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

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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 ethanols, of gradually decreasing nucleophilicity, that can be used to map how the stereoselectivity of a given glycosylation system is dependent on the nucleophilicity of the acceptor, 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 ethanols 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

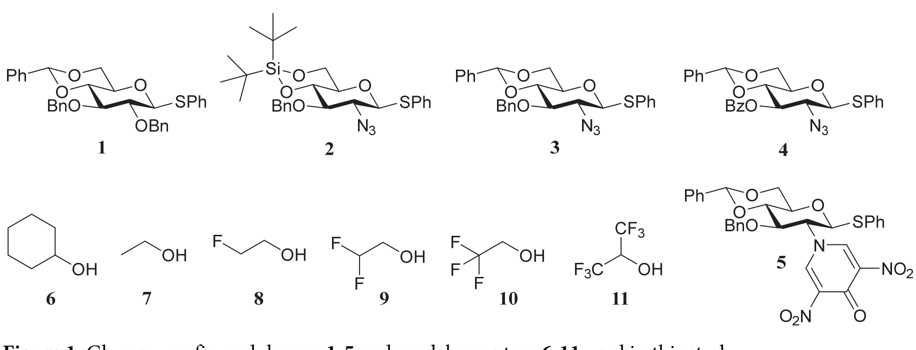


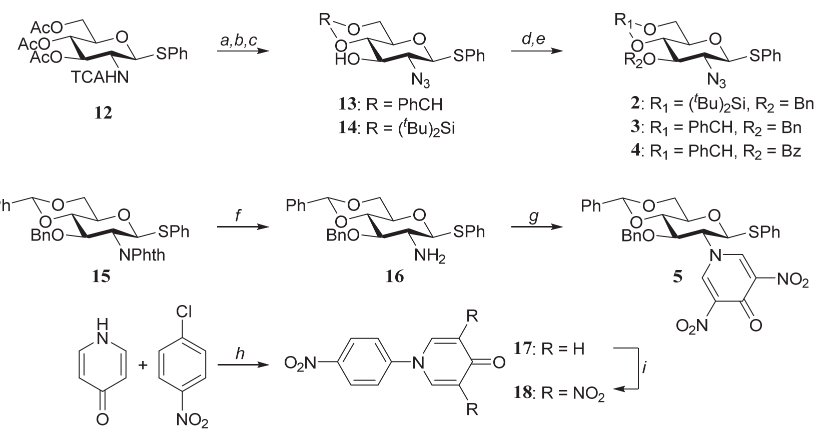
Figure 1. Glucose-configured donors **1-5** and model acceptors **6-11** used in this study.

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 stereoselecivity 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**.



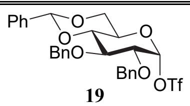
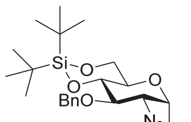
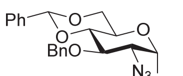
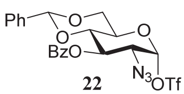
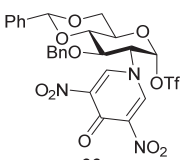
Reagents and conditions: (a) *i.* K_2CO_3, EtOH, H_2O; *ii.* $CuSO_4 \cdot 5H_2O$, imidazole-1-sulfonyl azide hydrochloride[34]; (b) di-*tert*-butylsilyl bis(trifluoromethanesulfonate), pyridine, **14**: 71% (three steps); (c) $PhCH(OMe)_2$, *p*-$TsOH \cdot H_2O$, **13**: 78% (three steps); (d) BnBr, 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 benzoylation of **13** gave the target donor compounds **2**, **3**, and **4**, respectively. Donor **5** was prepared in two steps from thioglucoside **15**[35] by exchange of the phthaloyl group for the DNPY functionality. To this end, compound **15** was treated with ethylenediamine to give amine **16**, wich was treated with DNPY reagent **18**[30,36] to furnish the target donor.

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 (Ph_2SO/Tf_2O)[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)	$^3J_{H1\text{-}H2}$^{a} (Hz)	^{13}C δ (ppm)	T_{decomp} (°C)
1	 **19**	6.09	3.4	106.1	-20
2	 **20**	6.00	3.4	104.8	-30
3	 **21**	6.07	3.5	105.0	-20
4	 **22**	6.23	3.5	104.5	-10
5	 **23**	6.06	n/a	102.2	-40

^{a}values determined at -40°C

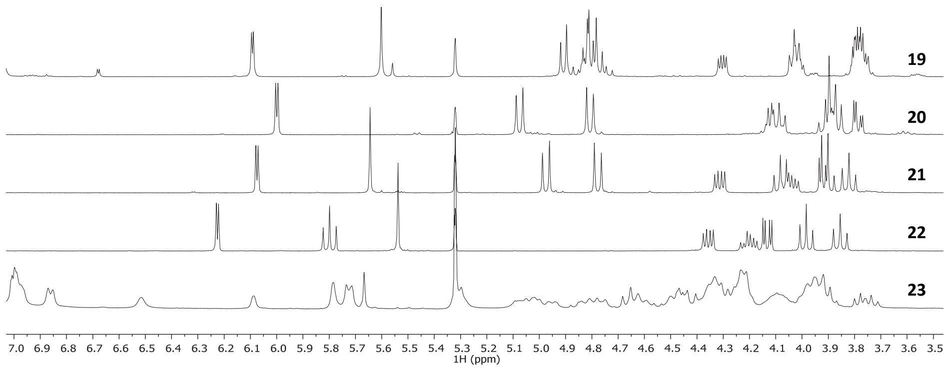
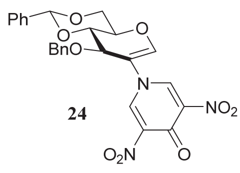


Figure 3. ^{1}H-NMR spectra at -40°C of activated donors **1-5** showing their respective anomeric triflates **19-23**.

to the formation of two species: In addition to the anomeric triflate **19**,[9] the oxosulfonium triflate **19α*** (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.



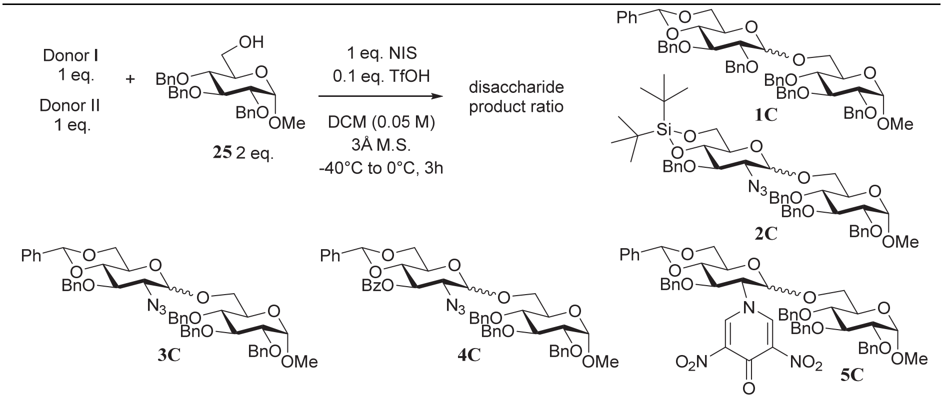
24

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.



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

[a]Determined by ^{1}H-NMR of the isolated disaccharide. [b]The disaccharide fraction was quantified after isolation by size-exclusion chromatography and related to the limiting amount of NIS (see experimental section). [c]The 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 (Et_3N).

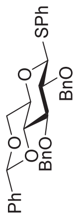
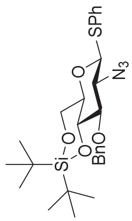
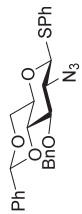
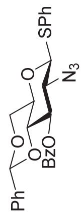
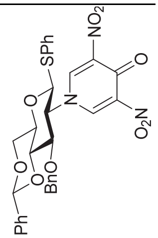
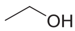
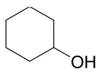
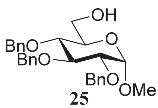
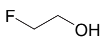
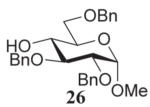
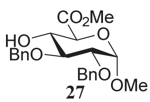
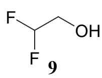
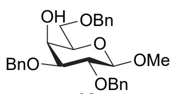
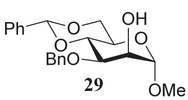
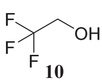
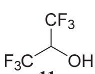
formed in a 6:1 ratio. C-3-*O*-Benzyl donor **3** in turn outcompetes benzoylated donor **4** slightly, as a result of the electron-withdrawing nature of the benzoate, giving a 1.6:1 ratio of the addition products **3C** and **4C**.[47–49] DNPY-protected donor **5** is the least reactive of the set of 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 Ph_2SO/Tf_2O 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] α:β (yield)[b]	Product α:β (yield)	Product α:β (yield)	Product α:β (yield)	Product α:β (yield)
A	 **7**	**1A** 1 : 10 (68 %)	**2A** < 1 : 20 (65 %)	**3A** < 1 : 20 (83 %)	**4A** < 1 : 20 (86 %)	**5A** < 1 : 20 (59 %)
B	 **6**	**1B** 1 : 5.1 (71 %)	**2B** < 1 : 20 (77 %)	**3B** < 1 : 20 (93 %)	**4B** < 1 : 20 (91 %)	**5B** < 1 : 20 (63 %)
C	 **25**	**1C** 1 : 2.7 (81 %)	**2C** 1 : 14 (92 %)	**3C** < 1 : 20 (89 %)	**4C** 1 : 14 (79 %)	**5C** < 1 : 20 (57 %)
D	 **8**	**1D** 1 : 2.8 (70 %)	**2D** 1 : 5 (79 %)	**3D** 1 : 6.7 (90 %)	**4D** 1 : 6.5 (83 %)	**5D** < 1 : 20 (43 %)
E	 **26**	**1E** 1 : 1 (79 %)	**2E** 1 : 3 (81 %)	**3E** 1 : 7 (88 %)	**4E** 1 : 6 (71 %)	**5E** 1 : 20 (55 %)
F	 **27**	**1F** 5 : 1 (90 %)	**2F** 3.3 : 1 (84 %)	**3F** 1.1 : 1 (93 %)	**4F** 1 : 1.4 (59 %)	**5F** 1 : 3.6 (30 %)
G	 **9**	**1G** 5 : 1 (70 %)	**2G** 2.7 : 1 (76 %)	**3G** 2.9 : 1 (64 %)	**4G** 2.7 : 1 (84 %)	**5G** 1 : 1 (59 %)
H	 **28**	**1H** > 20 : 1 (83 %)	**2H** 7 : 1 (52 %)	**3H** 9 : 1 (75 %)	**4H** 4 : 1 (51 %)	**5H** < 1 : 20 (52 %)
I	 **29**	**1I** > 20 : 1 (80 %)	**2I** > 20 : 1 (85 %)	**3I** 9 : 1 (74 %)	**4I** 5 : 1 (73 %)	**5I** 1 : 1.3 (53 %)
J	 **10**	**1J** > 20 : 1 (64 %)	**2J** > 20 : 1 (82 %)	**3J** > 20 : 1 (94 %)	**4J** > 20 : 1 (86 %)	**5J** 4 : 1 (58 %)
K	 **11**	**1K** > 20 : 1 (65 %)	**2K** > 20 : 1 (34 %)	**3K** > 20 : 1 (53 %)	-[c]	32% **24**

[a]Glycosylation results of donor **1**, are also reported in Chapter 2 of this thesis. [b]Ratio and yield of isolated product after column chromatography, anomers were not separated. [c]Only hydrolysed donor was found.

Mechanistic discussion

Two major trends become apparent from the table of glycosylations. First, with decreasing acceptor nucleophilicity the α/β ratio increases. 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

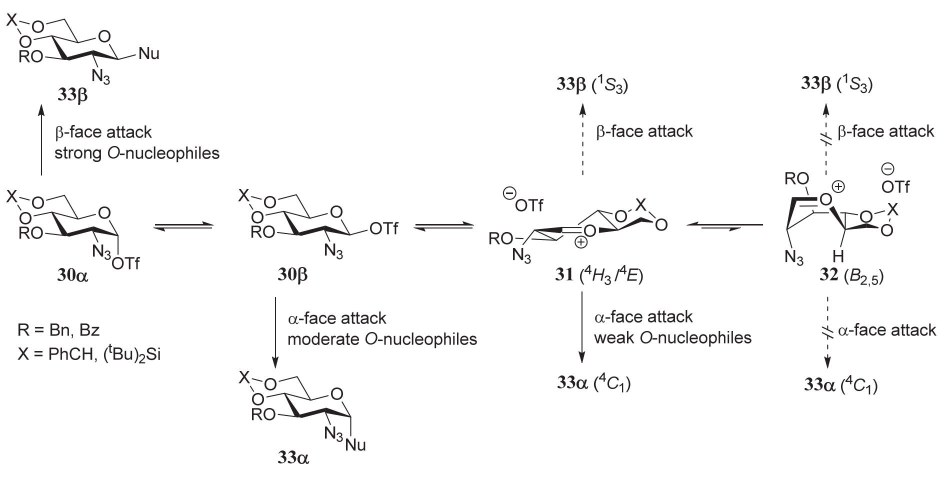


Figure 4. Reactive intermediates and reaction pathways for the 4,6-tethered glucosazide donors.

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

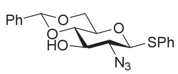
A set of model acceptors of gradually changing nucleophilicity has been used to investigate how the stereochemistry of glycosylations involving 4,6-tethered glucosamine donors relates to the nucleophilicity of the acceptor. The set of acceptors was complemented by a suite of carbohydrate alcohols to 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

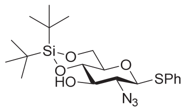
General procedure for Tf_2O/Ph_2SO mediated glycosylations: Donor (0.1 mmol), Ph_2SO (26 mg, 0.13 mmol, 1.3 eq.) and TTBP[60] (62 mg, 0.25 mmol, 2.5 eq.) were coevaporated twice with dry toluene and dissolved in dry DCM (2 mL, 0.05 M donor). Activated 3Å molecular sieves (rods, size 1/16 in.) were added,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

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

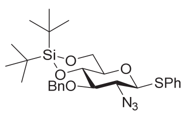
General procedure for the low temperature NMR experiments: A mixture of donor (30 µmol) and Ph_2SO (39 µmol) was coevaporated with dry toluene twice (for the activation of donor 1 also TTBP (75 µmol) was added). Under a nitrogen atmosphere, CD_2Cl_2 (0.6 mL) was added and the mixture transferred to a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



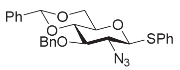
Phenyl 2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (13). To a suspension of thioglycoside **12**[33] (27.14 g, 50 mmol, 1 eq.) in EtOH (200 mL) was added K_2CO_3 (41.5 g, 300 mmol, 6 eq), and 20 mL H_2O and the mixture was refluxed overnight. The flask was cooled to r.t. and to the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



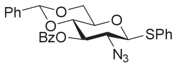
Phenyl 2-azido-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-1-thio-β-D-glucopyranoside (14). Crude triol phenyl 2-azido-2-deoxy-1-thio-β-D-glucopyranoside (synthesized as described for compound **13**) (≤10 mmol) was dissolved in pyridine (15 mL) and cooled to 0°C. Di-*tert*-butylsilyl bis(trifluoromethanesulfonate)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



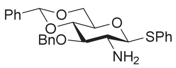
Phenyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-1-thio-β-D-glucopyranoside (2). Compound **14** (1.4 g, 3.2 mmol) was dissolved in DMF (15 mL) and cooled to 0°C. Benzyl bromide (421 µL, 3.52 mmol, 1.1 eq.) and NaH (60% dispersion in mineral oil, 166 mg, 4.16 mmol, 1.3 eq.) were added and the reaction was stirred for 2 h at 0°C and 1 h at r.t. The reaction mixture was quenched with MeOH and H_2O (100 mL) was added. The water phase was extracted three times with 30 mL Et_2O and the combined organic layers were washed with brine (2x), dried with Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography (1%-8% Et_2O/pentane) yielded compound **2** as a colorless oil (1.35 g, 2.56 mmol, 80%). Additional impurities as observed by ^{1}H NMR originating from the previous crude steps could be removed by size exclusion chromatography (Sephadex™ LH-20, 1/1 DCM/MeOH). R_f: 0.51 (19/1 pentane/Et_2O). $[\alpha]_D^{23}$ = -85.0° (*c* = 1.0, $CHCl_3$); IR (neat): 654, 694, 746, 766, 826, 1059, 1078, 1099, 1159, 1474, 2110, 2859, 2884, 2934, 2963; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.55 – 7.48 (m, 2H, CHarom), 7.43 – 7.37 (m, 2H, CHarom), 7.36 – 7.27 (m, 6H, CHarom), 4.99 (d, 1H, *J* = 10.7 Hz, C*H*H Bn), 4.81 (d, 1H, *J* = 10.7 Hz, CH*H* Bn), 4.41 (d, 1H, *J* = 10.2 Hz, H-1), 4.21 (dd, 1H, *J* = 10.3, 5.1 Hz, H-6), 3.90 (t, 1H, *J* = 10.2 Hz, H-6), 3.87 (dd, 1H, *J* = 9.5, 8.7 Hz, H-4), 3.48 – 3.38 (m, 2H, H-3, H-5), 3.28 (dd, 1H, *J* = 10.2, 9.2 Hz, H-2), 1.07 (s, 9H, CH_3 ^{t}Bu), 1.01 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.9 (C_q Bn), 133.9 (CH_{arom}), 130.9 (C_q SPh), 129.1, 128.7, 128.5, 128.5, 128.1 (CH_{arom}), 86.4 (C-1), 84.2 (C-3), 77.8 (C-4), 75.7 (CH_2 Bn), 74.7 (C-5), 66.2 (C-6), 64.2 (C-2), 27.5, 27.1 (CH_3 ^{t}Bu), 22.7, 20.0 (CH_3 ^{t}Bu); HRMS: $[M+H]^+$ calcd for $C_{27}H_{38}N_3O_4SSi$ 528.23468, found 528.23451. and $[M-N_2+H]^+$ calcd for $C_{27}H_{38}NO_4SSi$ 500.22853, found 500.22839.



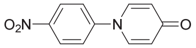
Phenyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (3). Compound **13** (4.36 g, 11.3 mmol) was coevaporated once with dry toluene and then dissolved in DMF (50 mL) and cooled to 0°C. Benzyl bromide (1.9 mL, 15.8 mmol, 1.4 eq.) and NaH (60% dispersion in mineral oil, 900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



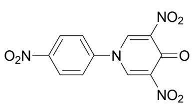
Phenyl 2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (4). To a 0°C solution of compound **13** (1.34 g, 3.48 mmol) in DCM (17 mL) and pyridine (1.4 mL, 34.8 mmol, 5 eq.) was added benzoyl chloride (0.61 mL, 5.22 mmol, 1.5 eq.) and DMAP (42 mg, 0.35 mmol, 0.1 eq.). The reaction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



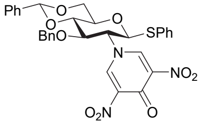
Phenyl 2-amino-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (16). Fully protected glycoside **15**[35] (9.11 g, 15.7 mmol) was dissolved in 160 ml EtOH and heated to reflux upon which ethylene diamine (52 mL, 785 mmol, 50 eq.) was added in three portions and reflux was maintained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



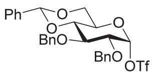
1-(4-nitrophenyl)-4-pyridone (17). Following the procedure of You and Twieg[64] 4-hydroxypyridine (14.3 g, 150 mmol), 4-chloronitrobenzene (22.9 g, 145 mmol) and K_2CO_3 (20.7 g, 150 mmol) were suspended in *N*-methyl-2-pyrrolidone (110 mL) and heated at 150°C for 2 h. The hot solution was then poured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



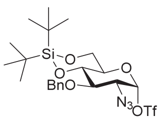
3,5-dinitro-1-(4-nitrophenyl)-4-pyridone (18). Modification of the procedure from Matsumura *et al.*[30], an ice cooled three-neck flask equipped with a condenser was charged with 120 mL H_2SO_4 (30% SO_3) followed by the slow addition of 120 mL fuming 99% HNO_3. To the cold mixture pyridone **17** (21.6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



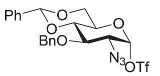
Phenyl 2-(3,5-dinitro-4-pyridone)-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (5). Free amine **16** (3.6 g, 8 mmol) and reagent **18** (2.7 g, 8.8 mmol, 1.1 eq.) were dissolved in pyridine (48 mL) and AcOH (4 mL) and left to stir for 30 min. The mixture was diluted with EtOAc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



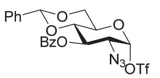
Trifluoromethanesulfonyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (19).[9] ^{1}H NMR (CD_2Cl_2, *T* = 213 K, 400 MHz, HH-COSY, HSQC): δ 6.08 (d, 1H, *J* = 3.5 Hz, H-1), 5.59 (s, 1H, C*H*Ph), 4.89 (d, 1H, *J* = 11.0 Hz, C*H*H Bn), 4.85 – 4.69 (m, 3H, CH*H* Bn, CH_2 Bn), 4.29 (dd, 1H,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



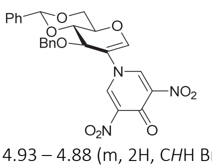
Trifluoromethanesulfonyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (20). ^{1}H NMR (CD_2Cl_2, *T* = 243 K, 400 MHz, HH-COSY, HSQC): δ 6.08 (d, 1H, *J* = 3.5 Hz, H-1), 5.64 (s, 1H, C*H*Ph), 4.98 (d, 1H, *J* = 10.6 Hz, C*H*H Bn), 4.78 (d, 1H, *J* = 10.6 Hz, CH*H* Bn), 4.32 (dd,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



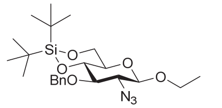
Trifluoromethanesulfonyl 2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (21). ^{1}H NMR (CD_2Cl_2, *T* = 243 K , 400 MHz, HH-COSY, HSQC): δ 6.23 (d, 1H, *J* = 3.5 Hz, H-1), 5.80 (t, 1H, *J* = 10.0 Hz, H-3), 5.54 (s, 1H, C*H*Ph), 4.36 (dd, 1H, *J* = 10.4, 4.9 Hz, H-6), 4.21 (td,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



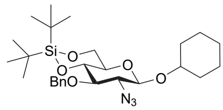
Trifluoromethanesulfonyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α-D-glucopyranoside (22). ^{1}H NMR (CD_2Cl_2, *T* = 233 K, 400 MHz, HH-COSY, HSQC, HMBC): δ 6.00 (d, 1H, *J* = 3.4 Hz, H-1), 5.08 (d, 1H, *J* = 10.1 Hz, C*H*H Bn), 4.81 (d, 1H, *J* = 10.2 Hz, CH*H* Bn), 4.15 – 4.06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



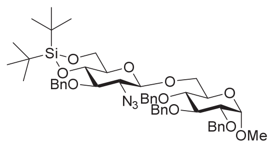
3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-D-glucal (24). Off-white solid. R_f: 0.20 (7/3 pentane/EtOAc). $[\alpha]_D^{23}$ = +85.9° (*c* = 0.32, DCM); IR (thin film): 698, 720, 753, 1007, 1059, 1095, 1192, 1247, 1304, 1351, 1516, 1679, 2880, 2924, 3072; ^{1}H NMR (Acetone-d_6,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



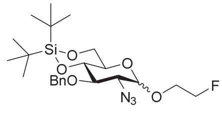
Ethyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-β-D-glucopyranoside (2A). Donor **2** and ethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (0% to 5% Et_2O in pentane) to yield glycosylation product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



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

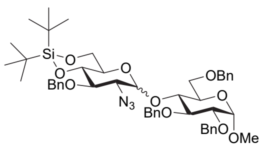


Methyl 6-*O*-(2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (2C). Donor **2** and acceptor **25** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and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

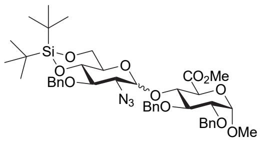


2-Fluoroethyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α/β-D-glucopyranoside (2D). Donor **2** and 2-fluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 2% Et_2O in toluene) to yield glycosylation product **2D** (37.8 mg, 79 µmol, 79%, α:β = 1:5.5) as a colorless oil. R*f*: 0.20

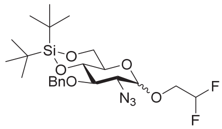
(toluene). Reported as a 1.00 : 0.18 mixture of anomers: IR (neat): 654, 768, 827, 962, 1080, 1161, 1472, 2112, 2859, 2932; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.45 – 7.40 (m, 2.36H, CH_{arom}), 7.39 – 7.27 (m, 3.54H, CH_{arom}), 5.06 (d, 0.18H, *J* = 10.7 Hz, C*H*H Bn_{α}), 4.99 (d, 1H, *J* = 10.9 Hz, C*H*H Bn_{β}), 4.86 (d, 0.18H, *J* = 3.6 Hz, H-1_{α}), 4.82 (d, 0.18H, *J* = 10.6 Hz, CH*H* Bn_{α}), 4.82 (d, 1H, *J* = 10.9 Hz, CH*H* Bn_{β}), 4.71 – 4.61 (m, 1.18H, C*H*HF_{α}, C*H*HF_{β}), 4.58 – 4.47 (m, 1.18H, CH*H*F_{α}, CH*H*F_{β}), 4.37 (d, 1H, *J* = 7.6 Hz, H-1_{β}), 4.17 (dd, 1H, *J* = 10.3, 5.1 Hz, H-6_{β}), 4.12 – 3.78 (m, 5.26H, CH_2-CH_2F_{α}, CH_2-CH_2F_{β}, H-3_{α}, H-4_{α}, H-4_{β}, H-5_{α}, H-6_{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, CH_3 $^{t}Bu_{\alpha}$), 1.08 (s, 9H, CH_3 $^{t}Bu_{\beta}$), 1.03 (s, 1.62H CH_3 $^{t}Bu_{\alpha}$), 1.01 (s, 9H, CH_3 $^{t}Bu_{\beta}$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.3 ($C_{q,\alpha}$), 138.2 ($C_{q,\beta}$), 128.6 (CH_{arom} Bn_{α}), 128.5 (CH_{arom} Bn_{β}), 128.5 (CH_{arom} Bn_{α}), 128.4 (CH_{arom} Bn_{β}), 128.0 (CH_{arom} $Bn_{\alpha,\beta}$), 102.4 (C-1_{β}), 98.3 (C-1_{α}), 82.7 (d, *J* = 170.0 Hz, CH_2F_{β}), 82.4 (d, *J* = 170.6 Hz, CH_2F_{α}), 82.3 (C-3_{β}), 79.3, 79.0 (C-3_{α}, C-4_{α}), 78.0 (C-4_{β}), 75.6 (CH_2 Bn_{α}), 75.5 (CH_2 Bn_{β}), 70.6 (C-5_{β}), 69.0 (d, *J* = 20.3 Hz, CH_2-CH_2F_{β}), 67.3 (d, *J* = 20.1 Hz, CH_2-CH_2F_{α}), 66.8 (C-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 (CH_3 $^{t}Bu_{\alpha,\beta}$), 23.1 (C_q $^{t}Bu_{\alpha}$), 22.8 (C_q $^{t}Bu_{\beta}$), 20.1 (C_q $^{t}Bu_{\alpha}$), 20.1 (C_q $^{t}Bu_{\beta}$); HRMS: $[M-N_2+H]^+$ calcd for $C_{23}H_{37}FNO_5Si$ 454.24195, found 454.24188.



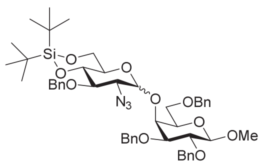
Methyl 4-*O*-(2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (2E). Donor **2** and acceptor **26** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and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



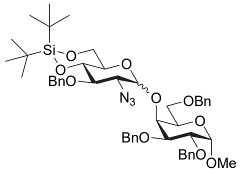
Methyl (methyl 4-*O*-[2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α/β-D-glucopyranosyl]-2,3-di-*O*-benzyl-α-D-glucopyranosyl uronate) (2F). Donor **2** and acceptor **27** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours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



2,2-Difluoroethyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α/β-D-glucopyranoside (2G). Donor **2** and 2,2-difluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 2% Et_2O in toluene) to yield glycosylation product **2G** (38.1 mg, 76 µmol, 76%, α:β = 2.7:1) in two fractions (24.3 mg α only, 13.8 mg α:β = 0.3:1) as white solids. R_f: 0.43 β, 0.31 α (toluene). IR (neat): 654, 766, 826, 1070, 1474, 2108, 2860, 2934; Data for the α-anomer: $[\alpha]_D^{23}$ = +35.6° (*c* = 0.86, $CHCl_3$); ^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, C*H*F_2), 5.06 (d, 1H, *J* = 10.6 Hz, C*H*H Bn), 4.85 (d, 1H, *J* = 3.6 Hz, H-1), 4.82 (d, 1H, *J* = 10.7 Hz, CH*H* Bn), 4.13 – 4.08 (m, 1H, H-6), 3.98 – 3.92 (m, 1H, H-3/4), 3.92 – 3.72 (m, 5H, CH_2-CHF_2, H-3/4, H-5, H-6), 3.35 (dd, 1H, *J* = 10.1, 3.6 Hz, H-2), 1.09 (s, 9H, CH_3 ^{t}Bu), 1.03 (s, 9H, CH_3 ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1 (C_q), 128.6, 128.5, 128.1 (CH_{arom}), 113.8 (t, *J* = 241.6 Hz, CHF_2), 98.7 (C-1), 79.0, 78.9 (C-3, C-4), 75.7 (CH_2 Bn), 67.3 (t, *J* = 28.6 Hz, CH_2-CHF_2), 67.1 (C-5), 66.6 (C-6), 62.4 (C-2), 27.5, 27.1 (CH_3 ^{t}Bu), 22.8, 20.1 (C_q ^{t}Bu); Data for the β-anomer: ^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, C*H*F_2), 4.99 (d, 1H, *J* = 10.9 Hz, C*H*H Bn), 4.81 (d, 1H, *J* = 11.0 Hz, CH*H* Bn), 4.35 (s, 1H, *J* = 7.7 Hz, H-1), 4.17 (dd, 1H, *J* = 10.3, 5.0 Hz, H-6), 4.02 – 3.74 (m, 4H, CH_2-CHF_2, H-4, H-6), 3.42 – 3.30 (m, 3H, H-2, H-3, H-5), 1.09 (s, 9H, CH_3 ^{t}Bu), 1.01 (s, 9H, CH_3, ^{t}Bu); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.1 (C_q), 128.5, 128.4, 128.1 (CH_{arom}), 114.1 (t, *J* = 241.4 Hz, CHF_2), 102.5 (C-1), 82.2 (C-3), 77.9 (C-4), 75.5 (CH_2 Bn), 70.7 (C-5), 68.8 (dd, *J* = 29.3, 28.8 Hz, CH_2-CHF_2), 66.2 (C-6), 65.4 (C-2), 27.5, 27.1 (CH_3 ^{t}Bu), 22.8, 20.1 (C_q ^{t}Bu); HRMS: $[M-N_2+H]^+$ calcd for $C_{23}H_{36}F_2NO_5Si$ 472.23253, found 472.23239.

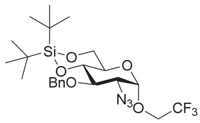


Methyl 4-*O*-(2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (2H). Donor **2** and acceptor **28** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C)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

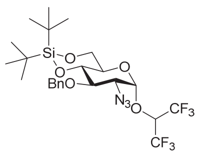


Methyl 2-*O*-(2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α-D-glucopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (2I). Donor **2** and acceptor **29** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (1/0 to 9/1 pentane/EtOAc) to yield glycosylation product **2I** (67 mg, 85 µmol, 85%, α:β = > 20:1) as a white solid. R_f: 0.54 (9/1 pentane/EtOAc). $[\alpha]_D^{20}$ = +44.3° (*c* = 1.34, $CHCl_3$); IR (thin film): 696, 827, 937, 1040, 1088, 1130, 1364, 2108, 2859, 2957; Data for the α-anomer: ^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, C*H*Ph), 5.23 (d, 1H, *J* = 3.6 Hz, H-1'), 5.09 (d, 1H, *J* = 10.6 Hz, C*H*H Bn), 4.89 – 4.82 (m, 2H, CH*H* Bn, C*H*H Bn), 4.74 – 4.65 (m, 2H, C*H*H Bn, H-1), 4.31 – 4.21 (m, 2H, H-4, H-6), 4.11 – 3.92 (m, 5H, H-2, H-3, H-3', H-4', H-6'), 3.92 – 3.76 (m, 4H, H-5, H-5', H-6, H-6'), 3.36 (s, 3H, CH_3 OMe), 3.27 (dd, 1H, *J* = 10.0, 3.7 Hz, H-2'), 1.09 (s, 9H), 1.05 (s, 9H); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ

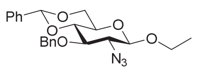
138.6, 138.4, 137.7 (C_q), 129.0, 128.5, 128.5, 128.4, 128.3, 128.3, 128.0, 127.6, 127.5, 127.4, 126.2, 126.1 (CH_{arom}), 101.7 (CHPh), 101.0 (C-1), 99.4 (C-1'), 79.3 (C-4), 79.1, 78.9 (C-3', C-4'), 76.0, 75.6 (C-2, C-3), 75.6, 73.0 (CH_2 Bn), 69.0 (C-6), 67.2 (C-5'), 66.6 (C-6'), 64.1 (C-5), 62.6 (C-2'), 55.2 (CH_3 OMe), 27.5, 27.2 (CH_3 ^tBu), 22.8, 20.2 (C_q ^tBu); Diagnostic peaks β-anomer: ^1H NMR ($CDCl_3$, 400 MHz): δ 5.60 (s, 1H, C*H*Ph), 4.98 (d, 1H, *J* = 11.3 Hz, C*H*H Bn), 4.39 (d, 1H, *J* = 8.2 Hz, H-1'), 3.57 – 3.48 (m, 1H); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 101.6, 99.6, 81.8, 78.5, 77.8, 76.4, 75.2, 74.4, 72.3, 70.9, 65.7, 55.1, 27.5, 27.1; HRMS: $[M+NH_4]^+$ calcd for $C_{42}H_{59}N_4O_{10}Si$ 807.39950, found 807.39931.



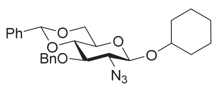
2,2,2-Trifluoroethyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylidene-α-D-glucopyranoside (2J). Donor **2** and 2,2,2-trifluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 30 min at -40°C) and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 2% Et_2O in toluene) to yield glycosylation product **2J** (42.4 mg, 82 µmol, 82%, α:β = >20:1) as a colorless oil. R_f: 0.36 (toluene). $[\alpha]_D^{23}$ = +32.6° (*c* = 1.0, $CHCl_3$); IR (neat): 654, 766, 826, 1036, 1082, 1159, 1279, 1472, 2108, 2859, 2930; ^1H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.45 – 7.39 (m, 2H, CH_{arom}), 7.38 – 7.27 (m, 3H, CH_{arom}), 5.07 (d, 1H, *J* = 10.6 Hz, C*H*H Bn), 4.88 (d, 1H, *J* = 3.6 Hz, H-1), 4.82 (d, 1H, *J* = 10.6 Hz, CH*H* Bn), 4.14 – 4.07 (m, 1H, H-6), 4.03 – 3.93 (m, 3H, C*H₂*-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, 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}), δ 123.5 (q, *J* = 278.4 Hz, CF3), 98.8 (C-1), 78.9 (C-3), 78.8 (C-4), 75.7 (CH_2 Bn), 67.4 (C-5), 66.5 (C-6), 65.2 (q, *J* = 35.4 Hz, CH_2-CF_3), 62.2 (C-2), 27.5, 27.1 (CH_3 ^tBu), 22.8, 20.1 (C_q ^tBu); HRMS: $[M-N_2+H]^+$ calcd for $C_{23}H_{35}F_3NO_5Si$ 490.22311, found 490.22292.



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

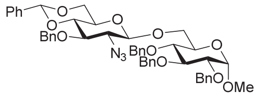


Ethyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (3A). Donor **3** and ethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 hexane/toluene to 5% EtOAc in toluene) to yield glycosylation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

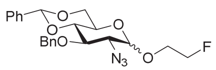


Cyclohexyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (3B). Donor **3** and cyclohexanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/1 to 0/1 hexane/toluene to 5% EtOAc in toluene) to yield glycosylation product **3B** (43 mg, 93 µmol, 93%, α:β = <1:20) as a white solid. R_f: 0.23 (toluene). $[\alpha]_D^{23}$ = -60.5° (*c* = 0.86, DCM); IR (neat): 696, 748, 998, 1092, 1275, 1365, 1452, 2108, 2858, 2933; Data for the β-anomer: ^1H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.50 – 7.44 (m, 2H, CH_{arom}), 7.42 – 7.27 (m, 8H, CH_{arom}), 5.56 (s, 1H, C*H*Ph), 4.90 (d, 1H, *J* = 11.4 Hz, C*H*H Bn), 4.79 (d, 1H, *J*

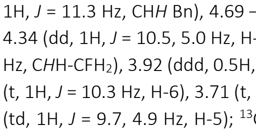
= 11.4 Hz, CH*H* Bn), 4.47 (d, 1H, *J* = 7.8 Hz, H-1), 4.32 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6), 3.79 (t, 1H, *J* = 10.3 Hz, H-6), 3.74 – 3.64 (m, 2H, H-4, CH Cyc), 3.50 (t, 1H, *J* = 9.2 Hz, H-3), 3.44 (dd, 1H, *J* = 9.6, 7.8 Hz, H-2), 3.36 (td, 1H, *J* = 9.7, 5.0 Hz, H-5), 1.99 – 1.87 (m, 2H, CH$_2$ Cyc), 1.82 – 1.72 (m, 2H, *J* = 15.2, 4.4 Hz, CH$_2$ Cyc), 1.56 – 1.37 (m, 3H, CH$_2$ Cyc), 1.36 – 1.20 (m, 3H, CH$_2$ Cyc); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC): δ 138.0, 137.3 (C$_q$), 129.1, 128.5, 128.4, 128.3, 127.9, 126.1 (CH$_{arom}$), 101.4 (CHPh), 101.0 (C-1), 81.6 (C-4), 79.0 (C-3), 78.5 (CH Cyc), 75.0 (CH$_2$ Bn), 68.8 (C-6), 66.5 (C-2), 66.3 (C-5), 33.6, 31.8, 25.6, 24.1, 23.9 (CH$_2$ Cyc); Diagnostic peaks α-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.59 (s, 0.04H, C*H*Ph), 5.03 (d, 0.04H, *J* = 3.7 Hz, H-1), 4.12 (t, 0.04H, *J* = 9.5 Hz, H-3), 4.00 (td, 0.04H, *J* = 9.9, 4.8 Hz, H-5), 3.28 (dd, 0.04H, *J* = 10.0, 3.7 Hz, H-2); ^{13}C-APT NMR (CDCl$_3$, 101 MHz): δ 101.4 (CHPh), 97.1 (C-1), 76.0 (C-3), 63.8 (C-2), 62.9 (C-5); HRMS: [M+NH$_4$]$^+$ calcd for $C_{26}H_{35}N_4O_5$ 483.26020 found 483.25991.



Methyl 6-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3C). Donor **3** and acceptor **25** were condensed using the general procedure for Tf$_2$O/Ph$_2$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 **3C** (73.7 mg, 89 µmol, 89%, α:β = <1:20) as a white solid. R$_f$: 0.42 (4/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[38] $[\alpha]_D^{23}$ = -32.2° (*c* = 1.0, CHCl$_3$); IR (neat): 696, 737, 999, 1028, 1070, 1090, 1277, 1362, 1497, 2108, 2876, 2926; ^{1}H NMR (CDCl$_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.47 (dd, 2H, *J* = 7.3, 2.5 Hz, CH$_{arom}$), 7.42 – 7.25 (m, 23H, CH$_{arom}$), 5.55 (s, 1H, C*H*Ph), 4.99 (d, 1H, *J* = 10.9 Hz, C*H*H 3-OBn), 4.95 (d, 1H, *J* = 11.2 Hz, C*H*H 4-OBn), 4.91 (d, 1H, *J* = 11.2 Hz, C*H*H 3'-OBn), 4.85 – 4.76 (m, 3H, CH*H* 3-OBn, C*H*H 2-OBn, CH*H* 3'-OBn), 4.70 – 4.63 (m, 2H, CH*H* 4-OBn, CH*H* 2-OBn), 4.61 (d, 1H, *J* = 3.6 Hz, H-1), 4.30 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6'), 4.23 (d, 1H, *J* = 7.9 Hz, H-1'), 4.07 (d, 1H, *J* = 8.9 Hz, H-6), 4.00 (t, 1H, *J* = 9.3 Hz, H-3), 3.81 – 3.72 (m, 3H, H-5, H-6, H-6'), 3.69 (t, 1H, *J* = 9.1 Hz, H-4'), 3.60 (t, 1H, *J* = 9.3 Hz, H-4), 3.59 – 3.46 (m, 3H, H-2, H-2', H-3'), 3.37 (s, 3H, CH$_3$ OMe), 3.36 – 3.29 (m, 1H, H-5'); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 138.8, 138.5, 138.2, 137.8, 137.2 (C$_q$), 129.2, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.1, 128.1, 128.0, 127.9, 127.9, 127.7, 126.1 (CH$_{arom}$), 102.4 (C-1'), 101.4 (CHPh), 98.4 (C-1), 82.2 (C-3), 81.5 (C-4'), 79.8 (C-2), 79.3 (C-3'), 77.6 (C-4), 75.9 (CH$_2$ 3-OBn), 75.0, 75.0 (CH$_2$ 3'-OBn, 4-OBn), 73.6 (CH$_2$ 2-OBn), 69.6 (C-5), 68.7, 68.6 (C-6, C-6'), 66.3 (C-5'), 66.1 (C-2'), 55.4 (OMe); HRMS: [M+NH$_4$]$^+$ calcd for $C_{48}H_{55}N_4O_{10}$ 847.39127, found 847.39224.

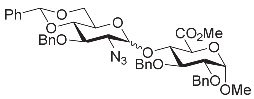


2-Fluoroethyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranoside (3D). Donor **3** and 2-fluoroethanol were condensed using the general procedure for Tf$_2$O/Ph$_2$SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 5% EtOAc in toluene) to yield glycosylation product **3D** (38.5 mg, 90 µmol, 90%, α:β = 1:6.7) as a white solid. R$_f$: 0.40 (19/1 toluene/EtOAc). IR (neat): 696, 748, 996, 1028, 1072, 1091, 1174, 1276, 1368, 1454, 2108, 2873, 2917; Data for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, HH-COSY, HSQC): δ 7.50 – 7.46 (m, 2H, CH$_{arom}$), 7.41 – 7.36 (m, 5H, CH$_{arom}$), 7.36 – 7.25 (m, 3H, CH$_{arom}$), 5.57 (s, 1H, C*H*Ph), 4.91 (d, 1H, *J* = 11.2 Hz, C*H*H Bn), 4.79 (d, 1H, *J* = 11.3 Hz, CH*H* Bn), 4.69 – 4.64 (m, 1H, C*H*HF), 4.55 (dt, 1H, *J* = 4.6, 2.9 Hz, CH*H*F), 4.42 (d, 1H, *J* = 7.9 Hz, H-1), 4.34 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6), 4.11 (ddd, 0.5H, *J* = 12.2, 4.8, 2.9 Hz, C*H*H-CFH$_2$), 4.03 (ddd, 0.5H, *J* = 12.2, 4.7, 3.0 Hz, C*H*H-CFH$_2$), 3.92 (ddd, 0.5H, *J* = 12.2, 5.9, 3.2 Hz, CH*H*-CFH$_2$), 3.86 (ddd, 0.5H, *J* = 12.2, 6.0, 3.3 Hz, CH*H*-CFH$_2$), 3.80 (t, 1H, *J* = 10.3 Hz, H-6), 3.71 (t, 1H, *J* = 9.2 Hz, H-4), 3.56 (t, 1H, *J* = 9.2 Hz, H-3), 3.48 (dd, 1H, *J* = 9.5, 7.9 Hz, H-2), 3.39 (td, 1H, *J* = 9.7, 4.9 Hz, H-5); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC): δ 137.8, 137.1 (C$_q$), 129.2, 128.5, 128.4, 128.3, 128.0, 126.1 (CH$_{arom}$), 102.7 (C-1), 101.4 (CHPh), 82.6 (d, *J* = 170.1 Hz, CFH$_2$), 81.5 (C-4), 79.0 (C-3), 75.1 (CH$_2$ Bn), 69.3 (d, *J* = 20.1 Hz, *CH$_2$*-CFH$_2$), 68.6 (C-6), 66.3 (C-5), 66.1 (C-2); ^{13}C-HMBC-GATED NMR (CDCl$_3$, 101 MHz): δ 102.7 ($J_{C1,H1}$ = 162 Hz, C-1); Diagnostic peaks α-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, HH-COSY, HSQC): δ 5.58 (s, 0.15H, C*H*Ph), 4.96 (d, 0.15H, *J* = 10.9 Hz, C*H*H Bn), 4.95 (d, 0.15H, *J* = 3.7 Hz, H-1), 4.81 (d, 0.15H, *J* = 11.0 Hz, CH*H* Bn), 4.29 (dd, 0.15H, *J* = 10.2, 4.9 Hz, H-6); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC): δ 101.5 (CHPh), 98.8 (C-1), 82.8 (C-4), 76.2 (C-3), 75.2 (CH$_2$ Bn), 68.9 (C-6), 63.0, 62.9 (C-2, C-5); ^{13}C-HMBC-GATED NMR (CDCl$_3$, 101 MHz): δ 98.8 ($J_{C1,H1}$ = 172 Hz, C-1); HRMS: [M+NH$_4$]$^+$ calcd for $C_{22}H_{28}FN_4O_5$ 447.20382 found 447.20355.

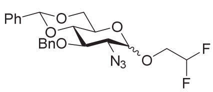


Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (3E). Donor **3** and acceptor **26** were condensed using the general procedure for Tf$_2$O/Ph$_2$SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 4/1 pentane/EtOAc) to yield glycosylation product **3E** (73.3 mg, 88 µmol, 88%, α:β = 1:7) as a white solid. R$_f$: 0.51 α, 0.43 β (4/1 pentane/EtOAc). IR (neat): 696, 737, 1049, 1092, 1362, 1454, 2110, 2868; Data for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, HH-COSY, HSQC, TOCSY): δ 7.68 – 7.60 (m, 2H, CH$_{arom}$), 7.52 – 7.18 (m, 23H, CH$_{arom}$), 5.47 (s, 1H, C*H*Ph), 4.89 (d, 1H, *J* = 11.2 Hz, C*H*H Bn), 4.87 (d, 1H, *J* = 10.9 Hz, C*H*H Bn), 4.81 (d, 1H, *J* = 10.9 Hz, CH*H* Bn), 4.78

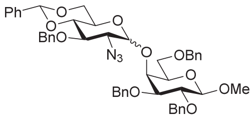
(d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.75 (d, 1H, *J* = 11.2 Hz, CH*H* Bn), 4.71 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.63 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.60 (d, 1H, *J* = 3.7 Hz, H-1), 4.41 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.19 (d, 1H, *J* = 7.6 Hz, H-1'), 4.11 (dd, 1H, *J* = 10.6, 5.0 Hz, H-6'), 4.00 – 3.90 (m, 2H, H-4, H-6), 3.85 (t, 1H, *J* = 9.3 Hz, H-3), 3.75 (dt, 1H, *J* = 9.8, 2.4 Hz, H-5), 3.69 (dd, 1H, *J* = 10.8, 1.9 Hz, H-6), 3.56 (t, 1H, *J* = 9.0 Hz, H-4'), 3.51 (dd, 1H, *J* = 9.5, 3.7 Hz, H-2), 3.45 – 3.38 (m, 4H, H-6', CH_3 OMe), 3.36 – 3.27 (m, 2H, H-2', H-3'), 3.00 (td, 1H, *J* = 9.8, 5.0 Hz, H-5'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 139.3, 138.3, 137.8, 137.8, 137.3 (C_q), 131.1, 129.4, 128.6, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 127.9, 127.9, 127.6, 126.0, 124.8 (CH_{arom}), 101.3, 101.2 (CHPh, C-1'), 98.4 (C-1), 81.7 (C-4'), 80.1 (C-3), 79.2 (C-3'), 79.0 (C-2), 76.9 (C-4), 75.4, 74.7, 73.6, 73.5 (CH_2 Bn), 69.7 (C-5), 68.6 (C-6'), 68.0 (C-6), 66.6 (C-2'), 65.8 (C-5'), 55.4 (OMe); Diagnostic peaks α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.71 (d, 1H, *J* = 4.0 Hz, H-1'), 5.53 (s, 1H, C*H*Ph), 5.11 (d, 1H, *J* = 10.7 Hz, C*H*H Bn), 4.95 (d, 1H, *J* = 10.9 Hz, C*H*H Bn); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 98.1, 97.8, 82.7, 82.1, 80.5, 76.2, 75.1, 73.3, 73.0, 69.4, 69.1, 68.7, 63.4, 62.9; HRMS: [M+Na]$^+$ calcd for $C_{48}H_{51}N_3O_{10}Na$ 852.34667, found 852.34668.



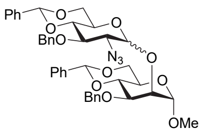
Methyl (Methyl 4-*O*-[2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl]-2,3-di-*O*-benzyl-α-D-glucopyranosyl uronate) (3F). Donor **3** and acceptor **27** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified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



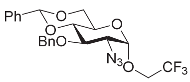
2,2-Difluoroethyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranoside (3G). Donor **3** and 2,2-difluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 5% EtOAc in toluene) to yield glycosylation product **3G** (28.8 mg, 64 µmol, 64%, α:β = 2.9:1) as a white solid. R_f: 0.15 and 0.18 (toluene). IR (neat): 698, 747, 998, 1070, 1093, 1372, 1454, 2109, 2867, 2934; Reported as a 1 : 0.35 mixture of anomers: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.52 – 7.45 (m, 2.70H, CH_{arom}), 7.43 – 7.26 (m, 10.80H, CH_{arom}), 5.95 (tt, 1H, *J* = 55.2, 4.2 Hz, CF_2*H*$_{\alpha}$), 5.94 (tt, 0.35H, *J* = 55.3, 3.8 Hz, CF_2*H*$_{\beta}$), 5.58 (s, 1H, C*H*Ph$_{\alpha}$), 5.57 (s, 0.35H, C*H*Ph$_{\beta}$), 4.96 (d, 1H, *J* = 10.9 Hz, C*H*H Bn$_{\alpha}$), 4.93 (d, 1H, *J* = 3.9 Hz, H-1$_{\alpha}$), 4.92 (d, 0.35H, *J* = 11.3 Hz, C*H*H Bn$_{\beta}$), 4.80 (d, 1H, *J* = 11.0 Hz, CH*H* Bn$_{\alpha}$), 4.79 (d, 0.35H, *J* = 11.3 Hz, CH*H* Bn$_{\beta}$), 4.40 (d, 0.35H, *J* = 7.9 Hz, H-1$_{\beta}$), 4.34 (dd, 0.35H, *J* = 10.5, 5.0 Hz, H-6$_{\beta}$), 4.29 (dd, 1H, *J* = 10.2, 4.8 Hz, H-6$_{\alpha}$), 4.08 (t, 1H, *J* = 9.5 Hz, H-3$_{\alpha}$), 4.02 – 3.67 (m, 6.4H, H-4$_{\alpha}$, H-4$_{\beta}$, H-5$_{\alpha}$, H-6$_{\alpha}$, H-6$_{\beta}$, C*H$_2$*-CF_2H$_{\alpha}$, C*H$_2$*-CF_2H$_{\beta}$), 3.56 (t, 0.35H, *J* = 9.2 Hz, H-3$_{\beta}$), 3.50 – 3.35 (m, 1.70H, H-2$_{\alpha}$, H-2$_{\beta}$, H-5$_{\beta}$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.8, 137.8, 137.1, 137.1 (C_q), 129.4, 129.3, 129.1, 128.6, 128.5, 128.5, 128.4, 128.1, 126.1 (CH_{arom}), 114.0 (t, *J* = 241.5 Hz, CF_2H$_{\beta}$), 113.8 (t, *J* = 241.6 Hz, CF_2H$_{\alpha}$), 102.8 (C-1$_{\beta}$), 101.6 (CHPh$_{\alpha}$), 101.5 (CHPh$_{\beta}$), 99.3 (C-1$_{\alpha}$), 82.6 (C-4$_{\alpha}$), 81.4 (C-4$_{\beta}$), 78.9 (C-3$_{\beta}$), 76.0 (C-3$_{\alpha}$), 75.3 (CH_2 Bn$_{\alpha}$), 75.1 (CH_2 Bn), 69.0 (t, *J* = 29.0 Hz, *CH$_2$*-CF_2H$_{\beta}$), 68.8 (C-6), 68.5 (C-6), 67.5 (t, *J* = 28.7 Hz, *CH$_2$*-CF_2H$_{\alpha}$), 66.4 (C-5$_{\beta}$), 66.0 (C-2$_{\beta}$), 63.3 (C-5$_{\alpha}$), 62.9 (C-2$_{\alpha}$); HRMS: [M+H]$^+$ calcd for $C_{22}H_{24}F_2N_3O_5$ 448.16785, found 448.16761.



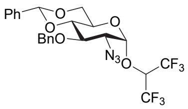
Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (3H). Donor **3** and acceptor **28** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash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



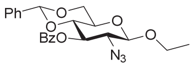
Methyl 2-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (3I). Donor **3** and acceptor **29** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 4/1 pentane/EtOAc) to yield glycosylation product **3I** (54.7 mg, 74 µmol, 74%, α:β = 9:1) as a white solid. R_f: 0.74 (7/2 pentane/EtOAc). IR (neat): 696, 746, 997, 1036, 1074, 1090, 1128, 1371, 1454, 2106, 2862, 2922; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, 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, C*H*Ph), 5.60 (s, 1H, C*H*Ph'), 5.39 (d, 1H, *J* = 3.7 Hz, H-1'), 5.00 (d, 1H, *J* = 11.0 Hz, C*H*H Bn), 4.90 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.84 (d, 1H, *J* = 10.9 Hz, CH*H* Bn), 4.73 – 4.66 (m, 2H, H-1, CH*H* Bn), 4.34 – 4.24 (m, 3H, H-4, H-6, H-6'), 4.17 (dd, 1H, *J* = 10.2, 9.0 Hz, H-3'), 4.09 (dd, 1H, *J* = 3.1, 1.7 Hz, H-2), 4.00 (dd, 1H, *J* = 9.9, 3.1 Hz, H-3), 3.95 – 3.86 (m, 2H, H-5', H-6), 3.83 – 3.70 (m, 3H, H-4', H-5, H-6'), 3.36 (s, 3H, CH_3 OMe), 3.32 (dd, 1H, *J* = 10.2, 3.8 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 138.7, 138.0, 137.7, 137.2 (C_q), 129.2, 129.0, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.6, 127.4, 126.2, 126.0 (CH_{arom}), 101.7 (CHPh), 101.5 (CHPh'), 101.0 (C-1), 99.8 (C-1'), 82.9 (C-4'), 79.4 (C-4), 75.9 (C-3), 75.6 (C-3'), 75.5 (C-2), 75.3, 73.3 (CH_2 Bn), 69.0, 68.9 (C-6, C-6'), 64.1 (C-5), 63.3 (C-5'), 63.0 (C-2'), 55.0 (OMe); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.43 (d, 0.1H, *J* = 8.0 Hz, H-1'), 3.62 (dd, 0.1H, *J* = 9.6, 8.0 Hz, H-2'), 3.51 (t, 0.1H, *J* = 9.3 Hz, H-4); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 102.0 (C-1'), 78.5 (C-4), 66.4 (C-2'); HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{47}N_4O_{10}$ 755.32867, found 755.32921.



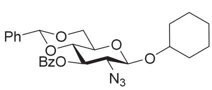
2,2,2-Trifluoroethyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (3J). Donor **3** and 2,2,2-trifluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 1 h at -40°C) and purified by flash column chromatography (1/0 to 0/1 pentane/toluene to 5% EtOAc in toluene) to yield glycosylation product **3J** (44 mg, 94 µmol, 94%, α:β = >20:1) as a colorless oil. R_f: 0.24 (toluene). $[\alpha]_D^{23}$ = +25.9° (*c* = 0.88, DCM); IR (neat): 697, 747, 1001, 1034, 1090, 1165, 1279, 1373, 2108, 2865, 2934; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.51 – 7.48 (m, 2H, CH_{arom}), 7.42 – 7.28 (m, 8H, CH_{arom}), 5.58 (s, 1H, C*H*Ph), 4.99 – 4.94 (m, 2H, C*H*H Bn, H-1), 4.80 (d, 1H, *J* = 10.9 Hz, CH*H* Bn), 4.29 (dd, 1H, *J* = 10.2, 4.8 Hz, H-6), 4.10 (dd, 1H, *J* = 10.0, 9.0 Hz, H-3), 3.98 (qd, 2H, *J* = 8.5, 3.1 Hz, C*H₂*-CF_3), 3.91 (td, 1H, *J* = 9.9, 4.8 Hz, H-5), 3.79 – 3.70 (m, 2H, H-4, H-6), 3.43 (dd, 1H, *J* = 10.0, 3.7 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 137.8, 137.1 (C_q), 129.3, 128.6, 128.5, 128.3, 128.1, 126.1 (CH_{arom}), 123.5 (q, *J* = 278.5 Hz), 101.6 (CHPh), 99.4 (C-1), 82.5 (C-4), 75.9 (C-3), 75.3 (CH_2 Bn), 68.7 (C-6), 65.4 (q, *J* = 35.4 Hz), 63.5 (C-5), 62.7 (C-2); ^{13}C-HMBC-GATED NMR ($CDCl_3$, 101 MHz): δ 102.5 ($J_{C1,H1}$ = 173 Hz, C-1); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.44 (d, 0.03H, *J* = 7.9 Hz, H-1), 4.34 (dd, 0.03H, *J* = 10.8, 5.3 Hz, H-6), 3.56 (t, 0.03H, *J* = 9.2 Hz), 3.48 (dd, 0.03H, *J* = 10.0, 7.9 Hz, H-2); ^{13}C-HMBC-GATED NMR ($CDCl_3$, 101 MHz): δ 102.4 (J_{C-H} = 150 Hz, C-1); HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{26}F_3N_4O_5$ 483.18498 found 483.18463.



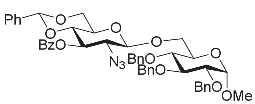
1,1,1,3,3,3-Hexafluoro-2-propyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (3K). Donor **3** and 1,1,1,3,3,3-hexafluoroisopropanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 72 h at -40°C) and purified by flash column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



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

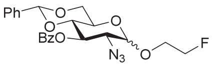


Cyclohexyl 2-azido-3-*O*-benozyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (4B). Donor **4** and cyclohexanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/1/0 to 0/1/0 to 0/19/1 pentane/toluene/EtOAc) to yield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

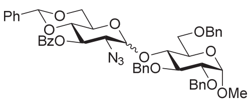


Methyl 6-*O*-(2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (4C). Donor **4** and acceptor **25** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 3/1 pentane/EtOAc) to yield glycosylation product **4C** (67 mg, 79 µmol, 79%, α:β = 1:14) as a white solid. R_f: 0.24 (4/1 pentane/EtOAc). $[\alpha]_D^{20}$ = -17.5° (*c* = 1.34, $CHCl_3$); IR (thin film): 696, 748, 1002, 1028, 1068, 1092, 1263, 1313, 1369, 1452, 1730, 2110, 2872, 2918; Data for the β-anomer: ^1H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.09 – 8.04 (m, 2H, CH_{arom}), 7.60 – 7.53 (m, 1H, CH_{arom}), 7.48 – 7.41 (m, 2H, CH_{arom}), 7.40 – 7.24 (m, 20H, CH_{arom}), 5.47 (s, 1H, C*H*Ph), 5.42 (t, 1H, *J* = 9.8 Hz, H-3'), 5.00 (d, 1H, *J* = 10.9 Hz, C*H*H Bn), 4.95 (d, 1H, *J* = 11.1 Hz, C*H*H Bn), 4.84 (d, 1H, *J* = 11.0 Hz, CH*H* Bn), 4.80 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.68 – 4.63 (m, 2H, 2xCH*H* Bn), 4.61 (d, 1H, *J* = 3.5 Hz, H-1), 4.43 (d, 1H, *J* = 8.0 Hz, H-1'), 4.33 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6'), 4.12 (d, 1H, *J* = 9.1 Hz, H-6), 4.02 (t, 1H, *J* = 9.3 Hz, H-3), 3.84 – 3.72 (m, 4H, H-4', H-5, H-6, H-6'), 3.69 (dd, 1H, *J* = 9.9, 8.0 Hz, H-2'), 3.57 (t, 1H, *J* = 9.2

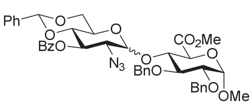
Hz, H-4), 3.54 (dd, 1H, *J* = 9.7, 3.6 Hz, H-2), 3.49 (td, 1H, *J* = 9.8, 5.0 Hz, H-5'), 3.39 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 165.4 (C=O), 138.7, 138.3, 138.2, 136.7 (CH_{arom}), 133.5, 130.0 (CH_{arom}), 129.4 (C_q Bz), 129.1, 128.6, 128.6, 128.5, 128.5, 128.3, 128.3, 128.1, 128.0, 128.0, 127.9, 127.9, 127.7, 126.1 (CH_{arom}), 102.6 (C-1'), 101.5 (CHPh), 98.3 (C-1), 82.1 (C-3), 79.8 (C-2), 78.7 (C-4'), 77.7 (C-4), 75.8, 75.0, 73.6 (CH_2 Bn), 71.9 (C-3'), 69.7 (C-5), 68.9 (C-6), 68.5 (C-6'), 66.6 (C-5'), 65.2 (C-2'), 55.4 (CH_3 OMe); Diagnostic peaks α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.79 (t, 0.07H, *J* = 9.9 Hz, H-3'), 5.50 (s, 0.07H, C*H*Ph), 5.08 (d, 0.07H, *J* = 3.5 Hz, H-1'), 4.24 (dd, 0.07H, *J* = 10.3, 4.8 Hz, H-6'), 3.41 (s, 0.21H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 101.7 (CHPh), 99.3 (C-1'), 98.1 (C-1), 82.1, 80.0, 79.7, 77.6, 75.8, 75.2, 70.0, 69.4, 67.0, 62.8, 62.1, 55.4; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{53}N_4O_{11}$ 861.37053, found 861.37064.



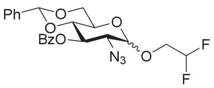
2-Fluoroethyl 2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranoside (4D). Donor **4** and 2-fluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/1/0 to 0/1/0 to 0/16/1 pentane/toluene/EtOAc) to yield glycosylation product **4D** (36.6 mg, 83 µmol, 83%, α:β = 1:6.5) as a white solid. R_f: 0.41 (19/1 toluene/EtOAc). IR (thin film): 700, 748, 879, 1001, 1026, 1070, 1093, 1179, 1261, 1722, 2108, 2868; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.10 – 8.05 (m, 2H, CH_{arom}), 7.61 – 7.54 (m, 1H, CH_{arom}), 7.49 – 7.43 (m, 2H, CH_{arom}), 7.41 – 7.36 (m, 2H, CH_{arom}), 7.33 – 7.27 (m, 3H, CH_{arom}), 5.50 (s, 1H, C*H*Ph), 5.41 (t, 1H, *J* = 9.8 Hz, H-3), 4.69 (ddt, 1H, *J* = 4.6, 3.2, 1.8 Hz, C*H*H-CH_2F), 4.65 (d, 1H, *J* = 7.9 Hz, H-1), 4.58 (ddt, 1H, *J* = 4.5, 3.3, 1.8 Hz, CH*H*-CH_2F), 4.38 (dd, 1H, *J* = 10.5, 4.9 Hz, H-6), 4.14 (dddd, 1H, *J* = 30.3, 11.9, 4.6, 3.1 Hz, C*H*HF), 3.95 (dddd, 1H, *J* = 27.1, 12.1, 5.5, 3.4 Hz, CH*H*F), 3.83 (t, 1H, *J* = 10.3 Hz, H-6), 3.79 (t, 1H, *J* = 9.5 Hz, H-4), 3.69 (dd, 1H, *J* = 10.0, 7.9 Hz, H-2), 3.57 (td, 1H, *J* = 9.7, 5.0 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 165.4 (C=O), 136.8 (C_q Ph), 133.5, 130.0 (CH_{arom}), 129.5 (C_q Bz), 129.2, 128.6, 128.5, 128.3, 126.3, 126.2 (CH_{arom}), 103.0 (C-1), 101.6 (CHPh), 82.5 (d, *J* = 170.5 Hz, *C*H_2F), 78.8 (C-4), 71.7 (C-3), 69.5 (d, *J* = 20.2 Hz, *C*H_2-CH_2F), 68.5 (C-6), 66.7 (C-5), 64.9 (C-2); Diagnostic peaks α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.89 (t, 0.17H, *J* = 9.9 Hz, H-3), 5.53 (s, 0.17H, C*H*Ph), 5.12 (d, 0.17H, *J* = 3.6 Hz, H-1), 4.33 (dd, 0.17H, *J* = 10.4, 5.0 Hz, H-6), 3.38 (dd, 0.17H, *J* = 10.4, 3.6 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 101.8, 99.5 (C-1), 82.4 (d, *J* = 170.8 Hz), 79.6, 68.9, 67.8 (d, *J* = 20.2 Hz), 63.1, 61.8; HRMS: $[M+NH_4]^+$ calcd for $C_{22}H_{26}FN_4O_6$ 461.18309 found 461.18292.



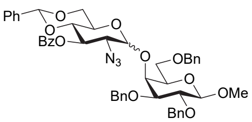
Methyl 4-*O*-(2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (4E). Donor **4** and acceptor **26** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by flash column chromatography (19/1 to 4/1 pentane/EtOAc) to yield glycosylation product **4E** (60 mg, 71 µmol, 71%, α:β = 1:6) as a white solid. R_f: 0.67 (4/1 pentane/EtOAc). IR (thin film): 696, 733, 914, 999, 1026, 1045, 1090, 1177, 1263, 1314, 1366, 1452, 1730, 2108, 2866, 2899; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.10 – 8.04 (m, 2H, CH_{arom}), 7.61 – 7.53 (m, 1H, CH_{arom}), 7.49 – 7.24 (m, 22H, CH_{arom}), 5.40 (s, 1H, C*H*Ph), 5.19 (t, 1H, *J* = 9.8 Hz, H-3'), 4.90 (d, 1H, *J* = 10.8 Hz, C*H*H Bn), 4.83 (d, 1H, *J* = 10.8 Hz, CH*H* Bn), 4.81 – 4.73 (m, 2H, 2xC*H*H Bn), 4.67 – 4.60 (m, 2H, CH*H* Bn, H-1), 4.42 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.31 (d, 1H, *J* = 8.0 Hz, H-1'), 4.17 (dd, 1H, *J* = 10.6, 5.0 Hz, H-6'), 4.08 – 3.98 (t, 1H, *J* = 9.4 Hz, H-4), 3.96 (dd, 1H, *J* = 10.8, 2.4 Hz, H-6), 3.86 (t, 1H, *J* = 9.3 Hz, H-3), 3.79 – 3.74 (m, 1H, H-5), 3.71 (dd, 1H, *J* = 10.7, 1.7 Hz, H-6), 3.61 (t, 1H, *J* = 9.5 Hz, H-4'), 3.54 (dd, 1H, *J* = 9.6, 3.7 Hz, H-2), 3.52 – 3.45 (m, 2H, H-2', H-6'), 3.39 (s, 3H, CH_3 OMe), 3.08 (td, 1H, *J* = 9.7, 5.0 Hz, H-5'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 165.3 (C=O), 139.3, 138.3, 137.6, 136.9 (C_q), 133.4, 129.9 (CH_{arom}), 128.9 (C_q Bz), 128.6, 128.5, 128.5, 128.3, 128.3, 128.2, 127.9, 127.8, 126.2 (CH_{arom}), 101.5, 101.4 (CHPh, C-1'), 98.4 (C-1), 80.1 (C-3), 79.1 (C-2), 78.9 (C-4'), 76.8 (C-4), 75.6, 73.7, 73.6 (CH_2 Bn), 72.0 (C-3'), 69.7 (C-5), 68.6 (C-6'), 67.8 (C-6), 66.1 (C-5'), 65.6 (C-2'), 55.5 (OMe); Diagnostic peaks α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.91 (d, 0.17H, *J* = 3.9 Hz, H-1'), 5.80 (t, 0.17H, *J* = 10.0 Hz, H-3'), 5.47 (s, 0.17H, C*H*Ph), 5.15 (d, 0.17H, *J* = 10.7 Hz, C*H*H Bn), 4.74 (d, 0.17H, *J* = 12.0 Hz, C*H*H Bn), 4.09 (t, 0.17H, *J* = 9.2 Hz), 3.29 (dd, 0.17H, *J* = 10.5, 3.9 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 165.6, 138.6, 138.1, 137.9, 137.0, 133.4, 130.0, 129.6, 129.0, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 127.6, 127.6, 127.4, 101.6 (CHPh), 98.6 (C-1'), 97.7 (C-1), 82.1, 80.7, 79.5, 75.0, 73.6, 73.3, 72.8, 69.5, 69.3, 68.9, 68.7, 63.7, 61.9, 55.5; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{53}N_4O_{11}$ 861.37053, found 861.37081.



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

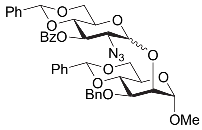


2,2-Difluoroethyl 2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranoside (4G). Donor **4** and 2,2-difluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations and purified by flash column chromatography (1/1/0 to 0/1/0 to 0/19/1 pentane/toluene/EtOAc) to yield glycosylation product **4G** (38.6 mg, 84 µmol, 84%, α:β = 2.7:1) as a white solid. R$_f$: 0.49 (19/1 toluene/EtOAc). IR (thin film): 709, 997, 1026, 1069, 1094, 1265, 1726, 2108, 2870; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.11 – 8.05 (m, 2H, CH$_{arom}$), 7.63 – 7.53 (m, 1H, CH$_{arom}$), 7.50 – 7.36 (m, 4H, CH$_{arom}$), 7.34 – 7.27 (m, 3H, CH$_{arom}$), 6.02 (tt, 1H, *J* = 55.1, 4.2 Hz, C*H*F_2), 5.91 – 5.81 (m, 1H, H-3), 5.53 (s, 1H, C*H*Ph), 5.11 (d, 1H, *J* = 3.6 Hz, H-1), 4.33 (dd, 1H, *J* = 10.4, 4.9 Hz, H-6), 4.07 (ddd, 1H, *J* = 14.8, 6.4, 3.7 Hz, H-5), 3.99 – 3.77 (m, 4H, H-4, H-6), 3.42 (dd, 1H, *J* = 10.4, 3.6 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 165.5 (C=O Bz), 136.8 (C$_q$), 133.5, 130.1 (CH$_{arom}$), 129.5 (C$_q$ Bz), 128.5, 128.3, 126.2 (CH$_{arom}$), 113.7 (t, *J* = 241.7 Hz, CHF_2), 101.8 (CHPh), 99.8 (C-1), 79.4 (C-4), 69.3 (C-3), 68.7 (C-6), 67.6 (t, *J* = 29.0 Hz, *C*H_2-CHF_2), 63.5 (C-5), 61.8 (C-2); Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.97 (tdd, 0.37H, *J* = 55.2, 4.8, 3.5 Hz, C*H*F_2), 5.51 (s, 0.37H, C*H*Ph), 5.42 (t, 0.37H, *J* = 9.8 Hz, H-3), 4.63 (d, 0.37H, *J* = 7.9 Hz, H-1), 4.38 (dd, 0.37H, *J* = 10.5, 5.0 Hz, H-6), 4.12 – 3.99 (m, 0.37H, C*H*H-CHF_2), 3.98 – 3.76 (m, 1.11H, CH*H*-CHF_2, H-4, H-6), 3.69 (dd, 0.37H, *J* = 10.0, 7.9 Hz, H-2), 3.58 (td, 0.37H, *J* = 9.8, 5.0 Hz, H-5); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 165.4, 136.7, 133.5, 130.0, 129.4, 129.2, 128.6, 126.2, 113.8 (t, *J* = 241.5 Hz), 103.1, 101.7, 78.7 (C-4), 71.5 (C-3), 69.1 (t, *J* = 29.0 Hz, *C*H_2-CHF_2), 68.4 (C-6), 66.8 (C-5), 64.9 (C-2); HRMS: $[M+H]^+$ calcd for $C_{22}H_{22}F_2N_3O_6$ 462.14712, found 462.14699.

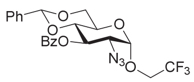


Methyl 4-*O*-(2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (4H). Donor **4** and acceptor **28** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified by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

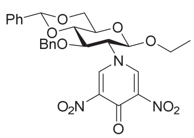
2.7 Hz, H-4); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 105.1 (C-1), 102.7 (C-1'), 101.5 (CHPh), 81.2, 79.6, 78.9, 75.3, 74.6, 73.9, 73.6, 73.3, 71.7, 69.4, 68.5, 66.2, 65.0, 57.3; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{53}N_4O_{11}$ 861.37053, found 861.37067.



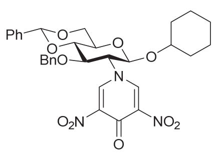
Methyl 2-*O*-(2-azido-3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (4I). Donor **4** and acceptor **29** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 h at -40°C) and purified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



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

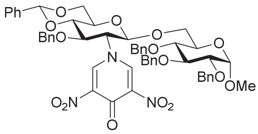


Ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-β-D-glucopyranoside (5A). Donor **5** and ethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 1 hour at -40°C) and purified by flash column chromatography (19/1 to 8/2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

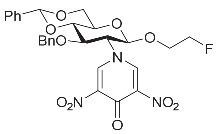


Cyclohexyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-β-D-glucopyranoside (5B). Donor **5** and cyclohexanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 1 hour at -40°C) and purified by flash column chromatography (19/1 to 8/2 pentane/EtOAc) to yield 51 mg of glycosylation product **5B** as an inseperable mixture with donor 5 (13 mg 5, 38 mg

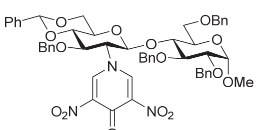
5B, 63 µmol, 63%, α:β = <1:20) as a yellow solid. R_f: 0.75 (7/3 pentane/EtOAc). R_f: 0.55 (7/3 pentane/EtOAc); IR: (thin film): 697, 718, 749, 789, 910, 997, 1092, 1212, 1302, 1330, 1516, 1623, 1674, 2931; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.60 (s, 2H, CH pyridone), 7.56 (d, 2H, *J* = 4.7 Hz, CH_{arom}), 7.48 – 7.33 (m, 3H, CH_{arom}), 7.10 – 6.96 (m, 5H, CH_{arom}), 5.65 (s, 1H, C*H*Ph), 5.41 (d, 1H, *J* = 8.2 Hz, H-1), 4.71 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.66 – 4.50 (m, 2H, CH*H* Bn, H-3), 4.44 (dd, 1H, *J* = 10.6, 5.2 Hz, H-6), 3.98 – 3.80 (m, 3H, H-4, H-5, H-6), 3.79 – 3.61 (m, 2H, C*H* Cy, H-2), 1.91 – 1.77 (m, 1H, CH_2 Cy), 1.71 – 1.54 (m, 2H, CH_2 Cy), 1.54 – 1.45 (m, 1H, CH_2 Cy), 1.43 – 0.96 (m, 6H, CH_2 Cy); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 160.5 (C=O pyridone), 141.6 (C_q NO_2 pyridone), 141.4 (CH pyridone), 137.1, 136.7 (C_q), 128.8, 128.6, 128.4, 126.3 (CH_{arom}), 101.9 (CHPh), 98.1 (C-1), 82.7 (C-4), 78.8 (CH Cy), 75.6 (C-3), 74.8 (CH_2 Bn), 74.0 (C-2), 68.8 (C-6), 65.7 (C-5), 33.3, 31.7, 25.3, 23.9, 23.6 (CH_2 Cy); HRMS: $[M+H]^+$ calcd for $C_{31}H_{34}N_3O_{10}$ 608.22387, found 608.22352.



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

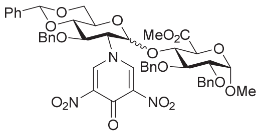


2-Fluoroethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-β-D-glucopyranoside (5D). Donor **5** and 2-fluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 1 hour at -40°C) and purified by flash column chromatography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

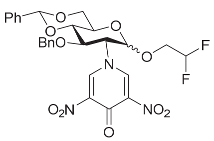


Methyl 4-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (5E). Donor **5** and acceptor **26** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (9/1 to 7/3 pentane/EtOAc) to yield glycosylation product **5E** (54 mg, 56 µmol, 56%, α:β = <1:20) as a yellow solid. R_f: 0.37 (7/3 pentane/EtOAc). $[\alpha]_D^{23}$ = +83.3° (*c* = 0.84, $CHCl_3$); IR (thin film): 696, 734, 997, 1028, 1039, 1092, 1209, 1302, 1327, 1454, 1522, 1682, 2862, 2900, 3030, 3065; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC, HMBC, NOESY): δ 7.74 (s, 2H, CH pyridone), 7.57 – 7.53 (m, 2H, CH_{arom}), 7.49 – 7.38 (m, 8H, CH_{arom}), 7.36 – 7.25 (m, 13H, CH_{arom}), 7.04 – 7.00 (m, 2H, CH_{arom}), 5.57 (s, 1H, C*H*Ph), 4.90 (d, 1H, *J* = 11.7 Hz, C*H*H

Bn), 4.77 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.74 (d, 1H, *J* = 12.3 Hz, C*H*H Bn), 4.69 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.66 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.63 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.56 (d, 1H, *J* = 12.3 Hz, CH*H* Bn), 4.54 (d, 1H, *J* = 3.6 Hz, H-1), 4.35 (d, 1H, *J* = 8.2 Hz, H-1'), 4.27 – 4.20 (m, 2H, CH*H* Bn, H-6'), 3.92 (t, 1H, *J* = 9.5 Hz, H-4), 3.70 (t, 1H, *J* = 9.3 Hz, H-3), 3.67 (t, 1H, *J* = 9.0 Hz, H-4'), 3.58 (t, 1H, *J* = 10.4 Hz, H-6'), 3.53 – 3.45 (m, 2H, H-2, H-3'), 3.43 (dd, 1H, *J* = 11.4, 1.5 Hz, H-6), 3.40 – 3.34 (m, 1H, H-5), 3.31 (s, 2H, CH_3 OMe), 3.18 (dd, 1H, *J* = 10.5, 8.3 Hz, H-2'), 3.04 (dd, 1H, *J* = 11.3, 2.6 Hz, H-6), 2.92 (td, 1H, *J* = 9.8, 5.1 Hz, H-5'); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC, HMBC): δ 159.3 (C=O pyridone), 141.8 (C_q NO_2 pyridone), 139.6 (CH pyridone), 139.4, 138.1, 137.8, 136.8, 135.7 (C_q), 129.6, 129.3, 129.2, 129.0, 128.9, 128.6, 128.6, 128.5, 128.4, 128.1, 128.1, 127.8, 126.1 (CH_{arom}), 101.8 (CHPh), 98.1 (C-1), 97.6 (C-1'), 82.4 (C-4'), 79.7 (C-2), 79.2 (C-3), 75.3 (CH_2 Bn), 74.4 (C-4), 73.9, 73.6, 73.5 (CH_2 Bn), 73.0 (C-3'), 72.5 (C-2'), 69.2 (C-5), 68.4 (C-6'), 68.1 (C-6), 65.6 (C-5'), 55.7 (OMe); HRMS: $[M+H]^+$ calcd for $C_{53}H_{54}N_3O_{15}$ 972.35494, found 972.35519.

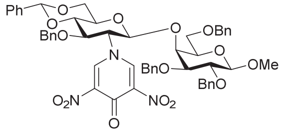


Methyl (Methyl 4-*O*-[3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-α/β-D-glucopyranosyl]-2,3-di-*O*-benzyl-α-D-glucopyranosyl uronate) (5F). Donor **5** and acceptor **27** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18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

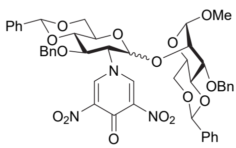


2,2-Difluoroethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-α/β-D-glucopyranoside (5G). Donor **5** and 2,2-difluoroethanol were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 1 hour at -40°C) and purified by flash column chromatography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

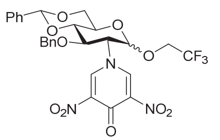
3), 75.1 (CH_2 Bn), 73.7 (C-2), 68.9 (t, *J* = 27.8 Hz, CH_2-CHF_2), 68.6 (C-6), 65.8 (C-5); HRMS: $[M+H]^+$ calcd for $C_{27}H_{26}F_2N_3O_{10}$ 590.15808, found 590.15741.



Methyl 4-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(3,5-dinitro-4-pyridone)-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (5H). Donor **5** and acceptor **28** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (for an additional 18 hours at -40°C) and purified by flash column chromatography (9/1 to 7/3 pentane/EtOAc) to yield glycosylation product **5H** (51 mg, 52 µmol, 52%, α:β = <1:20) as a yellow solid. R_f: 0.49 (7/3 pentane/EtOAc). $[\alpha]_D^{20}$ = +35.5° (*c* = 0.85, $CHCl_3$); IR (thin film): 698, 750, 999, 1072, 1094, 1213, 1454, 1522, 1682, 2868; ^1H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.20 (s, 2H, CH pyridone), 7.55 – 7.49 (m, 2H, CH_{arom}), 7.47 – 7.40 (m, 3H, CH_{arom}), 7.40 – 7.15 (m, 18H, CH_{arom}), 7.07 – 7.00 (m, 2H, CH_{arom}), 5.63 (s, 1H, C*H*Ph), 5.03 (d, 1H, *J* = 8.3 Hz, H-1'), 4.80 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.64 (d, 1H, *J* = 10.4 Hz, C*H*H Bn), 4.61 (d, 1H, *J* = 12.3 Hz, C*H*H Bn), 4.57 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 4.50 (s, 2H, CH_2 Bn), 4.47 (d, 1H, *J* = 12.3 Hz, CH*H* Bn), 4.29 (d, 1H, *J* = 10.4 Hz, CH*H* Bn), 4.20 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6'), 4.13 (d, 1H, *J* = 7.6 Hz, H-1), 3.91 (d, 1H, *J* = 2.6 Hz, H-4), 3.88 – 3.78 (m, 2H, H-3', H-4'), 3.74 (t, 1H, *J* = 10.3 Hz, H-6'), 3.70 (dd, 1H, *J* = 9.9, 8.4 Hz, H-2'), 3.66 – 3.52 (m, 2H, H-6, H-6), 3.46 (s, 4H, CH_3 OMe, H-5), 3.41 – 3.33 (m, 2H, H-3, H-5'), 2.93 (dd, 1H, *J* = 9.6, 7.6 Hz, H-2); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 159.4 (C_q pyridone), 141.6 (C_q NO_2 pyridone), 140.5 (CH pyridone), 138.2, 138.0, 137.6, 136.6, 135.6 (C_q), 129.6, 129.3, 129.1, 129.1, 128.9, 128.7, 128.6, 128.6, 128.4, 128.4, 128.1, 128.0, 127.7, 127.5, 126.1 (CH_{arom}), 104.8 (C-1), 101.8 (CHPh), 99.6 (C-1'), 82.3 (C-4'), 80.2, 80.2 (C-2, C-3), 75.4 (CH_2 Bn), 74.6 (C-4), 74.5, 74.4 (CH_2 Bn), 74.2 (C-3'), 73.5 (CH_2 Bn), 72.5 (C-5), 72.3 (C-2'), 68.6 (C-6), 68.2 (C-6'), 66.2 (C-5'), 57.3 (OMe); ^{13}C-HMBC-GATED NMR ($CDCl_3$, 101 MHz): δ 104.8 (*J* = 159 Hz, C-1), 99.6 (*J* = 165 Hz, C-1'); HRMS: $[M+H]^+$ calcd for $C_{53}H_{54}N_3O_{15}$ 972.35494, found 972.35542.



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



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

Footnotes and references

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