Chapter 6

Mapping glycosylation stereoselectivity by acceptor reactivity tuning

Introduction

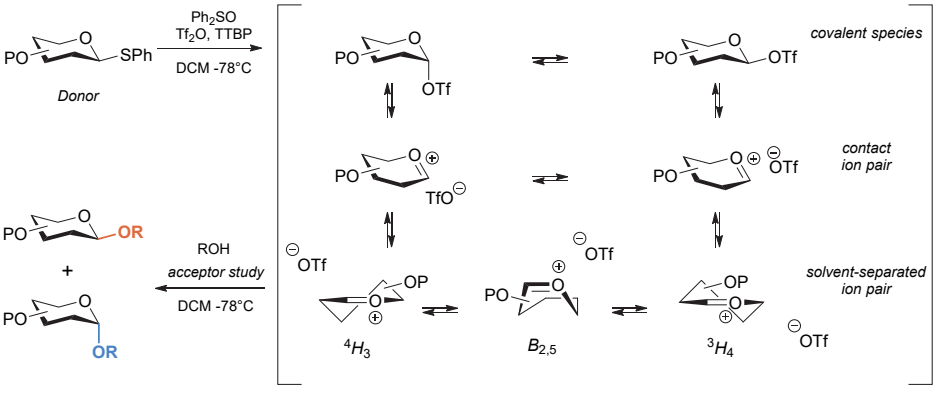
The union of two carbohydrates to generate larger oligosaccharides is arguably one of the most important reactions in glycochemistry.[1–4] Although the glycosylation reaction has been actively studied for more than half a century, many aspects that affect this reaction, both in terms of yield and stereoselectivity, remain enigmatic.[5–10] The reactivity of the carbohydrate building blocks is one of the most important determinants that influence the outcome of a glycosylation reaction.[11,12] The reactivity of donor glycosides has been very well documented: the relative reactivity value (RRV) of hundreds of thioglycosides has been established and hundreds of anomeric triflates and other covalent reactive species, key reactive intermediates formed *in situ* during the reaction, have been characterized.[13–18] The reactivity of acceptor glycosides is less well understood and systematic studies investigating this important reaction parameter are extremely scarce.[19–24] At the same time, it is common practice to change protecting groups on the acceptor building block to influence the yield or change the stereoselectivity of a

Published as part of: van der Vorm, S.; van Hengst, J. M. A.; Bakker, M.; Overkleeft, H. S.; van der Marel, G. A.; Codée, J. D. C. *Angew. Chem. Int. Ed.* **2018**, *57* (27), 8240–8244; *Angew. Chem.* **2018**, *130* (27), 8372–8376.

glycosylation reaction.[25–28] Often this is done in a time consuming, trial-and-error manner as well defined guidelines how to tune the reactivity of an acceptor and how this effects the glycosylation reaction are absent.[29–31]

In Chapters 3 and 4 of this thesis the profound influence acceptor nucleophilicity has on the stereoselectivity of glycosylation reactions with 4,6-*O*-benzylidene protected glucose and glucosamine donors was demonstrated.[32,33] In these studies a panel of partially fluorinated ethanols (ethanol, mono-, di- and trifluoroethanol) was used to reveal a donor's stereoselectivity dependency on acceptor nucleophilicity and described the change in the underlying continuum of mechanisms (Scheme 1).[21,34,35] An intimate relation between model acceptor reactivity and glycosylation stereoselectivity was evident. Whereas some donors are highly sensitive towards acceptor reactivity, other donors are more reluctant to changes in stereochemical outcome. They all have in common that eventually the poorest of *O*-nucleophiles lead them to converge to α-selectivity. These results have been explained by stereoelectronic properties of both the donor and acceptor molecules. In a general sense, the strongest acceptors are able to substitute an anomeric leaving group (α-triflate) in an S_N2-like substitution reaction. Somewhat weaker acceptors preferentially react with the more reactive β-triflate, and upon reducing acceptor reactivity further the mechanism shifts towards the S_N1-side of the reactivity spectrum as increasingly stronger electrophiles are required.

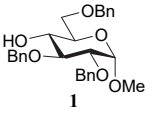
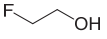
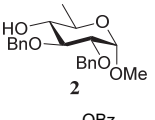
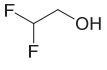
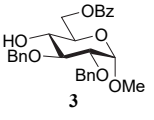
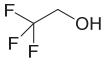
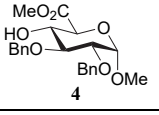
Scheme 1. General glycosylation mechanism, with distinct oxocarbenium ion conformations for the solvent-separated ion pairs. P = protecting group.



Results and discussion

Among the various donors evaluated in Chapters 3-5, the benzylidene glucose (**A**) and glucosazide donors (**B**) were identified to be the most susceptible to acceptor reactivity, based on the stereochemical results of the fluorinated ethanol model system and a few carbohydrate acceptors (See Table 1). An extension of the set of carbohydrate acceptors was envisioned, bearing protecting groups differing in electron-withdrawing properties to closely follow the trend set by the model nucleophiles, determined by the stereoselectivities in glycosylations with donors **A** and **B**. Simultaneously, the variety of acceptors can provide an accurate scale of relative acceptor reactivities to which any desired acceptor can be set against and reveal its potential stereoselectivity in glycosylation.

Table 1. Glycosylations of donor **A** and **B** with fluorinated model acceptors and carbohydrate acceptors **1**-**4**.

	 **A**	 **B**		 **A**	 **B**
Acceptor	Product[a] α:β (yield)	Product α:β (yield)	Acceptor	Product α:β (yield)	Product α:β (yield)
	1 : 10 (68%)	<1 : 20 (83%)	 **1**	**1A** 1 : 1 (82%)	**1B** 1 : 7 (88%)
	1 : 2.8 (70%)	1 : 6.7 (90%)	 **2**	**2A** 2 : 1 (85%)	**2B** 1 : 5 (69%)
	5 : 1 (70%)	2.9 : 1 (64%)	 **3**	**3A** 4 : 1 (92%)	**3B** 1 : 1.1 (67%)
	>20 : 1 (64%)	>20 : 1 (94%)	 **4**	**4A** 5 : 1 (90%)	**4B** 1.1 : 1 (93%)

[a]Ratios and yields of the isolated product after SiO_2 and LH-20 size-exclusion chromatography, anomers were not separated. Ratios were determined by integration of representative signals for each anomer in the mixture of anomers.

To keep steric and other structural effects to a minimum for comparison throughout the scope of acceptors, the primary focus was laid on a diverse set of C-4–OH glucoside acceptors (Figure 1, **1**-**20**). The other alcohol functions are protected as either *O*-benzyl or *O*-benzoyl groups, and in addition to these two groups, the primary alcohol is also either reduced or oxidized to give C-6-deoxy and C-6–CO_2Me species respectively to provide for a difference in electron-withdrawing properties. The glycosylation method used throughout this study is based on preactivation of donors **A** and **B** in DCM with the Ph_2SO/Tf_2O activation couple in the presence of hindered weak base TTBP at -80°C[36,37], followed by addition of a solution of the acceptor. Applying this protocol, the generation of an equilibrium of reactive species (Scheme 1) is ensured, enabling the rationalization of the stereoselectivity in terms of the set of reactive species, and furthermore avoids competitive alternative pathways present in the *in situ* activation scenarios (direct substitution of the activation thioglycoside, its ion pair or the first formed oxocarbenium ion conformer contribute to an increased complexity of the reaction mechanism).

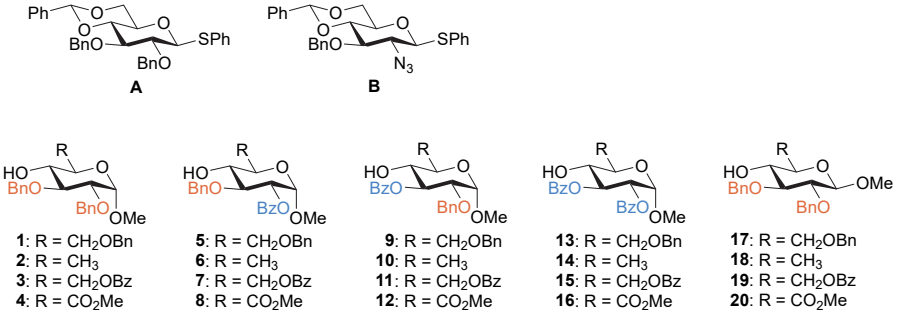
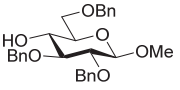
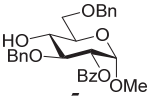
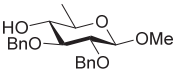
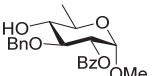
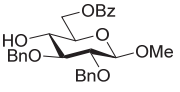
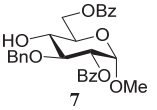
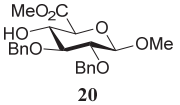
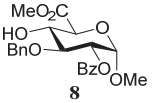
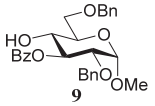
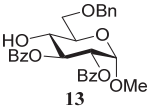
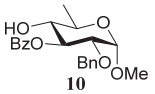
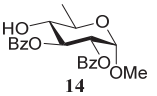
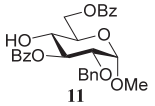
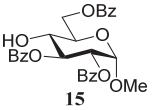
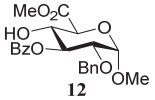
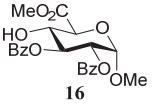
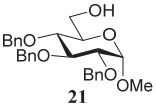
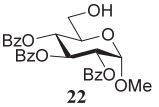


Figure 1. Donors and gluco C-4–OH acceptors used in this chapter.

In Table 1 results previously obtained with the fluorinated model alcohols are directly compared with glycosylation results of 2,3-di-*O*-benzyl acceptors **1**-**4**. A clear transition from β- to α-selectivity, following the electron-withdrawing tendency of the protecting group at the C-6 position, arises. The uronic acid having its electron-withdrawing carbonyl function closer to the acceptor's nucleophilic center than the 6-*O*-benzoyl has, is more α-directing than the latter, which in turn gives higher α-selectivity than the 6-*O*-benzyl. Changing the configuration of the remote anomeric position of the acceptor to a β-glucoside (**17**-**20**), or protecting the C-2 position with a benzoyl (**5**-**8**) rather than a benzyl has no apparent effect on the glycosylation stereoselectivities (Table 2).[38–41] However, the C-3 position has a dramatic effect on the stereoselectivity; complete

Table 2. Glycosylations of donor **A** and **B** with β-acceptors **17**-**20** and α-acceptors bearing a benzoyl on C-2 (**5**-**8**), C-3 (**9**-**12**), or both (**13**-**16**).

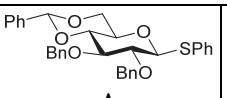
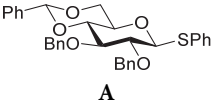
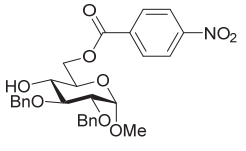
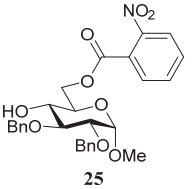
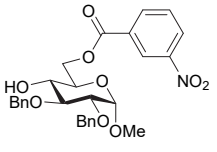
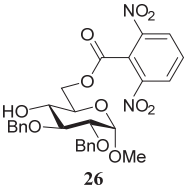
	 **A**	 **B**		 **A**	 **B**
Acceptor	Product α:β (yield)	Product α:β (yield)	Acceptor	Product α:β (yield)	Product α:β (yield)
 **17**	**17A** 1 : 1 (79%)	**17B** 1 : 7 (80%)	 **5**	**5A** 1 : 1.1 (81%)	**5B** 1 : 6 (88%)
 **18**	**18A** 1.1 : 1 (87%)	**18B** 1 : 5.6 (86%)	 **6**	**6A** 1.1 : 1 (86%)	**6B** 1 : 5 (88%)
 **19**	**19A** 3.3 : 1 (73%)	**19B** 1 : 1.2 (70%)	 **7**	**7A** 3.5 : 1 (88%)	**7B** 1.3 : 1 (87%)
 **20**	**20A** 5 : 1 (83%)	**20B** 1.2 : 1 (85%)	 **8**	**8A** 4.8 : 1 (96%)	**8B** 1.2 : 1 (82%)
 **9**	**9A** >20 : 1 (95%)	**9B** 6.7 : 1 (77%)	 **13**	**13A** >20 : 1 (90%)	**13B** 10 : 1 (93%)
 **10**	**10A** >20 : 1 (93%)	**10B** 14 : 1 (81%)	 **14**	**14A** >20 : 1 (83%)	**14B** >20 : 1 (96%)
 **11**	**11A** >20 : 1 (95%)	**11B** >20 : 1 (85%)	 **15**	**15A** >20 : 1 (91%)	**15B** >20 : 1 (69%)
 **12**	**12A** >20 : 1 (86%)	**12B** >20 : 1 (93%)	 **16**	**16A** >20 : 1 (84%)	**16B** >20 : 1 (99%)
 **21**	**21A** 1 : 2.7 (90%)	**21B** <1 : 20 (93%)	 **22**	**22A** 3 : 1 (86%)	**22B** 1 : 1.5 (95%)

α-selectivity is found only by changing the C-3–OBn group to a C-3–OBz group (Table 2, **9**-**12**). Even the more β-selective donor **B** reacts with high to complete α-selectivity with the C-3–OBz acceptors (**9**-**16**). Only exchanging the two C–H bonds for a C=O bond, by replacing a benzyl ether for a benzoyl ester, a marked change in stereoselectivity is achieved. This effect is most pronounced at the nearby C-3 position, whereas position C-6 offers slight fine-tuning of the acceptor reactivity, and position C-2 has only a negligible influence. [42]

The concept of reactivity tuning of the acceptors works consistently well for C-4–OH *gluco*-configured acceptors. The more reactive primary acceptors **21** and **22** (Table 2) showed similar behavior and upon benzoylation significantly more α-product is obtained, however the C-6 nucleophilic position remains too reactive to give complete α-selectivity.

To examine the extent of influence the protecting group on the C-6 position exerts, more electronegative elements were introduced on the benzoyl aromatic ring (Table 3, **23**-**26**).[43] A series of mono-nitrobenzoyl esters were found to marginally increase α-selectivity, but acceptor **26** bearing a 2,6-dinitrobenzoyl group enhanced α-selectivity even more than the uronic acid acceptor **4**.[44]

Table 3. Glycosylations of donor **A** and **B** with acceptor **23**-**26** bearing electron-withdrawing C-6 benzoates.

	 **A**		 **A**
Acceptor	Product α:β (yield)	Acceptor	Product α:β (yield)
 **23**	**23A** 3 : 1 (92%)	 **25**	**25A** 3.5 : 1 (83%)
 **24**	**24A** 3.3 : 1 (49%)	 **26**	**26A** 5.6 : 1 (83%)

Conclusions

The translation from a set of fluorinated model nucleophiles providing a reactivity-selectivity glycosylation picture, to a selection of carbohydrate acceptors occurs without difficulty. These carbohydrate acceptors can be tuned in reactivity just like donors have been in the past by manipulation of their protecting groups, and their reactivity exploited in obtaining stereoselectivity in glycosylations. Everyday protecting- and functional groups were successfully used to moderate the reactivity of the glycosyl acceptors. The most electron-withdrawing groups turned the acceptor into a poor nucleophile and steered the glycosyation utilizing these acceptors to the α-product. The concept of acceptor reactivity tuning holds for all the example acceptors displayed in this chapter. By using this panel of reference acceptors and the two model donors, any other relevant acceptor can have its reactivity compared with the current set of acceptors and appropriately adjusted for the desired reactivity and functional group pattern.

Experimental section

General experimental procedures:

A: reductive opening benzylidene acetal. The benzylidene protected compound (1 eq.) was coevaporated with dry toluene (2x) and dissolved at r.t. in dry THF (0.07 M). $NaCNBH_3$ (5 eq.) was added followed by drop-wise addition of a 4 M HCl solution in 1,4-dioxane (5.2 eq. pH<4). After stirring for an additional hour, the reaction was quenched by the addition of ice water (40 mL/mmol) and extracted with DCM (2x 15 mL/mmol). The combined organic layers were washed with sat.aq. $NaHCO_3$ and sat.aq. NaCl. The organic fraction was dried ($MgSO_4$), filtered, concentrated *in vacuo*, and purified by column chromatography (pentane/EtOAc mixtures).

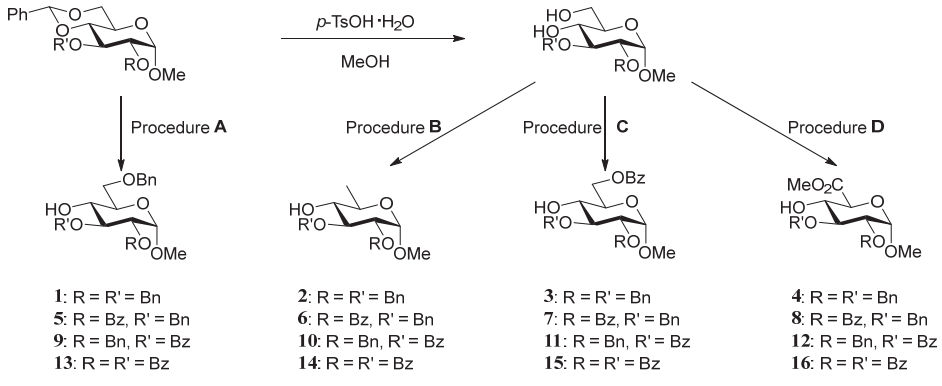
B: iodination-deoxygenation. To a 0°C solution of the diol (1 eq.) in pyridine (0.2 M) was added *p*-TsCl (1.5 eq.) and the reaction stirred until completion (TLC, 3-14 h). MeOH was added (1 mL/mmol), and the reaction mixture diluted with Et_2O (15 mL/mmol). The organic layer was washed with 5 M aq. HCl (3x), H_2O, sat.aq. $NaHCO_3$, and sat.aq. NaCl. The organic fraction was dried ($MgSO_4$), filtered and concentrated in vacuo. The crude compound was dissolved in butanone (0.2 M) and NaI (2 eq.) was added. The reaction mixture was heated for 3h at 80°C after which it was diluted with EtOAc and washed with 10% aq. $Na_2S_2O_3$ and H_2O. The organic fraction was dried ($MgSO_4$), filtered, concentrated *in vacuo*, and purified by column chromatography (pentane/EtOAc mixtures). The intermediate iodo compound (1 eq.) was coevaporated with dry toluene and dissolved in toluene (0.07 M) under a nitrogen atmosphere. AIBN (0.05 eq.) and Bu_3SnH (2 eq.) were added and the reaction refluxed (120°C) for 3-7 h. The cooled solution was diluted with EtOAc and washed with H_2O and sat.aq. NaCl. The organic fraction was dried ($MgSO_4$), filtered, concentrated *in vacuo*, and purified by column chromatography (pentane/EtOAc mixtures).

C: regioselective benzoylation. To a 0°C solution of the diol (1 eq.) in DCM (0.35 M) was added pyridine (5 eq.) followed by a solution of benzoyl chloride (1.05 eq.) in DCM (1.6 M), slowly added over 15 min. After stirring overnight, the reaction mixture was diluted with DCM, washed with 1 M HCl (2x), H_2O and sat.aq. $NaHCO_3$. The organic fraction was dried ($MgSO_4$), filtered, concentrated *in vacuo*, and purified by column chromatography (pentane/EtOAc mixtures).

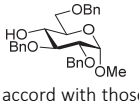
D: regioselective oxidation. To a 0°C solution of the diol (1 eq.) in DCM/H_2O (5/1, v/v, 0.20 M) was added (diacetoxy)iodobenzene (2.5 eq.) and TEMPO (0.2 eq.). The mixture was vigorously stirred for 2-5 h, and quenched by the addition of 10% aq. $Na_2S_2O_3$. The reaction mixture was extracted twice with DCM. The water layer was acidified (pH 1) with 1 M aq. HCl and extracted once with DCM. The combined organic layers were washed with H_2O, then dried ($MgSO_4$), filtered, and concentrated *in vacuo.* The crude carboxylic acid was coevaporated twice with dry toluene and dissolved in DMF (0.35 M). MeI (2 eq.) and K_2CO_3 (2 eq.) were added and stirred for 3 h. The reaction was quenched with AcOH (3 eq.), and diluted with H_2O. The mixture was extracted thrice with EtOAc, and the combined organic layers were washed with H_2O and sat.aq. NaCl. The organic fraction was dried ($MgSO_4$), filtered, concentrated *in vacuo*, and purified by column chromatography (pentane/EtOAc mixtures).

E: Tf_2O/Ph_2SO mediated pre-activation glycosylation. Donor (0.1 mmol), Ph_2SO (26 mg, 0.13 mmol, 1.3 equiv), and tri-*tert*-butylpyrimidine (TTBP) (62 mg, 0.25 mmol, 2.5 equiv) were coevaporated twice with dry toluene and dissolved in dry DCM (2 mL, 0.05 M donor). Activated 3 Å molecular sieves (rods, 1 /16 in. in size) were added, and the reaction mixture was stirred for 1 h at room temperature under a nitrogen atmosphere. The solution was cooled to −78 °C, and Tf_2O (22 μL, 0.13 mmol, 1.3 equiv) was added. The reaction mixture was allowed to warm to −60 °C and then recooled to −78 °C, after which the acceptor (0.2 mmol, 2 equiv) in DCM (0.4 mL, 0.5 M) was added. The reaction mixture was allowed to warm to −40 °C in approximately 90 min and stirred overnight at that temperature. The reaction was quenched with Et_3N (0.1 mL, 0.72 mmol, 5.5 equiv) at −40 °C, 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 $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by silica gel flash column chromatography and sephadex LH-20 size-exclusion chromatography yielded the glycosylation product as a mixture of anomers.

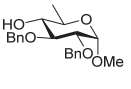
Scheme S1: Synthesis of all C-4–OH acceptors.[a,b]



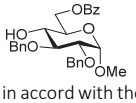
[a]Acceptors **17**-**20** follow the same four procedures from the corresponding β-methyl glycoside, acceptors **23**-**25** follow procedure C with the appropriate nitrobenzoyl chloride. [b]Acceptor **2** was made via an alternative route.



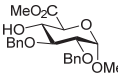
Methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (1). Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside[32] (4.67 g, 10 mmol) was converted to the title compound **1** following general procedure **A**. Yield: 3.5 g, 7.5 mmol, 75%. R_f 0.20 (9/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[32] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.40 – 7.24 (m, 15H, CH_{arom}), 5.00 (d, 1H, *J* = 11.4 Hz, C*H*H Bn), 4.77 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.73 (d, 1H, *J* = 11.4 Hz, CH*H* Bn), 4.66 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.63 (s, 1H, H-1), 4.59 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.54 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 3.78 (t, 1H, *J* = 9.1 Hz, H-3), 3.74 – 3.64 (m, 3H, H-5, H-6), 3.60 (td, 1H, *J* = 9.1, 2.3 Hz, H-4), 3.53 (dd, 1H, *J* = 9.5, 3.5 Hz, H-2), 3.38 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.9, 138.2 (C_q), 128.7, 128.6, 128.6, 128.5, 128.3, 128.3, 128.1, 128.1, 128.0, 127.8, 127.8 (CH_{arom}), 98.3 (C-1), 81.6 (C-3), 79.7 (C-2), 75.6, 73.7, 73.3 (CH_2 Bn), 70.9 (C-4), 70.0 (C-5), 69.6 (C-6), 55.4 (OMe).



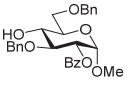
Methyl 2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (2). Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside[32] (581 mg, 1.5 mmol) and *p*-TsCl (343 mg, 1.8 mmol, 1.2 eq.) were dissolved in pyridine (3 mL) and stirred overnight. The reaction mixture was poured in 1 M aq. HCl and extracted twice with Et_2O. The organic layers were washed with 1 M aq. HCl, H_2O, and sat.aq. NaCl, then dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude was coevaporated twice with dry toluene and 12 mL Et_2O was added, followed by LiAlH4 (1 mL, 4 M in Et_2O, 2.6 eq.) and refluxed for 4 h. The reaction was quenched by addition of EtOAc and 1 M aq. HCl. The reaction mixture was washed with 1 M aq. HCl, H_2O and sat.aq. NaCl. The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo. Purificiation by column chromatography (5% to 30% EtOAc in pentane) gave the title compound **2** as an oil. (430 mg, 1.2 mmol, 80%). R_f 0.32 (3/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[45] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.42 – 7.23 (m, 10H, CH_{arom}), 5.03 (d, 1H, *J* = 11.5 Hz, C*H*H Bn), 4.76 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.72 – 4.63 (m, 2H, 2xCH*H* Bn), 4.56 (d, 1H, *J* = 3.5 Hz, H-1), 3.73 (t, 1H, *J* = 9.2 Hz, H-3), 3.69 – 3.54 (m, 1H, H-5), 3.55 – 3.48 (m, 1H, H-2), 3.37 (s, 3H, CH_3 OMe), 3.15 (t, 1H, *J* = 9.2 Hz, H-4), 2.19 (d, 1H, *J* = 18.3 Hz, 4-OH), 1.23 (d, 3H, *J* = 6.2 Hz, H-6); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.8, 138.1 (C_q), 128.8, 128.6, 128.2, 128.1, 128.1, 128.1 (CH_{arom}), 98.1 (C-1), 81.4 (C-3), 80.2 (C-2), 75.4 (CH_2 Bn), 75.4 (C-4), 73.1 (CH_2 Bn) , 66.9 (C-5), 55.2 (OMe), 17.8 (C-6).



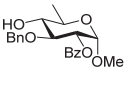
Methyl 2,3-di-*O*-benzyl-6-*O*-benzoyl-α-D-glucopyranoside (3). Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside[32] (3.37 g, 9 mmol) was converted to the title compound **3** following general procedure **C**. Yield: 3.94 g, 8.24 mmol, 92%. R_f 0.18 (4/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[45] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.03 (d, 2H, *J* = 7.6 Hz, CH_{arom}), 7.59 – 7.26 (m, 13H, CH_{arom}), 5.01 (dd, 1H, *J* = 11.3, 2.1 Hz, C*H*H Bn), 4.83 – 4.72 (m, 2H, CH*H* Bn, C*H*H Bn), 4.70 – 4.54 (m, 3H, H-1, CH*H* Bn, H-6), 4.51 (d, 1H, *J* = 11.7 Hz, H-6), 3.91 – 3.79 (m, 2H, H-5, H-3), 3.60 – 3.49 (m, 2H, H-4, H-2), 3.40 (s, 3H, CH_3 OMe), 2.64 (s, 1H, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 166.9 (C=O), 138.7, 138.1 (C_q), 133.3, 129.8, 128.8, 128.6, 128.5, 128.2, 128.2, 128.1, 128.1 (CH_{arom}), 98.3 (C-1), 81.3 (C-3), 79.8 (C-2), 75.8, 73.3 (CH_2 Bn), 70.2 (C-4), 69.6 (C-5), 63.8 (C-6), 55.4 (OMe).



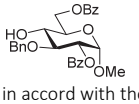
Methyl (methyl 2,3-di-*O*-benzyl-α-D-glucopyranosyl uronate) (4). Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside[32] (6.95 g, 18.6 mmol) was converted to the title compound **4** following general procedure **D**. Yield: 3.84 g, 9.54 mmol, 52%. Spectroscopic data were in accord with those previously reported.[32] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.39 – 7.26 (m, 10H, CH_{arom}), 4.92 (d, 1H, *J* = 11.3 Hz, C*H*H Bn), 4.81 (d, 1H, *J* = 11.4 Hz, CH*H* Bn), 4.79 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.67 – 4.62 (m, 2H, CH*H* Bn, H-1), 4.15 (d, 1H, *J* = 8.9 Hz, H-5), 3.87 – 3.76 (m, 5H, H-3, H-4, CH_3 CO_2Me), 3.53 (dd, 1H, J = 8.9, 3.4 Hz, H-2), 3.42 (s, 3H, CH_3 OMe), 2.89 (bs, 1H, 4-OH); ^{13}C-APT NMR (CDCl3, 101 MHz, HSQC): δ 170.8 (C=O CO_2Me), 138.7, 138.0 (C_q), 128.6, 128.3, 128.1, 128.0, 127.9 (CH_{arom}), 98.8 (C-1), 80.5 (C-3), 78.6 (C-2), 75.6, 73.7 (CH_2 Bn), 71.9 (C-4), 70.6 (C-5), 56.0 (OMe), 52.8 (CO_2Me); HRMS: $[M+Na]^+$ calcd for $C_{22}H_{26}O_7Na$ 425.15707, found 425.15649.



Methyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-α-D-glucopyranoside (5). Methyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside[46] (3.36 g, 7 mmol) was converted to the title compound **5** following general procedure **A**. Yield: 3.07 g, 6.42 mmol, 92%. R_f 0.38 (4/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[47] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.12 – 8.03 (m, 2H, CH_{arom}), 7.62 – 7.15 (m, 13H, CH_{arom}), 5.09 (dd, 1H, *J* = 9.7, 3.6 Hz, H-2), 5.05 (d, 1H, *J* = 3.7 Hz, H-1), 4.86 (d, 1H, *J* = 11.4 Hz, C*H*H Bn), 4.74 (d, 1H, *J* = 11.4 Hz, CH*H* Bn), 4.64 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.58 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.02 (dd, 1H, *J* = 9.7, 8.2 Hz, H-3), 3.86 – 3.71 (m, 4H, H-5, H-6, H-4, H-6), 3.38 (s, 3H, CH_3 OMe), 2.62 (d, 1H, *J* = 2.4 Hz, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 166.0 (C=O), 138.4, 138.0 (C_q), 133.5, 133.4, 129.9 (CH_{arom}), 129.8 (C_q), 128.6, 128.6, 128.5, 128.0, 128.0, 127.8, 127.8, 127.1 (CH_{arom}), 97.4 (C-1), 79.8 (C-3), 75.3 (CH_2 Bn), 74.0 (C-2), 73.8 (CH_2 Bn), 71.6 (C-5), 69.9 (C-4), 69.8 (C-6), 55.4 (OMe).

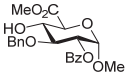


Methyl 2-*O*-benzoyl-3-*O*-benzyl-6-deoxy-α-D-glucopyranoside (6). Methyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside[46] (5.56 g, 17.96 mmol, 1 eq.) was dissolved in 100 ml MeOH and *p*-TsOH·H_2O (0.35 g) was added. The reaction mixture was stirred at 50°C for 3 h, after which it was quenched by addition of Et_3N (0.25 ml) and concentrated *in vacuo*. The crude product was purified by column chromatography (2:1 to 4:6 pentane/EtOAc) to yield Methyl 2-*O*-benzoyl-3-*O*-benzyl-α-D-glucopyranoside as a white solid (5.98 g, 15.39 mmol, 86%). R_f 0.26 (4/6 pentane/EtOAc). ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.13 – 8.04 (m, 2H, CH_{arom}), 7.63 – 7.56 (m, 1H, CH_{arom}), 7.51 – 7.42 (m, 2H, CH_{arom}), 7.31 – 7.19 (m, 5H, CH_{arom}), 5.08 – 5.01 (m, 2H, H-1, H-2), 4.88 (dd, 1H, *J* = 11.4, 1.0 Hz, C*H*H Bn), 4.70 (dd, 1H, *J* = 11.4, 0.9 Hz, CH*H* Bn), 4.07 – 4.00 (m, 1H, H-3), 3.91 – 3.78 (m, 2H, H-6, H-6), 3.77 – 3.67 (m, 2H, H-4, H-5), 3.38 (s, 3H, CH_3 OMe), 2.13 (d, 1H, *J* = 10.0 Hz, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 166.1 (C=O), 138.3 (C_q), 133.5, 130.0 (CH_{arom}), 129.7 (C_q), 128.7, 128.7, 128.1, 128.0 (CH_{arom}), 97.5 (C-1), 79.9 (C-3), 75.4 (CH_2 Bn), 74.2 (C-2), 70.9 (C-4), 70.7 (C-5), 62.5 (C-6), 55.5 (OMe). HRMS: $[M+Na]^+$ calcd for $C_{21}H_{24}O_7Na$ 411.1414, found 411.1421. Methyl 2-*O*-benzoyl-3-*O*-benzyl-α-D-glucopyranoside (3.01 g, 7.75 mmol) was converted to the 6-iodo intermediate following general procedure **B**. Yield: 3.21 g, 6.43 mmol, 83%. R_f 0.64 (3/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[48] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY): δ 8.13 – 8.06 (m, 2H, CH_{arom}), 7.64 – 7.26 (m, 8H, CH_{arom}), 5.12 – 5.03 (m, 2H, H-2, H-1), 4.88 (d, 1H, *J* = 11.4 Hz, C*H*H Bn), 4.65 (d, 1H, *J* = 11.4 Hz, CH*H* Bn), 4.02 (dd, 1H, *J* = 9.6, 8.1 Hz, H-3), 3.59 (dd, 1H, *J* = 10.6, 2.1 Hz, H-6), 3.56 – 3.52 (m, 1H, H-5), 3.52 – 3.46 (m, 1H, H-4), 3.44 (s, 3H, CH_3 OMe), 3.34 (dd, 1H, *J* = 10.5, 6.4 Hz, H-6), 2.33 (d, 1H, *J* = 2.5 Hz, 4-OH). Subsequent deoxygenation gave the title compound **6**. Yield: 2.03 g, 5.45 mmol, 85%. $[\alpha]_D^{20}$ = +112.3° (*c* = 0.90, $CHCl_3$); IR (thin film): 712, 1027, 1051, 1108, 1271, 1452, 1721, 2933, 3486; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.13 – 8.06 (m, 2H, CH_{arom}), 7.62 – 7.55 (m, 1H, CH_{arom}), 7.50 – 7.42 (m, 2H, CH_{arom}), 7.29 – 7.24 (m, 5H, CH_{arom}), 5.08 (dd, 1H, *J* = 9.9, 3.7 Hz, H-2), 4.98 (d, 1H, *J* = 3.7 Hz, H-1), 4.87 (d, 1H, *J* = 11.4 Hz, C*H*H Bn), 4.68 (d, 1H, *J* = 11.4 Hz, CH*H* Bn), 3.97 (dd, 1H, *J* = 9.9, 8.9 Hz, H-3), 3.76 (dq, 1H, *J* = 9.6, 6.2 Hz, H-5), 3.37 (s, 3H, CH_3 OMe), 3.33 (dd, 1H, *J* = 9.2, 2.7 Hz, H-4), 2.32 (d, 1H, *J* = 2.8 Hz, 4-OH), 1.32 (d, 3H, *J* = 6.2 Hz, H-6); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 166.0 (C=O), 138.3 (C_q), 133.4, 129.9 (CH_{arom}), 129.8 (C_q), 128.7, 128.6, 128.1, 128.1 (CH_{arom}), 97.3 (C-1), 80.0 (C-3), 75.6 (C-4), 75.3 (CH_2 Bn), 74.6 (C-2), 67.0 (C-5), 55.3 (OMe), 17.7 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{21}H_{24}O_6Na$ 395.1465, found 395.1472.

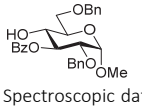


Methyl 2,6-di-*O*-benzoyl-3-*O*-benzyl-α-D-glucopyranoside (7). Methyl 2-*O*-benzoyl-3-*O*-benzyl-α-D-glucopyranoside (0.93 g, 2.4 mmol) was converted to the title compound **7** following general procedure **C**. Yield: 1.25 g, 2.4 mmol, 100%. R_f 0.25 (4/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[45] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.13 – 8.01 (m, 4H, CH_{arom}), 7.62 – 7.17 (m, 11H, CH_{arom}), 5.11 – 5.04 (m, 2H, H-1, H-2), 4.87 (d, 1H, *J* = 11.3 Hz, C*H*H Bn), 4.78 – 4.70 (m, 2H, CH*H* Bn, H-6), 4.54 (dd, 1H, *J* = 12.1, 2.2 Hz, H-6), 4.07 (t, 1H, *J* = 9.0 Hz, H-3), 3.97 (ddd, 1H, *J* = 10.0, 4.5, 2.1 Hz, H-5), 3.70 (t, 1H, *J* = 9.4 Hz, H-4), 3.40 (s, 3H, CH_3 OMe), 2.83 (s, 1H, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 167.1, 166.0

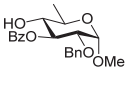
(C=O), 138.2 (C_q), 133.5, 133.4, 130.0, 129.9, 129.8 (CH_{arom}), 129.7 (C_q), 128.7, 128.6, 128.1, 128.1 (CH_{arom}), 97.5 (C-1), 79.6 (C-3), 75.6 (CH_2 Bn), 74.0 (C-2), 70.4 (C-4), 69.7 (C-5), 63.6 (C-6), 55.5 (OMe).



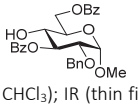
Methyl (methyl 2-*O*-benzoyl-3-*O*-benzyl-α-D-glucopyranosyl uronate) (8). Methyl 2-*O*-benzoyl-3-*O*-benzyl-α-D-glucopyranoside (1.55 g, 4 mmol) was converted to the title compound **8** following general procedure **D**. Yield: 1.01 g, 2.4 mmol, 61%. $[\alpha]_D^{20}$ = +137.4° (*c* = 0.95, $CHCl_3$); IR (thin film): 711, 1028, 1046, 1105, 1270, 1452, 1723, 1749, 2937, 3508; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.08 – 8.02 (m, 2H, CH_{arom}), 7.62 – 7.18 (m, 9H, CH_{arom}), 5.14 (d, 1H, *J* = 3.6 Hz, H-1), 5.08 (dd, 1H, *J* = 9.6, 3.6 Hz, H-2), 4.84 (s, 2H, CH_2 Bn), 4.24 (d, 1H, *J* = 9.6 Hz, H-5), 4.05 (dd, 1H, *J* = 9.7, 8.6 Hz, H-3), 3.98 (td, 1H, *J* = 9.2, 1.9 Hz, H-4), 3.86 (s, 3H, CH_3 CO_2Me), 3.43 (s, 3H, CH_3 OMe), 3.03 (s, 1H, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.8 (C=O CO_2Me), 166.0 (C=O OBz), 138.3 (C_q), 133.5, 130.0 (CH_{arom}), 129.6 (C_q), 128.6, 128.6, 128.1, 127.9 (CH_{arom}), 97.8 (C-1), 78.6 (C-3), 75.4 (CH_2 Bn), 73.1 (C-2), 72.4 (C-4), 70.2 (C-5), 56.0 (OMe), 53.0 (CO_2Me); HRMS: $[M+Na]^+$ calcd for $C_{22}H_{24}O_8Na$ 439.1363, found 439.1374.



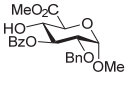
Methyl 3-*O*-benzoyl-2,6-di-*O*-benzyl-α-D-glucopyranoside (9). Methyl 3-*O*-benzoyl-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside[47] (3.34 g, 7 mmol) was converted to the title compound **9** following general procedure **A**. Yield: 2.11 g, 4.40 mmol, 63%. R_f 0.20 (4/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[47] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.07 – 8.00 (m, 2H, CH_{arom}), 7.64 – 7.21 (m, 13H, CH_{arom}), 5.50 (ddd, 1H, *J* = 9.9, 7.5, 1.3 Hz, H-3), 4.75 (d, 1H, *J* = 3.5 Hz, H-1), 4.69 – 4.52 (m, 4H, 2xCH_2 Bn), 3.86 – 3.66 (m, 5H, H-2, H-4, H-5, H-6, H-6), 3.42 (s, 3H, CH_3 OMe), 3.01 – 2.91 (m, 1H, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 167.7 (C=O), 138.0, 137.8 ($_{cq}$), 133.4, 130.1, 129.8, 128.5, 128.5, 128.1, 128.1, 127.8, 127.8 (CH_{arom}), 98.0 (C-1), 76.6 (C-2), 76.4 (C-3), 73.8 (CH_2 Bn), 73.1 (CH_2 Bn), 70.5 (C-4), 70.5 (C-5), 69.3 (C-6), 55.5 (OMe).



Methyl 2-*O*-benzyl-3-*O*-benzoyl-6-deoxy-α-D-glucopyranoside (10). Methyl 3-*O*-benzoyl-2-*O*-benzyl-α-D-glucopyranoside[49] (3.63 g, 9.34 mmol) was converted to the 6-iodo intermediate following general procedure **B**. Yield: 3.89 g, 7.80 mmol, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.06 – 7.99 (m, 2H, CH_{arom}), 7.65 – 7.23 (m, 8H, CH_{arom}), 5.47 (dd, 1H, *J* = 9.8, 8.5 Hz, H-3), 4.75 (d, 1H, *J* = 3.6 Hz, H-1), 4.69 (d, 1H, *J* = 12.4 Hz, C*H*H Bn), 4.63 (d, 1H, *J* = 12.4 Hz, CH*H* Bn), 3.69 (dd, 1H, *J* = 9.8, 3.6 Hz, H-6), 3.61 (dd, 1H, *J* = 10.7, 2.3 Hz, H-2), 3.57 – 3.52 (m, 1H, H-5), 3.52 – 3.48 (m, 1H, H-4), 3.48 (s, 3H, CH_3 OMe), 3.34 (dd, 1H, *J* = 10.6, 6.4 Hz, H-6), 3.19 (dq, 1H, *J* = 5.0, 1.6 Hz, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 168.1 (C=O), 137.7, 133.7(C_q), 130.1, 128.6, 128.1 (CH_{arom}), 97.9 (C-1), 76.7 (C-2), 76.1 (C-3), 74.0 (C-4), 73.2 (CH_2 Bn), 70.5 (C-5), 60.5 (C-6), 55.8 (OMe), 7.0 (C-6). Subsequent deoxygenation gave the title compound **10**. Yield: 1.08 g, 2.90 mmol, 37%. $[\alpha]_D^{20}$ = +93.3° (*c* = 1.0, $CHCl_3$); IR (thin film): 710, 748, 988, 1053, 1103, 1269, 1369, 1450, 1720, 2909, 3460; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.06 – 7.99 (m, 2H, CH_{arom}), 7.64 – 7.22 (m, 8H, CH_{arom}), 5.43 (t, 1H, *J* = 9.5 Hz, H-3), 4.71 – 4.61 (m, 3H, CH_2 Bn, H-1), 3.77 (dq, 1H, *J* = 9.5, 6.2 Hz, H-5), 3.68 (dd, 1H, *J* = 9.8, 3.6 Hz, H-2), 3.42 (s, 3H, CH_3 OMe), 3.34 (td, 1H, *J* = 9.3, 5.3 Hz, H-4), 2.82 (d, 1H, *J* = 5.3 Hz, 4-OH), 1.31 (d, 3H, *J* = 6.2 Hz, H-6); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 168.1 (C=O), 137.8, 133.5 (C_q), 130.1 (CH_{arom}), 129.8 (C_q), 128.6, 128.1, 128.1 (CH_{arom}), 97.8 (C-1), 76.9 (C-2), 76.7 (C-3), 75.7 (C-4), 73.1 (CH_2 Bn), 67.6 (C-5), 55.4 (OMe), 17.7 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{28}NO_6$ 390.19111, found 390.19132.

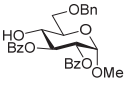


Methyl 2-*O*-benzyl-3,6-di-*O*-benzoyl-α-D-glucopyranoside (11). Methyl 3-*O*-benzoyl-2-*O*-benzyl-α-D-glucopyranoside[49] (1.36 g, 3.5 mmol) was converted to the title compound **11** following general procedure **C**. Yield: 1.47 g, 3.0 mmol, 85%. R_f 0.28 (4/1 pentane/EtOAc). $[\alpha]_D^{20}$ = +78.4° (*c* = 1.13, $CHCl_3$); IR (thin film): 709, 1051, 1070, 1097, 1107, 1275, 1452, 1724, 1749, 2945, 3493; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.08 – 8.02 (m, 4H, CH_{arom}), 7.65 – 7.54 (m, 2H, CH_{arom}), 7.49 – 7.41 (m, 4H, CH_{arom}), 7.30 – 7.22 (m, 5H, CH_{arom}), 5.54 (t, 1H, *J* = 9.5 Hz, H-3), 4.76 (d, 1H, *J* = 3.5 Hz, H-6), 4.73 – 4.63 (m, 3H, C*H*H Bn, H-1, H-6), 4.63 – 4.54 (m, 1H, CH*H* Bn), 4.02 (ddd, 1H, *J* = 10.0, 5.1, 2.3 Hz, H-5), 3.73 – 3.61 (m, 2H, H-2, H-4), 3.44 (s, 3H, CH_3 OMe), 3.35 – 3.20 (m, 1H, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 167.8, 166.9 (C=O), 137.8 (C_q), 133.5, 130.1, 129.9 (CH_{arom}), 129.7 (C_q), 128.6, 128.6, 128.5, 128.1, 128.1 (CH_{arom}), 97.9 (C-1), 76.7 (C-2), 76.1 (C-3), 73.2 (CH_2 Bn), 70.2 (C-4), 70.1 (C-5), 63.8 (C-6), 55.5 (OMe); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{28}O_8Na$ 515.1676, found 515.1680.

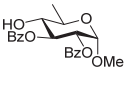


Methyl (methyl 2-*O*-benzyl-3-*O*-benzoyl-α-D-glucopyranosyl uronate) (12). Methyl 3-*O*-benzoyl-2-*O*-benzyl-α-D-glucopyranoside[49] (2.14 g, 5.5 mmol) was converted to the title compound **12** following general procedure **D**. Yield: 1.70 g, 4.08 mmol, 74%. $[\alpha]_D^{20}$ = +65.6° (*c* = 1.0, $CHCl_3$); IR (thin film): 714, 748, 910, 1049, 1111, 1200, 1269, 1450, 1724, 2932, 3472; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): 8.07 –

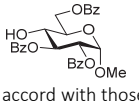
8.00 (m, 2H, CH_{arom}), 7.62 – 7.56 (m, 1H, CH_{arom}), 7.50 – 7.41 (m, 2H, CH_{arom}), 7.28 – 7.22 (m, 5H, CH_{arom}), 5.58 (t, 1H, *J* = 9.3 Hz, H-3), 4.79 (d, 1H, *J* = 3.4 Hz, H-1), 4.67 (d, 1H, *J* = 12.4 Hz, C*H*H Bn), 4.61 (d, 1H, *J* = 12.4 Hz, CH*H* Bn), 4.28 (d, 1H, *J* = 9.5 Hz, H-5), 3.96 (td, 1H, *J* = 9.4, 2.7 Hz, H-4), 3.80 (s, 3H, CH_3 CO_2Me), 3.70 (dd, 1H, *J* = 9.6, 3.4 Hz, H-2), 3.47 (s, 3H, CH_3 OMe), 3.28 (d, 1H, *J* = 4.3 Hz, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.4 (C=O CO_2Me), 166.8 (C=O OBz), 137.6 (C_q), 133.4, 130.0 (CH_{arom}), 129.7(C_q), 129.5, 128.6, 128.5, 128.2 (CH_{arom}), 98.4 (C-1), 76.0 (C-2), 74.3 (C-3), 73.3 (CH_2 Bn), 71.0 (C-4), 70.9 (C-5), 56.1 (OMe), 52.9 (CO_2Me); HRMS: $[M+NH_4]^+$ calcd for $C_{21}H_{28}NO_6$ 479.20643, found 479.20618.



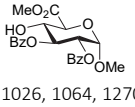
Methyl 2,3-di-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside (13). Methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside[50] (4.68 g, 9.54 mmol) was converted to the title compound **13** following general procedure **A**. Yield: 3.74 g, 7.62 mmol, 80%. R_f 0.30 (4/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[51] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.02 – 7.94 (m, 4H, CH_{arom}), 7.55 – 7.27 (m, 11H, CH_{arom}), 5.74 (dd, 1H, *J* = 10.1, 8.4 Hz, H-3), 5.26 (dd, 1H, *J* = 10.2, 3.7 Hz, H-2), 5.13 (d, 1H, *J* = 3.7 Hz, H-1), 4.67 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.61 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.03 – 3.91 (m, 2H, H-5, H-4), 3.86 (dd, 1H, *J* = 10.4, 3.9 Hz, H-6), 3.81 (dd, 1H, *J* = 10.4, 3.4 Hz, H-6), 3.43 (s, 3H, CH_3 OMe), 3.02 (d, 1H, *J* = 3.5 Hz, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 167.5, 166.1 (C=O), 137.0 (Cq), 133.5, 133.1, 130.0 (CH_{arom}), 129.9, 129.2 (C_q), 128.6, 128.4, 128.3, 126.3 (CH_{arom}), 97.2 (C-1), 74.3 (C-3), 73.9 (CH_2 Bn), 71.6 (C-2), 70.8 (C-4), 70.3 (C-5), 69.6 (C-6), 55.6 (OMe).



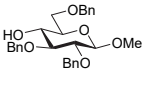
Methyl 2,3-di-*O*-benzoyl-6-deoxy-α-D-glucopyranoside (14). Methyl 2,3-di-*O*-benzoyl-α-D-glucopyranoside[50] (1.49 g, 3.7 mmol) was converted to the 6-iodo intermediate following general procedure **B**. Yield: 1.38 g, 2.7 mmol, 73%. ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.01 – 7.93 (m, 4H, CH_{arom}), 7.55 – 7.48 (m, 2H, CH_{arom}), 7.41 – 7.34 (m, 4H, CH_{arom}), 5.69 (dd, 1H, *J* = 10.1, 8.7 Hz, H-3), 5.29 (dd, 1H, *J* = 10.1, 3.7 Hz, H-2), 5.12 (d, 1H, *J* = 3.7 Hz, H-1), 3.76 – 3.63 (m, 3H, H-4, H-5, H-6), 3.49 (s, 3H, CH_3 OMe), 3.46 – 3.41 (m, 1H, H-6), 3.29 – 3.12 (m, 1H, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 168.0, 166.0 (C=O), 133.8, 133.6, 130.0, 130.0 (CH_{arom}), 129.2, 129.0 (C_q), 128.6, 128.6 (CH_{arom}), 97.2 (C-1), 74.4 (C-3), 73.9 (C-4), 71.3 (C-2), 70.6 (C-5), 55.8 (OMe), 6.5 (C-6). Subsequent deoxygenation gave the title compound **14**. Yield: 0.43 g, 1.12 mmol, 41%. Spectroscopic data were in accord with those previously reported.[52] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.02 – 7.93 (m, 4H, CH_{arom}), 7.56 – 7.47 (m, 2H, CH_{arom}), 7.42 – 7.32 (m, 4H, CH_{arom}), 5.65 (dd, 1H, *J* = 10.2, 9.2 Hz, H-3), 5.27 (dd, 1H, *J* = 10.1, 3.7 Hz, H-2), 5.05 (d, 1H, *J* = 3.6 Hz, H-1), 3.89 (dq, 1H, *J* = 9.5, 6.2 Hz, H-5), 3.55 (td, 1H, *J* = 9.3, 5.0 Hz, H-4), 3.43 (s, 3H, CH_3 OMe), 2.84 (d, 1H, *J* = 5.1 Hz, 4-OH), 1.40 (d, 3H, *J* = 6.2 Hz, CH_3-6); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 167.9, 166.1 (C=O), 133.6, 133.5, 130.0 (CH_{arom}), 130.0, 129.3 (Cq), 128.6, 128.5 (CH_{arom}), 97.1 (C-1), 75.4 (C-4), 74.8 (C-3), 71.7 (C-2), 67.7 (C-5), 55.4 (OMe), 17.6 (C-6).



Methyl 2,3,6-tri-*O*-benzoyl-α-D-glucopyranoside (15). Methyl 2,3-di-*O*-benzoyl-α-D-glucopyranoside[50] (2.84 g, 7 mmol) was converted to the title compound **15** following general procedure **C**. Yield: 2.3 g, 4.5 mmol, 66%. R_f 0.27 (4/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported.[53] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.05 (m, 2H, CH_{arom}), 8.03 – 7.93 (m, 4H, CH_{arom}), 7.64 – 7.12 (m, 9H, CH_{arom}), 5.79 (dd, 1H, *J* = 10.1, 9.2 Hz, H-3), 5.27 (dd, 1H, *J* = 10.2, 3.6 Hz, H-2), 5.14 (d, 1H, *J* = 3.6 Hz, H-1), 4.81 (dd, 1H, *J* = 12.1, 4.5 Hz, H-6), 4.63 (dd, 1H, *J* = 12.2, 2.3 Hz, H-6), 4.12 (ddd, 1H, *J* = 9.9, 4.5, 2.2 Hz, H-5), 3.88 (t, 1H, *J* = 9.6 Hz, H-4), 3.46 (s, 3H, CH_3 OMe), 3.39 (s, 1H, 4-OH). ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 167.5, 167.1, 166.1 (C=O), 133.6, 133.5, 133.5, 130.0, 130.0 (CH_{arom}), 129.7, 129.3, 129.2 (C_q), 128.6, 128.6, 128.5 (CH_{arom}), 97.2 (C-1), 74.0 (C-3), 71.4 (C-2), 70.2 (C-5), 69.8 (C-4), 63.6 (C-6), 55.6 (OMe).

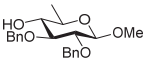


Methyl (methyl 2,3-di-*O*-benzoyl-α-D-glucopyranosyl uronate) (16). Methyl 2,3-di-*O*-benzoyl-α-D-glucopyranoside[50] (0.72 g, 1.8 mmol) was converted to the title compound **16** following general procedure **D**. Yield: 0.57 g, 1.49 mmol, 83%. $[\alpha]_D^{20}$ = +111.4° (*c* = 0.83, $CHCl_3$); IR (thin film): 710, 1026, 1064, 1270, 1452, 1701, 1719, 2895, 3486; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.03 – 7.92 (m, 4H, CH_{arom}), 7.55 – 7.30 (m, 6H, CH_{arom}), 5.85 (ddd, 1H, *J* = 11.2, 9.1, 1.7 Hz, H-3), 5.27 – 5.20 (m, 2H, H-1 H-2), 4.37 (d, 1H, *J* = 9.8 Hz, H-5), 4.16 (td, 1H, *J* = 9.6, 3.5 Hz, H-4), 3.88 (s, 3H, CH_3 CO_2Me), 3.49 (s, 3H, CH_3 OMe), 3.34 (d, 1H, *J* = 3.7 Hz, 4-OH). ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 170.4 (C=O CO_2Me), 166.7, 166.0 (C=O Bz), 133.6, 133.5, 130.0, 130.0 (CH_{arom}), 129.4, 129.1 (C_q), 128.6, 128.5 (CH_{arom}), 97.6 (C-1), 72.4 (C-3), 71.2 (C-2), 70.9 (C-4), 70.4 (C-5), 56.1 (OMe), 53.1 (CO_2Me); HRMS: $[M+Na]^+$ calcd for $C_{22}H_{22}O_9Na$ 453.1156, found 453.1165.

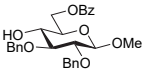


Methyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (17). Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside[54] (0.69 g, 1.5 mmol) was converted to the title compound **17** following

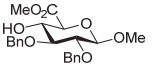
general procedure **A**. Yield: 0.45 g, 0.96 mmol, 64%. Spectroscopic data were in accord with those previously reported.[54] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.39 – 7.22 (m, 15H, CH_{arom}), 4.94 – 4.90 (m, 2H, 2xC*H*H Bn), 4.73 – 4.69 (m, 2H, 2xCH*H* Bn), 4.63 – 4.53 (m, 2H, CH_2 Bn), 4.33 (d, 1H, *J* = 7.4 Hz, H-1), 3.77 (dd, 1H, *J* = 10.4, 3.8 Hz, H-6), 3.70 (dd, 1H, *J* = 10.4, 5.3 Hz, H-6), 3.63 – 3.58 (m, 1H, H-5), 3.57 (s, 3H, CH_3 OMe), 3.50 – 3.37 (m, 3H, H-3, H-4, H-2), 2.55 (d, 1H, *J* = 2.1 Hz, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.7, 138.6, 138.0 (C_q), 128.7, 128.5, 128.5, 128.1, 128.1, 128.0, 127.8, 127.8, 127.8 (CH_{arom}), 104.9 (C-1), 84.1 (C-3), 81.9 (C-2), 75.4 (CH_2 Bn), 74.8(CH_2 Bn), 74.1 (C-4), 73.8 (CH_2 Bn), 71.6 (C-5), 70.4 (C-6), 57.3 (OMe).



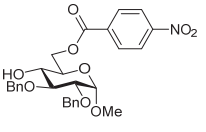
Methyl 2,3-di-*O*-benzyl-6-deoxy-β-D-glucopyranoside (18). Methyl 2,3-di-*O*-benzyl-β-D-glucopyranoside[54] (1.18 g, 3.15 mmol) was converted to the 6-iodo intermediate[55] following general procedure **B**. Yield: 1.03 g, 2.12 mmol, 67%. ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.44 – 7.18 (m, 10H, CH_{arom}), 5.01 – 4.89 (m, 2H, 2xC*H*H Bn), 4.73 – 4.58 (m, 2H, 2xCH*H* Bn), 4.38 – 4.34 (m, 1H, H-1), 3.61 (s, 3H, CH_3 OMe), 3.56 (dd, 1H, *J* = 10.6, 2.4 Hz, H-6), 3.46 – 3.41 (m, 2H, H-3, H-4), 3.37 – 3.30 (m, 1H, H-5), 3.25 (dd, 1H, *J* = 10.6, 7.8 Hz, H-2), 3.16 (ddd, 1H, *J* = 9.1, 7.8, 2.4 Hz, H-6), 2.18 (d, 1H, *J* = 2.4 Hz, OH). Subsequent deoxygenation gave the title compound **18**. Yield: 0.43 g, 1.21 mmol, 57%. $[\alpha]_D^{20}$ = -21.2° (*c* = 1.0, $CHCl_3$); IR (thin film): 698, 737, 988, 1065, 1146, 1354, 1454, 2905, 3345; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.54 – 7.03 (m, 10H, CH_{arom}), 5.00 – 4.91 (m, 2H, 2xC*H*H Bn), 4.74 – 4.61 (m, 2H, 2xCH*H* Bn), 4.33 – 4.27 (m, 1H, H-1), 3.57 (s, 3H, CH_3 OMe), 3.45 – 3.27 (m, 3H, H-3, H-2, H-5), 3.21 (ddt, 1H, *J* = 9.0, 6.7, 2.2 Hz, H-4), 1.31 (d, 3H, *J* = 6.1 Hz, CH_3 6); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.6 (C_q), 128.8, 128.5, 128.3, 128.1, 127.8 (CH_{arom}), 104.8 (C-1), 84.0 (C-2), 82.4 (C-3), 75.3 (CH_2 Bn), 75.0 (C-4), 74.7 (CH_2 Bn), 71.3 (C-5), 57.2 (OMe), 17.8 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{21}H_{26}O_5Na$ 381.1672, found 381.1677.



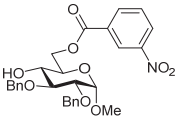
Methyl 2,3-di-*O*-benzyl-6-*O*-benzoyl-β-D-glucopyranoside (19). Methyl 2,3-di-*O*-benzyl-β-D-glucopyranoside[54] (0.56 g, 1.5 mmol) was converted to the title compound **19** following general procedure **C**. Yield: 0.70 g, 1.47 mmol, 98%. Spectroscopic data were in accord with those previously reported.[56] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.08 – 8.01 (m, 2H, CH_{arom}), 7.60 – 7.23 (m, 13H, CH_{arom}), 4.99 – 4.89 (m, 2H, 2xC*H*H Bn), 4.77 – 4.67 (m, 2H, 2xCH*H* Bn), 4.67 – 4.53 (m, 2H, H-6), 4.37 (d, 1H, *J* = 7.5 Hz, H-1), 3.62 – 3.53 (m, 5H, H-4, CH_3 OMe, H-5), 3.50 (td, 1H, *J* = 8.1, 7.2, 1.3 Hz, H-2), 3.42 (dd, 1H, *J* = 8.9, 7.5 Hz, H-3), 2.64 (s, 1H, OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 167.0 (C=O) 138.5, 133.3 (C_q), 130.0, 129.9 (CH_{arom}), 128.8 (C_q), 128.5, 128.5, 128.3, 128.2, 128.1, 127.9 (CH_{arom}), 105.0 (C-1), 83.8 (C-2), 81.9 (C-3), 75.6, 74.8 (CH_2 Bn), 73.7 (C-4), 70.1 (C-5), 63.9 (C-6), 57.3 (OMe).



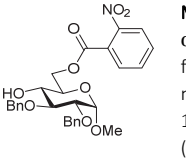
Methyl (methyl 2,3-di-*O*-benzoyl-β-D-glucopyranosyl uronate) (20). Methyl 2,3-di-*O*-benzyl-β-D-glucopyranoside[54] (745 mg, 2.0 mmol) was converted to the title compound **20** following general procedure **D**. Yield: 689 g, 1.71 mmol, 85%. Spectroscopic data were in accord with those previously reported.[57] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.37 – 7.21 (m, 10H, CH_{arom}), 4.92 – 4.84 (m, 2H, 2xC*H*H Bn), 4.80 (d, 1H, *J* = 11.3 Hz, CH*H* Bn), 4.68 (d, 1H, *J* = 11.1 Hz, CH*H* Bn), 4.34 (d, 1H, *J* = 7.5 Hz, H-1), 3.87 – 3.79 (m, 2H, H-3, H-4), 3.76 (s, 3H, CH3 CO_2Me), 3.55 (s, 3H, CH_3 OMe), 3.50 (ddd, 1H, *J* = 8.6, 6.7, 1.6 Hz, H-5), 3.42 (dd, 1H, *J* = 9.1, 7.5 Hz, H-2), 3.09 (s, 1H, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.7 (C=O CO_2Me), 138.4, 138.3 (C_q), 128.4, 128.3, 128.0, 127.9, 127.7, 127.7 (CH_{arom}), 104.9 (C-1), 83.0 (C-5), 81.1 (C-2), 75.3, 74.7 (CH_2 Bn), 74.3, 71.7 (C-3, C-4), 57.4 (OMe), 52.7 (CO_2Me).



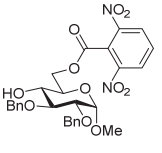
Methyl 2,3-di-*O*-benzyl-6-O-(4-nitrobenzoyl)-α-D-glucopyranoside (23). Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside[32] (374 mg, 1.0 mmol, 1 eq.) was converted to the title compound **23** following general procedure **C** (4-nitrobenzoyl chloride; 195 μL, 1.05 mmol, 1.05 eq.). Yield: 460 mg, 0.88 mmol, 88%. $[\alpha]_D^{20}$ = +28.3° (*c* = 0.6, $CHCl_3$); IR (thin film): 698, 719, 739, 1057, 1103, 1277, 1346, 1454, 1528, 1607, 1726, 2912, 3505; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 8.30 – 8.26 (m, 2H, CH_{arom} pNO_2Bz), 8.21 – 8.17 (m, 2H, CH_{arom} pNO_2Bz), 7.39 – 7.30 (m, 10H, CH_{arom} Bn), 5.04 (d, 1H, *J* = 11.3 Hz, C*H*H Bn), 4.79 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.73 (d, 1H, *J* = 11.3 Hz, CH*H* Bn), 4.68 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.64 (d, 1H, *J* = 3.5 Hz, H-1), 4.63 – 4.56 (m, 2H, H-6, H-6), 3.90 (ddd, 1H, *J* = 10.0, 4.6, 2.7 Hz, H-5), 3.83 (t, 1H, *J* = 9.2 Hz, H-3), 3.54 (dd, 1H, *J* = 9.5, 3.6 Hz, H-2), 3.52 (ddd, 1H, *J* = 10.0, 8.9, 2.7 Hz, H-4), 3.40 (s, 3H, CH_3 OMe), 2.43 (d, 1H, *J* = 2.8 Hz, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 164.8 (C=O), 150.8 (C_q NO_2), 138.6, 138.0, 135.3 (C_q), 131.0, 128.9, 128.7, 128.3, 128.2, 123.7 (CH_{arom}), 98.3 (C-1), 81.3 (C-3), 79.8 (C-2), 75.8, 73.3 (CH_2 Bn), 70.1 (C-4), 69.3 (C-5), 64.7 (C-6), 55.5 (OMe); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{29}NO_9Na$ 546.1740, found 546.1748.



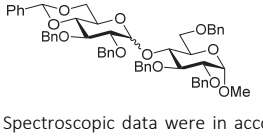
Methyl 2,3-di-*O*-benzyl-6-O-(3-nitrobenzoyl)-α-D-glucopyranoside (24). Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside[32] (300 mg, 0.8 mmol, 1 eq.) was converted to the title compound **24** following general procedure **C** (3-nitrobenzoyl chloride; 227 mg, 1.7 mmol, 1.6 eq.). Yield: 375 mg, 0.72 mmol, 90% (included 5% fully protected glycoside). $[\alpha]_D^{20}$ = +22.2° (*c* = 0.67, $CHCl_3$); IR (thin film): 698, 718, 741, 1059, 1121, 1261, 1294, 1350, 1454, 1533, 1616, 1728, 2920, 3520; ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 8.83 (ddd, 1H, *J* = 2.2, 1.6, 0.4 Hz, CH_{arom} NO_2Bz), 8.39 (ddd, 1H, *J* = 8.2, 2.3, 1.1 Hz, CH_{arom} NO_2Bz), 8.33 (ddd, 1H, *J* = 7.7, 1.6, 1.2 Hz, CH_{arom} NO_2Bz), 7.62 (td, 1H, *J* = 8.0, 0.4 Hz, CH_{arom} NO_2Bz), 7.40 – 7.27 (m, 10H, CH_{arom} Bn), 5.02 (d, 1H, *J* = 11.4 Hz, C*H*H Bn), 4.78 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.74 (d, 1H, *J* = 11.4 Hz, CH*H* Bn), 4.67 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.65 (d, 1H, *J* = 3.6 Hz, H-1), 4.61 – 4.58 (m, 2H, H-6, H-6), 3.91 (dt, 1H, *J* = 10.0, 3.9 Hz, H-5), 3.86 – 3.80 (m, 1H, H-3), 3.55 (dd, 1H, *J* = 9.5, 3.6 Hz, H-2), 3.53 – 3.48 (m, 1H, H-4), 3.42 (s, 3H, CH_3 OMe), 2.59 (d, 1H, *J* = 2.7 Hz, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 164.6 (C=O), 148.3 (C_q NO_2), 138.6, 138.0 (C_q Bn), 135.4 (CH_{arom}), 131.7 (C_q Bz), 129.7, 128.7, 128.6, 128.2, 128.2, 128.1, 128.1, 128.1, 128.1, 127.6, 124.7 (CH_{arom}), 98.2 (C-1), 81.2 (C-3), 79.8 (C-2), 75.6, 73.3 (CH_2 Bn), 70.2 (C-4), 69.3 (C-5), 64.8 (C-6), 55.4 (OMe); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{29}NO_9Na$ 546.1740, found 546.1752.



Methyl 2,3-di-*O*-benzyl-6-O-(2-nitrobenzoyl)-α-D-glucopyranoside (25). Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside[32] (374 mg, 1.0 mmol, 1 eq.) was converted to the title compound **25** following general procedure **C** (2-nitrobenzoyl chloride; 140 µL, 1.05 mmol, 1.05 eq.). Yield: 450 mg, 0.86 mmol, 86%. $[\alpha]_D^{20}$ = +15.8° (*c* = 0.6, $CHCl_3$); IR (thin film): 698, 737, 1059, 1117, 1257, 1292, 1350, 1533, 1734, 2907, 3503; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.85 – 7.81 (m, 1H, CH_{arom} NO_2Bz), 7.74 – 7.70 (m, 1H, CH_{arom} NO_2Bz), 7.64 – 7.55 (m, 2H, CH_{arom} NO_2Bz), 7.39 – 7.25 (m, 10H, CH_{arom} Bn), 4.99 (d, 1H, *J* = 11.4 Hz, C*H*H Bn), 4.78 – 4.73 (m, 2H, CH*H* Bn, C*H*H Bn), 4.64 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.62 (d, 1H, *J* = 3.5 Hz, H-1), 4.54 (d, 2H, *J* = 3.7 Hz, H-6, H-6), 3.86 – 3.78 (m, 2H, H-3, H-5), 3.51 (dd, 1H, *J* = 9.6, 3.5 Hz, H-2), 3.52 – 3.42 (m, 1H, H-4), 3.36 (s, 3H, CH_3 OMe), 2.65 (bs, 1H, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 165.3 (C=O), 148.3 (C_q-NO_2), 138.6, 137.9 (C_q Bn), 132.8, 132.0, 130.0, 128.6, 128.4, 128.0, 128.0, 127.9, 127.8 (CH_{arom}), 127.1 (C_q Bz), 123.8 (CH_{arom}), 98.1 (C-1), 81.1 (C-3), 79.5 (C-2), 75.4, 73.2 (CH_2 Bn), 69.9 (C-4), 69.0 (C-5), 65.3 (C-6), 55.4 (OMe); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{29}NO_9Na$ 546.1740, found 546.1755.

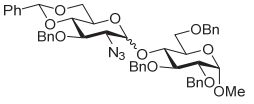


Methyl 2,3-di-*O*-benzyl-6-O-(2,6-dinitrobenzoyl)-α-D-glucopyranoside (26). Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside[32] (145 mg, 0.39 mmol, 1 eq.) was dissolved in 1.5 mL DCM and cooled to 0°C. To this solution was added 2,6-dinitrobenzoic acid (synthesized by $K_2Cr_2O_7/H_2SO_4$ oxidation of 2,6-dinitrotoluene)[58] (123 mg, 0.58 mmol, 1.5 eq.), Ph_3P (202 mg, 0.77 mmol, 2 eq.), and DEAD (~40% in toluene, ~0.8 mmol, 2 eq.). The reaction was stirred at room temperature for 2 days. The reaction mixture was diluted with H_2O and extracted with DCM twice. The combined organic layers were washed with sat. aq. $NaHCO_3$, and brine, then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Flash column chromatography (8/2 to 7/3 pentane/EtOAc) and size-exclusion chromatography (Sephadex LH-20, 1/1 MeOH/DCM) provide the title compound as a yellow oil. Yield: 165 mg, 0.29 mmol, 74%. $[\alpha]_D^{20}$ = +22.5° (*c* = 1.25, $CHCl_3$); IR (thin film): 698, 714, 743, 918, 1057, 1279, 1454, 1582, 1748, 2920, 3493; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.46 (d, 2H, *J* = 8.3 Hz, CH_{arom} NO_2Bz), 7.79 (t, 1H, *J* = 8.3 Hz, CH_{arom} NO_2Bz), 7.39 – 7.26 (m, 10H, CH_{arom} Bn), 5.00 (d, 1H, *J* = 11.4 Hz, C*H*H Bn), 4.79 (dd, 1H, *J* = 11.9, 4.8 Hz, H-6), 4.77 – 4.73 (m, 2H, C*H*H Bn, CH*H* Bn), 4.66 – 4.60 (m, 3H, CH*H* Bn, H-1, H-6), 3.89 (ddd, 1H, *J* = 10.0, 4.8, 2.1 Hz, H-5), 3.86 – 3.76 (m, 1H, H-3), 3.57 – 3.50 (m, 1H, H-4), 3.49 (dd, 1H, *J* = 9.6, 3.5 Hz, H-2), 3.37 (s, 3H, CH_3 OMe), 2.51 (d, 1H, *J* = 3.3 Hz, 4-OH); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 162.6 (C=O), 146.8 (C_q NO_2), 138.7, 138.0 (C_q Bn), 131.2, 129.8, 128.7, 128.5, 128.1, 128.1, 128.0, 128.0 (CH_{arom}), 125.6 (C_q Bz), 98.3 (C-1), 81.3 (C-3), 79.6 (C-2), 75.6, 73.2 (CH_2 Bn), 69.8 (C-4), 69.0 (C-5), 66.2 (C-6), 55.6 (OMe); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{28}N_2O_{11}Na$ 591.1591, found 591.1602.

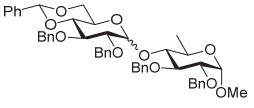


Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (1A). Donor **A** and acceptor **1** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **1A** (73 mg, 82 µmol, 82%, α:β = 1:1) as a white solid. R_f: 0.55 (4/1 pentane/EtOAc); Spectroscopic data were in accord with those previously reported.[32] ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.52 – 7.45 (m, 4H, CH_{arom}), 7.44 – 7.18 (m, 56H, CH_{arom}), 5.75 (d, 1H, J = 3.8 Hz, H-1'$_\alpha$), 5.52 (s, 1H, C*H*Ph$_\alpha$), 5.49 (s, 1H, C*H*Ph$_\beta$), 5.04 (d, 1H, *J* = 11.7 Hz, C*H*H Bn), 4.95 – 4.87 (m, 3H, 3xC*H*H Bn), 4.84 – 4.51 (m, 17H, 4xC*H*H Bn, 5xCH_2 Bn CH*H* Bn, H-1$_\alpha$, H-1$_\beta$), 4.36 (d, 1H, *J* = 7.8 Hz, H-1'$_\beta$), 4.30 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.19 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6'$_\beta$), 4.15 – 4.09 (m, 3H, H-3$_\alpha$, H-4$_\alpha$, H-6'$_\alpha$), 3.99 (t, 1H, *J* = 9.3 Hz, H-3'$_\alpha$), 3.94 (t, 1H, *J* = 9.4 Hz, H-4$_\beta$), 3.90 –

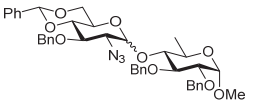
3.78 (m, 5H, H-2$_\beta$, H-5$_\alpha$, H-5'$_\alpha$, H-6$_\alpha$, H-6$_\beta$), 3.69 – 3.41 (m, 11H, H-2$_\alpha$, H-2'$_\alpha$, H-3$_\beta$, H-3'$_\beta$, H-4'$_\alpha$, H-4'$_\beta$, H-5$_\beta$, H-6$_\alpha$, H-6$_\beta$, H-6'$_\alpha$, H-6'$_\beta$), 3.40 – 3.31 (m, 7H, CH$_3$ OMe$_\alpha$, CH$_3$ OMe$_\beta$, H-2'$_\beta$), 3.10 (td, 1H, *J* = 9.5, 4.9 Hz, H-5'$_\beta$); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 139.4, 139.0, 138.7, 138.6, 138.5, 138.4, 138.2, 138.0, 137.9, 137.9, 137.6, 137.5 (C$_q$), 129.0, 128.9, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.7, 127.5, 127.5, 127.4, 127.3, 126.8, 126.1, 126.1 (CH$_{arom}$), 102.9 (C-1'$_\beta$), 101.2 (CHPh$_{\alpha,\beta}$), 98.5, 97.8 (C-1$_\alpha$, C-1$_\beta$), 97.2 (C-1'$_\alpha$), 82.7 (C-2'$_\beta$), 82.4 (C-4'$_\alpha$), 82.2 (C-3$_\alpha$), 81.8 (C-4'$_\beta$), 81.0 (C-3'$_\beta$), 80.3 (C-2$_\beta$), 80.3, 78.9 (C-2$_\alpha$, C-3'$_\alpha$), 78.8 (C-2'$_\alpha$, C-3$_\beta$), 76.9 (C-4$_\beta$), 75.6, 75.5, 75.4, 75.0, 74.4, 73.9, 73.7, 73.4, 73.4 (CH$_2$ Bn), 71.6 (C-4$_\alpha$), 70.0 (C-5$_\beta$), 69.4 (C-5$_\alpha$), 69.0, 68.9, 68.8 (C-6$_\alpha$, C-6'$_\alpha$, C-6'$_\beta$), 67.7 (C-6$_\beta$), 65.8 (C-5'$_\beta$), 63.4 (C-5'$_\alpha$), 55.5 (OMe$_\beta$), 55.3 (OMe$_\alpha$); HRMS: [M+NH$_4$]$^+$ calcd for $C_{55}H_{62}O_{11}N$ 912.43174, found 912.43282.



Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (1B). Donor **B** and acceptor **1** were condensed using the general procedure for Tf$_2$O/Ph$_2$SO mediated glycosylations (E) yielding product **1B** (mg, 88 µmol, 88% , α:β = 1:7) as a white solid. R$_f$ 0.51 α, 0.43 β (4:1 pentane/ EtOAc). Spectroscopic data were in accord with those previously reported.[11] IR (thin film): 696, 737, 1049, 1092, 1362, 1454, 2110, 2868. Data for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, HH-COSY, HSQC, TOCSY): δ 7.68−7.60 (m, 2H, CH$_{arom}$), 7.52−7.18 (m, 23H, CH$_{arom}$), 5.47 (s, 1H, C*H*Ph), 4.89 (d, 1H, *J* = 11.2 Hz, C*H*H Bn), 4.87 (d, 1H, *J* = 10.9 Hz, C*H*H Bn), 4.81 (d, 1H, *J* = 10.9 Hz, CH*H* Bn), 4.78 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.75 (d, 1H, *J* = 11.2 Hz, CH*H* Bn), 4.71 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.63 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.60 (d, 1H, *J* = 3.7 Hz, H-1), 4.41 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.19 (d, 1H, *J* = 7.6 Hz, H-1'), 4.11 (dd, 1H, *J* = 10.6, 5.0 Hz, H-6'), 4.00 – 3.90 (m, 2H, H-4, H-6), 3.85 (t, 1H, *J* = 9.3 Hz, H-3), 3.75 (dt, 1H, *J* = 9.8, 2.4 Hz, H-5), 3.69 (dd, 1H, *J* = 10.8, 1.9 Hz, H- 6), 3.56 (t, 1H, *J* = 9.0 Hz, H-4'), 3.51 (dd, 1H, *J* = 9.5, 3.7 Hz, H-2), 3.45−3.38 (m, 4H, H-6', CH$_3$ OMe), 3.36−3.27 (m, 2H, H-2', H-3'), 3.00 (td, 1H, *J* = 9.8, 5.0 Hz, H-5'). ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC): δ 139.3, 138.3, 137.8, 137.8, 137.3 (C$_q$), 131.1, 129.4, 128.6, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 127.9, 127.9, 127.6, 126.0, 124.8 (CH$_{arom}$), 101.3, 101.2 (*CH*Ph, C-1'), 98.4 (C-1), 81.7 (C-4'), 80.1 (C-3), 79.2 (C-3'), 79.0 (C-2), 76.9 (C-4), 75.4, 74.7, 73.6, 73.5 (CH$_2$ Bn), 69.7 (C-5), 68.6 (C-6'), 68.0 (C-6), 66.6 (C-2'), 65.8 (C-5'), 55.4 (OMe). Diagnostic peaks for the α-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.71 (d, 1H, J = 4.0 Hz, H-1'), 5.53 (s, 1H, C*H*Ph), 5.11 (d, 1H, J = 10.7 Hz, C*H*H Bn), 4.95 (d, 1H, J = 10.9 Hz, C*H*H Bn). ^{13}C-APT NMR (CDCl$_3$, 101 MHz): δ 98.1, 97.8, 82.7, 82.1, 80.5, 76.2, 75.1, 73.3, 73.0, 69.4, 69.1, 68.7, 63.4, 62.9; HRMS: [M+Na]$^+$ calcd for $C_{48}H_{51}N_3O_{10}Na$ 852.34667, found 852.34668.

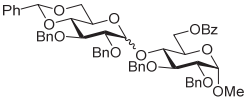


Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (2A). Donor **A** and acceptor **2** were condensed using the general procedure for Tf$_2$O/Ph$_2$SO mediated glycosylations (E) yielding product **2A** (67 mg, 85 µmol, 85%, α:β = 2:1) as a colorless oil. R$_f$: 0.50 (4/1 pentane/EtOAc); IR (thin film): 698, 737, 910, 995, 1029, 1049, 1088, 1369, 1454, 2870, 3032; Data reported for a 2:1 mixture of anomers. ^{1}H NMR (CDCl$_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.65 – 6.84 (m, 37.5H, CH$_{arom}$), 5.76 (d, 1H, *J* = 4.1 Hz, H-1'$_\alpha$), 5.55 (s, 1H, C*H*Ph$_\alpha$), 5.50 (s, 0.5H, C*H*Ph$_\beta$), 5.02 (d, 1H, *J* = 11.8 Hz, C*H*H Bn$_\alpha$), 4.96 – 4.88 (m, 2H, 2xCH*H* Bn$_\beta$, C*H*H Bn$_\alpha$), 4.87 – 4.81 (m, 1.5H, CH*H* Bn$_\beta$, CH*H* Bn$_\alpha$), 4.81 – 4.62 (m, 6.0H, CH*H* Bn$_\beta$, 2xC*H*H Bn$_\alpha$, 2xCH$_2$ Bn$_\beta$, CH$_2$ Bn$_\alpha$, H-1'$_\beta$), 4.55 (d, 1H, *J* = 12.0 Hz, CH*H* Bn$_\alpha$), 4.57 – 4.47 (m, 2.5H, CH*H* Bn$_\alpha$, H-1$_\alpha$, H-1$_\beta$), 4.26 (dd, 1H, *J* = 10.3, 4.8 Hz, H-6'$_\alpha$), 4.16 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6'$_\beta$), 4.08 – 3.99 (m, 2H, H-3$_\alpha$, H-3'$_\alpha$), 3.98 – 3.78 (m, 2H, H-5$_\alpha$, H-5'$_\alpha$), 3.78 – 3.66 (m, 2H, H-4'$_\beta$, H-6'$_\alpha$, H-5$_\beta$), 3.63 (m, 2H, m, H-4$_\alpha$, H-4'$_\alpha$), 3.58 – 3.50 (m, 2.5H, H-2'$_\alpha$, H-2$_\alpha$, H-2$_\beta$), 3.50 – 3.40 (m, 1.5H, H-6'$_\beta$, H-4$_\beta$, H-2'$_\beta$), 3.39 (s, 1.5H, CH$_3$ OMe$_\beta$), 3.37 (s, 3H, CH$_3$ OMe$_\alpha$), 3.29 (td, 0.5H, *J* = 9.7, 4.9 Hz, H-5'$_\beta$), 1.34 (d, 3H, *J* = 6.2 Hz, H-6$_\alpha$), 1.27 (d, 1.5H, *J* = 6.4 Hz, H-6$_\beta$); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 139.1, 138.7, 138.6, 138.4, 138.3, 138.0, 137.4 (C$_\alpha$), 129.0, 129.0, 128.5, 128.4, 128.3, 128.1, 127.7, 127.2, 126.6, 126.1, 126.1(CH$_{arom}$), 103.7(C-1'$_\beta$), 101.2(CHPh$_\alpha$), 101.2 (CHPh$_\beta$), 98.1 (C-1$_\beta$) , 97.9 (C-1'$_\alpha$), 97.6 (C-1$_\alpha$), 83.8 (C-4$_\beta$), 82.8 (C-2'$_\beta$), 82.3 (C-4$_\alpha$), 81.8 (C-3$_\alpha$), 81.4 (C-4'$_\beta$), 80.7 (C-2'$_\alpha$), 80.0 (C-3$_\beta$), 79.5 (C-3'$_\beta$), 79.0 (C-3'$_\alpha$), 78.8 (C-4'$_\alpha$), 78.3 (C-2$_\alpha$), 75.8, 75.5, 75.4, 75.2, 74.2, 74.0, 73.6, 73.3 (CH$_2$ Bn), 68.9 (C-6'$_\alpha$), 68.8 (C-6'$_\beta$), 66.6 (C-5$_\beta$), 66.0 (C-5'$_\beta$), 65.7 (C-5$_\alpha$), 63.3 (C-5'$_\alpha$), 55.4 (OMe$_\beta$), 55.2 (OMe$_\alpha$), 19.2 (C-6$_\alpha$), 18.0 (C-6$_\beta$); HRMS: [M+NH$_4$]$^+$ calcd for $C_{48}H_{56}NO_{10}$ 806.38987, found 806.39030.

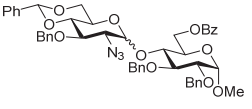


Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (2B). Donor **B** and acceptor **2** were condensed using the general procedure for Tf$_2$O/Ph$_2$SO mediated glycosylations (E) yielding product **2B** (50 mg, 69 µmol, 69%, α:β = 1:5) as a white solid. R$_f$: 0.50 (4/1 pentane/EtOAc); IR (thin film): 698, 737, 999, 1049, 1092, 1177, 1277, 1366, 1454, 2110, 2912, 3032; Data for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.51 – 7.20 (m, 20H, CH$_{arom}$), 5.48 (s, 1H, C*H*Ph), 4.94 –

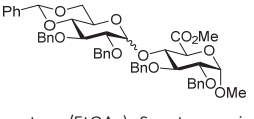
4.69 (m, 5H, 2xCH$_2$ Bn, C*H*H Bn), 4.66 – 4.58 (m, 1H, CH*H* Bn), 4.54 – 4.46 (m, 2H, H-1, H-1'), 4.07 – 3.98 (m, 1H, H-6'), 3.89 – 3.82 (m, 1H, H-3), 3.79 (dd, 1H, *J* = 9.7, 6.2 Hz, H-5), 3.63 (t, 1H, *J* = 9.1 Hz, H-4'), 3.57 (t, 1H, *J* = 9.1 Hz, H-3'), 3.51 – 3.48 (m, 1H, H-2), 3.48 – 3.39 (m, 3H, H-6', H-2', H-4), 3.38 (s, 3H, CH$_3$ OMe), 3.25 – 3.16 (m, 1H, H-5'), 1.35 (d, 3H, *J* = 6.2 Hz, H-6); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 139.4, 138.3, 137.8, 137.2 (C$_q$), 129.2, 128.5, 128.4, 128.3, 128.3, 128.2, 128.0, 128.0, 127.4, 127.2, 126.1 (CH$_{arom}$), 102.4 (C-1'), 101.3 (C*H*Ph), 97.9 (C-1), 84.0 (C-4), 81.7 (C-4'), 80.1 (C-3), 79.7 (C-2), 79.5 (C-3'), 75.3, 75.0, 73.5 (CH$_2$ Bn), 68.5 (C-6'), 67.2 (C-2'), 66.2 (C-5), 66.2 (C-5'), 55.3 (OMe), 18.1 (C-6); Diagnostic peaks for the α-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.66 (d, 1H, *J* = 4.2 Hz, H-1'), 5.57 (s, 1H, C*H*Ph), 5.10 (d, 1H, *J* = 10.6 Hz), 4.98 (d, 1H, *J* = 10.9 Hz), 4.22 (dd, 1H, *J* = 10.4, 4.9 Hz, H-6'), 3.92 (td, 1H, *J* = 10.1, 4.9 Hz, H-5'), 3.31 (dd, 1H, *J* = 10.1, 4.2 Hz, H-2'), 1.30 (d, 3H, *J* = 6.2 Hz, H-6); ^{13}C-APT NMR (CDCl$_3$, 101 MHz): δ 101.3, 98.8, 97.7, 82.6, 80.9, 79.9, 76.3, 75.2, 75.1, 73.3, 68.6, 65.5, 63.3, 62.8, 18.8; HRMS: [M+NH$_4$]$^+$ calcd for $C_{41}H_{49}N_4O_9$ 741.34941, found 741.34989.



Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-*O*-benzoyl-α-D-glucopyranoside (3A). Donor **A** and acceptor **3** were condensed using the general procedure for Tf$_2$O/Ph$_2$SO mediated glycosylations (E) yielding product **3A** (84 mg, 92 µmol, 92%, α:β = 5:1) as a colorless oil. R$_f$: 0.49 (4/1 pentane/EtOAc); IR (thin film): 737, 999, 1026, 1049, 1092, 1273, 1454, 1721, 2928; Data for the α-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.10 – 8.00 (m, 2H, CH$_{arom}$), 7.59 – 7.11 (m, 28H, CH$_{arom}$), 5.73 (d, 1H, *J* = 4.0 Hz, H-1'$_\alpha$), 5.47 (s, 1H, C*H*Ph), 4.99 (d, 1H, *J* = 11.5 Hz, C*H*H Bn), 4.89 (d, 1H, *J* = 11.1 Hz, C*H*H Bn), 4.80 (d, 1H, *J* = 8.3 Hz, C*H*H Bn), 4.76 – 4.69 (m, 3H, 2xCH*H* Bn, H-6), 4.66 (d, 1H, *J* = 8.7 Hz, C*H*H Bn), 4.60 (d, 1H, *J* = 3.5 Hz, H-1), 4.59 – 4.50 (m, 3H, 2xCH*H* Bn, H-6), 4.16 – 4.08 (m, 1H, H-3), 4.07 (m, 4H, H-5, H-3', H-4, H-6'), 3.81 (td, 1H, *J* = 9.9, 4.7 Hz, H-5'), 3.63 – 3.52 (m, 4H, H-2, H-4', H-6', H-2'), 3.39 (s, 3H, CH$_3$ OMe); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 166.2 (C=O), 138.9, 138.6, 137.8, 137.4 (C$_q$), 133.2 (CH$_{arom}$), 129.9 (C$_q$), 129.8, 128.9, 128.5, 127.7, 126.9, 126.2, 126.1 (CH$_{arom}$), 101.3 (CHPh), 98.2 (C-1'), 97.6 (C-1), 82.4 (C-2), 81.7 (C-3), 80.4 (C-4') , 78.7 (C-3'), 78.7 (C-2'), 75.3, 74.6, 74.2 (CH$_2$ Bn), 73.7 (C-4), 73.4 (CH$_2$ Bn), 68.8 (C-6'), 68.1 (C-5), 63.7 (C-5'), 62.8 (C-6), 55.4 (OMe); Diagnostic peaks β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.99 – 7.94 (m, 2H), 5.51 (s, 1H), 4.46 (dd, 1H, *J* = 12.1, 4.7 Hz), 4.19 (dd, 1H, *J* = 10.5, 5.0 Hz), 3.32 – 3.18 (m, 1H, H-5'$_\beta$); ^{13}C-APT NMR (CDCl$_3$, 101 MHz): δ 166.0, 139.1, 138.3, 138.2, 137.3, 129.6, 128.3, 127.3, 103.3, 101.2, 98.0, 82.7, 81.4, 80.1, 77.8, 75.8, 68.7, 66.1, 63.7, 41.1; HRMS: [M+NH$_4$]$^+$ calcd for $C_{55}H_{60}NO_{12}$ 926.41100, found 926.41196.

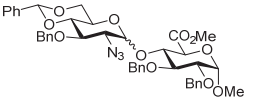


Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-*O*-benzoyl-α-D-glucopyranoside (3B). Donor **B** and acceptor **3** were condensed using the general procedure for Tf$_2$O/Ph$_2$SO mediated glycosylations (E) yielding product **3B** (61 mg, 67 µmol, 67%, α:β = 1:1.1) as a colorless oil. R$_f$: 0.50 (4/1 pentane/EtOAc); IR (thin film): 698, 741, 914, 999, 1030, 1092, 1273, 1369, 1454, 1721, 2110, 2870, 3032; Data reported for a 0.9:1 mixture of anomers. ^{1}H NMR (CDCl$_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.04 (ddd, 3.8H, *J* = 8.4, 6.7, 1.4 Hz, CH$_{arom}$), 7.61 – 7.15 (m, 43.7H, CH$_{arom}$), 5.71 (d, 0.9H, *J* = 4.2 Hz, H-1'$_\alpha$), 5.50 (s, 0.9H, C*H*Ph$_\alpha$), 5.49 (s, 1H, C*H*Ph$_\beta$), 5.13 (d, 1H, *J* = 10.4 Hz, C*H*H Bn), 5.00 – 4.83 (m, 5H, CH*H* Bn, 2xCH$_2$ Bn, C*H*H Bn), 4.83 – 4.68 (m, 4.9H, H-6$_\alpha$, H-6$_\beta$, CH*H* Bn, 2xCH*H* Bn), 4.68 – 4.54 (m, 4.8H, 2xCH*H* Bn, H-6$_\alpha$, H-1$_\alpha$, H-1$_\beta$), 4.51 – 4.40 (m, 2H, H-6$_\beta$, H-1'$_\beta$), 4.13 (dd, 1H, *J* = 9.5, 8.4 Hz, H-3$_\beta$), 4.08 – 3.88 (m, 7.5H, H-3$_\alpha$, H-3'$_\alpha$, H-4$_\beta$, H-4$_\alpha$, H-5$_\alpha$, H-5$_\beta$, H-6'$_\alpha$, H-6'$_\beta$), 3.83 (td, 0.9H, *J* = 9.9, 4.8 Hz, H-5'$_\alpha$), 3.71 – 3.51 (m, 5H, H-2$_\alpha$, H-2$_\beta$, H-3'$_\beta$, H-4'$_\beta$ H-4'$_\beta$, H-6'$_\alpha$), 3.49 (t, 1H, *J* = 10.3 Hz, H-6'$_\beta$), 3.46 – 3.41 (m, 1H, H-2'$_\beta$), 3.41 (s, 3H, CH$_3$ OMe$_\beta$), 3.40 (s, 2.7H, CH$_3$ OMe$_\alpha$), 3.35 (dd, 0.9H, *J* = 10.1, 4.2 Hz, H-2'$_\alpha$), 3.22 – 3.10 (m, 1H, H-5'$_\beta$); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 166.2, 166.1 (C=O), 139.1, 138.6, 138.2, 137.9, 137.8, 137.7, 137.2, 137.1 (C$_q$), 133.4, 133.3 (CH$_{arom}$), 129.9 (C$_q$), 129.7, 129.2, 129.1, 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.6, 127.5, 126.1, 126.0 (CH$_{arom}$), 102.0 (C-1'$_\beta$), 101.4 (CHPh$_\alpha$), 101.3 (CHPh$_\beta$), 99.0 (H-1$_\alpha$), 98.0, 97.7 (C-1$_\alpha$, C-1$_\beta$), 82.7 (C-4'$_\alpha$), 81.6, 81.6 (C-3$_\beta$, C-4'$_\beta$), 80.8 (C-2$_\alpha$), 80.1 (C-3$_\alpha$), 79.7 (C-3'$_\beta$), 79.6, (C-2$_\beta$), 78.0 (C-4$_\beta$), 76.1 (C-3'$_\alpha$), 75.7, 75.3, 75.2, 75.1 (CH$_2$ Bn), 74.9 (C-4$_\alpha$), 73.6, 73.4 (CH$_2$ Bn), 68.6, 68.5 (C-6'$_{\alpha,\beta}$) , 68.5, 68.0 (C-5$_\alpha$, C-5$_\beta$), 66.8 (C-2'$_\beta$), 66.3 (C-5'$_\beta$), 63.7 (C-5'$_\alpha$), 63.5 (C-6$_\beta$), 63.1 (C-6$_\alpha$), 62.8 (C-2'$_\alpha$), 55.6 (OMe$_\beta$), 55.5 (OMe$_\alpha$); HRMS: [M+Na]$^+$ calcd for $C_{48}H_{49}N_3O_{11}Na$ 866.3290, found 866.3259.

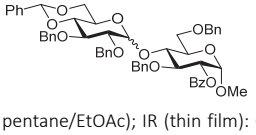


Methyl (methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-α-D-glucopyranosyl uronate) (4A). Donor **A** and acceptor **4** were condensed using the general procedure for Tf$_2$O/Ph$_2$SO mediated glycosylations (E) yielding product **4A** (75.2 mg, 90 µmol, 90%, α:β = 5:1) as a white solid. R$_f$: 0.77 (7/3 pentane/EtOAc); Spectroscopic data were in accord with those previously reported.[32] IR (thin film): 694, 732, 912, 988, 1026, 1043, 1074, 1086, 1358, 1454, 1749, 28866, 2932; Data for the α-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, HH-

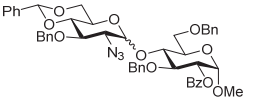
COSY, HSQC, HMBC): δ 7.48 – 7.43 (m, 2H, CH_{arom}), 7.40 – 7.16 (m, 23H, CH_{arom}), 5.51 (s, 1H, C*H*Ph), 5.44 (d, 1H, *J* = 3.8 Hz, H-1'), 4.95 – 4.86 (m, 3H, CH_2 Bn, C*H*H Bn), 4.78 (d, 1H, *J* = 11.2 Hz, CH*H* Bn), 4.71 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.67 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.59 – 4.53 (m, 3H, 2xCH*H* Bn, H-1), 4.28 (dd, 1H, *J* = 6.5, 3.8 Hz, H-6'), 4.25 (d, 1H, *J* = 9.5 Hz, H-5), 4.11 (t, 1H, *J* = 9.1 Hz, H-4), 4.05 (t, 1H, *J* = 8.9 Hz, H-3), 3.98 (t, 1H, *J* = 9.1 Hz, H-3'), 3.76 (s, 3H, CH_3 CO_2Me), 3.64 (t, 1H, *J* = 10.0 Hz, H-6'), 3.61 – 3.54 (m, 3H, H-2, H-4', H-5'), 3.48 (dd, 1H, *J* = 5.6, 3.9 Hz, H-2'), 3.40 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 170.1 (C=O CO_2Me), 139.0, 138.6, 138.0, 137.8, 137.6 (C_q), 129.0, 128.6, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 127.8, 127.7, 127.7, 127.3, 127.0, 126.1 (CH_{arom}), 101.3 (CHPh), 98.6 (C-1), 98.4 (C- 1'), 82.0 (C-4'), 80.8 (C-3), 79.2 (C-2), 78.7 (C-2'), 78.4 (C-3'), 76.1 (C-4), 75.3, 75.0, 73.7, 73.7 (CH_2 Bn), 70.3 (C-5), 68.6 (C-6'), 63.1 (C-5'), 55.8 (OMe), 52.9 (CO_2Me); ^{13}C-HMBC NMR ($CDCl_3$, 101 MHz): δ 98.4 ($J_{C1',H1'}$ = 174 Hz, C-1'$_\alpha$); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.47 (s, 1H, C*H*Ph), 4.62 (d, 1H, *J* = 12.1 Hz), 3.87 (dd, 1H, J = 9.6, 8.4 Hz), 3.50 (s, 3H, CH_3 CO_2Me), 3.44 (s, 0.54H, CH_3 OMe), 3.38 – 3.28 (m, 2H, H-2', H-5'); ^{13}CAPT NMR ($CDCl_3$, 101 MHz): δ 170.1, 139.2, 138.6, 138.2, 137.4, 129.0, 128.5, 128.3, 128.1, 127.7, 127.5, 126.1, 102.9 (C- 1'), 101.2 (CHPh), 99.0 (C-1), 82.3, 81.8, 81.3, 79.6, 78.5, 78.2, 75.6, 75.5, 75.2, 73.9, 70.0, 68.8, 65.9, 55.9, 52.7; ^{13}C-HMBC NMR ($CDCl_3$, 101 MHz): δ 102.9 ($J_{C1',H1'}$ = 164 Hz, C-1'$_\beta$); HRMS: $[M+Na]^+$ calcd for $C_{49}H_{52}O_{12}Na$ 855.33510, found 855.33496.



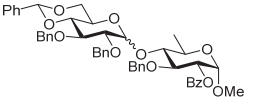
Methyl (methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-α-D-glucopyranosyl uronate (4B). Donor **B** and acceptor **4** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **4B** (mg, 93 μmol,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



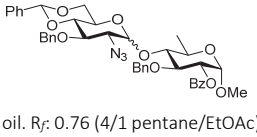
Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2-*O*-benzoyl-3,6-di-*O*-benzyl-α-D-glucopyranoside (5A). Donor **A** and acceptor **5** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **5A** (74 mg, 81 μmol, 81%, α:β = 1:1.1) as a white solid. R_f: 0.50 (4/1 pentane/EtOAc); IR (thin film): 696, 737, 916, 995, 1047, 1088, 1271, 1366, 1452, 1721, 2926; Data reported for a 1:1.1 mixture of anomers: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.02 (td, 4H, *J* = 8.2, 1.4 Hz, CH_{arom}), 7.60 – 6.99 (m, 56H, CH_{arom}), 5.64 (d, 1H, *J* = 3.8 Hz, H-1'$_\alpha$), 5.54 (s, 1H, C*H*Ph$_\alpha$), 5.49 (s, 1.1H, C*H*Ph$_\beta$), 5.18 (dd, 1H, *J* = 9.7, 3.7 Hz, H-2$_\alpha$), 5.11 – 5.02 (m, 3.2H, H-2$_\beta$, H-1$_\beta$, H-1$_\alpha$), 4.96 – 4.55 (m, 15.7H, 7xCH_2 Bn, C*H*H Bn$_\beta$), 4.45 (d, 1.1H, *J* = 7.8 Hz, H-1'$_\beta$), 4.38 (d, 1.1H, *J* = 12.0 Hz, CH*H* Bn$_\beta$), 4.32 (t, 1H, *J* = 9.2 Hz, H-3$_\alpha$), 4.25 (t, 1H, *J* = 9.0 Hz, H-4$_\alpha$), 4.21 – 4.08 (m, 3.2H, H-6α, H-6'$_\beta$, H-3$_\beta$), 4.08 – 3.99 (m, 2.1H, H-3'$_\alpha$, H-3$_\beta$), 3.99 – 3.82 (m, 4.1H, H-5'$_\alpha$, H-6$_\alpha$, H-6$_\beta$, H-5$_\alpha$), 3.78 – 3.66 (m, 2.2H, H-6$_\alpha$, H-5$_\beta$), 3.63 – 3.49 (m, 6.3H, H-6$_\beta$, H-4'$_\beta$, H-4$_\beta$, H-4'$_\alpha$, H-6$_\alpha$, H-2'$_\alpha$), 3.45 (t, 1.1H, *J* = 10.3 Hz, H-6'$_\beta$), 3.41 – 3.38 (m, 7.4H, H-2'$_\beta$, CH_3 OMe$_\beta$, CH_3 OMe$_\alpha$), 3.20 – 3.09 (m, 1.1H, H-5'$_\beta$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.0, 165.9 (C=O), 138.8, 138.8, 138.6, 138.5, 138.3, 138.3, 138.1, 138.0, 137.7 (C_q), 133.3, 133.2, 129.9, 129.9 (CH_{arom}), 129.7 (C_q), 129.1, 129.0, 128.6, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4, 127.0, 126.2 (CH_{arom}), 103.0 (C-1'$_\beta$), 101.2 (CHPh$_{\alpha,\beta}$), 97.7 (C-1'$_\alpha$), 97.3 (C-1$_\alpha$), 97.0 (C-1$_\beta$), 82.7 (C-2'$_\beta$), 82.4 (C-4'$_\alpha$), 81.9 (C-4'$_\beta$), 81.1 (C-3'$_\beta$), 80.6 (C-3$_\alpha$), 79.0 (C-2'$_\alpha$), 78.8 (C-3'$_\alpha$), 77.9 (C-3$_\beta$), 76.9 (C-4$_\beta$), 75.6, 75.4, 75.3, 75.1 (CH_2 Bn), 74.2 (C-2$_\alpha$), 74.1, 73.8, 73.6, 73.5 (CH_2 Bn), 73.4 (C-2$_\beta$), 72.7 (C-4$_\alpha$), 70.3 (C-5$_\beta$), 69.8 (C-5$_\alpha$), 69.0, 68.8, 68.8 (C-6'$_{\alpha,\beta}$, C-6$_\beta$), 67.6 (C-6$_\alpha$), 65.8 (C-5'$_\beta$), 63.5 (C-5'$_\alpha$), 55.5 (OMe$_\alpha$), 55.3 (OMe$_\beta$); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{60}NO_{12}$ 926.41100, found 926.41192.



Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2-*O*-benzoyl-3,6-di-*O*-benzyl-α-D-glucopyranoside (5B). Donor **B** and acceptor **5** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **5B** (74 mg, 88 µmol, 88%, α:β = 1:6) as a light yellow oil. R_f: 0.50 (4/1 pentane/EtOAc); IR (thin film): 698, 737, 999, 1092, 1173, 1273, 1366, 1454, 1721, 2110, 2870; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.05 – 7.98 (m, 2H, CH_{arom}), 7.60 – 7.10 (m, 23H, CH_{arom}), 5.47 (s, 1H, C*H*Ph), 5.12 – 5.03 (m, 2H, H-1, H-2), 4.90 (d, 1H, *J* = 11.2 Hz, C*H*H Bn), 4.85 (d, 1H, *J* = 11.0 Hz, C*H*H Bn), 4.78 (d, 1H, *J* = 4.3 Hz, C*H*H Bn), 4.75 (d, 1H, *J* = 3.5 Hz, CH*H* Bn), 4.70 (d, 1H, *J* = 11.0 Hz, CH*H* Bn), 4.47 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.29 – 4.24 (m, 1H, H-1'), 4.17 – 4.00 (m, 4H, H-3, H-6', H-3', H-6), 3.86 (dt, 1H, *J* = 9.4, 2.3 Hz, H-5), 3.77 (dd, 1H, *J* = 11.0, 1.8 Hz, H-6), 3.60 – 3.54 (m, 1H, H-4'), 3.44 – 3.34 (m, 2H, H-3', H-6', H-2', CH_3 OMe), 3.03 (td, 1H, *J* = 9.8, 5.0 Hz, H-5'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 165.9 (C=O), 138.7, 137.9, 137.3 (C_q), 133.3, 129.9 (CH_{arom}), 129.8 (C_q), 129.2, 128.7, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.7, 127.5, 126.1 (CH_{arom}), 101.3, 101.3 (C-1', CHPh), 97.3 (C-1), 81.8 (C-4'), 79.2 (C-3'), 77.9 (C-3), 76.9 (C-4), 75.3, 74.9, 73.6 (CH_2 Bn), 73.5 (C-2), 70.0 (C-5), 68.6 (C-6'), 67.9 (C-6), 66.7 (C-2'), 65.9 (C-5'), 55.5 (OMe); Diagnostic peaks for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 – 8.06 (m, 2H), 5.68 (d, 1H, *J* = 4.0 Hz, H-1'), 5.55 (s, 1H, C*H*Ph), 5.17 (dd, 1H, *J* = 9.8, 3.6 Hz, H-2), 4.98 (d, 1H, *J* = 10.9 Hz), 4.33 (dd, 1H, *J* = 9.8, 8.7 Hz), 3.67 (t, 1H, *J* = 9.3 Hz); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 165.9, 138.2, 137.9, 137.4, 133.4, 129.6, 129.1, 128.6, 127.6, 98.2, 97.1, 82.7, 80.9, 76.3, 75.2, 75.0, 74.7, 69.7, 69.1, 68.8, 63.5, 62.9; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{51}N_4O_{12}$ 861.37053, found 861.37082.

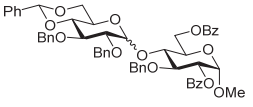


Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2-*O*-benzoyl-3-*O*-benzyl-6-deoxy-α-D-glucopyranoside (6A). Donor **A** and acceptor **6** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **6A** (69 mg, 86 µmol, 86%, α:β = 1.1:1) as a white solid. R_f: 0.55 (4/1 pentane/EtOAc); IR (thin film): 696, 737, 995, 1051, 1086, 1273, 1366, 1452, 1720, 2932; Data reported for a 1.1:1 mixture of anomers: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.05 – 8.01 (m, 2H, CH_{arom}), 8.01 – 7.95 (m, 2.2H, CH_{arom}), 7.60 – 7.16 (m, 42.8H, CH_{arom}), 7.14 – 7.08 (m, 3.3H, CH_{arom}), 7.04 – 6.97 (m, 2.2H, CH_{arom}), 5.66 (d, 1.1H, *J* = 4.0 Hz, H-1'$_\alpha$), 5.57 (s, 1.1H, C*H*Ph$_\alpha$), 5.50 (s, 1H, C*H*Ph$_\beta$), 5.12 (dd, 1.1H, *J* = 9.9, 3.7 Hz, H-2$_\alpha$), 5.06 (dd, 1H, *J* = 10.0, 3.8 Hz, H-2$_\beta$) 4.97 (d, 1.1H, *J* = 3.8 Hz, H-1$_\beta$), 4.95 (d, 1H, *J* = 4.0 Hz, H-1$_\beta$), 4.95 – 4.70 (m, 11.5H, 2xCH_2 Bn$_\alpha$, 3xCH_2 Bn$_\beta$, C*H*H Bn$_\alpha$), 4.67 (d, 1H, *J* = 7.7 Hz, H-1'$_\beta$), 4.57 (d, 1.1H, *J* = 11.8 Hz, CH*H* Bn$_\alpha$), 4.33 – 4.22 (m, 2.2H, H-3$_\alpha$, H-6'$_\alpha$), 4.18 (dd, 1H, *J* = 10.4, 4.8 Hz, H-6'$_\beta$), 4.12 – 4.00 (m, 2.1H, H-3'$_\alpha$, H-3$_\beta$), 4.03 – 3.89 (m, 2.2H, H-5$_\alpha$, H-5'$_\alpha$), 3.85 – 3.74 (m, 2H, H-3$_\beta$, H-5$_\beta$), 3.74 (t, 1.1H, *J* = 10.3 Hz, H-6'$_\alpha$), 3.68 (dd, 1.1H, *J* = 9.5, 8.6 Hz, H-4$_\alpha$), 3.68 – 3.61 (m, 2.1H, H-4'$_\alpha$, H-4'$_\beta$), 3.58 (dd, 1H, *J* = 9.7, 8.8 Hz, H-4$_\beta$), 3.56 (dd, 1.1H, *J* = 9.5, 4.1 Hz, H-2$_\alpha$), 3.48 (dd, 1H, *J* = 8.8, 7.7 Hz, H-2'$_\beta$), 3.45 (t, 1H, *J* = 10.2 Hz, H-6'$_\beta$), 3.38 (s, 3H, CH_3 OMe$_\beta$), 3.36 (s, 3.3H, CH_3 OMe$_\alpha$), 3.32 (dt, 0.9H, *J* = 9.7, 4.8 Hz, H-5'$_\beta$), 1.42 (d, 3H, *J* = 6.2 Hz, H-6$_\alpha$), 1.36 (d, 2.7H, *J* = 6.3 Hz, H-6$_\beta$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.0 (C=O), 138.8, 138.7, 138.6, 138.4, 138.3, 138.1, 137.4 (C_q), 133.3, 133.3 (CH_{arom}), 129.9 (C_q), 129.9, 129.1, 129.0, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 127.9, 127.8, 127.8, 127.7, 127.7, 127.5, 127.3, 126.7, 126.1, 126.1 (CH_{arom}), 103.8 (C-1'$_\beta$), 101.2 (CHPh$_\alpha$), 101.2 (CHPh$_\beta$), 98.3 (C-1'$_\alpha$), 97.0 (C-1$_\beta$), 96.9 (C-1$_\alpha$), 83.6 (C-4$_\beta$), 82.9 (C-2'$_\beta$), 82.3 (C-4'$_\alpha$), 81.8 (C-4'$_\beta$) , 81.4 (C-3'$_\beta$), 80.3 (C-3$_\alpha$), 79.2 (C-3'$_\alpha$), 78.9 (C-4$_\alpha$), 78.9 (C-2'$_\alpha$), 77.8 (C-3$_\beta$), 75.8, 75.4, 75.3 (CH_2 Bn), 74.7 (C-2$_\alpha$), 74.0 (CH_2 Bn), 73.8 (C-2$_\beta$), 68.9 (C-6'$_\alpha$), 68.8 (C-6'$_\beta$), 66.8 (C-5$_\beta$), 66.0 (C-5'$_\beta$), 65.9 (C-5$_\alpha$), 63.4 (C-5'$_\alpha$), 55.4 (OMe$_\beta$), 55.2 (OMe$_\alpha$) , 19.1 (C-6$_\alpha$), 17.9 (C-6$_\beta$); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{54}NO_{11}$ 820.36914, found 820.36967.

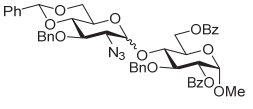


Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2-*O*-benzoyl-3-*O*-benzyl-6-deoxy-α-D-glucopyranoside (6B). Donor **B** and acceptor **6** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **6B** (65 mg, 88 µmol, 88%, α:β = 1:5) as a colorless oil. R_f: 0.76 (4/1 pentane/EtOAc); IR (thin film): 698, 737, 995, 1092, 1273, 1366, 1454, 1721, 2110, 2878; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.05 – 7.98 (m, 2H, CH_{arom}), 7.60 – 7.11 (m, 18H, CH_{arom}), 5.49 (s, 1H, C*H*Ph), 5.06 (dd, 1H, *J* = 10.0, 3.7 Hz, H-2), 4.97 (d, 1H, *J* = 3.8 Hz, H-1), 4.94 – 4.82 (m, 2H, 2xC*H*H Bn), 4.79 (d, 1H, *J* = 11.2 Hz, CH*H* Bn), 4.74 (d, 1H, *J* = 11.1 Hz, CH*H* Bn), 4.53 (d, 1H, *J* = 8.1 Hz, H-1'), 4.12 – 4.01 (m, 2H, H-6', H-3), 3.89 (qd, 1H, *J* = 6.3, 3.4 Hz, H-5), 3.65 (t, 1H, *J* = 9.0 Hz, H-4'), 3.62 – 3.52 (m, 2H, H-3', H-4), 3.49 – 3.40 (m, 2H, H-2', H-6'), 3.37 (s, 3H, CH_3 OMe), 3.25 (td, 1H, *J* = 9.6, 4.9 Hz, H-5'), 1.43 (d, 3H, *J* = 6.2 Hz, H-6); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.0 (C=O), 138.7, 137.8, 137.2 (C_q), 133.3, 129.9 (CH_{arom}), 129.8 (C_q), 129.2, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.0, 127.7, 127.5, 127.4, 126.1 (CH_{arom}), 102.4 (C-1'), 101.3 (CHPh), 96.9 (C-1), 83.8 (C-4), 81.7 (C-4'), 79.4 (C-3'), 78.1 (C-3), 75.3, 75.1 (CH_2 Bn), 74.0 (C-2), 68.5 (C-6'), 67.2 (C-2'), 66.4 (C-5), 66.2 (C-5'), 55.4 (OMe), 18.0 (CO_2Me); Diagnostic peaks for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 –

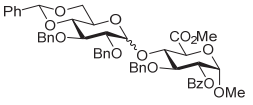
8.06 (m, 2H), 5.62 (d, 1H, *J* = 4.2 Hz, H-1'), 5.58 (s, 1H, C*H*Ph), 5.12 (dd, 1H, *J* = 9.8, 3.7 Hz, H-2), 4.31 – 4.23 (m, 2H), 3.78 – 3.66 (m, 2H) 1.39 (d, 3H, *J* = 6.2 Hz); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 166.0, 138.1, 137.9, 137.2, 133.5, 129.6, 127.7, 126.0, 98.8, 82.6, 80.4, 80.1, 76.4, 75.2, 75.0, 68.6, 65.6, 63.4, 62.8, 18.8; HRMS: $[M+Na]^+$ calcd for $C_{41}H_{43}N_3O_{10}Na$ 760.2841, found 760.2853.



Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,6-di-*O*-benzoyl-3-*O*-benzyl-α-D-glucopyranoside (7A). Donor **A** and acceptor **7** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **7A** (81 mg, 88 µmol, 88%, α:β = 3.5:1) as a white solid. R_f: 0.67 (4/1 pentane/EtOAc); IR (thin film): 698, 712, 737, 995, 1026, 1090, 1271, 1371, 1452, 1720, 2920; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC, HMBC): δ 8.12 – 8.06 (m, 2H, CH_{arom}), 8.01 – 7.97 (m, 2H, CH_{arom}), 7.61 – 6.99 (m, 26H, CH_{arom}), 5.57 (d, 1H, *J* = 3.9 Hz, H-1'$_\alpha$), 5.49 (s, 1H, C*H*Ph), 5.17 (dd, 1H, *J* = 9.9, 3.7 Hz, H-2), 5.02 (d, 1H, *J* = 3.5 Hz, H-1), 4.96 – 4.88 (m, 1H, C*H*H Bn), 4.87 – 4.82 (m, 1H, C*H*H Bn), 4.81 – 4.71 (m, 4H, C*H*H Bn, 2xCH*H* Bn, H-6), 4.65 – 4.55 (m, 2H, H-6, CH*H* Bn), 4.33 (ddd, 1H, *J* = 9.9, 6.5, 1.7 Hz, H-3), 4.17 – 4.02 (m, 4H, H-4, H-6', H-5, H-3'), 3.88 (td, 1H, *J* = 9.8, 4.7 Hz, H-5'), 3.63 – 3.57 (m, 2H, H-6', H-4'), 3.55 (dd, 1H, *J* = 9.5, 3.9 Hz, H-2'), 3.40 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC, HMBC): δ 166.2, 165.9 (C=O), 138.7, 138.3, 138.2, 137.5 (C_q), 133.4, 133.3 (CH_{arom}), 129.9 (C_q), 129.9, 129.7 (CH_{arom}), 129.6 (C_q), 129.0, 128.6, 128.5, 128.4, 128.3, 128.3, 128.1, 127.9, 127.7, 127.7, 127.4, 127.0, 126.2 (CH_{arom}), 101.4 (CHPh), 98.9 (C-1'), 97.0 (C-1), 82.4 (C-4'), 80.2 (C-3), 78.8 (C-2'), 78.7 (C-3'), 75.3 (CH_2 Bn) , 75.1 (C-4), 74.5 (CH_2 Bn) , 74.1 (C-2), 74.1 (CH_2 Bn), 68.9 (C-6'), 68.4 (C-5), 63.8 (C-5'), 63.7 (C-6), 55.5 (OMe); Diagnostic peaks for the β-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.06 – 8.01 (m, 2H), 5.50 (s, 1H, C*H*Ph), 5.08 (dd, 1H, *J* = 9.3, 3.8 Hz, H-2), 4.53 (dd, 1H, *J* = 12.1, 4.5 Hz, H-6), 3.76 (t, 1H, *J* = 9.0 Hz, H-3'), 3.27 (td, 1H, *J* = 9.1, 8.4, 4.3 Hz, H-5'); ^{13}C-APT NMR ($CDCl_3$, 126 MHz): δ 166.0, 165.9 (C=O), 138.5, 138.5, 137.3, 133.4, 130.0, 130.0, 129.8, 129.1, 128.6, 128.4, 128.1, 127.8, 127.8, 127.7, 126.1 (CH_{arom}), 103.4 (C-1'), 101.2 (CHPh), 97.1 (C-1), 82.8 (C-2'), 81.8 (C-4'), 81.4 (C-3'), 77.9, 77.8 (C-3, C-4), 75.9, 75.6, 75.3 (CH_2 Bn), 73.4 (C-2), 68.9 (C-5), 68.8 (C-6'), 66.2 (C-5'), 62.7 (C-6), 55.5 (OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{58}NO_{13}$ 940.39027, found 940.39106.

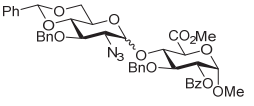


Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,6-di-*O*-benzoyl-3-*O*-benzyl-α-D-glucopyranoside (7B). Donor **B** and acceptor **7** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **7B** (75 mg, 87 µmol, 87%, α:β = 1.3:1) as a colorless oil. R_f: 0.66 (4/1 pentane/EtOAc); IR (thin film): 698, 737, 918, 995, 1026, 1092, 1173, 1269, 1369, 1450, 1721, 2110, 2866; Data reported for a 1.3:1 mixture of anomers: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.14 – 7.98 (m, 9.2H, CH_{arom}), 7.64 – 7.13 (m, 48.3H, CH_{arom}), 5.67 (d, 1.3H, *J* = 4.1 Hz, H-1'$_\alpha$), 5.51 (s, 1.3H, C*H*Ph$_\alpha$), 5.49 (s, 1H, C*H*Ph$_\beta$), 5.18 (dd, 1.3H, *J* = 9.8, 3.6 Hz, H-2$_\alpha$), 5.12 (dd, 1H, *J* = 9.6, 3.7 Hz, H-2$_\beta$), 5.05 (d, 1H, *J* = 3.7 Hz, H-1$_\beta$), 5.03 (d, 1.3H, *J* = 3.6 Hz, H-1$_\alpha$), 4.98 (d, 1.3H, *J* = 10.9 Hz, C*H*H Bn$_\alpha$), 4.96 – 4.85 (m, 4.6H, CH_2 Bn$_\alpha$, 2xC*H*H Bn$_\beta$), 4.80 – 4.73 (m, 5.6H, H-6$_\beta$, 2xCH*H* Bn$_\beta$, CH*H* Bn$_\alpha$ H-6$_\alpha$, H-6$_\beta$), 4.67 (dd, 1H, *J* = 12.2, 2.9 Hz, H-6$_\beta$), 4.53 (dd, 1.3H, *J* = 12.0, 2.6 Hz, H-6$_\alpha$), 4.49 (d, 1H, *J* = 8.0 Hz, H-1'$_\beta$), 4.42 – 4.33 (m, 1.3H, H-3$_\alpha$), 4.21 – 4.13 (m, 1H, H-3$_\beta$), 4.12 – 4.01 (m, 8.2H, H-3'$_\alpha$, H-4$_\alpha$, H-4$_\beta$, H-5$_\beta$, H-5$_\alpha$, H-6'$_\alpha$, H-6'$_\beta$), 3.87 (td, 1.3H, *J* = 9.9, 4.9 Hz, H-5'$_\alpha$), 3.72 – 3.53 (m, 4.6H, H-3'$_\beta$, H-4'$_\alpha$, H-4'$_\beta$, H-6'$_\alpha$), 3.51 – 3.40 (m, 8.9H, H-2'$_\beta$, H-6'$_\beta$, CH_3 OMe$_\alpha$, CH_3 OMe$_\beta$), 3.36 (dd, 1.3H, *J* = 10.0, 4.1 Hz, H-2'$_\alpha$), 3.18 (td, 1H, *J* = 9.4, 4.9 Hz, H-5'$_\beta$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.2, 166.2, 165.9, 165.9 (C=O), 138.4, 137.9, 137.8, 137.7, 137.2, 137.1 (C_q), 133.6, 133.5, 133.4, 133.3 (CH_{arom}), 129.9, 129.9 (C_q), 129.8 (CH_{arom}), 129.8, 129.7 (C_q), 129.7, 129.5, 129.2, 129.1, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.0, 127.8, 127.8, 127.7, 127.6, 126.2, 126.0 (CH_{arom}), 102.0 (C-1'$_\beta$), 101.4 (CHPh$_\alpha$), 101.3 (CHPh$_\beta$), 99.0 (C-1'$_\alpha$), 97.1 (C-1$_\alpha$). 97.1 (C-1$_\beta$), 82.6 (C-4'$_\alpha$), 81.7 (C-4'$_\beta$), 80.4 (C-3$_\alpha$), 79.7 (C-3'$_\beta$), 78.1 (C-3$_\beta$), 77.9 (C-4$_\beta$), 76.2 (C-3'$_\alpha$), 75.6, 75.2 (CH_2 Bn), 75.0(C-4$_\alpha$), 74.6 (C-2$_\alpha$), 73.5 (C-2$_\beta$), 68.6 (C-5$_\beta$), 68.5, 68.5 (C-6'$_\alpha$, C-6'$_\beta$), 68.1 (C-5$_\alpha$), 66.8 (C-2'$_\beta$), 66.3 (C-5'$_\beta$), 63.8 (C-5'$_\alpha$), 63.4 (C-6$_\alpha$), 62.9 (C-6$_\beta$), 62.8 (C-2'$_\alpha$), 55.6 (OMe$_\alpha$), 55.6 (OMe$_\beta$); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{49}N_4O_{13}$ 875.34980, found 875.35039.

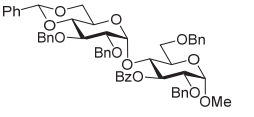


Methyl (methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2-*O*-benzoyl-3-*O*-benzyl-α-D-glucopyranosyl uronate) (8A). Donor **A** and acceptor **8** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **8A** (81 mg, 96 µmol, 96%, α:β = 4.8 : 1) as a colorless oil. R_f: 0.57 (4/1 pentane/EtOAc); IR (thin film): 698, 914, 995, 1045, 1088, 1200, 1267, 1369, 1452, 1722, 1751, 2938; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC, HMBC): δ 8.00 – 7.94 (m, 2H, CH_{arom}), 7.59 – 7.01 (m, 23H), 5.54 (s, 1H, C*H*Ph), 5.28 (d, 1H, *J* = 3.8 Hz, H-1'), 5.16 – 5.12 (m, 1H, H-2), 5.06 (d, 1H, *J* = 3.6 Hz, H-1), 4.95 – 4.68 (m, 5H, 2xCH_2 Bn, C*H*H Bn), 4.60 (d, 1H, *J* = 11.8 Hz, CH*H* Bn), 4.31 (dd, 1H, *J* = 8.9, 3.6 Hz, H-6'), 4.28 – 4.19 (m, 3H, H-3, H-4, H-5), 4.02 (t, 1H, *J* = 9.3 Hz, H-3'), 3.78 (s, 3H, CH_3 CO_2Me), 3.74 – 3.63 (m, 2H, H-5', H-6'), 3.60 (t, 1H, *J* = 9.2 Hz,

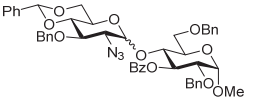
H-4'), 3.52 (dd, 1H, *J* = 9.5, 3.8 Hz, H-2'), 3.41 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC, HMBC): δ 169.5 (C=O CO_2Me), 165.9 (C=O OBz), 138.6, 138.3, 138.0, 137.6 (C_q), 133.4 (CH_{arom}), 130.0, 129.9 (CH_{arom}), 129.6 (C_q), 129.0, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.4, 127.4, 126.1 (CH_{arom}), 101.3 (CHPh), 98.9 (C-1'), 97.6 (C-1), 82.1 (C-4'), 79.0 (C-2), 78.4 (C-4), 78.2 (C-3'), 77.8 (C-3), 75.2, 74.9, 73.7 (CH_2 Bn), 73.1 (C-2), 70.7 (C-5), 68.6 (C-6'), 63.4 (C-5'), 55.9 (OMe), 52.8 (CO_2Me); Diagnostic peaks for the β-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05 – 8.00 (m, 1H), 5.46 (s, 1H, CHPh), 5.10 (dd, 1H, *J* = 9.4, 3.6 Hz, H-2), 4.09 (ddd, 1H, *J* = 9.4, 6.7, 1.5 Hz, H-3), 3.34 (td, 1H, *J* = 9.6, 4.7 Hz, H-5'); ^{13}C-APT NMR ($CDCl_3$, 126 MHz): δ 169.7 (C=O), 138.6, 138.5, 137.4 (C_q), 129.8, 128.3, 128.3, 128.1, 127.8, 127.7, 127.6, 126.1 (CH_{arom}), 103.1 (C-1'), 101.2 (CHPh), 97.6 (C-1), 82.4 (C-2'), 81.8, 81.3, 78.0, 77.0, 75.6 (C-3), 75.2, 72.6 (C-2), 70.4, 68.7, 65.9 (C-5'), 56.1 (OMe), 52.8 (CO_2Me); HRMS: $[M+NH_4]^+$ calcd for $C_{49}H_{54}NO_{13}$ 864.35897, found 864.36009.



Methyl (methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2-*O*-benzoyl-3-*O*-benzyl-α-D-glucopyranosyl uronate) (8B). Donor **B** and acceptor **8** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **8B** (64 mg, 82 µmol, 82%, α:β = 1.18 : 1) as a colorless oil. R_f: 0.73 (4/1 pentane/EtOAc); IR (thin film): 698, 737, 918, 991, 1045, 1092, 1200, 1265, 1366, 1454, 1724, 1751, 2110, 2940; Data reported for a 1.18 : 1 mixture of anomers: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.11 – 8.04 (m, 2H, CH_{arom}), 8.04 – 7.97 (m, 2.2H, CH_{arom}), 7.63 – 7.09 (m, 39.6H, CH_{arom}), 5.55 (s, 1H), 5.48 (d, 2H, *J* = 3.3 Hz), 5.16 (dd, 1H, *J* = 9.6, 3.6 Hz), 5.55 (s, 1.2H, C*H*Ph$_\alpha$), 5.50 – 5.44 (m, 2.2H, H-1'$_\alpha$, C*H*Ph$_\beta$), 5.16 (dd, 1H, *J* = 9.6, 3.6 Hz, H-2$_\alpha$), 5.12 – 5.07 (m, 3.2H, H-1$_\alpha$, H-1$_\beta$, H-2$_\beta$), 4.96 (d, 1.2H, *J* = 11.0 Hz, C*H*H Bn$_\alpha$), 4.93 – 4.83 (m, 4.4H, 2xC*H*H Bn$_\beta$, CH_2 Bn$_\alpha$), 4.82 – 4.74 (m, 2.2H, CH*H* Bn$_\alpha$, CH*H* Bn$_\beta$), 4.73 (d, 1H, *J* = 11.1 Hz, CH*H* Bn$_\beta$), 4.51 (d, 1H, *J* = 8.1 Hz, H-1'$_\beta$), 4.37 – 4.26 (m, 4.6H, H-5$_\alpha$, H-5$_\beta$, H-3$_\alpha$, H-6'$_\alpha$), 4.26 – 4.16 (m, 2.2H, H-4$_\alpha$, H-4$_\beta$), 4.16 – 4.05 (m, 2H, H-3$_\beta$, H-6'$_\beta$), 4.00 (dd, 1.2H, *J* = 10.0, 9.0 Hz, H-3'$_\alpha$), 3.86 (s, 3H, CH_3 CO_2Me_β), 3.85 (s, 3.6H, CH_3 CO_2Me_α), 3.71 – 3.64 (m, 2.4H, H-6'$_\alpha$, H-4'$_\alpha$), 3.63 – 3.50 (m, 3.2H, H-3'$_\beta$, H-5'$_\alpha$, H-4'$_\beta$), 3.47 – 3.33 (m, 8.8H, CH_3 OMe_α, CH_3 OMe_β, H-2'$_\alpha$ H-2'$_\beta$, H-6'$_\beta$), 3.29 (td, 1H, *J* = 9.5, 4.8 Hz, H-5'$_\beta$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 169.7, 169.6 (C=O CO_2Me), 165.9, 165.8 (C=O OBz), 138.4, 137.9, 137.9, 137.8, 137.4, 137.2 (C_q), 133.6, 133.4, 129.9, 129.9 (CH_{arom}), 129.6, 129.4 (C_q), 129.2, 129.1, 128.7, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.0, 128.0, 127.8, 127.8, 127.6, 127.6, 126.1, 126.1 (CH_{arom}), 102.3 (C-1'$_\beta$), 101.5 (CHPh$_\alpha$), 101.4 (CHPh$_\beta$), 98.6 (C-1'$_\alpha$), 97.7 (C-1$_\alpha$), 97.7 (C-1$_\beta$), 82.5 (C-4'$_\alpha$), 81.6 (C-3'$_\beta$), 79.6 (C-3$_\alpha$), 79.4 (C-4'$_\beta$), 79.3 (C-4$_\beta$), 77.3 (C-3$_\beta$), 76.4 (C-3'$_\alpha$), 75.7 (C-4$_\alpha$), 75.5, 75.4, 75.1, 75.1 (CH_2 Bn), 73.9 (C-2$_\alpha$), 72.9 (C-2$_\beta$), 70.1 (C-5$_\alpha$), 70.0 (C-5$_\beta$), 68.5 (C-6'$_\alpha$), 66.7(C-2'$_\beta$), 66.2 (C-5'$_\beta$), 63.2 (C-5'$_\alpha$), 62.9 (C-2'$_\alpha$), 56.0 ($OMe_{\alpha,\beta}$), 53.1 (CO_2Me_α), 52.9 (CO_2Me_β); HRMS: $[M+NH_4]^+$ calcd $C_{42}H_{47}N_4O_{12}$ for 799.31850, found 799.31937.

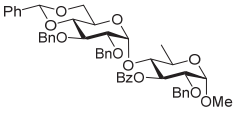


Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-2,6-di-*O*-benzyl-3-*O*-benzoyl-α-D-glucopyranoside (9A). Donor **A** and acceptor **9** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **9A** (86 mg, 95 µmol, 95%, α:β = >20:1) as a colorless oil. R_f: 0.26 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = -0.9° (*c* = 1.0, $CHCl_3$); IR (thin film): 696, 746, 912, 995, 1047, 1088, 1269, 1369, 1452, 1728, 2924; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.09 – 8.02 (m, 2H, CH_{arom}), 7.61 – 7.11 (m, 28H, CH_{arom}), 5.94 (t, 1H, *J* = 9.6 Hz, H-3), 5.46 (s, 1H, C*H*Ph), 5.03 (d, 1H, *J* = 3.5 Hz, H-1'), 4.79 – 4.72 (m, 2H, H-1, C*H*H Bn), 4.63 – 4.50 (m, 5H, 2xCH_2 Bn, CH*H* Bn), 4.40 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.21 (t, 1H, *J* = 9.4 Hz, H-4), 4.13 – 4.04 (m, 2H, CH*H* Bn, H-6'), 3.97 – 3.88 (m, 3H, H-3', H-5, H-6), 3.85 (dd, 1H, *J* = 9.9, 4.8 Hz, H-5'), 3.71 – 3.67 (m, 1H, H-6), 3.65 (t, 1H, *J* = 3.0 Hz, H-2'), 3.55 (t, 1H, *J* = 10.2 Hz, H-6'), 3.44 (t, 1H, *J* = 9.7 Hz, H-4'), 3.41 (s, 3H, CH_3 OMe), 3.26 (dd, 1H, *J* = 9.4, 3.5 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 165.4 (C=O), 138.8, 138.0, 137.9, 137.8, 137.6 (C_q), 132.9 (CH_{arom}), 130.7 (C_q), 129.9, 128.9, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 127.9, 127.9, 127.8, 127.7, 127.6, 126.2 (CH_{arom}), 101.3 (CHPh), 98.0 (C-1'), 97.7 (C-1), 81.9 (C-4), 78.8 (C-2'), 78.3 (C-3'), 77.2 (C-2), 75.4 (CH_2 Bn), 73.9 (C-3), 73.7 (C-4), 73.6, 72.9, 72.8 (CH_2 Bn), 69.7 (C-5), 69.0 (C-6'), 68.3 (C-6), 63.6 (C-5'), 55.4 (OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{60}NO_{12}$ 926.41100, found 926.41201.

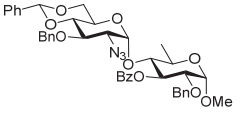


Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,6-di-*O*-benzyl-3-*O*-benzoyl-α-D-glucopyranoside (9B). Donor **B** and acceptor **9** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **9B** (65 mg, 77 µmol, 77%, α:β = 6.7:1) as a light yellow oil. R_f: 0.28 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = -25.5° (*c* = 1.0, $CHCl_3$); IR (thin film): 698, 745, 995, 1092, 1165, 1269, 1369, 1454, 1732, 2110, 2866; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.11 – 8.05 (m, 2H, CH_{arom}), 7.61 – 7.09 (m, 23H, CH_{arom}), 5.85 (t, 1H, *J* = 9.6 Hz, H-3), 5.50 (s, 1H, C*H*Ph), 5.04 (d, 1H, *J* = 3.7 Hz, H-1'), 4.82 (d, 1H,

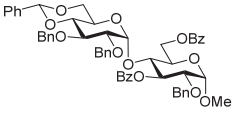
J = 10.6 Hz, C*H*H Bn), 4.75 (d, 1H, *J* = 3.5 Hz, H-1), 4.64 – 4.54 (m, 5H, CH*H* Bn, 2xCH$_2$ Bn), 4.10 (dd, 1H, *J* = 10.3, 4.8 Hz, H-6), 4.05 (t, 1H, *J* = 9.5 Hz, H-4), 3.96 – 3.81 (m, 4H, H-3', H-5', H-5, H-6), 3.76 – 3.67 (m, 1H, H-6'), 3.64 – 3.57 (m, 2H, H-2, H-6'), 3.56 (t, 1H, *J* = 9.3 Hz, H-4'), 3.42 (s, 3H, CH$_3$ OMe), 3.23 (dd, 1H, *J* = 9.9, 3.7 Hz, H-2'); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 165.4 (C=O), 137.9, 137.8, 137.7, 137.2 (C$_q$), 132.8 (CH$_{arom}$), 130.7 (C$_q$), 129.7, 129.1, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 126.1 (CH$_{arom}$), 101.5 (CHPh), 99.5 (C-1'), 97.7 (C-1), 82.5 (C-4'), 77.1 (C-4), 76.7 (C-3'), 76.5 (C-2), 75.3, 73.7 (CH$_2$ Bn), 73.5 (C-3), 72.8 (CH$_2$ Bn), 69.6 (C-5), 68.8 (C-6'), 68.7 (C-6), 63.8 (C-5'), 63.5 (C-2'), 55.6 (OMe); Diagnostic peaks for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.66 (dd, 1H, *J* = 10.0, 8.7 Hz, H-3), 5.19 (s, 1H, C*H*Ph), 4.70 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.69 (d, 1H, *J* = 11.4 Hz, CH*H* Bn), 4.44 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 3.99 (dd, 1H, *J* = 10.8, 2.5 Hz, H-6) 2.87 (td, 1H, *J* = 9.3, 4.9 Hz, H-5'), 2.52 (t, 1H, *J* = 10.4 Hz, H-6'); ^{13}C-APT NMR (CDCl$_3$, 101 MHz): δ 101.5 (C-1'), 101.0 (CHPh), 98.0 (C-1), 81.2, 79.1, 76.1, 74.6, 73.7, 72.8, 72.6, 69.4, 67.8, 67.6, 65.9, 65.7; HRMS: [M+NH$_4$]$^+$ calcd for $C_{48}H_{53}N_4O_{11}$ 861.37053, found 861.37106.



Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-2-*O*-benzyl-3-*O*-benzoyl-6-deoxy-α-D-glucopyranoside (10A). Donor **A** and acceptor **10** were condensed using the general procedure for Tf$_2$O/Ph$_2$SO mediated glycosylations (E) yielding product **10A** (67 mg, 83 µmol, 83%, α:β = >20:1) as a white solid. R$_f$: 0.38 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = -3.6° (*c* = 1.0, CHCl$_3$); IR (thin film): 698, 745, 995, 1053, 1092, 1269, 1454, 1728, 2866; ^{1}H NMR (CDCl$_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.07 – 8.01 (m, 2H, CH$_{arom}$), 7.62 – 7.06 (m, 23H, CH$_{arom}$), 5.98 – 5.87 (m, 1H, H-3), 5.48 (s, 1H, C*H*Ph), 5.10 (d, 1H, *J* = 3.8 Hz, H-1'), 4.80 (d, 1H, *J* = 11.1 Hz, C*H*H Bn), 4.70 – 4.62 (m, 2H, H-1, CH*H* Bn), 4.57 (d, 1H, *J* = 12.5 Hz, C*H*H Bn), 4.52 (d, 1H, *J* = 12.5 Hz, CH*H* Bn), 4.42 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.24 – 4.13 (m, 2H, H-6', CH*H* Bn), 4.02 – 3.85 (m, 3H, H-3', H-5, H-5'), 3.70 – 3.62 (m, 2H, H-4', H-6'), 3.62 – 3.55 (m, 1H, H-2), 3.49 (t, 1H, *J* = 9.5 Hz, H-4), 3.41 (s, 3H, CH$_3$ OMe), 3.33 (dd, 1H, *J* = 9.5, 3.8 Hz, H-2'), 1.36 (d, 3H, *J* = 6.2 Hz, H-6); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 165.2 (C=O), 138.7, 137.8, 137.4 (C$_q$), 133.0 (CH$_{arom}$), 130.6 (C$_q$), 129.9, 129.0, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 127.9, 127.7, 127.6, 126.1 (CH$_{arom}$), 101.3 (CHPh), 98.1 (C-1'), 97.3 (C-1), 81.9 (C-4), 79.4 (C-4'), 78.5 (C-2'), 78.4 (C-3'), 77.6 (C-2), 75.5 (CH$_2$ Bn), 73.9 (C-3), 73.1, 72.6 (CH$_2$ Bn), 68.9 (C-6'), 66.1 (C-5), 63.5 (C-5'), 55.3 (OMe), 18.7 (C-6); HRMS: [M+NH$_4$]$^+$ calcd for $C_{48}H_{54}NO_{11}$ 820.36914, found 820.36983.

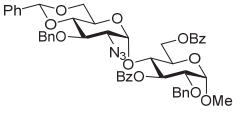


Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl)-2-*O*-benzyl-3-*O*-benzoyl-6-deoxy-α-D-glucopyranoside (10B). Donor **B** and acceptor **10** were condensed using the general procedure for Tf$_2$O/Ph$_2$SO mediated glycosylations (E) yielding product **10B** (60 mg, 81 µmol, 81%, α:β = 14:1) as a colorless oil. R$_f$: 0.25 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = -30.0° (*c* = 1.0, CHCl$_3$); IR (thin film): 698, 748, 995, 1053, 1096, 1269, 1373, 1454, 1732, 2110, 2931; Data for the α-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.07 – 8.01 (m, 2H, CH$_{arom}$), 7.61 – 7.09 (m, 18H, CH$_{arom}$), 5.84 (t, 1H, *J* = 9.6 Hz, H-3), 5.53 (s, 1H, C*H*Ph), 5.07 (d, 1H, *J* = 4.0 Hz, H-1'), 4.87 (d, 1H, *J* = 10.8 Hz, C*H*H Bn), 4.71 – 4.64 (m, 2H, CH*H* Bn, H-1), 4.61 – 4.47 (m, 2H, CH$_2$ Bn), 4.21 (dd, 1H, *J* = 10.4, 5.0 Hz, H-6'), 4.00 – 3.83 (m, 3H, H-3', H-5', H-5), 3.69 (t, 1H, *J* = 10.4 Hz, H-6'), 3.61 (t, 1H, *J* = 9.3 Hz, H-4'), 3.57 – 3.46 (m, 2H, H-2, H-4), 3.42 (s, 3H, CH$_3$ OMe), 3.19 (dd, 1H, *J* = 10.0, 4.0 Hz, H-2'), 1.35 (d, 3H, *J* = 6.2 Hz, H-6); ^{13}C-APT NMR (CDCl$_3$, 101 MHz, HSQC, HMBC): δ 165.3 (C=O), 137.8, 137.7, 137.1 (C$_q$), 132.8 (CH$_{arom}$), 130.6 (C$_q$), 129.6, 129.1, 128.5, 128.4, 128.4, 128.4, 128.3, 128.0, 127.9, 127.9, 126.0 (CH$_{arom}$), 101.3 (CHPh), 100.0 (C-1'), 97.5 (C-1), 82.4 (C-4'), 82.4 (C-4), 77.4 (C-2), 76.6 (C-3'), 75.2 (CH$_2$ Bn), 73.5 (C-3), 72.6 (CH$_2$ Bn), 68.5 (C-6'), 65.7 (C-5), 63.5 (C-5'), 63.0 (C-2'), 55.4 (OMe), 18.3 (C-6); Diagnostic peaks for the β-anomer: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.66 (t, 1H, *J* = 9.5 Hz, H-3), 5.23 (s, 1H, C*H*Ph), 3.04 (td, 1H, *J* = 9.7, 5.1 Hz, H-5'), 2.63 (t, 1H, *J* = 10.4 Hz, H-6'), 1.38 (d, 3H, *J* = 6.3 Hz, H-6); ^{13}C-APT NMR (CDCl$_3$, 101 MHz): δ 102.6 (C-1'), 101.0 (CHPh), 97.5 (C-1), 83.3, 81.3, 81.1, 79.2, 74.8, 72.7, 67.8, 66.4, 66.1, 65.9, 17.7; HRMS: [M+Na]$^+$ calcd for $C_{41}H_{43}N_3O_{10}Na$ 760.2841, found 760.2852.

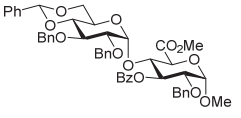


Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-2-*O*-benzyl-3,6-di-*O*-benzoyl-α-D-glucopyranoside (11A). Donor **A** and acceptor **11** were condensed using the general procedure for Tf$_2$O/Ph$_2$SO mediated glycosylations (E) yielding product **11A** (88 mg, 95 µmol, 95%, α:β = >20:1) as a white solid. R$_f$: 0.25 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = +21.1° (*c* = 1.0, CHCl$_3$); IR (thin film): 698, 712, 748, 995, 1026, 1090, 1267, 1371, 1452, 1724; ^{1}H NMR (CDCl$_3$, 400 MHz, HH-COSY, HSQC): δ 8.12 – 8.06 (m, 2H, CH$_{arom}$), 8.06 – 8.01 (m, 2H, CH$_{arom}$), 7.62 – 7.51 (m, 2H, CH$_{arom}$), 7.46 – 7.32 (m, 9H, CH$_{arom}$), 7.29 – 7.11 (m, 15H, CH$_{arom}$), 5.99 (dd, 1H, *J* = 9.9, 9.0 Hz, H-3), 5.42 (s, 1H, C*H*Ph), 4.97 (d, 1H, *J* = 3.6 Hz, H-1'), 4.84 – 4.68 (m, 3H, H-1, H-6, C*H*H Bn), 4.67 – 4.51 (m, 4H, CH*H* Bn, CH$_2$ Bn, H-6), 4.36 (d, 1H, *J* = 12.2 Hz, C*H*H Bn), 4.15 (ddd, 1H, *J* = 10.0, 4.4, 2.1 Hz, H-5), 4.11 – 4.01 (m, 3H, H-6', H-4, CH*H* Bn), 3.98 (t, 1H, *J* = 9.4 Hz, H-3'), 3.88 (td, 1H, *J* = 9.9, 4.8 Hz, H-5'), 3.67 (dd, 1H, *J* = 9.9, 3.5 Hz,

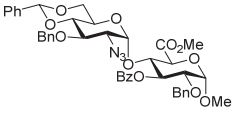
H-2), 3.54 (t, 1H, *J* = 10.3 Hz, H-6'), 3.46 (d, 1H, *J* = 9.5 Hz, H-4'), 3.44 (s, 3H, CH_3 OMe), 3.29 (dd, 1H, *J* = 9.5, 3.6 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.1, 165.3 (C=O), 138.7, 138.1, 137.7, 137.4 (C_q), 133.2, 133.0 (CH_{arom}), 130.7, 130.0 (C_q), 129.9, 129.8, 128.9, 128.5, 128.5, 128.4, 128.3, 128.2, 128.2, 128.2, 128.0, 127.9, 127.7, 127.6, 126.2 (CH_{arom}), 101.4 (CHPh), 99.2 (C-1'), 97.5 (C-1), 81.9 (C-4'), 78.5 (C-2'), 78.3 (C-3'), 77.3 (C-2), 75.9 (C-4), 75.4 (CH_2 Bn), 73.3 (C-3), 73.2 (CH_2 Bn), 72.8 (CH_2 Bn), 68.8 (C-6'), 68.6 (C-5), 63.9 (C-5'), 63.5 (C-6), 55.5 (OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{58}NO_{13}$ 940.39027, found 940.39105.



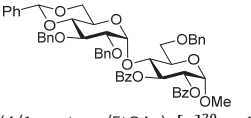
Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl)-2-*O*-benzyl-3,6-di-*O*-benzoyl-α-D-glucopyranoside (11B). Donor **B** and acceptor **11** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **11B** (73 mg, 85 µmol, 85%, α:β = >20:1) as a colorless oil. R_f: 0.31 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = +0.6° (*c* = 1.0, $CHCl_3$); IR (thin film): 748, 995, 1030, 1096, 1169, 1269, 1315, 1373, 1450, 1724, 2110, 2924; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.08 (td, 4H, *J* = 8.2, 1.4 Hz, CH_{arom}), 7.61 – 7.10 (m, 21H, CH_{arom}), 5.91 (t, 1H, *J* = 9.6 Hz, H-3), 5.49 (s, 1H, C*H*Ph), 5.07 (d, 1H, *J* = 3.9 Hz, H-1'), 4.85 (d, 1H, *J* = 10.7 Hz, C*H*H Bn), 4.76 (d, 1H, *J* = 3.4 Hz, H-1), 4.72 (dd, 1H, *J* = 12.2, 2.1 Hz, H-6), 4.67 (d, 1H, *J* = 10.7 Hz, CH*H* Bn), 4.63 – 4.53 (m, 2H, CH_2 Bn), 4.50 (dd, 1H, *J* = 12.1, 4.7 Hz, H-6), 4.23 (dd, 1H, *J* = 10.4, 4.9 Hz, H-6'), 4.12 (ddd, 1H, *J* = 9.9, 4.6, 2.0 Hz, H-5), 4.00 – 3.86 (m, 3H, H-3', H-4, H-5'), 3.67 – 3.53 (m, 3H, H-4', H-6', H-2), 3.45 (s, 3H, CH_3 OMe), 3.25 (dd, 1H, *J* = 10.0, 3.9 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.2, 165.4 (C=O), 137.8, 137.1 (C_q), 133.3, 132.9 (CH_{arom}), 130.5, 129.9 (C_q), 129.8, 129.1, 128.6, 128.5, 128.4, 128.3, 128.3, 128.0, 127.9, 127.9, 126.1 (CH_{arom}), 101.4 (CHPh), 100.5 (C-1'), 97.6 (C-1), 82.4 (C-4'), 77.8 (C-4), 77.2 (C-2), 76.6 (C-3'), 75.2 (CH_2 Bn), 73.2 (C-3), 72.7 (CH_2 Bn), 68.5 (C-6'), 68.3 (C-5), 64.0 (C-5'), 63.6 (C-6), 63.2 (C-2'), 55.6 (OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{51}N_4O_{12}$ 875.34980, found 875.35050.



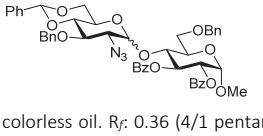
Methyl (methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-2-*O*-benzyl-3-*O*-benzoyl-α-D-glucopyranosyl uronate) (12A). Donor **A** and acceptor **12** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **12A** (73 mg, 86 µmol, 86%, α:β = >20:1) as a white solid. R_f: 0.40 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = -18.4° (*c* = 1.0, $CHCl_3$); IR (thin film): 698, 748, 914, 995, 1047, 1088, 1201, 1267, 1452, 1732, 2931; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.11 – 8.01 (m, 2H, CH_{arom}), 7.59 – 7.51 (m, 1H, CH_{arom}), 7.47 – 7.33 (m, 7H, CH_{arom}), 7.33 – 7.13 (m, 13H, CH_{arom}), 7.09 – 7.02 (m, 2H, CH_{arom}), 5.96 (t, 1H, *J* = 9.6 Hz, H-3), 5.45 (s, 1H, C*H*Ph), 4.93 (d, 1H, *J* = 3.7 Hz, H-1'), 4.80 (d, 1H, *J* = 11.1 Hz, C*H*H Bn), 4.75 (d, 1H, *J* = 3.4 Hz, H-1), 4.69 (d, 1H, *J* = 11.1 Hz, CH*H* Bn), 4.61 – 4.52 (m, 2H, CH_2 Bn), 4.40 – 4.28 (m, 2H, C*H*H Bn, H-5), 4.27 – 4.16 (m, 2H, H-4, H-6'), 3.99 (d, 1H, *J* = 12.2 Hz, CH*H* Bn), 3.92 (t, 1H, *J* = 9.4 Hz, H-3'), 3.74 (s, 3H, CH_3 CO_2Me), 3.69 (dd, 1H, *J* = 10.0, 3.4 Hz, H-2), 3.63 – 3.52 (m, 2H, H-5', H-6'), 3.46 (s, 3H, CH_3 OMe), 3.42 (d, 1H, *J* = 9.2 Hz, H-4'), 3.25 (dd, 1H, *J* = 9.4, 3.7 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 169.9 (C=O CO_2Me), 165.1 (C=O OBz), 138.7, 137.8, 137.5 (C_q), 133.1 (CH_{arom}), 130.5 (C_q), 129.9, 129.0, 128.5, 128.5, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 127.7, 127.6, 126.1 (CH_{arom}), 101.3 (CHPh), 98.8 (C-1'), 98.4 (C-1), 81.6 (C-4'), 78.2 (C-2'), 78.0 (C-3'), 76.5 (C-2), 76.1 (C-4), 75.4, 73.0, 72.8 (CH_2 Bn), 72.7 (C-3), 70.5 (C-5), 68.5 (C-6'), 63.5 (C-5'), 55.9 (OMe), 52.9 (CO_2Me); HRMS: $[M+NH_4]^+$ calcd for $C_{49}H_{54}NO_{13}$ 864.35897, found 864.36004.



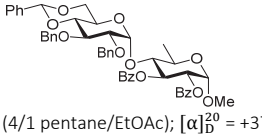
Methyl (methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl)-2-*O*-benzyl-3-*O*-benzoyl-α-D-glucopyranosyl uronate) (12B). Donor **B** and acceptor **12** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **12B** (73 mg, 93 µmol, 93%, α:β = >20:1) as a colorless oil. R_f: 0.33 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = -35.8° (*c* = 1.0, $CHCl_3$); IR (thin film): 698, 748, 914, 995, 1045, 1092, 1200, 1265, 1373, 1454, 1732, 2110, 2936; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.09 – 7.99 (m, 2H, CH_{arom}), 7.62 – 7.53 (m, 1H, CH_{arom}), 7.52 – 7.42 (m, 4H, CH_{arom}), 7.42 – 7.33 (m, 3H, CH_{arom}), 7.29 – 7.16 (m, 10H, CH_{arom}), 5.87 (t, 1H, *J* = 9.7 Hz, H-3), 5.50 (s, 1H, C*H*Ph), 4.96 (d, 1H, *J* = 3.8 Hz, H-1'), 4.84 (d, 1H, *J* = 10.8 Hz, C*H*H Bn), 4.74 (d, 1H, *J* = 3.4 Hz, H-1), 4.67 (d, 1H, *J* = 10.8 Hz, CH*H* Bn), 4.60 – 4.51 (m, 2H, CH_2 Bn), 4.30 (d, 1H, *J* = 9.8 Hz, H-5), 4.28 – 4.21 (m, 1H, H-6'), 4.12 (t, 1H, *J* = 9.5 Hz, H-4), 3.92 (dd, 1H, *J* = 10.0, 9.0 Hz, H-3'), 3.79 (s, 3H, CH_3 CO_2Me), 3.73 – 3.59 (m, 3H, H-5', H-6', H-2), 3.55 (t, 1H, *J* = 9.0 Hz, H-4'), 3.46 (s, 3H, CH_3 OMe), 3.20 (dd, 1H, *J* = 9.9, 3.8 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 169.4 (C=O CO_2Me), 165.2 (C=O OBz), 137.8, 137.5, 137.3 (C_q), 133.0 (CH_{arom}), 130.4 (C_q), 129.7, 129.1, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.1, 127.9, 126.1 (CH_{arom}), 101.5 (CHPh), 99.7 (C-1'), 98.5 (C-1), 82.3 (C-4'), 77.7 (C-4), 76.6 (C-3'), 76.4 (C-2), 75.2 (CH2 Bn), 73.0 (CH2 Bn), 72.3 (C-3), 70.4 (C-5), 68.4 (C-6'), 63.5 (C-5'), 63.1 (C-2'), 56.0 (OMe), 52.9 (CO_2Me); HRMS: $[M+NH_4]^+$ calcd for $C_{42}H_{47}N_4O_{12}$ 799.31850, found 799.31924.



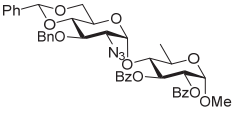
Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-2,3-di-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside (13A). Donor **A** and acceptor **13** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **13A** (83 mg, 90 µmol, 90%, α:β = >20:1) as a colorless oil. R_f: 0.53 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = +33.1° (*c* = 1.0, $CHCl_3$); IR (thin film): 698, 710, 748, 997, 1088, 1275, 1367, 1452, 1724, 2934; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.03 – 7.91 (m, 4H, CH_{arom}), 7.54 – 7.10 (m, 26H, CH_{arom}), 6.17 (dd, 1H, *J* = 10.2, 9.2 Hz, H-3), 5.48 (s, 1H, C*H*Ph), 5.23 (dd, 1H, *J* = 10.2, 3.6 Hz, H-2), 5.18 (d, 1H, *J* = 3.6 Hz, H-1), 5.05 (d, 1H, *J* = 3.5 Hz, H-1'), 4.78 (d, 1H, *J* = 11.1 Hz, C*H*H Bn), 4.67 – 4.56 (m, 3H, CH_2 Bn, CH*H* Bn), 4.43 – 4.33 (m, 2H, H-4, C*H*H Bn), 4.12 (dd, 1H, *J* = 10.1, 4.8 Hz, H-6'), 4.07 (d, 1H, *J* = 12.3 Hz, CH*H* Bn), 4.05 – 3.97 (m, 2H, H-5, H-6), 3.96 – 3.85 (m, 2H, H-3, H-5'), 3.74 (dd, 1H, *J* = 10.8, 1.6 Hz, H-6), 3.57 (t, 1H, *J* = 10.2 Hz, H-6'), 3.48 (t, 1H, *J* = 9.5 Hz, H-4'), 3.41 (s, 3H, CH_3 OMe), 3.29 (dd, 1H, *J* = 9.4, 3.5 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.1, 165.7 (C=O), 138.8, 138.0, 138.0, 137.6 (C_q), 133.3, 133.0 (CH_{arom}), 130.2 (C_q), 130.0, 129.8 (CH_{arom}), 129.2 (C_q), 129.0, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 127.8, 127.8, 127.7, 127.6, 126.2 (CH_{arom}), 101.3 (CHPh), 98.4 (C-1), 96.9 (C-1'), 81.9 (C-4'), 78.7 (C-2'), 78.3 (C-3'), 75.4 (CH_2 Bn), 73.9 (C-4), 73.6, 73.0 (CH_2 Bn), 72.4 (C-2), 72.3 (C-3), 70.0 (C-5), 69.0 (C-6'), 68.3 (C-6), 63.7 (C-5'), 55.4 (OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{58}NO_{13}$ 940.39027, found 940.39109.



Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl)-2,3-di-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside (13B). Donor **B** and acceptor **13** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **13B** (80 mg, 93 µmol, 93%, α:β = 10:1) as a colorless oil. R_f: 0.36 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = +27.3° (*c* = 1.0, $CHCl_3$); IR (thin film): 710, 748, 999, 1030, 1092, 1277, 1728, 2110, 2932; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.05 – 7.92 (m, 4H, CH_{arom}), 7.56 – 7.19 (m, 21H, CH_{arom}), 6.09 (dd, 1H, *J* = 10.2, 9.2 Hz, H-3), 5.53 (s, 1H, C*H*Ph), 5.18 – 5.06 (m, 3H, H-1, H-1', H-2), 4.86 (d, 1H, *J* = 10.8 Hz, C*H*H Bn), 4.68 – 4.63 (m, 3H, CH*H* Bn, CH_2 Bn), 4.25 (t, 1H, *J* = 9.5 Hz, H-4), 4.14 (dd, 1H, *J* = 10.3, 4.9 Hz, H-6'), 4.00 (ddd, 1H, *J* = 10.2, 3.9, 2.0 Hz, H-5), 3.96 – 3.86 (m, 3H, H-3', H-5', H-6), 3.79 (dd, 1H, *J* = 11.0, 1.8 Hz, H-6), 3.70 – 3.55 (m, 2H, H-6', H-4'), 3.42 (s, 3H, CH_3 OMe), 3.23 (dd, 1H, *J* = 10.0, 3.8 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.1, 165.6 (C=O), 138.1, 137.8, 137.2 (C_q), 133.4, 133.0, 130.1, 129.6 (CH_{arom}), 129.2 (C_q), 129.2, 128.5, 128.5, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7 (CH_{arom}), 101.5 (CHPh), 99.7 (C-1'), 96.9 (C-1), 82.5 (C-4'), 76.6 (C-3'), 76.1 (C-4), 75.2, 73.8 (CH_2 Bn), 72.4 (C-2), 72.3 (C-3), 69.8 (C-5), 68.8 (C-6'), 68.8 (C-6), 63.8 (C-5'), 63.3 (C-2'), 55.6 (OMe); Diagnostic peaks β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.90 (dd, 1H, *J* = 10.2, 9.1 Hz, H-3), 5.22 (dd, 1H, *J* = 10.1, 3.7 Hz, H-2), 4.77 (d, 1H, *J* = 11.9 Hz, C*H*H Bn), 4.51 (d, 1H, *J* = 11.9 Hz, CH*H* Bn), 2.97 – 2.88 (m, 1H, H-5'), 2.58 (t, 1H, *J* = 10.4 Hz, H-6'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 166.0, 165.5, 137.9, 137.2, 133.1, 130.5, 130.0, 129.8, 129.3, 128.7, 128.2, 126.0, 101.6 (CHPh), 101.1 (C-1'), 97.1, 81.3, 79.1, 75.9, 74.7, 71.9, 70.8, 69.7, 67.9, 67.6, 66.0, 65.7, 55.5; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{51}N_4O_{12}$ 875.34980, found 875.35038.

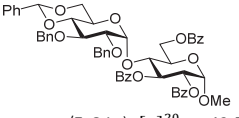


Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-2,3-di-*O*-benzoyl-6-deoxy-α-D-glucopyranoside (14A). Donor **A** and acceptor **14** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **14A** (68 mg, 83 µmol, 83%, α:β = >20:1) as a colorless oil. R_f: 0.50 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = +37.1° (*c* = 1.0, $CHCl_3$); IR (thin film): 696, 708, 748, 995, 1026, 1051, 1088, 1177, 1275, 1452, 1722, 2934; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.01 – 7.92 (m, 4H, CH_{arom}), 7.54 – 7.04 (m, 21H, CH_{arom}), 6.15 (dd, 1H, *J* = 10.2, 9.1 Hz, H-3), 5.51 (s, 1H, C*H*Ph), 5.15 (dd, 1H, *J* = 10.2, 3.6 Hz, H-2), 5.10 (d, 1H, *J* = 3.8 Hz, H-1'), 5.07 (d, 1H, *J* = 3.6 Hz, H-1), 4.83 (d, 1H, *J* = 11.1 Hz, C*H*H Bn), 4.67 (d, 1H, *J* = 11.1 Hz, CH*H* Bn), 4.36 (d, 1H, *J* = 12.1 Hz, C*H*H Bn), 4.25 (dd, 1H, *J* = 10.3, 4.9 Hz, H-6'), 4.16 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.06 (dq, 1H, *J* = 9.5, 6.2 Hz, H-5), 4.02 – 3.90 (m, 2H, H-3', H-5'), 3.80 (t, 1H, *J* = 9.3 Hz, H-4), 3.68 (t, 1H, *J* = 10.3 Hz, H-6'), 3.53 (t, 1H, *J* = 9.5 Hz, H-4'), 3.40 (s, 3H, CH_3 OMe), 3.35 (dd, 1H, *J* = 9.5, 3.8 Hz, H-2'), 1.45 (d, 3H, *J* = 6.2 Hz, H-6); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.2, 165.5 (C=O), 138.7, 137.9, 137.4 (C_q), 133.4, 133.1 (CH_{arom}), 130.1 (C_q), 130.0, 129.8 (CH_{arom}), 129.2 (C_q), 129.0, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 127.7, 127.7, 126.1 (CH_{arom}), 101.3 (CHPh), 98.7 (C-1'), 96.7 (C-1), 82.0 (C-4'), 79.8 (C-4), 78.5 (C-2'), 78.5 (C-3'), 75.5, 73.2 (CH_2 Bn), 72.9 (C-2), 72.4 (C-3), 68.9 (C-6'), 66.2 (C-5), 63.6 (C-5'), 55.3 (OMe), 18.6 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{52}NO_{12}$ 834.34840, found 834.34900.

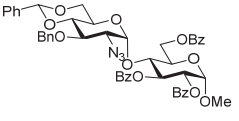


Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl)-2,3-di-*O*-benzoyl-6-deoxy-α-D-glucopyranoside (14B). Donor **B** and acceptor **14** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **14B** (72 mg, 96 µmol, 96%, α:β = 20:1) as a colorless oil. R_f: 0.40 (4/1

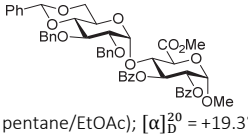
pentane/EtOAc); $[\alpha]_D^{20}$ = +22.9° (*c* = 1.0, $CHCl_3$); IR (thin film): 710, 753, 999, 1030, 1057, 1092, 1177, 1277, 1369, 1450, 1724, 2110, 2936; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.99 (dt, 4H, *J* = 8.3, 1.2 Hz, CH_{arom}), 7.54 – 7.18 (m, 16H, CH_{arom}), 6.11 – 6.01 (m, 1H, H-3), 5.56 (s, 1H, C*H*Ph), 5.15 (d, 1H, *J* = 4.0 Hz, H-1'), 5.09 – 5.02 (m, 2H, H-1, H-2), 4.90 (d, 1H, *J* = 10.8 Hz, C*H*H Bn), 4.72 (d, 1H, *J* = 10.8 Hz, CH*H* Bn), 4.26 (dd, 1H, *J* = 10.3, 4.9 Hz, H-6'), 4.06 – 3.89 (m, 3H, H-5, H-5', H-3'), 3.77 – 3.68 (m, 2H, H-4, H-6'), 3.65 (t, 1H, *J* = 9.3 Hz, H-4'), 3.41 (s, 3H, CH_3 OMe), 3.20 (dd, 1H, *J* = 10.1, 4.0 Hz, H-2'), 1.44 (d, 3H, *J* = 6.2 Hz, H-6); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.2, 165.5 (C=O), 137.8, 137.1 (C_q), 133.4, 133.0, 130.1 (CH_{arom}), 130.1 (C_q), 129.5 (CH_{arom}), 129.2 (C_q), 129.2, 128.5, 128.5, 128.4, 128.3, 128.0, 126.0 (CH_{arom}), 101.4 (CHPh), 100.1 (C-1'), 96.8 (C-1), 82.4 (C-4'), 82.1 (C-4), 76.5 (C-3'), 75.2 (CH_2 Bn), 72.8 (C-2), 72.3 (C-3), 68.5 (C-6'), 65.7 (C-5), 63.6 (C-5'), 62.9 (C-2'), 55.5 (OMe), 18.3 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{45}N_4O_{11}$ 769.30793, found 769.30861.



Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-2,3,6-tri-*O*-benzoyl-α-D-glucopyranoside (15A). Donor **A** and acceptor **15** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **15A** (85 mg, 91 µmol, 91%, α:β = >20:1) as a colorless oil. R_f: 0.47 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = +43.5° (*c* = 1.0, $CHCl_3$); IR (thin film): 710, 748, 997, 1028, 1090, 1271, 1452, 1724, 2936; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.11 – 8.06 (m, 2H, CH_{arom}), 8.03 – 7.95 (m, 4H, CH_{arom}), 7.63 – 7.57 (m, 1H, CH_{arom}), 7.52 – 7.41 (m, 6H, CH_{arom}), 7.39 – 7.23 (m, 13H, CH_{arom}), 7.19 – 7.14 (m, 3H, CH_{arom}), 7.12 – 7.07 (m, 2H, CH_{arom}), 6.21 (ddd, 1H, *J* = 10.2, 7.0, 1.8 Hz, H-3), 5.44 (s, 1H, C*H*Ph), 5.27 (dd, 1H, *J* = 10.3, 3.6 Hz, H-2), 5.15 (d, 1H, *J* = 3.6 Hz, H-1), 4.94 (d, 1H, *J* = 3.6 Hz, H-1'), 4.85 – 4.75 (m, 2H, C*H*H Bn, H-6), 4.69 – 4.58 (m, 2H, CH*H* Bn, H-6), 4.30 (d, 1H, *J* = 12.4 Hz, C*H*H Bn), 4.26 – 4.18 (m, 2H, H-5, H-4), 4.13 (dd, 1H, *J* = 10.2, 4.8 Hz, H-6'), 4.04 – 3.96 (m, 2H, CH*H* Bn, H-3'), 3.92 (td, 1H, *J* = 10.0, 4.8 Hz, H-5'), 3.57 (t, 1H, *J* = 10.3 Hz, H-6'), 3.49 (d, 1H, *J* = 9.5 Hz, H-4'), 3.44 (s, 3H, CH_3 OMe), 3.29 (dd, 1H, *J* = 9.5, 3.6 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.2, 165.6 (C=O), 138.7, 138.0, 137.4 (C_q), 133.5, 133.3, 133.1 (CH_{arom}), 130.1 (C_q), 130.1 (CH_{arom}), 129.9 (C_q), 129.8, 129.8 (CH_{arom}), 129.1 (C_q), 129.0, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 126.2 (CH_{arom}), 101.4 (CHPh), 99.7 (C-1'), 96.9 (C-1), 81.9 (C-4'), 78.4 (C-2'), 78.4 (C-3'), 76.2 (C-4), 75.4 (CH_2 Bn), 73.3 (CH_2 Bn), 72.2 (C-2), 71.7 (C-3), 68.8 (C-6'), 68.7 (C-5), 64.0 (C-5'), 63.4 (C-6), 55.6 (OMe); HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{56}NO_{14}$ 954.36953, found 954.37046.

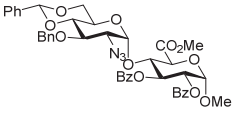


Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl)-2,3,6-tri-*O*-benzoyl-α-D-glucopyranoside (15B). Donor **B** and acceptor **15** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **15B** (60 mg, 69 µmol, 69%, α:β = >20:1) as a white solid. R_f: 0.42 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = +38.5° (*c* = 1.0, $CHCl_3$); IR (thin film): 710, 752, 999, 1030, 1096, 1269, 1450, 1724, 2110, 2936; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.15 – 7.94 (m, 6H, CH_{arom}), 7.64 – 7.20 (m, 19H, CH_{arom}), 6.14 (dd, 1H, *J* = 9.8, 8.7 Hz, H-3), 5.51 (s, 1H, C*H*Ph), 5.20 – 5.08 (m, 3H, H-1, H-1', H-2), 4.89 (d, 1H, *J* = 10.8 Hz, C*H*H Bn), 4.75 (dd, 1H, *J* = 12.2, 2.0 Hz, H-6), 4.70 (d, 1H, *J* = 10.8 Hz, CH*H* Bn), 4.59 (dd, 1H, *J* = 12.2, 4.1 Hz, H-6), 4.28 (dd, 1H, *J* = 10.4, 4.8 Hz, H-6'), 4.22 (ddd, 1H, *J* = 10.1, 4.1, 1.9 Hz, H-5), 4.20 – 4.12 (m, 1H, H-4), 4.03 – 3.89 (m, 2H, H-3', H-5'), 3.68 – 3.57 (m, 2H, H-6', H-4'), 3.45 (s, 3H, CH_3 OMe), 3.25 (dd, 1H, *J* = 10.0, 4.0 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.2, 166.1, 165.6 (C=O), 137.7, 137.1 (C_q), 133.5, 133.5, 133.4, 133.1, 130.1 (CH_{arom}), 130.0 (C_q), 129.9 (CH_{arom}), 129.8 (C_q), 129.5, 129.1 (CH_{arom}), 129.1 (C_q), 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 128.0, 126.1 (CH_{arom}), 101.4 (CHPh), 100.6 (C-1'), 96.9 (C-1), 82.4 (C-4'), 77.4 (C-4), 76.6 (C-3'), 75.2 (CH_2 Bn), 72.3 (C-2), 72.1 (C-3), 68.5 (C-6'), 68.2 (C-5), 64.0 (C-5'), 63.4 (C-6), 63.0 (C-2'), 55.7 (OMe); HRMS: $[M+Na]^+$ calcd for $C_{48}H_{45}N_3O_{13}Na$ 894.2845, found 894.2878.

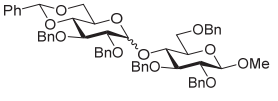


Methyl (methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-2,3-di-*O*-benzoyl-α-D-glucopyranosyl uronate) (16A). Donor **A** and acceptor **16** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **16A** (72 mg, 84 µmol, 84%, α:β = >20:1) as a colorless oil. R_f: 0.58 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = +19.3° (*c* = 1.0, $CHCl_3$); IR (thin film): 710, 748, 916, 997, 1049, 1090, 1271, 1452, 1732, 2938; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.05 – 7.91 (m, 4H, CH_{arom}), 7.53 – 7.43 (m, 4H, CH_{arom}), 7.41 – 7.24 (m, 12H, CH_{arom}), 7.21 – 7.15 (m, 3H, CH_{arom}), 7.07 – 7.02 (m, 2H, CH_{arom}), 6.17 (dd, 1H, *J* = 10.2, 8.8 Hz, H-3), 5.48 (s, 1H, C*H*Ph), 5.24 (dd, 1H, *J* = 10.1, 3.5 Hz, H-2), 5.20 (d, 1H, *J* = 3.5 Hz, H-1), 4.94 (d, 1H, *J* = 3.7 Hz, H-1'), 4.81 (d, 1H, *J* = 11.2 Hz, C*H*H Bn), 4.70 (d, 1H, *J* = 11.2 Hz, CH*H* Bn), 4.45 (d, 1H, *J* = 9.7 Hz, H-5), 4.39 (dd, 1H, *J* = 9.7, 8.9 Hz, H-4), 4.34 – 4.22 (m, 2H, C*H*H Bn, H-6'), 3.99 (d, 1H, *J* = 12.4 Hz, CH*H* Bn), 3.95 (t, 1H, *J* = 9.4 Hz, H-3'), 3.79 (s, 3H, CH_3 CO_2Me), 3.72 – 3.64 (m, 1H, H-5), 3.64 – 3.56 (m, 1H, H-6'), 3.52 – 3.40 (m, 4H, H-4', CH_3 OMe), 3.28 (dd, 1H, *J* = 9.4, 3.7 Hz, H-

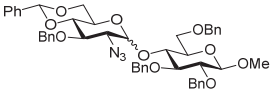
2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 169.4 (C=O CO_2Me), 166.0, 165.4 (C=O OBz), 138.7, 137.9, 137.5 (C_q), 133.5, 133.2, 130.1 (CH_{arom}), 130.0 (C_q), 129.8 (CH_{arom}), 129.0 (C_q), 129.0, 128.5, 128.4, 128.3, 128.2, 128.0, 127.7, 127.7, 126.1 (CH_{arom}), 101.3 (CHPh), 99.2 (C-1'), 97.5 (C-1), 81.6 (C-4'), 78.2 (C-2'), 78.0 (C-3'), 76.3 (C-4), 75.4, 72.8 (CH_2 Bn), 71.7 (C-2), 71.3 (C-3), 70.6 (C-5), 68.6 (C-6'), 63.6 (C-5'), 56.0 (OMe), 53.0 (CO_2Me); HRMS: $[M+NH_4]^+$ calcd for $C_{49}H_{52}NO_{14}$ 878.33823, found 878.33866.



Methyl (methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl)-2,3-di-*O*-benzoyl-α-D-glucopyranosyl uronate) (16B). Donor **B** and acceptor **16** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **16B** (79 mg, 99 µmol, 99%, α:β = >20:1) as a white solid. R_f: 0.51 (4/1 pentane/EtOAc); $[\alpha]_D^{20}$ = +13.1° (*c* = 1.0, $CHCl_3$); IR (thin film): 710, 752, 995, 1092, 1269, 1369, 1450, 1728, 2110, 2936; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.03 – 7.94 (m, 4H, CH_{arom}), 7.54 – 7.19 (m, 16H, CH_{arom}), 6.09 (dd, 1H, *J* = 10.2, 9.0 Hz, H-3), 5.53 (s, 1H, C*H*Ph), 5.21 (d, 1H, *J* = 3.5 Hz, H-1), 5.15 (dd, 1H, *J* = 10.2, 3.5 Hz, H-2), 5.06 (d, 1H, *J* = 3.9 Hz, H-1'), 4.87 (d, 1H, *J* = 10.8 Hz, C*H*H Bn), 4.70 (d, 1H, *J* = 10.8 Hz, CH*H* Bn), 4.45 – 4.26 (m, 3H, H-5, H-4, H-6'), 3.95 (dd, 1H, *J* = 10.0, 8.9 Hz, H-3'), 3.85 (s, 3H, CH_3 CO_2Me), 3.75 – 3.63 (m, 2H, H-5', H-6'), 3.59 (t, 1H, *J* = 9.1 Hz, H-4'), 3.47 (s, 3H, CH_3 OMe), 3.22 (dd, 1H, *J* = 10.0, 3.8 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 169.0 (C=O CO_2Me), 166.0, 165.5 (C=O OBz), 137.8, 137.3 (C_q), 133.5, 133.2, 130.1 (CH_{arom}), 129.8 (C_q), 129.6, 129.2 (CH_{arom}), 129.0 (C_q), 128.6, 128.5, 128.4, 128.3, 127.9, 126.1 (CH_{arom}), 101.5 (C*H*Ph), 99.8 (C-1'), 97.6 (C-1), 82.4 (C-4'), 77.4 (C-4), 76.5 (C-3'), 75.2 (CH_2 Bn), 71.8 (C-2), 71.1 (C-3), 70.3 (C-5), 68.5 (C-6'), 63.6 (C-5'), 63.0 (C-2'), 56.1 (OMe), 53.0 (CO_2Me); HRMS: $[M+NH_4]^+$ calcd for $C_{42}H_{45}N_4O_{13}$ 813.29776, found 813.29765.

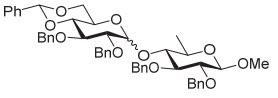


Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (17A). Donor **A** and acceptor **17** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **17A** (71 mg, 79 µmol, 79%, α:β = 1:1) as a colorless oil. R_f: 0.67 (4/1 pentane/EtOAc); IR (thin film): 698, 737, 910, 999, 1072, 1211, 1277, 1366, 1454, 2866; Data reported for a 1:1 mixture of anomers: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.55 – 7.05 (m, 60H, CH_{arom}), 5.71 (d, 1H, *J* = 3.9 Hz, H-1'$_\alpha$), 5.53 (s, 1H, C*H*Ph$_\alpha$), 5.49 (s, 1H, C*H*Ph$_\beta$), 5.00 – 4.84 (m, 6H, 6xC*H*H Bn), 4.84 – 4.66 (m, 9H, CH_2 Bn, 5xCH*H* Bn, 2xC*H*H Bn), 4.66 – 4.50 (m, 5H, 3xCH*H* Bn, C*H*H Bn, H-1'$_\beta$), 4.38 (d, 1H, *J* = 12.1 Hz, CH*H* Bn), 4.34 (d, 1H, *J* = 7.8 Hz, H-1$_\alpha$), 4.29 (d, 1H, *J* = 7.7 Hz, H-1$_\beta$), 4.23 – 4.14 (m, 2H, H-6'$_\beta$, H-6$_\alpha$), 4.12 (dd, 1H, *J* = 9.7, 8.7 Hz, H-3'$_\beta$), 4.02 – 3.94 (m, 2H, H-3$_\alpha$, H-3$_\beta$), 3.91 – 3.73 (m, 5H, H-5$_\alpha$, H-6$_\beta$, H-6$_\alpha$, H-6$_\alpha$, H-3'$_\alpha$), 3.68 (dd, 1H, *J* = 10.9, 1.8 Hz, H-6$_\beta$), 3.66 – 3.52 (m, 12H, H-2$_\alpha$, H-4'$_\beta$, H-4'$_\alpha$, H-4$_\alpha$, H-5$_\beta$, H-6'$_\alpha$, CH_3 OMe$_\alpha$, CH_3 OMe$_\beta$), 3.51 – 3.28 (m, 6H, H-2'$_\alpha$, H-2$_\beta$, H-2'$_\beta$, H-3$_\beta$, H-4$_\beta$, H-6'$_\beta$), 3.14 (td, 1H, *J* = 9.4, 4.9 Hz, H-5'$_\beta$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 139.1, 138.8, 138.8, 138.6, 138.4, 138.3, 138.2, 137.9, 137.7, 137.5 (C_q), 129.1, 128.9, 128.5, 128.4, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.5, 127.3, 126.7, 126.1 (CH_{arom}), 104.8 (C-1$_\beta$), 104.6 (C-1$_\alpha$), 102.9 (C-1'$_\beta$), 101.2 (CHPh$_{\alpha,\beta}$), 97.3 (C-1'$_\alpha$), 84.9 (C-3'$_\alpha$), 82.9 (C-2$_\alpha$), 82.6 (C-2'$_\beta$), 82.5, 82.4, 81.9, 81.8, 81.2 (C-4$_\alpha$ C-4'$_\beta$ C-5$_\alpha$ C-2$_\beta$ C-4'$_\alpha$), 78.8, 78.8 (C-2'$_\alpha$ C-3$_\beta$), 76.9 (C-3$_\alpha$), 75.5, 75.5, 75.4, 75.1, 75.1 (CH_2 Bn), 75.0 (C-4$_\beta$), 74.7, 74.3 (CH_2 Bn), 73.9 (C-5$_\beta$), 73.8, 73.5, 73.3 (CH_2 Bn), 72.0 (C-3'$_\beta$), 69.0 (C-6$_\alpha$), 68.9 (C-6'$_{\alpha,\beta}$) 68.0 (C-6$_\beta$), 65.9 (C-5'$_\beta$), 63.4 (C-5'$_\alpha$), 57.2 (OMe$_\alpha$), 57.1 (OMe$_\beta$); HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{56}NO_{10}$ 912.43174, found 912.43238.

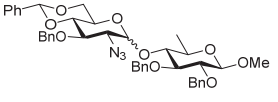


Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (17B). Donor **B** and acceptor **17** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **17B** (66 mg, 80 µmol, 80%, α:β = 1:7) as a colorless oil. R_f: 0.78 (4/1 pentane/EtOAc); IR (thin film): 698, 737, 914, 999, 1092, 1277, 1366, 1454, 2110, 2870; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.54 – 7.14 (m, 25H, CH_{arom}), 5.47 (s, 1H, C*H*Ph), 4.90 – 4.82 (m, 3H, CH_2 Bn, C*H*H Bn), 4.82 – 4.67 (m, 4H, CH*H* Bn, CH_2 Bn, C*H*H Bn), 4.48 (d, 1H, *J* = 12.0 Hz, CH*H* Bn), 4.35 (d, 1H, *J* = 7.8 Hz, H-1'), 4.30 (d, 1H, *J* = 7.7 Hz, H-1), 4.11 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6'), 4.02 (t, 1H, *J* = 9.4 Hz, H-4), 3.99 – 3.92 (m, 1H, H-6), 3.82 (dd, 1H, *J* = 11.0, 1.8 Hz, H-6), 3.60 – 3.52 (m, 5H, CH_3 OMe, H-3, H-4'), 3.49 – 3.29 (m, 5H, H-2, H-2', H-3', H-5, H-6'), 3.01 (td, 1H, *J* = 9.8, 5.0 Hz, H-5'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 139.1, 138.7, 138.1, 137.9, 137.3 (C_q), 129.2, 128.6, 128.5, 128.4, 128.3, 128.3, 128.1, 128.0, 128.0, 127.7, 127.7, 127.5, 126.1 (CH_{arom}), 104.8 (C-1), 101.3 (C*H*Ph), 101.3 (C-1'), 82.8 (C-4'), 81.8 (C-2), 81.8 (C-3), 79.2 (C-3'), 76.9 (C-4), 75.5, 75.0, 74.9 (CH_2 Bn), 74.7 (C-5), 73.5 (CH_2 Bn), 68.6 (C-6'), 68.2 (C-6), 66.7 (C-2'), 65.9 (C-5'), 57.3 (OMe); Diagnostic peaks for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.69 (d, 1H, *J* = 4.1 Hz, H-1'), 5.54 (s, 1H, C*H*Ph), 5.07 (d, 1H, *J* = 10.7 Hz), 3.26 (dd, 1H, *J* = 10.1, 4.0 Hz, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 138.5, 138.4, 138.3, 137.4,

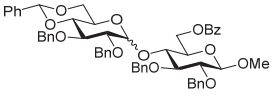
129.1, 128.5, 128.4, 128.2, 127.8, 127.6, 126.1, 104.7, 98.0, 85.0, 82.7, 76.2, 75.1, 74.3, 73.7, 73.1, 69.2, 68.8, 63.4, 62.8, 57.1; HRMS: $[M+NH_4]^+$ calcd for $C_{48}H_{55}N_4O_{10}$ 847.39127, found 847.39197.



Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-deoxy-β-D-glucopyranoside (18A). Donor **A** and acceptor **18** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **18A** (69 mg, 87 µmol, 87%, α:β = 1.1:1) as a colorless oil. R_f: 0.68 (4/1 pentane/EtOAc); IR (thin film): 698, 737, 999, 1030, 1072, 1454, 2870, 3032; Data reported for a 1.1:1 mixture of anomers: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.53 – 7.06 (m, 47.5H, CH_{arom}), 5.71 (d, 1H, *J* = 4.1 Hz, H-1'$_\alpha$), 5.55 (s, 1H, C*H*Ph$_\alpha$), 5.52 (s, 0.9H, C*H*Ph$_\beta$), 4.99 – 4.87 (m, 5H, 3xC*H*H Bn, CH_2 Bn), 4.87 – 4.74 (m, 6H, 2xCH*H* Bn, 2xCH_2 Bn), 4.74 – 4.62 (m, 3.9H, CH*H* Bn, 2xC*H*H Bn, H-1'$_\beta$), 4.57 (d, 1H, *J* = 10.9 Hz, CH*H* Bn), 4.52 (d, 1H, *J* = 11.7 Hz, CH*H* Bn), 4.34 – 4.28 (m, 1.9H, H-1$_\alpha$, H-1$_\beta$), 4.26 (dd, 1H, *J* = 10.3, 4.9 Hz, H-6'$_\alpha$), 4.18 (dd, 0.9H, *J* = 10.4, 4.9 Hz, H-6'$_\beta$), 4.02 (t, 1H, *J* = 9.3 Hz, H-3'$_\alpha$), 3.94 (td, 1H, *J* = 10.0, 4.8 Hz, H-5'$_\alpha$), 3.81 – 3.68 (m, 3H. H-3$_\alpha$, H-4$_\alpha$, H-6'$_\alpha$), 3.67 – 3.58 (m, 4.7H, H-3'$_\beta$, H-3$_\beta$, H-4'$_\beta$, H-5$_\alpha$, H-4'$_\alpha$), 3.57 (s, 3H, CH_3 OMe$_\alpha$), 3.56 (s, 2.7H, CH_3 OMe$_\beta$), 3.54 – 3.43 (m, 5.7H, H-2'$_\alpha$, H-2$_\alpha$, H-6'$_\beta$, H-4$_\beta$, H-5$_\alpha$, H-2'$_\beta$), 3.43 – 3.35 (m, 1.8H, H-2$_\beta$, H-5$_\beta$), 3.31 (td, 0.9H, *J* = 9.7, 4.9 Hz, H-5'$_\beta$), 1.42 (d, 3H, *J* = 5.8 Hz, H-6$_\alpha$), 1.38 (d, 2.7H, *J* = 6.1 Hz, H-6$_\beta$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 139.2, 139.0, 138.7, 138.7, 138.5, 138.4, 138.2, 137.9, 137.4 (C_q), 129.1, 129.0, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.1, 128.1, 127.9, 127.8, 127.7, 127.7, 127.7, 127.7, 127.5, 127.2, 126.5, 126.1, 126.0 (CH_{arom}), 104.5 (C-1$_\beta$), 104.5 (C-1$_\alpha$), 103.7 (C-1'$_\beta$), 101.2 (CHPh$_{\alpha,\beta}$), 97.8 (C-1'$_\alpha$), 84.6 (C-3$_\alpha$), 83.2 (C-4$_\beta$), 82.9, 82.7, 82.7, 82.3, 82.1 (C-3$_\beta$ C-3'$_\beta$ C-2$_\beta$ C-2'$_\beta$ C-2$_\alpha$), 81.8 (C-4'$_\beta$), 81.4 (C-4$_\alpha$), 78.9 (C-3'$_\alpha$), 78.7 (C-2'$_\alpha$), 78.2 (C-4'$_\alpha$), 75.7, 75.5, 75.4, 75.3, 75.0, 74.7, 74.0, 73.8 (CH_2 Bn), 71.4 (C-5$_\beta$), 70.4 (C-5$_\alpha$), 68.9 (C-6'$_\alpha$), 68.8 (C-6'$_\beta$), 66.0 (C-5'$_\alpha$), 63.3 (C-5'$_\alpha$), 57.2 (OMe$_\alpha$), 57.2 (OMe$_\beta$), 19.3 (C-6$_\alpha$), 18.1 (C-6$_\beta$); HRMS: $[M+Na]^+$ calcd for $C_{48}H_{52}O_{10}Na$ 811.3453, found 811.3475.

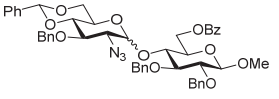


Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-deoxy-β-D-glucopyranoside (18B). Donor **B** and acceptor **18** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **18B** (62 mg, 86 µmol, 86%, α:β = 1:5) as a white solid. R_f: 0.84 (4/1 pentane/EtOAc); IR (thin film): 698, 737, 999, 1072, 1169, 1277, 1366, 1454, 2110, 2873; Data for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 7.54 – 7.11 (m, 20H, CH_{arom}), 5.49 (s, 1H, C*H*Ph), 4.91 (d, 1H, *J* = 11.3 Hz, C*H*H Bn), 4.87 (d, 1H, *J* = 11.1 Hz, C*H*H Bn), 4.85 – 4.81 (m, 2H, CH_2 Bn), 4.77 (d, 1H, *J* = 11.2 Hz, CH*H* Bn), 4.68 (d, 1H, *J* = 11.0 Hz, CH*H* Bn), 4.52 (d, 1H, *J* = 8.1 Hz, H-1'), 4.30 (d, 1H, *J* = 7.8 Hz, H-1), 4.06 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6'), 3.63 (t, 1H, *J* = 9.1 Hz, H-4'), 3.60 – 3.50 (m, 5H, CH3 OMe, H-3, H-3'), 3.50 – 3.36 (m, 6H, H-2, H-2', H-4, H-5, H-6'), 3.22 (td, 1H, *J* = 9.6, 5.0 Hz, H-5'), 1.44 (d, 2H, *J* = 5.5 Hz, H-6); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 139.1, 138.6, 137.8, 137.2 (C_q), 129.2, 128.5, 128.4, 128.4, 128.3, 128.3, 128.1, 128.0, 127.7, 127.6, 127.5, 127.3, 126.1 (CH_{arom}), 104.5 (C-1), 102.3 (C-1'), 101.3 (CHPh), 83.5 (C-4), 82.9 (C-3), 82.3 (C-2), 81.7 (C-4'), 79.4 (C-3'), 75.4, 75.0, 74.9 (CH_2 Bn), 71.0 (C-5), 68.5 (C-6'), 67.2 (C-2'), 66.2 (C-5'), 57.2 (OMe), 18.1 (C-6); Diagnostic peaks for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.64 (d, 1H, *J* = 4.2 Hz, (H-1'), 5.57 (s, 1H, C*H*Ph), 5.08 (d, 1H, *J* = 10.6 Hz, C*H*H Bn), 4.98 (d, 1H, *J* = 10.9 Hz, C*H*H Bn), 4.23 (dd, 1H, *J* = 10.4, 4.9 Hz, H-6'), 3.93 (td, 1H, *J* = 9.9, 4.9 Hz, H-5'), 3.29 (dd, 1H, *J* = 10.1, 4.2 Hz, H-2'), 1.39 (d, 3H, *J* = 5.2 Hz, H-6); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 138.6, 138.4, 137.9, 128.6, 128.2, 127.8, 126.0, 101.3, 98.6, 84.6, 83.1, 82.6, 79.5, 76.3, 75.2, 75.0, 74.7, 70.2, 68.6, 63.3, 62.8, 57.2, 19.0; HRMS: $[M+NH_4]^+$ calcd for $C_{41}H_{49}N_4O_9$ 741.34941, found 741.35004.

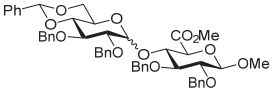


Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-*O*-benzoyl-β-D-glucopyranoside (19A). Donor **A** and acceptor **19** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **19A** (66 mg, 73 µmol, 73%, α:β = 3:1) as a white solid. R_f: 0.65 (4/1 pentane/EtOAc); IR (thin film): 698, 999, 1030, 1088, 1273, 1454, 1721, 2862, 3032; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.13 – 8.03 (m, 2H, CH_{arom}), 7.60 – 7.01 (m, 28H, CH_{arom}), 5.65 (d, 1H, *J* = 4.0 Hz, H-1'), 5.46 (s, 1H, C*H*Ph), 4.95 – 4.65 (m, 7H, 2xC*H*H Bn, 2xCH_2 Bn, H-6), 4.65 – 4.50 (m, 3H, 2x CH*H* Bn, H-6), 4.38 (d, 1H, *J* = 7.7 Hz, H-1), 4.12 – 4.00 (m, 3H, H-4', H-6', H-5'), 3.87 – 3.74 (m, 3H, H-3, H-5, H-3'), 3.62 – 3.45 (m, 7H, H-2', H-2, H-4, H-6', CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.2 (C=O), 138.8, 138.6, 138.3, 138.0, 137.4 (C_q), 133.2 (CH_{arom}), 130.0 (C_q), 129.9, 129.7, 129.0, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 126.8, 126.2 (CH_{arom}), 104.5 (C-1), 101.4 (CHPh), 98.3 (C-1'), 84.5 (C-3), 82.4 (C-4), 82.4 (C-2), 78.8 (C-5'), 78.6 (C-2'), 75.3, 74.7, 74.3 (CH_2 Bn), 74.2 (C-4'), 74.1 (CH_2 Bn), 72.6 (C-3'), 68.9 (C-6'), 63.8 (C-6), 63.7 (C-5), 57.2 (OMe); Diagnostic peaks for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.50 (s, 1H, C*H*Ph), 4.47 (dd, 1H, *J* = 12.0, 4.9 Hz), 4.33 (d, 1H, *J* = 7.7 Hz, H-1), 4.19 (dt, 1H, *J* = 9.3, 4.6 Hz), 3.72 (d, 1H, *J* = 8.9 Hz), 3.67 – 3.62 (m, 1H), 3.44 –

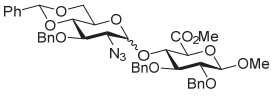
3.39 (m, 1H, H-2'), 3.23 (td, 1H, *J* = 9.7, 5.0 Hz, H-5'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 166.0, 138.8, 138.6, 138.5, 138.2, 137.3, 133.3, 129.7, 129.0, 128.5, 128.0, 127.4, 126.1, 104.6 (C-1), 103.1 (C-1'), 101.2 (CHPh), 82.7, 82.6, 81.8, 81.4, 77.4, 75.8, 75.7, 75.3, 75.0, 73.3, 66.1, 62.9; HRMS: $[M+Na]^+$ calcd for $C_{55}H_{56}O_{12}Na$ 931.3664, found 931.3695.



Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (19B). Donor **B** and acceptor **19** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **19B** (59 mg, 70 μmol, 70%, α:β = 1:1.2) as a colorless oil. R_f: 0.59 (4/1 pentane/EtOAc); IR (thin film): 698, 737, 999, 1030, 1069, 1092, 1273, 1369, 1454, 1721, 2110, 2870, 3032; Data reported for a 1:1.2 mixture of anomers: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.10 – 8.00 (m, 4.4H, CH_{arom}), 7.61 – 7.18 (m, 50.6H, CH_{arom}), 5.68 (d, 1H, *J* = 4.2 Hz, H-1'$_\alpha$), 5.49 (s, 1H, C*H*Ph$_\alpha$), 5.48 (s, 1.2H, C*H*Ph$_\beta$), 5.10 (d, 1H, *J* = 10.5 Hz, C*H*H Bn$_\alpha$), 4.95 (d, 1H, *J* = 11.0 Hz, C*H*H Bn$_\alpha$), 4.94 (d, 1H, *J* = 11.0 Hz, C*H*H Bn$_\alpha$), 4.92 – 4.82 (m, 7H, 2xC*H*H Bn$_\beta$, CH_2 Bn$_\beta$, CH*H* Bn$_\alpha$, H-6$_\beta$), 4.80 – 4.72 (m, 3.2H, CH*H* Bn$_\alpha$, CH*H* Bn$_\beta$, H-6$_\alpha$), 4.70 (d, 1.2H, *J* = 11.0 Hz,, CH*H* Bn$_\beta$), 4.68 (d, 1H, *J* = 11.0 Hz, CH*H* Bn$_\alpha$), 4.57 (dd, 1H, *J* = 12.2, 4.4 Hz, H-6$_\beta$), 4.51 – 4.43 (m, 2.2H, H-1'$_\beta$, H-6$_\alpha$), 4.43 – 4.33 (m, 2.2H, H-1$_\alpha$, H-1$_\beta$), 4.09 – 3.92 (m, 5.4H, H-3'$_\alpha$, H-4$_\alpha$, H-4$_\beta$, H-6'$_\alpha$, H-6'$_\beta$), 3.88 – 3.77 (m, 2.2H, H-3$_\beta$, H-5'$_\alpha$), 3.76 – 3.60 (m, 5.4H, H-3$_\alpha$, H-4'$_\alpha$, H-4'$_\beta$, H-5$_\alpha$, H-5$_\beta$), 3.60 – 3.39 (m, 13.4H, CH_3 OMe$_\alpha$, CH_3 OMe$_\beta$, H-2$_\alpha$, H-2$_\beta$, H-2'$_\beta$, H-3'$_\beta$, H-6'$_\alpha$, H-6'$_\beta$), 3.31 (dd, 1H, *J* = 10.1, 4.1 Hz, H-2'$_\alpha$), 3.13 (td, 1.2H, *J* = 9.6, 5.0 Hz, H-5'$_\beta$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 166.1 (C=O), 138.8, 138.5, 138.4, 138.3, 137.8, 137.7, 137.2, 137.1 (C_q), 133.4, 133.3, 129.9 (CH_{arom}), 129.9 (C_q), 129.7, 129.2, 129.1, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.5, 126.2, 126.0 (CH_{arom}), 104.7 (C-1$_\beta$), 104.6 (C-1$_\alpha$), 101.9 (C-1'$_\beta$), 101.4 (CHPh$_\alpha$), 101.3 (CHPh$_\beta$), 98.8 (C-1'$_\alpha$), 84.5 (C-3$_\beta$), 82.8 (C-2$_\beta$), 82.7 (C-4'$_\alpha$), 82.6 (C-3$_\alpha$), 81.9 (C-2$_\beta$), 81.6 (C-4'$_\beta$), 79.6 (C-3'$_\beta$), 77.7 (C-4$_\beta$), 76.0 (C-3'$_\alpha$), 75.7, 75.1, 75.1, 75.0 (CH_2 Bn), 74.8 (C-4$_\alpha$), 74.7, 74.7 (CH_2 Bn), 73.0 (C-5$_\beta$), 72.3 (C-5$_\alpha$), 68.5 (C-6$_{\alpha,\beta}$), 66.8 (C-2'$_\beta$), 66.3 (C-5'$_\beta$), 63.7 (C-5'$_\alpha$), 63.6 (C-6$_\alpha$), 63.1 (C-6$_\beta$), 62.8(C-2'$_\alpha$),, 57.3 (OMe$_\beta$), 57.2 (OMe$_\alpha$); HRMS: $[M+Na]^+$ calcd for $C_{48}H_{49}N_3O_{11}Na$ 866.3289, found 866.3259.

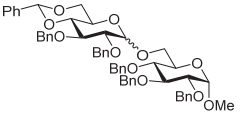


Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-β-D-glucopyranosyl uronate) (20A). Donor **A** and acceptor **20** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **20A** (69 mg, 83 μmol, 83%, α:β = 5:1) as a white solid. R_f: 0.75 (4/1 pentane/EtOAc); IR (thin film): 698, 737, 995, 1030, 1207, 1454, 1751, 2866, 3032; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.50 – 7.08 (m, 25H, CH_{arom}), 5.51 (s, 1H, C*H*Ph), 5.38 (d, 1H, *J* = 3.8 Hz, H-1'), 4.94 – 4.75 (m, 4H, 2xC*H*H Bn, CH_2 Bn), 4.67 – 4.50 (m, 4H, 2xCH*H* Bn, CH_2 Bn), 4.36 (d, 1H, *J* = 7.6 Hz, H-1), 4.32 – 4.25 (m, 1H, H-6'), 4.19 (t, 1H, *J* = 9.0 Hz, H-4), 4.00 (d, 1H, *J* = 9.5 Hz, H-5), 3.78 (s, 3H, CH_3 CO_2Me), 3.75 (t, 1H, *J* = 8.9 Hz, H-3), 3.65 – 3.55 (m, 3H, H-6', H-5', H-4'), 3.54 (s, 3H, CH_3 OMe), 3.52 – 3.43 (m, 3H, H-3', H-2, H-2'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 169.0 (C=O), 138.7, 138.6, 138.2, 137.9, 137.5 (C_q), 129.0, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.7, 127.3, 127.0, 126.1 (CH_{arom}), 104.9 (C-1), 101.3 (C*H*Ph), 98.4 (C-1'), 83.4 (C-3), 82.0 (C-4'), 81.5 (C-2), 78.6 (C-2'), 78.4 (C-3'), 76.3 (C-4), 75.3 (CH_2 Bn), 74.8 (C-5), 74.8, 74.7, 73.6 (CH_2 Bn), 68.6 (C-6'), 63.2 (C-5'), 57.5 (OMe), 52.9 (CO_2Me); Diagnostic peaks for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.48 (s, 1H, C*H*Ph), 4.39 (d, 1H, *J* = 7.6 Hz), 3.91 (d, 1H, *J* = 9.4 Hz), 3.41 – 3.29 (m, 1H); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 169.1, 138.9, 138.5, 138.5, 138.5, 137.4, 129.0, 127.6, 126.1, 105.0, 102.8, 101.2, 82.3, 81.8, 81.3, 78.0, 75.6, 75.4, 75.0, 74.8, 74.5, 68.8, 66.0, 52.7; HRMS: $[M+Na]^+$ calcd for $C_{49}H_{52}O_{12}Na$ 855.3351, found 855.3370.

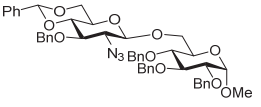


Methyl (methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-β-D-glucopyranosyl uronate) (20B). Donor **B** and acceptor **20** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **20B** (65 mg, 85 μmol, 85%, α:β = 1.2:1) as a white solid. R_f: 0.55 (4/1 pentane/EtOAc); IR (thin film): 698, 741, 999, 1030, 1211, 1277, 1369, 1454, 1751, 2110, 2870, 2932; Data reported for a 1.2:1 mixture of anomers: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 7.51 – 7.19 (m, 36H, CH_{arom}), 5.53 (s, 1H, C*H*Ph$_\alpha$), 5.50 (d, 1H, *J* = 3.9 Hz, H-1'$_\alpha$), 5.48 (s, 0.8H, C*H*Ph$_\beta$), 5.01 (d, 1H, *J* = 10.6 Hz, C*H*H Bn), 4.92 – 4.72 (m, 9H, C*H*H Bn, 4xCH_2 Bn), 4.69 (d, 1H, *J* = 4.8 Hz, C*H*H Bn), 4.66 (d, 1H, *J* = 4.8 Hz, CH*H* Bn), 4.46 (d, 0.8H, *J* = 8.1 Hz, H-1'$_\beta$), 4.42 – 4.34 (m, 1.8H, H-1$_\beta$, H-1$_\alpha$), 4.27 (dd, 1H, *J* = 10.3, 4.8 Hz, H-6'$_\alpha$), 4.19 – 4.04 (m, 2.8H, H-3$_\alpha$, H-5$_\alpha$, H-6'$_\beta$), 4.01 – 3.91 (m, 2.8H, H-5$_\beta$, H-4$_\alpha$, H-3'$_\alpha$), 3.85 (s, 2.4H, CH_3 CO_2Me$_\beta$), 3.83 (s, 3H, CH_3 OMe$_\alpha$), 3.76 (t, 1H, *J* = 8.9 Hz, H-3$_\beta$), 3.70 – 3.63 (m, 2H, H-6'$_\alpha$, H-4'$_\alpha$), 3.59 (dd, 0.8H, *J* = 9.1, 1.6 Hz, H-4'$_\beta$), 3.56 (s, 5.4H, CH_3 OMe$_{\alpha,\beta}$), 3.54 – 3.51 (m, 1.8H, H-2$_\alpha$, H-4$_\beta$) 3.51 – 3.47 (m, 0.8H, H-2$_\beta$), 3.47 – 3.40 (m, 2.6H, H-3$_\beta$, H-5'$_\alpha$, H-6'$_\beta$), 3.36 – 3.27 (m, 2.6H, H-2'$_\beta$, H-2'$_\alpha$, H-5'$_\beta$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 169.0, 169.0 (C=O),

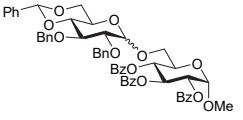
138.8, 138.3, 138.3, 138.2, 137.9, 137.9, 137.4, 137.2 (C_q), 129.2, 129.1, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5 (CH_{arom}), 105.1 (C-1$_\beta$), 105.0 (C-1$_\alpha$), 102.3 (C-1'$_\beta$), 101.5 (CHPh$_\alpha$), 101.4 (CHPh$_\beta$), 98.4 (C-1'$_\alpha$), 83.9 (C-3$_\beta$), 82.4 (C-4'$_\alpha$), 82.0 (C-4$_\beta$), 81.9 (C-2$_\alpha$), 81.6 (C-4'$_\beta$), 81.4 (C-2$_\beta$), 79.3 (C-5$_\alpha$), 79.2 (C-3'$_\beta$), 76.2 (C-3'$_\alpha$), 75.5, 75.4 (CH_2 Bn), 75.2 (C-3$_\alpha$), 75.1, 75.0, 75.0, 74.8 (CH_2 Bn), 74.4 (C-4$_\alpha$), 74.3 (C-5$_\beta$), 68.5 (C-6'$_{\alpha,\beta}$), 66.7 (C-2'$_\beta$), 66.2 (C-5'$_\beta$), 63.1 (C-5'$_\alpha$), 62.8 (C-2'$_\alpha$), 57.6 (OMe$_{\alpha,\beta}$), 53.0 (CO_2Me_β), 52.9 (CO_2Me_α); HRMS: $[M+Na]^+$ calcd for $C_{42}H_{45}N_3O_{11}Na$ 790.2946, found 790.2962.



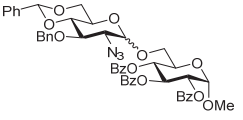
Methyl 6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (21A). See Chapter 3, compound **25** for synthesis and analytical data.



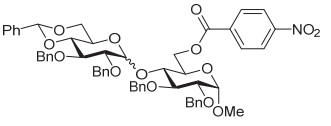
Methyl 6-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (21B). See Chapter 4, compound **3C** for synthesis and analytical data.



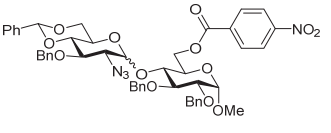
Methyl 6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (22A). Donor **A** and acceptor **22**[53] were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **22A** (80 mg, 86 µmol, 86%, α:β = 3 : 1) as a colorless oil. R_f: 0.40 (4/1 pentane/EtOAc). Spectroscopic data were in accord with those previously reported for the α-anomer.[59] IR (thin film): 648, 696, 708, 727, 906, 1026, 1053, 1068, 1088, 1261, 1277, 1452, 1726; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.91 (m, 4H, CH_{arom}), 7.90 – 7.82 (m, 2H, CH_{arom}), 7.56 – 7.43 (m, 4H, CH_{arom}), 7.43 – 7.16 (m, 20H, CH_{arom}), 6.24 – 6.12 (m, 1H, H-3), 5.57 – 5.46 (m, 2H, C*H*Ph, H-4), 5.33 – 5.19 (m, 2H, H-1, H-2), 4.94 – 4.64 (m, 5H, 2xCH_2 Bn, H-1'), 4.41 – 4.30 (m, 1H, H-5), 4.18 (dd, 1H, *J* = 10.0, 4.8 Hz, H-6'), 4.11 – 3.96 (m, 2H, H-3', H-5'), 3.91 – 3.82 (m, 1H, H-6), 3.78 – 3.52 (m, 5H, H-2', H-4', H-6, H-6'), 3.52 – 3.36 (m, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 165.9, 165.9, 165.5 (C=O), 138.8, 138.4, 137.7 (C_q), 133.5, 133.4, 133.2, 130.0, 130.0, 129.8 (CH_{arom}), 129.3, 129.2, 129.0 (C_q), 128.5, 128.5, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 128.1, 128.1, 128.0, 127.9, 127.6, 126.2 (CH_{arom}), 101.3 (CHPh), 98.3 (C-1'), 97.0 (C-1), 82.2 (C-4'), 79.4 (C-2'), 78.3 (C-3'), 75.2, 73.6 (CH_2 Bn), 72.2 (C-2), 70.6 (C-3), 69.7 (C-4), 69.0 (C-6'), 68.7 (C-5), 67.3 (C-6), 62.6 (C-5'), 55.8 (OMe); Diagnostic peaks β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01 (d, 1H, *J* = 10.7 Hz, H-), 4.59 (d, *J* = 7.6 Hz, 1H); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 165.9, 165.9, 165.5, 138.6 (C=O), 138.4, 137.4, 133.6 (C_q), 133.5-127.6 (CH_{arom}), 104.4 (C-1'), 101.2 (CHPh), 97.0 (C-1) 82.3, 81.4, 80.9, 75.4, 72.1, 70.5, 70.0, 69.2, 69.0, 66.1, 55.7; HRMS: $[M+Na]^+$ calcd for $C_{55}H_{52}O_{14}Na$ 959.3255, found 959.3292.



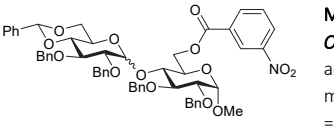
Methyl 6-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (22B). Donor **B** and acceptor **22**[53] were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **22B** (83 mg, 95 µmol, 95%, α:β = 1 : 1.5) as a colorless oil. R_f: 0.32 and 0.50 (4/1 pentane/EtOAc); product was contaminated with 10% of the 6-6 homocoupled acceptor. IR (thin film): 698, 706, 735, 999, 1026, 1069, 1090, 1175, 1250, 1261, 1450, 1724, 2110; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.01 – 7.93 (m, 10H, CH_{arom}), 7.89 – 7.84 (m, 5H, CH_{arom}), 7.54 – 7.25 (m, 47.5H, CH_{arom}), 6.22 – 6.14 (m, 2.5H, H-3$_\alpha$, H-3$_\beta$), 5.64 – 5.53 (m, 5H, C*H*Ph$_{\alpha,\beta}$, H-4$_\alpha$, H-4$_\beta$), 5.31 – 5.23 (m, 5H, H-1$_\alpha$, H-1$_\beta$, H-2$_\alpha$, H-2$_\beta$), 4.97 (d, 1H, *J* = 11.1 Hz, C*H*H Bn$_\alpha$), 4.95 – 4.89 (m, 2H, C*H*H Bn$_\beta$, H-1'$_\alpha$), 4.87 – 4.76 (m, 2H, CH*H* Bn$_\alpha$, CH*H* Bn$_\beta$), 4.44 (d, 1.5H, *J* = 8.0 Hz, H-1'$_\beta$), 4.34 – 4.26 (m, 4H, H-5$_\alpha$, H-5$_\beta$, H-6'$_\beta$), 4.20 – 4.11 (m, 2H, H-3', H-6'), 4.07 (dd, 1.5H, *J* = 11.2, 2.2 Hz, H-6), 3.99 – 3.89 (m, 2H, H-5', H-6), 3.80 (dd, 1.5H, *J* = 11.3, 6.3 Hz, H-6), 3.77 – 3.64 (m, 6H, H-4'$_\alpha$, H-4'$_\beta$, H-6$_\alpha$, H-6'$_\alpha$, H-6'$_\beta$), 3.57 (t, 1.5H, *J* = 9.3 Hz, H-3'$_\beta$), 3.50 (s, 4.5H, CH_3 OMe$_\beta$), 3.48 – 3.43 (m, 4.5H, CH_3 OMe$_\alpha$, H-2'$_\beta$), 3.41 – 3.33 (m, 2.5H, H-2'$_\alpha$, H-5'$_\beta$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 165.9, 165.9, 165.9, 165.5, 165.5 (C=O), 137.9, 137.4, 137.2 (C_q), 133.6, 133.5, 133.5, 133.2, 130.0, 130.0, 129.9, 129.8 (CH_{arom}), 129.3, 129.2, 129.1, 129.1, 129.0, 128.9 (C_q/CH_{arom}), 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.0, 126.2, 126.1 (CH_{arom}), 102.9 (C-1'$_\beta$), 101.4, 101.4 (CHPh$_{\alpha,\beta}$), 98.8 (C-1'$_\alpha$), 97.1, 97.0 (C-1$_\alpha$, C-1$_\beta$), 82.8 (C-4'$_\alpha$), 81.5 (C-4'$_\beta$), 79.0 (C-3'$_\beta$), 75.8 (C-3'$_\alpha$), 75.1 (CH_2 Bn), 72.1 (C-2, C-2$_\beta$), 70.5, 70.4 (C-3$_\alpha$, C-3$_\beta$), 69.7 (C-4$_\beta$), 69.5 (C-4$_\alpha$), 68.9 (C-5$_\alpha$), 68.8 (C-6$_\beta$), 68.6 (C-6'$_\alpha$, C-6'$_\beta$), 68.5 (C-5$_\alpha$), 67.0 (C-6$_\alpha$), 66.4 (C-2'$_\beta$), 66.3 (C-5'$_\beta$), 63.0 (C-2'$_\alpha$), 62.9 (C-5'$_\alpha$), 55.8 (OMe); HRMS: $[M+Na]^+$ calcd for $C_{48}H_{45}N_3O_{13}Na$ 894.2850, found 894.2874.



Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-*O*-(4-nitrobenzoyl)-α-D-glucopyranoside (23A). Donor **A** and acceptor **23** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **23A** (88 mg, 92 µmol, 92%, α:β = 3 : 1) as a colorless oil. R_f: 0.36 (4/1 pentane/EtOAc); IR (thin film): 696, 719, 735, 997, 1028, 1047, 1076, 1088, 1273, 1348, 1454, 1525, 1726, 2866, 2910, 2926; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.22 – 8.15 (m, 4H, pNO_2Bz), 7.44 – 7.17 (m, 25H, CH_{arom}), 5.71 (d, 1H, *J* = 4.0 Hz, H-1'), 5.47 (s, 1H, C*H*Ph), 5.00 (d, 1H, *J* = 11.5 Hz, C*H*H Bn), 4.94 – 4.88 (m, 1H, C*H*H Bn), 4.82 – 4.61 (m, 5H, 2xCH*H* Bn, 2x C*H*H Bn, H-6), 4.61 – 4.52 (m, 4H, 2x CH*H* Bn, H-1, H-6), 4.15 – 4.07 (m, 2H, H-3', H-5), 4.03 (t, 1H, *J* = 9.4 Hz, H-3), 4.01 – 3.95 (m, 2H, H-4, H-6'), 3.81 – 3.73 (m, 1H, H-5'), 3.63 – 3.52 (m, 4H, H-2, H-2', H-4', H-6'), 3.39 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 164.4 (C=O), 150.6, 138.8, 138.5, 137.9, 137.8, 137.3, 135.2 (C_q), 130.9, 128.6, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.0, 127.8, 127.8, 127.7, 127.7, 126.8, 126.1, 123.6 (CH_{arom}), 101.2 (CHPh), 98.1 (C-1'), 97.7 (C-1), 82.3 (C-4'), 81.6 (C-3'), 80.4 (C-2), 78.8, 78.7 (C-2', C-3), 75.3, 74.6, 74.3 (CH_2 Bn), 73.5 (C-4), 73.4 (CH_2 Bn), 68.8 (C-6'), 67.9 (C-5), 64.8 (C-6), 63.7 (C-5'), 55.5 (OMe); Diagnostic peaks for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 – 8.23 (m, 2H, pNO_2Bz), 8.10 – 8.06 (m, 2H, pNO_2Bz), 5.52 (s, 1H, C*H*Ph), 3.91 (dd, 1H, *J* = 9.5, 8.3 Hz), 3.66 (t, 1H, *J* = 9.3 Hz), 3.39 (s, 3H, CH_3 OMe), 3.27 (td, 1H, *J* = 9.8, 5.0 Hz, H-5'); ^{13}C-APT NMR ($CDCl_3$, 101 MHz): δ 164.1, 139.0, 138.4, 138.2, 138.1, 137.2, 135.2, 130.7, 129.0, 128.5, 128.3, 128.2, 128.2, 128.1, 127.8, 127.7, 127.4, 126.0, 103.6 (C-1'), 101.2 (CHPh), 98.0 (C-1), 82.7 (C-2'), 81.7 (C-4'), 81.4 (C-3'), 79.9 (C-3), 79.2 (C-2), 78.5 (C-4), 75.8, 75.1, 73.7 (CH_2 Bn), 68.8 (C-6'), 68.6 (C-5), 66.2 (C-5'), 63.9 (C-6), 55.5 (OMe); HRMS: $[M+H]^+$ calcd for $C_{55}H_{56}NO_{14}$ 954.3701, found 954.3745.

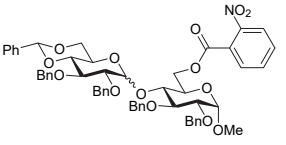


Methyl 4-*O*-(2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-*O*-(4-nitrobenzoyl)-α-D-glucopyranoside (23B). Donor **A** and acceptor **23** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **23B** (49 mg, 55 µmol, 55%, α:β = 1 : 1) as a colorless oil. R_f: 0.33 and 0.33 (4/1 pentane/EtOAc); IR (thin film): 698, 719, 739, 999, 1015, 1028, 1049, 1094, 1275, 1454, 1528, 1728, 2110, 2868, 2922; ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC, HMBC): δ 8.34 – 8.25 (m, 2H, pNO_2Bz), 8.24 – 8.15 (m, 8H, pNO_2Bz), 7.46 – 7.25 (m, 40H, CH_{arom}), 5.68 (d, 1H, *J* = 4.2 Hz, H-1'$_\alpha$), 5.51 (s, 1H, C*H*Ph$_\alpha$), 5.49 (s, 1H, C*H*Ph$_\beta$), 5.13 (d, 1H, *J* = 10.4 Hz, C*H*H Bn), 4.99 – 4.86 (m, 5H, 2xC*H*H Bn, CH*H* Bn, CH_2 Bn), 4.81 (dd, 1H, *J* = 12.0, 2.1 Hz, H-6$_\beta$), 4.81 – 4.73 (m, 4H, 2xCH*H* Bn, 2xC*H*H Bn), 4.71 (dd, 1H, *J* = 12.1, 2.4 Hz, H-6$_\alpha$), 4.65 (dd, 1H, *J* = 12.0, 4.8 Hz, H-6$_\beta$), 4.65 – 4.59 (m, 4H, 2xCH*H* Bn, H-1$_\alpha$, H-1$_\beta$), 4.53 (dd, 1H, *J* = 12.0, 4.2 Hz, H-6$_\alpha$), 4.45 (d, 1H, *J* = 8.1 Hz, H-1'$_\beta$), 4.13 (dd, 1H, *J* = 9.4, 8.8 Hz, H-3$_\alpha$), 4.06 – 3.94 (m, 6H, H-3$_\beta$, H-3'$_\alpha$, H-5$_\alpha$, H-5$_\beta$, H-6'$_\alpha$, H-6'$_\beta$), 3.90 – 3.78 (m, 3H, H-4$_\alpha$, H-4$_\beta$, H-5'$_\alpha$), 3.71 – 3.53 (m, 6H, H-2$_\alpha$, H-2$_\beta$, H-3'$_\beta$, H-4'$_\alpha$, H-4'$_\beta$, H-6'$_\alpha$), 3.48 (t, 1H, *J* = 10.3 Hz, H-6'$_\beta$), 3.43 (dd, 1H, *J* = 9.1, 8.3 Hz, H-2'$_\beta$), 3.40 (s, 3H, CH_3 OMe), 3.40 (s, 3H, CH_3 OMe), 3.36 (dd, 1H, *J* = 10.1, 4.2 Hz, H-2'$_\alpha$), 3.15 (ddd, 1H, *J* = 10.0, 9.0, 5.0 Hz, H-5'$_\beta$); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC, HMBC): δ 164.4, 164.3 (C=O), 150.7, 150.7 (C_q NO_2), 139.0, 138.5, 138.0, 137.8, 137.7, 137.6, 137.0, 137.0, 135.3, 135.1 (C_q), 130.9, 130.8, 129.2, 129.2, 128.7, 128.6, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.8, 127.6, 127.1, 126.1, 126.0, 123.8, 123.7 (CH_{arom}), 102.3 (C-1'), 101.3, 101.3 (CHPh), 99.0 (C-1'), 98.0, 97.8 (C-1, C-1), 82.5 (C-4'), 81.6 (C-3), 81.4 (C-4'), 80.7 (C-2), 80.1 (C-3), 79.7, 79.6 (C-2, C-3'), 78.5 (C-4), 76.1 (C-3'), 75.5, 75.3, 75.1 (CH_2 Bn), 75.1 (C-4), 75.0, 73.6, 73.4 (CH_2 Bn), 68.5 (C-6'), 68.4 (C-6'), 68.3 (C-5), 67.8 (C-5), 66.8 (C-2'), 66.4 (C-5'), 64.7 (C-6), 64.1 (C-6), 63.7 (C-5'), 62.8 (C-2'), 55.6, 55.6 (OMe); HRMS: $[M+H]^+$ calcd for $C_{48}H_{49}N_4O_{13}$ 889.3296, found 889.3331.

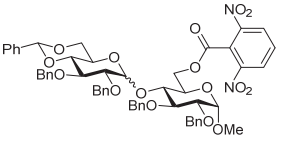


Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-*O*-(3-nitrobenzoyl)-α-D-glucopyranoside (24A). Donor **A** and acceptor **24** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **24A** (47 mg, 49 µmol, 49%, α:β = 3.3 : 1) as a colorless oil. R_f: 0.30 (4/1 pentane/EtOAc); IR (thin film): 696, 719, 737, 1028, 1047, 1076, 1088, 1261, 1350, 1454, 1533, 1730, 2868, 2908, 2926; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC, HMBC): δ 8.85 – 8.83 (m, 1H, CH_{arom} NO_2Bz), 8.37 (ddd, 1H, *J* = 8.2, 2.3, 1.1 Hz, CH_{arom} NO_2Bz), 8.33 (dt, 1H, *J* = 7.8, 1.3 Hz, CH_{arom} NO_2Bz), 7.57 (t, 1H, *J* = 8.0 Hz, CH_{arom} NO_2Bz), 7.45 – 7.17 (m, 25H, CH_{arom}), 5.70 (d, 1H, *J* = 4.0 Hz, H-1'), 5.47 (s, 1H, C*H*Ph), 5.00 (d, 1H, *J* = 11.5 Hz, C*H*H Bn), 4.90 (d, 1H, *J* = 11.2 Hz, C*H*H Bn), 4.79 – 4.72 (m, 4H, C*H*H Bn, 2xCH*H* Bn, H-6), 4.69 (d, 1H, *J* = 12.0 Hz, C*H*H Bn), 4.60 – 4.52 (m, 4H, 2xCH*H* Bn, H-1, H-6), 4.16 – 4.09 (m, 2H, H-3, H-5), 4.07 – 4.01 (m, 2H, H-3', H-6'), 3.97 (dd, 1H, *J* = 9.9, 8.7 Hz, H-4), 3.80 – 3.74 (m, 1H, H-5'), 3.63 – 3.57 (m, 3H, H-2, H-4', H-6'), 3.55 (dd, 1H, *J* = 9.4, 4.0 Hz, H-2'), 3.40 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC, HMBC): δ 164.2 (C=O), 148.4 (C_q NO_2), 138.9, 138.6, 138.0, 137.9 (C_q Bn), 137.3 (CH_{arom}),

135.4 (C_q Bz), 131.7, 129.7, 129.0, 128.6, 128.6, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 127.9, 127.8, 127.7, 127.7, 127.6, 127.4, 126.9, 126.1, 124.8 (CH_{arom}), 101.3 (CHPh), 98.2 (C-1), 97.8 (C-1'), 82.3 (C-4'), 81.6 (C-3), 80.5 (C-2), 78.8, 78.7 (C-2', C-3'), 75.4, 74.6, 74.2 (CH_2 Bn), 73.7 (C-4), 73.5 (CH_2 Bn), 68.8 (C-6'), 68.0 (C-5), 64.8 (C-6), 63.8 (C-5'), 55.5 (OMe); Diagnostic peaks for the β-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.76 – 8.72 (m, 1H, CH_{arom} NO_2Bz), 8.41 (ddd, 2H, *J* = 8.2, 2.3, 1.1 Hz, CH_{arom} NO_2Bz), 8.24 (dt, 1H, *J* = 7.7, 1.3 Hz, CH_{arom} NO_2Bz), 7.62 (t, 1H, *J* = 8.0 Hz, CH_{arom} NO_2Bz), 5.51 (s, 1H, C*H*Ph), 4.48 (dd, 1H, *J* = 11.8, 5.6 Hz, H-6), 4.19 (dd, 1H, *J* = 10.5, 5.0 Hz, H-6'), 3.93 – 3.87 (m, 1H, H-3), 3.65 (t, 1H, *J* = 9.3 Hz, H-4'), 3.41 (s, 3H, CH_3 OMe), 3.30 (td, 1H, *J* = 9.7, 5.0 Hz, H-5'); ^{13}C-APT NMR ($CDCl_3$, 126 MHz): δ 163.9 (C=O), 139.1 (C_q NO_2), 138.5, 138.2, 138.2, 135.2 (C_q) - 124.7 (CH_{arom}), 103.7 (C-1'), 101.2 (CHPh), 98.1 (C-1), 82.8 (C-2'), 81.8 (C-4'), 81.5 (C-3'), 80.0 (C-3), 79.3 (C-2), 78.6 (C-4), 75.8, 75.8, 75.2, 73.7 (CH_2 Bn), 68.8 (C-6'), 68.7 (C-5), 66.3 (C-5'), 63.9 (C-6), 55.5 (OMe); HRMS: $[M+Na]^+$ calcd for $C_{55}H_{55}NO_{14}Na$ 976.3520, found 976.3550.



Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-*O*-(2-nitrobenzoyl)-α-D-glucopyranoside (25A). Donor **A** and acceptor **25** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **25A** (79 mg, 83 µmol, 83%, α:β = 3.5 : 1) as a colorless oil. R_f: 0.20 (4/1 pentane/EtOAc); IR (thin film): 696, 733, 995, 1028, 1045, 1074, 1088, 1254, 1290, 1352, 1454, 1533, 1736, 2868, 2907; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz, HH-COSY, HSQC): δ 7.86 – 7.82 (m, 1H, CH_{arom}), 7.78 – 7.75 (m, 1H, CH_{arom}), 7.62 – 7.54 (m, 2H, CH_{arom}), 7.51 – 7.46 (m, 2H, CH_{arom}), 7.41 – 7.16 (m, 23H, CH_{arom}), 5.60 (d, 1H, *J* = 3.9 Hz, H-1'), 5.50 (s, 1H, C*H*Ph), 4.99 – 4.87 (m, 2H, 2xC*H*H Bn), 4.82 – 4.64 (m, 5H, 2xCH*H* Bn, 2xC*H*H Bn, H-6), 4.63 (d, 1H, *J* = 3.3 Hz, H-1), 4.61 – 4.50 (m, 3H, 2xCH*H* Bn, H-6), 4.11 – 4.05 (m, 2H, H-3', H-6'), 4.05 – 3.98 (m, 2H, H-3, H-5), 3.87 (dd, 1H, *J* = 9.8, 8.6 Hz, H-4), 3.84 – 3.77 (m, 1H, H-5'), 3.64 – 3.57 (m, 3H, H-2, H-4', H-6'), 3.52 (dd, 1H, *J* = 9.5, 3.9 Hz, H-2'), 3.39 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz, HSQC): δ 164.9 (C=O), 148.6 (C_q NO_2), 139.1, 138.7, 138.1, 137.9, 137.5 (C_q), 132.7, 132.0, 130.4, 129.0, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.2 (CH_{arom}), 127.0 (C_q Bz), 126.9, 126.2, 126.1, 123.8 (CH_{arom}), 101.4 (CHPh), 98.3 (C-1'), 97.7 (C-1), 82.3 (C-4'), 81.2 (C-3'), 80.2 (C-2), 78.8, 78.7 (C-2', C-3), 75.3 (CH_2 Bn), 74.5 (C-4), 74.4, 73.9, 73.4 (CH_2 Bn), 68.9 (C-6'), 68.1 (C-5), 65.3 (C-6), 63.6 (C-5'), 55.5 (OMe); Diagnostic peaks for the β-anomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.51 (s, 1H, C*H*Ph), 4.22 (dd, 1H, *J* = 9.8, 4.4 Hz, H-6'), 3.73 (dd, 1H, *J* = 10.0, 8.7 Hz, H-4), 3.37 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 126 MHz): δ 164.8, 148.6, 139.3, 138.4, 138.4, 132.7 - 123.8 (CH_{arom}), 103.2 (C-1'), 101.2 (CHPh), 98.2 (C-1), 82.9 (C-2'), 81.8 (C-4'), 81.6 (C-3'), 79.9 (C-3), 79.1 (C-2), 77.8 (C-4), 75.8, 75.5, 75.2, 73.7 (CH_2 Bn), 68.9 (C-6'), 68.5 (C-5), 65.9 (C-5'), 64.1 (C-6), 55.6 (OMe); HRMS: $[M+Na]^+$ calcd for $C_{55}H_{55}NO_{14}Na$ 976.3520, found 976.3566.



Methyl 4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-*O*-(2,6-dinitrobenzoyl)-α-D-glucopyranoside (26A). Donor **A** and acceptor **26** were condensed using the general procedure for Tf_2O/Ph_2SO mediated glycosylations (E) yielding product **26A** (83 mg, 83 µmol, 83%, α:β = 5.6 : 1) as a colorless oil. R_f: 0.12 (4/1 pentane/EtOAc); IR (thin film): 696, 735, 918, 1028, 1045, 1074, 1088, 1267, 1344, 1454, 1541, 1749, 2870; Data for the α-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.36 (d, 2H, *J* = 8.3 Hz, NO_2Bz_{meta}), 7.69 (t, 1H, *J* = 8.3 Hz, NO_2Bz_{para}), 7.40 – 7.17 (m, 25H, CH_{arom}), 5.52 (d, 1H, *J* = 3.9 Hz, H-1), 5.46 (s, 1H, C*H*Ph), 5.01 (dd, 1H, *J* = 11.8, 2.2 Hz, H-6), 4.95 – 4.74 (m, 4H, 2xCH_2 Bn), 4.73 – 4.62 (m, 4H, 2xC*H*H Bn, H-1, H-6), 4.59 – 4.51 (m, 2H, 2xCH*H* Bn), 4.09 (dd, 1H, *J* = 9.6, 8.5 Hz, H-3), 4.10 – 3.87 (m, 4H, H-3', H-5, H-5', H-6'), 3.82 (dd, 1H, *J* = 9.8, 8.5 Hz, H-4), 3.63 – 3.51 (m, 4H, H-2, H-2', H-4', H-6'), 3.40 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 162.3 (C=O), 146.7 (C_q NO_2), 139.1, 138.6, 138.1, 137.9, 137.5 (C_q), 129.7, 128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.0, 126.2 (CH_{arom}), 125.5 (C_q Bz), 101.3 (CHPh), 98.5 (C-1'), 97.7 (C-1), 82.2 (C-4'), 81.0 (C-3), 80.0 (C-2), 78.8 (C-2'), 78.6 (C-3'), 75.6 (C-4), 75.3, 74.6, 73.8, 73.4 (CH_2 Bn), 68.9 (C-6'), 68.5 (C-5), 66.2 (C-6), 63.5 (C-5'), 55.6 (OMe); Diagnostic peaks for the β-anomer: ^{1}H NMR ($CDCl_3$, 400 MHz, HH-COSY, HSQC): δ 8.42 (d, 2H, *J* = 8.3 Hz, NO_2Bz_{meta}), 7.75 (t, 1H, *J* = 8.3 Hz, NO_2Bz_{para}), 4.45 (dd, 1H, *J* = 12.1, 2.4 Hz, H-6), 4.19 (dd, 1H, *J* = 10.1, 4.7 Hz, H-6'), 3.79 – 3.72 (m, 1H), 3.47 (dd, 1H, *J* = 8.8, 7.7 Hz, H-2'), 3.42 (dd, 2H, *J* = 9.5, 3.6 Hz, H-2), 3.38 (s, 3H, CH_3 OMe); ^{13}C-APT NMR ($CDCl_3$, 101 MHz, HSQC): δ 162.2, 146.7, 139.1, 138.6, 138.5, 138.3, 137.5, 131.2, 129.8, 129.0, 128.9, 128.5, 128.4, 128.3, 128.1, 127.9, 127.9, 127.7, 127.5, 127.2, 126.1, 125.5, 103.0 (C-1'), 101.1 (CHPh), 98.2 (C-1), 82.9, 81.8, 81.6, 79.9, 78.8, 77.4, 75.7, 73.5, 68.3, 65.8, 65.5, 55.7; HRMS: $[M+NH_4]^+$ calcd for $C_{55}H_{58}N_3O_{16}$ 1016.3817, found 1016.3864.

Footnotes and references

(1) Sinnott, M. *Carbohydrate Chemistry and Biochemistry: Structure and Mechanism*; The Royal Society of Chemistry, 2007.

(2) Peng, P.; Schmidt, R. R. *Acc. Chem. Res.* **2017**, *50* (5), 1171–1183.

(3) Zhu, X.; Schmidt, R. R. *Angew. Chem. Int. Ed.* **2009**, *48* (11), 1900–1934.

(4) Mydock, L. K.; Demchenko, A. V. *Org. Biomol. Chem.* **2010**, *8* (3), 497–510.

(5) Demchenko, A. V. *Handbook of Chemical Glycosylation: Advances in Stereoselectivity and Therapeutic Relevance*; Wiley-VCH Verlag GmbH & Co. KGaA, 2008.

(6) Crich, D. *Acc. Chem. Res.* **2010**, *43* (8), 1144–1153.

(7) Lemieux, R. U.; Hendriks, K. B.; Stick, R. V.; James, K. *J. Am. Chem. Soc.* **1975**, *97* (14), 4056–4062.

(8) Bennett, C. S. *Selective Glycosylations: Synthetic Methods and Catalysts*; Wiley VCH Verlag GmbH, 2017.

(9) Nigudkar, S. S.; Demchenko, A. V. *Chem. Sci.* **2015**, *6* (5), 2687–2704.

(10) Whitfield, D. M.; Guo, J. *J. Carbohydr. Chem.* **2017**, *36* (2–3), 59–99.

(11) Paulsen, H. *Angew. Chem. Int. Ed. Engl.* **1982**, *21* (3), 155–173.

(12) Codée, J. D. C.; Litjens, R. E. J. N.; Bos, L. J. van den; Overkleeft, H. S.; Marel, G. A. van der. *Chem. Soc. Rev.* **2005**, *34* (9), 769–782.

(13) Fraser-Reid, B.; López, J. C. Armed–Disarmed Effects in Carbohydrate Chemistry: History, Synthetic and Mechanistic Studies. In *Reactivity Tuning in Oligosaccharide Assembly*; Fraser-Reid, B., Cristóbal López, J., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2011; pp 1–29.

(14) Frihed, T. G.; Bols, M.; Pedersen, C. M. *Chem. Rev.* **2015**, *115* (11), 4963–5013.

(15) Zhang, Z.; Ollmann, I. R.; Ye, X.-S.; Wischnat, R.; Baasov, T.; Wong, C.-H. *J. Am. Chem. Soc.* **1999**, *121* (4), 734–753.

(16) Douglas, N. L.; Ley, S. V.; Lücking, U.; Warriner, S. L. *J. Chem. Soc. [Perkin 1]* **1998**, No. 1, 51–66.

(17) Fraser-Reid, B.; Wu, Z.; Udodong, U. E.; Ottosson, H. *J. Org. Chem.* **1990**, *55* (25), 6068–6070.

(18) Walvoort, M. T. C.; Marel, G. A. van der; Overkleeft, H. S.; Codée, J. D. C. *Chem. Sci.* **2013**, *4* (3), 897–906.

(19) Krumper, J. R.; Salamant, W. A.; Woerpel, K. A. *Org. Lett.* **2008**, *10* (21), 4907–4910.

(20) Krumper, J. R.; Salamant, W. A.; Woerpel, K. A. *J. Org. Chem.* **2009**, *74* (21), 8039–8050.

(21) Beaver, M. G.; Woerpel, K. A. *J. Org. Chem.* **2010**, *75* (4), 1107–1118.

(22) Kalikanda, J.; Li, Z. *Tetrahedron Lett.* **2010**, *51* (12), 1550–1553.

(23) Kalikanda, J.; Li, Z. *Carbohydr. Res.* **2011**, *346* (15), 2380–2383.

(24) Crich, D.; Dudkin, V. *J. Am. Chem. Soc.* **2001**, *123* (28), 6819–6825.

(25) Sinaÿ, P. *Pure Appl. Chem.* **1978**, *50* (11–1), 1437–1452.

(26) Schmidt, T. H.; Madsen, R. *Eur. J. Org. Chem.* **2007**, *2007* (23), 3935–3941.

(27) Schumann, B.; Parameswarappa, S. G.; Lisboa, M. P.; Kottari, N.; Guidetti, F.; Pereira, C. L.; Seeberger, P. H. *Angew. Chem. Int. Ed.* **2016**, *55* (46), 14431–14434.

(28) Paulsen, H.; Lockhoff, O. *Chem. Ber.* **1981**, *114* (9), 3079–3101.

(29) Fraser-Reid, B.; López, J. C.; Gómez, A. M.; Uriel, C. *Eur. J. Org. Chem.* **2004**, *2004* (7), 1387–1395.

(30) Bohé L.; Crich D. *Trends Glycosci. Glycotechnol.* **2010**, *22* (123), 1–15.

(31) Green, L. G.; Ley, S. V.; Ernst, B.; Hart, G. W.; Sinaý, P. Protecting Groups: Effects on Reactivity, Glycosylation Stereoselectivity, and Coupling Efficiency. In *Carbohydrates in Chemistry and Biology*; Wiley-VCH Verlag GmbH, 2000; pp 427–448.

(32) van der Vorm, S.; Hansen, T.; Overkleeft, H. S.; van der Marel, G. A.; Codee, J. D. C. *Chem. Sci.* **2017**, *8* (3), 1867–1875.

(33) van der Vorm, S.; Overkleeft, H. S.; van der Marel, G. A.; Codée, J. D. C. *J. Org. Chem.* **2017**, *82* (9), 4793–4811.

(34) Hagen, B.; van Dijk, J. H. M.; Zhang, Q.; Overkleeft, H. S.; van der Marel, G. A.; Codée, J. D. C. *Org. Lett.* **2017**, *19* (10), 2514–2517.

(35) Hagen, B.; Ali, S.; Overkleeft, H. S.; van der Marel, G. A.; Codée, J. D. C. *J. Org. Chem.* **2017**, *82* (2), 848–868.

(36) Codée, J. D. C.; Litjens, R. E. J. N.; den Heeten, R.; Overkleeft, H. S.; van Boom, J. H.; van der Marel, G. A. *Org. Lett.* **2003**, *5* (9), 1519–1522.

(37) Crich, D.; Sun, S. *J. Org. Chem.* **1996**, *61* (14), 4506–4507.

(38) Zegelaar-Jaarsveld, K.; Smits, S. A. W.; van der Marel, G. A.; van Boom, J. H. *Bioorg. Med. Chem.* **1996**, *4* (11), 1819–1832.
(39) Magaud, D.; Dolmazon, R.; Anker, D.; Doutheau, A.; Dory, Y. L.; Deslongchamps, P. *Org. Lett.* **2000**, *2* (15), 2275–2277.
(40) de Jong, A.-R.; Hagen, B.; van der Ark, V.; Overkleeft, H. S.; Codée, J. D. C.; Van der Marel, G. A. *J. Org. Chem.* **2012**, *77* (1), 108–125.
(41) Zhang, Q.; van Rijssel, E. R.; Walvoort, M. T. C.; Overkleeft, H. S.; van der Marel, G. A.; Codée, J. D. C. *Angew. Chem. Int. Ed.* **2015**, *54* (26), 7670–7673.
(42) The C-6–OBn has the possibility to hydrogen-bond with the C-4–OH, rendering the acceptor more nucleophilic. This effect is seen for C-6–OBn protected acceptor **1** versus acceptor **2**, which based on the absence of the electronegative oxygen atom at C6 should be a more reactive acceptor than **1**. The hydrogen-bond may also be the contribution that prevents donor **B** in providing full α-selective condensations (Table 2; **9B**, **13B**).
(43) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91* (2), 165–195.
(44) The addition of a third nitro group on the benzoate did not lead to a further increase in α-selectivity. In fact, slightly more β-product was obtained with the C-6-trinitrobenzoate acceptor (Chapter 9 **57**; α/β = 2.1: 1).
(45) Burugupalli, S.; Shah, S.; van der Peet, P. L.; Arora, S.; White, J. M.; Williams, S. J. *Org Biomol Chem* **2016**, *14* (1), 97–104.
(46) Mulard, L. A.; Kováč, P.; Glaudemans, C. P. J. *Carbohydr. Res.* **1994**, *251*, 213–232.
(47) Daragics, K.; Szabó, P.; Fügedi, P. *Carbohydr. Res.* **2011**, *346* (12), 1633–1637.
(48) Rochepeau-Jobron, L.; Jacquinet, J.-C. *Carbohydr. Res.* **1997**, *303* (4), 395–406.
(49) Ward, D. E.; Kaller, B. F. *J. Org. Chem.* **1994**, *59* (15), 4230–4238.
(50) Rocheleau, S.; Pottel, J.; Huskić, I.; Moitessier, N. *Eur. J. Org. Chem.* **2017**, *2017* (3), 646–656.
(51) Shie, C.-R.; Tzeng, Z.-H.; Kulkarni, S. S.; Uang, B.-J.; Hsu, C.-Y.; Hung, S.-C. *Angew. Chem. Int. Ed.* **2005**, *44* (11), 1665–1668.
(52) Cicero, D.; Varela, O.; De Lederkremer, R. M. *Tetrahedron* **1990**, *46* (4), 1131–1144.
(53) Stévenin, A.; Boyer, F.-D.; Beau, J.-M. *J. Org. Chem.* **2010**, *75* (5), 1783–1786.
(54) Yoneda, Y.; Kawada, T.; Rosenau, T.; Kosma, P. *Carbohydr. Res.* **2005**, *340* (15), 2428–2435.
(55) Łopatkiewicz, G.; Mlynarski, J. *J. Org. Chem.* **2016**, *81* (17), 7545–7556.
(56) Zhang, X.; Ren, B.; Ge, J.; Pei, Z.; Dong, H. *Tetrahedron* **2016**, *72* (7), 1005–1010.
(57) Doi, R.; Shibuya, M.; Murayama, T.; Yamamoto, Y.; Iwabuchi, Y. *J. Org. Chem.* **2015**, *80* (1), 401–413.
(58) Warrener, R. N.; Russell, R. A.; Marcuccio, S. M. *Aust. J. Chem.* **1980**, *33* (12), 2777–2779.
(59) Kim, K. S.; Fulse, D. B.; Baek, J. Y.; Lee, B.-Y.; Jeon, H. B. *J. Am. Chem. Soc.* **2008**, *130* (26), 8537–8547.