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Environmentally friendly organic synthesis using bismuth(III) and iron(III) compounds as catalysts

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This review is dedicated to Dr. Rajender Varma whose seminal contributions to green chemistry have inspired the principal author (RSM) and his undergraduate students to incorporate green chemistry principles into their synthetic efforts, and into the chemistry curriculum at Illinois Wesleyan University

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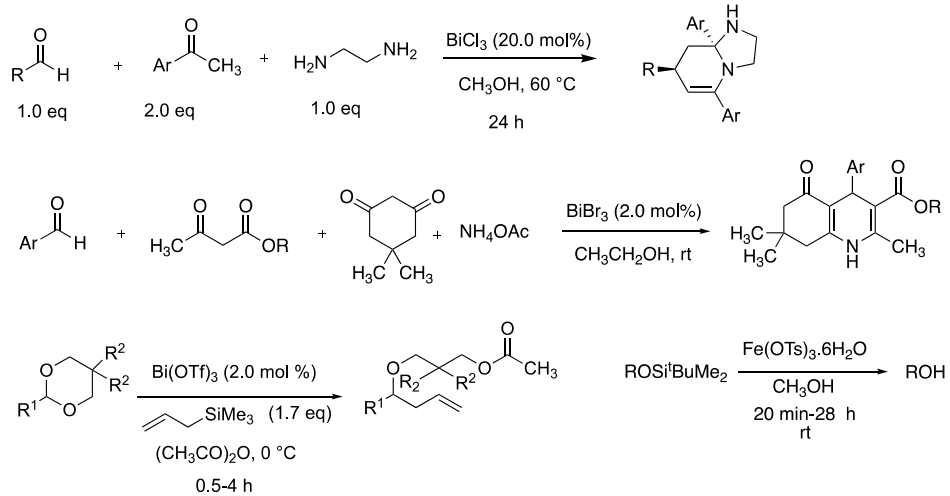
Abstract

Bismuth(III) salts are remarkably nontoxic, inexpensive, and easy to handle. This makes them attractive as Lewis acid catalysts from a green chemistry perspective. This account summarizes modest contributions from undergraduates in the Mohan research group to the applications of bismuth(III) salts as catalysts for a wide variety of reactions. These include synthesis of a variety of heterocycles, protection-deprotection chemistry, and C-C bond formations. A few examples of the first reported use of commercially available iron(III) tosylate as a non-corrosive catalyst are also reported.



Keywords: Bismuth, catalysis, green chemistry, Lewis acids, heterocycles

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1. Introduction

Bismuth, the 83rd element in the periodic table, is one of the least toxic elements despite its heavy metal status.[1] Bismuth(III) compounds are relatively nontoxic with many bismuth salts having LD_{50} values comparable to NaCl.[2] Bismuth-based compounds have increasingly found applications as pharmaceuticals, largely due to their nontoxic nature.[3] Bismuth in the +3 oxidation state exhibits Lewis acid properties. Bismuth also exhibits a +5 oxidation state, however the chemistry of bismuth(V) compounds is not as well explored.[4] It is the nontoxic nature of bismuth(III) salts coupled with their Lewis acidic nature that has prompted us to explore the utility of bismuth(III) salts as Lewis acids for environmentally friendly organic synthesis.

Several bismuth salts are commercially available and these include bismuth(III) acetate, $Bi(CH_3CO_2)_3$ (CAS 22306-37-2), bismuth(III) bromide, $BiBr_3$ (CAS 7787-58-8), bismuth(III) chloride, $BiCl_3$ (CAS 7787-60-2), bismuth(III) iodide, BiI_3 (CAS 7787-64-6), bismuth(III) nitrate pentahydrate, $Bi(NO_3)_3{\cdot}5H_2O$ (CAS 10035-06-0), Bismuth(III) sulfate, Bi2(SO4)3 (7787-68-0), and bismuth(III) triflate, $Bi(CF_3SO_3)_3$ (CAS 88189-03-1). Bismuth(III) triflate can also be synthesized in the laboratory from trifluoromethanesulfonic acid and bismuth(III) oxide in aqueous alcohol solutions.[5] Bismuth triflate is obtained or purchased as a hydrate (xH_2O, $0 < x < 4$). Heating the hydrate to prepare the anhydrous salt results in decomposition.[6] The hydrate is henceforth shown as $Bi(OTf)_3$ in this account. Besides their nontoxic nature, bismuth(III) salts have other advantages too. They are reasonably stable in air and do not require inert atmosphere conditions. Bismuth salts undergo reversible hydrolysis in water to generate triflic acid which can often be the true catalyst in a reaction,[7] unlike lanthanide triflates which do not undergo hydrolysis in water.[8] Ollevier and Nadeau have shown that the three-component Mannich reaction between an aldehyde, aniline and a silyl enol ether is catalyzed by both $Bi(OTf)_3$ and CF_3SO_3H. However, they also report that when the $Bi(OTf)_3$-catalyzed reaction is done in the presence of a proton scavenger such as 2,6-di-*tert*-butylpyridine, the reaction still occurred suggesting a Lewis acidic role for the Bi^{+3} cation.[9] Hinkle and coworkers have done elegant work studying an intramolecular silyl-modified Sakurai reactions leading to dihydropyrans using $Bi(OTf)_3$ to confirm that triflic acid is generated in reactions of $Bi(OTf)_3$.[10] The authors show that CF_3SO_3H is not formed just from adventitious water, and they propose that the the Bi^{+3} cation acts as a Lewis acid. It has been shown in many reactions that $Bi(OTf)_3$ can be recovered from the aqueous layer by evaporation of the water.[11] Since we typically use very small amounts of bismuth triflate as a catalyst in our reactions, we have not attempted to recover the catalyst.

In an extensive study on Friedel-Crafts acylation using metal triflates, Dubac and coworkers showed that $Bi(OTf)_3$ is more active than other metal triflates, and also more active than bismuth(III) halides.[12] Our general strategy has been to use bismuth(III) halides, especially $BiBr_3$ as we found $BiCl_3$ to be a bit more hygroscopic while BiI_3 was less active in most reactions. Only when these catalysts failed or when a nucleophilic anion was not desirable, such as in epoxide ring opening reactions, we attempted reactions with $Bi(OTf)_3$.

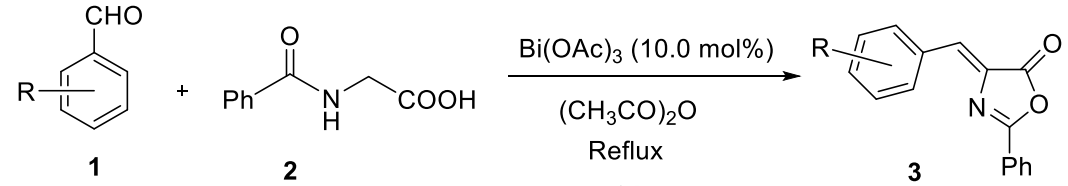
While attempting to prepare bismuth(III) tosylate, we discovered that iron(III) tosylate, $Fe(OTs)_3{\cdot}6H_2O$ (CAS 312619-41-3) is commercially available but surprisingly, there were no reports of its use as a catalyst for organic transformations. We have reported a few examples of the utility of iron(III) tosylate which are summarized herein.

While a few reviews have appeared on the utility of bismuth(III) salts in organic synthesis,[13,14,15,16] this account summarizes results from only our laboratory since 1998.

2. Results and Discussion

2.1. Synthesis of heterocylces using Bismuth(III) compounds

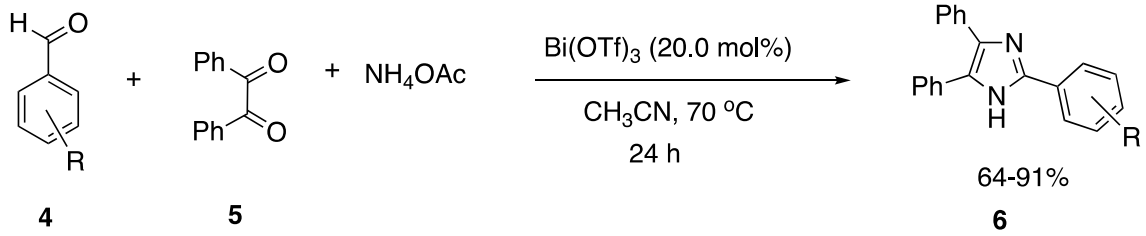
2.1.1. Bismuth(III) acetate catalyzed synthesis of azlactones. Azlactones or 2-oxazolin-5-ones are useful heterocyclic compounds, especially for the synthesis of α-amino acids.[17] The original synthesis of azlactones involved the condensation of an aldehyde with benzoyl glycine in the presence of a stoichiometric amount of fused anhydrous sodium acetate and acetic anhydride. The azlactone can then be converted to amino acids with an aromatic side chain by treatement with red phosphorous and HI.[18] We have reported a bismuth(III) acetate, $Bi(OAc)_3$ catalyzed synthesis of azlactones under mild conditions (Scheme 1).[19] The product is obtained in good purity without recrystallization of chromatographic purification, thus avoiding additional organic waste.



R = H, *m*-NO_2, *o*-NO_2, *p*-Cl, *m*-Cl
p-CH_3, *p*-CH_3O, *m*-CH_3O,
m-CH_3, 3,4-$(CH_3O)_2$

Scheme 1. Bismuth(III) acetate catalyzed synthesis of azlactones.

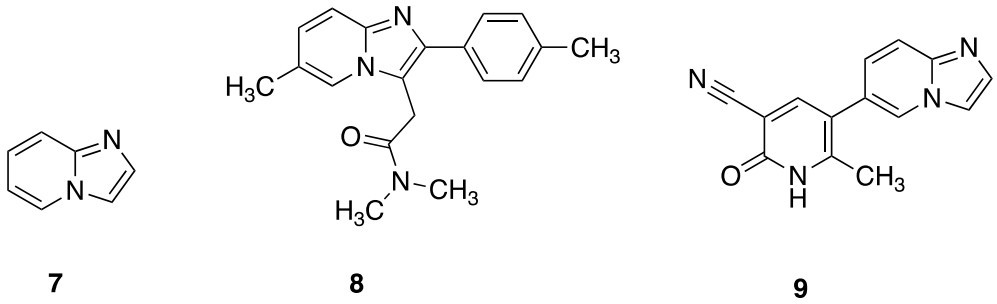
2.1.2. Bismuth(III) triflate catalyzed synthesis of 2,4,5-trisubstituted imidazoles. 2,4,5-trisubstituted imidazoles **6** have attracted attention due to the range of biological activities they exhibit. 2-substituted-4,5-diphenylimidazoles have been shown to exhibit antinociceptive and anti-inflammatory properties.[20] As a result several methods have been developed for the synthesis of 2,4,5-trisubstituted imidazoles, the oldest being a multicomponent reaction between an aldehyde **4**, benzil **5**, and ammonium acetate.[21] We have reported the multicomponent synthesis of 2,4,5-trisubstituted imidazoles via this route using bismuth(III) triflate, $Bi(OTf)_3$ as a catalyst (Scheme 2).[22] Other catalysts such as $BiO(NO_3)$, $BiBr_3$, $Bi(OTf)_3$, $FeCl_3$, and $Fe(OTf)_3$ in several solvents such as CH_3OH, CH_3CH_2OH, CH_3COOH and CH_3CN were tried, but the best results were obtained with $Bi(OTf)_3$ in CH_3CN.



R = H, *p*-OH, *p*-OCH_3, *p*-CH_3
p-Br, *p*-Cl, *p*-F, *m*-Cl, *m*-OCH_3,
m-CH_3, *m*-NO_2

Scheme 2. Bismuth(III) triflate catalyzed synthesis of 2,4,5-trisubstituted imidazoles.

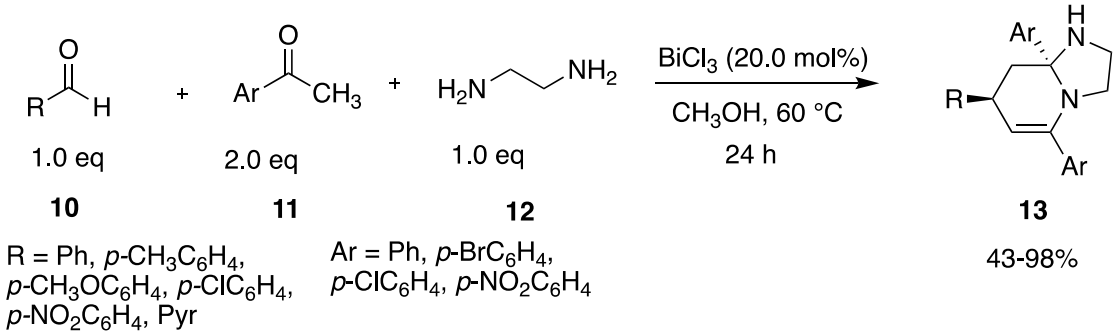
2.1.3. Bismuth(III) chloride catalyzed multicomponent synthesis of substituted hexahydroimidazo[1,2-a]pyridines. Bridgehead nitrogen heterocycles, such as imidazo[1,2-*a*]pyridines **7**, are of considerable interest due to their biological activities. The imidazo[1,2-*a*]pyridine moiety is seen in drugs such as zolpidem **8** (sedative)[23] and olprinone **9** (cardiotonic agent) (Figure 1).[24]



7 **8** **9**

Figure 1

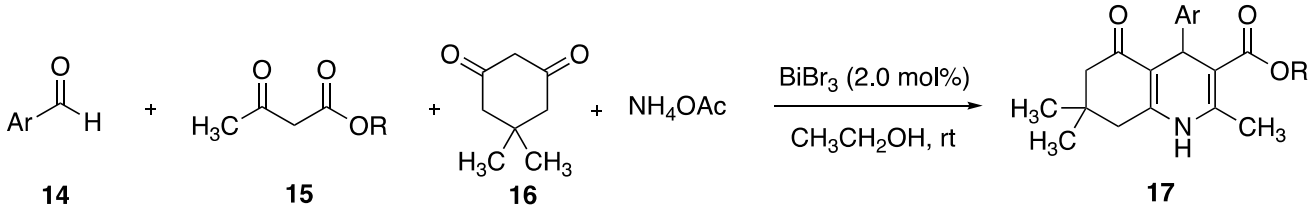
The first efficient synthesis of hexahydroimidazo[1,2-*a*]pyridines **13** utilized a *p*-toluenesulfonic acid (*p*-TsOH) as catalyst for a multicomponent reaction between an aldehyde **10**, a ketone **11**, and 1,2-diaminoethane **12**.[25] Although a commonly used catalyst, *p*-toluenesulfonic acid (*p*-TsOH·H_2O) is somewhat toxic (LD_{50} = 2.48 g/kg, rat oral) and highly irritating to the skin.[26] Li and co-workers report a similar synthesis using L-phenylalanine triflate as a catalyst, a compound that is not commercially available.[27] Other protocols that have been reported include a heteropolyacid containing ionic liquid-catalyzed multicomponent synthesis of hexahydroimidazo[1,2-*a*]pyridine derivatives.[28] The heteropolyacid-ionic liquid catalyst must be synthesized, which limits its utility. We have reported a bismuth(III) chloride, $BiCl_3$-catalyzed synthesis of a series of hexahydroimidazo[1,2-*a*]pyridines using a multicomponent reaction between an aldehyde, a ketone, and 1,2-diaminoethane in CH_3OH (Scheme 3).[29] Although other catalysts such as $BiBr_3$ and $Bi(OTf)_3$ were also effective in a variety of solvents (CH_3OH, CH_3CH_2OH, ^iPrOH, CH_2Cl_2 and CH_3CN) at reflux temperatures, the best results were obtained with $BiCl_3$ in CH_3OH. No reaction was observed at room temperature.



Scheme 3. Bismuth(III) chloride catalyzed synthesis of hexahydroimidazo[1,2-*a*]pyridines.

2.1.4. Bismuth(III) bromide catalyzed synthesis of polyhydroquinoline derivatives *via* The Hantzsch reaction. Polyhydroquinolines are derivatives of the 1,4-dihydropyridine skeleton. Their synthesis has attracted attention because they exhibit biological activities. Polyhydroquinolines hold promise in the search for therapies for Alzheimer's disease owing to their ability to reduce cellular tau levels.[30] A common route to polyhydroquinolines **17** involves a modified Hantzsch reaction,[31] featuring the coupling of an aldehyde **14** with a β-ketoester (such as ethyl acetoacetate) **15**, a diketone (such as dimedone) **16**, and ammonium acetate

(Scheme 3). Several catalysts such as I_2,[32] metal triflates,[33] ceric ammonium nitrate,[34] Baker's yeast,[35] organocatalysts,[36] zeolites,[37] Ph_3P,[38] and $GaCl_3$[39] have been used for the synthesis of polyhydroquinolines via this approach. We have reported the utility of bismuth bromide, $BiBr_3$ as a catalyst for the multicomponent synthesis of polyhydroquinolines in ethanol as a solvent (Scheme 4).[40]



Ar = *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$(CH_3)_2NC_6H_4$, *p*-ClC_6H_4, *p*-$NO_2C_6H_4$, *m*-$CH_3OC_6H_4$, *m*-$CH_3C_6H_4$, *m*-$NO_2C_6H_4$, 2-naphthyl, *p*-biphenyl, 2-furyl

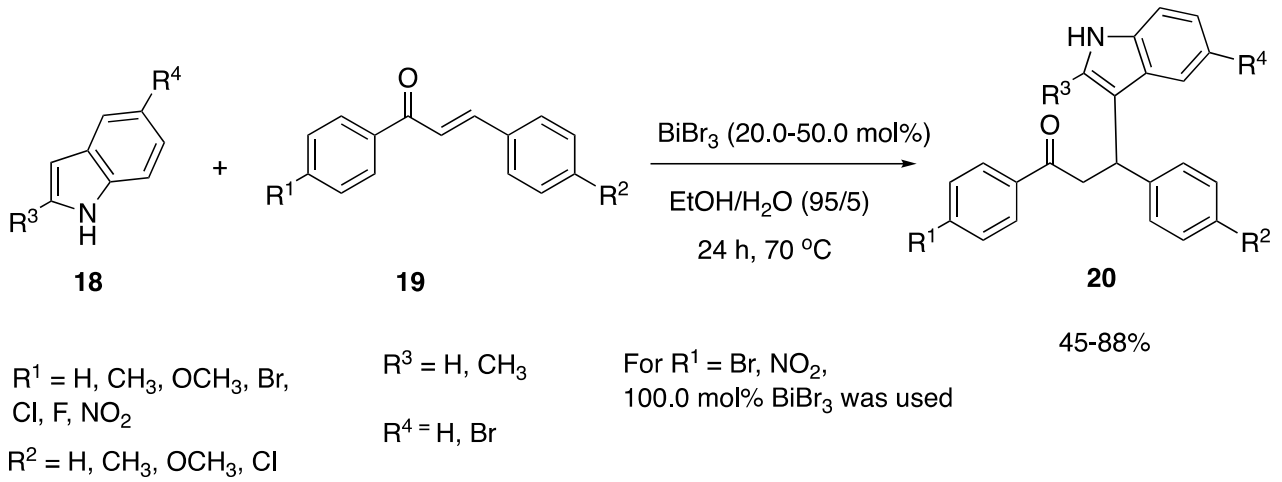
R = Et, Me

Scheme 4. Bismuth(III) bromide catalyzed synthesis of polyhydroquinoline derivatives.

The reactions were fast (1-3 h) and product was isolated by filtration of the reaction mixture, thus generating no aqueous waste stream. The reaction was also efficiently catalyzed by bismuth triflate (2.0 mol%). For example, *p*-tolualdehyde (R = *p*-$CH_3C_6H_4$) yielded 86% product (t = 2 h), but owing to the higher cost of bismuth(III) triflate ($225/25 g from Acros Organics) relative to bismuth(III) bromide ($25/25 g) and its increased moisture sensitivity, we chose bismuth(III) bromide. Ytterbium triflate, $Yb(OTf)_3$ (5.0 mol%) has also been reported as a catalyst for the formation of polyhydroquinolines, but a higher catalyst loading (5.0 mol%) and its high cost detract from its utility ($395/25 g for the anhydrous salt, and $136/25 g for the monohydrate).[33] Although we used anhydrous ethanol as the reaction solvent, one cannot rule out hydrolysis of $BiBr_3$ by adventitious water to generate HBr, which could act as a Brønsted acid catalyst. To get some insight into the role of $BiBr_3$ in the reaction, we carried out the reaction of *p*-chlorobenzaldehyde (Ar = *p*-ClC_6H_4) in the presence of $BiBr_3$ (2.0 mol%) and solid potassium carbonate (10.0 mol%). The pH of this reaction mixture was found to be ~ 6-7, and yet product was obtained in 86% yield, suggesting that $BiBr_3$ is acting as a Lewis acid and not just as a source of HBr. In addition, $BiBr_3$ is a lot easier to handle than HBr. In the absence of $BiBr_3$, significant product formation did not occur.

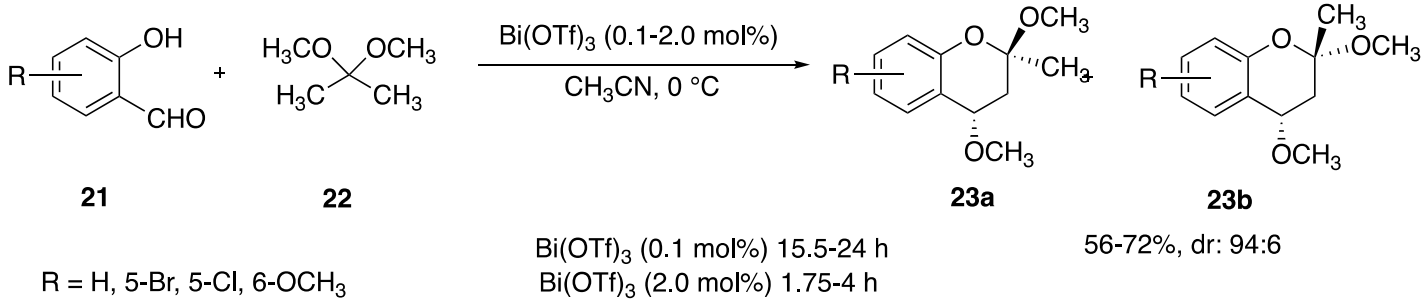
2.1.5. Bismuth(III) bromide catalyzed conjugate addition of indoles to *α,b* -unsaturated ketones. The synthesis of indoles and their derivatives has attracted considerable attention because they exhibit a wide range of biological activities.[41] Indoles undergo electrophilic substitution at the 3-position and hence a variety of methods have been developed for the synthesis of 3-substituted indoles **20**.[42,43] The conjugate addition of indole to chalcone has also been reported with $Bi(OTf)_3$ as a catalyst in CH_3CN.[44] However, in this case products are isolated by column chromatography which results in considerable waste generation. We have reported the conjugate addition of indoles **18** to a variety of chalcones **19** using bismuth bromide, $BiBr_3$, in a relatively green and inexpensive solvent, ethanol (190 proof) (Scheme 5).[45] The product was isolated by evaporation of the solvent, filtration of the residue through a short plug of silica to remove the catalyst, and concentration of the filtrate followed by trituration of the residue with ethanol (190 proof). This method avoids the use of elaborate chromatography for product purification and also eliminates an aqueous waste

stream. We chose ethanol (190 proof) over absolute ethanol or isopropanol as it is easier to remove than ^{i}PrOH, and is considerably cheaper and easier to obtain than absolute ethanol. When the reaction was carried out in the presence of Proton-Sponge®,[46] 1,8-bis(dimethylamino)naphthalene, (0.60 equivalents) or solid K_2CO_3, no product formed, and the starting materials were recovered. These results suggest that the primary role of $BiBr_3$ is to act as a source of HBr. Aqueous HBr is however very corrosive and difficult to handle, unlike $BiBr_3$, which is an air stable and easy to handle solid.



Scheme 5. Bismuth(III) bromide catalyzed addition of indoles to *α,β*-unsaturated ketones.

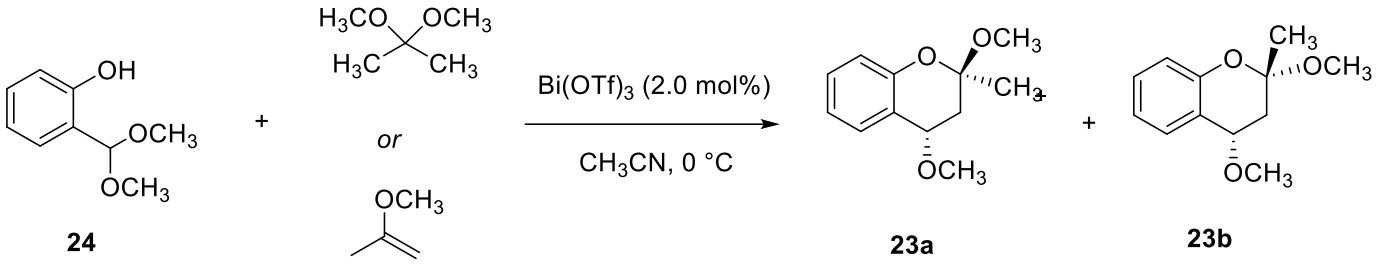
2.1.6. Bismuth(III) triflate catalyzed synthesis of 3,4-dihydro-2*H*-1-benzopyrans. 3.4-dihydro-2*H*-1-benzopyrans are useful scaffolds in organic synthesis[47] and hence their synthesis has attracted attention. Some of the catalysts used for their synthesis include $(Ph_3P)_2PdCl_2$,[48] I_2,[49] and $Sc(OTf)_3$.[50] While each method has its advantages, all these catalysts have drawbacks. Palladium compounds are toxic and expensive, while iodine vapor is very corrosive. Scandium salts are both expensive and hygroscopic. We have reported a bismuth(III) triflate catalyzed synthesis of 3,4-dihydro-2*H*-1-benzopyrans **23a-b** by condensation of substituted salicylaldehydes **21,** and 2,2-dimethoxypropane **22** (Scheme 6) in CH_3CN as the solvent.[51] The product was obtained in a 94:6 diastereomeric ratio. The identity of the major product was established by NOE spectroscopy.



Scheme 6. Bismuth(III) triflate catalyzed synthesis of 3,4-dihydro-2*H*-1-benzopyrans.

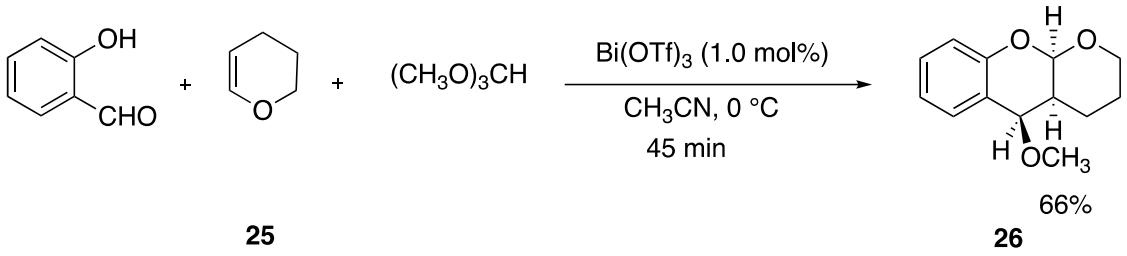
It was speculated that the reaction proceeds via an acetal intermediate **24** derived from salicylaldehyde and 2-methyoxypropene **23** (generated from 2,2-dimethoxypropane). When the dimethyl acetal of

salicylaldehyde was reacted independently with 2,2-dimethoxypropane or 2-methoxypropene, the corresponding 3,4-dihydro-2*H*-1-benzopyrans were obtained in the same diastereomeric ratio (Scheme 7).



Scheme 7. Mechanistic studies on dihydrobenzopyran formation.

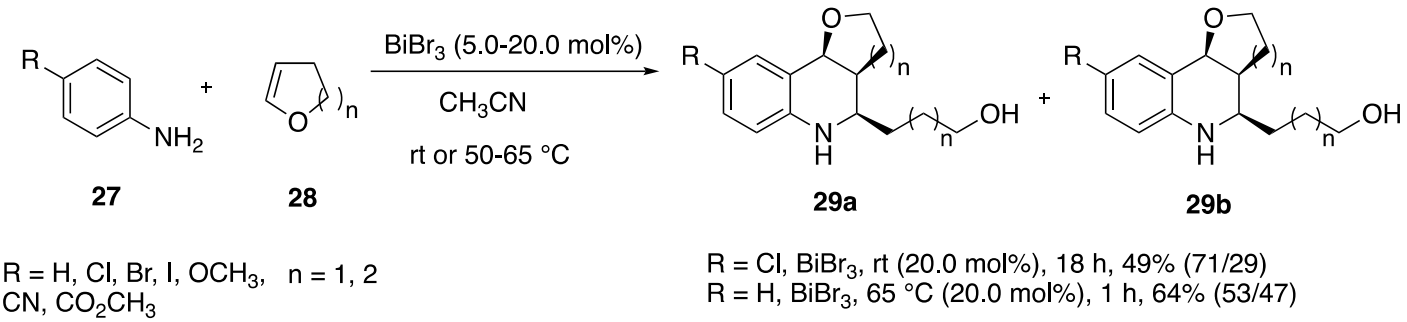
When salicyladehyde was treated with dihydropyran **25** and trimethylorthoformate the corresponding tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromene **26** was formed. The stereochemistry of the product was established by NOE spectroscopy (Scheme 8).



25 **26**

Scheme 8. Bismuth(III) triflate catalyzed synthesis of tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromene.

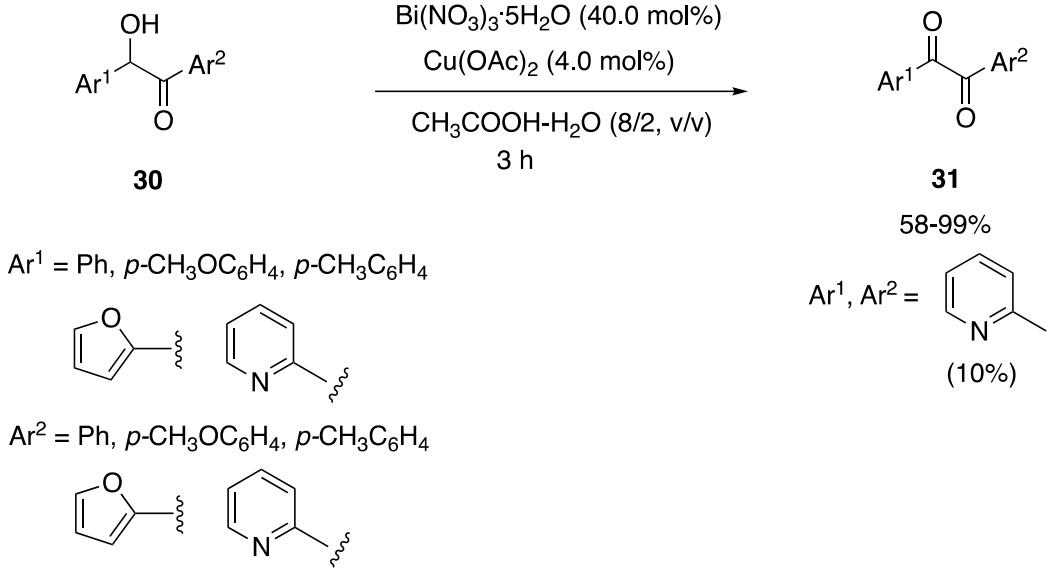
2.1.7. Bismuth(III) bromide catalyzed synthesis of substituted tetrahydroquinoline derivatives. Substituted tetrahydroquinolines have found applications as drugs[52] and pesticides.[53] Hence methods for their synthesis have attracted considerable attention. Among them the Povarov synthesis, which is the cyclocondensation of an amine with two equivalents of an enol ether, is the most common.[54,55] Several catalysts have been reported for the Povarov synthesis such as $AlCl_3$,[56] I_2,[57] $InCl_3$,[58] and $Sc(OTf)_3$.[59] Several of these catalysts have some drawbacks such as being corrosive ($AlCl_3$ and I_2), toxic ($InCl_3$), or expensive (scandium salts). We have reported the bismuth(III) bromide, $BiBr_3$, catalyzed synthesis of substituted tetrahydroquinoline derivatives **29a/29b** by condensation of a series of anilines **27** and enol ethers **28** in CH_3CN as a solvent (Scheme 9).The product was obtained as a diastereomeric mixture of products. The stereochemistry of the products were assigned using NOE spectroscopy.



Scheme 9. Bismuth(III) bromide catalyzed synthesis of substituted tetrahydroquinoline derivatives.

2.2. Bismuth(III) nitrate-copper(II) acetate oxidation of benzoins to benzils

Benzil (1,2-diphenyl-1,2-ethanedione) **30** and its derivatives exhibit photophysical properties.[60] Hence methods for their synthesis has attracted considerable attention.[61] A common route to their synthesis is the oxidation of the corresponding α-hydroxyketones or benzoins. Many of the oxidizing agents used for this reaction are toxic, such as thallium nitrate[62] and ammonium chlorochromate.[63] We have reported the oxidation of benzoins **31** to benzils using bismuth(III) nitrate, $Bi(NO_3)_3·5H_2O$-copper(II) acetate, $Cu(OAc)_2$ in aqueous acetic acid (Scheme 10).[64]

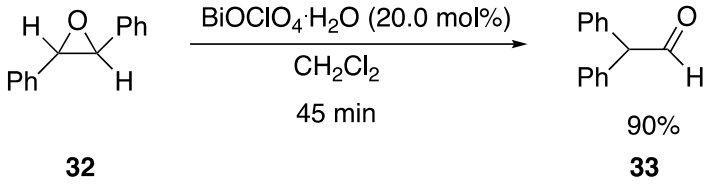


Scheme 10. Bismuth(III) nitrate-copper(II) acetate oxidation of benzoins to benzils.

2.3. Rearrangement of Epoxides

2.3.1. Bismuth(III) oxide perchlorate and bismuth(III) triflate catalyzed rearrangement of epoxides. The rearrangement of epoxides to carbonyl compounds is a useful transformation. Not surprisingly, many reagents have been used to effect these rearrangements.[65, 66] One of the most common reagents used for epoxide rearrangements is boron trifluoride etherate, $BF_3·Et_2O$.[67] Although a powerful Lewis acid, $BF_3·Et_2O$ is very corrosive and difficult to handle. We initially carried out the rearrangement of epoxides using bismuth(III) oxide perchlorate (20.0 mol%) as a catalyst. The reagent is a commercially available solid and smoothly catalyzed the rearrangement of epoxides. For example, the rearrangement of *trans*-stilbene oxide **32** gave diphenylacetaldehyde (migration of Ph) **33** as the only product (Scheme 11).[68] Unfortunately the

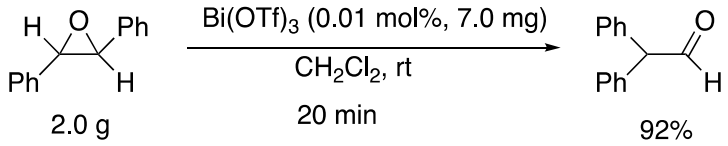
rearrangement worked best in the environmentally undesirable solvent, CH_2Cl_2. No rearrangement was observed in ether, while the reaction was very slow in benzene and THF.



32 **33**

Scheme 11. Bismuth(III) oxide perchlorate catalyzed rearrangement of epoxides.

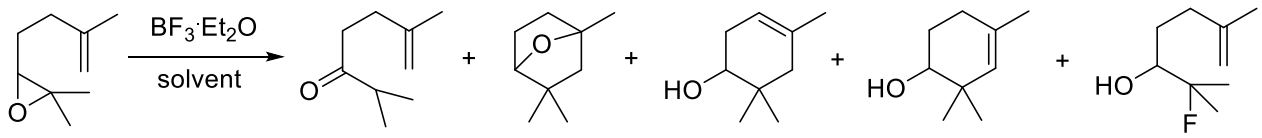
The search for a more efficient catalyst for the rearrangement of epoxides led us to bismuth(III) triflate, $Bi(OTf)_3$.[69] Although CH_2Cl_2 still remained the best solvent for this reaction, the reaction was remarkably catalytic. For example, the rearrangement of *trans*-stilbene oxide required as little as 0.01 mol% catalyst (Scheme 12).



Scheme 12. Bismuth(III) triflate catalyzed rearrangement of epoxides.

Unlike $BF_3{\cdot}Et_2O$, bismuth(III) triflate is easy to handle and stable in air. When the rearrangement of *trans*-stilbene oxide was attempted with 0.1 mol% triflic acid, CF_3SO_3H, the reaction mixture turned red and the resulting diphenylacetaldehyde **32** was found to be quite impure. Such a red color was not seen when $Bi(OTf)_3$ was used as a catalyst. This observation suggests that $Bi(OTf)_3$ is acting as a Lewis acid and not merely a source of triflic acid.

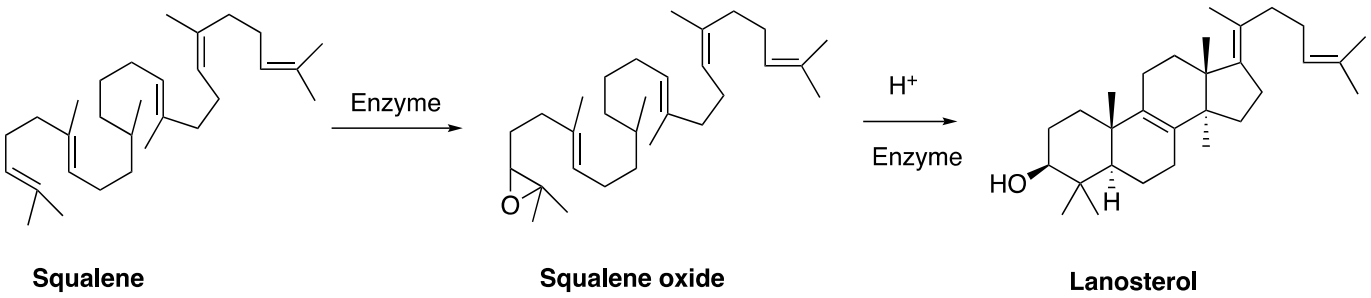
2.3.2. Bismuth(III) triflate catalyzed epoxyolefin cyclizations. The Lewis acid catalyzed cyclization of epoxyolefins has been well studied. In one of the early examples of this reaction, Goldsmith and coworkers reported the cyclization of geraniolene oxide **34** with $BF_3{\cdot}Et_2O$ to give a variety of products (**35-39**).[70]



34 **35** **36** **37** **38** **39**

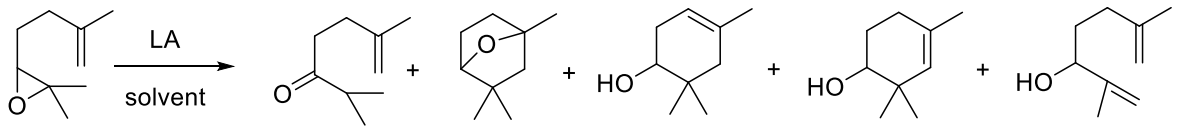
Scheme 13. Cyclization of geraniolene oxide catalyzed by $BF_3{\cdot}Et_2O$.

Van Tamelen and coworkers elegantly demonstrated that squalene oxide is an intermediate in the enzymatic cyclization of squalene to lanosterol (Scheme 14).[71]



Scheme 14. Enzymatic cyclization of squalene oxide to lanosterol.

Several non-enzymatic olefin-epoxide cyclizations have also been reported.[72] Since $BF_3{\cdot}Et_2O$ is very corrosive, we investigated the use of metal triflates for effecting epoxyolefin cyclizations.[73] The cyclization of geraniolene oxide was studied with several metal triflates such as $Bi(OTf)_3$, $Ga(OTf)_3$, $In(OTf)_3$, $K(OTf)_3$, $La(OTf)_3$, LiOTf, $Sc(OTf)_3$, and $Yb(OTf)_3$. the best results were obtained with $Bi(OTf)_3$. The cyclization gave multiple products whose ratios were determined by GC analysis of the crude product mixtures (Scheme 15). The cyclization was initially carried out at 0.36 M concentration (0.20 g of epoxide in 4.0 mL of solvent), and under these conditions two acyclic products **35** and **39** were also formed in significant amounts. These products result from simple Lewis acid catalyzed rearrangement of the epoxide (Scheme 15, product **35)** or via ring opening of the epoxide followed by elimination (Scheme 15, product **40**).



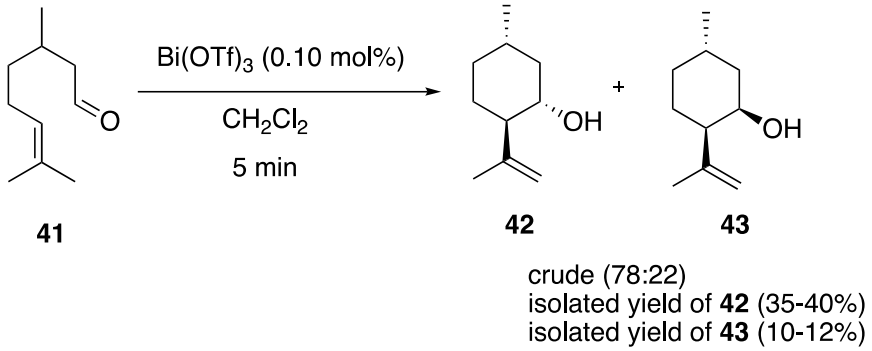
34 **35** **36** **37** **38** **40**

$Bi(OTf)_3$·(0.10 mol%), CH_2Cl_2, 5 min	22%	13%	36% (82:18)	29%
$Bi(OTf)_3$·(0.10 mol%), CH_2Cl_2, 24 hr Proton sponge (1.0 mol%)	NR			
$Bi(OTf)_3$·(0.10 mol%), CH_2Cl_2, 5 min K_2CO_3 (40.0 mol%)	19%	11%	39%	31%
$Bi(OTf)_3$· (1.0 mol%), pentane, 10 min	57%	6.0%	17%	20%
$Bi(OTf)_3$·(0.1 mol%), toluene, 45 min	25%	9.0%	16%	50%
$Bi(OTf)_3$·(1.0 mol%), THF, 10 min	55%	0%	6.0%	39%
$Bi(OTf)_3$·(0.1 mol%), dioxane, 10 min	49%	2.0%	6.0%	43%
$Bi(OTf)_3$· (0.1 mol%), DME, 20 min	59%	1.0%	4.0%	36%
CF_3SO_3H (0.1 mol%), CH_2Cl_2, 20 min	21%	10%	36%	33%
CF_3SO_3H (0.1 mol%), CH_2Cl_2, 16 h K_2CO_3 (40.0 mol%)	NR			

Scheme 15. Bismuth(III) triflate catalyzed cyclization of geraniolene oxide.

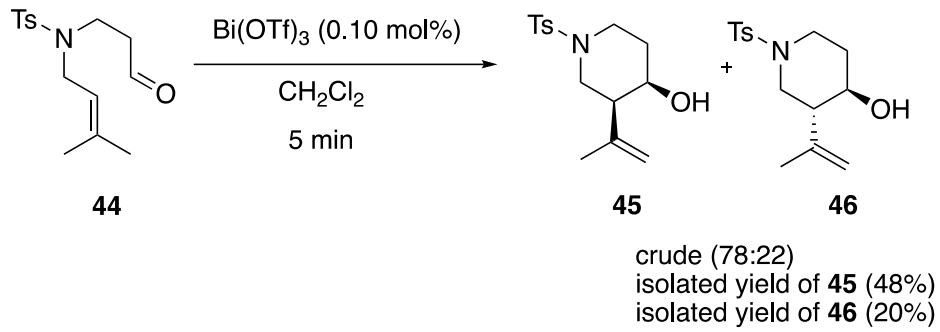
Since the reaction was also catalyzed by triflic acid, CF_3SO_3H (0.10 mol %), the possibility that the metal triflate was simply acting as a source of triflic acid was considered. When the reaction was carried out with $Bi(OTf)_3$ in the presence of Proton-Sponge® (*N*,*N*,*N*′,*N*′-tetramethyl-1,8-naphthalenediamine)®,[46] no rearrangement occurred, but similar product mixtures were obtained when the reaction was carried out with $Bi(OTf)_3$ in K_2CO_3. The efficacy of K_2CO_3 in neutralizing CF_3SO_3H was also ascertained. These observations suggested that $Bi(OTf)_3$ is acting as a Lewis acid though its role as a source of CF_3SO_3H cannot be ruled out. The lack of reaction in the presence of Proton Sponge® was attributed to the complexation of bismuth triflate to the amine nitrogens in Proton Sponge®. The effect of solvent on product composition was also studied and it was found that solvent influenced product composition more than the Lewis acid. Dichloromethane gave the greatest amounts of cyclization product while least amounts were formed in dioxane, DME, THF, and an ionic liquid [Bmim][OTf].

2.3.3. Bismuth(III) triflate catalyzed carbonyl-ene reaction. The intramolecular carbonyl-ene reaction is a useful synthetic method to generate cyclic systems.[74] The cyclization of citronellol to isopulegol is of considerable interest as isopuelgol can be easily converted to menthol, a common ingredient in many analgesics. Several catalysts such as $InCl_3$[75] and $Sc(OTf)_3$[76] have been used to catalyze this cyclization. However, indium salts are toxic while scandium salts are very expensive. Our interest in bismuth(III) compounds led us to investigate their utility in catalyzing the carbonyl-ene reaction. We have reported that bismuth(III) triflate is an efficient catalyst for the cyclization of citronellal **41** to a mixture (80:20) of isopulegol **42** and neoisopulegol **43**, respectively (Scheme 16).[77] Ytterbium(III) triflate, $Yb(OTf)_3$ proved to be less efficient for this transformation (10.0 mol %, 1 h) although the ratio of the products was the same as with $Bi(OTf)_3$.



Scheme 16. Bismuth(III) triflate catalyzed cyclization of citronellal.

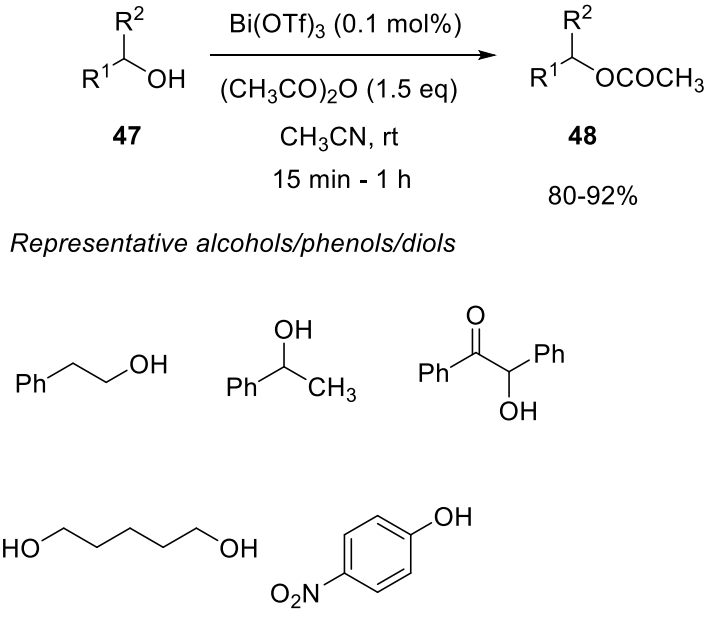
Snaith and coworkers have reported the methyl aluminum dichloride, Me_2AlCl_2-catalyzed synthesis of *cis*- and *trans*-3,4-disubstituted piperidines **45-46** via carbonyl-ene cyclization of sulfonamide **44**.[78] Inspired by this report, we have used bismuth(III) triflate for the synthesis of substituted piperidines (Scheme 17). Unlike with cyclization of citronellal, in this case the *cis* isomer **51** was the major product.



Scheme 17. Bismuth(III) triflate catalyzed synthesis of 3,4-substituted piperidines.

2.4. Bismuth(III) compounds catalyzed protection of alcohols, phenols, aldehydes and ketones

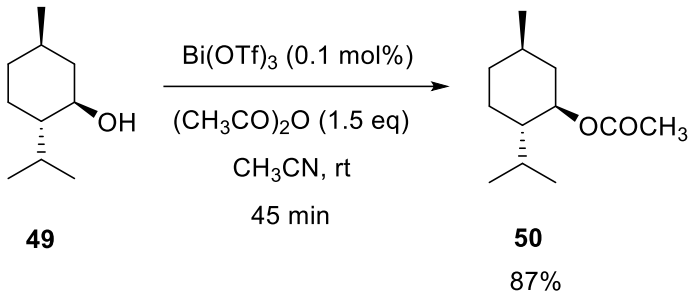
2.4.1. Bismuth(III) triflate catalyzed acetylation of alcohols, diols, and phenols. The acylation of alcohols and phenols to give an ester is a very useful reaction and several methods have been developed for effecting this transformation. A common method involves the reaction of an alcohol with acetic anhydride in the presence of pyridine or triethylamine.[79] 4-(Dimethylamino)pyridine (DMAP) is known to cause remarkable rate acceleration in this reaction.[80] Yamamoto and coworkers introduced scandium(III) triflate as an efficient catalyst for the acylation of alcohols with acetic anhydride and mixed anhydrides.[81] Two drawbacks of scandium(III) triflate are that it is very expensive and quite moisture sensitive. Orita and coworkers reported the bismuth(III) triflate catalyzed acylation of alcohols.[82] However the method only report GC yields and an excess of acetic anhydride is used. We have reported the bismuth(III) triflate catalyzed acetylation of alcohols, diols and phenols **47** to give the corresponding acetate **48** on a large scale (Scheme 18).[83]



Scheme 18. Bismuth(III) triflate catalyzed acetylation of alcohols, diols and phenols.

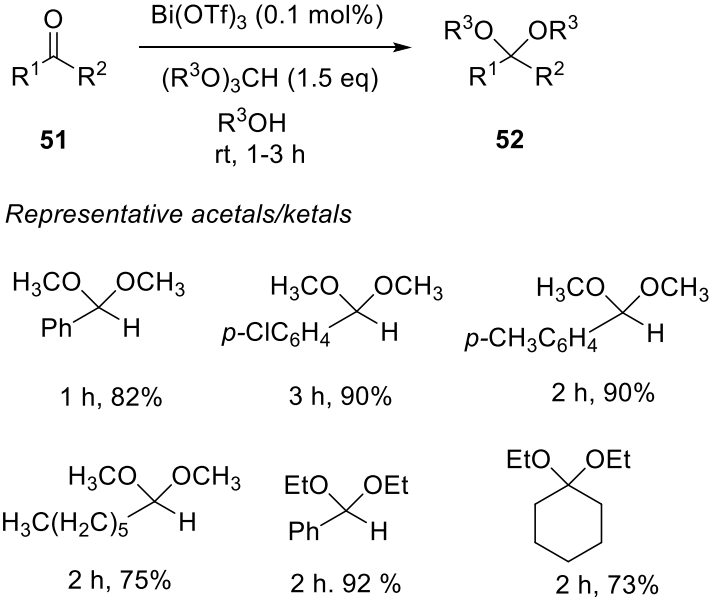
Attempts to make the monoacetate from symmetrical diols were unsuccessful, and instead a statistical mixture of monoacetate, diacetate and unreacted diol was obtained. With diols containing a 1° and 2° hydroxy group, a significant difference in the rate of acetylation was not observed. Acetonitrile was found to be the best solvent while the reaction was very slow in diethyl ether and THF. Tertiary alcohols (linalool and

triphenylmethanol) failed to undergo acetylation under the reaction conditions. Procopiou and coworkers have reported the trimethylsilyl triflate, TMSOTf-catalyzed acetylation of alcohols in CH_2Cl_2 as a solvent. As part of a mechanistic study they reported that when the acetylation of menthol was attempted using CF_3SO_3H (2.0 mol %) in CH_2Cl_2, no product was obtained.[84] In contrast, the $Bi(OTf)_3$-catalyzed acetylation of menthol **49** proceeded smoothly in CH_3CN to yield menthyl acetate **50** (Scheme 19). Based on these observations a referee suggested that a possible mechanism might involve exchange between $Bi(OTf)_3$ and $(CH_3CO)_2O$ to yield CH_3COOTf and CF_3SO_3H, with the latter acting as the true catalyst in CH_3CN.

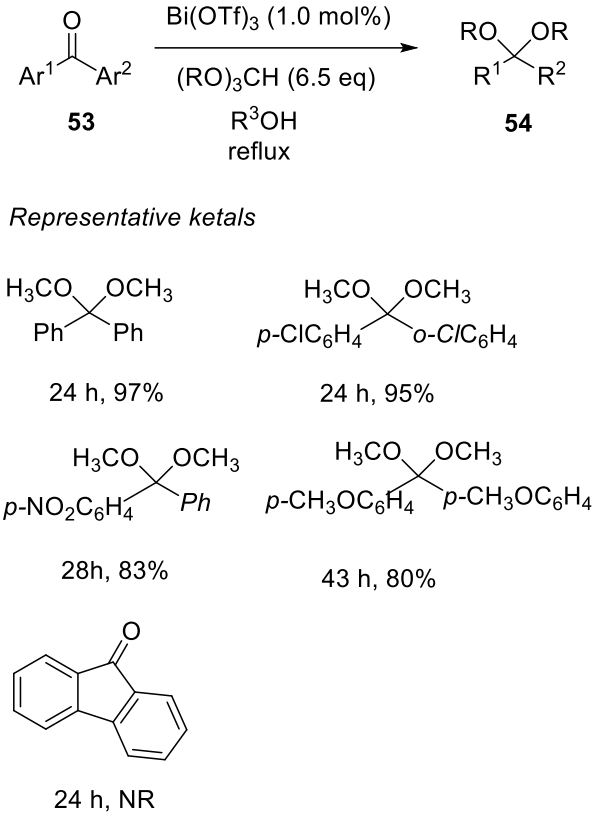


Scheme 19. Bismuth(III) triflate catalyzed acetylation of menthol.

2.4.2. Bismuth(III) triflate catalyzed synthesis of acetals. Aldehydes and ketones are frequently protected as acetals and ketals in the total synthesis of molecules. Hence facile methods for their efficient synthesis have attracted much attention[85,86,87] We have reported a simple bismuth(III) triflate catalyzed method for the synthesis of acyclic acetals and ketals **52** from aldehydes and ketones **51** (Scheme 20).[88] The use of orthoformates enabled acetal formation without the need for removal of the water by-product.



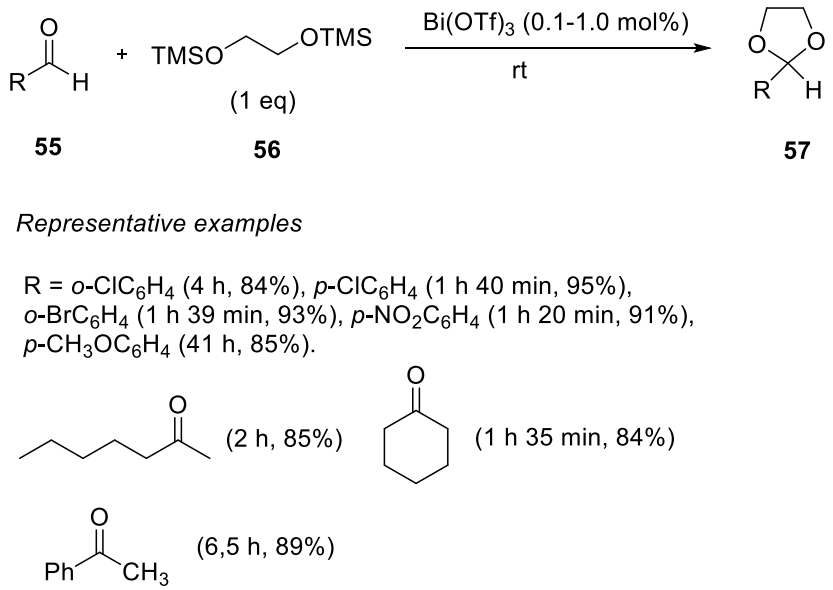
Scheme 20. Bismuth(III) triflate catalyzed synthesis of acyclic acetals and ketals.



Scheme 21. Bismuth(III) triflate catalyzed synthesis of ketals from diaryl ketones.

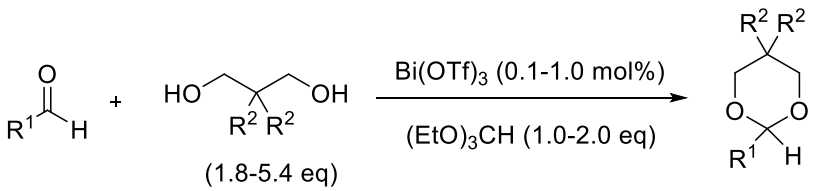
The synthesis of ketals from diaryl ketones requires harsher conditions. One reported procedure utilizes the highly corrosive triflic acid, CF_3SO_3H (20.0 mol%).[89] Using our method we were able to synthesis ketals **54** from diaryl ketones **53** under milder conditions (reflux conditions and 1.0 mol% of $Bi(OTf)_3$ (Scheme 21).

We have also reported a convenient bismuth(III) triflate catalyzed synthesis of dioxolanes **57** using aldehydes **55** and 1,2-bis(trimethylsilyloxy)ethane **56** (Scheme 22).[90]



Scheme 22. Bismuth(III) triflate catalyzed synthesis of dioxolanes using 1,2-bis(trimethylsilyloxy)ethane.

Since bis(trimethylsilyloxy)propane is not commercially available, it was synthesized in the lab. However the synthesis of dioxanes was not successful unlike dioxolanes. Hence dioxanes **59** were synthesized using 1,3-propane diol **58** along with triethylorthoformate as a water scavenger (Scheme 23).



58 **59**

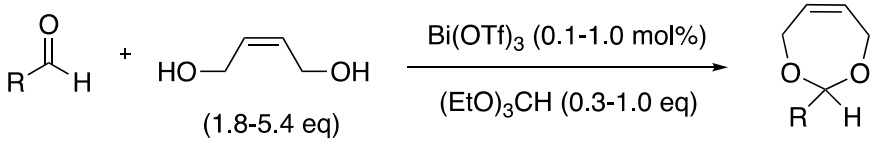
Representative examples

R^1 = *o*-BrC_6H_4, R^2 = H (2 h 35 min, 78%)
R^1 = *p*-ClC_6H_4, R^2 = H (1.5 h, 99%)
R^1 = *p*-OHC_6H_4, R^2 = H, (1 h 20 min, 72%)
R^1 = *p*-$TBSC_6H_4$, R^2 = H,(2 h 25 min h, 83%)

R^1 = *p*-ClC_6H_4, R^2 = CH_3 (4 h, 83%)
R^1 = *m*-BrC_6H_4, R^2 = CH_3, (1.5 h, 80%)
R^1 = PhCH=CH, R^2 = CH_3, (55 min, 99%)

Scheme 23. Bismuth(III) triflate catalyzed synthesis of dioxanes.

The use of aldehydes and *Z*-but-2-ene-1,4-diol **60** gave the corresponding dioxepines **61** (Scheme 24).

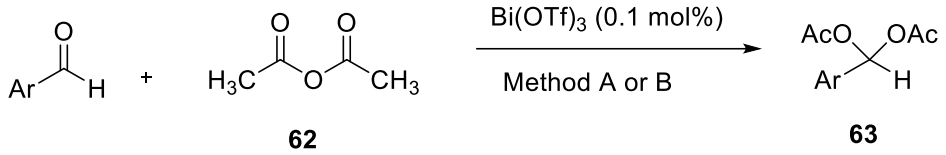


60 **61**

R = *o*-BrC_6H_4, 1 h 35 min, 56%
R = PhCH=CH-, 4 h 15 min, 60%
R = $CH_3(CH_2)_8$, 1 h 45 min, 86%

Scheme 24. Bismuth(III) triflate catalyzed synthesis of dioxepines.

2.4.3. Bismuth(III) nitrate and triflate catalyzed synthesis of acylals from aldehydes. When we were studying the bismuth(III) triflate-catalyzed acetylation of phenols with acetic anhydride, *p*-hydroxybenzaldehyde gave a product which did not have the aldehyde group. This led us to conclude that $Bi(OTf)_3$ had also catalyzed the formation of acylals (1,1-diesters) **63** from aldehydes and acetic anhydride **62**, which led to the development of a simple protocol for formation of acylals (Scheme 25).[91] With aliphatic aldehydes significant product formation occurred only under solvent-free conditions.



Ar = Ph, *p*-ClC_6H_4, *p*-$CH_3C_6H_4$
p-$CH_3OC_6H_4$, *m*-$NO_2C_6H_4$,
PhC=CH, $PhCH_2CH_2$-, *p*-HOC_6H_4

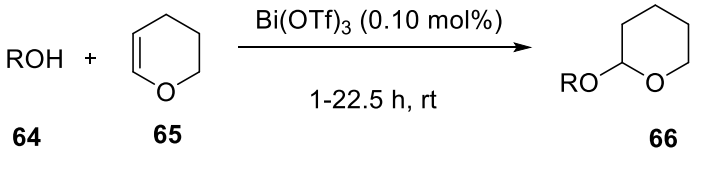
Method A: CH_3CN, rt (45 min - 4.5 h), 79-91%

Method B: rt (10 min-1.5 h), 64-95%

Scheme 25. Bismuth(III) triflate catalyzed synthesis of acylals from aldehydes.

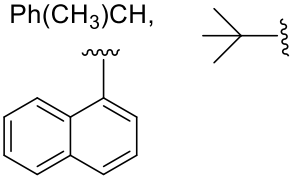
We have also reported the bismuth(III) nitrate, $Bi(NO_3)_3{\cdot}5H_2O$-catalyzed synthesis of acylals from aromatic aldehydes.[92] It was problematic to get acylals from activated aldehydes such as *p*-methoxybenzaldehyde and *p*-hydroxybenzaldehyde. Control studies and NMR analysis of crude products suggested that acylal product was undergoing ring nitration. However it was not possible to isolate the pure acylal or any nitration product by column chromatography of the crude product. Control experiments using HNO_3, and also $Bi(NO_3)_3{\cdot}5H_2O$ the presence of Proton Sponge® suggested that Bi(III) was acting as a Lewis acid in these reactions and not merely as a source of HNO_3.

2.4.4. Bismuth(III) triflate catalyzed synthesis of tetrahydropyranyl (THP) ethers. The tetrahydropyranyl (THP) ether group is a common protecting group for alcohols.[93] We have reported the formation of THP ethers **66** from alcohols **64** and dihydropyran **65** under solvent-free conditions (Scheme 26).[94] The procedure is simple and involves stirring the alcohol and dihydropyran (DHP) in the presence of $Bi(OTf)_3$ at room temperature.



R = n-pentyl, n-heptyl,
$PhCH_2CH_2$, $HC{\equiv}CCH_2CH_2$
p-$NO_2C_6H_4CH_2$, , PhCH=CH,

$Ph(CH_3)CH$,

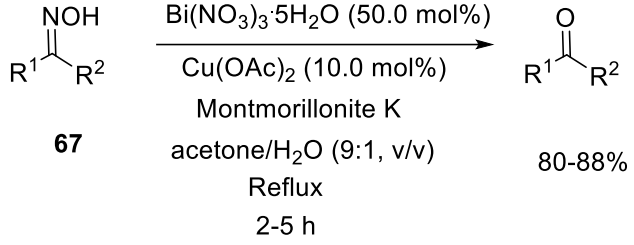


Scheme 26. Bismuth(III) triflate catalyzed synthesis of tetrahydropyranyl (THP) ethers.

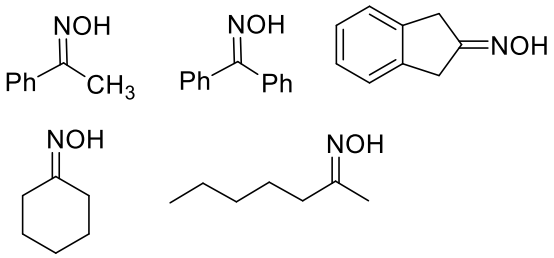
2.5. Bismuth(III) compounds catalyzed deprotection of various protecting groups

2.5.1. Bismuth(III) nitrate promoted deprotection of ketoximes. Although oximes are not commonly used as protecting groups for aldehydes/ketones, they can be formed from non-carbonyl compounds.[95] Hence their conversion to aldehydes/ketones provides a route to the latter. We have reported a bismuth nitrate,

$Bi(NO_3)_3{\cdot}5H_2O$ promoted deprotection of ketoximes **67** (Scheme 28).[96] The method works only for ketoximes and requires the presence of copper(II) acetate, $Cu(OAc)_2$ (0.10 eq). In the absence of $Cu(OAc)_2$, upto 10% acetone oxime formed, presumably by an exchange reaction the acetone solvent. The use of Montmorillonite K afforded products in better yield than without. Although smooth deprotection was observed in CH_2Cl_2, some oximes (acetophenone oxime and cyclohexanone oxime) underwent a very exothermic reaction. Hence it is suggested that CH_2Cl_2 not be used as a solvent for this method.

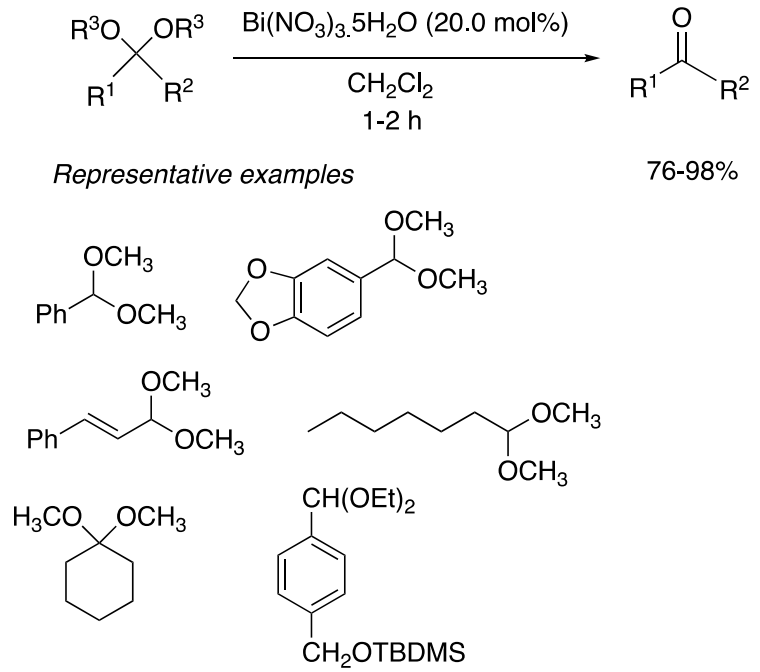


Representative oximes



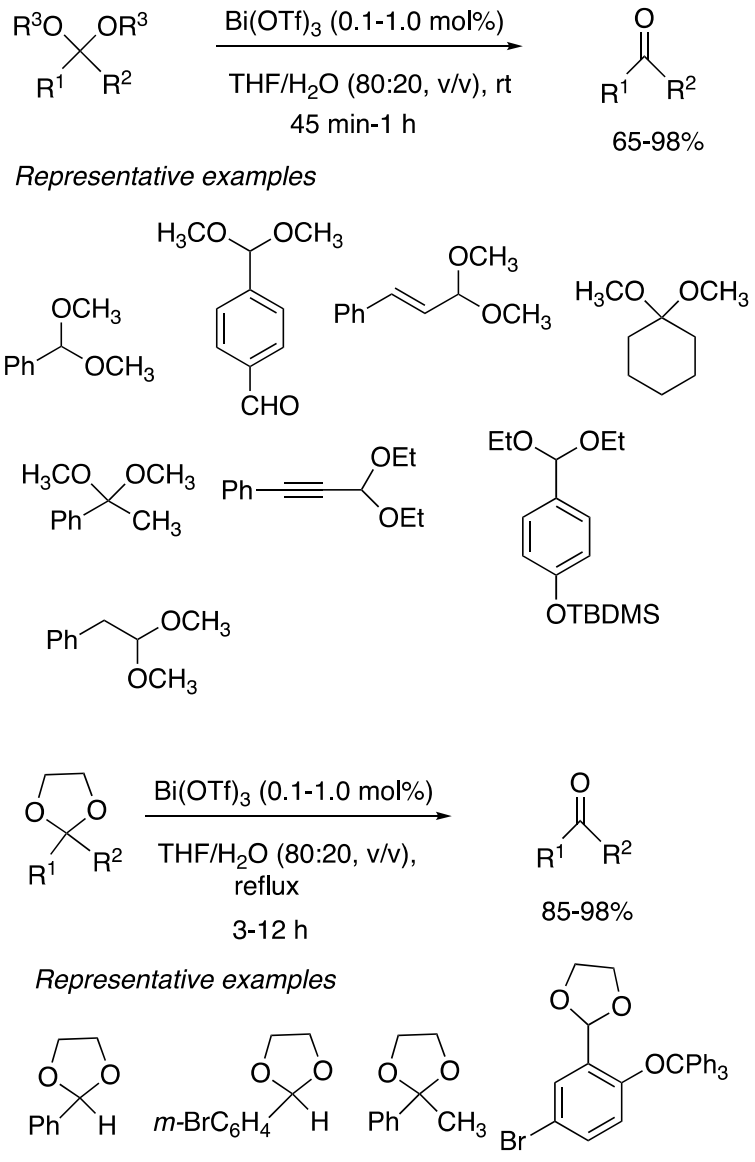
Scheme 27. Bismuth(III) nitrate promoted deprotection of ketoximes.

2.5.2. Bismuth(III) nitrate catalyzed deprotection of acetals and ketals. Bismuth(III) salts have been used for the cleavage of a variety of protecting groups. For example, we have reported the deprotection of a variety of protecting groups using bismuth(III) compounds. For example, bismuth(III) nitrate, $Bi(NO_3)_3{\cdot}5H_2O$, is an efficient catalyst for the deprotection of a variety of acetals and ketals (Scheme 28).[97] Reactions were carried out at room temperature, and under these conditions *tert*-butyldimethylsilyl (TBDMS) and THP ethers were not affected. This allowed for the chemoselective deprotection of an acetal in the presence of a TBDMS ether. The deprotection of cyclic acetals was very slow (~ 5 days).



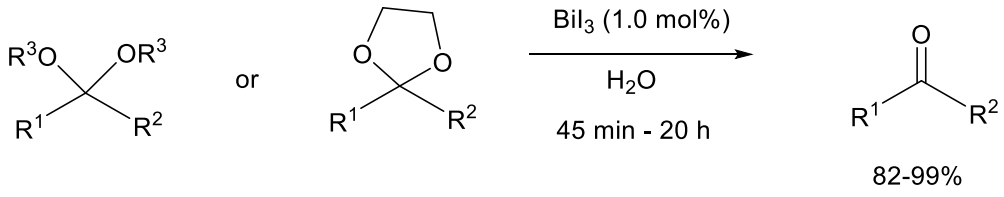
Scheme 28. Bismuth(III) nitrate catalyzed deprotection of acyclic acetals.

2.5.3. Bismuth(III) triflate catalyzed deprotection of acetals and ketals. One big drawback of the above of the above method is the use of CH_2Cl_2. In order to avoid CH_2Cl_2 we developed a bismuth(III) triflate catalyzed deprotection of acetals in aqueous THF as the solvent.[98] Under these conditions, acyclic aromatic acetals and ketals were deprotected at room temperature (using as little as 0.10 mol% catalyst) while cyclic acetals could be cleaved under reflux conditions using 1.0 mol% catalyst (Scheme 29). This is in contrast to $Bi(NO_3)_3{\cdot}5H_2O$, which was not an effective catalyst for the deprotection of cyclic acetals. The dimethyl acetal of heptanal could not be cleaved even after heating at reflux for 24 h but the dimethyl acetal of phenylacetaldehyde could be cleaved when heated at reflux for 3 h. THP ethers and TBDMS ethers were stable under these conditions but a trityl group could be easily cleaved.



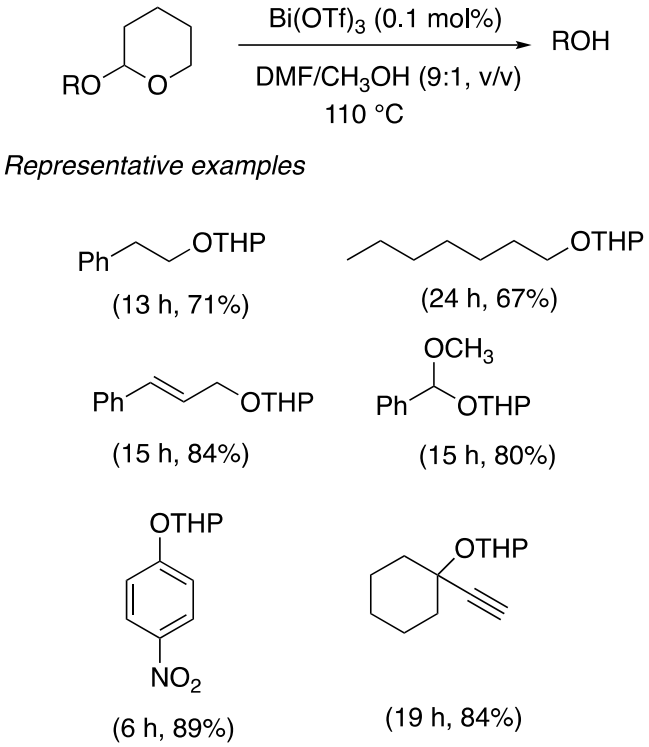
Scheme 29. Bismuth(III) triflate catalyzed deprotection of acetals.

2.5.4. Bismuth(III) iodide catalyzed deprotection of acetals in water. Bismuth(III) iodide, BiI_3, is an underutilized catalyst in synthetic methodology. Yasuike and coworkers have reported the BiI_3-catalyzed synthesis of 3-Selanylindoles via a regioselective selenation of indoles with diaryl diselenides.[99] We have reported the deprotection of acetals using BiI_3 in water (Scheme 31).[100] Like with $Bi(NO_3)_3{\cdot}5H_2O$, and $Bi(OTf)_3$, TBDMS ethers were not affected.



Scheme 30. Bismuth(III) iodide catalyzed deprotection of acetals in water.

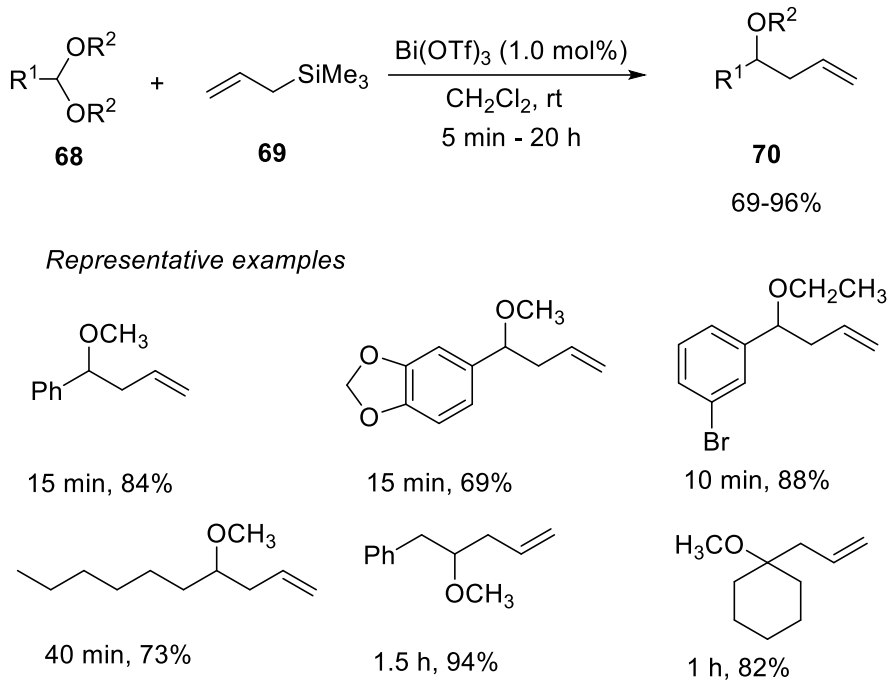
2.5.5. Bismuth(III) triflate catalyzed deprotection of tetrahydropyranyl (THP) ethers. As mentioned earlier bismuth(III) triflate efficiently catalyzed the deprotection of THP ethers.[94] In the same manuscript we also developed a method for the deprotection of THP ethers under non-aqueous conditions using $Bi(OTf)_3$ (Scheme 31).



Scheme 31. Bismuth(III) triflate catalyzed deprotection of THP ethers.

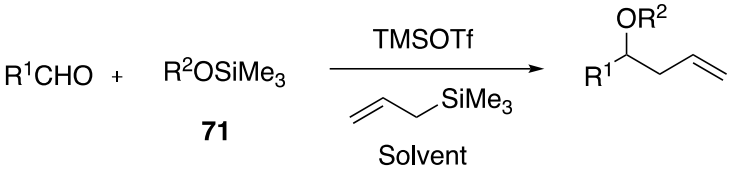
2.6. Bismuth(III) compounds catalyzed allylation of acetals, ketals and THP ethers

2.6.1 Bismuth(III) triflate catalyzed allylation of acyclic acetals. The allylation of aldehydes, ketones, acetals and ketals is an important way to form a C-C bond and hence has been the subject of numerous studies. In particular, allylations using allyltrimethylsilane has been studied extensively. Sakurai and coworkers reported the $TiCl_4$-promoted allylation of aldehydes and acetals (Sakurai reaction) to generate homoallyl alcohols and homoallyl ethers.[101] Several other catalysts have also been developed for this purpose including $AlCl_3$,[102] $BF_3{\cdot}Et_2O$,[103] $BiBr_3$,[104] $Sc(OTf)_3$,[105] and CuBr.[106] We have reported the bismuth(III) triflate, $Bi(OTf)_3$-catalyzed allylation of acetals **68** using allyltrimethylsilane **69** to yield the corresponding homoallyl ethers **70** (Scheme 32).[107] In contrast to corrosive Lewis acids such as $TiCl_4$, $AlCl_3$ and $BF_3{\cdot}Et_2O$, bismuth(III) triflate as an easy to handle white solid. Additionally, the reaction was highly catalytic with $Bi(OTf)_3$ (1.0 mol%) while $TiCl_4$ was required in catalytic amounts, and carried out at -78 °C. Unlike $TiCl_4$, bismuth(III) triflate however did not catalyze the addition of allyltrimethylsilane to aldehydes.



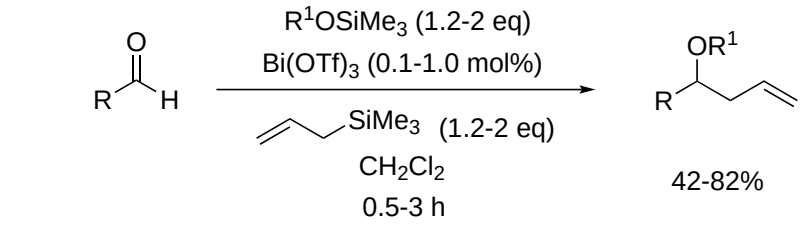
Scheme 32. Bismuth(III) triflate catalyzed allylation of acetals.

2.6.2. Bismuth(III) triflate catalyzed allylation of cyclic acetals and dithianes followed by *in situ* derivatization to generate highly functionalized esters. In an effort to convert aldehydes to the corresponding homoallyl ethers directly, we followed a protocol developed by Marko and coworkers in which an aldehyde is treated with alkoxysilanes **71** and allyltrimethylsilane. Marko's protocol used the highly toxic CCl_4 as the solvent and trimethylsilyl triflate (TMSOTf) as the catalyst (Scheme 33).[108]



Scheme 33. General strategy for one pot conversion of aldehydes to homoallyl ethers.

Using a similar methodology Oriyama and coworkers have reported an iron(III) chloride, $FeCl_3$-catalyzed one pot method for the conversion of aldehydes to homoallyl ethers.[109] We have reported similar conversions using bismuth(III) triflate as a catalyst (Scheme 34).[110]

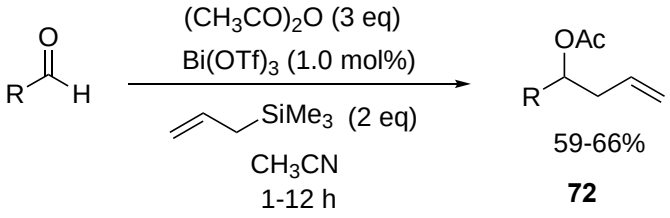


R^1 = *m*-BrC_6H_4, *p*-BrC_6H_4,
m-$CH_3C_6H_4$, *p*-ClC_6H_4,
^{t}Bu, Ph

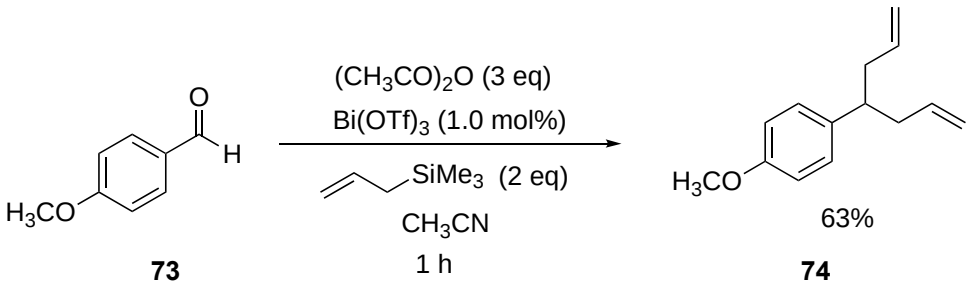
R^2 = Allyl, Bn, Me, Et,

Scheme 34. Bismuth(III) catalyzed one pot method for the conversion of aldehydes to homoallyl ethers.

Aggarwal and co-workers extended this methodology to the synthesis of homoallyl esters using scandium(III) triflate as a catalyst.[111] We also extended this methodology to the synthesis of homoallyl acetates **72** (Scheme 35). The one pot allylation of *p*-anisaldehyde **73** led to the corresponding diallylated product **74**.

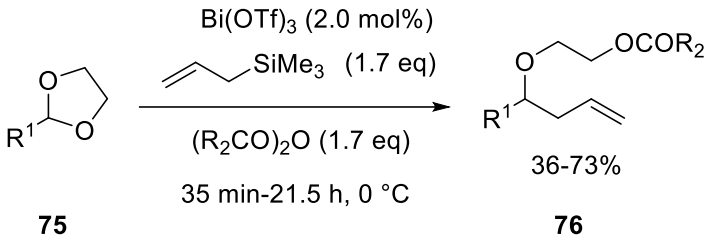


R = *p*-$CH_3C_6H_4$, *m*-$CH_3OC_6H_4$,
p-ClC_6H_4, Ph



Scheme 35. Bismuth(III) triflate catalyzed synthesis of homoallyl acetates.

Although as indicated above the allylation of acyclic acetals to generate homoallyl ethers has been well documented in the literature, there are fewer reports in the literature describing the corresponding allylation of cyclic acetals.[112, 113] We have reported the bismuth(III) triflate catalyzed allylation of cyclic acetals **75** followed by in situ derivatization to generate highly functionalized esters **76** (Scheme 36).[114]

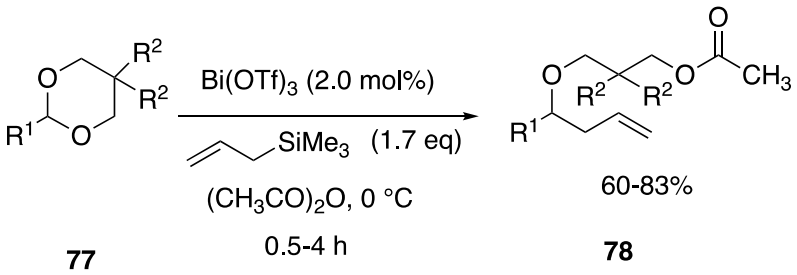


R^1 = *o*-BrC_6H_4, *m*-BrC_6H_4, *o*-ClC_6H_4, *p*-ClC_6H_4, *o*-FC_6H_4, *p*-$CH_3C_6H_4$, $PhCH_2$, $CH_3(CH_2)_8$

R^2 = CH_3, ^{i}Pr, ^{t}Bu

Scheme 36. Bismuth(III) triflate catalyzed allylation of cyclic acetals.

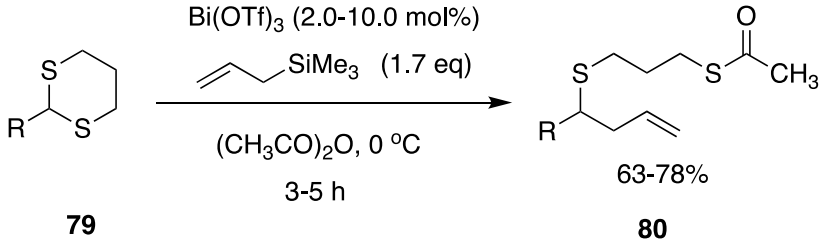
The methodology was extended to dioxanes **77** (Scheme 37) and dithianes **79** (Scheme 38) to give the corresponding functionalized esters, **78** and **80**. One drawback of this method was the use of a slight excess of allyltrimethyl silane for optimal reaction times but isolation of product by filtration through a silica column eliminated an aqueous waste stream, minimizing waste generation.



R^1 = *o*-BrC_6H_4, *p*-BrC_6H_4, *p*-ClC_6H_4, *p*-$CH_3C_6H_4$, *m*-$CH_3C_6H_4$, *m*-$CH_3OC_6H_4$, $CH_3(CH_2)_8$

R^2 = H, CH_3

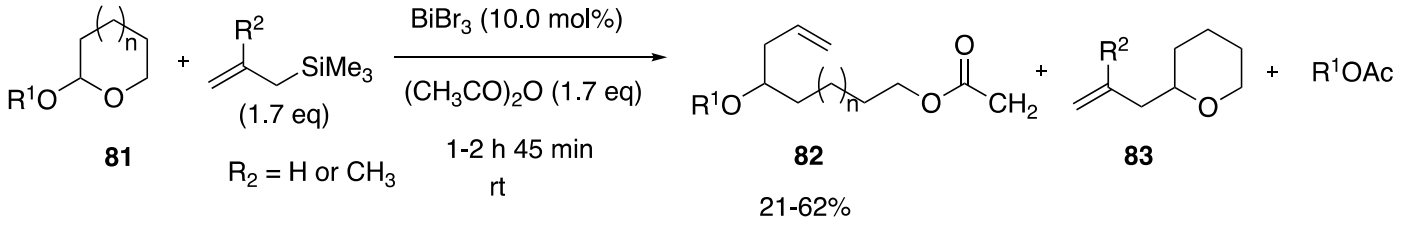
Scheme 37. Bismuth(III) triflate catalyzed allylation of dioxanes followed by *in situ* derivatization.



R = Ph, *p*-ClC_6H_4, *m*-$CH_3C_6H_4$, $CH_3(CH_2)_8$

Scheme 38. Bismuth(III) triflate catalyzed allylation of dithianes followed by *in situ* derivatization.

2.6.3. Bismuth(III) bromide catalyzed allylation of tetrahydrofuranyl and tetrahydropyrany ethers. Unlike allylation of acetals, the corresponding allylation of THP ethers has not been well studied. Maeda and coworkers have reported the titanium tetrachloride, $TiCl_4$-induced allylation of α-iodomixed acetals with allylsilanes.[115] The methodology utilizes a stoichiometric amount of $TiCl_4$. Hunter and coworkers have reported the TMSOTf-promoted allylation of 2-methoxytetrahydropyran using lithium *n*-butyltriallylborate as the allyl source.[116] We have reported a bismuth(III) bromide, $BiBr_3$-catalyzed allylation of tetrahydrofuranyl and tetrahydropyranyl ethers **81** followed by *in situ* derivatization with acetic anhydride to yield highly functionalized esters **82** (Scheme 39).[117] The reaction gave almost equal amounts of the open chain product **82** and 2-allyltetrahydro-2H-furan or 2-allyltetrahydro-2H-pyran. The two products could be easily separated by chromatography when allyltrimethylsilane was used but separation was a little more difficult when methallylsilane was used. When 3-phenylpropanol was used the corresponding acetate was isolated in 31% yield. The acetate product could be easily hydrolyzed, thus providing access to highly functionalized alcohols.

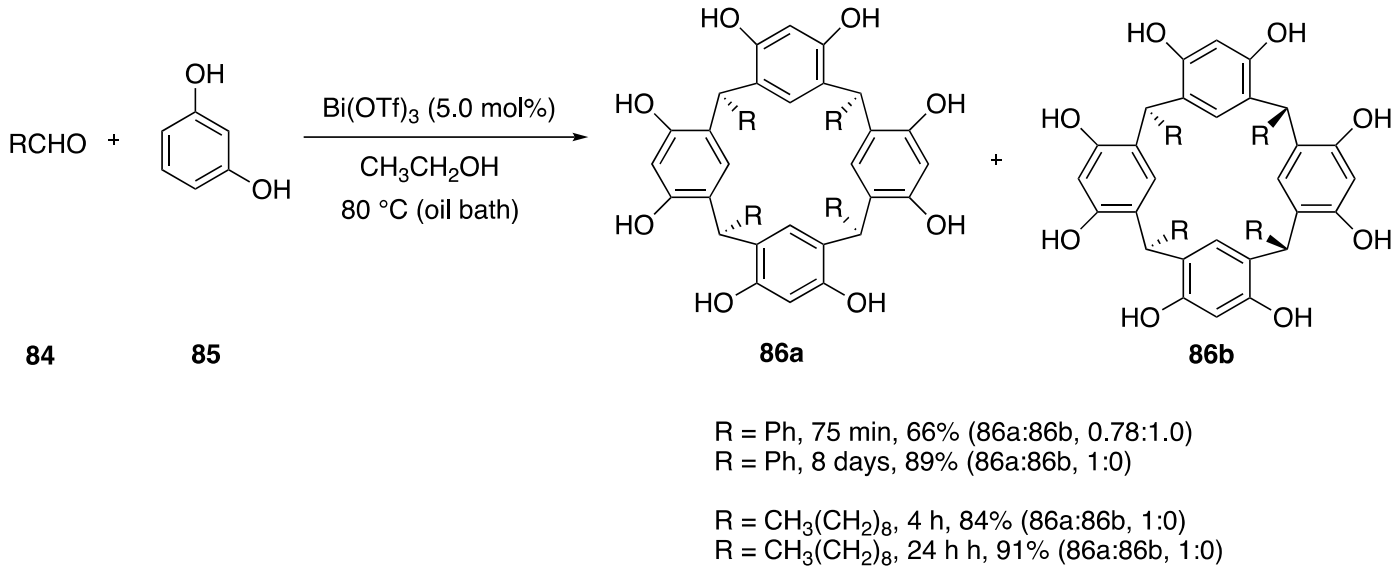


R^1 = CH_3, $CH_3(CH_2)_3$, $CH(CH_2)_6$, cyclohexyl, $PhCH_2(CH_2)_2$, $HC{\equiv}CCH_2CH_2$

Scheme 39. $BiBr_3$-catalyzed allylation of tetrahydrofuranyl and tetrahydropyranyl ethers.

2.7. Bismuth(III) triflate catalyzed synthesis of resorcinarenes

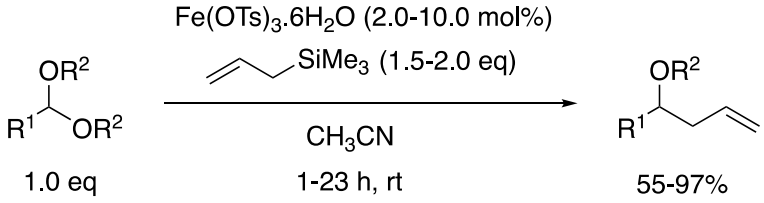
Resorcinarenes **86** are macrocyles formed by condensation of an aldehyde **84** with resorcinol **85**.[118] Resorcinarenes act as guests for a variety of host molecules.[119] Their synthesis has been reported using ytterbium(III) triflate, $Yb(OTf)_3$[120] as well as under solvent-free conditions using *p*-toluenesulfonic acid, *p*-TsOH.[121] One drawback of *p*-TsOH is that is quite corrosive. While Yb(OTf)3 is easy to handle the method serves from long reaction times (48 h). We have reported the bismuth(III) triflate, Bi(OTf)3-catalyzed synthesis of resorcinarenes (Scheme 40).[122] Unlike with $Yb(OTf)_3$, bismuth(III) triflate was more efficient and the reactions were complete in a short period of time. With benzaldehyde, after 75 min, the product was obtained as a mixture of **86a** (*all cis)* and **86b** (*cis-trans-trans)* while decanal gave only the thermodynamically more stable all *cis* isomer. Increasing the reaction time to 8 days with benzaldehyde results in the all cis isomer suggesting that isomerization occurs via ring opening. When the mixture of **86a** and **86b** was subjected to the reaction conditions for 10 days, the product was mostly the all *cis* isomer.



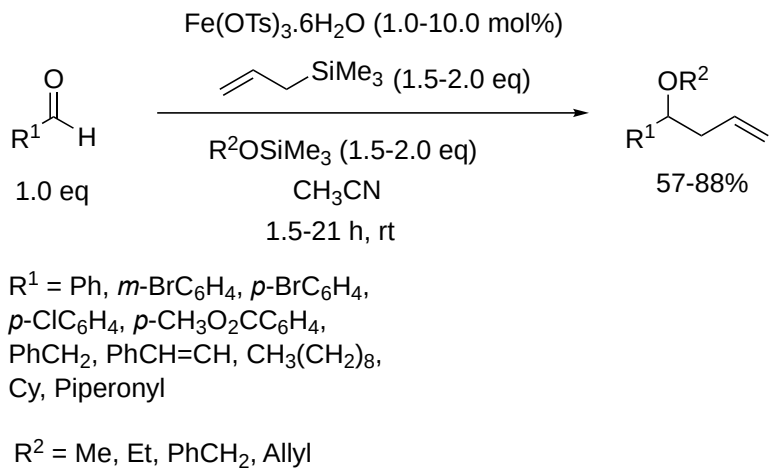
Scheme 40. Bismuth(III) triflate catalyzed synthesis of resorcinarenes.

2.8. Utility of iron(III) tosylate in organic synthesis

2.8.1. Iron(III) tosylate catalyzed synthesis of homoallyl ethers from acetals and aldehydes. While attempting to prepare bismuth(III) tosylate, we did a search for commercially available metal tosylates and discovered that iron(III) tosylate is readily available, noncorrosive, and easy to handle. Surprisingly, there were no reports of its use as a catalyst for organic transformations. The synthesis of homoallyl ethers from acetals has attracted considerable attention.[123] However many acetals have poor shelf lives and are often synthesized from the corresponding aldehyde. Hence a direct method for conversion of aldehydes to homoallyl ethers is desirable. Our interest in using iron(III) tosylate led us to develop a synthesis of homoallyl ethers from acetals (Scheme 41) and aldehydes (Scheme 42).[124]

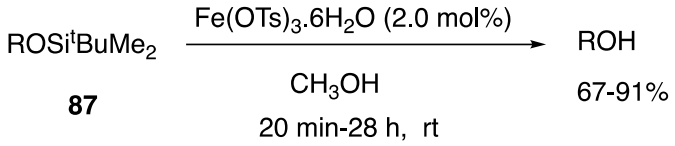


Scheme 41. Iron(III) tosylate catalyzed allylation of acetals.



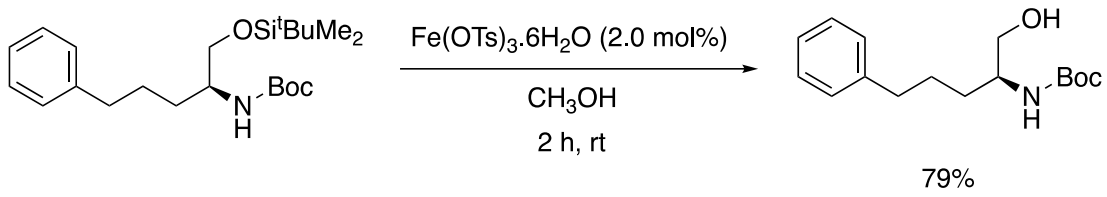
Scheme 42. Iron(III) tosylate catalyzed 3-component allylation of aldehydes.

2.8.2. Iron(III) tosylate catalyzed deprotection of *tert*-butyldimethylsilyl (TBDMS) ethers. The *tert*-butyldimethylsilyl (TBDMS) protecting group, introduced by Corey and coworkers, is one of the most common silyl protecting groups for alcohols and phenols.[125] The most common methods for the deprotection of the TBDMS group utilize reagents containing a fluoride ion, with *n*-$Bu_4N^+F^-$ often being the reagent of choice. However, the highly basic nature of *n*-$Bu_4N^+F^-$ can lead to side reactions with base-sensitive substrates.[126] In addition, *n*-$Bu_4N^+F^-$ is extremely corrosive to the mucosa and the upper respiratory tract,[127] a problem compounded by the fact that *n*-$Bu_4N^+F^-$ is required in stoichiometric amounts. We have reported a mild method for the deprotection of TBDMS ethers **87** using iron(III) tosylate as a catalyst (Scheme 43).[128]

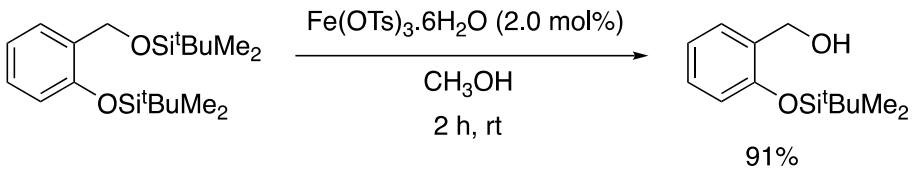


Scheme 43. Iron(III) tosylate catalyzed deprotection of TBDMS ethers.

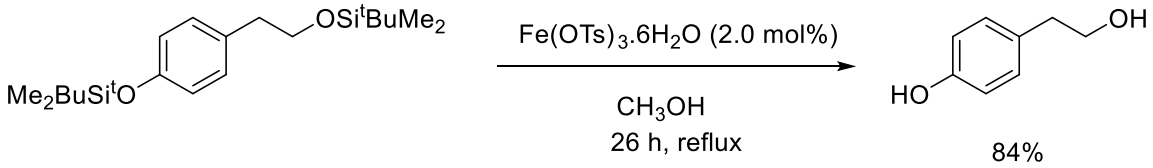
The experimental procedure was simple and consisted of stirring the silyl ether in methanol as the catalyst is added. The product was isolated by removal of methanol and filtration of the residue through a short silica column, thus avoiding an aqueous waste stream. A variety of chemoselective deprotections could be achieved under the reaction conditions. A TBDMS ether could be cleaved in the presence of a Boc (*tert*-butyloxycarbonyl) group (Scheme 44). Phenolic TBDMS ethers were unaffected while an alkyl TBDMS group was cleaved (Scheme 45). Both phenolic and alkyl TBDMS (*tert*-butyldimethylsilyl) groups were cleaved under reflux conditions (Scheme 46). We were also able to cleave a 1° TBDMS ether in the presence of a 1° TBDPS (*tert*-butyldiphenylsilyl ether) (Scheme 47).



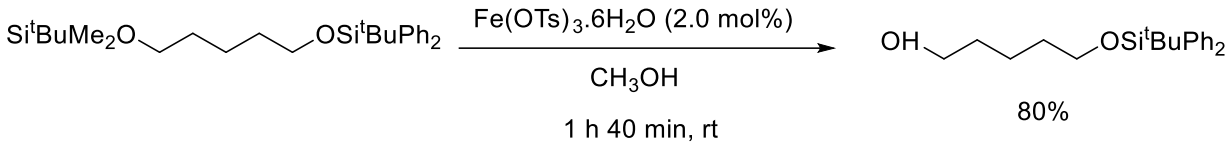
Scheme 44. Deprotection of TBDMS group in the presence of Boc group.



Scheme 45. Deprotection of aliphatic TBDMS group over phenolic TBDMS group.

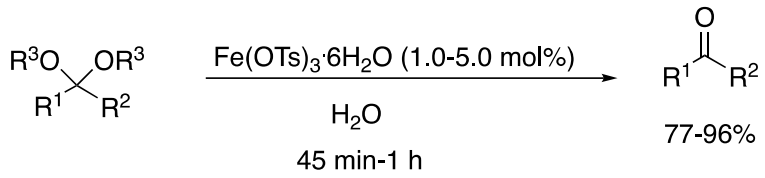


Scheme 46. Deprotection of aliphatic TBDMS and a phenolic TBDMS group.



Scheme 47. Deprotection of a TBDMS group over a TBDPS.

2.8.3. Iron(III) tosylate catalyzed deprotection of aromatic acetals in water. We have reported the iron(III) tosylate catalyzed deprotection of aromatic acetals in water as a solvent (Scheme 48).[129] Although we have previously demonstrated the iron(III) tosylate catalyzed deprotection of TBDMS ethers in methanol, no deprotection of a TBDMS group was observed when water is used as a solvent. Hence we could selectively cleave an acetal in the presence of a TBDMS ether (R^1 = *p*-^{t}BuMe$_2$SiOC$_6$H$_4$ in Scheme 48).

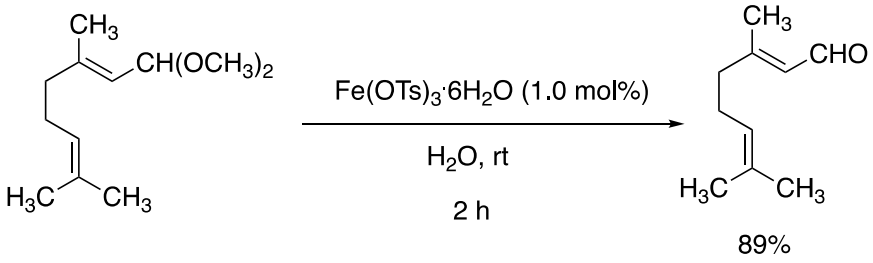


R^1 = *p*-ClC_6H_4, *m*-BrC_6H_4,
p-BrC_6H_4, *p*-$HOCC_6H_4$, *p*-$CH_3OC_6H_4$,
p-$Me_2NC_6H_4$, PhCH=CH,
p-$^tBuMe_2SiOC_6H_4$

R^2 = H, R^3 = Me or Et

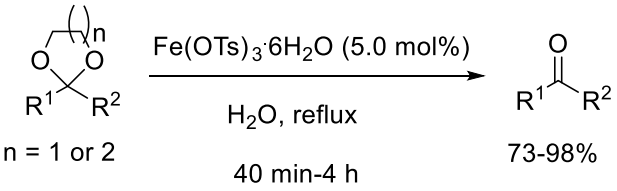
Scheme 48. Iron(III) tosylate catalyzed deprotection of aromatic acetals in water.

Although the deprotection of aliphatic acetals was sluggish under the reaction conditions, the deprotection of dimethyl acetal of a conjugated acetal derived from citral was successful (Scheme 49).



Scheme 49. Iron(III) tosylate catalyzed deprotection of citral dimethyl acetal.

The deprotection of cyclic acetals was also achieved in water under reflux conditions (Scheme 50).



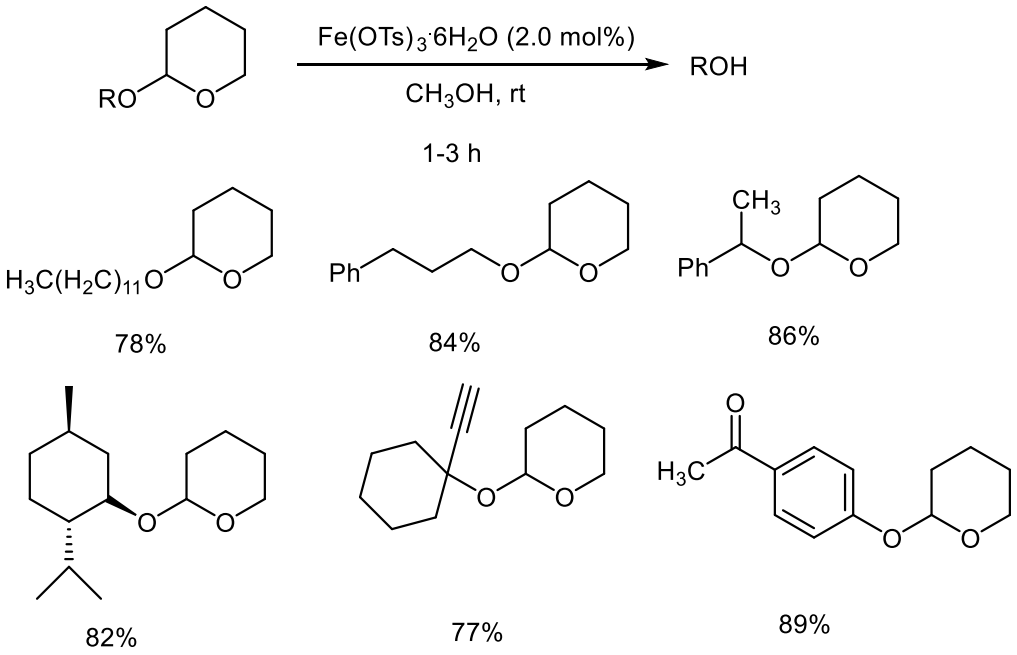
R^1 = 2-Ph_3CO-5-BrC_6H_3, *p*-$NO_2C_6H_4$,
p-ClC_6H_4, *m*-BrC_6H_4, *m*-$CH_3OC_6H_4$, *p*-$CH_3C_6H_4$
p-$CH_3OC_6H_4$, PhCH=CH, $PhCCH_3$

R^2 = H, CH_3

Scheme 50. Iron(III) tosylate catalyzed deprotection of cyclic acetals.

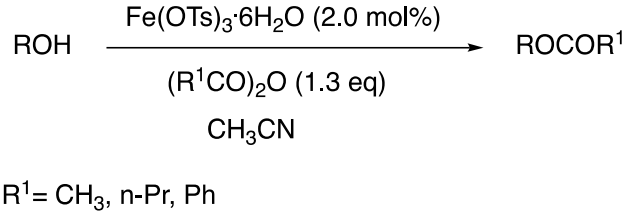
2.8.4. Iron(III) tosylate deprotection of tetrahydropyranyl ethers (THP). We have reported the deprotection of THP ethers using iron(III) tosylate as a catalyst (Scheme 51).[130] Product could be isolated via an aqueous work up or by evaporation of methanol followed by filtration through a plug of silica, thus avoiding an

aqueous waste stream. No deprotection was observed in water as the solvent. We have reported the deprotection of THP ethers using bismuth triflate, $Bi(OTf)_3$, as a catalyst under non aqueous conditions (DMF-CH_3OH) at 110 °C.[94] In contrast, the deprotection using iron(III) tosylate can be carried out in a more benign solvent, CH_3OH, and milder reaction conditions. This method also avoids DMF as a co-solvent, thus making the method greener.



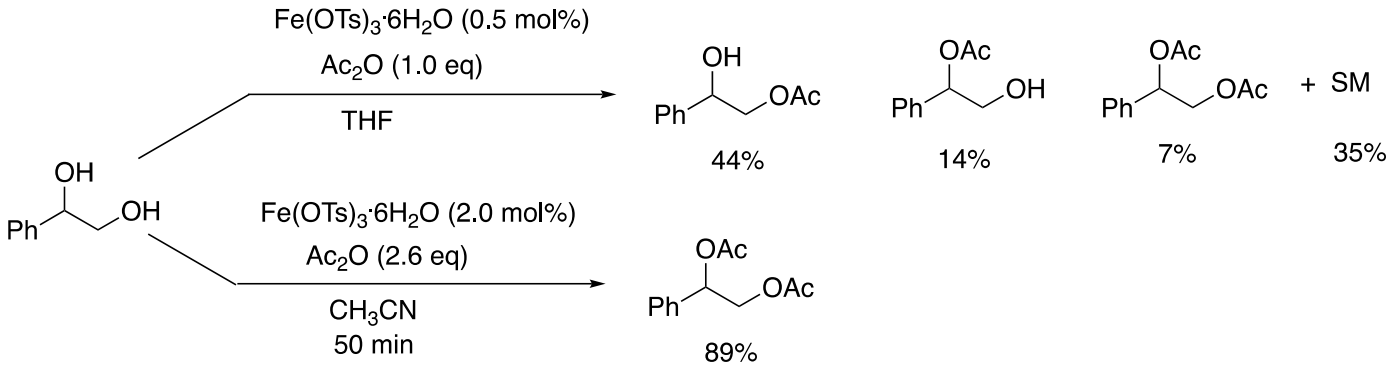
Scheme 51. Iron(III) tosylate catalyzed deprotection of THP ethers.

2.8.5. Iron(III) tosylate catalyzed acylation of alcohols, phenols, and aldehydes. We have reported that iron(III) tosylate is a mild catalyst for the acylation of a variety of alcohols, phenols, and diols (Scheme 52).[131] Not surprisingly, 1° and 2° alcohols reacted fast (10 min to 1 h) while some 3° alcohols required longer reaction times (4-21 h). Highly hindered alcohols, such as triphenylmethanol, failed to give the corresponding acetate even under reflux conditions. The mild reaction conditions make this an attractive procedure for conversion of alcohols to the corresponding acetate.



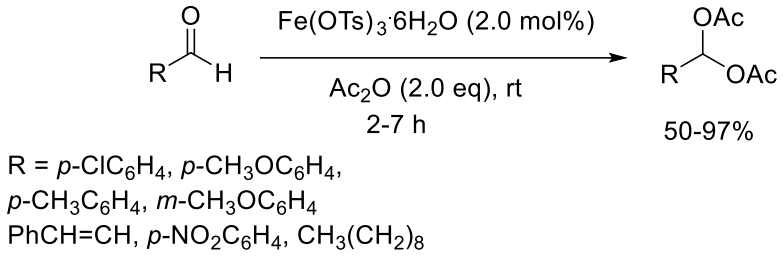
Scheme 52. Iron(III) tosylate catalyzed acylation of alcohols.

We found a difference in rates of acetylation of a 1° vs 2° alcohol in THF as the solvent. Attempts to selectively acetylate a 1° alcohol in the presence of a 2° alcohol were not very successful. Use of excess acetic anhydride afforded the diacetate in good yields (Scheme 53).



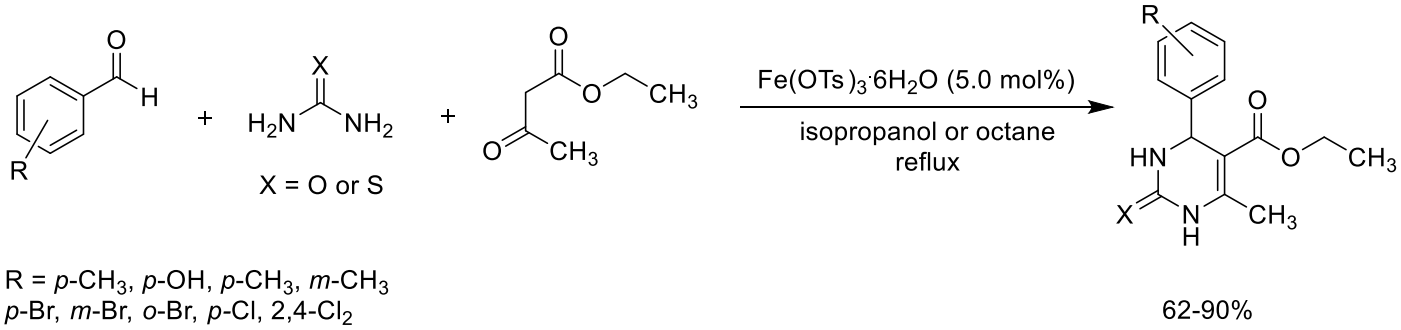
Scheme 53. Iron(III) tosylate catalyzed acylation of diols.

Aldehydes could also be converted to the corresponding 1,1-diesters (acylals) under the reaction conditions (Scheme 54).



Scheme 54. Iron(III) tosylate catalyzed synthesis of acylals.

2.8.6. Iron(III) tosylate catalyzed synthesis of 3, 4-dihydropyrimidin-2(1*H*)-ones/thiones via the Biginelli reaction. We have reported that iron(III) tosylate (5.0 mol %) is an efficient catalyst for the synthesis of dihydropyrimidinones and dihydropyrimidine thiones from a wide range of aldehydes via the Biginelli reaction (Scheme 55).[132] Dihydropyrimidinones are of interest due to the range of biological activity they exhibit.[133]



Scheme 55. Iron(III) tosylate catalyzed synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones.

Both isopropanol and octane worked as solvents. Although octane is less environmentally friendly than isopropanol, it was easily recovered using a rotary evaporator or by decantation and recycled. Both procedures avoided an aqueous work-up, thus adding to the green aspect of the methodology. The

methodology was expanded to acetals, which underwent in situ deprotection to yield the corresponding aldehydes under the reaction conditions.

Conclusions

Bismuth(III) compounds have shown promise as versatile Lewis acid catalysts for a range of organic transformations including protection-deprotection chemistry, C-C bond formations, and synthesis of a variety of heterocycles. The nontoxic nature of bismuth(III) salts makes them attractive from a green chemistry perspective. While in many examples bismuth compounds serve to generate the corresponding protic acid, they are also shown to act as a Lewis acid. When the reaction is favored by a lower pH, bismuth compounds are probably more advantageous than lanthanide salts which are not hydrolyzed to generate the protic acid. Bismuth(III) triflate is a stronger Lewis acid and is typically required in lower catalyst loading than the corresponding bismuth(III) halides. However, bismuth(III) triflate generates fluorine waste unlike the halide salts. Many of the early reactions developed in our laboratory often best in CH_2Cl_2. But with the recent ban on CH_2Cl_2, our goal is to find alternate safer solvents. Based on previous examples acetonitrile is a reasonable option for consideration. Additionally, we have demonstrated that iron(III) tosylate is also a versatile catalyst for a range of similar organic transformations. Inspired by green chemistry principles, reactions are typically worked up using ethyl acetate rather than diethyl ether for extraction. In addition, while our goals isare to develop reactions that are high yielding and give products that can be purified by recrystallization, occasionally column chromatographic purification is necessary. In such instance we use ethyl acetate-heptane mixtures rather than the toxic hexane.

Acknowledgements

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Dr. Ram Mohan got his BSc (Honors) in chemistry from Hansraj College in Delhi, India, a master's in organic chemistry from The University of Delhi, India and his PhD from The University of Maryland Baltimore under the supervision of Professor Dale Whalen. He did postdoctoral work in Dr. Robert Coates' lab at The University of Illinois Urbana Champaign. He is currently the Wendell and Loretta Hess Professor of Chemistry at Illinois Wesleyan University (IWU), an undergraduate liberal arts university. At IWU, Dr. Mohan teaches organic chemistry, advanced organic chemistry and green chemistry. His research, done exclusively with undergraduate students, is focused on developing environmentally friendly organic synthesis using bismuth(III) compounds as Lewis acid catalysts. Dr. Mohan is the recipient of multiple Fulbright grants which have allowed him to travel extensively in rural India to raise awareness about environmental issues. Dr. Mohan enjoys traveling by trains, cooking vegetarian food, drawing cartoons and doing origami.

Sophie Thorp is a native of St. Louis, Missouri and graduated from IWU in 2023 with a BS degree in chemistry. As an undergraduate, Sophie worked in Professor Ram Mohan's lab and published two manuscripts. They were the recipient of the ACS Collegiate Scholar Award for the Heartland, IL section. Currently, they attend the University of Missouri – Columbia and is pursuing a PhD in chemistry, designing ligands for organometallic catalysts in Dr. Wes Bernskoetter's lab. Sophie has several hobbies outside of chemistry, including knitting, sewing, 3D printing, thrifting, and attending renaissance festivals (in costume, of course!).

Rem Quintin David is a native of the Philippines and is currently a junior biochemistry major at IWU. Rem is currently working in Professor Ram Mohan's lab and has published two manuscripts as an undergraduate co-author. He works in the chemistry stockroom of IWU and helps set up the chemistry teaching labs at IWU. He plans to pursue a PhD in the future with an interest in natural product synthesis and the biochemical processes of plants. Rem likes to play volleyball, run, and listen to music in his free time.

