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REVIEW ARTICLE

Transition Metals Catalyzed Direct C-H Chalcogentaion of Arenes and Heteroarenes

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Abstract: Transition metals catalyzed C-H bond activation reactions have appeared as an emerging field to introduce different functional groups in the inactivated saturated and unsaturated C-H bonds. C-S and C-Se bond constructions in aromatic scaffolds are very interesting due to the important applications of organochalcogen reagents in pharmaceutical chemistry and the material world. The introduction of sulphur or selenium moiety to an inert C-H functionality of an arene under transition metal catalysis has become one of the prime challenges and targets in recent years. In this perspective, various transition metals such as Cu, Ni, Co, Pd, Rh, Ru *etc*. have been extensively studied. Aromatic arenes owning bearing suitable directing groups appeared as the most promising coupling partners to selectively synthesize differently substituted aryl sulfones and aryl sulfides/selenides. The synthetic strategies were highly convenient owing to the regioselectivity of products, broad substrate scope, mild reaction conditions and excellent functional group tolerance. The current review article comprehensively summarizes the extent of C-S/Se bond formation *via* transition metal-catalyzed C-H bond activation with the assistance of directing groups to govern the site selectivity.

Keywords: Transition metal catalysis, sulfenylation, selenylation, C-H activation, diaryl diselenides, directing groups.

1. INTRODUCTION

Transition metals promoted catalytic reactions have reached a paramount level of sophistication and have been enriched by the incorporation of chalcogen atoms into activated C-H bond functionalities, emerging as outstanding strategies in modern organic synthesis.[1-8] In addition to the significant advancements in organometallic chemistry, notable innovations have been achieved in the area of C-Z (Z = S, Se) bond constructions as these structural motifs demand massive applications in pharmaceutical chemistry, [9, 10] material science[11, 12**]** and fluorescence spectroscopy [13, 14]. Due to prevalent structural fragments, acceptable stability and excellent functionality, the C-H bond in the aromatic ring has been extensively analysed in organic chemistry [15-17]. In the past few years, researchers have successfully employed transition metal catalysis to achieve C(sp2)-H bond functionalization reactions such as C-H halogenation[18, 19] oxygenation [20, 21] acylation [22] and alkylation [23, 24]. Synthesis of aryl-substituted chalcogenides *via* traditional methods involves harsh reaction conditions, poor functional group tolerance, elevated reaction temperature and affording minimum yields. However, transition metal-catalyzed direct transformation of an unreactive C(sp2)-H functionality to a C-chalcogen framework has emerged as a powerful tool to realize enormous promising conversions as these methodologies require mild reaction conditions, step and atom economy, sustainable and environmentally benign green protocols.[25-27] The ease of selective cleavage of a particular C-H bond of arenes is overwhelmed by the presence of directing groups and assistance of coordinating ligands which directs a transition metal atom into the close proximity of a specific C-H centre.[28-30] Besides, the strong coordinating nature of the chalcogen atoms (S and Se) has enabled them to get incorporated into an inert C-H motif. The excellent regioselectivity, site-selectivity, wider substrate scope and outstanding functional group compatibility of the arenes undergoing C-H bond functionalization reactions under standard protocols have been at the forefront of our current investigations.

In the past few years, activated C-H bond functionalization reactions of arenes under metal- and solvent-free protocols have extensively been employed to highlight the significant contribution to the sustainable development of green chemistry [31-34]. It is worth mentioning that the advancement of novel and practical catalytic methods involving C-S/Se bond constructions through transition metal-promoted direct C-H activation is still less explored in comparison to C-C, C-N and C-O bond functionalization reactions. In con-

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trast to conventional transition metals assisted cross-coupling transformations, the strategy for direct C-H functionalization is notably convenient because it avoids prefunctionalized substrate, minimizes poisonous waste production, and always requires mild reaction conditions, step and atom-economic approach, eco-friendly and greener techniques.[26, 27, 35-38] Although an impressive number of catalytic approaches have been designed to focus on this issue, the most popular one involves the use of reactants anchored with various recognized directing groups (DGs) which represents an excellent methodology to achieve unique selectivity and reactivity patterns [39-43]. The role of a directing group is not only to promote the C-H activation but also to control the chemo- and regioselectivity of the reaction. In addition, the substrate acting as pincer-type ligand is found to stabilize the transition metal complexes.

It is of note that in recent times, the chemistry of C-H activation of arenes has been enriched by cobalt, [44, 45] nickel [46] copper [47, 48] ruthenium [49] rhodium [50, 51] and palladium [52] metal-based catalytic systems. The organometallic complexes of these transition metals have emerged as omnipresent and efficient catalysts for C-H bond functionalization and the subsequent construction of diversified carbon-chalcogen bonds. Indeed, the 3d and 4d transition metal catalysts by virtue of their electronic properties could complement the C-H functionalization with reference to activity, selectivity, substrate scope and functional group compatibility. This idea appears to be interesting and attractive from an eco-friendly and atom-economical viewpoint. Nevertheless, with these advantages, the development of viable and innovative catalytic protocols using 3d and 4d transition metals is still a growing field.

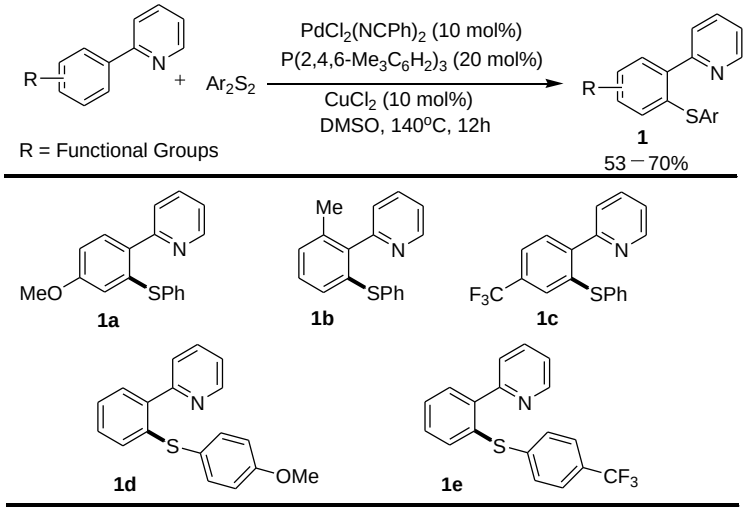
Based on the pioneering studies, although a plethora of transition metals mediated chelation guided *ortho*-directive C-H bond functionalization reactions of arenes has been documented in the literature, however, reports on *meta*- or *para*-directive C-H activations would remain comparatively less unveiled and are far restricted to a limited approach. The authors, with their long-standing curiosity, intended to explore a current comprehensive and organized overview for the construction of selective C-S/C-Se bond *via* transition metal promoted directing group assisted C-H bond activation of arenes. In this perspective, the catalytic transformations employed herein are subjected to be advantageous and environmentally friendly, which essentially involve the use of cost-effective, non-poisonous, commercial-grade reagents and environmentally benign solvents.

2. C(SP2)-H SULFENYLATION/SULFONYLATION OF ARENES

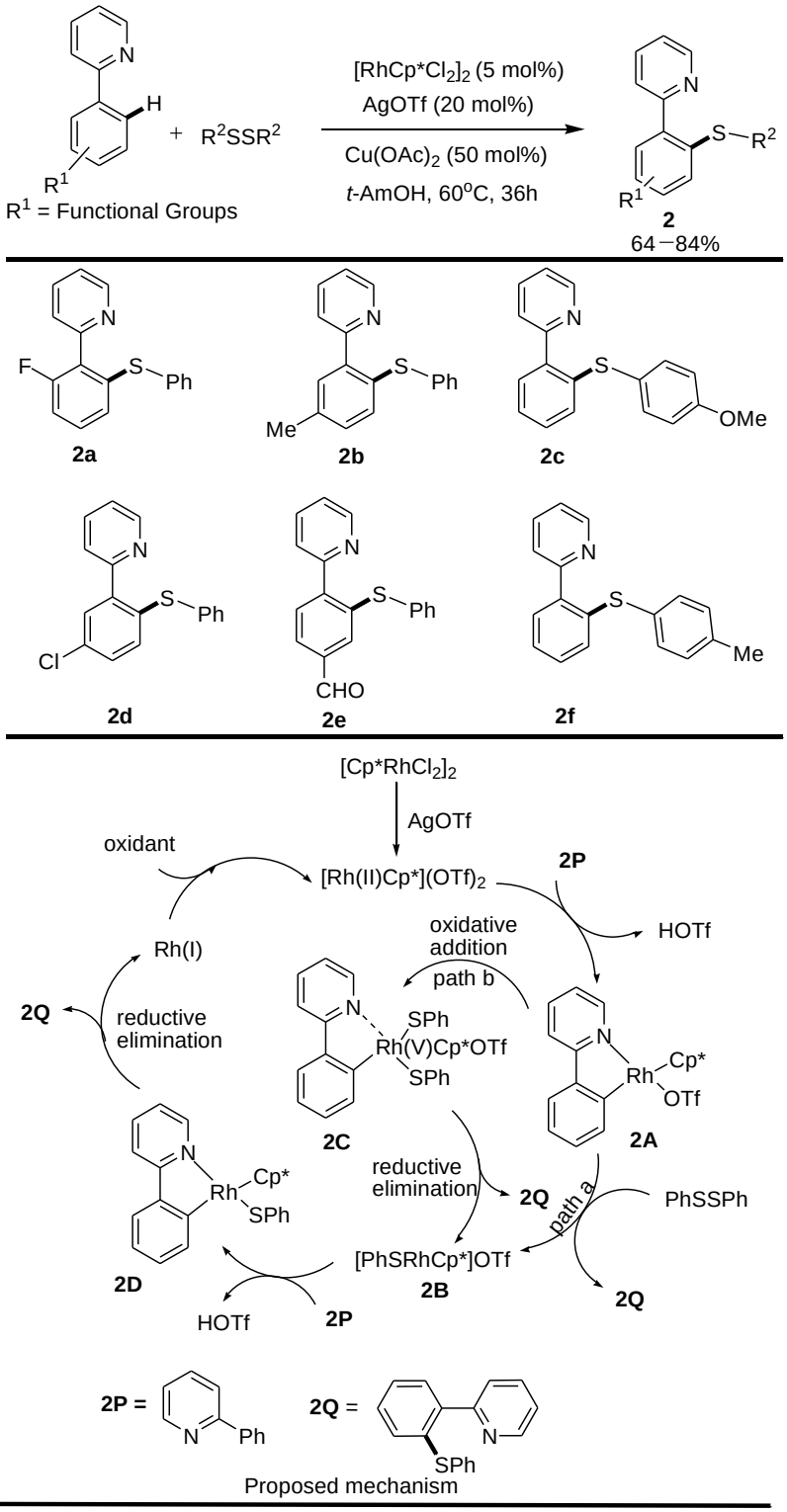
In the last decade, researchers have witnessed the decoration of numerous synthetic methods for site-selective sulfenylation and/or sulfonylation of aromatic compounds *via* activated C-H bond functionalization reactions. The classical approach involving chelation-assisted C-H sulfenylation is less unveiled, probably because the organosulfur reagents are supposed to act as a catalyst poison [53, 54]. However, significant innovations have been developed by various research communities to enrich this area to a great extent. In the forthcoming section, the authors made an endeavour to focus on the selective sulfenylation and/or sulfonylation at different positions of aromatic arenes.

2.1. Ortho Selective C-H Sulfenylation/Sulfonylation

Transition metal promoted direct thiolation at activated C(sp2)-H centres of directing groups anchored aromatic arenes emerged as the most powerful and practical approach for the preparation of well-functionalized aryl sulfide frameworks [55, 56]. In view of that, Iwasaki *et al.* designed and devised 2-phenylpyridine derivative and diaryl disulfide in the presence of copper and palladium co-catalysis (Scheme **1**) [57]. It was worth noting that the addition of phosphine ligand accelerated the catalytic route and influenced the reaction yields. A variety of desired monothiolated products were afforded by 2-phenylpyridines possessing various electron-rich and electron-deficient substituents at ortho and para positions. The catalytic path was anticipated to follow a Pd(II)/Pd(IV) mechanism. A detailed study on H/D exchange experiment as well as the kinetic isotope effect (KIE), also indicated that the cleavage of the C-H bond was not involved in the rate-determining step.



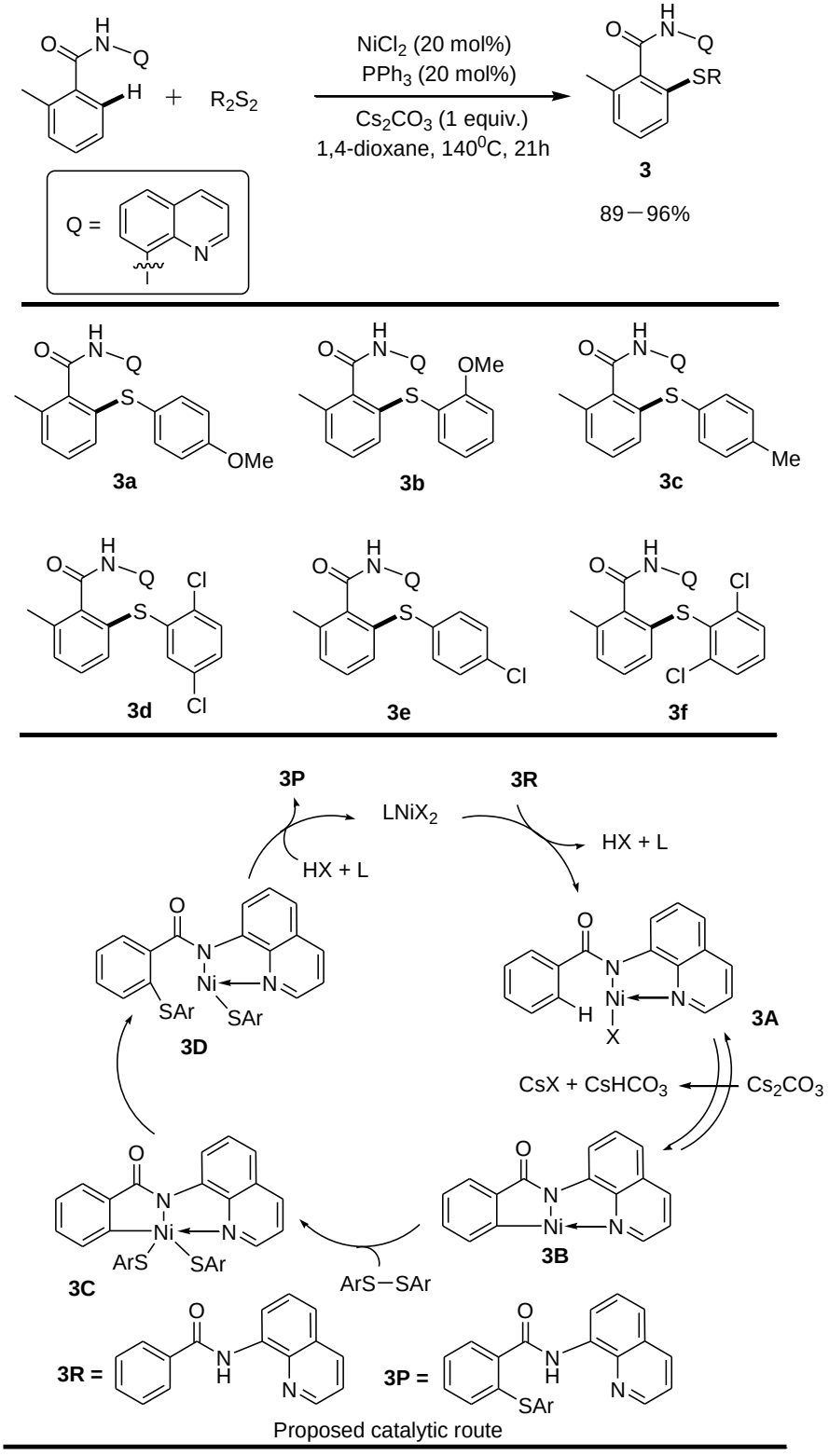
Scheme 1. Pd-promoted direct ortho sulfenylation of arenes with diaryl disulfides.



Scheme 2. Rhodium catalyzed ortho mono-thiolation of 2-phenyl pyridines.

Yang *et al*. developed an easy and practical rhodium-promoted catalytic route to derive aryl thioethers *via* direct C-H bond activation of directing group anchored arenes [58]. Addition of AgOTf as an additive and Cu(OAc)2 as an oxidant was found to improve the reaction yield remarkably. The substrates tolerated well with various -deficient and electron-releasing substituents at different positions of the phenyl ring were efficiently coupled with aryl sulfides, resulting in the desired ortho sulfenylated products in good to excellent yields (Scheme **2**). Besides, the aryl sulfides, irrespective of the electronic effects of the functional groups on the phenyl ring, displayed faster reaction rates. The site selectivity, broader substrate scope, functional group compatibility and optimal reaction protocol also enriched the phenomenon of direct C(sp2)-H sulfenylation.

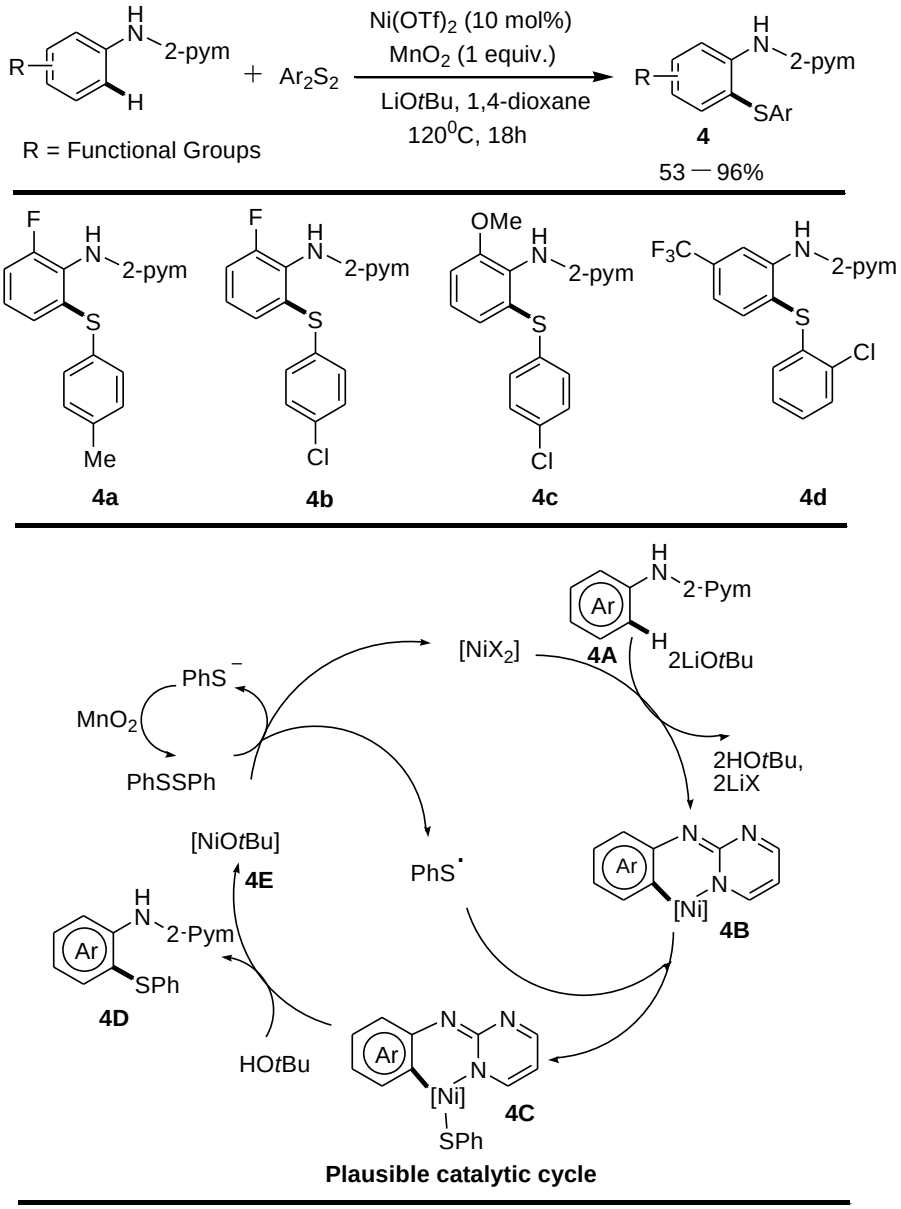
With a view to throwing some light on the direct sulfenylation of arenes *via* activated C(sp2)-H bond functionalization, Reddy and co-workers assembled bidentate directing group linked benzamide derivatives and diaryl disulfides to synthesize ortho sulfenylated thioethers in exclusively superior yields [59]. The authors also analysed the screening of solvents and bases and found that the presence of Ni(II) catalyst in combination with PPh3 ligand and Cs_2CO base facilitated the sulfenylation reaction predominantly. Diaryl disulfides bearing electron releasing and withdrawing substituent(s) afforded desired ortho selective coupling products in excellent yields (Scheme **3**).



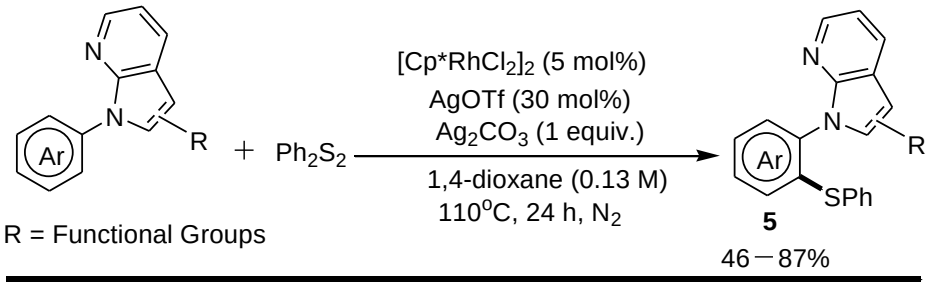
Scheme 3. Nickel catalyzed direct C-H activation of benzamide derivatives.

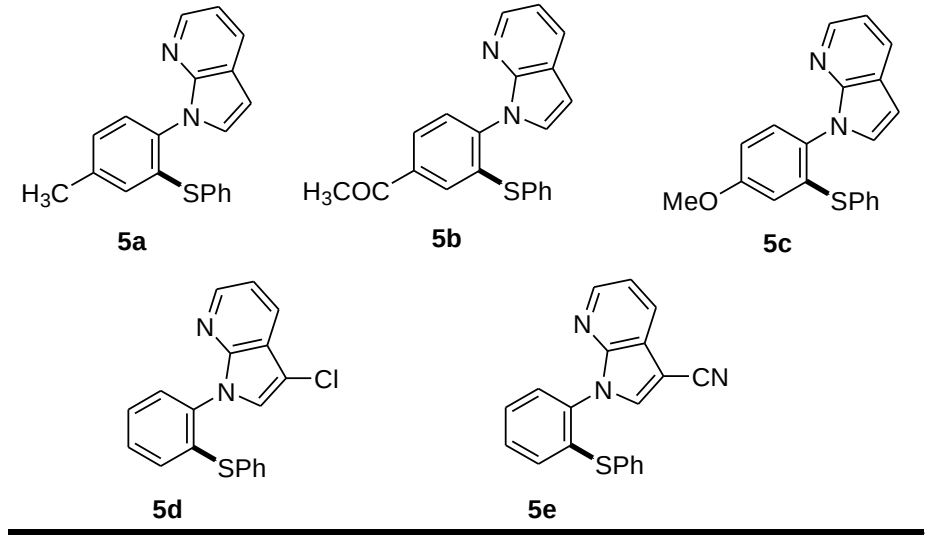
Müller and Ackermann introduced a ligand-free nickel(II) catalytic route to study the thiolation of pyrimidyl group anchored anilines *via* direct C-H bond activation under ligand-free situation (Scheme **4**) [60]. The site-selective ortho sulfenylation proceeded smoothly when well-tolerated anilines were subjected to react with diaryl disulfides. Notably, disulfides possessing electron donating andelectron-withdrawing groups in the phenyl ring preferred ortho-sulfenylation with highly regioselective yields. A detailed study on reaction mechanisms argued in favor of a single electron transfer (SET) type process and C-H bond activation in the rate-limiting step. The efficiency of this optimized protocol in C-H functionalization could be rationalized in terms of ample substrate scope, regioselectivity, and excellent functional group tolerance.

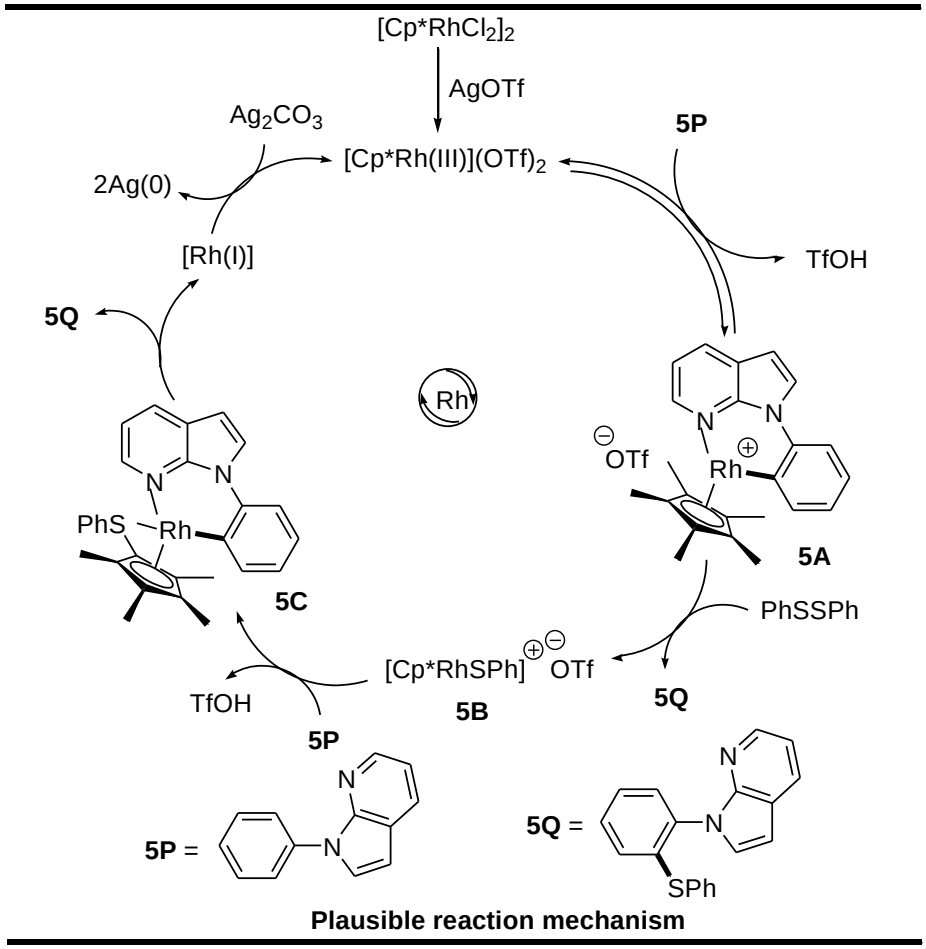
The 7-azaindole, a unique structural motif, widely exists in various pharmaceutical agents and natural products.[61, 62] In 2018, Deb and research group reported rhodium metal-catalyzed direct and selective thiolation at activated C(sp2)-H bond functionalization for the synthesis of *ortho* thiolated azaindole derivatives in the presence of silver triflate as an additive and silver carbonate as an oxidant in 1,4-dioxane solvent under nitrogen atmosphere [63]. C-H thio-functionalization of N-aryl azaindole at ortho position could remarkably be achieved when the substrate interacted with diphenyl disulphide under standard condition. This optimized reaction protocol furnished a variety of ortho products with desirable quantities (Scheme **5**). Moreover, azaindole derivatives possessing electron-deficient groups like chloro and cyano at the C-3 position resulted good to excellent yields. The catalytic protocol was also successful with diselenides performing C-H selenylation in the same substrates.



Scheme 4. Thiolation of arenes with differently substituted diaryl sulfides catalyzed by nickel.



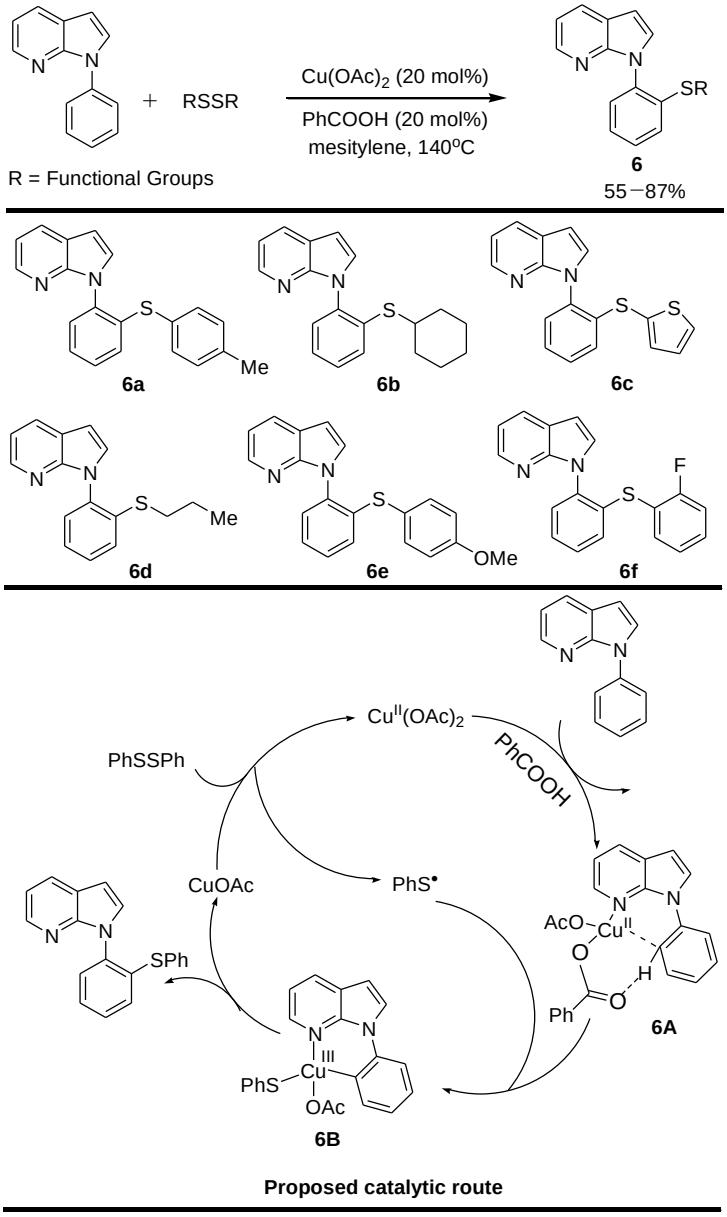




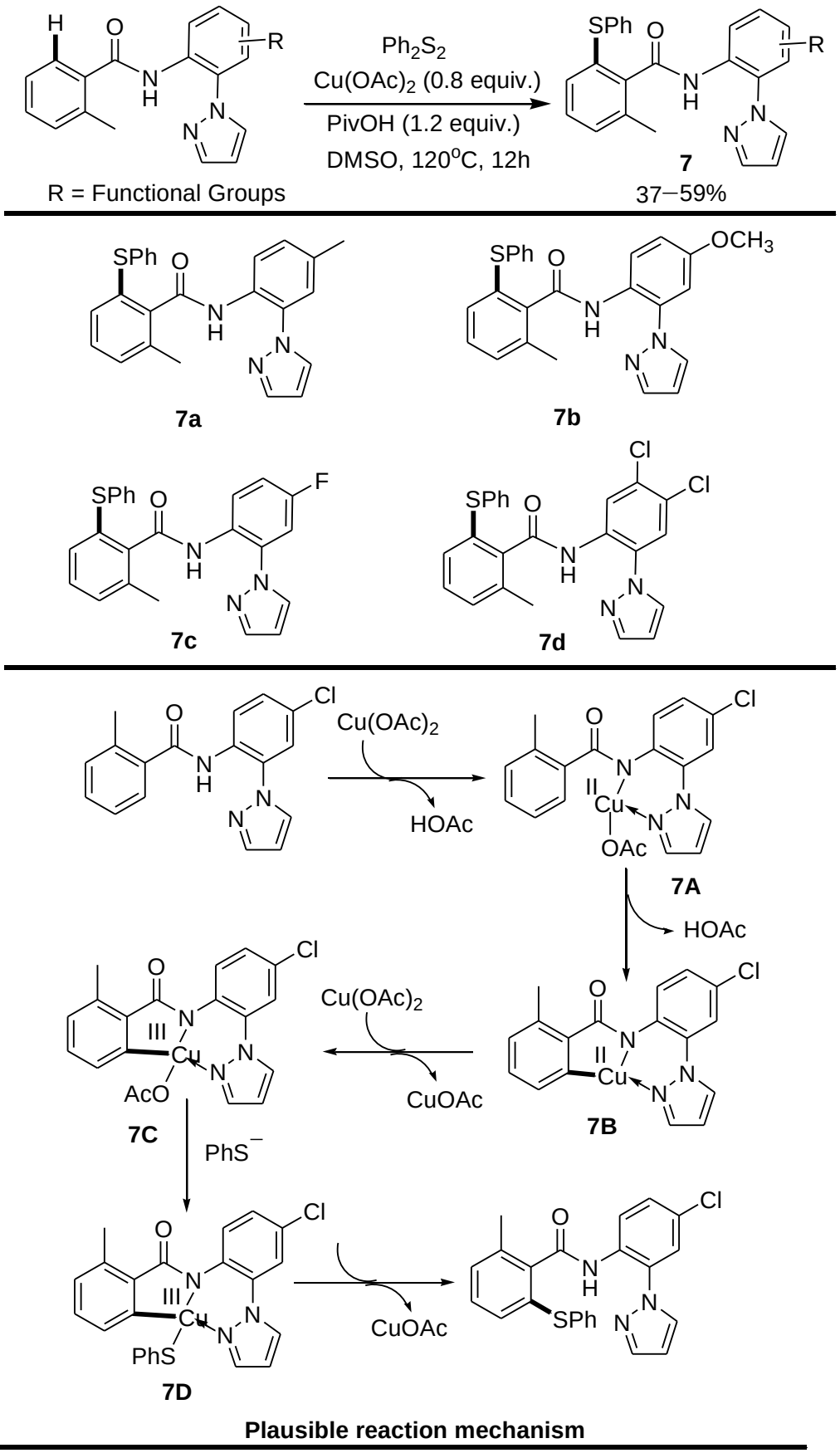
Scheme 5. Rhodium catalyzed thiolation of N-aryl azaindoles.

Inspired by the report of the Deb group, the Duan group described an explicit study with respect to copper-mediated *ortho*-C-H sulfenylation of N-aryl-7-azaindoles [64]. A wide variety of N-aryl-azaindole derivatives possessing electron-rich and electron-poor substituents underwent smooth coupling with disulfides in the presence of benzoic acid as an additive under heating at 140oC in mesitylene (Scheme **6**). This catalytic approach displayed ample substrate scope, high conversion efficiency and good compatibility with different substituents. Based on various evidential facts, the authors proposed a SET-type mechanism where the complexation of 7-azaindole with Cu(OAc)2 in the presence of C_6H_5COOH led to the formation of Cu(II) species **6A**. Subsequently, the sulfenyl radical obtained from the homolytic cleavage of Ph2S2 oxidized **6A** to deliver Cu(III) intermediate **6B**, which, after reductive elimination, furnished the desired *ortho*-selective product along with Cu(I) species. Oxidation of Cu(I) regenerated the active catalyst Cu(OAc)2 to run the next cycle.

Deng and his research colleagues demonstrated a copper-assisted selective and direct *ortho* sulfenylation of benzamide derivatives through the activation reaction of inert C-H bond functionalities (Scheme **7**) [65]. The synthetic protocol involving benzamides with broad substrate scope and well-functional group tolerance reacted smoothly with disulfides and afforded desired ortho-sulfenylated products in moderate yields. Careful screening on the solvents and catalysts indicated that dimethyl sulfoxide (DMSO) and stoichiometric quantity of Cu(OAc)2 were the best choices to monitor the reaction pathway. Various electronic substituents attached to the directing groups anchored benzamides affected the percentage of yields remarkably. Control experiments also revealed the preferential rate of reaction between electron poor benzamides and disulfides.



Scheme 6. Cu(II) mediated direct sulfenylation of N-aryl azaindoles with disulfides.

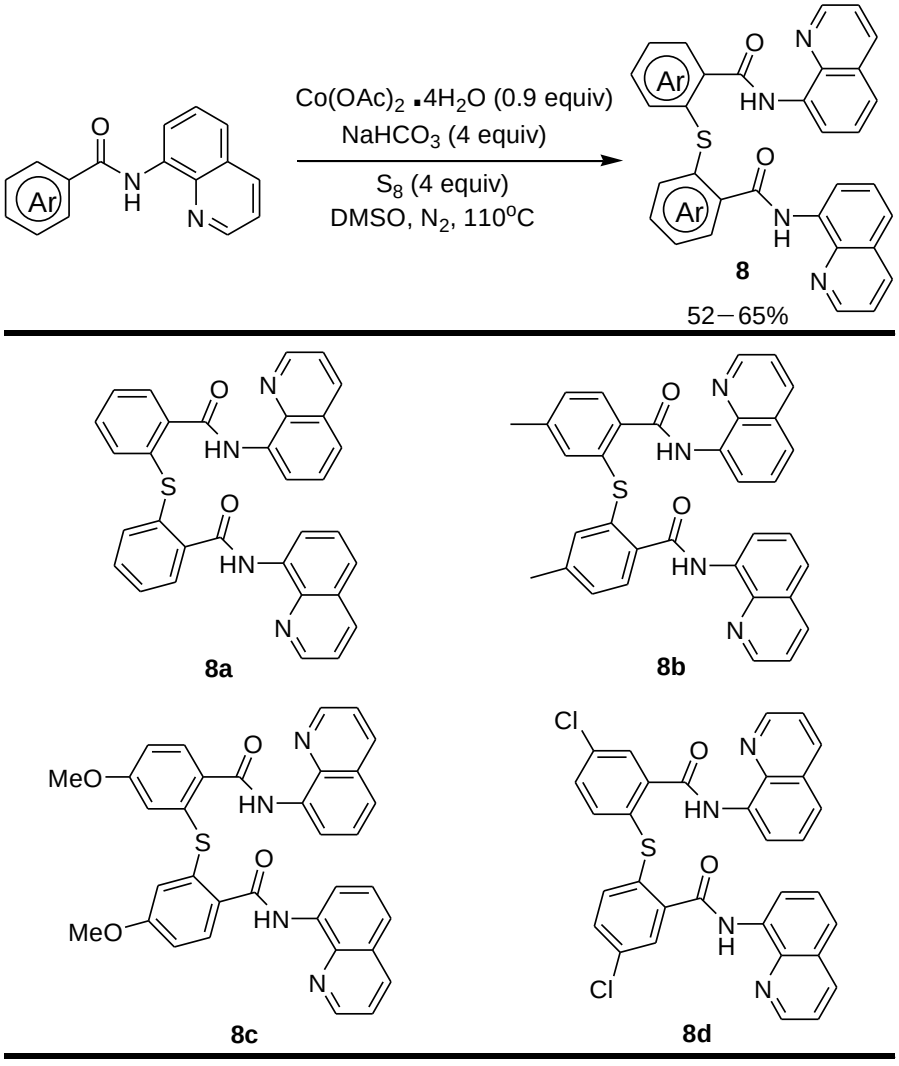


Scheme 7. Cu-catalyzed ortho thiolation of directing group anchored arenes.

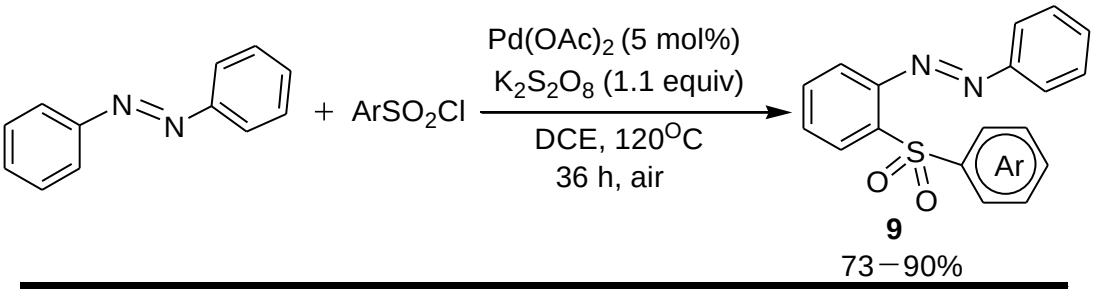
Wu and co-workers assembled aryl amides and elemental sulphur to reveal the cobalt-catalyzed synthesis of aryl sulfides through C(sp2)-H bond activation at 110oC under N2 atmosphere (Scheme **8**) [66]. The highly chemoselective catalytic process under mild reaction conditions followed a cobalt-sulphur free radical pathway where elemental sulphur played a key role in the reaction. The optimized protocol was substantially affected by both electronic and steric factors of the substituents attached to the benzene ring. A library of symmetrical diaryl sulfides was attained in moderate yields. The authors have extensively investigated that a combination of cobalt acetate, sodium bicarbonate and elemental sulphur was essential for the catalytic transformation.

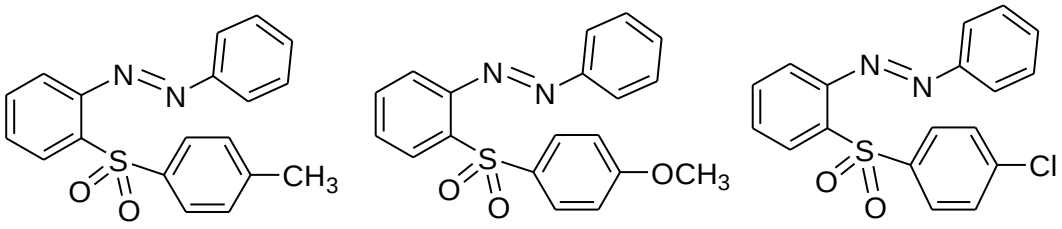
Azoarenes, an important class of chromophores derived from natural products, are found to be practically act as organic dyes, metal ion indicators, and molecular photoswitches [67-73]. With view of that, an *ortho*-selective C-H sulfonation of azobenzene derivatives employing palladium catalyst under base and ligand-free situation was reported by Zhang and co-workers [74]. The catalytic protocol was greatly influenced by the electronic nature of the substituents attached to the phenyl ring of aryl sulfonyl chloride. A series of sulfonated azobenzenes were afforded in excellent quantity. The authors have also illustrated addition and reductive elimination-based mechanistic pathways to unveil the catalytic transformation (Scheme **9**). As shown in the mechanism, the interaction of azobenzene with Pd(OAc)2 provided the Pd-species **9A** *via ortho*-palladation. Thereafter, **9A** reacted with sulfonyl radical to generate an active species **9B,** which then underwent reductive elimination to deliver the desired product *via* regeneration of active catalyst Pd(OAc)2 for the next cycle.

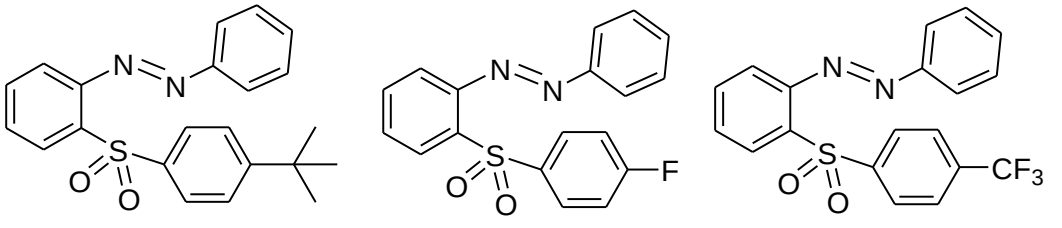
In 2018, an ortho-selective C-H arylsulfonylation of 2-arylpyridines using halogen-containing benzenesulfonyl chloride with the assistance of a palladium catalyst was reported by Sasmal and research colleagues [75]. Of particular note is that the use of Ag_2CO_3 in addition to $Cu(OAc)_2$ additive and a stoichiometric amount of $Pd(OAc)_2$ was found to improve the chemoselectivity of the products in remarkably good yields. The scope of both 2-arylpyridines and benzenesulfonyl chlorides was broad, with bromo, nitro, trifluoro methyl and chloro-substituted pyridines being excellently tolerated (Scheme **10**). Under optimized protocols, no cleavage of C-halogen moiety on both coupling partners was truly investigated by the authors.

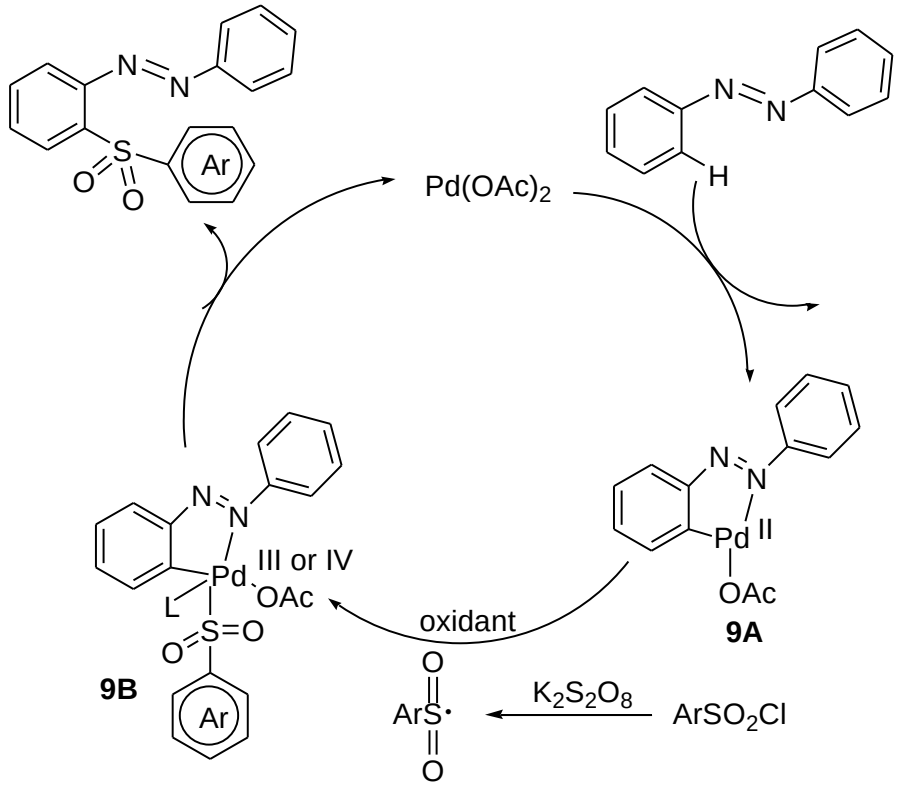


Scheme 8. Cobalt catalyzed C-H functionalization of arenes.



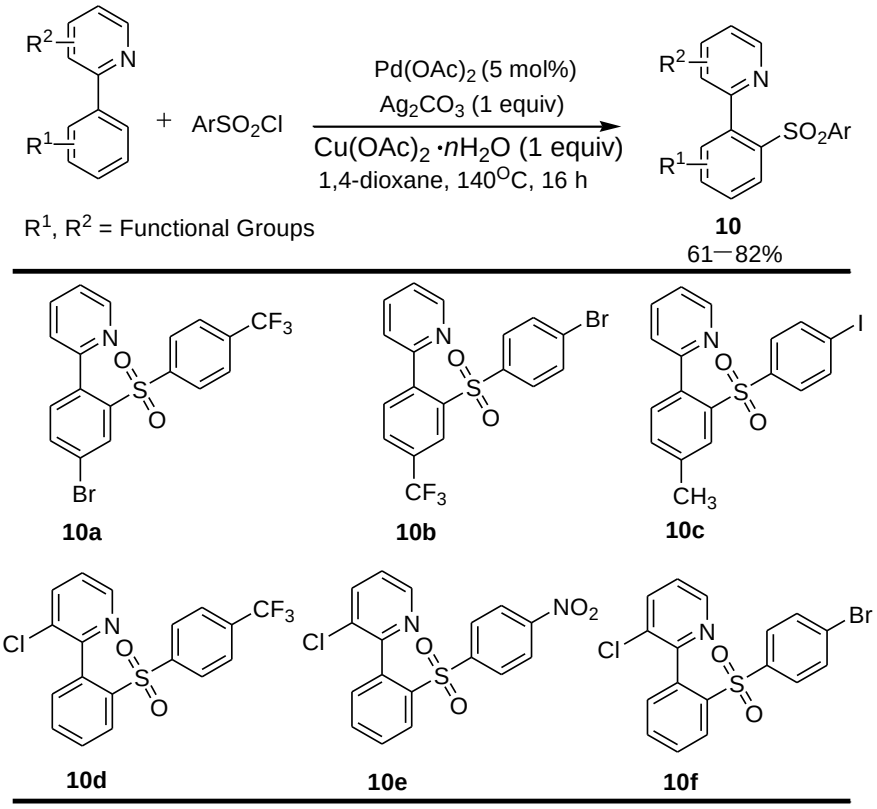






Proposed catalytic route

Scheme 9. Palladium assisted C-H sulfonylation of azobenzenes.



Scheme 10. Palladium catalyzed C-H sulfonylation of 2-arylpyridines with azobenzenes.

2.2. (Halo)-Benzenesulfonyl Chlorides

The research community has been focusing great attention on the phenol derivatives possessing diaryl sulfides as these structural frameworks are extensively employed to cure HIV, heart diseases and cancer [76-79]. Inspired by the fact, the Miura group described a direct ortho-selective sulfenylation of phenol derivatives using diphenyl disulfides as the coupling partners aided by phenanthroline auxiliary (Scheme **11**) [80]. The coupling reaction was conducted smoothly in the presence of the catalytic amount of $Cu(OAc)_2$ or CuTC (TC = 2-thiophenecarboxylate) in DMF solvent at 70oC whereby various phenolic compounds were efficiently coupled to afford both mono and dithiolated products with excellent regioselectivities. Moreover, this synthetic protocol was highly compatible with phenol derivatives and thus allowed for rapid synthesis of aryl thioethers.

In 2018, Li and Wang postulated a direct C(sp2)-H sulfenylation of aromatic amide derivatives with diaryl disulfides [81]. After scrutinizing different cobalt catalysts, CoBr2 was found to be the potential candidate to drive the catalytic transformation. It is pertinent here to note that the synthetic protocol tolerated both electron rich and electron-poor substituents on aryl sulfides as well as on the phenyl ring in benzamides which offered an easy and straightforward strategy for the synthesis of ortho-thiolated yields (Scheme **12**). This sulfenylation strategy was also applied successfully to achieve a potential antipsychotic agent called quetiapine. The authors proposed a free radical-type mechanism to be involved in the catalytic cycle. Firstly, the coordination of benzamide with CoBr2 furnished the active species **12A** which, on oxidation by DTBP delivered Co(III) species **12B**. Now, **12B** underwent reversible cobaltation leading to the formation of a cobalt cycle intermediate **12C**. Subsequently, **12C** coupled with thioether free radical to afford Co(IV) intermediate **12D**. Finally, **12D,** upon reductive elimination followed by protonation, delivered the desired sulfenylated product and led to the regeneration of CoBr2 for the next catalytic cycle.

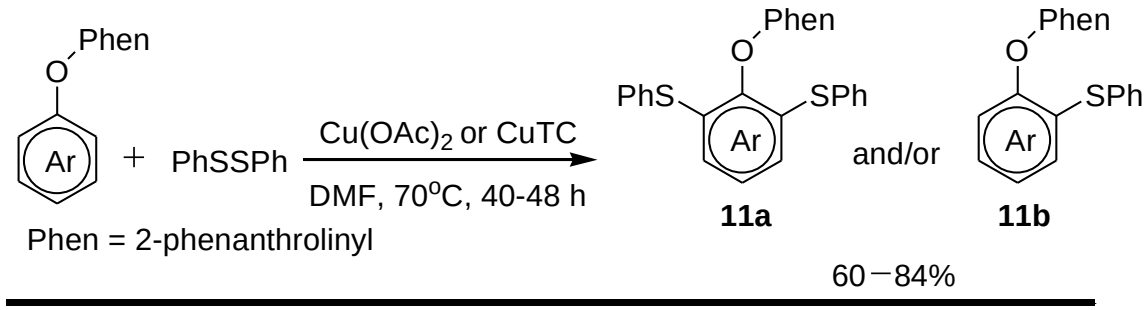
The Song group successfully employed *p*-Tosylmethyl isocyanide (TosMIC) as sulfonating agent and pyridine-N-oxide (PyO) as a removable auxiliary to address the *ortho* selective C(sp2)-H sulfonation of benzamides.**82** $NaHCO_3$ in concert with a stoichiometric amount of copper salts showed the better performance to promote the reaction and interestingly, a library of *ortho*-sulfonyl-substituted benzamide derivatives was documented with moderate to high yields (Scheme **13**). The reaction revealed a kinetic isotope effect (KIE) for deuterium-substituted benzamide and the fact indicated the involvement of ortho-C-H bond cleavage in the rate-controlling step. In addition, the authors also anticipated the mechanism where complexation between benzamide analogue and $Cu(OAc)_2$ followed by ligand-exchange delivered the species **13A**. Now, **13A** underwent intramolecular C-H bond activation to form Cu(II) complex **13B**. Subsequent oxidation of **13B** by $Cu(OAc)_2$ and tert-butyl hydroperoxide (TBHP) afforded a pincer type Cu(III) species **13C**. The sulfonyl anion formed by the dissociation of TosMIC reacted with **13C** to furnish the crucial intermediate **13D**, and finally **13D,** after reductive elimination released the desired product along with the Cu(I) species.

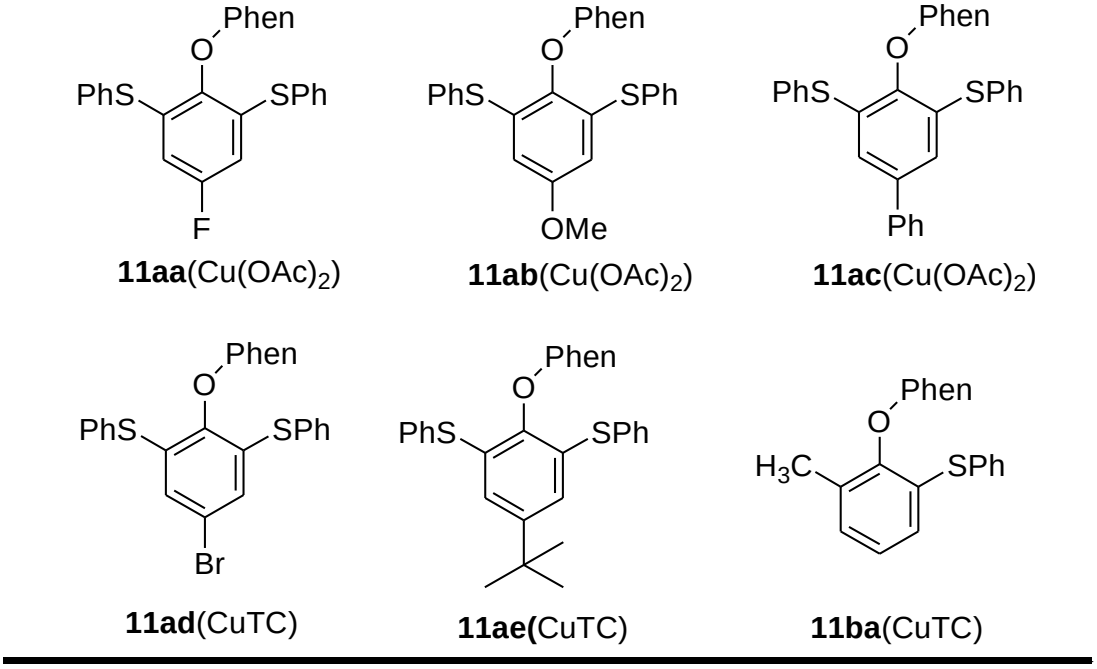
2.3. Meta Selective C-H Sulfenylation/Sulfonylation

The catalytic system owning both Ru(0) and Ru(II) complexes has unveiled a tremendously mounting topic of research in ruthenium-mediated versatile C-H bond functionalization approaches[82, 83, 84]In view of that, in 2011, Frost's research group assembled 2-phenylpyridine derivatives and aryl sulfonyl chloride to derive *meta*-selective aryl sulfones in acetonitrile medium [85]. The ruthenium promoted *meta*-selective C-H sulfonation involved chelation-mediated cyclometalation where the formation of Ru-Caryl σ-bond facilitated the para-directing effect. The coupling reaction was greatly influenced by the electronic substituents attached to the phenyl ring of both substrates. A library of sulfones meta to the chelating auxiliary resulted in moderate isolated yields (Scheme **14**). This chelation-induced synthetic protocol was found to be beneficial owing to its regioselectivity and ample substrate scope. Cleavage of the C-H bond in the rate determining step was also truly guided by a detailed survey of the kinetic isotope effect.

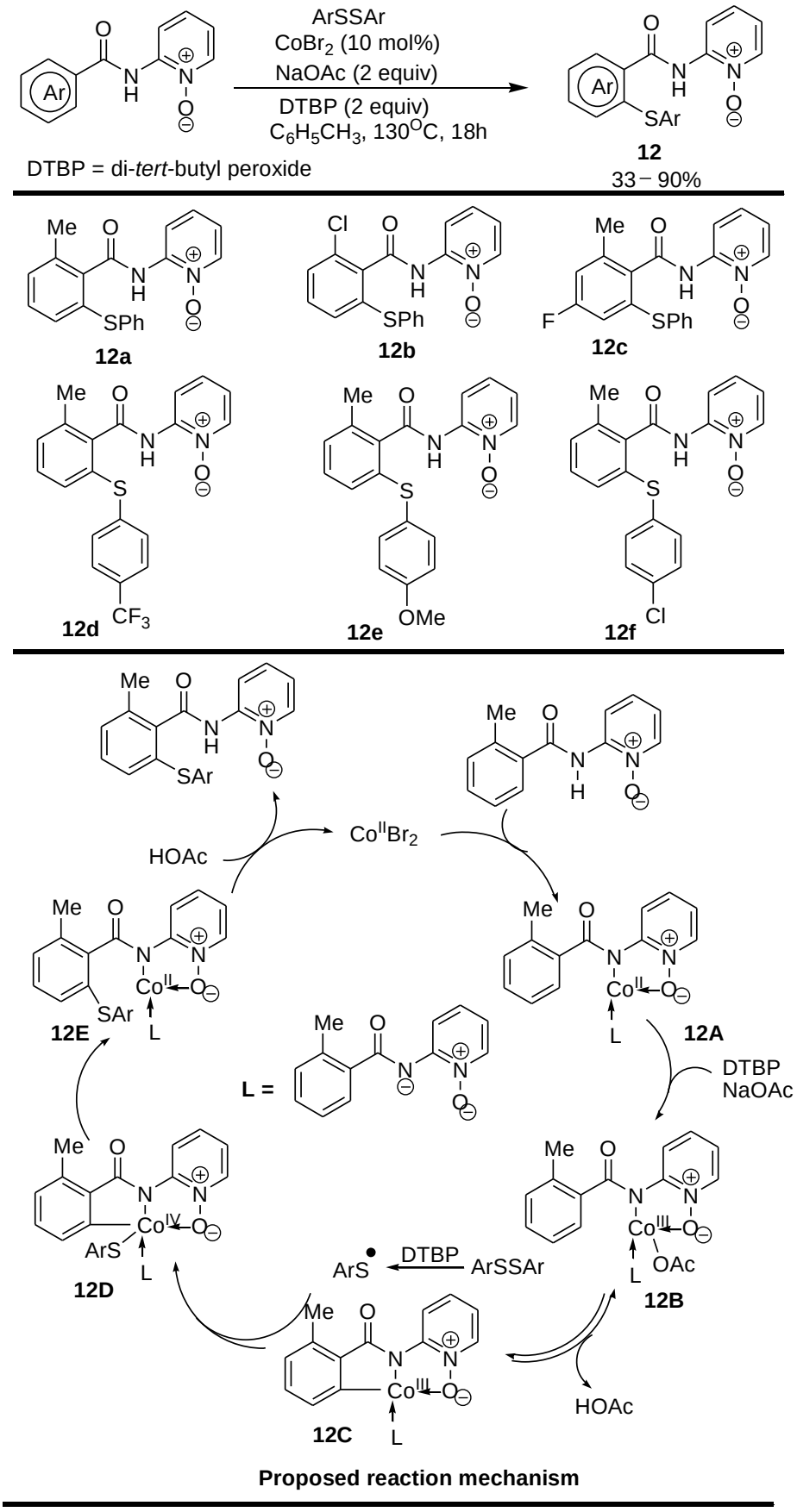
The intriguing results favouring radical trapping experiments inspired the Frost group to revise the previously hypothesized aromatic electrophilic substitution (SEAr) mechanism for *meta*-directive sulfonylation in 2016 [86]. The radical-induced catalytic pathway provided fundamental insights into each step by the isolation and characterization of active *meta*-sulfonated product, which showed evidence for preferential para-selectivity to the RuAr–C bond. The possibility of the SEAr pathway was precluded when negative aspects were caused with several sulfonating agents. Besides, the detrimental effects on the sulfonation reactions employing radical scavenger (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) were argued in favor of the reaction to proceed through the generation of a tosyl radical.

Li *et al*. documented the synthesis of aryl sulfones *via* ruthenium-catalyzed meta directive C(sp2)-H sulfonation of azoarenes by aryl sulfonyl chloride in the presence of Cs2CO3 base under N2 atmosphere (Scheme **15**) [87]. Screening of solvents would indicate that acetonitrile was a potential candidate for this catalytic transformation. A plausible catalytic route was predicted to explore the Ru(II) promoted electrophilic aromatic substitution reaction as depicted in the scheme. Ortho C-H ruthenation of azoarene by [Ru(p-cymene)Cl2]2 yielded a cycloruthenated species **15A**, which upon sulfonation by ArSO2+ ion at the para position of CAr-Ru linkage led to the formation of active species **15B**. Deprotonation of **15B** provided **15C,** which underwent proto-deruthenation to furnish the desired meta-selective sulfonated product.

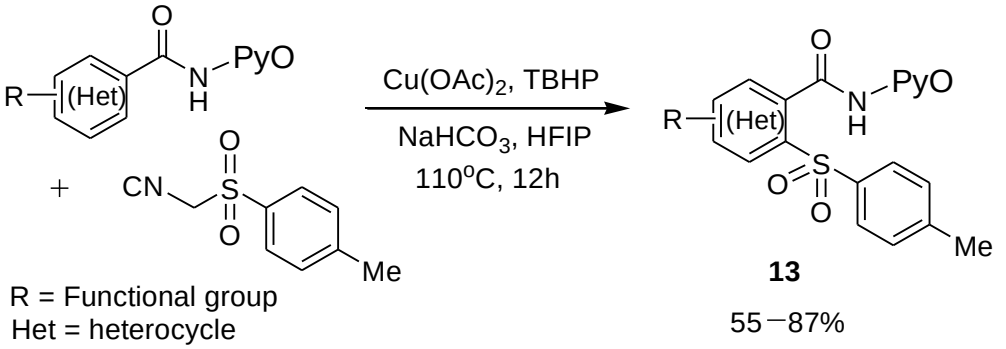


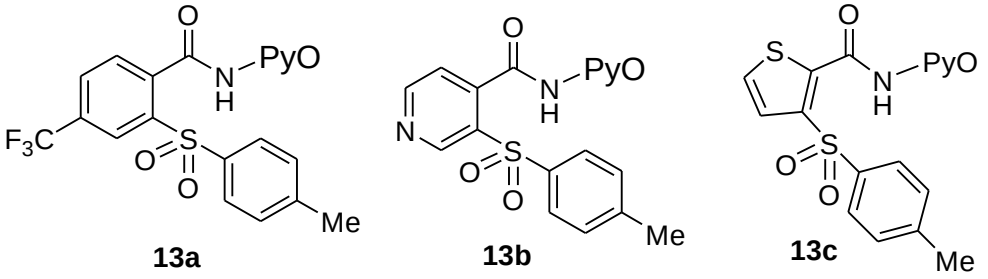


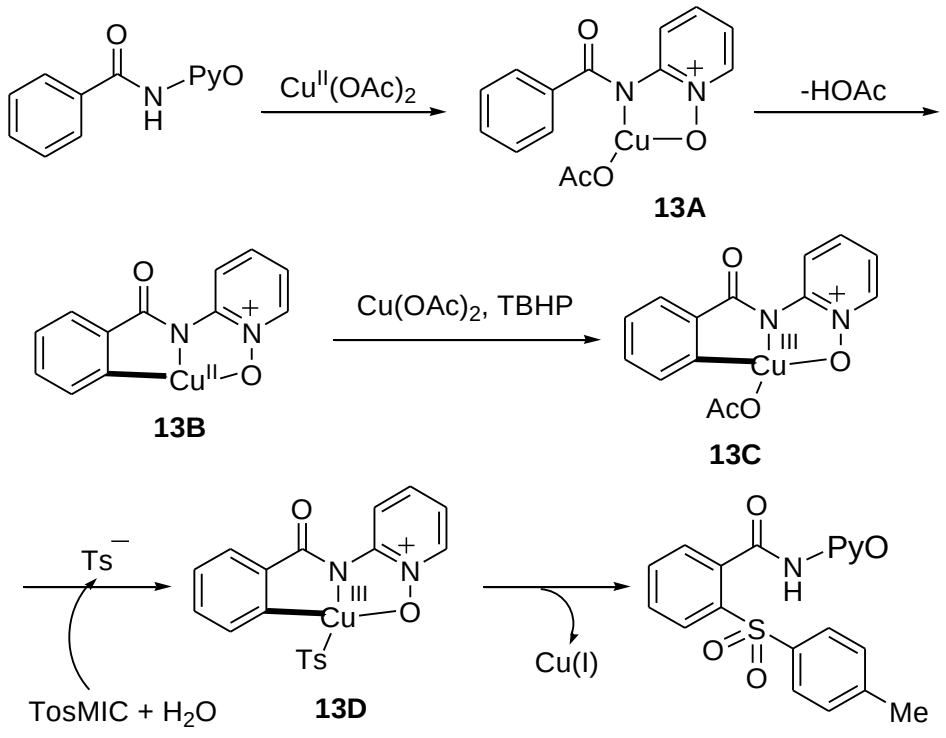
Scheme 11. Cu-promoted ortho-selective C-H sulfenylation of phenolic compounds by diphenyl disulfides.



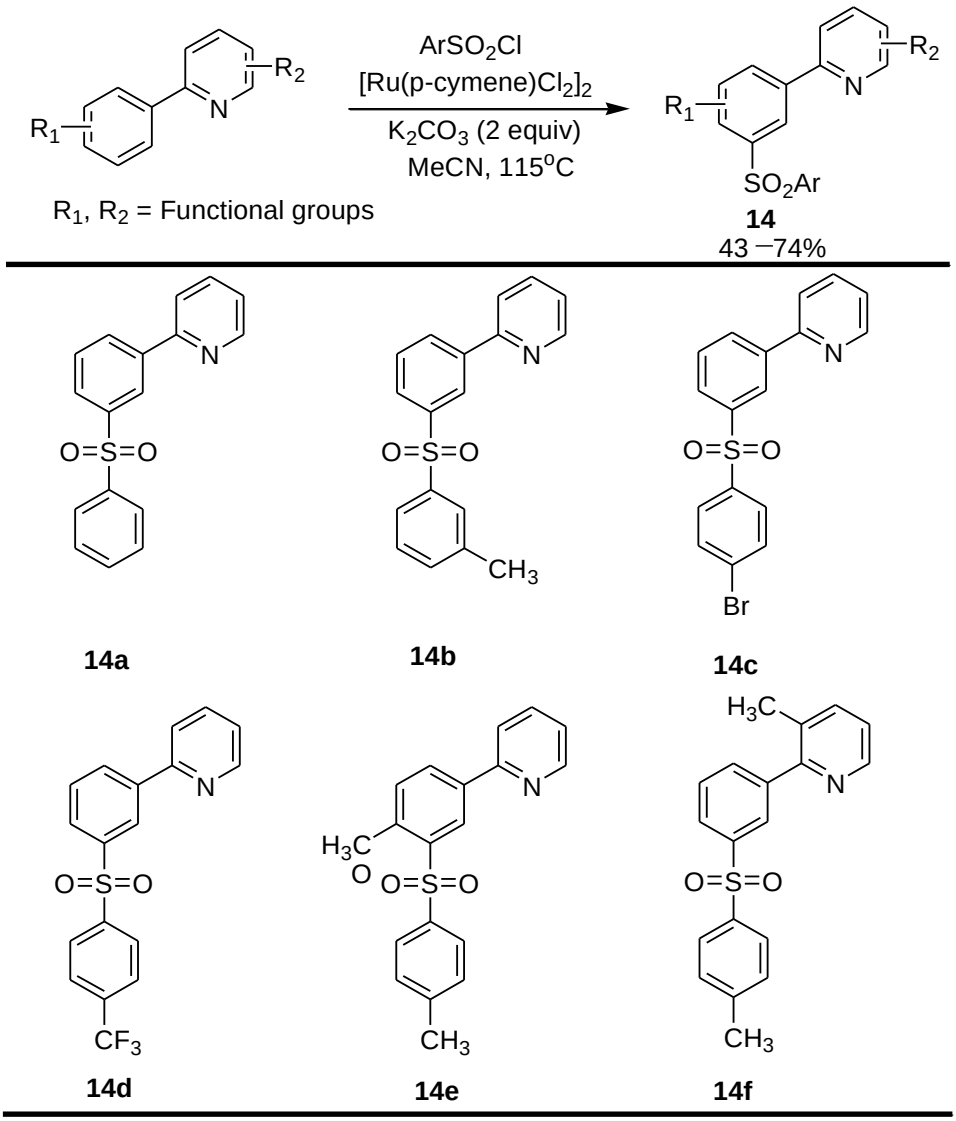
Scheme 12. Co(II) mediated direct C-H sulfenylation of benzamides.



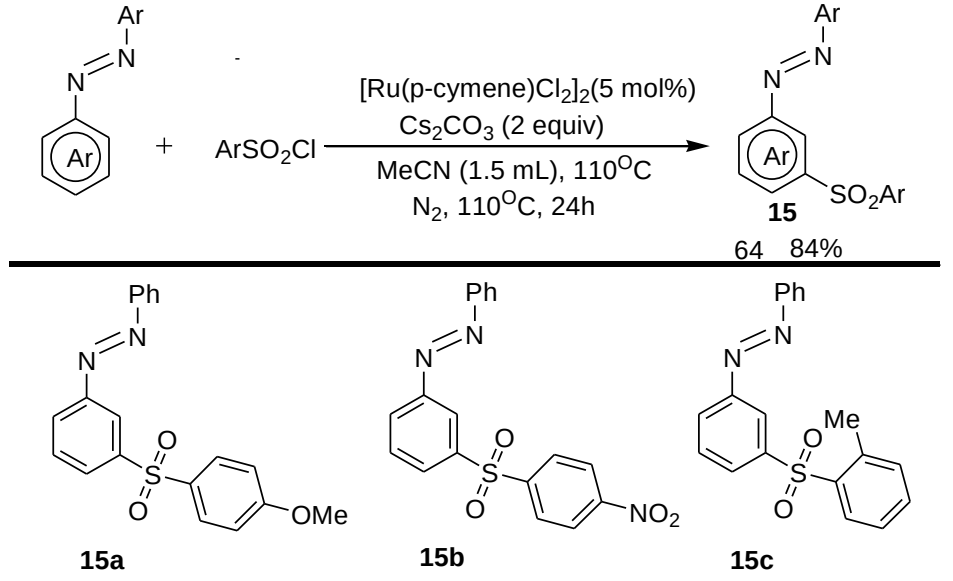




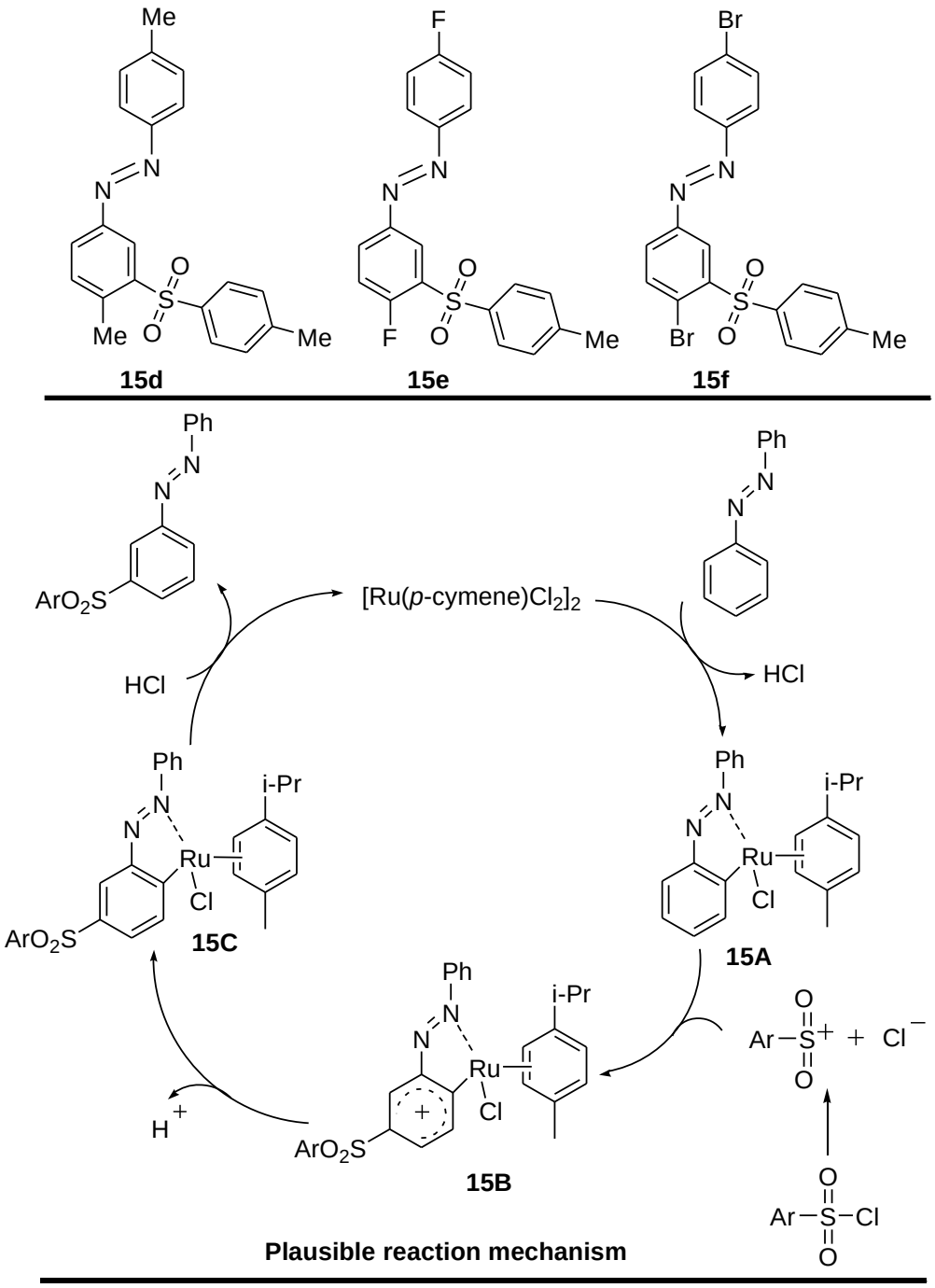
Scheme 13. Copper-catalyzed direct sulfonylation of benzamides.



Scheme 14. Ruthenium promoted meta sulfonylation of 2-phenylpyridines.



(Scheme 15) contd….



Scheme 15. Ruthenium(II) mediated meta directive sulfonylation of azoarenes.

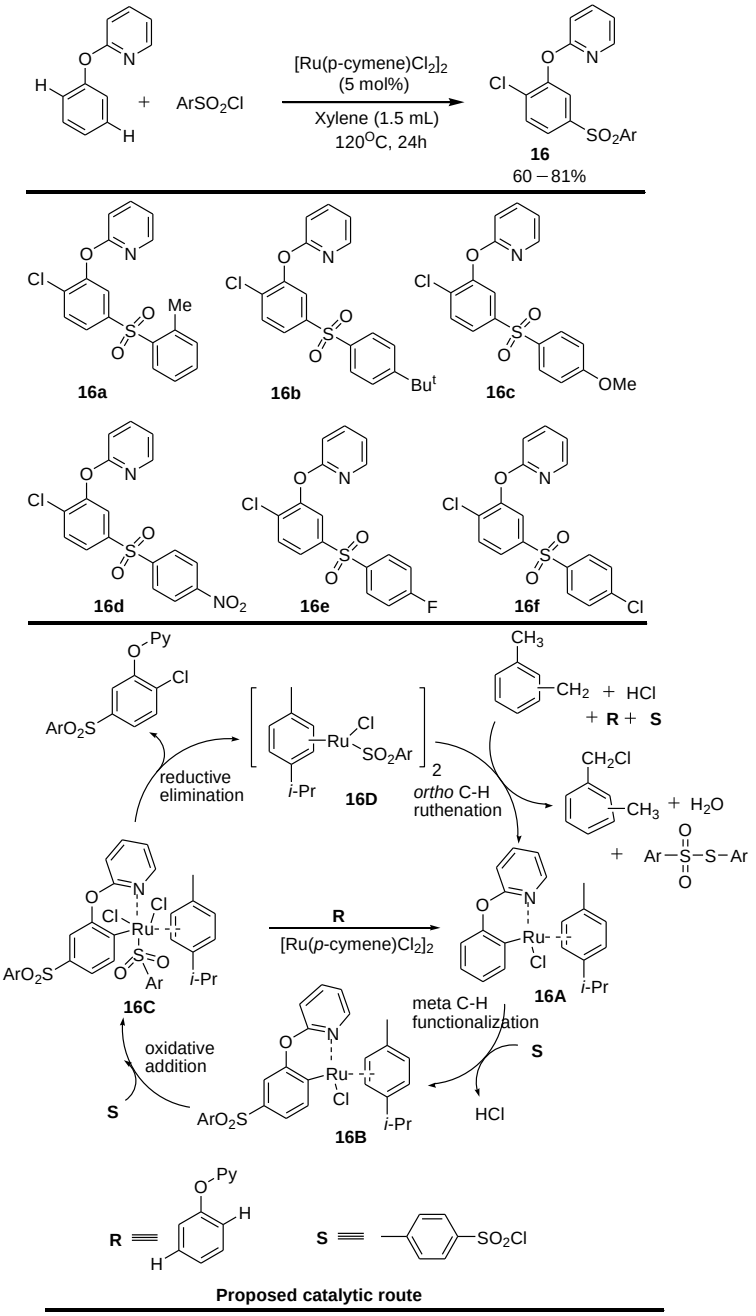
The research group of Yang explored ruthenium(II) mediated synthesis of meta-selective arylsulfonyl arenes by employing 2-phenoxy pyridine and arylsulfonyl chloride as coupling partners [41]. This catalytic protocol tolerated various electron rich as well as electron-poor substituent on arylsulfonyl chlorides and thus offered a bunch of desired meta-sulfonylated products in a remarkably higher percentage of yields (Scheme **16**). A detailed mechanistic survey unveiled that the catalytic path furnished the intermediate **16A** *via* an *ortho*-C(sp2)-H ruthenation. Thereafter, aromatic electrophilic substitution by arylsulfonyl chloride at the C-H centre para to the Ru-CAr σ-bond led to the generation of an active species **16B,** which underwent oxidative addition resulted Ru (IV) species **16C**. **16C** upon reductive elimination pathway gave Ru(II) intermediate **16D** *via* releasing the key product. The effect of chelation enhanced directing group, excellent functional group compatibility and high conversion efficiency of this catalytic system also facilitated the C-H sulfonylation strategy.

2.4. Para Selective C-H Sulfenylation/Sulfonylation

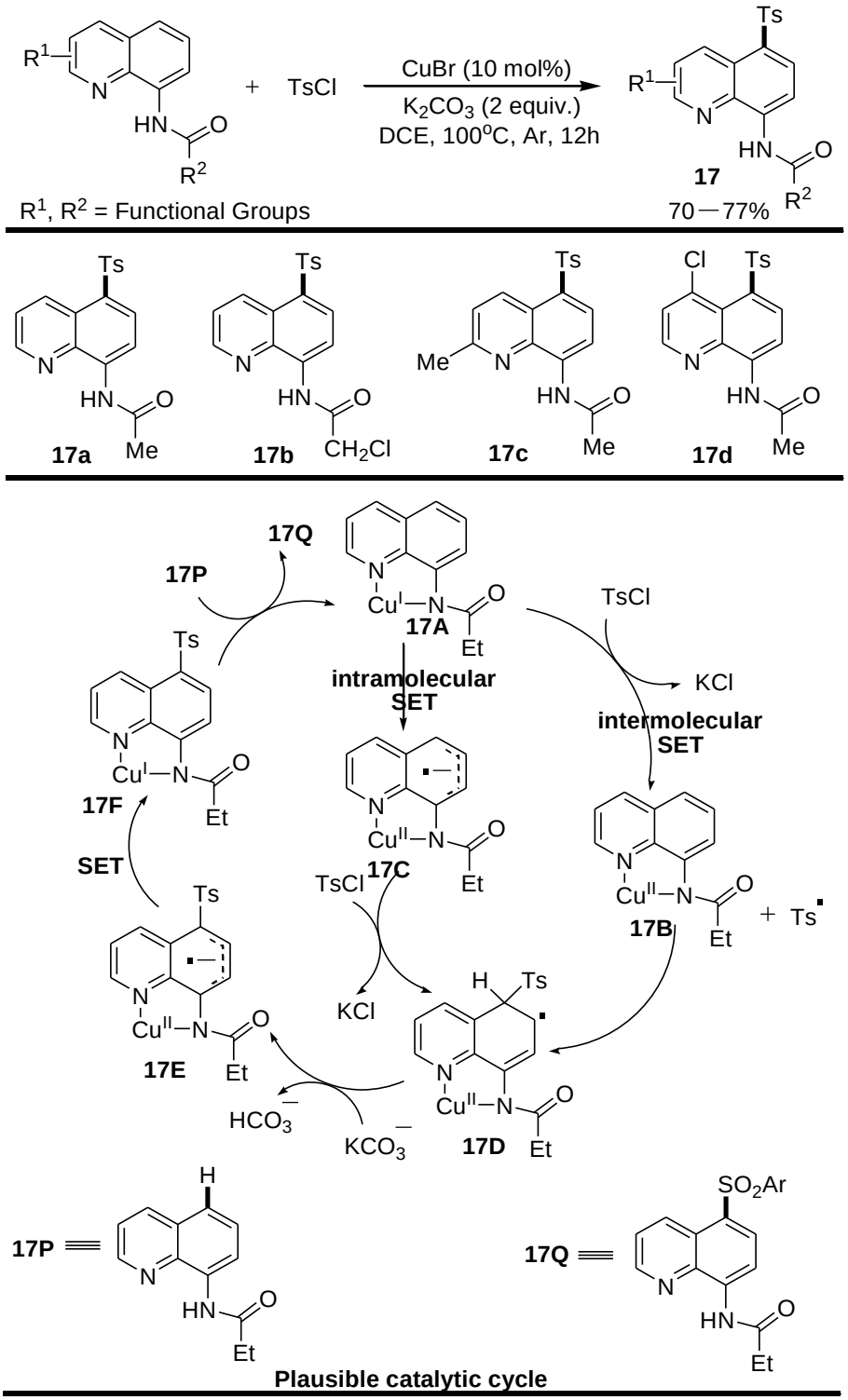
In contrast to significant improvements in transition metals-assisted direct *ortho*- and *meta*-selective C-H functionali-

zation, methodologies for *para*-selective C-H thiolation/ sulfonation remain less explored.

Zeng and research colleagues devised and decorated an easy and excellent copper promoted catalytic route for the para-selective sulfonylation of quinoline scaffolds [88]. The bidentate chelating group assisted C(sp2)-H sulfonation reaction under optimized protocol proceeded well in concert with copper(I) catalyst and K_2CO_3 base at 100oC heating under argon atmosphere (Scheme **17**). A combined study of experimental and density functional theory (DFT) calculations revealed that an excellent functional group tolerance also facilitated high conversion efficiency with moderately good yields. To explore the feasibility of the catalytic protocol, the authors also envisaged both intramolecular single electron transfer (SET) and intermolecular SET type mechanism. Firstly, 17A underwent intermolecular SET to TsCl to furnish a Cu(II) species 17B and tosyl radical whereas subsequent intramolecular SET from 17A resulted Cu(II) anchored anion radical 17C. Again, addition of tosyl radical with 17B led to the formation of a radical intermediate 17D which on deprotonation generated 17E. Now, a single electron transfer from heterocyclic anionic moiety to Cu(II) centre was initiated to generate Cu(I) species 17F and eventually the catalytic cycle came to an end *via* the release of the final product (17Q).



Scheme 16. Ru(II) catalyzed meta-selective sulfonylation of 2-phenoxy pyridine with arylsulfonyl chloride.



Scheme 17. Copper-mediated C-H sulfenylation of quinoline scaffolds with aryl sulfonyl chloride.

2.5. C(sp2)-H Selenylation of Arenes

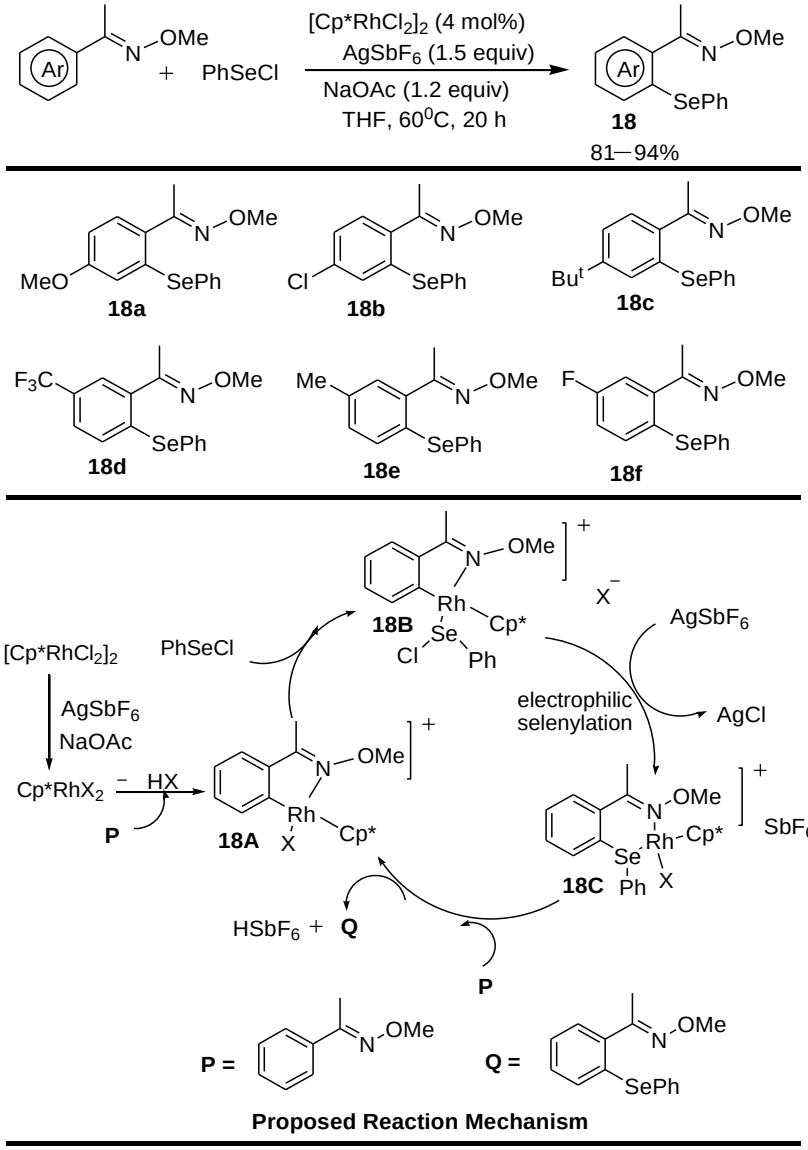
Traditional catalytic methodologies for C-Se bond construction *via* transition metals mediated direct selenylation of inert C-H functionalization of arenes are in high demand since aromatic frameworks bearing selenium moiety could be recognized to exhibit viable biological, medicinal and pharmaceutical activities [89-92].

2.6. Ortho Selective C-H Selenylation

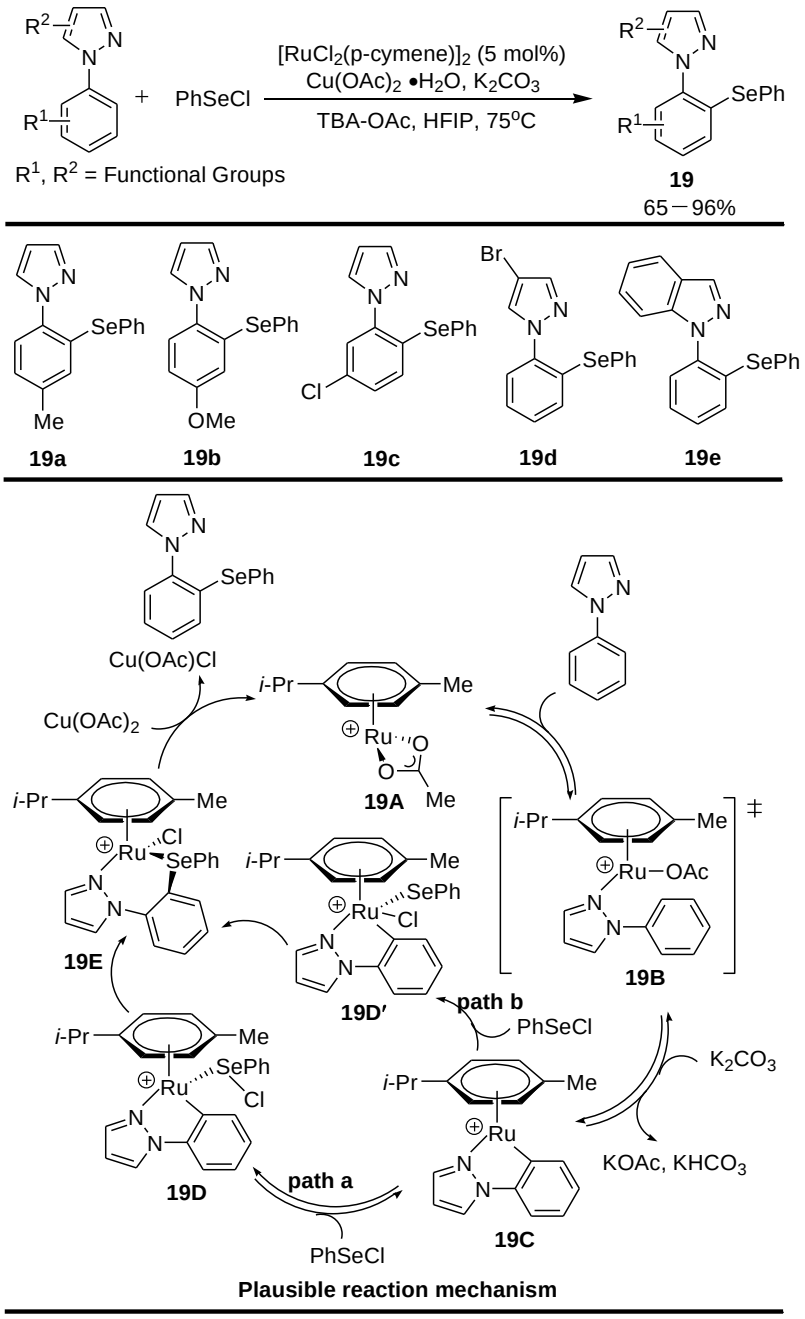
Significant advances in transition metal assisted selenoether synthesis *via* C-H bond functionalization employing substrates linked with various directing groups have revolutionized the field of organoselenium chemistry [5, 93-97]. Following this logic, Yu *et al*. in 2015, developed an excellent rhodium (III) based catalytic system to activate the C-H

bond functionality of arenes-bearing chelating ligands (Scheme **18**) [98]. This site-selective ortho-selenation was found to be operated smoothly in the presence of the stoichiometric amount of AgSbF6, NaOAc as base and tetrahydrofuran (THF) as potential solvent. This optimized reaction protocol resulted in moderate yields of diaryl selenides bearing electron donating and electron attracting functional groups at less hindered meta and para positions. Cleavage of activated C-H bond in the rate-determining step was also supported by a detailed study on the kinetic isotopic effect. The catalytic protocol proved to be highly advantageous due to the wide-ranging substrate scope with excellent functional group compatibility.

In 2016, the Zhang group employed benzeneselenyl chloride as a selenylating agent to selenate at the ortho $C(sp_2)$-H bonds of arenes tethered with pyrazoles as directing groups.**26** in the presence of stoichiometric quantity of $Cu(OAc)_2$ additive and hexafluoroisopropanol (HFIP) solvent, the ruthenium-promoted selenylation reaction was thought to undergo smoothly to deliver a bunch of ortho-selenylated products in 65-96% yields (Scheme **19**). Moreover, the catalytic method showed notable functional group compatibility and broad substrate scope under mild reaction criteria. The authors additionally reported the late-stage selenylation of potentially bioactive estrone derivative or clinically prescribed antidepressant drug to be acting as a selenylating agent. The mechanistic study unveiled that the interaction of 1-phenylpyrazole with the active catalyst **19A** delivered the ruthenated complex **19B** which, after ortho C-H bond cleavage, furnished five-membered ruthenacycle **19C**. In path, **a**, interplay of **19C** with PhSeCl and subsequent Se-Cl bond cleavage led to the formation of **19E**. However, in path **b**, the formation of **19E** was favoured by oxidative addition of PhSeCl with **19C** followed by reductive elimination. **19E,** upon treatment with $Cu(OAc)_2$ released the desired selenylated product with the regeneration of Ru(II) catalyst to be employed for the next catalytic cycle.



Scheme 18. Rh-catalyzed *ortho*-C-H selenylation of arenes with PhSeCl.

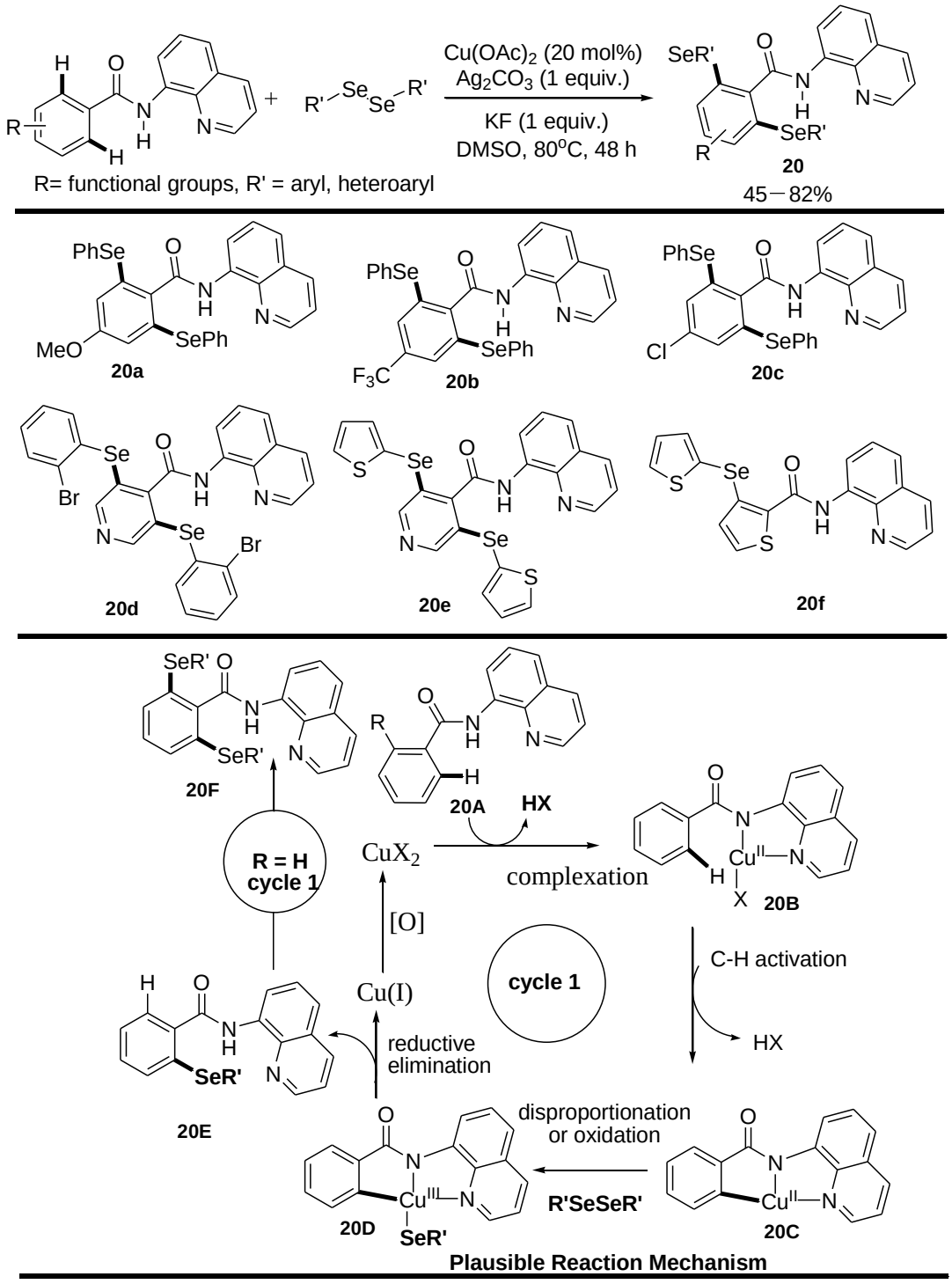


Scheme 19. Ruthenium catalyzed direct selenylation of arenes with PhSeCl.

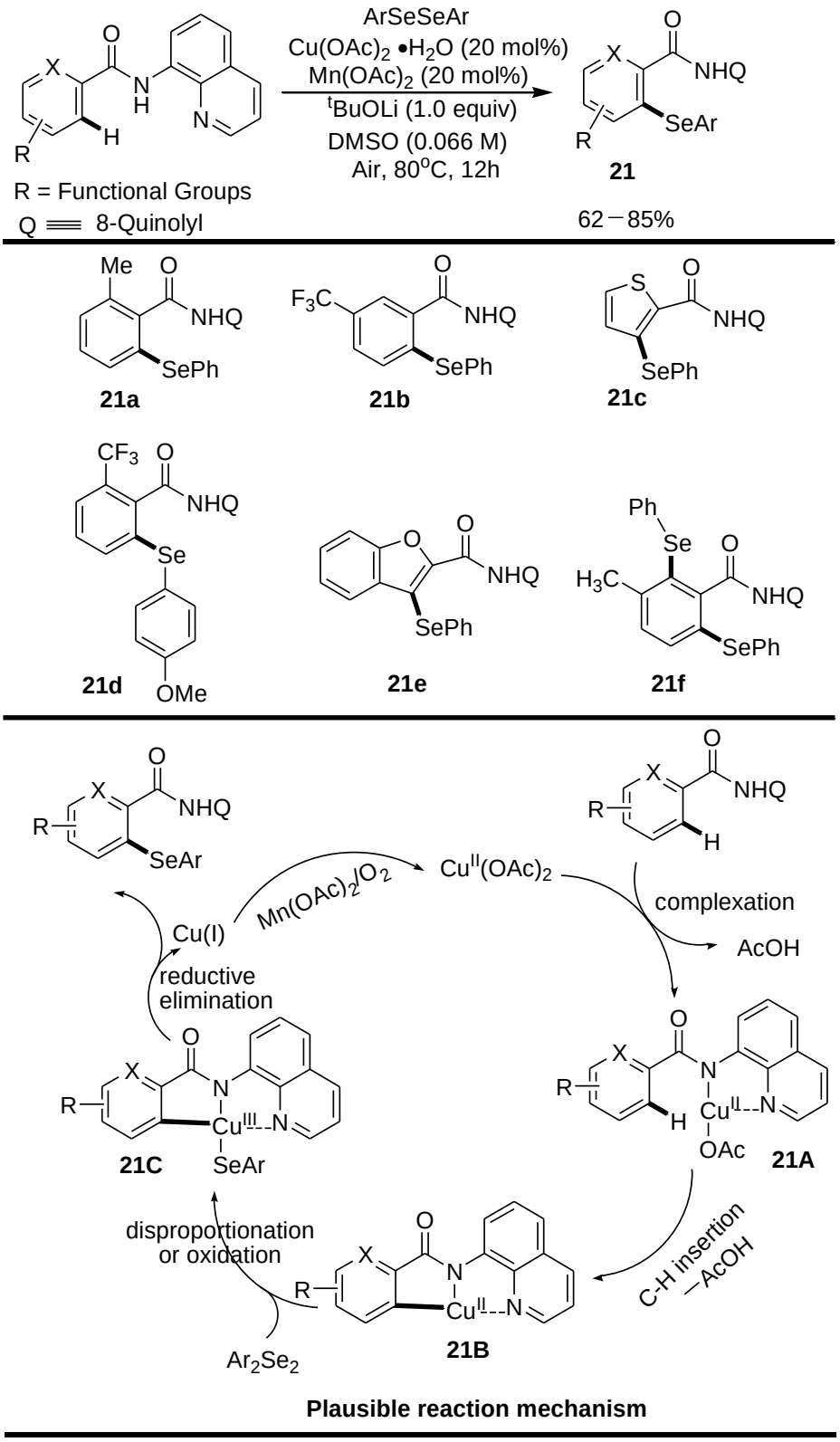
In the same year, Mandal and co-workers successfully designed a Cu(II) catalytic system to explore the N-directed *ortho*-C-H selenylation of arenes and heteroarenes in the presence of Ag2CO3 as an additive [99]. A good to excellent yields were afforded when a series of aryl and heteroaryl substituted amide derivatives assisted by 8-aminoquinoline auxiliary was subjected to couple with diaryl/heteroaryl diselenides (Scheme **20**). Under the optimized protocol, benzamides tethered with various electron-poor and electron-rich groups were well tolerated; however, the electron-donating substrates displayed better performances to furnish the desired yields. Moreover, the reaction delivered monoselenylated products when either one ortho-position was blocked or there was a meta-substituted bulky group. The proposed mechanism illustrated that coordination between the substrate (**20A**) and Cu(II) furnished the intermediate **20B** which, upon C-H activation gave **20C**. Thereafter, **20C** was oxidized by diselenide to form the active species **20D** which, after reductive elimination delivered the monoselenylated product (**20E**). Subsequently, **20E** would participate in the next catalytic cycle to generate the diselenated product (**20F**).

Later on, Jana and research colleagues designed a manganese-copper dual catalytic protocol to develop a chelation-guided direct C(sp2)-H selenylation of arene and heteroarene derived benzamide analogues under an air atmosphere at 80oC heating [100]. This synthetic method was operationally

simple and gram-scalable, displayed good compatibility over a broad range of electron-rich as well as electron-deficient functional groups. It is worth mentioning that the presence of meta substituted -CF3 and -Me group was likely to elucidate the chemo- and regioselectivity of C-H functionalization by affording both mono- and diselenylated products (Scheme **21**). Interestingly, the quinoline-based directing group could readily be deprotected and thus resulting *ortho*-selenylated benzoic acid. Moreover, the proposed catalytic route was also found to be in accordance with the literature precedents. Initially, the 8-quinoline anchored benzamide coordinated with Cu(OAc)2 to furnish the intermediate **21A**, which underwent *ortho*-C-H bond insertion to produce **21B**. Next, **21B,** upon disproportionation or oxidation, yielded Cu(III) pincer complex **21C**. Subsequent reductive elimination of **21C** released the desired product and Cu(I) species. Meanwhile, Cu(I) upon oxidation resulted in the Cu(II) species completing the catalytic path.



Scheme 20. Copper catalyzed selenylation of 8-aminoquinoline assisted (hetero)arenes with diselenides.



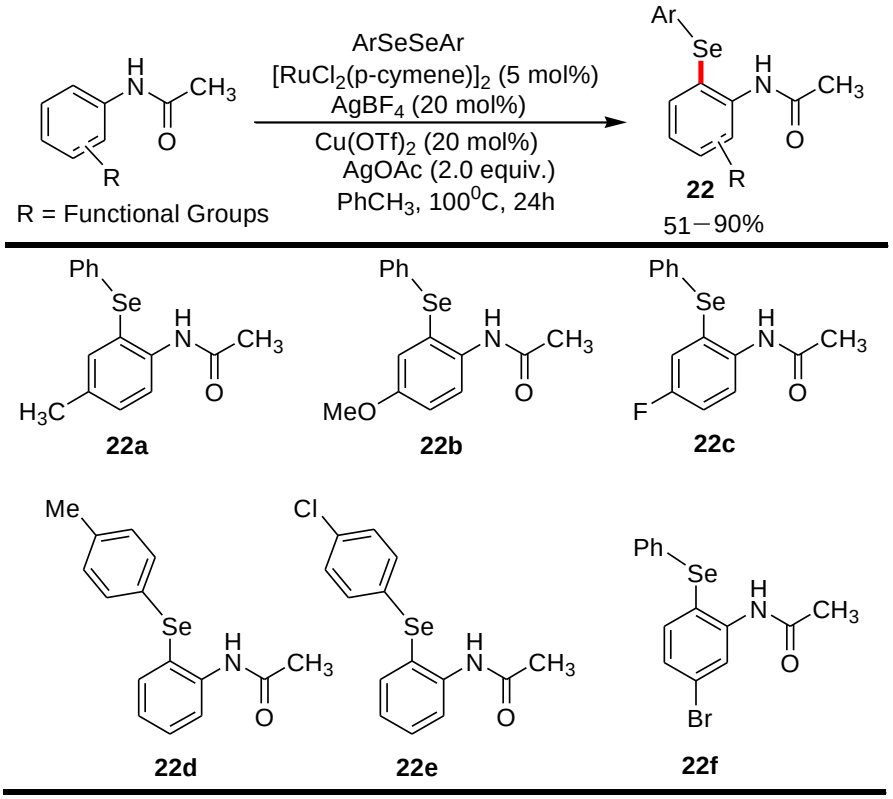
Scheme 21. Dual Cu-Mn catalyzed direct C-H selenylation of arenes and heteroarenes.

Ackermann's research group documented an easy and efficient catalytic route for the synthesis of ortho-silylated anilides *via* ruthenium(II)-promoted C-H functionalization reaction.**94** It is worth noting that anilides decorated with both electron-poor and electron-rich substituents at the para position reacted smoothly with diselenides to afford a wide range of monoselenylated products in good to excellent yields (Scheme **22**). The optimized synthetic protocol could

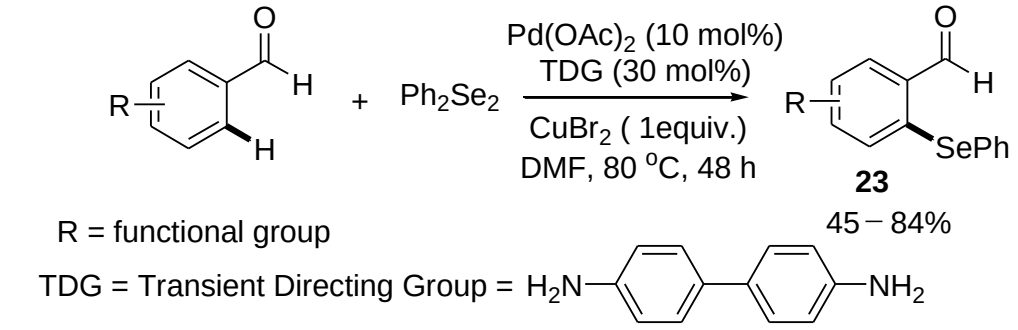
be employed to explore the versatility of the C-H functionalization with a broad substrate scope, excellent functional group compatibility and chemo- and regioselectivity. A detailed study on kinetic isotope effect truly confirmed the reversibility of the C-H activation step.

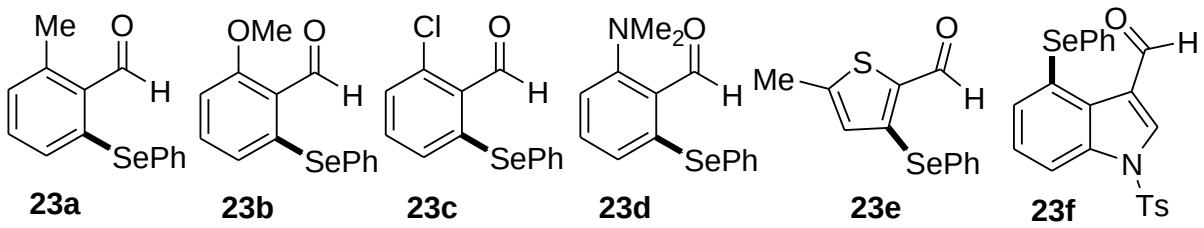
Qiao *et al*. [101] designed and established a novel ruthenium-based catalytic pathway to selenate at the ortho position of benzaldehyde derivatives bearing benzidine as transient directing group. It is worth noting that aromatic aldehydes with well-tolerated electron deficient substituents were selectively monoselenated and afforded good yields of products (Scheme **23**). However, the protocol was found to be completely insensitive towards C-H selenylation for pyrrole and furan systems under standard reaction condition. The authors also proposed a plausible reaction mechanism to clarify the catalytic route. Condensation between aldehyde **23A** and transient direction group (**TDG)** resulted in the imine **23B,** which underwent palladation *via* C-H bond functionalization to form the intermediate **23C**. Thereafter, **23C,** upon oxidative addition with diselenides furnished Pd(IV) species **23D,** which subsequently underwent reductive elimination to produce Pd(II) species **23E** and desired *ortho*-selective imine **23F**. Hydrolysis of **23F** delivered the expected *ortho*-selenylated aryl aldehyde (**23)**. Treatment of **23E** with AcOH led to the regeneration of active Pd(OAc)2 catalyst at the cost of PhSeH formation. In an another route **b,** the species **23C** reacted with benzeneselenol (PhSeH) obtained from route **a**, to generate palladacycle species **23H,** which followed a Pd(II)-Pd(0) reductive elimination again to produce *ortho*-selenylated imine **23F**. Pd(0) was further oxidized to Pd (II) by CuBr2 to monitor the next catalytic cycle.

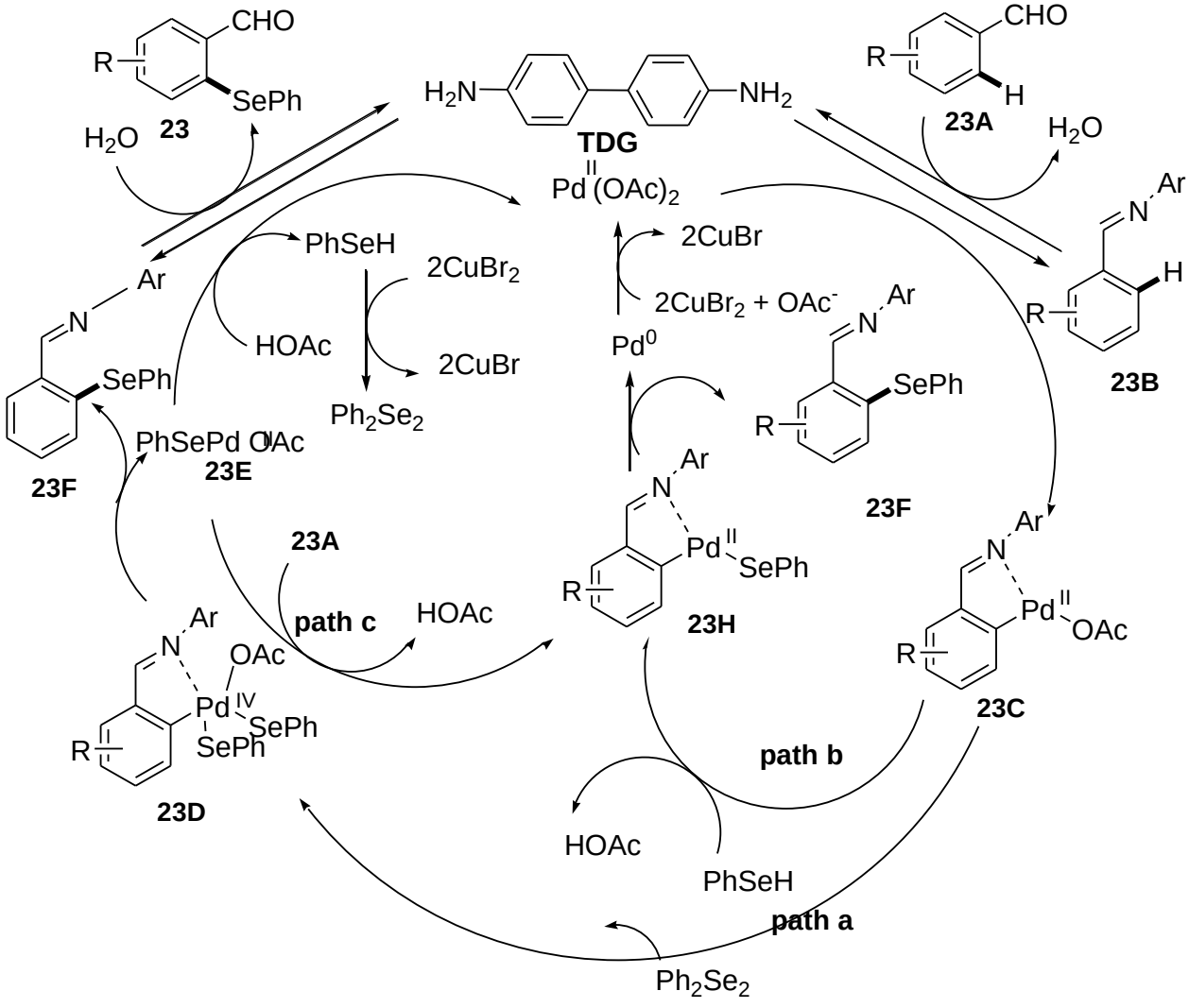
In 2019, a novel and unprecedented ruthenium(II) promoted catalytic protocol performing *ortho*-C(sp2)-H selenylation of benzamide derivatives was successfully designed by Ma and co-workers [102] The optimized reaction proceeded smoothly in the presence of silver additives in 2,2,2-trifluoroethanol (TFE) solvent under an argon atmosphere. The benzamides were functionalized with Ar2Se2 to afford the desired ortho-seleno ethers in good to excellent yields (Scheme **24**). Interestingly, diaryl diselenides owning electron-rich substituents showed no compatibility with this reaction. The authors employed a series of competition experiments to reveal the higher reactivity of electron-rich benzamides in comparison to electron-poor partners, indicating the involvement of a base-mediated intramolecular electrophilic substitution (BIES) at the C-H bond activation step event. Moreover, the H/D exchange experiment in CD3OD as a co-solvent indicated that the C-H bond activation step was reversible under the optimized reaction conditions. Initially, the catalytic cycle started with the formation of an active cationic Ru(II) intermediate **24A,** which initiated the reversible C-H bond activation of benzamide to afford the cycloruthenated species **24B**. Coordination of **24B** with diaryl diselenide delivered the Ru(IV) species **24F** which, after reductive elimination, released the desired product and Ru(II) species **24C**. Alternatively, intermediate **24B** reacted with diaryl diselenide to furnish the desired product along with the Ru(II) species **24C**. Thereafter, **24C** could interact with benzamide *via* the second C-H activation step to furnish the cycloruthenated benzamide **24D**, which subsequently underwent reductive elimination to generate the Ru(I) species **24E**. Finally, the oxidation of **24E** by AgOAC regenerated the active catalyst **24A** and completed the catalytic cycle.



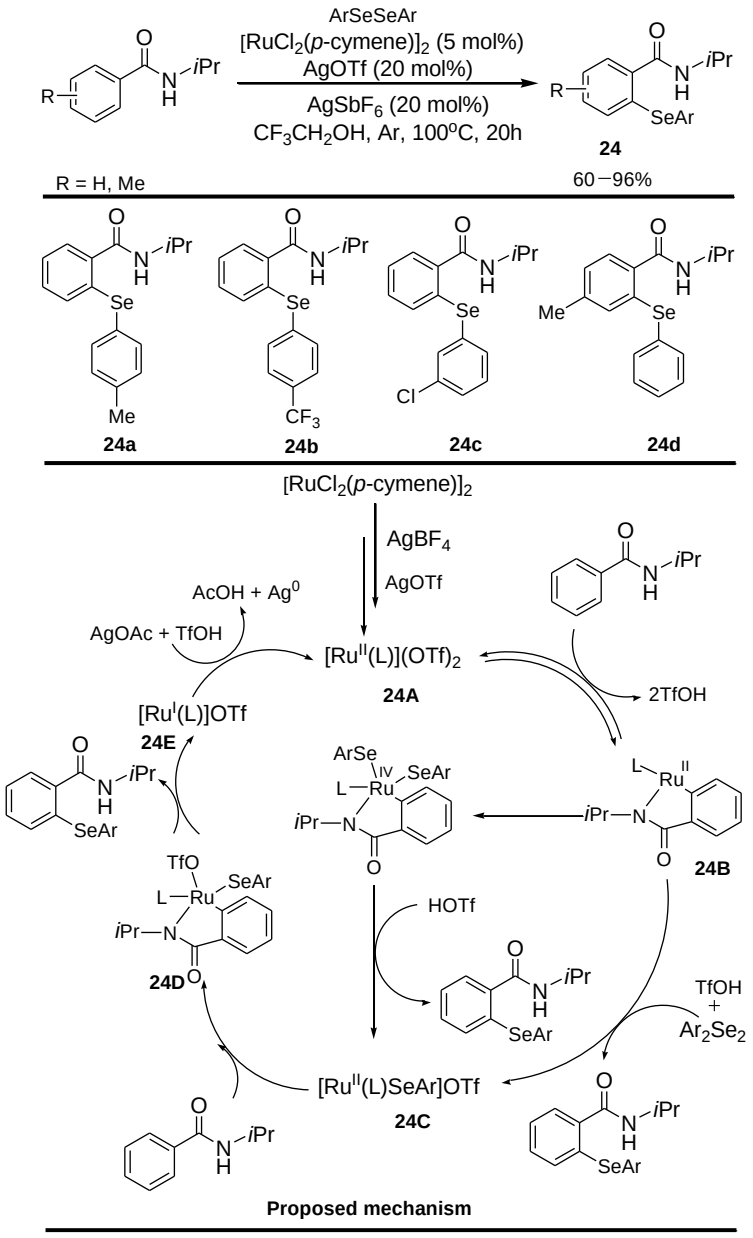
Scheme 22. Ruthenium catalysed direct C-H selenation of anilides.







Scheme 23. Palladium catalysed C-H selenation of benzaldehyde derivatives with Ph2Se2.

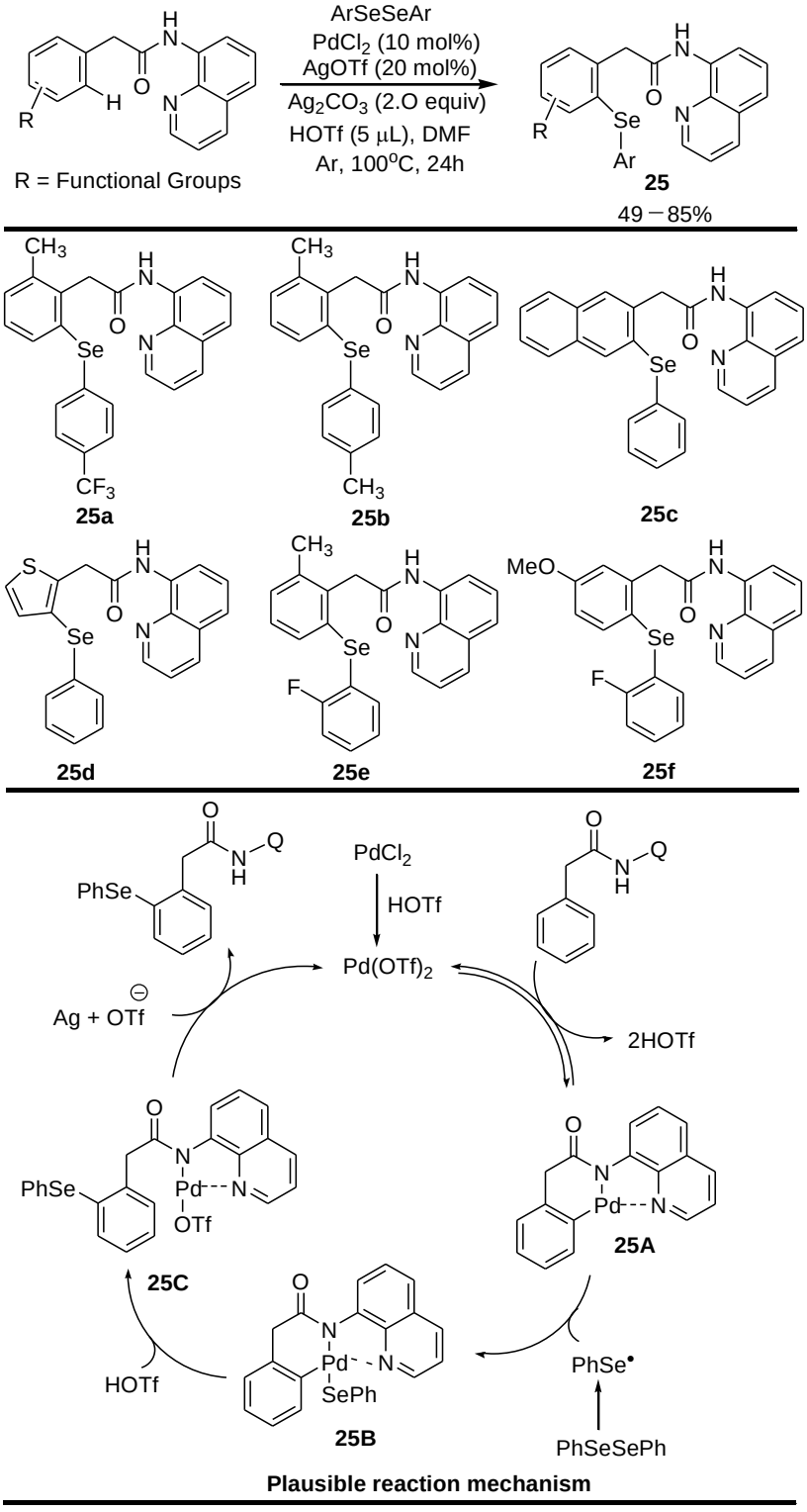


Scheme 24. Ru(II) mediated C-H selenylation of benzamide derivatives with Ar2Se2.

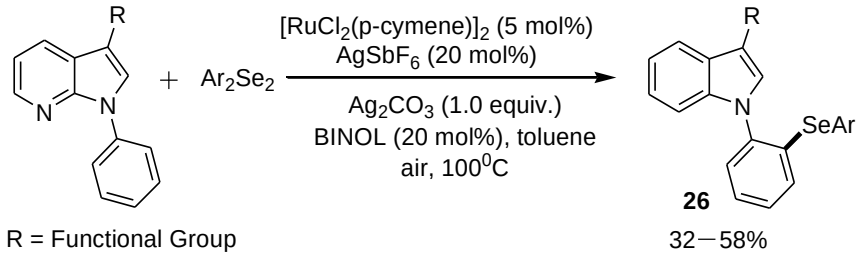
In a different study, Hu *et al* [103]. assembled diaryl diselenides and 2-aryl acetamides anchored with a removable 8-aminoquinoline auxiliary to design a novel and facile synthesis of unsymmetrical seleno ethers in excellent yields (Scheme **25**). After the screening of various representative oxidants and solvents, Ag2CO3 as oxidant and DMF as solvent turned out to show better performance to promote the palladium assisted selenylation reaction. The gram scalability, regioselectivity and a broad range of functional group tolerance also facilitated the catalytic transformation. The authors also proposed that a SET-induced radical type mechanism was likely to be operating in the selenylation process. Coordination of Pd catalyst with N, N-bidentate ligand furnished a cyclopalladated species **25A**. Oxidation of **25A** by selenyl radical produced palladium (III) intermediate **25B**, which upon reductive elimination, delivered the desired ortho-selenylated yield.

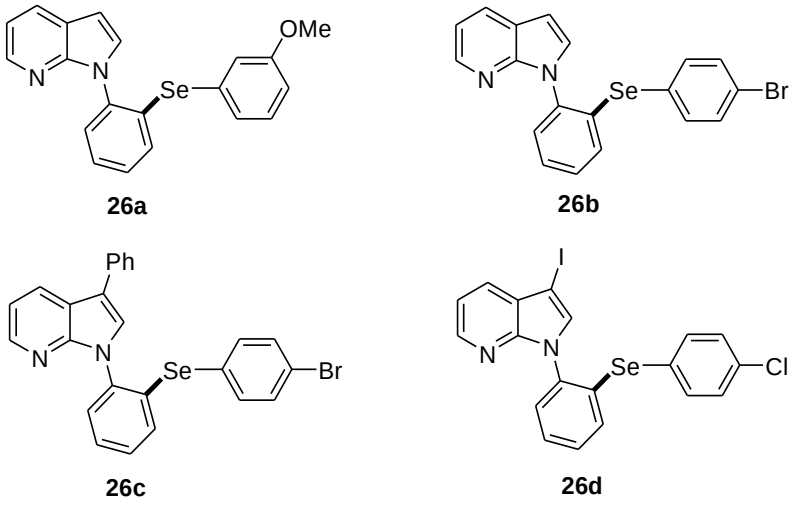
Owing to robustness and versatility, Ru-catalysis in direct C-H selenylation has attained attractive interest to researchers. Of this particular interest, Bag *et al*., by their inspiring research work, demonstrated the ruthenium metal assisted ortho selective C(sp2)-H functionalization reaction of arenes tethered to 7-azaindoles with diselenides under air atmosphere (Scheme **26**) [104]. This BINOL ligand modulated catalytic protocol proceeded smoothly in the presence of Ag_2CO_3 oxidant, AgSbF6 additive in toluene at 100°C. The diselenide analogue bearing various electron withdrawing and electron donating substituents underwent coupling at the activated C-H centre of N-phenyl-7-azaindole and monoselenation was found as a sole product. The authors also elucidated the large scalability and regioselectivity of the reaction with wider substrate scope and excellent functional group tolerance.

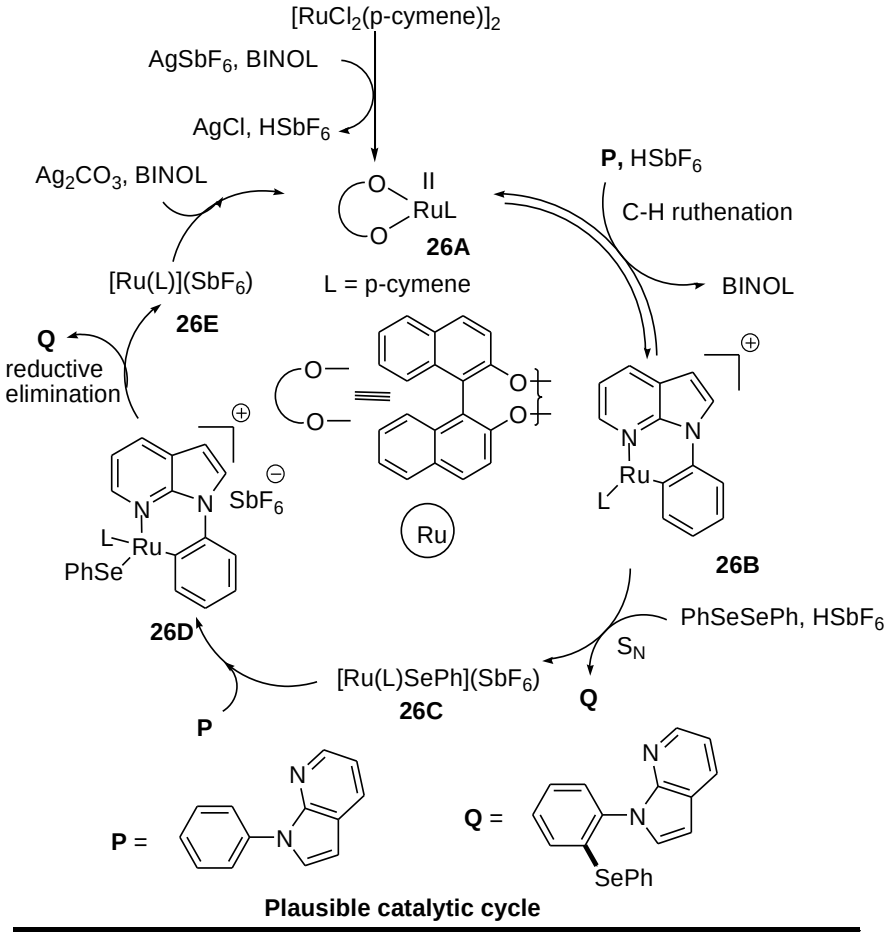
Thereafter, Nguyen and Daugulis derived aryl selenides by assembling commercially available diphenyl diselenides and N-aminopyridinium ylide in the presence of potassium persulfate ($K_2S_2O_8$) and hexafluoroisopropanol (HFIP) solvent under 110°C heating [105]. This copper catalyzed *ortho* selenylation at activated C(sp2)-H centre was found to afford good to moderate to yields (Scheme **27**). Interestingly, the ylide anchored with meta substituted -CH3 group furnished a substantially higher percentage of yield, whereas *m*-substituted -CF3 group decreased the rate of reaction. The regioselectivity of the C-H activation was also tested by lessening the reaction temperature and loading of diphenyl diselenide.



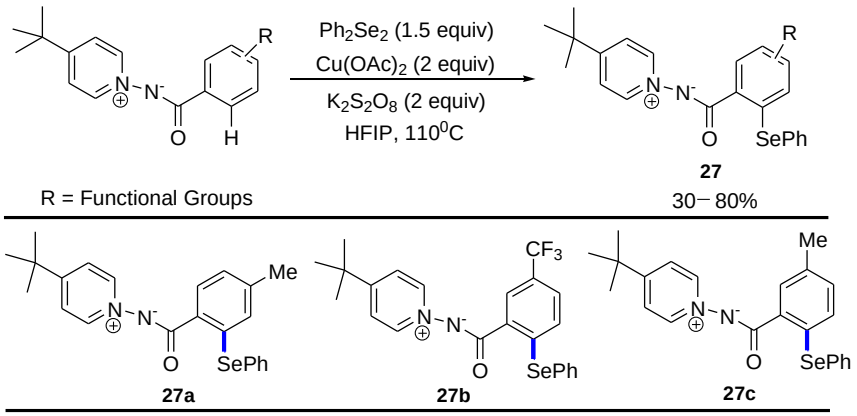
Scheme 25. Pd-catalyzed direct selenylation of differently substituted 2-aryl acetamides.



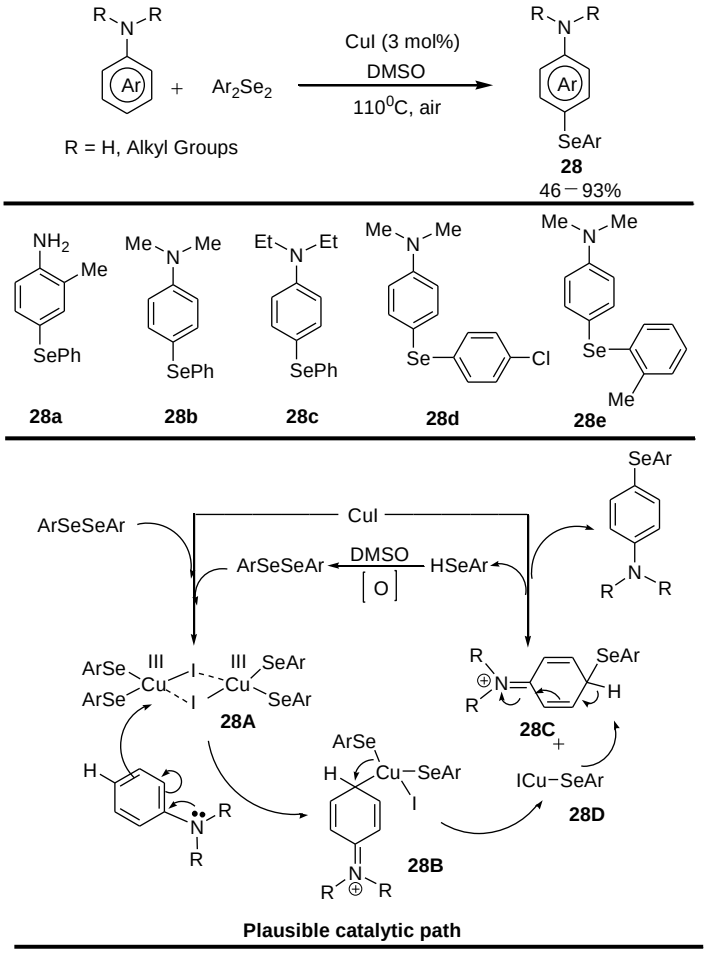




Scheme 26. Ru(II) catalyzed selenylation of N-phenyl-7-azaindoles with diaryl diselenides



Scheme 27. Copper catalyzed direct C-H selenylation of N-aminopyridinium ylides with Ph2Se2.



Scheme 28. Copper catalyzed direct selenylation of aniline derivatives.

2.7. Meta Selective C-H Selenylation

To the best of our knowledge, no research is to be reported on transition metals mediated chelation guided direct *meta*-C-H selenylation.

2.8. Para Selective C-H Selenylation

Alves and the research team developed an atom-economical and appropriate catalytic protocol to derive arylselanyl anilines in DMSO solvent at 110oC heating under air atmosphere [105, 106]. The cleavage of C-H bond of substituted aryl amines followed by the formation of C-Se functionality was found to be improved by employing CuI salt and thus a library of para-selenylated anilines was afforded in good yields (Scheme **28**). The regioselectivity, ample substrate scope and excellent compatibility by various electronic substituents on both diaryl diselenide and aniline moiety also enriched the synthetic strategy. A plausible mechanism involving Cu(I)/Cu(III) catalytic cycle revealed that coordination between diaryl diselenide and CuI furnished a Cu(III)

anchored tetracoordinate species **28A**. Now N, N-dialkyl aniline, through its *para*-position, interacted with the intermediate **28A** to generate **28B**, which after reductive elimination resulted in an intermediary iminium salt **28C** and an anionic species **28D**. Deprotonation of **28C** would release the desired selenylated product along with the formation of arylselenol (ArSeH) which on exposure with air and DMSO regenerated CuI and Ar_2Se_2.

In 2022, Beletskaya and Ananikov introduced an exhaustive study on the transition metals catalyzed C-Z bond formations (Z = S, Se and Te) under various catalytic protocols [107]. It is worth mentioning that higher atom economy, environmental concerns, higher selectivity, and conversion yields with respect to the catalytic transformations made this study more acceptable to the researchers.

Recently in 2023, Kong and co-workers designed and developed a terminal group-oriented self-assembly strategy for the preparation of a homogeneous layered $SnSe_2$ and MXene heterostructure (LBL-SnSe2@MXene) [108]. The authors also explained the massive applications of these synthesized heterostructured materials in the area of photo/electrocatalysis, rechargeable batteries and supercapacitors.

CONCLUSION

In summary, significant advances have been achieved in the area of chelation-guided transition metals mediated direct chalcogenation of activated C-H bond functionalities over the current ten years. Different nitrogen-based monodentate and bidentate auxiliaries have been effectively designed as active directing groups to address the site-selective synthesis of thioethers, sulfones and selenoethers. In contrast, the coordination of transition metal salts with the monodentate and/or bidentate chelating ligands has developed an innovative approach for the synthesis of C-S/Se motifs via C-H bond cleavage. We believe this review article could render a comprehensive and informative outline on this current issue and motivate researchers to design new and straight forward catalytic protocols.

LIST OF ABBREVIATIONS

BIES	=	Base-mediated Intramolecular Electrophilic Substitution
DFT	=	Density Functional Theory
DG	=	Directing Groups
DMSO	=	Dimethyl Sulfoxide
HFIP	=	Hexafluoroisopropanol
PyO	=	Pyridine-N-oxide
SET	=	Single Electron Transfer
TBHP	=	*tert*-butyl Hydroperoxide
TC	=	2-thiophenecarboxylate
TDG	=	Transient Direction Group
TEMPO	=	(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl
TFE	=	2,2,2-trifluoroethanol
THF	=	Tetrahydrofuran
TosMIC	=	*p*-Tosylmethyl Isocyanide

CONSENT FOR PUBLICATION

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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