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Bismuth(III) triflate as a novel and efficient activator for glycosyl halides

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Supporting Information Placeholder

ABSTRACT: Presented herein is the discovery that bismuth(III) trifluoromethanesulfonate ($Bi(OTf)_3$) is an effective catalyst for the activation of glycosyl bromides and glycosyl chlorides. The key objective for the development of this methodology is to employ only one promoter in lowest possible amount and avoid using any additive/co-catalyst/acid scavenger except molecular sieves. $Bi(OTf)_3$ works well in promoting the glycosidation of differentially protected glucosyl, galactosyl, and mannosyl halides with many classes of glycosyl acceptors. Most reactions complete within 1 h in the presence of only 35% of green and light-stable $Bi(OTf)_3$ catalyst.

First chemical glycosylations performed by Michael, Fischer, and Koenigs/Knorr[1-3] helped pave the path to modern glycosciences that now encompass many chemical, biomedical, and industrial aspects of carbohydrates. Glycosyl halides, once the glycosyl donors of choice to perform both single-stage glycosylations and multi-step glycan assembly, started losing dominance due to their instability and somewhat sluggish activation profile. To address the issues related to the activation of halides, many promoters have been introduced. Traditionally used silver salt[3-8] and mercury[9-14] salt-based promoters have been expanded to other metal salts including cadmium,[11,15-17] zinc,[11,18-21] tin,[22,23] indium,[24-26] and iron.[27] The activity of metal salt activators is defined by their halophilicity; however, the rate of glycosylation can be greatly influenced by many other factors.[28]

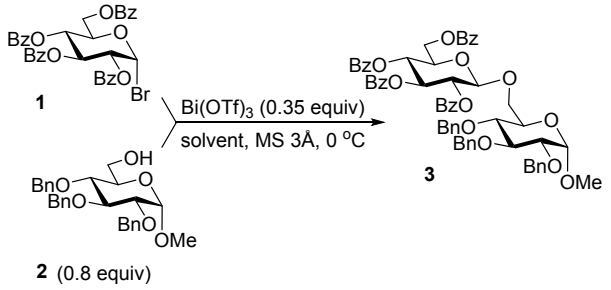
Many metal salt-based promoters for the activation of glycosyl halides experience limitations related to their inherent toxicity, light/air/moisture sensitivity, cost, excess requirement, and/or substrate compatibility. As a result, there has been a notable interest in studying non-metallic promoters including organic modulators,[29-34] halogens,[35-43] diarylborinic acid,[44] organocatalysts,[45,46] supercritical CO_2,[47] and blue light.[48] Most of the non-metallic activators function with an associative additive. Recent approaches introduced by Taylor,[49] Ye,[45] Jacobsen,[46] and Nguyen[34] have largely changed the way glycosyl halides have been activated by providing a catalytic means to their activation. However, these methods also have certain limitations related to multistep catalyst synthesis, long reaction time (even at high temperatures), requirement additives that are commonly used in excess, substrate limitations, and, in some cases, a complex reaction set up is needed.

In an ongoing effort to develop new glycosylation reactions suitable for traditional manual and automated synthetic approaches, we have recently developed a cooperative concept for the activation of glycosyl halides. Over the course of this study, we achieved a dramatic acceleration of a silver(I)-promoted glycosylation reaction the presence of catalytic Lewis or Bronsted acid additive.[50-52] In extension of this effort in identifying suitable activators, reported herein is our first dedicated effort to implement promoters based on other metal salts. The substrates of choice for the initial screening were common 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide donor **1**[53] and methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside acceptor **2**.[54] After preliminary screening of several halophilic metal salts as potential promoters for the activation of the bromide leaving group, we chose bismuth(III) trifluoromethanesulfonate, $Bi(OTf)_3$, as a promising candidate for further investigation. Other activators considered included Cu_2O, CuO, CaO, $ZnCO_3$, $Ni(acac)_2$, $(BiO)_2CO_3$, $Fe(OAc)_3$, and $Fe(OTf)_3$, but unfortunately all these reagents were practically ineffective as the desired disaccharide was produced in less than 5% under the tested reaction conditions. Good reaction rates and minimal side products were achieved in the presence of as little as 35 mol % of $Bi(OTf)_3$ in CH_2Cl_2 at rt. These, along with the moderate cost, low hygroscopicity, high stability, and greenness of $Bi(OTf)_3$, were all important traits of this reaction.

For comparison, silver triflate, arguably the most frequently used metallic promoter for the activation of glycosyl halides, has a very high reactivity profile. However, it has to be preactivated and dried directly prior to each application. AgOTf is highly sensitive towards moisture and light, it must be used in excess (2 equiv or higher), and it frequently requires an associative acid scavenger and low temperature conditions. In contrast, glycosidation of bromide **1** with acceptor **2** in the

presence of 35 mol % of $Bi(OTf)_3$ in CH_2Cl_2 in the absence of molecular sieves produced the desired disaccharide **3** (entry 1, Table 1).[55] The reaction performed at 0 °C was completed in 1.25 h. The isolated yield of disaccharide **3** was rather modest under these conditions (52%) even though donor **1** has been completely consumed. When the crude reaction mixture was subjected to mass spectrometry analysis, several side products were identified. Along with a variety of the hydrolysis products, one of the major side products was identified as methyl 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranoside. The formation of this compound could be rationalized by the direct intermolecular acceptor-to-donor aglycone transfer.[56] Alternatively, methyl glycoside hydrolysis followed by glycosylation of the liberated MeOH could not be excluded due to a relatively high acidity (TfOH) of the reaction medium. Indeed, along with glycosylation, TfOH is constantly being produced from $Bi(OTf)_3$. These observations led us to investigating the means for suppressing the formation of side products.

Table 1. Glycosylation of donor **1** (30 mg) and acceptor **2** with varying the amount of molecular sieves 3 Å and solvent.



Entry	MS 3Å (mg)	Solvent	Time (h)	Yield of **3**
1	--	CH_2Cl_2	1.25	52%
2	30	CH_2Cl_2	2	57%
3	90	CH_2Cl_2	20	84%
4	**120**	CH_2Cl_2	**20**	**92%**
5	150	CH_2Cl_2	20	93%
6	300	CH_2Cl_2	20	98%
7	120	Toluene	20	67%
8	120	Et_2O	1	45%
9	120	MeCN	1	50%
10	120	$MeNO_2$	1	95%
11	--	$MeNO_2$	1	55%
12	120	$MeNO_2/CH_2Cl_2$, 1/4, v/v	20	96%
13	120	$MeNO_2/CH_2Cl_2$, 1/1, v/v	20	98%
14	120	$MeNO_2/CH_2Cl_2$, 7/3, v/v	1	98%

Practically all chemical glycosylation reactions in modern times rely on molecular sieves as a desiccant (and acid scavenger) to suppress the formation of hydrolyzed by-products. When the aforementioned glycosylation (entry 1) was repeated in the presence of molecular sieves (3 Å, 30 mg, 1/1, w/w to donor **1**) we noted a slight increase of the yield of disaccharide **3** to 57% (entry 2). This result was indicative of the reaction-dependence on the presence of molecular sieves. To further investigate the role of the desiccant, we performed glycosylation in the presence of 90 mg of molecular sieves under otherwise identical reaction conditions. As a result, disaccharide **3** was obtained in a significantly improved yield of 84% (entry 3). We have also noted a significant increase in the reaction time to 20 h. Further increase of the amount of molecular sieves to 120, 150, and 300 mg led to the formation of disaccharide **3** in excellent yields of 92, 93, and 98%, respectively (entries 4-6). At the conclusion of this series of experiments, we chose to perform subsequent glycosylation reactions in the presence of 120 mg of molecular sieves (4/1, w/w to the donor). In our opinion, these reaction conditions offer the best combination between efficiency, sieve amount, and yield. Since this reaction required 20 h to complete, we turned our attention to investigating other factors with the primary purpose of enhancing the reaction rates.

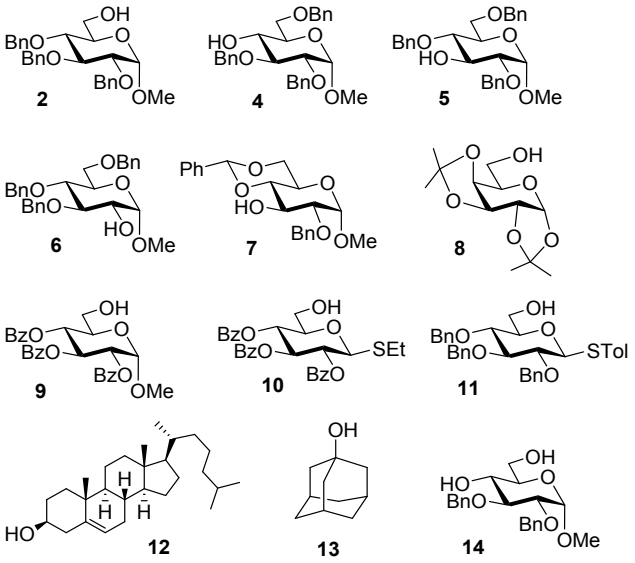
Keeping all other parameters constant, replacing CH_2Cl_2 with toluene showed no noticeable improvement in the rate of reaction between compounds **1** and **2**, but the yield of disaccharide **3** was reduced to 67% (entry 7). A notable enhancement rate was observed for reactions performed in diethyl ether or acetonitrile, reaction solvents known for their ability to affect the stereoselectivity of glycosylation via participation at the anomeric center. While rapid at the beginning, these reactions stalled after about 1 h and failed to proceed past this time point. As a result, disaccharide **3** was obtained in 45-50% yield (entries 8 and 9). In contrast, freshly distilled nitromethane ($MeNO_2$) was very effective in enhancing the rate of the reaction without having any detrimental effect on the reaction yield. Thus, the glycosylation reaction in $MeNO_2$ smoothly completed within 1 h and disaccharide **3** was isolated in 95% yield (entry 10). Reaction in $MeNO_2$ without molecular sieves produced disaccharide **3** in 55% yield (entry 11). Only side products resulted from donor hydrolysis have been observed in this reaction.

Over the course of the subsequent experiments, we investigated how modulating the ratios between the reaction solvents CH_2Cl_2 and $MeNO_2$ would affect the reaction time and product yields (entries 12-14). From this experimentation, we concluded that dichloromethane is a suitable reaction solvent. However, the rate of the reaction was low and 18-24 h were still needed for complete consumption of the glycosyl bromide. In terms of reactivity, yield of glycosides, and suppressing sides products, nitromethane seems a better choice among the investigated solvents. However, nitromethane alone is often a poor solvent for sugars. To develop a universal solvent system that would be suitable for most donor acceptor combinations, we concluded that $MeNO_2/CH_2Cl_2$ (7/3, v/v) offers an optimal balance between solubility, rates, and yields. Therefore, this solvent combination was chosen as the standard reaction solvent system for future experimentations.

Having optimized the basic reaction conditions, we extended $Bi(OTf)_3$-promoted reactions to glycosidation of donor **1** with various glycosyl acceptors **4-14** depicted in Figure 1. Glycosylation reactions of less reactive standard secondary glycosyl acceptors **4-6**[54] with glucosyl bromide **1** were rapid and efficient affording the respective disaccharides **15-17**[54,55] in 40-60 min in 92-94% (entries 1-3, Table 2). These and following

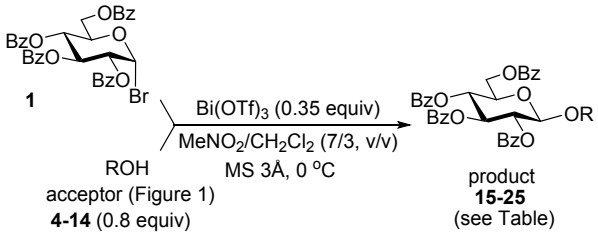
reactions were exclusively 1,2-trans stereoselective due to the participatory effect of the benzoyl ester group at C-2 of donor **1**.

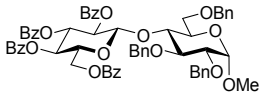
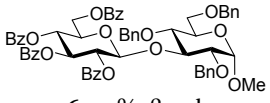
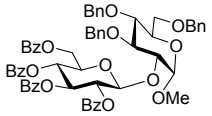
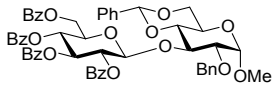
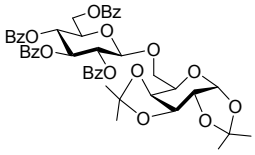
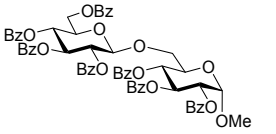
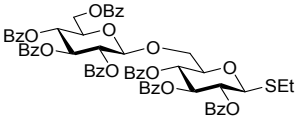
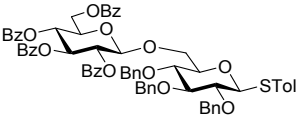
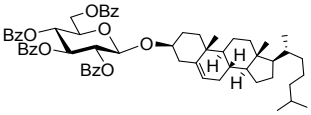
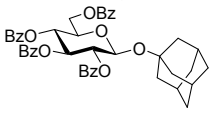
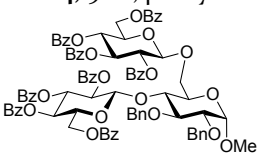
Figure 1. Glycosyl acceptors used in this study.



Further, the compatibility of the reaction conditions towards the acid-labile protecting groups was investigated by performing glycosylation reactions with benzylidene-protected acceptor **7**[57] and isopropylidene-protected acceptor **8**. The glycosylations proceeded smoothly and produced the respective disaccharides **18**[58-60] and **19**[61] in 1-2 h in 85-86% yield (entries 4 and 5). Glycosylation of electronically deactivated benzoylated glycosyl acceptor **9**[62] was also swift and efficient, but only if carried out in the presence of the increased amount of $Bi(OTf)_3$ (0.5 equiv) and in neat $MeNO_2$. As a result, the corresponding disaccharide **20**[63] was obtained in 85% yield in 15 min (entry 6).

Table 2. Glycosidation of donor **1** with acceptors **4-14**.



Entry	ROH	Time	Products, Yield
1	**4**	1 h	 **15,** 92%, β only
2	**5**	40 min	 **16,** 93%, β only
3	**6**	1 h	 **17,** 94%, β only
4	**7**	2 h	 **18,** 86%, β only
5	**8**	1 h	 **19,** 85%, β only
6[a]	**9**	15 min	 **20**, 85%, β only
7[b]	**10**	45 min	 **21,** 16%, β only
8[c]	**11**	1 h	 **22**, 42%, β only
9	**12**	2.5 h	 **23,** 77%, β only
10[d]	**13**	20 h	 **24,** 96%, β only
11[e]	**14**	2 h	 **25,** 41%, β only

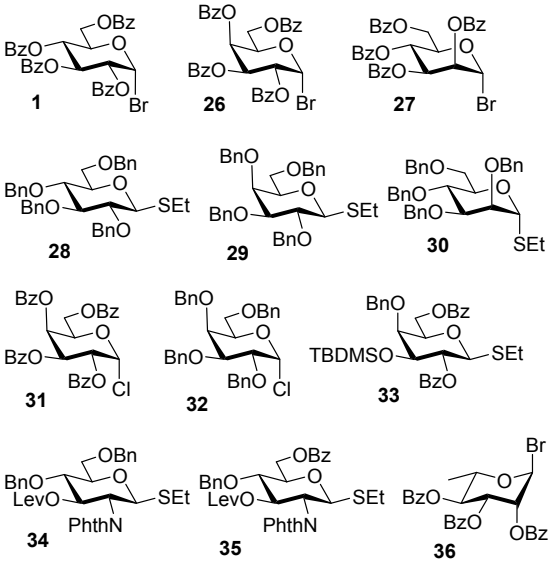
Deviations from standard reaction conditions: [a] – performed in the presence of 0.5 equiv $Bi(OTf)_3$ in neat $MeNO_2$; [b] – performed in the presence of 0.5 equiv $Bi(OTf)_3$; [c] – performed in the presence of 0.6 equiv $Bi(OTf)_3$; [d] – performed in neat CH_2Cl_2 [e] – performed with 0.4 equiv of acceptor at 0 °C for 5 min and then increased to rt

A selective activation approach[64] was then undertaken to activate glycosyl bromide **1** over thioglycoside acceptors **10**[65] and **11**.[66] These efforts still need improvement, and the respective disaccharides **21**[67] and **22**[68] were isolated in 16-42% yield (entries 7 and 8). It should be noted that these disaccharides equipped with the anomeric leaving group can be used as glycosyl donors for subsequent chain elongation directly. A lower efficiency of these reactions in comparison to that of glycosylation of standard acceptors was attributed to the competing aglycone transfer.[56] Presumably, this side reaction is accelerated due to interaction of the thiophilic bismuth cation with the anomeric sulfur atom of the glycosyl acceptor. Aliphatic glycosyl acceptors, secondary alcohol cholesterol **12**

and tertiary 1-adamantanol **13** were then studied. These glycosylations produced corresponding glycosides **23**[69] and **24**[70] in 77% and 96% yield, respectively (entries 9 and 10). Note that reaction in neat CH_2Cl_2 was found to be superior for glycosyl acceptor **13**. Finally, to execute multiple glycosylations to access branched structures in one pot, we conducted glycosylation of benzylated 4,6-diol acceptor **14**.[71] This reaction produced trisaccharide **25** in 41% yield (entry 11).

After the successful construction of a variety of glycosidic linkages from donor **1**, we explored the glycosylation reaction with other classes of glycosyl donors depicted in Figure 2. The purpose of this study was to further explore the scope of this reaction, determine compatibility with other classes of protecting groups, and to access its applicability to the assembly of complex glycans. Benzylated glycosyl acceptor **2** was chosen as a nucleophile for this study. The first series of experiments was conducted with glycosyl bromide donors bearing disarming protection (benzoyl group). Benzoylated glucosyl donor **1** was supplemented with benzoylated galactosyl bromide **26**[72] and mannosyl bromide **27**.[73] In comparison with the benchmark experiment involving bromide **1** and acceptor **2** that produced disaccharide **3** in 45 min in 98% yield (entry 1, Table 3), donors **26** and **27** provided a very similar outcome. Thus, glycosylation of acceptor **2** with donors **26** and **27** swiftly produced disaccharides **37**[74] and **38**[63] in 30 min in 97% and 92% yield, respectively (entries 2 and 3).

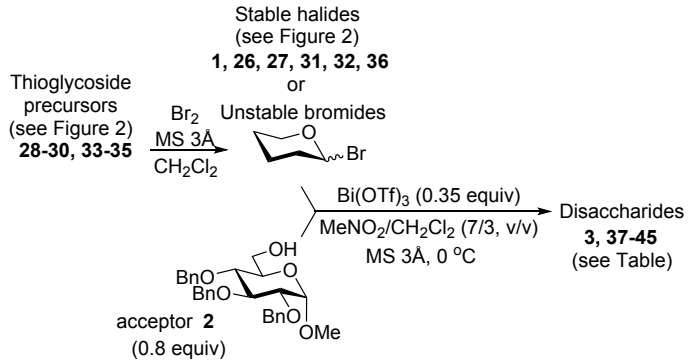
Figure 2. Glycosyl donors used in this study.

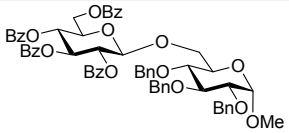
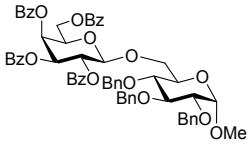
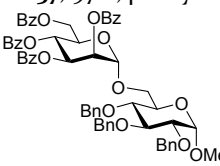
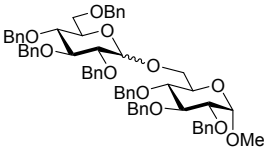


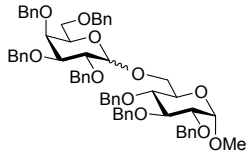
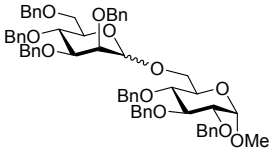
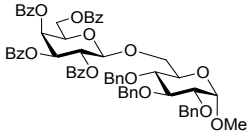
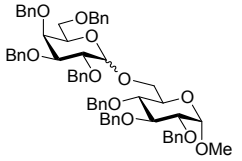
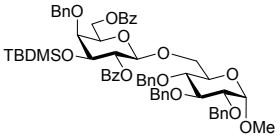
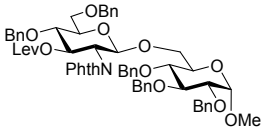
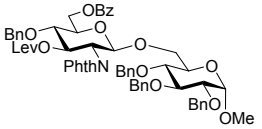
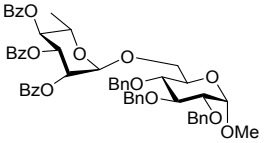
We then moved on to investigating the glycosylation reactions with per-benzylated (armed) glycosyl bromides that were generated from the corresponding ethyl thioglycoside precursors by reaction with bromine directly prior to application after treatment with stoichiometric molecular bromine. Glycosidation of armed glucosyl bromide generated from thioglycoside **28**[75] afforded disaccharide **39**[76] in 71% in 15 min (entry 4). The lower yield of **39** in comparison to those seen for reactions with benzoylated bromides could be attributed to competitive hydrolysis and the formation of the 1,6-anhydro derivative. Galactosyl and mannosyl bromides generated from the respective thioglycoside precursors **29**[37,77] and **30**[78] gave rise to disaccharides **40**[79] and **41**[80] in 78 and 91% yield, respectively (entries 5 and 6). The armed glycosyl bromide donors generated from thioglycoside precursors **28**-**30** produced disaccharides in poor stereoselectivity with α/β ratio ranging within 1/1.1-1.5 due to the lack of stereodirecting factors.

Following the efficient glycosylation reactions of various glycosyl bromide donors with the newly discovered metal salt, we investigated glycosyl chloride donors **31**[81] and **32.**[82] Glycosidation under the standard reaction conditions was also smooth and efficient in producing disaccharides **37** and **40** in 15 min in 93% and 97% yield, respectively (entries 7 and 8). Glycosidation of differentially protected glycosyl bromide donors obtained from thioglycosides **33**-**35** was then attempted to understand the compatibility of the new activation conditions with various protecting and functional groups. Of particular interest were aminosugars and temporary protecting groups (TBDMS and Lev) that are commonly used in glycan synthesis. These glycosylations were smooth and efficient producing disaccharides **42**-**44** in 73-93% yield (entries 9-11). Finally, glycosidation of the L-series sugar, rhamnosyl bromide donor **36**,[83] afforded disaccharide **45**[84] in 79% yield (entry 12).

Table 3. Glycosylation of acceptor **2** with various donors.



Entry	Donor	Time	Product, yield, ratio α/β
1	**1**	45 min	 **3**, 98%, β only
2	**26**	30 min	 **37**, 97%, β only
3	**27**	30 min	 **38**, 92%, α only
4	**28**	15 min	 **39**, 71%, α/β = 1/1.5

5	**29**	30 min	 **40**, 78%, α/β = 1/1.1
6	**30**	25 min	 **41**, 91%, α/β = 1/1.4
7	**31**	15 min	 **37**, 93%, β only
8	**32**	15 min	 **40**, 97%, α/β =1/1.2
9	**33**	10 min	 **42**, 93%, β only
10	**34**	1 h	 **43**, 73%, β only
11	**35**	1 h	 **44**, 79%, β only
12	**36**	15 min	 **45**, 79%, α only

In conclusion, $Bi(OTf)_3$ was found to be an effective metal salt capable of the activation of glycosyl bromides and chlorides. Successful glycosidation of per-benzoylated glucosyl bromide was carried out with a variety of glycosyl acceptors, and these reactions were relatively high yielding with swift reaction times. Additionally, glycosidations of benzylated/benzoylated glucosyl, galactosyl, and mannosyl bromides, along with benzylated/benzoylated galactosyl chlorides and a few differentially protected building blocks have been performed with high efficiency. This glycosylation method is favorable due to the low mol % of green and light-stable $Bi(OTf)_3$ required. One current limitation of this reaction is the use of thioglycoside acceptors that showed propensity to undergo the competing aglycone transfer reaction, which is not uncommon under other reaction conditions. Further investigation of this reaction is currently underway in our laboratory.

EXPERIMENTAL SECTION

General. Column chromatography was performed on silica gel 60 (70-230 mesh), reactions were monitored by TLC on Kieselgel 60 F_{254}. The compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol. Solvents were removed under reduced pressure at <40 °C. CH_2Cl_2 and $MeNO_2$ were distilled from CaH_2 directly prior to application. Molecular sieves (3 Å) used for reactions were crushed and activated *in vacuo* at 390 °C during 8 h in the first instance and then for 2-3 h at 390 °C directly prior to application. Optical rotations were measured using a Jasco P-1020 polarimeter. ^{1}H NMR spectra were recorded in $CDCl_3$ at 300 MHz and ^{13}C NMR spectra were recorded in $CDCl_3$ at 75 MHz. Accurate mass spectrometry determinations were preformed using Agilent 6230 ESI TOF LCMS mass spectrometer.

Synthesis of Glycosyl Halide Donors and Thioglycoside Precursors

2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (1) was obtained from 1,2,3,4,6-penta-*O*-benzoyl-D-glucopyranose as reported previously.[85] The analytical data for **1** was in accordance with that previously reported.[53]

2,3,4,6-Tetra-*O*-benzoyl-α-D-galactopyranosyl bromide (26) was obtained from 1,2,3,4,6-penta-*O*-benzoyl-D-galactopyranose as reported previously.[86] The analytical data for **26** was in accordance with that previously reported.[72]

2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl bromide (27) was obtained from 1,2,3,4,6-penta-*O*-benzoyl-D-mannpyranose as reported previously.[87] The analytical data for **27** was in accordance with that previously reported.[73]

Ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (28) was obtained as reported previously.[75]

Ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (29) was obtained as reported previously.[37,77]

Ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-mannopyranoside (30) was obtained as reported previously.[78]

2,3,4,6-Tetra-*O*-benzoyl-α-D-galactopyranosyl chloride (31) was obtained from 2,3,4,6-tetra-*O*-benzoyl-D-galactopyranose[88] as reported previously.[52] The analytical data for **31** was in accordance with that previously reported.[81]

2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl chloride (32) was obtained from 2,3,4,6-tetra-*O*-benzyl-D-galactopyranose[89] as reported previously.[27] The analytical data for **32** was in accordance with that previously reported.[81,82]

Ethyl 2,6-di-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-1-thio-β-D-galactopyranoside (33). Benzoyl chloride (3.93 mL, 33.78 mmol) was added to a solution of ethyl 2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-1-thio-β-D-galactopyranoside[90] (**46**, 12.0 g, 22.52 mmol) in pyridine (50 mL) and the resulting mixture was stirred under argon for 4 h at rt. Methanol (~5 mL) was added dropwise, the volatiles were removed under reduced pressure and the residue was co-evaporated with toluene (3 x 40 mL). The resulting residue was diluted with CH_2Cl_2 (~500 mL) and washed with 1

N aq. HCl (50 mL), sat. aq. $NaHCO_3$ (50 mL), and water (2 x 50 mL). The organic phase was separated, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate – hexane gradient elution) and crystallization (diethyl ether - hexane) to afford the title compound as white crystals in 86% yield (12.32 g). Analytical data for **33**: R_f = 0.66 (ethyl acetate/hexane, 1/4, v/v); m. p. 101.7-102.9 °C (diethyl ether - hexane); $[\alpha]_D^{20}$ +17.4 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05, 7.99 (2 d, 4H, aromatic), 7.20-7.63 (m, 11H, aromatic), 5.67 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 4.90 (dd, 2H, ^2J = 11.4 Hz, C*H*$_2$Ph), 4.45-4.60 (m, 2H, $J_{1,2}$ = 9.6, $J_{6a,6b}$ = 11.3 Hz, H-1, 6a), 4.42 (dd, 1H, H-6b), 4.02 (dd, 1H, $J_{3,4}$ = 1.0 Hz, H-3), 3.92 (m, 1H, $J_{5,6a}$ = 6.8, $J_{5,6b}$ = 5.6 Hz, H-5), 3.87 (br d, 1H, $J_{4,5}$ = 1.9 Hz, H-4), 2.72 (m, 2H, SC*H*$_2$), 1.22 (t, 3H, SCH$_2$C*H*$_3$), 0.80 (s, 9H, Si*t*Bu), 0.13, -0.06 (2 s, 6H, SiMe$_2$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 165.4, 138.4, 133.3, 133.1, 130.3, 129.9 (x2), 129.8, 129.7 (x2), 128.5 (x2), 128.4 (x4), 128.0 (x2), 127.7, 83.9, 77.1, 76.4, 75.7, 75.1 (x2), 71.0, 63.9, 25.6 (x3), 24.1, 15.0, -3.9, -5.0 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{35}H_{44}O_7SSiNa$ 659.2475, found 659.2465.

Ethyl 4,6-di-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-phthalimido-1-thio-β-D-glucopyranoside (34). Levulinic acid (0.336 g, 2.90 mmol), *N*,*N*'-diisopropylcarbodiimide (DIC, 0.449 mL, 2.90 mmol) and dimethylaminopyridine (DMAP, 35.0 mg, 0.29 mmol, 0.20 equiv) were added to a solution of ethyl 4,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[91] (**47**, 0.773 g, 1.45 mmol) in dry DCM (1.0 mL) and the resulting mixture was stirred under argon for 3 h at rt. After that, the reaction mixture was diluted with DCM (~100 mL), washed with saturated aq. $NaHCO_3$ (2 x 25 mL) and water (2 x 25 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) and crystallization (diethyl ether) to afford the title compound as white crystalline solid in 91% yield (0.83 g). Analytical data for **34**: R_f = 0.24 (ethyl acetate/hexane, 35/65, v/v); m.p. 133.2-133.8 °C (diethyl ether); $[\alpha]_D^{20}$ +17.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (br s, 2H, aromatic), 7.68-7.76 (m, 2H, aromatic), 7.15-7.42 (m, 10H, aromatic), 5.87 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 5.44 (d, 1H, $J_{1,2}$ = 10.6 Hz, H-1), 4.52-4.72 (m, 4H, 2 x C*H*$_2$Ph), 4.32 (dd, 1H, $J_{2,3}$ = 10.4 Hz, H-2), 3.69-3.90 (m, 4H, H-4, 5, 6a, 6b), 2.57-2.80 (m, 2H, SCH$_2$), 2.15-2.53 (m, 4H, CH$_2$CH$_2$), 1.91 (s, 3H, COCH$_3$), 1.21 (t, 3H, *J* = 7.4 Hz, SCH$_2$C*H*$_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.6, 171.8, 167.8, 167.5, 138.0, 137.9, 134.0, 133.9, 131.6, 131.5, 128.3 (x4), 127.8 (x2), 127.7 (x2), 127.6 (x2), 123.5, 123.4, 80.8, 79.1, 76.4, 74.5, 74.00, 73.4, 68.6, 54.0, 37.5, 29.4, 27.7, 24.1, 14.9 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{35}H_{37}NO_8SNa$ 654.2138, found 654.2140.

Ethyl 6-*O*-benzoyl-4-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-phthalimido-1-thio-β-D-glucopyranoside (35). Benzoyl chloride (3.63 mL, 31.24 mmol) was added to a solution of ethyl 4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[91] (**48**, 5.81 g, 10.42 mmol) in pyridine (40 mL) and the resulting mixture was stirred under argon for 12 h at rt. Methanol (~5 mL) was added dropwise, the volatiles were removed under reduced pressure and the residue was co-evaporated with toluene (3 x 20 mL). The resulting residue was diluted with CH_2Cl_2 (~300 mL) and washed with 1 N aq. HCl (50 mL), sat. aq. $NaHCO_3$ (50 mL), and water (2 x 50 mL). The organic phase was separated, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate-CH_2Cl_2-hexane gradient elution) to afford 6-*O*-benzoyl-4-*O*-benzyl-3-*O*-tert-butyldimethylsilyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**49**) as a white foam in 94% yield (6.46 g). Analytical data for **49**: R_f = 0.54 (ethyl acetate/hexane, 1/3, v/v); $[\alpha]_D^{20}$ +37.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, 2H, *J* = 7.3 Hz, aromatic), 7.87 (br s, 2H, aromatic), 7.71-7.79 (m, 2H, aromatic), 7.54-7.63 (m, 1H, aromatic), 7.42-7.52 (m, 2H, aromatic), 7.19-7.34 (m, 5H, aromatic), 5.39 (d, 1H, $J_{1,2}$ = 10.5 Hz, H-1), 4.86 (d, 1H, ^2J = 11.4 Hz, C*H*Ph), 4.49-4.71 (m, 3H, $J_{3,4}$ = 8.7 Hz, $J_{6a,6b}$ = 12 Hz, H-3, 6a), 4.40 (dd, 1H, H-6b), 4.31 (dd, 1H, $J_{2,3}$ = 10.2 Hz, H-2), 3.82-3.91 (m, 1H, $J_{5,6a}$ = 2.0, $J_{5,6b}$ = 4.7 Hz, H-5), 3.60 (dd, 1H, $J_{4,5}$ = 8.7 Hz, H-4), 2.49-2.73 (m, 2H, SCH$_2$), 1.15 (t, 3H, *J* = 7.4 Hz, SCH$_2$C*H*$_3$), 0.75 (s, 9H, Si*t*Bu), -0.20, -0.40 (2 s, 3H, SiMe$_2$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 168.6, 167.6, 166.1, 137.4, 134.2, 133.0, 131.9, 131.5, 129.8, 129.6 (x2), 128.3 (x4), 127.7, 127.3 (x3), 123.6, 123.2, 80.9, 80.1, 77.2, 75.0, 73.4, 63.6, 55.6, 25.6 (x3), 24.1, 17.6, 14.9, -4.2, -4.6 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{36}H_{43}NO_7SSiNa$ 684.2427, found 684.2434.

BF_3-Et_2O (1.23 mL, 9.97 mmol) was added to a solution of compound **49** (6.0 g, 9.06 mmol) in dry CH_3CN (50 mL) and the resulting mixture was stirred under argon for 2 h 45 min at 0 °C. Additional CH_3CN (25 mL) and BF_3-Et_2O (0.33 mL, 2.72 mmol) were added, and the reaction mixture was stirred for additional 15 min at 0 °C. After that, the reaction was quenched with sat. aq. $NaHCO_3$ (5 mL), and the volatiles were removed under reduced pressure. The residue was diluted with CH_2Cl_2 (~00 mL) and washed with brine (2 x 70 mL). The organic phase was separated, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to give ethyl 6-*O*-benzoyl-4-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**50**) as a white foam in 86% yield (4.26 g). Analytical data for **50**: R_f = 0.59 (ethyl acetate/hexane, 2/3, v/v); $[\alpha]_D^{20}$ +10.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (d, 2H, *J* = 7.6 Hz, aromatic), 7.85 (br s, 2H, aromatic), 7.69-7.77 (m, 2H, aromatic), 7.56-7.64 (m, 1H, aromatic), 7.44-7.53 (m, 2H, aromatic), 7.19-7.35 (m, 5H, aromatic), 5.37 (d, 1H, $J_{1,2}$ = 10.4 Hz, H-1), 4.63-4.81 (m, 3H, H-6b, C*H*$_2$Ph), 4.49-4.62 (m, 2H, $J_{3,4}$ = 9.3 Hz, H-3, 6a), 4.28 (dd, 1H, $J_{2,3}$ = 10.4 Hz, H-2), 3.81-3.91 (m, 1H, H-5), 3.64 (dd, 1H, $J_{4,5}$ = 9.3 Hz, H-4), 2.54-2.77 (m, 2H, -SC*H*$_2$), 2.25 (br s, 1H, OH), 1.18 (t, 3H, *J* = 7.4 Hz, SCH$_2$C*H*$_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ, 168.2, 167.9, 166.2, 137.5, 134.1, 133.1, 131.4 (x2), 129.7, 129.6 (x2), 128.6 (x3), 128.3 (x2), 128.1, 128.0 (x2), 123.7, 123.2, 81.1, 79.0, 77.1 75.0, 72.9, 63.7, 55.7, 24.2, 14.9 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{30}H_{29}NO_7SNa$ 570.1562, found 570.1571.

Levulinic acid (0.424 g, 3.65 mmol), DIC (0.566 mL, 3.65 mmol) and DMAP (44.0 mg, 0.36 mmol) were added to a solution of compound **50** (1.00 g, 1.83 mmol) in dry DCM (25 mL) and the resulting mixture was stirred under argon for 3 h at rt. The reaction mixture was then diluted with DCM (~100 mL) and washed with saturated aq. $NaHCO_3$ (2 x 25 mL) and water (2 x 25 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified

by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to afford the title compound (**35**) as a white foam in 94% yield (1.11 g). Analytical data for **35**: R_f = 0.37 (ethyl acetate/hexane, 2/3, v/v); $[\alpha]_D^{20}$ +25.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, 2H, *J* = 7.6 Hz, aromatic), 7.87 (br s, 2H, aromatic), 7.69-7.78 (m, 2H, aromatic), 7.56-7.65 (m, 1H, aromatic), 7.44-7.53 (m, 2H, aromatic), 7.16-7.32 (m, 5H, aromatic), 5.95 (dd, 1H, $J_{3,4}$ = 9.8 Hz, H-3), 5.52 (d, 1H, $J_{1,2}$ = 10.5 Hz, H-1), 4.59-4.74 (m, 3H, H-6a, CH_2Ph), 4.52 (dd, 1H, $J_{6a,6b}$ = 12.0 Hz, H-6b), 4.35 (dd, 1H, $J_{2,3}$ = 10.4 Hz, H-2), 3.91-4.00 (m, 1H, $J_{5,6a}$ = 4.5 Hz, H-5), 3.83 (dd, 1H, $J_{4,5}$ = 9.0 Hz, H-4), 2.56-2.76 (m, 2H, SCH_2), 2.22-2.55 (m, 4H, CH_2CH_2), 1.91 (s, 3H, $COCH_3$), 1.18 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.5, 171.9, 167.8, 167.5, 166.1, 137.2, 134.1, 133.9, 133.1, 131.5, 129.7, 129.6 (x2), 128.4 (x3), 128.3 (x2), 127.9 (x3), 123.6, 123.5, 81.0, 77.1, 76.4, 74.6, 74.1, 63.4, 54.0, 37.5, 29.3, 27.7, 24.4, 14.9 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{35}H_{35}NO_9SNa$ 668.1930, found 668.1939.

2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl bromide (36) was obtained from 1,2,3,4-tetra-*O*-benzoyl-L-rhamnopyranose[92] as reported previously. The analytical data for **36** was in accordance with that previously reported.[83,92]

Synthesis of Oligosaccharides

General Method A. A mixture of glycosyl donor (0.046 mmol), glycosyl acceptor (0.036 mmol), and freshly activated molecular sieves (3 Å, 120 mg) in $MeNO_2$ and CH_2Cl_2 (1.0 mL, 7/3, v/v) was stirred under argon for 1 h at rt. The mixture was cooled to 0 °C, $Bi(OTf)_3$ (0.016 mmol) was added, and the resulting mixture was stirred for the time specified in Tables at 0 °C. After that, the solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with water (2 × 10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate – hexane or toluene gradient elution) to afford the corresponding glycosides in yields and stereoselectivities listed in Tables and below. Anomeric ratios (or anomeric purity) were determined by comparison of the integral intensities of relevant signals in ^{1}H NMR spectra.

General Method B. A mixture of thioglycoside precursor (0.048–0.051 mmol) and freshly activated molecular sieves (3 Å, 120 mg) in CH_2Cl_2 (1.0 mL) was stirred under argon for 1 h at rt. The mixture was cooled to 0 °C, Br_2 (1.3 equiv) was added dropwise, and the resulting mixture was stirred for 15 min at 0 °C. The volatiles were then removed under reduced pressure, and the residue was dried in *vacuo* for 1 h. Glycosyl acceptor (0.038 – 0.041 mmol) was added and the resulting mixture was dried in *vacuo* for an additional 30 min. $MeNO_2$ and CH_2Cl_2 (1.0 mL, 7/3, v/v) were added, the resulting mixture was cooled to 0 °C, $Bi(OTf)_3$ (0.35 equiv or as indicated in Tables) was added, and the reaction mixture was stirred under argon for the time specified in Tables at 0 °C. After that, the solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with water (2 × 10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate – hexane or toluene gradient elution) to afford the corresponding glycosides in yields and stereoselectivities listed in Tables and below. Anomeric ratios (or anomeric purity) were determined by comparison of the integral intensities of relevant signals in ^{1}H NMR spectra.

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3) was obtained from donor **1** and acceptor **2**[54] under the general glycosylation method A in 98% yield (β only) as a white amorphous solid. The analytical data for **3** was in accordance with that previously reported.[55] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90-7.03 (m, 35H, aromatic), 5.89 (dd, 1H, $J_{3',4'}$ = 9.6 Hz, H-3'), 5.68 (dd, 1H, $J_{4',5'}$ = 9.7 Hz, H-4'), 5.60 (dd, 1H, $J_{2',3'}$ = 9.6 Hz, H-2'), 4.89 (d, 1H, ^2J = 10.9 Hz, C*H*Ph), 4.82 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1'), 4.73 (d, 1H, ^2J = 12.2 Hz, C*H*Ph), 4.67 (d, 1H, ^2J = 11.1 Hz, C*H*Ph), 4.63-4.57 (m, 2H, CH_2Ph), 4.54-4.46 (m, 3H, H-1, 6a', 6b'), 4.27 (d, 1H, ^2J = 11.1 Hz, C*H*Ph), 4.15 (d, 1H, H-5'), 4.11-4.08 (m, 1H, H-6a), 3.88 (dd, 1H, $J_{3,4}$ = 9.3 Hz, H-3), 3.77-3.70 (m, 2H, H-5, 6b), 3.43 (dd, 1H, $J_{2,3}$ = 9.6, $J_{1,2}$ = 3.6 Hz, H-2), 3.36 (dd, 1H, $J_{4,5}$ = 9.3 Hz, H-4), 3.20 (s, 3H, OCH_3) ppm.

Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (15) was obtained from donor **1** and acceptor **4**[54] under the general glycosylation method A in 92% yield (β only) as an off-white amorphous solid. The analytical data for **15** was in accordance with that previously reported.[54,55] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97-7.17 (m, 35H, aromatic), 5.59 (dd, 1H, $J_{3',4'}$ = 9.5 Hz, H-3'), 5.55 (dd, 1H, $J_{2',3'}$ = 9.6 Hz, H-2'), 5.46 (dd, 1H, $J_{4',5'}$ = 8.0 Hz, H-4'), 5.06 (d, 1H, ^2J = 11.2 Hz, C*H*Ph), 4.81-4.75 (m, 3H, 3 x C*H*Ph), 4.75 (d, 1H, $J_{1',2'}$ = 8.1 Hz, H-1'), 4.60 (d, 1H, ^2J = 12.2 Hz, C*H*Ph), 4.54 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.41 (dd, 1H, $J_{6a',6b'}$ = 12.1 Hz, H-6a'), 4.33 (d, 1H, ^2J = 12.2 Hz, C*H*Ph), 4.27 (dd, 1H, H-6b'), 3.94 (dd, 1H, H-4), 3.88 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 3.71-3.68 (m, 2H, $J_{5',6a'}$ = 3.6, $J_{5',6b'}$ = 5.0 Hz, H-5', 6a), 3.50-3.47 (m, 1H, H-5), 3.46-3.39 (m, 2H, $J_{2,3}$ = 9.1 Hz, H-2, 6b), 3.27 (s, 3H, OCH_3) ppm.

Methyl 3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,4,6-tri-O-benzyl-α-D-glucopyranoside (16) was obtained from donor **1** and acceptor **5**[54] under the general glycosylation method A in 93% yield (β only) as a white amorphous solid. The analytical data for **16** was in accordance with that previously reported.[54,55] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02-7.07 (m, 35H, aromatic), 5.94 (dd, 1H, $J_{3',4'}$ = 9.6 Hz, H-3'), 5.72 (dd, 1H, $J_{4',5'}$ = 9.7 Hz, H-4'), 5.65 (dd, 1H, $J_{2',3'}$ = 9.7 Hz, H-2'), 5.51 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 5.11 (d, 1H, ^2J = 10.7 Hz, C*H*Ph), 4.64 (d, 1H, ^2J = 12.2 Hz, C*H*Ph), 4.54-4.32 (m, 6H, $J_{3,4}$ = 9.7 Hz, H-3, H-6a', 6b', 3 x C*H*Ph), 4.26 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 4.14-4.10 (m, 2H, H-5', C*H*Ph), 3.65-3.51 (m, 4H, H-4, 5, 6a, 6b), 3.32 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.22 (s, 3H, OCH_3) ppm.

Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-3,4,6-tri-O-benzyl-α-D-glucopyranoside (17) was obtained from donor **1** and acceptor **6**[54] under the general glycosylation method A in 94% yield (β only) as a white amorphous solid. The analytical data for **17** was in accordance with that previously reported.[54,55] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05–6.95 ppm (m, 35H, aromatic), 5.90 (dd, 1H, $J_{3',4'}$ = 9.6 Hz, H-3'), 5.71 (dd, 2H, H-2', 4'), 5.16 (d, 1H, $J_{1',2'}$ = 7.7 Hz, H-1'), 5.05 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 4.74–4.69 (dd, 1H, H-6a'), 4.64–4.55 (m, 3H, 3 x C*H*Ph), 4.50–4.35 (m, 4H, H-6b', 3 x C*H*Ph), 4.16–4.13 (m, 1H, $J_{5',6a'}$ = 1.5, $J_{5',6b'}$ = 4.8 Hz, H-5'), 3.92 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 3.95–3.88

(dd, 1H, $J_{2,3}$ = 3.4 Hz, H-2), 3.82–3.58 (m, 4H, H-4, 5, 6a, 6b), 3.35 (s, 3H, OCH_3) ppm.

Methyl 3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (18) was obtained from donor **1** and acceptor **7**[57] under the general glycosylation method A in 86% yield (β only) as a white amorphous solid. The analytical data for **18** was in accordance with that previously reported.[58-60] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98-7.78 (m, 8H, aromatic), 7.53-7.22 (m, 22H, aromatic), 5.88 (dd, 1H, H-3'), 5.72-5.62 (m, 2H, $J_{2',3'}$ = 9.6 Hz, H-2', 4'), 5.55 (s, 1H, >C*H*Ph), 5.23 (d, 1H, $J_{1',2'}$ = 7.7 Hz, H-1'), 4.58 (d, 1H, ^2J = 12.7 Hz, C*H*Ph), 4.49 (dd, 1H, $J_{6a',6b'}$ = 12.3 Hz, H-6a'), 4.32-4.16 (m, 5H, $J_{1,2}$ = 3.6, H-1, 3, 6a, 6b', C*H*Ph), 3.98-3.93 (m, 1H, $J_{5',6b'}$ = 3.4 Hz, H-5'), 3.80-3.57 (m, 3H, H-4, 5, 6b), 3.41 (dd, 1H, $J_{2,3}$ = 9.1 Hz, H-2), 3.26 (s, 3H, OCH_3) ppm.

6-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (19) was obtained from donor **1** and acceptor **8** under the general glycosylation method A in 85% yield (β only) as an off-white amorphous solid. The analytical data for **19** was in accordance with that previously reported.[61] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04-7.81 (m, 8H, aromatic), 7.57-7.25 (m, 12H, aromatic), 5.90 (dd, 1H, $J_{3',4'}$ = 9.6 Hz, H-3'), 5.68 (dd, 1H, H-4'), 5.54 (dd, 1H, $J_{2',3'}$ = 9.6 Hz, H-2'), 5.42 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1), 5.05 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1'), 4.65 (dd, 1H, $J_{6a',6b'}$ = 12.2 Hz, H-6a'), 4.51-4.41 (m, 2H, H-3, 6b'), 4.23-4.15 (m, 2H, $J_{5',6b'}$ = 3.2 Hz, H-2, 5'), 4.10 (dd, 1H, $J_{4,5}$ = 8.1 Hz, H-4), 4.02 (dd, 1H, $J_{6a,6b}$ = 9.3 Hz, H-6a), 3.91-3.82 (m, 2H, $J_{5,6b}$ = 2.4 Hz, H-5, 6b), 1.37, 1.24, 1.21, 1.19 (4 s, 12H, 4 x CH_3) ppm.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-glucopyranoside (20) was obtained from donor **1** and acceptor **9**[62] under the general glycosylation method A in 85% yield (β only) as a white amorphous solid. The analytical data for **20** was in accordance with that previously reported.[63] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01-7.778 (m, 14H, aromatic), 7.52-7.26 (m, 21H, aromatic), 6.07 (dd, 1H, $J_{3,4}$ = 9.8 Hz, H-3), 5.93 (dd, 1H, $J_{3',4'}$ = 9.6 Hz, H-3'), 5.67 (dd, 1H, $J_{4',5'}$ = 9.7 Hz, H-4'), 5.57 (dd, 1H, $J_{2',3'}$ = 9.5 Hz, H-2'), 5.32 (dd, 1H, $J_{4,5}$ = 9.9 Hz, H-4), 5.09 (dd, 1H, $J_{2,3}$ = 10.2 Hz, H-2), 4.97 (d, 1H, $J_{1',2'}$ = 7.9 Hz, H-1'), 4.93 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.60 (dd, 1H, $J_{6a',6b'}$ = 12.0 Hz, H-6a'), 4.46 (dd, 1H, $J_{5',6a'}$ = 4.9 Hz, H-6b'), 4.22-4.09 (m, 3H, $J_{5',6b'}$ = 2.6 Hz, H-5, 5', 6a), 3.79 (dd, 1H, $J_{6a,6b}$ = 7.8 Hz, $J_{5,6a}$ = 3.4 Hz, H-6b), 2.94 (s, 3H, OCH_3) ppm.

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (21) was obtained from donor **1** and acceptor **10**[65] under the general glycosylation method A in 16% yield (β only) as an off-white amorphous solid. The analytical data for **21** was in accordance with that previously reported.[67] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02-7.23 (m, 35H), 5.88 (dd, 1H, $J_{3,4}$ = 9.6 Hz, H-3), 5.81 (dd, 1H, $J_{3',4'}$ = 9.5 Hz, H-3'), 5.63 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 5.51 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2), 5.40 (dd, 1H, $J_{2',3'}$ = 9.7 Hz, H-2'), 5.31 (dd, 1H, $J_{4',5'}$ = 9.7 Hz, H-4'), 4.99 (d, 1H, $J_{1,2}$ =7.8 Hz, H-1), 4.65 (d, 1H, $J_{1',2'}$ = 10.0 Hz, H-1'), 4.58 (dd, 1H, $J_{6a,6b}$ = 12.1 Hz, H-6a), 4.40 (dd, 1H, H-6b), 4.13-3.83 (m, 4H, $J_{5,6a}$ = 3.0, $J_{5,6b}$ = 5.0 Hz, H-5, H-5', 6a', 6b'), 2.52 (m, 2H, SCH_2CH_3), 1.10 (t, 3H, SCH_2CH_3) ppm.

***p*-Tolyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (22)** was obtained from donor **1** and acceptor **11**[66] under the general glycosylation method A in 42% yield (β only) as a white amorphous solid. The analytical data for **22** was in accordance with that previously reported.[68] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93-7.09 (m, 39H, aromatic), 5.84 (dd, 1H, $J_{3',4'}$ = 9.6 Hz, H-3'), 5.67 (dd, 1H, $J_{4',5'}$ = 9.6 Hz, H-4'), 5.58 (dd, 1H, $J_{2',3'}$ = 9.6 Hz, H-2'), 4.93 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1'), 4.86-4.80 (m, 2H, 2 x C*H*Ph), 4.74-4.39 (m, 7H, H-1, 6a', 6b', 4 x C*H*Ph), 4.13 (d, 1H, $J_{6a,6b}$ = 11.4 Hz, H-6a), 3.87-3.82 (m, 1H, H-5'), 3.85 (dd, 1H, H-6b), 3.57 (dd, 1H, $J_{3,4}$ = 8.3 Hz, H-3), 3.42-3.33 (m, 3H, $J_{5,6a}$ = 4.2 Hz, H-2, 4, 5), 2.34 (s, 3H, CH_3) ppm.

(3β)-Cholest-5-en-3-yl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (23) was obtained from donor **1** and acceptor **12** under the general glycosylation method A in 77% yield (β only) as a white solid. The analytical data for **23** was in accordance with that previously reported.[69] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01, 7.96, 7.90 and 7.84 (4 d, 8H, aromatic), 7.57-7.26 (m, 12H, aromatic), 5.90 (dd, 1H, $J_{3,4}$ = 9.7 Hz, H-3), 5.63 (dd, 1H, H-4), 5.50 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2), 5.22 (d, 1H), 4.94 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 4.60 (dd, 1H, $J_{6a,6b}$ = 12.0 Hz, H-6a), 4.52 (dd, 1H, H-6b), 4.18-4.12 (m, 1H, $J_{5,6a}$ = 3.3, $J_{5,6b}$ = 5.9 Hz, H-5), 3.53 (m, 1H), 2.17-2.16 (m, 2H), 2.02-1.69 (m, 2H), 1.60-1.57 (m, 1H), 0.91 (d, 3H, J = 6.5 Hz), 0.89 (s, 3H), 0.87 (d, 3H, J = 6.6 Hz), 0.86 (d, 3H, J = 6.6 Hz), 0.65 (s, 3H) ppm.

1-Adamantyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (24) was obtained from donor **1** and acceptor **13** under the general glycosylation method A in 96% yield (β only) as a white solid. The analytical data for **24** was in accordance with that previously reported.[70] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03-7.90 (m, 8H, aromatic), 7.85-7.26 (m, 12H, aromatic), 5.92 (dd, 1H, $J_{3,4}$ = 9.6 Hz, H-3), 5.55 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 5.49 (dd, 1H, $J_{2,3}$ = 8.0 Hz, H-2), 5.13 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 4.59 (dd, 1H, $J_{6a,6b}$ = 11.9 Hz, H-6a), 4.48 (dd, 1H, H-6b), 4.19 (ddd, 1H, $J_{5,6a}$ = 3.0 Hz, $J_{5,6b}$ = 7.1 Hz, H-5), 2.02 (s, 3H), 1.82 (d, 3H, J = 11.3 Hz), 1.63 (d, 3H, J = 11.4 Hz), 1.50 (dd, 6H) ppm.

Methyl 4,6-di-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3-di-O-benzyl-α-D-glucopyranoside (25) was obtained from donor **1** and acceptor **14**[71] under the general glycosylation method A in 41% yield (β only) as a white amorphous solid. Analytical data for **25**: R_f = 0.36 (ethyl acetate/hexane, 35/65, v/v); $[\alpha]_D^{23}$ +26.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12-7.77 (m, 16H, aromatic), 7.62-7.21 (m, 34H, aromatic), 5.75 (dd, 1H, $J_{3',4'}$= 9.5 Hz, H-3'), 5.66 (dd, 1H, $J_{3'',4''}$= 9.7 Hz, H-3"), 5.59-5.53 (m, 2H, H-4', 4"), 5.50-5.43 (m, 2H, $J_{2',3'}$= 9.5, $J_{2'',3''}$= 9.7 Hz, H-2', 2"), 4.90 (dd, 2H, CH_2Ph), 4.63 (d, 1H, $J_{1',2'}$= 7.6 Hz, H-1'), 4.59 (d, 1H, ^2J= 10.0 Hz, C*H*Ph), 4.49-4.38 (m, 4H, $J_{1,2}$= 3.4 Hz, H-1, 6a', 6b', C*H*Ph), 4.32 (d, 1H, $J_{1'',2''}$= 7.5 Hz, H-1"), 4.07 (dd, 1H, $J_{6a'',6b''}$= 12.7 Hz, H-6a"), 3.99 (dd, 1H, H-6b"), 3.91-3.83 (m, 2H, $J_{3,4}$= 10.7 Hz, H-3, 6a), 3.66-3.60 (m, 3H, H-5, 5', 6b'), 3.56 (dd, 1H, $J_{4,5}$= 3.7, H-4), 3.38 (dd, 1H, $J_{2,3}$= 9.4 Hz, H-2), 3.30 (m, 1H, $J_{5'',6a''}$= 2.0, $J_{5'',6b''}$= 3.6 Hz, H-5"), 3.18 (s, 3H, OCH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.1 166.0, 165.5 (×2), 165.4, 165.3, 165.2, 164.8, 138.2, 137.9, 133.4, 133.3, 133.2 (×2), 133.0 (×3), 132.9, 130.0, 129.8 (×4), 129.7 (×4), 129.6 (×5), 129.3, 129.2, 129.1 (×2), 128.9, 128.8, 128.5 (×2), 128.4 (×6), 128.3 (×6), 128.2 (×4), 128.1 (×3), 128.0 (×3), 127.9, 127.4 (×3), 127.1, 101.6, 101.5, 97.9, 80.0, 79.6, 79.2, 74.5, 73.6, 73.2, 72.9, 72.6, 72.3, 72.2, 71.8, 69.7, 69.2, 68.9, 68.3, 63.5, 62.4, 55.4 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{89}H_{78}O_{24}Na$ 1553.4781, found 1553.4755.

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (37) was obtained from donor **26** and acceptor **2** under the general glycosylation method A in 97% yield (β only) as a white amorphous solid. The analytical data for **37** was in accordance with that previously reported.[74] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09-7.11 (m, 35H, aromatic), 5.97 (d, 1H, $J_{4',5'}$ = 2.7 Hz, H-4'), 5.85, (dd, 1H, $J_{2',3'}$ = 10.4 Hz, H-2'), 5.60 (dd, 1H, $J_{3',4'}$ = 3.5, Hz, H-3') 4.90 (d, 1H, ^2J = 10.9 Hz, C*H*Ph), 4.76 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.72 (d, 1H, ^2J = 12.0 Hz, C*H*Ph), 4.69 (d, 1H, ^2J = 10.9 Hz, C*H*Ph), 4.67 (dd, 1H, $J_{6a',6b'}$ = 11.3 Hz, H-6a'), 4.58 (d, 1H, ^2J = 12.0 Hz, C*H*Ph), 4.56 (d, 1H, ^2J = 11.2 Hz, C*H*Ph), 4.51 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.40 (dd, 1H, H-6b'), 4.38 (d, 1H, ^2J = 11.2 Hz, C*H*Ph), 4.24-4.19 (m, 1H, $J_{5',6a'}$ = 6.4, $J_{5,6b'}$ = 6.8 Hz, H-5'), 4.21 (dd, 1H, $J_{6a,6b}$ = 12.7 Hz, H-6a), 3.89 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 3.77-3.74 (m, 2H, $J_{5,6a}$ = 4.2 Hz, H-5, H-6b), 3.40 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.38 (dd, 1H, H-4), 3.20 (s, 3H, OCH_3) ppm.

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (38) was obtained from donor **27** and acceptor **2** under the general glycosylation method A in 92% yield (α only) as a white amorphous solid. The analytical data for **38** was in accordance with that previously reported.[63] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09-7.25 (m, 35H, aromatic), 6.07 (dd, 1H, $J_{4',5'}$ = 10.0 Hz, H-4'), 5.86 (dd, 1H, $J_{3',4'}$ = 3.1 Hz, H-3'), 5.72 (dd, 1H, $J_{2',3'}$ = 1.7 Hz, H-2'), 5.15 (d, 1H, $J_{1',2'}$ = 1.5 Hz, H-1'), 5.00 (dd, 2H, CH_2Ph), 4.84-4.78 (m, 2H, 2 x C*H*Ph), 4.70-4.61 (m, 4H, $J_{1,2}$ = 3.6 Hz, H-1, 6a', CH_2Ph), 4.40-4.35 (m, 1H, $J_{5',6a'}$ = 4.3 Hz, H-5'), 4.30 (dd, 1H, H-6b'), 4.03 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 3.96-3.91 (dd, 1H, H-6a), 3.88-3.78 (m, 2H, $J_{5,6a}$ = 4.9 Hz, H-5, 6b), 3.58-3.49 (m, 2H, $J_{4,5}$ = 9.3 Hz, H-2, 4), 3.45 (s, 3H, OCH_3) ppm.

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (39) was obtained from donor **28** and acceptor **2** under the general glycosylation method B in 71% yield (α/β = 1/1.5) as a white amorphous solid. The analytical data for **39** was in accordance with that previously reported.[76] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.16 (m, 35H, aromatic), 4.98-4.35 (m, 15H), 4.34 (d, 1H, $J_{1',2'}$ = 7.7 Hz, H-1'), 4.20-3.42 (m, 12H), 3.35-3.32 (2 s, 6H, 2 x OCH_3) ppm.

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (40) was obtained from donor **32** and acceptor **2** under the general glycosylation method A in 97% yield (α/β = 1/1.1) as a white amorphous solid. The analytical data for **40** was in accordance with that previously reported.[79] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33-7.24 (m, 35H, aromatic), 4.99-4.33 (m, 15H), 4.32 (d, 1H, $J_{1',2'}$ = 7.6 Hz, H-1'), 4.16-3.41 (m, 12H), 3.28 (2 s, 6H, 3 x OCH_3) ppm.

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (41) was obtained from donor **30** and acceptor **2** under the general glycosylation method B in 91% yield (α/β = 1/1.4) as an off-white amorphous solid. The analytical data for **41** was in accordance with that previously reported.[80] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.12 (m, 35H, aromatic), 5.04-4.41 (m, 16H), 4.18-3.36 (m, 12H), 3.32-3.30 (2 s, 6H, 2 x OCH_3) ppm.

Methyl 6-*O*-(2,6-di-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (42) was obtained from donor **33** and acceptor **2** by general method A in 93% yield (β-only) as a white foam. Analytical data for **42**: R_f = 0.60 (ethyl acetate/toluene, 12/88, v/v); $[\alpha]_D^{23}$ +25.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (m, 4H, aromatic), 7.58-7.23 (m, 26H, aromatic), 7.11 (dd, 2H, aromatic), 5.66 (dd, 1H, $J_{2',3'}$ = 8.6 Hz, H-2'), 5.11 (d, 1H, ^2J = 11.3 Hz, C*H*Ph), 4.87 (d, 1H, ^2J = 11.0 Hz, C*H*Ph), 4.71-4.35 (m, 10H, $J_{1,2}$ = 3.3, $J_{1',2'}$ = 8.6 Hz, H-1, 1', 6a', 6b', 3 x CH_2Ph), 4.12 (m, 1H, H-6b), 3.97 (br d, 1H, H-3'), 3.89-3.82 (m, 3H, $J_{2,3}$ = 10.1 Hz, H-3, 4', 5'), 3.68-3.60 (m, 2H, H-5, 6a), 3.39-3.29 (m, 2H, H-2, 4), 3.13 (s, 3H, OCH_3), 0.79 (s, 9H, Si^{t}Bu), 0.12, -0.06 (2 s, 6H, $SiMe_2$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 165.0, 138.9, 138.3 (x2), 138.2, 133.2, 132.9, 130.2, 129.9, 129.8 (x2), 129.6 (x2), 128.5 (x2), 128.4 (x4), 128.3 (x5), 128.1 (x4), 127.9 (x3), 127.8, 127.7 (x2), 127.6, 127.5, 101.6, 97.7, 82.0, 80.0, 75.5, 75.1, 74.7, 73.3, 72.5, 69.5, 67.8, 63.7, 54.9 (x2), 29.8, 25.6 (x3), 17.9 (x2), -3.9, -5.0 ppm; HRMS $[M+Na]^+$ calcd for $[C_{61}H_{70}O_{13}SiNa]^+$ 1061.4483 found 1061.4500.

Methyl 6-*O*-(4,6-di-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-phthalimido-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (43) was obtained from donor **34** and acceptor **2** by general method B in 73% yield (β-only) as a white foam. Analytical data for **43**: R_f = 0.60 (ethyl acetate/hexane, 1/1, v/v); $[\alpha]_D^{23}$ +30.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18-7.75 (m, 27H, aromatic), 7.01 (dd, 2H, *J* = 3.2 Hz, aromatic), 5.82 (dd, 1H, $J_{3',4'}$ = 8.3 Hz, H-3'), 5.40 (d, 1H, $J_{1',2'}$ = 8.5 Hz, H-1'), 4.85 (d, 1H, ^2J = 10.8 Hz, C*H*Ph), 4.53-4.73 (m, 7H, 7 x C*H*Ph), 4.27-4.42 (m, 3H, $J_{1,2}$ = 3.5, $J_{2',3'}$ = 9.6, ^2J = 10.6 Hz, H-1, 2', C*H*Ph), 4.10-4.15 (m, 2H, H-6b, C*H*Ph), 3.74-3.87 (m, 5H, $J_{3,4}$ = 9.2 Hz, H-3, 4', 5', 6a', 6b'), 3.62-3.66 (m, 2H, H-5, 6a), 3.38 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2), 3.26 (dd, 1H, $J_{4,5}$ = 9.2 Hz, H-4), 3.13 (s, 3H, OCH_3), 2.20-2.45 (m, 4H, CH_2CH_2), 1.91 (s, 3H, $COCH_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.7, 172.0, 168.2, 167.5, 138.7, 138.2 138.1, 137.9, 137.8, 133.8, 131.5, 128.5 (x2), 128.4 (x6), 128.3 (x2), 128.2 (x2), 128.0 (x3), 127.9 (x4), 127.8 (x3), 127.7 (x5), 127.6, 123.4, 98.2, 97.9, 81.9, 79.7, 77.7, 75.8, 75.1, 74.8, 74.6, 73.5 (x2), 73.4, 73.3, 69.3, 68.6 (x2), 54.9, 37.6, 29.8, 29.5, 27.8 ppm; HRMS $[M+Na]^+$ calcd for $[C_{61}H_{63}NO_{14}Na]^+$ 1056.4146 found 1056.4164.

Methyl 6-*O*-(6-*O*-benzoyl-4-*O*-benzyl-2-deoxy-3-*O*-levulinoyl-2-phthalimido-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (44) was obtained from donor **35** and acceptor **2** by general method B in 79% yield (β-only) as a white foam. Analytical data for **44**: R_f = 0.60 (ethyl acetate/hexane, 45/55, v/v); $[\alpha]_D^{23}$ +33.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, 2H, *J* = 7.5 Hz, aromatic), 7.77-7.21 (m, 25H, aromatic), 7.01-6.99 (dd, 2H, *J* = 3.1 Hz, aromatic), 5.89 (dd, 1H, $J_{3',4'}$ = 8.8 Hz, H-3'), 5.46 (d, 1H, $J_{1',2'}$ = 8.5 Hz, H-1'), 4.83 (d, 1H, ^2J = 10.8 Hz, C*H*Ph), 4.72-4.51 (m, 7H, H-6a', 6b', 5 x C*H*Ph), 4.39-4.35 (m, 3H, $J_{1,2}$ = 3.4 Hz, H-1, 2', C*H*Ph), 4.11-4.05 (m, 2H, H-6b, C*H*Ph), 3.93 (m, 1H, H-5'), 3.87-3.78 (m, 2H, $J_{3,4}$ = 8.9 Hz, H-3, 4'), 3.68-3.61 (m, 2H, H-5, 6a), 3.37 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2), 3.23 (dd, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 3.11 (s, 3H, OCH_3), 2.48-2.29 (m, 4H, CH_2CH_2), 1.91 (s, 3H, $COCH_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.7 (x2), 172.0 (x2), 166.2, 138.7, 138.1, 137.7, 137.3, 133.9, 133.2, 131.4, 129.8 (x3), 128.5 (x7), 128.4 (x3), 128.3 (x3), 128.1 (x3), 128.0 (x6), 127.9 127.7 (x3), 127.6, 123.4, 98.3, 97.9, 81.9, 79.6, 76.6, 75.7, 74.8, 74.7, 73.4 (x2), 73.2, 69.2, 68.6, 63.4, 54.9, 37.6, 29.5, 27.8 ppm; HRMS $[M+Na]^+$ calcd for $[C_{61}H_{61}NO_{15}Na]^+$ 1070.3939 found 1070.3954.

Methyl 6-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (45) was obtained from donor **36** and acceptor **2** under the general glycosylation method A in 79% yield (α only) as a white foam. The analytical data for **47** was in accordance with that previously reported.[84] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (d, 2H, J = 7.6 Hz, aromatic), 7.97 (d, 2H, J = 7.6 Hz, aromatic), 7.81 (d, 2H, J = 7.7 Hz, aromatic), 7.61-7.23 (m, 24H, aromatic), 5.80 (dd, 1H, $J_{3',4'}$ = 10.1 Hz, H-3'), 5.67-5.60 (m, 2H, $J_{2',3'}$ = 3.4 Hz, $J_{4',5'}$ = 9.9 Hz, H-2', 4'), 5.05-4.93 (m, 3H, $J_{1',2'}$ = 5.3 Hz, H-1', CH_2Ph), 4.87-4.81 (m, 2H, CH_2Ph), 4.72-4.61 (m, 3H, $J_{1,2}$ = 2.9 Hz, H-1, CH_2Ph), 4.16 (m, 1H, $J_{5',6'}$ = 6.2 Hz, H-5'), 4.05 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 3.97-3.94 (m, 1H, H-6a), 3.86 (m, 1H, H-5), 3.65-3.52 (m, 3H, $J_{2,3}$ = 9.2 Hz, $J_{4,5}$ = 10.3 Hz, H-2, 4, 6b), 3.46 (s, 3H, OCH_3), 1.31 (d, 3H, H-6') ppm.

ASSOCIATED CONTENT

Supporting Information

NMR spectra for all new and selected known compounds. This material is available free of charge via the Internet at

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