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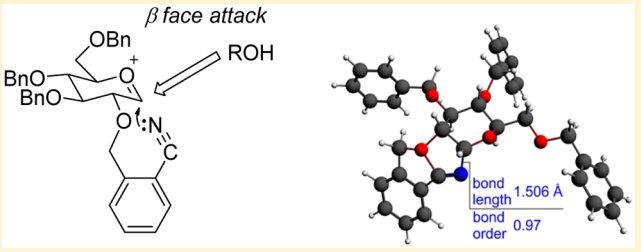
Application of 2-Substituted Benzyl Groups in Stereoselective Glycosylation

Szymon Buda, Mirosław Nawój, Patrycja Gołębiowska, Karol Dyduch, Artur Michalak, and Jacek Mlynarski*

Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland

Supporting Information

ABSTRACT: The use of 2-*O*-(2-nitrobenzyl) and 2-*O*-(2-cyanobenzyl) groups controls stereoselective formation of 1,2-*trans*-glycosidic linkages via the arming participation effect. The observed stereoselectivity likely arises from the intramolecular formation of cyclic intermediate between the electron-rich substituent and the donor oxacarbenium ion providing the expected facial selectivity for attack of the glycoside acceptor. The stereodirecting effect of the 2-nitro- and 2-cyanobenzyl groups attached at the remote position (C-3, C-4, and C-6) of the donor molecule have also been investigated. To prove the postulated mechanism based on the participation effect of 2-substituted benzyl groups in the glycosylation stereoselectivity we used DFT theoretical calculation methodology.



INTRODUCTION

Because of the importance and prominent role the oligosaccharides play in biology and pharmaceutical industry, stereoselective formation of glycosidic bond is probably the most important aspect of modern carbohydrate chemistry.[1] Despite many various strategies available for the efficient and stereocontrolled synthesis di- and oligosaccharides, this field still deserves additional attention.[2] The most commonly used strategy for the synthesis of glycosidic bond involves nucleophilic coupling of suitably protected glycosyl acceptor (ROH) with a fully protected donor bearing a leaving group (LG) at its anomeric center.[3] Nucleophilic attack of a hydroxyl moiety of a glycosyl acceptor to the flattened oxacarbenium ion resulting from the leaving group departure often leads to usually undesired α- and β-anomer mixtures.[4]

Stereocontrolled synthesis of one anomer requires special techniques, among which the most reliable is selective equipment of a donor molecule with the groups controlling glycosylation via intramolecular stereodirecting effects. Thus, the most studied application of 2-*O*-acyl functionality (Scheme 1, **I**) depends on neighboring group participation of an ester protecting group, which gives a more stable oxacarbenium ion shielded by protecting group from one site. An alcohol can attack the anomeric center from only one face to provide a 1,2-*trans*-glycoside. However, application of ester-type substituents which electronically deactivate donor molecules decrease the reaction yield in many cases. In contrast, application of ether-type substituents (Scheme 1, **II**) that electronically activate the donor usually lead to a mixture of both anomers, resulting from unhindered approach of the alcohol from both sites of the flattened oxacarbonium ion.

Interestingly, application of an electron-rich ether-type substituent that could control glycosylation via neighboring group participation has been neglected for many years. In 2005, Demchenko demonstrated 1,2-trans glycosylation by developing the neighboring 2-*O*-picolinyl (pyridylmethyl) ether.[5] Pyridine-based N-donor was demonstrated to be capable of efficient participation when attached at C-2, but also at the C-3, C-4, and C-6 positions of the glycosyl donor.[6] In the case of the remote picolinyl substituent, intermolecular H-bond tethering with a glycosyl acceptor instead of direct participation of nitrogen atom to the anomeric position has been postulated.[6] Stereoselective 1,2-*cis* glycosides with (*S*)-(phenylthiomethyl)benzyl and 2-*O*-(thiophen-2-yl)methyl protecting groups have been demonstrated by Boons[7] and Fairbanks,[8] respectively. According to the authors, the observed α-selectivity results from the intramolecular formation of a transition six-membered intermediate sulfonium/thiophenium ion, which then undergoes nucleophilic substitution by the glycosyl acceptor from the α-site. In parallel, some other nonbenzyl groups for participation-assisted or stereodirecting glycosylation have been recently introduced.[9] In contrast, successful examples of regular benzyl ethers substituted at the aromatic ring (Scheme 1, **III**) have never been deeply explored. This concept, however, seems to have great potential, and the use of neighboring group participation by using a benzyl-type group may have an important impact on the field by combining at least two advantages: the use of an activated (armed) donor and easy one-step deprotection of all benzyl-type groups at the most convenient stage.

Here, we report the first use of 2-substituted benzyl groups as stereodirecting substituents for the formation of 1,2-*trans*-glycosidic linkage. As the benzyls can be removed after glycosylation, they can be used as stereodirecting protecting groups,

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Scheme 1. Glycosyl Donors with 2-*O*-Acetyl- (1a), 2-*O*-Benzyl- (1b), 2-*O*-(2-Nitrobenzyl)- (1c), and 2-*O*-(2-Cyanobenzyl)- (1d) Groups

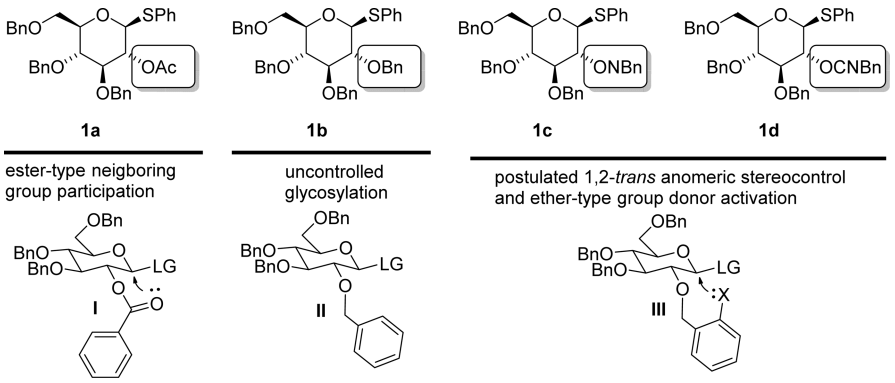
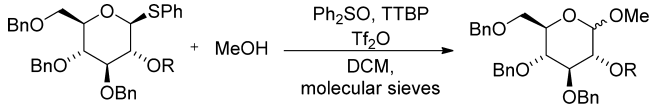
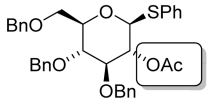
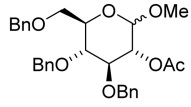
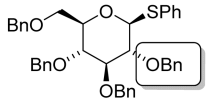
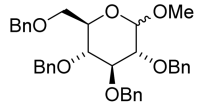
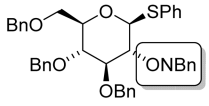
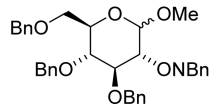
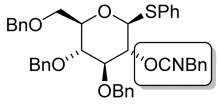
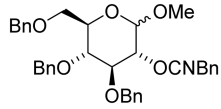


Table 1. Glycosylation Reaction of Donors Containing Various 2-*O*-Substituents with Methanol[a]



	Donor	Yield [α/β]	Product
1	 **1a**	44% (0:1)	 **2a**
2	 **1b**	91% (1:1)	 **2b**
3	 **1c**	95% (1:12)	 **2c**
4	 **1d**	82% (1:12)	 **2d**

[a]Reactions were performed with donor **1a–d** (0.074 mmol), MeOH (0.11 mmol), Ph_2SO (0.081 mmol), TTBP (0.185 mmol), and DCM (5 mL) at −40 °C to rt for 3 h.

broadly expanding application of benzyl groups in carbohydrate chemistry and chemical glycosylation.

RESULTS AND DISCUSSION

Previously we showed that that 1,2-*trans* stereoselectivity in glycosylation can be achieved by using 2-*O*-(2-nitrobenzyl) which can act as a neighboring glycosylation support of type **III** (Scheme 1).[10] Assuming that other substituted benzyl groups can show similar features and taking into account the relatively low stability of nitrobenzyl ethers, we decided to broaden the scope of this method and investigate whether a similar effect can be achieved by using other benzyl ethers. After initial trials, we selected 2-cyanobenzyl as a comparatively promising candidate to nitrobenzyl. The different geometry and electronic nature of both groups and different availability of electron pairs further encouraged comparison of both benzyl groups. Moreover, in

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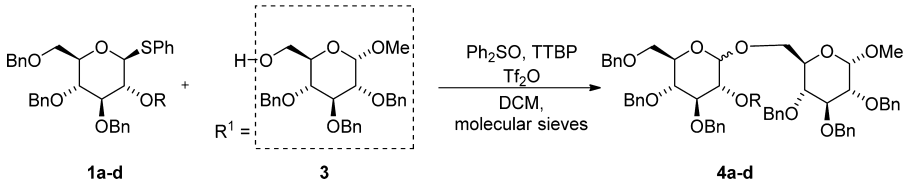
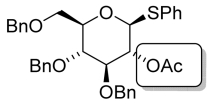
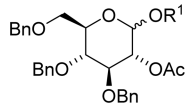
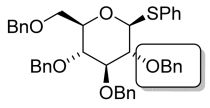
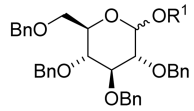
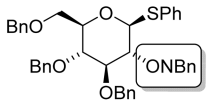
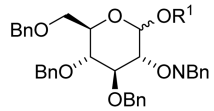
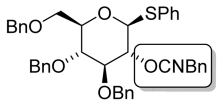
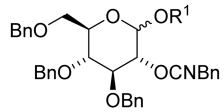
Table 2. Glycosylation Reaction with 6-OH Acceptor 3[s]



1a-d 3 4a-d

	Donor	Yield [α/β]	Product
1	 **1a**	42% (0:1)	 **4a**
2	 **1b**	60% (1:1)	 **4b**
3	 **1c**	88% (1:3)	 **4c**
4	 **1d**	86% (1:3)	 **4d**

[s]Reactions were performed with donor **1a–d** (0.074 mmol), acceptor **3** (0.11 mmol), Ph_2SO (0.081 mmol), TTBP (0.185 mmol), and CM (5 mL) at −40 °C to rt for 3 h.

contrast to the well-known external nitrile effect,[11] discovering the similar influence of a cyano substituent from the same sugar remote position was very exciting.

As the starting comparison points, we decided to use per-*O*-benzylated thioglucoside **1b** and 2-*O*-(2-nitrobenzyl)-(**1c**) as well as 2-*O*-(2-cyanobenzyl) thioglucoside (**1d**) donors. Both benzyl ethers (NBn, CNBn) could be efficiently prepared from the corresponding alcohols by using routine methodology like that used for regular benzyl ehers. All three donors **1b–d** as well as 2-*O*-(acetyl) thioglucoside (**1a**) were activated by treatment with Ph_2SO and triflic anhydride (Tf_2O) in the presence of 2,4,6-tri-*tert*-butylpyridine (TTBP) in dichloromethane as a standard condition[12] and coupled with methanol to afford methyl glucosides **2a–d** (Table 1). According to expectations, glycosidation of donor **1a** resulted in exclusive formation of *β*-methyl glucoside **2a** although in low yield (44%) as a combined effect of disarming the participating effect of the ester substituent (Table 1, entry 1). In contrast, glycosidation of per-*O*-benzylated donor **1b** was more efficient yet unselective, leading to a mixture of both anomers in a 1:1 ratio (Table 1, entry 2). This significant example of unselective glycosylation in the presence of regular benzyl ether attached to the C-2 position of the donor constitutes a comparison point for additional substituted benzyl groups. Indeed, reactions of both 2-*O*-(2-nitrobenzyl)- (**1c**) and 2-*O*-(2-cyanobenzyl)- (**1d**) thioglucosides turned out to be far more stereoselective. The desired 1,2-*trans* methyl glycosides **2c** and **2d** were isolated in high yields and with high levels of *β*-selectivity (Table 1, entries 3 and 4), thus confirming the assumed arming as well as participating effect of both substituted benzyl groups. The reactions with donors **1c**/**1d** and methanol as acceptor proceeded selectively in a range of solvents and additionally proved the prominent internal effect of 2-nitro- and 2-cyano substituents.[13]

The same series of donors **1a–d** have been submitted to more demanding glycosylation with methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (**3**) having a primary hydroxyl group at C-6. Results of this trial-by-fire for new benzyl ethers have been collected in Table 2. Glycosylation with **1a** as acceptor produced disaccharide **4a** in a modest yield but with complete *β*-stereoselectivity (Table 2, entry 1). Glycosylation of donors **1b–d** showed that the stereoselectivity of glycosylation was highly dependent on the electronic structure of benzyl ether at C-2. However, with all three armed donors the yields of the isolated disaccharides (**4b–d**) were high, and the *β*-stereoselectivity

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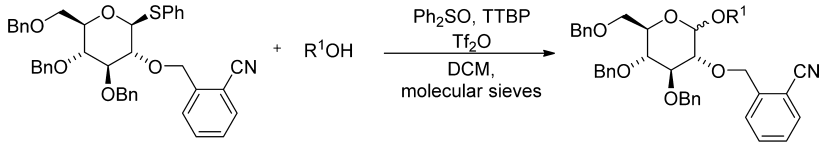
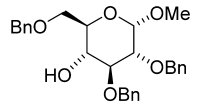
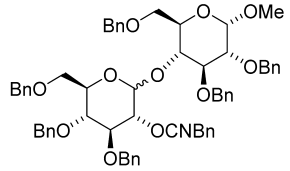
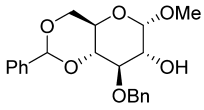
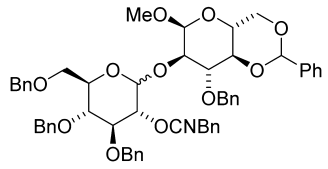
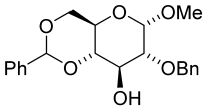
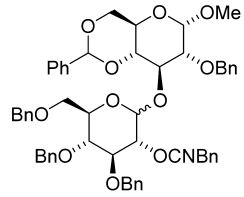
Table 3. Example of Various Glycosyl Acceptors Tested in Glycosylation with Donor 1d[a]



Entry	Acceptor	Yield (α/β)	Product	
1	 **5**	67% (1:5)		**8**
2	 **6**	34% (1:5)		**9**
3	 **7**	72% (1:4)		**10**
4	propan-2-ol	78% (0:1)	$R_1 = {}^{i}Pr$	**11**
5	benzyl alcohol	67% (1:10)	R_1 = Bn	**12**
6	nonan-1-ol	54% (0:1)	$R_1 = C_9H_{19}$	**13**

[a]Reactions were performed with donor **1d** (0.074 mmol), acceptor (0.11 mmol), Ph_2SO (0.081 mmol), TTBP (0.185 mmol), DCM (5 mL) at −40 °C to rt for 3 h.

of the process was considerable for 2-*O*-(2-nitrobenzyl)- (**1c**) and 2-*O*-(2-cyanobenzyl)- (**1d**) thioglucosides only (Table 2, entries 2 vs 3, 4). The fact that the glycosylation led principally to the formation of *β*-anomers provides strong support that the reactions proceed through neighboring participation of substituted benzyl ethers from the *α*-site of anomeric position in donor ring. The stereocontrolling effect of the 2-nitrobenzyl- and 2-cyanobenzyl groups was accompanied by a great influence on general reaction yield (Table 2, entry 1 vs 3, 4), which may refer to the arming effect of newly used benzyl ethers (NBn and CNBn).

Subsequent investigations focused on glycosylation of donor **1d** with 2-cyanobenzyl groups as relatively more stable and synthetically more useful when compared to their 2-nitro-counterpart. More investigations and results with donor **1c** have been presented in our previous work.[10] The synthetic scope of the current 2-cyanobenzyl protecting group was examined by changing the structure of acceptors (Table 3). The glycosylation of **1d** with **5**, which has a secondary hydroxyl group at C-4, proceeds smoothly and afforded the desired *O*-glycoside **8** with high *β*-selectivity and high yield (Table 3, entry 1). The glycosylation of **1d** with **6** and **7**, which have an equatorial hydroxyl group at C-2 and C-3, respectively, also afforded disaccharides **9** and **10** with predominant formation of *β*-anomers (Table 3, entries 2 and 3). Reaction of nonsugar alcohols (propan2-ol, benzyl alcohol, and nonan-1-ol) proceeded even better and resulted in the formation of expected *β*-anomers, exclusively (Table 3, entries 4−6).

In order to prove the applicability of the new methodology in organic synthesis, we examined the possibility of mild deprotection of thus-utilized 2-benzyl ethers from glucoside **2c** and **2d** (Scheme 2). Both ethers were easily cleaved when using standard debenzylation conditions (H_2/Pd−C). This methodology can be used for convenient deprotection of all benzyl substituents when necessary. Additionally, 2-nitrobenzyl protecting group can be also selectively cleaved in the presence of other

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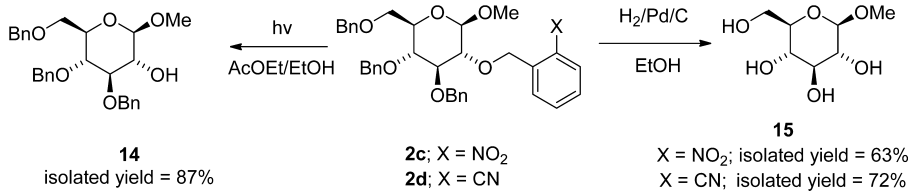
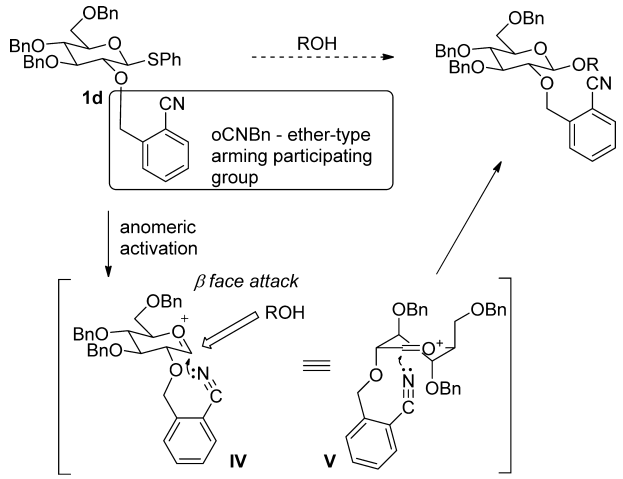
Scheme 2. Pd/C Hydrogenation and Selective UV-Light Deprotection of 2-Nitrobenzyl Group



benzyl groups by light irridation[14] affording methyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**14**) in high yield. This mild deprotection method can further open up new areas of application of 2-nitrobenzyl as arming participating protecting groups.

This successful application of 2-nitrobenzyl (NBn) and 2-cyanobenzyl (CNBn) as arming participating groups controlling 1,2-*trans*-glycosidic bond formation relies on the assumption of neighboring group participation of both tested benzyl ethers. Thus, we postulate that the oxocarbenium ion is controlled as a stable intermediate by electrons of 2-*O*-CNBn (Scheme 3) or 2-*O*-NBn protecting groups. Formal participation of the nitrogen (CN) or oxygen (NO_2) will give a more stable oxacarbenium ion providing β-glycosides after alcohol attack from only one face providing 1,2-*trans*-glycoside (Scheme 3).

Scheme 3. Proposed Participating Group Concept by Using Cyanobenzyl Group



To exclude alternative explanations[15] and to prove previously postulated mechanisms based on participation of 2-substituted benzyl groups in the glycosylation, we used DFT theoretical calculation methodology. The main goal of the theoretical (DFT) calculations was to investigate the electronic structure of the cationic form of **IV** (see Scheme 2) with and without the presence of leaving anion (OTf), to verify the possibility of formation of an intramolecular bond between the nitrile group and the cationic carbon center. The minimum energy structure of the cation is shown in Figure 1, structure **A**. In the absence of anion, a strong, "single" bond between nitrogen atom from nitrile group and carbon from glucose ring is formed: the distance is 1.506 Å, and the calculated bond-order is 0.968. As a result, the carbon−nitrogen bond in the nitrile group can be described as a "double" bond, with a bond order of 2.110 and a bond length equal to 1.236 Å. In addition, the significant interaction between the carbon atom of nitrile group and the ether oxygen can be observed, characterized by the bond order value of 0.670 and the distance of 1.625 Å. This may result from shifting electron density toward glucose ring and formation of a partial positive charge on the nitrile carbon atom. Thus, in the cationic structure **A** two additional five-membered rings are observed.

For neutral systems in which cationic glucose derivative is neutralized by OTf anion, two low energy structures were obtained from geometry optimization, presented in Figure 1 (panels B and C). Here, the structure with unbounded nitrile group is slightly lower in energy (by c.a. One kcal/mol), than the structure in which the bond between the nitrile nitrogen and the glucose carbon atom is preserved. However, since the energy difference is relatively low (below 1 kcal/mol), it can be expected that these structures can coexist.

Two conclusions emerge from comparison of the structures presented in Figure 1. First, the bond between the oxygen atom of the OTf anion and the respective glucose carbon is longer/weaker in structure B (bond length: 1.525 Å; bond order: 0.908) than in structure C (bond length: 1.413 Å; bond order: 1.077). Second, the comparison of structures A and C leads to the conclusion that the interaction between cationic species and anion results in strengthening of the nitrogen−carbon bond for C (increase in bond order from 0.968 to 1.065), while for structure B such an interaction is not observed; the distance between nitrogen atom and glucose carbon is 5.871 Å. These results support our assumption about participation of the nitrogen of CN group via formation of C−N bond with anomeric

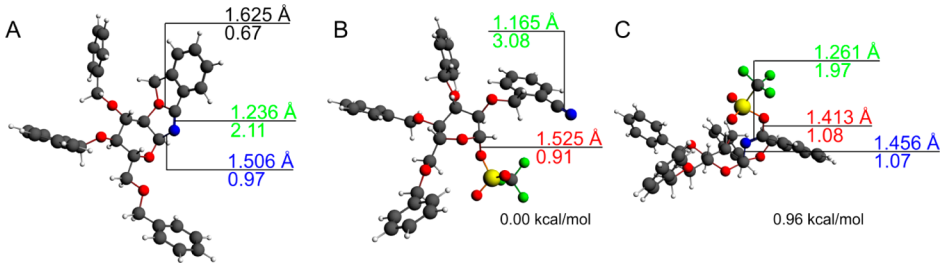


Figure 1. Comparison of bond lengths (top value) and bond orders (bottom value) for optimized models of structure **I** for cationic molecule (panel A) and neutral systems including anion (panels B and C). For structures B and C, the electronic energy difference is also presented.

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center of the oxacarbenium ion efficiently shielding the α-face to provide 1,2-*trans*-glycoside (Scheme 3).

In order to draw qualitative conclusions concerning the interaction of the analyzed system with nucleophiles, the molecular electrostatic potential (MEP) was characterized for compounds B and C, the color-coded contour is presented in Figure 2. A comparison clearly shows that in the vicinity of the

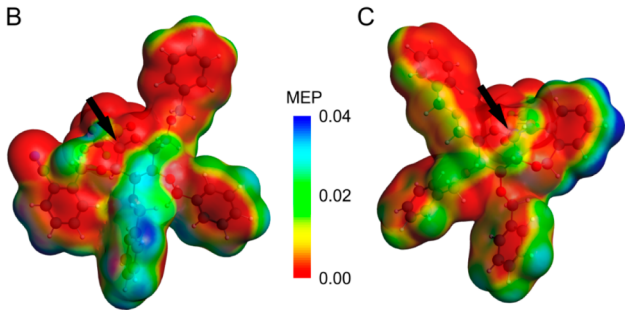


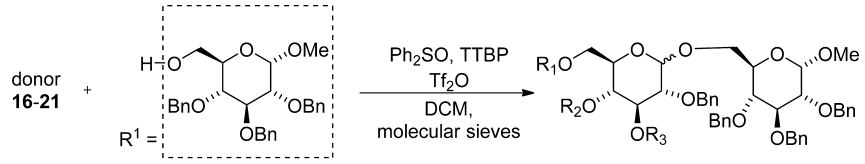
Figure 2. Molecular electrostatic potential (MEP), color-coded on the electron density isosurface (ρ = 0.001 au) for structures B (left) and C (right); the arrow points to the respective carbon atom that can be attacked by a nucleophile in the glycosylation reaction mechanism.

respective carbon atom undergoing the nucleophilic attack, the MEP is more positive for structure C than for B. Thus, it may be predicted that the structure C will be more reactive toward nucleophilic attack. This further strengthens the conclusion about the importance of the intramolecular bond between the nitrile nitrogen atom and the carbon atom of glucose, as a possible origin of the experimentally observed stereoselectivity.

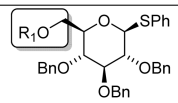
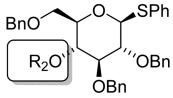
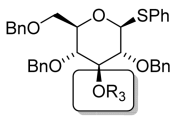
It was also interesting to investigate whether the participating effect of 2-substituted benzyl groups could be visible from remote positions of donors. The effect that these remote substituents may have on the reaction stereoselectivity was estimated at this stage. To assess this possibility, we tested a series of novel glycosyl donors equipped with 2-nitrobenzyl (NBn) and 2-cyanobenzyl (CNBn) groups at remote positions, i.e., C-6 (**16**, **17**), C-4 (**18**, **19**), and C-3 (**20**, **21**). The results of this study collected in Table 4 showed that the observed level of stereoselectivity controlled by remote benzyl groups is not exceptionally high, while formation of either α- or β-anomers supported our assumptions. Thus, 6-*O*-equipped thioglycoside **18** and **19** gave disaccharide **24** and **25** with reversed α-selectivity (Table 4, entry 1). In contrast, isomers with 4-*O*-substituted benzyl groups **18** and **19** showed a tendency for predominant formation of β-glycosides **24** and **25** (Table 4, entry 2) while 3-*O*-substituted donors were simply unselective (Table 4, entry 3).

An explanation for various modes of participating group effects is shown in Scheme 3. 2-Nitro- and 2-cyano-substituted benzyl groups attached to the C-4 position can interact with oxacarbenium ion in a *cis*-facial relationship, providing the expected β-selectivity for the attack of the glycoside acceptor. Direct

Table 4. Example of Remote Control in Glycosylation[a]



3 **22-27**

	Donor	Yield [α/β]	Product
1	 **16:** R_1=NBn **17:** R_1=CNBn	73% (2:1)	**22:** R_1=NBn, R_2=R_3=Bn
		85% (2:1)	**23:** R_1=CNBn, R_2=R_3=Bn
2	 **18:** R_2=NBn **19:** R_2=CNBn	79% (1:3)	**24:** R_2=NBn, R_1=R_3=Bn
		93% (1:2)	**25:** R_2=CNBn, R_1=R_3=Bn
3	 **20:** R_3=NBn **21:** R_3=CNBn	98% (1:1)	**26:** R_3=NBn, R_1=R_2=Bn
		80% (1:1)	**27:** R_3=CNBn, R_1=R_2=Bn

[a]Reaction were performed with donor **16**–**21** (0.074 mmol), **3** (0.11 mmol), Ph_2SO (0.081 mmol), TTBP (0.185 mmol), DCM (5 mL) at −40 °C to rt for 3 h.

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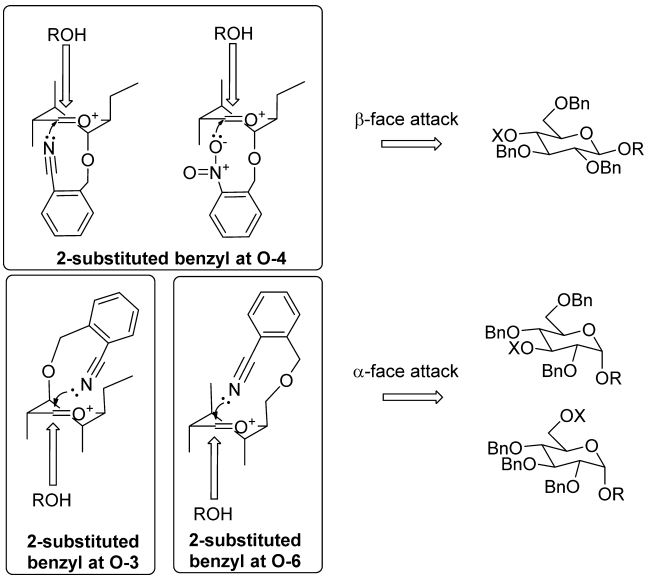
Scheme 4. Remote Participation of 2-Cyano- and 2-Nitrobenzyl Groups



interaction between 6-*O*-substituted benzyl groups with anomeric centers resulted in predominant formation of α-glycosides (Scheme 4), while nonselective reaction of 3-*O*-substituted thioglycoside resulted from ineffective shielding interaction of the substituent and the anomeric center.

CONCLUSIONS

In summary, we presented that 2-substituted benzyl protecting groups can efficiently control stereoselective formation of 1,2-*trans*-glycosidic linkage, thus acting as armed participating groups. We demonstrated that 1,2-*trans*-stereoselectivity can be achieved by using 2-*O*-(2-nitrobenzyl) and 2-*O*-(2-cyanobenzyl) ethers, which can act as neighboring glycosylation support. This ether group can also enhance the reaction yield by activation (arming) glycosyl donors, in contrast to broadly used deactivating esters. Similar yet lower stereoselectivity can be achieved by using remote benzyl groups. Easy protection and selective deprotection of presented 2-nitrobenzyl 2-cyanobenzyl group further confirms its usefulness in the synthesis.

EXPERIMENTAL SECTION

General Information. All starting materials and reagents were obtained from commercial sources and used as received unless otherwise noted. All solvents used were freshly distilled prior to use. Optical rotations were measured at room temperature with a polarimeter. High-resolution mass spectra were acquired using electrospray (ESI) ionization mode with a time-of-flight (TOF) detector. ^{1}H NMR spectra were recorded on spectrometers operating at 300, 500, and 600 MHz in $CDCl_3$. Data were reported as follows: chemical shifts in parts per million (ppm) from tetramethylsilane as an internal standard, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double−doublet, m = multiplet, br = broad), coupling constants (in hertz), and assignment. ^{13}C NMR spectra were measured at 75, 125, or 150 MHz with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. Reactions were controlled using TLC on silica [alu-plates (0.2 mm)]. Plates were visualized with UV light (254 nm) and by treatment with aqueous cerium(IV) sulfate solution with molybdic and sulfuric acid followed by heating. All organic solutions were dried over anhydrous sodium sulfate. Reaction products were purified by flash chromatography using silica gel 60 (240−400 mesh).

All the DFT calculations presented here are based on the Amsterdam Density Functional (ADF2013) program.[16−19] Structures were fully optimized using the Becke−Perdew exchange-correlation functional (BP86).[20,21] For obtained geometries dispersion correction to energy was calculated using BP86-D3 with Becke−Johnson damping.[22,23] A full electron basis set with a triple-ζ STO basis containing two sets of polarization functions was adopted for all of the elements (TZ2P). Auxiliary s, p, d, f, and g STO functions, centered on all nuclei, were used to fit electron density and obtain accurate Coulomb potentials in each SCF cycle. Relativistic effects were included using the ZORA formalism. The contours and the color-coded plots of the molecular electrostatic potential were plotted on the basis of the ADF-GUI interface.[24] Nalewajski−Mrozek bond-multiplicity indices[25,26] implemented in ADF program were used to quantify selected bond orders.

Synthesis and spectroscopic data for compound **1a−c**, **2a−c**, **3**, **4a−c**, **14**, and **15** were described previously.[10] Synthesis of known compound **5** have been performed on the basis of a method presented by Cheng,[27] known compounds **6** and **7** were prepared based on method presented by Potter.[28]

*Phenyl 3,4,6-Tri-O-benzyl-2-O-(o-cyanobenzyl)-1-thio-β-D-glucopyranoside (**1d**, Scheme 1).* Phenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (3 g, 5.1 mmol, 1 equiv) was dissolved in CH_3OH (15 mL), and KCN (36 mg, 0.5 mmol) was added. The reaction was stirred for 2 h, and another 36 mg KCN was added. After an additional 2 h, TLC indicated that the reaction was complete, and the mixture was concentrated in vacuo and dries in vacuo for 3 h. To the crude oil was added anhydrous MeCN (40 mL), and the solution was cooled to 0 °C. Sodium hydride (245 mg, 60% dispersion in mineral oil, 6.1 mmol, 1.2 equiv) was added carefully; the mixture was stirred at 0 °C for 30 min. Then *o*-cyanobenzyl bromide (1.21 g, 5.6 mmol, 1.1 equiv) was added in a 3 mL MeCN solution, and the mixture was allowed to warm to room temperature overnight. The mixture was quenched with methanol (3 mL). The phases were separated, and the aqueous phase was extracted with ethyl acetate (4 × 20 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification of the residue by crystallization from mixture EtOH/H_2O afforded phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(*o*-cyanobenzyl)-1-thio-β-D-glucopyranoside (**1d**) (2.7 g, 78%): mp 92−93 °C; $[\alpha]^{20}_D$ = −15.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.8 Hz, 1H), 7.63 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.61−7.50 (m, 3H), 7.42−7.19 (m, 20H), 5.08 (d, *J* = 12.5 Hz, 1H), 4.99 (d, *J* = 12.5 Hz, 1H), 4.86 (s, 2H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.69 (d, *J* = 9.7 Hz, 1H), 4.65 (d, *J* = 7.3 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.54 (d, *J* = 12.1 Hz, 1H), 3.86−3.64 (m, 4H), 3.55 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.9, 138.3, 138.2, 138.1, 133. 4, 132.7, 132.6, 132.0, 129.0, 128.6, 128.4, 127.9, 127.8, 127.7, 127.6, 117.2, 110.9, 87.1, 86.5, 81.1, 79.1, 77.9, 77.2, 75.7, 75.0, 73.4, 72.3, 69.0; HRMS (ESI-TOF) calcd for $C_{41}H_{39}NO_5S$ $[M + Na]^+$ 680.2447, found 680.2433.

Syntheses of donors **16−21** have been performed from the corresponding alcohols with free hydroxyl groups at C-3, C-4, and C-6. Synthesis and spectroscopic data for *phenyl 2,3,4-tri-O-benzyl-1-thio-β-D-glucopyranoside* was described by McGarrigle and co-workers.[29] Synthesis of *phenyl 2,3,6-tri-O-benzyl-1-thio-β-D-glucopyranoside* have been performed on the basis of a method presented by Møller.[30] *Phenyl 2,4,6-tri-O-benzyl-1-thio-β-D-glucopyranoside* has been prepared on the basis of a method presented by Kanie.[31]

General Procedure for the Preparation of 16, 18, and 20 (Procedure A). The sugar derivative with a free hydroxyl group (1 equiv) and tetrabutylammonium bromide (0.1 equiv) were dissolved in CH_2Cl_2 (10 mL). Then 33% KOH solution (10 mL) was added, and the mixture was vigorously stirred at room temperature for 30 min. After this time, *o*-nitrobenzyl bromide (1.5 equiv) was added, and the reaction was stirred until complete consumption of starting material (monitored by TLC). Then water (20 mL) was added, and the mixture extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification of the residue by crystallization from the mixture EtOH/H_2O gave the corresponding products.

General Procedure for the Preparation of 17, 19, and 21 (Procedure B). The starting material (1 equiv) was dissolved in

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anhydrous MeCN (15 mL), and the solution was cooled to 0 °C. Sodium hydride (60% dispersion in mineral oil, 2 equiv) was added carefully, and the mixture was stirred at 0 °C for 1 h. Then *o*-cyanobenzyl bromide (1.5 equiv) was added in 1 mL of MeCN solution, and the mixture was allowed to warm to room temperature overnight. The mixture was quenched with methanol (1 mL) and the aqueous phase extracted with ethyl acetate (4 × 20 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification of the residue by crystallization from mixture EtOH/H_2O afforded the corresponding products.

*Phenyl 2,3,4-Tri-O-benzyl-6-O-(o-nitrobenzyl)-1-thio-β-D-glucopyranoside (**16**, Table 4).* Compound **16** was obtained as a white solid (490 mg, 55%): mp 92−93 °C; $[\alpha]^{20}_D$ = −3.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.61 (td, *J* = 7.7, 1.2 Hz, 1H), 7.58−7.56 (m, 2H), 7.43 (ddd, *J* = 8.2, 1.4, 0.7 Hz, 1H), 7.41−7.39 (m, 2H), 7.35−7.22 (m, 16H), 4.95−4.89 (m, 3H), 4.88−4.84 (m, 3H), 4.75 (d, *J* = 10.3 Hz, 1H), 4.69 (d, *J* = 9.8 Hz, 1H), 4.62 (d, *J* = 11.1 Hz, 1H), 3.84 (dd, *J* = 10.7, 1.9 Hz, 1H), 3.79 (dd, *J* = 10.7, 4.7 Hz, 1H), 3.74 (t, *J* = 8.9 Hz, 1H), 3.67 (t, *J* = 9.4 Hz, 1H), 3.56−3.52 (m, 1H), 3.53 (dd, *J* = 9.7, 8.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.9, 138.3, 138.0, 137.9, 135.4, 133.8, 133.7, 133.7, 132.0, 128.9, 128.6, 128.5, 128.5, 128.5, 128.4, 128.2, 128.2, 127.9, 127.9, 127.8, 127.5, 124.8, 124.6, 87.4, 86.8, 80.8, 78.8, 77.7, 75.9, 75.4, 75.1, 69.8, 69.8; HRMS (ESI-TOF) calcd for $C_{40}H_{39}NO_7S$ $[M + Na]^+$ 700.2345, found 700.2329.

*Phenyl 2,3,4-Tri-O-benzyl-6-O-(o-cyanobenzyl)-1-thio-β-D-glucopyranoside (**17**, Table 4).* Compound **17** was obtained as a white solid (800 mg, 92%): mp 84 °C; $[\alpha]^{20}_D$ = +1.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.59 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.58−7.53 (m, 3H), 7.40−7.21 (m, 19H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.90 (d, *J* = 10.3 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 2H), 4.76 (d, *J* = 13.1 Hz, 1H), 4.74 (d, *J* = 10.3 Hz, 1H), 4.69 (d, *J* = 9.8 Hz, 1H), 4.69 (d, *J* = 12.6 Hz, 1H), 4.62 (d, *J* = 11.0 Hz, 1H), 3.84 (dd, *J* = 10.8, 1.9 Hz, 1H), 3.79 (dd, *J* = 10.8, 4.7 Hz, 1H), 3.72 (t, *J* = 8.9 Hz, 1H), 3.65 (t, *J* = 9.4 Hz, 1H), 3.55−3.51 (m, 1H), 3.52 (dd, *J* = 9.7, 8.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.1, 138.3, 138.0, 137.9, 133.7, 132.8, 132.6, 132.0, 128.9, 128.5, 128.4, 128.3, 128.2, 127.9, 127.9, 127.8, 127.7, 127.4, 117.2, 111.0, 87.4, 86.8, 80.9, 78.9, 77.6, 75.9, 75.4, 75.1, 70.9, 69.8; HRMS (ESI-TOF) calcd for $C_{41}H_{39}NO_5S$ $[M + Na]^+$ 680.2447, found 680.2407.

*Phenyl 2,3,6-Tri-O-benzyl-4-O-(o-nitrobenzyl)-1-thio-β-D-glucopyranoside (**18**, Table 4).* Compound **18** was obtained as a white solid (720 mg, 78%): mp 77 °C; $[\alpha]^{20}_D$ = +12.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.64 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.60−7.57 (m, 2H), 7.52 (td, *J* = 7.7, 1.2 Hz, 1H), 7.40−7.37 (m, 3H), 7.34−7.13 (m, 16H), 5.19 (d, *J* = 14.8 Hz, 1H), 4.99 (d, *J* = 14.8 Hz, 1H), 4.90 (d, *J* = 10.3 Hz, 1H), 4.86 (d, *J* = 11.1 Hz, 1H), 4.71 (d, *J* = 10.3 Hz, 1H), 4.69 (d, *J* = 9.8 Hz, 1H), 4.66 (d, *J* = 11.1 Hz, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.51 (d, *J* = 11.8 Hz, 1H), 3.77 (dd, *J* = 10.9, 1.9 Hz, 1H), 3.74−3.69 (m, 3H), 3.56−3.51 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.8, 138.1, 138.0, 135.0, 133.8, 133.5, 131.9, 128.9, 128.6, 128.4, 128.3, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.5, 124.8, 124.5, 87.5, 86.6, 80.9, 79.0, 78.0, 75.7, 75.4, 73.4, 71.0, 69.1; HRMS (ESI-TOF) calcd for $C_{40}H_{39}NO_7S$ $[M + Na]^+$ 700.2345, found 700.2338.

*Phenyl 2,3,6-Tri-O-benzyl-4-O-(o-cyanobenzyl)-1-thio-β-D-glucopyranoside (**19**, Table 4).* Compound **19** was obtained as a white solid (800 mg, 89%): mp 86 °C; $[\alpha]^{20}_D$ = −1.4 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60−7.57 (m, 3H), 7.45 (td, *J* = 7.7, 1.3 Hz, 1H), 7.38−7.21 (m, 20H), 4.97 (d, *J* = 12.2 Hz, 1H), 4.91 (d, *J* = 11.2 Hz, 1H), 4.90 (d, *J* = 10.3 Hz, 1H), 4.82 (d, *J* = 12.2 Hz, 1H), 4.78 (d, *J* = 11.2 Hz, 1H), 4.70 (d, *J* = 10.3 Hz, 1H), 4.67 (d, *J* = 9.8 Hz, 1H), 4.60 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 11.9 Hz, 1H), 3.81 (d, *J* = 3.2 Hz, 2H), 3.73−3.69 (m, 2H), 3.54−3.50 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.6, 138.3, 138.3, 138.0, 133.8, 132.8, 132.0, 128.9, 128.8, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.6, 127.5, 117.4, 111.3, 87.4, 86.5, 80.9, 78.9, 77.9, 75.6, 75.3, 73.3, 72.2, 69.0; HRMS (ESI-TOF) calcd for $C_{41}H_{39}NO_5S$ $[M + Na]^+$ 680.2447, found 680.2419.

*Phenyl 2,4,6-Tri-O-benzyl-3-O-(o-nitrobenzyl)-1-thio-β-D-glucopyranoside (**20**, Table 4).* Compound **20** was obtained as a white solid (690 mg, 75%): mp 103 °C; $[\alpha]^{20}_D$ = −7.1 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.84 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.60−7.57 (m, 2H), 7.54 (td, *J* = 7.7, 1.2 Hz, 1H), 7.39 (t, *J* = 7.1 Hz, 1H), 7.37−7.18 (m, 16H), 7.09−7.07 (m, 2H), 5.25 (d, *J* = 15.4 Hz, 1H), 5.20 (d, *J* = 15.4 Hz, 1H), 4.89 (d, *J* = 10.4 Hz, 1H), 4.67 (d, *J* = 9.8 Hz, 1H), 4.65 (d, *J* = 10.9 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 10.8 Hz, 1H), 4.57 (d, *J* = 11.0 Hz, 1H), 4.56 (d, *J* = 12.3 Hz, 1H), 3.79 (dd, *J* = 10.8, 1.9 Hz, 1H), 3.77−3.73 (m, 2H), 3.70 (t, *J* = 9.3 Hz, 1H), 3.53 (dd, *J* = 9.7, 8.7 Hz, 1H), 3.51−3.48 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.6, 138.2, 137.8, 137.7, 135.6, 133.9, 133.6, 131.9, 128.9, 128.4, 128.3, 128.3, 128.1, 127.8, 127.8, 127.8, 127.7, 127.6, 127.5, 124.6, 87.6, 86.6, 80.9, 79.0, 77.7, 75.4, 74.9, 73.5, 71.5, 68.9; HRMS (ESI-TOF) calcd for $C_{40}H_{39}NO_7S$ $[M + Na]^+$ 700.2345, found 700.2307.

*Phenyl 2,4,6-Tri-O-benzyl-3-O-(o-cyanobenzyl)-1-thio-β-D-glucopyranoside (**21**, Table 4).* Compound **21** was obtained as a white solid (1.05 g, 77%): mp 122 °C; $[\alpha]^{20}_D$ = +2.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59−7.57 (m, 2H), 7.56 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.53 (dd, *J* = 7.8, 0.5 Hz, 1H), 7.45 (td, *J* = 7.7, 1.3 Hz, 1H), 7.35−7.22 (m, 17H), 7.15−7.13 (m, 2H), 5.08 (d, *J* = 12.9 Hz, 1H), 5.02 (d, *J* = 12.9 Hz, 1H), 4.91 (d, *J* = 10.4 Hz, 1H), 4.72 (d, *J* = 11.0 Hz, 1H), 4.67 (d, *J* = 11.0 Hz, 1H), 4.67 (d, *J* = 9.7 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 11.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 3.77 (dd, *J* = 10.9, 1.9 Hz, 1H), 3.73−3.70 (m, 2H), 3.67 (t, *J* = 9.3 Hz, 1H), 3.53 (dd, *J* = 9.7, 8.5 Hz, 1H), 3.51−3.48 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.2, 138.2, 137.9, 137.9, 133.9, 132.7, 132.6, 131.9, 128.9, 128.3, 128.1, 127.8, 127.8, 127.7, 127.6, 127.4, 117.2, 110.8, 87.6, 87.0, 80.8, 79.0, 77.7, 75.2, 74.9, 73.4, 72.8, 68.9; HRMS (ESI-TOF) calcd for $C_{41}H_{39}NO_5S$ $[M + Na]^+$ 680.2447, found 680.2400.

General Procedures of Glycosylation for Compound 2a−d, 4a−d, 8−13, and 22−27. To a cooled solution (−40 °C) of donor (0.076 mmol, 1.0 equiv), Ph_2SO (0.084 mmol, 1.1 equiv), TTBP (0.19 mmol, 2.5 equiv), and freshly activated molecular sieves (3 Å, 100 mg) in 5 mL of CH_2Cl_2 was added Tf_2O (0.084 mmol, 1.1 equiv). The mixture was allowed to stir at the same temperature about 15 min, and then acceptor (0.114 mmol, 1.5 equiv) was added. The mixture was allowed to warm to rt. After 3 h, 5 equiv of Et_3N was added, and the mixture was stirred for 15 min at rt. The reaction was then quenched with aqueous NH_4Cl and extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel with hexane/EtOAc to afford the desired glycosides.

*Methyl 3,4,6-Tri-O-benzyl-2-O-(o-cyanobenzyl)-α/β-D-glucopyranoside (**2d**, Table 1).* Compound **2d** was obtained as a colorless oil (36 mg; 82%; α/β = 1:12): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.54 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.48 (td, *J* = 7.6, 1.4 Hz, 1H), 7.38−7.23 (m, 15H), 7.15 (m, 2H), 5.15 (d, *J* = 12.6 Hz, 1H), 4.88 (d, *J* = 12.6 Hz, 1H), 4.87 (d, *J* = 11.7 Hz, 1H), 4.80 (d, *J* = 11.7 Hz, 1H), 4.79 (d, *J* = 11.1 Hz, 1H), 4.63 (d, *J* = 12.9 Hz, 1H), 4.55 (d, *J* = 12.9 Hz, 1H), 4.52 (d, *J* = 11.1 Hz, 1H), 4.33 (d, *J* = 7.8 Hz, 1H, H1-*β*), 3.80−3.59 (m, 4H), 3.57 (s, 3H), 3.51−3.40 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2, 138.6, 138.2, 138.1, 132.8, 132.7, 129.1, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 117.4, 111.6, 104.4, 84.5, 82.4, 77.9, 77.2, 75.6, 75.0, 74.9, 73.5, 71.7, 68.9, 57.0; HRMS (ESI-TOF) calcd for $C_{36}H_{37}NO_6$ $[M + Na]^+$ 602.2519, found 602.2495.

*Methyl 2,3,4-Tri-O-benzyl-6-O-(3,4,6-tri-O-benzyl-2-O-(o-cyanobenzyl)-α/β-D-glucopyranosyl)-α-D-glucopyranoside (**4d**, Table 2).* Compound **4d** was obtained as a colorless oil (66 mg, 86%, α/β = 1:3): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (m, 1.6H), 7.40 (d, *J* = 7.7 Hz, 1.3H), 7.38−7.20 (m, 40H), 7.16 (d, *J* = 6.9 Hz, 5H), 5.18 (d, *J* = 13.2 Hz, 1.27H, HC*H*-*o*CBn, 0.27H, *J* = 1.8 Hz, H1′-*α*), 4.95 (m, 3.26H), 4.87−4.75 (m, 6.1H), 4.71 (d, *J* = 10.9 Hz, 1H), 4.65 (d, *J* = 11.9 Hz, 2H), 4.61−4.51 (m, 6H), 4.47 (m, 0.78H), 4.38 (d, *J* = 10.2 Hz, 1H), 4.36 (d, *J* = 7,8 Hz, 1H, H1′-*β*) 4.16 (d, *J* = 10.7 Hz, 1H), 3.96 (m, 1.74H), 3.87 (m, 0.3H), 3.82−3.62 (m, 7.45H), 3.62−3.55 (m, 2.85H), 3.51 (m, 1.24H), 3.46−3.41 (m, 1.2H), 3.41−3.37 (m, 6H), 3.35 (s, 0.8H), 3.32 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.2, 139.0, 138.5, 138.4, 138.3, 138.2, 138.1, 132.9, 132.7, 132.6, 132.4, 128.4, 128.3, 128.2, 128.1, 128.00, 127.9, 127.8, 127.7, 127.6, 127.5, 117.2, 117.1, 110.8, 110.6, 103.6, 98.1, 97.9, 96.9, 84.6, 82.2, 82.1, 81.9, 81.5, 80.3, 80.0, 78.1,

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77.9, 77.7, 75.7, 75.6, 75.4, 75.1, 74.9, 74.7, 73.5, 73.4, 73.1, 71.7, 70.4, 69.7, 69.3, 69.0, 68.6, 68.5, 65.8, 55.2; HRMS (ESI-TOF) calcd for $C_{63}H_{65}NO_{11}$ $[M + Na]^+$ 1034.4450, found 1034.4438.

*Methyl 2,3,6-Tri-O-benzyl-4-O-(3,4,6-tri-O-benzyl-2-O-(o-cyanobenzyl)-α/β-D-glucopyranosyl)-α-D-glucopyranoside (**8**, Table 3).* Compound **8** was obtained as a colorless oil (52 mg, 67%, α/β = 1:5): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63−7.58 (m, 0.2H), 7.57−7.55 (m, 1.2H), 7.54−7.46 (m, 3H), 7.44−7.40 (m, 3H), 7.39−7.26 (m, 42H), 7.18−7.11 (m, 3H), 5.16 (d, J = 12.8 Hz, 1H), 5.08 (d, J = 3.7 Hz, 0.2H, H1′-α), 4.99−4.91 (m, 3.8H), 4.87−4.79 (m, 7.2H), 4.78 (d, J = 2.1 Hz, 1.2H, H1-α), 4.68 (d, J = 6.5 Hz, 1H, H1′-β), 4.67−4.60 (m, 4.7H), 4.60−4.54 (m, 3H), 4.54−4.44 (m, 5H), 4.06 (t, J = 9.4 Hz, 0.2H), 3.98 (t, J = 9.3 Hz, 1H), 3.85−3.68 (m, 6H), 3.66−3.50 (m, 7.8H), 3.49−3.42 (m, 2H), 3.40 (s, 0.6H), 3.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 140.2, 139.9, 139.7, 139.6, 139.5, 139.3, 138.7, 138.0, 135.0, 134.1, 134.0, 132.8, 130.8, 130.3, 130.2, 129.9, 129.8, 129.6, 129.4, 129.3, 129.2, 129.1, 129.0, 118.8, 112.7, 103.6, 99.6, 97.1, 85.9, 83.83, 83.6, 82.0, 81.3, 79.4, 79.1, 79.0, 78.7, 78.4, 78.2, 77.2, 77.0, 76.4, 76.3, 74.9, 74.8, 73.2, 72.5, 72.0, 71.7, 71.5, 70.3, 69.9, 61.8, 56.6; HRMS (ESI-TOF) calcd for $C_{63}H_{65}NO_{11}$ $[M + Na]^+$ 1034.4450, found 1034.4435.

*Methyl 4,6-O-Benzylidene-3-O-benzyl-2-O-(3,4,6-tri-O-benzyl-2-O-(o-cyanobenzyl)-α/β-D-glucopyranosyl)-α-D-glucopyranoside (**9**, Table 3).* Compound **9** was obtained as a colorless oil (24 mg, 34%, α/β = 1:5): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72−7.67 (m, 0.5H), 7.56−7.47 (m, 5H), 7.39−7.18 (m, 39H), 7.17−7.12 (m, 2.6H), 5.59 (s, 0.16H), 5.55 (s, 1H), 5.19 (d, J = 13.0 Hz, 1H), 5.13 (d, J = 12.7 Hz, 0.2H), 5.02−4.76 (m, 8H), 4.70−4.67 (m, 0.5H), 4.61−4.48 (m, 6.5H), 4.43 (dd, J = 9.4, 3.8 Hz, 0.2H), 4.33−4.30 (m, 1.1H), 4.11−4.06 (m, 1.5H), 3.96−3.84 (m, 2.3H), 3.80−3.72 (m, 2H), 3.73−3.63 (m, 6H), 3.61 (d, J = 8.5 Hz, 0.8H), 3.60−3.52 (m, 2H), 3.55−3.45 (m, 1.5H), 3.44 (s, 4.2H), 3.38 (s, 0.5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.7, 142.3, 138.5, 138.0, 137.4, 132.7, 132.6, 132.5, 132.4, 131.1, 129.3, 129.0, 128.9, 128.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 126.0, 125.0, 124.8, 123.4, 117.4, 111.07, 104.1, 101.4, 100.4, 84.5, 84.4, 82.9, 82.3, 82.2, 78.5, 78.0, 77.9, 77.8, 77.2, 77.0, 76.8, 75.6, 75.5, 75.1, 75.0, 74.9, 74.7, 73.4, 73.3, 71.7, 69.2, 69.0, 62.2, 60.4, 55.4; HRMS (ESI-TOF) calcd for $C_{56}H_{57}NO_{11}$ $[M + Na]^+$ 942.3824, found 942.3791.

*Methyl 4,6-O-Benzylidene-2-O-benzyl-3-O-(3,4,6-tri-O-benzyl-2-O-(o-cyanobenzyl)-α/β-D-glucopyranosyl)-α/β-D-glucopyranoside (**10**, Table 3).* Compound **10** was obtained as a colorless oil (50 mg, 72%, α/β = 1:4): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58−7.55 (m, 2H), 7.51−7.48 (m, 3H), 7.46−7.41 (m, 2H), 7.40−7.26 (m, 37H), 7.18−7.10 (m, 2.4H), 5.55 (s, 1H), 5.16 (d, J = 12.7 Hz, 1H), 5.08 (d, J = 3.6 Hz, 0.25H, H1′-α), 5.05−5.02 (m, 0.25H), 4.98−4.90 (m, 3H), 4.88−4.76 (m, 6H), 4.76−4.60 (m, 4.2H), 4.59 (d, J = 3.7 Hz, 1.2H, H1-α), 4.58−4.54 (m, 1.6H), 4.52 (d, J = 7.8 Hz, 1H, H1′-β), 4.49 (dd, J = 11.4, 5.7 Hz, 1H), 4.27 (dd, J = 10.2, 4.8 Hz, 1H), 4.08−4.02 (m, 1.4H), 3.85−3.80 (m, 2.6H), 3.78−3.69 (m, 3.4H), 3.65−3.58 (m, 3.2H), 3.58−3.52 (m, 1.8H), 3.51−3.46 (m, 1.3H), 3.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 138.7, 138.5, 138.1, 137.4, 137.2, 136.60, 133.6, 132.8, 132.7, 132.6, 131.4, 129.7, 129.4, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 126.0, 117.4, 117.1, 111.5, 111.2, 102.1, 101.3, 99.2, 95.7, 84.5, 82.4, 82.1, 81.9, 81.3, 80.5, 79.8, 79.1, 78.6, 77.9, 77.9, 77.6, 75.6, 75.3, 75.1, 75.0, 74.9, 73.8, 73.5, 73.1, 71.8, 71.1, 70.6, 70.5, 70.3, 69.6, 69.1, 68.8, 68.3, 62.3, 55.3; HRMS (ESI-TOF) calcd for $C_{56}H_{57}NO_{11}$ $[M + Na]^+$ 942.3824, found 942.3807.

*Isopropyl 3,4,6-Tri-O-benzyl-2-O-(o-cyanobenzyl)-β-D-glucopyranoside (**11**, Table 3).* Compound **11** was obtained as solid (36 mg, 78%): mp 63−65 °C; $[\alpha]^{20}_D$ = −9.5 (c = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58−7.55 (m, 1H), 7.50−7.41 (m, 2H), 7.36−7.25 (m, 17H), 7.19−7.15 (m, 2H), 5.20 (d, J = 12.9 Hz, 1H), 4.93 (d, J = 12.9 Hz, 1H), 4.87 (d, J = 12.0 Hz, 1H), 4.81 (d, J = 12.0 Hz, 1H), 4.80 (d, J = 12.0 Hz, 1H), 4.61 (d, J = 12.2 Hz, 1H), 4.57 (dd, J = 12.2, 1H), 4.54 (d, J = 12.0, 1H), 4.49 (d, J = 7.8 Hz, 1H, H1-β), 4.03 (hept, J = 6.1 Hz, 1H), 3.73 (dd, J = 10.8, 2.0 Hz, 1H), 3.66 (m, 1H), 3.67 (t, J = 9.3 Hz, 1H), 3.57 (t, J = 9.3 Hz, 1H), 3.50−3.38 (m, 2H), 1.30 (d, J = 6.2 Hz, 3H), 1.21 (d, J = 6.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 138.6, 138.3, 138.1, 136.6, 132.7, 129.4, 128.9, 128.8, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.5, 117.4, 111.2, 101.8, 84.6, 82.4, 78.1, 75.6, 75.0, 74.8, 73.5, 72.2, 71.6, 69.1, 23.7, 22.0; HRMS (ESI-TOF) calcd for $C_{38}H_{41}NO_6$ $[M + Na]^+$ 630.2826, found 630.2796.

*Benzyl 3,4,6-Tri-O-benzyl-2-O-(o-cyanobenzyl)-α/β-D-glucopyranoside (**12**, Table 3).* Compound **12** was obtained as a colorless oil (33 mg, 67%, α/β = 1:10): ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63−7.55 (m, 1.86H), 7.52−7.48 (m, 1H), 7.45−7.27 (m, 24H), 7.18−7.15 (m, 2H), 5.17 (d, J = 12.7 Hz, 1H), 5.08 (d, J = 3.7 Hz, 0.18H), 4.98−4.91 (m, 2.32H), 4.88−4.72 (m, 4H), 4.71−4.60 (m, 3H), 4.60−4.54 (m, 1.73H), 4.53 (d, J = 7.8 Hz, 1.65H), 4.49 (dd, J = 11.4, 3.7 Hz, 0.58H), 4.09−4.03 (m, 0.2H), 3.82−3.50 (m, 6.41H), 3.49−3.45 (m, 1.13H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 138.5, 138.2, 138.1, 137.3, 136.6, 133.63, 132.8, 132.7, 132.6, 131.4, 129.5, 128.9, 128.8, 128.8, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 117.4, 111.3, 102.2, 95.7, 84.5, 82.4, 80.0, 80.6, 78.0, 77.6, 77.3, 77.0, 76.8, 75.6, 75.1, 75.0, 74.9, 73.5, 71.8, 71.1, 70.5, 70.3, 69.6, 68.9, 68.3; HRMS (ESI-TOF) calcd for $C_{42}H_{41}NO_6$ $[M + Na]^+$ 678.2826, found 678.2799.

*Nonyl 3,4,6-Tri-O-benzyl-2-O-(o-cyanobenzyl)-β-D-glucopyranoside (**13**, Table 3).* Compound **13** was obtained as a colorless oil (28 mg, 54%): $[\alpha]^{20}_D$ = −2.8 (c = 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60−7.56 (m, 1H), 7.48 (ddd, J = 7.7, 6.4, 1.2 Hz, 1H), 7.36−7.30 (m, 4H), 7.30−7.23 (m, 10H), 7.18−7.14 (m, 2H), 5.18 (d, J = 12.8 Hz, 1H), 4.92 (d, J = 12.8 Hz, 1H), 4.87 (d, J = 11.1 Hz, 1H), 4.81 (d, J = 10.8, 1H), 4.79 (d, J = 11.1, 1H), 4.62 (d, J = 12.2 Hz, 1H), 4.56 (d, J = 12.2 Hz, 1H), 4.54 (d, J = 10.8 Hz, 1H), 4.41 (d, J = 7.8 Hz, 1H, H1-β), 3.93 (dt, J = 9.4, 6.7 Hz, 1H), 3.75 (dd, J = 10.8, 1.9 Hz, 1H), 3.71−3.62 (m, 2H), 3.59 (t, J = 9.3 Hz, 1H), 3.54 (dt, J = 9.4, 6.9 Hz, 1H), 3.50−3.42 (m, 2H), 1.67−1.60 (m, 2H), 1.38−1.16 (m, 12H), 0.87 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.4, 138.6, 138.2, 138.1, 132.7, 132.6, 128.8, 128.4, 128.3, 128.0, 127.7, 127.6, 127.5, 117.3, 111.3, 103.4, 84.5, 82.4, 78.1, 75.6, 75.0, 74.9, 73.5, 71.6, 70.2, 69.0, 31.9, 29.7, 29.5, 29.4, 29.3, 26.1, 22.7, 14.1; HRMS (ESI-TOF) calcd for $C_{44}H_{53}NO_6$ $[M + Na]^+$ 714.3765, found 714.3742.

*Methyl 2,3,4-Tri-O-benzyl-6-O-(2,3,4-tri-O-benzyl-6-O-(o-nitrobenzyl)-α/β-D-glucopyranosyl)-α/β-D-glucopyranoside (**22**, Table 4).* Compound **22** was obtained as a colorless oil (57 mg, 73%, α/β = 2:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06−8.02 (m, 1.7H), 7.81 (dd, J = 7.8, 1.0 Hz, 0.7H), 7.75 (dd, J = 7.8, 1.1 Hz, 1.2H), 7.60−7.52 (m, 2.3H), 7.42−7.13 (m, 55H), 5.01−4.48 (m, 27.5H), 4.37 (d, J = 7.7 Hz, 0.6H), 4.17−4.07 (m, 1.6H), 3.99 (td, J = 9.3, 2.6 Hz, 2.7H), 3.87−3.41 (m, 18H), 3.36 (s, 3H), 3.33 (s, 1.7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9, 146.8, 138.8, 138.6, 138.4, 138.2, 138.1, 138.0, 135.3, 135.2, 133.7, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 124.5, 103.8, 98.1, 98.0, 97.1, 84.8, 82.1, 82.0, 81.7, 80.1, 79.8, 77.8, 75.8, 75.7, 75.6, 74.9, 73.3, 72.4, 70.4, 70.2, 69.9, 69.7, 66.1, 55.2, 55.2; HRMS (ESI-TOF) calcd for $C_{62}H_{65}NO_{13}$ $[M + Na]^+$ 1054.4354, found 1054.4336.

*Methyl 2,3,4-Tri-O-benzyl-6-O-(2,3,4-tri-O-benzyl-6-O-(o-cyanobenzyl)-α/β-D-glucopyranosyl)-α/β-D-glucopyranoside (**23**, Table 4).* Compound **23** was obtained as a colorless oil (65 mg, 85%, α/β = 2:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61−7.48 (m, 7H), 7.46 (dd, J = 7.7, 1.3 Hz, 0.3H), 7.35−7.15 (m, 59H), 5.18 (d, J = 3.4 Hz, 0.3H), 5.12 (d, qJ = 11.5 Hz, 0.3H), 5.00−4.53 (m, 28H), 4.51 (d, J = 11.2 Hz, 0.4H), 4.47 (d, J = 13.1 Hz, 0.3H), 4.37 (d, J = 7.8 Hz, 0.4H, H1-β), 4.20−4.16 (m, 0.7H), 4.13−4.10 (m, 0.6H), 3.98 (td, J = 9.3, 4.2 Hz, 2.5H), 3.85−3.47 (m, 17H), 3.44 (dd, J = 9.6, 3.6 Hz, 1H), 3.36 (s, 3H), 3.32 (s, 1.3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.0, 138.8, 138.7, 138.4, 138.2, 138.0, 133.1, 133.0, 132.8, 132.5, 129.3, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.8, 127.7, 127.7, 127.6, 127.5, 117.2, 110.9, 103.8, 98.1, 98.0, 97.2, 82.1, 82.0, 81.7, 80.2, 80.1, 79.8, 77.8, 77.7, 77.5, 77.4, 75.7, 75.6, 75.5, 75.0, 74.9, 74.9, 73.3, 73.2, 72.4, 70.9, 70.7, 70.4, 70.3, 69.9, 69.5, 66.1, 55.2, 55.2; HRMS (ESI-TOF) calcd for $C_{63}H_{65}NO_{11}$ $[M + Na]^+$ 1034.4455, found 1034.4410.

*Methyl 2,3,4-Tri-O-benzyl-6-O-(2,3,6-tri-O-benzyl-4-O-(o-nitrobenzyl)-α/β-D- glucopyranosyl)-α/β-D-glucopyranoside (**24**, Table 4.* Compound **24** was obtained as a white solid (62 mg, 79%, α/β = 1:3): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.1, 1.2 Hz, 0.3H), 8.02 (dd, J = 8.2, 1.2 Hz, 1.2H), 7.62 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 7.8 Hz, 0.7H), 7.51 (td, J = 7.7, 1.2 Hz, 1.3H), 7.46 (td, J = 7.7, 1.3 Hz, 0.5H), 7.42 (t, J = 7.7 Hz, 0.4H), 7.38 (t, J = 7.8 Hz, 1.8H), 7.34−7.14 (m, 44H),

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7.12−7.09 (m, 2H), 5.19 (d, J = 14.9 Hz, 0.3H), 5.17 (d, J = 14.8 Hz, 1H), 4.99−4.48 (m, 21H), 4.39 (d, J = 12.1 Hz, 0.3H), 4.36 (d, J = 7.8 Hz, 1H, H1-β), 4.18 (dd, J = 10.9, 2.0 Hz, 1H), 3.99 (t, J = 9.3 Hz, 1H), 3.94 (t, J = 9.3 Hz, 0.3H), 3.86−3.43 (m, 15H), 3.37 (s, 1H), 3.33 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.8, 146.7, 138.8, 138.8, 138.5, 138.4, 138.4, 138.3, 138.2, 138.2, 138.1, 138.1, 135.1, 134.9, 133.8, 133.5, 133.4, 128.6, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 124.6, 124.5, 124.4, 104.3, 103.8, 98.1, 98.0, 84.6, 82.2, 82.1, 82.0, 81.4, 80.0, 79.8, 78.1, 78.0, 77.8, 77.7, 76.2, 75.7, 75.7, 75.5, 74.9, 74.8, 74.1, 73.4, 73.3, 72.4, 71.9, 70.9, 70.3, 70.1, 69.9, 69.3, 69.1, 68.6, 66.2, 65.4, 55.2, 55.1; HRMS (ESI-TOF) calcd for $C_{62}H_{65}NO_{13}$ $[M + Na]^+$ 1054.4354, found 1054.4310.

*Methyl 2,3,4-Tri-O-benzyl-6-O-(2,3,6-tri-O-benzyl-4-O-(o-cyanobenzyl)-α/β-D- glucopyranosyl)-α/β-D-glucopyranoside (**25**, Table 4).* Compound **25** was obtained as a white solid (72 mg, 93%, α/β = 1:2): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59−7.56 (m, 1.7H), 7.47−7.40 (m, 3.3H), 7.35−7.17 (m, 55H), 4.99−4.90 (m, 7H), 4.82−4.45 (m, 19H), 4.35 (d, J = 7.8 Hz, 1H), 4.17 (dd, J = 10.9, 2.0 Hz, 1H), 4.01−3.93 (m, 2.3H), 3.85−3.41 (m, 17.3H), 3.36 (s, 1.7H), 3.32 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.1, 141.7, 138.9, 138.7, 138.5, 138.4, 138.3, 138.2, 138.1, 138.0, 132.7, 132.7, 132.6, 132.6, 131.0, 129.3, 128.8, 128.6, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 124.8, 117.4, 111.4, 103.8, 98.0, 98.0, 97.2, 84.5, 82.2, 82.0, 80.2, 80.1, 79.8, 78.1, 78.0, 77.8, 75.7, 75.6, 75.4, 75.3, 74.9, 74.8, 74.8, 73.3, 72.3, 72.1, 70.4, 70.1, 69.9, 69.0, 68.6, 66.1, 55.2, 55.1; HRMS (ESI-TOF) calcd for $C_{63}H_{65}NO_{11}$ $[M + Na]^+$ 1034.4455, found 1034.4427.

*Methyl 2,3,4-Tri-O-benzyl-6-O-(2,4,6-tri-O-benzyl-3-O-(o-nitrobenzyl)-α/β-D- glucopyranosyl)-α/β-D-glucopyranoside (**26** Table 4).* Compound **26** was obtained as a white solid (77 mg, 98%, α/β = 1:1): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.2, 1.2 Hz, 1H), 8.05 (dd, J = 8.2, 1.2 Hz, 1H), 7.81 (dd, J = 7.8, 0.8 Hz, 1H), 7.74 (t, J = 7.9 Hz, 2H), 7.65 (dd, J = 8.0, 1.6 Hz, 1H), 7.58−7.55 (m, 2H), 7.55−7.52 (m, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.41−7.19 (m, 70H), 7.17−7.15 (m, 2H), 5.25 (d, J = 3.6 Hz, 1H), 5.02 (d, J = 10.7 Hz, 1H), 5.00−4.84 (m, 12H), 4.82−4.75 (m, 7H), 4.74−4.63 (m, 8H), 4.61−4.56 (m, 5H), 4.50 (d, J = 11.2 Hz, 1H), 4.37 (d, J = 7.8 Hz, 1H), 4.23−4.20 (m, 1H), 4.18 (dd, J = 10.9, 2.0 Hz, 1H), 4.08 (t, J = 9.3 Hz, 1H), 4.01−3.96 (m, 2H), 3.85−3.58 (m, 16H), 3.56−3.49 (m, 4H), 3.47−3.42 (m, 2H), 3.36 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.9, 138.8, 138.7, 138.4, 138.2, 138.1, 138.0, 135.3, 135.2, 135.1, 133.7, 131.0, 129.3, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 124.8, 124.6, 124.5, 103.8, 98.1, 98.0, 97.1, 84.8, 82.1, 82.1, 82.0, 81.9, 81.8, 81.7, 80.2, 80.1, 79.8, 79.6, 78.0, 77.8, 77.7, 77.6, 75.8, 75.8, 75.7, 75.6, 75.6, 75.1, 75.0, 75.0, 74.9, 74.9, 74.8, 73.3, 73.3, 72.9, 72.4, 70.7, 70.4, 70.2, 69.9, 69.8, 69.7, 69.7, 69.3, 68.5, 66.1, 55.2, 55.2; HRMS (ESI-TOF) calcd for $C_{62}H_{65}NO_{13}$ $[M + Na]^+$ 1054.4354, found 1054.4320.

*Methyl 2,3,4-Tri-O-benzyl-6-O-(2,4,6-tri-O-benzyl-3-O-(o-cyanobenzyl)-α/β-D- glucopyranosyl)-α/β-D-glucopyranoside (**27**, Table 4).* Compound **27** was obtained as a white solid (62 mg, 80%, α/β = 1:1): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57−7.49 (m, 5H), 7.46−7.44 (m, 1H), 7.42 (td, J = 7.7, 1.3 Hz, 1H), 7.39 (td, J = 7.8, 1.3 Hz, 1H), 7.35−7.09 (m, 70H), 5.13 (d, J = 12.8 Hz, 1H), 5.09 (d, J = 13.0 Hz, 1H), 5.01−4.95 (m, 6H), 4.92 (d, J = 11.2 Hz, 1H), 4.82−4.49 (m, 22H), 4.45 (d, J = 11.1 Hz, 1H), 4.42 (d, J = 12.1 Hz, 1H), 4.35 (d, J = 7.8 Hz, 1H, H1-β), 4.17 (dd, J = 10.9, 2.0 Hz, 1H), 4.01−3.93 (m, 3H), 3.85−3.79 (m, 2H), 3.77 (dd, J = 10.9, 2.9 Hz, 2H), 3.70−3.40 (m, 18H), 3.35 (s, 3H), 3.32 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.6, 142.4, 138.8, 138.8, 138.4, 138.3, 138.2, 138.2, 138.1, 137.9, 137.9, 132.7, 132.6, 132.5, 132.5, 128.7, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4, 117.3, 117.2, 111.0, 110.6, 103.8, 98.0, 98.0, 97.0, 85.1, 82.1, 81.9, 81.7, 80.1, 79.8, 78.1, 77.7, 77.5, 77.4, 75.6, 74.9, 74.9, 74.8, 74.8, 74.6, 73.4, 73.4, 73.3, 72.5, 72.4, 72.1, 70.3, 70.1, 69.9, 68.9, 68.6, 68.4, 66.1, 55.2, 55.1; HRMS (ESI-TOF) calcd for $C_{63}H_{65}NO_{11}$ $[M + Na]^+$ 1034.4455, found 1034.4419.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all compounds presented in the paper and Cartesian coordinates for structures A−C. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jacek.mlynarski@gmail.com.

Notes

The authors declare no competing financial interest.

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(13) For donor **1c**: reaction carried out in DCM 88% (α/β, 1:3), MeCN 24% (α/β, 1:10), Et_2O 31% (β only), toluene 59% (α/β, 1:10). **1d**: reaction carried out in DCM 83% (α/β, 1:12), MeCN 74% (β only), Et_2O 47% (β only), toluene 72% (α/β, 1:10).

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(15) Alternative explanation for improved stereoselectivity over 2-*O*-(2-cyanobenzyl) might be due to the persistence of an α anomeric triflate intermediate possibly favoring by more electron-withdrawing substituents relative to benzyl. According to such a scenario, displacement with inversion would lead to the β-product, whereas leakage to an oxacarbenium intermediate would result in the formation of anomeric mixture. To exclude this possibility, we tested the donor with an electron-withdrawing group attached to benzyl at the *para* position. This would make the *ortho* group less liable to participate but would increase the electron-withdrawing effect. Thus, in control experiments, glycosylation between **3** and 2-*O*-(2-cyanobenzyl)-substituted donor **1d** was always more selective than a similar reaction in the presence of 2-*O*-benzyl-substituted donor **1a** or 2-*O*-(4-cyanobenzyl)-substituted donor. In a series of control experiments, unselective formation of anomeric products was observed for benzyl and *p*-CN-benzyl (α/β, 1:1−1:1.2), whereas the same reaction controlled by donor with *o*-CN-substituted benzyl (**1d**) always led to more selective formation of β-glycoside (α/β, 1:3−1:3.5).
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