

MINI-REVIEW ARTICLE

Recent Advances in Copper-Catalyzed Carbon Chalcogenides Cross-Coupling Reactions

Totan Roy¹, Atanu Mahata¹ and Debasish Kundu^{2,*}¹Department of Chemistry, Government General Degree College at Ranibandh, Bankura, WB-722135, India; ²Department of Chemistry, Government General Degree College at Mangalkote, Khudrun, Purba Bardhaman-713132, India

ARTICLE HISTORY

Received: August 6, 2021
Revised: January 2 2022
Accepted: January 8, 2022DOI:
10.2174/1570179419666220324122735

Abstract: Cu-catalyzed carbon-heteroatom bond formation is a powerful tool in the field of organic synthesis. In the past two decades, numerous Cu-based catalytic systems are developed in both homogeneous and heterogeneous forms. Important developments have been reported on Cu-based catalytic systems in the field of C-Chalcogenide cross-coupling in the last few decades. Where homogeneous Cu/L-based catalytic systems are found to perform reactions with high selectivity, heterogeneous supported-Cu and Cu-based nanoparticles are found to perform the reactions under sustainable conditions and high recyclability of catalytic systems. This present overview mainly focuses on the recent advances and applications in this fast-growing research field with an emphasis on copper-catalyzed cross-coupling generations of carbon-chalcogenide (S/Se/Te) bonds.

Keywords: Copper, selenium, sulfur, tellurium, cross-coupling, organo chalcogenides.

1. INTRODUCTION

The formation and necessity of carbon-heteroatom bond for the synthesis of organo-sulphides, selenides, and tellurides attract attention due to their profound applications in the field of catalysis [1], material science [2], biological, environmental, and pharmaceutical chemistry [3]. There has been an increasing interest in selenium and tellurium chemistry from the effective Se- and Te-based organocatalysts in several functional group transformations under sustainable conditions for the synthesis of bioactive molecules [4].

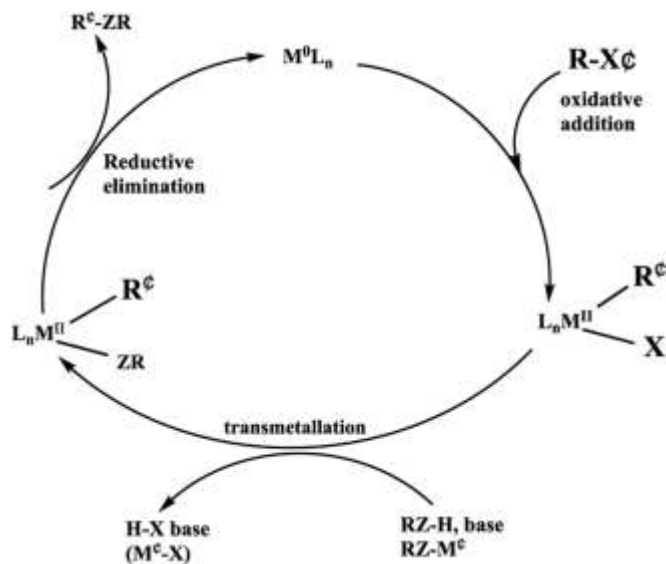
Transition metal-catalyzed cross-coupling reactions provide a powerful tool for the synthesis of a wide array of organic compounds *via* C-C and C-heteroatom cross-coupling within unsaturated carbon centres [3, 5-8]. However, the progress in carbon-chalcogen bond formation *via* copper-mediated or catalyzed cross-coupling reactions covers a variety of functional groups as well as the stability of starting materials and products due to the essentially required harsh reaction conditions, such as high temperatures-typically 150-200°C and for the extended reaction time from several hours to few days [9]. Recently, environment-friendly nanocrystals were successfully applied for C-Se cross-coupling under benign conditions [10]. Although the chemistry of C-Te bond formation is still in its early stages, the catalytic C-S and C-Se

cross-coupling reactions *via* decyanative cross-coupling or nucleophilic addition of ArSe to aryl halides, aryldiazonium salts, and arylboronic acids have received a lot of attention in recent years [3, 8, 11-14]. Due to the catalyst poisoning nature of sulphur-containing compounds, it becomes the most challenging factor for C-S cross-coupling, whereas a small number of thiols or disulphides can destroy the catalytic activity [15]. However, the recent development of efficient catalytic systems has successfully ruled out the mentioned problems to perform C-S coupling. Catalytic investigation was further extended in performing C-Se and C-Te cross-coupling.

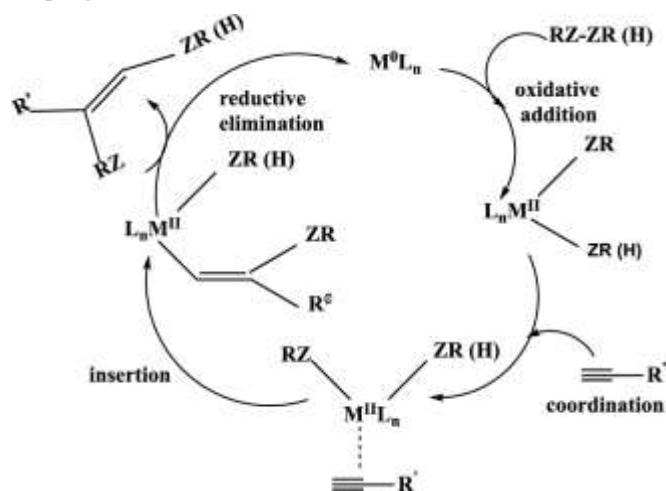
Catalytic systems with other transition metals like nickel [16], cobalt [17], and iron [18] have also been employed as catalysts; such systems suffer from serious drawbacks such as metal toxicity, low turnover numbers, *etc.* development of Cu-based heterogeneous catalytic systems were employed in such coupling reactions due to its low cost and ready accessibility. The use of Cu-based heterogeneous catalysts has the distinct benefit of decreasing the probability of Cu leaching from the surface. A large number of attractive Cu-catalyzed cross-coupling reactions have been reported by various research groups. In recent years, diarylchalcogenides-containing C-S and C-Se bonds occur as component of drugs like AZD4407 [19a, b] vortioxetine [19c], chlorpromazine [19d] *etc.* These are effective and biologically active molecules against various diseases like cancer, HIV, Alzheimer's, asthma, Parkinson's, *etc.*, demanding the continuous development in the synthesis of carbon-chalcogen compounds to meet the growing demand in many pharmaceutical applications [19]. As shown in

*Address correspondence to this author at Department of Chemistry, Government General Degree College at Mangalkote, Khudrun, Purba Bardhaman-713132, India; Tel: +91-9679326889; E-mail: chem.debasishkundu@mangalkotegovtcollege.org

Scheme 1, metal catalysed carbon-carbon and carbon heteroatom cross-coupling generally occurred *via* an oxidative addition-reductive elimination pathway involving transmetalation. However, in case of C-chalcogenide cross-coupling generally dichalcogenides (R₂Z₂) or Chalconols (RZH) were used as coupling partners with unsaturated halides (Scheme 2).



Scheme 1. General Mechanism for C-C and C-Heteroatom Cross-coupling.



Scheme 2. Addition of Z-Z bonds and Z-H bonds in the triple bond of alkynes.

A detailed, comprehensive, and updated study on recent methods for the synthesis of organochalcogen compounds using alternative solvents such as, water, polyethylene glycol, glycerol, ionic liquids, supercritical carbon dioxide, or solvent-free conditions was reported by Lenardaõ and co-workers [20]. Braga *et al.* [21] reported the efficient and mild synthesis of unsymmetrical diorganylchalcogenides employing CuI as a catalyst under ligand- and solvent-free conditions. According to the 'Chan-Lam coupling method', the carbon-heteroatom bond formation takes place *via* a copper-based cross-coupling reaction of arylboronates with electrophilic coupling partners [22]. Ranu *et al.* explored the copper-silver dual catalyzed nucleophilic displacement reaction for

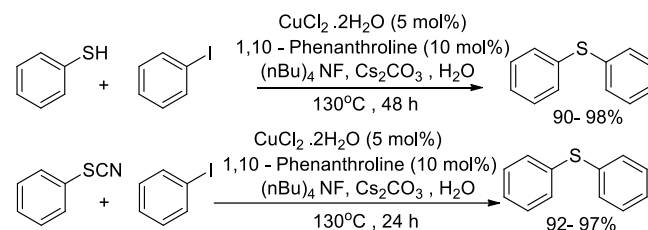
decyanative cross-coupling of aryl selenocyanate with aryl/alkyl acetylenes, boronic acids, and silanes [11]. They showed that cross-coupling reaction is initiated successfully by introducing both electron-donating groups such as -OMe, -NMe₂, 4-pentyl, and electron-withdrawing groups *e.g.* -OCF₃, -CF₃, -F in aryl alkynes. The interest of the present review article aims to focus on the perspective and recent advances in the cross-coupling reactions for the C-Z (Z = S, Se, and Te) bond formations toward the synthesis of aryl/heteroaryl sulphides, selenides, and tellurides in presence of a copper catalyst as well as nanostructured copper catalyst. Herein we highlighted the cross-coupling reactions by employing several green techniques such as microwave irradiation, and conventional and non-conventional methods.

2. DIFFERENT CATALYTIC SYSTEMS

Although the scope of transition metals catalyzed protocols for the synthesis of sulphides, selenides, and tellurides are small in number, in recent times scientists have been analyzing fundamental research with various catalytic systems. In this review, we have classified various catalytic systems in order to make a comparative study regarding the formation of organo-chalcogenides through copper-catalyzed cross-coupling reactions.

2.1. Cross-couplings *via* Homogeneous Catalyst

A copper catalysis is always a powerful tool in achieving C-S cross-coupling reactions due to getting maximum contact between reactants and catalysts as both are in the same phase. In the last few years, a number of research has been reported regarding this. CuPF₆(MeCN)₄ was found to show excellent catalytic activity in the synthesis of *ortho*-substituted aryl iodides and aryl thiols. An intramolecular mode of the reaction in synthesizing diaryl thioethers has also been reported [23].



Scheme 3. CuCl₂-phenanthroline catalyzed C-S cross-coupling in water.

Zhou *et al.* [24] introduced an effective copper catalytic system for the cross-coupling reaction of aryl halides and potassium thiocyanate in neat water. Aryl halides underwent a reaction with KSCN to give desired products and iodobenzenes afford a higher percentage of yields (Scheme 3). The authors reported excellent chemoselectivity between iodide, bromide, and chloride functional groups in the case of coupling of *p*-chloriodobenzene and *p*-bromiodobenzene with KSCN in presence under the standardized reaction conditions.

Venkatarman *et al.* reported a general synthetic protocol for the formation of diaryl selenides by the cross-coupling reaction of aryl iodides and phenylselenol using CuI/

neocuproinecatalytic system under 110°C heating [25]. Excellent yields are obtained by aryl iodides having electron-rich functional group tolerance. They recommended the use of K_2CO_3 in the place of NaO^t-Bu for electron-poor aryl iodides.

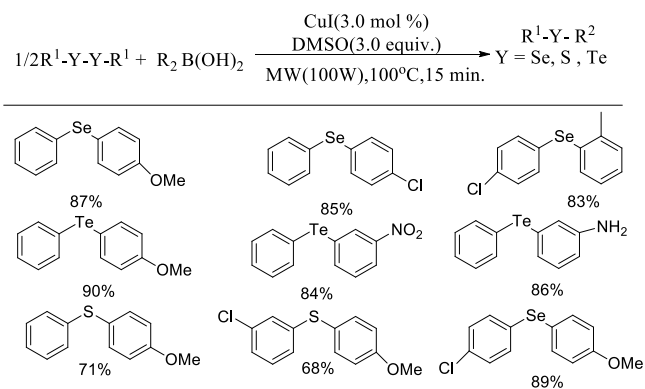
2.2. Cross-Couplings via Heterogeneous Catalyst

Heterogeneous catalysis is preferred over homogeneous catalysis due to several factors such as easy separation of catalyst from the reaction medium, catalyst recyclability, greater steric control, less exposure to metal salts in environment *etc.* [26]. Studies for effective and selective construction of C-S, C-Se, and C-Te bonds through metal-catalyzed cross-coupling reactions catalyzed *via* heterogeneous copper catalyst have received the attention of organic chemistry and thus several methodologies have been developed. Herein a comparative study has been performed on different copper-catalyzed carbon-chalcogenides cross-coupling reactions.

2.2.1 Cross-Coupling Reactions under Microwave Irradiation:

In the last two decades, microwave-assisted organic synthesis has been established as a sustainable tool for performing C-C and C-heteroatom bond formations [8, 13, 27-30]. The microwave technology under conventional heating sources has emerged as an excellent tool for organic reactions due to its high efficiency, reproducibility, and shortening of time. There are several advantages such as fulfilling the requirements of green chemistry, simplified synthetic reaction techniques, cheaper solvents, greatly reduced side reactions due to applying lower temperatures, *etc.*

Although the scope of transition metals catalyzed protocols for the synthesis of sulphides, selenides and tellurides are small in number but in recent times scientists are analyzing fundamental research with various catalytic systems. The applicability of copper-catalyzed cross-coupling of aryl boronic acids by diorganylchalcogenides was reported by Braga *et al.* [21] where aryl boric acids react with 0.5 equiv. of diorganyldichalcogenides (Te/Se/S) in the presence of 3 mol % of CuI and 3 equiv. of DMSO under microwave irradiation (Scheme 4).

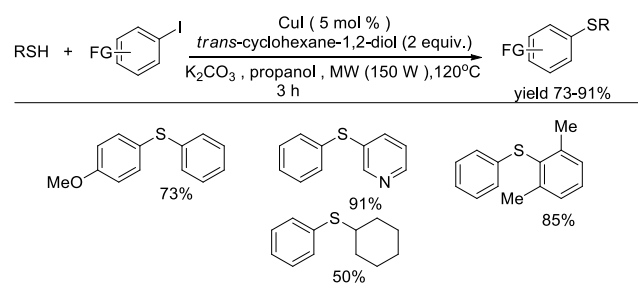


Scheme 4. Microwave-assisted CuI-catalyzed C-chalcogenide cross-coupling with boronic acids.

They investigated the choice of catalyst and also the effect of catalyst loading on the reaction condition. It was noted that among the copper halides and CuO nanoparticles, CuI shows

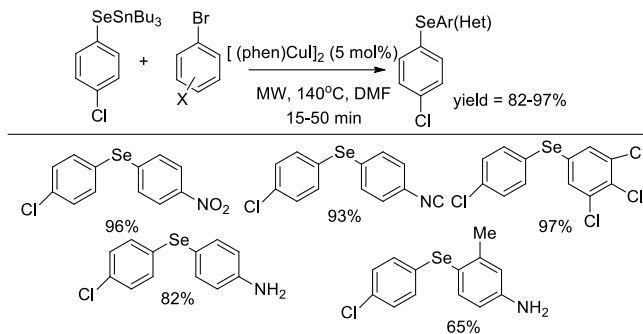
better catalytic activity. The reaction yield increases remarkably as the concentration of catalyst increases from 1 mol% to 3 mol% whereas the addition of 4 mol% CuI does not affect the yield. The authors explored here the scope of their protocol by employing various diorganylchalcogenides and aryl boronic acids. A wide range of electronic substituents *i.e.*, electron-donating groups like -OMe, -NH₂, *etc.* as well as electron-withdrawing groups like -Cl, -NO₂, *etc.* attached at different positions of the aromatic ring of boronic acid affect the reaction yield appreciably.

In 2009, Bagley *et al.* reported microwave-assisted Cu-catalyzed cross-coupling of thiols with iodoarenes for the synthesis of diaryl sulfides using *trans*-cyclohexane-1,2-diol as a ligand [31]. Iodoarenes bearing electron-donating and withdrawing groups in the aromatic ring are coupled with several aromatic thiols and cyclohexyl thiols to produce the corresponding products in good to excellent yields (Scheme 5).



Scheme 5. Microwave-assisted CuI-catalyzed C-S cross-coupling between thiols and iodoarenes.

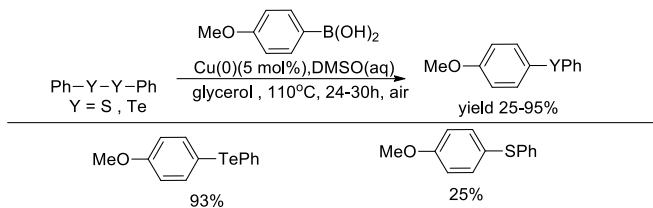
Beletskaya and co-workers [32] studied the synthesis of unsymmetrical diaryl selenides using a cross-coupling reaction between trialkyltin aryl selenides with aryl and hetaryl bromides. The reaction proceeds using a catalytic amount (5 mol%) of the copper catalyst ($[(phen)CuI]_2$) in DMF as a solvent, and the reaction mixture was then heated in a microwave oven at 140°C for 15-50 minutes to produce unsymmetrical diaryl selenides in moderate to excellent yields. The microwave activation drastically decreases the reaction time from 6-30 h to 15-50 minutes (Scheme 6).



Scheme 6. Microwave-assisted C-S cross-coupling between trialkyltin aryl selenides with aryl and hetaryl bromides.

Richodi and co-workers [33] used aryl boronic acids and different diarylchalcogenides in copper-catalyzed cross-coupling reactions to prepare chalcogenoethers under the optimized reaction conditions. The protocol was successfully utilized in the C-S, C-Se, and C-Te cross-coupling reaction

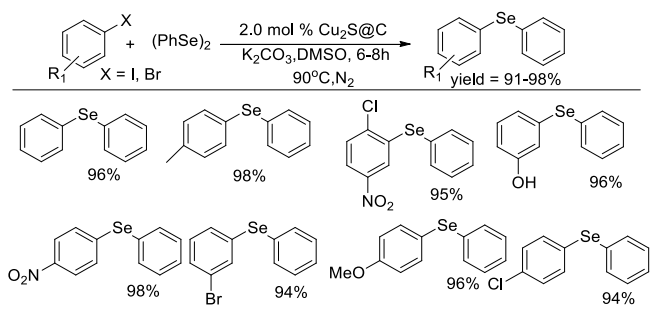
between the diaryl disulphides/diselenides/ditellurides and arylboronic acids and it revealed that the reactions worked well with a range of substituted arylboronic acids, affording good yields of the products. The excellent yield was obtained when 4-methoxyphenylboronic acid was efficiently coupled with diphenyl ditelluride rather than diphenyl disulfide or diselenide (Scheme 7).



Scheme 7. Copper-catalyzed cross-coupling between organo-dichalcogen-ides with boronic acids.

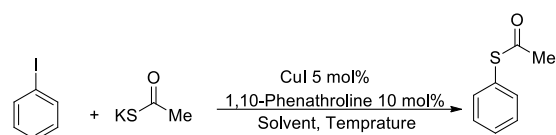
2.2.2. Cross-Coupling Reactions under Conventional and Non-conventional Method:

In the last two decades, ionic liquids have proved themselves as environmentally friendly green solvents because of their polarity, negligible vapor pressure, non-hydroxylic, non-volatility, nonflammability, reasonable thermal stability, easy separation, and recyclability, *etc.* [34]. Kim *et al.* studied the ligand-free cross-coupling reaction of aryl halide and diaryl diselenide using ionic liquid-based copper sulphide functionalized carbon ($\text{Cu}_2\text{S}@C$) catalyst [35]. The tri-cationic ionic liquid was used to synthesize $\text{Cu}_2\text{S}@C$ by the polymerization in presence of copper chloride salt as a precursor. The advantage of $\text{Cu}_2\text{S}@C$ over Cu_2S and $\text{Cu}_2\text{S}/C$ catalytic systems reflects that the former is highly efficient in reducing the reaction time from 15h to 8h by affording almost 96% yield (Scheme 8). The reaction is almost insensitive to the electronic effects of the substituents attached to the aryl ring.



Scheme 8. Synthesis of diaryl selenides by $\text{Cu}_2\text{S}@C$ -catalyzed C-Se cross-coupling.

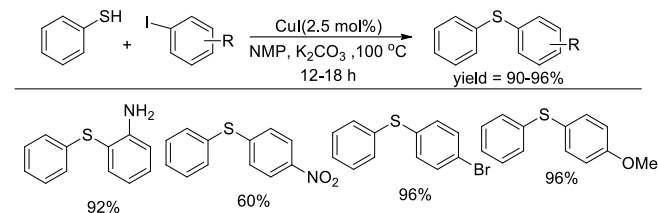
Ligand-assisted cross-coupling reactions are valuable transformations in organic synthesis. Soria-Castro and Peñeñory proposed the reaction of KSCOMe with aryl iodides under copper-free conditions to afford S-aryl thioacetates as thiol surrogates in good to excellent yields, under conventional heating [36]. The optimal reaction conditions (temperature and solvent) were determined by choosing PhI and KSCOMe as model substrates in presence of CuI and a 1,10-phenanthroline catalytic system (Scheme 9).



Scheme 9. CuI-Phenanthroline-catalyzed coupling of KSCOMe and iodoarenes.

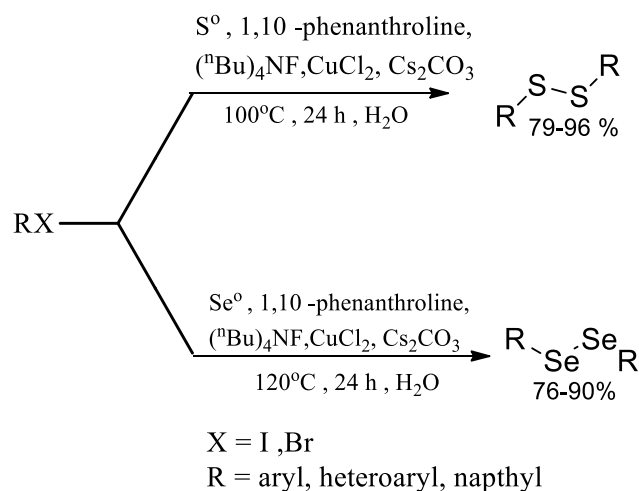
The group of Beloglazkina established a novel and synthetic copper-mediated cross-coupling reaction of 2-selenohydantoin and aryl boronic acid under base-free mild conditions [37]. The authors applied $\text{Cu}(\text{OAc})_2/1,10$ phenanthroline catalytic system to allow a broad array of 3,5-disubstituted-2-selenohydantoin to undergo coupling with boronic acids successfully with producing good to excellent yield.

Koten and co-workers have reported that CuI-catalyzed cross-coupling of iodoarenes with thiols in NMP solvent under ligand-free conditions [38]. The reactions were performed under 100 °C heating by using K_2CO_3 as a base. The reaction showed excellent functional group compatibility in the aryl rings and thus a library of diaryl sulfides has been synthesized by this procedure.



Scheme 10. CuI-catalyzed cross-coupling between thiols and iodoarenes.

Li and co-workers have reported Cu-catalyzed coupling of iodo- and bromoarenes with elemental S and Se in an aqueous medium for the synthesis of disulfides and diselenides [39]. The authors have used tetrabutyl ammonium fluoride as a phase transfer agent and 1,10 phenanthroline as a ligand for this reaction. A library of diaryl disulfides and diphenyl diselenides were afforded in good to excellent yields (76-96%) (Schemes 10 and 11).

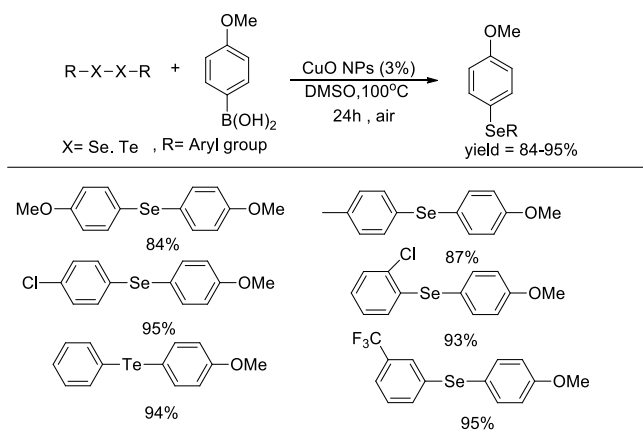


Scheme 11. Cu-catalyzed synthesis of disulfides and diselenides.

2.3 Copper Nanoparticles-Catalyzed Cross-Coupling Reactions

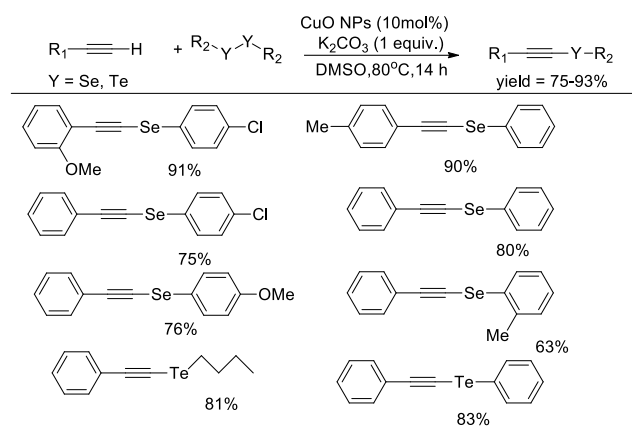
The application of metal nanoparticles for organic reactions has attracted the immense attention of organic chemists in the last two decades [40-43]. Furthermore, the metal nanoparticle-catalyzed reactions provide the advantages of high atom efficiency, simplified isolation of product, and easy recovery and recyclability of the catalysts. Recently, nanoparticles-catalyzed cross-coupling reactions have witnessed growing importance for the synthesis of organochalcogenides. Due to large surface area and low coordinated sites, metal-catalyzed nanoparticled show high catalytic efficiency which maximizes the rate of reaction, improves product yield and selectivity, shortens reaction time, decreases catalyst loading, and minimizes the consumption of the catalyst [44]. The relative comparison of the catalytic activity of CuO NPs with other copper catalysts such as CuI, CuO, and CuFe₂O₄ nanoparticles, established its superior comparability with them in terms of product yield. Moreover, CuO can be recovered from the reaction media and can be used for further catalytic reactions.

The applicability of nano-sized metal nanoparticles (NPs) in the selenation and telluration of boronic acids with diselenides/ditellurides was reported by Alves and co-workers [41] in 2009, where 4-methoxyphenyl boronic acid was efficiently coupled with diphenyl diselenide/ditelluride in the presence of the catalytic amount of CuO nanoparticles in DMSO as a solvent at 100°C under air atmosphere. The authors synthesized a good number of organic selenides through cross-coupling reactions. The results revealed that the reaction is sensitive to the electronic effects whereas steric effects show a little influence on the coupling process. The authors also extended the applicability of the protocol toward the synthesis of diaryl tellurides in excellent yields (Scheme 12).



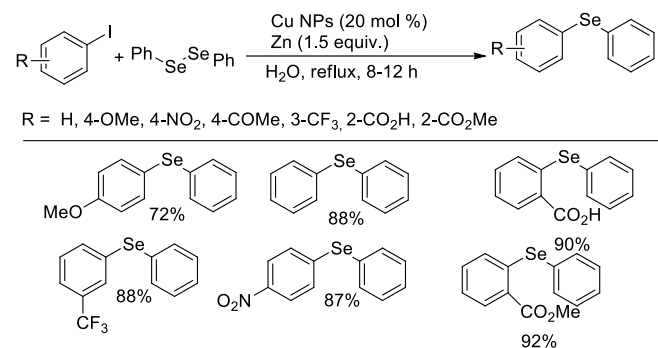
Scheme 12. CuO-catalyzed cross-coupling between boronic acids with diaryl diselenides and ditellurides.

Braga and co-workers demonstrated C–Se cross-coupling of terminal alkynes with diorganylselenides and tellurides in the presence of recyclable CuO nanopowder and K₂CO₃ as a base in DMSO at 80°C to obtain corresponding alkynyl selenides and tellurides [45] (Scheme 13). The electronic factors on diselenides do not have any remarkable effect on the product yield, however, the steric factors affect the reaction adversely.



Scheme 13. CuO nanoparticles-catalyzed synthesis of alkynyl selenides and tellurides.

Saha and co-workers [46] achieved Cu(0) nanoparticle catalyzed cross-coupling of iodoarenes with diaryl diselenides in water solvent under refluxing conditions in presence of Zn as additive. Zn was expected to form active seleno nucleophile from diselenides and thus the desired diaryl selenides were obtained in good to excellent yields (Scheme 14) with broad functional group compatibility in the aromatic rings.

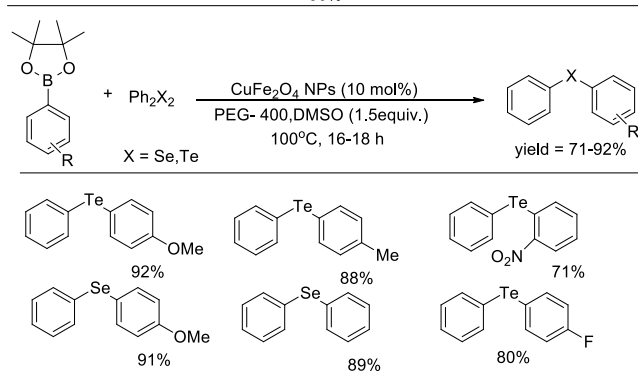
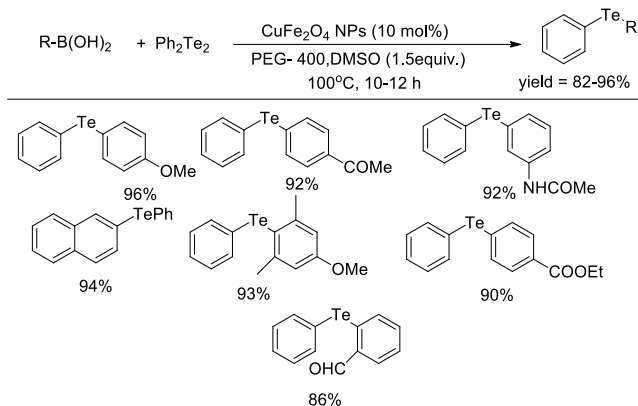


Scheme 14. Cu(0) NPs-catalyzed C-Se cross-coupling in water.

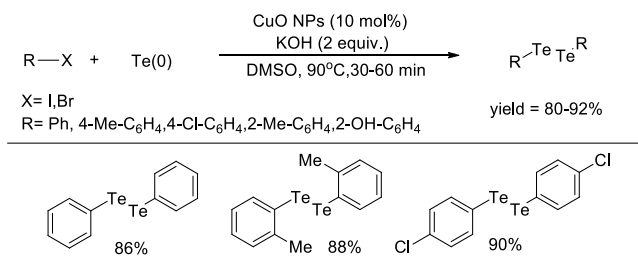
Magnetic nanocatalysts have attracted considerable attention in the field of organo-chalcogen chemistry due to their unique properties, such as large surface area and facile separation using external magnets [47]. The pioneering work of Ranu *et al.* [40] prompted the chemists to study the synthesis of organoselenides and tellurides by the reaction of boronic acid/boronic ester/trifluoroborate with diphenyl ditelluride/diselenide employing CuFe₂O₄ nanoparticles as efficient catalyst in eco-friendly Polyethylene Glycol (PEG-400) solvent and DMSO as an additive under ligand-free conditions (Scheme 15).

They utilized this green synthetic protocol by introducing various electron-withdrawing or electron-donating groups at 2 and 4-positions of the aromatic ring of aryl trifluoroborates or boronic acid pinacol esters which furnished the corresponding products in excellent yields. In 2010, Rodrigues and Braga along with their co-workers studied the possibility of synthesizing diorganyltellurides through a Cu NPs-catalyzed coupling reaction between organohalides and elemental Te(0) [48]. Careful analysis of the optimized reactions revealed that the C-Te cross-coupling reaction occurred by the addition of CuO NPs (10 mol%), KOH (2

equiv.) at 90°C, to a solution of halides, and Te(0) in DMSO under a nitrogen atmosphere (Scheme 16).



Scheme 15. CuFe₂O₄ NPs-catalyzed C-Se and C-Te Cross-coupling.

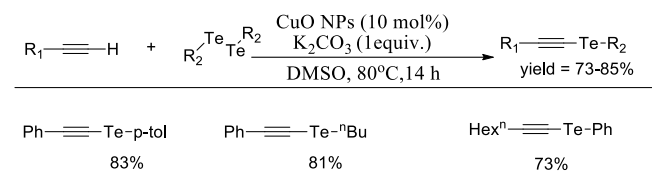


Scheme 16. CuO nanoparticle-catalyzed synthesis of ditellurides.

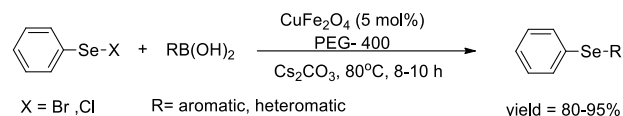
Some important information about the above-mentioned reactions is listed below: (i) organic iodides afford higher yields of the desired coupling products as compared to organic bromides; (ii) aryl halides gave a higher yield of products than alkyl halides and (iii) the electronic character of the substituents in aryl halides had little effect on the rate of the reaction. Following this work, Godoi *et al.* demonstrated that the cross-coupling reaction between terminal alkynes and diorganyltellurides occurred effectively in presence of CuO nanopowder (10 mol %) and K₂CO₃ (1 equiv.) under ligand-free conditions at 80°C [45] (Scheme 17).

Nageswar *et al.* applied magnetically separable CuFe₂O₄ nanoparticles [49] for performing cross-coupling of boronic acids with aryl selenium halides. The optimized reaction protocol significantly tolerated both aryl and heteroaryl boronic acids (Scheme 18). The authors were able to separate the catalyst from the reaction mixture easily and recycled it

several times without any significant loss of the catalytic activity. (Scheme 18). CuFe₂O₄ Nps-catalyzed coupling of boronic acids with phenyl selenium halide.

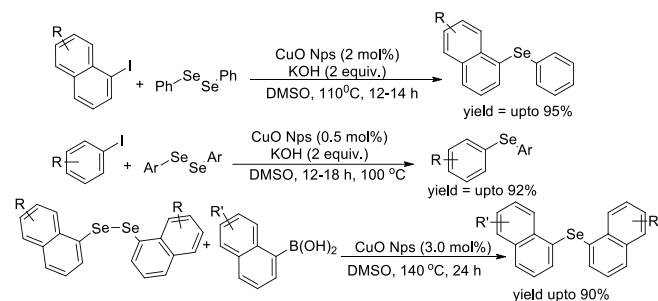


Scheme 17. CuO NPs-catalyzed synthesis of alkynyl tellurides.



Scheme 18. CuFe₂O₄ Nps-catalyzed coupling of boronic acids with phenyl selenium halide.

Khosroshahic and co-workers [10] also discussed the most important contributions of nanostructured copper-based catalysts for the synthesis of diaryl selenides from aryl boronic acids, acyl/aryl halides, and alkynes and diorganyldiselenides. They studied a series of cross-coupling reactions by employing various efficient nanocatalysts, bases, and solvents (Scheme 19).



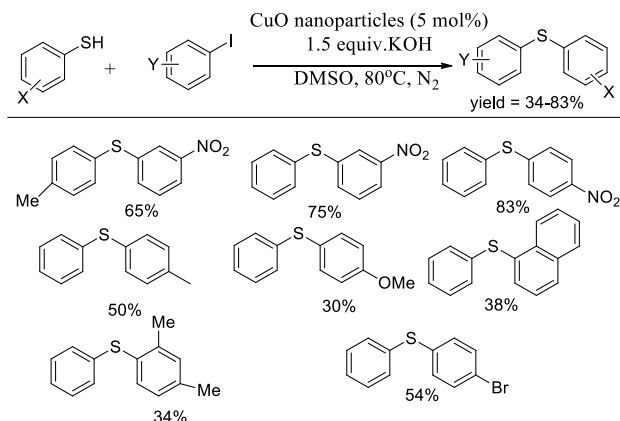
Scheme 19. CuO NPs-catalyzed various C-Se cross-couplings.

The number of reported articles on nanoparticle catalyzed C-S cross-coupling reactions is still fewer, so there is an urgent need to study the scope and limitations of these heterogeneous reactions. In 2009, Punniyamurthy *et al.* [50] highlighted an important aspect regarding the cross-coupling reactions between substituted thiols and aryl iodides having 3-NO₂, 4-NO₂, 4-Br, 4-Me, 4-OMe, and 2,4-di-Me substituents (Scheme 20). This work revealed that the attachment of electron-withdrawing groups to aryl iodides made them more reactive rather than having electron-donating substituents which indicate that the reactions occurred via oxidative addition–reductive elimination process (Scheme 21).

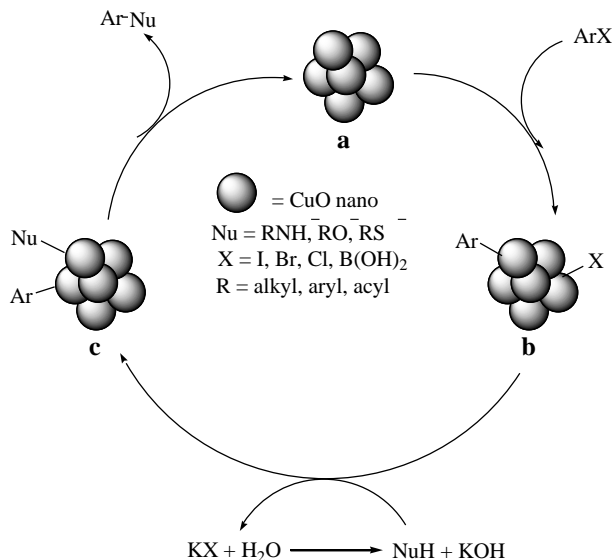
In another work, the research group of Punniyamurthy reported an efficient C-S bond formation pathway through the cross-coupling reaction of aryl and alkyl thiols with iodobenzene in presence of CuO nanoparticles [51]. The reaction proceeded well at 80 °C in DMSO in the presence of KOH under a nitrogen atmosphere. Electron-donating groups on thiols were found to be more reactive than electron-withdrawing groups. A higher extent of yield was obtained in the case of iodoarenes with electron withdrawing groups in the aromatic ring.

An effective nano copper oxide catalyzed reaction of an aryl halide with thiophenol in presence of KOH as a base dimethylacetamide (DMAc) at room temperature under ligand-free conditions was reported by Babu and Karvembu [52] (Scheme 22).

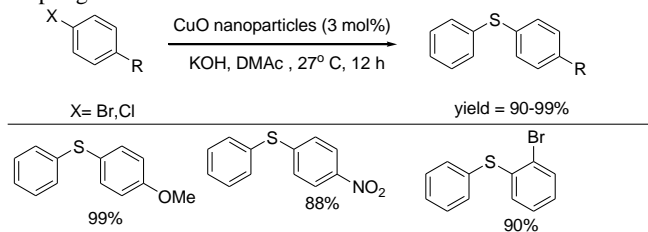
The combination of nanotechnology and ionic liquids to perform an effective C-S cross-coupling reaction with CuO nanopowder as a catalyst in [bmmim] BF₄ was reported by Braga *et al.* in 2011 [53]. The authors explored this efficient and ligand-free methodology to synthesize the organosulfides by cross-coupling reactions of aryl iodides with alkyl thiols under an ionic liquid medium (Scheme 23).



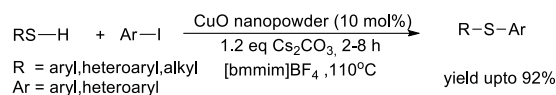
Scheme 20. CuO nanoparticle-catalyzed C-S cross-coupling.



Scheme 21. Mechanism for CuO nanoparticle catalyzed C-Se cross coupling.

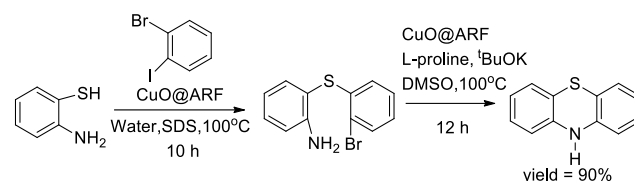


Scheme 22. CuO nanoparticle-catalyzed thiol-coupling with aryl iodides and bromides.



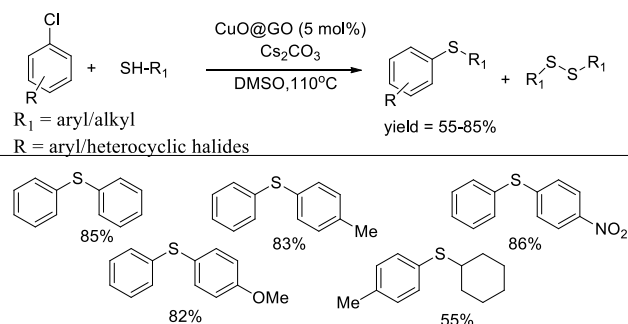
Scheme 23. Ionic liquid-mediated CuO nanoparticle-catalyzed C-S cross-coupling.

Sengupta and Basu [54] prepared poly-ionic amberlite resins embedded with CuO NPs, which efficiently catalyze the C-S cross-coupling reaction under on-water and ligand-free conditions. They performed the coupling reaction of haloarene and substituted thiol in water medium using different catalytic systems, and demonstrated the chemoselectivity in the synthesis of bioactive heterocyclic scaffold phenothiazine (Scheme 24).



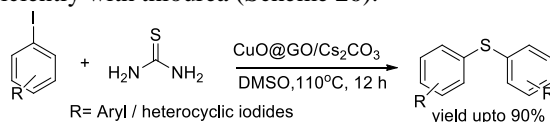
Scheme 24. Supported CuO nanoparticle-catalyzed synthesis of phenothiazine via C-S cross-coupling.

The efficient and optimized protocol for solvent- and ligand-free C-S cross-coupling reactions by using copper oxide supported graphene oxide nanoparticles under mild conditions has been explored by Kamal and co-workers [55]. A variety of aryl chlorides with good functional group tolerance underwent cross-coupling successfully with various aliphatic as well as aromatic thiols in DMSO leading to excellent yields and good selectivity (Scheme 25).



Scheme 25. Supported CuO NPs-catalyzed cross-coupling of chloroarenes with thiols.

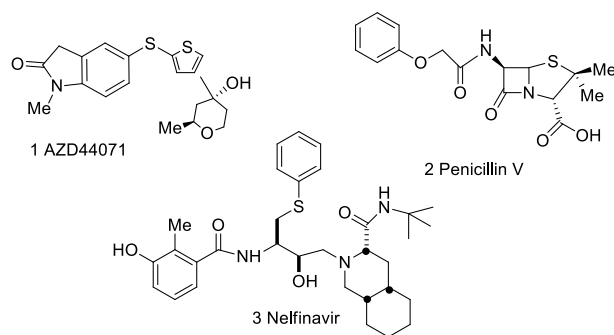
In addition, the same research group also established the scope of activity of this catalyst for the reaction of thiourea with different aryl and heterocyclic halides in the presence of Cs₂CO₃ and DMSO. The reactions afforded 90% yield after 18-20 hrs when heterocyclic halides are coupled smoothly and efficiently with thiourea (Scheme 26).



Scheme 26. Supported CuO NPs-catalyzed C-S Cross-coupling of thiourea.

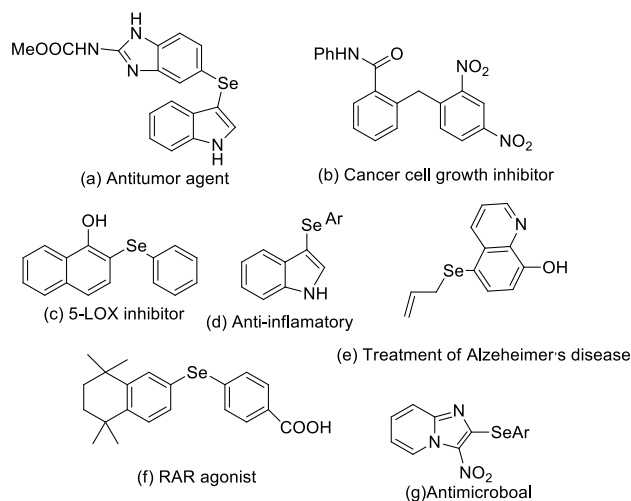
3. APPLICATION

Copper-catalyzed cross-coupling reactions are a very much effective path for the synthesis of carbon-chalcogen bonds. Copper catalysis has an important role in these cross-coupling reactions. Copper-catalyzed C-S bond-forming reactions give various molecules that are used in bio-active, pharmaceutical fields of study. AZD4407 drug [19b] is used as an anti-allergy agent, Penicillin V [56] is effective to reduce drug-resistant bacteria and Nelfinavir [57] possesses a function of treating human immunodeficiency virus (HIV) infection (Scheme 27).



Scheme 27. Different important organosulfides.

Se and Te containing compounds were also found to have interesting applications in semiconductors, magnets and NLO materials [58]. Recent developments of Se- and Te-based organocatalysts were also found to be effective in several functional group transformations under sustainable conditions for the synthesis of natural products and other biologically active molecules [59]. Organoselenides, less toxic than selenium, were found to have diverse applications in medicinal and biological fields by showing anticancer, anti-HIV, and anti-bacterial activities [60]. Aryl and heteroaryl selenides are found to have a large array of applications against several human diseases and thus have been applied to the human body as a potential therapy against them [61, 62] (Scheme 28).



Scheme 28. Different biologically important organoselenides.

CONCLUSION

The recent study of the article reveals the advent of copper-catalyzed cross-coupling reactions in tremendous development in modern organic synthesis. The article demonstrated clean, inexpensive, sustainable, and greener catalytic techniques to obtain aryl-aryl, aryl-alkyl, aryl-alkynyl, and aryl-heteroaryl organo-chalcogenides (S, Se, and Te) which are of high potential in the field of sustainable organic synthesis. Copper catalyst has proven its superiority in terms of ready availability, efficiency, and excellent functional group tolerance. The heterogeneous catalytic systems represent not only a greener approach but also retain their activity to complete the catalytic cycles significantly. The copper nanoparticle was also successfully applied in carbon-chalcogenide cross-coupling reactions. A deeper knowledge of the synthesis of carbon-chalcogenides allows a better understanding of the role of these compounds in different reaction protocols and it is important from a biomedical point of view since these types of compounds show relevant biological properties such as antitumor, antioxidant, antiviral, antimicrobial and neuroprotective effects. In conclusion, we believe that these results and knowledge about the carbon-chalcogenide cross-coupling chemistry will attract researchers to further research in the field of catalysis and organic synthesis.

LIST OF ABBREVIATIONS

DMAc	=	Dimethylacetamide
HIV	=	Human Immunodeficiency Virus
NPs	=	Nanoparticles
PEG	=	Polyethylene Glycol

CONSENT FOR PUBLICATION

Not Applicable.

FUNDING

The study was financially supported by WBDST, Govt. of West Bengal, India with an award of "GobesonaiBanga" Project funding to DK (Grant no. 43(sanc)/ST/P/S&T/15G-21/2018, dated 30/01/2019).

CONFLICT OF INTEREST

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

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support from WBDST, Govt. of West Bengal, India with an award of "GobesonaiBanga" Project funding to DK (Grant no. 43(sanc)/ST/P/S&T/15G-21/2018, dated 30/01/2019).

REFERENCES

- [1] (a) Besev, M.; Engman, L. Diastereocontrol by a hydroxyl auxiliary in the synthesis of pyrrolidines *via* radical cyclization. *Org. Lett.*, **2002**, *4*(18), 3023-3025.
<http://dx.doi.org/10.1021/ol026038t> PMID: 12201707

- (b) Berlin, S.; Ericsson, C.; Engman, L. Radical carbonylation/reductive cyclization for the construction of tetrahydrofuran-3-ones and pyrrolidin-3-ones. *J. Org. Chem.*, **2003**, *68*(22), 8386-8396.
<http://dx.doi.org/10.1021/jo030153f> PMID: 14575462
- (c) Freudendahl, D.M.; Santoro, S.; Shahzad, S.A.; Santi, C.; Wirth, T. Green chemistry with selenium reagents: Development of efficient catalytic reactions. *Angew. Chem. Int. Ed. Engl.*, **2009**, *48*(45), 8409-8411.
<http://dx.doi.org/10.1002/anie.200903893> PMID: 19802863
- (d) Srivastava, P.; Engman, L. A radical cyclization route to cyclic imines. *Tetrahedron Lett.*, **2010**, *51*(8), 1149-1151.
<http://dx.doi.org/10.1016/j.tetlet.2009.12.104>
- [2] (a) Patai, S.; Rappoport, Z. *The chemistry of organic selenium and tellurium compounds*; John Wiley and Sons: New York, **1987**, Vol. 2, .
 (b) Hellberg, J.; Remonen, T.; Johansson, M.; Inganas, O.; Theander, M.; Engman, L.; Eriksson, P. New monomers for polythiophenes. *Synth. Met.*, **1997**, *84*(1-3), 251-252.
[http://dx.doi.org/10.1016/S0379-6779\(97\)80737-0](http://dx.doi.org/10.1016/S0379-6779(97)80737-0)
 (c) Evano, G.; Blanchard, N.; Toumi, M. Copper-mediated coupling reactions and their applications in natural products and designed biomolecules synthesis. *Chem. Rev.*, **2008**, *108*(8), 3054-3131.
<http://dx.doi.org/10.1021/cr8002505> PMID: 18698737
 (d) Wirth, T. *Organoselenium Chemistry: Synthesis and Reactions*; Wiley-VCH: Weinheim, Germany, **2012**, pp. 1-65.
 (e) Manjare, S.T.; Kim, Y.; Churchill, D.G. Selenium- and tellurium-containing fluorescent molecular probes for the detection of biologically important analytes. *Acc. Chem. Res.*, **2014**, *47*(10), 2985-2998.
<http://dx.doi.org/10.1021/ar500187v> PMID: 25248146
 (f) Rampon, D.S.; Rodembusch, F.S.; Schneider, J.M.F.M.; Bechto, L.H.; Gonçalves, P.F.B.; Merlo, A.A.; Schneider, P.H. Novel selenoesters fluorescent liquid crystalline exhibiting a rich phase polymorphism. *J. Mater. Chem.*, **2010**, *20*(4), 715-722.
<http://dx.doi.org/10.1039/B917366H>
- [3] (a) Devillanova, F.A.; du Mont, W.W. *Handbook of Chalcogen Chemistry: New Perspectives in Sulfur, Selenium and Tellurium*, 2nd ed; RSC Publishing: Cambridge, **2013**.
 (b) Rappoport, Z. *PATAI's Chemistry of Functional Groups: The Chemistry of Organic Selenium and Tellurium Compounds*, 1st Ed; Wiley: Hoboken, New Jersey, **2014**.
- [4] Ruiz-Castillo, P.; Buchwald, S.L. Applications of palladium-catalyzed C-N cross-coupling reactions. *Chem. Rev.*, **2016**, *116*(19), 12564-12649.
<http://dx.doi.org/10.1021/acs.chemrev.6b00512> PMID: 27689804
- [5] Beletskaya, I.P.; Ananikov, V.P. Transition-metal-catalyzed C-S, C-Se, and C-Te bond formation via cross-coupling and atom-economic addition reactions. *Chem. Rev.*, **2011**, *111*(3), 1596-1636.
<http://dx.doi.org/10.1021/cr100347k> PMID: 21391564
- [6] Lee, C-F.; Liu, Y-C.; Badsara, S.S. Transition-metal-catalyzed C-S bond coupling reaction. *Chem. Asian J.*, **2014**, *9*(3), 706-722.
<http://dx.doi.org/10.1002/asia.201301500> PMID: 24443103
- [7] Abdoli, M.; Mirjafary, Z.; Saeidian, H.; Kakanejadifard, A. New developments in direct functionalization of C-H and N-H bonds of purine bases via metal catalyzed cross-coupling reactions. *RSC Adv.*, **2015**, *5*(55), 44371-44389.
<http://dx.doi.org/10.1039/C5RA04406E>
- [8] Kundu, D. Synthetic strategies for aryl/heterocyclic selenides and tellurides under transition-metal-catalyst free conditions. *RSC Adv.*, **2021**, *11*(12), 6682-6698.
<http://dx.doi.org/10.1039/D0RA10629A>
- [9] Giri, R.; Brusoe, A.; Troshin, K.; Wang, J.Y.; Font, M.; Hartwig, J.F. Mechanism of the ullmann biaryl ether synthesis catalyzed by complexes of anionic ligands: Evidence for the reaction of iodoarenes with ligated anionic Cu^I intermediates. *J. Am. Chem. Soc.*, **2018**, *140*(2), 793-806.
<http://dx.doi.org/10.1021/jacs.7b11853> PMID: 29224350
- [10] Didehban, K.; Vessally, E.; Hosseinian, A.; Edjlali, L.; Khosroshahic, E.S. Nanocatalysts for C-Se cross-coupling reactions. *RSC Adv.*, **2018**, *8*(1), 291-301.
<http://dx.doi.org/10.1039/C7RA12663H>
- [11] Mukherjee, N.; Kundu, D.; Ranu, B.C. Copper-Silver dual catalyzed decyanative C-Se cross-coupling. *Adv. Synth. Catal.*, **2017**, *359*(2), 329-338.
<http://dx.doi.org/10.1002/adsc.201600933>
- [12] Chatterjee, T.; Ranu, B.C. Solvent-controlled halo-selective selenylation of aryl halides catalyzed by Cu(II) supported on Al₂O₃. A general protocol for the synthesis of unsymmetrical organo mono- and bis-selenides. *J. Org. Chem.*, **2013**, *78*(14), 7145-7153.
<http://dx.doi.org/10.1021/jo401062k> PMID: 23786642
- [13] Kundu, D.; Ahammed, S.; Ranu, B.C. Microwave-assisted reaction of aryl diazonium fluoroborate and diaryl dichalcogenides in dimethyl carbonate: A general procedure for the synthesis of unsymmetrical diaryl chalcogenides. *Green Chem.*, **2012**, *14*(7), 2024-2030.
<http://dx.doi.org/10.1039/c2gc35328h>
- [14] Wang, L.; Wang, M.; Huang, F. A simple copper salt-catalyzed synthesis of unsymmetrical diaryl selenides and tellurides from arylboronic acids with diphenyl diselenide and ditelluride. *Synlett.*, **2005**, *13*(13), 2007-2010.
<http://dx.doi.org/10.1055/s-2005-871936>
- [15] (a) Kondo, T.; Mitsudo Ta, T.A. Metal-catalyzed carbon-sulfur bond formation. *Chem. Rev.*, **2000**, *100*(8), 3205-3220.
<http://dx.doi.org/10.1021/cr9902749> PMID: 11749318
 Hegedus, L.L.; McCabe, R.W. *Catalyst Poisoning*; Marcel Dekker: New York, **1984**, p. 128.
J. Chem. Soc., Faraday Trans., **1997**, *93*(14), 2445-2450.
<http://dx.doi.org/10.1039/a701293d>
 deactivation. *J. Catal.*, **1997**, *169*(1), 338-346.
<http://dx.doi.org/10.1006/jcat.1997.1709>
- [16] Zhang, Y.; Ngeow, K.C.; Ying, J.Y. The first N-heterocyclic carbene-based nickel catalyst for C-S coupling. *Org. Lett.*, **2007**, *9*(18), 3495-3498.
<http://dx.doi.org/10.1021/ol071248x> PMID: 17676857
- [17] Wong, Y-C.; Jayanth, T.T.; Cheng, C.H. Cobalt-catalyzed aryl-sulfur bond formation. *Org. Lett.*, **2006**, *8*(24), 5613-5616.
<http://dx.doi.org/10.1021/ol062344l> PMID: 17107085
- [18] Correa, A.; Carril, M.; Bolm, C. Iron-catalyzed S-arylation of thiols with aryl iodides. *Angew. Chem. Int. Ed. Engl.*, **2008**, *47*(15), 2880-2883.
<http://dx.doi.org/10.1002/anie.200705668> PMID: 18318033
- [19] (a) Bird, T.G.C.; Crawley, G.C.; Large, M.S.; Ple, P. 4-Aryl-4-hydroxy-tetrahydropyrans and 3-aryl-3-hydroxy-tetrahydrofurans as 5-lipoxygenase inhibitors. E.P. Patent No. 0623614 A1, **1998**.
 D.; Zakariya, M. P.; Perkins, J.; Rowan, P.; Sadler, P.; Singleton, J. T.; Tornos, J.; Watts, A. J.; Woodland, I. A. Efficient synthesis of AZD4407 via thioether formation by nucleophilic attack of organometallic species on sulphur. *Org. Process Res. Dev.*, **2005**, *9*, 555-569.
<http://dx.doi.org/10.1021/op0500483>
 Discovery of 1-[2-(2,4-dimethylphenylsulfanyl)phenyl]piperazine (Lu AA21004): a novel multimodal compound for the treatment of major depressive disorder. *J. Med. Chem.*, **2011**, *54*(9), 3206-3221.
<http://dx.doi.org/10.1021/jm101459g> PMID: 21486038
 (d) Basta-Kaim, A.; Budziszewska, B.; Jaworska-Feil, L.; Tetich, M.; Kubera, M.; Leśkiewicz, M.; Otczyk, M.; Lason, W. Antipsychotic drugs inhibit the human corticotropin-releasing-hormone gene promoter activity in neuro-2A cells-an involvement of protein kinases. *Neuropsychopharmacology*, **2006**, *31*(4), 853-865.
<http://dx.doi.org/10.1038/sj.npp.1300911> PMID: 16205782
- [20] Perin, G.; Alves, D.; Jacob, R.G.; Barcellos, A.; Soares, L.K.; Lenardão, E.J. Synthesis of organochalcogen compounds using non-conventional reaction media. *ChemistrySelect*, **2016**, *2*(2), 205-258.
<http://dx.doi.org/10.1002/slct.201500031>
- [21] Saba, S.; Botteselle, G.V.; Godoi, M.; Frizon, T.E.A.; Galetto, F.Z.; Rafique, J.; Braga, A.L. Copper-catalyzed synthesis of unsymmetrical diorganyl chalcogenides (Te/Se/S) from boronic acids under solvent-free conditions. *Molecules*, **2017**, *22*(8), 1367-1379.
<http://dx.doi.org/10.3390/molecules22081367> PMID: 28820487
- [22] (a) Chan, D.M.T.; Monaco, K.L.; Wang, R.; Winters, M.P. New N- and O-arylations with phenylboronic acids and cupric acetate. *Tetrahedron Lett.*, **1998**, *39*(19), 2933-2936.
[http://dx.doi.org/10.1016/S0040-4039\(98\)00503-6](http://dx.doi.org/10.1016/S0040-4039(98)00503-6)
 (b) Evans, D.A.; Katz, J.L.; West, T.R. Synthesis of diaryl ethers through the copper-promoted arylation of phenols with arylboronic

- acids. An expedient synthesis of thyroxine. *Tetrahedron Lett.*, **1998**, 39(19), 2937-2940.
[http://dx.doi.org/10.1016/S0040-4039\(98\)00502-4](http://dx.doi.org/10.1016/S0040-4039(98)00502-4)
- (c) Lam, P.Y.S.; Clark, C.G.; Saubern, S.; Adams, J.; Winters, M.P.; Chan, D.M.T.; Combs, A. New aryl/ heteroaryl C-N bond cross-coupling reactions via aryl-boronic acid/cupric acetate arylation. *Tetrahedron Lett.*, **1998**, 39(19), 2941-2944.
[http://dx.doi.org/10.1016/S0040-4039\(98\)00504-8](http://dx.doi.org/10.1016/S0040-4039(98)00504-8)
- (d) Combs, A.P.; Saubern, S.; Rafalski, M.; Lam, P.Y.S. Solid supported arylheteroaryl C-N cross-coupling reactions. *Tetrahedron Lett.*, **1999**, 40(9), 1623-1626.
[http://dx.doi.org/10.1016/S0040-4039\(99\)00026-X](http://dx.doi.org/10.1016/S0040-4039(99)00026-X)
- (e) Lam, P.Y.S.; Vincent, G.; Bonne, D.; Clark, C.G. Copper-promoted C-N bond cross-coupling with phenyl stannane. *Tetrahedron Lett.*, **2002**, 43(16), 3091-3094.
[http://dx.doi.org/10.1016/S0040-4039\(02\)00356-8](http://dx.doi.org/10.1016/S0040-4039(02)00356-8)
- (f) Combs, A.P.; Tadesse, S.; Rafalski, M.; Haque, T.S.; Lam, P.Y.S. N-arylation of primary and secondary aliphatic amines on solid supports. *J. Comb. Chem.*, **2002**, 4(2), 179-182.
<http://dx.doi.org/10.1021/cc0100767> PMID: 11886294
- (g) Lam, P.Y.S.; Bonne, D.; Vincent, G.; Clark, C.G.; Combs, A.P. N-Arylation of α -aminoesters with p-tolylboronic acid promoted by copper (II) acetate. *Tetrahedron Lett.*, **2003**, 44(8), 1691-1694.
[http://dx.doi.org/10.1016/S0040-4039\(02\)02882-4](http://dx.doi.org/10.1016/S0040-4039(02)02882-4)
- (h) Chan, D.M.T.; Monaco, K.L.; Li, R.; Bonne, D.; Clark, C.G.; Lam, P.Y.S. Copper promoted C-N and C-O bond cross-coupling with phenyl and pyridylboronates. *Tetrahedron Lett.*, **2003**, 44(19), 3863-3865.
[http://dx.doi.org/10.1016/S0040-4039\(03\)00739-1](http://dx.doi.org/10.1016/S0040-4039(03)00739-1)
- (i) Lam, P.Y.S.; Vincent, G.; Bonne, D.; Clark, C.G. Copper-promoted/catalyzed C-N and C-O bond cross-coupling with vinylboronic acid and its utilities. *Tetrahedron Lett.*, **2003**, 44(26), 4927-4931.
[http://dx.doi.org/10.1016/S0040-4039\(03\)01037-2](http://dx.doi.org/10.1016/S0040-4039(03)01037-2)
- [23] Kalinin, A. V.; Bower, J. F.; Riebel, P.; Snieckus, V.J. The directed ortho metalation-ullmann connection. A new Cu(I)-catalyzed variant for the synthesis of substituted diaryl ethers. *Org. Chem.*, **1999**, 64, 2986-2987.
- [24] Ke, F.; Qu, Y.; Jiang, Z.; Li, Z.; Wu, D.; Zhou, X. An efficient copper-catalyzed carbon-sulfur bond formation protocol in water. *Org. Lett.*, **2011**, 13(3), 454-457.
<http://dx.doi.org/10.1021/ol102784c> PMID: 21174396
- [25] Gujadhur, R.K.; Venkataraman, D. A general method for the formation of diaryl selenides using copper(I) catalysts. *Tetrahedron Lett.*, **2003**, 44(1), 81-84.
[http://dx.doi.org/10.1016/S0040-4039\(02\)02480-2](http://dx.doi.org/10.1016/S0040-4039(02)02480-2)
- [26] (a) Gates, B.C. Supported metal clusters: Synthesis, structure, and catalysis. *Chem. Rev.*, **1995**, 95(3), 511-522.
<http://dx.doi.org/10.1021/cr00035a003>
- (b) Bergbreiter, D.E. Alternative polymer supports for organic chemistry. *Med. Res. Rev.*, **1999**, 19(5), 439-450.
[http://dx.doi.org/10.1002/\(SICI\)1098-1128\(199909\)19:5<439: AID-MED9>3.0.CO;2-7](http://dx.doi.org/10.1002/(SICI)1098-1128(199909)19:5<439: AID-MED9>3.0.CO;2-7) PMID: 10502745
- [27] Ahammed, S.; Kundu, D.; Mukherjee, N.; Ranu, B.C. Microwave assisted synthesis of chalcogenides. *Curr. Microw. Chem.*, **2017**, 4, 25-35.
- [28] Kappe, C.O.; Pieber, B.; Dallinger, D. Microwave effects in organic synthesis: Myth or reality? *Angew. Chem. Int. Ed. Engl.*, **2013**, 52(4), 1088-1094.
<http://dx.doi.org/10.1002/anie.201204103> PMID: 23225754
- [29] Rathi, A. K.; Gawandea, M. B.; Zboril, R.; Varma, R.S. Microwave-assisted synthesis-catalytic applications in aqueous media. *Coord. Chem. Rev.*, **2015**, 291, 68-94.
<http://dx.doi.org/10.1016/j.ccr.2015.01.011>
- [30] Gawande, M.B.; Shelke, S.N.; Zboril, R.; Varma, R.S. Microwave-assisted chemistry: Synthetic applications for rapid assembly of nanomaterials and organics. *Acc. Chem. Res.*, **2014**, 47(4), 1338-1348.
<http://dx.doi.org/10.1021/ar400309b> PMID: 24666323
- [31] Bagley, M.C.; Dix, M.C.; Fusillo, V. Rapid Ullmann-type synthesis of aryl sulfides using a copper(I) catalyst and ligand under microwave irradiation. *Tetrahedron Lett.*, **2009**, 50(26), 3661-3664.
<http://dx.doi.org/10.1016/j.tetlet.2009.03.115>
- [32] Beletskaya, I.P.; Sigeev, A.S.; Peregodov, A.; Petrovskii, P.V.; Khrustalov, V.N. Microwave-assisted synthesis of diaryl selenides. Elucidation of Cu(I)-catalyzed reaction mechanism. *Chem. Lett.*, **2010**, 39(7), 720-722.
<http://dx.doi.org/10.1246/cl.2010.720>
- [33] Ricordi, V.G.; Freitas, C.S.; Perin, G.; Lenarda, E.J.; Jacob, R.G.; Savegnago, L.; Alves, D. Glycerol as a recyclable solvent for copper-catalyzed cross-coupling reactions of diaryl diselenides with aryl boronic acids. *Green Chem.*, **2012**, 14(4), 1030-1034.
<http://dx.doi.org/10.1039/c2gc16427b>
- [34] (a) Wasserscheid, P.; Welton, P. Ionic liquids in synthesis. *Org. Process Res. Dev.*, **2003**, 7, 223-224.
<http://dx.doi.org/10.1021/op0340210>
- (b) Welton, T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.*, **1999**, 99(8), 2071-2084.
<http://dx.doi.org/10.1021/cr980032t> PMID: 11849019
- (c) Dupont, J.; de Souza, R.F.; Suarez, P.A.Z. Ionic liquid (molten salt) phase organometallic catalysis. *Chem. Rev.*, **2002**, 102(10), 3667-3692.
<http://dx.doi.org/10.1021/cr010338r> PMID: 12371898
- (d) van Rantwijk, F.; Sheldon, R.A. Biocatalysis in ionic liquids. *Chem. Rev.*, **2007**, 107(6), 2757-2785.
<http://dx.doi.org/10.1021/cr050946x> PMID: 17564484
- (e) Martins, M.A.P.; Frizzo, C.P.; Moreira, D.N.; Zanatta, N.; Bonacorso, H.G. Ionic liquids in heterocyclic synthesis. *Chem. Rev.*, **2008**, 108(6), 2015-2050.
<http://dx.doi.org/10.1021/cr078399y> PMID: 18543878
- (f) Olivier-Bourbigou, H.; Magna, L.; Morvan, D. Ionic liquids and catalysis: Recent progress from knowledge to applications. *Appl. Catal. A Gen.*, **2010**, 373(1-2), 1-56.
<http://dx.doi.org/10.1016/j.apcata.2009.10.008>
- (g) Ranu, B.C.; Banerjee, S. Ionic liquid as catalyst and reaction medium. The dramatic influence of a task-specific ionic liquid, [bmIm]OH, in Michael addition of active methylene compounds to conjugated ketones, carboxylic esters, and nitriles. *Org. Lett.*, **2005**, 7(14), 3049-3052.
<http://dx.doi.org/10.1021/ol051004h> PMID: 15987202
- [35] Chaugule, A.A.; Pawar, A.A.; Tamboli, A.H.; Bandal, H.A.; Chung, W.J.; Kim, H. Ionic liquid based Cu₂S@C catalyst for effective coupling of diaryldiselenide with aryl halides under ligand-free conditions. *Chem. Eng. J.*, **2018**, 351, 490-497.
<http://dx.doi.org/10.1016/j.cej.2018.06.081>
- [36] Soria-Castro, S.M.; Peññory, A.B. Efficient Cu-catalyzed base-free C-S coupling under conventional and microwave heating. A simple access to S-heterocycles and sulfides. *Beilstein J. Org. Chem.*, **2013**, 9, 467-475.
<http://dx.doi.org/10.3762/bjoc.9.50> PMID: 23503063
- [37] Vyhivskiy, O.; Dlin, E. A.; Finko, A. V.; Stepanova, S.P.; Ivanenkov, Y.A.; Skvortsov, D.A.; Mironov, A.V.; Zyk, N.V.; Majouga, A.G.; Beloglazkina, E.K. Copper-promoted C-Se cross-coupling of 2-selenohydantoin with arylboronic acids in an open flask. *ACS Comb. Sci.*, **2019**, 21(6), 456-464.
<http://dx.doi.org/10.1021/acscombsci.9b00021> PMID: 31009196
- [38] Sperotto, E.; van Klink, G.P.M.; de Vries, J.G.; van Koten, G. Ligand-free copper-catalyzed C-S coupling of aryl iodides and thiols. *J. Org. Chem.*, **2008**, 73(14), 5625-5628.
<http://dx.doi.org/10.1021/jo800491k> PMID: 18570479
- [39] Li, Z.; Ke, F.; Deng, H.; Xu, H.; Xiang, H.; Zhou, X. Synthesis of disulfides and diselenides by copper-catalyzed coupling reactions in water. *Org. Biomol. Chem.*, **2013**, 11(18), 2943-2946.
<http://dx.doi.org/10.1039/c3ob40464a> PMID: 23538860
- [40] Kundu, D.; Mukherjee, N.; Ranu, B.C. A general and green procedure for the synthesis of organochalcogenides by CuFe₂O₄ nanoparticle catalyzed coupling of organoboronic acids and dichalcogenides in PEG-400. *RSC Adv.*, **2013**, 3(1), 117-125.
<http://dx.doi.org/10.1039/C2RA22415A>
- [41] Alves, D.; Santos, C.G.; Paixão, M.W.; Soares, L.C.; Souza, D.; Rodrigues, O.E.D.; Braga, A.L. CuO nanoparticles: An efficient and recyclable catalyst for cross-coupling reactions of organic diselenides with aryl boronic acids. *Tetrahedron Lett.*, **2009**, 50(48), 6635-6638.
<http://dx.doi.org/10.1016/j.tetlet.2009.09.052>
- [42] Mohammadi, S.; Musavi, M.; Abdollahzadeh, F.; Babadoust, S.; Hosseini, A. Application of nanocatalysts in C-Te cross-coupling reactions: An overview. *Chem. Rev. Lett.*, **2018**, 1, 49-55.
- [43] Astruc, D. *Nanoparticles and Catalysis*; Wiley-VCH: Weinheim, **2008**.

- [44] (a) Pacchioni, G. Quantum chemistry of oxide surfaces: From CO chemisorption to the identification of the structure and nature of point defects on MgO. *Surf. Rev. Lett.*, **2000**, *7*, 277-306.
<http://dx.doi.org/10.1142/S0218625X00000336>
(b) Durán-Pachón, L.; van Maarseveen, J.H.; Rothenberg, G. Click chemistry: Copper clusters catalyse the cycloaddition of azides with terminal alkynes. *Adv. Synth. Catal.*, **2005**, *347*(6), 811-815.
<http://dx.doi.org/10.1002/adsc.200404383>
(c) Vessally, E.; Babazadeh, M.; Hosseinian, A.; Arshadi, S.; Edjlali, L. Nanocatalysts for chemical transformation of carbon dioxide. *J. CO₂ Util.*, **2017**, *21*, 491-502.
(d) Vessally, E. A new avenue to the synthesis of highly substituted pyrroles: Synthesis from *N*-propargylamines. *RSC Adv.*, **2016**, *6*(22), 18619-18631.
<http://dx.doi.org/10.1039/C5RA20706A>
(e) Vessally, E.; Hosseinian, A.; Edjlali, L.; Bekhradnia, A.; Esrafil, M.D. New page to access pyridine derivatives: Synthesis from *N*-propargylamines. *RSC Adv.*, **2016**, *6*(75), 71662-71675.
<http://dx.doi.org/10.1039/C6RA08720E>
- [45] Godoi, M.; Ricardo, E. W.; Frizon, T. E.; Rocha, M.S.T.; Singh, D.; Paixão, M.W.; Braga, A.L. An efficient synthesis of alkynyl selenides and tellurides from terminal acetylenes and diorganyl diselenides or ditellurides catalyzed by recyclable copper oxide nanopowder. *Tetrahedron*, **2012**, *68*(51), 10426-10430.
<http://dx.doi.org/10.1016/j.tet.2012.08.086>
- [46] Saha, A.; Saha, D.; Ranu, B.C. Copper nano-catalyst: Sustainable phenyl-selenylation of aryl iodides and vinyl bromides in water under ligand free conditions. *Org. Biomol. Chem.*, **2009**, *7*(8), 1652-1657.
<http://dx.doi.org/10.1039/b819137a> PMID: 19343253
- [47] (a) Schätz, A.; Reiser, O.; Stark, W.J. Nanoparticles as semi-heterogeneous catalyst supports. *Chemistry*, **2010**, *16*(30), 8950-8967.
<http://dx.doi.org/10.1002/chem.200903462> PMID: 20645330
(b) Polshettiwar, V.; Luque, R.; Fihri, A.; Zhu, H.; Bouhrara, M.; Basset, J.M. Magnetically recoverable nanocatalysts. *Chem. Rev.*, **2011**, *111*(5), 3036-3075.
<http://dx.doi.org/10.1021/cr100230z> PMID: 21401074
- [48] Singh, D.; Deobald, A.M.; Camargo, L.R.S.; Tabarelli, G.; Rodrigues, O.E.; Braga, A.L. An efficient one-pot synthesis of symmetrical diselenides or ditellurides from halides with CuO nanopowder/Se⁰ or Te⁰/base. *Org. Lett.*, **2010**, *12*(15), 3288-3291.
<http://dx.doi.org/10.1021/ol100558b> PMID: 20586442
- [49] Reddy, K. H. V.; Satish, G.; Ramesh, K.; Karnakar, K.; Nageswar, Y.V.D. Magnetically separable CuFe₂O₄ Nanoparticle catalyzed C-Se cross coupling in reusable PEG medium. *Chem. Lett.*, **2012**, *41*(6), 585-587.
<http://dx.doi.org/10.1246/cl.2012.585>
- [50] Jammi, S.; Sakthivel, S.; Rout, L.; Mukherjee, T.; Mandal, S.; Mitra, R.; Saha, P.; Punniyamurthy, T. CuO nanoparticles catalyzed C-N, C-O, and C-S cross-coupling reactions: scope and mechanism. *J. Org. Chem.*, **2009**, *74*(5), 1971-1976.
<http://dx.doi.org/10.1021/jo8024253> PMID: 19173559
- [51] Rout, L.; Sen, T. K.; Punniyamurthy, T. Efficient CuO-nanoparticle-catalyzed CS cross-coupling of thiols with iodobenzene. *Angew. Chem. Int. Ed.*, **2007**, *46*, 5583-5586.
<http://dx.doi.org/10.1002/anie.200701282>
- [52] Babu, S.G.; Karvembu, R. Room temperature Ullmann type C-O and C-S cross coupling of aryl halides with phenol/thiophenol catalyzed by CuO nanoparticles. *Tetrahedron Lett.*, **2013**, *54*(13), 1677-1680.
<http://dx.doi.org/10.1016/j.tetlet.2013.01.063>
- [53] Schwab, R. S.; Singh, D.; Alberto, E. E.; Piquini, P.; Rodrigues, O.E.D.; Braga, A.L. C-S cross-coupling of thiols with aryl iodides under ligand-free conditions using nano copper oxide as a recyclable catalyst in ionic liquid. *Catal. Sci. Technol.*, **2011**, *1*(4), 569-573.
<http://dx.doi.org/10.1039/c1cy00091h>
- [54] Sengupta, D.; Basu, B. An efficient heterogeneous catalyst (CuO@ARF) for on-water C-S coupling reaction: An application to the synthesis of phenothiazine structural scaffold. *Org. Med. Chem. Lett.*, **2014**, *4*(1), 17.
<http://dx.doi.org/10.1186/s13588-014-0017-7> PMID: 26548993
- [55] Kamal, A.; Srinivasulu, V.; Murty, J.N.S.R.C.; Shankaraiah, N.; Nagesh, N.; Reddy, T.S.; Rao, A.V.S. Copper oxide nanoparticles supported on graphene oxide-catalyzed S-arylation: An efficient and ligand-free synthesis of aryl sulfides. *Adv. Synth. Catal.*, **2013**, *355*(11-12), 2297-2307.
<http://dx.doi.org/10.1002/adsc.201300416>
- [56] Sheehan, J.C.; Henery-Logan, K.R. The total synthesis of penicillin V. *J. Am. Chem. Soc.*, **1959**, *81*(12), 3089-3094.
<http://dx.doi.org/10.1021/ja01521a044>
- [57] Raghavan, S.; Krishnaiah, V.; Sridhar, B. Asymmetric synthesis of the potent HIV-protease inhibitor, nelfinavir. *J. Org. Chem.*, **2010**, *75*(2), 498-501.
<http://dx.doi.org/10.1021/jo902048t> PMID: 20000659
- [58] Ahluwalia, G.K. *Application of Chalcogenides: S, Se and Te*; Springer: New York City, **2017**.
<http://dx.doi.org/10.1007/978-3-319-41190-3>
- [59] Laitien, R.; Oilunkaniemi, R. *Selenium and Tellurium Reagents: In Chemistry and Material Science*; De Gruyter: Berlin, Germany, **2019**.
- [60] Jain, V.K.; Priyadarsini, K.I. *Organoselenium Compounds in Biology and Medicine: Synthesis, Biological and Therapeutic Treatments*; RSC Publishing: Cambridge, **2017**.
<http://dx.doi.org/10.1039/9781788011907>
- [61] (a) Sarma, B.K.; Mughesh, G. Thiol cofactors for selenoenzymes and their synthetic mimics. *Org. Biomol. Chem.*, **2008**, *6*(6), 965-974.
<http://dx.doi.org/10.1039/b716239a> PMID: 18327317
(b) Mughesh, G.; Singh, H.B. Synthetic organoselenium compounds as antioxidants: Glutathione peroxidase activity. *Chem. Soc. Rev.*, **2000**, *29*(5), 347-357.
<http://dx.doi.org/10.1039/a908114c>
(c) Woods, J.A.; Hadfield, J.A.; McGown, A.T.; Fox, B.W. Bioactivity and molecular modelling of diphenylsulfides and diphenylselenides. *Bioorg. Med. Chem.*, **1993**, *1*(5), 333-340.
[http://dx.doi.org/10.1016/S0968-0896\(00\)82139-2](http://dx.doi.org/10.1016/S0968-0896(00)82139-2) PMID: 8081863
- [62] (a) Pang, Y.; An, B.; Lou, L.; Zhang, J.; Yan, J.; Huang, L.; Li, X.; Yin, S. Design, synthesis, and biological evaluation of novel selenium-containing isocombretastatins and phenstatins as antitumor agents. *J. Med. Chem.*, **2017**, *60*, 7300-7314.
(b) Sancineto, L.; Mariotti, A.; Bagnoli, L.; Marini, F.; Desantis, J.; Iraci, N.; Santi, C.; Pannecouque, C.; Tabarrini, O. Design and synthesis of diselenobisbenzamides (DISEBAs) as nucleocapsid protein 7 (NCp7) inhibitors with anti-HIV activity. *J. Med. Chem.*, **2015**, *58*(24), 9601-9614.
<http://dx.doi.org/10.1021/acs.jmedchem.5b01183> PMID: 26613134
(c) de Souza, D.; Mariano, D. O. C.; Nedel, F.; Schultze, E.; Campos, V. F.; Seixas, F.; daSilva, R. S.; Munchen, T. S.; Ilha, V.; Dornelles, L.; Braga, A. L.; Rocha, J. B. T.; Collares, T.; Rodrigues, O.E.D. New organochalcogen multitarget drug: Synthesis and antioxidant and antitumor activities of chalcogenozidovudine derivatives. *J. Med. Chem.*, **2015**, *58*(8), 3329-3339.
<http://dx.doi.org/10.1021/jm5015296> PMID: 25811955

DISCLAIMER: The above article has been published, as is, ahead-of-print, to provide early visibility but is not the final version. Major publication processes like copyediting, proofing, typesetting and further review are still to be done and may lead to changes in the final published version, if it is eventually published. All legal disclaimers that apply to the final published article also apply to this ahead-of-print version.