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Review

# Glycosyl fluorides in glycosidations

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**Abstract**

This short review deals with the recent progress in chemical O-glycosidation and C-glycosylation methods using glycosyl fluorides as glycosyl donors. Pyranosyl and furanosyl fluorides were effectively activated by fluorophilic reagents such as $SnCl_2$–$AgClO_4$, $SnCl_2$–$TrClO_4$, $SnCl_2$–AgOTf, TMSOTf, $SiF_4$, $BF_3{\cdot}Et_2O$, $TiF_4$, $SnF_4$, $Cp_2MCl_2$–$AgClO_4$ (M = Zr or Hf), $Cp_2ZrCl_2$–$AgBF_4$, $Cp_2HfCl_2$–AgOTf, $Bu_2Sn(ClO_4)_2$, $Me_2GaCl$, $Tf_2O$, $LiClO_4$, $Yb(OTf)_3$, $La(ClO_4)_3{\cdot}nH_2O$, $La(ClO_4)_3{\cdot}nH_2O$–$Sn(OTf)_2$, Yb–Amberlyst 15, $SO_4/ZrO_2$, Nafion-H®, montmorillonite K-10, and $TrB(C_6F_5)_4$ to react with alcohols to give the corresponding *O*-glycosides in high yields. Furthermore, several types of *C*-glycosyl compounds, such as aryl, allyl and alkyl *C*-glycosyl derivatives, were also obtained by the glycosylation using glycosyl fluorides and the corresponding nucleophile with or without a Lewis acid. 

*Keywords:* O-Glycosidation; C-Glycosidation; Glycosyl fluoride; *O*-Glycoside; *C*-Glycoside

**Contents**



## 1. Introduction

Glycosidation is one of the most important and basic synthetic methods to prepare several types of glycosides and oligosaccharides. Therefore, highly effective chemical glycosidation reactions have attracted considerable attention in carbohydrate chemistry related to certain biomolecules and functional materials. From a synthetic standpoint, the efficiency of the glycosidation method generally involves a high chemical yield, regioselectivity, and stereoselectivity. This short review concentrates on recent progress (1981–1998) in chemical O-glycosidation and C-glycosylation methods using glycosyl fluorides as glycosyl donors, including historically indispensable protocols [1–3]. This article also particularly emphasizes the development of new activating methods for the glycosyl fluorides.

Glycosyl fluorides have now been widely and effectively used for O- and C-glycosidation reactions. One of the notable advantages of the glycosyl fluoride as a glycosyl donor is its high thermal and chemical stability as compared with the low stability of other glycosyl halides, such as glycosyl chlorides, bromides

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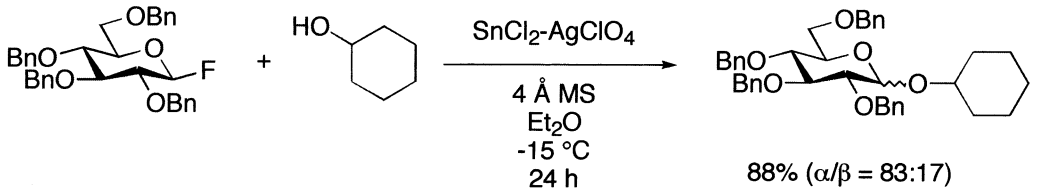



Scheme 1.

and iodides. Therefore, the glycosyl fluoride can be generally purified by the appropriate distillation and even by column chromatography with silica gel. Having such favorable synthetic attributes, the use of a glycosyl fluoride as a practical glycosyl donor in the glycosidation reaction was first developed by Mukaiyama and co-workers in 1981 [4]. After their significant advance, a number of effective chemical methods for O-glycosidations and C-glycosylations using a glycosyl fluoride have been developed.

## 2. Glycosyl fluorides in O-glycosidations

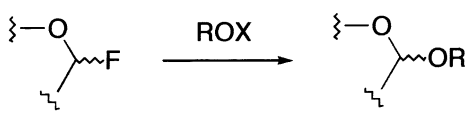
Since the use of glycosyl fluoride as a glycosyl donor with a fluorophilic activator, $SnCl_2$–$AgClO_4$, was introduced by Mukaiyama in 1981 (Scheme 1), a number of specific fluorophilic reagents have been developed for effective O-glycosidation reactions. These activators for O-glycosidations using glycosyl fluorides as glycosyl donors are summarized in Table 1. After $SnCl_2$ was first employed as an activator of the glycosyl fluorides in combination with $AgClO_4$, the other combined use of $SnCl_2$–$TrClO_4$ (Scheme 2) [5] and $SnCl_2$–AgOTf (Scheme 3) [6] were reported by Mukaiyama and Ogawa, respectively. In these cases, 1,2-*cis*-α-glycosides were predominantly obtained in high yields due to the anomeric effect.

In 1984, Noyori and co-workers announced that the silyl compounds, both $SiF_4$ and trimethylsilyl trifluoromethanesulfonate (TMSOTf), were very effective for catalytic glycosidation reactions of glucopyranosyl fluorides and trimethylsilylated alcohols (Scheme 4) [7]. In this study, it was found that the stereoselectivity of the glycosidation was highly dependent on the reaction solvent. Thus, glycosidation in MeCN exclusively gave the β-glycoside, while glycosidation performed in $Et_2O$ predominately afforded the α-glycoside in high yield. Furthermore, this general trend was not affected by the stereochemistry of the starting glycosyl fluoride.

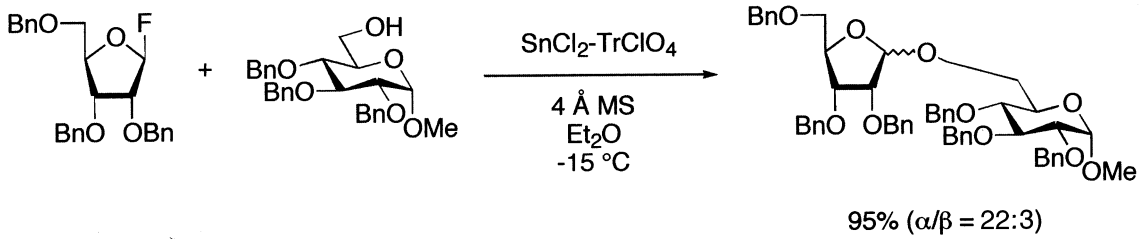
Nicolaou, Kunz and Vozny independently reported that glycosyl fluorides effectively coupled with a variety of free alcohols and silyl ethers using another Lewis acid, $BF_3{\cdot}Et_2O$, in $CH_2Cl_2$ to give the corresponding *O*-glycosides in moderate to good yields (Scheme 5) [8–11].

On the other hand, metal fluorides such as $TiF_4$ and $SnF_4$ were also used as effective promoters of glycosyl fluorides by Thiem and co-workers. The stereoselective glycosidation

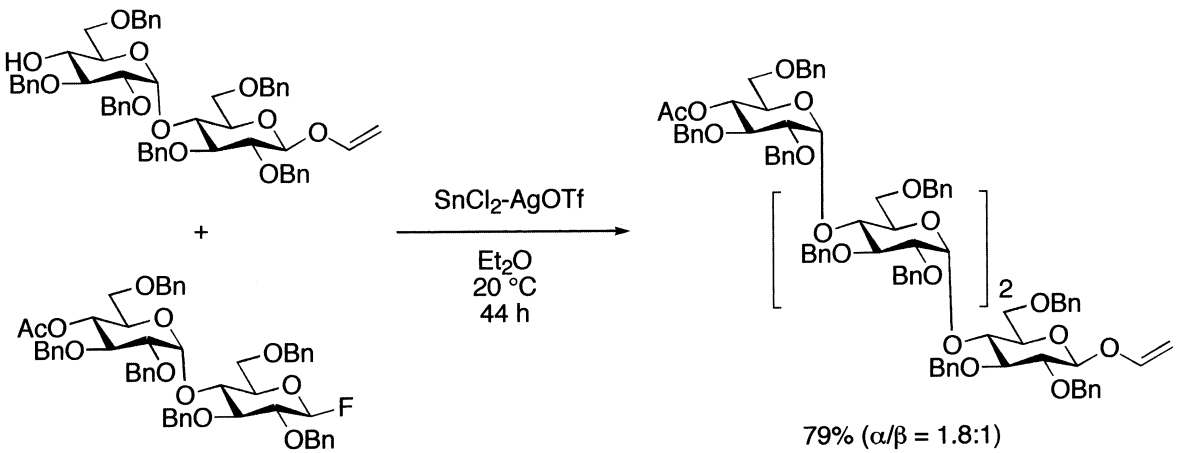
Table 1
O-Glycosidations of glycosyl fluorides



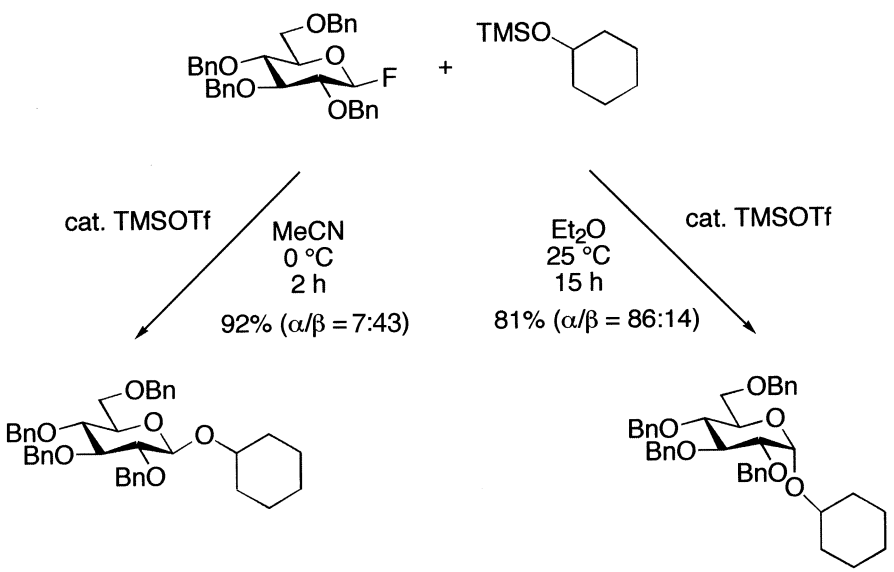

| Activator | X | Refs. |
|---|---|---|
| $SnCl_2$–$AgClO_4$ | H | [4] |
| $SnCl_2$–$TrClO_4$ | H | [5] |
| $SnCl_2$–AgOTf | H | [6] |
| TMSOTf (cat.) | TMS | [7] |
| $SiF_4$ (cat.) | TMS | [7] |
| $BF_3{\cdot}Et_2O$ | H | [8–11] |
| $TiF_4$ | H | [12] |
| $SnF_4$ | H | [12] |
| $Cp_2MCl_2$–$AgClO_4$ (M = Zr or Hf) | H | [13] |
| $Cp_2ZrCl_2$–$AgBF_4$ | H | [14] |
| $Cp_2HfCl_2$–AgOTf | H | [14,15] |
| $Bu_2Sn(ClO_4)_2$ | H | [16] |
| $Me_2GaCl$ | H | [17] |
| $Tf_2O$ | H | [18] |
| $LiClO_4$ | H | [19] |
| $Yb(OTf)_3$ | H | [20] |
| $La(ClO_4)_3{\cdot}nH_2O$ (cat.) | TMS | [21] |
| $La(ClO_4)_3{\cdot}nH_2O$–$Sn(OTf)_2$ | H | [22] |
| Yb–Amberlyst 15 | H | [24] |
| $SO_4/ZrO_2$ | H | [25] |
| Nafion-H | H | [25] |
| Montmorillonite K-10 | H | [25] |
| $TrB(C_6F_5)_4$ (cat.) | H | [26] |




Scheme 2.



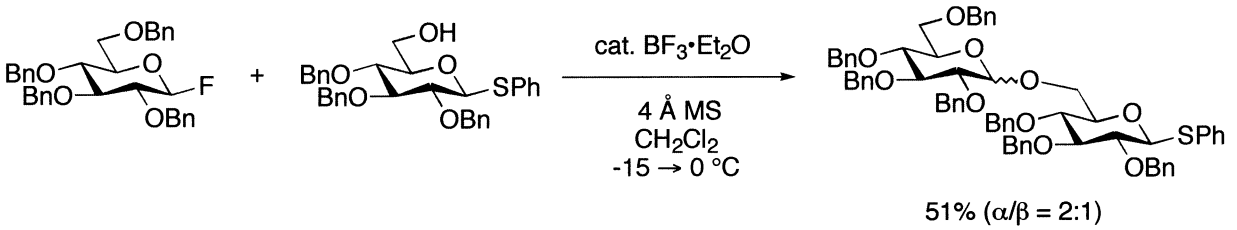

Scheme 3.



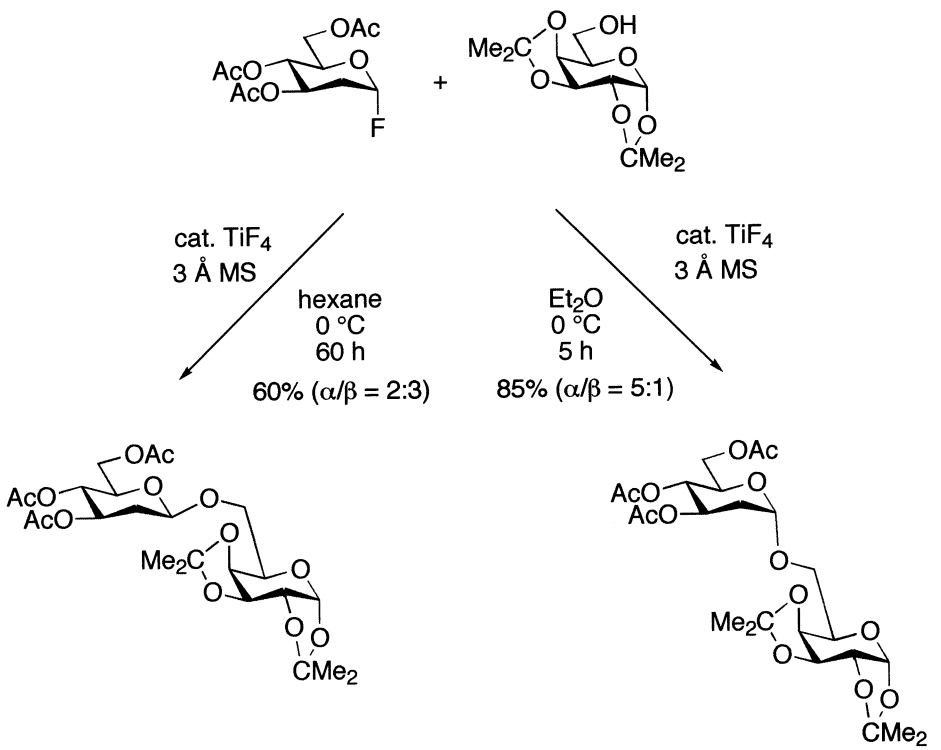

Scheme 4.

of 2-deoxyglycosyl fluoride was carried out using $TiF_4$. In the case of 2-deoxy-α-glycosyl fluoride, when hexane was used as the solvent, the β-glycoside was selectively produced with inversion of the anomeric center via an $S_N2$ mechanism. On the other hand, when the reaction was performed in $Et_2O$, the α-glycoside was obtained as the major product via a 'double $S_N2$' mechanism, which involved the formation of the oxionium cation–ether complex (Scheme 6) [12].

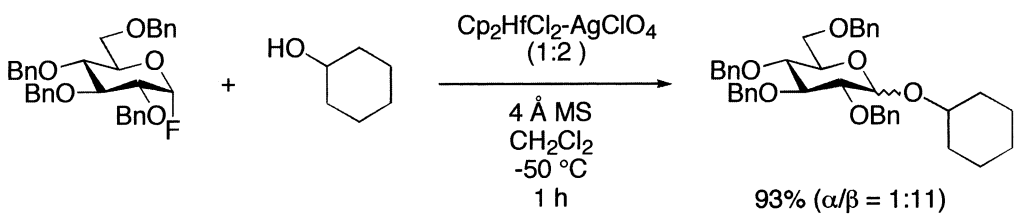
Suzuki and co-workers developed new and quite effective glycosidation protocols in which the combined activators including the



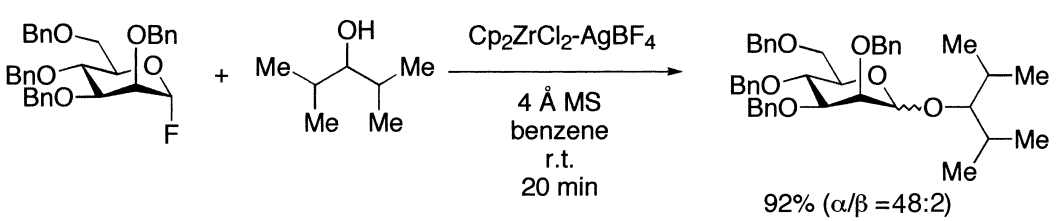

Scheme 5.



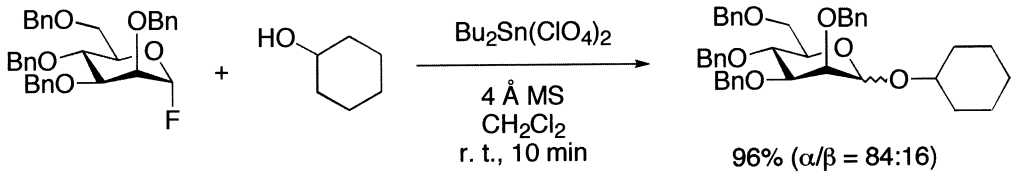

Scheme 6.



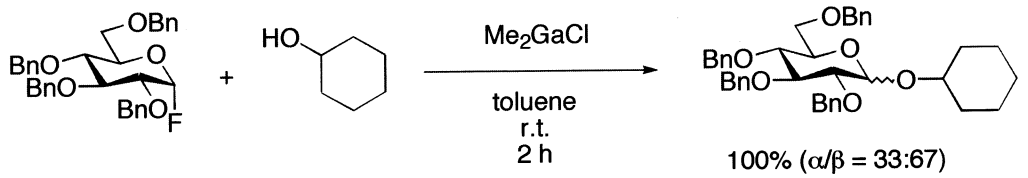

Scheme 7.



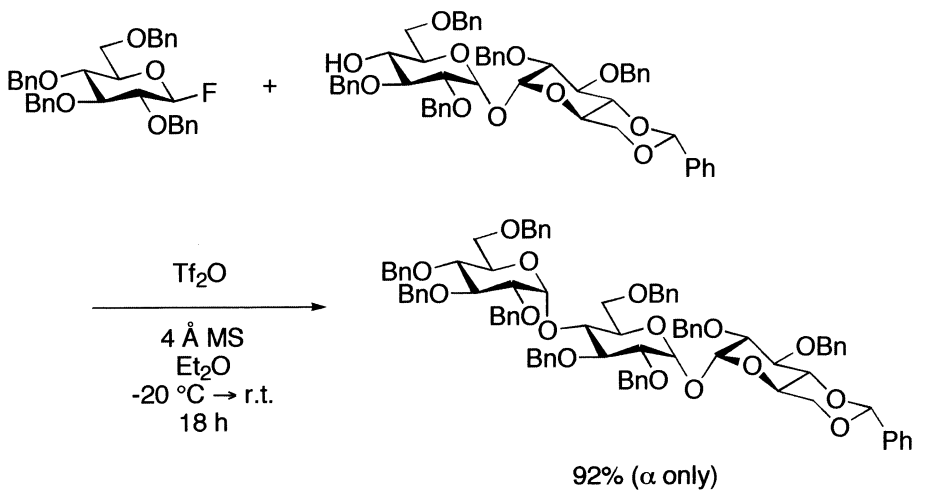

Scheme 8.




Scheme 9.




Scheme 10.




Scheme 11.

group $IV_B$ metallocenes such as $Cp_2MCl_2AgClO_4$ (M = Zr, Hf) (Scheme 7) [13], $Cp_2ZrCl_2$–$AgBF_4$ (Scheme 8) [14] and $Cp_2HfCl_2$–AgOTf [14,15] were used as milder reagents for promoting the glycosidations of glycosyl fluorides. It is interesting to note that the combinations of $Cp_2ZrCl_2$–$AgClO_4$ in benzene and $Cp_2HfCl_2$–$2AgClO_4$ in $CH_2Cl_2$ were very effective for the highly β-stereoselective glycosidations of D-mycinose and D-glucose derivatives, respectively. On the other hand, the combined use of $Cp_2ZrCl_2$–$AgBF_4$ was found to be useful for the stereoselective α-mannopyranoside synthesis from totally benzylated α-mannopyranosyl fluoride. Furthermore, Suzuki also reported the novel combined use of $Bu_2SnCl_2$–$AgClO_4$ as an effective promoter for the glycosidation of totally benzylated α-mannopyranosyl fluoride and several alcohols (Scheme 9) [16].

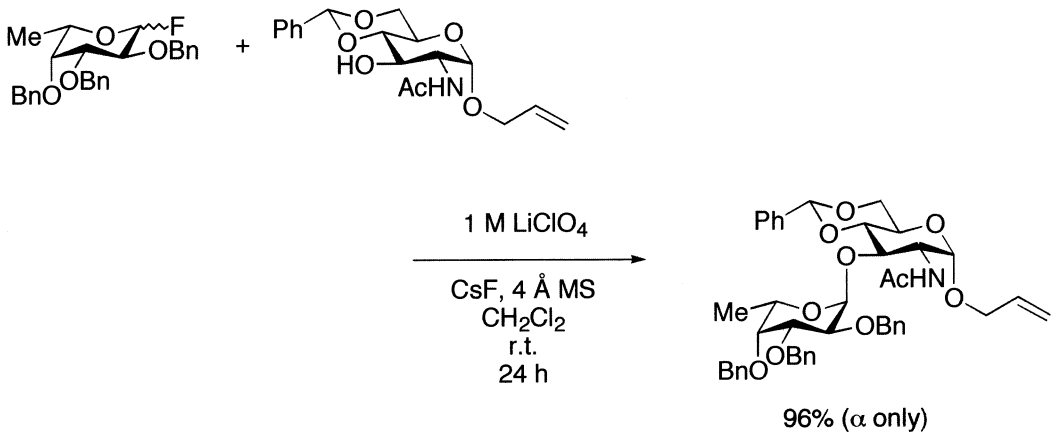
On the other hand, $Me_2GaCl$ and $Me_2GaOTf$ were introduced as new promoters of glycosyl fluorides by Kobayashi due to their strong affinity to fluoride. In this study, it was found that the readily available $Me_2GaCl$ was more effective for the glycosidation reactions of glycosyl fluorides, and *O*-glycosides were obtained in high yields with moderate stereoselectivities (Scheme 10) [17].

Wessel and co-workers announced that $Tf_2O$ was shown to be a highly reactive activator for the glycosidation of glycosyl fluorides (Scheme 11) [18]. In this report, it was interestingly suggested that the sequence of relative reactivity for catalysts examined for the glycosyl fluorides was TMSOTf < $SnCl_2$–AgOTf < $TiF_4$ < $Tf_2O$.

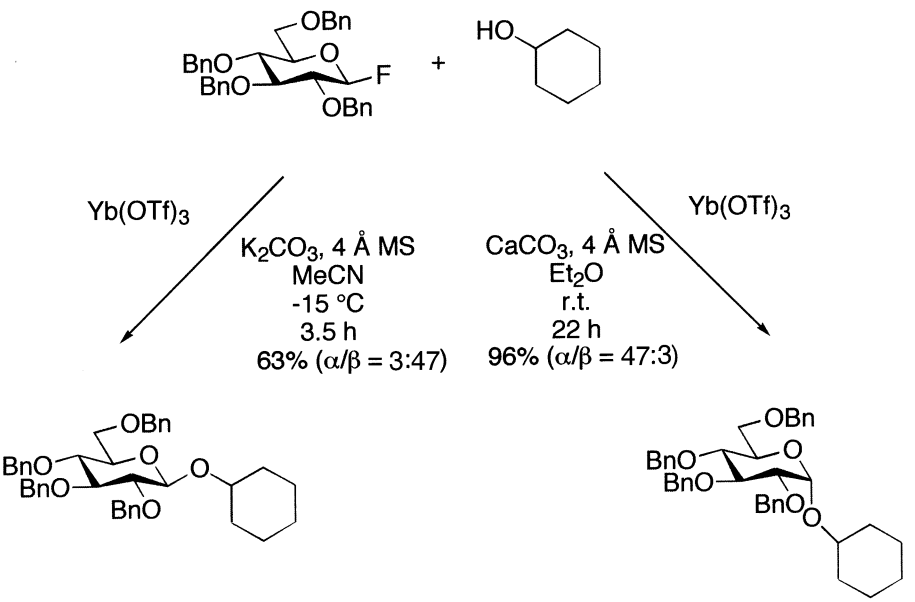
On the other hand, Waldmann and Böhm reported the use of 1 M solutions of $LiClO_4$ in $CH_2Cl_2$, which is a milder Lewis acid, for the glycosidation of fucosyl fluoride under neutral conditions (Scheme 12) [19]. In this glycosidation protocol, CsF was employed as an effective acid scavenger. Although $LiClO_4$ could be used for the activation of other glycosyl donors such as a glycosyl trichloroimidate, glycosyl fluorides were found to be most effectively activated.

Recently, Shibasaki and co-workers developed the rare earth metal salts, such as $La(ClO_4)_3 \cdot nH_2O$ and $Yb(OTf)_3$, for the glycosidations with glycosyl fluorides [20–23]. The use of either $Yb(OTf)_3$ or $YbCl_3$ in the presence of $CaCO_3$ and 4 Å molecular sieves in $Et_2O$ was found to be effective for α-selective glycosidation of the glucosyl fluoride. On the other hand, for β-selective glycosidation, the utilization of $Yb(OTf)_3$ in MeCN containing $K_2CO_3$ and 4 Å molecular sieves gave a good result (Scheme 13) [20]. Furthermore, it was found that glycosidations of glycosyl fluorides with trimethylsilylated alcohols were promoted more effectively using a catalytic amount of $La(ClO_4)_3 \cdot nH_2O$ [21], and the combined use of $La(ClO_4)_3 \cdot nH_2O$ and $Sn(OTf)_2$ was very useful for β-stereoselective mannosylation, which was one of the most difficult stereoselective glycosidations (Scheme 14) [22].

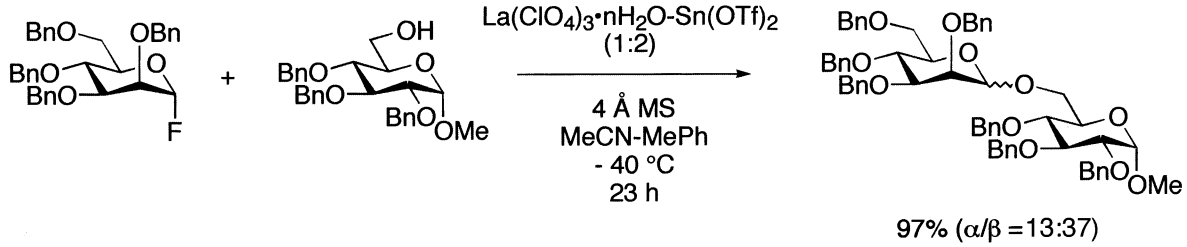
Along this line, Wang and co-workers reported the glycosidation of glucosyl fluoride in methanol promoted by the lanthanide(III) cat-



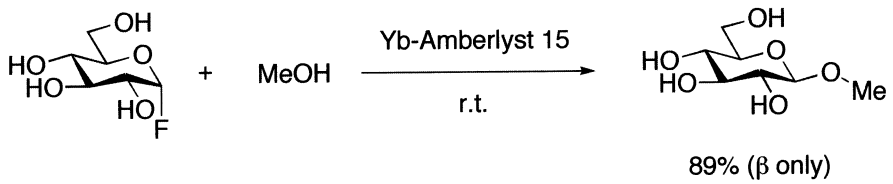

Scheme 12.



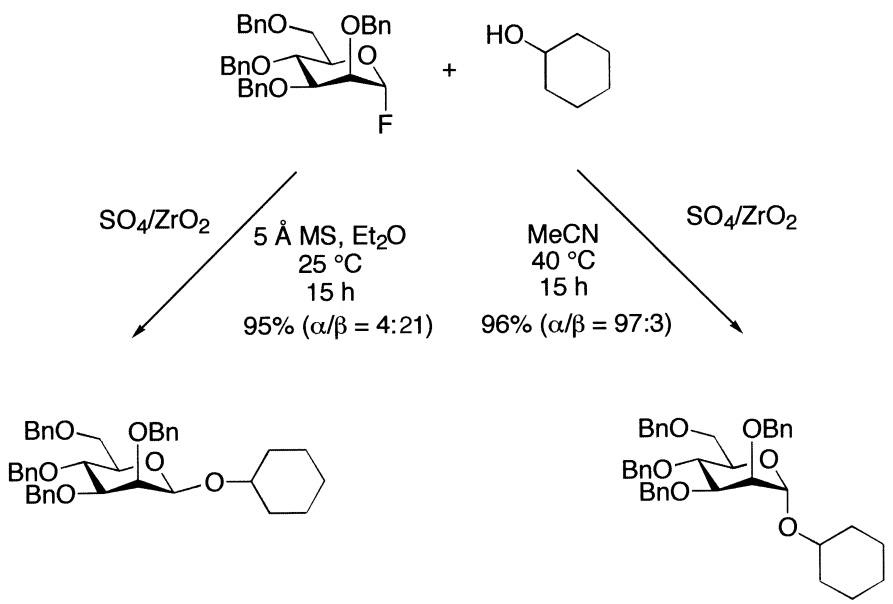

Scheme 13.




Scheme 14.




Scheme 15.




Scheme 16.

alyst supported on an ion-exchange resin, Yb–Amberlyst 15 (Scheme 15) [24]. Interestingly, it was found that methyl glucosides were stereospecifically produced with complete inversion of the anomeric center of the glucosyl fluoride.

Very recently, Toshima and co-workers demonstrated that environmentally friendly heterogeneous catalysts such as montmorillnite K-10, Nafion-H® and $SO_4/ZrO_2$ were very effective for practical glycosidations of glycosyl fluorides (Scheme 16) [25]. Among them, $SO_4/ZrO_2$ was shown to be superior for the stereocontrolled glycosidation with α-mannopyranosyl fluoride. Thus, the glycosidations of perbenzylated α-mannopyranosyl fluoride and alcohols using $SO_4/ZrO_2$ in MeCN at 40 °C gave exclusively the corresponding α-glycosides in high yields. On the other hand, the corresponding β-glycosides were obtained selectively by the glycosidations employing $SO_4/ZrO_2$ in the presence of 5 Å molecular sieves in $Et_2O$ at 25 °C.

Furthermore, Mukaiyama and Takeuchi quite recently reported the stereoselective β-glycosidation of glucopyranosyl fluoride and free alcohols using a catalytic amount of $TrB(C_6F_5)_4$ in $^t$BuCN–benzotrifluoride (BTF) (Scheme 17) [26]. This is the first example of activation of the anomeric C–F bond using a trityl cation.

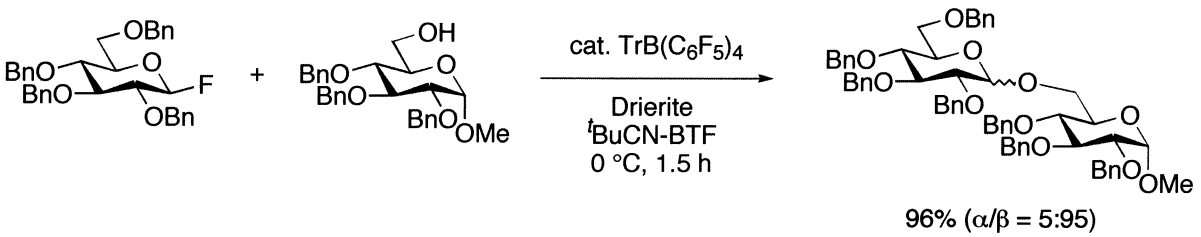
## 3. Glycosyl fluorides in C-glycosylations

An efficient chemical C-glycosylation with high regio- and stereoselectivity is of particular interest as well as O-glycosidations. Several types of *C*-glycosyl compounds such as alkyl, allyl and aryl *C*-glycosyl derivatives are now well recognized to be useful chiral building blocks for the syntheses of optically active biomolecules and functional materials. Furthermore, C-linked glycosyl compounds, stable analogs of naturally occurring *O*-glycosides and glycosylamines, have become the subject of considerable interest in medicinal chemistry. After Nicolaou and co-workers first announced the use of glycosyl fluorides in C-glycosylations in 1984 [27], several types of C-glycosylations using glycosyl fluorides have been reported.

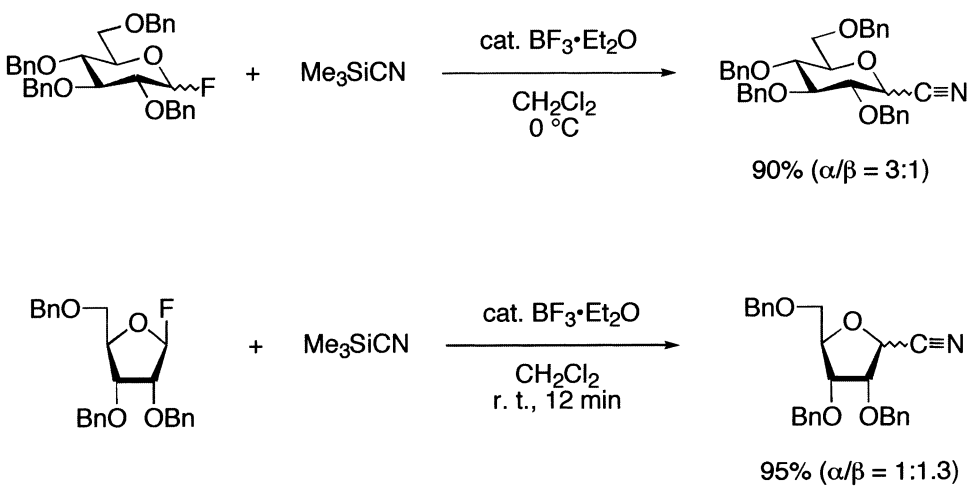
The reaction of glycosyl fluoride and trimethylsilyl cyanide with a Lewis acid was developed by two groups. Nicolaou and co-workers first reported that the C-glycosylation of totally benzylated glucopyranosyl fluoride and trimethylsilyl cyanide using $BF_3{\cdot}Et_2O$ as a Lewis acid gave the corresponding cyanoglycoside in high yield (Scheme 18) [27]. Along this line, Ishido and co-workers confirmed that the anomeric selectivity was dependent on the amount of Lewis acid, and increasing the amount of $BF_3{\cdot}Et_2O$ resulted in the highly stereoselective formation of the α anomer [28]. Ishido also reported the C-glycosylation of the totally benzylated ribofuranosyl fluoride with trimethylsilyl cyanide using a catalytic amount of $BF_3{\cdot}Et_2O$ (Scheme 18) [28].

The reaction of glycosyl fluoride and allylsilane with a Lewis acid was also announced from the same groups. Thus, the C-glycosylations of glycosyl fluoride and allyltrimethylsilane with a Lewis acid, $BF_3{\cdot}Et_2O$, was reported by Nicolaou (Scheme 19) [27] and a similar result was demonstrated by Ishido (Scheme 19) [28,29]. In most cases, the allyl *C*-glycosyl compounds was obtained with high α-stereoselectivity.

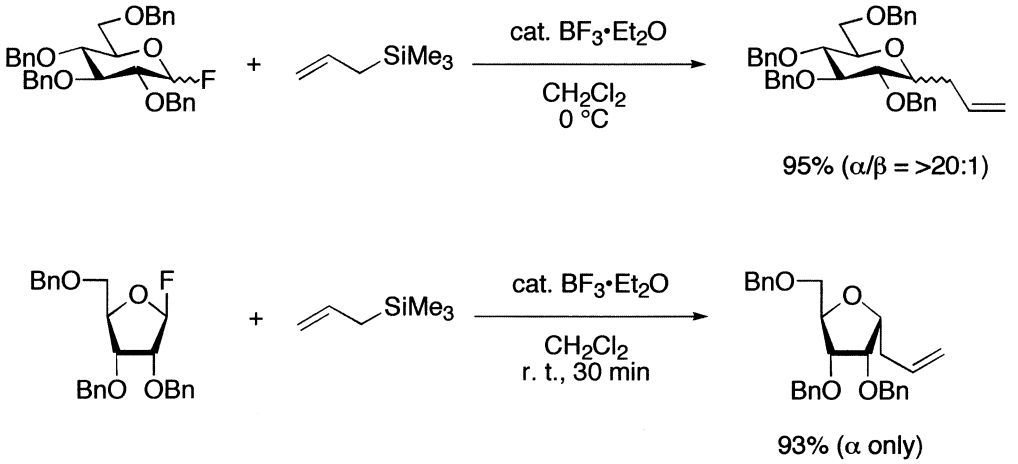
Nicolaou [27] and Ishido [30] also independently reported effective C-glycosylations of glycosyl fluorides and several types of silyl enol ethers. In these reactions, $BF_3{\cdot}Et_2O$ was



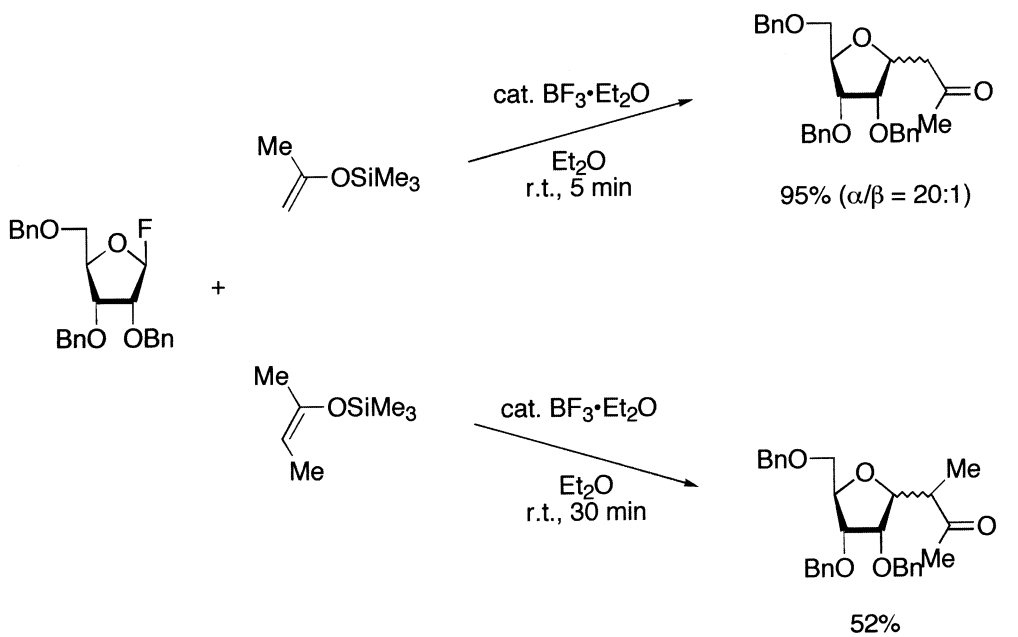

Scheme 17.



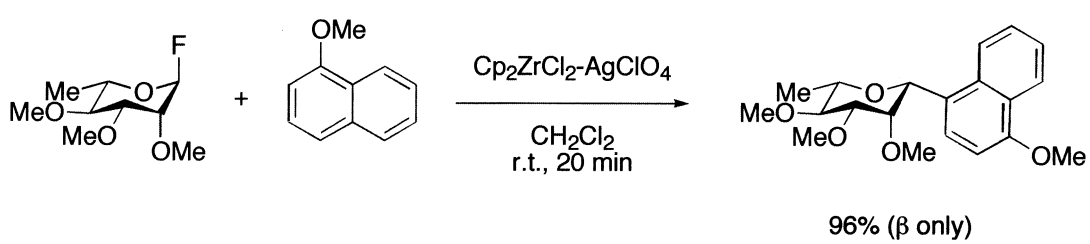

Scheme 18.




Scheme 19.




Scheme 20.




Scheme 21.

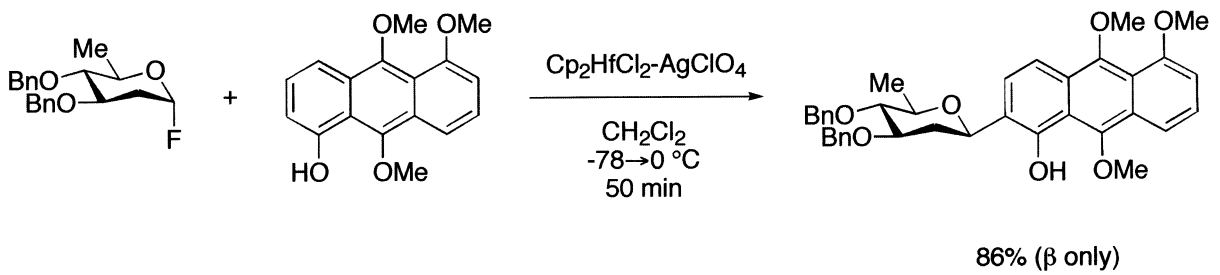
also found to be an effective catalyst. Ishido and co-workers clearly indicated that the α-glycoside was obtained exclusively with high stereoselectivity and the chemical yield and the stereoselectivity was highly independent of the amount of catalyst (Scheme 20) [30].

Furthermore, two different types of aryl C-glycosylations with glycosyl fluorides and electron-rich aromatic compounds using $Cp_2ZrCl_2$–$AgClO_4$ were reported by Suzuki and Matsumoto. One is the Friedel–Crafts type reaction (Scheme 21) [31], and another is

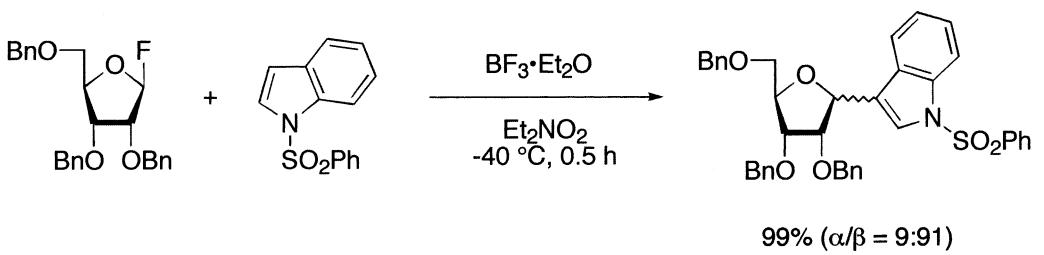
the C-glycosylation of naphthol derivatives via the O–C migration pathway (Scheme 22) [32]. In both cases, the thermodynamically stable aryl β-glycosides were generally obtained in high yields and excellent stereoselectivity.

Alternatively, the reaction of ribofuranosyl fluoride with some indoles using $BF_3{\cdot}Et_2O$ was reported by Yokoyama and co-workers (Scheme 23) [33]. The stereoselectivity was dependent on the reaction temperatures and solvents; the β-glycoside was selectively obtained under such conditions as −15 to −40 °C in $EtNO_2$, while the α-glycoside was preferred at −78 °C in EtCN.

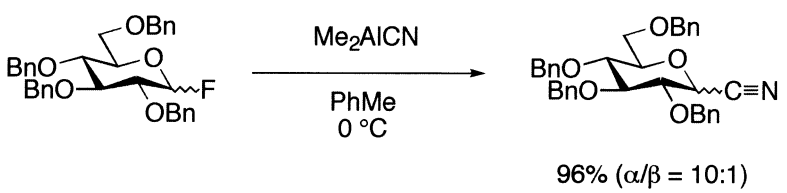
On the other hand, the reactions of glycosyl fluoride and organoaluminum reagents were developed. For example, cyanations of glycosyl fluorides using aluminated cyanides such as $Me_2AlCN$ (Scheme 24) [27] and $Et_2AlCN$ [34] were reported. In the case of the C-glycosylation of an α-mannopyranosyl fluoride with $Et_2AlCN$, a mixture of isocyanoglycoside and cyanoglycoside was produced in a 7:3 ratio [34]. Posner and Haines reported that several furanosyl and pyranosyl fluorides were smoothly reacted with alkyl, alkenyl, and alkynyl organoaluminum reagents under mild conditions to afford the corresponding *C*-gly-



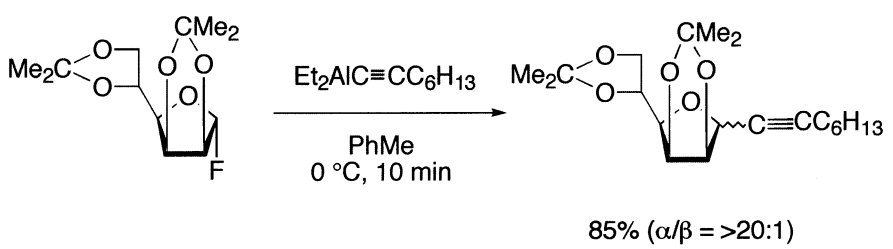

Scheme 22.



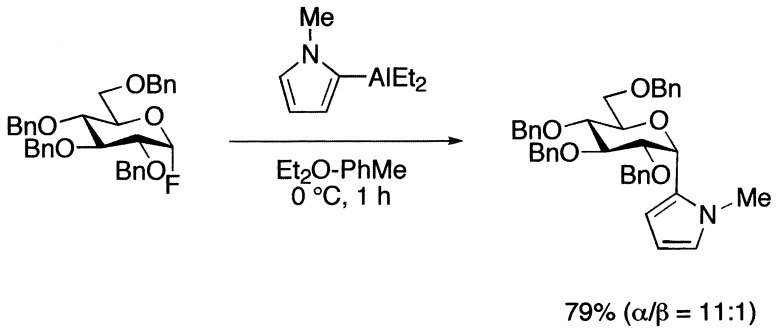

Scheme 23.



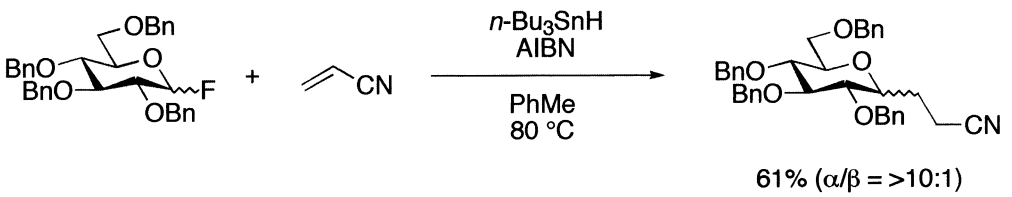

Scheme 24.



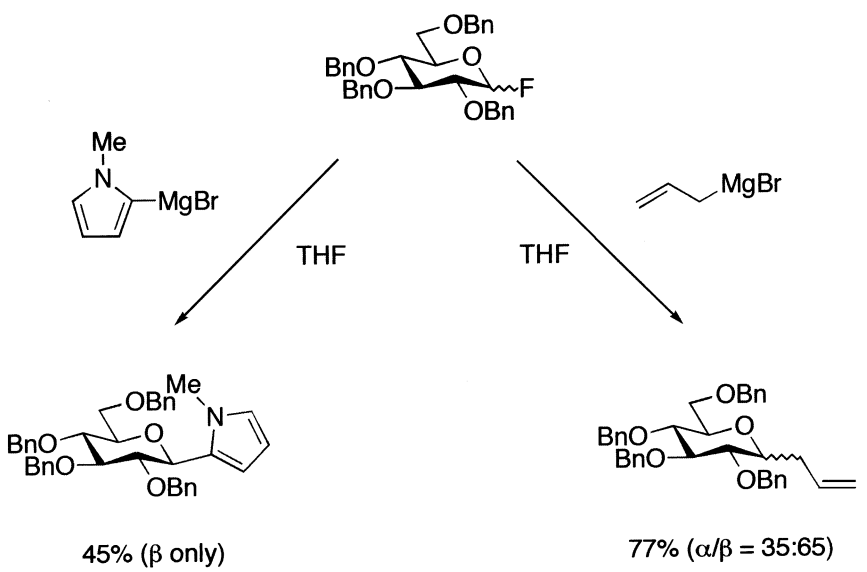

Scheme 25.




Scheme 26.




Scheme 27.




Scheme 28.

cosyl compounds in high to excellent yields (Scheme 25) [35]. Furthermore, the C-glycosylations of glycosyl fluorides and aluminated heterocycles were also demonstrated by McKenzie and co-workers. It was interesting to note that when glycopyranosyl fluorides were used as the glycosyl donors, the C-glycosylations proceeded with retention of configuration at the anomeric center. On the other hand, reactions of the same aluminated heterocycles with ribofuranosyl fluorides selectively afforded the β-ribofuranosyl heterocycles (Scheme 26) [36].

Glycosyl fluorides were also found to be excellent substrates for the radical mediated C-glycosylations. Thus, Nicolaou and coworkers reported that the C-glycosylation of totally benzylated glucopyranosyl fluoride and acrylonitrile using $Bu_3SnH$ and AIBN smoothly proceeded to afford the correspond ing *C*-glycosyl derivatives in moderate yield with high α-selectivity (Scheme 27) [27].

Very recently, Yokoyama and co-workers demonstrated C-glycosylations of glycosyl fluorides with several Grignard reagents without any activators. Thus, the glycosylations of aryl magnesium bromides with a totally benzylated furanosyl fluoride gave the corresponding aryl β-*C*-glycosyl derivatives in moderate yields. Furthermore, the totally benzylated glucopyranosyl fluoride was found to react with *N*-methylpyrrol-2-yl magnesium bromide and allyl magnesium bromide to afford the corresponding *C*-glycosyl derivatives in moderate to high yields (Scheme 28) [37].

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