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# C-F insertion reaction sheds new light on the construction of fluorinated compounds

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ABSTRACT

The atom-economical C-F insertion chemistry is emerged as a promising technology for the synthesis of various fluorinated scaffolds, which have wide applications both in the academic and the industrial communities. The past three years have witnessed rapid developments in this field. This highlight provides an overview on the evolution according to the fluorinating agents used.



## 1. Introduction

The selective incorporation of fluorine atoms onto organic compounds has emerged as a common and useful strategy to design agrochemicals, pharmaceuticals, medical imaging agents, and functional materials [1–7], since the fluorine substitution can often lead to a dramatic change in physical, chemical, and biological properties [8,9]. For example, vericiguat **1** demonstrates the superior pharmokinetic property [10], chiral fluorinated thalidomide **2** displays the enhanced metabolic stability [11], and fluorinated tolane **3** shows significantly enhanced photoluminescence efficiency [12] when compares with their respective non-fluorinated counterparts **4**, **5**, and **6** (Scheme 1). Therefore, given the beneficial effects bring about by fluorine atoms, organofluorine molecules have become popular synthetic targets over the years [13–21]. However, how to prepare fluorinated compounds is not as simple as it seems and has been daunting chemists for a long time. This is likely due to the following reasons: (1) The availability of natural fluorine-containing compounds that can potentially be used as starting materials is very limited; (2) the high electronegativity of fluorine atom and the high hydration energy of the fluoride anion makes the C-F bond formation very challenging. Consequently, strategies suitable for the synthesis of chlorinated, brominated, and iodinated compounds cannot be easily extended to fluorinated compounds.

Despite the challenges mentioned above, the wide applications of fluorinated compounds have stimulated extensive research on seeking for efficient strategies for their construction in the past decades. Three commonly used strategies are shown in Scheme 2. These include: (a) Nucleophilic, electrophilic and radical fluorination reaction of non-fluorinated precursors; (b) defluorinative functionalization reaction of poly-fluorinated substances; and (c) C-F bond insertion reaction. Of these strategies developed, the C-F bond insertion reaction which proceeds *via* the concomitant formation of C-C and C-F bonds is the most desirable as it allows the rapid construction of more complex organofluorine molecules using readily available organofluorine compounds with an atom economy of 100% and without requiring any exogenous fluorinating reagent. However, the merge of C-F bond cleavage and formation in a single transformation is a challenging task because of the high bond dissociation energy of both C-F and metal-F bonds as well as the low reactivity of the fluoride released upon C-F bond cleavage [22]. Considering the advantages of C-F insertion reactions, considerable efforts have been devoted to developing inno-

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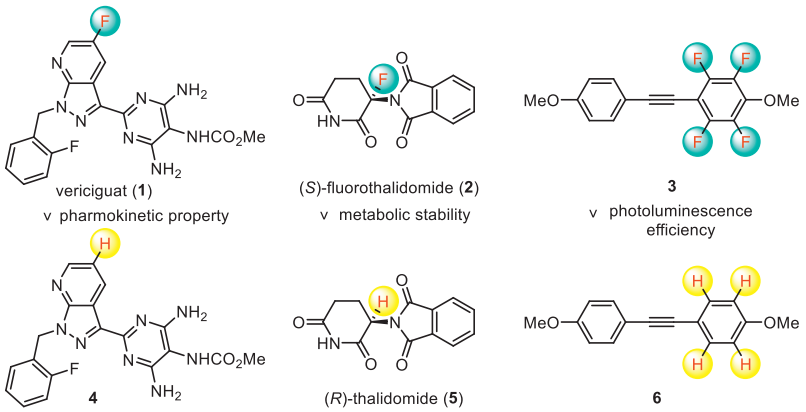
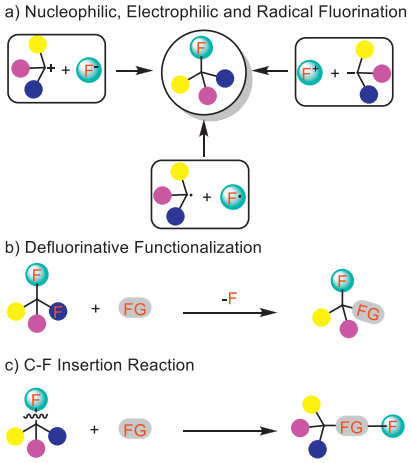
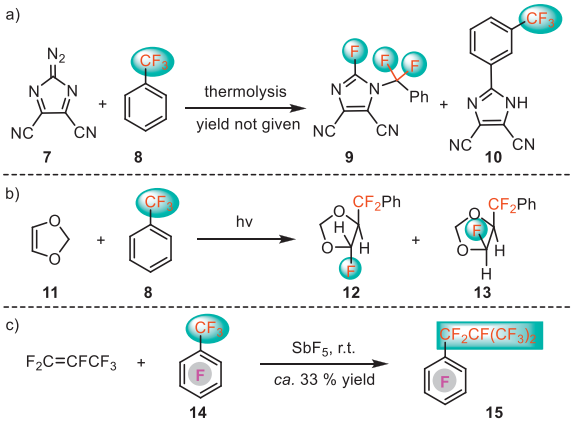



**Scheme 1.** Structures of representative drugs, materials and their corresponding analogues.




**Scheme 2.** Strategies for the construction of organofluorine molecules.




**Scheme 3.** Early reports of C-F insertion reactions.

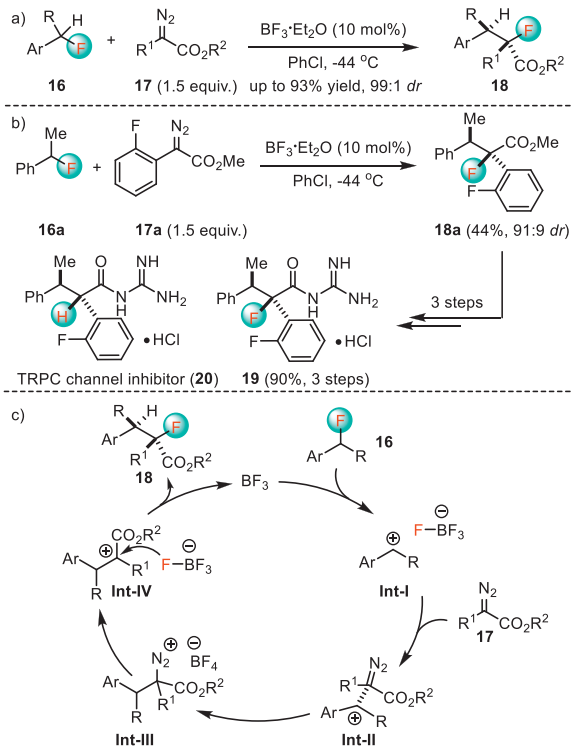
vative protocols to overcome these challenges, and breakthroughs have been achieved recently. Therefore, this highlight will focus on this emerging field, aiming to inspire and push for new developments. The contents of this highlight will be arranged by the fluorinating agents used.

## 2. Benzyl or propargyl fluorides as the fluorinating agents

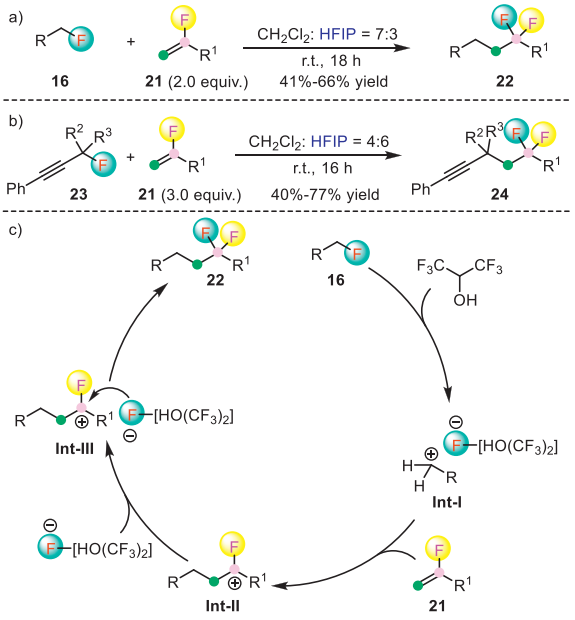
As mentioned above, C-F bond insertion is a highly challenging and complicated process. Therefore, so far, reports of such processes are scarce in the literature. In 1973, Sheppard and Webster found that a C-F bond of trifluoromethylbenzene insertion of a C-N unit with diazonium salt-derived reactive *N*-heterocyclic carbenes could occur under heating condition (Scheme 3a) [23]. In 1985, Mattay's group reported a photo-mediated insertion of alkenes into C-F bonds of trifluoromethylbenzene to give products **12** and **13** (Scheme 3b) [24]. Later in 2018, a $SbF_5$ promoted insertion of perfluoropropene into C-F bonds of perfluoroarenes **14** was accomplished by the Kapov's group (Scheme 3c) [25]. However, in these early reports, the yields are extremely low as the formation of the desired C-F insertion products was accompanied with substantial amounts of side products.

Although the C-F bond insertion reactions described above are not so successful, these pioneering reports demonstrated that it was possible to insert functional groups into a benzylic C-F bond of trifluoro- and perfluoro-arenes. Considering that C-F bond dissociation energy (BDE) increases with increasing fluorine substitution [26], the use of benzylic fluorides with lower BDEs might be amenable to the C-F bond insertion process. In this context, in 2021, Yasuda and Nishimoto reported the first example of a $BF_3$-catalyzed formal insertion of diazo esters **17** into the C-F bonds of benzylic fluorides **16**, which furnished the one-carbon elongation products, $\alpha$-fluoro-$\alpha$,$\beta$-diaryl esters **18**, in moderate to good yields and with high diastereoselectivities (Scheme 4) [27]. This catalytic method exhibits high chemoselectivity, broad substrate scope and good functional group tolerance, and can also be applied toward the synthesis of compound **19**, a fluorinated analogue of compound **20** that is utilized as a transient receptor and potential canonical (TRPC) channel inhibitor. DFT calculations suggested that the $BF_3$ catalyst initially abstracted $F^-$ from benzylic fluoride **16** to generate the benzylic cation and $BF_4^-$ (**Int-I**). This benzylic cation would thereafter be attacked by diazo esters **17** to form intermediate **Int-II**. $N_2$ Extrusion from **Int-II** afforded contact ion pair **Int-III**. The C-F bond re-formation *via* the nucleophilic attack of the F atom in $BF_4^-$ to the carbocation produced the desired $\alpha$-fluoro-$\alpha$,$\beta$-diaryl esters **18**.

Very recently, Hopkinson *et al.* described a hexafluoroisopropanol (HFIP) mediated C-F insertion of secondary benzyl fluorides **16** with $\alpha$-fluorinated styrenes **21** to produce *gem*-difluorinated products **22** in 41%-66% yield (Scheme 5) [28]. In addition, upon increasing the amount of **21** and changing the $CH_2Cl_2$:HFIP ratio from to 7:3 to 4:6, the propargylic fluorides **23** can also serve as suitable reaction partners and gave the corresponding products **24** in good yields. However, benzyl fluorides bearing strong electron-withdrawing groups (*e.g.*, $NO_2$, $CF_3$ and CN) at the *para*-position and primary propargylic fluorides were not

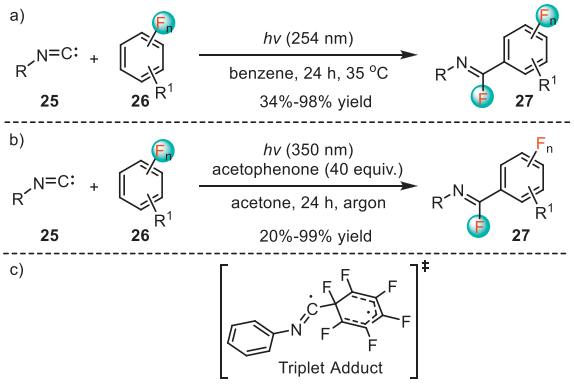



**Scheme 4.** $BF_3$-Catalyzed insertion of diazo esters into C-F bonds of benzylic fluorides.




**Scheme 5.** Hydrogen-bonding-mediated C-F insertion reactions of benzyl or propargyl fluorides with $\alpha$-fluorostyrenes.

compatible with the present reaction conditions likely because of the decreased stability of the *in situ* formed benzyl or propargyl cation. Interestingly, the authors found that the reactions should be conducted in a PTFE vial rather than in a glass Schlenk tube in that the HF or silicon fluoride species generated from the glass surface caused side reactions. Notably, the use of pure $CH_2Cl_2$ totally shut down the reaction. This result confirmed the key role of HFIP as a hydrogen bond donor. Accordingly, the authors proposed that HFIP served as the hydrogen bond donors to activate C-F bonds of benzyl fluorides. This process liberated a benzyl cation **Int-I** and a HFIP stabilized fluoride ion. Subsequent electrophilic addition of the benzyl cation to fluorinated alkenes generate a new cation **Int-II**, which can be trapped by fluoride ion to give the *gem*-difluorinated products **22**.



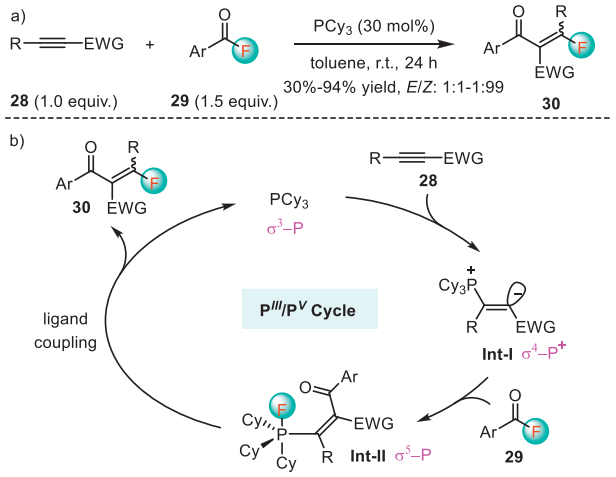

**Scheme 6.** Light-mediated insertion of isonitriles into the C-F bond of polyfluorinated arenes.

## 3. Perfluorinated arenes as the fluorinating agents

Polyfluorinated arenes constitute a unique class of molecules and play important roles in the fields of pharmaceuticals, pesticides and material science [29–31]. Typically, they can be synthesized by arene fluorination or by partial arene defluorination. However, these classic strategies suffer from lengthy reaction steps or low atom economy [32]. Therefore, the development of novel C-F insertion reactions that occur *via* mechanistically distinct pathways and also produce complimentary products are of great value. In this context, in 2015, Studer and co-workers disclosed the first light-mediated insertion of aryl and alkyl isonitriles **25** into the C-F bond of polyfluorinated arenes **26**, affording various imidoyl fluorides **27** in moderate to excellent yields (Scheme 6a) [33]. The versatile imidoyl fluorides can further be readily transformed into other valuable compounds that are otherwise difficult to prepare using the available methodologies. Unfortunately, high energy and pressure mercury lamp ($\lambda_{exc} = 254$ nm) was required for the efficient excitation of isonitriles, which resulted in a limited functional group tolerance.

In order to solve this issue, in 2020, the authors reported an alternative photosensitized C-F insertion reaction of polyfluorinated arenes **26** with isonitriles **25** to deliver benzimidoyl fluorides **27** in 20%-99% yields (Scheme 6b) [34]. In this case, acetophenone was proved to be a suitable external photosensitizer, which enabled the reaction to be performed upon irradiation at 350 nm. The mild light warrants the high functional group tolerance of this methodology. For example, this methodology tolerated the halogen functionality (*e.g.*, Cl, Br) in the isonitrile and polyfluorinated arene components, which are challenging substrates in the previous study since 254 nm irradiation caused C-halogen bond homolysis.

Mechanistic studies showed that these C-F insertion reactions proceeded through the triplet state of the isonitriles (Scheme 6c). As for the reaction shown in Scheme 6a, the triplet state was generated *via* 250 nm excitation, while the acetophenone-sensitized reaction likely proceeded through the Dexter energy transfer at 350 nm (Scheme 6b). However, the mechanism regarding the observed regioselectivity is currently not fully understood, and the precise control of regioselectivity is still an unsolved problem given that the arene contains multiple C-F bonds.

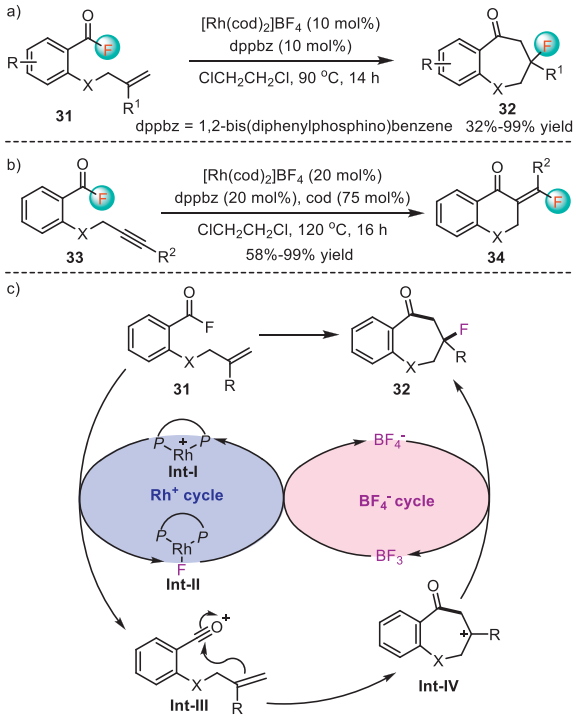



**Scheme 7.** $PCy_3$-catalyzed insertion of alkynoates into C-F bonds of acyl fluorides.

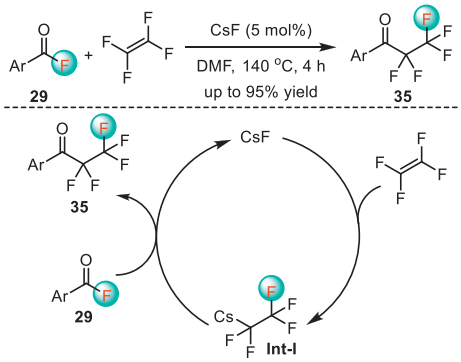
## 4. Acyl or carbamoyl fluorides as the fluorinating agents

Apart from benzylic and propargylic fluorides, acyl fluorides that display a good balance of highly electrophilic reactivity and stability are also popular substrates for atom-economical C-F insertion reactions as the corresponding fluoroaroylation products are useful for drug discovery [35,36]. In 2020, Tobisu's group reported an elegant phosphine-catalyzed intermolecular acylfluorination of alkynoates **28**, which provided rapid and straightforward access to a variety of highly functionalized monofluoroalkene derivatives **30** (Scheme 7) [37]. This transition metal free protocol operates at room temperature, thus permitting a good functional group tolerance. For example, a broad range of acyl fluorides **29** bearing electron-neutral, electron-deficient, or electron-rich groups readily participated in this reaction with (hetero)aryl-substituted alkynoates **28** to produce the corresponding monofluoroalkenes **30** in moderate to excellent yields (30%-94%). However, the alkyl-substituted alkynoates **28** were not compatible, which constituted the limitation of this method. It should be noted that the stereoselectivity of the reaction is substrate dependent. While most products were obtained as an inseparable *E* and *Z* isomers (1:1-1:1.6), the use of a 2-pyridyl alkynoate led to excellent *Z*:*E* selectivity (96:4 ~ >99:1). This is possibly due to the stabilizing n-$\pi^*$ interaction between the nitrogen lone pair of pyridyl ring and C=O $\pi^*$ orbital. Based on the control experimental results and density functional theory (DFT) calculations, the authors proposed that the reaction might occur *via* the addition of tertiary phosphines to alkynoates followed by the nucleophilic substitution with an acyl fluoride to generate the key P(V) intermediate **Int-II**, which was then underwent an unprecedented C-F bond-forming ligand coupling to afford the products **30** and release the catalyst.

More recently, Tobisu's group further disclosed a $[Rh(cod)_2]BF_4$ catalyzed intramolecular carbofluorination reaction of alkene tethered acyl fluorides (Scheme 8) [38]. The reaction allows access to complex tertiary alkyl fluorides **32** bearing a seven-membered heterocycle ring in 32%-99% yield. In addition to alkene tethered acyl fluorides, differently substituted alkyne tethered acyl fluorides **33** were competent substrates, giving the fluorinated 4-chromanone derivatives **34** with high yields. However, although acyl fluorides bearing 1,1-disubstituted alkenes were found to be well tolerated, substrates with an internal alkene or a mono-substituted alkene moiety failed to participate in this carbofluorination reaction, which constituted the limitations of this approach. Notably, the cationic character of the rhodium catalyst was a key factor for the success of this reaction as the electronically neutral $[RhCl(cod)]_2$ showed no catalytic activity. They proposed that a Lewis acidic rhodium cation initially abstracted a fluoride anion from acyl fluoride to form an acylium cation **Int-III** and a neutral rhodium(I)-fluoride complex **Int-II**. The interception of acylium cation **Int-III** with a tethered alkene led to the formation of a tertiary carbocation intermediate **Int-IV**. Subsequently, carbocation **Int-IV** abstracted a fluoride from $BF_4^-$ to give product **32** and $BF_3$, which reacted with complex **Int-II** to regenerate cationic rhodium catalyst. In this catalytic cycle, $BF_4^-$ can be viewed as the fluoride anion shuttle, which acts cooperatively with a rhodium cation to mediate the cleavage and formation of a C-F bond.

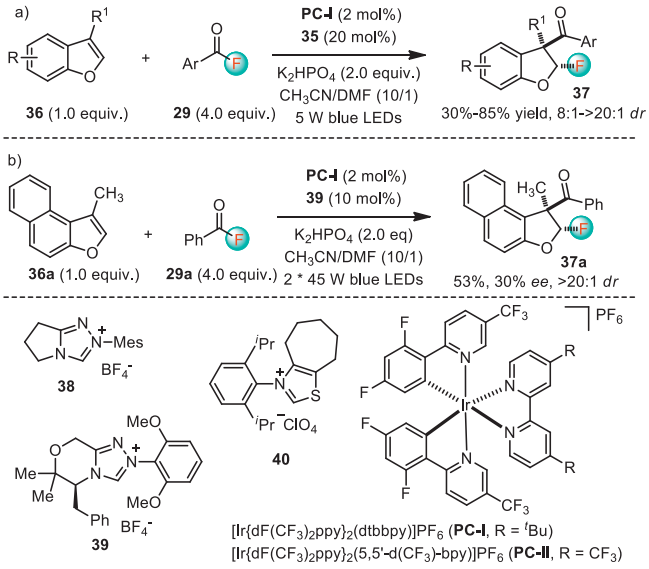



**Scheme 8.** $[Rh(cod)_2]BF_4$-catalyzed intramolecular carbofluorination of alkenes and alkynes.

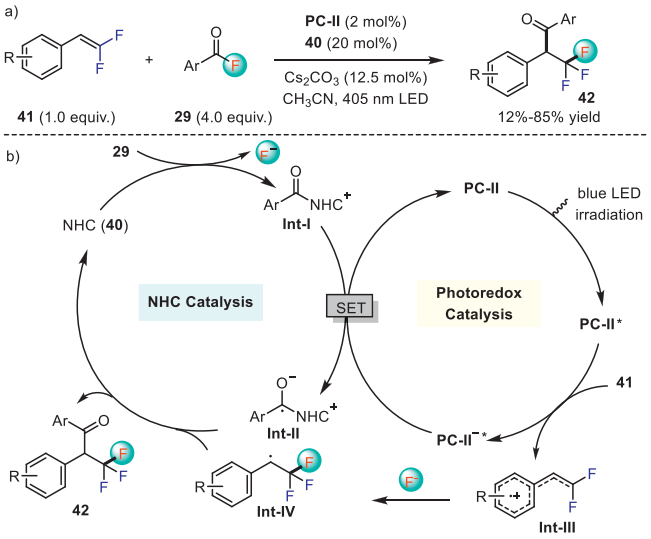



**Scheme 9.** CsF-catalyzed insertion of tetrafluoroethylene into C-F bonds of acyl fluorides.

In 2021, Ogoshi and co-workers reported a CsF-catalyzed fluoroacylation of tetrafluoroethylene with acyl fluorides **29** (Scheme 9) [39]. This reaction occurred *via* the addition of CsF across tetrafluoroethylene to generate intermediate **Int-I**, followed by the reaction with an acyl fluoride **29** to afford the pentafluoroethyl ketones **35**. However, the substrate scope of this reaction is largely limited to aromatic acyl fluorides, and high reaction temperature (140 °C) was required to avoid the formation of side products.




**Scheme 10.** Cooperative NHC and photoredox catalysis enabled access to 3-aroyl-2-fluoro-2,3-dihydrobenzofurans.



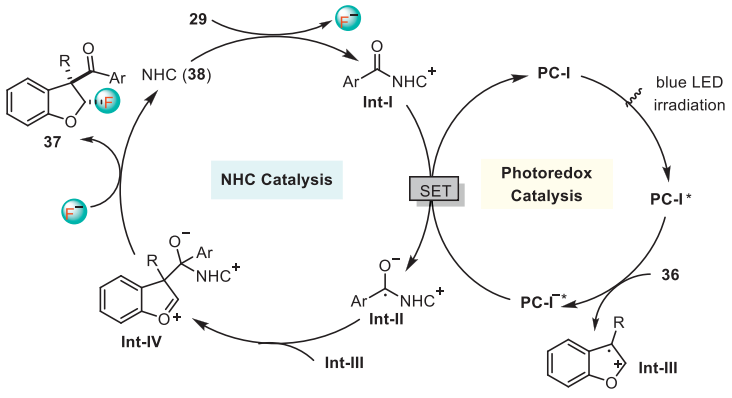

**Scheme 12.** The synthesis of $\alpha$-$CF_3$-substituted ketones by cooperative NHC and photoredox catalysis.

In 2022, Studer and colleagues developed a cooperative *N*-heterocyclic carbene (NHC)/photoredox catalysis strategy for the 2,3-fluoroaroylation of benzofurans with aroyl fluorides **29** as the bifunctional reagents (Scheme 10) [40]. In the presence of 2 mol% of photocatalyst **PC-1** and 20 mol% of NHC catalyst **38**, the dearomatization reactions proceeded smoothly to afford 3-aroyl-2-fluoro-2,3-dihydrobenzofurans **37** with 30%-85% yields and high diastereoselectivity (8:1 ~ >20:1 *dr*). Remarkably, upon running the reaction of **36a** and **29a** with chiral NHC catalyst **39**, the corresponding product **37a** could be furnished with 53% yield, 30% *ee* and >20:1 *dr*. In addition, it should be noted that reactions also took place with *N*-acyl indoles to afford 3-aroyl-2-fluoro-dihydroindoles with moderate yield and excellent diastereoselectivity, which demonstrated the high functional group compatibility of this methodology.

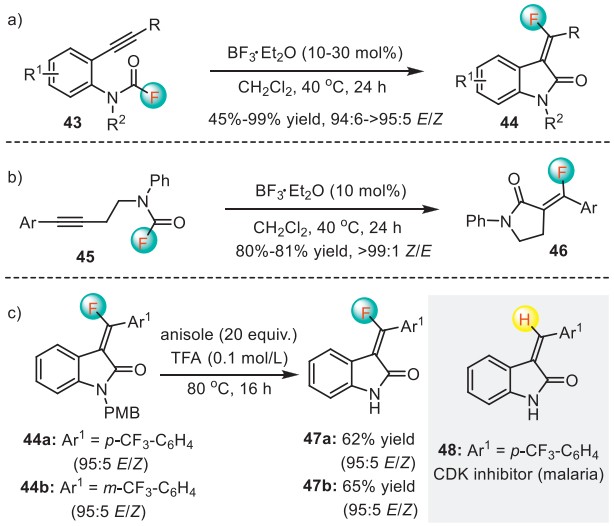
The authors proposed that a photoexcited $Ir^{III}$ species (**PC-I***) oxidized benzofuran **36** to a radical cation intermediate **Int-III** (Scheme 11). At the meantime, NHC catalyst **38** initially reacted with the acyl fluoride **29** to form an azolium ion intermediate **Int-I**, which was subsequently reduced by Ir(II) to give the persistent ketyl radical intermediate **Int-II**. C-C bond coupling of the radical cation **Int-III** and the ketyl radical **Int-II** led to formation of oxocarbenium intermediate **Int-IV**, which could be trapped by the fluoride anion *trans* to the bulky alcoholate moiety to provide the final fluoroacylation products **37** with high diastereoselectivity. This rare radical/radical cation cross-coupling strategy opens up new opportunities to develop reactions that are otherwise difficult to be realized by using other protocols.

Very recently, Studer *et al.* further successfully accomplished the fluoroaroylation of *gem*-difluoroalkenes [41]. The same catalytic strategy using $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)\text{-}bpy)]PF_6$ **PC-II** (2 mol%) as the photoredox catalyst and the triazolium salt **40** as the NHC precatalyst (20 mol%) was adopted to deliver the $\alpha$-trifluoromethylated ketones **42** with 12%-85% yields (Scheme 12). This method encompasses a broad range of alkenes (*e.g.*, *gem*-difluoroalkenes, $\alpha$-fluorostyrenes and simple styrenes) and aroyl fluorides. However, aliphatic acyl fluorides remain problematic substrates. The reaction is postulated to occur in a fashion similar to the mechanism depicted in Scheme 11. In this case, an $\alpha$-trifluoromethylated benzyl radical species **Int-IV** was involved, which finally give rise to the targeted $\alpha$-$CF_3$-substituted ketones through the cross-coupling with ketyl radical **Int-II** formed by the reaction of aroyl fluoride **29** with NHC catalyst **40** and the subsequent single electron transfer reduction by photocatalyst **PC-II**.

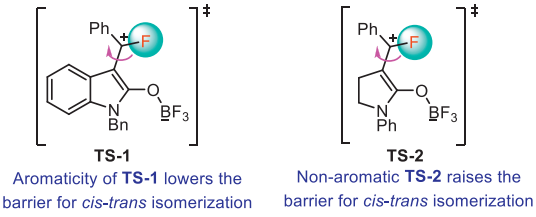
Compared with acyl fluorides, the catalytic C-F bond cleavage of carbamoyl fluorides was much more difficult due to their significantly less electrophilic reactivities [42]. Le and co-workers made a breakthrough in this field. They discovered that $BF_3{\cdot}OEt_2$ could catalyze the carbofluorination reaction of alkyne-tethered carbamoyl



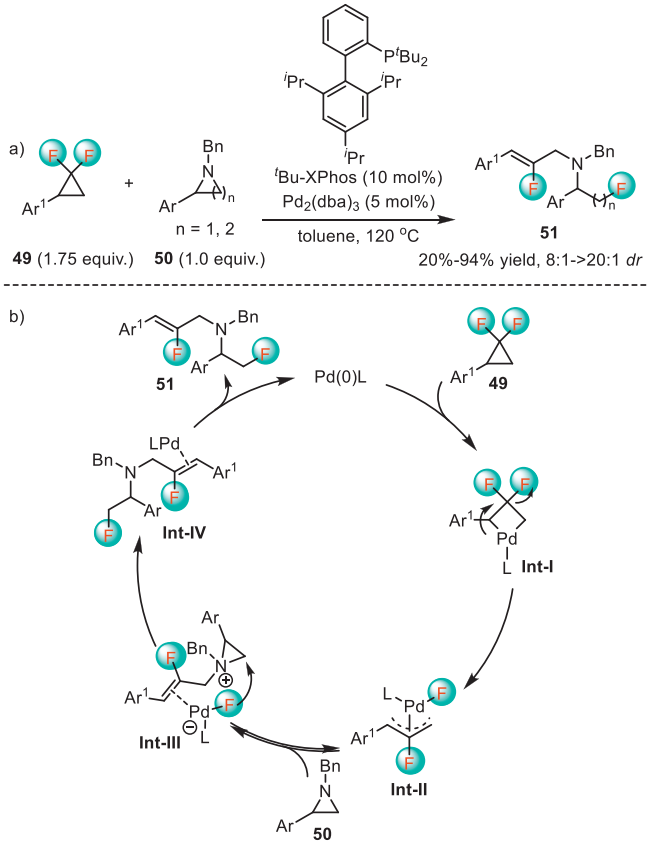

**Scheme 11.** Proposed catalytic cycle for the fluoroaroylation of benzofurans with aroyl fluorides.




**Scheme 13.** $BF_3$-catalyzed fluorocarbamoylation of alkyne-tethered carbamoyl fluorides.




**Scheme 14.** The possible transition states and origins of stereoselectivity of the fluorocarbamoylation reaction.




**Scheme 15.** Pd-catalyzed fluoroallylation of azardines with *gem*-difluorocyclopropanes.

fluorides to afford 3-(fluoromethylene)oxindoles **44** and $\gamma$-lactams **46** with 45%-99% yield, 94:6 ~ >95:5 *E*/*Z* and 80%-81% yield, >99:1 *Z*/*E*, respectively (Scheme 13) [22]. In particular, this method allowed compounds **47a** and **47b**, fluorinated derivatives of known protein kinase inhibitors, to be constructed rapidly with moderate yields and excellent stereoselectivities. The mild reaction conditions along with the readily available catalyst make this methodology attractive for drug development.

Experimental and computational studies suggested that the fluorocarbamoylation reaction proceeded through a turnover-limiting annulation step, followed by fluoride ion transfer from a $BF_3$-coordinated carbamoyl adduct to forge the C-F bond (Scheme 14). In addition, the calculations also provide insight into the origin of the opposite stereoselectivity observed for fluoromethylene oxindoles **44** and $\gamma$-lactams **46**. For methylene oxindoles, the transition state **TS-1** possesses significant aromatic character, and therefore, easing the barrier for C=C bond isomerization to produce the thermodynamically favored *E*-isomer as the major product. However, the transition state **TS-2** for the isomerization of $\gamma$-lactams **46** does not benefit from the aromatic stabilization effect, which leads to a significantly higher barrier for isomerization and the exclusive formation of the *Z*-$\gamma$-lactams.

## 5. *gem*-Difluorocyclopropanes as the fluorinating agents

In recent years, the readily available *gem*-difluorocyclopropanes have attracted considerable attention partly due to their ability to participate in various ring-opening reactions [42–45]. However, these reactions suffered from low atom economy as the fluorine atom scissored from *gem*-difluorocyclopropane could not be incorporated into the products. The breakthrough in this field was achieved by Liu *et al.*, they successfully realized an innovative palladium-catalyzed fluorinative bifunctionalization of aziridines and azetidines (Scheme 15) [46]. Under optimum conditions, the regioselective C-C and C-F bond cleavage of *gem*-difluorocyclopropanes **49** proceeded smoothly to afford various bisfluorinated amines **51** in moderate to excellent yields and with excellent *Z*/*E* ratio. This fluorinative bifunctionalization reaction exhibited a broad substrate scope and was easy to scale up. In addition, the products can serve as the important class of building blocks in organic synthesis, as the versatile carbon-carbon double bond permitted various follow-up transformations.

The proposed mechanism began with the oxidative addition of Pd(0)L into *gem*-difluorocyclopropanes **49** to form the four-membered-ring palladacycle complex **Int-I**. The subsequent $\beta$-F elimination generated 2-fluorinated $\eta^3$-allyl palladium complex **Int-II**. Afterward, cyclic tertiary amines **50** attacked the complex **Int-II** to produce $\eta^2$-coordinated *N*-tetrasubstituted allyl ammonium complex **Int-III**. Finally, difluorinated amines **51** were formed from ring opening of aziridinium ion at the electrophilic carbon by fluoride ligand on Pd(0) center. This work represents a notable advance in the C-F insertion chemistry, which opens up opportunities for designing new reactions.

## 6. Conclusion

As summarized in this review, C-F insertion reaction represents a reliable and powerful protocol for the rapid and atom-economical synthesis of various versatile fluorinated compounds and some related bioactive natural products and drugs. The past three years have witnessed rapid developments in this field. Nevertheless, despite these excellent achievements, this research area is still in its infancy compared to more established insertion reactions of C-X bonds of the other halogens. This emerging field is still

facing some challenges that need to be addressed in the future. First, the substrate scope of fluorinating reagents that can be utilized for C-F insertion reactions is not broad enough so far. The examples described in this highlight clearly shown that catalysts were significant for merging C-F bond cleavage and formation in a single transformation. As a result, the rational design and development of catalytic systems are at the heart of addressing this challenge and will be crucial for advancing this chemistry. Second, catalytic enantioselective C-F insertion reactions remain unknown, albeit this will provide new possibilities for C-F insertion chemistry. Therefore, the development of efficient strategies to achieve this goal could be an important direction for future studies. We hope this highlight allows readers to notice the advantages and drawbacks of current C-F insertion reactions and to identify new activation methods and concepts for addressing the remaining challenges. As this field has recently attracted tremendous research efforts, it can be expected that more and more breakthroughs will appear in the future, and it might become a popular choice for the synthesis of fluorinated compounds.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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