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Is an Acyl Group at O-3 in Glucosyl Donors Able to Control α-Stereoselectivity of Glycosylation? The Role of Conformational Mobility and the Protecting Group at O-6

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Abstract

The stereodirecting effect of a 3-*O*-acetyl protecting group, which is potentially capable of the remote anchimeric participation, and other protecting groups in 2-*O*-benzyl glucosyl donors with flexible and rigid conformations has been investigated. To this aim, an array of *N*-phenyltrifluoroacetimidoyl and sulfoxide donors bearing either 3-*O*-acetyl or 3-*O*-benzyl groups in combination with 4,6-di-*O*-benzyl, 6-*O*-acyl-4-*O*-benzyl or 4,6-*O*-benzylidene protecting groups was prepared. The conformationally flexible 3-*O*-acetylated glucosyl donor protected at other positions with *O*-benzyl groups demonstrated very low or no α-stereoselectivity upon glycosylation of primary or secondary acceptors. On the contrary, 3,6-di-*O*-acylated glucosyl donors proved to be highly α-stereoselective as well as the donor having a single potentially participating acetyl group at O-6. The 3,6-di-*O*-acylated donor was shown to be the best α-glucosylating block for the primary acceptor, whereas the best α-selectivity of glycosylation of the secondary acceptor was achieved with the 6-*O*-acylated donor. Glycosylation of the

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secondary acceptor with the conformationally constrained 3-*O*-acetyl-4,6-*O*-benzylidene-protected donor displayed under standard conditions (–35 °C) even lower α-selectivity as compared to the 3-*O*-benzyl analogue. However, increasing the reaction temperature essentially raised the α-stereoselectivities of glycosylation with both 3-*O*-acetyl and 3-*O*-benzyl donors and made them almost equal. The stereodirecting effects of protecting groups observed for *N*-phenyltrifluoroacetimidoyl donors were also generally proven for sulfoxide donors.

Keywords: Glycosylation; Remote anchimeric participation; α-Stereodirecting effect; 3-*O*-acetyl group; Glucosyl *N*-phenyltrifluoroacetimidate; Glucosyl sulfoxide

1. Introduction

Each of the protecting groups in pyranosyl donors has a considerable influence on stereoselectivity of glycosylations.[1-10] Investigation of the stereocontrolling properties of the protecting groups provides deeper insight into the mechanism of glycosylation[11] and can give rise to new technics for the synthesis of challenging[12] 1,2-*cis*-glycosides. One of the most intriguing types of stereocontrolling groups is non-vicinal or remote acyl groups, that is, the acyl groups at O-3, O-4 or O-6 of glycosyl donors with a non-participating alkyl group at O-2 or azide at C-2. The impact of such *O*-acyl groups may be explained in terms of the remote anchimeric participation.[13] Usually the presence of a non-vicinal potentially participating acyl group in the donor favors the formation of a glycosylation product with the *trans*-stereoselectivity relatively to the remote acyl group.[13] The notion to govern the selectivity of glycosylations by non-vicinal acyl protecting groups was successfully applied in our group for the synthesis of linear and branched fucoidans,[14] and oligosaccharides related to glycoforms I and II of LPS of *Pseudomonas aeruginosa*.[15-17] Glucosyl *N*-phenyltrifluoroacetimidates possessing α-stereodirecting acyl groups at O-3 and O-6 were employed in the latter syntheses based on the assumption that the combined effects of both acyl groups would provide the highest

α-selectivity.[17] But however attractive the remote anchimeric participation might be for the rationalization of the stereodirecting effect of non-vicinal acyl groups, it is still not proven and provokes a plenty of questions.[18,19] One of them is why the degree of the stereodirecting effect of a certain acyl group is different for different pyranoses. For example, an acyl group at O-3 in glucose affected very slightly the stereoselectivity of glycosylation,[14,15] while the same 3-*O*-acyl group in fucose provides almost complete α-selectivity.[20] Moreover, 3-*O*-acyl groups in mannose demonstrated a powerful α-directing effect, which switches the inherent β-selectivity of 4,6-*O*-benzylidene-protected mannosyl donors[21] to the complete α-selectivity on replacement of a single benzyl protecting group at O-3 by an acetyl one.[22,23] In principle, the 4,6-*O*-benzylidene group should disfavor in this case the plausible anchimeric assistance but in reality it does not impede the α-selectivity of mannosylation. This fact complicates even more an adequate explanation of the α-stereocontrolling effect of 3-*O*-acyl groups. In this communication we attempted to estimate the limits of the α-directing effect of the 3-*O*-acetyl group in conformationally rigid and flexible glucose donors bearing various protecting groups at O-4 and O-6 and define how stereocontrolling properties of the 3-*O*-acetyl substituent correlate with the presence of the 4,6-*O*-benzylidene group. Another goal of this investigation was a search for optimal glucosyl donors and conditions for α-(1→3)- and α-(1→6)-glucosylation for further application in the synthesis of oligosaccharides related to fungal α-glucans.

2. Results and discussion

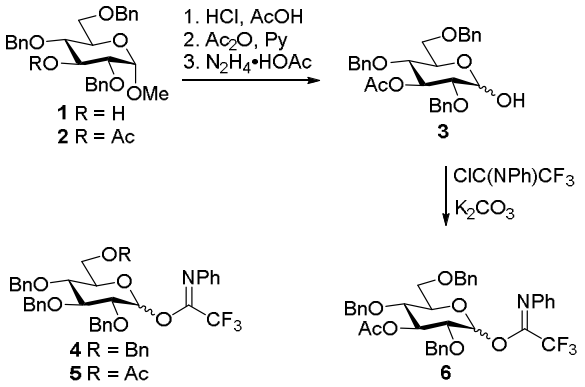
2.1. Preparation of glycosyl donors and acceptors

Primary and secondary alcohols, when coupled with the same glycosyl donor, often produce anomeric mixtures with different α:β ratios. On the other hand, as already mentioned above, we intended to find an optimal protecting group pattern in donor and acceptor molecules, which would facilitate a blockwise synthesis of α-(1→3)- and α-(1→6)-glucans. This protecting group pattern in glycosyl acceptors had to provide easy replacement of the anomeric protection

by a leaving group and a possibility to glycosylate the hydroxy group at either C-3 or C-6. Therefore, primary alcohol **13** and secondary alcohols **16** and **30** derived from ethylthio or *p*-methoxyphenyl glucosides were used as the model glycosyl acceptors.

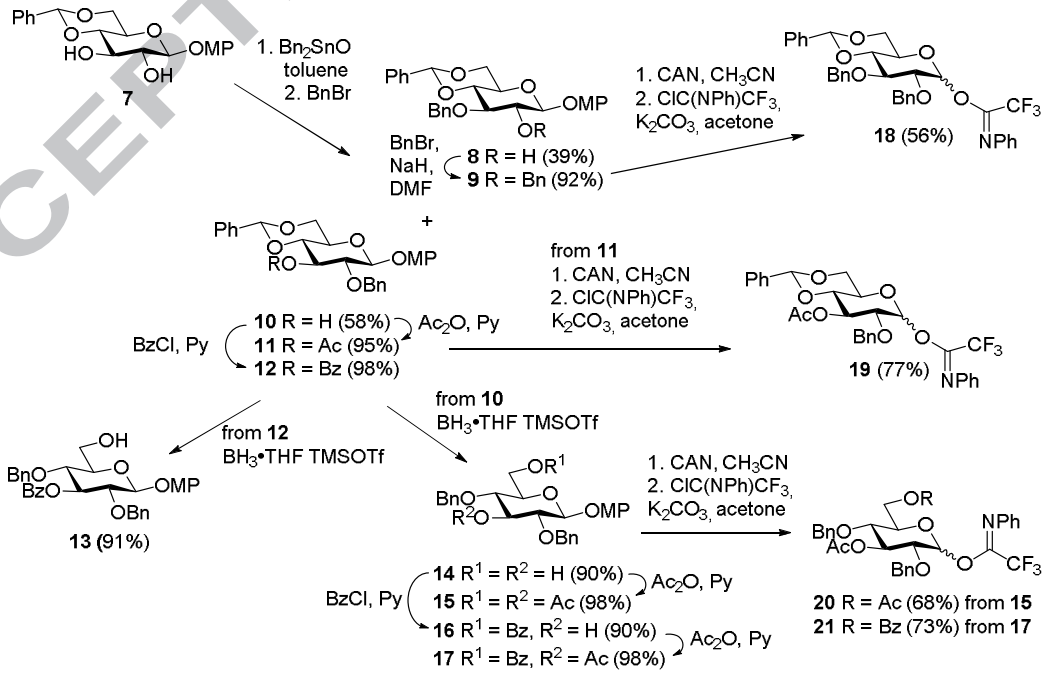
Application of partially acylated donors in a combination with the *N*-phenyltrifluoracetimidoyl leaving group always resulted in our hand in good to excellent yields of 1,2-*cis*-glycosides.[15-17] On the other hand, glycosyl sulfoxides are widely used in the recent oligosaccharide synthesis.[24-32] For these reasons, the present investigation of stereocontrolling properties of protecting groups was performed using both types of the leaving groups. Application of two different glycosylation protocols would allow us to differentiate the effect of the way of activation and the stereocontrol of protecting groups.

Preparation of the principal trifluoracetimidoyl donor **6** with the sole acetyl group at O-3 took advantage of the availability of methyl 2,4,6-tri-O-benzyl-α-glucoside **1** (Scheme 1).[33] Its acetylated derivative **2**[33,34] was subjected to acidic hydrolysis in the presence of HCl. Since this procedure led to partial 3-*O*-deacetylation, the reaction products was acetylated again to provide an anomeric mixture of 1,3-di-*O*-acetylated glucose.[35] Regioselective removal of the anomeric acetyl group with hydrazine acetate in DMF afforded hemiacetal **3**[36] in overall yield 21% for four steps. For the transformation of hemiacetals into *N*-phenyltrifluoroacetimidoyl donors and, in particular, for the preparation of the donor **6**, 1-OH derivatives were treated with *N*-phenyltrifluoroacetimidoyl chloride (PTAIC) in acetone in the presence of solid K_2CO_3.[37] Perbenzylated donor **4** and 6-acetate **5** were prepared as described.[16,38]



Scheme 1. Preparation of donor **6** and the structure of donors **4** and **5**.

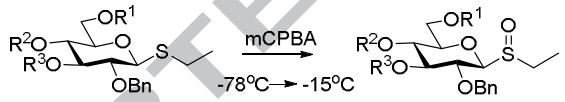
The synthesis of 4,6-*O*-benzylidene-protected donors **18**, **19**, 3,6-di-*O*-acylated donors **20**, **21**, and acceptors **13** and **16** was performed starting from the known diol **7**[39] as outlined in Scheme 2. The key step was stannylene-mediated monobenzylation[40] of **7**, which proceeded with moderate regioselectivity and provided 2-*O*-benzyl and 3-*O*-benzyl ethers **10** and **8** in 58 and 39% yield respectively. Transformation of **8** and **10** into glucosyl donors included introduction of necessary protecting groups into proper positions, removal of the anomeric *p*-methoxyphenyl group with CAN[41] and acylation with PTAIC. Thus, benzylation of **8** gave 2,3-di-*O*-benzyl ether **9**, which was converted into donor **18**.



Scheme 2. Synthesis of 4,6-*O*-benzylidene-protected glucosyl donors **18**, **19**, 3,6-di-*O*-acylated donors **20**,**21**, and acceptors **13** and **16** from diol **7**.

Similarly, compound **10** was acetylated with the formation of **11**, from which 3-*O*-acetylated donor **19** was obtained. Regioselective reductive opening of the acetal ring in **10** with BH_3·THF[42] provided 3,6-diol **14**; the latter was transformed into diacetate **15** and then – into 3,6-di-*O*-acetylated donor **20**. Selective benzoylation of the primary OH group in **14** provided monobenzoate **16**, which was used as a model secondary glycosyl acceptor and also as a starting compound for the preparation, via 3-acetate **17**, of donor **21**. Model primary acceptor **13** was synthesized from **10** by benzoylation followed by reductive opening of the 4,6-*O*-benzylidene group in **12**.

Variously protected sulfoxide donors **26**-**29** were prepared from the known ethyl thioglucoside precursors **22**,[43] **23**,[44] **24**[45] and **25**[46] by oxidation with mCPBA as shown on Scheme 3.



22 $R^1 = R^2 = R^3$ = Bn
23 R^1,R^2 = PhCH, R^3 = Bn
24 R^1,R^2 = PhCH, R^3 = Ac
25 $R^1 = R^3$ = Ac, R^2 = Bn

26 $R^1 = R^2 = R^3$ = Bn (88%)
27 R^1,R^2 = PhCH, R^3 = Bn (98%)
28 R^1,R^2 = PhCH, R^3 = Ac (86%)
29 $R^1 = R^3$ = Ac, R^2 = Bn (88%)

Scheme 3. Synthesis of sulfoxide donors **26**-**29**.

2.2. Glucosylation reactions

The ratio of anomers in disaccharide mixtures produced in glycosylation reactions given in Table 1 was measured by means of analytical HPLC. In all cases, each of the anomers was isolated and their structure was unambiguously proved by NMR techniques.

The first series of glucosylation reactions was made with *N*-phenyltrifluoracetimidoyl donors. Our experience[15-17] of application of such donors showed that they are preferentially

activated with methyl triflate. Probably, its way of action is similar to N-methylation of a C=N bond.[47]

Coupling of perbenzylated glucosyl donor **4** with secondary acceptor **30** led to disaccharide mixture **31** with an α:β ratio of 1.5:1, while glycosylation of primary acceptor **13** produced an α,β-mixture of disaccharides **35** in a ratio of 1:3 (Table 1, entries 1 and 5). Glycosylation of **30** with 3-*O*-acetylated donor **6** provided almost the same stereoselectivity of the formation of **32** as perbenzylated donor **4** (cf. entries 2 and 1). Similarly, only a negligible decrease of the proportion of the β-product was observed when primary acceptor **13** was glycosylated with 3-*O*-acetylated donor **6** instead of **4** (cf. entries 6 and 5). Thus, the single 3-*O*-acetyl group in *N*-phenyltrifluoroacetimidate **6** does not affect the stereoselectivity of glycosylation relatively to stereochemistry inherent to perbenzylated glucosyl donor **4**.

These results contradict published examples of α-directing properties of acyl groups at O-3 proved by comparative glycosylation with fully alkylated and 3-*O*-acylated donors of different configurations[3,20,22,23,48-50] including those closely related to glucose, such as 6-deoxyglucose,[48] xylose[49] and glucuronic acid.[50] Apparently, the negligible stereochemical effect of the 3-*O*-acetyl group in **6** as compared to the noticeable α-directing influence of that group in works cited above evidenced that the degree of the stereochemical effect of the 3-*O*-acyl group depends not only on the structure of the glycosyl donor but also on the structure of the glycosyl acceptor and reaction conditions.

The results of glycosylation with donor **6** clearly indicated that it is insufficiently α-stereoselective for the practical use in the synthesis of α-glucooligosaccharides. Therefore, then we studied 3,6-di-*O*-acetylated donor **20** assuming that the combined effect of two participating acetyl groups would essentially increase the α-stereoselectivity of glycosylation. 6-*O*-Acetylated donor **5** was also studied to estimate the contribution of the substituents at O-3 and O-6 to increasing the α-stereoselectivity.

Indeed, glycosylation of secondary acceptor **30** with donor **20** resulted in the considerable increase of the proportion of α-**33** as compared to glycosylation with 3-monoacetate **6** (cf. entries 2 and 3). Unexpectedly, 6-monoacetate **5** provided even higher α-stereoselectivity than 3,6-diacetate **20** (entries 3 and 4). From these results one might conclude that the 3-*O*-acetyl group does not contribute to the α-stereoselectivity and, moreover, can even reduce it. However, an opposite picture was observed on glycosylation of primary acceptor **13**: both 3,6-diacetate **20** and 6-monoacetate **5** provided considerably higher proportions of corresponding α-anomers than 3-acetate **6** (cf. entries 5 and 7, 8), but glycosylation with 3,6-diacetate **20** was more α-stereoselective than that with 6-monoacetate **5**. This indicated that the contribution of the acyl substituents at O-3 and O-6 to the overall α-stereoselectivity can vary depending on the structure of the glycosyl acceptor. As for the synthetic utility of the donors, both **5** and **20** demonstrated sufficiently high α-stereoselectivity of glycosylation and can used in the synthesis of α-(1→3)- and α-(1→6)-glucooligosaccharides. 3,6-Di-*O*-acylated donor **21**, which showed high efficiency and α-stereoselectivity on glycosylation of monocyclic secondary acceptor **16** (entry 9), can also be included in the group of glycosyl donors with a high synthetic potential.

Then we studied α-stereodirecting effect of the acetyl group at O-3 in conformationally rigid 4,6-*O*-benzylidene-protected donors. It is generally accepted[51-55] that the 4,6-*O*-benzylidene group in glucose donors facilitates the formation of α-linked glucosylation products. This feature was confirmed by practical application of such donors in several syntheses of oligosaccharides containing α-glucosyl residues.[56-59] However, the stereoselectivity of these glycosylation reactions can depend on the leaving group type[52] and the promoter system.[52,53] To the best of our knowledge, only one example of direct comparison of stereochemical results of glycosylation with conformationally free tetrabenzyl- and rigid 4,6-*O*-benzylidene-protected donors has been described so far.[52] Therefore, the stereochemistry of MeOTf-promoted glycosylation with 4,6-*O*-benzylidene-protected imidate **18** in comparison with that of tetrabenzyl counterpart **4** was initially studied. It turned out that the reaction of **18** with the secondary acceptor **30** was only

slightly more α-selective (α:β = 2.2:1, entry 10) than glycosylation with **4** (α:β = 1.5:1, entry 1), whereas the reaction with primary acceptor **13** changed its stereochemistry to the opposite one upon replacement of **4** (α:β = 1:3.3, entry 5) by **18** (α:β = 5.2:1, entry 15). Thus, again, the stereochemical impact of the certain structural element in the glycosyl donor is strongly dependent on the glycosyl acceptor.

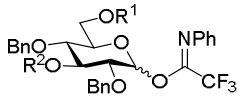
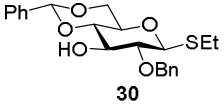
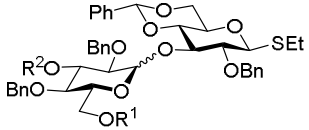
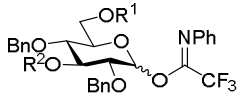
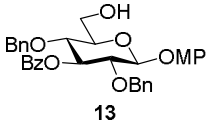
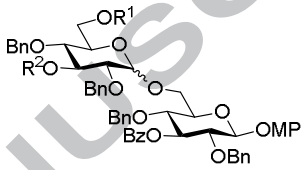
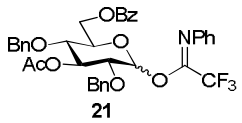
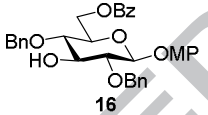
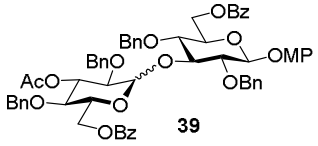
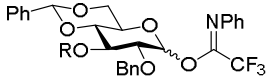
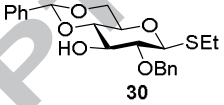
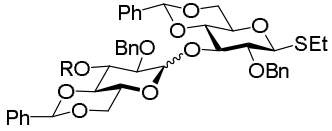
3-*O*-Acetyl group in the 4,6-*O*-benzylidene-protected donor **19** did not improved the α-stereoselectivity of glycosylation of acceptor **30** relatively to 2,3-dibenzyl **18** but, on the contrary, worsened it (α:β = 2.2:1 → 1:1.4, entries 10, 11). Probably, it indicates that the rigid 4,6-*O*-benzylidene-protected donor cannot change its conformation in such a way as to enable carbonyl oxygen of the 3-*O*-acetyl group to reach positively charged anomeric carbon. The change of stereochemistry in favor of β-**41** may be explained by the electron-withdrawing influence of the acetyl group similar to that of fluorine in the 2-*O*-benzyl-3-fluoro-3-deoxyglucosyl donor,[60] which provided a noticeable increase of the β-anomer proportion (α:β = 1:1.8) as compared to the 2,3-di-*O*-benzyl- donor (α:β = 3.2:1).

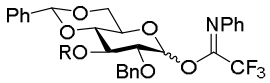
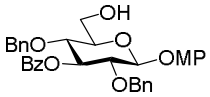
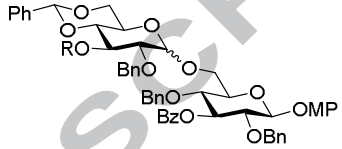
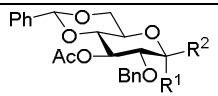
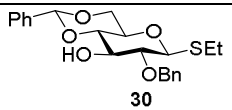
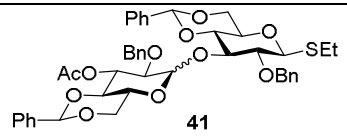
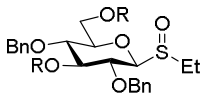
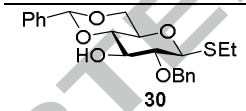
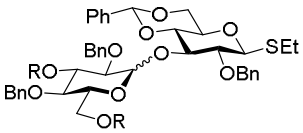
The MeOTf-promoted coupling of the donors **18** and **19** with the acceptor **30** was used to study the effect of the reaction temperature on the stereoselectivity. When the reaction was carried out at room temperature, the α:β ratio (3.8:1, entry 13) was somewhat higher than at –50 °C. The same α:β ratio was observed on glycosylation of **30** with 3-*O*-acetylated **19** (entry 14). The use of silver triflate as the reaction promoter only slightly affected the stereoselectivity of the coupling of **19** with **30** (entry 12). These results indicated that the presence of the acetyl group at the position 3 of the donor again did not improve the α-stereoselectivity, whereas increasing the reaction temperature facilitated the formation of α-anomers. However, it should be noted that the yields of the disaccharides **41** and **42** at room temperature were markedly lower than under standard glycosylation conditions (–35 °C).

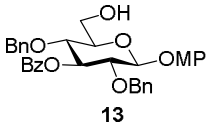
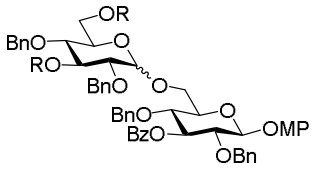
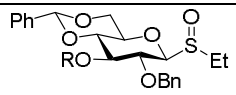
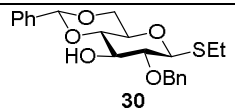
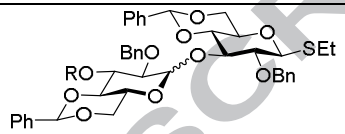
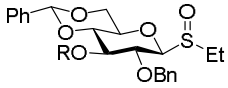
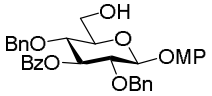
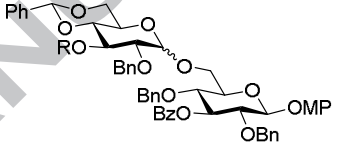
In order to rule out anomerization of the β-glycoside bond as a possible reason of the higher α-stereoselectivity at room temperature, a blank experiment was carried out (Scheme 4).

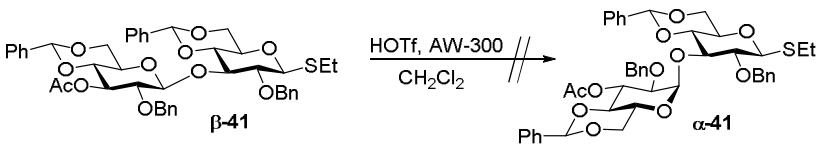
Disaccharide β-**41** was treated with 1 equiv. of TfOH in CH_2Cl_2 in the presence of mol. sieve AW-300 (Scheme 4). No formation of α-**41** was observed within 4 hours, thus indicating that the temperature-dependent stereoselectivity did not relate to anomerization. The dependence of the stereochemical outcome of glycosylation on the temperature is known.[61,62] Most likely, this phenomenon is a consequence of changes in the conformation of intermediate oxacarbenium ions occurring on increasing the temperature.[62]

Table 1. Stereochemical results of glucosylation with variously protected donors bearing an acetyl at O-3.

Entry	Donor	Acceptor	Conditions	Coupling product	α:β Ratio (yield)
		 **30**	MeOTf, CH_2Cl_2,		
1	**4** $R^1 = R^2 =$ Bn		AW-300,	**31** $R^1 = R^2 =$ Bn	1.5:1 (90%)
2	**6** $R^1 =$ Bn, $R^2 =$ Ac		-35 → -15 °C	**32** $R^1 =$ Bn, $R^2 =$ Ac	1.4:1 (98%)
3	**20** $R^1 = R^2 =$ Ac			**33** $R^1 = R^2 =$ Ac	5.3:1 (89%)
4	**5** $R^1 =$ Ac, $R^2 =$ Bn			**34** $R^1 =$ Ac, $R^2 =$ Bn	17:1 (77%)
		 **13**	MeOTf, CH_2Cl_2, AW-300,		
5	**4** $R^1 = R^2 =$ Bn		-35 → -15 °C	**35** $R^1 = R^2 =$ Bn	1:3.3 (99%)
6	**6** $R^1 =$ Bn, $R^2 =$ Ac			**36** $R^1 =$ Bn, $R^2 =$ Ac	1:2.3 (94%)
7	**20** $R^1 = R^2 =$ Ac			**37** $R^1 = R^2 =$ Ac	11.2:1 (93%)
8	**5** $R^1 =$ Ac, $R^2 =$ Bn			**38** $R^1 =$ Ac, $R^2 =$ Bn	4:1 (97%)
9	 **21**	 **16**	MeOTf, CH_2Cl_2, AW-300, -35 → -15 °C	 **39**	16.4:1 (93%)
		 **30**	MeOTf, CH_2Cl_2, AW-300, -50 → -15 °C,		

10	**18** R = Bn			**40** R = Bn	2.2:1 (95%)
11	**19** R = Ac			**41** R = Ac	1:1.4 (92%)
12	**19** R = Ac		AgOTf, CH_2Cl_2, AW-300, 20 °C	**41** R = Ac	3:1 (71%)
13	**18** R = Bn		MeOTf, CH_2Cl_2, AW-300, 20 °C	**40** R = Bn	3.8:1 (78%)
14	**19** R = Ac			**41** R = Ac	3.8:1 (64%)
		 **13**	MeOTf, CH_2Cl_2, AW-300, -35 → 20 °C		
15	**18** R = Bn			**42** R = Bn	5.2:1 (96%)
16	**19** R = Ac		MeOTf, CH_2Cl_2, AW-300, 20 °C	**43** R = Ac	5.9:1 (96%)
		 **30**	MeOTf, AW-300, -35 →-15 °C	 **41**	
17	**19a** R^1 = OC(=NPh)CF_3, R^2 = H				1:1.2 (91%)
18	**19b** R^1 = H, R^2 = OC(=NPh)CF_3				1:1.5 (91%)
		 **30**	Tf_2O, DTBMP, CH_2Cl_2, -78 → 0°C		
19	**22** R = Bn			**31** R = Bn	1.8:1 (63%)

20	**25** R = Ac			**33** R = Ac	6.8:1 (59%)
		 **13**	Tf_2O, DTBMP, CH_2Cl_2, -78 → 0 °C		
21	**22** R = Bn			**35** R = Bn	1.1:1 (79%)
22	**25** R = Ac			**37** R = Ac	5.9:1 (92%)
		 **30**	Tf_2O, DTBMP, CH_2Cl_2, -78 → 0 °C		
23	**27** R = Bn			**40** R = Bn	1:1.9 (45%)
24	**28** R = Ac			**41** R = Ac	No formation of **41**
		 **13**	Tf_2O, DTBMP, CH_2Cl_2, -78 → 0 °C		
25	**27** R = Bn			**42** R = Bn	2.3:1 (88%)
26	**28** R = Ac			**43** R = Ac	No formation of **43**



Scheme 4. An attempt at anomerization of the disaccharide β-**41**.

Finally, the role of the initial anomeric configuration was estimated by comparison of glycosylation of **30** with the α and β-anomers of the donor **19**. The reaction with the β-donor **19b** resulted in an insignificantly higher proportion of the β-isomer (entry 18) than the reaction with the α-donor **19a** (entry 17).

The study of the influence of the 4,6-*O*-benzylidene protecting group on the stereoselectivity of glycosylation was primarily carried out using glycosyl sulfoxides or thioglycosides activated with Tf_2O[24,25] or 1-benzenesulfinylpiperidine/Tf_2O[63] respectively. In both cases, *in situ* generated glycosyl trifluormethanesulfonates are believed to be the reactive species defining stereochemistry of products.[21,23,64,65] It is not obvious, whether a similar intermediate glycosyl trifluoromethanesulfonate is formed and can determine the stereochemical outcome, if glycosylation is made with a 3,6-di-*O*-acylated donor. Therefore, it was interesting to ascertain, whether the stereochemical results observed for trifluoroacetimidoyl donors can be reproduced with sulfoxide donors promoted with Tf_2O.

α-Stereoselectivity of Tf_2O-promoted glycosyaltion of the secondary acceptor **30** with the tetrabenzyl sulfoxide **22** (α:β = 1.8:1, entry 19) and the 3,6-di-*O*-acetyl sulfoxide **25** (α:β = 6.8:1, entry 20) was slightly higher than that for trifluoroacetimidoyl donors **4** (α:β = 1.5:1, entry 1) and **20** (α:β = 5.3:1, entry 3). However, the yields of glycosylation with sulfoxides were essentially lower than the yields achieved with the corresponding trifluoroacetimidates.

Glycosylation of the primary acceptor **13** with the sulfoxide donors **22** and **25** was somewhat contradictory: tetrabenzyl sulfoxide **22** produced a higher proportion of α-**35** (α:β =

1.1:1, entry 21) as compared to the corresponding trifluoracetimidate **4**, whereas 3,6-di-*O*-acetyl sulfoxide **25** appeared to be less α-stereselective (α:β = 5.9:1, entry 22) than the imidate **20**.

4,6-*O*-Benzylidene-2,3-di-*O*-benzyl sulfoxide **27** demonstrated lower α-selectivity upon glycosylation of both primary and secondary acceptors **13** and **30** (entries 25 and 23) than the trifluoracetimidate **18** (entries 10 and 15). Moreover, glycosylation with **27** provided lower yields of the corresponding disaccharides especially for the secondary acceptor **30**. It is noteworthy that no formation of disaccharides **41** and **43** (entries 24 and 26) was detected when the 3-*O*-acetylated sulfoxide **28** was coupled with the acceptors **30** and **13**.

To summarize, the stereochemical results of glycosylation with the sulfoxide donors **22**, **25**, and **27** resembled, with minor deviations, those with the corresponding *N*-phenyltrifluoroacetimidoyl donors **4**, **20**, and **18**, thus indicating the generality of stereodirecting effects of protecting groups, in particular remote acyl groups, in different glycosyl donors regardless of the leaving group type and activation protocol.

2.3. Conclusions

The effect of 3-*O*- and 6-*O*-acyl protecting groups on stereochemistry of glucosylation of primary and secondary glucose acceptor with conformationally flexible monocyclic and conformationally rigid 4,6-*O*-benzylidene-protected glucosyl *N*-phenyltrifluoroacetimidates and glucosyl sulfoxides has been investigated. The results obtained were sometimes contradictory (for example, a certain group in the glucosyl donor exerted an opposite stereochemical effect depending on the structure of the acceptor) and could not be rationalized in terms of a single concept, for example, the concept of the remote anchimeric assistance. Nevertheless, some important particular conclusions could be drawn. Thus, it has been found that, contrary to previous observations (see refs. 14-18, 20, 40, 50 and ref. 13 for a review), in studied cases a single 3-*O*-acetyl group in mono- and bicyclic glucosyl donors did not cause any appreciable α-directing effect but in one case even changed the stereoselectivity towards the β-anomer. The

latter fact may be attributed to the electron-withdrawing effect of the acetyl group (by analogy with fluorine in 3-fluoro-3-deoxydonors) or mismatched interaction of the donor and acceptor in glycosylation reaction[66] or other phenomena. On the other hand, the 3-*O*-acetyl group is able to increase the α-stereoselectivity of 3,6-di-*O*-acylated donors as compared to the donor with a single 6-*O*-acetyl group. The latter donor also demonstrated good α-stereoselectivity on glycosylation of the primary and especially the secondary acceptor.

α-Stereoselectivity of glycosylation with rigid 4,6-*O*-benzylidene-protected glucosyl donors turned out to be temperature-dependent and rose on increasing the reaction temperature irrespectively of the protecting group type at O-3.

From the synthetic standpoint, 6-*O*-acetyl and 3,6-di-*O*-acyl donors proved the most effective and α-stereoselective donors for the practical synthesis of α-(1→3)- and α-(1→6)-linked oligosaccharides.

3 Experimental Section

3.1 General methods

All glycosylation reactions were carried out under dry Ar. Molecular sieves for glycosylation reactions were activated prior to application at 180 ºC in vacuum of an oil pump during 2 h. Dichloromethane was successively distilled from diethanolamine, P_2O_5, and CaH_2 under Ar. For glycosylation reactions, dichloromethane was freshly redistilled from CaH_2. THF was distilled from sodium benzophenone ketyl. DMF was distilled under reduced pressure (17 mm Hg) from phthalic anhydride and then from CaH_2. Pyridine was dried by distillation from P_2O_5. Analytical thin-layer chromatography (TLC) was performed on Silica Gel 60 F254 aluminium sheets (Merck), and visualization was accomplished using UV light or by charring at ~150 ºC with 10% (v/v) H_3PO_4 in ethanol. Column chromatography was performed on Silica Gel 60, 40–63 μm (Merck). Analytical HPLC was carried out on a Supelcosil LC-SI column (5 μm, 250×4.6 mm) at a flow rate of 0.8 mL/min with a K-2301 refractive index detector (Knauer)

Data processing was performed using the MultiChrom Software. Preparative HPLC was performed on a Supelcosil LC-SI column (5 μm, 250×21.2 mm) at a flow rate of 8 mL/min with a K-2401 refractive index detector (Knauer). Optical rotation values were measured using a JASCO DIP-360 polarimeter at the ambient temperature in solvents specified. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX-400, Bruker DRX-500, and Bruker Avance spectrometers. Chemical shifts were referenced to residual solvent signals. Signal assignment in ^{1}H and ^{13}C NMR spectra was made using COSY, TOCSY, and ^{1}H–^{13}C HSQC techniques. High-resolution mass spectra were acquired by electrospray ionization on a MicrOTOF II (Bruker Daltonics) instrument.

3.2. 3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-D-glucopyranose (3)

A solution of the methyl glucoside **2** (0.91 mg, 1.95 mmol) in a mixture of AcOH (13 mL) and 1 M aq. HCl (3.45 mL) was boiled under reflux for 1 h and poured into a mixture of crushed ice and satd $NaHCO_3$. The resulting mixture was extracted with EtOAc (4 × 150 mL) and the combined organic extracts were dried and concentrated. Toluene was evaporated twice from the solid residue, which was then acetylated with Ac_2O (5 ml) in pyridine (5 mL) for 5 h. Pyridine and acetic acid anhydride were evaporated, and toluene was twice evaporated from the residue. After chromatographic purification on SiO_2 ($CHCl_3$ – Et_2O, 40:1), 1,3-di-*O*-acetyl-2,4,6-tri-*O*-benzyl-D- glucopyranose (398 mg, 38%) was obtained as a colorless foam; R_f 0.62 (petroleum ether – EtOAc, 1.8:0.5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-7.12 (m, Ar), 6.38 (d, $J_{1,2}$ = 3.5 Hz, H-1$^{\alpha}$), 5.65 (d, $J_{1,2}$ = 8.1 Hz, H-1$^{\beta}$), 5.48 (t, *J* 9.7 Hz, H-3$^{\alpha}$), 5.28 (t, *J* 9.4 Hz, H-3$^{\beta}$), 4.72-4.44 (m, C*H*$_2$Ph), 3.91 (m, H-5$^{\alpha}$), 3.77 (m, H-6A$^{\alpha}$), 3.74 (m, H-4$^{\alpha}$), 3.73 (m, H-6$^{\beta}$), 3.72 (m, H-4$^{\beta}$), 3.65 (m, H-6B$^{\alpha}$), 3.61 (m, H-5$^{\beta}$), 3.59 (m, H-2$^{\alpha}$), 3.53 (t, *J* 9.4 Hz, H-2$^{\beta}$), 2.12, 2.03, 1.94, 1.85 (4 s, CH_3CO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 169.7, 169.3, 168.9 (CH_3*C*O), 137.8, 137.5, (*ipso*-C, Ph), 129.0, 128.0, 127.9 (Ar), 94.0 (C-1$^{\beta}$), 89.5 (C-1$^{\alpha}$), 78.4 (C-2$^{\beta}$), 76.0 (C-2$^{\alpha}$), 75.6 (C-3$^{\beta}$), 75.5 (C-4$^{\alpha}$, C-5$^{\beta}$), 75.3 (C-4$^{\beta}$), 74.3, 74.2, 73.6 (3 *C*H$_2$Ph), 73.3 (C-

3^{α}), 72.6 (C-5^{α}), 72.5 (*C*H_2Ph), 67.8 (C-6^{α}, C-6^{β}), 21.0, 20.9 (*C*H_3CO). Hydrazine acetate (403 mg, 4.4 mmol) was added to a solution of the above 1,3-diacetate (1.53 g, 2.9 mmol) in DMF (16 mL), the mixture was stirred for 1.5 h at rt, and poured into cold aq satd $NaHCO_3$ solution. The solution was extracted with EtOAc (3 × 200 mL), the combined extracts were dried and concentrated. Chromatographic purification ($CHCl_3$ – Et_2O, 20:3) of the residue provided the hemiacetal **3** (773 mg, 55 %); R_f 0.59 and 0.47 (petroleum ether – EtOAc, 1.8:0.5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.10 (m, Ar), 5.50 (t, *J* 9.5 Hz, H-3^{α}) 5.28 (br. s, H-1^{α}), 5.21 (t, *J* 9.1 Hz, H-3^{β}), 4.84 (d, PhCH_2), 4.74 (dd, $J_{1,2}$ 7.5 Hz, $J_{1,OH}$ 5.2 Hz, H-1^{β}), 4.65-4.40 (m, PhCH_2), 4.30 (d, OH^{β}), 4.08 (m, H-5^{α}), 3.71 (dd, $J_{5,6A}$ 3.5 Hz, $J_{6A,6B}$ 10.7 Hz, H-$6A^{\alpha}$), 3.68-3.53 (m, H-6^{β}, H-$6B^{\alpha}$, H-4^{α}, H-4^{β}, H-5^{β}), 3.50 (dd, $J_{2,1}$ 3.4 Hz, $J_{2,3}$ 9.7 Hz, H-2^{α}), 3.29 (dd, $J_{2,3}$ 9.4 Hz, H-2^{β}), 1.91, 1.87 (2 s, CH_3CO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0 (CH_3*C*O), 138.2, 137.9, 137.7, 137.5 (*ipso*-C, Ph), 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6 (Ar), 97.4 (C-1^{β}), 90.8 (C-1^{α}), 80.0 (C-2^{β}), 77.5 (C-2^{α}), 76.2 (C-4^{β}), 76.0 (C-4^{α}), 75.5 (C-3^{β}), 74.4 (C-5^{β}), 74.2, 73.8, 73.5 (3 *C*H_2Ph), 73.3 (C-3^{α}), 72.6 (*C*H_2Ph), 69.9 (C-5^{α}), 68.5 (C-6^{β}), 68.2 (C-6^{α}), 21.0 (*C*H_3CO). Anal. Calcd. for $C_{29}H_{32}O_7$: C, 70.71; H, 6.55. Found: C, 70.72; H, 6.62.

3.3. *O*-(3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-D-glucopyranosyl) *N*-phenyltrifluoroacetimidate (6)

N-Phenyltrifluoroacetimidoyl chloride (PTAIC) (50 μL, 0.31 mmol) and K_2CO_3 (45 mg, 0.31 mmol) were added to a solution of the hemiacetal **3** (104 mg, 0.21 mmol) in acetone (4.4 mL), and the mixture was intensively stirred until TLC showed the absence of the starting material. The mixture was filtered through a Celite layer, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography to give the donor **6** (132 mg, 94%) as an amorphous solid, R_f 0.69 (petroleum ether – EtOAc, 2:1). Data for α-anomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60–6.71 (m, 20H, Ar), 6.55 (br. s, 1H, H-1), 5.57 (t, 1H, *J* 9.7 Hz, H-3), 4.71–4.50 (m, 6H, 3 PhCH_2), 4.01 (m, 1H, H-5), 3.82–3.65 (m, 4H, H-2, H-4, H-6A, H-6B), 1.96 (s, CH_3CO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.7 (CO), 143.5 (*ipso*-C,

NPh), 137.7, 137.5 (*ipso*-C, Bn), 129.5, 128.7, 128.4, 128.0, 127.9, 127.6 (Ar), 125.7, 124.2, 119.3 (NPh), 92.9 (C-1), 76.4 (C-2), 75.4 (C-4), 73.1 (C-3), 72.8 (C-5), 67.8 (C-6), 21.0 (CH_3CO). Data for β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–6.70 (m, Ar), 5.69 (br s, H-1), 5.22 (m, H-3), 4.82–4.50 (m, PhCH_2), 3.80–3.70 (m, H-4, H-6A, H-6B), 2.29 (s, CH_3CO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8 (CO), 143.3 (*ipso*-C, NPh), 137.8, 137.7 (*ipso*-C, Ph), 129.6, 128.9, 128.4, 128.0, 127.9, 127.6 (Ar), 125.8, 124.3, 119.3 (NPh), 97.2 (C-1), 78.1 (C-2), 75.2-75.3 (C-3, C-4, C-5), 67.8 (C-6), 21.9 (CH_3CO). Anal. Calcd. for $C_{37}H_{36}F_3NO_8$: C, 66.96; H, 5.47; N, 2.11. Found: C, 66.89; H, 5.49; N, 2.13.

3.4. *p*-Methoxyphenyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (8) and *p*-methoxyphenyl 2-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (10)

A mixture of the diol **7** (6.38 g, 17.06 mmol) and dibutyltin oxide (4.25 g, 17.06 mmol) in toluene (480 mL) was boiled under refluxed with aseotropic removal of water for 6 h. The solvent was evaporated and benzyl bromide (100 mL) was added. The resulting mixture was stirred at 80-90 °C until TLC indicated that the starting material had disappeared. Benzyl bromide was removed in vacuum of an oil pump and benzyl ethers **10** (4.61 g, 58%) and **8** (3.02 g, 38.6%) were isolated from the residue by column chromatography (petroleum ether – CH_2Cl_2 – acetone, 2:1:0.1→1.5:1:0.1). Data for **10**: white crystals, mp 150–153 °C; $[\alpha]_D$ +4.5 (*c* 1, $CHCl_3$); R_f 0.52 ($CHCl_3$ – acetone, 50:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52–7.28 (m, 10H, 2 Ph), 7.05 (d, 2H, *J* 9.1 Hz, $C_6H_4OCH_3$), 6.88 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.58 (s, 1H, PhC*H*), 5.07 (d, 1H, J_{gem} 11.3 Hz, PhCH_2A), 5.05 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.88 (d, 1H, PhCH_2B), 4.39 (dd, 1H, $J_{6A,5}$ 5.0 Hz, $J_{6A,6B}$ 10.5 Hz, H-6A), 3.95 (t, 1H, *J* 9.4 Hz, H-3), 3.84 (t, 1H, *J* 10.7 Hz, H-6B), 3.82 (s, 3H, CH_3O), 3.67-3.62 (m, 2H, H-2, H-4), 3.55 (m, 1H, H-5). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 129.2, 128.5, 128.3, 128.2, 128.0, 126.3 (Ar), 118.5 ($C_6H_4OCH_3$), 114.7 ($C_6H_4OCH_3$), 102.3 (C-1), 101.8 (Ph*C*H), 81.7 (C-2), 80.2 (C-4), 75.0 (Ph*C*H_2), 73.3 (C-3), 68.7

(C-6), 66.2 (C-5), 55.7 (CH_3O) Anal. Calcd. for $C_{27}H_{28}O_7$: C, 69.81; H, 6.08. Found: C, 69.91; H, 6.28.

Data for **8**: white crystals, mp 200-205 ºC; $[\alpha]_D$ +24.3 (*c* 1, $CHCl_3$); R_f 0.46 ($CHCl_3$ – acetone, 50:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52–7.25 (m, 10H, Ar), 7.05 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 6.87 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.62 (s, 1H, PhC*H*), 5.03 (d, 1H, J_{gem} 11.7 Hz, PhCH_2A), 4.93 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 4.86 (d, 1H, PhCH_2B), 4.40 (dd, 1H, $J_{6A,5}$ 4.9 Hz, $J_{6A,6B}$ 10.6 Hz, H-6A), 3.88–3.82 (m, 2H, H-2, H-6B), 3.81 (s, 1H, CH_3O), 3.80–3.74 (m, 2H, H-4, H-3), 3.56 (m, 1H, H-5). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 129.0, 128.5, 128.3, 128.1, 127.9, 126.0 (Ar), 118.8, 114.6 ($C_6H_4OCH_3$), 102.6 (C-1), 101.4 (Ph*C*H), 81.2, 80.3 (C-3, C-4), 74.7 (Ph*C*H_2), 74.1 (C-2), 68.7 (C-6), 66.6 (C-5), 55.7 (CH_3O). Anal. Calcd.for $C_{27}H_{28}O_7$: C, 69.81 H, 6.08. Found: C, 69.68; H, 6.29.

3.5. *p*-Methoxyphenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (9)

Benzyl bromide (380 µL, 3.2 mmol) and NaH (130 mg of 60% dispersion, 3.2 mmol) were added to a solution of **8** (500 mg, 1.08 mmol) in dry DMF (15 mL). The mixture was stirred until TLC indicated disappearance of the starting material, diluted with EtOAc and successively washed with 1 M HCl, water, aq satd $NaHCO_3$, and water. The organic layer was dried with Na_2SO_4, the solvent was removed under reduced pressure and the residue was purified by column chromatography (petroleum ether–EtOAc, 6:1). Dibenzyl ether **9** (549 mg, 92%) was isolated as white crystals; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.50 (m, 2H, Ar), 7.42–7.29 (m, 15H, Ar), 7.03 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 6.88 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.61 (s, 1H, PhC*H*), 5.03 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 5.01 (d, 1H, J_{gem} 10.9 Hz, PhCH_2A), 4.97 (d, 1H, J_{gem} 11.4 Hz, PhCH_2A'), 4.89 (d, 1H, PhCH_2B), 4.85 (d, 1H, PhCH_2B'), 4.40 (dd, 1H, $J_{5,6A}$ 5.2 Hz, $J_{6A,6B}$ 10.6 Hz, H-6A), 3.87–3.77 (m, 7H, H-6B, H-3 or H-4, H-2, CH_3O), 3.74 (t, 1H, *J* 8.3 Hz, H-3 or H-4), 3.53 (m, 1H, H-5). ^{1}H NMR data were in accordance with those published.[68]

3.6. *O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranosyl) *N*-phenyltrifluoroacetimidate (18)

Cerium(IV) ammonium nitrate (5.20 g, 9.48 mmol) was added to a solution of **9** (525 mg, 0.95 mmol) in a mixture of CH_3CN, toluene, and water (1:1:1, 75 mL). The mixture was intensively stirred at room temperature until TLC showed disappearance of the starting material, diluted with EtOAc, and washed with aq satd $NaHCO_3$ and water. The organic layer was dried with Na_2SO_4, concentrated, and the residue was purified by silica gel column chromatography (petroleum ether – EtOAc, 5:1) to afford 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranose (256 mg, 60%) as a 1:1 mixture of α- and β-anomers; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.55–7.28 (ArH), 5.60 (2 s, 1H, PhC*H*$^{\alpha,\beta}$), 5.22 (d, 0.5H, $J_{1,2}$ 4.4 Hz, H-1$^{\alpha}$), 5.00-4.75 (m, 4.5H, 2 PhCH_2, H-1$^{\beta}$), 4.38 (dd, 0.5 H, $J_{5,6A}$ 4.9 Hz, $J_{6A,6B}$ 10.4 Hz, H-6A), 4.33 (dd, 0.5 H, $J_{5,6A}$ 4.9 Hz, $J_{6A,6B}$ 10.3 Hz, H-6A), 4.11 (m, 0.5 H, H-5$^{\alpha}$), 4.04 (t, 0.5 H, *J* 9.3 Hz, H-3$^{\alpha}$), 3.81 (t, 1H, *J* 9.8 Hz, H-4$^{\alpha,\beta}$), 3.78-3.70 (m, 1H), 3.70-3.60 (m, 1H), 3.50 (m, 0.5 H, H-5$^{\beta}$), 3.45 (t, 0.5H *J* 8.2 Hz), 3.24 (br. s, 0.5H, OH), 3.12 (br. s, 0.5H, OH). ^{1}H NMR data were in agreement with those published.[67] The above hemiacetal (245 mg, 0.547 mmol) was dissolved in acetone (11.4 mL), PTAIC (105 μL, 0.656 mmol) and K_2CO_3 (118 mg, 0.821 mmol) were added and the reaction mixture was intensively stirred until TLC showed the absence of the starting material. The resulting mixture was filtered through a pad of Celite, the filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (petroleum ether – EtOAc, 12:1) to give **18** (319 mg, 94 %) as an α,β-mixture in a ratio of ~1:6. Pure anomers were isolated for characterization purposes. Data for **18α**: $[\alpha]_D$ +44.6 (*c* 1, $CHCl_3$); R_f 0.57 (petroleum ether–EtOAc, 2:1); ^{1}H NMR (500 MHz, C_6D_6): δ 7.68– 6.81 (m, 20H, 4 Ph), 6.67 (br. s, 1H, H-1), 5.43 (s, 1H, PhC*H*), 5.01 (d, 1H, J_{gem} 11.7 Hz, PhCH_2A), 4.83 (d, 1H, PhCH_2B), 4.77 (d, 1H, J_{gem} 12.0 Hz, PhCH_2A'), 4.67 (d, 1H, PhCH_2B'), 4.29 (t, 1H, *J* 9.3 Hz, H-3), 4.26-4.21 (m, 2H, H-5, H-6A), 3.68 (dd, 1H, $J_{2,1}$ = 3.4 Hz, $J_{2,3}$ = 9.2 Hz, H-2), 3.58 (t, 1H, *J* 9.3 Hz, H-4), 3.52 (t, 1H, *J* 10.4 Hz, H-6B).^{13}C NMR (150.9 MHz, C_6D_6): δ 144.5, 139.8, 138.9, 138.5, 129.4, 129.0,

128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 127.0, 124.9, 120.2 (ArH), 102.2 (Ph*C*H), 95.0 (C-1), 82.4 (C-4), 79.5 (C-2), 79.2 (C-3), 75.8 (Ph*C*H_2), 74.4 (Ph*C*H_2), 69.2 (C-6), 66.2 (C-5). Data for **18β**: $[\alpha]_D$ +48.4 (*c* 1, $CHCl_3$); R_f 0.66 (petroleum ether – EtOAc, 2:1); ^{1}H-NMR (500 MHz, C_6D_6): δ 7.62–6.82 (m, 20H, 4 Ph), 5.91 (br. s, 1H, H-1), 5.33 (s, 1H, PhC*H*), 4.99 (d, 1H, J_{gem} 11.9 Hz, PhCH_2A), 4.90 (s, 2H, PhCH_2), 4.82 (d, 1H, PhCH_2B), 4.17 (dd, 1H, $J_{6A,6B}$ 10.3 Hz, H-6A), 3.82-3.73 (m, 2H, H-2, H-3), 3.62 (t 1H, *J* 9.2, Hz H-4), 3.52 (t, 1H, *J* 10.1 Hz, H-6B), 3.21 (bs, 1H, H-5).^{13}C-NMR (150.9 MHz, C_6D_6): δ 144.3, 138.9, 138.5, 129.4, 129.3, 128.9, 128.8, 128.6, 128.1, 126.9, 125.0, 120.0 (ArH), 102.0 (Ph*C*H), 98.1 (C-1), 81.8 (C-4), 81.5 (C-3), 81.3 (C-2), 75.7 (Ph*C*H_2), 75.2 (Ph*C*H_2), 69.0 (C-6), 67.2 (C-5). HR ESI MS for the anomeric mixture of **18** calcd for $[M + Na]^+$ $C_{35}H_{32}F_3NO_6Na$: 2.2074, found: 642.2046.

3.7. *O*-(3-*O*-Acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranosyl) *N*-phenyltrifluoroacetimidate (19)

CAN (2.12 g, 9.48 mmol) was added to a solution of compound **11** (391 mg, 0.773 mmol) in 80% aq acetonitrile (65 mL) and the mixture was intensively stirred at rt until TLC showed disappearance of the starting material. The mixture was diluted with EtOAc and washed with aq satd $NaHCO_3$ and water, the organic layer was dried with Na_2SO_4 and concentrated. Purification of the residue on a silica gel column (petroleum ether – EtOAc, 3:1→2:1) provided 3-*O*-acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranose (256 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.10 (m, 10H, Ar), 5.44 (t, 1H, *J* 9.6 Hz H-3$^\beta$), 5.37(s, 1H, PhCH^β), 5.35 (s, 1H, PhCH^α), 5.22 (t, 1H, *J* 9.3 Hz, H-3$^\alpha$), 5.17 (d, $J_{1,2}$ 3.7 Hz, 1H, H-1$^\alpha$), 4.78 (d, 1H, J_{gem} 11.9 Hz, PhCH_2A$^\alpha$), 4.75 (d, $J_{1,2}$ 7.7 Hz, 1H, H-1$^\beta$), 4.55-4.60 (d, 3H, PhCH_2), 4.52 (d, 1H, PhCH_2B$^\beta$), 4.20 (m, 2H, H-6A$^\alpha$, H-6A$^\beta$), 4.04 (m, 1H, H-5$^\alpha$), 3.65 (t, 1H, *J* 10.2 Hz, H-6B$^\alpha$), 3.60 (t, 1H, *J* 10.3 Hz, H-6B$^\beta$), 3.51 (dd, 1H, $J_{2,3}$ 9.4 Hz, H-2$^\alpha$), 3.49 (t, *J* 9.6 Hz, 1H, H-4$^\alpha$), 3.45 (t, 1H, *J* 9.7 Hz, H-4$^\beta$), 3.39 (m, 1H, H-5$^\beta$), 3.31 (dd, 1H, $J_{2,3}$ 9.2 Hz, H-2$^\beta$), 1.96 (s, 3H, CH_3CO^β), 1.90 (s, 3H, CH_3CO^α). ^{13}C NMR (100.9 MHz, $CDCl_3$): δ 170.10 (CH_3CO), 138.0,

137.3, 137.1, 137.0, 129.01, 128.7, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 126.25, 126.20 (Ar), 101.6, 101.4 (Ph*C*H), 98.0 (C-1^{β}), 91.8 (C-1^{α}), 80.8 (C-2^{β}), 79.2 (C-2^{α}), 78.8 (C-4^{β}), 78.8 (C-4^{α}), 74.4 (Ph*C*H_2), 73.0 (Ph*C*H_2), 72.7 (C-3^{β}), 70.7 (C-3^{α}), 69.0 (C-6^{α}), 68.7 (C-6^{β}), 66.3 (C-5^{β}), 62.6 (C-5^{α}), 21.03, 20.95 (*C*H_3CO). Anal. Calcd.for $C_{22}H_{24}O_7$: C, 65.99 H, 6.04. Found: C, 65.88; H, 6.27.

Compound **19** (124 mg, 92.5%) was obtained as an α,β-mixture in a ratio of ~1:6 from the above hemiacetal (94 mg, 0.235 mmol) as described for preparation of **6** and purified by silica gel column chromatography (petroleum ether – EtOAc, 12:1→10:1). Pure anomers were isolated for characterization purposes. Data for **19α**: syrup, $[\alpha]_D$ +70.6 (*c* 1, $CHCl_3$); R_f 0.53 (petroleum ether–EtOAc, 3:1); ^{1}H NMR (400 MHz, C_6D_6): δ 7.65–6.78 (m, 15H, Ar), 6.70 (br. s, 1H, H-1), 5.63 (t, 1H, *J* 9.8 Hz, H-3), 5.38 (s, 1H, PhC*H*), 4,60 (d, J_{gem} 12,3 Hz, 1H, PhCH_2A), 4.49 (d, 1H, PhCH_2B), 4.29 (m, 1H, H-5), 4.19 (dd, 1H, $J_{6A,5}$ 5.0 Hz, $J_{6A,6B}$ 10.3 Hz, H-6A), 3.68 (dd, 2H, $J_{2,1}$ 3.1 Hz, $J_{2,3}$ 9.7 Hz, H-2), 3.55–3.47 (m, 2H, H-4, H-6B), 1.79 (s, 3H, CH_3CO). ^{13}C NMR (100.9 MHz, acetone-d_6): δ 129.7, 129.2, 128.9, 128.7, 128.6, 127.2, 125.2, 120.2 (Ar), 102.2 (Ph*C*H), 94.9 (C-1), 79.2 (C-4), 77.9 (C-2), 73.9 (Ph*C*H_2), 71.0 (C-3), 68.9 (C-6), 66.4 (C-5), 20.9 (*C*H_3CO). Data for **19β**: syrup, $[\alpha]_D$ +46.2 (*c* 1, $CHCl_3$); R_f 0.67 (petroleum ether – EtOAc, 3:1); ^{1}H NMR (600 MHz, C_6D_6): δ 7.62–6.79 (m, 15H, ArH), 5.93 (br. s, 1H, H-1), 5.62 (t, 1H, *J* 8.6 Hz, H-3), 5.30 (s, 1H, PhC*H*), 4.87 (d, 1H, J_{gem} 11.9 Hz, PhCH_2A), 4.74 (d, 1H, PhCH_2B), 4.12 (dd, 1H, $J_{5,6A}$ 4.9 Hz, $J_{6A,6B}$ 10.3 Hz, H-6A), 3.78 (t, 1H, *J* 7.6 Hz, H-2), 3.60 (t, 1H, *J* 9.6 Hz, H-4), 3.48 (t, 1H, *J* 10.2 Hz, H-6B), 3.29 (br. s, 1H, H-5), 1.78 (s, 3H, CH_3CO). ^{13}C NMR (150.9 MHz, C_6D_6): δ 169.5 (CH_3*C*O), 144.1, 138.5, 138.2, 129.5, 129.4, 129.1, 128.7, 128.6, 128.4, 128.2, 127.1, 125.2, 120.0 (Ar), 102.3 (Ph*C*H), 98.1 (C-1), 79.6 (C-2), 79.1 (C-4), 75.0 (Ph*C*H_2), 73.3 (C-3), 69.1 (C-6), 67.1 (C-5), 20.8 (*C*H_3CO). HR ESI MS calcd for $[M + Na]^+$ $C_{30}H_{28}F_3NNaO_7$ 594.1710, found 594.1631. Anal. Calcd.for $C_{30}H_{28}F_3NO_7$: C, 63.04, H, 4.94, N 2.45. Found: C, 62.93, H, 4.80, N, 2.52.

3.8. *p*-Methoxyphenyl 3-*O*-acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (11)

A solution of **10** (400 mg, 0.862 mmol) in a mixture of pyridine (0.85 mL) and acetic anhydride (0.65 mL) was kept at rt for 5 h and concentrated. Residual pyridine and Ac_2O were removed by coevaporation with toluene. The residue was purified by column chromatography (petroleum ether – EtOAc, 3:1) to give pure **11** (414 mg, 95 %); white crystals, mp 165-170 °C; $[\alpha]_D$ –7.3 (*c* 1, $CHCl_3$); R_f 0.67 (toluene – EtOAc, 6:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50–7.27 (m, 10H, Ar), 7.08 (d, 2H, *J* 8.9 Hz C_6H_4OMe), 6.89 (d, 2H, *J* 8.9 Hz C_6H_4OMe), 5.51 (s, 1H, PhC*H*), 5.42 (t, *J* 9.4 Hz, 1H, H-3), 5.12 (d, $J_{1,2}$ 7.6 Hz, 1H, H-1), 4.99 (d, 1H, J_{gem} 11.7 Hz, PhCH_2A), 4.79 (d, 1H, PhCH_2B), 4.40 (dd, 1H, $J_{6A,5}$ 6 Hz, $J_{6A,6B}$ 10.6 Hz, H-6A), 3.83 (br. t, 1H, H-6B), 3.82 (s, 3H, CH_3O), 3.74 (t, 1H, *J* 8.3 Hz, H-2), 3.71 (t, *J* 9.6 Hz, 1H, H-4), 3.62 (m, 1H, H-5), 2.03 (s, 3H, CH_3CO). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 169.8 (CH_3CO), 137.9, 136.9, 129.1, 128.4, 128.2, 127.9, 126.2 (Ar), 151.0, 155.8, 118.7, 114.7 ($C_6H_4OCH_3$), 103.4 (C-1), 101.45 (Ph*C*H), 79.6 (C-2), 78.6 (C-4), 74.7 (Ph*C*H_2), 72.6 (C-3), 68.7 (C-6), 66.3 (C-5), 55.7 (CH_3O), 20.9 (*C*H_3CO). Anal. Calcd. for $C_{29}H_{30}O_8$: C, 68.76, H, 5.97. Found: C, 68.73; H, 5.90.

3.9. *p*-Methoxyphenyl 3-*O*-benzoyl-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (12)

Benzoyl chloride (500 µL, 4.3 mmol) and DMAP (132 mg, 1.08 mmol) were added to a solution of **10** (500 mg, 1.08 mmol) in pyridine (10 mL). When TLC showed disappearance of the starting material, the reaction was quenched by adding aq satd $NaHCO_3$. The resulting mixture was extracted three times with CH_2Cl_2, the combined extracts were concentrated and residual pyridine was removed by coevaporation with toluene. After column chromatography (toluene – EtOAc, 30:1), compound **12** (600 mg, 98 %) was obtained; white crystals, mp 165–170°C; $[\alpha]_D$ +2.4 (*c* 1, $CHCl_3$); R_f 0.51 (petroleum ether – EtOAc, 3:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02–7.10 (m, 15H, 3 Ph), 7.08 (d, 2H, *J* 9.1 Hz, $C_6H_4OCH_3$), 6.89 (d, 2H, *J* 9.1 Hz, $C_6H_4OCH_3$), 5.68 (t, 1H, *J* 9.3 Hz, H-3), 5.51 (s, 1H, PhC*H*), 5.18 (d, 1H, $J_{1,2}$ 7.4 Hz, H-1), 4.92 (d, 1H, J_{gem} 11.5 Hz, PhCH_2A), 4.77 (d, 1H, PhCH_2B), 4.42 (dd, 1H, $J_{6A,5}$ 5.0 Hz, $J_{6A,6B}$ 10.5 Hz,

H-6A), 3.88–3.65 (m, 3H, H-2, H-4, H-6B), 3.81 (s, 3H, CH_3O), 3.68 (m, 1H, $J_{5,6A}$ 4.9 Hz, H-5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 137.5, 136.8, 133.0, 129.9, 129.0, 128.3, 128.2, 127.7, 126.1 (Ar), 118.7, 114.7 ($C_6H_4OCH_3$), 103.4 (C-1), 101.4 (Ph*C*H), 79.3 (C-2 or C-4), 78.7 (C-2 or C-4), 74.5 (Ph*C*H_2), 73.2 (C-3), 68.7 (C-6), 66.3 (C-5), 55.7 (CH_3O). Anal. Calcd.for $C_{34}H_{32}O_8$: C, 71.82, H, 5.67. Found: C, 71.90; H, 5.76.

3.10. *p*-Methoxyphenyl 2,4-di-*O*-benzyl-β-D-glucopyranoside (14)

1 M solution of BH_3·THF in THF (22.6 mL, 22.54 mmol) was added to a solution of **10** (5.23 g, 11.27 mmol) in dry CH_2Cl_2 (90 mL). Then TMSOTf (306 μL, 1.7 mmol) was added dropwise and the mixture was stirred under argon atmosphere at rt until TLC showed disappearance of the starting material. The reaction was quenched by adding MeOH (10 mL) and Et_3N (5 mL), the resulting mixture was concentrated, and MeOH (3×35 mL) was evaporated from the residue. Purification of the residue by silica gel column chromatography (toluene – EtOAc, 12:1) afforded diol **14** (4.71 g, 90%) as white crystals, mp 112–113 °C; $[\alpha]_D$+0.3 (*c* 1, $CHCl_3$); R_f 0.39 (toluene – EtOAc, 5:1); ^1H NMR (600 MHz, $CDCl_3$): δ 7.40–7.30 (m, 10H, Ar), 7.00 (d, 2H, *J* 9.1 Hz, C_6H_4OMe), 6.86 (d, 2H, *J* 9.1 Hz, C_6H_4OMe), 5.07 (d, 1H, J_{gem} 11.4 Hz, PhCH_2A), 4.95 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.92 (d, 1H, J_{gem} 11.3 Hz, PhCH_2A'), 4.79 (d, 1H, PhCH_2B), 4.71 (d, 1H, PhCH_2B'), 3.91 (ddd, 1H, $J_{5,6A}$ 2.9 Hz, $J_{6A,6B}$ 12.0 Hz, $J_{6A,OH}$ 6.1 Hz, H-6A), 3.84 (dt, 1H, $J_{3,OH}$ 2.3 Hz, *J* 8.9 Hz, H-3), 3.79 (s, 3H, CH_3O), 3.75 (ddd, 1H, $J_{5,6B}$ 4.9 Hz, $J_{6B,OH}$ 7.6 Hz, H-6B), 3.56 (t, 1H, *J* 9.3 Hz, H-4), 3.51 (dd, 1H, $J_{2,3}$ 9.0 Hz, H-2), 3.48 (m, 1H, H-5), 2.54 (d, 1H, 3-OH), 1.95 (br. t, 1H, 6-OH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 138.2, 128.7, 128.6, 128.3, 128.2, 128.1 (Ar), 118.2, 114.8 ($C_6H_4OCH_3$), 102.3 (C-1), 81.3 (C-2), 77.1 (C-4), 76.7 (C-3), 75.4 (C-5), 74.8 (Ph*C*H_2), 62.2 (C-6), 55.8 (CH_3O). Anal. Calcd.for $C_{27}H_{30}O_7$: C, 69.51 H, 6.48. Found: C, 69.71; H, 6.63.

3.11. *p*-Methoxyphenyl 3,6-di-*O*-acetyl-2,4-di-*O*-benzyl-β-D-glucopyranoside (15)

Acetylation of **14** (210 mg, 0.45 mmol) as described above for the preparation of **11** afforded, after column chromatography (toluene – EtOAc, 15:1), diacetate **15** (243 mg, 98%) as white crystals, mp 117–119°C; $[\alpha]_D$ +2.4 (*c* 1, $CHCl_3$); R_f 0.36 (petroleum ether – EtOAc, 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.22 (m, 10H, Ar), 7.02 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 6.84 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.33 (t, 1H, *J* 9.2 Hz, H-3), 4.96–4.92 (m, 2H, H-1, PhCH_2A), 4.73 (d, 1H, J_{gem} 11.9 Hz, PhCH_2B), 4.59 (d, 1H, J_{gem} 11.2 Hz, PhCH_2A'), 4.54 (d, 1H, PhCH_2B'), 4.36 (dd, 1H, $J_{6A,6B}$ 11.8 Hz, $J_{6A,5}$ 2.2 Hz, H-6A), 4.25 (dd, 1H, $J_{6B,6A}$ 12.0 Hz, $J_{6B,5}$ 5.4 Hz, H-6B), 3.78 (s, 3H, CH_3O), 3.68 (m, 1H, H-5), 3.64-3.58 (m, 2H, H-2, H-4), 2.05 (s, 3H, CH_3CO), 1.92 (s, 3H, CH_3CO). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 169.8 (CH_3CO), 128.5, 128.4, 128.1, 128.0, 127.8 (Ar), 118.7, 114.6 ($C_6H_4OCH_3$), 102.8 (C-1), 78.9 (C-2), 76.1 (C-4), 75.5 (C-3), 74.5 (PhCH_2), 74.2 (PhCH_2), 72.9 (C-5), 62.9 (C-6), 55.7 (CH_3O), 21.0 (CH_3CO), 20.8 (CH_3CO). Anal. Calcd.for $C_{31}H_{34}O_9$: C, 67.62, H, 6.22. Found: C, 67.77; H, 6.04.

3.12 *p*-Methoxyphenyl 6-*O*-benzoyl-2,4-di-*O*-benzyl-β-D-glucopyranoside (16)

Pyridine (6 mL) and benzoyl chloride (1.18 mL, 10.1 mmol) were added to a solution of **14** (3.93 g, 8.43 mmol) in dry CH_2Cl_2 (100 mL) at –20 ºC. When TLC showed full conversion of the starting material, the reaction mixture was diluted with CH_2Cl_2, washed successively with aq 1 M HCl, water, aq satd $NaHCO_3$, and water. The organic layer was dried over Na_2SO_4, the solvent was removed under reduced pressure and residue was purified by column chromatography (toluene – EtOAc, 15:1) to afford monobenzoate **16** (4.30 g, 89.5%) as white crystals, mp 107–108 °C; $[\alpha]_D$ +6.9 (*c* 1, $CHCl_3$); R_f 0.39 (toluene – EtOAc, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.15 (m, 15H, 3 Ph), 6.91 (d, 2H, *J* 8.9 Hz, C_6H_4OMe), 6.62 (d, 2H, *J* 8.9 Hz, C_6H_4OMe), 5.00 (d, 1H, J_{gem} 11.4 Hz, PhCH_2A), 4.84 (d, 1H, J_{gem} 11.2 Hz, PhCH_2A'), 4.79 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.71 (d, 1H, PhCH_2B), 4,61 (d, 1H, PhCH_2B'), 4.58 (m, 1H, H-6A), 4.35 (dd, 1H, $J_{6B,6A}$ 11.8 Hz, $J_{6B,5}$ 6.7 Hz, H-6B), 3.77 (t, 1H, *J* 8.9 Hz, H-3), 3.66 (m, 1H, H-5), 3.63 (s, 3H, CH_3O), 3.47 (m, 2H, H-2, H-4). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 166.2 (Ph*C*O),

138.2, 137.9, 133.1, 129.8, 129.1, 128.7, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9 (Ar), 118.5, 114.6 ($C_6H_4OCH_3$), 102.5 (C-1), 81.2 (C-2), 77.3 (C-4), 77.0 (C-3), 74.71 (Ph*C*H_2), 74.69 (Ph*C*H_2), 73.3 (C-5), 63.9 (C-6), 55.7 (CH_3O). Anal. Calcd. for $C_{34}H_{34}O_8$: C, 71.56, H, 6.01. Found: C, 71.33; H, 6.28.

3.13. *p*-Methoxyphenyl 3-*O*-acetyl-6-*O*-benzoyl-2,4-di-*O*-benzyl-β-D-glucopyranoside (17)

Compound **16** (284 mg, 0.50 mmol) was acetylated as described for **11**. After purification by silica gel column chromatography (toluene – EtOAc, 12:1), acetate **17** (300 mg, 98%) was obtained as a foam, $[\alpha]_D$ +9.2 (*c* 1, $CHCl_3$); R_f 0.48 (toluene – EtOAc, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–7.14 (m, 15H, 3 Ph), 6.91 (d, 2H, *J* 9.1 Hz, C_6H_4OMe), 6.63 (d, 2H, *J* 9.0 Hz, C_6H_4OMe), 5.29 (t, 1H, *J* 9.3 Hz, H-3), 4.90–4.86 (m, 2H, H-1, PhCH_2A), 4.66 (d, 1H, J_{gem} 11.9 Hz, PhCH_2B), 4.57–4.47 (m, 3H, H-6A, PhCH_2A', PhCH_2B'), 4,37 (dd, 1H, $J_{6B,5}$ 6.3 Hz, $J_{6B,6A}$ 11.8 Hz, H-6B), 3,74 (m, 1H, H-5), 3.65 (s, 3H, CH_3O), 3.62–3.53 (m, 2H, H-2, H-4), 1,84 (s, 3H, CH_3CO). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 169.9 (CH_3CO), 166.2 (Ph*C*O), 138.1, 137.3, 133.2, 129.8, 128.6, 128.4, 128.2, 128.1, 127.9 (Ar), 118.9, 114.6 ($C_6H_4OCH_3$), 102.9 (C-1), 79.1 (C-2), 76.6 (C-4), 75.6 (C-3), 74.6, 74.3 (Ph*C*H_2), 73.2 (C-5), 63.5 (C-6), 55.7 (CH_3O), 21.1 (CH_3CO). Anal. Calcd. for $C_{34}H_{34}O_8$: C, 70.58, H, 5.92. Found: C, 70.58; H, 5.74.

3.14. O-(3,6-Di-*O*-acetyl-2,4-di-*O*-benzyl-D-glucopyranosyl) *N*-phenyltrifluoroacetimidate (20)

CAN (1.00 g, 1.85 mmol) was added to a solution of **15** (203 mg, 0.369 mmol) in a mixture of CH_3CN (25 mL) and water (6.3 mL) at 0 °C. After being stirred for 10 min, the reaction mixture was diluted with EtOAc and washed with aq satd $NaHCO_3$ and water. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuum. Chromatographic purification (petroleum ether – EtOAc, 2:1) on silica gel provided 3,6-di-*O*-acetyl-2,4-di-*O*-benzyl-D-glucopyranose (129 mg, 79%) as a syrupy α,β-mixture in a ratio of 1.9:1; ^{1}H NMR

(600 MHz, $CDCl_3$): δ 7.40-7.20 (m, Ar), 5.53 (t, 1.9 H, *J* 9.4 Hz, H-3^{α}), 5.29 (t, 1H, *J* 9.4 Hz, H-3^{β}), 5.25 (d, 1.9H, $J_{1,2}$ 3.4 Hz, H-1^{α}), 4.87 (d, 1H, J_{gem} 11.9 Hz, $PhCH_2^{\beta}$), 4.83 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{1,OH}$ 4.9 Hz, H-1^{β}), 4.67-4.64 (m, 2.9H, $PhCH_2^{\alpha}$, $PhCH_2^{\beta}$), 4.61-4.55 (m, 3.8H, $2PhCH_2^{\alpha}$, $PhCH_2^{\beta}$), 4.54-4.50 (m, 2.9H, $PhCH_2^{\alpha}$, $PhCH_2^{\beta}$), 4.36 (dd, 1H, $J_{6A,5}$ 2.1Hz, $J_{6A,6B}$ 12.0 Hz, H-$6A^{\beta}$), 4.31 (dd, 1.9H, $J_{6A,5}$ 2.3 Hz, $J_{6A,6B}$ 11.8 Hz, H-$6A^{\alpha}$), 4.20-4.15 (m, 2.9H, H-$6B^{\beta}$, H-5^{α}), 3.63 (m, 1H, H-5^{β}), 3.57-3.49 (m, 3.8H, H-4^{β}, H-4^{α}, H-2^{α}), 3.31 (dd, $J_{2,3}$ 9.6 Hz, H-2^{β}), 3.18 (m, 2.9H, OH^{α}, OH^{β}), 2.07, 2.07, 1.99, 1.92 (4s, CH_3CO).

Transformation of the hemiacetal (102 mg, 0.230 mmol) into donor **20** was conducted according to the procedure described for the preparation of **6**. Pure **20** (121 mg, 86%) was isolated by column chromatography (petroleum ether – EtOAc, 10:1→8:1) as a syrupy mixture of α- and β-anomers in a ratio of 2:1; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40-7.10 (13H, Ar), 6.85 (d, 2H, $C(NPh)CF_3$), 6.25 (d, 2H, $C(NPh)CF_3$), 6.48 (br. s, 1H, H-1^{α}), 5.68 (br. s, 2H, H-1^{β}), 5.60 (t, 1H, *J* 9.6 Hz, H-3^{α}), 5.27 (t, 2H, *J* 8.5 Hz, H-3^{β}), 4.81 (d, 2H, J_{gem} 11.8 Hz, $PhCH_2^{\beta}$), 4.70 (d, 1H, J_{gem} 12.3 Hz, $PhCH_2^{\alpha}$), 4.66-4.51 (m, 9H, $3PhCH_2^{\alpha}$, $3PhCH_2^{\beta}$), 4.38-4.32 (m, 3H, H-$6A^{\alpha}$, H-$6A^{\beta}$), 4.26 (dd, 1H, $J_{6B,5}$ 4.4 Hz, $J_{6B,6A}$ 12.2 Hz, H-$6B^{\alpha}$), 4.20 (dd, 2H, $J_{6B,5}$ 4.5 Hz, $J_{6B,6A}$ 12.1 Hz, H-$6B^{\beta}$), 4.08 (m, 1H, H-5^{α}), 3.77 (br. s, 2H, H-5^{β}), 3.68-3.55 (m, 6H, H-4^{α}, H-4^{β}, H-2^{α}, H-2^{β}), 2.07, 2.05, 2.00, 1.92 (4 s, CH_3CO). HR ESI MS calcd. for $[M + Na]^+$ $C_{32}H_{32}F_3NNaO_8$: 638.1972, found: 538.1922.

3.15. *O*-(3-*O*-Acetyl-6-*O*-benzoyl-2,4-di-*O*-benzyl-D-glucopyranosyl) *N*-phenyltrifluoroacetimidate (21)

CAN (1.30 g, 2.37 mmol) was added to a solution of **17** (290 mg, 0.474 mmol) in a mixture of CH_3CN (32 mL) and H_2O (8 mL) at 0 °C. After 10 min, the reaction mixture was diluted with EtOAc and washed with aq satd $NaHCO_3$ and water. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuum. Chromatographic purification

(petroleum ether – EtOAc, 3:1) on silica gel provided 3-*O*-acetyl-6-*O*-benzoyl-2,4-di-*O*-benzyl-D-glucopyranose (186 mg, 78%) as a syrup. Data for α-anomer: R_f 0.19 (toluene – EtOAc, 6:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.10 (m, 15H, 3 Ph), 5.49 (t, 1H, *J* 9.4 Hz, H-3), 5.19 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1); 4.57–4.45 (m, 5H, H-6A, PhCH_2, PhCH_2'), 4.40 (dd, 1H, $J_{6B,5}$ 2.2 Hz, $J_{6B,6A}$ 13.8 Hz, H-6B), 4.20 (m, 1H, H-5), 3.55 (t, 1H, *J* 9.6 Hz, H-4), 3.43 (dd, 1H, $J_{2,3}$ 9.7 Hz, H-2), 1.90 (s, 3H, CH_3CO). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.0 (CH_3CO), 137.5, 137.3, 133.2, 130.0, 129.8, 128.6, 128.5, 128.1, 128.0, 127.9(Ar), 90.8 (C-1), 77.9 (C-2), 76.2 (C-4), 74.5 (PhCH_2), 73.4 (C-3), 72.8 (PhCH_2), 68.9 (C-5), 63.4 (C-6), 21.1 (CH_3CO). Data for β-anomer: R_f 0.12 (toluene – EtOAc, 6:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.10 (m, 15H, 3 Ph), 5.22 (t, 1H, *J* 9.3 Hz, H-3), 4.80 (d, 1H, J_{gem} 11.9 Hz, PhCH_2A), 4.74 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.60–4.47 (m, 3H, PhCH_2B, PhCH_2', H-6A), 4.41 (dd, 1H, $J_{6B,5}$ 2.2 Hz, $J_{6B,6A}$ 13.7 Hz, H-6B), 3.64 (m, 1H, H-5), 3.57 (t, 1H, *J* 9.1 Hz, H-4), 3.25 (dd, 1H, $J_{2,1}$ 1.9 Hz, $J_{2,3}$ 7.7 Hz, H-2), 1.82 (s, 3H, CH_3CO). ^{13}C-NMR (100,6 MHz, $CDCl_3$): δ 166.3 (Ph*C*O), 137.5, 137.3, 133.2, 129.9, 129.8, 128.5, 128.6, 128.1, 128.0, 127.8 (Ar), 97.6 (C-1), 80.3 (C-2), 76.3 (C-4), 75.6 (C-3), 74.6 (PhCH_2), 74.0 (PhCH_2), 73.1 (C-5), 63.4 (C-6), 21.0 (CH_3CO). Anal. Calcd. for $C_{29}H_{30}O_8$: C, 68.76, H, 5.97. Found: C, 68.59; H, 5.86.

Transformation of the above hemiacetal (160 mg, 0.316 mmol) into donor **21** was carried out according to the procedure described for the preparation of **6**. Pure **21** (200 mg, 93.5%) was isolated by column chromatography (petroleum ether – EtOAc, 12:1→10:1) as a syrupy α,β-mixture. Pure anomers were isolated for characterization purposes. Data for **21α**: syrup, $[\alpha]_D$ +71.4 (*c* 1, $CHCl_3$); R_f 0.21 (petroleum ether – EtOAc, 8:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05–6.70 (m, 20H, 4 Ph), 6.49 (br. s, 1H, H-1), 5.66 (t, 1H, *J* 9.6 Hz, H-3), 4.71 (d, 1H, J_{gem} 12.3 Hz, PhCH_2A), 4.67–4.59 (m, 4H, 3 PhCH_2, H-6A), 4.53 (dd, 1H, $J_{6B,5}$ 4.7 Hz, $J_{6B,6A}$ 12.2 Hz, H-6B), 3.80 (m, 1H, H-5), 3.73–3.67 (m, 2H, H-2, H-4), 1.93 (s, 3H, CH_3CO). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 169.3 (CH_3CO), 165.3 (Ph*C*O), 143.0, 137.8, 137.4, 133.3, 129.1, 128.6, 128.1, 127.7, 127.6, 127.5, 127.3, 124.2, 118.8 (Ar), 93.1 (C-1), 75.8 (C-2), 75.2 (C-4),

73.7 (Ph*C*H_2), 72.4 (C-3), 72.1 (Ph*C*H_2), 71.0 (C-5), 62.8 (C-6), 20.6 (*C*H_3CO). Data for **21β**: syrup, $[\alpha]_D$ +101.8 (*c* 1, $CHCl_3$); R_f 0,19 (petroleum ether – EtOAc, 8:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04–6.77 (m, 20H, 4 Ph), 5.77 (br. s, 1H, H-1), 5.34 (br s, 1H, H-3), 4.84 (d, 1H, J_{gem} 11.7 Hz, PhCH_2), 4.65 (d, 2H, J_{gem} 11.7 Hz, PhCH_2), 4.62–4.56 (m, 3H, 2 PhCH_2, H-6A), 4.46 (dd, 1H, $J_{6B,5}$ 4.4 Hz, $J_{6B,6A}$ 11.6 Hz, H-6B), 3.83–3.60 (m, 2H, H-5, H-4), 3.67 (t, 1H, *J* 9.4 Hz, H-2); 1,94 (s, 1H, CH_3CO). ^{13}C NMR (100.6 MHz, acetone-d_6): δ 170.1 (CH_3*C*O), 144.0, 139.1, 139.0, 134.1, 130.4, 129.7, 129.5, 129.2, 128.9, 128.7, 128.6, 125.3, 120.1 (Ar), 98.1 (C-1), 79.6 (C-2), 77.0 (C-4), 76.0 (C-3), 75.0, 74.7 ($PhCH_2$, C-5), 63.9 (C-6), 21.1 (*C*H_3CO). HR ESI MS for the anomeric mixture calcd. for $[M + Na]^+$ $C_{37}H_{34}F_3NNaO_8$: 700.2129, found: 700.2133.

3.16. *p*-Methoxyphenyl 3-*O*-benzoyl-2,4-di-*O*-benzyl-β-D-glucopyranoside (13)

Acceptor **13** (551 mg, 91%) was prepared from compound **12** (600 mg, 1.06 mmol) according to the procedure described for **14**. The product was purified by silica gel column chromatography (toluene – EtOAc, 15:1). Data for **13**: white crystals, mp 131–132 °C; $[\alpha]_D$ +31.5 (*c* 1, $CHCl_3$); R_f 0.19 (petroleum ether – EtOAc, 3:1), ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00–7.05 (m, 15H, 3 Ph), 7.03 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 6.89 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.62 (t, 1H, *J* 9.4 Hz, H-3), 5.10 (d, 1H, $J_{2,1}$ 7.7 Hz, H-1), 4.88 (d, 1H, J_{gem} 11.7 Hz, PhCH_2A), 4.72 (d, 1H, PhCH_2B), 4.60–4.55 (m, 2H, PhCH_2), 3.94 (ddd, 1H, $J_{5,6A}$ 2.6 Hz, $J_{6A,6B}$ 12.2 Hz, $J_{6A,OH}$ 5.1 Hz, H-6A), 3.84 (t, 1H, *J* 9.5 H, H-4), 3.82–3.77 (m, 4H, H-6B, CH_3O), 3.72 (dd, 1H, $J_{2,1}$ 7.7 Hz, $J_{2,3}$ 9.4 Hz, H-2), 3.60 (m, 1H, H-5) 1.90 (dd, 1H, $J_{OH,6A}$ 5.1 Hz, $J_{OH,6B}$ 8.1 Hz, OH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 165.5 (Ph*C*O), 137.6, 137.3, 133.1, 133.0, 129.8, 128.4, 128.3, 128.2, 127.9, 127.6 (Ar), 118.4, 114.8 ($C_6H_4OCH_3$), 102.6 (C-1), 78.6 (C-2), 76.1(C-3), 75.5 (C-4), 75.2 (C-5), 74.6 (Ph*C*H_2), 74.1 (Ph*C*H_2), 61.7 (C-6), 55.7 (CH_3O).). Anal. Calcd. for $C_{34}H_{34}O_8$: C, 71.56, H, 6.01. Found: C, 71.31; H, 5.99.

3.17. Ethyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl sulfoxide (26)

m-Chloroperbenzoic acid (63 mg, 0.365 mmol) was added to a solution of **22** (213 mg, 0.365 mmol) in CH_2Cl_2 (3.5 mL) at –78 °C. The reaction mixture was allowed to attain slowly –15 °C and kept at this temperature until TLC showed disappearance of the starting material. Then the reaction was quenched with Na_2SO_3 (92 mg, 0.73 mmol) and Et_3N (74 mg, 0.73 mmol). The resulting mixture was diluted with CH_2Cl_2 and washed with aq satd $NaHCO_3$ and water. The solvent was removed under reduced pressure and the product **26** (193 mg, 88%) was obtained by column chromatography (toluene – EtOAc, 4:1→3:1) as a mixture of two isomers. Individual isomers were isolated for characterization purposes. Data for isomer 1: crystalline solid, mp 105-107 °C; $[\alpha]_D$ +5.7 (*c* 1, $CHCl_3$); R_f 0.40 (toluene – EtOAc, 2:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40–7.18 (m, 20H, 4 Ph), 4.95–4.87 (m, 3H, PhCH_2), 4.86–4.79 (m, 2H, PhCH_2), 4.63–4.55 (m, 3H, PhCH_2), 4.32 (d, 1H, $J_{1,2}$ 8.9 Hz, H-1), 3.95 (t, 1H, *J* 8.5 Hz, H-2), 3.88 (t, 1H, *J* 8.3 Hz, H-3), 3,75 (br. d, 1H, $J_{6A,6B}$ 10.9 Hz, H-6A), 3.70 (dd, 1H, $J_{5,6B}$ 4.3 Hz, H-6B) 3.67 (t, 1H, *J* 9.5 Hz, H-4), 3.61 (m, 1H, H-5), 3.06 (m, 1H, S(O)CH_2CH$_3$A), 2,67 (m, 1H, S(O)CH_2CH$_3$B), 1.33 (t, 3H, *J* 7.7 Hz, S(O)CH$_2$CH_3). ^{13}C NMR (150,9 MHz, $CDCl_3$): δ 138.1, 138.0, 137.95, 137.8, 128.5, 128.4, 128.0, 127.9, 127.7, 127.7 (Ar), 92.3 (C-1), 86.3 (C-3), 79.4 (C-5), 76.3 (C-2), 75.4, 74.9, 74.6, 73.5 (PhCH_2), 68.6 (C-6), 41.2 (S(O)CH$_2$CH$_3$), 7.3 (S(O)CH$_2$$CH_3$). Data for isomer 2: crystalline solid, mp 127-129 °C; $[\alpha]_D$ –29.1 (*c* 1, $CHCl_3$); R_f 0.31 (toluene – EtOAc, 3:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40–7.18 (m, 20H, 4 Ph), 5.00–4.90 (m, 4H, PhCH_2), 4.84 (d, 1H, J_{gem} 10.9 Hz, PhCH_2), 4.61–4.55 (m, 2H, PhCH_2), 4.08 (t, 1H, *J* 9.4 Hz, H-2), 3.94 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1), 3.87 (t, 1H, *J* 8.2 Hz, H-3), 3.77 (t, 1H, 10.8 Hz, H-6A), 3.68 (dd, $J_{6B,6A}$ 10.8 Hz, 1H, $J_{6B,5}$ 4.8 Hz, H-6B), 3.62–3.57 (m, 2H, H-5, H-4), 3.19 (m, 1H, S(O)CH_2CH$_3$), 2.86 (m, 1H, S(O)CH_2CH$_3$), 1.34 (t, 3H, *J* 7.7 Hz, S(O)CH$_2$CH_3). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 138.2, 138.0, 137.6, 128.9, 128.5, 128.4, 128.3, 128.1, 128.0, 127.7, 127.6 (Ar), 89.1 (C-1), 86.6 (C-3), 80.2 (C-5), 77.6 (C-4), 76.1 (C-2), 75.7, 75.2, 73.5 (PhCH$_2$), 69.1 (C-6), 40.9 (S(O)CH$_2$CH$_3$), 7.4 (S(O)CH$_2$$CH_3$). Anal. for the mixture of the isomers. Calcd. for $C_{36}H_{40}O_6S$: C, 71.97, H, 6.71. Found: C, 71.81; H, 6.81.

3.18 Ethyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl sulfoxide (27)

Oxidation of the thioglucoside **23** (120 mg, 0.243 mmol) according to the procedure described for the preparation of **26** and purification by silica gel column chromatography (toluene – EtOAc, 3:1→2:1) provided **27** (122 mg, 98%) as a mixture of two isomers. Individual isomers were isolated for characterization purposes. Data for isomer 1: crystalline solid, mp 148-150 °C; $[\alpha]_D$ –27.9 (*c* 1, $CHCl_3$); R_f 0.24 (toluene – EtOAc, 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50–7.25 (m, 15H, 3 Ph), 5.60 (s, 1H, PhC*H*), 5.05–4.99 (m, 2H, 2PhCH_2), 4.90–4.84 (m, 2H, 2PhCH_2), 4.37 (dd, 1H, $J_{6A,6B}$ 10.5 Hz, $J_{6A,5}$ 4.9 Hz, H-6A), 4.14 (t, 1H, *J* 9.4 Hz, H-2), 4.03 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1), 3.97 (t, 1H, *J* 9.1 Hz, H-3), 3.93 (t, *J* 10.3 Hz, H-6B), 3.82 (t, 1H, *J* 9.3 Hz, H-4), 3.56 (m, 1H, H-5), 3.15 (m, 1H, S(O)C$H_2$$CH_3$), 2.81 (m, 1H, S(O)C$H_2$$CH_3$), 1.34 (t, 3H, *J* 7.6 Hz, S(O)CH_2CH_3). ^{13}C NMR (150.9 MHz, $CDCl_3$): *δ* 138.2, 137.6, 137.0, 129.0, 128.4, 128.3, 128.0, 127.9, 127.7, 126.0 (Ar), 101.3 (Ph*C*H), 89.4 (C-1), 82.6 (C-3), 81.1 (C-4), 76.1 (Ph*C*H_2), 75.5 (C-2), 75.0 (Ph*C*H_2), 71.2 (C-5), 68.2 (C-6), 41.0 (S(O)*C*$H_2$$CH_3$), 7.4 (S(O)$CH_2$*C*$H_3$). Data for isomer 2: crystalline solid, mp 184-186 °C; $[\alpha]_D$ –44.3 (*c* 1, $CHCl_3$); R_f 0.09 (toluene – EtOAc, 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50–7.25 (m, 15H, 3 Ph), 5.62 (s, 1H, Ph*C*H), 5.03 (d, 1H, J_{gem} 11.2 Hz, PhCH_2A), 4.94 (d, 1H, J_{gem} 10.6 Hz, PhCH_2A'), 4.87 (d, 1H, PhCH_2B), 4.83 (d, 1H, PhCH_2B'), 4.43–4.37 (m, 2H, H-6A, H-1), 4.05–4.00 (m, 2H, H-3, H-2), 3.80–3.72 (m, 2H, H-6B, H-4), 3.58 (m, 1H, H-5), 3.04 (m, 1H, S(O)C$H_2$$CH_3$), 2.61 (m, 1H, S(O)*C*$H_2$$CH_3$), 1.28 (t, 3H, S(O)$CH_2$*C*$H_3$). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 138.1, 137.4, 137.0, 129.0, 128.9, 128.5, 128.41, 128.36, 128.3, 128.0, 127.9, 127.8, 126.0 (Ar), 101.2 (Ph*C*H), 92.2 (C-1), 82.9 (C-3), 81.2 (C-4), 75.1 (C-2), 74.9 74.8 (2 Ph*C*H_2), 70.4 (C-5), 68.4 (C-6), 42.2 (S(O)*C*$H_2$$CH_3$), 7.4 (S(O)$CH_2$*C*$H_3$). Anal. for the mixture of the isomers. Calcd. for $C_{29}H_{32}O_6S$: C, 68.48, H, 6.34. Found: C, 68.40; H, 6.27.

3.19. Ethyl 3-*O*-acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl sulfoxide (28)

Sulfoxide **28** (137 mg, 86%) was prepared from **24** (154 mg, 0.347 mmol) according to the procedure described for **26**. The product was obtained by silica gel column chromatography (toluene – EtOAc, 2:1→1:1) as a mixture of two isomers. Individual isomers were isolated for characterization purposes. Data for isomer 1: $[\alpha]_D$ –20,8 (*c* 1, $CHCl_3$); R_f 0.30 (toluene – EtOAc, 2.5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50–7.28 (m, 10H, 2 Ph), 5.55 (t, 1H, *J* 9.3 Hz, H-3), 5.50 (s, 1H, PhC*H*), 4.91 (d, 1H, J_{gem} 11.1 Hz, PhCH_2A), 4.76 (d, 1H, PhCH_2B), 4.38 (dd, 1H, $J_{6A,6B}$ 10.4 Hz, H-6A), 4.22 (t, *J* 9.4 Hz, 1H, H-2), 4.14 (d, 1H, $J_{1,2}$ 9.7 Hz, H-1), 3.88 (t, 1H, *J* 10.2 Hz, H-6B), 3.72 (t, 1H, *J* 9.5 Hz, H-4), 3.66 (m, 1H, H-5), 3.22 (m, 1H, S(O)CH_2CH$_3$), 2.87 (m, 1H, S(O)CH_2CH$_3$), 2.05 (s, 3H, CH_3CO), 1.39 (t, 3H, *J* 7.5 Hz, S(O)CH$_2$CH_3). ^{13}C-NMR (150.9 MHz, $CDCl_3$): δ 169.9 (CH$_3$*C*O),137.1, 136.7, 133.5, 130.2, 129.8, 129.1, 128.5, 128.2, 128.2, 126.1 (Ar), 101.5 (Ph*C*H), 89.3 (C-1), 78.0 (C-4), 75.8 (Ph*C*H$_2$), 74.7 (C-2), 74.4 (C-3), 71.3 (C-5), 68.1 (C-6), 40.1 (S(O)*C*H$_2$CH$_3$), 20.9 (*C*H$_3$CO), 7.4 (S(O)CH$_2$*C*H$_3$). Data for isomer 2: $[\alpha]_D$ –91.1 (*c* 1, $CHCl_3$); R_f 0.15 (toluene – EtOAc, 2.5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50–7.28 (m, 10H, 2 Ph), 5.59 (t, 1H, *J* 8.3 Hz, H-3), 5.52 (s, 1H, PhC*H*), 4.90 (d, 1H, J_{gem} 10.2 Hz, PhCH_2), 4.76 (d, 1H, PhCH_2B), 4.45 (d, 1H, $J_{1,2}$ 8,5 Hz, H-1), 4.40 (dd, 1H, $J_{6A,5}$ 3.7 Hz, $J_{6A,6B}$ 10.3 Hz, H-6A), 4.24 (t, 1H, *J* 8.3 Hz, H-2), 3.77 (t, 1H, *J* 10.2 Hz, H-6B), 3.73–3.67 (m, 2H, H-5, H-4), 3.08 (m, 1H, S(O)CH_2CH$_3$A), 2.78 (m, 1H, S(O)CH_2CH$_3$B), 2.10 (s, 3H, *C*H$_3$CO), 1.32 (t, 3H, *J* 7.5 Hz, S(O)CH$_2$CH_3). ^{13}C NMR (150,9 MHz, $CDCl_3$): δ 169.9 (CH$_3$*C*O),137.1, 136.7, 129.1, 128.5, 128.2, 128.1, 126.1 (Ar), 101.5 (Ph*C*H), 92.0 (C-1), 78.1 (C-4), 74.8 (C-3), 74.6 (Ph*C*H$_2$), 74.2 (C-2), 70.2 (C-5), 68.4 (C-6), 43.2 (S(O)*C*H$_2$CH$_3$), 20.9 (*C*H$_3$CO), 7.5 (S(O)CH$_2$*C*H$_3$). Anal. for the mixture of the isomers. Calcd. for $C_{24}H_{28}O_7S$: C, 62.59, H, 6.13. Found: C, 62.54, H, 6.30.

3.20. Ethyl 3,6-di-*O*-acetyl-2,4-di-*O*-benzyl-β-D-glucopyranosyl sulfoxide (29)

Thioglucoside **25** (111 mg, 0.227 mmol) was oxidized according to the procedure described for **26**. The product **29** (100 mg, 88%) was obtained by silica gel column

chromatography (toluene – EtOAc, 2:1→1:1) as a mixture of two isomers. Individual isomers were isolated for characterization purposes. Data for isomer 1: crystalline solid, mp 127-129 °C; $[\alpha]_D$ –29.9 (*c* 1, $CHCl_3$); R_f 0.30 (toluene – EtOAc, 1:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40–7.25 (m, 10H, 2 Ph), 5.47 (t, 1H, *J* 9.2 Hz, H-3), 4.81 (d, 1H, J_{gem} 10.9 Hz, PhCH_2A), 4.68 (d, 1H, PhCH_2B), 4.62 (d, 1H, J_{gem} 11.2 Hz, PhCH_2A'), 4.57 (d, 1H, PhCH_2B'), 4.43 (dd, 1H, $J_{6A,5}$ 2.1 Hz, $J_{6A,6B}$ 12.1 Hz, H-6A), 4.19 (dd, 1H, $J_{6B,5}$ 5.7 Hz, H-6B), 4.06 (t, 1H, *J* 9.5 Hz, H-2), 4.00 (d, 1H, $J_{1,2}$ 9.7 Hz, H-1), 3.69 (m 1H, H-5), 3.60 (t, 1H, *J* 9.4 Hz, H-4), 3.14 (m, 1H, S(O)CH_2CH$_3$A), 2.86 (m, 1H, S(O)CH_2CH$_3$B), 2.09 (s, 3H, CH_3CO), 1.95 (s, 3H, CH_3CO); 1,34 (t, 3H, *J* 7.6 Hz, S(O)CH$_2$CH_3). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 170.5, 169.9 (2 CH_3*C*O), 137.2, 137.0, 128.6, 128.5, 128.2, 128.11, 128.06 (Ar), 88.7 (C-1), 78.0 (C-5), 77.2 (C-3), 75.7 (C-4), 75.4 (Ph*C*H$_2$), 74.8 (Ph*C*H$_2$), 74.4 (C-2), 62.7 (C-6), 40.9 (S(O)*C*H$_2$CH$_3$), 21.0, 20.8 (2 *C*H$_3$CO), 7.3 (S(O)CH$_2$*C*H$_3$). Data for isomer 2: crystalline solid, mp 161-164 °C; $[\alpha]_D$ +35.1 (*c* 1, $CHCl_3$); R_f 0.15 (toluene – EtOAc, 1:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40–7.25 (m, 10H, 2 Ph), 5.50 (t, 1H, *J* 8.2 Hz, H-3), 4.87 (d, 1H, J_{gem} 10.8 Hz, PhCH_2A), 4.69 (d, 1H, PhCH_2B), 4.64 (d, 1H, J_{gem} 11.2 Hz, PhCH_2A'), 4.58 (d, 1H, PhCH_2B'), 4.37 (dd, 1H, $J_{6A,5}$ 2.1 Hz, $J_{6A,6B}$ 12.3 Hz, H-6A), 4.35 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.20 (dd, 1H, $J_{6B,5}$ 4.9 Hz, H-6B), 4.13 (t, *J* 8.1 Hz, 1H, H-2), 3,75 (m 1H, H-5), 3.61 (t, 1H, *J* 8.4 Hz, H-4), 3.03 (m, 1H, S(O)CH_2CH$_3$A), 2.78 (m, 1H, S(O)CH_2CH$_3$B), 2.08 (s, 3H, CH_3CO), 2.01 (s, 3H, CH_3CO), 1.31 (t, 3H, *J* 7.5 Hz, S(O)CH$_2$CH_3). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 170.5, 169.9 (2 CH_3CO), 137.1, 128.6, 128.5, 128.2, 128.1, 128.0 (Ar), 91.7 (C-1). 77.0 (C-5), 76.7 (C-3), 75.3 (C-4), 74.4 (C-3), 74.3 (Ph*C*H$_2$), 74.2 (Ph*C*H$_2$, C-2), 62.7 (C-6), 43.1 (S(O)*C*H$_2$CH$_3$), 21.0, 20.8 (2 *C*H$_3$CO), 7.3 (S(O)CH$_2$*C*H$_3$). Anal. for the mixture of the isomers. Calcd. for $C_{26}H_{32}O_8S$: C, 61.89, H, 6.39. Found: C, 62.18; H, 6.25.

3.21. General procedure A: glycosylation by *N*-phenyltrifluoracetimidoyl donors

A solution of a glycosyl acceptor (1 equiv.) and an *N*-phenyltrifluoracetimidoyl donor (1.2 equiv.) in anhydrous CH_2Cl_2 (12 mL/1 mmol of the donor) was stirred with MS AW 300 (100 mg/1 mL of CH_2Cl_2) at rt for 1 h, cooled to –35 °C, and MeOTf (0.12 equiv.) was added. The reaction mixture was stirred at –35 °C for 5 min and then the temperature was increased to –15 °C within 30 min. By that time TLC showed that the reaction was completed. It was quenched by adding MeOH (2.3 equiv.) and triethylamine (2.3 equiv.). The resulting mixture was diluted with CH_2Cl_2, the solids were filtered off through a pad of Celite, washed with CH_2Cl_2, and the combined filtrates were washed with aq satd $NaHCO_3$ and water. The organic solution was dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. A disaccharide as a mixture of anomers was isolated by conventional silica gel column chromatography using elution with a gradient of EtOAc in petroleum ether. The ratio of the anomers (see Table 1) was determined by analytical HPLC, and the individual α- and β-disaccharides were isolated by preparative HPLC. Appropriate hexane – EtOAc mixtures were used as eluents.

3.22. General procedure B: glycosylation by sulfoxide donors

A solution of a glycosyl sulfoxide (1 equiv.) and 2,6-di-tert-butyl-4-methylpyridine (2 equiv.) in anhydrous CH_2Cl_2 (44 mL/1 mmol of the sulfoxide) was cooled to –78 °C and Tf_2O (1.1 equiv.) was added. After a few minutes, a solution of a glycosyl acceptor (2 equiv.) in dichloromethane (7 mL/1 mmol of the acceptor; total volume of CH_2Cl_2 corresponded to 0.02 M concentration of the glycosyl donor) was added. The reaction temperature was raised to 0 °C within 5 min, then the mixture was quenched by adding aq satd $NaHCO_3$, diluted with CH_2Cl_2, and the organic layer was washed with aq satd $NaHCO_3$ solution and water. The organic solution was dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. Determination of the α,β-ratio and isolation of the individual anomers were carried out as described in General procedure A.

3.23. Ethyl tetra-2,3,4,6-*O*-benzyl-α- and β-D-glucopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranosides (31α,β)

The title compounds were obtained according to General procedure A (table 1, entry 1) and General procedure B (entry 19).

Data for **31α**: white foam, $[\alpha]_D$ +31.4 (*c* 1, $CHCl_3$); R_f 0.43 (petroleum ether – EtOAc, 4:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40–6.96 (m, 30H, 6 Ph), 5.69 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1^b), 5.46 (s, 1H, PhC*H*), 5.03 (d, 1H, J_{gem} 10.9 Hz, PhCH_2A), 4.95 (d, 1H, J_{gem} 9.6Hz, PhCH_2A'), 4.87–4.82 (m, 2H, PhCH_2B, PhCH_2A''), 4.69 (d, 1H, PhCH_2B'), 4.60 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1^a), 4.59 (d, 1H, J_{gem} 12.4 Hz, PhCH_2A'''), 4.50 (d, 1H, J_{gem} 12.1 Hz, PhCH_2A''''), 4.39–4.36 (m, 2H, PhCH_2B'', PhCH_2B'''), 4.34 (dd, 1H, $J_{5,6A}$ 5.1 Hz, $J_{6A,6B}$ 10.5Hz, H-6A^a), 4.20 (d, 1H, PhCH_2B'''') 4.17 (t, 1H, *J* 9.2 Hz, H-3^a), 4.07 (m, 1H, H-5^b), 4.01 (t, 1H, *J* 9.4 Hz, H-3^b), 3.87 (t, 1H, *J* 9.4 Hz, H-4^a), 3.78 (t, 1H, *J* 10.2 Hz, H-3^a), 3.66 (t, *J* 9.6 Hz, 1H, H-4^b), 3.58–3.48 (m, 3H, H-2^a, H-5^a, H-2^b), 3.33 (dd, 1H, $J_{5,6A}$ 2.3 Hz, $J_{6A,6B}$ 10.9 Hz, H-6A^b), 3.29 (dd, 1H, $J_{5,6B}$ 1.7 Hz, H-6B^b), 2.81 (m, 2H, SCH_2CH$_3$), 1.36 (t, 3H, *J* 7.4 Hz, SCH$_2$CH_3). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 138.9, 138.8, 137.9, 137.8, 137.3, 136.9, 129.4, 128.8, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.5, 127,4, 126.4 (Ar), 102.0 (Ph*C*H), 96.1 (C-1^b), 86.1 (C-1^a), 82.4 (C-4^a), 81.7 (C-2^b), 79.7 (C-2^a), 78.8 (C-2^b), 77.6 (C-4^b), 76.6 (C-3^a), 76.0, 75.6, 75.1, 73.3, 71.2 (5 Ph*C*H$_2$), 69.9 (C-5^a), 69.8 (C-5^b), 68.9 (C-6^a), 67.9 (C-6^b), 25.1 (S*C*H$_2$CH$_3$), 15.1 (SCH$_2$*C*H$_3$). HR ESI MS calcd. for $[M + Na]^+$ $C_{56}H_{60}NaO_{10}S$ 947.3799, found 947.3808

Data for **31 β**: white foam, $[\alpha]_D$ –1.6 (*c* 1, $CHCl_3$), R_f 0.40 (petroleum ether – EtOAc, 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46–7.14 (m, 30H, 5 Ph), 5.50 (s, 1H, PhC*H*), 4.99 (d, 1H, J_{gem} 11.0 Hz, PhCH_2A), 4.93–4.88 (m, 2H, PhCH_2A', H-1^b), 4.83–4.73 (m, 5H, PhCH_2B, PhCH_2B', PhCH_2A'', PhCH_2B'', PhCH_2A'''), 4.56 (d, 1H, $J_{1,2}$ 9.9 Hz, H-1^a), 4.53 (d, 1H, J_{gem} 10.6 Hz, PhCH_2B'''), 4.50, 4.47 (2 d, 2H, J_{gem} 12.3 PhCH_2''''), 4.32 (dd, 1H, $J_{5,6A}$ 4.9 Hz, $J_{6A,6B}$ 10.5 Hz, H-6A^a), 4.15 (t, 1H, *J* 9.0 Hz, H-3^a), 3.78–3.72 (m, 2H, H-4^a, H-6B^a), 3.65–3.48 (m,

6H, 2H-6^b, H-4^b, H-3^b, H-2^a, H-2^b), 3.42 (m, 1H, $J_{5,6A}$ 4.8 Hz, H-5^a), 3.27 (m, 1H, H-5^b), 3.78 (m, 2H, SCH_2CH$_3$), 1.35 (t, 3H, J 7.5 Hz, SCH$_2$CH_3). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 138.6, 138.5, 138.4, 138.1, 137.0, 137.3, 128.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 126.2 (Ar), 102.1 (C-1^b), 101.3 (Ph*C*H), 85.8 (C-1^a), 84.9 (C-3^b), 83.0 (C-2^b), 81.9 (C-2^a), 79.9 (C-3^a), 79.3 (C-4^a), 78.1 (C-4^b), 75.6, 75.3, 75.1 (3 Ph*C*H$_2$), 74.9 (C-5^b), 74.8, 73.6 (2 Ph*C*H$_2$), 70.6 (C-5^a), 69.0 (C-6^b), 68.7 (C-6^a), 25.2 (S*C*H$_2$CH$_3$), 15.1 (SCH$_2$*C*H$_3$). HR ESI MS calcd. for $[M + NH_4]^+$ $C_{56}H_{64}NO_{10}S$ 942.4245, found 942.4282.

3.24. Ethyl 3-*O*-acetyl-2,4,6-tri-*O*-benzyl-α- and β-D-glucopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranosides (32α,β)

The title compounds were obtained according to General procedure A (table 1, entry 2).

Data for **32α**: white foam, $[\alpha]_D$ +58.4 (*c* 1, $CHCl_3$); R_f 0.13 (petroleum ether – EtOAc, 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41–6.38 (d, 25H, 5 Ph), 5.69 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1^b), 5.56 (t, 1H, J 9.7 Hz, H-3^b), 5.43 (s, 1H, PhC*H*), 4.99 (d, 1H, J_{gem} 9.7 Hz, PhCH_2A), 4.71 (d, 1H, J_{gem} 9.6 Hz, PhCH_2B), 4.60 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1^a), 4.56–4.50 (m, 2H, PhCH_2A', PhCH_2A''), 4.47 (d, 1H, J_{gem} 11.1Hz, PhCH_2A'''), 4.33 (dd, 1H, $J_{6A,6B}$ 10.5 Hz, $J_{6A,5}$ 5.0 Hz, H-6A^a), 4.30 (d, 1H, PhCH_2B'''), 4.22 (d, 1H, PhCH_2B''), 4.17 (d, 1H, PhCH_2B'''), 4.13 (t, 1H, J 9.1 Hz, H-3^a), 4.07 (m, 1H, $J_{5,4}$ 10.1 Hz, H-5^b), 3.84 (t, 1H, J 9.5 Hz, H-4^a), 3.77 (t, 1H, J 10.3Hz, H-6B^a), 3.63 (t, 1H, J 9.7 Hz, H-4^b), 3.57 (t, 1H, J 9.4 Hz, H-2^a), 3.51 (m, 1H, $J_{5,4}$ 9.6 Hz, $J_{5,6A}$ 5,1 Hz, H-5^a), 3.36 (dd, 1H, $J_{2,1}$ 3.6 Hz, $J_{2,3}$ 10.2 Hz, H-2^b), 3.24 (dd, 1H, $J_{5,6A}$ 2.0 Hz, $J_{6A,6B}$ 10.9 Hz, H-6A^b), 3.19 (dd, 1H, $J_{5,6B}$ 2.5 Hz, H-6B^b), 2.81 (m, 2H, SCH_2CH$_3$), 1.36 (t, 3H, J 7.3 Hz, SCH$_3$CH_3), 1.98 (s, 3H, CH$_3$CO). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 169.9 (CH$_3$*C*O), 138.3, 137.8, 137.6, 137.3, 137.0, 129.4, 128.8, 128.4, 128.2, 128.1, 128.0, 127.7, 127.6, 127.5, 127.2, 126.4 (Ar), 102.0 (Ph*C*H), 95.7 (C-1^b), 86.0 (C-1^a), 82.1 (C-4^a), 79.3 (C-2^a), 76.8 (C-3^a), 76.0, 75.9, 74.8 (C-2^b, C-4^b, Ph*C*H$_2$), 74.4 (Ph*C*H$_2$), 73.45, 73.39 (C-3^b, Ph*C*H$_2$), 70.5 (Ph*C*H$_2$), 69.9

(C-5[a]), 69.5 (C-5[b]), 68.9 (C-6[a]), 67.6 (C-6[b]), 24.9 (S*C*H$_2$CH$_3$), 21.1 (*C*H$_3$*C*O), 15.1 (SCH$_2$*C*H$_3$). HR ESI MS calcd. for [M + NH$_4$]$^+$ $C_{51}H_{60}NO_{11}S$ 894.3882, found 894.3890.

Data for **32β**: white foam, $[\alpha]_D$ +5.4 (*c* 1, CHCl$_3$); R_f 0.21 (petroleum ether – EtOAc, 5:1); ^{1}H NMR (600 MHz, CDCl$_3$): 7.46-7.14 (m, 25H, 5 Ph), 5.49 (s, 1H, PhC*H*), 5.21 (t, 1H, *J* 9.6 Hz, H-3[b]), 4.95 (d, 1H, $J_{1,2}$ 7.9 Hz H-1[b]), 4.91 (d, 1H, J_{gem} 11.8 Hz, PhC*H*$_2$A), 4.86 (d, 1H, J_{gem} 9.6 Hz, PhC*H*$_2$A'), 4.77 (d, 1H, PhC*H*$_2$B'), 4.61 (d, 1H, PhC*H*$_2$B), 4.58 (d, 1H, $J_{1,2}$ 9.9 Hz, H-1[a]), 4.51–4.44 (m, 4H, 2 PhCH$_2$), 4.33 (dd, 1H, $J_{6Aa,5a}$ 4.9 Hz, $J_{6Aa,6Ba}$ 10.4 Hz, H-6A[a]), 4.14 (t, 1H, *J* 8.8 Hz, H-3[a]), 3.76 (t, 1H, *J* 10.2 Hz, H-6B[a]), 3.74 (t, 1H, *J* 9.5 Hz, H-4[a]), 3.63 (t, 1H, *J* 9.6 Hz, H-4[b]), 3.61–3.56 (m, 2H, 2 H-6[b]), 3.53 (dd, 1H, $J_{2,3}$ 8.5 Hz, $J_{2,1}$ 9.7 Hz, H-2[a]), 3.44 (m, 1H, $J_{5,4}$ 9.7 Hz, $J_{5,6A}$ 4.9 Hz, H-5[a]), 3.42 (dd, 1H, $J_{2,1}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2[b]), 3.27 (m, 1H, H-5[b]), 2.80 (m, 2H, SC*H*$_2$CH$_3$), 1.85 (s, 3H, CH$_3$CO), 1.35 (t, 3H, *J* 7.3 Hz, SCH$_3$C*H*$_3$). ^{13}C NMR (150.9 MHz, CDCl$_3$): δ 169.9 (CH$_3$*C*O), 138.3, 137.9, 137.7, 137.2, 128.9, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.4, 126.2 (Ar), 102.3 (C-1[b]), 101.4 (Ph*C*H), 85.8 (C-1[a]), 81.8 (C-2[a]), 80.4 (C-2[b]), 80.1 (C-3[a]), 79.4 (C-4[a]), 76.2 (C-4[b]), 75.7 (C-3[b]), 75.3 (PhCH$_2$), 74.7 (C-5[b]), 74.5, 74.1, 73.6 (3 Ph*C*H$_2$), 70.5 (C-5[a]), 68.7 (C-6[a]), 68.5 (C-6[b]), 25.3 (S*C*H$_2$CH$_3$), 21.0 (*C*H$_3$*C*O), 15.1 (SCH$_2$*C*H$_3$). HR ESI MS calcd. for [M + NH$_4$]$^+$ $C_{51}H_{60}NO_{11}S$ 894.3882, found 894.3911.

3.25. Ethyl 3,6-di-*O*-acetyl-2,4-di-*O*-benzyl-α- and β-D-glucopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranosides (33α,β)

The title compounds were obtained according to General procedure A (table 1, entry 3) and General procedure B (entry 20).

For **33α**: white foam, $[\alpha]_D$ +6.7 (*c* 0.5, CHCl$_3$); R_f 0.30 (petroleum ether – EtOAc, 3:1); ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.42–6.90 (m, 20H, 4 Ph), 5.63 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1[b]), 5.59 (t, 1H, *J* 9.8 Hz, H-3[b]), 5.43 (s, 1H, PhC*H*), 5.04 (d, 1H, J_{gem} 9.8 Hz, PhC*H*$_2$A), 4.70 (d, 1H, PhC*H*$_2$B), 4,62 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1[a]), 4.56 (d, 1H, J_{gem} 12.6 Hz, PhC*H*$_2$A'), 4.53 (d, 1H, J_{gem}

11.1 Hz, PhCH_2A''), 4.40 (d, 1H, PhCH_2B''), 4.35 (dd, 1H, $J_{5,6A}$ 5.0 Hz, $J_{6A,6B}$ 10.7 Hz, H-6A[a]), 4.18–4.12 (m, 2H, H-5[b], PhCH_2B'), 4.11 (t, 1H, 9.1 Hz, H-3[a]), 3.90 (br. d, 1H, $J_{6A,6B}$ 12.4 Hz, H-6A[b]), 3.85 (t, 1H, *J* 9.4 Hz, H-4[a]), 3.76 (t, 1H, *J* 10.4 Hz, H-6B[a]), 3.74 (dd, 1H, $J_{5,6B}$ 2.7 Hz, H-6B[b]), 3.57 (t, 1H, *J* 9.6 Hz, H-2[a]), 3.53 (m, $J_{5,4}$ 9.6 Hz,1H, H-5[a]), 3.48 (t, 1H, *J* 9.7 Hz, H-4[b]), 3.33 (dd, 1H, $J_{2,1}$ 3.5 Hz, $J_{2,3}$ 10.2 Hz, H-2[b]), 2.79 (m, 2H, SCH_2CH$_3$), 2.01 (s, 3H, CH$_3$O), 1.96 (s, 3H, CH$_3$O), 1.38 (t, 3H, SCH$_2$CH_3). ^{13}C NMR (150.9 MHz, CDCl$_3$): δ 170.4, 169.8 (CH$_3$*C*O), 137.8, 137.6, 137.2, 137.0, 129.5, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.5, 127.2, 126.5, 126.1 (Ar), 102.2 (Ph*C*H), 95.5 (C-1[b]), 86.0 (C-1[a]), 82.1 (C-4[a]), 79.3 (C-2[a]), 77.0 (C-3[a]), 75.9 (Ph*C*H$_2$), 75.8 (C-2[b]), 75.7 (C-4[b]), 74.5 (Ph*C*H$_2$), 73.4 (C-3[b]), 70.5 (Ph*C*H$_2$), 69.9 (C-5[a]), 68.9 (C-6[a]), 68.2 (C-5[b]), 62.2 (C-6[b]), 25.0 (SCH$_2$CH$_3$), 21.1, 20.8 (2 *C*H$_3$CO), 15.1 (SCH$_2$*C*H$_3$). HR ESI MS calcd. for [M + NH$_4$]$^+$ $C_{46}H_{56}NO_{12}S$: 846.3518, found: 846.3518.

Data for **33β**: white foam, $[\alpha]_D$ +73.0 (*c* 1, CHCl$_3$); R_f 0.36 (petroleum ether – EtOAc, 3:1); ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.50–7.20 (m, 20H, 4 Ph), 5.58 (s, 1H, PhC*H*), 5.26 (t, 1H, *J* 9.3 Hz, H-3[b]), 4.97 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1[b]), 4.92 (d, 1H, J_{gem} 11.8 Hz, PhCH_2A), 4.84 (d, 1H, J_{gem} 9.2 Hz, PhCH_2A'), 4.73 (d, 1H, PhCH_2B'), 4.64 (d, 1H, PhCH_2B), 4.58 (d, 1H, $J_{1,2}$ 9.9 Hz, H-1[a]), 4.51 (d, 1H, J_{gem} 11.1 Hz, PhCH_2A''), 4.47 (d, 1H, PhCH_2B''), 4.34 (dd, 1H, $J_{5,6A}$ 4.9 Hz, $J_{6A,6B}$ 10.4 Hz, H-6A[a]), 4.25 (br. d, 1H, $J_{6A,6B}$ 12.0 Hz, H-6A[b]), 4.15-4.10 (m, 2H, H-6B[b], H-3[a]), 3.80 (t, 1H, *J* 10.3 Hz, H-6B[a]), 3.71 (t, 1H, *J* 9.8 Hz, H-4[a]), 3.56 (t, 1H, *J* 9.2 Hz, H-4[b]), 3.53 (t, 1H, *J* 8.6 Hz, H-2[a]), 3.47-3.39 (m, 1H, H-5[b], H-5[a], H-2[b]), 2.80 (m, 2H, SCH_2CH$_3$), 1.95 (s, 3H, CH$_3$CO), 1.89 (s, 3H, CH$_3$CO), 1.34 (t, 3H, *J* 7.4 Hz, SCH$_2$CH_3). ^{13}C NMR (150.9 MHz, CDCl$_3$): δ 170.7, 169.9 (CH$_3$*C*O), 138.2, 137.7, 137.1, 137.0, 129.5, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.5, 127.2, 126.5, 126.1 (Ar), 102.4 (C-1[b]), 101.7 (Ph*C*H), 85.9 (C-1[a]), 81.8 (C-2[a]), 80.6 (C-3[a]), 80.1 (C-2[b]), 78.9 (C-4[a]), 76.2 (C-4[b]), 75.80 (C-3[b]), 75.3, 74.7, 74.3 (3 Ph*C*H$_2$), 72.5 (C-5[b]), 70.6 (C-5[a]), 68.7 (C-6[a]), 63.3 (C-6[b]), 25.4 (S*C*H$_2$CH$_3$), 21.1, 20.8 (*C*H$_3$CO), 15.2 (SCH$_2$*C*H$_3$). HR ESI MS calcd. for [M + Na]$^+$ $C_{46}H_{52}NaO_{12}S$: 851.3072, found: 851.3064.

3.26. Ethyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α- and β-D-glucopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranosides (34α,β)

The title compounds were obtained according to General procedure A (table 1, entry 4).

Data for **34α**: white foam, $[\alpha]_D$ +49.8 (*c* 1, $CHCl_3$); R_f 0.45 (petroleum ether – EtOAc, 3:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40–6.95 (m, 25H, 5 Ph), 5.63 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1^b), 5.45 (s, 1H, PhC*H*), 5.08 (d, 1H, J_{gem} 10.9 Hz, PhCH_2A), 5.00 (d, 1H, J_{gem} 9.7 Hz, PhCH_2A'), 4.86 (d, 1H, J_{gem} 10.9 Hz, PhCH_2A''), 4.85 (d, 1H, J_{gem} 10.9 Hz, PhCH_2B), 4.69 (d, 1H, J_{gem} 9.7 Hz, PhCH_2B'), 4.63 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1^a), 4.61 (d, 1H, J_{gem} 11.9 Hz, PhCH_2A'''), 4.48 (d, 1H, J_{gem} 10.9 Hz, PhCH_2B''), 4.37 (d, 1H, J_{gem} 11.9 Hz, PhCH_2B'''),4.36 (dd, 1H, $J_{6A,5}$ 5.1 Hz, $J_{6A,6B}$ 10.4 Hz, H-6A^a), 4.18–4.12 (m, 2H, H-3^a, H-5^b), 4.04 (t, 1H, *J* 9.4 Hz, H-3^b), 3.94 (dd, 1H, $J_{5,6A}$ 2.3 Hz, $J_{6A,6B}$ 12.2 Hz, H-6A^b), 3.88-3.85 (m, 2H, H-6B^b, H-4^a), 3.79 (t, 1H, *J* 10.4 Hz, H-6B^a), 3.58–3.46 (m, 4H, H-2^a, H-5^a, H-4^b, H-2^b), 2.83 (m, 2H, SCH_2CH$_3$), 1.94 (s, 3H, CH_3CO), 1.39 (t, 3H, *J* 7.7 Hz, SCH$_2$CH_3). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 170.5 (CH_3*C*O), 138.7, 138.3, 137.7, 137.2, 136.9, 129.5, 128.9, 128.6, 128.4, 128.3, 128.24, 128.19, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5 (Ar), 102.3 (Ph*C*H), 95.9 (C-1^b), 86.1 (C-1^a), 82.3 (C-4^a), 81.6 (C-3^b), 79.6 (C-2^a), 78.8 (C-2^b), 77.0 (C-4^b), 76.8 (C-3^a), 75.9, 75.7, 75.1, 71.1 (4 Ph*C*H$_2$), 69.9 (C-5^a), 68.9 (C-6^a), 68.5 (C-5^b), 62.5 (C-6^b), 25.2 (S*C*H$_2$CH$_3$), 20.1 (*C*H$_3$CO), 15.0 (SCH$_2$*C*H$_3$). HR ESI MS calcd. for $[M + Na]^+$ $C_{51}H_{56}NaO_{11}S$ 899.3436, found 899.3449.

Data for **34β**: white foam, R_f 0.45 (Petroleum ether–EtOAc, 3:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49–7.20 (m, 25H, 5 Ph), 5.58 (s, 1H, PhC*H*), 4.99 (d, 1H, J_{gem} 11.1 Hz, PhCH_2A), 4.95 (d, 1H, J_{gem} 11.1 Hz, PhCH_2A'), 4.89 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1^b), 4.83–4.76 (m, 5H, PhCH_2B, PhCH_2B', PhCH_2'', PhCH_2A'''), 4.57 (d, 1H, $J_{1,2}$ 9.6 Hz, H-1^a), 4.52 (d, 1H, J_{gem}10.7 Hz, PhCH_2B'''), 4.33 (dd, 1H, $J_{6A,5}$ 5.0 Hz, $J_{6A,6B}$ 10.6 Hz, H-6A^a), 4.27 (dd, 1H, $J_{6A,5}$ 2.3 Hz, $J_{6A,6B}$ 12.1 Hz, H-6A^b), 4.15–4.11 (m, 2H, H-3^a, H-6B^b), 3.80 (t, 1H, *J* 10.3 Hz, H-6B^a), 3.72 (t, 1H, *J* 9.5 Hz, H-4^a), 3.61 (t, 1H, *J* 9.2 Hz, H-3^b), 3.55–3.50 (m, 2H, H-2^a, H-2^b, H-4^b), 3.45 (dt, *J*

10.0 Hz, $J_{5,6A}$ 5.0 Hz, H-5[a]), 3.35 (m, 1H, H-5[b]), 2.81 (m, 2H, SCH_2CH$_3$), 1.94 (s, 3H, CH$_3$CO), 1.36 (t, 3H, *J* 7.5 Hz, SCH$_2$CH_3). HR ESI MS calcd. for $[M + Na]^+$ $C_{51}H_{56}NaO_{11}S$ 899.3436, found 899.3437.

3.27. *p*-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-α- and β-D-glucopyranosyl-(1→6)-3-*O*-benzoyl-2,4-di-*O*-benzyl-β-D-glucopyranosides (35α,β)

The title compounds were obtained according to General procedure A (table 1, entry 5) and General procedure B (entry 21).

Data for **35α**: crystalline solid, mp 120–122 °C; $[\alpha]_D$ +47.8 (*c* 1, $CHCl_3$); R_f 0.19 (petroleum ether – EtOAc, 4:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92–7.05 (m, 37H, 7 Ph, C$_6H_4$OCH$_3$), 6.83 (d, 2H, *J* 9.0 Hz, C$_6H_4$OCH$_3$), 5.53 (t, 1H, *J* 9.5 Hz, H-3[a]), 5.15 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1[b]), 5.07 (d, 1H, J_{gem} 10.8 Hz, PhCH_2A), 4.97 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1[a]), 4.90 (d, 1H, J_{gem} 12.0 Hz, PhCH_2A'), 4.87 (d, 1H, J_{gem} 11Hz, PhCH_2A''), 4.86 (d, 1H, PhCH_2B), 4.79 (d, 1H, J_{gem} 11.7 Hz, PhCH_2A'''), 4.76 (d, 1H, PhCH_2B'), 4.63 (d, 1H, J_{gem} 12.1 Hz, PhCH_2A''''), 4.59 (s, 2H, PhCH_2), 4.55 (d, 1H, PhCH_2B'''), 4.51 (d, 1H, PhCH_2B''), 4.49 (d, 1H, PhCH_2B''''), 4.05 (t, 1H, *J* 9.1 Hz, H-3[b]), 3.94–3.87 (m, 4H, 2H-6[a], H-4[a], H-5[b]), 3.74 (dd, 1H, $J_{5,6A}$ 4.0 Hz, $J_{6A,6B}$ 10.9 Hz, H-6A[b]), 3.70–3.63 (m, 7H, OCH_3, H-4[b], H-5[a], H-6B[b], H-2[b]), 3.49 (dd, 1H, $J_{2,1}$ 7.8 Hz, $J_{2,3}$ 9.5 Hz, H-2[a]). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 165.5 (Ph*C*O), 138.9, 138.6, 138.4, 138.0, 137.8, 137.5, 132.9, 130.0, 129.8, 128.4, 128.34, 128.30, 128.2, 128.1, 128.04, 127.9, 127.8, 127.6, 127.5, 127.4 (Ar), 119,1, 114.7 (*C*$_6$H$_4$OCH$_3$), 103.3 (C-1[a]), 97.4 (C-1[b]), 81.9 (C-3[b]), 80.3 (C-2[b]), 79.1 (C-2[a]), 77.7 (C-4[b]), 76.0 (C-3[a]), 75.6 (Ph*C*H$_2$), 75.5 (C-4[a]), 75.1 (C-5[a]), 75.0, 74.4, 74.3, 73.4, 72.2 (5 Ph*C*H$_2$), 70.2 (C-5[b]), 68.5 (C-6[b]), 65.2 (C-6[a]), 55.5 (CH$_3$O). HR ESI MS calcd. for $[M + Na]^+$ $C_{68}H_{68}NaO_{13}$ 1115.4552, found 1115.4551

Data for **35β**: crystalline solid, mp 126–130 °C; $[\alpha]_D$ +26.6 (*c* 1, $CHCl_3$); R_f 0.24 (petroleum ether – EtOAc, 4:1); ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.99–7.08 (m, 35H, 7 Ph), 7.06 (d, 2H, *J* 9.0 Hz, C$_6H_4$OCH$_3$), 6.74 (d, 2H, *J* 9.0 Hz, C$_6H_4$OCH$_3$), 5.62 (t, 1H, *J* 9.4 Hz, H-3[a]),

5.06 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1[a]), 4.96 (d, 1H, J_{gem} 11.1 Hz, PhCH_2A), 4.95 (d, 1H, J_{gem} 10.9 Hz, PhCH_2A'), 4.89 (d, 1H, J_{gem} 11.7 Hz, PhCH_2A''), 4.82 (d, 1H, J_{gem} 10.5 Hz, PhCH_2A'''), 4.81 (d, 1H, PhCH_2B'), 4.73 (d, 2H, J_{gem} 11.5 Hz, PhCH_2B, PhCH_2B''), 4.61 (d, 1H, J_{gem} 12.1 Hz, PhCH_2A''''), 4.55 (d, 1H, PhCH_2B'''), 4.52 (d, 1H, PhCH_2B''''), 4.50 (d, 1H, J_{gem} 11.1 Hz, PhCH_2A'''''), 4.47 (d, 1H, PhCH_2B'''''), 4.45 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1[b]), 4.20 (br. d, 1H, J 9.6 Hz, H-6A[a]), 3.85–3.79 (m, 2H, H-5[a], H-6B[a]), 3.75–3.57 (m, 9H, H-2[a], H-4[a], 2H-6[b], CH_3O, H-4[b], H-3[b]), 3.49 (t, 1H, J 8.1 Hz, H-2[b]), 3.39 (m, 1H, H-5[b]). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 165.5 (Ph*C*O), 138.6, 138.5, 138.2, 137.7, 133.1, 130.0, 129.8, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5 (Ar), 118.1, 114.6 ($C_6H_4OCH_3$), 103.8 (C-1[b]), 102.4 (C-1[a]), 84.7 (C-3[b]), 82.3 (C-2[b]), 78.5 (C-2[a]), 77.9 (C-4[b]), 76.5 (C-4[a]), 76.3 (C-3[a]), 75.7 (Ph*C*H$_2$), 75.2 (C-5[a]), 74.9 (2 Ph*C*H$_2$), 74.95 (C-5[b]), 74.5, 74.0, 73.5 (Ph*C*H$_2$), 68.8 (C-6[b]), 68.1 (C-6[a]), 55.5 (CH_3O). HR ESI MS calcd. for $[M + Na]^+$ $C_{68}H_{68}NaO_{13}$ 1115.4552, found 1115.4559.

3.28. *p*-Methoxyphenyl 3-*O*-acetyl-2,4,6-tri-*O*-benzyl-α- and β-D-glucopyranosyl-(1→6)-3-*O*-benzoyl-2,4-di-*O*-benzyl-β-D-glucopyranosides (36α,β)

The title compounds were obtained according to General procedure A (table 1, entry 6).

Data for **36α**: white foam, R_f 0.14 (petroleum ether – EtOAc, 4:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88–7.02 (m, 32H, 6 Ph, $C_6H_4OCH_3$), 6.88 (d, 2H, J 9.0 Hz, $C_6H_4OCH_3$), 5.63 (t, 1H, J 9.7 Hz, H-3[b]), 5.49 (t, 1H, J 9.6 Hz, H-3[a]), 5.20 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1[b]), 4.96 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1[a]), 4.85 (d, 1H, J_{gem} 12.4 Hz, PhCH_2), 4.72 (d, 1H, J_{gem} 11.7 Hz, PhCH_2), 4.65–4.58 (m, 4H, 2 PhCH_2), 4.51 (d, 1H, J_{gem} 11.3 Hz, PhCH_2), 4.48–4.42 (m, 3H, PhCH_2), 3.92 (t, 1H, J 9.6 Hz, H-4[a]), 3.91–3.83 (m, 3H, 2H-6[a], H-5[b]), 3.76 (s, 3H, CH_3O), 3.72–3.67 (m, 2H, H-4[b], H-6A[b]), 3.63–3.59 (m, 2H, H-5[a], H-6B[b]), 3.52 (dd, 1H, $J_{2,1}$ 3.5 Hz, $J_{2,3}$ 10.0 Hz, H-2[b]), 3.37 (dd, 1H, $J_{2,1}$ 7.8 Hz, $J_{2,3}$ 9.6 Hz, H-2[a]), 2.00 (s, 3H, CH_3CO). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 169.9 (CH_3*C*O), 165.5 (Ph*C*O), 155.4 ($C_6H_4OCH_3$), 151.1 ($C_6H_4OCH_3$), 138.3, 138.0, 137.7, 137.6, 137.3, 132.9, 129.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.5, 127.4, 127.1 (Ar),

118.6 ($C_6H_4OCH_3$), 114.8 ($C_6H_4OCH_3$), 102.9 (C-1^a), 97.3 (C-1^b), 79.0 (C-2^a), 77.4 (C-2^b), 76.1 (C-4^b), 75.9 (C-3^a), 75.2 (C-4^a, C-5^a), 74.6, 74.3 (2 PhCH_2), 73.5 (C-3^b, PhCH_2), 71.6 (PhCH_2), 69.9 (C-5^b), 68.2 (C-6^b), 65.2 (C-6^a), 55.6 (CH_3O), 21.1 (CH_3CO). HR ESI MS calcd. for [M + Na]$^+$ $C_{63}H_{64}NaO_{14}$ 1067.4188, found 1067.4195

Data for **36β**: white foam, $[\alpha]_D$ +25.6 (*c* 0.5, $CHCl_3$); R_f 0.10 (petroleum ether – EtOAc 4:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98-7.04 (m, 32H, 6 Ph, $C_6H_4OCH_3$), 6.80 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.61 (t, 1H, *J* 9.2 Hz, H-3^b), 5.19 (t, 1H, *J* 9.5 H-3^a), 5.04 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1^b), 4.88 (d, 1H, J_{gem} 11.7 Hz, PhCH_2A), 4.84 (d, 1H, J_{gem} 11.8 Hz, PhCH_2A'), 4.72 (d, 1H, PhCH_2B), 4.62 (d, 1H, J_{gem} 12.1 Hz, PhCH_2A''), 4.58 (d, 1H, PhCH_2B'), 4.52–4.44 (m, 6H, PhCH_2B'', 2 PhCH_2, H-1^a), 4.18 (m, 1H, H-6A^b), 3.82–3.75 (m, 2H, H-5^b, H-6B^b), 3.73-3.66 (m, 8H, H-4^b, H-2^b, 2H-6^a, CH_3O), 3.66 (t, 1H, *J* 9.5 Hz, H-4^a), 3.38 (m, 1H, H-5^a), 3.36 (dd, 1H, $J_{2,3}$ 9.6 Hz, H-2^a), 1.86 (s, 3H, CH_3CO). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 170.0 (CH_3CO), 165.5 (PhCO), 155.6 ($C_6H_4OCH_3$), 151.3 ($C_6H_4OCH_3$), 138.4, 138.0, 137.9, 137.5, 137.6, 133.1, 129.8, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5 (Ar), 118.1 ($C_6H_4OCH_3$), 114.7 ($C_6H_4OCH_3$), 103.7 (C-1^a), 102.4 (C-1^b), 79.5 (C-2^a), 78.5 (C-2^b), 76.5 (C-4^b), 76.2 (C-4^a), 76.1 (C-3^b), 75.6 (C-3^a), 75.1 (C-5^b), 74.7 (C-5^a), 74.6, 74.34, 74.30, 74.0, 73.6 (5 PhCH_2), 68.5 (C-6^a), 68.3 (C-6^b), 55.6 (CH_3O), 20.1 (CH_3CO). HR ESI MS calcd. for [M + Na]$^+$ $C_{63}H_{64}NaO_{14}$: 1067.4188, found: 1067.4192.

3.28. *p*-Methoxyphenyl 3,6-di-*O*-acetyl-2,4-di-*O*-benzyl-α- and β-D-glucopyranosyl-(1→6)-3-*O*-benzoyl-2,4-di-*O*-benzyl-β-D-glucopyranosides (37α,β)

The title compounds were obtained according to General procedure A (table 1, entry 7) and General procedure B (entry 22).

Data for **37α**: white foam, $[\alpha]_D$ +74.1 (*c* 1, $CHCl_3$); R_f 0.15 (hexane – EtOAc, 3:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92–7.00 (m, 27H, 5 Ph, $C_6H_4OCH_3$), 6.89 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.68 (t, 1H, *J* 9.6 Hz, H-3^b), 5.51 (t, 1H, *J* 9.5 Hz, H-3^a), 5.19 (d, 1H, $J_{1,2}$ 3.5 Hz, H-

1[b]), 4.98 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1[a]), 4.88 (d, 1H, J_{gem} 12.6 Hz, PhCH_2A), 4.72 (d, J_{gem} 11.5 Hz, 1H, PhCH_2A'), 4.62 (d, 1H, PhCH_2B), 4.62 (s, 2H, PhCH_2), 4.60 (d, 1H, J_{gem} 11.3 Hz, PhCH_2A''), 4.53 (d, 1H, PhCH_2B''), 4.46 (d, 1H, PhCH_2B'), 4.28–4.23 (m, 2H, 2H-6[b]), 3.97 (m, 3H, H-4[a], H-5[b], H-6A[a]), 3.87 (dd, 1H, $J_{5,6B}$ 1.7 Hz, $J_{6A,6B}$ 12.6 Hz, H-6B[a]), 3.78 (s, 3H, CH_3O), 3.62 (m, 1H, H-5[a]), 3.55 (t, 1H, J 9.6 Hz, H-4[b]), 3.50 (dd, 1H, $J_{2,1}$ 3.5, $J_{2,3}$ 9.9 Hz, Hz, H-2[b]), 3.37 (dd, 1H, $J_{2,3}$ 9.6 Hz, H-2[a]), 2.08, 2.07 (2 s, 6H, 2 CH_3CO). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 170.6, 169.8 (CH_3CO), 165.5 (Ph*C*O), 138.3, 137.5, 132.9, 130.0, 129.9, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.5, 127.0 (Ar), 118.4 ($C_6H_4OCH_3$), 114.8 ($C_6H_4OCH_3$), 102.8 (C-1[a]), 97.2 (C-1[b]), 79.0 (C-2[a]), 77.3 (C-2[b]), 76.0 (C-3[a] or C-4[b]), 75.9 (C-3[a] or C-4[b]), 75.2 (C-4[a] or C-5[a]) , 75.1 (C-4[a] or C-5[a]), 74.7, 74.3 (2 Ph*C*H_2), 73.4 (C-3[b]), 71.5 (Ph*C*H_2), 68.5 (C-5[b]), 65.3 (C-6[a]), 62.8 (C-6[b]), 55.6 (*C*H_3O), 21.1, 20.8 (*C*H_3CO). HR ESI MS calcd. for $[M + NH_4]^+$ $C_{58}H_{64}NO_{15}$: 1014.4270, found: 1014.4269.

Data for **37β**: foam, $[\alpha]_D$ +36.5 (*c* 0.5, $CHCl_3$); R_f 0.24 (hexane – EtOAc, 3:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98–7.00 (m, 25H, 5 Ph, $C_6H_4OCH_3$), 6.81 (d, 2H, J 8.7 Hz, $C_6H_4OCH_3$), 5.60 (t, 1H, J 9.4 Hz, H-3[b]), 5.22 (t, 1H, J 9.3 Hz, H-3[a]), 5.04 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1[b]), 4.87 (d, 1H, J_{gem} 11.7 Hz, PhCH_2A), 4.83 (d, 1H, J_{gem} 11.9 Hz, PhCH_2A'), 4.72 (d, 1H, PhCH_2B), 4.58 (d, 1H, PhCH_2B'), 4.55 (d, 1H, J_{gem} 11.1 Hz, PhCH_2A''), 4.52 (d, 1H, J_{gem} 10.7 Hz, PhCH_2A'''), 4.50 (d, 1H,PhCH_2B''), 4.48 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1[a]), 4.44 (d, 1H, PhCH_2B'''), 4.34 (br. d, 1H, J 11.7 Hz H-6A[a]), 4.19–4.14 (m, 2H, H-6B[a], H-6A[b]), 3.82–3.68 (m, 6H, H-5[b], H-6B[b], H-2[b], CH_3O), 3.64 (t, 1H, J 9.2 Hz, H-4[b]), 3.53 (t, 1H, J 9.5 Hz, H-4[a]), 3.44 (m, 1H, H-5[a]), 3.36 (t, 1H, J 9.0 Hz, H-2[a]), 2.04, 1.91 (2 s, 6H, 2 CH_3CO). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ129.8, 128.5, 128.4, 128.3; 128.2, 128.0, 127.9, 127.6 (Ar), 118.1 ($C_6H_4OCH_3$), 114.7 ($C_6H_4OCH_3$), 103.6 (C-1[a]), 102.4 (C-1[b]), 79.4 (C-2[a]), 78.5 (C-2[b]),76.5 (C-4[b]) 76.2 (C-3[b]), 76.1 (C-4[a]), 75.5 (C-3[a]), 75.1 (C-5[b]), 74.6, 74.4, 74.1 (4 Ph*C*H_2), 72.7 (C-5[a]), 68.4 (C-6[b]), 62.8 (C-6[a]), 55.6 (CH_3O), 21.0, 20.9 (2 *C*H_3CO). Anal. for the mixture of the isomers. Calcd. for $C_{58}H_{60}O_{15}$: C, 69.87, H, 6.07. Found: C, 69.83; H, 6.08.

3.30. *p*-Methoxyphenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α- and β-D-glucopyranosyl-(1→6)-3-*O*-benzoyl-2,4-di-*O*-benzyl-β-D-glucopyranosides (38α,β)

The title compounds were obtained according to General procedure A (table 1, entry 8).

Data for **38α**: white foam, $[\alpha]_D$ +55.1 (*c* 1, $CHCl_3$); R_f 0.21 (petroleum ether – EtOAc, 3:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91–7.07 (m, 30 H, 6 Ph), 7.06 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 6.84 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.53 (t, 1H, *J* 9.5 Hz, H-3^a), 5.14 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1^b), 5.08 (d, 1H, J_{gem} 10.7 Hz, PhCH_2A), 4.97 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1^a), 4.92–4.87 (m, 2H, PhCH_2A', PhCH_2A''), 4.85 (d, 1H, J_{gem} 10.7 Hz, PhCH_2B), 4.77 (d, 1H, J_{gem} 11.6 Hz, PhCH_2A'''), 4.62–4.57 (m, 3H, PhCH_2B', 2PhCH_2''''), 4.53 (d, 1H, J_{gem} 11.6 Hz, PhCH_2B'''), 4.28 (dd, 1H, $J_{5,6A}$ 4.0 Hz, $J_{6A,6B}$ 12.1 Hz, H-6A^b), 4.25 (dd, 1H, $J_{5,6B}$ 2.2 Hz, H-6B^b), 4.06 (t, 1H, *J* 9.2 Hz, H-3^b), 3.94–3.85 (m, 4H, H-4^a, 2H-6^a, H-5^b), 3.72 (s, 3H, CH_3O), 3.65 (m, 1H, H-5^a), 3.61 (dd, 1H, $J_{2,1}$ 3.5 Hz, $J_{2,3}$ 9.5 Hz, H-2^b), 3.54 (t, 1H, *J* 9.4 Hz, H-3^b), 3.47 (dd, 1H, $J_{2,1}$ 7.9 Hz, $J_{2,3}$ 9.5 Hz, H-2^a), 2.02 (s, 3H, CH_3CO). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 170.7 (CH_3CO), 165.5 (Ph*C*O), 138.6, 138.5, 137.7, 137.4, 133.0, 130.1, 129.8, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5 (Ar), 118.9 ($C_6H_4OCH_3$), 114,7 ($C_6H_4OCH_3$), 103.1 (C-1^a), 97.3 (C-1^b), 81.8 (C-3^b), 80.2 (C-2^b), 79.1 (C-2^a), 77.2 (C-4^b), 76.0 (C-3^a), 75.7 (Ph*C*H$_2$), 75.4 (C-4^a), 75.1 (C-5^a), 75.0, 74.4, 74.3, 72.2 (4 Ph*C*H$_2$), 68.8 (C-5^b), 65.3 (C-6^a), 63.0 (C-6^b), 55.6 (CH_3O), 20.8 (*C*H$_3$CO). HR ESI MS calcd. for $[M + Na]^+$ $C_{63}H_{64}NaO_{14}$ 1067.4188, found 1067.4184.

Data for **38β**: crystalline solid, mp 104–106 °C; $[\alpha]_D$ +50.7 (*c* 1, $CHCl_3$); R_f 0.30 (petroleum ether – EtOAc, 3:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98–7.07 (m, 30H, 6 Ph), 7.03 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 6.74 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.61 (t, 1H, *J* 9.3 Hz, H-3^a), 5.04 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1^a), 4.96 (d, 1H, J_{gem} 11.1 Hz, PhCH_2A), 4.94 (d, 1H, J_{gem} 11.3 Hz, PhCH_2A'), 4.87 (d, 1H, J_{gem} 11.7 Hz, PhCH_2A''), 4.85 (d, 1H, J_{gem} 10.9 Hz, PhCH_2A'''), 4.80 (d, 1H, PhCH_2B), 4.72 (d, 1H, PhCH_2B'), 4.71 (d, 1H, PhCH_2B''), 4.57 (d, 1H, PhCH_2B'''), 4.51 (d, 1H, J_{gem} 11.1 Hz, PhCH_2A''''), 4.47 (2, 1H, PhCH_2B''''), 4.46 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1^b), 4.35 (dd, 1H, $J_{5,6A,}$ 2.1 Hz, $J_{6A,6B}$ 12.0 Hz, H-6A^b), 4.18 (dd, 1H, $J_{5,6B,}$ 5.0 Hz, H-6B^b), 4.15

(br. d, 1H, $J_{6A,6B}$ 11.1 Hz, H-6A[a]), 3.83 (m, 1H, H-5[a]), 3.79 (dd, 1H, $J_{5,6B}$ 6.7 Hz, H-6B[a]), 3.72 (dd, 1H, $J_{2,1}$ 7.8 Hz, $J_{2,3}$ 9.4 Hz, H-2[a]), 3.68 (s, 3H, CH_3O), 3.64 (t, 1H, *J* 9.3 Hz, H-4[a]), 3.59 (t, 1H, *J* 9.0 Hz, H-3[b]), 3.53 (t, 1H, *J* 9.0 Hz, H-4[b]), 3.47 (t, 1H, *J* 8.5 Hz, H-2[b]), 3.42 (m, 1H, H-5[b]), 2.01 (s, 3H, CH_3CO). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 170.6 (CH_3CO), 165.5 (Ph*C*O), 137.9, 137.3, 133.1, 130.1, 129.8, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6 (Ar), 118.2 ($C_6H_4OCH_3$), 114,7 ($C_6H_4OCH_3$), 103.8 (C-1[b]), 102.5 (C-1[a]), 84.7 (C-3[b]), 82.3 (C-2[b]), 78.7 (C-2[a]), 77.6 (C-4[b]), 76.7 (C-3[a]), 76.3, 75.7 (2 Ph*C*H_2), 75.3 (C-5[a]), 75.0, 74.5, 74.1 (3 Ph*C*H_2), 73.0 (C-3[b]), 68.4 (C-6[a]), 63.1 (C-6[b]), 55.6 (CH_3O), 20.8 (*C*H_3CO). HR ESI MS calcd. for $[M + Na]^+$ $C_{63}H_{64}NaO_{14}$ 1067.4188, found 1067.4195.

3.31. *p*-Methoxyphenyl 3-*O*-acetyl-6-*O*-benzoyl-2,4-di-*O*-benzyl-α- and β-D-glucopyranosyl-(1→3)-6-*O*-benzoyl-2,4-di-*O*-benzyl-β-D-glucopyranosides (39α,β)

The title compounds were obtained according to General procedure A (table 1, entry 9).

Data for **39α**: white foam, $[\alpha]_D$ +54.6 (*c* 1, $CHCl_3$); R_f 0.48 (toluene – EtOAc, 6:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04–7.06 (m, 30H, 6 Ph), 6.98 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 6.73 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.75 (t, 1H, *J* 9.7 Hz, H-3[b]), 5.60 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1[b]), 5.08 (d, 1H, J_{gem} 10.2 Hz, PhCH_2A), 4.99 (d, 1H, J_{gem} 11.8 Hz, PhCH_2A'), 4.90 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1[a]), 4.79 (d, 1H, PhCH_2B), 4.65 (dd, 1H, $J_{5,6A}$ 1.7 Hz, $J_{6A,6B}$ 11.9 Hz, H-6A[a]), 4.61–4.51 (m, 5H, PhCH_2B', PhCH_2'', PhCH_2A''', H-5[b]), 4.43 (d, 1H, J_{gem} 11.9 Hz, PhCH_2B'''), 4.34 (dd, 1H, $J_{5,6B}$ 6.1 Hz, H-6B[a]), 4.30 (dd, 1H, $J_{5,6A}$ 1.7 Hz, $J_{6A,6B}$ 12.3 Hz, H-6A[b]), 4.09 (dd, 1H $J_{5,6B}$ 14.3 Hz, H-6B[b]), 4.07 (t, 1H, *J* 8.8 Hz, H-3[a]), 3.85–3.76 (m, 3H, H-4[a], H-2[a], H-5[a]), 3.75 (s, 3H, CH_3O), 3.57 (t, 1H, *J* 9.8 Hz H-4[b]), 3.52 (dd, 1H, $J_{2,3}$ 10.3 Hz, H-2[b]), 1.96 (s, 3H, CH_3CO). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 169.9 (CH_3CO), 166.2 155.5 (Ph*C*O), 151.4 137.8, 137.7, 137.6, 133.2, 133.0, 130.1, 130.0, 129.8, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.2, 118.6, 118.4, 114.6 (Ar), 103.0 (C-1[a]), 97.0 (C-1[b]), 79.9(C-2[a]), 79.7(C-3[a]), 78.8(C-4[a]), 78.0(C-2[b]), 76.9(C-4[b]), 74.9, 74.8(2 Ph*C*H_2), 74.0(C-3[b]), 73.9, 73.6(2 Ph*C*H_2),

73.0(C-5^a), 69.0(C-5^b), 63.5(C-6^a), 63.3(C-6^b), 55.7 (CH_3O), 21.2 (CH_3CO). HR ESI MS calcd. for $[M + Na]^+$ $C_{63}H_{62}NaO_{15}$: 1081.3981, found: 1081.3983.

Data for **39β**: white foam, $[\alpha]_D$ +16.9 (*c* 0.5, $CHCl_3$); R_f 0.48 (toluene – EtOAc, 6:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92–6.05 (m, 30H, 6 Ph), 6.99 (d, 2H, *J* 9.1 Hz, $C_6H_4OCH_3$), 6.70 (d, 2H, *J* 9.1 Hz, $C_6H_4OCH_3$), 5.37 (t, 1H, *J* 9.3 Hz, H-3^b), 5.22 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1^b), 5.05–5.01 (m, 2H, PhCH_2A, PhCH_2A'), 4.93 (d, 1H, J_{gem} 9.4 Hz, PhCH_2A''), 4.83 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1^b),–4.82 (d, 1H, J_{gem} 11.8 Hz, PhCH_2B), 4.64 (d, 1H, PhCH_2B''), 4.61 (d, 1H, *J* 10.9 Hz, PhCH_2B'), 4.60–4.50 (m, 4H, 2PhCH_2, H-6A^a, H-6A^b), 4.46 (dd, 1H, $J_{5,6B}$ 4.5 Hz, $J_{6A,6B}$ 12.1 Hz, H-6B^b), 4.41 (dd, 1H, $J_{5,6B}$ 6.8 Hz, $J_{6A,6B}$ 11.7 Hz, H-6B^a), 4.17 (t, 1H, *J* 8.6 Hz, H-3^a), 3.76–3.70 (m, 4H, H-2^a, CH_3O), 3.69–3.65 (m, 2H, H-4^b, H-5^a), 3.62–3.55 (m, 2H, H-4^a, H-5^b), 3.45 (dd, 1H, $J_{2,3}$ 9.6 Hz, H-2^b), 1.98 (s, 3H, CH_3CO). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 133.0, 129.7, 129.2, 128.7, 128.5, 128.4, 128.3, 128,2, 128.1, 127.9, 127.8, 127.7 (Ar), 118.5 ($C_6H_4OCH_3$), 114.5 ($C_6H_4OCH_3$), 102.9 (C-1^b), 102.5 (C-1^a), 82.5 (C-2^a), 81.4 (C-3^a), 80.2 (C-2^b), 76.6 (C-4^b), 75.9 (C-3^b), 75.7 (C-4^a), 75.1, 74.8, 74.5, 74.3 (4 PhCH_2), 73.0 (C-5^a), 72.8 (C-5^b), 63.9 (C-6^a), 63.4 (C-6^b), 55.6 (CH_3O), 21.1 (CH_3CO). HR ESI MS calcd. for $[M + Na]^+$ $C_{63}H_{62}NaO_{15}$: 1081.3981, found: 1081.3979.

3.32. Ethyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α- and β-D-glucopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranosides (40α,β)

The title compounds were obtained according to General procedure A (table 1, entry 10) and General procedure B (entry 23).

Data for **40α**: crystalline solid, mp 60–63 °C; $[\alpha]_D$ +10.4 (*c* 1, $CHCl_3$); R_f 0.57 (petroleum ether – EtOAc, 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53–7.07 (m, 25H, 5 Ph), 5.68 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1^b), 5.53 (s, 1H, PhC*H*), 5.48 (s, 1H, PhC*H*), 4.96 (d, 1H, J_{gem} 11.3 Hz, PhCH_2A), 4.91 (d, 1H, J_{gem} 9.8 Hz, PhCH_2A'), 4.90 (d, 1H, PhCH_2B), 4.85 (d, 1H, PhCH_2B'), 4.67 (d, 1H, J_{gem} 12.2 Hz, PhCH_2A''), 4.64 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1^a), 4.53 (d, 1H, PhCH_2B''),

4.36 (dd, 1H, $J_{5,6A}$ 4.9 Hz, $J_{6A,6B}$ 10.7 Hz, H-6A[a]), 4.22–4.16 (m, 2H, H-5[b], H-3[a]), 4.13 (dd, 1H, $J_{5,6A}$ 5.0 Hz, $J_{6A,6B}$ 10.2 Hz, H-6A[b]), 4.10 (t, 1H, J 9.4 Hz, H-3[b]), 3.88 (t, 1H, J 9.4 Hz, H-4[a]), 3.79 (t, 1H, J 10.4 Hz, H-6B[a]), 3.63–3.57 (m, 3H, H-4[b,] H-6B[b], H-2[a]), 3.56–3.50 (m, 2H, H-2[b,] H-5[a]), 2.82 (m, 2H, SCH_2CH$_3$), 1.37 (t, 3H, J 7.4 Hz, SCH$_3$CH_3). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 138.9, 137.8, 137.0, 129.3, 129.0, 128.7, 128.4, 128.3, 128.2, 128.0, 127.9, 127.5, 127.4, 126.3, 126.2 (Ar), 101.9 (Ph*C*H), 101.1 (Ph*C*H), 96.8 (C-1[b]), 86.1 (C-1[a]), 82.5 (C-4[a]), 82.1 (C-4[b] or C-2[a]), 79.8 (C-2[a] or C-4[b]), 78.4 (C-2[b]), 77.8 (C-3[b]), 76.7 (C-3[a]), 76.3, 75.2, 71.9 (3 Ph*C*H$_2$), 69.7 (C-5[a]), 68.84, 68.78 (C-6[a], C-6[b]), 62.6 (C-5[b]), 25.2 (S*C*H$_2$CH$_3$), 15.1 (SCH$_2$*C*H$_3$). HR ESI MS calcd. for $[M + NH_4]^+$ $C_{49}H_{56}NO_{10}S$ 850.3619, found 850.3621.

Data for **40β**: crystalline solid, mp 108–110 °C; $[\alpha]_D$ –13.0 (*c* 1, $CHCl_3$); R_f 0.57 (petroleum ether – EtOAc, 3:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55–7.22 (m, 25H, 5 Ph), 5.57 (s, 1H, PhC*H*), 5.41 (s, 1H, PhC*H*), 5.02 (d, 1H, $J_{1,2}$ 7.1 Hz, H-1[b]), 4.92 (d, 1H, J_{gem} 11.6 Hz, PhCH_2A), 4.84 (d, 1H, J_{gem} 11.1 Hz, PhCH_2A'), 4.80 (d, 1H, J_{gem} 11.8 Hz, PhCH_2A'''), 4.79 (d, 1H, PhCH_2B), 4.77 (d, 1H, PhCH_2B'), 4.74 (d, 1H, PhCH_2B''), 4.57 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1[a]), 4.36 (dd, 1H, $J_{5,6A}$ 5.0 Hz, $J_{6A,6B}$ 11.6 Hz, H-6A[a]), 4.23 (dd, 1H, $J_{5,6A}$ 5.0 Hz, $J_{6A,6B}$ 11.3 Hz, H-6A[b]), 4.13 (t, 1H, J 9.0 Hz, H-3[a]), 3.82–3.77 (m, 2H, H-6B[a], H-4[b]), 3.75–3.65 (m, 3H, H-3[b], H-6B[b], H-4[a]), 3.56 (t, J 7.4 Hz, 1H, H-2[b]), 3.50 (dd, $J_{2,1}$ 9.8 Hz, $J_{2,3}$ 8.7 Hz, H-2[a]), 3.47 (m, 1H, H-5[a]), 3.30 (m, 1H, H-5[b]), 2.80 (m, 2H, SCH_2CH$_3$), 1.35 (t, 3H, J 7.5 Hz, SCH$_3$CH_3). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 138.5, 138.3, 137.9, 137.4, 137.3, 129.1, 128.8, 128.3, 128.17, 128.15, 128.0, 127.9, 127.7, 127.6, 127.5, 126.1, 126.0 (Ar), 102.4 (C-1[b]), 101.2 (Ph*C*H), 100.9 (Ph*C*H), 85.9 (C-1[a]), 82.5 (C-2[b]), 81.9 (C-2[a]), 81.4 (C-4[b]), 80.9 (C-3[b]), 80.0 (C-3[a]), 79.2 (C-4[a]), 75.2, 75.1, 74.6 (3 Ph*C*H$_2$), 70.5 (C-5[a]), 68.8 (C-6[b]), 68.7 (C-6[a]), 65.6 (C-5[b]), 25.2 (S*C*H$_2$CH$_3$), 15.1 (SCH$_2$*C*H$_3$). HR ESI MS calcd. for $[M + Na]^+$ $C_{49}H_{52}NaO_{10}S$ 855.3173, found 855.3176.

3.33. Ethyl 3-*O*-acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-α- and β-D-glucopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranosides (41α,β)

3.33.1. A solution of donor **19** (47 mg, 0.082 mmol) and acceptor **30** (27.4mg, 0.069 mmol) in CH_2Cl_2 (650 µL, anhydr.) was stirred with MS AW 300 (65 mg) for 1 h at rt. A solution of AgOTf (10.5 mg, 0.041 mmol) in dry toluene (100 µL) was added and the mixture was stirred at rt until TLC showed full consumption of **19**. The reaction was quenched by adding MeOH (3.3µL, 0.082 mmol) and Et_3N (11.5µL, 0.082 mmol), the mixture was diluted with CH_2Cl_2 and filtered trough a Celite pad. The filtrate was washed with aq sat $NaHCO_3$ and water, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to column chromatography (toluene – methyl *tert*-butyl ether, 35:1→15:1) to afford **41α** (28.7 mg, 53%) and **41β** (9.6 mg, 18%).

3.33.2. A solution of donor **19** (50 mg, 0.088 mmol) and acceptor **30** (29.5mg, 0.073 mmol) in CH_2Cl_2 (0.8 mL) was stirred with MS AW 300 (80 mg) for 1 h at rt, then MeOTf (10µL, 0.088 mmol) was added. The mixture was stirred for 5 min and quenched by adding MeOH (7µL, 0.176 mmol) and Et_3N (24.6µL, 0.176 mmol). The resulting mixture was worked-up and the title compounds were isolated as described in **3.33.1** to give **41α** (29.0 mg, 51%) and **41β** (7.6 mg, 13%).

The title compounds were also obtained according to General procedure A (table 1, entries 11, 17, 18).

Data for **41α**: crystalline solid, mp 194–197 °C; $[\alpha]_D$ +51.1 (*c* 1, $CHCl_3$); R_f 0.15 (toluene – methyl *tert*-butyl ether, 17:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60–6.90 (m, 20H, 4 Ph), 5.72 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1^a), 5.64 (t, 1H, *J* 9.8 Hz, H-3^b), 5.45 (s, 1H, PhC*H*), 5.43 (s, 1H, PhC*H*), 4.98 (d, 1H, J_{gem} 9.8 Hz, PhCH_2A), 4.93 (d, 1H, J_{gem} 9.0 Hz, PhCH_2B), 4.64 (d, 1H, $J_{1,2}$ 9.7 Hz, H-1^b), 4.61 (d, 1H, J_{gem} 12.6 Hz, PhCH_2A$'$), 4.36 (dd, 1H, $J_{6A,5}$ 5.0 Hz, $J_{6A,6B}$ 10.6 Hz, H-6A^a), 4.30 (d, 1H, J_{gem} 12.0 Hz, PhCH_2B$'$), 4.23 (m, 1H, $J_{5,6A}$ 5.0 Hz, $J_{5,6B}$ 10.0 Hz , H-5^b), 4.17 (t, 1H, *J* 9.0 Hz, H-3^a), 4.09 (dd, 1H, $J_{6A,5}$ 4.9 Hz, $J_{6A,6B}$ 10.2 Hz, H-6A^b), 3.86 (t, 1H, *J* 9.3 Hz, H-4^a), 3.78 (t, 1H, *J* 10.4 Hz, H-6B^a), 3.61 (t, 1H, *J* 9.2 Hz, H-2^a), 3.56 (t, 1H, *J* 10.2 Hz, H-6B^b), 3.51 (m, 1H, $J_{5,6A}$ 4.9 Hz, H-5^a), 3.49 (t, 1H, *J* 9.5 Hz, H-4^b), 3.48 (dd, 1H, $J_{2,1}$ 3.6 Hz, $J_{2,3}$ 9.6 Hz, H-

2[b]), 2.83 (m, 2H, SC*H*$_2$CH$_3$), 2.09 (s, 3H, CH$_3$CO), 1.38 (t, 3H, *J* 7.5 Hz, SCH$_2$C*H*$_3$). ^{13}C NMR (150,9 MHz, CDCl$_3$): δ 169.8 (CH$_3$*C*O), 137.5, 137.3, 137.0, 129.4, 129.0, 128.8, 128.4, 128.3, 128.2, 128.0, 127.8, 127.6, 127.3, 126.4, 126.3, 126.1 (Ar), 101.3, 101,2 (2 Ph*C*H), 96.4 (C-1[b]), 86.1 (C-1[a]), 82.3 (C-4[a]), 79.5 (C-2[a], C-4[b]), 77.0 (C-3[a]), 76.41, 76.36 (Ph*C*H$_2$, C-2[b]), 71.0 (Ph*C*H$_2$), 70.0 (C-3[b]), 69.7 (C-5[a]), 68.9 (C-6[a]), 68.7 (C-6[b]), 62.6 (C-5[b]), 25.1 (S*C*H$_2$CH$_3$), 21.0 (*C*H$_3$CO), 15.0 (SCH$_2$*C*H$_3$ HR ESI MS calcd. for [M + Na]$^+$ C$_{44}$H$_{48}$NaO$_{11}$S: 807.2810, found: 807.2830.

Data for **41β**: white foam, [α]$_D$ –13.9 (*c* 1, CHCl$_3$); R_f 0.33 (toluene – methyl *tert*-butyl ether, 17:1); ^{1}H NMR (600 MHz, CDCl$_3$): *δ*7.60–7.20 (m, 20H, 4 Ph), 5.59 (s, 1H, PhC*H*), 5.30–5.27 (m, 2H, H-3[b], PhC*H*), 5.09 (d, 1H, $J_{1,2}$ 7.0 Hz, H-1[b]), 4.89 (d, 1H, J_{gem} 11.8 Hz, PhC*H*$_2$A), 4.86 (d, 1H, J_{gem} 9.5 Hz, PhC*H*$_2$A'), 4.74–4.70 (m, 2H, PhC*H*$_2$B', PhC*H*$_2$B), 4.58 (d, 1H, $J_{1,2}$ 9.7 Hz, H-1[a]), 4.38 (dd, $J_{6A,6B}$ 10.5 Hz, $J_{6A,5}$ 5.3 Hz, 1H, H-6A[a]), 4.23 (dd, 1H, $J_{6A,6B}$ 10.5 Hz, $J_{6A,5}$ 4.9 Hz, H-6A[b]), 4.13 (t, 1H, *J* 9.0 Hz, H-3[a]), 3.82 (t, 1H, *J* 10,2 Hz, H-6B[a]), 3.71–3.65 (m, 3H, H-4[b], H-4[a], H-6B[b]), 3.55 (t, 1H, *J* 7.6 Hz, H-2[b]), 3.51 (t, 1H, *J* 9.1 Hz, H-2[a]), 3.47 (m, 1H, H-5[a]), 3.40 (m, 1H, H-5[b]), 2.81 (m, 2H, SC*H*$_2$CH$_3$), 2.01 (s, 3H, CH$_3$CO), 1.38 (t, 3H, *J* 7.4 Hz, SCH$_2$CH$_3$). ^{13}C NMR (150,9 MHz, CDCl$_3$): δ 169.9 (CH$_3$*C*O), 138.0, 137.6, 137.3, 137.1, 129.2, 128.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 126.1 (Ar), 102.4 (C-1[b]), 101.3, 101.2 (Ph*C*H), 86.0 (C-1[a]), 82.0 (C-2[a]), 80.6 (C-2[b]), 80.0 (C-3[a]), 79.1, 78.6 (C-4[b], C-4[a]), 75.3, 74.6 (2 Ph*C*H$_2$), 73.0 (C-3[b]), 70.5 (C-5[a]), 68.7, (C-6[b], C-6[a]), 65.7 (C-5[b]), 25.4 (S*C*H$_2$CH$_3$), 21.00 (*C*H$_3$CO), 15.1 (SCH$_2$*C*H$_3$). HR ESI MS calcd. for [M + Na]$^+$ C$_{44}$H$_{48}$NaO$_{11}$S: 807.2810, found: 807.2807.

3.34. *p*-Methoxyphenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α- and β-D-glucopyranosyl-(1→6)-3-*O*-benzoyl-2,4-di-*O*-benzyl-β-D-glucopyranosides (42α,β)

The title compounds were obtained according to General procedure A (table 1, entry 15) and General procedure B (entry 25).

Data for **42α**: crystalline solid, mp 175–177 °C; $[\alpha]_D$ +31.7 (*c* 1, $CHCl_3$); R_f 0.10 (petroleum ether – EtOAc, 4:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94–7.04 (m, 32H, 6 Ph, $C_6H_4OCH_3$), 6.83 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.59 (s, 1H, PhC*H*), 5.55 (t, 1H, *J* 9.5 Hz, H-3^a), 5.12 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1^b), 4.99 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1^a), 4.97–4.89 (m, 3H, PhCH_2), 4.84–4.79 (m, 2H, PhCH_2), 4.61–4.55 (m, 3H, PhCH_2), 4.30 (dd, 1H, $J_{5,6A}$ 4.9 Hz, $J_{6A,6B}$ 10.2 Hz, H-6A^b), 4.08 (t, 1H, *J* 9.3 Hz, H-3^b), 3.97–3.91 (m, 3H, H-5^b, H-6A^a, H-4^a), 3.88 (dd, 1H, $J_{5,6B}$ 1.7 Hz, H-6B^a), 3.73 (t, 1H, *J* 10.3 Hz, H-6B^b), 3.69–3.66 (m, 4H, H-5^a, CH_3O), 3.65 (t, 1H, *J* 9.8 Hz, H-4^b), 3.63 (dd, 1H, $J_{2,3}$ 9.2 Hz, H-2^b), 3.52 (dd, 1H, $J_{2,3}$ 9.5 Hz, H-2^a). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 165.5 (Ph*C*O), 138.8, 138.5, 137.7, 137.5 , 133.0, 130.0, 129.8, 128.9, 128.5, 128.3, 128.2, 128.1, 127.9, 127.8, 127.5, 127.4, 126.1 (Ar), 119.1 ($C_6H_4OCH_3$), 114.7 ($C_6H_4OCH_3$), 103.3 (C-1^a), 101.4 (Ph*C*H), 98.3 (C-1^b), 82.2 (C-4^b), 79.6 (C-2^b), 79.0 (C-2^a), 78.1 (C-3^b), 76.1 (C-3^a), 75.5 (C-5^b), 75.2 (PhCH_2), 75.0 (C-5^a), 74.5, 74.3, 72.7 (3 PhCH_2), 69.1 (C-6^b), 65.5 (C-6^a), 62.6 (C-5^b), 55.5 (CH_3O). HR ESI MS calcd. for $[M + Na]^+$ $C_{61}H_{60}NaO_{13}$ 1023.3926, found 1023.3935

Data for **42β**: crystalline solid, mp 147–149 °C; $[\alpha]_D$ +5.9 (*c* 1, $CHCl_3$); R_f 0.17 (petroleum ether – EtOAc, 4:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99–7.06 (m, 30H, 6 Ph), 7.03 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 6.74 (d, 2H, *J* 9.0 Hz, $C_6H_4OCH_3$), 5.61 (t, 1H, *J* 9.3 Hz, H-3^a), 5.58 (s, 1H, PhC*H*), 5.02 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1^a), 4.92 (d, 1H, J_{gem} 11.5 Hz, PhCH_2A), 4.90 (d, 1H, J_{gem} 11.1 Hz, PhCH_2A'), 4.88 (d, 1H, J_{gem} 11.7 Hz, PhCH_2A''), 4.81 (d, 1H, PhCH_2B), 4.77 (d, 1H, PhCH_2B'), 4.73 (d, 1H, PhCH_2B''), 4.54 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1^b), 4.51 (d, 1H, J_{gem} 11.1 Hz, PhCH_2A'''), 4.46 (d, 1H, PhCH_2B'''), 4.32 (dd, 1H, $J_{5,6A}$ 5.1 Hz, $J_{6A,6B}$ 10.4 Hz, H-6A^b), 4.15 (br. d, 1H, $J_{6A,6B}$ 10.4 Hz, H-6A^a), 3.83–3.66 (m, 10H, H-5^a, H-6B^a, H-6B^b, H-4^a, H-2^a, H-3^b, H-4^b, CH_3O), 3.50 (m, 1H, H-2^b), 3.32 (m, 1H, H-5^b). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 165.5 (Ph*C*O), 138.5, 138.4, 137.6, 137.3, 133.3, 129.9, 129.8, 128.9, 128.4, 128.3, 128.2, 128.0, 127.9, 127.6, 126.0 (Ar), 118.2 ($C_6H_4OCH_3$), 114.6 ($C_6H_4OCH_3$), 104.0 (C-1^b), 102.4 (C-1^a), 101.1 (Ph*C*H), 82.1 (C-2^b), 81.5 (C-3^b or C-4^b), 81.0 (C-4^b or C-3^b), 78.0 (C-2^a), 76.4 (C-4^a),

76.2 (C-2[a]), 75.4 (Ph*C*H$_2$), 75.1 (Ph*C*H$_2$, C-5[a]), 74.5, 74.0 (2 Ph*C*H$_2$), 68.7 (C-6[b]), 68.3 (C-6[a]), 66.0 (C-5[b]), 55.5 (CH$_3$O). HR ESI MS calcd. for [M + Na]$^+$ $C_{61}H_{60}NaO_{13}$ 1023.3926, found 1023.3924.

3.35. *p*-Methoxyphenyl 3-*O*-acetyl-2-*O*-benzyl-4,6-O-benzylidene-α- and β-D-glucopyranosyl-(1→6)-3-*O*-benzoyl-2,4-di-*O*-benzyl-β-D-glucopyranosides (43α,β)

The title compounds were obtained as described in **3.33.2** (table 1, entry 16).

Data for **43α**: white crystals, mp 175–185 °C; $[\alpha]_D$ +57.1 (*c* 1, $CHCl_3$); R_f 0.26 (petroleum ether – EtOAc, 3:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91–6.90 (m, 29H, 5 Ph, C$_6$*H*$_4$OCH$_3$), 5.68 (t, 1H, *J* 9.8 Hz, H-3[b]), 5.53 (t, 1H, *J* 9.5 Hz, H-3[a]), 5.48 (s, 1H, PhC*H*), 5.19 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1[b]), 4.99 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1[a]), 4.90 (d, 1H, J_{gem} 12.4 Hz, PhC*H*$_2$A), 4.75 (d, 1H, J_{gem} 11.5 Hz, PhC*H*$_2$A'), 4.67 (d, 1H, J_{gem} 12.4 Hz, PhC*H*$_2$B), 4.65–4.60 (m, 2H, 2PhC*H*$_2$), 4.50 (d, 1H, J_{gem} 11.6 Hz, PhC*H*$_2$B'), 4.27 (dd, 1H, $J_{5,6A}$ 5.0 Hz, $J_{6A,6B}$ 11.3 Hz, H-6A[b]), 3.97–3.93 (m, 3H, H-5[b], H-4[a], H-6A[a]), 3.87 (dd, 1H, $J_{5,6B}$ 1.6 Hz, H-6B[a]), 3.74 (s, 3H, CH$_3$O), 3.71 (t, 1H, *J* 10.4 Hz, H-6B[b]), 3.66 (m, 1H, H-5[a]), 3.60 (dd, 1H, $J_{2,1}$ 3.6 Hz, $J_{2,3}$ 9.6 Hz, H-2[b]), 3.57 (t, 1H, *J* 9.6 Hz, H-4[b]), 3.42 (dd, 1H, $J_{2,3}$ 9.6 Hz, $J_{2,1}$ 7.8 Hz, H-2[a]), 2.11 (s, 3H, CH$_3$CO). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 169.9 (CH$_3$*C*O), 165.5 (Ph*C*O), 138.2, 137.6, 137.4, 137.1, 133.0, 133.0, 129.9, 129.0, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.6, 127.5, 127.1, 126.2 (Ar), 118.5 (*C*$_6$H$_4$OCH$_3$), 114.8 (*C*$_6$H$_4$OCH$_3$), 102.9 (C-1[a]), 101.6 (PhC*H*), 98.1 (C-1[b]), 79.5 (C-4[b]), 78.9 (C-2[a]), 77.7 (C-2[b]), 75.9 (C-3[a]), 75.1 (C-4[a], C-5[a]), 74.7, 74.3, 71.8 (3 Ph*C*H$_2$), 70.3 (C-3[b]), 69.0 (C-6[b]), 65.4 (C-6[a]), 62.5 (C-5[b]), 55.6 (CH$_3$O), 21.0 (*C*H$_3$CO). HR ESI MS calcd. for [M + Na]$^+$ $C_{56}H_{56}NaO_{14}$ 975.3562, found 975.3565

Data for **43β**: white foam, $[\alpha]_D$ +7.4 (*c* 0.5, $CHCl_3$); R_f 0.33 (petroleum ether – EtOAc, 3:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00–7.00 (m, 27H, 5 Ph, C$_6$*H*$_4$OCH$_3$), 6.81 (d, 2H, *J* 9.0 Hz, C$_6$*H*$_4$OCH$_3$), 5.61 (t, 1H, *J* 9.4 Hz, H-3[a]), 5.45 (s, 1H, PhC*H*), 5.28 (t, 1H, *J* 9.4 Hz, H-3[b]), 5.05 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1[a]), 4.89 (d, 1H, J_{gem} 11.7 Hz, PhC*H*$_2$A), 4.83 (d, 1H, J_{gem} 11.8 Hz,

PhCH_2A'), 4.71 (d, 1H, PhCH_2B), 4.62 (d, 1H, PhCH_2B'), 4.61 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1^b), 4.52 (d, 1H, J_{gem} 11.1 Hz, PhCH_2A''), 4.45 (d, 1H, PhCH_2B''), 4.30 (dd, 1H, $J_{5,6A}$ 5.0 Hz, $J_{6A,6B}$ 10.5 Hz, H-6A^b), 4.16 (m, 1H, H-6A^a), 3.81–3.69 (m, 7H, H-6B^a, H-5^a, H-6B^b, H-2^a, CH_3O), 3.67 (t, 1H, *J* 9.4 Hz, H-4^b), 3.58 (t, 1H, *J* 9,6 Hz, H-4^b), 3.44 (dd, 1H, $J_{2,3}$ 8.9 Hz, H-2^b), 3.35 (m, 1H, H-5^b), 1.98 (s, 3H, CH_3CO). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 165.5 (Ph*C*O), 133.2, 129.8, 129.0, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6 (Ar), 118.1 ($C_6H_4OCH_3$), 114.7 ($C_6H_4OCH_3$), 103.9 (C-1^b), 102.4 (C-1^a), 101.4 (Ph*C*H), 79.9 (C-2^b), 78.7 (C-4^b), 78.4 (C-2^a), 76.3 (C-4^a), 76.1 (C-3^a), 75.1 (C-5^a), 74.7, 74.6, 74.0 (3 Ph*C*H_2), 72.5 (C-3^b), 68.6 (C-6^b), 68.3 (C-6^a), 66.0 (C-5^b), 55.6 (CH_3O), 20.9 (*C*H_3CO). HR ESI MS calcd. for $[M + Na]^+$ $C_{56}H_{56}NaO_{14}$ 975.3562, found 975.3556.

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Graphical Abstract

Is an acyl group at O-3 in glucosyl donors able to control α-stereoselectivity of glycosylation? The role of conformational mobility and the protecting group at O-6

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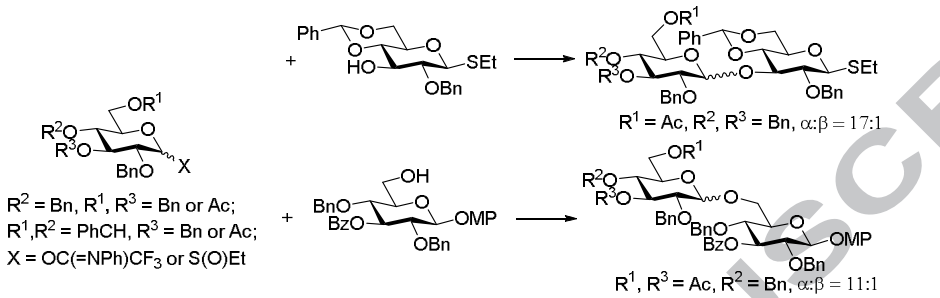

The effect of the acetyl groups at O-3 and/or O-6 and 4,6-*O*-benzylidene group in *N*-phenyltrifluoroacetimidoyl and sulfoxide glucosyl donors on stereoselectivity of glycosylation has been studied

Highlights

- Glucosylation with donors bearing acetyl groups at O-3 and/or O-6 has been studied.
- A sole acetyl group at O-3 did not cause any appreciable α-directing effect.
- 6-*O*-Acetyl and 3,6-di-*O*-acetyl donors demonstrated the highest α-stereoselectivity.
- Increasing the reaction temperature facilitated higher α-stereoselectivity.