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TMSOTf-Catalyzed Koenigs-Knorr Glycosylation Reaction

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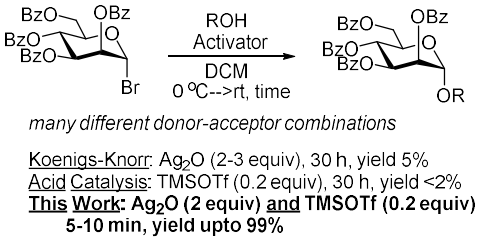
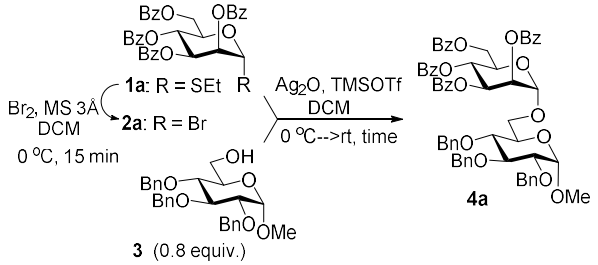


ABSTRACT: Presented herein is our discovery that traditional silver(I) oxide-promoted glycosidations of glycosyl bromides (Koenigs-Knorr reaction) can be greatly accelerated in the presence of catalytic TMSOTf. These reaction conditions are very mild and allow for maintaining a practically neutral pH while providing high rates and excellent glycosylation yields. In addition, unusual reactivity trends among a series of differentially protected glycosyl bromides have been documented. Also revealed is an unusual reactivity trend according to which benzoylated α-bromides are much more reactive than their benzylated counterparts under these conditions.

In spite of many methods developed for the synthesis of glycans, glycosyl halide donors discovered by Michael[1] continue to find wide application. Under classical Koenigs-Knorr reaction conditions,[2-4] a glycosyl bromide (or chloride) donor is coupled with a glycosyl acceptor (alcohol, ROH) in the presence of silver oxide (or carbonate). This reaction is slow, and even glycosidations of reactive, per-benzylated donors require many hours (or even days) to produce the respective glycoside products. This reaction is particularly sluggish with less reactive per-benzoylated bromides. To advance the classical Koenigs-Knorr glycosylation, many activators including salts of mercury,[5-8] cadmium,[9-11] tin,[12-13] zinc,[14-15] indium,[16-17] silver[18-26] have emerged.[27] Nevertheless, these modifications failed to adequately enhance the reaction that continued to suffer from fair yields, poor reactivity of donors, substrate scope, and the requirement to use excess of toxic or expensive reagents. This prompted the investigation of other, non-metallic activators and promoters including halide ions,[28] iodine or IBr with DDQ/DABCO,[29-30] bromine,[31] and 3,3-difluoroxindole (HOFox),[32-33] diarylborinic acid,[34] iodonium ions,[35] halogen bonding,[36] super critical CO2,[37] and organocatalysis.[38-39] Many of these conditions still fail to glycosidate per-benzoylated bromides.

Presented herein is our discovery that the addition of catalytic amounts of a Lewis acid to the Ag_2O-promoted glycosylation, dramatically speeds up the reaction and enhances the yields. For example, when per-benzoylated mannosyl bromide **2a**, freshly prepared from thioglycoside **1a**, was glycosidated with acceptor **3** under classical Koenigs-Knorr reaction conditions in the presence of Ag_2O (3.0 equiv) in DCM only trace amount (5%) of disaccharide **4a** was isolated, even after 30 h (entry 1, Table 1). In contrast, when essentially the same reaction was performed in the presence of 20 mol % of TMSOTf disaccharide **4a** was obtained practically instantaneously (<5 min) and nearly quantitatively (99% yield, entry 2). After preliminary screening of the additives (entries 3-5) we chose 20 mol % amount of TMSOTf for subsequent experimentation. Practically no reaction took place in the absence of Ag_2O (entry 6) and the gradual increase of Ag_2O (entries 7-11) showed that stoichiometric amount is required to obtain practical yields and at least 2.0 equiv of Ag_2O are needed to achieve rapid conversion (10 min, entry 11). Herein and below all reactions were performed in DCM that was found to be the best reaction solvent for these conditions based of our preliminary screening.

Table 1. TMSOTf-catalyzed glycosidation of bromide **2a**



Entry	Ag_2O (equiv)	TMSOTf (equiv)	Time, yield of 4a
1	3.00	--	30 h, 5%
2	3.00	0.20	5 min, 99%
3	3.00	0.15	10 min, 95%
4	3.00	0.10	1 h, 61%
5	3.00	0.05	22 h, 7%
6	--	0.20	18 h, <2%
7	1.00	0.20	18 h, 17%
8	1.25	0.20	18 h, 40%
9	1.50	0.20	18 h, 72%
10	1.75	0.20	18 h, 81%
11	2.00	0.20	10 min, 99%

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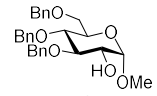
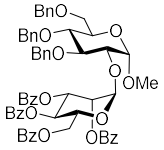
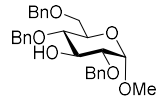
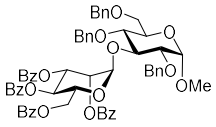
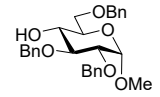
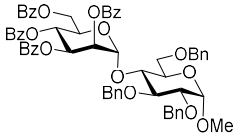
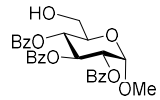
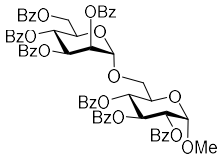
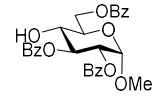
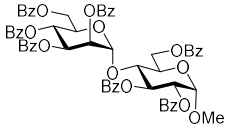
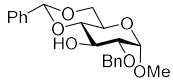
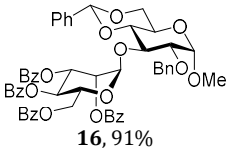
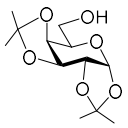
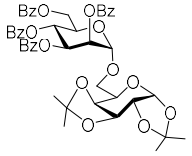
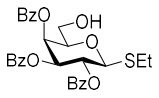
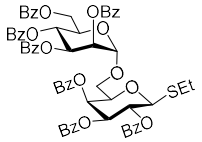
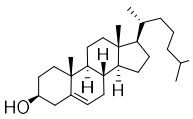
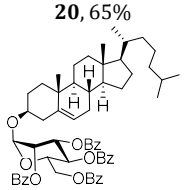
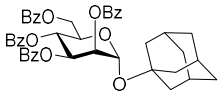
We then began studying the formation of other types of glycosidic linkages with donor **2a**. Glycosylation of partially benzylated secondary 2-OH acceptor **5** afforded disaccharide **6** in 98% yield in 10 min (entry 1, Table 2). In case of 3-OH acceptor **7** and 4-OH acceptor **9**, a higher amount of promoters (3.0 equiv of Ag_2O and 0.25 equiv of TMSOTf) was found beneficial to afford swift and nearly quantitative formation of disaccharides **8** and **10**, respectively (99% yield each, entries 2 and 3). Higher amounts of the promoters were helpful for all glycosylations of poorly nucleophilic acceptors to achieve the desired rates and yields. This trend can be traced in case of benzoylated acceptors **11** and **13.** While the primary 6-OH acceptor **11** afforded disaccharide **12** in 99% yield in 10 min (2.0 equiv of Ag_2O and 0.20 equiv of TMSOTf, entry 4), sterically hindered and deactivated 4-OH acceptor **13** needed additional amounts (3 equiv of Ag_2O and 0.5 equiv of TMSOTf) to afford a swift reaction (20 min) and a good yield of disaccharide **14** (87%, entry 5). Increasing only one activator, either Ag2O (from 2.0 to 3.0 equiv) or TMSOTf (from 0.20 to 0.25 equiv) resulted in no improvement. However, in some cases a significant increase in the amount of TMSOTf (from 0.2 to 0.5 equiv) allowed to reduce the amount of Ag_2O to 1.5 equiv.

Table 2. Glycosidation of bromide **2a** with various acceptors

Entry	Acceptor (0.8 equiv)	Ag_2O (equiv)/ TMSOTf (equiv) time	Product, Yield
1	 **5**	2.0/0.20 10 min	 **6**, 98%
2	 **7**	3.0/0.25 10 min	 **8**, 99%
3	 **9**	3.0/0.25 10 min	 **10**, 99%
4	 **11**	2.0/0.20 10 min	 **12**, 99%
5	 **13**	3.0/0.50 20 min	 **14**, 87%
6	 **15**	2.5/0.25 10 min	 **16**, 91%
7	 **17**	2.5/0.25 10 min	 **18**, 99%
8	 **19**	2.0/0.20 24 h	 **20**, 65%
9	 **21**	2.0/0.20 10 min	 **22**, 96%
10[a]	 **23**	2.0/0.20 10 min	 **24**, 91%

[a] – 0.9 equiv of acceptor **23** was used

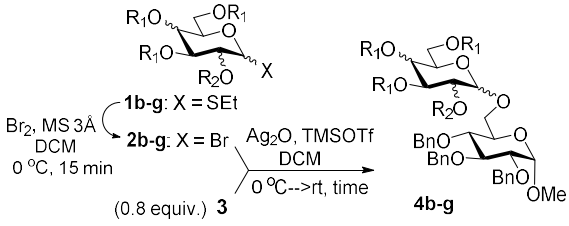
Acid-sensitive cyclic ketal/acetal protection in acceptors **15** and **17** are unaffected under these conditions and excellent yields of disaccharides **16** and **18** were achieved (91-99%, entries 6 and 7). Thioglycoside acceptor **19** also produced disaccharide **20** in a good yield of 65% (entry 8) ultimately demonstrating the applicability of these reaction conditions to iterative, selective activations for the synthesis of longer oligosaccharide sequences. Hindered aliphatic acceptors cholesterol **21** and 1-adamantanol **23** were also glycosylated affording the respective glycosides **22** and **24** in 10 min and in excellent yields (91-96%, entries 9 and 10).

We then explored differently protected glycosyl donors of other sugar series. Donors **2b-g** were obtained directly prior to glycosylation from the corresponding ethylthio glycosides **1b-g** by the reaction with bromine.[31, 40-42] In the benchmark experiment, glycosidation of mannosyl donor **2a** with acceptor **3** in the presence of 2 equiv. of Ag_2O and 20 mol % of TMSOTf afforded disaccharide **4a** in 99% yield in 10 min (entry 1, Table 3). Glycosyl bromides **2b** and **2c** produced only 48-49% of the respective disaccharides **4b** and **4c** under these reaction conditions (entries 2-3). When higher amounts of promoters were applied (3.0 equiv of Ag_2O and 0.25 equiv of TMSOTf), swift reaction times (10 min) and the excellent yields (99%) for the formation of disaccharides **4b** and **4c** have been recorded (entries 4 and 5).

We then performed glycosidations of 2-*O*-benzylated glycosyl donors **2d-g**. The stereoselectivity of these reactions was reduced due to the lack of the participating group at C-2. Very unexpectedly, we also noticed a significant drop in reactivity in all cases except per-benzylated galactosyl donor **2f** that was as reactive as its per-benzoylated counterpart **2c**. Slow glycosidation of donor **2d** (16 h, entry 6) could be attributed to the superdisarming nature of its protecting group pattern.[43] Nonetheless, disaccharide **4d** was produced in an excellent yield (92 %). In this context, we have also investigated glycosyl bromides equipped with the superarming 2-O-benzoyl-3,4,6-tri-O-benzyl protecting group pattern.[44] However, the reactivity of these compounds could not be differentiated from that of the per-benzoylated derivatives under these powerful activation conditions.

A comparatively slow reaction of the supposedly armed per-benzylated glucosyl donor **2e** (16 h, entry 7) versus glycosidation of the disarmed per-benzoylated counterpart **2b** was striking (10 min, entry 4). In addition, glycosyl donor **2e** produced disaccharide **4e** in a moderate yield (46%) even after 18 h. A similar reactivity trend was observed with mannosyl donors. Thus, glycosidation of per-benzylated donor **2g** was slow (4.5 h) and required excess activators to produce disaccharide **4g** in a respectable yield of 87% (entry 7). In contrast, the glycosidation of the supposedly disarmed, per-benzoylated donor **2a** was consistently swift. Glycosidation of per-benzylated galactosyl donor **2f** was swift and produced the desired disaccharide **4f** in 90% yield even with as little as 10 mol % of TMSOTf (entry 8).

Table 3. Glycosylation of acceptor **3** with bromides **2a-g**



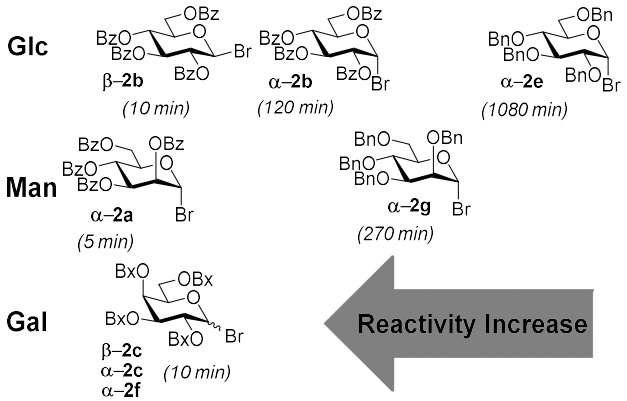
Entry	Donor (α/β)	Ag_2O (equiv)/TMSOTf (equiv), temp, time	Product yield, ratio α/β
1	**2a** (α only)	2.0/0.20, 0 °C, 10 min	**4a**, 99%, α only
2	**2b** (1/8.5)	2.0/0.20, 0 °C, 1 h	**4b**, 48%, β only
3	**2c** (1/3.7)	2.0/0.20, 0 °C, 1 h	**4c**, 49%, β only
4	**2b** (1/8.5)	3.0/0.25, 0 °C, 10 min	**4b**, 99%, β only
5	**2c** (1/3.7)	3.0/0.25, 0 °C, 10 min	**4c**, 99%, β only
6	**2d** (5.9/1)	3.0/0.20, 0 °C→rt, 16 h	**4d**, 92%, 2.7/1
7	**2e** (α only)	3.0/0.20, 0 °C→rt, 18 h	**4e**, 46%, 1/1.1
8	**2f** (α only)	3.0/0.10, 0 °C, 15 min	**4f**, 90%, >1/20
9	**2g** (α only)	3.0/0.20, 0 °C→rt, 4.5 h	**4g**, 87%, 1.9/1
10[a]	**2a** (α only)	2.0/0.20, 0 °C, 10 min	**4a**, 98%, α only
11[a]	**2b** (α only)	3.0/0.25, 0 °C, 2 h	**4b**, 96%, β only
12[a]	**2c** (α only)	3.0/0.25, 0 °C, 10 min	**4c**, 96%, β only

[a] – glycosyl bromide donors were presynthesized from the respective penta-benzoates by reaction with HBr in acetic acid

The discrepancies in the reactivities of bromides of the armed and disarmed series prompted us to investigate structures of the glycosyl bromide intermediates. The NMR measurements showed that mannosyl bromide **2a** and all per-benzylated bromides **2e-g** were pure α-anomers, whereas benzoylated glucosyl bromide **2b** (α/β = 1/8.5) and galactosyl bromide **2c** (α/β = 1/3.7) showed the prevalence of the β-linked isomers. Being aware that both the anomeric configuration and the relative orientation of the C-1 and C-2 substituents have effect on the reactivity, we also obtained pure α-configured donors **2a-c**. This was accomplished by presynthesizing glycosyl bromides from the respective penta-benzoates by the reaction with HBr in acetic acid. The presynthesized α-bromides **2a-c** were then glycosidated with acceptor **3** (entries 9-11). Not surprisingly, the outcome of glycosidation of α-**2a** was essentially the same although glycosidation of presynthesized glucosyl bromide α-**2b** was much more sluggish (2 h, entry 11, Table 3) compared to that of α/β-**2b** (α/β = 1/8.5) generated *in situ* (10 min, entry 4, Table 3).

The difference in reactivity lies within the orientation of the 2-*O*-participating group and the anomeric substituent and ultimately confirms common knowledge that α-bromide **2b** is less reactive than its β-counterpart. In case of the 1,2-trans-oriented glycosyl bromides α-**2a** or β-**2b**, the substituent at C-2 is able to provide the anchimeric assistance that aids in the leaving group departure. This is the rate-determining step (RDS) of most glycosylations, and therefore the effect on the reaction rate can be dramatic. There is no anchimeric assistance in case of glucosyl donor α-**2b** or in case of any 2-O-benzylated donors. As a result, the reactions with these substrates are much slower. In case of galactosyl bromide **2c** though, the anchimeric effect on the rate of the reaction is negligible because of high reactivity of galactosyl donors in general. Perhaps the reaction conditions developed herein are too powerful to differentiate the reactivity difference between α/β-**2c** and α-**2c**. Both glycosidations of α/β-**2c** and α-**2c** provided quantitative yields in 10 min (entries 5 and 12). Glycosidation of per-benzylated galactosyl donor **2f** proceeded β-stereoselectively. This result is indicative of an S_N2-like displacement, but it also implies that the anchimeric assistance is not the prevalent pathway in the D-galactosyl series.

Figure 1. Relative reactivity of glycosyl bromides

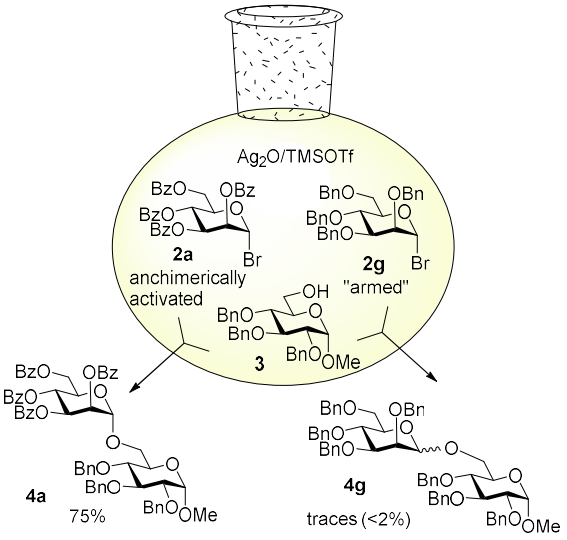


The relative reactivity of glycosyl bromides towards Ag_2O (3.0 equiv)/TMSOTf (0.25 equiv) activation are summarized in Figure 1. In the D-gluco series, donor β-**2b** is much more reactive than its α-linked counterpart α-**2b**. We specifically note a large gap in reactivity between structurally similar donors α-**2b** and **2e** that differ only by the electronics of their protecting groups. Also in the D-manno series, a large reactivity difference was observed between highly reactive benzoylated donor **2a** and its per-benzylated counterpart **2g**. Practically no donor reactivity difference was observed in the highly reactive D-galacto series. To acquire the ultimate evidence of the superior reactivity profile of the "disarmed" benzoylated mannosyl donor, we conducted a direct competition experiment, wherein two mannosyl donors **2a** and **2g** were set to compete for acceptor **3** in a single pot (Scheme 1). As a result of this experiment, disaccharide **4a** derived from benzoylated donor **2a** was isolated in 75% yield, whereas disaccharide **4g** was present only in trace amounts.

We also executed preliminary steps to evaluate the mechanism by which the Lewis acid additive enhances Koenigs-Knorr glycosylations. *First*, we investigated whether this enhancement is due to the direct interaction of the anomeric leaving group with the Lewis or Bronsted acid. A series of ^1H NMR experiments with donor **2a** in the absence/presence of TMSOTf in $CDCl_3$ showed no shift of the anomeric hydrogen indicating that no direct interaction between the leaving group and the additive takes place (see the SI for complete details).

Second, we investigated whether the initial interaction of TMSOTf with Ag_2O leads to the formation of AgOTf, a known effective activator for bromides. When equimolecular amounts of TMSOTf and Ag_2O were premixed, a hygroscopic material was obtained and its overall composition was confirmed by SEM/EDS (scanning electron microscopy/energy dispersive X-ray spectroscopy) semi-quantitative elemental analysis ($C_4H_9F_3O_4SSiAg_2$). Glycosidation of donor **2a** with acceptor **3** in presence of this presynthesized promoter was very effective in producing disaccharide **4a** in 99% in 10 min. The preformed promoter was also very effective in glycosidating per-benzoylated S-thiazolinyl (STaz)[45] and S-benzoxazolyl (SBox)[46-47] donors that are known to be readily activated by AgOTf. This result implies that the presynthesized promoter contains AgOTf.

Scheme 1. Competition experiments show superior reactivity of per-benzoylated bromide **2a**



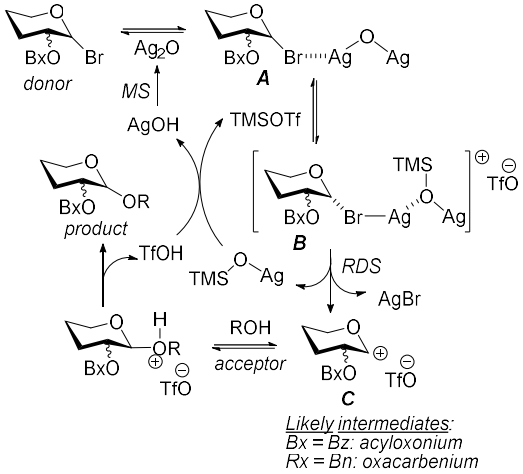
Third, we investigated whether AgOTf that might be forming in the reaction medium gets regenerated to perform subsequent catalytic cycles. Glycosidation of thioimidate donors in the presence of Ag_2O (2.0 equiv) and cat. TMSOTf (0.2 equiv) was practically ineffective and only small amounts of disaccharide **4b** (<10%) have been obtained with the SBox donor that is known to be slowly activated with TMSOTf.[46-47] Although we cannot entirely exclude a possibility of forming small amounts of AgOTf in situ, this results implies that it neither contributes in the acceleration of the reaction with bromide donors nor gets regenerated as shown in failed activations of thioimidates.

Fourth, previous studies dedicated to the activation of glycosyl bromide with AgOTf were effective in the presence of 1,1,3,3-tetramethylurea (TMU) as the proton scavenger. When our standard experiment was performed in the presence of TMU (1.0 equiv), only a small amount (<10%) of the disaccharide was produced. This observation suggests that TMU scavenges the protons needed to regenerate TMSOTf to run the catalytic cycle. This observation also reduces the likelihood of the involvement of AgOTf in the activation process.

Fifth, we investigated whether other Lewis acids that cannot form AgOTf would activate bromides. Similar experiments performed with Ag_2O and BF_3-Et_2O have ultimately confirmed that AgOTf is not involved in the acceleration of Koenigs-Knorr reactions. Nevertheless, the premixed Ag_2O and BF_3-Et_2O gave a swift and nearly quantitative glycosidations of donor **2a** with acceptor **3** (see the SI for details).

Therefore, we believe that this reaction proceeds via a cooperative catalysis with Ag_2O and a Lewis acid that originates from the classical pathway of bromide activation via the complexation of Ag_2O with the leaving group (**A**) as depicted in Scheme 2. While silver is thiophilic, Ag_2O is too weak a promoter to effectively pull the leaving group and pass the energy barrier required for the dissociation RDS to take place. Koenigs and Knorr[2] used mildly basic Ag_2O or Ag_2CO_3 as acid scavengers. It was not until the early 1930's when it was realized that the silver salts may play a more active role by assist in the leaving group departure.[4] The intermediate **A** will ultimately dissociate, but this reaction is slow, particularly with unreactive bromides (*vide supra*). When catalytic TMSOTf (0.2 equiv) is added, strongly ionized species **B** are formed as the result of silylation of the silver oxide oxygen. The intermediate **B** will readily break apart leading to the loss of the leaving group that is irreversible due to the rapid precipitation of AgBr. Also formed at this stage is AgOTMS and glycosyl cation **C** that can be stabilized via acyloxonium or oxacarbenium intermediate depending on the nature of the substituent at C-2.[48] As an alternative, some donors might be capable of a concerted leaving group displacement as observed in case of highly reactive galactosyl bromide **2f**. The reactive intermediate **C** is then attacked by acceptor (ROH) and after the proton exchange step affords the desired glycoside product and TfOH. The latter reacts with AgOTMS to produce TMSOTf that becomes available for the next catalytic cycle for the activation of complex **A**. Also generated is unstable AgOH that undergoes the loss of water, scavenged by the molecular sieves (MS), and contributes to the regeneration of Ag_2O and helps to maintain the overall neutral pH of the reaction medium. In our experience, AgOTf-promoted glycosidations of bromides are highly acidic and often provide only moderate yields due to occurrence of side reactions caused by the acidic medium.

Scheme 2. Plausible mechanistic pathway



In conclusion, the effective reaction conditions for rapid Koenigs-Knorr glycosylation catalyzed with TMSOTf are reported. The glycosylation products form in minutes and the neutral activation conditions are compatible with many protecting and leaving groups. Also revealed is an unusual reactivity trend according to which benzoylated α-bromides are much more reactive than their benzylated counterparts. The reactivity difference was demonstrated by the competition experiment. Also studied is the reaction mechanism by which the Koenigs-Knorr's promoter silver oxide acts in cooperation with the Lewis acid catalyst. Further studies dedicated to the

optimization of the reaction conditions in application to other donors and systems are underway in our laboratory.

ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data for all new compounds. This material is available free of charge via the Internet.

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