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

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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, $\alpha$-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\textsuperscript{1} and natural product chemistry.\textsuperscript{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.\textsuperscript{3} Synthetic applications of these reagents have seen exponential growth as realised by several books,\textsuperscript{4,5} chapters in books\textsuperscript{6,7} and comprehensive reviews\textsuperscript{8-11} published in this area. Both iodine(III) and iodine(V) compounds (also known as \(\lambda^3\)-iodane and \(\lambda^5\)-iodane) have been commonly used as reagents in the oxidative transformations of various simple and complex organic molecules.\textsuperscript{12-14} Most importantly, the unique reactivity and oxidizing ability of \(\lambda^3\)- and \(\lambda^5\)-iodanes has prompted their use as efficient oxidants in a variety of synthetic transformations including \(\alpha\)-functionalization of carbonyl compounds,\textsuperscript{15,16} oxidative rearrangements,\textsuperscript{17,18} alkene defunctionalization\textsuperscript{19,20} and cyclization reactions.\textsuperscript{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.\textsuperscript{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.\textsuperscript{24-26} Moreover, importance of heterocyclic compounds in material science\textsuperscript{27,28} and pharmaceutical\textsuperscript{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 \textit{et al.},\textsuperscript{30} Kandimalla \textit{et al.},\textsuperscript{31} and Singh \textit{et al.}\textsuperscript{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.\textsuperscript{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.\textsuperscript{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 \textit{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.\textsuperscript{30-32} Most of these reactions employ iodine(III)/(V) reagents as stoichiometric oxidants. Apart from this, several catalytic systems involving \textit{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 achieved using chiral iodoarenes as precatalyst. In this section, hypervalent iodine-mediated synthesis of three-\textendash five-\textendash 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 \textit{syn}-\textit{β}-fluoroaziridines 3 from cinnamylamine derivatives 1 using a catalytic amount of chiral aryl iodide 2 (Scheme 1).\textsuperscript{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 mCPBA. 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). 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 NH3) 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 15N2-diazirines was achieved from unlabelled amino acids using 15NH3 as a nitrogen source. Finally, hyperpolarization of 15N2-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 mCPBA-mediated oxidation of α-nitroiodobenzene (Scheme 3). The synthesized iodine(III/V) compound 10 proved to be effective oxidant in preparing 2H-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 2H-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). 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.

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 cycloisomerization-fluorination sequence (Scheme 5).\(^{39}\) This reaction occurs by employing either catalytic 4-iodoanisole 18/HF-pyridine/Selectfluor system (Method A) or stoichiometric p-TollF\(_2\)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(azides) 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).

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/mCPBA/Tf\(_2\)NH catalytic system (Scheme 6).\(^{42}\) This oxidative annulation represents the first example of iodine catalysis in multicomponent 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 mCPBA 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)NTf₂ involved was isolated as an aquo-[18C6] complex in 43% yield under the optimized conditions.

![Scheme 6](image)

**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. Reaction was carried out in the presence of BF₃·OEt₂ 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](image)

**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). 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. The first method involves intramolecular cyclization of N-propargylamides 17 while other involves cyclization of β-amidoketones 42 using 2-iodoanisole 18 as precatalyst with mCPBA 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.
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). In the presence of PIDA 6 (1.0 equiv) and Lil (1.0 equiv), iodo cyclization 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). The proposed mechanism for this inter-/intra aminohydroxylation reaction involves in situ generation of PhI(OAc)(NR1R2) or PhI(NR1R2)2 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.
Further, Scheidt et al. provided a direct route to 2-oxazolines 52 incorporating a fluoromethyl group from N-allylcarboxamides 45 following I(II)/I(III) catalysis (Scheme 12). The success of this fluoroxygenation reaction lies in its efficient generation of active iodine(III) species, p-TolIF₂ 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 Et₃N·3HF and Olah's reagent (Pyr·HF).

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). 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.
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). 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.

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 NH₂OH, NCS and alkynes 59 (Scheme 15). 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 NH₂OH·HCl with NH₂NHPh in the second step under similar conditions.

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-propargylocoumarin 66 via PIDA-mediated sequential oxidative cyclization and [3+2] cycloaddition reaction (Scheme 16). 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). Notably, activation of Phl(OAc)₂ 6 by BF₃·OEt₂ 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. 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 \( \beta,\gamma \)-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-iodosylbenzoic acid triflate (IBA-OTf) 75 as stoichiometric oxidant (Scheme 18).\(^5^6\) The reagent IBA-OTf 75 was previously prepared by the same group from iodosylbenzoic and trifluoromethanesulfonic acid.\(^5^7\) 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 electron-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-anisoly 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(sp³)–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(sp³)–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 Phl(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-iodobenzoamide 98 in the presence of co-oxidant oxone (Scheme 23). 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.

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-phosphoryloxylationactonatization of 4-pentenoic acid derivatives 101 (Scheme 24).62 Using stoichiometric or catalytic amount of C2 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 sulfonyloxylationactonization 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.
Minakata and co-workers investigated intramolecular lactonization of tertiary carbon containing carboxylic acids employing iodic acid (HIO$_3$) 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 $\gamma$-lactones 114 in respectable yields under metal-free conditions.

The same team prepared furan-2(5H)-ones 116 via oxidative cyclization of various $\beta,\gamma$-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$_3$SiOTf, plays crucial role of oxidant. Both aromatic and aliphatic substituents at the $\beta$-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(3H)-one products 118 in 54-68% yields.

Scheme 27. PIDA-induced synthesis of furan-2(5H)-ones 116 and furan-2(3H)-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(OOCOCF₃)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 \( \text{PhI(OAc)}_2 \) 6 and pyridine-HF complex as a fluorine source (Scheme 29). 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 \( \text{PhI(OCOF}_3\text{)}_2 \) 120 via Hofmann rearrangement–ring expansion cascade reaction (Scheme 30). 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-pyrrole derivatives 127 using \( \text{PhI(OCOF}_3\text{)}_2 \) 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). 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.

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 AcO$I$ from I$_2$ and PIDA 6 to yield iodide 135, which upon subsequent intramolecular $S_N$2-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 amidamidation of allyl ketone tosylhydrazones 136 by employing PIDA 6 as an oxidant and BF$_3$.OEt$_2$ as the promoter (Scheme 33). 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). This cascade reaction proceeds through the generation of N-centered radical 140 from corresponding N-H bond, that undergoes sequential radical cyclization and sulfonylation/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-allylamidines 141 using Et₃N.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 Ph[OOC(Pr)₂Me]₂ 142 as an oxidant.

In the following year Yu’s research group designed a domino azidation/C(sp³)−H amination strategy for the transformation of N-alkyl enamines 144 into 2,4,5-trisubstituted imidazoles 146 by reacting with TMSN₃ 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-trisubstituted 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 CF₃-group onto the lactam ring 149 via Cu-catalyzed intramolecular aminotrifluoromethylation
of unsaturated amides 147 (Scheme 37).\textsuperscript{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 CF₃-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.\textsuperscript{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.](image)

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).\textsuperscript{74} The proposed reaction mechanism possibly involves oxidation of Pd(OAc)₂ by PIFA 120 to generate Pd(O₂CCF₃)₄ in situ, which initiates allylic C–H activation to form η³-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 H2O2 (Scheme 40).75 This protocol provides an easy access to the biologically important 2-amino-1,3,4-thiadiazoles 159 in moderate to high yields. Aromatic, heteroaromatic and alkyl aldehydes were well tolerated.

Scheme 40. Synthesis of 2-amino-1,3,4-thiadiazoles 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, 
H₂O₂ oxidizes Phl 13 to generate Phl(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, Brogginì et al. performed Pd(II)-catalyzed inter-
intramolecular aminoacetoxylation of glycine allylamides 162 to prepare 5-acetoxymethyl-substituted
piperazinones 163 employing Phl(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 Phl(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 Phl(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). 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). 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 Phl 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 Phl(O2CCCH3)2 6 (Scheme 45).74 The reaction was carried out in the presence of AcONa and Bu4NH2SO4 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 λ3-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.
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)\textsubscript{2}/Phl(OAc)\textsubscript{2} catalytic system (Scheme 47).\textsuperscript{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 $\gamma$-C–H amination of substituted morpholinones 179 containing $\alpha$-ethyl group.\textsuperscript{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 $\alpha$-position to the amine were well tolerated, unlike in the previous developed protocol.\textsuperscript{79}

![Scheme 46](image-url)
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). The reaction was mediated by Phl(OAc)2 6 in the presence of Bu4NI 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). 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 mCPBA 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). 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 acetoxyductive (3 + 2) cycloaddition of 1,6-enynes 192 in a 6-exo manner via Pd(II)−Pd(IV) catalysis. 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 acetoxy palladation process, following which alkyne 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 Phl(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). The presence of the additional coordinating ligand for Pd(IV) obstruct the direct C–O bond reductive elimination and promotes reaction via a S$_n$2-type C–C reductive elimination pathway.
Scheme 52. Synthesis of 3-bicyclo[4.1.0]-heptan-5-one products 200 using oxidant Phl(OAc)$_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). 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). This transformation took place via Michael addition-[3 + 2] annulation of 2-substituted 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).\textsuperscript{87} Subsequent treatment with K\textsubscript{2}CO\textsubscript{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\textsubscript{3} \cdot OEt\textsubscript{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\textsubscript{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 Phl(OAc)$_2$ 6 with NH$_2$SO$_3$H 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-mCPBA 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-mCPBA-HFIP system. 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 Phl(OAc)2 6 as the catalyst and m-CPBA as the oxidant (Scheme 59). 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 Phl 13 (10 mol %) as precatalyst in the presence of terminal oxidant m-CPBA and additive trifluoroacetic acid in CHCl3.

**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. Intramolecular cyclization of 225 gives intermediate 226, which upon reductive elimination yields anticipated product 224 with the release of Phl 13. Further Phl 13 could be reoxidized to active iodine(III) species 6 in the presence of mCPBA 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). 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 Phl 13 and AcOH. Finally, oxidation of 230 in the presence of oxygen forms 231, which gives final product 228 with the elimination of CH₃COOH. Previously, Zheng and co-workers had constructed quinoxaline scaffolds through Phl(OAc)₂-mediated cascade cycloamination of N-aryl ketimines by employing sodium azide as the nitrogen source under copper catalysis.
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 \textit{in situ} generated chiral hypervalent iodine(III) species from diiodospirobiindane derivative 233 in the presence of \textit{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 \textit{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). 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$_6$H$_4$I(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 arylidene radical-mediated oxidation gives benzylic cation intermediate 242 with loss of ArI (4-FC$_6$H$_4$I). Finally, E1 elimination of 242 delivers desired product 237.

Scheme 64. Plausible mechanism of synthesis of 2-quinolinones 237 using 4-FC$_6$H$_4$I(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). Reaction employs HF-pyridine as a nucleophilic fluorinating reagents and mCPBA 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). 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]oxazines 249 from N-(2-hydroxaryl)enaminones 248 using PIDA 6 under air atmosphere (Scheme 67). 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 Et₃N-promoted oxidation of 252 under O₂ 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 O₂. 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). 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). 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). This tandem C−C/C−N bond forming reaction involves simultaneous functionalization of three C(sp²)−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. 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–mCPBA 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.
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). 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 iodo benzene 13 (20 mol %) and terminal oxidant mCPBA. 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 Cs₂CO₃ 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). This method comprises Phl(OAc)₂-promoted 1,2-C-to-N alkyl migration of secondary amines 274 followed by subsequent reduction using NaCNBH₃ 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-silyloxyhex-3-ene 276 promoted by lactate-based chiral iodine(III) reagent 277, 278 and 279 in the presence of BF$_3$·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 7H-chromeno[3,2-c]quinolones 288 from arylols 287 and substituted arylidine(III) reagents 286 through cascade O-arylation and palladium-catalyzed C(sp^3)-H arylation process (Scheme 77). 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 7H-chromeno[3,2-c]quinolones 288 and benzopyranone derivative 290 using trivalent arylidene 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).\(^\text{109}\) 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-λ³-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 dearomatizzative 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 dearomatizzative 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). 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-\(\lambda^3\)-iodanes generated \textit{in situ} through mCPBA-mediated oxidation of chiral iodoarene \(102\) catalyze this asymmetric spirocyclization reaction.

![Scheme 80](image)

**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). 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](image)

**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). 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 mCPBA as an oxidant (Scheme 83). 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. This method provided spirolactones 312 in variable yields and high enantioselectivity, facilitated by in situ generated hypervalent iodine(III) species using terminal oxidant mCPBA (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. 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). Further, Imrich and Ziegler prepared the first
carbohydrate-based chiral aryl iodide catalyst 315 by condensing partially protected glucosides with iodoresorcinol via Mitsunobu reaction. This catalyst was further employed for the oxidative spiro lactonisation of 309 to provide spiro lactone 312 in 77% yield with $er$ up to 80:20. Later, Quideau’s research group succeeded in constructing helicene-based chiral iodoarene catalyst 316 from inexpensive precursors (L)-(−)-tartaric acid and 4-methylstyrene. This novel chiral catalyst 316 served as catalyst for the dearomative spiro lactonization of 309 to afford chiral spiro lactones 312 with moderate selectivity. Notably, reaction catalyzed by catalyst 306 and 307 gives (R)-isomer 312.

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

Very recently, PhI(OOCF$_3$)$_2$-induced dearomatizing spirocyclization of various phenolic biarylic ketones 317 was by demonstrated by Wang’s research team (Scheme 86). 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](image)

**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). 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](image)

**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.
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 mCPBA (Scheme 89). 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 9H-fluoren-9-ol derivatives 330 promoted by iodosobenzene 331. 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 alkoxyiodine(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 1H-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_{2}O probably accounts for the high diastereoselectivity.\(^{123}\)

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 \(\lambda^3\)-iodane generated \textit{in-situ} from \(4\text{-MeC}_6\text{H}_4\)I \(51/m\)-CPBA catalytic system (Scheme 92).\(^{124}\) Authors predicted that the \(\lambda^3\)-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-arylpropanamides \(232\) via an asymmetric desymmetrization strategy (Scheme 93).\(^{95}\) The protocol was catalyzed by hypervalent iodine(III) species generated \textit{in situ} from chiral precatalyst diiodospirobiindane \(233\) in the presence of \(m\)CPBA as the terminal oxidant. \textit{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.
Odaghi 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). 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 to generate key aryl-λ3-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(sp2)–H amination of imidazopyridines 352 (Scheme 95). 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 \(\alpha\)-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(sp³)–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). This reaction proceeds through hypervalent iodine-induced oxidation of 361 generating pyrazole-4-arylliodyonium tosylate, [ArI(pyrazole)][OTs] in situ which undergoes facile deprotonation forming zwitterionic iodonium ylide 365. Finally, an intermolecular N-arylation mediated by 1,10-phenanthroline/K₂CO₃ 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(sp³)–H azidation of 3-substituted-2-oxindoles 366 (Scheme 99). This transformation employs TMSN₃ 367 as the azide reagent in the presence of PhI(OAc)₂ 6 and EtsN 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 Heterocycles

In 2017, Zhang’s research group demonstrated PIDA-mediated C−H perfluoroalkylation of 8-aminoquinoline amides 369 to yield perfluoroalkylated quinolones 371 (Scheme 100). Reaction scope was administered by using different perfluoroalkyl sources 370 such as TMSCF_5, TMSN-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). 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). 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). 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). 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(sp³)–H heteroarylation of aliphatic alcohols using perfluorinated hydroxybenziodoxole as an oxidant.
Scheme 104. PIDA-mediated C–H alkylation/acetylation of N-heterocycles 379.

Using ethynyl-1,2-benziodoxol-3(1H)-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). 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(1H)-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). This reaction provides 3-alkoxyoxindoles 389 in 43-93% yields under mild conditions in shorter reaction time. Further using PIFA/I₂ 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.

\[
\text{Phl(OCOCF}_3\text{)}_2 \quad 120 \text{ (2 equiv)} \\
\text{rt, 15 min} \\
\text{R = Me, Et, nPr, nBu, nPent, iPr, CH}_2\text{iPr, tBu, CH(Me)CH}_2\text{CH}_3, \text{ (CH}_2\text{)}_2\text{OMe, allyl, Cyp, Cy} \\
43-93\% \\
\]

\[
\text{Phl(OCOCF}_3\text{)}_2 \quad 120 \text{ (2 equiv)} \\
l_2, \text{ rt, 30 min} \\
\text{R = Me, Et, nPr, nBu, nPent, iPr, CH}_2\text{iPr, tBu, CH(Me)CH}_2\text{CH}_3, \text{ (CH}_2\text{)}_2\text{OMe, Cyp} \\
49-79\% \\
\]

\[
\text{Phl(OCOCF}_3\text{)}_2 \quad 120 \text{ (2 equiv)} \\
l_2, \text{ rt, 8 h} \\
\text{R = Me, Et, nPr, nBu, nPent, iPr, CH}_2\text{iPr, tBu, CH(Me)CH}_2\text{CH}_3, \text{ (CH}_2\text{)}_2\text{OMe, Cyclopentyl} \\
41-69\% \\
\]

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-2H-azirines 392 using PIDA 6 as the reagent. 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 2H-azirines 392 using rose bengal as the organophotoredox catalyst.

Very recently, Kumar and co-workers transformed imidazo[1,2-α]pyridine 394 into the corresponding N-acetoxyethyl/alkoxymethyl-N-arylimidazo[1,2-α]pyridine-3-amines 396 via PIDA-induced [1,2]-ipso migration
strategy (Scheme 108). This reaction was proposed to proceed via Wheland-type aziridine intermediate which upon subsequent ring opening assisted by acetate/alkoxy nucleophile delivers rearranged products.

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

3.4. Halogenation/cyanation of heterocycles
In 2018, a mild method for the selective C–H halogenation of indoles with Phl(OAc)\(_2\)/NaX system was developed by Rao and co-workers (Scheme 109). This method is applicable for the chlorination, bromination and iodination of functionally diverse indoles providing privileged scaffold, 3-haloindoles 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 and subsequent proton loss yields halo product.

Scheme 109. PIDA-mediated C–H halogenation of indoles 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 by grinding with alkali metal/ammonium salts (M-X) mediated by PIDA (Scheme 110). This method enabled greener synthesis of halogenated/thiocyanated imidazoheterocycles under solvent-free conditions. Reaction mechanism possibly involves in situ formation of [acetoxy(halo/thiocyanato)iodo]benzene from PIDA and M-X, which serve as source of X\(^+\) species facilitating electrophilic substitution on electron-rich substrates. Additionally, in situ bromination protocol was developed by utilizing HBr generated as by-product during the synthesis of fused N-heterocycles and from the condensation reaction of heterocyclic amine with bromoketone. The desired brominated products and 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-TollF₂ 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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**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 pursued his PhD in 2007 with Dr Atul Goel (CSIR-CDRI, Lucknow, India). After the completion of his doctoral studies, he started his first postdoctoral studies (FAPESP fellowship) with Prof. H A Stefani at USP, São Paulo, Brazil and worked with him for more than two years in the
area organotrifluoroborate chemistry. In 2010, he joined as Marie Curie postdoctoral fellow with Prof. Thomas Wirth at Cardiff University, UK and worked two years in the area of organoselenium and hypervalent iodine chemistry. He received Dr D S Kothari fellowship in 2013 and worked with Prof. G Mugesh at IISc Bangalore, India for a short stay. In 2014, he started his independent career and joined VIT University, Chennai as an Assistant Professor. Mainly, his research group is interested in the findings of new organoselenium and hypervalent catalysts for organic synthesis. Moreover, his research group is also involved in the development of new organic fluorescent molecules for OLEDs and chemical sensors. Currently, he is having different research grants from Government of India. He has already published more than 50 research papers, several book chapters and review articles.

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