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Metal-Mediated Oxidative Radical Processes for the Synthesis of Heterocycles

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Abstract This chapter describes recent development on synthesis of heterocycles via metal-mediated oxidative radical reactions. Oxidative radical processes enabling difunctionalization of carbon-carbon unsaturated bonds (alkenes or alkynes) or functionalization of carbon-hydrogen bonds for heterocycle synthesis will be discussed. The mechanistic insight of each transformation will also be addressed.

Keywords Cascade reactions • C-H functionalization • Difunctionalization of alkene • Heterocycles • Metals • Oxidation • Radicals • Single-electron transfer

Contents

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1 Introduction

Heterocyclic motifs are found in myriad of biologically active natural products and pharmaceutical compounds [1–4] as well as material-based application [5, 6]. There is therefore a high demand for efficient production of heterocycles of needs and interests [7–9]. Oxidative molecular transformations that incorporate heteroatom units into carbon-based organic scaffolds are one of the most frequently used methods to construct heterocyclic skeletons with enhancement of the molecular complexity. In this context, various radical species have been utilized under metal-mediated/catalyzed oxidative reaction conditions for the development of new methodologies to convert readily accessible substrates into highly oxidized targeted heterocycles. This chapter will cover the recent selected reports (mainly published in the last decade) on metal-mediated oxidative carbon-heteroatom bond formation for the construction of heterocycles via a free-radical mechanism.

2 Heterocycle Synthesis via Oxidative Difunctionalization of Alkenes or Alkynes

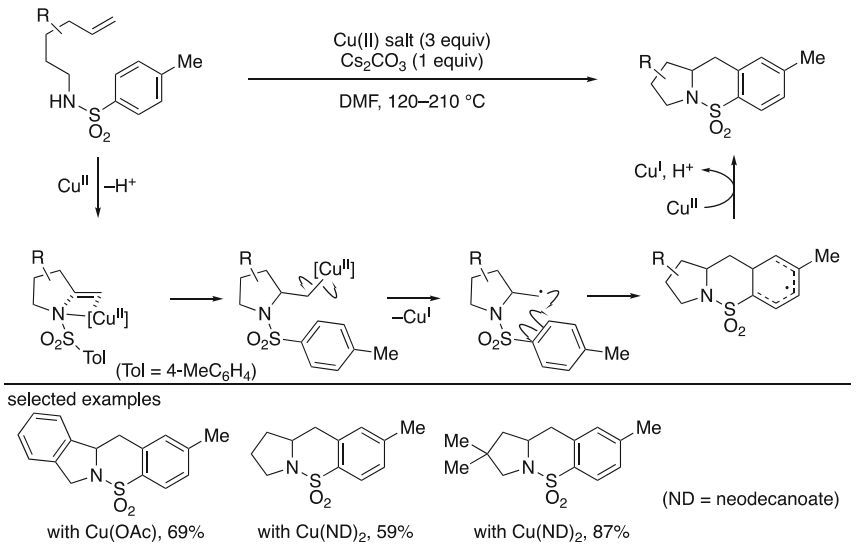
The construction of heterocycles triggered by cyclization or annulation onto alkenes or alkynes provides a variety of reaction patterns in terms of the functionality installed onto the heterocyclic scaffolds. The use of radical species or radical intermediates under metal-mediated/catalyzed oxidative reaction conditions enables facile oxidative difunctionalization of alkenes or alkynes.

2.1 Carboamination

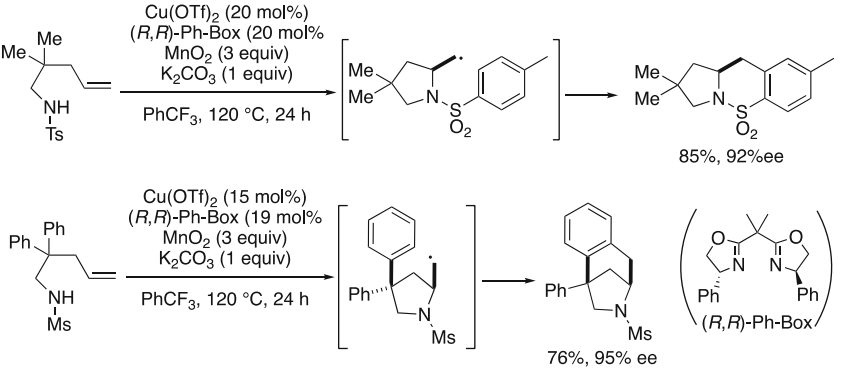
Chemler's group reported a Cu(II)-mediated intramolecular carboamination of *N*-alkenyl-*N*-arylsulfonamides for the synthesis of bicyclo[4.3.0]sultams (Scheme 1) [10]. Elucidation of the reaction mechanism revealed that the process is initiated by a concerted *syn* aminocupration of alkenes to provide organocopper(II) intermediates, which undergo homolysis of the C-Cu(II) bond to form the C-centered radicals [11]. Subsequent radical cyclization onto the aromatic ring followed by oxidation/re-aromatization affords bicyclo[4.3.0]sultams.

The catalytic asymmetric variant of this transformation was realized by using a combination of $Cu(OTf)_2$ and (*R*,*R*)-BOX ligand with MnO_2 as the terminal oxidant (Scheme 2) [12]. Interestingly, the reaction of *N*-mesyl-4-pentenylamines bearing the C2 geminal diphenyl moiety gave 6-azabicyclo[3.2.1]octanes [13, 14].

Matsunaga and Kanai reported the use of *N*-fluorobenzenesulfonylimide (NFSI) in the Cu(I)-catalyzed carboamination of unactivated alkenes, leading to the synthesis of sultam derivatives (Scheme 3) [15]. The process is initiated by a single-electron



Scheme 1 Cu(II)-catalyzed synthesis of bicyclo[4.3.0]sultams

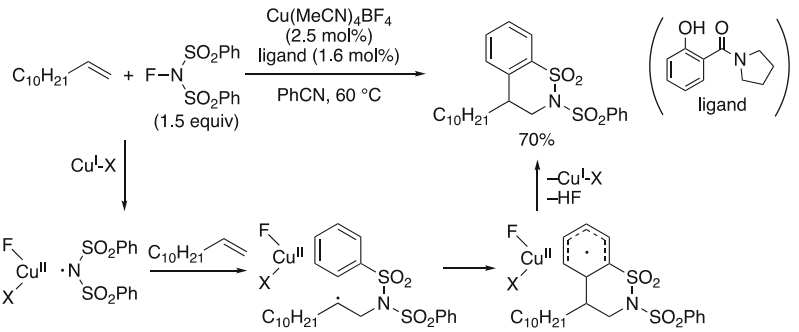


Scheme 2 Cu(II)-catalyzed enantioselective carboamination

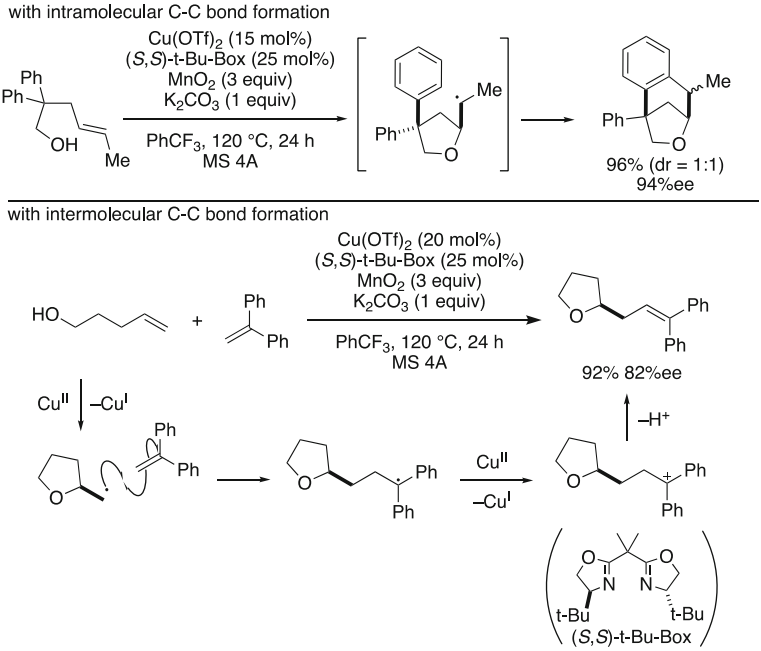
reduction of NFSI by the Cu(I) catalyst, generating a Cu(II)-bound sulfonylimide radical, which subsequently adds onto alkenes in an *anti*-Markovnikov fashion to provide C-centered radicals. The ensuing intramolecular radical cyclization onto the phenylsulfonyl moiety delivers sultams.

2.2 Carbooxygenation

Chemler's group successfully extended the Cu(II)-catalyzed MnO_2-mediated carboamination strategy to the corresponding carbooxygenation of alkenyl alcohols



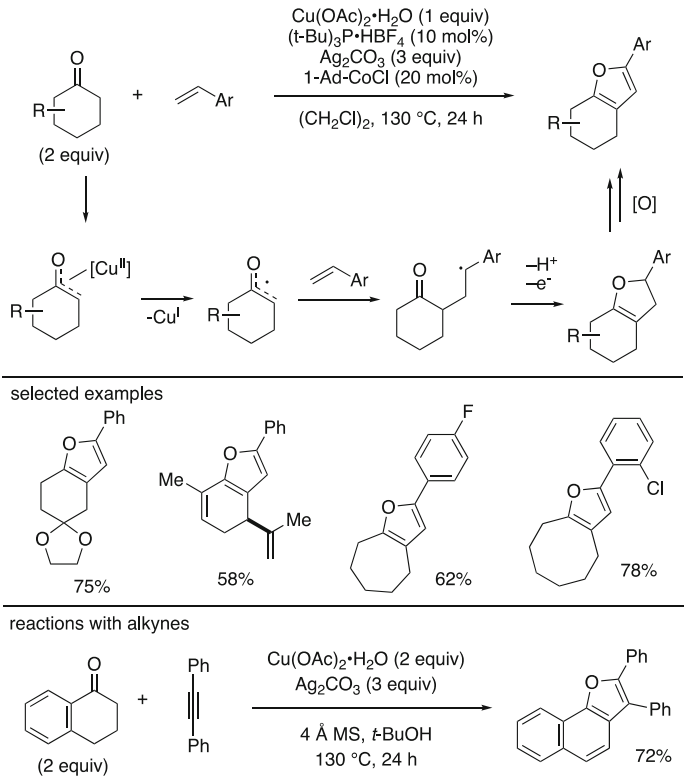
Scheme 3 Cu(I)-catalyzed carboamination with NSFI



Scheme 4 Cu(II)-catalyzed carbooxygenation of alkenes for the construction of furans

[16]. For example, the reaction of 4-pentenyl alcohol having a C2-geminal diphenyl moiety was transformed into 6-oxabicyclo[3.2.1]octanes through oxycupration of alkenes, followed by intramolecular radical C-C bond formation (Scheme 4). Moreover, the resulting C-centered radicals formed via oxycupration and ensuing C-Cu bond homolysis can be trapped by external aryl alkenes [17].

Recently, Maiti's group reported a $Cu(OAc)_2$-mediated intermolecular annulation between simple ketones and alkenes for the synthesis of furan derivatives (Scheme 5) [18]. The process is initiated by an oxidative generation of α-keto

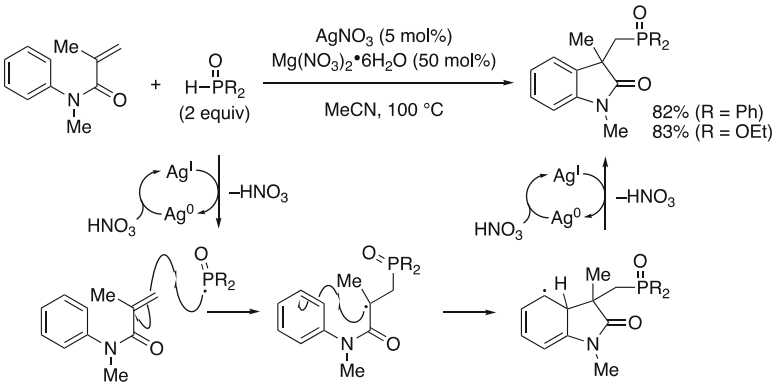


Scheme 5 Cu(II)-mediated carbooxygenation of alkenes and alkynes through annulation with ketones

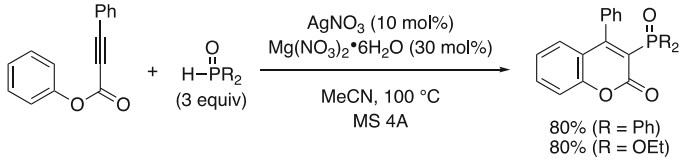
radicals, which subsequently add onto alkenes to generate the first C-C bond. The resulting C-centered radicals are oxidatively coupled intramolecularly with the carbonyl oxygen to form dihydrofurans, which are further aromatized under the reaction conditions. This method can also be applied to the annulation of ketones with alkynes.

2.3 Carbophosphination

Synthesis of oxindoles bearing a phosphine oxide moiety was realized by Yang's group through Ag-catalyzed carbophosphination of acrylamides with secondary phosphine oxides (Scheme 6) [19]. Single-electron oxidation of phosphine oxides by $AgNO_3$ generates P-centered radicals, which add onto acrylamides to form α-amido radicals. Subsequent radical cyclization with the aryl moiety, followed by oxidation/re-aromatization, delivers oxindoles. The catalytic cycle is supposed



Scheme 6 Ag-catalyzed radical carbophosphination of alkenes



Scheme 7 Ag-catalyzed radical carbophosphination of alkynes

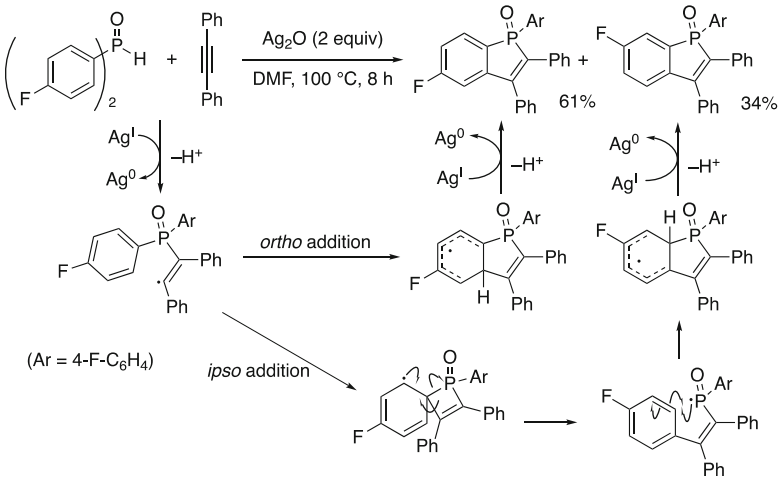
to be maintained by regeneration of $AgNO_3$ by oxidation of Ag(0) with HNO_3, $Mg(NO_3)_2$ supplying sufficient amount of nitrate ion in the reaction mixture.

Huang and Wu applied the Yang's reaction conditions to elaborate 3-phosphorated coumarins from phenyl alkynoates through radical carbophosphination of alkynes (Scheme 7) [20].

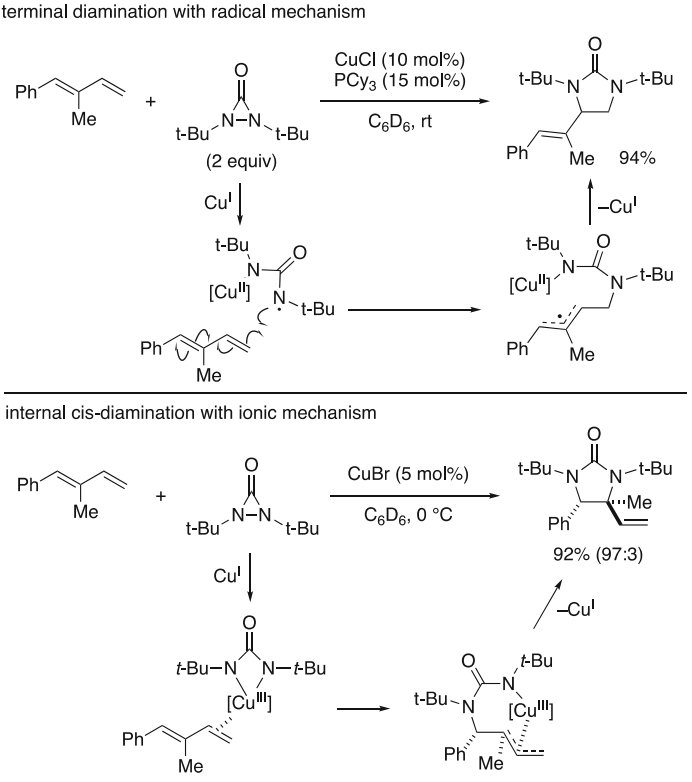
Duan's group developed an Ag(I)-mediated carbophosphination of alkynes with diarylphosphine oxides for the synthesis of benzo[*b*]phospholes (Scheme 8) [21]. The reaction started with the oxidative generation of P-centered radicals and their addition onto alkynes to form vinylic radicals. The ensuing radical cyclization onto the aryl moiety occurred through two different pathways, either on *ortho*- or *ipso*-carbons, leading to two different benzo[*b*]phosphole products after oxidative re-aromatization. The ratio of *ortho*- and *ipso*-cyclization products varied depending on the nature of the substituents on the aryl moiety.

2.4 Diamination

Shi's group disclosed intermolecular diamination of conjugated dienes with diaziridinone, catalyzed by the CuCl-phosphine system for the synthesis of cyclic ureas (Scheme 9) [22, 23]. Single-electron reduction of the diaziridinone by the CuCl-phosphine complex gave the Cu(II)-N radical species, which undergoes



Scheme 8 Ag-mediated carbophosphination of alkynes through annulation with diarylphosphine oxides

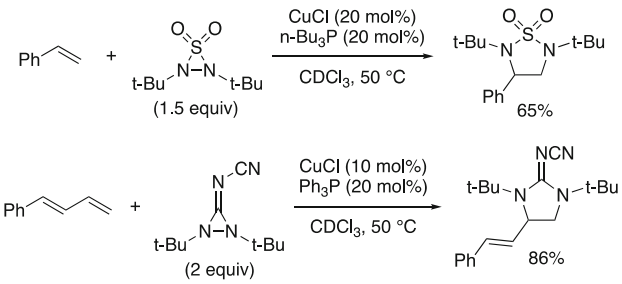


Scheme 9 Cu-catalyzed oxidative diamination of conjugated dienes with diaziridinone

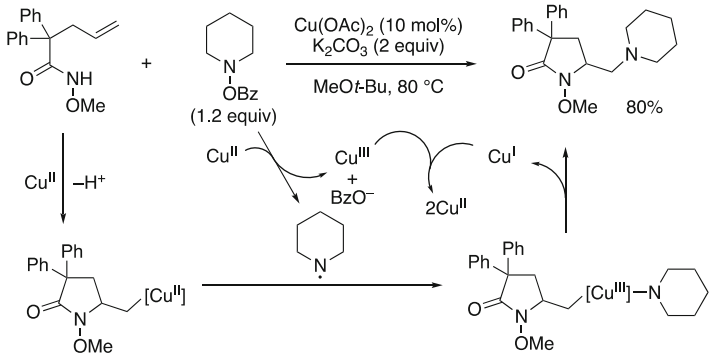
radical addition onto the sterically less hindered terminal carbon of conjugated dienes to construct the first C-N bond with generation of allylic radicals. The second C-N bond formation takes place by subsequent radical recombination of the allylic radicals with the Cu(II)-amide moiety to furnish cyclic urea products with regeneration of the Cu(I)-catalyst. It is worth of note that the reactions of conjugated dienes with diaziridinone using CuBr as the catalyst induce *cis*-diamination of internal alkenes through the four-membered Cu(III)-metallacycle, undergoing ionic migratory insertion, followed by C-N reductive elimination. This radical diamination method was extended to diamination of 1,1-disubstituted alkenes [24]. Asymmetric variants were developed using the Cu(I)-chiral phosphine/phosphate catalytic systems [25, 26].

Cu-catalyzed radical diamination of conjugate alkenes is also enabled by using *N*,*N*-di-*t*-butylthiadiaziridine 1,1-dioxide and *N*,*N*-di-*t*-butyl-3-(cyanimino)-diaziridine under the CuCl-phosphine catalysis systems [27, 28] (Scheme 10).

Wang's group developed a Cu-catalyzed synthesis of *N*-methoxylactams from alkenyl *N*-methoxyamides and *O*-benzoylhydroxylamines through diamination of alkenes (Scheme 11) [29]. In this process, *O*-benzoylhydroxylamines serve as the external nitrogen source and the stoichiometric oxidant to maintain the catalytic turnover. It was proposed that the Cu(II) species play two roles: one is to initiate



Scheme 10 Cu-catalyzed diamination of conjugated alkenes



Scheme 11 Cu(II)-catalyzed diamination of alkenylamides with hydroxylamines

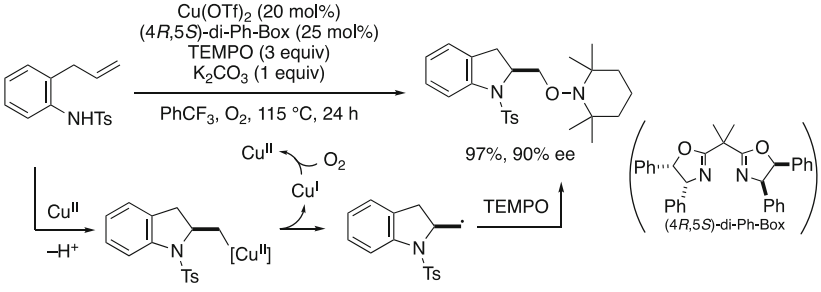
aminocupration of alkenyl *N*-methoxyamides to give organocopper intermediates; another is to reduce *O*-benzoylhydroxylamines to generate aminyl radicals and Cu(III) species. Subsequent radical recombination between the organocopper intermediates and aminyl radicals, followed by C-N reductive elimination, completes the diamination along with formation of Cu(I) species. Comproportionation of the resulting Cu(I) and Cu(III) species generates the active Cu(II) species.

2.5 *Aminooxygenation*

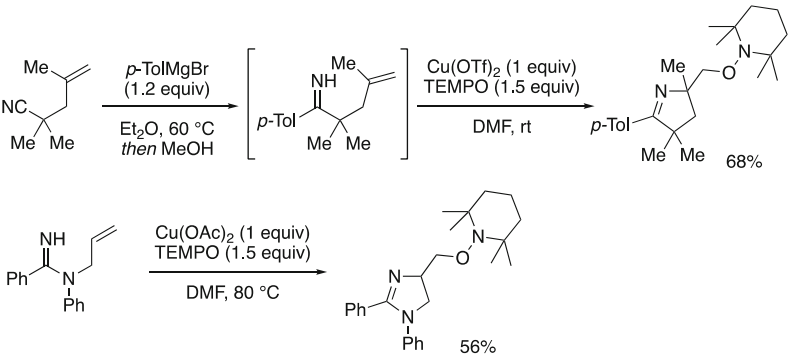
Chemler's group reported the Cu-catalyzed asymmetric synthesis of indolines from *o*-allyl-*N*-Ts-anilines and TEMPO through aminooxygenation of alkenes. Similarly with these authors' earlier studies, the reaction was initiated by aminocupration of alkenes. Subsequent homolysis of the C-Cu bond generates C-radicals, which are trapped by TEMPO to give the aminooxygenation products [30]. In this reaction, the Cu(I) species is reoxidized to the Cu(II) by molecular oxygen to maintain the catalytic turnover (Scheme 12).

Similarly, Chiba's group reported a synthesis of 2-(oxymethyl)dihydropyrroles by Cu(II)-mediated aminooxygenation of alkenyl *N*-H imines (generated from alkenyl carbonitriles and Grignard reagents) with TEMPO (Scheme 13) [31]. The method was extended to the use of *N*-allylamidines for synthesis of 2-(oxymethyl) dihydroimidazoles.

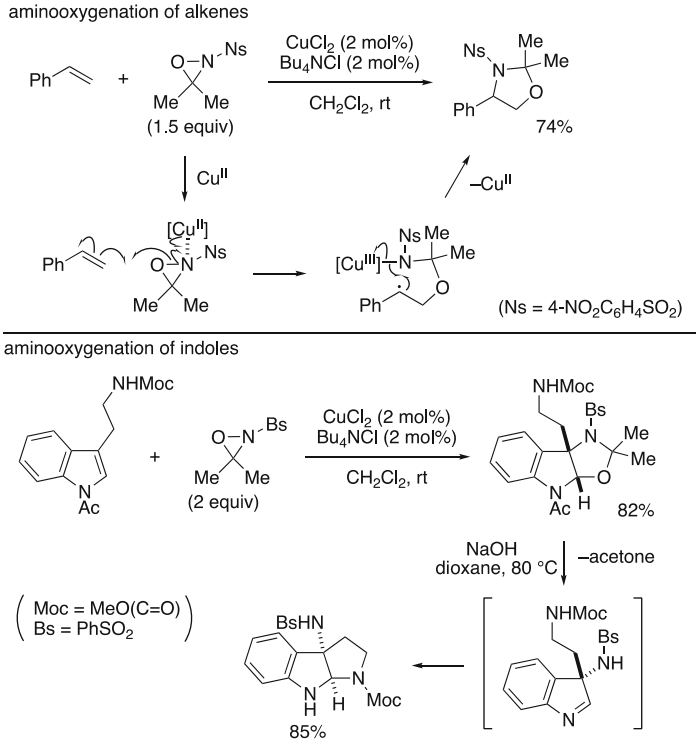
Yoon's group developed $CuCl_2$-catalyzed aminooxygenation of alkenes with *N*-sulfonyloxaziridine. The transient Cu(II)-oxaziridine complex undergoes radical C-O bond formation with alkenes to give C-centered radicals bearing the Cu(III)-sulfonamide moiety. Subsequent C-N bond formation with radical recombination provides oxazolidines with regeneration of the Cu(II) species (Scheme 14) [32–35]. This method is capable of converting indoles through aminooxygenation of the C2 and C3 positions. The resulting aminooxygenation products derived from *N*-acyltryptamines can be further transformed into the 3-aminopyrroloindoline derivatives through treatment with NaOH (Scheme 14) [36].



Scheme 12 Cu(II)-catalyzed aminooxygenation of *o*-allyl-*N*-Ts-anilines with TEMPO

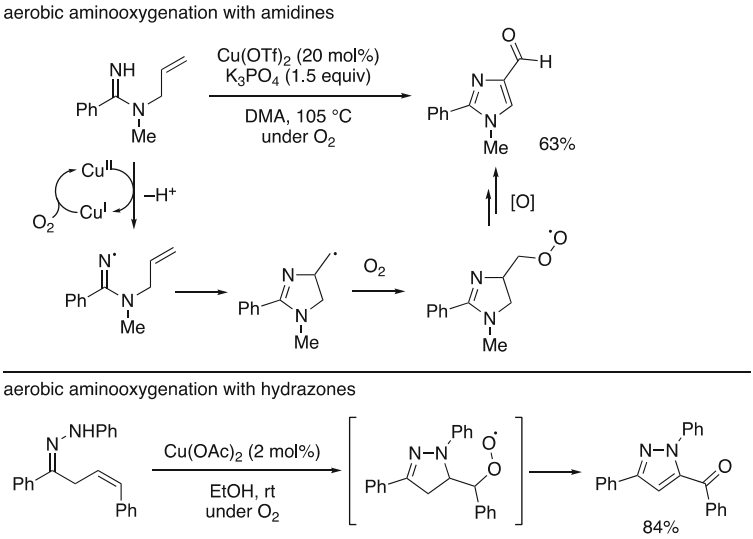


Scheme 13 Cu(II)-mediated aminooxygenation of alkenes with TEMPO



Scheme 14 Cu(II)-catalyzed aminooxygenation of alkenes and indoles with oxaziridines

Zhang and Zhu disclosed Cu(II)-catalyzed aerobic construction of formylimidazole scaffolds through aminooxygenation of *N*-allylamidines (Scheme 15) [37]. Single-electron oxidation of the amidine moiety by the Cu(II) species generates amidinyl radicals that cyclize with the pendant alkene to form the C-N bond with generation of C-centered radicals. Subsequent oxygenation of the C-radicals with molecular oxygen



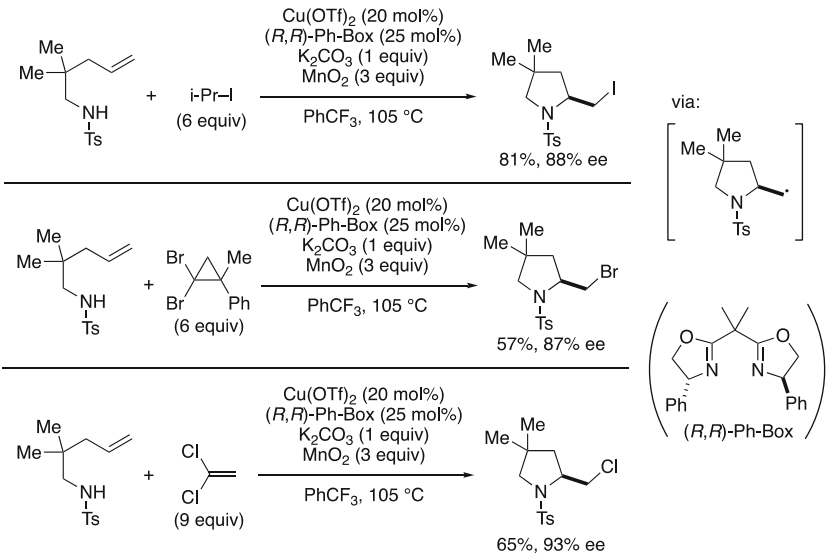
Scheme 15 Cu-catalyzed aerobic aminooxygenation with amidines or hydrazones

forms peroxy radicals. Further fragmentation of the peroxy moiety and oxidative aromatization of the dihydroimidazole part provide the final products. Similarly, Sodeoka's group recently adopted alkenylhydrazones for Cu-catalyzed aerobic aminooxygenation for the synthesis of pyrazoles [38].

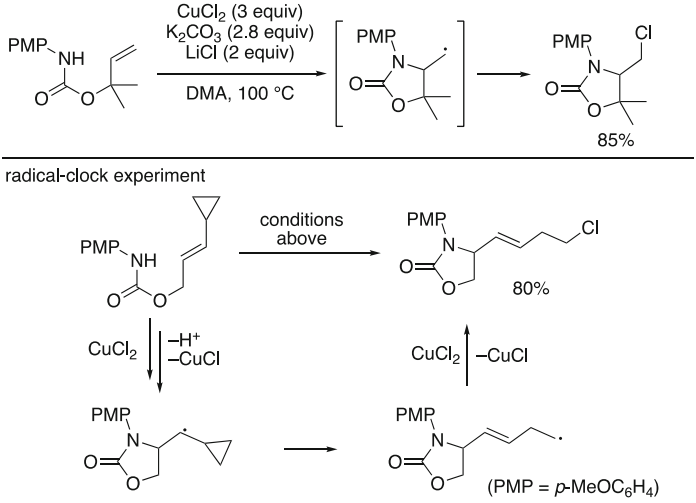
2.6 Haloamination

Chemler's group developed Cu(II)-catalyzed MnO_2-mediated enantioselective iodoamination of *N*-pentenylsulfonamides with 2-iodopropane as the iodine source for the synthesis of 2-(iodomethyl)pyrrolidines (Scheme 16) [39]. The transient C-centered radicals formed through aminocupration of alkenes and subsequent C-Cu bond homolysis finally capture the iodine atom from 2-iodopropane to afford the desired iodopyrrolidine. This system also allows for use of (2,2-dibromo-1-methylcyclopropyl)benzene and 1,1-dichloroethylene, enabling bromoamination and chloroamination, respectively.

Xu's group reported $CuCl_2$-mediated synthesis of 4-(chloromethyl)oxazolidin-2-ones through chloroamination of *O*-allylcarbamates (Scheme 17) [40]. The radical- clock experiment suggests that C-centered radical intermediates are involved, undergoing radical chlorination with $CuCl_2$. The initial aminocupration of alkenes/C-Cu bond homolysis takes place to form the C-radical intermediates. The method is amenable to chloroamination of *N*-allylureas, alkenylamides, and *N*-Ts-pentenylamine as well as to *O*-propargyl and *O*-allenylcarbamates (Scheme 18).



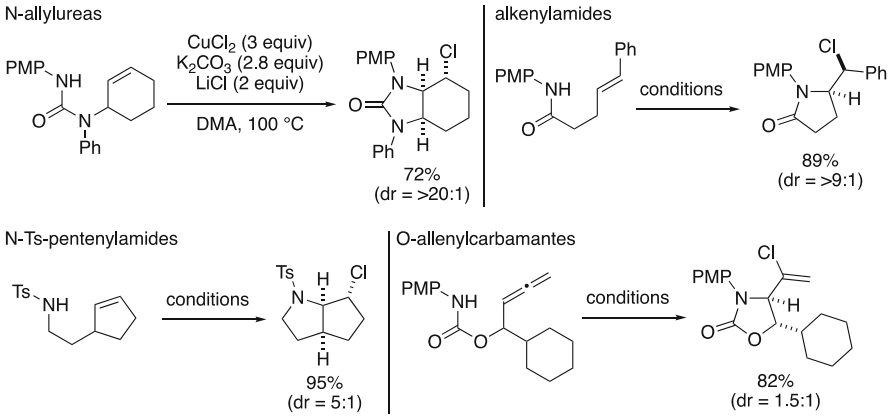
Scheme 16 Cu-catalyzed haloamination of alkenes



Scheme 17 Cu-mediated chloroamination of *O*-allylcarbamates

3 Heterocycle Synthesis via C-H Bond Oxidation

Intramolecular oxidative functionalization of a carbon-hydrogen (C-H) bond to form a new carbon-heteroatom bond offers an atom- and step-economical way to construct a heterocyclic scaffold. This section will highlight recent development on



Scheme 18 Cu-mediated chloroamination with ureas and amides as well as allenes

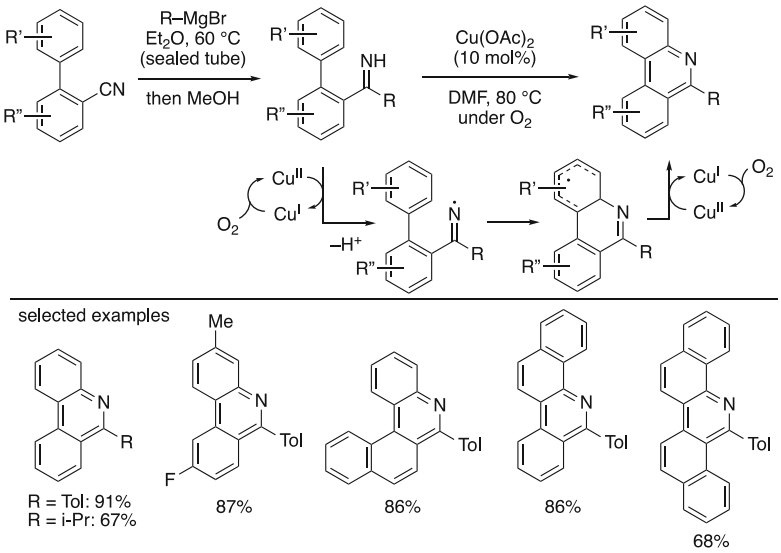
heterocycle synthesis through C-H oxidation using metal-mediated oxidative radical reactions.

3.1 C-H Amination

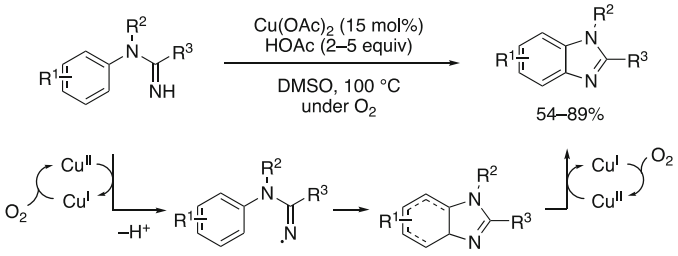
There is an increasing use of iminyl radicals that can be generated by single-electron oxidation of *N*-H imines and their derivatives for construction of nitrogen heterocycles [41]. In 2010, Chiba's group disclosed a one-pot synthesis of phenanthridines via Cu-catalyzed aerobic C-H amination of biaryl-*N*-H-imines, which can be generated in situ from 2-biarylcarbonitriles and Grignard reagents (Scheme 19) [42]. Single-electron oxidation of *N*-H imines by the Cu(II) species generates iminyl radicals, the addition of which onto the benzene ring followed by oxidative aromatization furnishes phenanthridines [43]. The catalytic turnover is maintained by reoxidation of Cu(I) to Cu(II) by molecular oxygen. This method allowed for efficient construction of aza-polynuclear aromatic hydrocarbons (aza-PAHs) such as aza-chrysene and aza-picene.

Buchwald's group disclosed Cu(II)-catalyzed aerobic oxidation of *N*-arylbenzyl-amidines that provides 2-arylbenzimidazoles through C-H amination (Scheme 20) [44]. As one of the possible reaction pathways, it is proposed that oxidative generation of amidinyl radicals and their cyclization onto the aromatic ring followed by oxidative aromatization furnish 2-arylbenzimidazoles, while other pathways involving organometallic intermediates or nitrene species are not ruled out.

Chiba's group in turn demonstrated the use of amidinyl radicals derived from *N*-alkylamidines under $Cu(OAc)_2$-catalyzed $PhI(OAc)_2$-mediated reaction conditions for synthesis of dihydroimidazoles via aliphatic C-H amination. Single-electron



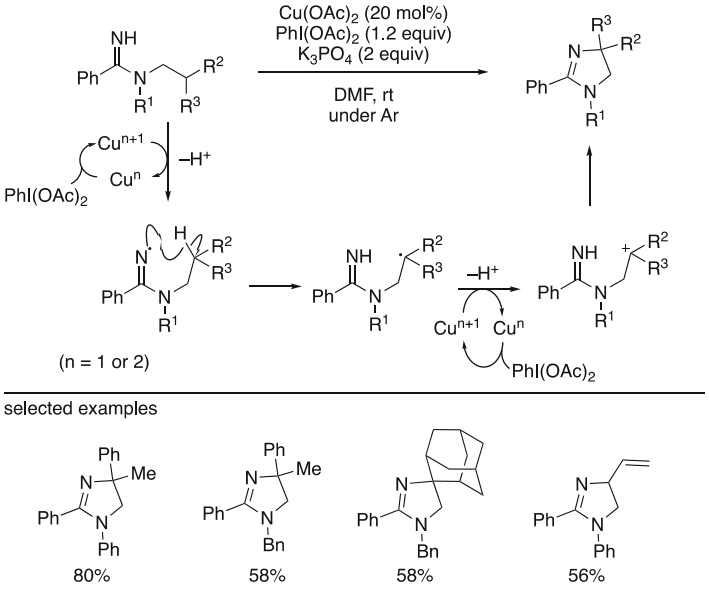
Scheme 19 Cu-catalyzed aerobic C-H amination of biaryl-*N*-H-imines for synthesis of phenanthridines and their derivatives



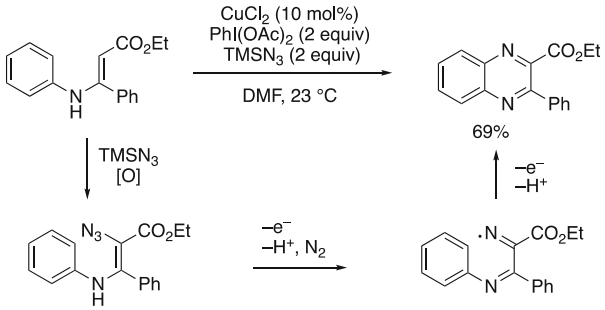
Scheme 20 Cu-catalyzed aerobic C-H amination of *N*-arylamidines

oxidation of *N*-alkylamidines generates amidinyl radicals, which undergo 1,5-H radical shift to form C-centered radicals. Subsequent C-N bond formation via oxidation of alkyl radicals into carbocations furnished dihydroimidazole products (Scheme 21) [45]. Another possibility for the C-N bond formation is radical recombination with the Cu species followed by C-N reductive elimination.

Yu's group reported synthesis of quinazoline derivatives from *N*-aryl enamine carboxylates and $TMSN_3$ in the presence of a catalytic amount of $CuCl_2$ and PhI $(OAc)_2$ (Scheme 22) [46]. The oxidative azidation of the enamine moiety first takes place to form vinylazides, the ensuing single-electron oxidation of the latter affording iminyl radicals with elimination of dinitrogen. Radical C-N bond formation followed by oxidative re-aromatization delivers the quinazoline derivatives. The role of $CuCl_2$ is likely to facilitate the electron-transfer processes. The overall process offers formal double C-H amination of alkenyl and aromatic C-H bonds.

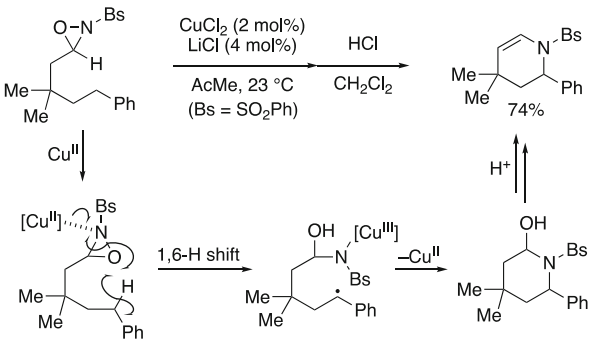


Scheme 21 Cu-catalyzed I(III)-mediated C-H amination of *N*-alkylamidines



Scheme 22 Cu-catalyzed I(III)-mediated amination of double C(sp^2)-H bonds of *N*-phenylenamine carboxylates

Yoon reported the synthesis of cyclic enamides from alkyl-tethered *N*-sulfonyloxaziridines under the $CuCl_2$-LiCl catalytic system (Scheme 23) [47]. The process is initiated by a 1,6-H radical shift onto the putative Cu(II)-oxaziridine complex to form C-centered radicals bearing the Cu(III)-amide moiety, which undergo radical recombination to give cyclic hemiaminals. Subsequent treatment with an acid promotes dehydration to afford cyclic enamides.



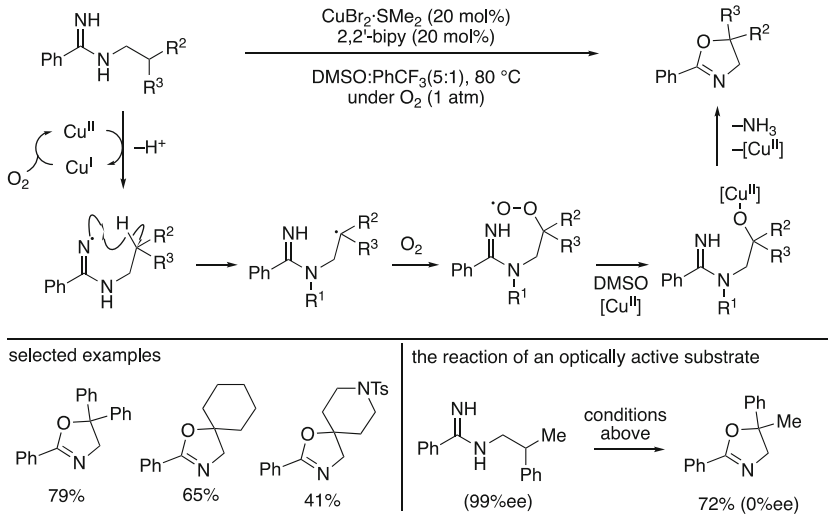
Scheme 23 Cu(II)-catalyzed C-H amination with *N*-sulfonyloxaziridines

3.2 C-H Oxygenation

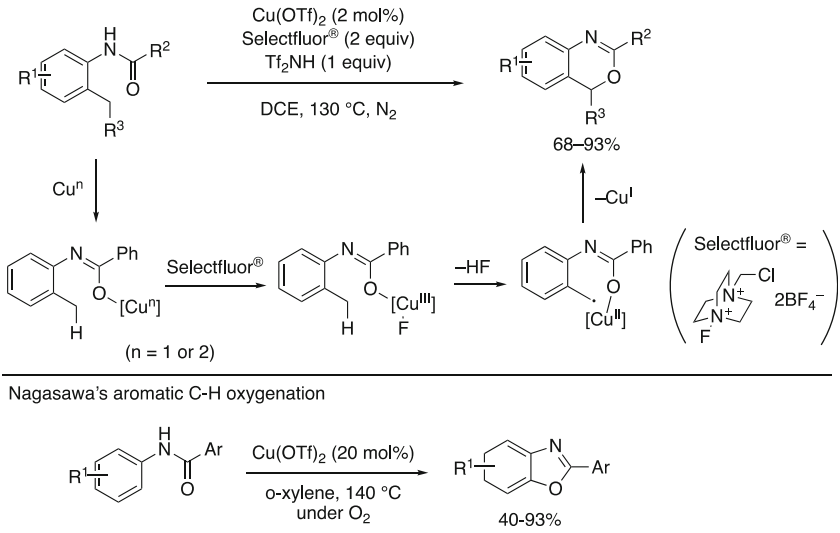
Chiba's group demonstrated that when *N*-alkylamidines are treated under Cu-catalyzed aerobic reaction conditions, the process delivered dihydroxazoles through aliphatic C-H oxygenation. In this case, the resulting C-centered radicals are captured by molecular oxygen to form peroxy radicals, which are reduced into alkoxy copper species, by the assist of DMSO. Final intramolecular condensation furnishes dihydroxazoles with elimination of ammonia (Scheme 24) [48]. The reaction of an optically active substrate resulted in racemization, which proves the presence of the C-centered radical species in the present process.

In 2012, Zhang's group reported a Cu-catalyzed oxidative intramolecular benzylic C-H oxygenation of *N*-arylamides in the presence of 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor®) for synthesis of 4*H*-3,1-benzoxazines (Scheme 25) [49]. The process is initiated by the oxidation of initially formed amide-Cu(II) enolates by Selectfluor® to generate higher valent Cu(III) species that undergo H-radical abstraction from the benzylic position with elimination of HF. The resulting benzylic radicals subsequently form the C-O bond probably through radical recombination, followed by C-O reductive elimination to afford 4*H*-3,1-benzoxazines. This approach is complementary to the Cu-catalyzed aerobic conversion of *N*-arylamides into benzoxazoles through aromatic C-H oxygenation reported by Nagasawa's group [50].

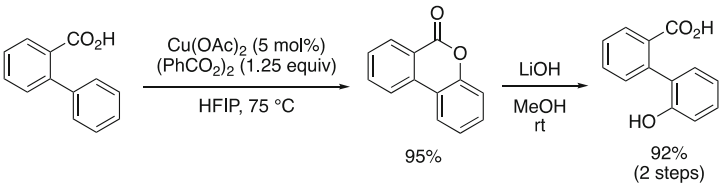
Martin's group developed a Cu-catalyzed oxidative synthesis of benzolactones from 2-arylbenzoic acids in the presence of benzoyl peroxide as the stoichiometric oxidant (Scheme 26) [51]. A series of mechanistic studies indicated the involvement of aryl radical species for the C-O bond formation, while concerted metalation-deprotonation process is not ruled out. Subsequent saponification of lactones provides hydroxylated arenes. The overall process thus offers remote aromatic C-H hydroxylation of 2-arylbenzoic acids.



Scheme 24 Cu-catalyzed aerobic aliphatic C-H oxygenation with amidines



Scheme 25 Cu-catalyzed oxidative aliphatic C-H oxygenation for synthesis of 4*H*-3,1-benzoxazines

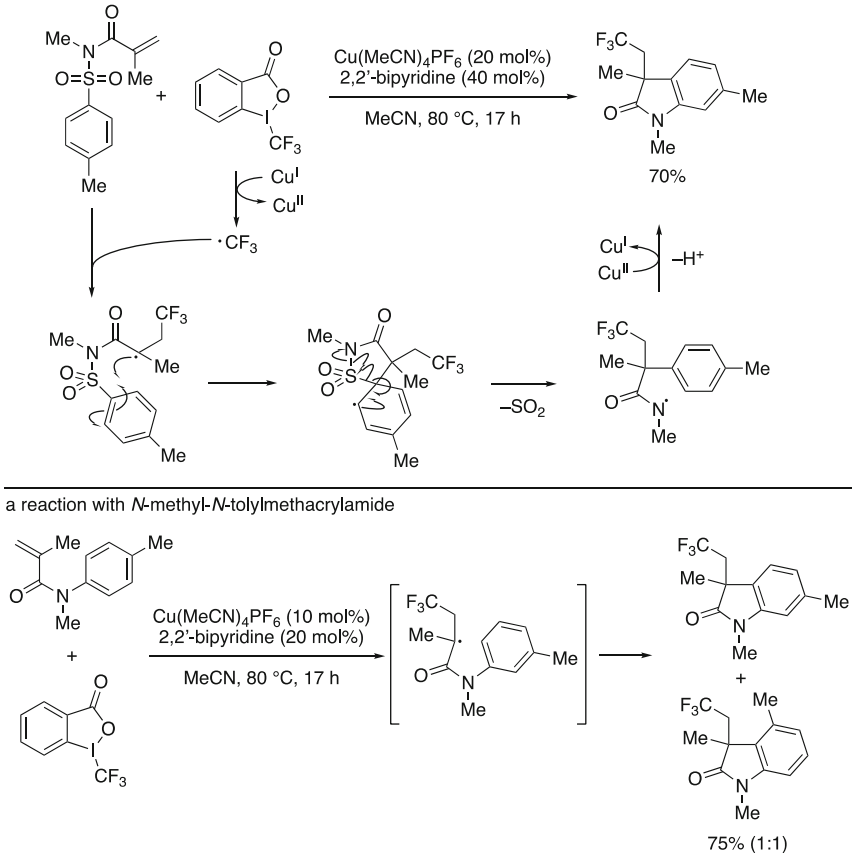


Scheme 26 Cu-catalyzed aromatic C-H oxygenation of 2-arylbenzoic acids

4 Heterocycle Synthesis via Oxidative Radical Cascades

Cascade processes enable facile construction of complex structures from readily available starting materials [52–57]. This section highlights recent development of metal-mediated oxidative radical cascade reactions, which include multi-steps of bond-forming/breaking processes, in the construction of heterocycles.

Nevado's group reported Cu-catalyzed radical cascade triggered by radical trifluoromethylation of *N*-arylsulfonylmethacrylamides (Scheme 27) [58]. This process is initiated by a single-electron reduction of the Togni reagent to deliver the CF_3 radical, which adds onto the methacrylamide moiety to give α-amido radicals. Subsequently, 1,4-aryl migration/desulfonylation is induced to give amidyl radicals that add onto the migrated tolyl group to form oxindoles as a single regioisomer. It is noteworthy that radical trifluoromethylation-cyclization cascade from *N*-methyl-*N*-tolylmethacrylamide affords an inseparable mixture of regioisomers of oxindoles through radical cyclization of the resulting α-amido radicals [59].

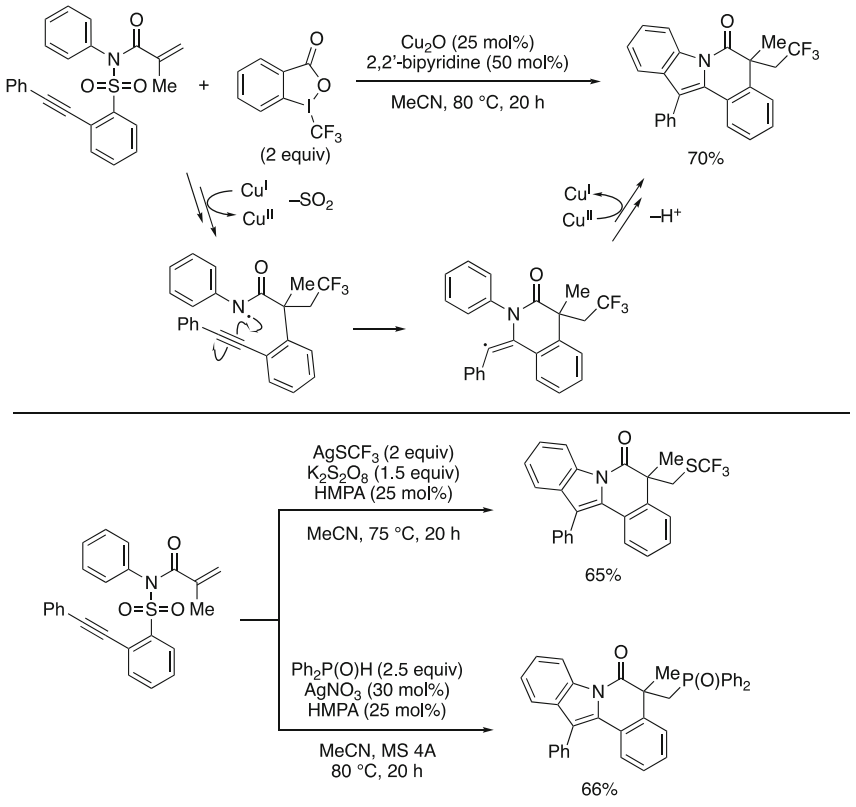


Scheme 27 Cu-catalyzed radical cascade from *N*-arylmethacrylamides and Togni reagent in the synthesis of oxindoles

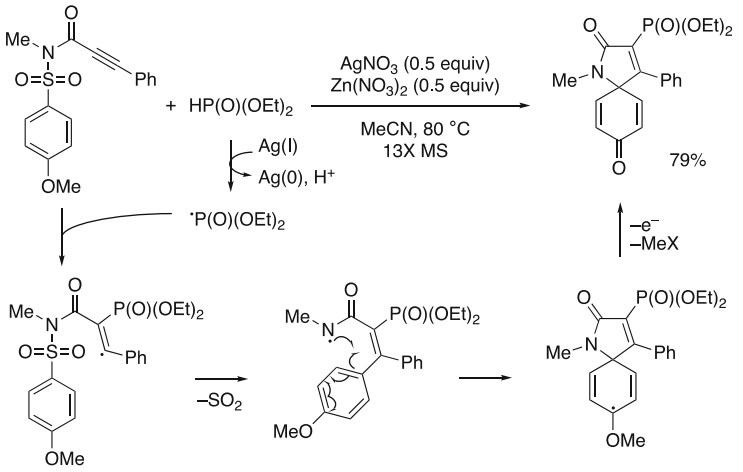
Nevado's group demonstrated further the use of 2-alkynylarylsulfonyl group to trap the *N*-amidyl radical generated through 1,4-migration/desulfonylation sequence and illustrated this cascade with the construction of indolo[2,1-*a*]isoquinoline-6(5*H*)-ones (Scheme 28) [60]. Other radical sources such as trifluoromethylthio and phosphonyl radicals were also employed under Ag-mediated oxidative reaction conditions.

Liang's group developed the desulfonylative radical cascade reaction of *N*-((4-methoxyphenyl)sulfonyl)-3-phenylpropiolamides with diethyl phosphite in the presence of $AgNO_3$ (Scheme 29) [61]. Interestingly, the resulting *N*-amidyl radical undergoes oxidative spirocyclization onto the methoxyphenyl moiety to give azaspirocyclohexadienone scaffolds.

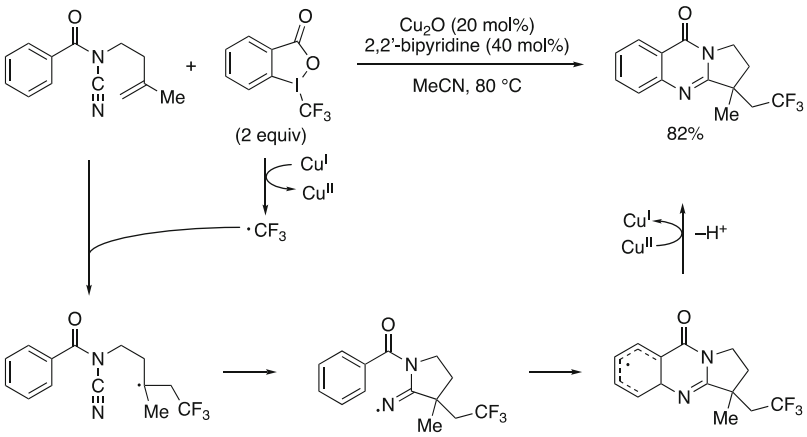
Cui's group reported an oxidative radical cascade to construct quinazolinone scaffolds from *N*-alkenyl-*N*-cyanobenzamides and the Togni reagent in the presence of Cu_2O as the catalyst (Scheme 30) [62]. Upon addition of the trifluoromethyl radical onto the alkene moiety, the resulting C-centered radical adds onto the cyano group to give an aminidyl radical, which in turn undergoes radical cyclization onto the benzoyl moiety to form the quinazolinone skeleton.



Scheme 28 Construction of indolo[2,1-*a*]isoquinoline-6(5*H*)-ones through radical cascade involving *N*-arylmethacrylamides



Scheme 29 Ag-mediated oxidative radical cascade for construction of azaspirocyclohexadienones



Scheme 30 Cu-catalyzed oxidative radical cascade of alkenylcyanamides for the synthesis of quinazolinones

5 Summary and Outlook

Metal-mediated oxidative radical cyclization/annulation has recently emerged as a robust strategy for the synthesis of various heterocycles. In such processes, copper salts are mainly utilized to generate the radical species, owing to their superior reactivity to induce the SET process to generate radical species. Employment of such first-row transition metals is advantageous from the viewpoint of sustainability as these base metals are ubiquitous in nature and lower in cost and toxicity [63].

Choice of stoichiometric oxidants, which often serve as to trigger bond-forming processes, is also important to design efficient synthesis of targeted heterocycles [64]. Thus, it is our strong belief that the leveraging of metal-mediated oxidative radical processes to exploit new routes for the synthesis of heterocycles of medicinal and material interests continues to flourish and thus enhance our synthetic capability.

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