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Silicon Fluorides for Acid-Base Catalysis in Glycosidations

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Abstract: Adduct formation between alcohols as glycosyl acceptors and phenylsilicon trifluoride ($PhSiF_3$) as catalyst permits acid-base-atalyzed glycosidations with *O*-glycosyl trichloroacetimidates as glycosyl donors. In this way, from various glycosyl donors and acceptors 1,2-*trans*- and some 1,2-*cis*-glycosides could be obtained with high anomeric selectivity. A preference for an intramolecular bimolecular nucleophilic substitution (S_N2-type) reaction course with concomitant donor and acceptor activation is supported by the results.

Keywords: arylsilicon fluorides; bifunctional catalysis; glycosidation; 1,2-*trans* glycosides; *O*-glycosyl trichloroacetimidates; mechanism

Introduction

Acid-base catalysis for the acceleration of chemical reactions is an important concept that is also extensively employed by nature, for instance, in glycosyltransferase reactions.[1] As the glycosyl donor and the acceptor are bound in the glycosyltransferase active site in such a way that an intramolecular S_N2-type process is possible, complete stereocontrol is obtained.

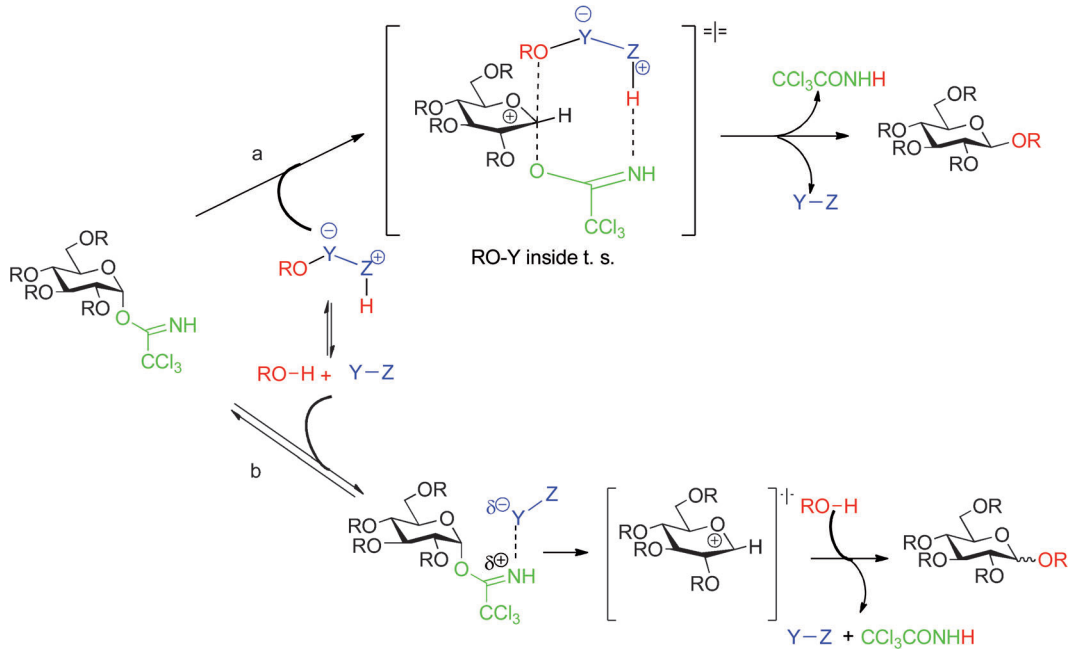
Glycosidation *via* first complex formation between a catalyst Y–Z, where Y is Lewis acidic and Z basic, and an alcohol RO–H as acceptor permits in the glycosidation step an activation of the glycosyl donor *via* proton transfer as well as an activation of the acceptor due to the transfer of a partial negative charge to the reacting oxygen.[2,3] When the donor and the acceptor-catalyst complex arrange in such a way that a hydrogen bond-mediated intramolecular S_N2-type process is available (path a, Scheme 1, "RO-Y inside" transition state), also in the i*n vitro* glycosidation, excellent stereocontrol should be observed. Thus, the stereochemical outcome is dependent on the configuration of the glycosyl donor. To support this conceptual approach to glycosidation, the catalyst Y–Z should not activate and thus eventually decompose the glycosyl donor (path b, Scheme 1), this should be only available to the fast and reversibly formed acceptor-catalyst complex that generates the increased proton acidity and concomitantly the increased acceptor nucleophilicity.[2]

As boron has a high affinity to oxygen, however, a markedly lower affinity to nitrogen, phenylboron fluorides as catalyst Y–Z fulfill these criteria; with their help and *O*-glycosyl trichloroacetimidates as glycosyl donors excellent results in 1,2-*trans*-glycoside bond formation were obtained, thus supporting the prevalence of a concerted S_N2-type transition state in these reactions.[3] As silicon forms much stronger bonds to fluorine and oxygen[4] than to nitrogen and the pentacoordinated (or eventually hexacoordinated)[5] silicon having a negative charge (see Scheme 2, a) is more prone to transfer the alkoxy group to the electrophilic anomeric carbon than the corresponding boron complexes that possess higher bond energies,[6] studies with phenylsilicon fluorides **I–III**[7] as glycosidation catalysts were undertaken. The detection of silicon fluoride-hydrogen bonds (Si–F···H) in fluoride-containing silicon complexes[8] favours S_N2-type reactions of the acceptor-catalyst adduct with the glycosyl donor.

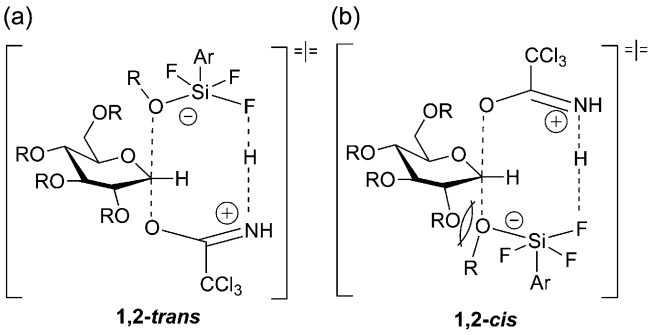
F_5C_6-SiF_3 (**I**) Ph_2SiF_2 (**II**) $PhSiF_3$ (**III**)

Results and Discussion

Compared with $PhBF_2$ as catalyst, **I–III** are weaker Lewis acids and NMR studies exhibited that complex formation, for instance, with 2-propanol (acceptor **A**), is fast, however the equilibrium is mainly on the left side. Hence, as expected, **I–III** do not activate and



Scheme 1. Reaction of acceptors RO–H in the presence of catalyst Y–Z.



Scheme 2. Postulated transition state for S_N2-type 1,2-*trans*- and 1,2-*cis*-product formation.

this way eventually decompose *O*-(α-D-glucopyranosyl) trichloroacetimidate **1α**[9] at 0 °C even after 2 h (or longer reaction time) (Table 1, entries 1, 4, and 6). Thus, side reactions due to direct activation of *O*-glycosyl trichloroacetimidates (Scheme 1, path b) leading eventually to α,β-mixtures of the desired product or to *O*-glycosyl trichloroacetimidate rearrangement reactions are minimized. Hence, an important precondition for the prevalence of an acid-base-catalyzed S_N2-type glycosidation is fulfilled.

However, when the acceptor **A** is added to the solution of catalyst **I** in CH_2Cl_2 and thereafter the donor **1α** (inverse procedure) a fast reaction takes place leading at 0 °C and even at −40 °C mainly to β-product **1Aβ** (Table 1, entries 2 and 3).[10] Thus, the desired proton acidity and concomitantly the acceptor nucleophilicity increase in the acceptor-catalyst complex is exhibited. The Lewis acidity of Ph_2SiF_2 (**II**) is too low to initiate glycosidation in the presence of **A** as acceptor (entry 5), however excellent results were obtained with $PhSiF_3$ (**III**) as catalyst and **A** as acceptor. At −40 °C practically only **1Aβ** was obtained (entry 7) and, in support of a concerted reaction, the results were only little influenced by solvent variation (entries 9 and 10), yet strongly by temperature and catalyst variation (entries 8, 11 and 12). Hence, $PhSiF_3$ as catalyst, CH_2Cl_2 as solvent and −40 °C as reaction temperature were chosen as standard reaction conditions. Similar results were obtained with allyl alcohol (**B**) as primary alcohol, cholesterol (**C**) and (+)-/(−)-menthol [(+)/(−)**D**] as secondary alcohol and *tert*-butanol (**E**) as tertiary alcohol (furnishing **1B**,[11] **1C**,[12] **1**(+)/(−)**D**,[12] and **1E**,[13] entries 13–18). Although the steric demand of the acceptors **B**–**E** is strongly increasing, only with *tert*-butanol (**E**, entry 18) did the yield and the β-selectivity drop slightly. But in line with an S_N2-type mechanism, the reaction rates are affected by the increasing steric bulk of the acceptors **B**–**E**. Also the relative placement of the acceptor substituents leading to diastereomeric transition states affects the reaction rate and the α/β-ratio as shown for (+)-/(−)-menthol [(+)/(−)**D**, entries 16 and 17]. Comparisons with $PhBF_2$ as catalyst at −40 °C under the same conditions (entries 11 and 14) demonstrate that both catalysts provide similar results.

Reaction of **A** with the anomeric *O*-β-D-glucopyranosyl trichloroacetimidate **1β**[10a] as glycosyl donor led only to low α-selectivity (entry 19), as the transition state for a concerted 1,2-*cis* glycoside bond formation is sterically disfavoured (Scheme 2, b). Hence, the ac-

Table 1. Phenylsilicon fluorides as glycosidation catalysts. Reaction of **1α** and **1β** with different acceptors.[a]

Entry	Donor	Acceptor	Promotor/Catalyst (0.1 equiv.)	Reaction Conditions Solvent	Temperature	Time	Product (Yield)	β/α-Ratio
1	**1α**	None	$F_5C_6SiF_3$	CH_2Cl_2	0	2 h	no reaction/no decomp. of **1α**	
2	**1α**	**A**	″	″	0	10 min	**1A** (86%)	6:1
3	**1α**	**A**	″	″	−40	10 min	**1A** (86%)	8:1
4	**1α**	none	Ph_2SiF_2	″	0	2 h	no reaction/no decomp. of **1α**	
5	**1α**	**A**	″	″	−40	4 h	no reaction/no decomp. of **1α**	
6	**1α**	none	$PhSiF_3$	″	0	12 h	no reaction/no decomp. of **1α**	
7	**1α**	**A**	″	″	−40	2 h	**1A** (92%)	24:1
8	**1α**	**A**	″	″	−78	4 h	no reaction/no decomp. of **1α**	
9	**1α**	**A**	″	MeCN	−30	5 h	**1A** (89%)	24:1
10	**1α**	**A**	″	toluene	−40	6 h	**1A** (88%)	20:1
11	**1α**	**A**	$PhBF_2$	CH_2Cl_2	−40	10 min	**1A** (76%)	8:1
12	**1α**	**A**	TMSOTf		−40	10 min.	**1A** (78%)	4:1
13	**1α**	**B**	$PhSiF_3$	″	−40	30 min	**1B** (90%)	24:1
14	**1α**	**B**	$PhBF_2$	″	−40	10 min	**1B** (85%)	20:1
15	**1α**	**C**	$PhSiF_3$	″	−40	1 h	**1C** (81%)	16:1
16	**1α**	(−)**D**	″	″	−40	1 h	**1**(−)**D** (88%)	24:1
17	**1α**	(+)**D**	″	″	−40	2 h	**1**(+)**D** (81%)	15:1
18	**1α**	**E**	″	″	−40	4 h	**1E** (78%)	9:1
19	**1β**	**A**	″	″	−40	3 h	**1A** (84%)	1:2
20	**1β**	**B**	$PhSiF_3$	″	−40	30 min	**1B** (82%)	1:12
21	**1β**	**B**	$PhBF_2$	″	−40	10 min	**1B** (86%)	1:15
22	**1β**	**F**	$PhSiF_3$	″	−40	1 h	**1F** (77%)	2:1

[a] Inverse procedure, temperature in °C.

ceptor-catalyst complex linked to the glycosyl donor *via* a hydrogen bond is forced in the transition state in an "RO–Y outside" arrangement that favours an acid catalyzed S_N1-type reaction course. Thus, formation of an α/β-product mixture is admitted. This hypothesis is strongly supported by the results with allyl alcohol (**B**) (entry 20); the lower steric demand of this acceptor favours formation of the inversion product, namely 1,2-*cis*-glycoside **1Bα** that is also obtained with $PhBF_2$ as catalyst (entry 21). However, already with **F** as acceptor the anomeric preference is reversed (entry 22).

To further demonstrate the efficacy of this method important 1,2-*trans* linked di- and trisaccharides were synthesized based on quite different carbohydrates such as, for instance, **F**,[10a] **G**,[14] **H**,[15] **I**,[16] **J** and **K** as acceptors (Figure 1, Figure 2 and Figure 3). Thus, with 6-*O*-unprotected glucoside **F** as acceptor and **1α** as glycosyl donor almost exclusive formation of gentiobioside **1Fβ**[17] was observed (Table 2, entry 1). However, the reaction of 4-*O*-unprotected glucoside **G** as acceptor and **1α** as donor was sluggish and led even after 8 h only in low yield to the desired cellobioside **1Gβ**;[18] in addition, also the corresponding maltoside **1Gα**[18] was formed (β/α = 3:1, entry 2). Obviously, the lower nucleophilicity of sugar hydroxy groups compared with simple alcohols and the steric bulk of a pentacoordinated (or hexacoordinated) silicon complex having fully protected sugars attached gave inferior results. Therefore, partially protected acceptors **H**, **I** and **J** were investigated; they provided much better results (entries 3–5). Reaction of **1α** with **H** led to β-selective reaction at 6-OH (**1Hβ**);[19] with **I** and **J** regioselective reactions at 3-OH were observed, that again furnished mainly β-linked disaccharides **1Iβ** and **1Jβ**. The structural assignments were confirmed by the NMR data of the per-*O*-acetylated derivatives

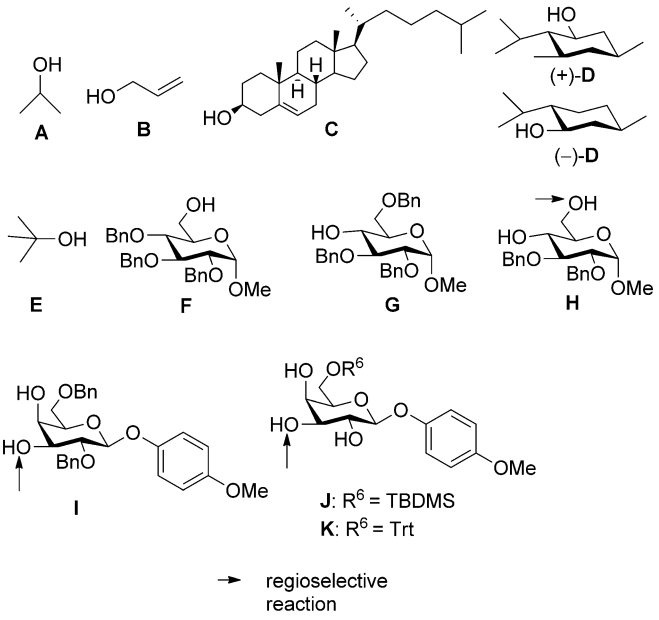


Figure 1. Hydroxy group containing acceptors **A**–**K**.

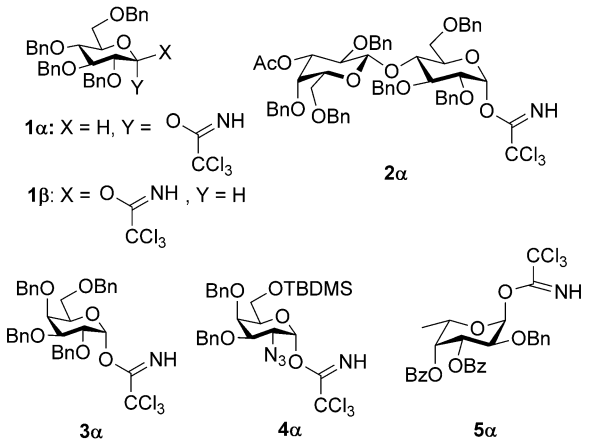


Figure 2. Donors **1α**, **1β**, **2α**–**5α**.

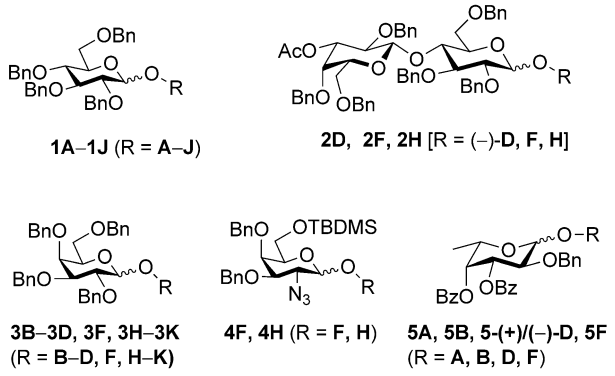


Figure 3. Products.

1Hβ′, **1Iβ′** and **1Jβ′**.[20] Comparisons with $PhBF_2$ as catalyst showed that diols **H** and **I** led to better results with $PhSiF_3$ as catalyst (entries 3 and 4) than with $PhBF_2$ (entries 6 and 7). This is presumably due to the generation of hexacoordinated intermediates with $PhSiF_3$. Similar results were obtained for the *O*-lactosyl trichloroacetimidate **2α**;[3] with acceptors **A**, **B**, (−)**D**, **F** and **H** the desired β-glycosides **2Aβ**,[3] **2Bβ**,[3] **2**(−)**Dβ**, **2Fβ**[3] and **2Hβ** were almost exclusively formed (Table 2, entries 8–12).

Nearly the same results, as obtained for glucose-derived glycosyl donor **1α** and **2α**, were found for galactosyl donor **3α** (Table 2, entries 14–22).[17] Reactions with alcohols **B**, **C** and (+)/(−)**D** and also with 6-*O*-unprotected glucoside **F** as acceptor led practically exclusively to β-glycoside bond formation furnishing **3Bβ**,[11] **3Cβ**,[21] **3**(+)/(−)**Dβ** and **3Fβ**.[22] Again, (+)-menthol [(+)**D**] as acceptor exhibited a slightly lower reactivity than (−)**D** (entries 16, 17). Also partially *O*-protected acceptors **H, I, J** and **K** furnished mainly the β-products **3Hβ**, **3Iβ**, **3Jβ** and **3Kβ**, respectively, although in partly lower yields (entries, 19–22). Good glycosidation results were also obtained for *O*-(2-azido-2-deoxy-α-D-galactopyranosyl) trichloroacetimidate **4α**[23] as glycosyl donor; with acceptors **F** and **H** under standard conditions preferentially the β-glycosides **4Fβ**[3] and **4Hβ**, respectively, were formed (entries 23 and 24).

Then we extended the scope of this glycosidation method to fucosyl donor **5α**,[24] a compound type that is generally employed for the synthesis of α-L-fucopyranosides (Table 3).[25] In the presence of **A** as acceptor donor **5α** could be even activated with Ph_2SiF_2 as catalyst affording **5A** at 0 °C in good β-selectivity (entries 1–3). Similar results were observed for $PhSiF_3$ as catalyst (entries 4–7) that readily activated **5α** even at −60 °C (entry 5). Also primary alcohol **B** as acceptor followed this S_N2-type reaction course furnishing with $PhSiF_3$ as catalyst essentially only β-product **5Bβ** (entry 9).[26] Similar glycosidation results were obtained for **A** and **B** with $PhBF_2$ as catalyst (entries 8 and 10). However, this outcome is in strong contrast to the TMSOTf-catalyzed reaction (entry 11) that generally favours an S_N1-type reaction course and hence led to a 1:1 ratio of **5Bα,β**. Sterically more hindered (−)-menthol [(−)**D**] as acceptor led to a β/α 2:3 mixture of **5**(−)**D** (entry 12), thus exhibiting the known tendency of **5α** to α-product formation with less reactive acceptors and at higher temperatures (entry 13). As **5α** is a pseudoenantiomer of **3α** it was expected that the match/mismatch situation is reversed and enantiomeric (+)-menthol [(+)**D**] will react faster than (−)**D** with **5α** and eventually also more β-product will be obtained; this was indeed observed (entries 14 and 15). After these findings it was not surprising that less reactive 6-*O*-unprotected glucoside acceptor **F** gave, as generally found for donors of **5α**-type,[25] exclusively the α-product **5Fα** (entry 16).[27] Hence, the S_N1-type mechanism (presumably *via* an "RO–Y outside" transition state) prevails in this case.

The structural assignments of new compounds were also confirmed through *O*-acetylation furnishing compounds **2Hβ′**, **3Hβ′**, **3Iβ′**, **3Jβ′**, **3Kβ′** and **4Hβ′**.[20]

Conclusions

$PhSiF_3$ does neither activate nor decompose *O*-glycosyl trichloroacetimidates, however it reversibly generates with alcohols adducts that activate the glycosyl donor *via* a proton transfer. Even at low temperature and with catalytic amounts of $PhSiF_3$ the reaction is quite fast, thus confirming the concomitant nucleophilicity increase of the acceptor. With structurally different, quite nucleophilic acceptors mainly 1,2-*trans*-glycosides were obtained in good yields. The solvent, temperature and the acceptor steric demand dependence of these reactions supports the proposed S_N2-type intramolecular reaction course. Practically no glycosyl fluorides are obtained, thus reflecting the dif-

Table 2. Reaction of donors **1α**–**4α** with different acceptors.[a]

Entry	Donor	Acceptor	Catalyst (0.1 equiv.)	Reaction Time	Product (Yield)	β/α-Ratio
1	**1α**	**F**	$PhSiF_3$	3 h	**1F** (81%)	24:1
2	**1α**	**G**	″	8 h	**1G** (30%)	3:1
3	**1α**	**H**	″	3 h	**1H** (73%)	24:1
4	**1α**	**I**	″	4 h	**1I** (70%)	8:1
5	**1α**	**J**	″	5 h	**1J** (52%)	5:1
6	**1α**	**H**	$PhBF_2$	30 min	1H (63%)	15:1
7	**1α**	**I**	″	30 min	several products	
8	**2α**	**A**	$PhSiF_3$	2.5 h	**2A** (72%)	3:1
9	**2α**	**B**	″	2 h	**2B** (78%)	15:1
10	**2α**	(−)**D**	″	6 h	**2**(−)**D** (78%)	24:1
11	**2α**	**F**	″	6 h	**2F** (76%)	24:1
12	**2α**	**H**	″	3 h	**2H** (74%)	8:1
13	**2α**	**A**	$PhBF_2$	15 min	**2A** (79%)	5:1
14	**3α**	**B**	$PhSiF_3$	30 min	**3B** (91%)	24:1
15	**3α**	**C**	″	2 h	**3C** (82%)	15:1
16	**3α**	(−)**D**	″	1 h	**3**(−)**D** (89%)	20:1
17	**3α**	(+)**D**	″	2 h	**3**(+)**D** (76%)	20:1
18	**3α**	**F**	″	6 h	**3F** (78%)	24:1
19	**3α**	**H**	″	3 h	**3H** (75%)	20:1
20	**3α**	**I**	″	4 h	**3I** (64%)	9:1
21	**3α**	**J**	″	6 h	**3J** (57%)	9:1
22	**3α**	**K**	″	5 h	**3K** (53%)	9:1
23	**4α**	**F**	″	18 h	**4F** (76%)	15:1
24	**4α**	**H**	″	3 h	**4H** (70%)	4:1

[a] All reactions were carried out in dichloromethane as solvent in the presence of $PhSiF_3$ or $PhBF_2$ (0.1 equivalents) as catalyst at −40 °C; the inverse procedure was applied.

Table 3. Reaction of fucosyl donor **5α** with various acceptors in the presence of different catalysts.[a]

Entry	Acceptor	Catalyst (0.1 equiv.)	Reaction Conditons		Product (Yield)	β/α-ratio
			Temperature [°C]	Time		
1	–	Ph_2SiF_2	r.t.	12 h	no reaction/no decomp.	
2	**A**	″	-40	12 h	no reaction/no decomp.	
3	**A**	″	0	30 min	**5A** (85%)	14:1
4	–	$PhSiF_3$	r.t.	12 h	no reaction/no decomp.	
5	**A**	″	−60	3 h	**5A** (84%)	12:1
6	**A**	″	−40	2 h	**5A** (86%)	9:1
7	**A**	″	−20	1 h	**5A** (82%)	6:1
8	**A**	$PhBF_2$	−40	30 min	**5A** (79%)	9:1
9	**B**	$PhSiF_3$	−40	2 h	**5B** (90%)	20:1
10	**B**	$PhBF_2$	−40		**5B**	15:1
11	**B**	TMSOTf	−40	10 min	**5B** (82%)	1:1
12	(−)**D**	$PhSiF_3$	−40	6 h	**5**(−)**D** (72%)	2:3
13	(−)**D**	″	−20	5 h	**5**(−)**D** (70%)	1:3
14	(+)**D**	″	−40	4 h	**5**(+)**D** (72%)	3:2
15	(+)**D**	″	−20	2.5 h	**5**(+)**D** (75%)	1:2
16	**F**	″	−40	10 h	**5F** (72%)	α only

[a] All reactions were carried out in CH_2Cl_2 with equimolar amounts of **5α** and acceptor; the inverse procedure was applied.

ferent bond strength and nucleophilicity of the negatively charged Si−OR *vs.* Si−F moieties. Other reaction courses, particularly an S_N1-type reaction, are only competitive with less nucleophilic acceptors. Hence, in most cases acid-base-catalyzed highly stereocontrolled S_N2-type intramolecular glycosidations are operative that are related to enzymatic glycosidations. Worth mentioning is the high regioselectivity that is observed for partially *O*-protected acceptors, where $PhSiF_3$ shows a clear preference over $PhBF_2$ as catalyst. Thus, protecting group manipulations, gener-

ally required in consecutive glycosidations, can be minimized.

Experimental Section

General Experimental Details

Solvents were purified by standard procedures. NMR spectra were recorded at 22 °C with a 400 MHz spectrometer; tetramethylsilane (TMS) or the resonance of the undeuterated solvent were used as internal standards (solvent $CDCl_3$, $\delta = 7.26$ ppm). Mass spectra were recorded with an ESI MS mass spectrometer. Thin-layer chromatography was performed on silica gel plastic plates; compounds were visualized by treatment with a solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (20 g) and $Ce(SO_4)_2$ (0.4 g) in sulfuric acid (10%, 400 mL) and then by heating to 120 °C. Flash chromatography was performed on silica gel (230–400 mesh) at a pressure of 0.2 bar. Optical rotations were measured at 22 °C using sodium D line light.

General Procedure for Glycosylation: Inverse Pocedure (A)

To a solution of acceptor (1 equiv. in CH_2Cl_2 was added catalyst (0.1 equiv.) (C_6F_5-SiF_3, Ph_2SiF_2 or $PhSiF_3$ in CH_2Cl_2) at room temperature. The reaction mixture was cooled to −40 °C. Donor (1 equiv.) was dissolved in minimum amount of CH_2Cl_2 and after cooling to −40 °C, was added into the reaction mixture at once. The mixture was allowed to stir at the same temperature until TLC indicated the complete consumption of the starting material. The reaction was quenched with aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by flash column chromatography with petroleum ether/EtOAc to afford the desired glycoside.

General Procedure for Acetylation (B)

To a stirred solution of the hydroxy compound in dry CH_2Cl_2 (2 mL) was added acetic anhydride (0.5 mL), dry pyridine (0.5 mL) and few crystals of DMAP at room temperature. The reaction mixture was stirred at room temperature until TLC indicated complete consumption of the starting material (12 h). Then the reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with diluted HCl. The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by flash column chromatography with petroleum ether/EtOAc.

p-Methoxyphenyl 6-*O*-(*tert*-Butyldimethylsilyl)-β-D-galactopyranoside (J)

To a solution of *p*-methoxyphenyl β-D-galactopyranoside[28] (2.0 g, 7.0 mmol) in dry pyridine (30 mL) was added TBDMS-Cl (1.35 g, 9.0 mmol) and the solution was stirred for 12 h at room temperature. Solvents were evaporated under vacuum and the residual syrup was purified by flash chromatography using petroleum ether/EtOAc (1:3) as eluent to afford pure compound **J** as a white solid; yield: 2.6 g (92%). $R_f = 0.4$ (petroleum ether/EtOAc, 2:8); $[\alpha]_D$: −86.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.96$ (d, $J = 9.0$ Hz, 2H, Ar-H), 6.72 (d, $J = 9.0$ Hz, 2H, Ar-H), 4.65 (d, $J = 7.7$ Hz, 1H, 1-H), 3.99 (*app* d, *Japp* = 3.0 Hz, 1H, 5-H), 3.89 (*app* t, *Japp* = 8.2 Hz, 1H, 2-H), 3.84–3.78 (m, 2H, 6a-H and 6a′-H), 3.70 (s, 3H, OMe), 3.60 (dd, $J = 9.6$, 3.2 Hz, 1H, 3-H), 3.49 (*app* t, *Japp* = 5.2 Hz, 1H, 4-H), 0.83 (s, 9H, *t*-Bu), 0.00 (s, 3H, -$SiCH_3$), −0.01 (s, 3H, -$SiCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.4$, 151.2, 118.7, 114.5, 102.5 (C-1), 74.9, 73.7, 71.7, 68.9, 62.6, 55.6, 25.8, 18.2, −5.40, −5.47; HR-MS: $m/z = 423.1800$, calcd. for ($C_{19}H_{32}NaO_7Si$) $[M+Na]^+$: 423.1810.

p-Methoxyphenyl 6-*O*-(Trityl)-β-D-galactopyranoside (K)

To a solution of *p*-methoxyphenyl β-D-galactopyranoside[28] (1.0 g, 3.5 mmol) in dry pyridine (20 mL) was added trityl-Cl (1.01 g, 4.0 mmol) and the solution was stirred for 12 h at room temperature. Solvents were evaporated under vacuum and the residual syrup was purified by flash chromatography using petroleum ether/EtOAc (1:3) as eluent to afford pure compound **K** as a white solid; yield: 1.5 g (81%). $R_f = 0.5$ (petroleum ether/EtOAc, 2:8); $[\alpha]_D$: −20.8 (*c* 4.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.49$ (d, $J = 7.4$ Hz, 6H, Ar-H), 7.34–7.27 (m, 9H, Ar-H), 7.13 (d, $J = 9.0$ Hz, 2H, Ar-H), 6.84 (d, $J = 9.0$ Hz, 2H, Ar-H), 4.76 (d, $J = 7.8$ Hz, 1H, 1-H), 4.02 (d, $J = 3.3$ Hz, 1H, 5-H), 3.93 (*app* t, *Japp* = 9.3 Hz, 1H, 2-H), 3.80 (s, 3H, OMe), 3.68 (*app* d, *Japp* = 3.3 Hz, 1H, 4-H), 3.65 (dd, $J = 7.4$, 4.0 Hz, 1H, 3-H), 3.60–3.56 (m, 1H, 6a-H), 3.42 (dd, $J = 9.8$, 5.0 Hz, 1H, 6a′-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.4$, 151.2, 143.7, 128.7, 127.9, 127.1, 118.7, 114.5, 102.4 (C-1), 86.9, 74.1, 73.9, 69.3, 63.1, 55.6; HR-MS: $m/z = 551.2032$, calcd. for ($C_{32}H_{32}NaO_7$) $[M+Na]^+$: 551.2040.

Methyl 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-α-D-glucopyranoside (1H): Following the general procedure **A** for glycosylation afforded **1H** as a white solid; yield: 73%. $R_f = 0.4$ (petroleum ether/EtOAc, 7:3); $[\alpha]_D$: +20.5 (*c* 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.32$–7.17 (m, 28H), 7.07 (dd, $J = 7.0$, 2.4 Hz, 2H), 4.92 (d, $J = 11.5$ Hz, 1H), 4.88 (d, $J = 11.0$ Hz, 1H), 4.83 (d, $J = 11.0$ Hz, 1H), 4.78–4.73 (m, 1H), 4.71 (br s, 1H), 4.67 (dd, $J = 7.5$, 4.9 Hz, 2H), 4.64–4.62 (m, 1H), 4.56–4.50 (m, 2H), 4.50 (br s, 1H), 4.45 (br s, 1H), 4.42 (t, $J = 5.6$ Hz, 1H), 4.37 (d, $J = 7.6$ Hz, 1H), 4.05 (dd, $J = 10.0$, 1.6 Hz, 1H), 3.75–3.68 (m, 2H), 3.66 (d, $J = 1.9$ Hz, 1H), 3.63 (d, $J = 1.8$ Hz, 1H), 3.60 (d, $J = 4.7$ Hz, 1H), 3.59–3.54 (m, 1H), 3.53 (d, $J = 5.9$ Hz, 1H), 3.50 (s, 1H), 3.44–3.41 (m, 1H), 3.40 (d, $J = 3.2$ Hz, 2H), 3.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.9$, 139.8, 139.7, 139.5, 139.1, 137.9, 128.5 −127.5 (m), 104.3, 98.1, 82.4, 81.5, 79.7, 79.4, 75.4, 75.1, 74.5, 73.6, 73.5, 73.4, 73.1, 73.0, 70.7, 70.0, 69.1, 68.7, 55.2; HR-MS: $m/z = 919.4019$, calcd. for ($C_{55}H_{60}NaO_{11}$) $[M+Na]^+$: 919.4028.

Methyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl-(1→6)-4-*O*-acetyl-2,3-di-*O*-benzyl-α-D-glucopyranoside (1H′): Acetylation under standard conditions (**B**) afforded **1H′** as a colourless solid; yield: 90%. $R_f = 0.6$ (petroleum ether/EtOAc, 7:3); $[\alpha]_D$: +11.0 (*c* 1.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.39$–7.26 (m, 28H, Ar-H), 7.22–7.11 (m, 2H, Ar-H), 5.00 (d, $J = 10.9$ Hz, 1H, benzylic-H), 4.91–4.86 (m,

3H, benzylic-H), 4.85 (d, $J=10.0$ Hz, 1H, benzylic-H), 4.79–4.73 (m, 2H, 4a-H and benzylic-H), 4.75 (d, $J=9.7$ Hz, 2H, benzylic-H), 4.66 (br s, 1H, benzylic-H), 4.64–4.60 (m, 3H, benzylic-H), 4.57 (br s, 1H, benzylic-H), 4.53 (d, $J=3.6$ Hz, 1H, 1a-H), 4.50 (d, $J=11.6$ Hz, 2H, benzylic-H), 4.41 (d, $J=7.8$ Hz, 1H, 1b-H), 3.93 (br d, $J=9.2$ Hz, 2H, 5a-H and 6b-H), 3.91 (br d, $J=2.8$ Hz, 1H, 6a-H), 3.72 (dd, $J=10.7$, 2.0 Hz, 1H, 6a′-H), 3.70–3.64 (m, 1H, 5b-H), 3.61 (dd, $J=8.1$, 6.4 Hz, 2H, 4b-H and 6b′-H), 3.56–3.54 (m, 2H, 3a-H and 2a-H), 3.44 (*app* t, *Japp* = 8.3 Hz, 2H, 2b-H and 3b-H), 3.30 (s, 3H, OMe), 1.88 (s, 3H, -$COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=169.9$, 138.6, 138.5, 138.18, 138.16, 138.0, 128.5–127.6 (m), 104.0 (C-1b), 97.9 (C-1a), 84.6, 82.3, 79.6, 79.2, 77.2, 75.7, 75.4, 74.9, 74.8, 74.7, 73.5, 70.8, 69.1, 68.9, 68.8, 55.3, 20.8; HR-MS: $m/z=961.4130$, calcd. for ($C_{57}H_{62}NaO_{12}$) $[M+Na]^+$: 961.4133.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranosyl-(1→3)-2,6-di-*O*-benzyl-β-D-galactopyranoside (1I): Following the general procedure **A** for glycosylation afforded **1I** as a white solid; yield: 70%. $R_f=0.5$ (petroleum ether/EtOAc, 6:4); $[\alpha]_D$: +18.2 (*c* 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.43$–7.30 (m, 29H), 7.23–7.29 (m, 5H), 7.07 (d, $J=9.1$ Hz, 2H), 6.84 (d, $J=9.1$ Hz, 2H), 5.30 (d, $J=3.6$ Hz, 1H), 5.07–4.99 (m, 2H), 4.98 (s, 1H), 4.95 (d, $J=4.4$ Hz, 1H), 4.93 (s, 1H), 4.90 (d, $J=2.6$ Hz, 1H), 4.88–4.86 (m, 1H), 4.85 (d, $J=1.5$ Hz, 1H), 4.84–4.82 (m, 1H), 4.81–4.77 (m, 3H), 4.76 (s, 1H), 4.67–4.64 (m, 1H), 4.62 (br s, 1H), 4.59 (br s, 2H), 4.57 (d, $J=5.3$ Hz, 2H), 4.53 (d, $J=8.0$ Hz, 2H), 4.16 (d, $J=2.8$ Hz, 1H), 4.07–4.02 (m, 2H), 3.89 (dd, $J=9.5$, 3.3 Hz, 1H), 3.84 (d, $J=2.9$ Hz, 1H), 3.82 (s, 4H), 3.78 (dd, $J=9.2$, 3.7 Hz, 1H), 3.71–3.63 (m, 7H), 3.52–3.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=163.5$, 155.2, 138.7=137.8 (m), 128.7–127.4, 118.5, 114.5, 103.3, 103.0, 91.3, 84.7, 81.8, 81.7, 81.2, 80.0, 78.4, 77.78, 77.73, 77.2, 75.74, 75.72, 75.2, 75.1, 75.0, 74.8, 74.5, 73.7, 73.57, 73.53, 73.0, 70.3, 69.6, 68.8, 68.7, 68.2, 55.6; HR-MS: $m/z=$ 1011.4283, calcd. for ($C_{61}H_{64}NaO_{12}$) $[M+Na]^+$: 1011.4290.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl-(1→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (1I′): Acetylation under standard conditions (**B**) afforded **1I′** as a white solid; yield: 85%. $R_f=0.4$ (petroleum ether/EtOAc, 7:3); $[\alpha]_D$: +13.8 (*c* 1.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.32$–7.11 (m, 29H, Ar-H), 7.11–7.02 (m, 2H, Ar-H), 6.97 (d, $J=9.1$ Hz, 2H, Ar-H), 6.72 (d, $J=9.1$ Hz, 2H, Ar-H), 5.44 (*app* d, *Japp* = 3.2 Hz, 1H, 4a-H), 4.86–4.85 (m, 3H, benzylic-H), 4.80 (d, $J=7.6$, 1H, 1a-H), 4.77 (d, $J=8.0$, 1H, 1b-H), 4.70 (d, $J=11.2$ Hz, 2H, benzylic-H), 4.68 (d, $J=11.8$ Hz, 1H, benzylic-H), 4.58 (d, $J=10.2$ Hz, 1H, benzylic-H), 4.53 (d, $J=12.0$ Hz, 1H, benzylic-H), 4.47–4.42 (m, 3H, benzylic-H), 3.98 (dd, $J=9.7$, 3.4 Hz, 1H, 3a-H), 3.93–3.91 (m, 1H, 2a-H), 3.76 (*app* t, *Japp* = 6.5 Hz, 1H, 3b-H), 3.70 (s, 3H, OMe), 3.61–3.59 (m, 2H, 6a-H and 6a′-H), 3.58–3.46 (m, 3H, 4b-H, 5b-H, 6b-H and 6b′-H), 3.36 (*app* t, *Japp* = 8.1 Hz, 1H, 2b-H), 3.27–3.25 (m, 1H, 5a-H), 2.05 (s, 3H, -$COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=169.9$, 155.3, 151.4, 138.6, 138.4, 138.3, 138.1,138.0, 128.7–127.5 (m), 118.3, 114.5, 102.97 (C-1a), 102.90 (C-1b), 84.5, 82.5, 79.8, 77.8, 77.1, 75.8, 77.4, 75.2, 75.0, 74.8, 74.7, 73.7, 73.2, 70.3, 68.9, 68.7, 55.6, 20.9; HR-MS: $m/z=1053.4399$, calcd. for ($C_{63}H_{66}NaO_{13}$) $[M+Na]^+$: 1053.4396.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-α,β-D-glucopyranosyl-(1→3)-6-*O*-*tert*-butyldimethylsilyl-α-D-galactopyranoside (1J): Following the general procedure **A** for glycosylation afforded **1J** as a white solid; yield: 52%. $R_f=0.5$ (petroleum ether/EtOAc, 5:5); $[\alpha]_D$: +25.0 (*c* 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.42$–7.22 (m, 35H), 7.16 (dd, $J=7.1$, 2.4 Hz, 3H), 7.04 (d, $J=9.0$ Hz, 3H), 6.81 (d, $J=9.2$ Hz, 3H), 5.05 (d, $J=10.9$ Hz, 1H), 4.94 (d, $J=10.9$ Hz, 2H), 4.86–4.78 (m, 4H), 4.75 (d, $J=7.9$ Hz, 2H), 4.69 (dd, $J=6.8$, 3.6 Hz, 2H), 4.55 (br s, 2H), 4.52 (d, $J=5.7$ Hz, 2H), 4.49–4.42 (m, 1H), 4.13 (d, $J=3.0$ Hz, 1H), 4.07 (qt, $J=9.3$ Hz, 2H), 3.97 (t, $J=8.3$ Hz, 1H), 3.88 (d, $J=7.1$ Hz, 3H), 3.77 (s, 4H), 3.72 (dd, $J=9.5$, 3.2 Hz, 2H), 3.66 (d, $J=8.1$ Hz, 5H), 3.59 (dd, $J=16.1$, 10.1 Hz, 4H), 3.51–3.45 (m, 1H), 0.90 (s, 2H), 0.89 (s, 10H), 0.07, 0.06 (2 s, 2H), 0.48, 0.40 (2 s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 155.7, 151.5, 138.4, 137.9, 137.8, 128.49, 128.46, 128.0, 127.8, 127.7, 118.6, 114.4, 103.9, 102.3, 84.6, 83.1, 81.6, 77.2, 75.7, 75.0, 74.7, 73.5, 70.4, 68.8, 67.9, 62.4, 25.9, 18.2, −5.31, −5.40; HR-MS: $m/z=945.4221$, calcd. for ($C_{53}H_{66}NaO_{12}Si$) $[M+Na]^+$: 945.4216.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl-(1→3)-2,4-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranoside (1J′): Acetylation under standard conditions (**B**) afforded **1J′** as a white solid; yield: 85%. $R_f=0.4$ (petroleum ether/EtOAc, 7:3); $[\alpha]_D$: +28.0 (*c* 0.7, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.40$–7.21 (m, 24H, Ar-H), 7.16 (d, $J=7.0$ Hz, 2H, Ar-H), 6.97 (d, $J=9.1$ Hz, 2H, Ar-H), 6.79 (d, $J=9.1$ Hz, 2H, Ar-H), 5.56–5.53 (m, 2H, 2a-H and 4a-H), 4.87 (d, $J=11.2$ Hz, 1H, benzylic-H), 4.83 (d, $J=11.5$ Hz, 1H, benzylic-H), 4.80 (d, $J=6.8$ Hz, 1H, 1a-H), 4.74 (d, $J=11.2$ Hz, 2H, benzylic-H), 4.60 (dd, $J=11.2$, 6.8 Hz, 2H, benzylic-H), 4.55–4.52 (m, 1H, 3a-H), 4.51 (d, $J=7.6$ Hz, 1H, 1b-H), 4.03 (dd, $J=12.5$, 6.3 Hz, 1H, 6a-H) 3.70 (s, 3H, OMe), 3.74–3.65 (m, 4H, 5a-H, 6a′-H′, 6b-H and 6b′-H), 3.58–3.54 (m, 2H, 3b-H and 4b-H), 3.47 (m, 1H, 5b-H), 3.38 (*app* t, *Japp* = 8.2 Hz, 1H, 2b-H), 2.11 (s, 3H, -$COCH_3$), 2.03 (s, 0.77H, -$COCH_3$), 1.91 (s, 3H, -$COCH_3$), 1.85 (s, 0.77H, -$COCH_3$), 0.89 (s, 11H, *t*-Bu), 0.02, 0.01 (2s, 8H, -$SiCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=169.8$, 169.5, 155.6, 151.7, 138.6 138.0, 128.4–127.6 (m), 118.1, 114.5, 104.1-(C-1a), 100.8 (C-1b), 84.3, 81.9, 77.8, 76.2, 75.5, 75.0, 73.4, 70.0, 69.2, 62.1, 55.6, 25.8, 20.88, 20.81, 18.2, −5.44, −5.53; HR-MS: $m/z=1029.4421$, calcd. for ($C_{57}H_{70}NaO_{14}Si$) $[M+Na]^+$: 1029.4427.

(−)-Menthyl 4-*O*-acetyl-2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside [2(−)D]: Following the general procedure **A** for glycosylation afforded **2(−)D** as a yellow oil; yield: 78%. $R_f=0.4$ (petroleum ether/EtOAc, 9:1); $[\alpha]_D$: −3.6 (*c* 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.43$–7.04 (m, 30H, Ar-H), 5.00 (d, $J=10.8$ Hz, 1H, benzylic-H), 4.90 (d, $J=10.8$ Hz, 1H, benzylic-H), 4.86 (d, $J=10.8$ Hz, 1H, benzylic-H), 4.76 (dd, $J=8.8$, 2.4 Hz, 1H, 3b-H), 4.70 (d, $J=11.1$ Hz, 1H benzylic-H), 4.62 (d, $J=10.8$ Hz, 2H, benzylic-H), 4.56 (d, $J=9.6$ Hz, 1H, 1b-H), 4.52 (d, $J=11.2$ Hz, 2H, benzylic-H), 4.45 (br. s, 1H, benzylic-H), 4.42–4.36 (m, 2H, 1a-H and benzylic-H), 4.25 (d, $J=12.0$ Hz, 1H, benzylic-H), 3.98–3.91 (m, 2H, 4b-H and 3a-H), 3.83–3.63 (m, 3H, 5b-H, 6b-H and 2b-H), 3.57–3.42 (m, 3H, 4a-H, 6a-H and 6b′-H), 3.38–3.32 (m, 3H, 2a-H, 5a-H and 6a′-H), 2.39–2.27 (m, 1H), 2.12 (q, $J=14.1$ Hz, 1H), 1.91 (s, 3H, -$COCH_3$), 1.66 (d, $J=10.8$ Hz, 2H), 1.38–1.14 (m, 3H), 1.04–0.68 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=171.1$, 139.3, 138.8, 138.5, 138.4,

138.0, 128.3–127.3 (m), 102.7 (C-1b), 100.7 (C-1a), 83.1, 81.7, 77.77, 77.73, 77.0, 75.4, 75.2, 75.1, 75.0, 74.8, 74.6, 73.4, 73.3, 72.8, 68.4, 67.7, 48.1, 40.9, 34.5, 31.5, 25.3, 23.3, 22.2, 21.0, 20.9, 16.0; HR-MS: $m/z = 1085.5373$, calcd. for ($C_{66}H_{78}NaO_{12}$) $[M+Na]^+$: 1085.5385.

Methyl 4-*O*-acetyl-2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α,β-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-α-D-glucopyranoside (2H): Following the general procedure **A** for glycosylation afforded **2H** as a white solid; yield: 74%. $R_f = 0.4$ (petroleum ether/EtOAc, 7:3); $[\alpha]_D$: +22.5 (*c* 1.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.38–7.26$ (m, 40H), 7.24 (d, $J = 1.9$ Hz, 4H), 7.20–7.08 (m, 5H), 5.19 (d, $J = 3.7$ Hz, 1H), 5.04–4.95 (m, 2H), 4.90 (d, $J = 10.9$ Hz, 1H), 4.80 (dd, $J = 10.1$, 3.1 Hz, 2H), 4.76 (d, $J = 4.9$ Hz, 1H), 4.73 (d, $J = 3.9$ Hz, 3H), 4.70 (d, $J = 2.7$ Hz, 2H), 4.64 (s, 1H), 4.63–4.59 (m, 4H), 4.56 (br s, 1H), 4.52 (d, $J = 6.5$ Hz, 2H), 4.49–4.43 (m, 3H), 4.37 (d, $J = 12.1$ Hz, 3H), 4.25 (t, $J = 9.2$ Hz, 2H), 4.06 (dd, $J = 10.8$, 2.1 Hz, 1H), 3.99–3.94 (m, 1H), 3.92 (br s, 2H), 3.80 (dd, $J = 9.8$, 2.6 Hz, 2H), 3.77–3.66 (m, 5H), 3.60 (d, $J = 9.3$ Hz, 1H), 3.58–3.54 (m, 1H), 3.52 (s, 1H), 3.52–3.48 (m, 5H), 3.35 (s, 1H), 3.34 (s, 3H), 1.93 (s, 1H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.3$, 139.0, 138.9, 138.6, 138.57, 138.1, 138.0, 128.7–127.5 (m), 127.1, 103.7, 102.7, 98.2, 82.9, 81.4, 81.3, 79.6, 77.7, 77.6, 75.4, 75.1, 75.0, 74.98, 74.94, 74.5, 73.5, 73.2, 73.1, 72.7, 70.4, 70.2, 68.4, 68.0, 67.6, 55.2, 20.9; HR-MS: $m/z = 1303.5609$, calcd. for ($C_{77}H_{84}NaO_{17}$) $[M+Na]^+$: 1303.5601.

Methyl 4-*O*-acetyl-2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→6)-4-*O*-acetyl-2,3-tri-*O*-benzyl-α-D-glucopyranoside (2H′): Acetylation under standard conditions (**B**) afforded **2H′** as a colourless solid; yield: 90%. $R_f = 0.6$ (petroleum ether/EtOAc, 8:2); $[\alpha]_D$: +18.8 (*c* 1.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.48–7.02$ (m, 44H, Ar-H), 4.97 (d, $J = 11.2$ Hz, 1H, benzylic-H), 4.91 (d, $J = 9.1$ Hz, 1H, benzylic-H), 4.87 (br s, 1H, benzylic-H), 4.84–4.75 (m, 3H, 3c-H and benzylic-H), 4.71 (dd, $J = 11.6$, 7.6 Hz, 2H, 4a-H and benzylic-H), 4.66 (d, $J = 11.6$ Hz, 1H benzylic-H), 4.63 (d, $J = 11.1$ Hz, 2H, benzylic-H), 4.60 (d, $J = 4.5$ Hz, 1H, 1a-H), 4.57–4.50 (m, 3H, benzylic-H), 4.45 (d, $J = 7.2$ Hz, 1H, 1b-H), 4.39 (d, $J = 7.2$ Hz, 2H, benzylic-H), 4.36 (d, $J = 7.5$ Hz, 1H, 1c-H), 4.24 (d, $J = 11.9$ Hz, 1H, benzylic-H), 3.92–3.88 (m, 5H, 4c-H, 5c-H, 3a-H, 6c-H and 4b-H), 3.70–3.65 (m, 3H, 6a-H, 6b-H and 3b-H), 3.60–3.47 (m, 3H, 2a-H, 6c′-H and 2b-H), 3.40–3.33 (m, 4H, 6a′-H, 6b′-H, 5b-H, and H-2c), 3.27 (s, 3H, OMe), 1.91 (s, 3H, -$COCH_3$), 1.88 (s, 3H,-$COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.3$, 170.0, 139.0, 138.7, 138.6, 138.5, 138.4, 138.1, 138.06, 138.02, 128.6–127.36 (m), 104.0 (C-1b), 102.6 (C-1c), 97.8 (C-1a), 82.7, 81.8, 79.7, 79.2, 77.7, 77.2, 75.4, 75.0, 74.9, 74.5, 73.4, 73.3, 73.1, 72.7, 70.9, 69.2, 68.9, 67.6, 55.3, 20.9, 20.8; HR-MS: $m/z = 1345.5710$, calcd. for ($C_{79}H_{86}NaO_{18}$) $[M+Na]^+$: 1345.5706.

Methyl 2,3,4,6-tetra-*O*-benzyl-α,β-D-galactopyranosyl-(1→6)-2,3-di-*O*-benzyl-α-D-glucopyranoside (3H): Following the general procedure **A** for glycosylation afforded **3H** as a white solid; yield: 75%. $R_f = 0.4$ (petroleum ether/EtOAc, 7:3); $[\alpha]_D$: +35.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.37–6.83$ (m, 30H), 4.89 (d, $J = 11.5$ Hz, 1H), 4.85 (d, $J = 2.0$ Hz, 1H), 4.82 (br s, 1H), 4.66 (d, $J = 2.0$ Hz, 1H), 4.65–4.60 (m, 4H), 4.54 (br s, 1H), 4.50 (t, $J = 3.6$ Hz, 1H), 4.47 (br s, 1H), 4.37–4.29 (m, 3H), 4.04–3.97 (m, 1H), 3.79 (d, $J = 2.7$ Hz, 1H), 3.78–3.70 (m, 1H), 3.67–3.63 (m, 3H), 3.53–3.47 (m, 2H), 3.47–3.41 (m, 2H), 3.39 (dd, $J = 7.5$, 4.2 Hz, 2H), 3.22 (s, 3H), 2.25 (d, $J = 2.2$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.9$, 139.8, 139.7, 139.5, 139.1, 137.9, 128.5–127.5 (m), 104.3, 98.1, 82.4, 81.5, 79.7, 79.4, 75.4, 75.1, 74.5, 73.6, 73.4, 73.1, 73.0, 70.7, 70.0, 69.1, 68.7, 55.1; HR-MS: $m/z = 919.4036$, calcd. for ($C_{55}H_{60}NaO_{11}$) $[M+Na]^+$: 919.4028.

Methyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl-(1→6)-4-*O*-acetyl-2,3-di-*O*-benzyl-α-D-glucopyranoside (3H′): Acetylation under standard conditions (**B**) afforded **3H′** as a white solid; yield: 90%. $R_f = 0.6$ (petroleum ether/EtOAc, 7:3); $[\alpha]_D$: +7.4 (c 2.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.27$ (m, 30H, Ar-H), 4.94 (d, $J = 10.8$ Hz, 1H, benzylic-H), 4.90 (d, $J = 11.6$ Hz, 1H, benzylic-H), 4.85 (d, $J = 11.6$ Hz, 1H, benzylic-H), 4.80 (br s, 1H, benzylic-H), 4.76 (*app* t, *Japp* = 8.4 Hz, 1H, 4a-H), 4.71 (d, $J = 12.3$ Hz, 2H, benzylic-H), 4.67 (br s, 1H, benzylic-H), 4.63 (d, $J = 9.7$ Hz, 2H, benzylic-H), 4.61–4.57 (m, 1H, benzylic-H), 4.52 (d, $J = 3.5$ Hz, 1H, 1a-H), 4.39 (d, $J = 8.5$ Hz, 1H, benzylic-H), 4.34 (d, $J = 7.7$ Hz, 1H, 1b-H), 3.95–3.91 (m, 2H, 4a-H and 3b-H), 3.86 (dd, $J = 6.2$, 3.4 Hz, 2H, 4b-H and 6b-H), 3.77 (*app* t, *Japp* = 7.7 Hz, 1H, 2b-H), 3.58 (*app* d, *Japp* = 9.0 Hz, 1H, 3a-H), 3.56–3.51 (m, 3H, 2a-H, 5a-H and 6a-H), 3.51–3.48 (m, 2H, 5b-H and 6b′-H), 3.48–3.45 (m, 1H, 6a′-H), 3.25 (s, 3H, OMe), 1.84 (s, 3H, -$COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.0$, 138.8, 138.6, 138.5, 138.0, 137.9, 128.6–127.3 (m), 104.3 (C-1b), 97.8 (C-1a), 82.0, 79.7, 79.6, 79.3, 77.2, 75.4, 75.0, 74.6, 73.59, 73.50, 73.4, 73.1, 71.0, 69.3, 68.9, 68.6, 55.3, 20.8; HR-MS: $m/z = 961.4123$, calcd. for ($C_{57}H_{62}NaO_{12}$) $[M+Na]^+$: 961.4133.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-α,β-D-galactopyranosyl-(1→3)-2,6-di-*O*-benzyl-β-D-galactopyranoside (3I): Following the general procedure **A** for glycosylation afforded **3I** as white solid; yield: 63 mg (64%). $R_f = 0.5$ (petroleum ether/EtOAc, 6:4); $[\alpha]_D$: +28.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.45–7.32$ (m, 26H), 7.24 (m, 8H), 7.07 (d, $J = 9.1$ Hz, 2H), 6.83 (d, $J = 9.1$ Hz, 2H), 5.33 (d, $J = 3.4$ Hz, 1H), 5.04–4.95 (m, 3H), 4.90 (d, $J = 7.8$ Hz, 1H), 4.87 (d, $J = 5.7$ Hz, 1H), 4.85–4.75 (m, 4H), 4.73 (d, $J = 7.9$ Hz, 2H), 4.69–4.61 (m, 2H), 4.58 (d, $J = 7.2$ Hz, 1H), 4.56–4.47 (m, 1H), 4.42 (br s, 2H), 4.11 (d, $J = 2.8$ Hz, 1H), 4.04 (dd, $J = 9.4$, 7.9 Hz, 2H), 3.94 (dd, $J = 6.5$, 2.9 Hz, 2H), 3.92–3.88 (m, 1H), 3.85 (dd, $J = 7.3$, 4.4 Hz, 2H), 3.81 (s, 3H), 3.79–3.74 (m, 1H), 3.65 (br s, 1H), 3.63–3.51 (m, 4H), 2.97 (d, $J = 14.9$ Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 155.2$, 151.6, 138.4, 138.3, 138.2, 137.7, 128.6–127.3 (m), 118.5, 114.5, 103.6, 102.9, 82.2, 81.0, 79.1, 78.7, 78.4, 77.2, 75.2, 75.19, 74.6, 73.7, 73.5, 73.4, 73.2, 69.6, 68.89, 68.1, 55.6; HR-MS: $m/z = 1011.4285$, calcd. for ($C_{61}H_{64}NaO_{12}$) $[M+Na]^+$: 1011.4290.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl-(1→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (3I′): Acetylation under standard conditions (**B**) afforded **3I′** as a white solid; yield: 90%. $R_f = 0.4$ (petroleum ether/EtOAc, 7:3); $[\alpha]_D$: +32.2 (*c* 2.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.30$ (m, 27H, Ar-H), 7.24 (m, 4H, Ar-H), 7.03 (d, $J = 9.1$ Hz, 2H, Ar-H), 6.78 (d, $J = 9.1$ Hz, 2H, Ar-H), 5.44 (*app* d, *Japp* = 2.4 Hz, 1H, 4a-H), 4.96–4.89 (m, 3H, 1b-H and benzylic-H), 4.86 (d, $J = 7.2$ Hz, 1H, 1a-H), 4.78 (*app* t, *Japp* = 9.9 Hz, 2H, benzylic-H), 4.71 (d, $J = 11.3$ Hz, 2H, benzylic-H), 4.67 (d, $J = 10.0$ Hz, 1H, benzylic-

H), 4.60 (d, $J=11.7$ Hz, 1H, benzylic-H), 4.51 (d $J=$ 11.2 Hz, 2H, benzylic-H), 4.39 (br s, 2H, benzylic-H), 4.02 (*app* t, *Japp*=7.2 Hz, 2H, 2a-H and 2b-H), 3.86–3.84 (m, 1H, 5a-H), 3.80 (*app* t, *Japp*=5.9 Hz, 1H, 3a-H), 3.77 (s, 3H, OMe), 3.64 (dd, $J=10.0$, 4.4 Hz, 1H, 3b-H), 3.58–3.49 (m, 3H, 5b-H, 6a-H and 6a′-H), 3.44–3.37 (m, 2H, 6b-H and 6b′-H), 2.10 (s, 3H, -$COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=170.2$, 155.3, 151.5, 138.8, 138.4, 137.9, 137.5, 128.7–127.7 (m), 118.2, 114.5, 102.9 (C-1b), 100.0 (C-1a), 87.3, 86.9, 79.9, 77.2, 75.8, 75.2, 73.6, 72.8, 70.3, 70.2, 70.0, 69.6, 69.1, 68.41, 68.40 68.0, 55.6, 20.9; HR-MS: $m/z=1053.4386$, calcd. for ($C_{63}H_{66}NaO_{13}$): $[M+Na]^+$: 1053.4396.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-α,β-D-galactopyranosyl-(1→3)-6-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranoside (3J): Following the general procedure **A** for glycosylation afforded **3J** as a white solid; yield: 54%. $R_f=0.5$ (petroleum ether/EtOAc, 5:5); $[\alpha]_D$: +45.5 (*c* 1.1, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.28$ (m, 23H), 7.01 (d, $J=9.1$ Hz, 2H), 6.77 (d, $J=9.1$ Hz, 2H), 5.33–5.11 (m, 1H), 4.97 (d, $J=10.8$ Hz, 1H), 4.91 (d, $J=11.5$ Hz, 1H), 4.80 (d, $J=10.7$ Hz, 1H), 4.74 (d, $J=6.3$ Hz, 1H), 4.70 (d, $J=4.1$ Hz, 2H), 4.61 (d, $J=7.6$ Hz, 1H), 4.59 (d, $J=11.6$ Hz, 1H), 4.45 (d, $J=11.9$ Hz, 1H), 4.38 (br s, 2H), 4.07- 4.00 (m, 2H), 3.94 (s, 1H), 3.92–3.85 (m, 2H), 3.82 (dd, $J=6.0$, 4.0 Hz, 2H), 3.74 (s, 3H), 3.64 (dd, $J=9.4$, 3.2 Hz, 1H), 3.59–3.47 (m, 6H), 2.70 (s, 1H), 2.65 (d, $J=2.3$ Hz, 1H), 0.85 (s, 1H), 0.84 (s, 9H), 0.04, 0.03 (2 s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta=155.2$, 151.4, 138.4, 138.3, 137.7, 128.7–127.4 (m), 118.6, 114.4, 104.4, 102.2, 91.9, 83.4, 82.3, 78.8, 77.3, 75.3, 75.2, 74.7, 73.6,73.5, 73.2, 73.0, 70.4, 68.6, 67.8, 62.1, 55.6, 25.9, 18.2, −5.3, −5.4; HR-MS: $m/z=$ 945.4218, calcd. for ($C_{53}H_{66}NaO_{12}Si$) $[M+Na]^+$: 945.4216.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl-(1→3)-6–2,4-di-*O*-acetyl-*O*-*tert*-butyldimethylsilyl-β-D-galactopyranoside (3J′): Acetylation under standard conditions (**B**) afforded **3J′** as a white solid; yield: 87%. $R_f=0.4$ (petroleum ether/EtOAc, 7:3); $[\alpha]_D$: +18.5 (*c* 1.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.45$–7.21 (m, 20H, Ar-H), 6.96 (d, $J=9.1$ Hz, 2H, Ar-H), 6.77 (d, $J=9.1$ Hz, 2H, Ar-H), 5.53 (*app* t, *Japp*=8.4 Hz, 1H, 2a-H), 5.45 (*app* d, *Japp*=3.6 Hz, 1H, 4a-H), 4.91 (d, $J=11.7$ Hz, 1H, benzylic-H), 4.79 (dd, $J=11.6$ Hz, 2H, benzylic-H), 4.66 (d, $J=$ 10.5 Hz, 3H, benzylic-H), 4.55 (d, $J=11.7$ Hz, 1H, benzylic-H), 4.50–4.42 (m, 3H, 1a-H, 1b-H and benzylic-H), 3.94 (dd, $J=10.0$, 3.6 Hz, 1H, 3b-H), 3.86 (*app* d, *Japp*=2.4 Hz, 1H, 4b-H), 3.75 (s, 3H, OMe), 3.73–3.66 (m, 3H, 3a-H, 5a-H and 6a-H), 3.63–3.58 (m, 3H, 5b-H, 6b-H and 6b′-H), 3.51 (*app* t, *Japp*=6.4 Hz, 1H, 2b-H), 3.45 (dd, $J=9.7$, 2.9 Hz, 1H, 6a′-H), 2.07 (s, 3H, -$COCH_3$), 1.84 (s, 3H, -$COCH_3$), 0.88 (s, 9H, *t*-Bu), 0.02, 0.05 (2s, 6H, $SiCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=171.0$, 169.5, 155.3, 151.6, 138.87, 138.81, 138.4, 138.0, 128.4–127.7 (m), 118.1, 114.4, 104.3 (C-1a), 100.9 (C-1b), 82.0, 79.2, 77.3, 75.6, 74.9, 74.4, 73.5, 72.8, 70.9, 70.0, 68.7, 62.3, 55.6, 25.8, 20.86, 20.84, 18.2, −5.46, −5.56; HR-MS: $m/z=1029.4432$, calcd. for ($C_{57}H_{70}NaO_{14}Si$) $[M+Na]^+$: 1029.4427.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-α,β-D-galactopyranosyl-(1→3)-6-*O*-trityl-β-D-galactopyranoside (3K): Following the general procedure **A** for glycosylation afforded **3K** as a white solid; yield: 54 mg (53%). $R_f=0.5$ (petroleum ether/EtOAc, 5:5); $[\alpha]_D$: +46.9 (*c* 2.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.41$–7.34 (m, 6H), 7.33–7.19 (m, 26H), 7.17–7.09 (m, 6H), 7.04 (d, $J=9.1$ Hz, 2H), 6.71 (d, $J=9.1$ Hz, 2H), 5.21 (s, 1H), 4.95–4.82 (m, 3H), 4.79–4.72 (m, 2H), 4.69 (dd, $J=5.7$, 2.7 Hz, 1H), 4.65 (d, $J=4.7$ Hz, 2H), 4.62 (s, 1H), 4.56 (d, $J=7.6$, 1H), 4.50 (dd, $J=11.6$, 2.5 Hz, 2H), 4.40 (d, $J=11.9$ Hz, 1H), 4.34 (d, $J=11.9$ Hz, 1H), 4.25 (br s, 2H), 4.09 (t, $J=6.5$ Hz, 1H), 4.0–3.98 (m, 1H), 3.90 (br s, 1H), 3.84–3.80 (m, 1H), 3.78 (d, $J=2.9$ Hz, 1H), 3.67 (s, 4H), 3.58–3.50 (m, 3H), 3.46 (ddd, $J=12.4$, 7.5, 2.8 Hz, 4H), 3.38 (dd, $J=11.0$, 4.0 Hz, 2H), 3.19 (dd, $J=8.2$, 2.7 Hz, 1H), 2.98 (d, $J=6.3$ Hz, 1H), 2.80 (s, 1H), 2.59 (d, $J=11.6$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=155.2$, 151.3, 143.9, 138.3, 138.2, 137.6, 128.7–127.4 (m), 126.9, 118.6, 114.4, 104.2, 102.0, 100.0, 86.7, 83.2, 82.3, 78.8, 77.2, 75.3, 74.6, 74.0, 73.7, 73.4, 73.3, 73.0, 68.5, 55.6; HR-MS: $m/z=1073.4429$, calcd. for ($C_{66}H_{66}NaO_{12}$) $[M+Na]^+$: 1073.4446.

Methyl 2-azido-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-D-2-deoxy-α,β-galactopyranosyl-(1→6)-2,3-di-*O*-benzyl-α-D-glucopyranoside (4H): Following the general procedure **A** for glycosylation afforded **4H** as a white solid; yield: 69 mg (53%). $R_f=0.4$ (petroleum ether/EtOAc, 8:2); $[\alpha]_D$: +12.5 (*c* 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.75$–7.55 (m, 8H), 7.34–7.23 (m, 30H), 7.21–7.16 (m, 10H), 7.14–7.08 (m, 4H), 5.19 (d, $J=3.5$ Hz, 1H), 4.93 (t, $J=10.9$ Hz, 2H), 4.85 (br s, 2H), 4.84–4.79 (m, 3H), 4.78–4.75 (m, 1H), 4.74 (br s, 1H), 4.72 (br s, 1H), 4.69 (s, 1H), 4.66 (app t, *Japp*= 5.7 Hz, 4H), 4.62 (d, $J=2.4$ Hz, 1H), 4.59 (t, $J=3.9$ Hz, 1H), 4.57 (d, $J=2.2$ Hz, 2H), 4.38 (d, $J=7.8$ Hz, 1H), 4.13 (d, $J=8.4$ Hz, 1H), 3.94–3.88 (m, 2H), 3.87–3.81 (m, 4H), 3.74 (d, $J=9.0$ Hz, 2H), 3.71–3.64 (m, 4H), 3.59 (d, $J=$ 9.0 Hz, 1H), 3.56 (d, $J=3.4$ Hz, 1H), 3.54 (d, $J=1.9$ Hz, 1H), 3.52 (s, 1H), 3.46 (br s, 1H), 3.44 (d, $J=3.4$ Hz, 1H), 3.43–3.41 (m, 1H), 3.34–3.31 (m, 1H), 3.28 (s, 3H), 3.28 (s, 1H), 3.25 (d, $J=3.0$ Hz, 1H), 0.99 (s, 3H), 0.96 (s, 10H): ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=135.9$, 138.63, 138.61, 138.0, 135.9, 135.8, 135.63, 135.60, 128.3–126.78 (m), 103.9, 99.2, 98.2, 84.8, 82.5, 81.8, 81.5, 80.6, 79.7, 77.2, 76.2, 75.87, 75.81, 75.3, 75.1, 74.8, 73.3, 73.1, 71.6, 70.2, 70.0, 68.6, 55.3 26.9, 26.8, 19.2 , 19.1; HR-MS: $m/z=1002.4336$, calcd. for ($C_{57}H_{65}N_3NaO_{10}Si$) $[M+Na]^+$: 1002.4331.

Methyl 2-azido-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-galactopyranosyl-(1→6)-4-*O*-acetyl-2,3-di-*O*-benzyl-α-D-glucopyranoside (4H′): Acetylation under standard conditions (**B**) afforded **4H′** as a colourless solid; yield: 90%. $R_f=0.6$ (petroleum ether/EtOAc, 8:2); $[\alpha]_D$: +8.2 (*c* 1.6, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.68$–7.64 (m, 4H, Ar-H), 7.41–7.25 (m, 28H, Ar-H), 7.16–7.10 (m, 2H, Ar-H), 5.04 (d, $J=10.9$ Hz, 1H, benzylic-H), 4.93–4.82 (m, 5H, 4a-H and benzylic-H), 4.73 (dd, $J=11.3$, 5.6 Hz, 2H, benzylic-H), 4.66–4.60 (m, 3H, benzylic-H), 4.56 (d, $J=$ 3.6 Hz, 1H, 1a-H), 4.43 (d, $J=7.7$ Hz, 1H, 1b-H), 3.94 (dd, $J=9.3$, 3.5 Hz, 3H, 5b-H, 6a-H and 6a′-H), 3.88 (br s, 2H, 3a-H and 4b-H), 3.68–3.62 (m, 2H, 2a-H and 2b-H), 3.53 (dd, $J=9.6$, 3.4 Hz, 2H, 3b-H and 5a-H), 3.44 (*app* t, *Japp*= 8.0 Hz, 1H, 6b-H), 3.31 (br s, 1H, 6b′-H), 3.30 (s, 3H, OMe), 1.85 (s, 1H, -$COCH_3$), 1.82 (s, 3H, -$COCH_3$), 1.02 (s, 9H, *t*-Bu), 1.00 (s, 2H, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=169.7$, 138.7, 138.6, 138.0, 135.8, 135.6, 133.2, 129.6, 128.6–127.2 (m), 103.9 (C-1b), 98.0 (C-1a), 84.6, 82.6, 79.6, 79.3, 77.5, 75.8, 75.7, 75.4, 75.1, 74.7, 73.5, 70.7, 69.0, 62.8, 55.4, 29.7, 26.8, 20.8, 19.3; HR-MS: $m/z=1044.4422$, calcd. for ($C_{59}H_{67}N_3NaO_{11}Si$) $[M+Na]^+$:1044.4437.

Isopropyl 3,4-di-*O*-benzoyl-2-*O*-benzyl-α,β-L-fucopyranoside (5A): Following the general procedure **A** for glycosylation afforded **5A** as a colourless solid; yield: 86%. R_f=0.5 (petroleum ether/EtOAc, 8:2); $[\alpha]_D$: −64.9 (c 1.1, $CHCl_3$). ^{1}H NMR (**β-Isomer**, 400 MHz, $CDCl_3$): δ=8.13 (dd, J=8.0, 1.2 Hz, 2H, Ar-H), 7.89 (dd, J=8.0, 1.0 Hz, 2H, Ar-H), 7.71 (dd, J=10.6, 4.3 Hz, 1H, Ar-H), 7.60–7.55 (m, 4H, Ar-H), 7.42–7.37 (m, 4H, Ar-H), 7.31 (dd, J=8.0, 1.8 Hz, 3.0H, Ar-H), 7.26–7.25 (m, 3H, Ar-H), 5.68 (br d, J=3.6 Hz, 1H, 4-H), 5.50 (dd, J=10.1, 3.6 Hz, 1H, 3-H), 5.00 (d, J=11.5 Hz, 1H, benzylic-H), 4.82 (d, J=11.6 Hz, 1H, benzylic-H), 4.75 (d, J=8.0 Hz, 1H, 1-H), 4.28–4.19 (m, 1H), 4.11–4.05 (m, 1H, 5-H), 3.97 (dd, J=10.1, 7.8 Hz, 1H, 2-H), 1.49 (d, J= 6.2 Hz, 4H, -CH_3), 1.43–139 (m, 7H); ^{1}H NMR (**α-Isomer**, 400 MHz, $CDCl_3$) δ 8.12–8.08 (m, 0.4H, Ar-H), 7.98–7.92 (m, 0.4H, Ar-H), 5.84 (dd, J=10.4, 3.3 Hz, 1H, 3-H), 5.79 (br d, J=2.4 Hz, 1H, 4-H), 5.73 (*app* t, *Japp*=2.4, Hz, 1H, 2-H), 5.20 (d, J=3.6 Hz, 1H, 1-H), 3.80–3.78 (m, 1H, 5-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=166.1, 165.5, 138.1, 133.2, 132.9, 129.9, 129.8–129.5 (m), 128.5–128.0 (m), 127.5, 102.3 (C-1β), 95.6(C-1α), 74.5, 73.2, 72.7, 71.7, 69.2, 64.7, 31.9, 29.7, 29.6, 29.3, 23.5, 22.7, 22.2, 16.4, 14.1; HR-MS: m/z= 527.2051, calcd. for ($C_{30}H_{32}NaO_7$) $[M+Na]^+$: 527.2040.

(−)-Menthyl 3,4-Di-*O*-benzoyl-2-*O*-benzyl-α,β-L-fucopyranoside [5(−)D]: Following the general procedure **A** for glycosylation afforded **5(−)D** as a colourless oil; yield: 72%. R_f=0.5 (petroleum ether/EtOAc, 9:1); $[\alpha]_D$: −80.9 (*c* 1.1, $CHCl_3$). ^{1}H NMR (**α-isomer**, 400 MHz, $CDCl_3$): δ=8.04 (d, J=7.2 Hz, 1H, Ar-H), 7.82 (d, J=7.2 Hz, 2H, Ar-H), 7.59 (t, J=7.4 Hz, 2H, Ar-H), 7.55–7.40 (m, 5H, Ar-H), 7.41–7.26 (m, 7H, Ar-H), 7.23–7.01 (m, 4H), 5.69 (br s, 1H, 4-H), 5.19 (d, J=3.8 Hz, 1H, 1-H), 4.69–4.61 (m, 3H, 3-H and benzylic-H), 4.40 (*app* q, *Japp*=6.6 Hz, 1H, 5-H), 4.14 (dd, J=11.0, 3.8 Hz, 1H, 2-H), 3.55–3.46 (m, 2H), 2.46–2.31 (m, 2H), 2.26 (d, J=12.7 Hz, 1H), 2.07 (d, J=12.3 Hz, 1H), 1.70–1.64 (m, 4H), 1.49 –1.36 (m, 4H, -CH_3), 1.32–1.24 (m, 4H), 1.18 (d, J=6.5 Hz, 4H), 1.07–0.79 (m, 21H), 0.72 (d, J=6.9 Hz, 2H); ^{1}H NMR (**β-isomer**, 400 MHz, $CDCl_3$): δ= 7.97 (d, J=7.2 Hz, 2H, Ar-H), 7.74 (d, J=7.2 Hz, 1H, Ar-H), 5.66 (d, J=3.2 Hz, 1H, Ar-H), 5.56 (*app* d, *Japp*= 3.4 Hz, 1H, 4-H), 5.39 (dd, J=8.2, 4.0 Hz, 1H, 3-H), 4.84 (d, J=8.2 Hz, 1H, 1-H), 3.95 (*app* q, *Japp*=6.5 Hz, 1H, 5-H), 3.87 (dd, J=8.2, 7.8 Hz, 1H, 2-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=165.9, 165.6, 138.0, 137.8, 133.2, 132.97, 132.90, 130.0, 129.9, 129.83, 129.81, 129.7, 129.69, 129.67, 128.4–127.8 (m), 127.4, 104.5 (C-1β), 93.9 (C-1α), 81.9, 77.2, 76.9, 76.2, 74.9, 73.6, 73.2, 72.9, 72.5, 71.8, 70.8, 69.1, 65.1, 48.8, 47.5, 43.4, 39.9, 34.4, 34.3, 31.8, 31.5, 25.5, 24.7, 22.8, 22.7,22.4, 22.3, 21.3, 21.1, 16.5, 16.2, 15.9, 15.1; HR-MS: m/z=623.2985, calcd. for ($C_{37}H_{44}NaO_7$) $[M+Na]^+$: 623.2979.

(+)-Menthyl 3,4-di-*O*-benzoyl-2-*O*-benzyl-α,β-L-fucopyranoside [5(+)D]: Following the general procedure **A** for glycosylation afforded **5(+)D** as a colourless oil; yield: 72%. R_f=0.5 (petroleum ether/EtOAc, 9:1); $[\alpha]_D$: −56.9 (*c* 1.1, $CHCl_3$). ^{1}H NMR (**β-isomer**, 400 MHz, $CDCl_3$): δ=8.03 (t, J=7.2 Hz, 2H, Ar-H), 7.88–7.77 (m, 3H, Ar-H), 7.55–7.44 (m, 5H, Ar-H), 7.40–7.14 (m, 12H, Ar-H), 5.71 (dd, J=10.4, 3.3 Hz 1H, 3-H), 5.60 (br d, J=3.3 Hz, 1H, 4-H), 4.89 (d, J=11.2 Hz, 1H, benzylic-H), 4.73–4.71 (m, 2H, 1-H and benzylic-H), 4.16- 4.10 (m, 1H, 5-H), 3.44 (m, 2H, 2-H), 2.48–2.43 (m, 1H), 2.27–2.12 (m, 3H), 1.99 (d, J=12.0 Hz, 2H), 1.83–1.64 (m, 7H), 0.99–0.95 (m, 14H), 0.85 (dd, J= 9.6, 5.5 Hz, 14H), 0.77 (d, J=6.9 Hz, 2H); ^{1}H NMR (**α-isomer**,400 MHz, $CDCl_3$): δ=7.99 (d, J=7.5 Hz, 1H, Ar-H), 7.63–7.61 (m, 2H, Ar-H), 5.51 (*app* d, *Japp*=3.6 Hz, 1H, 4-H), 5.43 (*app* d, *Japp*=8.2 Hz, 1H, 3-H), 5.17 (d, J=3.6 Hz, 1H, 1-H), 4.52–4.48 (m, 1H, benzylic-H), 4.09–4.00 (m, benzylic-H), 3.95–3.90 (m, 1H, 5-H), 3.80 (dd, J=8.2, 3.2 Hz, 1H, 2-H), 3.57–3.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=165.8, 165.6, 138.1, 137.7, 133.2, 132.97, 132.90, 130.0, 129.9, 129.83, 129.81, 129.7, 129.69, 129.67, 128.4–127.6 (m), 127.4, 104.5 (C-1β), 93.9 (C-1α), 81.9, 77.2, 76.9, 76.2, 74.9, 73.5, 73.2, 72.9, 72.6, 71.7, 70.8, 69.1, 65.1, 48.8, 47.5, 43.4, 39.9, 34.4, 34.3, 31.8, 31.5, 25.5, 24.7, 22.8, 22.7,22.4, 22.3, 21.3, 21.1, 16.5, 16.2, 15.8, 15.1; HR-MS: m/z=623.2974, calcd. for ($C_{37}H_{44}NaO_7$) $[M+Na]^+$: 623.2979.

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