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Review

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Recent progress in hypervalent iodine-mediated fluorination of organic compounds

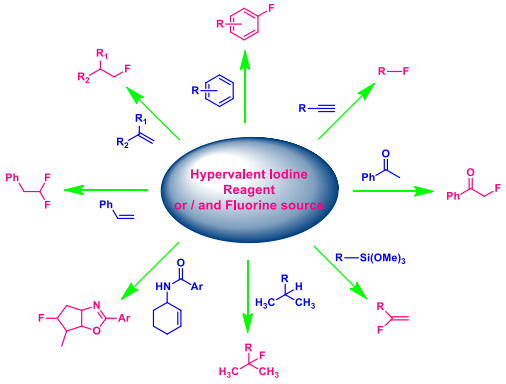
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Received 03-31-2023 **Accepted** 08-23-2023 **Published on line** 09-10-2023

Abstract

Fluorine is an essential element for the protection of teeth and bones. Number of fluorinated drug molecules is available in the literature. Mainly, the addition of fluorine atom increases the lipophilicity of the drugs that makes it unique in the field of medicinal chemistry. In past two decades, hypervalent iodine chemistry has received a particular attention in organic synthesis mainly due to their mild reaction conditions and environmental friendly nature of hypervalent iodine reagents. Although their use is not just restricted to oxidation reactions, these reagents were primarily recognized for their oxidative properties. Due to their use in catalysis, the demand for these reagents has recently surged significantly for green chemistry. The hypervalent iodine reagents were also been used to achieve number of synthetically valuable organic transformations. Recently, hypervalent iodine reagents have been successfully employed to achieve various fluorination reactions. In this review recent development of fluorination of organic compounds using hypervalent iodine reagent are described.



Keywords: fluorines, hypervalent reagents, fluorination, Olah's reagent.

DOI: https://doi.org/10.24820/ark.5550190.p011.996 ©AUTHOR(S)

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1. Introduction

Fluorine is an essential element found in teeth and bones to prevent their decay.[1] Chemistry of organofluorines is well now established and receives significant applications in pharmaceutical chemistry. Various fluorinated aromatic compounds have been used as drug to treat various diseases.[2] Fluorine compounds shows few other applications such as finishing agent for fabrics, components of extinguishing agents, electroplating baths, lubricating oils and oxygen carriers in blood substitutes.[3] Lipophilicity is one of the key parameters used in medicinal chemistry.[4] Inclusion of fluorine atom in bioactive aromatic compounds enhances the lipophilicity significantly.[2,5]

As a result, new methodology for introducing a fluoride ion into small molecules has become an urgent need. Much work has been done on systematic methodology for fluorination into various molecules.[6-8] HIRs are green catalysts, and electrophilic reagents in organic transformations.[9-18] Book chapters and review papers on the chemistry of HIRs are now widely available. The reagents can also be employed for reductive elimination reaction, ligand exchange, ligand coupling, homolytic reactions, radical type reactions, single electron transfer reactions and oxidation under the effective reaction condition.[19-35]

Generally, the installations of fluorine atom into organic compounds are occurring by two ways. The first one is fluorination of organic compounds using fluorine containing hydervalent iodine reagents such as 1-Fluoro-3,3-dimethyl-1,2-benziodoxole **1**, 1-fluoro-1,2-benziodoxol-3(1H)-one **2**, 1-fluoro-N-acetylbenziodazole **3**, (difluoroiodo)benzene **4** and 4–(difluoroiodo)toluene **5**. The next way to install fluorine into organic species is using hypervalent iodine reagents along with the fluorine sources like HF.Py, Et_3N–3HF. In this route, fluorination occurs by *in situ* formation of reactive fluoroiodine(III) by the treatment of fluorine sources with fluorine free hypervalent iodine reagent such as Phenyliodine(III) diacetate (PIDA) **6,** [bis(trifluoroacetoxyiodo)]benzene (PIFA) **7** and iodoarenes (Figure 1).

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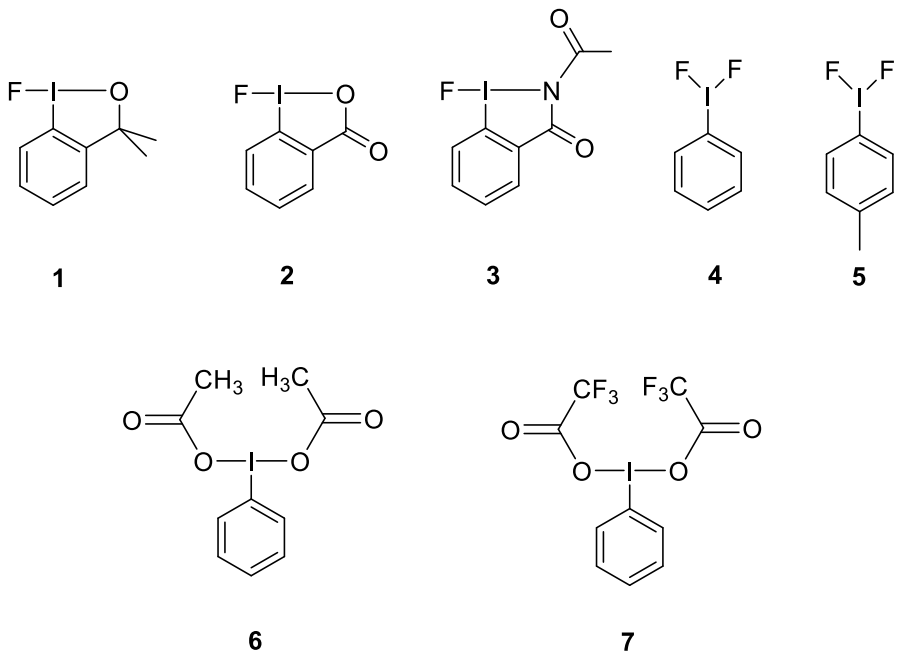
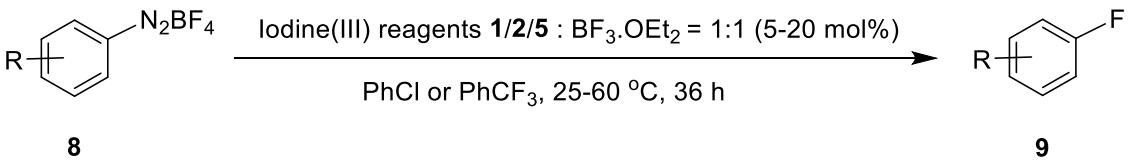


Figure 1. Structure of hypervalent iodine reagents used for fluorination.

This review encapsulates the literature data that includes transfer of fluorine group into different substrates with the assistance of hypervalent iodine reagents. Presentation of material is organized by the type of organo-fluorine moiety. This review covers literature published in or after 2015.

2. Synthesis of Aryl Fluorides

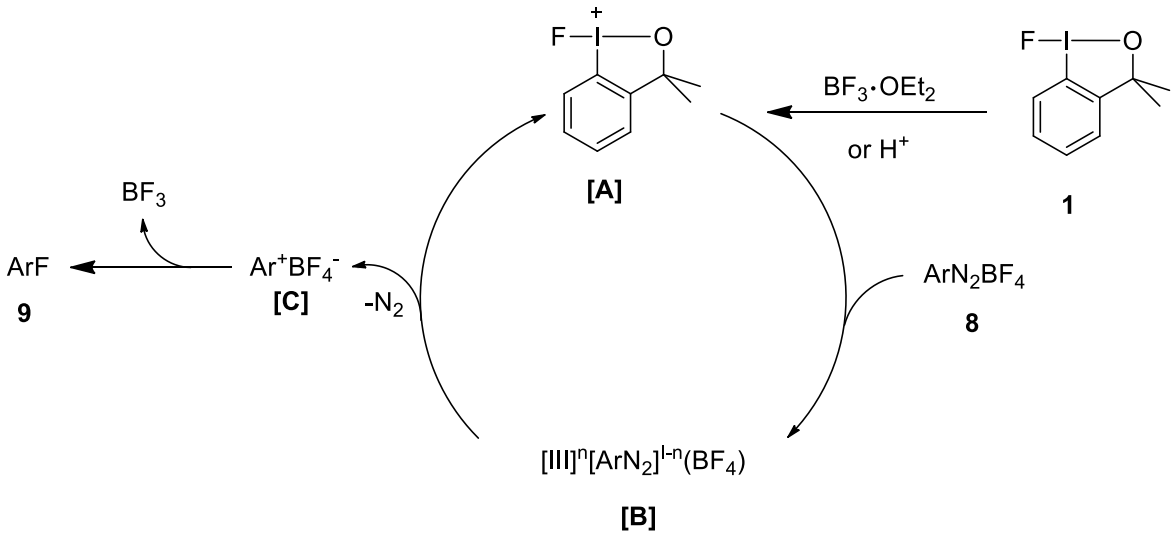
Aryl fluorides are important in several industries and hence there were significant studies done on development of aromatic C–F formation. The most commonly used method in the industrial production is the Balz-Schiemann reaction. Bo Xing et.al synthesized the fluoro benzene species **9** from benzenediazonium tetrafluoroborate **8** using Iodine (III) compound to promote fluorination using Balz-Schiemann reaction by activating the arene diazonium salts (Scheme 1). Using the reported reaction conditions, the expected products were produced well to afford excellent yields for substrates containing electron-neutral substituents, and it produced satisfactory yields for electron- withdrawing groups like iodo, keto, ester in the presence of **1**. This mild fluorination procedure was also found to be useful for fluorination of derivatives of molecules like androsterone, estrone, flavone, fluorene, menthol and tocopherol.[36]



Scheme 1. Catalytic Balz-Schiemann fluorination of substituted benzene **8**.

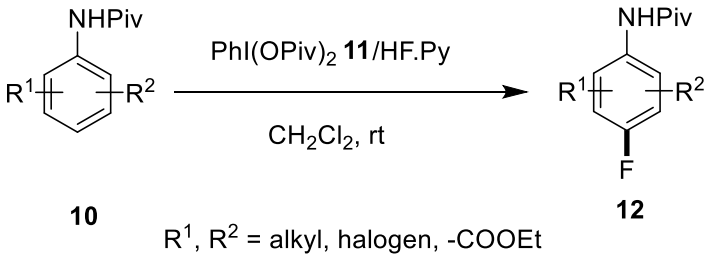
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The catalytic cycle of this reaction is given in Scheme 2. Reaction proceeds via aryliodonium(III)-catalyzed generation of aryl cation intermediates. The $BF_3.OEt_2$ or *in situ* generated H^+ activates the iodine(III) species **1** to form more active iodine(III) species [**A**] which may increase the leaving ability of the diazo functionality. After that the formation of an intermediate $Ar^+BF_4^-$ [**C**] occurs on the elimination of the diazo grup. Finally, intermediate [**C**] undergoes reductive elimination to form aryl fluoride **9**. Despite the fact that, the interaction between substrate **8** and the aryliodonium(III) catalyst is not clearly understood, while using fluorine contained hypervalent iodine compounds **1**, **2** and **5** leads to a very subtle difference in the amount of product, whereas PIDA **6** and PIFA **7** produced moderate yields.



Scheme 2. Proposed reaction mechanism for catalytic Balz-Schiemann fluorination of substituted benzene **8**.

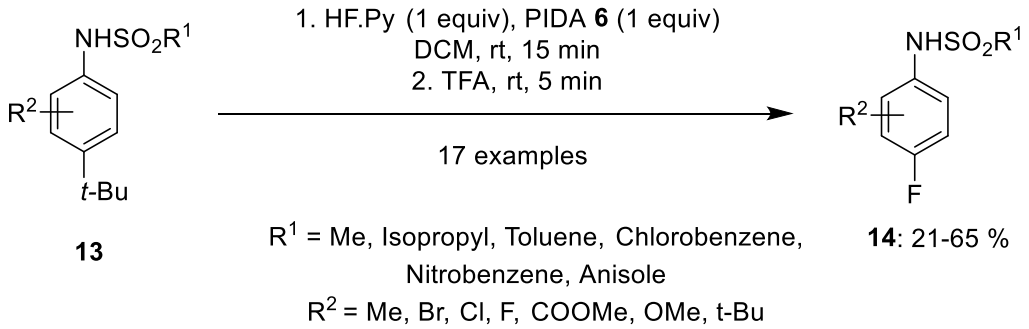
Tian Tian *et.al* reported a method for one pot fluorination of anilides using HIRs in the presence of fluorine source. Previously, Balz–Schiemann reaction was used to convert the diazonium tetrafluoroborate to fluorinated arenes. Halex process, Pd-catalysed nucleophilic fluorination are other methods which due to several drawbacks are being replaced. Here, the team has used HF.Py as fluorine source which resulted in the formation of fluorinated product and PIDA **6** due to its chemical stability and availability was specifically used as hypervalent iodine reagent (Scheme 3). Several substituted anilides having electron withdrawing groups like halogen, ester gave moderate yields and in addition to this, disubstituted anilides also smoothly produced para-fluorinated products.[37]



Scheme 3. Para fluorination of aniline **10** using Hypervalent iodine reagent **12**.

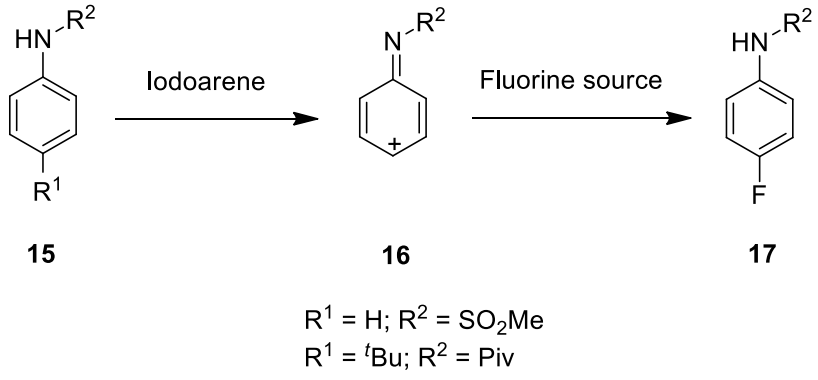
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A team discovered the oxidative nucleophilic fluorination of N-arylsulfonamides in 2015. They were proved that oxidative fluorination occurs regioselectively in the presence of HF.pyridine and PIDA **6** if the aniline **13** ring has a para-positioned tert butyl group. Moreover, the N-substituted aryl- and alkylsulfonyl groups were used to analyse the substrate's reactivity. The electrophilic position of the N-sulfonyl substituent, which is far from the aryl motie manifest to oxidative fluorination, produced moderate yield upto 54 to 65%. It is interesting to note that when electron-withdrawing $-NO_2$ groups inhibited the activation with PIDA **6**, thereby yielding less. Later, employing N-tosylated aniline precursors, experiments were conducted on the substitution pattern of the N-aryl sub-motif. The reaction was deemed to be tolerant to a numerous of *ortho* and *meta* positioned functional groups, including esters, halogens, and alkyl. Due to the lack of reactivity of ortho situated electron withdrawing groups, there was a negative impact on the reaction results the less amount of isolated yield. Amazingly, 2-tert-butyl-N-tosylaniline **13** only undergoes chemoselective fluorination at the para position without the *para*-located *tert*-butyl group. The mechanism reveals that reaction proceeded via an aryl-stabilised *N*-sulfonylnitrenium ion amenable to nucleophilic fluorination. The resultant fluorodienimine **14** is more easily aromatized with the addition of trifluoroacetic acid (TFA), by simultaneously losing the t-butyl carbocation (Scheme 4).[38]



Scheme 4. Nucleophilic fluorination of *para*–substituted aniline **13** using Hypervalent iodine reagent.

A plausible mechanism for the *para*-fluorination is that the iodoarene attacks the aniline resulting in the formation of charge delocalized intermediate **16**. Which further confined by HF to lead the formation of *para*-fluorinated amine **17** (Scheme 5).



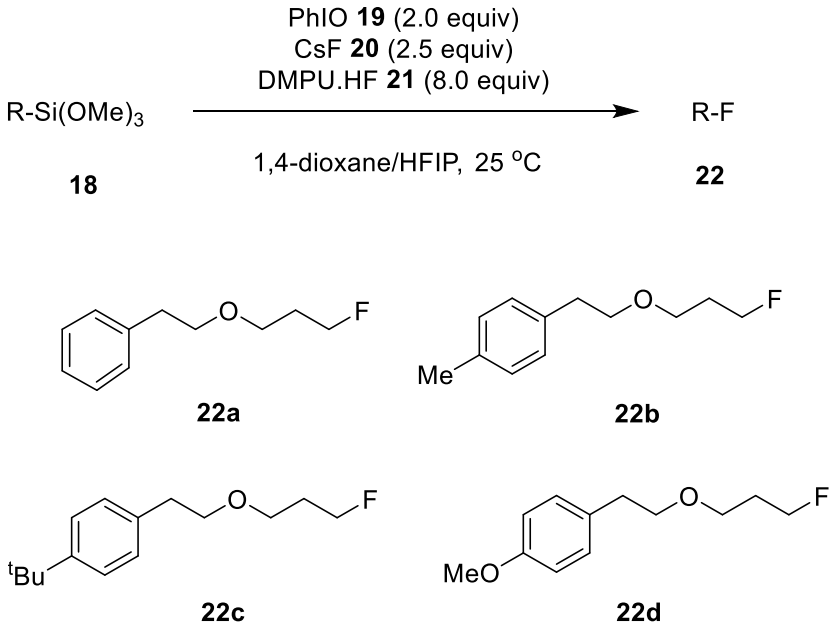
Scheme 5. Plausible reaction mechanism for the *para*-fluorination of aniline **13**.

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3. Synthesis of Alkyl and Alkenyl Fluorides

3.1. Primary fluorides

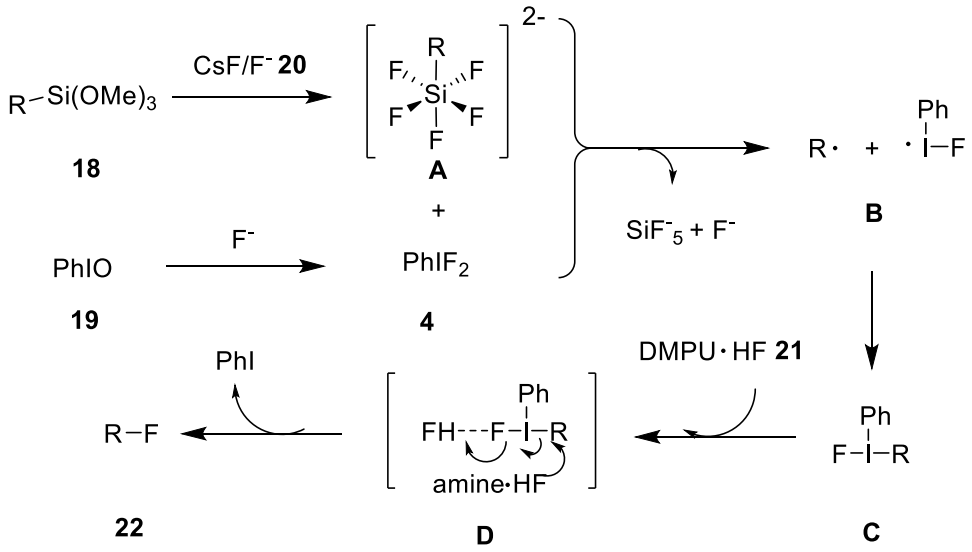
Introduction of fluorine into different molecules will change the properties and for this reason, new methods have been studied for incorporating fluorine into small molecules. In general, organo-silanes are useful intermediates. But, using fluoride ions for fluorination of organosilanes is uncommon because the Si-F bond dissociation energy is very high. Fluoride is stable and present abundant in nature and so it is highly desirable. Peng Xu et.al presented for the first time, iodine (III) mediated oxidative fluorination of alkylsilanes **18** with fluoride ions in the absence of any transition metal. Several fluorinating agents were used and when CsF **20** and DMPU·HF **21** were used together, the product **22** obtained was found to be of highest yield in the presence of 1,4-dioxane/HFIP as oxidant (Scheme 6). This method was tested with several primary alkylsilane substrates containing electron withdrawing and donating groups as substituents and these gave desired products. The reaction also tolerated several functional groups like alkene, bromide, chloride, ether, iodide, nitrile and sulfonyl. One of the disadvantages was that the secondary alkylsilanes were not fluorinated using this technique.[39]



Scheme 6. Oxidative fluorination of primary alkylsilanes **18** by fluoride ions using hypervalent iodine(III) reagent **19**.

The team depicted the mechanism shown in Scheme 7 based on this mechanistic research and related DFT calculations. The organopentafluorosilicate **A** and $PhIF_2$ were produced by the treatment of alkylsilane **18** with PhIO **19** in the presence of CsF **20** and DMPUHF **21**. Then, a carbon radical intermediate and an iodoarene radical (B) are produced as a result of a single-electron transfer from intermediate **A** to $PhIF_2$ **4**, which leads to the formation of the stable hypervalent iodine(III) species **C**. In order to create the final product **22**, the activation-displacement sequence by the transition-state **D** with the help of DMPUHF **21** is made possible by the production of this species.

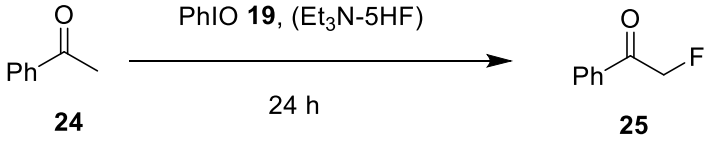
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Scheme 7. Proposed mechanism based on DFT calculations.

The organofluorine compounds are very important intermediates. Even though there are methods to replace the hydrogen and prepare the organofluorines, there are several drawbacks like explosion. Hence, other methods were tested, and it was found that usage of hypervalent iodine compounds as fluorinating agents were preferred because they are safer and cleaner.

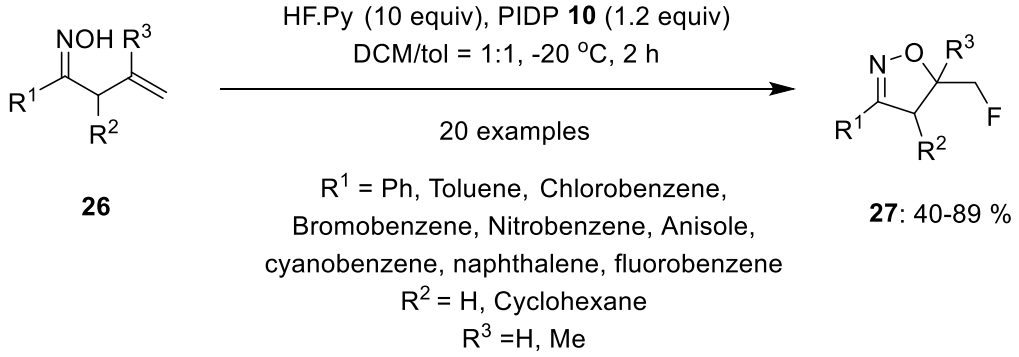
Recently, Tsugio Kitamura reported fluorination of 1,3-dicarbonyl compounds **23** using iodosylbenzene (PhIO) **19** and hydrofluoric acid. But one major drawback was that this method was not useful for monocarbonyl substrates. So, they utilized triethylamine.HF complexes as fluorine source for the fluorination of acetophenone **24** which resulted in the formation of α-fluoroacetophenones **25** in good yields but required expensive fluorinating agent. Hence other agents were screened and it was found that TEA·5HF gave good yields of α - fluoroacetophenones **25** (Scheme 8).[40]



Scheme 8. Fluorination of acetophenone **24** to α - fluoroacetophenones **25** using Hypervalent iodine(III) catalyst.

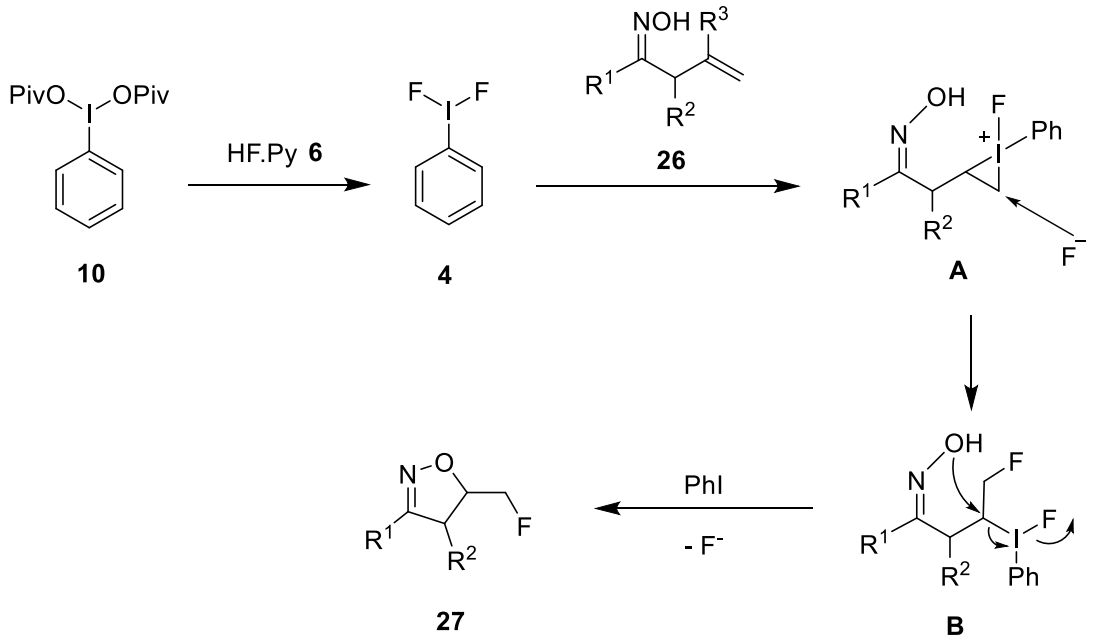
For the intramolecular oxidative oxyfluorination of unactivated terminal alkenes **26**, Kong and his team created a highly regioselective metal-free procedure in which HF·Py (HF-pyridine) is used as the fluorine source in the presence of PIDP ($PhI(OPiv)_2$) **10** oxidant. The development of monofluoromethyl-substituted isoxazolines **27** can be accomplished with the help of this novel transformation in an effective manner. The substrates containing different kinds of substituents admirably produced the expected products in moderate to high yields. Surprisingly, an oxime with an internal alkene produced the unusual product isolated yield of 86% (Scheme 9).[41]

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Scheme 9. Intramolecular oxidative oxyfluorination of terminal alkene **26** using Hypervalent iodine(III).

The proposed mechanism begins with *in situ* interaction of PIDP **10** and HF-Py leads to the formation of $PhIF_2$ **4** by ligand exchange reaction. The $PhIF_2$ **4** further reacted with an alkene cause the generation of an iodonium cation **A**, which was subsequently attacked by a F^- to form intermediate **B**. The intended product **27** was obtained by an intramolecular nucleophilic attack of −OH followed by the reductive ring opening reaction by elimination of iodoarene. The plausible mechanism of intramolecular oxidative oxyfluorination is demonstrated in Scheme 10.

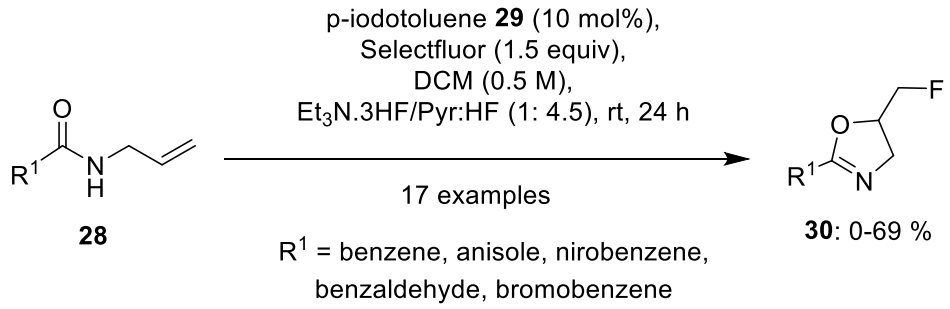


Scheme 10. Plausible mechanism of intramolecular oxidative oxyfluorination of terminal alkenes using Hypervalent iodine(III) catalyst.

Scheidt and team synthesized monofluoromethyl-substituted oxazolines using the Iodine(I)/Iodine(III) catalysis, by fluorooxygenation of *N*-allylcarboxamides **28** (Scheme 11). Similar to previous work, the reactive intermediate formed by the treatment of a catalytic amount of *p*-iodotoluene **29** in presence of fluoride source (mixture of TEA·3HF/ Py·HF). Then the intended product **30** was obtained by an intramolecular nucleophilic attack of −OH followed by the reductive ring opening reaction by elimination of iodoarene.

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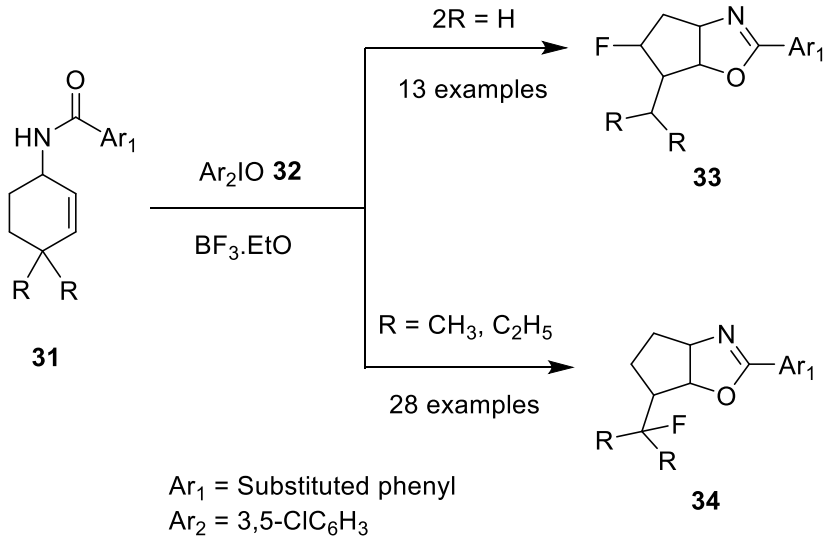
Unsprisingly, the formation of heterocyclic compounds such furan was obtained along with the expected 9-fluorenonyl-substituted oxazoline **30** occurred with 48% and 59%, respectively.[42]



Scheme 11. Fluorooxygenation reaction of terminal alkenes using Hypervalent iodine(III) catalyst.

3.2. Secondary fluorides

Initially Hara et al., synthesized gem-difluorinated product by ring contraction of cyclic alkenes. But, monofluorination by ring contraction mediated particularly by hypervalent iodine remained unexplored.[43] Yong-Chao Han and coworkers have done the synthesis of mono fluorinated five-membered ring fused with oxazolines with the help of hypervalent iodine (Scheme 12).[44]

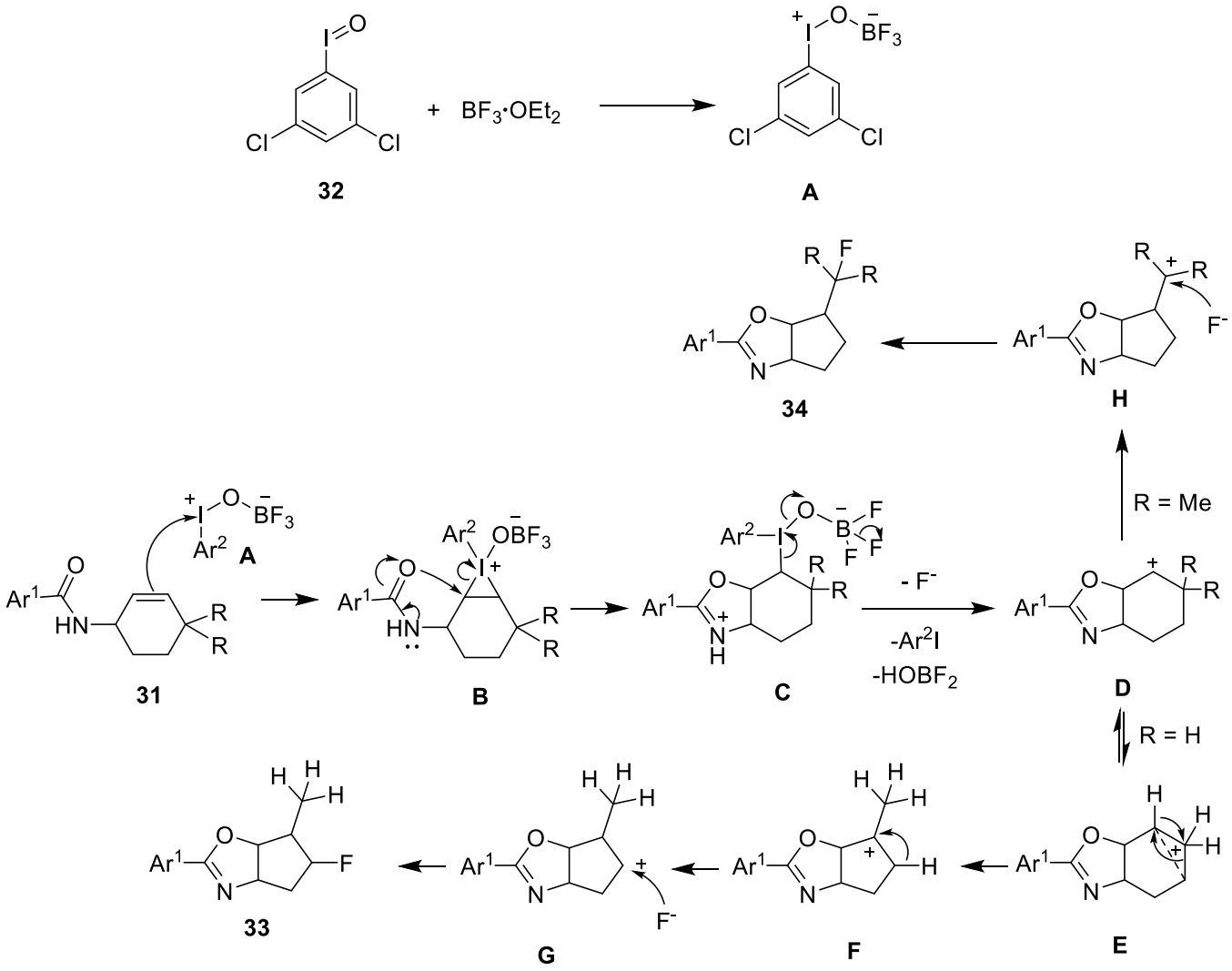


Scheme 12. Synthesis of monofluorinated five-membered ring fused oxazolines compound **33** and **34** from compound **31** using Hypervalent iodine(III) catalyst.

The reaction started with the activation of hypervalent iodine **32** using $BF_3{\cdot}Et_2O$ produced reactive intermediate **A,** which then combines with the substrate **31** to activate its double bond and produce iodonium intermediate **B**. The intermediate **C** is produced by an intramolecular nucleophilic attack on the amide group's oxygen atom and it goes through reductive elimination to become intermediate **D**, coupled with the release of an ion of fluoride. Here after, the R group will choose what happens next. If R is hydrogen, the intermediate carbocation **G** is formed via sequential alkyl and double hydride shifts. Monofluorinated product **33** is produced when intermediate **G** interacts with a fluoride ion. The author's hypothesis that **G** is more stable than **F** due to the oxygen atom's electron-withdrawing inductive function, which might account for how

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secondary carbocation intermediate **G** develops from tertiary carbocation intermediate **F**. If R is a methyl group, intermediate **D** proceeds through an alkyl migration to become a tertiary carbocation intermediate **H**, which is a lot more stable. A fluoride ion then captures carbocation of intermediate **H** to produce product **34** (Scheme 13).



Scheme 13. Plausible mechanism for the fluorination reaction.

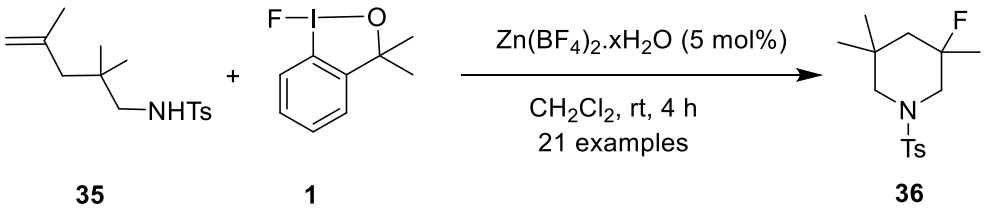
3.3. Tertiary fluorides

For the synthesis of heterocycles and functionalized carbocyclic compounds, electrophilic fluorocyclization is an important method. This was first reported by Liu and co-workers which then became an important method for the synthesis of heterocycles containing a nitrogen in them. Fluorocyclization method is an important technique for the introduction of fluorine into organic molecules. Only few methodologies were developed for the intermolecular aminofluorination and carbofluorination reaction.

As we discussed early, fluorination can be done with fluorine containing hypervalent iodine reagents. 1-Fluoro-3,3-dimethyl-1,2-benziodoxole **1** is the one where researchers used most commonly for fluorocyclization. There is need for catalyst to activate the hypervalent fluoroiodane reagent. The commercially available metal catalysts $Zn(BF_4)_2$ was used to activate hypervalent fluoroiodane reagent. The actived complex further underwent electrophilic addition with the terminal alkene resulted as iodonium ion

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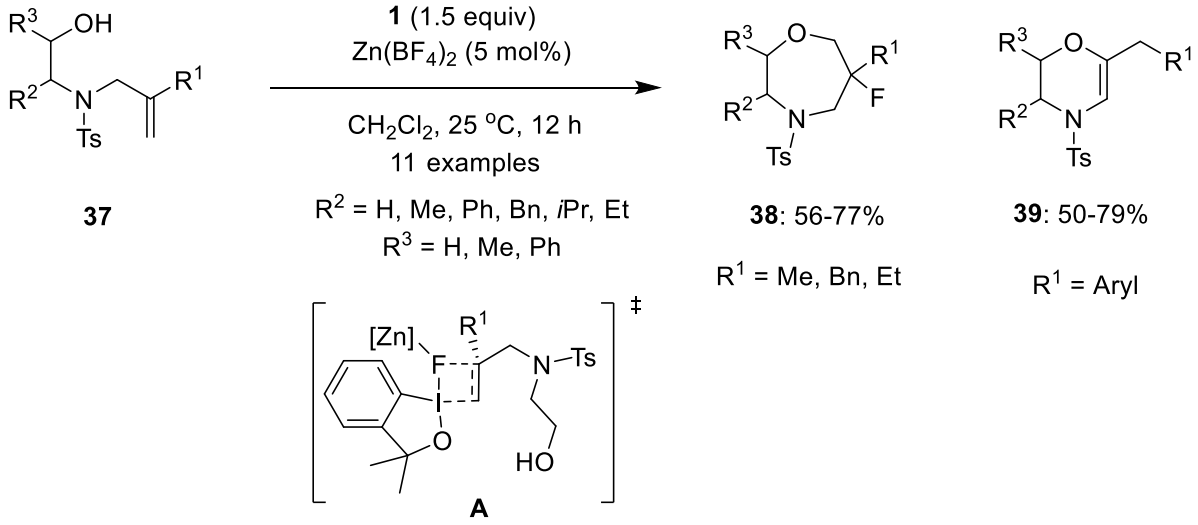
intermediate. A nucleophilic attack at the least hindered corner of the iodonium cation produced the expected products. On treatment of alkene tosylamide **35** with stoichiometric amount of hypervalent fluoroiodane reagent underwent aminofluorination resulted a fluoropiperidine derivatives (Scheme 14). While using alkenyl alcohol and alkenyl malonate derivatives as a substrate along with stoichiometric amount of hypervalent fluoroiodane reagent underwent oxy- and carbofluorination respectively, leads the formation of corresponding fluoro compounds. [45]



35 **1** **36**

Scheme 14. Aminofluorination of alkene tosylamide **35** to compound **36** using hypervalent fluoroiodane reagent.

Using the same protocol, Yang and team used substituted aminoethanols as a substrate. When the substrates underwent metathesis reaction with hypervalent iodine generates the intermediate via the four membered transition state **A**. Now, there are two reactive sites for further action. If R^1 is aryl group, then an intramolecular nucleophilic attack of the hydroxy group occurs at the more-substituted carbon leads the formation of dihydrooxazine **39**. If R^1 is an alkyl group, then the nucleophilic attack happened at least hindered corner of four membered transition state leads the formation of fluorinated oxazepanes **38** (Scheme 15). This reaction shows high stereoselectivity as fluorine atom and oxygen atom are on the same side of intermediate.[46]



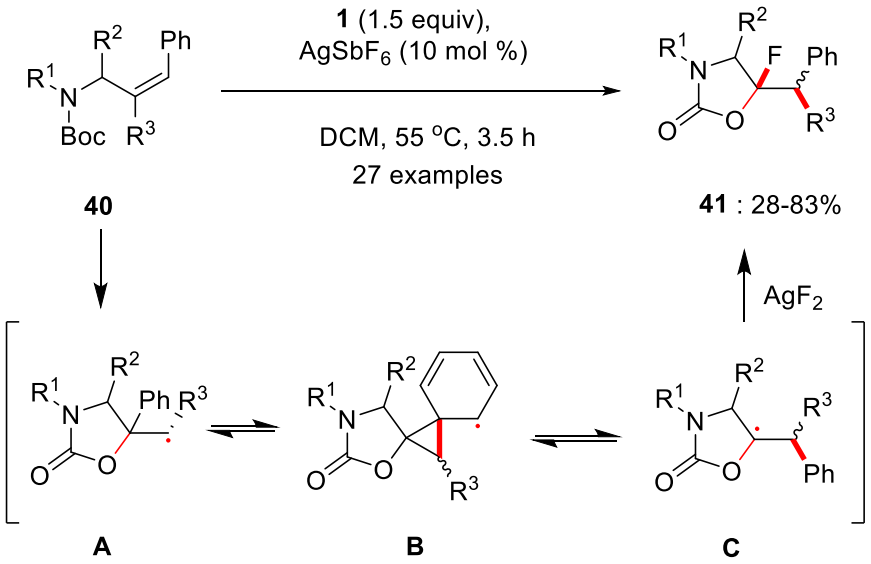
37 **A**

Scheme 15. Synthesis of fluorinated oxazepanes **38** from substituted allylaminoethanol **37**.

In an unique radical reaction, Yang and his team produced fluorinated oxazolidine-2,4-diones, 1,3-oxazinan-2-ones and oxazolidin-2-ones via intramolecular fluorocyclization of unsaturated carbamates. Silver hexafluoroantimonate, was used as a catalyst in the fluorination reaction, over substituted olefins and

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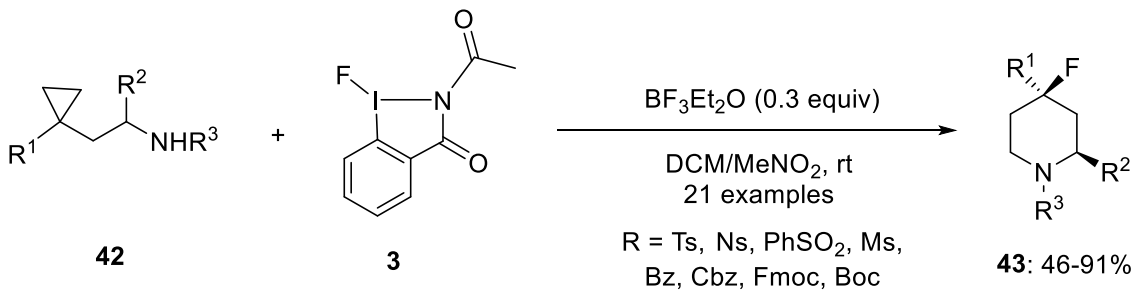
acrylamides as substrates. Both electron-withdrawing and electron- donating substituted phenyl groups on the nitrogen effectively transformed. With yields of 66-78%, even the alkyl substituted agents functioned admirably in this process. The yield was decreased rapidly when the radical trapping reagent 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was added to the reaction evidenced the formation of methyl radical **A** in the catalytic process. The radical rearrangement of radical intermediate **A** into three-membered ring cyclic structure **B** may use to overcome the minimal barrier with the migration of phenyl ring producing the radical intermediate **C**. After that, the fluorine atom of Ag(II)F_2 abstract by methylene radical **C** leads the formation of desired final product **41** (Scheme 16).[47]



Scheme 16. Synthesis of fluorinated oxazolidine derivatives **41** via intramolecular fluorocyclization of unsaturated carbamates **40**.

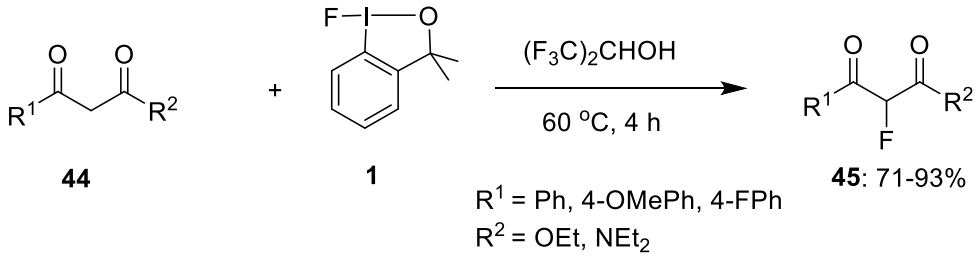
Unactivated cyclopropanes have been reported to be capable of intramolecular ring expansion fluorination. In this study, a newly created hypervalent fluoroiodane(III) reagent 1-fluoro-N-acetylbenziodazole **3** was used along with Lewis acid and the substrate **42** can generate a wide variety of 4-fully substituted fluoropiperidines **43** in a single step with high yields and outstanding regio- and diastereoselectivity. It's interesting to note that the cis isomer was always the main product (Scheme 17). The four- and five-membered fluorinated products could not be detected throughout the reaction, demonstrating the reaction's strong regioselectivity. The range of the substrate was also observed by switching the amine protecting groups to p-nitrobenzenesulfonyl, benzenesulfonyl, and methanesulfonyl, all of which produced smooth conversions with 64–83% yields, but benzoyl-protected and non–sulfonyl–protected substrates do not give the expected fluorinated piperidine products. Aside from this, the reaction was well tolerated and had a good yield when electron-donating and electron-withdrawing moieties were coupled to cyclopropanes carrying substituted phenyl groups. Cyclopropanes with a thiophene or naphthalene ring were also appropriate.[48]

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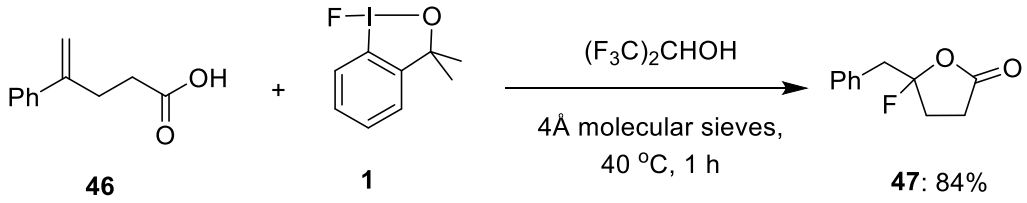
Scheme 17. Intramolecular ring expansion fluorination of cyclopropanes.

In order to replace the transition metals or TREAT-HF activators, Minhas and companions used hexafluoroisopropan-2-ol (HFIP) is an ideal solvent for fluorination of 1,3-ketones and to fluorocyclize unsaturated carboxylic acids in the presence of hypervalent fluoroiodane reagent. The comparative study was performed for the reaction with and without Lewis acid or $Et_3N{\cdot}HF$ in CH_2Cl_2 and in HFIP respectively. The percentage of obtained yield was elevated in HFIP. On treatment of 1,3-dicarbonyl compounds with this protocol produced respective monofluorinated compounds (Scheme 18).



Scheme 18. Fluorination of 1,3-ketoesters **44** using 1-Fluoro-3,3-dimethyl-1,2-benziodoxole **1**.

The metal-free intramolecular fluorocyclisations of unsaturated carboxylic acids **46** were performed with HFIP and produced high yields of fluorinated lactones **47** that were tolerant to the majority of the functional groups (Scheme 19).[49]

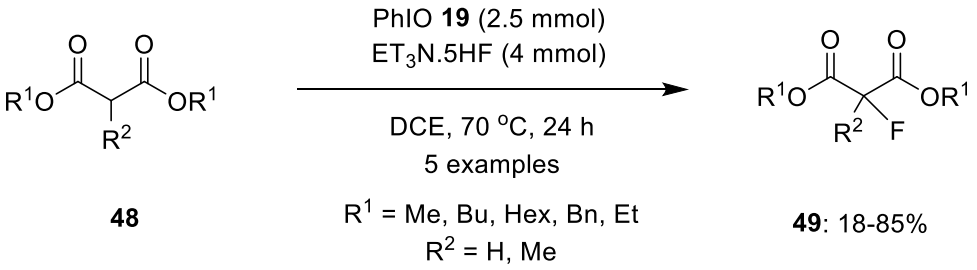


Scheme 19. The metal-free fluoro cyclizations of unsaturated carboxylic acids **46** to fluorinated lactones **47** using 1-fluoro-3,3-dimethyl-1,2-benziodoxole **1**.

Similarly, Kitamura and his coworkers fluorinated the malonic esters using fluorine free hypervalent iodine reagent with the assistance of external fluorine source. The stoichiometric amount of iodosybenzene **19** and $Et_3N.5HF$ in dichloroethane (DCE) at 70 °C for 24 hours directed to fluorinate the malonic ester **48**. The reaction proceeded effectively on dibenzyl malonate, dibutyl malonate, dihexyl malonate and dimethyl malonate substrates with a yield of 53–85% of corresponding 2-fluoromalonic esters **49** (Scheme 20). However

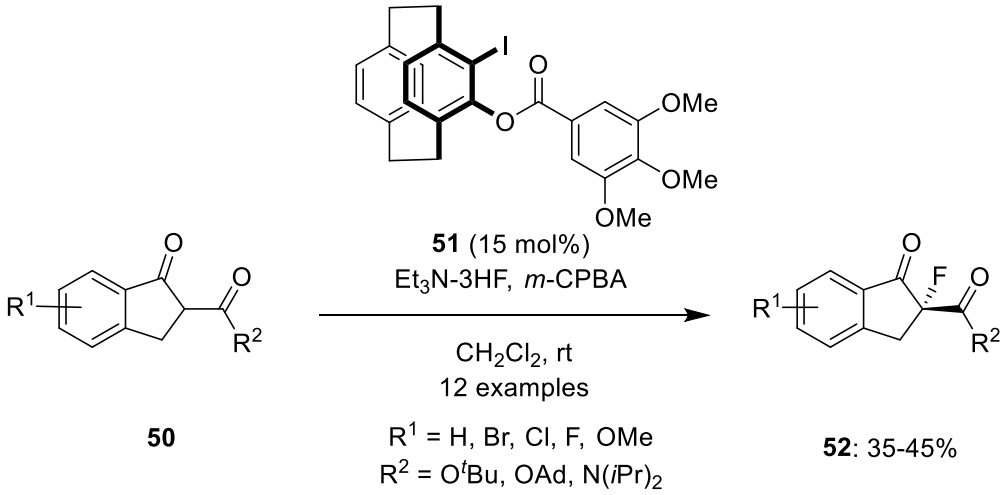
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disubstituted malonate ester showed lesser yield on fluorination due to steric effect. The mechanism of the reaction is that in the presence of HF, iodosylbenzene is transformed to difluoroiodobenzene, acidic condition helps to enolate the malonic ester. The resulting 2-fluoromalonic ester is produced by reaction on newly created enol of the malonic ester with difluoroiodobenzene.[50]



Scheme 20. Fluorination of malonic ester **48** to corresponding 2-fluoromalonic esters **49** using Hypervalent iodine reagent.

Wang and team reported the chiral hypovalent iodine catalyst for an effective enantioselective oxidative fluorination of β-ketoester. The fluorination of β -ketoester occurs at room temperature in the presence of catalytic amount of chiral iodoarene **51**, oxidant *m*-CPBA, and the nucleophilic source of fluoride hydrofluoride triethylamine. The β-ketoester is tolerant of both electron withdrawing and donating groups under optimal condition, providing the corresponding product with strong enantioselectivity (Scheme 21). Enantioselectivity was shown to be dependent on the size of the ester group. When compared to other tert-butyl esters and β-ketoamide, methyl ester only yields 21:79 *er*. Acyclic substrates, however, were not successful.[50]

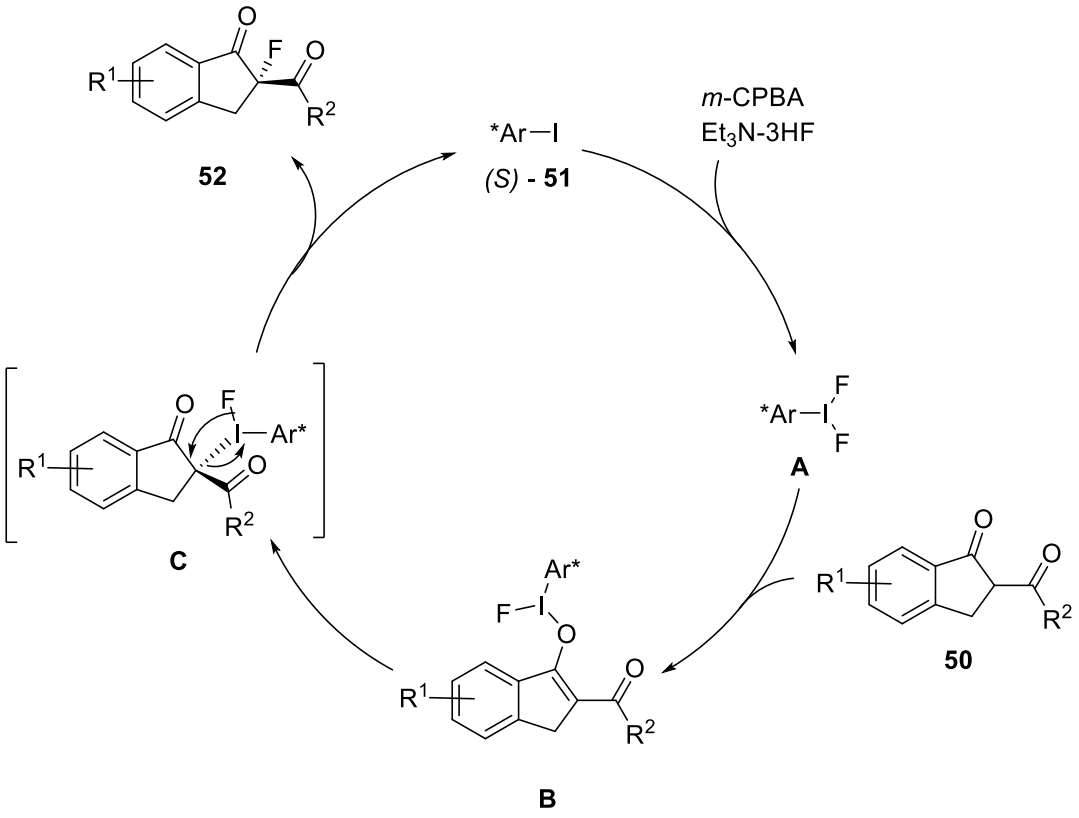


Scheme 21. Enantioselective oxidative fluorination of β–ketoester **50** using planar chiral hypervalent iodine catalyst.

According to the literature, the plausible mechanism starts with the oxidation of hypoiodoarene into hypervalent fluoro-iodine **A** by *m*-CPBA in presence of HF. On treatment of β-ketoester **50** with hypervalent iodine **A** underwent ligand exchange to form O-bonded hypervalent iodine species **B**. Which further caused intermediate **C** via 1,3-migration. This step would be an enantioselective and rate determining step in this

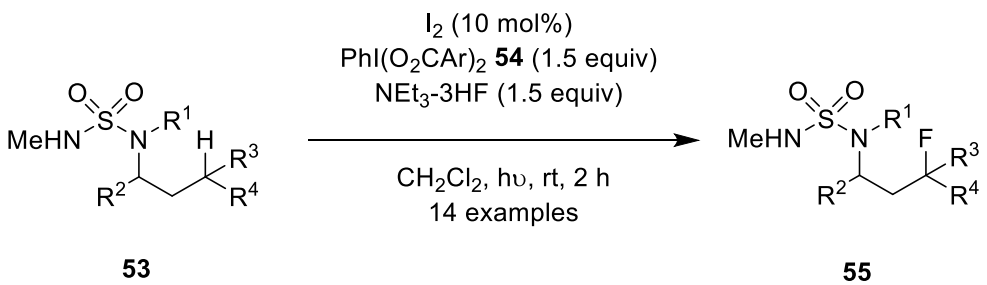
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reaction. Finally, the intended product **52** obtained by the reductive elimination iodoarene from intermediate **C**. The catalytic cycle demonstrated in Scheme 22.



Scheme 22. Plausible mechanism of an enantioselective oxidative fluorination of β–ketoester **47**.

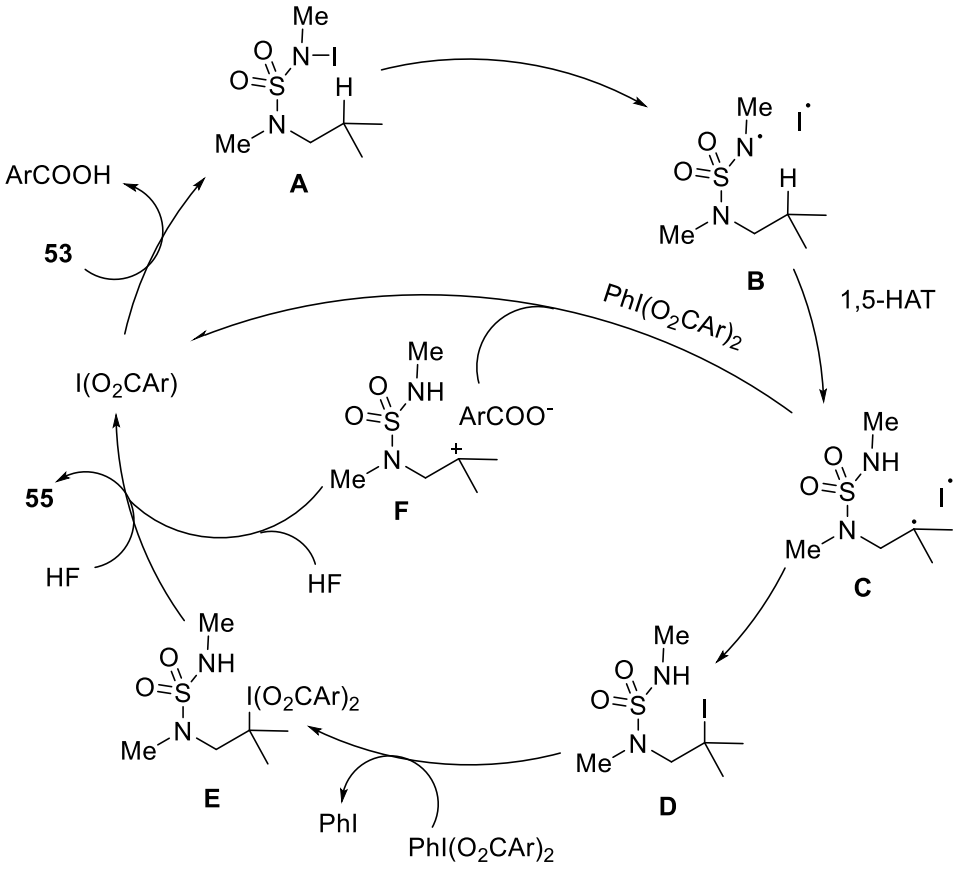
Several strategies were studied for the fluorination of alkanes among which SN_2-based deoxyfluorination of compounds containing alcohols were established. But due the harsh conditions needed for carrying out the reaction, alternatives were researched, and it was found that generating carbon-centered radicals and later trapping them using electrophilic fluorine transfer reagents was a better option. Daniel Bafaluy et al. reported C(sp^3)-H fluorination for radical-based functionalization of aliphatic hydrocarbon in the using molecular iodine and hypervalent iodine reagent (Scheme 23).[51] The similar fluorination reported using copper catalyst, the resulted product exhibit retention configuration.[52]



Scheme 23. The fluorination of compound **53** using Hypervalent iodine(III) catalyst.

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The comproportionation of molecular iodine and $PhI(O_2CAr)_2$ to generate the active iodine(I) catalyst, selective iodination of the NH group of the substrates **53** leads the formation of corresponding N-iodinated amide **A**. Upon light exposure, homolytic cleavage of the N-I bond generates the nitrogen centered radical **B**, which further 1,5-hydrogent atom transfer (HAT) for the sulfonamide produces the carbon centered tert-alkyl radical **C**. The essential alkyl iodide intermediate **D** can either arise by radical recombination or chain growth via intermolecular iodine atom abstraction, which consumes more **A** and regenerates nitrogen-centered radical intermediate **B**. Both of the routes could be active. The vital intermediate species **E**, which contains the essential alkyl iodine(III) supernucleofuge and allows for direct nucleophilic assault of fluoride to release products **55** and regenerate the original I-O_2CAr catalyst, is produced by further oxidising **D** with $PhI(O_2CAr)_2$. Currently, we also take into account the potential involvement of a different pathway that involves the direct regeneration of the original catalyst I-O_2CAr by the rapid oxidation of both the iodine radical and the tert-alkyl radical **C** by iodine(III). This pathway promotes a tertiary carbocation **F**. The nucleophilic fluoride capture cation **F** results in the synthesis of **58** (Scheme 24).



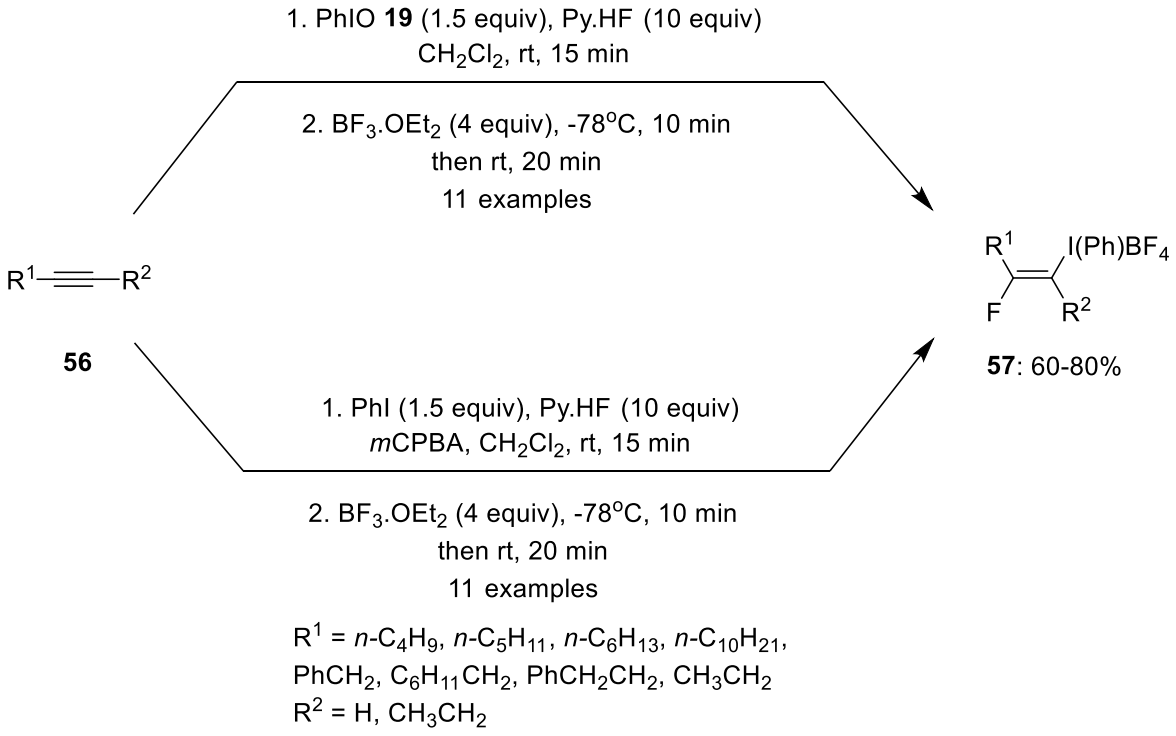
Scheme 24. The proposed mechanism for the fluorination reaction using iodine(III) catalyst.

3.4. Fluoro alkenes

The fluorination of alkenes produced vinyl fluorides. They have similar properties to that of amide group and are isopolar and isosteric mimics of the amide moiety in peptides. Hence, they play an important role in the field of medicinal chemistry. Tsugio Kitamura and co-workers considered β-fluorovinyliodonium salts as source for obtaining fluoroalkynes. The team made use of facile method to synthesize the β-fluorovinyliodonium salts from alkynes using hypervalent iodine reagents (Scheme 25). Several substrates were tested, and terminal

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alkynes gave good yields, internal alkynes gave moderate yields and alkynes functionalized with phenyl, methyl ester, tosylate gave 73-78% of their corresponding β-fluorovinyliodonium salts.[53]

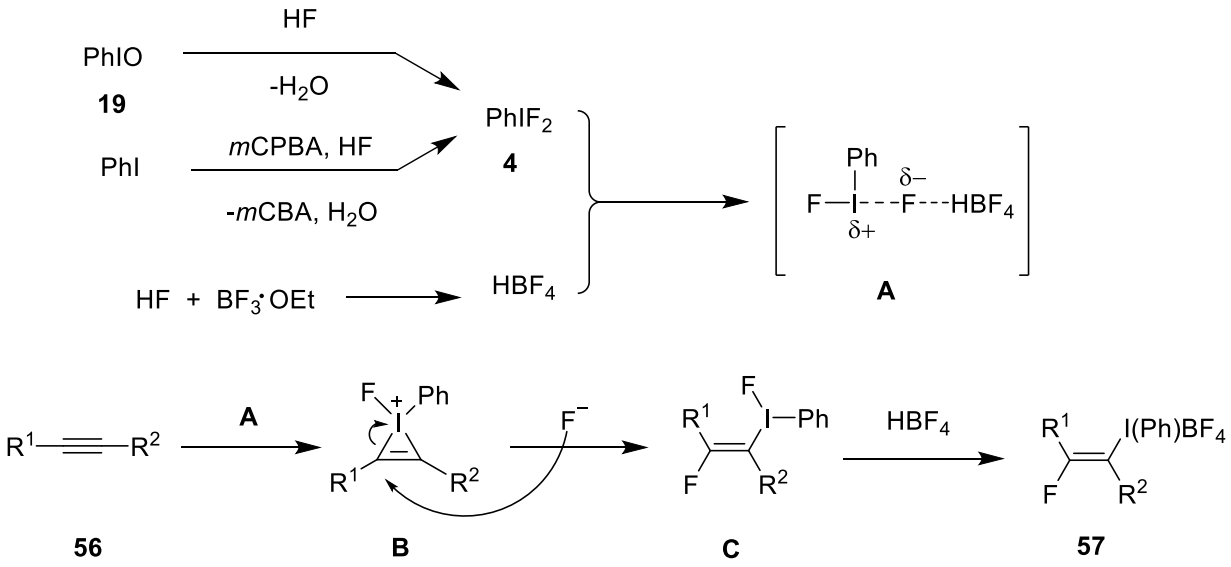


Scheme 25. Fluorination alkenes using hypervalent iodine reagent.

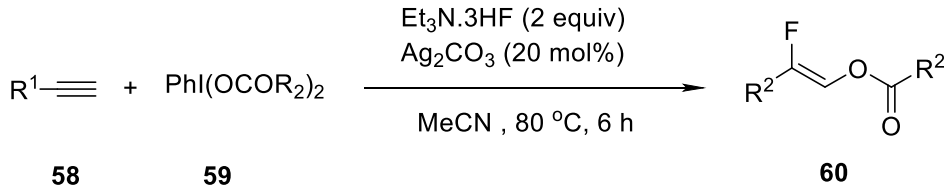
Reaction begins with the formation of active $PhIF_2$ in two ways, either direct treatment of PhIO with fluorine source or PhI oxidized by the well know oxidizing agent *m*CPBA then treated with fluorine source. The *in situ* generated $PhIF_2$ is activated by HBF_4 and undergoes electrophilic addition to alkynes **59** to form bridged iodonium species, which are subject to the nucleophilic attack of fluoride ion to form (E)-β-vinyliodonium fluorides. The ligand exchange with HBF_4 provides the final product **60**. The ring-opening of the bridging iodonium species with the fluoride ion controls the stereochemistry of compound **60** (Scheme 26).

Among various compounds fluoroalkenes and gem-difluoromethylenes are said to be important targets and building block for organic synthesis. Although these have biological importance, there has been very less advancements in their synthetic methods of preparation. Zhidong Song and Wenbin Yi developed one-pot synthesis of organofluorine molecule using hypervalent iodine compounds **59** along the fluorine source $Et_3N{\cdot}HF$ in presence silver catalyst. The reaction yielded fluorovinyl acetates **60** and β,β-difluoro carboxylates (Scheme 27).[54]

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Scheme 26. Mechanism for the fluorination of alkyne **56** to β-fluorovinyliodonium tetrafluoroborate **57** using PhIO and *m*-CPBA.

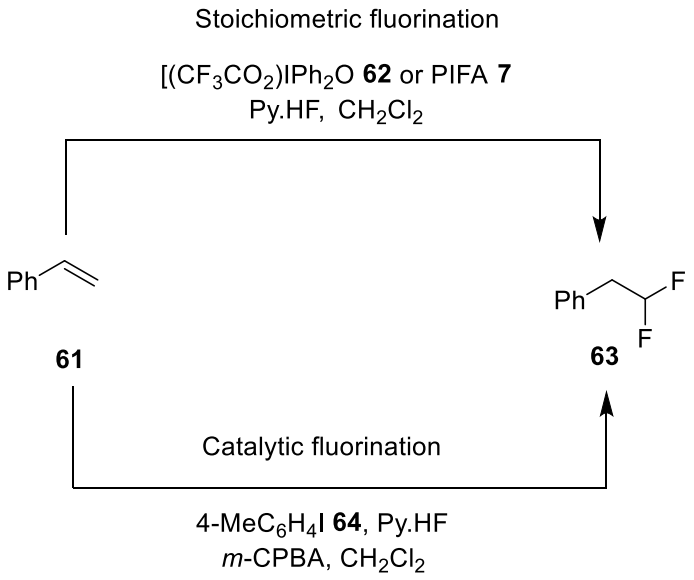


Scheme 27. Synthesis of fluorovinyl acetates **60** from terminal alkyne **58** using Hypervalent iodine(III) reagent **59**.

4. Synthesis of difluorides

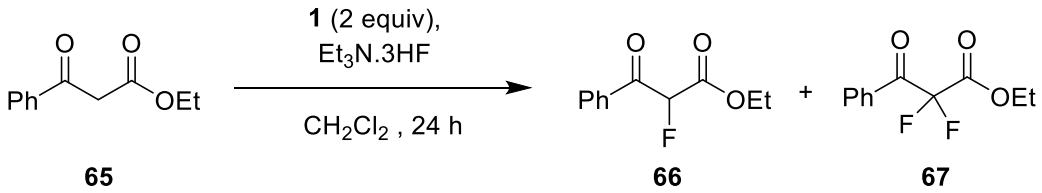
Trifluoromethyl and related groups are found to be an active component in pharmaceutical and agrochemical products. Tsugio Kitamura et al. reported an easy and convenient method to introduce 2,2-difluoroethyl group in various styrene derivative **61** using *in situ* generated hypervalent iodine reagent. Several of the iodine reagents were screened and $[(CF_3CO_2)IPh]_2O$ **62** gave the highest yield of the product. It was found that PIFA **7** also gave comparable yields and gave cleaner reaction mixture. Py·HF was used as fluorine source. With the optimized conditions, several substituted styrenes **61** were used as substrates to carry out the reactions (Scheme 28). Few drawbacks were that the products were volatile and had bad separation, styrene derivatives bearing HF sensitive groups like alcohols and amines couldn't be used as substrates.[55]

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Scheme 28. Difluorination of styrene **61** using hypervalent iodine reagents.

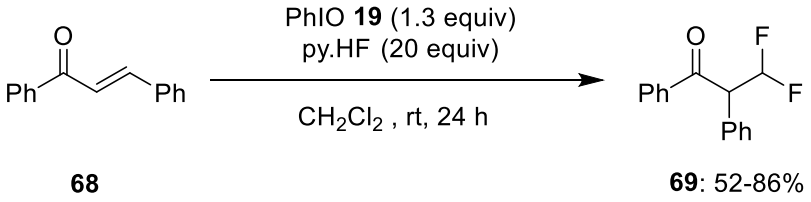
Geary et al. developed fluorinating agents based on cyclic hypervalent iodine(III) skeleton from cheap sources of fluorine. Reactivity of fluoroiodane **1** was tested using ethyl 3-oxo-3-phenylpropanoate **65** as substrate in the presence of triethylamine tris(hydrogen fluoride) (TREAT-HF) fluorine source. It was found that the nature of the products obtained using the fluorinating agent differed with change in temperature. At low temperature, for example 40 ^{O}C, monofluorinated β-fluoro-1,3-dicarbonyl compound **66** was formed, at a reaction temperature of 80 ^{O}C difluorinated product β,β'-difluoro-1,3-dicarbonyl compound **67** was obtained due to presence of base which abstracts the another hydrogen also at the β position (Scheme 29).[56]



Scheme 29. Difluorination of β–ketoester **65** using cyclic hypervalent iodine(III) reagent **1**.

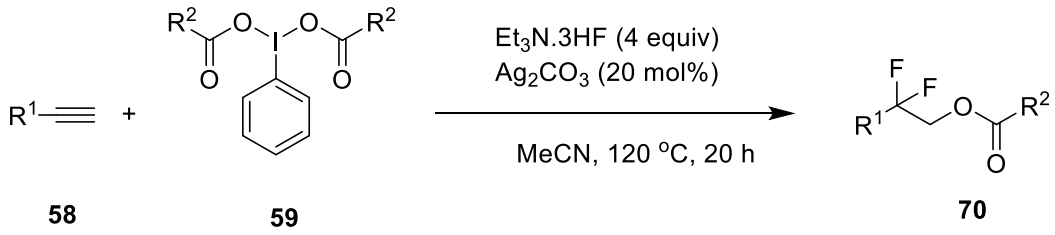
Kitamura et al. used ArIO/HF reagent to fluorinate 1,3-dicarbonyl compounds, malonic esters, aromatic ketones, and aromatic olefins. For the first time, the team had reported that reaction took place in the presence of terminal oxidant and ArI in catalytic amount. Hydroxyl and carbonyl are very important functional moieties and hence their tolerance for the reported method was checked. Here, the fluorination of alkenes with carbonyl and hydroxyl groups were tested. Fluorination of 1,3-diphenyl-2-propen-1-one **68** with py·HF in CH_2Cl_2 underwent difluorination with 1,2 phenyl migration produced 3,3-difluoro-1,2-diphenylpropan-1-one **69** in 85% yield. α,β-unsaturated ketones substituted with electron-withdrawing, electron-donating groups gave 52−86% of fluorinated product (Scheme 30).[57]

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Scheme 30. Difluorination of chalcone **68** using hypervalent iodine(III) catalyst.

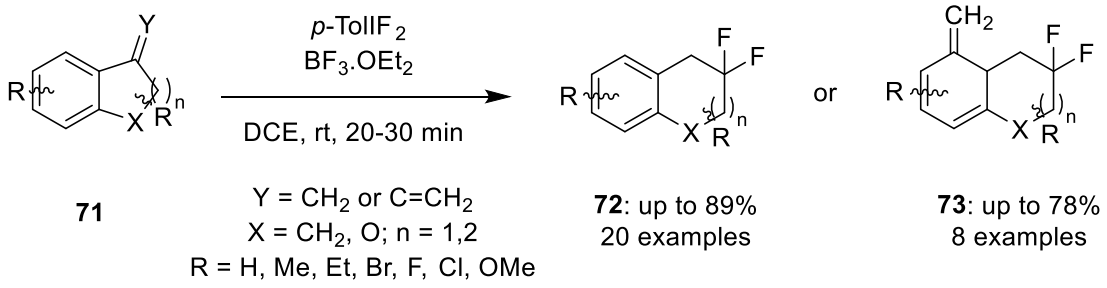
The fluorination of terminal alkyne **58** using hypervalent iodine **59** at 80 °C produced monofluorinated compound. When the same reaction was performed at higher temperature such as 120 °C, difluorination took place (Scheme 31). Arylacetylenes bearing electron-rich groups gave higher yields than the ones bearing electron deficient groups. It was found that slight modification to the existing reaction condition gave rise to the formation of β,β-difluoro carboxylate product. Aromatic substrates bearing electron rich and deficient groups gave good yields.[54]



Scheme 31. Synthesis of β,β-difluoro carboxylates **70** from difluorination of terminal alkyne **58**.

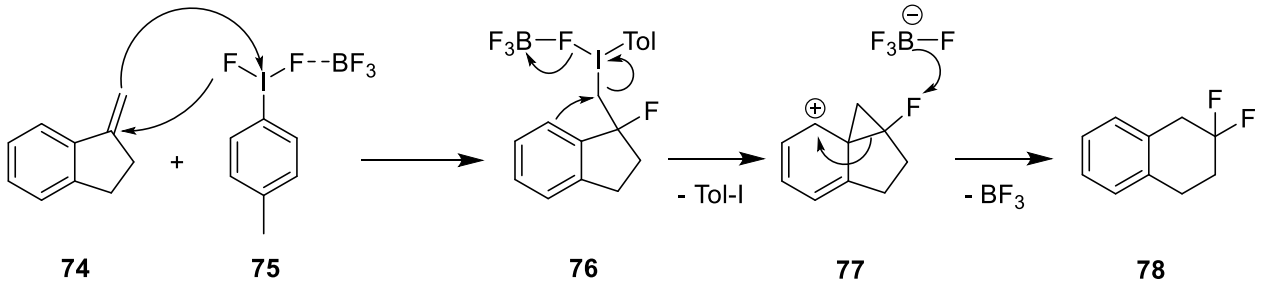
Zhao, To, and Murphy reported a rapid chemoselective fluorinative ring-expansion of benzo-fused alkene and allene by using p-(difluoroiodo)toluene (p-TolIF$_2$) to synthesise β,β-difluoroalkyl arenes and allylic gem-difluorides. The compounds containing α-exocyclic alkenes were transformed utilizing 2.5 equiv. of p-TolIF$_2$ in DCE with 5 mol % $BF_3.OEt_2$ as the activator over the course of 20 minutes at room temperature. With a yield of 72–77%, the process is tolerant to halogen substitution well. When methyl or methoxy groups were connected, the yield was only moderate, and there was no yield when a gem-Dimethyl was next to the reacting alkene. Additionally, chromane skeletons, 2,2-spirocyclic derivatives, and thiochromane derived alkenes were all capable of undergoing the reaction. Like alkenes, allenes were resistant to reactants with halogen substitution, but the yield for rearrangements that produced medium-ring scaffolds was greatly reduced (Scheme 32).[58]

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Scheme 32. Difluorination of phenylallene derivatives **71** using hypervalent iodine(III) in the presence of Lewis acid.

The Lewis acid activates the iodine(I) into iodine(III), which will attack the weak nucleophilic π-system of the styrene or phenylallene derivative **74** to produce intermediate **76**. From this intermediate **76**, the leaving group hypernucleofugal iodanyl is expelled to cause intermediate phenonium ion **77**. The intermediate **77** further undergoes ring expansion followed by the rearomatization leads the formation of allylic *gem*-difluorides **78**. The regioselectivity is controlled by the stabilising influence of the first fluorine atom (Scheme 33).



Scheme 33. Plausible mechanism of difluorination of phenylallene derivatives **74.**

Conclusions

Most often, the beneficial qualities linked to these compounds are systematically enhanced when a fluorine atom is introduced into a carbon framework. So, it should not be a surprise that compounds containing organofluorine have entered a number of scientific and technical fields and have a profound effect on everyone's daily lives. With the insistence for new fluorinated structural scaffolds developing quickly, it is necessary to create new, particularly gentle and selective, ways to install C-F bonds. Hypervalent iodine(III) compounds have the potential to meet these requirements. They are used as simple and distinct oxidants, but more recently, they have also proven to be of great value in other areas of organic chemistry, such as atom transfer processes. Hypervalent iodine reagents help to go both nucleophilic and electrophilic fluorination reaction of organic molecules. As a result, we are confident that fluorinations sparked by hypervalent iodine(III) will flourish soon and become a widely used technique in organic synthesis.

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Acknowledgements

Kokila S acknowledges the support from Vellore Institute of Technology, Chennai. Fateh V. Singh is thankful to CSIR New Delhi [Grant No.: 02/(0330)/17-EMR-II].

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Authors' Biographies



Kokila Sakthivel obtained her MSc degree in Chemistry (2018) from Bharathidasan University and MPhil in Chemistry (2019) from Mother Teresa Women's University. She is currently working as an Internal Full Time (IFT) research scholar to pursue her PhD at Vellore Institute of Technology, Chennai under the supervision of Dr Fateh V. Singh. Her research focus is mainly associated with application of hypervalent iodine reagents in organic synthesis.



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Ravi Kumar, Associate Professor at J C Bose University of Science and Technology, YMCA, India, received his M.Sc. degree in 2000 and, Ph.D. in 2005 (Prof Om Prakash and Prof Pawan K Sharma) from the Department of Chemistry, Kurukshetra University. He worked at School of Chemistry, Cardiff University, UK as Postdoctoral Research Fellow in Prof Thomas Wirth research group where he explored asymmetric synthesis with hypervalent iodine reagents. He was awarded the Young Scientist research grants under Fast track scheme by the Department of Science and Technology, India to work on Hypervalent Iodine reagents, the Commonwealth Academic Staff Fellowship by Commonwealth Scholarship Commission, UK and INSA-Visiting Scientist Fellowship by Indian National Science Academy. His research area includes oxidative transformations using hypervalent iodine reagents and heterocyclic chemistry.

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Toshifumi Dohi, a professor at Ritsumeikan University, received his MS degree in 2002 (Prof. S. Murai) from the Graduate School of Engineering of Osaka University, Japan, and PhD in 2005 (Prof. Y. Kita) from the Graduate School of Pharmaceutical Sciences of Osaka University, where he studied new reactivities of transition metal catalysts and synthetic chemistry using hypervalent iodine reagents. After finishing his PhD work, he became an assistant professor at Osaka University and was promoted to associate professor (PI) in 2014 at Ritsumeikan University. His current research interest is focused on reagent/catalyst design and the development of new reactions using hypervalent iodine reagents. T.D. has received the IUPAC-ICOS 15 Poster Award for most excellent presentation, the Pharmaceutical Society of Japan (PSJ) Award for Young Scientists (2009), Banyu Chemist Award (2013), Thieme Chemistry Journal Award (2014), GSC Encouragement Award (2015), and International Congress on Pure & Applied Chemistry (ICPAC) Lecture Award (2019). For more details, see his homepage at http://www.ritsumei.ac.jp/pharmacy/dohi/.



Fateh V Singh was born in Ravani Katiry, Bulandshahr, UP, India in 1976. He has completed his MSc in Chemistry from SSV College, Hapur, UP, India in 1998. He has persued his PhD in 2007 with Dr Atul Goel (CSIR-CDRI, Lucknow, India). After the completion of his doctoral studies, he started his first postdoctoral studies (FAPESP fellowship) with Prof. H A Stefani at USP, São Paulo, Brazil and worked with him for more than two years in the area organotrifluoroborate chemistry. In 2010, he joined as Marie Curie postdoctoral fellow with Prof. Thomas Wirth at Cardiff University, UK and worked two years in the area of organoselenium and hypervalent iodine chemistry. He received Dr D S Kothari fellowship in 2013 and worked with Prof. G Mugesh at IISc Bangalore, India for a short stay. In 2014, he started his independent career and joined VIT University, Chennai as an Assistant Professor. Mainly, his research group is interested in the findings of new

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organoselenium and hypervalent catalysts for organic synthesis. Moreover, his research group is also involved in the development of new organic fluorescent molecules for OLEDs and chemical sensors. Currently, he is having different research grants from Government of India. He has already published more than 55 research papers, several book chapters and review articles.

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