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Recent developments in the chemistry of iodine(III) compounds with nucleophiles

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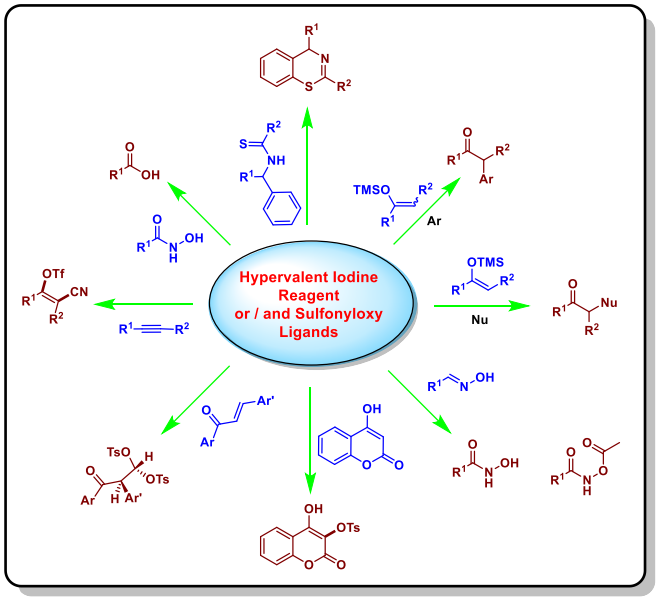
Abstract

Iodine(III) compounds gained interest due to their significant role in organic transformations. Despite the ligand bearing, some iodine(III) reagent along with external ligand source also played a similar role in organic transformations. The metal-free and benign reaction condition directs the iodine(III) reagents to the green chemistry approaches. Besides, the chemoselectivity plays an additional benefit in this case. Thus reduces the formation of byproduct leads good yield in all the reactions. In this study, recent developments in the chemistry of iodine(III) compounds with sulfonyloxy ligands reported in last decade have been highlighted.



Keywords: hypervalent reagents, Koser's reagent, cyclization, rearrangement, sulfonyloxy ligands

Table of Contents

1. Introduction

Hypervalent iodine compounds are the significant and effective tool in the modern synthesis of organic scaffolds. Contrary to traditional metal and other toxic catalysts, the hypervalent iodine reagents are gentle and benign to the environment. Additionally, the distinctive reactivity, commercial availability and typically reacts under metal-free atmosphere facilitates its substantial role in green synthesis and medicinal chemistry.[1-3]

Most commonly, hypervalent iodine with the oxidation state +3 and +5 are explored in many organic syntheses. The hypervalent iodine(V) reagents such as Dess Martin Periodinane (DMP) **1**, 2-Iodoxybenzoic acid (IBX) **2** and its analogues **3** and **4** are utilized as oxidant in many reactions.[4] Likewise, the hypervalent iodine(III) reagents (diacetoxyiodo)benzene (PIDA) **5**, [bis(trifluoroacetoxy)iodo]benzene (PIFA) **6**, [Hydroxy(tosyloxy)iodo]benzene (HTIB) known as Koser's reagent **7** and its cyano substituted variant **8** are extensively explored in oxidation reactions and in functionalization of organic scaffolds (Figure 1).[5-8]

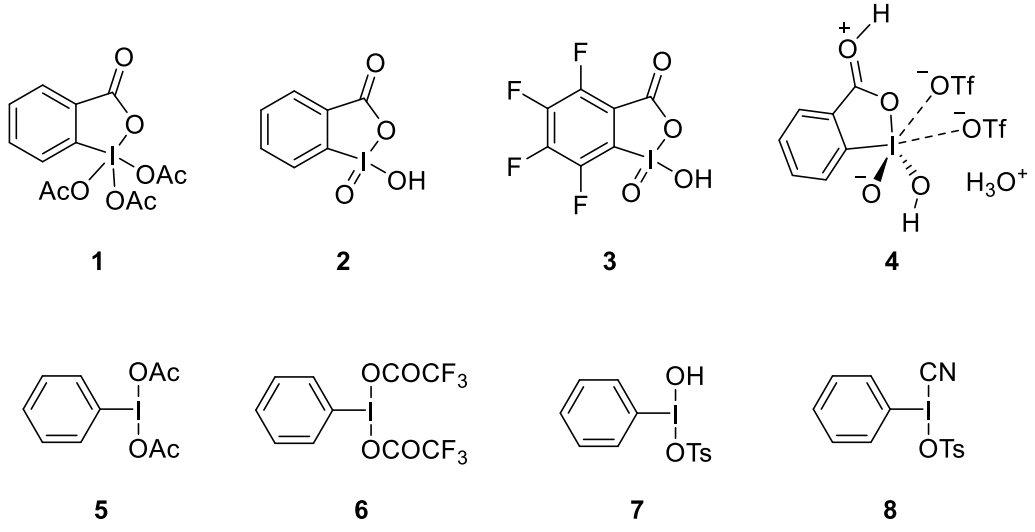


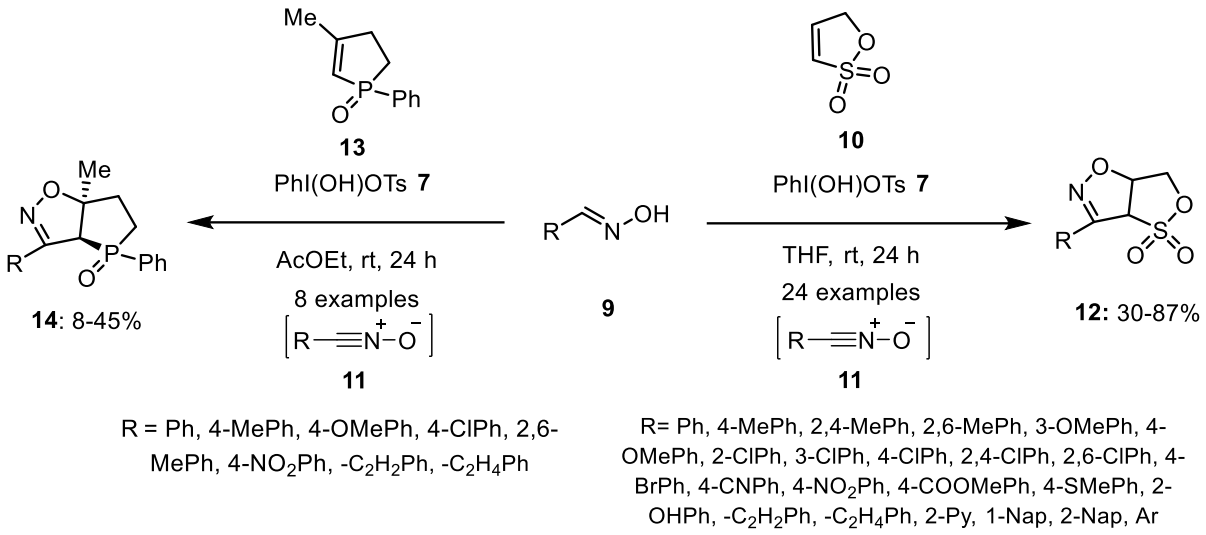
Figure 1. Examples of commonly explored hypervalent iodine reagents.

Typically, the hypervalent iodine(III) reagent participate in reaction by two ways, either hypervalent iodine(III) reagent embedded with ligands or hypervalent iodine(III) reagent with external nucleophiles/electrophiles.[9-12] Especially, when common iodine(III) reagents did not align with the targeted product newly modified iodine(III) reagents have been synthesized. Like, Koser type reagents typically used as electrophile and mild oxidizing reagent.[13,14] When, classic Koser's reagent misleads the formation of target scaffold, Koser's type reagents are employed to enhance selectivity and progressive yield.[15,16] In this context, we have discussed the utility of hypervalent iodine(III) reagent bearing ligands and hypervalent iodine(III) reagents along with external nucleophile sources. These systems supported in many organic reactions with the formation of C–C and C–X (X = heteroatoms like N, O, S) bonds.[17-19] In this review, literature described the reactions such as cyclization, carbonylation, rearrangement reaction, triflation, tosyloxylation, arylation, dehydrogenation and dearomatization reactions using hypervalent iodine(III) reagent bearing sulfonyloxy ligands and hypervalent iodine(III) reagents along with external sulfonyl sources reported in the last decade were highlighted.

2. Cyclization reactions using iodine(III) reagents

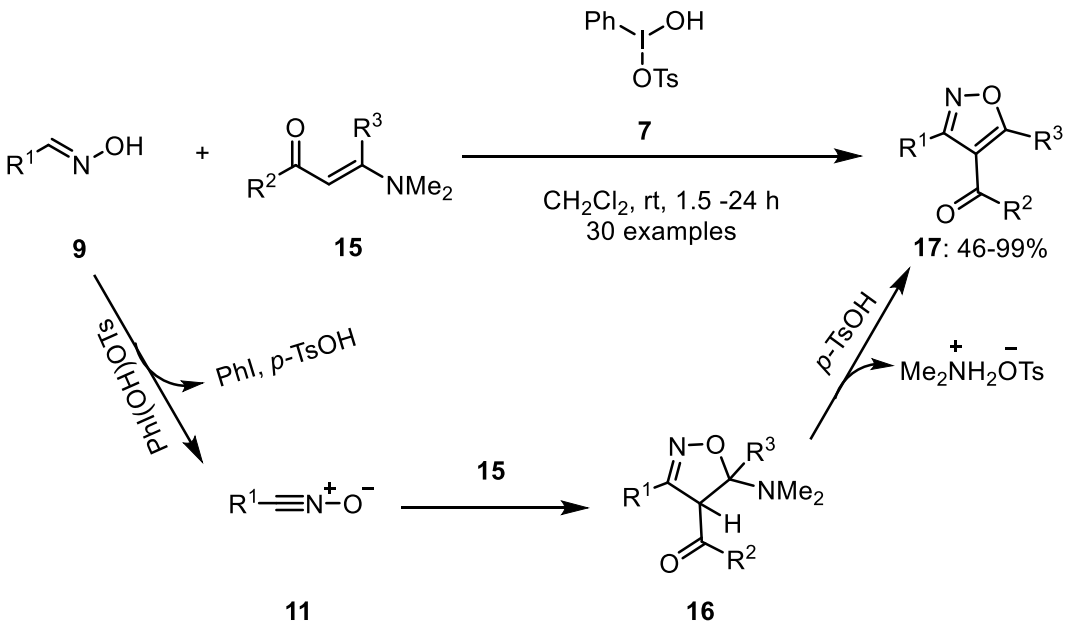
Iodine(III) reagents acquired interest in cyclization reactions. The reactions proceed through intramolecular oxidative cyclization by forming either radical species or reactive iodonium intermediates. These intermediates further promote the cyclization to build a new molecule. The ability to facilitate stereo and regioselectivity of iodine(III) reagents making them as a vital tool for constructing molecules.

In 2017, Yoshimura and others introduced an efficient synthetic method to access isoxazoline-ring fused heterobicyclic compounds by an oxidative cyclization of heterocyclic olefins with aldoximes **9** using [hydroxy(tosyloxy)iodo]benzene **7** in stoichiometric amounts.[20] Notably, 1-propene-1,3-sultone **10** showed a better participation during the cyclization process and corresponding heterobicyclic compounds were obtained in moderate to high yields (Scheme 1). In addition, the heterocyclic phospholenes **14** were obtained in moderate yields by reacting aldoximes **9** with cyclic phospholene-oxide **13** under similar conditions. Predominantly, the substituted benzaldoximes with electron withdrawing and donating groups showed good results during these cyclizations. It was observed that sterically hindered aldoximes gave the corresponding products in relatively poor yields. Notably, the cyclization reaction occurred via *in situ* generation of nitrile oxides **11** by the oxidation of corresponding aldoximes with Koser's reagent **7**. Course of the reaction was not influenced by the amount of Koser's reagent used and reaction temperature.



Scheme 1. Oxidative cyclization of aldoximes **9** with alkenes **10** & **13**, separately mediated by Koser's reagent **7**.

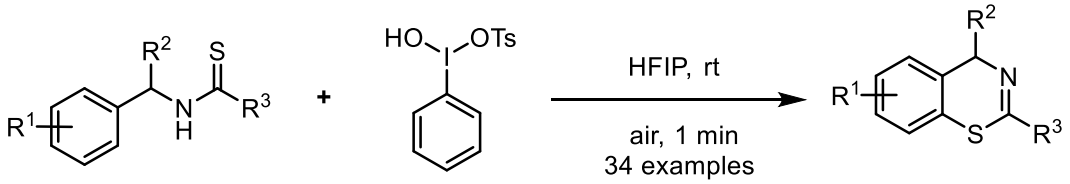
The same research group explored the potential of *in situ* generated nitrile oxides **11** from the corresponding aldoximes **9** with enaminones **15** using Koser's reagent **7** in dichloromethane at room temperature.[21] Various 3,4-disubstituted isoxazoles **17** were obtained in moderate to excellent yields using this synthetic approach (Scheme 2). The reaction tolerates substituted benzaldoximes **9** with both electron donating and withdrawing group successfully to give corresponding 3,4-disubstituted isoxazoles. Notably, the cycloaddition of 4-(methylthio)benzaldoxime **9** with enaminone **15** proceeds poorly and the corresponding isoxazole **17** was obtained in moderate yield due to competitive oxidation of sulfide functionality. Additionally, the cycloaddition with β-substituted enaminones **15** gave corresponding 3,4,5-trisubstituted isoxazoles **17** in excellent yields. The proposed reaction mechanism suggests that the reaction proceeds with the formation nitrile oxide **11** by the oxidation of aldoximes **9** using Koser's reagent **7**. Nitrile oxide **11** undergo 1,3-dipolar cycloaddition with enaminones **15** to form cyclic intermediate **16**. Finally, the cyclic intermediate **16** undergoes β-elimination by eliminating the dimethylamine group to give desired isoxazoles **17** (Scheme 2).



R^1= Ph, 4-MePh, 2,4-Me_2Ph, 2,6-Me_2Ph, 4-OMePh, 4-ClPh, 3-ClPh, 2-ClPh, 2,6-Cl_2Ph, 4-BrPh, 4-NO_2Ph, 4-CNPh, 4-MeO_2CPh, 4-OAcPh, 4-C_6H_6Ph, 4-SMePh, 1-Nap, 2-Nap, 5-benzodioxole, 5-NO_2Furyl, Propyl, $PhCH_2CH_2$, (*E*) PhCH=CH; R^2= H, Me, *i*Pr, *c*Pr, OEt, Ph; R^3= H, Me

Scheme 2. Iodine(III)-mediated cycloaddition of aldoximes **9** with enaminones **15** using Koser's reagent **7**.

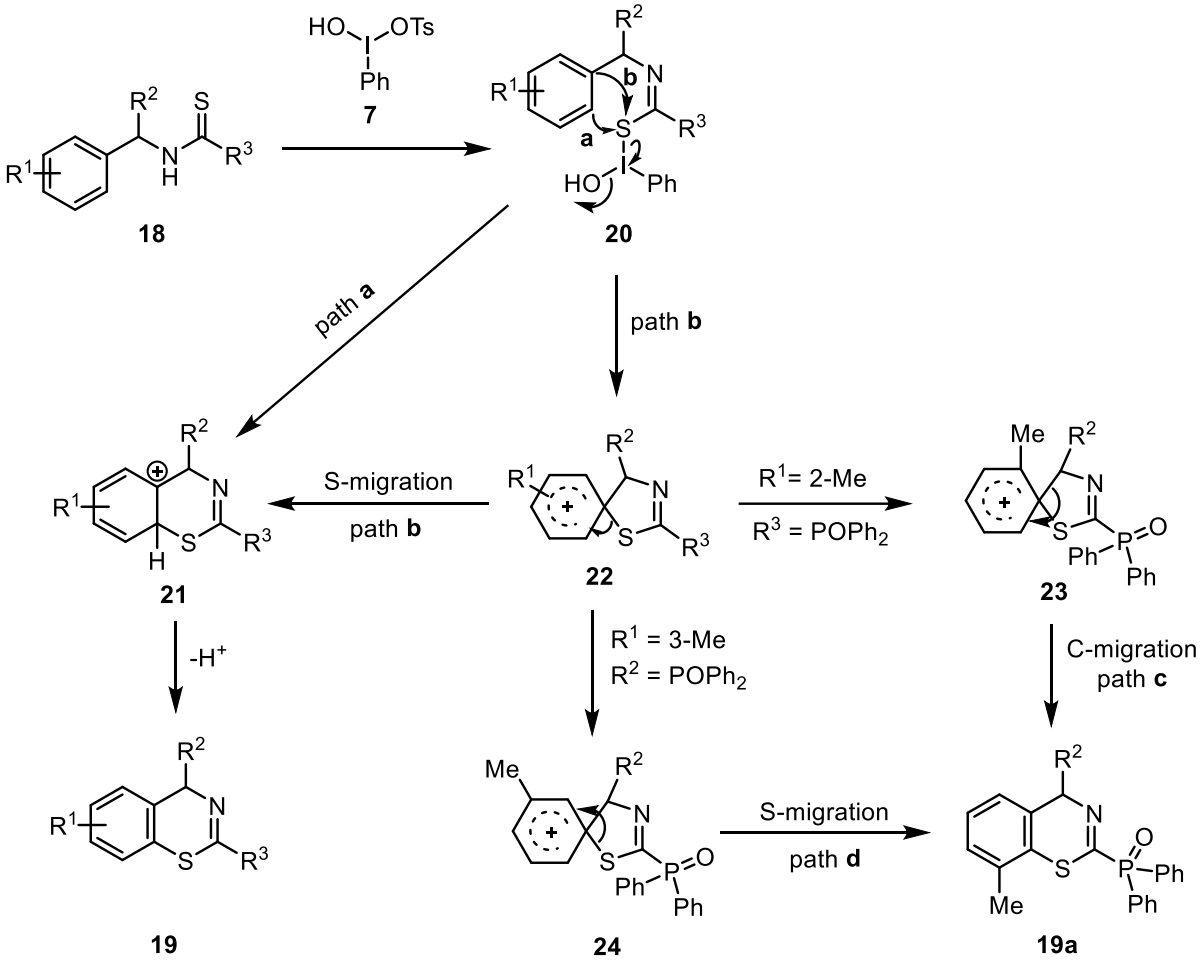
In 2019, Koser's reagent **7** was used to establish a new efficient protocol for the synthesis 1,3-benzothiazine derivatives **19** via direct intramolecular dehydrogenative C-S bond coupling reaction of thioamides **18**. Reaction proceeds readily at room temperature within one minute under metal free condition in hexafluoroisopropanol (HFIP) and reaction products **19** were isolated in excellent yields.[22] The protocol works smoothly with substrates having two substituents (R^1= 3,4-dimethoxy), branched substituents (*β*-Nap) and gives targeted product **19** with high yields (Scheme 3). Notably, *o*-methoxy substituted thioamides **19** undergo migration reaction and rearranged product obtained with 61% yield and 4-chloro and 4-bromo substituted thioamides do not give corresponding benzothiazines. Additionally, tricyclic products were obtained in excellent yields. Reaction showed good functional group tolerance in thioamides including phosphoryl groups such as methyl, methoxy, trifluoromethyl and halogen groups.



R^1 = H, OMe, cyclic, Ar, het-Ar; R^2 = H, Me, Ph, Cy, 4-ClPh, 4-FPh, cyclic, Ar; R^3 = $PO(Ph)_2$, $PO(4\text{-}MePh)_2$, $PO(4\text{-}OMePh)_2$, $PO(4\text{-}ClPh)_2$, $PO(4\text{-}FPh)_2$, CF_3, Ph, 4-OMePh, 4,3-$(OMe)_2$Ph, 4-ClPh, 4-CF_3Ph, Cy, ^{n}Pr

Scheme 3. Iodine(III)-mediated synthesis of 1,3-benzothiazines **19** by C-S coupling of thioamides **18** involving Koser's reagent **7**.

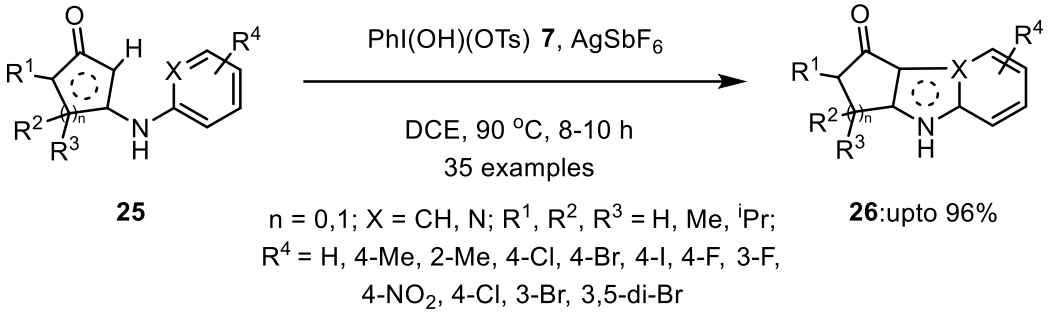
The mechanism for cyclization of thioamide **18** to benzothiazines **19** using Koser's reagent **7** is described in Scheme 4. Reaction proceeds by activating the sulfur atom of thioamide **18** to form intermediate **20** which is stabilised by the Koser's reagent. The targeted product **19** is obtained by an intramolecular cyclization of intermediate **21** (path **a**) via formation of another intermediate **22**. It can also proceed via path **b** by S-migration of spirocyclic intermediate **23** and it is observed that R^1 plays a vital role in the construction of the product. If *o*-methyl substrates were used intermediate **23** is formed and undergoes C-migration (path **c)** to generate **19a** as major product while *m*-methyl substrate forms intermediate **24** followed by S-migration (path **d**) which results in formation of **19a** as minor isomer.



Scheme 4. Mechanistic pathway for the synthesis of benzothiazines **19** from thioamides **18** involving Koser's reagent **7**.

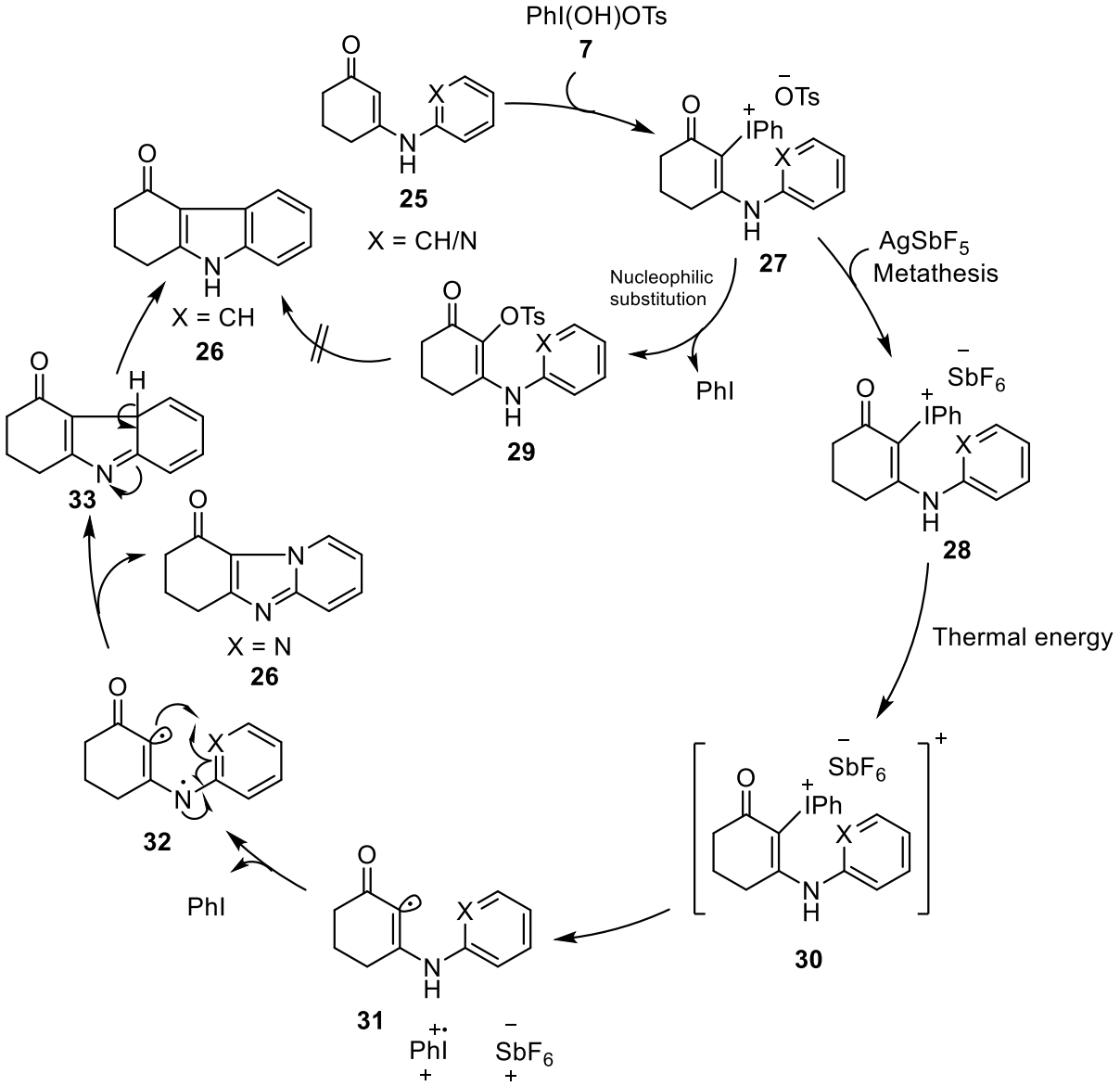
In 2019, an efficient novel synthetic protocol was developed to access carbazolones and imidazo[1,2-a]pyridines **26**.[23] This method involves intramolecular annulation of exocyclic-β-enaminones **25** to synthesize the corresponding carbazolones and imidazo[1,2-a]pyridines **26** through anion controlled free radical mechanism assisted by Koser's reagent **7**. Annulation reaction was performed smoothly and cyclized products **26** were isolated in excellent yields (Scheme 5). Co-operative behaviour of HITB [hydroxy(tosyloxy)iodobenzene] **7** and $AgSbF_6$ plays vital role in the intramolecular annulation via C-C and C-N bond formation to afford targeted products. Notably, the reaction rate is lowered by the effect of the vicinal bulky group in the rate determining C-H activation process. Thus, bulkiness at 4th position of exocyclic-*β*-enaminones **25** results the lowering in the product yields. Using this protocol, 2-aminopyridine derived exocyclic-β-enaminones **25** undergoes intramolecular annulation which involves C-N bond formation rather

than C-C formation to yield imidazo[1,2-a]pyridines **26** under identical condition. Various mono and di-substituted 2-aminopyridine enaminones gave excellent selectivity in C-N bond formation. In addition, variation in ring size (n = 0, 1) does not affect the yield much.



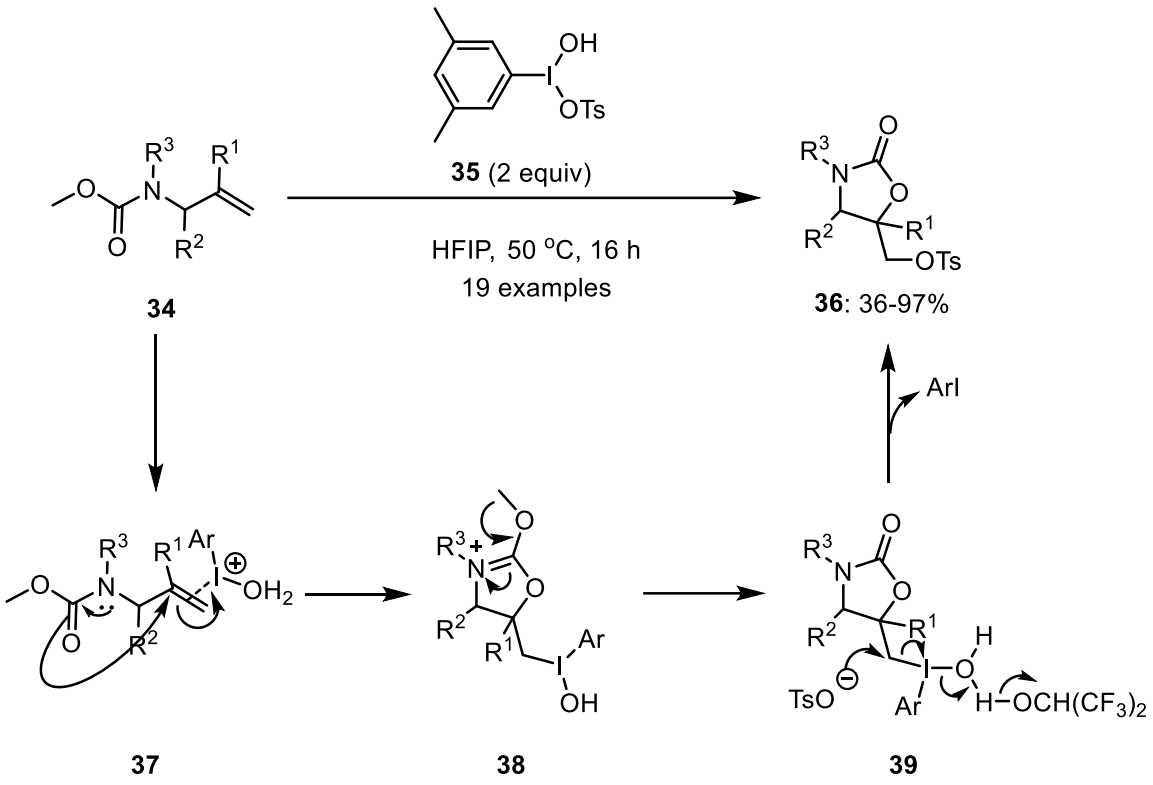
Scheme 5. Iodine(III)-mediated annulation of exocyclic-β-enaminones **25** to carbazolones and imidazo[1,2-a]pyridines **26**.

The reaction mechanism for the annulation of exocyclic-β-enaminones **25** to carbazolones **26** is depicted in Scheme 6. Initially, ligand exchange reaction takes between HTIB **7** and reactant **25** to give intermediate **27** which either undergoes metathesis or nucleophilic substitution to yield **28** and **29** respectively. Since metathesis is faster under the given reaction condition, intermediate **28** is formed over **29**. Intermediate **31** is formed via **30** by the homolytic cleavage which further undergoes cyclisation to furnish **33** via intermediate **32** along with the formation of product **26** (X = N). Finally, intermediate **33** undergoes aromatization with the migration of proton to give corresponding carbazolones **26** (X = CH).



Scheme 6. Mechanistic pathway for the synthesis of carbazolones and imidazo[1,2-a]pyridines **26** iodine(III)-mediated annulation of enaminones **25**.

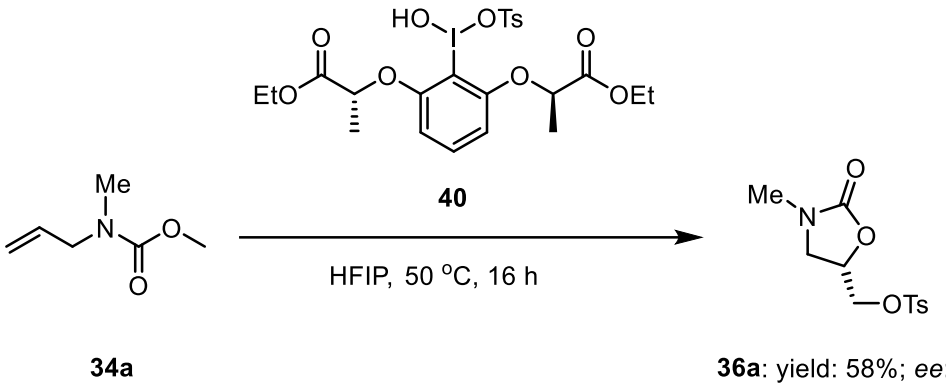
In 2021, Das and co-workers introduced new efficient methodology for the synthesis of oxazolidinones **36** by the cyclization of *N*-allyl carbamates **34** using hypervalent iodine reagent **35**.[24] Reactions were performed in polar solvent 1,1,1,3,3,3-hexafluoro-2-propanol and gave reaction products **36** in moderate to excellent yields (Scheme 7). A wide range of substrates **34** containing both electron donating and withdrawing groups were tolerated successfully and give corresponding oxazolidinones **36**. Furthermore, the tosyl group was replaced by amino functionality by S_N2 substitution with amines. The above cyclisation of *N*-allyl carbamates **36** mechanistically proceeds through an activation of olefinic functionally by the iodine(III) species **35** to form the intermediate **38** via formation of intermediate **37** (Scheme 7). HFIP reacts with intermediate **38** to form another intermediate **39** which undergoes S_N2 substitution by tosylate ion to the afford final product **36**. It was observed that solvent HFIP plays a vital role during these transformations. The classical Koser's reagent was examined in a screening study, and the targeted product was obtained in 76%yield. While modified Koser' reagent used in this reaction elevated the final product yield to 95%.



R^1, R^2 = Me; R^3 = H, Me, Et, Ph, 4-MePh, 2,6-Me_2Ph, 2-OCF_3Ph, 4-OMePh, 4-SO_2MePh, 4-NO_2Ph, 4-CNPh, 4-CO_2MePh, 4-Pz, Ph, 4-Br, 3-FPh

Scheme 7. Cyclization of *N*-allyl carbamates **34** to oxazolidinones **36** using hypervalent iodine reagent **35**.

Furthermore, the chiral Koser type reagent **40** was synthesized from the corresponding chiral PIDA derivative using reported procedure and used for the enantioselective cyclization of *N*-allyl carbamates **34a**. Reaction was not as effective as the with achiral iodine(III) reagent **35** and chiral corresponding oxazolidinone **36a** was obtained in 58% with 62% enantiomeric excess (Scheme 8).

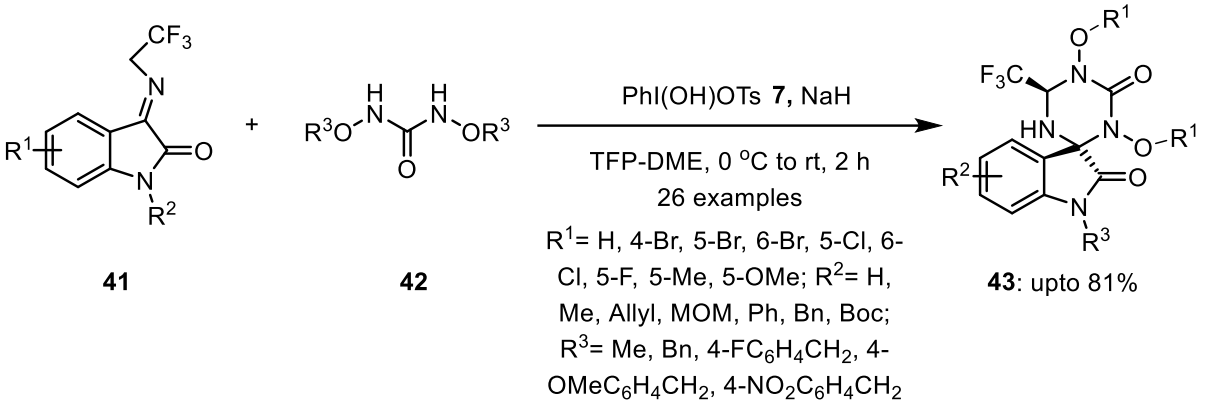


34a **36a**: yield: 58%; *ee*: 62%

Scheme 8. Iodine(III)-catalysed enantioselective cyclization of *N*-allyl carbamate **34a** to enantiomerically rich oxazolidinone **36a**.

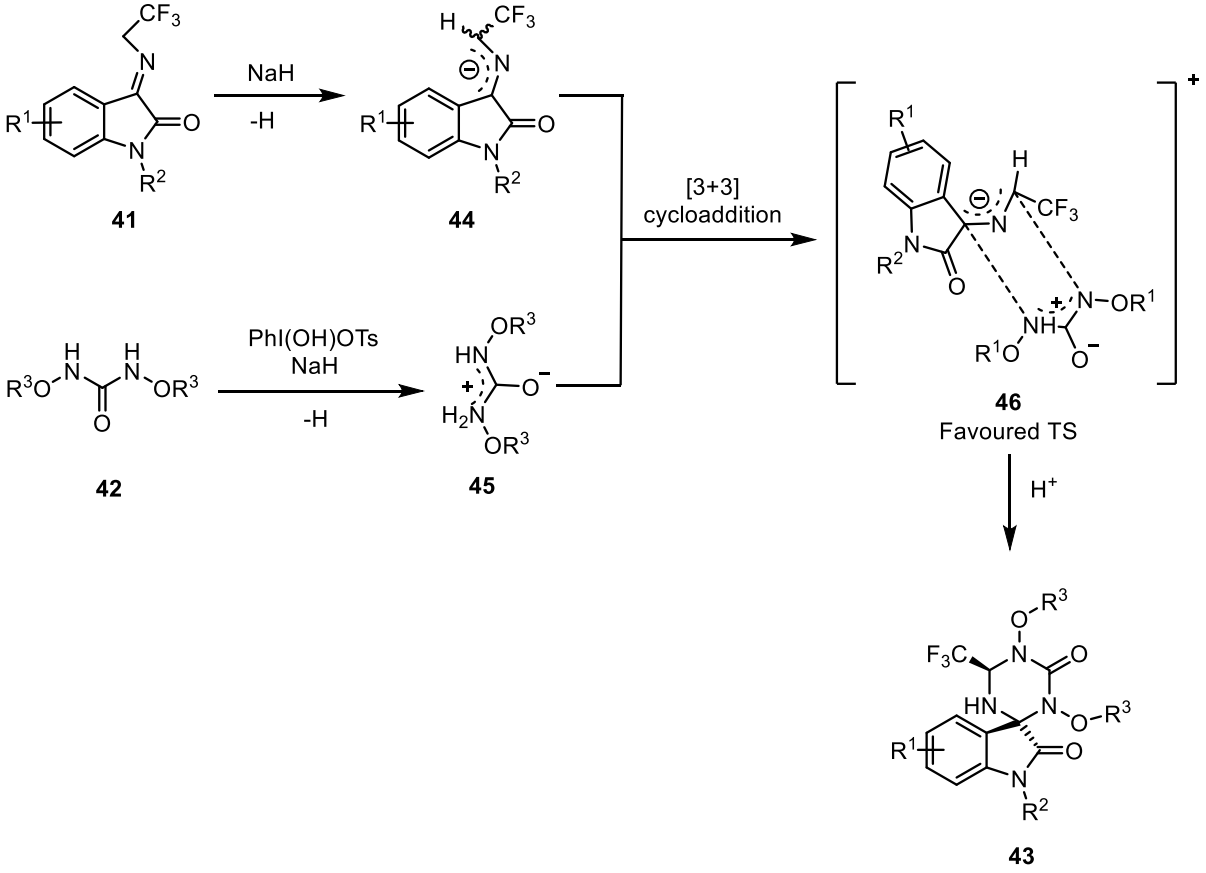
In 2019, Zhao et al. established a new efficient synthetic route to afford *trans*-configured spiro-1,3,5-triazinan-2-ones **43** in moderate yield (Scheme 9).[25] This methodology proceeds through the [3+3] cycloaddition

of isatin based α-(trifluoromethyl)imines **41** with *N*,*N*'-dialkyloxyureas **42** conciliated by PhI(OH)OTs (Koser's reagent) **3** and NaH and the obtained product's **43** configuration is confirmed as *trans* using single crystal X-ray analysis. Generally, substrate **41** tolerates a range of substituents and affords the corresponding product with reasonable yield but notably, substrate **41** with H and Boc as substituent failed to undergo [3+3] cycloaddition. Also, *N*,*N*'-dialkyloxyureas **42** involving 4-$OMeC_6H_4CH_2$ and 4-$NO_2C_6H_4CH_2$ as substituents were ineffective.



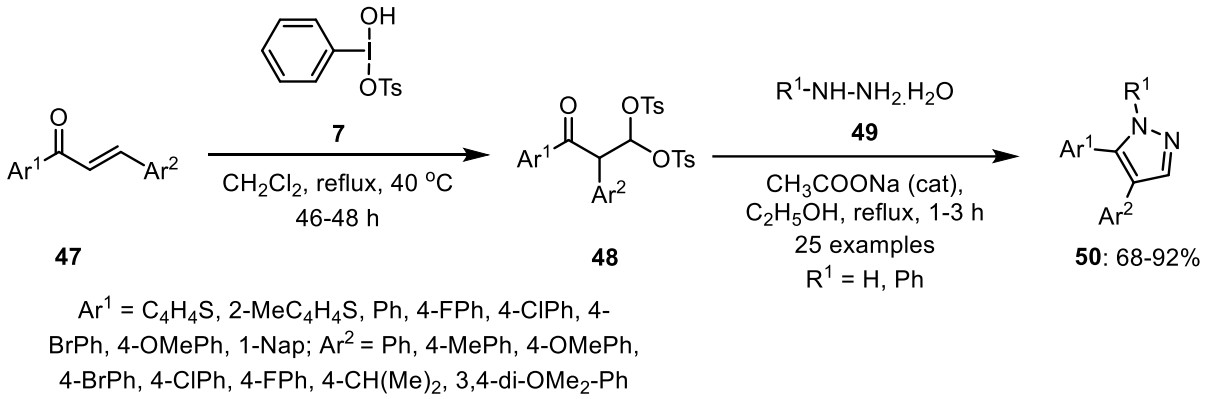
Scheme 9. Synthesis of spiro-1,3,5-triazinan-2-ones **43** mediated by Koser's reagent **7** and NaH.

This [3+3] cycloaddition mechanistically proceeds through the formation of ylide **44** from isatin analogue **41** and diaza-allyl cation **45** by oxidation of *N*,*N*'-dialkyloxyureas **42** (scheme 10)**.** These intermediates **44** and **45** undergo [3+3] cycloaddition via the formation of thermodynamically stable transition states **46** to yield the expected *trans*-configured spiro-1,3,5-triazinan-2-ones **43**.



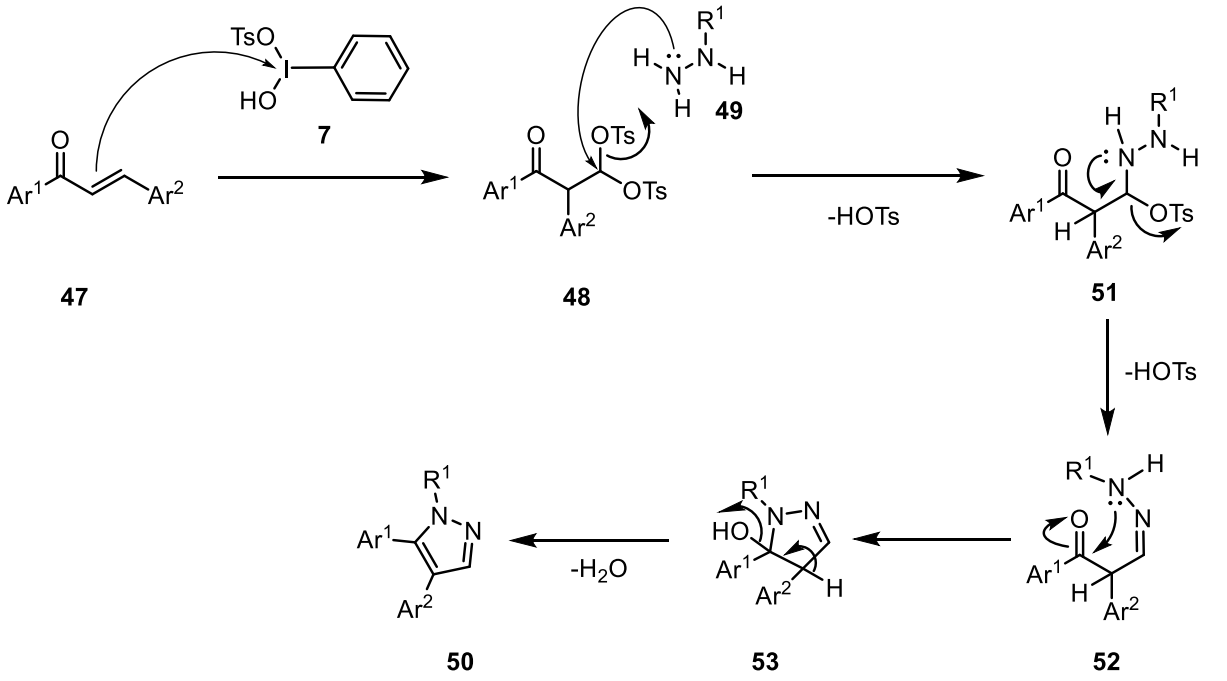
Scheme 10. Plausible mechanism for the synthesis of *trans*-configured spiro-1,3,5-triazinan-2-ones **43**.

In 2022, Kumar and others utilized the Koser's reagent **7** for the synthesis of 4,5-diaryl and 1,4,5-triaryl pyrazoles **47** from chalcones **44** in two chemical steps.[26] Chalcones 47 were converted to α-aryl-β, β-ditosyloxy ketones **45** on the reaction with iodine(III) reagent **11**, which was further utilized as 1,3-dielectrophilic three carbon atom versatile precursor further structural modifications. Subsequently, the isolated products **45** were treated with hydrazines **46** to construct 4,5-diarylpyrazoles **47** in excellent yields (Scheme 9). Actually, presence of two *p*-toluenesulfonyloxyl group in the substrates made this reaction more feasible due to the leaving property and electron withdrawing nature. Various electronically rich and poor substituents were successfully tolerated under given reaction conditions.



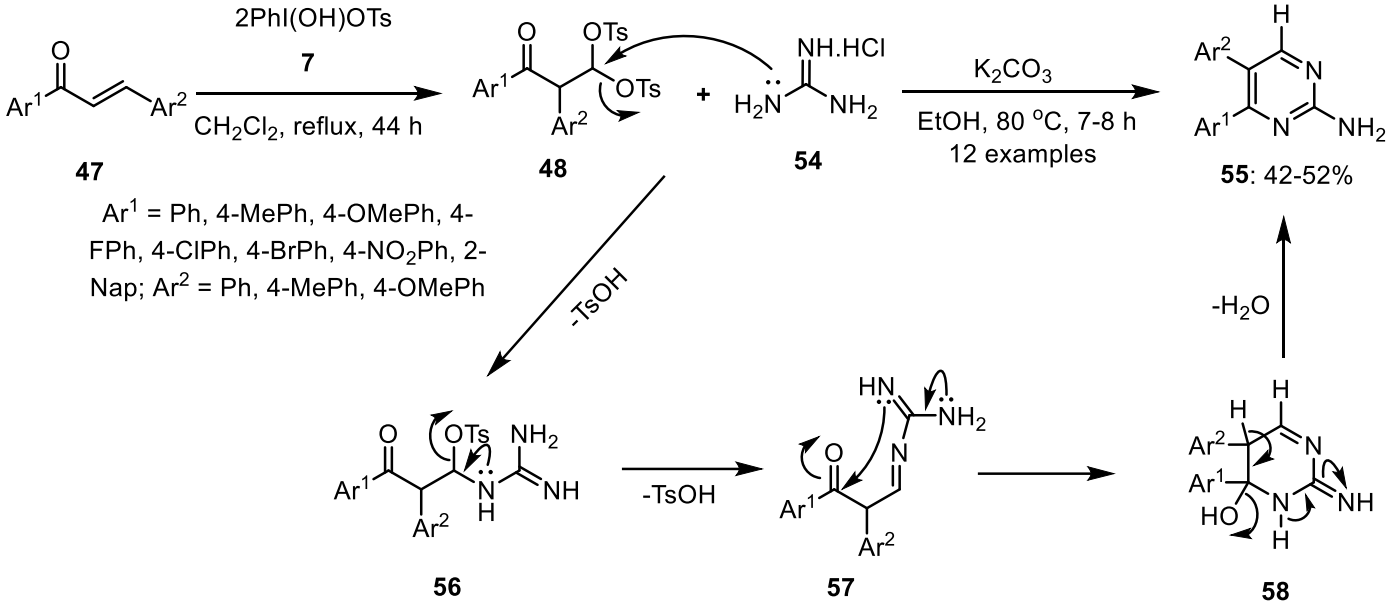
Scheme 11. Regioselective synthesis of 4,5-diarylpyrazoles **50** from chalcones **47** in two chemical steps.

The above cyclization possibly occurs via the mechanistic pathway described in Scheme 12. Reaction was initiated by the activation of olefinic double bond of substrate **47** by iodine(III) species **7** forms α-aryl-β,β-ditosyloxy ketones **48**. The good leaving property and electron withdrawing capability of the tosyl group played a vital role. Thus, a tosyl group at the β-position makes the substrate more susceptible towards the nucleophilic attack. The lone pair of the nitrogen atom of the hydrazine **49** attacks at the β-position removing the TsOH and generating intermediate **51**. Consequently, the intermediate **51** gave imine intermediate **52** by losing another TsOH. Then, the intramolecular cyclization between the lone pair of nitrogen and carbonyl carbon forms intermediate **52**. Further, loss of H_2O yields the arylated pyrazole derivatives **50**



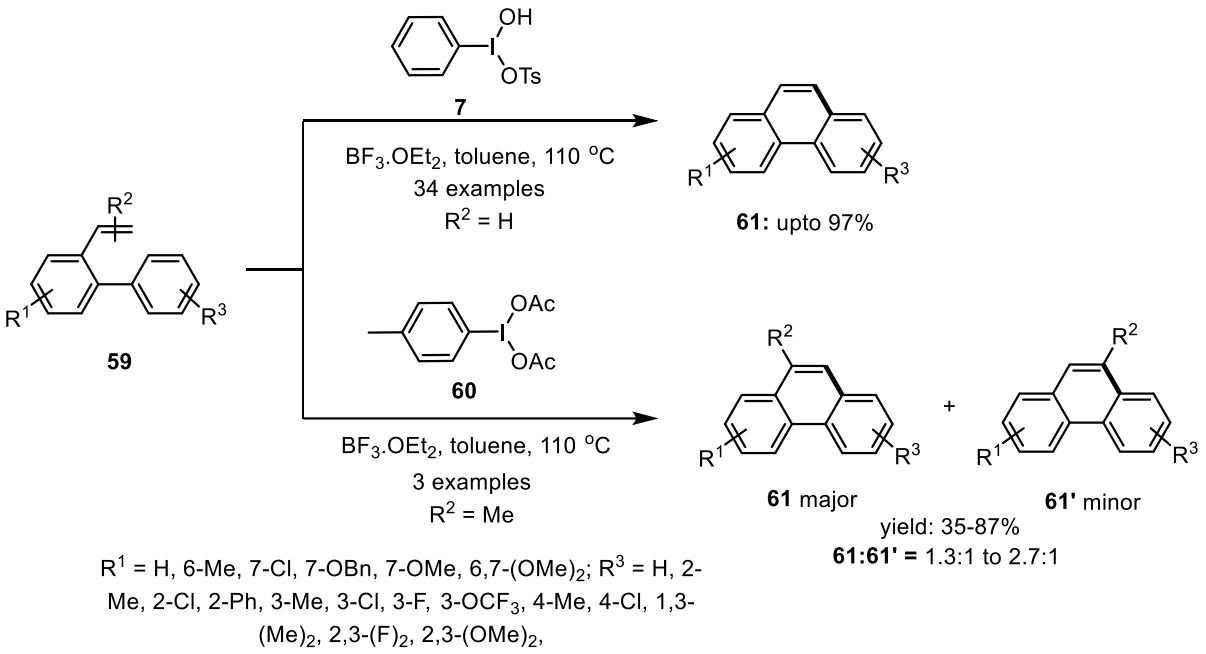
Scheme 12. Plausible mechanism for the synthesis of 4,5-diaryl pyrazoles **50** from chalcones **47** in two chemical steps.

The same group explored the guanidine hydrochloride **54** instead of hydrazine **49** under the same reaction conditions and obtained pyrimidines **55** (Scheme 13).[27] Similar to the previous reaction, the reaction proceeds through the formation of ditosyloxy ketones **48**, which further gets attacked by guanidine hydrochloride with loss of TsOH, intramolecular cyclization and loss of H_2O give the pyrimidine derivatives. High regioselectivity, shorter time and facile reactivity due to the existence of two tosyl group are considered as advantages. It was observed that all the derivatives reacted in the same manner to give the corresponding pyrimidine molecule with moderate yield.



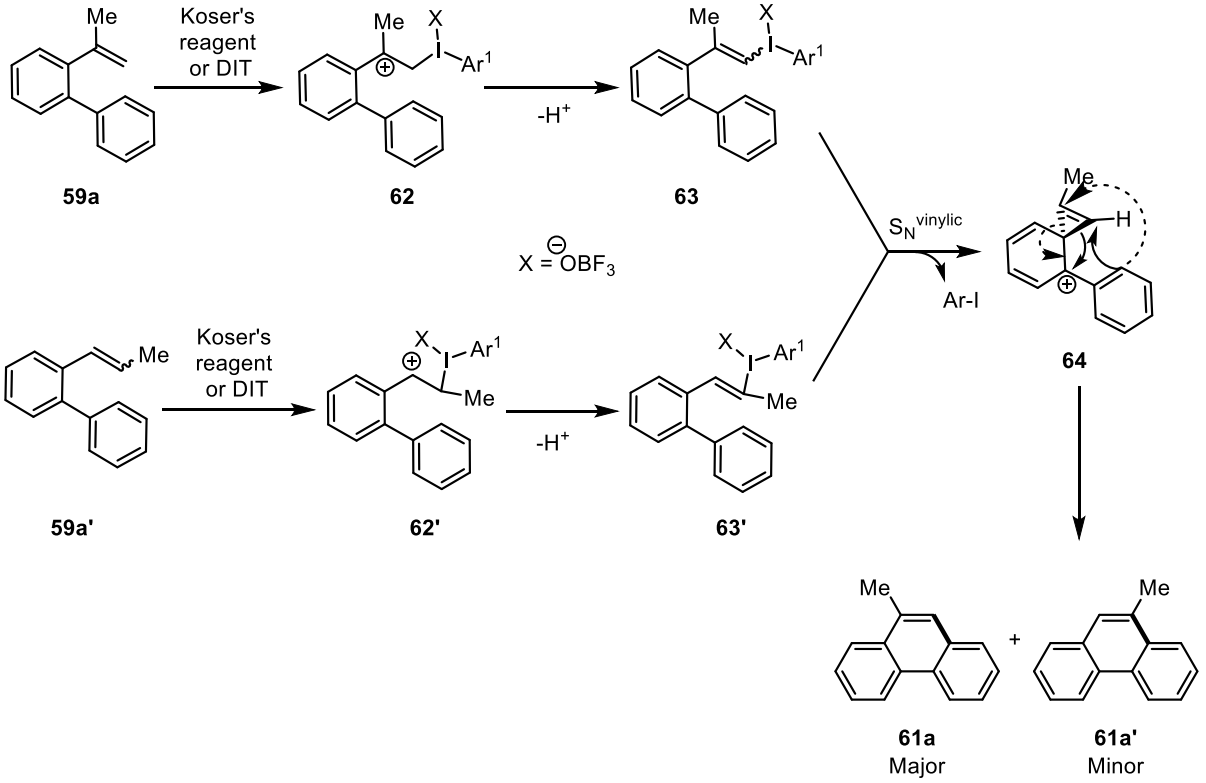
Scheme 13. Hypervalent iodine(III)-mediated synthesis of 2,4,5-trisubstituted pyrimidines **55** starting from chalcones **47**.

In 2022, Britt et al. achieved novel oxidative arylation of alkene mediated by Koser's reagent **7** and (Diacetoxyiodo)toluene (DIT).[28] This arylation involves the transformation of *ortho*-vinylbiphenyl **59** derivative to polycyclic aromatic hydrocarbons **61** with yield up to 97%. This protocol likely to operate via vinyliodonium salts decomposing into vinylene phenonium ions (Scheme 14). Formation of *E*-vinyliodonium ions as initial intermediate is supported by 1,2-phenyl shift. The yield was reduced up to 36 % when the substrate **59** bearing with electron withdrawing group as substituents are failed to undergo subsequent cyclization, may be due to the reactivity of proton with iodanes. Besides, the substrate bearing electron donating substituent at vinylic position were well tolerated.



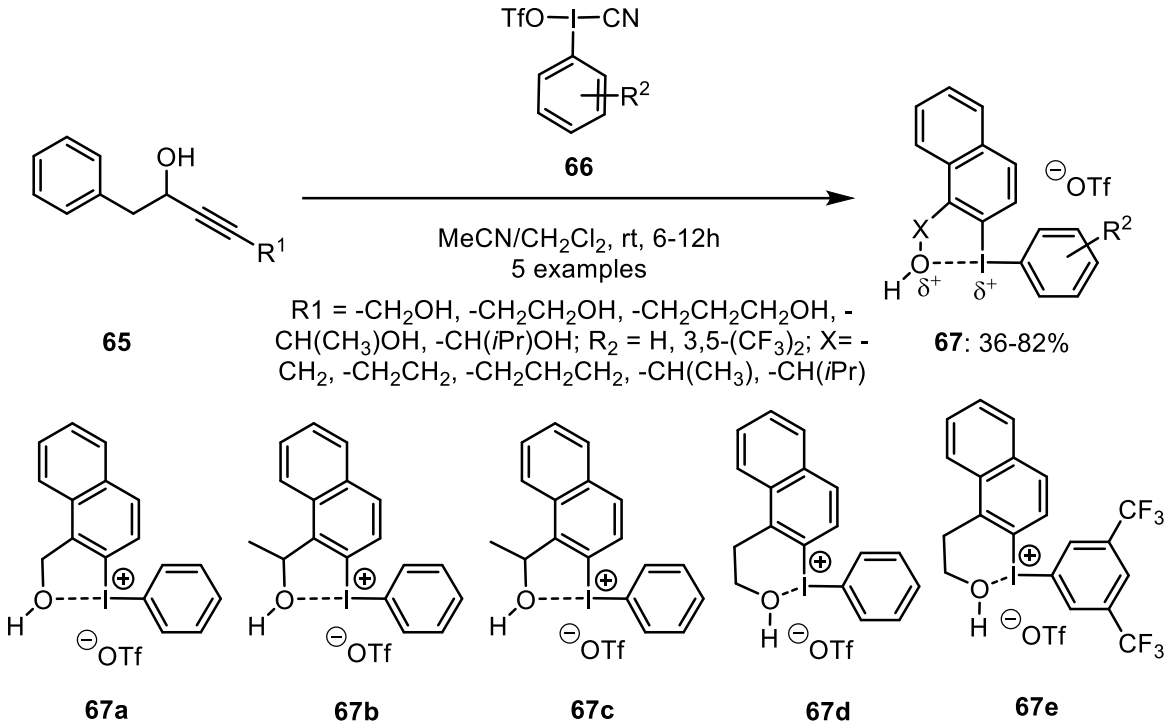
Scheme 14. Hypervalent iodine(III) reagent **7** mediated oxidative alkene arylation of compound **59**.

The above oxidative alkene arylation mechanistically proceed through the attack on hypervalent iodine reagent **7** or **60** to generate the benzylic cations **62** and **62'** followed by the deprotonation form **63** and **63'** respectively (Scheme 15). Subsequent discharge of the iodoarene via vinylic substitution gives common vinylene phenonium ion **64** which is attacked by the pendant arene to produce the observed phenanthrene isomers **61a** and **61a'**.



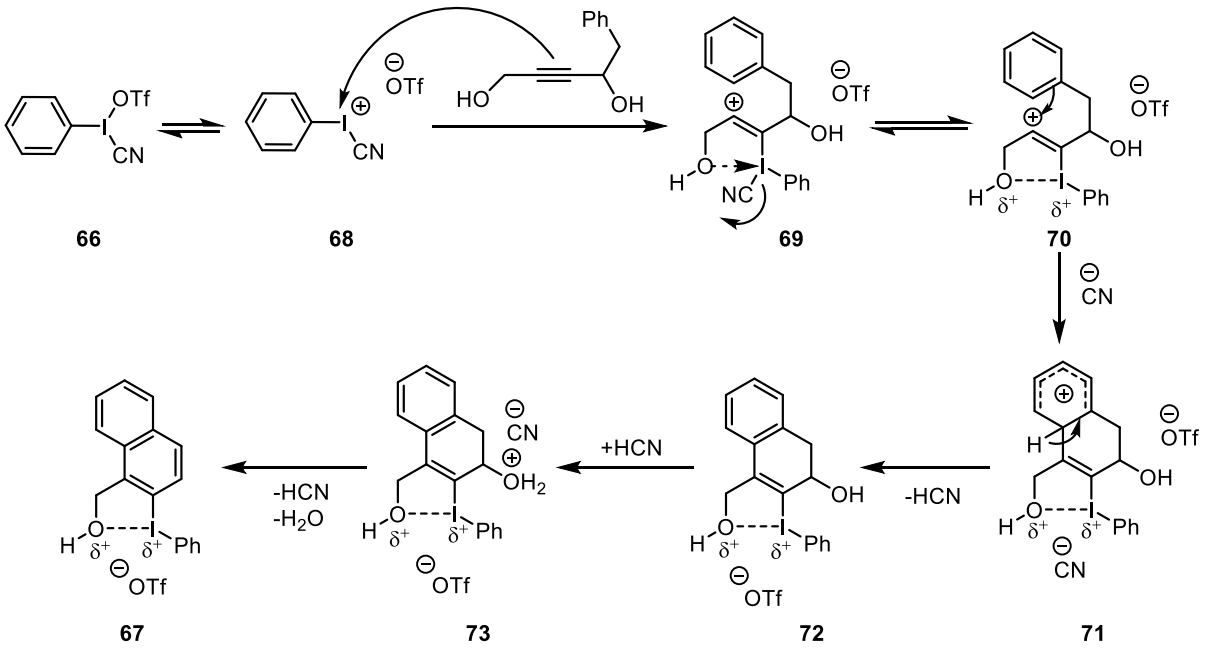
Scheme 15. Plausible mechanism for the hypervalent iodine (III) **7** mediated alkene arylation.

Furthermore, Stang's reagent **66** was treated with the phenyl alkynediols **65** derivatives in acetonitrile or chloroform at room temperature. The reaction results in the formation of range of naphthyl(aryl)iodonium triflates **67** in good yield by electrophilic cyclization.[29] The phenyl alkynediols were synthesized by the reaction of benzyl aldehyde with terminal alkynols in presence of *n*-BuLi in THF at -78 °C. The obtained phenyl alkynediols cyclized with the assistance of Stang's reagent **66** (Scheme 16). This methodology provides the X-ray quality crystals of naphthyl(aryl)iodonium triflates **67** with hydroxyl group and forming 5 and 6-membered chelation complexes **67** containing an iodine atom.



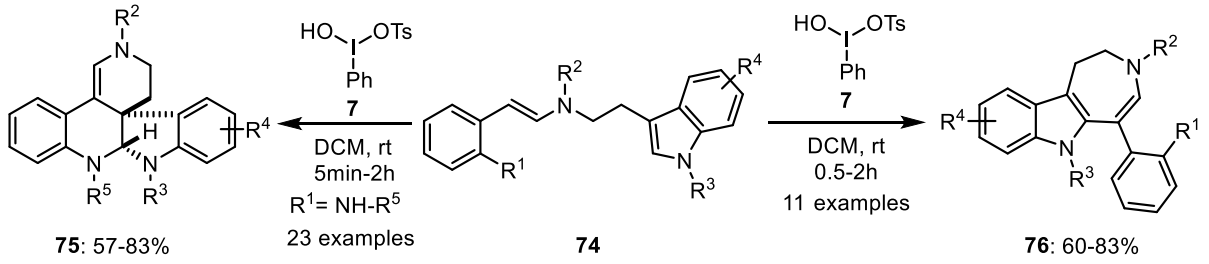
Scheme 16. Conversion of phenylalkynediols **65** to naphthy(aryl)iodonium triflates **67** by electrophilic cyclization using Stang's reagent **66**.

The alkynyl π-electrons attacks the electrophile [Ph-I$^+$-CN] **68** (which is generated as a result of large ionic nature of I-OTf) led to formation of incipient alkenyl cation **69.** Coordination with any alcohols could reinforce to form electrophile from alkyne and to loss of cyanide **69** (Scheme 17). Arenium ion **70** (rearomatized) is obtained by the attack of pendant phenyl followed by the subsequent protonation of propargylic alcohol by HCN and naphthyl moiety is obtained from the final dehydration also water and HCN as by-products.



Scheme 17. Plausible mechanism for electrophilic cyclization to naphthy(aryl)iodonium triflates **67**.

In 2025, Yoshimura et al. established new metal free, site-selective, chemo and regio-selective cross-nucleophilic coupling cascade of indole-enamine-aniline intermediates mediated by Koser's reagent **7** to synthesis a valuable benzo[c]indolo[3,2-j][2,6]naphthyridines **75** and azepino[4,5-b]indoles **76** (Scheme 18).[30] The presence of an electron donating group at indole's C_4 or C_5 position increases efficiency of the reaction whereas the electron withdrawing group diminishes the corresponding product **75** yield.



R^2 = Ts, 1-SO_2 4-FPh, 1-$SO_2$4-CF_3Ph, 1-$SO_2$4-ClPh,1-$SO_2$2,4,5-$(Cl)_3$Ph, 1-$SO_2$4-ClPh, SO_2-3-Py, SO_2-3-thiophenyl, SO_2-Nap-2, aryl, alkyl; R^3 = Me, Et, Bn; R^4 = H, 4-Cl; R^5 = Ts, 1-SO_2-4ClPh, 1-SO_2-4-COF_2Ph, Aryl

R^1 = H, $NHCOCF_3$, NO_2; R^2 = Ts, 1-SO_2-4ClPh, 1-SO_2-4CF_3Ph, 1-SO_2-Nap-2, aryl, alkyl; R^3 = Me, Bn; R^4 = H, 4-OMe

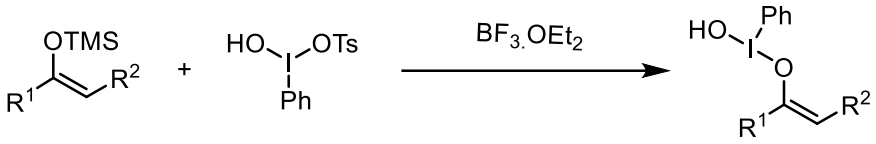
Scheme 18. Synthesis of azepino[4,5-b]indoles **75** and benzo[c]indolo[3,2-j][2,6]naphthyridines **76** conciliated by the hypervalent iodine(III).

3. Carbonylation reactions using iodine(III) reagents

Insertion of carbonyl to the molecules was easily and effectively achieved by iodine(III) reagent, avoiding expansive metal catalysts. The oxidative process facilitates the activation of alkene, and alkyl and other olefinic compounds.

Up on treating silylated enol species **77** with the Koser's reagent **7** in presence of Lewis acid leads the formation of readily reactive intermediate species **78** (Scheme 19). In the absence of Lewis acid, silylated enol species **77**

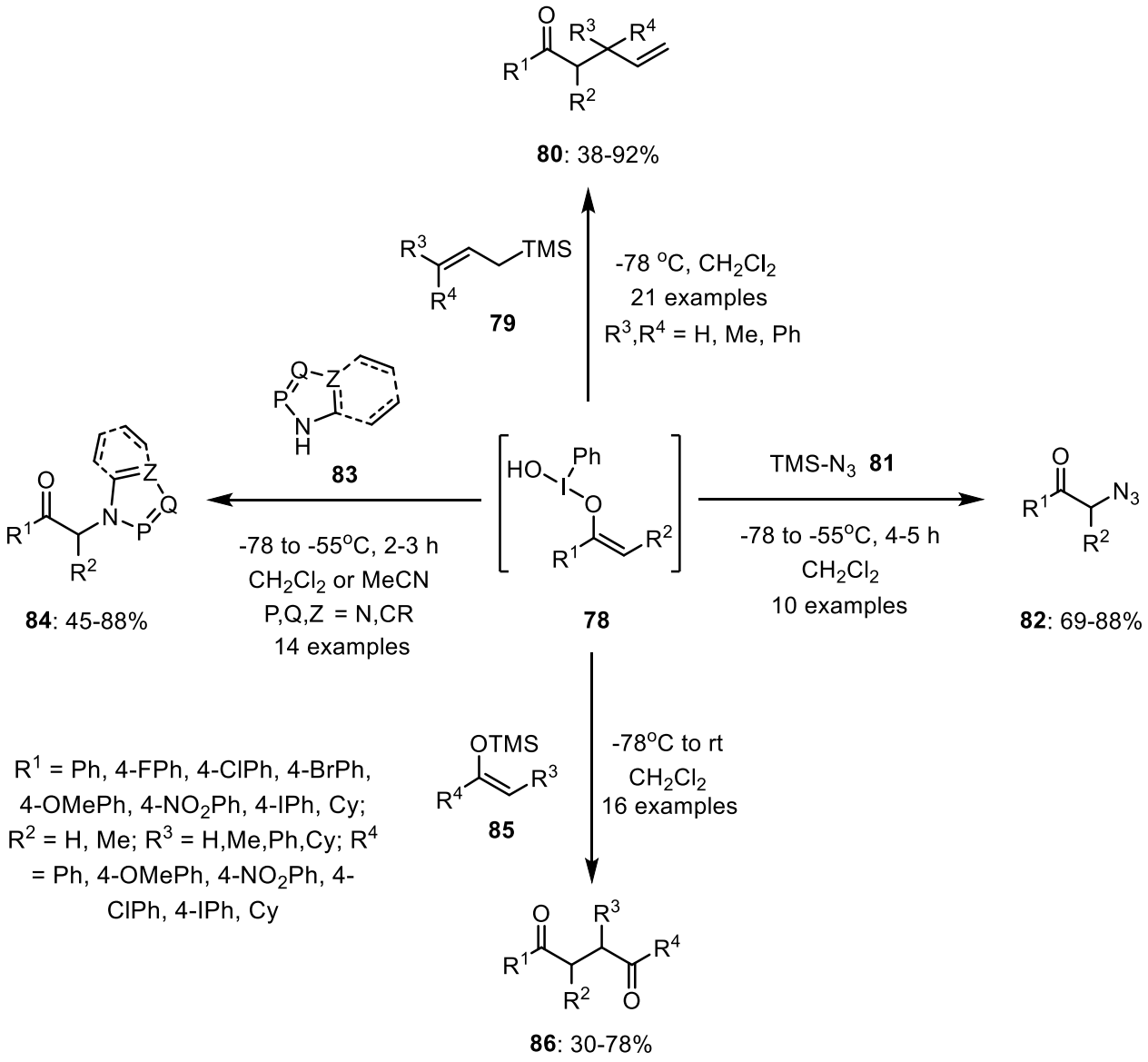
readily forms the dimer. Dimerization decreases the overall yield of the reaction. Thus, Lewis acid prevents dimer formation resulting in enhanced yield. Further, the intermediate **78** could be explored with the different nucleophiles at optimized condition results in the various set of scaffolds bearing with carbonyl group.



77 **7** **78**

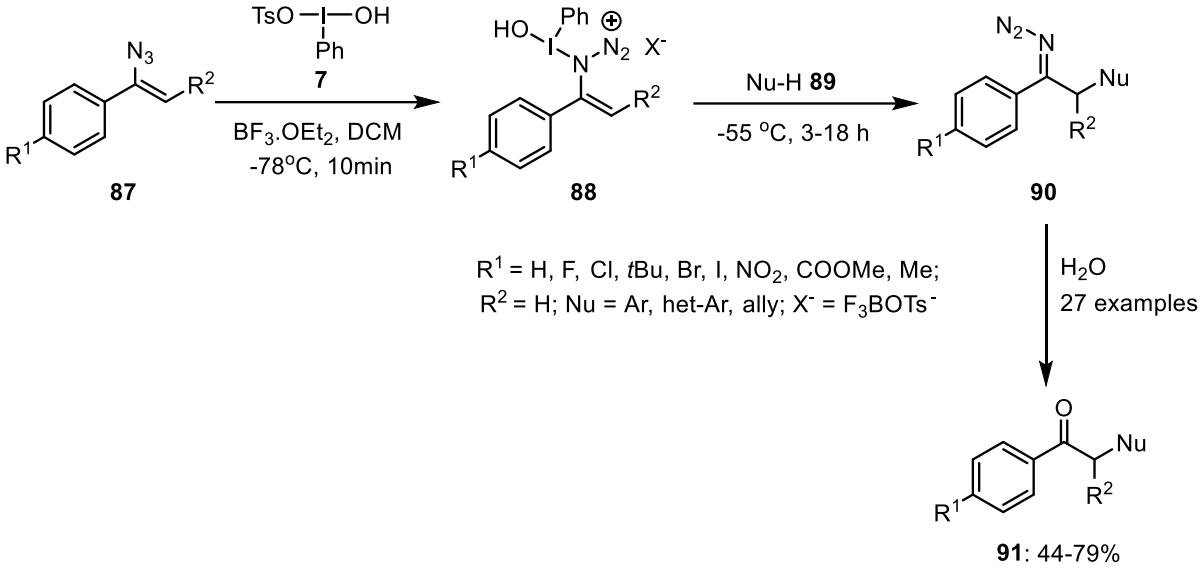
Scheme 19. Formation of iodine(III) intermediate species from Koser's reagent.

The reverse prenylation of ketone enolates **77** was achieved with the reaction of reactive intermediate **78** with the allyl silane **79** at -78 °C in dichloromethane. The prenylations occurs in a single step and results the results the formation of desired product in moderate to good yield.[31] When the reaction was performed under the same reaction conditions with $TMSN_3$ **81**, the α- azido-ketones **82** were obtained. Similarly, when the amino nucleophile **83** was used instead of azide, this synthetic method generated α-aminated ketones **84**.[32] Under mild reaction conditions, a variety of azoles participate in the reaction giving good to excellent yields with electron rich as well as electron poor ketones. Further in 2018, Parida et al. proposed the utility of Koser's reagent **7** for the formation of 1, 4-diketones **86** with good diastereoselectivity via oxidative intermolecular cross-coupling of dissimilar trimethylsilyl enol ethers **85**.[33] Despite its poor electronic nucleophilicity, the less hindered tosylate reacts faster with the enolonium species rendering significant increase in yield. The less sterically hindered TMS enol ether **77** (R^1 = Ph, R^2 = H) is preferably used to generated the enolonium species **78** followed by cross-coupling of more sterically hindered silyl enol **85** (R^3 = Ph, R^4 = Me) to render the 1,4 -diketone with good yield (scheme 20). When the order of addition is reversed, only a trace amount of the desired product is obtained.



Scheme 20. Functionalization of trimethylsilyl enol ethers **77** by using Koser's reagent **7** along with various nucleophiles.

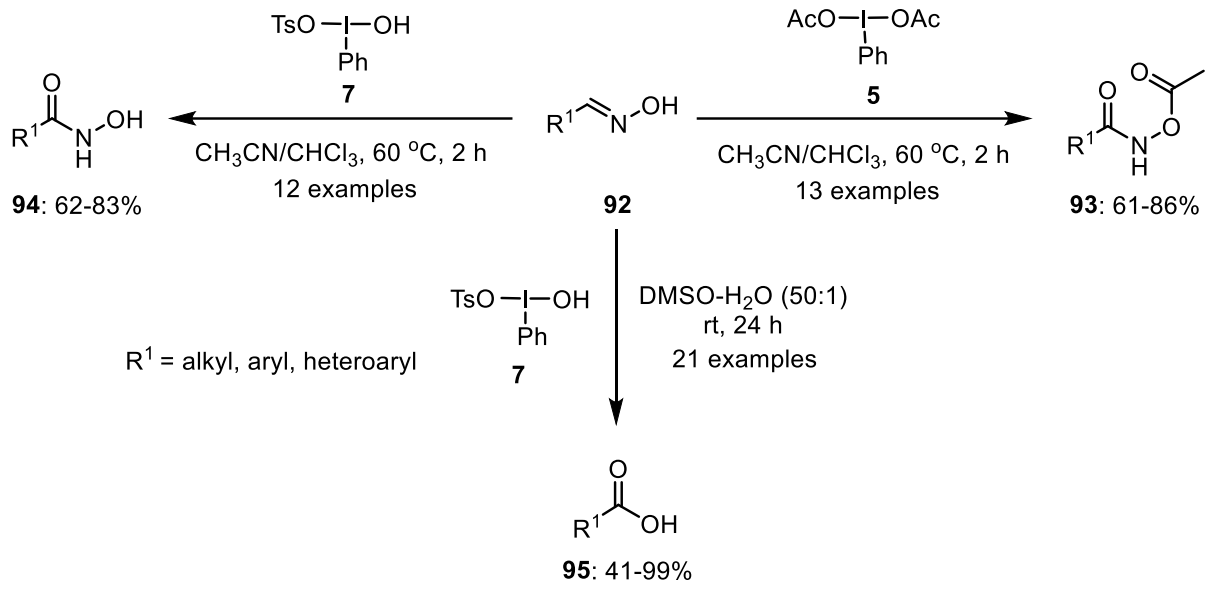
In 2020, More et al. proposed a methodology to synthesise a range of α-functionalized ketones **91** in good yield, by reacting the azido-enolonium species **88** with different nucleophiles such as aromatic, allyl and azoles.[34] The reaction of vinyl azides **87** with Koser's reagent affords the azido-enolonium species **88** which reacts with aromatic coupling partner **89**, the compound 90 was obtained which further hydrolyzed and the target α-functionalized ketones **91** was obtained (Scheme 21). The compatibility of electron rich group substituted indole and vinyl azide gives an excellent yield in comparison to indoles that are less prone to react twice under the given reaction conditions.



Scheme 21. The synthesis of α-functionalized ketones **91** from vinyl azides **87**.

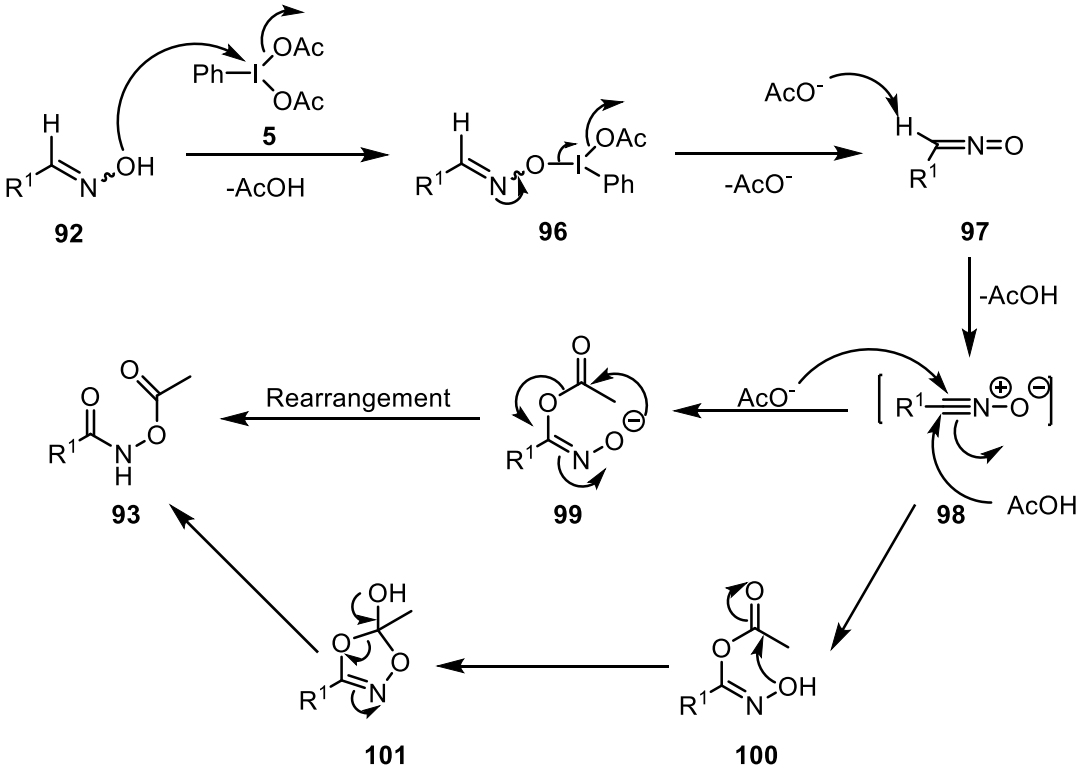
4. Rearrangement reactions using iodine(III) reagents

The selectivity of iodine(III) reagents plays a crucial role in rearrangement reactions. Thus, diminished formation of byproducts leads to outstanding yields. Upon treating aldoximes **92** with hypervalent iodine(III) reagent at different reaction condition yields the different products. By reacting with Koser's reagent **7** in acetonitrile or chloroform at 60 °C for 2 h yielded the *N*-hydroxy amide derivatives **94**. Whereas with the same reaction condition, the (diacetoxyiodo)benzene (PIDA) **5** used instead of Koser's reagent yielded *N*-acetoxy benzamide **93**.[35] Likewise, when the Koser's reagent used in different condition as DMSO:H_2O (50:1) for 24 h for room temperature yielded corresponding carboxaldehydes **95** (Scheme 22).[36] Variety of aliphatic and aromatic aldoximes **92** containing electron donating and withdrawing group were tolerated to give the corresponding *N*-acetoxy amide derivatives **93** and hydroxamic acid derivatives **94**. It was observed that aliphatic aldoximes were more reactive than aromatic and get converted into appropriate *N*-acetoxy amide **93** while treating DIB and hydroxamic acid **94** with HTIB.[35] Electron rich benzaldehyde oximes and the substrates possessing electron withdrawing substituents at the para position proceeded under the optimised mild reaction conditions rendering the respective carboxylic acids **95** in good to excellent yield. Whereas, 1-napthaldehyde oxime gave poor yield in comparison with 2-napthaldehyde oxime. Enduring these conditions Ts-protected indole moiety provided excellent yield of the respective carboxylic acids. In the presence of primary and secondary benzylic alcohols, the oxidation of aldoximes proceeded by giving moderate to good yield of the acids.[36]



Scheme 22. Reaction of aldoximes **92** with DIB **5** and HTIB **7** at different reaction condition.

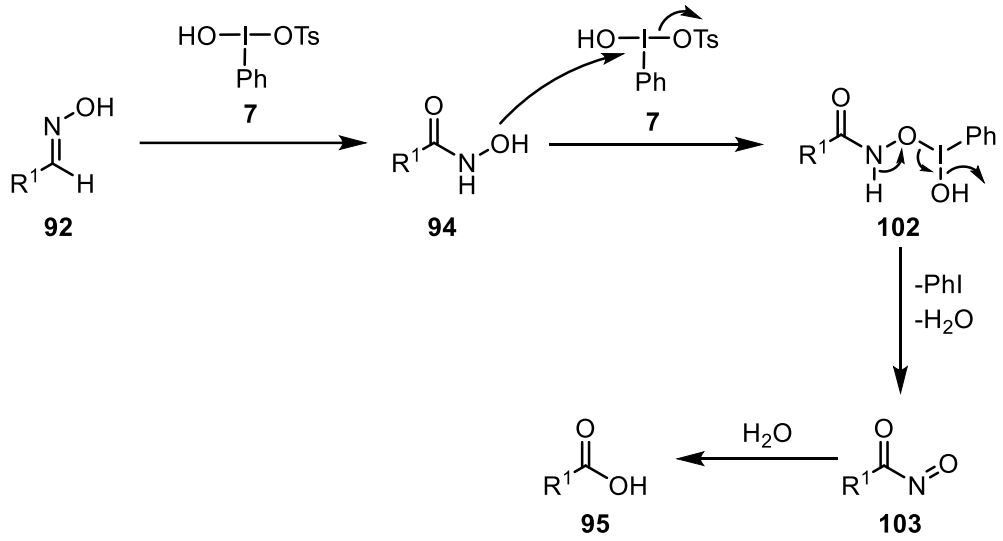
The nucleophilic attack on PIDA by aldoxime leads the nucleophilic displacement results the intermediate **97**. Further, the intermediate nitrile oxide **98** is generated from the deprotonation of **97**. This nitrile oxide **98** is further attacked by *in situ* liberated acetate or acetic acid facilitate the two types of intermediate species **99** and **100** respectively. The consequent intramolecular rearrangement of both intermediates results the targeted *N*-acetoxy amide **93**.[35]



Scheme 23. The plausible mechanism for the formation of *N*-acetoxy amides **93**.

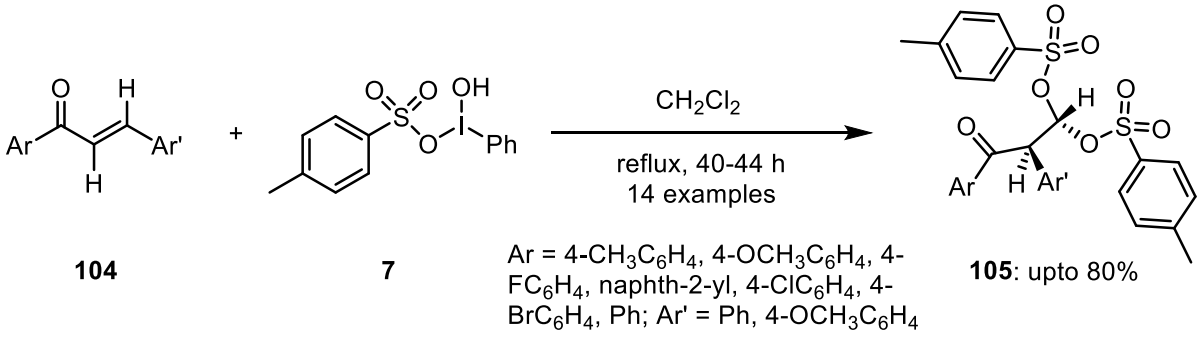
When the aldoxime 92 is treated with Koser's reagent hydroxamic acid derivatives **94** are produced. Further, the ligand exchange between hydroxamic acid **94** and Koser's reagent **7** from the compound **102**,

followed by the elimination of PhI and H_2O leads the formation of acyl-nitroso compound **103**. This on further hydrolysis gives carboxylic acid **95** (Scheme 24).[36]



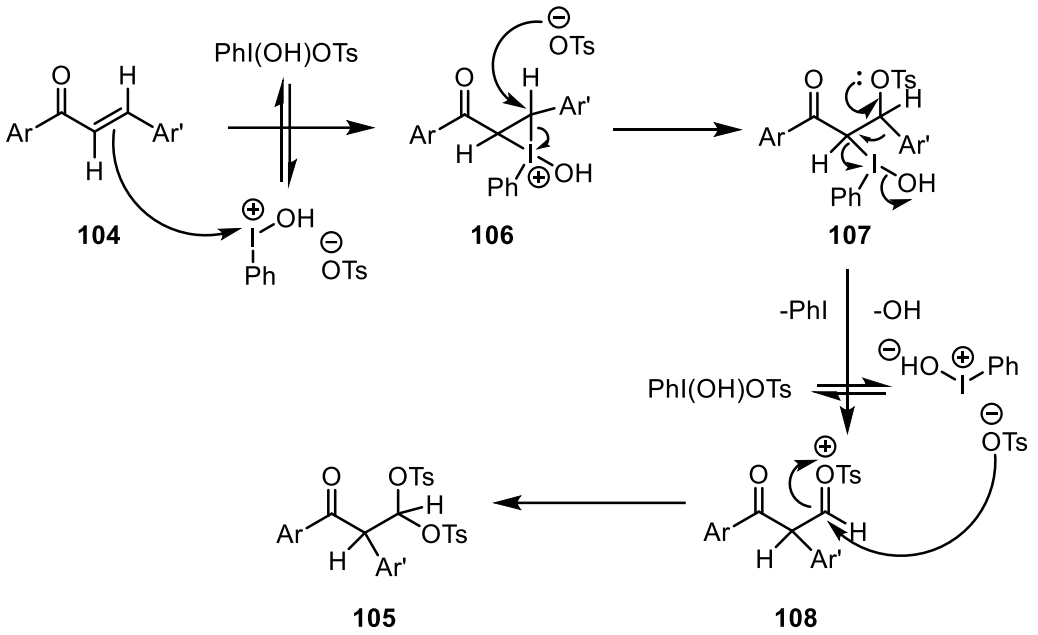
Scheme 24. The plausible mechanism to synthesis carboxylic acid **95**.

The 1,2-aryl shift is observed when chalcone is treated with Koser's reagent. In 2020, Kamal et al. explored the intriguing role of HTIB **7** to synthesis a series of geminal β,β-ditosyloxy ketones **105** in moderate to good yields. This was achieved by ditosyloxylation of α,β-unsaturated ketones **104** mediated by HTIB **7** (Scheme 25).[37] A stereoselective oxidation of α,β-unsaturated ketones **104** proceeds via 1,2-aryl migration upon reacting with Koser's reagent leads the formation of *gem*-β,β-ditosyloxy ketones **105.**



Scheme 25. Synthesis of geminal β,β-ditosyloxy ketones **105**.

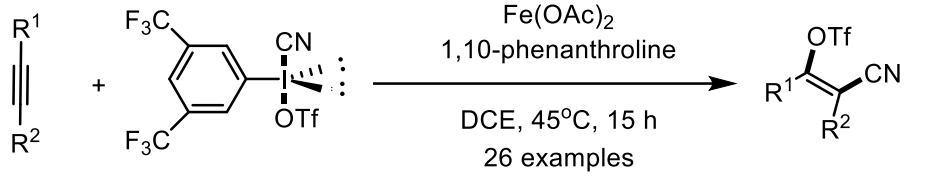
The electrophilic addition of $Ph(OH)I^+$ to the double bond of the chalcone results in formation of the cyclic organoiodine intermediate **107.** Due to the presence of electron-withdrawing carbonyl group, the nucleophilic attack at α-carbon is not favourable. Therefore, the nucleophile attacks at β-carbon and produces ring opened adduct **107**. The lone pair facilitates the 1,2 aryl migration followed by the release of a hydroxide ion (OH^-) and iodobenzene lead the formation of intermediate **108** (Scheme 26). On the β-carbon of the carbonyl group through the attack of a second tosylate ion, results in the formation of geminal ditosyloxy ketone **105**.



Scheme 26. Proposed mechanism for the ditosyloxylation of α, β-unsaturated ketones **104.**

5. Triflation reactions using iodine(III) reagents

Firstly, Zhdankin et al. introduced an iodine(III) reagent, aryl(cyano)iodonium triflates **110** for the direct triflation of organic substrate.[38] Later, Wang et al. used aryl(cyano)iodonium triflates **110** along with $Fe(OAc)_2$ and phenanthroline for the triflate of alkyne **109** (Scheme 27).[39] In this reaction, the OTf and CN substituted alkenes were obtained with excellent *cis*-selectivity and complete regioselectivity. 1-Aryl-1-pentynes bearing electron withdrawing or donating groups at para positions were converted, rendering high yield along with good. regio- and stereoselectivity to the acrylonitriles **111**. But significantly lower yields of the alkynes bearing substituents at the meta and ortho positions were produced.

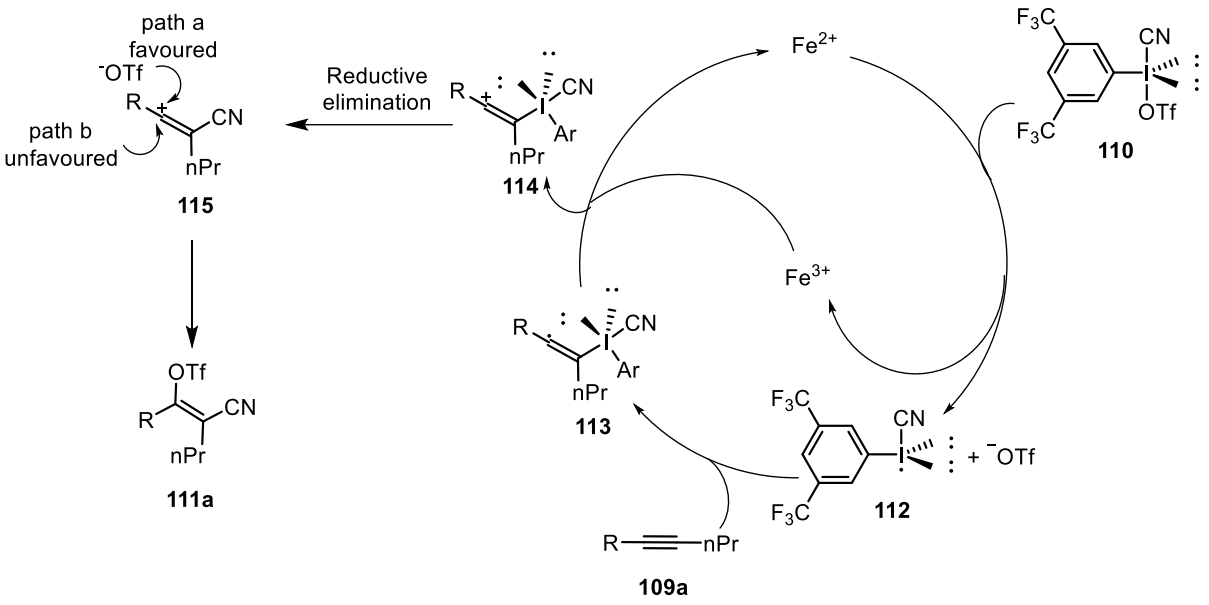


109 **110** **111**:13-93%

R^1 = H, CH_3, Ph, 4-MePh, 4-Cl-5-CH_3Ph, 4-BrPh, 4-FPh, 4-OAcPh, 4-PhthNPh, 4-OCF_3Ph, 4-SCF_3Ph, 5-CO_2EtPh, 5-CHOPh, 6-CH_3Ph, 4-BrPh, 4-ClPh; R^2 = *n*-Pr, C_3H_6Cl, C_2H_4OTs, C_4H_8NPhth, CH_3, *i*-Pr, *t*-Bu

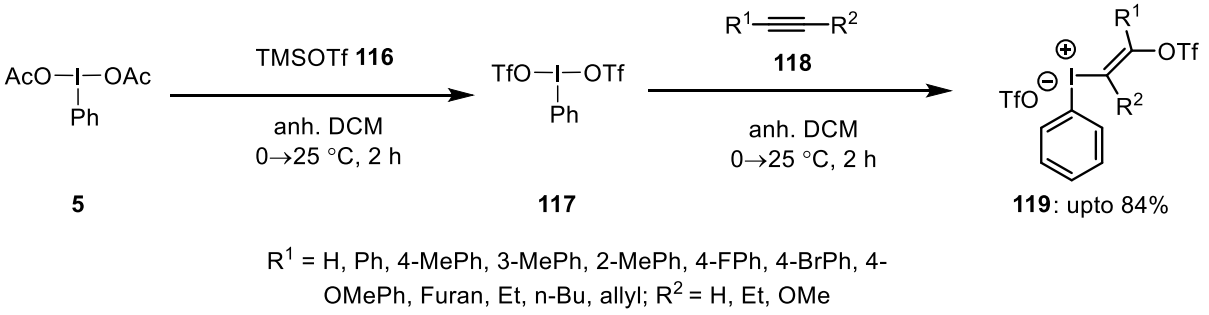
Scheme 27. Regio and stereoselective triflation of alkyne using iodine(III) reagent.

The suggested mechanism shows a radical species **112** obtained by the reaction of iodine(III) catalyst with Fe^{2+}. Which then interacted with alkynyl substrate **109a** produced **113**. The rapid oxidation of **113** with the assistance of Fe^{3+} produced the cationic species **114**. The intermediate further underwent reductive elimination to form **115**. Further, the attack of TfO^- could be a favoured, path a, leading to the *cis* product **111a** (Scheme 28).



Scheme 28. Proposed mechanism for the alkyne **109** cyanotriflation.

Another triflation reagent is prepared upon treated of PIDA with TMSOTf, which was further used for the triflation of alkyne **118** (Scheme 29).[40] The so-obtained salts possess electrophilic and nucleophilic functions and serve as novel C2 synthons for many organic transformations. The presence of methyl group influences the steric and electronic effects by reducing the yield and formation of *E* product was more pronounced than *Z* isomer. By increasing the length of side chains on the vinyl moiety through the application of different terminal alkylacetylenes resulted in better yields and higher stability.

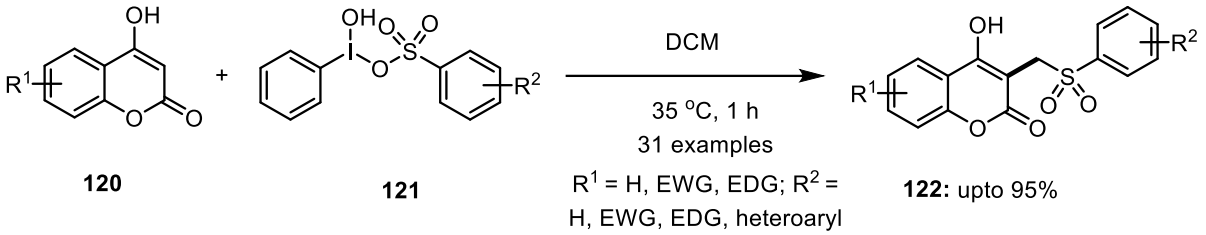


R^1 = H, Ph, 4-MePh, 3-MePh, 2-MePh, 4-FPh, 4-BrPh, 4-OMePh, Furan, Et, n-Bu, allyl; R^2 = H, Et, OMe

Scheme 29. Synthesis of aryl(trifloxyalkenyl)iodonium triflate salts **119** using DIB **5**.

6. Tosyloxylation reactions using iodine(III) reagents

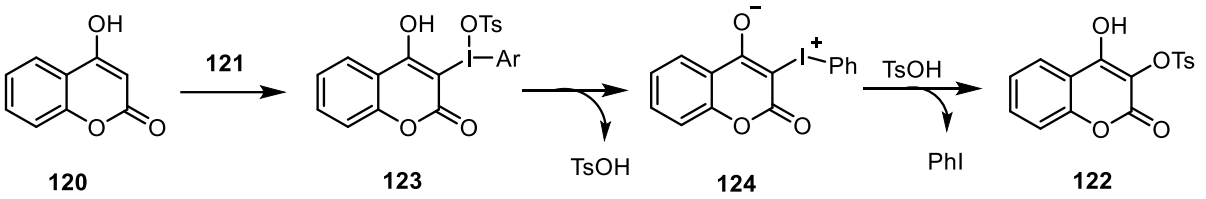
The Koser's reagent and its analogues **121** were used for the tosyloxylation of 4-hydroxycoumarins **120**. In 2019, Bowen Xu and team carried out an elegant study on the mechanistic insights of Koser's reagent for the synthesis of 3-tosylloxy-4-hydroxycoumarins **122** under mild reaction conditions (Scheme 30).[41] By varying the Koser's reagent viz. meta or para-halogen-substituted aryl motifs **121** rendered the expected product with good yield. The electron donating groups exist in the substrate rendered excellent yield. Whereas, the electron withdrawing groups on the Koser's reagent moderate to good yield was furnished. While the presence of a phenyl group produced moderated yield. This indicates that Koser's reagents bearing electron donating groups are the most favoured in tosyloxylation reactions. By tolerating various functional groups, the obtained product serves as useful aromatic building block.



120 121 122

Scheme 30. Synthesis of 3-tosyloxy-4-hydroxycoumarins **122** under mild conditions by using modified Koser's reagents **121**.

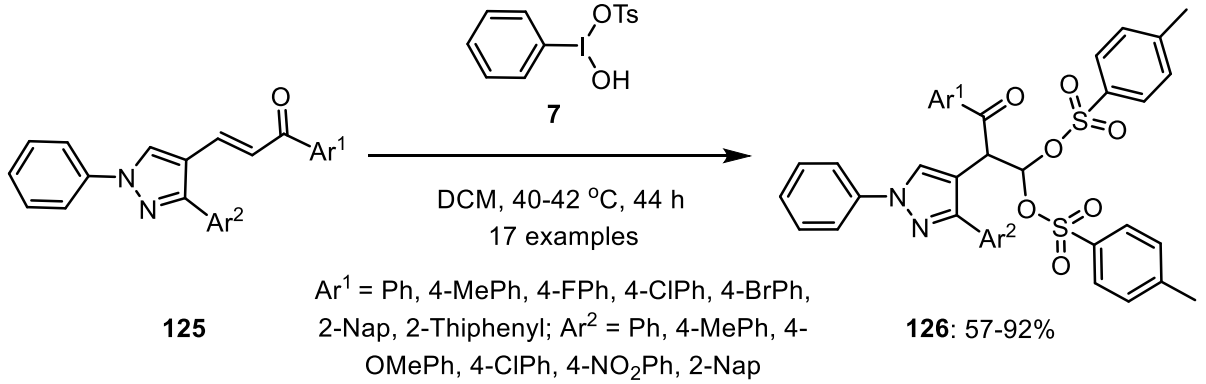
The positive iodine centre of modified Koser's reagent **121** gets attacked by the enol-keto tautomerism of 4-hydroxycoumarin to give **123**. Consequently, the elimination TsOH leads the formation of iodonium ylide **124** (Scheme 31). Further, the OTs anion facilitates the elimination of phenyl iodide from ylide and yields the targeted 3-tosyloxy-4hydroxycoumarins **122**.



120 123 124 122

Scheme 31. The plausible mechanism to synthesis 3-tosyloxy-4-hydroxycoumarins **122**.

Recently, Bains et al. established a tosyloxylation of chalcone derivative **125** using Koser's reagent **7**. Upon treating Koser's reagent **7** with the chalcone derivative **125**, the α-heteroaryl-β,β-ditosyloxy ketones **126** was obtained in moderate to excellent yield.[42] This methodology involves the 1,2-heteroaryl migration of pyrazolyl group of chalcones **125** upon treatment with HTIB **7** in dichloromethane (Scheme 32). The product which results from this migration leads the formation of series of α-heteroaryl-β, β-ditosyloxy ketones **126**. On top of that, the synthetic utility of α-heteroaryl-β, β-ditosyloxy ketones lies in the regioselective synthesis of five and six membered heterocyclic compounds.



125

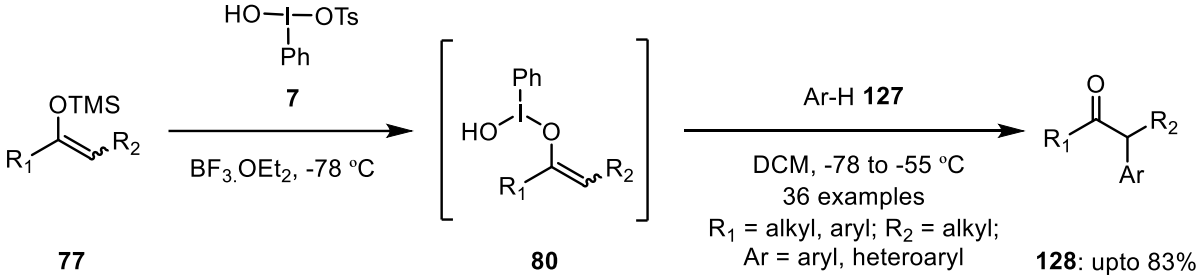
Scheme 32. Synthesis of α-heteroaryl-β, β-ditosyloxy ketones **126** driven by hypervalent iodine(III) reagent **7**.

It is observed that the 1,2-aryl migration efficiently takes place with all substituted aryl rings (including electron donating, electron withdrawing and sterically hindered groups) if the pyrazolyl group is bulkier. Pyrazole ring **126** having 4-nitro phenyl substituent at 3rd position upon reacting with HTIB leads to corresponding ditosyloxyketone **126**. Earlier it was observed that the phenyl group having an electron withdrawing substituent has very poor migratory aptitude. In the case of bulkier naphthyl, the chalcone **125** underwent the migration efficiently and gave the corresponding product with moderate yield. Overall, the 1,2-

aryl rearrangement of the bulkier pyrazolyl group was not influenced by the migratory aptitude of electronically and sterically different groups and the reaction proceeded efficiently by the 1,2-aryl C-C migration process for all the substrates to yield the corresponding ditosyloxyketones.

7. Arylation reactions using iodine(III) reagents

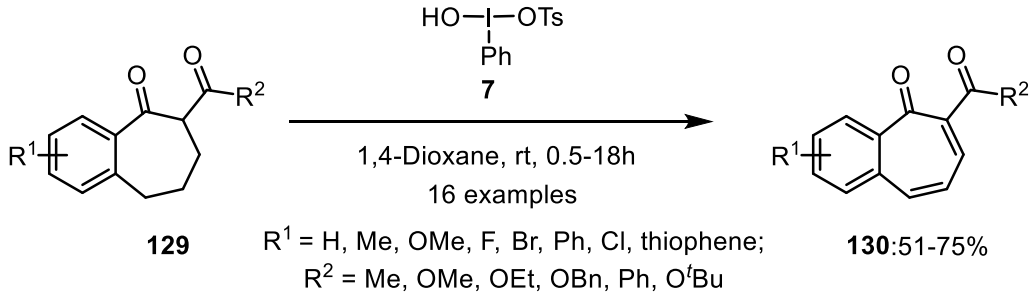
Overcoming the instability of enolonium species in 2017, Maksymenko and co-workers published a compatible method to afford α-arylated ketones **128** via reacting the electrophilic enolonium species **80** (generated from reacting TMS-enolates **77** and Koser's reagent **7**) with aromatic or heteroaromatic substrates **127** (Scheme 33).[43] To retard the rate of α-tosylation, BF_3 in excess amount coordinates with tosyl anion, rendering an excellent yield with the aromatic nucleophiles. Higher yields are obtained when more sterically hindered indoles are used. The presence of highly oxidizable halogens Br and I as functional groups are well tolerated. Not restricted only to methyl ketones, the reactions also give moderate to good yield in the presence of cyclic ketones. This reaction is well tolerated by various functional groups as well as polymerisation prone substrates.



Scheme 33. The α-arylation of ketone enolates **77** via the formation of enolonium species **80** using Koser's reagent **7**.

8. Dehydrogenation reactions using iodine(III) reagents

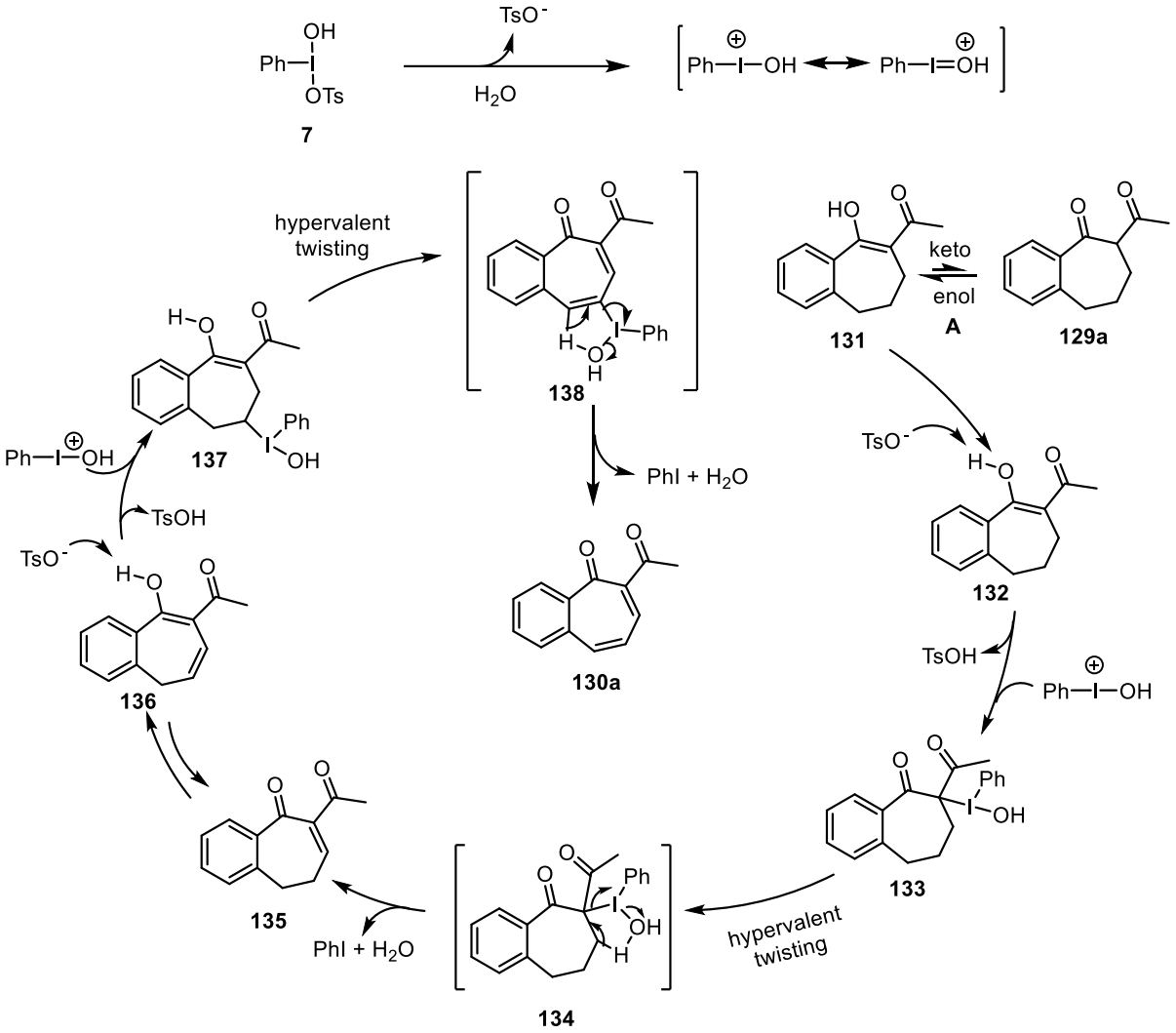
In 2019, Liu and team explored yet another reactivity of Koser's reagent 7 with carbocyclic carbonyl compounds **129**. Initiated by HITB, an efficient and mild oxidative double dehydrogenation occurs serving as an economical route to provide moderate to good yield of products.[44] The substrates containing electron-donating groups as well as the electron withdrawing groups were transformed to the respective dehydrogenated products in good yield (Scheme 34).



Scheme 34. Double dehydrogenation of carbocyclic carbonyl compounds **70** mediated by HTIB **3**.

First, the reference substrate **129a** exhibits keto-enol tautomerization, the tosylate anion deprotonates the enolated substrate **132** which interacts with PhI^+OH to yield an adduct **133**. Consequently, the intramolecular

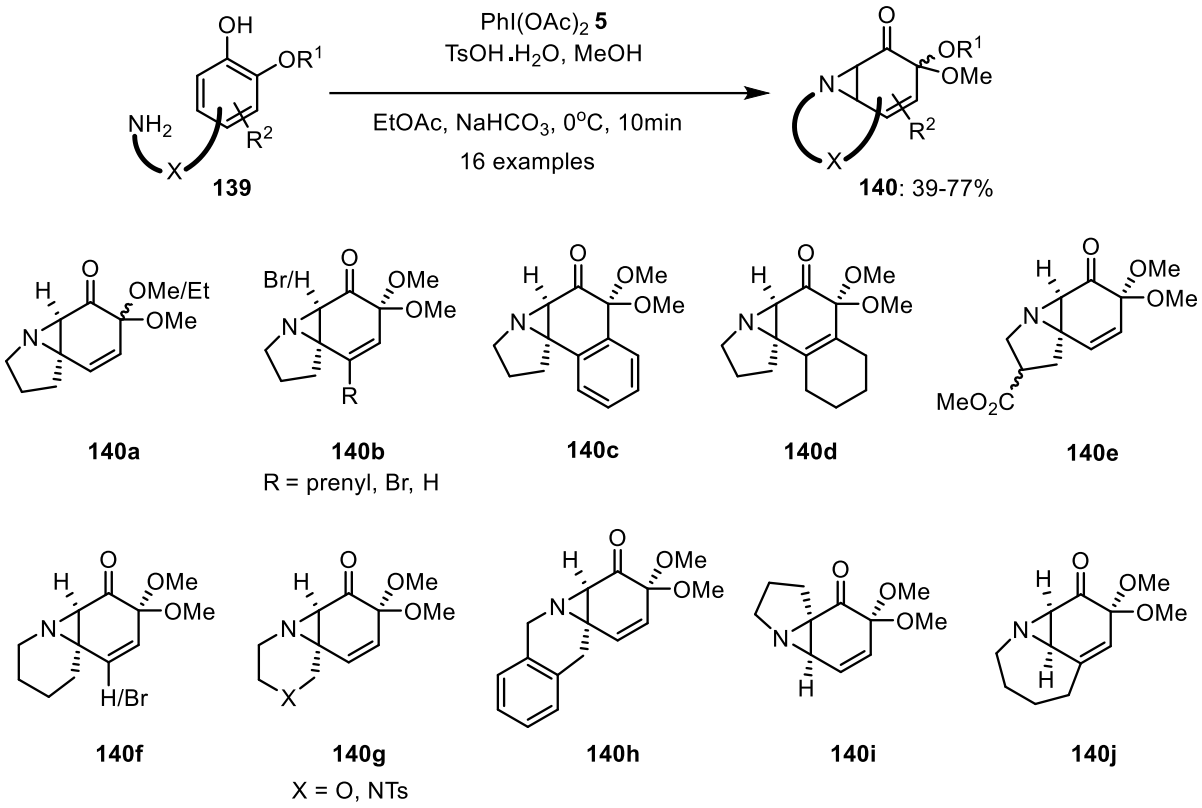
hydrogen abstraction at transition state **134** assists the formation of **135** with the elimination of PhI and H_2O. Like the initial substrate **129a**, the same procedure was followed by compound **135** and yields the dehydrogenated product **130a**.



Scheme 35. Mechanism for the double dehydrogenation reaction.

9. Dearomatization reactions using iodine(III) reagents

In 2021, Cao and co-workers introduced a new synthetic route to construct valuable aziridines **140** in moderate to good yield.[45] This method involves the PIDA **5** mediated tandem reaction consists oxidative dearomatization and *in situ* aziridination of phenolic amines **139**. In addition, the resulting aziridines provide a platform to access architecturally vast aza-heterocycles via transformations originated by selective ring opening of aziridines (Scheme 36). A series of *m*-phenolic amines **140** bearing primary amino pendant group at β-position of phenolic core were considered in order to topological connection of the phenol and amino having substituent. Bulkiness at α` decreases the yield of the corresponding aziridines (*e.g.,***140a**) while the substrates with γ-substituent were tolerated and targeted products **140b** obtained in reasonable yield with the exception of γ-Br group which could not deliver the desired product largely due to instability of bromoaziridine.



Scheme 36. Hypervalent iodine (III) reagent **5** mediated synthesis of functionalized unactivated aziridines **140**.

The phenolic amine bearing ester group substituted propyl amino side chain undergoes this cascade transformation to give 5,3,6-tricyclic aziridines **140e** rather than lactonized product. The 6,3,6-tricyclic aziridines having the morpholine and piperazine moiety **140g** can be synthesized from the substrates with oxygen and nitrogen having amino side chains. Interestingly, 7,3,6-tricyclic aziridine having bridgehead double bond were obtained from *p*-phenolic amine with primary pendant substituent at γ position of phenolic core.

Conclusions

Hypervalent iodine(III) reagents are widely used in modern organic chemistry because of their identical behaviour in mild reaction atmosphere. Hypervalent iodine(III) reagents facilitate the range of transformation by bond breaking and bond making between C–C and C–heteroatoms at metal-free and benign reaction condition. Additionally, the regio- and stereoselective nature of iodine(III) reagents used to functionalize many organic substrates. Using iodine(III) reagents cyclization, arrangement, functionalization, aromatization and dearomatization etc., has been unlocked. All the reported reactions were produced moderate to excellent percent of yield. Further, many reactions reported without use of additional co-catalyst, toxic environment and no byproduct have been generated. Despite these merits, there is a challenge about the cost and quantity of use of iodine(III) reagents. Apart from catalytic, many transformations enabled by using stoichiometric number of reagents. Thus cause, waste of chemicals and the recyclability remain further improvement. With this regard, the utility of hypervalent iodine(III) reagent in chemistry was explored to facilitate new synthetic approaches. Functional group tolerance gives hypervalent iodine(III) a significant and essential role in contemporary organic synthesis.

Acknowledgements

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