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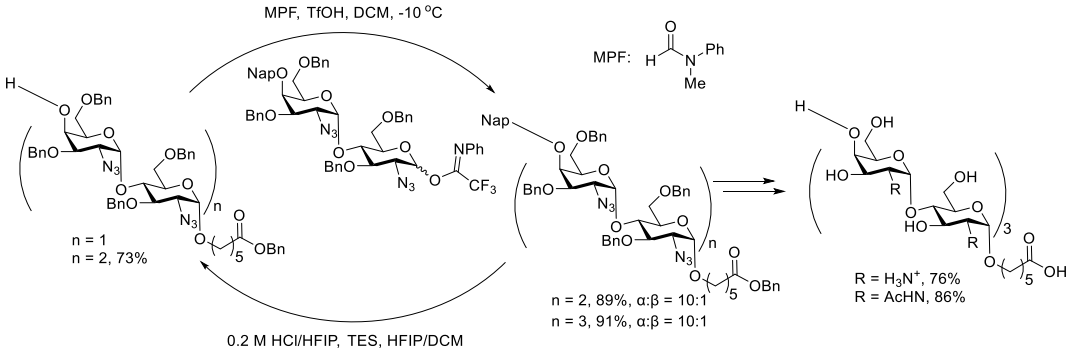
Leiden Institute of Chemistry, Leiden University, Einsteinweg 55, 2333 CC Leiden, The Netherlands.

Supporting Information Placeholder



ABSTRACT: A new additive, methyl(phenyl)formamide (MPF), is introduced for the glycosylation of 2-azido-2-deoxyglucose building blocks. A linear α-(1,4)-glucosamine tetrasaccharide was assembled to prove the utility of MPF. Next, a hexasaccharide fragment of the *Pseudomonas aeruginosa* exopolysaccharide Pel was assembled using a [2+2+2] strategy modulated by MPF. The used [galactosazide-α-(1,4)-glucosazide] disaccharide building blocks were synthesized using a 4,6-*O*-DTBS protected galactosyl azide donor.

Introduction

Pel is one of the exopolysaccharides that is involved in the biofilm formation of *Pseudomonas aeruginosa*, an opportunistic Gram-positive pathogen that is the major cause of morbidity and mortality in cystic fibrosis patients.[1] Pel is a linear polysaccharide composed of 1,4-linked α-*N*-acetyl galactosamine (GalNAc) and α-*N*-acetyl glucosamine (GlcNAc) residues, present in a ±6 : 1 ratio, of which some of the residues have been de-acetylated to generate positively charged galactosamine (GalN) and glucosamine (GlcN) moieties (Figure 1).[1b] Well-defined Pel fragments can be used to unravel their role in biofilm formation, to study their biosynthesis and possibly as synthetic antigens in the development of a (semi)-synthetic vaccine against *P. aeruginosa.* Because of the random distribution of the monosaccharides in Pel, it is impossible to isolate well-defined oligosaccharides from natural sources and therefore organic synthesis is necessary to provide these structures.

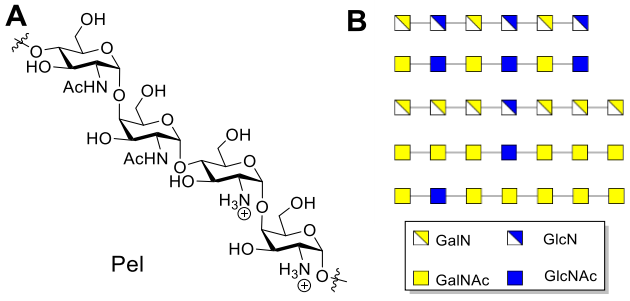
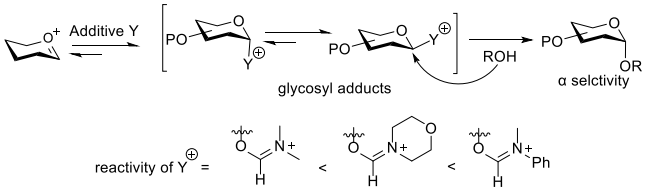


Figure 1. The repeating structures of Pel.

The key challenge in the generation of these oligosaccharides is the stereoselective construction of the 1,2-*cis*-glycosidic linkages. Four kinds of *cis*-glycosidic linkages, namely α-D-GlcN-(1 → 4)-D-GlcN, α-D-GlcN-(1 → 4)-D-GalN, α-D-GalN-(1→4)-D-GlcN and α-D-GalN-(1→4)-D-GalN, have to be constructed. Zhang *et al.* have recently reported an effective synthetic strategy to assembly galactosaminogalactans (GAGs), fungal polysaccharides composed of 1,4-linked α-D-Gal, α-D-GalN and α-D-GalNAc moieties.[2] For the formation of the 1,2-*cis*-linkages in these structures, 4,6-di-*tert*-

butylsilylene (4,6-*O*-DTBS) protected GalN-donors were used to control the selectivity.[3] This strategy allowed the use of galactosamine donors bearing differently masked amine functionalities. Galactosazide and trichloroacetyl protected GalN donors were used to combine GalN and GalNAc at pre-determined sites in the target GAG oligosaccharides. Of note, the stereodirecting capacity of the DTBS group in GalN donors effectively overrides the neighboring group participation by C2-particpating functionalities such as the trichloroacetamide. Thus, DTBS-GalN donors also represent attractive building blocks for Pel-assembly. For the stereoselective introduction of α-D-GlcN linkages no general solution exists, even though the construction of this type of glycosidic linkage has attracted significant attention,[4,5] as it is present in many important natural polysaccharides and glycoconjugates, such as heparin, heparan sulfate,[6] GPI anchors and various bacterial polysaccharides.[7]

Additive controlled glycosylations are gaining increasing interest for the stereoselective construction of glycosidic linkages.[8] In these approaches the nature of the additive determines the reactivity of *in situ* formed glycosylating species and the influence of the additive can be tuned to match the reactivity of the glycosyl donor[9] and acceptor[10] building blocks. We have recently reported on the fully stereoselective assembly of a branched α-glucan with an α-(1→4)-linked backbone from *Mycobacterium tuberculosis*, α-(1,3)-glucans from the *Aspergillus fumigatus* fungal cell wall as well as the assembly of α-(1,3)-glucans found attached to lipoteichoic acids of *Enterococcus faecalis*.[11] The synthetic strategy used in these approaches hinged on the use of additive controlled glycosylation reactions in combination with the use of a single benzyl-type protecting group (Bn, PMB, Nap). For glycosylations with relatively reactive primary alcohol acceptors, the trimethylsilyliodide (TMSI)-triphenylphosphine oxide ($Ph_3P=O$) activator couple was used, while the condensations with less reactive secondary alcohols required the use of the trifluoromethanesulfonic acid (TfOH)-dimethylformamide (DMF) pair. The successful construction of multiple 1,4-α-glucosidic linkages was an incentive to explore this strategy for the assembly of the Pel oligasaccharides. Mong and co-workers have previously described how formamide additives can be used for the construction of 1,2-*cis*-$GalN_3$ and $GlcN_3$ linkages. They introduced *N*-formyl-morpholine (NFM) to modulate the reactivity of tri-*O*-benzyl $GlcN_3$ and 4,6-benzylidene-$GalN_3$ donors and showed that glycosylations mediated by NFM proceeded with higher stereoselectivity than the corresponding DMF-modulated condensations.[7c] Because of the stronger electron withdrawing effect of the azide group with respect to a benzyl ether, 2-azido donors are generally less reactive than their 2-*O*-benzyl counterparts. This lower reactivity can be counterbalanced by the use of a somewhat less nucleophilic additive, resulting in a better leaving group Y, thereby explaining why NFM outperforms DMF in these glycosylations (See Scheme 1).



Scheme 1. The relative reactivity of DMF and NFM glycosyl adducts.

We here describe a strategy to synthesize Pel oligosaccharides using additive-controlled glycosylations to match the reactivities of the $GlcN_3$-donor and the Pel acceptors. Because of the relatively low nucleophilicity of the GlcN3-C4-OH and especially the GalN3-C4-OH, a new additive is introduced that generates intermediates that are more reactive than the previously introduced DMF and NFM-imidinium ions.

Results and discussion

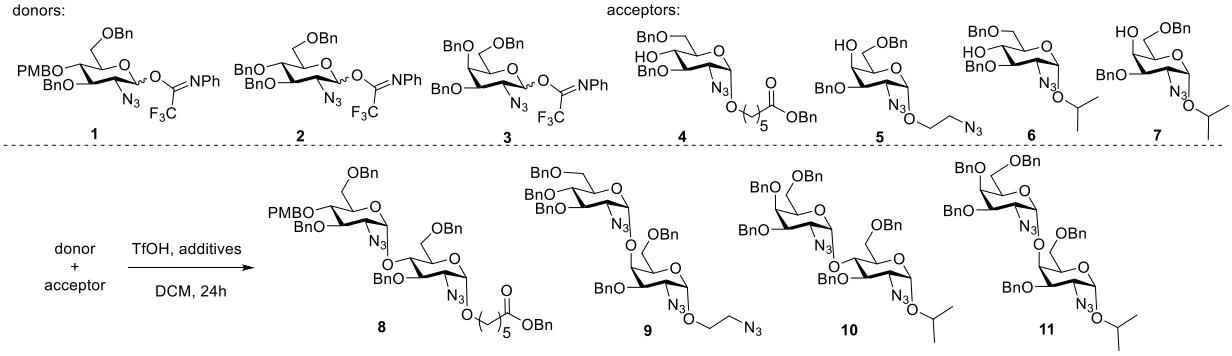
First, we paid attention to the formation of α-D-GlcN-(1→4)-D-GlcN linkages. In line with previous work, solely benzyl type protecting group (PMB, Nap, Bn) were used -besides the azide at C2- to generate orthogonally protected building blocks of uniform reactivity. With donor **1** and acceptor **4** (See SI for the syntheses of these building blocks), DMF was investigated as an additive to control the selectivity according to previous successful experiments. Thus, donor α-D-GlcN **1**, acceptor **4** and the additive were mixed in DCM with molecular sieves and cooled to -78 °C. Next, TfOH was added and after stirring for 0.5h, the mixture was placed at 0 °C and allowed to stir for 24h. As shown in Table 1, this produced the desired disaccharide product **8** with complete α-selectivity, but the yield was only 32% (entry 1). Performing the reaction at room temperature did not lead to erosion of stereoselectivity but only marginally improved the yield (entry 2). Likely, the low reactivity of the donor and acceptor led to the observed poor yield and therefore NFM was probed as additive.[6c] Use of this additive provided complete α-selectivity, and raised the yield of the condensation to 55% yield. To further improve the reaction, a slightly less nucleophilic additive was sought and *N*-methyl-*N*-phenylformamide (MPF) was explored. It was expected that the imidinium ion formed from this additive would be more reactive because the aniline-type nitrogen would be less capable of supporting the (partial) positive charge in the ion (See Scheme 1). The reaction of donor **1** and acceptor **4** proceeded with excellent yield (91%) when performed at 0 °C, and the disaccharide **8** was obtained with 15:1 α:β-selectivity (entry 4). Although the stereoselectivity of this condensation is somewhat less than the DMF or NFM mediated glycosylations, the improved yield allows for an overall more productive reaction.[12]

Next, our attention was turned to the formation of the α-GlcN-(1→4)-GalN-linkage exploring the additives as described above. First donor **2** was coupled with acceptor **5** using DMF to provide product **9** in low yield and poor selectivity (Table 1, entry 5). The use of NFM instead of DMF did not improve the outcome of this glycosylation (entry 6). Likely the poor reactivity of the $GalN_3$-C4-OH hampers the union of the two carbohydrate building blocks. Next, the use of MPF was explored. At 0 °C, disaccharide **9** was obtained in high yield (83%), but with moderate α:β-selectivity (5:1). Performing the same reaction at -10°C increased the α-selectivity (α:β = 10:1), but led to a relatively low yield (43%, entry 8). To increase the yield of the reaction, the concentration was raised from 0.1 M to 0.2 M (entry 9). This led to the formation of the desired compound **9** with a yield of 88% and a 10:1 α:β ratio. Having defined adequate conditions for

the construction of α-GlcN-(1→4)-GlcN and α-GlcN-(1→4)-GalN linkages, the use of MPF in combination with galactosazide donor **3** was explored for the construction of the target α-GalN-(1→4)-GlcN and α-GalN-(1→4)-GalN linkages. Under the conditions established above, donor **3** was coupled with glucosyl acceptor **6** to give the disaccharide **10** in excellent yield and 8:1 α/β-stereo selectivity (entry 10). Contrary, disaccharide **11**, formed from donor **3** and galactosyl acceptor **7**, was obtained with relatively poor selectivity (α:β = 4:1, entry 11). From these model reactions, it can be concluded that three out of four Pel-type linkages can effectively be installed using the MPF-mediated glycosylations. For the α-GalN-(1→4)-GalN linkages, the previously reported approach using 4,6-*O*-DTBS galactosamine donors is clearly superior.

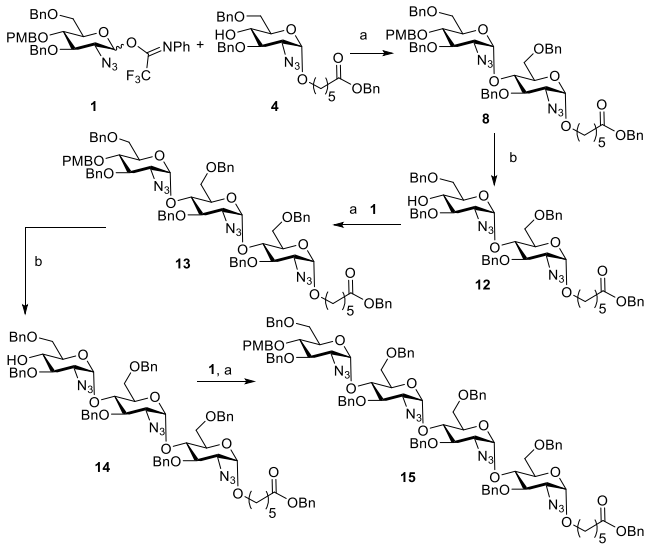
Next we probed the robustness of the MPF-mediated protocol in the synthesis of Pel-type oligosaccharides. First the assembly of an all-1,2-*cis* linked tetraglucosamine was explored as depicted in Scheme 2. Thus, donor **1** and acceptor **4** were coupled under the above identified reaction conditions to provide the desired disaccharide **8**. The PMB was removed using a catalytic amount of HCl to give disaccharide acceptor **12** in 88% yield.[13] Next, compound **12** was glycosylated with donor **1** under the MPF-conditions to form the desired trisaccharide **13** in 83% yield and excellent stereoselectivity (α:β > 19:1). Repetition of the deprotection and glycosylation reactions then uneventfully provided tetrasaccharide **15**. The successful assembly of this tetrasaccharide indicates that the yield and stereoselectivity do not decrease with the growing of the sugar chain.

Table 1. Glycosylation between 2-azido Glu/Gal donors and 4-OH-2-azido Glu/Gal acceptors.



entry	donor	acceptor	c(mmol/ml)	additive	eq	T(°C)	product	yield[a]	α:β[b]
1	**1**	**4**	0.1	DMF	16	0	**8**	32%	>20:1
2	**1**	**4**	0.1	DMF	16	rt	**8**	38%	>20:1
3	**1**	**4**	0.1	NFM	16	rt	**8**	55%	>20:1
4	**1**	**4**	0.1	MPF	16	0	**8**	91%	~15:1
5	**2**	**5**	0.1	DMF	16	0	**8**	23%	6:1
6	**2**	**5**	0.1	NFM	16	0	**9**	24%	6:1
7	**2**	**5**	0.1	MPF	16	0	**9**	83%	5:1
8	**2**	**5**	0.1	MPF	16	-10	**9**	43%	10:1
9	**2**	**5**	0.2	MPF	16	-10	**9**	88%	10:1
10	**3**	**6**	0.1	MPF	16	-10	**10**	88%	8:1
11	**3**	**7**	0.1	MPF	16	-10	**11**	80%	4:1

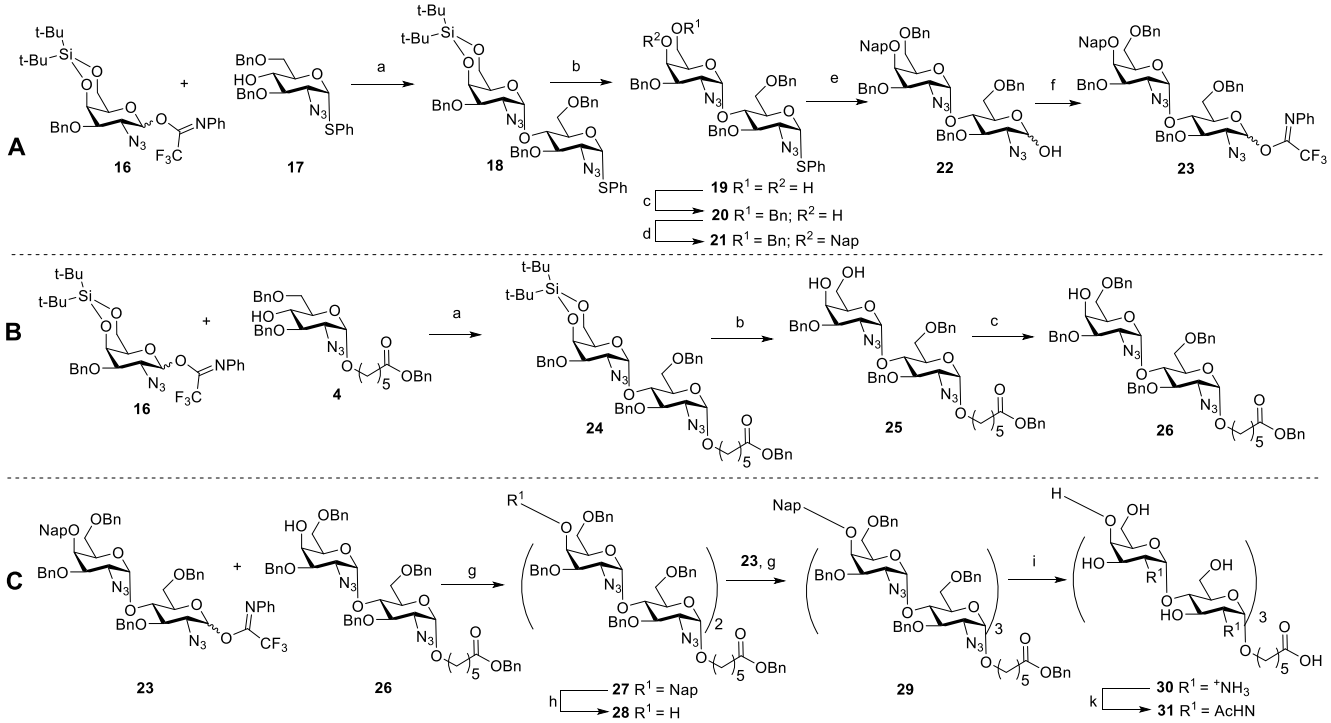
[a] Isolated yield. [b] The α:β ratio was determined by ^{1}H NMR.



(a) MPF, TfOH, DCM, -78-0 °C, **8**: 91%, α:β = 15:1; **13**: 83%, α:β > 19:1; **15**: 90%, α:β > 20:1. (b) 0.2 M HCl/HFIP, TES, HFIP/DCM, **12**: 88%; **14:** 78%.

Scheme 2. Assembly of an α-glucosazide tetrasaccharide using MPF mediated glycosylations.

Next the synthesis of a Pel hexasaccharide, featuring both GalN and GlcN residues, was undertaken. A [2+2+2] strategy was designed to streamline the assembly of the structures, building on MFP-mediated glycosylations of the $GalN_3$-$GlcN_3$ donor **23**. The procedure for the synthesis of the required building blocks **23** and **26** is depicted in Scheme 3 A and B. First donor **16** was coupled with glucoazide **17** in a chemoselective glycosylation to form disaccharide **18** as a single anomer. Next, the silylidene ketal was cleaved with HF-pyridine, after which a benzyl ether was regioselectively introduced under the aegis of Taylor's borinic acid catalyst.[14] Protection of the remaining C4'-OH with a naphthyl group delivered compound **21**. Next the anomeric thiophenol group was removed using *N*-iodosuccinimide in acetone/water, and the resulting hydroxyl group turned into the desired *N*-phenyltrifluoroimidate functionality to provide donor **23**. Acceptor **26** was obtained from donor **16** and acceptor **4**. These two building blocks were united to stereoselectively provide disaccharide **24**. Removal of the silylidene ketal and introduction of the C6'-*O*-benzyl ether as described above provided **26**. With building blocks **23** and **26** in hand, the assembly of the target hexasaccharides was undertaken (Scheme 3C). First, donor **23** was glycosylated with acceptor **26** using MPF as additive at -10 °C at a 0.2 M concentration to form tetrasaccharide **27** in 89% yield as a 10:1 α/β-mixture. Then the Nap ether was removed using HCl and triethylsilane in DCM/HFIP to give the tetrasaccharide acceptor **28**. Compound **28** was treated with donor **23** under the optimal MPF-mediated glycosylation conditions to deliver hexasaccharide **29** in high yield and stereoselectivity. Reduction of the six azides and removal of the benzyl ester and ethers were accomplished in a one-step reduction to give the compound **30**, of which the amino groups were acetylated with acetic anhydride to afford the Pel-structure **31**.



(a) TfOH, DCM, **18**: 70%; **24**: 92%. (b) HF-pyridine, THF, **19**: 98%, **25**: 91%. (c) BnBr, borinic acid-catalyzed, K_2CO_3, KI, CH_3CN, 60 °C, **20**: 96%; **26**: 95%. (d) NapBr, NaH, DMF, **21**: 93%. (e) NIS, acetone, H_2O. (f) 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride, Cs_2CO_3, acetone, **23**: 83% over two steps. (g) MPF, TfOH, DCM, -10 °C, 48 h, **27**: 89%, α:β = 10:1; **29**: 91%, α:β = 10:1. (h) 0.2 M HCl/HFIP, TES, HFIP/DCM, **28**: 73%. (i) H_2, $Pd(OH)_2$/C, CH_3COOH, THF/H_2O/t-BuOH, **30**: 76%. (k) Ac_2O, $NaHCO_3$, H_2O, **31**: 86%.

Scheme 3. A: Synthesis of donor **23**. B: synthesis of acceptor **26**. C: Assembly of Pel fragment **31**.

Conclusion

In conclusion, MPF is here reported for the first time as a moderator to enable the stereoselective construction of α-$GlcN_3$ linkages. This additive complements previously introduced glycosylation additives, such as DMF and NFM and expands the "nucleophilic additive toolbox", that can be used to match the reactivity of glycosyl donor-acceptor pairs. The applicability of the MPF-mediated glycosylations in oligosaccharide synthesis has been demonstrated by the hand of the assembly of Pel-type oligosaccharides. A linear glucosazide tetrasaccharide was assembled, through highly stereoselective glycosylation reactions, using building blocks, solely equipped with benzyl type (Bn and PMB) hydroxyl protecting groups. A [2+2+2] strategy was developed for the assembly of a $(GalN\text{-}GlcN)_3$ hexasaccharide in which the α-GlcN linkages were constructed in glycosylation reactions using MPF as an additive.

Experiment section

General experimental procedures

All reagents were of commercial grade and used as received. All moisture sensitive reactions were performed under an argon atmosphere. DCM used in the glycosylation reactions was dried with flamed 4Å molecular sieves before being used. Reactions were monitored by TLC analysis with detection by UV (254 nm) and where applicable by spraying with 20% sulfuric acid in EtOH or with a solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (25 g/L) and $(NH_4)_4Ce(SO_4)_4{\cdot}2H_2O$ (10 g/L) in 10% sulfuric acid (aq.) followed by charring at ~150 °C. Column chromatography was carried out using silica gel (0.040-0.063 mm). Size-exclusion chromatography was carried out using Sephadex LH-20. ^1H and ^{13}C spectra were recorded on a Bruker AV 400 and Bruker AV 500 in $CDCl_3$ or D_2O. Chemical shifts (δ) are given in ppm relative to tetramethylsilane as internal standard (^1H NMR in $CDCl_3$) or the residual signal of the deuterated solvent. Coupling constants (*J*) are given in Hz. All ^{13}C spectra are proton decoupled. NMR peak assignments were made using COSY and HSQC experiments, where applicable Clean TOCSY, HMBC and GATED experiments were used to further elucidate the structure. The anomeric product ratios were analyzed through integration of proton NMR signals.

Procedure A for the glycosylation of secondary alcohols:

A mixture of donor (1.0 eq), acceptor (0.7 eq) (donors and acceptors co-evaporated with toluene three times), MPF (16 eq) in dry DCM were stirred over fresh flame-dried molecular sieves 3A under nitrogen. The solution was cooled to -78 ℃, after which TfOH (1.0 eq) was added. After 30 min, the reaction was stirred at 0 or -10 ℃ until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The products were purified by size exclusion and silica gel column chromatography.

Procedure B for the glycosylation of primary alcohols:

A mixture of donor (1.0 eq), acceptor (0.7 eq) (donors and acceptors co-evaporated with toluene three times), $Ph_3P{=}O$ (6 eq) in dry DCM were stirred over fresh flame-dried molecular sieves 3A under nitrogen. Then TMSI (1.0 eq) was added slowly in the mixture. The reaction was stirred at room temperature until TLC-analysis indicated the reaction to be complete. The solution was diluted and the reaction quenched with saturated $Na_2S_2O_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The products were purified by size exclusion and silica gel column chromatography.

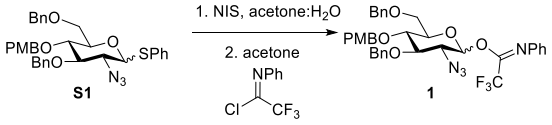
Procedure C for deprotection of the PMB and Nap protecting group:[13]

The starting material (1 eq) was dissolved in DCM:HFIP (1:1, 0.1 M). TES (2.0 eq) and 0.2M HCl/HFIP (0.1-1eq) were added to the mixture. The reaction stirred until TLC-analysis indicated full consumption of the starting material (15min-2h). Then the mixture was diluted with DCM and the reaction quenched with saturated $NaHCO_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography.

Experimental Procedures and Characterization Data of Products

For the synthesis procedure and data of known compounds **9**[15a], **S1**[15a], **S2**[15b], **S3**[15c] and **S10**[5e] see references. We used "a", "b", "c", "d", "e", "f", "g", "h" and "i" to specify the H-1 and C-13 NMR signals of sugar rings from the "reducing" to the "non-reducing" end and "°" to specify the H-1 and C-13 NMR signals of the spacer.

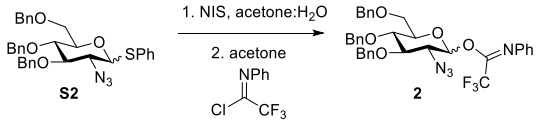
N-phenyl trifluoroacetimidate 2-N_3-glucose donor **1**:



Compound **S1** (9.1 g, 15.2 mmol) was dissolved in acetone:H_2O (10:1, 150 mL). N-Iodosuccinimide (NIS) (6.9 g, 30.5 mmol) was added in one portion and the reaction was stirred at room temperature for 2 hours. The solution was diluted with DCM and the reaction was quenched with saturated aqueous $Na_2S_2O_3$. Then the organic layer was washed with water and brine. The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacu*o, and the product purified by column chromatography (pentane : ethyl acetate (EA) = 3:1). The lactol (7.2 g, 14.3 mmol) was obtained as colourless syrup. Next, the lactol was dissolved in acetone (150 mL). Cs_2CO_3 (7.0 g, 21.3 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (3.4 mL, 21.3 mmol) were added to the solution respectively. The reaction was stirred overnight, then quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by column chromatography (pentane:EA = 40:1-20:1). Compound **1** (8.5 g, 79% over two steps, pentane:EA = 10:1, R*f* = 0.45-0.55) was obtained as yellow syrup. IR (neat, cm^{-1}) ν 697, 737, 1029, 1082, 1119, 1210, 1251, 1312, 1514, 1720, 2112 (N_3), 2872, 2912. ^1H-NMR ($CDCl_3$, 500 MHz, 60℃) δ 7.38-7.20 (m, aromatic *H*), 7.11-7.06 (m, aromatic *H*), 6.82-6.78 (m, aromatic *H*), 6.37 (bs, 1 H), 5.41 (bs, 1 H), 4.92-4.80 (m), 4.74-4.69 (m), 4.60-4.48 (m), 3.96 (t, J = 10.0 Hz, 1 H), 3.90 (bd, 1 H), 3.77-3.58 (m), 3.43 (t), 3.33 (bs, 1 H). ^{13} C-APT ($CDCl_3$, 125 MHz, 60℃) δ 159.8, 159.8, 143.6, 143.5, 138.3, 138.2, 138.1, 130.3 (aromatic *C*), 129.7, 128.9, 128.6, 128.6, 128.5, 128.1, 128.0, 1278.0, 127.9, 127.9, 127.8, 124.7, 124.6, 119.6, 114.2, 114.2 (aromatic *C*H), 96.2 (C-1), 94.4 (C-1), 83.3, 80.5, 77.7, 77.3, 76.4, 75.7, 75.0, 74.8, 73.9, 73.8,

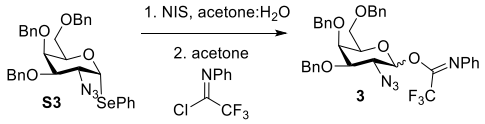
73.7, 68.5, 65.8, 63.5, 55.4. HRMS (ESI) m/z: Calculated for $[M-[O(C=NPh)CF_3]+OH+Na]^+$ $C_{28}H_{31}O_6N_3Na$: 582.21051, found: 582.20943.

Synthesis of *N*-phenyl trifluoroacetimidate 2-N_3-glucose donor **2**:



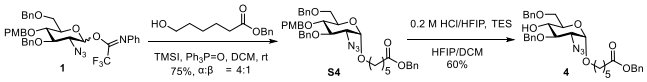
Compound **S2** (8.5 g, 15 mmol) was dissolved in acetone:H_2O (10:1, 150 mL). N-Iodosuccinimide (NIS) (6.7 g, 30 mmol) was added in one portion and the reaction was stirred at room temperature for 2 hours. The solution was diluted with DCM and the reaction was quenched with saturated aqueous $Na_2S_2O_3$. Then the organic layer was washed with water and brine. The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacu*o, and the product purified by column chromatography (pentane : ethyl acetate (EA) = 3:1). The lactol (6.1 g, 13 mmol) was obtained as colorless syrup. Next, the lactol was dissolved in acetone (150 mL). Cs_2CO_3 (6.4 g, 19.6 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (3.4 mL, 21.3 mmol) were added to the solution respectively. The reaction was stirred overnight, then quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by column chromatography (pentane:EA = 40:1-20:1). Compound **2** (7.3 g, 87%) was obtained as yellow syrup. IR (neat, cm^{-1}) ν 694, 734, 1027, 1073, 1116, 1150, 1208, 1312, 1361, 1452, 1490, 1497, 1598, 1717, 2110 (N_3), 2869, 3032. ^{1}H-NMR ($CDCl_3$, 500 MHz, 60℃) δ 7.52-6.81 (m, aromatic *H*), 6.37 (bs, 1 H, H-1α), 5.43 (bs, 1 H, H-1β), 4.89-4.76 (m, CH*H*), 4.60-4.48 (m, CH*H*), 3.98 (t, J = 9.5 Hz, 1 H), 3.91 (bd, 1 H), 3.80-3.59 (m), 3.46 (t), 3.36 (bs, 1 H). ^{13}C-APT ($CDCl_3$, 125 MHz, 60℃) δ 143.6, 143.5, 138.2, 138.2, 138.1, 138.1, 138.1 (aromatic *C*), 129.5, 128.9, 128.8, 128.6, 128.6, 128.5, 128.2, 128.1, 128.1, 128.0, 128.0, 127.97, 127.95, 127.91, 127.9, 126.5, 124.7, 124.6, 120.8, 119.6 (aromatic *C*H), 96.2 (C-1), 94.4 (C-1), 83.3, 80.5, 78.0, 77.6, 76.3, 75.7, 75.7, 75.4, 75.2, 73.9, 73.8, 73.7, 68.5, 65.8, 63.5. HRMS (ESI) m/z: Calculated for $[M-[O(C=NPh)CF_3]+OH+Na]^+$ $C_{27}H_{29}O_5N_3Na$: 498.19994, found: 498.19848.

Synthesis of *N*-phenyl trifluoroacetimidate 2-N_3-galactose donor **3**:



Compound **S3** (3.7 g, 6.0 mmol) was dissolved in acetone:H_2O (10:1, 150 mL). N-Iodosuccinimide (NIS) (2.7 g, 12 mmol) was added in one portion and the reaction was stirred at room temperature for 2 hours. The solution was diluted with DCM and the reaction was quenched with saturated aqueous $Na_2S_2O_3$. Then the organic layer was washed with water and brine. The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacu*o, and the product purified by column chromatography (pentane:EA = 3:1). The lactol was obtained as colourless syrup. Next, the lactol was dissolved in acetone. Cs_2CO_3 (3.0 g, 9 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (1.5 mL, 9 mmol) were added to the solution respectively. The reaction was stirred overnight, then quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by column chromatography (pentane:EA = 40:1-20:1). Compound **3** (3.3 g, 86%) was obtained as yellow syrup. IR (neat, cm^{-1}) ν 695, 734, 751, 986, 1027, 1153, 1316, 1364, 1454, 1490, 1497, 1590, 1717, 2114 (N_3), 2870, 2915. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.56-6.79 (m, aromatic *H*), 6.35 (bs, 1 H, H-1), 5.49 (bs, 1 H, H-1), 5.28 (d), 4.90-4.84 (m, CH*H*), 4.78-4.31 (m), 4.15-3.83 (m), 3.76 (dd), 3.65-3.31 (m). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 143.5, 143.4, 138.5, 138.3, 138.3, 138.2, 138.1, 137.7, 137.7, 137.6, 137.6, 137.4, 137.3, 135.2 (aromatic *C*), 129.5, 128.8, 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.43, 128.37, 128.3, 128.19, 128.17, 128.15, 128.14, 128.07, 128.03, 128.00, 127.95, 127.9, 126.48, 124.46, 120.6, 119.4 (aromatic *C*H), 96.5 (C-1), 92.5 (C-1), 80.9, 80.7, 77.4, 75.1, 74.9, 74.8, 74.7, 74.6, 73.8, 73.67, 73.65, 73.62, 73.5, 72.9, 72.7, 72.6, 72.5, 72.4, 72.3, 72.2, 71.9, 69.7, 69.3, 68.7, 68.3, 68.1, 64.7, 62.2, 60.4, 59.2. HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{27}H_{29}O_5N_3Na$: 669.22953, found: 669.22913.

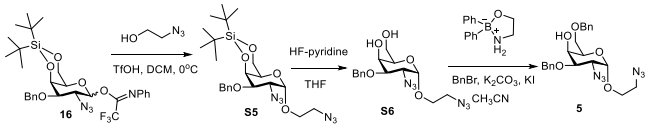
Synthesis of monosaccharide **4**:



The reaction was carried out according to the standard procedure B. A mixture of donor **1** (1.0 g, 1.5 mmol), benzyl 6-hydroxyhexanoate (520 mg) (donors and acceptors co-evaporated with toluene three times), $Ph_3P=O$ (2.6 g, 9.3 mmol) in dry DCM (15 mL) were stirred over fresh flame-dried molecular sieves 3A under nitrogen. Then TMSI (222 μL, 1.5 mmol) was added slowly in the mixture. The reaction was stirred at room temperature until TLC-analysis indicated the reaction to be complete. The solution was diluted and the reaction quenched with saturated $Na_2S_2O_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The products were purified by silica gel column chromatography (pentane:EA = 8:1, R*f* = 0.63). Compound **S4** (800 mg, 75% yield, α:β = 5:1) was obtained as a colorless syrup. IR (neat, cm^{-1}) ν 697, 736, 1002, 1029, 1037, 1075, 1150, 1248, 1358, 1454, 1611, 1733 (C=O), 2105 (N_3), 2866, 2933. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.40-7.21 (m, 15 H, aromatic *H*), 7.00 (bd, 2 H, aromatic *H*), 6.79 (bd, 2 H, aromatic *H*), 5.09 (s, 2 H, PhCH_2), 4.90 (d, *J* = 3.6 Hz, 1 H, H-1a), 4.88 (s, 2 H, PhCH_2),4.71 (d, *J* = 10.4 Hz, 1 H, C*H*H), 4.63 (d, *J* = 12.4 Hz, 1 H, CH*H*), 4.49 (d, *J* = 12.4 Hz, 1 H, C*H*H), 4.43 (d, *J* = 10.4 Hz, 1 H, CH*H*), 3.975 (t, t, *J* = 9.6 Hz, 1 H, H-3a), 3.79-3.63 (m, 5 H, H-2a, H-4a, H-5a, H-6a, H-1º$_a$), 3.47-3.37 (m, 1 H, H-1º$_b$), 3.33 (dd, 1 H, J_1 = 10.0 Hz, J_2 = 2.0 Hz, H-2a), 2.36 (t, *J* = 7.6 Hz, 2H, H-5º), 1.70-1.58 (m, 4 H, H-2º, H-4º), 1.43-1.36 (m, 2 H, H-3º). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 173.4 (*C*=O), 159.4, 138.1, 137.9, 130.1 (aromatic *C*), 129.6, 128.6, 128.5, 128.5, 128.2, 127.99, 127.96, 127.9, 127.8, 113.9 (aromatic *C*H), 97.9 (C-1a), 80.2 (C-3a), 78.0 (C-4a), 75.3, 74.8, 73.6 (*C*H$_2$), 70.7 (C-5a), 68.3 (C-6a), 68.0 (C-1º), 66.1 (Ph*C*H$_2$), 63.4 (C-2a), 55.3 (O*C*H$_3$), 34.2 (C-5º), 29.1 (C-2º), 25.7 (C-3º), 24.7 (C-4º). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{41}H_{51}N_4O_8$: 727.37014, found: 727.37015.

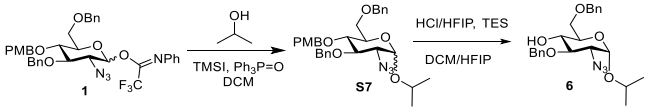
Then the reaction was carried out according to the standard procedure C. The starting material **S4** (700 mg, 0.99 m mol) was dissolved in DCM:HFIP (1:1, 0.1 M). TES (314 mL) and 0.2M HCl/HFIP (0.5 mL) were added to the mixture. The reaction stirred until TLC-analysis indicated full consumption of the starting material (15min). Then the mixture was diluted with DCM and the reaction quenched with saturated $NaHCO_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EA = 4:1, R*f* = 0.34). Compound **4** (350 mg, 60% yield) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +59.3 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 737, 1050, 1147, 1455, 1734 (C=O), 2105 (N_3), 2866, 2926, 3478. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.41-7.23 (m, 15 H, aromatic *H*), 5.10 (s, 2 H, PhC*H*$_2$), 4.90 (d, *J* = 11.2 Hz, 1 H, C*H*H), 4.87 (d, *J* = 3.6 Hz, 1 H, H-1a), 4.81 (d, *J* = 11.2 Hz, 1 H, CH*H*), 4.59 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.53 (d, *J* = 12.0 Hz, 1 H, CH*H*), 3.86-3.64 (m, 6 H, H-2a, H-3a, H-4a, H-5a, H-6a, H-1º$_a$), 3.47-3.41 (m, 1 H, H-1º$_b$), 3.25 (dd, 1 H, J_1 = 10.0 Hz, J_2 = 2.0 Hz, H-2a), 2.37 (t, *J* = 7.6 Hz, 2H, H-5º), 1.72-1.61 (m, 4 H, H-2º, H-4º), 1.47-1.37 (m, 2 H, H-3º). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 173.6 (*C*=O), 138.2, 137.9, 136.1 (aromatic *C*), 128.7, 128.6, 128.5, 128.3, 128.3, 128.1, 128.05, 127.9, 127.7, 127.5 (aromatic *C*H), 98.0 (C-1a), 79.8 (C-3a), 75.0 (C-6a), 73.7 (*C*H$_2$), 72.2 (c-4a), 70.2 (c-5a), 69.8 (Ph*C*H$_2$), 68.1 (C-1º), 66.2 (Ph*C*H$_2$), 62.8 (C-2a), 34.2 (C-5º), 29.1 (C-2º), 25.7 (C-3º), 24.7 (C-4º). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{33}H_{43}O_7N_4$: 607.31263, found: 607.31238.

Synthesis of acceptor **5**



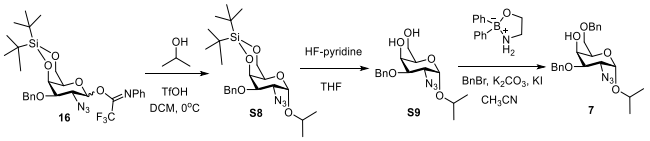
Donor **16** (620 mg, 1.0 mmol) and 2-azidoethanol (178 mg, 2.0 mmol) were dissolved in DCM, cooled to 0 ºC and TfOH (15 µL, 0.1 mmol) was added. The reaction was stirred at 0 ℃ until TLC-analysis showed complete conversion of the donor. The reaction was quenched with Et_3N after completed checking by TLC, filtered and concentrated *in vacuo*. Compound **S5** (370 mg, 73%) was obtained with full α-selectivity. Then compound **S5** was dissolved in THF. HF-pyridine was added to the solution. After TLC-analysis showed complete consumption of the starting material, the reaction was quenched with saturated $NaHCO_3$. The mixture was diluted with ethyl acetate, washed with H_2O and brine, dried with anhydrous $MgSO_4$, filtered, concentrated *in vacuo*. Crude compound **S6**, K_2CO_3, KI, and borinic acid-catalyzed were mixed in CH_3CN, and then BnBr was added in the solution. The reaction was stirred at 60 ℃ until TLC-analysis showed complete conversion of the starting material. The reaction was quenched with H_2O after completed checking by TLC, filtered and concentrated *in vacuo*, purified by column chromatography (pentane:EA = 5:1). Compound **5** (280 mg, 84% yield over two steps) was obtained as colorless syrup. $[\alpha]_D^{20}$ +89.9 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 738, 1052, 1096, 1146, 1454, 2108 (N_3), 2873, 2923, 3483. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 7.40-7.28 (m, 10 H, aromatic *H*), 4.95 (d, *J* = 3.5 Hz, 1 H, H-1a), 4.71 (d, *J* = 11.5 Hz, 1 H, C*H*H), 4.68 (d, *J* = 11.5 Hz, 1 H, C*H*H), 4.60 (d, *J* = 12.0 Hz, 1 H, CH*H*), 4.57 (d, *J* = 12.0 Hz, 1 H, CH*H*), 4.12 (t, *J* = 1.5 Hz, 1 H, H-4a), 3.98 (t, *J* = 6.0 Hz, 1 H, H-5a), 3.93 (dd, 1 H, J_1 = 10.5 Hz, J_2 = 3.0 Hz, H-3a), 3.90-3.86 (m, 1 H, H-1º$_a$), 3.77-3.63 (m, 4 H, H-2a, H-6ª, H-1º$_b$), 3.57-3.52 (m, 1 H, H-2º$_a$), 3.37-3.33 (m, 1 H, H-2º$_b$), 2.61 (bt, 1 H, O*H*), 1.21-1.18 (bt, 6 H, 2 C*H*$_3$). ^{13}C-APT ($CDCl_3$, 125 MHz) δ 137.9, 137.3 (aromatic *C*), 128.8, 128.6, 128.4, 128.2, 127.9, 127.8 (aromatic *C*H), 98.5 (C-1a), 76.0 (C-3a), 73.8, 72.1 (*C*H$_2$), 69.6 (C-6a), 69.2 (C-5a), 67.2 (C-1º), 66.8 (C-4a), 59.0 (C-2a), 50.8 (C-2º). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{22}H_{30}O_5N_7$: 472.23029, found: 472.23003.

Synthesis of acceptor **6**:



Donor **1** (820 mg, 1.2 mmol), isopropanol (200 µL, 2.6 mmol) and Ph_3P=O (2 g) were dissolved in DCM (12 mL), and TMSI (173 µL) was added at room temperature. The reaction was stirred at rt until TLC-analysis showed complete conversion of the donor. The reaction was quenched with Et_3N after completed checking by TLC, filtered and concentrated *in vacuo*, purified by column chromatography. Compound ***S7*** was obtained with α:β = 5:1. Then compound ***S7*** was dissolved in DCM/HFIP (1.5 mL: 1.5 mL). TES (380 µL) and 0.2M HCl/HFIP (600 µL) were added to the mixture. The reaction stirred until TLC-analysis indicated full consumption of the starting material (30min). Then the mixture was diluted with DCM and the reaction quenched with saturated $NaHCO_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EA = 5:1). Compound **6** (240 mg, 47% yield over two steps) was obtained as colorless syrup. $[\alpha]_D^{20}$ +83.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 735, 1029, 1047, 1120, 1454, 2105 (N_3), 2920, 2974, 3476. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.40-7.20 (m, 10 H, aromatic *H*), 4.97 (d, *J* = 3.6 Hz, 1 H, H-1a), 4.88 (d, *J* = 11.2 Hz, 1 H, C*H*H), 4.78 (d, *J* = 11.2 Hz, 1 H, CH*H*), 4.57 (d, *J* = 12.0 Hz, 1 H, CH*H*), 4.50 (d, *J* = 12.0 Hz, 1 H, C*H*H), 3.93-3.82 (m, 3 H, H-3a, H-5a, H-1º), 3.73-3.61 (m, 3 H, H-4a, H-6a), 3.18 (dd, 1 H, J_1 = 10.0 Hz, J_2 = 3.6 Hz, H-2a), 2.76 (bs, 1 H, O*H*), 1.23, (d, *J* = 8.4 Hz, 3 H, C*H*$_3$), 1.21 (d, *J* = 8.4 Hz, 3 H, C*H*$_3$). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.2, 137.8 (aromatic *C*), 128.5, 128.4, 128.0, 127.9, 127.7, 127.6 (aromatic *C*H), 96.4 (C-1a), 79.6 (C-3a), 74.9, 73.6 (*C*H$_2$), 72.1 (C-4a), 70.8 (C-1º), 70.1 (C-5a), 69.7 (C-6a), 62.5 (C-2a), 23.2 (*C*H$_3$), 21.5 (*C*H$_3$). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{23}H_{33}O_5N_4$: 445.24455, found: 445.24441.

Synthesis of acceptor **7**:



Donor **16** (2.77 g, 4.6 mmol) and isopropanol were dissolved in DCM (40 mL), cooled to 0 ºC and TfOH (40 µL) was added. The reaction was stirred at 0 ℃ until TLC-analysis showed complete conversion of the donor. The reaction was quenched with Et_3N after completed checking by

TLC, filtered and concentrated *in vacuo*. Compound **S8** was obtained with full α-selectivity. Then compound **S8** was dissolved in THF (20 mL). HF-pyridine (1 mL) was added to the solution. After TLC-analysis showed complete consumption of the starting material, the reaction was quenched with saturated $NaHCO_3$. The mixture was diluted with ethyl acetate, washed with H_2O and brine, dried with anhydrous $MgSO_4$, filtered, concentrated *in vacuo*, purified by column chromatography (pentane:EA = 3:1). Compound **S9 (**1.45 g) was obtained with 94% yield over two steps. Then compound ***S9*** **(**665 mg, 1.97 mmol), K_2CO_3 (293 mg), KI (327 mg), and borinic acid-catalyzed (44 mg) were mixed in CH_3CN (20 mL), and then BnBr was added in the solution. The reaction was stirred at 60 ℃ in oil bath until TLC-analysis showed complete conversion of the starting material. The reaction was quenched with H_2O after completed checking by TLC, filtered and concentrated *in vacuo*, purified by column chromatography (pentane:EA = 5:1). Compound **7** (745 mg, 80% yield) was obtained as colorless syrup. $[\alpha]_D^{20}$ +102.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 737, 1052, 1454, 2108 (N_3), 2892, 2926. 2972. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.42-7.27 (m, 10 H, aromatic *H*), 5.02 (d, *J* = 3.6 Hz, 1 H, H-1a), 4.71 (bs, 2 H, PhC*H*$_2$), 4.58 (bs, 2 H, PhC*H*$_2$), 4.15 (t, *J* = 1.6 Hz, 1 H, H-4a), 4.01 (bt, 1 H, H-5a), 3.95-3.89 (m, 2 H, H-3a, H-1º), 3.76 (dd, 1 H, J_1 = 10.0 Hz, J_2 = 6.0 Hz, H-6a$_a$), 3.70-3.62 (m, 2 H, H-6a$_b$, H-2a), 2.60 (bs, 1 H, O*H*), 1.23 (d, 3 H, *J* = 10.4 Hz, C*H*$_3$), 1.21 (d, 3 H, *J* = 10.4 Hz, C*H*$_3$). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.0, 137.5 (aromatic *C*), 128.8, 128.6, 128.3, 128.1, 127.9, 127.8 (aromatic *C*H), 96.7 (C-1a), 76.1 (C-3a), 73.8, 72.0 (*C*H$_2$), 70.9 (C-1º), 69.6 (C-6a), 68.7 (C-5a), 66.8 (C-4a), 59.0 (C-2a), 23.3 (*C*H$_3$), 21.6 (*C*H$_3$). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{23}H_{33}O_5N_4$: 445.24455, found: 445.24455.

Synthesis of disaccharide **8**: The reaction was carried out according to the standard procedure A. A mixture of donor **1** (320 mg, 0.47 mmol), acceptor **4** (185 mg, 0.31 mmol) (donors and acceptors co-evaporated with toluene three times), MPF (610 μL) in dry DCM (3 mL) were stirred over fresh flame-dried molecular sieves 3A under nitrogen. The solution was cooled to -78 ℃, after which TfOH (42 μL) was added. After 30 min, the reaction was stirred at -10 ℃ until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **8** (304 mg, 88% yield, α:β = 15:1, PE:EA = 4:1, R*f* = 0.51) was obtained as a colorless syrup. IR (neat, cm^{-1}) ν 697, 736, 1027, 1147, 1249, 1358, 1454, 1514, 1734 (C=O), 2103 (N_3), 2866, 2928. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.39-7.21 (m, 25 H, aromatic *H*), 7.00 (bd, 2 H, aromatic *H*), 6.79 (bd, 2 H, aromatic *H*), 5.66 (d, *J* = 4.0 Hz, 1 H, H-1b), 5.11 (s, 2 H, PhC*H*$_2$), 4.98(d, *J* = 10.4 Hz, 1 H, C*H*H), 4.93 (d, *J* = 4.0 Hz, 1 H, H-1a), 4.89-4.82 (m, 3 H, 3 CH*H*), 4.66 (d, *J* = 10.0 Hz, 1 H, C*H*H), 4.54-4.47 (m, 3 H, 3 CH*H*), 4.37 (d, *J* = 10.4 Hz, 1 H, C*H*H), 4.23 (d, *J* = 10.4 Hz, 1 H, C*H*H), 4.07 (t, *J* = 9.2 Hz, 1 H, H-3a), 3.98 (t, *J* = 9.2 Hz, 1 H, H-4a), 3.87-3.61 (m, 10 H, H-3b, H-4b, H-5a, H-5b, H-6a, H-6b$_a$, OC*H*$_3$), 3.54-3.44 (m, 2 H, H-6b$_b$, H-1º$_a$), 3.35-3.29 (m, 3 H, H-2a, H-2b, H-1º$_b$), 2.38 (t, *J* = 7.6 Hz, 2H, H-5º), 1.73-1.63 (m, 4 H, H-2º, H-4º), 1.46-1.38 (m, 2 H, H-3º). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 173.5 (*C*=O), 159.4, 138.2, 138.0, 137.84, 137.82, 136.2, 130.2 (aromatic *C*), 129.7, 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.84, 127.78, 127.6, 127.4, 113.9 (aromatic *C*H), 97.8 (C-1b), 97.7 (C-1a), 80.9 (C-3a), 80.3 (C-3b), 77.8 (C-4b), 75.5, 74.7, 74.5, 73.6, 73.5 (Ph*C*H$_2$), 73.4 (c-4a), 71.6 (c-5b), 70.2 (C-5a), 69.1 (C-6a), 68.2 (C-6b), 67.9 (C-1º), 66.2 (Ph*C*H$_2$), 63.8 (C-2), 63.4 (C-2), 55.4 (O*C*H$_3$), 34.2 (C-5º), 29.2 (C-2º), 25.8 (C-3º), 24.8 (C-4º). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{61}H_{72}N_7O_{12}$: 1094.52335, found: 1094.52388.

Synthesis of disaccharide **9**: The reaction was carried out according to the standard procedure A. A mixture of donor **2** (146 mg, 0.22 mmol), acceptor **5** (50 mg, 0.11 mmol) (donors and acceptors co-evaporated with toluene three times), MPF (216 μL) in dry DCM were stirred over fresh flame-dried molecular sieves 3A under nitrogen. The solution was cooled to -78 ℃, after which TfOH (19 μL) was added. After 30 min, the reaction was stirred at -10 ℃ until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **9** (86 mg, 87%, α:β = 10:1) was obtained as a colorless syrup. IR (neat, cm^{-1}) ν 697, 736, 1027, 1046, 1093, 1127, 1150, 1259, 1359, 1454, 2105 (N_3), 2869, 2923. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.40-7.05 (m, 25 H, aromatic *H*), 4.99 (bt, 2 H, H-1a and H-1b), 4.90-4.76 (m, 3 H, 3 C*H*H), 4.69 (d, *J* = 10.8 Hz, 1 H, C*H*H), 4.63 (d, *J* = 10.8 Hz, 1 H, CH*H*), 4.59-4.53 (m, 2 H, 2 C*H*H), 4.39 (bt, 2 H, 2 CH*H*), 4.31 (d, *J* = 2.4 Hz, 1 H), 4.13-3.49 (m, 13 H), 3.39-3.29 (m, 2 H), 3.22 (dd, J_1 = 12.4 Hz, J_2 = 2.0 Hz, 1 H), 2.96 (dd, J_1 = 10.8 Hz, J_2 = 2.0 Hz, 1 H), 4.48 (d, J_1 = 10.8 Hz, J_2 = 1.6 Hz, 1 H). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.1, 137.8, 137.7, 137.5 (aromatic *C*), 128.6, 128.5, 128.4, 128.4, 128.2, 128.07, 128.06, 127.9, 127.82, 127.78, 127.75, 127.7, 127.2 (aromatic *C*H), 98.9 (C-1), 98.5 (C-1), 80.2, 78.1, 75.6, 75.4, 74.9, 73.7, 73.3, 73.3, 72.0, 70.9, 69.6, 67.3, 67.3, 67.0, 64.0, 59.4, 50.7. HRMS (ESI) m/z: $[M+NH_4]^+$: Calculated for $C_{49}H_{57}O_9N_{10}$: 929.43045, found: 929.43039.

Synthesis of disaccharide **10**: The reaction was carried out according to the standard procedure A. A mixture of donor **3** (77 mg, 0.12 mmol), acceptor **6** (34 mg, 0.08 mmol) (donors and acceptors co-evaporated with toluene three times), MPF (156 μL) in dry DCM were stirred over fresh flame-dried molecular sieves 3A under nitrogen. The solution was cooled to -78 ℃, after which TfOH (8 μL) was added. After 30 min, the reaction was stirred at -10 ℃ until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **10** (56 mg, 88% yield, α:β = 8:1) was obtained as a colorless syrup. IR (neat, cm^{-1}) ν 697, 737, 1050, 1097, 1122, 1258, 1454, 2108 (N_3), 2869, 2928. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.41-7.19 (m, 25 H, aromatic *H*), 5.64 (d, *J* = 3.6 Hz, 1 H, H-1a), 5.03 (d, *J* = 3.6 Hz, 1 H, H-1b), 4.96 (d, *J* = 10.0 Hz, 1 H, C*H*H), 4.91 (d, *J* = 10.0 Hz, 1 H, CH*H*), 4.81 (d, *J* = 11.2 Hz, 1 H, CH*H*), 4.67 (d, *J* = 11.2 Hz, 1 H, C*H*H), 4.61 (d, *J* = 11.2 Hz, 1 H, CH*H*), 4.56 (d, *J* = 12.4 Hz, 1 H, CH*H*), 4.48 (d, *J* = 11.2 Hz, 1 H, CH*H*), 4.44 (d, *J* = 12.4 Hz, 1 H, CH*H*), 4.29 (d, *J* = 11.6 Hz, 1 H, CH*H*), 4.22 (d, *J* = 11.6 Hz, 1 H, CH*H*), 4.07 (dd, *J* = 8.0, 10.0 Hz, 1 H, H-3b), 3.98-3.78 (m, 7 H), 3.72-3.63 (m, 2 H, H-6), 3.48-3.37 (m, 2 H, H-6), 3.29 (dd, *J* = 3.6, 10.0 Hz, 1H, H-2b), 1.28 (d, *J* = 6.4 Hz, 1 H, C*H*$_3$), 1.24 (d, *J* = 6.4

Hz, 1 H, C*H*$_3$). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.4, 138.2, 137.9, 137.6 (aromatic *C*), 128.62, 128.57, 128.5, 128.42, 128.37, 128.3, 128.0, 127.92, 127.89, 127.85, 127.8, 127.5, 127.4 (aromatic *C*H), 98.0 (C-1a), 96.2 (C-1b), 80.8 (C-3b), 77.6 (C-3a), 74.9, 74.5 (Ph*C*H$_2$), 74.0 (C-2a), 73.6, 73.2 (Ph*C*H$_2$), 72.9 (C-4b), 72.2 (Ph*C*H$_2$), 71.1 (C-4a), 70.2 (C-5b), 70.1 (C-5a), 69.5 (C-6), 68.5 (C-6), 63.6 (C-2b), 59.8 (C-1º), 23.4 (*C*H$_3$), 21.7 (*C*H$_3$). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{50}H_{60}O_9N_7$: 902.44470, found: 902.44467.

Synthesis of disaccharide **11**: The reaction was carried out according to the standard procedure A. A mixture of donor **3** (77 mg, 0.12 mmol), acceptor **7** (34 mg, 0.08 mmol) (donors and acceptors co-evaporated with toluene three times), MPF (156 μL) in dry DCM were stirred over fresh flame-dried molecular sieves 3A under nitrogen. The solution was cooled to -78 ℃, after which TfOH (8 μL) was added. After 30 min, the reaction was stirred at -10 ℃ until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **11** (62 mg, 80% yield, α:β = 4:1) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +85.8 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 736, 986, 1037, 1117, 1209, 1261, 1454, 2106 (N_3), 2870, 2925. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.43-7.12 (m, 25 H, aromatic *H*), 5.05 (d, *J* = 3.6 Hz, 1 H, H-1a), 4.98 (d, *J* = 3.6 Hz, 1 H, H-1b), 4.88 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.80 (d, *J* = 10.8 Hz, 1 H, CH*H*), 4.72 (d, *J* = 11.2 Hz, 1 H, CH*H*), 4.63 (d, *J* = 11.2 Hz, 1 H, C*H*H), 4.54 (bd, 3 H,3 CH*H*), 4.47 (d, *J* = 10.8 Hz, 1 H, CH*H*), 4.36 (dd, *J* = 5.2, 9.2 Hz, 1 H, H-5a), 4.28 (d, *J* = 2.8 Hz, 1 H, H-4a), 4.10 (s, 1 H, H-4b), 4.03-3.85 (m, 8 H, H-6b$_a$, H-5b, H-3b, H-3a, H-2b, H-2a, H-1º), 3.60 (dd, *J* = 3.6, 11.2 Hz, 1H, H-2a), 3.56-3.49 (m, 2 H, H-6b$_b$, H-6a$_a$), 3.14-3.09 (m, 2 H, H-6a$_b$), 1.20 (d, *J* = 6.0 Hz, 1 H, C*H*$_3$), 1.19 (d, *J* = 6.0 Hz, 1 H, C*H*$_3$). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.7, 138.0, 137.7, 137.6 (aromatic *C*), 128.64, 128.58, 128.55, 128.4, 128.3, 128.2, 128.12, 128.09, 128.0, 127.90, 127.87, 127.75, 127.74, 127.6, 127.3 (aromatic *C*H), 98.2 (C-1b), 96.8 (C-1a), 77.4 (C-3b), 75.9 (C-3a), 75.0, 73.7, 73.2 (Ph*C*H$_2$), 73.0 (C-4b), 72.9 (C-4a), 71.9, 71.9 (Ph*C*H$_2$), 71.0 (C-1º), 69.4 (C-5b), 69.2 (C-5a), 67.7 (C-6a), 67.2 (C-6b), 60.4 (C-2b), 59.5 (C-2a), 23.4 (*C*H$_3$), 21.7 (*C*H$_3$). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{50}H_{60}O_9N_7$: 902.44470, found: 902.44482.

Synthesis of disaccharide **12**: The reaction was carried out according to the standard procedure C. Compound **8** (200 mg, 0.18 mmol) was dissolved in DCM:HFIP (1:1, 0.1 M). TES (60 μL) and 0.2M HCl/HFIP (100 μL) were added to the mixture. The reaction stirred until TLC-analysis indicated full consumption of the starting material (30 min). Then the mixture was diluted with DCM and the reaction quenched with saturated $NaHCO_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EA = 5:1, R*f* = 0.22). Compound **12** (152 mg, 88% yield) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +62.9 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 736, 1029, 1043, 1146, 1261, 1454, 1734 (C=O), 2105 (N_3), 2868, 2926, 3491. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.42-7.20 (m, 25 H, aromatic *H*), 5.64 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.11 (s, 2 H, PhC*H*$_2$), 4.98 (d, *J* = 10.4 Hz, 1 H, C*H*H), 4.93 (d, *J* = 3.6 Hz, 1 H, H-1a), 4.89-4.82 (m, 3 H, 3 CH*H*), 4.55 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.51 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.08 (dd, *J*$_1$ = 8.8 Hz, *J*$_2$ = 10.0 Hz, 1 H, H-3a), 3.99 (t, *J* = 8.8 Hz, 1 H, H-4a), 3.86-3.65 (m, 7 H, H-3b, H-4b, H-5a, H-5b, H-6b, H-6a$_a$), 3.53-3.44 (m, 2 H, H-6a$_b$, H-1º$_a$), 3.40-3.33 (m, 2 H, H-2a, H-1º$_b$), 3.24 (dd, *J*$_1$ = 3.6 Hz, *J*$_2$ = 10.0 Hz, 1 H, H-2b), 2.68 (bs, 1 H, O*H*), 2.38 (t, *J* = 7.6 Hz, 2H, H-5º), 1.73-1.64 (m, 4 H, H-2º, H-4º), 1.47-1.39 (m, 2 H, H-3º). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 173.56 (*C*=O), 138.23, 138.17, 137.8, 137.7, 136.2 (aromatic *C*), 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.83, 127.79, 127.6, 127.4 (aromatic *C*H), 97.7 (C-1a), 97.6 (C-1b), 80.9 (C-3a), 79.7 (C-3b), 75.2, 74.5, 73.7, 73.4 (Ph*C*H$_2$), 73.1 (C-4b), 72.8 (c-4a), 70.6 (c-5b), 70.2 (C-5a), 69.9 (C-6a), 69.0 (C-6b), 68.2 (C-1º), 66.3 (Ph*C*H$_2$), 63.8 (C-2a), 62.8 (C-2b), 34.3 (C-5º), 29.2 (C-2º), 25.8 (C-3º), 24.8 (C-4º). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{53}H_{64}N_7O_{11}$: 974.46583, found: 974.46576.

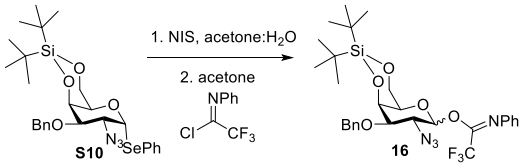
Synthesis of trisaccharide **13**: The reaction was carried out according to the standard procedure A. A mixture of donor **1** (160 mg, 0.24 mmol), acceptor **12** (150 mg, 0.16 mmol) (donors and acceptors co-evaporated with toluene three times), MPF (307 mL) in dry DCM (1.5 mL) were stirred over fresh flame-dried molecular sieves 3A under nitrogen. The solution was cooled to -78 ℃, after which TfOH (300 μL) was added. After 30 min, the reaction was stirred at -10 ℃ until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **13** (186 mg, 81% yield, α:β > 19:1, PE:EA = 4:1, R*f* = 0.40) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +75.8 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 736, 1029, 1147, 1249, 1359, 1454, 1514, 1734 (C=O), 2106 (N_3), 2866, 2932. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.39-7.21 (m, 35 H, aromatic *H*), 7.00 (bd, 2 H, aromatic *H*), 6.79 (bd, 2 H, aromatic *H*), 5.69 (d, *J* = 3.6 Hz, 1 H, H-1), 5.67 (d, *J* = 3.6 Hz, 1 H, H-1), 5.11 (s, 2 H, PhC*H*$_2$), 5.02-4.82 (m, 7 H, 6 C*H*H, H-1a), 4.66 (d, *J* = 10.0 Hz, 1 H, C*H*H), 4.56-4.46 (m, 3 H, 3 CH*H*), 4.39-4.33 (m, 2 H, 2 CH*H*), 4.26 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.18 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.14-3.98 (m, 4 H), 3.90-3.59 (m, 11 H), 3.56-3.44 (m, 3 H), 3.37-3.24 (m, 3 H), 2.38 (t, *J* = 7.6 Hz, 2H, H-5º), 1.73-1.63 (m, 4 H, H-2º, H-4º), 1.47-1.39 (m, 2 H, H-3º). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 173.5 (*C*=O), 159.4, 138.3, 138.2, 138.0, 137.8, 137.7, 137.6, 136.1, 130.3 (aromatic *C*), 129.6, 128.6, 128.57, 128.55, 128.4, 128.3, 128.26, 128.1, 127.9, 127.86, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 113.8 (aromatic *C*H), 97.8, 97.7, 97.4 (C-1a, 1b and 1c), 81.0, 80.7, 79.9 (C-3a, 3b and 3c), 77.7 (C-4c), 75.3, 74.7, 74.6, 74.2, 73.6, 73.5 (Ph*C*H$_2$), 73.0, 72.5 (C-4a and 4b), 71.5, 71.1, 70.2 (c-5a, 5b and 5c), 68.9, 68.7 (2 C-6), 68.2 (C-1º), 67.7 (C-6), 66.2 (Ph*C*H$_2$), 63.9, 63.6, 63.1 (C-2a, 2b and 2c), 55.3 (O*C*H$_3$), 34.2 (C-5º), 29.1 (C-2º), 25.7 (C-3º), 24.7 (C-4º). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{81}H_{93}N_{10}O_{16}$: 1461.67655, found: 1461.67594.

Synthesis of trisaccharide acceptor **14**: The reaction was carried out according to the standard procedure C. The starting material **13** (320 mg, 0.22 mmol) was dissolved in DCM:HFIP (1:1, 0.1 M). TES (71 μL) and 0.2M HCl/HFIP (110 μL) were added to the mixture. The reaction stirred

until TLC-analysis indicated full consumption of the starting material (15min). Then the mixture was diluted with DCM and the reaction quenched with saturated $NaHCO_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EA = 4:1). Compound **14** (230 mg, 78% yield) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +51.0 (c=3mg/mL, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 737, 1028, 1148, 1454, 1736 (C=O), 2106 (N_3), 2866, 2926. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.42-7.17 (m, 35 H, aromatic *H*), 5.67-5.65 (m, 2 H, H-1b and H-1c), 5.12 (s, 2 H, PhC*H*$_2$), 5.01-4.85 (m, 7 H, 6 C*H*H, H-1a), 4.56 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.50 (d, *J* = 12.0 Hz, 1 H, CH*H*), 4.37-4.32 (m, 3 H, 3 CH*H*), 4.22 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.14-3.99 (m, 4 H), 3.87-3.62 (m, 8 H), 3.56-3.43 (m, 3 H), 3.37-3.30 (m, 4 H), 3.18 (dd, J_1 = 3.6 Hz, J_2 = 10.0 Hz, 1 H, H-2c), 2.76 (bs, 1 H, O*H*), 2.39 (t, *J* = 7.6 Hz, 2H, H-5º), 1.74-1.64 (m, 4 H, H-2º, H-4º), 1.47-1.41 (m, 2 H, H-3º). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 173.6 (*C*=O), 138.3, 138.20, 138.17, 137.8, 137.6, 137.5, 136.2 (aromatic *C*), 138.7, 128.7, 128.6, 128.55, 128.5, 128.4, 128.3, 128.13, 128.09, 128.0, 127.95, 127.9, 127.8, 127.7, 127.5, 127.48, 127.3 (aromatic *C*H), 97.8, 97.7, 97.4 (C-1a, 1b and 1c), 81.1, 80.8, 79.1 (C-3a, 3b and 3c), 75.0, 74.6, 74.3, 73.7, 73.5, 73.4 (Ph*C*H$_2$), 73.0, 72.9, 72.3 (C-4a, 4b and 4c), 71.1, 70.3, 70.2 (c-5a, 5b and 5c), 70.0, 68.9, 68.6 (C-6a, 6b and 6c), 68.3 (C-1º), 66.26 (Ph*C*H$_2$), 63.9, 63.7, 62.5 (C-2a, 2b and 2c), 34.3 (C-5º), 29.2 (C-2º), 25.8 (C-3º), 24.8 (C-4º). HRMS (ESI) m/z: Calculated for $C_{73}H_{85}N_{10}O_{15}$: 1341.61904, found: 1341.61923.

Synthesis of tetrasaccharide **15**: The reaction was carried out according to the standard procedure A. A mixture of donor **1** (40 mg, 0.06 mmol), acceptor **14** (35 mg, 0.03 mmol) (donors and acceptors co-evaporated with toluene three times), MPF (52 µL) in dry DCM (0.3 mL) were stirred over fresh flame-dried molecular sieves 3A under nitrogen. The solution was cooled to -78 ℃, after which TfOH (5 µL) was added. After 30 min, the reaction was stirred at -10 ℃ until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **15** (43 mg, 87% yield, α:β > 20:1) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +94.8 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 737, 1029, 1148, 1251, 1359, 1454, 1514, 1735 (C=O), 2106 (N_3), 2868, 2928. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.42-7.15 (m, 45 H, aromatic *H*), 7.00 (bd, 2 H, aromatic *H*), 6.79 (bd, 2 H, aromatic *H*), 5.70-5.67 (m, 3 H, H-1b, 1c, 1d), 5.11 (s, 2 H, PhC*H*$_2$), 5.02-4.87 (m, 8 H, 7 C*H*H, H-1a), 4.81 (d, *J* = 10.4 Hz, 1 H, C*H*H), 4.66 (d, *J* = 10.4 Hz, 1 H, C*H*H), 4.54 (s, 2 H, PhC*H*$_2$), 4.65 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.38-4.28 (m, 4 H, 4 CH*H*), 4.22-4.00 (m, 8 H), 3.90-3.59 (m, 15 H), 3.52-3.44 (m, 3 H), 3.39-3.34 (m, 7 H), 2.38 (t, *J* = 7.6 Hz, 2H, H-5º), 1.73-1.64 (m, 4 H, H-2º, H-4º), 1.47-1.38 (m, 2 H, H-3º). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 173.5 (*C*=O), 159.4, 138.3, 138.2, 138.0, 137.84, 137.78, 137.6, 136.2, 130.3 (aromatic *C*), 129.7, 128.7, 128.65, 128.61, 128.59, 128.48, 128.45, 128.4, 128.33, 128.30, 128.2, 128.02, 127.98, 127.93, 127.87, 127.8, 127.74, 127.71, 127.6, 127.5, 127.4, 127.3, 113.9 (aromatic *C*H), 97.9, 97.8, 97.5, 97.48 (C-1a, 1b, 1c and 1d), 81.0, 80.9, 80.8, 80.0 (C-3a, 3b, 3c and 3d), 77.8 (C-4), 75.3, 74.7, 74.4, 74.3, 73.6, 73.6, 73.54, 73.51 (Ph*C*H$_2$), 73.1 (C-4), 72.4 (C-4), 72.1 (C-4), 71.5, 71.2, 71.1, 70.2 (c-5a, 5b, 5c and 5d), 68.9, 68.6, 68.3 (3 C-6), 68.29 (C-1º), 67.8 (C-6), 66.3 (Ph*C*H$_2$), 63.8, 63.7, 63.6, 63.2 (C-2a, 2b, 2c and 2d), 55.4 (O*C*H$_3$), 34.3 (C-5º), 29.2 (C-2º), 25.8 (C-3º), 24.8 (C-4º).

Synthesis of *N*-phenyl trifluoroacetimidate 2-N_3-galactose donor **16**:



NIS (9.15 g, 40.68 mmol) was added to the solution of compound **S3** (18 g, 31.3 mmol) in Acetone/H_2O (210 ml/72ml) at 0 ºC. The reaction was slowly warmed to room temperature and stirred until TLC-analysis indicated full consumption of the starting material (± 1h). Then the mixture was diluted with DCM and washed with saturated $Na_2S_2O_3$ and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The lactol was purified by silica gel column chromatography (pentane:EA = 4:1). Cs_2CO_3 was added to the solution of The lactol (10.59g, 24.33 mmol) in 140 ml acetone. The mixture was stirred at 0 ºC for 15 minutes. Then CF_3C(=NPh)Cl (6.06 g, 29.2 mmol) was added to the solution. which was slowly warmed to room temperature and stirred overnight. The reaction was quenched with Et_3N and concentrated *in vacuo*. The product **16** was purified by silica gel column chromatography (pentane:Et_2O = 30:1 – 10:1). Compound **16** (13.3 g, a/b = 2:1, 90% yield, PE: Et_2O = 10:1, R*f* = 0.45-0.55) was obtained as white solid. α isomer: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.50 – 7.24 (m, 7H, aromatic H), 7.15 – 7.05 (m, 1H, aromatic H), 6.84 (d, *J* = 7.7 Hz, 2H, aromatic H), 6.47 (bs, 1H, H-1), 4.78 (d, *J* = 11.4 Hz, 1H, *C*H$_2$*Ph*), 4.69 (d, *J* = 11.4 Hz, 1H, *C*H$_2$*Ph*), 4.63 (s, 1H, H-4), 4.22 (q, *J* = 12.8 Hz, 2H. H-6), 4.10 (t, *J* = 6.3 Hz, 1H, H-2), 3.89 (d, *J* = 9.5 Hz, 1H, H-3), 3.76 (s, 1H, H-5), 1.09-1.02 (m, 18H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.29, 137.45, 128.74, 128.56, 128.01, 127.91, 124.40, 119.35 (aromatic C/C*H*), 94.73 (C-1), 76.04 (C-3), 70.71 (C*H*$_2$*Ph*), 69.89 (C-5), 69.16 (C-4), 66.76 (C-6), 57.71 (C-2), 27.59 (C*H*$_3$), 27.23 (C*H*$_3$), 23.38 (C-*Si*), 20.73 (C-*Si*). β isomer: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.48 – 7.25 (m, 7H, aromatic H), 7.14 – 7.04 (m, 1H, aromatic H), 6.85 (d, *J* = 7.7 Hz, 2H, aromatic H), 5.50 (bs, 1H, H-1), 4.77 (d, *J* = 11.9 Hz, 1H, *C*H$_2$*Ph*), 4.66 (d, *J* = 11.9 Hz, 1H, *C*H$_2$*Ph*), 4.43 (s, 1H, H-5), 4.19 (s, 2H, H-6), 4.02 (s, 1H, H-4), 3.30 (s, 2H, H-2, 3), 1.15 – 1.00 (m, 18H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 137.5, 128.8, 128.7, 128.2, 128.0, 124.5, 119.4 (aromatic C/C*H*), 95.8 (C-1), 79.6 (C-3), 72.2 (C-2), 71.0 (C*H*$_2$*Ph*), 68.6 (C-5), 66.8 (C-6), 60.8 (C-4), 27.7 (C*H*$_3$), 27.4 (C*H*$_3$), 23.6 (C-*Si*), 20.9 (C-*Si*). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{21}H_{37}N_3O_5Si$: 629.2383, found: 629.2376.

Synthesis of disaccharide **18**: Donor **16** (5 g, 8.2 mmol) and acceptor **17** (3.32 g, 6.95 mmol) (donors and acceptors co-evaporated with toluene three times) were dissolved in DCM (65 mL), cooled to 0 ºC and TfOH (60 µL) was added. The reaction was stirred at 0 ℃ until TLC-analysis showed complete conversion of the donor. The reaction was

quenched with Et_3N after completed checking by TLC, filtered and concentrated *in vacuo*. The product **16** was purified by silica gel column chromatography (pentane:Et_2O = 10:1). Compound **18** (4.36g, 70% yield) was obtained with full α-selectivity as a colorless syrup. $[\alpha]_D^{20}$ +153.3 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 651, 698, 738, 797, 826, 984, 1043, 1066, 1100, 1171, 1364, 1473, 2107 (N_3), 2859, 2933. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.53-7.51 (m, 2 H, aromatic *H*), 7.44-7.22 (m, 18 H, aromatic *H*), 5.64 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.59 (d, *J* = 5.2 Hz, 1 H, H-1a), 5.00 (d, *J* = 10.4 Hz, 1 H, C*H*H), 4.91 (d, *J* = 10.4 Hz, 1 H, CH*H*), 4.73 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.63 (d, *J* = 11.6 Hz, 1 H, CH*H*), 4.43-4.37 (m, 4 H, 2 CH*H*, H-4b, H-5a), 3.96-3.77 (m, 6 H, H-2a, H-2b, H-3a, H-4a, H-6), 3.72-3.64 (m, 2 H, H-3b, H-6$_a$), 3.53 (dd, J_1 = 2.0 Hz, J_2 = 10.8 Hz, 1 H, H-6$_b$), 3.42 (s, 1 H, H-5b), 1.03 (s, 9 H, 3 CH_3), 0.97 (s, 9 H, 3 CH_3). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 137.9, 137.8, 137.4, 133.5 (aromatic *C*), 132.1, 129.2, 128.62, 128.58, 128.51, 128.48, 128.00. 127.98, 127.8, 127.5 (aromatic *C*H), 97.7 (C-1b), 87.1 (C-1a), 82.3 (C-3a), 75.5 (C-3b), 75.0, 73.3 (Ph*C*H$_2$), 72.8 (c-4a), 71.3 (c-5a), 70.5 (Ph*C*H$_2$), 69.6 (C-4b), 68.9 (C-6), 68.0 (C-5b), 66.9 (C-6), 64.6 (C-2a), 58.1 (C-2b), 27.7 (3 *C*H$_3$), 27.3 (3 *C*H$_3$), 23.4, 20.7. HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{47}H_{62}N_7O_8SSi$: 912.41444, found: 912.41409.

Synthesis of disaccharide **20**: Compound **18** (4.1 g, 4.6 mmol) was dissoveld in THF (40 mL) in a round flusk. Then HF-pyridine (1.2 mL) was added in the solution. The reaction stirred until TLC-analysis indicated full consumption of the starting material (30 min). Then the mixture was diluted with DCM and the reaction quenched with saturated $NaHCO_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude compound **19** was dissloved in CH_3CN (47 mL). Then BnBr (880 µL), borinic acid-catalyzed (110 mg), K_2CO_3 (710 mg), KI (800 mg) were added in the mixture. The reaction stirred at 60 °C in oil bath until TLC-analysis indicated full consumption of the starting material (24 h). Then the mixture was diluted with ethyl acetate and the reaction quenched with saturated $NaHCO_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:Et_2O = 5:1). Compound **20** (3.6 g, 94% yield with two steps) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +11.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 737, 1029, 1046, 1077, 1266, 2106 (N_3), 2870, 2919, 3493. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.54-7.51 (m, 2 H, aromatic *H*), 7.41-7.23 (m, 23 H, aromatic *H*), 5.61 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.60 (d, *J* = 5.2 Hz, 1 H, H-1a), 5.00 (d, *J* = 10.4 Hz, 1 H, C*H*H), 4.94 (d, *J* = 10.4 Hz, 1 H, CH*H*), 4.66 (s, 2 H, PhC*H*$_2$), 4.50-4.37 (m, 3 H, 2 CH*H*, 5a), 4.08 (s, 1 H, H-4b), 3.97-3.91 (m, 2 H, H-2b, H-4a), 3.85-3.37 (m, 5 H), 3.66 (dd, J_1 = 2.4 Hz, J_2 = 10.8 Hz, 1 H, H-6$_b$), 3.59 (dd, J_1 = 5.6 Hz, J_2 = 9.6 Hz, 1 H), 3.51 (dd, J_1 = 5.6 Hz, J_2 = 9.6 Hz, 1 H), 2.63 (s, 1 H, O*H*). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.3, 137.8, 137.6, 137.2, 133.5 (aromatic *C*), 132.3, 128.8, 128.6, 128.5, 128.4, 128.3, 128.1, 128.o, 127.9, 127.86, 127.85, 127.6, 127.55 (aromatic *C*H), 98.2 (C-1b), 87.1 (C-1a), 82.1 (C-3a), 76.3 (C-3b), 75.1 (Ph*C*H$_2$), 74.4 (c-4a), 73.8, 73.2, 71.8 (Ph*C*H$_2$), 71.3 (c-5a), 69.5 (C-6), 69.4 (C-6), 69.3 (C-5b), 66.5 (C-4b), 64.8 (C-2b), 59.0 (C-2a). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{46}H_{52}N_7O_8S$: 862.35926, found: 862.35895.

Synthesis of thio-disaccharide **21**: The compound **20** (3.83 g, 4.53 mmol) was dissloved in DMF (10 mL). Then NaH (544 mg) and NapBr (1.5 g) were added in the mixture. The reaction stirred until TLC-analysis indicated full consumption of the starting material (2 h). Then the mixture was diluted with ethyl acetate and the reaction quenched with ice water. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:Et_2O = 10:1). Compound **21** (4.15 g, 93% yield) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +208.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 737, 1028, 1049, 1093, 1123, 1362, 1454, 2106 (N_3), 2870. 2914. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.80-7.11 (m, 32 H, aromatic *H*), 5.64 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.59 (d, *J* = 5.2 Hz, 1 H, H-1a), 5.01-4.89 (m, 3 H, 3 C*H*H), 4.70-4.62 (m, 3 H, 3 C*H*H), 4.50 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.44-4.40 (m, 2 H, CH*H*, 5b), 4.27 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.17 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.04 (s, 1 H, H-4b), 3.97-3.81 (m, 6 H, H-2a, H-2b, H-3a, H-3b, H-4a, H-5a), 3.77-3.65 (m, 2 H, H-6), 3.51-3.40 (m, 2 H, H-6). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 138.3, 137.8, 137.60, 137.58, 135.6, 133.6, 133.2, 133.1 (aromatic *C*), 133.08, 129.2, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.99, 127.97, 127.93, 127.80, 127.6, 127.4, 127.2, 126.5, 126.2, 126.1 (aromatic *C*H), 98.3 (C-1b), 87.1 (C-1a), 82.2 (C-3a), 77.5 (C-3b), 75.2, 74.9 (Ph*C*H$_2$), 74.1 (c-4a), 73.6, 73.1 (Ph*C*H$_2$), 72.8 (C-4b), 72.3 (Ph*C*H$_2$), 71.3 (C-5b), 70.4 (C-5a), 69.4 (C-6), 68.6 (C-6), 64.8 (C-2a), 69.8 (C-2b). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{57}H_{60}N_7O_8S$: 1002.42186, found: 1002.42125.

N-phenyl trifluoroacetimidate disaccharide donor **23**: Compound **21** (4.15 g, 4.21 mmol) was dissolved in acetone:H_2O (10:1, 44 mL). N-Iodosuccinimide (NIS) (2.0 g, 8.8 mmol) was added in one portion and the reaction was stirred at room temperature for 2 hours. The solution was diluted with DCM and the reaction was quenched with saturated aqueous $Na_2S_2O_3$. Then the organic layer was washed with water and brine. The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacu*o, and the product purified by column chromatography (pentane:EA = 3:1). The lactol **22** was obtained as colourless syrup. Next, the lactol was dissolved in acetone (40 mL). Cs_2CO_3 (1.9 g) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (960 µL) were added to the solution respectively. The reaction was stirred overnight, then quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by column chromatography (pentane:EA = 40:1-20:1). Compound **23** (3.7 g, 81% over two steps) was obtained as yellow syrup. IR (neat, cm^{-1}) ν 695, 734, 818, 1027, 1116, 1209, 1312, 1454, 1489, 1497, 1717, 2107, 2870, 2918. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 7.80-7.09 (m, aromatic *H*), 6.81 (bt, 1 H), 5.65 (dd, 1 H), 5.01-4.87 (m), 4.68-4.54 (m), 4.45-4.42 (m), 4.33-4.18 (m), 4.03-3.41 (m). ^{13} C-APT ($CDCl_3$, 125 MHz) δ 143.4, 143.2, 138.20, 138.18, 137.8, 137.6, 137.55, 137.5, 135.6, 133.3, 133.2 (aromatic *C*), 128.9, 128.7, 128.53, 128.52, 128.44, 128.43, 128.3, 128.08, 128.05, 128.0, 127.97, 127.9, 127.84, 127.81, 127.69, 127.66, 127.65, 127.6, 127.2, 127.17, 124.7, 124.6 (aromatic *C*H), 119.4 (C-1), 98.3 (C-1),

98.2 (C-1), 83.6, 81.0, 77.6, 77.3, 75.5, 75.18, 75.16, 75.0, 74.9, 73.64, 73.60, 73.30, 73.2, 73.1, 73.0, 72.8, 72.7, 72.3, 72.2, 70.4, 70.3, 69.0, 68.5, 65.8, 63.7, 59.7, 59.6. HRMS (ESI) m/z: $[M-[O(C=NPh)CF3]+OH+Na]^+$ Calculated for $C_{59}H_{56}F_3N_7O_9Na$: 910.41340, found: 910.41374.

Synthesis of disaccharide **24**: Donor **16** (1.09 g) and acceptor **4** (790 mg) (donors and acceptors co-evaporated with toluene three times) were dissolved in DCM (12 mL), cooled to 0 °C and TfOH (12 μL) was added. The reaction was stirred at 0 ℃ until TLC-analysis showed complete conversion of the donor. The reaction was quenched with Et_3N after completed checking by TLC, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **24** (1.24 g, 92% yield) was obtained with full α-selectivity as a colorless syrup. $[\alpha]_D^{20}$ +95.9 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 651, 698, 737, 765, 797, 826, 984, 1004, 1040, 1130, 1144, 1171, 1455, 1474, 1735 (C=O), 2106 (N_3), 2860, 2933. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.44-7.24 (m, 20 H, aromatic *H*), 5.67 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.12 (s, 2 H, PhC*H*$_2$), 4.96 (d, *J* = 10.4 Hz, 1 H, C*H*H), 4.92 (d, *J* = 3.6 Hz, 1 H, H-1a), 4.86 (d, *J* = 10.4 Hz, 1 H, C*H*H), 4.71 (d, *J* = 11.6 Hz, 1 H, CH*H*), 4.61 (d, *J* = 11.6 Hz, 1 H, C*H*H), 4.48 (s, 2 H, PhC*H*$_2$), 4.36 (d, *J* = 2.0 Hz, 1 H, H-4b), 4.06 (dd, J_1 = 10 Hz, J_2 = 8.4 Hz, 1 H, H-3a), 3.91-3.78 (m, 4 H), 3.74-3.45 (m, 6 H), 3.34-3.30 (m, 2 H, H-2a, H-1º$_b$), 2.39 (t, *J* = 7.6 Hz, 2H, H-5º), 1.74-1.64 (m, 4 H, H-2º, H-4º), 1.48-1.42 (m, 2 H, H-3º), 1.03 (s, 9 H, 3 C*H*$_3$), 0.95 (s, 9 H, 3 C*H*$_3$). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 173.5 (*C*=O), 138.0, 137.9, 137.7, 136.2 (aromatic *C*), 128.7, 128.6, 128.3, 128.0, 127.96, 127.9, 127.86, 127.6 (aromatic *C*H), 97.9 (C-1b), 97.5 (C-1a), 81.0 (C-3a), 75.5 (C-3b), 74.3, 73.5 (Ph*C*H$_2$), 72.4 (c-4a), 70.5 (Ph*C*H$_2$), 70.1 (c-5a), 69.6 (C-4b), 69.1 (C-6), 68.3 (C-1º), 67.9 (C-5b), 66.9 (C-6), 66.3 (Ph*C*H$_2$), 63.6 (C-2a), 58.1 (C-2b), 34.3 (C-5º), 29.2 (C-2º), 27.7 (3 *C*H$_3$), 27.3 (3 *C*H$_3$), 25.8 (C-3º), 24.8 (C-4º), 23.4, 20.7. HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{54}H_{74}N_7O_{11}Si$: 1024.52101, found: 1024.52157.

Synthesis of disaccharide **25**: Compound **24** (1.16 g, 1.15 mmol) was dissoveld in THF (11 mL) in a round flusk. Then HF-pyridine (300 μL) was added in the solution. The reaction stirred until TLC-analysis indicated full consumption of the starting material (30 min). Then the mixture was diluted with DCM and the reaction quenched with saturated $NaHCO_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:Et_2O = 3:1). Compound **25** (910 mg, 91% yield) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +80.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 738, 1040, 1145, 1262, 1354, 1455, 1733 (C=O), 2106 (N_3), 2872, 2932, 3461. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.38-7.25 (m, 20 H, aromatic *H*), 5.65 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.12 (s, 1 H, PhC*H*$_2$), 4.97 (d, *J* = 10.4 Hz, 1 H, C*H*H), 4.92 (d, *J* = 3.6 Hz, 1 H, H-1a), 4.88 (d, *J* = 10.4 Hz, 1 H, C*H*H), 4.67-4.54 (m, 4 H, 4 CH*H*), 4.05 (dd, J_1 = 10.0 Hz, J_2 = 8.4 Hz, 1 H, H-3a), 3.91-3.80 (m, 2 H, H-4a, H-5), 3.74-3.57 (m, 8 H), 3.51-3.44 (m, 1 H, H-1º$_b$), 3.31 (dd, J_1 = 10.0 Hz, J_2 = 3.6 Hz, 1 H, H-2a), 2.65 (s, 1 H, O*H*), 2.39 (t, *J* = 7.6 Hz, 2H, H-5º), 2.29 (s, 1 H, O*H*), 1.74-1.64 (m, 4 H, H-2º, H-4º), 1.47-1.40 (m, 2 H, H-3º). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 173.60 (*C*=O), 138.1, 137.80, 137.1, 136.1 (aromatic *C*), 128.8, 128.7, 128.6, 128.5, 128.4, 128.31, 128.29, 128.1, 127.9, 127.8, 127.7 (aromatic *C*H), 97.9 (C-1b), 97.7 (C-1a), 80.8 (C-3a), 76.1 (C-3b), 74.5 (Ph*C*H$_2$), 73.8 (c-4a), 73.7 (Ph*C*H$_2$), 71.9 (Ph*C*H$_2$), 70.3 (c-5b), 70.2 (C-5a), 69.7 (C-6), 68.3 (C-1º), 67.2 (C-4b), 66.3 (Ph*C*H$_2$), 63.8 (C-2a), 62.9 (C-6), 58.8 (C-2b), 34.3 (C-5º), 29.2 (C-2º), 25.8 (C-3º), 24.8 (C-4º). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{46}H_{60}N_7O_{11}$: 884.41888, found: 884.41942.

Synthesis of disaccharide acceptor **26**: The compound **25** (865 mg, 1.0 mmol) was dissloved in CH_3CN (10 mL). Then BnBr (182 μL), borinic acid-catalyzed (22 mg), K_2CO_3 (148 mg), KI (166 mg), were added in the mixture. The reaction stirred at 60 °C in oil bath until TLC-analysis indicated full consumption of the starting material (24 h). Then the mixture was diluted with ethyl acetate and the reaction quenched with saturated $NaHCO_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:Et_2O = 5:1). Compound **26** (910 mg, 95%) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +66.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 736, 1040, 1096, 1259, 1455, 1734 (C=O), 2106 (N_3), 2869, 2928. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.40-7.21 (m, 25 H, aromatic *H*), 5.64 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.11 (s, 1 H, PhC*H*$_2$), 4.96 (d, *J* = 10.4 Hz, 1 H, C*H*H), 4.91 (d, *J* = 3.6 Hz, 1 H, H-1a), 4.88 (d, *J* = 10.4 Hz, 1 H, C*H*H), 4.63 (bs, 2 H, 2 CH*H*), 4.55 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.45 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.47-4.36 (m, 3 H, 3 CH*H*), 4.07-4.03 (m, 2 H, H-3a, H-5a), 3.91-3.44 (m, 12 H), 3.32 (dd, J_1 = 11.2 Hz, J_2 = 3.6 Hz, 1 H, H-2a), 2.65 (s, 1 H, O*H*), 2.38 (t, *J* = 7.6 Hz, 2H, H-5º), 1.73-1.63 (m, 4 H, H-2º, H-4º), 1.47-1.39 (m, 2 H, H-3º). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 173.5 (*C*=O), 138.3, 137.8, 137.3, 136.1 (aromatic *C*), 129.1, 128.7, 128.65, 128.54, 128.50, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 127.6, 127.3 (aromatic *C*H), 97.9 (C-1b), 97.7 (C-1a), 80.8 (C-3a), 76.3 (C-3b), 74.5 (Ph*C*H$_2$), 73.9 (C-4a), 73.8, 73.3, 71.7 (Ph*C*H$_2$), 70.1 (C-4b), 69.5, 69.4 (C-6), 69.2 (C-5b), 68.2 (C-1º), 66.4 (C-5a), 66.2 (Ph*C*H$_2$), 63.7 (C-2a), 58.9 (C-2b), 34.2 (C-5º), 29.1 (C-2º), 25.7 (C-3º), 24.8 (C-4º). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{53}H_{64}N_7O_{11}$: 974.46583, found: 974.46660.

Synthesis of tetrasaccharide **27**: The reaction was carried out according to the standard procedure A. A mixture of donor **23** (520 mg, 0.49 mmol), acceptor **26** (238 mg, 0.25 mmol) (donors and acceptors co-evaporated with toluene three times), MPF (490 μL) in dry DCM (1 mL) were stirred over fresh flame-dried molecular sieves 3A under nitrogen. The solution was cooled to -78 ℃, after which TfOH (40 μL) was added. After 30 min, the reaction was stirred at -10 ℃ until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **27** (280 mg, 89%, α:β = 10:1) was obtained as a colorless syrup. IR (neat, cm^{-1}) ν 697, 736, 1028, 1096, 1258, 1319, 1356, 1454, 1497, 1731 (C=O), 2105 (N_3), 2868, 2925. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.77-7.69 (m, 3 H, aromatic *H*), 7.60 (bs, 1 H, aromatic *H*), 7.42-7.17 (m, 48 H, aromatic *H*), 5.73 (d, *J* = 3.6 Hz, 1 H, H-1d), 5.65 (d, *J* = 3.6 Hz, 1 H, H-1b), 5.10 (s, 1 H,

PhC*H*$_2$), 4.96-4.90 (m, 7 H), 4.74-4.48 (m, 7 H), 4.36-3.61 (m, 22 H), 3.51-3.26 (m, 6 H), 3.20 (d, *J* = 10.0 Hz, 1 H), 3.03 (d, *J* = 10.0 Hz, 1 H), 2.36 (t, *J* = 7.6 Hz, 2H, H-5º), 1.71-1.61 (m, 4 H, H-2º, H-4º), 1.45-1.37 (m, 2 H, H-3º). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 173.4 (*C*=O), 138.4, 138.2, 137.7, 137.68, 137.6, 137.54, 137.47, 136.1, 135.6, 133.1, 133.0 (aromatic *C*), 128.6, 128.5, 128.4, 128.38, 128.35, 128.27, 128.25, 128.2, 128.1, 128.07, 128.0, 127.9, 127.88, 127.86, 127.78, 127.76, 127.66, 127.6, 127.4, 127.3, 127.1, 127.0, 126.4, 126.0, 125.9 (aromatic *C*H), 98.7 (C-1), 98.1 (C-1), 97.8 (C-1), 97.7 (C-1), 81.0 (C-3), 80.7 (C-3), 76.8 (C-3), 75.1 (C-3), 74.9, 74.5, 74.4 (*C*H$_2$), 73.5 (C-4), 73.5, 73.3 (*C*H$_2$), 73.2 (C-4), 72.9 (C-4), 72.8 (C-4), 72.8, 72.2, 71.7 (*C*H$_2$), 70.6 (C-5), 70.1 (C-5), 69.9 (C-5), 69.8 (C-5), 69.2, 68.4, 68.1, 67.9, 66.8, 66.1 (*C*H$_2$), 64.7 (C-2), 63.7 (C-2), 59.5 (C-2), 59.4 (C-2), 34.1 (C-5º), 29.0 (C-2º), 25.6 (C-3º), 24.7 (C-4º). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{104}H_{114}N_{13}O_{19}$: 1848.83484, found: 1848.83541.

Synthesis of tetrasaccharide acceptor **28**: The reaction was carried out according to the standard procedure C. Compound **27** (700 mg, 0.38 mmol) was dissolved in DCM:HFIP (1:1, 0.1 M). TES (304 µL, 1.91 mmol) and 0.2M HCl/HFIP (1.9 mL) were added to the mixture. The reaction stirred until TLC-analysis indicated full consumption of the starting material (15min). Then the mixture was diluted with DCM and the reaction quenched with saturated $NaHCO_3$. The organic phase was washed with water and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:Et_2O = 5:1). Compound **28** (297mg, 73% yield) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +106.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 696, 737, 1040, 1100, 1261, 1454, 1735 (C=O), 2106 (N_3), 2869, 2926. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 7.42-7.17 (m, 45 H, aromatic *H*), 5.71 (d, *J* = 3.5 Hz, 1 H, H-1d), 5.65 (d, *J* = 3.5 Hz, 1 H, H-1b), 5.10 (s, 1 H, PhC*H*$_2$), 4.95-4.89 (m, 6 H, H-1a, H-1c, 4 CH*H*), 4.72 (d, *J* = 12.0 Hz, 1 H, C*H*H), 4.68 (s, 2 H, 2 CH*H*), 4.57-4.48 (m, 3 H), 4.36-4.17 (m, 7 H), 4.09-3.58 (m, 17 H), 3.51-3.30 (m, 3 H), 3.36-3.30 (m, 3 H), 3.91-3.44 (m, 12 H), 3.17 (dd, J_1 = 11.5 Hz, J_2 = 2.5 Hz, 1 H), 3.02 (dd, J_1 = 11.5 Hz, J_2 = 2.5 Hz, 1 H), 2.66 (s, 1 H, O*H*), 2.37 (t, *J* = 7.5 Hz, 2H, H-5º), 1.71-1.63 (m, 4 H, H-2º, H-4º), 1.45-1.39 (m, 2 H, H-3º). ^{13}C-APT ($CDCl_3$, 125 MHz) δ 173.5 (*C*=O), 138.5, 138.3, 137.8, 137.7, 137.68, 137.6, 137.4, 136.2 (aromatic *C*), 128.8, 128.7, 128.6, 128.6, 128.5, 128.3, 128.2, 128.18, 128.0, 127.9, 127.9, 127.86, 127.8, 127.7, 127.69, 127.5, 127.5, 127.3, 127.2 (aromatic *C*H), 98.8 (C-1), 98.1 (C-1), 97.9 (C-1), 97.8 (C-1), 80.9 (C-3), 80.8 (C-3), 76.1 (C-3), 75.8 (C-3), 74.54, 74.46, 73.7 (*C*H$_2$), 73.6 (C-4), 73.56, 73.4 (*C*H$_2$), 73.1 (2 C-4), 73.07 71.8, 71.75 (*C*H$_2$), 70.7 (C-4), 70.2 (C-5), 69.9 (C-5), 69.3, 69.1 (*C*H$_2$), 68.8 (C-5), 68.5, 68.3, 68.9 (*C*H$_2$), 66.5 (C-5), 66.3 (Ph*C*H$_2$), 64.7 (C-2), 63.8 (C-2), 59.6 (C-2), 58.8 (C-2), 34.3 (C-5º), 29.2 (C-2º), 25.8 (C-3º), 24.8 (C-4º). HRMS (ESI) m/z: $[M+NH_4]^+$ Calculated for $C_{93}H_{106}N_{13}O_{19}$: 1708.77224, found: 1708.77299.

Synthesis of hexasaccharide **29**: The reaction was carried out according to the standard procedure A. A mixture of donor **23** (540 mg, 0.5 mmol), acceptor **28** (360 mg, 0.21 mmol) (donors and acceptors co-evaporated with toluene three times), MPF (400 µL) in dry DCM (1 mL) were stirred over fresh flame-dried molecular sieves 3A under nitrogen. The solution was cooled to -78 ℃, after which TfOH (44 µL) was added. After 30 min, the reaction was stirred at -10 ℃ until TLC-analysis showed complete conversion of the acceptor (48 h). The reaction was quenched with Et_3N, filtered and concentrated *in vacuo*. The product was purified by size exclusion (DCM:MeOH = 1:1). Compound **29** (500 mg, 91%, α:β = 10:1) was obtained as a colorless syrup. $[\alpha]_D^{20}$ +123.0 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 736, 1039, 1099, 1261, 1319, 1359, 1454, 1734 (C=O), 2106 (N_3), 2870, 2926. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.77-7.69 (m, 3 H, aromatic *H*), 7.60 (bs, 1 H, aromatic *H*), 7.44-7.07 (m, 68 H, aromatic *H*), 5.73 (d, *J* = 3.6 Hz, 1 H, H-1), 5.71 (d, *J* = 3.2 Hz, 1 H, H-1), 5.65 (d, *J* = 3.6 Hz, 1 H, H-1), 5.09 (s, 1 H, PhC*H*$_2$), 4.96-4.91 (m, 9 H), 4.77-4.65 (m, 5 H), 4.58-4.48 (m, 4 H), 4.33-3.62 (m, 37 H), 3.52-3.16 (m, 10 H), 3.05 (d, *J* = 10.0 Hz, 1 H), 2.99 (d, *J* = 10.0 Hz, 1 H), 2.36 (t, *J* = 7.6 Hz, 2H, H-5º), 1.71-1.61 (m, 4 H, H-2º, H-4º), 1.45-1.37 (m, 2 H, H-3º). ^{13}C-APT ($CDCl_3$, 100 MHz) δ 173.4 (*C*=O), 138.5, 138.4, 138.2, 137.7, 137.7, 137.6, 137.59, 137.57, 137.5, 137.4, 136.1, 135.7, 133.2, 133.0 (aromatic *C*), 128.6, 128.5, 128.49, 128.48, 128.45, 128.39, 128.36, 128.3, 128.2, 128.1, 128.05, 128.1, 128.0, 127.94, 127.90, 127.86, 127.82, 127.78, 127.77, 127.72, 127.67, 127.6, 127.42, 127.35, 127.3, 127.12, 127.11, 127.03, 127.0, 126.4, 126.0, 125.9 (aromatic *C*H), 98.8 (C-1), 98.7 (C-1), 98.1 (C-1), 97.9 (C-1), 97.8 (C-1), 97.7 (C-1), 80.9 (C-3), 80.8 (C-3), 80.7 (C-3), 76.9 (C-3), 76.1 (C-3), 75.7 (C-3), 74.9, 74.5, 74.4, 73.5, 73.3 (*C*H$_2$), 73.3 (C-4), 73.2 (C-4), 73.0 (*C*H$_2$), 72.83 (C-4), 72.80 (*C*H$_2$), 72.7 (C-4), 72.2, 71.9, 71.7 (*C*H$_2$), 70.6 (C-5), 70.5 (C-5), 70.1 (C-5), 69.9 (C-5), 69.8 (C-5), 69.6 (C-5), 69.2, 68.3, 68.1, 67.9, 66.8, 66.5, 66.1 (*C*H$_2$), 64.7 (2 C-2), 63.7 (C-2), 59.5 (C-2), 59.47 (C-2), 59.4 (C-2), 34.2 (C-5º), 29.1 (C-2º), 2575 (C-3º), 24.7 (C-4º).

Synthesis of hexasaccharide **30**: Compound **29** (20 mg, 0.0078 mmol) was dissolved in THF/H_2O/*tert*-BuOH (2 mL/2 mL/1 mL) before a catalytic amount of $Pd(OH)_2$/C was added. The reaction mixture was stirred for 3 days under a H_2 atmosphere, filtered and concentrated *in vacuo*. A white powder **30** (6.7 mg, 76%) was obtained after purification by gel filtration (HW-40, 0.15M NH_4OAc in H_2O). ^{1}H-NMR (D_2O, 500 MHz) δ 5.40-5.35 (m, 3 H, 3 H-1), 4.85-4.81 (m, 3 H, 3 H-1), 4.13-4.06 (m, 2 H), 3.97-3.50 (m, 35 H), 3.41-3.37 (m, 1 H), 3.15-3.08 (m, 2 H), 2.81 (dd, 2 H), 2.72-2.70 (m, 2 H), 2.06 (t, 2 H), 1.55-1.43 (m, 5 H), 1.29-1.23 (m, 2 H). ^{13}C-APT ($CDCl_3$, 125 MHz) δ 99.6 (C-1), 99.5 (C-1), 99.5 (C-1), 99.2 (2 C-1), 97.4 (C-1), 76.9, 76.7, 76.6, 76.7, 73.7, 73.3, 72.4, 72.3, 71.9, 71.1, 71.0, 70.5, 69.2, 68.8, 68.4, 68.3, 61.2, 60.6, 60.4, 55.3, 55.3, 54.6, 51.1, 51.1, 51.0, 37.5, 28.3, 25.7, 25.4. HRMS (ESI) m/z: $[M+2H]^+/2$ Calculated for $C_{42}H_{80}N_6O_{27}$: 550.25302; found: 550.25247.

Synthesis of hexasaccharide **31**: Compound **30** (5 mg) was dissoled in H_2O. Then Ac_2O and $NaHCO_3$ were added in the solution. The reaction mixture was stirred for 3 days until TLC-analysis showed complete conversion of the starting martials. The product was purified by gel filtration (HW-40, 0.15M NH_4OAc in H_2O). Compound **31** (5.5 mg, 86%) was obtained as a white solid. ^{1}H-NMR (D_2O, 500 MHz) δ 5.36-5.34 (m, 4 H, 4 H-1), 5.27 (d, *J* = 4.0 Hz, 1 H, H-1), 4.79 (bt, 2

H, 2 H-1), 4.73 (d, *J* = 3.0 Hz, 1 H, H-1), 4.21-4.06 (m, 5 H), 3.97-3.57 (m, 37 H), 3.40-3.35 (m, 1 H), 2.24 (bt, 2 H), 1.97-1.91 (m, 18 H, 6 C*H*$_3$), 1.80-1.74 (m, 2 H), 1.54-1.46 (m, 4 H), 1.32-1.26 (m, 2 H). ^{13}C-APT ($CDCl_3$, 125 MHz) δ 180.2, 174.7, 174.69, 174.6, 174.5, 174.46 (6 C=O), 98.2, 98.15, 96.6 (6 C-1), 77.4, 77.2, 76.1, 75.7, 75.4, 72.5, 72.4, 71.8, 71.7, 71.3, 71.2, 70.7, 70.7, 70.4, 68.5, 68.1, 67.9, 67.6, 66.9, 61.6, 60.7, 60.3, 60.0, 54.4, 54.2, 49.9, 34.6, 28.2, 25.0, 24.4, 22.1 (*C*H$_3$), 22.0 (*C*H$_3$), 22.0 (*C*H$_3$), 21.9 (*C*H$_3$), 21.9 (2 *C*H$_3$). HRMS (ESI) m/z: $[M+2H]^+/2$ Calculated for $C_{54}H_{92}O_{33}N_6$: 676.28472; found: 676.28489.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Full experimental details and characterization of all new compounds (PDF). NMR spectra of all new compounds (PDF)

AUTHOR INFORMATION

Corresponding Author

* jcodee@chem.leidenuniv.nl

Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

Notes

Any additional relevant notes should be placed here.

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