A Platinum Open Access Journal for Organic Chemistry

Review

Free to Authors and Readers | DOAJ Seal | *Arkivoc* **2026** (2) 202612590

Expanding the role of organoiodine(III) reagents as a versatile tool for various synthetic transformations

Sushma,[a] Rashmi Pundeer[b*]

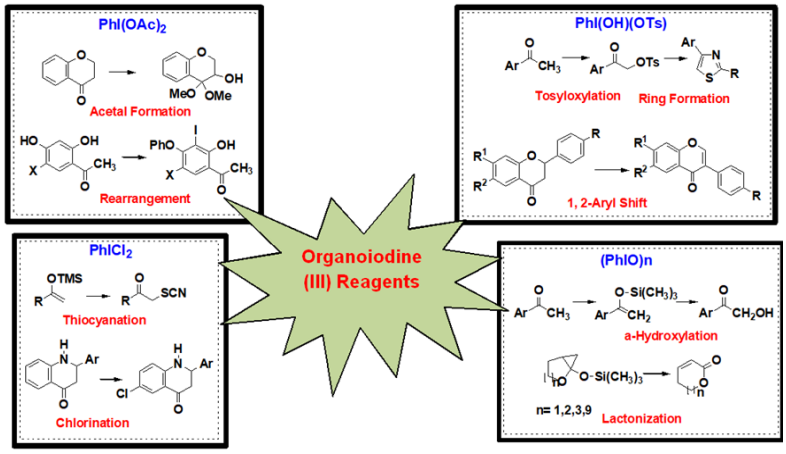
[a]Department of Chemistry, GGJ Government College Hisar, Haryana, 125001, India
[b]Department of Chemistry, Indira Gandhi University, Meerpur, Rewari 122502, Haryana, India*
Email : rashmi.chem@igu.ac.in

Dedicated to Professor Om Prakash

Received 03-31-2026 **Accepted** 05-24-2026 **Published on line** 07-08-2026

Abstract

This review elaborates the significance of organoiodine (III) reagents in the organic transformations authored by Prof. Om Prakash. His work is particularly focused on iodobenzene diacetate, [hydroxy(tosyloxy)iodo]benzene, (dichloroiodo)benzene, and iodosobenzene. His contributions have extended into the pharmaceutical sciences, where compounds developed in his laboratory have been evaluated for their biological and medicinal relevance. His many grateful students are proudly carrying on his legacy.



Keywords: Organoiodine (III) reagents, iodobenzene diacetate, [hydroxy(tosyloxy)iodo]benzene, (dichloroiodo)benzene, iodosobenzene

Table of Contents

1. Introduction

The use of hypervalent iodine (III) reagents has emerged as a powerful and versatile strategy in organic transformations, offering mild reaction conditions, high selectivity, and environmentally benign alternatives to metal-based oxidants. The rapid expansion of this field is reflected in the large number of comprehensive review articles, monographs, and book chapters published over the past decades, which systematically document the reactivity, mechanisms, and synthetic applications of hypervalent iodine reagents. Seminal contributions, including authoritative books by Viktor V. Zhdankin and edited volumes by Thomas Wirth, along with numerous high-impact review articles, underscore the sustained global interest and continuing evolution of hypervalent iodine chemistry as a vital area of modern synthetic research.[1–22]

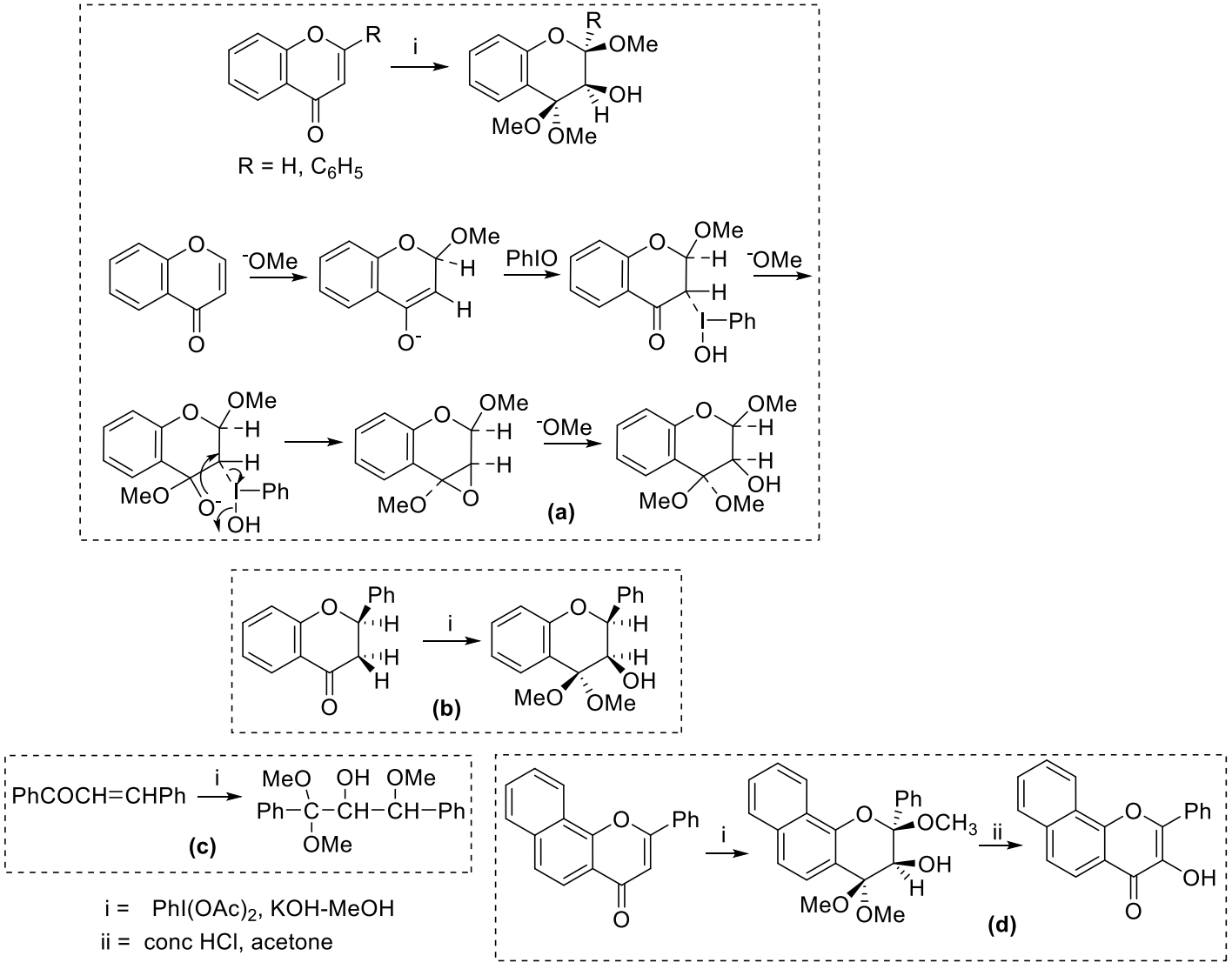
This review aims to highlight the significant contributions of Prof. Om Prakash, former Professor in the Department of Chemistry, Kurukshetra University, Kurukshetra (KUK), whose pioneering work has advanced the synthetic utility of iodine (III) reagents in diverse organic reactions. His collaborative investigations with Prof. R. M. Moriarity at the University of Chicago further augmented this field, leading to impactful contributions that bridged fundamental reactivity with practical synthetic applications.[23–31] The reactions are presented in reagent-specific manner commencing with iodobenzene diacetate (IBD) and [hydroxy(tosyloxy)iodo]benzene (HTIB), followed by (dichloroiodo)benzene and finally iodosobenzene.

2. Iodobenzene Diacetate

Iodobenzene diacetate ($PhI(OAc)_2$), commonly referred to as IBD or DIB, is a prototypical iodine(III) reagent capable of promoting diverse oxidative transformations.[32–34] It serves as an efficient reagent for the formation of C–C and C–heteroatom (C–O, C–N, C–X) bonds involving ligand transfer, oxidative activation, and generation of reactive intermediates such as iodonium ions and radicals.[35–37] Consequently, IBD has been extensively employed in α-functionalization of carbonyl compounds, oxidative dearomatization of phenols, difunctionalization of alkenes, and oxidative cyclization reactions leading to structurally complex carbocycles and heterocycles.[38–46] Recent developments have expanded its utility into catalytic iodine(I)/iodine(III) cycles, electrochemical and photoredox processes,[47–49] thereby reinforcing its role as a key reagent in green and contemporary synthetic methodologies.

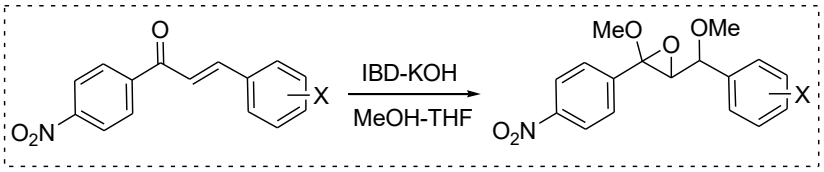
2.1. Reactions under basic condition (IBD-KOH-MeOH): acetal formation

2.1.1. α-Hydroxy-β-methoxydimethyl acetalization. One of the major areas of interest is the use of iodobenzene diacetate under basic conditions and the $PhI(OAc)_2$-KOH-MeOH trio is used frequently. The reaction is applied to systems that cannot form an anion by α-hydrogen abstraction. Treatment of α, β-unsaturated ketones, chromones, flavones, chalcones and flavanones lead to α-hydroxydimethylacetal β-methoxy products regiospecifically and stereospecifically (Scheme 1a-c).[50,51] The reaction proceed by initial Michael addition of MeO^- followed by electrophilic anti addition of PhIO to the thus formed enolate anion, with sequential addition of methoxy anion to the carbonyl group and intramolecular reductive elimination of iodine as iodobenzene with inversion of configuration. Further, the addition of MeO^- to oxirane completes the reaction. The α-hydroxy-β-methoxydimethylacetals so formed, are hydrolyzed to 3-hydroxychromone and 3-hydroxyflavone, respectively, with the loss of three molecules of methanol (Scheme 1a). The reaction is extended for the hydroxylation of α-naphthoflavone without isolating the intermediate acetal (Scheme 1d).[52]



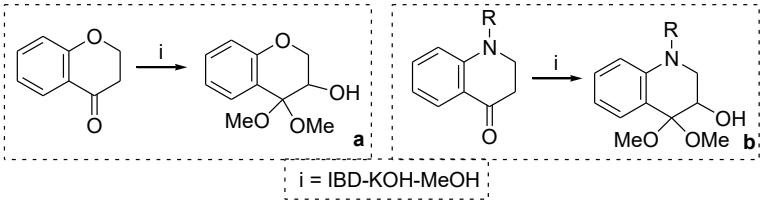
Scheme 1. IBD-mediated oxidation of chromones, flavones, chalcones and flavanones.

The use of IBD in the oxidation of 1-(4-nitrophenyl)-3-arylprop-2-en-1-ones is reported for the isolation of oxiranes, e.g., 2-methoxy-3 (methoxy(aryl)methyl)-2-(4-nitrophenyl)oxiranes (Scheme 2). The oxiranes were earlier proposed to be intermediates in such oxidation reactions.[53]



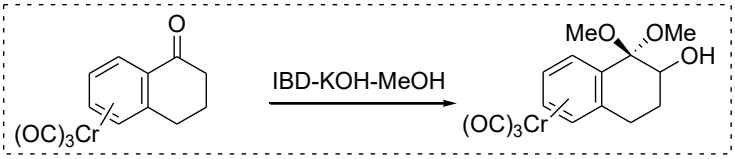
Scheme 2. Oxidation of 1-(4-nitrophenyl)-3-arylprop-2-en-1-ones to oxiranes.

2.1.2. α-Hydroxydimethyl acetalization. The hydroxylation of chromanone using IBD in methanolic base provides a convenient route for the synthesis of 3-hydroxy-4-chromanone through the corresponding dimethylacetal (Scheme 3a).[54] In this connection, β-aminoketone substrates are also converted into α-hydroxy dimethylacetals without oxidation at primary, secondary or tertiary amino groups or at sulfur in the case of morpholino group.[55] The approach is extended to N-containing heterocycles also offering the corresponding α-hydroxydimethylacetals (Scheme 3b).[56]



Scheme 3. α-Hydroxydimethyl acetalization of chromanone and β-aminoketones.

The oxidative method is used for the synthesis of *cis*-3-hydroxyflavanone from flavanone through the intermediate dimethylacetal;, vigorous hydrolytic conditions afford trans-3-hydroxyflavanone instead of the *cis* derivative.[57] The application of the reaction is studied for η^6-tricarbonyl chromium (0) complexes of 1-tetralone, indan-1-one and acetophenone to study the compatibility of the easily oxidized $Cr(CO)_3$ group with the oxidizing agent, and also to get the benefit of the steric effect of the $Cr(CO)_3$ tripod in achieving distereoselectivity. In all of the cases, single diasteromers are easily obtained with the $Cr(CO)_3$ group intact (Scheme 4).[58] The formation of α-hydroxydimethyl acetals is highly sterospecific as the hyperiodination of the ketones involves the introduction of the large $–I(OH)C_6H_5$ group , alpha to the carbonyl group[59]. Heteroaryl ketones, thiazolyl, and benzothiazolyl ketones furnish α-hydroxydimethylacetals using IBD in basic conditions.[60] Tropan-3-one is oxidized by IBD in methanolic KOH to afford α-hydroxytropan-3-one dimethyl acetal.[61] The application of IBD to the functionalization of fused bi- and tricyclopentane derivatives has also been explored. Bicyclic derivatives afforded the predicted, α-hydroxy dimethylacetals *via* the intermediacy of epoxides. The tricyclic ketone does not follow the usual pathway, however, because of steric hindrance associated with the epoxide. Furthermore, both types of fused derivatives undergo α-tosyloxylation successfully using HTIB.[62]

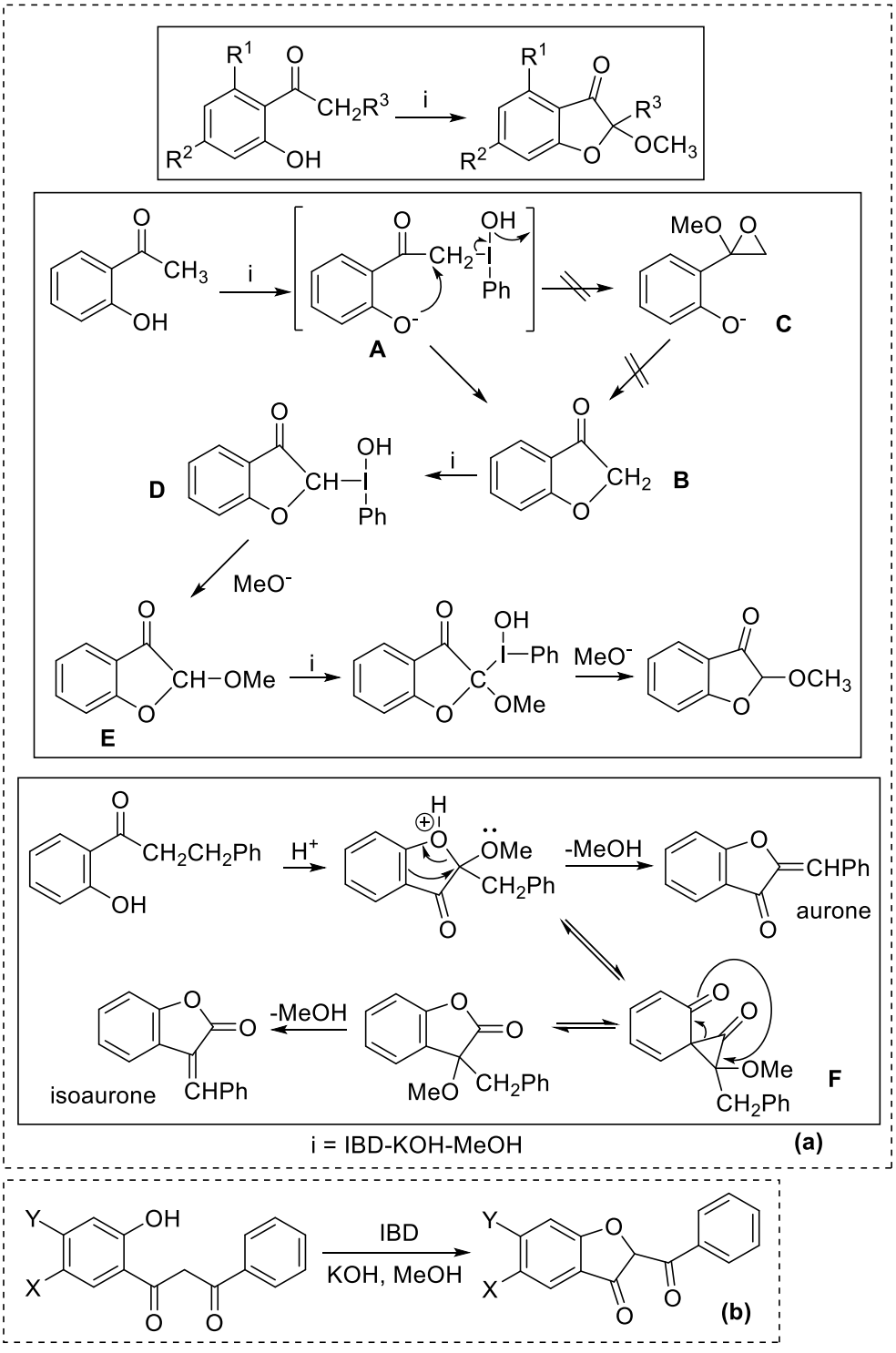


Scheme 4. Oxidation of η^6-tricarbonyl chromium(0) complex of 1-tetralone.

2.2 Intramolecular cyclization: reaction of o-hydroxy/amino aryl ketones/chalcones

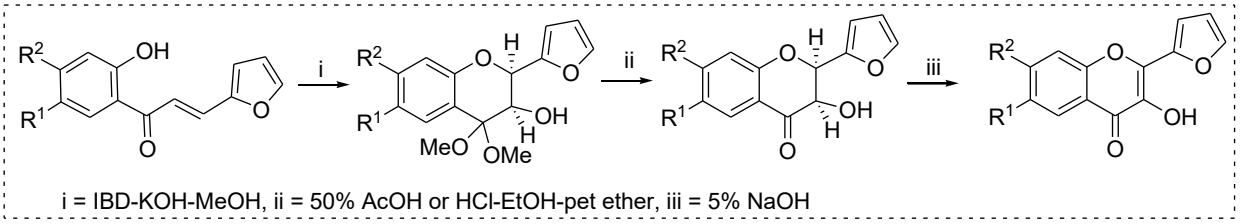
2.2.1 Synthesis of benzofuran-3-ones. The reaction is applied to a series of substituted o-hydroxyacetophenones at a temperature of 0 ^oC, the hydroxy group acted as intramolecular nucleophile in the reductive cleavage of the C-I bond. Intramolecular displacement with reductive elimination [A to B, a 5-*exo*-*tet*

process] is stereochemically favorable. The alternative nucleophilic attack by methoxy [A to C] is possible but, C to B, is stereoelectronically unfavorable. Hyperiodination [B to D], bimolecular reductive displacement [D to E], followed by the same sequence give the coumaran-3-one product. Formation of aurone from coumaran-3-one results from the acid catalyzed removal of methanol. Isoaurone is made by rearrangement of the phenonium type intermediate F (Scheme 5a).[63] A direct method for obtaining 2-benzoylcoumaran-3-ones is provided by IBD-KOH-MeOH oxidation of α-benzoyl-o-hydroxyacetophenones involving neighboring group participation (Scheme 5b).[64]



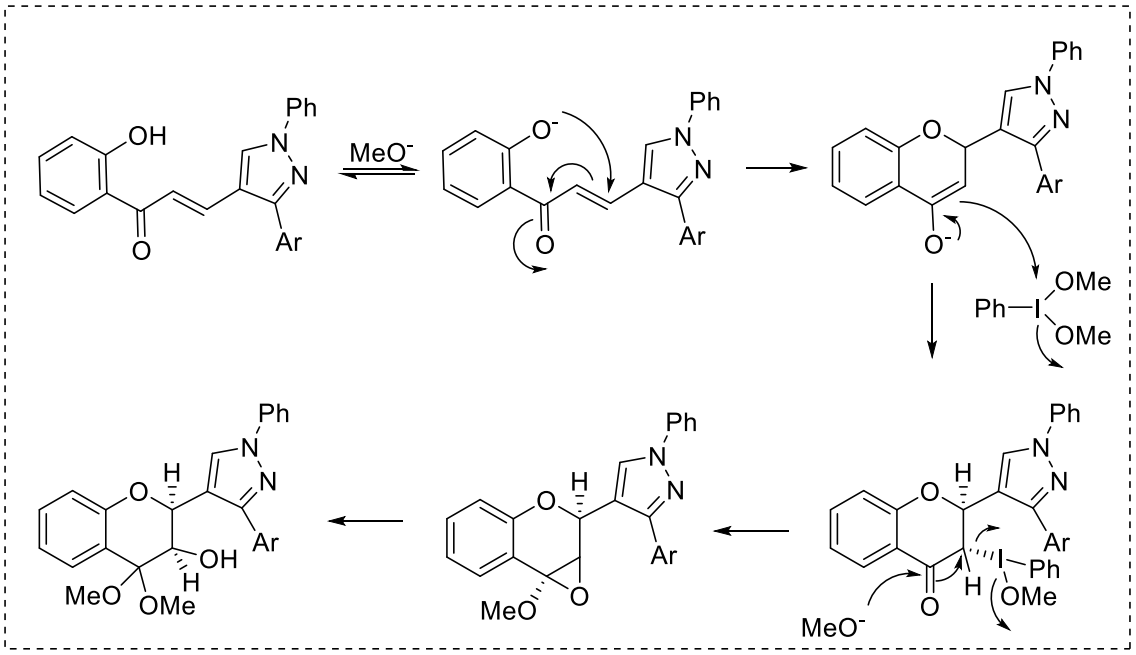
Scheme 5. NGP in the intramolecular cyclization of o-hydroxyacetophenones and α-benzoyl-o-hydroxyacetophenones.

2.2.2. Synthesis of chromanones. 3-(Furan-2-yl)-1-(2-hydroxyphenyl)prop-2-en-1-ones are cyclized to the respective dimethylacetal chromanones by treating with IBD in methanolic base. The acidic hydrolysis of the acetal provides a route for the synthesis of 2-(2-furyl)-*cis*-3-hydroxychromanones, the subsequent basic hydrolysis of which in dilute conditions offers 2-(2-furyl)-3-hydroxychromones (Scheme 6).[65]



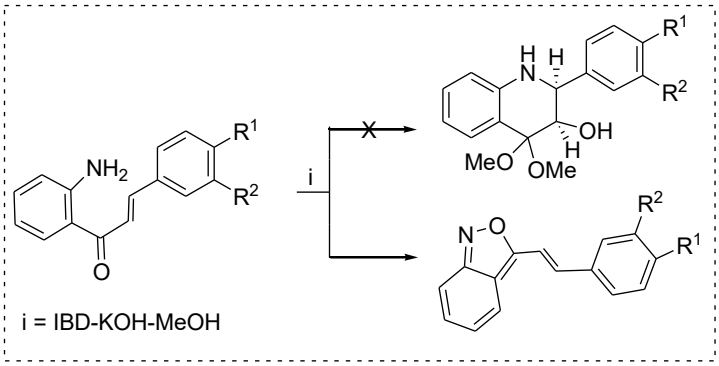
Scheme 6. Cyclization of 3-(furan-2-yl)-1-(2-hydroxyphenyl)prop-2-en-1-ones to α-hydroxydimethylacetal chromanones.

2'-Hydroxychalcone analogues of pyrazoles lead to the IBD-KOH-MeOH mediated formation of *cis*-3-hydroxy-2-(1-phenyl-3-aryl-4-pyrazolyl) chromanone dimethylacetals. The acetals, upon hydrolysis, afford either *trans*-3-hydroxy-2-(1-phenyl-3-aryl-4-pyrazolyl) chromanones or *cis*-3-hydroxy-2-(1-phenyl-3-aryl-4-pyrazolyl) chromanones depending upon the hydrolytic conditions (Scheme 7).[66]



Scheme 7. 2'-Hydroxychalcone analogues of pyrazoles to α-hydroxydimethylacetal chromanones.

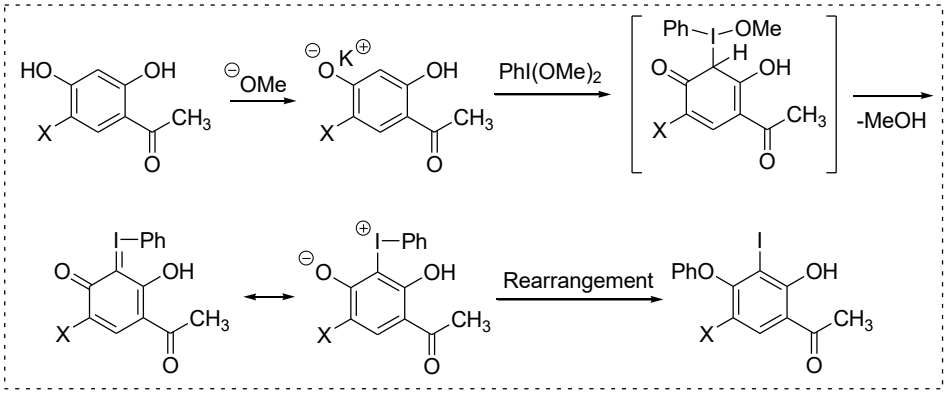
Prompted by the reaction of o-hydroxychalcones with IBD-KOH-MeOH to afford *cis*-3-hydroxyflavanone dimethylacetals, and then *cis*-3-hydroxyflavanones upon acidic hydrolysis,[67] o-aminochalcones and 1-(2-aminophenyl)-3-phenylprop-2-enones are treated with the I(III) reagent to obtain N-analogs of *cis*-3-hydroxyflavanones. The reaction offered 3-styrylbenzo[c]isoxazoles unexpectedly (Scheme 8).[68]



Scheme 8. 1-(2-Aminophenyl)-3-phenylprop-2-enones to 3-styrylbenzo[c]isoxazoles.

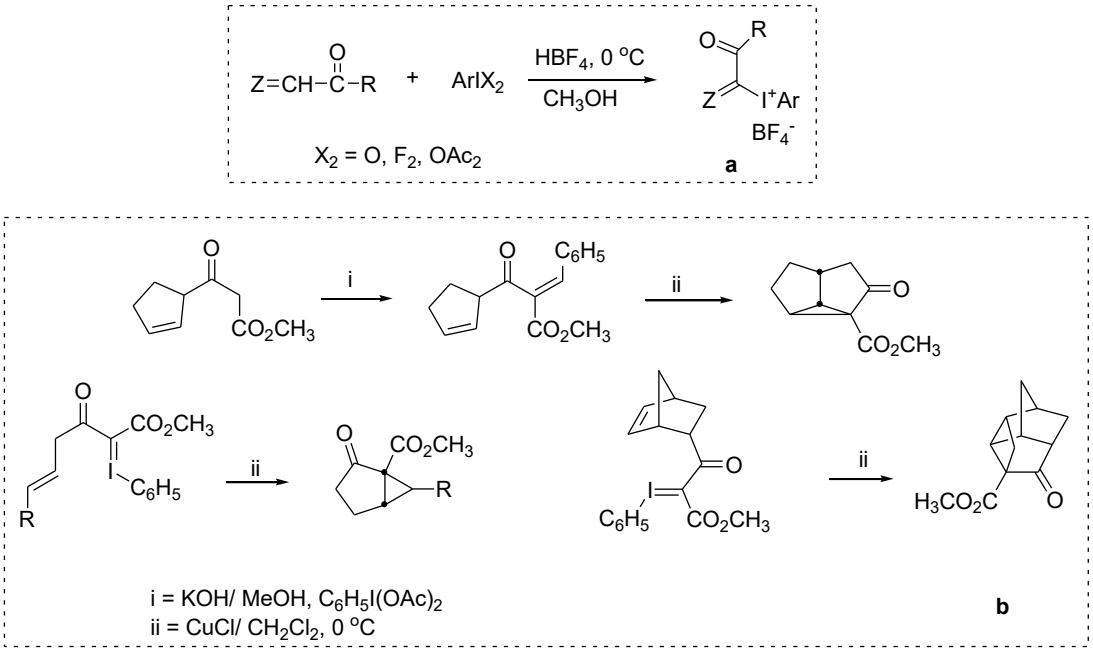
2.3. Rearrangement

2.3.1. Ylides. Treatment of 2,4-dihydroxyacetophenones with IBD-KOH/MeOH provides a novel route for the synthesis of 2-hydroxy-3-iodo-4-phenoxyacetophenones (Scheme 9). The transformation occurs by the rearrangement of the iodonium ylide which results from electrophilic attack of the I(III) reagent $PhI(OMe)_2$ on the phenolate ion, followed by the loss of methanol from the resultant intermediate.[69] Oxidation of α-substituted-2,4-dihydroxyacetophenones using IBD under acidic, basic or neutral conditions leads to o-iodophenoxy ethers through a rearrangement of the respective iodonium ylides (Scheme 9).[70]



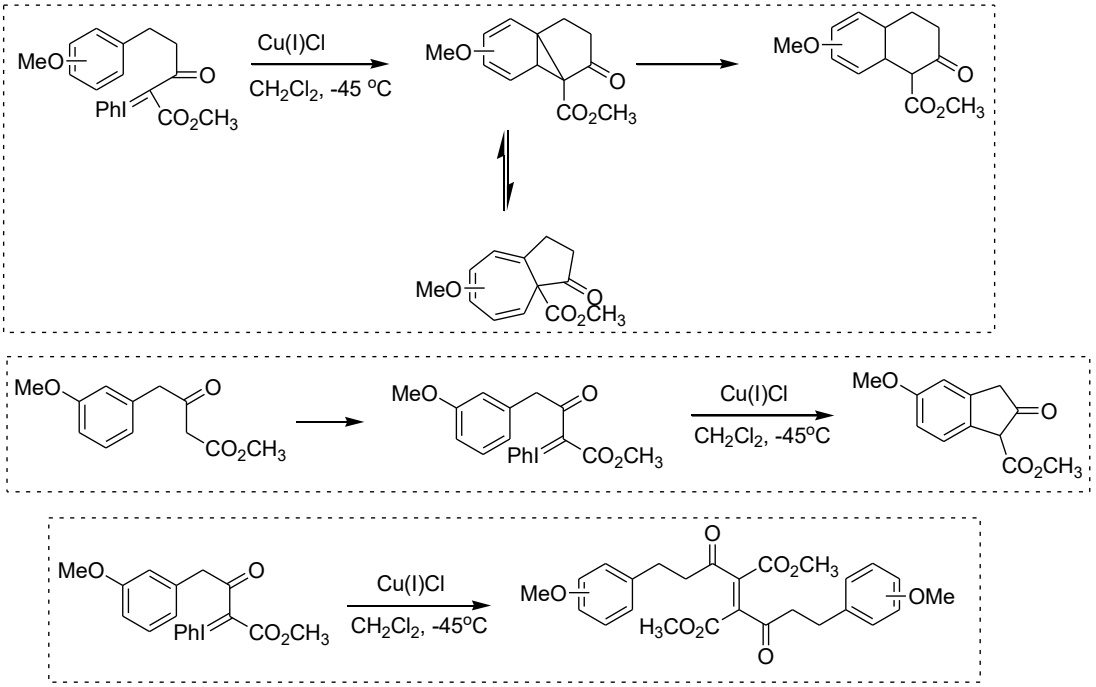
Scheme 9. 2,4-Dihydroxyacetophenones to o-iodophenoxy ethers through iodonium ylides.

Synthesis of some new stable iodonium ylides was achieved in which one of the stabilizing groups contains atom Z. The atom Z is phosphorus or nitrogen; phosphorus is capable of d-orbital stabilization while nitrogen offers p-orbital delocalization. The ylides are synthesized by the reaction of the appropriate starting ylide Z=CHCOR with either the I(III) reagent, ArI=O, $ArI(OAc)_2$ or $ArIF_2$ in $MeOH/HBF_4$ at 0 °C. Reaction of the starting ylide with $ArICl_2$ gives C-chlorinated derivatives (Scheme 10a).[71] The high-yielding method using the iodonium ylides, instead of the hazardous diazo ketones for intramolecular cyclopropanation, is shown by different examples (Scheme 10b).[72]



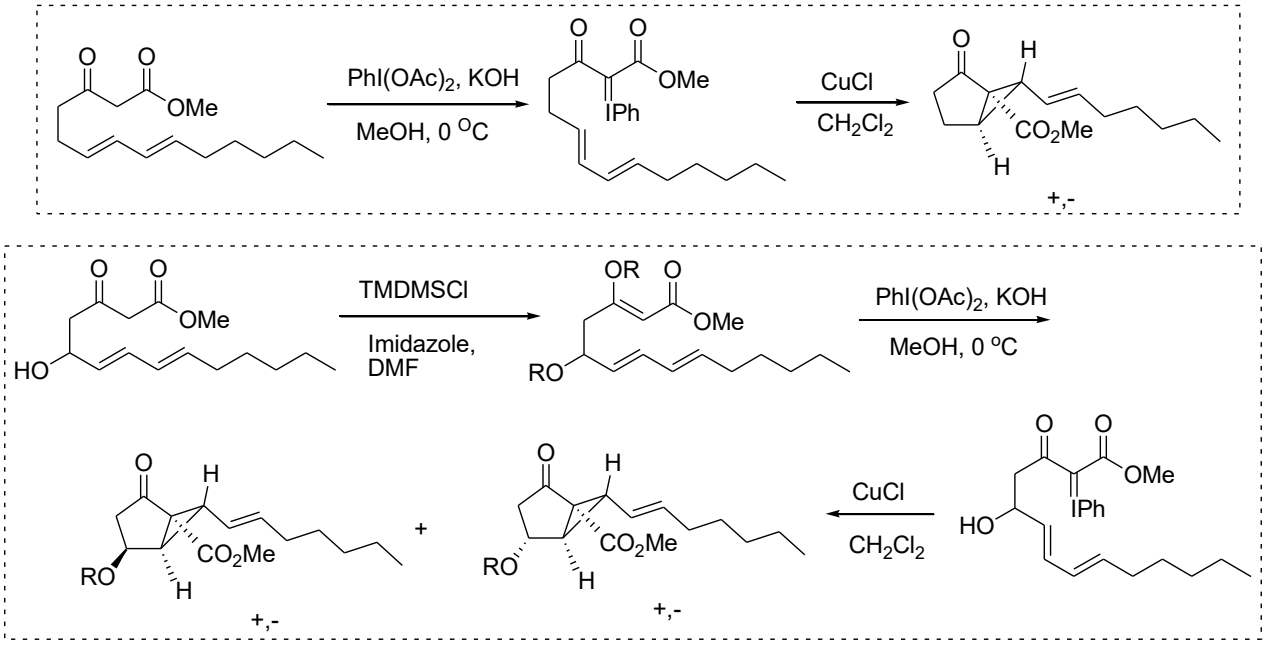
Scheme 10. Preparation and intramolecular cyclization of ylides.

Ylides of o-, m- and p-methoxyphenyl-3-ketopentanoic acid methyl esters, obtained by the reaction of aryl-substituted β-keto esters with IBD/KOH, are decomposed in preparative yields by Cu(I)Cl in DCM at -45 °C to afford 5-, 6- and 7-methoxy-1-carbomethoxy-2-tetralones. However, with lower homologous ylides from o-, m- and p-methoxyphenyl-3-ketbutyric acid methyl esters, the analogous 1-carbomethoxy-2-indanone is obtained only with the m-methoxyphenyl derivative; the other two ylides offer the dimeric products (Scheme 11).[73]



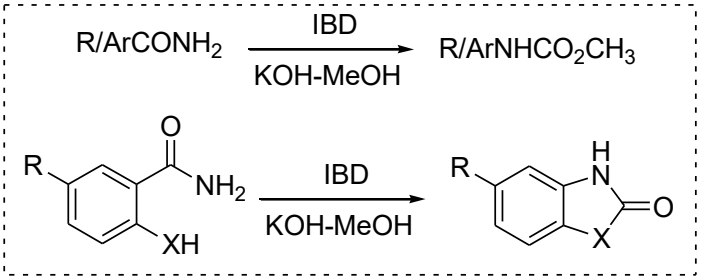
Scheme 11. Decomposition of ylides by Cu(I)Cl.

The iodonium ylide of methyl-3-oxo-*trans*, *trans*-6,8-tetradecadienoate is made by the reaction with IBD-KOH in methanol at 0 °C. The ylide undergoes decomposition with Cu(I)Cl catalyst in DCM at room temperature to afford a racemic endo/exo mixture of methyl 6-(*trans*-1-heptenyl)-2-oxobicyclo[3.1.0]hexane-1-carboxylate which can be converted to 11-deoxyprostaglandin E_1 or prostaglandin A_2. Also, another iodonium ylide is obtained from the protected silyl enol ether made from methyl 5-hydroxy-3-oxo-*trans*, *trans*-6,8-tetradecadienonate, t-butyl dimethylsilyl chloride and imidazole in dry DMF. The ylide is decomposed with a catalytic amount of Cu(I)Cl in dry DCM to give the two bicycle[3.1.0]hexane products (Scheme 12).[74]



Scheme 12. Formation of ylides using IBD-KOH-MeOH and their reaction.

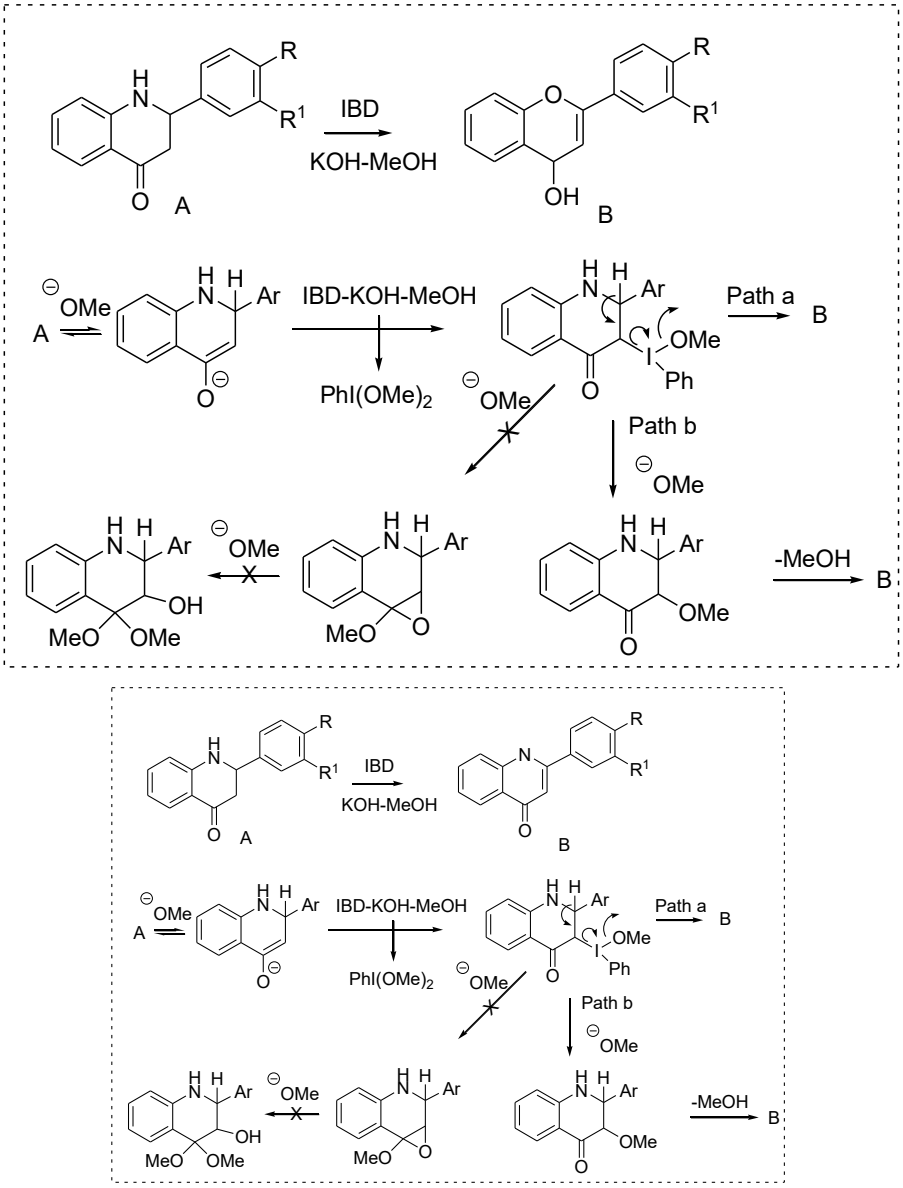
2.3.2. 1,2 Shift: hoffmann-type rearrangement. In some cases, the flavanones undergo facile ring contraction by a 1,2-aryl shift, thereby yielding methyl 2-aryl-2,3-dihydrobenzofuran-3-carboxylates as major products, and *cis*-3-methoxyflavanones and flavones as the minor products formed in variable ratios.[75] A number of different primary alkyl and arylcarboxamides rearranged to the corresponding methyl carbonate products in good-to-excellent yields by treatment with IBD in KOH-MeOH. The reaction is believed to follow a Hofmann-type rearrangement of the amide, affording the N-(phenyliodonio) intermediate, which then rearranges to an isocyanate. Under acidic conditions, the isocyanate hydrolyzes to the amine which is further hydrolysed in the case of arylamines.[76] The syntheses of 2-benzimidazolones, benzoxazolones and related compounds are accomplished by the treatment of carboxamides bearing nucleophilic substituents at the β-position with IBD-KOH-MeOH at 0 °C. The reaction results in a Hofmann-type rearrangement to generate an isocyanate *in situ*, which undergoes intramolecular nucleophilic attack by the XH group to afford the cyclized products (Scheme 13).[77]



Scheme 13. IBD-mediated Hofmann-type rearrangement.

2.4. Dehydrogenation

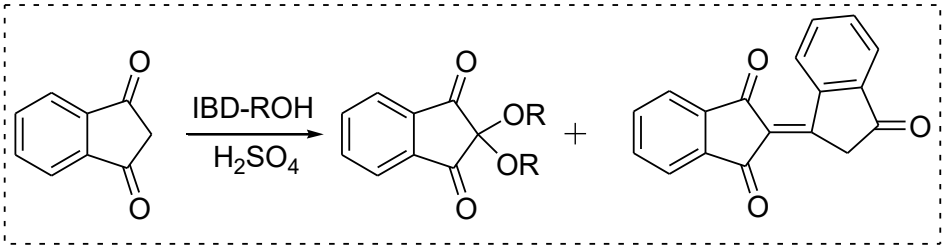
2-Aryl-1,2,3,4-tetrahydro-4-quinolones are dehydrogenated using iodobenzene diacetate in methanolic potassium hydroxide to obtain 2-aryl-4-quinolones. The reaction involves an iodine(III) intermediate which is generated by the electrophilic attack of $PhI(OMe)_2$ (from IBD-KOH-MeOH) at C3 of the enolate which, in turn, is generated from the tetrahedroquinolone by methoxide ion (Scheme 14).[78]



Scheme 14. Dehydrogenation of 2-aryl-1,2,3,4-tetrahydro-4-quinolones to 2-aryl-4-quinolones.

2.5. Acetalization in acidic conditions

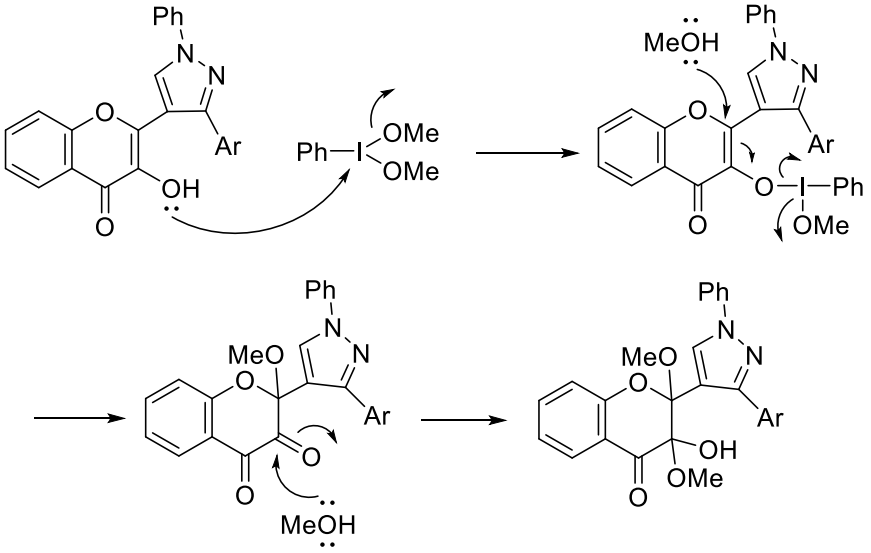
IBD-ROH-H_2SO_4 oxidized indane-1,3-dione to give the ketals and dimeric products. Under acidic conditions, the ketals afforded ninhydrin (Scheme 15).[79]



Scheme 15. Oxidation of indane-1,3-dione using IBD-ROH-H_2SO_4.

2.6. Addition: chromone to 2,3-dimethoxychromanone

When 3-hydroxy-2-(1-phenyl-3-aryl-4-pyrazolyl)chromones are treated with iodobenzene diacetate in methanol, the formation of 2,3-dimethoxy-3-hydroxy-2-(1-phenyl-3-aryl-4-pyrazolyl)chromanones takes place (Scheme 16).[80] All of the products were tested *in vitro* against Gram-positive and Gram-negative bacteria.



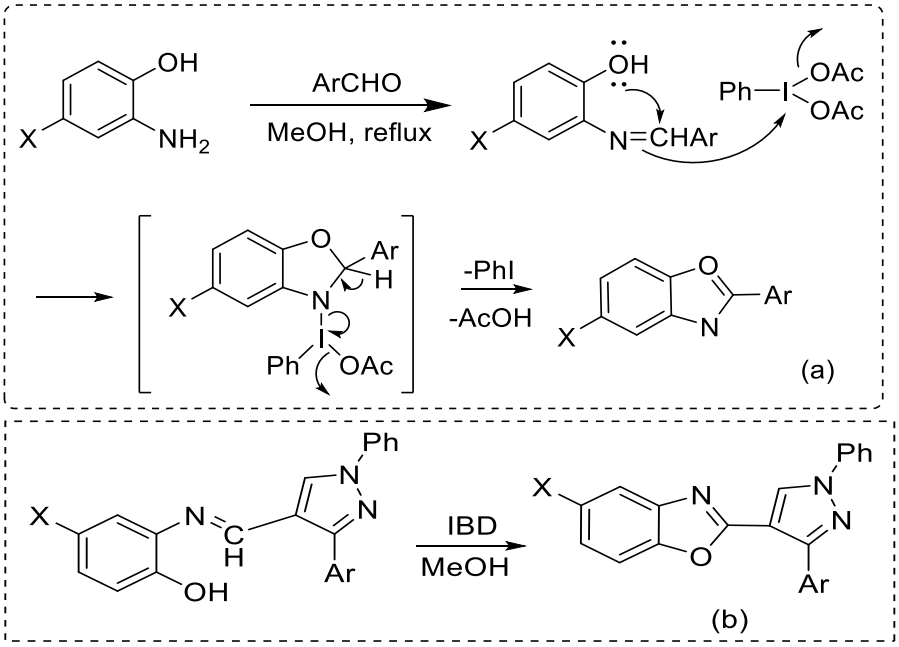
Scheme 16. Addition to a double bond to produce dimethoxy derivatives.

2.7. Intramolecular cyclization of Schiff's bases: synthesis of benzoxazoles

Phenolic Schiff's bases underwent oxidative intramolecular cyclization using IBD as oxidant in methanol or acetonitrile. The reaction resulted in the formation of 2-arylbenzoxazoles in high yields (Scheme 17a).[81] The Schiff's bases of o-aminothiophenol, *p*-chloro-*o*-aminothiophenol and aldehydes were subjected to oxidative intramolecular cyclization using IBD as an oxidant in dry methanol to furnish 2-substituted benzoxazoles. The reaction works in one-pot without isolating the intermediate Schiff's bases.[82]

Similarly, 2-(3-aryl-1-phenyl-4-pyrazolyl)benzoxazoles have been synthesized from the corresponding Schiff's bases using IBD-CH_3OH.[83] Schiff's bases, made with o-amino, p-chloro-o-aminophenol and aryl/hetaryl aldehydes, experience oxidative intramolecular annulation by the application of IBD in methanol to provide the respective benzoxazoles (Scheme 17b). All of these 2-aryl/hetaryl-benzoxazoles were evaluated *in vitro* for

their antibacterial and antifungal activities.[84,85] Pyrazolyl isoxazolines were synthesized by the 1,3-dipolar cycloaddition reactions of pyrazolyl nitrile oxide with various activated alkenes in the presence of IBD/MeOH containing a catalytic amount of TFA at room temperature.[86]



Scheme 17. Intramolecular annulation for benzoxazole preparation.

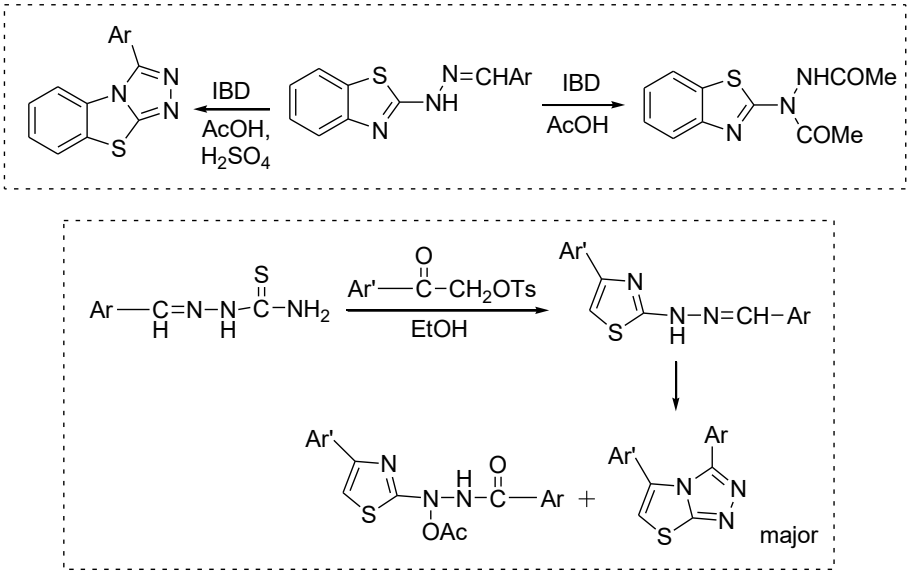
2.8. Intramolecular cyclization of hydrazones: Synthesis of fused triazoles

In most of the intramolecular cyclizations of hydrazones, the syntheses of fused triazoles was achieved. 2-Pyridyl and 2-quinylhydrazones were oxidatively cyclized to fused 1-aryl/hetryl-1,2,4-triazolo[4,3-*a*]pyridines and 1-aryl/heteroaryl-5-methyl-1,2,4-triazolo[4,3-*a*]quinolines by using IBD-dichloromethane. Seven compounds were tested for their antibacterial activity *in vitro*.[87,88] Similarly, 4,6-dimethyl-2-pyrimidinylhydrazones were successfully cyclized with IBD to afford 3-aryl/hetaryl-5,7-dimethyl-1,2,4-triazolo[4,3-*a*]pyrimidines. The compounds were tested *in vitro* for the antibacterial activity.[89]

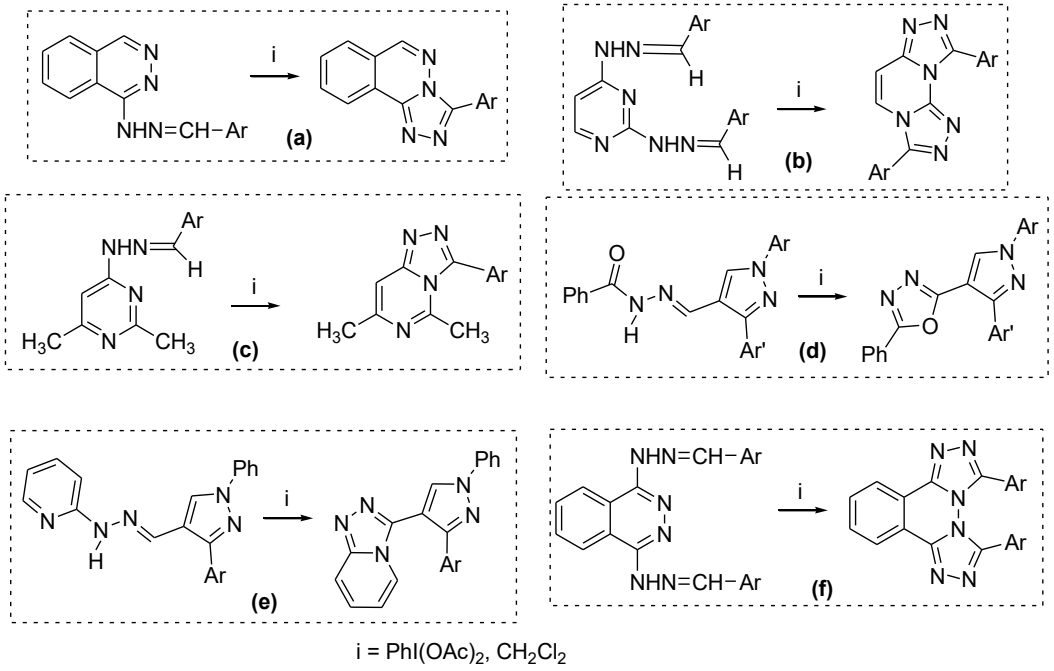
Treatment of arenecarbaldehyde benzothiazol-2-ylhydrazones with IBD in AcOH provided 1-acetyl-1-(benzothiazol-2-yl)-2-aroylhydrazines as the products. Furthermore, the reaction in AcOH-H_2SO_4 gave the bridgehead heterocycles, 1,2,4-triazolo[3,4-*b*]benzothiazoles. The acetylated product can also be converted to the bridgehead heterocycle by refluxing in phenol.[90] IBD-mediated oxidation of arenecarbaldehyde-4-arylthiazol-2-ylhydrazones in DCM resulted in 3,5-diarylthiazolo[2,3-*c*]-S-triazoles as the major product by an intramolecular cyclization (Scheme 18).[91]

Phthalazine hydrazones are oxidized by IBD in DCM to afford ring construction giving cyclic triazolophthalazine derivatives (Scheme 19 a-f).[92] Bishydrazones of 1,3-dihydrazinylbenzene are treated with two equivalents of IBD to give 9-diaryl-bis-1,2,4-triazolo[4,3-*a*][4,3-*c*]pyrimidines (Scheme 19a).[93] Analogously, bishydrazones of 2,4-dihydrazinopyrimidine are made with various araldehydes (and furfural) and treated with IBD to synthesize 3,9-diaryl- and 3,9-difuryl-bis-1,2,4-triazolo[4,3-*a*][4,3-*c*]pyrimidines (Scheme 19b). The products were tested for antibacterial activity.[94] Oxidation of the pyrimidinylhydrazones of various aryl/heteroaryl aldehydes using 1.1 equiv. of IBD in dichloromethane gave the cyclization products 3-aryl/heteroaryl-5,7-dimethyl-1,2,4-triazolo[4,3-*c*]pyrimidines (Scheme 19c).[95] Pyrazolylaldehyde N-acylhydrazones were cyclized in the presence of IBD-DCM to deliver the analogous oxadiazoles, 2-phenyl-5-

(1,3-diaryl-4-pyrazolyl)-1,3,4-oxadiazoles (Scheme 19d). The hydrazones obtained by the condensation of 2-pyridylhydrazine and the appropriate 4-formylpyrazole were oxidized using IBD-DCM to give the cyclized fused-triazole products, 3-(3-aryl-1-phenyl-1*H*-pyrazol-4-yl)-[1,2,4]triazolo[4,3-*a*]pyridines (Scheme 19e).[96] The synthesized compounds were tested for antibacterial and antifungal activity.[97] Hydrazones of dihydrazinophthalazine, 1,4-bis(substituted benzalhydrazino)phthalazines were cyclized by IBD under mild conditions to offer symmetrical 3,6-bis(aryl)bis([1,2,4]triazolo)[3,4-*a*:4',3'-*c*]phthalazines (Scheme 19f).[98]

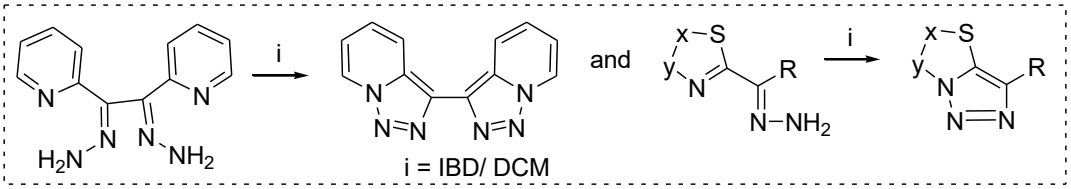


Scheme 18. Acetylation and fused triazole formation.



Scheme 19. Use of IBD in the construction of 1,2,4-triazole and 1,3,4-oxadiazole loop.

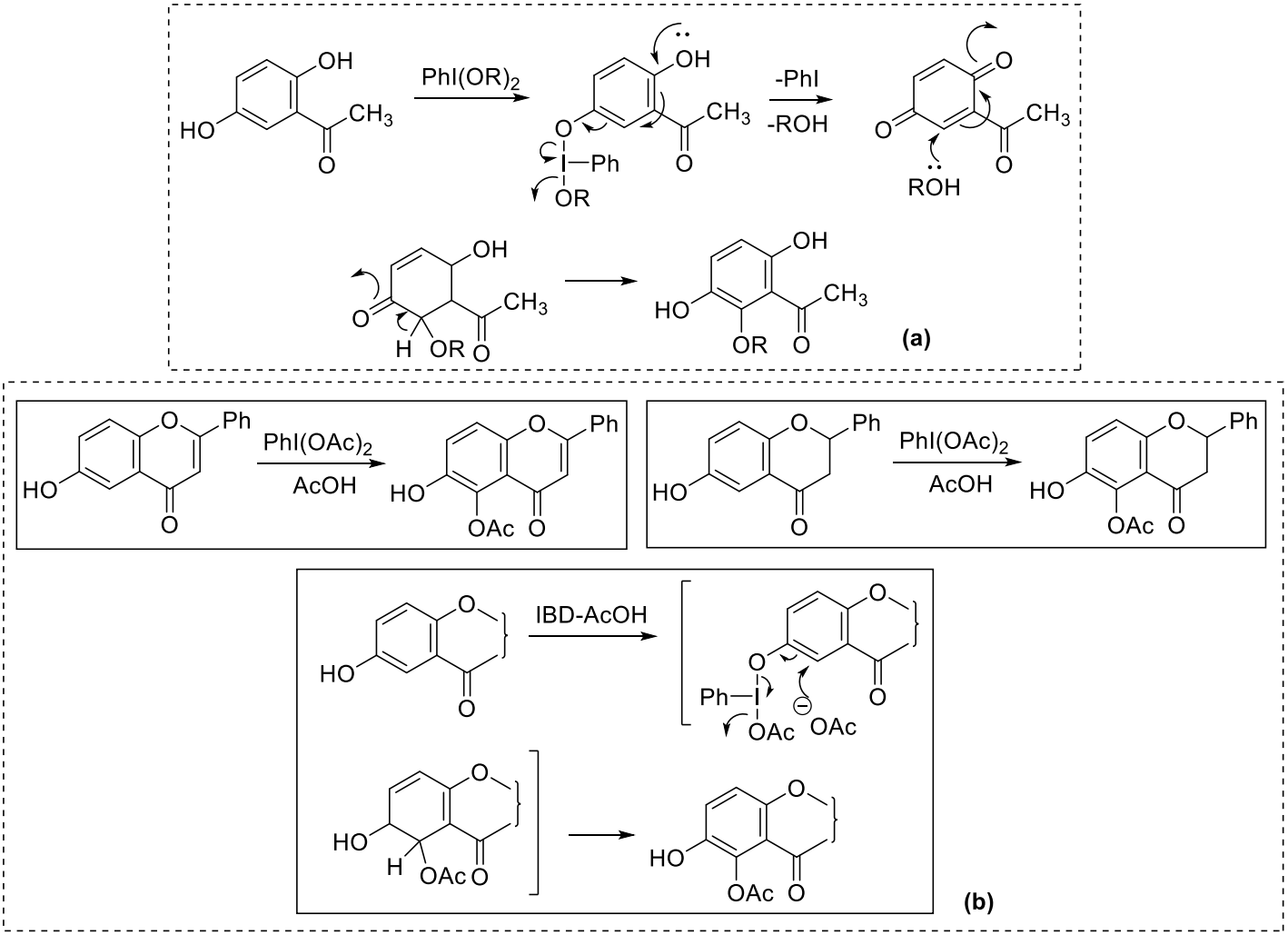
Intramolecular cyclization of hydrazones of N-heterocyclic ketones and aldehydes is effected by using IBD-DCM to achieve the synthesis of fused 1,2,3-triazoloheterocycles (Scheme 20).[99]



Scheme 20. Intramolecular cyclization for fused 1,2,3-triazole formation.

2.9. Alkoxylation/acetoxylation

While 2,4-dihydroxyacetophenones give o-iodophenoxy ethers through the rearrangement of iodonium ylides, 2,5-dihydroxyacetophenones undergo a regioselective alkoxylation in different alcohols, thereby, providing a new route for the synthesis of 6-alkoxy-2,5-dihydroxyacetophenones (Scheme 21a).[100] Similarly, regioselective acetoxylation of 6-hydroxyflavone and 6-hydroxyflavanones was effected with IBD-AcOH to obtain the 5-acetoxylated products (Scheme 21 b).[101]

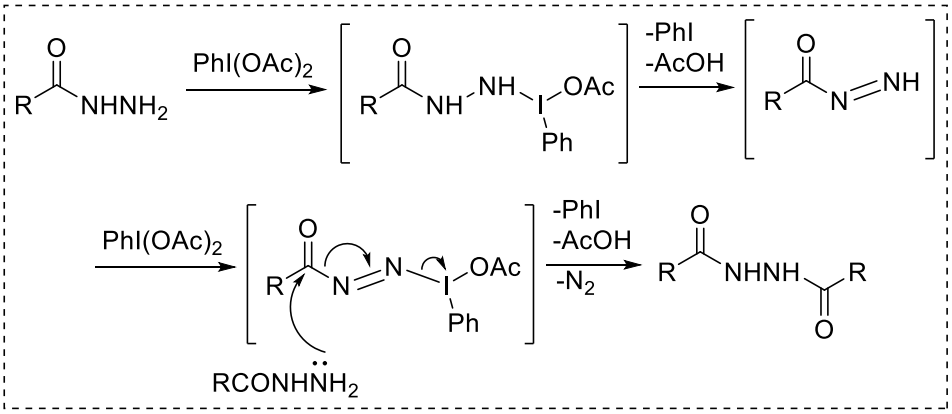


Scheme 21. Regioselective alkoxylation and acetoxylation.

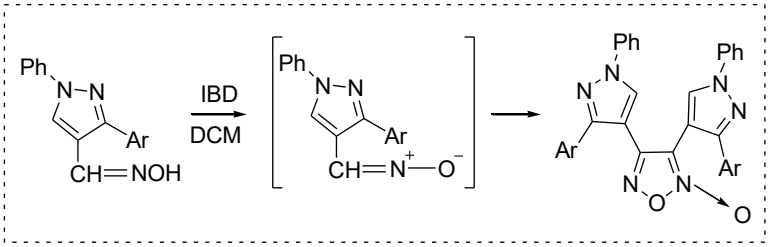
2.10. Dimerization

IBD was utilized in the dimerization of hydrazides in dry DCM or acetonitrile. Phenylactohydrazide, p-substituted benzohydrazides and heterocyclic acid hydrazides were successfully dimerized to N,N-diacylhydrazines (Scheme 22). The reaction involves the electrophilic attack of IBD on the lone pair of terminal nitrogen of hydrazide to give the intermediate which undergoes reductive loss of PhI alongwith expulsion of AcOH to generate acylimide. The acylimide is oxidized with second molecule of IBD followed by nucleophilic attack by hydrazide at carbonyl to offer the product.[102]

Solid-state dimerization of acid hydrazides to N,N'-diacylhydrazines was effected using IBD. The contents were thoroughly mixed in a conical flask for 1-5 min and pulverized by rubbing with a spatula against walls of the flask, thus resulting in the evolution of nitrogen gas and a change of colour of the mixture from white to dirty red. The completion of the reaction was marked by a change in state from solid to semi-solid, giving the characteristic smell of iodobenzene. Alternatively, heating the solid reaction mixture on a water bath completed the reaction in less than one minute.[103] Treatment of pyrazole-4-carboxaldehyde oximes with IBD gave the dimerization products, 3, 4-bis-(1-phenyl-3-arylpyrazolyl)-1,2,5-oxadiazole-N-oxides, of the initially formed nitrile oxides (Scheme 23).[104]



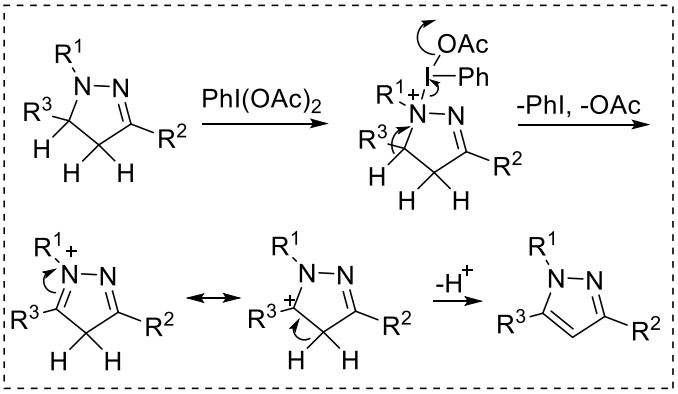
Scheme 22. Dimerization of hydrazides to N,N-diacylhydrazines.



Scheme 23. Pyrazole-4-carboxaldehyde oximes dimerized to 3, 4-bispyrazolyl-1, 2, 5-oxadiazole-N-oxides.

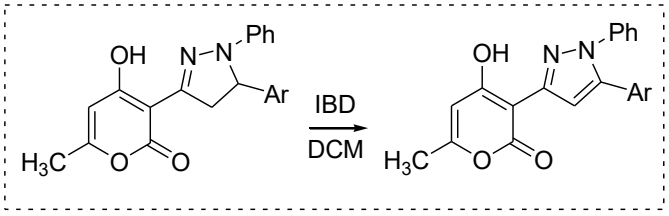
2.11. Oxidation of single bond

IBD-mediated facile oxidation of 1,3,5-trisubstituted pyrazolines to the corresponding pyrazoles was successfully achieved (Scheme 24).[105]



Scheme 24. Oxidation of pyrazoline to pyrazole.

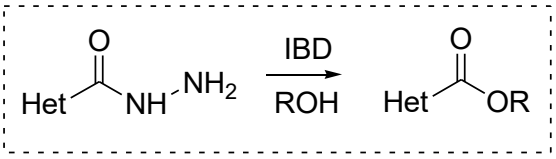
Pyrazolines are made by the condensation of 1,3-diarylprop-2-en-1-ones with phenylhydrazines, and oxidized to the corresponding pyrazoles by using IBD-DCM. Some of the synthesized pyrazoles were tested for antifungal acitivity.[106] In a similar manner, pyrazolines, made by combining 3-cinnamoyl-4-hydroxy-6-methyl-2-pyrones (chalcone analogs of DHA) with phenylhydrazine, undergo dehydrogenation to the corresponding pyrazoles, 5-aryl-3-(4-hydroxy-6-methyl-2*H*-pyran-2-oxo-3-yl)-1-phenylpyrazoles, while stirring the reaction mixture with IBD-DCM for 2 hours (Scheme 25).[107] Analogously, the pyrazolines obtained from chalcone analogs of Cl-DHA were converted to the homologous pyrazoles, 5-aryl-3-(4-chloro-6-methyl-2*H*-pyran-2-on-3-yl)-1-phenylpyrazoles by the application of IBD.[108]



Scheme 25. Oxidation of pyrazoline from DHA-chalcone to pyrazole.

2.12. C-N cleavage

Heterocyclic acid hydrazides, when treated with IBD in nucleophilic solvents, afforded the products of C-N cleavage, the corresponding esters or carboxylic acids (Scheme 26).[109]

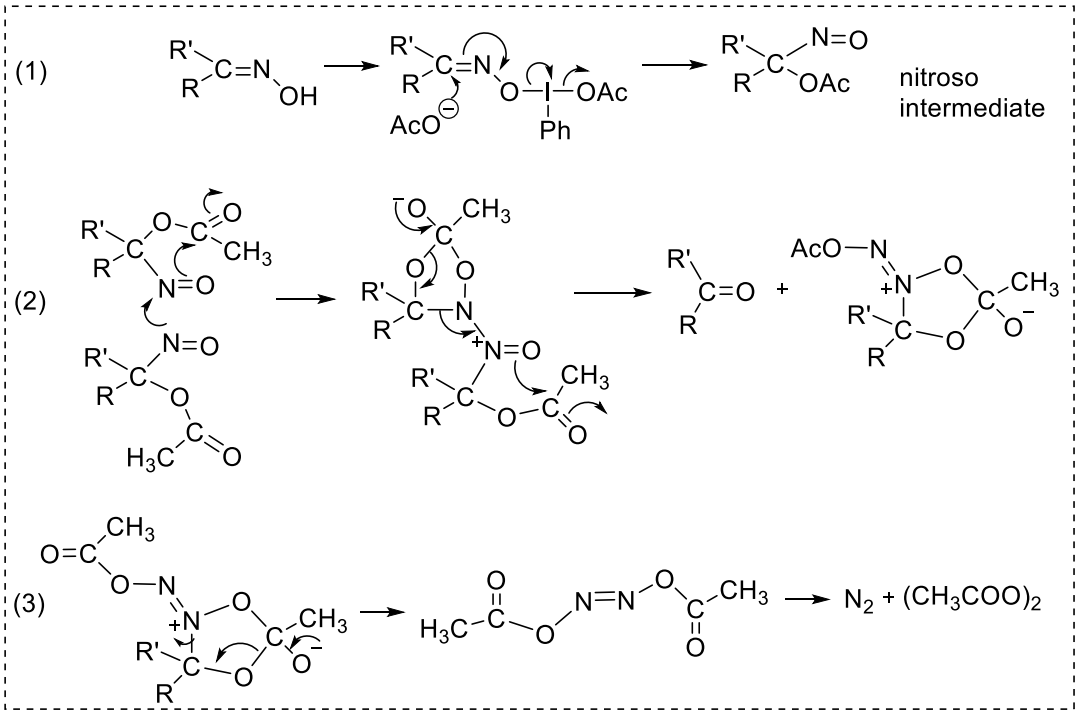


Scheme 26. Conversion of acid hydrazides to esters or acids.

2.13. Regeneration of carbonyl moiety

Ketoximes undergo C-N bond cleavage when treated with IBD in DCM to afford the corresponding ketones (Scheme 27) The mechanism for the deoximation reaction may involve the formation of nitroso intermediate.

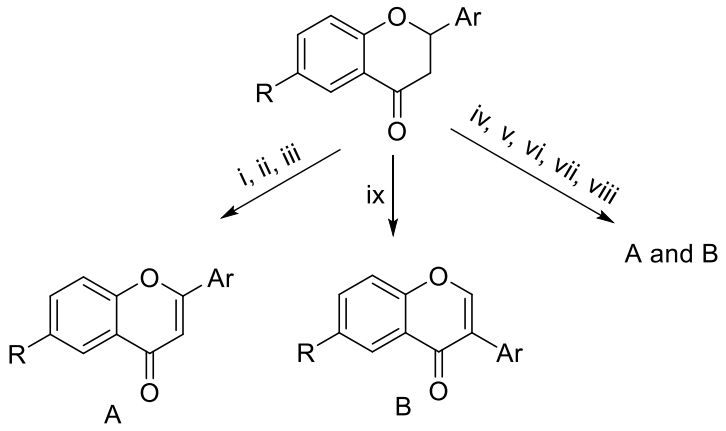
Evolution of nitrogen gas was observed in aromatic ketoximes. Probably, the nitroso intermediate undergoes dimerization and the resulting dimer gives nitrogen gas on decomposition.[110]



Scheme 27. Carbonyl regeneration from its derivatives.

2.14. Miscellaneous

Various flavanones were converted to flavones and isoflavones depending upon the reaction conditions. Appropriate reaction conditions can be selected to obtain the desired flavone or isoflavone product (Scheme 28).[111]



Scheme 28. Organoiodine(III) reagents in the conversions of flavanones.

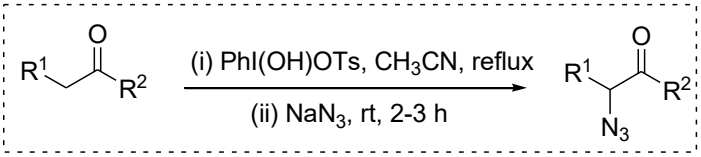
3. [Hydroxy(tosyloxy)iodo]benzene

Hydroxy(tosyloxy)iodobenzene (HTIB), widely recognized as Koser's reagent, functions both as an oxidant and versatile group-transfer reagent. In addition to its classical application in α-tosyloxylation of enolizable

ketones, HTIB has been effectively employed in oxidative rearrangements, including ring contraction and expansion processes, as well as in oxidative cyclization reactions for the construction of oxygen and nitrogen-containing heterocycles.[112–118] It also plays a significant role in the dearomatization of phenols, oxyfunctionalization and difunctionalization of alkenes (such as oxytosyloxylation), and oxidative cleavage of carbon–carbon bonds.[119,120] Furthermore, HTIB-mediated transformations include the synthesis of α-functionalized carbonyl compounds, intramolecular cyclizations, and tandem or cascade reactions that enable the rapid assembly of complex molecular architectures.[121–125] Contributions from various research groups have expanded its scope to include ligand-exchange processes and the generation of reactive iodine(III) intermediates for novel bond-forming reactions.[126,127] Owing to its operational simplicity, high regio- and chemoselectivity, and reduced toxicity compared to conventional metal-based oxidants, HTIB continues to serve as a powerful and reliable reagent in the synthesis of structurally diverse, and biologically important, molecules.

3.1. α-Functionalization: tosyloxylation

A remarkable reaction of HTIB is to effect α-tosyloxylation of enolizable ketones, i.e., to introduce the formal equivalent of the tosyloxyenium ion (TsO^+) directly onto the α-carbon.[128] α-Tosyloxyketones offer a superior alternative to large number of syntheses that make the use of highly-lachrymatory α-haloketones used conventionally. Reaction of various enolizable ketones with HTIB followed by treatment of the *in situ* generated α-tosyloxyketone with sodium azide offered a one-pot procedure for the synthesis of α-azido ketones in high yields (Scheme 29).

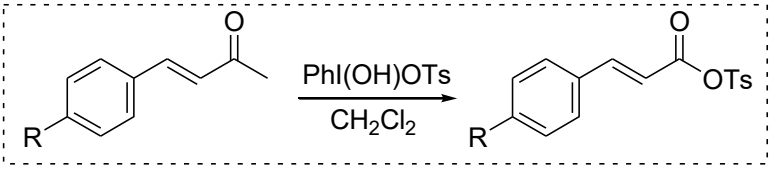


Scheme 28. Preparation of α-azidoketones through α-tosyloxyketones.

Generally, the tosyloxy-compounds are used as precursors for the formation of different heterocyclic compounds, discussed in the upcoming section. Furthermore, in most of the cases, the approach provides the direct synthesis of heterocycles without isolating the intermediate tosylates.

In addition to monotosyloxylation, HTIB promotes multiple tosylation pathways depending on substrate structure and reaction conditions. For instance, α,α-ditosyloxyketones (gem-ditosylates) are formed *via* successive tosyloxylation at the same α-carbon and α,β-ditosyloxylation, leading to the formation of α,β-ditosyloxyketones (vic-ditosylates) through electrophilic addition across the enol/enone framework[129]. The ditosylates constitute valuable bifunctional synthons, as the presence of two excellent tosyloxy leaving groups enables diverse chemical transformations.

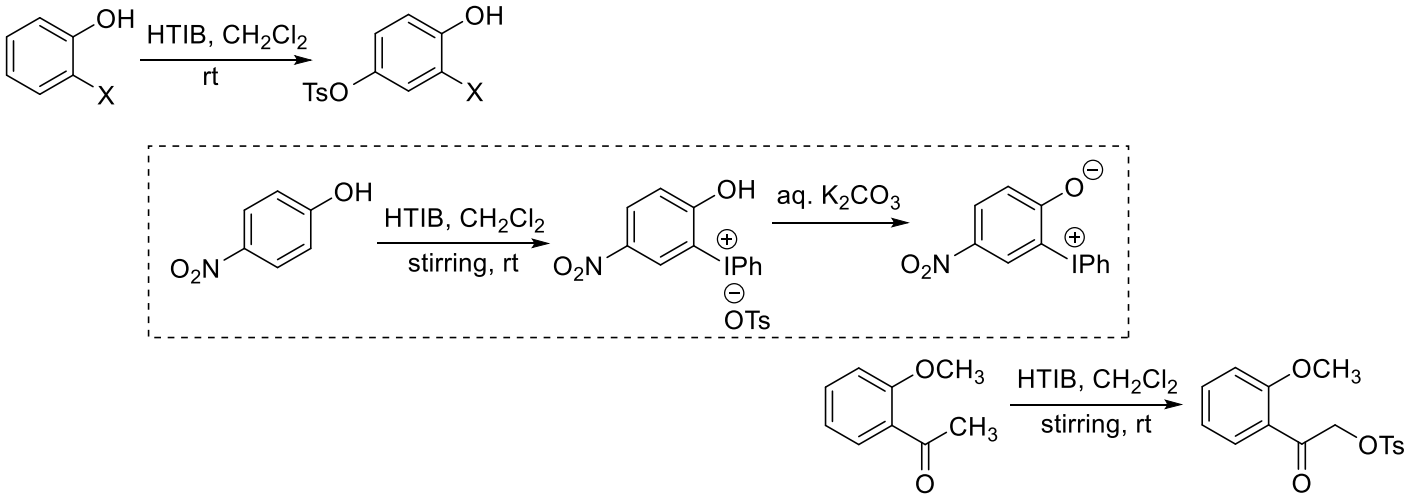
The reaction of enolizable ketones having a double bond, i.e., α,β-unsaturated ketones (benzalacetones) with HTIB leads to regioselective tosyloxylation, giving α-tosyloxybenzalacetones, in good yields. This study established that HTIB, a tosyloxylating agent, possessed selectivity for ketones in the presence of an α,β-unsaturated conjugated double bond. The products obtained are potential precursors for various chemical modifications to synthesize biologically-active heterocyclic compounds (Scheme 30).[130]



Scheme 29. Regioselective tosyloxylation of benzalacetones.

Tosyloxylation of aromatic rings bearing electron-withdrawing groups at the *ortho* position to a phenolic group have been conducted to achieve the straightforward synthesis of 4-tosyloxy-2-substituted phenols. The oxidation of *ortho* substituted phenols with HTIB in DCM at room temperature offers a novel and regioselective approach for the tosyloxylation of *ortho*-substituted phenols. The monohydric phenols which contained electron-withdrawing substituents (-NO_2, -CHO, -$CONH_2$, -$COOCH_3$, -COOPh) at the *ortho* position, underwent smooth tosyloxylation to the corresponding 4-tosyloxy-2-substituted phenols.[131]

The reaction of *p*-nitrophenol under similar reaction conditions, however, afforded 2-hydroxy-5-nitrodiphenyliodonium tosylate which, upon basification with aqueous potassium carbonate, resulted in the formation of stable ylides. Under similar reaction conditions, the reaction of *o*-methoxyacetophenone (an electron-releasing group) afforded the α-tosyloxyketone. Therefore, it was concluded that the presence of the *o*-hydroxy group is necessary to carry out nuclear tosyloxylation of the ring (Scheme 31).



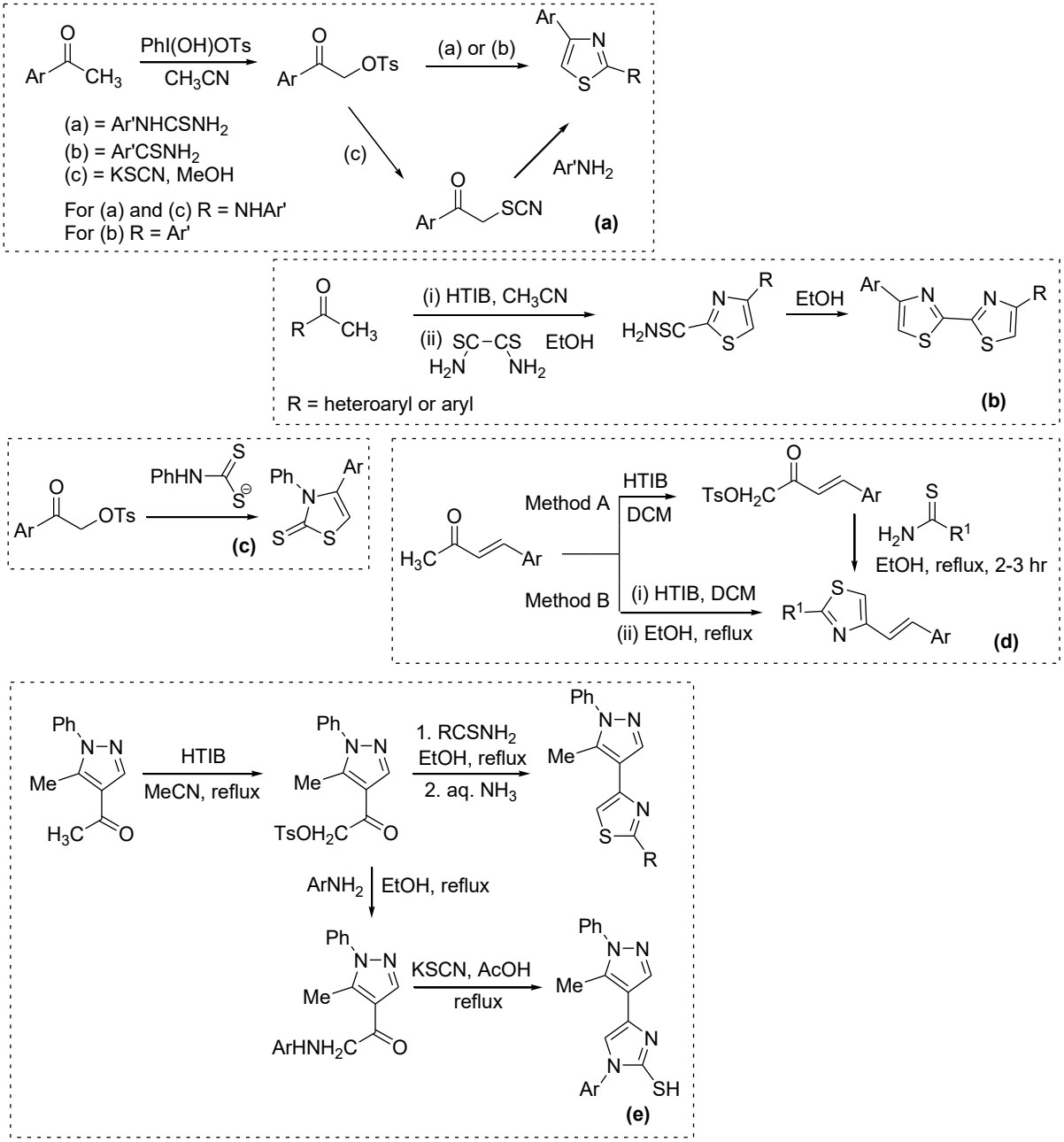
Scheme 30. Ring tosyloxylation and ylide formation.

3.2. Tosyloxyketones-mediated cyclization: Synthesis of heterocycles

3.2.1. Synthesis of unfused heterocycles. α-Tosyloxyketones, obtained by α-functionalization of enolizable ketones using HTIB, were used for constructing the thiazole nucleus in a modified Hantzsch thiazole synthesis. A considerable amount of work has been done on this reaction.

Tosyloxyketones, upon treatment with various binucleophiles such as thioureas and thioamides, result in the formation of *N*-substituted-2-aminothiazoles (R = NHAr'), and 2-substituted thiazoles (R = Ar'), respectively.[132–134] Many *N*-substituted-2-aminothiazoles (R = NHAr') have been synthesized by the treatment of α-thiocyanatoacetophenones, obtained from the corresponding tosylates and potassium thiocyanate, with the appropriate anilines.[135,136] Also, these syntheses are successfully effected by a direct one-pot procedure, thereby, omitting the step of isolation of the intermediate α-tosyloxyketones (Scheme 32a-e). The

construction of new thiazole derivatives, 4-aryl-2-(2-(1-arylethylidene)hydrazinyl)thiazoles and 2-*N*-acetylhydrazino-4-arylthiazoles, starting from aryl methyl ketones and thiosemicarbazones or *N*-acetylthiosemicarbazide, respectively, have been reported (Scheme 32a).[137,138] In a similar fashion, α-tosyloxy



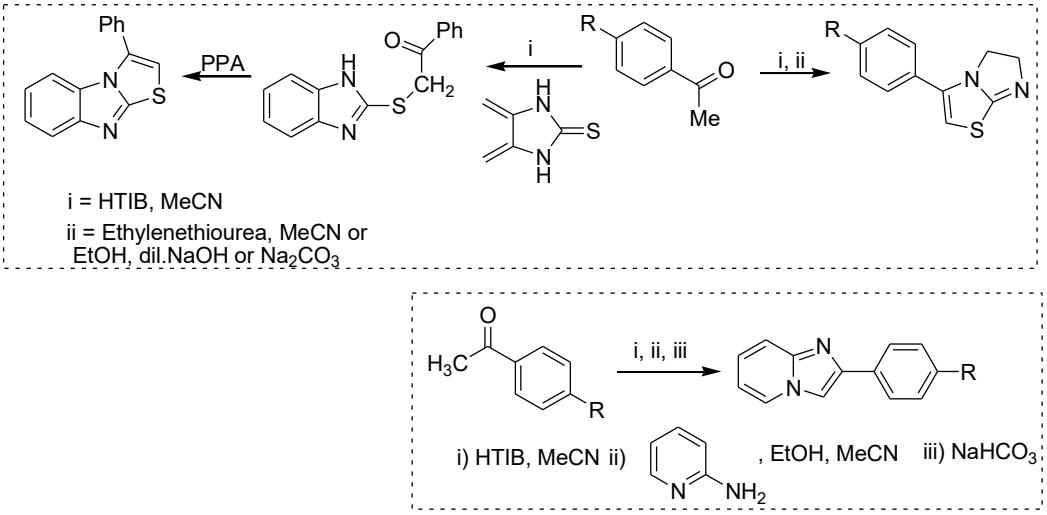
Scheme 31. α-Tosyloxyketones in (i) modified Hantzsch thiazole and (ii) imidazole synthesis.

derivatives of heteroaryl/aryl methyl ketones on treatment with rubeanic acid (dithiocarboxamide) lead to the formation of 2-thiocarboxamidethiazoles which provides a useful method for the convenient synthesis of bi-, ter- and quarter-heterocycles (Scheme 32b). Examples of such reactions include the synthesis of aryl(thienyl)- and bis(thienyl)bithiazoles.[139] α-Tosyloxy derivative have been converted to 3,4-diarylthiazole-2(3*H*)-thiones by the action of phenylammonium dithiocarbamate salt in ethanol (Scheme 32c).[140] The reaction of (*E*)-4-arylbut-3-en-2-ones with HTIB followed by treatment with thioureas, thioamide, and thiobenzamide has offered a one-pot synthesis of 2-substituted 4-styrylthiazoles (Scheme 32d).[141] 4-Pyrazolylthiazoles and 4-

pyrazolylmercaptoimidazoles have been synthesized by the treatment of 4-acylpyrazoles with HTIB *via* the intermediate 4-(α-tosyloxyacetyl)pyrazole (Scheme 32e).[142] There is one report of the formation of a pyrazole heterocycle by the reaction of α,β-chalcone ditosylates with various reagents, such as phenylhydrazine hydrochloride, semicarbazide hydrochloride and thiosemicarbazide in suitable conditions leading to a 1,2-aryl shift. Similarly, the reaction of ditosylates with hydroxylamine hydrochloride leads to 4,5-disubstituted-isoxazoles.[143]

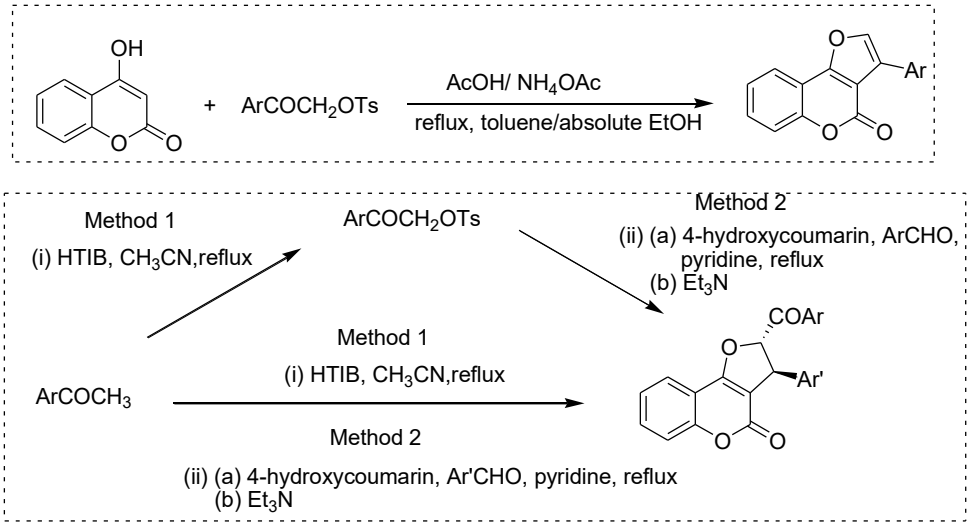
3.2.2. Synthesis of fused heterocycles

3.2.2.1. Imidazo- and thiazolo-fused heterocycles. The synthesis of 3-substituted-5,6-dihydroimidazo[2,1-*b*]thiazoles has been carried out by exploiting the hypervalent-iodine oxidation of acetophenones with [hydroxy(tosyloxy)iodo] benzene, followed by the treatment of the resultant α-tosyloxyacetophenones (generated *in situ)* with ethylenethiourea. The same approach, starting from a carbonyl compound and a 2-mercaptobenzimidazole, also afforded 3-phenylthiazolo[3,2-*a*]benzimidazole *via* the intermediate 2-phenacylmercaptobenzimidazole.[144] Similarly, HTIB-mediated syntheses of substituted imidazo[1,2-*a*]pyridines which showed prominent antifungal activity have been reported (Scheme 33).[145]



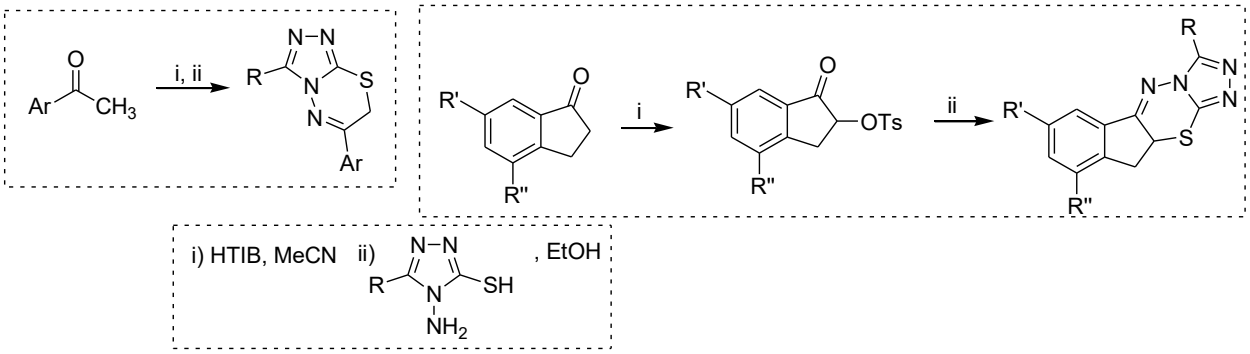
Scheme 32. Synthesis of 3-substituted-5,6-dihydroimidazo[2,1-*b*]thiazoles and 3-phenylthiazolo[3,2-*a*]benzimidazoles.

3.2.2.2. Furo[3,2-*c*]coumarins. The cyclocondensation of α-tosyloxyketones with 4-hydroxycoumarin has been reported for the synthesis of furo[3,2-*c*]coumarins *via* initial C–C bond formation, followed by a 5-exo-tet-cyclization (2012).[146] Based on this strategy, a modified one-pot multi-component protocol was subsequently developed for the diastereoselective synthesis of variously-substituted *trans*-2,3-dihydrofuro[3,2-c]coumarins using α-tosyloxyacetophenones, aromatic aldehydes and 4-hydroxycoumarin in the presence of pyridine and triethylamine (Scheme 34).[147]



Scheme 33. One-step and two-step syntheses of furo[3,2-*c*]coumarins via α-tosyloxyketones.

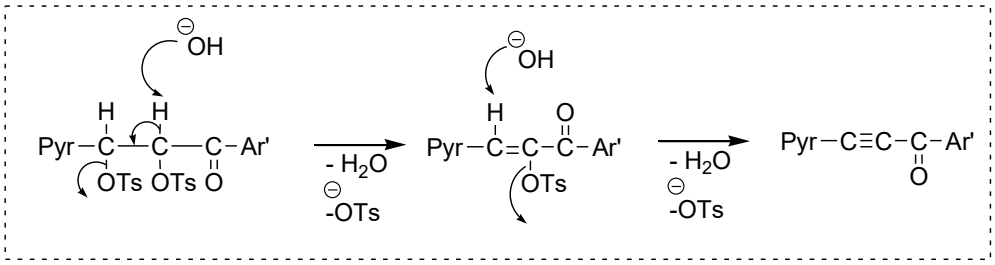
3.2.2.3. Synthesis of indeno-fused triazolo-thiadiazines. The HTIB-mediated synthesis of symmetrical triazolo-[3,4-*b*]-1,3,4-thiadiazines has been achieved by a one-pot, two-step process. The products were tested for their antibacterial properties.[148] The synthesis of a series of 3-alkyl/aryl-7/9-methyl-10,10a-dihydroindeno[1,2-*e*][1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazines has been achieved by the cyclocondensation between 4/6-methyl-2-tosyloxy-1-indanones (obtained using HTIB in acetonitrile) and 3-alkyl/aryl-4-amino-5-mercapto-1,2,4-s-triazoles (Scheme 35).[149]



Scheme 34. HTIB-mediated synthesis of triazolo-thiadiazines.

3.3. Elimination

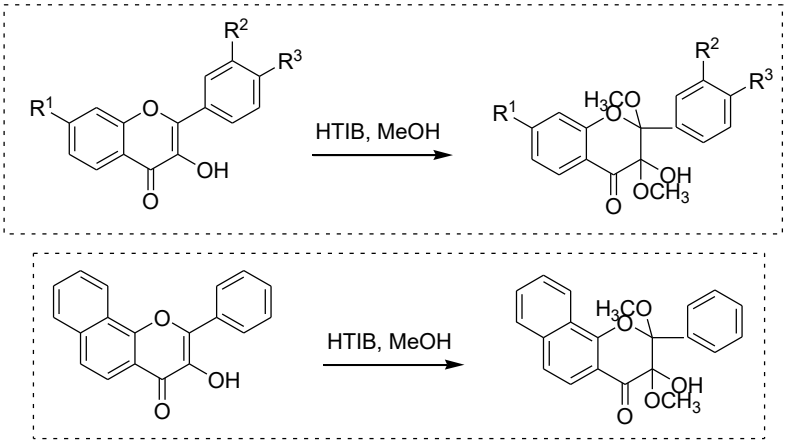
A facile route for the synthesis of acetylenic ketones by the elimination of ditosyloxy groups of ditosylates derived from α,β-chalcone has been described (Scheme 36). The acetylenic ketones are stable compounds which are, otherwise, challenging to synthesize by other methods (Scheme 36).[150]



Scheme 35. Synthesis of acetylenic ketones.

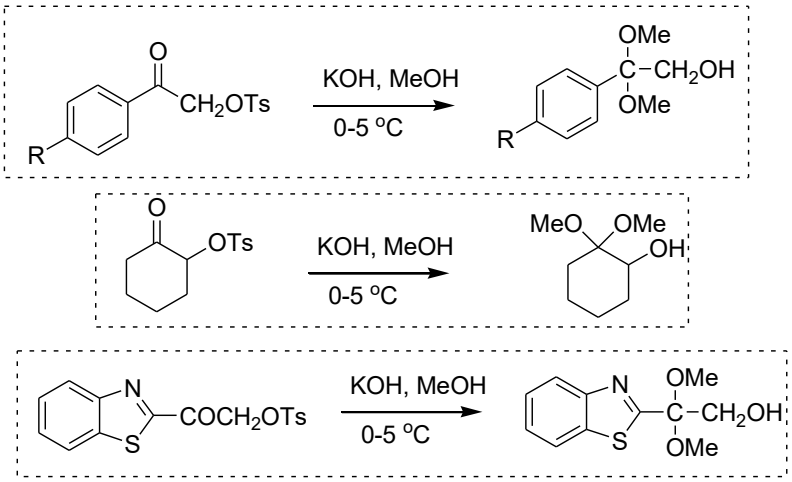
3.4. Acetalization

HTIB-mediated oxidation of various flavonols and o-naphthoflavonol leads to the formation of 2,3-dimethoxy-3-hydroxyflavanones and 2,3-dimethoxy-3-hydroxy- α -naphthoflavanone, respectively. HTIB resembles periodic acid in its oxidative behavior towards flavonols. The reaction, with a slight excess of HTIB in methanol, occurs spontaneously, and the corresponding 2,3-dimethoxy-3-hydroxyflavanones [methyl 3- hemiacetals of 2-methoxy 3,4-flavandione] are formed. α-Naphthoflavonol also undergoes the same type of oxidation, and the methyl 3-hemiacetals of 2-methoxy 3,4-naphthoflavandione are formed in good yield (Scheme 37).[151]



Scheme 36. Addition to double bond in flavanols.

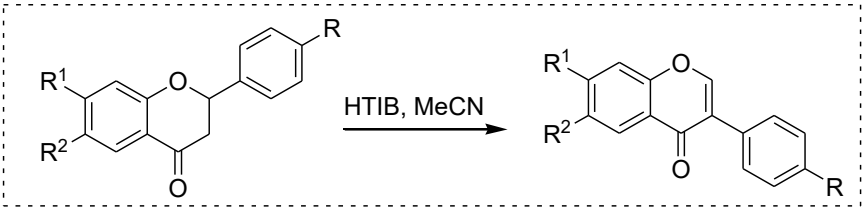
Upon reaction with methanolic potassium hydroxide, different α-tosyloxyketones afford the corresponding α-hydroxy-dimethylacetals (Scheme 38).[152]



Scheme 37. Synthesis of α-hydroxy-dimethylacetals from tosyloxyketones in basic medium.

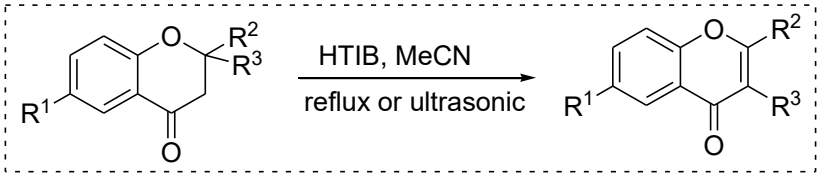
3.5. Rearrangement

3.5.1. 1,2-aryl shift. Oxidation of flavanones using HTIB/MeOH affords the corresponding flavones[153] whereas HTIB/MeCN-mediated oxidation of flavanones (2-aryl-2*H*-1-benzopyran-4(3*H*)-ones), leads to a 1,2-aryl shift, providing an efficient route to isoflavones (3-aryl-4*H*-1-benzopyran-4-ones) (Scheme 39).[154]



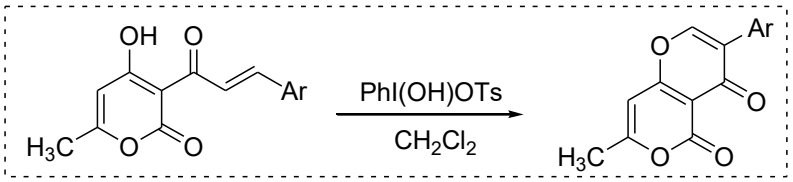
Scheme 38. Rearrangement of flavanones to isoflavones.

Oxidation of chromanones and 2-spirochromanones using HTIB in refluxing acetonitrile, as well as using ultrasound, provides a convenient route for the synthesis of chromones, tetrahydroxanthones and their higher homologues *via* dehydrogenation and 2,3-alkyl migration. The ultrasound also substantially enhanced the rate of the above transformations (Scheme 40).[155]



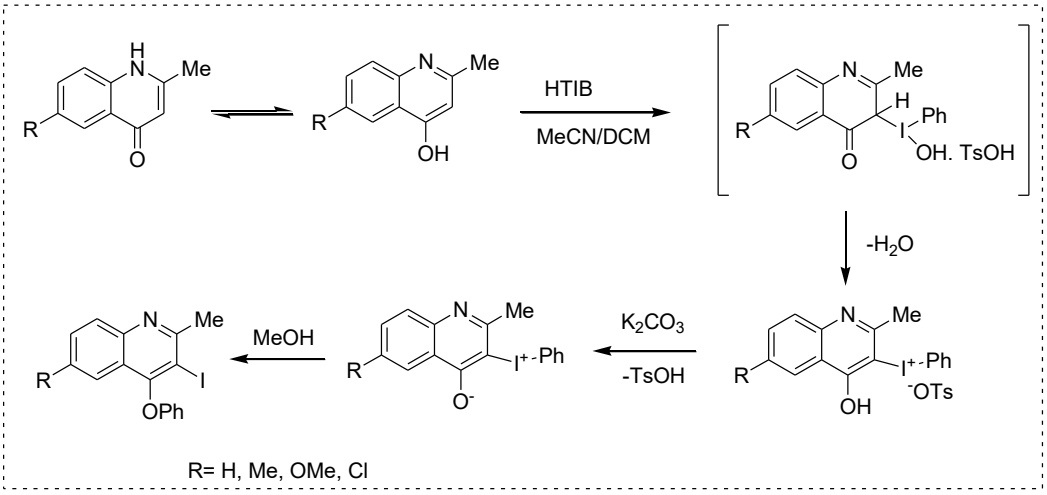
Scheme 39. Dehydrogenation and alkyl migration in chromanones.

The oxidation of 3-cinnamoyl-4-hydroxy-6-methyl-2*H*-pyran-2-ones with HTIB in DCM led to cyclization, thereby, providing a new and convenient route for the synthesis of 3-aryl-7-methylpyrano[4,3-*b*]pyran-4*H*,5*H*-diones (Scheme 41).[156]



Scheme 40. Intramolecular cyclization and migration in DHA-chalcones.

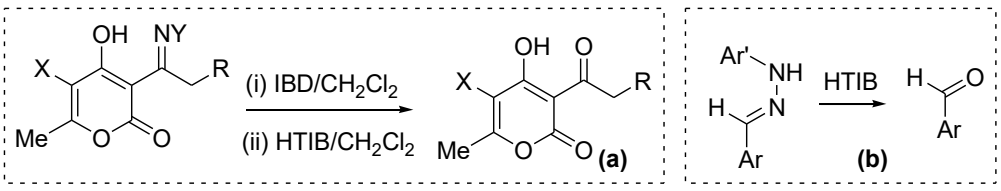
3.5.2. Rearrangement through an ylide. The oxidation of 2-methyl-4-quinolones by HTIB in acetonitrile or DCM gave phenyliodonio tosylate, and then monocarbonyl iodonium ylides, which rearranged to 2-methyl-3-iodo-4-phenoxyquinolines (Scheme 42).[157]



Scheme 41. Rearrangement of 4-quinolones to 3-iodo-4-phenoxyquinoline derivatives.

3.6. Regeneration of carbonyl moiety

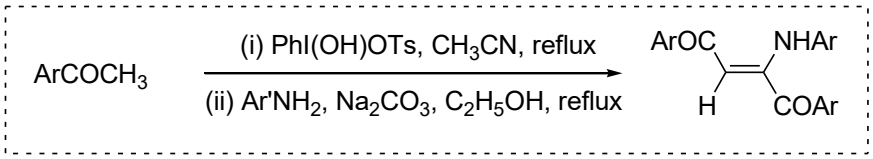
Hypervalent iodine oxidation of carbonyl derivatives of dehydroacetic acid and its analogs, leads to a mild and efficient regeneration of the parent carbonyl compounds leaving the pyrone moiety intact (Scheme 43a).[158] The HTIB-mediated regeneration of carbonyl compounds from various derivatives of carbonyl compounds of aryl and heteroaryl hydrazines containing adjacent nitrogen atoms has been reported. These types of hydrazones are cleaved oxidatively by HTIB, giving back the carbonyl compounds, while cyclisation occurred with iodobenzene diacetate (IBD) (Scheme 43b).[159]



Scheme 42. Hypervalent iodine(III)-mediated regeneration of carbonyl group.

3.7. Dimerization

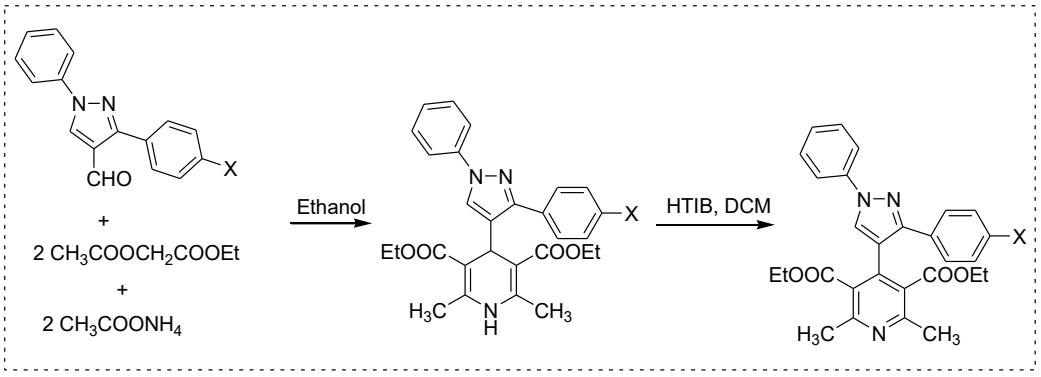
α-Anilinoacetophenones efficiently undergo oxidative dimerization to give 1,4-diaryl-2-(arylamino)but-2-ene-1,4-diones using HTIB (Scheme 44).[160]



Scheme 43. HTIB in the dimerization of α-anilinoacetophenones.

3.8. Aromatization

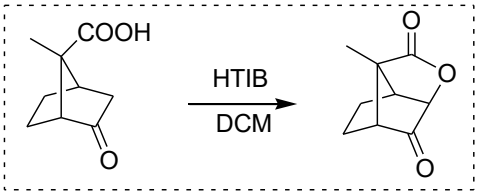
The synthesis of a series of diethyl-1,4-dihydro-2,6-dimethyl-4-(3-aryl-1-phenyl-4-pyrazolyl)pyridine-3,5-dicarboxylates by the multicomponent-cyclocondensation reaction of ethylacetoacetate, 3-aryl-1-phenylpyrazole-4-carboxaldehyde, and ammonium acetate, was carried out in 2011. The dihydropyridines were smoothly converted to diethyl-2,6-dimethyl-4-(3-aryl-1-phenyl-4-pyrazolyl)pyridine-3,5-dicarboxylates using HTIB as the oxidizing agent (Scheme 45). The compounds were evaluated for their antimicrobial activity.[161]



Scheme 44. HTIB-mediated aromatization of dihydropyridines.

3.9. Oxidative lactonization

Oxidation of 5-ketoacids and 4,6-diketoacids using HTIB in DCM afforded keto-γ-lactones, and diketo-δ-lactones, under refluxing conditions and at room temperature, respectively (Scheme 46).[162]



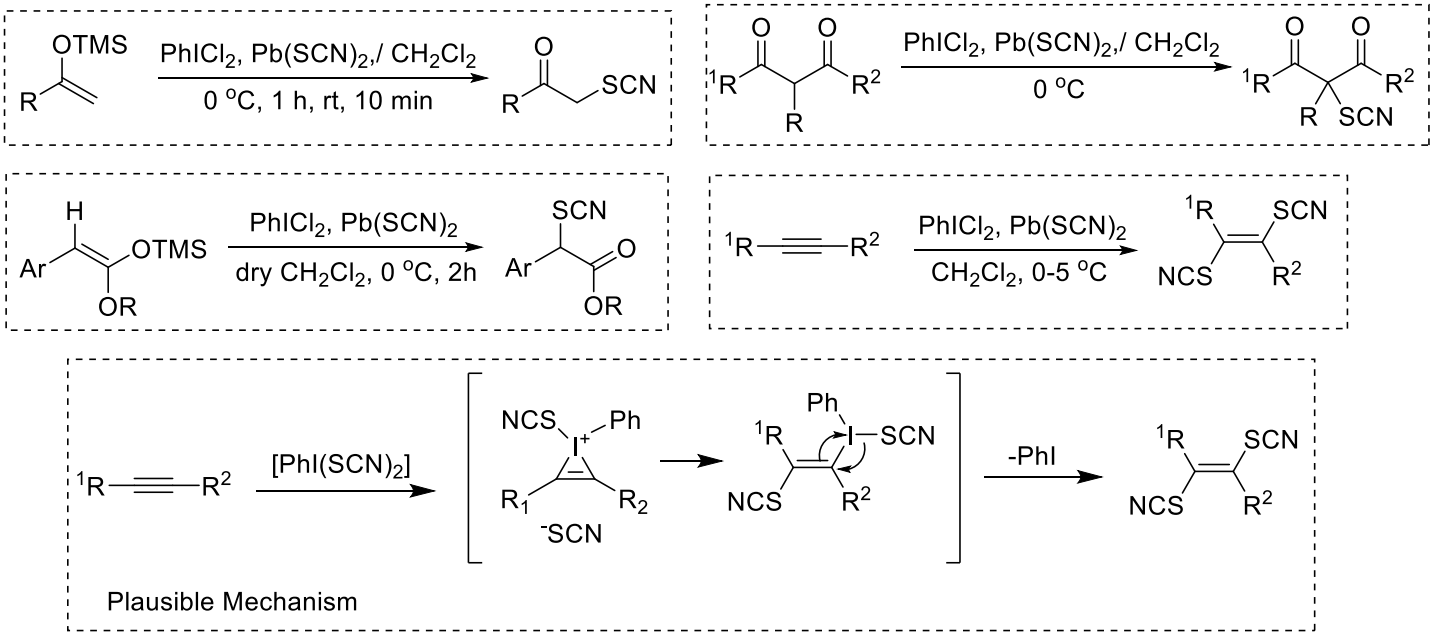
Scheme 45. Lactonization of 5-ketoacid to a keto-γ-lactone.

4. Dichloroiodobenzene

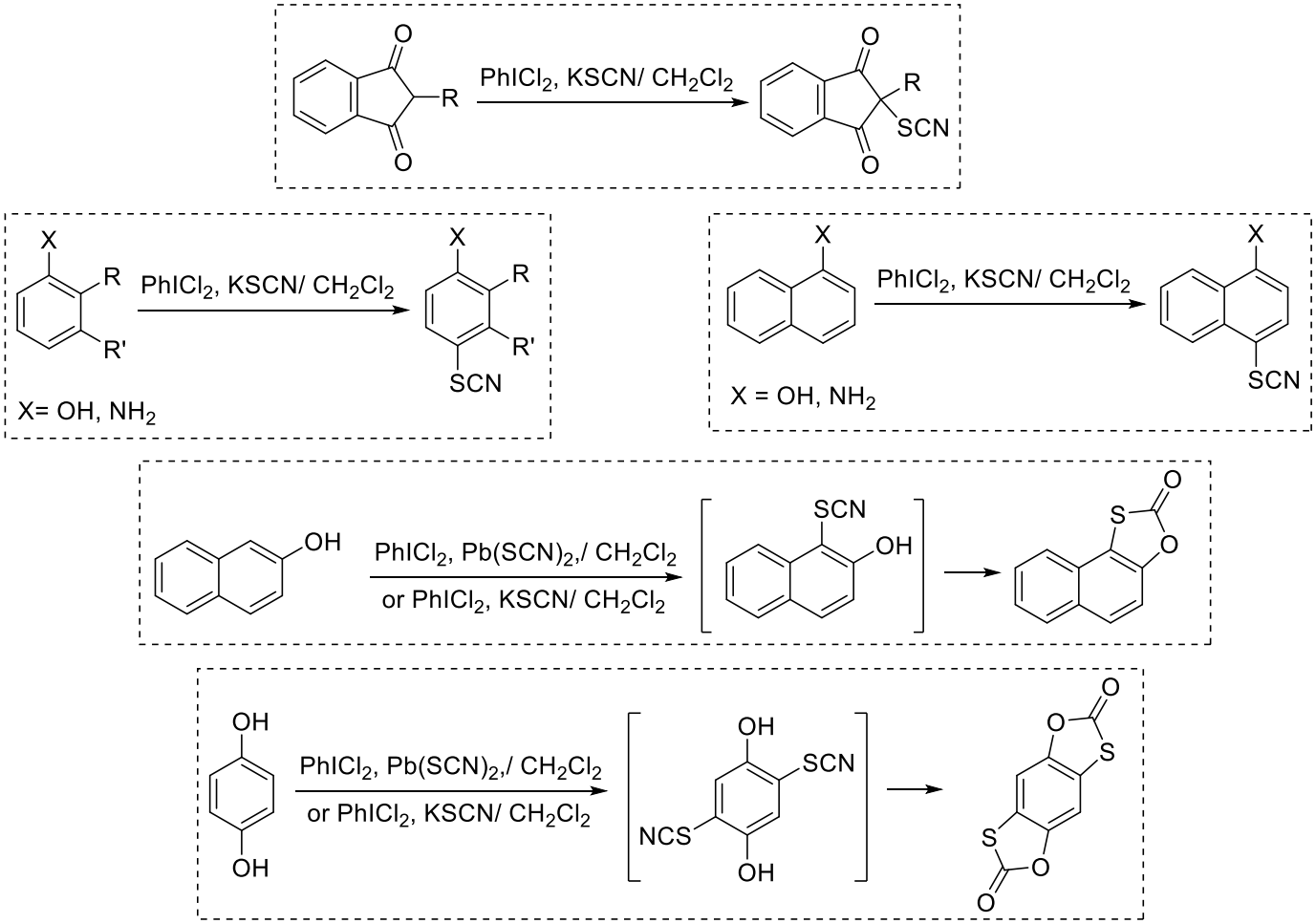
(Dichloroiodo)benzene ($PhICl_2$), an iodine(III) reagent, is a versatile electrophilic chlorinating and oxidizing agent widely employed in organic synthesis. Due to its highly polarized I–Cl bonds, and strong electrophilic character, it facilitates a variety of transformations, including electrophilic chlorination of arenes and activated-methylene compounds, α-chlorination of carbonyl compounds, and vicinal dichlorination of alkenes.[163,164] In addition, $PhICl_2$, also participates in oxidative cyclization reactions leading to heterocycles, oxidative rearrangements, and C–heteroatom bond-forming reactions, such as chloroamination and chlorolactonization.[165,166] $PhICl_2$is also utilized in tandem halogenation–functionalization reactions and in combination systems (e.g., with thiocyanate salts) for oxidative thiocyanation.

4.1. Thiocyanation

α-Thiocyanation of carbonyl compounds and esters is achieved by the reaction of enol silyl ethers of acetophenone, 2-acetylfuran, 2-acetylthiophene, 2-acetyl pyridine, cyclopentanone and ketene silyl acetals of arylacetic esters in combination with $PhICl_2$ and lead(II) thiocyanate, thus affording the corresponding α-thiocyanated ketones and esters.[167] Following this method, α-thiocyanation of various enol silyl ethers, ketene silyl acetals, and β-dicarbonyl compounds has been successfully performed.[168] A stereoselective 1,2-dithiocyanation of various alkynes was accomplished by using the reagent combination of $PhICl_2$ and lead(II) thiocyanate in DCM at 0–5°C (Scheme 47).[169]



Scheme 46. Thiocyanation by using combination of (dichloroiodo)benzene and lead(II) thiocyanate.

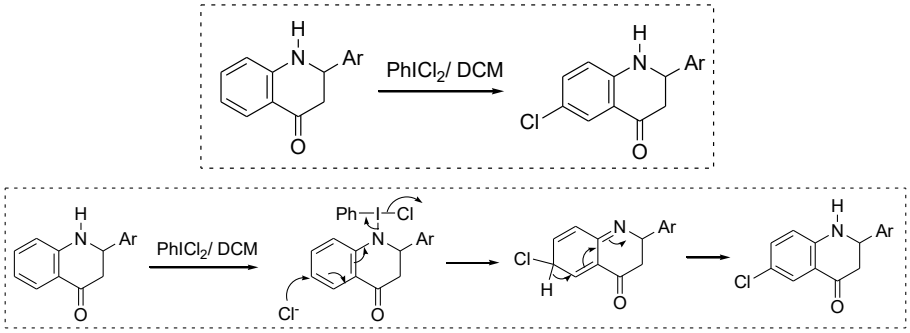


Scheme 47. Thiocyanation using $PhICl_2$-KSCN/CH_2Cl_2: Formation of oxathiole and bis-oxathiole products.

The thiocyanation of α-substituted-β-dicarbonyl compounds using $PhICl_2$-KSCN/CH_2Cl_2 was carried out to afford the corresponding 2-thiocyanato derivatives. The scope of this reagent system was subsequently extended to the thiocyanation of phenols and anilines. Substrates such as phenol, catechol, α-naphthol, aniline, substituted anilines, and α-naphthylamine were successfully converted into their respective *p*-thiocyanato derivatives. Interestingly, in certain cases, namely β-naphthol and hydroquinone, the reaction did not stop at simple thiocyanation. Instead, it led to the formation of oxathiole and bis-oxathiole products, respectively, by an intramolecular cyclization of the initially formed thiocyanato or dithiocyanato intermediates (Scheme 48).[170]

4.2. Electrophilic chlorination

Oxidation of 2-aryl-2,3-dihydro-4(1*H*)-quinolones with $PhICl_2$in DCM at room temperature resulted in regioselective chlorination, thereby, offering an efficient method for the synthesis of new 2-aryl-6-chloro-2,3-dihydro-4(1*H*)-quinolones (Scheme 49). [171]

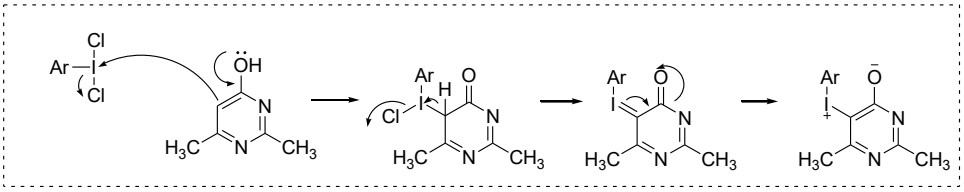


Scheme 48. Regioselective chlorination of 2-aryl-2,3-dihydro-4(1H)-quinolones.

4.3. Formation of ylides

Using (dichloroiodo)arenes, formation of synthetically useful aryliodonium ylides of 2,6-dimethylpyrimidin-4-ol, in aqueous medium at room temperature, was achieved. The mechanistic pathway for the formation of iodonium ylides involves the electrophilic attack of (dichloroiodo)benzene at the C-5 position of pyrimidine to form the intermediate which subsequently undergoes elimination of one molecule of HCl under basic conditions to give the ylide.

The ylide products were evaluated for antibacterial activity against *Escherichia coli* and *Bacillus licheniformis* (Scheme 50).[172]



Scheme 49. Formation of aryliodonium ylides from 2,6-dimethylpyrimidin-4-ol.

5. Iodosobenzene

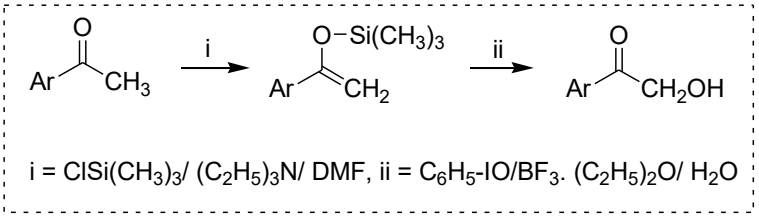
Iodosobenzene (PhIO) is a prominent iodine(III) reagent that functions primarily as an oxygen-transfer oxidant in organic synthesis. Possessing a polarized I=O bond and polymeric structure, PhIO exhibits significant electrophilic and oxidizing character, enabling a variety of synthetically useful transformations. It is widely employed in oxygen-transfer reactions such as epoxidation of alkenes, and oxidation of sulfides to sulfoxides, often in the presence of metal catalysts. In addition, PhIO participates in oxidative cyclization reactions, dehydrogenation reactions, and oxidative functionalization of C–H bonds. It is also known for facilitating nitrene-transfer reactions (in combination with suitable nitrogen sources) leading to aziridination of alkenes and amination reactions. Furthermore, PhIO is utilized in the generation of high-valent metal–oxo species, making it valuable in biomimetic-oxidation chemistry. Owing to its versatility and relatively mild reaction conditions, PhIO remains an important reagent in both synthetic and mechanistic organic chemistry.

5.1. α-Functionalization of carbonyl compounds from the oxidation of silyl enol ethers

The wide applicability of IBD-KOH/MeOH to bring about α-hydroxylations of ketones and some α,β-unsaturated ketones suffers from the following shortcomings: (i) hydrolysis of some acetals to ketones is problematic, (ii) certain compounds that contain groups sensitive to strongly basic conditions are affected

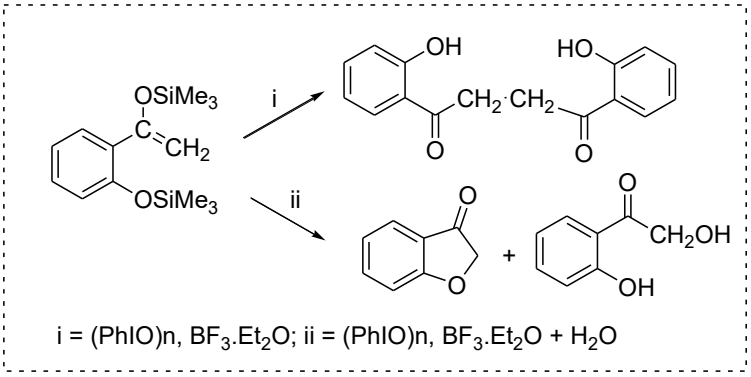
during oxidation, thereby, giving poor results, and (iii) the method is limited to α-hydroxyketones. Iodosobenzene lacks the above said shortcomings and is, therefore, used in many α-hydroxylation reactions.

5.1.1. α-Hydroxylation. Hypervalent-iodine oxidation of various silyl enol ethers (aromatic, heteroaromatic, and aliphatic) using PhIO-BF_3.OEt_2-H_2O- provides a general and direct route for the α-hydroxylation of ketones. Enol silyl ethers of ketones are oxidized to hydroxymethyl aryl ketones (Scheme 51).[173–175]



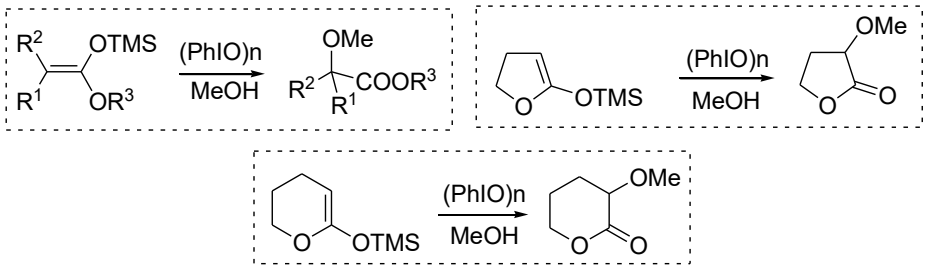
Scheme 50. Formation of α-hydroxymethyl aryl ketones from enol silyl ethers.

The oxidation of 1-trimethylsilyloxy,1-(2′-trimethylsilyloxyphenyl)ethene with PhIO-BF_3.OEt_2-H_2O affords two major products, namely, 3-coumaranone and 2, 2′-dihydroxyacetophenone. Formation of the coumaranone is explained by neighboring-group participation of the adjacent hydroxyl group. The 1,4-diketone and o-hydroxyacetophenone are minor products (Scheme 52).[176]



Scheme 51. Oxidation of 1-trimethylsilyloxy-1-(2′-trimethylsilyloxyphenyl)ethane using (PhIO)n, BF_3.Et_2O.

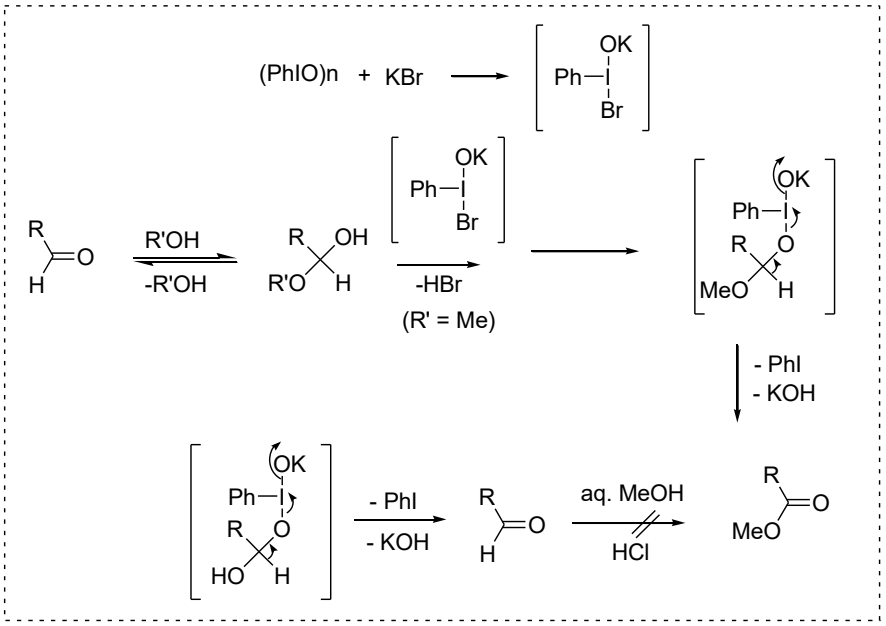
5.1.2. α-Methoxylation. Hypervalent-iodine oxidation of methylsilyl ketene acetals of esters and lactones, using PhIO in methanol, affords the corresponding methoxylated carbonyl compounds in good yields (Scheme 53).[177]



Scheme 52. (PhIO)n-MeOH in the oxidation of methylsilyl ketene acetals of esters and lactones.

5.2. Aldehydes to esters

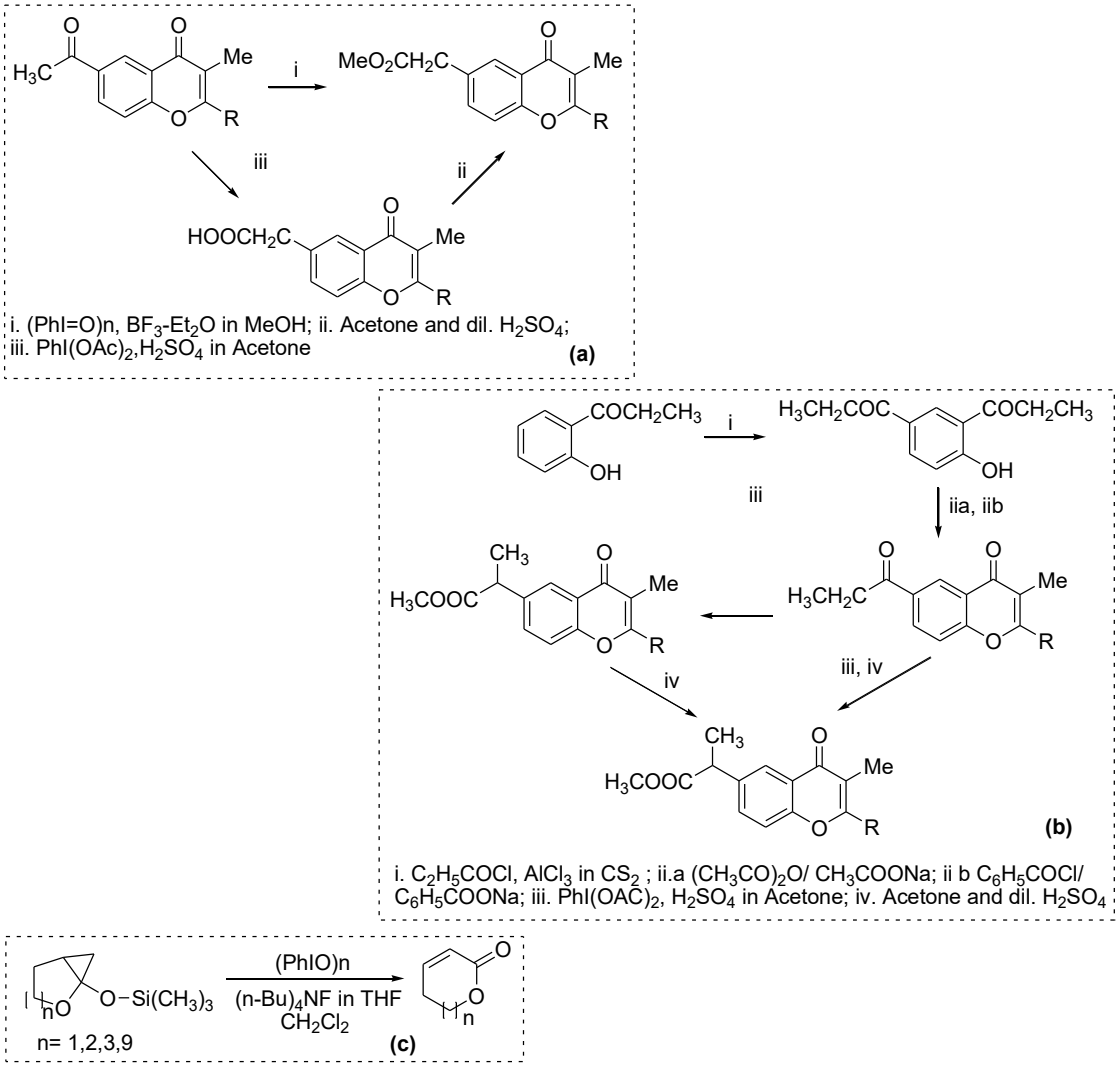
Various aliphatic and aromatic aldehydes are oxidized with PhIO in combination with KBr in aqueous MeOH to offer the corresponding methyl esters. However, the method is not straightforward for the synthesis of heteroaryl esters (Scheme 54).[178]



Scheme 53. Oxidation of aliphatic/aromatic aldehydes by (PhIO)n-KBr-MeOH.

5.3. Rearrangement

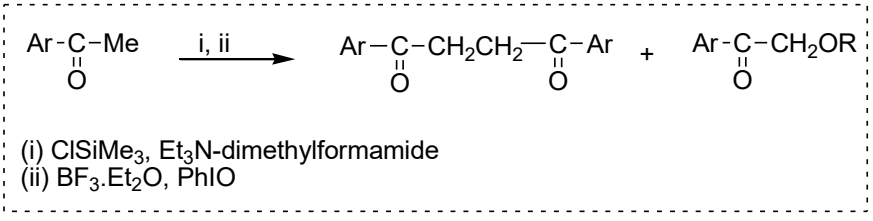
Various chalcones, acetophenones and styrenes react in the presence of PhIOMeOH as well as HTIB/MeOH, in combination with a catalyst such as FSO_3H, CF_3SO_3H or BF_3Et_2O, to yield rearranged products.[179] The use of hypervalent-iodine reagents for the synthesis of chromon-6-ylalkanoic acids from the corresponding 6-acylchromones, by a 1,2-aryl migration, has been described (Scheme 55a-b).[180] The ring expansion of lactones *via* oxidation of the derived trimethylsilyloxycyclopropanols to the higher homologous a,β-unsaturated lactones was reported by Moriarty *et al*. in 1990 (Scheme 55c).[181]



Scheme 54. Organoiodine(III) reagents to offer rearranged products.

5.4. Carbon-Carbon bond formation

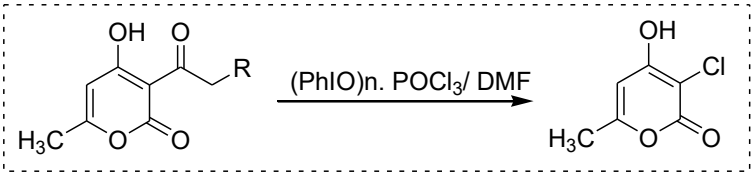
Hypervalent-iodine-mediated oxidation of silyl enol ethers under Lewis-acid conditions leads to an intermediate that is the synthetic equivalent of a carbonium ion. Upon addition of H_2O, MeOH, and EtOH, the respective α-substituted products are produced in excellent yield (Scheme 56). [182]



Scheme 55. Role of (PhIO)n-$BF_2O.Et_2O$ in C-C bond formation.

5.5. Carbon-Carbon bond Cleavage

PhIO in combination with the Vilsmeier–Haack reagent offers a novel and convenient method for C-C bond cleavage of dehydroacetic acid, with the formation of 3-chloro-4-hydroxy-6-methyl-2*H*-pyran-2-one (Scheme 57).[183]



Scheme 56. PhIO-mediated C-C bond cleavage.

6. Conclusion

Prof. Om Prakash's scientific contributions span an impressive breadth of synthetic organic chemistry, with his most distinguished work centered on the development and application of hypervalent iodine reagents in diverse organic transformations. The research has furnished valuable methodologies for oxidative cyclizations, heterocyclic construction, and functional group interconversions and rearrangements, significantly advancing the synthetic utility of iodine (III) systems.

Acknowledgements

We gratefully acknowledge the students, research scholars, and collaborators of Prof. Om Prakash for their valuable contributions to the advancement of this body of work in hypervalent iodine chemistry.

References

1. Zhdankin, V. *Resour.-Effic. Technol.* **2021**, 1. http://doi.org/10.18799/2405652 9/2021/1/286
2. Zhdankin, V. V. *Arkivoc* **2021**, *2020*, (iv), 1. https://doi.org/10.24820/ark.5550190.p011.145
3. Zhdankin, V. *Arkivoc* **2023**, *2022*, (vii), 1. https://doi.org/10.24820/ark.5550190.p001.488
4. Zhdankin, V. *Arkivoc* **2022**, *2022*, 1. https://doi.org/10.24820/ark.5550190.p001.488
5. Singh, F. V.; Wirth, T. *Arkivoc* **2021**, *2021*, 12. https://doi.org/10.24820/ark.5550190.p011.483
6. Venkata Durga Nageswar, Y.; Ramesh, K.; Rakhi, K. *Front. Chem.* **2022**, *10*, 841751. https://doi.org/10.3389/fchem.2022.841751.
7. Soni, S.; Rimi; Kumar, V.; Kikushima, K.; Dohi, T.; Zhdankin, V. V.; Kumar, R. *Arkivoc* **2022**, *2022*, 27. https://doi.org/10.24820/ark.5550190.p011.800
8. Singh, F. V.; Shetgaonkar, S. E.; Krishnan, M.; Wirth, T. *Chem. Soc. Rev.* **2022**, *51*, 8102. https://doi.org/10.1039/D2CS00206J
9. Kumar, R.; Nguyen, Q. H.; Um, T.-W.; Shin, S. *Chem. Rec*. **2022**, *22*, e202100172.

https://doi.org/10.1002/tcr.202100172
10. Rani, N.; Soni, R.; Sihag, M.; Kinger, M.; Aneja, D. K. *Adv. Synth. Catal.* **2022**, *364*, 1798. https://doi.org/10.1002/adsc.202200088
11. Ishihara, K.; Muniz, K. *Iodine catalysis in organic synthesis*; John Wiley & Sons, **2022**.
12. Sihag, M.; Soni, R.; Rani, N.; Kinger, M.; Kumar Aneja, D. *Org. Prep. Proced. Int.* **2023**, *55*, 1. https://doi.org/10.1080/00304948.2022.2113964.
13. Sihag, M.; Soni, R.; Rani, N.; Kinger, M.; Aneja, D. K. *Org. Prep. Proced. Int.* **2023**, *55*, 2, 99. https://doi.org/10.1080/00304948.2022.2114236
14. Sihag, M.; Soni, R.; Rani, N.; Kinger, M.; Aneja, D. K. *Org. Prep. Proced. Int.* **2023** *, 55*, 199. https://doi.org/10.1080/00304948.2022.2114239
15. König, B. *Org. Chem. Front.* **2023**, *10*, 1577. https://doi.org/10.1039/D3QO00039G
16. Yoshimura, A.; Saito, A.; Zhdankin, V. V. *Adv. Synth. Catal.* **2023**, *365*, 2653. https://doi.org/10.1002/adsc.202300275.
17. Yoshimura, A.; Zhdankin, V.V. *Chem. Rev.* **2024**, *124, 11108*. https://doi.org/10.1021/acs.chemrev.4c00303.
18. Varala, R.; Seema, V.; Dubasi, N. *Organics* **2022**, *4*, 1. https://doi.org/10.3390/org4010001.
19. Vittal, S.; Mujahid Alam, M.; Hussien, M.; Amanullah, M.; Pisal, P. M.; Ravi, V. *Chemistry Select* **2023**, *8*, e202204240. http://doi.org/10.1002/slct.202204240
20. Sakthivel, K.; J., S.; Raju, A.; Kumar, R.; Dohi, T.; Singh, F. V. *Arkivoc* **2023**, *2022*, 138. https://doi.org/10.24820/ark.5550190.p011.996.
21. Varala, R.; Seema, V.; Amanullah, M.; Ramanaiah, S.; Alam, M. M. *Curr. Org. Chem.* **2024**, *28*, 489. https://doi.org/10.2174/0113852728296345240215111730.
22. Mironova, I. A.; Noskov, D. M.; Yoshimura, A.; Yusubov, M. S.; Zhdankin, V. V. *Molecules* **2023**, *28*, 2136. https://doi.org/10.3390/molecules28052136.
23. Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. http://doi.org/10.1021/ar00128a003
24. Prakash, O.; Saini, N.; Tanwar, M. P.; Moriarty, R. M. *Contemp. Org. Synth.* **1995**, *2*, 121. https://doi.org/10.1039/CO9950200121.
25. Moriarty, R. M.; Prakash, O. In *Advances in Heterocyclic Chemistry*; Elsevier, **1997**; Vol. 69, 1. https://doi.org/10.1016/S0065-2725(08)60080-X.
26. Prakash, O.; Saini, N.; K. Sharma, P. *Heterocycles* **1994**, *38*, 409. https://doi.org/10.3987/REV-93-458.
27. Prakash, O.; Saini, N.; Sharma, P. K. *Synlett* **1994**, *1994*, 221. https://doi.org/10.1055/s-1994-22803.
28. Prakash, O.; Singh, S. P. *Aldrichim Acta* **1994**, *27*, 15.
29. Moriarty, R. M.; Prakash, O. *In Organic Reactions;* Denmark, S. E., Ed.; Wiley, **2001**; 327. https://doi.org/10.1002/0471264180.or057.02.
30. Moriarty, R. M.; Prakash, O. I*n Organic Reactions*; Denmark, S. E., Ed.; Wiley, **1999**; 273. https://doi.org/10.1002/0471264180.or054.02.
31. Moriarty, R. M.; Prakash, O. **2001**, 57, 315
32. Varala, R.; Seema, V.; Dubasi, N. *Organics* **2022**, *4*, 1. https://doi.org/10.3390/org4010001.
33. Alam, M. M.; Bollikolla, H. B.; Amanullah, M.; Hussein, M.; Varala, R. *Curr. Org. Chem.* **2023**, *27*, 93. https://doi.org/10.2174/1385272827666230330105241.

34. Yan, J.; Wang, J.; Yuan, J.; Lu, J.; Jiang, Y.; Li, X.; Ni, T. *Tetrahedron* **2025**, *188*, 134996. https://doi.org/10.1016/j.tet.2025.134996.
35. Yang, M.; Shao, Y.; Zhang, W.; Wan, Y.; Zhou, P.; Tang, D. *Tetrahedron Lett.* **2024**, *144*, 155135. https://doi.org/10.1016/j.tetlet.2024.155135.
36. Segura-Quezada, L. A.; Torres-Carbajal, K. R.; Juárez-Ornelas, K. A.; Navarro-Santos, P.; Granados-López, A. J.; González-García, G.; Ortiz-Alvarado, R.; De León-Solis, C.; Solorio-Alvarado, C. R. *Curr. Org. Chem.* **2022**, *26*, 1954. https://doi.org/10.2174/1385272826666220621142211.
37. Banerjee, S.; Bhoyare, V. W.; Patil, N. T. *Chem. Commun.* **2020**, *56*, 2677. https://doi.org/10.1039/D0CC00106F.
38. Miyamoto, N.; Koseki, D.; Sumida, K.; Elboray, E. E.; Takenaga, N.; Kumar, R.; Dohi, T. *Beilstein J. Org. Chem.* **2024**, *20*, 1020. https://doi.org/10.3762/bjoc.20.90.
39. Mamgain, R.; Sakthivel, K.; Singh, F. V. *Beilstein J. Org. Chem.* **2024**, *20*, 2891. https://doi.org/10.3762/bjoc.20.243.
40. Sumran, G.; Aggarwal, R. *Arkivoc* **2025**, *2025*. https://doi.org/10.24820/ark.5550190.p012.469.
41. Opai, I. A.; Shirsath, P. D.; Kalbandhe, A. H.; Karade, N. N. *Arkivoc* **2021**, *2021*, 101. https://doi.org/10.24820/ark.5550190.p011.579.
42. Peng, S.; He, J.; Yang, L.; Zhang, H.; Li, H.; Lang, M.; Chen, C.; Wang, J. *J. Org. Chem.* **2022**, *87*, 6247. https://doi.org/10.1021/acs.joc.2c00482.
43. Tang, P.; Wen, L.; Ma, H.-J.; Yang, Y.; Jiang, Y. *Org. Biomol. Chem.* **2022**, *20*, 3061. https://doi.org/10.1039/D2OB00364C.
44. Kumar Yadav, A.; Yadav, D.; Kumar, V.; Ray, S.; Singh, M. S. *Org. Biomol. Chem.* **2024**, *22*, 4326. https://doi.org/10.1039/D4OB00438H.
45. Wang, S.; Li, R.; Chen, S.; Mao, G.; Shao, W.; Deng, G.-J. *Green Synth. Catal.* **2024**, *5*, 112. https://doi.org/10.1016/j.gresc.2023.01.002.
46. Chaudhri, V.; Lakhia, R.; Sushma; Pundeer, R. Arkivoc **2026**, *2025*. https://doi.org/10.24820/ark.5550190.p012.543.
47. Ibarra-Gutiérrez, J. G.; Segura-Quezada, L. A.; Hernández-Velázquez, E. D.; García-Dueñas, A. K.; Millán-Cortés, J. A.; Mondragón-Hernández, K.; Miranda-Navarrete, L. K.; Valtierra-Camarena, E. M.; Yebra-Rivera, S. Y.; Alférez-Carmona, O. E.; Ávalos-Otero, O. E.; Chávez-Rivera, R.; De León-Solís, C.; Ortíz-Alvarado, R.; Solorio-Alvarado, C. R. *Molecules* **2025**, *30*, 784. https://doi.org/10.3390/molecules30040784.
48. Zhou, N.; Liu, R.; Shi, C.; Wang, Z.; Xie, C.; Liu, C.; Qin, H.; Zhao, Y.; Xu, Y.; Chen, J.; Li, X.; Shi, D. *Org. Lett.* **2026**, acs.orglett.6c00652. https://doi.org/10.1021/acs.orglett.6c00652.
49. Ibarra-Gutiérrez, J. G.; Segura-Quezada, L. A.; Hernández-Velázquez, E. D.; García-Dueñas, A. K.; Millán-Cortés, J. A.; Mondragón-Hernández, K.; Miranda-Navarrete, L. K.; Valtierra-Camarena, E. M.; Yebra-Rivera, S. Y.; Alférez-Carmona, O. E.; Ávalos-Otero, O. E.; De León-Solís, C.; Ortíz-Alvarado, R.; Solorio-Alvarado, C. R. **2025**. https://doi.org/10.20944/preprints202501.0211.v1.
50. Moriarty, R. M.; Prakash, O.; Freeman, W. A. *J. Chem. Soc. Chem. Commun.* **1984**, 927. https://doi.org/10.1039/C39840000927.
51. Prakash, O.; Ahuja, S.; Tanwar, M. P. **1994**, 33B, 272.
52. Moriarty, R. M.; Prakash, O.; Musallam, H. A. *J. Heterocycl. Chem.* **1985**, *22*, 583. https://doi.org/10.1002/jhet.5570220275.
53. Prakash, O.; Moriarty, R. M.; Chaudhri, V.; Pannu, K.; Pundeer, R. *Indian J. Heterocycl. Chem.* **2017**, *27*,

327.
54. Moriarty, R. M.; Prakash, O.; Thachet, C. T. *Synth. Commun.* **1984**, *14*, 1373. https://doi.org/10.1080/00397918408057678.
55. Moriarty, R. M.; Prakash, O.; Karalis, P.; Prakash, I. *Tetrahedron Lett.* **1984**, *25*, 4745. https://doi.org/10.1016/S0040-4039(01)81508-2.
56. Moriarty, R. M.; Prakash, O.; T. Thachet, C.; A. Musallam, H. *Heterocycles* **1985**, *23*, 633. https://doi.org/10.3987/R-1985-03-0633.
57. Moriarty, R. M.; Prakash, O. *J. Org. Chem.* **1985**, *50*, 151. https://doi.org/10.1021/jo00202a001.
58. Moriarty, R. M.; Engerer, S. G.; Prakash, O.; Prakash, I.; Gill, U. S.; Freeman, W. A. *J. Chem. Soc. Chem. Commun.* **1985**, 1715. https://doi.org/10.1039/C39850001715.
59. Moriarty, R. M.; Engerer, S. C.; Prakash, O.; Prakash, I.; Gill, U. S.; Freeman, W. A. *J. Org. Chem.* **1987**, *52*, 153. https://doi.org/10.1021/jo00377a028.
60. Prakash, O.; Goyal, S.; Sehgal, S.; Singh, S. P.; Moriarty, R. M. *ChemInform* **1989**, *20*, no.
61. Moriarty, R. M.; Prakash, O.; Vavilikolanu, P. R.; Vaid, R. K.; Freeman, W. A. *J. Org. Chem.* **1989**, *54*, 4008. https://doi.org/10.1021/jo00277a055.
62. Moriarty, R.; Rani, N.; Eric J. May; Liang Guo; Prakash, O. *J. Chem. Res. (S)*, 1998, 32. https://doi.org/10.1039/A701440F
63. Moriarty, R. M.; Prakash, O.; Prakash, I.; Musallam, H. A. *J. Chem. Soc. Chem. Commun.* **1984**, 1342. https://doi.org/10.1039/C39840001342.
64. Prakash, O.; Goyal, S.; Pahuja, S.; Singh, S. P. *Synth. Commun.* **1990**, *20*, 1409. https://doi.org/10.1080/00397919008052856.
65. Prakash, O.; Mendiratta, S. *Synth. Commun.* **1992**, *22*, 327. https://doi.org/10.1080/00397919208021310.
66. Prakash, O.; Kumar, R. *ARKIVOC* **2006**, *16*, 57. http://doi.org/10.3998/ARK.5550190.0007.G07
67. Prakash, O.; PAHUJA, S.; Sawhney, S. N.; *Indian J. Chem.* **1991**, 30B, 1023
68. Prakash, O.; Saini, R. K.; Singh, S. P.; Varma, R. S. *Tetrahedron Lett.* **1997**, *38*, 3147. https://doi.org/10.1016/S0040-4039(97)00564-9.
69. Prakash, O.; Tanwar, M. P.; Goyal, S.; Pahuja, S. *Tetrahedron Lett.* **1992**, *33*, 6519. https://doi.org/10.1016/S0040-4039(00)79031-9.
70. Prakash, O.; Sharma, V.; Tanwar, M. P. *Can. J. Chem.* **1999**, *77*, 1191. https://doi.org/10.1139/v99-097.
71. Moriarty, R. M.; Prakash, I.; Prakash, O.; Freeman, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 6082. https://doi.org/10.1021/ja00332a057.
72. Moriarty, R. M.; Prakash, O.; Vaid, R. K.; Zhao, L. *J. Am. Chem. Soc.* **1989**, *111*, 6443. https://doi.org/10.1021/ja00198a078.
73. Moriarty, R. M.; May, E. J.; Prakash, O. *Tetrahedron Lett.* **1997**, *38*, 4333. https://doi.org/10.1016/S0040-4039(97)00967-2.
74. Moriarty, R. M.; May, E. J.; Guo, L.; Prakash, O. *Tetrahedron Lett.* **1998**, *39*, 765. https://doi.org/10.1016/S0040-4039(97)10620-7.
75. Prakash, O.; Tanwar, M. P. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1168. https://doi.org/10.1246/bcsj.68.1168.
76. Moriarty, R. M.; Chany, C. J.; Vaid, R. K.; Prakash, O.; Tuladhar, S. M. *J. Org. Chem.* **1993**, *58*, 2478. https://doi.org/10.1021/jo00061a022.
77. Prakash, O.; Batra, H.; Kaur, H.; Sharma, P. K.; Sharma, V.; Singh, S. P.; Moriarty, R. M. *Synthesis* **2001**,

2001, 0541.
https://doi.org/10.1055/s-2001-12346.
78. Prakash, O.; Kumar, D.; Saini, R. K.; Singh, S. P. *Synth. Commun.* **1994**, *24*, 2167. https://doi.org/10.1080/00397919408010231.
79. Prakash, O.; Sharma, P.; Saini, N. *Indian J. Chem.* **1995**, *34 B*, 632
80. Prakash, O.; Kumar, R.; Sehrawat, R. *Eur. J. Med. Chem.* **2009**, *44*, 1763. https://doi.org/10.1016/j.ejmech.2008.03.028.
81. Varma, R. S.; Saini, R. K.; Prakash, O. *Tetrahedron Lett.* **1997**, *38*, 2621. https://doi.org/10.1016/S0040-4039(97)00444-9.
82. Prakash, O.; Batra, A.; Sharma, V.; Saini, R. K.; Verma, R. S. J.-*Indian Chem. Soc.* **2003**, *80*, 1031.
83. Prakash, O.; Pannu, K.; Kumar, A. *Molecules* **2006**, *11*, 43. https://doi.org/10.3390/11010043.
84. Kumar, R.; Nair, R. R.; Dhiman, S. S.; Sharma, J.; Prakash, O. *Med. Chem. Res.* **2010**, *19*, 541. https://doi.org/10.1007/s00044-009-9211-y.
85. Kumar, R.; Bhardwaj, V.; Prakash, O. *Indian J. of Het. Chem.* **2020,** *30*, 87.
86. Kumar, R.; Kumar, M.; Prakash, O. *Heteroat. Chem.* **2016**, *27*, 228. https://doi.org/10.1002/hc.21320.
87. Ak, S.; Y, M.; Kr, A.; O, P. *Eur. J. Med. Chem.* **2003**, *38*, 533. https://doi.org/10.1016/s0223-5234(03)00061-8.
88. Prakash, O.; Hussain, K.; Aneja, D. K.; Sharma, C.; Aneja, K. R. *Org. Med. Chem. Lett.* **2011**, *1*, 1. https://doi.org/10.1186/2191-2858-1-1.
89. Prakash, O.; Bhardwaj, V.; Kumar, R.; Tyagi, P.; Aneja, K. R. *Eur. J. Med. Chem.* **2004**, *39*, 1073. https://doi.org/10.1016/j.ejmech.2004.06.011.
90. Kumar, D.; Prakash, O.; Singh, S. *J. Chem. Res. Synop. Print* **1993**, 244.
91. Prakash, O.; Saini, R. K.; Kumar, D.; Singh, S. P. *Synth. Commun.* **1995**, *25*, 3363. https://doi.org/10.1080/00397919508013857.
92. Prakash, O.; Batra, H.; Sharma, V.; Singh, S. P. *Indian J. Chem.* **1998**, *37B*, 583.
93. Prakash, O.; Kumar, R.; Sharma, D.; Naithani, R.; Kumar, R. *Heteroat. Chem.* **2006**, *17*, 653. https://doi.org/10.1002/hc.20250.
94. Prakash, O., Kumar, R., Kumar, R., & Kuhad, R. C. *Eur. J. Med. Chem.* **2007**, *42*, 868. https://doi.org/10.1016/j.ejmech.2006.11.019.
95. Kumar, R.; Nair, R. R.; Dhiman, S. S.; Sharma, J.; Prakash, O. *Eur. J. Med. Chem.* **2009**, *44*, 2260. https://doi.org/10.1016/j.ejmech.2008.06.004.
96. Prakash, O.; Hussain, K.; Aneja, D. K.; Sharma, C.; Aneja, K. R. *Org. Med. Chem. Lett.* **2011**, *1*, 1. https://doi.org/10.1186/2191-2858-1-1.
97. Prakash, O., Kumar, M., Kumar, R., Sharma, C., & Aneja, K. R. *Eur. J. Med. Chem.* **2010**, *45*, 4252. https://doi.org/10.1016/j.ejmech.2010.06.023.
98. Prakash, O.; Aneja, D. K.; Hussain, K.; Kumar, R.; Arora, S.; Sharma, C.; Aneja, K. R. *J. Heterocycl. Chem.* **2012**, *49*, 1091. https://doi.org/10.1002/jhet.943.
99. Prakash, O.; Gujral, H. K.; Rani, N.; Singh, S. P. *Synth. Commun.* **2000**, *30*, 417. https://doi.org/10.1080/00397910008087337.
100. Prakash, O.; Pundeer, R.; Kaur, H. *Synthesis* **2003**, *2003*, 2768. https://doi.org/10.1055/s-2003-42461
101. Prakash, O.; Kaur, H.; Sharma, V.; Bhardwaj, V.; Pundeer, R. *Tetrahedron Lett.* **2004**, *45*, 9065. https://doi.org/10.1016/j.tetlet.2004.10.037.
102. Prakash, O.; Sharma, V.; Sadana, A. *Synth. Commun.* **1997**, *27*, 3371.

https://doi.org/10.1080/00397919708005637.
103. Prakash, O.; Sharma, V. Indian J. Chem. **1999**, *38B*, 229.
104. Prakash, O.; Pannu, K. Arkivoc **2007**, *13*, 28. https://doi.org/10.3998/ark.5550190.0008.d04
105. Singh, S. P.; Kumar, D.; Prakash, O.; Kapoor, R. P. *Synth. Commun.* **1997**, *27*, 2683. https://doi.org/10.1080/00397919708004136.
106. Singh, S. P.; Naithani, R.; Aggarwal, R.; Prakash, O. *Indian J. Heterocycl. Chem.* **2001**, *11*, 27.
107. Prakash, O.; Kumar, A.; Kinger, M.; Singh, S. P. *Indian J. Chem.* **2006**, *45B*, 456.
108. Lohan, P.; Aneja, D. K.; Prakash, O. *Asian J. Org. Med. Chem.* **2017**, *2*, 81. https://doi.org/10.14233/ajomc.2017.AJOMC-P41.
109. Moriarty, R. M.; Prakash, O.; Duncan, M. P.; Vaid, R. K.; Rani, N. *J. Chem. Res.-Part Synop.* **1996**, 432.
110. Moriarty, R. M.; Prakash, O.; Vavilikolanu, P. R. *Synth. Commun.* **1986**, *16*, 1247. https://doi.org/10.1080/00397918608056372.
111. Prakash, O.; Tanwar, M. P. *J. Chem. Res. (S)* **1995**, 213.
112. Kamal, R.; Omkar; Kumar, V.; Kumar, R. *Chemistry Select* **2022**, *7*, e202103719. https://doi.org/10.1002/slct.202103719.
113. Bennett, J. A.; Socash, T.; Khamis, N.; Justik, M. W. *ACS Omega* **2024**, *9*, 47361. https://doi.org/10.1021/acsomega.4c09236.
114. Khan, A.; Silva, L. F.; Rabnawaz, M. *New J. Chem.* **2021**, *45*, 2078. https://doi.org/10.1039/D0NJ04700G.
115. Khan, A.; Silva, L. F.; Rabnawaz, M. *Asian J. Org. Chem.* **2021**, *10*, 2549. https://doi.org/10.1002/ajoc.202100497.
116. Bhattacharjee, S.; Laru, S.; Hajra, A. *Chem. Commun.* **2022**, *58*, 981. https://doi.org/10.1039/D1CC06129A.
117. Lussari, N.; Khan, A.; Pilli, R. A.; Dos Santos, A. A.; Silva, L. F.; Braga, A. A. C. *New J. Chem.* **2022**, *46*, 20817. https://doi.org/10.1039/D2NJ04393A.
118. Sodoor, M.; Selvakumar, S. *Eur. J. Org. Chem.* **2023**, *26*, e202300925. https://doi.org/10.1002/ejoc.202300925.
119. Rani, N.; Aneja, D. K.; Kinger, M.; Soni, R.; Sihag, M.; Malik, S. *Lett. Org. Chem.* **2024**, *21*, 456. https://doi.org/10.2174/0115701786275866231117113843.
120. Sihag, M.; Soni, R.; Rani, N.; Kinger, M.; Aneja, D. K. *Lett. Org. Chem.* **2023**, *20*, 696. https://doi.org/10.2174/1570178620666230209145324.
121. Rani, N.; Aneja, D. K.; Kinger, M.; Soni, R.; Sihag, M.; Malik, S. *Lett. Org. Chem.* **2024**, *21*, 456. https://doi.org/10.2174/0115701786275866231117113843.
122. Jadhav, A. P.; Legault, C. Y. *Beilstein J. Org. Chem.* **2024**, *20*, 1286. https://doi.org/10.3762/bjoc.20.111.
123. Zhang, L.; Song, Z. *Org. Lett.* **2024**, *26*, 2192. https://doi.org/10.1021/acs.orglett.4c00294.
124. Li, B.; Zhang, Z.; Tio, R.; Li, J.; Loh, T.-P. *Proc. Natl. Acad. Sci.* **2024**, *121*, e2405337121. https://doi.org/10.1073/pnas.2405337121.
125. Hu, L.; Gao, T.; Deng, Q.; Xiong, Y. *Tetrahedron* **2021**, *95*, 132334. https://doi.org/10.1016/j.tet.2021.132334.
126. Bains, O.; Jangra, R.; Kumar, A.; Kumar, R.; Kataria, R.; Sharma, P.; Kamal, R. *J. Mol. Struct.* **2026**, *1351*, 144103. https://doi.org/10.1016/j.molstruc.2025.144103.
127. Parkash, J.; Saini, S.; Saini, V.; Bains, O.; Kamal, R. *Beilstein J. Org. Chem.* **2025**, *21*, 2703. https://doi.org/10.3762/bjoc.21.208.
128. Prakash, O.; Pannu, K.; Prakash, R.; Batra, A. *Mol. J. Synth. Chem. Nat. Prod. Chem.* **2006**, *11*, 523.

https://doi.org/10.3390/11070523.
129. Prakash, O.; Sharma, D.; Kamal, R.; Kumar, R.; Nair, R. R. *Tetrahedron* **2009**, *65*, 10175. https://doi.org/10.1016/j.tet.2009.10.001.
130. Prakash, O.; Sharma, N.; Ranjan, P. *Synth. Commun.* **2010**, *40*, 2875. https://doi.org/10.1080/00397910903321090.
131. Prakash, O.; Kumar, M.; Kumar, R. *Tetrahedron* **2010**, *66*, 5827. https://doi.org/10.1016/j.tet.2010.05.042.
132. Prakash, O. *Indian J. Heterocycl. Chem.* **1992**, *2*, 111.
133. Prakash, O.; Goyal, S. *Indian J. of Het. Chem.* 1991,99.
134. Prakash, O.; Batra, A.; Pundeer, R. *Indian J. Chem.* **2020**, *59B*, 247.
135. Moriarty, R. M.; Vaid, B. K.; Duncan, M. P.; Levy, S. G.; Prakash, O.; Goyal, S. *Synthesis* **1992**, *1992*, 845. https://doi.org/10.1055/s-1992-26243.
136. Prakash, O.; Saini, S.; Saini, N.; Prakash, I.; Singh, S. P. *ChemInform* **1995**, *26*, no.
137. Prakash, O.; Pundeer, R.; Chaudhri, V. *Indian. Chem. Soc.* 2004, 786.
138. Prakash, O.; Saini, N. *Synth. Commun.* **1993**, *23*, 1455. https://doi.org/10.1080/00397919308011236.
139. Singh, S. P.; Naithani, R.; Aggarwal, R.; Prakash, O. *Synth. Commun.* **2001**, *31*, 3747. https://doi.org/10.1081/SCC-100108224.
140. Aggarwal, R.; Pundeer, R.; Kumar, V.; Chaudhri, V.; Singh, S. P.; Prakash, O. *Synth. Commun.* **2004**. https://doi.org/10.1081/SCC-200025631.
141. Prakash, O.; Sharma, N.; Ranjan, P. *Synth. Commun.* **2013**, *43*, 582. https://doi.org/10.1080/00397911.2011.604815.
142. Singh, S. P.; Batra, H.; Sharma, P. K.; Prakash, O. *ChemInform* **1999**, *30*, chin.199903136. https://doi.org/10.1002/chin.199903136.
143. Kamal, R.; Sharma, D.; Wadhwa, D.; Prakash, O. *Synlett* **2012**, *2012*, 93. https://doi.org/10.1055/s-0031-1290109.
144. Prakash, O.; Rani, N.; Goyal, S. *J. Chem. Soc. Perkin 1* **1992**, 707. https://doi.org/10.1039/p19920000707.
145. Singh, S. P.; Naithani, R.; Prakash, O. *ChemInform* **1999**, *30*, chin.199949135. https://doi.org/10.1002/chin.199949135.
146. Prakash, O.; Wadhwa, D.; Hussain, K.; Kumar, R. *Synth. Commun.* **2012**, *42*, 2947. https://doi.org/10.1080/00397911.2011.570471.
147. Kumar, R.; Wadhwa, D.; Hussain, K.; Prakash, O. *Synth. Commun.* **2013**, *43*, 1802. https://doi.org/10.1080/00397911.2012.671435.
148. Singh, S. P.; Naithani, R.; Aggarwal, R.; Prakash, O. *ChemInform* **1998**, *29*, chin.199849207. https://doi.org/10.1002/chin.199849207.
149. Prakash, O.; Aneja, D. K.; Wadhwa, D.; Kumar, R.; Arora, S. *J. Heterocycl. Chem.* **2012**, *49*, 566. https://doi.org/10.1002/jhet.815.
150. Ranjan, P.; Arora, L.; Prakash, R.; Aneja, D. K.; Prakash, O. *Lett. Org. Chem.* **2017**, *14*, 1. https://doi.org/10.2174/1570178614666170321121411.
151. M. Moriarty, R.; Prakash, O.; A. Musallam, H.; K. Mahesh, V. *Heterocycles* **1986**, *24*, 1641. https://doi.org/10.3987/R-1986-06-1641.
152. Prakash, O.; Saini, N.; Sharma, P. K. J. *Chem. Res. Synop. Print* **1993**, 430.
153. Prakash, O.; Pahuja, S.; Moriarty, R. M. *Synth. Commun.* **1990**, *20*, 1417. https://doi.org/10.1080/00397919008052857.
154. Prakash, O.; Pahuja, S.; Goyal, S.; Sawhney, S. N.; Moriarty, R. M. *Synlett* **1990**, *1990*, 337. https://doi.org/10.1055/s-1990-21084.
155. Kumar, D.; Singh, O. V.; Prakash, O.; Singh, S. P. *Synth. Commun.* **1994**, *24*, 2637.

https://doi.org/10.1080/00397919408010576.
156. Prakash, O.; Kumar, A.; Sadana, A. K.; Singh, S. P. *Synthesis* **2006**, *2006*, 21. https://doi.org/10.1055/s-2005-921751.
157. Prakash, O.; Kumar, D.; Saini, R. K.; Singh, S. P. *Tetrahedron Lett.* **1994**, *35*, 4211. https://doi.org/10.1016/S0040-4039(00)73154-6.
158. Pundeer, R.; Chaudhri, V.; Kinger, M.; Prakash, O. *Indian J. Chem.* **2007**, *46B*, 834.
159. Aneja, D. K.; Ranjan, P.; Arora, L.; Prakash, O. *Comptes Rendus Chim.* **2014**, *17*, 881. https://doi.org/10.1016/j.crci.2013.10.013.
160. Prakash, O.; Batra, A.; Chaudhri, V.; Prakash, R. *Tetrahedron Lett.* **2005**, *46*, 2877. https://doi.org/10.1016/j.tetlet.2005.02.129.
161. Aneja, D. K.; Lohan, P.; Arora, S.; Sharma, C.; Aneja, K. R.; Prakash, O. *Org. Med. Chem. Lett.* **2011**, *1*, 15. https://doi.org/10.1186/2191-2858-1-15.
162. Moriarty, R. M.; Vaid, R. K.; Hopkins, T. E.; Vaid, B. K.; Prakash, O.; Moriarty, R. M.; Vaid, R. K.; Hopkins, T. E.; Vaid, B. K.; Prakash, O. *Tetrahedron Lett.* **1990**, *31*, 201.
163. Patra, T.; Arepally, S.; Seitz, J.; Wirth, T. *Nat. Commun.* **2024**, *15*, 6329. https://doi.org/10.1038/s41467-024-50643-z.
164. Davis, B. A.; Tania; Dutton, J. L. *Dalton Trans.* **2022**, *51*, 12384. https://doi.org/10.1039/D2DT01842J.
165. Rohe, S.; Révol, G.; Marmin, T.; Barriault, D.; Barriault, L. *J. Org. Chem.* **2020**, *85*, 2806. https://doi.org/10.1021/acs.joc.9b03237.
166. Robidas, R.; Legault, C. Y. *Helv. Chim. Acta* **2021**, *104*, e2100111. https://doi.org/10.1002/hlca.202100111.
167. Prakash, O.; Rani, N.; Sharma, V.; Moriarty, R. *Synlett* **1997**, *1997*, 1255. https://doi.org/10.1055/s-1997-1027.
168. Prakash, O.; Kaur, H.; Batra, H.; Rani, N.; Singh, S. P.; Moriarty, R. M. *J. Org. Chem.* **2001**, *66*, 2019. https://doi.org/10.1021/jo001504i.
169. Prakash, O.; Sharma, V.; Batra, H.; Moriarty, R. M. *Tetrahedron Lett.* **2001**, *42*, 553. https://doi.org/10.1016/S0040-4039(00)01909-2.
170. Prakash, O.; Kaur, H.; Pundeer, R.; Dhillon, R. S.; Singh, S. P. *Synth. Commun.* **2003**, *33*, 4037. https://doi.org/10.1081/SCC-120026343.
171. Sharma, D.; Ranjan, P.; Prakash, O. *Synth. Commun.* **2009**, *39*, 596. https://doi.org/10.1080/00397910802413865.
172. Kumar, R.; Nair, R. R.; Prakash, O. *Heteroat. Chem.* **2010**, *21*, 339. https://doi.org/10.1002/hc.20608.
173. Moriarty, R. M.; Prakash, O.; Duncan, M. P. *Synthesis* **1985**, *1985*, 943. https://doi.org/10.1055/s-1985-31394.
174. Moriarty, R. M.; Duncan, M. P.; Prakash, O. *J. Chem. Soc. Perkin 1* **1987**, 1781. https://doi.org/10.1039/P19870001781.
175. Moriarty, R. M.; Prakash, O.; Duncan, M. P.; Vaid, R. K.; Musallam, H. A. *J. Org. Chem.* **1987**, *52*, 150. https://doi.org/10.1021/jo00377a027.
176. Moriarty, R. M.; Prakash, O.; Duncan, M. P. *Synth. Commun.* **1986**, *16*, 1239. https://doi.org/10.1080/00397918608056371.
177. Moriarty, R. M.; Rani, N.; Condeiu, C.; Duncan, M. P.; Prakash #, O. *Synth. Commun.* **1997**, *27*, 3273. https://doi.org/10.1080/00397919708004187.
178. Arora, L.; Prakash, R.; Prakash, O.; Sharma, N. *Arkivoc* **2015**, *2015*, 354. https://doi.org/10.3998/ark.5550190.p009.267.
179. Moriarty, R. M.; Khosrowshahi, J. S.; Prakash, O. *Tetrahedron Lett.* **1985**, *26*, 2961. https://doi.org/10.1016/S0040-4039(00)98592-7.

180. Singh, O.; Prakash, O.; Garg, C.; Kapoor, R. *ChemInform* **1990**, *21*, no.
181. Moriarty, R. M.; Vaid, R. K.; Hopkins, T. E.; Vaid, B. K.; Prakash, O. *Tetrahedron Lett.* **1990**, *31*, 197. https://doi.org/10.1016/S0040-4039(00)94369-7.
182. Moriarty, R. M.; Prakash, O.; Duncan, M. P. *J. Chem. Soc. Chem. Commun.* **1985**, 420. https://doi.org/10.1039/C39850000420.
183. Prakash, O.; Chaudhri, V.; Kinger, M. *Synth. Commun.* **2005**, *35*, 2819. https://doi.org/10.1080/00397910500290573.

Authors' Biographies

Sushma (ORCID iD 0000-0001-6008-489X) received M.Sc. degree in 2007 from Guru Jambheshwar University of Science & Technology, Hisar (GJUS&T). She completed Ph.D. in 2014 from Kurukshetra University, Kurukshetra under the guidance of Prof. Om Prakash and Prof. Rashmi Pundeer. Presently she is working as an Associate Professor in Govt. College Hisar (Department of Higher Education, Panchkula Haryana, since 2011). Her area of interests in research is exploring the new techniques in synthesis of heterocyclic compounds.

Rashmi Pundeer completed her Ph.D. degree under the supervision of Prof. Om Prakash from Kurukshetra University, Kurukshetra, Haryana in 2004. She worked as Assistant Professor in the Department of Chemistry, Kurukshetra University up to 2020. Presently, she is a Professor in the Department of Chemistry, Indira Gandhi University, Meerpur, Rewari, Haryana. Her research work deals with the applications of hypervalent iodine(III) reagents and the synthesis and biological evaluation of nitrogen containing heterocycles.