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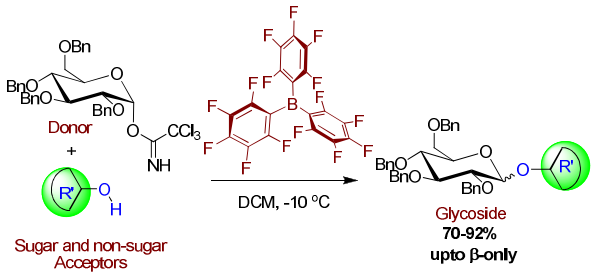
TOC



Abstract: Tris(pentafluorophenyl)borane promoted stereoselective glycosylation with trichloroacetimidate glycosyl donors is described. The reactions proceed efficiently with a wide range of acceptors, from sugar to non-sugar, under mild conditions in the presence of a catalytic amount of $B(C_6F_5)_3$. The perbenzylated glucosyl α-imidate provides β-selective glycosides in 70-92% yields.

Structurally well-defined glycosides are crucial for understanding various biological functions of carbohydrates.[1] Glycosylation is an important reaction through which enantiomerically pure oligosaccharides and glycoconjugates are synthesized.[2] Indeed, stereoselective formation of a glycosyl linkage is a challenging task which is controlled by many factors including the nature of donor and acceptor, activator, solvent, temperature, etc.[2,3] Nevertheless, the interaction of the activator with the glycosyl donor or acceptor plays a crucial role in stereoselective glycosylation.[3c,4] Recently, Schmidt *et.al* have introduced a novel conceptual approach for the stereoselective glycoside bond formation by acid-base catalysis, where some promoter shows high affinity towards the acceptor rather than donor while the adduct of acceptor-promoter activates the glycosyl donor and deliver the acceptor in a stereocontrolled manner.[5]

Among the different glycosyl donors, Schmidt's trichloroacetimidates are most used in glycosylation due to their high reactivity and easy preparation.[2-6] Activation of trichloroacetimidate is typically accomplished by Lewis acids such as TMSOTf and boron trifluoride etherate.[4,6] However, these catalysts do not provide stereoselectivity in glycosylation reactions in the absence of anchimeric assistance. Recently, significant efforts

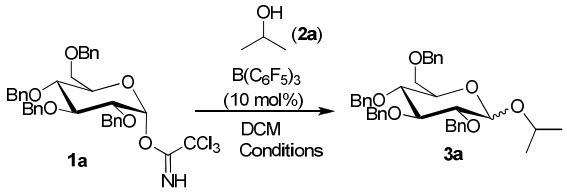
have been made towards the development of transition metal catalysts as well as organocatalysts to achieve high stereoselectivity in glycosylation reactions.[7] Notably, cationic palladium complexes,[8] (salen) cobalt complex,[9] gold chlorides,[5b] silicon fluorides,[5c] phenyl boron fluorides,[5d] thioureas,[5e,10] and TMSNTf2[11] have been recently established. Nevertheless, each method of glycosylation has its own advantages and disadvantages and thus the development of new promoters for the glycosylation reaction that offer high stereoselectivity and good yield under optimum condition is of great interest.

Tris-(pentafluorophenyl)borane ($B(C_6F_5)_3$ or BCF) is a versatile Lewis acid catalyst explored in hydrogenation, hydrosilylation, borylation, polymerization reactions, etc.[12] Indeed, $B(C_6F_5)_3$ is a key reagent leading to the concept of frustrated Lewis pairs.[13] Although some applications of $B(C_6F_5)_3$ were explored in carbohydrate synthesis,[14] its application in glycosylation reactions are not well studied.[15] Recently, the Schmidt group has investigated the activation of glycosyl imidates by using phenyl boron difluoride which provides good to excellent stereoselectivity in the glycosylation reaction.[5d] Nevertheless, these catalysts are expected to be strong Lewis acids owing to direct boron-fluoride (B-F) bonds which may be the reason for requirement of low temperature for the activation of imidates (i.e. -78 ^{o}C). In this context, $B(C_6F_5)_3$ would possess relatively less Lewis acidity and thus we have envisioned that the imidates may be activated at a more optimal temperature. Moreover, steric bulk and the electron-withdrawing nature of the three C_6F_5 groups around the boron also inspired us to investigate the activation of trichloroacetimidate glycosyl donors with BCF.

At the outset, glycosylation of perbenzylated glucose α-imidate (**1a**) was investigated with *iso*-propanol (**2a**) in dichloromethane (Table 1). The reaction was carried out at room temperature (~ 23 $^{\circ}$C) with 10 mol% of tris(pentafluorophenyl)borane in the presence of molecular sieves (4Å) (Table 1, entry 1). To our delight, the desired glycoside **3a** was obtained in 59% yield within 45 mins while the anomeric selectivity was observed in α:β=1:3.5 ratio. To our surprise, the glycosylation also proceeds efficiently in the absence of molecular sieves and gave **3a** in 88% yield within 15 mins (Table 1, entry 2). However, there was no significant change observed in the stereoselectivity. Encouraged, further optimization of the glycosylation reaction was carried out by varying the reaction conditions in the absence of molecular sieves. At 0°C, the desired glycoside **3a** was obtained in 86% yield with a significant increase in the β-selectivity *i.e.* from 1:3.5 to 1:9 (α:β) (Table 1, entry 3). To further explore the effect of temperature, the glycosylation reaction was additionally tested at -10°C, -20°C, -30°C and -78°C. The reaction proceeds smoothly at -10°C to provide the glycoside **3a** in 89% yield with α:β=1:11.5 ratio (Table 1, entry 4). Unfortunately, the glycosylation reactions were found to be slow at -20 °C, -30 °C and -78 °C (Table 1, entries

5-7). For instance, the reaction did not proceed to completion even after 14 hours at -78 °C (Table 1, entry 7) while -20°C and -30°C also gave the products in reduced yields. However, there was a slight increment in the β-selectivity with decrease in temperature.

Table 1. Optimization of the reaction condition.



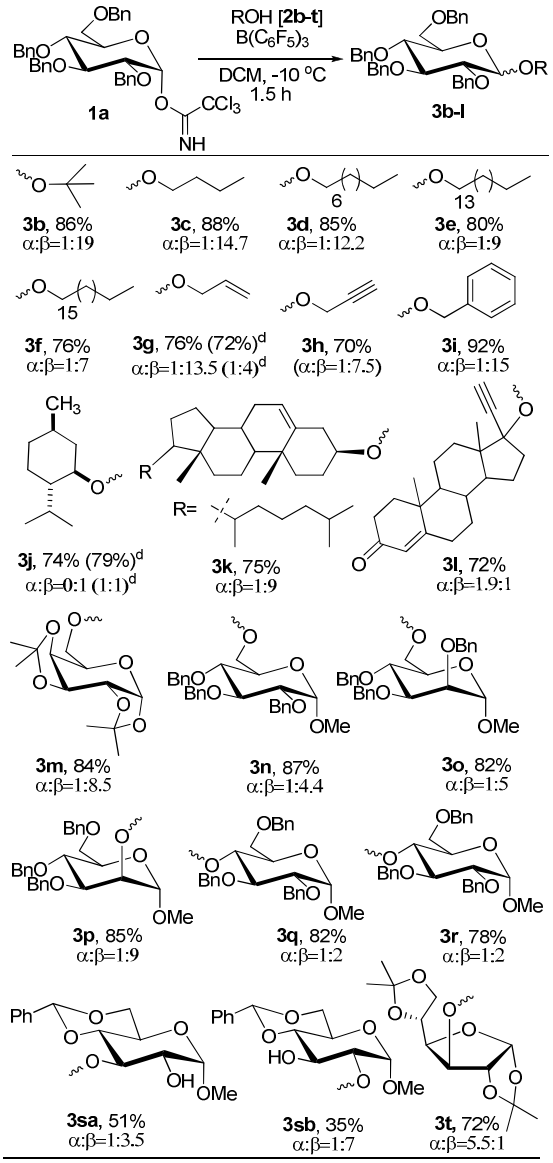
Entry	Tem (^oC)	Time	Yield (%)[a]	α:β[b]
1[c]	23	45 mins	59	1:3.5
2	23	15 mins	88	1:3.5
3	0	30 mins	86	1:9
4	-10	1.5 h	89	1:11.5
5	-20	5.0 h	72	1:13
6	-30	5.0 h	60	1:19
7	-78	14.0 h	42	β-only
8[d]	-10	1.5 h	82	1:11.5
9[d]	-10	1.5 h	<10	nd[e]
10[f]	-10	3.0 h	<10	nd[e]
11[g]	-10	3.0 h	17	nd[e]
12[h]	-10	1.5 h	82	1:3

[a]Isolated yield. [b]Measured using ^{1}HNMR. [c]Molecular sieves was added. [d]Reaction was carried out in reverse mode. [e]nd:Not determined. [f]Reaction was carried out in CH_3CN. [g]Reaction was carried out in THF. [h]$BF_3.OEt_2$ is used instead of BCF

All the above mentioned reactions were carried out in normal mode, where the acceptor and donor were stirred in dichloromethane prior to activator addition. Some recent reports suggest that reverse mode addition is efficient for glycosylation reactions.[5] Thus, the reaction was tested in two other conditions, namely, i) addition of acceptor and catalyst followed by donor (Table 1, entry 8) and ii) addition of donor and catalyst followed by acceptor (Table 1, entry 9). In the first case, almost the same yield and stereoselectivity was observed while the latter condition gave the desired glycoside in <10% yield. Further, the glycosylation reaction was executed in other solvents such as acetonitrile and THF at -10^{o}C. Both solvents gave the desired glycoside **3a** in a low yield (Table 1, entries 10 and 11). Finally, the glycosylation was performed with catalytic amount of $BF_3.OEt_2$ (instead of $B(C_6F_5)_3$) in order to identify

the credential of BCF in seteroselective glycosylation (Table 1, entry 12). The reaction provides the glycoside **3a** in a comparable yield to that of BCF, however with poor stereoselectivity, *i.e.* α:β=1:3.

Scheme 1. $B(C_6F_5)_3$-promoted glycosylation of non-sugar and sugar acceptors with donor **1a**.[a,b,c]



[a]Donor **1a** (1 equiv.), ROH (1.5 equiv. [**2b-l**] or 0.67 equiv. [**2m-t**]) and BCF (10 mol%) were stirred in DCM at -10°C; [b]Isolated yields. [c]α:β ratio was measured using ^{1}HNMR. [d]Reaction was carried out with $BF_3.OEt_2$ instead of BCF.

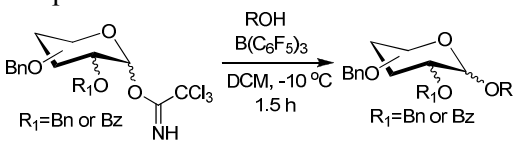
Having established the optimized condition, glycosylation of various non-sugar (**2b-2l**) as well as sugar acceptors (**2m-2t**) with perbenzylated glucose α-imidate (**1a**) was investigated

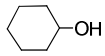
(Scheme 1). Glycosylation of *tert*-butanol with donor **1a** gave the desired glycoside **3b** in 86% yield with α:β ratio 1:19. Further, different linear alcohols including *n*-butanol, nonan-1-ol, hexadecan-1-ol, and octadecan-1-ol were subjected to the glycosylation with donor **1a** under the optimized condition (Scheme 1, **2c-f**). The reactions provide the corresponding glycosides **3c-3f** in >76% yields with up to α:β=1:14.7 ratio. It is also noteworthy that the long chain linear alcohols also showed a comparable reactivity to that of small alcohols in glycosylation reactions. However, a decrease in β-selectivity was observed with the increased carbon chain length.

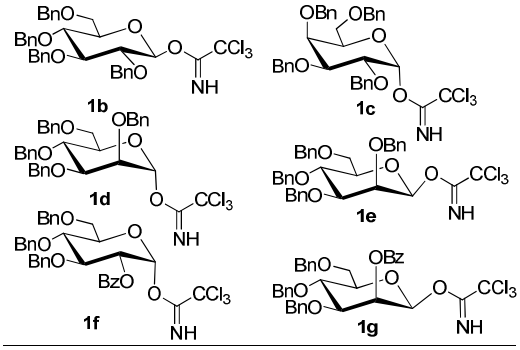
Similar to alkanols, allyl, propargyl and benzyl alcohols also underwent glycosylation smoothly to provide glycosides **3g-3i** with good to excellent β-selectivity (up to α:β=1:15). It is important to note that glycosylation of donor **1a** with allyl alcohol catalyzed by $BF_3.OEt_2$ provides α:β selectivity only in 1:4 ratio. Remarkably, L-menthol glycoside **3j** was obtained with complete β-selectivity with BCF while $BF_3.OEt_2$ provides 1:1 anomeric mixture. Steroid containing glycosides have received considerable attention in various fields.[16] The glycosylation of cholesterol (**2k**) with donor **1a** gave the glycoconjugates **3k** in 75% yield with α:β=1:9 ratio. However, to our surprise, ethisterone (**2l**) underwent α-selective glycosylation (i.e. α:β =1.9:1), which might be due to the steric hindrance around the hydroxyl group (Scheme 1, **3l**).

Encouraged, glycosylation between sugar alcohols (**2m-2t**) and donor **1a** was investigated under the optimized condition**.** Initially, the glycosylation was tested with galactose (**2m**), glucose (**2n**) and mannose (**2o**) acceptors possessing primary alcohols. To our delight, the reaction proceeds smoothly and gave the disaccharides **3m-3o** in >82% yield while α:β selectivity was observed up to 1:8.5 ratio. Similarly, glycosylation of secondary alcohol possessing mannopyranose (**2p**) and glucopyranose acceptors (**2q** and **2r)** was successfully accomplished in >78% yield with α:β=1:2 to 1:9 ratio (Scheme 1, **3p-3r**). The reaction also proceeds with diol containing acceptor such as 2,6-benzylidene α-methylglucoside (**2s**) and gave β-selective disaccharides **3sa** (3-OH glycosylated) and **3sb** (2-OH glycosylated) in 51% and 29% yield, respectively. However, *iso*-propylidene protected D-glucose acceptor (**2t**) gave the α-selective glycoside (**3t**) (α:β =5.5:1). In fact, a similar observation was previous reported by Schmidt *et.al* where acceptor **2t** provides preferentially α-selective glycoside with perbenzyl glucosyl α-imidate due to steric hindrance and poor reactivity of hydroxyl group (i.e. 3-OH).[6c]

Scheme 2. $B(C_6F_5)_3$-promoted glycosylation of various glycosyl imidates with different acceptors.[a]



Entry	Donor	R-OH	Product	Yield (%)[b]	α:β[c]
1	**1b**	**2a**	**3a**	90	3 : 1
2	**1b**	**2j**	**3j**	72	1: 1.6
3	**1b**	**2n**	**3n**	85	1 : 1.7
4	**1c**	**2a**	**3u**	84	1 : 8.6
5	**1d**	**2a**	**3v**	92	1 : 3
6	**1e**	**2a**	**3v**	85	8 : 1
7	**1f**	**2c**	**4a**	87	β-only
8	**1f**	 **(2s)**	**4b**	91	β-only
9	**1g**	**2c**	**4c**	92	α-only
10	**1g**	**2s**	**4d**	85	α-only

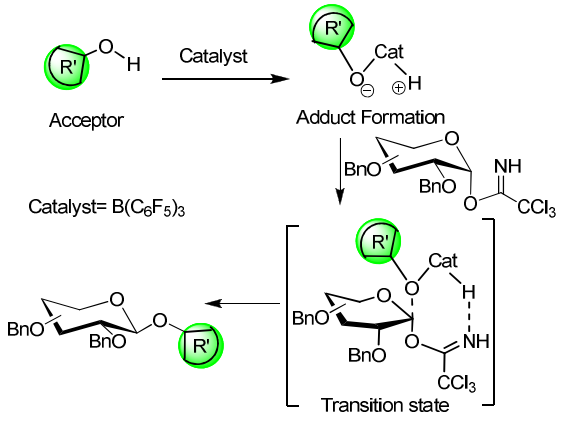


[a]Donor **1a** (1 equiv.), ROH (1.5 equiv.,) for **2n** (0.67 equiv.) and BCF (10 mol%) were stirred in DCM -10°C. [b]Isolated yield. [c]Measured using ^{1}HNMR.

Having studied the acceptor scope with perbenzylated glucose α-imidate, the scope of donors was investigated with other commonly used glycosyl imidates **1b-1g** (Scheme 2). Initially, glycosylation of different acceptors with perbenzylated glucose β-imidate (**1b**) was studied. Glycosylation of *iso*-propanol with donor **1b** gave the glycoside **3a** in 90% yield, however with high α-selectivity (α:β=3:1). Similarly, acceptors L-menthol **(2j)** and α-methylglucoside **2n** were also gave the glycosides **3j** and **3n** with increased α-selectivity in comparison to the reactions of these acceptors with glucose α-imidate (**1a**). Further, the glycosylation of *iso*-propanol (**2a**) was investigated with perbenzylated glalactosyl and mannosyl α/β-imidates to understand the anomeric selectivity (Scheme, **1c**-**1e**). Similar to our previous observation, galactose α-imidate (**1c**) underwent glycosylation with high β-selectivity (Scheme 3, **3u**)**.** On the other hand, perbenzylated mannose α- and β-imidates (**1d** and **1e**) gave high β- and α-selective glycosides **3v** and **3w**, respectively. Further, the glycosylation was investigated with

participating group containing donor such as 2-*O*-benzoyl-3,4,6-tri-*O*-benzylglucose α-imidate (**1f**) and 2-*O*-benzoyl-3,4,6-tri-*O*-benzylmannose β-imidate (**1g**) donors in the presence of *n*-butanol (**2c**) and cyclohexanol (**2s**) acceptors. All the reactions proceeded smoothly to provide the desired products **4a-4d** in >87% yield with complete stereocontrol (either α or β).

The mechanism of the reaction is unclear to us at this point of time. However, from scheme 1 and 2, it is clear that the α-imidates provide high β-selectivity while increased α-selectivity is observed with β-imidates. Therefore, we believe that the reaction might proceed through S_N2 or acid-base mechanism rather than S_N1 (i.e. through carbonium ion intermediate). In this context, ^{1}H NMR study was performed with the acceptor (*iso*-propanol) in the presence of and absence of promoter $B(C_6F_5)_3$ (1.0 equiv.) at room temperature in $CDCl_3$. It reveals that there is a formation of acceptor-activator adduct which can be seen from the shift of the OH peak of *iso*-propanol in the presence of $B(C_6F_5)_3$ (Figure SI-1 in ESI). In addition, under moisture free condition, the donor **1a** did not undergo decomposition at -10^{o}C in the presence of 10 mol% of $B(C_6F_5)_3$. In fact, similar observations were previously reported with other acid-base catalysts such as phenylboron difluoride as well as gold chloride.[5b,5d] Therefore, overall it lends support to the assumption that the BCF may act as an acid-base type rather than simple SN_2 type reaction. At first, acceptor forms adduct with catalyst which activates the imidate in a stereoselective manner to provide β-selective glyscosides from perbenzylated α-glucosyl imidate as shown in scheme 3.



Scheme 3. Plausible mechanism for the activation of imidates with BCF.

In conclusion, we have demonstrated the application of tris(pentafluorophenyl)borane as an efficient catalyst for stereoselective glycosylation with glycosyl imidates. A wide range of sugar and non-sugar acceptors were examined with perbenzylated α-glucosyl imidate as well as different α- and β-glycosyl imidates. All the reactions proceed in a stereoselective manner

where α-imidates give β-selective glycosides while β-imidates provide α-selective glycosides in high yields. This simple method does not require molecular sieves or extremely low temperatures, and thus shows promise to find wide applications in oligosaccharide synthesis.

Experimental Section

General methods

All the reactions were executed using anhydrous solvents under an argon atmosphere in oven-dried glassware at 100°C. All the reagents and solvents were of pure analytical grade. Thin-layer chromatography (TLC) was performed on 60 F254 silica gel, pre-coated on aluminum plates and revealed with either a UV lamp (λ_{max} = 254 nm) or a specific colour reagent (iodine vapours) or by spraying with methanolic H_2SO_4 solution and subsequent charring by heating at 100°C. ^1H and ^{13}C NMR were recorded at 500 MHz and 125 MHz, respectively on Bruker Advance 500 MHz NMR spectrometer. Chemical shifts given in ppm downfield from internal TMS; *J* values in Hz. HRMS spectra was recorded on UHD Q-TOF using water's Quattro Micro V 4.1. Column chromatography was performed using 100-200 mess silica gel.

Experimental Procedures

Optimization Table 1, Entry 1: Anhydrous DCM (6 mL) was added to a powdered, flame-dried 4 Å molecular sieves (250 mg), followed by the addition of donor **1a** (120 mg, 0.18 mmol) and *iso*-propanol (acceptor) **2a** (0.016 ml, 0.27 mmol). The reaction mixture was stirred for 5 mins at room temperature to which the activator BCF (10 mg, 0.018 mmol) was added. The reaction was further stirred for 45 minutes at this temperature. After completion, the reaction was quenched by addition of triethylamine (0.1 ml) and diluted with 50 mL of DCM. The organic layer was washed with $NaHCO_3$ (aq.), brine and dried over Na_2SO_4. Further the organic layer was filtered, concentrated and subjected for the column chromatography purification (hexane/ethyl acetate) using silica gel (SiO_2:100-200) to afford the glycoside **3a**.

Optimization Table 1, Entries 2-7: Glucosyl donor **1a** (120 mg, 0.18 mmol) and *iso*-propanol **2a** (0.016 ml, 0.27 mmol) were stirred in freshly dried DCM (4 mL) at room temperature for 5 mins. After that, the reaction mixture was cooled to appropriate temperature as stated in Optimization Table 1. The reaction mixture was stirred for 5 mins at the same temperature to which the activator BCF (10 mg, 0.018 mmol) was added. The reaction mixture was further stirred for appropriate time as stated in Optimization Table 1 and quenched by addition of triethylamine (0.1 ml) and diluted with 50 mL of DCM. The organic layer was washed with $NaHCO_3$ (aq.), brine and dried over Na_2SO_4. Further the organic layer

was filtered, concentrated and subjected for the column chromatography purification (hexane/ethyl acetate) using silica gel (SiO_2:100-200) to afford the glycoside **3a** in different yields as stated in optimization Table.

Optimization Table 1, Entry 8: *iso*-Propanol **2a** (0.016 ml, 0.27 mmol) and the activator BCF were stirred in freshly dried DCM (3 mL) at room temperature for 5 mins. After that the reaction mixture was cooled to -10^{o}C. The reaction mixture was stirred for 5 mins at the same temperature to which the solution glucosyl donor **1a** (120 mg, 0.18 mmol) in DCM (1 mL) was added. The reaction mixture was further stirred for 1.5 h at the same temperature, and quenched by addition of triethylamine and diluted with 50 mL of DCM. The organic layer was washed with $NaHCO_3$ (aq.), brine and dried over Na_2SO_4. Further the organic layer was filtered, concentrated and subjected for the column chromatography purification (hexane/ethyl acetate) using silica gel (SiO_2:100-200) to afford the glycoside **3a**.

Optimization Table 1, Entry 9: Glucosyl donor **1a** (120 mg, 0.18 mmol) and the activator BCF were stirred in freshly dried DCM (3 mL) at room temperature for 5 mins. After that the reaction mixture was cooled to -10^{o}C. The reaction mixture was stirred for 5 mins at the same temperature to which the solution of *iso*-propanol **2a** (0.016 ml, 0.27 mmol) in DCM (1 mL) was added. The reaction mixture was further stirred for 1.5 h at the same temperature. Decomposition of the donor was observed.

Optimization Table 1, Entries 10-11: A similar procedure was adopted as stated above in optimization table 1, entry 2-7. However, in the place of DCM, other solvents such as THF and acetonitrile were used for the glycosylation reaction.

Optimization Table 1, Entry 12: Anhydrous DCM (6 mL) was added to a powdered, flame-dried 4 Å molecular sieves (250 mg), followed by the addition of donor **1a** (120 mg, 0.18 mmol) and *iso*-propanol (acceptor) **2a** (0.016 ml, 0.27 mmol). The reaction mixture was stirred for 5 mins at -10^{o}C to which the activator BF_3. OEt_2 (cat.) was added. The reaction was further stirred for 90 minutes at this temperature. After completion, the reaction was quenched by addition of triethylamine (0.1 ml) and diluted with 50 mL of DCM. The organic layer was washed with $NaHCO_3$ (aq.), brine and dried over Na_2SO_4. Further the organic layer was filtered, concentrated and subjected for the column chromatography purification (hexane/ethyl acetate) using silica gel (SiO_2:100-200) to afford the glycoside **3a**.

General Glycosylation Procedures:

Glycosylation Procedure A (for nonsugar acceptors **2b-2l** and **2s**, Scheme 1 and 2**)**: Donor (1 equiv.) and acceptor (1.5 equiv) were stirred in freshly dried DCM (3-5 mL) for 5 mins at room temperature. After 5 mins, the reaction mixture was cooled to -10 ^{o}C and allowed to stir for 5 mins, to which the activator BCF (0.1 equv. with respect to donor) was added. The reaction was further stirred for 1.5 h at the same temperature and quenched by addition of triethylamine (0.1 mL) and diluted with 50 mL of DCM. The organic layer was washed with $NaHCO_3$ (aq.) and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate) using silica gel (SiO_2:100-200) to afford glycosides.

Glycosylation Procedure B (For sugar acceptors **2m-2t,** Scheme 1 and 2): Glycosyl donor (1 equiv) and acceptor (0.67 equiv.) were stirred in freshly dried DCM (3-5 mL) for 5 mins at room temperature. After 5 mins, the reaction mixture was cooled to -10 ^{o}C and allowed to stir for 5 mins, to which the activator BCF (0.1 equiv. with respect to acceptor) was added. The reaction was further stirred for 1.5 h at the same temperature and quenched by addition of triethylamine (0.1 mL) and diluted with 50 mL of DCM. The organic layer was washed with $NaHCO_3$ (aq.) and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate) using silica gel (SiO_2:100-200) to afford glycosides.

2-Propyl 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranoside [3a][5c]: The compound **3a** was prepared using the glycosylation procedure A. The reaction was carried out between donor **1a** (120 mg, 0.18 mmol) and *iso*-propanol **2a** (0.016 ml, 0.27 mmol) in freshly dried DCM (4 mL) in the presence of BCF (10 mg, 0.018 mmol) at -10 ^{o}C. Column chromatography purification was performed using 5% ethyl acetate in hexane to obtain **3a** as white solid (83 mg, 89%); α:β=1:11.5; TLC R_f = 0.35 (12% ethyl acetate/88% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.16 (m, 18H), 7.09 (d, *J* = 6.3 Hz, 2H), 4.87 (dd, *J* = 25.5, 10.5 Hz, 2H), 4.72 (dd, *J* = 18.5, 10.5 Hz, 2H), 4.63 (d, *J* = 10.5 Hz, 1H), 4.52-4.44 (m, 3H), 4.39 (d, *J* = 7.5 Hz, 1H), 3.96-3.93 (m, 1H), 3.65 (d, *J* = 10.5 Hz, 1H), 3.59-3.54 (m, 2H), 3.47 (t, *J* = 9.5 Hz, 1H), 3.39-3.37 (m, 2H), 1.24 (d, *J* = 6.0 Hz, 3H), 1.17 (d, *J* = 9.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 138.5, 138.2, 138.1, 128.3, 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5, 102.1, 84.8, 82.2, 77.9, 75.6, 74.9, 74.8, 74.7, 73.4, 72.3, 69.1, 23.7, 22.2.

***t*-Butyl 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranoside [3b]**[17a]: The compound **3b** was prepared using the glycosylation procedure A. The reaction was carried out between donor **1a** (100 mg, 0.15 mmol) and *t*-butanol **2b** (17 mg, 0.23 mmol) in freshly dried DCM (3 mL) in the presence of BCF (8 mg, 0.015 mmol) at -10 ^{o}C. Column chromatography purification was

performed using 8% ethyl acetate in hexane which furnished **3b** as white solid (76 mg, 86%); α:β= 1:19; TLC R_f = 0.45 (15% ethyl acetate/85% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.17 (m, 18H), 7.10 (d, *J* = 6.0 Hz, 2H), 4.90 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 10.5 Hz, 1H), 4.72 (dd, *J* = 19.5, 11.0 Hz, 2H), 4.63 (d, *J* = 11.0 Hz, 1H), 4.52-4.45 (m, 4H), 3.63 (d, *J* = 10.5 Hz, 1H), 3.59-3.53 (m, 2H), 3.45 (t, *J* = 9.0 Hz, 1H), 3.39-3.33 (m, 2H), 1.50 (s, 0.76H), 1.25 (s, 8.52H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 138.4, 138.3, 138.1, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.5, 127.4, 97.8, 85.1, 82.3, 78.1, 76.0, 75.7, 74.9, 74.8, 74.6, 73.3, 69.3, 28.8.

Butyl 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranoside [3c][17b]: The compound **3c** was prepared using the glycosylation procedure A. The reaction was carried out between donor **1a** (112 mg, 0.16 mmol) and n-butanol **2c** (0.019 ml, 0.24 mmol) in freshly dried DCM (4 mL) in the presence of BCF (8 mg, 0.016 mmol) at -10 ^{o}C. Column chromatography purification was performed using 5% ethyl acetate/hexane which furnished **3c** as white solid (83 mg, 88%); α:β=1:14.7; TLC R_f = 0.35 (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.28 (m, 18H), 7.20 (d, *J* = 7.5 Hz, 2H), 4.98 (t, *J* = 11.5 Hz, 2H), 4.84 (dd, *J* = 15.5, 10.5 Hz, 2H), 4.76 (d, *J* = 11.0 Hz, 1H), 4.64-4.56 (m, 3H), 4.43 (d, *J* = 7.5, 1H), 4.02-4.00 (m, 1H), 3.79 (d, *J* = 11 Hz, 1H), 3.73-3.66 (m, 2H), 3.63-3.58 (m, 2H), 3.50 (dd, *J* = 15.5, 6.5 Hz, 2H), 1.71-1.67 (m, 2H), 1.49-1.46 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.5, 138.2, 138.1, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.7, 127.6, 127.6, 103.7, 84.7, 82.3, 78.0, 75.7, 75.0, 74.9, 74.8, 73.5, 69.8, 69.0, 31.8, 19.3, 13.9.

Nonyl 2,3,4,6-tetra-O-benzyl-*β,α*-D-glucopyranoside, [3d]: The compound **3d** was prepared using the glycosylation procedure A. The reaction was carried out between donor **1a** (120 mg, 0.18 mmol) and acceptor **2d** (0.048 ml, 0.27 mmol) in freshly dried DCM (4 mL), in the presence of BCF (9 mg, 0.018 mmol) at -10 ^{o}C. Column chromatography purification was performed using 3% ethyl acetate in hexane which furnished **3d** as semi solid (104 mg, 85%); α:β=1:12.2; TLC R_f = 0.35 (8% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.32 (m, 18H), 7.23 (dd, *J* = 8.0, 2.0 Hz, 2H), 5.02 (dd, *J* = 15.0, 11.0 Hz, 2H), 4.87 (dd, *J* = 14.5, 10.5 Hz, 2H), 4.79 (d, *J* = 11.0 Hz, 1H), 4.69-4.59 (m, 3H), 4.46 (d, *J* = 8.0 Hz, 1H), 4.06-4.01 (m, 1H), 3.81 (dd, *J* = 11.0, 2.0 Hz, 1H), 3.75-3.70 (m, 2H), 3.65 (m, 2H), 3.54-3.52 (m, 2H), 1.75-1.68 (m, 2H), 1.49-1.44 (m, 2H), 1.38-1.33 (m, 10H), 0.95 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 138.4, 138.1, 138.0, 128.2, 128.2, 128.2, 128.0, 127.8, 127.7, 127.6, 127.4, 103.6, 84.6, 82.2, 77.8, 75.6, 74.9, 74.8, 74.7, 73.4, 70.0, 68.9, 31.8, 29.7, 29.4, 29.4, 29.2, 26.1, 22.6, 14.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{43}H_{55}O_6$ 667.3999, found 667.4001.

Hexadecanyl 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranoside, [3e][17c]: The compound **3e** was prepared using the glycosylation procedure A. The reaction was carried out between

donor **1a** (110 mg, 0.16 mmol) and hexadecanol acceptor **2e** (58 mg, 0.24 mmol) in freshly dried DCM (5 mL) in the presence of BCF (8 mg, 0.016 mmol) at -10 ^{o}C. Column chromatography purification was performed using 3% ethyl acetate in hexane which furnished **3e** as White Semi solid (97 mg, 80%); α:β=1:9; TLC R_f = 0.4 (8% ethyl acetate/92% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.28 (m, 18H), 7.18 (dd, *J* = 7.5, 2.0 Hz, 2H), 4.97 (dd, *J* = 13.5, 11.0 Hz, 2H), 4.82 (dd, *J* = 15.5, 10.9 Hz, 2H), 4.74 (d, *J* = 11.0 Hz, 1H), 4.63-4.54 (m, 3H), 4.41 (d, *J* = 7.5 Hz, 1H), 4.01-3.97 (m, 1H), 3.78 (dd, *J* = 10.5, 2.0 Hz, 1H), 3.70-3.65 (m, 2H), 3.60 (m, 2H), 3.49-3.47 (m, 2H), 1.71-1.65 (m, 2H), 1.44-1.38 (m, 2H), 1.32-1.27 (m, 21H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 138.5, 138.2, 138.1, 128.3, 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 127.5, 103.6, 84.7, 82.2, 77.9, 75.6, 74.9, 74.8, 74.7, 73.4, 70.1, 69.0, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 26.1, 22.6, 14.1.

Octadecayl 2,3,4,6-tetra-*O*-benzyl-*ß,α*-D-glucopyranoside, [3f]: The compound **3f** was prepared using the glycosylation procedure A. The reaction was carried out between donor **1a** (100 mg, 0.15 mmol) and ocatdecanol acceptor **2f** (62 mg, 0.23 mmol) in freshly dried DCM (5 mL) in the presence of BCF (8 mg, 0.015 mmol) at - 10 ^{o}C. Column chromatography purification was performed using 3% ethyl acetate in hexane which furnished **3f** as semi solid (95 mg, 76%); α:β=1:7; TLC R_f=0.45 (8% ethyl acetate/92% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.29 (m, 20H), 4.97 (dd, *J* = 13.5, 11.0 Hz, 2H), 4.82 (dd, *J* = 15.0, 10.5 Hz, 2H), 4.74 (d, *J* = 10.5 Hz, 1H), 4.65-4.54 (m, 3H), 4.41 (d, *J* = 7.5 Hz, 1H), 4.01-3.96 (m, 1H), 3.76 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.71-3.65 (m, 2H), 3.61-3.58 (m, 2H), 3.49-3.47 (m, 2H), 1.67 (m, 2H), 1.42-1.40 (m, 2H), 1.32-1.28 (m, 27H), 0.90 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 138.5, 138.2, 138.1, 128.3, 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 127.5, 103.6, 84.7, 82.2, 77.9, 75.6, 74.9, 74.8, 74.7, 73.4, 70.1, 69.0, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 26.2, 22.6, 14.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{52}H_{72}O_6Na$ 815.5227, found 815.5267.

Allyl 2,3,4,6-tetra-*O*-benzyl-*ß,α*-D-glucopyranoside, [3g][5c]: The compound **3g** was prepared using the glycosylation procedure A. The reaction was carried out between donor **1a** (115 mg, 0.17 mmol) and ocatdecanol acceptor **2g** (0.023 ml, 0.34 mmol) in freshly dried DCM (5 mL) in the presence of BCF (9 mg, 0.017 mmol) at - 10 ^{o}C. Column chromatography purification was performed using 5% ethyl acetate in hexane which furnished **3g** as semi solid (81 mg, 83%); α:β=1:13.5; TLC R_f=0.45 (8% ethyl acetate/92% hexane);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 18H), 7.23 – 7.21 (m, 2H), 6.07 – 5.99 (m, 1H), 5.43-5.39 (m, 1H), 5.28 – 5.25 (m, 1H), 5.02 (dd, *J* = 17.5, 11.0 Hz, 2H), 4.87 (dd, *J* = 15.0, 11.0 Hz, 2H), 4.79 (d, *J* = 11.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.61 (dd, *J* = 11.5, 9.0 Hz, 2H), 4.53 – 4.49 (m, 2H), 4.24-4.19 (m, 1H), 3.82 – 3.65 (m, 4H), 3.58 – 3.51

(m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 138.4, 138.1, 138.0, 134.0, 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 117.1, 102.6, 84.6, 82.2, 77.8, 75.6, 74.9, 74.8, 73.4, 70.2, 68.9.

***Propargyl* 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranoside, [3h]**[5e]: The compound **3h** was prepared using the glycosylation procedure A: The reaction was carried out between donor **1a** (118 mg, 0.17 mmol) and propargyl alcohol acceptor **2h** (0.014 ml, 0.25 mmol) in freshly dried DCM (4 mL) in the presence of BCF (10 mg, 0.017 mmol) at -10 ^{o}C. Column chromatography purification was performed using 7% ethyl acetate in hexane which furnished **3h** as viscous oil (68 mg, 70%); α:β=1:7.5; TLC R_f = 0.35 (10% ethyl acetate/90% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.31 (m, 18H), 7.22-7.20 (m, 2H), 5.01 (dd, *J* = 23.5, 11.0 Hz, 2H), 4.85 (dd, *J* = 19.0, 10.5 Hz, 2H), 4.75 (d, *J* = 10.5 Hz, 1H), 4.70-4.65 (m, 2H),4.60 (d, *J* = 3.5 Hz, 1H), 4.58 (d, *J* = 2.0 Hz, 2H), 4.51-4.50 (m, 1H), 4.32 (d, *J* = 2.0 Hz, 0.18H), 3.78-3.67 (m, 4H), 3.54-3.53 (m, 2H), 2.51 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 138.3, 138.0, 138.0, 128.3, 128.3, 128.2, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5, 101.4, 84.5, 81.9, 79.0, 77.6, 75.6, 74.9, 74.8, 74.8, 74.7, 73.4, 68.7, 55.9.

Benzyl 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranoside, [3i][17d]: The compound **3i** was prepared using the glycosylation procedure A. The reaction was carried out between donor **1a** (115 mg, 0.17 mmol) and benzyl alcohol acceptor **2i** (0.025 ml, 0.25 mmol) in freshly dried DCM (4 mL) in the presence of BCF (8 mg, 0.017 mmol) at -10 ^{o}C. Column chromatography purification was performed using 7% ethyl acetate in hexane which furnished **3i** as white solid (98 mg, 92%); α:β=1:15; TLC R_f = 0.4 (10% ethyl acetate/90% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.16 (m, 22H), 7.08 (dd, *J* = 7.5, 2.0 Hz, 2H), 4.91-4.83 (m, 3H), 4.72 (dd, *J* = 19.0, 10.5 Hz, 2H), 4.64 (d, *J* = 11.0 Hz, 1H), 4.60-4.53 (m, 2H), 4.49-4.42 (m, 3H), 3.68 (dd, *J* = 10.5, 2.0 Hz, 1H), 3.62 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.57-3.51 (m, 2H), 3.45 (t, *J* = 8.0 Hz, 1H), 3.40-3.38 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 138.3, 138.1, 138.0, 137.4, 128.3, 128.3, 128.3, 128.2, 128.1, 127.9, 127.8, 127.8, 127.7, 127.6, 102.5, 84.6, 82.2, 77.8, 75.6, 74.9, 74.8, 74.8, 73.4, 71.0, 68.8.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranoside, [3j][17e]: The compound **3j** was prepared using the glycosylation procedure A: The reaction was carried out between donor **1a** (71 mg, 0.15 mmol) and L-menthol acceptor **2j** (35 mg, 0.22 mmol) in freshly dried DCM (4 mL) in the presence of BCF (7 mg, 0.015 mmol) at -10 ^{o}C. Column chromatography purification was performed using 4% ethyl acetate in hexane which furnished **3j** as White solid (71 mg, 71%); β-only; TLC R_f = 0.35 (10% ethyl acetate/90% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 18H), 7.26-7.25 (m, 2H), 5.00 (dd, *J* = 13.0, 11.0 Hz, 2H), 4.86 (dd, *J* = 13.0, 11.0 Hz, 2H), 4.75 (d, *J* = 11.0 Hz, 1H), 4.68 – 4.58 (m, 3H), 4.54 (d, *J* = 8.0 Hz, 1H), 3.76-3.75 (m, 2H), 3.71 – 3.64

(m, 2H), 3.59 – 3.54 (m, 1H), 3.49-3.46 (m, 2H), 2.43 – 2.40 (m, 1H), 2.20 (d, *J* = 12.5 Hz, 1H), 1.73-1.70 (m, 2H), 1.32 (m, 2H), 0.99 – 0.88 (m, 13H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.5, 138.3, 138.2, 128.3, 128.2, 128.2, 128.0, 127.7, 127.6, 127.6, 127.5, 127.4, 127.4, 100.7, 84.9, 82.1, 77.9, 77.7, 75.5, 74.9, 74.7, 73.6, 69.3, 48.1, 40.9, 34.4, 31.4, 25.2, 23.1, 22.2, 21.0, 15.9.

Cholesterol 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranoside, [3k][5c]: The compound **3k** was prepared using the glycosylation procedure A. The reaction was carried out between donor **1a** (110 mg, 0.16 mmol) and cholesterol **2k** (92 mg, 0.24 mmol) in freshly dried DCM (5 mL) in the presence of BCF (8 mg, 0.016 mmol) at -10 ^{o}C. Column chromatography purification was performed using 5% ethyl acetate in hexane which furnished **3k** as a white solid (108 mg, 75%); α:β=1:9; TLC R_f= 0.35 (8% ethyl acetate/92% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.29 (m, 18H), 7.22-7.21 (m, 2H), 5.38 (d, *J* = 5.0 Hz, 1H), 4.99 (dd, *J* = 28.0, 10.9 Hz, 2H), 4.84 (dd, *J* = 18.0, 10.5 Hz, 2H), 4.76 (d, *J* = 11.0 Hz, 1H), 4.65-4.53 (m, 4H), 3.76 (m, 1H), 3.70-3.59 (m, 4H), 3.50-3.48 (m, 2H), 2.48 (m, 2H), 2.07-2.05 (m, 3H), 1.91-1.89 (m, 2H), 1.61-1.33 (m, 14H), 1.21-1.11 (m, 8H), 1.07-1.05 (m, 4H), 0.96 (d, *J* = 6.0 Hz, 3H), 0.91 (d, *J* = 2.0 Hz, 3H), 0.90 (d, *J* = 2.0 Hz, 3H), 0.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 138.6, 138.5, 138.3, 138.1, 128.3, 128.3, 128.2, 128.2, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5, 121.9, 102.2, 84.8, 82.3, 79.6, 78.0, 75.6, 74.9, 74.9, 74.7, 73.3, 69.1, 56.7, 56.1, 50.1, 42.3, 39.7, 39.5, 39.1, 37.3, 36.7, 36.1, 35.7, 31.9, 31.8, 29.9, 29.6, 28.0, 24.2, 23.8, 22.8, 22.5, 21.0, 19.4, 18.7, 14.1, 11.8.

Ethisterone-2,3,4,6-tetra-O-benzyl-*β,α*-D-glucopyranoside, [3l]: The compound **3l** was prepared using the glycosylation procedure A. To a solution of donor **1a** (90 mg, 0.13 mmol) and ethisterone **2l** (37 mg, 0.12 mmol) in freshly dried DCM (4 mL), BCF (6 mg, 0.013 mmol) was added at -10 ^{o}C. Column chromatography purification was performed using 20% ethyl acetate in hexane which furnished **3l** as white solid (72 mg, 71%); α:β=1.9:1; TLC R_f= 0.3 (15% ethyl acetate/85% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.398-7.28 (m, 18H), 7.18-7.16 (m, 2H), 5.77 (s, 0.35H), 5.26 (d, *J* = 3.0 Hz, 0.65H), 5.04-4.49 (m, 8.65H), 4.08-3.98 (m, 1.37H), 3.74-3.54 (m, 4.55H), 3.35-3.16 (m, 0.65H), 2.60-2.04 (m, 5.32H), 1.75-1.35 (m, 9H), 1.22 (s, 3H), 1.12-0.98 (m, 2H), 0.92-0.90 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 171.1, 139.2, 138.6, 138.4, 138.1, 137.9, 137.8, 137.7, 128.4, 128.3, 128.3, 128.3, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.6, 123.8, 114.0, 97.4, 91.2, 87.2, 84.5, 83.1, 81.7, 79.9, 79.6, 77.7, 75.6, 75.6, 74.9, 74.7, 74.1, 73.4, 73.4, 73.2, 70.2, 68.8, 68.5, 53.3, 49.8, 46.6, 38.8, 38.5, 36.1, 35.6, 33.9, 33.7, 32.7, 32.3, 29.6, 29.6, 29.5, 29.4, 29.3, 29.1, 28.9, 23.0, 22.6, 20.6, 17.3, 14.1, 12.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{55}H_{63}O_7$ 835.4574, found 835.4640.

2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-*isopropylidene*-*α*-D-galactopyranoside, [3m][17f]: The compound **3m** was prepared using the glycosylation procedure B. The reaction was carried out between acceptor **2m** (35 mg, 0.13 mmol) and donor **1a** (135 mg, 0.2 mmol) in freshly dried DCM (4 mL) in the presence of BCF (7 mg, 0.013 mmol) at -10 ^{o}C. Column chromatography purification was performed using 12% ethyl acetate in hexane which furnished **3m** as viscous oil (85 mg, 84%); α:β=1:8.5; TLC R_f = 0.3 (18% ethyl acetate/82% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.43 (m, 2H), 7.37-7.28 (m, 16H), 7.17-7.15 (m, 2H), 5.59 (d, *J* = 5.0 Hz, 1H), 5.08 (d, *J* = 11.0 Hz, 1H), 4.98 (d, *J* = 11.0 Hz, 1H), 4.84-4.73 (m, 3H), 4.65-4.61 (m, 2H), 4.60-4.47 (m, 3H), 4.34 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.27 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.18 (dd, *J* = 11.0, 3.5 Hz, 1H), 4.12 (dd, *J* = 5.5, 1.5 Hz, 1H), 3.77-3.72 (m, 3H), 3.66-3.63 (m, 2H), 3.49-3.47 (m, 2H), 1.52 (s, 3H), 1.48 (s, 3H), 1.34 (s, 3x2=6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.1, 138.1, 128.6, 128.3, 128.3, 128.3, 128.2, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 127.4, 109.3, 108.5, 104.4, 96.4, 84.5, 81.6, 77.7, 75.6, 74.9, 74.7, 74.3, 73.5, 71.4, 70.8, 70.5, 69.7, 68.8, 67.3, 26.0, 26.0, 25.0, 24.4.

Methyl 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside, [3n][5c]: The compound **3n** was prepared using the glycosylation procedure B. The reaction was carried out between acceptor **2n** (80 mg, 0.17 mmol) and donor **1a** (170 mg, 0.25 mmol) in freshly dried DCM (4 mL) in the presence of BCF (8 mg, 0.017 mmol) at -10 ^{o}C. Column chromatography purification was performed using 8% ethyl acetate in hexane which furnished **3n** as white solid (145 mg, 87%); α:β=1:4.5; TLC R_f = 0.3 (15% ethyl acetate/85% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.24 (m, 29H), 7.22-7.15 (m, 6H), 4.96 (dd, *J* = 11.0, 4.5 Hz, 2H), 4.89 (m, 1H), 4.81-4.70 (m, 6H), 4.65-4.51 (m, 7H), 4.35-4.33 (m, 1H), 4.17 (dd, *J* = 11.0,2.0 Hz, 1H), 3.98 (td, *J* = 9.3, 5.4 Hz, 1H), 3.84-3.79 (m, 1H), 3.62-3.50 (m, 9H), 3.34 (m, 1H), 3.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.5, 138.3, 138.3, 138.2, 138.1, 138.1, 128.4, 128.3, 128.3, 128.3, 128.1, 127.9, 127.9, 127.8, 127.8, 103.8, 98.0, 84.7, 82.0, 81.9, 79.7, 78.0, 77.9, 75.6, 75.6, 75.0, 74.9, 74.8, 73.4, 73.3, 69.8, 69.0, 68.5, 55.1.

Methyl 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-*α*-D-mannopyranoside, [**3o**]**]**[17g]: The compound **3o** was prepared using the glycosylation procedure B. The reaction was carried out between acceptor **2o** (65 mg, 0.14 mmol) and donor **1a** (143 mg, 0.21 mmol) in freshly dried DCM (4 mL) in the presence of BCF (7 mg, 0.014 mmol) at -10 ^{o}C. Column chromatography purification was performed using 8% ethyl acetate in hexane which furnished **3o** as brownish solid (112 mg, 82%); α:β=1:5; TLC R_f = 0.35 (15% ethyl acetate/85% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.25 (m, 27H), 7.24-7.12 (m, 8H), 5.04 (d, *J* = 11.0 Hz, 1H), 4.94-4.90 (m, 2H), 4.80-4.76 (m, 3H), 4.70-

4.67 (m, 3H), 4.61 (d, *J* = 2.5 Hz, 1H), 4.59-4.58 (m, 2H), 4.54 (s, 1H), 4.52-4.51 (m, 1H), 4.49 (m, 1H), 4.40 (d, *J* = 8.0, 1H), 4.25 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.93 (d, *J* = 9.0 Hz, 1H), 3.90-3.88 (m, 1H), 3.82-3.80 (m, 2H), 3.76-3.74 (m, 1H), 3.72-3.69 (m, 2H), 3.64-3.58 (m, 2H), 3.49 (*t*, *J* = 8.0 Hz, 1H), 3.45-3.42 (m, 1H), 3.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 138.5, 138.5, 138.2, 138.2, 138.2, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 104.1, 98.9, 84.6, 82.1, 80.2, 77.9, 75.6, 75.0, 74.9, 74.9, 74.7, 74.6, 73.4, 72.7, 72.0, 71.4, 69.0, 54.7.

Methyl 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranoside, [3p]: The compound **3p** was prepared using the glycosylation procedure B. The reaction was carried out between acceptor **2p** (65 mg, 0.14 mmol) and donor **1a** (143 mg, 0.21 mmol) in freshly dried DCM (4 mL) in the presence of BCF (8 mg, 0.014 mmol) at -10 ^{o}C. Column chromatography purification was performed using 12% ethyl acetate/hexane which furnished **3p** as white solid (117 mg, 85%); α:β=1:9; TLC R_f = 0.35 (15% ethyl acetate/85% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.20 (m, 35H), 4.88-4.86 (m, 2H), 4.84-4.79 (m, 3H), 4.76-4.69 (m, 4H), 4.63-4.57 (m, 3H), 4.49-4.44 (m, 4H), 4.34-4.29 (m, 1H), 3.89-3.83 (m, 2H), 3.78 (t, *J* = 3.0 Hz, 1H), 3.74-3.66 (m, 3H), 3.62-3.55 (m, 3H), 3.6 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 138.5, 138.5, 138.4, 138.4, 138.2, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 127.4, 127.3, 127.3, 127.3, 102.9, 99.6, 84.8, 82.8, 78.0, 77.9, 75.8, 75.6, 75.2, 75.0, 74.8, 74.8, 73.5, 73.1, 72.8, 72.6, 71.7, 68.8, 68.7, 54.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{62}H_{66}O_{11}Na$ 1009.4503, found 1009.4503.

Methyl 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside, [3q][5c]: The compound **3q** was prepared using the Glycosylation Procedure B. The reaction was carried out between acceptor **2q** (58 mg, 0.13 mmol) and donor **1a** (136 mg, 0.2 mmol) in freshly dried DCM (4 mL) in the presence of BCF (7 mg, 0.013 mmol) at -10 ^{o}C. Column chromatography purification was performed using 8% ethyl acetate in hexane which furnished **3q** as semi solid (99 mg, 78%); α:β=1:2; TLC R_f = 0.3 (15% ethyl acetate/85% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.39 (m, 34H), 7.14-7.12 (m, 1H), 5.05-4.70 (m, 9H), 4.64-4.52 (m, 5H), 4.45-4.40 (m, 2H), 4.12-4.07 (m, 0.60H), 3.87 (m, 2H), 3.78-3.49 (m, 8H), 3.40 (s, 3H), 3.34-3.30 (m, 0.51H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 138.6, 138.5, 138.5, 138.3, 138.3, 138.2, 137.8, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.3, 127.2, 127.1, 126.7, 102.5, 99.3, 98.4, 97.7, 96.6, 84.8, 84.6, 82.8, 82.2, 82.0, 80.4, 80.2, 79.5, 78.8, 78.0, 75.1, 75.0, 75.0, 74.9, 74.8, 74.6, 73.6, 73.4, 73.3, 73.2, 73.1, 72.3, 71.0, 70.0, 69.5, 69.0, 68.9, 67.8, 55.3, 55.1.

Methyl 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-*α*-D-glucopyranoside, [3r]: The compound **3r** was prepared using the glycosylation procedure B. The reaction was carried out between acceptor **2r** (35 mg, 0.07 mmol) and donor **1a** (70 mg, 0.11 mmol) in freshly dried DCM (4 mL) in the presence of BCF (5 mg, 0.007 mmol) at -10 ^{o}C. Column chromatography purification was performed using 15% ethyl acetate in hexane which furnished **3r** as semi solid (58 mg, 82%); α:β=1:2; TLC R_f = 0.3 (20% ethyl acetate/80% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00-7.91 (m, 4H), 7.52-7.46 (m, 3H), 7.43-7.28 (m, 25H), 7.21-7.09 (m, 8H), 5.17-5.16 (m, 2H), 5.10 (d, *J* = 11.0 Hz, 1H), 5.06-5.02 (m, 1H), 4.96 (d, *J* = 10.5 Hz, 1H), 4.86-4.84 (m, 3H), 4.63-4.57 (m, 3H), 4.50-4.48 (m, 2H), 4.48 (m, 1H), 4.28 (dd, *J* = 11.0, 2.0 Hz, 1H), 4.08-3.95 (m, 2H), 3.90-3.87 (m, 1H), 3.83-3.79 (m, 1H), 3.77-3.74 (m, 1H), 3.73-3.70 (m, 1H), 3.69-3.66 (m, 1H), 3.64 (m, 1H), 3.58 (*t*, *J* = 8.0 Hz, 1H), 3.50-3.45 (m, 1H), 3.39 (s, 1H), 3.38 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 165.6, 165.6, 165.6, 138.4, 138.1, 133.2, 129.9, 129.7, 129.6, 129.18, 128.4, 128.3, 128.3, 128.3, 128.2, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 103.9, 96.9, 84.7, 82.1, 77.9, 77.6, 77.2, 76.5, 75.8, 75.7, 75.5, 75.0, 75.0, 74.8, 74.6, 74.4, 73.4, 72.7, 72.6, 72.3, 69.7, 68.9, 68.2, 55.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{62}H_{63}O_{13}$ 1015.4269, found 1015.4222.

Methyl 2,3,4,6-tetra-O-benzyl-*β,α*-D-glucopyranosyl-(1→3)-4,6-O-benzylidene-*α*-D-glucopyranoside [3sa][17h] and **Methyl 2,3,4,6-tetra-O-benzyl-*β,α*-D-glucopyranosyl-(1→2)-4,6-O-benzylidene-*α*-D-glucopyranoside [3sb]**[17h]: The compound **3sa** and **3sb** was prepared using the glycosylation procedure B. To a solution of donor **1a** (120 mg, 0.18 mmol) and acceptor **2s** (72 mg, 0.27 mmol) in freshly dried DCM (5 mL), BCF (10 mg, 0.018 mmol) was added at -10 ^{o}C. Column chromatography purification furnished **3sa** and **3sb**. Data for **3sa**: Yellowish Solid (75 mg, 51%); α:β=1:3.5; TLC R_f = 0.5 (17% ethyl acetate/83% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.39-7.29 (m, 21H), 7.20-7.18 (m, 2H), 5.56 (s, 1H), 5.00-4.92 (m, 3H), 4.84-4.79 (m, 4H), 4.69 (d, *J* = 8.0 Hz, 1H), 4.58-4.55 (m, 2H), 4.53-4.49 (m, 1H), 4.32 (dd, *J* = 10.0, 5.0 Hz, 1H), 4.21 (t, *J* = 9.0 Hz, 1H), 3.92-3.86 (m, 1H), 3.76 (m, 1H), 3.71-3.65 (m, 4H), 3.61-3.55 (m, 3H), 3.53-3.49 (m, 1H), 3.45-3.43 (each s, (0.65 and 2.19 H) 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.1, 137.9, 137.9, 137.1, 129.1, 128.4, 128.4, 128.3, 128.3, 128.2, 127.9, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 126.3, 104.6, 102.0, 100.2, 84.8, 81.8, 81.7, 81.4, 77.7, 75.6, 74.9, 74.9, 74.7, 73.4, 69.6, 69.1, 62.0, 55.4; HRMS: Calcd for $C_{48}H_{53}O_{11}$ $[M+H]^+$: 805.3588; found: 805.3526. Data for **3sb**. White solid (42 mg, 29%); α:β=1:7; TLC R_f = 0.3 (17% ethyl acetate/83% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.0, 2.5 Hz, 2H), 7.35-7.28 (m, 20H), 7.16-7.15 (m, 3H), 5.54 (s, 1H), 4.93-4.86 (m, 4H), 4.79-4.73 (m, 3H), 4.56 (d, *J* = 2.0 Hz, 1H), 4.54 (d, *J* = 3.5 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.28 (dd, *J*

= 10.0, 5.0 Hz, 1H), 4.10 (t, *J* = 9.0 Hz, 1H), 3.88-3.84 (m, 1H), 3.76 (t, *J* = 10.0 Hz, 1H), 3.68-3.50 (m, 8H), 3.45-3.40 (m, 4H);^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 138.2, 137.9, 137.7, 137.3, 128.8, 128.4, 128.3, 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.5, 127.3, 126.4, 126.2, 103.2, 101.4, 99.8, 85.1, 82.1, 80.7, 79.0, 77.9, 75.5, 75.2, 75.0, 74.9, 73.6, 72.6, 68.9, 68.8, 62.8, 55.3.

2,3,4,6-tetra-*O*-benzyl-*β,α*-D-glucopyranosyl-(1→3)-1,2:5,6-di-*O-isopropylidene-α*-D-glucofuranoside, [3t][6c]: The compound **3t** was prepared using the glycosylation procedure B. The reaction was carried out between acceptor **2t** (40 mg, 0.15 mmol) and donor **1a** (157 mg, 0.23 mmol) in freshly dried DCM (4 mL) in the presence of BCF (8 mg, 0.015 mmol) at -10 ^{o}C. Column chromatography purification was performed using 12% ethylacetate in hexane which furnished **3t** as white solid (84 mg, 72%); α:β=5.5:1; TLC R_f = 0.25 (15% ethyl acetate/85% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.28 (m, 17H), 7.23-7.15 (m, 3H), 5.91 (d, *J* = 3.5 Hz, 1H), 5.27 (d, *J* = 3.5 Hz, 1H), 5.00-4.82 (m, 4H), 4.76-4.70 (m, 3H), 4.64-4.48 (m, 5H), 4.25 (d, *J* = 2.0 Hz, 1H), 4.17-4.15 (m, 1H), 4.07 (d, *J* = 5.5 Hz, 1H), 3.96 (t, *J* = 9.0 Hz, 1H), 3.82 (d, *J* = 10.0 Hz, 1H), 3.74 (m, 2H), 3.65-3.60 (m, 2H), 1.51 (s, 3H), 1.44 (s, 3H), 1.28 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 138.0, 137.9, 137.7, 128.4, 128.3, 128.3, 128.3, 128.0, 127.9, 127.8, 127.5, 111.8, 109.0, 105.1, 97.9, 83.6, 81.4, 81.1, 80.7, 79.9, 77.7, 75.6, 75.2, 73.5, 73.0, 72.3, 71.2, 68.6, 66.9, 26.9, 26.7, 26.0, 25.4.

2-Propyl 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-galactopyranoside, [3u][5c]: The compound **3u** was prepared using the glycosylation procedure A. The reaction was carried out between donor **1c** (100 mg, 0.15 mmol) and *iso*-propanol **2a** (0.017 ml, 0.23 mmol) in freshly dried DCM (4 mL) in the presence of BCF (8 mg, 0.015 mmol) at -10 ^{o}C. Column chromatography purification was performed using 7% ethyl acetate in hexane which furnished **3u** as white solid (73 mg, 84%); TLC R_f = 0.35 (10% ethyl acetate/90% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.31 (m, 20H), 5.01-4.98 (m, 2H), 4.82-4.74 (m, 3H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.51-4.45 (m, 3H), 4.05-4.03 (m, 1H), 3.93 (d, *J* = 2.5 Hz, 1H), 3.85 (dd, *J* = 9.5, 7.5 Hz, 1H), 3.64-3.55 (m, 4H), 1.33 (d, *J* = 6.0 Hz, 3H), 1.27 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.6, 138.5, 137.9, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.0, 127.8, 127.4, 127.4, 102.4, 82.3, 79.5, 75.1, 74.4, 73.5, 73.4, 73.3, 73.0, 72.0, 69.0, 23.6, 22.0.

Propyl 2,3,4,6-tetra-*O*-benzyl-*β,α*-D-mannopyranoside, [3v][17i]: The compound **3v** was prepared using the glycosylation procedure A. The reaction was carried out between donor 1**d** (116 mg, 0.17 mmol) and *iso*-propanol acceptor **2a** (0.019 ml, 0.25 mmol) in freshly dried DCM (4 mL) in the presence of BCF (9 mg, 0.017 mmol) at -10 ^{o}C. Column chromatography purification was performed using 7% ethyl acetate in hexane which furnished **3v** as white

solid (91 mg, 92%). TLC R_f = 0.35 (10% ethyl acetate/90% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 6.5 Hz, 2H), 7.41-7.32 (m, 16H), 7.31-7.23 (m, 2H), 5.05-5.03 (m, 1H), 4.96-4.92 (m, 1.72H), 4.82 (d, *J* = 12.0 Hz, 0.23H), 4.75 (d, *J* = 12.0 Hz, 0.23H), 4.71 (d, *J* = 12.0 Hz, 0.24H), 4.67-4.64 (m, 1.76H), 4.59-4.54 (m, 2H), 4.50-4.46 (m, 1.46H), 4.06 (m, 1H), 3.89-3.84 (m, 3H), 3.79-3.77 (m, 1.22H), 3.54 (dd, *J* = 9.3, 3.0 Hz, 0.72H), 3.50-3.47 (m, 0.73H), 1.34 (d, *J* = 6.0 Hz, 3H), 1.20 (dd, *J* = 6.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.4, 138.4, 138.3, 138.2, 128.4, 128.2, 128.2, 128.0, 127.9, 127.7, 127.7, 127.5, 127.5, 127.5, 127.4, 99.5, 95.7, 82.5, 80.3, 75.8, 75.2, 75.1, 75.1, 75.0, 74.9, 74.0, 73.7, 73.3, 73.2, 72.6, 72.1, 71.6, 71.3, 71.1, 69.8, 69.2, 68.8, 23.6, 21.7.

Butyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside, [4a]: The compound **4a** was prepared using the glycosylation procedure A. The reaction was carried out between donor **1f** (100 mg, 0.14 mmol) and *n*-butanol **2c** (0.019 ml, 0.21 mmol) in freshly dried DCM (4 mL) in the presence of BCF (7 mg, 0.014 mmol) at -10 ^{o}C. The reaction was further stirred for 30 minutes at this temperature. Column chromatography purification was performed using 7% ethyl acetate/hexane which furnished **4a** as white solid (74 mg, 87%); TLC R_f = 0.45 (20% ethyl acetate/80% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.59 (t, *J* = 7.5, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.40-7.31 (m, 8H), 7.22 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.16 (m, 5H), 5.30 (dd, *J* = 9.0, 8.0 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.77 (d, *J* = 11.0 Hz, 1H), 4.71-4.66 (m, 2H), 4.63-4.60 (m, 2H), 4.53 (d, *J* = 8.0 Hz, 1H), 3.91-3.76 (m, 5H), 3.61-3.57 (m, 1H), 3.51-3.46 (m, 1H), 1.45 (m, 2H), 1.24 (m, 2H), 0.75 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 138.1, 137.9, 137.8, 132.9, 130.0, 129.6, 128.3, 128.3, 128.2, 128.2, 127.9, 127.9, 127.8, 127.7, 127.5, 101.1, 82.7, 78.0, 75.2, 75.0, 74.9, 73.8, 73.4, 69.4, 68.8, 31.4, 18.8, 13.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{38}H_{42}O_7Na$ 633.2828, found 633.2877.

Cyclohexyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside, [4b][17j]: The compound **4b** was prepared using the glycosylation procedure A. The reaction was carried out between donor **1f** (125 mg, 0.18 mmol) and cyclohexanol acceptor **2s** (0.028 ml, 0.27 mmol) in freshly dried DCM (4 mL) in the presence of BCF (9 mg, 0.018 mmol) at -10 ^{o}C. Column chromatography purification was performed using 7% ethyl acetate in hexane which furnished **4b** as white solid (104 mg, 91%). TLC R_f = 0.45 (20% ethyl acetate/80% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04-8.03 (m, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.39-7.28 (m, 8H), 7.24-7.22 (m, 2H), 7.17-7.14 (m, 5H), 5.27 (t, *J* = 9.0 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.76 (d, *J* = 11.5 Hz, 1H), 4.69-4.60 (m, 5H), 3.84-3.80 (m, 2H), 3.76-3.72 (m, 2H), 3.67 (m, 2H), 1.90-1.88 (m, 1H), 1.68 (m, 2H), 1.57-1.55 (m, 1H), 1.45-1.42 (m, 2H), 1.23 (m, 2H), 1.15-1.13 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 138.2,

137.9, 137.8, 132.8, 130.2, 129.6, 128.4, 128.3, 128.3, 128.2, 128.0, 128.0, 127.8, 127.7, 127.5, 99.6, 82.8, 78.1, 77.5, 75.2, 75.0, 74.9, 74.01, 73.4, 68.9, 33.2, 31.5, 25.4, 23.7, 23.4.

Butyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranoside, [4c]: The compound **4c** was prepared using the glycosylation procedure A. The reaction was carried out between donor **1g** (150 mg, 0.21 mmol) and *n*-butanol **2c** (0.027 ml, 0.32 mmol) in freshly dried DCM (4 mL) in the presence of BCF (11 mg, 0.021 mmol) at -10 ^{o}C. Column chromatography purification was performed using 7% ethyl acetatein hexane which furnished **4c** as viscous oil (117 mg, 92%); TLC R_f = 0.55 (20% ethyl acetate/85% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.41-7.20 (m, 17H), 5.63 (t, *J* = 2.5 Hz, 1H), 4.97 (d, *J* = 2.0 Hz, 1H), 4.89 (d, *J* = 10.5 Hz, 1H), 4.82 (d, *J* = 11.0 Hz, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.61-4.54 (m, 3H), 4.13-4.10 (m, 2H), 3.91 (m, 2H), 3.80 (dd, *J* = 10.0, 1.5 Hz, 1H), 3.76-3.71 (m, 1H), 3.49-3.45 (m, 1H), 1.59-1.58 (m, 2H), 1.43-1.36 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 138.4, 138.3, 138.0, 133.0, 129.9, 128.3, 128.3, 128.2, 128.0, 128.0, 127.6, 127.5, 127.5, 127.4, 97.7, 78.3, 75.3, 74.4, 73.4, 71.5, 71.5, 69.1, 69.0, 67.7, 31.4, 19.3, 13.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{38}H_{42}O_7Na$ 633.2828, found 633.2877.

Cyclohexyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranoside, [4d][17k]: The compound **4d** was prepared using the glycosylation procedure A. The reaction was carried out between donor **1g** (110 mg, 0.16 mmol) and cyclohexanol acceptor **2s** (0.025 ml, 0.24 mmol) in freshly dried DCM (4 mL) in the presence of BCF (8 mg, 0.016 mmol) at -10 ^{o}C. Column chromatography purification was performed using 7% ethyl acetate in hexane which furnished **4d** as viscous oil (86 mg, 85%); TLC R_f = 0.55 (20% ethyl acetate/80% hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10-8.09 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.41-7.21 (m, 16H), 5.59-5.58 (m, 1H), 5.13 (d, *J* = 1.5 Hz, 1H), 4.89 (d, *J* = 11.0 Hz, 1H), 4.83 (d, *J* = 11.0 Hz, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.61-4.54 (m, 3H), 4.16-4.11 (m, 2H), 3.94-3.91 (m, 2H), 3.80 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.68-3.64 (m, 1H), 1.88 (m, 2H), 1.73-1.72 (m, 2H), 1.53-1.52 (d, *J* = 5.2 Hz, 1H), 1.41-1.38 (m, 1H), 1.33 (m, 1H), 1.31 (s, 1H), 1.26-1.24 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 138.5, 138.3, 138.1, 133.0, 130.0, 129.9, 128.3, 128.3, 128.3, 128.2, 128.0, 128.0, 127.6, 127.5, 127.4, 127.4, 95.8, 78.3, 75.3, 74.5, 73.3, 71.5, 71.5, 69.7, 69.1, 33.2, 31.3, 25.5, 24.0, 23.7.

ASSOCIATED CONTENT

Supporting Information

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

Copies of ^{1}H NMR of *iso*-propanol in the presence of and absence of $B(C_6F_5)_3$ and ^{1}H and ^{13}C NMR of glycoside **3a-3v** and **4a-4d**.

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NOTES

The authors declare no competing financial interest

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