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Diaryliodonium salts: Emerging reagents for arylations and heterocycles synthesis

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Abstract: Since the last one decade, a substantial research has been developed in the synthetic applications of diaryliodonium salts. They provide mild and general protocols for the construction of C-C and C-heteroatom bonds which are indispensable in many useful medicinal, agrochemicals and industrial molecules. This review is focused on the recent advances in synthetic utilities of diaryliodonium salts leading to the formation of heterocyclic frameworks, arylation using C-H functionalization strategies and their related mechanistic details.

Keywords: Diaryliodonium salts, heterocycles, metal-catalysts, C-H functionalization.

1.1 Introduction

Diaryliodonium salts are well renowned for their powerful electrophilic arylating behaviour. They have been used as aryl coupling partners for diverse range of alkenes, alkynes and heterocycles under metal and metal-free reaction conditions.[1-3] In current scenario diaryliodonium salts are frequently used as arylating agents besides their interesting applications in the construction of valuable heterocycles with five- and six-membered ring systems. The salient features of diaryliodonium salts are easy to synthesize, non-toxic, benign safety profile, air and moisture stability.[4]

1.1.1 Structure and Geometry

Diaryliodonium salts **1** (Ar_2IX) are a class of iodine (III) reagents with two aryl moieties and an anionic part (X). with ten electrons. The geometry of Ar_2IX is pseudo trigonal bipyramidal with the weakly bonded anionic part at apical position, two aryl groups at apical and equatorial and two lone pairs occupied at equatorial position. X-ray studies showed diaryliodonium salts are T-shaped geometry (figure 1) with the bond angle of Ar-I-Ar is 90°. The I-X bond

in **2** is longer than the average covalent bond length. The high reactivity of iodonium salts **1** is illustrated by the leaving group ability of iodobenzene (106 times > triflate) released from the corresponding diaryliodonium salt. Given the superior solubility and non-nucleophilic character, diaryliodonium salts **1** with triflate and tetrafluoroborate anions are most frequently employed in synthetic transformations.[5]

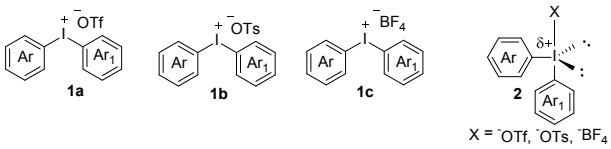


Figure 1 Structures and geometry of commonly used diaryliodonium salts

1.1.2 Preparation of diaryliodonium salts

In general, preparation of diaryliodonium salts involves two steps, first oxidation of an aryl iodide (I) to iodine (III) species and next ligand exchange with arenes or organometallic reagents. Diaryliodonium salts **1** were first prepared by Meyer and Hartmann in 1894.[4a] Nevertheless, the synthetic procedure was time-consuming and low-yielding. In 20th century this reagent was rediscovered with the myriad of synthetic transformations. In 1950, Beringer reported the synthesis of symmetrical and unsymmetrical diaryliodonium salts using hypervalent iodine (III) compounds namely, iodosylarenes (ArI=O), (diacetoxyiodo)benzene (IBD), iodoxyarenes ($ArIO_2$) and electron-rich arenes in the presence of sulphuric acid.[6] Later, in 1980 Koser and co-workers prepared diaryliodonium tosylates by employing hydroxy(tosyloxy)iodobenzene and arylsilanes.[7] Afterwards, Kitamura et al. disclosed an improved procedure to access diaryliodonium salts by involving the reaction of (diacetoxyiodo)arenes and electron-rich arenes in triflic acid. Notably, triflic acid was found to be an effective alternative to sulfuric acid, acetic acid and *p*-toluenesulfonic acid in the terms of reactivity and isolation of diaryliodonium triflate salts. Next, Widdowson and co-workers prepared

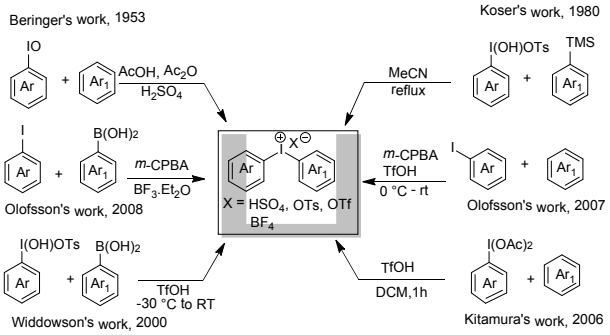


Figure 2 Methods to prepare diaryliodonium salts

diaryliodonium salts by employing IBD and arylboronic acids in triflic acid.[8] Recently, Olofsson's group developed an operationally simple, one-pot general protocol to achieve diaryliodonium triflates in good to excellent yields.[9] This convenient method uses the reaction of aryl iodides and arenes in the presence of *m*-chloroperbenzoic acid (*m*-CPBA) and triflic acid. Use of mild oxidant *m*-CPBA is advantageous due to its less solubility in organic solvents which facilitates its removal from the reaction mixture. The protocol is applicable to a range of iodoarenes and arenes. In an alternative route, the same research group[10] prepared various symmetrical and unsymmetrical diaryliodonium salts from iodoarenes and arylboronic acids as outlined in Figure 2.

1.1.3 Plausible catalytic cycle

The reactivity of diaryliodonium salts could be enhanced in the presence of copper and palladium catalysts. Research groups of Gaunt and Sanford disclosed the metal-catalyzed (Cu and Pd) arylation of indoles using diaryliodonium salts, and investigated the mechanistic pathways. In 2008, Gaunt et al. proposed an elegant hypothesis that Cu(I) reduce the iodonium salt with the release of

highly electrophilic arylcopper(III) species and iodoarenes.[11] This *in situ* generated reactive species could rapidly undergo functionalization with the nucleophile under fairly mild reaction conditions (Figure 3a).

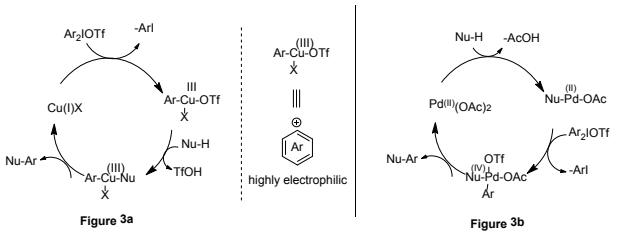


Figure 3 Plausible catalytic pathways involving Cu and Pd

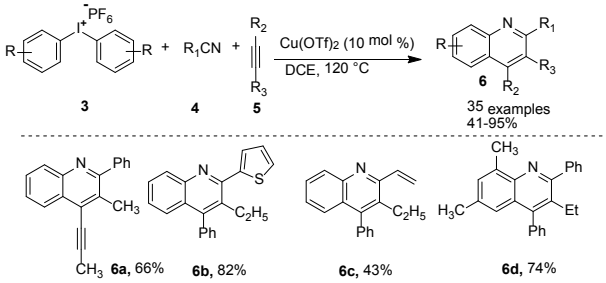
In 2006, Sanford and co-workers described a Pd(II)-catalyzed C-H arylation of indoles and proposed a persuasive $Pd^{II/IV}$ catalytic pathway for the formation of 2-arylindoles (Figure 3b).[12]

1.2 Heterocycles synthesis

Heterocyclic compounds are extensively distributed in many natural products, life saving drugs and organic materials. Owing to the high significance and applications in drug discovery research construction of heterocycles is a long-standing interest. Assembly of heterocyclic compounds particularly, five- and six-membered ring systems and arylated heterocycles with interesting biological properties and for being important building blocks which are frequently encountered in natural products and various therapeutic agents. Though there are plethora of protocols to construct useful five and six-membered heterocycles but still straightforward and eco-friendly methods to access these heterocycles are highly desirable. In view of significant advantages, diaryliodonium salts have been widely utilized in the direct arylation and preparation of bio-active heterocycles. In this review article, we have summarized the recent applications of diaryliodonium salts in the arylation of heterocycles and construction of quinolines, phenanthridines, oxindoles, arylcoumarins, acridines, and acridones.

1.2.1 Quinolines

Chen's group[13] developed a general and elegant pathway for the synthesis of quinolines **6** using multicomponent approach by employing diaryliodonium salts **3**, nitriles **4** and alkynes **5**. The reaction proceeded *via* [2+2+2] regioselective cascade annulation strategy to generate quinoline derivatives in good to excellent yields. Iodonium salts **3** bearing non-coordinating anion PF_6 gave better yields than the salts with $^-$OTf, Br^- and $^-$OTs counter ions. Use of electron deficient nitriles like ethyl cyanoformate and diethyl cyanophosphate failed to deliver the annulated products. Identified reaction conditions covers variety of internal alkynes, asymmetric alkynes, 1,3-hexadiyenes and diaryliodonium salts to prepare various quinolines (Scheme 1.1).

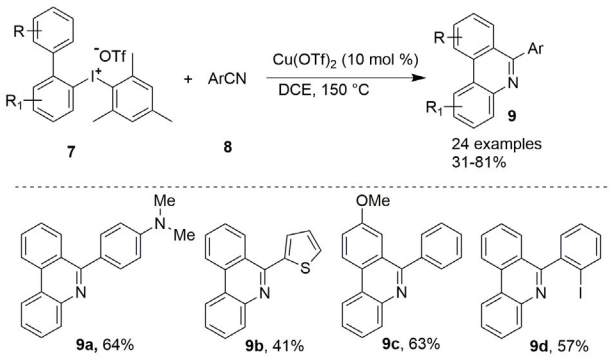


Scheme 1.1 Synthesis of quinolines and representative examples

1.2.2 Phenanthiridines

Li et al.[14] reported a copper-catalyzed cascade coupling strategy for the synthesis of phenanthiridine derivatives **9** using diaryliodonium salts as an aryl source. The reaction was smoothly proceeded in the presence of $Cu(OTf)_2$ and dichloroethane at 150 °C to produce **9** in good yields. Mechanistically, *in situ* generated copper(I) species from $Cu(OTf)_2$ underwent oxidative insertion with diaryliodonium salt to furnish a highly

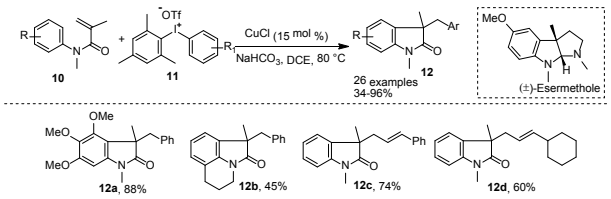
electrophilic Ar-Cu(III) species. Consecutive nucleophilic addition of nitriles and annulation led to the corresponding phenanthiridines in moderate to excellent yields (Scheme 1.2).



Scheme 1.2 Synthesis of phenanthiridine derivatives

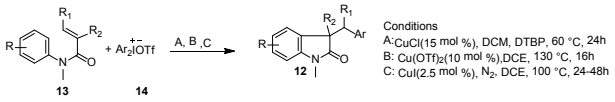
1.2.3 Oxindoles

Zhou co-workers described the copper-catalyzed arylation/vinylation of electron-deficient alkenes **10** to furnish highly substituted oxindoles **12** using diaryliodonium salts **11** as coupling partners.[15] After exploring various parameters, cuprous chloride in the presence of sodium bicarbonate found to be the best catalytic conditions. Formation of C-C bond proceeded with electrophilic addition of Cu(III)-aryl intermediate, followed by aromatization and reductive elimination to produce oxindoles **12** in good yields. The obtained oxindoles **12** were utilized to prepare complex bio-active natural product (±)-esermethole (Scheme 1.3).



Scheme 1.3 Synthesis of oxindoles

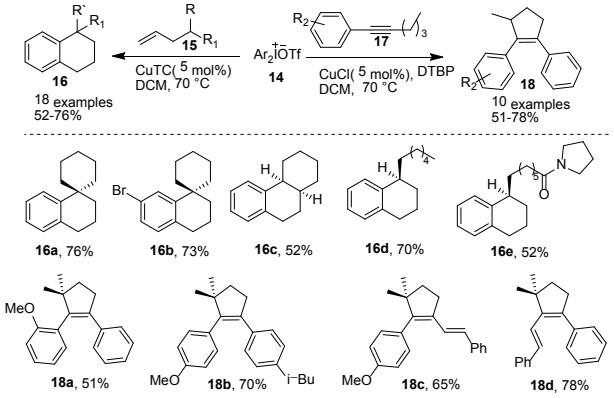
Likewise, Tang et al.[16] explored the synthesis of oxindoles **12** using diaryliodonium salts **14** and 2,6-ditertbutylpyidine (DTBP) as a base. Later, two different research groups [17-18] have independently reported the synthesis of oxindoles **12** under base-free conditions in the presence of a copper catalyst and diaryliodonium salts **14** (Scheme .131).



Scheme 1.31 Synthesis of oxindoles

1.2.4 Carbocyclization

Interestingly, Gaunt and co-workers[19] described the efficient transformation of easily available alkenes and alkynes into substituted tetralins and cyclopentenes in good yields. Air-stable, copper(I) thiophene-2-carboxylate (CuTC), copper(I) chloride and sterically-hindered 2,6-ditertbutylpyidine (DTBP) are the suitable catalysts and base for the carbocyclization of **15** and **17**. Detailed mechanistic investigations revealed that concerted 1,2-hydride and 1,5-hydride shifts led to the desired products **16** and **18** in good yields (Scheme 1.4).

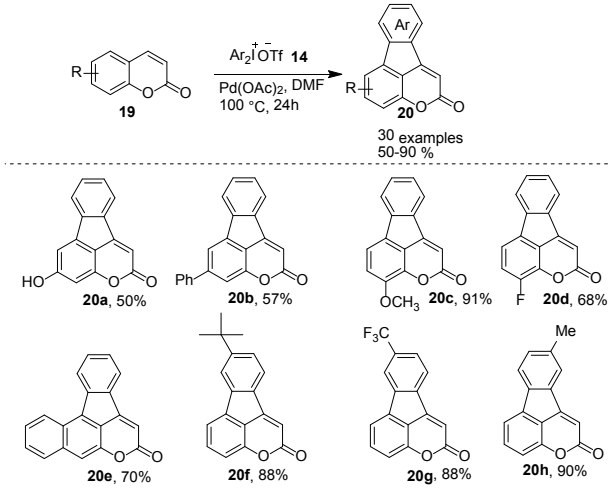


Scheme 1.4 Synthesis of substituted tetralins and cyclopentenes

1.2.5 Benzocoumarins

An unprecedented, Pd-catalyzed two consecutive C-C bonds forming strategy was employed between diaryliodonium salts **14** and coumarins

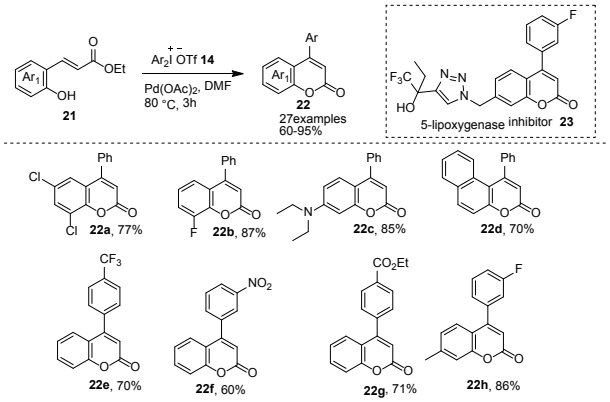
19 to construct π-expanded 4,5-dibenzo-coumarins **20**. Formation of dibenzocoumarins **20** was smoothly proceeded without any external oxidant, ligand or directing groups. Interestingly, coumarins with hydroxyl group produced **20** without any *O*-arylation. However, sterically-hindered bis(2,4,6,-trimethylphenyl) iodonium triflate failed to afford the desired fused product **20**. The proposed diarylation proceeded *via* Pd(II/IV) catalytic cycles with the synergistic activations of C-I and vicinal C-H bonds in diaryliodonium salts (Scheme 1.5).[20]



Scheme 1.5 Synthesis of 4,5-dibenzocoumarins and their representative examples

1.2.6 4-Arylcoumarins

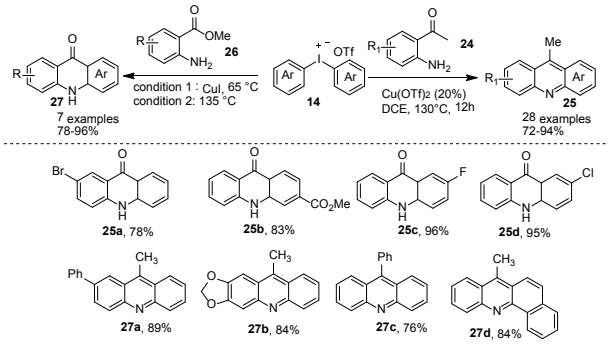
Yang et al.[21] extended the synthetic utility of diaryliodonium salts in the construction of 4-arylcoumarins **23** *via* Pd-catalyzed arylations and cyclizations of *o*-hydroxylcinnamates **21**. In the presence of CuI and $Cu(OTf)_2$, *O*-phenylated cinnamates were obtained rather than expected arylcoumarins **22**. By changing the catalyst from copper to palladium the reaction progressed in anticipated manner to afford 4-arylcoumarins **23** in better yields. This ligand and base-free approach is well-suited for diverse diaryliodonium salts and *o*-hydroxyl cinnamates and provided an alternative convenient route for 5-lipoxygenase inhibitor **23** (Scheme 1.6).



Scheme 1.6 Synthesis and selected examples of 4-arylcoumarins

1.2.7 Acridines and Acridones

Recently, Pang et al.[22] reported a domino arylation and Friedel-Crafts acylation between *o*-acylanilines **24** and diaryliodonium salts **14** to achieve valuable acridine derivatives **25**. Interestingly, this reaction proceeded effectively either under copper-catalyzed or metal-free conditions at an elevated temperature (130-135 °C). The reaction of *o*-aminobenzoates **26** with diaryliodonium salts **14** generated acridone framework **27** in high yields (Scheme 1.7).

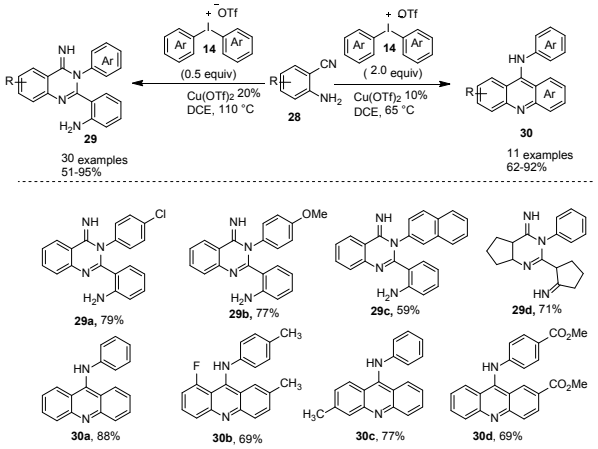


Scheme 1.7 Some selected examples of prepared acridines and acridones

1.2.8 Quinazolinimines

Recently, a new tandem approach was developed by Chen and co-workers[23] for the synthesis of quinazolinimines **29** and acridines **30** from easily accessible *o*-cyanoanilines **28**

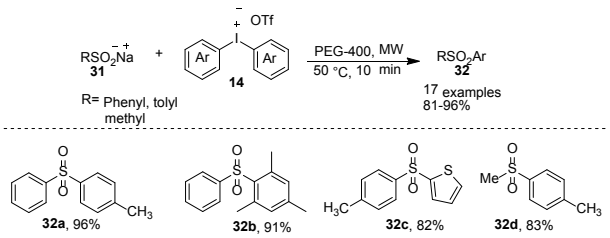
and diaryliodonium salts **14**. With the more favourable cyano group in cyanoanilines for arylation , the protocol is well-suited for 1-amino-2-cynaocyclopentene and cyclohexene to afford pyrimidine **29d** analogues. Detailed optimization reaction conditions and mechanistic experiments disclosed that half an equivalent of **14** afforded quinazolinones **29**, whereas**,** its excess quantity (2.0 equiv) led to acridines **30** in good yields (Scheme 1.8).



Scheme 1.8 Synthesis of quinazolinimines and acridines

1.2.9 Diaryl sulfones

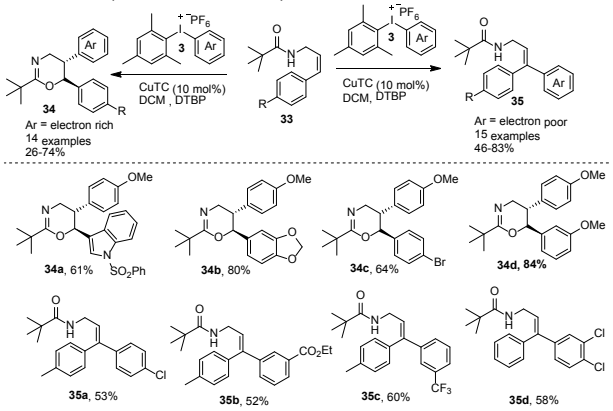
Kumar et al.[24] disclosed a microwave-assisted, metal-free protocol for the synthesis of diaryl sulfones **32** using easily available diaryliodonium salts **14** and arenesulfinates **31**. This high yielding protocol proceeded in benign and bio-degradable solvent polyethyleneglycol-400 (PEG-400). Iodonium salts bearing different substitutents (Cl, Br, Me, COOH, OMe) were smoothly coupled to afford the corresponding sulfones in good to excellent yields. In the presence of cuprous iodide, unsymmetrical iodonium salts selectively transferred the electron-rich aryl moiety to produce appropriate sulfones in good yields. Under the optimized conditions, alkyl sulfone **32d** was also achieved in high yield (Scheme 1.9).



Scheme 1.9 Synthesis of diaryl sulfones and their representative examples

1.2.10 Diaryloxazines

A chiral copper(II)bisoxazoline-catalyzed reaction of readily available allylic amides **33** and diaryliodonium salts **3** led to enantioselective synthesis of 1,3-oxazines **34** and *β,β'*-diaryl enamides **35**. Sterically hindered base 2,6-ditertbutylpyidine (DTBP) was used in order to avoid the decomposition of chiral catalyst by the release of HPF_6. The electronic nature of diaryliodonium salts was found to be crucial for the enantioselective synthesis of **34** and **35**. (Scheme 1.10).[25]

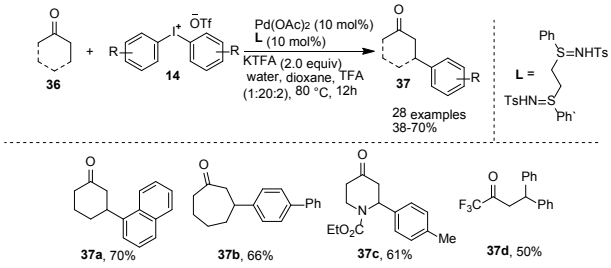


Scheme 1.10 Synthesis of various 1,3-oxazines and *β,β'*-diaryl enamides

1.2.11 β-arylation of ketones

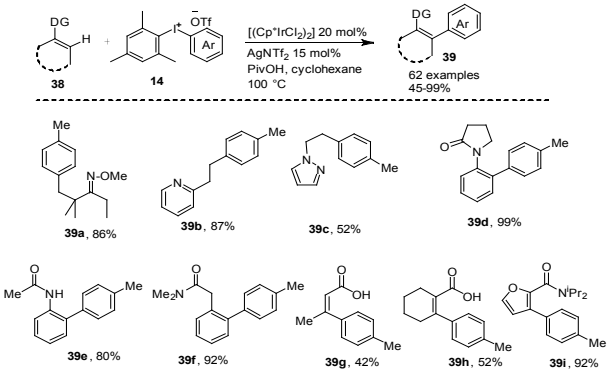
Huang and co-workers illustrated the application of diaryliodonium salts **14** in the selective *β*-arylation of ketones **36** using Pd-catalyst.[26] This method enabled to arylate various cyclic and linear ketones in excellent yields under oxidant free conditions. Under the reaction conditions, potassium trifluoroacetate (KTFA)

and trifluoroacetic acid (TFA) behaved as buffer pair to maintain the required acidity of reaction medium. From the detailed mechanistic investigation and control experiments, involvement of Pd nanoparticles was suggested in the present catalytic system (Scheme 1.11).



Scheme 1.11 Synthesis of *β*-arylated ketones and their representative examples

1.2.12 Arylheterocyles

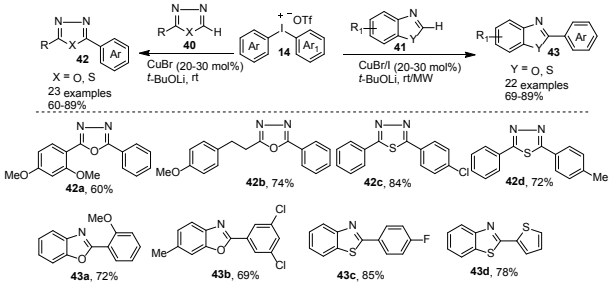


Scheme 1.12 Synthesis of arylheterocycles

First example of Ir(III)-catalyzed β-arylation of aliphatic sp^3 C-H bonds present in oximes and nitrogen-containing heterocycles like pyrazines, pyrazoles, quinolines, isoxazole, pyridine derivatives, substituted enamides and carboxylic acids, has been discovered. This protocol displayed high functional groups tolerance and also proved an effective synthetic tool for late-stage regioselective C-H arylation of complex triterpenoid molecules, for example, Lanosterol and Oleanolic acid. Outcome of the detailed mechanistic studies and density functional theory calculations suggested that sp^3 C-H bond present in the substrates **38** were activated by the concerted metallation–deprotonation process and oxidation of Ir(III) to Ir(IV) (Scheme 1.12).[27]

1.2.13 2-Arylazoles

Kumar and co-workers[28] developed a general and high-yielding protocol for the C-H arylation of various azaheterocycles such as oxadiazoles, thiadiazoles, benzoxazoles and benzothiazoles using diaryliodonium salts **14** at room temperature. The C-H arylation required simple catalytic system (CuBr/*t*-BuOLi) with reduced reaction time (15 min) to produce arylated azoles **42-43** in fairly good yields. The reactivity order of different heterocycles **40-41** was rationalized by the variable acidity of C2-H (oxadiazoles = benzoxazoles (pKa = 24.8) > thiadiazoles >benzothiazoles (pKa = 27.3). Under the optimized conditions, C2-H arylation of benzothiazole could not be achieved. Modified reaction conditions involving the use of MW successfully afforded 2-arylbenzothiazoles in good yields. The synthetic utility of developed protocol was extended to prepare a Tafamidis analogue **43b** which is a well known drug for neurodegenerative diseases (Scheme 1.13).

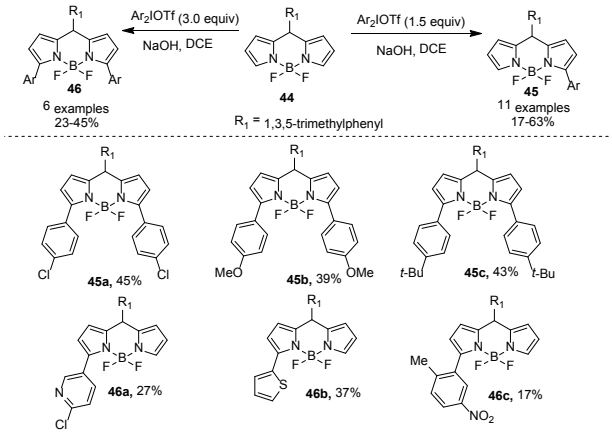


Scheme 1.13 Synthesis of various 2-arylazoles

1.2.14 Arylation of boron dipyrromethenes

Jiao et al.[29] developed a metal-free, *α*-selective C-H arylation of boron dipyrromethenes **44** by employing mild coupling partners, diaryliodonium salts **14**. The developed protocol furnished an array of mono **45** and di-arylated **46** boron dipyrromethenes in moderate to good

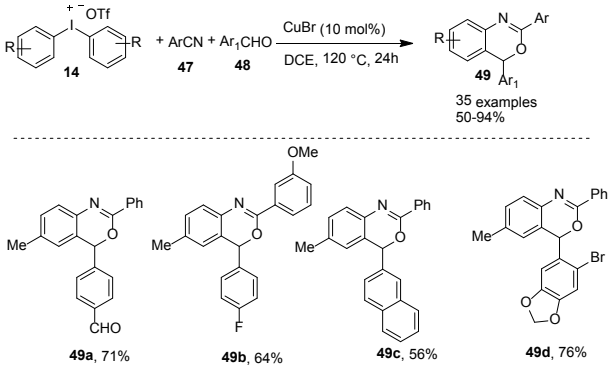
yields. No product was formed upon addition of radical inhibitor (BHT) 2,6-di-*tert*-butyl-4-methylphenol suggested the involvement of an aryl radical. The arylated compounds **45** and **46** displayed promising photophysical properties (Scheme1.14).



Scheme 1.14 Synthesis of *α*-arylated boron dipyrromethenes

1.2.15 Benzoxazines

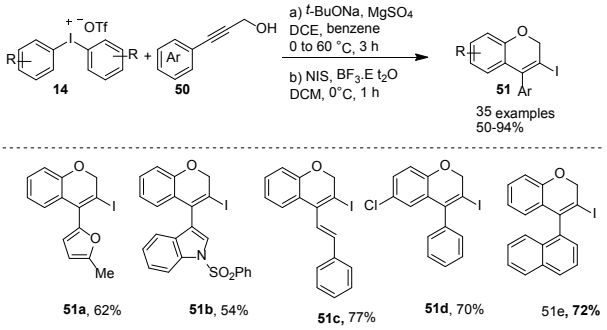
Very recently, an interesting Cu-catalyzed one-pot [2+2+2] cascade annulation of nitriles **47**, aldehydes **48** and diaryliodonium salts **14** has been developed by Jinhu et al. to construct benzoxazines **49** frameworks.[30] Iodonium salts **14** bearing functional groups such as aldehyde, halogens, alkyl and naphthyl were tolerated to afford **49** under the optimized reaction conditions. When two aldehyde groups were present in *p*-phthalaldehyde, then selectively one of –CHO underwent cyclization to give corresponding product (Scheme 1.15).



Scheme 1.15 Synthesis of benzoxazines and their representative examples

1.2.16 3-Iodochromenes

Togo and his co-workers[31] developed an efficient metal-free synthesis of 3-iodochromenes **51** from easily accessible diaryliodonium salts and aryl/alkly-propyn-1-ols **50**. This elegant transformation proceeded *via* one-pot *O*-arylation of aryl/alkly-propyn-1-ols in the presence of base *t*-BuONa and subsequent iodocyclization using *N*-iodosuccinimide and Lewis acid BF_3Et_2O. Iodochromenes **51** could be converted into beneficial molecules using metal-catalyzed C-C bond forming strategies (Scheme 1.16).

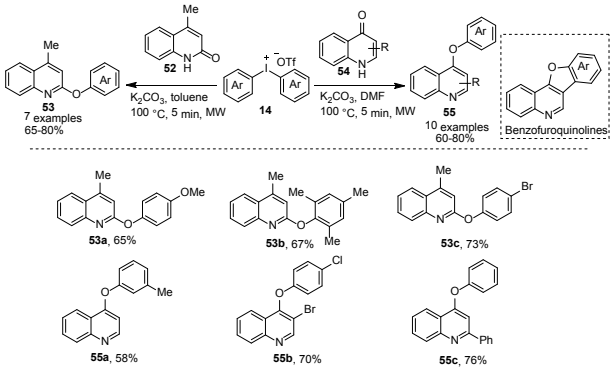


Scheme 1.16 Synthesis of iodochromenes

1.2.17 2/4-Aryloxyquinolines

Kumar et al.[32] disclosed a metal- and ligand-free approach for the synthesis of aryloxyquinolines **53** and **55** by the direct O-arylation of readily accessible quinolones

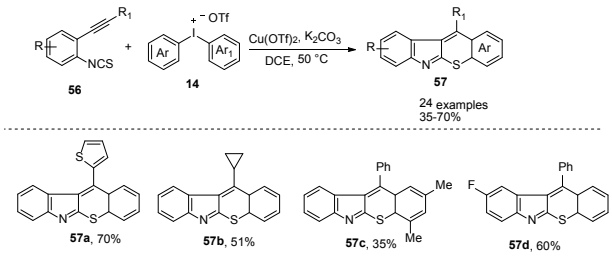
52/54 using diaryliodonium salts **14** as aryl source. The reaction conditions were compatible with 2-/4-quinolones **52/54** and diaryliodonium salts **14** bearing sterically congested and sensitive functional substituents such as mesityl and halides. Moreover, use of microwave energy, mild reaction conditions, good product yields (55-80%) and short reaction time (5 min) are significant features of the protocol. Prepared 4-aryloxyquinolines **55** were utilized in the construction of biologically important benzofuro[3,2-*c*]quinolines (Scheme 1.17).



Scheme 1.17 Synthesis of 2-and 4-aryloxyquinolines

1.2.18 Thiochromeno[2,3-*b*]indoles

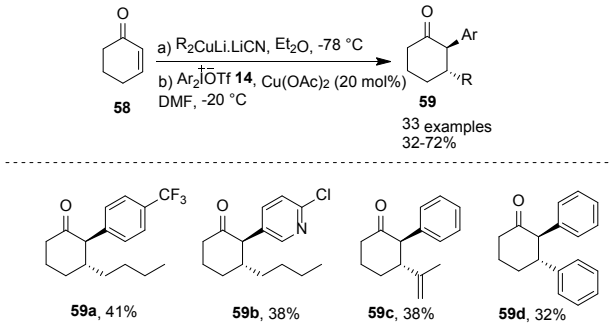
An efficient $Cu(OTf)_2$-promoted synthesis of thiochromeno[2,3-*b*]indoles **57** was developed from alkynylaryl isothiocyanates **56** and diaryliodonium salts **14.** The reaction involves successive *S*-arylation and cyclization to furnish fused heterocycles **57.** Under the optimized conditions both electron-rich and electron-poor iodonium salts were smoothly coupled with isothiocyanates **56** to afford the corresponding fused heterocycles **57**.in 35-70% yields. Addition of a radical inhibitor led to **57** in excepted yield which suggested the involvement of carbocation mechanism (Scheme 1.18).[33]



Scheme 1.18 Synthesis of thiochromeno[2,3-*b*] indoles

1.2.19 α-Aryl-β-substituted cyclic ketones

Pan et al.[34] reported an efficient method for the construction of *α*-aryl-*β*-substituted cyclic ketones **58** using diaryliodonium salts **14**. The current transformation involved Cu-promoted one-pot Michael addition followed by stereoselective arylation of cyclohexene-1-one and cyclohepten-1-one using alkyl, aryl and sterically challenging lithium reagents as Michael donors and different diaryliodonium salts **14** as aryl partner. Proposed mechanistic pathway involves reaction of Cu(I) species and diaryliodonium salts to generate an highly electrophilic Cu(III)-aryl species, which believed to react with enolate to produce the desired substituted cyclic ketones **59** in excellent yields (Scheme 1.19).

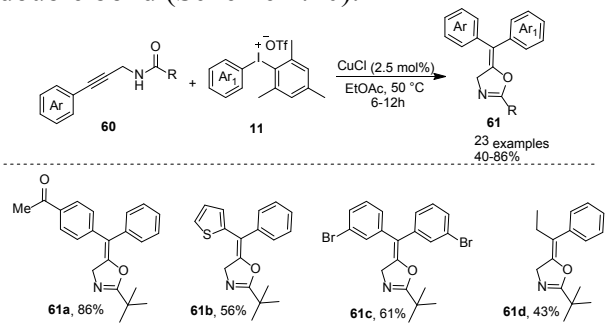


Scheme 1.19 Synthesis of α-aryl-β-substituted cyclic ketones

1.2.20 Oxazolines

Adam et al. demonstrated a novel copper-catalyzed ring closure-carboarylation strategy for the construction of oxazoline derivatives **61**

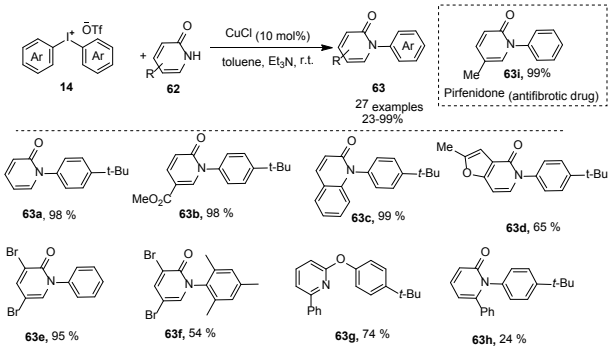
using easily accessible alkylpropargylamides **60** and diaryliodonium salts **11**. Iodonium salts **11** having *ortho* and *para* substitutents delivered **61** in relatively better yields. This one-pot method provides access to novel oxazolines heterocyclic core with highly substituted exo double bond (Scheme 1.20).[35]



Scheme 1.20 Synthesis of oxazolines and their representative examples

1.2.21 Pyridones

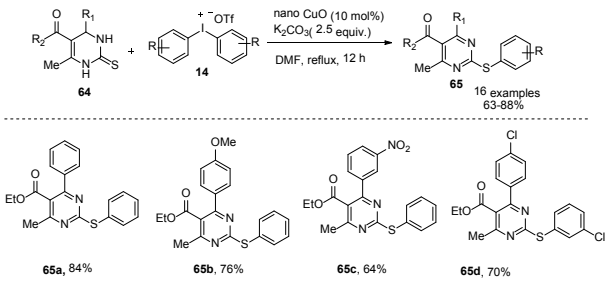
Recently, Kim and co-workers reported the copper-catalyzed *N*-arylation of 2-pyridones **62** using solid aryl coupling partner diaryliodonium salts **14** at room temperature. Various symmetrical and unsymmetrical diaryliodonium salts have been employed with 2-pyridones, to furnish the desired products in excellent yields. Pyridones with bulkier C6-phenyl, for example, 2-hydroxy-6-phenylpyridine,upon treatment with iodonium salt produced *O*-arylate **63g** as the major product.. Further investigation of counter ion effect in diaryliodonium salts revealed that OTf, BF_4 and PF_6 ions yielded the desired products in **63** good yields in shorter time, while OTs, Cl, and Br showed the negative impact on the reaction and delivered the desired products low yields and longer reaction times. Next, the developed protocol was effectively utilized to prepare an antifibrotic drug, Pirfenidone (**63i**) which is used in the treatment of idiopathic pulmonary fibrosis (Scheme 1.21).[36]



Scheme 1.21 *N*-arylation of 2-pyridones using diaryliodonium salts

1.2.22 2-(Phenylthio)pyrimidine

In 2013, Karade et al.[37] reported the synthesis of biologically important scaffold 2-(phenylthio)pyrimidine (**65**) *via* C-S coupling of 4-aryl-3,4-dihydropyrimidine-2(1*H*)-thione (**64**) using diaryliodonium salts **14** in the presence of catalytic amount of CuO nanoparticles. This protocol showed good compatibility towards various functional groups and furnished **65** in good to excellent yields. In the case of unsymmetrical iodonium salts, mixture of S-arylated products were obtained. The CuO nanoparticles was recycled and reused for three times without any loss of catalytic activity (Scheme 1.22).

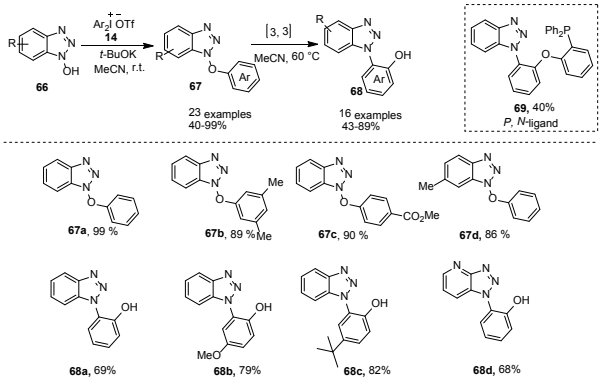


Scheme 1.22 Synthesis of 4-aryl-3,4-dihydropyrimidine-2(*1H*)-thiones

1.2.23 *N*-(2-Hydroxyaryl)benzotriazoles

Very recently, Dong-Liang Mo and his research group developed a metal-free approach for the synthesis of *N*-(2-hydroxyaryl)benzotriazoles **68** using *N*-hydroxybenzotriazoles **66** and

diaryliodonium salts **14**.[38] Initially, reaction of *N*-hydroxybenzotriazoles **66** with **14** at room temperature delivered the *O*-arylated product **67**, which underwent [3,3] sigmatropic rearrangement at 60 °C to provide *N*-(2-hydroxyaryl)benzotriazoles **68** in good yields. A variety of diaryliodonium salts and *N*-hydroxybenzotriazoles were examined to show the generality of developed protocol. Authors also showed practical utility of the protocol by the synthesis of novel *P*, *N*-type ligands **69** in two steps (Scheme 1.23).



Scheme 1.23 Synthesis of ***N***-(2-hydroxyaryl) benzotriazoles and representative examples

Conclusions

In summary, we have described the recent achievements of diaryliodonium salts in the constructions of various C-C, C-N, C-S and C-O bonds enabling to access valuable heterocycles under mild reaction conditions. The impressive features of diaryliodonium salts are enhanced electrophilicity, stable solid compounds, no special precaution to handle, easy to prepare and recyclability of released iodoarenes during the reaction. Hopefully, these unique advantageous properties are highly favourable for synthetic community. In recent years, a range of new substrates have been explored for the arylation and manifold novel transformations for the assembly of heterocyclic frameworks. Undoubtedly, the distinctive properties of diaryliodonium salts will open a new avenue for the design of novel transformations in the fields of metal-free and transition-metal-catalyzed reactions in the future.

Acknowledgments

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