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PERSPECTIVE

Enantioselective organocatalytic fluorination using organofluoro nucleophiles

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Synthetic fluorinated compounds are enormously useful in areas such as materials, agrochemicals, pharmaceuticals and fine chemicals. While methods of electrophilic fluorination have been extensively developed to stereoselectively install fluorine atoms onto molecules, nucleophilic fluorination is a much less explored approach. Recently, several organofluoro reagents have been designed and used as nucleophiles in the asymmetric synthesis of fluorinated compounds, significantly expanding the scope of enantio-enriched fluorine-containing compounds that can be synthesised. Such organofluoro nucleophiles are particularly useful in organocatalytic transformations. In this review, recent advances in the application of organofluoro nucleophiles in organocatalysis are summarised.

Introduction

Powerful probes for revealing the workings of biological systems can be prepared through the judicious replacement of hydrogen with fluorine.[1] Due to the unique properties of the fluorine atom, fluorine-containing compounds have many important applications in the pharmaceutical industry and other related fields. In the past few years, some fluorine-containing drugs such as Lipitor® and Seretide® were ranked as top-selling.[1] These huge successes stimulate the research on fluorine in medicinal chemistry for drug discovery.

The C–F bond brings about significant effect on the reactivity, stability and bioavailability of molecules. While natural organofluoro compounds are rare, synthetic fluorinated compounds are widely used in a variety of fields due to the fact that molecules containing fluorine atoms or fluorinated groups often display unique properties that cannot be accomplished using other elements. Hence, the demand is strong for the development of versatile fluorine-containing building blocks as well as synthetic strategies leading to fluorinated compounds.

Several strategies have been developed for the construction of chiral fluorinated compounds utilizing both nucleophilic (F^-) and electrophilic (F^+) sources. However, due to the small size of F^- and its low polarizability, F^- usually behaves more like a base rather than a nucleophile. Hence, nucleophilic fluorination always occurs under harsh conditions.[2] On the other hand, with the development of various F^+-sources, electrophilic fluorination plays a key role in the formation of C–F bonds.[3] More recently, there has been much interest in the development of organofluoro nucleophiles as an alternative approach to electrophilic fluorination for the asymmetric synthesis of fluorinated compounds. The replacement of a hydrogen by fluorine atom in a molecule results in neighbouring protons becoming more acidic, due to the strong electron-withdrawing property of fluorine atom. The acidic organofluoro compounds performed well under the nucleophilic additions.[4] It was often observed that the presence of fluorine in organofluoro nucleophiles increased their reactivity compared to similar species where the fluorine atom is absent, and these organofluoro nucleophiles are particularly suitable for organocatalytic transformations. Herein, we will focus on the recent progress in using organofluoro nucleophiles for organocatalytic asymmetric synthesis.

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Synthesis of organofluoro nucleophiles

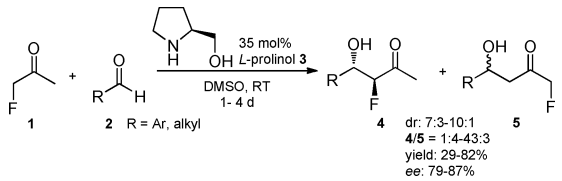
The organofluoro nucleophiles are easily prepared by electrophilic fluorination reactions in presence of fluorinating agents such as Selectfluor® and *N*-fluorobenzenesulfonimide (NFSI). There are two general synthetic routes to achieve the target products, the most common one depends on the formation of metal enolates under strong base condition, followed by the fluorination with fluorinating agents.[5a] These transformations could be also achieved by conventional heating or microwave irradiation methods in polar solvents.[5b,c]

Organofluoro nucleophiles in organocatalysis

Fluoroacetone as nucleophile

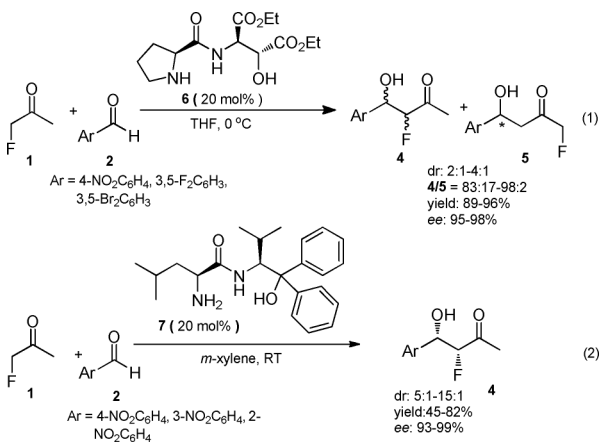
Fluoroacetone is one of the most useful organofluoro building blocks and is a promising nucleophile in asymmetric aldol reactions. This methodology provides a useful and direct route for the synthesis of optically active α-fluoro-β-hydroxyl ketones. The direct asymmetric aldol reactions of fluoroacetone **1** with aldehydes **2** using chiral prolinol **3** as catalyst was reported by Barbas and co-workers.[6a] L-Prolinol was selected from a screen of

various amine catalysts for its ability to form the reactive enamine with fluoroacetone **1** instead of the aldehydes, which allows the reaction to proceed. Reaction time of 1–4 days was required in presence of 35 mol% of the catalyst. Both aromatic and aliphatic aldehydes were tolerated, and adducts were formed with high regioselectivities. The *anti*-α-fluoroaldol products **4** were obtained in moderate yields with good enantioselectivities (up to 87% *ee*) (Scheme 1).



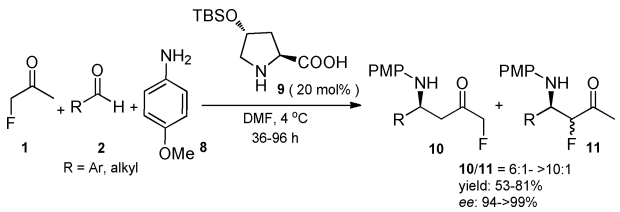
Scheme 1 Aldol reaction of aldehydes with fluoroacetone catalysed by prolinol.

While direct asymmetric aldol reaction between aldehydes and fluoroacetone provides convenient and direct access to chiral α-fluoro-β-hydroxyl ketones, the challenge lies in controlling the selectivity of the reaction, as up to six different isomers can possibly be generated. Recently, Gong's group has developed a highly enantioselective aldol reaction with fluoroacetone catalysed by L-proline amide **6**.[6b] The reaction predominantly afforded **4** with regioisomeric ratios of **4** : **5** ranging from 83 : 17 to 98 : 2 and excellent enantioselectivities ranging from 94 to 98%. However, only aromatic aldehydes with strong electron-withdrawing groups can act as the aldol acceptor (Scheme 2, eqn (1)). Similarly, Guillena *et al.* also reported a solvent-free asymmetric direct aldol reaction between fluoroacetone and 4-nitrobenzaldehyde catalysed by (*S*)-binam-L-prolinamide,[7a] obtaining the *anti* aldol product with 80% ee. The use of secondary amine-based organocatalysts provided predominantly the *anti* diastereoisomers, so that highly enantioselective *syn*-direct aldol reaction remained an important challenge.[7b] To address this, Gong and co-workers also designed a new organocatalyst **7**, which was easily synthesised from primary amino acids and β-amino alcohols.[6c] Using nitro-substituted aromatic aldehydes as aldol acceptors, the *syn*-aldol adducts **4** were obtained in good yields with excellent enantioselectivity (up to 99% *ee*) (Scheme 2, eqn (2)).



Scheme 2 Aldol reaction of aldehydes with fluoroacetone.

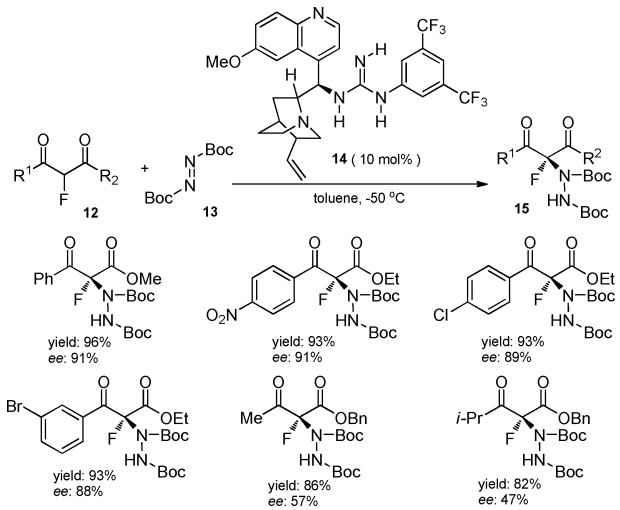
More recently, Zhong and co-workers reported the highly enantioselective direct Mannich reaction of fluoroacetone, catalysed by 4-siloxyproline **9** (Scheme 3).[8] This method allows pharmaceutically important fluorinated β-amino ketones to be accessed easily, with the linear Mannich adduct **10** being observed to be the major product over the branched adduct. The authors' initial investigation using DFT calculations showed that in the gas phase (generalised to non-polar solvents), the selectivity for either one of the two possible enamine intermediates formed between **1** and catalyst **9** is very low. However, in polar solvents such as DMSO there is a preference for the enamine which leads to product **10**.



Scheme 3 Direct Mannich reaction with fluoroacetone.

Fluorinated 1,3-dicarbonyl compounds as nucleophiles

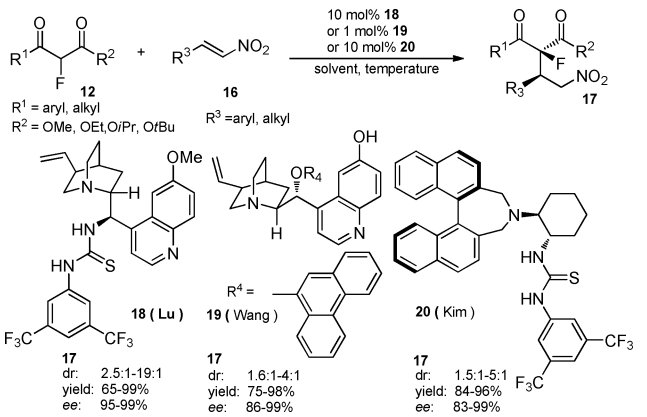
Fluorinated 1,3-dicarbonyl compounds have relatively low pK_a values and can be easily activated using chiral organic bases. Lu and co-workers investigated the use of fluorinated 1,3-dicarbonyl compounds in enantioselective amination reactions between β-keto esters **12** and azodicarboxylates **13**, catalysed by a chiral guanidine derived from Cinchona alkaloids **14**.[9a] Excellent *ee* values were obtained for aromatic α-fluoro-β-ketoesters **15** while their aliphatic counterparts gave lower enantioselectivities (Scheme 4). Maruoka and co-workers reported one single entry for asymmetric amination reaction catalyzed by quaternary phosphonium salts as PTC catalysts.[9f,g]



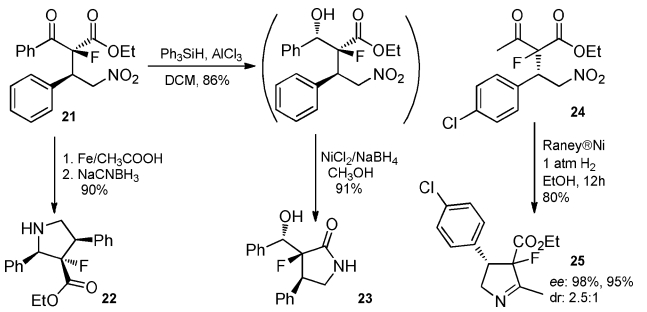
Scheme 4 Asymmetric amination of β-keto esters with azodicarboxylates.

Both Lu[9b] and Wang[10] reported highly enantioselective Michael reactions of α-fluoro-β-ketoesters with nitroalkenes catalysed by Cinchona alkaloid-derived organocatalysts. Lu and co-workers examined the reactions of α-fluoro-β-ketoesters **12** with a wide range of aryl and alkyl nitroolefins **16** catalysed by Cinchona

alkaloid-based thiourea bifunctional organocatalyst **18**. Quantitative yields and excellent enantioselectivities were achieved but diastereoselectivities were moderate in most of the cases (Scheme 5). The Michael adducts containing fluorinated quaternary carbon centres can be converted into useful chiral scaffolds **22** and **23** containing three contiguous stereogenic centers after one or two synthetic steps starting from adduct **21** (Scheme 6).



Scheme 5 Asymmetric Michael reaction of α-fluoro-β-ketoesters and nitroalkenes.



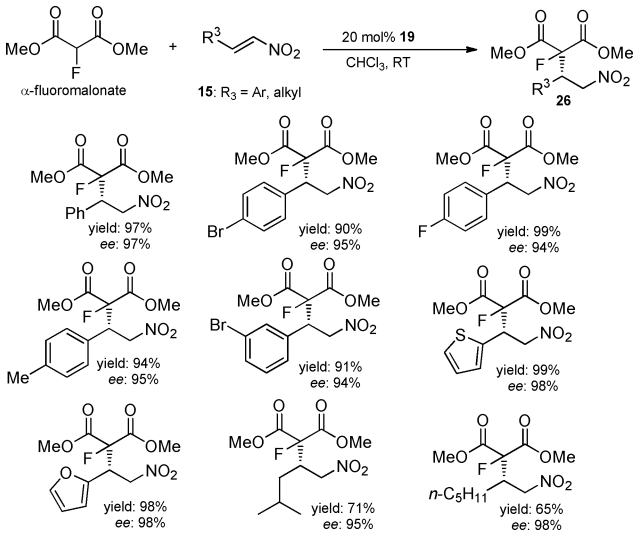
Scheme 6 Modification of Michael adducts **21** and **24**.

Wang and co-workers reported the use of alkyl α-fluoro-β-ketoesters **12** as Michael donors with various nitroolefins **16**, catalysed by a Cinchona alkaloid derivative **19** with a low catalyst loading (1 mol%).[10a] The reaction afforded Michael adducts with moderate diastereoselectivities and excellent enantioselectivities. The adduct **24** was converted to synthetically useful chiral Δ^1-pyrrolidine **25** by a simple hydrogenation reaction (Scheme 6).

The Wang group also reported a similar reaction; the Michael addition of nitroolefins using commercially available α-fluoromalonate as the nucleophile.[10b] Highly enantio-enriched Michael adduct **26** (up to 98% *ee*) were obtained with high yields in the presence of **19** (Scheme 7). Furthermore, the use of aliphatic nitro-olefins also gave products with excellent enantioselectivities, albeit moderate yields.

Rios and co-workers reported the highly enantioselective fluoromalonate addition to α,β-unsaturated aldehydes. Excellent enantioselectivities were achieved.[10c]

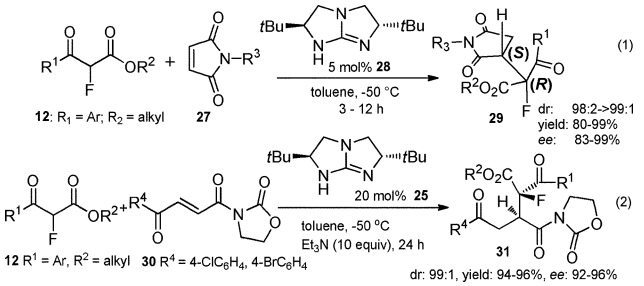
Kim and co-workers reported similar Michael reactions using a bifunctional thiourea-type organocatalyst **20** bearing both central and axial chiral elements.[11] The Michael adducts were obtained



Scheme 7 Asymmetric Michael reaction of α-fluoromalonate and nitroalkenes.

in high yields with moderate diastereoselectivities and excellent enantioselectivities (up to >99% *ee*) (Scheme 5).

Tan and co-workers developed a highly enantioselective and diastereoselective Michael addition reaction of α-fluoro-β-ketoesters **12** (R^1 = Ar) with *N*-alkyl maleimides **27**, catalysed by chiral guanidine **28**.[12] Aryl α-fluoro-β-ketoesters **12** acted as nucleophiles in the presence of 5 mol% of chiral guanidine catalyst, affording adducts **29** with high yields, excellent diastereoselectivities (dr: >99 : 1) and *ee* values (up to 99%) (Scheme 8, eqn (1)). Substrates **12** were also found to be good Michael donors for the addition to linear acceptors such as *trans*-4-oxo-4-arylbutenamides **30**. With 10 equivalents triethylamine as additive and a catalyst loading of 20 mol% **28**, adducts **31** were obtained with excellent enantioselectivities (up to 96%) and diastereoselectivities (99 : 1) (Scheme 8, eqn (2)).



Scheme 8 Asymmetric Michael reaction between α-fluoro-β-ketoesters and *N*-alkyl maleimides.

To understand the mechanism, density functional theory (DFT) calculations at the B3LYP/6-31* level were performed. An ion-pair complex between guanidinium cation and α-fluoro-β-ketoester was first formed, before the maleimide approaches the complex to form a pre-transition-state complex. Two possible structures for the pre-transition-state complex were hypothesized: face-on or side-on. The side-on TS was strongly preferred over the face-on TS because of the stronger hydrogen-bond association with the maleimide carbonyl group. For the four plausible side-on transition states, the calculated preference for the

(*S*,*R*)-stereoisomer was in agreement with the observed high enantioselectivity and diastereoselectivity (Fig. 1).

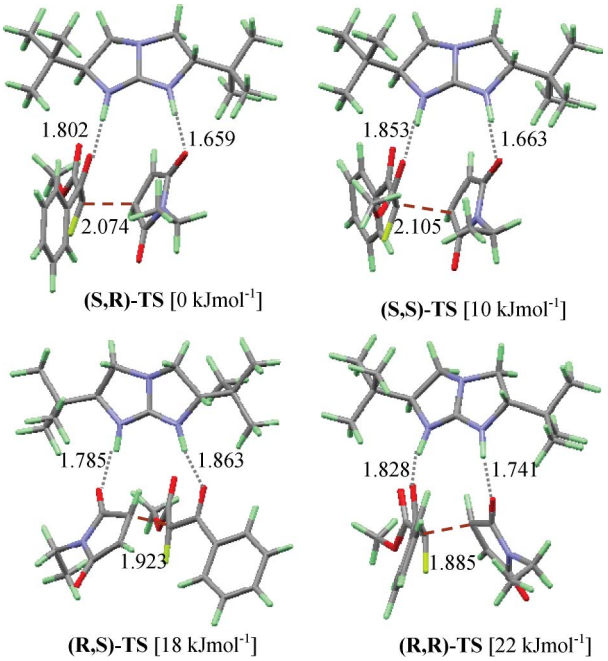
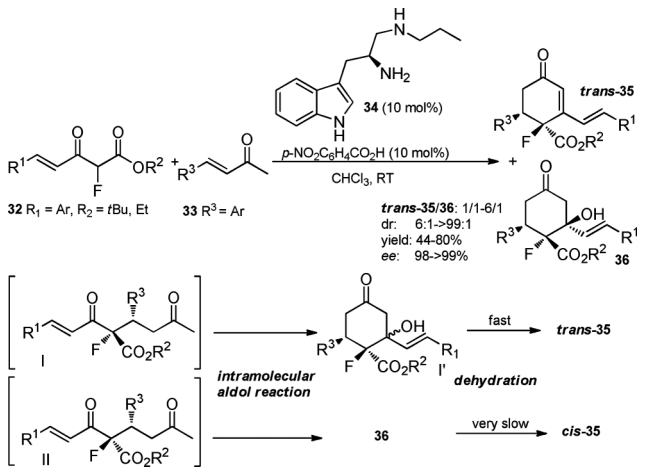


Fig. 1 Optimized (B3LYP/6-31G*) geometries of the four transition states leading to the (*S*,*R*)-, (*S*,*S*)-, (*R*,*S*)- and (*R*,*R*)-products. Calculated relative energies of the transition states are given in square brackets and the bond lengths are given in Å.

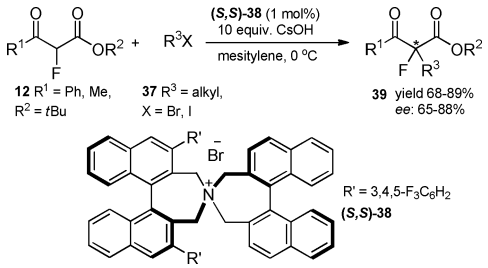
Most recently, Zhao and co-workers reported the asymmetric Robinson annulation reaction of α-fluoro-β-ketoesters **32** catalysed by primary/secondary diamine catalysts **34**.[13a] The multiple-substituted fluorinated chiral cyclohexenones *trans*-**35** and **36** were synthesised by the combination of Michael addition, intramolecular aldol reaction and dehydration. The highly enantioselective products *trans*-**35** (up to >99% *ee*) were obtained in good yields when 10 mol% of diamine catalyst **34** was used together with 10 mol% *p*-nitrobenzoic acid as additive (Scheme 9). They also performed the asymmetric Michael reaction of α-fluoro-α-enone.[13b]



Scheme 9 Asymmetric Robinson annulations of α-fluoro-β-ketoesters **29**.

Besides *trans*-**35** as the major products, the reaction also yielded the un-dehydrated product **36**, with the ratio of *trans*-**35**:**36** ranging from 1:1 to 6:1. From the observed results, a possible mechanism was proposed where intermediates **I** and **II** were first achieved by the Michael reaction between α-fluoro-β-ketoesters **32** and α,β-unsaturated ketones **33**. This was followed by an intramolecular aldol reaction which gave **I′** and **36**, respectively. The intermediate **I′** underwent rapid dehydration to deliver the product *trans*-**35**, while dehydration of **36** was very slow due to the intramolecular hydrogen-bond interaction between the hydroxyl group and the ester carbonyl group (Scheme 9).

The asymmetric alkylation of α-fluoro-β-ketoesters **12** with alkyl halide **37** utilising a *N*-spiro chiral quaternary ammonium bromide **(*S*,*S*)-38** was reported by Maruoka and co-workers.[14] Under phase-transfer conditions, organofluoro nucleophiles exhibited good reactivities towards various alkyl halides such as allylic and simple alkyl halides, achieving enantioselectivity of up to 88% *ee* for the products **39** (Scheme 10).

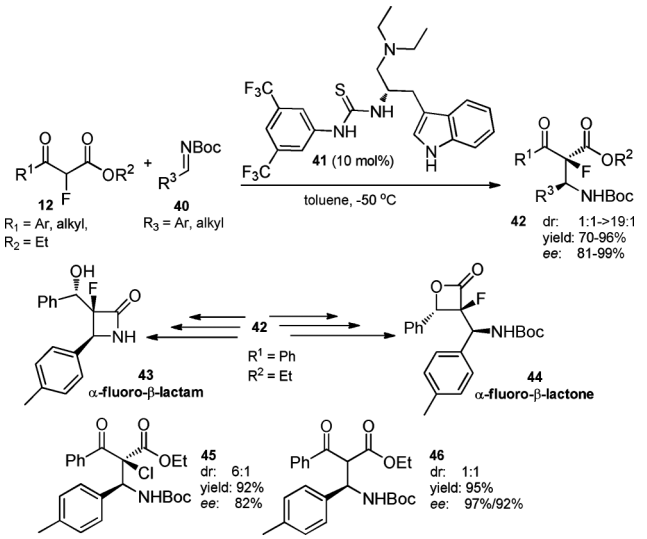


Scheme 10 Asymmetric alkylation of α-fluoro-β-ketoesters.

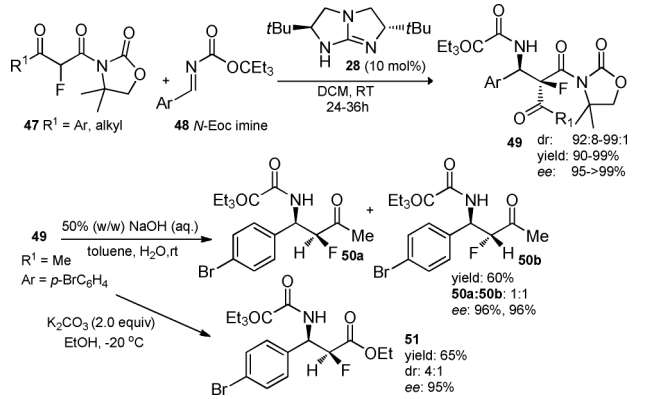
Organofluoro nucleophiles were also found to be excellent donors for the Mannich reaction catalysed by chiral organic bases. Lu and co-workers reported the asymmetric Mannich reaction of α-fluoro-β-ketoesters **12** with *N*-Boc imine **40** catalysed by a tryptophan-derived bifunctional thiourea catalyst **41**.[9c] Highly enantioselective Mannich products **42** with good diastereoselectivities were observed for a wide range of aromatic and alkyl α-fluoro-β-ketoesters used. To demonstrate the utility of this reaction, α-fluoro-β-lactam **43** and α-fluoro-β-lactone **44** were prepared in three steps from the Mannich products **37**. By using a α-chloro-β-ketoester as the nucleophile, product **45** was obtained with a slightly lower enantioselectivity (82% *ee*). For the non-fluorinated β-ketoester, the product **46** was obtained with high enantioselectivities for both diastereomers although the dr value was only 1:1 (Scheme 11).

Kim and co-workers reported the similar work using bifunctional catalysts, good yields and enantioselectivities were achieved.[9d,e]

The use of β-keto-acetyloxazolidinones **47** as organofluoro nucleophiles was first developed by Tan's group for the asymmetric Mannich reaction with *N*-3-ethylpentan-3-yloxycarbonyl (Eoc) imines **48**, catalysed by chiral guanidine catalyst **28**.[15] Excellent diastereoselectivities (up to 99:1) and enantioselectivities (up to 99% *ee*) were achieved for the Mannich adducts **49**. Treatment of product **49** with 50% aqueous sodium hydroxide generated α-fluoro-β-amino ketones **50a** and **50b** *via* decarboxylative protonation; while the use of two equivalents of a weaker base (potassium carbonate) in EtOH, resulted in a de-acylation reaction to yield the α-fluoro-β-amino ester **51** (Scheme 12).



Scheme 11 Asymmetric Mannich reaction of α-fluoro-β-ketoesters.



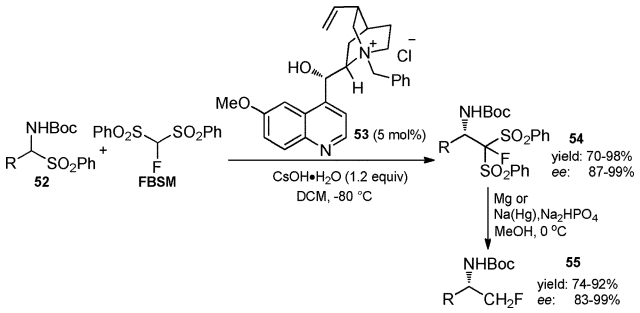
Scheme 12 Asymmetric Mannich reaction of β-keto-acetyloxazolidinones.

FBSM and FSM derivatives as nucleophiles

1-Fluorobis(phenylsulfonyl)methane (FBSM) and fluoro-(phenylsulfonyl) methane (FSM) derivatives are effective synthetic equivalents of monofluoromethide species in asymmetric catalysis. The presence of electron-withdrawing sulfonyl or nitro functionalities in the organofluoro carbon lowers the pK_a value of the molecule and it can be easily activated by even weak bases.

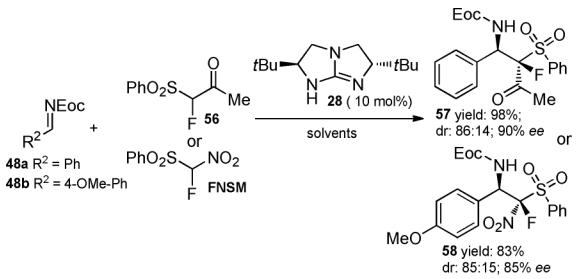
Shibata and co-workers reported a Mannich-type reaction of FBSM under phase-transfer conditions, catalysed by *N*-benzylquinidinium chloride **53**.[16] In the presence of a catalytic amount of **53**, *in situ* generated imines from α-amino sulfones **52** reacted with FBSM to give Mannich products **54** in good yields and excellent enantioselectivity (up to 99% *ee*). Removal of the two phenylsulfonyl groups from products **54** using Mg/MeOH or Na(Hg)/Na_2HPO_4/MeOH generated the corresponding monofluoromethylated amines **55** with good yields and enantioselectivities (Scheme 13).

Tan's group has also reported asymmetric Mannich reactions between fluoro(phenylsulfonyl)methane (FSM) derivative (**56** and FNSM) and *N*-Eoc imine **48** catalysed by the chiral guanidine catalyst **28**.[15] The Mannich products were achieved with good



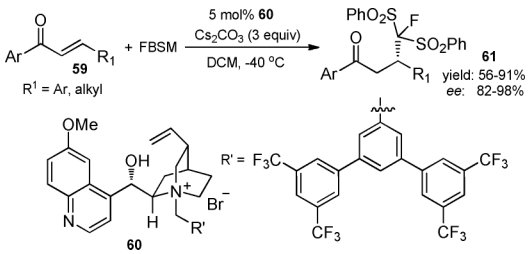
Scheme 13 Asymmetric Mannich-type reaction of FBSM.

ee values (**57**: 90% *ee*; **58**: 85% *ee*) and diastereoselectivities (**57**: 86 : 14; **58**: 85 : 15) (Scheme 14).



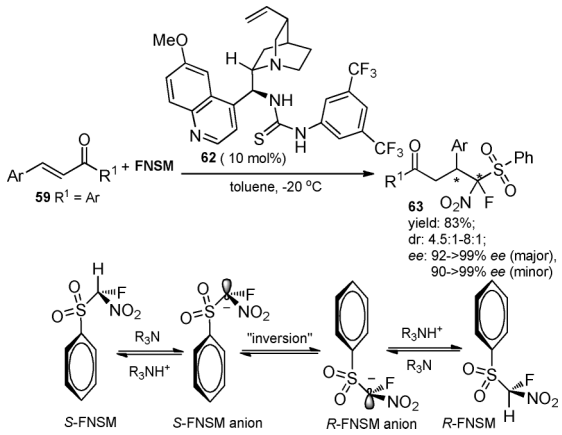
Scheme 14 Asymmetric Mannich reaction of FSM derivatives.

Shibata and co-workers demonstrated that FBSM performed well as nucleophile in the catalytic enantioselective Michael addition to chalcone derivatives **59** employing the Cinchona alkaloid-derived salt **60**.[17] Carrying out the reactions at low temperature (–40 °C) under phase-transfer conditions using 3 equivalents of base (Cs_2CO_3), the Michael adducts **61** were afforded in good yields with *ee* values ranging from 82 to 98% (Scheme 15).



Scheme 15 Asymmetric Michael reaction of FBSM.

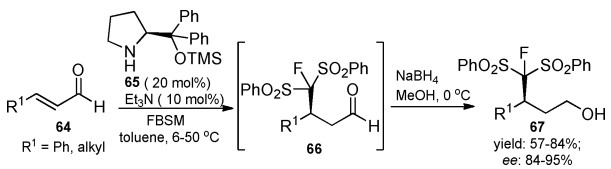
Simultaneously, Olah and co-workers reported a Michael reaction between FNSM and chalcone derivatives with Cinchona-based bifunctional chiral catalyst **62**.[18] The bifunctional catalyst is capable of activating FNSM without the need of additional bases, and also catalysed the addition of activated FNSM to the chalcone derivatives in a stereoselective fashion (Scheme 16). The Michael adducts **63** were achieved with high diastereomeric ratio (up to 8 : 1) and excellent enantiomeric excesses (up to >99% *ee*). The authors also proposed that the resulting FNSM carbanion containing fluorine in the α-position assumes a tetrahedral structure rather than a planar one, which was suggested for non-fluorinated α-nitromethane derivatives. This would enhance the diasteroselectivity of the reaction through a possible inversion. The presence of an inversion step between *S*-FNSM and



Scheme 16 Enantioselective Michael addition of FNSM to chalcones.

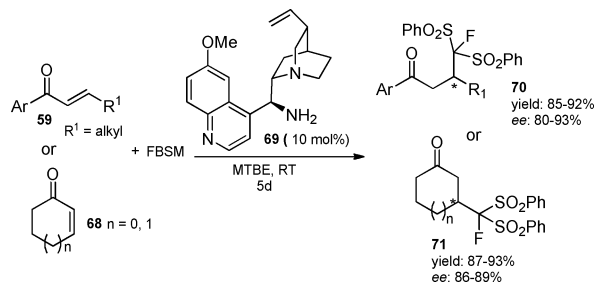
R-FNSM after deprotonation indicated that the stereoselectivity on the α-carbon did not originate from the deprotonation step, but rather from the interaction between FNSM and the chalcone–**62** complex.

The Michael addition of FBSM to α,β-unsaturated aldehydes **64** was reported by Córdova' group,[19a] Wang's group[19b] and Rios' group[19c] in 2009. The reaction was catalysed by 20 mol% of diarylprolinol **65**, and required triethylamine as an additive to accelerate the reaction. The intermediate Michael adduct **66** was reduced *in situ* to yield the final products **67** with high *ee* values (Scheme 17).



Scheme 17 Asymmetric Michael addition between FNSM and α,β-unsaturated aldehydes.

Kim and co-workers reported the asymmetric Michael reaction of FBSM and α,β-unsaturated ketones in the presence of bifunctional catalyst **69**.[20] Both linear as well as cyclic α,β-unsaturated ketones **59** and **68** were effective acceptors of the organofluoro nucleophile FBSM using this organocatalytic approach. The desired products **70** and **71** were achieved in high yields with good to high enantioselectivities (Scheme 18).



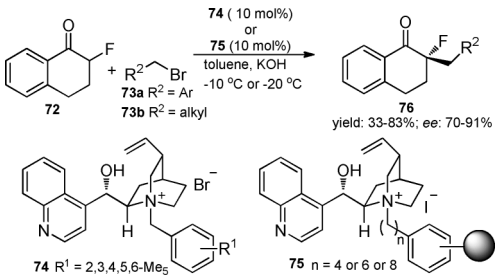
Scheme 18 Asymmetric Michael reaction of FBSM and α,β-unsaturated ketones.

Fluorinated aromatic ketones as nucleophiles

Compared to their linear aliphatic counterparts, the study and application of fluorinated aromatic ketones in asymmetric organocatalysis has received little attention; although the use of fluorinated silyl enol ethers derived from α-fluorinated cyclic ketones as nucleophiles in enantioselective transitional-metal catalysed reactions has been reported.[21]

The use of α-fluorotetralone as a nucleophile in asymmetric alkylation reactions was first demonstrated by Shioiri and co-workers in 1999.[22] The reactions were conducted using α-fluorotetralone **72** with various aryl or alkyl methyl bromides **73**, catalysed by phase-transfer catalyst **74** in the presence of a strong base (KOH). The desired alkylated adducts **76** were obtained with moderate to high *ee* values, but the yields were not satisfactory in many cases.

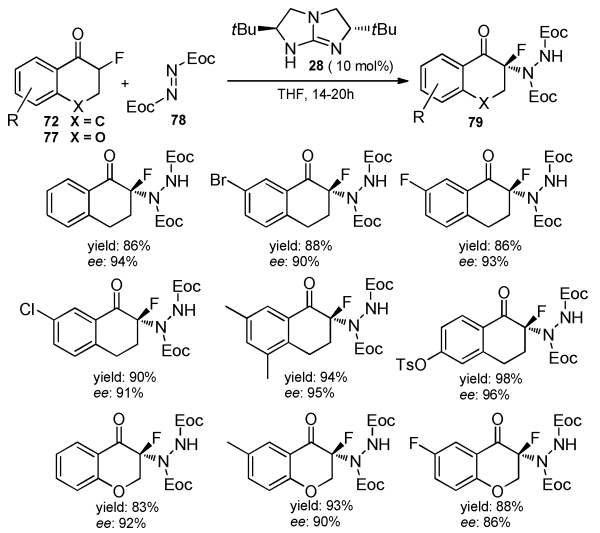
Subsequently, Cahard and co-workers reported a single example of asymmetric alkylation reaction between α-fluorotetralone **72** and benzyl bromide (**73a**: R^2 = Ph) using a polymer-supported phase-transfer catalyst **75**.[23] The reaction was carried out in presence of 21 equivalents of KOH and afforded 2-benzyl-2-fluoro-1-tetralone (**76**: R^2 = Ph) in 73% yield and 62% *ee* (Scheme 19).



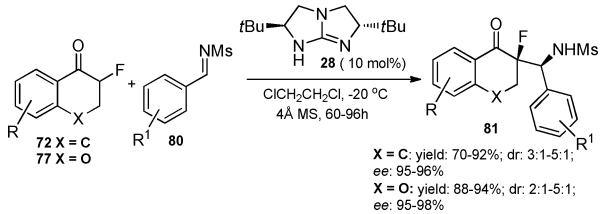
Scheme 19 Asymmetric alkylation of α-fluorotetralone.

Tan and co-workers investigated the use of α-fluorotetralones as nucleophiles in the asymmetric direct α-amination of α-fluorinated aromatic cyclic ketones, catalysed using chiral guanidine **28**[24] (Scheme 20). A bulkier version of azodicarboxylate, di-3-ethylpentan-3-yl azodicarboxylate **78** (EocN=NEoc) was developed by Tan's group to improve the enantioselectivity of the reaction. A variety of cyclic ketones **72** with varying substituents on the aromatic ring was prepared from α-tetralone derivatives. Excellent yields and high *ee* values were achieved irrespective of the electronic nature or positions of the substituents on the aromatic ring. Similarly, the α-fluorinated 4-chromanones derivatives **77** also reacted efficiently with azodicarboxylate **78**, affording the chiral α-hydrazino-α-fluorinated 4-chromanones derivatives in good yields and enantioselectivies

Tan and co-workers extended the methodology for asymmetric Mannich reactions using these organofluoro nucleophiles, obtaining excellent enantioselectivities and high yields with *N*-mesyl (Ms) imines **80** but the diastereoselectivities of products **81** were moderate. The enantioselectivities of the minor *anti*-isomers were typically less than 33% *ee*; however, the two diastereoisomers were easily separated by flash chromatography.



Scheme 20 Asymmetric amination of α-fluorotetralone and α-fluorinated 4-chromanones.



Scheme 21 Asymmetric Mannich reaction of α-fluorotetralone and α-fluorinated 4-chromanones.

Conclusions

The development of simple and efficient strategies to introduce fluorine into organic molecules has attracted much attention due to the value of organofluoro-compounds. During the past few years, organocatalytic approaches employing organofluoro compounds as nucleophiles in asymmetric C–C bond forming reactions has been an active area of research. Much of these efforts have been focused on reactive organofluoro nucleophiles such as fluorinated dicarbonyl compounds, FBSM and FSM derivatives. For α-fluorinated ketone nucleophiles, some progress has been made by utilizing fluoroacetone as a donor, mainly depending on the formation of reactive enamine intermediates. The use of fluorinated aromatic ketones as nucleophiles is less studied although several examples have been reported recently. On the other hand, due to their low reactivities, acyclic fluorinated aromatic ketones have yet to be investigated as nucleophiles. In view of the importance of fluorinated compounds for various applications, the use of organofluoro nucleophiles in organocatalysed asymmetric synthesis of organofluoro-compounds will continue to flourish and more exciting developments in this area are expected.

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