Structure-reactivity relationships in glycosylation chemistry

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Chapter 5: Influence of N-protecting groups on the reactivity of glycosyl acceptors

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Results from this chapter are published in

Chemical Science, 2023, 14, 1532-1542

Introduction

2-Deoxy-2-aminosugars are important constituents of many biologically relevant carbohydrates and glycoconjugates, such as the glycosaminoglycans,[1, 2] various cell surface carbohydrate antigens, such as the blood group determinants, bacterial oligosaccharides,[3, 4] including pathogenic bacteria such as *Acinetobacter Baumannii,* an opportunistic pathogen with high rates of antibiotic resistance[5] or *Vibrio vulnificus,* a bacterium that causes sepsis and necrotizing fasciitis, related to *Vibrio cholera,* the causative agent of cholera[6] as well as in many secondary metabolites.[7] (***Figure 1)***. Many different aminosugars are found in nature, varying in the position on the carbohydrate ring (with a C-2-amino group occurring most often), the stereochemistry, as well as the nature of the substituent on the amine, which can be an *N*-alkyl, *N*-acyl/acetyl, *N*-sulfate, *N*-phosphate group. Non-substituted amines also commonly occur.

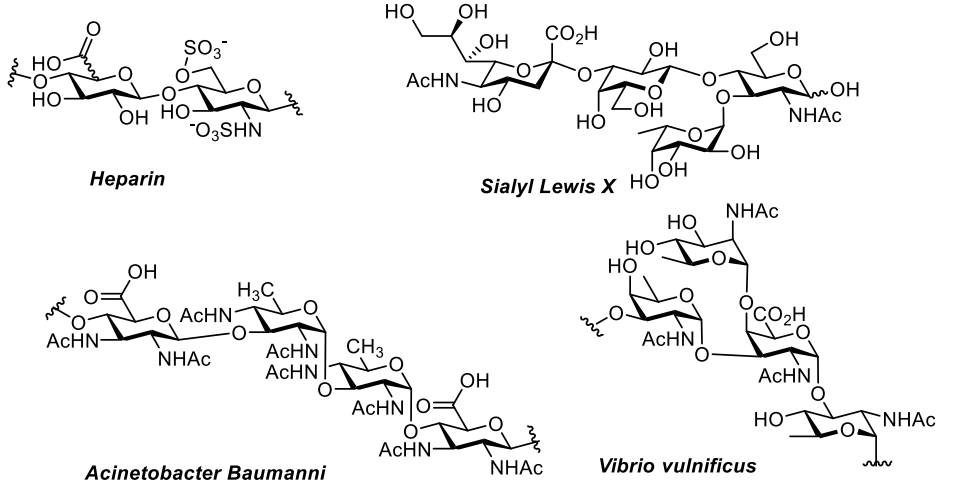


Figure 1*: Representative structures of glycosaminoglycans (Heparin), carbohydrate antigens (sialyl Lewis X) and bacterial oligosaccharides (A. Baumannii and V. vulnificus) containing deoxy-amino sugars.*

Because of their biological relevance, many 2-deoxy-2-aminosugar containing oligosaccharides have been synthesised to date.[8, 9] To mask the amino group in the building blocks different types of protecting groups have been used. The *N*-protecting group in the donor glycoside is primarily selected based on the type of glycosidic linkage that has to be constructed. To install *cis*-glycosidic linkages, an azide on C-2 is by far the most commonly applied (and indeed almost solely used), while the construction of *trans*-linkages can be controlled by the use carbamate functionalities of amide groups. The previous chapter has shown that the nature of the functional groups on the carbohydrate ring also critically influence the nucleophilicity of the alcohol

function in the acceptor. A systematic series of 60 ether and ester protected acceptors was tested and showed that the reactivity of the acceptor is dependent on both the configuration and the protecting group pattern of the acceptor: equatorial alcohols in acceptors are more reactive than axial alcohols. Also, the configuration of the protected alcohols next to the OH-group are important, and acceptors in which the neighbouring protected alcohols take up an equatorial position, are more reactive than acceptors in which one of the flanking protected alcohols is axial. With regard to protecting group patterns, benzoyl protected acceptors are less reactive than benzyl protected acceptors. It is important to note that the configuration of the ester is also important, and substituting an axial ether for an ester has significantly less effect on the reactivity of the acceptor than substituting an equatorial ether for an ester.

It has long been recognized that the nature of the *N*-protecting group can have a significant effect on the reactivity of the aminosugar alcohol acceptor, although systematic investigations are relatively scarse.[10] A prime example is presented by the *N*-acetyl glucosamine C-4-OH, which is a notoriously difficult acceptor to glycosylate.[11-16] Through a systematic survey Crich and Dudkin determined that intramolecular hydrogen bonding by the acetamide functionality was a prime factor in reducing the reactivity of the C-4-OH. Through the use of different *N*-protecting groups (a phthalimide or azide) the reactivity of the GlcN-C-4-OH could be effectively enhanced.

This chapter describes the influence of three different *N*-protecting groups on the reactivity of glycosyl alcohol nucleophiles: an azide, a trifluoroacetyl (TFA) and trichloroacetyl (TCA) group, as these are amongst the most commonly employed *N*-protecting groups.[17-19] The influence of these protecting groups on the reactivity of the acceptor is investigated for both the C-3-OH and C-4-OH glucosamine acceptors. To investigate whether the orientation of the *N*-protecting groups is important for its effect on the reactivity of the acceptor, just like in the *O*-protecting groups in ether/ester protected acceptors, both glucosamine and mannosamine acceptors are probed.

The method used for measuring the reactivity of the acceptors is based on the stereoselectivity observed in glycosylation reactions with phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**Donor A**, ***Figure 2A***) and phenyl 2-deoxy-2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**Donor B**). As described before, the stereoselectivity of glycosylation reactions of these is a measure for the reactivity of the acceptor.[20] More nucleophilic acceptors, provide β-selective glycosylations, while less nucleophilic acceptors lead to α-selectivity. The mechanism to explain the change in stereoselectivity is shown in ***Figure 2***. Both thioglycoside donors form an α-triflate upon activation with Ph_2SO and Tf_2O. The more reactive acceptors can substitute this triflate in an S_N2 like mechanism, while less nucleophilic acceptors react with the corresponding β-triflate or an oxocarbenium ion-like species to form the α-product.[21] **Donor B** shows higher β-selectivity with the same acceptor than **Donor A**

because the electron-withdrawing azide on C-2 stabilises the anomeric triflate rendering the S_N2 substitution of the α-triflate more predominant.[22]

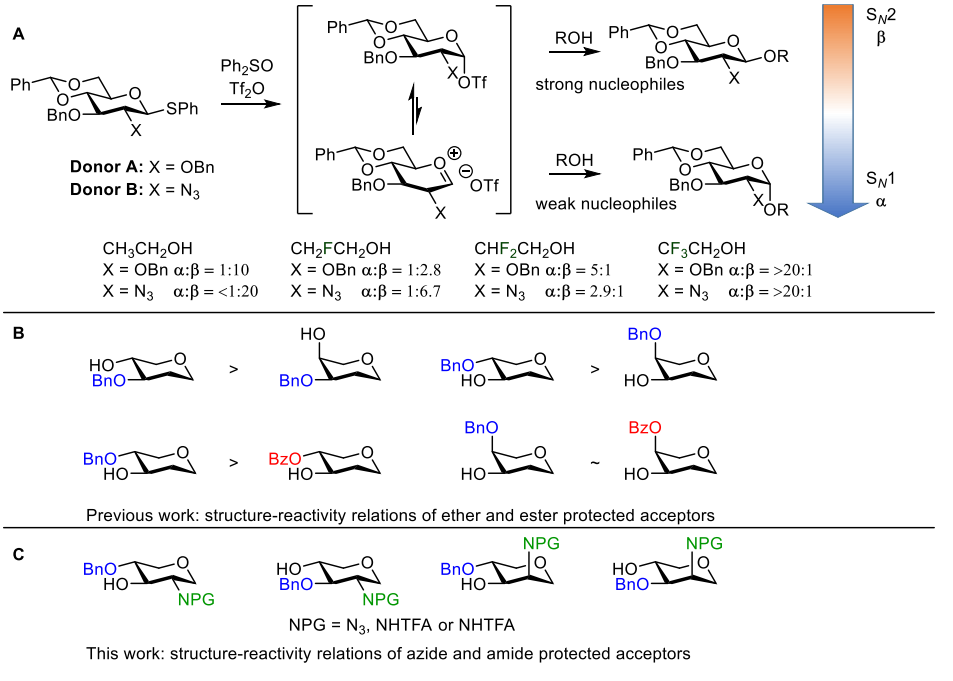


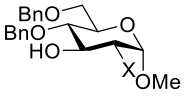
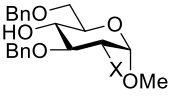
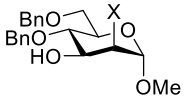
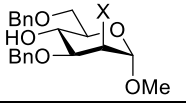
Figure 2: A: *Glycosylation mechanisms and the relation between stereoselectivity of* ***donor A*** *and* ***Donor B*** *and nucleophilicity of the acceptor,* ***B:*** *the reactivity trends found in chapter 4 and* ***C:*** *the structure-reactivity relations investigated in this work.*

Results and discussion

In this study, 12 acceptors that can be divided in four groups based on the type of 2-deoxy-2-aminosugar and the position of the hydroxyl function, were reacted with **Donor A** and **Donor B**: 1) glucosamine C-3-OH acceptors **1c**-**1e**; 2) glucosamine C-4-OH acceptors **2b**-**2d**; 3) mannosamine C-3-OH acceptors **3c**-**3e** and 4) mannosamine C-4-OH acceptors **2b**-**2d**. The results are summarized in ***table 1***, in which also the results of the corresponding glucose and mannose acceptors **1a**, **1b**, **2a**, **3a**, **3b** and **4a** are provided a reference (see Chapter 4). When looking at the results of the glucosamine C-3-OH acceptors, it becomes apparent that the nature of the protecting group next to the alcohol has a significant influence its reactivity. An azide flanking the free hydroxy group decreases the reactivity of the acceptor more than a neighboring benzyl ether and about as much as as a benzoyl group (acceptors **1a**-**1c**). The trichloro-

and trifluoroacetamides next to the alcohol decrease the reactivity of the acceptor even more, with the disarming effect of the trifluoroacetamide being stronger than that of the trichloroacetamide (acceptors **1d** and **1e**). Note how switching an *O*-benzyl group to a *N*-trifuoroacetyl group completely reverses the stereoselectivity of the acceptor, with acceptor **1a** giving full β-selectivity with **Donor B**, while acceptor **1d** gives nearly full α-selectivity with **Donor B**. On the other hand, the nature of the *N*-protecting group has an almost negligible effect on the reactivity of the C-4-OH glucose acceptors. All tested C-4-OH acceptors tested in this work provide high yielding glycosylations with very similar stereoselectivity with both **Donor A** and **Donor B**, regardless of the nature of the group on C-2 being an *O*-benzyl, an azide, a *N*-trifluoroacetamide or a *N*-trichloroacetamide (acceptors **2a**-**2d**). The results in the C-3-OH mannosamine series, show that, in line with the survey on *O*-protecting groups, not only the nature of the *N*-protecting groups is important, but also the configuration of the *N*-functional group next to the acceptor alcohol is relevant for the reactivity of the acceptor. Similar to the differences in reactivity observed between glucose and mannose (acceptors **1a** and **3a**), where the alcohol next to an axial benzyl group is less reactive than the alcohol next to the equatorial one, the acceptor next to the equatorial azide (acceptor **1a**) is more reactive than the acceptor next to the axial azide (acceptor **3a**). Furthermore, in line with the reactivity of benzoylated glucose/galactose/mannose systems of the previous chapter, it turns out that the difference in reactivity between an axial benzyl group and an axial azide is less than the difference between an equatorial benzyl group and the corresponding azide (acceptor **1a** vs **1c** and acceptor **3a** vs **3c**). Similarly, there is little difference between the axial azide and the axial *N*-trifluoroacetyl or *N*-trichloroacetyl groups (acceptors **3c**-**3e**) in contrast to the different effects when these groups are flanking the nucleophilic hydroxy group in an equatorial orientation (acceptor **1c**-**1e**). It is noteworthy however, that in acceptors **3c**-**3e** the *N*-trifluoroacetyl protected acceptor (**3d**) seems to be more reactive than *N*-trichloroacetyl protected acceptor **3e**, which is more reactive than azide acceptor **3c**. Finally, the nature of the protecting group has very little effect on the reactivity of the mannosamine C-4-OH acceptors. In line with the glucose/glucosamine series above, the mannose C-4-OH is not strongly effected by the nature of the function group at C-2. Whether it is an *O*-benzyl, an azide, a *N*-trifluoroacetamide or a *N*-trichloroacetamide (acceptors **4a**-**4d**) the stereoselectivity with both **Donor A** and **Donor B** is all very similar, and all glycosylations are high yielding.

Table 1: *Results of glucosamine and mannosamine acceptors with different protecting groups. The results for glucose and mannose acceptors are given for reference*

Position	Acceptor	Donor A		Donor B	
		Product (yield)	α:β	Product (yield)	α:β
3-OH glucose 	**1a** X = OBn	**1aA** (78%)	**1:2.7**	**1aB** (70%)	**<1:20**
	1b X = OBz	**1bA** (99%)	**1.8:1**	**1bB** (93%)	**1:4**
	1c X = N_3	**1cA** (83%)	**1.6:1**	**1cB** (85%)	**1:2.5**
	1d X = NHTFA	**1dA** (96%)	**>20:1**	**1dB** (100%)	**12:1**
	1e X = NHTCA	**1eA** (65%)	**11:1**	**1eB** (63%)	**3:1**
4-OH glucose 	**2a** X = OBn	**2aA** (82%)	**1:1**	**2aB** (88%)	**1:7**
	2b X = N_3	**2bA** (94%)	**1:1.1**	**2bB** (100%)	**1:3.3**
	2c X = NHTFA	**2cA** (82%)	**1.3:1**	**2cB** (100%)	**1:2.5**
	2d X = NHTCA	**2dA** (81%)	**1.1:1**	**2dB** (100%)	**1:3.5**
3-OH mannose 	**3a** X = OBn	**3aA** (82%)	**8:1**	**3aB** (70%)	**1.1:1**
	3b X = OBz	**3bA** (82%)	**10:1**	**3bB** (93%)	**1:1**
	3c X = N_3	**3cA** (100%)	**7:1**	**3cB** (75%)	**1.8:1**
	3d X = NHTFA	**3dA** (80%)	**2.3:1**	**3dB** (92%)	**1:1.2**
	3e X = NHTCA	**3eA** (57%)	**5:1**	**3eB** (80%)	**1:1**
4-OH mannose 	**4a** X = OBn	**4aA** (76%)	**1:2**	**4aB** (72%)	**<1:20**
	4b X = N_3	**4bA** (100%)	**1:2.5**	**4bB** (100%)	**1:14**
	4c X = NHTFA	**4cA** (71%)	**1:1.4**	**4cB** (77%)	**1:10**
	4d X = NHTCA	**4dA** (77%)	**1:2.7**	**4dB** (100%)	**<1:20**

Conclusion

In conclusion, structure-reactivity relationships for a set of glycosyl acceptors with different *N*-protecting groups have been established, based on the stereoselectivity of these acceptors in glycosylations with two conformationally restricted glucosyl donors. Three different *N*-protecting groups were used in this study: an azide, a trifluoroacetamide and a trichloroacetamide group. These were surveyed on the 2-position of both glucosamine and mannosamine acceptors, to investigate the difference between equatorially and axially oriented *N*-functional groups, as it was found previously that the orientation of the flanking *O*-functional groups has a large influence on the reactivity of the acceptor alcohol. Both the C-3-OH and C-4-OH acceptors in the glucosamine and mannosamine series were investigated. The orientation of the *N*-protecting group proved to be important for its effect on the reactivity of the acceptor. It was found that, in line with the previsouly studied ether/ester protected acceptors, the influence of the protecting group on the reactivity is much larger when the group

next to the alcohol is equatorial then when it is placed axial. The nature of the protecting group is also important for the reactivity with the disarming effect of an azide being similar to that of an benzoyl ester and the trichloroacetamide and trifluoroacetamide group having an larger influence on the reactivity. The difference in reactivity between the mannosamine acceptor having either an axial azide or amide is smaller with the *N*-trifluoroacetamide mannosamine C-3-OH being the most reactive in the series. The different *N*-protecting groups do not significantly influence the reactivity of the glucosamine and mannosamine C-4-OH acceptors. Overall this study has shown that the reactivity of glycosamine acceptors can be tuned by the changing the nature of the *N*-protecting group, if this is suitable positioned. The effects observed in this study can likely be transposed to galactosamine and fucosamine systems and aid in the assembly of bacterial glycans.[23, 24]

Experimental

General experimental procedures

General experimental procedures: All chemicals were of commercial grade and used as received unless stated otherwise. Dichloromethane (DCM) was stored over activated 4 Å molecular sieves for at least 24 h before use. Trifluoromethanesulfonic anhydride (Tf_2O) was distilled over P_2O_5 and stored at -20°C under a nitrogen atmosphere. Overnight temperature control was achieved by a FT902 Immersion Cooler (Julabo). Flash column chromatography was performed on silica gel 60 Å (0.04 – 0.063 mm, Screening Devices B.V.). Size-exclusion chromatography was performed on Sephadex (LH-20, GE Healthcare Life Sciences) by isocratic elution with DCM/MeOH (1/1, v/v). Thin-layer chromatography (TLC) analysis was conducted on TLC silica gel 60 plates (Kieselgel 60 F254, Merck) with UV detection by (254 nm) and by spraying with 20% sulfuric acid in ethanol or by spraying with a solution of $(NH_4)_6Mo_7O_{24}{\cdot}H_2O$ (25 g/L) and $(NH_4)_4Ce(SO4)_4{\cdot}2H_2O$ (10 g/L) in 10% aq. sulfuric acid followed by charring at ±250 °C. High-resolution mass spectrometry (HRMS) was performed on a Thermo Finnigan LTQ Orbitrap mass spectrometer equipped with an electrospray ion source in positive-ion mode (source voltage 3.5 kV, sheath gas flow 10, capillary temperature 275 °C) with resolution R = 60.000 at m/z 400 (mass range of 150-4000) and dioctylphtalate (m/z=391.28428) as lock mass, or on a Waters Synapt G2-Si (TOF) equipped with an electrospray ion source in positive mode (source voltage 3.5 kV) and LeuEnk (m/z = 556.2771). as internal lock mass. 1H and 13C NMR spectra were recorded on Bruker AV-400, Bruker DMX-400, and Bruker AV-500 NMR instruments. Chemical shifts (δ) are given in parts per million (ppm) relative to tetramethylsilane as an internal standard or the residual signal of the deuterated solvent. Coupling constants (J) are given in Hertz (Hz). All presented 13C-APT spectra are proton-decoupled. NMR peak assignments were made using COSY and HSQC. When necessary, additional NOESY, HMBC and HMBC-GATED experiments were used to further elucidate the structure. The anomeric product ratios were based on careful analysis of the crude reaction mixture and the purified reaction product by integration of representative 1H NMR signals. IR spectra were recorded on a Shimadzu FTIR-

8300 IR spectrometer and are reported in cm-1. Specific rotations were measured on a Propol automatic polarimeter or an Anton-Paar MCP-100 modular circular polarimeter at 589 nm unless otherwise stated.

General procedure I: Ph_2SO/Tf_2O meditated glycosylations

Donor (0.1 mmol, 1 eq), Ph_2SO (0.13 mmol, 1.3 eq) and TTBP (0.25 mmol, 2.5 eq) were coevaporated twice with toluene, dissolved in 2 mL DCM and stirred for 30 min at RT with 3A molecular sieves. The solution was cooled to -80 ^{0}C and Tf_2O (22 µL, 0.13 mmol, 2 eq) was added. The reaction mixture was allowed to warm to −60 ^{0}C and then recooled to −78 ^{0}C, after which the acceptor (0.2 mmol, 2 eq) in DCM (0.4 mL, 0.5 M) was added. The reaction mixture was allowed to warm to −40 ^{0}C for and stirred between 4-24 hr at that temperature. The reaction was quenched with 1 mL sat aq $NaHCO_3$, and the mixture was diluted with DCM. The solution was transferred to a separatory funnel, water was added, the layers were separated, and the water phase was extracted once more with DCM. The combined organic layers were dried over MgSO4, filtered, and concentrated in vacuo. Purification by silica gel flash column chromatography and/or sephadex LH-20 size-exclusion chromatography yielded the glycosylation product as a mixture of anomers.

General procedure II: azide reduction

The azide (1 eq) was dissolved in anhydrous THF, after which $LiAlH_4$ (1.5 eq, soln in Et_2O, THF or 2-MeTHF) was added dropwise while gaseous by-products were allowed to escape. After full conversion, the reaction mixture was cooled to 0 °C, and excess reagents were destroyed by careful and dropwise addition of water. The precipitated aluminium salts were filtered off and the solution was concentrated under reduced pressure. The residue was purified over silica or used directly in subsequent reactions.

General procedure III: TFA installation

The amine (1 eq) was dissolved in DCM, after which TEA (1.5 eq) and TFAA (1.5 eq) were added. After TLC indicates full conversion, the reaction mixture was diluted with DCM and washed with water. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica chromatography to yield the title compound.

General procedure IV: TCA installation

The amine (1 eq) was dissolved in DCM, after which TEA (1.5 eq) and trichloroacetyl chloride (1.5 eq) were added. After TLC indicates full conversion, the reaction mixture was diluted with DCM and washed with water. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica chromatography to yield the title compound.

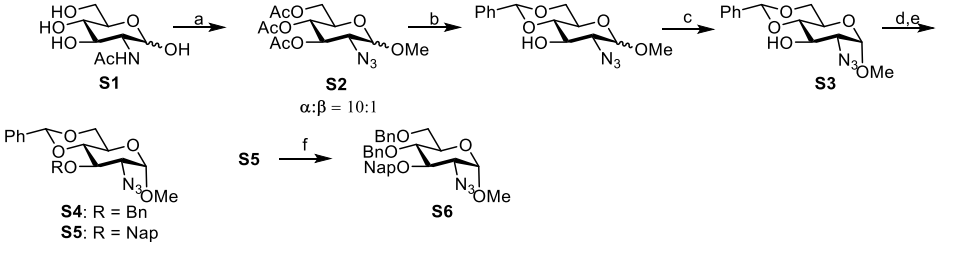
General procedure V: DDQ mediated Nap deprotection

Nap protected acceptor (1 eq) was dissolved in 9:1 DCM/H_2O with DDQ (2 eq). After After TLC indicates full conversion, the reaction mixture was diluted with DCM and washed twice with sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica chromatography to yield the title compound.

General procedure VI: reductive benzylidene opening

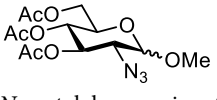
The benzylidene (1 eq) was dissolved in DCM and cooled to 0 °C, after which triethylsilane (10 eq) and TFA (10 eq) were added. After TLC indicates full conversion, the reaction mixture was quenched with sat. aq. $NaHCO_3$ and extracted twice with DCM. Combined organic phases were washed with sat .aq $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica chromatography to yield the title compound.

Preparations of acceptors



Scheme S1*: preparation of α-OMe glucosazide intermediates: reagents and conditions: a) i: amberlite-H⁺, methanol, reflux, ii: $Ba(OH)_2$, water, reflux, iii: Imidazole-1-sulfonyl azide-H_2SO_4, K_2CO_3, $CuSO_4(H_2O)_5$, methanol, iv: Ac_2O, pyridine, DMAP, 65% over 4 steps; b) i: Na, methanol, ii: PTSA, $PhCH(OMe)_2$, acetonitrile, 60 °C, 300 mbar, 71% over 2 steps; c) recrystallization from acetone/pentane; d) for* ***S4****: BnBr, NaH, DMF, 87%, e) for* ***S5****: NapBr, NaH, DMF, 88%; f) i: PTSA, methanol, 50 °C, ii: BnBr, NaH, DMF, 100% over 2 steps*

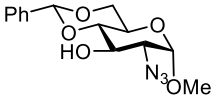
Methyl 2-deoxy-2-azido-3,4,6-tri-*O*-acetyl-α,β-D-glucopyranoside (S2)



N-acetylglucosamine (**S1**, 30 g, 136 mmol) was dissolved in 700 mL methanol with 50 g amberlite-H^+ and heated to a reflux overnight, after which the reaction mixture was filtered and concentrated under reduced pressure. The residue was dissolved in 1 L water with 50 g $BaOH(H_2O)_8$. After overnight reflux, the reaction mixture was cooled to RT and neutralised with dry ice (pH 7). Salts were removed by filtration and the solution was concentrated under reduced pressure. The residue was dissolved in methanol with K_2CO_3 (47 g, 340 mmol, 2.5 eq) and imidazole-1-sulfonyl azide hydrogen sulfate[25] (42,1 g, 163 mmol, 1.2 eq) and $CuSO_4(H_2O)_5$ (340 mg, 1.36 mmol, 0.01 eq). When TLC (EA/MeOH/H_2O 8:1:1, Rf = 0.6) shows a single spot, the reaction mixture was concentrated and dissolved in pyridine (274 mL, 3.4 mol, 25 eq). The solution was cooled to 0 °C and Ac_2O (103 mL, 1.08 mol, 8 eq) and DMAP (1.66 g, 13.6 mmol, 0.1 eq) were added. The reaction mixture was allowed to warm to RT overnight and concentrated. The residue was dissolved in ethyl acetate and washed with 1M HCl and sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure, yielding the title compound as a red oil. Yield: 30.6 g, 89 mmol, 65%, α:β = 10:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (dd, *J* = 10.6, 9.2 Hz, 1H, H-3), 5.05 (dd, *J* = 10.2, 9.2 Hz, 1H, H-4), 4.88 (d, *J* = 3.5 Hz, 1H, H-1), 4.29 (dd, *J* = 12.4, 4.6 Hz, 1H, H-6), 4.10 (dd, *J* = 12.4,

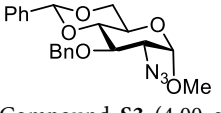
2.3 Hz, 1H, H-6), 4.01 (ddd, *J* = 10.1, 4.6, 2.3 Hz, 1H, H-5), 3.47 (s, 3H, CH_3 OMe), 3.38 (dd, *J* = 10.6, 3.5 Hz, 1H, H-2), 2.10 (s, 3H, CH_3 Ac), 2.09 (s, 3H, CH_3 Ac), 2.04 (s, 3H, CH_3 Ac); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 170.1, 169.8 (C=O), 98.8 (C-1), 70.6 (C-3), 68.6 (C-4), 67.6 (C-5), 62.0 (C-6), 61.1 (C-2), 55.7 (CH_3 OMe), 20.8, 20.8, 20.7 (CH_3 Ac). Spectra in agreement with literature.[26]

Methyl 2-deoxy-2-azido-4,6-*O*-benzylidene-α-D-glucopyranoside (S3)



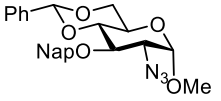
Compound **S2** (30.7 g, 89.0 mmol) was dissolved in MeOH, and a catalytic amount of sodium was added. When TLC shows full deacetylation, the reaction mixture was acidified (pH = 5) using amberlite-H^+, filtered, concentrated and coevaporated twice with toluene. The residue was dissolved in acetonitrile with PTSA-H_2O (1.69 g, 8.90 mmol, 0.1 eq) and benzaldehyde dimethyl acetal (18.8 mL, 125 mmol, 1.4 eq) and heated to 60 °C at 300 mbar. After full conversion, the reaction mixture was quenched with Et_3N (1.88 mL, 13.4 mL, 0.15 eq) and concentrated under reduced pressure. Silica chromatography (10%→20% acectone in pentane) yields the title compound as white solid. Yield: 19.5 g, 63.5 mmol, 71%, α:β = 10:1. Recrystallization from acetone/pentane yields 10 g of pure α-anomer as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H, CH_{arom}), 7.41 – 7.35 (m, 3H, CH_{arom}), 5.52 (s, 1H, C*H*Ph), 4.78 (d, *J* = 3.6 Hz, 1H, H-1), 4.27 (dd, *J* = 10.0, 4.6 Hz, 1H, H-6), 4.16 (ddd, *J* = 10.0, 9.1, 2.8 Hz, 1H, H-3), 3.82 (td, *J* = 9.7, 4.6 Hz, 1H, H-5), 3.73 (t, *J* = 10.2 Hz, 1H, H-6), 3.49 (t, *J* = 9.3 Hz, 1H, H-4), 3.43 (s, 3H, CH_3 OMe), 3.31 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2), 2.93 (d, *J* = 2.9 Hz, 1H, 3-OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0 (C_q), 129.5, 128.5, 126.4 (CH_{arom}), 102.2 (CHPh), 99.5 (C-1), 81.9 (C-4), 69.2 (C-3), 68.9 (C-6), 63.3 (C-2), 62.3 (C-5), 55.6 (CH_3 OMe). Spectra in agreement with literature.[27]

Methyl 2-deoxy-2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (S4)



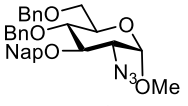
Compound **S3** (4.00 g, 13.0 mmol) was dissolved in DMF, after which BnBr (2.32 mL, 19.5 mmol, 1.5 eq) and NaH (60% dispersion in mineral oil, 781 mg, 19.5 mmol, 1.5 eq) were added. After TLC shows full conversion, the reaction mixture was quenched with 5x the volume in water. Precipitated solids were collected by filtration, dissolved in $CHCl_3$ and washed with water. The organic phase was dried with $MgSO_4$ and concentrated to yield the title compound as white powder. Yield: 4.52 g, 11.3 mmol, 87%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 2H, CH_{arom}), 7.38 (ddt, *J* = 7.0, 5.8, 1.0 Hz, 5H, CH_{arom}), 7.34 – 7.27 (m, 3H, CH_{arom}), 5.58 (s, 1H, C*H*Ph), 4.94 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.80 (d, *J* = 11.1 Hz, 1H, CH*H* Bn), 4.78 (d, *J* = 3.6 Hz, 1H, H-1), 4.29 (dd, *J* = 10.2, 4.8 Hz, 1H, H-6), 4.06 (dd, *J* = 9.9, 9.0 Hz, 1H, H-3), 3.87 (td, *J* = 9.9, 4.7 Hz, 1H, H-5), 3.76 (t, *J* = 10.3 Hz, 1H, H-6), 3.70 (t, *J* = 9.3 Hz, 1H, H-4), 3.46 – 3.42 (m, 4H, H-2, CH_3 OMe); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 137.3 (C_q), 129.2, 128.5, 128.4, 128.4, 128.0, 126.1 (CH_{arom}), 101.6 (CHPh), 99.5 (C-1), 82.9 (C-4), 76.5 (C-3), 75.2 (CH_2 Bn), 69.0 (C-6), 63.3 (C-2), 62.7 (C-5), 55.5 (CH_3 OMe). Spectra in agreement with literature.[28]

Methyl 2-deoxy-2-azido-3-*O*-(2-naphtyl)methyl-4,6-*O*-benzylidene-α-D-glucopyranoside (S5)

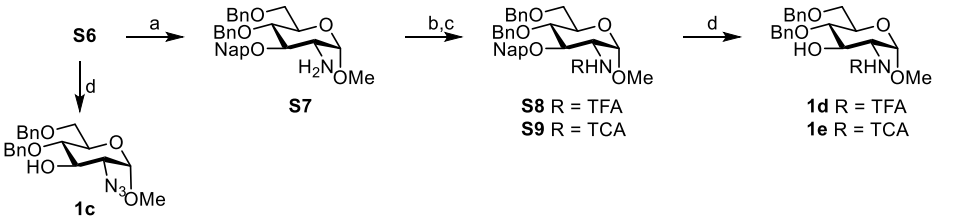


The title compound was synthesised from **S3** as described for **S4** but 2-(Bromomethyl)naphthalene was used instead of benzyl bromide. Yield: 7.73 g, 17.3 mmol, 88%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (td, *J* = 6.0, 5.4, 3.5 Hz, 3H, CH_{arom}), 7.77 – 7.73 (m, 1H, CH_{arom}), 7.53 – 7.48 (m, 3H, CH_{arom}), 7.47 – 7.43 (m, 2H, CH_{arom}), 7.40 (dt, *J* = 4.6, 2.8 Hz, 3H, CH_{arom}), 5.60 (s, 1H, C*H*Ph), 5.09 (d, *J* = 11.3 Hz, 1H, C*H*H Nap), 4.97 (d, *J* = 11.3 Hz, 1H, CH*H* Nap), 4.79 (d, *J* = 3.6 Hz, 1H, H-1), 4.30 (dd, *J* = 10.2, 4.7 Hz, 1H, H-6), 4.11 (dd, *J* = 9.9, 9.0 Hz, 1H, H-3), 3.88 (td, *J* = 9.9, 4.7 Hz, 1H, H-5), 3.80 – 3.71 (m, 2H, H-4, H-6), 3.47 (dd, *J* = 9.9, 3.6 Hz, 1H, H-2), 3.43 (s, 3H, CH_3 OMe); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.3, 135.4, 133.4, 133.2 (C_q), 129.2, 128.5, 128.3, 128.1, 127.8, 127.2, 126.3, 126.2, 126.1, 126.0 (CH_{arom}), 101.7 (CHPh), 99.5 (C-1), 82.9 (C-4), 76.5 (C-3), 75.2 (CH_2 Nap), 69.1 (C-6), 63.4 (C-2), 62.7 (C-5), 55.6 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{25}H_{25}N_3O_5NH_4$ 465.21325, found 465.21285

Methyl 2-deoxy-2-azido-4,6-di-*O*-benzyl-3-O-(2-naphtyl)methyl-α-D-glucopyranoside (S6)

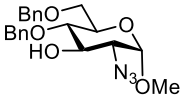


Compound **S5** (7.70 g, 17.2 mmol) was dissolved in methanol with PTSA-H_2O (327 mg, 1.72 mmol, 0.1 eq) and heated to 50 °C. After removal of the benzylidene, Et_3N (0.48 mL, 3.44 mmol, 0.2 eq) was added and the reaction mixture was concentrated under reduced pressure. The residue was coevaporated with toluene and dissolved in DMF, after which benzyl bromide (6.13 mL, 51.6 mmol, 3 eq) and sodium hydride (60% dispersion in mineral oil, 2.07 g, 51.6 mmol, 3 eq) were added. After full conversion, the reaction was quenched with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated. The residue was purified over silica (10% acetone in pentane) to yield the title compound as a colourless oil that slowly solidifies. Yield: 9.29 g, 17.4 mmol, 100%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 4H, CH_{arom}), 7.51 – 7.43 (m, 3H, CH_{arom}), 7.35 – 7.30 (m, 4H, CH_{arom}), 7.30 – 7.25 (m, 4H, CH_{arom}), 7.14 (dd, *J* = 6.7, 2.9 Hz, 2H, CH_{arom}), 5.04 (d, *J* = 10.9 Hz, 1H, C*H*H Bn/Nap), 4.99 (d, *J* = 10.9 Hz, 1H, CH*H* Bn/Nap), 4.87 – 4.78 (m, 2H, H-1, C*H*H Bn/Nap), 4.63 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.56 – 4.47 (m, 2H, 2x CH*H* Bn/Nap), 4.03 (dd, *J* = 10.2, 8.6 Hz, 1H, H-3), 3.84 – 3.71 (m, 3H, H-4, H-5, H-6), 3.68 (dd, *J* = 10.6, 1.9 Hz, 1H, H-6), 3.48 (dd, *J* = 10.2, 3.5 Hz, 1H, H-2), 3.42 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 137.9, 135.5, 133.4, 133.2 (C_q), 128.5, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.0, 126.1, 126.1, 126.0 (CH_{arom}), 98.8 (C-1), 80.7 (C-3), 78.3 (C-4), 75.6, 75.1, 73.7 (CH_2 Bn/Nap), 70.7 (C-5), 68.4 (C-6), 63.8 (C-2), 55.3 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{33}N_3O_5NH_4$ 557.27585, found 557.25700



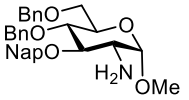
Scheme S2**: preparation of 3-OH glucosamine acceptors: reagents and conditions: a) $LiAlH_4$, THF, 99%; b) for **S8**: TFAA, Et_3N, DCM, 77%; c) for **S9**: trichloroacetyl chloride, Et_3N, DCM, 98%; d) DDQ, 9:1 DCM/H_2O 88% for **1c**, 93% for **1d**, 70% for **1e

Methyl 2-deoxy-2-azido-4,6-di-*O*-benzyl-α-D-glucopyranoside (1c)



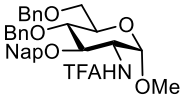
Title compound was synthesised from **S6** according to general procedure V as a colourless oil. Yield: 1.05 g, 2.64 mmol, 88%. $[\alpha]_D^{25}$ = 106.0° (c = 0.91, $CHCl_3$); IR (thin film): 698, 737, 1047, 1105, 2106; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.17 (m, 10H, CH_{arom}), 4.80 (d, *J* = 3.6 Hz, 1H, H-1), 4.72 – 4.63 (m, 2H, 2x C*H*H Bn), 4.58 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.52 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.05 (ddd, *J* = 10.3, 8.7, 3.4 Hz, 1H, H-3), 3.79 – 3.71 (m, 2H, H-5, H-6), 3.71 – 3.66 (m, 1H, H-6), 3.57 (dd, *J* = 9.8, 8.7 Hz, 1H, H-4), 3.40 (s, 3H, CH_3 OMe), 3.28 (dd, *J* = 10.3, 3.6 Hz, 1H, H-2), 2.49 (d, *J* = 3.4 Hz, 1H, 3-OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 137.8 (C_q), 128.7, 128.5, 128.1, 128.1, 128.0, 127.9 (CH_{arom}), 98.8 (C-1), 78.3 (C-4), 74.9, 73.7 (CH_2 Bn), 72.3 (C-3), 70.2 (C-5), 68.4 (C-6), 63.3 (C-2), 55.4 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{25}N_3O_5NH_4$ 417.21325, found 417.21254

Methyl 2-deoxy-2-amino-4,6-di-*O*-benzyl-3-O-(2-naphtyl)methyl-α-D-glucopyranoside (S7)



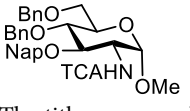
Title compound was synthesised form **S6** according to general procedure II as a colourless oil. Yield: 7.11 g, 13.8 mmol, 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.72 (m, 4H, CH_{arom}), 7.48 – 7.42 (m, 3H, CH_{arom}), 7.37 – 7.24 (m, 8H, CH_{arom}), 7.19 – 7.14 (m, 2H, CH_{arom}), 5.09 (d, *J* = 11.7 Hz, 1H, C*H*H Bn/Nap), 4.86 (d, *J* = 11.6 Hz, 1H, CH*H* Bn/Nap), 4.81 (d, *J* = 10.9 Hz, 1H, C*H*H Bn/Nap), 4.75 (d, *J* = 3.6 Hz, 1H, H-1), 4.66 (d, *J* = 12.1 Hz, 1H, C*H*H Bn/Nap), 4.58 – 4.47 (m, 2H, 2x CH*H* Bn/Nap), 3.82 – 3.75 (m, 2H, H-5, H-6), 3.71 – 3.65 (m, 2H, H-4, H-6), 3.60 (t, *J* = 9.3 Hz, 1H, H-3), 3.35 (s, 3H, CH_3 OMe), 2.85 (dd, *J* = 9.7, 3.6 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 138.0, 136.1, 133.3, 133.0 (C_q), 128.4, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 126.5, 126.2, 125.9, 125.8 (CH_{arom}), 100.7 (C-1), 84.0 (C-3), 78.9 (C-4), 75.6, 74.7, 73.6 (CH_2 Bn/Nap), 70.9 (C-5), 68.6 (C-6), 56.0 (C-2), 55.1 (CH_3 OMe); HRMS: $[M+H]^+$ calcd for $C_{32}H_{35}NO_5H$ 514.25880, found 514.25759

Methyl 2-deoxy-2-*N*-trifluoroacetyl-4,6-di-*O*-benzyl-3-O-(2-naphtyl)methyl-α-D-glucopyranoside (S8)



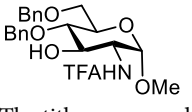
The title compound was prepared from **S7** according to general procedure III as a white solid. Yield: 1.40 g, 2.23 mmol, 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 3H, CH_{arom}), 7.65 (d, *J* = 1.6 Hz, 1H, CH_{arom}), 7.47 (dt, *J* = 6.9, 3.5 Hz, 2H, CH_{arom}), 7.40 – 7.27 (m, 9H, CH_{arom}), 7.19 (dt, *J* = 5.5, 2.2 Hz, 2H, CH_{arom}), 6.22 (d, *J* = 9.5 Hz, 1H, NH), 4.96 (d, *J* = 11.5 Hz, 1H, C*H*H Bn/Nap), 4.83 (d, *J* = 7.0 Hz, 1H, C*H*H Bn/Nap), 4.80 (d, *J* = 7.6 Hz, 1H, CH*H* Bn/Nap), 4.74 (d, *J* = 3.6 Hz, 1H, H-1), 4.65 (d, *J* = 12.1 Hz, 1H, C*H*H Bn/Nap), 4.55 (dd, *J* = 11.5, 9.9 Hz, 2H, 2x CH*H* Bn/Nap), 4.30 (td, *J* = 9.4, 3.4 Hz, 1H, H-2), 3.84 – 3.74 (m, 4H, H-3, H-4, H-5, H-6), 3.73 – 3.66 (m, 1H, H-6), 3.35 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 135.2, 133.3, 133.2 (C_q), 128.6, 128.6, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 127.1, 126.3, 126.2, 126.0 (CH_{arom}), 97.9 (C-1), 79.4, 78.6 (C-3, C-4), 75.3, 75.2, 73.7 (CH_2 Bn/Nap), 71.1 (C-5), 68.3 (C-6), 55.2 (CH_3 OMe), 53.3 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{34}H_{34}F_3NO_6$ 627.26765, found 627.26665

Methyl 2-deoxy-2-*N*-trichloroacetyl-4,6-di-*O*-benzyl-3-O-(2-naphtyl)methyl-α-D-glucopyranoside (S9)



The title compound was prepared from **S7** according general procedure IV as a yellow oil that slowly solidifies. Yield: 1.93g, 2.93 mmol, 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 3H, CH_{arom}), 7.71 – 7.68 (m, 1H, CH_{arom}), 7.47 – 7.43 (m, 2H, CH_{arom}), 7.41 (dd, *J* = 8.4, 1.7 Hz, 1H, CH_{arom}), 7.37 – 7.31 (m, 4H, CH_{arom}), 7.31 – 7.26 (m, 4H, CH_{arom}), 7.18 – 7.12 (m, 2H, CH_{arom}), 6.81 (d, *J* = 9.3 Hz, 1H, NH), 4.94 (d, *J* = 11.2 Hz, 1H, C*H*H Bn/Nap), 4.88 (d, *J* = 11.2 Hz, 1H, CH*H* Bn/Nap), 4.82 – 4.77 (m, 2H, H-1, C*H*H Bn/Nap), 4.65 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.57 – 4.50 (m, 2H, 2x CH*H* Bn), 4.29 (td, *J* = 9.6, 3.7 Hz, 1H, H-2), 3.89 – 3.75 (m, 4H, -3, H-4, H-5, H-6), 3.75 – 3.68 (m, 1H, H-6), 3.40 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (C=O), 138.0, 137.9, 135.3, 133.3, 133.1 (C_q), 128.6, 128.4, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 126.8, 126.2, 126.0, 126.0 (CH_{arom}), 98.1 (C-1), 80.3, 78.3 (C-3, C-4), 75.5, 75.1, 73.7 (CH_2 Bn/Nap), 71.0 (C-5), 68.4 (C-6), 55.4 (CH_3 OMe), 55.0 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{34}H_{34}Cl_3NO_6NH_4$ 675.17900, found 675.17786

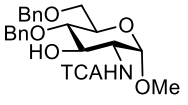
Methyl 2-deoxy-2-*N*-trifluoroacetyl-4,6-di-*O*-benzyl-α-D-glucopyranoside (1d)



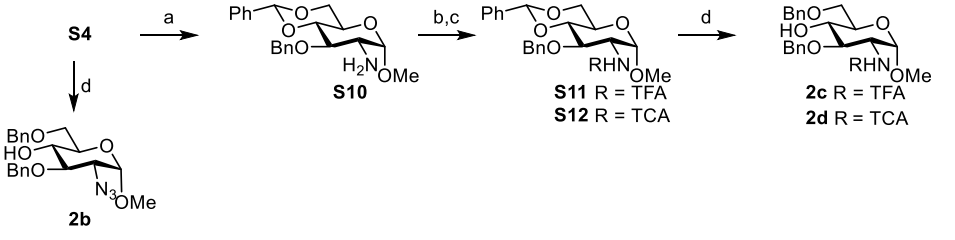
The title compound was prepared from **S8** according to general procedure V as colourless oil that slowly solidifies. Yield: 980 mg, 2.08 mmol, 93%. $[\alpha]_D^{25}$ = 46.3° (c = 1.01, $CHCl_3$); IR (thin film): 698, 1051, 1152, 1717; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 8H, CH_{arom}), 7.23 – 7.18 (m, 2H, CH_{arom}), 6.54 (d, *J* = 9.0 Hz, 1H, NH), 4.78 (d, *J* = 3.7 Hz, 1H, H-1), 4.71 (d, *J* = 11.2 Hz, 1H,

C*H*H Bn), 4.66 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.58 (d, *J* = 11.2 Hz, 1H, CH*H* Bn), 4.54 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.15 (ddd, *J* = 10.4, 9.0, 3.7 Hz, 1H, H-2), 3.86 – 3.80 (m, 1H, H-3), 3.80 – 3.68 (m, 3H, H-5, 2x H-6), 3.64 – 3.56 (m, 1H, H-4), 3.37 (s, 3H, CH_3 OMe), 2.45 (d, *J* = 4.7 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8 (q, *J* = 37.4 Hz, C=O), 138.0, 137.9 (C_q), 128.7, 128.6, 128.2, 128.1, 128.0, 127.9 (CH_{arom}), 115.9 (d, *J* = 287.9 Hz, CF_3) 97.6 (C-1), 78.3 (C-4), 75.0, 73.7 (CH_2 Bn), 73.1 (C-3), 70.6 (C-5), 68.4 (C-6), 55.3 (CH_3 OMe), 54.1 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{23}H_{26}F_3NO_6$ 487.20505, found 487.20455

Methyl 2-deoxy-2-*N*-trichloroacetyl-4,6-di-*O*-benzyl-α-D-glucopyranoside (1e)

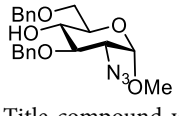


The title compound was prepared from **S9** according to general procedure V as yellow oil. Yield: 1.04 g, 2.00 mmol, 70%. $[\alpha]_D^{25}$ = 56.5° (c = 1.14, $CHCl_3$); IR (thin film): 698, 738, 820, 1053, 1118, 1515, 1713; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 8H, CH_{arom}), 7.22 (dd, *J* = 7.6, 1.9 Hz, 2H, CH_{arom}), 6.90 (d, *J* = 8.8 Hz, 1H, NH), 4.81 (d, *J* = 3.7 Hz, 1H, H-1), 4.75 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.66 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.58 (d, *J* = 11.2 Hz, 1H, CH*H* Bn), 4.54 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.10 (ddd, *J* = 10.5, 8.9, 3.8 Hz, 1H, H-2), 3.88 (ddd, *J* = 10.4, 8.6, 4.3 Hz, 1H, H-3), 3.80 – 3.68 (m, 3H, H-5, 2x H-6), 3.62 (t, *J* = 9.0 Hz, 1H, H-4), 3.39 (s, 3H, CH_3 OMe), 2.47 (d, *J* = 4.8 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (C=O), 138.1, 137.9 (C_q), 128.7, 128.5, 128.1, 128.0, 127.9 (CH_{arom}), 97.7 (C-1), 92.5 (CCl_3), 78.4 (C-4), 75.0, 73.7 (CH_2 Bn), 73.6 (C-3), 70.6 (C-5), 68.5 (C-6), 55.5, 55.4 (C-2, CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{23}H_{26}Cl_3NO_6NH_4$ 535.11640, found 535.11599



Scheme S3**: preparation of 4-OH glucosamine acceptors: reagents and conditions: a) $LiAlH_4$, THF, 98%; b) for **S11**: TFAA, Et_3N, DCM, 77%; c) for **S12**: trichloroacetyl chloride, Et_3N, DCM, 77%; d) TES-H, TFA, DCM, 0 °C, 83% for **2b**, 78% for **2c**, 67% for **2d

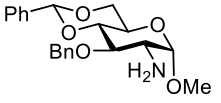
Methyl 2-deoxy-2-azido-3,6-di-*O*-benzyl-α-D-glucopyranoside (2b)



Title compound was prepared from **S4** according to general procedure VI as a colourless oil. Yield: 661 mg, 1.66 mmol, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 10H, CH_{arom}), 4.91 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.83 – 4.76 (m, 2H, H-1, CH*H* Bn), 4.61 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.54 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 3.80 (dd, *J* = 10.0, 8.1 Hz, 1H, H-3), 3.77 – 3.64 (m, 4H,

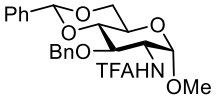
H-4, H-5, 2x H-6), 3.42 (s, 3H, CH_3 OMe), 3.37 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2), 2.51 (d, *J* = 2.5 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 137.8 (C_q), 128.8, 128.6, 128.3, 128.2, 128.0, 127.8 (CH_{arom}), 98.9 (C-1), 80.2 (C-3), 75.2, 73.8 (CH_2 Bn), 72.2 (C-4), 70.1 (C-5), 69.8 (C-6), 63.2 (C-2), 55.4 (CH_3 OBn). Spectra in agreement with literature.[28]

Methyl 2-deoxy-2-amino-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (S10)



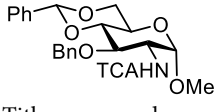
Title compound was prepared from **S4** according to general procedure II as a white solid. 3.40 g, 9.15 mmol, 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H, CH_{arom}), 7.41 – 7.26 (m, 8H, CH_{arom}), 5.58 (s, 1H, C*H*Ph), 5.01 (d, *J* = 11.5 Hz, 1H, C*H*H Bn), 4.74 (d, *J* = 3.7 Hz, 1H, H-1), 4.68 (d, *J* = 11.4 Hz, 1H, CH*H* Bn), 4.29 (dd, *J* = 9.8, 4.4 Hz, 1H, H-6), 3.85 (ddd, *J* = 10.3, 8.5, 4.3 Hz, 1H, H-5), 3.80 – 3.74 (m, 1H, H-6), 3.70 – 3.58 (m, 2H, H-3, H-4), 3.39 (s, 3H, CH_3 OMe), 2.84 (dd, *J* = 9.3, 3.7 Hz, 1H, H-2), 1.49 (s, 2H, NH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 137.6 (C_q), 129.0, 128.6, 128.4, 128.2, 127.9, 126.1 (CH_{arom}), 101.3, 101.2 (C-1, CHPh), 83.3, 80.1 (C-3, C-4), 75.0 (CH_2 Bn), 69.3 (C-6), 62.9 (C-5), 56.0 (C-2), 55.4 (CH_3 OMe). Spectra in agreement with literature.[29]

Methyl 2-deoxy-2-*N*-trifluoroacetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (S11)



Title compound was prepared from **S10** according to general procedure III as white solid. Yield: 790 mg, 1.69 mmol, 77%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H, CH_{arom}), 7.44 – 7.37 (m, 3H, CH_{arom}), 7.35 – 7.28 (m, 3H, CH_{arom}), 7.27 – 7.23 (m, 2H, CH_{arom}), 6.24 (d, *J* = 9.3 Hz, 1H, NH), 5.61 (s, 1H, C*H*Ph), 4.89 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.75 (d, *J* = 3.8 Hz, 1H, H-1), 4.66 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.33 – 4.22 (m, 2H, H-2, H-6), 3.85 – 3.72 (m, 4H, H-3, H-4, H-5, H-6), 3.37 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 137.3 (C_q), 129.2, 128.6, 128.5, 128.2, 128.1, 126.1 (CH_{arom}), 101.5 (CHPh), 98.4 (C-1), 82.8 (C-3), 75.1 (C-4), 74.3 (CH_2 Bn), 68.9 (C-6), 62.8 (C-5), 55.5 (CH_3 OMe), 53.1 (C-2). Spectra in agreement with literature.[30]

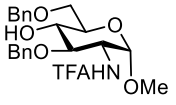
Methyl 2-deoxy-2-*N*-trichloroacetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (S12)



Title compound was prepared from **S10** according to general procedure IV as white solid. Yield: 870 mg, 1.68 mmol, 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 2H, CH_{arom}), 7.47 – 7.36 (m, 3H, CH_{arom}), 7.34 – 7.27 (m, 5H, CH_{arom}), 6.76 (d, *J* = 9.1 Hz, 1H, NH), 5.61 (s, 1H, C*H*Ph), 4.90 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.80 (d, *J* = 3.7 Hz, 1H, H-1), 4.71 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.34 – 4.28 (m, 1H, H-6), 4.23 (td, *J* = 9.3, 3.8 Hz, 1H, H-2), 3.87 – 3.80 (m, 4H, H-3, H-4, H-5, H-6), 3.41 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (C=O), 138.0, 137.3 (C_q),

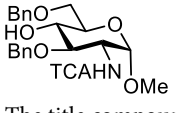
129.2, 128.6, 128.4, 128.1, 127.9, 126.1 (CH_{arom}), 101.5 (CHPh), 98.5 (C-1), 82.8 (C-3), 75.8 (C-4), 74.5 (CH_2 Bn), 69.0 (C-6), 62.8 (C-5), 55.6 (CH_3 OMe), 54.7 (C-2); HRMS: $[M+Na]^+$ calcd for $C_{23}H_{24}Cl_3NO_6NH_4$ 538.05614, found 538.05516

Methyl 2-deoxy-2-*N*-trifluoroacetyl-3,6-di-*O*-benzyl-α-D-glucopyranoside (2c)

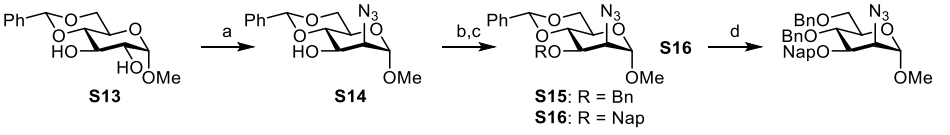


The title compound was prepared from **S11** according to general procedure VI as a white solid. Yield: 600 mg, 1.28 mmol, 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 10H, CH_{arom}), 6.28 (d, *J* = 9.3 Hz, 1H, NH), 4.76 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.75 – 4.67 (m, 2H, H-1, CH*H* Bn), 4.63 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.56 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.21 (td, *J* = 9.9, 3.6 Hz, 1H, H-2), 3.81 (td, *J* = 8.8, 2.7 Hz, 1H, H-4), 3.77 – 3.68 (m, 3H, H-5, 2x H-6), 3.60 (dd, *J* = 10.5, 8.5 Hz, 1H, H-3), 3.37 (s, 3H, CH_3 OMe), 2.71 (d, *J* = 2.7 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 137.7 (C_q), 128.8, 128.7, 128.2, 128.1, 127.9 (CH_{arom}), 97.9 (C-1), 79.2 (C-3), 74.6, 73.9 (CH_2 Bn), 72.7 (C-4), 70.2 (C-6), 70.0 (C-5), 55.4 (CH_3 OMe), 52.7 (C-2). Spectra in agreement with literature.[30]

Methyl 2-deoxy-2-*N*-trichloroacetyl-3,6-di-*O*-benzyl-α-D-glucopyranoside (2d)

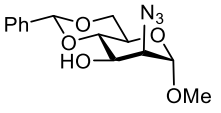


The title compound was prepared from **S12** according to general procedure VI as colourless oil. Yield: 570 mg, 1.10 mmol, 67%. $[\alpha]_D^{25}$ = 52.8° (c = 0.73, $CHCl_3$); IR (thin film): 698, 737, 820, 1029, 1055, 1515, 1713; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 10H, CH_{arom}), 6.83 (d, *J* = 9.3 Hz, 1H, NH), 4.81 – 4.76 (m, 2H, H-1, C*H*H Bn), 4.72 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.63 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.56 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.20 (ddd, *J* = 10.3, 9.2, 3.7 Hz, 1H, H-2), 3.82 – 3.70 (m, 4H, H-4, H-5, 2x H-6), 3.66 (dd, *J* = 10.4, 8.1 Hz, 1H, H-3), 3.41 (s, 3H, CH_3 OMe), 2.66 (d, *J* = 2.4 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (C=O), 138.1, 137.8 (C_q), 128.7, 128.6, 128.1, 128.1, 128.0, 127.9 (CH_{arom}), 98.2 (C-1), 92.6 (CCl_3), 80.0 (C-3), 74.7, 73.9 (CH_2 Bn), 72.1 (C-4), 70.2 (C-5), 70.0 (C-6), 55.5 (CH_3 OMe), 54.4 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{23}H_{26}Cl_3NO_6NH_4$ 535.11640, found 535.11593



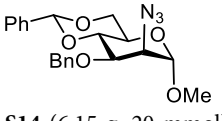
***Scheme S4**: preparation of α-OMe mannosazide intermediates: reagents and conditions: a) i: Tf_2O, pyridine, DCM, -20 °C, ii: NaN_3, DMF, 70 °C, 51% over 2 steps; b) for **S15**: BnBr, NaH, DMF, 80%; c) for **S16**: NapBr, NaH, DMF 76%; d) i: PTSA, methanol, 50 °C, ii: BnBr, NaH, DMF, 79% over 2 steps*

Methyl 2-deoxy-2-azido-4,6-*O*-benzylidene-α-D-mannopyranoside (S14)



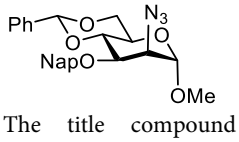
S13 (28.2 g, 100 mmol) and pyridine (16.1 mL, 200 mmol, 2 eq) were dissolved in DCM and cooled to -20 °C, after which triflic anhydride (19.3 mL, 115 mmol, 1.15 eq) was added dropwise. The reaction mixture was allowed to warm to RT and subsequently quenched with water. Phases were separated and the organic phase was dried with $MgSO_4$ and concentrated. The residue was dissolved in DMF with NaN_3 (19.5 g, 300 mmol, 3 eq) and heated to 70 °C. After 18 hr, the reaction mixture was cooled to RT, diluted with water and extracted twice with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated. The residue was purified over silica (10%→20% acetone in pentane) to yield the title compound as yellow oil. Yield: 15.7 g, 51.2 mmol, 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H, CH_{arom}), 7.38 (dd, *J* = 5.0, 2.0 Hz, 3H, CH_{arom}), 5.56 (s, 1H, C*H*Ph), 4.67 (d, *J* = 1.4 Hz, 1H, H-1), 4.28 – 4.18 (m, 2H, H-3, H-6), 3.92 (dd, *J* = 4.0, 1.5 Hz, 1H, H-2), 3.88 (t, *J* = 9.4 Hz, 1H, H-4), 3.83 – 3.71 (m, 2H, H-5, H-6), 3.37 (s, 3H, CH_3 OMe), 2.77 (s, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1 (C_q), 129.5, 128.5, 126.4 (CH_{arom}), 102.4 (CHPh), 100.2 (C-1), 79.1 (C-4), 69.0 (C-3), 68.8 (C-6), 63.7 (C-2), 63.4 (C-5), 55.3 (CH_3 OMe). Data in agreement with literature.[31]

Methyl 2-deoxy-2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (S15)



S14 (6.15 g, 20 mmol) was dissolved in DMF and cooled to 0°C, after which benzyl bromide (3.56 mL, 30 mmol, 1.5 eq) and sodium hydride (60% dispersion in mineral oil, 1.20 g, 30 mmol, 1.5 eq) were added. After full conversion, the reaction was quenched with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated. The residue was purified over silica (5% acetone in pentane) to yield the title compound as yellow oil. Yield: 6.35 g, 16.0 mmol, 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H, CH_{arom}), 7.41 – 7.27 (m, 8H, CH_{arom}), 5.62 (s, 1H, C*H*Ph), 4.88 (d, *J* = 12.3 Hz, 1H, C*H*H bn), 4.73 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.65 (d, *J* = 1.5 Hz, 1H, H-1), 4.25 (dd, *J* = 9.7, 4.3 Hz, 1H, H-6), 4.15 – 4.06 (m, 2H, H-3, H-4), 4.00 – 3.97 (m, 1H, H-2), 3.88 – 3.79 (m, 1H, H-6), 3.80 – 3.73 (m, 1H, H-5), 3.34 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 137.5 (C_q), 129.1, 128.5, 128.3, 127.8, 127.6, 126.2 (CH_{arom}), 101.7 (CHPh), 100.3 (C-1), 79.2, 75.7 (C-3, C-4), 73.3 (CH_2 Bn), 68.8 (C-6), 63.8 (C-5), 62.8 (C-2), 55.1 (CH_3 OMe). Spectra in agreement with literature.[32]

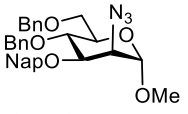
Methyl 2-deoxy-2-azido-3-*O*-(2-naphtyl)methyl-4,6-*O*-benzylidene-α-D-mannopyranoside (S16)



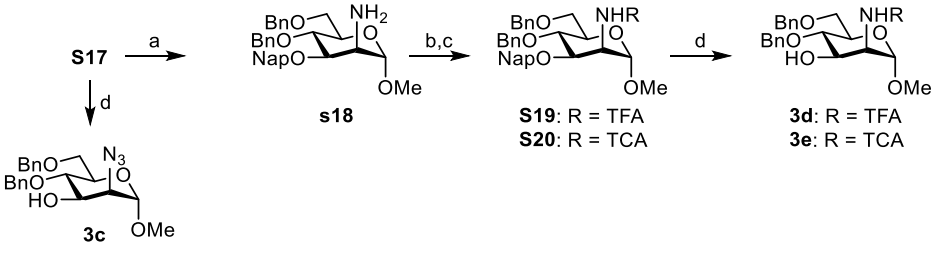
The title compound was prepared from **S14** as described for **S15**, but 2-(Bromomethyl)naphthalene was used instead of benzyl bromide. Yield: 4.98 g, 11.1 mmol, 76%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 3H, CH_{arom}), 7.74 – 7.68 (m, 1H, CH_{arom}), 7.53 – 7.43 (m, 5H, CH_{arom}), 7.41 – 7.36 (m, 3H, CH_{arom}), 5.64 (s, 1H, C*H*Ph), 5.01 (d, *J* = 12.3 Hz, 1H, C*H*H Nap), 4.89 (d, *J* = 12.4 Hz, 1H, CH*H* Nap), 4.65 (d, *J* = 1.4 Hz, 1H, H-1), 4.25 (dd, *J* = 9.8, 4.4 Hz, 1H, H-6), 4.17 – 4.11 (m, 2H, H-3, H-4), 4.04 – 3.98 (m, 1H, H-2), 3.88 – 3.81 (m, 1H, H-6), 3.77 (ddd, *J* = 10.8, 5.5, 4.1 Hz, 1H, H-5), 3.32 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 135.6, 133.4, 133.1 (C_q), 129.1, 128.4, 128.3, 128.1, 127.8, 126.3, 126.3, 126.2, 126.2, 126.0, 125.5 (CH_{arom}), 101.8 (CHPh), 100.2 (C-1), 79.1, 75.6 (C-3, C-4), 73.2 (CH_2 Nap), 68.8 (C-6), 63.7 (C-5), 62.7 (C-2), 55.1 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{25}H_{25}N_3O_5NH_4$ 465.21325, found 465.21276

Methyl 2-deoxy-2-azido-4,6-di-*O*-benzyl-3-O-(2-naphtyl)methyl-α-D-mannopyranoside (S17)

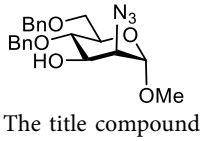


The title compound was prepared from **S16** as described for **S6**. Yield: 4.67 g, 8.65 mmol, 79%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 3H, CH_{arom}), 7.78 – 7.73 (m, 1H, CH_{arom}), 7.51 – 7.44 (m, 3H, CH_{arom}), 7.38 – 7.29 (m, 4H, CH_{arom}), 7.30 – 7.23 (m, 4H, CH_{arom}), 7.16 – 7.09 (m, 2H, CH_{arom}), 4.92 – 4.82 (m, 3H, C*H*H Bn/Nap, CH_2 Bn/Nap), 4.71 (d, *J* = 1.8 Hz, 1H, H-1), 4.66 (d, *J* = 12.2 Hz, 1H, C*H*H Bn/Nap), 4.53 (d, *J* = 12.3 Hz, 1H, CH*H* Bn/Nap), 4.50 (d, *J* = 10.8 Hz, 1H, CH*H* Bn/Nap), 4.09 (dd, *J* = 9.2, 3.7 Hz, 1H, H-3), 3.95 (dd, *J* = 3.7, 1.8 Hz, 1H, H-2), 3.91 (t, *J* = 9.4 Hz, 1H, H-4), 3.78 – 3.62 (m, 3H, H-5, 2x H-6), 3.32 (s, 3H, CH_3 OMe); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.3, 138.3, 135.4, 133.4, 133.2 (C_q), 128.5, 128.4, 128.1, 128.0, 128.0, 127.8, 127.8, 127.7, 126.7, 126.2, 126.1, 125.9 (CH_{arom}), 99.2 (C-1), 79.9 (C-3), 75.4 (CH_2 Bn/Nap), 74.6 (C-4), 73.6, 72.7 (CH_2 Bn/Nap), 71.6 (C-5), 68.8 (C-6), 61.4 (C-2), 55.0 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{32}N_{33}N_3O_5NH_4$ 557.27585, found 557.27509



Scheme S5**: preparation of 3-OH mannosamine acceptors: reagents and conditions: a) $LiAlH_4$, THF, 93%; b) for **S19**: TFAA, Et_3N, DCM, 80%; c) for **S20**: trichloroacetyl chloride, Et_3N, DCM, 97%; d) DDQ, 9:1 DCM/H_2O 65% for **3c**, 61% for **3d**, 61% for **3e

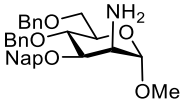
Methyl 2-deoxy-2-azido-4,6-di-*O*-benzyl-α-D-mannopyranoside (3c)



The title compound was prepared from **S17** according to general procedure V. Yield: 391 mg, 0.98 mmol, 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 8H, CH_{arom}), 7.22 (dd, *J* = 7.7, 1.9

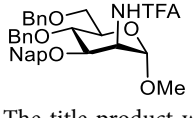
Hz, 2H, CH_{arom}), 4.75 (d, *J* = 1.7 Hz, 1H, H-1), 4.73 – 4.65 (m, 2H, 2x C*H*H Bn), 4.60 – 4.51 (m, 2H, 2x CH*H* Bn), 4.10 (ddd, *J* = 9.1, 5.4, 3.9 Hz, 1H, H-3), 3.88 (dd, *J* = 4.0, 1.7 Hz, 1H, H-2), 3.79 – 3.73 (m, 2H, H-4, H-6), 3.71 – 3.65 (m, 2H, H-5, H-6), 3.36 (s, 3H, CH_3 OMe), 2.27 (d, *J* = 5.4 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1 (C_q), 128.7, 128.5, 128.1, 128.1, 128.0, 127.8 (CH_{arom}), 99.2 (C-1), 76.1 (C-4), 75.0, 73.7 (CH_2 Bn), 71.6 (C-3), 71.3 (C-5), 68.8 (C-6), 63.8 (C-2), 55.2 (CH_3 OMe). Spectra in agreement with literature.[33]

Methyl 2-deoxy-2-amino-4,6-di-*O*-benzyl-3-O-(2-naphtyl)methyl-α-D-mannopyranoside (S18)



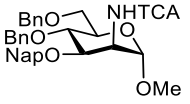
The title compound was prepared from **S17** according to general procedure II. Yield: 3.34 g, 6.50 mmol, 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 3H, CH_{arom}), 7.75 (dd, *J* = 6.1, 3.4 Hz, 1H, CH_{arom}), 7.49 – 7.42 (m, 3H, CH_{arom}), 7.37 – 7.31 (m, 4H, CH_{arom}), 7.31 – 7.25 (m, 4H, CH_{arom}), 7.19 – 7.14 (m, 2H, CH_{arom}), 4.87 (d, *J* = 10.9 Hz, 1H, C*H*H Bn/Nap), 4.82 (d, *J* = 11.7 Hz, 1H, C*H*H Bn/Nap), 4.77 (d, *J* = 11.8 Hz, 1H, CH*H* Bn/Nap), 4.73 (d, *J* = 1.6 Hz, 1H, H-1), 4.65 (d, *J* = 12.1 Hz, 1H, C*H*H Bn/Nap), 4.56 – 4.45 (m, 2H, 2x C*H*H Bn/Nap), 3.93 (dd, *J* = 9.0, 3.9 Hz, 1H, H-3), 3.84 (t, *J* = 9.2 Hz, 1H, H-4), 3.80 – 3.72 (m, 2H, H-5, H-6), 3.71 – 3.67 (m, 1H, H-6), 3.36 – 3.31 (m, 4H, H-2, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.3, 135.9, 133.4, 133.1 (C_q), 128.5, 128.5, 128.4, 128.3, 128.0, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 126.5, 126.2, 126.0, 125.9 (CH_{arom}), 102.0 (C-1), 80.5 (C-3), 75.1 (CH_2 Bn/Nap), 74.1 (C-4), 73.6, 71.8 (CH_2 Bn/Nap), 71.1 (C-5), 69.0 (C-6), 55.0 (CH_3 OMe), 52.1 (C-2); HRMS: $[M+H]^+$ calcd for $C_{32}H_{35}NO_5H$ 514.25880, found 514.25811

Methyl 2-deoxy-2-*N*-trifluoroacetyl-4,6-di-*O*-benzyl-3-O-(2-naphtyl)methyl-α-D-mannopyranoside (S19)



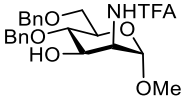
The title product was prepared from **S18** according to general procedure III as colourless oil. Yield: 777 mg, 1.28 mmol, 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.68 (m, 4H, CH_{arom}), 7.50 – 7.39 (m, 3H, CH_{arom}), 7.38 – 7.22 (m, 8H, CH_{arom}), 7.14 (dd, *J* = 6.6, 3.0 Hz, 2H, CH_{arom}), 6.97 (d, *J* = 9.2 Hz, 1H, NH), 4.91 (d, *J* = 11.2 Hz, 1H, C*H*H Bn/Nap), 4.86 (d, *J* = 10.8 Hz, 1H, C*H*H Bn/Nap), 4.78 (d, *J* = 1.7 Hz, 1H, H-1), 4.70 (ddd, *J* = 9.4, 4.5, 1.7 Hz, 1H, H-2), 4.66 – 4.58 (m, 2H, C*H*H Bn/Nap, CH*H* Bn/Nap), 4.49 – 4.40 (m, 2H, 2x CH*H* Bn/Nap), 4.14 (dd, *J* = 8.4, 4.4 Hz, 1H, H-3), 3.81 – 3.63 (m, 4H, H-4, H-5, 2x H-6), 3.36 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 137.7, 135.2, 133.4, 133.2 (C_q), 128.6, 128.5, 128.3, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.2, 126.3, 126.2, 126.1 (CH_{arom}), 99.4 (C-1), 77.4 (C-3), 75.3 (CH_2 Bn/Nap), 73.7 (C-4), 73.7, 71.8 (CH_2 Bn/Nap), 70.7 (C-5), 68.5 (C-6), 55.3 (CH_3 OMe), 50.0 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{34}H_{34}F_3NO_6NH_4$ 627.26765, found 627.26653

Methyl 2-deoxy-2-*N*-trichloroacetyl-4,6-di-*O*-benzyl-3-O-(2-naphtyl)methyl-α-D-mannopyranoside (S20)



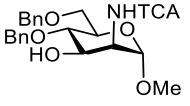
The title product was prepared from **S18** according to general procedure IV as colourless oil. Yield: 1.03 g, 1.56 mmol, 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 4H, CH_{arom}), 7.49 – 7.41 (m, 3H, CH_{arom}), 7.33 – 7.23 (m, 8H, CH_{arom}), 7.16 (dd, *J* = 6.7, 3.0 Hz, 2H, CH_{arom}), 7.01 (d, *J* = 9.1 Hz, 1H, NH), 4.95 (d, *J* = 11.1 Hz, 1H, C*H*H Bn/Nap), 4.87 (d, *J* = 10.9 Hz, 1H, C*H*H Bn/Nap), 4.84 (d, *J* = 1.8 Hz, 1H, H-1), 4.67 – 4.57 (m, 3H, H-2, C*H*H Bn/Nap, CH*H* Bn/Nap), 4.48 (d, *J* = 10.9 Hz, 1H, CH*H* Bn/Nap), 4.44 (d, *J* = 11.7 Hz, 1H, CH*H* Bn/Nap), 4.18 (q, *J* = 4.4 Hz, 1H, H-3), 3.81 – 3.74 (m, 3H, H-4, H-5, H-6), 3.70 (d, *J* = 9.7 Hz, 1H, H-6), 3.38 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (C=O), 138.2, 138.0, 135.3, 133.4, 133.1 (C_q), 128.5, 128.5, 128.2, 128.1, 127.9, 127.8, 127.8, 127.2, 126.4, 126.1, 126.0 (CH_{arom}), 99.3 (C-1), 77.7 (C-3), 75.3 (CH_2 Bn/Nap), 73.6 (C-4), 73.6, 71.5 (CH_2 Bn/Nap), 70.9 (C-5), 68.6 (C-6), 55.4 (CH_3 OMe), 51.1 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{34}H_{34}Cl_3NO_6NH_4$ 675.17900, found 675.17798

Methyl 2-deoxy-2-*N*-trifluoroacetyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (3d)



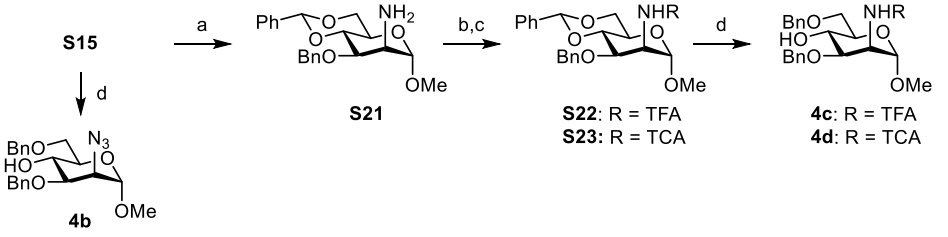
The title product was prepared from **S19** according to general procedure V as colourless oil. Yield: 350 mg, 0.746 mmol, 61%. $[\alpha]_D^{25}$ = 56.6° (c = 0.35, $CHCl_3$); IR (thin film): 689, 1065, 1133, 1160,1209, 1721; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 8H, CH_{arom}), 7.22 (dd, *J* = 7.7, 1.8 Hz, 2H, CH_{arom}), 7.03 (d, *J* = 8.6 Hz, 1H, NH), 4.78 – 4.71 (m, 2H, H-1, C*H*H Bn), 4.64 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.54 (d, *J* = 11.2 Hz, 1H, CH*H* Bn), 4.49 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.40 (ddd, *J* = 8.7, 4.6, 1.6 Hz, 1H, H-2), 4.23 (ddd, *J* = 9.2, 4.5, 3.2 Hz, 1H, H-3), 3.80 (dd, *J* = 10.3, 2.8 Hz, 1H, H-6), 3.76 – 3.67 (m, 2H, H-5, H-6), 3.62 (t, *J* = 9.3 Hz, 1H, H-4), 3.36 (s, 3H, CH_3 OMe), 2.34 (d, *J* = 3.3 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 137.6 (C_q), 128.7, 128.6, 128.1, 128.1, 128.0 (CH_{arom}), 99.2 (C-1), 75.1 (C-4), 75.0, 73.8 (CH_2 Bn), 70.5 (C-5), 70.2 (C-3), 68.5 (C-6), 55.4 (CH_3 OMe), 53.7 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{23}H_{26}F_3NO_6$ 487.20505, found 487.20455

Methyl 2-deoxy-2-*N*-trichloroacetyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (3e)



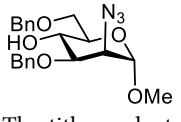
The title product was prepared from **S20** according to general procedure V as colourless oil. Yield: 482 mg, 0.929 mmol, 61%. $[\alpha]_D^{25}$ = 42.1° (c = 0.35, $CHCl_3$); IR (thin film): 697, 821, 1069, 1515, 1720; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 10H, CH_{arom}), 6.95 (d, *J* = 8.3 Hz, 1H, NH), 4.78 (d, *J* = 1.8 Hz, 1H, H-1), 4.76 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.64 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.59 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.49 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.32 (ddd, *J* = 8.3, 4.3, 1.7 Hz, 1H, H-2), 4.27 (ddd, *J* = 8.9, 4.3, 3.1 Hz, 1H, H-3), 3.84 – 3.70 (m, 3H, H-5, 2x H-6), 3.68 (t, *J* = 9.2 Hz, 1H, H-4), 3.39 (s, 3H, CH_3 OMe), 2.26 (d, *J* = 3.3 Hz, 1H, OH); ^{13}C NMR

(101 MHz, $CDCl_3$) δ 162.9 (C=o), 138.1, 138.0 (C_q), 128.7, 128.5, 128.3, 128.2, 127.9, 127.8 (CH_{arom}), 99.1 (C-1), 74.9 (CH_2 Bn), 74.9 (C-4), 73.6 (CH_2 Bn), 70.8 (C-5), 70.5 (C-3), 68.6 (C-6), 55.4 (CH_3 OMe), 54.9 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{23}H_{26}Cl_3NO_6NH_4$ 535.11640, found 535.11565



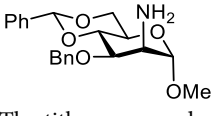
Scheme S6**: preparation of 4-OH mannosamine acceptors: reagents and conditions: a) $LiAlH_4$, THF, 85%; b) for **S22**: TFAA, Et_3N, DCM, 100%; c) for **S23**: trichloroacetyl chloride, Et_3N, DCM, 100%; d) TES-H, TFA, DCM, 0 °C, 70% for **4b**, 60% for **4c**, 73% for **4d

Methyl 2-deoxy-2-azido-3,6-di-*O*-benzyl-α-D-mannopyranoside (4b)



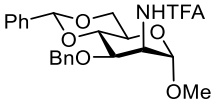
The title product was prepared from **S15** according to general procedure VI as colourless oil. Yield: 705 mg, 1.77 mmol, 70%. $[\alpha]_D^{25}$ = 19.5° (c = 0.28, $CHCl_3$); IR (thin film): 698, 970, 1070, 1138, 1365, 1454, 2105; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 10H, CH_{arom}), 4.75 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.69 (d, *J* = 1.7 Hz, 1H, H-1), 4.66 – 4.60 (m, 2H, C*H*H Bn, CH*H* Bn), 4.57 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 3.98 – 3.91 (m, 2H, H-2, H-4), 3.86 (dd, *J* = 9.2, 3.6 Hz, 1H, H-3), 3.76 – 3.67 (m, 3H, H-5, 2x H-6), 3.35 (s, 3H, CH_3 OMe), 2.58 (d, *J* = 2.4 Hz, 1H, OH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.1, 137.7 (C_q), 128.8, 128.5, 128.2, 128.1, 127.8, 127.8 (CH_{arom}), 99.4 (C-1), 79.4 (C-3), 73.7, 72.6 (CH_2 Bn), 71.1 (C-5), 70.2 (C-6), 68.0 (C-4), 60.4 (C-2), 55.1 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{25}N_3O_5NH_4$ 417.21325, found 417.21277

Methyl 2-deoxy-2-amino-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (S21)



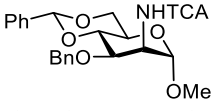
The title compound was prepared from **S15** according to general procedure II as colourless oil. Yield: 4.23 g, 11.4 mmol, 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H, CH_{arom}), 7.41 – 7.27 (m, 8H, CH_{arom}), 5.62 (s, 1H, C*H*Ph), 4.81 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.73 – 4.64 (m, 2H, H-1, CH*H* Bn), 4.29 – 4.24 (m, 1H, H-6), 4.07 – 4.00 (m, 1H, H-4), 3.92 (dd, *J* = 9.7, 4.2 Hz, 1H, H-3), 3.87 – 3.80 (m, 2H, H-5, H-6), 3.41 (dd, *J* = 4.3, 1.3 Hz, 1H, H-2), 3.36 (s, 3H, CH_3 OMe), 1.45 (s, 2H, NH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 137.7 (C_q), 129.0, 128.5, 128.3, 127.8, 127.8, 126.2 (CH_{arom}), 103.1 (C-1), 101.8 (CHPh), 79.0 (C-4), 75.7 (C-3), 72.8 (CH_2 Bn), 69.1 (C-6), 63.6 (C-5), 55.1 (CH_3 OMe), 53.7 (C-2). Spectra in agreement with literature.[34]

Methyl 2-deoxy-2-*N*-trifluoroacetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (S22)



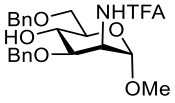
The title compound was prepared from **S21** according to general procedure II as yellowish oil. Yield: 1.20 g, 2.57 mmol, 100 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H, CH_{arom}), 7.42 – 7.36 (m, 3H, CH_{arom}), 7.34 – 7.26 (m, 5H, CH_{arom}), 6.56 (d, *J* = 7.6 Hz, 1H, NH), 5.62 (s, 1H, C*H*Ph), 4.85 (d, *J* = 1.3 Hz, 1H, H-1), 4.70 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.65 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.57 – 4.49 (m, 1H, H-2), 4.28 (dd, *J* = 9.4, 3.8 Hz, 1H, H-6), 4.13 (dd, *J* = 10.0, 4.9 Hz, 1H, H-3), 3.88 (ddd, *J* = 10.4, 9.0, 4.0 Hz, 1H, H-5), 3.85 – 3.78 (m, 1H, H-6), 3.76 – 3.70 (m, 1H, H-4), 3.38 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 137.2 (C_q), 129.2, 128.6, 128.4, 128.1, 127.9, 126.2 (C_q), 102.0 (CHPh), 99.7 (C-1), 78.7 (C-4), 72.7 (C-3), 72.3 (CH_2 Bn), 68.8 (C-6), 63.0 (C-5), 55.4 (CH_3 OMe), 51.9 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{23}H_{24}F_3NO_6NH_4$ 485.18940, found 485.18902

Methyl 2-deoxy-2-*N*-trichloroacetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (S23)



The title compound was prepared from **S21** according to general procedure III as yellowish oil. Yield: 1.30 g, 2.52 mmol, 100%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H, CH_{arom}), 7.42 – 7.26 (m, 8H, CH_{arom}), 7.02 (d, *J* = 7.3 Hz, 1H, NH), 5.63 (s, 1H, C*H*Ph), 4.90 (d, *J* = 1.3 Hz, 1H, H-1), 4.71 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.64 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.48 (ddd, *J* = 7.4, 5.0, 1.4 Hz, 1H, H-2), 4.28 (dd, *J* = 9.7, 4.2 Hz, 1H, H-6), 4.15 (dd, *J* = 10.0, 4.9 Hz, 1H, H-3), 3.93 – 3.86 (m, 1H, H-5), 3.85 – 3.79 (m, 1H, H-6), 3.73 (t, *J* = 9.6 Hz, 1H, H-4), 3.39 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (C=O), 137.6, 137.2 (C_q), 129.2, 128.5, 128.3, 127.9, 127.8, 126.2 (CH_{arom}), 101.9 (CHPh), 99.7 (C-1), 92.4 (CCl_3), 78.8 (C-4), 72.9 (C-3), 72.0 (CH_2 Bn), 68.9 (C-6), 62.9 (C-5), 55.4 (CH_3 OMe), 52.9 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{23}H_{24}Cl_3NO_6NH_4$ 533.10075, found 533.10041

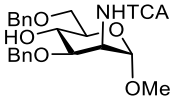
Methyl 2-deoxy-2-*N*-trifluoroacetyl-3,6-di-*O*-benzyl-α-D-mannopyranoside (4c)



The title product was prepared from **S22** according to general procedure VI as colourless oil. Yield: 700 mg, 1.49 mmol, 60%. $[\alpha]_D^{25}$ = 20.2° (c = 0.55, $CHCl_3$); IR (thin film): 698, 1072, 1135, 1162, 1453, 1724 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 10H, CH_{arom}), 6.95 (d, *J* = 9.1 Hz, 1H, NH), 4.81 – 4.74 (m, 2H, H-1, C*H*H Bn), 4.65 – 4.59 (m, 2H, H-2, C*H*H Bn), 4.56 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.41 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 3.92 – 3.84 (m, 1H, H-3), 3.83 – 3.68 (m, 4H, H-4, H-5, 2x H-6), 3.38 (s, 3H, CH_3 OMe), 2.55 (d, *J* = 1.5 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 137.3 (C_q), 128.7, 128.6, 128.5, 128.3, 128.0, 127.8 (CH_{arom}), 99.6 (C-1), 77.0 (C-

3), 73.8, 71.8 (CH_2 Bn), 70.6 (C-4), 69.1 (C-6), 66.7 (C-6), 55.4 (CH_3 OMe), 49.6 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{23}H_{26}F_3NO_6NH_4$ 487.20505, found 487.20446

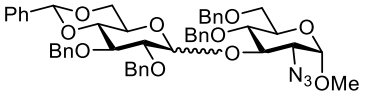
Methyl 2-deoxy-2-*N*-trichloroacetyl-3,6-di-*O*-benzyl-α-D-mannopyranoside (4d)



The title product was prepared from **S23** according to general procedure VI as colourless oil. Yield: 950 mg, 1.83 mmol, 73%. $[\alpha]_D^{25}$ = -1.26° (c = 1.35, $CHCl_3$); IR (thin film): 698, 819, 1073, 1133, 1203, 1281, 1367, 1454, 1515, 1720; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 10H, CH_{arom}), 6.95 (d, *J* = 8.8 Hz, 1H, NH), 4.85 (d, *J* = 1.7 Hz, 1H, H-1), 4.80 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.63 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.60 – 4.51 (m, 2H, H-2, CH*H* Bn), 4.42 (d, *J* = 10.8 Hz, 1H, CH*H* Bn), 3.92 (dd, *J* = 8.6, 4.2 Hz, 1H, H-3), 3.85 – 3.73 (m, 4H, H-4, H-5, 2x H-6), 3.41 (s, 3H, CH_3 OMe), 2.52 (d, *J* = 1.9 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (C=O), 138.1, 137.4 (C_q), 128.7, 128.5, 128.5, 128.3, 127.8, 127.6 (CH_{arom}), 99.5 (C-1), 92.5 (CCl_3), 77.2 (C-3), 73.8, 71.6 (CH_2 Bn), 70.8 (C-4), 69.2 (CH_2 Bn), 66.8 (C-5), 55.5 (CH_3 OMe), 50.6 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{23}H_{26}Cl_3NO_6NH_4$ 535.11640, found 535.11757

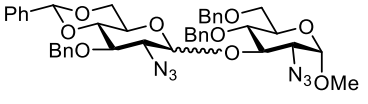
Characterisation of glycosylation products

Disaccharide 1cA



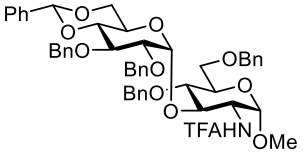
The title compound was synthesised from donor **A** and acceptor **1c** according to general procedure I as colourless oil. Yield: 69 mg, 83 μmol, 83%, α:β = 1.6:1. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.10 (m, 50H), 5.55 (s, 1H, C*H*Phα), 5.51 (s, 1H, C*H*Phβ), 5.44 (d, *J* = 3.8 Hz, 1H, H-1'α), 4.98 – 4.85 (m, 7H), 4.85 – 4.75 (m, 3H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.61 – 4.54 (m, 2H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.46 – 4.35 (m, 3H), 4.31 (d, *J* = 12.6 Hz, 1H), 4.28 – 4.12 (m, 5H), 3.84 – 3.69 (m, 5H), 3.69 – 3.50 (m, 6H), 3.47 (dd, *J* = 8.7, 7.6 Hz, 1H, H-2'β), 3.42 (d, *J* = 4.1 Hz, 7H), 3.33 (dd, *J* = 10.2, 3.5 Hz, 1H, H-2β), 3.25 (dd, *J* = 10.3, 3.6 Hz, 1H, H-2α); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.6, 138.5, 138.4, 138.4, 138.0, 137.9, 137.8, 137.6, 137.4, 135.4, 134.4, 131.9, 131.5, 131.2, 130.3, 130.3, 129.0, 128.9, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.4, 126.7, 126.2, 126.1, 125.3, 102.9 (C-1'β), 101.4 (CHPhα), 101.2 (CHPhβ), 99.5 (C-1'α), 99.3 (C-1α), 98.9 (C-1β, 82.8, 82.7, 81.8, 81.3, 78.9, 78.6, 78.5, 77.0, 76.8, 76.0, 75.6, 75.4, 75.3, 75.0, 74.2, 73.7, 73.7, 73.6, 70.2, 70.1, 69.5, 68.8, 68.3, 68.3, 65.9, 63.9, 63.5, 62.2, 55.3 (CH_3 OMeβ), 55.2 (CH_3 OMeα); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{51}N_3O_{10}$ 847.39127, found 847.38982

Disaccharide 1cB



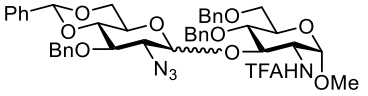
The title compound was synthesised from donor **B** and acceptor **1c** according to general procedure I as colourless oil. Yield: 65 mg, 85 µmol, 85%, α:β = 1:2.5. Data for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 20H, CH_{arom}), 5.52 (s, 1H, C*H*Ph), 4.95 – 4.86 (m, 3H, H-1, CH_2 Bn), 4.84 – 4.76 (m, 2H, H-1', C*H*H Bn), 4.63 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.51 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.42 (d, *J* = 10.6 Hz, 1H, CH*H* Bn), 4.25 – 4.08 (m, 3H), 3.82 – 3.71 (m, 2H), 3.70 – 3.63 (m, 2H, H-4', H-6'), 3.60 (t, *J* = 9.1 Hz, 1H), 3.55 – 3.44 (m, 3H, H-2, H-2', H-6'), 3.42 (s, 3H, CH_3 OMe), 3.40 – 3.29 (m, 1H, H-5'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 137.9, 137.9, 137.2 (C_q), 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 126.1 (CH_{arom}), 102.2 (C-1'), 101.4 (CHPh), 98.7 (C-1'), 81.7 (C-4'), 79.3, 78.7, 76.0, 75.2, 75.0, 73.7, 70.3, 68.6, 68.3, 66.7, 66.1, 64.1, 55.3 (CH_3 OMe); diagnostic peaks for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57 (s, 1H, C*H*Ph), 5.45 (d, *J* = 3.9 Hz, 1H, H-1'), 4.68 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 3.17 (dd, *J* = 10.4, 3.6 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 101.5 (CHPh), 99.3, 99.3 (C-1, C-1'), 82.9, 78.9, 76.3, 76.3, 74.1, 73.8, 69.4, 68.1, 63.5, 63.0, 61.7, 55.3; product contaminated with TTBP; HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{44}N_6O_9NH_4$ 782.35080, found 782.34978

Disaccharide 1dA



The title compound was synthesised from donor **A** and acceptor **1d** according to general procedure I as colourless oil. Yield: 86 mg, 96 µmol, 96%, α:β > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.61 (m, 3H, CH_{arom}), 7.57 – 7.52 (m, 1H, CH_{arom}), 7.50 – 7.43 (m, 3H, CH_{arom}), 7.41 – 7.30 (m, 8H, CH_{arom}), 7.30 – 7.17 (m, 16H, CH_{arom}), 7.09 – 7.02 (m, 2H, CH_{arom}), 6.54 (d, *J* = 9.6 Hz, 1H, NH), 5.50 (s, 1H, C*H*Ph), 5.07 (d, *J* = 3.6 Hz, 1H, H-1'), 5.00 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.86 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.78 – 4.70 (m, 3H, H-1, C*H*H Bn, CH*H* Bn), 4.62 – 4.54 (m, 2H, C*H*H Bn, CH*H* Bn), 4.48 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.38 – 4.25 (m, 3H, H-2, H-6', CH*H* Bn), 4.02 (t, *J* = 9.2 Hz, 1H, H-3'), 3.94 (ddt, *J* = 10.8, 5.2, 2.7 Hz, 1H, H-3), 3.88 (dt, *J* = 10.0, 5.0 Hz, 1H, H-5'), 3.78 – 3.75 (m, 2H, H-4, H-5), 3.74 – 3.69 (m, 1H, H-6), 3.66 – 3.55 (m, 3H, H-4', H-6, H-6'), 3.53 (dd, *J* = 9.3, 3.6 Hz, 1H, H-2'), 3.37 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.4, 138.2, 137.9, 137.6 (C_q), 135.3, 134.5, 131.6, 131.6, 131.0, 130.3, 128.9, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.5, 126.2 (CH_{arom}), 101.5 (CHPh), 99.8 (C-1'), 97.9 (C-1), 82.3 (C-4'), 79.8 (C-3), 79.2 (C-2'), 78.3 (C-3'), 77.6 (C-4), 75.2, 74.7, 73.8, 73.6 (CH_2 Bn), 70.5 (C-5), 68.8 (C-6'), 68.4 (C-6), 63.7 (C-5'), 55.3 (CH_3 OMe), 53.2 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{50}H_{52}F_3NO_{11}NH_4$ 917.38307, found 917.38163.

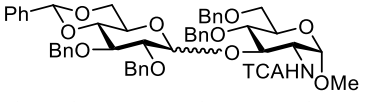
Disaccharide 1dB



The title compound was synthesised from donor **B** and acceptor **1d** according to general procedure I as colourless oil. Yield: 83 mg, 100 µmol, 100%, α:β = 12:1. Data for the α-anomer: ^{1}H

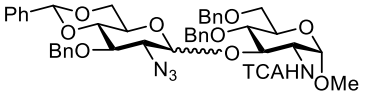
NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 20H, CH_{arom}), 6.52 (d, *J* = 9.7 Hz, 1H, NH), 5.50 (s, 1H, C*H*Ph), 5.40 (d, *J* = 3.9 Hz, 1H, H-1'), 4.97 – 4.88 (m, 2H, 2x C*H*H Bn), 4.76 – 4.71 (m, 2H, H-1, CH*H* Bn), 4.67 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.58 – 4.50 (m, 2H, CH*H* Bn), 4.34 (td, *J* = 10.0, 3.7 Hz, 1H, H-2), 4.24 (dd, *J* = 10.3, 4.6 Hz, 1H, H-6), 4.04 – 3.94 (m, 2H, H-3, H-4), 3.86 (t, *J* = 9.2 Hz, 1H, H-3'), 3.83 – 3.73 (m, 3H, H-5, H-5', H-6), 3.71 (dd, *J* = 10.6, 1.8 Hz, 1H, H-6), 3.68 – 3.60 (m, 2H, H-4', H-6'), 3.42 – 3.34 (m, 4H, H-2', CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4 (d, *J* = 37.3 Hz, C=O), 137.8, 137.7, 137.3 (C_q), 131.6, 131.0, 129.1, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.3, 128.0, 128.0, 127.9, 127.9, 127.5, 126.3 (CH_{arom}), 115.8 (d, *J* = 288.4 Hz, CF_3), 101.9 (CHPh), 98.9 (C-1'), 97.8 (C-1), 82.8 (C-4'), 78.6 (C-3'), 77.2 (C-4), 76.1 (C-3), 75.2, 74.3, 73.7 (CH_2 Bn), 70.7 (C-5), 68.6 (C-6'), 68.1 (C-6), 63.5 (C-5'), 63.0 (C-2'), 55.3 (CH_3 OMe), 52.7 (C-2); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 (d, *J* = 9.3 Hz, 1H, NH), 5.48 (s, 1H, C*H*Ph); ^{13}C NMR (101 MHz, $CDCl_3$) δ 103.2 (C-1'), 101.3 (CHPh), 81.6, 80.2, 79.6, 75.0, 66.4; HRMS: $[M+NH_4]^+$ calcd for $C_{43}H_{45}F_3N_4O_{10}NH_4$ 852.34260, found 852.34131.

Disaccharide 1eA



The title compound was synthesised from donor **A** and acceptor **1e** according to general procedure I as colourless oil. Yield: 62 mg, 65 μmol, 65%, α:β = 11:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 3H, CH_{arom}), 7.40 – 7.16 (m, 20H, CH_{arom}), 7.08 – 7.02 (m, 2H, CH_{arom}), 6.74 (d, *J* = 9.6 Hz, 1H, NH), 5.51 (s, 1H, C*H*Ph), 5.20 (d, *J* = 3.7 Hz, 1H, H-1'), 4.94 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.86 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.81 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.75 – 4.71 (m, 2H, H-1, CH*H* Bn), 4.61 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.56 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.49 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.41 – 4.32 (m, 2H, H-6, C*H*H Bn), 4.23 (td, *J* = 9.9, 3.7 Hz, 1H, H-2), 4.06 (t, *J* = 9.3 Hz, 1H, H-3'), 4.04 – 3.93 (m, 2H, H-3, H-5'), 3.82 – 3.76 (m, 2H, H-4, H-5), 3.72 (dd, *J* = 11.4, 2.1 Hz, 1H, H-6), 3.69 – 3.56 (m, 3H, H-4', H-6, H-6'), 3.53 (dd, *J* = 9.3, 3.7 Hz, 1H, H-2'), 3.39 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (C=O), 138.6, 138.3, 138.3, 137.9, 137.6 (C_q), 128.9, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 127.7, 127.7, 127.5, 127.4, 126.2 (CH_{arom}), 101.4 (CHPh), 99.1 (C-1'), 97.9 (C-1), 92.6 (CCl_3), 82.5 (C-4'), 79.3 (C-2'), 78.2, 78.1, 78.0 (C-3, C-3', C-4), 75.2, 74.3, 74.0, 73.6 (CH_2 Bn), 70.5 (C-5), 69.1 (C-6'), 68.4 (C-6), 63.4 (C-5'), 55.5 (CH_3 OMe), 54.6 (C-2); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (s, 1H, C*H*Ph); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (C=O), 103.3 (C-1'), 101.2 (CHPh), 98.1 (C-1), 81.9, 81.6; HRMS: $[M+NH_4]^+$ calcd for $C_{50}H_{52}Cl_3NO_{11}NH_4$ 965.29442, found 965.29281.

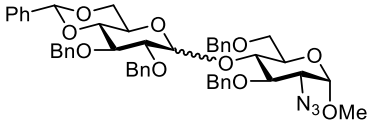
Disaccharide 1eB



The title compound was synthesised from donor **A** and acceptor **1e** according to general procedure I as colourless oil. Yield: 56 mg, 63 μmol, 63%, α:β = 3:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.25 (m, 20H, CH_{arom}), 5.53 (d, *J* = 3.9 Hz, 1H, H-1'), 5.51 (s, 1H, C*H*Ph), 4.96 – 4.86 (m, 2H, 2x C*H*H Bn), 4.80 – 4.73 (m, 2H, H-1, CH*H* Bn), 4.69 (d, *J* = 12.0

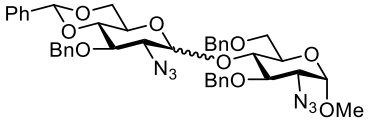
Hz, 1H, C*H*H Bn), 4.61 – 4.53 (m, 2H, 2x CH*H* Bn), 4.31 – 4.21 (m, 2H, H-2, H-6'), 4.10 – 4.01 (m, 2H, H-3, H-3'), 3.95 (td, *J* = 9.9, 4.9 Hz, 1H, H-5'), 3.89 (dd, *J* = 9.7, 8.6 Hz, 1H, H-4), 3.83 – 3.59 (m, 5H, H-4', H-5, 2x H-6, H-6'), 3.40 (s, 3H, CH_3 OMe), 3.34 (dd, *J* = 10.0, 3.9 Hz, 1H, H-2'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (C=O), 137.8, 137.8, 137.7, 137.3 (C_q), 131.6, 131.0, 129.1, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.0, 128.0, 127.9, 127.9, 127.9, 127.5, 126.2 (CH_{arom}), 101.6 (CHPh), 98.4 (C-1'), 97.9 (C-1), 92.4 (CCl_3), 82.9 (C-4'), 79.1 (C-4), 75.9, 75.8 (C-3, C-3'), 75.2, 74.1, 73.7 (CH_2 Bn), 70.7 (C-5), 68.8 (C-6'), 68.1 (C-6), 63.1 (C-5'), 63.0 (C-2'), 55.5 (CH_3 OMe), 54.4 (C-2); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (d, *J* = 9.5 Hz, 1H, NH), 4.64 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.46 (d, *J* = 10.6 Hz, 1H, CH*H* Bn), 4.34 (ddd, *J* = 10.5, 9.5, 3.6 Hz, 1H, H-2), 4.15 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6), 3.28 – 3.21 (m, 1H, H-5'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6 (C=O), 102.7 (C-1'), 101.3 (CHPh), 98.0 (C-1), 81.6, 79.6, 79.0, 76.1, 74.9, 73.6, 68.5, 68.4, 66.5, 66.4, 55.4, 55.0; HRMS: $[M+NH_4]^+$ calcd for $C_{43}H_{45}Cl_3N_4O_{10}NH_4$ 900.25395, found 900.25272.

Disaccharide 2bA



The title compound was synthesised from donor **A** and acceptor **2b** according to general procedure I as colourless oil. Yield: 87 mg, 94 μmol, 94%, α:β = 1.1:1. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.23 (m, 50H), 5.56 (d, *J* = 3.5 Hz, 1H, H-1'α), 5.54 (s, 1H, C*H*Phα), 5.48 (s, 1H, C*H*Phβ), 4.99 (d, *J* = 10.3 Hz, 1H), 4.90 (d, *J* = 11.3 Hz, 2H), 4.87 – 4.53 (m, 14H), 4.39 (d, *J* = 7.9 Hz, 1H, H-1'β), 4.34 (d, *J* = 12.0 Hz, 1H), 4.21 – 4.10 (m, 3H), 4.09 – 3.96 (m, 3H), 3.94 – 3.79 (m, 6H), 3.70 – 3.54 (m, 7H), 3.53 – 3.33 (m, 11H), 3.10 (q, *J* = 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.1, 138.0, 137.6, 137.5, 131.6, 131.1, 129.1, 129.0, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.3, 126.1, 102.9 (C-1'β), 101.3, 101.2 (CHPhαβ), 98.7 (C-1αβ), 97.8 (C-1'α), 82.7, 82.3, 81.8, 81.1, 80.6, 78.9, 78.8, 78.5, 76.9, 75.7, 75.4, 75.3, 75.1, 74.0, 73.5, 73.5, 73.5, 72.8, 70.5, 70.1, 69.0, 68.8, 68.7, 67.5, 65.9, 63.5, 63.5, 63.0, 55.5, 55.4; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{51}N_3O_{10}NH_4$ 847.39127, found 847.39020.

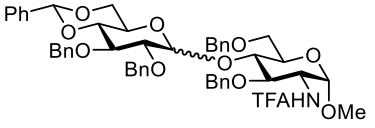
Disaccharide 2bB



The title compound was synthesised from donor **B** and acceptor **2b** according to general procedure I as colourless oil. Yield: 76 mg, 100 μmol, 100%, α:β = 1:3.3. Data for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 20H, CH_{arom}), 5.46 (s, 1H, C*H*Ph), 4.96 – 4.87 (m, 2H, 2x C*H*H Bn), 4.79 – 4.70 (m, 4H, H-1, C*H*H Bn, 2x CH*H* Bn), 4.43 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.20 (d, *J* = 8.0 Hz, 1H, H-1'), 4.12 – 3.98 (m, 3H, H-4, H-6, H-6'), 3.88 (dd, *J* = 10.2, 8.9 Hz, 1H, H-3), 3.83 – 3.76 (m, 1H, H-5), 3.74 – 3.66 (m, 1H, H-6), 3.61 – 3.53 (m, 1H, H-4'), 3.49 – 3.41 (m, 4H, H-2, CH_3 OMe), 3.36 – 3.29 (m, 3H, H-2', H-3', H-6'), 3.00 (td, *J* = 9.8, 5.0 Hz, 1H, H-5'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 137.8, 137.7, 137.2 (C_q), 135.3, 134.5, 131.7, 131.6,

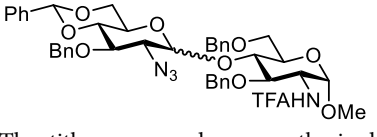
131.0, 130.3, 129.2, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.0, 127.9, 127.9, 127.7, 127.5, 126.1, 126.1 (CH_{arom}), 101.3 (CHPh), 101.2 (C-1'), 98.6 (C-1), 81.7 (C-4'), 79.1 (C-3'), 78.4 (C-3), 76.9 (C-3), 75.2, 74.8, 73.6 (CH_2 Bn), 70.3 (C-5), 68.4 (C-6'), 67.7 (C-6), 66.5 (C-2'), 65.9 (C-5'), 63.1 (C-2), 55.5 (CH_3 OMe); diagnostic peaks for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (d, *J* = 4.0 Hz, 1H, H-1'), 5.54 (s, 1H, C*H*Ph), 4.85 (d, *J* = 3.5 Hz, 1H, H-1), 4.65 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.59 (d, *J* = 12.1 Hz, 1H, CH*H* Bn); HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{44}N_6O_9NH_4$ 782.35080, found 782.34972.

Disaccharide 2cA



The title compound was synthesised from donor **A** and acceptor **2c** according to general procedure I as colourless oil. Yield: 74 mg, 82 μmol, 82%. α:β = 1.3:1. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.42 (m, 6H), 7.44 – 7.17 (m, 41H), 7.20 – 7.12 (m, 3H), 6.31 (d, *J* = 9.3 Hz, 1H, NHα), 6.19 (d, *J* = 9.2 Hz, 1H, NHβ), 5.55 (s, 1H, C*H*Phα), 5.48 (s, 1H, C*H*Phβ), 5.46 (d, *J* = 3.8 Hz, 1H, H-1'α), 4.94 – 4.89 (m, 2H), 4.89 – 4.82 (m, 2H), 4.81 – 4.71 (m, 7H), 4.68 (d, *J* = 7.9 Hz, 1H), 4.64 – 4.56 (m, 5H), 4.52 (d, *J* = 11.2 Hz, 1H), 4.43 (d, *J* = 7.8 Hz, 1H, H-1'β), 4.43 – 4.32 (m, 2H), 4.25 – 4.12 (m, 4H), 4.09 (dd, *J* = 9.9, 8.9 Hz, 1H), 3.99 (t, *J* = 9.3 Hz, 1H), 3.95 – 3.89 (m, 3H), 3.89 – 3.81 (m, 3H), 3.70 (dd, *J* = 10.9, 2.1 Hz, 1H), 3.68 – 3.52 (m, 5H), 3.56 – 3.48 (m, 2H), 3.43 (t, *J* = 10.3 Hz, 1H), 3.40 – 3.32 (m, 7H), 3.21 – 3.05 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.5, 138.4, 138.4, 138.1, 137.9, 137.8, 137.6, 137.5, 137.5, 131.6, 131.0, 129.1, 129.0, 128.7, 128.7, 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 126.1, 102.9 (C-1'β), 101.3 (CHPhα), 101.2 (CHPhβ), 97.9 (C-1'α), 97.6 (C-1β), 97.6 (C-1α), 82.7, 82.2, 81.8, 81.1, 79.5, 78.9, 78.5, 77.1, 76.8, 75.7, 75.3, 75.1, 74.4, 73.8, 73.5, 73.4, 72.7, 72.6, 70.8, 70.6, 69.0, 68.8, 68.6, 67.4, 65.8, 63.6, 55.4, 55.3, 52.8, 52.3; HRMS: $[M+NH_4]^+$ calcd for $C_{50}H_{52}F_3NO_{11}NH_4$ 917.38307, found 917.38154.

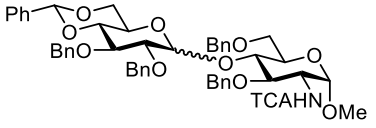
Disaccharide 2cB



The title compound was synthesised from donor **A** and acceptor **2c** according to general procedure I as colourless oil. Yield: 84 mg, 100 μmol, 100%. α:β = 1:2.5. Data for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H, CH_{arom}), 7.47 – 7.30 (m, 18H, CH_{arom}), 6.26 (d, *J* = 9.2 Hz, 1H, NH), 5.52 (s, 1H, C*H*Ph), 4.96 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.88 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.83 – 4.76 (m, 3H, H-1, C*H*H Bn, CH*H* Bn), 4.61 (d, *J* = 11.4 Hz, 1H, CH*H* Bn), 4.51 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.32 – 4.23 (m, 2H, H-1', H-2), 4.23 – 4.14 (m, 2H, H-4, H-6), 4.09 – 4.03 (m, 1H, H-2'), 3.84 – 3.72 (m, 2H, H-5, H-6), 3.69 (dd, *J* = 10.6, 8.9 Hz, 1H, H-3), 3.62 (t, *J* = 9.2 Hz, 1H, H-4'), 3.45 – 3.37 (m, 6H, H-2', H-3', H-6', CH_3 OMe), 3.08 (td, *J* = 9.8, 5.0 Hz, 1H, H-5'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 137.8, 137.8, 137.2 (C_q), 129.2, 128.7, 128.7, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 126.1,

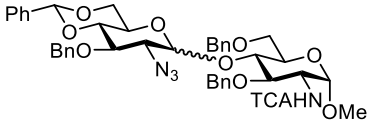
126.1 (CH_{arom}), 101.3 (CHPh), 101.2 (C-1'), 97.7 (C-1), 81.8 (C-4'), 79.2 (C-3'), 77.1 (C-3), 76.8 (C-4), 74.9, 74.6, 73.6 (CH_2 Bn), 70.5 (C-5), 68.5 (C-6'), 67.7 (C-6), 66.6 (C-2'), 65.9 (C-5'), 55.4 (CH_3 OMe), 52.9 (C-2); diagnostic peaks for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (d, *J* = 9.7 Hz, 1H, NH), 5.64 (d, *J* = 4.0 Hz, 1H, H-1'), 5.60 (s, 1H, CHPh), 5.02 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.78 (d, *J* = 3.7 Hz, 1H, H-1); ^{13}C NMR (101 MHz, $CDCl_3$) δ 97.9, 97.8 (C-1, C-1'), 82.6, 81.1, 76.3, 75.1, 74.5, 73.7, 72.3, 70.4, 68.7, 68.7, 63.6, 62.9, 53.3 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{43}H_{45}F_3N_4O_{10}NH_4$ 852.34260, found 852.34132.

Disaccharide 2dA



The title compound was synthesised from donor **A** and acceptor **2c** according to general procedure I as colourless oil. Yield: 77 mg, 82 μmol, 81%. α:β = 1.1:1. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.42 (m, 6H), 7.40 – 7.17 (m, 44H), 6.83 (d, *J* = 9.4 Hz, 1H, NHα), 6.73 (d, *J* = 8.9 Hz, 1H, NHβ), 5.54 (s, 1H, C*H*Phα), 5.52 (d, *J* = 3.8 Hz, 1H, H-1'α), 5.45 (s, 1H, C*H*Phβ), 4.93 – 4.87 (m, 3H), 4.85 – 4.74 (m, 7H), 4.69 – 4.55 (m, 7H), 4.44 (d, *J* = 7.8 Hz, 1H, H-1β), 4.40 – 4.34 (m, 2H), 4.25 (dd, *J* = 9.7, 8.8 Hz, 1H), 4.21 – 4.07 (m, 4H), 4.01 – 3.96 (m, 2H), 3.95 – 3.83 (m, 4H), 3.73 – 3.64 (m, 2H), 3.63 – 3.52 (m, 6H), 3.48 (dd, *J* = 9.5, 3.8 Hz, 1H), 3.41 – 3.35 (m, 7H), 3.32 (t, *J* = 10.3 Hz, 1H), 3.14 – 3.08 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7, 161.7 (C=Oαβ), 138.7, 138.5, 138.5, 138.5, 138.1, 137.9, 137.9, 137.7, 137.6, 137.5, 135.3, 134.3, 131.9, 131.5, 131.2, 130.3, 129.0, 129.0, 128.6, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.6, 127.6, 127.4, 126.1, 102.9 (C-1β), 101.2, 101.1 (CHPhαβ), 97.8, 97.8 (C-1αβ), 97.6 (C-1'α), 92.6, 92.5 (CCl_3αβ), 82.7, 82.2, 81.8, 81.1, 80.3, 78.8, 78.6, 77.9, 76.6, 75.6, 75.3, 75.0, 74.4, 73.6, 73.6, 73.5, 72.2, 71.9, 70.8, 70.4, 69.0, 68.7, 67.5, 65.8, 63.5, 55.6, 55.4, 54.3, 53.9; HRMS: $[M+NH_4]^+$ calcd for $C_{50}H_{52}Cl_3NO_{11}NH_4$ 965.29442, found 965.29364.

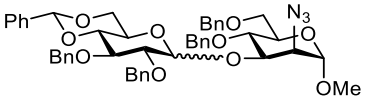
Disaccharide 2dB



The title compound was synthesised from donor **A** and acceptor **2c** according to general procedure I as colourless oil. Yield: 88 mg, 100 μmol, 100%. α:β = 1:3.5. Data for the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 20H, CH_{arom}), 6.74 (d, *J* = 9.0 Hz, 1H, NH), 5.43 (s, 1H, C*H*Ph), 4.90 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.85 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.82 (d, *J* = 3.7 Hz, 1H, H-1), 4.77 – 4.73 (m, 2H, C*H*H Bn, CH*H*Bn), 4.61 (d, *J* = 11.0 Hz, 1H, CH*H* Bn), 4.46 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.25 (d, *J* = 7.7 Hz, 1H, H-1'), 4.20 (ddd, *J* = 10.5, 9.1, 3.7 Hz, 1H, H-2), 4.12 (dd, *J* = 10.0, 8.9 Hz, 1H, H-4), 4.06 (dd, *J* = 10.6, 5.0 Hz, 1H, H-6'), 4.02 (dd, *J* = 11.0, 2.9 Hz, 1H, H-6), 3.79 (dt, *J* = 9.9, 2.3 Hz, 1H, H-5), 3.76 – 3.68 (m, 2H, H-3, H-6), 3.53 (t, *J* = 9.2 Hz, 1H, H-4'), 3.41 (s, 3H, CH_3 OMe), 3.37 – 3.32 (m, 2H, H-2', H-3'), 3.25 (t, *J* = 10.3 Hz, 1H, H-6'), 3.00 (td, *J* = 9.7, 5.0 Hz, 1H, H-5'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7 (C=O), 138.4, 137.8, 137.8, 137.2 (C_q), 131.9, 131.6, 129.1, 128.7, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3,

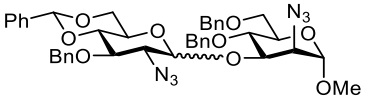
128.3, 128.2, 128.2, 128.0, 128.0, 127.9, 127.6, 127.6, 127.5, 126.1, 126.1 (CH_{arom}), 101.3 (CHPh), 101.1 (C-1'), 97.9 (C-1), 92.6 (CCl_3), 81.7 (C-4'), 79.1 (C-3'), 77.9 (C-3), 76.7 (C-4), 74.8, 74.7, 73.6 (CH_2 Bn), 70.5 (C-5), 68.4 (C-6'), 67.8 (C-6), 66.6 (C-2'), 65.8 (C-5'), 55.6 (CH_3 OMe) 54.4 (C-2); diagnostic peaks for the α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (d, *J* = 9.7 Hz, 1H, NH), 5.61 (d, *J* = 4.0 Hz, 1H, H-1'), 5.54 (s, 1H, C*H*Ph), 4.96 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.36 (td, *J* = 9.9, 3.7 Hz, 1H, H-2); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6 (C=O), 101.3 (CHPh), 98.0 (C-1'), 82.6, 81.5, 76.3, 75.1, 74.4, 72.3, 70.2, 68.8, 68.7, 63.5, 62.8, 55.5 (CH_3 OMe), 55.0 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{43}H_{45}Cl_3N_4O_{10}NH_4$ 900.25395, found 900.25318.

Disaccharide 3cA



The title compound was synthesised from donor **A** and acceptor **3c** according to general procedure I as colourless oil. Yield: 83 mg, 100 μmol, 100%. α:β = 7:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.8, 1.9 Hz, 2H, CH_{arom}), 7.41 – 7.16 (m, 21H, CH_{arom}), 7.10 – 7.05 (m, 2H, CH_{arom}), 5.55 (s, 1H, C*H*Ph), 5.09 (d, *J* = 3.7 Hz, 1H, H-1'), 5.01 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.92 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.83 – 4.77 (m, 2H, H-1, CH*H* Bn), 4.73 (d, *J* = 12.2 Hz, 1H, CH*H* Bn), 4.65 – 4.58 (m, 2H, C*H*H Bn, CH*H* Bn), 4.49 (d, *J* = 12.2 Hz, 1H, CH*H* Bn), 4.42 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.32 (dd, *J* = 10.3, 4.9 Hz, 1H, H-6'), 4.19 – 4.07 (m, 3H, H-3, H-3', H-5'), 3.93 (dd, *J* = 3.8, 1.8 Hz, 1H, H-2), 3.89 (t, *J* = 9.5 Hz, 1H, H-4), 3.77 – 3.59 (m, 5H, H-4', H-5, 2x H-6, H-6'), 3.55 (dd, *J* = 9.4, 3.7 Hz, 1H, H-2'), 3.37 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.6, 138.2, 138.1, 137.5 (C_q), 129.0, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 126.2, 126.1 (C_q), 101.4 (CHPh), 100.3 (C-1'), 99.0 (C-1), 82.4 (C-4'), 79.7 (C-3), 78.9 (C-2'), 78.3 (C-3'), 75.3, 74.8 (CH_2 Bn), 74.0 (C-4), 73.6, 73.6 (CH_2 Bn), 71.7 (C-5), 69.2, 68.8 (C-6, C-6'), 63.9 (C-5'), 63.2 (C-2), 55.1 (CH_3 OMe); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (s, 1H, C*H*PH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 101.9 (C-1'), 101.2 (CHPh), 99.1 (C-1), 81.9, 81.7, 81.4, 79.1, 77.9, 75.1, 75.0, 73.7, 71.6, 68.5, 66.1; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{51}N_3O_{10}NH_4$ 847.39127, found 847.39022.

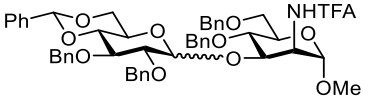
Disaccharide 3cB



The title compound was synthesised from donor **B** and acceptor **3c** according to general procedure I as colourless oil. Yield: 57 mg, 75 μmol, 75%. α:β = 1.8:1. Data reported for a 2:1 mixture of anomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.14 (m, 60H), 5.58 (s, 2H, C*H*Phα), 5.55 (s, 1H, C*H*Phβ), 5.28 (d, *J* = 3.8 Hz, 2H, H-1'α), 4.95 (dd, *J* = 10.8, 5.3 Hz, 5H), 4.87 (d, *J* = 10.6 Hz, 1H), 4.83 – 4.77 (m, 4H), 4.74 – 4.64 (m, 6H), 4.59 – 4.45 (m, 6H), 4.43 – 4.38 (m, 2H, H-1'β, CH*H* Bn), 4.31 (dd, *J* = 10.4, 4.9 Hz, 2H), 4.24 (dd, *J* = 9.3, 3.7 Hz, 3H), 4.21 – 4.11 (m, 3H), 4.05 – 3.94 (m, 5H), 3.91 (dd, *J* = 3.8, 1.8 Hz, 2H), 3.87 (t, *J* = 9.2 Hz, 1H), 3.79 – 3.58 (m, 17H), 3.53 – 3.42 (m, 3H, H-2'αβ)), 3.35 (d, *J* = 1.6 Hz, 10H, H-5'β, CH_3 OMeαβ); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 138.1, 137.8, 137.2, 137.1, 129.2, 128.6, 128.5, 128.5, 128.4, 128.4, 128.1,

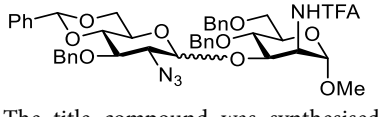
128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 126.2, 126.1, 101.6 (CHPhα), 101.5 (CHPhβ), 101.4 (C-1'β), 99.9 (C-1'α), 99.3 (C-1β), 99.0 (C-1α), 82.9, 81.7, 80.3, 79.8, 77.7, 76.2, 75.3, 75.0, 74.9, 74.8, 73.7, 73.6, 73.4, 71.7, 71.7, 68.9, 68.7, 68.6, 68.5, 66.5, 66.4, 63.9, 63.5, 63.2, 62.0, 55.1 (CH_3 OMeαβ); HRMS: $[M+NH_4]^+$ calcd for $C_{41}N_{44}N_6O_9NH_4$ 782.35080, found 782.34970.

Disaccharide 3dA



The title compound was synthesised from donor **A** and acceptor **3c** according to general procedure I as colourless oil. Yield: 72 mg, 80 μmol, 80%. α:β = 2.3:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.17 (m, 25H), 5.50 (s, 1H, C*H*Ph), 5.06 (d, *J* = 3.7 Hz, 1H, H-1'), 5.01 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.88 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.82 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.71 (d, *J* = 2.5 Hz, 1H, H-1), 4.62 – 4.55 (m, 2H, C*H*H Bn, CH*H* Bn), 4.54 – 4.47 (m, 2H, H-2, C*H*H Bn), 4.44 – 4.39 (m, 2H, 2x CH*H* Bn), 4.31 – 4.19 (m, 2H, H-3, H-6'), 4.02 (t, *J* = 9.4 Hz, 1H, H-3'), 3.87 (td, *J* = 9.9, 4.7 Hz, 1H, H-5'), 3.82 – 3.69 (m, 3H, H-4, H-5, H-6), 3.66 – 3.60 (m, 2H, H-6, H-6'), 3.57 (t, *J* = 9.5 Hz, 1H, H-4'), 3.52 (dd, *J* = 9.5, 3.7 Hz, 1H, H-2'), 3.37 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.4, 138.1, 137.7 (C_q), 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 127.8, 127.7, 127.6, 127.6, 127.5, 126.3, 126.1 (CH_{arom}), 101.6 (CHPh), 100.3 (C-1'), 99.1 (C-1), 82.4 (C-4'), 78.8 (C-2'), 78.3 (C-3'), 77.6 (C-3), 75.2, 74.9 (CH_2 Bn), 73.9 (C-4), 73.8, 73.7 (CH_2 Bn), 70.9 (C-5), 69.0 (C-6'), 68.4 (C-6), 64.0 (C-5'), 55.4 (CH_3 OMe), 53.0 (C-2); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (s, 1H, C*H*Ph), 4.67 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.37 (d, *J* = 11.0 Hz, 1H, CH*H* Bn), 3.45 (t, *J* = 7.2 Hz, 1H, H-2'), 3.35 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 101.2 (CHPh), 99.7 (C-1'), 99.3 (C-1), 81.5, 81.2, 81.0, 74.8, 74.7, 74.4, 74.3, 73.7, 73.5, 70.7, 68.5, 65.9, 50.0; HRMS: $[M+NH_4]^+$ calcd for $C_{50}H_{52}F_3NO_{11}NH_4$ 917.38307, found 917.38211.

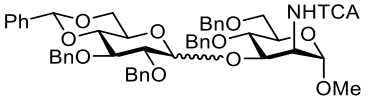
Disaccharide 3dB



The title compound was synthesised from donor **B** and acceptor **3c** according to general procedure I as colourless oil. Yield: 77 mg, 92 μmol, 92%. α:β = 1:1.2. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dtt, *J* = 14.2, 4.4, 2.1 Hz, 5H), 7.41 – 7.25 (m, 32H), 7.20 (ddd, *J* = 7.4, 5.9, 1.7 Hz, 3H), 5.56 (s, 1H, C*H*Phβ), 5.54 (s, 1H, C*H*Phα), 5.28 (d, *J* = 3.7 Hz, 1H, H-1'α), 4.94 (d, *J* = 11.2 Hz, 1H), 4.90 (d, *J* = 11.2 Hz, 2H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.80 – 4.75 (m, 2H), 4.73 (d, *J* = 11.1 Hz, 1H), 4.68 (d, *J* = 1.6 Hz, 1H, H-1α), 4.66 (d, *J* = 8.0 Hz, 1H), 4.64 – 4.59 (m, 2H), 4.53 – 4.44 (m, 7H), 4.41 (d, *J* = 10.7 Hz, 1H), 4.36 – 4.26 (m, 3H), 4.11 (td, *J* = 9.9, 4.9 Hz, 1H), 4.03 (t, *J* = 9.6 Hz, 1H), 3.87 – 3.72 (m, 7H), 3.72 – 3.61 (m, 7H), 3.45 – 3.34 (m, 8H), 3.31 (dd, *J* = 10.1, 3.8 Hz, 1H, H-2'α); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 137.9, 137.8, 137.8, 137.5, 137.5, 137.4, 137.1, 135.4, 134.3, 132.0, 131.5, 131.3, 130.3, 129.2, 129.1, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 126.4, 126.1, 101.7, 101.4 (CHPhαβ), 99.9 (C-1'α), 99.4, 99.3 (C-1αβ), 98.4 (C-1'β), 82.8, 81.8, 79.4, 75.6, 75.2, 75.1, 75.1, 75.0, 74.9, 74.9, 74.7, 73.8, 73.7, 72.8, 71.0, 70.5, 68.8, 68.6, 68.2,

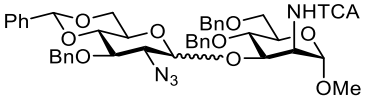
68.2, 66.6, 66.3, 63.5, 63.0, 55.3, 53.1, 49.5; HRMS: $[M+NH_4]^+$ calcd for $C_{43}H_{45}F_3N_4O_{10}NH_4$ 852.34260, found 852.34134.

Disaccharide 3eA



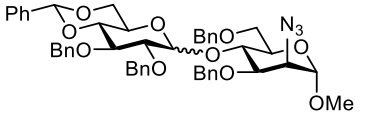
The title compound was synthesised from donor **A** and acceptor **3c** according to general procedure I as colourless oil. Yield: 54 mg, 57 µmol, 57%. α:β = 5:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.11 (m, 25H, CH_{arom}), 5.50 (s, 1H, C*H*Ph), 5.07 (d, *J* = 3.8 Hz, 1H, H-1'), 5.04 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.88 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.79 – 4.69 (m, 3H, H-1, C*H*H Bn, CH*H* Bn), 4.61 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.56 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.50 – 4.36 (m, 3H, H-2, 2x CH*H* Bn), 4.35 – 4.26 (m, 2H, H-3, H-6'), 4.05 (t, *J* = 9.4 Hz, 1H, H-3'), 3.92 (td, *J* = 9.9, 4.8 Hz, 1H, H-5'), 3.85 – 3.75 (m, 2H, H-4, H-5), 3.72 (dd, *J* = 10.5, 2.9 Hz, 1H, H-6), 3.70 – 3.53 (m, 3H, H-4', H-6, H-6'), 3.52 (dd, *J* = 9.5, 3.8 Hz, 1H, H-2'), 3.39 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (C=O), 138.7, 138.4, 138.1, 138.0, 137.7 (C_q), 131.6, 131.1, 128.9, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.6, 127.6, 127.5, 127.1, 126.4 (CH_{arom}), 101.4 (CHPh), 100.7 (C-1'), 98.9 (C-1), 92.5 (CCl_3), 82.4 (C-4'), 78.9 (C-2'), 78.3, 78.2 (C-3, C-3'), 75.1, 75.0 (CH_2 Bn), 73.7 (C-4), 73.7, 73.5 (CH_2 Bn), 71.1 (C-5), 69.0 (C-6'), 68.5 (C-6), 63.8 (C-5'), 55.4 (CH_3 OMe), 54.4 (C-2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (s, 1H, C*H*Ph), 4.99 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.23 (dd, *J* = 10.2, 4.8 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 101.1 (CHPh), 99.7 (C-1'), 99.1 (C-1), 81.4, 81.3, 81.0, 79.1, 76.4, 75.4, 74.7, 74.5, 74.3, 74.2, 73.2, 72.6, 71.4, 71.2, 54.5; HRMS: $[M+NH_4]^+$ calcd for $C_{50}H_{52}Cl_3NO_{11}NH_4$ 965.29442, found 965.29366.

Disaccharide 3eB



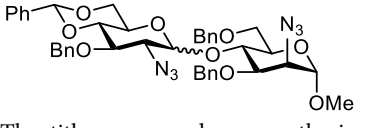
The title compound was synthesised from donor **B** and acceptor **3c** according to general procedure I as colourless oil. Yield: 70 mg, 80 µmol, 80%. α:β = 1:1.1. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.20 (m, 40H), 7.08 – 6.98 (m, 2H, NHαβ), 5.56 (s, 1H, C*H*Phα), 5.54 (s, 1H, C*H*Phβ), 5.24 (d, *J* = 3.7 Hz, 1H, H-1'α), 4.97 (d, *J* = 10.5 Hz, 1H), 4.94 – 4.89 (m, 2H), 4.85 (d, *J* = 10.8 Hz, 1H), 4.81 (d, *J* = 1.7 Hz, 1H, H-1α/β), 4.78 (d, *J* = 11.0 Hz, 1H), 4.75 – 4.71 (m, 2H), 4.65 (d, *J* = 10.3 Hz, 1H), 4.62 (d, *J* = 10.1 Hz, 1H), 4.56 (d, *J* = 7.9 Hz, 1H, H-1'β), 4.54 – 4.43 (m, 5H), 4.40 (ddd, *J* = 8.9, 4.3, 1.8 Hz, 1H), 4.37 – 4.29 (m, 3H), 4.14 – 4.02 (m, 2H), 3.88 (t, *J* = 9.6 Hz, 1H), 3.84 – 3.64 (m, 12H), 3.46 – 3.35 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 162.1 (C=O), 138.1, 137.9, 137.9, 137.8, 137.8, 137.5, 137.1 (C_q), 135.4, 134.5, 131.7, 131.6, 131.0, 130.4, 130.3, 129.2, 129.0, 129.0, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 126.4, 126.1 (CH_{arom}), 101.6, 101.4 (CHPhαβ), 100.2 (C-1'α), 99.1, 99.1 (C-1αβ), 98.2 (C-1'β), 82.8, 81.8, 79.5, 75.9, 75.8, 75.2, 75.0, 75.0, 74.8, 73.6, 73.6, 72.9, 71.2, 70.8, 68.8, 68.7, 68.3, 66.6, 66.3, 63.5, 63.2, 55.4, 55.3, 54.5, 50.8; HRMS: $[M+NH_4]^+$ calcd for $C_{43}H_{45}Cl_3N_4O_{10}NH_4$ 900.25395, found 900.25352.

Disaccharide 4bA



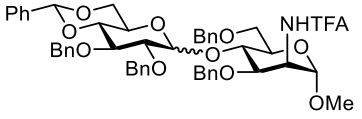
The title compound was synthesised from donor **A** and acceptor **4b** according to general procedure I as colourless oil. Yield: 83 mg, 100 µmol, 100%. α:β = 1:2.5. Data for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 25H, CH_{arom}), 5.46 (s, 1H, C*H*Ph), 4.92 – 4.84 (m, 2H, 2x C*H*H Bn), 4.79 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.74 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.69 – 4.65 (m, 2H, H-1, CH*H* Bn), 4.61 – 4.56 (m, 2H, 2x CH*H* Bn), 4.43 (d, *J* = 7.7 Hz, 1H, H-1'), 4.36 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.21 – 4.09 (m, 2H, H-4, H-6'), 3.92 – 3.87 (m, 2H, H-2, H-3), 3.80 (dd, *J* = 10.8, 4.0 Hz, 1H, H-6), 3.62 – 3.54 (m, 4H, H-3', H-4', H-5, H-6), 3.45 – 3.38 (m, 1H, H-6'), 3.36 (s, 3H, CH_3 OMe), 3.34 – 3.30 (m, 1H, H-2'), 3.16 (td, *J* = 9.4, 5.0 Hz, 1H, H-5'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 138.5, 138.4, 138.2, 137.5 (C_q), 135.3, 134.3, 131.9, 131.5, 131.2, 130.3, 129.0, 128.6, 128.5, 128.4, 128.3, 128.3, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 127.4, 127.3, 127.1, 126.1 (CH_{arom}), 103.2 (C-1'), 101.1 (CHPh), 99.1 (C-1), 82.6 (C-2'), 81.7 (C-4'), 81.1 (C-3'), 77.3 (C-3), 75.5 (CH_2 Bn), 75.0 (C-4), 75.0, 73.4, 73.1 (CH_2 Bn), 71.5 (C-5), 68.8 (C-6'), 68.0 (C-6), 65.7 (C-5'), 62.2 (C-2), 55.2 (CH_3 OMe); diagnostic peaks for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (d, *J* = 3.9 Hz, 1H, H-1'), 5.52 (s, 1H, C*H*Ph), 4.54 (d, *J* = 11.9 Hz, 1H), 4.31 (d, *J* = 9.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 101.1 (CHPh), 99.0 (C-1), 97.8 (C-1'), 82.2, 80.5, 78.9, 78.6, 75.3, 71.7, 70.9, 70.1, 69.1, 68.9, 63.4, 60.5, 55.0; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{51}N_3O_{10}NH_4$ 847.39127, found 847.39012.

Disaccharide 4bB



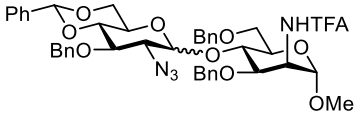
The title compound was synthesised from donor **B** and acceptor **4b** according to general procedure I as colourless oil. Yield: 83 mg, 100 µmol, 100%. α:β = 1:14. Data for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.60 (m, 3H, CH_{arom}), 7.46 (dq, *J* = 4.4, 2.4 Hz, 3H, CH_{arom}), 7.42 – 7.26 (m, 19H, CH_{arom}), 5.45 (s, 1H, C*H*Ph), 4.89 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.80 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.78 – 4.72 (m, 2H, C*H*H Bn, CH*H* Bn), 4.70 (d, *J* = 1.6 Hz, 1H, H-1), 4.66 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.49 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.25 (d, *J* = 8.1 Hz, 1H, H-1'), 4.18 (t, *J* = 9.3 Hz, 1H, H-4'), 4.10 (dd, *J* = 10.6, 5.0 Hz, 1H, H-6'), 3.96 – 3.90 (m, 2H, C-3, C-6), 3.88 (dd, *J* = 3.8, 1.7 Hz, 1H, H-2'), 3.76 – 3.68 (m, 2H, H-5, H-6), 3.54 (t, *J* = 9.2 Hz, 1H, H-4'), 3.42 – 3.37 (m, 2H, H-4', H-6'), 3.36 (s, 3H, CH_3 OMe), 3.28 (dd, *J* = 9.4, 8.1 Hz, 1H, H-2'), 3.07 (td, *J* = 9.7, 5.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 138.1, 137.8, 137.3 (C_q), 135.4, 134.4, 131.8, 131.5, 131.2, 130.3, 130.3, 129.1, 128.6, 128.5, 128.4, 128.3, 128.3, 128.0, 127.9, 127.5, 127.0, 126.1 (CH_{arom}), 101.6 (C-1'), 101.3 (CHPh), 99.2 (C-1), 81.7 (C-4'), 79.3 (C-3'), 77.5 (C-3), 75.0 (C-4), 74.9, 73.6, 73.1 (CH_2 Bn), 71.1 (C-5), 68.6 (C-6'), 68.2 (C-6), 66.7 (C-2'), 65.9 (C-5'), 62.1 (C-2), 55.1 (CH_3 OMe); diagnostic peaks for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (d, *J* = 4.0 Hz, 1H, H-1'), 5.54 (s, 1H, C*H*Ph); HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{44}N_6O_9NH_4$ 782.35080, found 782.34981.

Disaccharide 4cA



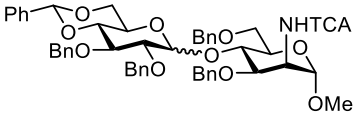
The title compound was synthesised from donor **A** and acceptor **4c** according to general procedure I as colourless oil. Yield: 64 mg, 71 µmol, 71%. α:β = 1:1.4. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.18 (m, 50H), 7.04 (d, *J* = 9.1 Hz, 1H, NHα), 6.87 (d, *J* = 8.6 Hz, 1H, NHβ) 5.70 (d, *J* = 3.9 Hz, 1H, H-1'α), 5.54 (s, 1H, C*H*Phα), 5.51 (s, 1H, C*H*Phβ), 4.93 – 4.88 (m, 2H), 4.85 – 4.72 (m, 7H), 4.70 – 4.64 (m, 4H), 4.61 (s, 2H), 4.58 – 4.49 (m, 3H), 4.39 (d, *J* = 7.7 Hz, 1H, H-1'β), 4.36 – 4.31 (m, 2H), 4.25 (dd, *J* = 9.0, 4.3 Hz, 1H), 4.21 – 4.07 (m, 3H), 4.00 – 3.88 (m, 5H), 3.83 (dd, *J* = 10.7, 3.2 Hz, 1H), 3.76 (ddd, *J* = 12.4, 8.5, 3.7 Hz, 1H), 3.73 – 3.69 (m, 1H), 3.67 – 3.57 (m, 6H), 3.57 – 3.52 (m, 1H), 3.51 – 3.46 (m, 2H), 3.41 – 3.33 (m, 7H), 3.18 (tt, *J* = 9.3, 4.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 138.5, 138.4, 138.1, 137.9, 137.8, 137.7, 137.5, 137.5, 137.3, 135.4, 134.2, 132.0, 131.4, 131.3, 130.3, 130.2, 129.1, 129.0, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.5, 127.4, 126.1, 126.1, 125.7, 103.4 (C-1'β), 101.2 (CHPhαβ), 99.1 (C-1αβ), 97.4 (C-1'α), 82.5, 82.2, 81.7, 81.2, 78.9, 78.5, 78.2, 75.6, 75.4, 75.1, 75.0, 74.5, 73.6, 73.4, 73.3, 71.9, 71.0, 70.6, 70.0, 69.0, 69.0, 68.9, 68.9, 68.0, 65.9, 63.6, 55.5, 55.4, 50.6, 49.5; HRMS: $[M+NH_4]^+$ calcd for $C_{50}H_{52}F_3NO_{11}NH_4$ 917.38307, found 917.38203.

Disaccharide 4cB



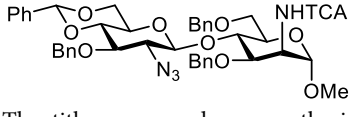
The title compound was synthesised from donor **B** and acceptor **4c** according to general procedure I as colourless oil. Yield: 64 mg, 77 µmol, 77%. α:β = 1:10. Data for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.60 (m, 3H, CH_{arom}), 7.49 – 7.45 (m, 3H, CH_{arom}), 7.42 – 7.26 (m, 19H, CH_{arom}), 6.94 (d, *J* = 8.8 Hz, 1H, NH), 5.49 (s, 1H, C*H*Ph), 4.90 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.78 – 4.74 (m, 2H, H-1, CH*H* Bn), 4.72 – 4.66 (m, 2H, 2x C*H*H Bn), 4.60 – 4.49 (m, 3H, H-2, 2x CH*H* Bn), 4.24 (d, *J* = 8.1 Hz, 1H, H-1'), 4.05 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6'), 4.01 – 3.92 (m, 3H, H-3, H-4, H-5), 3.79 (d, *J* = 8.8 Hz, 1H, H-5), 3.74 (dd, *J* = 10.6, 1.8 Hz, 1H, H-6), 3.60 (t, *J* = 9.2 Hz, 1H, H-4'), 3.53 (t, *J* = 10.3 Hz, 1H, H-6'), 3.44 (t, *J* = 9.3 Hz, 1H, H-3'), 3.38 (s, 3H, CH_3 OMe), 3.30 (dd, *J* = 9.4, 8.2 Hz, 1H, H-2'), 3.06 (td, *J* = 9.7, 5.0 Hz, 1H, H-5'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 137.8, 137.6, 137.2 (C_q), 135.4, 134.4, 131.9, 131.5, 131.2, 130.3, 129.2, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 127.7, 127.3, 126.1, 126.0 (CH_{arom}), 101.7 (C-1'), 101.4 (CHPh), 99.1 (C-1), 81.7 (C-4'), 79.3 (C-3'), 75.4 (C-3), 74.9 (CH_2 Bn), 74.6 (C-4), 73.7, 71.8 (CH_2 Bn), 70.2 (C-5), 68.6 (C-6'), 68.1 (C-6), 66.8 (C-2'), 66.0 (C-5'), 55.4 (CH_3 OMe), 50.3 (C-2); diagnostic peaks for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (d, *J* = 4.1 Hz, 1H, H-1'), 5.56 (s, 1H, C*H*Ph); HRMS: $[M+NH_4]^+$ calcd for $C_{43}H_{45}F_3N_4O_{10}NH_4$ 852.34260, found 875.34206.

Disaccharide 4dA



The title compound was synthesised from donor **A** and acceptor **4d** according to general procedure I as colourless oil. Yield: 73 mg, 77 µmol, 77%. α:β = 1:2.7. Data for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.15 (m, 25H, CH_{arom}), 6.92 (d, *J* = 8.5 Hz, 1H, NH), 5.48 (s, 1H, C*H*Ph), 4.89 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.85 – 4.80 (m, 2H, H-1, C*H*H Bn), 4.76 – 4.68 (m, 2H, C*H*H Bn, CH*H* Bn), 4.62 – 4.54 (m, 2H, 2x CH*H* Bn), 4.55 – 4.45 (m, 3H, H-1', H-2, C*H*H Bn), 4.35 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 4.07 (dd, *J* = 10.5, 5.1 Hz, 1H, H-6'), 4.02 – 3.94 (m, 2H, H-3, H-4), 3.84 (dd, *J* = 10.7, 3.3 Hz, 1H, H-6), 3.72 (td, *J* = 9.2, 2.3 Hz, 1H, H-5), 3.65 – 3.51 (m, 4H, H-2', H-3', H-6, H-6'), 3.40 – 3.33 (m, 4H, H-4', CH_3 OMe), 3.13 (td, *J* = 9.3, 4.9 Hz, 1H, H-5'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (C=O), 138.5, 138.4, 138.3, 138.1, 137.4 (C_q), 129.1, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.1, 128.0, 127.9, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.5, 127.5, 127.3, 127.3, 126.1, 126.1 (CH_{arom}), 103.3 (C-1'), 101.2 (CHPh), 99.0 (C-1'), 82.6 (C-4'), 81.7, 81.2 (C-2', C-3'), 75.5 (CH_2 Bn), 75.4 (C-3), 75.1 (CH_2 Bn), 74.5 (C-4), 73.3, 71.5 (CH_2 Bn), 70.8 (C-5), 68.8 (C-6'), 68.2 (C-6), 65.8 (C-5'), 55.5 (CH_3 OMe), 51.6 (C-2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (d, *J* = 4.0 Hz, 1H, H-1'), 5.51 (s, 1H, C*H*Ph); ^{13}C NMR (101 MHz, $CDCl_3$) δ 97.5 (C-1'), 82.2, 78.8, 78.5, 78.3, 77.5, 75.4, 75.4, 73.5, 73.2, 70.2, 69.1, 69.1, 68.9, 63.6, 55.5, 50.6; HRMS: $[M+NH_4]^+$ calcd for $C_{50}H_{52}Cl_3NO_{11}NH_4$ 965.29442, found 965.29360.

Disaccharide 4dB



The title compound was synthesised from donor **B** and acceptor **4d** according to general procedure I as colourless oil. Yield: 88 mg, 100 µmol, 100%, α:β < 1:20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H, CH_{arom}), 7.42 – 7.26 (m, 18H, CH_{arom}), 6.96 (d, *J* = 8.8 Hz, 1H, NH), 5.47 (s, 1H, NH), 4.89 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.83 (d, *J* = 1.9 Hz, 1H, H-1), 4.77 (d, *J* = 9.7 Hz, 1H, C*H*H Bn), 4.74 (d, *J* = 9.7 Hz, 1H, CH*H* Bn), 4.67 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.58 – 4.46 (m, 3H, H-2, 2x CH*H* Bn), 4.33 (d, *J* = 8.1 Hz, 1H, H-1'), 4.06 – 3.93 (m, 4H, H-3, H-4, H6, H-6'), 3.83 – 3.80 (m, 1H, H-5), 3.77 (dd, *J* = 10.6, 1.9 Hz, 1H, H-6), 3.59 (t, *J* = 9.2 Hz, 1H, H-4'), 3.56 – 3.42 (m, 2H, H-3', H-6'), 3.40 (s, 3H, CH_3 OMe), 3.32 (dd, *J* = 9.4, 8.2 Hz, 1H, H-2'), 3.02 (td, *J* = 9.8, 5.0 Hz, 1H, H-5'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (C=O), 138.1, 138.0, 137.8, 137.2 (C_q), 134.9, 133.4, 132.3, 131.9, 131.6, 131.5, 131.1, 129.2, 128.6, 128.5, 128.4, 128.3, 128.3, 128.1, 128.0, 127.9, 127.6, 127.2, 126.1 (CH_{arom}), 101.8 (C-1'), 101.3 (CHPh), 99.0 (C-1), 81.7 (C-4'), 79.3 (C-3'), 75.7 (C-3), 74.9 (CH_2 Bn), 74.7 (C-4), 73.6, 71.4 (CH_2 Bn), 70.3 (C-5), 68.5, 68.3 (C-6, C-6'), 66.9 (C-2'), 66.0 (C-5'), 55.5 (CH_3 OMe), 51.3 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{43}H_{45}Cl_3N_4O_{10}NH_4$ 900.25395, found 900.25314.

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