Glycosylation

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S-Benzimidazolyl Glycosides as a Platform for Oligosaccharide Synthesis by an Active–Latent Strategy**

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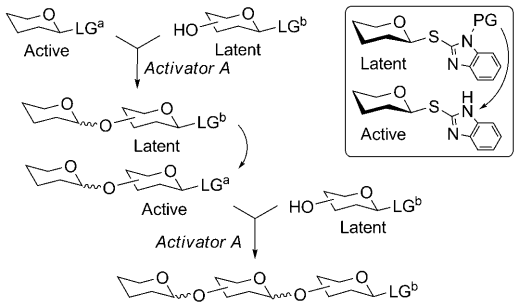
The involvement of complex carbohydrates in a wide variety of disease-related cellular processes has given this class of natural compounds tremendous diagnostic and therapeutic potential.[1] While scientists have been able to successfully isolate certain classes of natural carbohydrates, the availability of pure natural isolates is still inadequate to address the challenges offered by modern glycosciences. As a consequence, chemical glycosylation has become a viable means to obtain both natural complex carbohydrates and nonnatural analogues thereof.[2–4] Unfortunately, chemical synthesis of oligosaccharides of even moderate complexity still remains a considerable challenge, and many more complex structures are not available at all. As such, the development of efficient strategies for oligosaccharide and glycoconjugate synthesis stands out as a demanding area of research.[5]

As a part of the ongoing research effort in our laboratory to develop versatile methods for chemical glycosylation and expeditious oligosaccharide synthesis, we became interested in glycosyl thioimidates, glycosyl donors equipped with the $SCR^1{=}NR^2$ leaving group. Among a variety of thioimidates studied by us and others,[6,7] S-benzoxazolyl (SBox),[8] and S-thiazolinyl (STaz)[9] moieties were found to be excellent building blocks for oligosaccharide synthesis. We determined that the SBox and STaz glycosides fit into existing progressive strategies for oligosaccharide synthesis, such as selective (including one-pot[10–12] and solid-phase synthesis),[13–15] chemoselective (armed–disarmed),[16–18] and orthogonal[19–22] strategies. In addition, the glycosyl thioimidates led us to the development of conceptually new strategies for oligosaccharide synthesis: the inverse armed–disarmed strategy,[23,24] temporary deactivation concept,[25,26] O2/O5 cooperative effect (superarmed and superdisarmed glycosyl donors),[17,27–29] coordination-assisted glycosylation,[30] and surface-tethered iterative carbohydrate synthesis (STICS).[31]

At the core of the study presented herein is the development of a new method for chemical glycosylation and expeditious oligosaccharide synthesis based on S-benzimidazolyl (SBiz) glycosides. The SBiz moiety was previously investigated as a leaving group for phosphorylation of unprotected glycosyl donors.[32,33] We envisaged that the SBiz moiety may also be compatible with a very attractive active–latent concept pioneered by Roy,[34] Fraser-Reid,[16] Boons,[35] and more recently further advanced by Kim[36,37] and others.[38–40] According to this concept, an active (reactive) leaving group (LG^a) is selectively activated over its latent (unreactive) counterpart (LG^b, Scheme 1). Subsequently, the latent LG^b of the formed disaccharide is converted into the active LG^a. This modification does not involve substitution at the anomeric center like in the two-step activation strategy;[5] rather it is achieved by a modification of the leaving group, usually at a remote position. We assumed that in the case of the SBiz glycosides, deactivation of the leaving group could be achieved by placing an easily removable protecting group (PG) at the nitrogen atom of the imidazolium ring. The active SBiz leaving group can then be regenerated by simple deprotection as needed.



Scheme 1. Outline of the active–latent strategy and the SBiz leaving group explored in this work.

To pursue this concept we obtained a range of differently protected SBiz glucosides including perbenzylated **1a**, perbenzoylated **1b**, and derivative **1c** equipped with the superarming protecting-group pattern.[28] We also obtained the SBiz donor of the D-galacto and D-glucosamino series **1d** and **1e**, respectively. With glycosyl donors **1a–e** in hand, we began evaluating their applicability to chemical glycosidation with standard glycosyl acceptors **2–5**.[41] Encouragingly, reaction of glycosyl donor **1a** with the primary glycosyl acceptor **2** in the presence of silver(I) triflate completed in 15 min and provided the corresponding disaccharide **6a** in 98% yield (Table 1, entry 1). Copper(II) triflate is a significantly milder promoter for thioimidates, and although a significantly lower reaction rate was observed (60 h) **6a** was isolated in an

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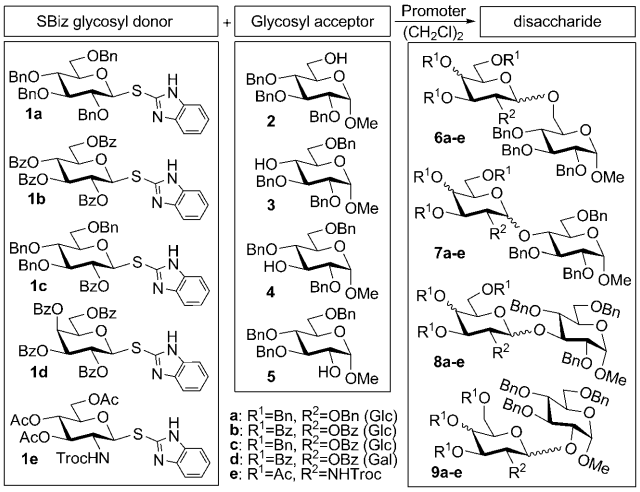
Table 1: Glycosidation of SBiz glycosyl donors **1a–e** with glycosyl acceptors **2–5**.



Entry	Donor + acceptor	Promoter[a]	*t*	Product (yield, α/β ratio)
1	**1a**+**2**	AgOTf	15 min	**6a** (98%, 1.1:1)
2	**1a**+**2**	$Cu(OTf)_2$	60 h	**6a** (93%, 1.3:1)
3	**1a**+**2**	AllBr, BnBr MeI (55°C)[b]	12 h	**6a** (84–90%, 3.3–5.3:1)
4	**1a**+**3**	AgOTf	15 min	**7a** (81%, 1.8:1)
5	**1a**+**4**	AgOTf	15 min	**8a** (91%, 1.3:1)
6	**1a**+**5**	AgOTf	15 min	**9a** (95%, 1.6:1)
7	**1b**+**2**	AgOTf	2 h	**6b** (86%, β only)
8	**1b**+**2**	$Cu(OTf)_2$	144 h	**6b** (83%, β only)
9	**1b**+**2**	AllBr, BnBr MeI (55°C)	120 h	no reaction
10	**1b**+**3**	AgOTf	45 min	**7b** (94%, β only)
11	**1b**+**4**	AgOTf	2 h	**8b** (87%, β only)
12	**1b**+**5**	AgOTf	2 h	**9b** (84%, β only)
13	**1c**+**2**	AgOTf	<5 min	**6c** (98%, β only)
14	**1c**+**2**	$Cu(OTf)_2$	2 h	**6c** (93%, β only)
15	**1c**+**3**	AgOTf	<5 min	**7c** (84%, β only)
16	**1c**+**4**	AgOTf	<5 min	**8c** (90%, β only)
17	**1c**+**5**	AgOTf	<5 min	**9c** (88%, β only)
18	**1d**+**2**	AgOTf	2 h	**6d** (97%, β only)
19	**1d**+**3**	AgOTf	2 h	**7d** (94%, β only)
20	**1d**+**4**	AgOTf	3 h	**8d** (89%, β only)
21	**1d**+**5**	AgOTf	3.5 h	**9d** (89%, β only)
22	**1e**+**2**	AgOTf	30 min	**6e** (94%, β only)
23	**1e**+**3**	AgOTf	30 min	**7e** (92%, β only)
24	**1e**+**4**	AgOTf	30 min	**8e** (86%, β only)
25	**1e**+**5**	AgOTf	30 min	**9e** (92%, β only)

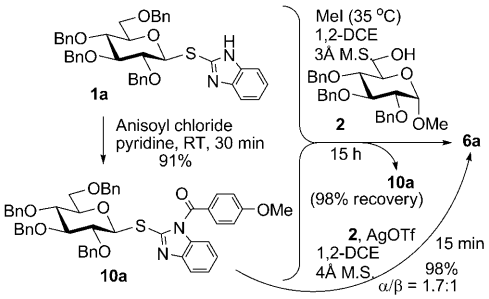
[a] Performed in the presence of 3 Å molecular sieves at room temperature, unless noted otherwise. [b] Reaction at room temperature was much more sluggish. Bn = benzyl, Bz = benzoyl, Tf = triflate, All = allyl.

excellent yield of 93% (Table 1, entry 2). Subsequently, we demonstrated that the SBiz moiety can be efficiently activated under alkylation conditions at elevated temperature, similarly to STaz glycosides.[22] No significant difference between AllBr-, BnBr-, or MeI-promoted glycosidations of **1a** was detected, and **6a** was obtained in 84–90% yield (Table 1, entry 3). We noticed a significantly improved α stereoselectivity (up to 5.3:1 with AllBr) in comparison to that of the metal-assisted glycosylations. Glycosylation of the secondary glycosyl acceptors **3–5** was also proven feasible, and the corresponding disaccharides **7a–9a** were obtained in the presence of AgOTf in 81–95% yield (Table 1, entries 4–6).

Having investigated the reactivity of perbenzylated (armed) glycosyl donor **1a**, we turned our attention to testing its perbenzoylated (disarmed) counterpart **1b**. As anticipated, the reactivity of **1b** was significantly lower than that of **1a**, and only AgOTf-promoted glycosidations were proven to be of preparative value. Thus, the desired disaccharides **6b–9b** were isolated in 84–94% yield (Table 1, entries 7, 10–12). Copper(II) triflate-promoted glycosidation was very slow (144 h; Table 1, entry 8) while alkyl halide-promoted reactions did not proceed at all (Table 1, entry 9). These results suggest that the SBiz glycosides can be applied in accordance with the classic armed–disarmed strategy.[42] To develop a more flexible route to the synthesis of 1,2-*trans* glycosides we also investigated SBiz glycosyl donor **1c**, which bears the superarming protecting-group pattern.[28] As expected, AgOTf-promoted glycosidation produced disaccharides **6c–9c** almost instantaneously in 84–98% yield (Table 1, entries 13, 15–17). Also in the presence of $Cu(OTf)_2$, the reaction rate was significantly higher than that observed with either the armed glycosyl donor **1a** or its disarmed counterpart **1b** (2 h, 93%; Table 1, entry 14).

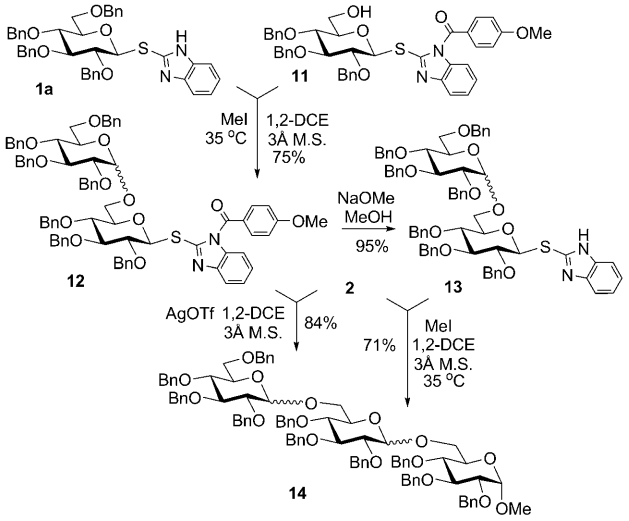
To broaden the scope of this glycosylation approach, we tested its applicability to the synthesis of D-galactosides and 2-amino-2-deoxyglucosides, highly important and abundant sugar series.[43–45] Glycosidation of SBiz galactose donor **1d** with glycosyl acceptors **2–5** in the presence of AgOTf proceeded smoothly and the corresponding disaccharides **6d–9d** were obtained in 89–97% yield (Table 1, entries 18–21). Also, glycosidation of *N*-(2,2,2-trichloroethoxy)carbamoyl (*N*-Troc) glycosyl donor **1e** with acceptors **2–5** in the presence of AgOTf was successfully accomplished. The resulting disaccharides **6e–9e** were isolated in 86–94% yields (Table 1, entries 22–25).

Having investigated the applicability of the SBiz glycosides for chemical glycosylation, we next investigated the effects that N-substitution may have on the reactivity of the leaving group. For this purpose, we investigated a variety of N-acyl substituents (acetyl, haloacetyls, benzoyl, substituted benzoyls), and the most prominent results were achieved with the N-anisoylated SBiz building block **10a** obtained from **1a** by reaction with anisoyl chloride in the presence of pyridine (Scheme 2). As projected, no product was formed in glycosidations of **10a** under alkylation conditions (up to 120 h at 55°C). In addition, competitive glycosylation wherein two glycosyl donors (**1a** and **10a**) were allowed to compete for glycosyl acceptor **2** allowed differentiation of the reactivities of SBiz and anisoylated SBiz leaving groups. Thus, the competition experiment in the presence of MeI allowed for nearly complete recovery of the unreacted **10a** (98%), while only traces of **1a** (2%) remained. Less expectedly, AgOTf-promoted activation of the N-anisoylated glycosyl donor **10a** was as efficient as that of its SBiz counterpart **1a** and disaccharide **6a** was rapidly produced (15 min) in 98% yield.



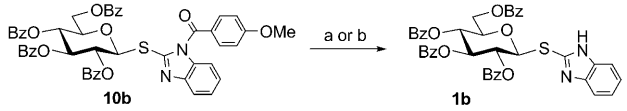
Scheme 2. Synthesis and glycosidation of N-anisoylated glycosyl donor **10a**; competition experiment with SBiz donor **1a**. 1,2-DCE = 1,2-dichloroethane.

With these promising results, we next began investigating whether SBiz donor **1a** could be selectively activated in the presence the N-anisoylated SBiz acceptor, which represents the key step for executing the SBiz-based active–latent concept. For this purpose we obtained glycosyl acceptor **11** (see the Supporting Information). Very encouragingly, MeI-promoted glycosylation between building blocks **1a** and **11** produced the expected latent disaccharide **12** in 75% yield (α:β = 1:1.8, Scheme 3). After that, the N-anisoyl group was removed by treatment with NaOMe in MeOH and the resulting active disaccharide **13** was subsequently activated with MeI to afford trisaccharide **14** in 71% yield. This two-step SBiz activation sequence mimics the traditional active–latent concept.[5]



Scheme 3. Activation of SBiz donor **1a** over N-anisoylated SBiz acceptor **11** in the active–latent fashion.

It should be noted that although the removal of the *N*-anisoyl moiety in **12** with NaOMe/MeOH is suitable for the synthesis of benzylated building blocks, it would represent a hurdle if the application of the active–latent methodology were attempted with acylated compounds. To broaden the scope of this transformation, we investigated other reaction conditions that would not trigger concomitant O-deacylation. As depicted in Scheme 4, we discovered that N-anisoyl in O-

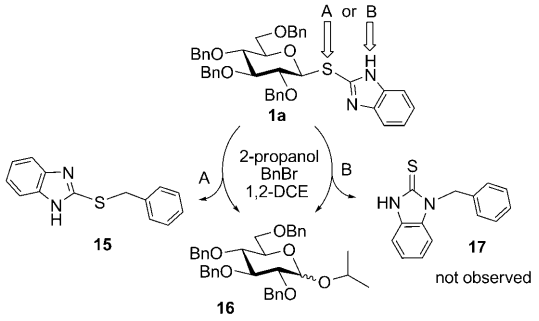


Scheme 4. Removal of the N-anisoyl group in the presence of the O-benzoyl group. Conditions: a) 0.5 M guanidine/MeOH (0.5 equiv) in CH_2Cl_2/MeOH (9:1, v/v), RT, 5 min; b) 2 equiv 1 M TBAF/THF in THF, RT, 3 h; quantitative yield of **1b** in both procedures.

benzoylated compound **10b** can be effectively removed in the presence of guanidine in MeOH or, alternatively, tetra-*n*-butylammonium fluoride (TBAF) in THF. No competitive O-benzoyl group removal was detected under these reaction conditions and the desired SBiz donor **1b** was obtained quantitatively. In this context, we anticipate that other acyl groups, for example, 2-(azidomethyl)benzoyl,[46] 3-(2′-benzyloxyphenyl)-3,3-dimethylpropanoate,[47] or (2-nitrophenyl)acetyl,[48] which can be reductively cleaved in the presence of conventional O-acyl substituents (benzoyl), would also be suitable for the purpose of the temporary N-acylation.

Since the N-protected latent SBiz moiety can be activated with a stronger promoter (Scheme 2), we pursued this pathway also. AgOTf-promoted activation of latent disaccharide **12** led to trisaccharide **14** in 84% yield (Scheme 3). By exploring this two-way activation approach we showed that the SBiz moiety serves as a suitable new platform for the active–latent-like activations, but also allows for the direct activation of the latent N-acylated leaving group using stronger promoter.

What remained unknown is why alkylating reagents are able to activate SBiz but not its N-anisoylated counterpart. Based on the anticipation that the SBiz is activated by the direct activation pathway A (Scheme 5) through the anome-



Scheme 5. Direct pathway A versus remote pathway B for SBiz activation.

ric sulfur, like in S-alkyl/aryl[49] or SBox glycosides,[22,50] one possible explanation is the electronic effect. It is possible that upon N-anisoylation the sulfur atom in compound **10a** will become too weak a nucleophile to displace the halogen atom of the alkylating reagent. Alternatively, the activation of the SBiz may also take place through the nitrogen atom of the imidazole ring representing the remote activation pathway B,

like in S-pyridyl[51,52] or STaz[22] derivatives. In this case, the effect of the N-anisoyl group is steric as it will block the N-activation site of the SBiz moiety.

To differentiate the two pathways we set up a model experiment wherein SBiz donor **1a** reacted with 2-propanol in the presence of BnBr (Scheme 5). Upon completion of the reaction, judged by the disappearance of **1a** and formation of **16**,[53] we separated and analyzed all components of the reaction mixture. 2-Benzylsulfanyl-1*H*-benzimidazole **15**[54,55] was isolated and its identity was proven by spectral and X-ray methods, whereas no trace of its N-benzylated counterpart **17**[56,57] was detected. The result of this study indicates that activation of SBiz under alkylation conditions takes place through the sulfur atom, similarly to that found previously for SBox glycosides.[22,50] Therefore, we conclude that the deactivation effect of the N-anisoyl moiety in **10a** is electronic. However, whether this effect results from simple electron withdrawal or distortion of the aromaticity of the imidazole ring is yet to be determined. What makes this disarming effect different from the well-documented disarming effect in glycosylation[42] is that herein the disarming is achieved by acylation of the leaving group, not by introducing the neighboring acyl substituents in the sugar moiety.

In conclusion, we have investigated the S-benzimidazolyl (SBiz) anomeric moiety as a new leaving group that can be activated for chemical glycosylation under a variety of conditions including metal-assisted and alkylation pathways. Differentiation between the two possible reaction pathways for activation of the SBiz moiety was achieved by an extended mechanistic study. We also demonstrated that the application of the substituted SBiz moiety allows execution of rapid oligosaccharide assembly through active–latent- and armed–disarmed-like concepts.

Experimental Section

1a: A solution of ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside[58] (2.19 g, 3.75 mmol) and activated molecular sieves (3 Å, 1.88 g) in CH_2Cl_2 (56 mL) was stirred under argon for 1 h at room temperature. A freshly prepared solution of Br_2 in CH_2Cl_2 (36 mL, 1:165, v/v) was then added and the reaction mixture was stirred for 5 min at room temperature. After that, the solid was isolated by filtration and the filtrate was concentrated in vacuo at room temperature. The crude residue was dissolved in dry MeCN (80 mL) and KSBiz (1.76 g, 9.36 mmol) and [18]crown-6 (0.20 g, 0.75 mmol) were added. The resulting reaction mixture was stirred under argon for 16 h at room temperature. The solid was then isolated by filtration and the filtrate was concentrated in vacuo. The residue was diluted with CH_2Cl_2 (200 mL) and washed successively with 10% aq. NaOH (20 mL) and water (3 × 20 mL). The organic layer was separated, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/toluene gradient elution) to afford compound **1a** (1.85 g, 73%) as an off-white foam. $R_f = 0.54$ (ethyl acetate/toluene, 3:17, v/v); $[\alpha]_D^{28} = -28.7°$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR: $\delta = 3.45$ (dd, 1H, $J_{2,3} = 8.5$ Hz; H-2), 3.58–3.82 (m, 5H; H-3, 4, 5, 6a, 6b), 4.57 (dd, 2H, $J^2 = 11.5$ Hz; CH_2Ph), 4.64 (dd, 2H, $J^2 = 11.1$ Hz; CH_2Ph), 4.76 (d, 1H, $J_{1,2} = 9.6$ Hz; H-1), 4.76 (dd, 2H, $J^2 = 10.0$ Hz; CH_2Ph), 4.82 (dd, 2H, $J^2 = 10.9$ Hz; CH_2Ph), 6.38–7.38 ppm (m, 25H; aromatic, NH); ^{13}C NMR: $\delta = 68.8$, 74.0, 75.3, 75.8, 76.0, 77.2, 78.3, 80.9, 84.1, 86.0, 122.5, 127.9 (×3), 128.1 (×4), 128.4, 128.5 (×3), 128.6 (×10), 128.9 (×3), 129.0, 137.4, 137.5, 137.7, 138.1, 146.5 ppm; HR-FAB MS: *m/z* calcd for $C_{41}H_{41}N_2O_5S$: 673.2736 $[M+H]^+$; found: 673.2732.

10: Anisoyl chloride (0.58 mL, 4.29 mmol) was added dropwise to a stirred solution of **1a** (0.962 g, 1.4 mmol) in pyridine (10 mL). The resulting reaction mixture was stirred under argon for 15 min at room temperature. After that, the volatiles were removed in vacuo and the residue was co-evaporated with toluene (3 × 10 mL). The residue was diluted with CH_2Cl_2 (200 mL), and washed with water (20 mL), 1N aq. HCl (20 mL), water (20 mL), sat. aq. $NaHCO_3$ (2 × 20 mL), and water (3 × 10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/toluene gradient elution) to afford compound **10** (1.05 g, 91%) as an off-white foam. $R_f = 0.50$ (ethyl acetate/toluene, 1:9, v/v); $[\alpha]_D^{27} = +119.5°$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR: $\delta = 3.66$ (dd, 1H, $J_{2,3} = 8.67$ Hz; H-2), 3.70–3.87 (m, 5H; H-3, 4, 5, 6a, 6b), 3.88 (s, 3H; OCH_3), 4.54 (dd, 2H, $J^2 = 11.9$ Hz; CH_2Ph), 4.71 (dd, 2H, $J^2 = 10.7$ Hz; CH_2Ph), 4.87 (dd, 2H, $J^2 = 10.7$ Hz; CH_2Ph), 4.88 (dd, 2H, $J^2 = 10.9$ Hz; CH_2Ph), 5.83 (d, 1H, $J_{1,2} = 10.2$ Hz; H-1), 6.89–7.71 ppm (m, 28H; aromatic); ^{13}C NMR: $\delta = 55.8$, 68.8, 73.5, 75.1, 75.5, 75.9, 77.9, 79.6, 81.2, 85.1, 86.9, 113.4, 114.4 (×3), 119.3, 123.4, 124.2, 124.9, 127.7, 127.9 (×3), 128.0 (×7), 128.5 (×3), 128.6 (×4), 129.2, 132.8 (×2), 134.7, 138.1, 138.3 (×2), 138.6, 143.9, 151.8, 164.5, 167.3 ppm; HR-FAB MS: *m/z* calcd for $C_{49}H_{47}N_2O_7S$: 807.3104 $[M+H]^+$; found: 807.3081.

Typical AgOTf-promoted glycosylation procedure: A mixture of glycosyl donor (0.045 mmol), glycosyl acceptor (0.030 mmol), and freshly activated molecular sieves (3 Å, 125 mg) in 1,2-dichloroethane (1 mL) was stirred under argon for 1 h. AgOTf (0.090 mmol) was added and the reaction mixture was monitored by TLC. Upon completion (see Table 1), the solid was isolated by filtration and the filtrate was diluted with CH_2Cl_2 (15 mL), and washed with 5% aq NaOH (5 mL) and water (3 × 5 mL). The organic layer was separated, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate/toluene gradient elution) to afford the corresponding oligosaccharide.

Typical alkyl halide-promoted glycosylation procedure: A mixture of glycosyl donor (0.045 mmol), glycosyl acceptor (0.030 mmol), and freshly activated molecular sieves (4 Å, 125 mg) in 1,2-dichloroethane (1 mL) was stirred under argon for 1 h. Alkyl halide (0.027 mmol) was added and the reaction mixture was monitored by TLC. Upon completion (see Table 1), the solid was isolated by filtration and the filtrate was diluted with CH_2Cl_2 (15 mL), and washed with 5% aq NaOH (5 mL) and water (3 × 5 mL). The organic layer was separated, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate/toluene gradient elution) to afford the corresponding disaccharide.

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