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Nucleophilic trifluoromethylation tamed☆

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Abstract

The paper reviews our recent findings on the trifluoromethylation of organic compounds using $TMSCF_3$. Direct preparation of trifluoromethylated ketones from esters, amides from alcohols and amines from imines is described. Trifluoromethylated amino alcohols are also prepared using a three-component condensation chemistry.

Keywords: Amides; Amines; Amino alcohols; Enones; Esters; Nucleophilic trifluoromethylation; $TMSCF_3$

1. Introduction

The development of methods for the efficient synthesis of fluorinated molecules is blossoming because of fluorine's ability to exert special properties (high electronegativity and its relatively close size to hydrogen) on organic molecules. Last decades have witnessed the profound use of the perfluorinated compounds in material science, agrochemistry and in pharmaceutical industry [1]. Although methods for mono and perfluorinations are well developed similar approach are not compatible for the preparation of corresponding trifluoromethylated compounds. We have discovered that $TMSCF_3$, a compound first reported by Ruppert et al. [2], but never synthetically explored as an efficient trifluoromethylating agent for a variety of electrophiles under nucleophilic conditions. A comprehensive review on the work carried out before 1997 is published [3]. A recent review covers work after 1997 [4]. In this review, we will summarize our recent findings in this field.

2. Preparation of $TMSCF_3$

The Gilman's general method [5,6] for the preparation of perfluorinated silanes from silyl halides and perfluoroalkyl metals is not suitable for the preparation of $TMSCF_3$ because of the inherent instability of trifluoromethyl organometalic precursors that decompose to difluorocarbene with the formation of metal fluorides with a strong M–F bond. A conceptually different route for the preparation of $TMSCF_3$ (**1**) was developed by Ruppert et al. [2] which involves the condensation of CF_3Br with TMSCl in presence of $(Et_3N)_3P$. Our modification [7] for the preparation of **1** greatly simplifies the Ruppert's original method (Scheme 1).

Pawelke also reported [8] that in presence of tetrakis(dimethylamino)ethylene CF_3I trifluoromethylates TMSCl to yield $TMSCF_3$ (via single electron transfer chemistry). Under similar reaction conditions, CF_3Br was ineffective.

The high toxicity of $(Et_3N)_3P$ led us to search other methods for the facile preparation of $TMSCF_3$. Following the work by Yoshida et al. [9,10] on the electrochemical trimethylsilylation of iodoarenes and more recently by Bordeau's group on the electrochemical silylation of polychloromethanes [11], arenes [12] and chloroarenes [13,14], we have prepared [15] $TMSCF_3$ using Al as the sacrificial anode in an undivided cell under constant current density (Scheme 2). Thus, CF_3Br underwent efficient trimethylsilylation with TMSCl in presence of PhOMe as a solvent and $Bu_4N^+ \cdot PF_6^-$ as an electrolyte. We have found that a small amount of HMPA was necessary for a good yield of the product. DMF, a common solvent for electroorganic synthesis, was avoided because of the possible side reaction generating CF_3CHO. This electro-assisted Barbier reaction provides an efficient way for the preparation of $TMSCF_3$.

Subsequently, Grobe and Hegge [16] have found even a simpler way to prepare $TMSCF_3$ using Al/NMP without electrochemical activation (Scheme 3).

Alternative trifluoromethylation procedures have been developed recently using trifluoromethane as the trifluoromethide source [17–19].

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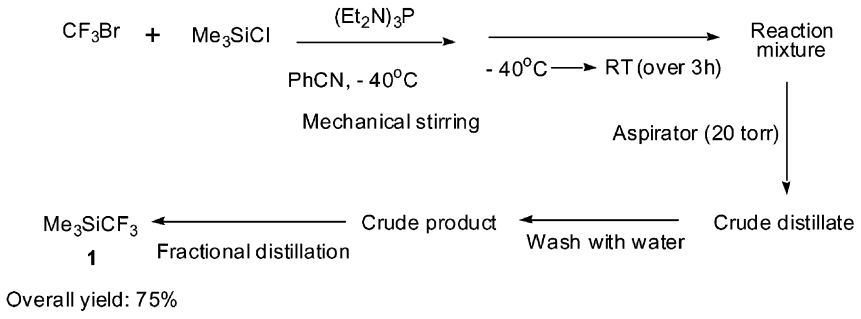
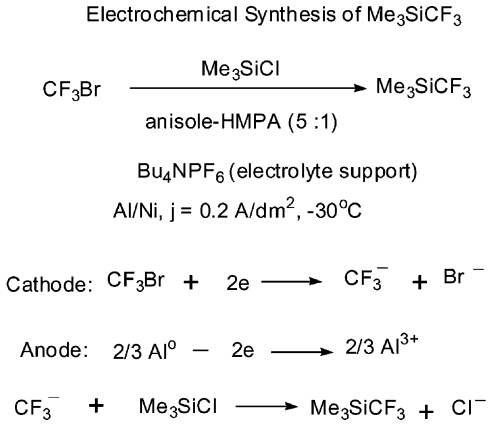


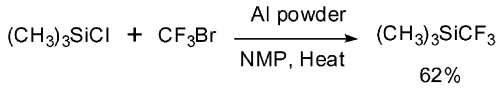
Scheme 1.



Scheme 2.

3. Synthetic application of trifluoromethyltrimethylsilane

Although $TMSCF_3$ was reported in 1984 [2], it did not find synthetic application until our own disclosure in 1989 [20]. Unlike Grignard-reagents, which are stable in the reaction medium, metal trifluoromethide decomposes readily to difluorocarbene with the formation of metal fluoride

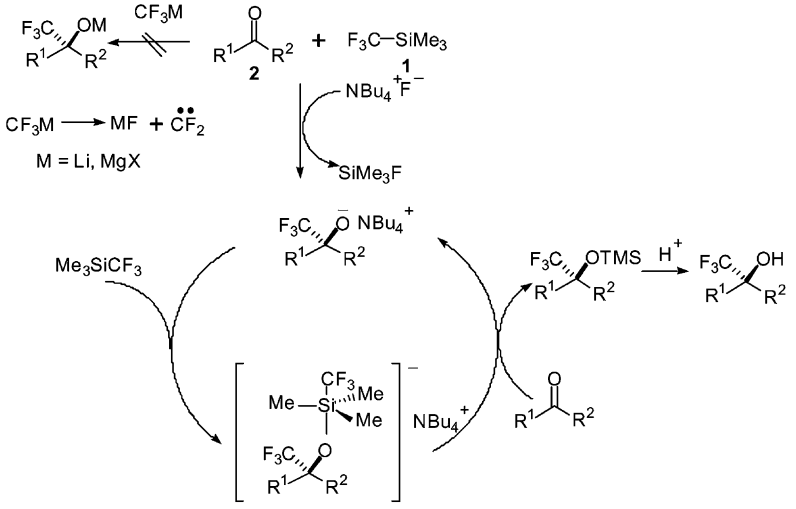


Scheme 3.

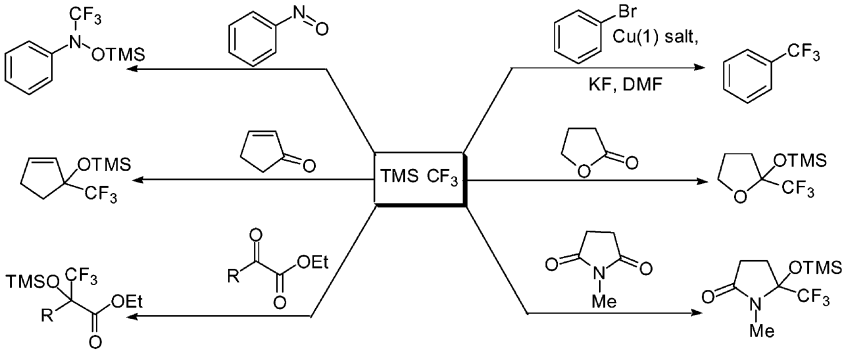
[21]. Lewis acid catalysts that found wide use as activating agents for electrophiles, such as carbonyl compounds and imines, have an adverse effect on the trifluoromethylation reaction. Only under nucleophilic conditions could the transient trifluoromethide ion be transferred to the electrophilic centers. Thus, **2** (Scheme 4) undergoes efficient trifluoromethylation in the presence of catalytic amounts of TBAF (Scheme 4). Several other electrophiles undergo efficient trifluoromethylation under these conditions [3] (Scheme 5).

4. Preparation of trifluoromethylated ketones from esters

Because of their high electrophilicity trifluoromethylated ketones form stable hydrates and mimic the transition-state analogues of substrates for proteolytic enzymes. Although



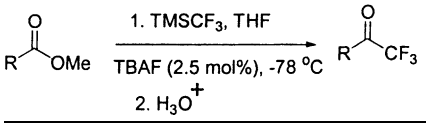
Scheme 4.

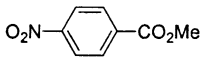
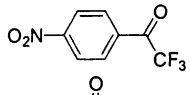
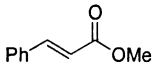
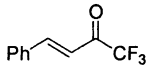
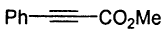
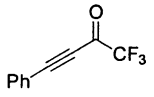
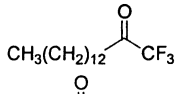
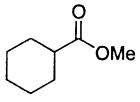
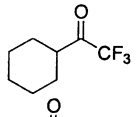
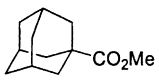
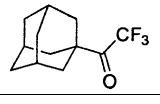


Scheme 5.

the aryl trifluoromethyl ketones can be obtained *via* Friedel–Crafts acylations (albeit, in low yields), the alicyclic and aliphatic trifluoromethyl ketones are available through multi-step operations. We had launched an investigation for the direct preparation of trifluoromethylated ketones from the corresponding esters using $TMSCF_3$. Because of the low electrophilicity of the ester compared to aldehydes and ketones, special conditions were required. When commercially available TBAF was used for the trifluoromethylation of esters no detectable amount of the desired compound was obtained. The prerequisite for successful reaction is careful drying of all solvents and reagents. Therefore, the commercial solution of TBAF was dried under argon atmosphere over activated 4 Å molecular sieves prior to use. When the reaction was performed under inert conditions with pre-dried solvent and reagent at 0°C both trifluoromethylated ketones and bistrifluoromethylated alcohols were obtained. Performing the reaction at −78°C gave exclusively the ketones (Table 1). Although THF could be used as a solvent, slow ring opening to a detectable amount of 5,5,5-trifluoro-1-trimethylsiloxypentane was observed. In general, non-polar aprotic solvents such as pentane, toluene, benzene and dichloromethane could be used. For low boiling trifluoromethylated ketones pentane is a good reaction medium, which nevertheless could be substituted by dichloromethane when solubility problems arise. Aliphatic,

Table 1
Preparation of trifluoromethylated ketones



Substrate	Solvent	*t* (h)	Product	Yield (%)
$PhCO_2Me$	Toluene	18		95
	CH_2Cl_2	18		81
	Pentane	24		85
	Pentane	24		0
$CH_3(CH_2)_{12}CO_2Me$	Pentane	24		75
	Pentane	48		72
$tBuCO_2Me$	Pentane	72		68
	Pentane	72		70

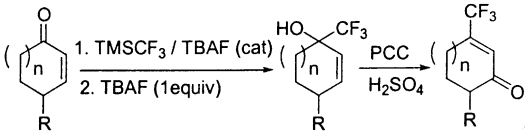
aromatic and α,β-unsaturated carboxylic esters react smoothly and gave the corresponding ketones in good to excellent yields [22]. However, under these conditions alkylnyl carboxylic esters underwent extensive polymerization. In this respect, the CsF catalyzed trifluoromethylation developed by Shreeve and co-workers allows a variety of esters, including alkynyl esters, to undergo efficient reaction with $TMSCF_3$ [23].

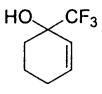
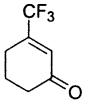
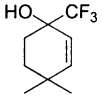
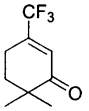
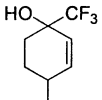
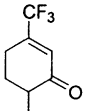
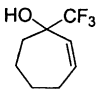
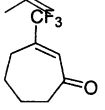
5. Preparation of 3-trifluoromethyl-2-cycloalkenones

As an application of our methodology, we have prepared α,β-unsaturated β-trifluoromethyl ketones *via* Dauben rearrangement. The ready availability α,β-unsaturated tertiary alcohols, by addition of $TMSCF_3$ to conjugate enones led us to investigate whether oxidative rearrangement of this class of compounds to 3-trifluoromethyl-2-alkenones (Table 2) takes place. Such compounds could be used as dienophiles for the preparation of polycyclic compounds such as steroids with an angular CF_3 group.

Initial oxidation of the cyclic alcohols with reagents, such as PCC, PDC, Collins and Jones reagent, were unsuccessful. Interestingly, when the reaction was carried out with PCC in the presence of small amount of conc. H_2SO_4, the desired product was obtained in 20–30% yield [24]. Attempts to improve the yield by using a stoichiometric amount of acid led to decomposition of PCC. It should be mentioned that in the presence of acid alone (catalytic or stoichiometric) no rearranged product was obtained. The present reaction is only limited to cyclic enones. Acyclic trifluoromethylated tertiary alcohols did not give any rearranged products.

Table 2
Preparation of α,β-unsaturated β-trifluoromethyl cycloalkenones

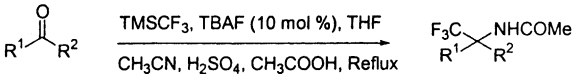


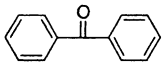
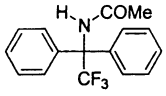
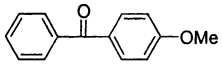
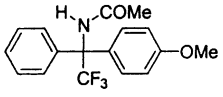
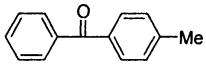
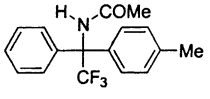
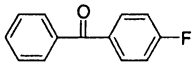
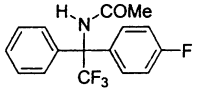
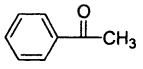
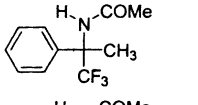
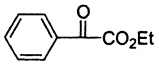
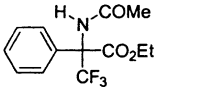
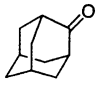
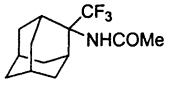
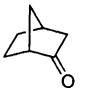
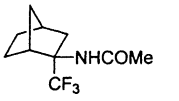
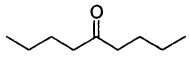
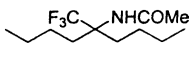
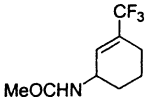
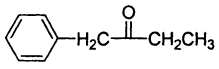
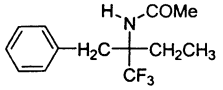
Substrate	Product	Yield (%)
		28
		25
		34
		20

6. Preparation of trifluoromethylated amides

Since the direct preparation of trifluoromethylated amines from the corresponding imines and $TMSCF_3$ was not previously successful because of the low electrophilicity of imines, we undertook conversion of the alcohol to the amide via a Ritter reaction using acetonitrile (Table 3). When in situ generated trifluoromethylated alcohol was treated in acetonitrile with excess H_2SO_4 and acetic acid under refluxing conditions, corresponding trifluoromethylated amide was obtained in good yield [25]. Reaction time and conditions differ slightly for different substrates. In general, ketones undergo smooth amidation reactions. α,β-Unsaturated carbonyl compounds undergo amidation at the double

Table 3
Preparation of trifluoromethyl acetamides



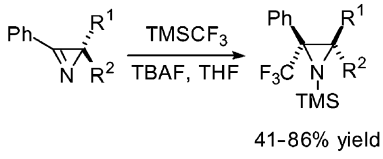
Substrate	Product	Yield (%)
		68
		66
		81
		57
		54
		59
		40
		32
		32
		54
		49

bond. Aldehydes under the above conditions do not undergo the amidation reaction.

7. Trifluoromethylation of imines

Since most of the drugs and drug candidates contain nitrogen, and fluorinated molecules often exhibit special properties, fluorinated amines are interesting building blocks for pharmaceutical research. Although successful methods for trifluoromethylation of carbonyl compounds have been known for several years, efficient nucleophilic trifluoromethylation of imines has only been recently reported [26–30]. The low electrophilicity of imines compared to carbonyl compounds inhibits the nucleophilic transfer of de facto 'CF_3^-' to them. In this context, Laurent and co-workers [26] for the first time showed that azirines underwent efficient trifluoromethylation using TBAF as well as TEAF as fluoride sources (Scheme 6). Reported yields were good to excellent. Most interestingly, the reaction is catalytic in fluoride ion initiators. Most probably the high strain release upon addition of 'CF_3' to the azirine facilitates the thermodynamically unfavorable silicon nitrogen bond formation, thus rendering the reaction catalytic.

Nelson et al. [27,28] have reported an interesting approach for direct preparation of trifluoromethylated amines (Scheme 7). Since nitrone is strongly electrophilic, it readily accepts trifluoromethide ion. Upon addition of the trifluoromethide, a negative charge on oxygen develops, resulting in an efficient catalytic initiator. The best results were obtained when *t*BuOK was used as initiator and addition–elimination was predominant when other initiators

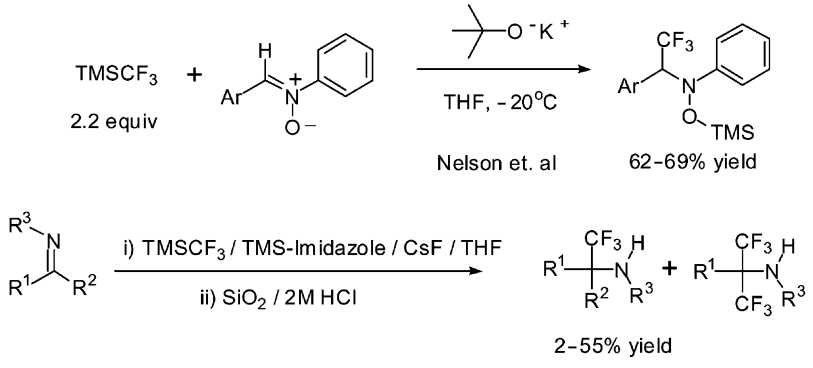


Scheme 6.

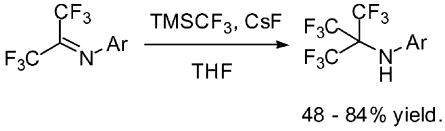
such as KF and TBAF were used. Aryl nitrones gave good to excellent yields under these conditions.

Blazejewski et al. [29] have claimed success in the addition of trifluoromethide ion to normal imines in the presence of TMS-imidazole using a stoichiometric amount of CsF (Scheme 7). The trick behind their success is the use of TMS-imidazole as an additional silylating auxiliary. However, imines with a α-hydrogen gave lower yields of the addition products. Very recently, Petrov reported [30] that *N*-aryl imines of hexafluoroacetone react efficiently with $TMSCF_3$ in the presence of CsF (Scheme 8). The reaction requires stoichiometric amount of fluoride source and proceeds rapidly in THF or monoglyme. The yields of this reaction are good to excellent.

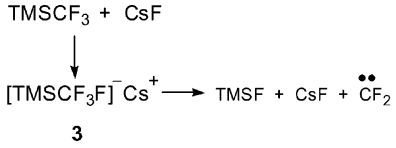
Our systematic investigation in this area began as an extension of our earlier work based on the fact that imines are less electrophilic than carbonyl compounds and the Si–N bond is weaker than the Si–O bond, i.e. propagation in the presence of a catalytic amount of the initiator is not possible. We surmised that we would be able to transfer trifluoromethide ion to the strongly electrophilic imines under non-catalytic conditions. Sulfonaldimines in the presence of a stoichiometric amount of TBAF (because of its strongly hygroscopic nature) gave mostly trifluoromethane. CsF, a successful initiator for the generation of trifluoromethide ion [23], because of its easy availability in anhydrous form, was used in a stoichiometric amount for the generation of trifluoromethide ion. Because of its basic nature and the high instability of the pentavalent intermediate **3** (Scheme 9), moderate to good yields were obtained only for the aryl-sulfonaldimines. This led us to search for a non-hygroscopic, non-metallic fluoride source. DeShong and co-workers reported that TBAT [31], a non-hygroscopic form of TBAF, serves as an effective reagent for nucleophilic displacement reactions. When we used TBAT for trifluoromethide ion generation for nucleophilic transfer to sulfonaldimines the corresponding adducts were obtained in good to excellent yields [32]. Aromatic sulfonaldimines containing no α-proton next to imine moiety reacted smoothly (Table 4). Electron withdrawing or electron donating groups on the benzene ring do not show much effect on reaction yields.



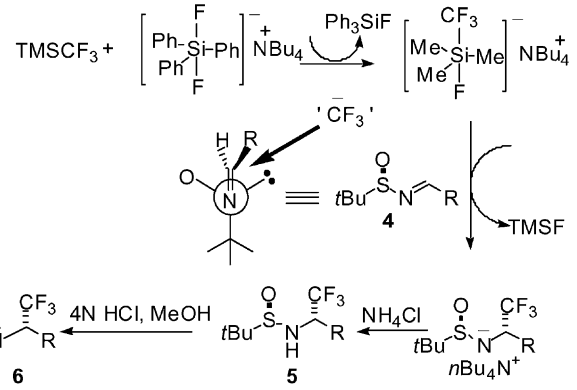
Scheme 7.



Scheme 8.



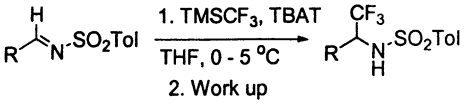
Scheme 9.

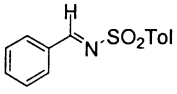
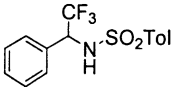
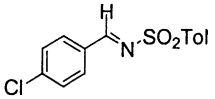
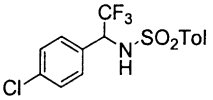
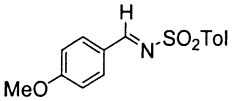
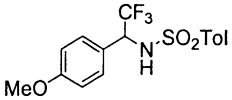
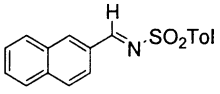
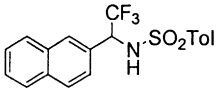
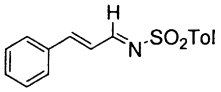
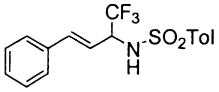
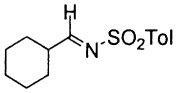
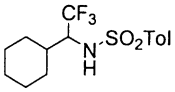
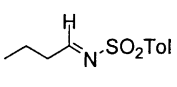
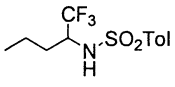
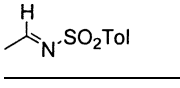
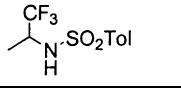


Scheme 10.

α,β-Unsaturated sulfonaldimines gave exclusively the 1,2-addition product. Even sulfonaldimines containing an enolizable proton, such as cyclohexylsulfonamide gave the trifluoromethylated adduct in 80% yield. Aliphatic imines, however, gave lower yields because of their inherent instability.

Table 4
Preparation of trifluoromethyl sulfonaldamines



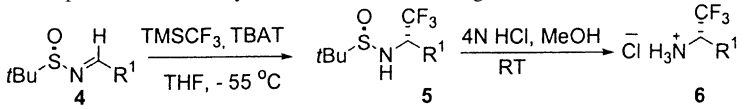
Substrate	Product	Yield (%)
		90
		87
		85
		95
		83
		80
		50
		45

Next we turned our attention to an asymmetric version of this reaction. *p*-Toluenesulfinimines [33] and *tert*-butanesulfinimines [34,35] enjoy wide use in organic synthesis for asymmetric preparation of amines. We have prepared both types of imines and have found that chiral *tert*-butanesulfinimines gave higher diastereoselectivities and, thus, higher e.e.s in trifluoromethylation reactions (Scheme 10 and Table 5). When CsF was used as the fluoride source low yields, as well as low e.e.s were obtained. Sulfinimines being less reactive compared to sulfonaldimines the decomposition pathway predominated (Scheme 9). TBAT gave higher e.e.s as well as a higher yield of the trifluoromethylated adducts [36]. The reaction is very general. Aromatic, heterocyclic and aliphatic imines react smoothly and give trifluoromethylated adducts in good to excellent yields (Table 5). The observed high diastereoselectivity can be surmised by the presence of a non-competitive open transition state (Scheme 10).

8. Trifluoromethylated amino alcohols

Trifluoromethylated amino alcohols like their non-fluorinated analogs are currently being used in peptidomimetics and transition state mimics in drug design. These alcohols could be used as novel chiral auxiliary or as ligands in asymmetric synthesis. As an application of our trifluoromethylation methodology, we have also prepared trifluoromethylated amino alcohols [38] utilizing the Petasis three component condensation reaction [37]. The main precursor of the three components reaction, the trifluorolactaldehyde was prepared according to Scheme 11. Thus, cinnamaldehyde underwent efficient trifluoromethylation in presence of a catalytic amount of CsF. Ozonolysis of the allylic alcohol in a 1:1 dichloromethane/methanol mixture gave trifluorolactaldehyde in the oligomeric form that was used directly without further purification for the coupling reaction. Aromatic, heterocyclic and styryl boronic acids undergo smooth coupling reaction in the presence of secondary amines and gave exclusively one diastereomer (Table 6).

Table 5
Nucleophilic trifluoromethylation of sulfinimines using CsF as well as TBAT as fluoride source

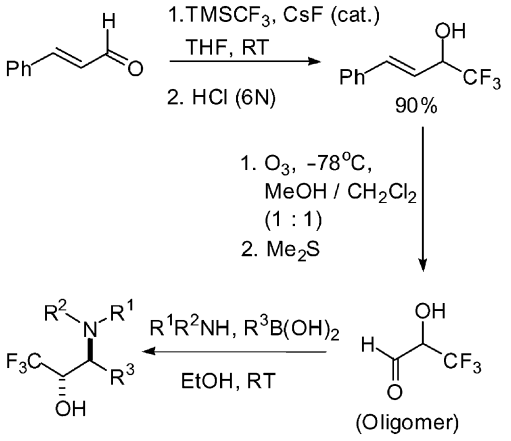


70-95% yield, 80-99% *ee*.

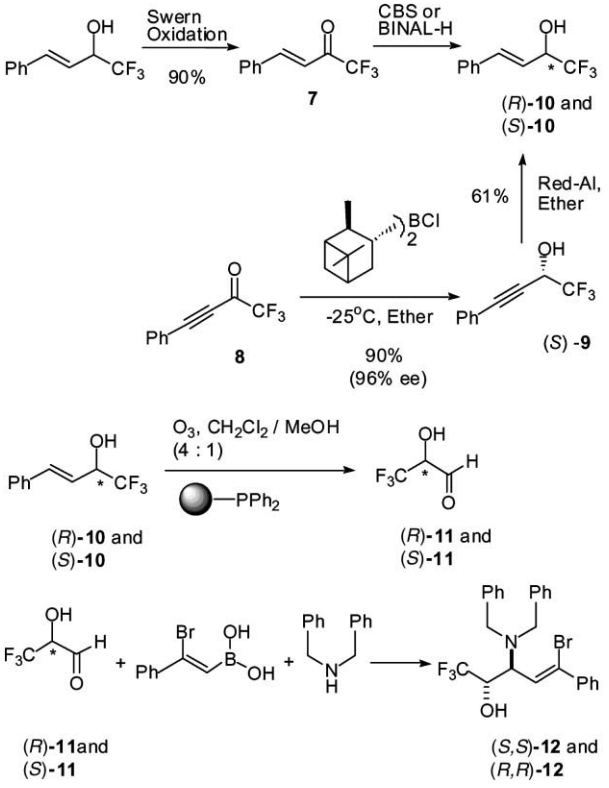
Entry	R^1	Sulfinamide **5** Yield (%)[a]	(R_s, *S*)/(R_s, *R*)[b]	Amine **6** Configuration[c]	$[\alpha]_D^{25}$[d]
1	*p*-ClPh	95 (53)[e]	>99 (85:15)[f]	*S*	+25.9 ($c = 0.72$)
2	*p*-BrPh	90 (50)[e]	>99 (80:0)[f]	*S*	+11.2 ($c = 1.5$)
3	*p*-CF_3Ph	84 (57)[e]	95:05 (85:15)[f]	*S*	+8.4 ($c = 1.5$)
4	2-Pyridyl	95 (60)[e]	99:01 (90:10)[f]	*S*	+11.7 ($c = 2.0$)
5	3-Pyridyl	92 (60)[e]	99:01 (85:15)[f]	*S*	+14.9 ($c = 1.0$)
6	2-Furyl	85 (55)[e]	97:03 (80:20)[f]	*S*	+6.6 ($c = 2.0$)
7	Ph	80 (65)[e]	97:03 (75:25)[f]	*S*[g]	+28.6 ($c = 0.65$)
8	2-Napthyl	83	94:06	*S*	+26.0 ($c = 0.75$)
9	9-Anthracyl	90	99:01	*S*	+28.8 ($c = 3.0$)
10	Cyclohexyl	88	99:01	*S*	−2.2 ($c = 3.0$)
11	*t*-Bu	75	99:01	*S*	+11.3 ($c = 0.65$)
12	$PhCH_2CH_2$	84	90:10	*S*	−15.7 ($c = 1.5$)

[a] Isolated yields of the analytically pure material. TBAT: tetrabutyl-ammonium triphenyldifluorosilicate.
[b] Diastereomeric ratios are determined by ^{19}F NMR of the crude reaction mixture.
[c] Configurations are assigned from transition state model.
[d] Optical rotations are measured in methanol and concentrations are given in the parenthesis.
[e] Yield when CsF is used as a fluoride source.
[f] Diastereomeric ratio when CsF is used as a fluoride source. Unless otherwise mentioned all the other yields and drs are when TBAT is used as fluoride source.
[g] Configuration is determined by correlation with the known compound.

For the enantioselective version of this reaction, we undertook the following two strategies for generation of the trifluorolactaldehyde in enantiomerically pure form. Reduction of alkenyl ketone **7** using Noyori's procedure gave unsatisfactorily low e.e. (Scheme 12). Corey's CBS oxazoborolidine method gave the required alcohol in 85% e.e. The best result was obtained following Brown's approach. Thus, the 1,1,1-trifluoro-4-phenyl-3-butyn-2-one **8** was reduced by (−)-DIP-chloride to (*S*)-1,1,1-trifluoro-4-phenyl-3-butyn-2-ol in 96% e.e. (*S*)-**8** was then reduced to the alkenyl alcohol using Red-Al without any stereochemical loss. We have found that the concentration of methanol during ozonolysis is crucial for

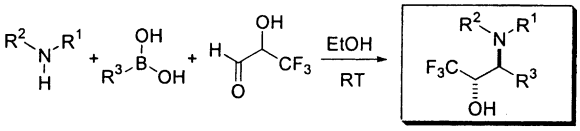


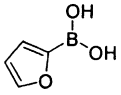
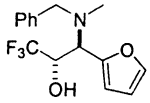
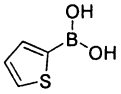
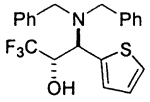
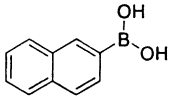
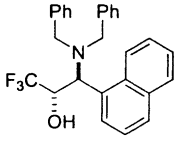
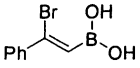
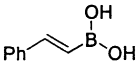
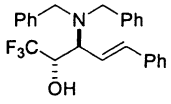
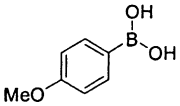
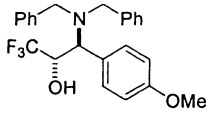
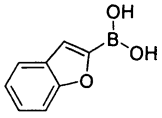
Scheme 11.



Scheme 12.

Table 6
Preparation of α-trifluoromethyl-β-amino alcohols



Amine	Boronic acid	Product	Yield (%)	d.e. (%)
			85	>99
			67	>99
			73	>99
			80	>99
			75	>99
			70	>99
			75	>99

maintaining the enantiopurity of the trifluoromethylactaldehyde. The optimum solvent concentration, 4:1 mixture of dichloromethane and methanol, is found to be superior. It should be mentioned that column chromatography after ozonolysis causes racemization of the hydroxy aldehyde **11**. Thus, when allylic alcohol (*S*)-**10** with 96% e.e. was ozonolyzed under above-mentioned optimum solvent conditions and taken directly for coupling reaction, the amino alcohol (*S*,*S*)-**12** was obtained in 92% e.e.

In summary, we have shown that $TMSCF_3$ is a versatile reagent for nucleophilic trifluoromethylation of a variety of substrates leading to potentially useful intermediates such as trifluoromethylated ketones, enones, amides, amines and amino alcohols.

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