Recent advances in reagent-controlled stereoselective/stereospecific glycosylation

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ABSTRACT

The formation of *O*-glycosidic linkage is arguably one of the most important topics in glycoscience due to the prevalence of *O*-glycosides in nature. Great efforts have been devoted to this field by many carbohydrate chemists to develop stereoselective/stereospecific glycosylation methodologies. Although glycosyl donor- and acceptor-controlled strategies have significantly progressed, the tedious design and pre-synthesis of substrates could not be avoided. On the other hand, reagent-controlled glycosylation can overcome these challenges and produce the desired selectivity by only altering external factors such as concentration, reagents or other reaction conditions. This mini-review discusses selected recent novel methodologies on reagent-mediated stereo-controlled glycosylation in the last decade, classified by the types of glycosyl donors.

1. Introduction

In the pursuit to better understand glycobiology, there is great demand to obtain a variety of oligosaccharide and glycoconjugate libraries [1,2]. This fuels the need to develop efficient glycosylation methodologies with excellent regio- and stereo-selectivity [3–7]. Notably, most of these chemical approaches focus on designing and tuning the nature of the glycosyl donors to target the selectivity directly and indirectly [8–11]. Through an indirect manner, for examples, hydrogen bonding, steric blocking, ring locking and conformational restrictions, stereocontrol could be realized [12]. On the other hand, direct approaches, which include anomeric effect, tuning of anomeric leaving group, neighboring group participation and intramolecular aglycon delivery, were also reported to be successful in targeting stereoselectivity [13–15]. While donor-controlled stereoselectivity has been efficient, tedious multi-step syntheses of glycosyl donors are often unavoidable. Recently, alternative approaches directing the stereoselectivity by glycosyl acceptors were successfully developed by Woerpel, Liu and Seeberger [16–19]. The innate properties of these acceptors determine their product stereoselectivities through different reaction pathways, with/without intermolecular interactions such as hydrogen bonding or coordination with palladium complexes.

However, both glycosyl donor-controlled and accepter-controlled glycosylation rely on the nature of the substrates. Moreover, additional efforts are essential for the design and synthesis of the specific starting materials. To extend the stereochemical control without modifying the target glycosides, a preferable approach is to change the reaction conditions by employing different reagents/activators. In the past decade, carbohydrate chemists have reviewed glycosylation reactions mediated by transition-metal [20], exo-nucleophiles [21] and organocatalysts [22,23]. Though quite a lot of efficient reagent-controlled methods towards 2-deoxyguars have been developed recently [22,24–29], we are not going to them here. It encompassed a vast field of numerous efforts dedicated by carbohydrate chemists deserved to be reviewed in a separate article. Herein, we select to review some typical reagent-controlled *O*-glycosylation methodologies developed in recent ten years. This mini-review will discuss the methods based on the different types of glycosyl donors.

2. Thioglycoside donors

Thioglycoside may be the most widely explored glycosyl donor in glycosylation owing to its stability and ease of preparation. The thioether moiety leaving group can be activated under various conditions. The resulting oxocarbenium intermediate usually gives α-glycosides as the major product due to anomeric effect. Several activators have been applied, but it is a remaining challenge to obtain β-glycosides.

Recently, Davis's group successfully developed new activators to furnish dual selectivity for both α- and β-glycosides with thioglycoside donor and 2 hydroxyl-mannose as the acceptor, as shown in Scheme 1

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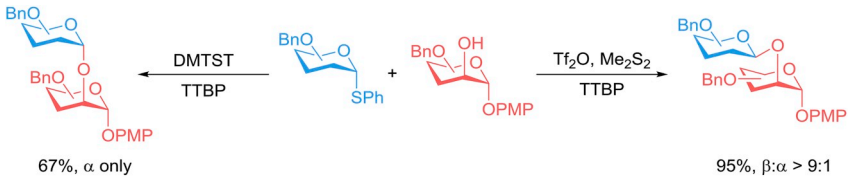


Scheme 1. Different stereoselectivities of mannosylation were achieved by varying reagents.

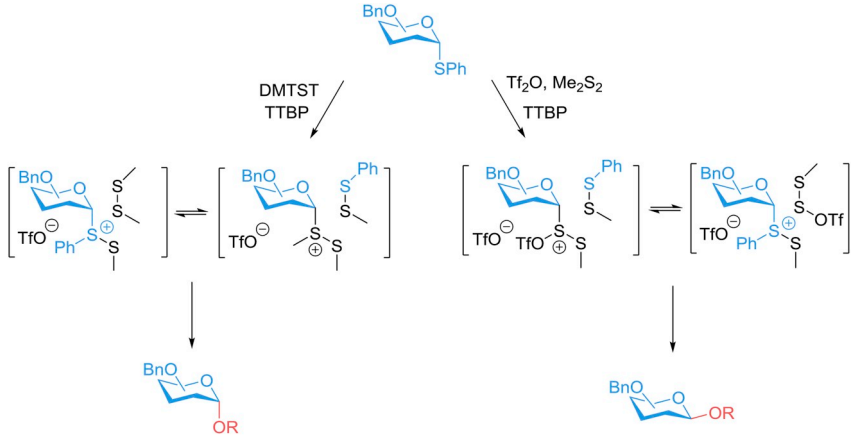


Fig. 1. Proposed mechanism of achieving α- or β-mannosides respectively from thioglycosides.

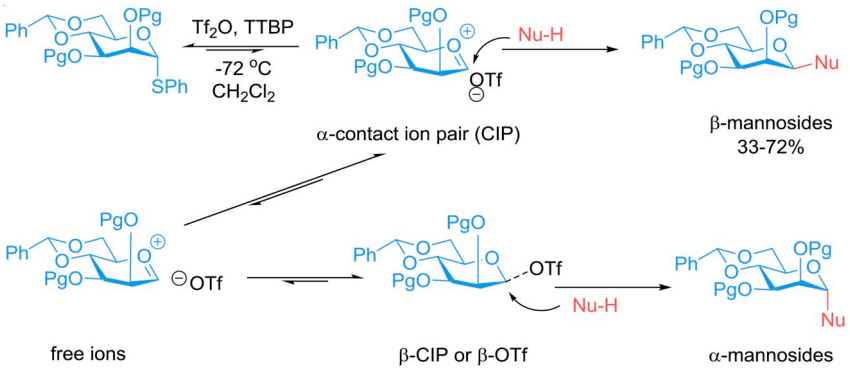
[30]. While they could obtain the α only mannoside in 67% using dimethyl(methylthio) sulfonium triflate, the β-mannoside was generated in 95% as the major product (β/α > 9:1) by dimethyl disulfide and triflic anhydride. Although this result of the switchable method is very interesting, the glycosyl acceptor scope is limited to 2-OH mannose derivatives.

Based on the results and their previous work, they proposed a mechanism for selectivity, as delineated in Fig. 1. Triflic anhydride/Me_2S_2 and DMTST could help to generate different sulfonium *in situ* from thiomannoside starting material. After the activation, equilibrium established between other types of intermediates can lead to different selectivity during the nucleophilic attack from acceptors. The intermediate of triflic anhydride condition can promote a cleaner S_N2 reaction to generate the β-selectivity.

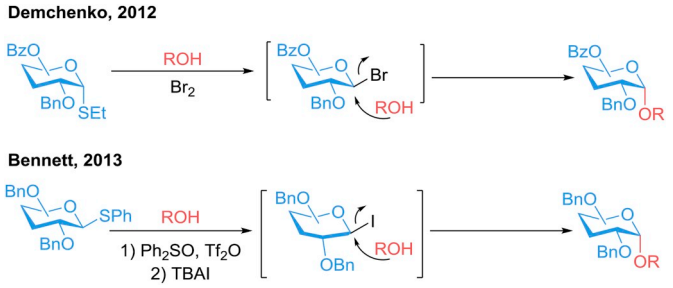
Triflic anhydride has been applied widely in glycosylation and well-studied by Crich et al., giving high selectivity of mannosylation with 4,6-*O*-benzylidene protection [31,32]. As shown in Scheme 2, with the specific protection, the sugar conformation can be locked after activation by Tf_2O. The concept of α-contact ion pair (CIP), which was favored and stabilized by this locked conformation, was proposed. Then glycosyl acceptors would prefer attacking from the opposite face giving β-mannosides selectively. Numerous detailed mechanistic studies were performed by Crich's group [31,33,34]. The intermediate glycosyl triflates have actually been demonstrated by using primary ^{13}C kinetic isotope effects and supported by computational chemistry [32].

As being discussed above, the specific protection 4,6-*O*-benzylidene is necessary to confirm the selectivity of Tf_2O-catalyzed glycosylation from thioglycosides, which means additional steps cannot be avoided. In order to overcome this challenge, Demchenko and Bennett developed protocols using Tf_2O to form 1,2-*cis*-glycosides selectively without specific protecting groups as shown in Scheme 3 [35,36].

Demchenko employed bromine to mediate α-stereoselective glycosylation with thioglycoside donors [35]. By elucidating Lemieux's previous study of *in situ* anomerization concept, Demochenko developed a similar and complementary glycosylation method. It was demonstrated that β only glycosyl bromide can be achieved from the disarmed donor 2-*O*-benzyl-3,4,6-tri-*O*-benzoyl thioglycoside. The mechanism of bromine-mediated glycosylation was illustrated in Fig. 2. Firstly, the electron lone pair of thiol moiety attacks bromine forming sulfonium cation. The generated bromide anion undergoes nucleophilic attack to the cation, furnishing β-bromide glycosides, which was confirmed by NMR study. However, the approach is not applicable to all 1,2-cis glycosides, as being discussed in the article, 2-*O*-benzyl-3,4,6-tri-*O*-benzoyl glucosyl donor and 1,2-cis mannosides cannot be accessed. On the other hand, Bennet adapted Ph_2SO/Tf_2O as the catalyst on the similar disarmed donors. In addition, they applied TBAI to reverse the



Scheme 2. The mechanism of triflic anhydride applied in 4,6-*O*-benzylidene thioglycoside donors.



Scheme 3. 1,2-*cis*-glycosides obtained without specific protection group from thioglycosides.

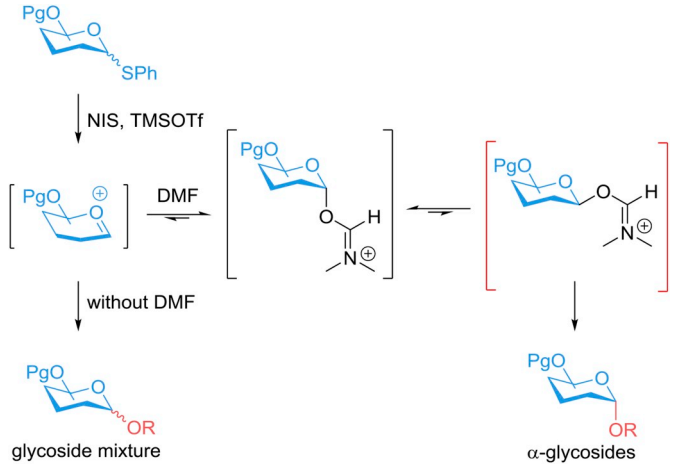
selectivity to α and *N*-methylmaleimide to block the regeneration of thioglycoside donor caused by TBAI [36].

Another interesting discovery of reagent-controlled glycosylation from thioglycosides was contributed by Mong's group using DMF as an effective additive (Scheme 4) [37]. The common solvent DMF can be used to trap the oxocarbenium cation after thioglycoside activated by TMSOTf and NIS. A mixture of α/β-glycosides will be formed without locked conformation or DMF. However, in the presence of DMF, α-glycosides will be produced as the major product because DMF reacts with oxocarbenium to get glycosyl imidate intermediates. β-Glycosyl imidates are more reactive compared to the α counterparts, thus the dynamic kinetic control delivered dominant α-selectivity.

3. Acetimidate donors

Trichloroacetimidates have become another type of common glycosyl donors since first introduced in 1980, due to its easy preparation [38], high reactivity and ability to provide desirable stereoselective outcomes. In 2010, Fairbanks and co-workers reported chiral Brønsted acid catalyzed stereoselective glycosylation to achieve β-galactosides [39]. BINOL-derived phosphoric acid (*S*)-**A** was found to deliver absolute selectivity when methanol was used as an acceptor. In comparison, the traditional activator TMSOTf only gave β-selectivity in the ratio of 10:1. Nevertheless, increasing the bulkiness level of acceptor showed detrimental effect to the selectivity. The scope of secondary-alcohol-containing acceptors was limited, with rather poor selectivity.

Three years later, Toshima presented a catalytic protocol using the same Brønsted acid (*S*)-**A** that induced chirality recognition of racemate mixture of chiral acceptors [40]. A diastereoisomeric mixture composed of 4 isomers of 2-phenyl cyclohexanol underwent stereoselective glycosylation with benzyl protected glucosyl trichloroacetimidate to furnish a single *O*-glucoside. Other chiral simple alcohols were tested and provided very high selectivity; however, there was no successful example of carbohydrate acceptor. It is worth noting that the reactivity of glycosyl donor is totally dependent on which enantiomer of the chiral acid was used. Only (*S*)-**A** was able to facilitate an efficient stereoselective glycosylation, while (*R*)-isomer gave low yield and poor selectivity. Mechanistic study indicated that the selectivity results from



Scheme 4. DMF-controlled stereoselective glycosylation.

kinetic control, and the acceptor approaches in S_N2 manner, proposedly directed by the chiral acid catalyst (Scheme 5).

Achiral phosphoric acid **B** was also employed together with thiourea **C** for stereoselective glycosylation, as demonstrated by Schmidt [41]. The reaction requires purified α-trichloroacetimidate glycosides as the donor because its mechanism resembles S_N2 mediated by acid. The formation of oxonium cation is inconclusive, and the proposed mechanism is depicted in Fig. 3.

In 2016, Toshima developed concentration controlled dual stereoselective glycosylation facilitated by organo-photoacid [42]. Once again, thiourea **C** was utilized, and it exhibits significantly enhanced acidity upon UV-irradiation (365 nm). The reaction concentration plays a pivotal role in determining the mechanistic pathway. High concentration of substrates promotes the S_N2 type substitution while diluted concentration encourages the S_N1 pathway. Although the diastereoisomeric ratio (dr) is merely in the range of 10:1, the concept was proved to work for both small alcohols and carbohydrate acceptors.

Most recently, Codée and co-workers employed a modified version of traditional trichloroacetimidate for stereoselective 1,2-*cis*-glycosylation reaction [43]. Different activation conditions are required for primary and secondary hydroxyl acceptors. For secondary alcohol acceptors, DMF was found to be the best nucleophilic additive to promote selectivity on the oxocarbenium cation, in line with Mong's observation aforementioned in Scheme 4. In contrast, primary alcohol acceptors required trimethylsilyl iodide as the activator and Ph_3PO additive, as inspired by Mukaiyama's report [44,45]. The mechanistic studies revealed that anomeric iodide was involved as an intermediate. Under the activation condition, α-glycosyl iodide would be formed and could further undergo the first substitution with the phosphine derivative, delivering the more reactive β-phosphonium iodide, which was the actual glycosylating reagent. The generality of this method showed its great potential application. A *Mycobacterium tuberculosis* nonasaccharide α-glycan was successfully synthesized as an example.

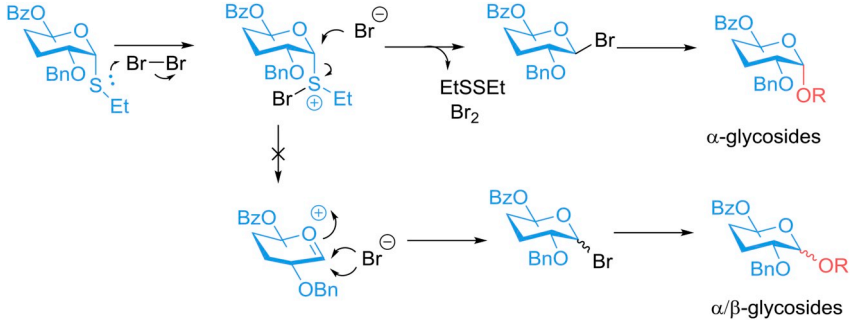
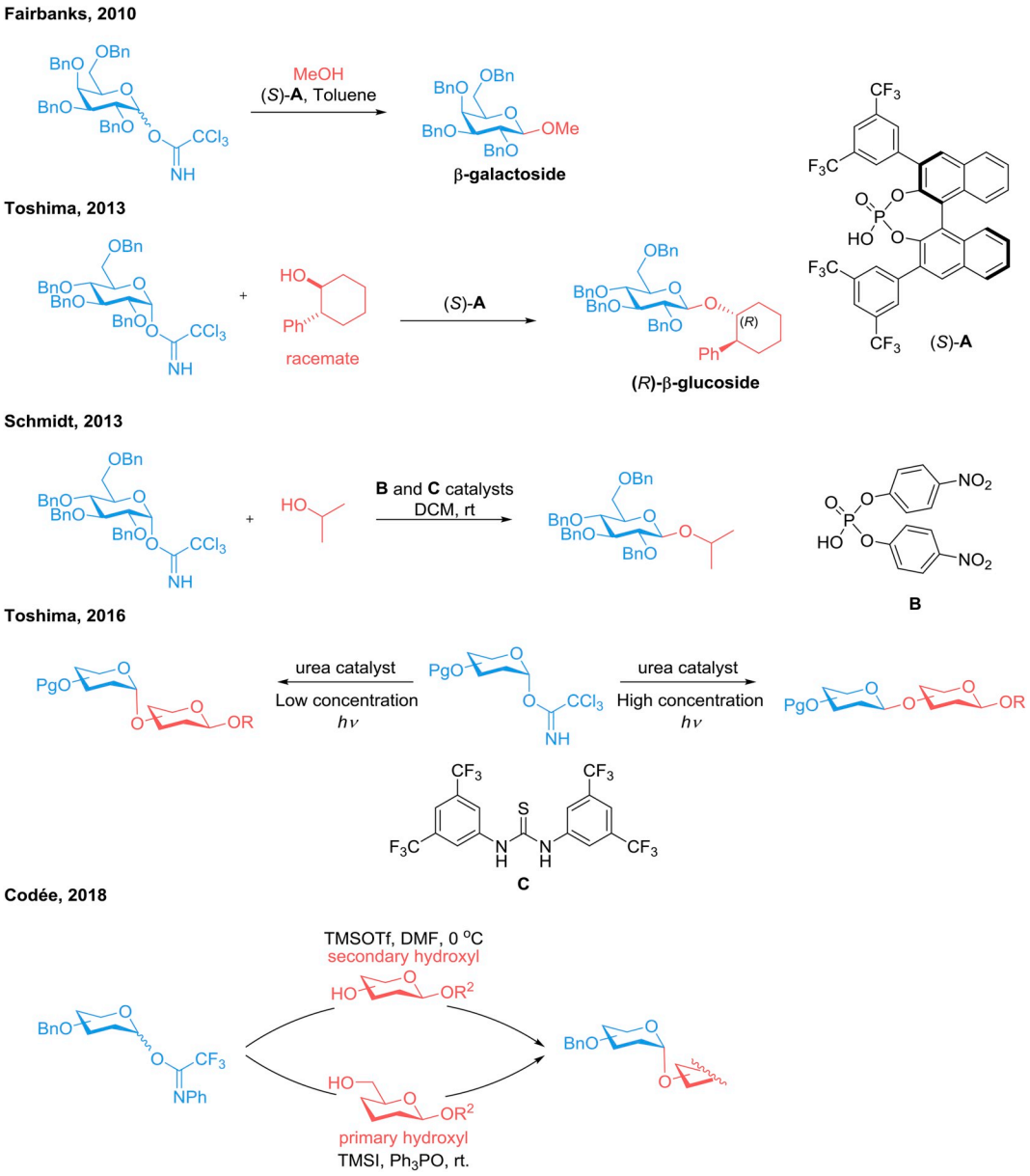


Fig. 2. Proposed mechanism of bromide-mediated glycosylation.



Scheme 5. Selected recent reagent-controlled glycosylation with acetimidate donors.

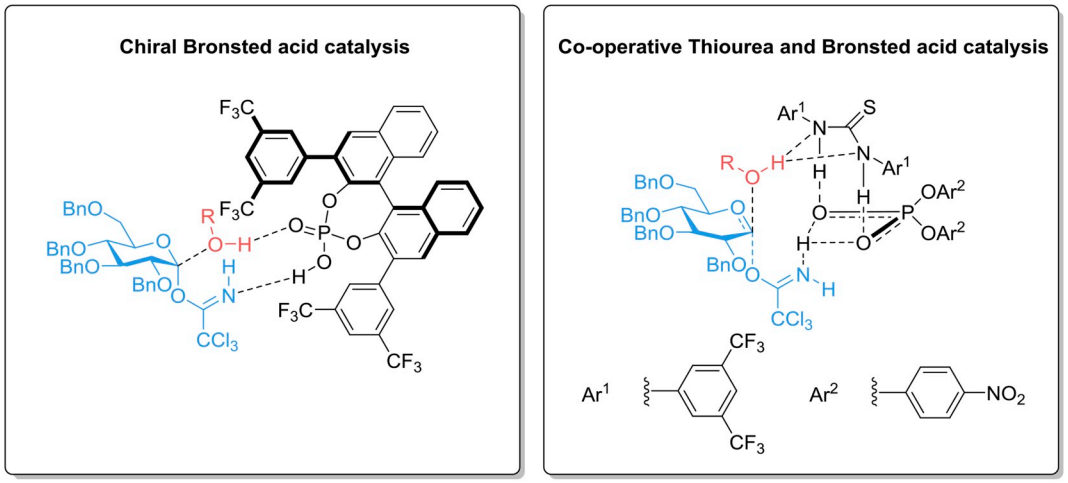
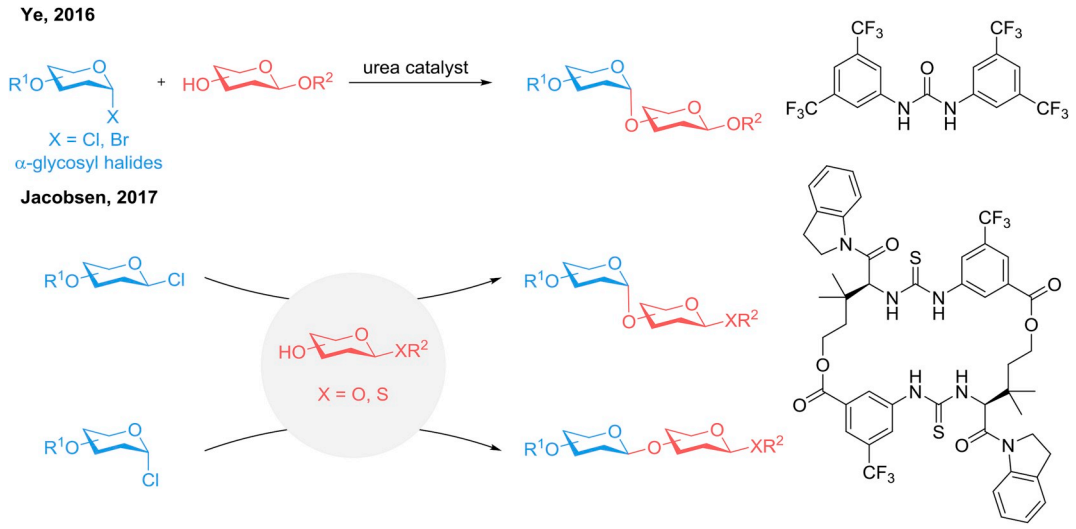


Fig. 3. Proposed mechanism of Bronsted acid/thiourea-controlled glycosylation.



Scheme 6. Urea/thiourea catalyst-controlled glycosylation with glycosyl halide donors.

4. Halide donors

Koenigs–Knorr glycosylation that employs glycosyl halide donors and silver salt activators is among the traditional methods promoting high yield glycosylation albeit with low selectivity. In 2016, Ye and co-workers developed the first stereoselective Koenigs–Knorr glycosylation facilitated by urea organocatalysis (Scheme 6) [46]. Absolute α-selectivity was observed on the products from galactosyl, mannosyl and rhamnosyl chloride under the reaction with a wide range of acceptors. The rationale of the reactivity was explained by the activation of glycosyl donor via hydrogen-bonding with urea catalyst. Similar activation was reported by Jacobsen in enantioselective addition to halide derived oxocarbenium ions [47]. The necessity of active hydrogen on urea catalyst together with mechanistic ^{1}H NMR studies reaffirmed the theory of hydrogen-bonding activation. Notably, the presence of a phosphine additive was found to facilitate the glycosylation selectivity on challenging cases (benzoyl protected donors), although the detailed mechanism has not been investigated.

Subsequently, Jacobsen and co-worker discovered the intriguing catalytic property of macrocyclic bis-thioureas in the glycosylation that allows stereospecific construction of glycosidic bonds [48]. The mechanism was studied by the computational study as shown in Fig. 4, the stereoselectivity was controlled by the hydrogen-bonding between sugar and catalyst. A broad scope of glycosyl donors with good to excellent yield and selectivity shows the wide applicability of this strategy. Another central advantage of this method is that it works well on disaccharide donor and thioglycoside containing acceptors without compromising selectivity. This facilitates the future application to complex glycan synthesis.

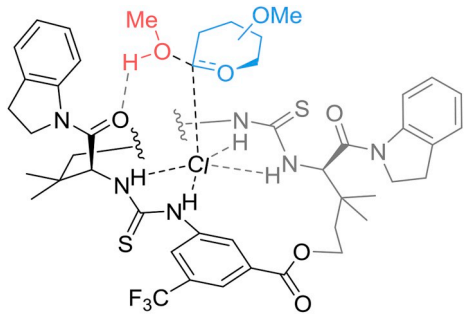


Fig. 4. Mechanism of bis-thiourea-catalyzed glycosylation.

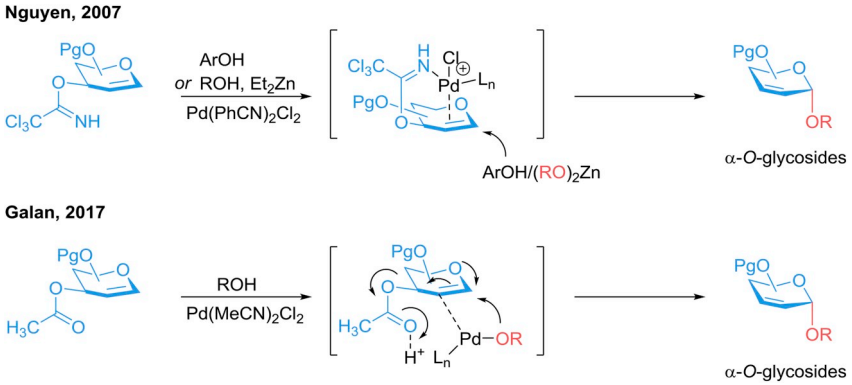
5. Glycal donors

In contrast to all the thioglycoside, acetimidates and halide donors that have no unsaturated bond on the ring structure, another type of general donor is the unsaturated saccharide derivatives with a double bond between C_1 and C_2, named as glycals. They have shown diverse reactivities and broad applications in organic synthesis. As the rapid development of transition metal in organic chemistry, glycals play more important roles in glycosylation due to its ability to coordinate to metal catalysts. Herein, we only review some typical reagent-controlled stereoselective *O*-glycosylation using glycal donors. A few efficient reagent-controlled methods to 2-deoxyguars have been developed by Galan and some other chemists [22,24,25,28,49], but due to the scope of this mini-review as being stated in the introduction, 2-deoxy glycosylation would not be discussed here in further details.

Nguyen's group reported a successful use of catalytic Pd(II) complex with trichloroacetimidate glycal donor for achieving stereoselective glycosylation [50]. According to Nguyen's study, glycosylation reactions proceeded readily with phenol acceptors, while aliphatic acceptors, including monosaccharides, had to be activated by $ZnEt_2$ additive for better reactivity (Scheme 7) [50]. They proposed that the strategic positioning of C_3-trichloroacetimidate could direct the bulky palladium complex to the β–face through Pd-N coordination, which in turn blocked the β face of the sugar to yield selectively α-*O*-glycosides (Fig. 5). To circumvent the need for activating additives for donor or acceptor, Galan reported last year a direct glycosylation from commercially available glycals catalyzed by $Pd(MeCN)_2Cl_2$ (Scheme 7) [51]. The authors proposed that palladium's insertion into ROH acceptor generated alkoxypalladium species and proton, as an acid, to catalyze the Ferrier rearrangement. Subsequently, the palladium complex coordinated to the α-face, and the α-*O*-glycoside products were the results possibly from steric hindrance at the C_3-moiety and anomeric effect.

In order to confirm the mechanism pathway through Pd(0) or Pd(II), Nguyen also applied the Pd(0) catalyst $Pd_2(dba)_3$ to test this method. As shown in Scheme 8, the result demonstrated that Pd(0) catalyst could only produce low yield and poor selectivity (α/β = 3:2). This experiment not only proved the proposed mechanism but also indicated the difference in catalytic nature of Pd(0) and Pd(II) cycles.

The varying nature of catalysts could be exploited to effect α- and β-anomeric selectivity easily. Recently, Liu's group designed highly reactive 3,4-*O*-carbonate glycal donors which can selectively produce both α- and β-products controlled by various Pd catalysts (Scheme 9) [52]. In Pd(II) condition, while aliphatic alcohols including



Scheme 7. Pd(II) catalyst-controlled stereoselective glycosylation.

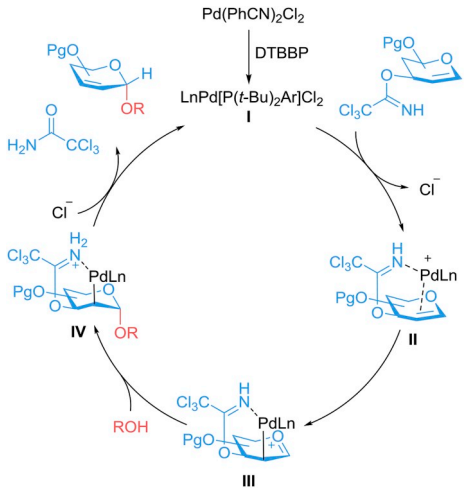


Fig. 5. Proposed Mechanism of $Pd(PhCN)_2Cl_2$ catalyzed stereoselective *O*-glycosylation.

monosaccharide derivatives gave β-selectivity, aromatic phenols produce α-selectivity only. On the other hand, in Pd(0) condition both aliphatic and aromatic acceptors generate β-glycosides exclusively in high yields. This methodology is applicable to broad substrate scope. Five types of glycals were tested. Twenty-four β-*O*-glycosides were obtained from alcohols and phenols catalyzed by Pd(0) species in high yield. While eleven aromatic α-*O*-glycosides were achieved from Pd(II) catalytic system, twenty-four aromatic β-*O*-glycosides were synthesized via Pd(0) catalyst. The method allows facile stereoselective synthesis of the target glycosides by only switching catalysts.

The possible mechanism was proposed based on the resulting selectivity and reported literature, as shown in Fig. 6. While Pd(0) prefer to coordinate with the olefin of glycal directly from α-face due to the steric effect, Pd(II) would like to coordinate with the carbonate moiety and the double bond simultaneously to form a complex. In Pd(0) condition, all the acceptors attack from the β-face because of H-bonding. In Pd(II) condition, hard nucleophiles (ROH) yield β-glycosides through the inner-sphere pathway and softer nucleophile (ArOH) produce α-glycosides from the outer-sphere pathway [18].

As the organocatalysis has been attracting a huge attention from organic chemists in the last decade, it has been applied in a few catalytic protocols using glycal donors. Yoshida developed a bifunctional chiral thiourea, which can catalyze stereoselective glycosylation between 2-nitro-glycal and phenols. α-Glycosides can be achieved in good selectivity (10:1 to ≥ 20:1) and high yields (Scheme 10) [53]. They proposed the –NH moieties of thiourea catalyst could form H-bonds with the nitro group of glycal donors (Fig. 7). The other hand of the chiral organocatalyst is pyrrole that can direct the direction of acceptor attack.

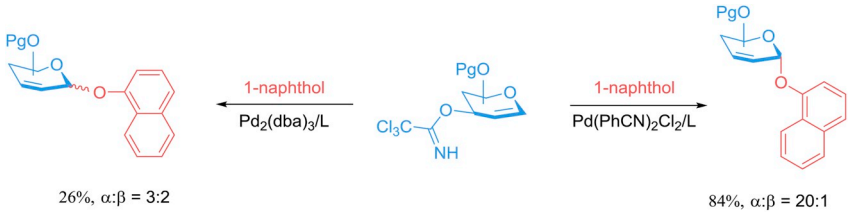
6. Epoxide donors

A series of 1,2-*cis*-stereoselective glycosylation was successfully carried out by Takahashi, Toshima and co-workers since 2016, utilizing 1,2-anhydroglycosyl donor (epoxide) and borinic/boronic acid promoter (Scheme 11) [54–59]. The methodology was first tested on the synthesis of 1,2-*cis*-α-glucosides and 1,2-*cis*-β-mannosides [57,58]. It is worth to mention that the glycosylation scope has been extended to a wide array of unprotected glycosyl acceptors, giving excellent regioisomeric control [56]. This elegant protocol has been applied to the total synthesis of carbohydrate-containing natural products, for examples, acremomannolipin A [57], GSL-1 and GSL-1' [58], and oligosaccharides [55,56].

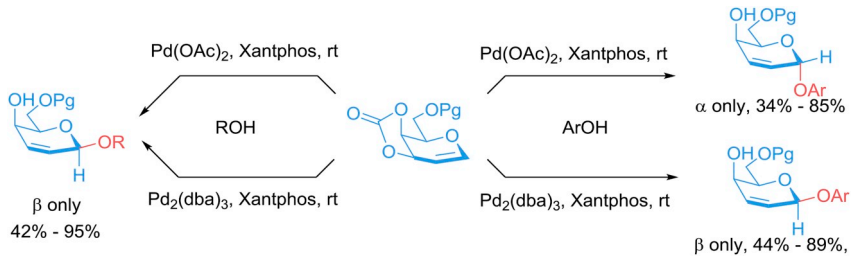
The proposed mechanism of the reaction involves the formation of a boronic/borinic ester between glycosyl acceptors and the organoboron catalyst (Fig. 8). These intermediates possess Lewis acid property that could efficiently activate epoxide electrophile, forming the short-lived oxonium cation *in situ*. The delivery of glycosyl acceptor aided by tetravalent boron partially resembles the intramolecular aglycon delivery (IAD) strategy firstly introduced by Hindsgaul [60].

7. Other donors

Beside the donors we described above, some other universal donors are also applied in reagent-controlled glycosylation. For instance, exploitation of solvent effect might be one of the oldest methods applied in glycosylation, but some interesting and new results are reported recently [61–63]. As we discussed before, Mong et al. applied DMF as an additive to control the selectivity in thioglycosyl donor successfully.



Scheme 8. Pd(0) catalyst demonstrated difference selectivity from Pd(II) catalyst.



Scheme 9. Pd(0)/Pd(II) catalyst-controlled glycosidic bond formation selectively.

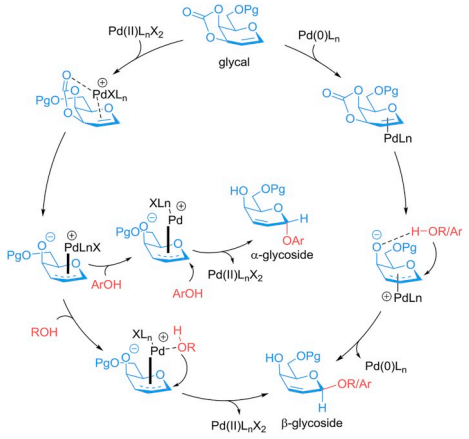


Fig. 6. The possible mechanism of Pd catalyst-controlled glycosylation.

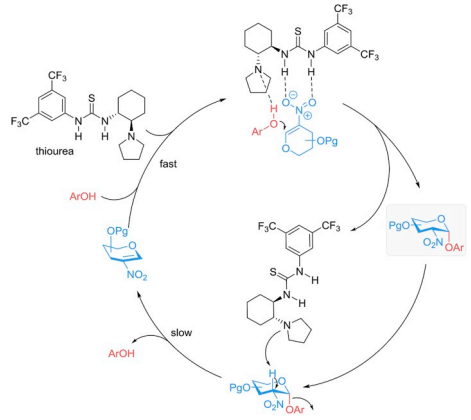


Fig. 7. The possible mechanism of chiral thiourea catalyst-controlled glycosylation.

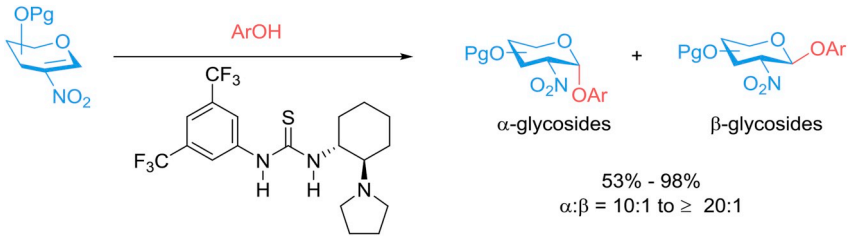
Recently, they applied solvent effect in various glycosyl donors simultaneously and one-pot strategy to synthesize oligosaccharides [64]. DMF was also applied to control the selectivity of synthesizing α- and β-*O*-glycosyl serine conjugates with anomeric-protection-free glycosyl donors by Gin's group (Scheme 12) [61]. They discovered that KH and DMF system could generate α-glycosides as the major product (α/β = 10:1). On the other hand, NaH and THF system could reverse the selectivity to dominantly β (α/β = 1:20). This method provides a brand-new pathway to glycoprotein synthesis.

Zhu and his coworkers also reported a successful glycosylation using anomeric protection free glycosyl donor with stereoselectivity controlled by an additional reagent [65]. As shown in Scheme 13, they developed a stereoselective β-mannosylation directed by the cesium ion coordination using 1,2-dihydroxyl free mannoses as the donor. Cesium carbonate serves as a strong base which first deprotonates the 1,2-dihydroxy group and then forms a five-membered ring transition state between cesium ion and the 1,2-dioxy groups. This method was applied to synthesize two trisaccharides which are the core structure of *N*-glycans and glycosphingolipid [65,66].

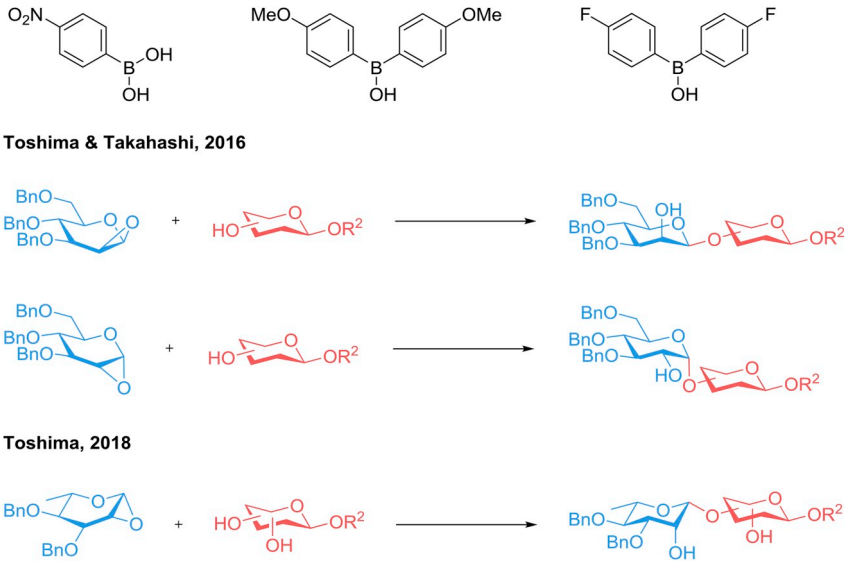
Taylor's group has been studying boron reagent in carbohydrate chemistry for a long time. Recently, they discovered one diarylborinic acid which could catalyze glycosylation between protection-less glycosyl donors and acceptors. anomeric hydroxyl free sugars could be employed directly as the donors (Scheme 14) [67]. Methanesulfonate glycosyl donors were generated *in situ* with methanesulfonic anhydride. While β-selectivity (α/β = 1:10) was generated from the reaction with protection-less acceptor 2,3,4-trihydroxy-mannose directly catalyzed by borinic acid, α-selectivity (α/β = 2:1) was obtained from the same reaction without boron catalyst. Based on their results from reaction kinetic analysis and NMR exchange spectroscopy, they proposed a mechanism to explain the selectivity difference as shown in Fig. 9. After the formation of methanesulfonate glycosyl donors, an equilibrium shows that α-glycosyl donor is more reactive and upon nucleophilic attacked by the acceptor affords the major product. This glycosyl donor reacts with tetracoordinate borinic ester generated from 2,3,4-trihydroxy free acceptors and borinic acid catalyst. Then the major product is formed as the β-selectivity due to the steric effect from this borinic ester complex.

8. Conclusion and outlook

Glycosylation with product stereochemistry controlled by additional reagents is considered to be the most effective method regardless of donor or acceptor structures. In the past decade, considerable effort has been dedicated to this field and many efficient strategies working on various glycosyl donors have been developed. Stereochemistry of glycosylation products from thioglycosides, acetimidates, glycosyl halides, glycals and glycosyl epoxides can all be controlled by different reagents



Scheme 10. Chiral thiourea catalyst-controlled glycosidic bond formation selectively.



Scheme 11. Boronic/borinic acid-controlled glycosylation.

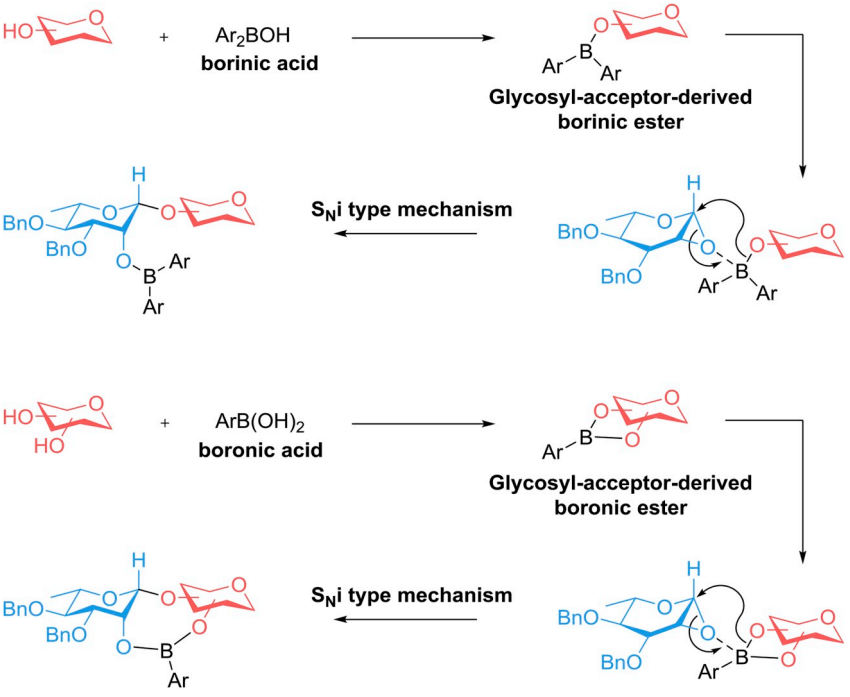
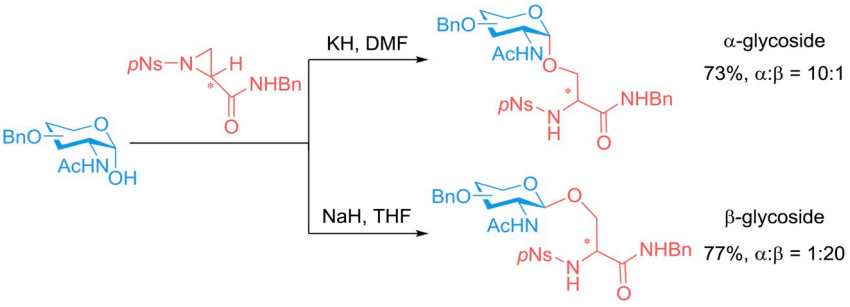
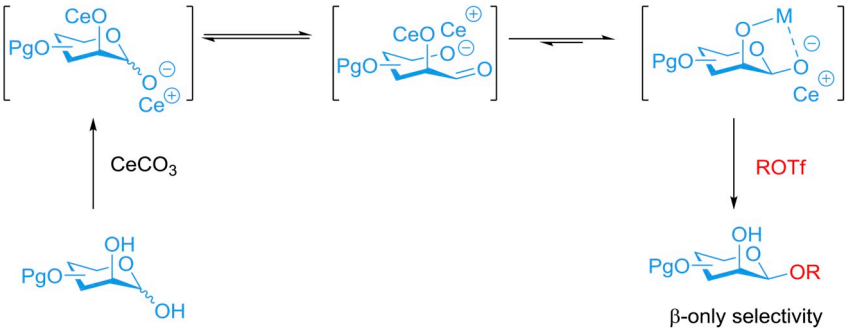


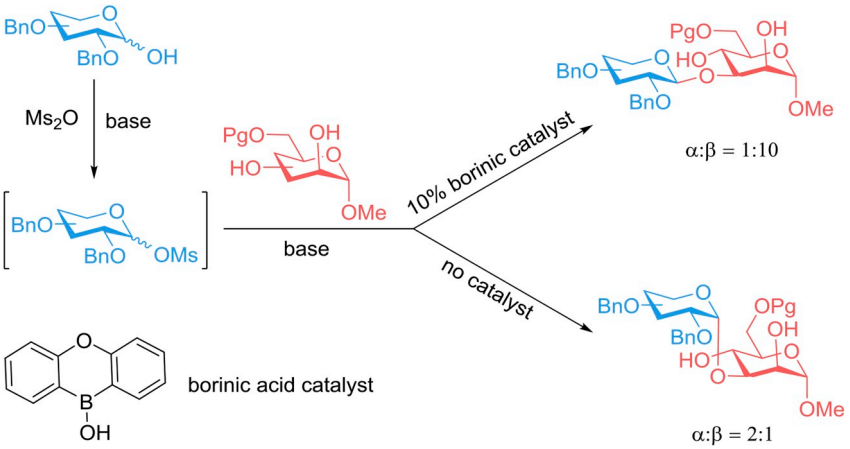
Fig. 8. Mechanism of boronic/borinic acid-controlled glycosylation.



Scheme 12. Solvent and metal hydride-controlled glycosylation stereoselectively.



Scheme 13. Cesium chelation-controlled β-mannosylation.



Scheme 14. Borinic acid catalyst-controlled glycosidic bond formation selectively.

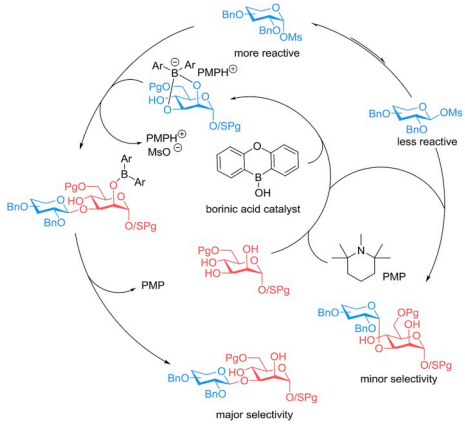


Fig. 9. Mechanism of borinic acid catalyst-controlled glycosylation form methanesulfonate glycosyl donors.

such as additives, solvents and catalysts to produce the desirable target stereoselectivity. Some of the reagents, for example, borinic acid are applicable to reactions employing protection-less donors and acceptors. Most of the developed methodologies only work for a limited scope of glycosyl donors and some strategies can only provide a single selectivity (either α or β). Overall, we envision that the reagent-controlled glycosylation holds a great promise in addressing the stereoselectivity issues currently associated with the automated synthesis of oligosaccharides, polysaccharides or glycoconjugates. Potential future outlook would be to design new efficient universal reagents, which can control the regio- and stereoselectivity of glycosylation effectively in high efficiency, especially for protection-less glycosyl donors and acceptors.

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