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Recent progress in the application of fluorinated chiral sulfinimine reagents

Haibo Mei[a], Jianlin Han[a,*], Santos Fustero[b,c,*], Raquel Román[b], Renzo Ruzziconi[d,*], Vadim A. Soloshonok[e,f,*]

[a] College of Chemical Engineering, Nanjing Forestry University, Nanjing, 210037, China
[b] Departamnerto de Química Orgánica, Universidad de Valencia, E-46100, Burjassot, Valencia, Spain
[c] Laboratorio de Moléculas Orgánicas, Centro de Investigaión Príncipe Felipe, E-46012, Valencia, Spain
[d] Department of Chemistry, Biology and Biotechnologies, University of Perugia, via Elce di Sotto 8, 06123, Perugia, Italy
[e] Department of Organic Chemistry I, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel Lardizábal 3, 20018, San Sebastián, Spain
[f] IKERBASQUE, Basque Foundation for Science, María Díaz de Haro 3, Plaza Bizkaia, 48013, Bilbao, Spain

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This paper is dedicated to Professor Norio Shibata on the occasion of receiving the 2019 ACS Award for Creative Work in Fluorine Chemistry.

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ABSTRACT

The development of synthetic methodology allowing for a strategic incorporation of fluorine into target compounds is in a high demand in many areas of the chemical and pharmaceutical industries. In this regard, application of fluorinated chiral sulfinimine reagents, in particularly, *N-tert*-butylsulfinyl-3,3,3-trifluoroacetaldimine, is one of the most general and practical approaches for preparation of compounds containing pharmacophoric fluoro-amino-keto/hydroxy moieties. This article provides a timely and comprehensive overview of the recent synthetic applications of fluorinated chiral sulfinimine reagents for asymmetric synthesis of fluoro-containing polyfunctional amino-compounds of biological interest. Where it is possible, we emphasize the synthetic versatility and practicality of the reported methods.

1. Introduction

Nowadays, a designed substitution of fluorine atoms and fluorine-containing groups for hydrogen is rather an established concept in the development of new pharmaceuticals [1], agrochemicals [2], and materials [3] possessing some advanced desirable properties. Thus, the presence of fluorine atoms in healthcare products is becoming an increasingly common structural feature [1,4], motivating the development of fluoro-organic synthesis [5]. Over past decade, introduction of trifluoromethyl groups, such as C-CF_3, O-CF_3 and S-CF_3, has received some augmented interest, due to the apparently advantageous pharmaceutical profile of CF_3-containing drugs [1,5,6]. However, to access the full biological potential of trifluoromethylation, significant scientific efforts are needed to provide for strategic introduction of these moieties into the structures of organic molecules. Some success was already achieved for preparation of aromatic/heteroaromatic compounds containing CF_3-groups [5–7]. By contrast, synthesis of aliphatic CF_3-containing compounds is still significantly underdeveloped. One of the most active areas of research is focusing on the synthesis of fluorine-containing amines and amino acids [8], which, along with other tailor-made amino acids [9] are playing an increasingly important role in new drug development [10,11]. For example, introduction of fluorine atoms and fluorine-containing groups into the strategic positions relatively to the amino group, is an efficient approach for fine-tuning the molecular properties of biologically active amino compounds by rational adjustment their physicochemical characteristics, such as, their acid/base properties [11,12]. For example, the 1-amino-2,2,2-trifluoroethyl [$CF_3-CH(NH_2)$–] moiety is of considerable interest as a proven pharmacophore unit [13] found in the structure of recently developed new drug Odanacatib (**1**, Fig. 1), introduced to the market for treatment for osteoporosis and bone metastasis [14].

The pharmaceutical potential of compounds containing the 1-amino-2,2,2-trifluoroethyl system is far from being fully explored, motivating the development of chemistry allowing for practical synthesis of this and related fluorinated moieties. Among currently available methodology for preparation of $CF_3-CH(NH_2)$– bearing compounds, one can mention the reductive amination [14,15] and biomimetic transamination [16,17], utilizing the corresponding carbonyl compounds; nucleophilic additions to fluorinated [18] and fluoro-alkylation of non-fluorinated imines [19]. However, over the recent decade nucleophilic additions to (*S*)- and (*R*)-*N-tert*-butylsulfinyl-3,3,3-trifluoroacetaldimines (**2**) (Fig. 1) have become the most widely used

* Corresponding authors.
E-mail addresses: hanjl@nju.edu.cn (J. Han), santos.fustero@uv.es (S. Fustero), renzo.ruzziconi@unipg.it (R. Ruzziconi), vadym.soloshonok@ehu.es (V.A. Soloshonok).

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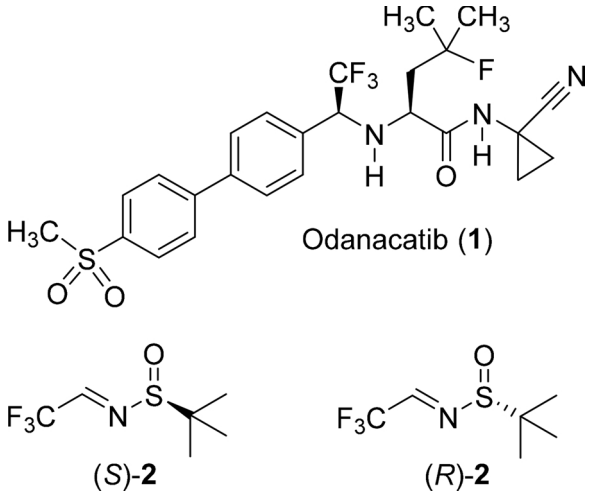


Fig. 1. Structure of Odanacatib (**1**), (*S*)- and (*R*)-*N*-*tert*-butylsulfinyl-3,3,3-trifluoroacetaldimine (**2**).

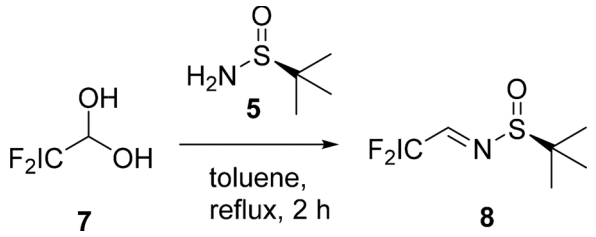
approach for preparation of various fluoro-amino derivatives [20,21]. Advantages of these imines applications include fascinating synthetic versatility provided by high electrophilicity of the C═N bond; usually very high level of diastereoselectivity executed by combination of stereocontrolling properties of *tert*-butanesulfinamide [20,21] and trifluoromethyl [22] groups.

The early reports on synthetic applications of imines **2** and related reagents have been discussed in the review articles [20,21]. Here we provide the overview of the most recent works published since 2016 as well as some papers missed in the previous coverage.

2. Synthesis of fluorinated chiral sulfinimine reagents

Synthesis of fluorinated imines is not an ordinary feat. Due to the highly electrophilic nature of C═N bond these derivatives are very reactive towards nucleophiles [23]. Thus any traces of water or alcohols can easily react with these imines affording stable gem-amino-alcohols or -ethers [24]. Accordingly, the early reports on chemistry and applications of reagents **2** resorted to the in situ formation of the imine species [21,25]. Recently, Han and coworkers [26] devoted a special study examining various procedures for preparation of structurally different *N*-*tert*-butylsulfinyl-imines [26].

As presented in Scheme 1, the authors [26] recommend procedure



Scheme 2. Preparation of imine **8** bearing chemically and thermally sensitive CIF_2 group.

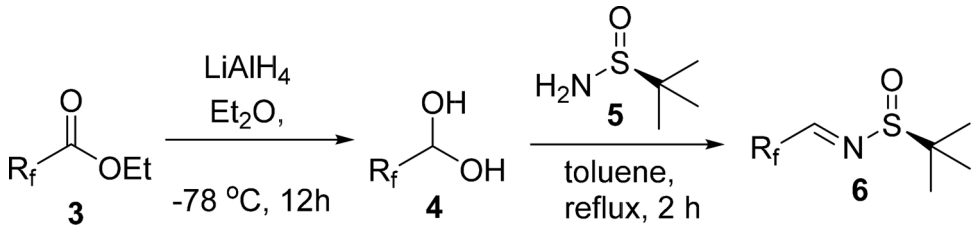
starting with readily available esters **3**, which are, first, reduced with $LiAlH_4$ to furnish *gem*-diols **4**, which are easily isolated by extraction. Due to the quantitative yields on this stage, intermediates **4** do not require any purification and can be reacted with (*S*)- or (*R*)-*tert*-butanesulfonamide **5** under the usual Dean–Stark conditions. Drawing inspiration form the work reported by the Tosoh group [24] the authors suggest the isolation of the target imines via distillation under reduced pressure. For example, imines **6a-f** are distilled at about 60 °C/3.0 mmHg. Chemical yields of thus prepared imines **6a-f** are not spectacular, but the method allows for preparation of highly chemically and optically pure products (> 99%).

It was shown that this distillation protocol has some limitation depending on chemical stability or physicochemical properties of the target imines. For example, as shown in Scheme 2, imine **8** bearing very sensitive CIF_2 group cannot be distilled without noticeable thermal decomposition.

In this case, the authors [26] suggest using imine **8** without isolation. They indicate that, based on the ^{19}F-NMR analysis of the crude reaction mixture, one can estimate at least 70% purity of thus in situ prepared imine **8**.

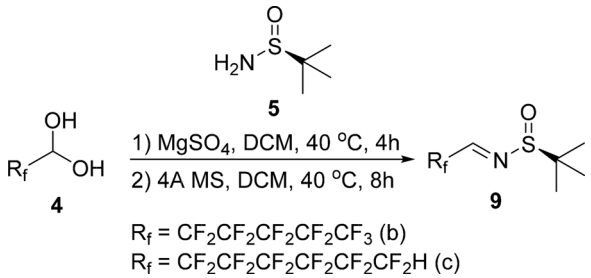
Similar problem with the distillation of the target imines was observed in the case of derivatives bearing long-chain poly-fluoro-alkyl groups (Scheme 3).

In particular, compounds **9**, possessing C_5F_{11}, and C_6HF_{12} groups, require too high temperature for practical purification via distillation, resulting in partial thermal decomposition. The authors [26] suggest an alternative procedure for their preparation described in Scheme 3. Applications of $MgSO_4$ in dichloromethane, on the condensation step, and molecular sieves, for the dehydration stage, were found to be quite efficient for in situ synthesis of this type of long-chain *N*-*tert*-butylsulfinyl-aldimines [26].



R_f	CF_2H	CF_2Cl	CF_2Br
	6a, 40%	**6b**, 33%	**6c**, 21%
	CF_2CF_3	$CF_2CF_2CF_3$	$CF_2CF_2CF_2CF_3$
	6d, 62%	**6e**, 58%	**6f**, 55%

Scheme 1. Synthesis of *N*-*tert*-butylsulfinyl-imines containing CHF_2, $CClF_2$, $CBrF_2$, C_2F_5, C_3F_7, C_4HF_8.



Scheme 3. Synthesis of *N-tert*-butylsulfinyl-imines containing C_5F_{11}, and C_6HF_{12} groups.

3. Reactions with detrifluoroacetylatively in situ generated enolates

Detrifluoroacetylative generation of fluoro-enolates is an emerging area of high impact research in the past several years. This detrifluoroacetylative reaction was developed by Colby and coworkers in 2011 [27]. They found that the selective cleavage of C—C bond of the difluoro *gem*-diols happens under mild conditions. The corresponding fluorinated enolates could be generated in the presence of base through the release of trifluoroacetate. These *in situ* generated fluorinated enolates were successfully used as nucleophiles in many types of asymmetric reactions, using stoichiometric or catalytic mode, which allows for rather synthetically simple and practical installation of CF_2, CHF and quaternary CF structural units into various types of organic compounds [28].

In 2016, Han and coworkers reported the discovery of detrifluoroacetylative in situ generation of the new type of fluorinated amide enolates derived from 3-fluoroindolin-2-one and their asymmetric Mannich additions with sulfinyl-aldimines bearing fluoroalkyl groups (Scheme 4) [29]. It should be mentioned that the fluorinated amide enolate is unstable and difficult to generate, and has never been explored in the detrifluoroacetylative reaction. These fluorinated amide enolates could be easily generated from the *gem*-diols **10** in the presence of LiBr and DIPEA (*N*,*N*-diisopropylethylamine). They reacted with the fluorinated sulfinyl-aldimines **6** smoothly without the use of any additives at −40 °C within 5 min, which gave rise to the α-fluoro-β-fluoroalkyl-β-amino-indolin-2-ones containing C–F quaternary stereogenic centers **11** with 79–97% yields and high diastereoselectivities. The reaction showed a wide substrate scope, and a series of substituted 3-fluoroindolin-2-one derived *gem*-diols **10** and fluorinated imines could all be well tolerated in this system. In particular, only one diastereomer was obtained for the imines bearing CF_2Cl, CF_2Br, C_2F_5 and C_3F_7 perfluoro-alkyl groups.

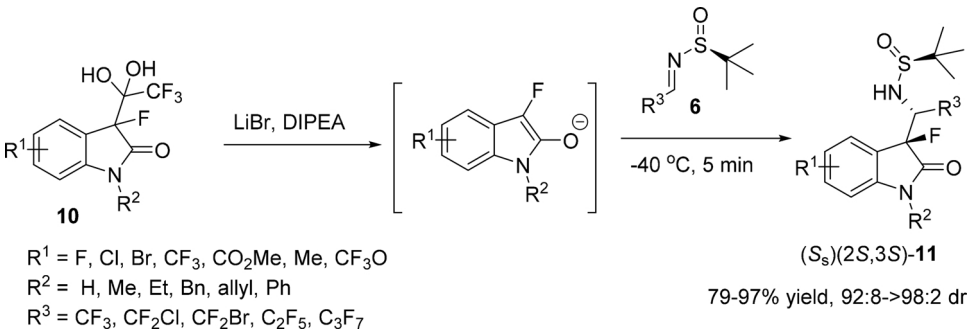
After that, the same group developed the similar detrifluoroacetylative Mannich reaction of in situ generation of fluorinated amide enolates derived from 3-fluoroindolin-2-one with several fluoroalkyl imines (**6**, **9**) [26]. In this work, the scope of imine was extensively extended, and the imines bearing C_4F_9, C_4HF_8, C_5F_{11}, $C_6F_{12}H$ all worked very well in the detrifluoroacetylative asymmetric Mannich addition reaction with 2-Me-THF as solvent at −40 °C, resulting in the corresponding product **12** in 73–81% yield and almost completely controlled diastereoselectivities (> 98:2 dr) (Scheme 5).

To realize the synthetic potential of this asymmetric detrifluoroacetylative Mannich methodology, Han, Soloshonok and co-workers tried to use the non-fluorinated imines **13** in this asymmetric detrifluoroacetylative Mannich reaction of 3-fluoroindolin-2-one derived *gem*-diols **10** in 2017 [30]. After the reaction condition optimization, they found the reaction could be conducted with acetonitrile as the solvent at 0 °C. Several types of regular sulfinyl aldimines, including aryl, heterocyclic, alkyl, alkenyl and alkynyl groups, were well tolerated in this reaction, which afforded the corresponding product in 64–97% yields and > 98:2 diastereoselectivities (Scheme 6).

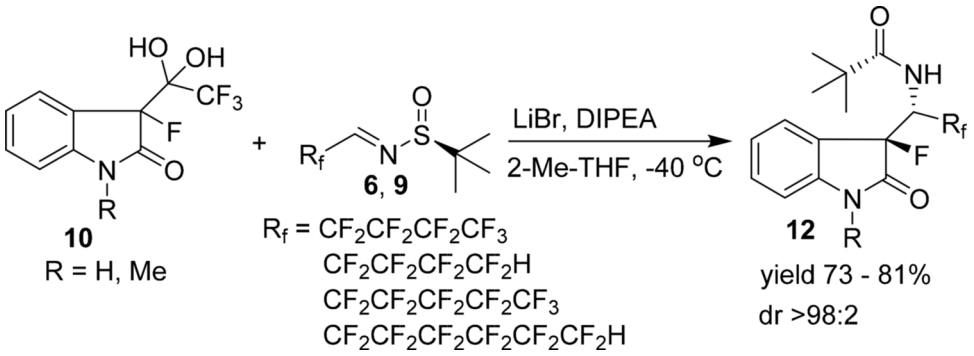
They determined the absolute configuration of the expected product by a crystallographic analysis, and the result indicates a different configuration was obtained in sharp contrast to the configuration reported for the reactions of (S_s)-CF_3-sufinylimine [28e,29]. The imines used in this reaction do not contain the strong electron-withdrawing group, such as a trifluoromethyl, thus, the additional stabilization via Li-coordination to the S—O oxygen in the transition-state could occur, which is never observed in the case of CF_3-sulfenylimines (Fig. 2). This work could be looked at as a successful supplement for the research on fluorinated imines.

In 2017, Han, Soloshonok, and co-workers designed a new type of fluorine imine, *N-tert*-butylsulfinyl-(perfluoro)benzaldimine **15**, which was synthesized via direct condensation of pentafluorobenzaldehyde and sulfonamide with dichloromethane as solvent and Cs_2CO_3 as a base [31a]. The reactivity and stereocontrolling properties of this new designed imine **15** were investigated by the asymmetric detrifluoroacetylative reaction with 3-fluoroindolin-2-one derived *gem*-diols **10**. The reaction could be conducted under simple reaction conditions and tolerated a wide range of *gem*-diols, which afforded the corresponding β-perfluorophenyl-β-amino-indolin-2-ones **16** in good to excellent yields and diastereoselectivity (Scheme 7). In particular, the *N*-H free *gem*-diols also worked well in this reaction, resulting in slightly lower chemical yields. They also did the deprotection reaction of the obtained product by the removal of the sulfinamide chiral auxiliary under HCl/methanol conditions. As the [$C_6F_5CH(NH_2)$-] structural feature is expected to have pharmacophoric properties, thus this reaction provides an easy access to such pentaflurophenyl-containing amino compounds [31b,c].

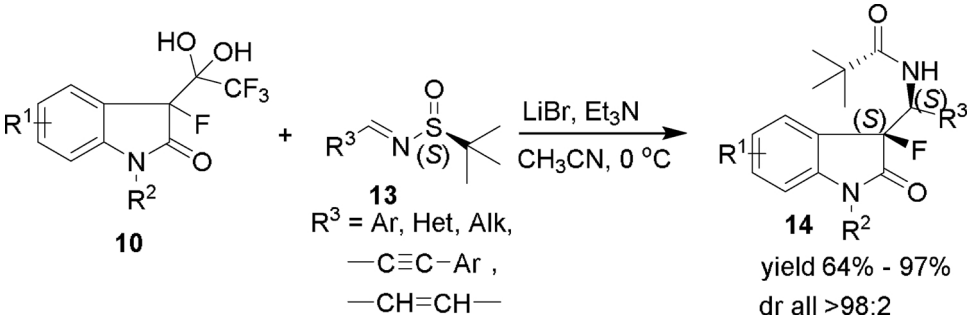
In 2015, Han and coworkers reported a Ni-catalyzed asymmetric decarboxylative Mannich reaction between chiral sulfinyl-3,3,3-trifluoro-acetaldimine and β-keto-acids, which was performed at room temperature affording β-trifluoromethyl-β-amino ketones with excellent yields and diastereoselectivities [32]. In 2017, the Cossío group developed another type of decarboxylative Mannich reactions of β-keto acids **17**, by use of non-fluorinated *N-tert*-butanesulfinyl aldimines **18** as electrophiles (Scheme 8) [33]. The reaction did not use any metal-catalyst, affording the β-amino ketones **19** in the presence of LiOH with



Scheme 4. Detrifluoroacetylative Mannich reaction of fluorinated imines.



Scheme 5. Detrifluoroacetylative Mannich reaction of fluoroalkyl imines.



Scheme 6. Detrifluoroacetylative Mannich reaction of imines.

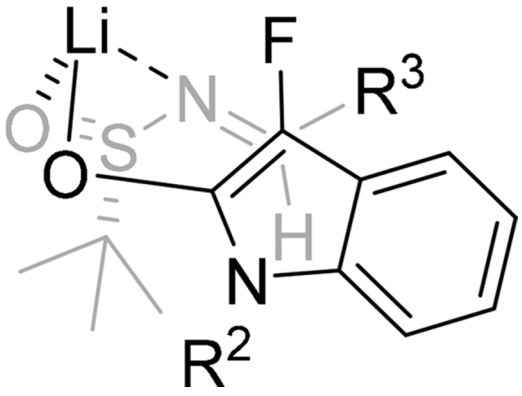


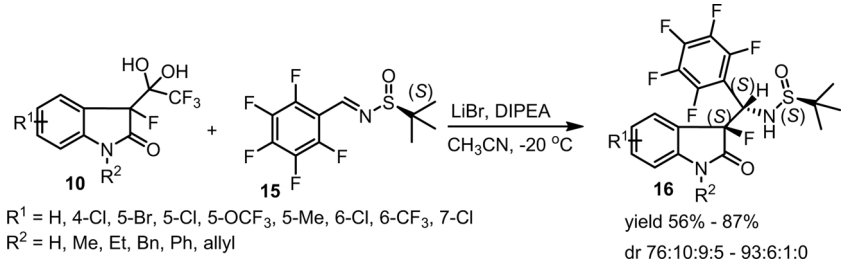
Fig. 2. Transition state.

high levels of diastereocontrol and high yields. They also did the DFT calculations of this reaction, which indicated the existence of coordination between the lithium atom and the oxygen of sulfinyl moiety. They also proposed an eight-membered cyclic transition state involved in this reaction, which is different from the previous reported results from the fluorinated imines. It should be mentioned that this synthetic strategy has been used in the synthesis of the piperidine alkaloid (−)-pelletierine starting from 3-oxobutanoic acid with total 66% chemical yields.

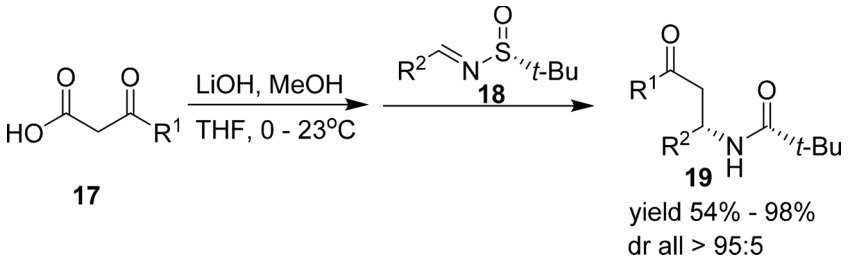
4. Ene-type reactions

The use of ene reactions is one of the most adopted strategies in the carbon-carbon bond formation, especially when very electrophilic species are involved as enophiles. Some years ago, Ruzziconi and coworkers showed that properly substituted 3-methyleneindolines **22**, easily prepared from Boc-protected 2-bromoanilines **20** by a two-steps procedure, including nitrogen propargylation (**21**), proved to be a valuable building blocks for the synthesis of highly functionalized 3-alkylsubstituted indoles **23**, Thus, regioselectively fluorinated diethyl 2-hydroxy-2-[(1*H*-indol-3-yl)methyl]malonates (**23**, R = CO_2Et), racemic ethyl 2-hydroxy-3-(1*H*-indol-3-yl)propionates (**23**, R=H) and ethyl 2-hydroxy-3-(1*H*-indol-3-yl)-2-trifluormethylpropionates (**23**, R = CF_3) were obtained in good yield by simply heating 1-(*tert*-butoxycarbonyl)-3-methyleneindoline **22**, with an equimolar amount of diethyl ketomalonate, ethyl glyoxalate and ethyl 3,3,3-trifluoropyruvate, respectively, at 100 °C, for 0.5–2 h, under solvent free condition (Scheme 9) [34].

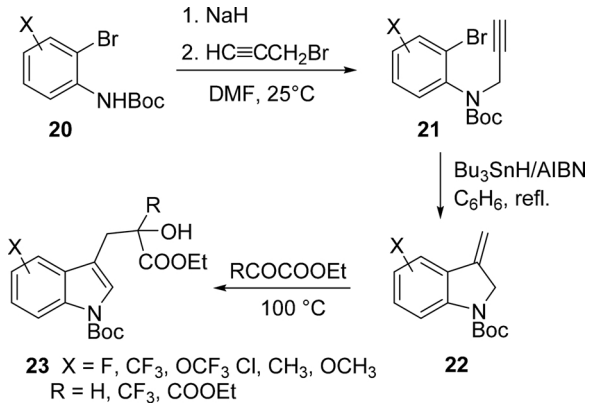
Taking into account that the chemistry of trifluoroacetaldimines is rather well-studied [5b,5f,8b,21a,21d,35], it was very surprising that only a single example of the corresponding ene-type reactions has been reported so far [36]. Thus, regardless of the apparent synthetic opportunities for the preparation of polyfunctional biologically relevant



Scheme 7. Detrifluoroacetylative Mannich reaction of (perfluoro)benzaldimine.



Scheme 8. Decarboxylative Mannich reactions of β-keto acids.



Scheme 9. The synthesis of functionalized 3-alkylsubstituted indoles **23**.

compounds, ene reactivity remained a virtually unexplored area of *N*-sulfinyl imines [20b], until Han, Soloshonok, Ruzziconi and coworkers thought about facing this challenge, especially in its the most difficult, uncatalyzed and solvent-free mode [37]. They assumed that the insufficient reactivity of the C=N bond could be counterbalanced by the electron rich carbon–carbon double bond of the corresponding reaction partner. Thus, while the electrophilicity of the C=N bond in *N*-sulfinyltrifluoroacetaldimines is substantially lower, as compared with the above-mentioned carbonyl compounds, the exceptional reactivity of the 3-methyleneindolines might be sufficient for the ene reaction to take place. Accordingly, they found that simple heating of regioselectively substituted *N*-Boc-protected 3-methyleneindolines (**22**) with (*R*)-*N*-*tert*-butylsulfinyl-3,3,3-trifluoroacetaldimine (**2**), under solvent-free conditions, leads to the corresponding ene (S,R_S)- and (R,R_S)-adducts (**24**), respectively, in good yields and diastereoselectivities (Scheme 10).

Noteworthy, the absolute configuration of the major product was assigned by comparing the experimental VCD spectrum with those reproduced by DFT calculations effected on the basis of arbitrarily assigned configuration [38,39].

From the mechanistic point of view, the observed stereoselectivity was rationalized by considering the *ene* reaction like a [4 + 2] pericyclic reaction running across a unique transition state. As shown in Fig. 3 (*a*), attack of the exocyclic methylene of indoline occurs preferentially at the *re* face of C=N double bond through a distorted skew-boat conformed transition state in which the bulky trifluoromethyl group occupies an equatorial position.

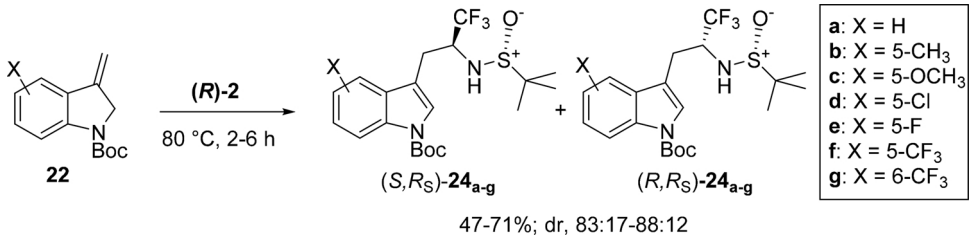
The authors also proved that the different protection (Boc and –SO^{t}Bu) at the two nitrogen atoms of the resulting tryptamines can be chemoselectively removed under different reaction conditions, allowing the remaining protecting group to carry on its specific regio- (Boc) or stereoselective (–S*O^{t}Bu) orientation in further synthetic transformations. Deprotection of both the nitrogen atoms gave optically pure α-(trifluoromethyl)tryptamines, suitable for the asymmetric synthesis of high pharmaceutical interest (Scheme 11). For example, deprotection of the adduct (R,R_S)-**24$_c$** (X = 5-OMe) with 6*M* HCl in methanol in the presence of 1.2 eq formaldehyde gave the corresponding carboline (*R*)-**25$_c$** in moderate yield, while under the same conditions adduct (R,R_S)-**24d** (X = 5-Cl) react with pyridine-3-carbaldehyde to give a 2:1 diastereomeric mixture of carbolines (1*R*,3*R*)-**25** and (1*S*,3*R*)- **25**, respectively.

5. Mannich-type additions

The asymmetric Mannich-type reaction is another powerful synthetic tool for carbon-carbon bond-forming processes in the synthesis of β-amino carbonyl compounds [40]. Due to the high selectivity described in this addition and the fact that the resulting nitrogen-containing compounds have been used as building-blocks in the construction of many biologically important molecules, this methodology represents an indispensable tool in total synthesis [41]. In this sense, the addition of different nucleophile derivatives to fluorinated chiral sulfinimines should be taken into account in this work, given that it is directly related to the objective of this review.

In a contribution concerning the addition of C-nucleophiles to fluorinated imines [18c,21a], Fanhong Wu and coworkers reported the 1,2-addition of organolithium reagents to chiral fluorinated α,β-unsaturated *N*-*tert*-butylsulfinyl ketimines **26** without any additives (Scheme 12) [42]. Starting their investigation with the addition of a 2.0 M solution of PhLi in Et_2O at −78 °C, the corresponding α-tertiary fluoroalkyl allylic amine **27** was obtained in excellent diastereoselectivity (98:2) and good yield (78%). A further increase in the reaction temperature to −40 °C and lowering the concentration for organolithium reagent to 0.2 M allowed a regio- and diastereoselective 1,2-addition (70–98% *de*) of diverse aryllithium, alkyllithium and alkynyllithium reagents to a variety of fluoroalkyl (CF_3, HCF_2, $ClCF_2$, *n*-C_3F_7, *n*-C_5F_{11}) α,β-unsaturated *N*-*tert*-butanesulfinyl ketimines **26**, affording various α-fluoroalkylated allylic amines **27** in good to high yields (48–99%).

The synthetic utility of these compounds was highlighted when



Scheme 10. Ene reaction between *N*-Boc-protected 3-methyleneindolines (**22**) with (*R*)-*N*-*tert*-butylsulfinyl-3,3,3-trifluoroacetaldimine (**2**).

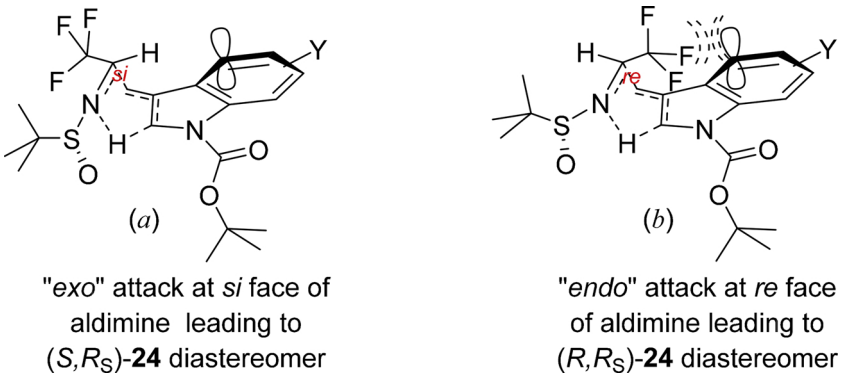
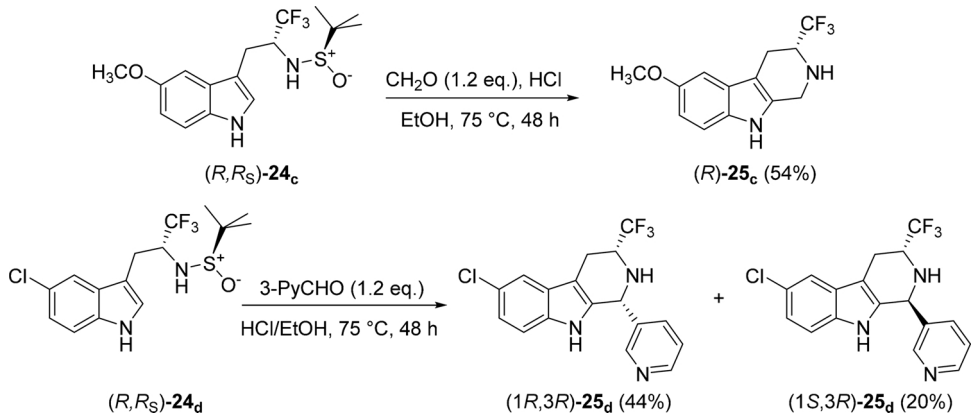


Fig. 3. Transition state of the ene reaction.

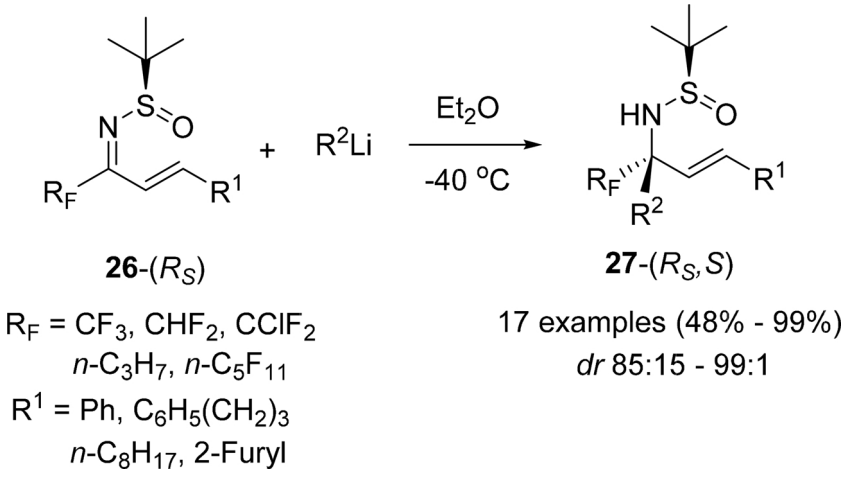


Scheme 11. Deprotection and cyclization reaction of **24** (ref. Scheme 10).

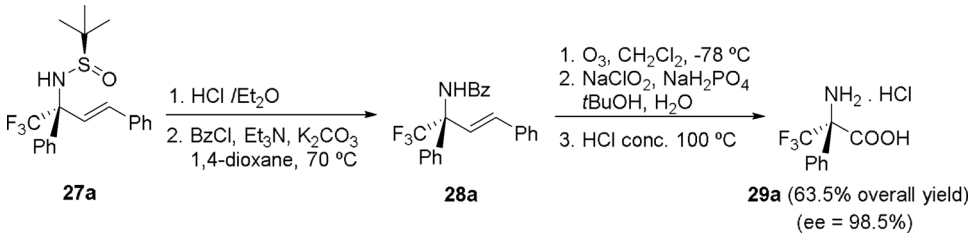
trifluoromethyl-adduct **27a** was used for the enantiomerically pure synthesis (*ee* = 98.5%) of the corresponding α-trifluoromethyl α-amino acid **29a**, through subsequent functionalization of the double bond in a high overall yield (Scheme 13).

Continuing with the C–H functionalization strategy to access synthetically useful structural motifs, in 2016 Ellman and coworkers described an efficient route for Co^{III}-catalyzed three-component addition to *N-tert*-butanesulfinyl imines [43]. After optimization of previous research employing the preformed catalyst $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ for the direct C–H bond addition to aldehydes, using LiOAc as the most efficient acetate salt and studying the most suitable number of equivalents of aldehyde, the transformation was adapted for the addition to chiral *N-tert*-butanesulfinyl imines **30**. This Co^{III}-catalyzed asymmetric three-component coupling process proceeded with high diastereoselectivities (88–92% *de*) to afford the corresponding branched amine products **31** (Scheme 14).

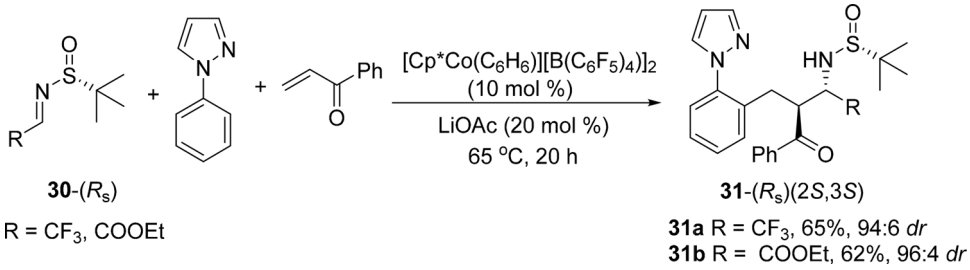
In order to contribute to the direct addition processes to imines as electrophile reagents, Qing and co-workers have explored the asymmetric vinylogous Mannich reaction (VMR) which involves γ-addition to fluorinated imines and provides access to optically active δ-amino-δ-fluoroalkyl-α,β-unsaturated carbonyl compounds [44]. The corresponding enolates of 3-alkenyl-2-oxindoles **33** reacted regioselectively through the γ-position with CF_3- and CHF_2-sulfinyl aldimines **32** with moderate to high diastereoselectivities (68–96% *de*) (Scheme 15). Furthermore, taking into account the stereoselectivity related to the geometric configuration of the olefinic moiety, it should be noted that



Scheme 12. The 1,2-addition of organolithium reagents to fluoroalkyl α,β-unsaturated *N-tert*-butanesulfinyl ketimines **26**.



Scheme 13. Application of α-trifluoromethylated allylic amine **27a** for the synthesis of optically active α-trifluoromethyl α-amino acid.



Scheme 14. Co^{III}-catalyzed asymmetric three-component coupling process applied to *N-tert*-butanesulfinyl imines **30**.

this addition was completed with satisfactory stereocontrol. The reaction was carried out with Ti(O*i*Pr)$_4$ and KHMDS to afford structurally complex derivatives **34**, α-alkylidene-δ-amino-δ-fluoroalkyl oxindoles, with (*Ss*,*S*) as absolute configuration.

More recently, an asymmetric VMR between fluoroalkylsulfinyl imines **32** and dicyanoalkenes **35** was reported by Fustero and coworkers (Scheme 16) [45]. As excellent vinylogous donors, α,α-dicyanoalkenes **35** act as nucleophiles through the γ-position using *t*-BuOK, to afford vinylogous adducts **36** with moderate to good yields (30–95%) and excellent diastereoselectivity (*dr* = > 99:1). However, the authors observed a surprising inversion in the stereochemistry of the final compounds in comparison with previously described asymmetric VMR using similar fluorinated imines. The proposed chelated transition state could explain the *cis* relative relationship of the fluorinated group and the *tert*-butyl sulfoxide group.

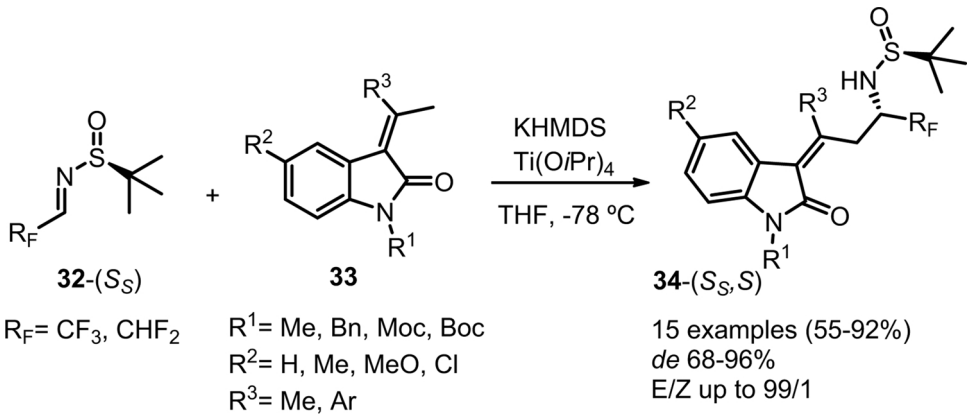
In addition, in order to prove the applicability of this methodology and the utility of compounds **36** as synthetic intermediates, further transformations were carried out. The authors evaluated allylation to give γ- or α-addition products depending on the base used, and hydrogenation of the alkylidene double bond. Finally, the authors also carried out the oxidation of the double bond, with previous sulfoxide oxidation, to afford Bus-protected amino ketones **37** (Scheme 16).

6. Reformatsky-type reactions

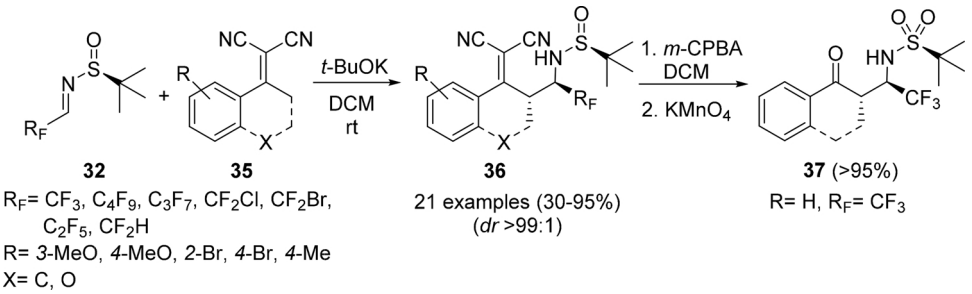
Although being one of the oldest organometal involving processes, Reformatsky reaction is always topical, especially when the target product is required on a large scale [46].

As weak nucleophilic species, organozinc reagents demand reaction partners exhibiting a marked electrophilic character. In this respect, owing to the presence of strong electron withdrawing groups, such as CF_3 and sulfinyl, around C=N double bonds, aromatic trifluoromethyl *N-tert*-butanesulfinyl ketoimines proves to be the ideal partners of the Reformatsky reagents. On the other hand, the substantial instability of these reagents to the hydrolytic processes and their decomposition during workup, requires a fast and careful manipulation as well as a quick use after their preparation with significant limitation of their synthetic potentiality [47]. Nevertheless, Grellepois showed that quite stable hemiaminals ethers **39**, easily prepared *in situ* from trifluoacetyl derivatives **38** and optically pure (*S*)-*tert*-butanesulfinylamide (*S*)-**5**, in aprotic solvents and in the presence of catalytic amount of titanium tetraethoxide (Scheme 17) could be the eligible precursors, of a number of chiral α-trifluoromethylamines [48].

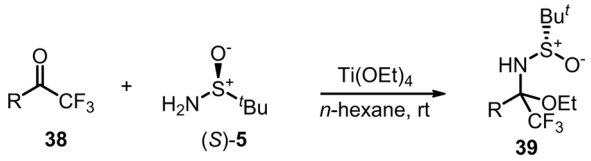
The authors adopted this strategy for the synthesis of chiral targets, such as trifluoromethylated β-amino acids, a class of compounds nowadays extensively studied as peptidomimetic of great biologic interest [49]. The asymmetric synthesis of β-alkyl(aryl)-β-trifluoromethylamino esters has been described occurring *via* a highly stereoselective imino-Reformatsky reaction with stable trifluoromethyl ketone *N-tert*-butanesulfinyl aminals (*S*)-**39** (Scheme 18). 2-Me-THF at 0 °C appeared to be the best conditions for the synthesis of the target $\beta^{3,3}$-amino esters.



Scheme 15. Vinylogous Mannich addition of 3-alkenyl-2-oxindoles **33** to fluoroalkyl *N-tert*-butanesulfinyl aldimines **32**.



Scheme 16. Asymmetric VMR of fluorinated *N-tert*-butanesulfinyl imines **32** with dicyanoalkenes **35**.



Scheme 17. Synthesis of the hemiaminals ethers.

The observed diastereoselectivity was realistically rationalized by assuming a preferential attack of the Reformatsky reagent at the *si* face of the C=N double bond through a chair conformed six member cyclic TS, where both the bulky ^{t}Bu and CF_3 groups hold the equatorial position (Scheme 19).

The effectiveness and versatility of the above strategy was clearly stressed by coupling the optically pure β-trifluoromethyl-β-amino esters with different α-amino acids to attain, by conventional procedures, *C*- and *N*-coupled heterodi- (**42**) and tripeptides (**43**) of indubitable biological interest (Scheme 20).

Thereafter, Reformatsky protocol was successful adopted in the synthesis of optically pure β-amino acids using chiral *N-tert*-butanesulfinyl-trifluoromethylketoimines as suitable partner of organozinc reagents. Very recently, Milcent, Retailleau, Soloshonok and coworkers [50], proposed an elegant synthesis of optically pure trifluoromethyl-substituted cyclic five- and six-member β-amino acids of relevant utility in the synthesis of foldamers, by their incorporation into various peptides. Following the Mimura protocol [24], these authors performed Zn-mediated allylation to (*S*)-*N-tert*-butanesulfinyltrifluoroectaldimine [(*S*)-**44**] with several allyl bromides **45** to obtain a variety of diastereomeric *N-tert*-butanesulfynyl-1,1,1-trifluoropent-4-en-2-ylamines **46** in satisfactory yields. High diastereoselectvities were achieved when primary allylzinc bromides were used as the Reformatsky reagents whilst secondary allylzinc bromides seem to be much less selective excepted cinnamylzinc bromide which provided the corresponding adduct (R^1 = H, R^2 = Ph,) with high yield and stereoselectivity (Scheme 21).

The Reformatsky product from the reactions of aldimine (*S*)-**44** with 2-(ethoxycarbonyl)allylzinc bromide (**46**, R^1 = COOEt; R^2 = H) assumes a particular importance as valuable precursor of stereoselectively trifluoromethyl-substituted nitrogen heterocycles of relevant pharmacological interest. Accordingly, a satisfactory yield of a 48:52 diastereomeric mixture of ethyl (S_S,3*S*,5*S*)-**47** and (S_S,3*R*,5*S*)-**47**, respectively] was smoothly obtained from the acrylate (S,S_S)-**46** (R^1 = CO_2Et, R^2 = H) by NaH-promoted intramolecular aza-Michael addition. Finally, optically pure 5-trifluoromethyl-β-proline (2*S*,4*R*)-**48** was obtained in high yield after separation of the two *N*-Cbz-substituted diastereomeric esters, followed by alkaline hydrolysis (Scheme 22).

A different strategy was adopted to attain stereoselectively trifluoromethylated six membered nitrogen heterocycles from the same adduct (S,S_S)-**46**. After oxidation of the sulfinyl group with *m*CPBA, the resulting sulfonamide (*S*)-**49** was *N*-allylated and the resulting aminodiene (*S*)-**50** was subject to metathesis catalyzed by a second-generation Grubbs catalyst to give optically pure 2-trifluoromethyltetrahydropyridines (*S*)-**51**. Finally, the latter was successfully transformed into optically pure (*S*)-2-trifluoromethylisonipecotic acids and (2*S*)-6-trifluoromethylnipecotic acids by tested procedures (Scheme 23).

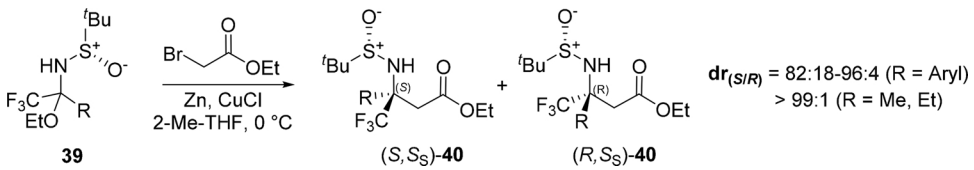
The very low diastereomeric ratio observed in the hydrogenation step, could be rationalized by considering that sulfonamide (*S*)-**51** can adopt two possible conformations **A** and **B** (Fig. 4), the latter of which, by far the most stable, provides for the bulky trifluoromethyl group occupying the equatorial position. In such conformation, trifluoromethyl group exerts a very little effect, if not null, in orientating the hydrogen attack on the one or the other diastereotopic face of the carbon-carbon double bond, both looking in fact equally accessible.

By the same way (2*S*,3*S*)-*N-tert*-butanesulfonyl-3-phenyl-2-trifluoromethylpiperidine [(2*S*,3*S*)-**56**] was smoothly prepared in 90% yield over several steps including Sharpless oxidation [51] (Scheme 24).

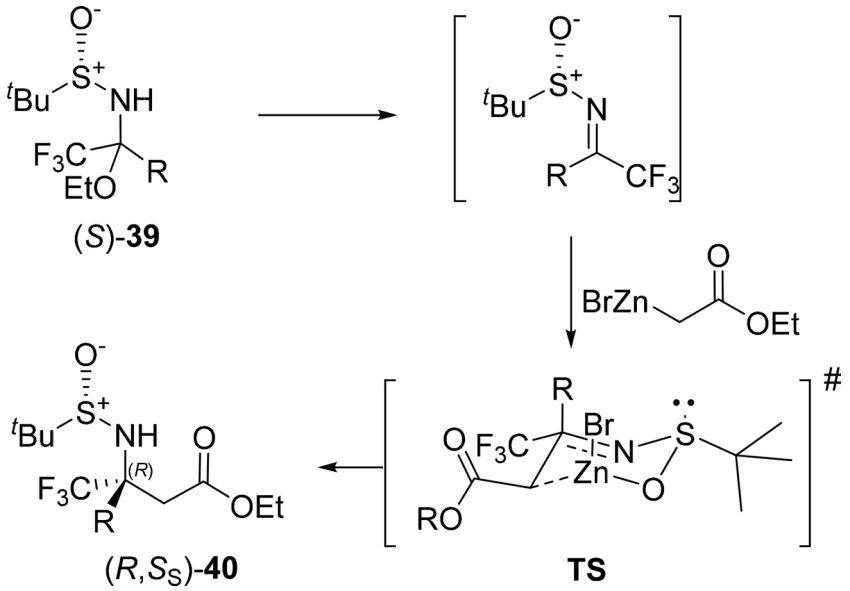
7. Application of other types of chiral auxiliaries

In 2015, Fioravanti and coworkers developed a Zr-catalyzed Mannich reaction of N-protected trifluoromethyl aldimines **58** and β-keto esters **59** under solvent-free conditions affording the fluorinated β'-amino β-dicarbonyl compounds **60** in moderate to good chemical yields [52] In this Zr-catalyzed reaction, they also conducted the reaction in the asymmetric manner with (*R*)-α-methylbenzylamine-derived trifluoromethyl aldimine **61** as starting material. A series of cyclic and linear β-keto esters were well tolerated, and reacted smoothly with this imine, resulting in the corresponding chiral product **62** in excellent diastereoselectivities for most cases. The decarboxylative reaction of the obtained chiral products was carried out via two-step reaction (Scheme 25).

In 2015, Fioravanti, Pellacani and co-authors designed and synthesized a series of new functionalized trifluoromethyl aldimines **63** via the condensation reaction of L-α-Amino esters with trifluoroacetaldehyde (fluoral) ethyl hemiacetal [53]. The reactivity of these obtained trifluoromethyl aldimines **63** was performed by the Mannich reaction of isovaleraldehyde with L-proline as catalyst under solvent free conditions (Scheme 26). It was very interesting that the



Scheme 18. Reformatsky reaction with trifluoromethyl ketone *N-tert*-butanesulfinyl aminals.



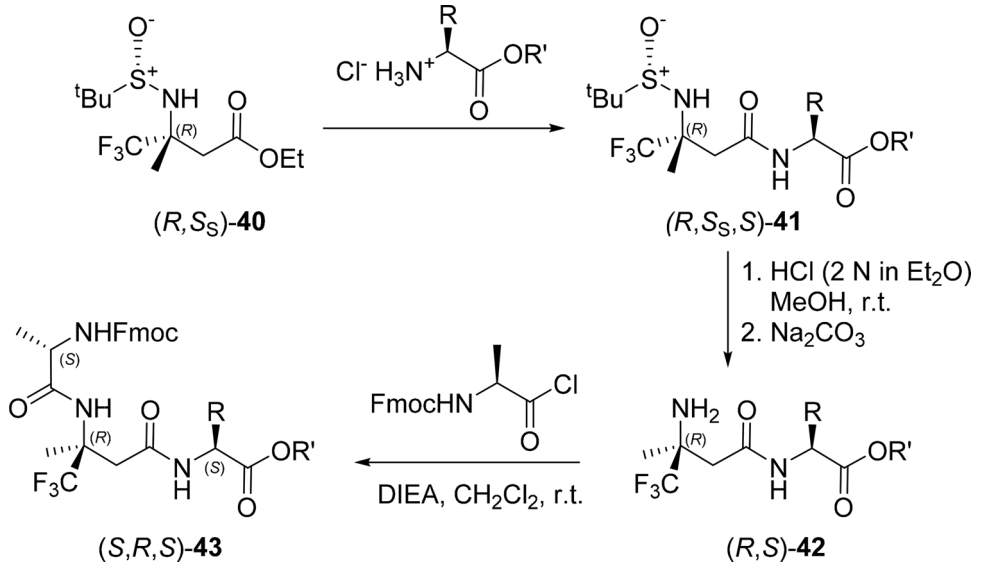
Scheme 19. Transition station.

different stereo outcomes were observed when the Mannich reaction was conducted under different reaction temperature. When the Mannich reaction was carried out at room temperature followed by reduction at 0 °C, only the syn diastereomers **64** were obtained but with poor diastereoselectivity (dr = 1:1). In the sharp contrast, only the anti diastereomer **64** was obtained when the reaction was conducted at −20 °C for seven days. Furthermore, the diastereoselectivity is excellent, and only one anti-isomer was detected for the four cases.

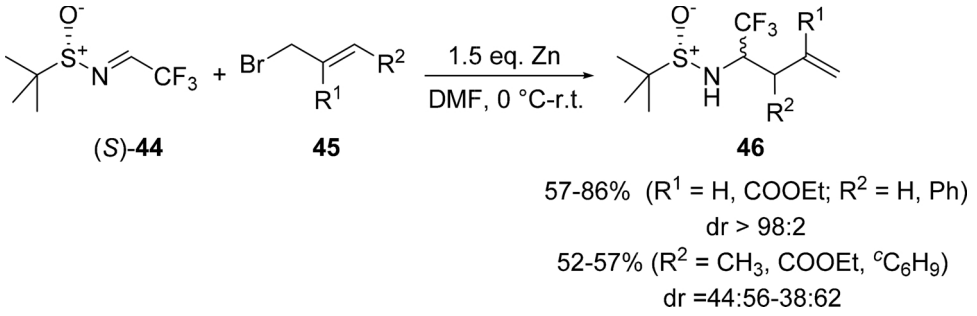
8. Synthesis of β-amino-α,α-difluoro-phosphonic acids

In 2016, the chiral *N-tert*-butanesulfinyl-phosphoryldifluoro-imine **66** was developed as a new reagent for the asymmetric installation of bioactive chiral 2-(alkoxyphosphono)-1-amino-2,2-difluoroethyl group into organic compounds [54]. This imine was prepared via the direct condensation of β-(alkoxyphosphono)-α,α-difluoroethyl and sulfonamide in the presence of dehydrating agents. They also mentioned that such imine was directly used for the reaction without the purification. This new obtained imine was firstly applied in the Friedel-Crafts reaction to examine its reactivity. The Friedel-Crafts reactions of this imine **66** was conducted with indoles **65** in the presence of $BF_3{\cdot}OEt_2$ at room temperature (Scheme 27). It was found that the reaction proceeded smoothly, and tolerated a wide range of indole derivatives, affording the corresponding product **67** in up to 81% chemical yield. It should be mentioned that the diastereoselectivities were almost completely controlled, and the enantiomerically pure product was obtained for all the cases.

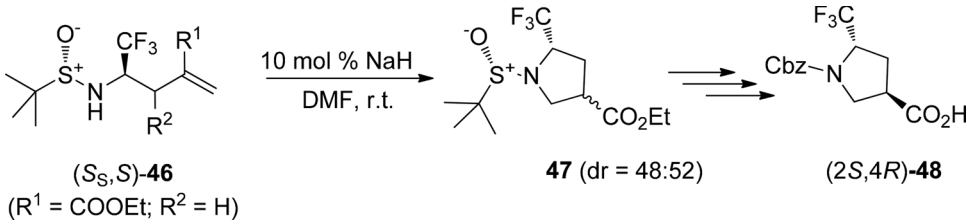
After the success in the use of the *N-tert*-butanesulfinyl-phosphoryldifluoro-imine in the Friedel-Crafts reaction, the same group extended the study of such imine by reaction with properly protected glycinates in 2017 [55]. After the optimization of reaction conditions, they found the asymmetric Mannich reaction could be performed with Cs_2CO_3 as catalyst in THF at room temperature (Scheme 28). This Mannich reaction showed good substrate generality, and a series of glycinates **68** reacted very well with *N-tert*-butanesulfinyl-phosphoryldifluoro-imine **66**, resulting in the desired diamino acid derivatives **69** in good yields (49–81%) and excellent diastereoselectivity (95:5-99:1). The further chemistry of the obtained product was also conducted, a novel type of



Scheme 20. Synthesis of the peptide.



Scheme 21. The Reformatsky reaction of imine.



Scheme 22. The further chemistry of product **46** for the synthesis of heterocycle.

biologically useful compounds, including the α- and β-amino acid, vicinal diamino acid, carboxylic acid, and phophonic acid, peptide was achieved [56].

9. Cascade reactions

In 2017, Han and coworkers developed a cascade reactions of (*S*)- and (*R*)-*N*-*tert*-butylsulfinyl-3,3,3-trifluoro-acetaldimine **2** by using α-thiocyanate ketones **70** as nucleophiles (Scheme 29) [57]. Interestingly, they found that different products could form when the reaction was

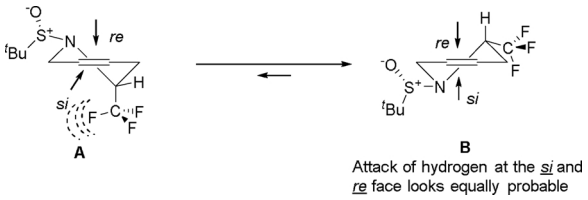
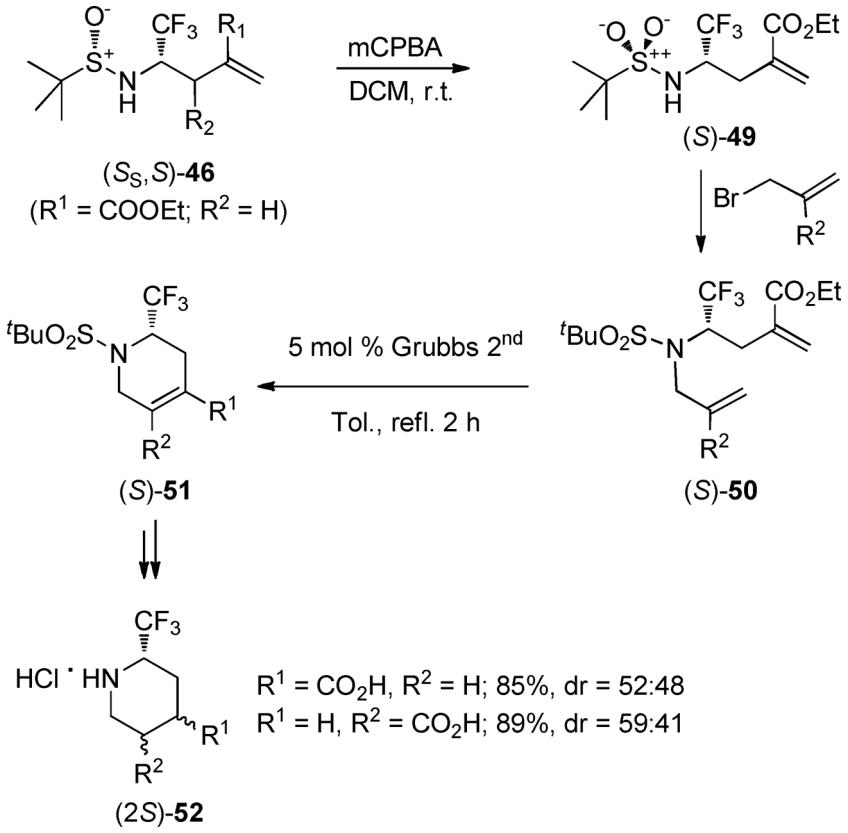
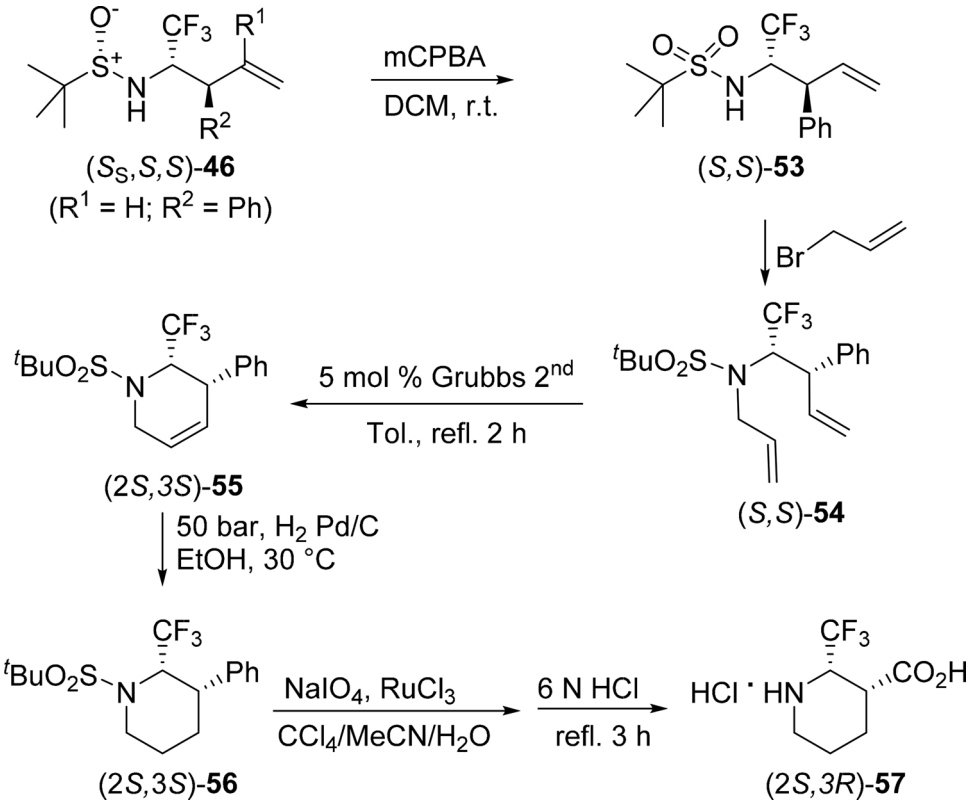


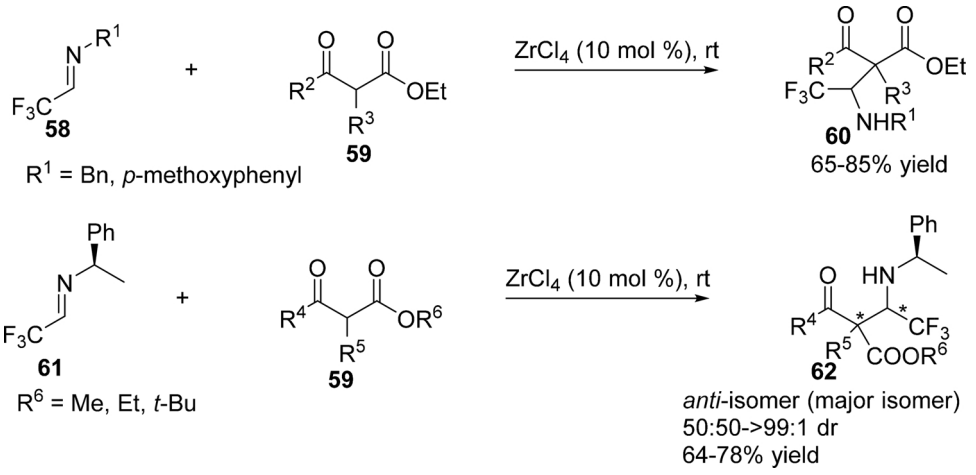
Fig. 4. Reactive conformation of sulfonamide (*S*)-**51**.



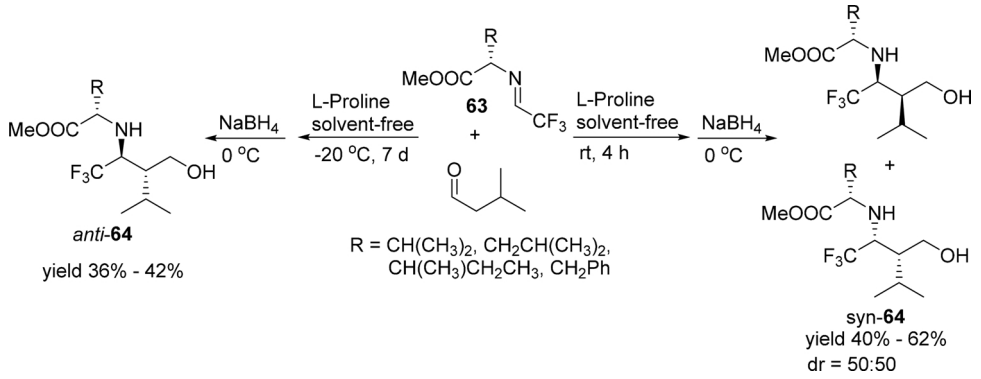
Scheme 23. The further chemistry of product **46** for the synthesis of trifluoromethylisonipecotic acids.



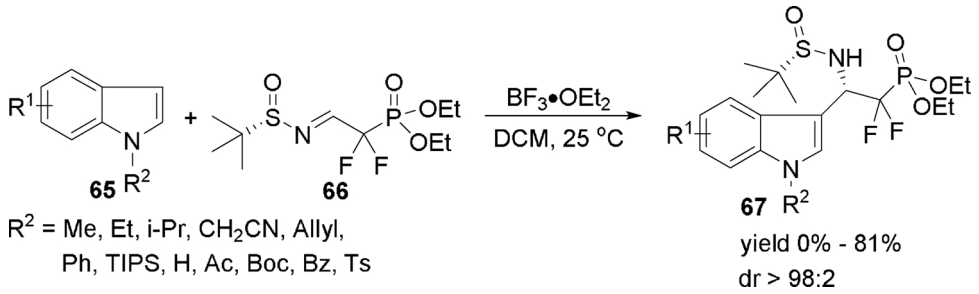
Scheme 24. The synthesis of trifluoromethylnipecotic acid.



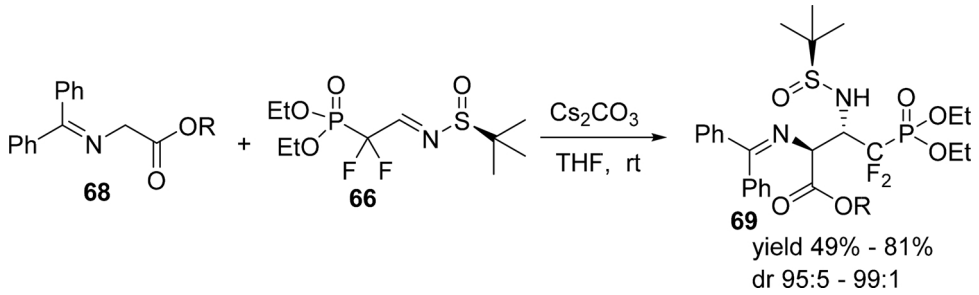
Scheme 25. Zr-catalyzed Mannich reaction of trifluoromethyl aldimines.



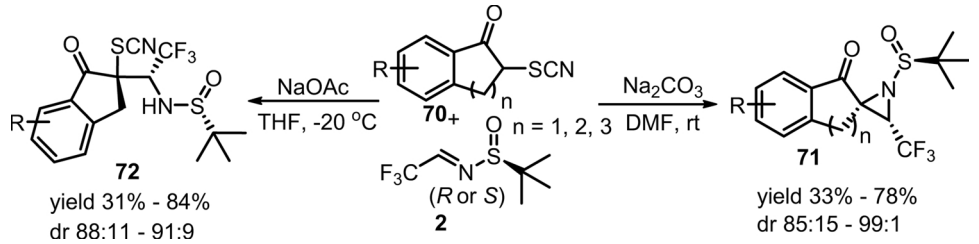
Scheme 26. L-proline-catalyzed Mannich reaction with isovaleraldehyde.



Scheme 27. The Friedel-Crafts reactions of this *N-tert*-butanesulfinyl-phosphoryldifluoro-imine.



Scheme 28. The Mannich reaction of *N-tert*-butanesulfinyl-phosphoryldifluoro-imine.



Scheme 29. The Mannich and Mannich-cyclization reaction of α-thiocyanate ketones.

conducted under different reaction conditions. The direct Mannich adducts **72** were obtained in the presence of NaOAc/THF with 31–84% chemical yields and 88:11–91:9 diastereoselectivities. However, the tandem Mannich addition-cyclization reaction was found in the presence of Na_2CO_3/DMF, and the cyclic product was found with 33–78% yields and 85:15-99:1 diastereoselectivities. Although the use of different bases gave the usual Mannich addition product **72** and aziridine product **71**, the chemoselectivity for each reaction was excellent. Most important is that the latter offers a new method to synthesize chiral spirocyclic trifluoromethyl-containing aziridines unavailable by usual approaches.

10. Conclusions

Considering the data discussed in this review article, one may agree that the application of chiral sulfinimine reagents continue to attract a tremendous attention due to their synthetic versatility and usually very high level of the stereocontrol. Of particular interest are results that underscore the difference between alkyl and fluoro-alkyl groups in terms of reactivity and stereochemical outcome. New methodological aspects are represented in the recent literature by the examples of tri-component reactions, cascade processes as well as advantageous detrifluoroacetylative *in situ* generation of tertiary fluoro-enolates. The chemistry reported so far provides very practical approaches to various types of fluorinated amines, α-, β-amino acids, as well as many heterocyclic compounds of high pharmaceutical importance. However, it is obviously clear that the full synthetic potential of chiral sulfinimine reagents is far from being explored leaving plenty of room for further exciting and creative synthetic discoveries. For example, one of the unsolved problems or unexplored areas is cycloaddition reactions leading to chiral five- or six-membered heterocyclic systems which could be of great interest for pharmaceutical and agrochemical industries.

Acknowledgments

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