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Hypervalent iodine-mediated synthesis and late-stage functionalization of heterocycles

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Dedicated to Prof Thomas Wirth

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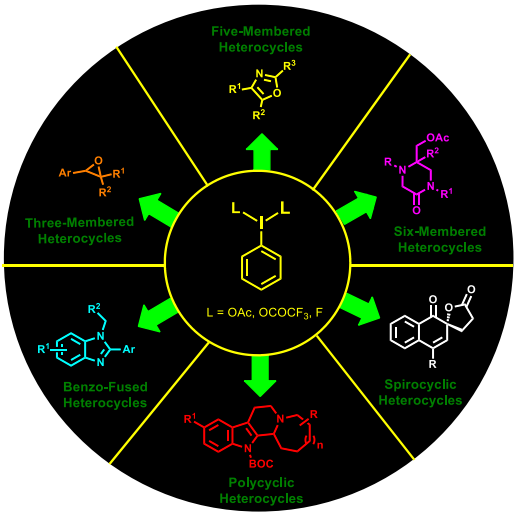
Abstract

Hypervalent iodine chemistry has witnessed exponential growth in organic synthesis in recent times. Because of the electrophilic and good-leaving nature of hypervalent iodine reagents, they react with different nucleophiles in various synthetic transformations such as rearrangements, α-functionalization of carbonyl compounds, alkene difunctionalization and oxidation reactions. Importantly, the application of hypervalent iodine reagents in the construction of heterocycles is of great interest and has been well studied over the years. This review article highlights the recent developments accomplished by hypervalent iodine reagents in the synthesis and functionalization of heterocyclic compounds.



Keywords: Hypervalent iodine, late-stage functionalization, monocyclic, bicyclic, polycyclic, spirocyclic heterocycles

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1. Introduction

Hypervalent iodine chemistry has become a focus of valuable research for designing robust methodologies in synthetic[1] and natural product chemistry.[2] Hypervalent iodine reagents are promising alternatives to the heavy-metal oxidants due to their ready availability, easy handling, low toxicity and environmentally-benign nature.[3] Synthetic applications of these reagents have seen exponential growth as realised by several books,[4,5] chapters in books[6,7] and comprehensive reviews[8-11] published in this area. Both iodine(III) and iodine(V) compounds (also known as λ^3-iodane and λ^5-iodane) have been commonly used as reagents in the oxidative transformations of various simple and complex organic molecules.[12-14] Most importantly, the unique reactivity and oxidizing ability of λ^3- and λ^5-iodanes has prompted their use as efficient oxidants in variety of synthetic transformations including α-functionalization of carbonyl compounds,[15,16] oxidative rearrangements,[17,18] alkene defunction-alization[19,20] and cyclization reactions.[21,22] However, most of this transformation requires stoichiometric

amounts of these reagents, generating the same molar quantity of iodoarenes as by-product thus limiting their scope. In order to combat this issue, several catalytic protocols including stereoselective variants have been developed extensively by employing various chiral/achiral iodoarenes as organocatalysts.[6,23]

Heterocycles constitute one of the widely studied classes of organic compounds as they are key to the structural units in various biologically and medicinally-important natural and synthetic products.[24-26] Moreover, importance of heterocyclic compounds in material science[27,28] and pharmaceutical[29] applications led their preparation and functionalization as topic of interest in organic synthesis. Owing to their wide scale importance, several researchers have devoted their studies in developing novel methodologies to access oxygen-, nitrogen- and sulphur-containing heterocyclic scaffolds. Along these lines, hypervalent iodine chemistry has evolved as a powerful green strategy for their synthesis. Significant achievements have been accomplished in various hypervalent iodine-mediated or catalysed synthesis of heterocycles as discussed in the review articles by Sun *et al*.,[30] Kandimalla *et al.,*[31] and Singh *et al*.[32] Further, late-stage functionalization constitute a powerful strategy for the manipulation of X–H (X = C, N) bonds of a complex molecule into novel carbon–carbon and carbon–heteroatom bond.[33] Within this context, hypervalent iodine reagents have emerged as promising alternate candidates for transition metals in the direct C–H functionalizations of diverse heterocycles via various synthetic transformations such as oxidative amination, alkylation, arylation, acetoxylation, halogenation, etc.[33] This review article gives brief overview of the recent development of hypervalent iodine reagents in the synthesis and reactions of heterocyclic compounds. This review article is broadly divided into two categories *i.e*. synthesis of heterocycles and late-stage functionalization of heterocycles.

2. Hypervalent Iodine-Mediated Synthesis of Heterocycles

Synthesis of heterocycles using hypervalent iodine reagents has seen dramatic progress in the last couple of decades. Having excellent electrophilic and oxidizing properties, iodine(III)/(V) compounds are choice of reagents to substitute toxic heavy metals. The use of these reagents in the construction of heterocyclic systems via C−C, C−O, C−N, C−S, N−N, N−S or N−O bond formation reactions have been well explored by several researchers.[30-32] Most of these reactions employs iodine(III)/(V) reagents as stoichiometric oxidants. Apart from this, several catalytic systems involving *in situ* generation of hypervalent iodine species from aryl iodides in the presence of suitable terminal oxidant are well explored. Further this section is classified based on synthesis of monocyclic, bicyclic, polycyclic and spirocyclic heterocycles using different hypervalent iodine reagents.

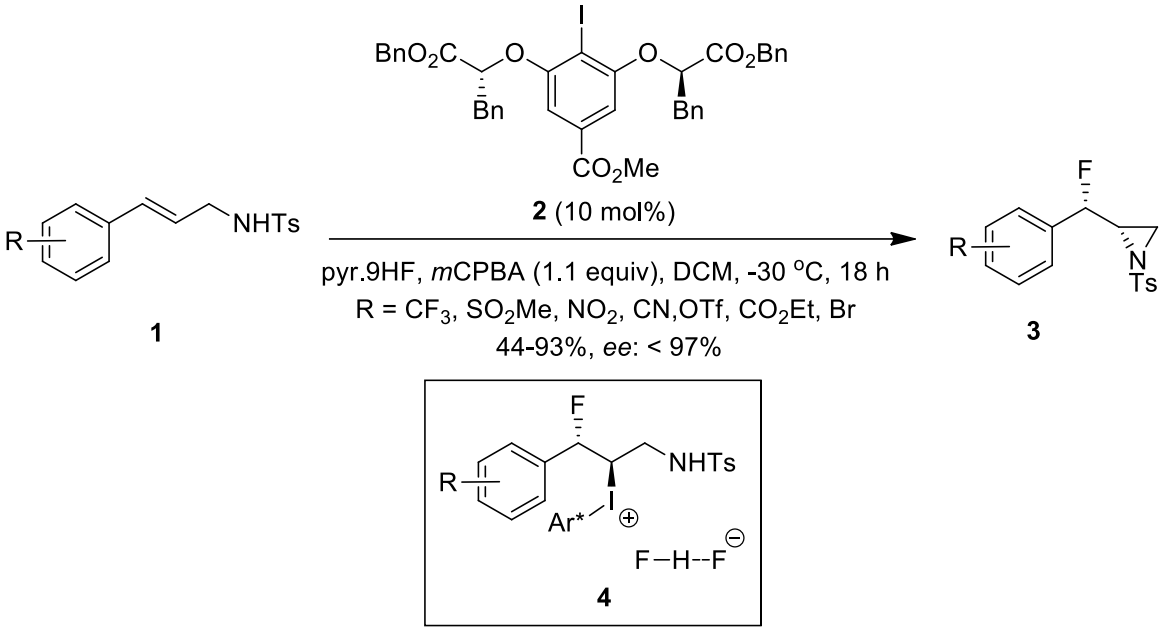
2.1. Synthesis of monocyclic heterocycles

Various cyclization reactions employing hypervalent iodine reagents as oxidants are developed for the synthesis of monocyclic heterocycles in distinguish yields. Most of the approaches are free from metal catalyst while few require presence of copper or palladium species as catalysts. Moreover, enantioselective synthesis of heterocycles has been was achieved using chiral iodoarenes as precatalyst. In this section, hypervalent iodine-mediated synthesis of three-, five-, six- and seven-membered heterocycles will be covered.

2.1.1. Synthesis of three-membered heterocycles

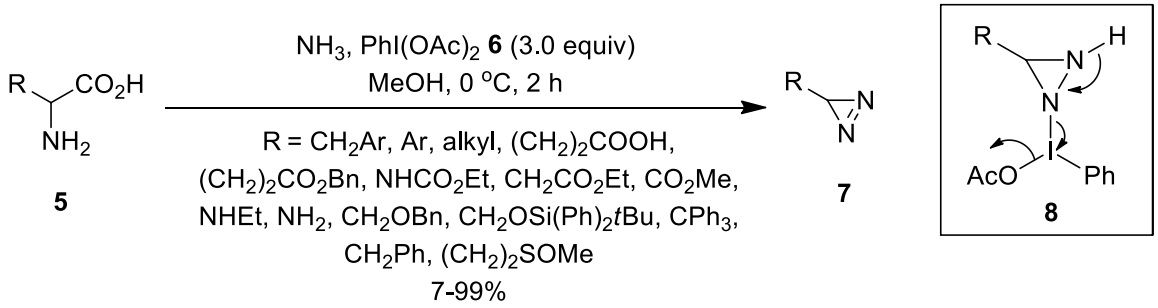
2.1.1.1. Synthesis of aziridines. In 2018, Jacobsen and co-workers demonstrated an elegant method for the diastereospecific synthesis of *syn-β*-fluoroaziridines **3** from cinnamylamine derivatives **1** using a catalytic amount of chiral aryl iodide **2** (Scheme 1).[34] Reaction was hypothesized to proceed via trapping of key intermediate **4** by internal nitrogen nucleophile. The present fluoroaziridination reaction employs HF-pyridine

as the nucleophilic fluoride source in the presence of stoichiometric oxidant *m*CPBA. Substrates with electron-withdrawing substituents yielded the desired products as single diastereoisomers with high enantioselectivity. Additionally, the scope of the reaction was extended to the synthesis of the five-membered heterocycle *anti-β*-fluoropyrrolidine in 82% yield with *ee* up to 86%.



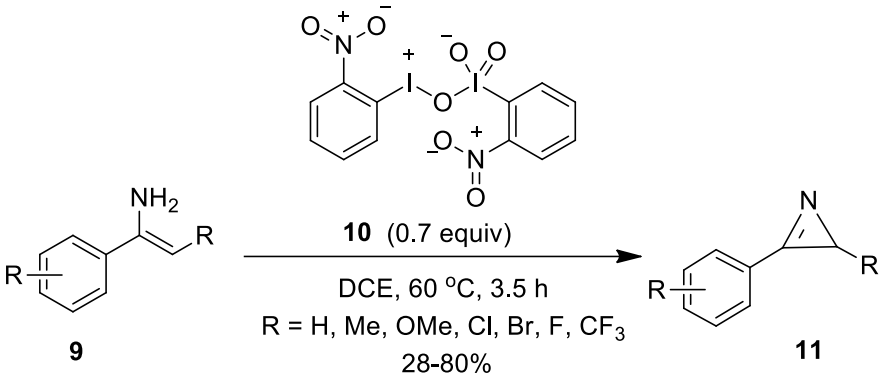
Scheme 1. Synthesis of *syn-β*-fluoroaziridines **3** using chiral iodide **2** as precatalyst.

Later, Reboul's team developed an unprecedented approach towards the synthesis of terminal diazirines **7** from amino acids **5** using ammonia as the nitrogen source (Scheme 2).[35] This one-pot reaction involves PIDA-mediated decarboxylation of amino acid **5** giving an imine intermediate, followed by insertion of the iodonitrene (formed *in situ* from the reaction of PIDA **6** and NH_3) to form a diaziridine **8** and final oxidation to provide the desired diazirines **7**. Several functional groups such as arene, heteroarene, ester, carboxylic acid, amide, sulfide, sulfoxide, etc. present in the amino acid side chain were well tolerated. Additionally, synthesis of terminal $^{15}N_2$-diazirines was achieved from unlabelled amino acids using $^{15}NH_3$ as a nitrogen source. Finally, hyperpolarization of $^{15}N_2$-diazirine derivative was investigated using the SABRE-SHEATH method, demonstrating its potential application as hyperpolarized molecular tag.



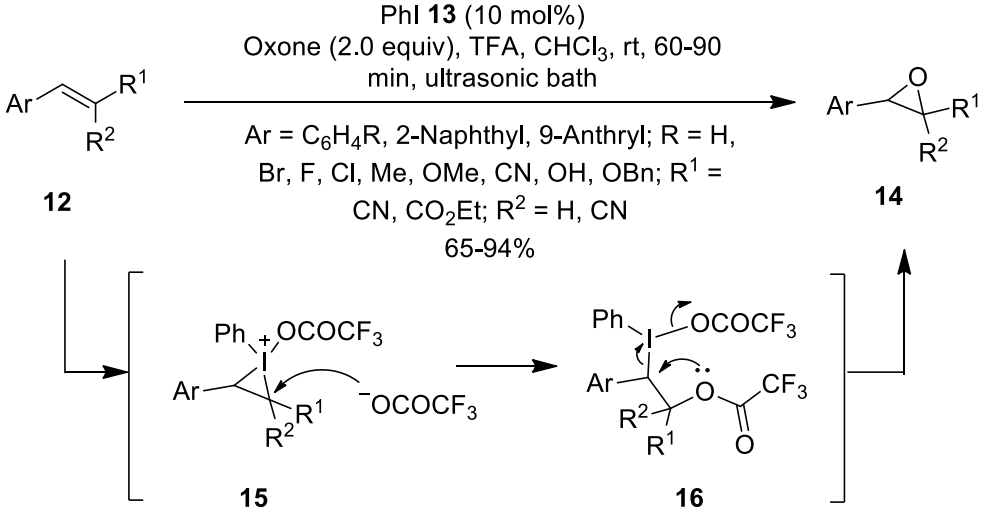
Scheme 2. Synthesis of terminal diazirines **5** using PIDA **6** as an oxidant.

Very recently, Du and co-workers reported the synthesis of first novel hypervalent iodine reagent **10** bearing both iodine(III) and iodine(V) moieties through *m*CPBA-mediated oxidation of *o*-nitroiodobenzene (Scheme 3).[36] The synthesized iodine(III/V) compound **10** proved to be effective oxidant in preparing 2*H*-azirines **11** from α-substituted enamines **9** via intramolecular oxidative azirination process. Reaction tolerated variety of substituents at the *ortho*-, *meta*- or *para*-position of the phenyl ring affording the desired products in moderate to good yields.



Scheme 3. Synthesis of 2*H*-azirines **11** using iodine(III/V) compound **10** as an oxidant.

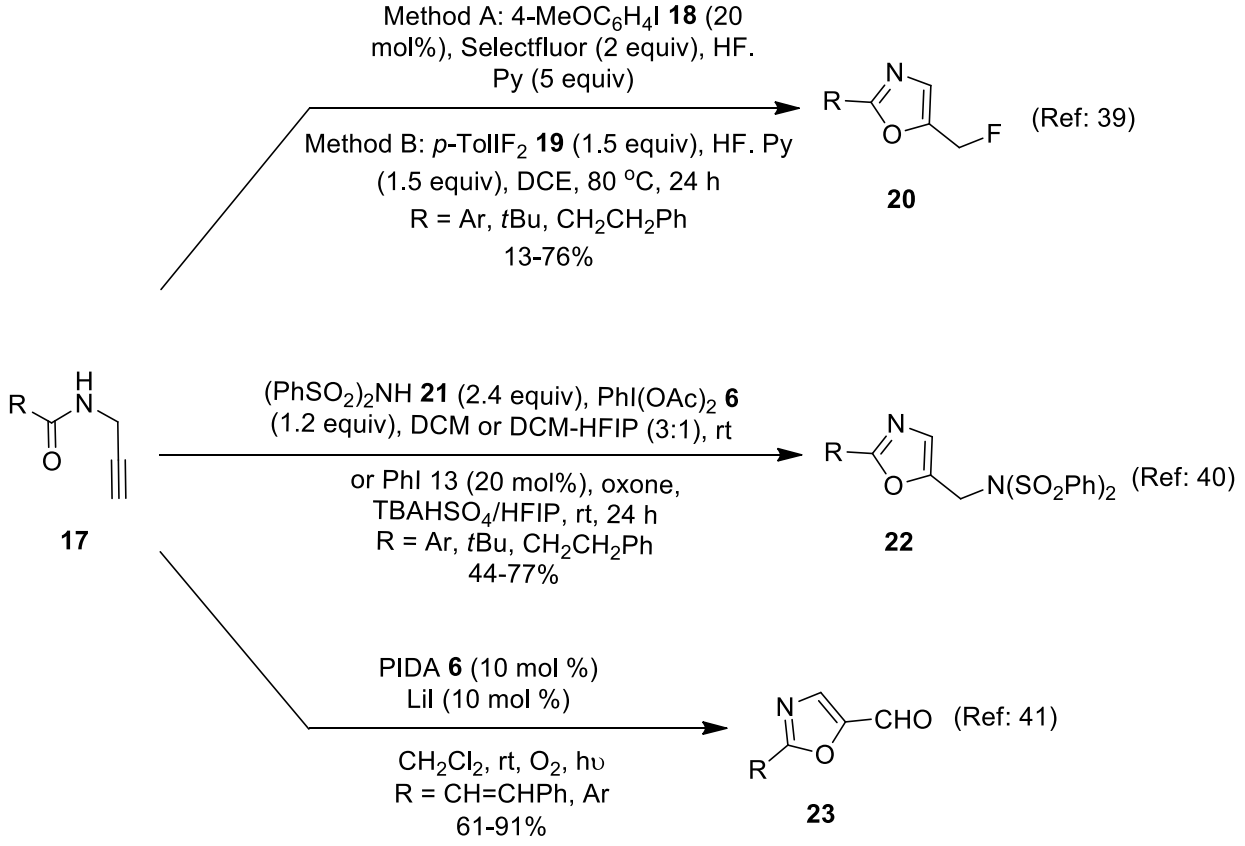
2.1.1.2. Synthesis of epoxides. Mangaonkar and Singh developed a convenient ultrasound-assisted catalytic route to access β-cyanoepoxides **14** through epoxidation of β-cyanostyrenes **12** using iodobenzene **13** as precatalyst at room temperature (Scheme 4).[37] The presence of oxone as terminal oxidant and TFA as an additive are crucial for the *in situ* generation of active iodine(III) species which reacts with alkene **12** and generates three-membered iodonium intermediate **15** followed by ring opening and cyclization to give anticipated product **14**. Reaction featured excellent functional group compatibility, high product yields and shorter reaction time. Previously, the same group also described epoxidation of β-cyanostyrenes with stoichiometric PIDA **6** under ultrasound irradiation conditions.[38]



Scheme 4. Iodine(III)-catalyzed epoxidation of β-cyanostyrenes **12** using iodobenzene **13** as precatalyst.

2.1.2. Synthesis of five-membered heterocycles.

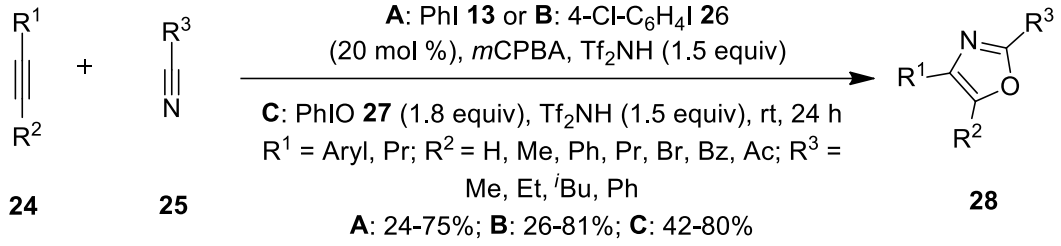
2.1.2.1. Synthesis of oxazoles and oxazolines. In 2016, Saito's research group reported synthesis of fluorinated oxazoles **20** through hypervalent iodine(III)-induced activation of *N*-propargyl amides **17** via a cyclo-isomerization-fluorination sequence (Scheme 5).[39] This reaction occurs by employing either catalytic 4-iodoanisole **18**/HF-pyridine/Selectfluor system (Method A) or stoichiometric *p*-TolIF$_2$**19**/HF·Py system (Method B). Notably, stoichiometric method was found more effective for halogenated substrates. Later, the same group prepared 5-[(*N*,*N*-disulfonylamino)methyl]-oxazoles **22** by reacting *N*-propargyl carboxamides **17** with bisulfonyl(imides) **21** promoted by PhI(OAc)$_2$ **6** via cycloisomerization-amination sequence.[40] The catalytic version of this method was developed using PhI **13** as precatalyst with oxone as oxidant and TBAHSO$_4$ as phase transfer reagent. Furthermore, Yi *et al.*[41] combined iodocyclization and oxidative deiodination process for the conversion of *N*-propargylamides **17** into oxazole-5-carbaldehydes **23** using PIDA **6** (10 mol %)/LiI/visible light system under oxygen atmosphere (Scheme 5).



Scheme 5. Hypervalent iodine(III)-mediated synthesis of oxazoles **20**, **22** and **23.**

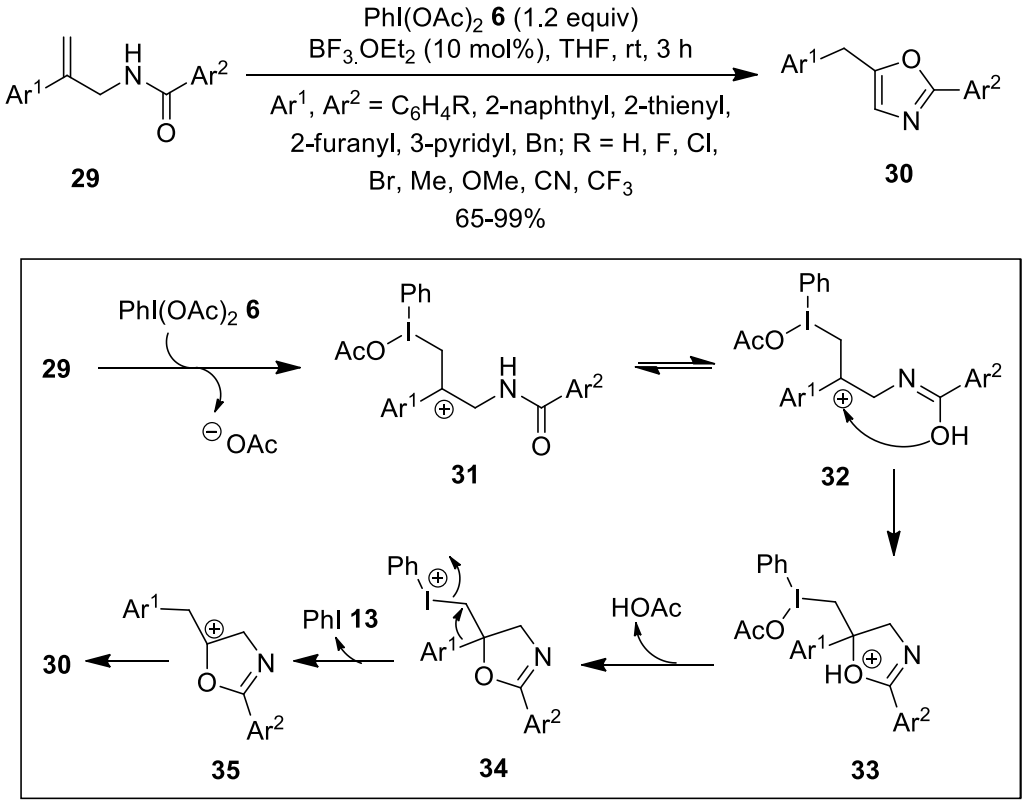
In continuation, Saito's research group reported [2 + 2 + 1] cycloaddition-type reaction of internal/terminal alkynes **24**, nitriles **25** and oxygen atom from ArI(OH)NTf$_2$, which is generated *in situ* from ArI/*m*CPBA/Tf$_2$NH catalytic system (Scheme 6).[42] This oxidative annulation represents the first example of iodine catalysis in multi-component reactions enabling facile synthesis of 2,4-disubstituted and 2,4,5-trisubstituted oxazoles **28**. The reaction employed either PhI **13** (Condition A) or 4-ClC$_6$H$_4$I **26** (Condition B) as precatalysts along with *m*CPBA and Tf$_2$NH. Additionally, reaction scope was also administered using iodosylbenzene **27** (1.8 equiv) and Tf$_2$NH (Condition C). Notably, catalytic conditions **A** or **B** provided almost same results as stoichiometric condition **C**.

Further active iodine(III) species PhI(OH)NTf_2 involved was isolated as an aquo-[18C6] complex in 43% yield under the optimized conditions.



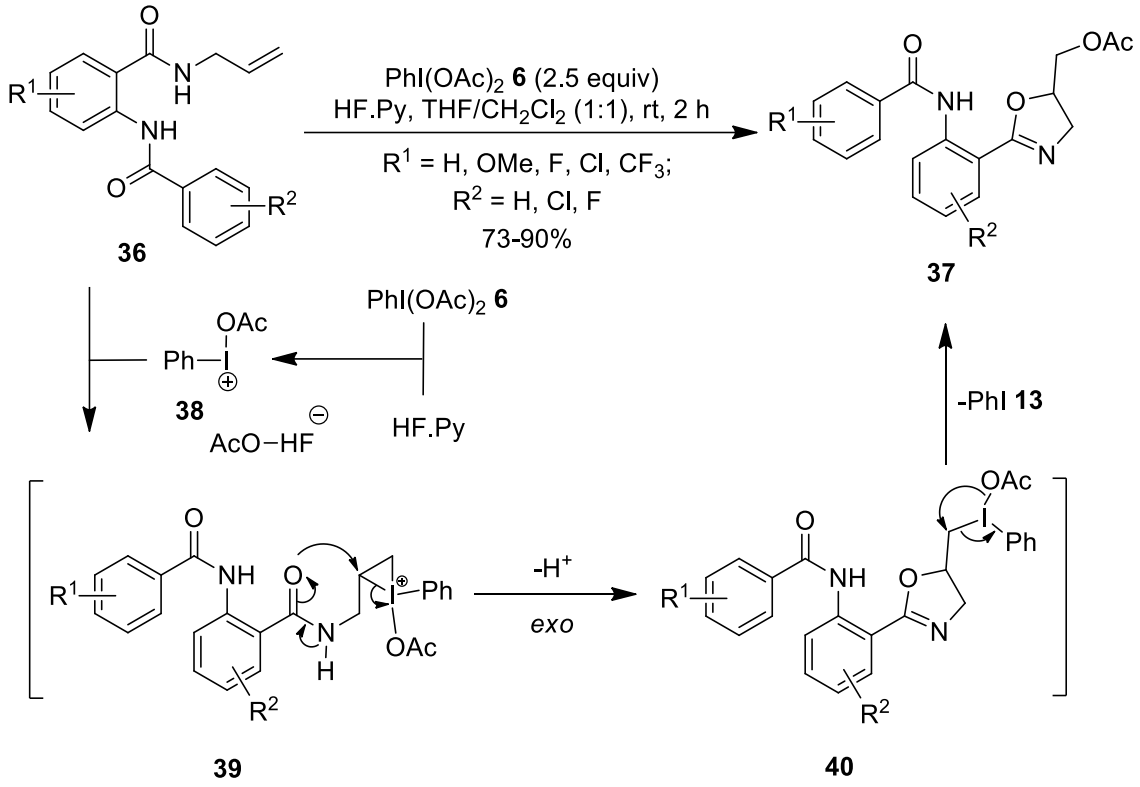
Scheme 6. Iodine(III)-mediated synthesis of 2,4-disubstituted and 2,4,5-trisubstituted oxazoles **28.**

Ding's group recently published a divergent protocol to access 2,5-disubstituted oxazole derivatives **30** via $PhI(OAc)_2$-induced oxidative rearrangement of several allylic amides **29**.[43] Reaction was carried out in the presence of $BF_3{\cdot}OEt_2$ as an additive in THF at room temperature. Both aromatic and heteroaromatic substituents were well tolerated under optimized reaction conditions and products were obtained in variable yields (Scheme 7). Possible mechanistic approach initiates with the reaction of allylic amide **29** with $PhI(OAc)_2$ **6** to form iodinated intermediate **31** which further gives intermediate **32**. Next, nucleophilic attack by hydroxyl group at the carbocation of **32** generates cyclic intermediate **33** followed by subsequent aryl migration with the loss of PhI **13** gives species **35**, which later gets converted into desired product **30**.



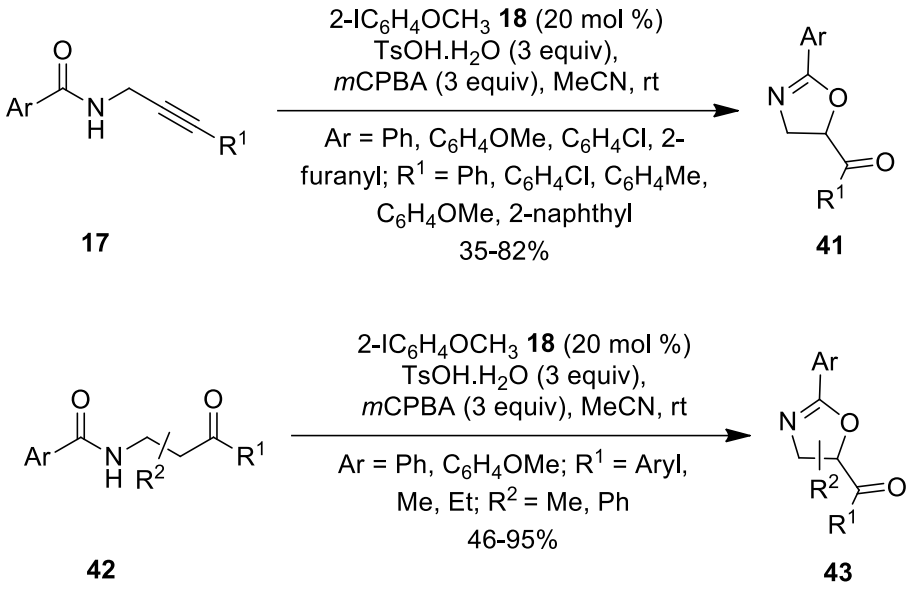
Scheme 7. PIDA-mediated oxidative rearrangements of amides **29** to oxazoles **30.**

Another interesting heterocycle, oxazoline **37**, was synthesized by Ranjith *et al.* via PIDA-mediated intramolecular oxyacetoxylation of substituted *N*-allylamides **36** using HF·py as the promoter (Scheme 8).[44] Reaction mechanism initiates with the conversion of PIDA **6** into aryliodinium ion **38** influenced by HF·py, which further interacts with the alkene to form cyclic iodonium ion **39**. Next, *exo* attack by the amide moiety transforms cyclic iodonium ion **39** into alkyl iodane **40**. Finally, nucleophilic attack by acetyl group liberates PhI **13** and delivers oxazolines **37** following S_N2-like bimolecular reductive elimination.



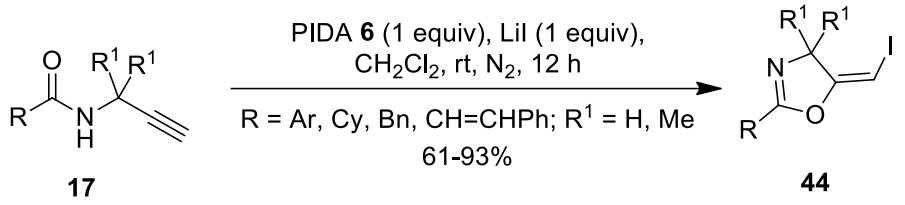
Scheme 8. Synthesis of substituted oxazolines **37** using PIDA **6** as an oxidant.

Later, two catalytic methods to prepare 2-oxazolines **41** and **43** were developed by Kamouka and Moran.[45] The first method involves intramolecular cyclization of *N*-propargylamides **17** while other involves cyclization of β-amidoketones **42** using 2-iodoanisole **18** as precatayst with *m*CPBA and $TsOH.2H_2O$ (Scheme 9). Both these approaches employ easily available starting materials, tolerates wide range of functional groups and operate under mild reaction conditions. The same group previously synthesized oxazolines through iodoarene-catalyzed cyclization of *N*-alkenylamides using selectfluor as an oxidant.[46]



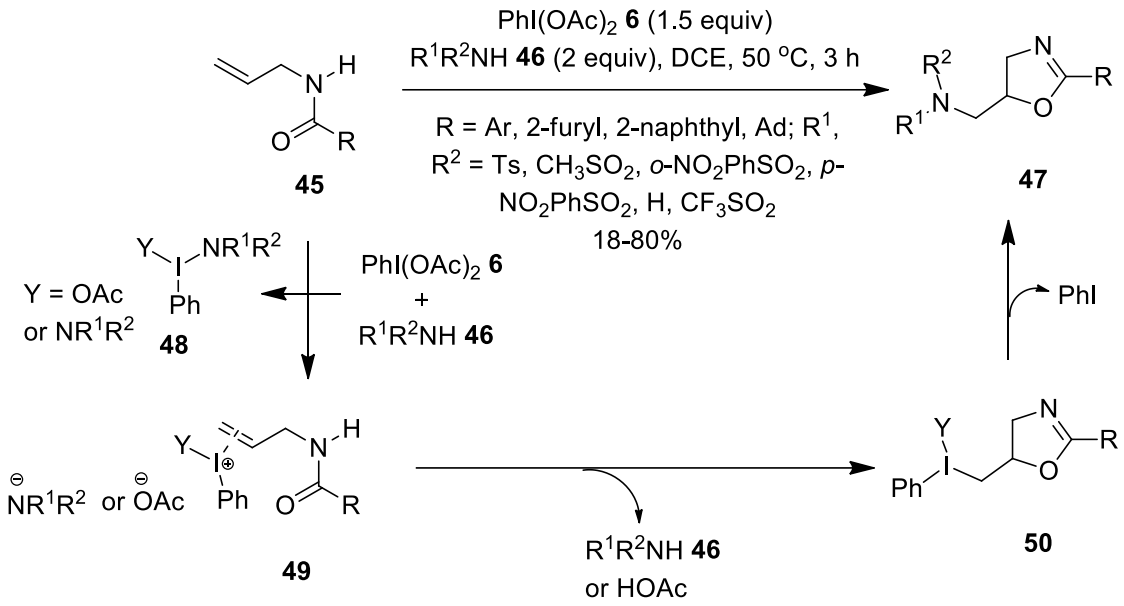
Scheme 9. 2-Iodoanisole-catalyzed cyclization of *N*-propargylamides **17** and *β*-amidoketones **42.**

In 2018, Liu and co-workers designed a simple and efficient method for the preparation of oxazolines **44** via *5-exo-dig* process (Scheme 10).[41] In the presence of PIDA **6** (1.0 equiv) and LiI (1.0 equiv), iodocyclization of various *N*-propargylamides **17** was performed, providing iodomethylene-2-oxazolines **44** in significant yields. Synthesis of 5-halomethyloxazolines was previously accomplished by the same group through PIDA-promoted cyclization of *N*-allylamides.[47]



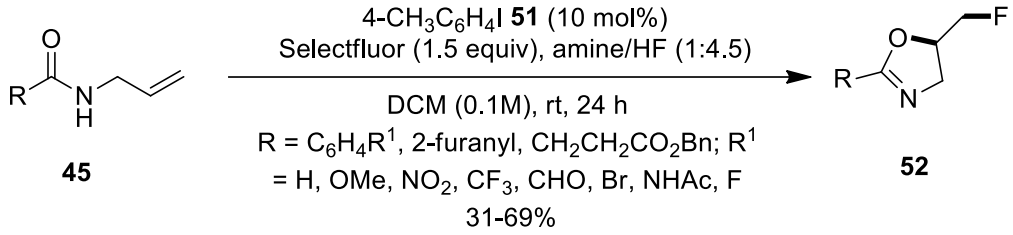
Scheme 10. PIDA-induced preparation of oxazolines **44.**

Later, another iodine(III)-mediated route to prepare oxazolines **47** was developed by Hong and co-workers by treating *N*-allylamides **45** with bis(sulfonyl)imides **46** as the nitrogen source (Scheme 11).[48] The proposed mechanism for this inter-/intra aminohydroxylation reaction involves *in situ* generation of PhI(OAc)(NR^1R^2) or PhI(NR^1R^2)$_2$ **48** which activates double bond of **45** followed by subsequent cyclization and substitution to yield heterocyclic products **47**. Several electron deficient amines **46** were evaluated and validated that the desired reactivity originates from attached (benzene)sulfonyl group.



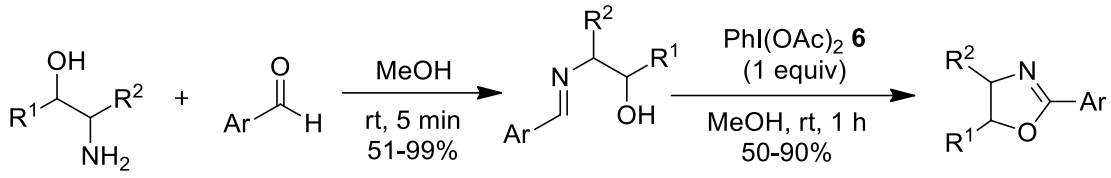
Scheme 11. Synthesis of oxazolines **47** using PIDA **6** as an oxidant.

Further, Scheidt *et al.* provided a direct route to 2-oxazolines **52** incorporating a fluoromethyl group from *N*-allylcarboxamides **45** following I(I)/I(III) catalysis (Scheme 12).[49] The success of this fluorooxygenation reaction lies in its efficient generation of active iodine(III) species, *p*-TolIF$_2$ **19** *in situ* from precatalyst 4-iodotoluene **51** using Selectfluor as an oxidant. The amine/HF ratio of 1:4.5 was obtained by combining Et$_3$N·3HF and Olah's reagent (Pyr·HF).



Scheme 12. 4-iodotoluene-catalyzed fluorocyclization of *N*-allylcarboxamides **45** to form 2-oxazolines **52.**

In the same year, a convenient synthesis of 2-oxazolines **56** via PIDA-promoted cyclization of imine intermediate **55** was demonstrated by Carlucci *et al.* (Scheme 13).[50] The imines **55** were obtained subsequently by treating amino alcohols **53** with aldehydes **54** in methanol solution. Also, synthesis of 3-oxazolines was accomplished albeit in lower yields under similar reaction conditions.

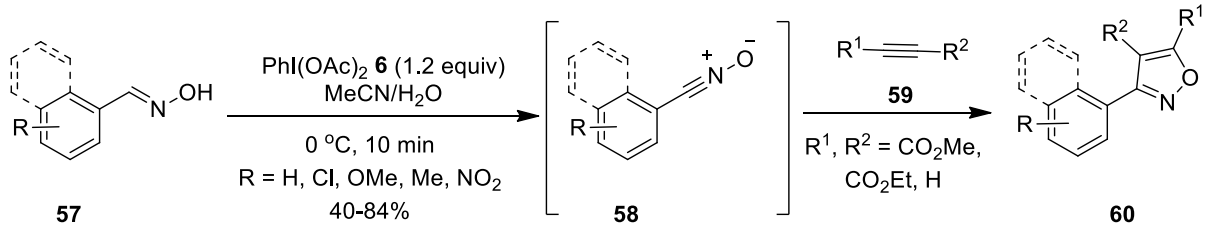


53 **54** **55** **56**

R^1 = H, Ph; R^2 = H, Me, CO_2Me; Ar = Ph, 1-nap, 4-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, CH=CHPh,CH=CH(4-$OMeC_6H_4$), 3-pyridyl

Scheme 13. PIDA-promoted synthesis of 2-oxazolines **56.**

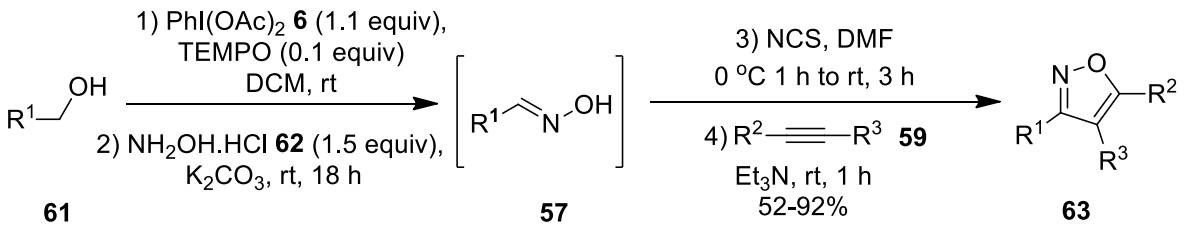
2.1.2.2. Synthesis of Isoxazole and Isoxazolines. In 2016, Peddinti and co-workers developed a strategy to access isoxazole derivatives **60** via PIDA-mediated [3+2] cycloaddition of *in situ* formed nitrile oxides **58** from aldoximes **57** with alkynes **59** (Scheme 14).[51] Scope of the reaction was explored using dimethyl acetylenedicarboxylate (DMAD), diethyl acetylenedicarboxylate (DEAD) and methyl propiolate as dipolarophiles. Different substituents on aryl moiety of aldoximes **57** were well tolerated and anticipated products were isolated in shorter reaction time.



57 **58** **60**

Scheme 14. Synthesis of isoxazole derivatives **60** using PIDA **6** as an oxidant.

Later in 2019, Kobayashi and Togo reported one-pot synthesis of 3-aryl- or 3-alkylisoxazoles **63** through the reaction of primary alcohols **61** with $PhI(OAc)_2$ **6** and then sequential reactions with NH_2OH, NCS and alkynes **59** (Scheme 15).[52] This reaction involves PIDA-mediated oxidation of primary alcohols **61** to aldehydes which reacts with hydroxylamine **62** to form oximes **57** (Step 1 and 2). Further, reaction of oximes **57** with NCS generates nitrile *N*-oxides *in situ* which then reacts with alkynes **59** to yield isoxazoles **63** *via* 1,3-dipolar cycloaddition (Step 3 and 4). Additionally, synthesis of 3-aryl-/3-alkylpyrazoles was achieved by replacing $NH_2OH{\cdot}HCl$ with NH_2NHPh in the second step under similar conditions.

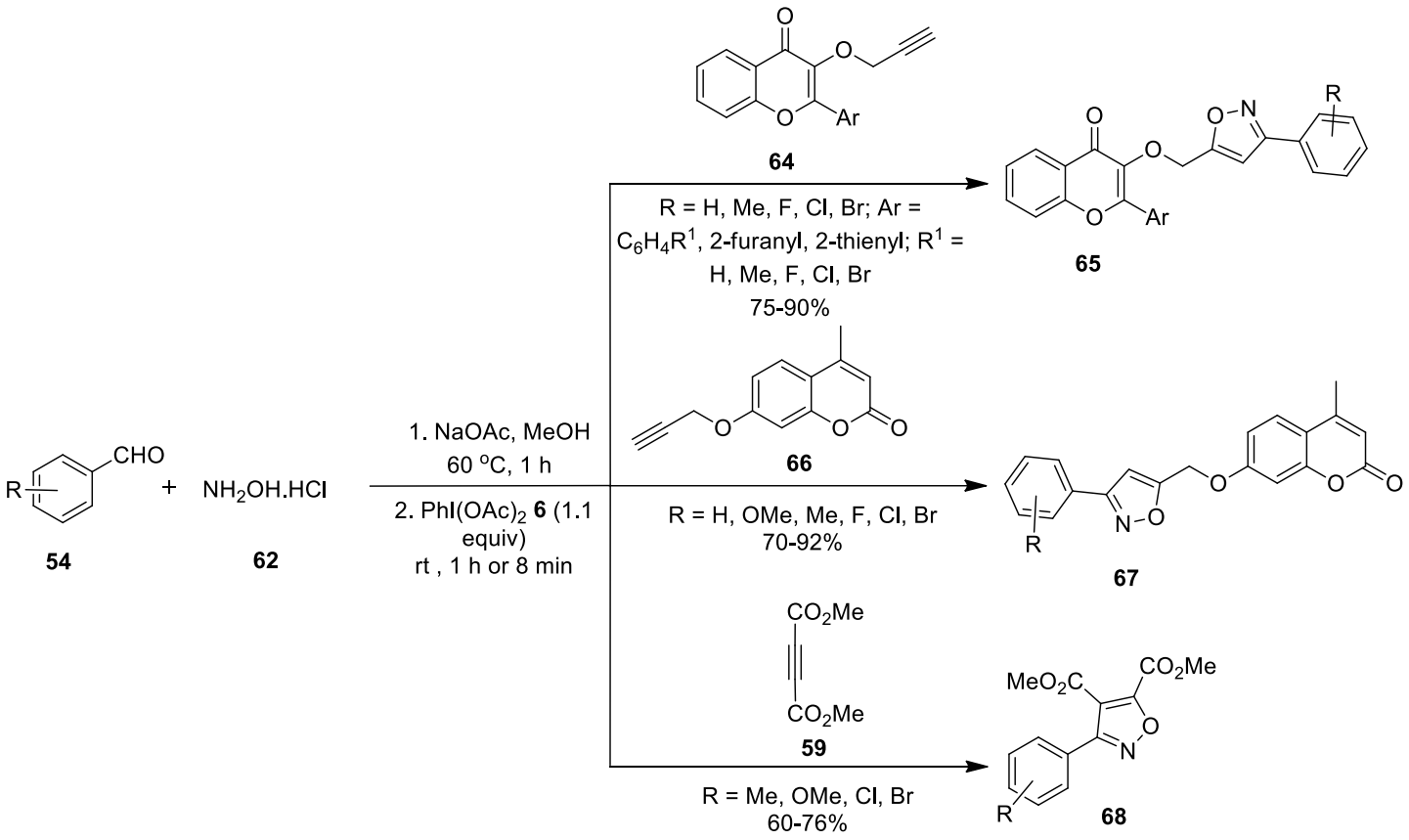


61 **57** **63**

R^1 = Aryl, CH=CHPh; R^2 = CO_2Et, Ph, n-Hex; R^3 = CO_2Et, H

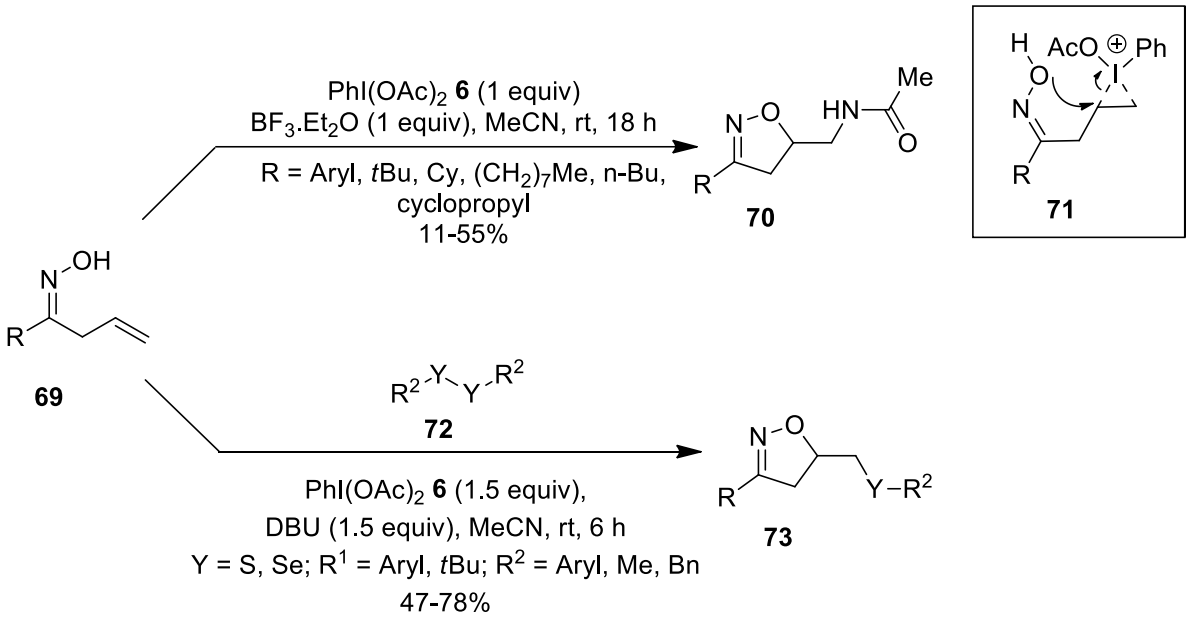
Scheme 15. PIDA-mediated synthesis of 3-aryl- and 3-alkylisoxazoles **63** from primary alcohols **61.**

Subsequently, Mukthar and co-workers described synthesis of flavone- and coumarin-based isoxazoles **65** and **67** through one-pot reaction of aryl aldehydes **54**, hydroxylamine **62** and 3-*O*-propargylflavones **64**/3-*O*-propargylcoumarin **66** via PIDA-mediated sequential oxidative cyclization and [3+2] cycloaddition reaction (Scheme 16).[53] Further synthesis of tri-substituted isoxazoles **68** was accomplished by using dimethyl acetylenedicarboxylate (DMAD) **59** as an alkyne source. High product yields, excellent functional group tolerance, shorter reaction time, easy-workup and purification are key advantages of developed protocol. Further, synthesized compounds have been tested for the antibacterial activity.



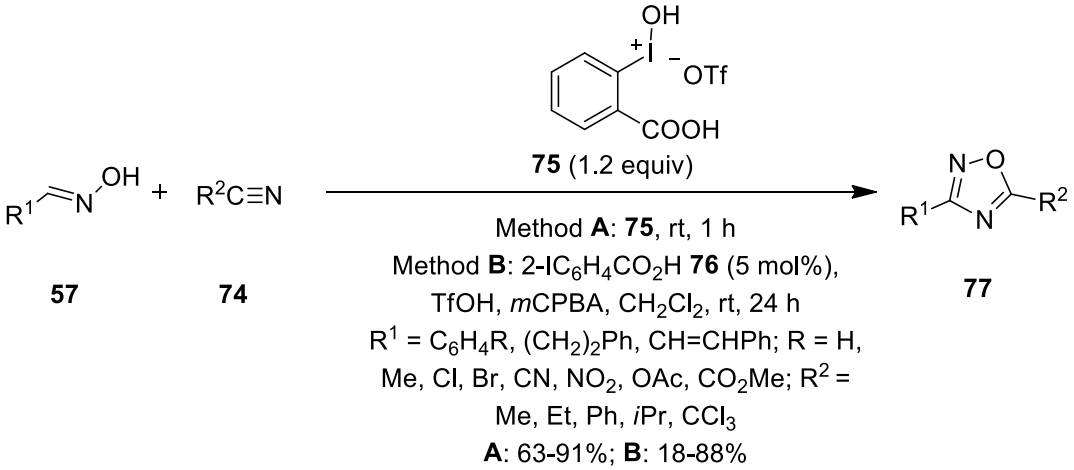
Scheme 16. PIDA-induced one-pot synthesis of isoxazoles **65**, **67** and **68.**

Park *et al.* constructed isoxazolines **70** through PIDA-induced Ritter-type amidation of terminal olefins **69**. Acetonitrile plays dual role of solvent and the amine source (Scheme 17).[54] Notably, activation of $PhI(OAc)_2$ **6** by $BF_3{\cdot}OEt_2$ generates active iodine(III) species *in situ*, that reacts with **69** to form electrophilic iodonium intermediate **71** which could give desired product **70** through sequential 5-*exo*-type cyclization and Ritter-type-substitution using excess acetonitrile as the nucleophile. A variety of ketone oximes with aryl, heteroaryl and alkyl substituents were well tolerated. Specifically, electron-deficient aryl ketone oximes displayed robust reactivity thereby giving corresponding products in moderate yields while electron-rich ones gave inferior results. Further a similar method for the construction of heteroatom-containing isoxazolines **73** was demonstrated by Cai and co-workers.[55] This cascade reaction featured PIDA-mediated sulfeno-/seleno-/functionalization of several β,γ-unsaturated oximes **69** using substituted disulfides/diselenides **72** as S/Se-sources.



Scheme 17. Preparation of isoxazolines **70** and **73** from β,γ-unsaturated oximes **69** using PIDA **6.**

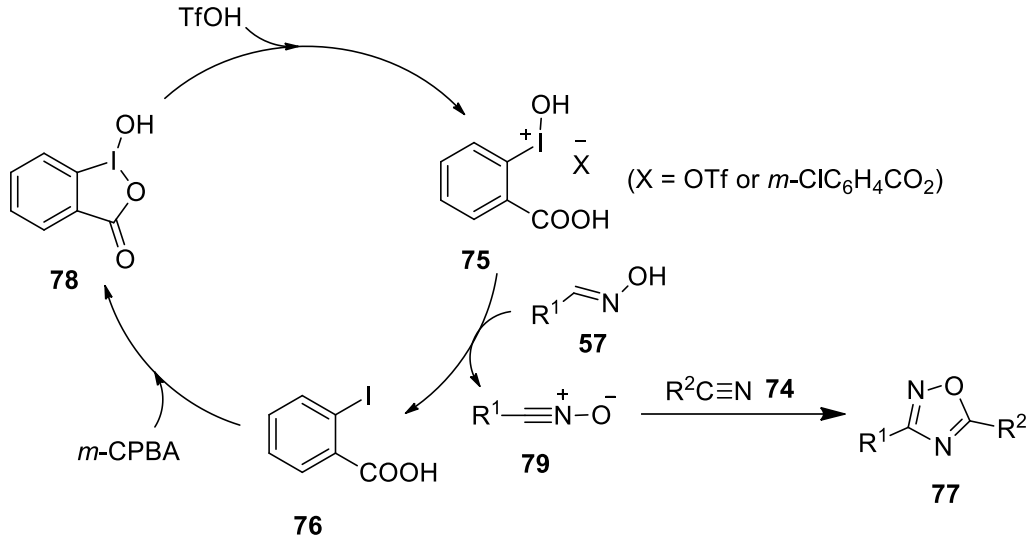
2.1.2.3. Synthesis of oxadiazoles. Meanwhile, Zhdankin's research group reported convenient synthesis of 1,2,4-oxadiazoles **77** via oxidative cycloaddition of substituted aldoximes **57** with nitriles **74** using 2-iodosyl-benzoic acid triflate (IBA-OTf) **75** as stoichiometric oxidant (Scheme 18).[56] The reagent IBA-OTf **75** was previously prepared by the same group from iodosylbenzoic and trifluoromethanesulfonic acid.[57] Further a catalytic system comprising 2-iodobenzoic acid **76** (5 mol %) as precatalyst in the presence of *m*-CPBA and TfOH was also developed for the cyclization of aldoximes **57** and nitriles **74**. Both stoichiometric and catalytic conditions gave desired products in moderate to high yields and electron-rich and -deficient substituents were well tolerated.



Scheme 18. Hypervalent iodine(III)-mediated oxidative cyclization of aldoximes **57** with nitriles **74** to yield 1,2,4-oxadiazoles **77.**

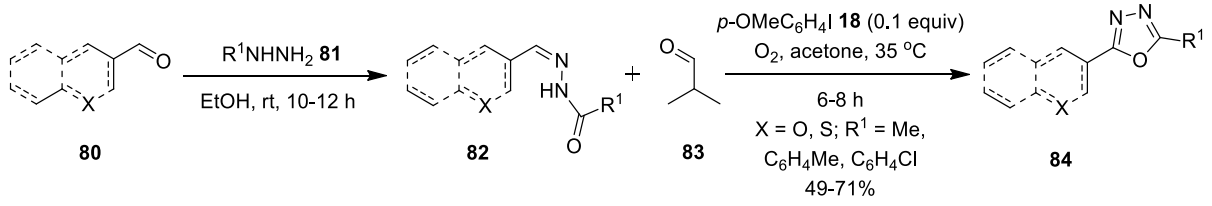
The mechanism for the catalytic reaction is depicted in Scheme 19. Cationic species **75** is formed *in situ* through oxidation of 2-iodobenzoic acid **76** by *m*-CPBA in the presence of TfOH. This active iodine(III) species **75**

reacts with aldoximes **57** via ligand exchange and generates nitrile oxides **79**, which further react with nitriles **74** to deliver desired product **77**. The regenerated precatalyst **76** is reoxidized by *m*-CPBA to continue the catalytic cycle.



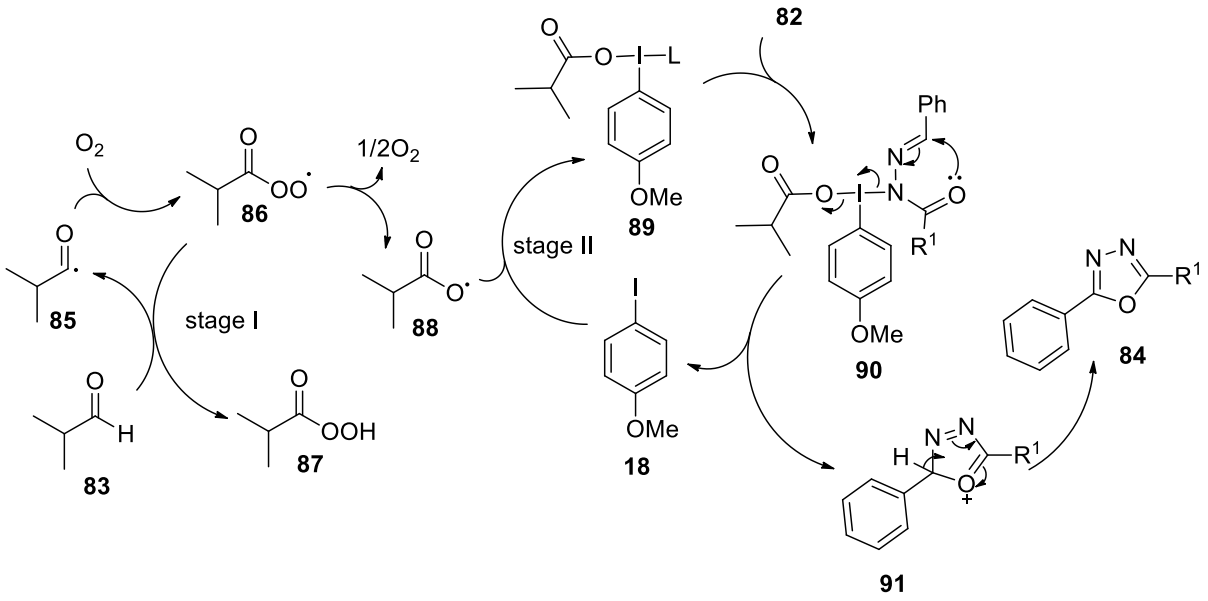
Scheme 19. The proposed catalytic cycle for the oxidative cyclization of aldoximes **57** using **76** as precatalyst.

In 2019, Sen and coworkers prepared 1,3,4-oxadiazoles **84** from variety of *N*′-arylidene acetohydrazides **82** in the presence of isobutyraldehyde **83** and *p*-anisolyl iodide **18**. In this reaction, autoxidation of isobutyraldehyde **83** forms acyloxy radical that oxidizes *p*-anisolyl iodide **18** into active hypervalent iodine species *in situ* which promotes the cyclization reaction (Scheme 20).[58] The precursors **82** were synthesized through condensation of variety of aromatic or heteroaromatic aldehydes **80** with acetyl, *p*-chlorobenzoyl, or tolyl hydrazides **81** in ethanol at room temperature. This method exhibits broad substrates scope and amenable for scale up reaction.



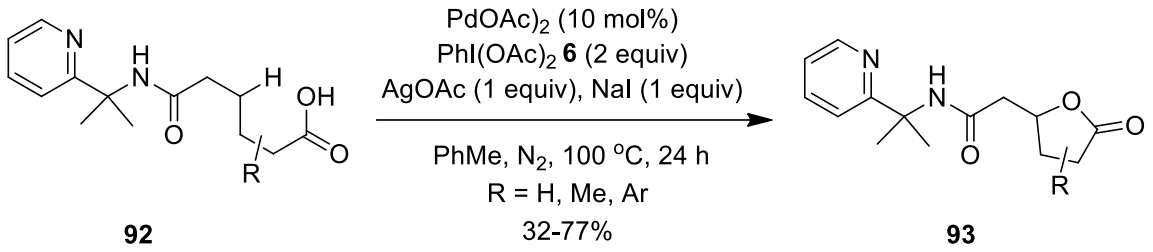
Scheme 20. Synthesis of 1,3,4-oxadiazole **84** using *p*-anisolyl iodide **18** as precatalyst.

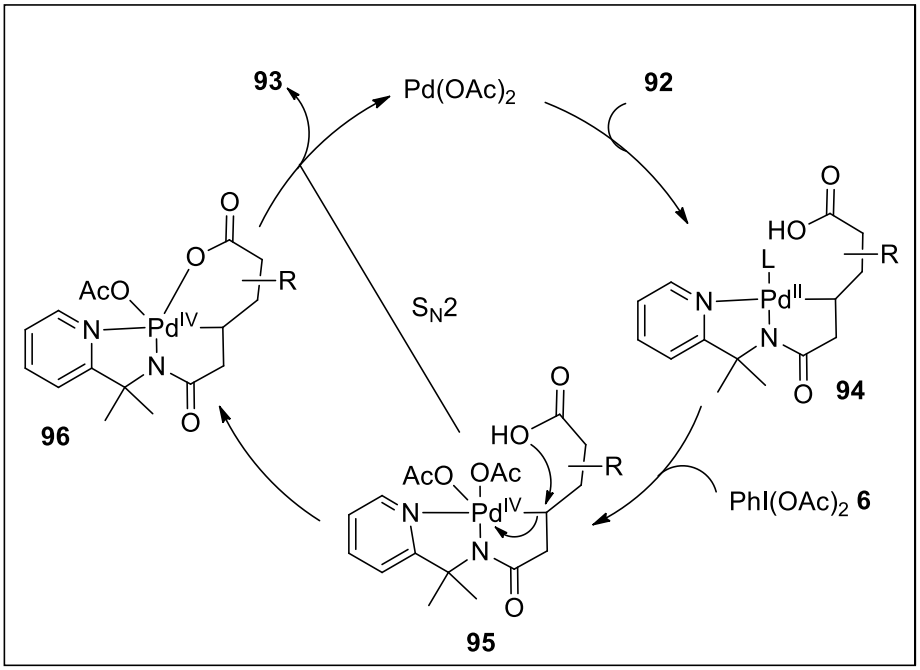
The postulated mechanism for this transformation follows two main stages as shown in Scheme 21. In the preliminary stage, autoxidation of isobutyraldehyde **83** forms per acid **87** through acyl radical **85** and acyl peroxy radical **86** respectively. Further acyloxy radical **88** generated from acyl peroxy radical **86**, enacts as oxidant for the oxidation of *p*-anisolyl iodide **18** leading to the *in situ* formation of hypervalent iodines(III) species **89**. Finally, **89** react with substrate **82** to afford **90**, which cyclizes to give **91** and aromatizes to afford **84**. The regenerated *p*-anisolyl iodide **18** later continues the catalytic cycle.



Scheme 21. The proposed catalytic cycle for the cyclization of *N*′-arylidene acetohydrazides **82** using using *p*-anisolyl iodide **18** as the precatalyst.

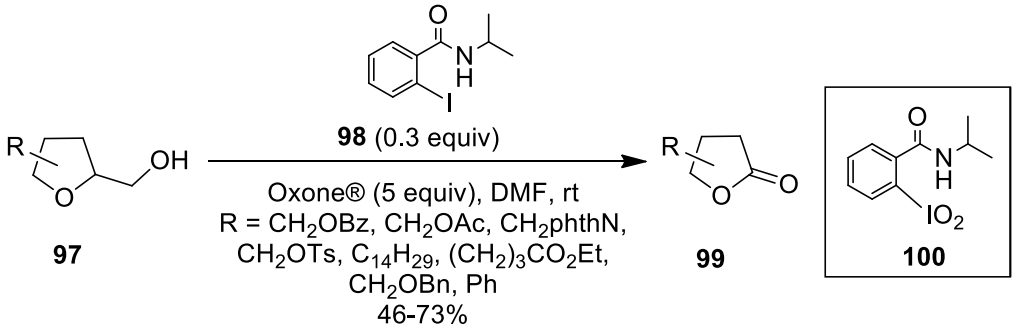
2.1.2.4. **Synthesis of Lactones.** Liu and Shi have reported straightforward routes to access γ-lactones **93** via palladium (II)-catalyzed intramolecular dehydrogenative lactonization between carboxylic acids and γ-C(sp^3)–H bond of substrates **92** using $PhI(OAc)_2$ **6** as the oxidant and (pyridin-2-yl)isopropyl amine (PIP) as the directing group (Scheme 22).[59] Among the various solvent and inorganic salts screened, toluene and NaI provided the best results. A variety of substituents on the alkyl chain of **92** were well tolerated. The proposed mechanism initiates with the Pd-catalyzed activation of methylene C(sp^3)–H assisted by PIP-auxillary to form palladacycle **94**, followed by PIDA-induced oxidation to give Pd(IV) intermediate **95** which undergoes ligand exchange to provide **96**. Finally, **96** upon reductive elimination releases target product **93** and regenerates Pd(II) catalyst to complete the catalytic cycle. Also, lactone **93** could be generated via direct intramolecular S_N2-type attack of carboxylate group onto the Pd(IV)–C bond of intermediate **95**.





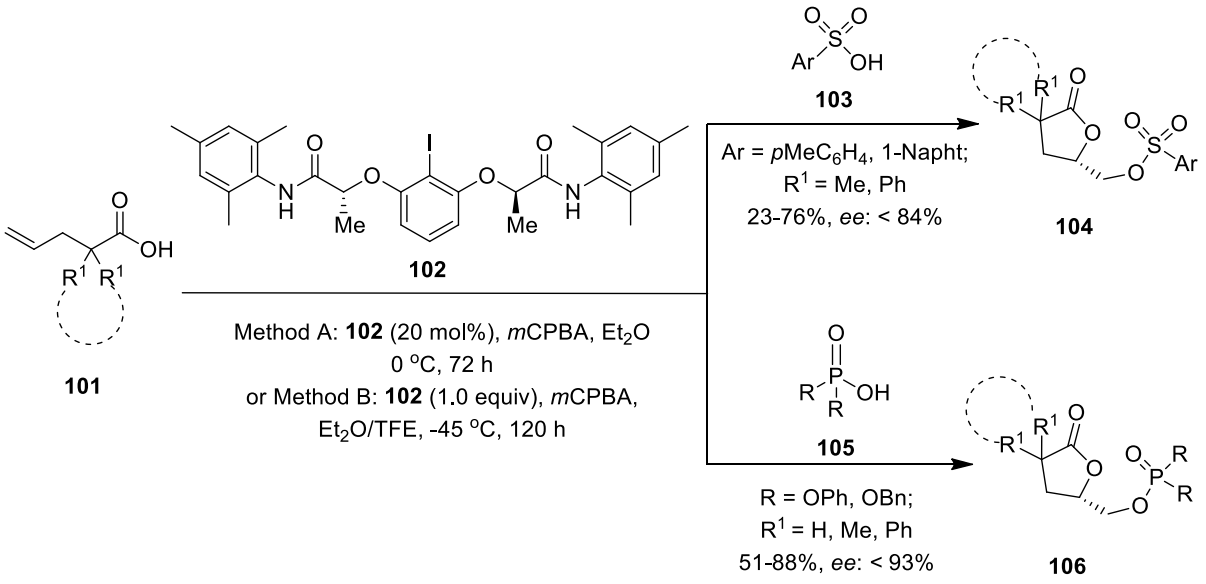
Scheme 22. Synthesis of γ-lactones **93** via intramolecular lactonization of **92** using $PhI(OAc)_2$ **6.**

Further, Fujiwara and co-workers reported direct conversion of tetrahydrofuran-2-methanols **97** into γ-lactones **99** via oxidative cleavage by employing precatalyst, 2-iodobenzamide **98** in the presence of co-oxidant oxone (Scheme 23).[60] Reaction proceeds through *in situ* generation of active hypervalent iodine(V) species **100** which facilitates the oxidation of substrates **97**. This reaction occurs at room temperature under mild conditions without using any toxic heavy metals and desired products were isolated in significant yields. Later, the same group developed a new catalyst, [4-Iodo-3-(isopropylcarbamoyl)phenoxy]acetic acid for the oxidation of tetrahydrofuran-2-methanols **97** and showed its reactivity greater than the previously employed catalyst **98**.[61]



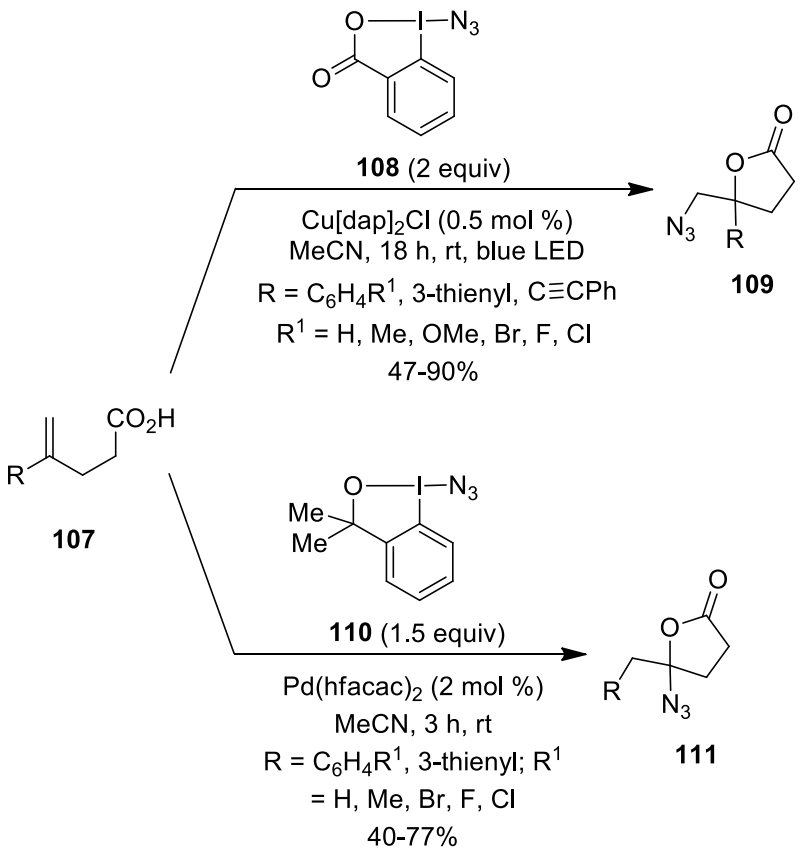
Scheme 23. Oxidation of tetrahydrofuran-2-methanols **97** to **99** using **100** as precatalyst.

Another interesting strategy to prepare γ-butyrolactones was reported by Gelis *et al.,* featuring enantioselective *γ*-sulfonyl- and *γ*-phosphoryloxylactonatization of 4-pentenoic acid derivatives **101** (Scheme 24).[62] Using stoichiometric or catalytic amount of C_2 symmetric chiral iodoarene **102**, a facile synthesis of sulfonyloxy-γ-butyrolactones **104** or phosphoryloxy-γ-butyrolactones **106** were achieved in variable yields. Notably, higher enantioselectivity was observed for phosphoryl-oxylactonatization (*ee* up to 93%) as compared to the sulfonyloxylactonization of 4-pentenoic acids **101** (*ee* up to 84%). Interestingly, *gem*-disubstituted- and spiro-lactones were obtained in high yields with good enantioselectivities.



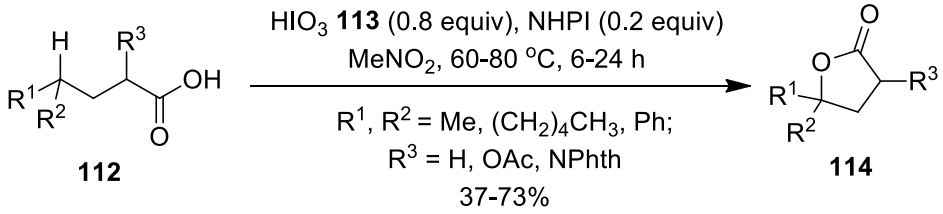
Scheme 24. Synthesis of γ-butyrolactones using chiral iodoarene **102** as precatalyst.

In 2017, Waser's research group synthesised (1,2)-azidolactones **109** through azidation and cyclization of unsaturated carboxylic acids **107** by employing azidobenziodoxolone (ABX) **108** as azide-transfer reagent with 0.5 mol % of the $Cu(dap)_2Cl$ as photoredox catalyst under blue LED irradiation (Scheme 25).[63] Both electron-rich and -deficient arenes as well as thiophene heterocycles were well tolerated. Furthermore, replacing ABX **108** with azidodimethylbenziodoxole (ADBX) **110** resulted in the formation of (1,1)-azidolactones **111** in the presence of Lewis acid catalyst, $Pd(hfacac)_2$ (2 mol %). Reactions were performed at room temperature, require low catalyst loading and exhibit broad substrate scope.



Scheme 25. Synthesis of azidolactones **109** and **111** using benziodoxol(on)e reagents **108** and **110** as azide source.

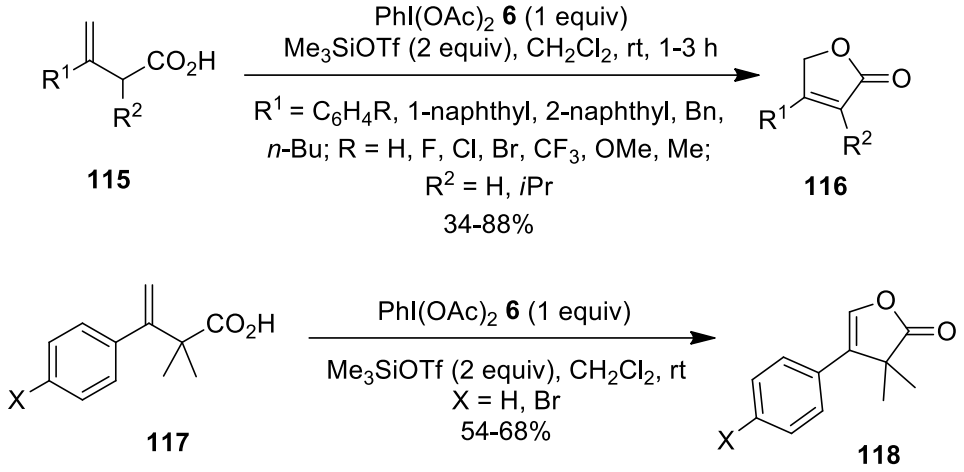
Minakata and co-workers investigated intramolecular lactonization of tertiary carbon containing carboxylic acids employing iodic acid (HIO_3) **113** as an oxidant in the presence of catalyst *N*-hydroxyphthalimide (NHPI) as hydrogen-atom transfer mediator (Scheme 26).[64] Notably, NHPI is oxidized to the phthalimide N-oxyl radical which facilitates the site selective C–H bond cleavage. The present oxidation system was found very effective for the preparation of γ-lactones **114** in respectable yields under metal-free conditions.



Scheme 26. Synthesis of γ-lactones **112** using iodic acid **114** as an oxidant.

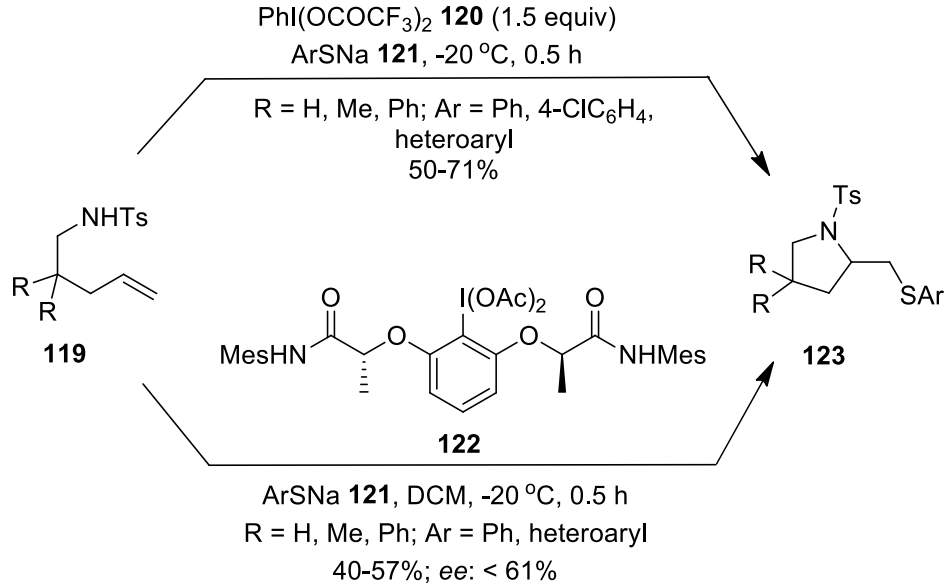
The same team prepared furan-2(5*H*)-ones **116** via oxidative cyclization of various β,γ-unsaturated carboxylic acid derivatives **115** induced by hypervalent iodine reagent (Scheme 27).[65] In this reaction, highly electrophilic species $PhI(OTf)_2$ generated *in situ* from $PhI(OAc)_2$ **6** and Me_3SiOTf, plays crucial role of oxidant. Both aromatic and aliphatic substituents at the β-position were well tolerated. Further cyclization of 3-aryl-2,2-

dimethylbut-3-enoic acids **117** in the presence of $PhI(OTf)_2$ furnished furan-2(3*H*)-one products **118** in 54-68% yields.



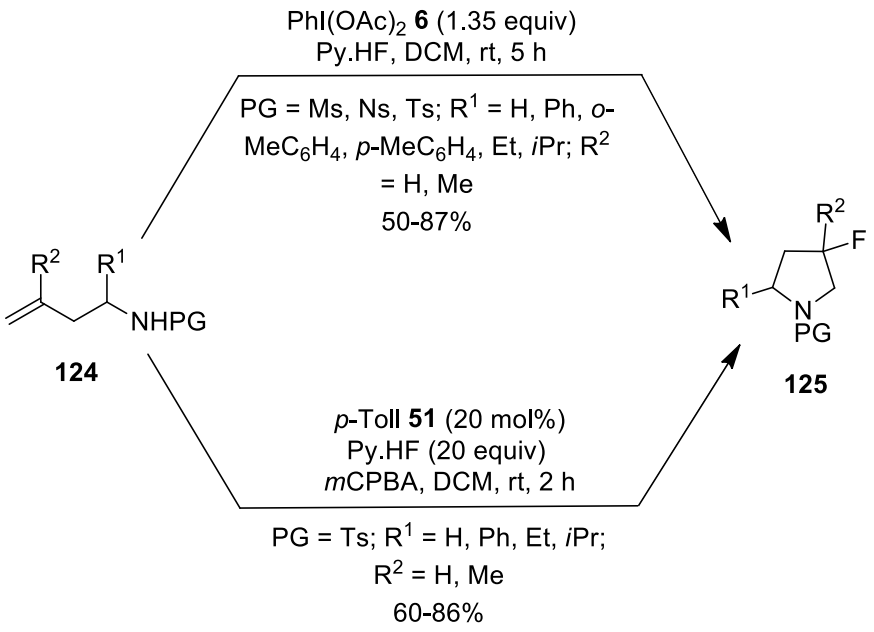
Scheme 27. PIDA-induced synthesis of furan-2(5*H*)-ones **116** and furan-2(3*H*)-one **118.**

2.1.2.5. Synthesis of pyrrolidines, dihydropyrroles and pyrroles. Wirth's research group disclosed thioamination of terminal alkenes **119** with [bis(trifluoroacetoxy)iodo]benzene ($PhI(OCOCF_3)_2$) **120** using thiolates **121** as an external nucleophile. This protocol provides flexible synthesis of pyrrolidines **123** in significant yields (Scheme 28).[66] Further a stereoselective version of this reaction was developed by employing lactate-based chiral iodine(III) reagent **122**, and thioamination products **123** were isolated in useful yields with up to 61% enantiomeric excess. Additionally, synthesis of indolines from corresponding *N*-(2-allylphenyl)-4-methyl benzene sulfonamides was achieved under both conditions.



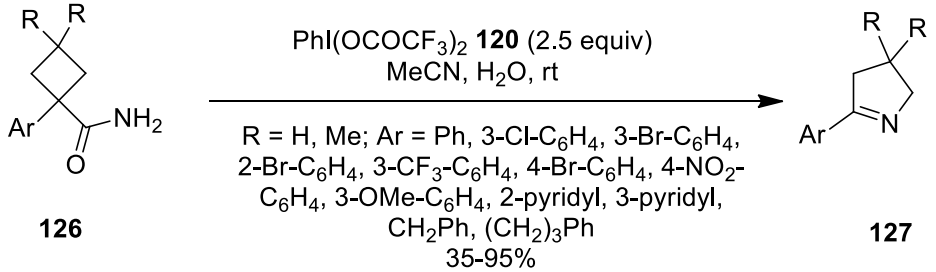
Scheme 28. Iodine(III)-mediated synthesis of pyrrolidines **123.**

Later, Kitamura *et al.* synthesized *N*-tosyl-3-fluoropyrrolidines **125** through intramolecular aminofluorination reaction of homoallylamines **124** using stoichiometric $PhI(OAc)_2$ **6** and pyridine·HF complex as a fluorine source (Scheme 29).[67] Further catalytic aminofluorination was achieved using *p*-iodotoluene **51** as the catalyst in the presence of Py·HF and *m*CPBA. Moreover, synthesis of *N*-tosyl-3-fluoropiperidine from *N*-tosyl-4-pentenylamine was accomplished in 89% yield under identical conditions.



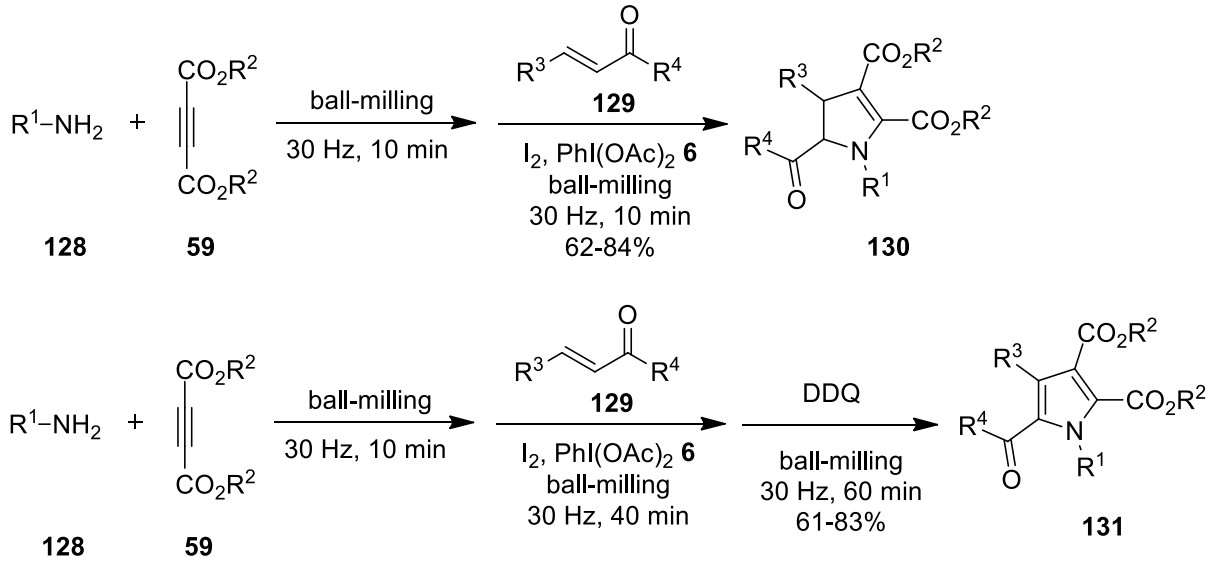
Scheme 29. Synthesis of *N*-tosyl-3-fluoropyrrolidines **125** from homoallylamines **124** using hypervalent iodine reagent.

Chang and co-workers prepared 2-aryl-1-pyrrolines **127** by treating 1-arylcyclobutanecarboxamides **126** with ($PhI(OCOCF_3)_2$) **120** via Hofmann rearrangement–ring expansion cascade reaction (Scheme 30).[68] Substrates **126** with aromatic ring bearing *ortho*-, *meta*- and *para* substituents reacted cleanly under mild conditions to deliver products in 35-95% yields. However, substrates with electron withdrawing groups delivered products in lower yields. Further this method has been adapted for the synthesis of 2,3-dihydro-1*H*-pyrrolo[2,1-*a*]isoquinolinium salts through cyclization of synthesized bromophenylpyrroline with alkynes using nickel catalyst.



Scheme 30. Synthesis of 2-aryl-1-pyrroline derivatives **127** using $PhI(OCOCF_3)_2$ **120** as an oxidant.

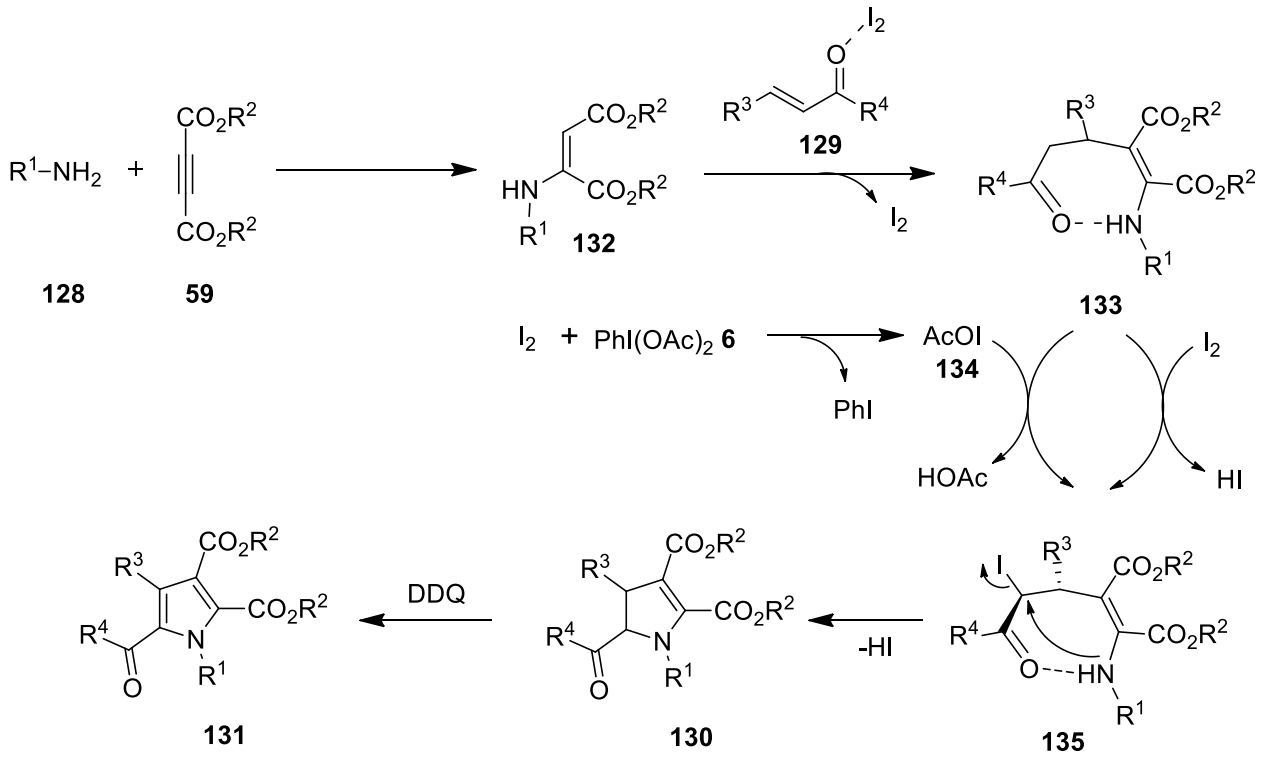
Wang and co-workers demonstrated I_2/PIDA-promoted one-pot synthesis of polysubstituted *trans*-2,3-dihydropyrroles **130** through multi-component reaction of aryl/alkyl amines **128** with alkyne esters **59** and chalcone derivatives **129** under ball-milling conditions (Scheme 31).[69] Further using DDQ as an oxidant, one pot-three step synthesis of multi-substituted pyrroles **131** were achieved under similar conditions. The present reaction featured broad substrates scope, shorter reaction time, and provides feasibility for larger-scale preparation.



R^1 = Aryl, *n*Butyl, *n*pent, *n*Hex, CH_2*i*Pr, Bn; R^2 = Et, Me; R^3, R^4 = Ph, C_6H_4Me, C_6H_4OMe, C_6H_4Cl, C_6H_4Br, Me, 2-naphthyl

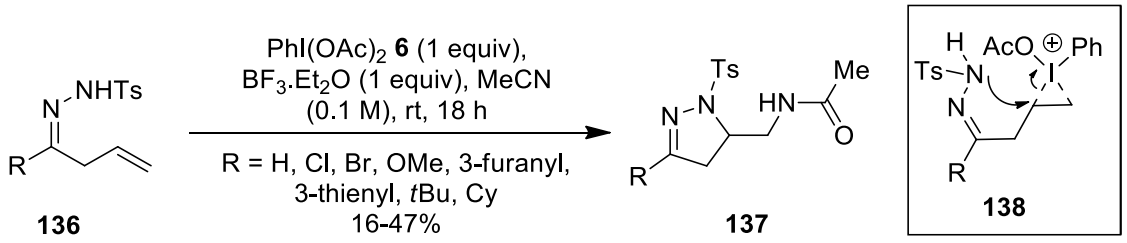
Scheme 31. Synthesis of dihydropyrroles **130** and pyrroles **131** using PIDA **6** as an oxidant.

The proposed reaction mechanism is shown in scheme 32. Initially, amine **128** reacts with alkyne ester **59** to give *β*-enamino ester **132**, followed by Michael addition between **132** and **129** to give intermediate **133**. Next, intermediate **133** reacts with I_2 or *in situ* generated AcOI **134** from I_2 and PIDA **6** to yield iodide **135**, which upon subsequent intramolecular S_N2-type nucleophilic substitution affords polysubstituted *trans*-2,3-dihydropyrrole **130** with the elimination of HI. Finally, DDQ mediated dehydrogenation aromatization of **130** gives corresponding pyrrole **131**.



Scheme 32. The proposed mechanism for the synthesis of dihydropyrroles **130** and pyrroles **131** using PIDA **6** as an oxidant.

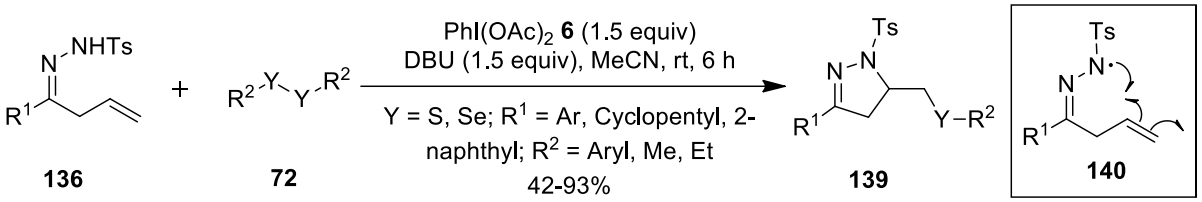
2.1.2.6. **Synthesis of pyrazolines, imidazolines and imidazoles.** In 2018, Park *et al*. explored Ritter-type amido-amidation of allyl ketone tosylhydrazones **136** by employing PIDA **6** as an oxidant and $BF_3.OEt_2$ as the promoter (Scheme 33).[54] This reagent system in combination with acetonitrile as the solvent and the amine source has led to the synthesis of pyrazoline scaffolds **137** at ambient temperature. Proposed mechanism involved activation of PIDA **6** by the Lewis acid generating active hypervalent iodine(III) species *in situ* that forms cyclic iodonium intermediate **138** with the alkene, which subsequently undergoes 5-*exo*-type cyclization and Ritter-type-substitution to deliver product **137**.



Scheme 33. Preparation of pyrazolines **137** using PIDA **6** as an oxidant.

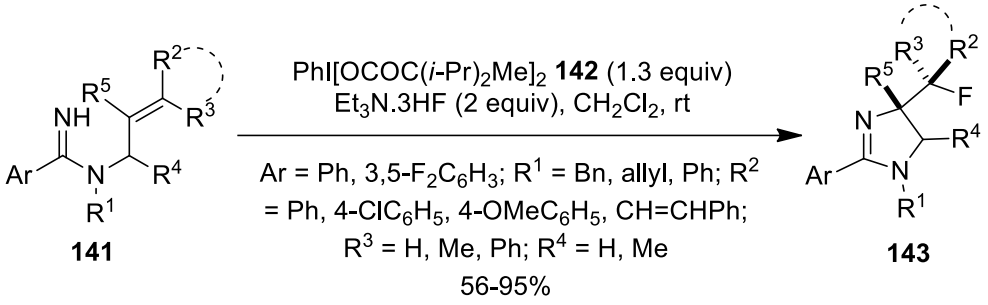
Later, a similar methodology was developed for the construction of heteroatom-containing pyrazolines **139** from β,γ-unsaturated tosyl hydrazones **136** using PIDA **6** as the sole oxidant (Scheme 34).[55] This cascade reaction proceeds through the generation of *N*-centered radical **140** from corresponding N-H bond, that undergoes sequential radical cyclization and sulfenylation/selenylation using disulfides/diselenides **72** as the S/Se-

nucleophiles to form desired product **139**. Aliphatic, aromatic and heteroaromatic disulfides/diselenides were well tolerated.



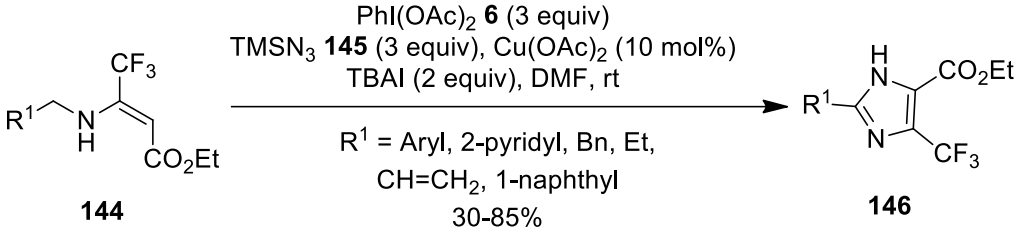
Scheme 34. PIDA-mediated synthesis of pyrazolines **139** using PIDA **6** as the sole oxidant.

In 2016, Chiba and co-workers reported iodine(III)-mediated intramolecular aminofluorination of *N*-allyl-amidines **141** using $Et_3N.3HF$ as the fluoride nucleophile (Scheme 35).[70] This reaction enabled *anti*-selective preparation of 4-fluoroalkyl-2-imidazolines **143** from a series of *di-*, *tri-* and *tetra*-substituted *E*- or *Z*-alkenes **141**. Moreover, synthesized 2-imidazoline moiety were subjected to reductive ring-opening to deliver 3-fluoropropane-1,2-diamines in significant yields.



Scheme 35. Synthesis of 4-fluoroalkyl-2-imidazolines **143** using $PhI[OCOC(i\text{-}Pr)_2Me]_2$ **142** as an oxidant.

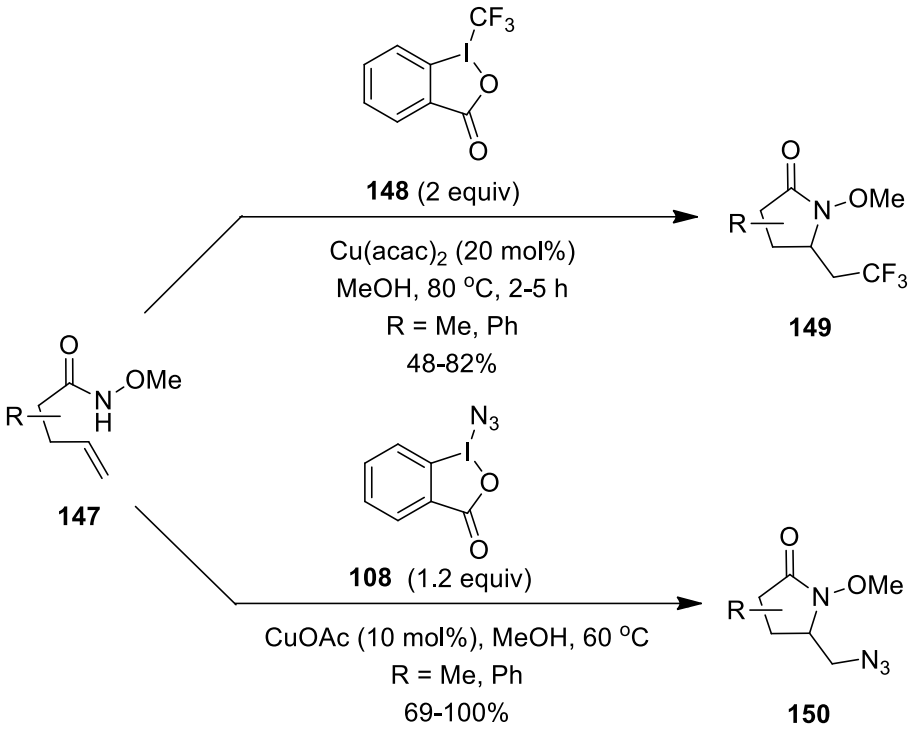
In the following year Yu's research group designed a domino azidation/C(sp^3)−H amination strategy for the transformation of *N*-alkyl enamines **144** into 2,4,5-trisubsituted imidazoles **146** by reacting with $TMSN_3$ **145** as an azide source in the presence of PIDA **6** under copper catalysis (Scheme 36).[71] Presence of tetrabutyl ammonium iodide (TBAI) was essential for obtaining higher yields.



Scheme 36. Synthesis of 2,4,5-trisubsituted imidazoles **146** using PIDA **6** as oxidant.

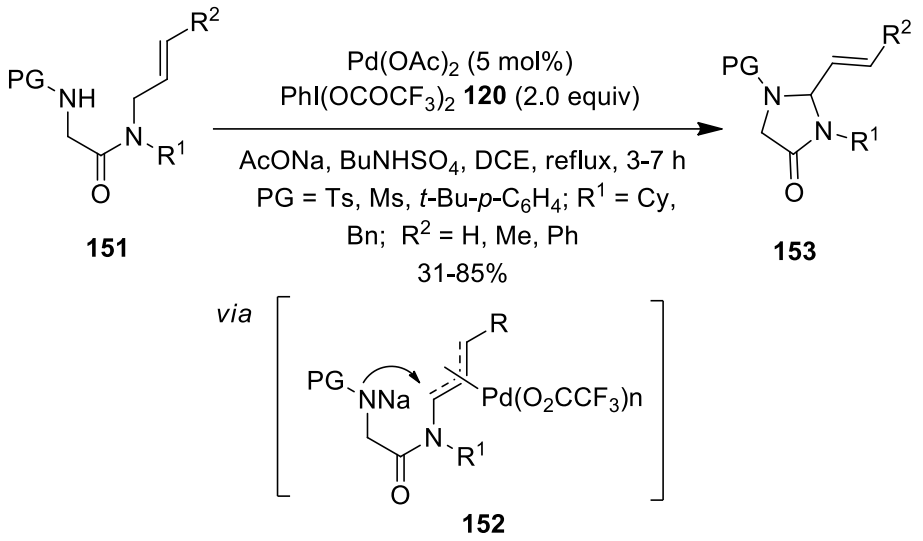
2.1.2.7. **Synthesis of lactam and imidazolidinones.** Shen and Wang reported the first example of the introduction of a CF_3-group onto the lactam ring **149** via Cu-catalyzed intramolecular aminotrifluoromethylation

of unsaturated amides **147** (Scheme 37).[72] A series of *N*-methoxyamides **147** smoothly underwent 5-*exo* cyclization followed by C–N bond formation by using Togni's reagent **148** to provide desired CF_3-containing γ-lactam **149** in 48–82% yields. Later, the same team demonstrated aminoazidation of several unactivated alkenes **147** by employing azidoiodinane **108** as an azide precursor.[73] This diamination reaction enabled the installation of two distinct amino groups onto the alkenes with excellent regio- and stereoselectivity.



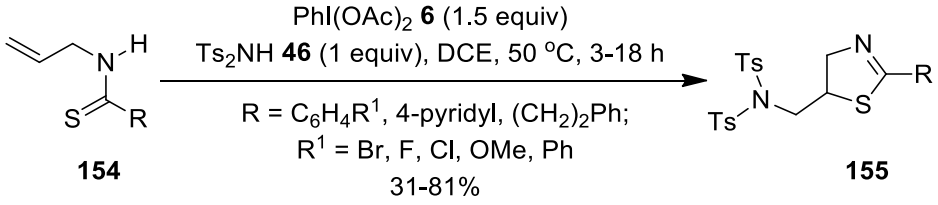
Scheme 37. Hypervalent iodine-mediated synthesis of lactams **149** and **150.**

Further, Borelli *et al*. employed PIFA **120** as an oxidant in the cyclization of allyl or crotyl *N*-sulfonyl-amides **151** to yield 2-propenylimidazolidinones **153** (Scheme 38).[74] The proposed reaction mechanism possibly involves oxidation of $Pd(OAc)_2$ by PIFA **120** to generate $Pd(O_2CCF_3)_4$ *in situ*, which initiates allylic C–H activation to form η^3-allylcomplex **152** and subsequent intramolecular cyclization gives cyclic product **153**.



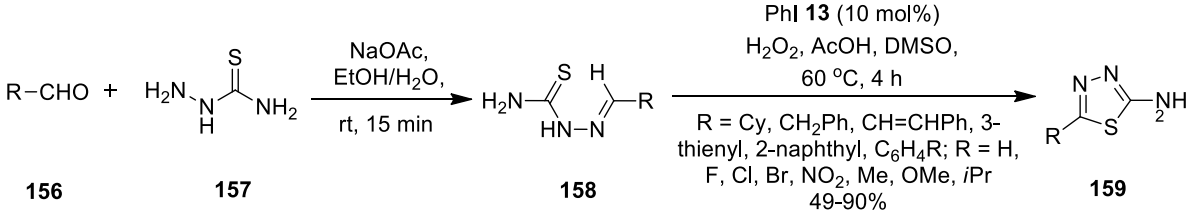
Scheme 38. Synthesis of 2-propenylimidazolidinones **153** using PIFA **120** as an oxidant.

2.1.2.8. Synthesis of thiazoles and thiadiazoles. An inter-/intra-molecular thioamination of *N*-allylthioamides **154** has been demonstrated by Hong and co-workers (Scheme 39). This reaction system featured the use of *bis*-tosylimide **46** as the nitrogen source and PIDA **6** as the oxidant to deliver 5-amino-thiazolines **155** via 5-*exo* cyclization in useful yields.[48]



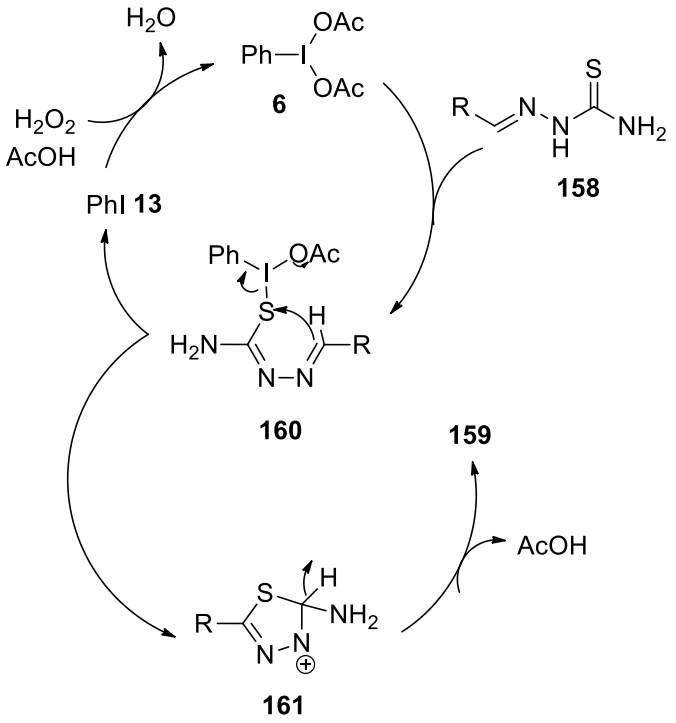
Scheme 39. PIDA-mediated synthesis of oxazolines **155** from *N*-allylthioamides **154.**

Further, Han *et al*. reported catalytic oxidative coupling of thiosemicarbazide **157** mediated by *in situ* generated PIDA **6** from PhI **13** in the presence of external oxidant H_2O_2 (Scheme 40).[75] This protocol provides an easy access to the biologically important 2-amino-1,3,4-thiadizoles **159** in moderate to high yields. Aromatic, heteroaromatic and alkyl aldehydes were well tolerated.



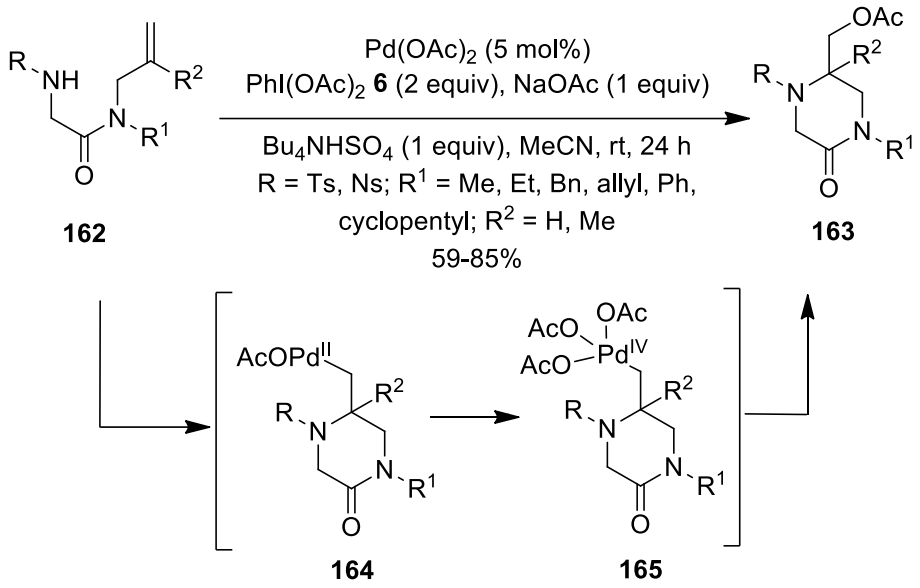
Scheme 40. Synthesis of 2-amino-1,3,4-thiadizoles **159** using iodobenzene **13** as precatalyst.

A plausible mechanism for the synthesis of 2-amino-1,3,4-thiadizoles **159** is depicted in scheme 41. Initially, H_2O_2 oxidizes PhI **13** to generate $PhI(OAc)_2$ **6** *in situ*, which reacts with **158** to give intermediate **160**. Cationic species **161** formed through intramolecular cyclization of intermediate **160**, losses hydrogen ions to deliver desired product **159**.



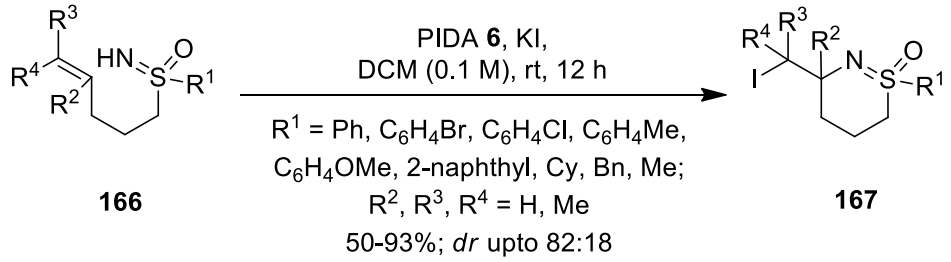
Scheme 41. The proposed mechanism for the synthesis of 2-amino-1,3,4-thiadizoles **159** using iodobenzene **13** as precatalyst.

2.1.3. Synthesis of six/seven-membered heterocycles. In 2015, Broggini *et al*. performed Pd(II)-catalyzed inter-intramolecular aminoacetoxylation of glycine allylamides **162** to prepare 5-acetoxymethyl-substituted piperazinones **163** employing $PhI(OAc)_2$ **6** as the oxidizing agent (Scheme 42).[76] Reaction initiates with the formation of σ-alkyl Pd-complex **164** through Pd(II)-mediated aminopalladation process, which is further oxidized to alkyl-Pd(IV) intermediate **165** by $PhI(OAc)_2$ **6**. Finally, intermediate **165** undergoes reductive elimination via C–O bond formation to yield desired product **163** with the regeneration of catalyst.



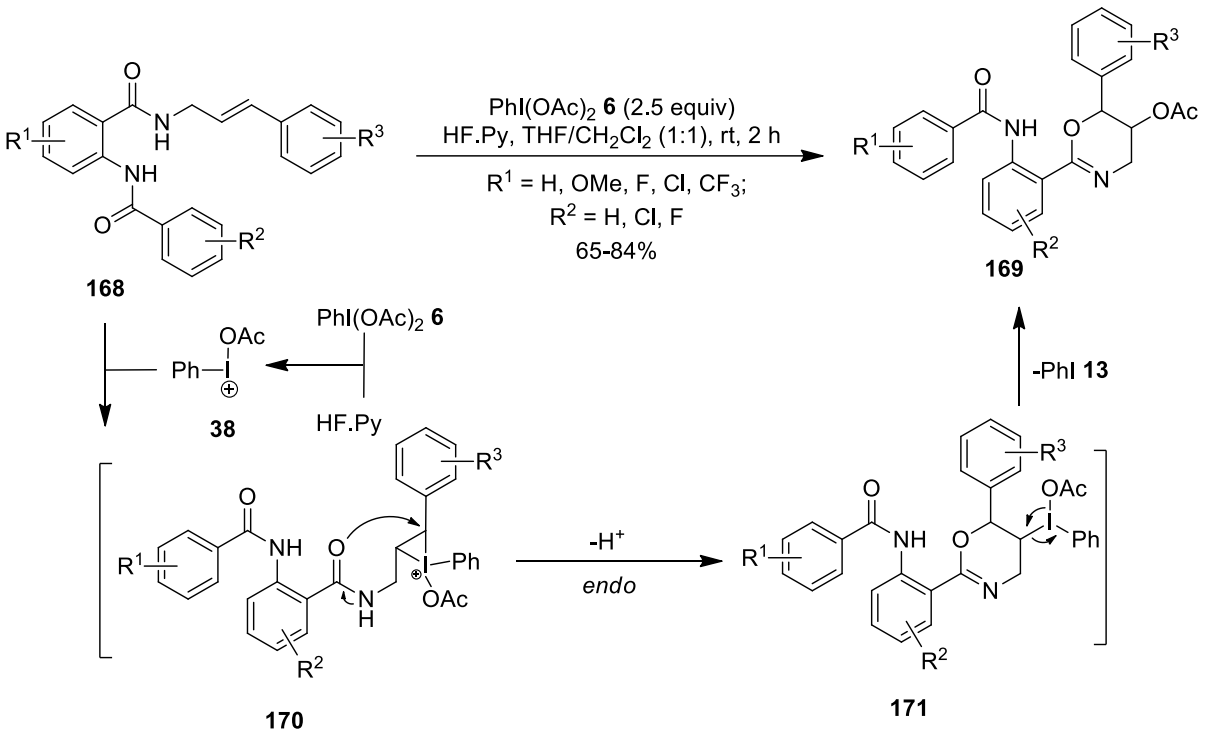
Scheme 42. Synthesis of 5-acetoxymethyl-substituted piperazinones **163** using $PhI(OAc)_2$ **6** as an oxidant.

An elegant method featuring PIDA-mediated halocyclization of *S*-alkenylsulfoximines **166** was developed by Bolm's research group (Scheme 43).[77] Among the various iodine sources screened, potassium iodide provided the best result. The present intramolecular iodoamination process enabled synthesis of tetrahydro-1,2-thiazine-1-oxides **167** in variable yields with remarkable regioselectivities and diastereoselectivities. However, substrates with tri-substituted double bonds were unsuitable for this cyclization reaction. Additionally, preparation of dihydro isothiazoles was achieved in 69–90% yields with high *dr* (71:29−80:20) under identical conditions.



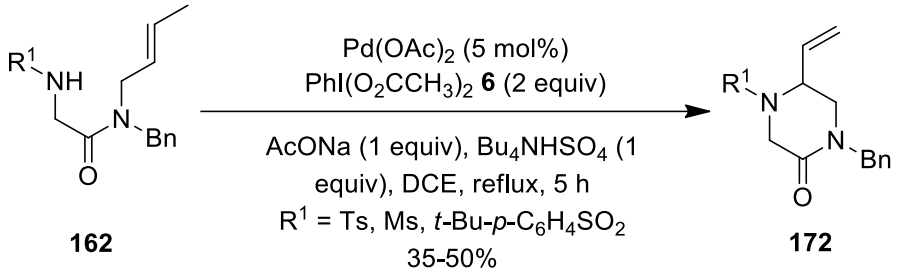
Scheme 43. Synthesis of tetrahydro-1,2-thiazine-1-oxides **167** using oxidant PIDA **6.**

In 2016, an intramolecular cyclization of *N*-(*E*)-alkenylamides **168** to the corresponding 6-aryl-5-acetoxy-2-oxazines **169** induced by PIDA **6** was described by Ranjith *et al.* (Scheme 44).[44] In the proposed mechanism, aryliodinium ion **38** formed from PIDA **6** and HF·py interacts with the alkene **168** and generates cyclic iodonium ion **170** which is attacked by the amide moiety to give alkyl iodane **171**. Notably, the presence of aryl group at the end of the alkene stabilizes the incipient carbocation thereby facilitating *endo*-cyclization of intermediate **171**. Finally, nucleophilic attack by the acetyl group via S_N2-like bimolecular reductive elimination furnishes desired oxazine **169** and releases PhI **13**.



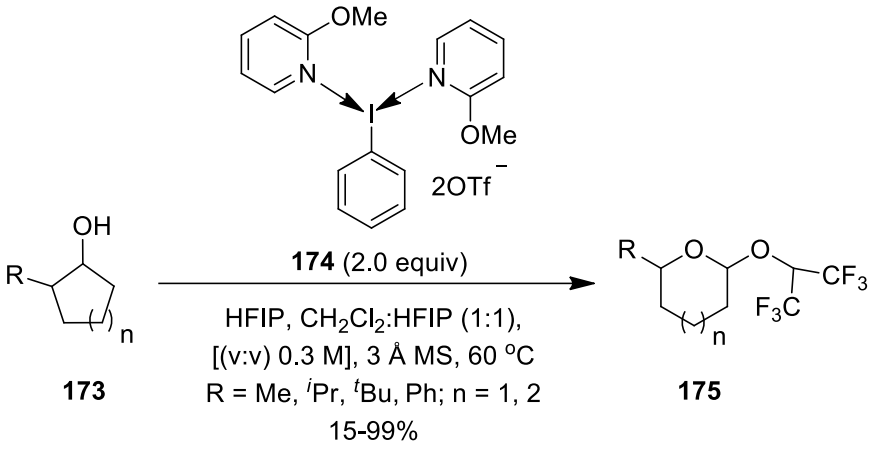
Scheme 44. Synthesis of 6-aryl-5-acetoxy-2-oxazines **169** using PIDA **6** as an oxidant.

Later, Borelli *et al.* reported Pd-catalyzed intramolecular cyclization of *N*-sulfonyl-*N*''-crotyl-benzylamides **162** via aminopalladation/dehydropalladation process using terminal oxidant $PhI(O_2CCH_3)_2$ **6** (Scheme 45).[74] The reaction was carried out in the presence of AcONa and Bu_4NHSO_4 in DCE under refluxing conditions. The expected product vinyl piperazinones **172** were obtained in moderate yields.



Scheme 45. Synthesis of vinyl piperazinones **172** using PIDA **6** as an oxidant.

Wengryniuk's research group prepared six or seven membered cyclic ethers **175** by employing (poly)cationic λ^3-iodane (*N*-HVI) **174** as electrophilic reagent for the activation of secondary alcohols **173** (Scheme 46).[78] Presence of *N*-HVI **174** was crucial for the excellent selectivity achieved for C–O bond migration over direct oxidation via α-elimination pathways. Additionally, ring expansion strategy was successfully applied in the late-stage derivatization of several natural products. Further synthesized HFIP-acetals could be easily derivatized with different nucleophiles, providing scope for subsequent manipulations.

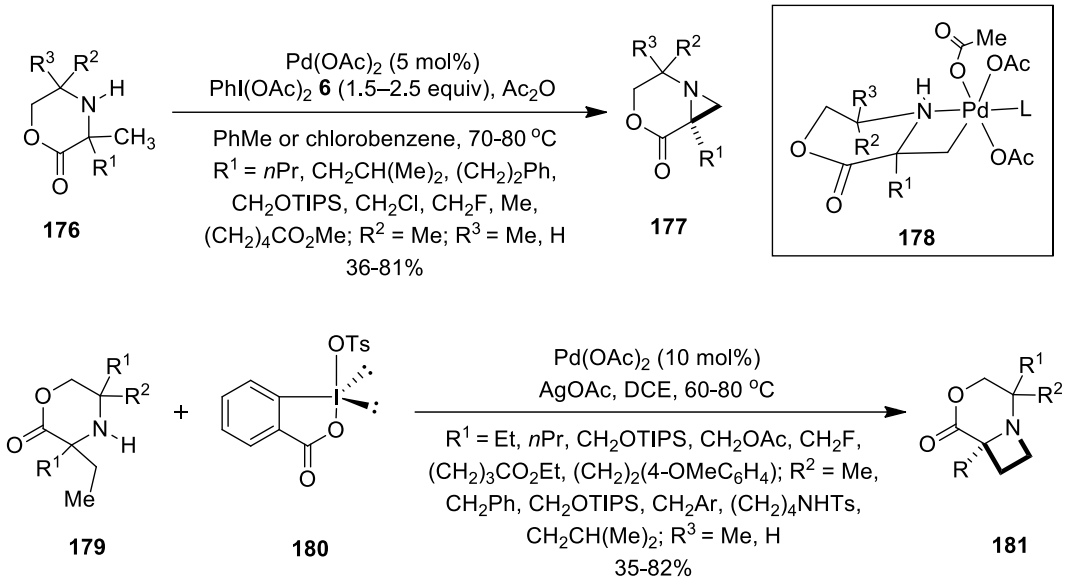


Scheme 46. Synthesis of six or seven membered cyclic ethers **175** using (poly)cationic λ^3-iodanes **174.**

2.1. Synthesis of bicyclic heterocycles

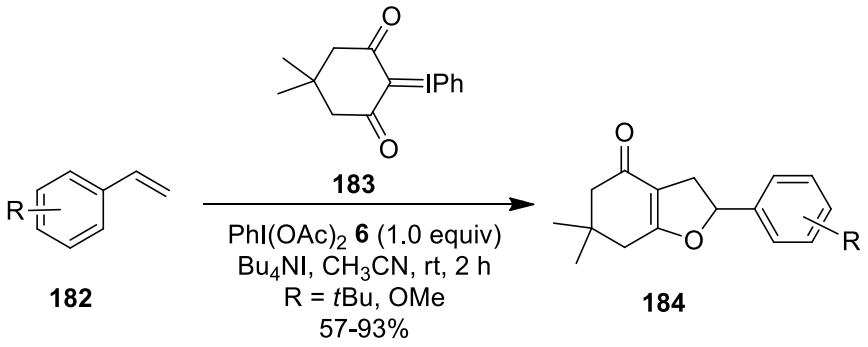
In recent years, various intra- and inter-molecular approaches have been developed for the preparation of bicyclic heterocycles. Most of these reactions require stoichiometric hypervalent iodine reagents as oxidants while few employ chiral/achiral aryl iodides as precatalysts. In this section, all hypervalent-mediated or catalysed reactions for the construction of bicyclic heterocycles will be discussed.

The group of Gaunt has designed a novel C–H activation strategy for the transformation of aliphatic secondary amines **176** possessing adjacent methyl group into the corresponding bicyclic heterocycles **177** using $Pd(OAc)_2$/$PhI(OAc)_2$ **6** catalytic system (Scheme 47).[79] This C–H aziridination process proceeds via Pd(IV) intermediate **178** which upon subsequent C–N bond reductive elimination delivers aziridines **177**. In continuation, the same team prepared azetidines **181** via Pd-catalyzed intramolecular γ-C–H amination of substituted morpholinones **179** containing α-ethyl group.[80] Presence of the oxidant benziodoxole tosylate **180** with additive AgOAc played a crucial role in controlling selective C–N reductive elimination pathway leading to azetidines **181**. The present protocol tolerated range of substituents, including enantio-enriched substrates which yield chiral azetidines **181** with excellent diastereoselectivity. Interestingly, substrates **179** possessing C–H bond at the α-position to the amine were well tolerated, unlike in the previous developed protocol.[79]



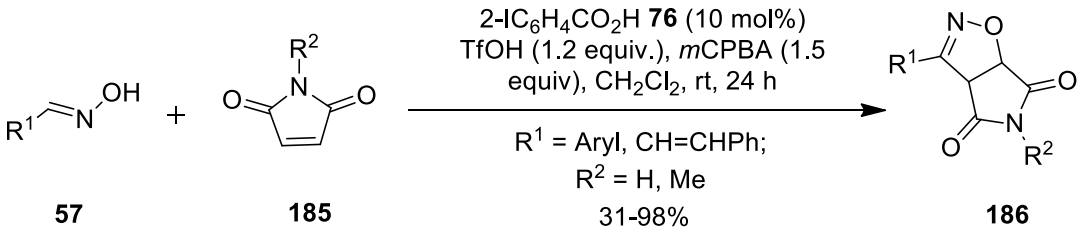
Scheme 47. Synthesis of fused aziridines **177** and azetidines **181** via C–H activation strategy.

Murphy's group reported preparation of dihydrofurans **184** by reacting electron-rich styrenes **182** with cyclic iodonium ylides **183** (Scheme 48).[81] The reaction was mediated by $PhI(OAc)_2$ **6** in the presence of Bu_4NI as an iodine source. Though only few examples were reported, the present method provided bicyclic products **184** in significant yields.



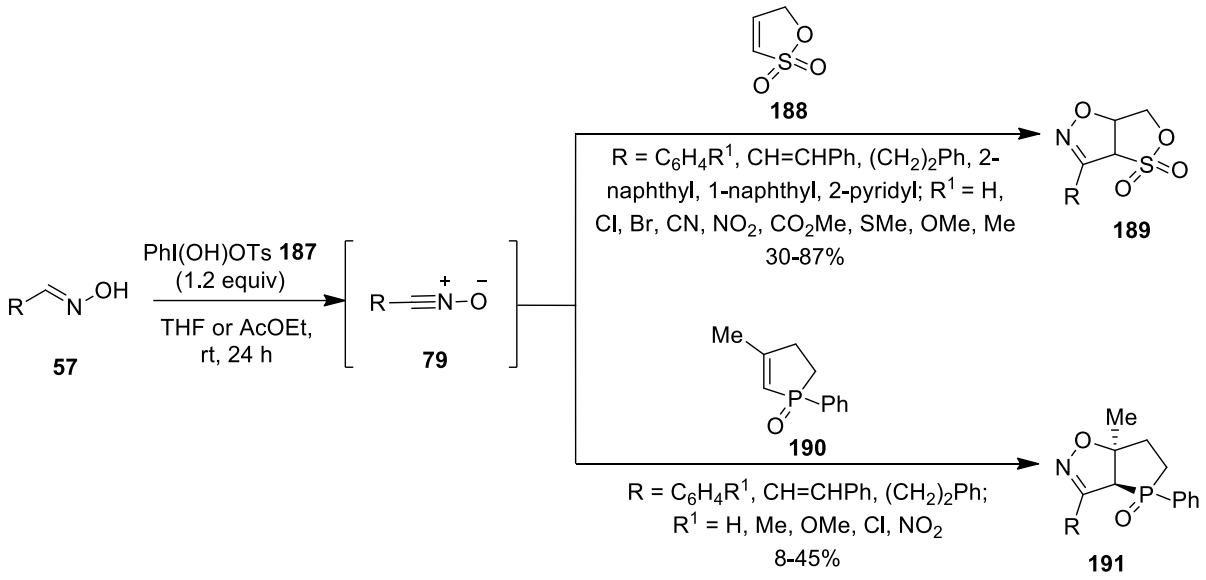
Scheme 48. Synthesis of dihydrofurans **184** by reacting iodonium ylides **183** with styrenes **182.**

An efficient catalytic protocol featuring hypervalent iodine(III)-induced oxidative cycloaddition of various aldoximes **57** with maleimides **185** to prepare pyrrolo-isoxazolines **186** was described by Yoshimura *et al*. (Scheme 49).[82] This cyclization reaction involves *in situ* generation of hydroxy(aryl)iodonium species (IBA-OTf) **75** from corresponding 2-iodobenzoic acid **76** in the presence of *m*CPBA and TfOH. The proposed mechanism is similar to that discussed in Scheme 19 wherein oxidation of aldoximes generates nitrile oxide which later undergoes cycloaddition with **185** to deliver product **186**.



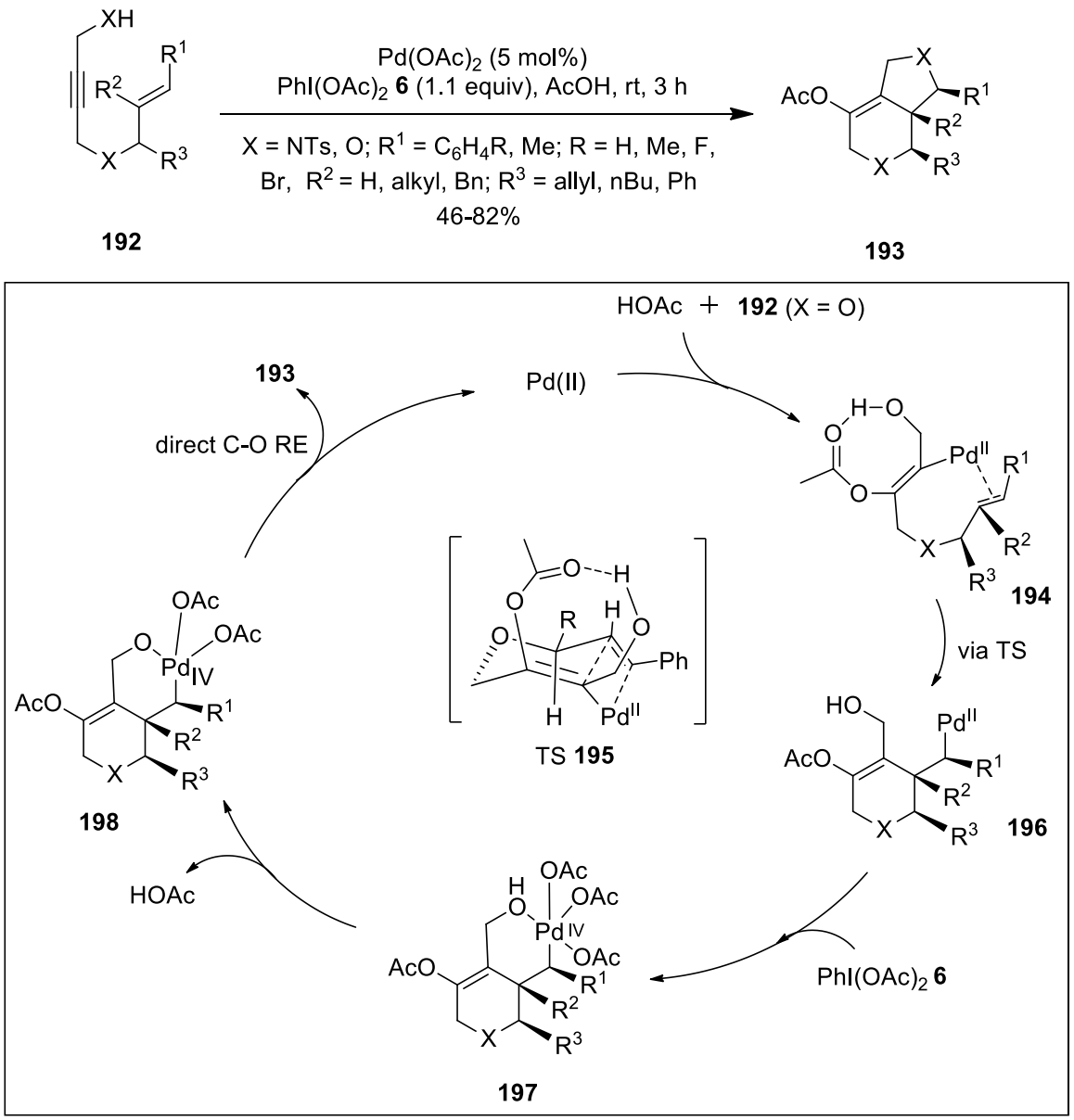
Scheme 49. Synthesis of pyrrolo-isoxazolines **186** using precatalyst 2-iodobenzoic acid **76.**

Later, the same group reported oxidative heterocyclization of aldoximes **57** with 1-propene-1,3-sultone **188** mediated by Koser's reagent **187** furnishing isoxazoline-ring-fused heterobicyclic products **189** (Scheme 50).[83] Furthermore, reaction of aldoximes **57** with 3-methyl-1-phenyl-2-phospholene-1-oxide **190** enabled synthesis of isoxazoline-fused phospholene oxides **191** under identical conditions. The proposed mechanism involves Koser's reagent-induced oxidation of aldoximes **57** to generate nitrile oxides **79** *in situ*, which undergoes subsequent intermolecular 1,3-dipolar cycloaddition with heterocyclic alkenes to deliver respective heterobicyclic products.



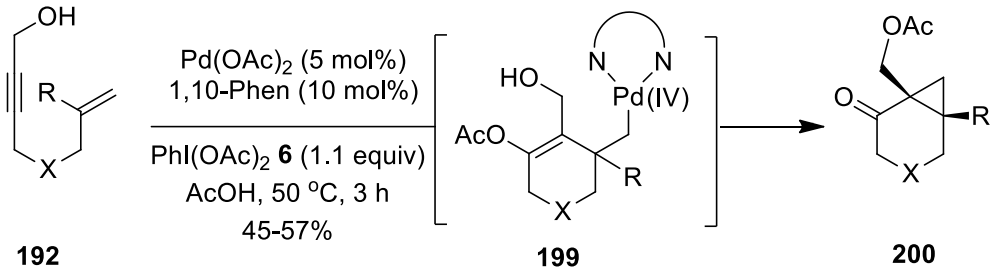
Scheme 50. Synthesis of heterobicyclic products **189** and **191** using Koser's reagent **187** as an oxidant.

In 2019, Tong's group performed a PIDA-induced intramolecular acetoxylative (3 + 2) cycloaddition of 1,6-enynes **192** in a 6-exo manner via Pd(II)−Pd(IV) catalysis.[84] This cyclization reaction afforded bicyclic heterocycles **193** in variable yields (Scheme 51). The proposed mechanism begins with the formation of alkenyl-Pd(II) intermediate **194** via alkyne acetoxypalladation process, following which alkene insertion occurs to form alkyl-Pd(II) intermediate **196** through chair-like transition state **195**. Further **196** is oxidized to bicyclic Pd(IV) intermediate **197** using oxidant $PhI(OAc)_2$ **6**, which gives cyclometalated alkoxyPd(IV)-alkyl intermediate **198** with the loss of AcOH. Finally, direct C−O reductive elimination of **198** delivers product **193** and regenerate palladium catalyst.



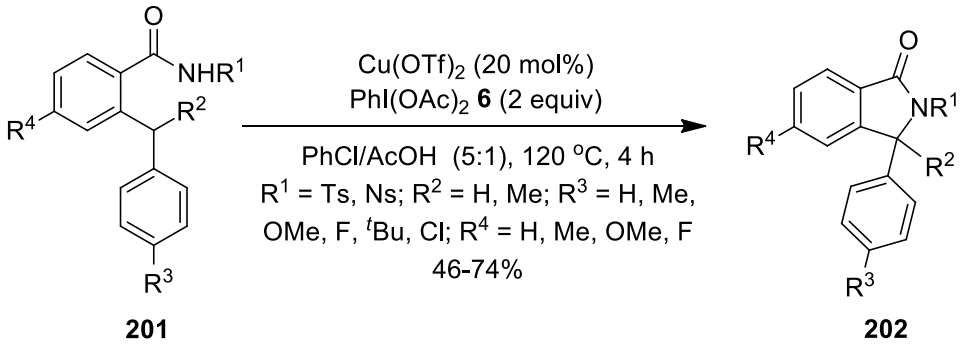
Scheme 51. Synthesis of bicyclic heterocycles **193** using oxidant $PhI(OAc)_2$ **6.**

Further, when the ligand 1,10-phenanthroline was introduced, 1,6-enynes **192** were converted into 3-bicyclo[4.1.0]-heptan-5-one products **200** *via* ligated Pd(IV) intermediate **199** (Scheme 52).[84] The presence of the additional coordinating ligand for Pd(IV) obstruct the direct C−O bond reductive elimination and promotes reaction *via* a S_N2-type C−C reductive elimination pathway.



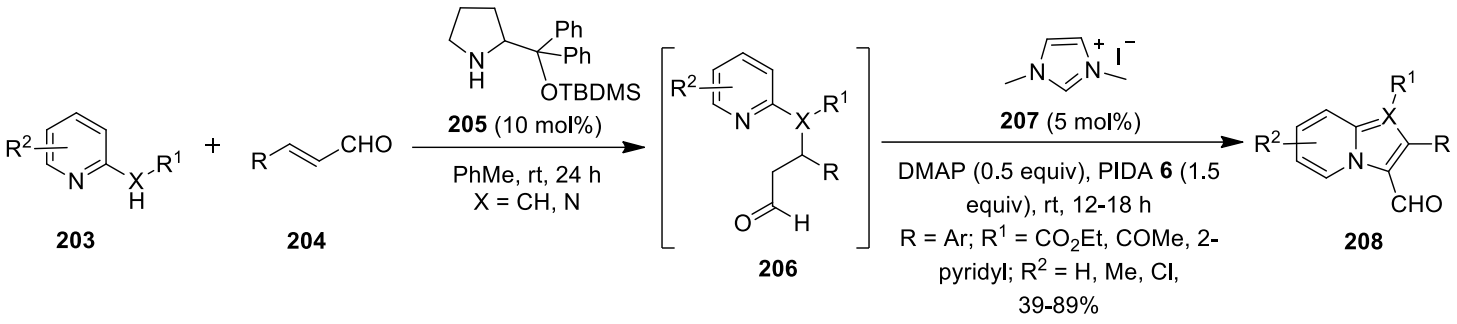
Scheme 52. Synthesis of 3-bicyclo[4.1.0]-heptan-5-one products **200** using oxidant $PhI(OAc)_2$ **6.**

The synthesis of benzo-fused heterocycles has been well studied using different hypervalent iodine reagents. Further in this section, we will be discussing the synthesis of variety of heterocyclic compounds in which benzene ring is fused with five-, six- and seven-membered heterocycles in briefly. In 2017, Bedford *et al.* performed intramolecular benzylic C–H sulfamidation of 2-benzyl-*N*-sulfonylbenzamide substrates **201** catalysed by $Cu(OTf)_2$ in the presence of PIDA **6** as the terminal oxidant (Scheme 53).[85] The present method leads to the synthesis of *N*-arylsulfonyl-1-arylisoindolinones **202** in useful yields. Interestingly, sulfonamide moiety behaves as directing group as well as functionalizing reagent in this reaction. Further samarium iodide-mediated deprotection of **202** provides valuable free 1-arylisoindolinone.



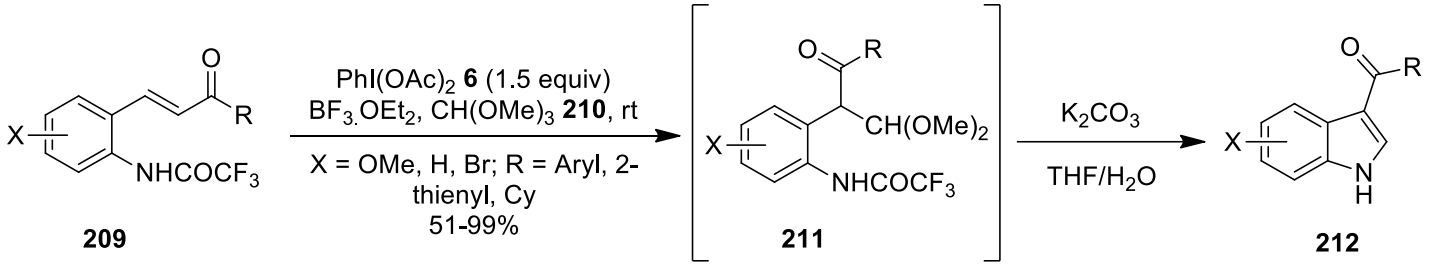
Scheme 53. Synthesis of *N*-arylsulfonyl-1-arylisoindolinones **202** using PIDA **6** as the terminal oxidant.

In the same year, an elegant catalytic strategy to prepare biologically important scaffolds indolizines **208** (X = C) and imidazopyridines **208** (X = N) was developed by Wang and co-workers (Scheme 54).[86] This transformation took place via Michael addition-[3 + 2] annulation of 2-substitued azaarenes **203** and α,β-unsaturated aldehydes **204**. The reactions are promoted by amine catalyst **205** and *N*-heterocyclic carbene (NHC) **207** relay catalysis in the presence of oxidant PIDA **6** and base DMAP. Notably, preformation of the Michael adduct **206** from **203** and **204** was necessary which could be used without further purification. Furthermore, preparative power of this method was demonstrated for synthesizing an anxiolytic drug, Saripidem in 45% yield.



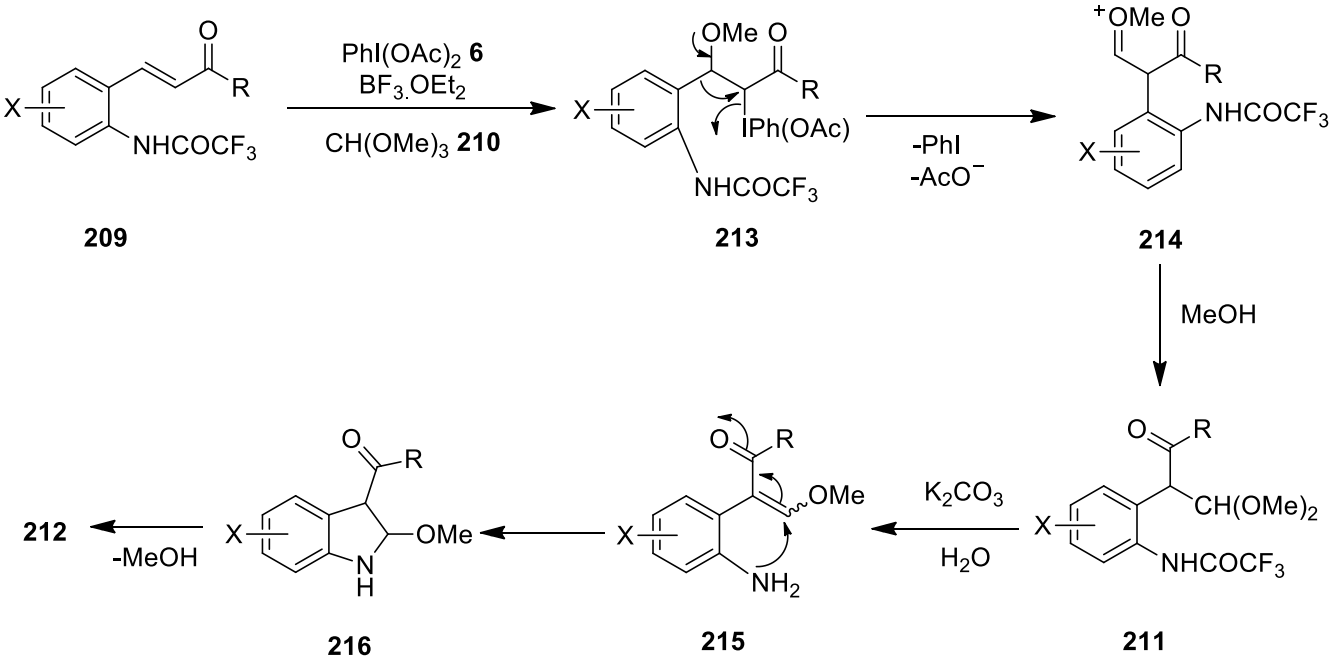
Scheme 54. Synthesis of indolizines and imidazopyridines **208** using PIDA **6** as an oxidant.

Later, Miki's research team described a concise route to access 3-acylindole derivatives **212** by performing PIDA-mediated oxidative rearrangement of 2-aminochalcones **209** to form acetal intermediate **211** (Scheme 55).[87] Subsequent treatment with K_2CO_3 at room temperature resulted in 3-acylindoles **212** via intramolecular cyclization process. Chalcones **209** bearing substituted phenyl, thiophene and alkyl groups were well tolerated. Furthermore, scope of this method was extended towards the rapid synthesis of SCB01A, currently evaluated as a potential anticancer drug.



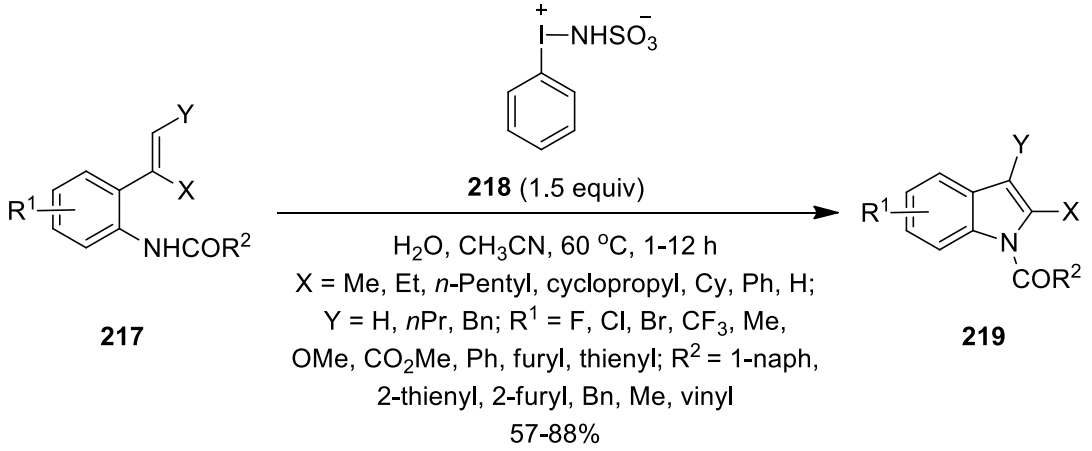
Scheme 55. PIDA-mediated synthesis of 3-acylindoles **212.**

The proposed mechanism for the synthesis of 3-acylindoles **212** is depicted in scheme 56. Reaction begins with the electrophilic addition of PIDA **6** to the double bond alkene **209** mediated by $BF_3 \cdot OEt_2$ and MeOH to form adduct **213**. Subsequent oxidative rearrangement assisted by the lone pair of oxygen causes aryl group migration to yield oxonium intermediate **214**, which could be converted into corresponding acetal **211** in the presence of methanol. Further, deprotection of N-$COCF_3$ group and elimination of methoxy group under basic conditions furnishes intermediate **215** which then undergo subsequent cyclization and aromatization to deliver anticipated product **212**.



Scheme 56. The proposed mechanism for the PIDA-mediated synthesis of 3-acylindoles **212.**

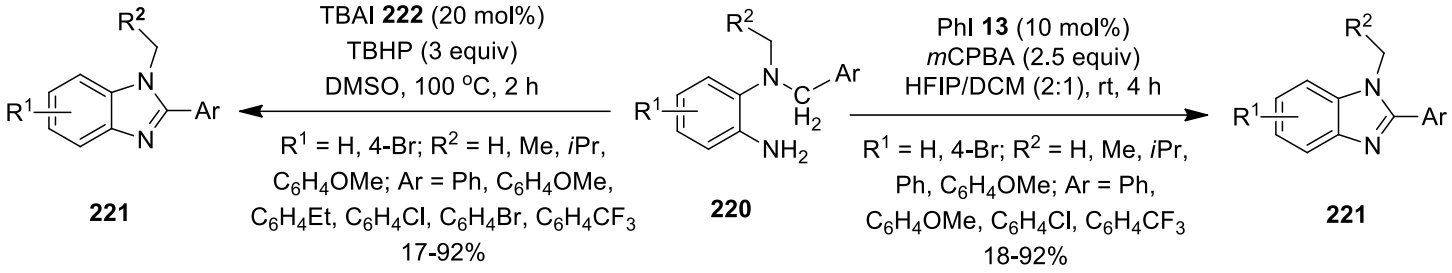
In 2018, Xia *et al.* synthesized a new water-soluble and highly acidic hypervalent iodine(III) reagent, (phenyliodonio)sulfamate (PISA) **218** by reacting $PhI(OAc)_2$ **6** with NH_2SO_3H in MeCN at room temperature.[88] Using PISA, synthesis of various substituted indoles **219** from 2-alkenylanilines **217** involving aryl migration/intramolecular C–H cyclization cascade process was demonstrated successfully (Scheme 57). PISA **218** behaves as both oxidant and lewis acid in this reaction. Further developed methodology has been utilized for the synthesis of the bioactive molecule Pravadoline and anti-inflammatory drug molecules such as Indometacin and Zidometacin.



Scheme 57. Synthesis of indoles **219** using (phenyliodonio)sulfamate **218** as an oxidant.

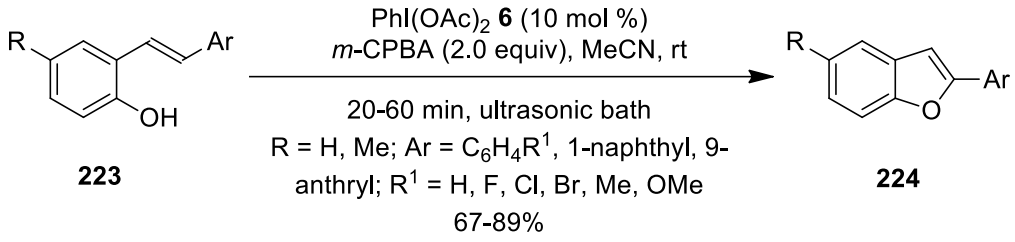
Further for the synthesis of 1,2-disubstituted benzimidazoles **221**, an intramolecular benzylic C(sp^3)–H imination strategy involving 4-H elimination was designed by Mal's research group.[89] This method enabled selective functionalization of two aliphatic-C(sp^3)H and two aryl-N(sp^3)H at 1,5 position facilitated by *in situ*

generated hypervalent iodine(III) species from PhI-*m*CPBA catalytic system (Scheme 58). Later, the same group developed another catalytic route employing precatalyst tetrabutylammonium iodide **222** in combination with *t*-BuOOH in DMSO as relatively inexpensive replacement for the previously designed PhI-*m*CPBA-HFIP system.[90] Symmetrical dibenzylamines **220** gave single isomer of benzimidazoles while unsymmetrical ones yielded mixture of isomers of imination product under both catalytic conditions.



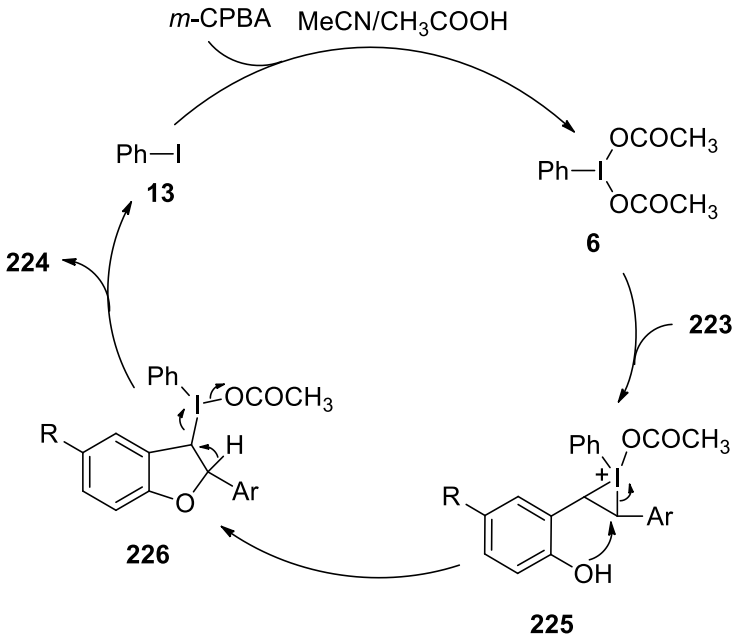
Scheme 58. Iodine(III)-catalyzed synthesis of 1,2-disubstituted benzimidazoles **221.**

Furthermore, Singh and Mangaonkar demonstrated an efficient method for the oxidative cyclization of 2-hydroxystilbenes **223** using $PhI(OAc)_2$ **6** as the catalyst and *m*-CPBA as the oxidant (Scheme 59).[91] This metal-free route gave access to a variety of functionally diverse 2-arylbenzofurans **224** at room temperature. Reaction time was reduced by performing the reaction under ultrasound-irradiation conditions and desired products were obtained in high yields. Very recently, the same group prepared 2-arylbenzofurans **224** by employing PhI **13** (10 mol %) as precatalyst in the presence of terminal oxidant *m*-CPBA and additive trifluoroacetic acid in $CHCl_3$.[92]



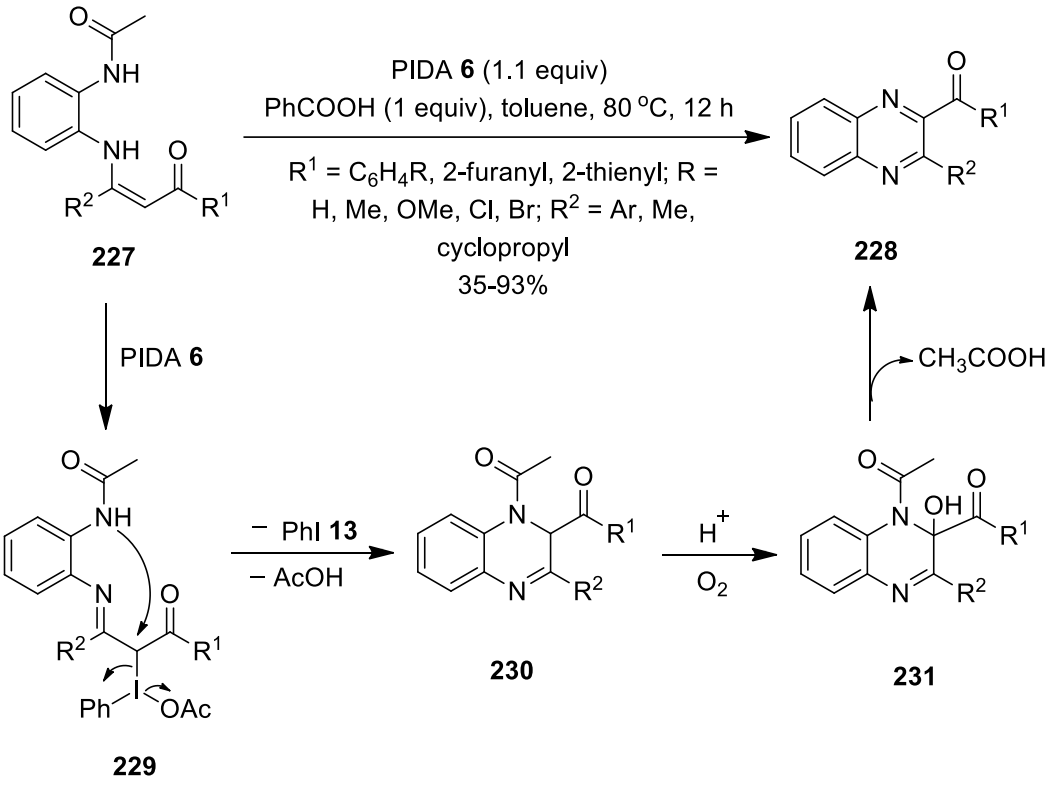
Scheme 59. Synthesis of 2-arylbenzofurans **224** using PIDA **6** as the catalyst.

A plausible catalytic cycle for this cyclization reaction initiates with the activation of double bond of **223** by PIDA **6** to form three-membered iodonium intermediate **225**.[91] Intramolecular cyclization of **225** gives intermediate **226**, which upon reductive elimination yields anticipated product **224** with the release of PhI **13**. Further PhI **13** could be reoxidized to active iodine(III) species **6** in the presence of *m*CPBA and acetic acid (Scheme 60).



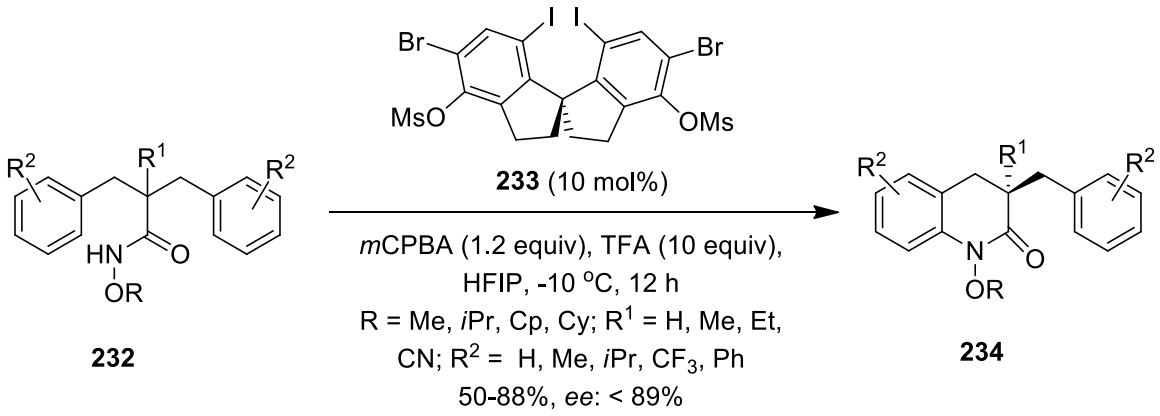
Scheme 60. The proposed catalytic cycle for the synthesis of 2-arylbenzofurans **224** using catalytic PIDA **6.**

In 2019, Cui's research group developed an expedient strategy to prepare quinoxalines **228** from *N*-(2-acetaminophenyl)enaminones **227** via hypervalent iodine(III)-induced intramolecular oxidative C–N bond forming tandem process (Scheme 61).[93] Inspection of various substrates revealed that electron-rich substrates gave desirable product yields while electron-deficient ones provided relatively lower yields. The proposed mechanism initiates with the reaction of **227** with PIDA **6** that generates α-iodo iminoketone **229**, which undergoes intramolecular condensation cyclization to afford **230** with the release of PhI **13** and AcOH. Finally, oxidation of **230** in the presence of oxygen forms **231**, which gives final product **228** with the elimination of CH_3COOH. Previously, Zheng and co-workers had constructed quinoxaline scaffolds through $PhI(OAc)_2$-mediated cascade cycloamination of *N*-aryl ketimines by employing sodium azide as the nitrogen source under copper catalysis.[94]



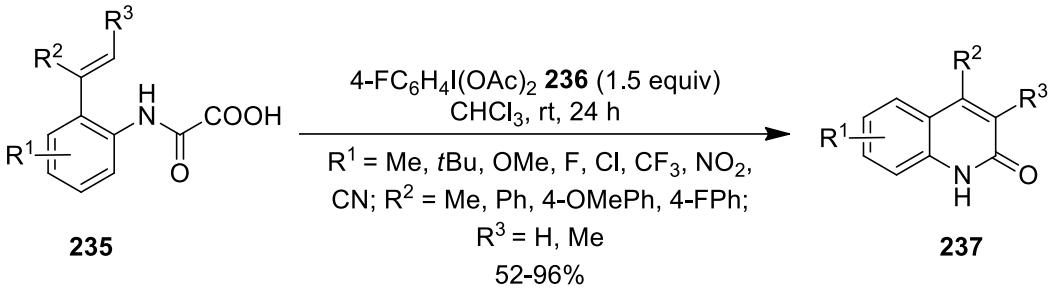
Scheme 61. Synthesis of quinoxalines **228** using PIDA **6** as the oxidant.

Meanwhile, Cai's research group described asymmetric intramolecular C−N bond forming reaction of substituted amides **232** via catalytic desymmetrization process (Scheme 62).[95] This reaction was promoted by *in situ* generated chiral hypervalent iodine(III) species from diiodospirobiindane derivative **233** in the presence of *m*CPBA. Addition of TFA as acid promoter and HFIP as solvent media provided the best result. The desired lactams **234** were obtained in decent yields with enantiomeric excess up to 89%. Notably, cyclopentoxy substituent on the nitrogen of amide gave products with better enantioselectivity than with other alkoxy substituents.



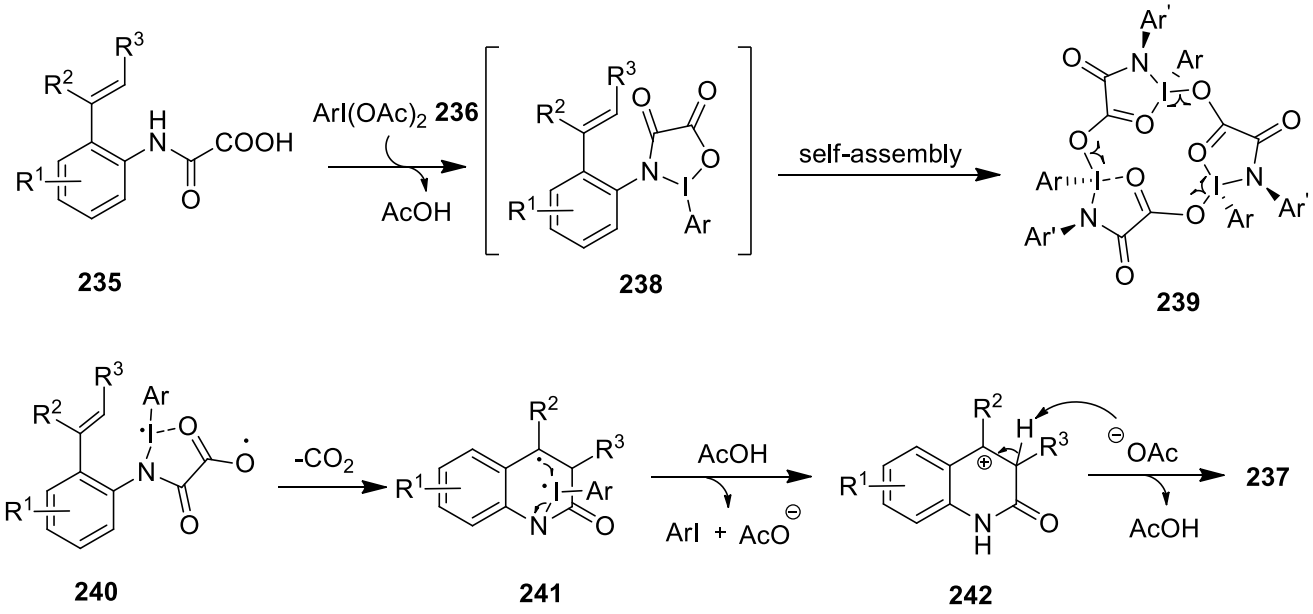
Scheme 62. Synthesis of *N*-alkoxy-lactams **234** using **233** as precatalyst.

Wang and co-workers employed hypervalent iodine(III) reagent **236** as an efficient oxidant for the intramolecular decarboxylative Heck-type reaction of readily accessible 2-vinyl-phenyl oxamic acids **235** (Scheme 63).[96] This operationally simple lactamization method enabled preparation of various 2-quinolinones **237** in variable yields with excellent chemoselectivity.



Scheme 63. Synthesis of 2-quinolinones **237** using 4-$FC_6H_4I(OAc)_2$ **236** as the oxidant.

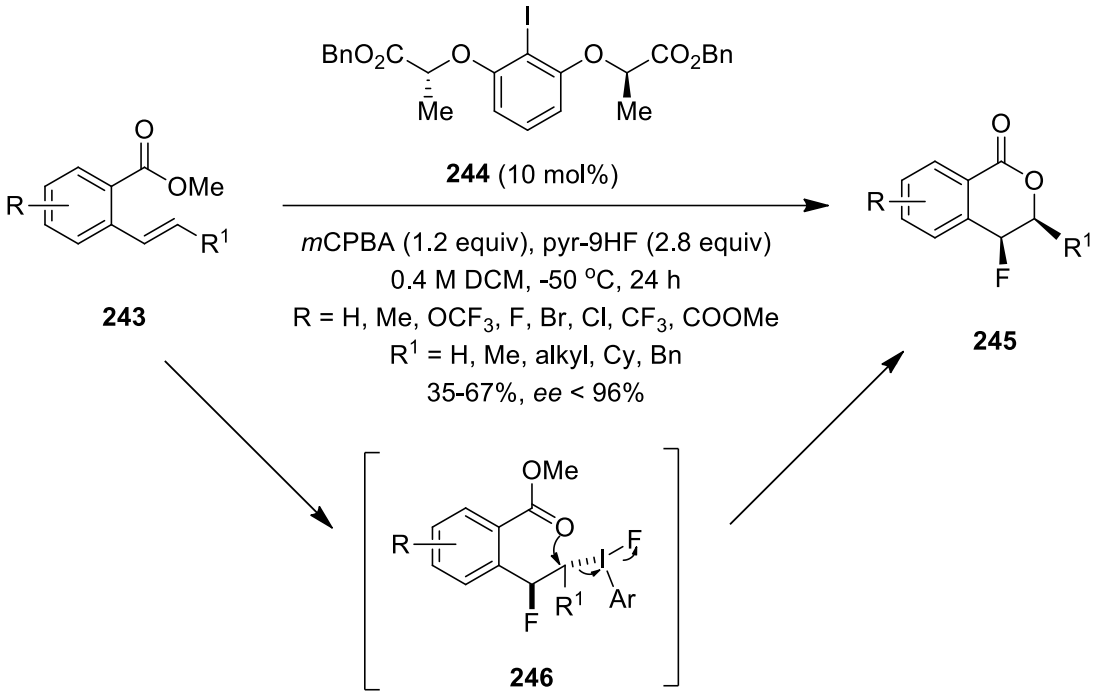
A plausible mechanism is elucidated in scheme 64. Initially, substrates **235** reacts with hypervalent iodine(III) reagent **236** giving cyclic iodine(III) monomer **238** which subsequently self-assembles to form macrocyclic trimer **239**. The diradical intermediate **240** generated through ring-strain-induced homolysis of iodine−oxygen bond, undergoes decarboxylation and radical addition to the alkene to give intermediate **241**. Next, intermediate **241** upon intramolecular aryliodine radical-mediated oxidation gives benzylic cation intermediate **242** with loss of ArI (4-FC_6H_4I). Finally, E1 elimination of **242** delivers desired product **237**.[96]



Scheme 64. Plausible mechanism of synthesis of 2-quinolinones **237** using 4-$FC_6H_4I(OAc)_2$ **236** as the oxidant.

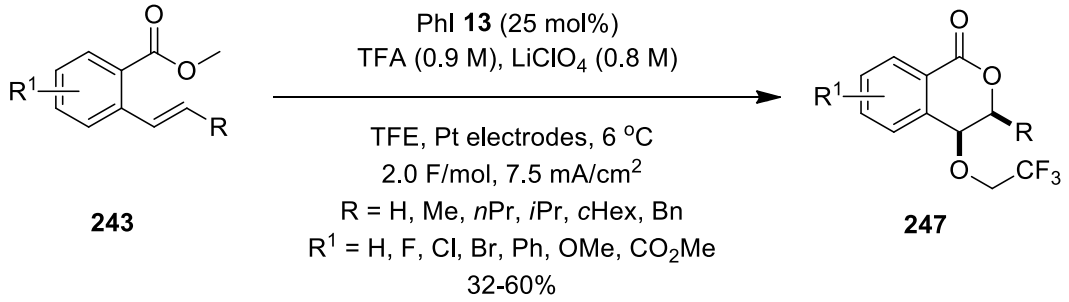
Jacobsen and coworkers developed a catalytic route to prepare 4-fluoroisochromanones **245** through enantioselective fluorolactonization of vinyl benzoates **243** using chiral aryl iodide **244** as precatalyst (Scheme 65).[97] Reaction employs HF-pyridine as a nucleophilic fluorinating reagents and *m*CPBA as the terminal oxidant. This nucleophilic fluorination protocol enabled introduction of fluorine-containing stereogenic center, which

constitute a frontier endeavor in organic synthesis. Moreover, reaction products are formed in the *syn* configuration as determined by X-ray crystallographic analysis. Reaction possibly occurs through intermediate **246**, wherein anchimeric assistance of carboxylate group lead to the displacement of aryliodo group giving desired products.



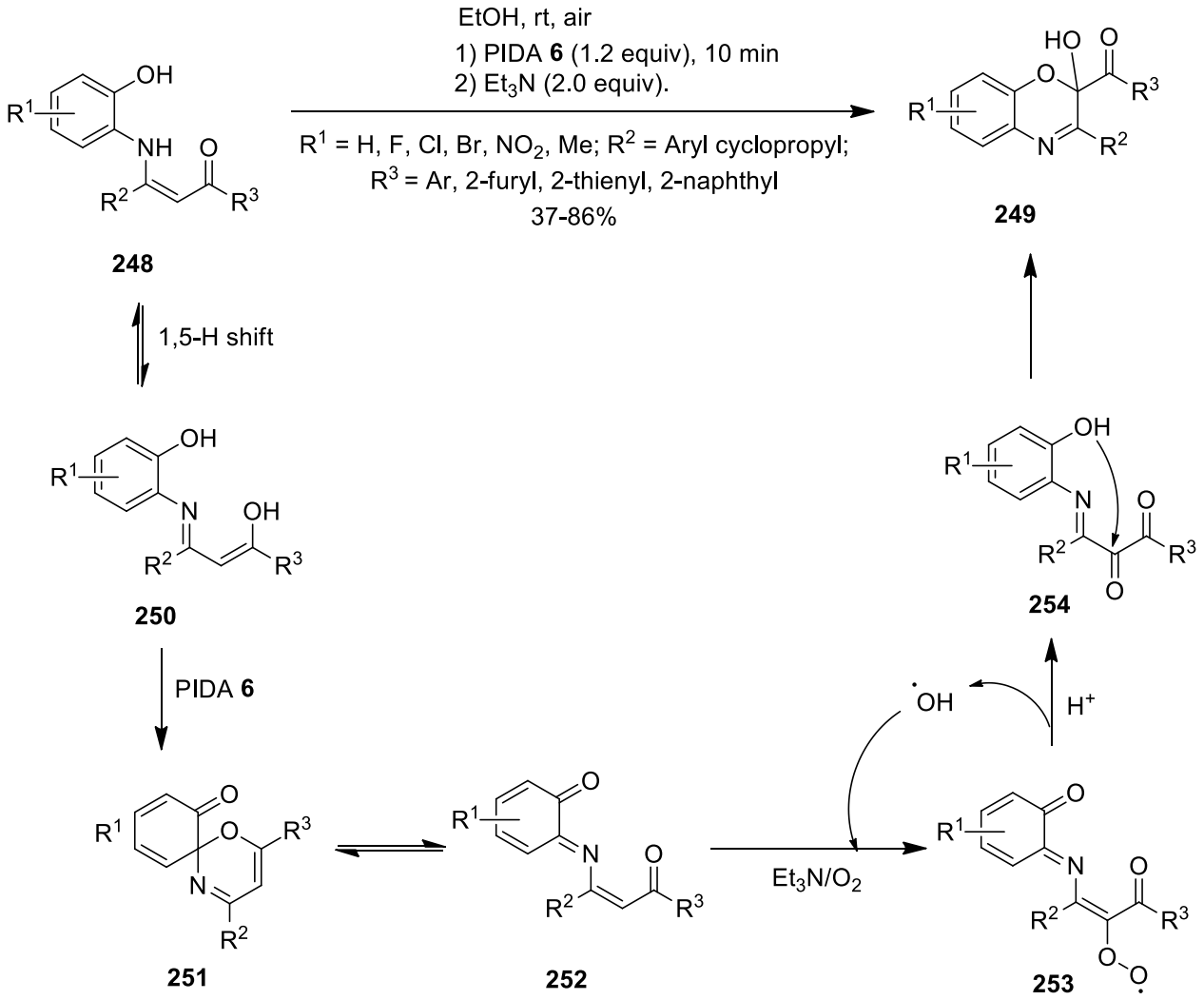
Scheme 65. Enantioselective synthesis of 4-fluoroisochromanones **245** using chiral aryl iodide **244** as catalyst.

Later, Möckel *et al.* developed a novel electrochemical method for the lactonization of vinyl benzoates **243** using as precatalyst iodobenzene **13**. The reaction was performed in the presence of lithium perchlorate and trifluoroacetic acid as electrolyte and supporting acid respectively. Trifluoroethoxy-substituted isochromanones **247** were isolated in appreciable yields (Scheme 66).[98] Reaction scope was administered by changing the steric and electronic components of the substrates. Further functional group tolerance was determined using compatibility test and it indicated that functional groups labile to oxidative conditions show low yields. In case of vinyl substituted substrates, satisfying diastereomeric ratio were observed.



Scheme 66. Synthesis of isochromanones **247** using iododobenzene **13** as precatalyst.

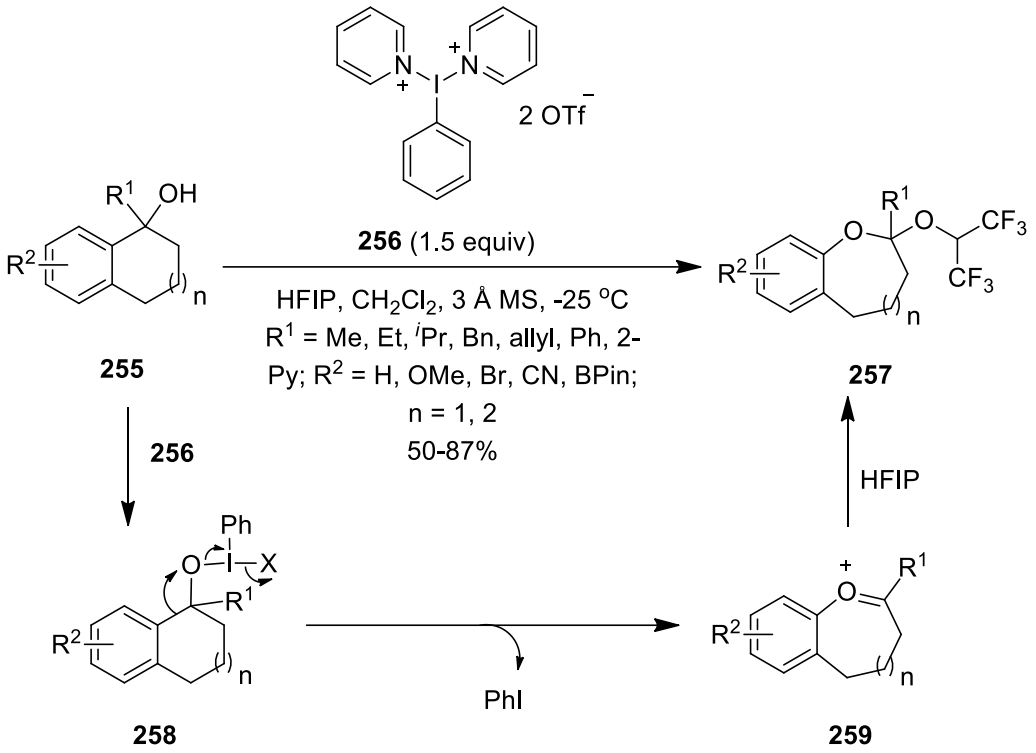
Cui's research group developed a metal-free route to prepare 2-hydroxy-benzo[*b*][1,4]oxazins **249** from *N*-(2-hydroxylaryl)enaminones **248** using PIDA **6** under air atmosphere (Scheme 67).[99] This one-pot synthesis exhibits excellent functional group compatibility with broad substrates scope and significant product yields. The proposed mechanism initiates with the 1,5-H shift of **248** to give iminoenolate intermediate **250**, followed by PIDA-induced oxidation to provide spirolactone intermediate **251** which reversibly forms **252**. Further Et_3N-promoted oxidation of **252** under O_2 gives superoxide radical intermediate **253** which upon subsequent dismutation generates intermediate **254** and releases hydroxyl radical. This radical could be then trapped by **252** to continue the radical chain growth in the presence of O_2. Finally, intramolecular cyclization of **254** furnishes desired product **249**.



Scheme 67. Preparation of 2-hydroxy-benzo[*b*][1,4]oxazines **249** using PIDA **6** as an oxidant.

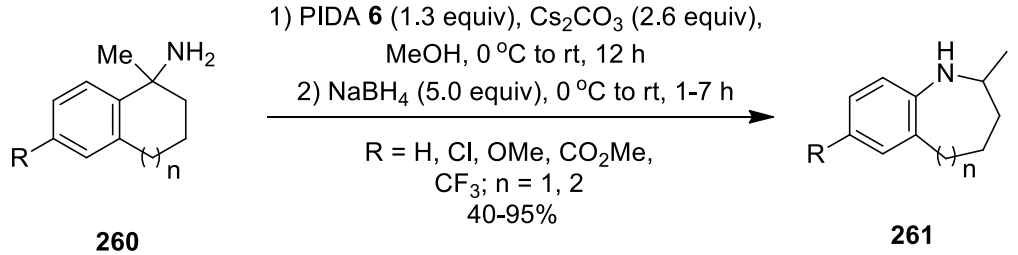
In 2016, Wengryniuk's research group reported synthesis of benzo-fused oxygen heterocycles **257** via oxidative rearrangement of benzylic tertiary alcohols **255**. This reaction was facilitated by (poly)cationic hypervalent iodine reagent **256** promoting C-to-O alkyl migration and represents the first example showing the unique reactivity of this class of reagents (Scheme 68).[100] Although detailed mechanism is not provided, authors envisioned attack of the alcohol on the iodine center that would generate an activated intermediate **258** followed by carbon to oxygen alkyl migration to generate oxonium ion **259** which could be trapped by a

nucleophile to give cyclic ethers **257**. Reaction was highly scalable, demonstrated by gram scale reaction and also HFIP-derived acetals **257** were subjected to subsequent derivatization under different reaction conditions.



Scheme 68. Synthesis of Benzo-fused oxygen heterocycles **257** using polycationic hypervalent iodine reagent **256.**

In 2019, PIDA-induced oxidative rearrangement of primary amines **260** via 1,2-C to N migration was developed by Murai's research group. This method enabled facile synthesis of cyclic amines such as benzoazepine **261** (n = 1) and benzosuberan **261** (n = 2) in significant yields (Scheme 69).[101] Substituents such as chloro, methoxy, ester and trifluoromethyl groups were well tolerated.

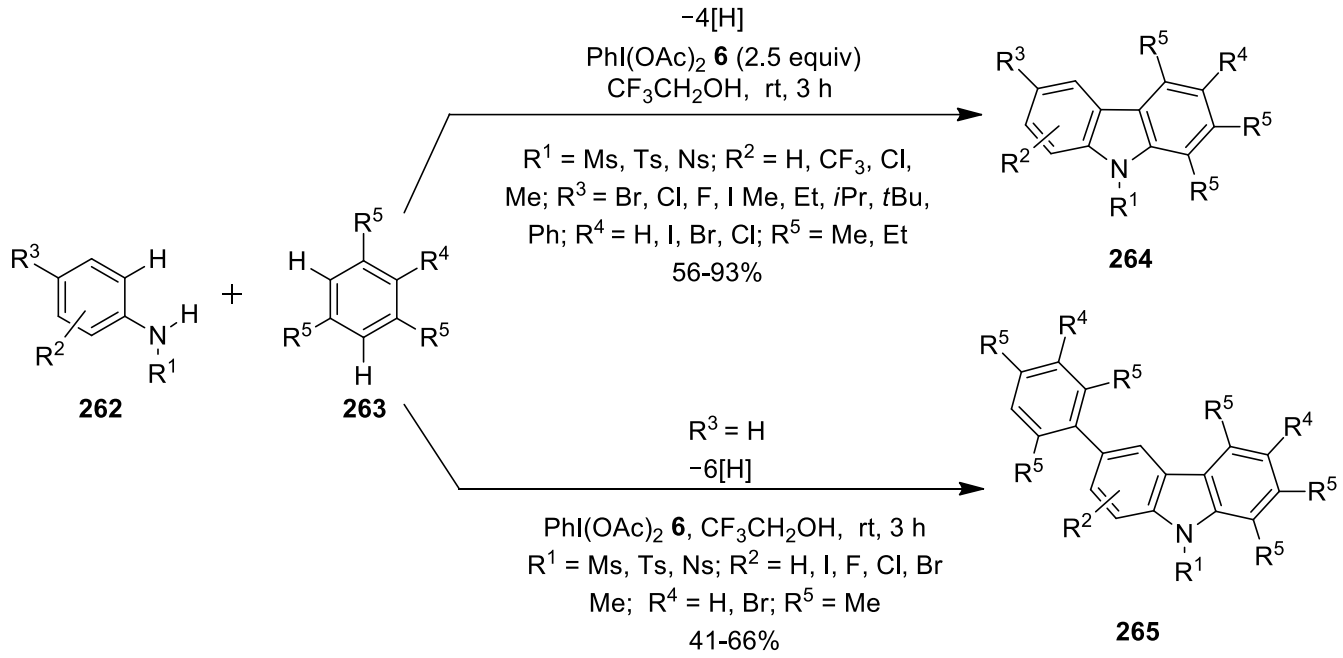


Scheme 69. Synthesis of cyclic amines **261** using PIDA **6** as an oxidant.

2.3. Synthesis of polycyclic heterocycles

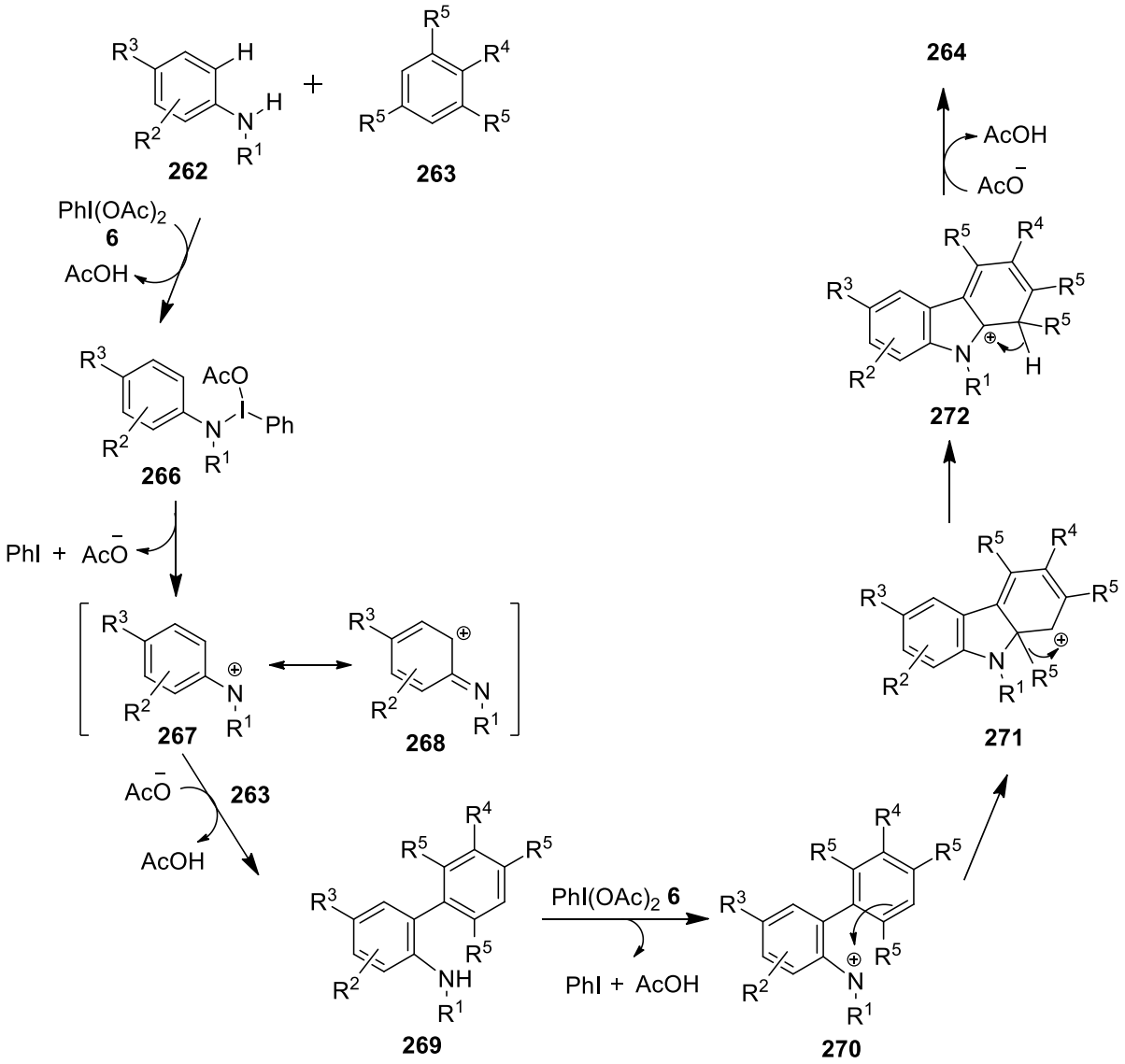
Maiti and Mal designed a PIDA-induced intermolecular dehydrogenative annulation strategy for the synthesis of carbazoles **264** from non-prefunctionalized *N*-sulfonylanilides **262** and 1,3,5-trialkylbenzenes **263** (Scheme 70).[102] This tandem C−C/C−N bond forming reaction involves simultaneous functionalization of three C(sp^2)−H

and one N(sp^3)−H bonds followed by one alkyl migration. Further scope of this annulation method was extended with substrates **262** containing −H at the *para*-position (R^3 = H), enabling synthesis of multi-substituted carbazols **265** via sequential five C−H and one N−H bond functionalization.



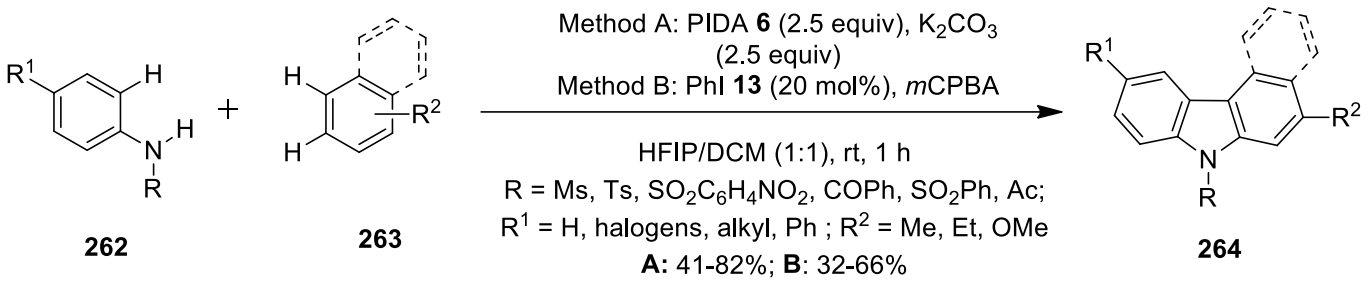
Scheme 70. Synthesis of multi-substituted carbazoles **264** and **265** using oxidant PIDA **6.**

The proposed mechanism for this intermolecular reaction is depicted in scheme 71.[102] Initially, anilide **262** interacts with PIDA **6** to form nitrenium ion intermediate **267** which later stabilizes through charge delocalization to give carbenium ion **268**. C-arylated intermediate **269**, obtained through nucleophilic addition of arene **263** to the **268**, undergoes further oxidation with PIDA **6** to generate ionic intermediate **270**. Subsequent electrophilic aromatic substitution furnishes carbenium intermediate **271** which is stabilized by neighbouring quaternary methyl group migration. Finally, conversion of cationic intermediate **272** into the heterocyclic product **264** occurs via abstraction of proton by acetate ion.



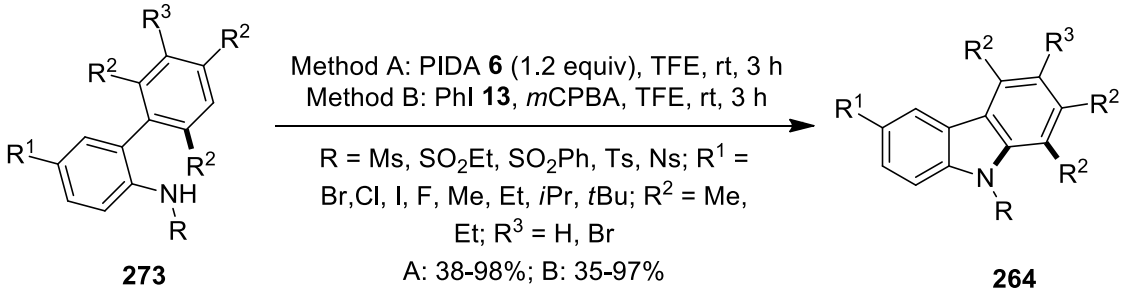
Scheme 71. Proposed mechanism for the synthesis of multi-substituted carbazoles **264.**

In continuation, Mal's group employed iodine(III) reagent as sole oxidant to prepare multi-substituted carbazoles from anilides **262** and simple arenes **263** either by using stoichiometric PIDA **6** (Method A) or catalytic PhI–*m*CPBA system (Method B) (Scheme 72).[103] Reactions were performed at ambient temperature and tolerates range of functional groups. Notably, stoichiometric pathway provided better yields as compared to catalytic ones. Further synthetic utility of this method was well documented in the synthesis of bio-active natural products.



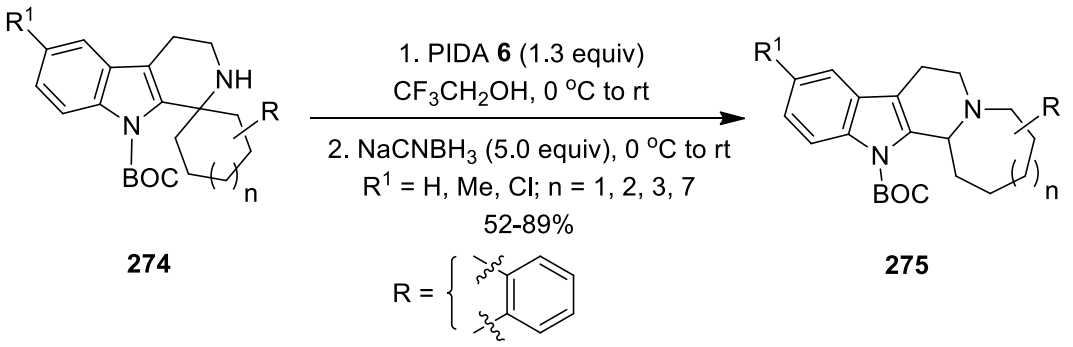
Scheme 72. Hypervalent iodine(III)-mediated synthesis of multi-substituted carbazoles **264.**

Later, the same group developed intramolecular dehydrogenative C−N coupling reaction for the synthesis of carbazoles **264** by reacting biarylsulfonanilides **273** with iodine(III) reagent (Scheme 73).[104] This method enabled distal (-*meta*) C−H bond functionalization with the aid of 1,2-alkyl migration. Reactions were performed either by using stoichiometric phenyliodine diacetate **6** or *in situ* generated iodine(III) reagent from precatalyst iodobenzene **13** (20 mol %) and terminal oxidant *m*CPBA. Substrates **273** with electron-rich arene moiety gave higher products yield as compared to electron-deficient ones. Both reaction pathways worked perfectly well at room temperature under open atmosphere condition. Further conversion of *N*-protected carbazole **264** into the corresponding NH-carbazole derivative was done by treating with Cs_2CO_3 in THF-MeOH under refluxing condition.



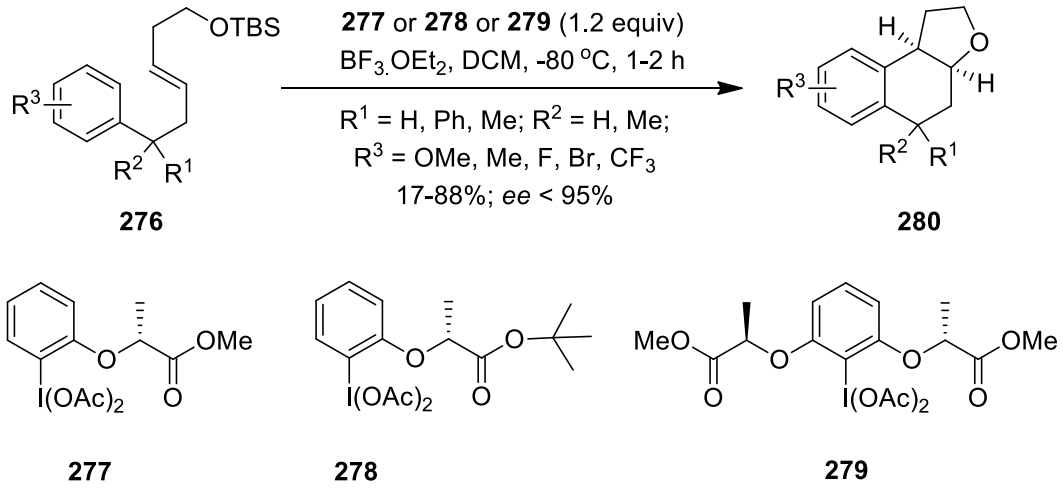
Scheme 73. Synthesis of carbazoles **264** using hypervalent iodine(III) reagent as an oxidant.

Murai and co-workers performed the first oxidative rearrangement of cyclic secondary amines **274** using hypervalent iodine reagent **6** (Scheme 74).[105] This method comprises $PhI(OAc)_2$-promoted 1,2-C-to-N alkyl migration of secondary amines **274** followed by subsequent reduction using $NaCNBH_3$ to provide tetracyclic compounds **275.** Further scope of the reaction was extended towards the synthesis of macrocyclic indole-fused compounds.



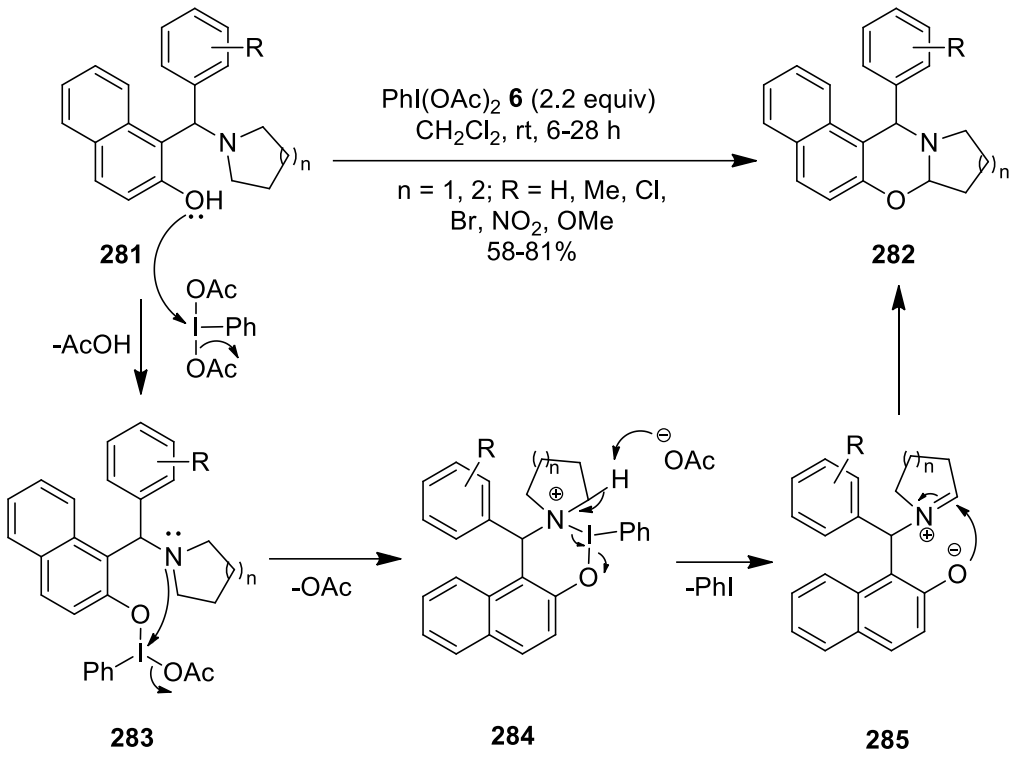
Scheme 74. Synthesis of tetracyclic indole-fused compounds **275** using PIDA **6** as an oxidant.

Meanwhile, Sugimura's team presented an enantioselective intramolecular oxyarylation of (*E*)-6-aryl-1-silyloxylhex-3-ene **276** promoted by lactate-based chiral iodine(III) reagent **277, 278** and **279** in the presence of $BF_3{\cdot}OEt_2$ (Scheme 75).[106] Tricyclic products **280** were obtained in variable yields under metal-free conditions. Further experimental evidences revealed that silyl group as a protecting group accelerates this oxidative cyclization reaction and also contribute for high enantioselectivity. Additionally, aminoarylation of methane-sulfonylamide provided hexahydrobenz[*e*]indole in 85% yield (*ee* 80%) using tris(pentafluorophenyl)borane as promoter.



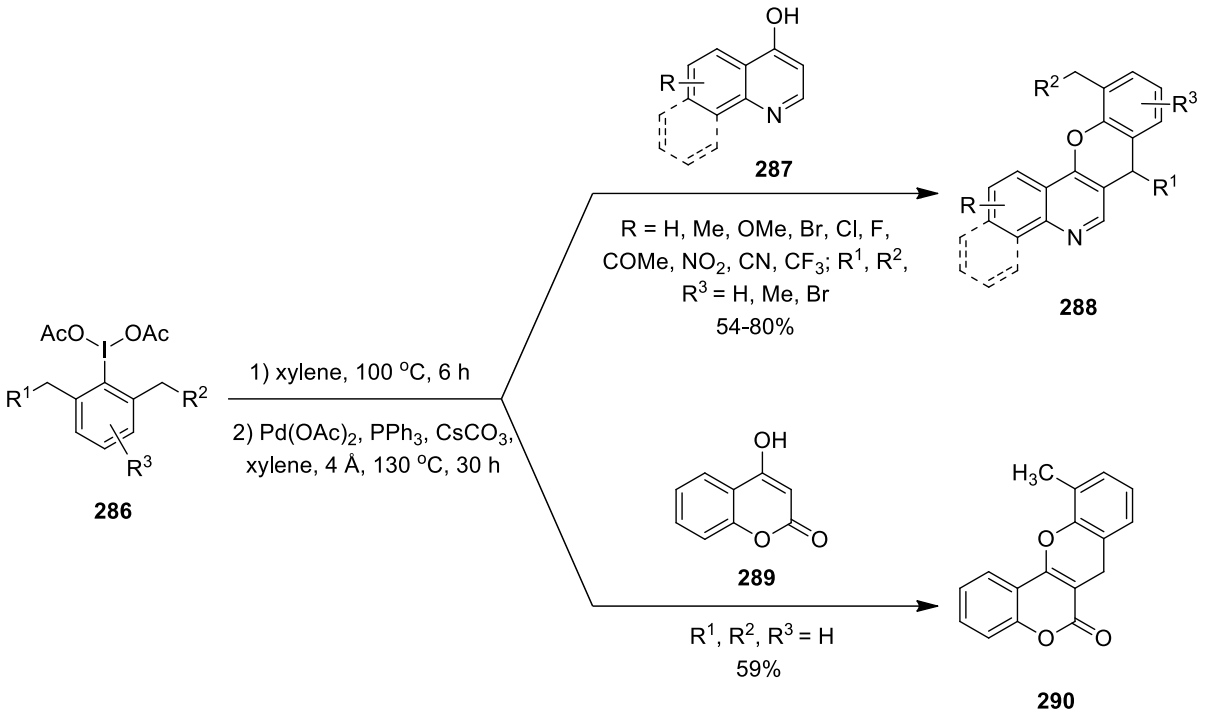
Scheme 75. Enantioselective synthesis of tricyclic products **280** using lactate-based chiral iodine(III) reagent.

In 2016, Waghmode *et al.* employed PIDA **6** as an oxidant to prepare 1,3-napthoxazines **282** through cross dehydrogenative-coupling of 1-(α-aminoalkyl)-2-naphthols **281** (Scheme 76).[107] The precursors **281** were synthesized via three-component condensation of β-naphthol, aldehydes and cyclic secondary amines *via* Betti reaction. The proposed mechanism initiates with the reaction of **281** with PIDA **6** to form intermediate **283** via ligand exchange, which further gives six membered iodine(III) heterocycle **284**. Intermediate **284** upon reductive elimination of PhI generates imminium ion **285** followed by subsequent trapping by phenoxide anion to yield product **282**.



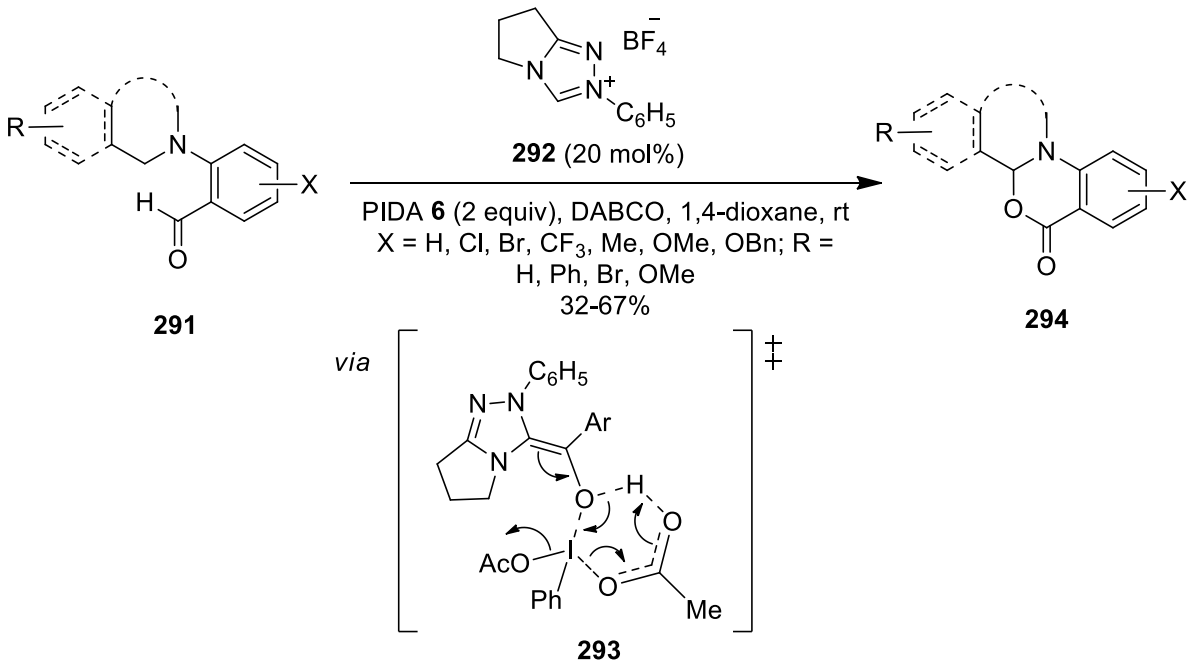
Scheme 76. Synthesis of 1,3-napthoxazines **282** using as oxidant PIDA **6.**

In 2017, Hong *et al.* established an efficient protocol for the one-pot synthesis of 7*H*-chromeno[3,2-*c*]quinolones **288** from arylols **287** and substituted aryliodine(III) reagents **286** through cascade *O*-arylation and palladium-catalyzed C(sp^3)-H arylation process (Scheme 77).[108] Both electron-donating and -withdrawing substituents on the quinoline ring were well tolerated. Further 4-hydroxycoumarin **289** was converted into benzopyranone derivative **290** using bis(acetoxy)iodoarene **286** under similar conditions in 59% yield.



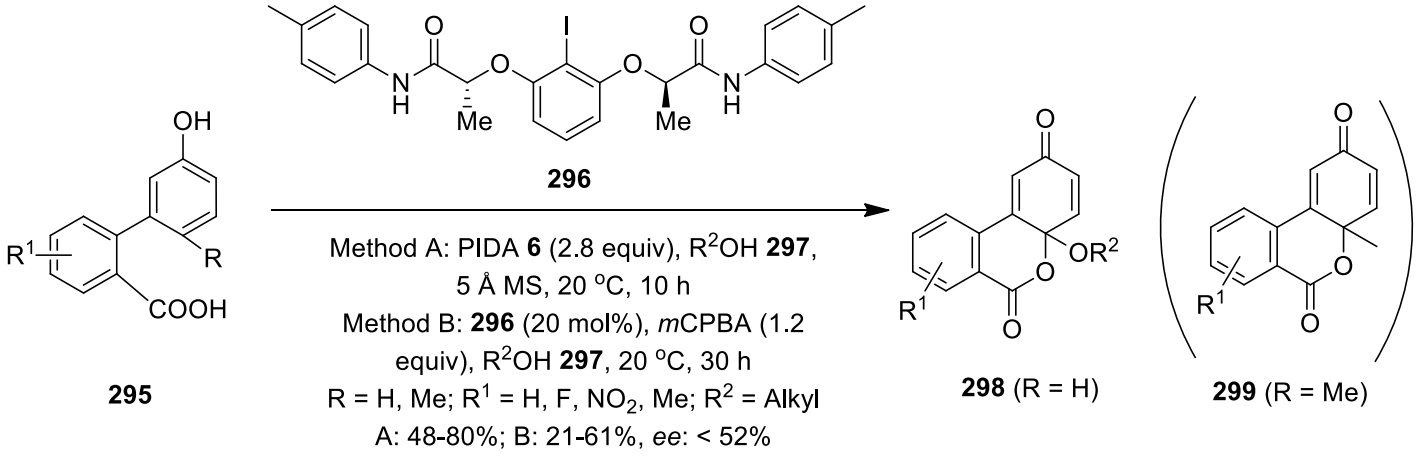
Scheme 77. Synthesis of 7*H*-chromeno[3,2-*c*]quinolones **288** and benzopyranone derivative **290** using trivalent aryliodine reagents **286.**

In 2019, Chen *et al*. disclosed an interesting *N*-heterocyclic carbene (NHC) **292**-catalyzed intramolecular domino reaction of aryl aldehyde **291** using PIDA **6** (Scheme 78).[109] Based on the control experiments and DFT studies, a domino two-stage mechanism was proposed involving NHC-catalyzed oxidation of the aldehyde to the corresponding carboxylic acid via acyl azolium intermediate formed from Breslow intermediate **293** and subsequent addition of carboxylate to the iminium intermediate to give desired product **294**. Several cyclic amines such as piperidine, pyrrolidine, morpholine and azepine-derived aldehydes were well reacted under optimized conditions.



Scheme 78. Synthesis of α-oxygenated products **294** using PIDA **6** as an oxidant.

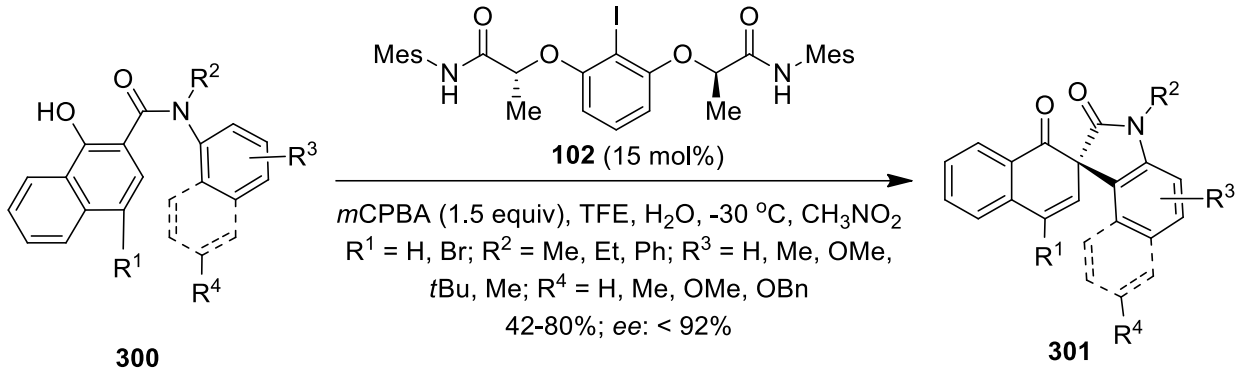
Deng *et al.* established a new strategy to construct polycyclic cyclohexadienones **298** through intramolecular alkoxy-oxylactonization/dearomatization of 3'-hydroxy-[1,1'-biphenyl]-2-carboxylic acid **295** promoted by stoichiometric oxidant PIDA **6** (Scheme 79).[110] Further asymmetric version of this method was developed by using *in situ* generated aryl-λ^3-iodane from chiral aryl iodide **296** in the presence of *m*-CPBA in MeOH. Reaction scope was investigated by employing different alcohols **297** as nucleophile. Notably, decrease in product yields and enantioselectivities was observed for sterically hindered alcohols and therefore reaction was found sensitive to the size of the alcohol. Further methyl-substituted substrate **295** (R = Me) enabled synthesis of core unit of dehydroaltenusin **299**, which is an inhibitor of DNA polymerase.



Scheme 79. Hypervalent iodine(III)-mediated synthesis of polycyclic cyclohexadienones **298.**

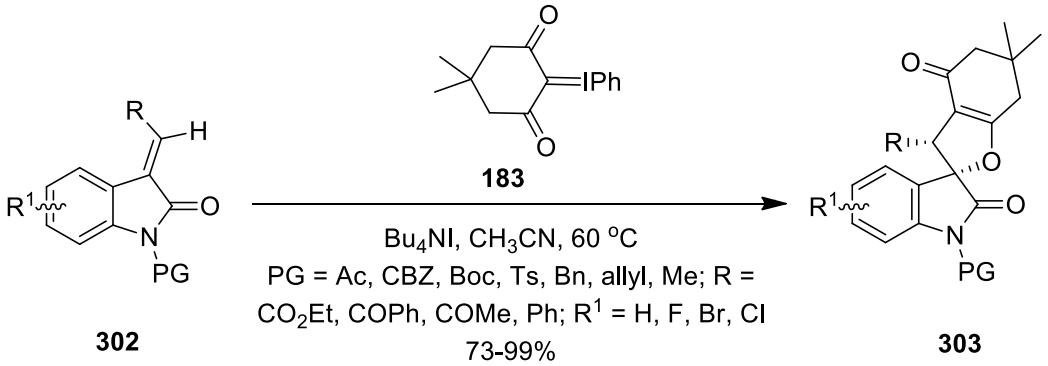
2.4. Synthesis of spirocyclic heterocycles

Oxidative dearomatizative spirocyclization constitutes an important platform for the preparation of functionalized spirocyclic skeletons. Chiral hypervalent iodine reagents are frequently employed as reagents or catalyst to achieve asymmetric dearomatization of phenols and other related electron-rich organic compounds. The current section of the review highlights the recent progress made in the enantioselective dearomatizative spirocyclization reactions. In 2015, Zhang *et al.* constructed spirooxindole derivatives **301** from 1-hydroxy-*N*-aryl-2-naphthamides **300** via chiral organoiodine-catalyzed enantioselective oxidative dearomatization process (Scheme 80).[111] This reaction enabled stereoselective creation of all-carbon stereogenic center containing spiro products **301** in good yields with excellent enantioselectivities (up to 92% *ee*). Notably, the active hypervalent species, phenyl-λ^3-iodanes generated *in situ* through *m*CPBA-mediated oxidation of chiral iodoarene **102** catalyze this asymmetric spirocyclization reaction.



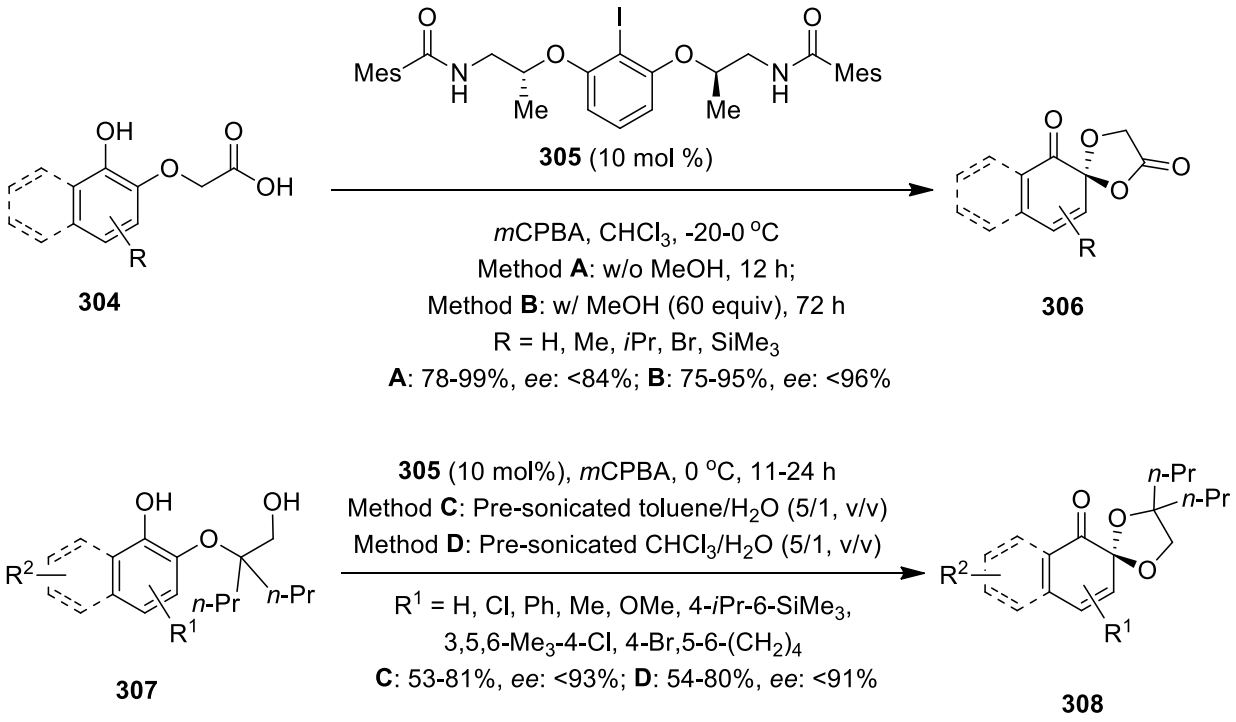
Scheme 80. Synthesis of spirooxindoles **301** using chiral iodoarene **102** as precatalyst.

Later, Murphy's research team presented an unprecedented metal-free approach to access 3,3'-spirooxindolo dihydrofurans **303** by reacting cyclic iodonium ylides **183** with 3-alkylidene-2-oxindoles **302** using Bu_4NI catalysis (Scheme 81).[112] The reaction was tolerant to a variety of electron-poor and electron-neutral substituents on the alkylidene substrates and the products were isolated in high to excellent yields. Other iodonium ylides derived from 1,3-diketones, pyrimidines and 1,3-ketoesters smoothly gave spirocyclic products in significant yields.



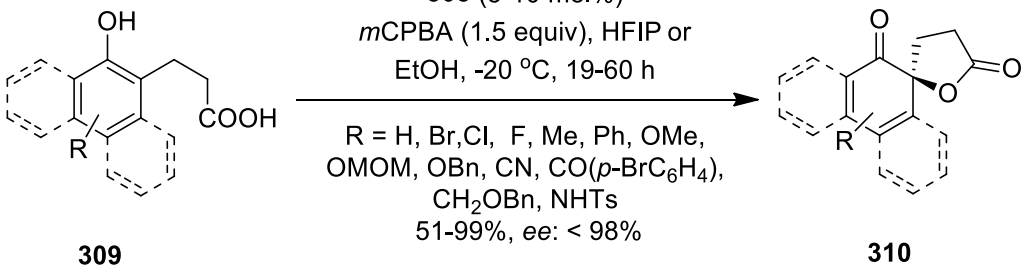
Scheme 81. Synthesis of spirooxindolo dihydrofurans **303** by reacting cyclic iodonium ylides **183** with 3-alkylidene-2-oxindoles **302.**

In 2017, Ishiara's group adapted oxidative dearomatization strategy to prepare enantioselective masked *ortho*-benzoquinones **306** and **308** from *ortho*-hydroquinone derivatives using chiral organoiodine(III) catalysis (Scheme 82).[113] Reactions works well with both phenols *O*-tethered to an acetic acid **304** or to an ethanol unit **307** by employing chiral iodoarene **305** as precatalyst. Further the use of synthesized spiroketal in the asymmetric synthesis of natural product, bis(monoterpene) (-)-biscarvacrol highlights the potential scope of this method. Additionally, synthesis of dioxolanone-type masked *para*-benzoquinones from *para*-hydroquinone derivatives were achieved under similar conditions with *ee* up to 89%.



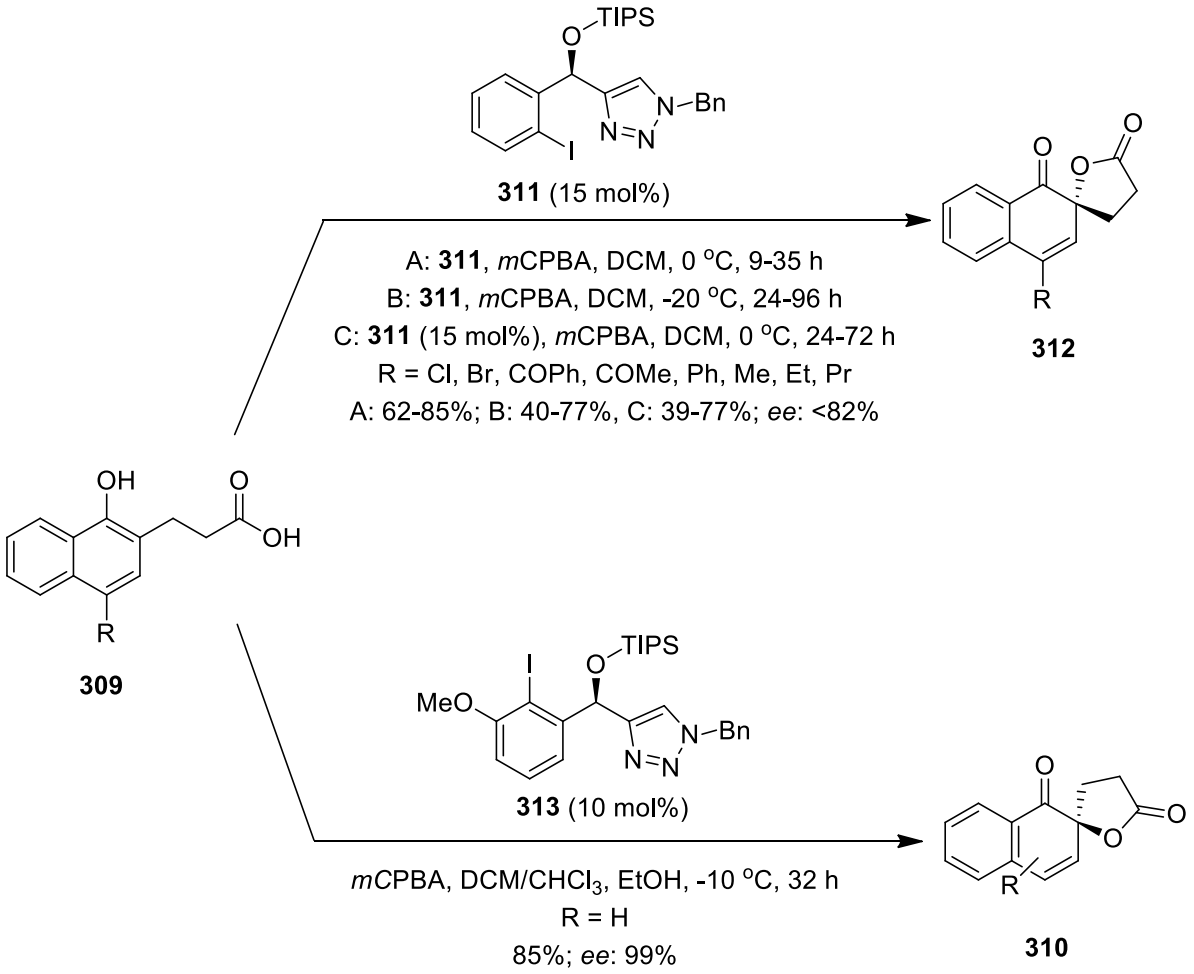
Scheme 82. Synthesis of masked *ortho*-benzoquinones **306** and **308** using chiral organoiodine(III) catalyst **305.**

In continuation, the same team employed organoiodine catalyst **305** for the enantioselective intramolecular oxidative dearomatization of naphthol derivatives **309** using *m*CPBA as an oxidant (Scheme 83).[114] This conformationally flexible catalyst **305** was found very effective for inducing excellent enantioselectivities to the corresponding spirolactones **310** (*ee* up to 98%). Notably, presence of HFIP and ethanol as an additive for the oxidation of 2-naphthols and 1-naphthols respectively was necessary for achieving high enantioselectivity.



Scheme 83. Synthesis of spirolactones **310** using organoiodine catalyst **305.**

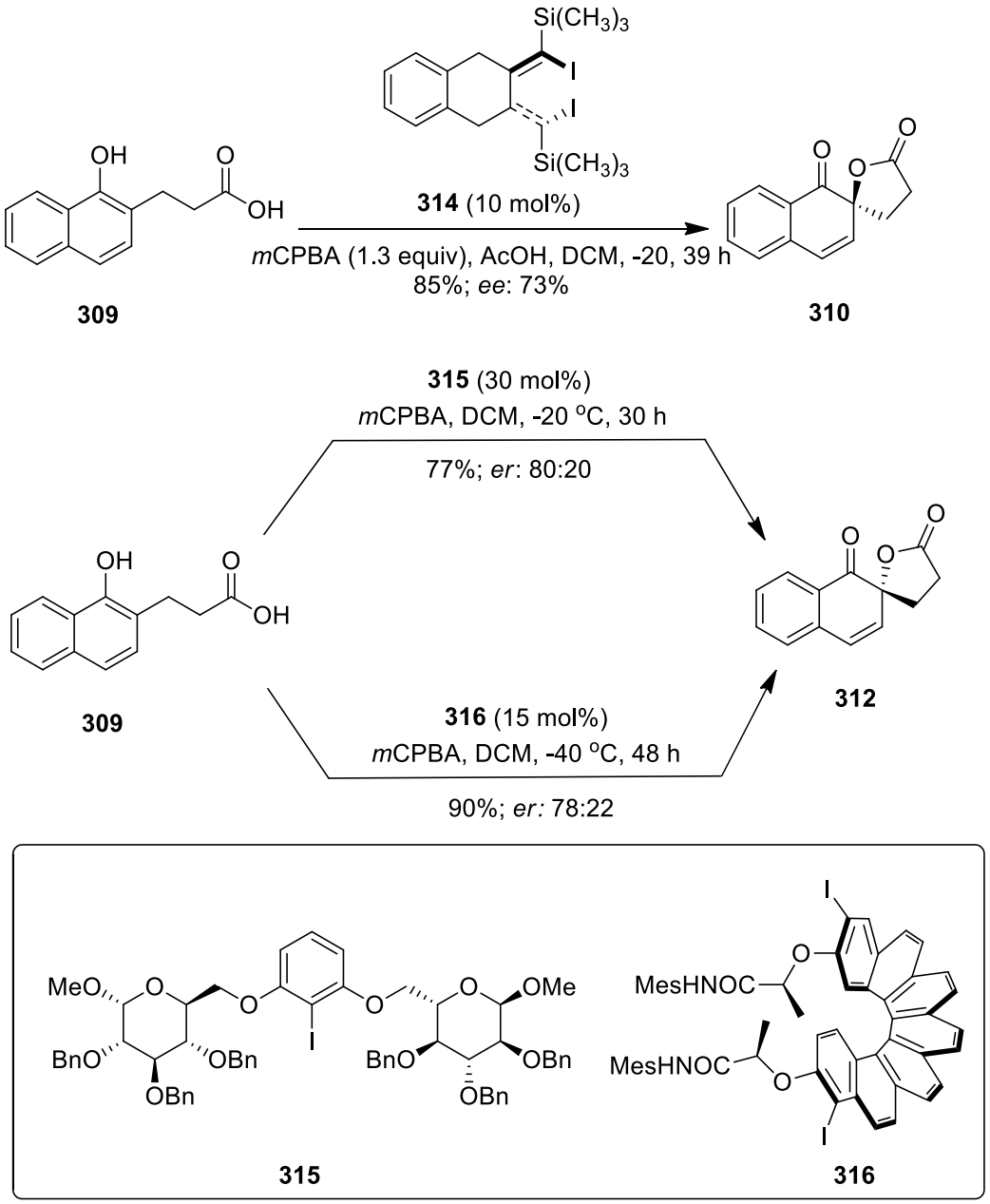
In the same year, Nachtsheim and co-workers designed a new C1 symmetric triazole-based chiral iodoarene catalyst **311** and successfully utilized this compound for the intramolecular asymmetric Kita-type spirolactonization of 4-substituted 1-naphthols **309**.[115] This method provided spirolactones **312** in variable yields and high enantioselectivity, facilitated by *in situ* generated hypervalent iodine(III) species using terminal oxidant *m*CPBA (Scheme 84). Reaction scope was investigated under distinct conditions that is by maintaining reaction temperature to 0 °C (Method A) and -20 °C (Method B), and by using catalytic amount of **311** (Method C). Though this "first-generation" triazole-based catalyst provided highest enantioselectivities for this reaction compared to other C1-symmetric iodoarenes, their reactivities were comparatively low. Therefore, the same group synthesized "second-generation" triazole-based catalyst **313** by introducing *ortho*-substituent at the aryl iodide.[116] This catalyst showed remarkable reactivity and excellent selectivity in the oxidative spirocyclization of **309**. The spirolactone **310** was obtained in 85% yield with 99% *ee*, the highest enantioselectivities observed for this reaction.



Scheme 84. Synthesis of spirolactones **312** and **310** using catalytic amount of chiral iodoarene **311** and **313.**

Several groups designed novel chiral iodoarene reagents for the asymmetric Kita-spirolactonization. For instance, Ogasawara *et al*. synthesized conformationally rigid C2-symmetric atropisomeric chiral diiododiene **314** and successfully applied as chiral organocatalyst in the dearomatizing spirolactonization of 1-naphthols **309** to yield (*S*)-spirolactone **310** with *ee* up to 73% (Scheme 85).[117] Further, Imrich and Ziegler prepared the first

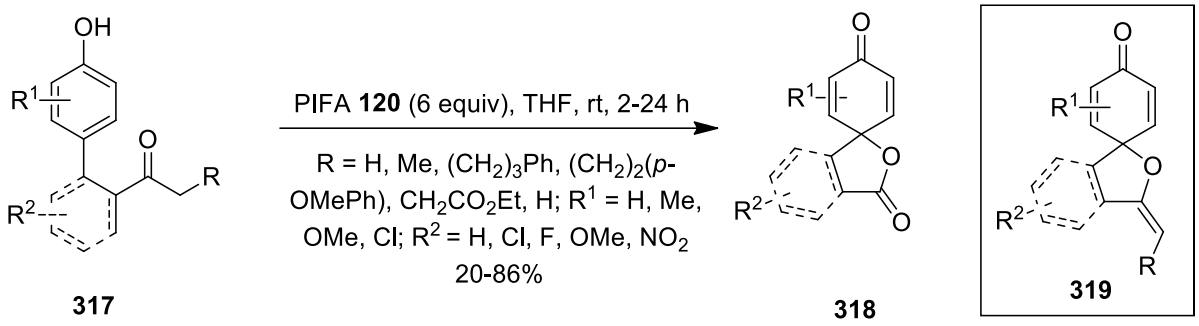
carbohydrate-based chiral aryl iodide catalyst **315** by condensing partially protected glucosides with iodoresorcinol *via* Mitsunobu reaction.[118] This catalyst was further employed for the oxidative spriolactonisation of **309** to provide spirolactone **312** in 77% yield with *er* up to 80:20. Later, Quideau's research group succeeded in constructing helicine-based chiral iodoarene catalyst **316** from inexpensive precursors (L)-(+)-tartaric acid and 4-methylstyrene.[119] This novel chiral catalyst **316** served as catalyst for the dearomative spirolactonization of **309** to afford chiral spirolactones **312** with moderate selectivity. Notably, reaction catalyzed by catalyst **306** and **307** gives (*R*)-isomer **312**.



Scheme 85. Enantioselective synthesis of spirolactones **310** and **312** using iodoarenes **314-316** as precatalysts.

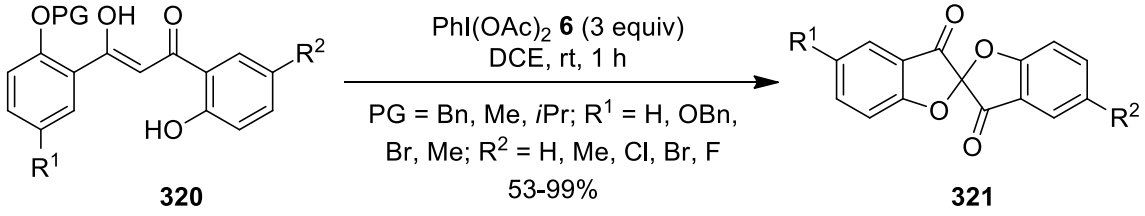
Very recently, $PhI(OCOCF_3)_2$-induced dearomatizative spirocyclization of various phenolic biarylic ketones **317** was by demonstrated by Wang's research team (Scheme 86).[120] This is the first example employing ketone group as internal nucleophile for the spirocyclization reaction. Mechanistic details revealed formation of key

intermediate exocyclic enol ether **319** that further undergoes PIFA-induced oxidation and C-C bond cleavage to yield cyclohexadienones **318**. Notably, spiroannulation of ketonic substrates with long alkyl chain gave moderate yields. Moreover, biaryl substrates **317** bearing β-ketoester and aldehyde groups delivered corresponding spiro-products albeit in low yields.



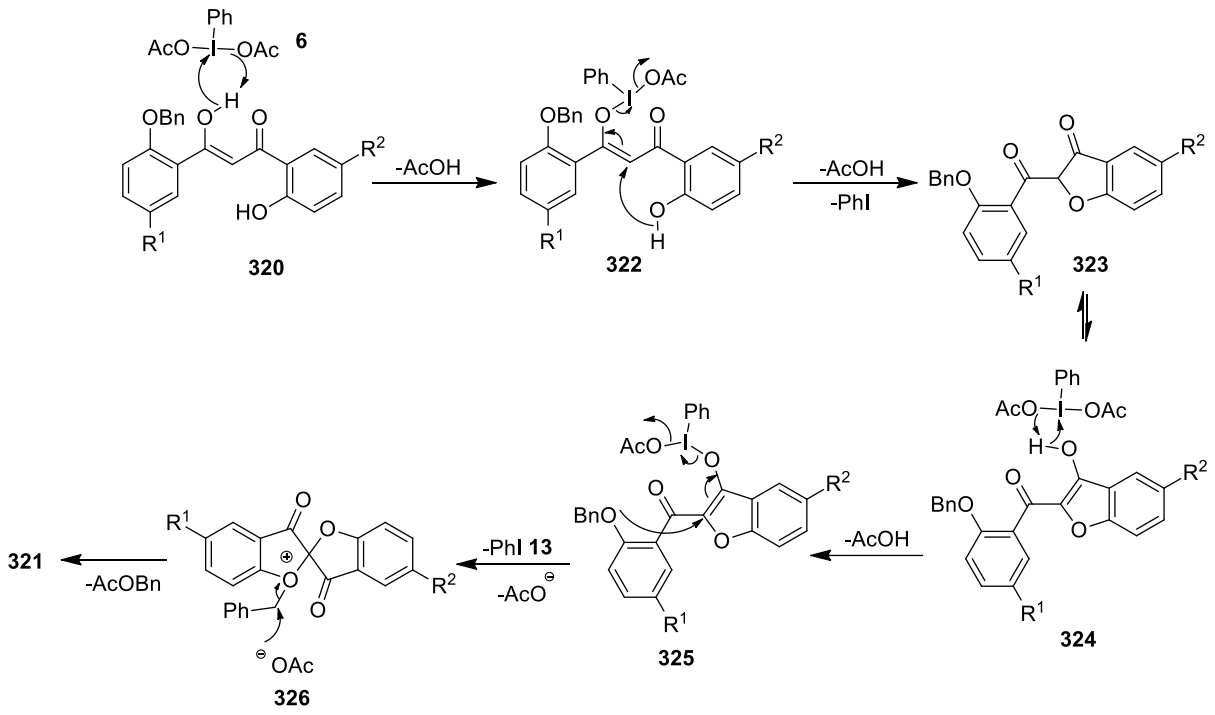
Scheme 86. Synthesis of spirolactones **318** using PIFA **120** as an oxidant.

Zhao and co-workers performed the reaction of protected 3-hydroxy1,3-bis(2-hydroxyaryl)prop-2-en-1-ones **320** with PIDA **6** that enabled synthesis of spiro-2,2'-benzo[*b*]furan-3,3'-ones **321** in quantitative yields at ambient temperature(Scheme 87).[121] This cascade intramolecular spirocyclization process involves dual oxidative C-O bond formation. A variety of substituents in both the phenyl rings were well tolerated.



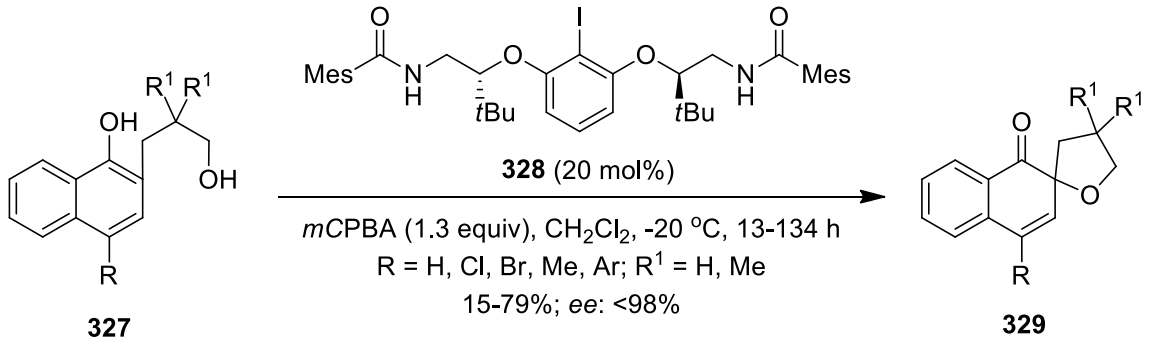
Scheme 87. Synthesis of spiro-2,2'-benzo[*b*]furan-3,3'-ones **321** using $PhI(OAc)_2$ **6** as an oxidant.

Scheme 88 depicts the proposed mechanism for this cyclization reaction. Initially, nucleophilic attack of enolic oxygen of **320** at the iodine center of PIDA **6** generates intermediate **322**, which cyclizes intramolecularly with the loss of PhI and acetate anion resulting in the formation of first C-O bond. Intermediate **323** tautomerizes into **324** which later reacts with PIDA **6** to give intermediate **325**. Then cyclization of **325** enables formation of second C-O bond to furnish oxonium ion intermediate **326**, which is finally attack by the acetate anion at the benzylic carbon resulting in the formation of spirocyclic product **321**.[121]



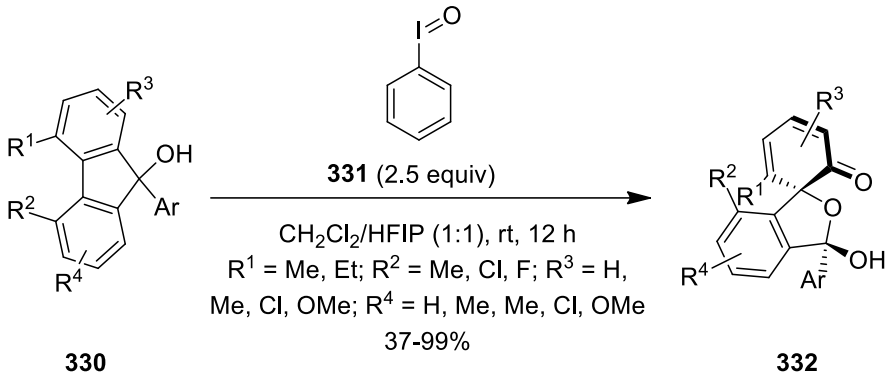
Scheme 88. The plausible mechanism for the synthesis of spiro-2,2'-benzo[*b*]furan-3,3'-ones **321** using $PhI(OAc)_2$ **6** as an oxidant.

Meanwhile, Ciufolini and co-workers disclosed catalytic, enantioselective intramolecular oxidative cyclization of naphtholic alcohols **327** promoted by newly designed chiral aryl iodide **328** and *m*CPBA (Scheme 89).[122] Using the present cycloetherification process, an efficient synthesis of spirocyclic products **329** bearing different substituents were achieved in high yields (*ee* upto 98%). Interestingly, presence of chiral center nearer to the H-bonding amido group in **328** was found useful for effective optical induction. Also, asymmetric oxidative cyclization of naphtholic sulphonamide was accomplished using catalyst **328** under identical conditions.



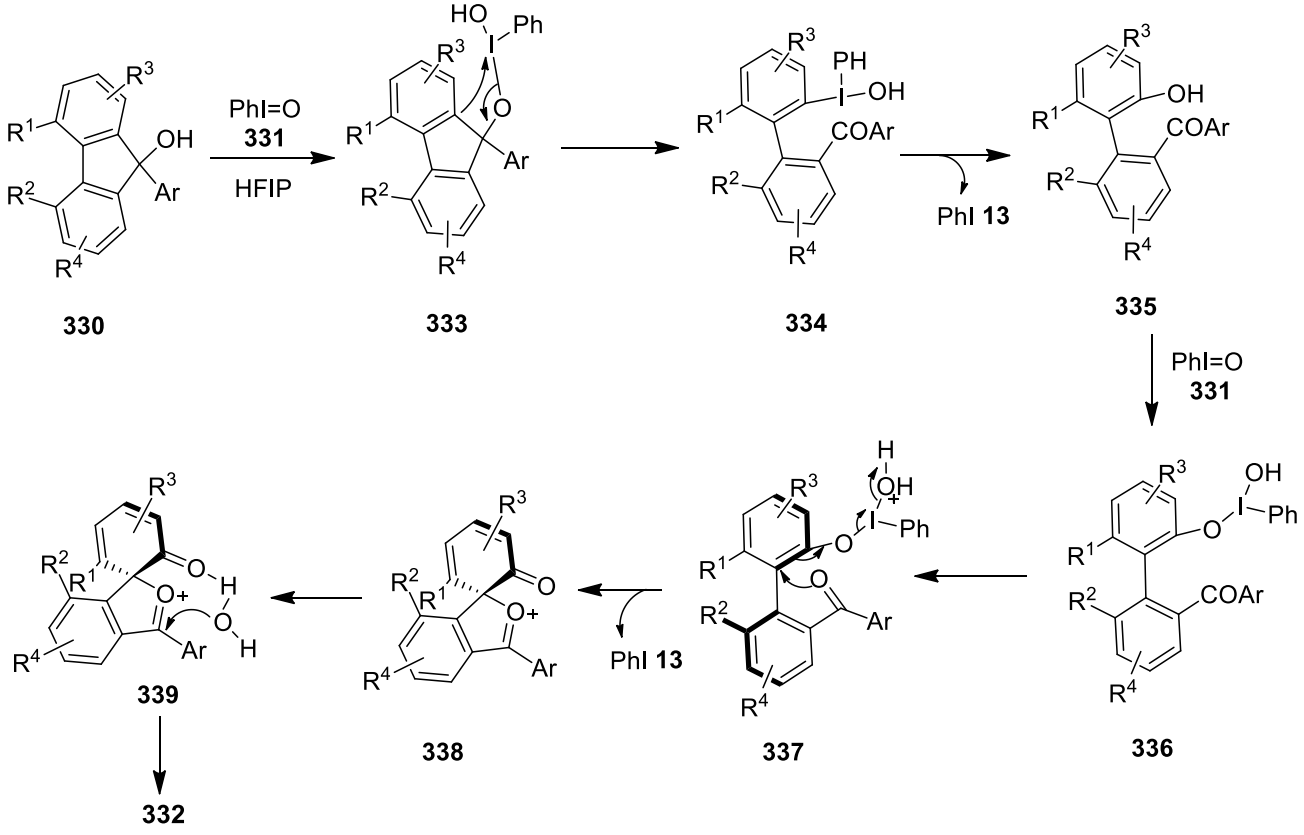
Scheme 89. Enantioselective synthesis of spirocyclic products **329** using chiral aryl iodide **328** as precatalyst.

Very recently, Deng *et al.* have reported a synthesis of spiro-ethers **332** *via* ring-opening/dearomatization of 9*H*-fluoren-9-ol derivatives **330** promoted by iodosobenzene **331**.[123] A variety of substituents on the 9-aryl ring were well tolerated. Reaction occurs under mild condition with excellent substrates scope, regio- and diastereochemistry (Scheme 90).



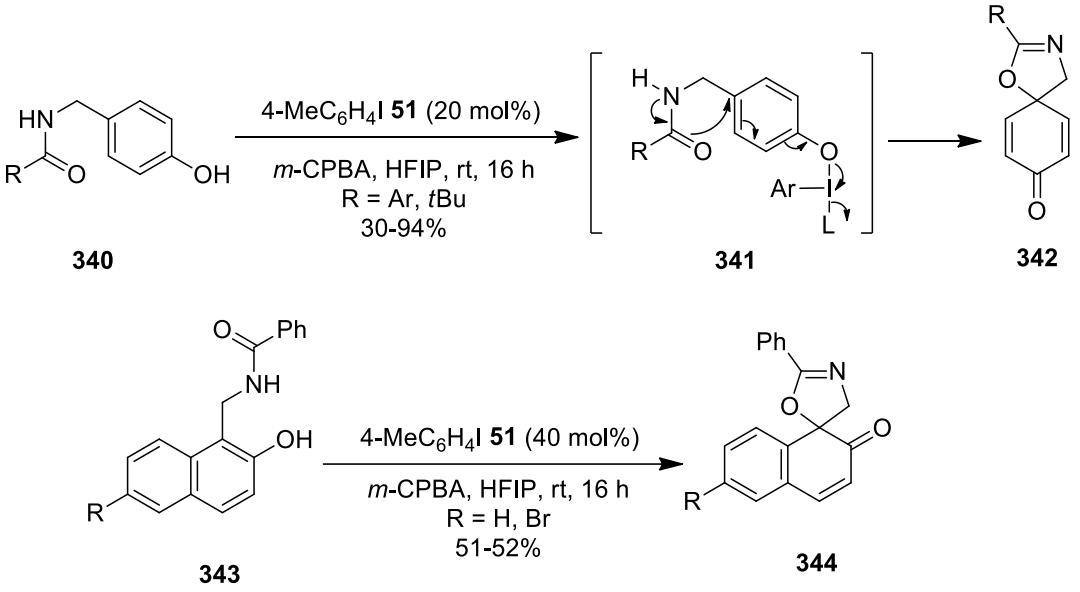
Scheme 90. Synthesis of oxo-spiro scaffolds **332** promoted by iodosobenzene **331.**

A plausible mechanism for this transformation is depicted in Scheme 91. Reaction begins with the interaction of substrate **330** with iodosobenzene **331** in HFIP to form alkoxyliodine(III) intermediate **333**, following which β-carbon cleavage produces diaryliodonium salt **334**. Reductive elimination of **334** provides oxygenated intermediate **335** with the loss of PhI **13**. Further **335** reacts with PhI=O **331** to form intermediate **336**, which undergoes nucleophilic attack by carbonyl group and subsequent dearomatization to give 1*H*-isobenzofuran-2-ium type product **338**. Finally, nucleophilic attack by water delivers the oxo-spiro compound **332** as a *cis*-isomer. Notably, the hydrogen bonding between the carbonyl group and H_2O probably accounts for the high diastereochemistry.[123]



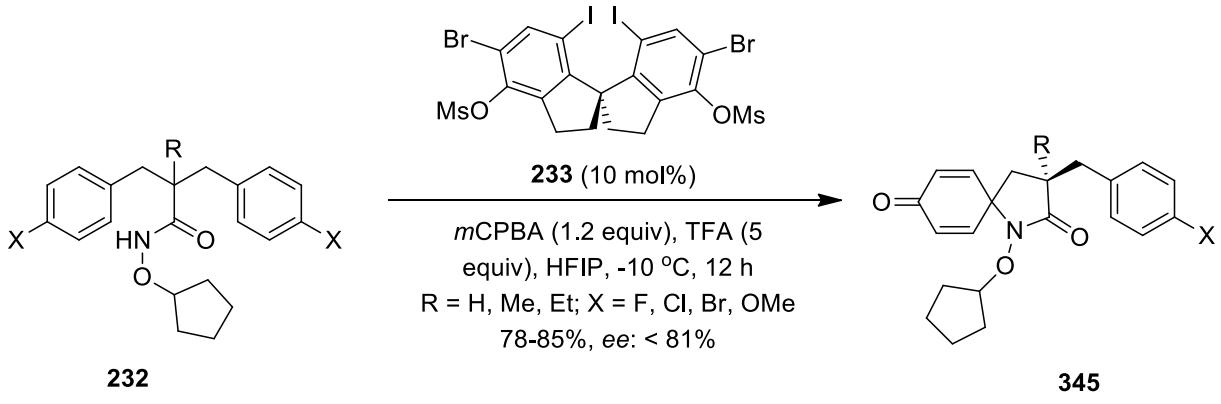
Scheme 91. The proposed mechanism for the synthesis of oxo-spiro scaffolds **332** promoted by **331.**

Very recently, Tariq and Moran synthesized spirooxazolines **342** via oxidative dearomatization of amide-tethered phenols **340** facilitated by active λ^3-iodane generated *in-situ* from 4-MeC_6H_4I **51**/*m*-CPBA catalytic system (Scheme 92).[124] Authors predicted that the λ^3-iodane would activate the phenolic oxygen to form intermediate **341** and subsequent cyclization of pendent amide on to the aromatic ring results in the formation of desired product **342**. Scope of the reaction was investigated with a range of aryl, alkyl and heteroaryl amide-based phenols under optimized conditions. Additionally, oxidative dearomatization of naphthol derivatives **343** yielded spirocycles **344** in moderate yields using 40 mol % of 4-iodotoluene **51**. Moreover, synthetic utility of this approach in the preparation of dihydrooxazines was successfully demonstrated.



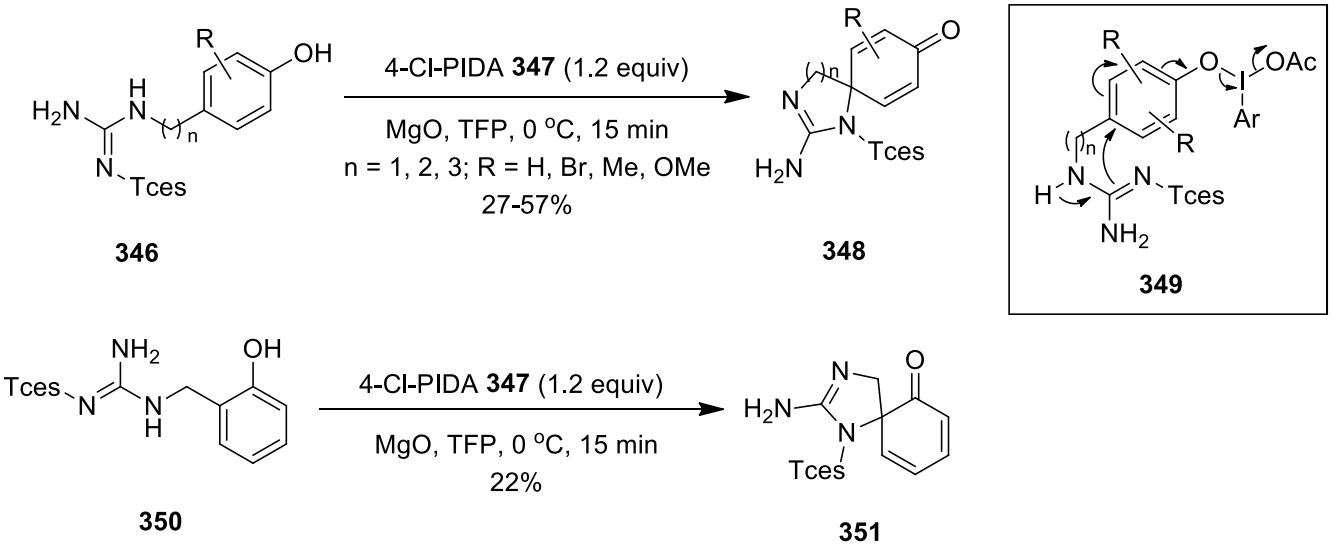
Scheme 92. Synthesis of spirooxazolines **342** using 4-iodotoluene **51.**

Cai and co-workers demonstrated synthesis of *N*-fused spirolactams **345** from corresponding 3-aryl-propanamides **232** via an asymmetric desymmetrization strategy (Scheme 93).[95] The protocol was catalyzed by hypervalent iodine(III) species generated *in situ* from chiral precatalyst diiodospirobiindane **233** in the presence of *m*CPBA as the terminal oxidant. *para*-substituted substrates **232** with halide or −OR groups smoothly underwent cyclization reaction to deliver products in high yields and moderate to good enantioselectivities.



Scheme 93. Synthesis of spirolactams **345** using **233** as precatalyst.

Odagi *et al.* constructed spirocyclic guanidines **348** from guanidine phenols **346** via dearomative spiroguanidination strategy by using oxidant 4-chloro-1-(diacetoxyiodo)benzene **347** (Scheme 94).[125] The reaction was performed in 2,2,2,3,3,3-hexafluoro-2-propanol (HFIP) and trichloroethoxysulfonyl (Tces) group was found a suitable protecting group for the guanidine. In the proposed mechanism, phenol reacts with PIDA **6** to generate key aryl-λ^3-iodane intermediate **349**, which is further attacked by the guanidine moiety at the *para*-position providing desired spiroguanidine **348** via dearomatization process. Additionally, *ortho*-spiroguanidination of substrate **350** yields spiroguanidine **351** under similar conditions.



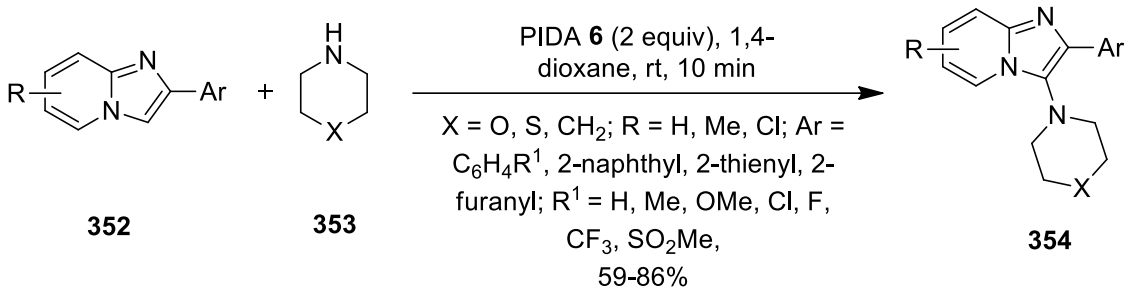
Scheme 94. Preparation of spiroguanidine derivatives **348** and **351** using 4-chloro-1-(diacetoxyiodo)benzene **347** as an oxidant.

3. Hypervalent Iodine-Mediated Late-Stage Functionalization of Heterocycles

Direct functionalization of heterocycles using hypervalent iodine reagents is fast-growing field in organic chemistry. These reagents find profound applications in the functionalization of variety heterocyles via synthetic transformations such as oxidative amination, alkylation, acetoxylation, halogenation, etc. In this section, all recent developments acheived in this area will be covered.

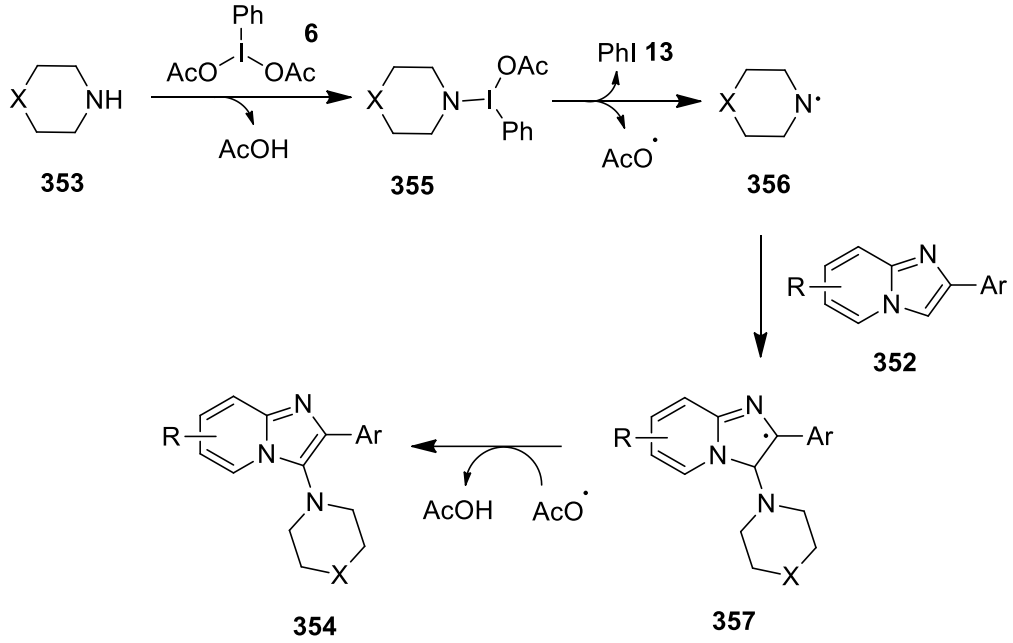
3.1. Amination/azidation of heterocycles

In 2017, Mondal *et al*. disclosed PIDA-induced intermolecular oxidative C(sp^2)−H amination of imidazopyridines **352** (Scheme 95).[126] Various cyclic amines **353** such as piperidine, morpholine and thiomorpholine reacted smoothly with imidazo[1,2-*a*]pyridines **352** to provide 3-amino substituted imidazopyridines **354** at room temperature. Moreover, regioselective C−H amination of indolizines was achieved under identical conditions.



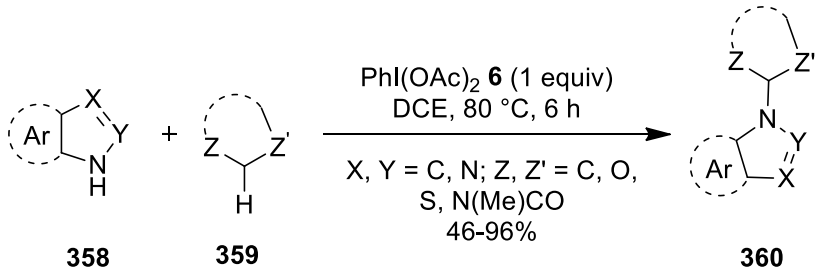
Scheme 95. PIDA-mediated reaction of imidazopyridines **352** with cyclic amines **353.**

Based on the experimental results, the proposed mechanism likely follows radical pathway as depicted in Scheme 96. Reaction of cyclic amine **353** with PIDA **6** forms *N*-iodoamido species **355** which gives radical **356** that further reacts with imidazo[1,2-*a*]pyridine **352** to furnish radical intermediate **357**. Finally, product **354** was obtained through the loss of AcOH.[126]



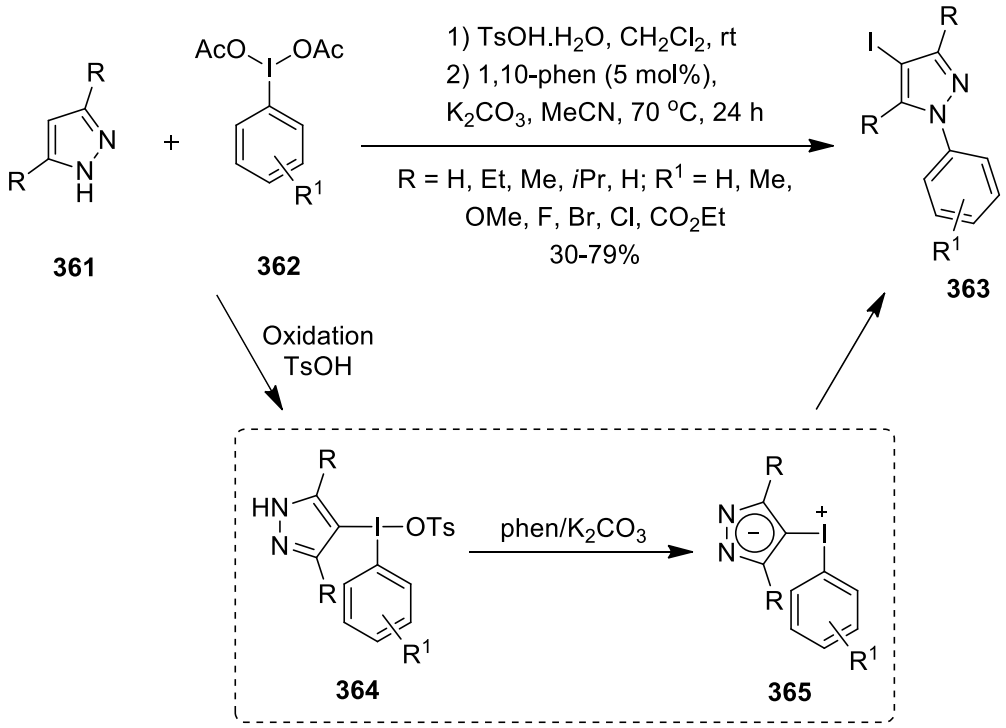
Scheme 96. The proposed mechanism for the synthesis of 3-amino substituted imidazopyridines **354** using PIDA **6** as oxidant.

Later, in 2018 Su's research group performed *cross*-dehydrogenative coupling of α-C(sp^3)–H bond of substrates **359** with azoles **358** using sole oxidant PIDA **6** (Scheme 97).[127] This protocol provides an easy access to a variety of N-alkylated azoles **360** by employing ethers, tetrahydrothiophene or N-Methyl-2-pyrrolidone as coupling reagents. Further synthetic utility was demonstrated by performing a gram scale reaction, which extends the practicality of this oxidative coupling reaction. Reaction follows radical pathway as indicated by various radical-trapping experiments.



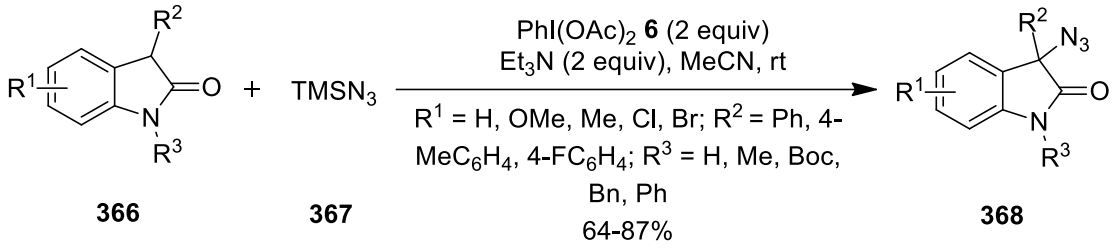
Scheme 97. PIDA-mediated C(sp^3)–H amination of substrates **359** with azoles **358.**

In 2018, an interesting one-pot protocol for the iodoarylation of NH-pyrazoles **361** with aryliodine diacetates **362** was developed by Cheng and co-workers (Scheme 98).[128] This reaction proceeds through hypervalent iodine-induced oxidation of **361** generating pyrazole-4-arylliodonium tosylate, [ArI(pyrazole)][OTs] **364** *in situ* which undergoes facile deprotonation forming zwitterionic iodonium ylide **365**. Finally, an intermolecular *N*-arylation mediated by 1,10-phenanthroline/K_2CO_3 yields the expected 1,4-disubstituted pyrazoles **363**. Further, the proposed intermediate **365** could be easily prepared and transformed into the target the iodoarylation product in high yield.



Scheme 98. Iodoarylation of various pyrazoles **361** using aryliodine diacetates **362** as coupling partner.

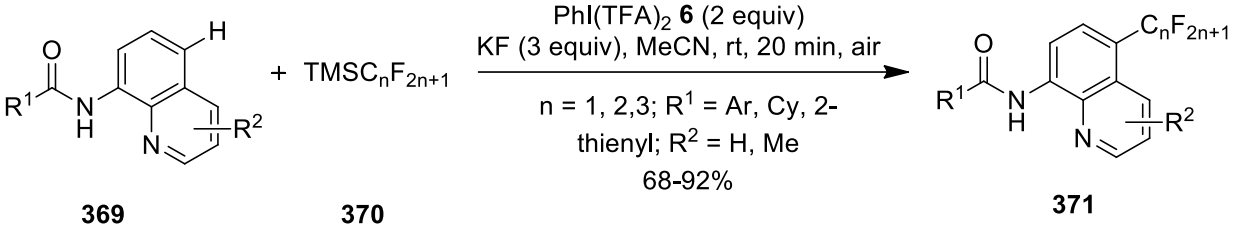
Further, radical-based strategy to prepare 3-azido-2-oxindoles **368** was developed by Chen *et al*. *via* C(sp^3)−H azidation of 3-substituted-2-oxindoles **366** (Scheme 99).[129] This transformation employs $TMSN_3$ **367** as the azide reagent in the presence of $PhI(OAc)_2$ **6** and Et_3N as an oxidant and additive respectively. Notably, azidation reaction proceeds smoothly with 3-aryl-2-oxindoles whereas 3-alkyl-2-oxindole showed no reactivity.



Scheme 99. PIDA-induced synthesis of 3-azido-2-oxindoles **368** through C(sp^3)−H azidation of 3-substituted-2-oxindoles **366.**

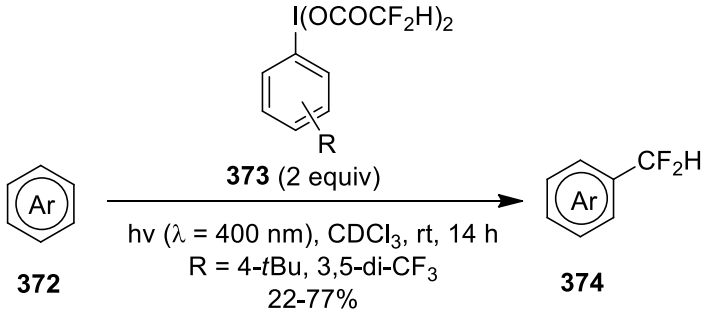
3.2. Alkylation/Alkynylation of Heterocyles

In 2017, Zhang's research group demonstrated PIDA-mediated C–H perfluoroalkylation of 8-aminoquinoline amides **369** to yield perfluoroalkylated quinolones **371** (Scheme 100).[130] Reaction scope was administered by using different perfluoroalkyl sources **370** such as $TMSC_2F_5$, TMS*n*-C_3F_7 and $TMSCF_3$. Based on the various control experiments, it was confirmed that reaction proceeds via single electron transfer mechanism.



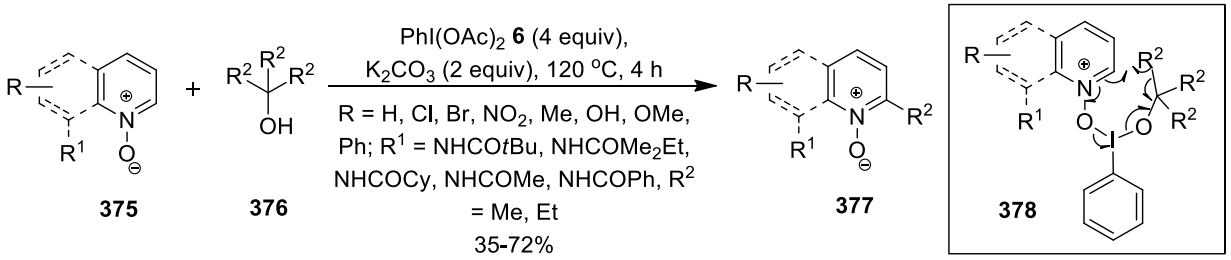
Scheme 100. PIDA-mediated C–H perfluoroalkylation of 8-aminoquinoline amides **369.**

Later, Maruoka and co-workers employed [bis(difluoroacetoxy)iodo]benzene **373** as the difluoromethylating agent for the C−H difluoromethylation of heteroarenes **372** (Scheme 101).[131] This reaction involves photolytic cleavage of iodine(III) reagent **373** on exposure to visible light (λ = 400 nm) generating difluoromethyl radical via decarboxylation that would react with heteroarenes **372** to deliver difluoromethylated products **374**. A series of heteroarenes **372** such as pentoxifylline, uraciles, pyridines, pyridazine, pyrimidines, triazine, pyrazine and pyrazole smoothly reacted under the optimized reaction conditions.



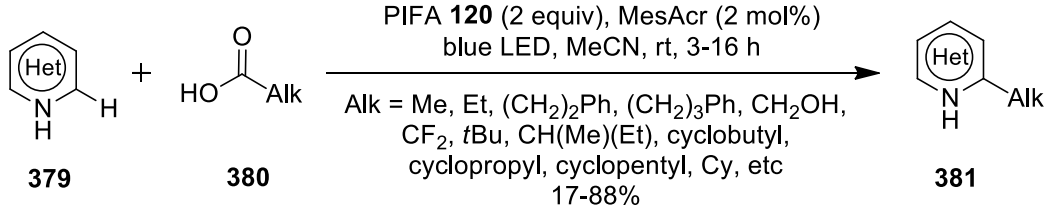
Scheme 101. C−H difluoromethylation of heteroarenes **372** using [bis(difluoroacetoxy)iodo]benzene **373** as difluoromethylating agent.

A regioselective C2-alkylation of N-heteroaromatic N-oxides **375** using *tert*-/sec-alkyl alcohol **376** as an alkylating reagent has been reported by Sen and Ghosh (Scheme 102).[132] This PIDA-promoted reaction involves formation of intermediate **378**, which upon homolytic C−C bond cleavage of alcohols (*via* SET pathway), followed by alkylation and final aromatization to deliver 2-alkylated products **377** in useful yields.



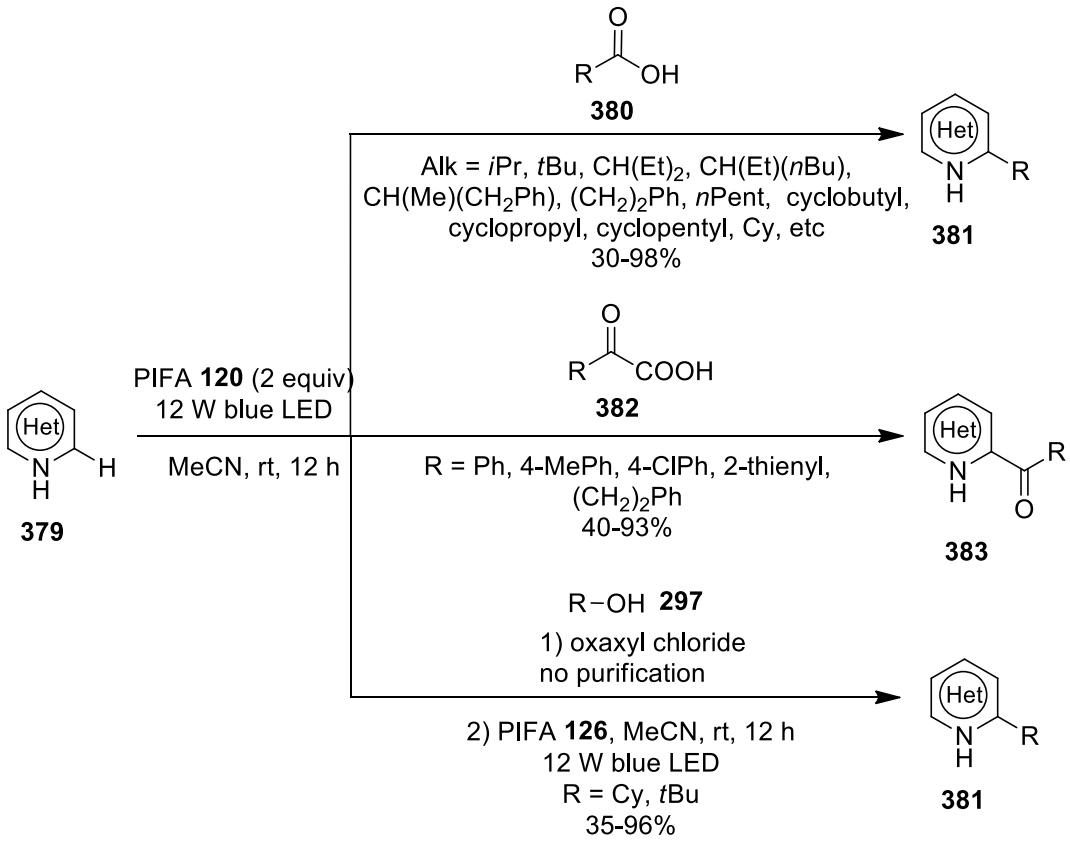
Scheme 102. PIDA-promoted C2-alkylation of N-heteroaromatic *N*-oxides **375** using secondary/tertiary alcohols **376** as an alkylating reagent.

Frenette's team developed a photoredox protocol featuring visible light-induced C−H alkylation of heteroaromatics **379** by using carboxylic acids **380** as coupling partner (Scheme 103).[133] The present decarboxylative coupling method employs organic photocatalyst, 9-mesityl-10-methyl acridinium and oxidant PIFA **120**. This catalytic system converts carboxylic acids **380** (primary, secondary and tertiary) into alkyl radicals that undergo radical substitution process to deliver corresponding alkylated products **381** in variable yields. Several heteroaromatic compounds **379** such as quinaldine, benzimidazole, benzothiazole, 2,6-dichloropurine, pyridines, pyrimidine, pyrazine and phthalazines were successfully tested under the optimized reaction conditions. Additionally, late-stage C−H functionalization of drugs such as Voriconazole, quinine and Varenicline were also achieved in variable yields.



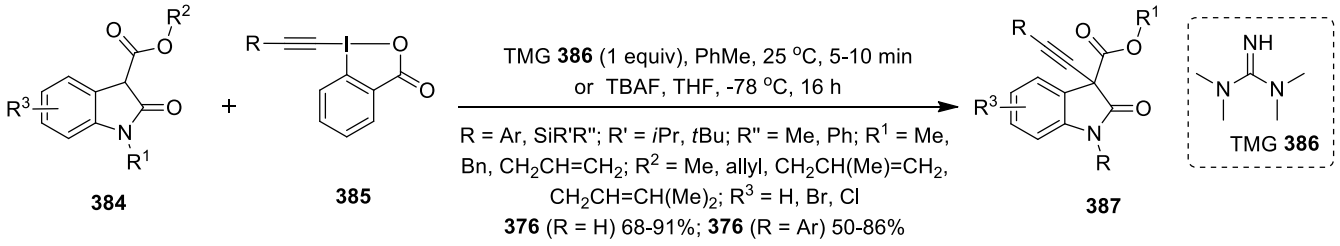
Scheme 103. PIDA-mediated C−H alkylation of heteroaromatics **379** using carboxylic acids **380** as coupling partner.

A similar decarboxylative coupling protocol was developed for the C−H alkylation of *N*-heterocycles **379** with carboxylic acids **380** as C-centered radical source and PIFA **120** as the oxidant (Scheme 104).[134] A variety of *N*-heterocycles **379** including quinolone, isoquinoline, and pyridine derivatives were smoothly transformed into the corresponding C2-alkylated products **381**. Moreover, decarboxylative C−H alkylation of *N*-heterocycles **379** with other carboxylic acid derivatives such as α-oxocarboxylates **382** and alcohol **297**-derived oxalates were also demonstrated under identical conditions. Very recently, Chen and co-workers disclosed similar photoredox catalysed C(sp^3)–H heteroarylation of aliphatic alcohols using perfluorinated hydroxybenziodoxole as an oxidant.[135]



Scheme 104. PIDA-mediated C−H alkylation/acylation of *N*-heterocycles **379.**

Using ethynyl-1,2-benziodoxol-3(1*H*)-one (EBX) **385** as an alkynylating reagent, Roy *et al.* carried out direct C3-alkynylation of 3-substituted-2-oxindoles **384** under metal-free conditions (Scheme 105).[136] Reaction works efficiently on variety of 2-oxindole-3-alkylcarboxylates **384** providing anticipated 3-alkynyl-3-alkyl/aryl 2-oxindoles **387** in significant yields. Further synthesized alkynylated products **387** were transformed into enantioenriched 2-oxindoles via Pd-catalyzed decarboxylative allylation in good yields with *ee* up to 96%.

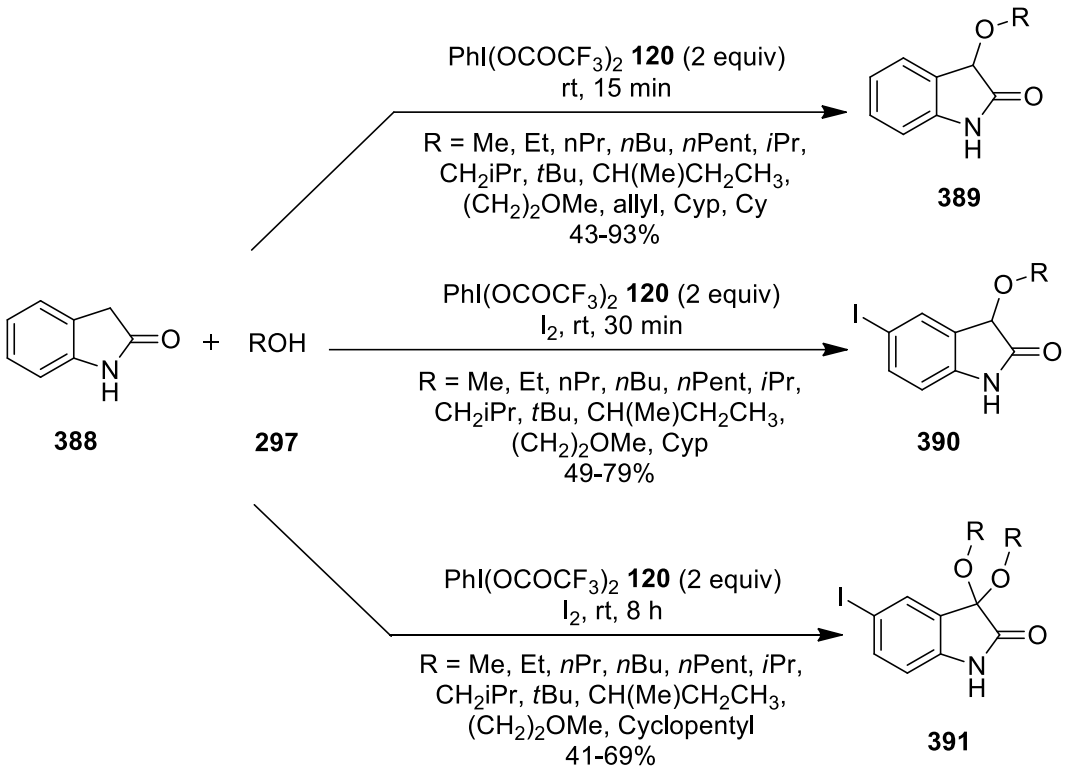


Scheme 105. Oxidative alkynylation of 3-substituted-2-oxindoles **384** using ethynyl-1,2-benziodoxol-3(1*H*)-one **385** as an alkynylating reagent.

3.3. Alkoxylation and acetoxylation of heterocycles

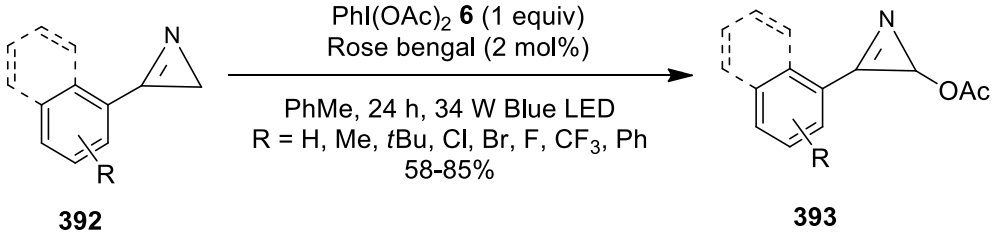
Kotagiri's group reported C-3 alkoxylation of simple oxindoles **388** *via* PIFA-mediated oxidative cross-coupling with different linear or branched alcohols **297** (Scheme 106).[137] This reaction provides 3-alkoxyoxindoles **389** in 43-93% yields under mild conditions in shorter reaction time. Further using PIFA/I_2 system, *in situ* iodo-

alkoxylation of oxindoles **388** resulted in the one-pot synthesis of 5-iodo-3-monoalkoxyoxindoles **390** or 5-iodo-3,3-dialkoxyoxindoles **391** in appreciable yields.



Scheme 106. PIFA-mediated oxidative cross-coupling of oxindoles **388** with alcohols **297.**

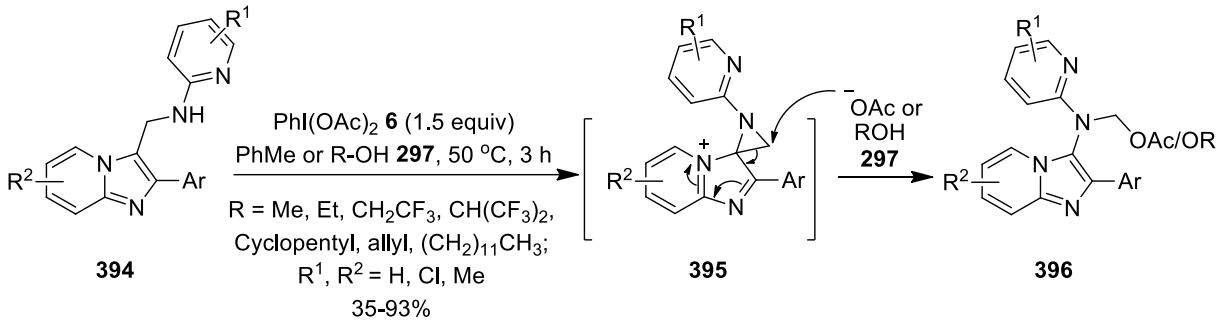
Later, Majee's research group performed visible-light-promoted C(sp^3)-H acetoxylation of aryl-2*H*-azirines **392** using PIDA **6** as the reagent.[138] Rose Bengal was used as the organophotoredox catalyst (Scheme 107). Reaction proceeds through radical pathway involving single electron transfer mechanism that requires presence of light irradiation. A library of acyloxylated azirines **393** was isolated in variable yields with excellent regioselectivity and functional group compatibility. Moreover, reaction occurs at room temperature under aerobic condition and applicable for gram scale synthesis.



Scheme 107. PIDA-mediated C(sp^3)-H acetoxylation of 2*H*-azirines **392** using rose bengal as the organophotoredox catalyst.

Very recently, Kumar and co-workers transformed imidazo[1,2-*a*]pyridine **394** into the corresponding *N*-acetoxymethyl/alkoxymethyl-*N*-arylimidazo[1,2-*a*]pyridine-3-amines **396** via PIDA-induced [1,2]-*ipso* migration

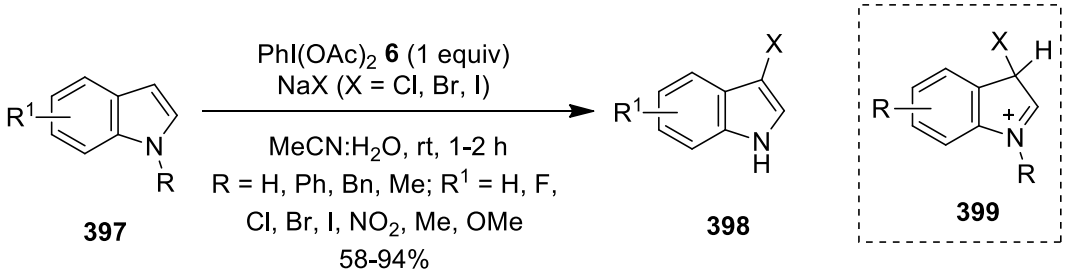
strategy (Scheme 108).[139] This reaction was proposed to proceed via Wheland-type aziridine intermediate **395** which upon subsequent ring opening assisted by acetate/alkoxy nucleophile delivers rearranged products **396**.



Scheme 108. PIDA-promoted synthesis of *N*-acetoxymethyl- and *N*-alkoxymethyl-N-arylimidazo[1,2-*a*]pyridine-3-amines **396.**

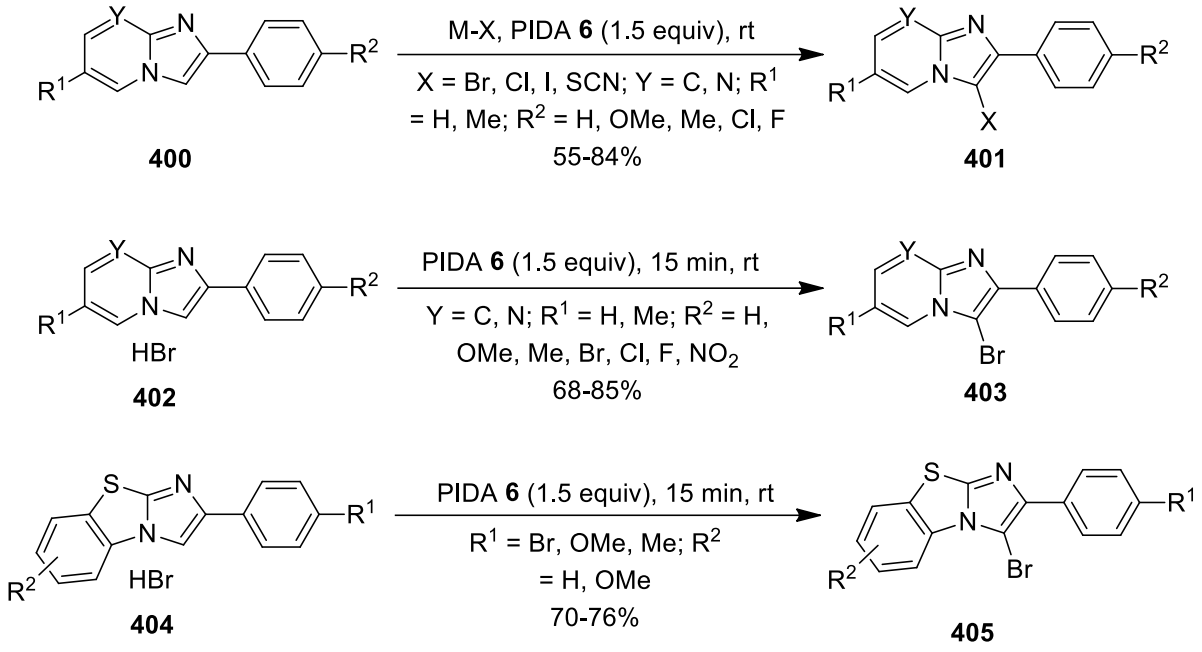
3.4. Halogenation/cyanation of heterocycles

In 2018, a mild method for the selective C–H halogenation of indoles **397** with $PhI(OAc)_2$ **6**/NaX system was developed by Rao and co-workers (Scheme 109).[140] This method is applicable for the chlorination, bromination and iodination of functionally diverse indoles providing privileged scaffold, 3-haloindoles **398** in moderate to excellent yields. Reaction mechanism involves PIDA-mediated oxidation of NaX generating positive halogen species (X^+) which is attacked by indole regioselectively at the C-3 position to form intermediate **399** and subsequent proton loss yields halo product **398**.



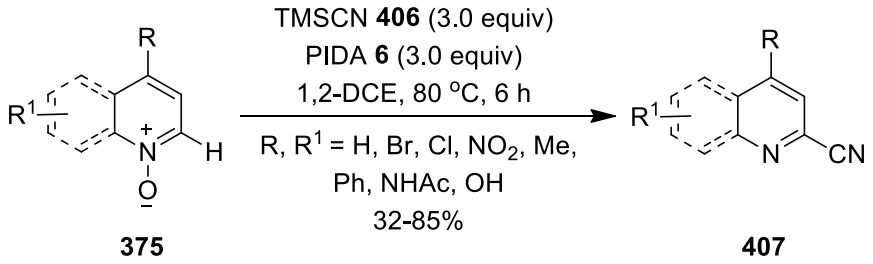
Scheme 109. PIDA-mediated C–H halogenation of indoles **397** using NaX as the halide source.

Further, Indukuri *et al.* devised a regioselective protocol for the C-3 halogenation/thiocyanation of imidazo[1,2-*a*]pyridines/pyrimidine **400** by grinding with alkali metal/ammonium salts (M-X) mediated by PIDA **6** (Scheme 110).[141] This method enabled greener synthesis of halogenated/thiocyanated imidazoheterocycles **401** under solvent-free conditions. Reaction mechanism possibly involves *in situ* formation of [acetoxy(halo/thiocyanato)iodo]benzene from PIDA **6** and M-X, which serve as source of X^+ species facilitating electrophilic substitution on electron-rich substrates **400**. Additionally, *in situ* bromination protocol was developed by utilizing HBr generated as by-product during the synthesis of fused *N*-heterocycles **402** and **404** from the condensation reaction of heterocyclic amine with bromoketone. The desired brominated products **403** and **405** are obtained in good yields.



Scheme 110. PIDA-mediated C-3 halogenation/thiocyanation of fused *N*-heterocycles **400**, **402** and **404.**

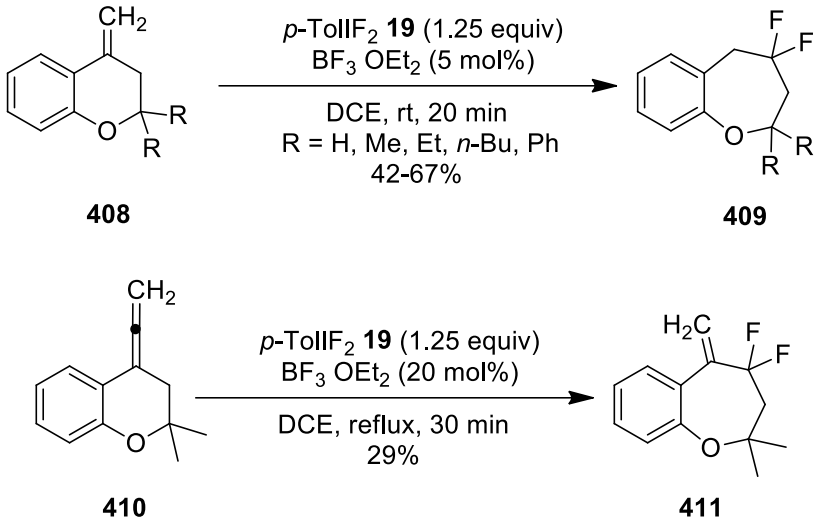
In 2019, Sun and co-workers developed a regioselective C-2 cyanation of quinoline *N*-oxides **375** by using trimethylsilyl cyanide **406** as an cyanating reagent with PIDA **6** as the oxidant (Scheme 111).[142] Notably, PIDA activates the substrates and accelerates cleavage of N-O bond. The present system showed remarkable compatibility for a wide range of substituents**;** particularly electron-rich substrates **375** produce 2-cyanoquinolines **407** in better yields as compared to electron-deficient ones. Moreover, the scope of the reaction was extended towards pyridine *N*-oxide and isoquinoline *N*-oxide and desired products were obtained in useful yields.



Scheme 111. PIDA-induced C-2 cyanation of quinoline N-oxides **375** by employing trimethylsilyl cyanide **406** as an cyanating reagent.

3.5. Ring expansion of heterocycles

In 2019, Murphy's research group realized fluorinative ring expansion of benzo-fused heterocycles **408** containing α-exocyclic alkene using *p*-(difluoroiodo)toluene **19** as fluorinating reagent (Scheme 112).[143] Anticipated ring expansion products **409** containing the β,β-difluoride moiety were isolated in valuable yields with shorter reaction time. Further fluorinative rearrangement of allene-based heterocycle **410** proceeded smoothly under similar conditions via 1,2-phenyl migration, to provide allylic gem-difluorides **411** in 29% yield.



Scheme 112. Synthesis of benzo-fused heterocycles **409** and **411** through ring expansion of **408** and **410** using *p*-TolIF$_2$ **19** as fluorinating reagent.

4. Conclusions

Hypervalent iodine compounds are valuable reagents in organic synthesis due to their ready availability, easy handling, environment benign nature and low toxicity. Excellent electrophilic nature and versatile oxidizing ability of these reagents makes them promising alternate candidates for the heavy metal oxidants/catalysts. This review article summarizes the recent developments in the construction of heterocyclic scaffolds using hypervalent iodine reagents. Various stoichiometric or catalytic protocols have been developed to achieve synthesis of monocyclic, bicyclic, polycyclic and spirocyclic heterocycles under mild reaction conditions. More importantly, substantial work in the stereoselective synthesis of different heterocycles using chiral hypervalent reagents has been done with excellent enantioselectivities. Moreover, the application of hypervalent iodine reagents in the late-stage functionalization of heterocycles has been discussed briefly. Furthermore, development of new catalytic transformations that generates iodine(III) species *in situ* would be area of main focus in future. Apart from this, designing chiral hypervalent iodine-mediated enantioselective reactions still remains a great challenge because of the limited availability of chiral reagents, unsatisfactory enantioselectivity and limited substrate scope. Thus, development of novel asymmetric transformations promoted by chiral iodine(III) species provides an interesting field of research.

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References

1. Yoshimura, A.; Zhdankin, V. V. *Chem. Rev.* **2016**, *116*, 3328. https://doi.org/10.1021/acs.chemrev.5b00547
2. Silva, Jr.; L. F.; Olofsson, B. *Nat. Prod. Rep.* **2011**, *28*, 1722. https://doi.org/10.1039/C1NP00028D
3. Yusubov, M. S.; Zhdankin, V. V. *Curr. Org. Synth.* **2012**, *9*, 247. https://doi.org/10.2174/157017912799829021
4. Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis, ed. T. Wirth, Topics in Current Chemistry, Springer-Verlag, **2016**, vol. 373.
5. Patai's Chemistry of Functional Groups: The Chemistry of Hypervalent Halogen Compounds, ed. B. Olofsson, I. Marek and Z. Rappoport, Wiley, **2019**.
6. Singh**,** F. V.; Wirth, T. Catalytic oxidation with hypervalent iodine In: *Catalytic Oxidation in Organic Synthesis*; Thieme; **2017**, *1*, 29. DOI 10.1055/sos-SD-225-23
7. Singh, F. V.; Wirth, T. Stereoselective reactions In *Patai's Chemistry of Functional Groups*, Eds. I.; John Wiley & Sons, Ltd: Chichester, **2018**.
8. Grelier, G.; Darses, B.; Dauban, P. *Beilstein J. Org. Chem.* **2018**, *14*, 1508. https://doi.org/10.3762/bjoc.14.128
9. Elsherbini, M.; Wirth, T. *Chem. Eur. J.* **2018**, *24*, 13399. https://doi.org/10.1002/chem.201801232
10. Hyatt, I. F. D.; Dave, L.; David, N.; Kaur, K.; Medard, M.; Mowdawalla, C. *Org. Biomol. Chem.* **2019**, *17*, 7822. https://doi.org/10.1039/C9OB01267B
11. Banerjee, S.; Bhoyare, V. W.; Patil, N. T. *Chem. Commun.* **2020**, *56*, 2677. https://doi.org/10.1039/D0CC00106F
12. Tohma, H.; Kita, Y. *Adv. Synth. Catal.* **2004**, *346*, 111. https://doi.org/10.1002/adsc.200303203
13. Mangaonkar, S. R.; Kole, P. B.; Singh, F. V. *Synlett* **2018**, *18*, 199. https://doi.org/10.1055/s-0036-1588575
14. Zhdankin, V. V. *ARKIVOC* **2009**, (*i*), 1. https://doi.org/10.3998/ark.5550190.0010.101
15. Merritt, E. A.; Olofsson, B. *Synthesis* **2011**, *4*, 517. https://doi.org/10.1055/s-0030-1258328
16. Dong, D.-Q.; Hao, S.-H.; Wang, Z.-L.; Chen, C. *Org. Biomol. Chem.* **2014**, *12*, 4278. https://doi.org/10.1039/C4OB00318G
17. Singh, F.V.; Wirth, T. *Synthesis*, **2013**, *45*, 2499. https://doi.org/10.1055/s-0033-1339679
18. Shetgaonkar, S. E.; Krishnan, M.; Singh, F. V. *Mini Rev. Org. Chem.* **2020**, *17*. https://doi.org/10.2174/1570193X17999200727204349
19. Li, X.; Chen, P.; Liu, G. *Beilstein J. Org. Chem.* **2018**, *14*, 1813. https://doi.org/10.3762/bjoc.14.154
20. Lee, J. H.; Choi, S.; Hong, K. B. *Molecules* **2019**, *24*, 2634. https://doi.org/10.3390/molecules24142634

21. Singh, F. V.; Wirth, T. *Synthesis* **2012**, *44*, 1171. https://doi.org/10.1055/s-0031-1290588
22. Singh**,** F. V.; Wirth, T. *Org. Lett.* **2011**, *13*, 6504. https://doi.org/10.1021/ol202800k
23. Singh, F. V.; Wirth, T. *Chem. Asian J.* **2014**, *9*, 950. https://doi.org/10.1002/asia.201301582
24. Heterocycles in Natural Product Synthesis Editor(s): Prof. Krishna C. Majumdar Prof. Shital K. Chattopadhyay https://doi.org/10.1002/9783527634880
25. Martins, P.; Jesus, J.; Santos, S.; Raposo, L. R.; Roma-Rodrigues, C.; Baptista, P. V.; Fernandes, A. R. *Molecules* **2015**, *20*, 16852. https://doi.org/10.3390/molecules200916852
26. Cabrele, C.; Reiser, O. *J. Org. Chem.* **2016**, *81*, 10109. https://doi.org/10.1021/acs.joc.6b02034.
27. Smith, C. A.; Narouz, M. R.; Lummis, P. A.; Singh, I.; Nazemi, A.; Li, C.-H.; Crudden, C. M. *Chem. Rev.* **2019**, *119*, 4986. https://doi.org/10.1021/acs.chemrev.8b00514
28. Gao, H.; Zhang, Q.; Shreeve, J. M. *J. Mater. Chem. A* **2020**, *8*, 4193. https://doi.org/10.1039/C9TA12704F
29. Taylor, A. P.; Robinson, R. P.; Fobian, Y. M.; Blakemore, D. C.; Jones, L. H.; Fadeyi, O. *Org. Biomol. Chem.* **2016**, *14*, 6611. https://doi.org/10.1039/C6OB00936K
30. Sun, J.; Zhang-Negrerie, D.; Du, Y.; Zhao, K. *Rep. Org. Chem.* **2016**, *6*, 25. https://doi.org/10.2147/ROC.S84894
31. Kandimalla, S. R.; Parvathaneni, S. P.; Sabitha, G.; Reddy, B. V. S. *Eur. J. Org. Chem.* **2019**, 1687. https://doi.org/10.1002/ejoc.201801469
32. Singh, F. V.; Kole, P. B.; Mangaonkar, S. R.; Shetgaonkar, S. E. *Beilstein J. Org. Chem.* **2018**, *14*, 1778. https://doi.org/10.3762/bjoc.14.152
33. Budhwan, R.; Yadav, S.; Murarka, S. *Org. Biomol. Chem.* **2019**, *17*, 6326. https://doi.org/10.1039/C9OB00694J
34. Mennie, K. M., Banik, S. M., Reichert, E. C.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2018**, *140*, 4797. https://doi.org/10.1021/jacs.8b02143
35. Glachet, T.; Marzag, H.; Rosa, N. S.; Colell, J. F. P.; Zhang, G.; Warren, W. S.; Franck, X.; Theis, T.; Reboul, V. *J. Am. Chem. Soc.* **2019**, *141*, 13689. https://doi.org/10.1021/jacs.9b07035
36. Zhang, G.; Wang, Y.; Xu, J.; Sun, J.; Sun, F.; Zhang, Y.; Zhang, C.; Du, Y. *Chem. Sci.* **2020**, *11*, 947. https://doi.org/10.1039/c9sc05536c
37. Mangaonkar, S.; Singh, F. V. *Synthesis* **2019**, *51*, 4473. https://doi.org/10.1055/s-0039-1690621
38. Singh, F. V.; Mangaonkar, S. R.; Kole, P. B. *Synth. Commun.* **2018**, *48*, 2169. https://doi.org/10.1080/00397911.2018.1479760
39. Asari, N., Takemoto, Y., Shinomoto, Y., Yagyu, T.; Yoshimura, A.; Zhdankin, V. V.; Saito, A. *Asian J. Org. Chem.* **2016**, *5*, 1314.

https://doi.org/10.1002/ajoc.201600383
40. Okamura, Y.; Sato, D.; Yoshimura, A.; Zhdankin, V.V.; Saito, A. *Adv. Synth. Catal.* **2017**, *359*, 3243. http://dx.doi.org/10.1002/adsc.201700587
41. Yi, W., Liu, Q.-Y., Fang, X.-X., Lou, S.-C.; Liu, G.-Q. *Org. Biomol. Chem.* **2018,** *16*, 7012. https://doi.org/10.1039/C8OB01474D
42. Yagyu, T., Takemoto, Y., Yoshimura, A., Zhdankin, V. V.; Saito, A. *Org. Lett.* **2017**, *19*, 2506. https://doi.org/10.1021/acs.orglett.7b00742
43. Xu, K.; Yang, S.; Ding, Z. *Org. Chem. Front.* **2020**, *7*, 69. https://doi.org/10.1039/c9qo01298b
44. Ranjith, J.; Rajesh, N.; Sridhar, B.; Krishna, P. R.; *Org. Biomol. Chem.* **2016**, 14, 10074. https://doi.org/10.1039/c6ob01752e
45. Kamouka, S.; Moran, W. J. *Beilstein J. Org. Chem.* **2017**, *13*, 1823. https://doi.org/10.3762/bjoc.13.177
46. Alhalib, A.; Kamouka, S.; Moran, W. J. *Org. Lett.* **2015**, *17*, 1453. https://doi.org/10.1021/acs.orglett.5b00333
47. Liu, G.-Q.; Yang, C.-H.; Li, Y.-M. *J. Org. Chem.* **2015**, *80*, 11339. https://doi.org/10.1021/acs.joc.5b01832
48. Jeon, H.; Kima, D.; Lee, J. H.; Song, J.; Lee, W. S.; Kang, D. W.; Kang, S.; Lee, S. B.; Choi, S.; Hong, K. B. *Adv. Synth. Catal.* **2018**, *360*, 779. https://doi.org/10.1002/adsc.201701087
49. Scheidt, F.; Thiehoff, C.; Yilmaz, G.; Meyer, S.; Daniliuc, C. G.; Kehr, G.; Gilmour, R. *Beilstein J. Org. Chem.* **2018**, *14*, 1021. https://doi.org/10.3762/bjoc.14.88
50. Carlucci, C.; Tota, A.; Colella, M.; Ronamazzi, G.; Clarkson, G. J.; Luisi, R.; Degennaro, L. *Chem. Heterocycl. Com.* **2018**, *54*, 428. https://doi.org/10.1007/s10593-018-2288-9
51. Singhal, A.; Parumala, S. K. R.; Sharma, A.; Peddinti, R. K. *Tetrahedron Lett.* **2016**, *57*, 719. http://dx.doi.org/10.1016/j.tetlet.2015.10.038
52. Kobayashi, E.; Togo, H. *Synthesis* **2019**, *51*, 3723. http://dx.doi.org/10.1055/s-0039-1690102.
53. Waheed, M., Ahmed, N., Alsharif, M. A.; Alahmdi, M. I.; Mukhtar, S. *ChemistrySelect* **2019**, *4*, 1872. https://doi.org/10.1002/slct.201803927
54. Park, S. W.; Kim, S.-H.; Song, J.; Park, G. Y.; Kim, D.; Nam, T.-G.; Hong, K. B. *Beilstein J. Org. Chem.* **2018**, *14*, 1028. https://doi.org/10.3762/bjoc.14.89
55. Yu, J.-M.; Cai, C. *Org. Biomol. Chem.* **2018**, *16*, 490. https://doi.org/10.1039/C7OB02892J
56. Yoshimura, A.; Nguyen, K. C.; Klasen, S. C.; Postnikov, P. S.; Yusubov, M. S.; Saito, A.; Nemykin, V. N.; Zhdankin, V. V. *Asian J. Org. Chem.* **2016**, *5*, 1128. http://dx.doi.org/10.1002/ajoc.201600247
57. Yoshimura, A.; Nguyen, K. C.; Klasen, S. C.; Saito, A.; Nemykina, V. N.; Zhdankin, V. V. *Chem. Commun.* **2015**, *51*, 7835. http://dx.doi.org/10.1039/c5cc02009c

58. Chauhan, J.; Ravva, M. K.; Sen, S. *Org. Lett.* **2019**, *21*, 6562. http://dx.doi.org/10.1021/acs.orglett.9b02542
59. Liu, B.; Shi, B.-F. *Synlett* **2016**, *27*, 2396. http://dx.doi.org/10.1055/s-0035-1562508
60. Yakura, T.; Horiuchi, Y.; Nishimura, Y.; Yamada, A.; Nambu, H.; Fujiwara, T. *Adv. Synth. Catal.* **2016**, *358*, 869. http://dx.doi.org/10.1002/adsc.201500795
61. Yakura, T.; Fujiwara, T.; Nishi, H.; Nishimura, Y.; Nambu, H. *Synlett* **2018**, *29*, 2316. http://dx.doi.org/10.1055/s-0037-1610657
62. Gelis, C., Dumoulin, A., Bekkaye, M., Neuville, L.; Masson, G. *Org. Lett.* **2017**, *19*, 278. http://dx.doi.org/10.1021/acs.orglett.6b03631
63. S.; Alazet, Vaillant, F. L.; Nicolai, S.; Courant, T.; Waser, J. *Chem. Eur. J.* **2017**, *23*, 9501. http://dx.doi.org/10.1002/chem.201702599
64. Kiyokawa, K.; Ito, R.; Takemoto, K.; Minakata, S. *Chem. Commun.* **2018**, *54*, 7609. http://dx.doi.org/10.1039/c8cc03735c
65. Kiyokawa, K.; Takemoto, K.; Yahata, S.; Kojima, T.; Minakata, S. *Synthesis* **2017**, *49*, 2907. http://dx.doi.org/10.1055/s-0036-1588987
66. Mizar, P.; Niebuhr, R.; Hutchings, M.; Farooq, U.; Wirth, T. *Chem. Eur. J.* **2016**, *22*, 1614. http://dx.doi.org/10.1002/chem.201504636
67. Kitamura, T.; Miyake, A.; Muta, K.; Oyamada, J. *J. Org. Chem.* **2017**, *82*, 11721. http://dx.doi.org/10.1021/acs.joc.7b01266
68. Huang, H.; Yang, Q.; Zhang, Q.; Wu, J.; Liu, Y.; Song, C.; Chang, J. *Adv. Synth. Catal.* **2016**, *358*, 1130. http://dx.doi.org/10.1002/adsc.201501071
69. Xu, H.; Liu, H.-W.; Chen, K.; Wang, G.-W. *J. Org. Chem.* **2018**, *83*, 6035. http://dx.doi.org/10.1021/acs.joc.8b00665.
70. Chen, H.; Kaga, A.; Chiba, S. *Org. Biomol. Chem.* **2016**, *14*, 5481. https://doi.org/10.1039/C5OB01854D
71. Ma, H.; Zhang, X.; Chen, L.; Yu, W. *J. Org. Chem.* **2017**, *82*, 11841. https://doi.org/10.1021/acs.joc.7b01361
72. Shen, K.; Wang, Q. *Org. Chem. Front*. **2016**, 3, 222. https://doi.org/10.1039/C5QO00353A
73. Shen, K.; Wang, Q. *J. Am. Chem. Soc.* **2017**, *139*, 13110. https://doi.org/10.1021/jacs.7b06852
74. T.; Borelli, S.; Brenna, G.; Broggini, J.; Oble, Poli, G., *Adv. Synth. Catal.* **2017**, *359*, 623. https://doi.org/10.1002/adsc.201600813
75. Han, Y.; Sun, Y.; Abdukader, A.; Liu, B.; Wang, D. *Catal. Lett.* **2018**, *148*, 3486. https://doi.org/10.1007/s10562-018-2541-y
76. Broggini, G.; Beccalli, E. M.; Borelli, T.; Brusa, F.; Gazzola, S.; Mazza, A. *Eur. J. Org. Chem.* **2015**, 4261. https://doi.org/10.1002/ejoc.201500386
77. Wang, H.; Frings, M.; Bolm, C. *Org. Lett.* **2016**, *18*, 2431. https://doi.org/10.1021/acs.orglett.6b00958
78. Walters, J. C.; Tierno, A. F.; Dubin, A. H.; Wengryniuk, S. E. *Eur. J. Org. Chem.* **2018**, 1460. http://dx.doi.org/10.1002/ejoc.201800118

79. McNally, A.; Haffemayer, B.; Collins, B. S. L.; Gaunt, M. J. *Nature*, **2014**, *510*, 129. http://dx.doi.org/10.1038/nature13389
80. Nappi, M.; He, C.; Whitehurst, W. G.; Chappell, B. G. N.; Gaunt, M. J. *Angew. Chem.* **2018**, *130*, 3232. http://dx.doi.org/10.1002/anie.201800519
81. Tao, J.; Estrada, C. D.; Murphy, G. K. *Chem. Commun.* **2017**, *53*, 9004. https://doi.org/10.1039/C7CC04859A
82. Yoshimura, A.; Nguyen, K. C.; Rohde, G. T.; Saito, A.; Yusubov, M. S.; Zhdankin, V. V. *Adv. Synth. Catal.* **2016**, *358*, 2340. http://dx.doi.org/10.1002/adsc.201600331
83. Yoshimura, A.; Nguyen, K. C.; Rohde, G. T.; Postnikov, P. S.; Yusubov, M. S.; Zhdankin, V. V. *J. Org. Chem.* **2017***, 82,* 11742. http://dx.doi.org/10.1021/acs.joc.7b01462
84. Xu, T.; Wang, D.; Tong, X. *Org. Lett.* **2019**, *21*, 5368. http://dx.doi.org/10.1021/acs.orglett.9b02096
85. Bedford, R. B.; J. G.; Bowen, Méndez-Gálvez, C. *J. Org. Chem.* **2017**, *82*, 1719. http://dx.doi.org/10.1021/acs.joc.6b02970
86. Li, H.; Li, X.; Yu, Y.; Li, J.; Liu, Y.; Li, H.; Wang, W. *Org. Lett.* **2017**, *19*, 2010. http://dx.doi.org/10.1021/acs.orglett.7b00566
87. Nakamura, A.; Tanaka, S.; Imamiya, A.; Takane, R.; Ohta, C.; Fujimura, K.; Maegawa, T.; Miki, Y. *Org. Biomol. Chem.* **2017**, *15*, 6702. https://doi.org/10.1039/C7OB01536D
88. Xia, H.-D.; Zhang, Y.-D.; Wang, Y.-H.; Zhang, C. *Org. Lett.* **2018**, *20*, 4052. https://doi.org/10.1021/acs.orglett.8b01615
89. Bose, A.; Maiti, S.; Sau, S.; Mal, P. *Chem. Commun.* **2019**, *55*, 2066. https://doi.org/10.1039/c8cc09100e
90. Bose, A., Sau, S.; Mal, P. *Eur. J. Org. Chem.* **2019**, 4105. https://doi.org/10.1002/ejoc.201900732
91. Singh, F. V.; Mangaonkar, S. R. *Synthesis* **2018**, *50*, 4940. https://doi.org/10.1055/s-0037-1610650
92. Mangaonkar, S. R.; Shetgaonkar, S. E.; Vernekar, A. A.; Singh. F. V. *ChemistrySelect* **2020**, *5*, 10754. https://doi.org/10.1002/slct.202002860
93. Zhang, H.; Shen, J.; Yang, Z.; Cui, X. *RSC Adv.* **2019**, *9*, 7718. https://doi.org/10.1039/c9ra01200a
94. Chen, T.; Chen, X.; Wei, J.; Lin, D.; Xie, Y.; Zeng, W. *Org. Lett.* **2016**, *18*, 2078. https://doi.org/10.1021/acs.orglett.6b00709
95. Ding, Q., He, H.; Cai, Q. *Org. Lett.* **2018**, *20*, 4554. https://doi.org/10.1021/acs.orglett.8b01849
96. Fan, H.; Pan, P.; Zhang, Y.; Wang, W. *Org. Lett.* **2018**, *20*, 7929. https://doi.org/10.1021/acs.orglett.8b03503
97. Woerly, E. M.; Banik, S. M.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2016**, *138*, 13858. https://doi.org/10.1021/jacs.6b09499
98. Möckel, R., Babaoglu, E.; Hilt, G. *Chem. Eur. J.* **2018**, *24*, 15781. https://doi.org/10.1002/chem.201804152

99. Zhang, H.; Shen, J.; Cheng, G.; Feng, Y.; Cui, X. *Org. Lett.* **2018**, *20*, 664. https://doi.org/10.1021/acs.orglett.7b03804
100. Kelley, B. T.; Walters, J. C.; Wengryniuk, S. E. *Org. Lett.* **2016**, *18*, 1896. https://doi.org/10.1021/acs.orglett.6b00672
101. Yamakoshi, W.; Arisawa, M.; Murai, K. *Org. Lett.* **2019**, *21*, 3023. https://doi.org/10.1021/acs.orglett.9b00559
102. Maiti, S.; Mal, P. *Org. Lett.* **2017**, *19*, 2454. https://doi.org/10.1021/10.1021/acs.orglett.7b01117
103. Maiti, S., Achar, T. K.; Mal, P. *Org. Lett.* **2017**, *19*, 2006. https://doi.org/10.1021/acs.orglett.7b00562
104. Bal, A., Maiti, S., Mal, P. *J. Org. Chem.* **2018**, *83*, 11278. https://doi.org/10.1021/acs.joc.8b01857
105. Murai, K.; Kobayashi, T.; Miyoshi, M.; Fujioka, H. *Org. Lett.* **2018**, *20*, 2333. https://doi.org/10.1021/acs.joc.8b01857
106. Shimogaki, M.; Fujita, M.; Sugimura, T. *Angew. Chem. Int. Ed.* **2016**, *55*, 15797. http://dx.doi.org/10.1002/anie.201609110
107. Waghmode, N. A.; Kalbandhe, A. H.; Thorat, P. B.; Karade N. N.; *Tetrahedron Lett.* **2016**, *57*, 680. https://doi.org/10.1016/j.tetlet.2015.12.117
108. Hong, F.; Lu, N.; Lu, B.; Cheng, J. *Adv. Synth. Catal.* **2017**, *359*, 3299. https://doi.org/10.1002/adsc.201700761
109. Chen, X.-Y.; Zhang, C.-Shen.; Yi, L.; Gao, Z.-H.; Wang, Z.-X.; Ye, S. *CCS Chem.* **2019**, *1*, 343. http://dx.doi.org/10.31635/ccschem.019.20190020
110. Deng, Q.; Xia, W.; Hussain, M. I.; Zhang, X.; Hu, W.; Xiong, Y. *J. Org. Chem.* **2020**, *85*, 3125. https://dx.doi.org/10.1021/acs.joc.9b03012
111. Zhang, D.-Y.; Xu, L.; Wu, H.; Gong, L.-Z. *Chem. Eur. J.* **2015**, *21*, 10314. http://dx.doi.org/10.1002/chem.201501583
112. Laevens, B. A.; Tao, J.; Murphy, G. K. *J. Org. Chem.* **2017**, *82*, 11903. http://dx.doi.org/10.1021/acs.joc.7b01639
113. Uyanik, M.; Sasakura, N.; Mizuno, M.; Ishihara, K. *ACS Catal.* **2017**, *7*, 872. https://doi.org/10.1021/acscatal.6b03380
114. Uyanik, M., Yasui, T.; Ishihara, K. *J. Org. Chem.* **2017**, *82*, 11946. https://doi.org/10.1021/acs.joc.7b01941
115. Hempel, C., Maichle-mössmer, C.; Pericas, M. A.; Nachtsheim, B. J. *Adv. Synth. Catal.* **2017**, *359*, 2931. http://dx.doi.org/10.1002/adsc.201700246
116. Abazid, A. H.; Nachtsheim, B. J. *Angew. Chem. Int. Ed.* **2020**, *59*, 1479. https://doi.org/10.1002/anie.201912023
117. Ogasawara, M.; Sasa, H.; Hu, H.; Amano, Y.; Nakajima, H.; Takenaga, N.; Nakajima, K.; Kita, Y.; Takahashi, T.; Dohi, T. *Org. Lett.* **2017**, *19*, 4102. https://doi.org/10.1021/acs.orglett.7b01876
118. Imrich, M. R.; Ziegler, T. *Tetrahedron Lett.* **2019**, *60*, 150954. https://doi.org/10.1016/j.tetlet.2019.150954
119. Antien, A. K., Pouysegu, L., Deffieux, D., Peixoto, P. A.; Quideau, S. *Chem. Eur. J.* **2019**, *25*, 2852. https://doi.org/10.1002/chem.201805761

120. Zhao, G.-H.; Li, B.-Q.; Wang, S.-S.; Liu, M.; Chen, Y.; Wang, B. *J. Org. Chem.* **2020**, *85*, 14, 9367. https://doi.org/10.1021/acs.joc.0c00971
121. Xing, Q.; Liang, H.; Bao, M.; Li, X.; Zhang, J.; Bi, T.; Zhang, Y.; Xu, J.; Du, Y.; Zhao, K. *Adv. Synth. Catal.* **2019**, *361*, 4669. https://doi.org/10.1002/adsc.201900652
122. Jain, N., Xu, S.; Ciufolini, M. A. *Chem. A Eur. J.* **2017**, *23*, 4542. https://doi.org/10.1002/chem.201700667
123. Deng, R.; Zhan, S.; Li, C.; Gu, Z. *Angew. Chem.* **2020**, *59*, 3093. https://doi.org/10.1002/ange.201913373
124. Tariq, M. U.; Moran, W. J. *Eur. J. Org. Chem.* **2020**, 5153. https://doi.org/10.1002/ejoc.202000840
125. Odagi, M.; Okuda, K.; Ishizuka, H.; Adachi, K.; Nagasawa, K. *Asian J. Org. Chem* **2020**, *9*, 218. https://doi.org/10.1002/ajoc.201900726
126. Mondal, S.; Samanta, S.; Jana, S.; Hajra, A. *J. Org. Chem.* **2017**, *82*, 4504. https://doi.org/10.1021/acs.joc.7b00564
127. Sun, B.; Yan, Z.; Jin, C.; Su, W. *Synlett* **2018**, *29*, 2432. https://doi.org/10.1055/s-0037-1610293
128. Lu, N. ; Huang, L.; Xie, L.; Cheng, J. *Eur. J. Org. Chem.* **2018**, 3437. http://dx.doi.org/10.1002/ejoc.201800416
129. Chen, W.-T.; Gao, L.-H.; Bao, W.-H.; Wei, W.-T. *J. Org. Chem.* **2018**, *83*, 11074. https://doi.org/10.1021/acs.joc.8b01678
130. Xu, J.; Qiao, L.; Ying, B.; Zhu, Xi.; C. Shen, Zhang, P. *Org. Chem. Front.* **2017**, *4*, 1116. https://doi.org/10.1039/c6qo00655h
131. Sakamoto, R.; Kashiwagi, H.; Maruoka, K. *Org. Lett.* **2017**, *19*, 5126. https://doi.org/10.1021/acs.orglett.7b02416
132. Sen, C.; Ghosh, S. C. *Adv. Synth. Catal.* **2018**, *360*, 905. https://doi.org/10.1002/adsc.201701330
133. Genovino, J.; Lian, Y.; Zhang, Y.; Hope, T. O.; Juneau, A.; Gagné, Y.; Ingle, G.; Frenette, M. *Org. Lett.* **2018**, *20*, 3229. https://doi.org/10.1021/acs.orglett.8b01085
134. Zhang, X.-Y.; Weng, W.-Z.; Liang, H.; Yang, H.; Zhang, B. *Org. Lett.* **2018**, *20*, 4686. https://doi.org/10.1021/acs.orglett.8b02016
135. Li, G.-X.; Hu, X.; He G.; Chen, G. *Chem. Sci.* **2019**, *10*, 688. https://doi.org/10.1039/c8sc04134b
136. Roy, A.; Das, M. K.; Chaudhuri, S.; Bisai, A. *J. Org. Chem.* **2018**, *83*, 403. https://doi.org/10.1021/acs.joc.7b02797
137. Kotagiri, R.; Adepu, R. *Eur. J. Org. Chem.* **2018**, 4556. https://doi.org/10.1002/ejoc.201800723
138. De, A.; Santra, S.; Hajra, A.; Zyryanov, G. V.; Majee, A. *J. Org. Chem.* **2019**, *84*, 11735. http://dx.doi.org/110.1021/acs.joc.9b01625
139. Patel, O. P. S.; Jaspal, S.; Shinde, V. N.; Nandwana, N. K.; Rangan, K.; Kumar A. *J. Org. Chem.* **2020**, *85*, 7309. https://dx.doi.org/10.1021/acs.joc.0c00674

140. Himabindu, V.; Parvathaneni, S. P.; Rao, V. J. *New J. Chem.* **2018**, *42*, 18889. https://dx.doi.org/10.1039/c8nj03822h
141. Indukuri, D. R.; Potuganti, G. R.; Alla, M. *Synlett* **2019**, *30*, 1573. https://dx.doi.org/10.1055/s-0037-1611856
142. Xua, F.; Li, Y.; Huang, X.; Fang, X.; Li, Z.; Jiang, H.; Qiao, J.; Chu, W.; Sun, Z. *Adv. Synth. Catal.* **2019**, *361*, 520. https://doi.org/10.1002/adsc.201801185
143. Zhao, Z.; To, A. J.; Murphy, G. K. *Chem. Commun.* **2019**, *55*, 14821. https://doi.org/10.1039/C9CC08310C

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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

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