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Structure-reactivity relationships in glycosylation chemistry

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Citation

Hengst, J. M. A. van. (2023, December 7). *Structure-reactivity relationships in glycosylation chemistry*. Retrieved from https://hdl.handle.net/1887/3665922

Version:	Publisher's Version
License:	Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden
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Note: To cite this publication please use the final published version (if applicable).

4

Chapter 4: How configuration and protecting group pattern influence glycosyl acceptor reactivity

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Results from this chapter are published in

Chemical Science, 2023, 14, 1532-1542

Introduction

Typically, the optimization of glycosylation reactions in the context of oligosaccharide total synthesis is done in a target-oriented approach and despite decades of research no universal guidelines exist to ensure general stereoselective and high yielding glycosylations.[1-5] Many different protocols for the synthesis of oligosaccharides have been developed, with most of them taking the same approach (***Figure 1***). First, a donor with a latent leaving group (LG) is activated with an activator (E-X) to form an activated donor. This electrophile then reacts with a nucleophile, the acceptor, in the glycosylation reaction, forming a glycosidic bond.[6] Not surprisingly, the outcome of a glycosylation reaction, in terms of both stereoselectivity and yield, is dependent on many variables. Both external factors such as temperature, solvent, concentration and activator as well as inherent properties of the donor and the acceptor play a determining role.[7]

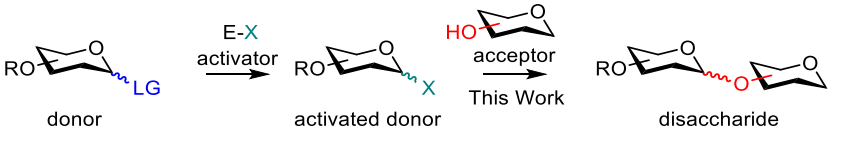


Figure 1: *A typical synthesis of a disaccharide*

Two important parameters are the reactivity of the donor,[8-10] as well as the nucleophilicity of the acceptor.[8, 11-14] Donor reactivity has been thoroughly investigated: countless relative reactivity values of thioglycosides have been determined,[15-17] various reactive species have been observed and characterized by variable temperature NMR,[18] and the reactivity of oxocarbenium-like intermediates has been probed via a combination of experiments, computational chemistry and spectroscopy.[14, 19, 20] Thanks to systematic mechanistic studies, the effect of both stereochemistry and protecting group pattern on the reactivity of the donor is relatively well understood. On the other hand, factors influencing the reactivity of the acceptor are less well understood, because systematic studies regarding the reactivity of the acceptor in the glycosylation reaction are much more scarce. Quite often acceptors with multiple variations are compared, making it unclear which structural modification is responsible for the difference in reactivity.[21] By carefully choosing a set of acceptors and changing the structure in a systematic way, it is possible to determine the effect of a single variation in the stereochemistry or protecting group pattern on the reactivity of the acceptor. This work investigates the reactivity of glycosyl acceptors of C-2, C-3, or C-4 hydroxyls of D-glucose, D-mannose, D-galactose, L-rhamnose and L-fucose acceptors, having different protecting group patterns of ether and ester groups. In order to limit steric effects when comparing different ether/ester protecting groups, sterically similar benzyl and benzoyl groups were used.

Model "stripped" carbohydrate-like acceptors and glycerol alcohols are probed for comparison. The glycerol acceptors in this series resemble typical carbohydrate acceptors as they are cyclic and secondary alcohols, flanked by protected alcohols. However, unlike carbohydrate acceptors, they are not chiral, eliminating the effect of double stereodifferentiation in the glycosylation reaction.

The method used for measuring the reactivity of the acceptors is based on the stereoselective outcome in a glycosylation reaction with the acceptors and two donors: phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**Donor A**) and phenyl 2-deoxy-2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**Donor B**). Recently the stereoselectivity of glycosylation reactions of these donors was reported to be a measure for the reactivity of the acceptor.[13] 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. More nucleophilic acceptors react with 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.[12] **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.[8]

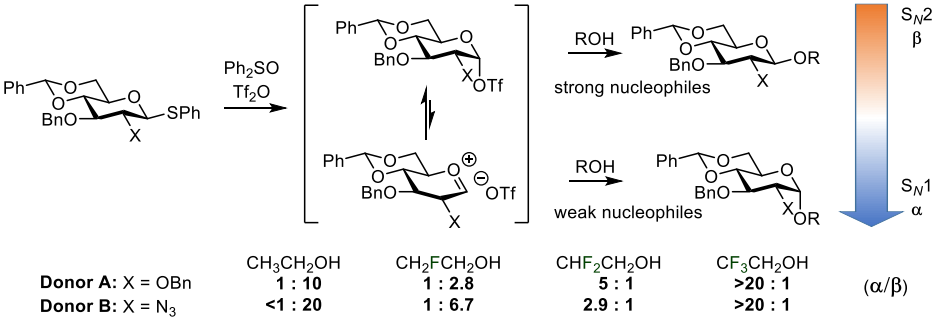


Figure 2: *Glycosylation mechanisms and the relation between stereoselectivity of* ***donor A*** *and* ***Donor B*** *and nucleophilicity of the acceptor*

Results and discussion

Stereoselectivity

In this study, 60 acceptors were reacted with **Donor A** and **Donor B**. The acceptors can be divided in six groups based on their configuration. The results of the glucose series (acceptors **1**-**12**), are reported in ***Table 1***, the mannose series (**13**-**23**) in ***Table 2***, the galactose series (**24**-**35**) in ***Table 3***, the rhamnose series (**36**-**42**) in ***Table 4***, the fucose series (**43**-**50**) in ***Table 5*** and the model acceptors (**51**-**60**) in ***Table 6***. When analysing these results, several trends became clear. In the previous study,[13] the reactivity of glucosyl C-4-hydroxy groups was thoroughly investigated (***Table 1***). It was found that the protecting groups on the C-6-position and on the C-3-position have an effect on the reactivity, with the protecting group on the C-3-position having a larger influence, due to the closer proximity. When both positions are changed from benzyl ethers to benzoyl esters, the deactivating effects work in concert leading the following order of reactivity of the glucosyl C-4-OH acceptors: **1** > **2** >**3** > **4**. A similar effect is found for the mannosyl C-4-OH (***Table 2*** acceptors **13**-**16**). Also, in this series the protecting group on the C-3-position has a larger influence on the reactivity of the acceptor than the protecting group on the 6-position, and again the effects of the C-3/C-6 benzyl/benzoyl groups are additive, leading to the order of reactivity for the mannosyl C-4-OH acceptors **13** > **14** > **15** > **16.** Of note, the mannosyl C-4-OH acceptors are all more reactive than their glucosyl C-4-OH equivalents.

The axial galactosyl C-4-OH is significantly less reactive (***Table 3*** acceptor **24**). When the protection groups on the C-6-position or the C-3-position of the galactose acceptors are changed from benzyl ethers to benzoyl esters (acceptors **25** and **26** respectively) the reactivity does not change significantly. Only when all protecting groups are changed to benzoyl esters, a significant effect is found and the reactivity decreases to provide highly α-selective glycosylations (acceptor **27**). The C-4-hydroxyls of D- and L-rhamnose and D- and L-fucose (acceptors **36**, **37**, **43**, **44**, ***Table 4*** and ***Table 5***) were used to investigate double stereodifferention effects in this glycosylation system. Although there are minor differences in stereoselectivity between the D- and L-isomers, the configuration of the acceptor seems to be more important than the absolute stereochemistry. The D-rhamnose and fucose acceptors have similar reactivity as their mannose and galactose counterparts, which is in line with what was previously found for C-4-OH glucose and C-4-OH 6-deoxyglucose acceptors.[13]

Regarding the reactivity of the C-3-hydroxyls, it is remarkable that the glycosylation with the glucose C-3-OH (acceptor **5**) is much more β-selective than the mannosyl, galactosyl, rhamnosyl and fucosyl C-3-OH (acceptor **17**, **28**, **38**, and **45** respectively), which all provide similar stereoselectivity. The main structural difference that distinguishes the glucosyl C-3-OH from the other alcohols, is that this alcohol has two equatorially oriented neighboring groups, while in mannose, galactose, rhamnose and fucose one of the neighboringing groups is axial, suggesting that this is important for the reactivity of the acceptor. Another difference is that benzoylation of the 2- and 4-position of glucose (acceptors **6** and **7**) has a similar effect on the reactivity and that the effects are additive (acceptor **8**). While the glycosylation of all per-benzoylated acceptors (acceptors **20**, **31**, **41** and **48**) show great α-selectivity, the effects of single benzoyl group (as in mannosyl acceptors **18** and **19**, galactosyl acceptors **29** and **30**, rhamnosyl acceptors **39** and **40** and fucosyl acceptors **46** and **47**), depends strongly on which position it is placed. In mannose and rhamnose, benzoylation of the equatorial C-4-OH significantly diminishes the reactivity (acceptors **18** and **39**) while benzoylation of the axial C-2-alcohol has little effect on the reactivity (acceptors **19** and **40**). This effect was also observed for the galactosyl and fucosyl acceptors were benzoylation of the axial C-4-OH (acceptors **29** and **46**) has a lower effect on the reactivity of the free alcohol than benzoylation of the equatorial C-2-OH (acceptors **30** and **47**). These results show that the electron withdrawing effect of the benzoate esters critically depends on the orientation of this protecting group relative to the free OH-group.

The results of the glycosylations with the C-2-OH acceptors show the same trend. The reactivity of the equatorial alcohols (acceptors **9**, **12**, **32**, **35**, **49**, **50**) is higher than that of the axial alcohols (acceptors **21** and **42**). Substitution of benzyl groups for benzoyl groups also decreases the reactivity of the glucosyl, mannosyl and galactosyl C-2-OH (acceptors **9**-**11, 21**-**23** and **32**-**34**). When regarding the reactivity of α-OMe *vs* β-OMe acceptors (**9** *vs* **12**, **32** *vs* **35** and **49** *vs* **50**) it becomes clear that alcohols next to equatorial ethers are more reactive than those next to one axial ether, in line with the reactivity trend revealed above for the C-3-OH acceptors. Furthermore, the β-OMe acceptors **12**, **35** and **50** have a similar reactivity as the other acceptors having the free alcohol next to two equatorial ethers (acceptors **1, 5, 13, 36, 37, 50**) and the α-OMe acceptors **9** and **32** react in a similar fashion to the other acceptors having one axial and one equatorial ether (acceptors **17**, **28**, **38** and **45**), again showing that the configuration of functional groups next to the alcohol is important for the reactivity with acceptors alcohols next to only equatorial benzyl ethers being more nucleophilic than those next to an axial benzyl ethers. From all the tested acceptors, only acceptor **49** shows a higher β-selectivity than what could be expected based on the above-described configuration-reactivity trends between.

Finally, two sets of model acceptors were introduced to 'isolate' the effect of the different neighboring groups and serve as benchmark to aid in (future) calculations to get more quantitative grip on the relative reactivity of the tested acceptors and provide a mechanistic explanation for the reactivity differences between acceptors. The first set consists of 'stripped' carbohydrate acceptors with a single substituent next to the alcohol. The experimental data obtained with these nucleophiles show that the same reactivity trends found for the carbohydrate acceptors above: equatorial acceptors are more reactive than axial acceptors (**51**, **53** and **55** *vs* **56**), alcohols next to equatorial benzyl ethers are more nucleophilic than those next to axial benzyl ethers (**51** and **55** vs **53**) and equatorial esters decrease the nucleophilicity much more than axial esters as compared to corresponding ethers (**51** *vs* **52** and **53** *vs* **54**). The second set of model acceptors consist of four glycerol C-2-OH acceptors, which were designed to investigate the effect of different protecting groups on non-chiral cyclic acceptors containing a secondary alcohol next to two protected oxygen atoms. Not surprisingly, the reactivity of the glyceroyl alcohols in the acceptors is heavily dependent on the protecting groups. The isopropylidene protected acceptor (**59**) is the most reactive, followed by the *cis*-benzylidene protected acceptor (**58**), the *trans*-benzylidene protected acceptor (**57**) and finally the carbonate protected acceptor (**60**)

***Table 1**: Glucose acceptors and their stereoselectivities with **donor A** and **donor B**. a: results are taken from ref 13*

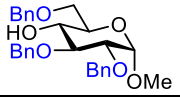
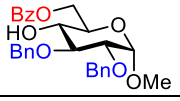
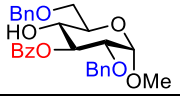
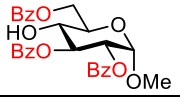
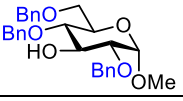
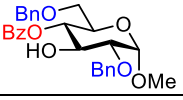
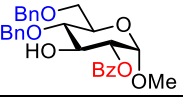
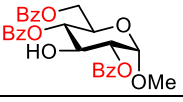
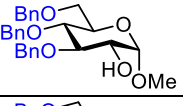
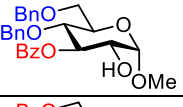
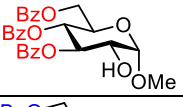
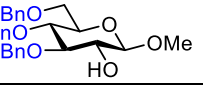
Acceptor	structure	Donor A		Donor B	
		Product (yield)	**α:β**	**Product** (yield)	**α:β**
1[a]		**1A** (82%)	**1:1**	**1B** (88%)	**1:7**
2[a]		**2A** (92%)	**4:1**	**2B** (67%)	**1:1.1**
3[a]		**3A** (95%)	**>20:1**	**3B** (77%)	**6.7:1**
4[a]		**4A** (91%)	**>20:1**	**4B** (69%)	**>20:1**
5[a]		**5A** (78%)	**1:2.7**	**5B** (70%)	**<1:20**
6		**6A** (98%)	**2.6:1**	**6B** (99%)	**1:5**
7		**7A** (99%)	**1.8:1**	**7B** (93%)	**1:4**
8[a]		**8A** (100%)	**>20:1**	**8B** (83%)	**>20:1**
9[a]		**9A** (76%)	**9:1**	**9B** (66%)	**1.6:1**
10		**10A** (78%)	**>20:1**	**10B** (82%)	**6:1**
11[a]		**11A** (85%)	**>20:1**	**11B** (92%)	**13:1**
12		**12A** (96%)	**1:1.9**	**12B** (78%)	**1:6**

Table 2: *Mannose acceptors and their stereoselectivities with* ***donor A*** *and* ***donor B****. a: results are taken from ref 13*

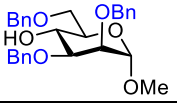
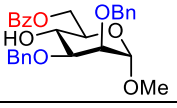
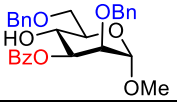
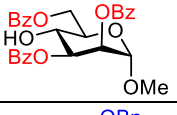
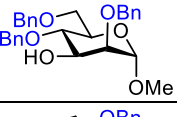
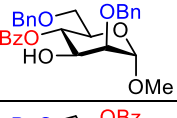
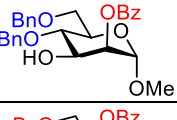
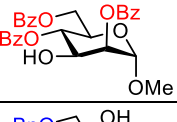
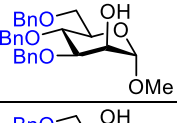
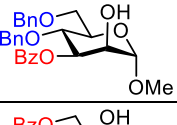
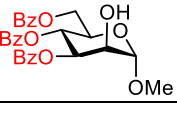
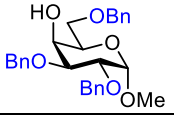
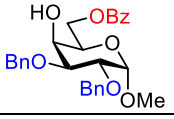
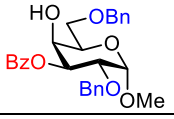
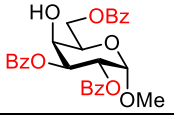
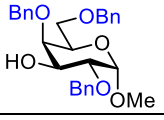
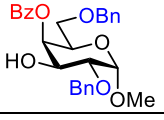
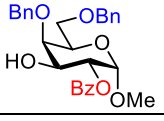
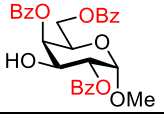
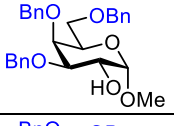
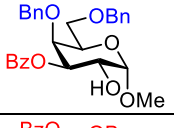
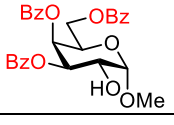
Acceptor	structure	Donor A		Donor B	
		Product (yield)	**α:β**	**Product** (yield)	**α:β**
13 [a]		**13A** (76%)	**1:2**	**13B** (72%)	**<1:20**
14		**14A** (76%)	**1.3:1**	**14B** (92%)	**1:8**
15		**15A** (62%)	**9:1**	**15B** (93%)	**1.5:1**
16		**16A** (66%)	**>20:1**	**16B** (98%)	**10:1**
17 [a]		**17A** (82%)	**8:1**	**17B** (70%)	**1.1:1**
18		**18A** (87%)	**>20:1**	**18B** (87%)	**>20:1**
19		**19A** (82%)	**10:1**	**19B** (93%)	**1:1**
20 [a]		**20A** (100%)	**>20:1**	**20B** (100%)	**>20:1**
21 [a]		**21A** (95%)	**>20:1**	**21B** (65%)	**7:1**
22		**22A** (76%)	**>20:1**	**22B** (51%)	**7:1**
23		**23A** (77%)	**>20:1**	**23B** (51%)	**>20:1**

***Table 3**: Galactose acceptors and their stereoselectivities with **donor A** and **donor B**. a: results are taken from ref 13*

Acceptor	structure	Donor A		Donor B	
		Product (yield)	**α:β**	**Product** (yield)	**α:β**
24 [a]		**24A** (72%)	**12:1**	**24B** (86%)	**3:1**
25		**25A** (85%)	**>20:1**	**25B** (100%)	**3:1**
26		**26A** (78%)	**11:1**	**26B** (67%)	**3:1**
27		**27A** (70%)	**>20:1**	**27B** (100)	**>20:1**
28 [a]		**28A** (85%)	**6:1**	**28B** (88%)	**1:1.3**
29		**29A** (76%)	**16:1**	**29B** (60%)	**1.3:1**
30		**30A** (84%)	**>20:1**	**30B** (82%)	**13:1**
31 [a]		**31A** (83%)	**>20:1**	**31B** (90%)	**11:1**
32 [a]		**32A** (87%)	**10:1**	**32B** (73%)	**1:1.3**
33		**33A** (89%)	**>20:1**	**33B** (51%)	**3:1**
34		**34A** (88%)	**>20:1**	**34B** (87%)	**6:1**

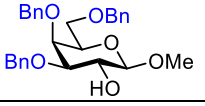
35		**35A** (83%)	**1.5:1**	**35B** (86%)	**1:10**

Table 4**: Rhamnose acceptors and their stereoselectivities with **donor A** and **donor B

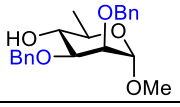
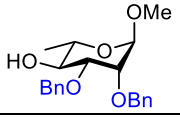
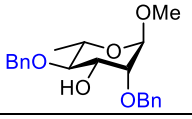
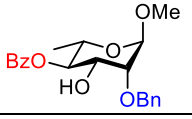
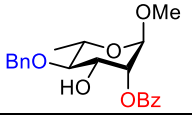
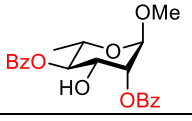
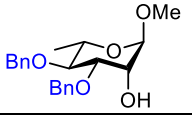
Acceptor	structure	Donor A		Donor B	
		Product (yield)	**α:β**	**Product** (yield)	**α:β**
36		**36A** (89%)	**1:2.4**	**36B** (75%)	**<1:20**
37		**37A** (90%)	**1.7:1**	**37B** (99%)	**1:10**
38		**38A** (100%)	**7:1**	**38B** (68%)	**1.4:1**
39		**39A** (69%)	**>20:1**	**39B** (50%)	**12:1**
40		**40A** (66%)	**6:1**	**40B** (55%)	**1:1**
41		**41A** (83%)	**>20:1**	**41B** (100%)	**12:1**
42		**42A** (59%)	**>20:1**	**42A** (77%)	**3:1**

Table 5: *Fucose acceptors and their stereoselectivities with* ***donor A*** *and* ***donor B***

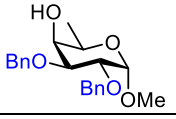
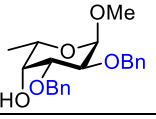
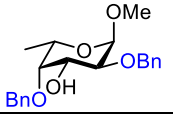
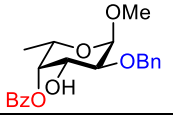
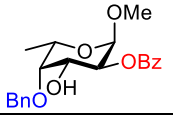
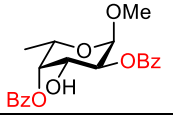
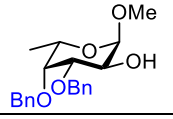
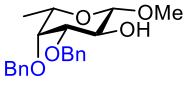
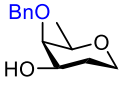
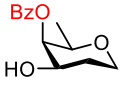
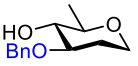
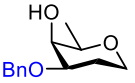
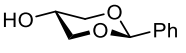
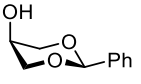
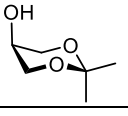
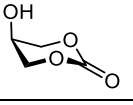
Acceptor	structure	Donor A		Donor B	
		Product (yield)	**α:β**	**Product** (yield)	**α:β**
43		**43A** (98%)	**>20:1**	**43B** (100%)	**1.3:1**
44		**44A** (85%)	**14:1**	**44B** (100%)	**3:1**
45		**45A**(100%)	**3.2:1**	**45B** (88%)	**1:2**
46		**46A** (100%)	**>20:1**	**46B** (100%)	**2:1**
47		**47A** (100%)	**>20:1**	**47B** (92%)	**9:1**
48		**48A** (100%)	**>20:1**	**48B** (100%)	**>20:1**
49		**49A** (55%)	**1:1**	**49B** (95%)	**1:5.5**
50		**50A** (86%)	**1:1.2**	**50B** (93%)	**<1:20**

Table 6**: Model acceptors and their stereoselectivities with **donor A** and **donor B

Acceptor	structure	Donor A		Donor B	
		Product (yield)	**α:β**	**Product** (yield)	**α:β**
51		**51A** (81%)	**1:1.6**	**51B** (85%)	**1:13**
52		**52A** (53%)	**5:1**	**52B** (60%)	**1.4:1**
53		**53A** (97%)	**4:1**	**53B** (60%)	**1:1.4**
54		**54A** (100%)	**8:1**	**54B** (100%)	**1.5:1**
55		**55A** (98%)	**1:1.6**	**55B** (97%)	**1:16**
56		**56A** (100%)	**11:1**	**56B** (93%)	**1.4:1**
57		**57A** (100%)	**6:1**	**57B** (100%)	**2.9:1**
58		**58A** (79%)	**1.6:1**	**58B** (31%)	**1:3**
59		**59A** (96%)	**1:1**	**59B** (100%)	**1:10**
60		**60A** (97%)	**>20:1**	**60B** (99%)	**>20:1**

Structure-reactivity relationships

In order to reveal structure-reactivity relationships for the large collection of acceptors, they were divided in groups based on their configuration and protecting group pattern and their reactivity of acceptors plotted as percentage β-product formed with both **donor A** and **donor B**.

Figure 3 shows the importance of configuration on the reactivity of the acceptor. Equatorial acceptors are generally more reactive than axial acceptors (light blue circles and blue squares bar vs black triangles). Furthermore, the orientation of the group next to the alcohol is important for the reactivity of the acceptor. When the nucleophilic alcohol only has equatorial neighbours (light blue circles) the acceptor is more nucleophilic than an acceptor with an axial neighbour (blue squares)

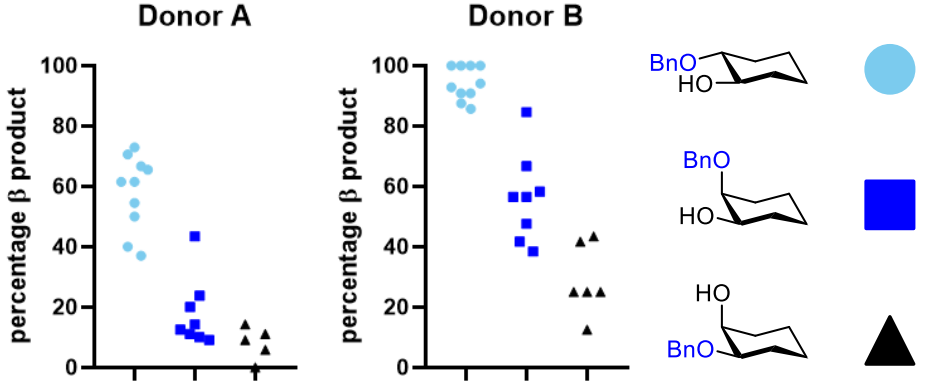


Figure 3*: Configuration vs reactivity (measured as percentage β-product for* ***Donor A*** *and* ***Donor B****) of glycosyl acceptors. Light blue circles: equatorial alcohol acceptors with only equatorial neighboring OBn and OMe groups, i.e. acceptors* ***1, 5, 12, 13, 35, 36, 37, 50, 51*** *and* ***55****. Blue squares: equatorial alcohol with one axial neighboring OBn or OMe group, i.e. acceptors* ***9, 17, 28, 32, 38, 45, 49*** *and* ***53.*** *Black triangles: axial alcohols, i.e. acceptors* ***21, 24, 42, 43, 44*** *and* ***56****.*

Figure 4 shows the effect of the orientation of a benzoyl group on the reactivity of the acceptors. When the neighboring benzoyl is axial (red diamonds) the effect on the reactivity is smaller than that of an equatorial benzoyl (yellow triangles). Benzyl protected acceptors with one axial neighboring OBn or OMe group (blue circles) and acceptors with one axial and one equatorial benzoyl group (green inverted triagles) are provided as a reference.

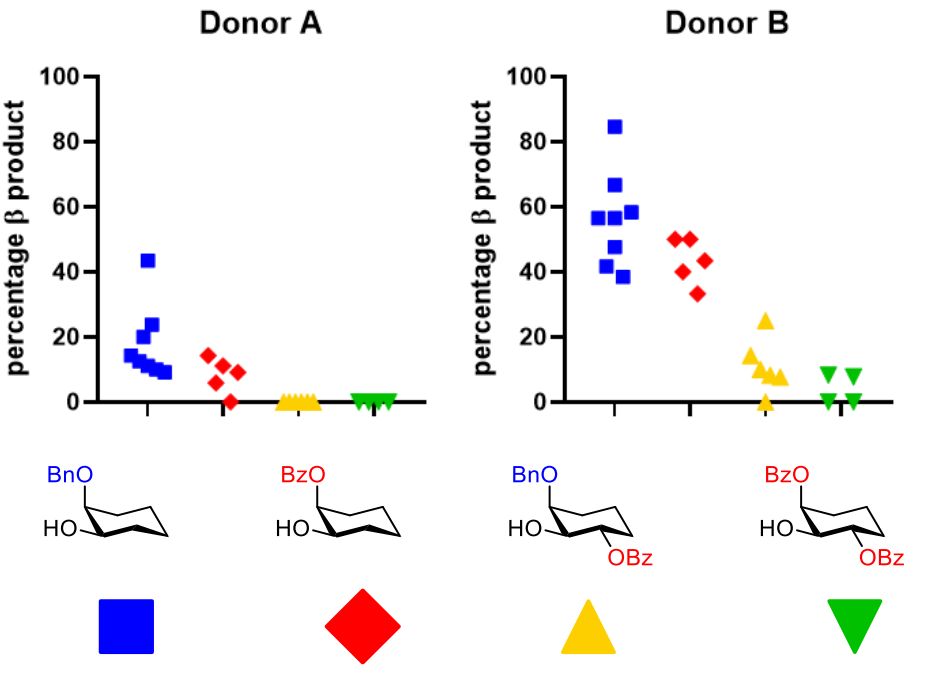


***Figure 4**: Protecting group pattern vs reactivity (measured as percentage β-product for **Donor A** and **Donor B**) of glycosyl acceptors. Blue circles: equatorial alcohol acceptors with one axial neighboring OBn or OMe group, i.e. acceptors **9, 17, 28, 32, 38, 45, 49** and **53.** Red diamonds: equatorial alcohol acceptors with one axial neighboring OBz group, i.e. acceptors **19, 29, 40, 46** and **54.** Yellow triangles: equatorial alcohol acceptors with one axial neighboring OBn or OMe group and one equatorial neighboring OBz group, i.e. acceptors **10, 18, 30, 34, 40** and **47**. Green triangles: equatorial alcohol acceptors with one axial and one equatorial neighboring OBz group, i.e. acceptors **20, 31, 41** and **48**.*

Proton affinity

Next, a method was sought to establish acceptor reactivity in a more quantitiative manner. To this end the proton affinity of the model acceptors **59**-**68** and partially fluorinated ethanols was calculated. The computed proton affinity (ΔH_{PA}) is defined as the enthalpy for the reaction described in ***equation 1*** in the gas phase.

$$ROH \rightarrow RO^- + H^+ \ (1)$$

The proton affinity of a given alcohol serves as a measure for the electron density of the alcohol, and thus relates to the nucleophilicity of the acceptor alcohols. First the proton affinities were computed for ethanol, 2-fluoroethanol, 2,2-difluoroethanol and 2,2,2-

trifluoroethanol and compared to experimental values from literature.[23-25] For each acceptor and the corresponding alkoxide the enthalpy of the lowest energy conformer was computed at DLPNO-CCSD(T)/CBS(3/4,def2)[26-29] //DLPNO-MP2/def2-TZVP[26-28, 30, 31] at T=298.15K using ORCA5.0.1.[32] This general purpose method[33] has recently been shown to provide energies similar to the 'golden standard', canonical CCSD(T) calculations, for carbohydrate conformations.[34] First the ΔH_{PA} of the fluorinated ethanol derivates were computed at both DLPNO-CCSD(T) and canonical CCSD(T) level, and compared to the experimental value to gauge the accuracy of the method. The DLPNO-CCSD(T) computations provided excellent agreement with both computed canonical CCDT(T) calculations and experimental values (***Table 7***).

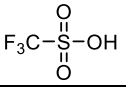
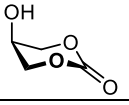
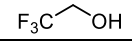
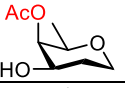
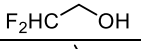
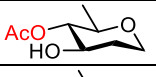
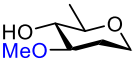
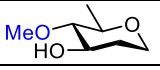
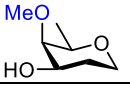
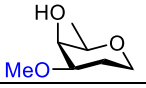
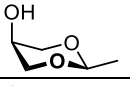
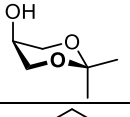
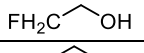
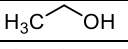
Table 7: *calculated proton affinities of ethanol acceptors compared to their experimental values from literature*

Acceptor	Calculated ΔH_{PA} DLNPO-CCDS(T) (Kcal/mol)	Calculated ΔH_{PA} CCDS(T) (Kcal/mol)	experimental ΔH_{PA} (Kcal/mol)
Ethanol	379.1	379.4	379.1 ± 1.0[23]
MFE	372.1	372.5	370.9 ± 2.9[24]
DFE	366.6	367.0	366.2 ± 2.2[25]
TFE	361.4	361.7	361.4 ± 2.4[25]

Next the proton affinities for the other acceptors were calculated. In these computations, the relatively large benzyl, benzoyl and benzylidene protecting groups were replaced for smaller but electronically similar methyl, acetyl and ethylidene groups. For ease of comparison, the proton affinities are shown as the relative proton affinity to triflic acid ($\Delta\Delta H_{PA}$), which can be defined by ***equation 2.*** The results of these calculations are depicted in ***Table 8*** and listed in order of increasing relative proton affinity.

$$\Delta\Delta H_{PA}\,(ROH) = \Delta H_{PA}\,(ROH) - \Delta H_{PA}\,(TfOH) \quad (2)$$

Table 8: *Proton affinity vs stereoselectivity for the studied model acceptors.*

Acceptor	structure	$\Delta\Delta H_{PA}$ (Kcal/mol)	Percentage β Donor A	Percentage β Donor B
TfOH		0	0[b]	0[b]
60		58.3	0	0
TFE		64.4	0	0
61		68.0	14[a]	26[a]
62		68.7	11[a]	40[a]
DFE		69.4	17	26
63		69.5	17[a]	42[a]
64		69.6	62[a]	94[a]
65		70.5	62[a]	93[a]
66		70.9	20[a]	58[a]
67		71.4	8[a]	42[a]
68		76.0	38[a]	75[a]
59		76.2	50	91
MFE		74.9	74	87
EtOH		81.9	91	100

[a]*Stereoselectivity based on experimental data from benzyl, benzoyl or benzylidene protected analogues, see above.* [b]*Determined by NMR at – 40 °C*

The correlation between proton-affinity and reactivity of the acceptor (as measured by the percentage of β-product in a glycosylation reaction with **Donor A** or **Donor B**) is plotted in ***Figure 5A-C***. When the proton affinity of all acceptors is plotted agains the β-selectivity of the acceptors, a coefficient of determination (R^2) of 0.57 was obtained for the reactions with both **Donor A** and **Donor B** (***Figure 5A***). When only the data was used obtained for the simpler non-chiral alcohols (*i.e.* **59**, **60**, **61**, **68**, EtOH, MFE, DFE and TFE) the value for R^2 was much higher (0.85 for **Donor A** and 0.92 for **Donor B**), indicating a good correlation between the calculated proton affinity and the reactivity of the acceptor (***Figure 5B***). There is no correlation between the proton affinity of the chiral 'stripped carbohydrate' acceptors and the stereoselectivity of the reactions ($R^2 < 0.01$, ***Figure 5C***), showing that reactivity of these acceptors in the glycosylations with donors **A** and **B** is not solely determined by the electron density of the alcohol, as determined by the ΔH_{PA}, but rather by the more complex interplay of both steric and electronic factors. Although the computations listed in ***Table 8*** show that the method used to compute the proton affinity can accurately reconstitute this parameter for simple alcohols in the gas phase, it is not surprising that there is poorer correlation with the reactivity of the more complex alcohols in solution.

Another recent study has attempted to describe acceptor reactivity with a parameter (Aka) relating to the reaction rate of acceptors with 3,4-dihydropyran (DHP) under acidic conditions.[22] The authors found relatively good correlations between this parameter, the reactivity of the donor and the outcome of the glycosylation reaction. So for future research it would be interesting to measure the Aka of this set of acceptors and investigate if the same trends can be found as described in this work.

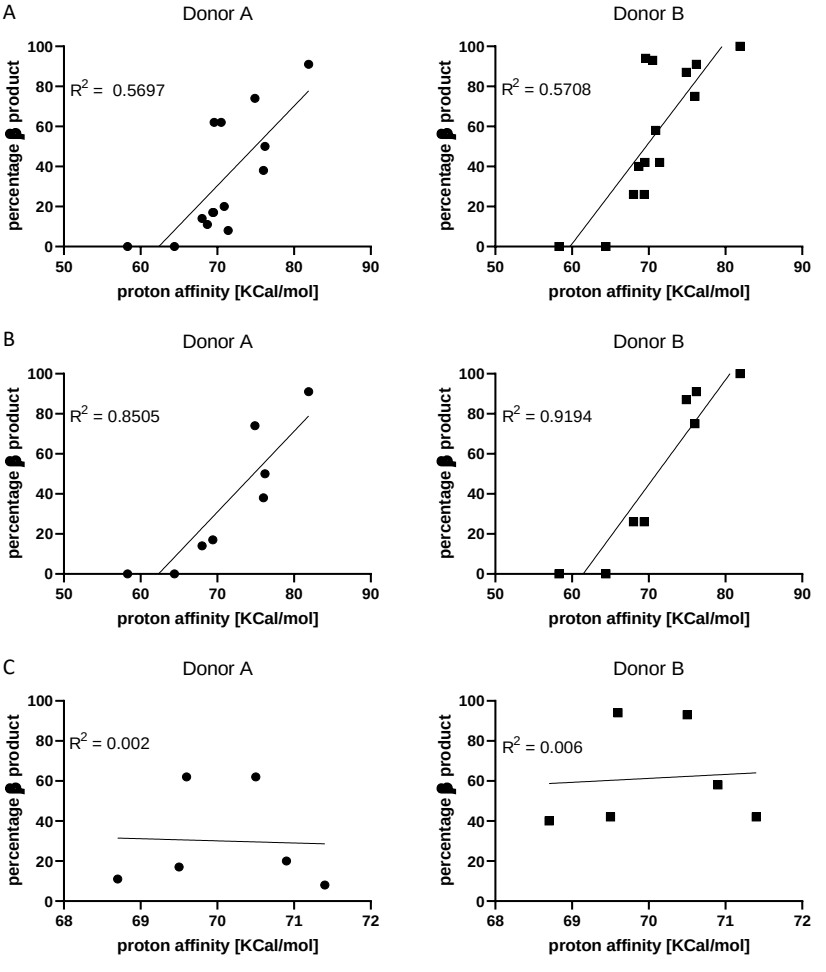


Figure 5: *Calculated proton affinity vs experimental stereoselectivity with R^2 displayed for A: all acceptors for which proton affinity was calculated; B: for the set of non-chiral acceptors and C: 'stripped carbohydrate-like' acceptors. Acceptor* ***60*** *was excluded for the calculation of R^2 because of non-linearity of the graph in that area, since the amount of β-product can not be lower than 0%, and acceptors with a higher proton affinity already show full α-selectivity. Experimental values of β-selectivity are based on benzyl, benzoyl and benzylidene protected acceptors, the calculated proton affinity is based on methyl, acetyl and ethylidene protected analogues.*

Conclusions

In conclusion, structure-reactivity relationships for a large set of glycosyl acceptors have been established, based on the stereoselectivity of these acceptors in glycosylations with two conformationally restricted glucosyl donors. The reactivity-stereoselectivity correlation is based on the premise that reactive acceptors predominantly provide the β-product via an S_N2 like mechanism in which a covalent anomeric α-triflate is displaced, while less reactive acceptors give more α-product via a glycosylation proceeding with more S_N1 like character. In total, 60 acceptors were tested, and this systematic series of nucleophiles has revealed several factors that influence the reactivity of the acceptor. With regards to configuration, equatorial 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 neighboring protected alcohols take up an equatorial position, are more reactive than acceptors in which one of the flanking protected alcohols is axial. The protecting group pattern also plays an important role, since switching benzyl ethers to sterically similar benzoyl esters decreases the reactivity of the acceptor. However, 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. To better understand the stereoelectronic effects of exerted by the different configuration and protecting group patterns, a set of model acceptors was introduced to serve as a benchmark for computational studies. Proton affinities were calculated in an attempt to explain differences in reactivity, and for simple non-chiral alcohol nucleophiles relatively good correlation was found between calculated proton affinity and reactivity. For the more complex, chiral carbohydrate-like acceptors, the differences in proton affinity proved to be relatively small, and these could not fully account for the experimentally observed differences in reactivity. Overall, this has shown that proton affinity is important for the reactivity of acceptors, but other factors may also contribute and future research efforts will focus on the investigation of steric and hydrogen bonding effects.

Experimental

Calculation of proton affinities

Spartan'14[35] was used to construct a conformer library of the neutral acceptor by a Monte-Carlo search. Each conformation was optimzed and evaluated using the MMFF[36] force field, and the 100 lowest energy structures were included in the conformer library. The conformer library of the corresponding anion was constructed by converting all hydroxyl conformers in the neutral conformer library to the corresponding alkoxide conformer. All conformers in both libraries were optimized using ORCA5.0.1[32] by DFT at B3LYP-D3(BJ)/def2-TZVP(-f)[26, 37-40] level of theory, utilizing the TighSCF and Defgrid2 keywords. All conformers with a ΔE < 1 kcal mol^{-1} were re-optimized by WFT at DLPNO-MP2/def2-TZVP[26-28, 30, 31] level of theory. Final single point energies of all re-optimized structures were computed by WFT at DLPNO-CCSD(T)/CBS(3/4,def2)[26-31] level of theory, utilizing the TightSCF, Defgrid2 and NormalPNO keywords. This method has been shown to provide energies similar to canonical CCSD(T) for diverse systems,[34] aswell as for carbohydrate conformations specifically.[33] The final enthalpy of each conformer was constructed as DLPNO-MP2/def2-TZVP//DLPNO-CCSD(T)/CBS(3/4,def2) at T=298.15K. ΔH_{PA} was derived by equation 1.

$$\Delta H_{PA} = H_{alkoxide} - H_{alcohol} \quad (1)$$

The ΔH_{PA} was expressed as $\Delta\Delta H_{PA}$, relative to the lowest computed ΔH_{PA} in this study; triflic acid.

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.

Acceptor **58** was purchased from Sigma Aldrich and used without further purification. Acceptors **26**,[41] **44**,[42] **57**,[43] **59**[43] and **60**[44] and donors **A**[12] and **B**[8] were synthesized according to literature procedures

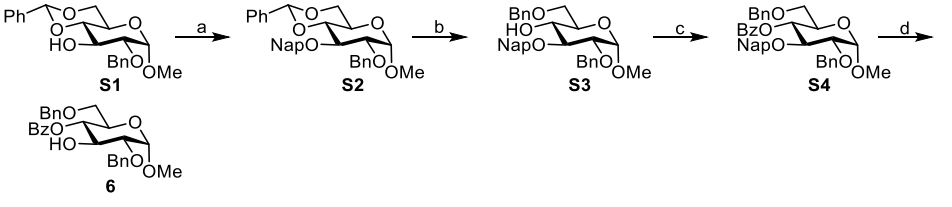
General procedure for Ph_2SO/Tf_2O meditated glycosylations

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 1-24 hr at that temperature. The reaction was quenched with 2 mL sat aq $NaHCO_3$ or 0.3 mL 1M Et_3N in DCM, 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.

Preparations of acceptors

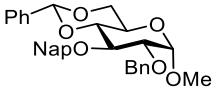
Glucose acceptors

Preparation of acceptor **6**



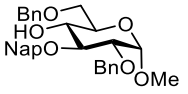
***Scheme S1**: preparation of acceptor (**6**): reagents and conditions: a) NapBr, NaH, DMF 100%; b) TES-H, TFA, DCM, 0^{0}C 84% c) BzCl, pyridine, 76% d) DDQ, DCM/H_2O (9:1), 90%*

Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2-naphthyl)methyl-α-D-glucopyranoside (S2)



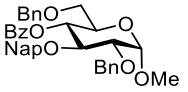
methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2-naphthyl)methyl-α-D-glucopyranoside[45] (**S1**, 1.50 g, 4.03 mmol) was dissolved in DMF and cooled to 0 °C. NaH (60% dispersion in mineral oil, 241 mg, 6.04 mmol, 1.5 eq) was added and after 15 minutes 2-(Bromomethyl)naphthalene (1.11 g, 5.03 mmol, 1.25 eq) was added. The reaction mixture was allowed to warm to room temperature. When TLC showed full conversion, the reaction mixture was quenched with 0.1 M HCl, diluted with EtOAc and washed with sat. aq. $NaHCO_3$ and brine. The organic phase is dried with $MgSO_4$ and concentrated under reduced pressure. The residue is purified over silica (10%→40% EtOAc in pentane) yielding the product as a white wax in quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 3H, CH_{arom}), 7.72 – 7.66 (m, 1H, CH_{arom}), 7.53 – 7.46 (m, 3H, CH_{arom}), 7.46 – 7.42 (m, 2H, CH_{arom}), 7.39 – 7.27 (m, 8H, CH_{arom}), 5.57 (s, 1H, C*H*Ph), 5.07 (d, *J* = 11.7 Hz, 1H, C*H*H Bn/Nap), 5.00 (d, *J* = 11.6 Hz, 1H, CH*H* Bn/Nap), 4.87 (d, *J* = 12.1 Hz, 1H, C*H*H Bn/Nap), 4.72 (d, *J* = 12.2 Hz, 1H, CH*H* Bn/Nap), 4.61 (d, *J* = 3.7 Hz, 1H, H-1), 4.27 (dd, *J* = 10.1, 4.7 Hz, 1H, H-6), 4.10 (t, *J* = 9.3 Hz, 1H, H-3), 3.84 (td, *J* = 9.9, 4.7 Hz, 1H, H-5), 3.71 (t, *J* = 10.2 Hz, 1H, H-6), 3.66 – 3.56 (m, 2H, H-2, H-4), 3.40 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 137.5, 136.3, 133.4, 133.1 (C_q), 129.1, 128.6, 128.4, 128.2, 128.1, 128.1, 128.1, 127.7, 126.8, 126.3, 126.2, 126.0, 125.8 (CH_{arom}), 101.5 (CHPh), 99.3 (C-1), 82.2 (C-4), 79.4 (C-2), 78.7 (C-3), 75.5, 73.9 (CH_2 Bn/Nap), 69.2 (C-6), 62.5 (C-5), 55.5 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{32}O_6NH_4$ 530.25371, found 530.25279.

Methyl 2,6-di-*O*-benzyl-3-*O*-(2-naphthyl)methyl-α-D-glucopyranoside (S3)



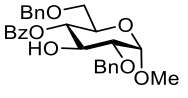
methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2-naphthyl)methyl-α-D-glucopyranoside (**S2**, 1.48 g, 2.89 mmol) and TES-H (2.15 mL, 28.9 mmol, 10 eq) were dissolved in DCM and cooled to 0 °C. After 15 min of stirring TFA (4.60 mL 28.9 mmol, 10 eq) was added dropwise. When TLC showed full conversion, the reaction was quenched with sat. aq. $NaHCO_3$. The organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified over silica (25% EtOAc in pentane) to obtain the title compound as colourless oil Yield: 1.25 g, 2.43 mmol, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 4H, CH_{arom}), 7.48 (ddd, *J* = 9.3, 6.1, 1.6 Hz, 3H, CH_{arom}), 7.39 – 7.25 (m, 10H, CH_{arom}), 5.15 (d, *J* = 11.7 Hz, 1H, C*H*H Bn/Nap), 4.91 (d, *J* = 11.7 Hz, 1H, CH*H* Bn/Nap), 4.78 (d, *J* = 12.1 Hz, 1H, C*H*H Bn/Nap), 4.68 (d, *J* = 12.1 Hz, 1H, CH*H* Bn/Nap), 4.65 (d, *J* = 3.6 Hz, 1H, H-1), 4.59 (d, *J* = 12.2 Hz, 1H, C*H*H Bn/Nap), 4.53 (d, *J* = 12.2 Hz, 1H, CH*H* Bn/Nap), 3.84 (dd, *J* = 9.6, 8.5 Hz, 1H, H-3), 3.73 – 3.62 (m, 4H, H-4, H-5, H-6, H-6), 3.57 (dd, *J* = 9.5, 3.6 Hz, 1H, H-2), 3.39 (s, 3H, CH_3 OMe), 2.37 (d, *J* = 2.3 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 138.1, 136.3, 133.5, 133.1 (C_q), 128.6, 128.5, 128.5, 128.3, 128.1, 127.8, 127.8, 127.8, 126.9, 126.3, 126.1, 126.0 (CH_{arom}), 98.3 (C-1), 81.5 (C-3), 79.7 (C-2), 75.6, 73.7, 73.3 (CH_2 Bn/Nap), 70.9, 70.0 (C-4, C-5), 69.6 (C-6), 55.4 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{34}O_6NH_4$ 532.26936, found 532.26839.

Methyl 4-*O*-benzoyl-2,6-di-*O*-benzyl-3-*O*-(2-naphthyl)methyl-α-D-glucopyranoside (S4)



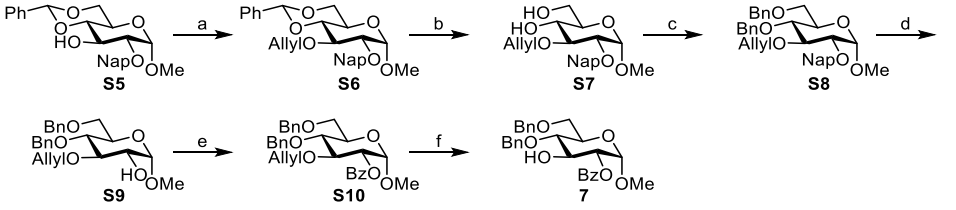
Methyl 2,6-di-*O*-benzyl-3-*O*-(2-naphthyl)methyl-α-D-glucopyranoside (**S3**, 1.20 g, 2.33 mmol) was dissolved in 5 mL pyridine, after which benzoyl chloride (0.406 mL, 3.50 mmol, 1.5 eq) was added. When TLC indicated full conversion, the reaction mixture was diluted with diethyl ether, washed with 1M aq. HCl, sat. aq. $NaHCO_3$ and brine. The organic phase was dried with sodium sulfate and concentrated under reduced pressure. The residue was purified with silica chromatography (15% EtOAc in pentane) to yield the title compound as colourless oil. Yield: 1.10 g, 1.78 mmol, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 2H, CH_{arom}), 7.66 – 7.62 (m, 1H, CH_{arom}), 7.60 – 7.57 (m, 2H, CH_{arom}), 7.50 (ddt, *J* = 8.7, 7.3, 1.3 Hz, 1H, CH_{arom}), 7.45 (d, *J* = 8.4 Hz, 1H, CH_{arom}), 7.41 – 7.28 (m, 9H, CH_{arom}), 7.24 – 7.12 (m, 6H, CH_{arom}), 5.33 (dd, *J* = 10.3, 9.2 Hz, 1H, H-4), 4.99 (d, *J* = 11.6 Hz, 1H, C*H*H Bn/Nap), 4.85 (d, *J* = 12.1 Hz, 1H, C*H*H Bn/Nap), 4.79 (d, *J* = 11.7 Hz, 1H, CH*H* Bn/Nap), 4.71 (d, *J* = 12.1 Hz, 1H, CH*H* Bn/Nap), 4.68 (d, *J* = 3.6 Hz, 1H, H-1), 4.46 (s, 2H, CH_2 Bn/Nap), 4.11 (t, *J* = 9.4 Hz, 1H, H-3), 3.96 (ddd, *J* = 10.2, 5.1, 2.7 Hz, 1H, H-5), 3.71 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2), 3.55 (dd, *J* = 10.8, 2.7 Hz, 1H, H-6), 3.49 (dd, *J* = 10.8, 5.1 Hz, 1H, H-6), 3.44 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4 (C=O), 138.1, 137.9, 135.8, 133.2 (C_q, 133.2 (CH_{arom}), 132.9, 129.8(C_q), 129.8, 128.6, 128.4, 128.3, 128.3, 128.1, 128.1, 128.0, 127.8, 127.7, 127.6, 126.9, 126.3, 125.9, 125.7 (CH_{arom}), 98.4 (C-1), 79.8 (C-2), 79.1 (C-3), 75.5 (CH_2 Bn/Nap), 73.7 (2xCH_2 Bn/Nap), 71.0 (C-4), 69.1 (C-6), 69.1 (C-5), 55.6 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{39}H_{38}O_7NH_4$ 636.29558, found 636.29453.

Methyl 4-*O*-benzoyl-2,6-di-*O*-benzyl-α-D-glucopyranoside (6)



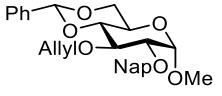
Methyl 4-*O*-benzoyl-2,6-di-*O*-benzyl-3-*O*-(2-naphthyl)methyl-α-D-glucopyranoside (**S4**, 1.05 g, 1.70 mmol) was dissolved in 20 mL 19:1 DCM/water, after which DDQ (770 mg, 3.39 mmol, 2 eq) was added. When TLC indicated full conversion, the organic phase was diluted with DCM, washed twice with sat. aq. $NaHCO_3$, dried with sodium sulfate and concentrated under reduced pressure. The residue was purified with silica chromatography (15%→25% EtOAc in pentane) to yield the title compound as a colourless oil. Yield: 731 mg, 1,53 mmol, 90%. $[\alpha]_D^{25}$ = 55.6° (c = 0.73, $CHCl_3$); IR (thin film): 698, 713, 1027, 1043, 1097, 1269, 1452, 1724; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H, CH_{arom}), 7.59 – 7.53 (m, 1H, CH_{arom}), 7.45 – 7.28 (m, 7H, CH_{arom}), 7.24 – 7.10 (m, 5H, CH_{arom}), 5.24 (dd, *J* = 10.2, 9.3 Hz, 1H, H-4), 4.77 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.70 (d, *J* = 12.2 Hz, 1H, CH*H* Bn), 4.67 (d, *J* = 3.5 Hz, 1H, H-1), 4.52 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.45 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.17 (td, *J* = 9.4, 2.8 Hz, 1H, H-3), 3.99 (ddd, *J* = 10.2, 4.6, 2.7 Hz, 1H, H-5), 3.61 – 3.50 (m, 3H, H-2, H-6, H-6), 3.40 (s, 3H, CH_3 OMe), 2.59 (d, *J* = 3.2 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (C=O), 138.0, 137.7 (C_q), 133.4, 130.0 (CH_{arom}), 129.7 (C_q), 128.7, 128.5, 128.3, 128.3, 128.2, 127.8, 127.6 (CH_{arom}), 97.9 (C-1), 79.5 (C-2), 73.7 , 73.5 (CH_2 Bn), 71.7, 71.7 (C-3, C-4), 68.7 (C-6), 68.6 (C-5), 55.6 (CH_3 OMe); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{30}O_7Na$ 501.18837, found 501.18733.

Preparation of acceptor **7**



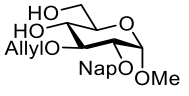
***Scheme S2**: preparation of acceptor **7**: reagents and conditions: a) AllylBr, NaH, DMF, 94%; b) pTsOH•H_2O, MeOH, 50 °C, quant.; c) BnBr, NaH, DMF, 95%; d) DDQ, DCM/H2O (9:1), 80%; e) BzCl, pyridine, 87%; f) $Pd(PPh_3)_4$, DMBA, MeOH, 40 °C, 90%.*

Methyl 3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-(2-naphtyl)methyl-α-D-glucopyranoside (S6)



Methyl 4,6-*O*-benzylidene-2-*O*-(2-naphtyl)methyl-α-D-glucopyranoside[46] (**S5**, 9.3 g, 22.0 mmol, 1 eq) was dissolved in 75 ml DMF and stirred at 0 °C until the sugar was fully dissolved. To the solution was added NaH (60 % dispersion in mineral oil, 0.48 g, 33 mmol, 1.5 eq) and the mixture was stirred for another 15 min before slowly adding AllylBr (2.9 ml, 33 mmol, 1.5 eq) and the reaction was stirred at RT until TLC indicated full conversion. The reaction mixture was quenched with H_2O and extracted with Et_2O. The organic layer was washed twice with H_2O. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (10% EtOAc in pentane) to provide the title compound as an oil. Yield: 9.58 g, 20.7 mmol, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.77 (m, 4H, CH_{arom}), 7.60 – 7.46 (m, 5H, CH_{arom}), 7.41 – 7.31 (m, 3H, CH_{arom}), 6.01 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H, CH_2-C*H*=CH_2), 5.52 (s, 1H, C*H*Ph), 5.34 (dq, *J* = 17.2, 1.7 Hz, 1H, CH_2-CH=C*H*H), 5.19 (dq, *J* = 10.4, 1.3 Hz, 1H, CH_2-CH=CH*H*), 5.02 (d, *J* = 12.0 Hz, 1H, C*H*H Nap), 4.87 (d, *J* = 12.4 Hz, 1H, CH*H* Nap), 4.57 (d, *J* = 3.7 Hz, 1H, H-1), 4.43 (ddt, *J* = 12.7, 5.8, 1.4 Hz, 1H, C*H*H-CH=CH_2), 4.34 (ddt, *J* = 12.6, 5.7, 1.4 Hz, 1H, CH*H*-CH=CH_2), 4.24 (dd, *J* = 10.1, 4.8 Hz, 1H, H-6), 3.96 (t, *J* = 9.2 Hz, 1H, H-3), 3.80 (td, *J* = 9.9, 4.7 Hz, 1H, H-5), 3.67 (t, *J* = 10.3 Hz, 1H, H-6), 3.57 – 3.50 (m, 2H, H-2, H-4), 3.40 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 135.8 (C_q), 135.4 (CH_2-*C*H=CH_2), 133.3, 133.2 (C_q), 129.0, 128.4, 128.4, 128.1, 127.9, 127.2, 126.3, 126.2 (CH_{arom}), 117.0 (CH_2-CH=*C*H_2), 101.4 (CHPh), 99.4 (C-1), 82.2 (C-4), 78.9 (C-2), 78.2 (C-3), 74.2 (*C*H_2-CH=CH_2), 74.1(CH_2 Nap), 69.2 (C-6), 62.4 (C-5), 55.5 (CH_3 OMe); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{30}O_6Na$ 485.19346, found 485.19269.

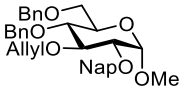
Methyl 3-*O*-allyl-2-*O*-(2-naphtyl)methyl-α-D-glucopyranoside (S7)



Methyl 3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-(2-naphtyl)methyl-α-D-glucopyranoside (**S6**, 9.57 g, 20.7 mmol, 1 eq) was dissolved in 100 ml MeOH and stirred at RT for 15 min. To the solution was added pTsOH·H_2O (0.39 g, 2.07 mmol, 0.1 eq) and the mixture was stirred for 1 h at 50 °C after which TLC indicated full conversion. The reaction mixture was set to cool down to RT and

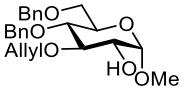
was quenched with TEA (2.3 ml, 6.18 mmol, 0.25 eq). Solvents were evaporated under reduced pressure and purification was performed on flash column chromatography (3/2 pentane/EtOAc) to provide the title compound as a solid. Yield: 7.8 g, 20.7 mmol, quant. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 4H, CH_{arom}), 7.53 – 7.43 (m, 3H, CH_{arom}), 5.99 (ddt, *J* = 17.3, 10.4, 5.8 Hz, 1H, CH_2-C*H*=CH_2), 5.31 (dq, *J* = 17.2, 1.6 Hz, 1H, CH_2-CH=C*H*H), 5.19 (dq, *J* = 10.4, 1.4 Hz, 1H, CH_2-CH=CH*H*), 4.89 (d, *J* = 12.3 Hz, 1H, C*H*H Nap), 4.78 (d, *J* = 12.3 Hz, 1H, CH*H* Nap), 4.57 (d, *J* = 3.5 Hz, 1H, H-1), 4.50 (ddt, *J* = 12.6, 5.5, 1.5 Hz, 1H, C*H*H-CH=CH_2), 4.28 (ddt, *J* = 12.6, 5.9, 1.3 Hz, 1H, CH*H*-CH=CH_2), 3.80 – 3.75 (m, 2H, H-6, H-6), 3.71 (dd, *J* = 9.5, 8.7 Hz, 1H, H-3), 3.60 (dt, *J* = 9.8, 3.7 Hz, 1H, H-5), 3.52 (ddd, *J* = 9.9, 8.7, 3.0 Hz, 1H, H-4), 3.47 (dd, *J* = 9.5, 3.5 Hz, 1H, H-2), 3.35 (s, 3H, CH_3 OMe), 3.07 (d, *J* = 3.2 Hz, 1H, 4-OH), 2.36 (t, *J* = 6.2 Hz, 1H, 6-OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5 (C_q), 135.2 (CH_2-*C*H=CH_2), 133.2, 133.1 (C_q), 128.3, 127.9, 127.7, 126.9, 126.3, 126.1, 125.9 (CH_{arom}), 117.2 (CH_2-CH=*C*H_2), 98.3 (C-1), 81.0 (C-3), 79.6 (C-2), 74.3 (*C*H_2-CH=CH_2), 73.3 (CH_2 Nap), 70.8 (C-5), 70.2 (C-4), 62.2 (C-6), 55.3 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{26}O_6NH_4$ 392.20676, found 392.20584.

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



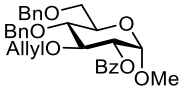
Methyl 3-*O*-allyl-2-*O*-(2-naphtyl)methyl-α-D-glucopyranoside (**S7**, 7.7 g, 20.56 mmol, 1 eq) was dissolved in 75 ml DMF and stirred at 0 °C until the sugar was fully dissolved. To the solution was added NaH (60% dispersion in mineral oil, 2.47 g, 61.69 mmol, 3 eq) and the reaction was stirred for 30 min at 0 °C after which BnBr (7.33 ml, 61.69 mmol, 3 eq) was slowly added. After 30 min the temperature was increased to RT. Once TLC indicated full conversion the reaction mixture was quenched with water and extracted twice with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc) to provide the title compound as an oil. Yield: 10.85 g, 19.55 mmol, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 4H, CH_{arom}), 7.55 – 7.42 (m, 3H, CH_{arom}), 7.35 – 7.23 (m, 8H, CH_{arom}), 7.21 – 7.15 (m, 2H, CH_{arom}), 6.03 (ddt, *J* = 17.3, 10.4, 5.6 Hz, 1H, CH_2-C*H*=CH_2), 5.33 (dq, *J* = 17.2, 1.7 Hz, 1H, CH_2-CH=C*H*H), 5.18 (dq, *J* = 10.4, 1.3 Hz, 1H, CH_2-CH=C*H*H), 4.94 (d, *J* = 12.3 Hz, 1H, C*H*H Bn), 4.84 (d, *J* = 8.2 Hz, 1H, C*H*H Nap), 4.81 (d, *J* = 9.9 Hz, 1H, CH*H* Bn), 4.62 – 4.56 (m, 2H, H-1, C*H*H Bn), 4.53 – 4.42 (m, 3H, CH*H* Bn, CH*H* Nap, C*H*H-CH=CH_2), 4.34 (ddt, *J* = 12.4, 5.7, 1.4 Hz, 1H, CH*H*-CH=CH_2), 3.86 (t, *J* = 9.3 Hz, 1H, H-3), 3.77 – 3.65 (m, 2H, H-5, H-6), 3.64 – 3.52 (m, 3H, H-2, H-4, H-6), 3.35 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 138.0, 135.8 (C_q), 135.4 (CH_2-*C*H=CH_2), 133.3, 133.2 (C_q), 128.4, 128.4, 128.3, 128.1, 128.0, 127.8, 127.8, 127.1, 126.2, 126.1, 126.1 (CH_{arom}), 116.7 (CH_2-CH=*C*H_2), 98.3 (C-1), 81.8 (C-3), 79.6 (C-2), 77.7 (C-4), 75.2 (CH_2 Nap), 74.5 (*C*H_2-CH=CH_2), 73.6, 73.6 (CH_2 Bn), 70.1 (C-5), 68.5 (C-6), 55.2 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{35}H_{38}O_6NH_4$ 572.30066, found 572.29941.

Methyl 3-*O*-allyl-4,6-di-*O*-benzyl-α-D-glucopyranoside (S9)



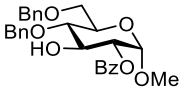
Methyl 3-*O*-allyl-4,6-di-*O*-benzyl-2-*O*-(2-naphtyl)methyl-α-D-glucopyranoside (**S8**, 2.77 g, 5.0 mmol, 1 eq) was dissolved in 40 ml 9/1 DCM/H_2O and stirred at RT until the sugar was fully dissolved. To the solution was added DDQ (2.27 g, 10.0 mmol, 2 eq) and the reaction was stirred for 60 min at RT after which TLC indicated full conversion. The reaction mixture was quenched with aq. Bicarb solution and extracted with DCM. The organic layer was washed twice with aq. Bicarb solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (7/3 pentane/EtOAc) to provide the title compound as an oil. Yield: 1.67 g, 4.01 mmol, 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 8H, CH_{arom}), 7.18 (dd, *J* = 7.6, 1.9 Hz, 2H, CH_{arom}), 5.98 (ddt, *J* = 17.3, 10.4, 5.7 Hz, 1H, CH_2-C*H*=CH_2), 5.30 (dq, *J* = 17.3, 1.7 Hz, 1H, CH_2-CH=C*H*H), 5.17 (dt, *J* = 10.3, 1.5 Hz, 1H, CH_2-CH=CH*H*), 4.83 – 4.78 (m, 2H, H-1, C*H*H Bn), 4.64 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.56 – 4.45 (m, 2H, 2x CH*H* Bn), 4.41 – 4.29 (m, 2H, C*H*$_2$-CH=CH_2,), 3.76 – 3.70 (m, 2H, H-5, H-6), 3.69 – 3.63 (m, 2H, H-2, H-6), 3.63 – 3.54 (m, 2H, H-3, H-4), 3.41 (s, 3H, CH_3 OMe), 2.14 (d, *J* = 7.7 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 138.0 (C_q), 135.3 (CH_2-*C*H=CH_2), 128.5, 128.0, 127.8, 127.8 (CH_{arom}), 117.1 (CH_2-CH=*C*H_2), 99.5 (C-1), 82.9 (C-3), 77.5 (C-4), 75.0 (CH_2 Bn), 74.3 (*C*H_2-CH=CH_2), 73.7 (CH_2 Bn), 72.8 (C-2), 70.2 (C-5), 68.6 (C-6), 55.3 (CH_3 OMe). Data is in agreement with literature.[47]

Methyl 3-*O*-allyl-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-glucopyranoside (S10)



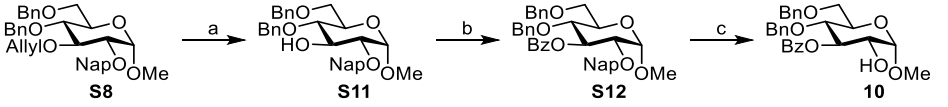
Methyl 3-*O*-allyl-4,6-di-*O*-benzyl-α-D-glucopyranoside (**S9**, 1.60 g, 3.86 mmol, 1 eq) was dissolved in 30 ml pyridine and stirred at 0 °C until the sugar was fully dissolved. To the solution was added BzCl (0.58 ml, 5.02 mmol, 1.3 eq) and the reaction was stirred for 30 min at 0 °C after which the temperature was increased to RT. Once TLC indicated full conversion the reaction mixture was diluted with DCM and washed twice with 1M HCl and with sat. aq. $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc) to provide the title compound as a light-yellow oil. Yield: 1.74 g, 3.36 mmol, 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 2H, CH_{arom}), 7.63 – 7.53 (m, 1H, CH_{arom}), 7.46 (dd, *J* = 8.4, 7.1 Hz, 2H, CH_{arom}), 7.40 – 7.18 (m, 10H, CH_{arom}) , 5.84 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H, CH_2-C*H*=CH_2), 5.18 (dq, *J* = 17.2, 1.6 Hz, 1H, CH_2-CH=C*H*H), 5.10 – 5.02 (m, 3H, H-1, H-2, CH_2-CH=CH*H*), 4.85 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.66 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.56 – 4.51 (m, 2H, 2x CH*H* Bn), 4.28 (dd, *J* = 5.8, 1.4 Hz, 2H, C*H*$_2$-CH=CH_2), 4.03 (t, *J* = 9.1 Hz, 1H, H-3), 3.85 – 3.79 (m, 1H, H-5), 3.79 – 3.68 (m, 3H, H-4, 2x H-6), 3.35 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0 (C=O), 138.3, 138.1, 134.9 (C_q), 133.3 (CH_2-*C*H=CH_2), 129.9, 128.5, 128.5, 128.1, 128.0, 127.9, 127.8 (CH_{arom}), 117.0 (CH_2-CH=*C*H_2), 97.3 (C-1), 79.9 (C-3), 77.9 (C-4), 75.2 (CH_2 Bn), 74.4 (*C*H_2-CH=CH_2), 74.2 (C-2), 73.6 (CH_2 Bn), 70.3 (C-5), 68.5 (C-6), 55.3 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{31}H_{34}O_7NH_4$ 536.26428, found 536.26337.

Methyl 2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-glucopyranoside (7)



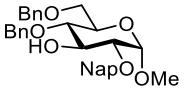
Methyl 2-*O*-benzoyl-*3*-*O*-allyl-4,6-di-*O*-benzyl-α-D-glucopyranoside (**S10**, 1.65 g, 3.18 mmol, 1 eq) and DMBA (1.00 g, 6.36 mmol, 2 eq) were dissolved in 20 ml MeOH and flushed for 30 min with N_2. To the solution was added $Pd(PPh_3)_4$ (0.18 g, 0.16 mmol, 0.05 eq) and the mixture was heated for 1h at 40 °C, after which TLC indicated full conversion. The mixture was diluted in EtOAc and washed with saturated Bicarb sol. The aqueous layer was extracted three times with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (8/2 pentane/EtOAc) to provide the title compound as a yellow oil. Yield: 1.27 g, 2.66 mmol, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 2H, CH_{arom}), 7.61 – 7.52 (m, 1H, CH_{arom}), 7.50 – 7.20 (m, 12H, CH_{arom}), 5.05 (d, *J* = 3.7 Hz, 1H, H-1), 4.98 (dd, *J* = 10.0, 3.7 Hz, 1H, H-2), 4.79 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.69 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.61 (d, *J* = 11.2 Hz, 1H, CH*H* Bn), 4.55 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.25 (ddd, *J* = 9.7, 8.5, 2.8 Hz, 1H, H-3), 3.87 – 3.76 (m, 2H, H-5, H-6), 3.77 – 3.69 (m, 1H, H-6), 3.68 (dd, *J* = 9.9, 8.8 Hz, 1H, H-4), 3.37 (s, 3H,CH_3 OMe), 2.30 (d, *J* = 3.5 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4 (C=O), 138.3, 138.0, 133.4 (C_q), 130.0, 129.7, 128.6, 128.5, 128.5, 128.0, 128.0, 128.0, 127.8 (CH_{arom}), 97.2 (C-1), 78.1 (C-4), 74.9 (CH_2 Bn), 74.1 (C-2), 73.7 (CH_2 Bn), 72.3 (C-3), 70.0 (C-5), 68.5 (C-6), 55.4 (CH_3 OMe). Data is in agreement with literature.[48]

Preparation of acceptor **10**



***Scheme S3**: preparation of acceptor **10**: reagents and conditions: a) $Pd(PPh_3)_4$, DMBA, MeOH, 40 °C, 83%; b) BzCl, pyridine, 86%; c) DDQ, DCM/H2O (9:1), 68%.*

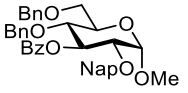
Methyl 4,6-di-*O*-benzyl-2-*O*-(2-naphtyl)methyl-α-D-glucopyranoside (S11)



Methyl 3-*O*-allyl-4,6-*O*-benzyl-2-*O*-(2-naphtyl)methyl-α-D-glucopyranoside (**S8**, 2.77 g, 5.0 mmol, 1 eq) and DMBA (1.57 g, 10.0 mmol, 2 eq) were dissolved in 20 ml MeOH and flushed for 30 min with N_2. To the solution was added $Pd(PPh_3)_4$ (0.29 g, 0.25 mmol, 0.05 eq) and the mixture was heated for 1h at 40 °C, after which TLC indicated full conversion. The mixture was diluted with EtOAc and washed with saturated Bicarb sol. The aqueous layer was extracted three times with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (8/2 pentane/EtOAc) to provide the title compound as a yellow oil. Yield: 2.12 g, 4.13 mmol, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.75 (m, 4H, CH_{arom}), 7.55 – 7.43 (m, 3H, CH_{arom}), 7.34 – 7.22 (m, 8H, CH_{arom}), 7.20 (dd, *J* = 7.8, 1.8 Hz, 2H, CH_{arom}), 4.87 (d, *J* = 12.3 Hz, 1H, C*H*H Bn/Nap), 4.86 – 4.76 (m, 2H, C*H*H Bn/Nap, CH*H* Bn/Nap), 4.64 (d, *J* = 3.5 Hz, 1H, H-1), 4.59 (d, *J* = 12.1 Hz, 1H, C*H*H Bn/Nap), 4.51 (d, *J* = 11.2 Hz, 1H, CH*H* Bn/Nap), 4.46 (d, *J* = 12.2 Hz, 1H, CH*H* Bn/Nap), 4.10 (td, *J* = 9.2, 2.1 Hz, 1H, H-3), 3.75 – 3.66 (m, 2H, H-5, H-6), 3.67 – 3.58 (m, 1H, H-6), 3.55 (dd, *J* = 10.2, 8.2 Hz, 1H, H-4), 3.45 (t, *J* = 9.6, 3.5 Hz, 1H, H-2), 3.32 (s, 3H, CH_3 OMe), 2.51 (d, *J* = 2.2 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 137.9,

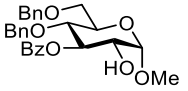
135.4, 133.2, 133.2 (C_q), 128.5, 128.4, 128.4, 128.0, 127.9, 127.8, 127.7, 127.1, 126.3, 126.2, 125.9 (CH_{arom}), 97.6 (C-1), 79.5 (C-2), 77.5 (C-4), 74.6 (CH_2 Bn/Nap), 73.7 (C-3), 73.5, 73.3 (CH_2 Bn/Nap), 69.7 (C-5), 68.5 (C-6), 55.3 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{34}O_6NH_4$ 532.26936, found 532.843.

Methyl 3-*O*-benzoyl-4,6-di-*O*-benzyl-2-*O*-(2-naphtyl)methyl-α-D-glucopyranoside (S12)



Methyl 4,6-di-*O*-benzyl-2-*O*-(2-naphtyl)methyl-α-D-glucopyranoside (**S11**, 2.00 g, 3.9 mmol, 1 eq) was dissolved in 30 ml pyridine and stirred at 0 °C until the sugar was fully dissolved. To the solution was added BzCl (0.59 ml, 5.10 mmol, 1.3 eq) and the reaction was stirred for 30 min at 0 °C after which the temperature was increased to RT. Once TLC indicated full conversion the reaction mixture was diluted with EtOAc and washed twice with 1M HCl and once with sat. aq. $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc) to provide the title compound as a light-yellow oil. Yield: 2.06 g, 3.35 mmol, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 2H, CH_{arom}), 7.76 – 7.70 (m, 1H, CH_{arom}), 7.67 – 7.60 (m, 2H, CH_{arom}), 7.60 – 7.52 (m, 2H, CH_{arom}), 7.46 – 7.35 (m, 4H, CH_{arom}), 7.35 – 7.25 (m, 6H, CH_{arom}), 7.14 – 7.08 (m, 3H, CH_{arom}), 7.01 – 6.96 (m, 2H, CH_{arom}), 5.83 (dd, *J* = 10.0, 8.8 Hz, 1H, H-3), 4.80 (d, *J* = 3.5 Hz, 1H), 4.75 (d, *J* = 12.7 Hz, 1H, C*H*H Bn/Nap), 4.68 (d, *J* = 12.4 Hz, 1H, CH*H* Bn/Nap), 4.63 (d, *J* = 12.1 Hz, 1H, C*H*H Bn/Nap), 4.51 – 4.43 (m, 2H, C*H*H Bn/Nap, CH*H* Bn/Nap), 4.35 (d, *J* = 10.7 Hz, 1H, CH*H* Bn/Nap), 3.89 – 3.73 (m, 3H, H-4, H-5, H-6), 3.70 – 3.62 (m, 2H, H-2, H-6), 3.41 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (C=O), 137.8, 137.6, 135.2, 133.1, 133.1 (C_q), 133.0 (CH_{arom}), 130.4 (C_q), 129.8, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 127.9, 127.9, 127.7, 126.9, 126.1, 126.0 (CH_{arom}), 97.9 (C-1), 77.1 (C-2), 76.1 (C-4), 74.5 (CH_2 Bn/Nap), 74.3 (C-3), 73.7, 72.8 (CH_2 Bn/Nap), 69.8 (C-5), 68.3 (C-6), 55.4 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{39}H_{38}O_7NH_4$ 636.29558, found 636.29410.

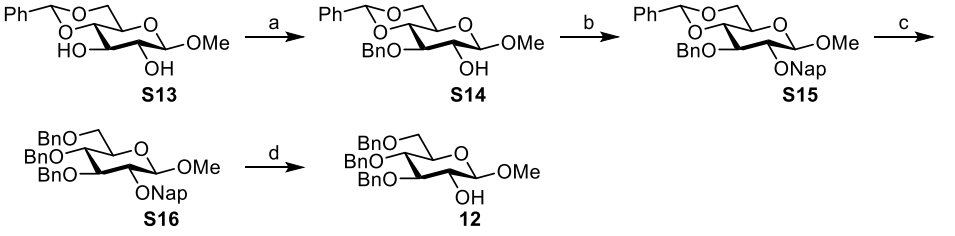
Methyl 3-O-benzoyl-4,6-di-O-benzyl-α-D-glucopyranoside (10)



Methyl 3-*O*-benzoyl-4,6-di-*O*-benzyl-2-*O*-(2-naphtyl)methyl-α-D-glucopyranoside (**S11**, 2.0 g, 3.23 mmol, 1 eq) was dissolved in 30 ml 9/1 DCM/H_2O and stirred at RT until the sugar was fully dissolved. To the solution was added DDQ (1.47 g, 6.46 mmol, 2 eq) and the reaction was stirred for 60 min at RT after which TLC indicated full conversion. The reaction mixture was quenched with aq. Bicarb solution and extracted with DCM. The organic layer was washed twice with aq. Bicarb solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (7/3 pentane/EtOAc) to provide the title compound as an oil. Yield: 0.901 g, 1.88 mmol, 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 2H, CH_{arom}), 7.62 – 7.52 (m, 1H, CH_{arom}), 7.48 – 7.27 (m, 8H, CH_{arom}), 7.14 (dd, *J* = 5.0, 2.0 Hz, 3H, CH_{arom}), 7.14 (dd, *J* = 5.0, 2.0 Hz, 3H, CH_{arom}), 7.05 – 6.97 (m, 2H, CH_{arom}), 5.55 (dd, *J* = 9.9, 7.4, Hz, 1H, H-3), 4.86 (d, *J* = 3.8 Hz, 1H, H-1), 4.68 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.57 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.53 (d, *J* = 12.1 Hz, 1H, CH*H* Bn),

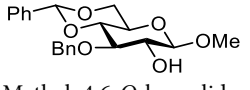
4.44 (d, *J* = 10.8 Hz, 1H, CH*H* Bn), 3.90 – 3.83 (m, 2H, H-4, H-5), 3.83 – 3.73 (m, 2H, H-2, H-6), 3.71 (dd, *J* = 10.4, 1.2 Hz, 1H, H-6), 3.45 (s, 3H, CH_3 OMe), 2.21 (d, *J* = 11.3 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9 (C=O), 137.9, 137.7(C_q), 133.2 (CH_{arom}), 130.1 (C_q), 129.9, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8 (CH_{arom}), 99.7 (C-1), 76.7 (C-3), 75.6 (C-4), 74.8, 73.8 (CH_2 Bn), 71.8 (C-2), 70.4 (C-5), 68.3 (C-6), 55.6 (CH_3 OMe). Data is in agreement with literature.[49]

preparation of acceptor **12**



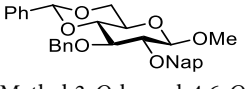
Scheme S4*: preparation of acceptor* ***12****: reagents and conditions: a) i: DBTO, toluene, reflux, ii: CsF, BnBr, DMF, 58% over 2 steps; b) NapBr, NaH, DMF, 96%; c) i: PTSA, MeOH, 60 °C, ii: BnBr, NaH, DMF, 91% over 2 steps; d) DDQ, DCM/H2O (9:1), 75%.*

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (S14)



Methyl 4,6-*O*-benzylidene-β-D-glucopyranoside[50] (**S13**, 1.60 g, 5.67 mmol) and di-n-butyltin oxide (1.83 g, 7.37 mmol, 1.3 eq) were refluxed in a Dean-Stark setup for 2 hr, after which the solvent was removed under reduced pressure. The residue was dissolved in DMF. Benzyl bromide (0.88 mL, 7.37 mmol, 1.3 eq) and CsF (1.12 g, 7.37 mmol) were added and the reaction mixture was stirred overnight, after which it was diluted with water and extracted twice with diethyl ether. Combined organic phases were dried and concentrated under reduced pressure. The residue was recrystallized from EA/pentane, yielding the title compound as white solid. Yield: 1.22 g, 3.28 mmol, 58%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H, CH_{arom}), 7.42 – 7.26 (m, 8H, CH_{arom}), 5.58 (s, 1H, C*H*Ph), 4.98 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.79 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.37 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6), 4.33 (d, *J* = 7.7 Hz, 1H, H-1), 3.81 (t, *J* = 10.3 Hz, 1H, H-6), 3.75 – 3.64 (m, 2H, H-3, H-4), 3.57 (s, 4H, H-2, CH_3 OMe), 3.50 – 3.42 (m, 1H, H-5), 2.49 (d, *J* = 2.2 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 137.3 (C_q), 129.2, 128.6, 128.4, 128.2, 128.0, 126.1 (CH_{arom}), 104.3 (C-1), 101.4 (CHPh), 81.6 (C-4), 80.3 (C-3), 74.8 (CH_2 Bn, 74.3 (C-2), 68.8 (C-6), 66.5 (C-5), 57.6 (CH_3 OMe). Spectra in agreement with literature.[51]

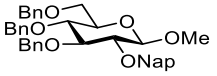
Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(2-naphtyl)methyl-β-D-glucopyranoside (S15)



Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**S14**, 1.20 g, 3.22 mmol) and NapBr (1.07 g, 4.83 mmol, 1.5 eq) were dissolved in DMF, after which NaH (60% dispersion in mineral oil, 193 mg, 4.83 mmol, 1.5 eq) was added. After completion of the reaction, water was added to quench the excess reagent. The formed precipitate was collected by filtration, washed with water

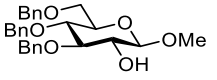
and with pentane and dried under vacuum, yielding the title compound as white solid. Yield: 1.59 g, 3.10 mmol, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dtd, *J* = 11.7, 6.3, 3.3 Hz, 4H, CH_{arom}), 7.52 (dtd, *J* = 10.9, 6.9, 6.3, 3.0 Hz, 5H, CH_{arom}), 7.46 – 7.35 (m, 5H, CH_{arom}), 7.33 – 7.26 (m, 4H, CH_{arom}), 5.62 (s, 1H, C*H*Ph), 5.08 (d, *J* = 11.2 Hz, 1H, C*H*H Bn/Nap), 5.01 – 4.93 (m, 2H, C*H*H Bn/Nap, CH*H* Bn/Nap), 4.86 (d, *J* = 11.4 Hz, 1H, CH*H* Bn/Nap), 4.51 (d, *J* = 7.7 Hz, 1H, H-1), 4.42 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6), 3.88 – 3.80 (m, 2H, H-4, H-6), 3.74 (t, *J* = 9.2 Hz, 1H, H-3), 3.55 (dd, *J* = 8.6, 7.7 Hz, 1H, H-2), 3.48 (td, *J* = 9.6, 5.0 Hz, 1H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 137.3, 135.9, 133.3, 133.0 (C_q), 129.0, 128.3, 128.3, 128.1, 128.1, 128.0, 127.7, 127.7, 126.8, 126.2, 126.0, 125.9 (CH_{arom}), 105.3 (C-1), 101.2 (CHPh), 82.2 (C-2), 81.6 (C-3), 80.8 (C-4), 75.3, 75.2 (CH_2 Bn, CH_2 Nap), 68.8 (C-6), 66.0 (C-5), 57.5 (CH_3 OMe). Spectra in agreement with literature.[52]

Methyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-naphtyl)methyl-β-D-glucopyranoside (S16)



Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(2-naphtyl)methyl-β-D-glucopyranoside (**S15**, 1.55 g, 3.02 mmol) was dissolved with PTSA-H_2O (58 mg, 0.30 mmol, 0.1 eq) and heated to 50 °C. After TLC indicates full conversion, the reaction mixture was quenched with triethylamine (0.06 mL, 0.45 mmol, 0.15 eq) and concentrated under reduced pressure. The residue was dissolved in DMF and treated with benzyl bromide (1.08 mL, 9.07 mmol, 3 eq) and sodium hydride (60% dispersion in mineral oil, 0.36 g, 9.07 mmol, 3 eq). After 1 hr, the reaction was quenched with water and extracted twice with diethyl ether. Combined organic phases were dried with $MgSO_4$ and concentrated. The residue was purified over silica (10% EtOAc in pentane) to obtain the title compound as colourless oil that slowly solidifies. Yield: 1.66 g, 2.74 mmol, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.79 (m, 4H, CH_{arom}), 7.57 – 7.48 (m, 3H, CH_{arom}), 7.44 – 7.38 (m, 4H, CH_{arom}), 7.38 – 7.30 (m, 10H, CH_{arom}), 7.25 – 7.20 (m, 2H, CH_{arom}), 5.15 (d, *J* = 11.2 Hz, 1H, C*H*H Bn/Nap), 5.02 (d, *J* = 11.0 Hz, 1H, C*H*H Bn/Nap), 4.94 (d, *J* = 11.2 Hz, 1H, CH*H* Bn/Nap), 4.91 – 4.85 (m, 2H, C*H*H Bn/Nap, CH*H* Bn/Nap), 4.70 (d, *J* = 12.2 Hz, 1H, C*H*H Bn/Nap), 4.65 – 4.57 (m, 2H, 2x CH*H* Bn/Nap), 4.42 (d, *J* = 7.8 Hz, 1H, H-1), 3.83 (dd, *J* = 10.7, 2.0 Hz, 1H, H-6), 3.79 – 3.75 (m, 1H, H-6), 3.75 – 3.65 (m, 5H, H-3, H-4, CH_3 OMe), 3.60 – 3.52 (m, 2H, H-2, H-5); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.3, 138.2, 136.1, 133.4, 133.1 (C_q), 128.5, 128.5, 128.2, 128.1, 128.1, 127.9, 127.9, 127.9, 127.8, 127.7, 127.7, 126.9, 126.4, 126.1, 125.9 (CH_{arom}), 104.9 (C-1), 84.8 (C-4), 82.4 (C-2), 78.0 (C-3), 75.8, 75.1 (CH_2 Bn/Nap), 75.0 (C-5), 74.9, 73.6 (CH_2 Bn/Nap), 69.0 (C-6), 57.3 (CH_3 Me); HRMS: $[M+NH_4]^+$ calcd for $C_{39}H_{40}O_6NH_4$ 622.31631, found 622.31478.

Methyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (12)

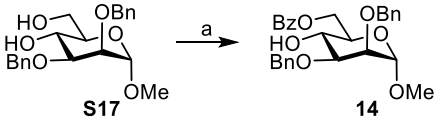


Methyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-naphtyl)methyl-β-D-glucopyranoside (**S16**, 1.63 g, 2.70 mmol) and DDQ (1.23 g, 5.40 mmol, 2 eq) were dissolved in 30 mL 9:1 DCM/H_2O and vigorously stirred. When TLC showed full conversion, the reaction mixture was diluted with DCM and washed twice with sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (20% EtOAc in pentane) to give the titel compound as white solid. Yield: 945 mg, 2.03 mmol, 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45

– 7.30 (m, 13H, CH_{arom}), 7.25 – 7.17 (m, 2H, CH_{arom}), 4.97 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.93 – 4.84 (m, 2H, C*H*H Bn, CH*H* Bn), 4.68 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.64 – 4.53 (m, 2H, CH*H* Bn), 4.23 (d, *J* = 7.3 Hz, 1H, H-1), 3.81 (dd, *J* = 10.8, 2.2 Hz, 1H, H-6), 3.76 (dd, *J* = 10.8, 4.5 Hz, 1H, H-6), 3.71 – 3.58 (m, 6H, H-2, H-3, H-4, CH_3 OMe), 3.54 (ddt, *J* = 9.4, 4.6, 2.4 Hz, 1H, H-5), 2.49 (d, *J* = 2.1 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 138.1, 138.1 (C_q), 128.5, 128.5, 128.4, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7 (CH_{arom}), 103.7 (C-1), 84.5 (C-4), 77.6 (C-3), 75.2 (CH_2 Bn), 75.2 (C-2), 75.1 (CH_2 Bn), 74.6 (C-5), 73.6 (CH_2 Bn), 68.8 (C-6), 57.2 (CH_3 OMe). Spectra in agreement with literature.[53]

Mannose acceptors

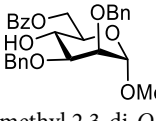
Preparation of acceptor **14**



S17 **14**

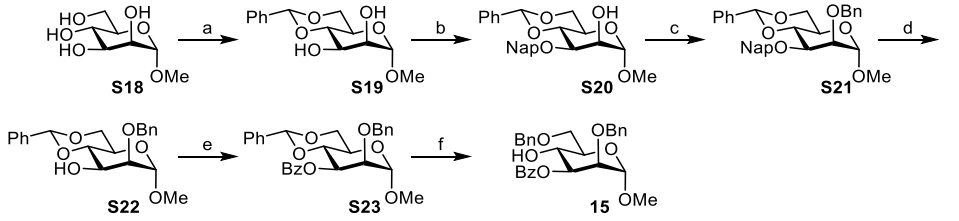
Scheme S5*: preparation of acceptor* ***14****: reagents and conditions a) BzCl, pyridine, DCM, 0 °C, 83%*

methyl 6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-mannopyranoside (14)



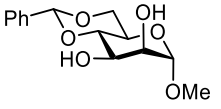
methyl 2,3-di-*O*-benzyl-α-D-mannopyranoside[54] (**S17,** 1.51 g, 4.03 mmol) and pyridine (1.63 mL, 20.2 mmol, 5 eq) were dissolved in 12 mL DCM and cooled to 0^{0}C, after which benzoyl chloride (0.492 mL, 4.23 mmol, 1.05 eq) was added dropwise as a 1.6 M solution in DCM. The reaction was allowed to warm to RT overnight and diluted with DCM, washed with 1M aq. HCl and sat. aq. $NaHCO_3$. The organic phase was sodium sulfate and concentrated under reduced pressure. The residue was purified with silica chromatography (20% EA in pentane) to yield the title compound (1.60 g, 3.34 mmol, 83%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 2H, CH_{arom}), 7.53 (ddt, *J* = 8.7, 7.0, 1.3 Hz, 1H, CH_{arom}), 7.40 – 7.25 (m, 12H, CH_{arom}), 4.82 (d, *J* = 1.7 Hz, 1H, H-1), 4.70 – 4.59 (m, 5H, H-6, H-6, C*H*H Bn, CH_2 Bn), 4.51 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 4.11 (t, *J* = 9.7 Hz, 1H, H-4), 3.86 (dt, *J* = 9.8, 3.6 Hz, 1H, H-5), 3.81 (dd, *J* = 3.1, 1.8 Hz, 1H, H-2), 3.75 (dd, *J* = 9.5, 3.1 Hz, 1H, H-3), 3.37 (s, 3H, CH_3 OMe), 2.61 (s, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8 (C=O), 138.2 (C_q), 138.1 (CH_{arom}), 133.1 (C_q), 130.1, 129.9, 128.6, 128.5, 128.4, 128.0, 127.9, 127.8, 127.8 (CH_{arom}), 99.1 (C-1), 79.6 (C-3), 74.1 (C-2), 72.7, 71.9 (CH_2 Bn), 70.8 (C-5), 66.6 (C-4), 64.2 (C-6), 55.0 (CH_3 OMe); Spectra in agreement with literature.[55]

Preparation of acceptor **15**



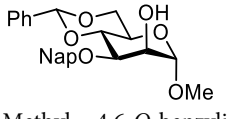
***Scheme S6**: preparation of acceptor **15**: reagents and conditions: a) $PhCH(OMe)_2$, $HBF_4 \bullet Et_2O$, DMF 96%; b) i) Bu_2SnO, toluene, reflux 3h; ii) NapBr, CsF, DMF, 79%; c) BnBr, NaH, DMF, 90%; d) DDQ, DCM/H2O (9:1), 80%; e) BzCl, pyridine 83%; f) TES-H, TFA, DCM, 0 °C, 92%.*

Methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (S19)



Methyl-α-D-mannopyranoside (**S18**, 3.88 g, 20.0 mmol, 1 eq) was dissolved in 20 ml DMF and stirred until the sugar was fully dissolved. To the solution was added benzaldehyde dimethyl acetal (3.22 ml, 21.4 mmol, 1.07 eq) and $HBF_4 \cdot Et_2O$ (32.74 ml, 20.0 mmol, 1 eq), the mixture was stirred for 4h at RT after which TLC indicated full conversion. The reaction mixture was quenched with TEA. Solvents were evaporated under reduced pressure and purification was performed on flash column chromatography (3/2pentane/EtOAc) to provide the title compound as a solid. Yield: 5.00 g, 17.8 mmol, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H, CH_{arom}), 7.40 – 7.35 (m, 3H, CH_{arom}), 5.56 (s, 1H, C*H*Ph), 4.73 (d, *J* = 1.4 Hz, 1H, H-1), 4.31 – 4.25 (m, 1H, H-6), 4.04 (dd, *J* = 9.4, 3.6 Hz, 1H, H-3), 4.00 (dd, *J* = 3.5, 1.5 Hz, 1H, H-2), 3.91 (t, *J* = 9.2 Hz, 1H, H-4), 3.84 – 3.77 (m, 2H, H-5, H-6), 3.39 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3 (C_q), 129.4, 128.6, 128.5, 128.5, 126.7, 126.4, 126.2 (CH_{arom}), 102.4 (CHPh), 101.4 (C-1), 79.0 (C-4), 70.9 (C-2), 68.9 (C-6), 68.8 (C-3), 63.0 (C-5), 55.2 (OMe). Data in agreement with literature.[56]

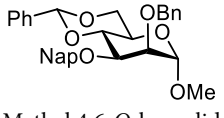
Methyl 4,6-*O*-benzylidene-3-*O*-(2-naphtyl)methyl-α-D-mannopyranoside (S20)



Methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**S19**, 5.44 g, 19.3 mmol) and di-n-butyltin(IV) oxide (6.24 g, 25.06 mmol, 1.3 eq) were dissolved in 100 ml toluene and refluxed for 3 hours, after which solvents where evaporated under reduced pressure. To the crude mixture was added NapBr (5.54 g, 25.06 mmol, 1.3 eq) and CsF (3.81 g, 25.06 mmol, 1.3 eq) and dissolved in 100 ml DMF. The reaction was stirred overnight at RT. The reaction mixture was diluted in Et_2O and washed twice with H_2O. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (3/1 pentane/EtOAc) to provide the title compound as a light-yellow oil. Yield: 6.47 g, 15.2 mmol, 79%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 3H, CH_{arom}), 7.75 – 7.70 (m, 1H, CH_{arom}), 7.55 – 7.44 (m, 5H, CH_{arom}), 7.42 – 7.35 (m, 3H, CH_{arom}), 5.63 (s, 1H, C*H*Ph),

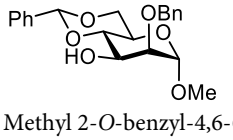
4.98 (d, *J* = 12.1 Hz, 1H, C*H*H Nap), 4.88 (d, *J* = 12.2 Hz, 1H, CH*H* Nap), 4.75 (d, *J* = 1.5 Hz, 1H, H-1), 4.28 (dd, *J* = 9.7, 4.3 Hz, 1H, H-6), 4.13 (t, *J* = 9.3 Hz, 1H, H-4), 4.07 (dt, *J* = 3.3, 1.6 Hz, 1H, H-2), 3.94 (dd, *J* = 9.6, 3.4 Hz, 1H, H-3), 3.90 – 3.84 (m, 1H, H-6), 3.81 (ddd, *J* = 10.3, 9.0, 4.2 Hz, 1H, H-5), 3.35 (s, 3H, CH_3 OMe), 2.78 (d, *J* = 1.6 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 135.4, 133.2, 133.1 (C_q), 129.0, 128.3, 128.3, 128.0, 127.7, 126.6, 126.2, 126.2, 126.0, 125.8 (CH_{arom}), 101.7 (CHPh), 101.2 (C-1), 78.9 (C-4), 75.6 (C-3), 72.9 (CH_2 Nap), 69.9 (C-2), 68.9 (C-6), 63.3 (C-5), 54.9 (CH_3 OMe). Data in agreement with literature.[57]

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



Methyl 4,6-*O*-benzylidene-3-*O*-(2-naphtyl)methyl-α-D-mannopyranoside (**S20**, 5.09 g, 15.2 mmol) was dissolved in 75 ml DMF and stirred at 0 °C until the sugar was fully dissolved. To the solution was added NaH (60% dispersion in mineral oil, 0.92 g, 23.0 mmol, 1.5 eq) and the reaction was stirred for 30 min at 0 °C after which BnBr (2.73 ml, 23.0 mmol, 1.5 eq) was slowly added. After 30 min the temperature was increased to RT. Once TLC indicated full conversion, the reaction mixture was quenched with water and extracted twice with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (8/2 pentane/EtOAc) to provide the title compound as an oil. Yield: 5.55 g, 13.77 mmol, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 3H, CH_{arom}), 7.74 – 7.64 (m, 1H), 7.59 – 7.27 (m, 14H, CH_{arom}), 5.67 (s, 1H, C*H*Ph), 4.93 (d, *J* = 12.3 Hz, 1H, C*H*H Bn/Nap), 4.87 – 4.75 (m, 3H, CH*H* Bn/Nap, CH_2 Bn/Nap), 4.70 (d, *J* = 1.7 Hz, 1H, H-1), 4.31 – 4.24 (m, 2H, H-4, H-6), 3.99 (dd, *J* = 10.0, 3.3 Hz, 1H, H-3), 3.90 (t, *J* = 10.3 Hz, 1H, H-6), 3.86 (dd, *J* = 3.3, 1.7 Hz, 1H, H-2), 3.77 (ddd, *J* = 10.4, 9.1, 4.7 Hz, 1H, H-5), 3.30 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 137.8, 136.2, 133.4, 133.0 (C_q), 129.0, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 126.2, 126.2, 126.1, 125.8, 125.7 (CH_{arom}), 101.7 (CHPh), 100.5 (C-1), 79.2 (C-4), 76.3 (C-3), 76.2 (C-2), 73.7, 72.9 (CH_2 Bn, CH_2 Nap), 69.0 (C-6), 64.1 (C-5), 54.9 (CH_3 OMe).

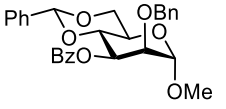
Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (S22)



Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2-naphtyl)methyl-α-D-mannopyranoside. (**S21**, 1.72 g, 3.36 mmol) was dissolved in 25 ml 9/1 DCM/H_2O and stirred at RT until the sugar was fully dissolved. To the solution was added DDQ (1.52 g, 6.71 mmol, 2 eq) and the reaction was stirred for 60 min at RT after which TLC indicated full conversion. The reaction mixture was quenched with sat. aq. Bicarb solution and extracted with DCM. The organic layer was washed twice with sat. aq. Bicarb solution, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (8/2 pentane/EtOAc) to provide the title compound as an oil. Yield: 1.00 g, 2.69 mmol, 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 2H, CH_{arom}), 7.41 – 7.28 (m, 8H, CH_{arom}), 5.56 (s, 1H, C*H*Ph), 4.77 – 4.72 (m, 2H, H-1, C*H*H Bn), 4.68 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 4.26 (dd, *J* = 9.3, 3.9 Hz, 1H, H-6), 4.07 (ddd, *J* =

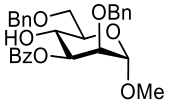
9.9, 7.9, 3.7 Hz, 1H, H-5), 3.90 (t, *J* = 9.4 Hz, 1H, H-4), 3.86 – 3.82 (m, 2H, H-2, H-6), 3.81 – 3.72 (m, 1H, H-3), 3.36 (s, 3H, CH_3 OMe), 2.39 (d, *J* = 8.0 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 137.4 (C_q), 129.2, 128.7, 128.3, 128.2, 128.0, 126.4 (CH_{arom}), 102.2 (CHPh), 99.5 (C-1), 79.6 (C-4), 78.5 (C-2), 73.8 (CH_2 Bn), 68.9 (C-6), 68.8 (C-5), 63.4 (C-3), 55.1 (CH_3 OMe). Data in agreement with literature[58]

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



Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**S22**, 0.95 g, 2.55 mmol) was dissolved in 10 ml pyridine and stirred at 0 °C until the sugar was fully dissolved. To the solution was added BzCl (0.39 ml, 3.32 mmol, 1.3 eq) and the reaction was stirred at RT until TLC indicated full conversion. The reaction mixture was diluted in DCM and washed twice with aq. 1M HCl and twice with aq. Bicarb solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (8/2 pentane/EtOAc) to provide the title compound as an oil. Yield: 1.28 g, 2.54 mmol, 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H, CH_{arom}), 7.60 – 7.52 (m, 1H, CH_{arom}), 7.47 – 7.40 (m, 4H, CH_{arom}), 7.23 – 7.17 (m, 3H, CH_{arom}) 7.35 – 7.26 (m, 5H, CH_{arom}), 5.62 (s, 1H, C*H*Ph), 5.55 (dd, *J* = 10.4, 3.4 Hz, 1H, H-3), 4.77 (d, *J* = 1.6 Hz, 1H, H-1), 4.64 (s, 2H, CH_2 Bn), 4.35 (dd, *J* = 10.6, 9.1 Hz, 1H, H-4), 4.32 – 4.28 (m, 1H, H-6), 4.09 (dd, *J* = 3.5, 1.6 Hz, 1H, H-2), 4.00 – 3.89 (m, 2H, H-5, H-6), 3.40 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (C=O), 137.6, 137.4 (C_q), 133.2 (CH_{arom}), 130.1 (C_q), 129.9, 129.0, 128.5, 128.5, 128.3, 128.0, 126.3 (CH_{arom}), 101.8 (CHPh), 100.2 (C-1), 76.5 (C-2, C-4), 73.9 (CH_2 Bn), 71.3 (C-3), 69.0 (C-6), 64.1 (C-5), 55.2 (CH_3 OMe). Data in agreement with literature.[59]

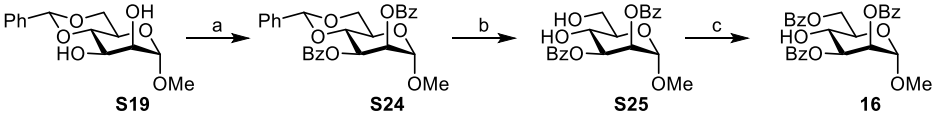
Methyl 3-*O*-benzoyl-2,6-di-*O*-benzyl-α-D-mannopyranoside (15)



Methyl 3-*O*-benzoyl-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**S23**, 0.54 g, 1.13 mmol) was dissolved in 20 ml anhydrous DCM and stirred at 0 °C until the sugar was fully dissolved. To the solution was added TES-H (1.8 ml, 11.3 mmol, 10 eq) and the mixture was stirred for another 15 min before slowly adding TFA (0.84 ml, 11.3 mmol, 10 eq) and the reaction was stirred at 0 °C until TLC indicated full conversion. The reaction mixture was quenched with aq. Bicarb solution and extracted with DCM. The organic layer was washed twice with aq. Bicarb solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (8/2 pentane/EtOAc) to provide the title compound as an oil. Yield: 0.49 g, 1.03 mmol, 92 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H, CH_{arom}), 7.61 – 7.55 (m, 1H, CH_{arom}), 7.47 – 7.41 (m, 2H, CH_{arom}), 7.38 – 7.32 (m, 4H, CH_{arom}), 7.32 – 7.26 (m, 3H, CH_{arom}), 7.20 (tt, *J* = 3.9, 2.4 Hz, 3H, CH_{arom}), 5.36 (dd, *J* = 9.9, 3.3 Hz, 1H, H-3), 4.79 (d, *J* = 1.7 Hz, 1H, H-1), 4.70 – 4.64 (m, 3H, C*H*H Bn, CH_2 Bn), 4.60 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.26 (t, *J* = 9.0 Hz, 1H, H-4), 3.94 (dd, *J* = 3.3, 1.8 Hz, 1H, H-2), 3.90 – 3.74 (m, 3H, H-5, 2x H-6), 3.40 (s, 3H, CH_3 OMe), 2.67 (s, 1H, OH); ^{13}C NMR (101 MHz,

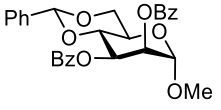
$CDCl_3$) δ 166.7 (C=O), 138.1, 137.9 (C_q), 133.3 , 130.0 (CH_{arom}), 129.9 (C_q), 128.5, 128.4, 127.8 (CH_{arom}), 99.2 (C-1), 75.9 (C-2), 74.8 (C-3), 73.8, 73.3 (CH_2 Bn), 71.3 (C-5), 70.7 (C-6), 67.8 (C-4), 55.1 (CH_3 OMe). Data in agreement with literature[60]

Preparation of acceptor **16**



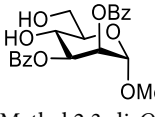
***Scheme S7**: preparation of acceptor **16**: reagents and conditions: a) BzCl, pyridine, 95%; b) pTsOH•H_2O, MeOH, 50 °C, 62%; c) BzCl, pyridine, DCM, 0 °C, 38%.*

Methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranoside (S24)



Methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**S19**, 1.04 g, 3.68 mmol) was dissolved in 20 ml pyridine and stirred at 0 °C until the sugar was fully dissolved. To the solution was added BzCl (1.28 ml, 11.04 mmol, 3.0 eq) and the reaction was stirred for 30 min at 0 °C after which the temperature was increased to RT. Once TLC indicated full conversion the reaction mixture was diluted with EtOAc and washed twice with sat. aq. $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc) to provide the title compound as a light-yellow oil. Yield: 1.73 g, 3.51 mmol, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 2H, CH_{arom}), 7.94 – 7.88 (m, 2H, CH_{arom}), 7.61 – 7.55 (m, 1H, CH_{arom}), 7.50 – 7.40 (m, 5H, CH_{arom}), 7.32 – 7.24 (m, 5H, CH_{arom}), 5.83 (dd, *J* = 10.3, 3.6 Hz, 1H, H-3), 5.72 (dd, *J* = 3.6, 1.6 Hz, 1H, H-2), 5.67 (s, 1H, C*H*Ph), 4.88 (d, *J* = 1.6 Hz, 1H, H-1), 4.42 – 4.32 (m, 2H, H-4, H-6), 4.10 (td, *J* = 9.8, 4.7 Hz, 1H, H-5), 3.96 (t, *J* = 10.3 Hz, 1H, H-6), 3.42 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4 (C=O), 137.1 (C_q), 133.5, 133.0, 129.8, 129.7 (CH_{arom}), 129.7, 129.4, 129.0, 128.6, 128.5, 128.4, 128.4, 128.4, 128.2, 128.2, 126.2, 126.2 (CH_{arom}), 101.9 (CH Ph), 99.6 (C-1), 76.8 (C-4), 70.9 (C-2), 69.0 (C-3), 68.8 (C-6), 63.8 (C-5), 55.3 (CH_3 OMe). Data in agreement with literature.[61]

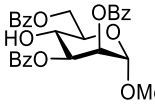
Methyl 2,3-di-*O*-benzoyl-α-D-mannopyranoside (S25)



Methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**S24**, 1.65 g, 3.36 mmol, 1 eq) was dissolved in 25 ml MeOH and stirred at RT for 15 min. To the solution was added pTsOH·H_2O (64.0 mg, 0.34 mmol, 0.1 eq) and the mixture was stirred for 1h at 50 °C after which TLC indicated full conversion. The reaction mixture was set to cool down to RT and was quenched with TEA (0.25 ml, 0.8 mmol, 0.25 eq). Solvents were evaporated under reduced pressure and purification was performed on flash column chromatography (3/2 pentane/EtOAc) to provide the title compound as a solid. Yield: 0.842 g, 2.10 mmol, 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.4, 1.4 Hz, 2H, CH_{arom}), 7.91 (dd, *J* = 8.4, 1.4 Hz, 2H, CH_{arom}), 7.65 – 7.58

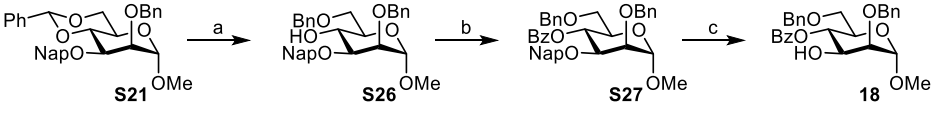
(m, 1H, CH_{arom}), 7.55 – 7.45 (m, 3H, CH_{arom}) 7.38 – 7.31 (m, 2H, CH_{arom}), 5.64 – 5.49 (m, 2H, H-2, H-3), 4.90 (d, *J* = 1.4 Hz, 1H, H-1), 4.33 (t, *J* = 9.4 Hz, 1H, H-4), 3.98 (dd, *J* = 3.8, 1.1 Hz, 2H, 2x H-6), 3.85 (dt, *J* = 9.7, 3.7 Hz, 1H, H-5), 3.47 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 165.6 (C=O), 133.7, 133.6, 129.9, 129.9 (CH_{arom}), 129.5, 129.3 (C_q), 128.7, 128.5 (CH_{arom}), 98.8 (C-1), 73.2 (C-3), 72.4 (C-5), 70.67 (C-2), 67.0 (C-4), 62.4 (C-6), 55.4 (CH_3 OMe). Data in agreement with literature.[62]

Methyl 2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside (16)



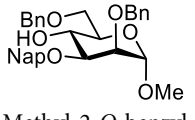
Methyl 2,3-di-*O*-benzoyl-α-D-mannopyranoside (**S25**, 800 mg, 1.99 mmol) and pyridine (0.80 mL, 9.94 mmol, 5 eq) were dissolved in 7 mL DCM and cooled to 0 °C. Benzoyl chloride (0.24 mL, 2.09 mmol, 1.05 eq) was added over 15 minutes, after which the reaction mixture was allowed to warm to RT. After 16 hr stirring, the reaction mixture was diluted with dichloromethane and washed twice with 1M HCl and 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 (5% EtOAc in pentane), yielding the title compound as colourless oil. Yield: 0.38 g, 0.76 mmol, 38 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.4, 1.3 Hz, 2H, CH_{arom}), 7.98 (dd, *J* = 8.3, 1.3 Hz, 2H, CH_{arom}), 7.92 (dd, *J* = 8.4, 1.3 Hz, 2H, CH_{arom}), 7.65 – 7.60 (m, 1H, CH_{arom}), 7.59 – 7.54 (m, 1H, CH_{arom}), 7.53 – 7.49 (m, 1H, CH_{arom}), 7.48 – 7.44 (m, 2H, CH_{arom}), 7.39 – 7.30 (m, 4H, CH_{arom}), 5.70 – 5.58 (m, 2H, H-2, H-3), 4.93 (s, 1H, H-1), 4.91 (dd, *J* = 12.2, 4.0 Hz, 1H, H-6), 4.65 (dd, *J* = 12.0, 2.2 Hz, 1H, H-6), 4.28 (dd, *J* = 10.7, 8.5 Hz, 1H, H-4), 4.10 (ddd, *J* = 9.9, 3.9, 2.2 Hz, 1H, H-5), 3.50 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 166.9, 165.5 (C=O), 133.5, 133.5, 133.4, 130.0, 129.9, 129.9 (CH_{arom}), 129.6, 129.4 (C_q), 128.7, 128.6, 128.5 (CH_{arom}), 98.8 (C-1), 72.8 (C-2), 71.3 (C-5), 70.6 (C-3), 66.5 (C-4), 63.5 (C-6), 55.5 (CH_3 OMe). Data in agreement with literature.[63]

Preparation of acceptor **18**



***Scheme S8**: preparation of acceptor **18**: reagents and conditions: a) TES-H TFA, DCM, 0 °C, 92%; b) BzCl, pyridine, 55%; c) DDQ, DCM/H_2O 9:1, 77%*

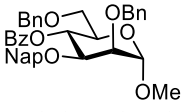
Methyl 2,6-di-*O*-benzyl-3-*O*-(2-naphtyl)methyl-α-D-mannopyranoside (S26)



Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2-naphtyl)methyl-α-D-mannopyranoside (**S21**, 3.33 g, 6.50 mmol) was dissolved in 40 ml anhydrous DCM and stirred at 0 °C until the sugar was fully dissolved. To the solution was added TES-H (10.38 ml, 65 mmol, 10 eq) and the mixture was stirred for another 15 min before slowly adding TFA (4.84 ml, 65 mmol, 10 eq). The reaction was

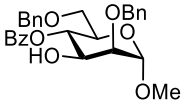
kept at 0 °C until TLC indicated full conversion. The reaction mixture was quenched with sat. aq. $NaHCO_3$ and extracted with DCM. The organic layer was washed twice with sat. aq. $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (7/3 pentane/EtOAc) to provide the title compound as an oil. Yield: 2.42 g, 4.70z mmol, 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.75 (m, 4H, CH_{arom}), 7.51 – 7.42 (m, 3H, CH_{arom}), 7.38 – 7.25 (m, 12H, CH_{arom}), 4.79 (d, *J* = 1.7 Hz, 1H, H-1), 4.75 – 4.69 (m, 2H, 2x CH*H* Bn/Nap), 4.67 – 4.61 (m, 3H, C*H*H Bn/Nap, 2x CH*H* Bn/Nap), 4.59 (d, *J* = 12.1 Hz, 1H, CH*H* Bn/Nap), 4.15 – 4.04 (m, 1H, H-4), 3.83 – 3.76 (m, 3H, H-2, 2x H-6) 3.76 – 3.70 (m, 2H, H-3, H-5), 3.34 (s, 3H,CH_3 OMe), 2.63 – 2.58 (m, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 138.2, 135.8, 133.3, 133.0 (C_q), 128.4, 128.4, 128.3, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 126.5, 126.3, 126.0, 125.8 (CH_{arom}), 99.2 (C-1), 79.7 (C-3), 73.9 (C-2), 73.6, 72.7, 71.9 (CH_2 Bn, CH_2 Nap), 71.4 (C-5), 70.5 (C-6), 68.0 (C-4), 54.9 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{34}O_6NH_4$ 532.26936, found 532.26887.

Methyl 4-*O*-benzoyl-2,6-di-*O*-benzyl-3-*O*-(2-naphtyl)methyl-α-D-mannopyranoside (S27)



Methyl 2,6-di-*O*-benzyl-3-*O*-(2-naphtyl)methyl-α-D-mannopyranoside (**S27**, 2.30 g, 4.47 mmol) was dissolved in 25 ml pyridine and stirred at 0 °C until the sugar was fully dissolved. To the solution was added BzCl (0.70 ml, 5.81 mmol, 1.3 eq) and the reaction was stirred for 30 min at 0 °C after which the temperature was increased to RT. Once TLC indicated full conversion the reaction mixture was diluted with EtOAc and washed twice with 1M HCl and with sat. aq. $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc) to provide the title compound as a light-yellow oil. Yield: 1.53 g, 2.46 mmol, 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H, CH_{arom}), 7.77 – 7.71 (m, 1H, CH_{arom}), 7.56 (dd, *J* = 16.2, 7.5 Hz, 4H, CH_{arom}), 7.47 – 7.34 (m, 6H, CH_{arom}), 7.34 – 7.27 (m, 3H, CH_{arom}), 7.26 – 7.14 (m, 7H, CH_{arom}), 5.66 (t, *J* = 9.8 Hz, 1H, H-4), 4.86 – 4.80 (m, 2H, H-1, C*H*H Bn/Nap), 4.76 (d, *J* = 12.5 Hz, 1H, CH*H* Bn/Nap), 4.71 (d, *J* = 12.5 Hz, 1H, C*H*H Bn/Nap), 4.55 (d, *J* = 12.5 Hz, 1H, CH*H* Bn/Nap), 4.51 (d, *J* = 2.7 Hz, 2H, CH_2 Bn/Nap), 4.01 – 3.91 (m, 2H, H-3, H-6), 3.88 (dd, *J* = 3.3, 1.8 Hz, 1H, H-2), 3.68 (dd, *J* = 10.8, 6.2 Hz, 1H, H-6), 3.62 (dd, *J* = 10.8, 2.9 Hz, 1H, H-5), 3.37 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7 (C=O), 138.3, 138.2, 135.6, 133.2 (C_q), 133.1 (CH_{arom}), 133.0, 130.1 (C_q), 129.9, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.7, 127.4, 126.5, 126.1, 125.9, 125.9 (CH_{arom}), 99.5 (C-1), 76.8 (C-3), 74.0 (C-2), 73.6, 73.0, 71.8 (CH_2 Bn, CH_2 Nap), 70.7 (C-5), 70.1 (C-6), 69.5 (C-4), 55.1 (OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{39}H_{38}O_7NH_4$ 636.29461, found 636.29461.

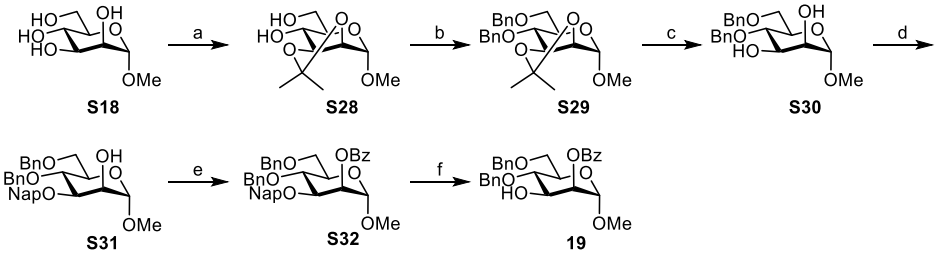
Methyl 4-*O*-benzoyl-2,6-di-*O*-benzyl-α-D-mannopyranoside (18)



Methyl 4-*O*-benzoyl-2,6-di-*O*-benzyl-3-*O*-(2-naphtyl)methyl-α-D-mannopyranoside (**S27**, 1.45 g, 2.34 mmol) was dissolved in 20 ml 9/1 DCM/H_2O and stirred at RT until the sugar was fully

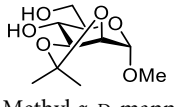
dissolved. To the solution was added DDQ (1.06 g, 4.69 mmol, 2 eq) and the reaction was stirred for 60 min at RT after which TLC indicated full conversion. The reaction mixture was diluted with DCM and washed twice with sat. aq. $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc) to provide the title compound as an oil. Yield: 0.86 g, 1.80 mmol, 77%. $[\alpha]_D^{25}$ = +22.9° (*c = 0.6*, $CHCl_3$); IR (thin film): 416, 699, 716, 750, 1037, 1060, 1106, 1270, 1731, 2350; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H, CH_{arom}), 7.59 – 7.49 (m, 1H, CH_{arom}), 7.46 – 7.29 (m, 7H, CH_{arom}), 7.24 – 7.10 (m, 5H, CH_{arom}), 5.38 (t, *J* = 9.9 Hz, 1H, H-4), 4.87 (d, *J* = 1.5 Hz, 1H, H-1), 4.77 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.61 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.57 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.50 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.07-3.95 (m, 2H, H-3, H-5), 3.79 (dd, *J* = 3.7, 1.6 Hz, 1H, H-2), 3.70 – 3.58 (m, 2H, 2x H-6), 3.41 (s, 3H, CH_3 OMe), 2.45 (d, *J* = 10.6 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6 (C=O), 138.0, 137.6 (C_q), 133.2, 129.9 (CH_{arom}), 129.8 (C_q), 128.6, 128.4, 128.3, 128.1, 128.0, 127.6, 127.54 (CH_{arom}), 98.2 (C-1), 78.2 (C-2), 73.6, 73.2 (CH_2 Bn), 71.0 (C-4), 70.1, 69.8 (C-3, C-5), 69.4 (C-6), 55.2(CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{28}H_{30}O_7NH_4$ 496.23298, found 496.23176.

Preparation of acceptor **19**



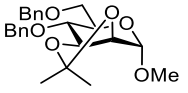
***Scheme S9**: preparation of acceptor **19**: reagents and conditions: a) 2,2-dimethoxypropane, PTSA, acetone, water, 54%; b) BnBr, NaH, DMF, 64%; c) TFA, H_2O, $CHCl_3$, quant; d) i: Bu_2SnO, toluene reflux, ii: NapBr, CsF, DMF, 74%; e) BzCl, pyridine, 94%; f) DDQ, DCM/H_2O (9:1), 74%*

Methyl 2,3-*O*-isopropylidene-α-D-mannopyranoside (S28)



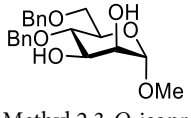
Methyl α-D-mannopyranoside (**S18**, 3.88 g, 20.0 mmol), 2,2-dimethoxypropane (36.8 ml, 300 mmol, 15 eq) and pTsOH·H_2O (0.38 g, 2 mmol, 0.1 eq) were dissolved in 40 ml Acetone and stirred at RT for 15 min. To the solution was added 80 ml H_2O and the mixture was stirred for 4h at RT. The reaction mixture was quenched with aq. Bicarb sol. Solvents were evaporated under reduced pressure and purification was performed on flash column chromatography (1/1 pentane/EtOAc) to provide the title compound as a solid. Yield: 2.48 g, 10.59 mmol, 53 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 (s, 1H, H-1), 4.21-4.09 (m, 2H, H-2, H-3), 3.86 (t, *J* = 3.2 Hz, 2H, 2x H-6), 3.74 (dd, *J* = 9.6, 5.9 Hz, 1H, H-4), 3.60 (dt, *J* = 9.5, 4.0 Hz, 1H, H-5), 3.39 (s, 3H, CH_3 OMe), 3.19 (s, 1H, 4-OH), 2.43 (s, 1H, 6-OH), 1.53 (s, 3H, CH_3 isopropylidene), 1.35 (s, 3H, CH_3 isopropylidene); ^{13}C NMR (101 MHz, $CDCl_3$) δ 109.5 (C_q isopropylidene), 98.2 (C-1), 78.5, 75.6 (C-2, C-3), 69.6 (C-5), 68.8 (C-4), 61.7 (C-6), 54.9 (CH_3 OMe), 27.9 (CH_3 isopropylidene), 26.1 (CH_3 isopropylidene). Data in agreement with literature.[64]

Methyl 4,6-di-*O*-benzyl-2,3-*O*-isopropylidene-α-D-mannopyranoside (S29)



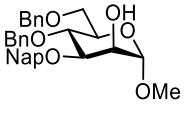
Methyl 2,3-*O*-isopropylidene-α-D-mannopyranoside (**S28**, 0.50 g, 2.13 mmol) was dissolved in 20 ml DMF and stirred at 0 °C until the sugar was fully dissolved. To the solution was added NaH (60% dispersion in mineral oil, 0.26 g, 6.40 mmol, 3 eq) and the reaction was stirred for 30 min at 0 °C after which BnBr (0.76 ml, 6.40 mmol, 3 eq) was slowly added. After 30 min the temperature was increased to RT. Once TLC indicated full conversion the reaction mixture was quenched with water and extracted twice with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (19/1 pentane/EtOAc) to provide the title compound as an oil. Yield: 0.62 g, 1.49 mmol, 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 10H, CH_{arom}), 4.95 (d, *J* = 0.8 Hz, 1H, H-1), 4.86 (d, *J* = 11.5 Hz, 1H, C*H*H Bn), 4.63 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.58 – 4.52 (m, 2H, 2x CH*H* Bn), 4.30 (dd, *J* = 6.9, 5.9 Hz, 1H, H-3), 4.13 (dd, *J* = 5.8, 0.9 Hz, 1H, H-2), 3.79 – 3.65 (m, 3H, H-5, 2x H-6), 3.56 (dd, *J* = 9.9, 6.9 Hz, 1H, H-4), 3.39 (s, 3H, CH_3 OMe), 1.51 (s, 3H, CH_3 isopropylidene)), 1.37 (s, 3H, CH_3 isopropylidene); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 138.3 (C_q), 128.3, 128.2, 127.9, 127.6, 127.6, 127.5 (*C*H_{arom}), 109.4 (C_q isopropylidene), 98.3 (C-1), 78.9 (C-3), 75.8 (C-2), 75.8 (C-4), 73.5, 72.8 (*C*H_2 Bn), 69.3 (C-6), 68.3 (C-5), 54.9 (CH_3 OMe), 27.9 (CH_3 isopropylidene), 26.3 (CH_3 isopropylidene). Data in agreement with literature[65]

Methyl 4,6-di-*O*-benzyl-α-D-mannopyranoside (S30)



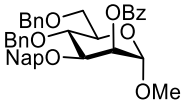
Methyl 2,3-*O*-isopropylidene-4,6-di-*O*-benzyl-α-D-mannopyranoside (**S29**, 0.55 g, 1.33 mmol) was dissolved in 10 ml $CHCl_3$ and stirred until the sugar was fully dissolved. To the solution was added TFA (0.82 ml, 10.62 mmol, 8.0 eq) and H_2O (0.07 ml, 3.58 mmol, 2.7 eq), the reaction was stirred for 4h at RT. Once TLC indicated full conversion the reaction mixture was quenched with TEA, the reaction mixture was concentrated under reduced pressure. Purification was performed on flash column chromatography (1/1 pentane/EtOAc) to provide the title compound as a solid. Yield: 0.50 g, 1.33 mmol, quant. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.23 (m, 10H, CH_{arom}), 4.75 (s, *J* = 1.1 Hz, 1H, H-1), 4.74 – 4.65 (m, 2H, 2x C*H*H Bn), 4.59 – 4.52 (m, 2H, 2x CH*H* Bn), 3.97 – 3.87 (m, 2H, H-2, H-5), 3.78 (dd, 1H, H-6), 3.75 – 3.69 (m, 3H, H-3, H-4, H-6), 3.36 (s, 3H, CH_3 OMe), 2.37 (s, 2H, 2-OH, 3-OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 138.1 (C_q), 128.7, 128.5, 128.1, 128.1, 128.1, 127.9 (CH_{arom}), 100.7 (C-1), 75.9 (C-4), 74.7, 73.7 (CH_2 Bn), 71.9 (C-5), 71.1 (C-2), 70.7 (C-3), 68.9 (C-6), 55.1 (CH_3 OMe). Data in agreement with literature.[66]

Methyl 4,6-di-*O*-benzyl-3-*O*-(2-naphtyl)methyl-α-D-mannopyranoside (S31)



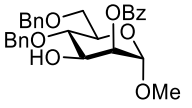
Methyl 4,6-di-*O*-benzyl-α-D-mannopyranoside (**S30**, 1.94 g, 5.18 mmol) and dibutyltin(IV) oxide (1.68 g, 6.74 mmol, 1.3 eq) were dissolved in 75 ml toluene and refluxed for 3 hours, after which solvents where evaporated under reduced pressure. The residue was dissolved in DMF and NapBr (1.49 g, 6.74 mmol, 1.3 eq) and CsF (1.02 g, 6.74 mmol, 1.3 eq) were added. The reaction was stirred overnight at RT. The reaction mixture was diluted with Et_2O and washed twice with H_2O. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (3/1 pentane/EtOAc) to provide the title compound as a light-yellow oil. Yield: 1.98 g, 3.85 mmol, 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.70 (m, 4H, CH_{arom}), 7.51 – 7.42 (m, 3H, CH_{arom}), 7.38 – 7.26 (m, 8H, CH_{arom}), 7.19 – 7.13 (m, 2H, CH_{arom}), 4.89 – 4.79 (m, 4H, H-1, 2x C*H*H Bn/Nap, CH*H* Bn/Nap), 4.66 (d, *J* = 12.1 Hz, 1H, C*H*H Bn/Nap), 4.55 (d, *J* = 9.6 Hz, 1H, CH*H* Bn/Nap), 4.52 (d, *J* = 8.3 Hz, 1H, CH*H* Bn/Nap), 4.07 (t, *J* = 1.7 Hz, 1H, H-2), 3.92 (dd, *J* = 9.1, 3.1 Hz, 1H, H-3), 3.87 (t, *J* = 8.9 Hz, 1H, H-4), 3.80 – 3.67 (m, 3H, H-5, 2x H-6), 3.36 (s, 3H, CH_3 OMe), 2.50 (d, *J* = 2.2 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 138.3 , 135.4, 133.3, 133.1 (C_q), 128.4, 128.4, 128.0, 127.9, 127.8, 127.7, 127.7, 126.7, 126.3, 126.1, 125.9 (CH_{arom}), 100.4 (C-1), 80.3 (C-3), 75.2 (CH_2 Bn/Nap), 74.4 (C-4), 73.6, 72.1 (CH_2 Bn/Nap), 71.1 (C-5), 69.1 (C-6), 68.5 (C-5), 55.0 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{34}O_6$ 532.26936, found 532.26888.

Methyl 2-*O*-benzoyl-4,6-di-*O*-benzyl-3-*O*-(2-naphtyl)methyl-α-D-mannopyranoside (S32)



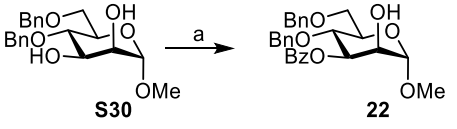
Methyl 4,6-di-*O*-benzyl-3-*O*-(2-naphtyl)methyl-α-D-mannopyranoside (**S31**, 1.90 g, 3.69 mmol) was dissolved in 20 ml pyridine and stirred at 0 °C until the sugar was fully dissolved. To the solution was added BzCl (0.56 ml, 4.8 mmol, 1.3 eq) and the reaction was stirred for 30 min at 0 °C after which the temperature was increased to RT. Once TLC indicated full conversion the reaction mixture was diluted with EtOAc and washed twice with 1M HCl and once with sat. aq. $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc) to provide the title compound as a light-yellow oil. Yield: 2.15 g, 3.47 mmol, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 2H, CH_{arom}), 7.83 – 7.74 (m, 2H, CH_{arom}), 7.71 (d, *J* = 8.4 Hz, 1H, CH_{arom}), 7.65 – 7.60 (m, 1H, CH_{arom}), 7.59 – 7.52 (m, 1H, CH_{arom}), 7.46 – 7.23 (m, 14H, CH_{arom}), 7.18 (ddd, *J* = 6.0, 2.5, 1.5 Hz, 2H, CH_{arom}), 5.67 (dd, *J* = 2.9, 2.0 Hz, 1H, H-2), 4.95 – 4.89 (m, 2H, 2x C*H*H Bn/Nap), 4.88 (d, *J* = 1.9 Hz, 1H, H-1) 4.77 – 4.69 (m, 2H, C*H*H Bn/Nap, CH*H* Bn/Nap), 4.60 – 4.48 (m, 2H, 2x CH*H* Bn/Nap), 4.15 (dd, *J* = 9.2, 2.9 Hz, 1H, H-3), 4.10 (t, *J* = 9.2 Hz, 1H, H-4), 3.90 (dd, *J* = 10.5, 3.9 Hz, 1H, H-6), 3.85 (dt, *J* = 9.2, 2.8 Hz, 1H, H-5), 3.80 (dd, *J* = 10.5, 1.7 Hz, 1H, H-6), 3.39 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (C=O), 138.5, 138.4, 135.5, 133.3 (CH_{arom}), 133.2 (C_q), 132.9 (CH_{arom}), 130.0 (C_q), 129.9, 128.4, 128.4, 128.3, 128.0, 127.9, 127.9, 127.6, 127.5, 127.5, 126.7, 126.0, 125.9, 125.8 (CH_{arom}), 98.9 (C-1), 78.2 (C-3), 75.3 (CH_2 Bn/Nap), 74.3 (C-4), 73.5, 71.5(CH_2 Bn/Nap), 71.5 (C-5), 69.1 (C-6), 68.9 (C-2), 55.0 (CH_3 OMe); HRMS: $[M+Na]^+$ calcd for $C_{39}H_{38}O_7NH_4$ 636.29558, found 636.29475.

Methyl 2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (19)



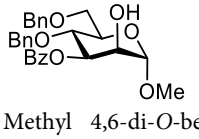
Methyl 2-*O*-benzoyl-4,6-di-*O*-benzyl-3-*O*-(2-naphtyl)methyl-α-D-mannopyranoside. (**S32**, 2.05 g, 3.31 mmol) was dissolved in 25 ml 9/1 DCM/H_2O and stirred at RT until the sugar was fully dissolved. To the solution was added DDQ (1.50 g, 6.63 mmol, 2 eq) and the reaction was stirred for 60 min at RT after which TLC indicated full conversion. The reaction mixture was quenched with aq. Bicarb solution and extracted with DCM. The organic layer was washed twice with aq. Bicarb solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc) to provide the title compound as an oil. Yield: 1.17 g, 2.44 mmol, 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.3, 1.3 Hz, 2H, CH_{arom}), 7.60 – 7.52 (m, 1H, CH_{arom}), 7.44 – 7.18 (m, 12H, CH_{arom}), 5.35 (dd, *J* = 3.4, 1.8 Hz, 1H, H-2), 4.85 (d, *J* = 1.8 Hz, 1H, H-1), 4.80 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.75 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.63 (d, *J* = 11.1 Hz, 1H, CH*H* Bn), 4.56 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.24 (dd, *J* = 9.4, 3.4 Hz, 1H, H-3), 3.99 (t, *J* = 9.6 Hz, 1H, H-4), 3.91 (dd, *J* = 10.9, 3.9 Hz, 1H, H-6), 3.85 – 3.74 (m, 2H, H-5, H-6), 3.39 (s, 3H, CH_3 OMe) 2.24 (s, 1H, OH);^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3 (C=O), 138.4, 138.3 (C_q), 133.3, 130.0 (CH_{arom}), 129.7 (C_q), 128.5, 128.5, 128.4, 128.1, 127.9, 127.6, 127.6 (CH_{arom}), 98.6 (C-1), 75.8 (C-4), 74.9, 73.6 (CH_2 Bn), 72.9 (C-2), 71.3 (C-5), 70.6 (C-3), 69.1 (C-6), 55.2 (CH_3 OMe). Data in agreement with literature.[67]

Preparation of acceptor **22**



*Scheme **S10**: preparation of acceptor **22**: reagents and conditions: a) BzCl, 2-aminoethyl diphenylborinate, Dipea, ACN, 61%*

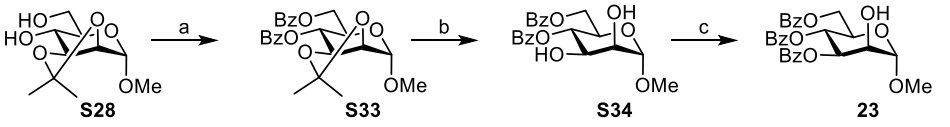
Methyl 3-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (22)



Methyl 4,6-di-*O*-benzyl-α-D-mannopyranoside (**S30**, 0.51 g, 1.27 mmol) and 2-aminoethyl diphenylborinate (0.03 g, 0.12 mmol, 0.1 eq) where dissolved in 10 ml anhydrous CH_3CN. To the solution was added DIPEA (0.31 ml, 1.80 mmol, 1.5 eq) and BzCl (0.21 ml, 1.80 mmol, 1.5 eq) the mixture was stirred for 4 hours, after which TLC indicated full conversion. The mixture was diluted in EtOAc and washed with H_2O. The aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc) to provide the title compound as a yellow oil. Yield: 0.35 g, 0.74 mmol, 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.00 (m, 2H, CH_{arom}), 7.64 – 7.54 (m, 1H, CH_{arom}), 7.50 – 7.42 (m, 3H, CH_{arom}), 7.39 – 7.28 (m, 5H, CH_{arom}), 7.20 – 7.12 (m, 3H, CH_{arom}), 7.09 – 6.99 (m, 2H, CH_{arom}), 5.50 (dd, *J*

= 9.6, 3.1 Hz, 1H, H-3), 4.79 (d, *J* = 1.9 Hz, 1H, H-1), 4.70 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.64 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.55 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.48 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.21 – 4.12 (m, 2H, H-2, H-4), 3.88 (ddt, *J* = 10.5, 4.4, 2.1 Hz, 1H, H-5), 3.82 (dd, *J* = 10.7, 3.9 Hz, 1H, H-6), 3.73 (dd, *J* = 10.6, 2.0 Hz, 1H, H-6), 3.42 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7 (C=O), 138.1, 137.8 (C_q), 133.3 (CH_{arom}), 130.0 (C_q), 129.8, 129.8, 128.7, 128.6, 128.5, 128.4, 128.1, 128.0, 127.8, 127.8, 127.1 (CH_{arom}), 100.9 (C-1), 75.1 (C-3), 74.9, 73.7 (CH_2 Bn), 73.0 (C-4), 71.2 (C-5), 69.7 (C-2), 68.6 (C-6), 55.2 (CH_3 OMe). Data in agreement with literature.[67]

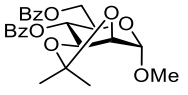
Preparation of acceptor **23**



S28 **S33** **S34** **23**

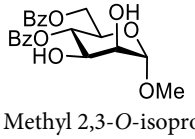
Scheme S11*: preparation of acceptor* ***23****: reagents and conditions: a) BzCl, pyridine, 96%; b) acetic acid, reflux, 85%; c) BzCl, 2-aminoethyl diphenylborinate, Dipea, ACN, 55%*

Methyl 4,6-di-*O*-benzoyl-2,3-*O*-isopropylidene-α-D-mannopyranoside (S33)



Methyl 2,3-*O*-isopropylidene-α-D-mannopyranoside (**S28**, 0.43 g, 1.84 mmol) was dissolved in 20 ml pyridine and stirred at 0 °C until the sugar was fully dissolved. To the solution was added BzCl (0.75 ml, 6.40 mmol, 3.0 eq) and the reaction was stirred for 30 min at 0 °C after which the temperature was increased to RT. Once TLC indicated full conversion the reaction mixture was diluted with EtOAc and washed twice with 1M HCl and with sat. aq. $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc) to provide the title compound as a light-yellow oil. Yield: 0.78 g, 1.77 mmol, 96%. ^1H NMR (400 MHz, $CDCl_3$) 8.07 – 7.97 (m, 4H, CH_{arom}), 7.58 – 7.49 (m, 2H, CH_{arom}), 7.45 – 7.34 (m, 4H, CH_{arom}), 5.42 (dd, *J* = 10.3, 7.6 Hz, 1H, H-4), 5.03 (s, 1H, H-1), 4.54 (dd, *J* = 12.0, 3.1 Hz, 1H, H-6), 4.47 – 4.34 (m, 2H, H-3, H-6), 4.23 (dd, *J* = 5.5, 0.8 Hz, 1H, H-2), 4.18 – 4.09 (m, 1H, H-5), 3.44 (s, 3H, CH_3 OMe), 1.64 (s, 3H, CH_3 isopropylidene), 1.37 (s, 3H, CH_3 isopropylidene). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 165.7 (C=O), 133.4, 133.1, 130.0 (CH_{arom}), 129.9 (C_q), 129.7 (CH_{arom}), 129.5 C_q), 128.5, 128.5 (CH_{arom}), 110.3 (C_q isopropylidene), 98.3 (C-1), 76.1 (C-3), 75.9 (C-2), 70.7 (C-4), 66.4 (C-5), 63.8 (C-6), 55.3 (CH_3 OMe), 27.9 (CH_3 isopropylidene), 26.5 (CH_3 isopropylidene). Data in agreement with literature.[68]

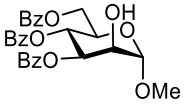
Methyl 4,6-di-*O*-benzoyl-α-D-mannopyranoside (S34)



Methyl 2,3-*O*-isopropylidene-4,6-di-*O*-benzoyl-α-D-mannopyranoside (**S33**, 0.73 g, 1.65mmol) was dissolved in 10 ml Acetic acid and refluxed for 1 h. Once TLC indicated full conversion the

reaction mixture was cooled down to RT and concentrated under reduced pressure. Purification was performed on flash column chromatography (3/2 pentane/EtOAc) to provide the title compound as a solid. Yield: 0.56 g, 1.40 mmol, 85 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.95 (m, 4H, CH_{arom}), 7.62 – 7.49 (m, 2H, CH_{arom}), 7.48 – 7.35 (m, 4H, CH_{arom}), 5.39 (dd, *J* = 10.1, 9.3 Hz, 1H, H-4), 4.86 (d, *J* = 1.6 Hz, 1H, H-1), 4.60 (dd, *J* = 11.9, 2.7 Hz, 1H, H-6), 4.46 (dd, *J* = 11.9, 5.9 Hz, 1H, H-6), 4.22 (ddd, *J* = 10.2, 5.9, 2.7 Hz, 1H, H-5), 4.11 (dd, *J* = 9.4, 3.6 Hz, 1H, H-3), 4.03 (dd, *J* = 3.5, 1.7 Hz, 1H, H-2), 3.44 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 166.4 (C=O), 133.8, 133.2, 130.1 (CH_{arom}), 129.8 (C_q), 129.8 (CH_{arom}), 129.2 (C_q), 128.7, 128.5 (CH_{arom}), 100.6 (C-1), 71.5 (C-4), 70.7 (C-2), 70.6 (C-3), 67.9 (C-5), 63.9 (C-6), 55.4 (CH_3 OMe). Data in agreement with literature.[68]

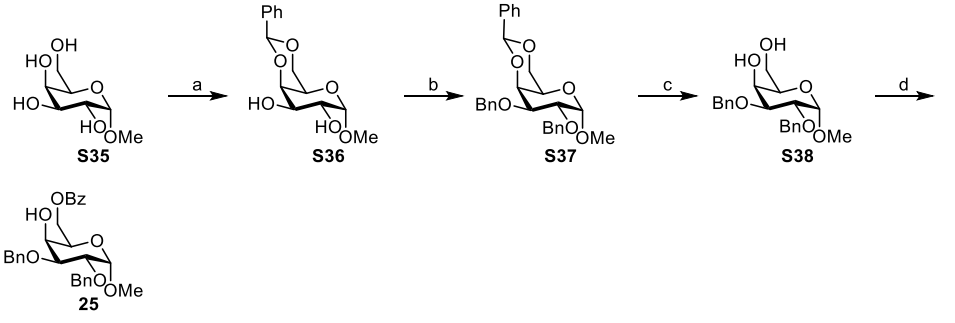
Methyl 3,4,6-tri-*O*-benzoyl-α-D-mannopyranoside (23)



Methyl 4,6-di-*O*-benzoyl-α-D-mannopyranoside (**S34**, 0.45 g, 1.20 mmol) and 2-aminoethyl diphenylborinate (0.03 g, 0.13 mmol, 0.1 eq) where dissolved in 10 ml anhydrous CH_3CN. To the solution was added DIPEA (0.27 ml, 1.52 mmol, 1.2 eq) and BzCl (0.18 ml, 1.52 mmol, 1.2 eq) the mixture was stirred for 4 hours, after which TLC indicated full conversion. The mixture was diluted in EtOAc and washed with H_2O. The aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc) to provide the title compound as a yellow oil. Yield: 0.35 g, 0.70 mmol, 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.00 (m, 2H, CH_{arom}), 7.95 (ddt, *J* = 11.8, 7.0, 1.4 Hz, 4H, CH_{arom}), 7.61 – 7.45 (m, 3H, CH_{arom}), 7.43 – 7.31 (m, 6H, CH_{arom}), 5.93 (t, *J* = 10.0 Hz, 1H, H-4), 5.67 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3), 4.89 (d, *J* = 1.8 Hz, 1H, H-1), 4.60 (dd, *J* = 12.0, 3.0 Hz, 1H, H-6), 4.49 (dd, *J* = 12.0, 5.5 Hz, 1H, H-6), 4.44 – 4.28 (m, 2H, H-2, H-5), 3.50 (s, 3H, CH_3 OMe), 2.35 (s, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 165.7, 165.6 (C=O), 133.5, 133.5, 133.2 (C_q), 129.9, 129.9, 129.9, 129.8, 129.3, 129.2, 128.6, 128.6, 128.5, 128.5 (CH_{arom}), 100.8 (C-1), 72.7 (C-3), 69.5 (C-2), 68.7 (C-5), 67.1 (C-4), 63.7 (C-6), 55.5 (CH_3 OMe). Data in agreement with literature.[67]

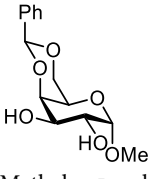
Galactose acceptors

Preparation of acceptor **25**



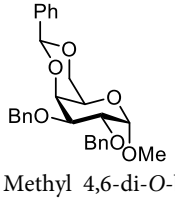
***Scheme S12**: preparation of acceptor **25**: reagents and conditions: a) $PhCH(OMe)_2$, HBF_4-Et_2O, DMF, 89%; b) BnBr, NaH, DMF, 65%; c) PTSA, MeOH, 50 °C, 94%; d) BzCl, pyridine, DCM, 0 °C, 48%*

Methyl 4,6-*O*-benzylidene-α-D-galactopyranoside (S36)



Methyl-α-D-galactopyranoside (**S35**, 4.85 g, 25.0 mmol) was dissolved in 25 ml DMF and stirred until the sugar was fully dissolved. To the solution was added benzaldehyde dimethyl acetal (4.03 ml, 26.75 mmol, 1.07 eq) and HBF_4-Et_2O (3.43 ml, 25.0 mmol, 1 eq), the mixture was stirred for 4h at RT after which TLC indicated full conversion. The reaction mixture was quenched with TEA (4.2 ml, 50.0 mmol, 2 eq). Solvents were evaporated under reduced pressure and purification was performed on flash column chromatography (3/2pentane/EtOAc) to provide the title compound as a solid. Yield: 6.3 g, 22.3 mmol, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.33 (m, 5H, CH_{arom}), 5.55 (s, 1H, C*H*Ph), 4.91 (d, *J* = 3.2 Hz, 1H, H-1), 4.31 – 4.22 (m, 2H, H-2, H-6), 4.06 (d, *J* = 1.8 Hz, 1H, H-6), 3.99 – 3.88 (m, 2H, H-3, H-5), 3.68 (d, *J* = 1.6 Hz, 1H, H-4), 3.45 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7 (C_q), 129.1, 128.2, 126.3 (CH_{arom}), 101.2 (CHPh), 100.4 (C-1), 76.0 (C-2), 69.7 (C-3), 69.6 (C-5), 69.4 (C-6), 62.7 (C-4), 55.7 (OMe). Data in agreement with literature.[69]

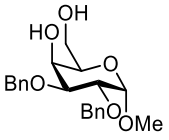
Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (S37)



Methyl 4,6-di-*O*-benzylidene-α-D-galactopyranoside. (**S36**, 7.0 g, 24.8 mmol) was dissolved in 75 ml DMF and stirred at 0 °C until the sugar was fully dissolved. To the solution was added NaH

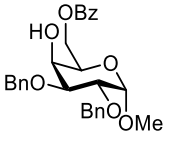
(60% dispersion in mineral oil, 2.98 g, 74.39 mmol, 3 eq) and the reaction was stirred for 30 min at 0 °C after which BnBr (8.84 ml, 74.39 mmol, 3 eq) was slowly added. After 30 min the temperature was increased to RT. Once TLC indicated full conversion the reaction mixture was quenched with water and extracted twice with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (8/2 pentane/EtOAc) to provide the title compound as an oil. Yield: 11.47 g, 16.12 mmol, 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.22 (m, 15H, CH_{arom}), 5.48 (s, 1H, C*H*Ph), 4.88 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.84 (d, *J* = 12.4 Hz, 1H, C*H*H Bn), 4.78 – 4.72 (m, 2H, CH*H* Bn, H-1), 4.68 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.21 (dd, *J* = 12.4, 1.6 Hz, 1H, H-6), 4.18 (dd, *J* = 3.5, 1.2 Hz, 1H, H-4), 4.06 (dd, *J* = 10.1, 3.5 Hz, 1H, H-3), 4.03 – 3.99 (m, 1H, H-6), 3.99 – 3.94 (m, 1H, H-2), 3.58 (q, *J* = 1.6 Hz, 1H, H-5), 3.38 (s, 3H, CH_3 OMe);^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 138.7, 137.9 (C_q), 129.0, 128.5, 128.2, 128.2, 127.8, 127.8, 127.7, 126.5 (CH_{arom}), 101.2 (CHPh), 99.6 (C-1), 76.2 (C-2), 75.6 (C-3), 74.9 (C-4), 73.9 (CH_2 Bn), 72.3 (CH_2 Bn), 69.5 (C-6), 62.5 (C-5), 55.6 (CH_3 OMe). Data in agreement with literature.[70]

Methyl 2,3-di-*O*-benzyl-α-D-galactopyranoside (S38)



Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (**S37**, 2.31 g, 5.0 mmol) was dissolved in 30 ml MeOH and stirred at RT for 15 min. To the solution was added pTsOH·H_2O (95.1 mg, 0.50 mmol, 0.1 eq) and the mixture was stirred for 1h at 50 °C after which TLC indicated full conversion. The reaction mixture was set to cool down to RT and was quenched with TEA. Solvents were evaporated under reduced pressure and purification was performed on flash column chromatography (3/2pentane/EtOAc) to provide the title compound as a solid. Yield: 1.75 g, 4.70 mmol, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 10H, CH_{arom}), 4.80 (dd, *J* = 11.8, 2.8 Hz, 2H, 2x C*H*H Bn), 4.72 – 4.63 (m, 3H, H-1, 2x CH*H* Bn), 4.03 (s, 1H, H-4), 3.90 – 3.84 (m, 3H, H-2, H-3, H-6), 3.79 – 3.71 (m, 2H, H-5, H-6), 3.37 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 138.1 (C_q), 128.6, 128.5, 128.1, 128.0, °127.9 (CH_{arom}), 98.7 (C-1), 77.4 (C-2), 75.7 (C-3), 73.6, 73.0 (CH_2 Bn), 69.1 (C-4), 69.0 (C-5), 63.0 (C-6), 55.4 (CH_3 OMe). Data in agreement with literature.[71]

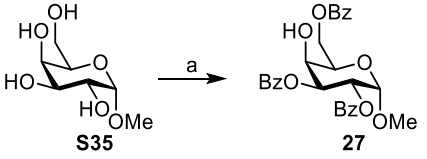
Methyl 6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (25)



Methyl 2,3-di-*O*-benzyl-α-D-galactopyranoside (**S38**, 0.75 g, 2.00 mmol) and pyridine (0.81 mL, 10.0 mmol, 5 eq) were dissolved in 6 mL DCM and cooled to 0 °C, after which BzCl (0.25 mL, 2.10 mmol, 1.05 eq) was added over 15 min. The reaction mixture was allowed to warm to RT overnight, before being diluted with DCM and washed with 1M HCl and sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (10% EtOAc in pentane) to yield the title compound as colourless oil. Yield:

468 mg, 0.96 mmol, 48% ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H, CH_{arom}), 7.59 – 7.54 (m, 1H, CH_{arom}), 7.43 (dd, *J* = 8.3, 7.1 Hz, 2H, CH_{arom}), 7.39 – 7.27 (m, 10H, CH_{arom}), 4.87 – 4.78 (m, 2H, 2x C*H*H Bn), 4.71 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.69 – 4.65 (m, 2H, H-1, CH*H* Bn), 4.55 (dd, *J* = 11.5, 5.0 Hz, 1H, H-6), 4.49 (dd, *J* = 11.5, 7.4 Hz, 1H, H-6), 4.10 – 4.01 (m, 2H, H-4, H-5), 3.91 (dd, *J* = 9.7, 3.0 Hz, 1H, H-3), 3.86 (dd, *J* = 9.8, 3.3 Hz, 1H, H-2), 3.37 (s, 3H, CH_3 OMe), 2.55 (s, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5 (C=O), 138.4, 138.1 (C_q), 133.2 (CH_{arom}), 130.0 (C_q), 129.8, 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 128.0 (CH_{arom}), 98.6 (C-1), 77.5 (C-3), 75.7 (C-2), 73.7, 73.2 (CH_2 Bn), 68.0, 67.6 (C-4, C-5), 64.1 (C-6), 55.4 (CH_3 OMe). Spectra in agreement with literature.[72]

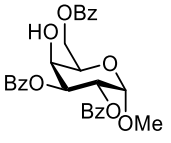
Preparation of acceptor **27**



S35 **27**

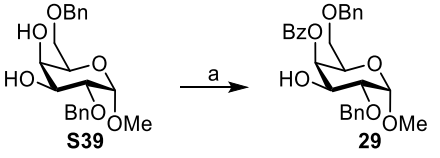
Scheme S13*: preparation of acceptor* ***27****: reagents and conditions: a) BzCl, pyridine, 63%*

Methyl 2,3,6-tri-*O*-benzoyl-α-D-galactopyranoside (27)



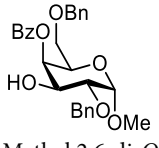
Methyl-α-D-galactopyranoside (**S35**, 0.78 g, 4.0 mmol) was dissolved in 20 ml pyridine and stirred at 0 °C until the sugar was fully dissolved. To the solution was added BzCl (2.14 ml, 18.4 mmol, 4.6 eq) over a 30 min time frame and the reaction was stirred for 4 h at RT after which TLC indicated full conversion. The reaction mixture was quenched with H_2O and extracted with Toluene. The organic layer was washed twice with aq. 1M HCl solution and once with aq. Bicarb solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc → 8/2 pentane/EtOAc) to provide the title compound as an oil. Yield: 1.28 g, 2.54 mmol, 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 7.88 (m, 6H, CH_{arom}), 7.58 (ddt, *J* = 8.8, 6.9, 1.3 Hz, 1H, CH_{arom}), 7.54 – 7.48 (m, 2H, CH_{arom}), 7.47 – 7.42 (m, 2H, CH_{arom}), 7.37 (td, *J* = 7.8, 1.6 Hz, 4H, CH_{arom}) 5.76 (dd, *J* = 10.7, 3.0 Hz, 1H, H-3), 5.69 (dd, *J* = 10.7, 3.5 Hz, 1H, H-2), 5.22 (d, *J* = 3.6 Hz, 1H, H-1), 4.68 (dd, *J* = 11.5, 5.8 Hz, 1H, H-6), 4.57 (dd, *J* = 11.4, 6.9 Hz, 1H, H-6), 4.41 (d, *J* = 1.8 Hz, 1H, H-4), 4.36 (t, *J* = 6.3 Hz, 1H, H-5), 3.45 (s, 3H, CH_3 OMe), 2.68 (s, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 166.2, 165.9 (C=O), 133.6, 133.4, 133.4, 129.9, 129.9, 129.8 (CH_{arom}), 129.7, 129.5, 129.4 (C_q), 128.6, 128.5 (CH_{arom}), 97.7 (C-1), 70.9 (C-3), 69.0 (C-2), 68.3 (C-4), 67.8 (C-5), 63.5 (C-6), 55.6 (CH_3 OMe). Data in agreement with literature.[73]

Preparation of acceptor **29**



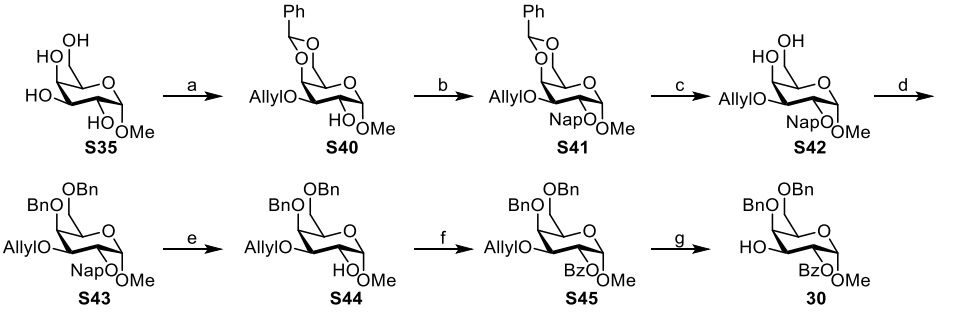
***Scheme S14**: preparation of acceptor **29**: reagents and conditions: a) Benzoyl cyanide, DMAP, DCM, - 78 °C, 65%*

Methyl 4-*O*-benzoyl-2,6-di-*O*-benzyl-α-D-galactopyranoside (29)



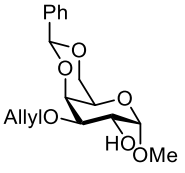
Methyl 2,6-di-*O*-benzyl-α-D-galactopyranoside[74] (**S39**, 1.30 g, 3.47 mmol) was dissolved in 20 ml anhydrous DCM. The solution was cooled down to -78 °C and BzCN (0.46 g, 3.47 mmol, 1 eq) and DMAP (43.4 mg, 0.35 mmol, 0.1 eq) were added. After 4 h TLC indicated full conversion and the reaction was quenched with aq. NH_4Cl, filtered over a celite pad and extracted with DCM. The organic phase was washed twice with aq. $Na_2S_2O_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (3/1 pentane/EtOAc) to provide the title compound as an oil. Yield: 1.08 g, 2.26 mmol, 65%. $[\alpha]_D^{25}$ = +46.5° (c = 0.60, $CHCl_3$); IR (thin film): 412, 699, 714, 738, 985, 1027, 1046, 1097, 1177, 1193, 1272, 1313, 1349, 1452, 1720; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.98 (m, 2H, CH_{arom}), 7.65 – 7.51 (m, 1H, CH_{arom}), 7.48 – 7.40 (m, 2H, CH_{arom}), 7.42 – 7.25 (m, 5H, CH_{arom}), 7.26 – 7.13 (m, 4H, CH_{arom}), 5.66 (dd, *J* = 3.6, 1.3 Hz, 1H, H-4), 4.81 (d, *J* = 3.5 Hz, 1H, H-1), 4.74 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.68 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.50 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.40 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.27 (dt, *J* = 10.0, 3.2 Hz, 1H, H-3), 4.17 (td, *J* = 6.1, 1.3 Hz, 1H, H-5), 3.82 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2), 3.55 (d, *J* = 6.2 Hz, 2H, 2x H-6), 3.40 (s, 3H, CH_3 OMe), 2.41 (d, *J* = 3.0 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4 (C=O), 138.0, 137.8 (C_q), 133.3, 130.0 (CH_{arom}), 129.9 (C_q), 128.6, 128.5, 128.4, 128.3, 128.2, 127.7 (CH_{arom}), 98.2 (C-1), 76.8 (C-2), 73.6 73.2 (CH_2 Bn), 71.4 (C-4), 68.9 (C-6), 68.5 (C-3), 68.2 (C-5), 55.6 (CH_3 OMe); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{30}O_7$ 501.18837, found 501.18754.

Preparation of acceptor **30**



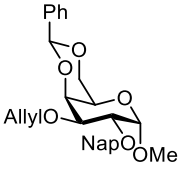
***Scheme S15**: preparation of acceptor **30**: reagents and conditions: a) i: DBTO, toluene reflux, ii: allyl bromide, TBAI, toluene, 75 °C, iii: $PhCH(OCH_3)_2$, PTSA, acetonitrile, 60 °C, 300 mbar, 27% over 3 steps; b) NapBr, NaH, DMF, 81%; c) PTSA, MeOH, 50 °C, 82%; d) BnBr, NaH, DMF, 86%; e) DDQ, DCM/H_2O (9:1), 79%; f) BzCl, pyridine, 90%; g) $Pd(Ph_3P)_4$, DMBA, MeOH, 40 °C, quant*

Methyl 3-*O*-allyl-4,6-*O*-benzylidene-α-D-galactopyranoside (S40)



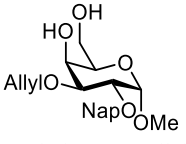
Methyl α-D-galactopyranoside (**S35**, 9.71 g, 50 mmol) and di-n-butyltin oxide (13.7 g, 55 mmol, 1.1 eq) were refluxed in toluene for 3 hr, while water was removed with a Dean-Stark trap. After this, the reaction mixture was cooled to 60 °C and TBAI (20.3 g, 55 mmol, 1.1 eq) and allyl bromide (5.18 mL, 60 mmol, 1.2 eq) were added. The reaction mixture was stirred overnight at this temperature and subsequently concentrated under reduced pressure. Silica chromatography (4% MeOH in DCM) yields impure Methyl 3-*O*-allyl-α-D-galactopyranoside (9.9 g, max. 42.3 mmol, 85%) as red oil. This was dissolved in acetonitrile with PTSA-H_2O (0.80 g, 4.23 mmol, ca. 0.1 eq) and benzaldehyde dimethyl acetal (8.92 mL, 59.2 mmol, ca. 1.4 eq). The reaction mixture was heated to 60 °C at 300 mbar until TLC showed full conversion. The reaction was then concentrated under reduced pressure. The residue was dissolved in EtOAc and washed with sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. Recrystallisation from EA/pentane yields the title compound as yellowish solid. Yield: 4.3 g, 13.3 mmol, 27% based on **S35**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 2H, CH_{arom}), 7.45 – 7.30 (m, 3H, CH_{arom}), 5.99 (ddt, *J* = 17.3, 10.3, 5.8 Hz, 1H, CH_2-C*H*=CH_2), 5.57 (s, 1H, C*H*Ph), 5.35 (dq, *J* = 17.3, 1.6 Hz, 1H, CH_2-CH=C*H*H), 5.23 (dq, *J* = 10.3, 1.3 Hz, 1H, CH_2-CH=CH*H*), 4.97 (d, *J* = 3.7 Hz, 1H, H-1), 4.34 (dd, *J* = 3.5, 1.2 Hz, 1H, H-4), 4.30 (dd, *J* = 12.5, 1.6 Hz, 1H, H-6), 4.30 – 4.21 (m, 1H, C*H*H-CH=CH_2), 4.24 – 4.14 (m, 2H, H-2, CH*H*-$CHCH_2$), 4.10 (dd, *J* = 12.5, 1.8 Hz, 1H, H-6), 3.76 (dd, *J* = 10.1, 3.5 Hz, 1H, H-3), 3.68 (q, *J* = 1.6 Hz, 1H, H-5), 3.48 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8 (C_q), 135.0(CH_2-*C*H=CH_2), 129.0, 128.2, 126.4 (CH_{arom}), 117.7 CH_2-CH=*C*H_2), 101.1 (CHPh), 100.2 (C-1), 76.1 (C-3), 73.7 (C-4), 70.6 (*C*H_2-CH=CH_2), 69.6 (C-6), 68.0 (C-2), 62.9 (C-5), 55.7 (CH_3 OMe). Spectra in agreement with literature.[75]

Methyl 3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-(2-naphtyl)methyl-α-D-galactopyranoside (S41)



Methyl 3-*O*-allyl-4,6-*O*-benzylidene-α-D-galactopyranoside (**S40**, 4.25 g, 13.18 mmol) was dissolved in 50 ml DMF and stirred at 0 °C until the sugar was fully dissolved. To the solution was added NaH (60 % dispersion in mineral oil, 0.69 g, 17.14 mmol, 1.3 eq) and the mixture was stirred for another 15 min before slowly adding NapBr (3.79 g, 17.14 mmol, 1.3 eq) and the reaction was stirred at RT until TLC indicated full conversion. The reaction mixture was quenched with H_2O and extracted with Et_2O. The organic layer was washed twice with H_2O. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (8/2 pentane/EtOAc) to provide the title compound as an oil. Yield: 4.85 g, 10.48 mmol, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 4H, CH_{arom}), 7.55 – 7.43 (m, 5H, CH_{arom}), 7.35 – 7.28 (m, 3H, CH_{arom}), 6.07 – 5.92 (m, 1H, CH_2-C*H*=CH_2), 5.53 (s, 1H, C*H*Ph), 5.36 (dq, *J* = 17.2, 1.6 Hz, 1H, CH_2-CH=C*H*H), 5.20 (dq, *J* = 10.4, 1.4 Hz, 1H, CH_2-CH=CH*H*), 5.06 – 4.97 (m, 1H, C*H*H Nap), 4.82 (d, *J* = 12.2 Hz, 1H, CH*H* Nap), 4.77 (d, *J* = 3.5 Hz, 1H, H-1), 4.35 – 4.24 (m, 2H, H-4, C*H*$_2$-CH=CH_2), 4.21 (dd, *J* = 12.5, 1.6 Hz, 1H, H-6), 4.08 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2), 4.03 (dd, *J* = 12.5, 1.8 Hz, 1H, H-6), 3.95 (dd, *J* = 10.2, 3.4 Hz, 1H, H-3), 3.62 (d, *J* = 1.5 Hz, 1H, H-5), 3.39 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 136.1 (C_q), 135.4 (CH_2-*C*H=CH_2), 133.3, 133.1 (C_q), 129.0, 128.2, 128.0, 127.8, 127.0, 126.5, 126.2, 126.1, 126.0 (CH_{arom}), 117.2 (CH_2-CH=*C*H_2), 101.3 (CHPh), 99.6 (C-1), 75.6 (C-3), 75.5 (C-2), 75.1 (C-4), 74.0 (CH_2 Nap), 71.6 (*C*H_2-CH=CH_2), 69.5 (C-6), 62.7 (C-5), 55.7 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{28}H_{30}O_6NH_4$ 480.23806, found 480.23749.

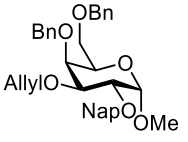
Methyl 3-*O*-allyl-2-*O*-(2-naphtyl)methyl-α-D-galactopyranoside (S42)



Methyl 3-*O*-allyl-4,6-di-*O*-benzylidene-2-*O*-(2-naphtyl)methyl-α-D-galactopyranoside (**S41**, 4.76 g, 10.3 mmol) was dissolved in 50 ml MeOH and stirred at RT for 15 min. To the solution was added pTsOH·H_2O (0.20 g, 1.03 mmol, 0.1 eq) and the mixture was stirred for 1h at 50 °C after which TLC indicated full conversion. The reaction mixture was set to cool down to RT and was quenched with TEA. Solvents were evaporated under reduced pressure and purification was performed on flash column chromatography (1/1 pentane/EtOAc) to provide the title compound as a solid. Yield: 3.17 g, 8.46 mmol, 82 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 4H, CH_{arom}), 7.54 – 7.43 (m, 3H, CH_{arom}), 5.96 (ddt, *J* = 17.3, 10.4, 5.7 Hz, 1H, CH_2-C*H*=CH_2), 5.33 (dq, *J* = 17.2, 1.6 Hz, 1H, CH_2-CH=C*H*H), 5.22 (dq, *J* = 10.3, 1.3 Hz, 1H, CH_2-CH=CH*H*), 4.95 (d, *J* = 12.3, 1H, C*H*H Nap), 4.81 (d, *J* = 12.3 Hz, 1H, CH*H* Nap), 4.69 (d, *J* = 3.3 Hz, 1H, H-1), 4.29 (ddt, *J* = 12.7, 5.4, 1.5 Hz, 1H, C*H*H-CH=CH_2), 4.22 (ddt, *J* = 12.7, 5.9, 1.4 Hz, 1H, CH*H*-CH=CH_2), 4.10 (dd, *J* = 3.1, 1.3 Hz, 1H, H-4), 3.91 (dd, *J* = 12.7, 6.9 Hz, 1H, H-6), 3.87 – 3.80 (m,

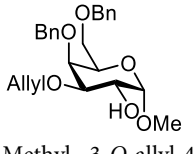
2H, H-2, H-3), 3.80 – 3.76 (m, 2H, H-5, H-6), 3.38 (s, 3H, CH_3 OMe), 2.72 (s, 1H, OH), 2.37 (s, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9 (C_q), 134.7(CH_2-*C*H=CH_2), 133.3, 133.2 (C_q), 128.3, 128.0, 127.8, 126.9, 126.3, 126.1, 126.1 (CH_{arom}), 117.6 (CH_2-CH=*C*H_2), 98.7 (C-1), 76.9 (C-3), 75.5 (C-2), 73.8 (CH_2 Nap), 71.8 (*C*H_2-CH=CH_2), 69.2 (C-4), 69.0 (C-5), 63.2 (C-6), 55.5 (CH_3 OMe); HRMS: $[M+Na]^+$ calcd for $C_{21}H_{26}O_6Na$ 397.16216, found 397.16144.

Methyl 3-*O*-allyl-4,6-di-*O*-benzyl-2-*O*-(2-naphtyl)methyl-α-D-galactopyranoside (S43)



Methyl 3-*O*-allyl-2-*O*-(2-naphtyl)methyl-α-D-galactopyranoside (**S42**, 2.62 g, 7.0 mmol, 1 eq) was dissolved in 40 ml DMF and stirred at 0 °C until the sugar was fully dissolved. To the solution was added NaH (60% dispersion in mineral oil, 0.84 g, 21.0 mmol, 3 eq) and the reaction was stirred for 30 min at 0 °C after which BnBr (2.49 ml, 21.0 mmol, 3 eq) was slowly added. After 30 min the temperature was increased to RT. Once TLC indicated full conversion the reaction mixture was quenched with water and extracted twice with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc) to provide the title compound as an oil. Yield: 3.35 g, 6.02 mmol, 86%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.76 (m, 4H, CH_{arom}), 7.55 – 7.42 (m, 3H, CH_{arom}), 7.38 – 7.21 (m, 10H, CH_{arom}) , 5.99 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1H, CH_2-C*H*=CH_2), 5.37 (dq, *J* = 17.2, 1.8 Hz, 1H, CH_2-CH=C*H*H), 5.20 (dq, *J* = 10.4, 1.5 Hz, 1H, CH_2-CH=CH*H*), 4.98 (d, *J* = 12.3 Hz, 1H, C*H*H Bn), 4.94 (d, *J* = 11.4 Hz, 1H, C*H*H Nap), 4.84 (d, *J* = 12.3 Hz, 1H, CH*H* Bn), 4.67 (d, *J* = 3.6 Hz, 1H, H-1), 4.56 (d, *J* = 11.4 Hz, 1H, CH*H* Nap), 4.47 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.39 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.32 (ddt, *J* = 13.0, 5.1, 1.6 Hz, 1H, C*H*H-CH=CH_2), 4.23 (ddt, *J* = 13.0, 5.4, 1.6 Hz, 1H, CH*H*-CH=CH_2), 4.03 (dd, *J* = 10.1, 3.7 Hz, 1H, H-2), 3.93 (d, *J* = 2.8 Hz, 1H, H-4), 3.89 (t, *J* = 6.5 Hz, 1H, H-5), 3.84 (dd, *J* = 10.1, 2.9 Hz, 1H, H-3), 3.51 (d, *J* = 6.5 Hz, 2H, 2x H-6), 3.36 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 138.1, 136.2 (C_q), 135.3 (CH_2-*C*H=CH_2), 133.4, 133.2 (C_q), 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.8, 127.7, 126.9, 126.2, 126.1, 125.9 (CH_{arom}), 116.6 (CH_2-CH=*C*H_2), 98.9 (C-1), 78.7 (C-3), 76.4 (C-2), 75.0 (C-4), 74.8 (CH_2 Nap), 73.8 (CH_2 Bn), 73.6 (CH_2 Bn), 72.0 (*C*H_2-CH=CH_2), 69.3 (C-5), 69.2 (C-6), 55.5 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{35}H_{38}O_6$ 572.30066, found 572.29988.

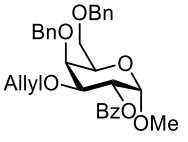
Methyl 3-*O*-allyl-4,6-di-*O*-benzyl-α-D-galactopyranoside (S44)



Methyl 3-*O*-allyl-4,6-di-*O*-benzyl-2-*O*-(2-naphtyl)methyl-α-D-galactopyranoside (**S43**, 1.66 g, 3.0 mmol) was dissolved in 30 ml 9/1 DCM/H_2O and stirred at RT until the sugar was fully dissolved. To the solution was added DDQ (1.36 g, 3.0 mmol, 2 eq) and the reaction was stirred for 60 min at RT after which TLC indicated full conversion. The reaction mixture was quenched with aq. Bicarb solution and extracted with DCM. The organic layer was washed twice with aq.

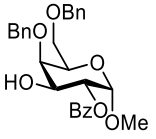
Bicarb solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (7/3 pentane/EtOAc) to provide the title compound as an oil. Yield: 0.973 g, 2.36 mmol, 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.17 (m, 10H, CH_{arom}), 5.94 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H, CH_2-C*H*=CH_2), 5.32 (dq, *J* = 17.2, 1.6 Hz, 1H, CH_2-CH=C*H*H), 5.20 (dq, *J* = 10.4, 1.4 Hz, 1H, CH_2-CH=CH*H*), 4.87 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.84 (d, *J* = 3.9 Hz, 1H, H-1), 4.56 (d, *J* = 11.4 Hz, 1H, CH*H* Bn), 4.52 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.44 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 4.18 (ddt, *J* = 12.7, 5.5, 1.5 Hz, 1H, C*H*H-CH=CH_2), 4.17 – 4.07 (m, 2H, H-2, CH*H*-CH=CH_2), 3.95 (dd, *J* = 2.9, 1.3 Hz, 1H, H-4), 3.90 (t, *J* = 2.7 Hz, 1H, H-5), 3.64 – 3.52 (m, 3H, H-3, 2x H-6), 3.42 (s, 3H, CH_3 OMe), 2.22 (d, *J* = 7.1 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 138.0 (C_q), 134.7 (CH_2-*C*H=CH_2), 128.6, 128.4, 128.3, 127.9, 127.9, 127.8 (CH_{arom}), 117.4 (CH_2-CH=*C*H_2), 99.7 (C-1), 79.1 (C-3), 74.7 (CH_2 Bn), 73.7 (C-4), 73.7 (CH_2 Bn), 71.2 (*C*H_2-CH=CH_2), 69.7 (C-5), 69.1 (C-6), 68.9 (C-2), 55.6 (OMe); HRMS: $[M+Na]^+$ calcd for $C_{24}H_{30}O_6Na$ 437.19346, found 437.19295.

Methyl 3-*O*-allyl-2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-galactopyranoside (S45)



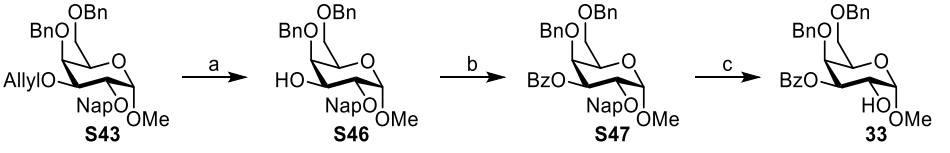
Methyl 3-*O*-allyl-4,6-di-*O*-benzyl-α-D-galactopyranoside (**S44**, 0.92 g, 2.22 mmol) was dissolved in 25 ml pyridine and stirred at 0 °C until the sugar was fully dissolved. To the solution was added BzCl (0.35 ml, 2.89 mmol, 1.3 eq) and the reaction was stirred for 30 min at 0 °C after which the temperature was increased to RT. Once TLC indicated full conversion the reaction mixture was diluted with EtOAc and washed twice with 1M HCl and once with sat. aq. $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc) to provide the title compound as a light-yellow oil. Yield: 1.04 g, 2.0 mmol, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 2H, CH_{arom}), 7.61 – 7.52 (m, 1H, CH_{arom}), 7.49 – 7.40 (m, 2H, CH_{arom}), 7.39 – 7.24 (m, 10H, CH_{arom}), 5.94 – 5.79 (m, 1H, CH_2-C*H*=CH_2), 5.49 (dd, *J* = 10.2, 3.7 Hz, 1H, H-2), 5.28 (dq, *J* = 17.2, 1.7 Hz, 1H, CH_2-CH=C*H*H), 5.14 (dq, *J* = 10.4, 1.4 Hz, 1H, CH_2-CH=CH*H*), 5.10 (d, *J* = 3.7 Hz, 1H, H-1), 4.97 (d, *J* = 11.5 Hz, 1H, C*H*H Bn), 4.60 (d, *J* = 11.5 Hz, 1H, CH*H* Bn), 4.52 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.44 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 4.17 (d, *J* = 5.5 Hz, 1H, C*H*$_2$-CH=CH_2), 4.06 – 3.95 (m, 3H, H-3, H-4, H-5), 3.68 – 3.57 (m, 2H, 2x H-6), 3.35 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (C=O), 138.6, 138.1 (C_q), 134.8 (CH_2-*C*H=CH_2), 133.1 (CH_{arom}), 130.3 (C_q), 129.9, 128.6, 128.5, 128.4, 128.4, 128.0, 127.9, 127.8 (CH_{arom}), 117.2 (CH_2-CH=*C*H_2), 97.7 (C-1), 76.6 (C-4), 74.9 (CH_2 Bn), 74.7 (C-3), 73.7 (CH_2 Bn), 71.9 (*C*H_2-CH=CH_2) 71.9 (C-2), 69.4 (C-5), 69.1 (C-6), 55.5 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{31}H_{34}O_7NH_4$ 536.26428, found 536.26380.

Methyl 2-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-galactopyranoside (30)



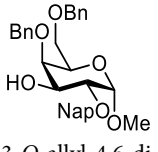
Methyl 2-*O*-benzoyl-3-*O*-allyl-4,6-di-*O*-benzyl-α-D-galactopyranoside (**S45**, 0.95 g, 1.83 mmol) and DMBA (0.57 g, 3.66 mmol, 2 eq) were dissolved in 20 ml MeOH and flushed for 30 min with N_2. To the solution was added $Pd(PPh_3)_4$ (0.11 g, 0.09 mmol, 0.05 eq) and the mixture was heated for 1h at 40 °C, after which TLC indicated full conversion. The mixture was diluted in EtOAc and washed with saturated Bicarb sol. The aqueous layer was extracted three times with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (8/2 pentane/EtOAc) to provide the title compound as a yellow oil. Yield: 0.88 g, 1.83 mmol, quant. $[\alpha]_D^{25}$ = +168.6° (*c = 0.6*, $CHCl_3$); IR (thin film): 698, 714, 1048, 1103, 1280, 1717; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H, CH_{arom}), 7.59 – 7.53 (m, 1H, CH_{arom}), 7.46 – 7.39 (m, 2H, CH_{arom}), 7.39 – 7.27 (m, 10H, CH_{arom}), 5.25 (dd, *J* = 10.3, 3.7 Hz, 1H, H-2), 5.02 (d, *J* = 3.7 Hz, 1H, H-1), 4.73 (s, 1H, CH_2 Bn), 4.58 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.50 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 4.17 (ddd, *J* = 10.3, 9.3, 3.5 Hz, 1H, H-3), 4.10 – 4.04 (m, 1H, H-5), 4.02 (dd, *J* = 3.6, 1.2 Hz, 1H, H-4), 3.75 – 3.59 (m, 2H, 2x H-6), 3.38 (s, 3H, CH_3 OMe), 2.17 (d, *J* = 9.4 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0 (C=O), 138.2, 137.9 (C_q), 133.4, 130.1 (CH_{arom}), 129.9 (C_q), 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 128.0 (CH_{arom}), 97.8 (C-1), 77.7 (C-4), 75.6 (CH_2 Bn), 73.7 (CH_2 Bn), 72.9 (C-2), 69.0, 68.9 (C-3, C-5), 68.7 (C-6), 55.6 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{28}H_{30}O_7NH_4$ 496.23298, found 496.23242.

Preparation of acceptor **33**



***Scheme S16**: preparation of acceptor **33**: reagents and conditions: a) $Pd(Ph_3P)_4$, DMBA, methanol, 40 °C, 95%; b) BzCl, pyridine, 97%; c) DDQ, DCM/H_2O (9:1), 84%*

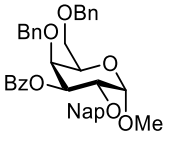
Methyl 4,6-di-*O*-benzyl-2-*O*-(2-naphtyl)methyl-α-D-galactopyranoside (S46)



3-*O*-allyl-4,6-di-*O*-benzyl-2-*O*-(2-naphtyl)methyl-α-D-galactopyranoside (**S43** 1.59 g, 2.87 mmol) and DMBA (0.90 g, 5.73 mmol, 2 eq) where dissolved in 50 ml MeOH and flushed for 30 min with N_2. To the solution was added $Pd(PPh_3)_4$ (0.17 g, 0.14 mmol, 0.05 eq) and the mixture was heated for 1h at 40 °C, after which TLC indicated full conversion. The mixture was diluted in EtOAc and washed with saturated aq. Bicarb sol. The aqueous layer was extracted three times with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated

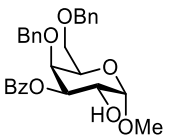
under reduced pressure. Purification was performed on flash column chromatography (17/3 pentane/EtOAc) to provide the title compound as a yellow oil. Yield: 1.40 g, 2.72 mmol, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 4H, CH_{arom}), 7.53 – 7.46 (m, 3H, CH_{arom}), 7.35 – 7.22 (m, 5H, CH_{arom}), 4.88 (d, *J* = 12.2 Hz, 1H, C*H*H Bn/Nap), 4.85 – 4.76 (m, 2H, CH*H* Bn/Nap, C*H*H Bn/Nap), 4.69 (d, *J* = 3.5 Hz, 1H, H-1), 4.60 (d, *J* = 11.5 Hz, 1H, CH*H* Bn/Nap), 4.51 (d, *J* = 11.8 Hz, 1H, C*H*H Bn/Nap), 4.42 (d, *J* = 11.8 Hz, 1H, CH*H* Bn/Nap), 4.08 (ddd, *J* = 10.0, 4.9, 3.2 Hz, 1H, H-3), 3.98 – 3.91 (m, 2H, H-4, H-5), 3.84 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2), 3.55 (d, *J* = 6.4 Hz, 2H, 2x H-6), 3.32 (s, 3H, CH_3 OMe), 2.26 (d, *J* = 4.9 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.0, 135.7, 133.3, 133.3 (C_q), 128.5, 128.5, 128.3, 128.1, 127.9, 127.8, 127.2, 126.3, 126.2, 126.1 (CH_{arom}), 98.1 (C-1), 77.5 (C-2), 76.8 (C-4), 75.3, 73.6, 73.3 (CH_2 Bn, CH_2 Nap), 70.4 (C-3), 69.2 (C-5), 69.1 (C-6), 55.5 (CH_3 OMe). HRMS: $[M+Na]^+$ calcd for $C_{32}H_{34}O_6Na$ 537.22531, found 537.22250.

Methyl 3-*O*-benzoyl-4,6-di-*O*-benzyl-2-*O*-(2-naphtyl)methyl-α-D-galactopyranoside (S47)



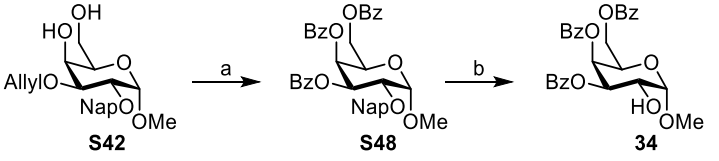
Methyl 4,6-di-*O*-benzyl-2-*O*-(2-naphtyl)methyl-α-D-galactopyranoside (**S46**, 1.30 g, 2.53 mmol) was dissolved in 25 ml pyridine and stirred at 0 °C until the sugar was fully dissolved. To the solution was added BzCl (0.38 ml, 3.28 mmol, 1.3 eq) and the reaction was stirred for 30 min at 0 °C after which the temperature was increased to RT. Once TLC indicated full conversion the reaction mixture was diluted with EtOAc and washed twice with 1M HCl. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (9/1 pentane/EtOAc) to provide the title compound as a light-yellow oil. Yield: 1.51 g, 2.45 mmol, 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.3, 1.4 Hz, 2H, CH_{arom}), 7.82 – 7.75 (m, 1H, CH_{arom}), 7.75 – 7.65 (m, 3H, CH_{arom}), 7.55 (ddt, *J* = 8.7, 7.1, 1.3 Hz, 1H, CH_{arom}), 7.49 – 7.41 (m, 2H, CH_{arom}), 7.41 – 7.37 (m, 3H, CH_{arom}), 7.36 – 7.24 (m, 5H, CH_{arom}), 7.20 – 7.08 (m, 5H, CH_{arom}), 5.59 (dd, *J* = 10.6, 3.1 Hz, 1H, H-3), 4.83 (d, *J* = 3.7 Hz, 2H, H-1, CH_2 Bn/Nap), 4.62 (d, *J* = 11.4 Hz, 1H, C*H*H Bn/Nap), 4.51 (d, *J* = 11.9 Hz, 1H, C*H*H Bn/Nap), 4.45 – 4.36 (m, 2H, 2x CH*H* Bn/Nap), 4.24 (dd, *J* = 10.5, 3.6 Hz, 1H, H-2), 4.16 (dd, *J* = 3.1, 1.3 Hz, 1H, H-4), 4.12 (t, *J* = 6.5, 1.3 Hz, 1H, H-5), 3.55 (dd, *J* = 6.6, 1.2 Hz, 2H, 2x H-6), 3.43 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (C=O), 138.0, 138.0, 135.7, 133.3 (C_q), 133.2 (CH_{arom}), 133.2, 130.0 (C_q), 129.9, 128.5, 128.4, 128.3, 128.1, 128.1, 127.8, 127.8, 127.0, 126.2, 126.1, 126.0 (CH_{arom}), 98.6 (C-1), 75.7 (C-4), 75.3 (CH_2 Bn/Nap), 74.3 (C-2), 73.5, 73.4 (CH_2 Bn/Nap), 73.0 (C-3), 68.9 (C-5), 68.7 (C-6), 55.6 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{39}H_{38}O_7NH_4$ 636.29558, found 636.29474.

Methyl 3-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-galactopyranoside (33)



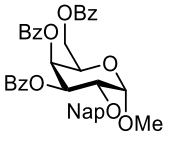
Methyl 3-*O*-benzoyl-4,6-di-*O*-benzyl-2-*O*-(2-naphtyl)methyl-α-D-galactopyranoside (**S47**, 1.45 g, 2.34 mmol) was dissolved in 25 ml 9/1 DCM/H_2O and stirred at RT until the sugar was fully dissolved. To the solution was added DDQ (1.06 g, 4.69 mmol, 2 eq) and the reaction was stirred for 60 min at RT after which TLC indicated full conversion. The reaction mixture was quenched with aq. Bicarb solution and extracted with DCM. The organic layer was washed twice with aq. Bicarb solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (3/1 pentane/EtOAc) to provide the title compound as a solid. Yield: 0.94 g, 1.96 mmol, 84%. $[\alpha]_D^{25}$= +97.9° (c = 0.60, $CHCl_3$); IR (thin film): 698, 738, 1027, 1056, 1070, 1094, 1124, 1149, 1273, 1315, 1352, 1452, 1717; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H, CH_{arom}), 7.57 (ddt, *J* = 8.7, 7.1, 1.3 Hz, 1H, CH_{arom}), 7.48 – 7.38 (m, 2H, CH_{arom}), 7.39 – 7.18 (m, 10H, CH_{arom}), 5.39 (dd, *J* = 10.4, 3.0 Hz, 1H, H-3), 4.89 (d, *J* = 3.9 Hz, 1H, H-1), 4.77 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.54 (d, *J* = 9.1 Hz, 1H, C*H*H Bn), 4.51 (d, *J* = 8.7 Hz, 1H, CH*H* Bn), 4.44 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.27 (ddd, *J* = 11.3, 10.4, 3.9 Hz, 1H, H-2), 4.13 – 4.04 (m, 2H, H-4, H-5), 3.60 (d, *J* = 6.6 Hz, 2H, 2x H-6), 3.46 (s, 3H, CH_3 OMe), 2.03 (d, *J* = 11.2 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7 (C=O), 138.12, 137.9 (C_q), 133.4, 130.0 (CH_{arom}), 129.9 (C_q), 128.6, 128.6, 128.5 128.1, 127.9, 127.9 (CH_{arom}), 99.9 (C-1), 75.6 (C-4), 75.3 (CH_2 Bn), 74.4 (C-3), 73.6 (CH_2 Bn), 69.5 (C-5), 68.7 (C-6), 68.1 (C-2), 55.7 (CH_3 OMe); HRMS: $[M+Na]^+$ calcd for 501.18837, found 501.18772.

Preparation of acceptor **34**



***Scheme S17**: preparation of acceptor **34**: reagents and conditions: a) i) Pd(Ph$_3$P)$_4$, DMBA, methanol, 40 °C, ii: BzCl, pyridine, 89% over 2 steps; b) DDQ, DCM/H$_2$O (9:1), 61%*

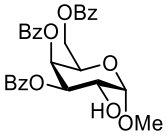
Methyl 3,4,6-tri-*O*-benzoyl-2-*O*-(2-naphtyl)methyl-α-D-galactopyranoside (S48)



Methyl 3-*O*-allyl-2-*O*-(2-naphtyl)methyl-α-D-galactopyranoside (**S42**, 0.5 g, 1.34 mmol) and DMBA (0.42 g, 2.67 mmol, 2 eq) were dissolved in 25 ml MeOH and flushed for 30 min with N_2. To the solution was added $Pd(PPh_3)_4$ (0.08 g, 0.07 mmol, 0.05 eq) and the mixture was heated for 1h at 40 °C, after which TLC indicated full conversion. The mixture conventrated under reduced pressure and the crude intermediate was dissolved in 25 ml pyridine and stirred at 0 °C until it was dissolved. To the solution was added BzCl (0.63 ml, 5.36 mmol, 4 eq) and stirred for 30 min at 0 °C, after which the temperature was increased to RT. The reaction was stirred overnight and diluted in DCM, once TLC indicated full conversion. The organic layer was washed three times with 1M aq. HCl and once with sat. aq. Bicarb. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (4/1 pentane/EtOAc) to provide the slightly impure title compound as a yellow oil. Yield: 0.772 g, 1.19 mmol, 89% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 –

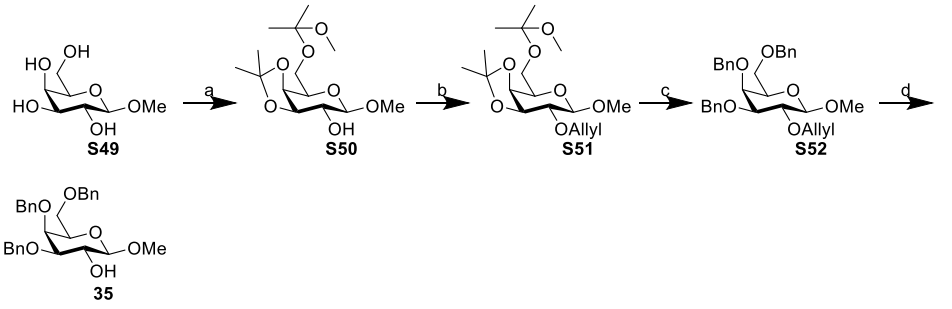
7.95 (m, 2H), 7.90 – 7.84 (m, 2H), 7.82 – 7.76 (m, 3H), 7.72 – 7.66 (m, 3H), 7.60 – 7.51 (m, 3H), 7.50 – 7.45 (m, 3H), 7.40 (dd, *J* = 8.7, 7.0 Hz, 3H), 7.35 – 7.26 (m, 7H), 5.92 (d, *J* = 3.4 Hz, 1H, H-4), 5.81 (dd, *J* = 10.4, 3.4 Hz, 1H, H-3), 4.96 (d, *J* = 3.6 Hz, 1H, H-1), 4.86 (d, *J* = 12.5 Hz, 1H, C*H*H Nap), 4.81 (d, *J* = 12.5 Hz, 1H, CH*H* Nap), 4.59 – 4.46 (m, 2H, H-5, H-6), 4.35 – 4.24 (m, 1H, H-6), 4.22 (dd, *J* = 10.5, 3.4 Hz, 1H, H-2), 3.50 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.6, 165.5 (C=O), 135.4, 135.2, 134.4, 133.5, 133.3, 133.2, 133.2 (C_q), 130.8, 130.7, 130.3, 129.9, 129.8, 129.8, 129.7, 129.6, 129.5, 129.3, 129.0, 128.6, 128.6, 128.5, 128.4, 128.0, 127.9, 127.2, 126.3, 126.2, 126.1 (CH_{arom}), 98.7 (C-1), 73.4 (CH_2 Nap), 73.4 (C-2), 70.3 (C-3), 69.7 (C-4), 66.9 (C-5), 62.8 (C-6), 55.8 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{39}H_{34}O_9NH_4$ 664.25411, found 664.25339.

Methyl 3,4,6-tri-*O*-benzoyl-α-D-galactopyranoside (34)



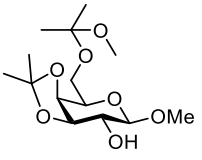
Methyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-naphtyl)methyl-α-D-galactopyranoside (0.82 g, 1.27 mmol) was dissolved in 25 ml 9/1 DCM/H_2O and stirred at RT until the sugar was fully dissolved. To the solution was added DDQ (0.58 g, 2.54 mmol, 2 eq) and the reaction was stirred for 60 min at RT after which TLC indicated full conversion. The reaction mixture was quenched with aq. Bicarb solution and extracted with DCM. The organic layer was washed twice with aq. Bicarb solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification was performed on flash column chromatography (4/1 pentane/EtOAc) to provide the title compound as a solid. Yield: 0.39 g, 0.78 mmol, 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.04 (m, 2H, CH_{arom}), 8.05 – 7.98 (m, 2H, CH_{arom}), 7.90 – 7.83 (m, 2H, CH_{arom}), 7.62 (ddt, *J* = 8.7, 7.1, 1.3 Hz, 1H, CH_{arom}), 7.60 – 7.51 (m, 1H, CH_{arom}), 7.53 – 7.44 (m, 3H, CH_{arom}), 7.46 – 7.37 (m, 2H, CH_{arom}), 7.35 – 7.26 (m, 2H, CH_{arom}), 5.91 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4), 5.59 (dd, *J* = 10.3, 3.4 Hz, 1H, H-3), 5.05 (d, *J* = 3.8 Hz, 1H, H-1), 4.58 (dd, *J* = 11.0, 7.0 Hz, 1H, H-6), 4.50 (ddd, *J* = 6.8, 5.4, 1.3 Hz, 1H, H-5), 4.36 (dd, *J* = 11.0, 5.6 Hz, 1H, H-6), 4.28 (td, *J* = 10.7, 3.8 Hz, 1H, H-2), 3.54 (s, 3H, CH_3 OMe), 2.19 (d, *J* = 11.0 Hz, 1H, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 166.2, 165.7 (C=O), 133.7, 133.4, 133.3, 130.0, 129.9 (CH_{arom}), 129.8 (C_q), 129.5, 128.7, 128.6, 128.4 (CH_{arom}), 99.9 (C-1), 71.5 (C-3), 69.4 (C-4), 68.1 (C-2), 67.3 (C-5), 62.7 (C-6), 55.9 (CH_3 OMe). Data in agreement with literature.[76]

Preparation of acceptor **35**



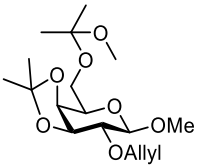
***Scheme S18**: preparation of acceptor **35**: reagents and conditions: a) 2,2-dimethoxypropane, PTSA, 78%; b) allyl bromide, NaH, DMF, 71%; c) i: PTSA, MeOH, 50 °C, ii: BnBr, NaH, DMF, 76% over 2 steps; d) Pd(Ph$_3$P)$_4$, DMBA, MeOH, 85%*

Methyl 3,4-*O*-isopropylidene-6-(1'-methoxy-1'-methyl)ethyl-β-D-galactopyranoside (S50)



Methyl β-D-galactopyranoside (**S49**, 3.88 g, 20 mmol) was suspended in 2,2-dimethoxypropane (49 mL, 400 mmol, 20 eq) and PTSA-H_2O (380 mg, 2 mmol, 0.1 eq) was added. The reaction mixture was stirred for 72 hr before being quenched with triethylamine (0.42 mL, 3 mmol, 0.15 eq) and concentrated under reduced pressure. The residue was purified over silica (20% → 40% acetone in pentane with 1% triethylamine), to provide the title compound as colourless oil. Yield: 4.79 g, 15.6 mmol, 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18 (dd, *J* = 5.5, 2.2 Hz, 1H, H-4), 4.11 (d, *J* = 8.2 Hz, 1H, H-1), 4.07 (dd, *J* = 7.3, 5.4 Hz, 1H, H-3), 3.87 (td, *J* = 6.1, 2.1 Hz, 1H, H-5), 3.72 (d, *J* = 6.1 Hz, 2H, 2x H-6), 3.60 – 3.50 (m, 4H, H-2, CH_3 OMe), 3.24 (s, 3H, CH_3 OMe), 2.80 (d, *J* = 2.3 Hz, 1H, OH), 1.52 (s, 3H, CH_3 isopropylidene), 1.38 – 1.36 (m, 6H, 2x CH_3 isopropylidene), 1.34 (s, 3H, CH_3 isopropylidene) ^{13}C NMR (101 MHz, $CDCl_3$) δ 110.2 (C_q isopropylidene), 103.3 (C-1), 100.2 (C_q isopropylidene), 78.9 (C-3), 73.8 (C-2, C-4), 72.6 (C-5), 60.4 (C-6), 56.9, 48.6 (CH_3 OMe), 28.2, 26.3, 24.5, 24.5 (CH_3 isopropylidene). Spectra in agreement with literature[77]

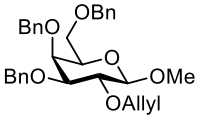
Methyl 2-*O*-allyl-3,4-*O*-isopropylidene-6-(1'-methoxy-1'-methyl)ethyl-β-D-galactopyranoside (S51)



Methyl 3,4-*O*-isopropylidene-6-(1'-methoxy-1'-methyl)ethyl-β-D-galactopyranoside (**S50)** 4.75 g, 15.5 mmol) was dissolved in DMF and allyl bromide (2 mL, 23.3 mmol, 1.5 eq) and sodium hydride (60% dispersion in mineral oil, 0.93 g, 23.3 mmol, 1.5 eq) were added. When TLC shows

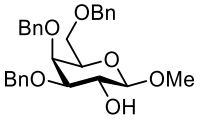
full conversion, the reaction was quenched with water. The aquatic phase was extracted twice with diethyl ether. Combined organic phases were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (10% acetone in pentane with 1% triethylamine) to provide the title compound as colourless oil. Yield: 3.79g, 10.9 mmol, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (ddt, *J* = 17.3, 10.4, 5.8 Hz, 1H, CH_2-C*H*=CH_2), 5.30 (dq, *J* = 17.2, 1.7 Hz, 1H, CH_2-CH=C*H*H), 5.18 (dq, *J* = 10.4, 1.3 Hz, 1H, CH_2-CH=CH*H*), 4.33 – 4.21 (m, 2H, C*H*$_2$-CH=CH_2), 4.18 (d, *J* = 8.1 Hz, 1H, H-1), 4.17 – 4.15 (m, 1H, H-4), 4.11 (dd, *J* = 6.8, 5.5 Hz, 1H, H-3), 3.82 (td, *J* = 6.2, 2.0 Hz, 1H, H-5), 3.70 (dd, *J* = 6.0, 0.9 Hz, 2H, 2x H-6), 3.53 (s, 3H, CH_3 OMe), 3.34 (dd, *J* = 8.0, 6.8 Hz, 1H, H-2), 3.24 (s, 3H, CH_3 OMe), 1.51 (s, 3H, CH_3 isopropylidene), 1.37 (s, 3H, CH_3 isopropylidene), 1.36 (s, 3H, CH_3 isopropylidene), 1.33 (s, 3H, CH_3 isopropylidene) ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9 (CH_2-*C*H=CH_2), 117.3 (CH_2-CH=*C*H$_2$), 109.8 (C_q isopropylidene), 103.6 (C-1), 100.1 (C_q isopropylidene), 79.6 (C-2), 79.1 (C-3), 73.9 (C-4), 72.5 (*C*H$_2$-CH=CH_2), 72.1 (C-5), 60.4 (C-6), 56.6, 48.5 (CH_3 OMe), 27.9, 26.3, 24.4, 24.4 (CH_3 isopropylidene). Spectra in agreement with literature.[78]

Methyl 2-*O*-allyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (S52)



Methyl 2-*O*-allyl-3,4-*O*-isopropylidene-6-(1'-methoxy-1'-methyl)ethyl-β-D-galactopyranoside (**S51**, 1.5 g, 4.33 mmol) and PTSA-H_2O (82 mg, 0.43 mmol, 0.1 eq) were dissolved in methanol and heated to 50 °C. When TLC shows full removal of isopropylidenes, the reaction is quenched with Et_3N (0.12 mL, 0.87 mmol, 0.2 eq) and concentrated under reduced pressure. After residual methanol and water were removed by azeotropic distillation with toluene, the residue was dissolved in DMF. Benzyl bromide (2.31 mL, 19.5 mmol, 4.5 eq) and NaH (60% dispersion in mineral oil, 779 mg, 19.5 mmol, 4.5 eq) were added. When TLC shows full conversion, the reaction was quenched with water and extracted with diethyl ether. The organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified over silica (10% EtOAc in pentane), yielding the title compound as colourless oil. Yield: 1.67 g, 3.30 mmol, 76% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.21 (m, 15H, CH_{arom}), 5.97 (ddt, *J* = 17.3, 10.4, 5.8 Hz, 1H, CH_2-C*H*=CH_2), 5.28 (dt, *J* = 17.3, 1.7 Hz, 1H, CH_2-CH=C*H*H), 5.15 (dq, *J* = 10.3, 1.3 Hz, 1H, CH_2-CH-CH*H*), 4.92 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.76 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.70 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.61 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 4.44 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.43 – 4.33 (m, 2H, C*H*H-CH=CH_2, CH*H* Bn), 4.28 – 4.18 (m, 2H, H-1, CH*H*-CH=CH_2), 3.86 (dd, *J* = 3.0, 1.0 Hz, 1H, H-4), 3.67 (dd, *J* = 9.7, 7.6 Hz, 1H, H-2), 3.60 – 3.56 (m, 2H, 2x H-6), 3.55 – 3.49 (m, 4H, H-5, CH_3 OMe), 3.46 (dd, *J* = 9.8, 2.9 Hz, 1H, H-3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 138.7, 138.1 (C_q), 135.5 (CH_2-*C*H=CH_2), 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.7, 127.7, 127.6 (CH_{arom}), 116.8 (CH_2-CH=*C*H$_2$), 104.9 (C-1), 82.2 (C-3), 79.4 (C-2), 74.5, 74.1 (CH_2 Bn), 73.7 (*C*H$_2$-CH=CH_2), 73.6 (C-4), 73.5 (C-5), 73.2 (CH_2 Bn), 69.0 (C-6), 57.1 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{31}H_{36}O_6NH_4$ 522.28501, found 522.28412.

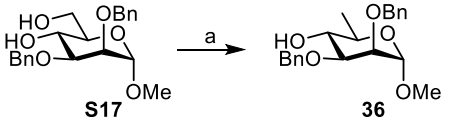
Methyl 3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (35)



Methyl 2-*O*-allyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (**S52**, 1.6 g, 3.17 mmol) and DMBA (990 mg, 6.34 mmol, 2 eq) were dissolved in methanol and heated to 40 °C. After degassing with N_2 for 30 min, $Pd(Ph_3P)_4$ (183 mg, 0.159 mmol, 0.05 eq) was added. When TLC shows full conversion, the reaction mixture concentrated under reduced pressure. The residue was dissolved in diethyl ether and washed twice with sat. aq. $NaHCO_3$. The organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified over silica (30% EA in pentane), yielding the title compound as yellowish powder. Yield: 1.25 g, 2.69 mmol, 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 6.98 (m, 15H, CH_{arom}), 4.88 (d, *J* = 11.6 Hz, 1H, C*H*H Bn) 4.72 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.66 – 4.57 (m, 2H, 2x CH*H* Bn), 4.48 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.43 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.18 (d, *J* = 7.6 Hz, 1H, H-1), 4.00 – 3.89 (m, 2H, H-2, H-4), 3.66 – 3.56 (m, 3H, H-5, 2x H-6), 3.52 (s, 3H, CH_3 OMe), 3.43 (dd, *J* = 9.8, 2.8 Hz, 1H, H-3), 2.50 (d, *J* = 2.0 Hz, 1H, OH) ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 138.1, 137.9 (C_q), 128.6, 128.5, 128.3, 128.3, 128.0, 127.9, 127.8, 127.7 (CH_{arom}), 104.2 (C-1), 82.1 (C-3), 74.6 (CH_2 Bn), 73.8 (C-5), 73.7 (CH_2 Bn), 72.8 (C-4), 72.4 (CH_2 Bn), 71.3 (C-4), 68.8 (C-6), 57.1 (CH_3 OMe); spectra in agreement with literature.[79]

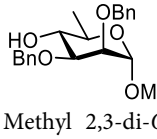
Rhamnose acceptors

Preparation of acceptor **36**



***Scheme S19**: preparation of acceptor **36**: reagents and conditions: a) i: TsCl, pyridine, ii: $LiAlH_4$, THF, reflux, 52% over 2 steps*

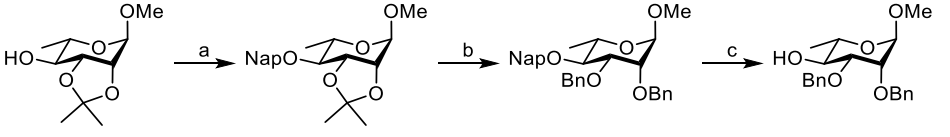
Methyl 2,3-di-*O*-benzyl-α-D-rhamnopyranoside (36)



Methyl 2,3-di-*O*-benzyl-α-D-mannopyranoside (**S17**, 1.80 g, 4.81 mmol, 1 eq) and TsCl (1.1 g, 5.77 mmol, 1.2 eq) were dissolved in 30 ml pyridine and stirred at RT overnight. The reaction mixture was diluted in EtOAc and washed three times with 1M aq. HCl. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to obtain crude intermediate. The crude intermediate was dissolved in 30 ml THF and a solution of $LiAlH_4$ (2.4 M in THF, 8.01 ml, 19.22 mmol, 4 eq) was slowly added. The reaction mixture was refluxed for 10 min, set to cool down to RT and quenched with 1M aq. HCl and extracted with EtOAc. The organic layer was washed once with 1M aq. HCl and twice aq. Bicarb solution. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The Purification was

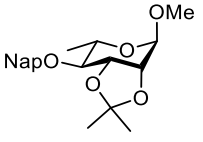
performed on flash column chromatography (8/2 pentane/EtOAc) to provide the title compound as an oil. Yield: 0.88 g, 2.50 mmol, 52%. $[\alpha]_D^{25}$ = -10.9° (c = 0.34, $CHCl_3$); IR (thin film): 698, 738, 1027, 1059, 1268, 1367, 1454; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 10H, CH_{arom}), 4.74 – 4.66 (m, 2H, H-1, C*H*H Bn), 4.63 (d, *J* = 12.3 Hz, 1H, C*H*H Bn), 4.56 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.41 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 3.79 (dd, *J* = 3.1, 1.8 Hz, 1H, H-2), 3.77 – 3.68 (m, 1H, H-4), 3.67 – 3.56 (m, 2H, H-3, H-5), 3.32 (s, 3H, CH_3 OMe), 2.33 (s, 1H, OH), 1.33 (d, *J* = 6.1 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 138.2 (C_q), 128.6, 128.5, 128.0, 127.9, 127.8, 127.8, 127.8 (CH_{arom}), 99.2 (C-1), 79.9 (C-3), 73.8 (C-2), 72.7 (CH_2 Bn), 71.7 (C-4), 71.5 (CH_2 Bn), 68.3 (C-5), 54.8 (CH_3 OMe), 17.9 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{21}H_{26}O_5Na$ 381.16725, found 381.16640.

Preparation of acceptor **37**



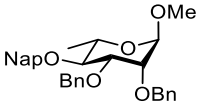
***Scheme S20**: preparation of acceptor **37**: reagents and conditions: a) NapBr, NaH, DMF, 71%; b) i: PTSA, methanol, 60 °C, ii: BnBr, NaH, DMF, 70% over 2 steps; DDQ, DCM/H_2O (9:1), 79%*

Methyl 2,3-*O*-isopropylidene-4-*O*-(2-naphthyl)methyl-α-L-rhamnopyranoside (S54)



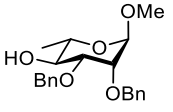
Methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside[80] (**S53**, 4.00 g, 18.3 mmol) was dissolved in DMF and cooled to 0 °C after which NaH (60% dispersion in mineral oil, 953 mg, 23.8 mmol, 1.3 eq) was added. After stirring for 10 minutes, 2-(Bromomethyl)naphthalene (5.27 g, 23.8 mmol, 1.3 eq) was added. The reaction mixture was allowed to warm to RT and upon completion (as indicated by TLC) quenched with water. The aqueous phase was extracted twice with diethyl ether, the combined organic phases were dried with $MgSO_4$ and concentrated. The residue is purified over silica (3% EtOAc in pentane), yielding the desired product as yellow oil. Yield: 4.68 g, 13.1 mmol, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.76 (m, 4H, CH_{arom}), 7.53 – 7.35 (m, 3H, CH_{arom}), 5.05 (d, *J* = 11.8 Hz, 1H, C*H*H Nap), 4.85 (app. s, 1H, H-1), 4.79 (d, *J* = 11.8 Hz, 1H, CH*H* Nap), 4.29 (dd, *J* = 7.1, 5.8 Hz, 1H, H-3), 4.14 (d, *J* = 5.8 Hz, 1H, H-2), 3.69 (dq, *J* = 9.7, 6.2 Hz, 1H, H-5), 3.35 (s, 3H, CH_3 OMe), 3.25 (dd, *J* = 9.8, 7.1 Hz, 1H, H-4), 1.50 (s, 3H, CH_3 isopropylidene), 1.38 (s, 3H, CH_3 isopropylidene), 1.31 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 133.3, 133.1 (C_q), 128.7, 128.5, 128.1, 128.0, 127.8, 127.6, 127.5, 126.9, 126.2, 126.1, 126.0, 125.9, 125.6 (CH_{arom}), 109.3 (C_q isopropylidene), 98.1 (C-1), 81.1 (C-4), 78.8 (C-3), 76.1 (C-2), 73.0 (CH_2 Nap), 64.5 (C-5), 54.9 (CH_3 OMe), 28.1, 26.4 (CH_3 isopropylidene), 18.0 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{21}H_{26}O_5NH_4$ 381.16725, found 381.16670.

Methyl 2,3-di-*O*-benzyl-4-*O*-(2-naphtyl)mehtyl-α-L-rhamnopyranoside (S55)



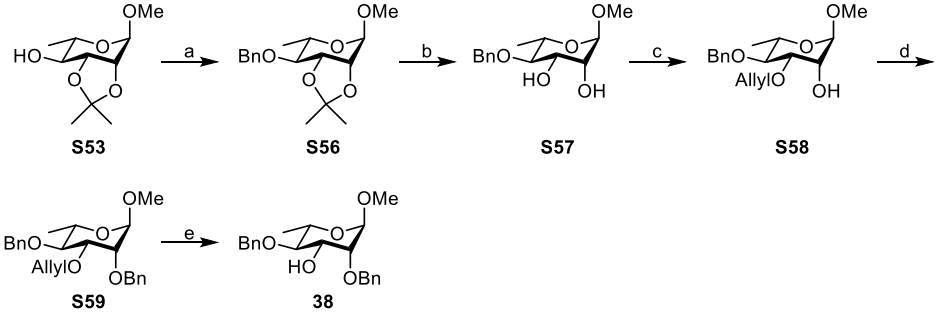
Methyl 2,3-*O*-isopropylidene-4-*O*-(2-naphthyl)methyl-α-L-rhamnopyranoside (**S54**, 1.40 g, 3.91 mmol) was dissolved in methanol with PTSA-H_2O (74 mg, 0.39 mmol, 0.1 eq) and heated to 60 °C. When TLC shows full removal of the isopropylidene, the reaction is quenched with triethylamine (0.13 mL, 0.98 mmol, 0.2 eq) and concentrated under reduced pressure. The residue is coevaporated with toluene and dissolved in DMF. The resulting solution is cooled to 0 °C, after which NaH (60% dispersion in mineral oil, 469 mg, 11.7 mmol, 3 eq) was added. After stirring for 10 minutes, benzyl bromide (1.93 mL, 11.7 mmol, 3 eq) was added. The reaction mixture was allowed to warm to RT and upon completion (as indicated by TLC) quenched with water. The aqueous phase was extracted twice with diethyl ether, the combined organic phases were dried with $MgSO_4$ and concentrated. The residue is purified over silica (5→10% EtOAc in pentane), yielding the desired product as yellowish oil. Yield: 1.365 g, 2.74 mmol, 70% over 2 steps.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.72 (m, 4H, CH_{arom}), 7.47 – 7.41 (m, 3H, CH_{arom}), 7.40 – 7.25 (m, 10H, CH_{arom}), 5.10 (d, *J* = 11.1 Hz, 1H, C*H*H Bn/Nap), 4.81 (d, *J* = 11.2 Hz, 1H, CH*H* Bn/Nap), 4.77 – 4.70 (m, 2H, CH_2 Bn/Nap), 4.67 (d, *J* = 1.8 Hz, 1H, H-1), 4.62 (s, 2H, CH_2 Bn/Nap), 3.88 (dd, *J* = 9.0, 3.1 Hz, 1H, H-3), 3.80 (dd, *J* = 3.2, 1.9 Hz, 1H, H-2), 3.72 – 3.67 (m, 2H, H-4, H-5), 3.29 (s, 3H, CH_3 OMe), 1.37 (d, *J* = 5.7 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.4, 136.3, 133.4, 133.0 (C_q), 128.5, 128.1, 128.1, 128.0, 127.8, 127.7, 127.6, 126.6, 126.2, 126.1, 125.9 (CH_{arom}), 99.2 (C-1), 80.6 (C-4), 80.3 (C-3), 75.5 (CH_2 Bn/Nap), 74.8 (C-2), 72.9, 72.2 (CH_2 Bn/Nap), 68.0 (C-5), 54.7 (CH_3 OMe), 18.2 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{34}O_5NH_4$ 516.27445, found 516.27370.

Methyl 2,3-di-*O*-benzyl-4-*O*-(2-naphtyl)mehtyl-α-L-rhamnopyranoside (37)



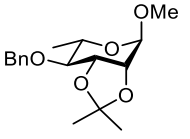
Methyl 2,3-di-*O*-benzyl-4-*O*-(2-naphtyl)mehtyl-α-L-rhamnopyranoside (**S55**, 1.30 g, 2.61 mmol) was dissolved in 20 mL 9:1 DCM/water, after which DDQ (1.184 g, 5.21 mmol, 2 eq) was added. When TLC shows full conversion, the reaction mixture is diluted with DCM and washed twice with sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue is purified over silica, yielding the title compound as colourless oil. Yield: 740 mg, 2.07 mmol, 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 10H, CH_{arom}), 4.74 – 4.68 (m, 2H, H-1, C*H*H Bn), 4.64 (d, *J* = 12.3 Hz, 1H, CH*H* Bn), 4.56 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.41 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 3.79 (dd, *J* = 3.1, 1.8 Hz, 1H, H-2), 3.72 (td, *J* = 9.3, 1.6 Hz, 1H, H-4), 3.66 – 3.59 (m, 2H, H-3, H-5), 3.33 (s, 3H, CH_3 OMe), 2.31 (d, *J* = 1.9 Hz, 1H, OH), 1.33 (d, *J* = 6.1 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 138.2 (C_q), 128.7, 128.5, 128.0, 128.0, 127.9, 127.9 (CH_{arom}), 99.2 (H-1), 79.9 (H-3), 73.8 (H-2), 72.8 (CH_2 Bn), 71.8 (C-4), 71.6 (CH_2 Bn), 68.3 (C-5), 54.9 (CH_3 OMe), 17.9 (C-6). spectra in agreement with literature.[81]

Preparation of acceptor **38**



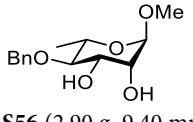
Scheme S21*: preparation of acceptor* ***38****: reagents and conditions: a) BnBr, NaH, DMF 81%; b) MeOH, PTSA,* 50 °C *,93%; c) i: DBTO, toluene, reflux, ii: CsF, allyl bromide, DMF, 93% over 2 steps; d) BnBr, NaH, DMF, 80%; e) Pd(Ph₃P)₄, DMBA, MeOH,* 40 °C, *84%*

Methyl 4-*O*-benzyl-2,3-*O*-ispropylidene-α-L-rhamnopyranoside (S56)



S53 (2.62 g, 12 mmol) was dissolved in DMF and cooled to 0 °C, after which NaH (60% dispersion in mineral oil, 720 mg, 18 mmol, 1.5 eq) was added. The solution was stirred for 10 minutes at 0 °C, benzyl bromide (2.14 mL, 18 mmol, 1.5 eq) was added and the reaction mixture was allowed to warm to RT. When TLC shows full conversion of the starting material, the reaction is quenched with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (10% diethyl ether in pentane), yielding the desired product as colourless oil. Yield: 2.99 g, 9.69 mmol, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 5H, CH_{arom}), 4.90 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.85 (app. s, 1H, H-1), 4.62 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.25 (dd, *J* = 7.1, 5.8 Hz, 1H, H-3), 4.12 (dd, *J* = 5.8, 0.7 Hz, 1H, H-2), 3.66 (dq, *J* = 9.8, 6.2 Hz, 1H, H-5), 3.35 (s, 3H, CH_3 OMe), 3.21 (dd, *J* = 9.8, 7.1 Hz, 1H, H-4), 1.50 (s, 3H, CH_3 isopropylidene), 1.37 (s, 3H, CH_3 isopropylidene), 1.29 (d, *J* = 6.2 Hz, 3H, H-6) ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4 (C_q), 128.3, 128.0, 127.6 (CH_{arom}), 109.2 (C_q isopropylidene), 98.1 (C-1), 81.1 (C-4), 78.7 (C-3), 76.0 (C-2), 72.9 (CH_2 Bn), 64.4 (C-5), 54.8 (CH_3 OMe), 28.0 (CH_3 isopropylidene), 26.3 (CH_3 isopropylidene), 17.9 (C-6). Spectra in agreement with literature.[82]

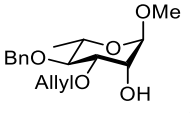
Methyl 4-*O*-benzyl-α-L-rhamnopyranoside (S57)



S56 (2.90 g, 9.40 mmol) was dissolved in methanol with PTSA-H_2O (179 mg, 0.94 mmol, 0.1 eq) and heated to 50 °C. When TLC shows full conversion, the reaction is quenched with triethylamine (0.26 mL, 1.88 mmol, 0.2 eq) and concentrated under reduced pressure. The residue is purified over silica (25% acetone in pentane) yielding the title compound as white powder. Yield: 2.437 g, 8.75 mmol, 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.14 (m, 5H,

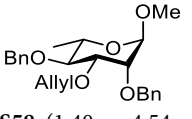
CH_{arom}), 4.76 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.71 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.63 (d, *J* = 1.4 Hz, 1H, H-1), 3.93 – 3.84 (m, 2H, H-2, H-3), 3.69 (dq, *J* = 9.5, 6.3 Hz, 1H, H-5), 3.39 – 3.29 (m, 4H, CH_3 OMe, H-4), 2.84 (d, *J* = 3.8 Hz, 1H, OH), 2.67 (d, *J* = 5.2 Hz, 1H, OH), 1.35 (d, *J* = 6.3 Hz, 3H, H-6) ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4 (C_q), 128.7, 128.1, 128.0 (CH_{arom}), 100.5 (C-1), 81.7 (C-4), 75.1 (CH_2 Bn), 71.6, 71.2 (C-2 and C-3), 67.1 (C-5), 54.9 (CH_3 OMe), 18.1 (C-6). Spectra in agreement with literature.[82]

Methyl 3-*O*-allyl-4-*O*-benzyl-α-L-rhamnopyranoside (S58)



S57 (1.43 g, 5 mmol) and dibutyltin oxide (1.618 g, 6.5 mmol, 1.3 eq) were refluxed in toluene for 2 hr with a Dean-Stark setup. The reaction mixture was concentrated under reduced pressure and the residue dissolved in DMF, after which Caesium fluoride (987 mg, 6.5 mmol, 1.3 eq) and allyl bromide (0.56 mL, 6.5 mmol, 1.3 eq) were added. The reaction mixture was stirred overnight, diluted with water and extracted twice with diethyl ether. Combined organic phases were dried and concentrated under reduced pressure. The residue was purified using flash chromatography (20% EtOAc in pentane) yielding the product as colourless oil. Yield: 1.428 g, 4.63 mmol, 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H, CH_{arom}), 5.95 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H, CH_2-C*H*=CH_2), 5.32 (dq, *J* = 17.2, 1.6 Hz, 1H, CH_2-CH=C*H*H), 5.20 (dq, *J* = 10.4, 1.4 Hz, 1H, CH_2-CH=CH*H*), 4.87 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.70 (d, *J* = 1.6 Hz, 1H, H-1), 4.63 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.19 (ddt, *J* = 12.7, 5.8, 1.4 Hz, 1H, C*H*H-CH=CH_2), 4.13 (ddt, *J* = 12.6, 5.5, 1.5 Hz, 1H, CH*H*-CH=CH_2), 4.00 (dt, *J* = 3.6, 1.8 Hz, 1H, H-2), 3.74 – 3.63 (m, 2H, H-3, H-5), 3.41 (t, *J* = 9.3 Hz, 1H, H-4), 3.34 (s, 3H, CH_3 OMe), 2.53 (d, *J* = 2.0 Hz, 1H, OH), 1.31 (d, *J* = 6.2 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5 (C_q), 134.6 (CH_2-CH=CH_2), 128.4, 128.0, 127.7 (CH_{arom}), 117.4 (CH_2-CH=*C*H_2), 100.0 (C-1), 79.9 (C-4), 79.6 (C-3), 75.3 (CH_2 Bn), 70.9 (*C*H_2-CH=CH_2), 68.6 (C-2), 67.1 (C-5), 54.8 (CH_3 OMe), 17.9 (C-6). Spectra in agreement with literature.[83]

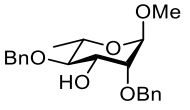
Methyl 3-*O*-allyl-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (S59)



S58 (1.40 g, 4.54 mmol) was dissolved in DMF and cooled to 0 °C, after which NaH (60% dispersion in mineral oil, 272 mg, 6.81 mmol, 1.5 eq) was added. The solution was stirred for 10 minutes at 0 °C, benzyl bromide (0.81 mL, 6.81 mmol, 1.5 eq) was added and the reaction mixture was allowed to warm to RT. When TLC shows full conversion of the starting material, the reaction is quenched with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (10% diethyl ether in pentane), yielding the desired product as colourless oil. Yield: 1.454 g, 3.65 mmol, 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.25 (m, 10H, CH_{arom}), 5.93 (ddt, *J* = 17.3, 10.6, 5.4 Hz, 1H, CH_2-C*H*=CH_2), 5.32 (dq, *J* = 17.2, 1.7 Hz, 1H, CH_2-CH=C*H*H), 5.17 (dq, *J* = 10.5, 1.5 Hz, 1H, CH_2-CH=CH*H*), 4.94 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.79 (d, *J* = 12.6 Hz, 1H, C*H*H Bn), 4.74 (d, *J* = 12.5 Hz, 1H, CH*H* Bn), 4.67 – 4.59 (m, 2H, CH*H* Bn, H-1), 4.08 (dq, *J* = 5.4, 1.4 Hz,

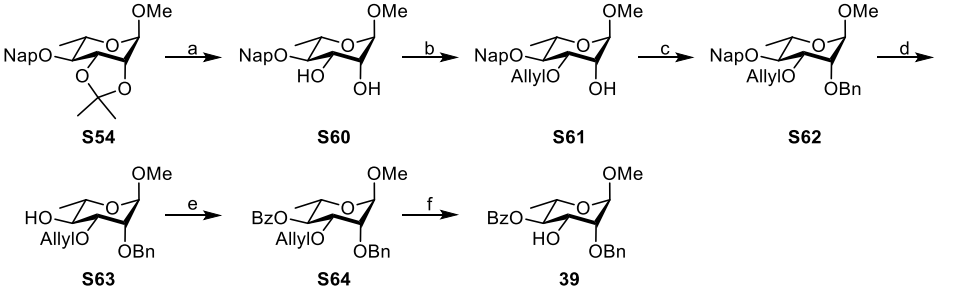
2H, C*H*$_2$-CH=CH$_2$), 3.77 – 3.69 (m, 2H, H-2, H-3), 3.68 – 3.60 (m, 1H, H-5), 3.59 – 3.54 (m, 1H, H-4), 3.29 (s, 3H, CH$_3$ OMe), 1.33 (d, *J* = 6.1 Hz, 3H, H-6) ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.8, 138.5 (C$_q$), 135.1 (CH$_2$-*C*H=CH$_2$), 128.5, 128.5, 128.1, 128.0, 127.8, 127.7 (CH$_{arom}$), 116.7 (CH$_2$-CH=CH$_2$), 99.2 (C-1), 80.5 (C-4), 79.9 (C-3), 75.5 (CH$_2$ Bn), 74.8 (C-2), 72.9 (CH$_2$ Bn), 71.1 (*C*H$_2$-CH=CH$_2$), 67.9 (C-5), 54.7 (CH$_3$ OMe), 18.1 (C-6). Spectra in agreement with literature.[84]

Methyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside (38)



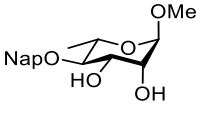
S59 (1.40 g, 3.51 mmol) and 1,3-dimethylbarbituric acid (1.097 g, 7.03 mmol, 2 eq) were dissolved in methanol, flushed with nitrogen and heated to 40 °C. Tetrakis(triphenylphosphine)palladium(0) (203 mg, 0.176 mmol, 0.05 eq) was added under a flow of nitrogen. When TLC shows full conversion, the reaction mixture was concentrated to ca. 20% of the original volume, diluted with ethyl acetate and wash twice with sat. aq. NaHCO$_3$. The organic phase was dried with MgSO$_4$ and concentrated under reduced pressure. The residue was purified over silica (15% acetone in pentane) yielding the title compound as colourless oil. Yield: 1.06 g, 2.96 mmol, 84 %. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 – 7.25 (m, 10H, CH$_{arom}$), 4.90 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.74 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.71 (d, *J* = 1.5 Hz, 1H, H-1), 4.65 (d, *J* = 11.1 Hz, 1H, CH*H* Bn), 4.58 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 3.92 (td, *J* = 9.2, 3.8 Hz, 1H, H-3), 3.71 (dd, *J* = 3.9, 1.6 Hz, 1H, H-2), 3.65 (dq, *J* = 9.5, 6.2 Hz, 1H, H-5), 3.37 – 3.25 (m, 4H, CH$_3$ OMe, H-4), 2.33 (d, *J* = 9.3 Hz, 1H, OH), 1.34 (d, *J* = 6.2 Hz, 3H, H-6) ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.7, 137.8 (C$_q$), 128.7, 128.5, 128.2, 128.1, 128.0, 127.8 (CH$_{arom}$), 98.0 (C-1), 82.4 (C-4), 78.7 (C-2), 75.1 (CH$_2$ Bn), 73.1 (CH$_2$ Bn), 71.7 (C-3), 67.1 (C-5), 54.8 (CH$_3$ OMe), 18.1 (C-6). Spectra in agreement with literature.[84]

Preparation of acceptor **39**



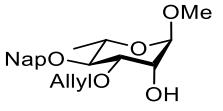
***Scheme S22**: preparation of acceptor **39**: reagents and conditions: a) PTSA, MeOH, 50 °C, 77%; b) i: DBTO, toluene, reflux, ii: allyl bromide, CsF, DMF, 100% over 2 steps; c) BnBr, NaH, DMF, 78%; d) DDQ, DCM/H$_2$O (9:1), 92%; e) BzCl, pyridine 87%; f) Pd(Ph$_3$P)$_4$, DMBA, MeOH, 40 °C, 100%*

Methyl 4-*O*-(2-naphthyl)methyl-α-L-rhamnopyranoside (S60)



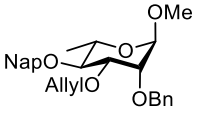
2,3-*O*-isopropylidene-4-*O*-(2-naphthyl)methyl-α-L-rhamnopyranoside (**S54**, 2.56 g, 7.14 mmol) and PTSA-H_2O (136 mg, 0.71 mmol, 0.1 eq) were dissolved in MeOH and heated to 50 °C. When TLC showed full conversion, the reaction was quenched with trimethylamine (0.2 mL, 1.43 mmol, 0.2 eq) and concentrated under reduced pressure. The residue is purified over silica (50% EA/pentane), yielding the title compound as white powder. Yield: 1.76 g, 5.53 mmol, 77%. ^{1}H NMR (400 MHz, DMSO) δ 7.92 – 7.78 (m, 4H, CH_{arom}), 7.50 (td, *J* = 5.9, 3.0 Hz, 3H, CH_{arom}), 5.02 (d, *J* = 11.8 Hz, 1H, C*H*H Nap), 4.99 (d, *J* = 4.4 Hz, 1H, OH), 4.88 (d, *J* = 6.9 Hz, 1H, OH), 4.75 (d, *J* = 11.8 Hz, 1H, CH*H* Nap), 4.46 (d, *J* = 1.4 Hz, 1H, H-1), 3.68 – 3.62 (m, 2H, H-2, H-3), 3.48 (dq, *J* = 9.5, 6.2 Hz, 1H, H-5), 3.31 (t, *J* = 9.2 Hz, 1H, H-4), 3.23 (s, 3H, CH_3 OMe), 1.17 (d, *J* = 6.3 Hz, 3H, H-6); ^{13}C NMR (101 MHz, DMSO) δ 136.8, 132.8, 132.4 (C_q), 127.7, 127.6, 127.6, 126.2, 126.1, 125.9, 125.8 (CH_{arom}), 101.0 (C-1), 80.8 (C-4), 73.8 (CH_2 Nap), 71.1, 70.8 (C-2, C-3), 66.9 (C-5), 54.1 (CH_3 OMe), 18.1 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{18}H_{22}O_5Na$ 341.13594, found 341.13544.

Methyl 3-*O*-allyl-4-*O*-(2-naphthyl)methyl-α-L-rhamnopyranoside (S61)



Methyl 4-*O*-(2-naphthyl)methyl-α-L-rhamnopyranoside (**S60**, 1.59 g, 5 mmol) and dibutyltin oxide (1.49 g, 6 mmol, 1.2 eq) are suspended in toluene and heated to reflux in a Dean-Stark setup for 2 hr, after which the reaction mixture was concentrated under reduced pressure. The residue is dissolved in DMF after which caesium fluoride (911 mg, 6 mmol, 1.2 eq) and allyl bromide (0.52 mL, 6 mmol, 1.2 eq) were added. After overnight stirring at room temperature, the reaction mixture was diluted with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. Silica chromatography (20% EtOAc in pentane) yields the title compound in quantitative yield as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 4H, CH_{arom}), 7.49 – 7.44 (m, 3H, CH_{arom}), 5.95 (ddt, *J* = 17.2, 10.3, 5.6 Hz, 1H, CH_2-C*H*=CH_2), 5.32 (dq, *J* = 17.2, 1.6 Hz, 1H, CH_2-CH=C*H*H), 5.20 (dq, *J* = 10.4, 1.4 Hz, 1H, CH_2-CH=CH*H*), 5.02 (d, *J* = 11.0 Hz, 1H, C*H*H Nap), 4.79 (d, *J* = 11.2 Hz, 1H, CH*H* Nap), 4.71 (d, *J* = 1.7 Hz, 1H, H-1), 4.21 (ddt, *J* = 12.7, 5.7, 1.4 Hz, 1H, C*H*H-CH=CH_2), 4.15 (ddt, *J* = 12.7, 5.6, 1.5 Hz, 1H, CH*H*-CH=CH_2), 4.01 (dt, *J* = 3.6, 1.9 Hz, 1H, H-2), 3.80 – 3.66 (m, 2H, H-3, H-5), 3.47 (t, *J* = 9.4 Hz, 1H, H-4), 3.35 (s, 3H, CH_3 OMe), 2.59 (d, *J* = 2.1 Hz, 1H, OH), 1.34 (d, *J* = 6.2 Hz, 3H, H-5); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1 (C_q), 134.7 (CH_2-*C*H=CH_2), 133.4, 133.1 (C_q), 128.2, 128.0, 127.8, 126.7, 126.1, 126.1, 126.0 (CH_{arom}), 117.5 (CH_2-CH=*C*H_2), 100.2 (C-1), 80.0 (C-4), 79.7 (C-3), 75.5 (CH_2 Nap), 71.0 (*C*H_2-CH=CH_2), 68.7 (C-2), 67.2 (C-5), 54.9 (CH_3 OMe), 18.1 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{21}H_{26}O_5Na$ 381.16725, found 381.166652

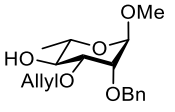
Methyl 3-*O*-allyl-2-*O*-benzyl-4-*O*-(2-naphthyl)methyl-α-L-rhamnopyranoside (S62)



S61 (1.70 g, 4.74 mmol) was dissolved in DMF and cooled to 0 °C after which NaH (60% dispersion in mineral oil, 285 mg, 7.11 mmol, 1.5 eq) was added. After stirring for 10 minutes, benzyl bromide (0.84 mL, 7.11 mmol, 1.5 eq) was added. The reaction mixture was allowed to

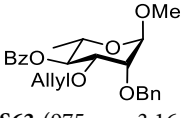
warm to RT and upon completion (as indicated by TLC) quenched with water. The aqueous phase was extracted twice with diethyl ether, the combined organic phases were dried with $MgSO_4$ and concentrated. The residue is purified over silica (10% diethyl ether in pentane), yielding the desired product as colourless oil. Yield: 1.67 g, 3.72 mmol, 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.72 (m, 4H, CH_{arom}), 7.53 – 7.25 (m, 8H, CH_{arom}), 5.95 (ddt, *J* = 17.2, 10.6, 5.4 Hz, 1H, CH_2-CH=CH_2), 5.33 (dq, *J* = 17.2, 1.7 Hz, 1H, CH_2-CH=C*H*H), 5.18 (dq, *J* = 10.4, 1.5 Hz, 1H, CH_2-CH=CH*H*), 5.10 (d, *J* = 11.2 Hz, 1H, C*H*H Bn/Nap), 4.86 – 4.71 (m, 3H, CH*H* Bn/Nap, CH_2 Bn/Nap), 4.65 (d, *J* = 1.5 Hz, 1H, H-1), 4.10 (dq, *J* = 5.3, 1.3 Hz, 2H, C*H*$_2$-CH=CH_2), 3.82 – 3.73 (m, 2H, H-2, H-3), 3.73 – 3.59 (m, 2H, H-4, H-5), 3.29 (s, 3H, CH_3 OMe), 1.36 (d, *J* = 5.9 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 136.4 (C_q), 135.1 (CH_2-*C*H=CH_2), 133.4, 133.1 (C_q), 128.5, 128.2, 128.0, 127.8, 126.6, 126.2, 126.1, 125.9 (CH_{arom}), 116.7 (CH_2-CH=*C*H$_2$), 99.2 (C-1), 80.6 (C-4), 80.0 (C-3), 75.5 (CH_2 Bn/Nap), 74.8 (C-2), 72.9 (CH_2 Bn/Nap), 71.1 (*C*H$_2$-CH=CH_2), 67.9 (C-5), 54.7 (CH_3 OMe), 18.2 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{28}H_{32}O_5NH_4$ 466.25880, found 466.25794.

Methyl 3-*O*-allyl-2-*O*-benzyl-α-L-rhamnopyranoside (S63)



S62 (1.6 g, 3.57 mmol) was dissolved in 20 mL 9:1 DCM/H_2O, after which DDQ (1.62 g, 7.13 mmol, 2 eq) was added. When TLC shows full conversion, the reaction mixture was diluted with DCM and washed twice with sat. aq. Bicarb. The organic phase was dried and concentrated under reduced pressure. Silica chromatography (10% acetone in pentane) yield the title compound as yellowish oil. Yield: 1.01 g, 3.28 mmol, 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 5.90 (ddt, *J* = 17.1, 10.3, 5.6 Hz, 1H), 5.28 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.19 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.76 – 4.58 (m, 3H), 4.01 (ddt, *J* = 12.5, 5.5, 1.5 Hz, 1H), 3.90 (ddt, *J* = 12.6, 5.8, 1.4 Hz, 1H), 3.75 (dd, *J* = 3.1, 1.8 Hz, 1H), 3.69 (td, *J* = 9.3, 2.0 Hz, 1H), 3.63 (dq, *J* = 9.3, 6.0 Hz, 1H), 3.53 (dd, *J* = 9.2, 3.1 Hz, 1H), 2.43 (d, *J* = 2.0 Hz, 1H), 1.34 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 134.5, 128.4, 128.0, 127.8, 117.5, 99.2, 79.4, 73.4, 72.6, 71.6, 70.3, 68.2, 54.8, 17.8; HRMS: $[M+Na]^+$ calcd for $C_{17}H_{24}O_5Na$ 331.15160, found 331.15103.

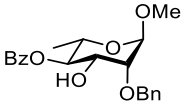
Methyl 3-*O*-allyl-4-*O*-benzoyl-2-*O*-benzyl-α-L-rhamnopyranoside (S64)



S63 (975 mg, 3.16 mmol) is dissolved in 5 mL pyridine after which benzoyl chloride (0.55 mL, 4.74 mmol, 1.5 eq) was added slowly. When TLC shows that the reaction is complete, the mixture is diluted with ethyl acetate and washed with 2 x 100 mL 1M aq. HCl and with 100 mL sat. aq. $NaHCO_3$. The organic phase was dried and concentrated under reduced pressure. The residue is purified with silica chromatography (5% → 10% ethyl acetate in pentane) to yield the desired compound as a colourless oil. Yield: 1.13 g, 2.74 mmol, 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 2H, CH_{arom}), 7.60 – 7.54 (m, 1H, CH_{arom}), 7.45 (dd, *J* = 8.4, 7.1 Hz, 2H, CH_{arom}), 7.42 – 7.38 (m, 2H, CH_{arom}), 7.36 – 7.32 (m, 2H, CH_{arom}), 7.30 – 7.26 (m, 1H, CH_{arom}), 5.72 (ddt, *J* = 17.2, 10.3, 5.5 Hz, 1H, CH_2-C*H*=CH_2), 5.44 (t, *J* = 9.7 Hz, 1H, H-4), 5.16 (dq, *J* = 17.2, 1.7 Hz, 1H, CH_2-

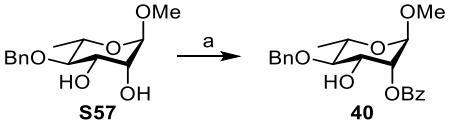
CH=C*H*H), 5.04 (dq, *J* = 10.4, 1.4 Hz, 1H, CH_2-CH=CH*H*), 4.85 (d, *J* = 12.5 Hz, 1H, C*H*H Bn), 4.75 (d, *J* = 12.5 Hz, 1H, CH*H* Bn), 4.71 (d, *J* = 1.8 Hz, 1H, H-1), 4.03 (ddt, *J* = 13.0, 5.4, 1.5 Hz, 1H, C*H*H-CH=CH_2), 3.92 (ddt, *J* = 13.1, 5.7, 1.5 Hz, 1H, CH*H*-CH=CH_2), 3.89 – 3.82 (m, 2H, H-3, H-5), 3.81 (dd, *J* = 3.2, 1.9 Hz, 1H, H-2), 3.36 (s, 3H, CH_3 OMe), 1.27 (d, *J* = 6.3 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (C=O), 138.4 (C_q), 134.8 (CH_2-*C*H=CH_2), 133.1 (CH_{arom}), 130.3 (C_q), 129.8, 128.5, 128.4, 128.1, 127.7 (CH_{arom}), 117.1 (CH_2-CH=*C*H_2), 99.8 (C-1), 77.2 (C-3), 74.6 (C-2), 73.8 (C-4), 73.2 (CH_2 Bn), 71.3 (*C*H_2-CH=CH_2), 67.0 (C-5), 55.0 (CH_3 OMe), 17.8 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{24}H_{28}O_6NH_4$ 430.22241, found 430.22153.

Methyl 4-*O*-benzoyl-2-*O*-benzyl-α-L-rhamnopyranoside (39)



Nr. (1.10 g, 2.67 mmol) and 1,3-Dimethylbarbituric acid (833 mg, 5.33 mmol, 2 eq) were dissolved in methanol. The solution was flushed with nitrogen and heated to 40 °C, after which $Pd(PPh_3)_4$ (154 mg, 0.133 mmol, 0.05 eq) was added under a flow of nitrogen. When TLC shows full conversion, the reaction mixture is cooled to RT, diluted with ethyl acetate and washed with sat. aq. $NaHCO_3$. The aqueous phase was extracted with ethyl acetate, combined organic phases were dried with $MgSO_4$ and concentrated under reduced pressure. The residue is purified over silica (30% diethyl ether in pentane), yielding the title compound in quantitative yield as a yellowish oil that solidifies over a few days. $[\alpha]_D^{25}$ = -0.29° (c = 0.34, $CHCl_3$); IR (thin film): 711, 1069, 1269, 1316, 1452, 1724; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.00 (m, 2H, CH_{arom}), 7.56 (ddt, *J* = 8.7, 7.0, 1.3 Hz, 1H, CH_{arom}), 7.47 – 7.41 (m, 2H, CH_{arom}), 7.39 – 7.29 (m, 5H, CH_{arom}), 5.14 (t, *J* = 9.8 Hz, 1H, H-4), 4.83 – 4.70 (m, 2H, H-1, C*H*H Bn), 4.62 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 3.98 (ddd, *J* = 11.0, 9.8, 3.7 Hz, 1H, H-3), 3.89 (dq, *J* = 9.7, 6.3 Hz, 1H, H-5), 3.78 (dd, *J* = 3.8, 1.6 Hz, 1H, H-2), 3.38 (s, 3H, CH_3 OMe), 2.40 (d, *J* = 11.0 Hz, 1H, OH), 1.27 (d, *J* = 6.3 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7 (C=O), 137.6 (C_q), 133.3 (CH_{arom}), 130.0 (C_q), 129.9, 128.7, 128.5, 128.2, 128.0 (CH_{arom}), 98.3 (C-1), 78.5 (C-2), 75.6 (C-3), 73.3 (CH_2 Bn), 69.9 (C-3), 66.1 (C-5), 55.1 (CH_3 OMe), 17.7 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{21}H_{24}O_6Na$ 395.14651, found 395.14590

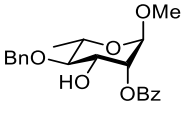
Preparation of acceptor **40**



S57 **40**

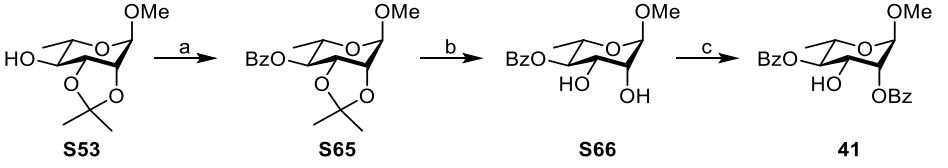
***Scheme S23**: preparation of acceptor **40**: reagents and conditions: a) BzCN, DMAP, DCM, -78 °C, 81%*

Methyl 2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (40)



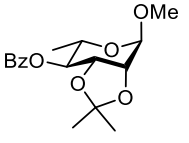
Nr. (805 mg, 3 mmol) and benzoyl cyanide (433 mg, 3.30 mmol, 1.1 eq) were dissolved in dichloromethane. 3A molecular sieves were added, the solution was stirred for 30 min at room temperature and subsequently cooled to -78 °C. DMAP (37 mg, 0.30 mmol, 0.1 eq) was added and the reaction mixture kept at that temperature for 2 hr after which it was slowly allowed to warm to RT. When TLC showed full conversion, the reaction was quenched with MeOH and sat aq. NH_4Cl, diluted with dichloromethane, washed with sat aq. NH_4Cl and sat aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (15% EA in pentane) yielding the title compound as colourless oil. Yield: 900 mg, 2.42 mmol, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 7.97 (m, 2H, CH_{arom}), 7.59 (ddt, *J* = 8.7, 6.9, 1.3 Hz, 1H, CH_{arom}), 7.53 – 7.43 (m, 2H, CH_{arom}), 7.40 – 7.28 (m, 5H, CH_{arom}), 5.33 (dd, *J* = 3.6, 1.7 Hz, 1H, H-2), 4.86 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.77 – 4.71 (m, 2H, CH*H* Bn, H-1), 4.20 (ddd, *J* = 9.0, 5.1, 3.5 Hz, 1H, H-3), 3.79 (dq, *J* = 9.5, 6.2 Hz, 1H, H-5), 3.46 (t, *J* = 9.4 Hz, 1H, H-4), 3.37 (s, 3H, CH_3 OMe), 2.28 (d, *J* = 5.1 Hz, 1H, OH), 1.40 (d, *J* = 6.3 Hz, 3H, H-6) ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4 (C=O), 138.3 (C_q), 133.5, 130.0 (CH_{arom}), 129.8 (C_q), 128.6, 128.6, 128.1, 128.0 (CH_{arom}), 98.5 (C-1), 81.8 (C-4), 75.2 (CH_2 Bn), 73.3 (C-2), 70.6 (C-3), 67.4 (C-5), 55.1 (CH_3 OMe), 18.3 (C-6). Spectra in agreement with literature.[83]

Preparation of acceptor **41**



***Scheme S24**: preparation of acceptor **41**: reagents and conditions: a) BzCl, pyridine, 100%; PTSA, MeOH, 50 °C, 78%; c) BzCN, DMAP, DCM, -78 °C, 44%*

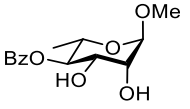
Methyl 4-*O*-benzoyl-2,3-isopropylidene-α-L-rhamnopyranoside (S65)



S53 (2.18 g, 10 mmol) was dissolved in 10 mL pyridine, after which benzoyl chloride (1.74 mL, 15 mmol, 1.5 eq) was added dropwise. When TLC shows full consumption of the starting material, the reaction mixture is diluted with ethyl acetate and washed twice with water. The organic phase is dried with $MgSO_4$ and concentrated under reduced pressure. Residual pyridine was removed by coevaporation with toluene. The residue was purified over silica (10% EtOAc in pentane) yielding the title compound in quantitative yield as colourless oil that slowly solidifies. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H, CH_{arom}), 7.60 – 7.50 (m, 1H, CH_{arom}), 7.44 (dd, *J* = 8.4, 7.1 Hz, 2H, CH_{arom}), 5.13 (dd, *J* = 10.1, 7.8 Hz, 1H, H-4), 4.96 (app. s, 1H, H-1), 4.34 (dd, *J* = 7.8, 5.4 Hz, 1H, H-3), 4.20 (dd, *J* = 5.4, 0.7 Hz, 1H, H-2), 3.87 (dq, *J* = 10.1, 6.3 Hz, 1H, H-5), 3.42 (s, 3H, CH_3 OMe), 1.63 (s, 3H, CH_3 isopropylidene), 1.36 (s, 3H, s, 3H, CH_3 isopropylidene), 1.23 (d, *J* = 6.4 Hz, 3H, H-6) ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (C=O), 133.3, 129.9, 128.5 (CH_{arom}), 110.0 (C_q isopropylidene), 98.2 (C-1), 76.1 (C-2), 76.0 (C-3), 75.1 (C-4), 64.1 (C-5), 55.1 (CH_3

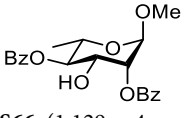
OMe), 27.9 (CH_3 isopropylidene), 26.5 (CH_3 isopropylidene), 17.2 (C-6). Spectra in agreement with literature.[85]

Methyl 4-*O*-benzoyl-α-L-rhamnopyranoside (S66)



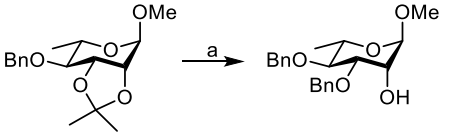
S65 (3.5 g, 10.9 mmol) was dissolved in methanol with PTSA-H_2O (207 mg, 1.09 mmol, 0.1 eq) and heated to 50 °C. When TLC shows full conversion, the reaction is quenched with triethylamine (0.31 mL, 2.17 mmol, 0.2 eq) and concentrated under reduced pressure. The residue is purified over silica (20% acetone in pentane) yielding the title compound as viscous colourless oil. Yield: 2.38 g, 8.43 mmol, 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 7.91 (m, 2H, CH_{arom}), 7.63 – 7.53 (m, 1H, CH_{arom}), 7.44 (dd, *J* = 8.6, 7.0 Hz, 2H, CH_{arom}), 5.09 (t, *J* = 9.3 Hz, 1H, H-4) 4.76 (d, *J* = 1.2 Hz, 1H, H-1), 4.04 – 3.99 (m, 2H, H-2, H-3), 3.94 (dq, *J* = 9.8, 6.3 Hz, 1H, H-5), 3.40 (s, 3H, CH_3 OMe), 1.28 (d, *J* = 6.3 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5 (C=O), 133.5, 130.0 (CH_{arom}), 129.6 (C_q), 128.6 (CH_{arom}), 100.7 (C-1), 76.1 (C-4), 71.0, 70.4 (C-2, C-3), 65.8 (C-5), 55.2 (CH_3 OMe), 17.7 (C-6). Spectra in agreement with literature.[86]

Methyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (41)



S66 (1.129g, 4 mmol) and benzoyl cyanide (557 mg, 4.40 mmol, 1.1 eq) were dissolved in dichloromethane. 3 Å molecular sieves were added, the solution was stirred for 30 min at room temperature and subsequently cooled to -78 °C. DMAP (49 mg, 0.40 mmol, 0.1 eq) was added and the reaction mixture kept at that temperature for 2 hr after which it was slowly allowed to warm to RT. When TLC showed full conversion, the reaction was quenched with MeOH and sat aq. NH_4Cl, diluted with dichloromethane, washed with sat aq. NH_4Cl and sat aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (15% EA in pentane) yielding the title compound as colourless oil. Yield: 672 mg, 1.74 mmol, 44% ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.05 (m, 4H, CH_{arom}), 7.64 – 7.57 (m, 2H, CH_{arom}), 7.52 – 7.44 (m, 4H, CH_{arom}), 5.38 (dd, *J* = 3.5, 1.7 Hz, 1H, H-2), 5.26 (t, *J* = 9.8 Hz, 1H, H-4), 4.87 (d, *J* = 1.6 Hz, 1H, H-1), 4.30 (ddd, *J* = 9.9, 8.1, 3.5 Hz, 1H, H-3), 4.11 – 3.99 (m, 1H, H-5), 3.45 (s, 3H, CH_3 OMe), 2.44 (d, *J* = 8.2 Hz, 1H, OH), 1.33 (d, *J* = 6.2 Hz, 3H, H-6) ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 166.2 (C=O), 133.7, 133.6, 130.0, 130.0 (CH_{arom}), 129.6, 129.5 (C_q), 128.7, 128.6 (CH_{arom}), 98.5 (C-1), 75.7 (C-4), 73.3 (C-2), 69.1 (C-3), 66.2 (C-5), 55.4 (CH_3 OMe), 17.8 (C-6). Spectra in agreement with literature.[87]

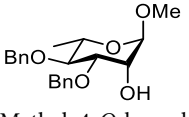
Preparation of acceptor **42**



S56 **42**

***Scheme S25**: preparation of acceptor **42**: reagents and conditions: a) i: PTSA, MeOH, 50 °C, ii: DBTO, toluene, reflux, iii: CsF, BnBr, DMF, 77% over 3 steps*

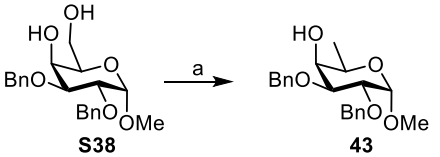
Methyl 3,4-di-*O*-benzyl-α-L-rhamnopyranoside (42)



Methyl 4-*O*-benzyl-2,3-*O*-ispropylidene-α-L-rhamnopyranoside (**S56**, 1.12 g, 3.63 mmol) and PTSA-H_2O (69 mg, 0.36 mmol, 0.1 eq) were dissolved in methanol. The reaction mixture was heated to 50 °C. When TLC shows full removal of the isopropylidene, triethylamine (0.1 mL, 0.73 mmol, 0.2 eq) was added and the mixture was concentrated under reduced pressure. The residue was dissolved in toluene with dibutyltin oxide (1.18 g, 4.72 mmol, 1.3 eq) and refluxed for 2.5 hr in a Dean-Stark setup. The reaction mixture was cooled to RT and concentrated under reduced pressure. The residue was dissolved in DMF and caesium fluoride (717 mg, 4.72 mmol, 1.3 eq) and benzyl bromide (0.56 mL, 4.72 mmol, 1.3 eq) were added. After 72 hr stirring, the reaction mixture was diluted with water and extracted twice with diethyl ether. Combined organic phases were dried with $MgSO_4$ and concentrated. The residue was purified over silica (10% Et_2O in pentane) yielding the title compound as colourless oil. Yield: 1.00 g, 2.79 mmol, 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 10H, CH_{arom}), 4.88 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.70 (d, *J* = 1.7 Hz, 1H, H-1), 4.68 (s, 2H, CH_2 Bn), 4.64 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.02 (dt, *J* = 3.6, 1.8 Hz, 1H, H-2), 3.82 (dd, *J* = 9.1, 3.4 Hz, 1H, H-3), 3.70 (dq, *J* = 9.6, 6.2 Hz, 1H, H-5), 3.45 (t, *J* = 9.4 Hz, 1H, H-4), 3.34 (s, 3H, CH_3 OMe), 2.53 (d, *J* = 1.9 Hz, 1H, OH), 1.32 (d, *J* = 6.3 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.0 (C_q), 128.7, 128.5, 128.1, 128.0, 127.8 (CH_{arom}), 100.1 (C-1), 80.2, 80.0 (C-3, C-4), 75.5, 72.1 (CH_2 Bn), 68.6 (C-2), 67.2 (C-5), 54.9 (CH_3 OMe), 18.0 (C-6). Spectra in agreement with literature.[88]

Fucose acceptors

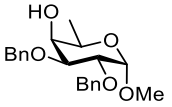
Preparation of acceptor **43**



S38 **43**

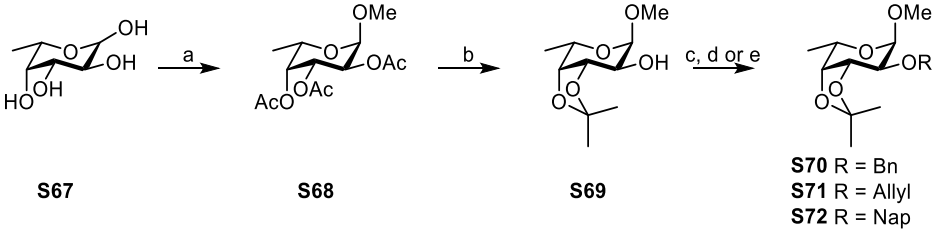
***Scheme S26**: preparation of acceptor **43**: reagents and conditions: a) i: TsCl, pyridine, ii: $LiAlH_4$, THF, reflux, 52% over 2 steps*

Methyl 2,3-di-*O*-benzyl-α-D-fucopyranoside (43)



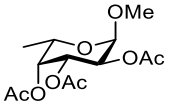
Methyl 2,3,-di-*O*-benzyl-α-D-galactopyranoside (**S38**, 0.75 g, 2 mmol) was dissolved in pyridine (3.3 mL, 40 mmol, 20 eq.) and cooled to 0 °C. Tosyl chloride (0.458 g, 2.4 mmol, 1.2 eq) was added and the reaction mixture was allowed to warm to RT overnight, diluted with ethyl acetate and washed with 1 M HCl and sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure to yield the crude tosylate which was used without further purification. The tosylate was dissolved in THF, $LiAlH_4$ (2.50 mL of a 2.4M solution in 2-methyltetrahydrofuran, 6 mmol, 3 eq) was added and the reaction mixture was heated to a gentle reflux. When TLC shows full conversion, the reaction mixture was cooled to 0 °C and carefully quenched with sat. aq. $NaHCO_3$. Solids were filtered off over celite and the filtrate was extracted with ethyl acetate. The organic phase was washed with 1M HCl, sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated. The residue was purified over silica (30%→50% EA in pentane) to give the title compound as colourless oil. Yield: 373 mg, 1.04 mmol, 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.21 (m, 10H, CH_{arom}), 4.80 (d, *J* = 11.9 Hz, 2H, 2x C*H*H Bn), 4.68 (dd, *J* = 13.6, 11.9 Hz, 2H, 2x CH*H* Bn), 4.62 (d, *J* = 3.4 Hz, 1H, H-1), 3.91 – 3.75 (m, 4H, H-2, H-3, H-4, H-5), 3.36 (s, 3H, CH_3 OMe), 2.49 (s, 1H, OH), 1.26 (d, *J* = 6.6 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.3 (C_q), 128.6, 128.4, 128.1, 127.9, 127.9, 127.8 (CH_{arom}), 98.6 (C-1), 78.0 (C-3), 75.6 (C-2), 73.5, 72.8 (CH_2 Bn), 70.4 (C-4), 65.1 (C-5), 55.4 (CH_3 OMe), 16.2 (C-6). Spectra in agreement with literature.[89]

Preparation of isopropylidene intermediates of fucose acceptors



***Scheme S27**: preparation of isopropylidene intermediates: reagents and conditions: a) i: MeOH, amberlite-H$^+$, reflux, ii: Ac_2O, pyridine, 52% over 2 steps; b) i: NaOMe, MeOH, ii: PTSA, 2,2-dimethoxypropane, 76% over 2 steps; c) Benzyl bromide, NaH, DMF, 82%; d) allyl bromide, NaH, DMF, 97%; e) NapBr, NaH, DMF, 77%*

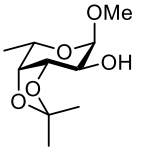
Methyl 2,3,4-tri-*O*-acetyl-α-L-fucopyranoside (S68)



Fucose (**S67**, 5.0 g, 30.5 mmol) was dissolved in methanol, after which 8 g Amberlite IR-120 H-form was added. The mixture was refluxed for 24 hr, cooled to RT and filtered to remove the Amberlite. The filtrate was concentrated under reduced pressure, coevaporated with toluene and

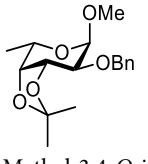
dissolved in 30 mL pyridine. Ac_2O (17.3 mL, 183 mmol, 6 eq) was added and the mixture was reacted overnight, after which it was diluted with ethyl acetate and washed with 1 M HCl and sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure, yielding a mixture of both anomers. The desired α-anomer was isolated via silica chromatography (20% diethyl ether in pentane, first eluting product) as a colourless oil. Yield: 4.92 g, 16.2 mmol, 53%.[1]H NMR (300 MHz, $CDCl_3$) δ 5.36 (dd, *J* = 10.8, 3.4 Hz, 1H, H-3), 5.30 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4), 5.15 (dd, *J* = 10.8, 3.7 Hz, 1H, H-2), 4.94 (d, *J* = 3.7 Hz, 1H, H-1), 4.18 – 4.10 (m, 1H, H-5), 3.40 (s, 3H, CH_3 OMe), 2.18 (s, 3H, CH_3 Ac), 2.09 (s, 3H, CH_3 Ac), 1.99 (s, 3H, CH_3 Ac), 1.16 (d, *J* = 6.5 Hz, 3H, H-6). Spectra in agreement with literature.[90]

Methyl 3,4-*O*-isopropylidene-α-L-fucopyranoside (S69)



Methyl 2,3,4-tri-*O*-acetyl-α-L-fucopyranoside (**S68**, 9.95 g, 32.7 mmol) and sodium methoxide (353 mg, 6.54 mmol, 0.2 eq) were dissolved in methanol. When TLC shows full deprotection, the solution was acidified with Amberlite IR-120 H-form to a pH of 5 and filtered over a short path of celite. The filtrate was concentrated under reduced pressure and residual water and methanol were removed by azeotropic distillation with toluene. The residue was suspended in 2,2-dimehtoxypropane (40 mL, 327 mmol, 10 eq) and PTSA-H_2O (622 mg, 3.27 mmol, 0.1 eq) was added. After overnight stirring, triethylamine (0.92 mL, 6.54 mmol, 0.2 eq) was added and the mixture was concentrated under reduced pressure. Silica chromatography (10% acetone in pentane) yields the title compound as colourless oil. Yield: 5.40 g, 24.7 mmol, 76%. [1]H NMR (400 MHz, $CDCl_3$) δ 4.72 (d, *J* = 3.9 Hz, 1H, H-1), 4.19 (t, *J* = 6.3 Hz, 1H, H-3), 4.11 (qd, *J* = 6.7, 2.4 Hz, 1H, H-5), 4.05 (dd, *J* = 5.9, 2.4 Hz, 1H, H-4), 3.79 (td, *J* = 6.7, 3.8 Hz, 1H, H-2), 3.44 (s, 3H, CH_3 OMe), 2.43 (d, *J* = 6.7 Hz, 1H, OH), 1.52 (s, 3H, CH_3 isopropylidene), 1.36 (s, 3H, CH_3 isopropylidene), 1.33 (d, *J* = 6.7 Hz, 3H, H-6); [13]C NMR (101 MHz, $CDCl_3$) δ 109.3 (C_q isopropylidene), 98.8 (C-1), 76.4 (C-3), 75.8 (C-4), 69.6 (C-2), 63.8 (C-5), 55.5 (CH_3 OMe), 28.0, 26.1 (, CH_3 isopropylidene), 16.4 (C-6). Spectra in agreement with literature.[91]

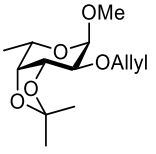
Methyl 2-*O*-benzyl-3,4-*O*-isopropylidene-α-L-fucopyranoside (S70)



Methyl 3,4-*O*-isopropylidene-α-L-fucopyranoside (**S69**, 1.5 g, 6.87 mmol), benzyl bromide (1.22 mL, 10.3 mmol, 1.5 eq) and sodium hydride (60% dispersion in mineral oil, 412 mg, 10.3 mmol, 1.5 eq) were dissolved in dimethylformamide. When TLC shows full conversion, the reaction was quenched with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (10% diethyl ether in pentane), yielding the title compound as colourless oil. Yield: 1.74 g, 5.65 mmol, 82%. [1]H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 5H, CH_{arom}), 4.82 (d, *J* = 12.6 Hz, 1H, C*H*H Bn), 4.72 (d, *J* =

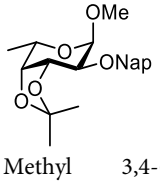
12.7 Hz, 1H, CH*H* Bn), 4.61 (d, *J* = 3.5 Hz, 1H, H-1), 4.32 (dd, *J* = 7.9, 5.4 Hz, 1H, H-3), 4.11 – 4.01 (m, 2H, H-4, H-5), 3.50 (dd, *J* = 7.9, 3.6 Hz, 1H, H-2), 3.38 (s, 3H, CH_3 OMe), 1.40 (s, 3H, CH_3 isopropylidene), 1.35 (s, 3H, CH_3 isopropylidene), 1.32 (d, *J* = 6.7 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3 (C_q), 128.5, 128.1, 127.9 (CH_{arom}), 108.9 (C_q isopropylidene), 98.5 (C-1), 76.3, 76.2, 76.2 (C-2, C-3, C-4), 72.4 (CH_2 Bn), 62.9 (C-5), 55.6 (CH_3 OMe), 28.3, 26.6 (CH_3 isopropylidene), 16.4 (C-6). Spectra in agreement with literature.[92]

Methyl 2-*O*-allyl-3,4-*O*-isopropylidene-α-L-fucopyranoside (S71)



Methyl 3,4-*O*-isopropylidene-α-L-fucopyranoside (**S69**, 1.5 g, 6.87 mmol), allyl bromide (0.89 mL, 10.3 mmol, 1.5 eq) and sodium hydride (60% dispersion in mineral oil, 247 mg, 10.3 mmol, 1.5 eq) were dissolved in DMF. After full conversion, the reaction was quenched with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. Silica chromatography (10% acetone in pentane) yields the title compound as colourless oil. Yield: 1.71 g, 6.64 mmol, 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (dddd, *J* = 17.3, 10.3, 6.3, 5.5 Hz, 1H, CH_2-C*H*=CH_2), 5.28 (dq, *J* = 17.3, 1.6 Hz, 1H, CH_2-CH=C*H*H), 5.19 (dq, *J* = 10.3, 1.3 Hz, 1H, CH_2-CH=CH*H*), 4.73 (d, *J* = 3.5 Hz, 1H, H-1), 4.32 – 4.23 (m, 2H, H-3, C*H*H-CH=CH_2), 4.18 (ddt, *J* = 13.0, 6.3, 1.3 Hz, 1H, CH*H*-CH=CH_2), 4.12 – 4.02 (m, 2H, H-4, H-5), 3.52 (dd, *J* = 7.9, 3.6 Hz, 1H, H-2), 3.41 (s, 3H, CH_3 OMe), 1.53 (s, 3H, CH_3 isopropylidene), 1.39 – 1.30 (m, 6H, H-6, CH_3 isopropylidene), ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0 (CH_2-*C*H=CH_2), 117.8 (CH_2-CH=*C*H_2), 108.9 (C_q isopropylidene), 98.5 (C-1), 76.5, 76.3, 76.1 (C-2, C-3, C-4), 71.9 (*C*H_2-CH=CH_2), 62.9 (C-5), 55.6 (CH_3 OMe), 28.4, 26.5 (CH_3 isopropylidene), 16.4 (C-6). Spectra in agreement with literature.[93]

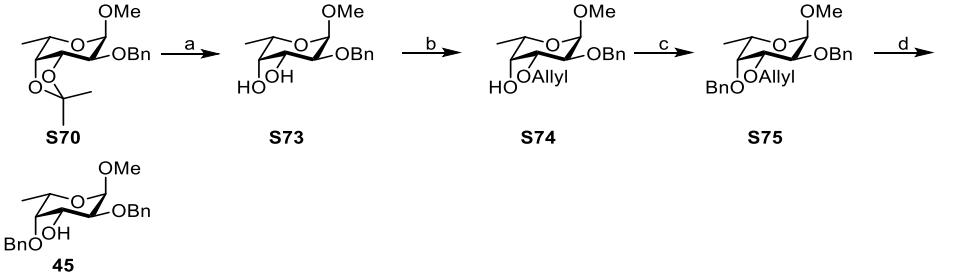
Methyl 3,4-*O*-isopropylidene-2-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (S72)



Methyl 3,4-*O*-isopropylidene-α-L-fucopyranoside (1 g, 4.58 mmol), 2-(Bromomethyl)naphthalene (1.52 g, 6.87 mmol, 1.5 eq) and sodium hydride (60% dispersion in mineral oil, 275 mg, 6.87 mmol, 1.5 eq) were dissolved in DMF. When TLC shows full conversion, the reaction was quenched with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (10% diethyl ether in pentane) to yield the title compound as colourless oil. Yield: 1.27 g, 3.54 mmol, 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 4H, CH_{arom}), 7.55 (dd, *J* = 8.4, 1.7 Hz, 1H, CH_{arom}), 7.52 – 7.45 (m, 2H, CH_{arom}), 5.01 (d, *J* = 12.2 Hz, 1H, C*H*H Nap), 4.91 (d, *J* = 12.7 Hz, 1H, CH*H* Nap), 4.66 (d, *J* = 3.6 Hz, 1H, H-1), 4.39 (dd, *J* = 7.9, 5.5 Hz, 1H, H-3), 4.17 – 4.05 (m, 2H, H-4, H-5), 3.58 (dd, *J* = 7.9, 3.5 Hz, 1H, H-2), 3.41 (s, 3H, CH_3 OMe), 1.41 (s, 3H, CH_3 isopropylidene), 1.38 (s, 3H, CH_3 isopropylidene), 1.34 (d, *J* = 6.7 Hz, 3H, H-6), ^{13}C NMR

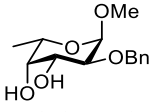
(101 MHz, $CDCl_3$) δ 135.8, 133.3, 133.2 (C_q), 128.3, 128.0, 127.8, 127.0, 126.2, 126.1, 126.0 (CH_{arom}), 108.9 (C_q isopropylidene), 98.5 (C-1), 76.3, 76.2, 76.2 (C-2, C-3, C-4), 72.6 (CH_2 Nap), 62.9 (C-5), 55.6 (CH_3 OMe, 28.3, 26.5 (CH_3 isopropylidene), 16.4 (C-6). Spectra in agreement with literature.[94]

Preparation of acceptor **45**



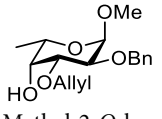
*Scheme **S28**: preparation of acceptor **45**: reagents and conditions: a) PTSA, MeOH, 91%; b) i: DBTO, toluene reflux, ii: allyl bromide, CsF, DMF, 58%; c) BnBr, NaH, DMF, %; d) DMBA, $Pd(Ph_3P)_4$, MeOH, 40 °C, 96%*

Methyl 2-*O*-benzyl-α-L-fucopyranoside (S73)



Methyl 2-*O*-benzyl-3,4-*O*-isopropylidene-α-L-fucopyranoside (**S70**, 1.40 g, 4.54 mmol) and PTSA-H_2O (86 mg, 0.45 mmol, 0.1 eq) were dissolved in methanol and stirred until TLC showed full conversion of the starting material. 0.19 mL triethylamine was added and the reaction mixture was concentrated under reduced pressure. The residue was purified over silica (30% EtOAc in pentane) to give the title compound as colourless oil. Yield: 1.11 g, 4.14 mmol, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H, CH_{arom}), 4.68 – 4.63 (m, 3H, H-1, CH_2 Bn), 3.97 (dt, *J* = 9.8, 3.1 Hz, 1H, H-3), 3.94 – 3.88 (m, 1H, H-5), 3.81 – 3.75 (m, 1H, H-4), 3.69 (dd, *J* = 9.9, 3.5 Hz, 1H, H-2), 3.34 (s, 3H, CH_3 OMe), 2.79 (d, *J* = 3.2 Hz, 1H, 3-OH), 2.63 (d, *J* = 2.7 Hz, 1H, 4-OH), 1.27 (d, *J* = 6.6 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0 C_q), 128.6, 128.2, 128.1 (CH_{arom}), 97.7 (C-1), 76.5 (C-2), 72.8 (CH_2 Bn), 71.6 (C-4), 69.5 (C-3), 65.3 (C-5), 55.3 (CH_3 OMe), 16.1 (C-6). Spectra in agreement with literature.[95]

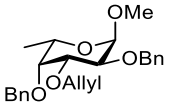
Methyl 3-*O*-allyl-2-*O*-benzyl-α-L-fucopyranoside (S74)



Methyl 2-*O*-benzyl-α-L-fucopyranoside (**S73**, 671 mg, 2.5 mmol) and dibutyltin oxide (809 mg, 3.25 mmol, 1.3 eq) were refluxed in toluene for 2 hr, while water was removed using a Dean-Stark trap. The reaction mixture was cooled to RT and concentrated under reduced pressure. The residue was dissolved in DMF, after which CsF (494 mg, 3.25 mmol, 1.3 eq) and allyl bromide (0.28 mL, 3.25 mmol, 1.3 eq) were added. The reaction mixture was stirred overnight, after which

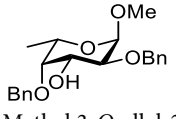
it was diluted with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. Silica chromatography (30% diethyl ether in pentane) yield the title compound as colourless oil. Yield: 446 mg, 1.45 mmol, 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.19 (m, 5H, CH_{arom}), 5.95 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H, CH_2-C*H*=CH_2), 5.32 (dq, *J* = 17.2, 1.7 Hz, 1H, CH_2-CH=C*H*H), 5.20 (dt, *J* = 10.3, 1.5 Hz, 1H, CH_2-CH=CH*H*), 4.78 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.64 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.61 (d, *J* = 2.7 Hz, 1H, H-1), 4.29 – 4.16 (m, 2H, C*H*$_2$-CH=CH_2), 3.89 (q, *J* = 6.6 Hz, 1H, H-5), 3.83 (q, *J* = 1.5 Hz, 1H, H-4), 3.79 – 3.72 (m, 2H, H-2, H-3), 3.36 (s, 3H, CH_3 OMe), 2.60 – 2.31 (m, 1H, OH), 1.28 (d, *J* = 6.6 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5 (C_q), 134.9 (CH_2-*C*H=CH_2), 128.5, 128.1, 127.9 (CH_{arom}), 117.4 (CH_2-CH=*C*H_2), 98.7 (C-1), 77.5, 75.3 (C-2, C-3), 73.5 (CH_2 Bn), 71.6 (*C*H_2-CH=CH_2), 70.4 (C-4), 65.1 (C-5), 55.4 (CH_3 OMe), 16.2 (C-6); HRMS: $[M+H]^+$ calcd for $C_{17}H_{24}O_5H$ 309.16965, found 309.14832.

Methyl 3-*O*-allyl-2,4-di-*O*-benzyl-α-L-fucopyranoside (S75)



Methyl 3-*O*-allyl-2-*O*-benzyl-α-L-fucopyranoside (**S74**, 425 mg, 1.38 mmol), benzyl bromide (0.33 mL, 2.76 mmol, 1.5 eq) and sodium hydride (60% dispersion in mineral oil, 110 mg, 2.76 mmol, 1.5 eq) were dissolved in DMF. After full conversion of the starting material, the reaction was quenched with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. Silica chromatography (25% diethyl ether in pentane) yield the title compound as colourless oil. Yield: 438 mg, 1.10 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 10H, CH_{arom}), 5.98 (ddt, *J* = 17.2, 10.5, 5.2 Hz, 1H, CH_2-C*H*=CH_2), 5.36 (dq, *J* = 17.2, 1.8 Hz, 1H, CH_2-CH=C*H*H), 5.19 (dq, *J* = 10.5, 1.5 Hz, 1H, CH_2-CH=CH*H*), 4.98 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.82 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.70 – 4.62 (m, 3H, H-1, 2x CH*H* Bn), 4.31 (ddt, *J* = 13.0, 5.0, 1.6 Hz, 1H, C*H*H-CH=CH_2), 4.20 (ddt, *J* = 13.1, 5.5, 1.5 Hz, 1H, CH*H*-CH=CH_2), 3.97 (dd, *J* = 10.1, 3.7 Hz, 1H, H-2), 3.88 – 3.77 (m, 2H, H-3, H-5), 3.63 (dd, *J* = 2.9, 1.3 Hz, 1H, H-4), 3.34 (s, 3H, CH_3 OMe), 1.12 (d, *J* = 6.5 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8 (C_q), 135.4 (CH_2-*C*H=CH_2), 128.6, 128.4, 128.3, 128.2, 127.7, 127.7 (CH_{arom}), 116.4 (CH_2-CH=*C*H_2), 99.0 (C-1), 79.1 (C-3), 77.6 (C-4), 76.1 (C-2), 74.8, 73.6 (CH_2 Bn), 72.0 (*C*H_2-CH=CH_2), 66.1 (C-5), 55.4 (CH_3 OMe), 16.7 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{24}H_{30}O_5Na$ 421.19909, found 421.19662.

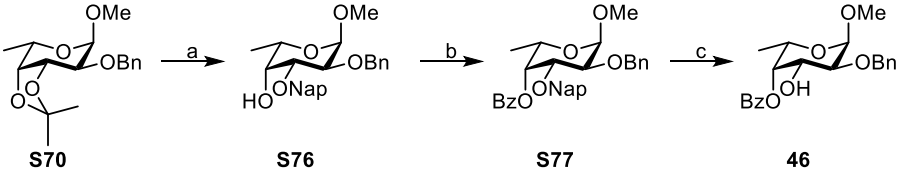
Methyl 2,4-di-*O*-benzyl-α-L-fucopyranoside (45)



Methyl 3-*O*-allyl-2,4-di-*O*-benzyl-α-L-fucopyranoside (**S75**, 418 mg, 1.05 mmol) and DMBA (328 mg, 2.10 mmol, 2 eq) were dissolved in methanol. The reaction mixture was flushed with N_2 for 30 min and heated to 40 °C, after which $Pd(Ph_3P)_4$ (61 mg, 0.05 mmol, 0.05 eq) was added under a flow of N_2. Upon completion, the reaction mixture was concentrated under reduced pressure and the residue was purified by silica chromatography (15% acetone in pentane), yielding the title compound as colourless oil. Yield: 361 mg, 1.01 mmol, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 –

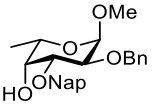
7.14 (m, 10H, CH_{arom}), 4.84 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.73 – 4.63 (m, 4H, H-1, CH*H* Bn, CH_2 Bn), 4.06 (ddd, *J* = 10.0, 4.7, 3.2 Hz, 1H, H-3), 3.92 – 3.86 (m, 1H, H-5), 3.78 (dd, *J* = 10.1, 3.5 Hz, 1H, H-2), 3.64 (dd, *J* = 3.4, 1.3 Hz, 1H, H-5), 3.32 (s, 3H, CH_3 OMe), 2.28 (d, *J* = 4.7 Hz, 1H, OH), 1.17 (d, *J* = 6.6 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.3 (C_q), 128.6, 128.5, 128.4, 128.3, 128.1, 127.9 (CH_{arom}), 98.1 (C-1), 79.5 (C-4), 77.2 (C-2), 75.6, 73.0 (CH_2 Bn), 70.6 (C-3), 66.1 (C-5), 55.4 (CH_3 OMe), 16.8 (C-6). Spectra in agreement with literature.[95]

Preparation of acceptor **46**



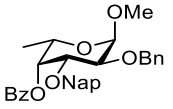
***Scheme S29**: preparation of acceptor **46**: reagents and conditions: a) i: PTSA, MeOH, 50 °C, ii: DBTO, toluene reflux, iii: NapBr, CsF, DMF, 76%; b) BzCl, pyridine, 98%; c) DDQ, DCM/H_2O (9:1), 84%*

Methyl 2-*O*-benzyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (S76)



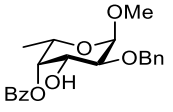
Methyl 2-*O*-benzyl-3,4-*O*-isopropylidene-α-L-fucopyranoside (**S70**, 1.72 g, 5.58 mmol) and PTSA-H_2O (106 mg, 0.56 mmol, 0.1 eq) were dissolved in methanol and stirred until TLC showed full conversion of the starting material. 0.16 mL triethylamine was added and the reaction mixture was concentrated under reduced pressure. The residue was dissolved in toluene with dibutyltin oxide (1.81 g, 7.25 mmol, 1.3 eq) and heated to a reflux while removing water with a Dean-Stark trap. After 2 hr, the reaction mixture was cooled to RT and concentrated under reduced pressure. The residue was dissolved in DMF and NapBr (1.60 g, 7.25 mmol, 1.3 eq) and CsF (1.10 g, 7.25 mmol, 1.3 eq) were added. After stirring overnight, the reaction mixture was diluted with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. Silica chromatography (10% acetone in pentane) yields the title compound as colourless oil. Yield: 1.72 g, 4.22 mmol, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.81 (m, 5H, CH_{arom}), 7.56 – 7.49 (m, 4H, CH_{arom}), 7.45 – 7.30 (m, 5H, CH_{arom}), 5.00 (d, *J* = 12.6 Hz, 1H, C*H*H Bn/Nap), 4.91 (d, *J* = 11.8 Hz, 1H, CH*H* Bn/Nap), 4.86 (d, *J* = 12.2 Hz, 1H, C*H*H Bn/Nap), 4.74 (d, *J* = 12.1 Hz, 1H, CH*H* Bn/Nap), 4.68 (d, *J* = 3.5 Hz, 1H, H-1), 3.95 (dd, *J* = 9.8, 3.2 Hz, 1H, H-3), 3.92 – 3.87 (m, 2H, H-2, H-5), 3.85 (dt, *J* = 3.1, 1.5 Hz, 1H, H-4), 3.41 (s, 3H, CH_3 OMe), 2.55 (t, *J* = 1.5 Hz, 1H, OH), 1.30 (d, *J* = 6.6 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 135.7, 133.3, 133.2 (C_q), 128.5, 128.4, 128.4, 128.2, 128.0, 127.9, 127.8, 126.8, 126.3, 126.3, 126.1, 126.0, 125.9 (CH_{arom}), 98.6 (C-1), 77.8 (C-3), 75.7 (C-2), 73.5, 73.0 (CH_2 Bn, CH_2 Nap), 70.6 (C-4), 65.1 (C-5), 55.4 (CH_3 OMe), 16.2 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{25}H_{28}O_5NH_4$ 426.22750, found 426.22659.

Methyl 4-*O*-benzoyl-2-*O*-benzyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (S77)



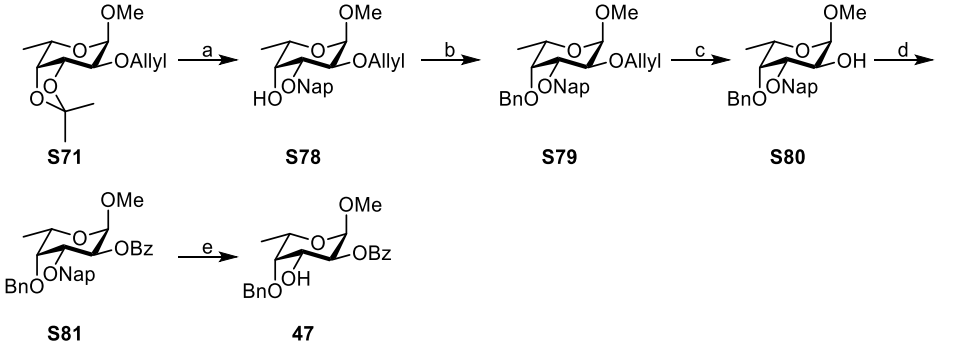
Methyl 2-*O*-benzyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (**S76**, 1.67 g, 4.09 mmol) was dissolved in 5 mL pyridine, after which benzoyl chloride (0.71 mL, 6.13 mmol, 1.5 eq) was added. Upon full conversion of the starting material, the reaction mixture was diluted with ethyl acetate and washed with 1M HCl and with sat. aq. $NaHCO_3$. The organic phase was dried and concentrated under reduced pressure. Silica chromatography (25% diethyl ether in pentane) yields the title compound as colourless oil. Yield: 2.06 g, 4.09 mmol, 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.10 (m, 2H, CH_{arom}), 7.87 – 7.78 (m, 3H, CH_{arom}), 7.75 – 7.71 (m, 1H, CH_{arom}), 7.66 – 7.60 (m, 1H, CH_{arom}), 7.53 – 7.43 (m, 5H, CH_{arom}), 7.42 – 7.32 (m, 5H, CH_{arom}), 5.69 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4), 5.00 (d, *J* = 11.7 Hz, 1H, C*H*H Bn/Nap), 4.91 (d, *J* = 12.1 Hz, 1H, C*H*H Bn/Nap), 4.83 (d, *J* = 11.7 Hz, 1H, CH*H* Bn/Nap), 4.79 – 4.73 (m, 2H, H-1, CH*H* Bn/Nap), 4.19 – 4.11 (m, 2H, H-3, H-5), 4.00 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2), 3.46 (s, 3H, CH_3 OMe), 1.23 (d, *J* = 6.5 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4 (C=O), 138.5, 135.9, 133.4 (C_q), 133.2 (CH_{arom}), 133.0, 130.2 (C_q), 130.2, 130.1, 128.5, 128.5, 128.4, 128.2, 128.1, 128.1, 127.9, 127.7, 126.7, 126.0, 126.0, 125.8 (CH_{arom}), 99.2 (C-1), 76.4 (C-3), 75.0 (C-2), 73.7, 72.1 (CH_2 Bn, CH_2 Nap), 71.8 (C-4), 64.9 (C-5), 55.6 (CH_3 OMe), 16.4 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{32}O_6NH_4$ 530.25371, found 530.25291.

Methyl 4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranoside (46)



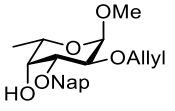
Methyl 4-*O*-benzoyl-2-*O*-benzyl-α-L-fucopyranoside (2.00 g, 3.90 mmol) and DDQ (1.77 g, 7.80 mmol, 2 eq) were dissolved in DCM/H_2O (9:1). After full conversion, the reaction mixture was diluted with DCM and washed twice with sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (15% acetone in pentane) to give the title compound as colourless oil. Yield: 1.22 g, 3.28 mmol, 84%. $[\alpha]_D^{25}$ = -99.0° (c = 0.60, $CHCl_3$); IR (thin film): 668, 713, 751, 1050, 1274, 1452, 1721; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.05 (m, 2H, CH_{arom}), 7.65 – 7.58 (m, 1H, CH_{arom}), 7.48 (dd, *J* = 8.4, 7.1 Hz, 2H, CH_{arom}), 7.44 – 7.31 (m, 5H, CH_{arom}), 5.50 (dd, *J* = 3.6, 1.3 Hz, 1H, H-4), 4.80 (d, *J* = 3.5 Hz, 1H, H-1), 4.77 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.73 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.30 (dt, *J* = 10.0, 3.3 Hz, 1H, H-3), 4.14 (qd, *J* = 6.5, 1.3 Hz, 1H, H-5), 3.85 (dd, *J* = 10.1, 3.5 Hz, 1H, H-2), 3.42 (s, 3H, CH_3 OMe), 2.45 (d, *J* = 3.2 Hz, 1H, OH), 1.20 (d, *J* = 6.6 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6 (C=O), 137.9 (C_q), 133.2, 129.9 (CH_{arom}), 129.8 (C_q), 128.6, 128.4, 128.2, 128.1 (CH_{arom}), 98.1 (C-1), 76.5 (C-2), 73.8 (C-4), 72.9 (CH_2 Bn), 68.3 (C-3), 64.9 (C-5), 55.5 (CH_3 OMe), 16.2 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{21}H_{24}O_6Na$ 395.14651, found 395.14616.

Preparation of acceptor **47**



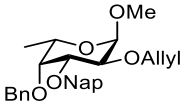
***Scheme S30**: preparation of acceptor **47**: reagents and conditions: a) i: PTSA, MeOH, 50 °C, ii: DBTO, toluene reflux, iii: NapBr, CsF, DMF, 98%; b) BnBr, NaH, DMF, 65%; c) $Pd(Ph_3P)_4$, DMBA, MeOH, 40 °C, 71%; d) BzCl, pyridine, 100%; e) DDQ, DCM/H_2O (9:1), 84%*

Methyl 2-*O*-allyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (S78)



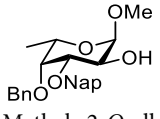
Methyl 2-*O*-allyl-3,4-*O*-isopropylidene-α-L-fucopyranoside (**S71**, 1.7 g, 6.58 mmol) and PTSA-H_2O (125 mg, 0.66 mmol, 0.1 eq) were dissolved in methanol and heated to 50 °C. After full conversion, 0.2 mL triethylamine was added and the reaction mixture was concentrated under reduced pressure. The residue was dissolved in toluene with dibutyltin oxide (2.1 g, 8.45 mmol, 1.3 eq) and heated to a reflux for 2 hr, while removing water with a Dean-Stark trap. The reaction mixture was then cooled to RT and concentrated under reduced pressure. The residue was dissolved in DMF and NapBr (1.87 g, 8.45 mmol, 1.3 eq), CsF (1.28 g, 8.45 mmol, 1.3 eq) were added. After overnight stirring, the reaction mixture was diluted with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (10% acetone in pentane) yielding the slightly impure title compound as yellowish oil. Yield: 2.27 g, 6.34 mmol, 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.78 (m, 4H, CH_{arom}), 7.55 – 7.45 (m, 3H, CH_{arom}), 6.00 (dddd, *J* = 17.2, 10.3, 6.3, 5.4 Hz, 1H, CH_2-C*H*=CH_2), 5.34 (dq, *J* = 17.2, 1.6 Hz, 1H, CH_2-CH=C*H*H), 5.23 (dq, *J* = 10.3, 1.3 Hz, 1H, CH_2-CH=CH*H*), 4.98 (d, *J* = 11.8 Hz, 1H, C*H*H Nap), 4.88 (d, *J* = 11.9 Hz, 1H, CH*H* Nap), 4.83 (d, *J* = 3.4 Hz, 1H, H-1), 4.31 (ddt, *J* = 12.8, 5.4, 1.4 Hz, 1H, C*H*H-CH=CH_2), 4.23 (ddt, *J* = 12.8, 6.3, 1.3 Hz, 1H, CH*H*-CH=CH_2), 3.95 – 3.80 (m, 4H, H-2, H-3, H-4, H-5), 3.43 (s, 3H, CH_3 OMe), 2.54 (t, *J* = 1.5 Hz, 1H, OH), 1.31 (d, *J* = 6.7 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8 (C_q), 135.0 (CH_2-*C*H=CH_2), 133.3, 133.2 (C_q), 128.4, 128.0, 127.8, 126.8, 126.3, 126.1, 125.9 (CH_{arom}), 117.7 (CH_2-CH=*C*H_2), 98.6 (C-1), 77.7 (C-3), 75.6 (C-2), 73.1 (CH_2 Nap), 72.7 (*C*H_2-CH=CH_2), 70.7 (C-4), 65.2 (C-5), 55.4 (CH_3 OMe), 16.2 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{21}H_{26}O_5Na$ 381.16725, found 381.16656.

Methyl 2-*O*-allyl-4-*O*-benzyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (S79)



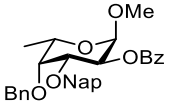
Methyl 2-*O*-allyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (**S78**, 1.26 g, 3.50 mmol) was dissolved in DMF after which benzyl bromide (0.62 mL, 5.25 mmol, 1.5 eq) and sodium hydride (60% dispersion in mineral oil, 210 mg, 5.25 mmol, 1.5 eq) were added. After full conversion, the reaction was quenched with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (10% diethyl ehter in pentane) yielding the title compound as colourless oil. Yield: 1.02 g, 2.26 mmol, 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 4H, CH_{arom}), 7.57 – 7.44 (m, 3H, CH_{arom}), 7.37 (ddt, *J* = 5.2, 3.8, 1.5 Hz, 2H, CH_{arom}), 7.35 – 7.26 (m, 3H, CH_{arom}), 5.97 (dddd, *J* = 17.0, 10.3, 6.3, 5.4 Hz, 1H, CH_2-C*H*=CH_2), 5.31 (dq, *J* = 17.2, 1.6 Hz, 1H, CH_2-CH=C*H*H), 5.18 (dq, *J* = 10.4, 1.3 Hz, 1H, CH_2-CH=CH*H*), 5.09 – 4.97 (m, 2H, C*H*H Bn, C*H*H Nap), 4.86 (d, *J* = 12.1 Hz, 1H, CH*H* Nap), 4.82 (d, *J* = 3.6 Hz, 1H, H-1), 4.71 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.31 (ddt, *J* = 12.7, 5.4, 1.5 Hz, 1H, C*H*H-CH=CH_2), 4.22 (ddt, *J* = 12.8, 6.3, 1.3 Hz, 1H, CH*H*-CH=CH_2), 4.02 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2), 3.92 (dd, *J* = 10.1, 2.9 Hz, 1H, H-3), 3.82 (qd, *J* = 6.4, 1.2 Hz, 1H, H-5), 3.63 (dd, *J* = 2.9, 1.3 Hz, 1H, H-4), 3.39 (s, 3H, CH_3 OMe), 1.12 (d, *J* = 6.5 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 136.6 (C_q), 135.2 (CH_2-*C*H=CH_2), 133.4, 133.0 (C_q), 128.6, 128.3, 128.2, 128.0, 127.8, 127.7, 126.3, 126.2, 125.9, 125.9 (CH_{arom}), 117.6 (CH_2-CH-*C*H_2), 98.9 (C-1), 79.3 (C-3), 78.2 (C-2), 76.5 (C-4), 75.0 (CH_2 Bn), 73.6 (CH_2 Nap), 72.8 (*C*H_2-CH=CH_2), 66.2 (C-5), 55.4 (CH_3 OMe), 16.7 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{28}H_{32}O_5NH_4$ 466.25880, found 466.25832.

Methyl 4-*O*-benzyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (S80)



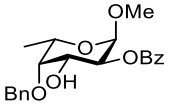
Methyl 2-*O*-allyl-4-*O*-benzyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (**S79**, 1.00 g, 2.23 mmol) and DMBA (696 mg, 4.46 mmol, 2eq) were dissolved in methanol, heated to 40 °C and flushed with N_2 for 30 minutes after which $Pd(Ph_3P)_4$ was added under a flow of N_2. After full conversion, as indicated by TLC, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in ethyl acetate 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 over silica (15% acetone in pentane) yielding the title compound as off-white powder. Yield: 650 mg, 1.59 mmol, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.79 (m, 4H, CH_{arom}), 7.54 – 7.45 (m, 3H, CH_{arom}), 7.41 – 7.36 (m, 2H, CH_{arom}), 7.34 – 7.26 (m, 3H, CH_{arom}), 4.97 (d, *J* = 11.6 Hz, 1H, C*H*H Bn/Nap), 4.89 (s, 2H, CH_2 Bn/Nap), 4.82 (d, *J* = 3.9 Hz, 1H, H-1), 4.70 (d, *J* = 11.6 Hz, 1H, CH*H* Bn/Nap), 4.21 (ddd, *J* = 9.9, 7.6, 4.0 Hz, 1H, H-2), 3.84 (qd, *J* = 6.3, 1.4 Hz, 1H, H-5), 3.73 (dd, *J* = 9.9, 2.8 Hz, 1H, H-3), 3.68 (dd, *J* = 2.9, 1.2 Hz, 1H, H-4), 3.39 (s, 3H, CH_3 OMe), 2.19 (d, *J* = 7.7 Hz, 1H, OH), 1.19 (d, *J* = 6.5 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 135.9, 133.4, 133.1 (C_q), 128.4, 128.4, 128.4, 128.0, 127.9, 127.8, 126.5, 126.3, 126.1, 125.8 (CH_{arom}), 99.9 (C-1), 80.0 (C-3), 76.9 (C-4), 74.4, 73.4 (CH_2 Bn, CH_2 Nap), 69.1 (C-2), 66.7 (C-5), 55.5 (CH_3 OMe), 16.9 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{25}H_{28}O_5$ 426.22750, found 426.22664.

Methyl 2-*O*-benzoyl-4-*O*-benzyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (S81)



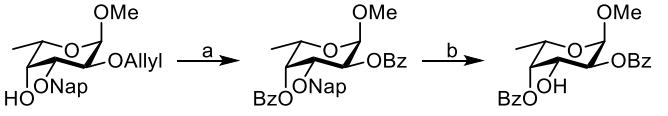
Methyl 4-*O*-benzyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (**S80**, 625 mg, 1.53 mmol) was dissolved in 5 mL pyridine, after which benzoyl chloride (0.27 mL, 2.30 mol, 1.5 eq) was added. After full conversion of the starting material (TLC), the reaction mixture was diluted with ethyl acetate and washed with 1M HCl and sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (5%→10% acetone in pentane) yielding the title compound as oil that solidifies upon standing. Yield: 784 mg, 1.53 mmol, 100%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 2H, CH_{arom}), 7.82 – 7.78 (m, 1H, CH_{arom}), 7.73 (d, *J* = 8.8 Hz, 2H, CH_{arom}), 7.71 – 7.67 (m, 1H, CH_{arom}), 7.59 – 7.53 (m, 1H, CH_{arom}), 7.48 – 7.38 (m, 7H, CH_{arom}), 7.34 – 7.26 (m, 3H, CH_{arom}), 5.60 (dd, *J* = 10.5, 3.8 Hz, 1H, H-2), 5.07 (d, *J* = 3.8 Hz, 1H, H-1), 5.04 (d, *J* = 11.7 Hz, 1H, C*H*H Bn/Nap), 4.86 (s, 2H, CH_2 Bn/Nap), 4.72 (d, *J* = 11.7 Hz, 1H, CH*H* Bn/Nap), 4.14 (dd, *J* = 10.5, 2.9 Hz, 1H, H-3), 3.91 (q, *J* = 6.3 Hz, 1H, H-5), 3.75 (dd, *J* = 2.9, 1.3 Hz, 1H, H-4), 3.32 (s, 3H, CH_3 OMe), 1.20 (d, *J* = 6.5 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3 (C=O), 138.5, 135.9, 133.3 (C_q), 133.1 (CH_{arom}), 133.1, 130.3 (C_q), 130.0, 128.6, 128.5, 128.4, 128.3, 128.0, 127.8, 126.5, 126.2, 126.0, 125.9 (CH_{arom}), 97.8 (C-1), 77.3 (C-3, C-4), 75.0, 73.0 (CH_2 Bn, CH_2 Nap), 71.8 (C-2), 66.3 (C-5), 55.5 (CH_3 OMe), 16.8 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{32}O_6NH_4$ 530.25371, found 530.25265.

Methyl 2-*O*-benzoyl-4-*O*-benzyl-α-L-fucopyranoside (47)



Methyl 2-*O*-benzoyl-4-*O*-benzyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (**S81**, 750 mg, 1.46 mmol) and DDQ (664 mg, 2.93 mmol, 2eq) were dissolved in DCM/H_2O (9:1). After full conversion, indicated by TLC, 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 over silica (5%→10% acetone in pentane) yielding the title compound as oil that solidifies upon standing. Yield: 455 mg, 1.22 mmol, 84%. $[\alpha]_D^{25}$ = -126.0° (c = 0.35, $CHCl_3$); IR (thin film): 711, 756, 1049, 1279, 1452, 1720; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.02 (m, 2H, CH_{arom}), 7.65 – 7.53 (m, 1H, CH_{arom}), 7.49 – 7.28 (m, 8H, CH_{arom}), 5.25 (dd, *J* = 10.4, 3.7 Hz, 1H, H-2), 4.99 (d, *J* = 3.7 Hz, 1H, H-1), 4.83 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.76 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.19 (ddd, *J* = 10.5, 9.4, 3.5 Hz, 1H, H-3), 4.01 (qd, *J* = 6.6, 1.5 Hz, 1H, H-5), 3.73 (dd, *J* = 3.7, 1.3 Hz, 1H, H-4), 3.38 (s, 3H, CH_3 OMe), 2.23 (d, *J* = 9.4 Hz, 1H, OH), 1.30 (d, *J* = 6.6 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0 (C=O), 138.1, 133.3 (CH_{arom}), 130.0 (C_q), 129.9, 128.7, 128.5, 128.2, 128.2 (CH_{arom}), 97.8 (C-1), 80.9 (C-4), 76.3 (CH_2 Bn), 72.7 (C-2), 69.3 (C-3), 66.2 (C-5), 55.6 (CH_3 OMe), 16.9 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{24}O_6NH_4$ 390.19111, found 390.19054.

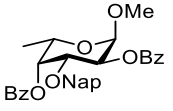
Preparation of acceptor **48**



S78 **S82** **48**

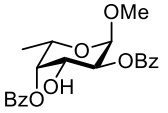
*Scheme **S31**: preparation of acceptor **48**: reagents and conditions: a) i: DMBA, Pd(Ph$_3$P)$_4$, methanol, 40 °C, ii: BzCl, pyridine, 73%; b) DDQ, DCM/H$_2$O (9:1), 58%*

Methyl 2,4-di-*O*-benzoyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (S82)



Methyl 2-*O*-allyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (**S78**, 896 mg, 2.50 mmol) and DMBA (781 mg, 5.00 mmol, 2 eq) were dissolved in methanol, heated to 40 °C and flushed with N_2 for 30 minutes after which Pd(Ph$_3$P)$_4$ (144 mg, 0.125 mmol, 0.05 eq) was added under a flow of N_2. After full conversion, as indicated by TLC, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in 7.5 mL pyridine and benzoyl chloride (0.87 mL, 7.50 mmol, 3 eq) was added. After overnight reaction, the reaction mixture was diluted with 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. The residue was purified over silica to give the title compound. Yield: 632 mg, 1.20 mmol, 48%. Further elution gave methyl 2-*O*-benzoyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside. Yield: 323 mg, 0.77 mmol, 31%. The latter was converted to the title compound with BzCl/pyridine in 89%, to give a total yield of 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.19 (m, 2H, CH_{arom}), 8.08 – 8.02 (m, 2H, CH_{arom}), 7.85 – 7.79 (m, 1H, CH_{arom}), 7.74 – 7.68 (m, 2H, CH_{arom}), 7.67 – 7.58 (m, 3H, CH_{arom}), 7.56 – 7.36 (m, 7H, CH_{arom}), 5.79 (dd, *J* = 3.5, 1.3 Hz, 1H, H-4), 5.52 (dd, *J* = 10.4, 3.8 Hz, 1H, H-2), 5.17 (d, *J* = 3.7 Hz, 1H, H-1), 4.92 (d, *J* = 12.6 Hz, 1H, C*H*H Nap), 4.77 (d, *J* = 12.6 Hz, 1H, CH*H* Nap), 4.26 (dd, *J* = 10.4, 3.5 Hz, 1H, H-3), 4.21 (qd, *J* = 6.6, 1.2 Hz, 1H, H-5), 3.40 (s, 3H, CH_3 OMe), 1.30 (d, *J* = 6.6 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 166.3 (C=O), 135.5 (C_q), 133.4, 133.3 (CH_{arom}), 133.1 (C_q), 130.2, 130.0 (CH_{arom}), 130.0, 129.9 (C_q), 128.6, 128.6, 128.5, 128.2, 128.0, 127.7, 126.7, 126.1, 125.9 (CH_{arom}), 97.8 (C-1), 73.2 (C-3), 71.4 (CH_2 Nap), 71.0, 71.0 (C-2, C-4), 64.9 (C-5), 55.6 (CH_3 OMe), 16.5 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{30}O_7NH_4$ 544.23298, found 544.23201.

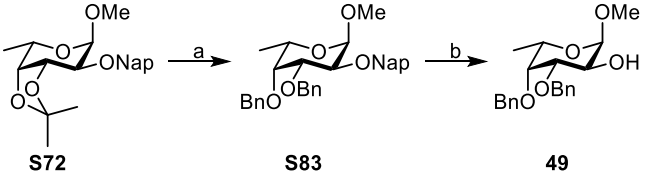
Methyl 2,4-di-*O*-benzoyl-α-L-fucopyranoside (48)



Methyl 2,4-di-*O*-benzoyl-3-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (**S82**, 950 mg, 1.80 mmol) and DDQ (819 mg, 3.61 mmol, 2 eq) were dissolved in 9:1 DCM/H$_2$O. After 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 over silica (10% acetone in pentane) to give the title compound as white solid. Yield: 403 mg, 1.04

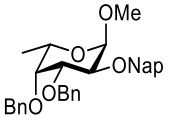
mmol, 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.12 (m, 2H, CH_{arom}), 8.11 – 8.04 (m, 2H, CH_{arom}), 7.64 – 7.53 (m, 2H, CH_{arom}), 7.52 – 7.39 (m, 4H, CH_{arom}), 5.56 (dd, *J* = 3.6, 1.3 Hz, 1H, H-4), 5.35 (dd, *J* = 10.5, 3.6 Hz, 1H, H-2), 5.11 (d, *J* = 3.7 Hz, 1H, H-1), 4.48 (dd, *J* = 10.4, 3.5 Hz, 1H, H-3), 4.22 (qd, *J* = 6.5, 1.4 Hz, 1H, H-5), 3.43 (s, 3H, CH_3 OMe), 2.39 (s, 1H, OH), 1.25 (d, *J* = 6.6 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 166.9 (C=O), 133.6, 133.5, 130.1, 130.0 (CH_{arom}), 129.7, 129.5 (C_q), 128.7, 128.6 (CH_{arom}), 97.8 (C-1), 74.5 (C-4), 72.4 (C-2), 67.6 (C-3), 65.1 (C-5), 55.7 (CH_3 OMe), 16.4 (C-6). Spectra in agreement with literature.[96]

Preparation of acceptor **49**



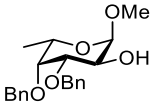
***Scheme S32**: preparation of acceptor **49**: reagents and conditions: a) i: PTSA, MeOH, 50 °C, ii: BnBr, NaH, DMF, 72%; b) DDQ, DCM/H_2O (9:1), 82%*

Methyl 3,4-di-*O*-benzyl-2-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (S83)



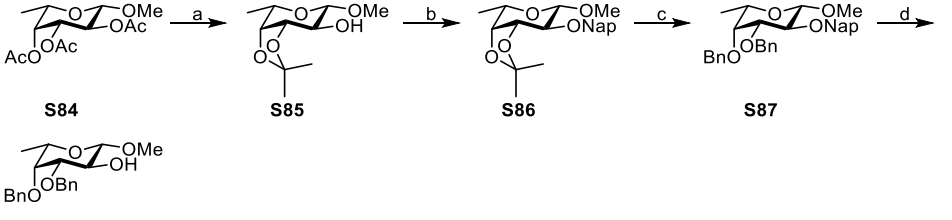
Methyl 3,4-*O*-isopropylidene-2-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (**S72**, 1.25 g, 3.49 mmol) and PTSA-H_2O (66 mg, 0.35 mmol, 0.1 eq) were dissolved in methanol and heated to 50 °C. After full conversion, 0.1 mL of triethylamine was added and the mixture was concentrated under reduced pressure. The residue was dissolved in DMF and benzyl bromide (1.24 mL, 10.5 mmol, 3 eq) and sodium hydride (60% dispersion in mineral oil, 418 mg, 10.5 mmol, 3 eq) were added. After stirring for 2.5 hr, the reaction was quenched with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (5% acetone in pentane) to give the title compound as colourless oil. Yield: 1.25 g, 2.51 mmol, 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 4H, CH_{arom}), 7.50 (dd, *J* = 8.4, 1.7 Hz, 1H, CH_{arom}), 7.48 – 7.39 (m, 4H, CH_{arom}), 7.38 – 7.25 (m, 7H, CH_{arom}), 5.01 – 4.96 (m, 2H, 2x C*H*H Bn/Nap), 4.91 (d, *J* = 11.8 Hz, 1H, C*H*H Bn/Nap), 4.86 (d, *J* = 12.3 Hz, 1H, CH*H* Bn/Nap), 4.77 (d, *J* = 11.8 Hz, 1H, CH*H* Bn/Nap), 4.68 – 4.62 (m, 2H, H-1, CH*H* Bn/Nap), 4.09 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2), 3.96 (dd, *J* = 10.1, 2.9 Hz, 1H, H-3), 3.88 – 3.79 (m, 1H, H-5), 3.65 (dd, *J* = 2.9, 1.2 Hz, 1H, H-4), 3.36 (s, 3H, CH_3 OMe), 1.10 (d, *J* = 6.5 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 138.7, 136.1, 133.4, 133.2 (C_q), 128.6, 128.5, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.0, 126.2, 126.1, 125.9 (CH_{arom}), 98.9 (C-1), 79.5 (C-3), 78.0 (C-4), 75.8 (C-2), 75.0, 73.7, 73.5 (CH_2 Bn, CH_2 Nap), 66.2 (C-5), 55.5 (CH_3 OMe), 16.7 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{34}O_5NH_4$ 516.27445, found 516.27365.

Methyl 2,3-di-*O*-benzyl-α-L-fucopyranoside (49)



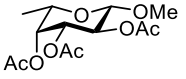
Methyl 3,4-di-*O*-benzyl-2-*O*-(2-naphthyl)methyl-α-L-fucopyranoside (**S83**, 1.12 g, 2.25 mmol) and DDQ (1.02 g, 4.50 mmol, 2 eq) were dissolved in DCM/H_2O 9:1. After full conversion of the starting material, the reaction mixture was diluted with dichloromethane and washed twice with sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (10%→15% acetone in pentane) to give the title compound as white solid. Yield: 665 mg, 1.86 mmol, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.23 (m, 10H, CH_{arom}), 4.94 (d, *J* = 11.5 Hz, 1H, C*H*H Bn), 4.81 (d, *J* = 3.9 Hz, 1H, H-1), 4.75 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.72 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.65 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.17 (ddd, *J* = 9.8, 7.3, 3.9 Hz, 1H, H-2), 3.88 – 3.81 (m, 1H, H-5), 3.70 (dd, *J* = 9.9, 2.8 Hz, 1H, H-3), 3.67 (dd, *J* = 2.9, 1.1 Hz, 1H, H-4), 3.40 (s, 3H, CH_3 OMe), 2.17 (d, *J* = 7.3 Hz, 1H, OH), 1.19 (d, *J* = 6.5 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.3 (C_q), 128.5, 128.3, 128.3, 127.8, 127.7 (CH_{arom}), 99.7 (C-1), 80.0 (C-3), 76.7 (C-4), 74.0, 72.1 (CH_2 Bn), 68.9 (C-2), 66.1 (C-5), 54.9 (CH_3 OMe), 15.7 (C-6). Spectra in agreement with literature.[97]

Preparation of acceptor **50**



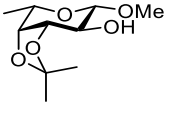
***Scheme S33**: preparation of acceptor **50**: reagents and conditions: a) i: NaOMe, MeOH, ii: 2,2-dimethoxypropane, PTSA, 76%; b) NapBr, NaH, DMF, 92%; c) i: PTSA, MeOH, 50 °C, ii: BnBr, NaH, DMF, 79%; d) DDQ, DCM/H_2O (9:1), 77%*

Methyl 2,3,4-tri-*O*-acetyl-β-L-fucopyranoside (S84)



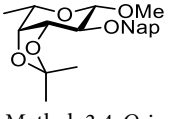
Title compound was isolated as a side product during multiple preparations of the α-anomer (**S68**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 (dd, *J* = 3.5, 1.2 Hz, 1H, H-4), 5.18 (dd, *J* = 10.4, 7.9 Hz, 1H, H-2), 5.02 (dd, *J* = 10.4, 3.4 Hz, 1H, H-3), 4.38 (d, *J* = 7.9 Hz, 1H, H-1), 3.82 (qd, *J* = 6.4, 1.1 Hz, 1H, H-5), 3.52 (s, 3H, CH_3 OMe), 2.18 (s, 3H, CH_3 Ac), 2.06 (s, 3H, CH_3 Ac), 1.99 (s, 3H, CH_3 Ac), 1.24 (d, *J* = 6.5 Hz, 3H, H-6); Spectra in agreement with literature.[90]

Methyl 3,4-*O*-isopropylidene-β-L-fucopyranoside (S85)



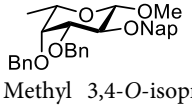
Methyl 2,3,4-tri-*O*-acetyl-β-L-fucopyranoside (**S84**, 3.00 g, 9.86 mmol) and NaOMe (53 mg, 0.99 mmol, 0.1 eq) were dissolved in methanol. After full deprotection, the pH of the reaction mixture was adjusted to 5 with amberlite. The solution was filtered over a short path of celite and concentrated under reduced pressure. Residual methanol and water were removed by coevaporation with toluene. The residue was suspended in 2,2-dimethoxypropane (30.2 mL, 246 mmol, 25 eq), after which PTSA-H_2O (188 mg, 0.99 mmol, 0.1 eq) was added. After 16 hr, triethylamine (0.28 mL, 1.97 mmol, 0.2 eq) was added and the reaction mixture was concentrated under reduced pressure. The residue was purified over silica (35% ethyl acetate in pentane) yields the title compound as colourless oil that slowly solidifies. Yield: 1.63 g, 7.47 mmol, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 – 4.01 (m, 2H, H-1, H-2), 4.01 (dd, *J* = 5.5, 2.2 Hz, 1H, H-4), 3.87 (qd, *J* = 6.6, 2.1 Hz, 1H, H-5), 3.56 – 3.47 (m, 4H, H-3, CH_3 OMe), 2.79 (d, *J* = 2.5 Hz, 1H, OH), 1.53 (s, 3H, CH_3 isopropylidene), 1.43 (d, *J* = 6.6 Hz, 3H, H-6), 1.36 (s, 3H, CH_3 isopropylidene), ^{13}C NMR (101 MHz, $CDCl_3$) δ 109.9 (C_q isopropylidene), 103.2 (C-1), 78.9 (C-2), 76.4 (C-4), 73.7 (C-3), 69.2 (C-5), 56.9 (CH_3 OMe), 28.3, 26.4, (CH_3 isopropylidene) 16.6 (C-6). Spectra in agreement with literature.[91]

Methyl 3,4-*O*-isopropylidene-2-*O*-(2-naphthyl)methyl-β-L-fucopyranoside (S86)



Methyl 3,4-*O*-isopropylidene-β-L-fucopyranoside (**S85**, 1.25 g, 5.73 mmol) was dissolved in DMF, after which NapBr (1.90 g, 8.59 mmol, 1.5 eq) and NaH (60% dispersion in mineral oil, 344 mg, 8.59 mmol, 1.5 eq) were added. Upon full conversion, the reaction was quenched with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (15% diethyl ether in pentane) to give the title compound as yellowish oil. Yield: 1.89 g, 5.27 mmol, 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 4H, CH_{arom}), 7.52 (dd, *J* = 8.6, 1.7 Hz, 1H, CH_{arom}), 7.48 – 7.41 (m, 2H, CH_{arom}), 4.99 (d, *J* = 12.0 Hz, 1H, C*H*H Nap), 4.95 (d, *J* = 12.0 Hz, 1H, CH*H* Nap), 4.22 (d, *J* = 8.0 Hz, 1H, H-1), 4.16 (dd, *J* = 7.0, 5.5 Hz, 1H, H-3), 3.98 (dd, *J* = 5.5, 2.1 Hz, 1H, H-4), 3.82 (qd, *J* = 6.6, 2.1 Hz, 1H, H-5), 3.56 (s, 3H, CH_3 OMe), 3.42 (dd, *J* = 8.1, 7.1 Hz, 1H, H-2), 1.40 (d, *J* = 6.6 Hz, 3H, H-6), 1.33 (s, 3H, CH_3 isopropylidene), 1.29 (s, 3H, CH_3 isopropylidene); HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{26}O_5NH_4$ 376.21185, found 376.21136.

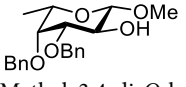
Methyl 3,4-di-*O*-benzyl-2-*O*-(2-naphthyl)methyl-β-L-fucopyranoside (S87)



Methyl 3,4-*O*-isopropylidene-2-*O*-(2-naphthyl)methyl-β-L-fucopyranoside (**S86**, 1.85 g, 5.16 mmol) and PTSA-H_2O (98 mg, 0.52 mmol, 0.1 eq) were dissolved in methanol and heated to 50 °C. After full conversion, triethylamine (0.15 mL, 1.03 mmol, 0.2 eq) was added and the mixture was concentrated under reduced pressure. Residual methanol and water were removed by coevaporation with toluene. The residue was dissolved in DMF, after which benzyl bromide (1.84 mL, 15.5 mmol, 3 eq) and sodium hydride (60% dispersion in mineral oil, 619 mg, 15.5 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 under reduced

pressure. The residue was purified over silica (25% diethyl ether in pentane) to give the title compound as white solid. Yield: 2.03 g, 4.07 mmol, 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 4H, CH_{arom}), 7.50 (dd, *J* = 8.4, 1.6 Hz, 1H, CH_{arom}), 7.48 – 7.43 (m, 2H, CH_{arom}), 7.39 – 7.25 (m, 10H, CH_{arom}), 5.07 (d, *J* = 11.2 Hz, 1H, C*H*H Bn/Nap), 4.98 (d, *J* = 11.7 Hz, 1H, C*H*H Bn/Nap), 4.92 (d, *J* = 11.2 Hz, 1H, CH*H* Bn/Nap), 4.81 (d, *J* = 11.9 Hz, 1H, C*H*H Bn/Nap), 4.74 (d, *J* = 12.0 Hz, 1H, CH*H* Bn/Nap), 4.69 (d, *J* = 11.7 Hz, 1H, CH*H* Bn/Nap), 4.28 (d, *J* = 7.6 Hz, 1H, H-1), 3.86 (dd, *J* = 9.7, 7.7 Hz, 1H, H-2), 3.58 – 3.52 (m, 5H, H-3, H-4, CH_3 OMe), 3.47 (qd, *J* = 6.3, 1.1 Hz, 1H, H-5), 1.20 (d, *J* = 6.4 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 138.7, 136.6, 133.5, 133.1 (C_q), 128.6, 128.5, 128.2, 128.1, 128.0, 127.8, 127.7, 127.7, 127.6, 126.8, 126.5, 126.0, 125.8 (CH_{arom}), 105.0 (C-1), 82.2 (C-3), 79.7 (C-2), 76.4 (C-4), 75.2, 74.7, 73.3 (CH_2 Bn, CH_2 Nap), 69.8 (C-5), 55.6 (CH_3 OMe), 15.1 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{34}O_5NH_4$ 516.27445, found 516.27379.

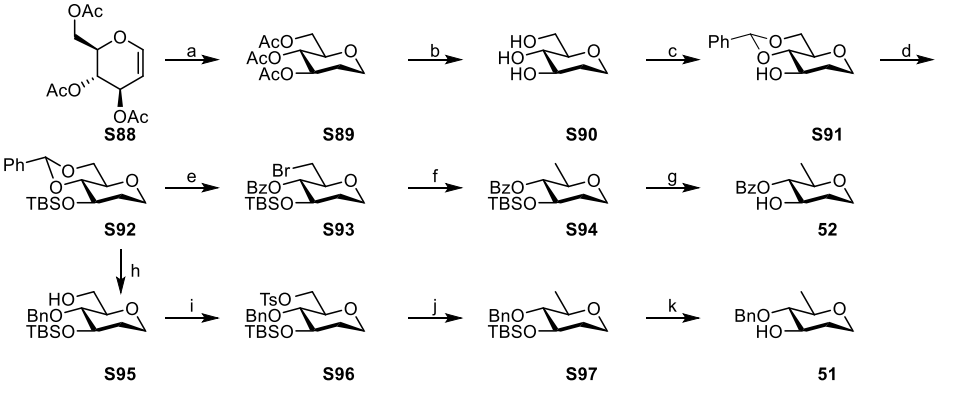
Methyl 3,4-di-*O*-benzyl-β-L-fucopyranoside (50)



Methyl 3,4-di-*O*-benzyl-2-*O*-(2-naphthyl)methyl-β-L-fucopyranoside (**S87**, 1.10 g, 2.21 mmol) and DDQ (1.00 g, 4.41 mmol, 2 eq) were dissolved in DCM/H_2O 9:1. After full conversion of the starting material, the reaction mixture was diluted with dichloromethane 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 over silica (15% acetone in pentane) to give the title compound as white solid. Yield: 607 mg, 1.69 mmol, 77%. $[\alpha]_D^{25}$ = 2.76° (c = 0.25, $CHCl_3$); IR (thin film): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.24 (m, 10H, CH_{arom}), 4.93 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.75 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.72 – 4.66 (m, 2H, 2x CH*H* Bn), 4.14 (d, *J* = 7.6 Hz, 1H, H-1), 3.93 (ddd, *J* = 9.7, 7.6, 1.9 Hz, 1H, H-2), 3.61 (dd, *J* = 2.9, 1.1 Hz, 1H, H-4), 3.55 – 3.48 (m, 4H, H-5, CH_3 OMe), 3.44 (dd, *J* = 9.8, 2.9 Hz, 1H, H-3), 2.41 (d, *J* = 2.0 Hz, 1H, OH), 1.24 (d, *J* = 6.4 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 138.2 (C_q), 128.7, 128.5, 128.3, 128.0, 127.8, 127.7 (CH_{arom}), 104.1 (C-1), 82.5 (C-3), 75.7 (C-4), 74.8, 73.1 (CH_2 Bn), 71.3 (C-2), 70.8 (C-5), 58.0 (CH_3 OMe), 10.8 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{26}O_5NH_4$ 376.21185, found 376.21140.

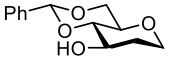
Model acceptors

Preparation of acceptors **51** and **52**



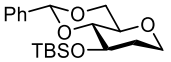
***Scheme S34**: preparation of acceptors **51** and **52**: reagents and conditions: a) Pd/C, H_2, EtOAc; b) NaOMe/MeOH; c) $PhCH(OMe)_2$, PTSA, 85% over 3 steps; d) TBSCl, imidazole, DMF, 98%; e) NBS, $BaCO_3$, cyclohexane, reflux, 75%; f) Bu_3SnH, cat AIBN, toluene, reflux 94%; g) PTSA, MeOH, 95%; h) BH_3-$NH(CH_3)_2$, BF_3-Et_2O, 89%; i) TsCl, pyridine; j) LAH, THF, reflux, 79% over 2 steps; k) PTSA, MeOH, 91%*

1,2-di-deoxy-4,6-*O*-benzylidene-D-glucopyranose (S91)



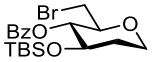
commercially available tri-*O*-acetly-D-glucal (**S88**, 20 g, 73.5 mmol) and Pd/C (10%, 500 mg) were dissolved in ethyl acetate and flushed with nitrogen gas, flushed with hydrogen gas and kept under hydrogen atmosphere overnight. The reaction mixture was flushed with nitrogen, filtered over celite and concentrated, yielding **S89**. The residue was dissolved in methanol and NaOMe (794 mg, 14.7 mmol, 0.2 eq) was added. When TLC shows full conversion, the reaction was quenched with amberlite, concentrated under reduced pressure and residual methanol and water were removed by azeotroping with toluene. The crude triol (**S90**) was then dissolved in acetonitrile with PTSA-H_2O (1.40 g, 7.35 mmol, 0.1 eq) and benzaldehyde dimethyl acetal (15.5 mL, 103 mmol, 1.4 eq). The reaction was heated to 60 °C at 275 mbar. After 45 min, the reaction was concentrated under reduced pressure. The residue was dissolved in ethyl acetate and washed with sat aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated. The residue was purified by precipitation form EA/pentane yielding the title compound white solid. Yield: 14.7 g, 62.2 mmol, 85% over 3 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dq, *J* = 4.9, 2.7 Hz, 2H, CH_{arom}), 7.38 (qd, *J* = 4.7, 1.7 Hz, 3H, CH_{arom}), 5.55 (s, 1H, C*H*Ph), 4.28 (dd, *J* = 10.4, 4.9 Hz, 1H, H-6), 3.98 (ddd, *J* = 11.8, 5.3, 1.6 Hz, 1H, H-1_{eq}), 3.86 (tdt, *J* = 11.4, 5.9, 2.9 Hz, 1H, H-3), 3.69 (td, *J* = 10.3, 3.9 Hz, 1H, H-6), 3.55 (tt, *J* = 11.9, 2.9 Hz, 1H, H-1_{ax}), 3.43 (t, *J* = 9.0 Hz, 1H, H-4), 3.33 (td, *J* = 9.6, 4.9 Hz, 1H, H-5), 2.65 (t, *J* = 2.8 Hz, 1H, OH), 2.09 – 1.92 (m, 1H, H-2_{eq}), 1.80 (tdd, *J* = 13.1, 11.0, 5.2 Hz, 1H, H-2_{ax}). Spectra in agreement with literature.[98]

1,2-di-deoxy-4,6-*O*-benzylidene-3-*O*-dimethyltertbutylsilyl-D-glucopyranose (S92)



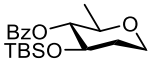
S91 (2 g, 8.46 mmol) was dissolved in DMF and imidazole (1.15 g, 16.9 mmol, 2 eq) and TBSCl (1.91 g, 12.7 mmol, 1.5 eq) were added. When TLC shows full conversion, the reaction is quenched with 5 mL methanol, diluted with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$, concentrated and the residue was purified over silica (10% diethyl ether in pentane) yielding the product as colourless oil. Yield: 2.90 g, 8.27 mmol, 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H, CH_{arom}), 7.41 – 7.30 (m, 3H, CH_{arom}), 5.56 (s, 1H, C*H*Ph), 4.27 (dd, *J* = 10.3, 4.9 Hz, 1H, H-6), 3.95 (ddd, *J* = 11.8, 5.1, 1.6 Hz, 1H, H-1_{eq}), 3.87 (ddd, *J* = 10.6, 8.6, 5.4 Hz, 1H, H-3), 3.70 (t, *J* = 10.2 Hz, 1H, H-6), 3.55 (td, *J* = 12.2, 2.6 Hz, 1H, H-1_{ax}), 3.44 (t, *J* = 8.9 Hz, 1H, H-4), 3.31 (td, *J* = 9.6, 4.9 Hz, 1H, H-5), 1.97 – 1.76 (m, 2H, H-2_{ax}, H-2_{eq}), 0.87 (s, 9H, C(CH_3) TBS), 0.08 (s, 3H, CH_3 TBS), 0.04 (s, 3H, CH_3 TBS) ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8 (C_q), 128.9, 128.2, 126.2 (CH_{arom}), 101.6 (CHPh), 84.0 (C-4), 71.9 (C-5), 70.4 (C-3), 69.1 (C-6), 66.6 (C-1), 35.6 (C-2), 25.9 (C(*C*H_3)$_3$ TBS), 18.4 (*C*(CH_3)$_3$ TBS), -4.3 (CH_3 TBS), -4.7 (CH_3 TBS). spectra in agreement with literature.[99]

1,2,6-tri-deoxy-6-bromo-4-*O*-benzoyl-3-*O*-dimethyltertbutylsilyl-D-glucopyranose (S93)



S92 (1.4 g, 3.99 mmol), N-bromosuccinimide (782 mg, 4.39 mmol, 1.1 eq) and barium carbonate (1.58 g, 7.99 mmol, 2 eq) were suspended in cyclohexane and heated to a reflux, after which the reaction mixture turns red. After the red colour fades, the progress was checked with TLC. Since some starting material was still present, another 0.2 eq of NBS was added and the reaction progress was checked again after the red colour faded again. TLC showed full consumption of the starting material, so the solids in the reaction mixture were removed by filtration and washed with ethyl acetate. The filtrate was washed with sat. aq. $Na_2S_2O_3$, dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (3% EA in pentane) yielding the title compound as colourless oil. Yield: 1.29 g, 3 mmol, 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 7.96 (m, 2H, CH_{arom}), 7.66 – 7.54 (m, 1H, CH_{arom}), 7.52 – 7.40 (m, 2H, CH_{arom}), 5.01 (dd, *J* = 9.3, 8.5 Hz, 1H, H-4), 4.07 (ddd, *J* = 11.9, 4.7, 2.2 Hz, 1H, H-1_{eq}), 3.91 (ddd, *J* = 10.7, 8.5, 5.2 Hz, 1H, H-3), 3.62 (ddd, *J* = 9.4, 7.5, 2.7 Hz, 1H, H-5), 3.54 (td, *J* = 11.6, 11.1, 2.1 Hz, 1H, H-1_{ax}), 3.51 – 3.47 (m, 1H, H-6), 3.41 (dd, *J* = 11.1, 7.5 Hz, 1H, H-6), 2.01 – 1.80 (m, 2H, H-2_{ax}, H-2_{eq}), 0.74 (s, 9H C(CH_3)$_3$ TBS), 0.01 (s, 3H, CH_3 TBS), -0.14 (s, 3H, CH_3 TBS) ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (C=O), 133.4, 129.9 (CH_{arom}), 129.8 (C_q), 128.5 (CH_{arom}), 78.2 (C-5), 75.3 (C-4), 71.5 (C-3), 65.4 (C-1), 34.9 (C-2), 32.4 (C-6), 25.6 (C(*C*H_3)$_3$ TBS), 17.8 (*C*(CH_3)$_3$ TBS), -4.3 (CH_3 TBS), -4.8 (CH_3 TBS). spectra in agreement with literature.[99]

1,2,6-tri-deoxy-4-*O*-benzoyl-3-*O*-dimethyltertbutylsilyl-D-glucopyranose (S94)



S93 (1.25 g, 2.91 mmol), AIBN (0.2 M solution in toluene, 1.46 mL, 0.29 mmol, 0.1 eq) and tri-n-butyltin hydride (1,10 mL, 4.08 mmol, 1.4 eq) were dissolved in toluene and heated to a reflux. When TLC shows full conversion, the reaction mixture was concentrated and the residue was purified over silica (3→6% diethyl ether in pentane) yielding the slightly impure title compound

as colourless oil. Yield: 974 mg, 2.75 mmol, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dt, *J* = 7.1, 1.4 Hz, 2H, CH_{arom}), 7.61 – 7.52 (m, 1H, CH_{arom}), 7.51 – 7.38 (m, 2H, CH_{arom}), 4.88 (t, *J* = 9.1 Hz, 1H, H-4), 3.96 (ddd, *J* = 11.8, 4.8, 1.9 Hz, 1H, H-1_{eq}), 3.85 (ddd, *J* = 10.7, 8.7, 5.5 Hz, 1H, H-3), 3.55 – 3.33 (m, 2H, H-1_{ax}, H-5), 1.98 – 1.77 (m, 2H, H-2), 1.21 (d, *J* = 6.2 Hz, 3H, H-6), 0.74 (s, 9H, C(CH_3)$_3$ TBS), 0.01 (s, 3H, CH_3 TBS), -0.14 (s, 3H, CH_3 TBS) ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (C=O), 133.1 (CH_{arom}), 130.4 (C_q), 129.8, 128.4 (CH_{arom}), 78.3 (C-4), 75.0 (C-5), 71.8 (C-3), 65.6 (C-1), 35.5 (C-2), 25.6 (C(*C*H$_3$)$_3$ TBS), 18.2 (C-6), 17.9 (*C*(CH$_3$)$_3$ TBS), -4.3 (CH_3 TBS), -4.8 (CH_3 TBS); HRMS: $[M+H]^+$ calcd for $C_{19}H_{30}O_4SiH$ 351.19861, found 351.19794.

1,2,6-tri-deoxy-4-*O*-benzoyl-D-glucopyranose (52)

S94 (925 mg, 2.64 mmol) and PTSA-H_2O (50 mg, 0.26 mmol, 0.1 eq) were dissolved in methanol. When TLC indicates full conversion, the reaction was quenched with triethylamine (0.08 mL, 0.53 mmol, 0.2 eq) and concentrated. The residue was purified over silica (25% EtOAc in pentane) to give the title compound as a colourless oil that slowly solidifies. Yield: 595 mg, 2.52 mmol, 95%. $[\alpha]_D^{25}$ = 33.4° (c = 0.39, $CHCl_3$); IR (thin film): 711, 1069, 1118, 1271, 1721; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.97 (m, 2H, CH_{arom}), 7.59 (ddt, *J* = 8.7, 6.9, 1.3 Hz, 1H, CH_{arom}), 7.52 – 7.42 (m, 2H, CH_{arom}), 4.71 (t, *J* = 9.2 Hz, 1H, H-4), 3.98 (ddd, *J* = 11.8, 5.0, 1.7 Hz, 1H, H-1_{eq}), 3.84 (ddt, *J* = 11.3, 8.9, 5.1 Hz, 1H, H-3), 3.57 – 3.41 (m, 2H, H-1_{ax}, H-5), 2.71 (d, *J* = 5.0 Hz, 1H, OH), 2.10 (ddt, *J* = 13.2, 5.3, 1.9 Hz, 1H, H-2_{eq}), 1.83 (tdd, *J* = 12.9, 11.3, 5.0 Hz, 1H, H-2_{ax}), 1.26 (d, *J* = 6.2 Hz, 3H, H-6) ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4 (C=O), 133.6, 129.9 (CH_{arom}), 129.7 (C_q), 128.6 (CH_{arom}), 79.9 (C-4), 74.6 (C-5), 71.8 (C-3), 65.7 (C-1), 34.6 (C-2), 18.3 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{13}H_{16}O_4Na$ 259.09408, found 259.09365.

1,2-di-deoxy-4-*O*-benzyl-3-*O*-dimethyltertbutylsilyl-D-glucopyranose (S95)

S92 (1.4 g, 3.99 mmol) was dissolved in dichloromethane and cooled to 0 °C, after which borane dimethylamine complex (1.18 g, 20.0 mmol, 5 eq) and BF_3-etherate (2.47 mL, 20.0 mmol, 5 eq) were added. When TLC shows full conversion of the starting material, the reaction was quenched with sat. aq. $NaHCO_3$, diluted and extracted twice with DCM. Combined organic phases were washed with sat. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated. The residue was purified over silica (20% EA in pentane) to yield the title compound as colourless oil. Yield: 1.25 g, 3.55 mmol, 89% ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H, CH_{arom}), 4.91 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.61 (d, *J* = 11.2 Hz, 1H, CH*H* Bn), 3.91 (ddd, *J* = 11.7, 4.9, 1.8 Hz, 1H, H-1_{eq}), 3.84 – 3.75 (m, 2H, H-3, H-6), 3.63 (ddd, *J* = 11.6, 6.8, 4.7 Hz, 1H, H-6), 3.41 (ddd, *J* = 12.7, 11.7, 2.2 Hz, 1H, H-1_{ax}), 3.28 (dd, *J* = 9.6, 8.1 Hz, 1H, H-4), 3.21 (ddd, *J* = 9.5, 4.8, 2.7 Hz, 1H, H-5), 1.92 (dd, *J* = 6.9, 6.0 Hz, 1H, OH), 1.86 (ddt, *J* = 13.3, 5.2, 2.0 Hz, 1H, H-2_{eq}), 1.77 – 1.64 (m, 1H, H-2_{ax}), 0.93 (s, 9H, C(CH_3)$_3$ TBS) 0.11 (s, 3H, CH_3 TBS), 0.10 (s, 3H, CH_3 TBS) ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5 (C_q), 128.5, 128.1, 127.8 (CH_{arom}), 79.9, 79.8 (C-4/C-5), 75.2 (CH_2 Bn), 74.6 (C-3), 65.5 (C-1), 62.8 (C-6), 35.6 (C-2), 26.0 (C(*C*H$_3$)$_3$ TBS), 18.1 (*C*(CH$_3$)$_3$ TBS), -4.2 (CH_3 TBS), -4.4 (CH_3 TBS). spectra in agreement with literature.[99]

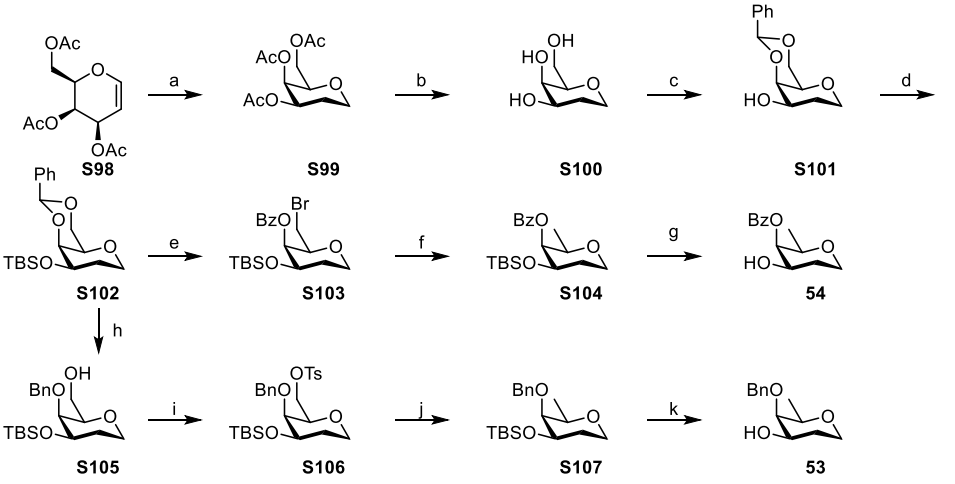
1,2,6-tri-deoxy-4-*O*-benzyl-3-*O*-dimethyltertbutylsilyl-D-glucopyranose (S97)

S95 (1.20 g, 3.40 mmol) was dissolved in 5.5 mL pyridine, after which *p*-toluenesulfonyl chloride (1.30 g, 6.81 mmol, 2 eq) was added. When TLC shows full conversion, the reaction mixture is diluted with ethyl acetate and washed with 2x 100 mL 1M HCl and with sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure, yielding the crude tosylate (**S96)** which was used without further purification. The tosylate was dissolved in THF, lithium aluminium hydride (2.4 M in 2-methyltetrahydrofuran, 5.67 mL, 13.6 mmol, 4 eq) was added and the mixture was heated to reflux. When TLC shows full conversion, the reaction mixture was cooled to 0 °C and excess reagent was very carefully quenched with 1M aq HCl and extracted twice with ethyl acetate. Combined organic phases were washed with sat. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (3→6% diethyl ether in pentane), yielding the title compound as colourless oil. Yield: 906 mg, 2.69 mmol, 79% over 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 5H, CH_{arom}), 4.93 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.61 (d, *J* = 11.1 Hz, 1H, CH*H* Bn), 3.85 (ddd, *J* = 11.7, 4.8, 1.8 Hz, 1H, H-1$_{eq}$), 3.74 (ddd, *J* = 11.0, 8.3, 5.2 Hz, 1H, H-3), 3.37 (td, *J* = 12.2, 2.2 Hz, 1H, H-1$_{ax}$), 3.24 (dq, *J* = 9.2, 6.2 Hz, 1H, H-5), 2.95 (t, *J* = 8.8 Hz, 1H, H-4), 1.85 (ddt, *J* = 13.2, 5.2, 2.0 Hz, 1H, H-2$_{eq}$), 1.72 (tdd, *J* = 12.9, 11.0, 4.9 Hz, 1H, H-2$_{eq}$), 1.25 (d, *J* = 6.2 Hz, 3H, H-6), 0.92 (s, 9H, C(CH_3)$_3$ TBS), 0.16 – 0.06 (m, 6H, 2x CH_3 TBS) ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7 (C_q), 128.4, 128.0, 127.7 (CH_{arom}), 85.7 (C-4), 76.1 (C-5), 75.5 (CH_2 Bn), 74.6 (C-3), 65.4 (C-1), 35.9 (C-2), 26.0 (C(*C*H$_3$)$_3$ TBS), 18.7 (C-6), 18.1 (*C*(CH$_3$)$_3$ TBS), -4.2 (CH_3 TBS), -4.3 (CH_3 TBS); HRMS: $[M+Na]^+$ calcd for $C_{19}H_{32}O_3SiNa$ 359.20129, found 359.20078.

1,2,6-tri-deoxy-4-*O*-benzyl-D-glucopyranose (51)

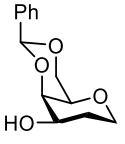
S97 (875 mg, 2.60 mmol) and PTSA-H_2O (50 mg, 0.26 mmol, 0.1 eq) were dissolved in methanol. When TLC shows full conversion, the reaction was quenched with triethylamine (0.07 mL, 0.52 mmol, 0.2 eq) and concentrated under reduced pressure. The residue was purified over silica (25% EtOAc in pentane) to give the desired compound as white solid. Yield: 528 mg, 2.38 mmol, 91%. $[\alpha]_D^{25}$ = -13.0° (c = 0.35, $CHCl_3$); IR (thin film): 689, 839, 1070, 1090, 1105, 1454; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 5H, CH_{arom}), 4.79 (d, *J* = 11.2 Hz, 1H, CH*H* Bn), 4.70 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 3.90 (ddd, *J* = 11.7, 5.0, 1.6 Hz, 1H, H-1$_{eq}$), 3.67 (tdt, *J* = 8.4, 5.1, 2.9 Hz, 1H, H-3), 3.41 (ddd, *J* = 12.6, 11.7, 2.2 Hz, 1H, H-1$_{ax}$), 3.27 (dq, *J* = 9.2, 6.2 Hz, 1H, H-5), 2.95 (t, *J* = 8.9 Hz, 1H, H-4), 2.19 (d, *J* = 2.9 Hz, 1H, OH), 1.94 (ddt, *J* = 13.0, 5.2, 1.9 Hz, 1H, H-2$_{eq}$), 1.69 (tdd, *J* = 12.9, 11.4, 5.0 Hz, 1H, H-2$_{ax}$), 1.35 (d, *J* = 6.2 Hz, 3H, H-6) ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4 (C_q), 128.8, 128.2, 128.0 (CH_{arom}), 86.7 (C-4), 76.0 (C-5), 75.4 (CH_2 Bn), 72.9 (C-3), 65.7 (C-1), 33.8 (C-2), 18.8 (C-6). HRMS: $[M+Na]^+$ calcd for $C_{13}H_{18}O_3Na$ 245.11482, found 245.11489.

Preparation of acceptors **53** and **54**



***Scheme S35**: preparation of acceptors **53** and **54**: reagents and conditions: a) Pd/C, H_2, EtOAc; b) NaOMe/MeOH; c) $PhCH(OMe)_2$, PTSA, 55% over 3 steps; d) TBSCl, imidazole, DMF, 73%; e) NBS, $BaCO_3$, cyclohexane, reflux, 70%; f) Bu_3SnH, cat AIBN, toluene, reflux 89%; g) PTSA, MeOH, 91%; h) BH_3-$NH(CH_3)_2$, BF_3-Et_2O, 62%; i) TsCl, pyridine; j) LAH, THF, reflux, 39% over 2 steps; k) PTSA, MeOH, 67%*

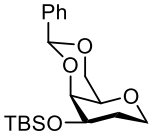
1,2-di-deoxy-4,6-*O*-benzylidene-D-galactopyranose (S101)



commercially available tri-*O*-acetly-D-galactal (**S98**, 10 g, 36.5 mmol) and Pd/C (5%, 500 mg) were dissolved in ethyl acetate and flushed with nitrogen gas, flushed with hydrogen gas and kept under hydrogen atmosphere overnight. The reaction mixture was flushed with nitrogen, filtered over celite, concentrated, yielding **S99**. The residue was dissolved in methanol and NaOMe (394 mg, 7.29 mmol, 0.2 eq) was added. When TLC shlows full conversion, the reaction was quenched with Amberilte IR-120 H-form to a pH of ~5, concentrated under reduced pressure and residual methanol and water were removed by azeotroping with toluene. The crude triol (**S100**) was then dissolved in acetonitrile with PTSA-H_2O (694 mg, 3.65 mmol, 0.1 eq) and benzaldehyde dimethyl acetal (7.7 mL, 51 mmol, 1.4 eq). The reaction was heated to 60 °C at 275 mbar. After 60 min, the reaction was concentrated under reduced pressure. The residue was dissolved in ethyl acetate and washed with sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated. The residue was recrystallized from EA/pentane to yield the title compound as fluffy white solid. Yield: 4.72 g, 20 mmol, 55% over 3 steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H, CH_{arom}), 7.44 – 7.37 (m, 3H, CH_{arom}), 5.62 (s, 1H, C*H*Ph), 4.30 (dd, *J* = 12.4, 1.6 Hz, 1H, H-6), 4.16 – 4.10 (m, 2H, H-1_{eq}, H-4), 4.04 (dd, *J* = 12.5, 1.8 Hz, 1H, H-6), 3.78 (dddd, *J* = 11.8, 10.8, 5.1, 3.5 Hz, 1H, H-3), 3.48 (td, *J* = 12.2, 2.0 Hz, 1H, H-1_{ax}), 3.33 (q, *J* = 1.6 Hz, 1H, H-5), 2.52 (d, *J* = 10.8 Hz, 1H, OH), 2.02 (qd, *J* = 12.4, 4.6 Hz, 1H, H-2_{ax}), 1.81 – 1.74 (m, 1H, H-2_{eq}); ^{13}C NMR

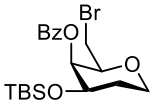
(101 MHz, $CDCl_3$) δ 137.8 (C_q), 129.1, 128.2, 126.4 (CH_{arom}), 101.2 (CHPh), 75.3 (C-4), 70.3 (C-5), 70.1 (C-6), 68.8 (C-3), 65.8 (C-1), 30.2 (C-2). Spectra in agreement with literature.[100]

1,2-di-deoxy-4,6-*O*-benzylidene-3-*O*-dimethyltertbutylsilyl-D-galactopyranose (S102)



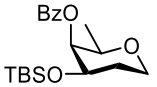
1,2-di-deoxy-4,6-*O*-benzylidene-D-galactopyranose (**S101**, 4.70 g, 19.9 mmol) was dissolved in DMF with imidazole (3.39 g, 49.8 mmol, 2.5 eq). TBSCl (3.90 g, 25.9 mmol, 1.3 eq) was added and the mixture was stirred at room temperature. When TLC shows full conversion, the reaction mixture was diluted with water and extracted twice with diethyl ether. Combined organic phases were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (10% acetone in pentane) yielding the title compound as white powder. Yield: 5.12 g, 14.6 mmol, 73% ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H, CH_{arom}), 7.37 – 7.28 (m, 3H, CH_{arom}), 5.57 (s, 1H, C*H*Ph), 4.27 (dd, *J* = 12.4, 1.6 Hz, 1H, H-6), 4.10 (ddd, *J* = 11.7, 4.6, 1.8 Hz, 1H, H-1_{eq}), 4.01 (dd, *J* = 12.3, 1.8 Hz, 1H, H-6), 3.96 (d, *J* = 3.2 Hz, 1H, H-4), 3.84 (ddd, *J* = 11.7, 4.8, 3.4 Hz, 1H, H-3), 3.49 (ddd, *J* = 12.6, 11.6, 2.0 Hz, 1H, H-1_{ax}), 3.26 (q, *J* = 1.5 Hz, 1H, H-5), 2.21 (tdd, *J* = 12.8, 11.6, 4.6 Hz, 1H, H-2_{ax}), 1.55 (ddq, *J* = 12.8, 4.7, 1.7 Hz, 1H, H-1_{eq}), 0.91 (s, 9H, C(CH_3)$_3$ TBS), 0.20 – 0.00 (m, 6H, 2x CH_3 TBS), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3 (C_q), 128.6, 128.0, 126.3 (CH_{arom}), 100.7 (CHPh), 76.5 (C-4), 70.7 (C-3), 70.6 (C-6), 70.4 (C-5), 66.2 (C-1), 30.0 (C-2), 25.9 (C(*C*H_3)$_3$ TBS), 18.3 (*C*(CH_3)$_3$ TBS), -4.2, -4.3 (CH_3 TBS); HRMS: $[M+Na]^+$ calcd for $C_{19}H_{30}O_4SiNa$ 373.18056, found 373.17989.

1,2,6-tri-deoxy-6-bromo-4-*O*-benzoyl-3-*O*-dimethyltertbutylsilyl-D-galactopyranose (S103)



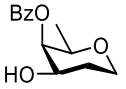
1,2-di-deoxy-4,6-*O*-benzylidene-3-*O*-dimethyltertbutylsilyl-D-galactopyranose (**S102**, 2.28 g, 6.50 mmol), barium carbonate (2.57 g, 13.0 mmol, 2 eq) and N-bromosuccinimide (1.27g, 7.15 mmol, 1.1 eq) were suspended in cyclohexane and heated to a reflux. Upon heating, the solution becomes red and then colourless after a few minutes. After the fading of the red colour, TLC showed full conversion. Solids were filtered off and washed with ethyl acetate. The organic phase was washed with sat. aq. $Na_2S_2O_3$, dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (5% diethyl ether in pentane) to obtain the title compound as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.04 (m, 2H, CH_{arom}), 7.61 – 7.54 (m, 1H, CH_{arom}), 7.48 – 7.41 (m, 2H, CH_{arom}), 5.51 – 5.46 (m, 1H, H-4), 4.14 (ddd, *J* = 11.9, 4.7, 2.2 Hz, 1H, H-1_{eq}), 3.95 (ddd, *J* = 10.9, 4.8, 3.2 Hz, 1H, H-3), 3.77 (ddd, *J* = 7.3, 5.7, 1.5 Hz, 1H, H-5), 3.57 (td, *J* = 12.1, 2.3 Hz, 1H, H-1_{ax}), 3.47 – 3.36 (m, 2H, 2x H-6), 2.10 (qd, *J* = 12.4, 4.7 Hz, 1H, H-2_{ax}), 1.69 (dddt, *J* = 13.0, 4.8, 2.5, 1.2 Hz, 1H, H-2_{eq}), 0.77 (s, 9H, C(CH_3)$_3$ TBS), 0.06 (s, 3H, CH_3 TBS), 0.05 (s, 3H, CH_3 TBS), ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1 (C=O), 133.2 (CH_{arom}), 130.2 (C_q), 130.0, 128.5 (CH_{arom}), 79.7 (C-5), 72.9 (C-4), 68.6 (C-3), 65.3 (C-1), 30.8, 30.7 (C-2, C-6), 25.7 (C(*C*H_3)$_3$ TBS), 18.0 (*C*(CH_3)$_3$ TBS), -4.7, -4.8 (CH_3 TBS); HRMS: $[M+H]^+$ calcd for $C_{19}H_{29}BrO_4SiH$ 429.10913; 431.10708, found 429.10855; 431.10647.

1,2-di-deoxy-4-*O*-benzoyl-3-*O*-dimethyltertbutylsilyl-D-fucopyranose (S104)



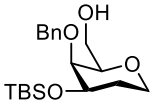
1,2,6-tri-deoxy-6-bromo-4-*O*-benzoyl-3-*O*-dimethyltertbutylsilyl-D-galactopyranose (**S103**, 1.90 g, 4.42 mmol), tributyltin hydride (1.67 mL, 6.19 mmol, 1.4 eq) and AIBN (0.2 M in toluene, 2.21 mL, 0.44 mmol, 0.1 eq) were dissolved in toluene and heated to a reflux. After 4 hr, the reaction was incomplete and showed no further conversion, so an extra 0.5 eq tributyltin hydride and 0.05 eq AIBN were added. After completion, the reaction mixture was concentrated under reduced pressure. The residue was purified over silica (5% diethyl ether in pentane) to give the title compound as colourless oil. Yield: 1.38 g, 3.93 mmol, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.11 (m, 2H, CH_{arom}), 7.63 – 7.55 (m, 1H, CH_{arom}), 7.51 – 7.42 (m, 2H, CH_{arom}), 5.27 (dd, *J* = 3.1, 1.4 Hz, 1H, H-4), 4.10 (ddd, *J* = 11.8, 4.8, 1.8 Hz, 1H, H-1_{eq}), 3.94 (ddd, *J* = 11.5, 5.0, 3.3 Hz, 1H, H-3), 3.68 (qd, *J* = 6.4, 1.2 Hz, 1H, H-5), 3.56 (ddd, *J* = 12.8, 11.8, 2.1 Hz, 1H, H-1_{ax}), 2.12 (tdd, *J* = 12.8, 11.4, 4.8 Hz, 1H, H-2_{ax}), 1.72 – 1.64 (m, 1H, H-2_{eq}), 1.23 (d, *J* = 6.4 Hz, 3H, H-6), 0.79 (s, 9H, C(CH_3)$_3$ TBS), 0.08 (s, 3H, CH_3 TBS), 0.07 (s, 3H, CH_3 TBS), ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6 (C=O), 132.9 (CH_{arom}), 130.7 (C_q), 129.9, 128.4 (CH_{arom}), 73.8 (C-5), 73.4 (C-4), 69.7 (C-3), 66.0 (C-1), 30.8 (C-2), 25.7 (C(CH_3)$_3$ TBS) , 18.1 (*C*(CH_3)$_3$ TBS), 17.5 (C-6), -4.6, -4.8 (CH_3 TBS); HRMS $[M+H]^+$ calcd for $C_{19}H_{30}O_4SiH$ 351.19861, found 351.19802.

1,2-di-deoxy-4-*O*-benzoyl-D-fucopyranose (54)



1,2-di-deoxy-4-*O*-benzoyl-3-*O*-dimethyltertbutylsilyl-D-fucopyranose (**S104**, 1.30 g, 3.71 mmol) and PTSA-H_2O (71 mg, 0.37 mmol, 0.1 eq) were dissolved in methanol. After full conversion, triethylamine (0.10 mL, 0.74 mmol, 0.2 eq) was added and the reaction mixture was concentrated under reduced pressure. Silica chromatography (25% EtOAc in pentane) yields the title compound as colourless oil. Yield: 800 mg, 3.39 mmol, 91%. $[\alpha]_D^{25}$ = 30.8° (c = 1.12, $CHCl_3$); IR (thin film): 713, 1086, 1115, 1274, 1717; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.08 (m, 2H, CH_{arom}), 7.65 – 7.55 (m, 1H, CH_{arom}), 7.53 – 7.41 (m, 2H, CH_{arom}), 5.37 – 5.18 (m, 1H, H-4), 4.09 (ddd, *J* = 11.8, 4.8, 1.8 Hz, 1H, H-1_{eq}), 3.99 (dtd, *J* = 11.7, 4.9, 3.2 Hz, 1H, H-3), 3.64 (qd, *J* = 6.5, 1.2 Hz, 1H, H-5), 3.53 (ddd, *J* = 12.6, 11.8, 2.3 Hz, 1H, H-1_{ax}), 2.42 (d, *J* = 4.9 Hz, 1H, OH), 2.08 – 1.91 (m, 1H, H-2_{ax}), 1.83 – 1.72 (m, 1H, H-2_{eq}), 1.22 (d, *J* = 6.4 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6 (C=O), 133.5, 130.0 (CH_{arom}), 129.8 (C_q), 128.6 (CH_{arom}), 73.8 (C-4), 73.5 (C-5), 69.6 (C-3), 66.1 (C-1), 29.6 (C-2), 17.6 (C-6); HRMS $[M+H]^+$ calcd for $C_{13}H_{16}O_4H$ 237.11214, found 237.11150.

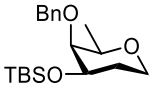
1,2-di-deoxy-4-*O*-benzyl-3-*O*-dimethyltertbutylsilyl-D-galactopyranose (S105)



1,2-di-deoxy-4,6-*O*-benzylidene-3-*O*-dimethyltertbutylsilyl-D-galactopyranose (**S102**, 2.28 g, 6.50 mmol) and BH_3-$NH(CH_3)_2$ (1.92 g, 32.5 mmol, 5 eq) were dissolved in DCM and cooled to 0 °C

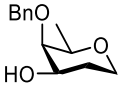
after which BF_3-Et_2O (4.0 mL, 32.5 mol, 5 eq) was added dropwise. After full conversion, the reaction was quenched with sat. aq. $NaHCO_3$. The aquatic phase was extracted twice with dichloromethane. Organic phases were combined, washed with sat. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated under reduced pressure. Silica chromatography (15% acetone in pentane) yields the title compound as colourless oil. Yield: 1.41 g, 4.00 mmol, 62%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H, CH_{arom}), 4.99 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.64 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 4.03 (ddd, *J* = 11.6, 4.8, 2.1 Hz, 1H, H-1_{eq}), 3.84 (ddd, *J* = 11.3, 4.6, 2.7 Hz, 1H, H-3), 3.78 (ddd, *J* = 11.2, 7.0, 3.0 Hz, 1H, H-6), 3.59 (dt, *J* = 2.6, 1.3 Hz, 1H, H-4), 3.49 – 3.40 (m, 2H, H-1_{ax}, H-6), 3.34 (ddd, *J* = 7.1, 4.7, 1.4 Hz, 1H, H-5), 2.19 (tdd, *J* = 14.1, 11.8, 4.8 Hz, 1H, H-2_{ax}), 1.82 (dd, *J* = 8.8, 3.5 Hz, 1H, OH), 1.58 (dddd, *J* = 12.9, 4.6, 2.3, 1.4 Hz, 1H, H-2_{eq}), 0.94 (s, 9H, $C(CH_3)_3$ TBS), 0.14 (s, 3H, CH_3 TBS), 0.12 (s, 3H, CH_3 TBS), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8 (C_q), 128.6, 128.5, 127.9 (CH_{arom}), 79.1 (C-5), 76.1 (C-4), 74.5 (CH_2 Bn), 72.8 (C-3), 66.0 (C-1), 63.2 (C-6), 30.8 (C-2), 26.0 ($C(CH_3)_3$ TBS), 18.2 ($C(CH_3)_3$ TBS), -4.3, -4.5 (CH_3 TBS); HRMS: $[M+Na]^+$ calcd for $C_{19}H_{32}O_4SiNa$ 375.19621, found 375.19571

1,2-di-deoxy-4-*O*-benzyl-3-*O*-dimethyltertbutylsilyl-D-fucopyranose (S107)



1,2-di-deoxy-4-*O*-benzyl-3-*O*-dimethyltertbutylsilyl-D-galactopyranose (1.35 g, 3.83 mmol) and tosyl chloride (1.46 g, 7.66 mmol, 2 eq) were dissolved in pyridine and reacted for 4 hr, after which the reaction mixture was diluted with 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 **S106**. The residue was dissolved in THF and lithium aluminiumhydride (4 M in Et_2O, 3.83 mL, 15.3 mmol, 4 eq) was added dropwise. The reaction mixture was refluxed overnight, before being cooled to 0 °C. Excess reagent was carefully quenched with 1M HCl. The aquatic phase was extracted twice with ethyl acetate. Combined organic phases were washed with sat. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated under reduced pressure. Silica chromatography (10% diethyl ether in pentane) gives the title compound as colourless oil. Yield: 506 mg, 1.50 mmol, 39%. Further elution also gave 29% of recovered starting material. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H, CH_{arom}), 7.34 – 7.30 (m, 2H, CH_{arom}), 7.28 – 7.24 (m, 1H, CH_{arom}), 5.01 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.64 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 3.97 (ddd, *J* = 11.6, 4.9, 1.8 Hz, 1H, H-1_{eq}), 3.82 (ddd, *J* = 11.5, 4.7, 2.6 Hz, 1H, H-3), 3.49 – 3.32 (m, 3H, H-1_{ax}, H-4, H-5), 2.16 (tdd, *J* = 12.7, 11.5, 4.9 Hz, 1H, H-2_{ax}), 1.58 – 1.48 (m, 1H, H-2_{eq}), 1.16 (d, *J* = 6.3 Hz, 3H, H-6), 0.94 (s, 9H, $C(CH_3)_3$ TBS), 0.12 (s, 3H, CH_3 TBS), 0.11 (s, 3H, CH_3 TBS), ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3 (C_q), 128.5, 128.2, 127.5 (CH_{arom}), 79.2 (C-4), 75.0 (CH_2 Bn), 75.0 (C-5), 73.4 (C-3), 66.0 (C-1), 30.4 (C-2), 26.0 ($C(CH_3)_3$ TBS), 18.2 ($C(CH_3)_3$ TBS), 17.9 (C-6), -4.3, -4.5 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{19}H_{32}O_3SiNH_4$ 354.24590, found 354.24526

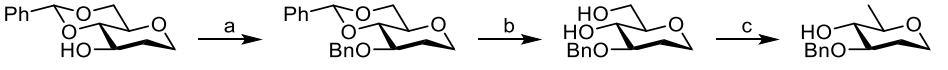
1,2-di-deoxy-4-*O*-benzyl-D-fucopyranose (53)



1,2-di-deoxy-4-*O*-benzyl-3-*O*-dimethyltertbutylsilyl-D-fucopyranose (**S107**, 450 mg, 1.34 mmol) and PTSA-H_2O (25 mg, 0.13 mmol, 0.1 eq) were dissolved in methanol. After full conversion,

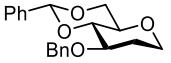
triethylamine (38 µL, 0.27 mmol, 0.2 eq) was added and the reaction mixture was concentrated under reduced pressure. Silica chromatography (25% ethyl acetate in pentane) yield the title compound as colourless oil. Yield: 200 mg, 0.90 mmol, 67%. $[\alpha]_D^{25}$ = 54.4° (c = 0.33, $CHCl_3$); IR (thin film): 714, 1027, 1086, 1275, 1454; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H, CH_{arom}), 4.85 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.64 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 3.98 (ddd, *J* = 11.7, 4.8, 2.0 Hz, 1H, H-1_{eq}), 3.68 (dddd, *J* = 11.5, 10.1, 5.1, 3.4 Hz, 1H, H-3), 3.51 – 3.49 (m, 1H, H-4), 3.48 – 3.35 (m, 2H, H-1_{ax}, H-5), 1.91 – 1.78 (m, 2H, H-2_{ax}, OH), 1.69 (ddtd, *J* = 12.7, 5.3, 2.2, 1.0 Hz, 1H, H-2_{eq}), 1.30 (d, *J* = 6.5 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4 (C_q), 128.8, 128.2, 128.2 (CH_{arom}), 80.1 (C-4), 76.1 (CH_2 Bn), 75.0 (C-5), 70.1 (C-3), 65.8 (C-1), 30.7 (C-2), 17.9 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{13}H_{18}O_3Na$ 245.11482, found 245.11441.

Preparation of acceptor **55**



*Scheme **S36**: preparation of acceptor **55**: reagents and conditions: a) BnBr, NaH, DMF, 86%; b) MeOH, 60 °C, 100%; c) i: TsCl, pyridine, ii: $LiAlH_4$, THF, reflux, 68% over 2 steps*

1,2-di-deoxy-3-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranose (S108)



1,2-di-deoxy-4,6-*O*-benzylidene-D-glucopyranose (**S91**, 1.18 g, 5 mmol), benzyl bromide (0.89 mL, 7.50 mmol, 1.5 eq) and sodium hydride (60% dispersion in mineral oil, 300 mg, 7.50 mmol, 1.5 eq) were dissolved in DMF. When TLC shows full conversion, the reaction is quenched with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (15% diethyl ether in pentane), yielding the title compound as white solid. Yield: 1.41 g, 4.30 mmol, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H, CH_{arom}), 7.43 – 7.25 (m, 8H, CH_{arom}), 5.62 (s, 1H, C*H*Ph), 4.84 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.72 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.29 (dd, *J* = 10.4, 4.9 Hz, 1H, H-6), 3.98 (ddd, *J* = 11.8, 5.3, 1.5 Hz, 1H, H-1_{eq}), 3.77 – 3.64 (m, 3H, H-3, H-4, H-6), 3.52 (ddd, *J* = 12.8, 11.8, 2.4 Hz, 1H, H-1_{ax}), 3.34 (ddd, *J* = 10.1, 8.7, 4.9 Hz, 1H, H-5), 2.06 (dddd, *J* = 13.5, 5.0, 2.3, 1.5 Hz, 1H, H-2_{eq}), 1.82 (tdd, *J* = 13.1, 10.6, 5.3 Hz, 1H, H-2_{ax}), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 137.8 (C_q), 129.0, 128.5, 128.3, 127.8, 127.7, 126.2 (CH_{arom}), 101.4 (CHPh), 84.0 (C-4), 76.0 (C-3), 72.7 (CH_2 Bn), 71.8 (C-5), 69.1 (C-6), 66.6 (C-1), 32.5 (C-2); HRMS: $[M+Na]^+$ calcd for $C_{20}H_{22}O_4Na$ 349.14103, found 349.14054.

1,2-di-deoxy-3-*O*-benzyl-D-glucopyranose (S109)

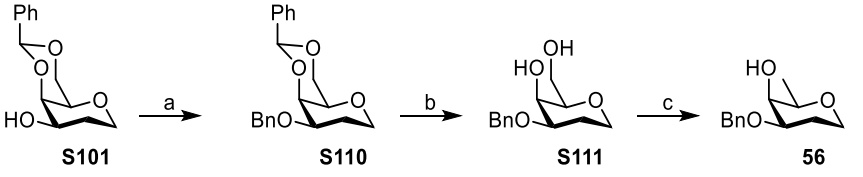
1,2-di-deoxy-3-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranose (**S108**, 1.40 g, 4.3 mmol) and PTSA-H_2O (82 mg, 0.43 mmol, 0.1 eq) were dissolved in methanol and heated to 60 °C. When TLC shows full conversion, triethylamine (0.12 mL, 0.86 mmol, 0.2 eq) was added and the reaction mixture was concentrated under reduced pressure. The residue was purified over silica (15% acetone in DCM) yielding the title compound as colourless oil in quantitative yield. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H, CH_{arom}), 4.71 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.52 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.00 (ddd, *J* = 11.8, 4.9, 1.7 Hz, 1H, H-1_{eq}), 3.87 (ddd, *J* = 11.7, 6.0, 3.5 Hz, 1H, H-6), 3.74 (ddd, *J* = 11.7, 6.6, 5.2 Hz, 1H, H-6), 3.56 – 3.37 (m, 3H, H-1_{ax}, H-3, H-4), 3.24 (ddd, *J* = 8.9, 5.2, 3.4 Hz, 1H, H-5), 2.79 (d, *J* = 2.2 Hz, 1H, 4-OH), 2.27 (t, *J* = 6.3 Hz, 1H, 6-OH), 2.07 (ddt, *J* = 12.8, 4.0, 1.9 Hz, 1H, H-2_{eq}), 1.62 (tdd, *J* = 12.7, 10.7, 4.9 Hz, 1H, H-2_{ax}), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2 (C_q), 128.6, 127.9, 127.8 (CH_{arom}), 80.5 (C-3), 79.7 (C-5), 71.6 (C-4), 70.9 (CH_2 Bn), 65.7 (C-1), 63.1 (C-6), 30.5 (C-2). Spectra in agreement with literature.[101]

1,2,6-tri-deoxy-3-*O*-benzyl-D-glucopyranose (55)

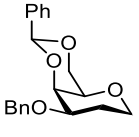
1,2-di-deoxy-3-*O*-benzyl-D-glucopyranose (**S109**, 1.03 g, 4.30 mmol) was dissolved in 25 mL pyridine, after which para-toluenesulfonyl chloride (1.23 g, 6.45 mmol, 1.5 eq) was added. The reaction mixture was stirred overnight, diluted with ethyl acetate and washed with 1M HCl and sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The crude tosylate was dissolved in THF and lithium aluminiumhydride (2.4 M in THF, 7.2 mL, 17.2 mmol, 4 eq) was added. The reaction mixture was heated to a reflux. When complete, the reaction mixture was cooled to 0 °C, carefully quenched with 1M HCl and extracted twice with ethyl acetate. The combined organic phases were washed with sat. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica chromatography (10% acetone in pentane) to give the title compound as colourless oil. Yield: 645 mg, 2.90 mmol, 68% over 2 steps. $[\alpha]_D^{25}$ = -65.0° (c = 0.10, $CHCl_3$); IR (thin film): 668, 699, 1093, 1276, 1455; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H, CH_{arom}), 4.71 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.50 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 3.95 (ddd, *J* = 11.9, 4.9, 1.7 Hz, 1H, H-1_{eq}), 3.47 – 3.35 (m, 2H, H-1_{ax}, H-3), 3.28 – 3.15 (m, 2H, H-4, H-5), 2.53 (d, *J* = 1.7 Hz, 1H, OH), 2.07 (ddt, *J* = 12.8, 4.4, 2.0 Hz, 1H, H-2_{eq}), 1.64 (tdd, *J* = 12.7, 11.1, 4.9 Hz, 1H, H-2_{ax}), 1.30 (d, *J* = 5.5 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2 (C_q), 128.6, 127.9, 127.8 (CH_{arom}), 80.6 (C-3), 76.2, 76.2 (C-4, C-5), 70.7 (CH_2 Bn), 65.5 (C-1), 30.7 (C-2), 18.3 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{13}H_{18}O_3Na$ 245.11482, found 245.11450.

Preparation of acceptor **56**



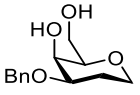
*Scheme **S37**: preparation of acceptor **56**: reagents and conditions: a) BnBr, NaH, DMF, 89%; b) MeOH, 60 °C, 97%; c) i: TsCl, pyridine, ii: $LiAlH_4$, THF, reflux, 70% over 2 steps*

1,2-di-deoxy-3-*O*-benzyl-4,6-*O*-benzylidene-D-galactopyranose (S110)



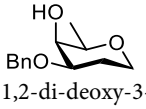
1,2-di-deoxy-4,6-*O*-benzylidene-D-galactopyranose (**S101**, 1.18 g, 5 mmol), benzyl bromide (0.89 mL, 7.50 mmol, 1.5 eq) and sodium hydride (60% dispersion in mineral oil, 300 mg, 7.50 mmol, 1.5 eq) were dissolved in DMF. When TLC shows full conversion, the reaction is quenched with water and extracted with diethyl ether. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified over silica (10%→15% acetone in pentane), yielding the title compound as white powder. Yield: 1.45 g, 4.43 mmol, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H, CH_{arom}), 7.41 – 7.26 (m, 8H, CH_{arom}), 5.58 (s, 1H, C*H*Ph), 4.67 (s, 2H, CH_2 Bn), 4.26 (dd, *J* = 12.3, 1.6 Hz, 1H, H-2), 4.20 – 4.12 (m, 2H, H-1_{eq}, H-4), 4.01 (dd, *J* = 12.4, 1.8 Hz, 1H, H-6), 3.57 (ddd, *J* = 11.9, 4.7, 3.1 Hz, 1H, H-3), 3.47 (ddd, *J* = 12.6, 11.7, 2.0 Hz, 1H, H-1_{ax}), 3.23 (q, *J* = 1.6 Hz, 1H, H-5), 2.25 (qd, *J* = 12.5, 4.6 Hz, 1H, H-2_{ax}), 1.74 (dddd, *J* = 12.4, 4.6, 2.8, 1.3 Hz, 1H, H-2_{eq}), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 138.1 (C_q), 128.9, 128.6, 128.2, 127.8, 127.8, 126.5 (CH_{arom}), 101.1 (*C*HPh), 75.5 (C-3), 73.4 (C-4), 70.6 (C-6), 70.2 (C-5), 69.6 (C-1), 66.2 (CH_2 Bn), 26.9 (C-2); HRMS: $[M+Na]^+$ calcd for $C_{20}H_{22}O_4Na$ 349.14103, found 349.14066.

1,2-di-deoxy-3-*O*-benzyl-D-galactopyranose (S111)



1,2-di-deoxy-3-*O*-benzyl-4,6-*O*-benzylidene-D-galactopyranose (**S110)** 1.63 g, 5 mmol) and PTSA-H_2O (95 mg, 0.5 mmol, 0.1 eq) were dissolved in methanol and heated to 60 °C. When TLC shows full conversion, triethylamine (0.14 mL, 1 mmol, 0.2 eq) was added and the reaction mixture was concentrated under reduced pressure. The residue was purified over silica (25% acetone in DCM) yielding the title compound as white powder. Yield: 1.16 g, 4.85 mmol, 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H, CH_{arom}), 4.61 (d, *J* = 1.7 Hz, 2H, CH_2 Bn), 4.07 (ddd, *J* = 11.7, 5.1, 1.7 Hz, 1H, H-1_{eq}), 4.03 – 3.98 (m, 1H, H-4), 3.92 (ddd, *J* = 11.7, 6.7, 3.7 Hz, 1H, H-6), 3.75 (ddd, *J* = 11.7, 8.5, 4.3 Hz, 1H, H-6), 3.53 (ddd, *J* = 11.6, 5.0, 3.0 Hz, 1H, H-3), 3.41 (ddd, *J* = 12.7, 11.7, 2.3 Hz, 1H, H-1_{ax}), 3.33 (ddt, *J* = 6.6, 4.2, 1.2 Hz, 1H, H-5), 2.61 (dd, *J* = 2.5, 1.2 Hz, 1H, 4-OH), 2.54 (dd, *J* = 8.5, 3.8 Hz, 1H, 6-OH), 2.01 (tdd, *J* = 12.8, 11.5, 5.0 Hz, 1H, H-2_{ax}), 1.75 (ddq, *J* = 13.0, 5.0, 1.9 Hz, 1H, H-2_{eq}), ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9 (C_q), 128.7, 128.1, 127.8 (CH_{arom}), 78.5 (C-5), 75.9 (C-3), 69.8 (CH_2 Bn), 67.0 (C-4), 66.0 (C-6), 63.6 (C-1), 26.5 (C-2). HRMS $[M+Na]^+$ calcd for $C_{13}H_{18}O_4Na$ 261.10973, found 261.10949.

1,2-di-deoxy-3-*O*-benzyl-D-fucopyranose (56)

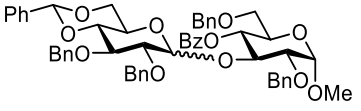


1,2-di-deoxy-3-*O*-benzyl-D-galactopyranose (**S111**, 1.13 g, 4.74 mmol) was dissolved in 25 mL pyridine, after which para-toluenesulfonyl chloride (1.36 g, 7.11 mmol, 1.5 eq) was added. The reaction mixture was stirred overnight, diluted with ethyl acetate and washed with 1M HCl and sat. aq. $NaHCO_3$. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The crude tosylate was dissolved in THF and lithium aluminiumhydride (2.4 M in THF, 7.9 mL, 19 mmol, 4 eq) was added. The reaction mixture was heated to a reflux. When complete, the reaction mixture was cooled to 0 °C, carefully quenched with 1M HCl and extracted twice with ethyl acetate. The combined organic phases were washed with sat. aq.

$NaHCO_3$, dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica chromatography (10% acetone in pentane) to give the title compound as colourless oil. Yield: 740 mg, 3.33 mmol, 70% over 2 steps. $[\alpha]_D^{25}$ = 33.9° (c = 0.43, $CHCl_3$); IR (thin film): 668, 700, 980, 1027, 1086, 1183; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H, CH_{arom}), 4.64 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.60 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.00 (ddd, *J* = 11.7, 5.1, 1.7 Hz, 1H, H-1_{eq}), 3.82 – 3.74 (m, 1H, H-4), 3.52 (ddd, *J* = 11.6, 5.1, 3.0 Hz, 1H, H-3), 3.43 – 3.34 (m, 2H, H-1_{ax}, H-5), 2.22 (dd, *J* = 3.3, 1.0 Hz, 1H, OH), 1.94 (tdd, *J* = 12.9, 11.6, 5.1 Hz, 1H, H-2_{ax}), 1.73 (dddd, *J* = 11.8, 6.3, 2.4, 1.3 Hz, 1H, H-2_{eq}), 1.31 (d, *J* = 6.5 Hz, 3H, H-6), ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1 (C_q), 128.7, 128.0, 127.8 (CH_{arom}), 76.5 (C-3), 74.6 (C-5), 69.7 (CH_2 Bn), 68.8 (C-4), 65.9 (C-1), 26.3 (C-2), 17.5 (C-6); HRMS $[M+Na]^+$ calcd for $C_{13}H_{18}O_3Na$ 245.11482, found 245.11451.

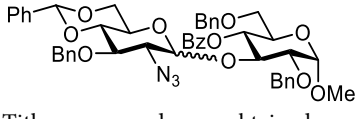
Characterisation of glycosylation products

Disaccharide 6A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **6**. Yield: 93 mg, 98 µmol, 98%, α:β = 2.6:1. Data reported for a 1:0.4 mixture of anomers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 1H), 7.98 – 7.93 (m, 2H), 7.60 – 7.00 (m, 38H), 5.49 – 5.41 (m, 2H, H-4α, C*H*Phα), 5.30 (dd, *J* = 10.3, 9.1 Hz, 0.4H, H-4β), 5.24 (s, 0.4H, C*H*Phβ), 5.19 (d, *J* = 3.5 Hz, 1H, H-1'α), 4.97 (d, *J* = 11.5 Hz, 0.4H), 4.89 – 4.85 (m, 0.8H, H-1'β, C*H*H Bnβ), 4.82 (d, *J* = 10.9 Hz, 1H), 4.79 – 4.73 (m, 2H), 4.66 (d, *J* = 12.0 Hz, 0.4 H), 4.59 – 4.50 (m, 5H), 4.48 – 4.41 (m, 2H), 4.40 – 4.26 (m, 4H), 4.18 (d, *J* = 12.1 Hz, 1H), 4.04 – 3.93 (m, 3H), 3.68 – 3.47 (m, 7H), 3.37 (d, *J* = 2.9 Hz, 4H, CH_3 Meαβ), 3.35 – 3.30 (m, 1H), 3.28 (t, *J* = 9.3 Hz, 0.4H, H-3'β), 3.20 (td, *J* = 9.7, 5.0 Hz, 0.4H, H-5'β), 2.90 (t, *J* = 10.1 Hz, 0.4H, H-6'β); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 165.2, 138.8, 138.7, 138.2, 138.0, 137.9, 137.8, 137.8, 137.7, 137.4, 133.2, 133.1, 130.6, 129.9, 129.9, 129.9, 129.0, 128.8, 128.8, 128.6, 128.6, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.6, 127.6, 127.5, 127.5, 127.5, 126.2, 126.0, 102.9 (C-1'β), 101.3 (CHPhα), 100.9 (CHPhβ), 98.6 (C-1'α), 98.1 (C-1β), 97.7 (C-1α), 82.7, 82.3, 81.5, 81.0, 80.3, 78.8, 78.6, 78.6, 77.4, 77.2, 76.9, 76.2, 75.5, 75.3, 75.0, 73.9, 73.7, 73.7, 73.6, 72.9, 72.2, 69.6, 69.4, 69.1, 68.8, 68.6, 68.5, 65.5, 63.0, 55.5, 55.4, HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{56}O_{12}NH_4$ 926.41100, found 926.40958.

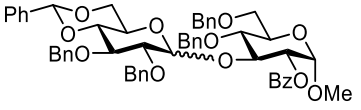
Disaccharide 6B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **6**. Yield: 86 mg, 99 µmol, 99%, α:β = 1:5. IR (thin film): 696, 711, 749, 998, 1027, 1043, 1070, 1091, 1174, 1269, 1452, 1727, 2109; Data for β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.14 (m, 25H, CH_{arom}), 5.27 (dd, *J* = 10.3, 9.1 Hz, 1H, H-4), 5.23 (s, 1H, CH Ph), 4.89 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.83 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.73 (d, *J* = 11.4 Hz, 1H, CH*H* Bn), 4.67 (d, *J* = 8.0 Hz, 1H, H-1'), 4.60 (d, *J* = 11.8 Hz, 1H,

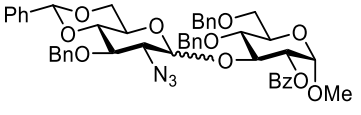
CH*H* Bn), 4.56 (d, *J* = 3.6 Hz, 1H, H-1), 4.53 – 4.47 (m, 2H, C*H*H Bn, CH*H* Bn), 4.26 (t, *J* = 9.3 Hz, 1H, H-3), 4.02 – 3.92 (m, 1H, H-5), 3.85 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6'), 3.72 (dd, *J* = 9.7, 3.6 Hz, 1H, H-2), 3.63 – 3.51 (m, 2H, H-6 x2), 3.47 – 3.42 (m, 1H, H-3'), 3.37 (d, *J* = 4.2 Hz, 4H, CH_3 OMe, H-2'), 3.34 – 3.28 (m, 1H, H-4'), 3.17 – 3.11 (m, 1H, H-5'), 2.76 (t, *J* = 10.3 Hz, 1H, H-6'). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1 (C=O), 138.1, 138.0, 137.8, 137.2, 133.1, 130.5, 129.9, 129.7, 129.1, 128.9, 128.7, 128.7, 128.6, 128.6, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.3, 128.2, 128.1, 127.8, 127.8, 127.8, 127.6, 127.6, 126.1, 126.0 (CH_{arom}), 102.2 (C-1'), 101.1 (CH Ph), 97.8 (C-1), 81.4 (C-4'), 79.8 (C-2), 79.2 (C-3'), 77.7 (C-3), 74.9 (CH_2 Bn), 73.8 (CH_2 Bn), 73.7 (CH_2 Bn), 69.5 (C-4), 68.9 (C-6), 68.7 (C-5), 68.1 (C-6'), 66.2 (C-2'), 65.6 (C-5'), 55.5 (CH_3 OMe). Diagnostic peaks for α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.50 (s, 1H, CH Ph), 5.36 (dd, *J* = 10.3, 9.2 Hz, 1H, H-4), 5.04 (d, *J* = 3.8 Hz, 1H, H-1'), 4.65 – 4.63 (m, 1H, H-1), 4.15 (dd, *J* = 10.2, 4.9 Hz, 1H, H-5), 3.37 (s, 3H, CH_3 OMe). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3 (C=O), 137.5, 137.5, 133.3, 131.8, 131.2, 129.7, 124.8, 124.5 (CH_{arom}), 101.3 (CHPh), 99.5 (C-1'), 97.5 (C-1), 82.7 (C-4'), 78.0, 77.6, 76.7, 75.1 (CH_2 Bn), 73.3 (CH_2 Bn), 72.1 (C-4), 69.3 (C-6'), 68.8 (C-6), 63.3, 63.0, 55.4 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{49}N_3O_{11}NH_4$ 861.37053, found 861.36976.

Disaccharide 7A



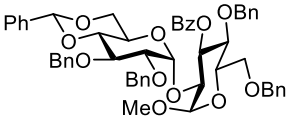
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **7**. Yield: 94 mg, 99 μmol, 99%, α:β = 1.8:1. Data reported for a 2:1 mixture of anomers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 4H), 7.95 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.45 (m, 4H), 7.41 – 7.15 (m, 66H), 7.10 (ddt, *J* = 7.8, 4.8, 2.2 Hz, 6H), 5.50 (s, 1H, C*H*Phβ), 5.39 (s, 2H, C*H*Phα), 5.21 (dd, *J* = 9.7, 3.8 Hz, 2H, H-2α), 5.14 (dd, *J* = 9.9, 3.6 Hz, 3H, H-1'α, H-2β), 5.10 – 5.06 (m, 3H, H-1β, C*H*H Bnα)), 4.95 (d, *J* = 10.5 Hz, 1H), 4.92 (d, *J* = 3.8 Hz, 2H, H-1α), 4.90 (d, *J* = 7.7 Hz, 1H, H-1'β), 4.82 (d, *J* = 11.4 Hz, 2H), 4.77 – 4.70 (m, 6H), 4.67 (d, *J* = 12.1 Hz, 1H), 4.65 – 4.57 (m, 5H), 4.57 – 4.50 (m, 4H), 4.48 – 4.40 (m, 3H), 4.39 – 4.31 (m, 3H), 4.14 (dd, *J* = 10.2, 4.9 Hz, 2H), 3.99 (t, *J* = 9.4 Hz, 2H), 3.94 (td, *J* = 10.0, 4.9 Hz, 2H), 3.89 – 3.79 (m, 6H), 3.78 – 3.73 (m, 2H), 3.70 (td, *J* = 10.6, 1.8 Hz, 3H), 3.63 – 3.55 (m, 2H), 3.53 (t, *J* = 8.9 Hz, 1H), 3.48 – 3.42 (m, 4H), 3.40 – 3.33 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0 (C=Oα), 165.9 (C=Oβ), 138.7, 138.6, 138.5, 138.5, 138.3, 138.3, 138.1, 138.1, 137.6, 137.4, 133.2, 133.1, 130.1, 129.9, 129.8, 129.7, 129.0, 128.8, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 127.8, 127.6, 127.5, 127.4, 126.2, 126.1, 103.9 (C-1'β), 101.2 (CHPhα), 101.1 (CHPhβ), 98.9 (C-1'α), 97.2 (C-1α), 97.0 (C-1β), 82.3, 82.3, 81.7, 81.2, 79.6, 79.5, 78.1, 77.8, 77.7, 77.4, 77.2, 76.9, 76.0, 75.2, 75.1, 75.1, 75.0, 74.9, 74.7, 73.7, 73.7, 73.7, 73.0, 70.1, 69.8, 68.9, 68.7, 68.6, 68.6, 66.1, 63.2, 55.3, 55.3; HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{56}O_{12}NH_4$ 926.41100, found 926.40981

Disaccharide 7B



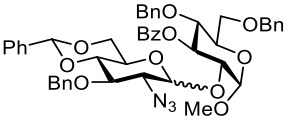
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **7.** Yield: 81 mg, 93 µmol, 93%, α:β = 1:4. Data for the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.4, 1.3 Hz, 2H, CH_{arom}), 7.62 – 7.56 (m, 1H, CH_{arom}), 7.49 – 7.43 (m, 4H, CH_{arom}), 7.41 – 7.20 (m, 18H, CH_{arom}), 5.51 (s, 1H, C*H*Ph), 5.23 (dd, *J* = 10.0, 3.7 Hz, 1H, H-2), 5.05 (d, *J* = 3.6 Hz, 1H, H-1), 4.94 (d, *J* = 10.6 Hz, 1H, C*H*H Bn), 4.75 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.71 (d, *J* = 8.0 Hz, 1H, H-1'), 4.66 (d, *J* = 12.0 Hz, 1H, , C*H*H Bn), 4.60 (d, *J* = 11.2 Hz, 1H, CH*H* Bn), 4.54 (d, *J* = 12.2 Hz, 1H, CH*H* Bn), 4.49 – 4.43 (m, 2H, H-3, CH*H* Bn), 4.26 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6'), 3.84 (ddd, *J* = 10.0, 3.7, 1.9 Hz, 1H, H-5), 3.80 – 3.73 (m, 2H, H-4, H-6), 3.70 (dd, *J* = 10.7, 1.9 Hz, 1H, H-6), 3.61 (t, *J* = 9.2 Hz, 1H, H-4'), 3.55 (t, *J* = 10.2 Hz, 1H, H-6'), 3.38 – 3.32 (m, 5H, H-2', H-5', CH_3 OMe), 3.29 (t, *J* = 9.2 Hz, 1H, H-3'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8 (C=O), 138.5, 138.1, 137.8, 137.1 (C_q), 133.3 (CH_{arom}), 129.9 (C_q), 129.8, 129.8, 129.2, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.1, 128.1, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 126.2, 126.0 (CH_{arom}), 102.9 (C-1'), 101.3 (CHPh), 97.1 (C-1), 81.6 (C-4'), 79.4 (C-3), 79.2 (C-3'), 76.0 (C-4), 75.0, 74.9 (CH_2 Bn), 74.2 (C-2), 73.7 (CH_2 Bn), 70.2 (C-5), 68.6, 68.5 (C-6, C-6'), 66.5, 66.3 (C-2', C-5'), 55.3 (CH_3 OMe); diagnostic peaks for the α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.41 (d, *J* = 3.8 Hz, 1H, H-1'), 5.35 (s, 1H, C*H*Ph), 4.82 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.38 (dd, *J* = 10.0, 8.4 Hz, 1H, H-3), 4.08 (dd, *J* = 10.2, 4.8 Hz, 1H, H-6'), 3.94 (dd, *J* = 10.0, 9.1 Hz, 1H), 3.46 (t, *J* = 10.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1 (C=O), 98.4 (C-1'), 97.2 (C-1), 82.8, 78.8, 76.6, 76.2, 75.0, 74.5, 73.8, 72.3, 70.1, 68.3, 63.4, 63.0, 55.3 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{49}N_3O_{11}NH_4$ 861.37053, found 861.36933.

Disaccharide 10A



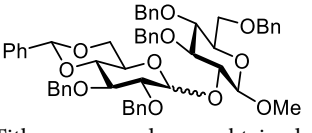
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **10**. Yield: 75 mg, 78 µmol, 78%, α:β > 20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 7.98 (m, 2H, CH_{arom}), 7.41 – 7.17 (m, 23H, CH_{arom}), 7.13 – 7.08 (m, 3H, CH_{arom}), 7.01 – 6.97 (m, 2H, CH_{arom}), 5.88 (dd, *J* = 10.1, 8.9 Hz, 1H, H-3), 5.30 (s, 1H, C*H*Ph), 4.92 (d, *J* = 3.4 Hz, 1H, H-1), 4.84 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.80 – 4.76 (m, 2H, H-1', C*H*H Bn), 4.71 (d, *J* = 11.2 Hz, 1H, CH*H* Bn), 4.67 (d, *J* = 8.7 Hz, 1H, C*H*H Bn), 4.64 (d, *J* = 8.6 Hz, 1H, CH*H* Bn), 4.52 (d, *J* = 9.0 Hz, 1H, CH*H* Bn), 4.50 (d, *J* = 7.8 Hz, 1H, C*H*H Bn), 4.40 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 3.95 – 3.86 (m, 4H, H-2, H-3', H-4, H-5), 3.84 – 3.78 (m, 2H, H-6, H-6'), 3.72 – 3.66 (m, 2H, H-5', H-6), 3.44 (dd, *J* = 9.3, 3.5 Hz, 1H, H-2'), 3.41 – 3.38 (m, 4H, H-4', CH_3 OMe), 3.37 – 3.33 (m, 1H, H-6'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5 (C=O), 138.8, 138.6, 137.8, 137.6, 137.5, 133.0 (C_q), 130.1, 129.7, 128.8, 128.6, 128.5, 128.5, 128.3, 128.3, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.6, 126.3 (CH_{arom}), 101.2 (CHPh), 98.0 (C-1'), 97.3 (C-1), 82.1 (C-4'), 78.7 (C-3'), 78.2 (C-2'), 76.5 (C-4), 76.2 (C-2), 75.2 (CH_2 Bn), 74.5 (CH_2 Bn), 73.8 (CH_2 Bn), 73.7 (C-3), 73.5 (CH_2 Bn), 69.9 (C-5), 68.6 (C-6'), 68.3 (C-6), 63.0 (C-5'), 55.4 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{56}O_{12}NH_4$ 926.41100, found 926.40995.

Disaccharide 10B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **10.** Yield: 69 mg, 82 µmol, 82%, α:β = 6:1. Data for α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 2H, CH_{arom}), 7.47 – 7.19 (m, 18H, CH_{arom}), 7.15 – 7.08 (m, 3H, CH_{arom}), 7.01 (dt, *J* = 4.6, 3.4 Hz, 2H, CH_{arom}), 5.86 (dd, *J* = 10.0, 8.9 Hz, 1H, H-3), 5.33 (s, 1H, C*H*Ph), 4.98 (d, *J* = 3.5 Hz, 1H, H-1), 4.88 (d, *J* = 3.6 Hz, 1H, H-1'), 4.80 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.68 (d, *J* = 5.9 Hz, 1H, C*H*H Bn), 4.65 (d, *J* = 4.7 Hz, 1H, CH*H* Bn), 4.53 (d, *J* = 8.9 Hz, 1H, CH*H* Bn), 4.50 (d, *J* = 7.7 Hz, 1H, C*H*H Bn), 4.42 (d, *J* = 10.8 Hz, 1H, CH*H* Bn), 3.97 – 3.87 (m, 4H, H-2, H-3', H-4, H-5), 3.84 – 3.77 (m, 2H, H-6, H-6'), 3.75 – 3.65 (m, 2H, H-5', H-6), 3.52 – 3.46 (m, 4H, H-4', CH_3 OMe), 3.39 (t, *J* = 10.2 Hz, 1H, H-6'), 3.27 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (C=O), 138.0, 137.9, 137.6, 137.3, 133.15 (C_q), 130.0, 129.7, 129.7, 129.0, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 126.3, 126.0 (CH_{arom}), 101.3 (CHPh), 98.1 (C-1'), 97.3 (C-1), 82.6 (C-4'), 76.9 (C-2), 76.1 (C-4), 75.7 (C-3'), 75.1 (CH_2 Bn), 74.6 (CH_2 Bn), 73.8 (CH_2 Bn), 73.6 (C-3), 70.0 (C-5), 68.5 (C-6'), 68.3 (C-6), 63.4 (C-5'), 63.0 (C-2'), 55.6 (CH_3 OMe); Diagnostic peaks for β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (s, 1H, C*H*Ph), 4.95 (d, *J* = 3.5 Hz, 1H, H-1), 4.28 – 4.21 (m, 2H, H-1', H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 103.9 (C-1'), 101.3 (CHPh), 99.5 (C-1), 81.2, 80.1, 79.7, 76.2, 74.9, 73.3, 68.5, 66.2 (C-6), 65.7, 55.5 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{49}N_3O_{11}NH_4$ 861.37053, found 861.36950.

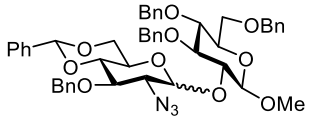
Disaccharide 12A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **12**. Yield: 86 mg, 96 µmol, 96%, α:β = 1:1.9. Data reported for a 1:2 mixture: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.08 (m, 90H, CH_{arom}), 5.68 (d, *J* = 3.8 Hz, 1H, H-1'α), 5.61 (s, 2H, C*H*Phβ), 5.53 (s, 1H, C*H*Phα), 5.11 (d, *J* = 7.6 Hz, 2H, H-1'β), 5.01 (d, *J* = 11.0 Hz, 1H, C*H*H Bnα), 4.97 – 4.86 (m, 9H), 4.86 – 4.82 (m, 8H), 4.77 (d, *J* = 11.2 Hz, 2H), 4.68 (dd, *J* = 12.2, 3.9 Hz, 3H), 4.64 – 4.56 (m, 6H), 4.49 (dd, *J* = 5.4, 2.2 Hz, 1H, H-1α), 4.41 (d, *J* = 7.5 Hz, 2H, H-1β), 4.37 (dd, *J* = 10.4, 5.0 Hz, 2H, H-6'β), 4.26 – 4.19 (m, 2H), 4.08 (t, *J* = 9.4 Hz, 1H), 3.90 – 3.85 (m, 3H), 3.84 – 3.71 (m, 14H), 3.66 – 3.61 (m, 3H), 3.60 (s, 6H, CH_3 OMeβ), 3.59 (s, 3H, CH_3 OMeα), 3.56 (t, *J* = 7.9 Hz, 3H), 3.41 (td, *J* = 9.8, 5.0 Hz, 2H, H-5'β); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8, 138.6, 138.5, 138.3, 138.2, 138.2, 138.1, 138.0, 137.9, 137.8, 137.8, 137.4, 135.4, 131.7, 131.4, 130.4, 129.0, 128.7, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 126.4, 126.1, 104.6 (C-1α), 102.7 (C-1β), 102.5 (C-1'β), 101.2 (CHPhα), 101.1 (CHPhβ), 96.2 (C-1'α), 85.3, 83.0, 82.5, 82.4, 81.5, 81.1, 78.9, 78.7, 78.6, 78.3, 78.2, 76.2, 75.5, 75.4, 75.3, 75.2, 75.1, 75.0, 75.0, 75.0, 74.9, 73.6, 73.0, 69.0, 68.9, 68.8, 68.7, 66.0 (C-5'β), 62.5 (C-5'α),

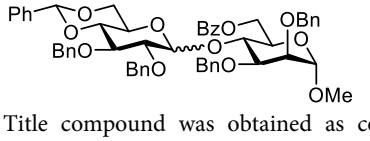
56.8 (CH_3 OMeα), 56.5 (CH_3 OMeβ); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{58}O_{11}NH_4$ 912.43174, found 912.43016.

Disaccharide 12B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **12**. Yield: 65 mg, 78 μmol, 78%, α:β = 1:6. Data for the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 25H, CH_{arom}), 5.56 (s, 1H. C*H*Ph), 4.95 (d, *J* = 10.6 Hz, 1H, C*H*H Bn), 4.92 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.88 (d, *J* = 10.6 Hz, 1H, CH*H* Bn), 4.82 – 4.77 (m, 3H, H-1', C*H*H Bn, CH*H* Bn), 4.62 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.58 – 4.51 (m, 2H, CH*H* Bn), 4.32 (d, *J* = 7.2 Hz, 1H, H-1), 4.29 (dd, *J* = 10.5, 5.1 Hz, 1H, H-6'), 3.81 (t, *J* = 10.3 Hz, 1H, H-6'), 3.77 – 3.69 (m, 5H, H-2, H-4, H-4', 2x H-6), 3.68 – 3.64 (m, 1H, H-3), 3.56 (t, *J* = 9.2 Hz, 1H, H-3'), 3.53 (s, 3H, CH_3 OMe), 3.51 – 3.46 (m, 2H, H-2', H-5), 3.30 (td, *J* = 9.7, 5.0 Hz, 1H, H-5'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.3, 138.2, 138.0, 137.8, 137.2 (C_q), 129.2, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 127.7, 126.3, 126.1 (CH_{arom}), 102.6 (C-1), 101.5 (C-1'), 101.3 (CHPh), 84.9 (C-4), 81.6 (C-4'), 79.7, 79.6 (C-2, C-3'), 78.3 (C-3), 75.6, 75.0 (CH_2 Bn), 74.9 (C-2'), 74.9, 73.6 (CH_2 Bn), 68.8, 68.7 (C-6, C-6'), 66.3, 66.3 (C-5, C-5'), 56.7 (CH_3 OMe); diagnostic peaks for the α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.59 (d, *J* = 3.8 Hz, 1H, H-1'), 5.52 (s, 1H, C*H*Ph), 4.37 (d, *J* = 7.1 Hz, 1H, H-1), 3.98 (dd, *J* = 10.0, 9.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 104.6 (C-1), 101.4 (CHPh), 97.1 (C-1'), 83.0, 78.6, 76.2, 76.1, 75.6, 63.0, 62.8, 57.2 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{51}N_3O_{10}NH_4$ 847.39127, found 847.38954.

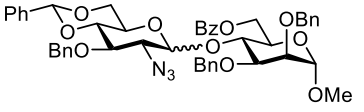
Disaccharide 14A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **14**. Yield: 75 mg, 79 μmol, 79%, α:β = 1.3:1. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.06 (m, 2H), 8.02 – 7.94 (m, 2H), 7.54 – 7.10 (m, 56H), 5.73 (d, *J* = 4.0 Hz, 1H, H-1'α), 5.48 (s, 1H, C*H*Phβ), 5.47 (s, 1H, C*H*Phα), 4.90 – 4.83 (m, 4H), 4.82 – 4.71 (m, 9H), 4.70 – 4.62 (m, 4H), 4.62 – 4.56 (m, 8H), 4.55 – 4.46 (m, 4H), 4.30 (t, *J* = 9.2 Hz, 1H, H-4β), 4.17 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6'β), 4.11 – 3.97 (m, 6H), 3.86 (ddd, *J* = 14.7, 9.2, 4.1 Hz, 3H), 3.82 – 3.77 (m, 2H, H-2αβ), 3.74 (t, *J* = 9.0 Hz, 1H), 3.62 (t, *J* = 9.3 Hz, 1H), 3.58 – 3.53 (m, 2H), 3.51 (dd, *J* = 9.5, 4.0 Hz, 1H, H-2'α), 3.45 (t, *J* = 8.2 Hz, 1H, H-2'β), 3.37 (s, 3H, CH_3 OMeα), 3.36 (s, 3H, CH_3 OMeβ), 3.24 (td, *J* = 9.7, 5.0 Hz, 1H, H-5'β); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 166.2, 139.1, 138.8, 138.5, 138.5, 138.3, 138.3, 138.1, 137.5, 137.4, 133.0, 133.0, 130.2, 130.1, 129.9, 129.9, 129.8, 129.7, 129.0, 128.9, 128.9, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.2, 126.9, 126.3, 126.1, 103.5 (C-1'β), 101.3 (CHPhα), 101.2 (CHPhβ), 99.1 (C-1β), 98.6 (C-1α), 98.4 (C-1'α), 82.7, 82.3, 81.7, 81.5, 80.3, 78.8, 78.6, 77.9, 75.9, 75.7, 75.6, 75.4, 75.2, 74.2, 73.3, 73.0, 72.7, 72.6, 71.7, 71.0,

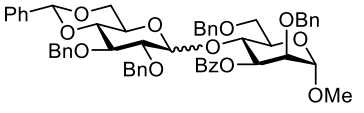
70.2, 69.4, 68.9, 66.0, 64.2, 63.6, 63.6, 55.1;); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{56}O_{12}NH_4$ 926.41100, found 926.40949

Disaccharide 14B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **14**. Yield: 78 mg, 92 µmol, 92%, α:β = 1:8. Data for β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.3, 1.4 Hz, 2H, CH_{arom}), 7.54 (ddt, *J* = 8.7, 7.3, 1.3 Hz, 1H, CH_{arom}), 7.44 – 7.22 (m, 22H, CH_{arom}), 5.47 (s, 1H, C*H*Ph), 4.89 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.79 – 4.76 (m, 2H, H-1, H-6), 4.75 – 4.70 (m, 3H, 2x C*H*H Bn, CH*H* Bn), 4.66 – 4.60 (m, 3H, H-6, 2x CH*H* Bn), 4.52 (d, *J* = 8.1 Hz, 1H, H-1'), 4.35 (t, *J* = 9.4 Hz, 1H, H-4), 4.01 – 3.94 (m, 2H, H-5, H-6'), 3.91 (dd, *J* = 9.1, 3.2 Hz, 1H, H-3), 3.78 (dd, *J* = 3.2, 2.0 Hz, 1H, H-2), 3.64 – 3.57 (m, 2H, H-3', H-4'), 3.52 (t, *J* = 10.3 Hz, 1H, H-6'), 3.41 (dd, *J* = 9.3, 8.1 Hz, 1H, H-2'), 3.36 (s, 3H, CH_3 OMe), 3.18 – 3.11 (m, 1H, H-5'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4 (C=O), 138.8, 138.4, 137.7, 137.2 (C_q), 133.1 (CH_{arom}), 129.8 (C_q), 129.1, 128.5, 128.4, 128.4, 128.4, 128.3, 128.0, 127.7, 127.6, 127.0, 126.1 (CH_{arom}), 102.2 (C-1'), 101.3 (CHPh), 98.9 (C-1), 81.7 (C-4'), 79.7 (C-3'), 78.4 (C-3), 76.0 (C-4), 75.2 (C-2), 75.0, 72.9, 72.4 (CH_2 Bn), 69.7 (C-5), 68.6 (C-6'), 67.0 (C-2'), 66.2 (C-5'), 63.6 (C-6), 55.1 (CH_3 OMe); diagnostic peaks for the α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67 (d, *J* = 4.1 Hz, 1H, H-1'), 5.51 (s, 1H, C*H*Ph), 3.83 (dd, *J* = 3.1, 2.0 Hz, 1H, H-2); ^{13}C NMR (126 MHz, $CDCl_3$) δ 101.4 (CHPh), 99.2 (C-1), 98.7 (C-1'), 82.7, 80.6, 77.4, 76.3, 63.0, 56.1 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{49}N_3O_{11}NH_4$ 861.37053, found 861.36936.

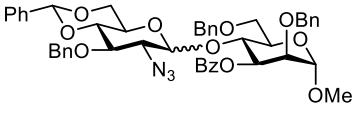
Disaccharide 15A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **15**. Yield: 59 mg, 62 µmol, 62%, α:β = 9:1. Data for α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.3, 1.4 Hz, 2H, CH_{arom}), 7.57 – 7.52 (m, 1H, CH_{arom}), 7.49 – 7.45 (m, 2H, CH_{arom}), 7.41 – 7.33 (m, 7H, CH_{arom}), 7.31 – 7.22 (m, 10H, CH_{arom}), 7.19 – 7.05 (m, 8H, CH_{arom}), 5.65 (dd, *J* = 8.7, 3.3 Hz, 1H, H-3), 5.49 (s, 1H, C*H*Ph), 5.35 (d, *J* = 3.8 Hz, 1H, H-1'), 4.85 (d, *J* = 2.3 Hz, 1H, H-1), 4.78 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.68 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.64 – 4.57 (m, 4H, H-4, C*H*H Bn, 2x CH*H* Bn), 4.55 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.38 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.30 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.07 (dd, *J* = 10.2, 4.9 Hz, 1H, H-6'), 4.00 (dd, *J* = 3.3, 2.3 Hz, 1H, H-2), 3.98 – 3.92 (m, 2H, H-5, H-6), 3.90 (t, *J* = 9.4 Hz, 1H, H-3'), 3.84 (dt, *J* = 10.0, 5.1 Hz, 1H, H-5'), 3.80 – 3.76 (m, 1H, H-6), 3.57 (t, *J* = 10.2 Hz, 1H, H-6'), 3.52 (t, *J* = 9.5 Hz, 1H, H-4'), 3.41 (s, 3H, CH_3 OMe), 3.40 – 3.36 (m, 1H, H-2'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6 (C=O), 138.8, 138.5, 138.0, 137.8, 137.6 (C_q), 133.2 (CH_{arom}), 130.2 (C_q), 129.9, 128.9, 128.6, 128.4, 128.4, 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 126.2 (CH_{arom}), 101.2 (CHPh), 99.0 (C-1), 97.8 (C-1'), 82.1 (C-4'), 79.0

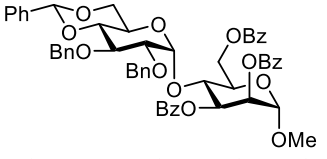
(C-2'), 78.5 (C-3'), 76.0 (C-2), 75.4 (CH_2 Bn), 74.5 (C-3), 73.6, 73.3, 72.9 (CH_2 Bn), 71.1 (C-4), 70.9 (C-5), 69.4 (C-6), 69.0 (C-6'), 63.6 (C-5'), 55.1 (CH_3 OMe); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.31 (s, 1H, C*H*Ph), 3.25 (dd, *J* = 8.9, 7.8 Hz, 1H, H-2'), 3.12 – 3.02 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6 (C=O), 103.3 (C-1'), 101.0 (CHPh), 99.1 (C-1), 82.5, 81.5, 81.0, 76.2, 75.6, 74.9, 73.4, 73.2, 72.0, 71.5, 68.6, 68.2, 65.7, 55.1 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{56}O_{12}NH_4$ 926.41100, found 926.40924.

Disaccharide 15B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **15**. Yield: 83 mg, 87 μmol, 87%, α:β = 1.5:1. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 4H), 7.60 – 7.54 (m, 2H), 7.47 – 7.13 (m, 34H), 5.60 (dd, *J* = 9.0, 3.3 Hz, 1H, H-3α), 5.53 – 5.47 (m, 2H, H-3β, C*H*Phα), 5.31 – 5.27 (m, 2H, H-1'α, C*H*Phβ), 4.88 – 4.76 (m, 4H, H-1αβ, 2x C*H*H Bn), 4.73 – 4.61 (m, 8H), 4.58 (d, *J* = 12.2 Hz, 1H, CH*H* Bn), 4.51 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.45 – 4.36 (m, 2H, H-4αβ), 4.17 (d, *J* = 8.1 Hz, 1H, H-1'β), 4.09 (dd, *J* = 10.3, 4.9 Hz, 1H, H-6'α), 4.03 (dd, *J* = 11.0, 3.7 Hz, 1H, H-6'β), 3.95 (dd, *J* = 3.3, 2.1 Hz, 1H), 3.96 – 3.82 (m, 6H), 3.80 (ddd, *J* = 11.0, 6.6, 1.8 Hz, 2H), 3.66 – 3.57 (m, 2H), 3.42 (s, 3H, CH_3 OMeα), 3.39 (s, 3H, CH_3 OMeβ), 3.39 – 3.29 (m, 2H), 3.27 – 3.19 (m, 2H), 3.03 – 2.93 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 165.5 (C=O), 138.4, 138.3, 138.1, 138.0, 137.9, 137.9, 137.3, 137.3, 133.2, 133.1, 131.3, 130.7, 130.1, 130.0, 129.7, 129.2, 129.1, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 126.2, 126.1, 126.1, 125.4, 121.9, 121.9, 101.7 (C-1'β), 101.4 (CHPhα), 101.2 (CHPhβ), 99.1, 99.1, 99.0 (C-1αβ, C-1'α), 82.6, 81.4, 79.2, 76.6, 76.3, 76.1, 75.2, 74.7, 74.2, 73.9, 73.8, 73.7, 73.4, 73.2, 73.1, 71.9, 71.2, 70.9, 69.8, 68.7, 68.4, 68.3, 66.3, 65.8, 63.6, 63.3, 55.2, 55.1; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{49}N_3O_{11}NH_4$ 861.37053, found 861.36906.

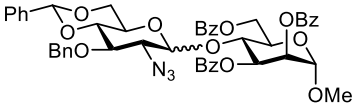
Disaccharide 16A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **16.** Yield: 62 mg, 66 μmol, 66%, α:β > 20: 1. Data for the α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.3, 1.4 Hz, 2H, CH_{arom}), 8.00 (dd, *J* = 8.3, 1.4 Hz, 2H, CH_{arom}), 7.89 (dd, *J* = 8.3, 1.3 Hz, 2H, CH_{arom}), 7.63 – 7.56 (m, 2H, CH_{arom}), 7.49 – 7.40 (m, 5H, CH_{arom}), 7.37 – 7.21 (m, 13H, CH_{arom}), 7.15 – 7.05 (m, 3H, CH_{arom}), 7.02 – 6.96 (m, 2H, CH_{arom}), 5.94 (dd, *J* = 9.5, 3.3 Hz, 1H, H-3), 5.69 (dd, *J* = 3.3, 1.9 Hz, 1H, H-2), 5.46 (s, 1H, C*H*Ph), 5.25 (d, *J* = 3.9 Hz, 1H, H-1'), 4.94 – 4.88 (m, 2H, H-1, H-6), 4.82 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.71 – 4.63 (m, 3H, H-4, H-6, CH*H* Bn), 4.30 – 4.24 (m, 2H, H-5, C*H*H Bn), 4.18 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.10 (dd, *J* = 10.2, 4.8 Hz, 1H, H-6'), 3.99 (t, *J* = 9.4 Hz, 1H, H-3'), 3.91 (dt, *J* = 9.9, 5.0 Hz, 1H, H-5'), 3.57 (t, *J* = 10.3 Hz, 1H, H-6'), 3.52 (t, *J* = 9.5 Hz, 1H, H-

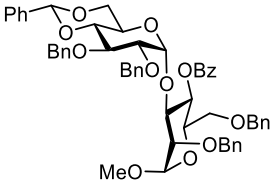
4'), 3.49 (s, 3H CH_3 OMe), 3.37 (dd, *J* = 9.5, 3.9 Hz, 1H, H-2'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 165.3, 165.2 (C=O), 138.7, 137.8, 137.4 (C_q), 133.5, 133.2, 133.2 (CH_{arom}), 130.1, 129.9, 129.9 (C_q), 129.9, 129.8, 129.8, 129.7, 129.0, 128.7, 128.7, 128.7, 128.6, 128.6, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.1, 127.7, 127.7, 127.6, 126.2 (CH_{arom}), 101.4 (CHPh), 99.1 (C-1'), 98.6 (C-1), 82.1 (C-4'), 78.7 (C-3'), 78.4 (C-2'), 75.4, 73.5 (CH_2 Bn), 72.4 (C-3), 72.1 (C-4), 70.6 (C-2), 69.5 (C-5'), 68.8 (C-6), 64.0 (C-5'), 63.4 (C-6), 55.5 (CH_3 OMe); diagnostic peaks for the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (dd, *J* = 9.8, 3.2 Hz, 1H, H-3), 5.59 (dd, *J* = 3.5, 1.8 Hz, 1H, H-2), 5.28 (s, 1H, C*H*Ph), 5.15 (t, *J* = 9.8 Hz, 1H), 4.57 (d, *J* = 7.6 Hz, 1H), 4.40 (t, *J* = 9.7 Hz, 1H), 3.75 (dd, *J* = 10.5, 4.9 Hz, 1H), 3.70 – 3.63 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 103.6 (C-1'), 101.0 (CHPh), 98.7 (C-1), 82.5, 81.3, 76.0, 75.1, 72.7, 71.1, 69.1, 68.3, 67.0, 65.9, 62.5.HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{52}O_{14}NH_4$ 954.36953, found 954.36920.

Disaccharide 16B



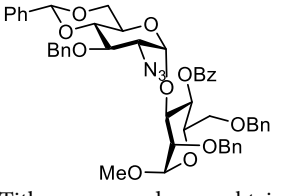
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **16**. Yield: 86 mg, 98 μmol, 98%, α:β = 10:1. Data for α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.3, 1.4 Hz, 2H, CH_{arom}), 8.01 – 7.96 (m, 2H, CH_{arom}), 7.97 – 7.91 (m, 2H, CH_{arom}), 7.59 (dtt, *J* = 11.7, 7.4, 1.3 Hz, 2H, CH_{arom}), 7.54 – 7.47 (m, 1H, CH_{arom}), 7.49 – 7.40 (m, 5H, CH_{arom}), 7.41 – 7.31 (m, 9H, CH_{arom}), 7.31 – 7.22 (m, 6H, CH_{arom}), 5.87 (dd, *J* = 9.6, 3.4 Hz, 1H, H-3), 5.63 (dd, *J* = 3.4, 1.9 Hz, 1H, H-2), 5.52 (s, 1H, C*H*Ph), 5.25 (d, *J* = 4.1 Hz, 1H, H-1'), 4.92 (d, *J* = 1.9 Hz, 1H, H-1), 4.88 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.80 (dd, *J* = 12.1, 2.0 Hz, 1H, H-6), 4.70 (d, *J* = 10.8 Hz, 1H, CH*H* Bn), 4.65 (dd, *J* = 12.1, 3.7 Hz, 1H, H-6), 4.51 (t, *J* = 9.7 Hz, 1H, H-4), 4.27 (dd, *J* = 10.3, 4.9 Hz, 1H, H-6'), 4.22 (ddd, *J* = 9.8, 3.7, 2.0 Hz, 1H, H-5), 4.00 – 3.92 (m, 2H, H-3', H-5'), 3.65 – 3.59 (m, 2H, H-4', H-6'), 3.51 (s, 3H, CH_3 OMe), 3.25 (dd, *J* = 10.0, 4.1 Hz, 1H, H-2'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 165.3 (C=O), 137.7, 137.2 (C_q), 135.4, 133.7, 133.5, 133.3, 133.2, 131.7, 131.6, 131.1 (CH_{arom}), 130.4, 130.0, 130.0 (C_q), 129.9, 129.9, 129.8, 129.8, 129.7, 129.6, 129.6, 129.1, 128.8, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.0, 126.1, 124.6 (CH_{arom}), 101.4 (CHPh), 100.2 (C-1'), 98.6 (C-1), 82.5 (C-4'), 76.6 (C-3'), 75.2 (CH_2 Bn), 74.1 (C-4), 72.2 (C-3), 70.6 (C-2), 69.2 (C-5), 68.5 (C-6'), 64.0 (C-5'), 63.5 (C-6), 63.1 (C-2'), 55.6 (CH_3 OMe); diagnostic peaks for the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.68 (dd, *J* = 3.4, 1.8 Hz, 1H, H-2), 5.28 (s, 1H, C*H*Ph), 4.42 (t, *J* = 9.7 Hz, 1H, H-4), 4.37 (d, *J* = 8.1 Hz, 1H, H-1'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 102.3 (C-1'), 101.2 (CHPh), 98.7 (C-1), 81.2, 79.6, 74.9, 74.8, 72.7, 71.1, 61.7. HRMS: $[M+NH_4]^+$ calcd for $C_{46}H_{46}O_{13}N_3NH_4$: 866.33689, found 866.33809.

Disaccharide 18A



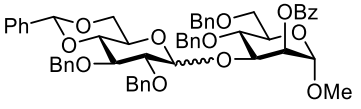
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **18**. Yield: 83 mg, 87 µmol, 87% α:β > 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H, CH_{arom}), 7.50 (t, *J* = 7.5 Hz, 1H, CH_{arom}), 7.42 (td, *J* = 7.6, 2.8 Hz, 5H, CH_{arom}), 7.38 – 7.31 (m, 6H, CH_{arom}), 7.27 – 7.14 (m, 19H, CH_{arom}), 7.06 – 6.99 (m, 2H, CH_{arom}), 5.70 (t, *J* = 9.5 Hz, 1H, H-4), 5.48 (s, 1H, C*H*Ph), 5.06 (d, *J* = 3.6 Hz, 1H, H-1'), 4.84 – 4.70 (m, 4H, H-1, 2x C*H*H Bn, CH*H* Bn), 4.60 (d, *J* = 11.2 Hz, 1H, CH*H* Bn), 4.52 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.47 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.38 – 4.26 (m, 2H, H-3, C*H*H Bn), 4.24 – 4.13 (m, 2H, H-6', CH*H* Bn), 4.06 – 3.95 (m, 3H, H-6, H-3',H-5'), 3.82 (t, *J* = 2.7 Hz, 1H, H-2), 3.75 – 3.59 (m, 3H, H-5, H-6, H-6'), 3.50 (t, *J* = 9.4 Hz, 1H, H-4'), 3.42 (s, 1H, CH_3 OMe), 3.37 (dd, *J* = 9.3, 3.6 Hz, 1H, H-2'). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4 (C=O), 138.8, 138.2, 138.1, 138.0, 137.6 (C_q), 133.1, 131.6, 131.1, 130.1, 130.0, 129.0, 128.6, 128.5, 128.4, 128.3, 128.2, 128.2, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 126.2 (CH_{arom}), 101.4 (CHPh), 99.2 (C-1'), 99.0 (C-1), 82.1 (C-4'), 78.6 (C-2'), 78.2 (C-3'), 77.1 (C-2), 76.2 (C-3), 75.2 (CH_2 Bn), 73.6 (CH_2 Bn), 73.1 (CH_2 Bn), 72.5 (CH_2 Bn), 70.7 (C-5), 70.2 (C-6), 70.0 (C-4), 69.1 (C-6'), 63.5 (C-5'), 55.2 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{56}O_{12}NH_4$ 926.41100, found 926.40970.

Disaccharide 18B



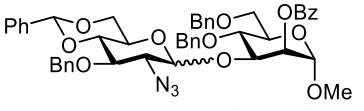
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **18.** Yield: 74 mg, 87 µmol, 87%, α:β > 20: 1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 2H, CH_{arom}), 7.58 – 7.53 (m, 1H, CH_{arom}), 7.47 – 7.37 (m, 10H, CH_{arom}), 7.32 – 7.16 (m, 13H, CH_{arom}), 5.70 (t, *J* = 9.8 Hz, 1H, H-4), 5.52 (s, 1H, C*H*Ph), 5.03 (d, *J* = 3.8 Hz, 1H, H-1'), 4.85 (dd, *J* = 6.4, 4.4 Hz, 2H, H-1, C*H*H Bn), 4.76 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.71 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.66 (d, *J* = 10.8 Hz, 1H, CH*H* Bn), 4.55 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.50 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.22 (dd, *J* = 9.5, 3.1 Hz, 1H, H-3), 4.17 (dd, *J* = 10.3, 4.8 Hz, 1H, H-6'), 4.04 – 3.90 (m, 3H, H-5, H-3', H-5'), 3.80 (dd, *J* = 3.2, 2.0 Hz, 1H, H-2), 3.74 – 3.63 (m, 3H, H-6 2x, H-6'), 3.60 (t, *J* = 9.4 Hz, 1H, H-4'), 3.43 (s, 3H, CH_3 OMe), 3.20 (dd, *J* = 9.9, 3.8 Hz, 1H, H-2'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6 (C=O), 138.1, 137.9, 137.7, 137.4 (C_q), 133.1, 131.5, 130.1, 129.7, 129.1, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.0, 127.9, 127.9, 127.7, 127.7, 127.5, 126.2 (CH_{arom}), 101.5 (CHPh), 100.3 (C-1'), 98.7 (C-1), 82.8 (C-4'), 77.4 (C-2), 77.4 (C-3), 76.3 (C-3'), 75.1 (CH_2 Bn), 73.7 (CH_2 Bn), 72.9 (CH_2 Bn), 70.7 (C-5), 70.2 (C-6), 69.7 (C-4), 68.9 (C-6'), 63.4 (C-5'), 63.1 (C-2'), 55.2 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{49}N_3O_{11}NH_4$ 861.37053, found 861.36924.

Disaccharide 19A



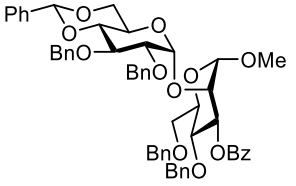
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **19**. Yield: 79 mg, 82 µmol, 82%, α:β = 10:1. Data for α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 7.14 (m, 30H, CH_{arom}), 5.42 (dd, *J* = 3.2, 2.0 Hz, 1H, H-2), 5.36 (s, 1H, C*H*Ph), 5.17 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 5.03 (d, *J* = 3.7 Hz, 1H, H-1'), 4.90 (d, *J* = 2.0 Hz, 1H, H-1), 4.80 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.73 (d, *J* = 11.5 Hz, 1H, CH*H* Bn), 4.71 – 4.61 (m, 3H, 2x C*H*H Bn, CH*H* Bn), 4.57 (d, *J* = 11.1 Hz, 1H, CH*H* Bn), 4.52 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.24 (dd, *J* = 9.3, 3.1 Hz, 1H, H-3), 4.18 (t, *J* = 9.4 Hz, 1H, H-4), 4.03 – 3.95 (m, 2H, H-3', H-6'), 3.90 – 3.84 (m, 2H, H-5, H-6), 3.81 – 3.74 (m, 2H, H-6, H-5'), 3.53 – 3.46 (m, 3H, H-2', H-4', H-6'), 3.41 (s, 3H, CH_3 OMe); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3 (C=O), 138.8, 138.8, 138.5, 138.2, 137.6, 135.4, 134.2, 133.3, 131.9, 131.4, 131.3, 130.3, 130.0, 129.9, 128.9, 128.7, 128.5, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.6, 127.6, 127.5, 127.5, 126.3, 126.1 (CH_{arom}), 101.3 (CHPh), 100.5 (C-1'), 98.1 (C-1), 82.1 (C-4'), 80.7 (C-3), 79.1 (C-2'), 78.2 (C-3'), 75.1 (CH_2 Bn), 73.8 (CH_2 Bn), 73.6 (C-4), 73.4 (CH_2 Bn), 72.4 (CH_2 Bn), 71.5 (C-2), 69.2 (C-5), 69.0 (C-6), 63.7 (C-6'), 55.3 (CH_3 OMe); Diagnostic peaks for β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.50 (dd, *J* = 3.1, 2.1 Hz, 1H, H-2'), 5.49 (s, 1H, C*H*Ph), 4.94 (d, *J* = 10.6 Hz, 1H, C*H*H Bn), 4.29 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6'), 3.69 – 3.65 (m, 1H), 3.65 – 3.61 (m, 1H, H-6'), 3.40 (s, 3H, CH_3 OMe); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7 (C=O), 101.2 (CHPh), 100.6 (C-1'), 98.4 (C-1), 82.0 (C-4'), 81.7, 81.0, 75.5, 75.2 (CH_2 Bn), 74.6, 73.7 (CH_2 Bn), 72.1, 70.8, 69.5, 69.4 (CH_2 Bn), 69.1 (CH_2 Bn), 66.0, 55.2 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{56}O_{12}NH_4$ 926.41100, found 926.40968.

Disaccharide 19B



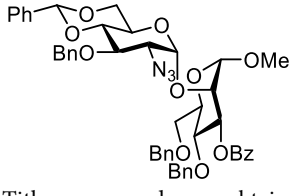
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **19**. Yield: 78 mg, 93 µmol, 93%, α:β = 1:1. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 4H), 7.60 – 7.53 (m, 2H), 7.50 – 7.45 (m, 2H), 7.42 – 7.20 (m, 42H), 5.55 (s, 1H, C*H*Phβ), 5.54 (dd, *J* = 3.4, 2.0 Hz, 1H, H-2β), 5.46 (s, 1H, C*H*Phα), 5.40 (dd, *J* = 3.2, 1.9 Hz, 1H, H-2α), 5.22 (d, *J* = 3.8 Hz, 1H, H-1'α), 5.03 (d, *J* = 10.4 Hz, 1H), 4.91 (d, *J* = 10.6 Hz, 1H), 4.89 – 4.85 (m, 3H), 4.83 (d, *J* = 11.0 Hz, 1H), 4.73 (dd, *J* = 11.5, 7.5 Hz, 3H), 4.65 (s, 1H), 4.59 – 4.51 (m, 6H), 4.47 (dd, *J* = 9.3, 3.3 Hz, 1H), 4.33 – 4.27 (m, 2H), 4.24 – 4.11 (m, 3H), 3.98 – 3.87 (m, 4H), 3.84 (ddt, *J* = 9.8, 3.9, 2.0 Hz, 2H), 3.78 (dt, *J* = 10.7, 1.9 Hz, 2H), 3.73 – 3.55 (m, 5H), 3.44 – 3.38 (m, 8H), 3.32 (dd, *J* = 9.4, 8.0 Hz, 1H, H-2'β); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 138.5, 138.5, 138.4, 138.3, 137.9, 137.9, 137.5, 137.2, 133.4, 133.3, 131.6, 131.1, 130.1, 130.0, 130.0, 129.9, 129.7, 129.2, 129.0, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.7, 127.7, 126.3, 126.1, 101.5, 101.4 (CHPhαβ), 100.2 (C-1'α), 99.3 (C-1'β), 98.6, 98.3 (C-1αβ), 82.7, 81.8, 79.4, 77.9, 77.4, 77.2, 76.9, 76.6, 76.3, 75.1, 75.1, 75.0, 74.7, 73.6, 73.6, 73.5, 72.4, 71.7, 71.4, 69.0, 68.9, 68.8, 68.8, 68.7, 66.9, 66.3, 63.5, 63.4, 55.2, 55.2; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{49}N_3O_{11}NH_4$ 861.37053, found 861.36959.

Disaccharide 22A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **22**. Yield: 77 mg, 76 µmol, 76%, α:β = 17:1. Data for α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H, CH_{arom}), 7.52 – 7.46 (m, 3H, CH_{arom}), 7.41 – 7.34 (m, 5H, CH_{arom}), 7.33 – 7.15 (m, 18H, CH_{arom}), 7.09 – 7.04 (m, 2H, CH_{arom}), 5.59 – 5.52 (m, 2H, H-3, C*H*Ph), 4.91 (d, *J* = 3.7 Hz, 1H, H-1'), 4.86 – 4.82 (m, 2H, H-1, C*H*H Bn), 4.79 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.69 (d, *J* = 11.2 Hz, 1H, CH*H* Bn), 4.64 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.61 (s, 2H, CH_2 Bn), 4.58 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.52 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.31 (t, *J* = 9.5 Hz, 1H, H-4), 4.27 (dd, *J* = 10.2, 4.9 Hz, 1H, H-6'), 4.25 (dd, *J* = 3.1, 2.1 Hz, 1H, H-2), 4.12 (t, *J* = 9.3 Hz, 1H, H-3'), 4.06 (td, *J* = 10.0, 4.9 Hz, 1H, H-5'), 3.93 – 3.85 (m, 2H, H-5, H-6), 3.79 – 3.72 (m, 1H, H-6), 3.67 (t, *J* = 10.3 Hz, 1H, H-6'), 3.59 (t, *J* = 9.5 Hz, 1H, H-4'), 3.49 (dd, *J* = 9.3, 3.7 Hz, 1H, H-2'), 3.41 (s, 3H, CH_3 OMe); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0 (C=O), 138.8, 138.6, 138.5, 138.1, 137.5 (C_q), 133.2 (CH_{arom}), 130.1 (C_q) , 129.9, 129.0, 128.5, 128.4, 128.4, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4, 126.2 (CH_{arom}), 101.4 (CHPh), 99.8 (C-1), 99.5 (C-1'), 82.3 (C-4'), 78.9 (C-2'), 78.6 (C-3'), 76.1 (C-2), 75.3, 75.1 (CH_2 Bn), 74.5 (C-3), 73.7 (CH_2 Bn), 73.6 (C-4), 72.9 (CH_2 Bn), 72.0 (C-5), 69.2 (C-6), 69.0 (C-6'), 63.2 (C-5'), 55.1 (CH_3 OMe); Diagnostic peaks for β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.39 (dd, *J* = 9.7, 3.5 Hz, 1H, H-3), 5.28 (s, 1H, C*H*Ph), 5.04 (d, *J* = 10.4 Hz, 1H, C*H*H Bn), 4.41 (d, *J* = 7.7 Hz, 1H, H-1'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 104.2 (C-1'), 101.0 (CHPh), 99.4 (C-1), 81.5, 81.3, 80.8, 76.5, 74.1, 72.9, 72.4, 65.5, 55.0 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{56}O_{12}NH_4$ 926.41100, found 926.40906.

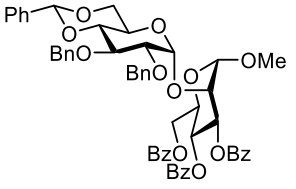
Disaccharide 22B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **22**. Yield: 44 mg, 51 µmol, 51%, α:β = 7:1. Data for α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.2, 1.4 Hz, 2H, CH_{arom}), 7.62 – 7.54 (m, 1H, CH_{arom}), 7.53 – 7.43 (m, 5H, CH_{arom}), 7.40 – 7.25 (m, 15H, CH_{arom}), 7.22 – 7.14 (m, 3H), 7.13 – 7.07 (m, 2H, CH_{arom}), 5.62 – 5.53 (m, 2H, H-3, C*H*Ph), 4.94 (d, *J* = 3.7 Hz, 1H, H-1'), 4.88 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.79 – 4.76 (m, 2H, H-1, C*H*H Bn), 4.71 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.63 (d, *J* = 11.0 Hz, 1H, CH*H* Bn), 4.58 (dd, *J* = 11.6, 2.8 Hz, 2H, 2x CH*H* Bn), 4.34 (t, *J* = 9.4 Hz, 1H, H-4), 4.27 (dd, *J* = 10.4, 4.9 Hz, 1H, H-6'), 4.20 (dd, *J* = 3.2, 2.0 Hz, 1H, H-2), 4.14 – 4.04 (m, 2H, H-3', H-5'), 3.92 – 3.86 (m, 2H, H-5, H-6), 3.79 – 3.67 (m, 3H, H-4', H-6, H-6'), 3.42 (s, 3H, CH_3 OMe), 3.26 (dd, *J* = 10.1, 3.7 Hz, 1H, H-2'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0

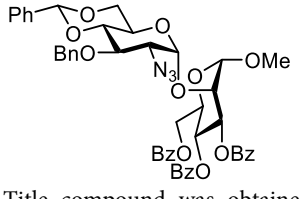
(C=O), 138.6, 138.0, 138.0, 137.3 (C_q), 133.4 (CH_{arom}), 131.7 (C_q), 131.4, 129.9, 129.9, 129.2, 128.7, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 127.8, 127.8, 127.6, 127.6, 127.6, 126.2, 126.1 (CH_{arom}), 101.6 (CHPh), 100.7 (C-1'), 99.9 (C-1), 82.9 (C-4'), 77.5 (C-2), 75.6 (C-3'), 75.2 (CH_2 Bn x2), 74.2 (C-3), 73.6 (CH_2 Bn), 73.4 (C-4), 71.9 (C-5), 69.1 (C-6), 68.7 (C-6'), 63.3 (C-5'), 62.9 (C-2'), 55.2 (CH_3 OMe); Diagnostic peaks for the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.36 (dd, *J* = 9.5, 3.5 Hz, 1H, H-3), 5.30 (s, 1H, C*H*Ph), 3.17 – 3.09 (m, 1H), 2.79 (t, *J* = 10.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 102.4 (C-1'), 101.5 (CHPh), 99.2 (C-1); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{49}N_3O_{11}NH_4$ 861.37053, found 861.36930.

Disaccharide 23A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **23**. Yield: 73 mg, 77 μmol, 77%, α:β >20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H, CH_{arom}), 8.02 – 7.94 (m, 4H, CH_{arom}), 7.51 – 7.44 (m, 3H, CH_{arom}), 7.42 – 7.16 (m, 21H, CH_{arom}), 6.18 (t, *J* = 10.1 Hz, 1H, H-4), 5.73 (dd, *J* = 10.1, 3.1 Hz, 1H, H-3), 5.51 (s, 1H, C*H*Ph), 4.96 (d, *J* = 3.7 Hz, 1H, H-1'), 4.93 (d, *J* = 1.9 Hz, 1H, H-1), 4.82 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.72 – 4.63 (m, 3H, H-6, C*H*H Bn, CH*H* Bn), 4.56 – 4.48 (m, 2H, H-6, C*H*H Bn), 4.39 (dd, *J* = 3.2, 1.9 Hz, 1H, H-2), 4.33 (ddd, *J* = 10.1, 4.7, 2.7 Hz, 1H, H-5), 4.25 (dd, *J* = 10.3, 4.9 Hz, 1H, H-6'), 4.10 (t, *J* = 9.3 Hz, 1H, H-3'), 3.99 (td, *J* = 10.0, 4.9 Hz, 1H, H-5'), 3.66 (t, *J* = 10.4 Hz, 1H, H-6'), 3.57 (t, *J* = 9.5 Hz, 1H, H-4'), 3.51 (s, 3H, CH_3 OMe), 3.48 (dd, *J* = 9.4, 3.8 Hz, 1H, H-2'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 166.1, 165.4 (C=O), 138.9, 138.3, 137.4 (C_q), 133.4, 133.3, 133.0, 130.0, 129.9, 129.8 (CH_{arom}), 129.4, 129.4 (C_q), 129.0, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.0, 128.0, 128.0, 127.8, 127.6, 127.6, 126.2 (CH_{arom}), 101.4 (CHPh), 100.1 (C-1), 99.7 (C-1'), 82.1 (C-4'), 78.5, 78.5 (C-2', C-3'), 75.5 (C-2), 75.4, 72.7 (CH_2 Bn), 72.3 (C-3), 69.0 (C-5), 68.9 (C-6'), 67.1 (C-4), 63.4 (C-5'), 63.3 (C-6), 55.5 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{52}O_{14}NH_4$ 954.36953, found 954.36815.

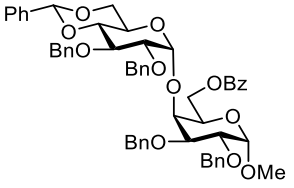
Disaccharide 23B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **23**. Yield: 42 mg, 51 μmol, 51%, α:β > 20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dq, *J* = 7.0, 1.6 Hz, 4H, CH_{arom}), 8.00 – 7.93 (m, 2H, CH_{arom}), 7.54 – 7.45 (m, 4H, CH_{arom}), 7.40 – 7.27 (m, 15H, CH_{arom}), 6.04 (t, *J* = 10.1 Hz, 1H, H-4), 5.72 (dd, *J* = 10.1, 3.2 Hz, 1H, H-3), 5.56 (s, 1H, C*H*Ph), 4.99 (d, *J* = 3.8 Hz, 1H, H-1'), 4.92 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.88 (d, *J* = 1.8 Hz, 1H, H-1), 4.71 (d, *J* = 10.8 Hz, 1H, CH*H* Bn), 4.65 (dd, *J* = 12.1,

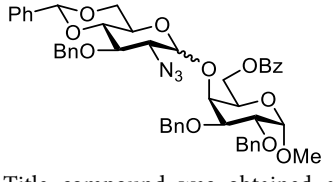
2.9 Hz, 1H, H-6), 4.50 (dd, *J* = 12.1, 5.5 Hz, 1H, H-6), 4.37 – 4.30 (m, 2H, H-2, H-5), 4.27 (dd, *J* = 10.4, 4.9 Hz, 1H, H-6'), 4.13 (dd, *J* = 10.1, 9.1 Hz, 1H, H-3'), 4.02 (td, *J* = 10.0, 4.9 Hz, 1H, H-5'), 3.71 (dt, *J* = 11.5, 9.9 Hz, 2H, H-4', H-6'), 3.51 (s, 3H, CH_3 OMe), 3.34 (dd, *J* = 10.1, 3.8 Hz, 1H, H-2'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 166.0, 165.4 (C=O), 138.0, 137.1, 133.5 (C_q), 133.4, 133.1, 131.7, 131.3, 130.0, 129.9, 129.9, 129.8, 129.3, 129.3, 129.2, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.4, 128.2, 128.0, 126.2, 126.1 (CH_{arom}), 101.6 (CHPh), 100.7 (C-1'), 100.0 (C-1), 82.7 (C-4'), 76.7 (C-2), 76.2 (C-3'), 75.3 (CH_2 Bn), 71.7 (C-3), 68.8 (C-5), 68.7 (C-6'), 67.3 (C-4), 63.6 (C-6), 63.4 (C-5'), 63.1 (C-2'), 55.5 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{45}N_3O_{13}NH_4$ 889.32906, found 889.32759

Disaccharide 25A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **25**. 79 mg, 85 µmol, 85%, α:β > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.14 (m, 30H, CH_{arom}), 5.53 (s, 1H, C*H*Ph), 4.97 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.93 – 4.84 (m, 3H, H-1', 2x C*H*H Bn), 4.82 – 4.74 (m, 5H, C*H*H Bn, 4x CH*H* Bn), 4.66 (q, *J* = 3.9 Hz, 2H, H-1, H-6'), 4.59 (dd, *J* = 11.1, 6.4 Hz, 1H, H-6'), 4.27 (td, *J* = 10.0, 4.9 Hz, 1H, H-5), 4.05 – 3.94 (m, 4H, H-3, H-4, H-6, H-3'), 3.91 (dd, *J* = 10.3, 2.5 Hz, 1H, H-2), 3.82 (dd, *J* = 10.1, 4.9 Hz, 1H, H-5'), 3.66 – 3.54 (m, 2H, H-2', H-4'), 3.50 (t, *J* = 10.2 Hz, 1H, H-6), 3.36 (s, 3H, CH_3 OMe). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1 (C=O), 138.9, 138.4, 138.1, 137.9, 137.8, 133.2 (C_q), 129.9, 129.6, 128.8, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.2, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 126.1 (CH_{arom}), 101.2 (CHPh), 101.0 (C-1'), 99.1 (C-1), 82.7 (C-4'), 79.3 (C-3'), 78.8 (C-2'), 78.0 (C-4), 77.5 (C-2), 75.3 (CH_2 Bn), 74.5 (CH_2 Bn), 74.1 (C-3), 73.6 (CH_2 Bn), 73.2 (CH_2 Bn), 69.0 (C-6), 68.5 (C-5'), 63.2 (C-5), 62.8 (C-6'), 55.4 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{56}O_{12}NH_4$ 926.41100, found 926.40964.

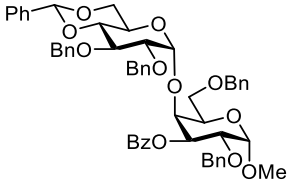
Disaccharide 25B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **25**. Yield: 84 mg, 100 µmol, 100%, α:β = 3:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.3, 1.5 Hz, 2H, CH_{arom}), 7.48 – 7.22 (m, 23H, CH_{arom}), 5.55 (s, 1H, C*H*Ph), 4.97 (d, *J* = 10.7 Hz, 1H, C*H*H Bn), 4.93 (d, *J* = 3.7 Hz, 1H, H-1'), 4.90 – 4.75 (m, 4H, 2x C*H*H Bn, 2x CH*H* Bn), 4.72 (d, *J* = 2.8 Hz, 1H, H-1), 4.69 – 4.57 (m, 3H, 2x H-6, CH*H* Bn), 4.35 – 4.27 (m, 1H, H-5'), 4.07 (d, *J* = 2.2 Hz, 1H, H-4), 4.03 (t, *J* = 6.9 Hz, 1H, H-5), 4.01 – 3.92 (m, 3H, H-2, H-3, H-3'), 3.83 (dd, *J* = 10.2, 4.9 Hz, 1H, H-6'), 3.69 (t, *J* = 9.5 Hz, 1H, H-4'), 3.58 – 3.50 (m, 2H, H-2', H-6'), 3.38 (s, 3H, CH_3 OMe); ^{13}C NMR (101

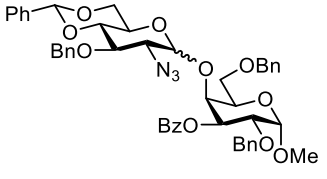
MHz, $CDCl_3$) δ 166.1 (C=O), 138.3, 138.1, 138.0, 137.6 (C_q), 133.4, 129.7, 129.6, 129.0, 128.6, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.4, 126.1, 126.1 (CH_{arom}), 101.3 (CHPh), 99.7 (C-1'), 98.9 (C-1), 82.9 (C-4'), 77.2, 77.2, 77.2 (C-3, C-3', C-4), 75.3 (CH_2 Bn), 74.5 (C-2), 73.5, 73.5 (CH_2 Bn), 68.8 (C-6'), 68.5 (C-5), 64.1 (C-2'), 63.3 (C-5'), 62.8 (C-6), 55.5 (CH_3 OMe); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (s, 1H, C*H*Ph), 4.47 (dd, *J* = 11.4, 5.7 Hz, 1H, H-6), 3.35 (s, 3H, CH_3 OMe); 3.17 (td, *J* = 9.7, 5.0 Hz, 1H, H-5'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (C=O), 102.1 (C-1'), 99.0 (C-1), 81.4, 78.9, 78.1, 74.9, 74.4, 74.0, 68.5, 67.6, 66.5, 66.0, 63.8; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{49}N_3O_{11}NH_4$ 861.37053, found 861.36949.

Disaccharide 26A



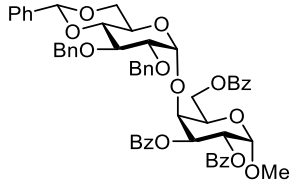
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **26**. Yield: 66 mg, 78 μmol, 78%, α:β = 11:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.02 (m, 2H, CH_{arom}), 7.59 – 7.53 (m, 1H, CH_{arom}), 7.51 – 7.47 (m, 2H, CH_{arom}), 7.44 – 7.16 (m, 25H, CH_{arom}), 5.51 – 5.42 (m, 2H, H-3, C*H*Ph), 4.94 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.86 – 4.76 (m, 4H, H-1, H-1', C*H*H Bn, C*H*H Bn), 4.73 (d, *J* = 10.6 Hz, 1H, C*H*H Bn), 4.68 (d, *J* = 12.3 Hz, 1H, CH*H* Bn), 4.62 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.38 – 4.31 (m, 2H, H-4, C*H*H Bn), 4.25 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.16 – 4.09 (m, 2H, H-2, H-5), 4.07 – 3.99 (m, 2H, H-3', H-5'), 3.86 (dd, *J* = 10.2, 6.5 Hz, 1H, H-6), 3.59 (dd, *J* = 10.3, 6.7 Hz, 1H, H-6'), 3.53 (t, *J* = 9.5 Hz, 1H, H-4'), 3.49 – 3.43 (m, 2H, H-2', H-6'), 3.42 (s, 3H, CH_3 OMe), 3.34 (t, *J* = 10.3 Hz, 1H, H-6'); 13C NMR (101 MHz, $CDCl_3$) δ 166.4 (C=O), 138.7, 138.2, 138.1, 137.8, 137.6, 133.2 (Cq), 129.9, 129.9, 128.9, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.6, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 126.0, 126.0 (CH_{arom}), 101.0 (CHPh), 100.2 (C-1'), 98.3 (C-1), 82.8 (C-4'), 79.5 (C-2'), 78.5 (C-3'), 77.2 (C-4), 75.1 (CH_2 Bn), 74.4 (CH_2 Bn), 73.5 (C-2), 73.1 (CH_2 Bn), 73.2 (CH_2 Bn), 72.6 (C-3), 69.2 (C-5), 68.7 (C-6'), 68.5 (C-6), 63.4 (C-5'), 55.4 (CH_3 OMe). Diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (dd, *J* = 10.4, 3.1 Hz, 1H, H-3), 5.10 (dd, *J* = 10.5, 2.9 Hz, 1H), 5.05 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.52 (d, *J* = 12.0 Hz, 1H), 4.47 – 4.43 (m, 2H, H-1'), 3.44 (s, 3H, CH_3 OMe). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (C=O), 103.4 (C-1'), 101.1 (CHPh), 98.4 (C-1), 82.7, 82.2, 81.5, 80.7, 76.3, 75.2 (CH_2 Bn), 75.0 (CH_2 Bn), 74.6 (CH_2 Bn), 74.1, 73.8, 73.3 (CH_2 Bn), 69.8, 68.9, 65.8, 63.3, 55.5 (CH_3 OMe); HRMS: $[M+Na]^+$ calcd for $C_{55}H_{56}O_{12}Na$ 931.36640, found 931.36295.

Disaccharide 26B



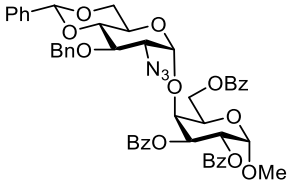
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **26**. Yield: 56 mg, 67 µmol, 67%, α:β = 3:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 2H, CH_{arom}), 7.62 – 7.51 (m, 1H, CH_{arom}), 7.49 – 7.15 (m, 22H, CH_{arom}), 5.52 (dd, *J* = 10.9, 2.9 Hz, 1H, H-3), 5.43 (s, 1H, C*H*Ph), 4.97 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.86 – 4.82 (m, 2H, H-1, H-1'), 4.78 (d, *J* = 10.7 Hz, 1H, CH*H* Bn), 4.72 (d, *J* = 8.9 Hz, 1H, C*H*H Bn), 4.68 (d, *J* = 12.2 Hz, 1H, CH*H* Bn), 4.61 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.47 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.43 (d, *J* = 2.9 Hz, 1H, H-4), 4.17 – 4.09 (m, 2H, H-2, H-5), 4.07 – 4.00 (m, 1H, H-5'), 3.97 (dd, *J* = 9.9, 9.1 Hz, 1H, H-3'), 3.92 (t, *J* = 9.0 Hz, 1H, H-6), 3.61 – 3.54 (m, 2H, H-4', H-6), 3.42 (s, 3H, CH_3 OMe), 3.30 (t, *J* = 10.3 Hz, 1H, H-6'), 3.24 – 3.17 (m, 2H, H-2', H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (C=O), 138.0, 137.8, 137.6 (C_q), 137.5, 133.4, 130.0, 129.9, 129.0 (CH_{arom}), 128.8 (C_q), 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.0, 127.4, 126.1, 126.0 (CH_{arom}), 101.1 (CHPh), 98.6, 98.4 (C-1, C-1'), 82.9 (C-4'), 76.3 (C-3'), 75.2 (CH_2 Bn), 75.0 (C-4), 73.6 (CH_2 Bn), 73.3 (C-2), 73.1 (CH_2 Bn), 72.1 (C-2), 68.5 (C-5), 68.4 (C-6'), 67.0 (C-6), 63.4 (C-2'), 63.2 (C-5'), 55.6 (CH_3 OMe); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 (dd, *J* = 10.5, 3.0 Hz, 1H, H-3), 5.49 (s, 1H, C*H*Ph), 4.36 (d, *J* = 8.0 Hz, 1H, H-1'), 4.34 (dd, *J* = 3.1, 1.2 Hz, 1H, H-4), 4.24 (dd, *J* = 10.5, 3.6 Hz, 1H, H-2), 3.43 (s, 3H, CH_3 OMe), 3.09 (td, *J* = 9.8, 5.0 Hz, 1H, H-5'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (C=O), 102.4 (C-1'), 101.4 (CHPh), 98.6 (C-1), 81.5, 78.9, 75.4, 74.9, 74.2, 73.4, 72.4, 69.5, 68.7, 68.3, 66.4, 66.0, 55.6; HRMS: $[M+Na]^+$ calcd for $C_{48}H_{49}N_3O_{11}Na$ 866.32593, found 866.32307.

Disaccharide 27A



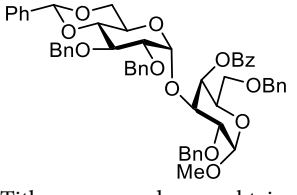
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **27**. Yield: 70 mg, 70 µmol, 70%, α:β > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.93 (m, 6H, CH_{arom}), 7.65 – 7.54 (m, 1H, CH_{arom}), 7.52 – 7.12 (m, 23H, CH_{arom}), 5.73 – 5.64 (m, 2H, H-2, H-3), 5.43 (s, 1H, C*H*Ph), 5.25 (d, *J* = 2.9 Hz, 1H, H-1), 5.00 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.90 (d, *J* = 4.7 Hz, 1H, C*H*H Bn), 4.87 (d, *J* = 4.1 Hz, 1H, CH*H* Bn), 4.82 (d, *J* = 3.7 Hz, 1H, H-1'), 4.77 – 4.70 (m, 3H, CH*H* Bn, 2x H-6), 4.48 – 4.45 (m, 1H, H-4), 4.35 (t, *J* = 6.5 Hz, 1H, H-5), 4.22 (t, *J* = 9.4 Hz, 1H, H-3'), 4.15 (dt, *J* = 10.0, 5.0 Hz, 1H, H-5'), 3.60 (dd, *J* = 10.2, 4.7 Hz, 1H, H-6'), 3.58 – 3.52 (m, 2H, H-2', H-4'), 3.42 (s, 3H, CH_3 OMe), 3.36 (t, *J* = 10.2 Hz, 1H, H-6'). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 166.1, 166.0 (C=O), 138.8, 137.9, 137.6, 133.5, 133.3 (C_q), 129.9, 129.7, 129.5, 129.3, 128.9, 128.7, 128.6, 128.6, 128.5, 128.4, 128.2, 128.2, 127.9, 127.7, 126.2 (CH_{arom}), 101.3 (CHPh), 100.9 (C-1'), 97.5 (C-1), 82.7 (C-4'), 78.9 (C-2'), 78.7 (C- 3'), 77.2 (C-4), 75.4 (CH_2 Bn), 74.6 (CH_2 Bn), 70.7 (C-2), 69.2 (C-3), 68.8 (C-6'), 68.4 (C-5), 63.7 (C-5'), 63.1 (C-6), 55.5 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{52}O_{14}NH_4$ 954.36953, found 954.36827.

Disaccharide 27B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **27**. Yield: 87 mg, 100 µmol, 100%, α:β > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.05 (m, 2H, CH_{arom}), 8.04 – 8.00 (m, 2H, CH_{arom}), 7.97 (dd, *J* = 7.1, 1.4 Hz, 2H, CH_{arom}), 7.61 – 7.27 (m, 19H, CH_{arom}), 5.76 (dd, *J* = 11.0, 2.8 Hz, 1H, H-2), 5.69 (dd, *J* = 11.0, 3.5 Hz, 1H, H-3), 5.43 (s, 1H, C*H*Ph), 5.28 (d, *J* = 3.5 Hz, 1H, H-1), 5.01 (d, *J* = 10.7 Hz, 1H, C*H*H Bn), 4.98 (d, *J* = 3.8 Hz, 1H, H-1'), 4.87 (d, *J* = 10.8 Hz, 1H, CH*H* Bn), 4.82 – 4.70 (m, 2H, 2x H-6), 4.54 (d, *J* = 2.8 Hz, 1H, H-4), 4.42 (t, *J* = 7.0 Hz, 1H, H-6), 4.21 (t, *J* = 9.6 Hz, 1H, H-3'), 4.15 (dt, *J* = 10.0, 5.0 Hz, 1H, H-5'), 3.63 (t, *J* = 9.4 Hz, 1H, H-4'), 3.55 – 3.46 (m, 2H, H-2', H-6'), 3.45 (s, 3H, CH_3 OMe), 3.37 (t, *J* = 10.2 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 166.1, 166.0 (C=O), 137.9, 137.3, 133.6, 133.4, 133.3 (C_q), 129.9, 129.8, 129.8, 129.8, 129.7, 129.6, 129.4, 129.0, 129.0, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 127.9, 126.2 (CH_{arom}), 101.3 (CHPh), 99.5 (C-1'), 97.6 (C-1), 82.7 (C-4'), 76.6 (C-3'), 76.1 (C-4), 75.3 (CH_2 Bn), 70.4 (C-2), 68.9 (C-3), 68.4 (C-6'), 68.1 (C-5), 63.8 (C-5'), 63.6 (C-2'), 62.5 (C-6), 55.6 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{45}N_3O_{13}NH_4$ 889.32906, found 889.32801.

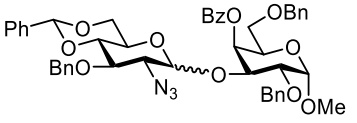
Disaccharide 29A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **29**. Yield: 72 mg, 76 µmol, 76%, α:β = 16:1. Data for α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H, CH_{arom}), 7.54 – 7.49 (m, 1H, CH_{arom}), 7.42 – 7.31 (m, 10H, CH_{arom}), 7.28 – 7.12 (m, 17H, CH_{arom}), 5.83 (dd, *J* = 3.3, 1.2 Hz, 1H, H-4), 5.49 (s, 1H, C*H*Ph), 5.27 (d, *J* = 3.6 Hz, 1H, H-1'), 4.84 – 4.80 (m, 2H, H-1, C*H*H Bn), 4.76 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.68 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.63 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.58 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.49 – 4.39 (m, 3H, C*H*H Bn, 2x CH*H* Bn), 4.34 (dd, *J* = 10.2, 3.2 Hz, 1H, H-3), 4.28 (dd, *J* = 10.1, 4.9 Hz, 1H, H-6'), 4.16 – 4.07 (m, 2H, H-5, H-5'), 4.03 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2), 3.98 (t, *J* = 9.3 Hz, 1H, H-3'), 3.64 (t, *J* = 10.2 Hz, 1H, H-6'), 3.56 (t, *J* = 9.5 Hz, 1H, H-4'), 3.54 – 3.51 (m, 3H, H-2', 2x H-6), 3.43 (s, 3H, CH_3 OMe); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1 (C=O), 138.7, 138.3, 138.0, 137.9, 137.8 (C_q), 133.2, 130.0 (CH_{arom}), 129.9 (C_q), 128.9, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.2, 128.2, 128.2, 128.1, 127.9, 127.8, 127.8, 127.7, 127.5, 127.4, 126.3 (CH_{arom}), 101.4 (CHPh), 98.7 (C-1), 94.1 (C-1'), 82.2 (C-4'), 78.6 (C-3'), 78.3 (C-2'), 75.0 (CH_2 Bn), 74.3 (C-2), 73.7, 73.5, 72.7 (CH_2 Bn), 71.3 (C-3), 69.1, 69.0 (C-6, C-6'), 68.2 (C-5), 67.9 (C-4), 62.8 (C-5'), 55.5 (CH_3 OMe); diagnostic peaks for

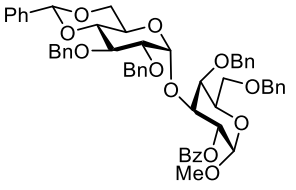
the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (dd, *J* = 3.6, 1.2 Hz, 1H, H-4), 5.53 (s, 1H, C*H*Ph), 4.98 (d, *J* = 7.6 Hz, 1H, H-1'), 4.86 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 3.75 (t, *J* = 10.3 Hz, 1H), 3.41 (s, 3H), 3.30 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 103.1 (C-1'), 101.1 (CHPh), 98.6 (C-1), 82.5, 81.5, 80.8, 77.3, 75.4, 74.9, 74.9, 74.8, 73.8, 73.2, 72.4, 71.9, 68.3, 65.9, 55.7; HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{56}O_{12}NH_4$ 926.41100, found 926.40952.

Disaccharide 29B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **29**. Yield: 52 mg, 60 μmol, 60%, α:β = 1.3:1. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.06 (m, 2H), 8.05 – 8.02 (m, 2H), 7.61 – 7.55 (m, 2H), 7.49 – 7.40 (m, 8H), 7.39 – 7.31 (m, 12H), 7.29 – 7.19 (m, 20H), 5.84 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4α), 5.67 (dd, *J* = 3.6, 1.2 Hz, 1H, H-4β), 5.54 (s, 1H, C*H*Phα), 5.53 (s, 1H, C*H*Phβ), 5.30 (d, *J* = 3.7 Hz, 1H, H-1'α), 4.90 – 4.82 (m, 4H), 4.81 – 4.77 (m, 2H, H-1'β, C*H*H Bn), 4.75 – 4.70 (m, 2H, H-1α, CH*H* Bn), 4.67 – 4.62 (m, 2H, H-1β, CH*H* Bn), 4.58 (d, *J* = 11.8 Hz, 1H), 4.52 – 4.46 (m, 2H), 4.44 – 4.38 (m, 2H), 4.38 – 4.27 (m, 3H), 4.19 – 4.10 (m, 3H), 4.08 (dd, *J* = 10.1, 3.6 Hz, 1H), 3.96 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.95 – 3.91 (m, 1H), 3.76 (t, *J* = 10.3 Hz, 1H), 3.71 – 3.62 (m, 3H), 3.59 – 3.49 (m, 4H), 3.43 (s, 4H), 3.40 (s, 3H), 3.34 – 3.26 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 165.9, 138.1, 138.0, 137.9, 137.8, 137.7, 137.6, 137.3, 133.3, 133.2, 130.0, 130.0, 129.9, 129.9, 129.8, 129.1, 129.0, 129.0, 128.7, 128.7, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 128.1, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 126.3, 126.1, 125.1, 102.4 (C-1β), 101.5 (CHPhα), 101.3 (CHPhβ), 98.7 (C-1α), 98.2 (C-1β), 94.0 (C-1'α), 82.8, 81.5, 78.9, 77.4, 77.2, 77.0, 76.9, 75.5, 75.0, 74.8, 74.6, 73.9, 73.7, 73.6, 73.5, 71.8, 70.9, 69.2, 68.8, 68.7, 68.6, 68.4, 67.8, 66.7, 66.5, 66.0, 62.8, 62.7, 55.6, 55.6; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{49}N_3O_{11}NH_4$ 861.37053, found 861.36925.

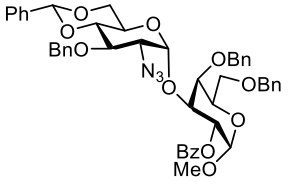
Disaccharide 30A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **30.** Yield: 81 mg, 84 μmol, 84%, α:β >20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 7.16 (m, 30H, CH_{arom}), 5.59 (dd, *J* = 10.5, 3.7, 0.8 Hz, 1H, H-2), 5.41 (s, 1H, C*H*Ph), 5.05 (dd, *J* = 5.9, 3.7 Hz, 2H, H-1, H-1'), 4.99 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.86 (d, *J* = 11.5 Hz, 1H, C*H*H Bn), 4.77 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.66 (t, *J* = 11.2 Hz, 2H, C*H*H Bn, CH*H* Bn), 4.47 (dd, *J* = 11.7, 2.8 Hz, 2H, 2x CH*H* Bn), 4.37 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.22 (dd, *J* = 10.4, 2.8 Hz, 1H, H-3), 4.07 – 4.03 (m, 1H, H-4), 3.99 – 3.90 (m, 3H, H-5, H-3', H-5'), 3.82 (dd, *J* = 10.2, 4.9 Hz, 1H, H-6'), 3.60 – 3.45 (m, 4H, 2x H-6, H-2', H-4'), 3.42 – 3.36 (m, 1H, H-6'), 3.35 (s, 3H, CH_3 OMe); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.19 (C=O), 138.8, 138.6, 138.2, 138.1, 137.6, 133.1, 130.0, 130.0, 128.9, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3,

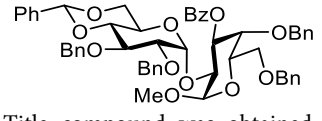
128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 126.3 (CH_{arom}), 101.3 (CHPh), 99.4 (C-1'), 97.7 (C-1), 82.5 (C-4'), 79.6 (C-2'), 78.5 (C-3'), 77.8 (C-3), 75.2 (C-4), 75.2 (CH_2 Bn), 75.0 (CH_2 Bn), 74.6 (CH_2 Bn), 73.6 (CH_2 Bn), 71.0 (C-2), 69.5 (C-5), 69.1 (C-6), 68.8 (C-6'), 63.3 (C-5'), 55.5 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{56}O_{12}NH_4$ 926.41100, found 926.40731.

Disaccharide 30B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **30.** Yield: 69 mg, 82 µmol, 82%, α:β = 13:1. Data for α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 7.18 (m, 25H, CH_{arom}), 5.62 (dd, *J* = 10.5, 3.7 Hz, 1H, H-2), 5.45 (s, 1H, C*H*Ph), 5.10 (d, *J* = 3.6 Hz, 1H, H-1'), 5.04 (d, *J* = 3.8 Hz, 1H, H-1), 4.99 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.76 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.59 (dd, *J* = 11.2, 3.7 Hz, 2H, 2x CH*H* Bn), 4.51 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.44 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 4.31 (dd, *J* = 10.5, 2.9 Hz, 1H, H-3), 4.15 (dd, *J* = 2.9, 1.2 Hz, 1H, H-4), 4.09 – 3.95 (m, 3H, H-5, H-5', H-6'), 3.89 (dd, *J* = 9.9, 9.1 Hz, 1H, H-3'), 3.66 – 3.56 (m, 3H, 2x H-6, H-4'), 3.53 – 3.45 (m, 2H, H-2', H-6'), 3.35 (s, 3H, CH_3 OMe); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1 (C=O), 138.6, 138.0, 137.7, 137.4 (C_q), 133.1, 129.9, 129.9, 129.1, 129.0, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 126.2, 126.1 (CH_{arom}), 101.4 (CHPh), 97.7 (C-1), 97.3 (C-1'), 82.8 (C-4'), 76.2 (C-3'), 75.7 (C-3), 75.2 (CH_2 Bn), 75.0 (CH_2 Bn), 74.6 (C-4), 73.7 (2x CH_2 Bn), 70.7 (C-2), 69.3 (C-5), 68.8 (C-6'), 68.6 (C-6), 63.6 (C-2'), 63.3 (C-5), 55.6 (CH_3 OMe); Diagnostic peaks for β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) 5.57 (s, 1H, CHPh), 5.13 (d, *J* = 3.8 Hz, 1H, H-1), 4.65 (d, *J* = 8.0 Hz, 1H, H-1'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 104.3 (C-1'), 101.4 (CH Ph), 98.0 (C-1); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{40}N_3O_{11}NH_4$ 861.37053, found 861.36922.

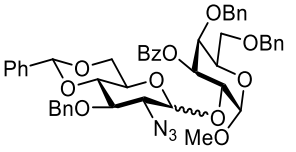
Disaccharide 33A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **33**. Yield: 85 mg, 89 µmol, 89%, α:β > 20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H, CH_{arom}), 7.41 – 7.14 (m, 28H, CH_{arom}), 5.63 (dd, *J* = 10.7, 3.1 Hz, 1H, H-3), 5.44 (s, 1H, C*H*Ph), 4.98 (d, *J* = 3.5 Hz, 1H, H-1), 4.90 (d, *J* = 3.6 Hz, 1H, H-1'), 4.82 (d, *J* = 12.1 Hz, 1H, C*H*H Ph), 4.77 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.70 (d, *J* = 11.2 Hz, 1H, CH*H* Bn), 4.67 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.63 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.54 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.47 – 4.42 (m, 3H, H-2, 2x CH*H* Bn), 4.24 (d, *J* = 2.4 Hz, 1H, H-4), 4.15 (t, *J* = 6.5 Hz, 1H, H-5), 4.06 – 3.94 (m, 3H, H-3', H-5', H-6'), 3.63 – 3.48 (m, 6H, H-2', H-4', H-5, 2x H-6, H-6'), 3.43 (s, 3H, CH_3 OMe); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9 (C=O), 138.7, 138.4, 137.9, 137.9, 137.5, 133.1 (C_q), 129.7, 129.6, 128.8, 128.6, 128.5, 128.4, 128.3, 128.3, 128.1, 128.0, 128.0, 127.8, 127.8, 127.5, 126.2 (CH_{arom}), 101.2 (CHPh), 97.2 (C-1), 96.6 (C-1'), 82.1 (C-

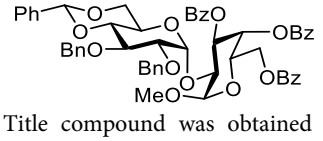
4'), 78.8 (C-2'), 78.3 (C-3'), 75.4 (C-4), 75.3, 75.2, 73.5, 73.4 (CH_2 Bn), 72.3 (C-3), 71.6 (C-2), 68.9 (C-5), 68.8(C-6), 68.7 (C-6'), 62.8 (C-5'), 55.4 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{56}O_{12}NH_4$ 926.41100, found 926.40964.

Disaccharide 33B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **33**. 44 mg, 51 µmol, 51%, α:β = 3:1. Data for the α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 2H, CH_{arom}), 7.49 – 7.17 (m, 23H, CH_{arom}), 5.63 (dd, *J* = 10.6, 3.1 Hz, 1H, H-3), 5.44 (s, 1H, C*H*Ph), 5.01 (d, *J* = 3.5 Hz, 1H, H-1), 4.97 (d, *J* = 3.8 Hz, 1H, H-1'), 4.78 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.72 – 4.60 (m, 2H, C*H*H Bn, CH*H* Bn), 4.54 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.50 – 4.39 (m, 3H, H-2, 2x CH*H* Bn), 4.19 (d, *J* = 2.6 Hz, 1H, H-4), 4.16 (t, *J* = 6.5 Hz, 1H, H-5), 4.01 (dd, *J* = 10.1, 4.9 Hz, 1H, H-6'), 3.99 – 3.89 (m, 2H, H-3', H-5'), 3.61 – 3.52 (m, 5H, H-4', H-5, 2x H-6, H-6'), 3.48 (s, 3H, CH_3 OMe), 3.34 (dd, *J* = 10.1, 3.4 Hz, 1H, H-2'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8 (C=O), 138.0, 137.9, 137.8, 137.3 (C_q), 133.3, 129.8, 129.7 (CH_{arom}), 129.6 (C_q), 129.0, 128.7, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 127.9, 127.9, 127.9, 127.9, 127.8, 127.8, 126.2, 126.0 (CH_{arom}), 101.4 (CHPh), 97.4 (C-1), 97.2 (C-1'), 82.7 (C-4'), 75.8 (C-3'), 75.6 (C-4), 75.4, 75.1, 73.6 (CH_2 Bn), 72.8 (C-2), 72.0 (C-3), 68.9 (C-5), 68.7, 68.6 (C-6, C-6'), 63.2 (C-5'), 63.0 (C-2'), 55.7 (CH_3 OMe); diagnostic peaks for the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.59 (dd, *J* = 10.7, 3.2 Hz, 1H, H-3), 5.54 (s, 1H, C*H*Ph), 4.29 (td, *J* = 10.5, 4.3 Hz, 2H, H-5'), 4.23 (d, *J* = 3.2 Hz, 1H, H-4), 3.75 (t, *J* = 10.3 Hz, 1H), 3.69 – 3.64 (m, 1H), 3.44 (s, 3H, CH_3 OMe); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9 (C=O), 104.4 (C-1'), 101.3 (CHPh), 99.8 (C-1), 81.3, 79.2, 75.5, 74.8, 68.7, 68.6, 68.5, 66.2, 65.7, 55.6; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{40}N_3O_{11}NH_4$ 861.37053, found 861.36914.

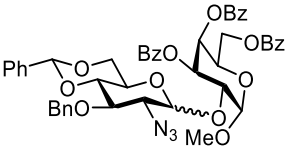
Disaccharide 34A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **34.** Yield: 89 mg, 88 µmol, 88%, α:β > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (ddd, *J* = 8.5, 2.6, 1.3 Hz, 4H, CH_{arom}), 7.83 – 7.73 (m, 2H, CH_{arom}), 7.66 – 7.59 (m, 1H, CH_{arom}), 7.57 – 7.52 (m, 1H, CH_{arom}), 7.50 – 7.12 (m, 22H, CH_{arom}) , 5.99 (dd, *J* = 3.5, 1.3 Hz, 1H, H-4), 5.84 (dd, *J* = 10.6, 3.4 Hz, 1H, H-3), 5.36 (s, 1H, C*H*Ph), 5.10 (d, *J* = 3.4 Hz, 1H, H-1), 4.92 – 4.85 (m, 2H, H-1', C*H*H Bn), 4.78 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.71 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.67 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.64 – 4.52 (m, 2H, H-5, H-6), 4.41 (dd, *J* = 10.6, 3.4 Hz, 1H, H-2), 4.34 (dd, *J* = 10.8, 5.2 Hz, 1H, H-6), 3.96 (t, *J* = 9.3 Hz, 1H, H-3'), 3.90 – 3.78 (m, 2H, H-5', H-6'), 3.54 – 3.42 (m, 6H, CH_3 OMe, H-2', H-4', H-6'). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 165.5, 165.5 (C=O), 138.7, 138.5, 137.4, 133.6, 133.3, 133.0 (C_q), 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 128.9, 128.7, 128.7, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 128.0, 128.0, 127.6, 126.2 (CH_{arom}), 101.2 (CHPh), 97.6 (C-1), 97.3 (C-1'), 82.1 (C-4'), 78.9 (C-2'),

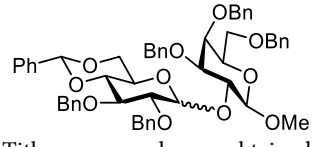
78.3 (C-3'), 75.2 (CH_2 Bn), 73.8 (CH_2 Bn), 72.1 (C-2), 69.5 (C-4), 69.3 (C-3), 68.7 (C-6'), 66.9 (C-5), 62.8 (C-5'), 62.7 (C-6), 55.7 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{52}O_{14}NH_4$ 954.36953, found 954.36787.

Disaccharide 34B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **34**. Yield: 76 mg, 87 µmol, 87%, α:β = 6:1. Data for α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.98 (m, 4H, CH_{arom}), 7.87 – 7.78 (m, 2H, CH_{arom}), 7.63 (ddt, *J* = 8.1, 7.0, 1.4 Hz, 1H, CH_{arom}), 7.55 (ddt, *J* = 8.1, 7.0, 1.3 Hz, 1H, CH_{arom}), 7.51 – 7.19 (m, 17H, CH_{arom}), 5.96 (dd, *J* = 3.6, 1.2 Hz, 1H, H-4), 5.83 (dd, *J* = 10.5, 3.5 Hz, 1H, H-3), 5.37 (s, 1H, C*H*Ph), 5.15 (d, *J* = 3.5 Hz, 1H, H-1), 4.98 (d, *J* = 3.6 Hz, 1H, H-1'), 4.82 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.67 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.64 – 4.54 (m, 2H, H-5, H-6), 4.36 (m, 2H, H-2, H-6), 4.02 – 3.96 (t, *J* = 9.1 Hz, 1H, H-3'), 3.87 - 3.77 (m, 2H, H-5', H-6'), 3.56 (m, 4H, H-4', CH_3 OMe), 3.48 – 3.41 (m, 1H, H-6'), 3.33 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2'). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 165.5, 165.4 (C=O), 137.8, 137.1, 133.6, 133.3, 133.2 (C_q), 129.9, 129.8, 129.6, 129.4, 129.3, 129.0, 128.7, 128.7, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.1, 128.1, 127.9, 126.1, 126.0 (CH_{arom}), 101.3 (CHPh), 98.0 (C-1'), 97.8 (C-1), 82.6 (C-4'), 75.6 (C-3'), 75.1 (CH_2 Bn), 73.6 (C-2), 69.4 (C-4), 69.2 (C-3), 68.4 (C-6'), 66.8 (C-5), 63.3 (C-5'), 62.9 (C-2'), 62.6 (C-6), 55.9 (CH_3 OMe). Diagnostic peaks for β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (dd, *J* = 3.6, 1.2 Hz, 1H, H-4), 5.55 (s, 1H, C*H*Ph), 5.12 (d, *J* = 3.6 Hz, 1H, H-1), 4.45 (d, *J* = 7.7 Hz, 1H, H-1'), 4.26 (dd, *J* = 10.5, 3.4 Hz, 1H, H-2), 3.52 (s, 3H, CH_3 OMe). ^{13}C NMR (101 MHz, $CDCl_3$) δ 104.3 (C-1'), 101.5 (CHPh), 99.8 (C-1), 76.7 (C-2), 55.8 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{45}N_3O_{13}NH_4$ 889.32906, found 889.32747.

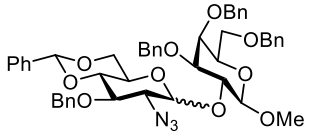
Disaccharide 35A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **35**. Yield: 75 mg, 83 mmol, 83%, α:β = 1.5:1. Data reported for a 1:1 mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 6.94 (m, 60H), 5.56 (s, 1H, C*H*Phβ), 5.53 – 5.49 (m, 2H, H-1'α, C*H*Phα), 5.08 (d, *J* = 7.5 Hz, 1H, H-1'β), 4.94 – 4.71 (m, 9H), 4.67 (d, *J* = 2.4 Hz, 2H), 4.63 (d, *J* = 10.6 Hz, 1H), 4.60 – 4.52 (m, 3H), 4.50 – 4.38 (m, 6H), 4.35 – 4.30 (m, 1H), 4.21 – 4.07 (m, 3H), 3.99 (t, *J* = 9.3 Hz, 1H), 3.93 (d, *J* = 2.8 Hz, 1H, H-4α), 3.90 (d, *J* = 2.8 Hz, 1H, H-4β), 3.85 – 3.80 (m, 1H), 3.80 – 3.75 (m, 1H), 3.72 (dd, *J* = 9.2, 7.9 Hz, 1H), 3.66 – 3.53 (m, 10H), 3.50 (d, *J* = 8.5 Hz, 7H), 3.42 (ddd, *J* = 10.0, 8.9, 5.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 138.7, 138.7, 138.2, 137.9, 137.9, 137.9, 137.5, 137.5, 129.0, 128.8, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 126.3, 126.1, 104.8 (C-1α), 103.5 (C-

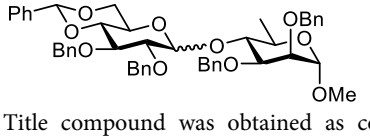
1β), 103.2 (C-1'β), 101.3 (CHPhα), 101.2 (CHPhβ), 96.8 (C-1'α), 82.8, 82.7, 82.3, 81.5, 81.3, 80.4, 79.1, 78.6, 77.2, 75.3, 75.0, 75.0, 74.7, 74.5, 73.7, 73.7, 73.5, 73.4, 73.3, 73.0, 73.0, 72.9, 72.8, 72.5, 69.1, 69.0, 68.8, 68.7, 66.0, 62.1, 56.7 (CH_3 OMeα), 56.6 (CH_3 OMeβ); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{58}O_{11}NH_4$ 912.43174, found 912.42989.

Disaccharide 35B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **35**. Yield: 80 mg, 96 μmol, 96%, α:β = 1:10. Data for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.20 (m, 25H), 5.54 (s, 1H, C*H*Ph), 4.93 – 4.84 (m, 3H, H-1', 2x C*H*H Bn), 4.77 (d, *J* = 11.4 Hz, 1H, CH*H* Bn), 4.74 – 4.68 (m, 2H, CH_2 Bn), 4.55 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 4.45 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.40 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 4.33 – 4.27 (m, 2H, H-1, H-6'), 4.08 (dd, *J* = 9.6, 7.6 Hz, 1H, H-2), 3.93 (d, *J* = 2.8 Hz, 1H, H-4), 3.79 (t, *J* = 10.3 Hz, 1H, H-6'), 3.76 – 3.70 (m, 1H, H-4'), 3.63 (dd, *J* = 9.6, 2.8 Hz, 1H, H-3), 3.60 – 3.57 (m, 3H, H-3', 2x H-6), 3.55 – 3.46 (m, 5H, H-2', H-5, CH_3 OMe), 3.34 (td, *J* = 9.9, 4.9 Hz, 1H, H-5'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 138.0, 137.9, 137.3 (C_q), 131.5, 129.1, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.6, 126.1 (CH_{arom}), 102.6 (C-1), 102.2 (C-1'), 101.3 (CHPh), 83.0 (C-3), 81.6 (C-4'), 79.4 (C-2'), 77.2 (C-2), 74.9, 74.6, 73.6 (CH_2 Bn), 73.3 (C-3'), 72.8 (C-4), 72.7 (CH_2 Bn), 68.7, 68.7 (C-6, C-6'), 66.5, 66.2 (C-5, C-5'), 56.3 (CH_3 OMe); Diagnostic peaks for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (s, 1H, C*H*Ph), 5.46 (d, *J* = 3.8 Hz, 1H, H-1'), 4.14 (dd, *J* = 10.2, 5.0 Hz, 1H), 4.01 (dd, *J* = 10.0, 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 104.9 (C-1), 101.4 (CHPh), 97.6 (C-1'), 82.9, 80.3, 76.0, 74.3, 73.4, 69.3, 63.2, 62.4, 58.0 (CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{51}N_3O_{10}NH_4$ 847.39127, found 847.38959.

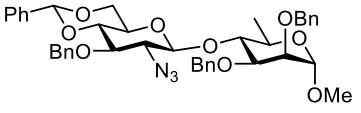
Disaccharide 36A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **36**. Yield: 70 mg, 80 μmol, 89%, α:β = 1:2.4. Data reported for a 1:2 mixture of anomers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.01 (m, 75H), 5.77 (d, *J* = 4.1 Hz, 1H, H-1'α), 5.55 (s, 1H, C*H*Phα), 5.48 (s, 2H, C*H*Phβ), 4.91 (d, *J* = 11.3 Hz, 3H), 4.84 (d, *J* = 2.8 Hz, 4H), 4.81 – 4.74 (m, 8H), 4.72 – 4.67 (m, 6H), 4.65 – 4.58 (m, 7H), 4.57 – 4.49 (m, 3H), 4.44 (d, *J* = 12.1 Hz, 1H), 4.29 (dd, *J* = 10.4, 4.9 Hz, 1H, H-6'α), 4.15 (dd, *J* = 10.5, 5.0 Hz, 2H, H-6'β), 4.04 – 3.94 (m, 3H), 3.90 (td, *J* = 9.7, 1.4 Hz, 2H, H-4β), 3.80 – 3.72 (m, 8H), 3.71 – 3.65 (m, 2H), 3.61 (td, *J* = 9.4, 4.6 Hz, 3H), 3.56 – 3.49 (m, 3H), 3.43 (dd, *J* = 8.8, 7.7 Hz, 2H, H-4'β), 3.33 (s, 9H, CH_3 OMeαβ), 3.27 (td, *J* = 9.9, 5.0 Hz, 2H, H-5'β), 1.42 (d, *J* = 6.2 Hz, 3H, H-6α), 1.36 (d, *J* = 6.3 Hz, 6H, H-6β); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4, 138.8, 138.6, 138.5, 138.4, 138.2, 138.0, 137.5, 137.5, 129.9, 129.6, 129.0, 129.0, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.4, 127.3, 127.0, 126.7, 126.1, 126.1, 103.9 (C-1'β), 101.2 (CHPhαβ), 99.5 (C-1β), 98.8 (C-1α), 98.0

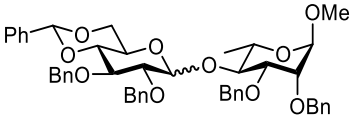
(C-1'α), 83.0 (C-4'β), 82.2 (C-4'α), 81.8, 81.5, 81.4, 80.7, 78.8, 78.7, 78.2, 77.4, 77.2, 76.9, 76.1, 75.7, 75.7, 75.4, 75.2, 73.9, 73.2, 73.0, 72.8, 72.6, 70.5, 69.0, 68.9, 67.9, 66.9, 65.9, 63.3, 54.9 (CH_3 OMeβ), 54.8 (CH_3 OMeα), 19.3 (C-6α), 18.2 (C-6β); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{52}O_{10}NH_4$ 806.38987, found 806.38846.

Disaccharide 36B



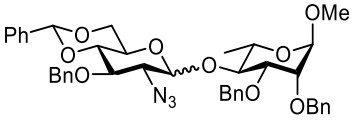
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **36**. Yield: 54 mg, 75 µmol, 75%, α:β < 1:20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.22 (m, 20H, CH_{arom}), 5.48 (s, 1H, C*H*Ph), 4.91 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.77 (d, *J* = 11.2 Hz, 1H, CH*H* Bn), 4.72 (d, *J* = 12.4 Hz, 1H, C*H*H Bn), 4.69 – 4.63 (m, 3H, H-1, C*H*H Bn, CH*H* Bn), 4.60 – 4.54 (m, 2H, H-1', CH*H* Bn), 4.00 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6'), 3.89 (t, *J* = 9.1 Hz, 1H, H-4), 3.80 – 3.69 (m, 3H, H-2, H-3, H-5), 3.66 – 3.55 (m, 2H, H-3', H-4'), 3.52 (t, *J* = 10.3 Hz, 1H, H-6'), 3.38 (dd, *J* = 9.0, 7.9 Hz, 1H, H-2'), 3.31 (s, 3H, CH_3 OMe), 3.19 (td, *J* = 9.4, 5.0 Hz, 1H, H-5'), 1.43 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 138.4, 137.9, 137.3 (C_q), 131.5, 131.2, 129.1, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.0, 128.0, 127.7, 127.4, 126.8, 126.1 (CH_{arom}), 102.4 (C-1'), 101.3 (CHPh), 99.2 (C-1), 81.7 (C-4'), 81.4 (C-4), 79.5 (C-3'), 78.6 (C-3), 75.2 (C-2), 75.0, 73.1, 72.2 (CH_2 Bn), 68.6 (C-6'), 67.5 , 67.4 (C-2', C-5), 66.1 (C-5'), 54.9 (CH_3 OMe), 18.1 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{45}N_3O_9NH_4$ 741.34941, found 741.34849.

Disaccharide 37A



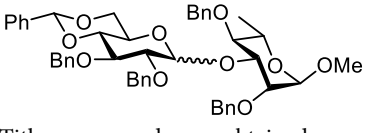
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **37**. Yield: 91 mg, 90 µmol, 90%, α:β = 1.7:1. Data reported for a 2:1 mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.06 (m, 75H), 5.61 (s, 1H, C*H*Phβ), 5.57 (s, 2H, C*h*Phα), 5.14 – 5.06 (m, 3H, H-1'αβ), 5.02 – 4.97 (m, 3H), 4.93 (d, *J* = 11.6 Hz, 1H), 4.90 – 4.84 (m, 5H), 4.79 (d, *J* = 11.6 Hz, 2H), 4.76 – 4.64 (m, 8H), 4.60 (s, 4H), 4.51 (d, *J* = 10.9 Hz, 1H), 4.40 (d, *J* = 11.1 Hz, 1H), 4.38 – 4.31 (m, 2H), 4.12 (dd, *J* = 10.2, 4.9 Hz, 2H, H-6'α), 4.07 (t, *J* = 9.3 Hz, 2H, H-4α), 3.95 (t, *J* = 9.3 Hz, 1H, H-4β), 3.86 – 3.81 (m, 6H), 3.81 – 3.73 (m, 3H), 3.73 – 3.60 (m, 6H), 3.45 (dd, *J* = 9.2, 6.9 Hz, 1H, H-2'β), 3.43 – 3.37 (m, 4H), 3.35 (s, 6H, CH_3 OMeα), 1.42 (d, *J* = 5.9 Hz, 6H, H-6α), 1.39 (d, *J* = 6.2 Hz, 3H, H-6β); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 138.4, 138.0, 138.0, 137.8, 131.7, 129.0, 128.9, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 126.2, 126.1, 103.1 (C-1'β), 101.2 (CHPhα), 101.2 (CHPhβ), 99.0 (C-1β, 99.0, 98.9 (C-1α, C-1'α), 82.8, 82.6, 81.9, 81.1, 80.5, 79.6, 79.1, 79.0, 77.9, 76.6, 75.3, 75.2, 75.1, 74.6, 74.4, 74.3, 72.9, 72.8, 72.2, 71.5, 69.1, 68.9, 68.0, 67.3, 65.7, 62.8, 54.9 (CH_3 OMeβ), 54.7 (CH_3 OMeα), 18.3 (C-6α), 18.0 (C-6β); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{52}O_{10}NH_4$ 806.38987, found 806.38859.

Disaccharide 37B



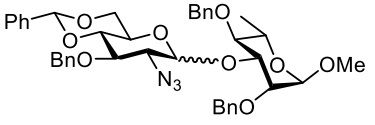
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **37**. Yield: 72 mg, 99 µmol, 99%, α:β = 1:10. Data for β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.64 (m, 2H, CH_{arom}), 7.47 (dd, *J* = 7.6, 2.2 Hz, 2H, CH_{arom}), 7.43 – 7.25 (m, 16H, CH_{arom}), 5.55 (s, 1H, C*H*Ph), 4.94 – 4.86 (m, 2H, H-1', C*H*H Bn), 4.78 (d, *J* = 11.4 Hz, 1H, CH*H* Bn), 4.68 – 4.60 (m, 4H, H-1, C*H*H Bn, CH_2 Bn), 4.51 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.30 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6'), 3.92 – 3.82 (m, 2H, H-3, H-4), 3.77 (dd, *J* = 3.0, 1.8 Hz, 1H, H-2), 3.72 (t, *J* = 10.3 Hz, 1H, H-6'), 3.68 – 3.62 (m, 2H, H-4', H-5), 3.47 (t, *J* = 9.2 Hz, 1H, H-3'), 3.39 (dd, *J* = 9.6, 7.9 Hz, 1H, H-2'), 3.36 – 3.29 (m, 4H, H-5', CH_3 OMe), 1.31 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 138.2, 138.1, 137.3 (C_q), 131.6, 129.1, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.0, 127.9, 127.9, 127.8, 126.1 (CH_{arom}), 102.1 (C-1'), 101.3 (CHPh), 98.9 (C-1), 81.9 (C-4'), 80.1 (C-3), 79.1 (C-3'), 77.4 (C-4), 74.9 (CH_2 Bn), 74.1 (C-2), 72.8, 72.0 (CH_2 Bn), 68.7 (C-6), 67.0 (C-5), 66.5 (C-2'), 65.8 (C-5'), 54.9 (CH_3 OMe), 17.9 (C-6); diagnostic peaks for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (s, 1H, C*H*Ph), 5.06 (d, *J* = 3.8 Hz, 1H, H-1'), 4.03 (dd, *J* = 10.2, 4.9 Hz, 1H), 3.98 (t, *J* = 9.5 Hz, 1H), 1.41 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 101.3 (CHPh), 98.7 (C-1'), 82.9, 81.3, 80.8, 75.1, 74.3, 71.3, 68.0, 63.7, 62.8, 21.9 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{45}N_3O_9NH_4$ 741.34941, found 741.34836.

Disaccharide 38A



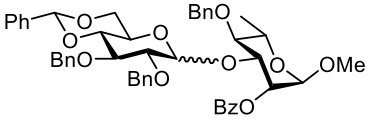
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **38**. Yield: 79 mg, 100 µmol, 100%, α:β = 7:1. Data for α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.12 (m, 25H, CH_{arom}), 5.53 (s, 1H, C*H*Ph), 5.11 (d, *J* = 3.5 Hz, 1H, H-1'), 4.96 – 4.89 (m, 2H, 2x C*H*H Bn), 4.83 – 4.77 (m, 3H, 2x C*H*H Bn, CH*H* Bn), 4.74 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.61 – 4.54 (m, 3H, H-1, 2x CH*H* Bn), 4.19 – 4.10 (m, 3H, H-4, H-5', H-6'), 4.09 – 4.05 (m, 1H, H-3), 3.86 (dd, *J* = 2.9, 2.1 Hz, 1H, H-2), 3.70 – 3.58 (m, 5H, H-2', H-3', H-4', H-5, H-6'), 3.28 (s, 3H, CH_3 OMe), 1.33 (d, *J* = 5.4 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.6, 138.2, 138.1, 137.7 (C_q), 131.6, 131.1, 128.9, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 126.3 (CH_{arom}), 101.3 (CHPh), 99.2 (C-1), 96.5 (C-1'), 82.6 (C-4'), 80.2, 79.2 (C-2', C-3'), 78.6 (C-4), 76.9 (C-3), 75.7 (CH_2 Bn), 75.3 (C-2), 75.2, 73.9, 73.3 (CH_2 Bn), 69.1 (C-6'), 68.2 (C-5), 63.0 (C-5'), 54.8 (CH_3 OMe), 18.1 (C-6); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 (s, 1H, C*H*Ph), 5.00 (d, *J* = 11.3 Hz, 1H), 4.40 (d, *J* = 10.6 Hz, 1H), 4.31 (dd, *J* = 10.4, 5.0 Hz, 1H), 3.79 (dd, *J* = 3.3, 1.8 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 103.9 (C-1'), 99.5 (C-1), 81.9, 81.4, 81.0, 79.6, 74.8, 73.6, 73.2, 67.8, 66.0; HRMS: $[M+NH_4]^+$ calcd for 806.38987, found 806.38793.

Disaccharide 38B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **38**. Yield: 49 mg, 68 µmol, 68%, α:β = 1.4:1. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.59 (m, 4H), 7.51 – 7.23 (m, 32H), 7.20 – 7.09 (m, 4H), 5.59 – 5.46 (m, 2H, C*H*Phαβ), 5.02 (d, *J* = 10.6 Hz, 1H), 4.96 – 4.91 (m, 3H), 4.85 (d, *J* = 10.6 Hz, 1H), 4.82 – 4.76 (m, 3H), 4.72 (d, *J* = 11.0 Hz, 4H), 4.65 (d, *J* = 8.1 Hz, 1H, H-1'β), 4.62 (d, *J* = 10.7 Hz, 1H), 4.57 (d, *J* = 1.8 Hz, 1H, H-1β), 4.54 (d, *J* = 10.6 Hz, 1H), 4.29 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6'β), 4.22 (dd, *J* = 10.2, 4.9 Hz, 1H, H-6'α), 4.15 – 4.09 (m, 2H), 4.07 – 4.01 (m, 2H), 3.82 (dd, *J* = 3.2, 2.0 Hz, 1H, H-2α), 3.77 (dd, *J* = 3.3, 1.7 Hz, 1H, H-2β), 3.74 – 3.62 (m, 6H), 3.59 (t, *J* = 8.4 Hz, 1H), 3.46 (dd, *J* = 9.4, 8.1 Hz, 1H, H-2'β), 3.38 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2'α), 3.33 (dt, *J* = 9.6, 4.9 Hz, 1H), 3.30 (s, 3H, CH_3 OMeα), 3.29 (s, 3H, CH_3 OMeβ), 1.37 – 1.31 (m, 6H, H-6αβ); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 138.5, 137.9, 137.9, 137.8, 137.7, 137.5, 137.2, 135.4, 134.4, 131.8, 131.7, 131.5, 131.3, 131.2, 130.4, 130.3, 129.2, 129.0, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 126.3, 126.1, 103.0 (C-1'β), 101.4, 101.4 (CHPhαβ), 99.5 (C-1β), 98.3 (C-1α), 94.2 (C-1'α), 83.0, 81.8, 80.6, 79.9, 79.7, 79.5, 78.3, 76.1, 75.7, 75.2, 75.1, 75.0, 74.7, 73.6, 73.0, 72.6, 68.9, 68.0, 67.9, 66.9, 66.1, 62.9, 62.8, 54.8, 54.6, 18.1, 18.0; HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{45}N_3O_9NH_4$ 741.34941, found 741.34778.

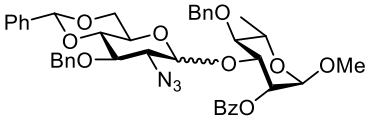
Disaccharide 39A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **39**. Yield: 53 mg, 66 µmol, 66%, α:β = 6:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 2H, CH_{arom}), 7.57 – 7.52 (m, 1H, CH_{arom}), 7.43 – 7.34 (m, 9H, CH_{arom}), 7.27 – 7.22 (m, 3H, CH_{arom}), 7.20 – 7.15 (m, 4H, CH_{arom}), 7.14 – 7.06 (m, 6H, CH_{arom}), 5.58 (dd, *J* = 3.2, 1.9 Hz, 1H, H-2), 5.51 (s, 1H, C*H*Ph), 5.18 (d, *J* = 3.6 Hz, 1H, H-1'), 4.98 (d, *J* = 10.4 Hz, 1H, C*H*H Bn), 4.81 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.77 (d, *J* = 1.9 Hz, 1H, H-1), 4.68 (d, *J* = 11.4 Hz, 1H, CH*H* Bn), 4.64 (d, *J* = 10.4 Hz, 1H, CH*H* Bn), 4.53 (d, *J* = 12.1 Hz, 1H C*H*H Bn), 4.44 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.29 (dd, *J* = 9.5, 3.3 Hz, 1H, H-3), 4.23 (dd, *J* = 10.1, 4.9 Hz, 1H, H-6'), 4.10 – 4.01 (m, 2H, H-3', H-5'), 3.82 (dq, *J* = 9.4, 6.2 Hz, 1H, H-5), 3.71 – 3.67 (m, 1H, H-4), 3.67 – 3.63 (m, 1H, H-6'), 3.60 (t, *J* = 9.5 Hz, 1H, H-4'), 3.54 (dd, *J* = 9.3, 3.6 Hz, 1H, H-2'), 3.37 (s, 3H, CH_3 OMe), 1.40 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2 (C=O), 138.7, 138.1, 137.8, 137.7 (C_q), 133.4, 130.1 (CH_{arom}), 129.9 (C_q), 129.9, 128.9, 128.8, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.6, 127.5, 126.4, 126.1 (CH_{arom}), 101.3 (CHPh), 98.6 (C-1), 93.6 (C-1'), 82.3 (C-4'), 79.7 (C-4), 78.4, 78.3 (C-2', C-3'), 76.3, 75.1 (CH_2 Bn), 72.8 (C-3), 72.7 (CH_2 Bn), 69.1 (C-6'), 68.4 (C-2), 67.9 (C-5), 62.9 (C-5'), 55.1 (CH_3 OMe), 18.2 (C-6); diagnostic peaks for the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 (s, 1H, C*H*Ph), 5.41 (dd, *J* = 3.5, 1.8 Hz, 1H, H-2), 4.36 (dd, *J* = 9.4, 3.5 Hz,

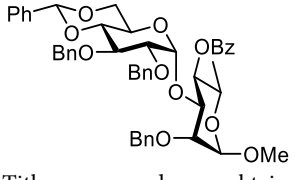
1H, H-3), 1.37 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9 (C=O), 103.7 (C-1'), 101.1 (CHPh), 98.5 (C-1), 81.6, 81.3, 80.8, 76.0, 74.9, 72.9, 68.8, 67.2, 66.0, 18.1 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{50}O_{11}NH_4$ 820.36914, found 820.36629.

Disaccharide 39B



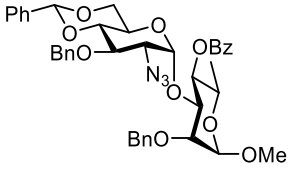
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **39**. Yield: 41 mg, 55 µmol, 55%, α:β = 1:1. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 – 8.12 (m, 2H), 8.09 – 8.05 (m, 2H), 7.51 – 7.26 (m, 36H), 5.61 (dd, *J* = 3.3, 1.9 Hz, 1H, H-2α/β), 5.57 (s, 1H, C*H*Ph α/β), 5.50 (s, 1H, C*H*Ph α/β), 5.34 (dd, *J* = 3.5, 1.8 Hz, 1H, H-2α/β), 5.23 (d, *J* = 3.7 Hz, 1H, H-1'α), 5.04 (d, *J* = 10.5 Hz, 1H), 4.90 (d, *J* = 11.3 Hz, 1H), 4.87 – 4.83 (m, 2H), 4.77 – 4.70 (m, 5H), 4.69 (d, *J* = 11.1 Hz, 1H), 4.65 (d, *J* = 8.1 Hz, 1H, H-1'β), 4.59 (d, *J* = 10.4 Hz, 1H), 4.35 – 4.25 (m, 4H), 4.09 (td, *J* = 9.9, 4.8 Hz, 1H), 4.01 (dd, *J* = 10.0, 9.1 Hz, 1H), 3.86 – 3.75 (m, 3H), 3.74 – 3.59 (m, 6H), 3.54 (t, *J* = 9.3 Hz, 1H), 3.42 – 3.36 (m, 7H), 3.34 – 3.30 (m, 1H), 3.27 (dd, *J* = 10.0, 3.7 Hz, 1H), 1.42 – 1.37 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 149.8, 137.2, 135.4, 134.5, 133.5, 133.3, 131.9, 131.7, 131.2, 130.4, 130.3, 130.0, 130.0, 129.1, 129.0, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.2, 128.2, 128.1, 128.0, 127.9, 126.3, 126.1, 125.1, 119.3, 102.4 (C-1'β), 101.4, 101.3 (CHPhαβ), 98.7, 98.3 (C-1αβ), 93.9 (C-1'α), 82.8, 81.5, 80.7, 79.9, 79.2, 76.4, 75.3, 75.2, 74.9, 74.8, 72.9, 72.7, 68.8, 68.5, 67.7, 67.5, 67.3, 66.5, 66.1, 62.9, 62.5, 55.0, 55.0, 18.2, 18.1; HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{43}N_3O_{10}NH_4$ 755.32867, found 755.32641

Disaccharide 40A



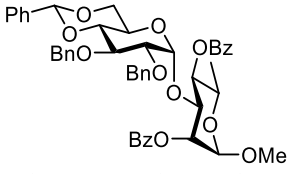
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **40**. Yield: 55 mg, 69 µmol, 69%, α:β >20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 7.98 (m, 2H, CH_{arom}), 7.50 – 7.45 (m, 1H, CH_{arom}), 7.40 – 7.35 (m, 2H, CH_{arom}), 7.34 (d, *J* = 0.9 Hz, 4H, CH_{arom}), 7.31 – 7.25 (m, 10H, CH_{arom}), 7.25 – 7.19 (m, 5H, CH_{arom}), 5.50 (t, *J* = 9.6 Hz, 1H, H-4), 5.36 (s, 1H, C*H*Ph), 4.87 – 4.84 (m, 2H, H-1', C*H*H Bn), 4.83 – 4.78 (m, 2H, 2x C*H*H Bn), 4.69 (d, *J* = 11.4 Hz, 1H, CH*H* Bn), 4.66 – 4.62 (m, 2H, 2x CH*H* Bn), 4.61 (d, *J* = 2.0 Hz, 1H, H-1), 4.09 (dd, *J* = 9.6, 3.0 Hz, 1H, H-3), 3.96 – 3.90 (m, 2H, H-2, H-3'), 3.87 – 3.76 (m, 3H, H-5, H-5', H-6'), 3.48 (dd, *J* = 9.4, 3.7 Hz, 1H, H-2'), 3.43 (t, *J* = 9.3 Hz, 1H, H-4'), 3.36 (s, 3H, CH_3 OMe), 3.30 – 3.21 (m, 1H, H-6'), 1.25 (d, *J* = 6.3 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7 (C=O), 138.7, 138.7, 138.3, 137.6 (C_q), 133.1 (CH_{arom}), 130.2 (C_q), 129.8, 128.9, 128.5, 128.4, 128.2, 128.1, 128.1, 128.1, 127.9, 127.6, 127.5, 126.3 (CH_{arom}), 101.2 (CHPh), 100.3 (C-1), 100.2 (C-1'), 82.3 (C-4'), 79.7 (C-3), 79.5 (C-2'), 78.3 (C-3'), 76.2 (C-2), 75.1, 74.0, 73.8 (CH_2 Bn), 73.8 (C-4), 68.7 (C-6'), 66.9 (C-5), 63.4 (C-5'), 55.0 (CH_3 OMe), 17.8 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{50}O_{11}NH_4$ 820.36914, found 820.36724.

Disaccharide 40B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **40**. Yield: 37 mg, 50 µmol, 50%, α:β = 12:1. Data for the α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.02 (m, 2H, CH_{arom}), 7.43 (dt, *J* = 7.4, 1.4 Hz, 3H, CH_{arom}), 7.35 (qt, *J* = 5.2, 2.7 Hz, 8H, CH_{arom}), 7.31 – 7.23 (m, 9H, CH_{arom}), 5.51 (t, *J* = 9.7 Hz, 1H, H-4), 5.38 (s, 1H, C*H*Ph), 4.91 (d, *J* = 3.6 Hz, 1H, H-1'), 4.83 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.78 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.73 (d, *J* = 12.2 Hz, 1H, CH*H* Bn), 4.71 (d, *J* = 1.9 Hz, 1H, H-1), 4.62 (d, *J* = 11.0 Hz, 1H, CH*H* Bn), 4.15 (dd, *J* = 9.7, 3.1 Hz, 1H, H-3), 4.00 (dd, *J* = 10.2, 4.9 Hz, 1H, H-6'), 3.92 (dd, *J* = 3.2, 2.0 Hz, 1H, H-2), 3.90 – 3.78 (m, 3H, H-3', H-5, H-5'), 3.50 (t, *J* = 9.4 Hz, 1H, H-4'), 3.40 (t, *J* = 10.3 Hz, 1H, H-6'), 3.37 (s, 3H, CH_3 OMe), 3.32 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2'), 1.27 (d, *J* = 6.3 Hz, 3H, CH_3 OMe); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6 (C=O), 138.2, 137.8, 137.4 (C_q), 133.2 (CH_{arom}), 130.0 (C_q), 129.7, 129.7, 129.0, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.2, 128.1, 128.1, 128.0, 127.9, 126.3 (CH_{arom}), 101.3 (CHPh), 99.3 (C-1), 97.8 (C-1'), 82.7 (C-4'), 77.0 (C-3), 75.9 (C-3'), 75.2 (C-2), 75.0, 73.4 (CH_2 Bn), 73.3 (C-4), 68.5 (C-6), 66.8 (C-5), 63.4, 63.3 (C-2', C-5'), 55.1 (CH_3 OMe), 17.7 (C-6); diagnostic peaks for the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.95 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.39 (d, *J* = 7.9 Hz, 1H, H-1'), 4.30 (dd, *J* = 10.4, 5.0 Hz, 1H, H-6'), 3.73 (t, *J* = 8.9 Hz, 1H), 3.68 (t, *J* = 10.3 Hz, 1H), 3.62 (t, *J* = 9.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 104.0 (C-1'), 99.9 (C-1), 81.5, 81.1, 80.9, 79.6, 79.5, 75.2, 74.9, 73.6, 66.4, 66.1, 64.8, 55.0(CH_3 OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{43}N_3O_{10}NH_4$ 755.32867, found 755.32744.

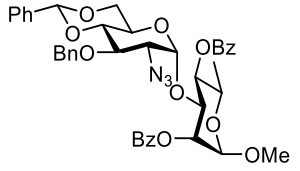
Disaccharide 41A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **42.** Yield: 68 mg, 83 µmol, 83%, α:β >20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 2H, CH_{arom}), 8.07 – 8.04 (m, 2H, CH_{arom}), 7.57 – 7.51 (m, 1H, CH_{arom}), 7.43 (t, *J* = 7.7 Hz, 2H, CH_{arom}), 7.40 – 7.36 (m, 1H, CH_{arom}), 7.34 – 7.28 (m, 5H, CH_{arom}), 7.21 – 7.09 (m, 13H, CH_{arom}), 5.59 (t, *J* = 9.8 Hz, 1H, H-4), 5.55 (dd, *J* = 3.5, 1.9 Hz, 1H, H-2), 5.29 (s, 1H, C*H*Ph), 4.91 (d, *J* = 1.8 Hz, 1H, H-1), 4.88 (d, *J* = 3.6 Hz, 1H, H-1'), 4.55 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.49 – 4.40 (m, 3H, CH*H* Bn, CH_2 Bn), 4.33 (dd, *J* = 9.9, 3.4 Hz, 1H, H-3), 4.03 (dq, *J* = 9.7, 6.2 Hz, 1H, H-5), 3.82 (dd, *J* = 10.1, 4.8 Hz, 1H, H-6'), 3.72 (t, *J* = 9.4 Hz, 1H, H-3'), 3.67 (dt, *J* = 9.9, 5.0 Hz, 1H, H-5'), 3.46 (s, 3H, CH_3 OMe), 3.40 (t, *J* = 10.2 Hz, 1H, H-6'), 3.37 – 3.32 (m, 2H, H-2', H-4'), 1.33 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 165.8 (C=O), 138.7, 138.2, 137.6 (C_q), 133.4, 133.3, 130.2 (CH_{arom}), 129.8 (C_q), 129.8 (CH_{arom}), 129.6 (C_q), 128.8, 128.7, 128.6, 128.6, 128.3, 128.2, 128.1, 128.0, 128.0, 128.0, 127.5, 127.5, 126.3

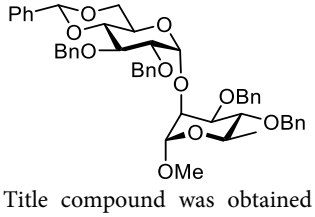
(CH_{arom}), 101.1 (CHPh), 98.7 (C-1), 96.4 (C-1'), 81.9 (C-4'), 78.4 (C-3'), 78.0 (C-2'), 75.1 (CH_2 Bn), 73.0 (C-3), 72.9 (CH_2 Bn, 72.8 (C-4), 69.5 (C-2), 68.7 (C-6'), 66.7 (C-5), 63.2 (C-5'), 55.4 (CH_3 OMe), 17.8 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{48}O_{12}NH_4$ 834.34840, found 834.34724.

Disaccharide 41B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **42.** Yield: 79 mg, 100 µmol, 100%, α:β = 12:1. Data for the α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 – 8.15 (m, 2H, CH_{arom}), 8.10 – 8.02 (m, 2H, CH_{arom}), 7.74 – 7.63 (m, 3H, CH_{arom}), 7.61 – 7.52 (m, 2H, CH_{arom}), 7.52 – 7.44 (m, 3H, CH_{arom}), 7.39 – 7.27 (m, 6H, CH_{arom}), 7.21 (pd, *J* = 4.2, 2.0 Hz, 3H, CH_{arom}), 7.18 – 7.15 (m, 1H, CH_{arom}), 7.14 – 7.08 (m, 2H, CH_{arom}), 5.62 (dd, *J* = 3.5, 1.9 Hz, 1H, H-2), 5.56 (t, *J* = 9.9 Hz, 1H, H-4), 5.32 (s, 1H, C*H*Ph), 5.05 (d, *J* = 3.7 Hz, 1H, H-1'), 4.87 (d, *J* = 1.9 Hz, 1H, H-1), 4.64 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.46 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.38 (dd, *J* = 9.9, 3.4 Hz, 1H, H-3), 4.06 (dq, *J* = 9.7, 6.2 Hz, 1H, H-5), 3.98 (dd, *J* = 10.1, 4.8 Hz, 1H, H-6'), 3.71 (dd, *J* = 10.0, 9.1 Hz, 1H, H-3'), 3.66 (dt, *J* = 9.9, 5.0 Hz, 1H, H-5'), 3.51 (t, *J* = 10.2 Hz, 1H, H-6'), 3.48 – 3.43 (m, 4H, H-4', CH_3 OMe), 3.21 (dd, *J* = 10.0, 3.7 Hz, 1H, H-2'), 1.35 (d, *J* = 6.3 Hz, 3H, CH_3 OMe); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 165.6 (C=O), 137.8, 137.3 (C_q), 135.3, 134.5, 133.5, 133.4, 131.8, 131.6, 131.1, 130.3, 130.3, 130.1, 130.0, 129.7 (CH_{arom}), 129.5, 129.4 (C_q), 128.9, 128.9, 128.7, 128.6, 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 126.2 (CH_{arom}), 101.2 (CHPh), 98.8 (C-1), 95.4 (C-1'), 82.3 (C-4'), 75.8 (C-3'), 74.9 (CH_2 Bn), 72.5 (C-4), 72.2 (C-3), 68.5 (C-6'), 68.2 (C-2), 66.5 (C-5), 63.2 (C-5'), 62.7 (C-2'), 55.4 (CH_3 OMe), 17.8 (C-6); diagnostic peaks for the α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70 (dd, *J* = 3.5, 1.8 Hz, 1H, H-2), 4.96 (dd, *J* = 9.8, 3.5 Hz, 1H, H-3), 4.33 – 4.27 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7 (C=O), 103.1 (C-1'), 98.6 (CHPh), 98.3 (C-1), 81.2 (, 79.2, 71.8, 70.7, 66.8, 66.7, 17.8 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{41}N_3O_{11}NH_4$ 769.30793, found 769.30679.

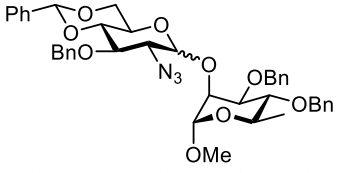
Disaccharide 42A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **42**. Yield: 47 mg, 59 µmol, 59%, α:β >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.21 (m, 25H, CH_{arom}), 5.54 (s, 1H C*H*Ph), 4.97 – 4.88 (m, 3H, H-1', 2x C*H*H Bn), 4.86 – 4.80 (m, 2H, C*H*H Bn, CH*H* Bn), 4.74 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.70 – 4.66 (m, 2H, 2x CH*H* Bn), 4.65 – 4.60 (m, 2H, H-1, CH*H* Bn), 4.21 (td, *J* = 10.0, 4.9 Hz, 1H, H-5'), 4.12 (t, *J* = 9.3 Hz, 1H, H-3'), 4.02 – 3.95 (m, 2H, H-2, H-6'), 3.85 (dd, *J* = 9.2, 3.2 Hz, 1H, H-3), 3.70 – 3.57 (m, 4H, H-2', H-4', H-5, H-6'), 3.55 (t, *J* = 8.4 Hz, 1H, H-4), 3.31 (s, 3H,

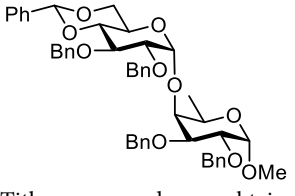
CH_3 OMe), 1.33 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 138.6, 138.6, 138.5, 137.7 (C_q), 135.4, 134.3, 131.9, 131.5, 131.2, 130.4, 129.0, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.0, 128.0, 127.8, 127.7, 127.7, 127.6, 127.6, 126.2, 126.1 (CH_{arom}), 101.3 (CHPh), 98.5 (C-1), 97.9 (C-1'), 82.5 (C-4'), 80.1 (C-4), 79.5 (C-2'), 79.0 (C-3), 78.4 (C-3'), 75.3, 75.2 (CH_2 Bn), 75.0 (C-2), 73.0, 72.2 (CH_2 Bn), 69.1 (C-6'), 68.2 (C-5), 62.8 (C-5'), 54.8 (CH_3 OMe), 18.2 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{52}O_{10}NH_4$ 806.38987, found 806.38837.

Disaccharide 42B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **42**. Yield: 56 mg, 77 µmol, 77%, α:β = 3:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.23 (m, 20H, CH_{arom}), 5.56 (s, 1H, C*H*Ph), 5.02 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.97 – 4.89 (m, 2H, H-1', C*H*H Bn), 4.83 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.76 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.73 (d, *J* = 1.8 Hz, 1H, H-1), 4.68 – 4.62 (m, 2H, 2x CH*H* Bn), 4.31 (tt, *J* = 10.5, 5.1 Hz, 1H, H-5'), 4.19 (dd, *J* = 10.2, 9.0 Hz, 1H, H-3'), 4.07 (dd, *J* = 3.3, 1.8 Hz, 1H, H-2'), 3.97 (dd, *J* = 10.3, 4.9 Hz, 1H, H-6'), 3.87 (dd, *J* = 9.4, 3.1 Hz, 1H, H-3), 3.75 – 3.70 (m, 1H, H-4'), 3.68 – 3.60 (m, 2H, H-5, H-6'), 3.54 (t, *J* = 9.5 Hz, 1H, H-4), 3.35 (s, 3H, CH_3 OMe), 3.25 (dd, *J* = 10.1, 3.7 Hz, 1H, H-2'), 1.34 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 138.2, 138.0, 137.4 (C_q), 135.3, 134.4, 131.7, 131.5, 131.1, 130.3, 130.2, 129.0, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4, 126.1, 126.0 (CH_{arom}), 101.3 (CHPh), 98.1, 98.0 (C-1, C-1'), 83.0 (C-4'), 80.0(C-4), 78.5 (C-3), 75.3 (CH_2 Bn), 75.2 (C-3'), 75.0 (CH_2 Bn), 74.6 (C-2), 72.3 (CH_2 Bn), 68.8 (C-6'), 68.1 (C-5), 62.9, 62.7 (C-2', C-5'), 54.8 (CH_3 OMe), 17.8 (C-6); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 (s, 1H, C*H*Ph), 4.59 (d, *J* = 7.8 Hz, 1H, H-1'), 3.32 (s, 3H, CH_3 OMe), 3.10 (qd, *J* = 7.4, 4.8 Hz, 1H), 1.31 (d, *J* = 5.8 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 81.4, 80.2, 74.9, 66.2; HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{45}N_3O_9NH_4$ 741.34941, found 741.34786.

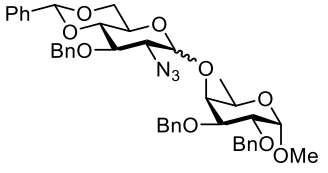
Disaccharide 43A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **43**. Yield: 76 mg, 98 µmol, 98%, α:β > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.10 (m, 25H, CH_{arom}), 5.52 (s, 1H, C*H*Ph), 4.94 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.89 – 4.75 (m, 7H, H-1', 3x C*H*H Bn, 3x CH*H* Bn), 4.72 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.61 (d, *J* = 3.4 Hz, 1H, H-1), 4.30 (td, *J* = 10.0, 4.8 Hz, 1H, H-5'), 4.03 (t, *J* = 9.3 Hz, 1H, H-3'), 3.95 – 3.77 (m, 4H, H-2, H-3, H-5, H-6'), 3.74 (d, *J* = 2.4 Hz, 1H, H-4), 3.63 – 3.54 (m, 2H, H-2', H-4'), 3.50 (t, *J* = 10.2 Hz, 1H, H-6'), 3.36 (s, 3H, CH_3 OMe), 1.28 (d, *J* = 6.6 Hz, 3H, H-

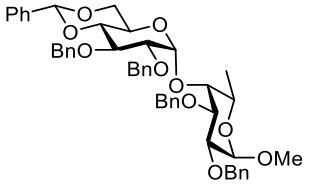
6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 138.8, 138.4, 138.3, 137.9 (C_q), 128.9, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.7, 127.7, 126.2 (CH_{arom}), 101.2 (CHPh), 101.0 (C-1'), 99.1 (C-1), 82.9 C-4'), 80.7 (C-4), 79.6 (C-2'), 79.1 (C-3'), 78.0 (C-2), 75.3 (CH_2 Bn), 74.4 (CH_2 Bn), 74.3 (C-3), 73.5 (CH_2 Bn), 73.1 (CH_2 Bn), 69.1 (C-6'), 66.6 (C-5), 63.2 (C-5'), 55.4 (CH_3 OMe), 16.4 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{52}O_{10}NH_4$ 806.38987, found 806.38813.

Disaccharide 43B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **43**. Yield: 73 mg, 100 μmol, 100%, α:β = 1.3:1. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.19 (m, 40H), 5.60 – 5.48 (m, 2H, C*H*Phαβ), 5.01 – 4.88 (m, 4H), 4.88 – 4.74 (m, 8H), 4.72 – 4.62 (m, 3H), 4.57 (d, *J* = 3.7 Hz, 1H, H-1β), 4.38 (td, *J* = 10.0, 4.9 Hz, 1H, H-5'α), 4.25 (dd, *J* = 10.5, 4.9 Hz, 1H, H-6'β), 4.09 (dd, *J* = 9.3, 3.6 Hz, 1H, H-2β), 3.99 (t, *J* = 9.5 Hz, 1H), 3.94 – 3.80 (m, 8H), 3.76 – 3.62 (m, 3H), 3.54 (t, *J* = 10.3 Hz, 1H), 3.50 – 3.42 (m, 3H, CH_3 OMeα), 3.36 (s, 3H, CH_3 OMeβ), 3.35 (s, 3H), 3.23 (td, *J* = 9.7, 5.0 Hz, 1H,), 3.09 (t, *J* = 6.3 Hz, 1H), 1.33 (d, *J* = 6.6 Hz, 3H, H-6α), 1.16 (d, *J* = 6.4 Hz, 3H, H-6β); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 138.6, 138.6, 138.2, 138.0, 137.6, 137.2, 135.3, 134.4, 132.0, 131.5, 131.3, 130.3, 130.2, 129.1, 128.9, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.5, 127.2, 126.1, 126.0, 125.3, 102.0 (C-1'β), 101.3 (CHPhβ), 101.2 (CHPhα), 99.7 (C-1'α), 99.0 (C-1β), 98.7 (C-1α), 82.9, 81.6, 79.4, 79.0, 78.5, 77.3, 76.9, 76.7, 76.3, 75.2, 74.9, 74.6, 73.7, 73.6, 73.3, 73.2, 68.8, 68.6, 66.4, 66.3, 65.9, 65.4, 63.8, 62.9, 55.4, 55.3, 16.6; HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{45}N_3O_9NH_4$ 741.34941, found 741.34811.

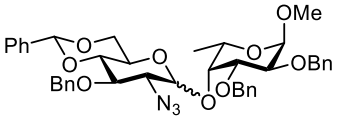
Disaccharide 44A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **44.** Yield: 67 mg, 85 μmol, 85%, α:β = 14:1. Data for α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.14 (m, 25H, CH_{arom}), 5.82 (d, *J* = 4.1 Hz, 1H, H-1'), 5.54 (s, 1H, C*H*Ph), 4.96 – 4.64 (m, 8H, H-1, 3x C*H*H Bn, 2x CH*H* Bn), 4.56 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.48 (d, *J* = 12.3 Hz, 1H, CH*H* Bn), 4.36 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.24 (dd, *J* = 10.3, 5.0 Hz, 1H, H-6'), 4.14 – 3.93 (m, 6H, H-2, H-3, H-4, H-5, H-3', H-5'), 3.72 (t, *J* = 10.3 Hz, 1H, H-6'), 3.64 – 3.56 (t, *J* = 9.8 Hz, 1H, H-4'), 3.51 (dd, *J* = 9.5, 4.1 Hz, 1H, H-2'), 3.36 (s, 3H, CH_3 OMe), 1.31 (d, *J* = 6.6 Hz, 3H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 138.8, 138.6, 138.5, 137.6 (C_q), 129.0, 128.6, 128.6, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1,

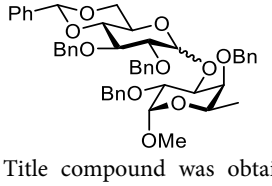
128.0, 128.0, 128.0, 127.9, 127.9, 127.7, 127.5, 127.4, 127.4, 126.1 (CH_{arom}), 101.2 (CHPh), 98.8 (C-1), 97.3 (C-1'), 82.1 (C-4'), 79.8 (C-2), 79.2 (C-2'), 78.2 (C-3'), 76.8 (C-3), 75.4 (CH_2 Bn), 74.7 (C-4), 74.2 (CH_2 Bn), 73.4 (CH_2 Bn), 72.2 (CH_2 Bn), 69.0 (C-6'), 66.2 (C-5), 63.0 (C-5'), 55.4 (CH_3 OMe), 17.8 (C-6). Diagnostic peaks for β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (s, 1H, C*H*Ph), 3.40 (s, 1H, CH_3 OMe), 1.40 (d, *J* = 6.4 Hz, 3H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 105.38 (C-1'), 101.29 (CHPh), 97.54 (C-1), 82.94, 81.98, 81.38, 79.41, 79.06, 78.10, 75.43 (CH_2 Bn), 74.85 (CH_2 Bn), 74.09, 73.95 (CH_2 Bn), 72.09 (CH_2 Bn), 70.38, 68.94 (C-6'), 66.42, 55.37 (CH_3 OMe), 17.86 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{52}O_{10}NH_4$ 806.38987, found 806.38843.

Disaccharide 44B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **44**. Yield: 73 mg, 100 μmol, 100%, α:β = 3:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.26 (m, 20H, CH_{arom}), 5.70 (d, *J* = 4.0 Hz, 1H, H-1'), 5.57 (s, 1H, C*H*Ph), 4.96 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.90 – 4.84 (m, 2H, C*H*H Bn, CH*H* Bn), 4.80 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.74 (d, *J* = 9.8 Hz, 1H, C*H*H Bn), 4.68 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.64 (d, *J* = 3.7 Hz, 1H, H-1), 4.27 – 4.14 (m, 2H, H-3, H-6'), 4.07 (t, *J* = 9.6 Hz, 1H, H-3'), 4.04 – 3.98 (m, 1H, H-5'), 3.97 – 3.91 (m, 3H, H-2, H-4, H-5), 3.77 – 3.65 (m, 2H, H-4', H-6'), 3.44 (dd, *J* = 10.1, 4.1 Hz, 1H, H-2'), 3.38 (s, 3H, CH_3 OMe), 1.26 (d, *J* = 6.3 Hz, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.6, 138.1, 137.3 (C_q), 129.1, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.2, 128.2, 128.2, 128.1, 127.9, 127.9, 127.6, 127.4, 126.1, 126.1 (CH_{arom}), 101.4 (CHPh), 99.1 (C-1), 98.0 (C-1'), 82.7 (C-4'), 79.3 (C-2), 76.4 (C-3'), 75.8, 75.7 (C-3, C-4), 75.2, 73.8, 73.6 (CH_2 Bn), 68.8 (C-6'), 65.9 (C-5), 63.7 (C-2'), 63.1 (C-5'), 55.5 (CH_3 OMe), 17.5 (C-6); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (s, 1H,C*H*Ph), 4.49 (d, *J* = 7.5 Hz, 1H, H-1'), 1.35 (d, *J* = 6.7 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 102.8 (C-1'), 101.4 (CHPh), 98.8 (C-1), 81.4, 79.5, 78.0, 75.9, 74.9, 72.7, 68.6, 67.0, 66.5, 65.7, 16.8 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{45}N_3O_9NH_4$ 741.34941, found 741.34831.

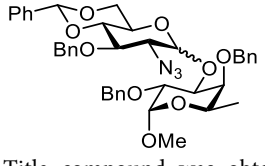
Disaccharide 45A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **45**. Yield: 79 mg, 100 μmol, 100%, α:β = 3.2:1. Data for the α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.14 (m, 25H, CH_{arom}), 5.61 (d, *J* = 3.7 Hz, 1H, H-1'), 5.56 (s, 1H, C*H*Ph), 5.02 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.85 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.80 – 4.73 (m, 2H, C*H*H Bn, CH*H* Bn), 4.70 (dd, *J* = 11.6, 4.4 Hz, 2H, 2x CH*H* Bn), 4.61 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.57 – 4.52 (m, 2H, H-1, CH*H* Bn), 4.31 – 4.23 (m, 2H, H-3, H-6'), 4.11 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2), 4.07 (t, *J* = 9.3 Hz, 1H, H-3'), 3.96 (td, *J* =

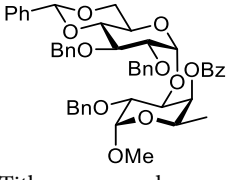
10.4, 5.2 Hz, 1H, H-5'), 3.90 (qd, *J* = 6.3, 1.2 Hz, 1H, H-5), 3.75 (t, *J* = 10.4 Hz, 1H, H-6'), 3.65 (t, *J* = 9.4 Hz, 1H, H-4'), 3.63 – 3.60 (m, 2H, H-2', H-4), 3.30 (s, 3H, CH_3 OMe), 1.17 (d, *J* = 6.5 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.6, 138.5, 138.5, 138.4, 137.5 (C_q), 128.7, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 127.8, 127.8, 127.8, 127.6, 127.5, 127.5, 126.1 (CH_{arom}), 101.3 (CHPh), 98.4, 98.3 (C-1, C-1'), 82.2 (C-4'), 80.0 (C-4), 79.1 (C-2'), 77.9 (C-3'), 77.4 (C-2), 75.5, 75.1 (CH_2 Bn), 74.3 (C-3), 72.7, 72.5 (CH_2 Bn), 69.2 (C-6'), 66.3 (C-5), 63.6 (C-5'), 55.4 (CH_3 OMe), 16.7 (C-6); diagnostic peaks for the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.98 – 4.94 (m, 2H, 2x C*H*H Bn), 4.90 (d, *J* = 11.9 Hz, 1H, C*H* Bn), 3.56 – 3.51 (m, 2H), 3.47 – 3.40 (m, 1H, H-5'), 1.02 (d, *J* = 6.5 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 101.8 (C-1'), 101.2 (CHPh), 98.8 (C-1), 83.0, 81.6, 78.0, 77.1, 75.0, 74.7, 73.7, 69.1, 66.0, 16.6 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{52}O_{10}NH_4$ 806.38987, found 806.38824.

Disaccharide 45B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **45.** Yield: 64 mg, 88 μmol, 88%, α:β = 1:2. Data reported for a 1:2 mixture of anomers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.23 (m, 60H, CH_{arom}), 5.60 (s, 1H, C*H*Phα), 5.58 (s, 2H, C*H*Phβ), 5.51 (d, *J* = 3.7 Hz, 1H, H-1'α), 5.04 (d, *J* = 11.5 Hz, 2H), 4.97 (d, *J* = 11.1 Hz, 2H), 4.95 – 4.90 (m, 2H), 4.86 – 4.77 (m, 6H), 4.68 – 4.61 (m, 6H), 4.58 – 4.53 (m, 5H, H-1α, H-1β, H-1'β), 4.30 – 4.20 (m, 3H), 4.18 (dd, *J* = 10.8, 2.8 Hz, 2H), 4.13 (dd, *J* = 10.2, 3.5 Hz, 1H), 4.05 (dd, *J* = 10.1, 9.0 Hz, 1H), 3.97 (dd, *J* = 10.1, 3.9 Hz, 3H), 3.90 – 3.83 (m, 3H), 3.80 – 3.72 (m, 8H), 3.68 (t, *J* = 9.2 Hz, 2H), 3.58 (dd, *J* = 2.8, 1.2 Hz, 1H), 3.50 (dd, *J* = 9.3, 8.1 Hz, 2H, H-2'β), 3.39 – 3.33 (m, 2H), 3.31 (d, *J* = 10.4 Hz, 10H, H-2'α, CH_3 OMeαβ), 1.14 – 1.10 (m, 9H, H-6αβ); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8, 138.6, 138.3, 138.2, 137.8, 137.7, 137.3, 137.2, 135.3, 134.2, 132.0, 131.4, 131.3, 130.3, 129.2, 128.7, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.0, 128.0, 128.0, 128.0, 127.9, 127.8, 127.7, 126.1, 126.0, 101.8 (C-1'β), 101.5 (CHPhα), 101.3 (CHPhβ), 99.5 (C-1'α), 98.8 (C-1β), 98.2 (C-1α), 83.0, 81.8, 79.8, 79.8, 79.8, 78.2, 77.6, 75.5, 75.4, 75.2, 75.1, 75.0, 74.9, 73.7, 73.3, 69.0, 68.8, 67.1, 66.4, 66.2, 66.0, 63.6, 62.8, 55.4 (CH_3 OMeα), 55.4 (CH_3 OMeβ), 16.7 (C-6α), 16.6 (C-6β); HRMS: $[M+NH_4]^+$ calcd for 741.34941, found 741.34841.

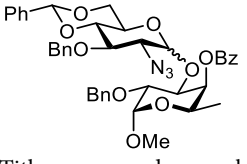
Disaccharide 46A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **46**. Yield: 80 mg, 100 μmol, 100%, α:β >20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.03 (m, 2H, CH_{arom}), 7.61 – 7.56 (m, 1H, CH_{arom}), 7.46 – 7.40 (m, 4H, CH_{arom}), 7.38 – 7.33 (m, 3H, CH_{arom}), 7.32 – 7.28 (m, 5H, CH_{arom}), 7.25 – 7.16 (m,

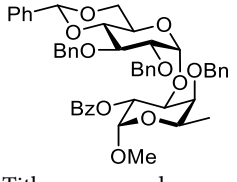
13H, CH_{arom}), 5.50 (dd, *J* = 3.4, 1.2 Hz, 1H, H-4), 5.46 (s, 1H, C*H*Ph), 5.28 (d, *J* = 3.8 Hz, 1H, H-1'), 4.74 – 4.70 (m, 2H, 2x C*H*H Bn), 4.69 – 4.63 (m, 3H, C*H*H Bn, 2x CH*H* Bn), 4.62 – 4.59 (m, 2H, H-1, CH*H* Bn), 4.33 – 4.26 (m, 2H, H-3, H-6'), 4.17 – 4.09 (m, 1H, H-5), 3.99 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2), 3.91 (td, *J* = 9.9, 4.8 Hz, 1H, H-5'), 3.85 (t, *J* = 9.4 Hz, 1H, H-3'), 3.62 (t, *J* = 10.2 Hz, 1H, H-6'), 3.56 – 3.46 (m, 2H, H-2', H-4'), 3.40 (s, 3H, CH_3 OMe), 1.16 (d, *J* = 6.6 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4 (C=O), 138.8, 138.5, 138.4, 137.9 (C_q), 133.2 (CH_{arom}), 130.2 (C_q), 130.1, 128.9, 128.5, 128.5, 128.5, 128.3, 128.3, 128.2, 128.2, 128.0, 127.9, 127.6, 127.5, 126.5 (CH_{arom}), 101.4 (CHPh), 99.9 (C-1'), 98.9 (C-1), 82.1 (C-4'), 78.9 (C-2'), 78.1 (C-3'), 75.4 (C-3), 75.2 (C-2), 75.1 (CH_2 Bn), 74.4 (C-4), 73.3, 72.6 (CH_2 Bn), 69.1 (C-6'), 65.1 (C-5), 63.4 (C-5'), 55.6 (CH_3 OMe), 16.4 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{50}O_{11}NH_4$ 820.36914, found 820.36771.

Disaccharide 46B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **46**. Yield: 74 mg, 100 µmol, 100%, α:β = 2:1. Data reported for a 2:1 mixture of anomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.09 (m, 4H), 8.08 – 8.04 (m, 2H), 7.65 – 7.19 (m, 54H), 5.62 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4β), 5.55 (s, 1H, C*H*Phβ), 5.53 (s, 2H, C*H*Phα), 5.51 (dd, *J* = 3.6, 1.3 Hz, 2H, H-4α), 5.36 (d, *J* = 3.6 Hz, 2H, H-1'α), 4.90 – 4.82 (m, 4H), 4.78 (d, *J* = 11.2 Hz, 2H), 4.75 – 4.67 (m, 6H), 4.63 (d, *J* = 11.8 Hz, 2H), 4.57 (d, *J* = 7.9 Hz, 1H, H-1'β), 4.50 (d, *J* = 11.0 Hz, 2H), 4.38 – 4.26 (m, 5H), 4.18 – 4.07 (m, 5H), 4.05 (dd, *J* = 10.1, 3.5 Hz, 2H), 3.96 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.84 (dd, *J* = 10.2, 9.0 Hz, 2H), 3.76 (t, *J* = 10.3 Hz, 1H), 3.69 (td, *J* = 9.8, 4.2 Hz, 3H), 3.61 (td, *J* = 9.2, 3.6 Hz, 3H), 3.44 – 3.35 (m, 10H), 3.32 (dd, *J* = 9.3, 8.0 Hz, 1H, H-2'β), 3.19 (dd, *J* = 10.2, 3.6 Hz, 2H, H-2'α), 1.21 – 1.16 (m, 9H, H-6αβ); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 166.3 (C=O), 138.4, 138.1, 138.0, 137.9, 137.7, 137.2, 135.4, 134.4, 133.3, 131.8, 131.7, 131.5, 131.3, 131.1, 130.3, 130.3, 130.1, 130.0, 129.9, 129.7, 129.1, 129.0, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 126.4, 126.1, 126.1, 101.6 (CHPhα), 101.3 (CHPhβ), 99.9 (C-1'α), 99.2 (C-1β), 98.5 (C-1'β), 98.4 (C-1α), 82.9, 76.9, 75.5, 75.0, 73.7, 73.3, 73.3, 68.9, 64.9, 64.8, 63.4, 62.9, 55.6, 16.3, 16.2; HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{43}N_3O_{10}$ 755.32867, found 755.32722.

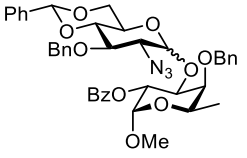
Disaccharide 47A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **47.** Yield: 80 mg, 100 µmol, 100%, α:β >20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H, CH_{arom}), 7.73 – 7.63 (m, 3H, CH_{arom}), 7.59 – 7.51 (m, 2H, CH_{arom}), 7.46 (ddt, *J* = 7.0, 4.8, 2.2 Hz, 5H, CH_{arom}), 7.41 – 7.34 (m, 5H, CH_{arom}), 7.29

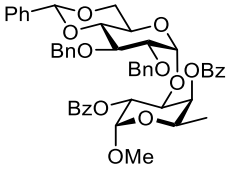
– 7.19 (m, 9H, CH_{arom}), 7.18 – 7.13 (m, 6H, CH_{arom}), 7.02 – 6.95 (m, 2H, CH_{arom}), 5.65 (dd, *J* = 10.4, 3.7 Hz, 1H, H-2), 5.55 (s, 1H, C*H*Ph), 5.46 (d, *J* = 3.7 Hz, 1H, H-1'), 5.08 (d, *J* = 3.7 Hz, 1H, H-1), 5.03 (d, *J* = 11.3 Hz, 1H, C*H*H Bn 4.74 – 4.69 (m, 2H, C*H*H Bn, CH*H* Bn), 4.64 (d, *J* = 11.4 Hz, 1H, CH*H* Bn), 4.53 (dd, *J* = 10.4, 2.9 Hz, 1H, H-3), 4.35 – 4.26 (m, 3H, H-6', CH_2 Bn), 4.05 – 3.91 (m, 3H, H-3', H-5, H-5'), 3.76 (t, *J* = 10.4 Hz, 1H, H-6'), 3.72 (dd, *J* = 3.0, 1.2 Hz, 1H, H-4), 3.62 (t, *J* = 9.5 Hz, 1H, H-4'), 3.53 (dd, *J* = 9.3, 3.7 Hz, 1H, H-2'), 3.33 (s, 3H, CH_3 OMe), 1.25 (d, *J* = 6.5 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7 (C=O), 138.5, 138.3, 137.9, 137.4 (C_q), 135.3, 134.6, 133.2, 131.7, 131.7, 131.6, 131.0, 130.4, 130.3 (CH_{arom}), 130.0 (C_q), 129.8, 129.0, 128.6, 128.6, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.2, 127.8, 127.6, 127.4, 127.3, 126.1, 124.9 (CH_{arom}), 101.4 (CHPh), 98.0 (C-1'), 97.4 (C-1), 81.9 (C-4'), 79.5 (C-4), 79.1 (C-2'), 77.6 (C-3'), 75.6, 75.1 (CH_2 Bn), 73.2 (C-3), 72.9 (C-2), 72.1 (CH_2 Bn), 69.1 (C-6'), 66.5 (C-5), 63.8 (C-5'), 55.5 (CH_3 OMe), 16.7 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{50}O_{11}NH_4$ 820.36914, found 820.36792.

Disaccharide 47B



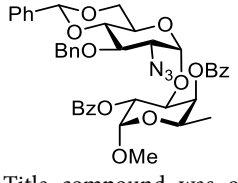
Title compound was obtained as white foam via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **47**. Yield: 68 mg, 92 µmol, 92%, α:β = 9:1. Data for the α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dt, *J* = 8.4, 1.8 Hz, 2H, CH_{arom}), 7.73 – 7.69 (m, 2H, CH_{arom}), 7.68 – 7.63 (m, 1H, CH_{arom}), 7.61 – 7.52 (m, 2H, CH_{arom}), 7.48 – 7.41 (m, 7H, CH_{arom}), 7.41 – 7.35 (m, 3H, CH_{arom}), 7.33 – 7.19 (m, 9H, CH_{arom}), 5.70 (dd, *J* = 10.5, 3.7 Hz, 1H, H-2), 5.57 (s, 1H, C*H*Ph), 5.29 (d, *J* = 3.8 Hz, 1H, H-1'), 5.04 (d, *J* = 3.7 Hz, 1H, H-1), 4.95 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.82 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.74 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.65 (d, *J* = 11.1 Hz, 1H, CH*H* Bn), 4.40 (dd, *J* = 10.6, 2.8 Hz, 1H, H-3), 4.29 (dd, *J* = 10.4, 4.8 Hz, 1H, H-6'), 4.06 – 3.95 (m, 2H, H-5, H-5'), 3.90 (t, *J* = 9.6 Hz, 1H, H-3'), 3.77 (t, *J* = 10.4 Hz, 1H, H-6'), 3.70 (d, *J* = 2.8 Hz, 1H, H-4), 3.67 (t, *J* = 9.3 Hz, 1H, H-3'), 3.35 (s, 3H, CH_3 OMe), 3.20 (dd, *J* = 10.0, 3.7 Hz, 1H, H-2'), 1.25 (d, *J* = 6.5 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9 (C=O), 138.1, 137.7, 137.2 (C_q), 135.3, 134.5, 133.2, 131.7, 131.6, 131.1, 130.3, 130.3 (CH_{arom}), 130.0 (C_q), 129.9, 129.7, 129.2, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 127.9, 127.9, 126.1, 126.0 (CH_{arom}), 101.6 (CHPh), 100.1 (C-1'), 97.6 (C-1), 82.8 (C-4'), 80.2 (C-4), 75.7 (C-3), 75.5 (CH_2 Bn), 75.4 (C-3'), 74.9 (CH_2 Bn), 71.8 (C-2), 68.9 (C-6'), 66.6 (C-5'), 63.8 (C-5), 62.8 (C-2'), 55.5 (CH_3 OMe), 16.8 (C-6); diagnostic peaks for the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.42 (s, 1H, C*H*Ph), 5.00 (d, *J* = 3.8 Hz, 1H, H-1), 4.69 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 3.58 (dd, *J* = 9.9, 4.5 Hz, 1H), 3.46 – 3.41 (m, 1H), 1.20 (d, *J* = 6.5 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 102.6 (C-1'), 101.2 (CHPh), 97.8 (C-1), 81.5, 79.7, 79.6, 78.5, 75.4, 74.9, 70.2, 66.8, 66.3, 16.6 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{43}N_3O_{10}NH_4$ 755.32867, found 755.32747.

Disaccharide 48A



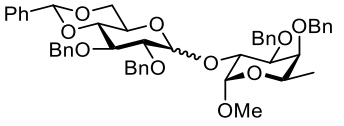
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **48**. Yield: 82 mg, 100 µmol, 100%, α:β >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.16 (m, 2H, CH_{arom}), 8.10 – 8.03 (m, 2H, CH_{arom}), 7.77 – 7.65 (m, 2H, CH_{arom}), 7.60 – 7.53 (m, 2H, CH_{arom}), 7.52 – 7.42 (m, 4H, CH_{arom}), 7.40 – 7.32 (m, 8H, CH_{arom}), 7.21 – 7.11 (m, 8H, CH_{arom}), 6.99 – 6.94 (m, 2H, CH_{arom}), 5.64 – 5.58 (m, 2H, H-2, H-4), 5.40 (s, 1H, C*H*Ph), 5.17 (d, *J* = 3.7 Hz, 1H, H-1), 5.07 (d, *J* = 3.6 Hz, 1H, H-1'), 4.57 – 4.47 (m, 2H, H-3, C*H*H Bn), 4.37 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.31 – 4.19 (m, 3H, H-5, CH_2 Bn), 4.12 (dd, *J* = 10.1, 4.8 Hz, 1H, H-6'), 3.86 (td, *J* = 9.9, 4.8 Hz, 1H, H-5'), 3.73 (t, *J* = 9.3 Hz, 1H, H-3'), 3.55 (t, *J* = 10.2 Hz, 1H, H-6'), 3.47 – 3.39 (m, 4H, H-4', CH_3 OMe), 3.35 (dd, *J* = 9.4, 3.6 Hz, 1H, H-2'), 1.26 (d, *J* = 6.6 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 166.0 (C=O), 138.9, 138.3, 137.8 (C_q), 134.5, 133.4, 133.2, 131.6, 131.2, 130.2, 130.1, 130.0, 129.9, 128.9, 128.7, 128.5, 128.3, 128.2, 128.2, 128.0, 127.5, 126.4 (CH_{arom}), 101.5 (CHPh), 99.2 (C-1'), 97.8 (C-1), 81.9 (C-4'), 78.9 (C-2'), 78.2 (C-3'), 75.2 (CH_2 Bn), 73.5, 73.4 (C-3, C-4), 72.4 (CH_2 Bn), 71.4 (C-2), 69.0 (C-6), 65.2 (C-5), 63.6 (C-5'), 55.8 (CH_3 OMe), 16.5 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{48}O_{12}NH_4$ 834.34840, found 834.34735.

Disaccharide 48B



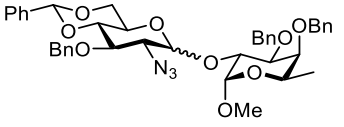
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **48**. Yield: 75 mg, 100 µmol, 100%, α:β >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.17 (m, 2H, CH_{arom}), 8.14 – 8.08 (m, 2H, CH_{arom}), 7.74 – 7.65 (m, 3H, CH_{arom}), 7.62 – 7.53 (m, 3H, CH_{arom}), 7.50 – 7.44 (m, 6H, CH_{arom}), 7.41 – 7.35 (m, 5H, CH_{arom}), 7.20 – 7.11 (m, 5H, CH_{arom}), 5.65 (dd, *J* = 3.5, 1.3 Hz, 1H, H-4), 5.62 (dd, *J* = 10.5, 3.6 Hz, 1H, H-2), 5.46 (s, 1H, C*H*Ph), 5.19 – 5.10 (m, 2H, H-1, H-1'), 4.65 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.49 (dd, *J* = 10.5, 3.5 Hz, 1H, H-3), 4.38 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.34 – 4.21 (m, 2H, H-5, H-6'), 3.93 (td, *J* = 9.9, 4.8 Hz, 1H, H-5'), 3.70 (dd, *J* = 10.1, 9.1 Hz, 1H, H-3'), 3.65 (t, *J* = 10.2 Hz, 1H, H-6'), 3.54 (t, *J* = 9.3 Hz, 1H, H-4'), 3.42 (s, 3H, CH_3 OMe), 3.15 (dd, *J* = 10.0, 3.7 Hz, 1H, H-2'), 1.26 (d, *J* = 6.5 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 166.1 (C=O), 137.8, 137.6 (C_q), 135.4, 134.5, 133.5, 133.3, 131.7, 131.6, 131.1, 130.4, 130.3, 130.2, 129.9, 129.8, 129.6, 129.1 (CH_{arom}), 128.7 (C_q), 128.6 (CH_{arom}), 128.4 (C_q), 128.4, 128.3, 128.2, 128.2, 127.8, 126.4 (CH_{arom}), 101.6 (CHPh), 100.8 (C-1'), 97.7 (C-1), 82.6 (C-4'), 75.8 (C-3'), 75.0 (CH_2 Bn), 74.7 (C-3), 73.7 (C-4), 71.1 (C-2), 68.8 (C-6'), 65.2 (C-5), 63.6 (C-5'), 62.9 (C-2'), 55.7 (CH_3 OMe), 16.4 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{41}N_3O_{11}$ 769.30793, found 769.30661

Disaccharide 49A



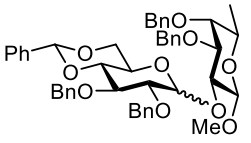
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **49** Yield: 70 mg, 89 μmol, 89%, α:β = 1.3:1. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (h, *J* = 7.0 Hz, 3H), 7.56 – 7.44 (m, 5H), 7.44 – 7.21 (m, 40H), 7.18 (dt, *J* = 4.7, 1.7 Hz, 2H), 5.55 (s, 1H, C*H*Phα), 5.52 (s, 1H, C*H*Phβ), 5.05 – 4.98 (m, 5H), 4.97 – 4.85 (m, 5H), 4.82 (d, *J* = 3.6 Hz, 1H, H-1α), 4.81 – 4.75 (m, 2H), 4.72 – 4.63 (m, 7H), 4.44 (dd, *J* = 10.1, 3.5 Hz, 1H, H-3β), 4.22 – 4.16 (m, 2H), 4.15 – 4.09 (m, 2H), 4.05 (dt, *J* = 10.0, 5.0 Hz, 1H), 3.95 – 3.90 (m, 2H), 3.88 – 3.80 (m, 2H), 3.76 (t, *J* = 8.9 Hz, 1H), 3.73 – 3.56 (m, 6H), 3.55 – 3.48 (m, 2H, H-2'αβ), 3.37 (s, 4H), 3.27 (s, 3H), 1.14 (dd, *J* = 6.6, 4.0 Hz, 6H, H-6αβ); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 139.4, 138.9, 138.7, 138.7, 138.6, 138.3, 137.6, 137.5, 135.4, 134.6, 131.8, 131.7, 131.2, 130.4, 130.3, 129.0, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.4, 127.4, 127.4, 127.3, 127.3, 126.2, 126.1, 124.9, 102.4 (C-1'β), 101.4 (CHPhα), 101.1 (CHPhβ), 100.8 (C-1'α), 99.8 (C-1α), 97.9 (C-1β), 82.4, 82.3, 81.6, 81.1, 79.3, 79.2, 78.5, 78.3, 78.2, 77.9, 77.6, 75.8, 75.2, 75.2, 75.2, 75.1, 75.0, 73.7, 73.3, 73.0, 69.3, 68.9, 66.3, 66.1, 66.1, 63.0, 55.2, 55.2, 16.7, 16.6; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{52}O_{10}NH_4$ 806.38987, found 806.38802.

Disaccharide 49B



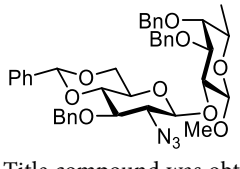
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **49**. Yield: 69 mg, 95 μmol, 95%, α:β = 1:5.5. Data for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.25 (m, 20H, CH_{arom}), 5.53 (s, 1H, C*H*Ph), 4.98 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.94 – 4.88 (m, 2H, 2x C*H*H Bn), 4.87 (d, *J* = 3.7 Hz, 1H, H-1), 4.79 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.68 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.63 (d, *J* = 11.5 Hz, 1H, CH*H* Bn), 4.47 (d, *J* = 7.9 Hz, 1H, H-1'), 4.35 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2), 4.12 (dd, *J* = 10.6, 5.0 Hz, 1H, H-6'), 3.94 – 3.83 (m, 2H, H-3, H-5), 3.71 – 3.62 (m, 3H, H-4, H-4', H-6'), 3.58 (t, *J* = 9.2 Hz, 1H, H-3'), 3.49 (dd, *J* = 9.3, 7.8 Hz, 1H, H-2'), 3.42 (s, 3H, CH_3 OMe), 3.30 (td, *J* = 9.7, 5.0 Hz, 1H, H-5'), 1.14 (d, *J* = 6.4 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.6, 137.9, 137.3 (C_q), 135.4, 134.3, 131.5, 129.1, 128.6, 128.5, 128.4, 128.3, 128.3, 128.3, 128.0, 127.8, 127.5, 127.3, 126.1 (CH_{arom}), 101.6 (C-1'), 101.3 (CHPh), 98.2 (C-1), 81.6 (C-4'), 79.4 (C-3'), 78.1 (C-4), 77.9 (C-3), 76.7 (C-2), 75.2, 75.0, 73.3 (CH_2 Bn), 68.6 (C-6'), 66.7 (C-2'), 66.4, 66.3 (C-5, C-5'), 55.5 (CH_3 OMe), 16.7 (C-6); diagnostic peaks for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (s, 1H, C*H*Ph), 5.21 (d, *J* = 3.8 Hz, 1H, H-1'), 4.21 (dd, *J* = 10.4, 4.9 Hz, 1H, H-6'), 4.01 (td, *J* = 10.0, 4.9 Hz, 1H, H-5'), 3.40 (s, 3H, CH_3 OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ 101.5 (CHPh), 100.4 (C-1'), 99.6 (C-1), 82.9, 78.8, 75.1, 73.4, 70.0, 63.4, 61.9, 55.3; HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{45}N_3O_9$ 741.34941, found 741.34828.

Disaccharide 50A



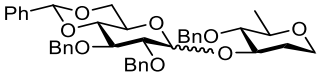
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **50**. Yield: 68 mg, 86 µmol, 86%, α:β = 1:1.2. Data reported for a 1:1 mixture: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 50H), 5.53 (s, 1H, C*H*Phα), 5.52 (d, *J* = 4.0 Hz, 1H, H-1'α), 5.50 (s, 1H, C*H*Phβ), 5.04 (d, *J* = 7.6 Hz, 1H, H-1'β), 4.96 (d, *J* = 11.7 Hz, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.91 (d, *J* = 7.8 Hz, 1H), 4.90 – 4.86 (m, 3H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.79 – 4.75 (m, 3H), 4.72 – 4.58 (m, 5H), 4.51 (d, *J* = 12.1 Hz, 1H), 4.35 (d, *J* = 7.6 Hz, 1H), 4.34 – 4.29 (m, 1H), 4.29 – 4.23 (m, 1H), 4.18 – 4.16 (m, 2H), 4.12 (dd, *J* = 9.7, 7.6 Hz, 1H), 4.05 (t, *J* = 9.3 Hz, 1H), 3.78 (t, *J* = 8.9 Hz, 1H), 3.73 (dd, *J* = 9.8, 2.8 Hz, 1H), 3.68 – 3.59 (m, 4H), 3.58 – 3.53 (m, 5H), 3.51 – 3.42 (m, 4H), 3.41 (s, 3H), 3.35 (td, *J* = 9.7, 5.1 Hz, 1H), 1.22 (d, *J* = 6.4 Hz, 3H, H-6α), 1.19 (d, *J* = 6.4 Hz, 3H, H-6β); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 138.9, 138.9, 138.7, 138.4, 138.3, 137.8, 137.6, 135.3, 134.2, 131.9, 131.4, 131.2, 130.3, 130.2, 128.9, 128.9, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 127.8, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.3, 126.5, 126.2, 126.1, 104.5 (C-1β), 102.8 (C-1α), 102.7 (C-1'β), 101.2 (CHPhα), 101.1 (CHPhβ), 98.2 (C-1'α), 83.9, 83.0, 82.2, 81.8, 81.4, 81.2, 79.1, 78.7, 77.2, 76.6, 75.3, 75.1, 75.0, 74.9, 74.7, 74.6, 74.6, 73.1, 72.8, 71.5, 70.4, 70.2, 69.1, 65.7, 62.4, 56.9, 56.8, 17.1, 16.8; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{52}O_{10}NH_4$ 806.38987, found 806.38795.

Disaccharide 50B



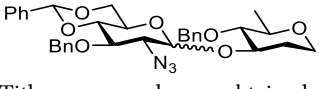
Title compound was obtained as white solid via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **51.** Yield: 68 mg, 93 µmol, 93%, α:β <1:20. Data for the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.24 (m, 20H, CH_{arom}), 5.53 (s, 1H, C*H*Ph), 4.97 (d, *J* = 11.7 Hz, 1H, C*H*Ph), 4.92 – 4.87 (m, 3H, H-1', 2x CH*H* Bn), 4.79 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.69 – 4.64 (m, 2H, 2x CH*H* Bn), 4.33 – 4.26 (m, 2H, H-1, H-6'), 4.11 (dd, *J* = 9.7, 7.8 Hz, 1H, H-2), 3.67 – 3.62 (m, 2H, H-4', H-6'), 3.58 – 3.53 (m, 5H, H-3', H-4, CH_3 OMe), 3.50 – 3.45 (m, 2H, H-3, H-5), 3.41 (dd, *J* = 9.5, 8.1 Hz, 1H, H-2'), 3.36 (td, *J* = 9.7, 5.0 Hz, 1H, H-5'), 1.19 (d, *J* = 6.4 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 138.7, 138.1, 137.4 (C_q), 135.4, 134.4, 131.8, 131.6, 131.1, 130.3, 129.1, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 127.9, 127.6, 127.5, 127.4, 126.1 (CH_{arom}), 104.3 (C-1), 102.1 (C-1'), 101.4 (CHPh), 81.9 (C-4'), 81.0 (C-3), 79.1 (C-3'), 78.4 (C-2), 76.9 (C-4), 75.0, 74.7, 73.4 (CH_2 Bn), 70.5 (C-5'), 68.8 (C-6'), 66.8 (C-2'), 66.0 (C-5'), 57.0 (CH_3 OMe), 16.8 (C-6); Diagnostic peaks for the α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.56 (s, 1H, C*H*Ph), 5.41 (d, *J* = 3.9 Hz, 1H, H-1'), 3.99 (dd, *J* = 9.8, 7.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 102.5 (C-1), 101.5 (CHPh), 98.9 (C-1'), 84.1, 82.7, 75.0, 72.6, 63.2, 62.5, 56.8 (CH_3 OMe), 17.0 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{45}N_3O_9NH_4$ 741.34941, found 741.34826.

Disaccharide 51A



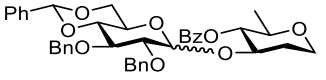
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **51**. Yield: 53 mg, 81 µmol, 81%, α:β = 1:1.6. Data reported for a 1:1 mixture: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.22 (m, 27H), 5.56 (s, 2H, C*H*Phαβ), 5.12 – 5.07 (m, 2H, H-1'α, C*H*H Bn), 4.99 (d, *J* = 10.7 Hz, 1H), 4.97 – 4.91 (m, 2H), 4.89 (d, *J* = 10.9 Hz, 1H), 4.85 (d, *J* = 11.4 Hz, 1H), 4.82 – 4.78 (m, 2H), 4.74 (d, *J* = 12.1 Hz, 1H), 4.68 – 4.63 (m, 2H, H-1'β, CH*H* Bn), 4.62 – 4.58 (m, 2H), 4.29 (dd, *J* = 10.5, 5.0 Hz, 1H), 4.23 (dd, *J* = 10.3, 4.9 Hz, 1H), 4.12 (t, *J* = 9.3 Hz, 1H), 3.97 (tdd, *J* = 8.6, 7.2, 5.0 Hz, 2H), 3.88 (dddd, *J* = 20.8, 11.8, 4.9, 1.7 Hz, 2H), 3.80 – 3.68 (m, 4H), 3.64 (t, *J* = 9.4 Hz, 1H), 3.54 (dd, *J* = 9.4, 3.7 Hz, 1H, H-2'α), 3.47 (dd, *J* = 8.6, 7.6 Hz, 1H, H-2'β), 3.42 – 3.32 (m, 3H), 3.28 (ddt, *J* = 9.2, 6.5, 5.7 Hz, 2H), 3.15 – 3.01 (m, 2H), 2.15 – 2.03 (m, 2H), 1.84 (tdd, *J* = 12.8, 11.3, 5.0 Hz, 1H), 1.68 (tdd, *J* = 12.8, 11.4, 5.9 Hz, 1H), 1.32 (d, *J* = 6.1 Hz, 3H), 1.25 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 138.8, 138.7, 138.6, 138.3, 138.1, 137.5, 137.4, 135.4, 134.4, 131.9, 131.5, 131.2, 130.4, 130.3, 129.1, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.5, 126.1, 125.3, 101.3 (CHPhα), 101.2 (CHPhβ), 100.9 (C-1'β), 100.0 (C-1'α), 83.4, 83.1, 82.5, 82.5, 82.5, 81.8, 81.2, 79.6, 79.1, 78.5, 76.2, 76.1, 75.6, 75.2, 75.1, 75.0, 73.7, 69.0, 69.0, 66.1, 65.3, 65.2, 63.1, 33.9, 31.4, 18.7, 18.6; HRMS: $[M+NH_4]^+$ calcd for $C_{40}H_{44}O_8NH_4$ 670.33744, found 670.33579.

Disaccharide 51B



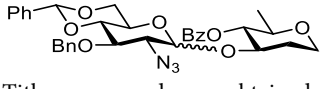
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **51.** Yield: 50 mg, 85 µmol, 85%, α:β =1:13. Data for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H, CH_{arom}), 7.42 – 7.27 (m, 13H, CH_{arom}), 5.57 (s, 1H, C*H*Ph), 4.96 (d, *J* = 10.7 Hz, 1H, C*H*H Bn), 4.92 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.80 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.61 (d, *J* = 10.7 Hz, 1H, CH*H* Bn), 4.51 (d, *J* = 7.9 Hz, 1H, H-1'), 4.27 (dd, *J* = 10.6, 5.0 Hz, 1H, H-6'), 3.99 – 3.88 (m, 2H, H-1_{eq}, H-3), 3.74 – 3.67 (m, 2H, H-4', H-6'), 3.54 (t, *J* = 9.3 Hz, 1H, H-3'), 3.43 (dd, *J* = 9.5, 7.9 Hz, 1H, H-2'), 3.41 – 3.32 (m, 2H, H-1_{ax}, H-5'), 3.27 (dq, *J* = 9.5, 6.1 Hz, 1H, H-5), 3.09 (t, *J* = 8.9 Hz, 1H, H-4), 2.12 (ddd, *J* = 13.2, 4.6, 2.2 Hz, 1H, H-2_{eq}), 1.77 (tdd, *J* = 12.8, 11.4, 4.9 Hz, 1H, H-2_{ax}), 1.31 (d, *J* = 6.1 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 137.9, 137.1 (C_q), 129.1, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 127.9, 127.7, 126.0 (CH_{arom}), 101.3 (CHPh), 99.9 (C-1'), 82.9 (C-4), 81.7 (C-4'), 80.3 (C-3), 78.9 (C-3'), 76.0 (C-5), 75.1, 74.9 (CH_2 Bn), 68.6 (C-6'), 66.7 (C-2'), 66.2 (C-5'), 65.1 (C-1), 31.1 (C-2), 18.5 (C-6); diagnostic peaks for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (s, 1H, C*H*Ph), 5.23 (d, *J* = 3.8 Hz, 1H, H-1'), 5.07 (d, *J* = 10.5 Hz, 1H, C*H*H Bn), 4.15 – 4.07 (m, 1H), 2.30 (tt, *J* = 8.7, 5.3 Hz, 2H, 2x H-2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 99.5 (C-1'), 87.0, 84.8, 70.7, 69.6, 63.2, 63.1, 29.7 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{33}H_{37}N_3O_7NH_4$ 605.29698, found 605.29618.

Disaccharide 52A



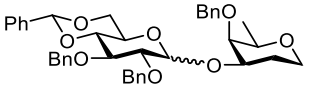
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **52**. Yield: 35 mg, 53 mmol, 53%, α:β = 5:1. Data for the α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.3, 1.4 Hz, 2H, CH_{arom}), 7.54 – 7.50 (m, 1H, CH_{arom}), 7.48 – 7.43 (m, 3H, CH_{arom}), 7.42 – 7.30 (m, 7H, CH_{arom}), 7.28 – 7.22 (m, 7H, CH_{arom}), 7.20 – 7.09 (m, 3H, CH_{arom}), 6.95 (dt, *J* = 6.6, 1.6 Hz, 2H, CH_{arom}), 5.50 (s, 1H, C*H*Ph), 5.12 (t, *J* = 9.3 Hz, 1H, H-4), 4.97 (d, *J* = 3.7 Hz, 1H, H-1'), 4.80 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.67 (d, *J* = 11.1 Hz, 1H, CH*H* Bn), 4.31 (d, *J* = 12.4 Hz, 1H, C*H*H Bn), 4.23 (dd, *J* = 10.2, 4.9 Hz, 1H, H-6'), 4.15 (d, *J* = 12.3 Hz, 1H, CH*H* Bn), 4.04 – 3.98 (m, 2H, H-1_{eq}, H-3'), 3.96 – 3.89 (m, 2H, H-3, H-5'), 3.67 (t, *J* = 10.3 Hz, 1H, H-6'), 3.55 – 3.46 (m, 3H, H-1_{ax}, H-4', H-5), 3.34 (dd, *J* = 9.3, 3.7 Hz, 1H, H-2'), 2.14 – 1.96 (m, 2H, H-2_{ax}, H-2_{eq}), 1.24 (d, *J* = 6.2 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5 (C=O), 138.8, 138.1, 137.4 (C_q), 133.2, 129.8, 129.0, 128.6, 128.3, 128.2, 128.2, 127.7, 127.6, 127.5, 126.1 (CH_{arom}), 101.3 (CHPh), 99.4 (C-1), 82.2 (C-4'), 78.4 (C-3'), 78.3 (C-2'), 77.8 (C-3), 76.8 (C-4), 75.4 (CH_2 Bn), 75.4 (C-5), 72.6 (CH_2 Bn), 69.0 (C-1), 65.5 (C-6'), 63.2 (C-5'), 33.5 (C-2), 18.2 (C-6); diagnostic peaks for the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (s, 1H, C*H*Ph), 4.86 – 4.83 (m, 2H, 2x C*H*H Bn), 4.77 – 4.71 (m, 2H, 2x CH*H* Bn), 4.52 (d, *J* = 7.6 Hz, 1H, H-1'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8 (C=O), 102.9 (C-1'), 101.0 (CHPh), 81.4, 80.9, 79.1, 76.3, 75.6, 75.1, 75.0, 68.4, 66.0, 32.1 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{40}H_{42}O_9NH_4$ 684.31671, found 684.31496.

Disaccharide 52B



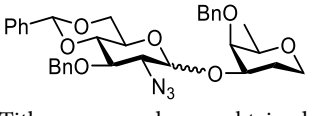
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **52**. Yield: 36 mg, 60 μmol, 60%, α:β = 1.4:1. Data reported for a 1:1 mixture: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 5H), 7.75 – 7.70 (m, 6H), 7.69 – 7.65 (m, 4H), 7.62 – 7.54 (m, 6H), 7.52 – 7.46 (m, 11H), 7.43 – 7.27 (m, 24H), 5.57 (s, 1H, C*H*Phα), 5.36 (s, 1H, C*H*Phβ), 5.07 (t, *J* = 9.3 Hz, 1H, H-4α), 5.02 – 4.94 (m, 2H, H-1'α, H-4β), 4.90 (d, *J* = 10.8 Hz, 1H), 4.86 (d, *J* = 11.5 Hz, 1H) 4.75 (d, *J* = 11.5 Hz, 1H), 4.71 (d, *J* = 10.8 Hz, 1H), 4.38 (d, *J* = 7.9 Hz, 1H, h-1'β), 4.26 (dd, *J* = 10.3, 4.9 Hz, 1H), 4.06 – 3.92 (m, 6H), 3.88 (ddd, *J* = 11.3, 9.2, 5.3 Hz, 1H), 3.74 (t, *J* = 10.4 Hz, 1H), 3.65 (t, *J* = 9.3 Hz, 1H), 3.61 – 3.58 (m, 1H), 3.56 – 3.47 (m, 6H), 3.45 (t, *J* = 9.0 Hz, 1H), 3.36 (dd, *J* = 9.3, 8.0 Hz, 1H), 3.25 (dd, *J* = 9.9, 3.8 Hz, 1H, H-2'α), 3.16 – 3.06 (m, 2H), 2.19 (ddt, *J* = 13.1, 5.3, 1.9 Hz, 1H), 2.13 – 2.07 (m, 1H), 2.05 – 1.93 (m, 2H), 1.38 – 0.98 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 165.6, 149.6, 137.9, 137.9, 137.2, 137.1, 135.3, 134.5, 133.3, 133.1, 131.8, 131.7, 131.6, 131.1, 130.5, 130.3, 130.3, 130.2, 129.8, 129.6, 129.2, 129.1, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 127.9, 126.1, 126.0, 125.1, 119.4, 102.2 (C-1'β), 101.5 (CHPhα), 101.2 (CHPhβ), 100.2 (C-1'α), 82.8, 81.3, 80.3, 79.4, 78.9, 76.6, 76.5, 76.1, 75.3, 75.1, 75.1, 74.8, 68.8, 68.0, 66.5, 66.1, 65.5, 65.4, 63.2, 63.2, 33.6, 32.2, 18.2, 18.1; HRMS: $[M+NH_4]^+$ calcd for $C_{33}H_{35}N_3O_8NH_4$ 619.27624, found 619.27524.

Disaccharide 53A



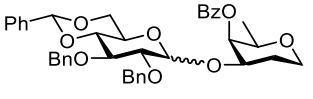
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **53.** Yield: 63 mg, 97 µmol, 97%, α:β =4:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.20 (m, 20H, CH_{arom}), 5.57 (s, 1H, C*H*Ph), 5.01 – 4.96 (m, 2H, H-1', C*H*H Bn), 4.93 – 4.86 (m, 2H, 2x C*H*H Bn), 4.81 (d, *J* = 11.5 Hz, 1H, CH*H* Bn), 4.70 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.62 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.24 (dd, *J* = 10.2, 4.8 Hz, 1H, H-6'), 4.09 (t, *J* = 9.3 Hz, 1H, H-3'), 4.03 – 3.94 (m, 2H, H-1, H-5'), 3.71 (t, *J* = 10.3 Hz, 1H, H-6'), 3.68 – 3.57 (m, 3H, H-2', H-3, H-4'), 3.47 (d, *J* = 2.7 Hz, 1H, H-4), 3.43 – 3.30 (m, 2H, H-1, H-5), 2.28 (qd, *J* = 12.2, 4.7 Hz, 1H, H-2), 1.74 – 1.67 (m, 1H, H-2), 1.11 (d, *J* = 6.3 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 138.6, 138.4, 137.5 (C_q), 131.6, 129.0, 128.8, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 127.9, 127.9, 127.7, 127.5, 126.1, 126.1 (CH_{arom}), 101.3 (CHPh), 99.4 (C-1'), 82.4 (C-4'), 81.1 (C-3), 79.7 (C-2'), 78.4 (C-3'), 76.2 (C-4), 75.2 (CH_2 Bn), 75.0 (C-5), 74.6, 73.9 (CH_2 Bn), 69.0 (C-6'), 65.9 (C-1), 63.1 (C-5'), 28.8 (C-2), 17.7 (C-6); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (s, 1H, C*H*Ph), 4.66 (d, *J* = 7.7 Hz, 1H, H-1), 4.37 (dd, *J* = 10.4, 5.0 Hz, 1H, H-6'), 4.16 (ddd, *J* = 8.6, 6.5, 3.1 Hz, 1H), 3.90 (ddd, *J* = 11.9, 4.6, 2.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 102.5 (C-1), 101.2 (CHPh), 82.3, 81.6, 80.9, 79.0, 78.0, 75.5, 75.2, 74.8, 17.6; HRMS: $[M+NH_4]^+$ calcd for $C_{40}H_{44}O_8NH_4$ 670.33744, found 670.33601.

Disaccharide 53B



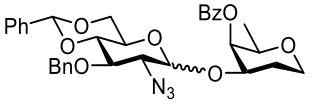
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **53**. Yield: 39 mg, 67 µmol, 67%, α:β =1:1.4. Data reported for a 1:1 mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.60 (m, 7H, CH_{arom}), 7.56 – 7.23 (m, 28H, CH_{arom}), 5.59 (s, 2H, 2x C*H*Ph), 5.06 (d, *J* = 3.6 Hz, 1H, H-1'α), 4.99 – 4.88 (m, 4H), 4.80 (d, *J* = 11.3 Hz, 1H), 4.75 (d, *J* = 11.1 Hz, 1H), 4.66 (t, *J* = 11.3 Hz, 2H), 4.51 (d, *J* = 7.9 Hz, 1H, H-1'β), 4.36 (dd, *J* = 10.5, 5.0 Hz, 1H), 4.25 (dd, *J* = 10.3, 4.9 Hz, 1H), 4.10 – 3.97 (m, 3H), 3.88 (ddd, *J* = 11.9, 4.6, 2.6 Hz, 1H), 3.84 – 3.68 (m, 5H), 3.59 – 3.52 (m, 3H), 3.51 – 3.35 (m, 7H), 2.42 – 2.17 (m, 2H), 1.82 – 1.68 (m, 2H), 1.22 – 0.90 (m, 6H, H-6αβ); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 137.9, 137.7, 137.3, 137.1, 135.4, 134.4, 131.9, 131.6, 131.5, 131.2, 130.3, 130.2, 129.2, 129.2, 128.7, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 128.0, 128.0, 127.7, 127.6, 126.1, 126.1, 125.3, 101.5 (CHPhα), 101.4 (CHPhβ), 101.3 (C-1'β), 98.7 (C-1'α), 83.0, 81.6, 80.8, 79.8, 78.9, 77.9, 76.7, 76.1, 75.0, 75.0, 75.0, 75.0, 74.8, 68.8, 68.7, 66.6, 66.3, 65.9, 65.8, 63.4, 63.3, 28.5, 26.5, 17.7, 17.7; HRMS: $[M+NH_4]^+$ calcd for $C_{33}H_{37}N_3O_7NH_4$ 605.29698, found 605.29612.

Disaccharide 54A



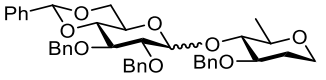
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **54**. Yield: 67 mg, 100 µmol, 100%, α:β = 8:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 2H, CH_{arom}), 7.77 – 7.59 (m, 3H, CH_{arom}), 7.56 – 7.34 (m, 10H, CH_{arom}), 7.28 – 7.09 (m, 12H, CH_{arom}), 5.55 (d, *J* = 3.2 Hz, 1H, H-4), 5.53 (s, 1H, C*H*Ph), 5.28 (d, *J* = 3.5 Hz, 1H, H-1'), 4.78 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.67 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.55 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.45 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.28 (dd, *J* = 9.6, 4.1 Hz, 1H, H-6'), 4.15 (ddd, *J* = 11.8, 4.9, 1.7 Hz, 1H, H-1_{eq}), 4.00 – 3.92 (m, 2H, H-3, H-3'), 3.81 – 3.75 (m, 1H, H-5'), 3.71 (t, *J* = 9.9 Hz, 1H, H-6'), 3.67 – 3.62 (m, 1H, H-5), 3.61 – 3.54 (m, 2H, H-4', H-6'), 3.52 (dd, *J* = 9.3, 3.7 Hz, 1H, H-2'), 2.34 (qd, *J* = 12.6, 4.9 Hz, 1H, H-2_{ax}), 1.80 (ddt, *J* = 11.1, 5.0, 1.7 Hz, 1H, H-2_{eq}), 1.21 (d, *J* = 6.4 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6 (C=O), 138.8, 138.1, 137.4 (C_q), 135.3, 134.4, 133.2, 131.9, 131.5 (CH_{arom}), 131.2 (C_q), 130.3, 130.2, 130.1, 129.9 (CH_{arom}), 129.9 (C_q), 129.0, 128.5, 128.3, 128.3, 128.3, 128.2, 128.2, 128.0, 128.0, 127.9, 127.8, 127.5, 127.5, 126.1, 126.0, 125.2 (CH_{arom}), 101.2 (CHPh), 94.0 (C-1'), 82.1 (C-4'), 78.6 (C-2'), 78.2 (C-3'), 75.3 (CH_2 Bn), 73.8 (C-5), 72.7 (CH_2 Bn), 71.8 (C-3), 69.0 (C-6'), 68.8 (C-4), 66.3 (C-1), 63.1 (C-5'), 28.2 (C-2), 17.5 (C-6); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (d, *J* = 3.1 Hz, 1H, H-4), 4.85 (d, *J* = 11.5 Hz, 1H, C*H*H Bn), 4.73 (d, *J* = 11.5 Hz, 1H, CH*H* Bn), 4.62 (d, *J* = 9.1 Hz, 1H, H-1'), 4.34 (dd, *J* = 10.5, 5.0 Hz, 1H), 1.96 – 1.89 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0 (C=O), 101.1 (CHPh), 100.8 (C-1'), 82.0, 81.3, 80.8, 75.2, 75.0, 74.7, 74.1, 64.7, 26.9; HRMS: $[M+NH_4]^+$ calcd for $C_{40}H_{42}O_9NH_4$ 684.31671, found 684.31519.

Disaccharide 54B



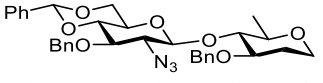
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **54**. Yield: 60 mg, 100 µmol, 100%, α:β = 1.5:1. Data reported for a 1:1 mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.14 (m, 2H), 8.13 – 8.08 (m, 1H), 7.75 – 7.62 (m, 6H), 7.61 – 7.51 (m, 3H), 7.48 – 7.42 (m, 8H), 7.37 (ddd, *J* = 5.3, 3.3, 2.1 Hz, 4H), 7.34 – 7.20 (m, 12H), 5.56 (s, 1H, C*H*Phα), 5.52 – 5.49 (m, 2H, H-4α, C*H*Phβ), 5.42 (d, *J* = 3.1 Hz, 1H, C-4β), 5.26 (d, *J* = 3.7 Hz, 1H, H-1'α), 4.88 – 4.81 (m, 2H), 4.73 (d, *J* = 11.4 Hz, 1H), 4.65 (d, *J* = 10.9 Hz, 1H), 4.49 (d, *J* = 7.9 Hz, 1H, H-1'β), 4.36 – 4.25 (m, 2H), 4.14 (dtd, *J* = 11.7, 3.9, 1.7 Hz, 1H), 4.03 (dddd, *J* = 13.5, 12.0, 4.9, 3.2 Hz, 2H), 3.96 (dd, *J* = 9.9, 9.0 Hz, 1H), 3.84 (td, *J* = 9.8, 4.4 Hz, 1H), 3.75 (t, *J* = 10.1 Hz, 1H), 3.71 – 3.51 (m, 6H), 3.45 (t, *J* = 9.3 Hz, 1H), 3.39 – 3.29 (m, 2H), 2.33 – 2.16 (m, 2H), 1.93 (dd, *J* = 13.4, 4.4 Hz, 1H), 1.79 (ddt, *J* = 11.3, 5.2, 1.7 Hz, 1H), 1.22 (d, *J* = 6.4 Hz, 3H), 1.20 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 166.4, 137.9, 137.9, 137.2, 137.2, 135.3, 134.6, 133.2, 133.0, 131.7, 131.7, 131.0, 130.4, 130.3, 130.3, 130.0, 130.0, 129.1, 129.1, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 127.9, 126.1, 126.0, 124.9, 101.4 (CHPhα), 101.3 (CHPhβ), 100.4 (C-1'β), 94.7 (C-1'α), 82.6, 81.3, 78.8, 76.2, 76.1, 75.0, 74.8, 74.0, 73.6, 72.2, 71.6, 68.9, 68.5, 68.2, 66.3, 66.1, 66.1, 65.8, 63.2, 62.8, 28.1, 27.1, 17.5, 17.4; HRMS: $[M+NH_4]^+$ calcd for $C_{33}H_{35}N_3O_8NH_4$ 619.27624, found 619.27510.

Disaccharide 55A



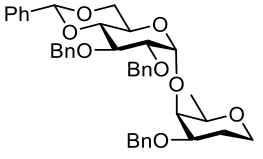
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **55**. Yield: 64 mg, 98 μmol, 98%, α:β =1:1.6. Data reported for a 1:1 mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.17 (m, 40H), 5.87 (d, *J* = 4.1 Hz, 1H, H-1'α), 5.54 (s, 1H, C*H*Phα), 5.53 (s, 1H, C*H*Phβ), 4.94 – 4.88 (m, 2H), 4.84 (s, 2H), 4.81 (d, *J* = 11.4 Hz, 1H), 4.79 – 4.71 (m, 3H, H-1'β, 2x C*H*H Bn), 4.70 – 4.62 (m, 3H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.40 (d, *J* = 11.8 Hz, 1H), 4.32 – 4.19 (m, 2H), 4.00 (t, *J* = 9.4 Hz, 1H), 3.96 – 3.87 (m, 2H), 3.84 – 3.74 (m, 2H), 3.72 – 3.66 (m, 1H), 3.65 – 3.58 (m, 2H), 3.53 (ddd, *J* = 11.7, 5.5, 2.6 Hz, 2H), 3.50 – 3.37 (m, 4H), 3.37 – 3.28 (m, 2H), 2.15 – 2.02 (m, 2H), 1.79 – 1.58 (m, 2H), 1.39 (d, *J* = 6.0 Hz, 3H), 1.34 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.8, 138.6, 138.3, 138.1, 137.5, 137.4, 135.3, 134.4, 131.8, 131.6, 131.6, 131.1, 130.3, 130.2, 129.0, 129.0, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.1, 128.1, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.3, 127.0, 127.0, 126.1, 126.1, 103.7 (C-1'β), 101.2 (CHPhβ), 101.1 (CHPhα), 97.8 (C-1'α), 84.2, 82.9, 82.1, 81.8, 81.7, 81.5, 79.2, 78.8, 78.7, 78.6, 76.2, 75.7, 75.4, 75.2, 75.1, 72.9, 71.9, 69.8, 68.9, 66.0, 65.4, 65.3, 63.2, 32.0, 31.3, 19.8, 18.7; HRMS: $[M+NH_4]^+$ calcd for $C_{40}H_{44}O_8NH_4$ 670.33744, found 670.33617.

Disaccharide 55B



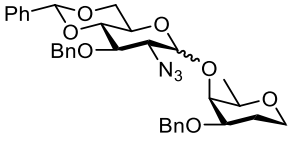
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **55**. Yield: 57 mg, 97 μmol, 97%, α:β =1:16. Data for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.26 (m, 15H, CH_{arom}), 5.52 (s, 1H, C*H*Ph), 4.92 (d, *J* = 11.1 Hz, 1H, C*H*H Bn), 4.78 (d, *J* = 11.1 Hz, 1H, CH*H* Bn), 4.69 – 4.61 (m, 2H, CH_2 Bn), 4.60 (d, *J* = 8.1 Hz, 1H, H-1'), 4.13 (dd, *J* = 10.5, 4.9 Hz, 1H, H-6'), 3.95 – 3.85 (m, 1H, H-1_{eq}), 3.67 (t, *J* = 9.2 Hz, 1H, H-4'), 3.64 – 3.50 (m, 3H, H-3, H-3', H-6'), 3.45 – 3.30 (m, 4H, H-1_{ax}, H-2', H-4, H-5), 3.24 (td, *J* = 9.7, 5.0 Hz, 1H, H-5'), 2.06 (dd, *J* = 13.1, 5.0 Hz, 1H, H-2_{eq}), 1.76 – 1.60 (m, 1H, H-2_{ax}), 1.40 (d, *J* = 5.9 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 137.8, 137.2 (C_q), 129.1, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.0, 127.9, 127.6, 127.1, 126.0 (CH_{arom}), 102.2 (C-1'), 101.3 (CHPh), 84.4 (C-4), 81.7 (C-4'), 79.4, 79.2 (C-3, C-3'), 75.7 (C-5), 75.0, 71.6 (CH_2 Bn), 68.6 (C-6'), 67.4 (C-2'), 66.1 (C-5'), 65.4 (C-1), 31.8 (C-2), 18.6 (C-6); Diagnostic peaks for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (d, *J* = 4.1 Hz, 1H, H-1'), 5.57 (s, 1H, C*H*Ph), 4.24 (dd, *J* = 10.4, 4.9 Hz, 1H), 4.04 (t, *J* = 9.5 Hz, 1H), 2.16 (dd, *J* = 12.8, 5.1 Hz, 1H, H-2_{eq}); ^{13}C NMR (101 MHz, $CDCl_3$) δ 101.9 (CHPh), 98.8 (C-1'), 84.3, 83.0, 82.6, 81.6, 80.9, 78.8, 75.9, 75.7, 72.2, 71.0, 70.8, 66.9, 63.2, 62.9, 62.4; HRMS: $[M+NH_4]^+$ calcd for $C_{33}H_{37}N_3O_7NH_4$ 605.29698, found 605.29595.

Disaccharide 56A



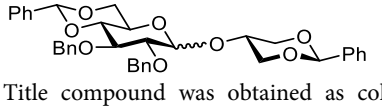
Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **56.** Yield: 65 mg, 100 µmol, 100%, α:β =11:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.43 (m, 5H, CH_{arom}), 7.42 – 7.25 (m, 15H, CH_{arom}), 5.50 (s, 1H, C*H*Ph), 4.97 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.92 – 4.87 (m, 2H, C-1', C*H*H Bn), 4.84 (d, *J* = 11.2 Hz, 1H, CH*H* Bn), 4.76 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.61 – 4.56 (m, 2H, CH_2 Bn), 4.32 (td, *J* = 10.0, 4.9 Hz, 1H, H-5'), 4.21 (t, *J* = 9.3 Hz, 1H, H-3'), 4.04 (ddd, *J* = 11.6, 4.8, 2.0 Hz, 1H, H-1_{eq}), 3.90 (dd, *J* = 10.1, 5.0 Hz, 1H, H-6), 3.70 (dd, *J* = 2.6, 1.3 Hz, 1H, H-4), 3.62 – 3.56 (m, 2H, H-2', H-4'), 3.51 (t, *J* = 10.2 Hz, 1H, H-6), 3.47 – 3.34 (m, 3H, H-1_{ax}, H-3, H-5), 2.14 – 2.01 (m, 1H, H-2), 1.77 – 1.65 (m, 1H, H-2), 1.34 (d, *J* = 6.4 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 138.5, 138.3, 137.8 (C_q), 135.3, 134.6, 131.7, 131.6, 131.0, 130.4, 128.8, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.2, 128.0, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 126.1 (CH_{arom}), 101.1 (CHPh), 100.5 (C-1'), 82.9 (C-4'), 79.6 (C-2'), 78.9 (C-3'), 78.2 (C-4), 77.6 (C-3), 75.2 (CH_2 Bn), 75.1 (C-5), 74.2 (CH_2 Bn), 70.2 (CH_2 Bn), 69.2 (C-6'), 66.0 (C-1), 62.8, 27.1 (C-2), 17.7 (C-6); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 (s, 1H, CHPh), 5.17 (d, *J* = 11.1 Hz, 1H, C*H*H Bn); ^{13}C NMR (101 MHz, $CDCl_3$) δ 103.3 (C-1'), 101.1 (CHPh), 82.6, 81.6, 81.0; HRMS: $[M+NH_4]^+$ calcd for $C_{40}H_{44}O_8NH_4$ 670.33744, found 670.33600.

Disaccharide 56B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **56**. Yield: 55 mg, 93 µmol, 93%, α:β = 1.4:1. Data reported for a 1:1 mixture of anomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 4H), 7.51 – 7.44 (m, 6H), 7.41 – 7.27 (m, 26H), 5.56 (s, 1H, C*H*Phβ), 5.53 (s, 1H, C*H*Phα), 5.03 – 4.96 (m, 2H, H-1'α, C*H*H Bn), 4.94 – 4.88 (m, 1H), 4.84 – 4.77 (m, 3H, H-1'β, 2x CH*H* Bn), 4.71 (d, *J* = 12.3 Hz, 1H), 4.61 (d, *J* = 1.4 Hz, 2H), 4.53 (d, *J* = 12.2 Hz, 1H), 4.41 (td, *J* = 10.0, 5.0 Hz, 1H), 4.28 (dd, *J* = 10.5, 5.0 Hz, 1H), 4.19 (t, *J* = 9.6 Hz, 1H), 4.09 – 4.00 (m, 2H), 3.92 – 3.86 (m, 2H), 3.79 – 3.73 (m, 2H), 3.68 (dd, *J* = 10.3, 8.8 Hz, 2H), 3.59 – 3.35 (m, 10H), 3.33 – 3.25 (m, 1H), 2.22 (td, *J* = 12.4, 4.9 Hz, 1H), 2.04 (qd, *J* = 12.4, 4.9 Hz, 1H), 1.85 – 1.67 (m, 2H), 1.38 (d, *J* = 6.6 Hz, 3H, H-6α), 1.22 (d, *J* = 6.5 Hz, 3H, H-6β); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 138.1, 137.6, 137.3, 135.4, 134.6, 131.7, 131.6, 131.0, 130.4, 130.3, 129.8, 129.1, 129.0, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.3, 127.3, 126.1, 126.1, 124.8, 102.1 (C-1'β), 101.3 (CHPhβ), 101.2 (CHPhα), 99.7 (C-1'α), 83.1, 81.7, 79.2, 78.0, 77.3, 77.2, 76.8, 75.5, 75.2, 75.0, 74.9, 74.5, 70.3, 70.0, 68.9, 68.7, 66.5, 66.1, 65.9, 63.9, 63.9, 62.8, 27.0, 26.4, 17.8; HRMS: $[M+NH_4]^+$ calcd for $C_{33}H_{37}N_3O_7NH_4$ 605.29698, found 605.29626.

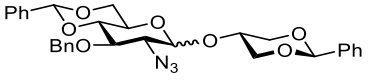
Disaccharide 57A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **57**, with the exceptions that 2,4,6-Tri-*tert*-butylpyridine was used instead of TTBP. Yield: 61 mg, 100 µmol, 100%, α:β = 6:1. Data for the α-

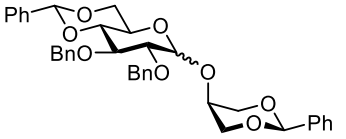
anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 5H, CH_{arom}), 7.48 – 7.31 (m, 15H, CH_{arom}), 5.62 (s, 1H, C*H*Ph), 5.47 (s, 1H, C*H*Ph), 4.99 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.92 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.89 (d, *J* = 11.5 Hz, 1H, CH*H* Bn), 4.82 (d, *J* = 3.9 Hz, 1H, H-1), 4.69 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.44 – 4.36 (m, 2H, 2x C*H*H glycerol), 4.31 (dd, *J* = 10.2, 4.8 Hz, 1H, H-6), 4.05 (t, *J* = 9.3 Hz, 1H, H-3), 4.00 – 3.87 (m, 2H, H-5, CH Glycerol), 3.86 – 3.73 (m, 3H, H-6, 2x CH*H* glycerol), 3.68 (t, *J* = 9.4 Hz, 1H, H-4), 3.60 (dd, *J* = 9.4, 3.9 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.1, 137.5, 137.3 (C_q), 129.4, 129.1, 129.0, 128.7, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 126.1, 126.0, 124.8 (CH_{arom}), 101.3 (CHPh), 101.2 (CHPh), 98.2 (C-1), 82.0 (C-4), 79.2 (C-2), 78.4 (C-3), 75.4, 74.1 (CH_2 Bn), 70.6, 69.5 (CH_2 glycerol), 68.8 (C-6), 67.9 (CH glycerol), 63.0 (C-5); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.65 (d, *J* = 7.7 Hz, 1H, H-1), 4.49 (ddd, *J* = 10.8, 5.0, 2.1 Hz, 1H, C*H*H Glycerol); ^{13}C NMR (101 MHz, $CDCl_3$) δ 103.9 (C-1), 81.9, 81.4, 80.9, 75.6, 75.2, 71.1, 69.6, 69.5, 68.7, 66.2; HRMS: $[M+NH_4]^+$ calcd for $C_{37}H_{38}O_8NH_4$ 628.29049, found 628.28946.

Disaccharide 57B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **57**, with the exceptions that 2,4,6-Tri-*tert*-butylpyridine was used instead of TTBP. Yield: 55 mg, 100 µmol, 100%, α:β = 2.9:1. Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 3H, CH_{arom}), 7.42 – 7.29 (m, 12H, CH_{arom}), 5.59 (s, 1H, C*H*Ph), 5.42 (s, 1H, C*H*Ph), 5.00 (d, *J* = 3.7 Hz, 1H, H-1), 4.97 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.80 (d, *J* = 11.0 Hz, 1H, CH*H* Bn), 4.44 – 4.37 (m, 2H, 2x C*H*H glycerol), 4.28 (dd, *J* = 10.3, 4.8 Hz, 1H, H-6), 4.04 (dd, *J* = 9.9, 9.2 Hz, 1H, H-3), 4.01 – 3.94 (m, 1H, CH glycerol), 3.90 (td, *J* = 9.9, 4.6 Hz, 1H, H-5), 3.80 – 3.70 (m, 4H, H-4, H-6, 2x CH*H* glycerol), 3.35 (dd, *J* = 10.0, 3.8 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 137.4, 137.1, 129.2 (C_q), 128.6, 128.4, 128.3, 128.1, 126.2, 126.1, 126.0 (CH_{arom}), 101.5, 101.4 (CHPh), 98.9 (C-1), 82.6 (C-4), 75.8 (C-3), 75.2 (CH_2 Bn), 70.5, 69.3 (CH_2 glycerol), 68.7 (C-6), 68.6 (CH glycerol), 63.4 (C-5), 62.8 (C-2); diagnostic peaks for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 (s, 1H, C*H*Ph), 5.41 (s, 1H, C*H*Ph), 4.91 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 3.53 (t, *J* = 9.3 Hz, 1H), 3.40 (dd, *J* = 9.5, 8.0 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 102.5 (C-1), 101.4 (CHPh), 101.3 (CHPh), 81.4, 78.8, 75.1, 70.9, 70.3, 69.7, 68.5, 66.4, 66.1, 65.0; HRMS: $[M+NH_4]^+$ calcd for $C_{30}H_{31}N_3O_7NH_4$ 563.25003, found 563.24913.

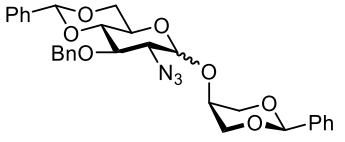
Disaccharide 58A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **58**, with the exceptions that 2,4,6-Tri-*tert*-butylpyridine was used instead of TTBP. Yield: 48 mg, 79 µmol, 79%, α:β = 1.6:1. Data reported for a 2:1 mixture of anomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 20H), 7.41 – 7.24 (m, 40H), 5.58 (s, 1H, C*H*Phβ), 5.57 (s, 2H, C*H*Phα), 5.57 (s, 1H, C*H*Phβ), 5.56 (s, 2H, C*H*Phα), 5.16 (d, *J* = 10.6 Hz, 1H, C*H*H Bnβ), 5.07 (d, *J* = 3.8 Hz, 2H, H-1α), 4.92 (d, *J* = 11.3 Hz, 1H), 4.86 –

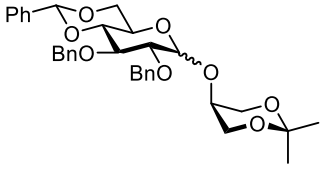
4.82 (m, 5H), 4.79 (d, *J* = 10.7 Hz, 1H, CH*H* Bnβ), 4.71 (d, *J* = 11.8 Hz, 2H), 4.38 (d, *J* = 12.1 Hz, 6H, 2x C*H*H glycerolαβ), 4.32 (dd, *J* = 10.5, 5.0 Hz, 1H), 4.26 – 4.12 (m, 7H), 4.11 – 4.01 (m, 6H), 3.82 – 3.68 (m, 7H), 3.67 – 3.58 (m, 5H), 3.53 (d, *J* = 1.6 Hz, 2H, CH glycerolα), 3.39 (dt, *J* = 9.8, 4.9 Hz, 1H, H-5β); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 138.6, 138.4, 138.2, 137.6, 137.4, 135.4, 134.6, 131.6, 131.0, 130.4, 130.3, 129.1, 129.0, 129.0, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.1, 128.0, 128.0, 127.8, 127.7, 127.6, 126.4, 126.3, 126.2, 126.1, 102.5 (C-1β), 101.6 (CHPhα), 101.4 (CHPhβ), 101.4 (CHPhα), 101.2 (CHPhβ), 96.8 (C-1α), 82.3, 81.8, 81.3, 80.9, 79.5, 78.5, 75.4, 75.4, 75.3, 73.0, 70.8, 70.1, 70.0, 69.6, 69.1, 68.8, 68.3, 68.1, 66.2, 62.9; HRMS: $[M+NH_4]^+$ calcd for $C_{37}H_{38}O_8NH_4$ 628.29049, found 628.28956.

Disaccharide 58B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **58**, with the exceptions that 2,4,6-Tri-*tert*-butylpyridine was used instead of TTBP. Yield: 17 mg, 31 μmol, 31%, α:β = 1:3. Data for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 5H, CH_{arom}), 7.43 – 7.29 (m, 10H, CH_{arom}), 5.57 (s, 1H, C*H*Ph), 5.42 (s, 1H, C*H*Ph), 4.91 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.79 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.45 (d, *J* = 8.0 Hz, 1H, C-1), 4.40 (dd, *J* = 11.3, 5.2 Hz, 2H, 2x C*H*H glycerol), 4.33 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6), 4.05 – 3.99 (m, 1H, CH glycerol), 3.83 – 3.65 (m, 4H, H-4, H-6, 2x CH*H* glycerol), 3.54 (t, *J* = 9.3 Hz, 1H, H-3), 3.44 – 3.36 (m, 2H, H-2, H-5); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 137.5, 137.1 (C_q), 129.3, 128.5, 128.5, 128.4, 128.1, 126.2, 126.1 (CH_{arom}), 102.5 (C-1), 101.5, 101.4 (CHPh), 81.5 (C-4), 78.8 (C-3), 75.1 (CH_2 Bn), 72.0 (CH_2 glycerol), 69.5 (CH glycerol), 69.5 (CH_2 glycerol), 68.6 (C-6), 66.8, 66.1 (C-2, C-5); diagnostic peaks for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 (s, 1H, C*H*Ph), 5.43 (s, 1H, C*H*Ph), 5.02 (d, *J* = 3.7 Hz, 1H, H-1), 4.97 (d, *J* = 11.0 Hz, 1H), 4.29 (dd, *J* = 10.3, 4.8 Hz, 1H), 3.90 (td, *J* = 9.9, 4.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 101.5 (CHPh), 99.0 (C-1), 82.7, 75.8, 75.2, 70.6, 69.4, 68.8, 68.7, 63.4, 62.8; HRMS: $[M+NH_4]^+$ calcd for $C_{30}H_{31}N_3O_7NH_4$ 563.25003, found 563.24936.

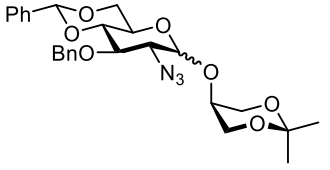
Disaccharide 59A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **59**, with the exceptions that 2,4,6-Tri-*tert*-butylpyridine was used instead of TTBP. Yield: 54 mg, 96 μmol, 96% α:β = 1:1. Data reported for a 1:1 mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.48 (m, 8H), 7.47 – 7.30 (m, 28H), 5.60 – 5.59 (m, 2H, C*H*Phαβ), 5.01 – 4.93 (m, 3H), 4.88 (dd, *J* = 12.2, 7.6 Hz, 3H), 4.83 – 4.79 (m, 2H, H-1α, CH*H* Bn), 4.68 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 7.7 Hz, 1H, H-1β), 4.35 (dd, *J* = 10.5, 5.0 Hz, 1H), 4.27 (dd, *J* = 10.2, 4.9 Hz, 1H), 4.12 – 4.04 (m, 2H), 4.03 – 3.93 (m, 3H), 3.92 – 3.83 (m, 6H), 3.82 – 3.69 (m, 5H), 3.65 (t, *J* = 9.4 Hz, 1H), 3.59 (dd, *J* = 9.4, 3.9 Hz, 1H, H-2α), 3.55 – 3.50 (m, 1H),

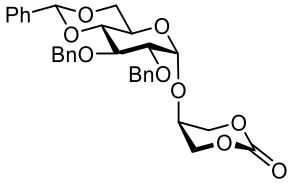
3.43 (td, *J* = 9.9, 5.0 Hz, 1H), 1.51 (s, 3H), 1.49 (s, 3H), 1.46 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 138.5, 138.3, 138.2, 137.4, 137.3, 135.3, 134.6, 131.8, 131.7, 131.6, 131.1, 131.0, 130.4, 130.3, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.7, 126.1, 126.1, 103.4 (C-1β), 101.3, 101.2 (CHPhα, CHPhβ)98.3, 98.3 (C_q isopropylidene α, C_q isopropylidene β), 97.9 (C-1α,) 82.1, 81.9, 81.4, 80.9, 79.3, 78.5, 75.6, 75.4, 75.2, 73.9, 71.0, 69.5, 68.9, 68.8, 66.2, 63.9, 63.5, 62.9, 62.4, 62.1, 26.4, 24.3, 23.1, 21.0.; HRMS: $[M+NH_4]^+$ calcd for $C_{33}H_{38}O_8NH_4$ 580.29049, found 580.29002

Disaccharide 59B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **59**, with the exceptions that 2,4,6-Tri-*tert*-butylpyridine was used instead of TTBP**.** Yield: 50 mg, 100 μmol, 100% α:β = 1:10. Data for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 3H, CH_{arom}), 7.55 – 7.52 (m, 1H, CH_{arom}), 7.47 (qd, *J* = 5.7, 4.9, 2.3 Hz, 3H, CH_{arom}), 7.42 – 7.26 (m, 10H, CH_{arom}), 5.56 (s, 1H, C*H*Ph), 4.90 (d, *J* = 11.3 Hz, 1H, C*H*H Bn), 4.79 (d, *J* = 11.3 Hz, 1H, CH*H* Bn), 4.42 (d, *J* = 7.8 Hz, 1H, H-1), 4.30 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6), 4.05 – 3.94 (m, 2H, 2x C*H*H Glycerol), 3.85 – 3.74 (m, 4H, H-6, CH glycerol, 2x CH*H* glycerol), 3.69 (t, *J* = 9.1 Hz, 1H, H-4), 3.53 (t, *J* = 9.2 Hz, 1H, H-3), 3.45 (dd, *J* = 9.5, 7.9 Hz, 1H, H-2), 3.37 (td, *J* = 9.8, 5.0 Hz, 1H, H-5), 1.46 (s, 3H, CH_3 isopropylidene), 1.40 (s, 3H, CH_3 isopropylidene); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 137.1 (C_q), 135.3, 134.6, 131.7, 131.6, 131.0, 130.4, 129.2, 128.5, 128.4, 128.4, 128.3, 128.0, 126.1 (CH_{arom}), 102.2 (C-1), 101.4 (CHPh), 98.4 (C_q isopropylidene), 81.4 (C-4), 78.9 (C-3), 75.0 (CH_2 Bn), 71.4 (CH glycerol), 68.6 (C-6), 66.3 (C-5), 66.1 (C-2), 63.7, 62.2 (CH_2 glycerol), 25.2, 22.0 (CH_3 isopropylidene); diagnostic peaks for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (s, 1H, C*H*Ph), 5.03 – 4.98 (m, 2H, H-1, C*H*H Bn), 4.16 (dd, *J* = 10.0, 9.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 101.5 (CHPh), 98.4 (C-1), 84.5, 75.9, 69.9, 63.2, 62.8, 24.2, 23.3.; HRMS: $[M+NH_4]^+$ calcd for $C_{26}H_{31}N_3O_7NH_4$ 515.25003, found 515.24996.

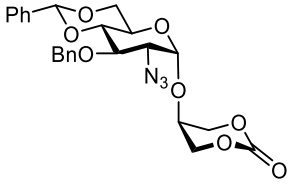
Disaccharide 60A



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **A** and acceptor **60,** with the exceptions that 2,4,6-Tri-*tert*-butylpyridine was used instead of TTBP and that the acceptor was added neat, rather than in solution. Yield: 53 mg, 97 μmol, 97%, α:β >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.5, 2.1 Hz, 2H, CH_{arom}), 7.42 – 7.26 (m, 13H, CH_{arom}), 5.54 (s, 1H, C*H*Ph), 4.91 (d, *J* = 11.2 Hz, 1H, C*H*H Bn), 4.86 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.84 – 4.79 (m, 2H, H-1, CH*H* Bn), 4.61 (d, *J* = 12.0

Hz, 1H, CH*H* Bn), 4.49 – 4.45 (m, 2H, 2x C*H*H glycerol), 4.41 (t, *J* = 2.8 Hz, 2H, 2x CH*H* glycerol), 4.23 (dd, *J* = 10.2, 4.8 Hz, 1H, H-6), 4.04 (t, *J* = 9.3 Hz, 1H, H-3), 3.95 (p, *J* = 2.8 Hz, 1H, CH glycerol), 3.85 (td, *J* = 10.0, 4.8 Hz, 1H, H-5), 3.69 (t, *J* = 10.3 Hz, 1H, H-6), 3.65 – 3.60 (m, 1H, H-4), 3.60 – 3.57 (m, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6 (C=O), 138.6, 138.3, 137.2 (C_q), 129.1, 128.7, 128.4, 128.3, 128.2, 128.1, 128.1, 127.8, 126.1 (CH_{arom}), 101.4 (CHPh), 97.7 (C-1), 81.9 (C-4), 79.2 (C-2), 78.2 (C-3), 75.5, 74.1 (CH_2 Bn), 70.6, 69.1 (CH_2 glycerol), 68.8 (C-6), 66.2 (CH glycerol), 63.5 (C-5); HRMS: $[M+NH_4]^+$ calcd for $C_{31}H_{32}O_9NH_4$ 566.23846, found 566.23774.

Disaccharide 60B



Title compound was obtained as colourless oil via the general procedure for Ph_2SO/Tf_2O mediated glycosylations with donor **B** and acceptor **60,** with the exceptions that 2,4,6-Tri-*tert*-butylpyridine was used instead of TTBP and that the acceptor was added neat, rather than in solution. Yield: 48 mg, 99 μmol, 99%, α:β >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.3, 2.3 Hz, 2H, CH_{arom}), 7.43 – 7.28 (m, 8H, CH_{arom}), 5.57 (s, 1H, C*H*Ph), 5.05 (d, *J* = 3.8 Hz, 1H, H-1), 4.96 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.79 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.51 (d, *J* = 2.4 Hz, 4H, 2x CH_2 glycerol), 4.27 (dd, *J* = 10.3, 4.9 Hz, 1H, H-6), 4.15 – 4.05 (m, 2H, H-3, CH glycerol), 3.94 (td, *J* = 9.9, 4.8 Hz, 1H, H-5), 3.78 – 3.69 (m, 2H, H-4, H-6), 3.42 (dd, *J* = 10.1, 3.8 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4 (C=O), 137.7, 137.0 (C_q), 129.3, 128.6, 128.4, 128.3, 128.1, 126.1 (CH_{arom}), 101.6 (CHPh), 98.5 (C-1), 82.5 (C-4), 75.8 (C-3), 75.3 (CH_2 Bn), 70.3, 69.9 (CH_2 glycerol), 68.6 (C-6), 67.2 (CH glycerol), 63.9 (C-5), 62.6 (C-2); HRMS: $[M+NH_4]^+$ calcd for $C_{24}H_{25}N_3O_8NH_4$ 501.19799, found 501.19736.

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