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Coinage metal-catalyzed or-mediated oxidative heteroarylation of arenes

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ABSTRACT

This review explores the coinage metal-catalyzed or-mediated oxidative heteroarylation of activated arenes or arenes possessing DG and focuses on the role of directing groups in influencing the efficiency and selectivity of product conversions. This leads to the construction of new C—C and C—N bonds. The synthesized heteroaryl products by this method are part of the many natural products, and have significance in pharmaceuticals, agrochemicals, and advanced material chemistry.

Introduction

The synthesis of substituted heteroaryl compounds has shown great interest in synthetic organic chemistry due to their utility in pharmaceuticals, natural products, agrochemicals, and advanced material chemistry [1]. Traditionally, these compounds were synthesized using pre-functionalized substrates and produced stoichiometric amounts of toxic by-products under transition metal catalysis (Scheme 1; Path-I) [2]. Recently, oxidative heteroarylation strategies have emerged as one of the hottest research interests in double C—H bond activation chemistry because such reactions do not require pre-functionalization of substrates and can significantly reduce the number of additional steps (Scheme 1; Path-II) [3]. Despite, these reactions often suffer from poor selectivity because the C—H bond in one molecule exhibits similar reactivity to others, making it challenging to obtain the desired product. To improve selectivity in such reactions, many researchers have employed activated arenes or arenes activated by attaching directing group (DG) (Scheme 1) [4].

The directing group (DG) induces the metal to activate the proximal C—H bond through the formation of a cyclometallated intermediate, thereby enhancing the regioselectivity of the transformations. Significant progress has been made in this method using precious noble metals such as Pd, Rh, Ru, and Ir [5]. However, these metals are associated with high costs and toxicity, thus, Cu, Ag, and Au, also known as coinage metal catalysts, have been explored for catalyzing the oxidative C—H bond heteroarylation of arenes. This approach has shown usefulness due to its cost-effective, low toxicity, sustainable, and environmentally friendly nature [6].

The coupling products formed by this pathway are ubiquitous in biologically active compounds, including antibiotics, natural products, plant hormones of the auxin family, female sex hormones, antioxidants, agricultural and pharmaceutical agents, fluorescent sensors for biological media, organic solar cells, and others (Fig. 1) [7].

As reported by literature, the general mechanism for DG-assisted coinage metal-catalyzed or-mediated oxidative heteroarylation of arenes is outlined in Fig. 2 (path-a). This is initiated by DG-assisted metalation *via* C—H bond activation of substrate (**1**) in the presence of active catalyst or mediator **A** and base, generating complex **B**, which is converted to complex **C**, where metal gets oxidized followed by binding of substrate (**2**) to complex **C** *via* C—H bond activation. Finally, reductive elimination generates final product **3** and pre-active catalyst or mediator **E**, which is oxidized to active catalyst or mediator **A**. In addition, the mechanism for coinage metal-catalyzed oxidative heteroarylation of activated arenes (Fig. 2; path-b), initiated by base-promoted metalation

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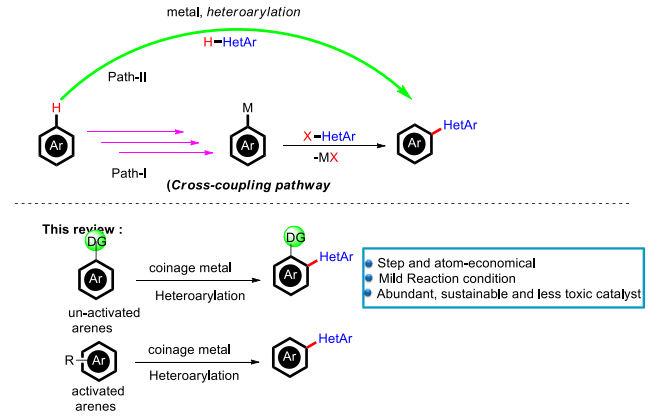


Scheme 1. Different routes of heteroarylation of arenes.

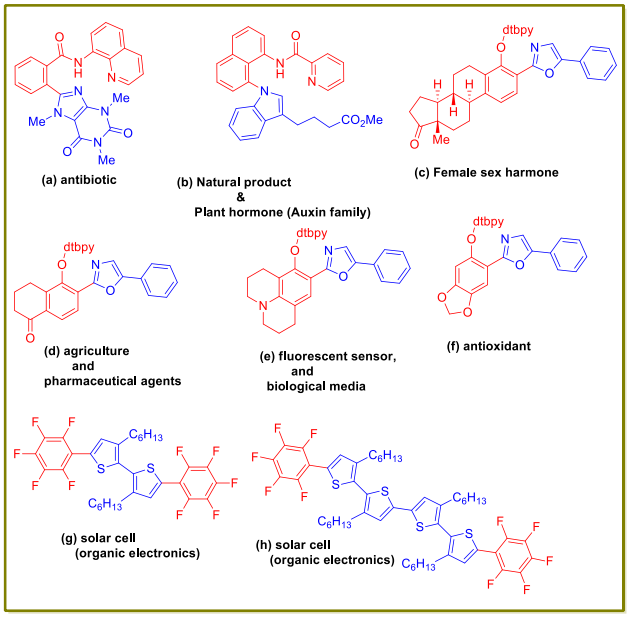


Fig. 1. Examples of biologically active heteroarylated products.

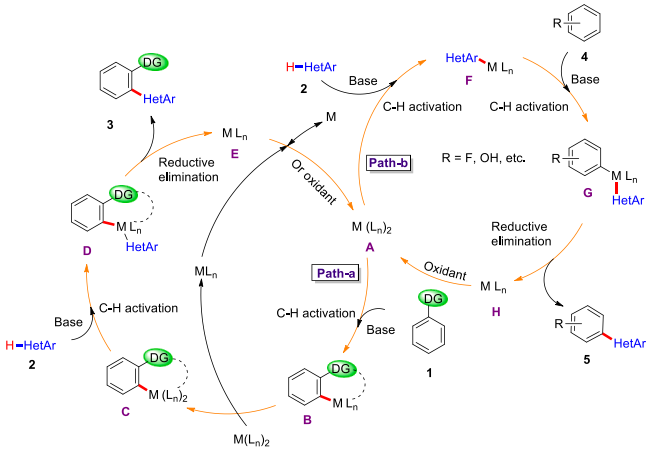


Fig. 2. General mechanism of DG assisted (path-a) and non-directed (path-b) coinage-metal catalyzed or-mediated oxidative heteroarylation of arenes.

of heteroarenes (**2**) *via* C—H bond activation generates complex **F**, which is coupled with arenes (**4**) by C—H activation to form complex **G**. Finally, complex **G** affords the desired product (**5**) and reduced catalyst or mediator **H** through reductive elimination. The active catalyst or mediator is regenerated by the oxidation of H in the presence of an oxidant.

In this review, we give a summary of the coinage metal-catalyzed or-mediated heteroarylation of arenes. Because the C—H bond of many benzenoids is un-reactive, we can functionalize them through the DG strategy. Herein, we covered the heteroarylation of both types of arenes, activated arenes, and the arenes activated by DG.

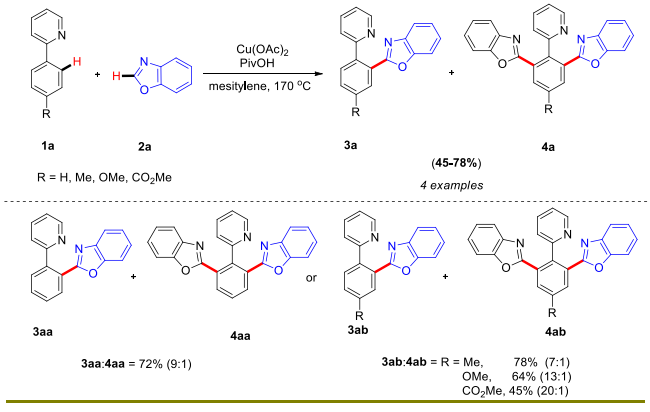
DG-assisted coinage metal-catalyzed or-mediated oxidative heteroarylation of arenes

DG-assisted Cu-catalyzed or-mediated oxidative heteroarylation of arenes to form new C—C bonds

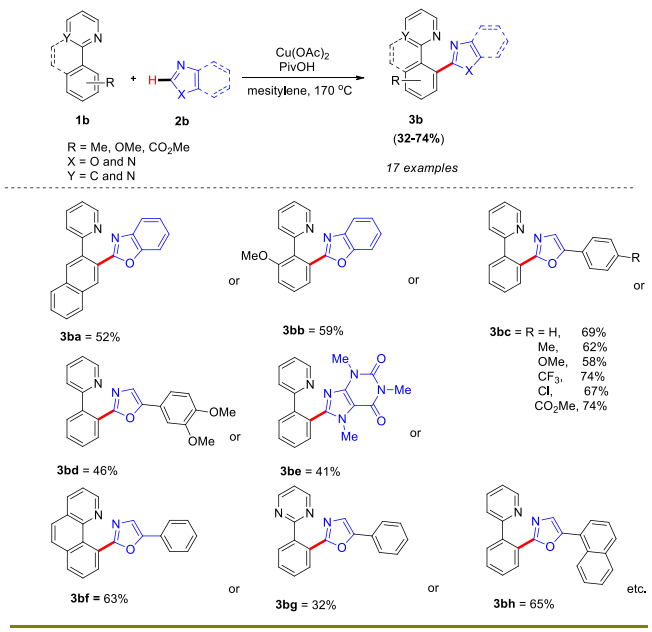
DG-assisted Cu-catalyzed or-mediated reactions are powerful tool for the synthesis of heteroaryl compounds, which are important in organic synthesis. In these reactions, DG coordinated with the Cu-catalyst or-mediator, which facilitates the stabilization of the active catalytic species and enhances the reactivity. DG can also control regioselectivity through the metallacycle intermediate and improve the product efficiency of the transformation. DG provides attributes such as ease of installation and removal, small in terms of mass and relatively weak coordination with metal-catalysts or-mediator [8].

The first report on DG-assisted Cu-mediated oxidative heteroarylation of arenes to form new C—C bonds was given by Hirano and co-workers in 2011 [9]. They reported azine as the DG in the Cu-mediated coupling of arylazines with azoles. After optimizing the reaction conditions, a 72 % combined yield (1:2 ratio) of **3a** and **4a** was obtained by the reaction of 2-phenylpridine (**1a**) with benzoxazole (**2a**) in the presence of $Cu(OAc)_2$ as mediator and PivOH as additives in mesitylene as solvent at 170 °C (Scheme 2; **3aa**:**4aa**). It was observed that arylazines with both electron-donating and electron-withdrawing groups at the *p*-position of the benzene ring were compatible under the reaction conditions (**3ab**: **4ab**).

To explore the scope of substrates for this reaction, different 2-arylazines were reacted with various azoles under optimized reaction conditions, gave low-to-high yields (32–74 %) of the desired product (Scheme 3; **3b**). 5-aryloxazoles bearing different substituents on the aryl ring react smoothly with 2-phenylpyridine and give low-to-good yields (58–74 %) of the target product (**3bc**). The reaction involving caffeine also produced synthetically useful yield of the desired product (**3be**). Experimental studies suggest that the mechanism for this reaction may include (i) reversible C—H cupration of azoles, (ii) C—H metalation of arylazine, and (iii) reductive elimination.

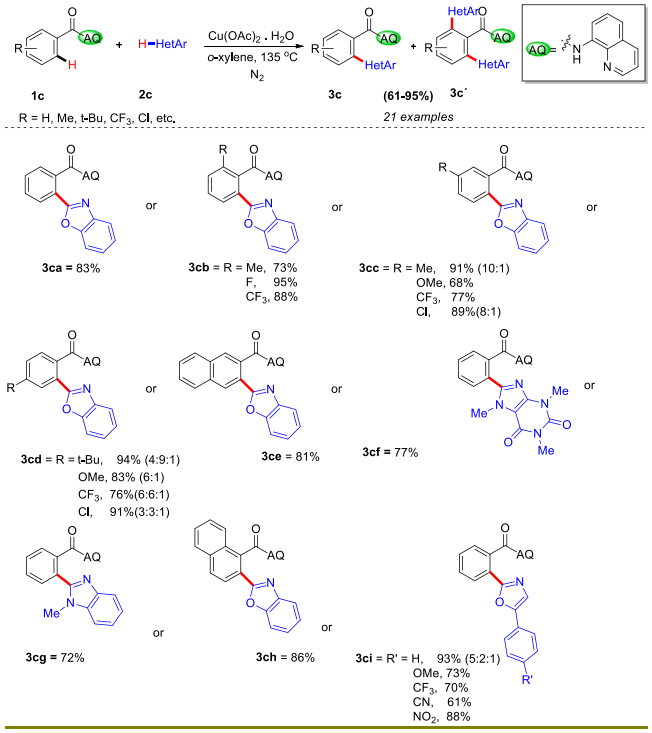


Scheme 2. Cu-mediated heteroarylation of 2-arylazines.



Scheme 3. Cu-mediated heteroarylation of 2-arylazines (**1b**).

Later in 2013, Hirano and co-workers also reported 8-aminoquinoline directed Cu-mediated heteroarylation of benzamide (**1c**) using benzoxazole (**2c**) with $Cu(OAc)_2{\cdot}H_2O$ as mediator and *o*-xylene as solvent at 135 °C. The reaction gave the corresponding hetero-biaryl product with 83 % yield, along with a trace amount of homo-coupling product (Scheme 4) [10]. After optimizing the reaction condition, they found that the yield of the product was improved to 93 % by using 1:2 ratio of **1a** and **2a**, 50 mol% of $Cu(OAc)_2{\cdot}H_2O$ in *o*-xylene solvent at 135 °C under nitrogen atmosphere for 4 h. Optimization showed that bidentate DG such as 8-amioquninoline are more efficient than monodentate DG. It has also been found that the anhydrous $Cu(OAc)_2$ is more efficient than hydrated $Cu(OAc)_2{\cdot}H_2O$.



Scheme 4. Cu-mediated heteroarylation of benzamide (**1c**) (The ratio of **3c**: **3ć** is given in parenthesis).

Next, to evaluate the scope of substrates for this reaction they tried reaction of different substituted benzamide (**1c**) with benzoxazole (**2c**) under optimized reaction conditions, gave low-to-high yields (61–95 %) of the desired product (Scheme 4; **3ca-3ce**). The various substituents like -methyl, -methoxy, -*t*butyl, -chloro, -fluoro, and -trifluoromethyl substituents on *o*-, *m*-, and *p*-positions of benzamide were tolerated under the reaction condition. Substrates bearing two reactive C—H bonds gave doubly heteroarylated products (**3ć**). They also synthesized hetero-biaryls containing caffeine and benzimidazoles with excellent yield (Scheme 4; **3cf-3cg**).

The plausible mechanism for this reaction (Fig. 3) begins with cupration of **2c** to form azolyl Cu-intermediate (**I**), followed by ligand exchange with **1c**, generates anionic and neutral doubly *N,N'*-chelated complex **J**. In the presence of $Cu(OAc)_2$, oxidation (disproportionation) of complex **J** gave Cu(III)-complex **K**. Now, C—H cupration of the benzene ring of complex **K** afforded intermediate **L**. Subsequently, reductive elimination liberates the desired product (**3c**).

To remove the 8-aminoquinoline DG from the coupling product **3ca** (Scheme 5), they used a two-step pathway. The first step was the Boc protection of secondary amide then ethanolysis in the presence of NaOEt in Et_2O-EtOH which furnished ethyl ester (**4c**) with 63 % yield in the next step.

In the same year, picolinamide-directed Cu-mediated direct heteroarylation of 1-naphthylamines (**1d**) using benzoxazole (**2d**) in the presence of PivOH as an additive was reported by Odani *et al.* [11]. Initially, they performed the reaction between 1-naphthylamines (**1d**) and benzoxazole (**2d**) in the presence of 20 mol% $Cu(OAc)_2$ in *o*-xylene at 150 °C under N_2 atmosphere using AcOH as additive to gave the desired product (**3d**) in 20 % yields. To improve the yield of **3d**, they optimized the reaction with respect to amount of $Cu(OAc)_2$, additives, solvents, temperature, and other reaction conditions, by using 1-naphthylamines (0.25 equiv.), benzoxazole (0.50 equiv.), 75 mol% of Cu $(OAc)_2$ as mediator, PivOH (0.25 equiv.) as additive in mesitylene as solvent at 165 °C under nitrogen atmosphere. The reaction gave the desired product with 73 % yields (Scheme 6; **3da**).

To analyze the scope of azoles for this reaction, they conducted the reaction of 1-naphthylamines derivatives (**1d**) with different azoles (**2d**) under the optimized reaction condition, gave low-to-high yield (35–78 %) of the desired product (Scheme 6; **3d**). They observed that electron-deficient group at the C-4 position of naphthylamines has little effect on reaction efficiency. Whereas, there were decrease in the product yield if the electron-rich group is present at the C-4 position of naphthylamines. Notably, 1-aminopyrene furnished desired heteroarylated pyrenes with 71 % yield (**3di**).

The proposed mechanism for this reaction (Fig. 4) is initiated by cupration of **2d** to form intermediate **M** followed by *N,N'*-bidentate

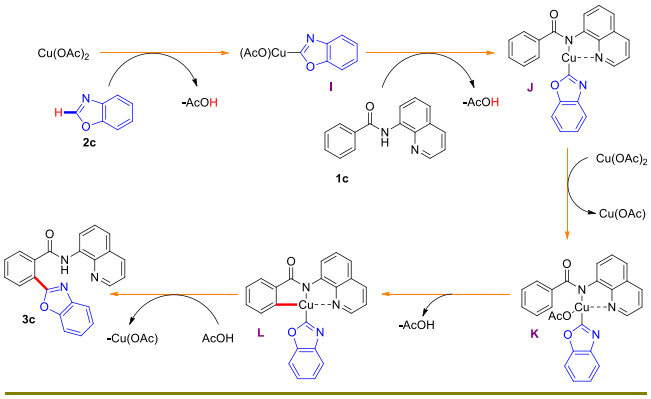
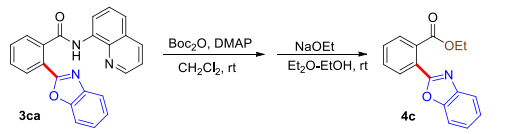
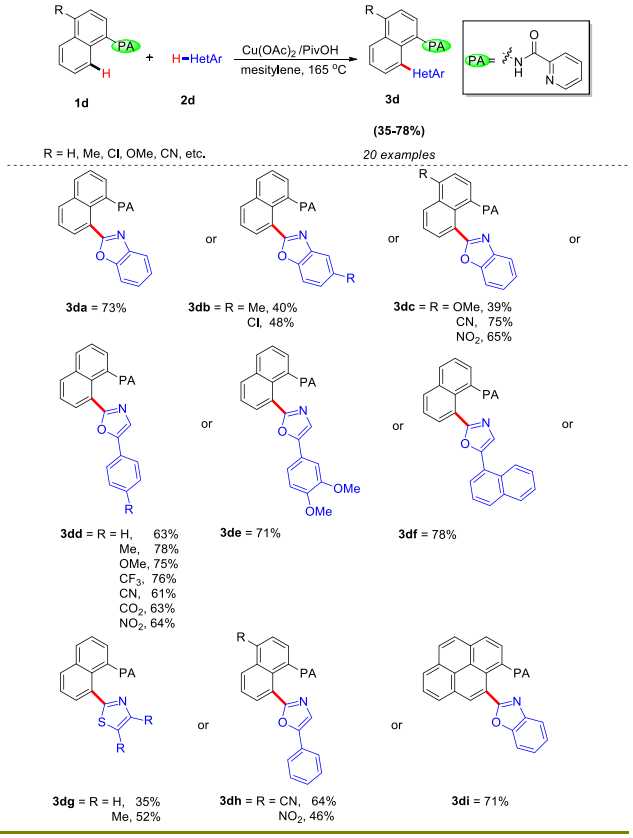


Fig. 3. Plausible mechanism for the Cu-mediated heteroarylation of benzamide (**1c**).



Scheme 5. Removal of aminoquinoline DG from **3ca**.



Scheme 6. Scope of heteroarenes for picolinamide-assisted Cu-mediated heteroarylation of 1-naphthylamines (**1d**).

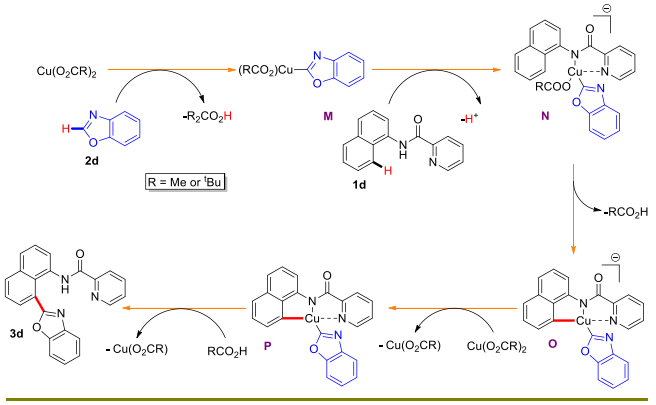


Fig. 4. Plausible mechanism for the Cu-mediated heteroarylation of 1-naphthylamines (**1d**).

coordination with **1d** to form organo-copper intermediate **N**. Then, C—H bond cleavage of naphthalene gives intermediate **O**, followed by oxidation (disproportionation) step in the presence of Cu(II), which forms the Cu(III)-metallacycle **P**. The reductive elimination of **P** produces the final product (**3d**).

The removal of the picolinamide DG from the product (**3dd**) was carried out by the Boc protection of NH-moiety in **3d** followed by ethanolysis using NaOEt in Et_2O-EtOH (Scheme 7).

Shi and co-workers in 2015 established pyridinylisopropyl (PIP)-directed Cu-catalyzed direct heteroarylation of benzamides using thiophenes [12]. Initially, they tried reaction between benzamide and 2-methyl thiophene in the presence of CuOAc (20 mol%) as catalyst, $AgNO_3$ (2.0 equiv.) as oxidant, and Li_2CO_3 (3.0 equiv.) as Lewis base, furnished the target product with 37 % yield. After optimization, the yield of the desired product was improved to 78 % by using CuOAc (20 mol%), Li_2CO_3 (3.0 equiv.), $Zn(OAc)_2$ (1.2 equiv.) with $AgNO_3$ (4.0 equiv.) in DMF under nitrogen atmosphere at 120 °C for 24 h (Scheme 8; **3ea**).

To investigate the scope of substituted benzamides for this reaction. They performed reaction of substituted benzamides (**1e**) with 2-methylthiophene (**2e**) under optimized conditions afforded low to high yield (41–79 %) of the desired product (Scheme 8; **3e**). Both electron-donor (-alkyl, -methoxy) and electron-acceptor (-trifluoromethyl, -fluoro, -methoxycarbonyl, -chloro, -iodo) substituents were compatible at *o*-, *m*-, and *p*- positions on aryl ring of benzamides (Scheme 8; **3eb-3ec**). They found that sterically hindered benzamide such as alkoxy-substituted benzamide provided a lower yield of product (**3ed**).

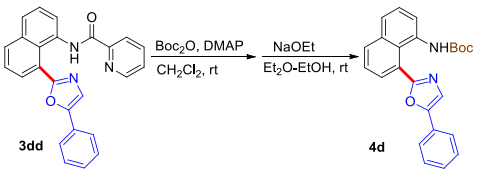
They also examined the reaction of benzamide (**1f**) with different substituted thiophenes (**2f**) under the same optimized reaction condition, which afforded low to high yields (20–90 %) of the desired products (Scheme 9; **3f**). Thiophenes bearing electron-rich and electron-poor groups were tolerated under the reaction conditions (Scheme 9; **3fa-3fc**). Thiophene possessing strong electron-deficient groups such as 2-acyl thiophene gave a lower yield (20 %) of the desired product (**3fd**) may be due to the electron-deficient nature of the acyl group.

Based on experimental results for mechanistic study, they proposed the mechanism (Fig. 5) for this reaction, which begins with the oxidation of Cu(I) to Cu(II) by Ag-salt. Now C—H cupration of **1f** to give Cu(II)-complex (**Q**), followed by oxidation or disproportionation, gives Cu (III)-aryl intermediate **R** that reacts with thiophene through electrophilic aromatic substitution (S_EAr) to produce intermediate **S**. Finally, reductive elimination of **S** afforded the desired product **3f** and Cu(I) to complete the catalytic cycle.

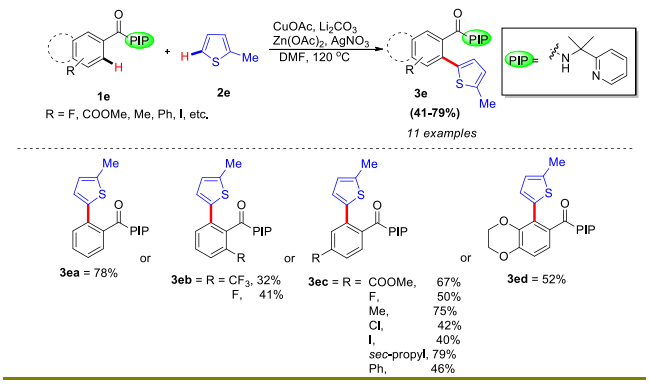
The removal of the PIP DG from coupling products (**3ea**) was done (Scheme 10) by nitrosylation of secondary amide in the first step followed by hydrolysis using LiOH and H_2O_2 in the subsequent step produced corresponding 2-heterobenzoic acid product (**4f**) with 85 % yield.

In 2021, Miura and co-workers developed a bipyridine-type bidentate (dtbpy) auxiliary group assisted Cu-mediated oxidative coupling of substituted phenols with 1,3-azoles [13]. After optimizing the DGs for this reaction, bipyridine DG gave the highest yield (71 %) of the desired product when reacting *o*-cresol with 5-phenyloxazole in the presence of $Cu(OAc)_2{\cdot}H_2O$ as mediator in *o*-xylene solvent at 130 °C (Scheme 11; **3ga**).

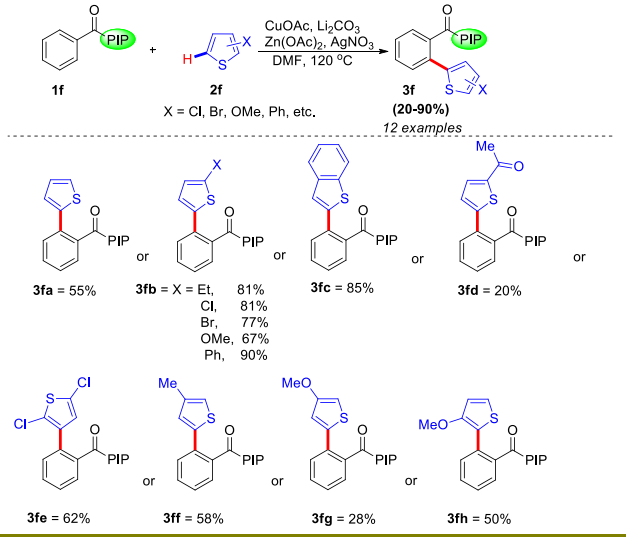
To see the scope of substrates for this reaction, they tried the reaction of different substituted phenols with different heteroarenes under optimized reaction conditions, gave low-to-good yields (20–71 %) of the desired product (Scheme 11; **3g**). It was found that 5-aryloxazoles and 1,3,4-oxadiazoles bearing electronically and sterically different groups were tolerated under the reaction conditions (**3ga-3gf**). The *p*-



Scheme 7. Removal of picolinamide DG from **3dd**.



Scheme 8. Scope of substituted benzamides for Cu-catalyzed heteroarylation of benzamide (**1e**).



Scheme 9. Scope of substituted thiophene for Cu-catalyzed heteroarylation of benzamide (**1f**).

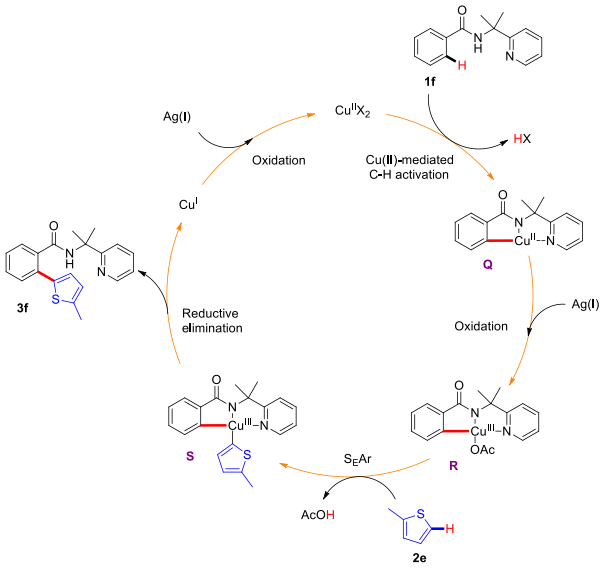
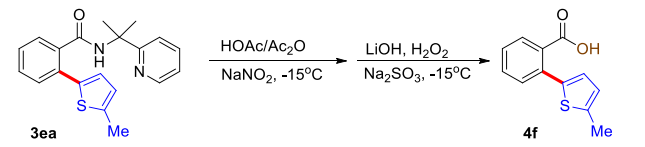
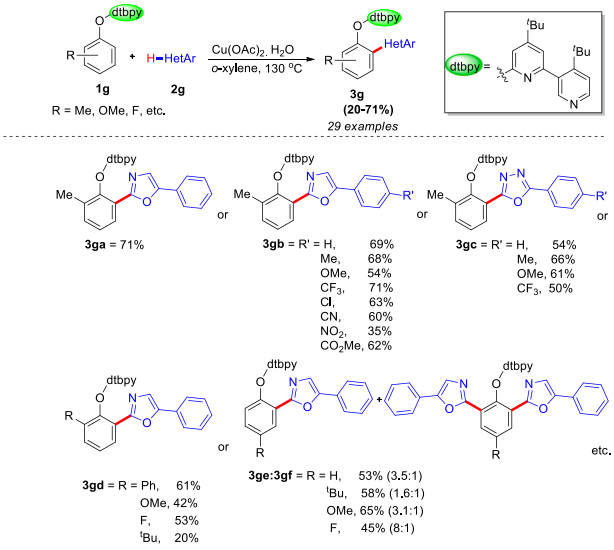


Fig. 5. Plausible mechanism for Cu-catalyzed coupling of benzamide (**1f**) and 2-methylthiophene (**2e**).



Scheme 10. Removal of PIP DG from **3ea.**



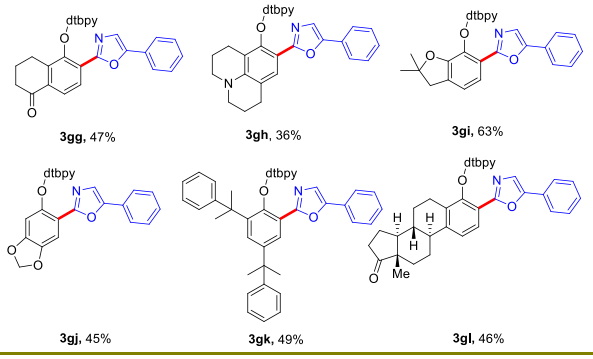
Scheme 11. Cu-mediated heteroarylation of different substituted phenols.

substituted phenol gave a mixture of mono- and di-hetero-arylated products (**3ge:3gf**).

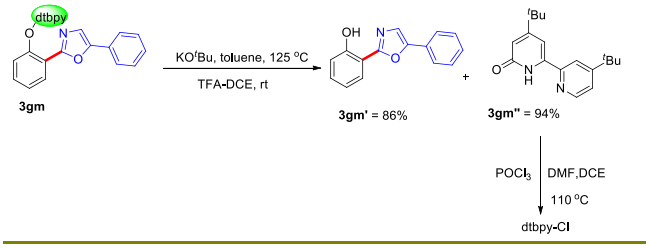
The tetralone (**3gg**), julolidine (**3gh**), dihydrobenzofuran (**3gi**), and sesamole (**3gj**) ring systems were tolerated under the reaction condition (Scheme 12). The optimized reaction conditions are useful for hetero-arylation of 2,4-bis(α,α'-dimethylbenzyl)phenol (**3gk**), which is a core moiety of UV absorption material, and bioactive compounds like estrone (**3gl**).

The removal of bipyridine auxiliary from the coupling product was obtained (Scheme 13) by reaction of **3gm** with KO*t*Bu in heated toluene at 125 °C, followed by TFA, gave 86 % yield of **3gm′** along with 94 % yield of pyridone derivative (**3gm′′**), which can be converted into dtbpy-Cl by treating with $POCl_3$, DMF-DCE at 110 °C.

Based on literature information, they proposed tentative mechanisms for this reaction (Fig. 6), which start with *N,N'*-bidentate coordination-assisted C—H bond cleavage of **1g** with $Cu(OAc)_2$ to form complex **T,** followed by coordination of azole (**2g**) with complex **T** through C—H bond cleavage to form complex **U**. Now the oxidation



Scheme 12. Cu-mediated heteroarylation of different phenol derivatives.



Scheme 13. Removal of bipyridine auxiliary from **3gm**.

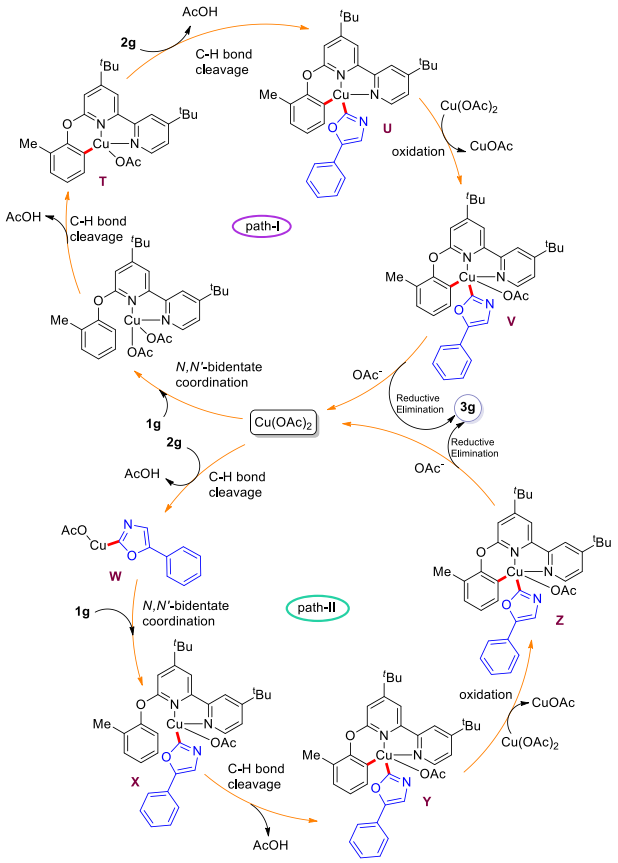


Fig. 6. Tentative mechanism for Cu-mediated heteroarylation of phenols derivative.

(disproportionation) step in the presence of $Cu(OAc)_2$ forms complex **V**. Finally, reductive elimination of complex **V** produces the final product (**3g**), as shown in path I. The reaction may follow path II, which begins with the cupration of azole (**2g**) to form Cu-intermediate (**W**), followed by ligand exchange with **1g**, which generates the *N,N'*-chelated complex **X**. Now the C—H bond cupration of the benzene ring of complex **X** generates complex **Y**. Oxidation (disproportionation) of complex **Y** in the presence of $Cu(OAc)_2$ gave complex **Z**. Finally, reductive elimination afforded the desired product (**3g**).

DG-assisted Cu-mediated oxidative heteroarylation of arenes to form new C—N bonds

The C—N bond-forming reaction from inert C—H bonds is an efficient transformation in organic synthetic chemistry [14]. The formation of C—N bonds through Cu-mediated oxidative heteroarylation offers more opportunities to introduce nitrogen-containing moieties in organic synthesis [15].

In 2016, Punniyamurthy and co-workers reported the 8-aminoquinoline amide-directed Cu-mediated *N*-arylation of *N*-(quinolin-8-yl)benzamide using pyrroles, indoles, pyrazoles, and carbazoles [16]. Initially they started the reaction of *N*-(quinolin-8-yl)benzamide with pyrrole in the presence of 1.0 equiv. $Cu(OAc)_2$ and 2.0 equiv. K_2CO_3 in DMSO at 70 °C, gave 34 % yield of the target product (**3h**). To increase the yield of the **3h**, the reaction conditions were optimized by varying Cu-salts, bases, and solvents. The best reaction condition was achieved by using 1.5 equiv. $Cu(OAc)_2$ as mediator and 2.0 equiv. Cs_2CO_3 as base in DMF solvent at 70 °C, which afforded 79 % yield of the desired product.

To study the scope of *N*-(quinolin-8-yl)benzamide derivatives for this reaction, the reaction of different *N*-(quinolin-8-yl)benzamide derivatives (**1h**) with pyrrole (**2h**) under optimized reaction conditions gave moderate to good yields (51–84 %) of the desired product (Scheme 14; **3h**). It was found that *N*-(quinolin-8-yl)benzamide derivatives bearing electron-donating and electron-withdrawing groups at different positions were tolerated under reaction conditions (**3ha**-**3hd**).

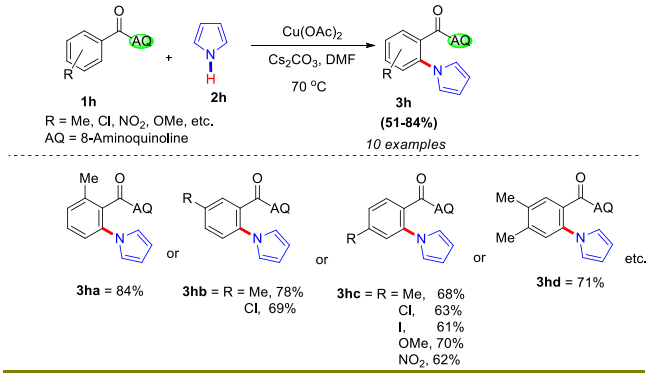
Next, to see the scope of indoles for this reaction, they tried the reaction of *N*-(quinolin-8-yl)benzamide with substituted indoles under optimized reaction conditions, gave moderate to high yields (51–84 %) of the desired product (Scheme 15; **3i**). It was examined that indoles bearing different substituents like bromo, methoxy, and 2-(2-(1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione efficiently provide the target products (**3ie** and **3if**). Azaindole also gave the desired product in good yields (**3ig**).

Furthermore, to extend the scope of the substrates for this reaction, they attempted the reaction of *N*-(quinolin-8-yl)benzamide with pyrazole, methylpyrazole, and carbazoles under optimized reaction conditions, which gave moderate yields (41–58 %) of the desired *N*-arylated product (Scheme 16; **3j**).

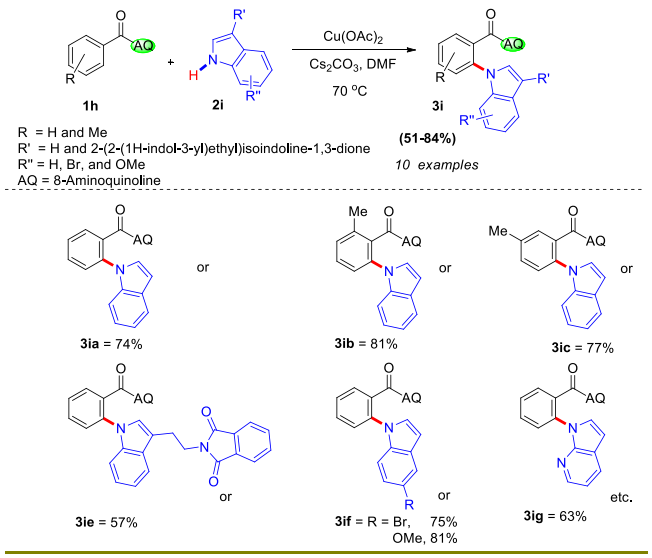
The removal of the DG from coupling product **3h** was achieved by hydrolysis using NaOH in ethanol at 110 °C to give 84 % yield of 2-(1*H*-pyrrol-1-yl) benzoic acid (Scheme 17).

A proposed mechanism for this reaction is outlined in Fig. 7, which starts the reaction of azole (**2h**) with $Cu(OAc)_2$ in the presence of base and generates Cu(II) intermediate **A′**. Then, ligand exchange of intermediate **A′** with *N*-(quinolin-8-yl)benzamide (**1h**) leads to the formation of Cu(II)-intermediate **B′**. Now $Cu(OAc)_2$-mediated oxidation of intermediate **B′** generates intermediate **C′**, followed by C—H cupration of the aryl ring to give intermediate **D′**. Finally, reductive elimination followed by protonation yields the desired product (**3h**).

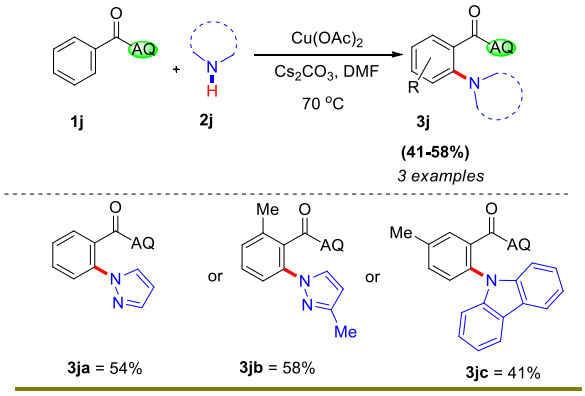
Pradhan *et al.,* in the following year reported picolinamide-directed Cu-mediated heteroarylation of naphthylamines with azoles to form a new C—N bond [17]. They tried to initiate reaction between *N*-(naphthalen-1-yl)picolinamide with indole using $CuCl_2$ as mediator, Ag_2CO_3 as additive, NMO (*N*-methylmorpholine oxide) as oxidant, and K_3PO_4 as base at 140 °C in DMSO under air to gave only 10 % yield of the desired coupling product. To raise the reaction yield, they optimized the



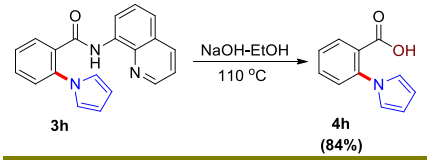
Scheme 14. Scope of *N*-(quinolin-8-yl)benzamide derivatives for Cu-mediated *N*-arylation reaction.



Scheme 15. Scope of indoles for Cu- mediated *N*-arylation of *N*-(quinolin-8-yl) benzamide derivatives (**1h**).



Scheme 16. Scope of azoles for Cu-mediated *N*-arylation of *N*-(quinolin-8-yl) benzamide (**1j**).



Scheme 17. Removal of 8-aminoquinoline DG from **3h**.

reaction condition with respect to Cu-salts, additives, bases, and solvents, the reaction gave 72 % yield of coupling product by reacting *N*-(naphthalen-1-yl)picolinamide (**1k**, 1.0 equiv.) with indole (2.0 equiv.) in presence of $Cu(OAc)_2$ (40 mol%) as mediator, Ag_2CO_3 (5 mol%) as additive, NMO (2.0 equiv.) as oxidant, and K_3PO_4 (2.0 equiv.) as base at 140 °C in DMSO solvent under air for 7 h (Scheme 18; **3ka**).They also found that 2-substituted indoles fail to give the desired product, due to the steric effect (**3kf**).

To explore the scope of indoles for this reaction they tried reaction of *N*-(naphthalen-1-yl)picolinamide with different indole derivatives, under optimized reaction conditions, afforded low-to-high yield (39–76 %) of the coupling products (Scheme 18; **3k**). A variety of substituents including methyl, methoxy, bromo, cyano, fluoro, ester, styrenyl, and allyl on indole ring tolerated under the reaction condition (**3kb**). Chloro

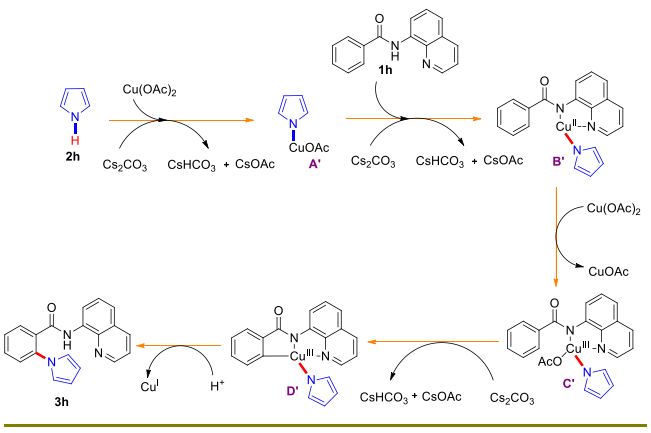
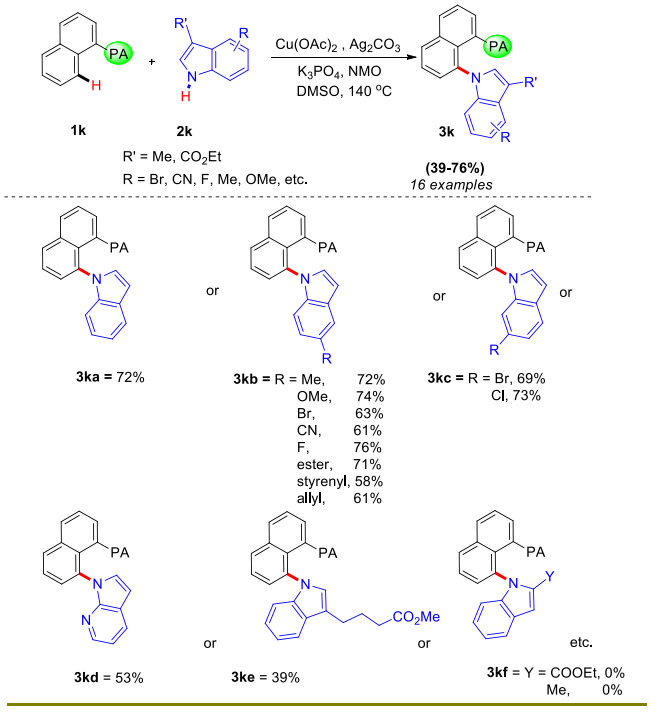


Fig. 7. Proposed mechanism for Cu-mediated heteroarylation of *N*-(quinolin-8-yl)benzamide (**2h**).

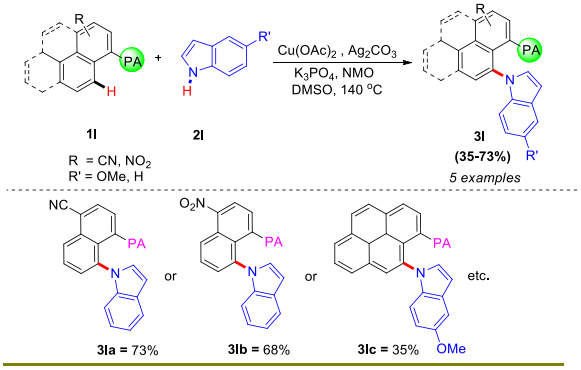


Scheme 18. Scope of indole for Cu-mediated heteroarylation of *N*-(naphthalen-1-yl)picolinamide (**1k**).

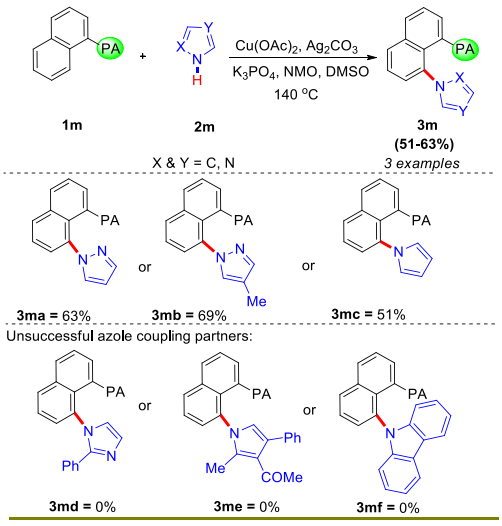
and bromo functional groups present at the C-6 position of indole quickly transformed the product (**3kc**). Also, coupling of *N*-(naphthalen-1-yl)picolinamide with 7-azaindole gave the desired product (**3kd**) with 53 % yield. The formation of indole-3-butyric acid (**3ke**) is part of natural products (plant hormones).

They also investigated the scope of different *N*-(naphthalen-1-yl) picolinamides (**1l**) with substituted indole, gave low to high yield (35–73 %) of the desired product under the optimized reaction condition (Scheme 19; **3l**). The substrates containing electron-acceptor groups at the C-4-position of **1l** smoothly transformed to the desired product (**3la-3lb**). It was noticed that conjugate π-cycles like *N*-(pyrene-1-yl)picolinamide gave a lower yield of the desired product (**3lc**).

This strategy was extended to the coupling of naphthalenylpicolinamide with various azoles under the same optimized condition, afforded moderate to good yields (51–63 %) of the desired products (Scheme 20; **3m**). The reaction carried out with pyrazole, 3-methylpyrazole, and pyrrole furnished the desired product in good



Scheme 19. Scope of *N*-(naphthalen-1-yl)picolinamides for Cu-mediated heteroarylation of *N*-(naphthalen-1-yl)picolinamide derivative (**1l**).



Scheme 20. Scope of azoles for Cu-mediated oxidative heteroarylation of *N*-(naphthalen-1-yl)picolinamide (**1m**).

yields (**3ma-3mc**). The reaction condition failed to give the desired product (**3md-3mf**) when the reaction was performed using 2-phenylimidazole, trisubstituted pyrrole, and carbazole as coupling partners, due to the steric effect generated by substituents.

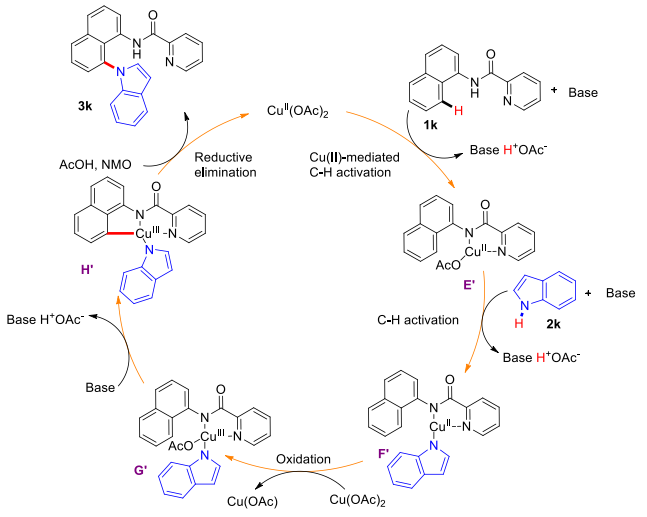


Fig. 8. Plausible mechanism for the Cu-mediated heteroarylation of *N*-(naphthalen-1-yl)picolinamide (**1k**).

Based on the experimental study, they proposed a mechanism for this reaction (Fig. 8). The reaction begins with *N*-cupration of naphthylamines (**1k**) in the presence of $Cu(OAc)_2$ leads intermediate **E′**, followed by substitution with indole (**2k**) generates Cu(II) intermediate **F′**. Then oxidation of **F′** forms Cu(III) intermediate **G′**, gave organo-Cu(III) intermediate **H′** through C—H cupration. Subsequently, reductive elimination of **H′** afforded the desired *N*-naphthyl azoles product (**3k**).

To remove the picolinamide DG from the coupling product (**3ka**), they used NaOH in EtOH for 6 h, obtained 91 % yield of 8-(1-indole-1-yl) naphthalen-1-amine (**4k**) (Scheme 21).

Wang and co-workers in 2019 reported oxazoline-aniline directed Cu-mediated heteroarylation of arene monocarboxylic acid derivatives with aza-heteroarenes [18]. Initially, they reacted the 2-methyl-benzoic acid derivative with imidazole, which gave only 11 % yield of coupled product in the presence of 30 mol% $Cu(OAc)_2$ and 2.0 equiv. Na_2CO_3 in DMSO solvent at 90 °C for 4 h. After optimizing the reaction conditions, they achieved 82 % yield of the desired product (R = Me; Scheme 22; **3na**) in the presence of $Cu(OAc)_2$ (100 mol%) as mediator and Na_2CO_3 (2 equiv.) as base in DMSO at 90 °C for 4 h.

To see the scope of benzoic acid derivatives for this reaction, they tried the coupling of various benzoic acid derivatives (**1n**) with imidazole under optimized reaction conditions, which gave low-to-good yields (45–82 %) of the desired product (Scheme 22; **3n**). Both electron-rich and electron-poor substituents at the *o*- and *m*-positions of benzoic acid derivatives are well tolerated (**3na** & **3nb**) and give moderate to good yields of the desired products. Additionally, *p*-substituted benzoic acid derivatives react smoothly with imidazole and give both mono- and di-heteroarylatred products in good yields (**3nc**).

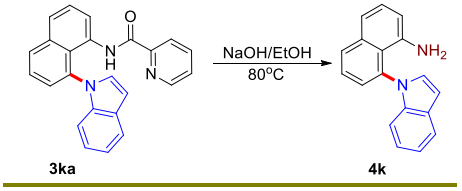
To see the scope of aza-heteroarenes, they tried coupling of 2-methylbenzoic acid derivatives with a variety of aza-heteroarenes under optimized reaction conditions, which gave low to high yields (39–84 %) of the desired products (Scheme 23; **3o**). Various aza-heteroarenes, including imidazole, pyrazole, indole, azindole, indazole, benzimidazole, purine, carbazole, and pyridone, react smoothly and give desired coupled products in moderate to good yields (**3o**).

Coinage metal-catalyzed or-mediated oxidative heteroarylation of activated arenes

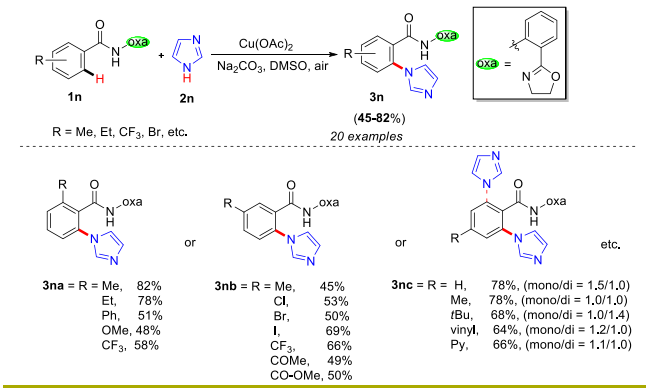
Cu-catalyzed or-mediated oxidative heteroarylation of activated arenes to form new C—C bonds

If arenes are activated then there is no need of DG for their activation. There are many reports known in the literature where activated arenes directly give heteroarylation reactions *via* C—H bond activation reaction, which lead to the synthesis of a variety of organic molecules [19].

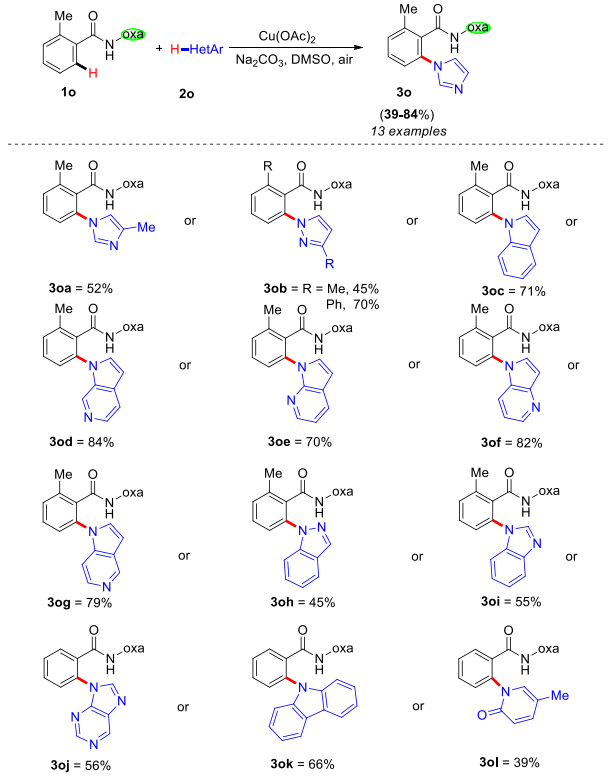
The first report on Cu-catalyzed oxidative heteroarylation of activated arenes to form new C—C bonds was given by Daugulis and coworkers in 2011 [20]. They reported the Cu-catalyzed oxidative cross-coupling of electron-rich and electron-poor arenes with five- and six-membered heteroarenes. Apart from aryl-heteroaryl cross-coupling, they also described heteroaryl-heteroaryl and aryl-aryl cross-couplings. They revealed the optimal reaction conditions for this reaction to be 10 mol% of both CuI as catalyst and phenanthroline as ligand, 1.2–2.5 equiv. of I_2 as oxidant, 0.5–1.0 equiv. of pyridine as additives, and 3.5



Scheme 21. Removal of picolinamide DG from **3ka**.



Scheme 22. Scope of benzoic acid derivatives (**1n**) for Cu-mediated heteroarylation.

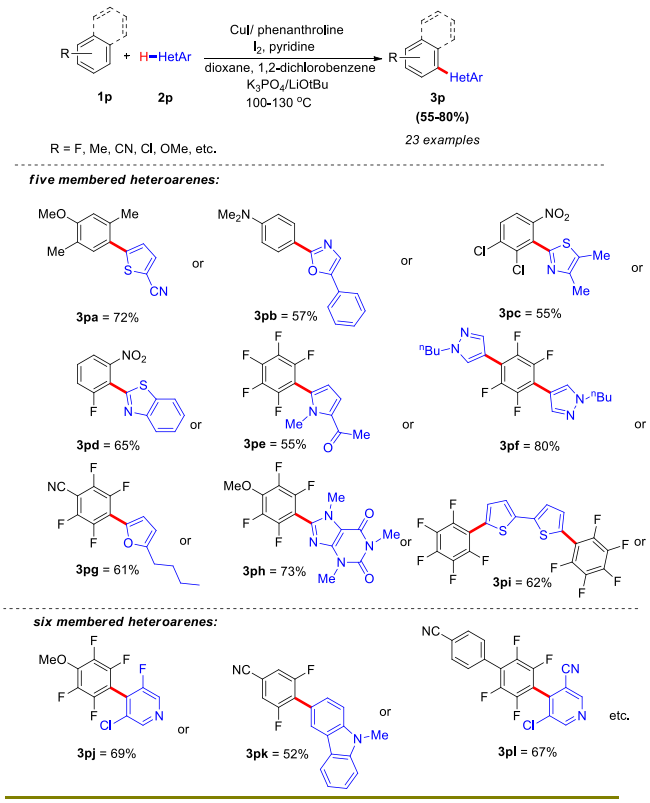


Scheme 23. Scope of aza-heteroarenes (**2o**) for Cu- mediated heteroarylation of 2-methyl benzoic acid derivatives (**1o**).

equiv. of K_3PO_4 as base in 1,2-dichlorobenzene solvent at 130 °C. Under optimized reaction conditions, a 72 % yield of the target heteroarylated product was obtained by reacting 2,5-dimethylanisole with 2-cyanothiophene (Scheme 24; **3pa**).

To observe the scope of substrates for this reaction, they tried the reaction of different substituted arenes with a variety of heteroarenes under similar reaction conditions, giving moderate to high yields (55–80 %) of the desired product (Scheme 24; **3p**). Substrate-bearing electron-withdrawing and electron-donating groups were tolerated under the reaction conditions (**3pa-3pl**).

In the following year, Zhang and co-workers used CuCl as catalyst for the heteroarylation of pentafluoroarenes with benzothiazoles under mild conditions [21]. Apart from Aryl-heteroaryl coupling, they were also shown heteroaryl-heteroaryl coupling between thiazole and benzothiazole. Under optimized reaction conditions, 71 % yield of the

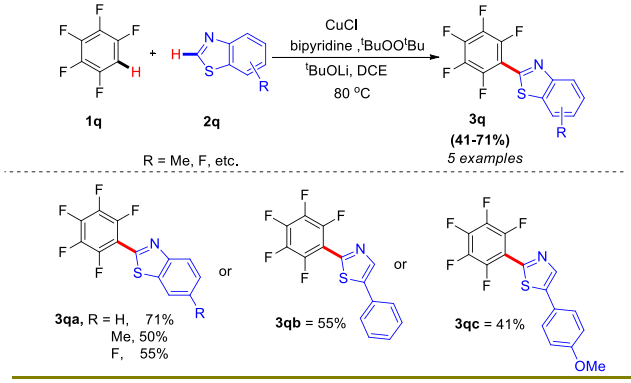


Scheme 24. Cu-catalyzed heteroarylation of different substituted arenes (**1p**).

desired product was obtained by using 20 mol% CuI as catalyst, 4,4́-dimethoxy-2,2́-bipyridine (bpy) (0.2 equiv.) as ligand, *t*BuOO*t*Bu (3.0 equiv.) as an oxidant, *t*BuOLi (0.5 equiv.) as base, 1,2-dichloroethane (DCE) as solvent at 80 °C for 6 h (Scheme 25; **3qa**).

Next, to observe the scope of benzothiazoles for this reaction, they carried out coupling of different benzothiazoles with pentafluoroarenes under similar reaction conditions afforded lower-to-higher yields (41–71 %) of the product (Scheme 25; **3q**). The reaction gave lower yields where benzothiazoles contained both electron-accepting and electron-donating groups. It was observed that 5-arylthiazoles gave reasonable yield of the product (**3qb & 3qc**).

On the basis of previous research, they proposed a mechanism for this reaction. The reaction starts with the cupration of either pentafluoroarenes or benzothiazoles in the presence of *t*BuOLi, which then react either with benzothiazole/pentafluoroarylCu-species or with benzothiazole/pentafluoroarylLi-species generated from the reaction of benzothiazole/pentafluoroarene with *t*BuOLi to form



Scheme 25. Scope of benzothiazoles for Cu-catalyzed heteroarylation of polyfluoroarene (**1q**).

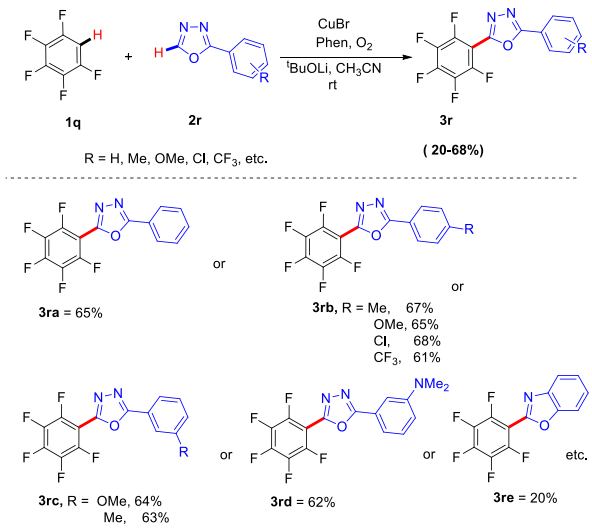
benzothiazolepentafluoroarylCu-complex, which undergoes reductive elimination to form desired product and active copper catalyst in the presence of oxidant like silver salt or *t*BuOO*t*Bu.

In the following year, Bolm and co-workers described Cu-mediated heteroarylation of pentafluoroarenes (**1q**) with 2-substituted 1,3,4-oxadiazoles (**2r**) under mild and ambient reaction conditions [22]. Initially, they tried reaction between pentafluorobenzene and 2-phenyl-1,3,4-oxadiazole (5:1 ratio) using CuBr (1.0 equiv.) as mediator, *t*BuOLi (3.0 equiv.) as base, 1,10-phenanthroline (1.0 equiv.) as ligand, CH_3CN as solvent at room temperature under oxygen atmosphere for 14 h afforded only 34 % yield of cross-coupling product. To reduce the chances of homo-coupling of 2-phenyl-1,3,4-oxadiazole and to improve the yield of cross-coupled product (**3r**), they used 30 equiv. of pentafluorobenzene, 20 mol% of CuBr, 1,10-phenanthroline (0.2 equiv.), *t*BuOLi (0.6 equiv.), in CH_3CN solvent at room temperature for 14 h, gave 65 % yield of desired heteroarylated product.

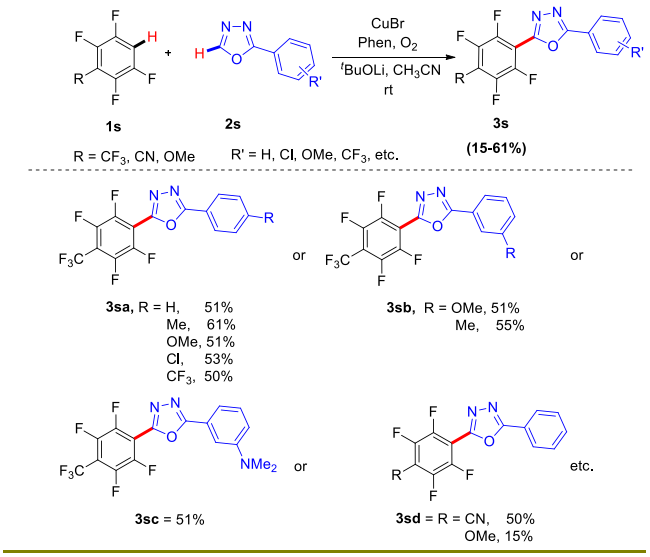
To see the scope of 1,3,4-oxadiazole for this reaction, they examined reaction with 1,3,4-oxadiazole bearing electron-donating (-Me, -OMe) as well as electron-withdrawing (-Cl, -CF_3) substituents at C-2 position and found that all substituents are tolerated under the reaction condition and gave low-to-high (20–68 %) yield of the desired products under similar reaction conditions (Scheme 26; **3r**). It was noticed that, using 5 equiv. of pentafluorobenzene as coupling partner gave a lower yield (20 %) of the product (**3re**).

They extended the protocol for coupling of substituted tetrafluoroarenes (**1s**) and several 2-aryl oxadiazoles (**2s**) gave the corresponding product in low-to-moderate (15–61 %) yields (Scheme 27; **3s**). Electron-acceptor substituents like -CF_3 in the tetrafluoroarenes favoured heteroarylation reaction and gave corresponding products in good yields (**3sa-3sc**). It was found that 10 equiv. of 1-methoxy-2,3,5,6-tetrafluorobenzene having electron-donor group, furnished only 15 % yield of product (**3sd,** R = OMe).

The proposed mechanism for this reaction (Fig. 9) showed that the desired product can be obtained through two possible pathways. The reaction is initiated by the formation of Cu-benzoxazole intermediate (**J′**) through the base-promoted addition of **2r** to active mediator (**I′**). Now the addition of **1q** to intermediate **J′** in the presence of base generates Cu (azole) (fluoroayl)Ln complex (**K′**) (Fig. 7; path-I). While path-II begins with the base-promoted addition of **1q** to active mediator (**I′**) to form, Cu-pentafluoroarene intermediate (**L′**). Now base-promoted addition of **2r** to intermediate **L′** provides intermediate **K′**. Afterwards, the reductive elimination of **K′** afforded the final product (**3r**).



Scheme 26. Scope of 1,3,4-oxadiazole for Cu-mediated heteroarylation of pentafluoroarene (**1q**).



Scheme 27. Scope of 2-aryl oxadiazoles (**2s**) for Cu-mediated heteroarylation of tetrafluoroarene (**1s**).

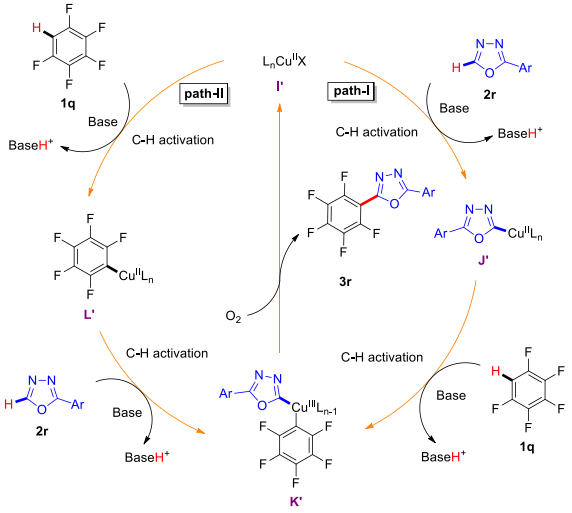


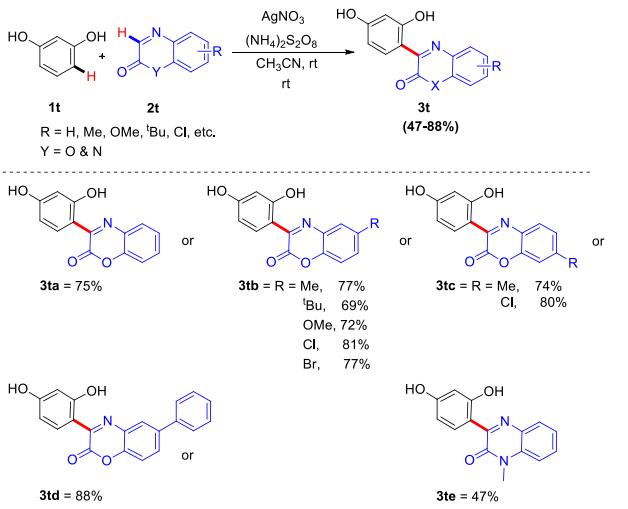
Fig. 9. Possible catalytic cycle for the Cu-mediated direct heteroarylation of pentafluoroarene (**1q**).

Ag-catalyzed oxidative heteroarylation of activated arenes to form new C—C bonds

Silver has been used for various organic transformations in the last few decades, due to its less expensive nature and also gives many reactions through C—H bond activation reaction [23]. In the literature, there is only one report on the Ag-catalyzed oxidative heteroarylation of arenes.

Pandit and co-workers in 2022 reported Ag-catalyzed oxidative heteroarylation of resorcinol using benzoxazine-2-ones under mild and ambient reaction conditions [24]. They start their study by reacting resorcinol (**1t**) with 2H-benzo[b][1,4]oxazin-2-one (**2t**) using 20 mol% of $AgNO_3$ as catalyst, $(NH_4)_2S_2O_8$ (2.0 equiv.) as oxidant, and CH_3CN as solvent at 80 °C for 3 h, which yielded only 20 % of the desired product (**3t**). After optimization of the reaction conditions, the product yield was improved to 75 % when the reaction was carried out at room temperature for 12 h using the same catalytic conditions (Scheme 28; **3ta**).

The scope of benzoxazine-2-ones for this reaction was examined by reacting resorcinol with different substituted benzoxazine-2-ones under



Scheme 28. Scope of benzoxazine-2-ones for Ag-catalyzed heteroarylation of resorcinol (**1t**).

the optimized condition, which provided low-to-high yields (47–88 %) of the desired products (Scheme 28; 3t). They observed that the aryl ring of benzoxazine-2-ones with electron-withdrawing groups like -chloro and -bromo as well as electron-donating groups such as -methyl, methoxy, and t-butyl reacts smoothly and furnishes the desired product (3tb and 3tc) in high yields. It was noticed that the reactant was easily transformed into the desired product when 2H-naphtho[2,3–b][1,4] oxazin-2-one and 1-methylquinoxalin-2(1H)-one were used as substrates to couple with resorcinol (3td and 3te).

Based on the experimental studies, they suggested a plausible mechanism for this reaction (Fig. 10). The reaction starts with the oxidation of Ag(I) to Ag(II) by $(NH_4)_2S_2O_8$ which induces abstraction of proton from **1t** to generate radical **M′**. Now, silver-coordinated 2*H*-benzo[b][1,4]oxazin-2-ones (**N′**) reacted with **M′** to give another radical **O′**. Finally, oxidation by sulphate radical anion, gave the desired product (**3t**).

Au-catalyzed oxidative heteroarylation of activated arenes to form new C—C bonds

Au-catalyzed C—H bond activation of organic molecules is extensively used in synthetic chemistry, due to the orthogonal selectivity of C—H activation reaction [25]. In recent years, this feasibility has provided great attention in double C—H bond activation reactions [26].

The first report on Au-catalyzed oxidative heteroarylation of activated arenes to form new C—C bonds was given by Larrosa and coworkers in 2015 [27]. They explored the Au-catalyzed heteroarylation of electron-poor arenes with electron-rich heteroarenes. Several optimizations for substrates such as *N*-protecting groups on indole, oxidants, additives, catalysts, and temperature were studied. Under optimal condition, when the reaction was carried out between tetrafluoroarene (**1u**) and *N*-triisopropylsilane (TIPS)-indole (**2u**) in the presence of 5 mol% PPh_3AuCl as catalyst, 1-pivaloyloxy-1,2-benziodoxol-3(1*H*)-one (PBX) as oxidant, AgOPiv as additives, 1,4-dioxane as solvent at 110 °C, gave 77 % yield of the desired product.

To explore the scope of different substituted fluoroarenes (sustituted di/tri/tetra-fluoroarenes), they tried the reaction of different substituted fluoroarenes with *N*-TIPS-indole under optimized reaction conditions which afforded low-to-high yields (25–85 %) of the desired products (Scheme 29; **3u**). The excellent yield (85 %) of the product (R = F, **3ua**) was obtained by reacting pentafluoroarenes with *N*-TIPS-indole. The substituents like -OMe, -Me, -SBu, $-CF_3$, -CHO, -CN, $-CO_2Bn$, –NPhth on tetrafluoroarene were tolerated under the reaction condition and gave good yields of the corresponding products (Scheme 29; **3ua**). The C-X (X = F, Cl, Br, I) bonds on aryl moieties were tolerated under the reaction condition and gave moderate yields of the corresponding products (**3ub**).

Next, to see the scope of heteroarenes, they tried the reaction of pentafluoroarene with different substituted heteroarenes, gave low-to-good yields (52–75 %) of the corresponding products under optimized condition (Scheme 30; **3v**) with C-X (X = F, Cl, Br, I) tolerance. *N*-TIPS indoles having different substituents present in C-4 (-bromo and -methyl), C-5 (-chloro, -iodo, and -methoxy) as well as C-6 (-bromo and -methoxy) furnished good yields of the desired product (Scheme 30; **3va-3vc**). It was also found that different heterocycles like benzothiophene, 2-methylthiophene, 2,3-dimethylfuran, and TIPS-protected pyrrole showed good reactivity to generate the desired product (**3vd-3vf**).

The plausible mechanism (Fig. 11) for this reaction represented that the reaction initiated by the C—H bond activation of **1u** in the presence of Au(I) catalyst to form Au-aryl complex (**P′**). Au-aryl complex (**P′**) oxidized to complex **Q′** followed by coupling of heteroarenes (**2u**) with complex **Q′** through C—H bond activation which generates complex **R′**. Finally, the reductive elimination affords the desired product (**3u**) and

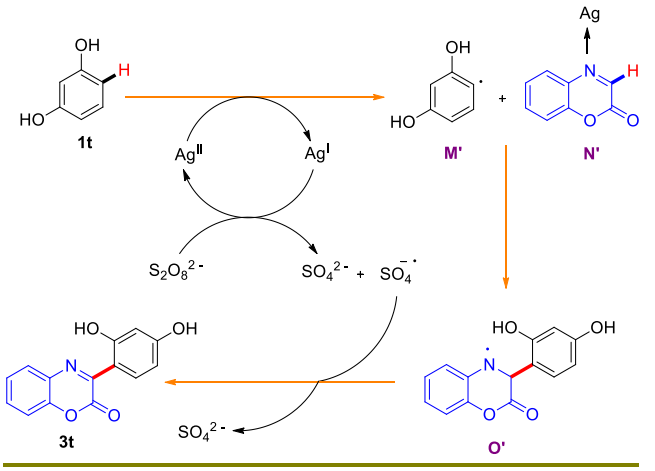
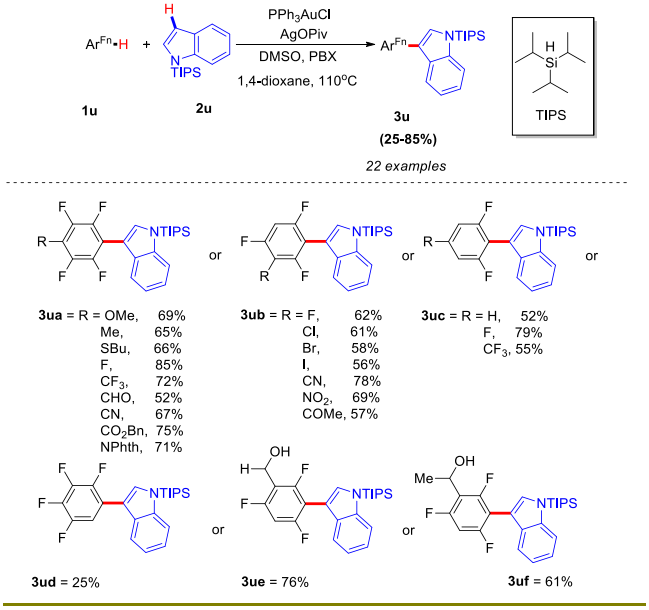
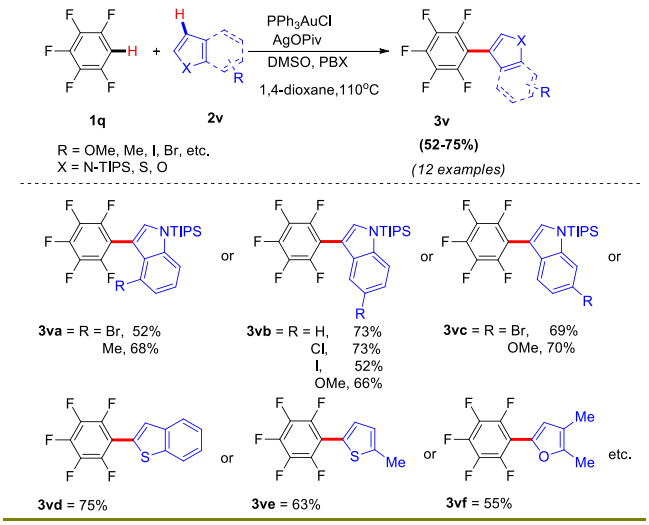


Fig. 10. Proposed mechanism for Ag-catalyzed direct heteroarylation of resorcinol (**1t**).



Scheme 29. Au-catalyzed heteroarylation of substituted electron-poor arenes (**1u**).



Scheme 30. Scope of substituted heteroarenes for Au-catalyzed heteroarylation of pentafluoroarenes (**1q**).

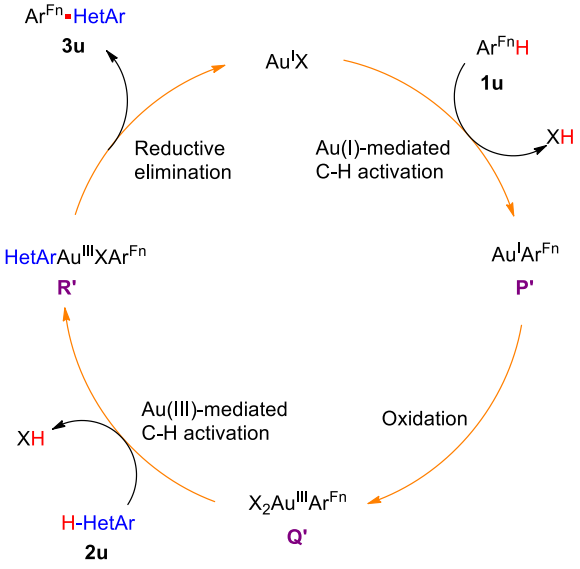
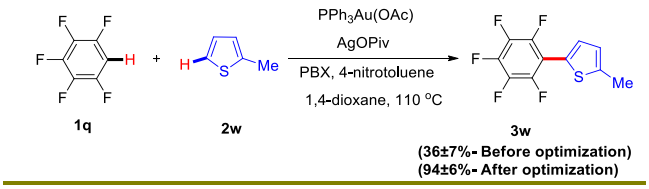


Fig. 11. Possible mechanism for Au-catalyzed direct heteroarylation of fluoroarenes (**1u**).

active catalyst.

In 2019, Luscombe and co-workers described Au-catalyzed heteroarylation of pentafluoroarenes for the synthesis of donor–acceptor polymer materials [28]. Initially, they performed the reaction between pentafluorobenzene (**1q**, 5 equiv.) and 2-methylthiophene (**2w**, 1 equiv.) using 5 mol % PPh_3AuCl as catalyst, 0.35 equiv. AgOPiv as additive and 1.5 equiv. of 1- pivaloyloxy-1,2-benziodoxol-3(1*H*)-one (PBX) as oxidant, in 1,4-dioxane solvent at 110 °C for 20 h using 4-nitrotoluene as internal standard afforded 36 ± 7 % yield of target product and trace amount (5 %) of homo-coupled product. To improve the reaction yield, the reaction was optimized with respect to the ligand attached to the Au-catalyst, amount of arenes, amount of additive, and reaction time, the reaction gave the highest yield (94 ± 6 %) of the desired product by using 5 equiv. of pentafluorobenzene (**1q**), 5 mol % of PPh_3AuOAc as catalyst, 1.0 equiv. AgOPiv as additive and 1.5 equiv. of 1- pivaloyloxy-1,2-benziodoxol-3(1*H*)-one (PBX) as oxidant, in 1,4-dioxane solvent at 110 °C for 20 h using 4-nitrotoluene as internal standard (Scheme 31).

They performed the application of this method for the synthesis of donor–acceptor polymer materials. They tried a reaction between



Scheme 31. Gold-catalyzed direct heteroarylation of pentafluoroarene (**1q**).

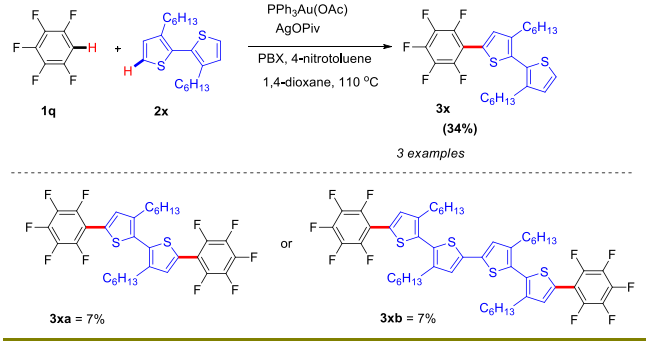
pentafluoroarene (**1q**) and 3,3′-dihexyl-2,2′-bithiophene (**2x**) under optimized reaction conditions to afford desired product, π-conjugated polymer (**3x**, 7 & 34 %) through homo-and hetero-coupling (Scheme 32; **3x**).

As established from experimental studies, they proposed a plausible mechanism (Fig. 12) for this transformation. Initially, there is C—H bond activation of pentafluoroarene (**1q**) by AgOPiv to form a metal-aryl complex (**U′**). Complex **U′** by *trans*-metallation generates complex **V′**. Complex **V′** oxidizes to complex **W′** in the presence of oxidant. Complex **W′** combines with 2-methylthiophene (**2w**) through S_EAr providing complex **X′**. Reductive elimination of complex **X′** afforded the desired product (**3w**) and active catalyst (***S′***).

In the same year, Xie and co-workers reported both experimentally and theoretically unprecedented Ag-Au bimetallic catalyzed heteroarylation of polyfluoroarenes using *N*-phenylpyrazoles [29]. After the theoretical study, they proposed that AgOAc is responsible for C—H bond activation of electron-poor arenes rather than Au(I), as reported by many groups earlier.

They optimized the reaction for a two-fold C—H activation reaction between tetrafluoropyridine and *N*-phenylpyrazoles (**2y**) and used a similar optimized condition for cross-dehydrogenative coupling between polyfluoroarenes (**1y**) and *N*-phenylpyrazoles (**2y**). They tried reaction with different substituted polyfluoroarenes (**1y**) and concluded that polyfluoroarenes (**1y**) could be an effective coupling partner for this reaction and yielded corresponding coupling product in good-to-excellent yields (51–84 %) by using 5 mol% of DMSAuCl and 20 mol% AgOAc as dual catalyst, 1.5 equiv. of phenyliodine diacetate (PIDA) as oxidant in 1,4-dioxane solvent at 100 °C for 15 h under Ar-atmosphere (Scheme 33; **3y**). Substituents like bromo, chloro, cyano, formyl, nitro, trifluoromethyl, iodo, and nitro group on polyfluorobenzene were tolerated under the reaction condition. It was found that in many cases electron deficient polyfluoroarenes gave a higher yield of products that may be due to more acidity of aromatic C—H bond (Scheme 33; **3y**). It was also found that polyfluoroarenes have two different C—H bonds, those C—H bonds were activated which were present between two C-F bonds (**3yb**, **3yd**, **3ye**, **3yf**, **3yh**). The less reactive 1,3,5-trifluorobenzene also reacts smoothly under the reaction condition (**3yi**).

Based on the DFT studies, they proposed a possible mechanism for the heteroarylation reaction of polyfluoroarene (**1y**) using *N*-phenylpyrazoles (**2y**) as depicted in Fig. 13. The reaction initiates with the formation of Ag-ArFn complex (**A′′**) by the C—H bond activation of



Scheme 32. Au-catalyzed homo- and hetero-coupling reactions.

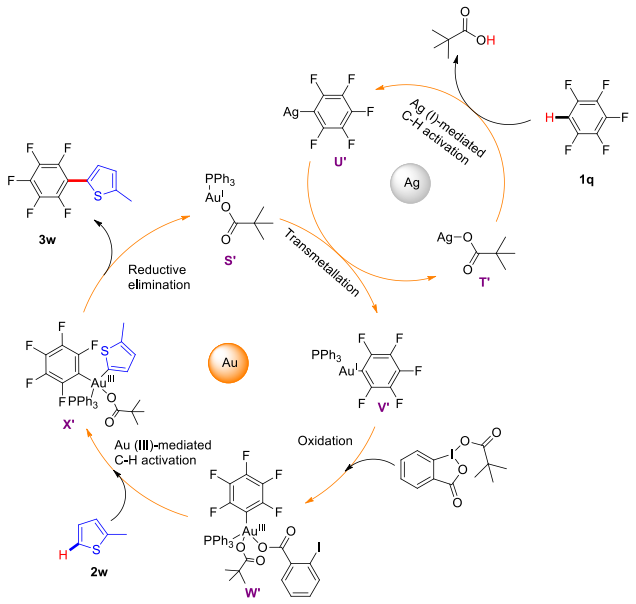
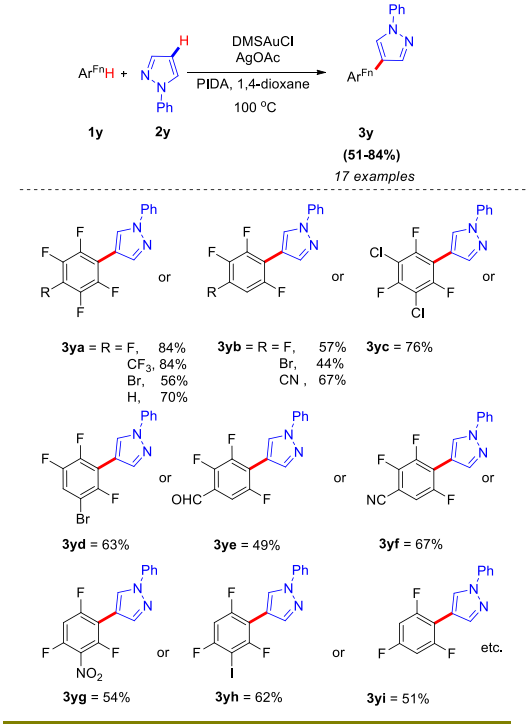


Fig. 12. Proposed mechanism for Au-catalyzed heteroarylation of pentafluorobenzene (**1q**).



Scheme 33. Au-Ag dual catalyst for heteroarylation of polyfluoroarene (**1y**).

polyfluoroarene (**1y**). Subsequent, *trans*-metallation generates Au(I)-ArFn intermediate (**B′′**) which after oxidation by PIDA gave intermediate **C′′**. Now, C—H bond activation of pyrazole ring of intermediate **C′′**, generates Ar-FnAu(III)pyrazole intermediate (**D′′**). Finally, reductive elimination liberates the desired product (**3y**) and pre-catalyst (DMSAuCl).

Conclusions and future outlook

Through this review, we covered coinage metal-catalyzed or-mediated oxidative heteroarylation of activated arenes or arenes containing

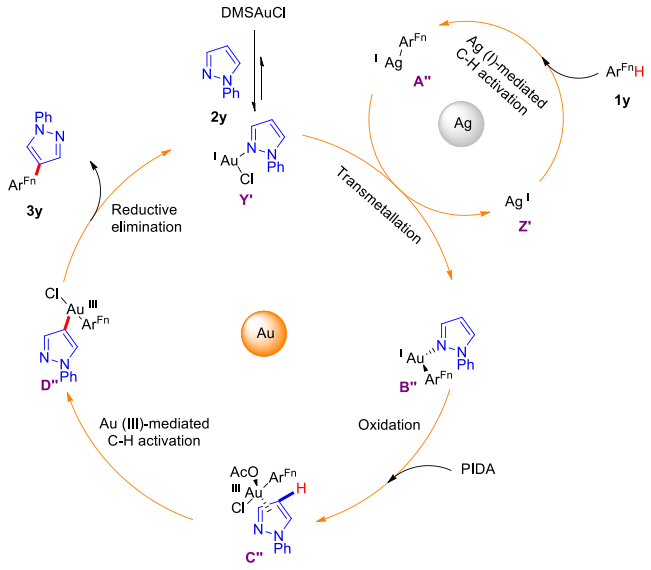


Fig. 13. Possible mechanism for Au-Ag dual catalyzed heteroarylation of polyfluoroarene (**1y**).

DG. The utilization of directing groups has enabled the oxidative heteroarylation of arenes by coordinating the directing group, which controls the selectivity and efficiency of the reaction. This led to the synthesis of a variety of heteroarenes-containing molecules. On the other hand, the development of strategies employing activated arenes has expanded the scope of substrates amenable to these conversions, offering new opportunities for the construction of diverse bioactive compounds. Since oxidative C—H bond activation has gained considerable attention for economic transformation, future development is expected, including m- and p-selectivity.

CRediT authorship contribution statement

Abadh Kishor Jha: Writing – review & editing, Supervision. **Shankar Kumar:** . **Rangnath Ravi:** Writing – review & editing. **Akanksha:** . **Sahil Roy:** Writing – original draft. **Vikesh Kumar Jha:** Writing – review & editing. **Sangeeta Gupta:** Writing – original draft. **Poonam Yadav:** Writing – review & editing. **Akshaya Kumar Rauta:** Supervision. **Anil K. Aggarwal:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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