Synthesis of Oxazoline and Oxazole Derivatives by Hypervalent-Iodine-Mediated Oxidative Cycloaddition Reactions

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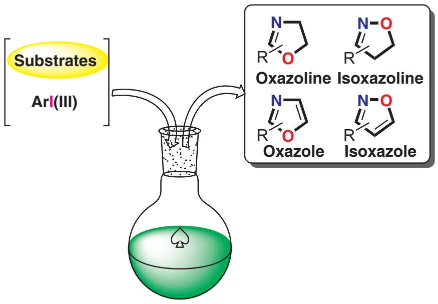

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Abstract Organohypervalent iodine reagents are widely used for the preparation of various oxazolines, oxazoles, isoxazolines, and isoxazoles. In the formation of these heterocyclic compounds, hypervalent iodine species can serve as the activating reagents for various substrates, as well as the heteroatom donor reagents. In recent research, both chemical and electrochemical approaches toward generation of hypervalent iodine species have been utilized. The in situ generated active species can react with appropriate substrates to give the corresponding heterocyclic products. In this short review, we summarize the hypervalent-iodine-mediated preparation of oxazolines, oxazoles, isoxazolines, and isoxazoles starting from various substrates.

Key words hypervalent iodine, oxidative cyclization, oxidative cycloaddition, oxazoles, oxazolines, isoxazoles, isoxazolines

1 Introduction

Heterocyclic structural blocks can be found in various biologically active natural and non-natural products and are widely employed in the synthesis of pharmaceuticals, agrochemicals, dyes, and polymeric materials.[1–8] Numerous reviews and books on the synthesis and properties of heterocyclic compounds have been published.[9–23] Five-membered heterocycles with nitrogen and oxygen atoms in the ring, such as oxazolines, oxazoles, isoxazolines, and isoxazoles, are particularly important in life-saving drugs, bioactive natural compounds, products of the pharmaceutical industry, synthetic building blocks, and as metal catalyst ligands.[10–12,14,16,24–29] Therefore, the reactions forming these heterocyclic rings and those introducing functional groups into these rings represent a hot topic, and numerous important synthetic procedures based on these reactions have been developed. The known procedures often have serious drawbacks, such as harsh reaction conditions, long reaction times, limited substrate scope, or poor yields. In particular, numerous synthetic procedures utilizing metal reagents have been developed for efficient and mild syntheses of oxazoline and oxazole derivatives.[10–12,14,16,23–28,30] However, some of the metal reagents are expensive, toxic, and rare; therefore, new synthetic methodologies under metal-free and mild conditions have been extensively studied.

Organohypervalent iodine compounds are known as non-toxic and environmentally friendly reagents that are utilized in many green and sustainable organic reactions.[31–33] The reactivity pattern of hypervalent iodine compounds is similar to that of transition-metal reagents.[34–40] Therefore, hypervalent iodine compounds have found wide application as efficient oxidative reagents and ligand transfer reagents in many reactions.[41–49] In fact, numerous oxidative reactions, benzyne-mediated reactions, and new bond-forming reactions, such as carbon–carbon, carbon–heteroatom, or hetero–heteroatom bonds, have been accomplished using hypervalent iodine reagents under metal-free conditions. In particular, these reagents have been used for various ring construction reactions. Numerous classes of heterocyclic compounds have been prepared under mild

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Akio Saito (second left) received his M.S. (1999) and Ph.D. (2003) degrees from the Tokyo University of Pharmacy and Life Sciences. In 2001, he joined Professor Takeo Taguchi's group as a research associate at the same university. From 2005, he worked as an assistant professor with Professor Yuji Hanzawa at the Showa Pharmaceutical University. In 2012, he moved to his present position as an Associate Professor at the Tokyo University of Agriculture and Technology.

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conditions using hypervalent iodine reagents.[50–52] In the present review, synthetic approaches to the azole derivatives, oxazolines **1**, oxazoles **2**, isoxazolines **3**, and isoxazoles **4** (Figure 1), starting from various substrates using hypervalent iodine species are summarized, and recent developments in chemical and electrochemical synthetic procedures toward these heterocycles are discussed.

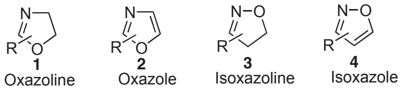
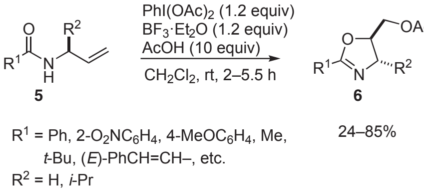


Figure 1 Important azole derivatives

2 Synthesis of Oxazolines

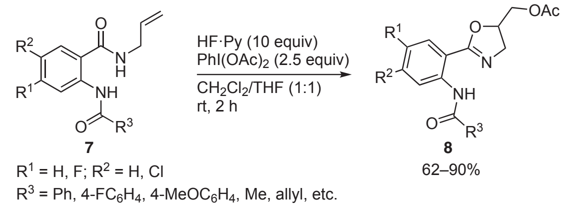
The oxazoline nucleus is present in many heterocyclic compounds that have found important applications in medicinal and materials chemistry.[14,51,53,54] Numerous synthetic strategies for the construction of the oxazoline ring have been explored. Particularly important are synthetic approaches using hypervalent iodine reagents, such as (diacetoxyiodo)arenes,[55–65] iodosylarenes,[66] (difluoroiodo)arenes,[67] in situ generated iodine(III) species,[68–73] or iodonium ylides.[74,75] This section covers synthetic methodologies for the preparation of various oxazoline derivatives from appropriate substrates using hypervalent iodine species.

The reactions of *N*-allylamides or *N*-propargylamides with hypervalent iodine species results in an oxidative cyclization leading to oxazolines with various substituents. For example, Harned's group reported the oxidative cyclization reaction of *N*-allylamides **5** using (diacetoxyiodo)benzene in the presence of $BF_3 \cdot Et_2O$ and acetic acid to give the respective oxazoline compounds **6** in moderate to good yields (Scheme 1).[55] The cyclization of chiral *N*-allylamides afforded the corresponding oxazolines in good yields and diastereoselectivities.



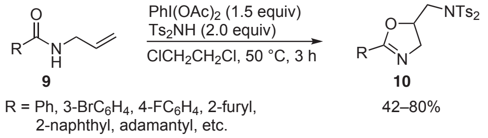
Scheme 1 Oxidative cyclization of *N*-allylamides **5**

A similar (diacetoxyiodo)benzene-mediated cyclization of *N*-allylamides **7** in the presence of HF·Py, instead of $BF_3 \cdot Et_2O$ and acetic acid, gave the respective acetoxymethyl-containing oxazolines **8** in moderate to good yields (Scheme 2).[61] Incidentally, when using substituted *N*-(*E*)-allylamides under the same conditions, the reaction resulted in *endo*-cyclization due to the carbocation stability to afford the oxazine products instead of oxazolines.



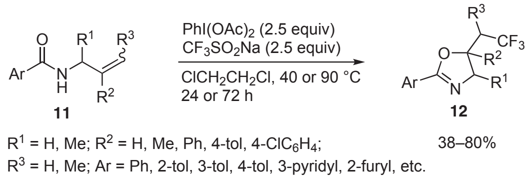
Scheme 2 Preparation of acetoxymethylated oxazolines **8**

The reaction of *N*-allylamides **9** using (diacetoxyiodo)benzene and bis(tosylimide) gave 5-amino-oxazolines **10** in moderate to good yields (Scheme 3).[60] The authors proposed that either PhI(OAc)(NTs$_2$) or PhI(NTs$_2$)$_2$ was generated in situ from (diacetoxyiodo)benzene and bis(tosylimide), and the generated active species reacted with the olefin followed by intramolecular cyclization to produce the final oxazoline products.



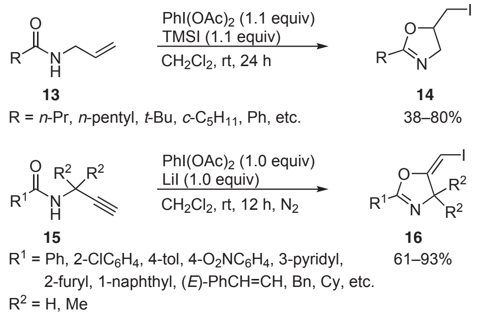
Scheme 3 Preparation of 5-amino-oxazolines from *N*-allylamides **9**

Fu and co-workers reported the metal-free trifluoromethylation of *N*-allylamides **11** by treatment with (diacetoxyiodo)benzene and sodium trifluoromethanesulfinate as the trifluoromethyl source (Scheme 4).[58] The reaction mechanism probably involved formation of a free-radical intermediate, which reacted with the alkenes to give the CF$_3$-containing oxazolines **12** in moderate to good yields.



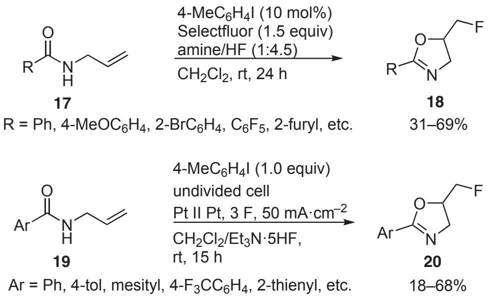
Scheme 4 Trifluoromethylation of *N*-allylamides **11**

The combination of (diacetoxyiodo)benzene and trimethylsilyl iodide promotes intramolecular iodocyclization of *N*-allylamides **13** leading to the respective 5-iodomethyl-2-oxazoline compounds **14** in good yields (Scheme 5).[56] Trimethylsilyl iodide serves as the iodine source and the activating reagent. When using trimethylsilyl bromide or trimethylsilyl chloride as the halogen source, the respective 5-bromo- or 5-chloromethyl-2-oxazoline compounds were also obtained in good yields. A similar iodocyclization reaction of *N*-propargylamides **15** using (diacetoxyiodo)benzene with lithium iodide instead of trimethylsilyl iodide gave the corresponding (*E*)-5-iodomethylene-2-oxazoline compounds **16** in good yields.[57] This reaction probably involved initial generation of acetyl hypoiodite (AcOI) from (diacetoxyiodo)benzene and lithium iodide. Nagib and co-workers reported the use of acetyl hypoiodite generated from (diacetoxyiodo)benzene and elemental iodine in the cyclization reaction of imidate compounds leading to the respective oxazolines in good yields.[65] The obtained products could be converted into β-amino alcohols by acidic hydrolysis.



Scheme 5 Iodocyclization of *N*-allylamides and *N*-propargylamides

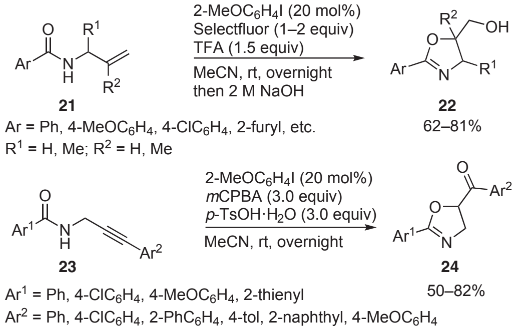
Recently, synthetic procedures for the preparation of 5-fluoromethyl-2-oxazolines from *N*-allylamides using in situ generated hypervalent iodine species in the presence of a fluorine source have been developed. For example, Gilmour and co-workers reported the fluorocyclization reaction of *N*-allylamides **17** using 4-iodotoluene as a precatalyst and Selectfluor as a terminal oxidant in the presence of amine/HF, producing the respective 5-fluoromethyl-2-oxazolines **18** in moderate to good yields (Scheme 6).[73] When the reaction of a chiral *N*-allylamide was performed under the same conditions, the desired oxazoline product was obtained in good yield and high diastereoselectivity. The authors proposed that the mechanism of this catalytic reaction probably involved (difluoroiodo)toluene generation from 4-iodotoluene, Selectfluor and the HF source. Another synthetic approach to 5-fluoromethyl-2-oxazolines from *N*-allylamides employed an electrochemical protocol. Very recently, Waldvogel and co-workers reported the generation



Scheme 6 Preparation of 5-fluoromethyl-2-oxazolines using in situ generated hypervalent iodine species

of a hypervalent iodine species from stoichiometric amounts of 4-iodotoluene by electrochemical oxidation in the presence of $Et_3N{\cdot}5HF$. This active species promotes the oxidative cyclization of *N*-allylamides **19** to give the respective 5-fluoromethyl-2-oxazolines **20** in moderate yields.[71]

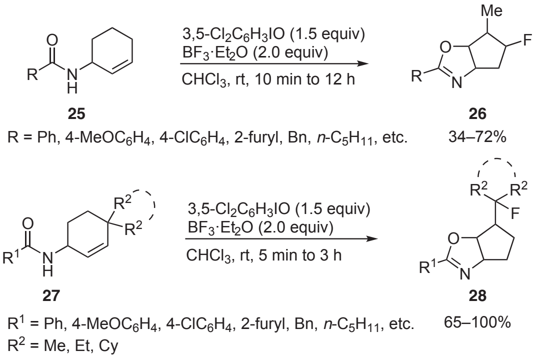
Moran and co-workers reported the catalytic hypervalent iodine species mediated oxidative cyclization of various *N*-allylamides **21** or *N*-propargylamides **23** to give the respective oxazoline compounds **22** and **24** in moderate to good yields (Scheme 7).[68,69] The same group also reported that when using β-amidoketones as substrates oxazoline products were obtained in moderate to good yields. A mechanistic investigation of the cyclization of *N*-allylamides with in situ generated hypervalent iodine reagents by DFT calculations and kinetic experiments was reported. It was found that the rate-limiting step in this reaction was the substrate cyclization.[70] Recently, a similar oxidative cyclization of *N*-allylamides using electrochemically generated hypervalent iodine species was developed by Francke and co-workers.[72]



Scheme 7 Catalytic cyclization of *N*-allylamides **21** or *N*-propargylamides **23**

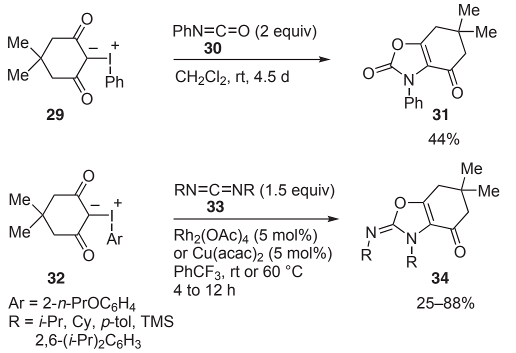
An efficient synthetic procedure for the preparation of bicyclic oxazoline compounds mediated by hypervalent iodine reagents has been developed. For example, Zhang and co-workers reported the reaction of *N*-cyclohexenylamides **25** and **27** with an iodosylarene in the presence of $BF_3{\cdot}Et_2O$ to give the respective monofluorinated ring-fused oxazolines **26** and **28** in moderate to excellent yields (Scheme 8).[66] $BF_3{\cdot}Et_2O$ served as the Lewis acid and also as a fluorine source in this reaction. The authors proposed that the mechanism of the introduction of fluorine into products **26** and **28** involved initial formation of carbocationic intermediates from the *N*-cyclohexenylamides.

In another example of the preparation of oxazoline compounds, an iodonium ylide was used for the construction of a bicyclic oxazoline (Scheme 9). Koser and co-workers reported the preparation of ring-fused 4-oxazoline **31** from cyclic iodonium ylide **29** and phenyl isocyanate (**30**).[74]



Scheme 8 Preparation of ring-fused oxazoline compounds from *N*-cyclohexenylamides

Our group has also reported the cycloaddition reaction of carbodiimides **33** mediated by cyclic iodonium ylide **32** to give the corresponding ring-fused 4-oxazolines **34** in moderate to good yields.[75]



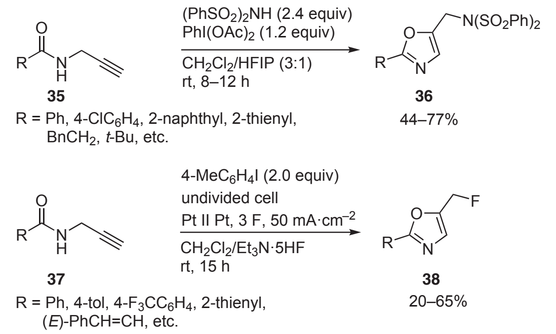
Scheme 9 Preparation of 4-oxazoline compounds from iodonium ylides

3 Synthesis of Oxazoles

Oxazoles have found numerous applications in chemical and biomedical sciences, and many synthetic procedures for oxazole ring formation from various precursors have been developed.[10,16,28,30,51] Particularly important are methods based on the use of hypervalent iodine reagents such as (diacetoxyiodo)benzene,[76–87] [bis(trifluoroacetoxy)iodo]benzene,[79,88–91] iodosylbenzene,[92–95] [hydroxy(tosyloxy)iodo]arenes,[96–99] recyclable iodine(III) compounds,[100] in situ generated iodine(III) species,[76,101–106] and iodonium ylides.[107–113]

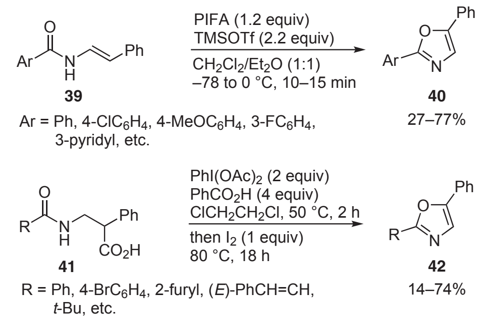
The hypervalent-iodine(III)-mediated cyclization of *N*-propargylamides represents a useful synthetic methodology for the construction of the oxazole nucleus. This methodology is applicable to the synthesis of substituted oxazoles bearing nitrogen-containing groups,[76] fluoride,[101,102] iodide,[95] or acetoxy groups.[77] For example, the reaction of

N-propargylamides **35** with (diacetoxyiodo)benzene in the presence of bis(sulfonyl)imides affords the respective oxazoles **36** bearing sulfonamide groups in moderate to good yields (Scheme 10).[76] The sulfonyl group in products **36** can be easily removed to give the respective amines. The reaction mechanism has been investigated by NMR spectroscopy using the deuterated alkyne variant of *N*-propargylamide. This cyclization reaction of *N*-propargylamides has also been accomplished using the in situ generated catalytic hypervalent iodine species derived from iodobenzene and Oxone. Similar oxidative cyclizations of *N*-propargylamides **37** were reported by Waldvogel and co-workers using electrochemically generated (difluoroiodo)arene, which gave the fluorinated products **38** in moderate yields.[102]



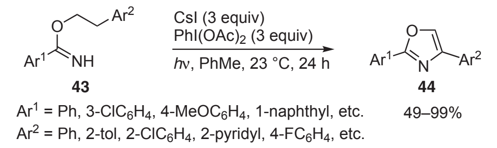
Scheme 10 Preparation of oxazoles from *N*-propargylamides

Enamides have been converted into the corresponding oxazole compounds using hypervalent iodine reagents under metal-free conditions.[78,79,88–90] Nachtsheim and Hempel developed an efficient method for the oxidative cyclization of *N*-styrylbenzamides **39** to give the corresponding oxazoles **40** using [bis(trifluoroacetoxy)iodo]benzene in the presence of TMSOTf (Scheme 11).[90] The key active iodine(III) species in this reaction, $PhI(OTf)_2$, is probably generated from [bis(trifluoroacetoxy)iodo]benzene and TMSOTf. A one-pot synthesis of oxazoles **42** from *N*-acylamino acids **41** was reported by Boto and co-workers.[80] In this reaction, the enamide intermediates were initially formed from *N*-acylamino acids **41** via decarboxylation and were further converted into the respective oxazole compounds **42** by iodine-mediated oxidative cyclization.



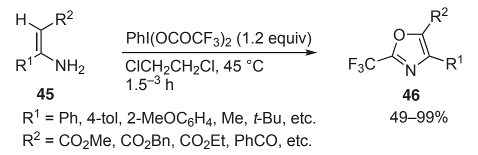
Scheme 11 Oxidative cyclization of enamides and *N*-acylamino acids

Very recently, Nagib and co-workers reported the reaction of arylimidates **43** with (diacetoxyiodo)benzene in the presence of cesium iodide under fluorescent light irradiation leading to the corresponding oxazole products **44** in moderate to good yields (Scheme 12).[114] The key step in this reaction involved the double hydrogen atom transfer (HAT) reaction by in situ generated radical species. The same group has also achieved a one-pot procedure for the synthesis of oxazoles from alcohols and nitriles.



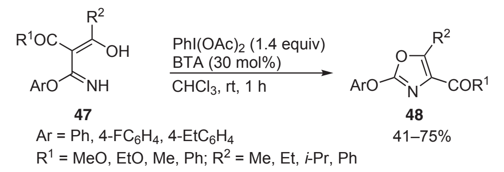
Scheme 12 Oxidative cyclization of arylimidates

Du and co-workers reported the reaction of enamines **45** with [bis(trifluoroacetoxy)iodo]benzene giving β-trifluoroacetoxy enamines, which were further converted into 2-(trifluoromethyl)oxazoles **46** in moderate to good yields (Scheme 13).[91] The same group has also developed the acyloxylation reaction of enamines using iodosylbenzene with various carboxylic acids. The obtained β-acyloxylated products can be further transformed into the corresponding oxazoles under acetic acid reflux conditions.[92]



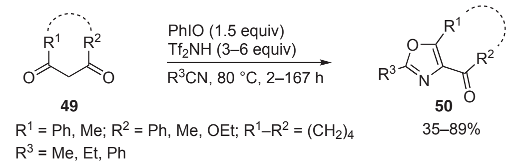
Scheme 13 Preparation of 2-(trifluoromethyl)oxazoles from enamines

The reaction of 3-hydroxybut-2-enimidates **47** with (diacetoxyiodo)benzene in the presence of benzotriazole (BTA) as an additive affords the rearranged 2,4,5-trisubstituted oxazoles **48** in moderate to good yields (Scheme 14).[81] The product structure was confirmed by X-ray crystallography. This reaction proceeds via initial isoxazole formation followed by ring opening and recyclization to produce oxazoles **48**.



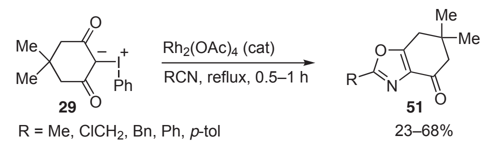
Scheme 14 (Diacetoxyiodo)benzene-mediated oxidative rearrangement of 3-hydroxybut-2-enimidates

Convenient practical approaches for the preparation of oxazoles from monocarbonyl substrates and nitrile solvents as the nitrogen source in the presence of hypervalent iodine reagents have been reported by several groups.[86,87,93,96,97,100,103–105] Furthermore, the reaction of dicarbonyl compounds **49** using iodosylbenzene in the presence of bis(trifluoromethanesulfonyl)imide also proceeded as an oxidative cycloaddition reaction to give the respective carbonyl-substituted oxazoles **50** (Scheme 15).[93] The reaction of carbonyl compounds with amides as the nitrogen source instead of nitrile afforded the respective oxazoles in moderate to good yields.[98,99]



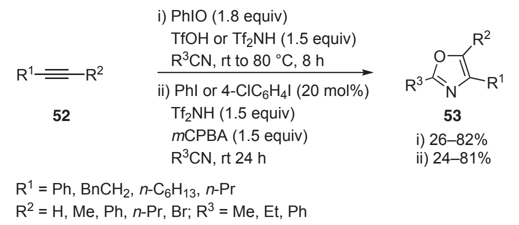
Scheme 15 Oxidative cycloaddition of dicarbonyl compounds with nitriles

Iodonium ylides and various nitriles can be converted into the corresponding oxazoles in moderate to good yields.[107–113] For example, dimedone-derived iodonium ylide **29**, reacting with nitriles in the presence of a metal catalyst, can be easily transformed into ring-fused oxazole compounds bearing a monocarbonyl group **51** (Scheme 16).[108] The key nitrilium intermediates are probably generated from iodonium salts reacting with nitrile in the presence of the rhodium catalyst, followed by cyclization to form the respective ring-fused oxazoles.



Scheme 16 Rhodium-catalyzed cycloaddition of iodonium ylides with nitriles

The metal-free, regioselective hypervalent-iodine-mediated [2+2+1] cycloaddition reactions of alkynes, nitriles and oxygen atoms leading to substituted oxazoles have been developed.[94,106] Reactions of alkynes **52** with iodosylbenzene in nitrile solution in the presence of trifluoromethanesulfonic acid or bis(trifluoromethane)sulfonimide gave the corresponding oxazole products **53** (Scheme 17).[94] Iodosylbenzene works in this reaction as the oxygen source and also as the activating reagent. Deuterium labeling experiments indicate that alkenyliodonium and alkynyliodonium intermediates are initially formed from iodosylbenzene and alkynes. A catalytic version of this [2+2+1] cycloaddition was also reported.[106] The oxygen source in the catalytic version of this reaction was *m*CPBA, and the yields of products **53** were comparable to those of the stoichiometric reaction. According to the deuterium labeling experiments, this catalytic [2+2+1] cycloaddition involved only alkenyliodonium intermediates.

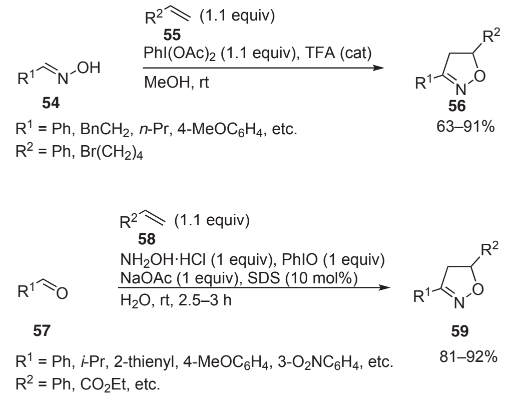


Scheme 17 Metal-free [2+2+1] oxidative cycloaddition reactions

4 Synthesis of Isoxazolines

The isoxazoline ring is present in many important heterocycles that are widely used in several areas of chemistry and biomedical sciences.[24–26,52] Hypervalent iodine reagents such as (diacetoxyiodo)benzene,[115–129] [hydroxy(tosyloxy)iodo]benzene,[130,131] iodosylbenzene,[132–135] [bis(trifluoroacetoxy)iodo]benzene,[136] (dichloroiodo)benzene,[137] and also in situ generated iodine(III) species,[138–141] can be used as efficient tools for construction of the isoxazoline ring.

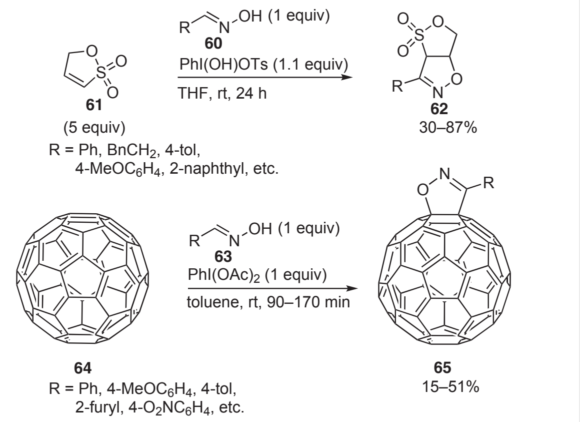
The hypervalent-iodine-mediated oxidative cycloaddition of aldoximes with unsaturated substrates represents a powerful methodology for the synthesis of isoxazoline compounds.[52,115–120,132–134,136,137] For example, the reactions of various aldoximes **54** with alkenes **55** and (diacetoxyiodo)benzene afford the corresponding isoxazolines **56** in generally high yields (Scheme 18).[116] The key intermediate in this reaction, nitrile oxide, is generated by oxidation of the aldoxime with (diacetoxyiodo)benzene, and then the generated nitrile oxide reacts with alkenes to produce the isoxazoline products. The reactions of disubstituted or trisubstituted alkenes with aldoximes using hypervalent iodine reagents can proceed through oxidative cycloaddition leading to the corresponding substituted isoxazolines.[120,133]



Scheme 18 Iodine(III)-mediated preparation of isoxazolines

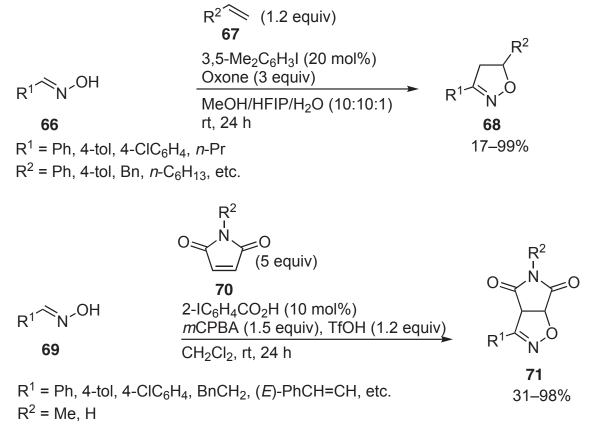
The treatment of aldoxime-bearing purine structures and various alkenes with an iodine(III) reagent also leads to the respective isoxazoline products in moderate to good yields.[136] A convenient one-pot synthesis of isoxazolines **59** from aldehydes **57**, hydroxylamine, and alkenes **58** using hypervalent iodine reagents also produces products **59** in good yields.[132] This reaction involves initial formation of aldoximes from aldehydes and hydroxylamine, followed by oxidative cycloaddition with alkenes to give the final products (Scheme 18).

Hypervalent-iodine-mediated oxidative cycloadditions of aldoximes with cyclic alkenes has been used for the preparation of bicyclic isoxazoline compounds in moderate to good yields.[116,117,132] Likewise, the treatment of heterocyclic alkenes with various aldoximes using hypervalent iodine reagents affords the respective bicyclic isoxazoline compounds.[130] For example, the oxidative cycloaddition of various aldoximes **60** with sultone **61** in the presence of [hydroxy(tosyloxy)iodo]benzene proceeds smoothly to produce the corresponding products **62** (Scheme 19). A similar reaction using cyclic phospholene-oxide instead of sultone resulted in the respective bicyclic products in moderate yields. In addition, Yang and co-workers reported a practical procedure for the preparation of fulleroisoxazolines **65** from various aldoximes **63** and fullerene **64** using (diacetoxyiodo)benzene.[121] This procedure can also be used for the synthesis of fulleropyrazolines from various hydrazones and fullerene.



Scheme 19 Oxidative cycloaddition of aldoximes with cyclic unsaturated compounds

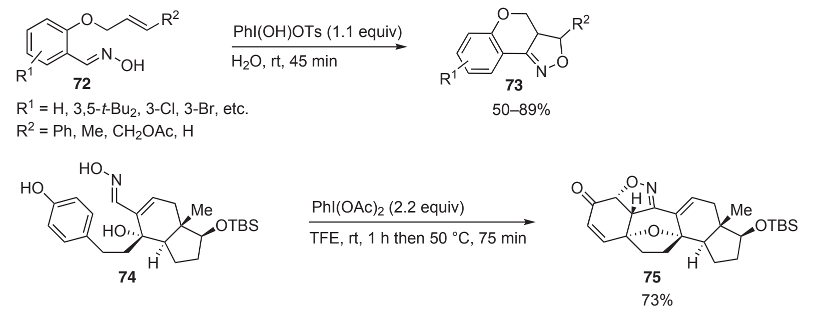
A catalytic, hypervalent-iodine-mediated oxidative cycloaddition of aldoximes with various alkenes has been developed by our group and others.[138–141] For example, we demonstrated that a catalytic hypervalent iodine species, generated in situ from an iodoarene and Oxone, can promote the oxidative cycloaddition of aldoximes **66** with alkenes **67** to give the respective isoxazoline compounds **68** (Scheme 20).[138] A similar, catalytic hypervalent-iodine-mediated synthesis of isoxazolines was reported by Yan and co-workers.[139,140] Our group has also performed the oxidative cycloaddition of aldoximes **69** with maleimides **70** using catalytic hypervalent iodine species to give the corresponding bicyclic isoxazoline compounds **71**.[141] The mechanism of this reaction involved initial formation of the active hydroxy(aryl)iodonium species from 2-iodobenzoic acid and *m*CPBA, followed by oxidative cycloaddition to give the final products. Experimental evidence toward the intermediate generation of hydroxy(aryl)iodonium species was provided by ^{1}H NMR spectroscopy and ESI-mass spectrometry.



Scheme 20 Catalytic hypervalent-iodine-mediated oxidative cycloaddition of aldoximes with alkenes

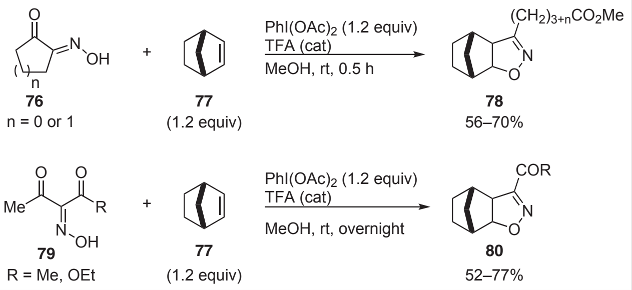
The intramolecular cyclization of aldoximes to produce fused isoxazolines was reported by several research groups.[116,117,122–124,131] In the reaction of 2-(allyloxy)benzaldoximes **72** with [hydroxy(tosyloxy)iodo]benzene in water, an intramolecular cyclization of the aldoximes led to the tricyclic fused products **73** (Scheme 21).[131] Das and co-workers reported a similar intramolecular oxidative cyclization reaction of a furanose-based aldoxime using (diacetoxyiodo)benzene leading to furopyrano-2-isoxazoline products in good yields.[123] Sorensen and co-workers reported a tandem oxidative cyclization reaction forming a pentacyclic product **75** by the treatment of aldoxime **74** with (diacetoxyiodo)benzene.[124] This reaction mechanism probably involved initial formation of quinone derivatives from the phenol moiety and nitrile oxide species, then followed by cyclization of the quinone and nitrile oxide to give the desired pentacyclic compound.

Ciufolini and co-workers have reported the (diacetoxyiodo)benzene-mediated generation of nitrile oxide species from α-oxo-oximes.[125] The reaction of α-oxo-ketoximes **76** with norbornene (**77**) and (diacetoxyiodo)benzene in methanol gave the corresponding isoxazolines **78** in moderate yields (Scheme 22). This reaction mechanism involved initial formation of the nitrile oxide from the α-oxo-ketoximes via ligand exchange and solvolysis, followed by the cycloaddition with the alkene to form the final products.



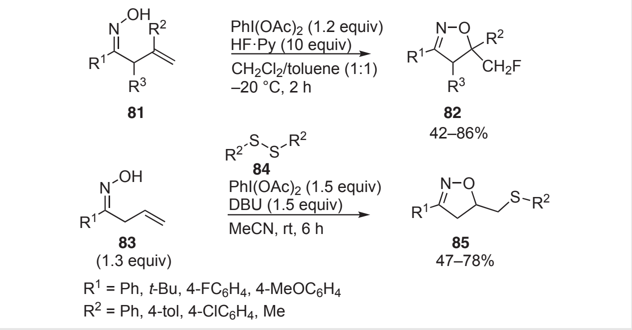
Scheme 21 Hypervalent-iodine-promoted intramolecular cyclization of aldoximes

The reaction of α,α′-dioxo-ketoximes **79** with norbornene under the same conditions also gave the corresponding isoxazoline compounds **80**.



Scheme 22 Oxidative cycloaddition of ketoximes with norbornene

The oxidative cyclization of allyl ketoximes using (diacetoxyiodo)benzene can produce the corresponding isoxazolines bearing various functional groups.[126–129] For example, the reaction of allyl ketoximes **81** using (diacetoxyiodo)benzene in the presence of HF·Py as the fluoride source gave the corresponding oxyfluorination compounds **82** (Scheme 23).[128] The obtained isoxazolines **82** can be converted into the monofluoromethyl-substituted β-hydroxy ketones via a ring-opening reaction. Cai and Yu reported a (diacetoxyiodo)benzene-induced oxidative cycloaddition of allyl ketoximes **83** in the presence of disulfides **84**, which produced the corresponding isoxazolines **85**.[129] A similar reaction using diselenides instead of disulfides afforded the selenium-containing isoxazolines in good yields. The authors suggested that this oxidative cyclization of allyl ketoximes proceeds via a radical mechanism.

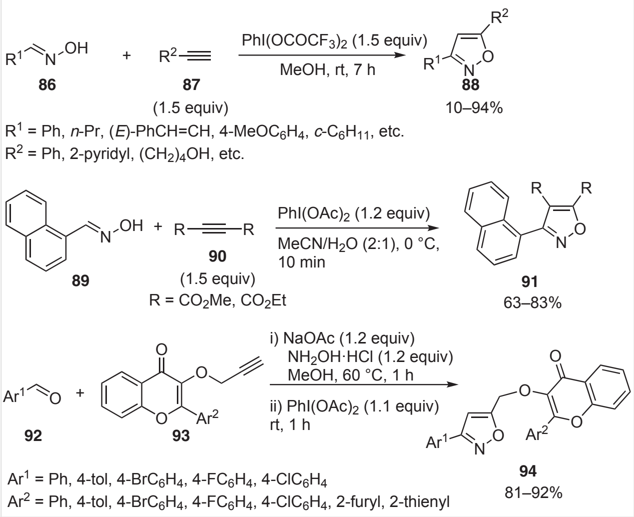


Scheme 23 (Diacetoxyiodo)benzene-mediated oxidative cyclizations of allyl ketoximes

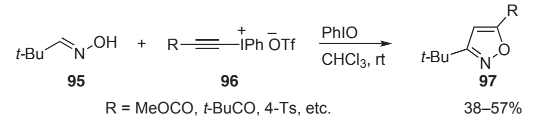
5 Synthesis of Isoxazoles

Isoxazoles belong to an important class of heteroaromatic compounds with many practical applications.[52] Hypervalent iodine reagents such as (diacetoxyiodo)benzene,[116,122,142–147] [bis(trifluoroacetoxy)iodo]benzene,[136,148–151] iodosylbenzene,[134,135] [hydroxy(tosyloxy)iodo]benzene,[152,153] and in situ generated iodine(III) species[138,154] have been commonly used for isoxazole ring construction.

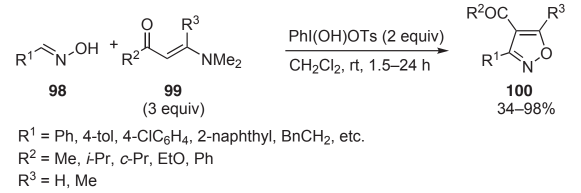
Hypervalent-iodine-mediated oxidative cycloadditions of aldoximes with unsaturated substrates represents an efficient procedure for the construction of isoxazoles. For example, the reaction of aldoximes **86** with terminal alkynes



Scheme 24 Iodine(III)-mediated preparation of isoxazoles



Scheme 25 Cycloaddition of aldoxime **95** and alkynyliodonium salts **96**



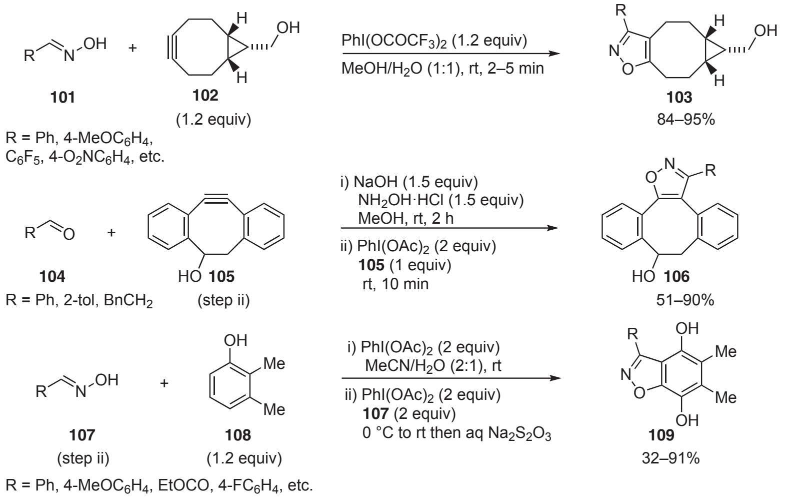
Scheme 26 Regioselective cycloaddition of aldoximes with enaminones

87, in the presence of [bis(trifluoroacetoxy)iodo]benzene, affords the corresponding 3,5-disubstituted isoxazoles **88** (Scheme 24).[151] This reaction is also applicable for the synthesis of isoxazole-derived nucleoside and peptide analogues. The cycloaddition reaction of aldoximes and alkynes under similar conditions was used for the efficient preparation of various types of isoxazole compounds. This reaction involves the initial generation of a nitrile oxide followed by cycloaddition with the alkyne to form the isoxazoles. The reaction of internal alkynes **90** with 1-naphthyl aldoxime **89** in the presence of a hypervalent iodine reagent gave the respective 3,4,5-trisubstituted isoxazole compounds **91** in moderate to good yields.[136,144] A convenient one-pot synthesis of flavone-derived isoxazoles **94** from aromatic aldehydes **92**, hydroxylamine and alkynes **93** using (diacetoxyiodo)benzene has also been reported (Scheme 24).[143]

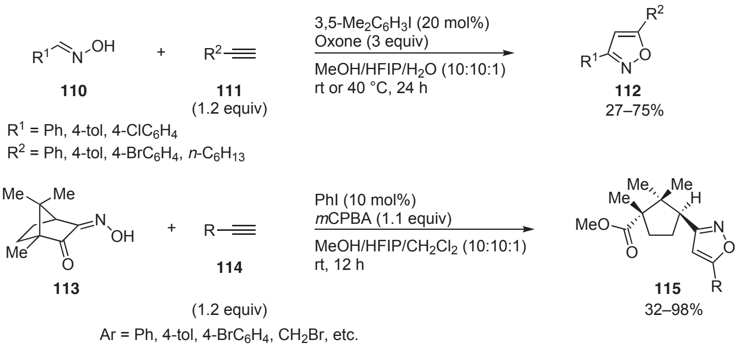
3,5-Disubstituted oxazole compounds **97** can be prepared from the respective alkynyliodonium salts **96** and a nitrile oxide generated from aldoxime **95** and iodosylbenzene (Scheme 25).[135] The mechanism of this reaction involves oxidative cycloaddition and loss of the iodonium group.

Very recently, our group reported the regioselective cycloaddition reaction of aldoximes with enaminones.[153] The reaction of aldoximes **98** with enaminones **99** and [hydroxy(tosyloxy)iodo]benzene afforded the 3,4-disubstituted isoxazoles **100** (Scheme 26). This reaction involves the regioselective cycloaddition of enaminones with the generated nitrile oxide followed by elimination of dialkylamine to produce 3,4-disubstituted isoxazole products **100**. The reaction of β-substituted enaminones under similar conditions afforded the respective 3,4,5-trisubstituted isoxazoles in moderate yields.

The hypervalent-iodine-mediated preparation of ring-fused isoxazoles from aldoximes and cyclic alkynes has been reported.[142,145,146,151] For example, the reaction of bicyclo[6.1.0]nonyne **102** with various aldoximes **101** and [bis(trifluoroacetoxy)iodo]benzene gave the corresponding bicyclic 3,4,5-trisubstituted isoxazole compounds **103** in good yields (Scheme 27). A one-pot synthesis of bicyclic isoxazoles has been developed by Boons and co-workers.[145] The reaction of aldehydes **104** with hydroxylamine and cyclic alkyne **105** using (diacetoxyiodo)benzene gave isoxazoles **106** in generally good yields. Another convenient one-pot synthetic approach to bicyclic isoxazoles using phenolic compounds (instead of cyclic alkynes) was reported by Liu and co-workers.[147] The reaction of aldoximes **107** with 2,3-dimethylphenol (**108**) and (diacetoxyiodo)benzene gave the corresponding isoxazoles **109** (Scheme 27). In this reaction, the hypervalent iodine reagent serves as the oxidant for both the aldoxime and the phenol.



Scheme 27 Iodine(III)-promoted preparation of bicyclic isoxazole compounds



Scheme 28 Catalytic hypervalent-iodine-mediated preparation of isoxazoles from alkynes and aldoximes or ketoximes

Catalytic procedures for the hypervalent-iodine-mediated synthesis of isoxazoles have been developed.[138,154] For example, the reaction of aldoximes **110** with alkynes **111**, in the presence of an iodoarene and Oxone, affords the respective 3,5-isoxazole products **112** in low to good yields (Scheme 28).[138] This reaction probably involves initial formation of a nitrile oxide, which further reacts with the alkyne to give the final isoxazole. Recently, Kaliappan and Subramanian reported the oxidation of a cyclic α-ketoxime to a nitrile oxide using an in situ generated hypervalent iodine species.[154] The reaction of cyclic α-ketoxime **113** and alkynes **114** with a catalytic amount of iodobenzene using *m*CPBA in methanol solution afforded the corresponding isoxazole compounds **115** bearing a cyclopentyl group in low to excellent yields. The key intermediate in this reaction, the nitrile oxide, is probably generated by iodine(III)-mediated methanolysis of the α-ketoxime, and then the resulting nitrile oxide is converted into product **115** by oxidative cycloaddition with the alkyne.

6 Conclusion

This short review summarizes organohypervalent-iodine-mediated synthetic procedures for the preparation of five-membered heterocycles with oxygen and nitrogen atoms in the ring. Intramolecular or intermolecular oxidative cyclization reactions of appropriate substrates provide efficient synthetic approaches to oxazolines, oxazoles, isoxazolines, and isoxazoles. Various hypervalent iodine compounds have been utilized as efficient reagents for the preparation of these heterocyclic compounds. Furthermore, the preparation of heterocyclic compounds using in situ generated hypervalent iodine species has been developed. We expect that hypervalent-iodine-mediated syntheses of heterocyclic compounds will continue to attract significant research activity in the future.

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References

(1) Vargas, D. F.; Larghi, E. L.; Kaufman, T. S. *Nat. Prod. Rep.* **2019**, *36*, 354.
(2) Miao, Y.-h.; Hu, Y.-h.; Yang, J.; Liu, T.; Sun, J.; Wang, X.-j. *RSC Adv.* **2019**, *9*, 27510.
(3) Madawali, I. M.; Gaviraj, E. N.; Kalyane, N. V.; Shivakumar, B. *Am. J. PharmTech Res.* **2019**, *9*, 256.
(4) Soor, H. S.; Appavoo, S. D.; Yudin, A. K. *Bioorg. Med. Chem.* **2018**, *26*, 2774.
(5) Afzal, O.; Kumar, S.; Haider, M. R.; Ali, M. R.; Kumar, R.; Jaggi, M.; Bawa, S. *Eur. J. Med. Chem.* **2015**, *97*, 871.
(6) Khan, I.; Ibrar, A.; Abbas, N.; Saeed, A. *Eur. J. Med. Chem.* **2014**, *76*, 193.
(7) Singh, G. S.; Mmatli, E. E. *Eur. J. Med. Chem.* **2011**, *46*, 5237.
(8) Galliford, C. V.; Scheidt, K. A. *Angew. Chem. Int. Ed.* **2007**, *46*, 8748.
(9) Gulevich, A. V.; Dudnik, A. S.; Chernyak, N.; Gevorgyan, V. *Chem. Rev.* **2013**, *113*, 3084.
(10) Ibrar, A.; Khan, I.; Abbas, N.; Farooq, U.; Khan, A. *RSC Adv.* **2016**, *6*, 93016.
(11) Pellissier, H. *Tetrahedron* **2007**, *63*, 3235.
(12) Nair, V.; Suja, T. D. *Tetrahedron* **2007**, *63*, 12247.
(13) Hashimoto, T.; Maruoka, K. *Chem. Rev.* **2015**, *115*, 5366.
(14) Gant, T. G.; Meyers, A. I. *Tetrahedron* **1994**, *50*, 2297.
(15) Wang, D.-S.; Chen, Q.-A.; Lu, S.-M.; Zhou, Y.-G. *Chem. Rev.* **2012**, *112*, 2557.
(16) Yeh, V. S. C. *Tetrahedron* **2004**, *60*, 11995.
(17) Carson, C. A.; Kerr, M. A. *Chem. Soc. Rev.* **2009**, *38*, 3051.
(18) Debnath, P. *Curr. Org. Chem.* **2019**, *23*, 2402.
(19) Wu, Y.-J. *Prog. Heterocycl. Chem.* **2017**, *29*, 315.
(20) Lu, L.-Q.; Chen, J.-R.; Xiao, W.-J. *Acc. Chem. Res.* **2012**, *45*, 1278.
(21) Sridharan, V.; Suryavanshi, P. A.; Menendez, J. C. *Chem. Rev.* **2011**, *111*, 7157.

(22) Katritzky, A.; Ramsden, C. A.; Joule, J. A.; Zhdankin, V. V. *Handbook of Heterocyclic Chemistry, 3rd ed*; Elsevier: Amsterdam, **2010**.
(23) de Andrade, V. S. C.; de Mattos, M. C. S. *Synthesis* **2019**, *51*, 1841.
(24) Maiuolo, L.; De Nino, A. *Targets Heterocycl. Syst.* **2015**, *19*, 299.
(25) Rane, D.; Sibi, M. *Curr. Org. Synth.* **2011**, *8*, 616.
(26) Browder, C. C. *Curr. Org. Synth.* **2011**, *8*, 628.
(27) Kozikowski, A. P. *Acc. Chem. Res.* **1984**, *17*, 410.
(28) Turchi, I. J.; Dewar, M. J. S. *Chem. Rev.* **1975**, *75*, 389.
(29) Sperry, J. B.; Wright, D. L. *Curr. Opin. Drug Discovery Dev.* **2005**, *8*, 723.
(30) Hu, Y.; Xin, X.; Wan, B. *Tetrahedron Lett.* **2015**, *56*, 32.
(31) Wirth, T. *Top. Curr. Chem.* **2016**, *373*, 1.
(32) Zhdankin, V. V. *Hypervalent Iodine Chemistry: Preparation, Structure and Synthetic Application of Polyvalent Iodine Compounds*; John Wiley & Sons: Chichester, **2014**.
(33) Yoshimura, A.; Zhdankin, V. V. *Chem. Rev.* **2016**, *116*, 3328.
(34) Morimoto, K.; Dohi, T.; Kita, Y. *Synlett* **2017**, *28*, 1680.
(35) Stuart, D. R. *Chem. Eur. J.* **2017**, *23*, 15852.
(36) Wang, M.; Chen, S.; Jiang, X. *Chem. Asian J.* **2018**, *13*, 2195.
(37) Merritt, E. A.; Olofsson, B. *Angew. Chem. Int. Ed.* **2009**, *48*, 9052.
(38) Hyatt, I. F. D.; Dave, L.; David, N.; Kaur, K.; Medard, M.; Mowdawalla, C. *Org. Biomol. Chem.* **2019**, *17*, 7822.
(39) Dohi, T.; Kita, Y. *Curr. Org. Chem.* **2016**, *20*, 580.
(40) Wang, X.; Studer, A. *Acc. Chem. Res.* **2017**, *50*, 1712.
(41) Le Vaillant, F.; Waser, J. *Chem. Sci.* **2019**, *10*, 8909.
(42) Li, Y.; Hari, D. P.; Vita, M. V.; Waser, J. *Angew. Chem. Int. Ed.* **2016**, *55*, 4436.
(43) Huang, X.; Groves, J. T. *ACS Catal.* **2016**, *6*, 751.
(44) Budhwan, R.; Yadav, S.; Murarka, S. *Org. Biomol. Chem.* **2019**, *17*, 6326.
(45) Yoshimura, A.; Saito, A.; Zhdankin, V. V. *Chem. Eur. J.* **2018**, *24*, 15156.
(46) Aradi, K.; Toth, B. L.; Tolnai, G. L.; Novak, Z. *Synlett* **2016**, *27*, 1456.
(47) Ghosh, M. K.; Rajkiewicz, A. A.; Kalek, M. *Synthesis* **2019**, *51*, 359.
(48) Hari, D. P.; Caramenti, P.; Waser, J. *Acc. Chem. Res.* **2018**, *51*, 3212.
(49) Charpentier, J.; Fruh, N.; Togni, A. *Chem. Rev.* **2015**, *115*, 650.
(50) Maiti, S.; Alam, M. T.; Bal, A.; Mal, P. *Adv. Synth. Catal.* **2019**, *361*, 4401.
(51) Saito, A. *ARKIVOC* **2017**, *(i)*, 84.
(52) Yoshimura, A.; Zhdankin, V. V. *ARKIVOC* **2017**, *(i)*, 99.
(53) Hargaden, G. C.; Guiry, P. J. *Chem. Rev.* **2009**, *109*, 2505.
(54) Reuman, M.; Meyers, A. I. *Tetrahedron* **1985**, *41*, 837.
(55) Moon, N. G.; Harned, A. M. *Tetrahedron Lett.* **2013**, *54*, 2960.
(56) Liu, G.-Q.; Yang, C.-H.; Li, Y.-M. *J. Org. Chem.* **2015**, *80*, 11339.
(57) Yi, W.; Liu, Q.-Y.; Fang, X.-X.; Lou, S.-C.; Liu, G.-Q. *Org. Biomol. Chem.* **2018**, *16*, 7012.
(58) Yu, J.; Yang, H.; Fu, H. *Adv. Synth. Catal.* **2014**, *356*, 3669.
(59) Mondal, B.; Hazra, S.; Naktode, K.; Panda, T. K.; Roy, B. *Tetrahedron Lett.* **2014**, *55*, 5625.
(60) Jeon, H.; Kim, D.; Lee, J. H.; Song, J.; Lee, W. S.; Kang, D. W.; Kang, S.; Lee, S. B.; Choi, S.; Hong, K. B. *Adv. Synth. Catal.* **2018**, *360*, 779.
(61) Ranjith, J.; Rajesh, N.; Sridhar, B.; Radha Krishna, P. *Org. Biomol. Chem.* **2016**, *14*, 10074.
(62) Guo, T.; Huang, F.; Jiang, Q.; Yu, Z. *Chem. Eur. J.* **2018**, *24*, 14368.
(63) Carlucci, C.; Tota, A.; Colella, M.; Ronamazzi, G.; Clarkson, G. J.; Luisi, R.; Degennaro, L. *Chem. Heterocycl. Compd.* **2018**, *54*, 428.
(64) Wappes, E. A.; Nakafuku, K. M.; Nagib, D. A. *J. Am. Chem. Soc.* **2017**, *139*, 10204.
(65) Stateman, L. M.; Wappes, E. A.; Nakafuku, K. M.; Edwards, K. M.; Nagib, D. A. *Chem. Sci.* **2019**, *10*, 2693.
(66) Han, Y.-C.; Zhang, Y.-D.; Jia, Q.; Cui, J.; Zhang, C. *Org. Lett.* **2017**, *19*, 5300.
(67) Edmunds, J. J.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1348.
(68) Alhalib, A.; Kamouka, S.; Moran, W. J. *Org. Lett.* **2015**, *17*, 1453.
(69) Kamouka, S.; Moran, W. J. *Beilstein J. Org. Chem.* **2017**, *13*, 1823.
(70) Butt, S. E.; Das, M.; Sotiropoulos, J.-M.; Moran, W. J. *J. Org. Chem.* **2019**, *84*, 15605.
(71) Haupt, J. D.; Berger, M.; Waldvogel, S. R. *Org. Lett.* **2019**, *21*, 242.
(72) Roesel, A. F.; Broese, T.; Majek, M.; Francke, R. *ChemElectroChem* **2019**, *6*, 4229.
(73) Scheidt, F.; Thiehoff, C.; Yilmaz, G.; Meyer, S.; Daniliuc, C. G.; Kehr, G.; Gilmour, R. *Beilstein J. Org. Chem.* **2018**, *14*, 1021.
(74) Koser, G. F.; Yu, S.-M. *J. Org. Chem.* **1975**, *40*, 1166.
(75) Zhu, C.; Yoshimura, A.; Solntsev, P.; Ji, L.; Wei, Y.; Nemykin, V. N.; Zhdankin, V. V. *Chem. Commun.* **2012**, *48*, 10108.
(76) Okamura, Y.; Sato, D.; Yoshimura, A.; Zhdankin, V. V.; Saito, A. *Adv. Synth. Catal.* **2017**, *359*, 3243.
(77) Saito, A.; Matsumoto, A.; Hanzawa, Y. *Tetrahedron Lett.* **2010**, *51*, 2247.
(78) Zheng, Y.; Li, X.; Ren, C.; Zhang-Negrerie, D.; Du, Y.; Zhao, K. *J. Org. Chem.* **2012**, *77*, 10353.
(79) Shishlyk, O. S.; Shcherbatiuk, A. V.; Iminov, R. T.; Tverdokhlebov, A. V.; Tolmachev, A. A.; Mykhailiuk, P. K.; Biitseva, A. V. *J. Fluorine Chem.* **2017**, *196*, 88.
(80) Romero-Estudillo, I.; Batchu, V. R.; Boto, A. *Adv. Synth. Catal.* **2014**, *356*, 3742.
(81) Liu, Q.; Zhang, X.; He, Y.; Hussain, M. I.; Hu, W.; Xiong, Y.; Zhu, X. *Tetrahedron* **2016**, *72*, 5749.
(82) Varma, R. S.; Saini, R. K.; Prakash, O. *Tetrahedron Lett.* **1997**, *38*, 2621.
(83) Prakash, O.; Pannu, K.; Kumar, A. *Molecules* **2006**, *11*, 43.
(84) Jung, M. H.; Choi, S.-W.; Cho, K.-W. *J. Heterocycl. Chem.* **2000**, *37*, 969.
(85) Jung, M. H.; Park, J.-G.; Ryu, B.-S.; Cho, K.-W. *J. Heterocycl. Chem.* **1999**, *36*, 429.
(86) Varma, R. S.; Kumar, D. *J. Heterocycl. Chem.* **1998**, *35*, 1533.
(87) Kang, I.-J.; Wang, H.-M.; Lin, M.-L.; Chen, L.-C. *J. Chin. Chem. Soc.* **2002**, *49*, 1031.
(88) Yu, Z.; Ma, L.; Yu, W. *Synlett* **2012**, *23*, 1534.
(89) Yu, P.; Zheng, S.-C.; Yang, N.-Y.; Tan, B.; Liu, X.-Y. *Angew. Chem. Int. Ed.* **2015**, *54*, 4041.
(90) Hempel, C.; Nachtsheim, B. J. *Synlett* **2013**, *24*, 2119.
(91) Zhao, F.; Liu, X.; Qi, R.; Zhang-Negrerie, D.; Huang, J.; Du, Y.; Zhao, K. *J. Org. Chem.* **2011**, *76*, 10338.
(92) Liu, X.; Cheng, R.; Zhao, F.; Zhang-Negrerie, D.; Du, Y.; Zhao, K. *Org. Lett.* **2012**, *14*, 5480.
(93) Saito, A.; Hyodo, N.; Hanzawa, Y. *Molecules* **2012**, *17*, 11046.
(94) Saito, A.; Taniguchi, A.; Kambara, Y.; Hanzawa, Y. *Org. Lett.* **2013**, *15*, 2672.
(95) Suzuki, S.; Saito, A. *J. Org. Chem.* **2017**, *82*, 11859.
(96) Lee, J. C.; Seo, J.-W.; Baek, J. W. *Synth. Commun.* **2007**, *37*, 2159.
(97) Kumar, D.; Sundaree, S.; Petel, G.; Kumar, A. *J. Heterocycl. Chem.* **2010**, *47*, 1425.
(98) Lee, J. C.; Choi, H. J.; Lee, Y. C. *Tetrahedron Lett.* **2003**, *44*, 123.
(99) Lee, J. C.; Kim, S.; Lee, Y. C. *Synth. Commun.* **2003**, *33*, 1611.
(100) Chen, J. M.; Wu, L. L.; Huang, X. *Chin. Chem. Lett.* **2004**, *15*, 143.
(101) Asari, N.; Takemoto, Y.; Shinomoto, Y.; Yagyu, T.; Yoshimura, A.; Zhdankin, V. V.; Saito, A. *Asian J. Org. Chem.* **2016**, *5*, 1314.
(102) Herszman, J. D.; Berger, M.; Waldvogel, S. R. *Org. Lett.* **2019**, *21*, 7893.

(103) Kawano, Y.; Togo, H. *Tetrahedron* **2009**, *65*, 6251.
(104) Ishiwata, Y.; Togo, H. *Tetrahedron* **2009**, *65*, 10720.
(105) Kawano, Y.; Togo, H. *Synlett* **2008**, 217.
(106) Yagyu, T.; Takemoto, Y.; Yoshimura, A.; Zhdankin, V. V.; Saito, A. *Org. Lett.* **2017**, *19*, 2506.
(107) Asouti, A.; Hadjiarapoglou, L. P. *Tetrahedron Lett.* **1998**, *39*, 9073.
(108) Gogonas, E. P.; Hadjiarapoglou, L. P. *Tetrahedron Lett.* **2000**, *41*, 9299.
(109) Spyroudis, S.; Tarantili, P. *J. Org. Chem.* **1993**, *58*, 4885.
(110) Batsila, C.; Kostakis, G.; Hadjiarapoglou, L. P. *Tetrahedron Lett.* **2002**, *43*, 5997.
(111) Matveeva, E. D.; Podrugina, T. A.; Pavlova, A. S.; Mironov, A. V.; Gleiter, R.; Zefirov, N. S. *Eur. J. Org. Chem.* **2009**, 2323.
(112) Matveeva, E. D.; Podrugina, T. A.; Pavlova, A. S.; Mironov, A. V.; Zefirov, N. S. *Russ. Chem. Bull.* **2008**, *57*, 2237.
(113) Nekipelova, T. D.; Kuzmin, V. A.; Matveeva, E. D.; Gleiter, R.; Zefirov, N. S. *J. Phys. Org. Chem.* **2013**, *26*, 137.
(114) Chen, A. D.; Herbort, J. H.; Wappes, E. A.; Nakafuku, K. M.; Mustafa, D. N.; Nagib, D. A. *Chem. Sci.* **2020**, *11*, 2479.
(115) Das, B.; Holla, H.; Mahender, G.; Banerjee, J.; Reddy, M. R. *Tetrahedron Lett.* **2004**, *45*, 7347.
(116) Mendelsohn, B. A.; Lee, S.; Kim, S.; Teyssier, F.; Aulakh, V. S.; Ciufolini, M. A. *Org. Lett.* **2009**, *11*, 1539.
(117) Liang, H.; Ciufolini, M. A. *Tetrahedron* **2010**, *66*, 5884.
(118) Kumar, R.; Kumar, M.; Prakash, O. *Heteroat. Chem.* **2016**, *27*, 228.
(119) Maiti, S.; Samanta, P.; Biswas, G.; Dhara, D. *ACS Omega* **2018**, *3*, 562.
(120) Harding, S. L.; Marcuccio, S. M.; Paul, S. G. *Beilstein J. Org. Chem.* **2012**, *8*, 606.
(121) Yang, H.-T.; Ruan, X.-J.; Miao, C.-B.; Sun, X.-Q. *Tetrahedron Lett.* **2010**, *51*, 6056.
(122) Bhosale, S.; Kurhade, S.; Vyas, S.; Palle, V. P.; Bhuniya, D. *Tetrahedron* **2010**, *66*, 9582.
(123) Das, B.; Holla, H.; Mahender, G.; Venkateswarlu, K.; Bandgar, B. P. *Synthesis* **2005**, 1572.
(124) Frie, J. L.; Jeffrey, C. S.; Sorensen, E. J. *Org. Lett.* **2009**, *11*, 5394.
(125) Jen, T.; Mendelsohn, B. A.; Ciufolini, M. A. *J. Org. Chem.* **2011**, *76*, 728.
(126) Park, S. W.; Nam, T.-G.; Kim, S.-H.; Song, J.; Park, G. Y.; Kim, D.; Hong, K. B. *Beilstein J. Org. Chem.* **2018**, *14*, 1028.
(127) Hu, X.-Q.; Feng, G.; Chen, J.-R.; Yan, D.-M.; Zhao, Q.-Q.; Wei, Q.; Xiao, W.-J. *Org. Biomol. Chem.* **2015**, *13*, 3457.
(128) Kong, W.; Guo, Q.; Xu, Z.; Wang, G.; Jiang, X.; Wang, R. *Org. Lett.* **2015**, *17*, 3686.
(129) Yu, J.-M.; Cai, C. *Org. Biomol. Chem.* **2018**, *16*, 490.
(130) Yoshimura, A.; Nguyen, K. C.; Rohde, G. T.; Postnikov, P. S.; Yusubov, M. S.; Zhdankin, V. V. *J. Org. Chem.* **2017**, *82*, 11742.
(131) Raihan, M. J.; Kavala, V.; Kuo, C.-W.; Raju, B. R.; Yao, C.-F. *Green Chem.* **2010**, *12*, 1090.
(132) Pal, G.; Paul, S.; Ghosh, P. P.; Das, A. R. *RSC Adv.* **2014**, *4*, 8300.
(133) Chatterjee, N.; Pandit, P.; Halder, S.; Patra, A.; Maiti, D. K. *J. Org. Chem.* **2008**, *73*, 7775.
(134) Tanaka, S.; Ito, M.; Kishikawa, K.; Kohmoto, S.; Yamamoto, M. *Nippon Kagaku Kaishi* **2002**, 471.
(135) Stang, P. J.; Murch, P. *Tetrahedron Lett.* **1997**, *38*, 8793.
(136) Balalas, T.; Peperidou, C.; Hadjipavlou-Litina, D. J.; Litinas, K. E. *Synthesis* **2016**, *48*, 281.
(137) Radhakrishna, A. S.; Sivaprakash, K.; Singh, B. B. *Synth. Commun.* **1991**, *21*, 1625.
(138) Yoshimura, A.; Middleton, K. R.; Todora, A. D.; Kastern, B. J.; Koski, S. R.; Maskaev, A. V.; Zhdankin, V. V. *Org. Lett.* **2013**, *15*, 4010.
(139) Xiang, C.; Li, T.; Yan, J. *Synth. Commun.* **2014**, *44*, 682.
(140) Han, L.; Zhang, B.; Xiang, C.; Yan, J. *Synthesis* **2014**, *46*, 503.
(141) Yoshimura, A.; Nguyen, K. C.; Rohde, G. T.; Saito, A.; Yusubov, M. S.; Zhdankin, V. V. *Adv. Synth. Catal.* **2016**, *358*, 2340.
(142) Wendeln, C.; Singh, I.; Rinnen, S.; Schulz, C.; Arlinghaus, H. F.; Burley, G. A.; Ravoo, B. J. *Chem. Sci.* **2012**, *3*, 2479.
(143) Waheed, M.; Ahmed, N.; Alsharif, M. A.; Alahmdi, M. I.; Mukhtar, S. *ChemistrySelect* **2019**, *4*, 1872.
(144) Singhal, A.; Parumala, S. K. R.; Sharma, A.; Peddinti, R. K. *Tetrahedron Lett.* **2016**, *57*, 719.
(145) Sanders, B. C.; Friscourt, F.; Ledin, P. A.; Mbua, N. E.; Arumugam, S.; Guo, J.; Boltje, T. J.; Popik, V. V.; Boons, G.-J. *J. Am. Chem. Soc.* **2011**, *133*, 949.
(146) Ledin, P. A.; Kolishetti, N.; Boons, G.-J. *Macromolecules* **2013**, *46*, 7759.
(147) Hou, Y.; Lu, S.; Liu, G. *J. Org. Chem.* **2013**, *78*, 8386.
(148) Kim, M.; Hwang, Y. S.; Cho, W.; Park, S. B. *ACS Comb. Sci.* **2017**, *19*, 407.
(149) Niu, T.-f.; Lv, M.-f.; Wang, L.; Yi, W.-b.; Cai, C. *Org. Biomol. Chem.* **2013**, *11*, 1040.
(150) von Zons, T.; Brokmann, L.; Lippke, J.; Preusse, T.; Huelsmann, M.; Schaate, A.; Behrens, P.; Godt, A. *Inorg. Chem.* **2018**, *57*, 3348.
(151) Jawalekar, A. M.; Reubsaet, E.; Rutjes, F. P. J. T.; van Delft, F. L. *Chem. Commun.* **2011**, *47*, 3198.
(152) Jadhav, R. D.; Mistry, H. D.; Motiwala, H.; Kadam, K. S.; Kandre, S.; Gupte, A.; Gangopadhyay, A. K.; Sharma, R. *J. Heterocycl. Chem.* **2013**, *50*, 774.
(153) Yoshimura, A.; Jarvi, M. E.; Shea, M. T.; Makitalo, C. L.; Rohde, G. T.; Yusubov, M. S.; Saito, A.; Zhdankin, V. V. *Eur. J. Org. Chem.* **2019**, 6682.
(154) Subramanian, P.; Kaliappan, K. P. *Chem. Asian J.* **2018**, *13*, 2031.