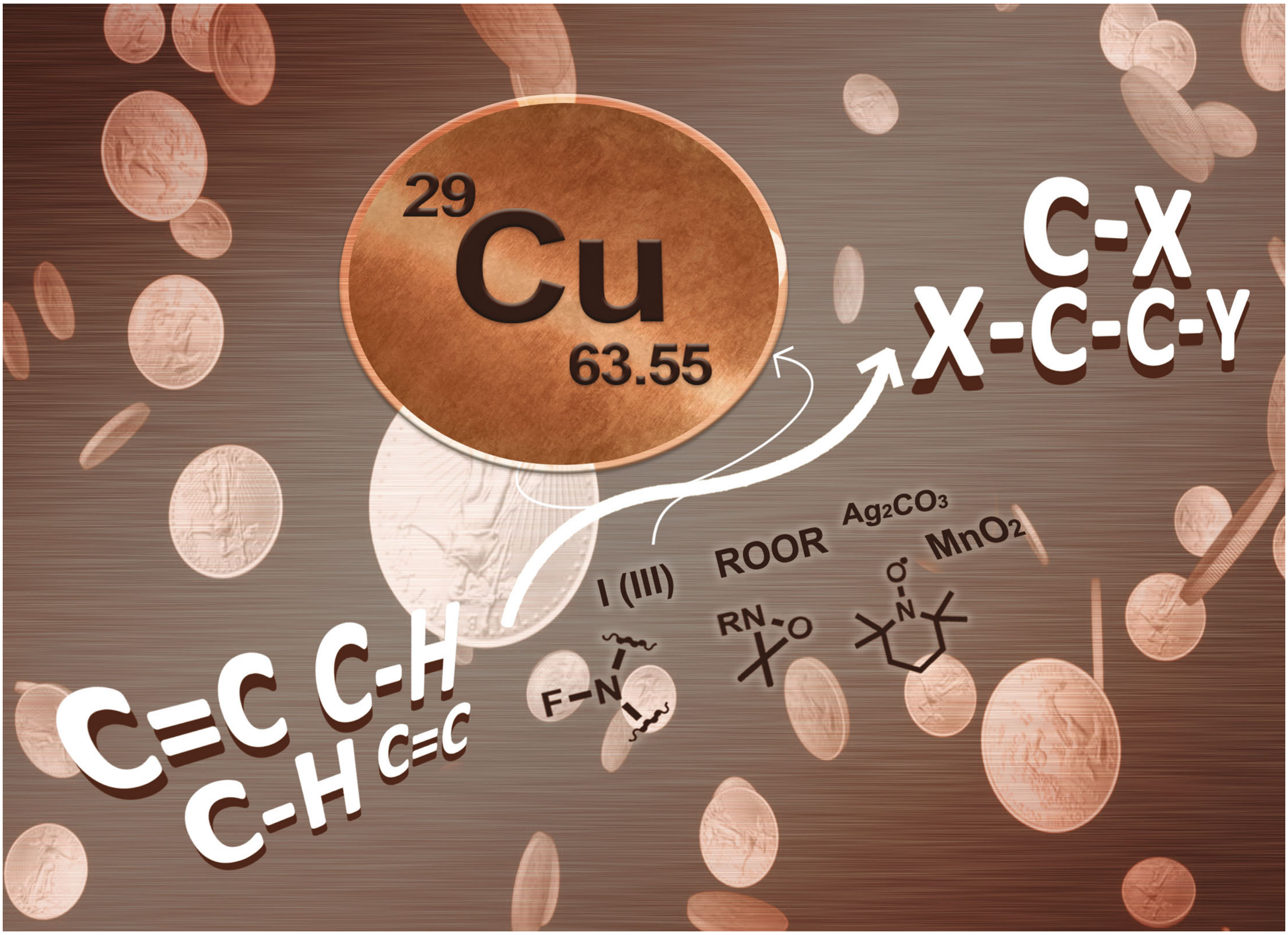

Featuring work from the research group of Professor Shunsuke Chiba, Nanyang Technological University, Singapore.

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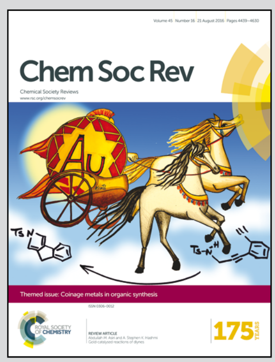

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Copper-catalyzed oxidative carbon–heteroatom bond formation: a recent update

Xu Zhu and Shunsuke Chiba*

This review updates recent advances in Cu-catalyzed (anaerobic) oxidative carbon–heteroatom bond formation on sp^3- and sp^2-C–H bonds as well as alkenes, classified according to the types of stoichiometric oxidants.

1. Introduction

Oxidative molecular transformation that incorporates heteroatom units into carbon-based organic scaffolds is one of the most fundamental and important synthetic transformations, enhancing the molecular complexity. Therefore, development of new oxidative synthetic methodologies that convert readily available substrates in lower oxidation states into highly functionalized (oxidized) molecules in a chemo- and stereo-selective manner is a long-standing goal in chemical synthesis. In this context, direct installation of carbon–heteroatom bonds on ubiquitous C–H bonds (both sp^3- and sp^2-hybridized) is of great significance to streamline the multi-step molecular transformations needed for the synthesis of target functional molecules. However, it is challenging to functionalize such C–H bonds selectively unless otherwise adjacent activating groups are installed because of the inherent inert property and the ubiquitous nature of the C–H bonds. On the other hand, oxidative difunctionalization of alkenes provided another efficient method to address highly oxidized molecular complexity through installing two distinct functional groups in a one-pot fashion. Thus, development of chemo-, regio-, and stereoselective difunctionalization of alkenes is the major concern to be addressed in chemical synthesis.

Transition-metals are capable of realizing various state-of-the-art processes for C–H oxidation[1] and oxidative difunctionalization of alkenes.[2] For the catalysis of choice, ubiquitous first row transition metals have recently attracted much attention not only as alternatives to precious late transition metals, but also for exploration of their unprecedented catalytic processes.[3]

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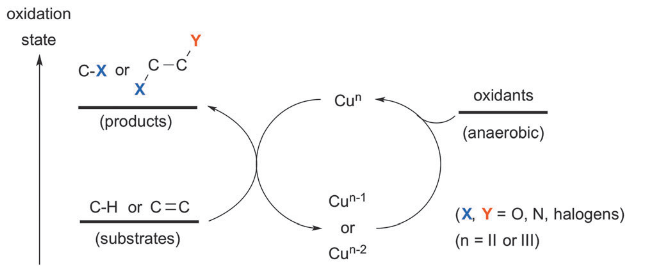


Scheme 1 Cu-Catalyzed oxidative carbon–heteroatom bond formation on C–H bonds and alkenes.

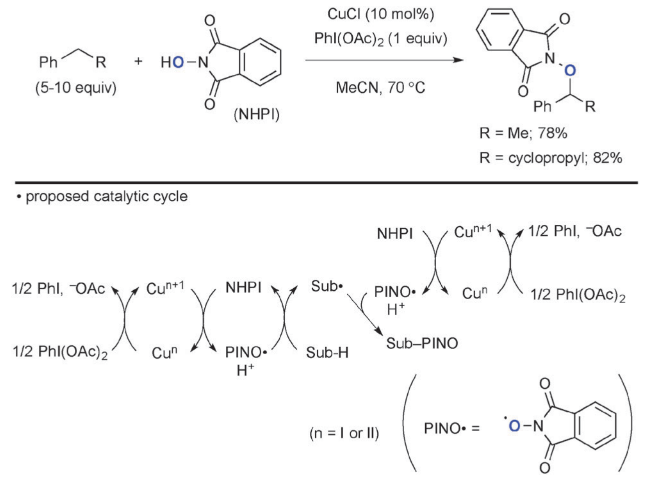
Among such first row transition metals, copper complexes exhibit unique and versatile reactivity and good functional group tolerance.[4] A broad range of oxidation states of copper complexes (mainly from Cu^0 to Cu^{III} applied in chemical synthesis)[5,6] enables the promotion of redox reactions in either a single-electron or a two-electron-transfer fashion (or both in the sequential processes), depending on the reaction conditions and types of substrates used. A variety of stoichiometric terminal oxidants have been devised and applied for realizing the catalytic turnover in Cu-mediated oxidative molecular transformation and/or serving as the sources of heteroatoms introduced into the products (Scheme 1).

This review focuses on recent advances in copper-catalyzed oxidative carbon–heteroatom bond forming reactions on C–H bonds as well as alkenes. These reactions are classified according to the different types of stoichiometric terminal oxidants employed in the processes. Among the available oxidants in copper-catalyzed oxidative molecular transformation, molecular oxygen (O_2) has been extensively employed as the terminal oxidant for catalytic turnover, enabling a variety of oxidative reactions. As these achievements are reviewed elsewhere in detail,[7] this review will exclude copper-catalyzed aerobic reactions.

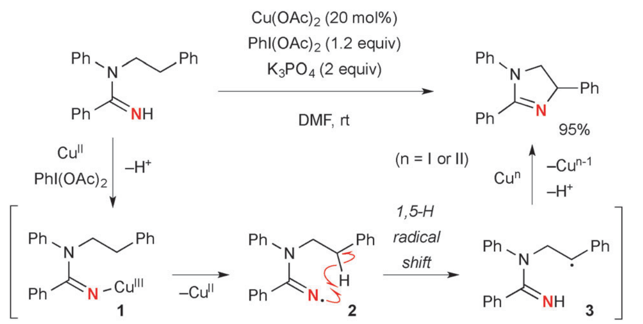
2. With I(III) reagents

2.1. PhI(OAc)$_2$

The combination of Cu complexes and PhI(OAc)$_2$ could generate higher oxidation state Cu^n species (n = II or III), which mediate unprecedented single-electron-oxidation processes. Chang reported benzylic/allylic sp^3-C–H oxygenation with *N*-hydroxyphthalimide (NHPI) under CuCl-catalyzed-PhI(OAc)$_2$-mediated reaction conditions (Scheme 2).[8] The radical mechanism is proposed, where the oxidatively formed phthalimide *N*-oxyl (PINO) radical undergoes H-radical abstraction from the substrates (Sub-H) to generate the corresponding C-radicals (Sub$^•$). Their subsequent recombination with the PINO radical affords the products. The role of PhI(OAc)$_2$ is to maintain the catalytic cycle by re-oxidizing lower valent Cu species. Interestingly, a radical-clock substrate, cyclopropylmethylbenzene was coupled with the PINO radical keeping the cyclopropyl moiety intact, indicating kinetically faster radical recombination or alternative organometallic mechanism involved.



Scheme 2 Cu-Catalyzed-PhI(OAc)$_2$-mediated sp^3-C–H oxygenation with NHPI.

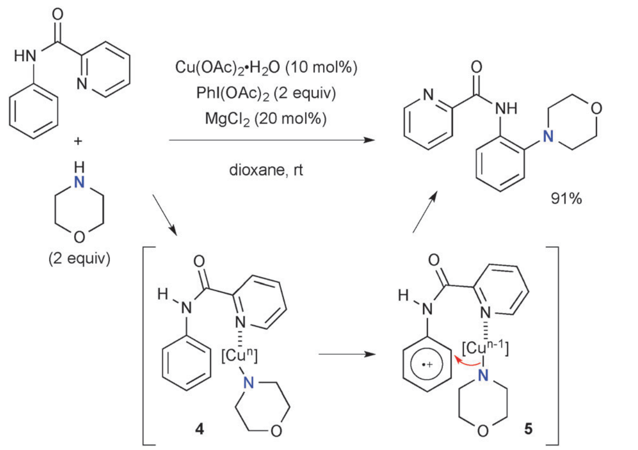


Scheme 3 Aliphatic C–H amination with amidines under Cu-catalyzed-PhI(OAc)$_2$-mediated reaction conditions.

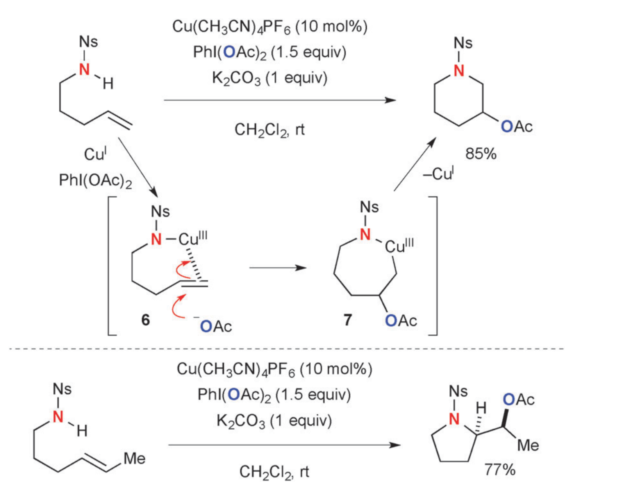
Chiba reported intramolecular aliphatic C–H amination of *N*-alkylamidines under Cu(OAc)$_2$-catalyzed-PhI(OAc)$_2$-mediated reaction conditions (Scheme 3).[9] The reaction is initiated by generation of amidinyl radical **2** probably through formation of Cu(III)-amidine intermediate **1** followed by homolysis of the N–Cu bond. A subsequent 1,5-*H* radical shift[10] of the amidinyl radical affords the corresponding C-radical **3**, further single-electron-oxidation of which with Cu(II) or Cu(III) species generates a carbocation and subsequent C–N bond formation to furnish dihydroimidazole. The radical recombination mechanism is not ruled out for C–N bond formation.

The Cu–PhI(OAc)$_2$ system is capable of oxidizing the aromatic sp^2-C–H bond with the assistance of appropriate *ortho*-directing groups. For example, *ortho*-C–H amination of aniline derivatives was developed using the picolinamide directing group under Cu-catalyzed-PhI(OAc)$_2$-mediated reaction conditions (Scheme 4).[11] The single-electron-oxidation of the benzene ring in chelate complex **4** followed by morpholine transfer to cation radical **5** is proposed for the C–H amination.

Various modes of oxidative functionalization of alkenes have been realized using Cu-catalyzed-PhI(OAc)$_2$-mediated reaction systems, in which the acetate moiety on PhI(OAc)$_2$ is incorporated during the process. The mechanisms for alkene functionalization



Scheme 4 Cu-Catalyzed-PhI(OAc)$_2$-mediated directed sp^2-C–H amination.

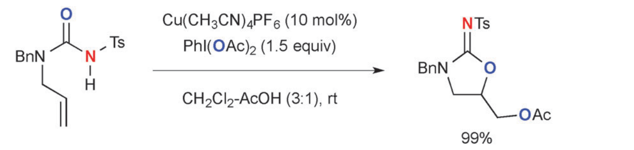


Scheme 5 Cu-Catalyzed-PhI(OAc)$_2$-mediated aminoacetoxylation of alkenes.

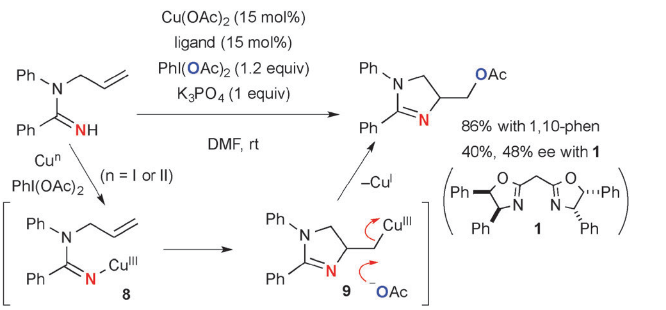
vary with the substrates used. Blakey disclosed intramolecular Cu-catalyzed-PhI(OAc)$_2$-mediated aminoacetoxylation of alkenylsulfonamides for synthesis of nitrogen heterocycles (Scheme 5).[12] The mode of cyclization (either *endo* or *exo*) depends on the alkene substituents. The process is proposed to be initiated by electrophilic activation of alkenes by amide–Cu(III) species **6**. Subsequently, acetoxy-cupration of alkenes takes place to afford metallacycle intermediate **7**, in which more substituted carbon is preferentially acetoxylated. Reductive elimination of the C–N bond finally furnishes the heterocyclic products.

Interestingly, the reactions of alkenylureas under similar reaction conditions give oxyacetoxylation products (Scheme 6).[13]

On the other hand, Cu(OAc)$_2$-catalyzed-PhI(OAc)$_2$-mediated reactions of *N*-allylamidines afford acetoxymethyl dihydroimidazoles *via* aminoacetoxylation of alkenes (Scheme 7).[14] When 2,2′-methylene bis[(4*R*,5*S*)-4,5-diphenyl-2-oxazoline] **1** is employed instead of 1,10-phenanthroline, chirality induction of 48% ee is observed in aminoacetoxylation. This observation implicates that the process might involve aminocupration of alkenes by the putative amidinyl copper(III) intermediate **8** *via* an organometallic pathway to form an organocopper(III)



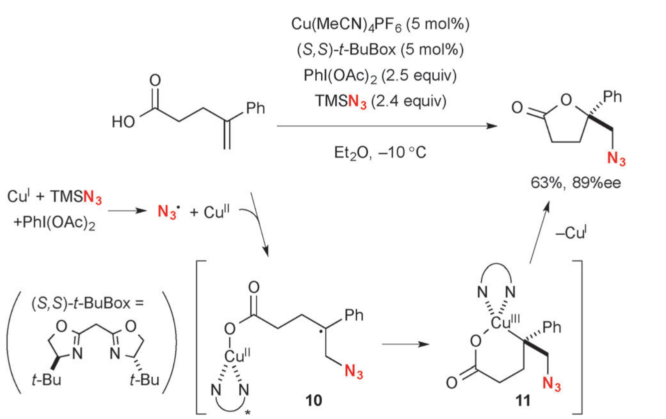
Scheme 6 Cu-Catalyzed-PhI(OAc)$_2$-mediated oxyacetoxylation of alkenylureas.



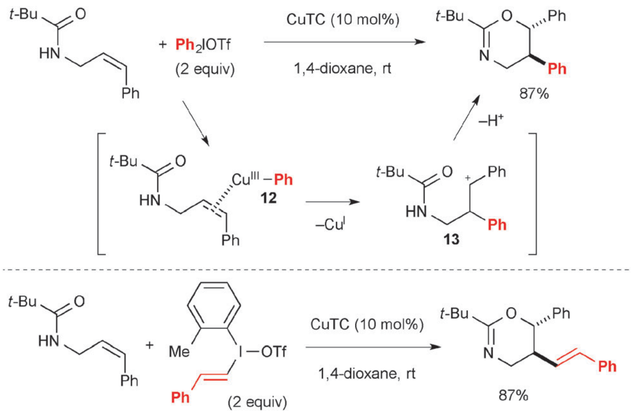
Scheme 7 Cu-Catalyzed-PhI(OAc)$_2$-mediated aminoacetoxylation of alkenylamidines.

intermediate that is unlike the aliphatic CH amination of *N*-alkylamidines involving free radical intermediates (Scheme 3). Finally, nucleophilic displacement of organocopper(III) moiety **9** with an acetate ion gives the final product.

Recently, Buchwald reported Cu-catalyzed enantioselective synthesis of functionalized lactones from alkenylcarboxylic acids through oxyfunctionalization of alkenes as the key step (Scheme 8).[15] For example, oxyazidation is enabled using a catalytic amount of Cu(MeCN)$_4$PF$_6$ with TMSN$_3$ and PhI(OAc)$_2$ (Scheme 8). The azido radical and higher valent Cu(II) species are initially formed by the redox reaction between TMSN$_3$, Cu(I) complex, and PhI(OAc)$_2$. The resulting azido radical then adds onto alkenes to generate tertiary radical **10** that recombines with the intramolecular Cu^{II}–carboxylate moiety in a stereoselective fashion with the chiral Box ligand. Finally, C–O reductive elimination from metallacycle **11** gives the lactone product with regeneration of the Cu(I) catalyst.



Scheme 8 Cu-Catalyzed-PhI(OAc)$_2$-mediated asymmetric oxyazidation of alkenes.



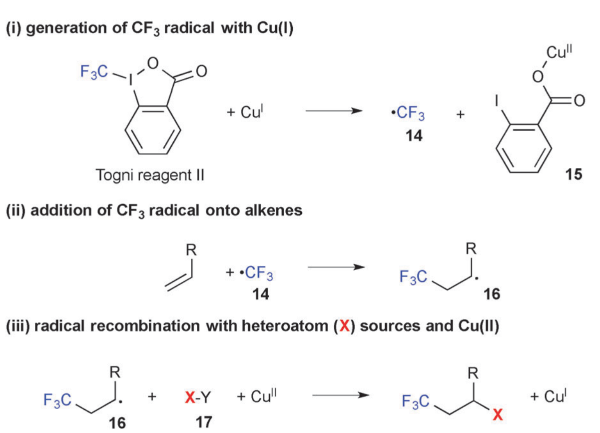
Scheme 9 Cu-Catalyzed oxy-arylation and -vinylation of allylamides with iodonium salts.

2.2. Diaryliodonium salts [Ar_2IX]

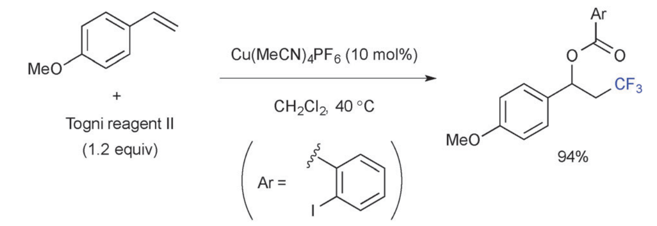
Treatment of Cu(I) complexes with diaryliodonium salts results in formation of aryl-Cu(III) species like **12** in Scheme 9 that could be used for electrophilic activation of alkenes to induce their carbo-functionalization. For example, Gaunt reported that the reaction of *N*-allylamides could afford oxyarylation products in a diastereoselective fashion through the transient carbocation **13** (Scheme 9).[16] Similarly, oxyvinylation was enabled by using vinyl(aryl)iodonium salts. The enantioselective variant was also devised using chiral Cu–bisoxazoline complexes as the catalyst.[17]

2.3. The Togni reagents

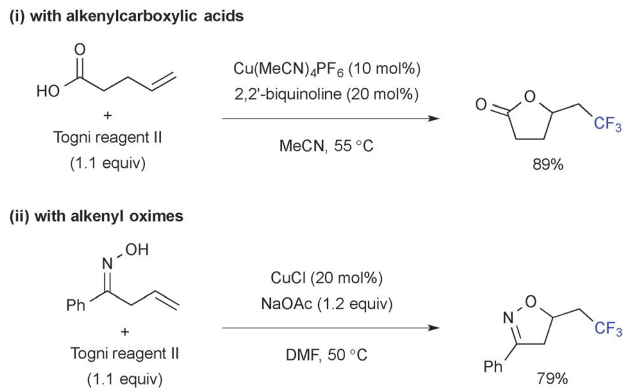
It has been shown that single-electron-reduction of 1-trifluoromethyl-1,2-benziodoxol-3(1*H*)-one (known as Togni reagent II) by Cu(I) complexes generates CF_3 radical **14** along with Cu(II) 2-iodobenzoate **15** (Scheme 10). This reductive process could be combined with the subsequent oxidative alkene difunctionalization through addition of the CF_3 radical onto alkenes followed by recombination of the resulting C-radical **16** with external heteroatom sources **17**, furnishing the final product and Cu(I) species. The overall process is thus able to have a catalytic turnover.



Scheme 10 Cu-Catalyzed trifluoromethylation of alkenes with the Togni reagent.



Scheme 11 Cu-Catalyzed intermolecular oxytrifluoromethylation.

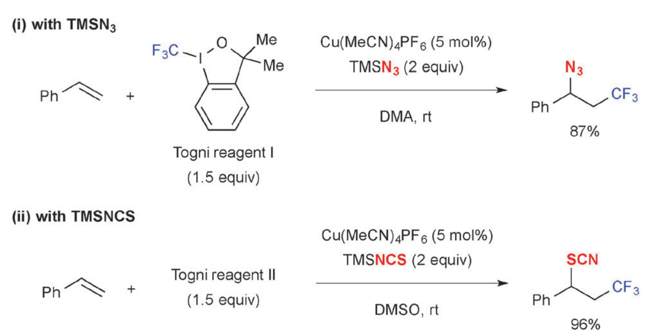


Scheme 12 Cu-Catalyzed intramolecular oxytrifluoromethylation.

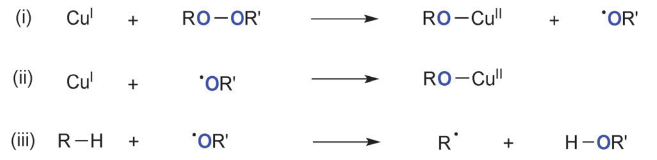
For example, intermolecular oxytrifluoromethylation was realized by radical recombination with the Cu(II) 2-iodobenzoate derived from the Togni reagent (Scheme 11).[18]

Intramolecular C–O bond formation upon trifluoromethylation was enabled by using alkenylcarboxylic acids (Scheme 12-i)[19] and alkenyloximes (Scheme 12-ii), delivering the corresponding trifluoromethylated lactones and isoxazolines, respectively.

Similarly, trifluoromethylazidation (Scheme 13-i)[20] and trifluoromethylthiocyanation (Scheme 13-ii)[21] were reported using $TMSN_3$ and TMSNCS, respectively, as the external heteroatom sources. In the case of trifluoromethylazidation, use of 3,3-dimethyl-1,2-benziodoxole (known as Togni reagent I) provided better yields of the desired azidation products as the reaction with 1,2-benziodoxol-3-one generated 2-iodobenzoyloxylaiton product as the side product.



Scheme 13 Cu-Catalyzed trifluoromethylazidation and trifluoromethylthiocyanation of alkenes.



Scheme 14 The reaction of peroxides with Cu(I) species.

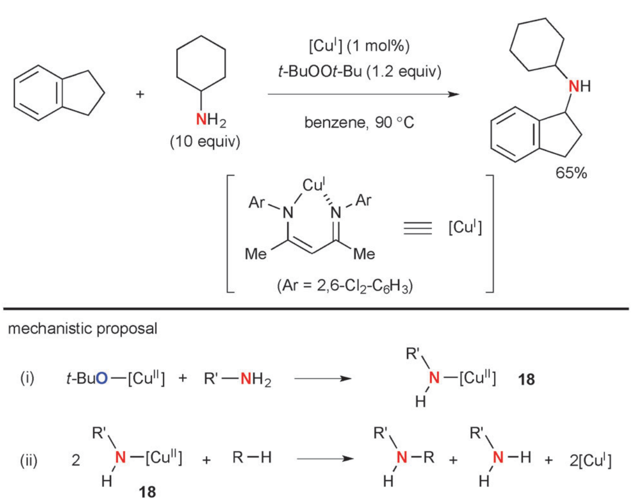
3. With peroxides

Various types of peroxides have been employed as the stoichiometric oxidants and often as the sources of oxygen functionality in Cu-catalyzed oxidative molecular transformation.[4d] In principle, reduction of peroxides by lower valent Cu(I) species provides the corresponding higher valent Cu(II) alkoxide and highly reactive alkoxy radical (Scheme 14) that cooperate synergistically to mediate subsequent Kharasch–Sosnovsky[22] type oxidative functionalization of the substrates. The resulting alkoxy radical could further oxidize Cu(I) species to give another Cu(II) alkoxide (path-ii) or undergo H-radical abstraction from the substrates to form the C-radical (path-iii).

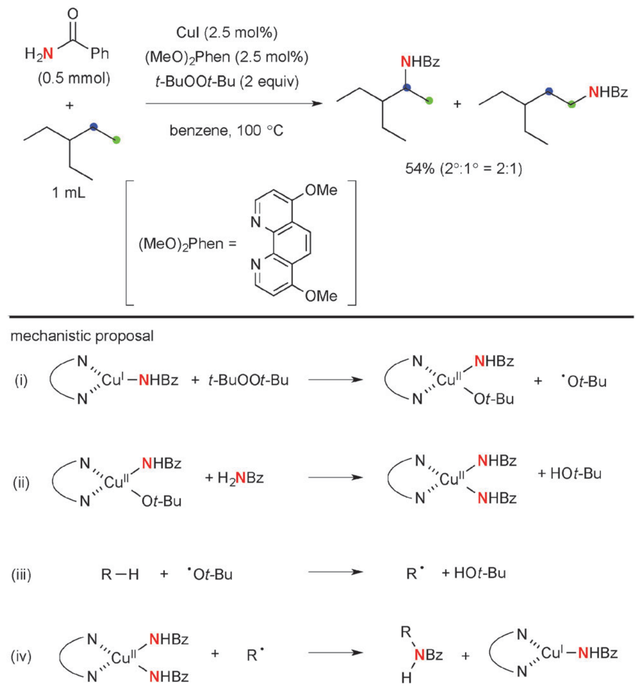
3.1. With di-*t*-butylperoxide (*t*-BuOO*t*-Bu)

Warren reported seminal studies on aliphatic C–H amination with simple amines using the well-defined Cu(I) β-diketiminate complex and *t*-BuOO*t*-Bu as well as their detailed mechanistic studies by kinetic, spectroscopic, and structural analyses of possible intermediates (Scheme 15).[1e,23] It is conceivable that Cu(II) amide complex **18** formed by the alkoxy-amide exchange (path-i) undergoes C–H bond amination of alkanes *via* aliphatic H-radical abstraction and subsequent C–N bond formation with the resulting C-radical (path-ii) along with generation of Cu(I) species that maintains the catalytic cycle with *t*-BuOO*t*-Bu.

More recently, Hartwig disclosed Cu-catalyzed aliphatic C–H amidation and imidation using *t*-BuOO*t*-Bu as the stoichiometric oxidant (Scheme 16).[24] The reactions prefer to oxidize secondary C–H bonds than primary ones, while tertiary C–H



Scheme 15 Cu-Catalyzed-*t*-BuOO*t*-Bu-mediated aliphatic C–H amination.

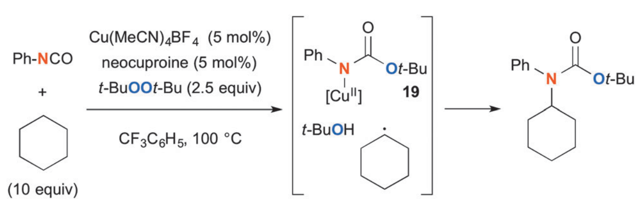


Scheme 16 Cu-Catalyzed-*t*-BuOO*t*-Bu-mediated aliphatic C–H amidation.

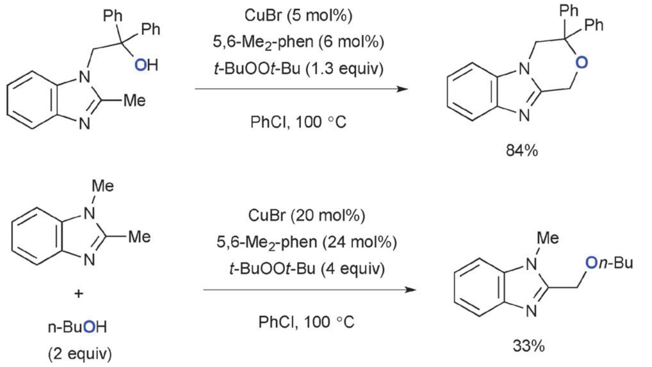
bonds are interestingly the least reactive. The stoichiometric reaction analyses using the isolated well-defined copper amidate complexes implicated that the C–H amidation is enabled by H-radical abstraction with the *t*-butoxy radical (path-iii) and radical recombination of the resulting C-radical with transient Cu(II) amidate complexes (path-iv). Analogous ligand-free Cu-catalyzed aliphatic C–H amidation and imidation with *t*-BuOO*t*-Bu were developed independently by Huang and Yu/Cheng.[25]

This type of Cu-catalyzed-*t*-BuOO*t*-Bu-mediated aliphatic C–H oxidation strategy could be further applied for synthesis of tertiary carbamates using isocyanates as the amide source (Scheme 17).[26] The reaction of Cu(I) species with *t*-BuOO*t*-Bu and isocyanate generates Cu(II)–amide complex **19**, which is coupled with the C-radical derived from alkanes *via* H-radical abstraction by the transient *t*-butoxy radical, affording tertiary carbamates.

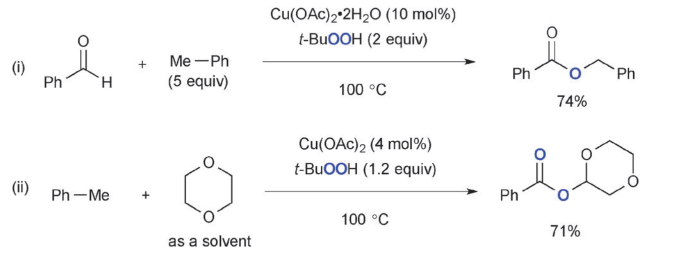
Intramolecular benzylic C–H alkoxylation of aromatic heterocycles having a hydroxyalkyl tether was devised under Cu-catalyzed-*t*-BuOO*t*-Bu-mediated reaction conditions (Scheme 18).[27] The intermolecular variant also worked in the same system, while the yields of the C–H alkoxylation products were moderate.



Scheme 17 Cu-Catalyzed-*t*-BuOO*t*-Bu-mediated synthesis of tertiary carbamates with isocyanates as the amide source.



Scheme 18 Cu-Catalyzed-*t*-BuOO*t*-Bu-mediated sp^3 C–H oxygenation.



Scheme 21 Cu-Catalyzed-TBHP-mediated ester synthesis.

Zhu recently reported carboetherification of aryl alkenes with solvent amounts of acetonitrile and alcohol under Cu-catalyzed-*t*-BuOO*t*-Bu-mediated reaction conditions (Scheme 19).[28] The radical clock experiment implicated that benzylic radical intermediate **20** is formed by the addition of acetonitrile through either carbocupration followed by homolysis of the resulting C–Cu bond or addition of the α-cyanomethyl radical. The final product is delivered through formation of the C–O bond *via* radical recombination of the benzylic radical intermediate with alcohol.

3.2. With *t*-butylhydroperoxide (*t*-BuOOH: TBHP)

t-Butylhydroperoxide (TBHP) exhibits reactivity analogous with that of di-*t*-butylperoxide for Cu-catalyzed aliphatic C–H oxidation with various heteroatom sources such as amides *via* radical intermediates (Scheme 20). For example, Guerra recently reported that Cu–Al mixed oxide could be utilized as a heterogeneous catalyst for Kharasch–Sosnovsky type allylic C–H oxygenation with TBHP as the stoichiometric oxidant.[29,30]

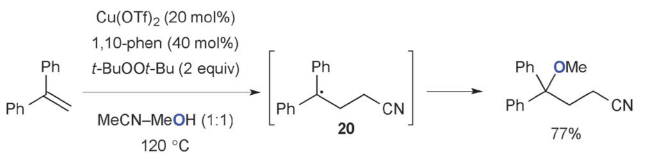
In addition, TBHP uniquely serves as an oxygen source for enhancing the oxidation state of the substrates in aliphatic C–H oxidation. Patel developed Cu-catalyzed-TBHP-mediated synthesis of esters from aldehydes and alkylarenes such as toluene (Scheme 21-i),[31] in which Cu–alkoxides formed *via* benzylic oxygenation with the TBHP couple with aldehydes to deliver esters. Toluene could serve as a benzoate precursor in synthesis of esters *via* C–H oxygenation of cyclic ethers (Scheme 21-ii).[32,33]

As a mechanistically distinct example of aliphatic C–H oxidation, Loh developed unique α-amination of aldehydes with secondary amines under Cu-catalyzed-TBHP-mediated reaction conditions that provides α-amino acetals as the products (Scheme 22).[34] The process is composed of a multi-step sequence including two successive single-electron-oxidations of enamine intermediate **21** derived from condensation of aldehydes and amines. The resulting α-methoxy aziridinium ion **22** undergoes ring-opening with methanolysis, giving α-amino acetal. The detailed roles of CuI and TBHP in the single-electron-transfer processes are not certain.

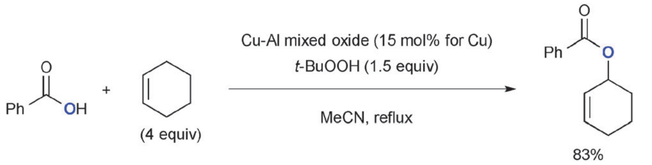
The Cu–TBHP system is also capable of oxidizing sp^2-C–H bonds. Jiao disclosed *ortho*-azidation of anilines with $TMSN_3$ under Cu-catalyzed-TBHP-mediated reaction conditions at ambient temperature (Scheme 23).[35] The single-electron-oxidation of the benzene ring by higher valent Cu(II) species **23** adjacent to the primary amine moiety followed by azido ion transfer in cation radical **24** is proposed for the C–H azidation. This is a rare example of the directed *ortho* C–H functionalization of anilines.

Benzaldimines **25** derived from condensation of anilines and aldehydes could be used for analogous *ortho*-azidation and the resulting 2-azidoarylimines **26** undergo subsequent denitrogenative cyclization to give benzimidazoles (Scheme 24).[36] A 2-pyridyl group has also been utilized as the directing group in aromatic C–H oxidation under Cu-catalyzed-TBHP-mediated reaction conditions.[37]

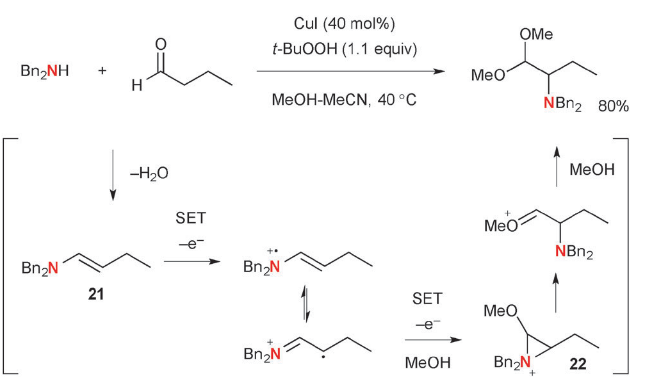
Bolm developed Cu-catalyzed oxidative *N*-acylation of sulfoximines with aldehydes (Scheme 25).[38] The *t*-butoxy radical derived



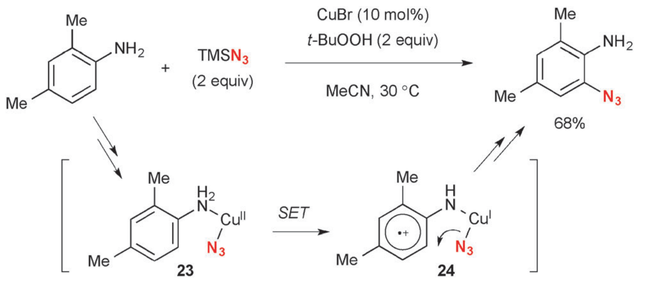
Scheme 19 Cu-Catalyzed carboetherification of alkenes.



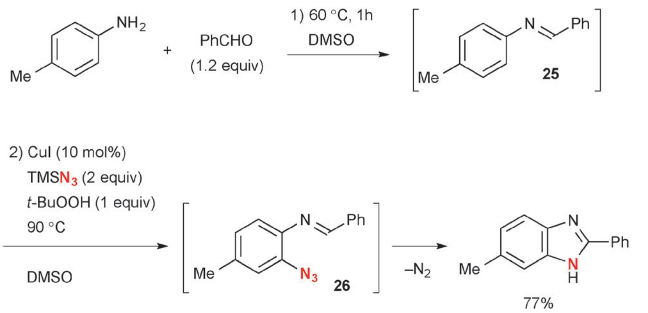
Scheme 20 Cu-Catalyzed allylic C–H oxygenation.



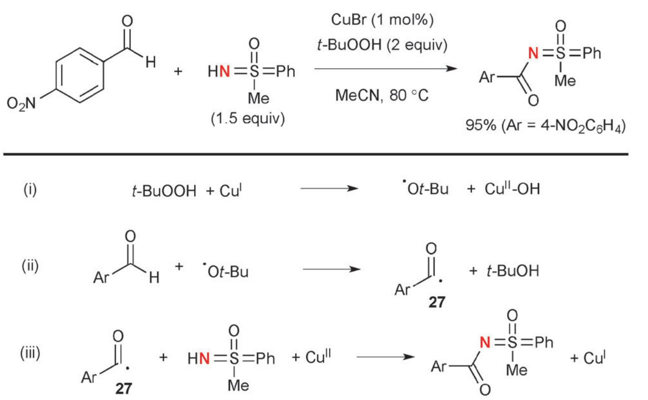
Scheme 22 Cu-Catalyzed α-amination of aldehydes.



Scheme 23 Cu-Catalyzed *ortho*-C–H azidation.



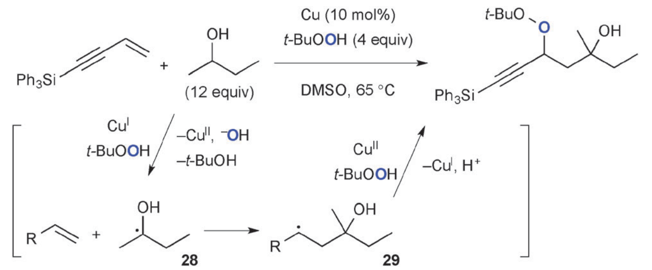
Scheme 24 Cu-Catalyzed-*t*-BuOOH-mediated aromatic *ortho*-azidation.



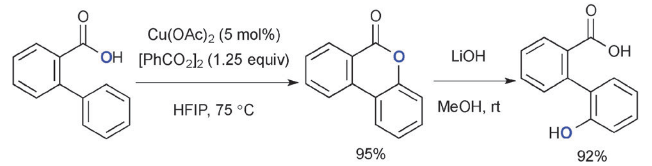
Scheme 25 Cu-Catalyzed oxidative *N*-acylation of sulfoximines.

from decomposition of TBHP by Cu(I) complexes (Scheme 25-i) could abstract the H-radical from aldehydes to generate the corresponding acyl radicals **27** (Scheme 25-ii). The transient acyl radicals **27** undergo radical recombination with sulfoximines mediated by higher valent Cu(II) species to give the products along with re-generation of lower valent Cu(I) species (Scheme 25-iii).

In the presence of Cu(I) complexes, TBHP can serve as the source of the *t*-butoxy radical that mediates H-radical abstraction to give the C-radical, whereas TBHP itself can also be introduced as the new oxygen functionality *via* the C–O bond forming process. Loh demonstrated Cu-catalyzed three-component coupling of alkenes, aliphatic alcohols, and TBHP for construction of the corresponding carbooxygenation products. In this process, α-hydroxy radicals **28** generated from aliphatic alcohols add to alkenes to give secondary radicals **29** that recombine with TBHP mediated by Cu(II) species (Scheme 26).[39] Patel reported analogous Cu-catalyzed



Scheme 26 Cu-Catalyzed carbooxygenation of alkenes.



Scheme 27 Cu-Catalyzed aromatic C–H oxygenation.

three-component coupling of electron-deficient alkenes, cycloalkanes, and TBHP.[40]

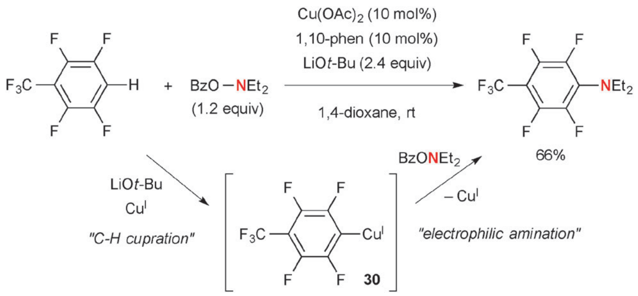
3.3. With benzoyl peroxide (BPO)

While benzoyl peroxide (BPO) has rarely been utilized as the partner with Cu-catalyzed oxidative molecular transformation, Martin recently reported Cu-catalyzed intramolecular aromatic C–H oxygenation of 2-arylbenzoic acids specifically mediated by BPO as the terminal oxidant (Scheme 27).[41] The reaction could not be facilitated by TBHP. Together with treatment of the biaryl lactones with LiOH for hydrolysis, the overall process is considered as formal aromatic C–H hydroxylation.

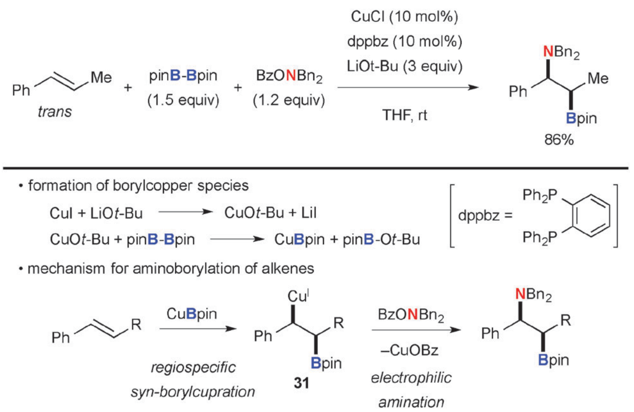
4. With *O*-benzoyl-*N*,*N*-dialkylhydroxylamines

Among various types of hydroxyl amine derivatives, *O*-benzoyl-*N*,*N*-dialkylhydroxylamines (BzO–NR_2) have been of particular use for electrophilic amination of organocopper(I) species. For example, Hirano/Miura reported direct aromatic C–H amination of electron-deficient arenes with BzO–NEt_2 by the $Cu(OAc)_2$-1,10-phen catalytic system in the presence of LiO*t*-Bu (Scheme 28).[42] The process is composed of aromatic C–H cupration for the formation of aryl-Cu(I) species **30** and subsequent electrophilic amination with BzO–NEt_2. The mechanism of electrophilic amination was previously investigated by Johnson and suggested as the S_N2 mechanism.[43] This strategy was applied for C2-amination of quinoline-*N*-oxides by Li/Wu.[44]

Hirano/Miura demonstrated the combination of borylcupration of alkenes with subsequent electrophilic amination of the resulting alkyl-Cu species with BzO–NR_2, offering elegant aminoboration of alkenes in stereo- and regio-selective manners. For example, the reactions of arylalkenes such as *trans*-β-methylstyrene with bis(pinacolato)diboron (pinB-Bpin) and BzO–NBn_2 under the CuCl-dppbz catalytic system in the presence of



Scheme 28 Cu-Catalyzed aromatic C–H amination with hydroxylamines.

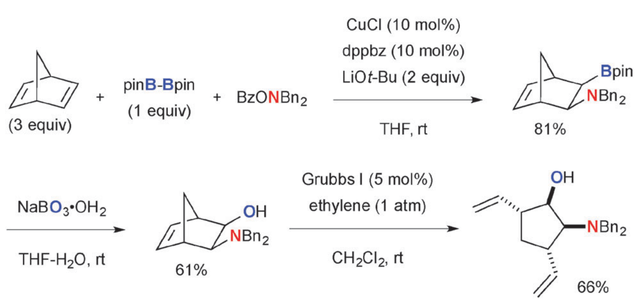


Scheme 29 Cu-Catalyzed aminoboration of alkenes.

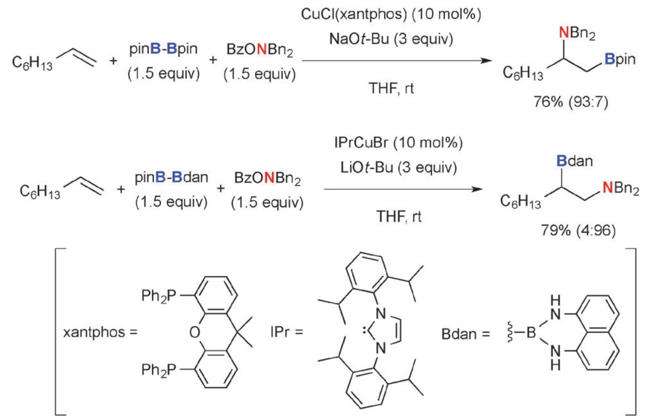
LiO*t*-Bu resulted in the formation of aminoboration products (Scheme 29).[45] As boryl-cupration of alkenes takes place in *syn*-selective and regiospecific fashions to form organocopper intermediate **31** and the subsequent electrophilic amination proceeds with retention of the configuration of the organocopper moiety, the overall stereochemical outcome of the process is regioselective *syn*-aminoboration of alkenes.

This Cu-catalyzed aminoboration of alkenes was capable of functionalizing bicyclic alkenes (Scheme 30).[46] The 1,2-aminoborane product from norbornadiene could be further converted into the corresponding diastereomerically pure cyclopentane derivative *via* hydroxylation of the C–B bond by sodium perborate followed by ring-opening cross metathesis with ethylene.

As for the aminoboration of non-activated terminal alkenes, its regioselectivity could be controlled by switching the ligands



Scheme 30 Cu-Catalyzed aminoboration of norbornadiene and further molecular transformation.

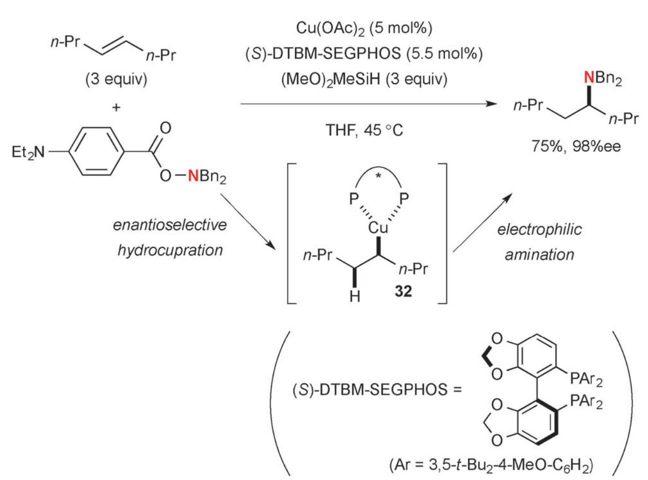


Scheme 31 Cu-Catalyzed regiodivergent aminoboration of non-activated terminal alkenes.

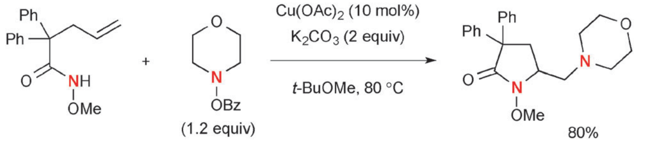
on the Cu(I) catalysts (Scheme 31).[47] Namely, the CuCl–xantphos system installs the amine moiety at the internal carbon, while the CuBr-*N*-heterocyclic carbene (IPrCuBr) complex induces the amination at the terminal carbon.

Buchwald, Hirano/Miura, and Hartwig independently reported formal hydroamination of alkenes by the sequence of Cu-catalyzed hydrocupration of alkenes with hydrosilanes and electrophilic amination of the resulting alkylcopper species **32** with BzO–NR_2. Various types of alkenes such as aryl alkenes,[48] unactivated 1,1-disubstituted alkenes,[49] unactivated internal alkenes (Scheme 32),[50] oxa/aza-bicyclic alkenes,[51] and alkenylsilanes[52] have been employed for regio- and enantioselective hydroamination, in which choice of ligands on copper catalysts is crucial to control the reactions (*i.e.* to prevent the side reactions such as hydride reduction of hydroxyl amines).

Wang recently developed Cu-catalyzed diamination of alkenes using alkenyl *O*-Me-hydroxamic acids and BzO–NR_2 that afforded functionalized nitrogen heterocycles (Scheme 33).[53] The process is composed of intramolecular aminocupration of alkenes and subsequent electrophilic amination. As a deuterium-labeling



Scheme 32 Cu-Catalyzed enantioselective formal hydroamination of non-activated internal alkenes.



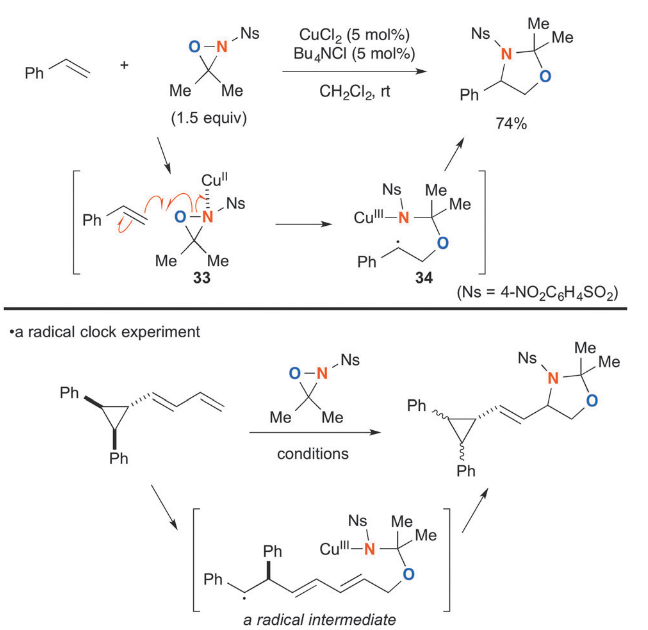
Scheme 33 Cu-Catalyzed diamination of alkenyl *O*-Me hydroxamic acids with *O*-benzoyl hydroxylamines.

experiment on the terminal alkenyl carbon revealed that the reaction does not retain the original stereochemistry of alkenes, the radical intermediates are supposed to be involved prior to the electrophilic amination.

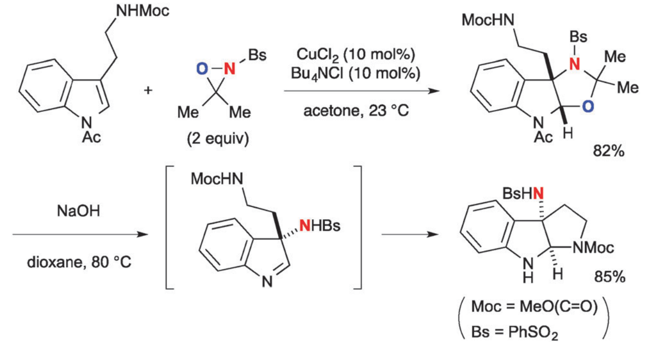
5. With oxaziridines

Highly strained three-membered ring oxaziridines work with copper complexes to facilitate aminooxygenation of alkenes. Yoon developed $CuCl_2$-catalyzed aminooxygenation of alkenes with *N*-sulfonyloxaziridines that could be dramatically facilitated by chloride additives such as Bu_4NCl (Scheme 34).[54] The detailed mechanistic investigation elucidated that Cu(II)–oxaziridine complex **33** undergoes C–O bond forming radical addition onto alkenes to generate C-radical intermediate **34** tethered with a Cu(III) sulfonamide moiety. Subsequent radical recombination forms the C–N bond and regenerates Cu(II) species that can maintain catalytic turnover further. The presence of the radical intermediate was proved by a radical clock experiment.

This aminooxygenation strategy with *N*-sulfonyl oxaziridines was capable of functionalizing indoles (Scheme 35).[55] It is worthy to note that the resulting aminal product derived from *N*-acyl-tryptamine was readily transformed to 3-aminopyrroloindoline by base treatment.



Scheme 34 $CuCl_2$-catalyzed aminooxygenation of alkenes with *N*-sulfonyloxaziridines.



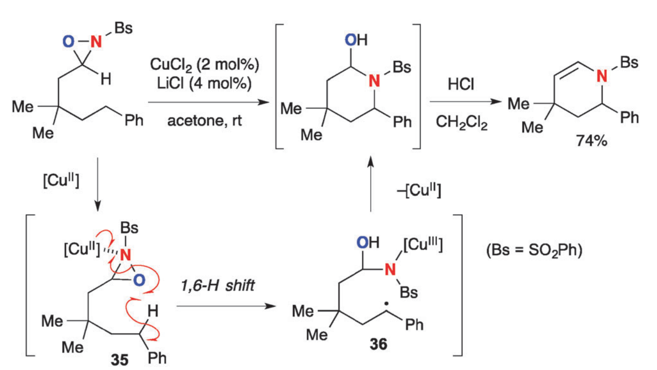
Scheme 35 Cu-Catalyzed aminooxygenation of indoles with *N*-sulfonyloxaziridines.

The Cu(II)–oxaziridine complexes also undergo the remote H-radical abstraction to enable aliphatic C–H amination (Scheme 36).[56] The reaction of *N*-sulfonyl oxaziridines having an alkyl tether under the $CuCl_2$–LiCl catalytic system provides intramolecular C–H amination products *via* 1,6-*H*-radical abstraction by Cu(II)–oxaziridine complex **35** followed by subsequent radical recombination of the resulting C-radical **36** to form the C–N bond. The resulting hemiaminal product could be converted into cyclic enamide by acid treatment.

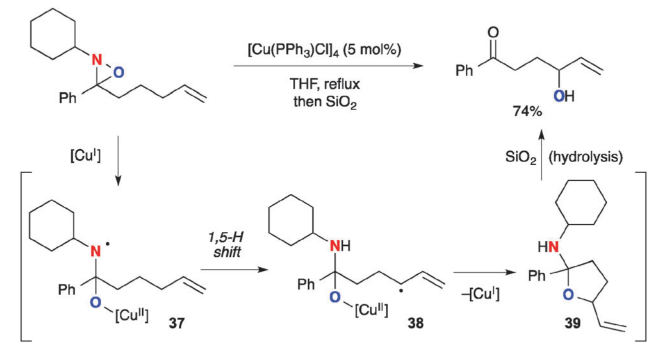
On the other hand, Aubé recently reported Cu(I)-catalyzed allylic sp^3 C–H oxygenation with *N*-alkyl oxaziridines (Scheme 37).[57] This method could oxidize the allylic position *via* the sequence of (1) formation of aminyl radical **37** having a Cu(II)–alkoxide tether through single-electron-reduction of *N*-alkyl oxaziridines by the Cu(I) complex; (2) generation of the allylic radical by a 1,5-*H* radical shift to form C-radical **38** and subsequent radical recombination with the Cu(II)–alkoxide moiety to form cyclic hemiaminal **39** with regeneration of Cu(I) species; (3) hydrolysis to form the final product, γ-hydroxy ketone.

6. With diaziridinone derivatives

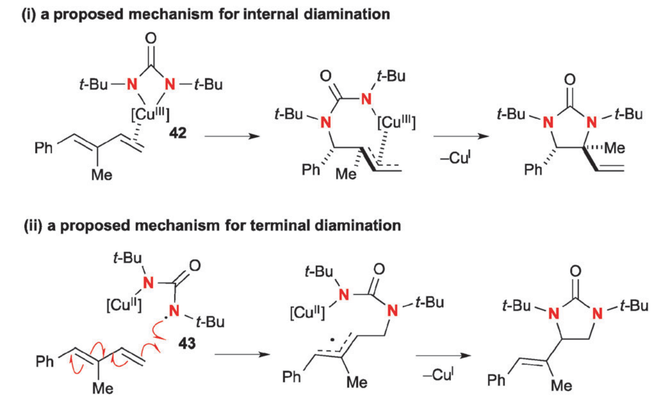
Similar to oxaziridines, *N*,*N*-di-*t*-butyldiaziridinone shows strain-driven oxidative reactivity towards Cu(I) complexes, enabling catalytic diamination of various types of alkenes.[4b] Shi revealed



Scheme 36 Cu(II)-catalyzed C–H amination with *N*-sulfonyloxaziridines.



Scheme 37 Cu(I)-catalyzed C–H oxygenation with *N*-alkyloxaziridines.

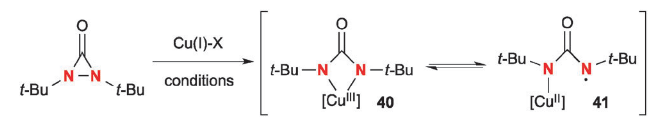


Scheme 40 The proposed reaction mechanisms for diamination.

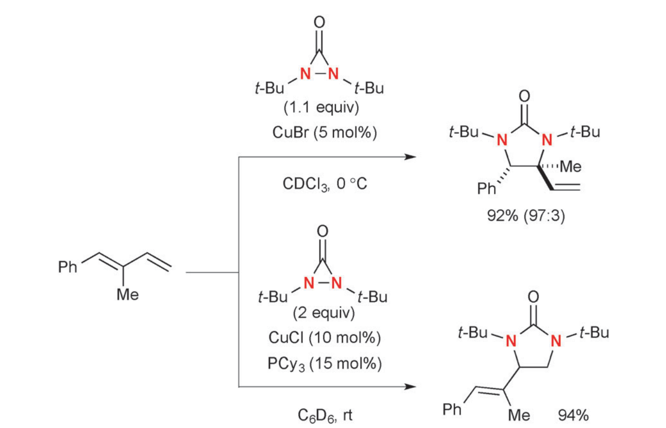
that *N*,*N*-di-*t*-butyldiaziridinone oxidizes Cu(I) complexes to form an equilibrium mixture of four-membered Cu(III) species **40** and Cu(II))–N radical species **41** (Scheme 38).

Of particular interest is that the regioselectivity in diamination of conjugated dienes could be switched by the choice of Cu(I) catalyst systems and electronic nature of dienes with the different reaction mechanisms.[58] Namely, conjugated dienes and *N*,*N*-di-*t*-butyldiaziridinone in the presence of a catalytic amount of CuBr generally undergo diamination of internal alkenes, whereas terminal alkenes could be functionalized under the CuCl–phosphine ligand catalytic system (Scheme 39).

Detailed mechanistic investigation suggested that internal diamination proceeds with the four-membered Cu(III) species **42** *via* (1) coordination and migratory insertion to dienes; (2) C–N reductive elimination that renders the overall process *cis*-diamination (Scheme 40-i). On the other hand, diamination of terminal alkenes involves Cu(II)–N radical species **43** that initiates radical C–N bond formation to the sterically less hindered terminal carbon to generate an allyl radical. The second C–N bond formation is enabled by the radical recombination of the allyl radical with an N–Cu(II) moiety to afford the diamination product along with regeneration of the Cu(I) catalyst (Scheme 40-ii).



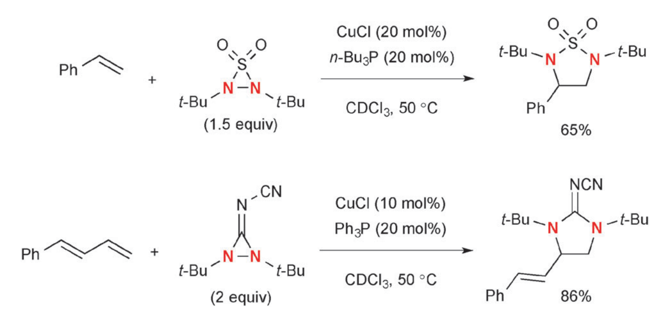
Scheme 38 The reaction of di-*t*-butyldiaziridinone with Cu(I) complexes.



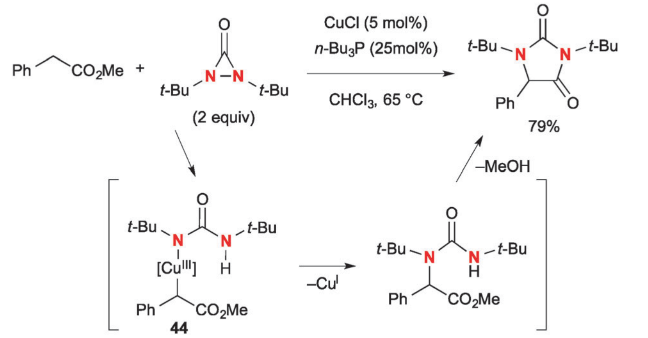
Scheme 39 Regioselectivity in Cu(I)-catalyzed diamination of conjugated dienes with *N*,*N*-di-*t*-butyldiaziridinone.

This stepwise radical-mediated diamination of alkenes with *N*,*N*-di-*t*-butyldiaziridinone by the Cu(I)–phosphine ligand catalytic system is amenable to functionalize not only conjugated dienes but also 1,1-disubstituted alkenes.[59] Asymmetric terminal diamination of conjugated dienes was also developed by the CuCl–chiral phosphine[60] and Cu(I)–chiral phosphate systems.[61] Analogous to *N*,*N*-di-*t*-butyldiaziridinone, *N*,*N*-di-*t*-butylthiadiaziridine 1,1-dioxide[62] and *N*,*N*-di-*t*-butyl-3-(cyanimino)-diaziridine[63] could be utilized for catalytic radical diamination of conjugated alkenes under the CuCl–phosphine ligand systems (Scheme 41).

In addition to diamination of alkenes, *N*,*N*-di-*t*-butyldiaziridinone could be utilized for Cu(I)-catalyzed α-amination of esters (Scheme 42).[64] The reaction of esters with *N*,*N*-di-*t*-butyldiaziridinone under the CuCl-*n*-Bu_3P catalytic system provides the corresponding hydantoins. The proposed mechanism involves α-cupration of esters by the transient Cu(II)–N radical species or four-membered Cu(III) species derived from *N*,*N*-di-*t*-butyldiaziridinone and CuCl. The resulting α-cupro(III)-esters **44** undergo C–N reductive elimination that is followed by cyclization to afford hydantoins.



Scheme 41 The reaction of di-*t*-butyldiaziridinone with Cu(I) complexes.



Scheme 42 Synthesis of hydantoins from esters and *N*,*N*-di-*t*-butyl-diaziridinone *via* α-amination.

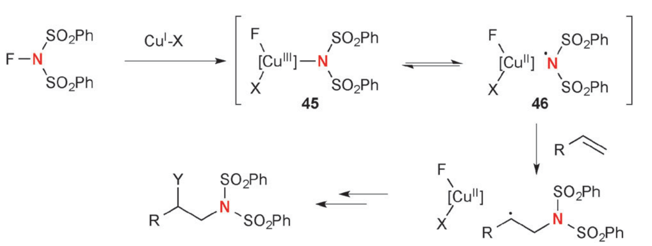
7. With fluoroamine derivatives

7.1. With *N*-fluorobenzenesulfonimide (NFSI)

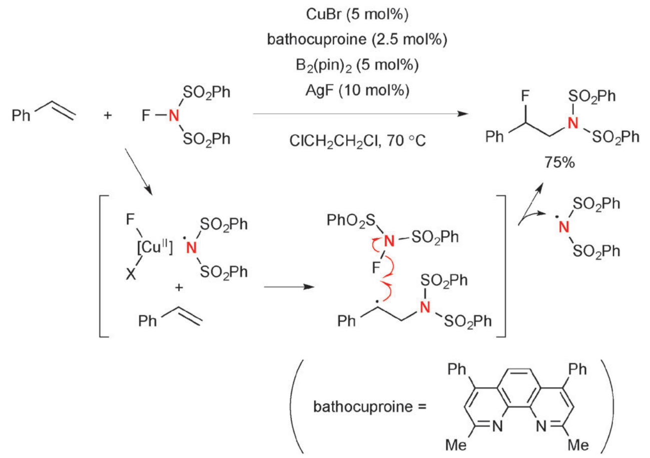
A highly reactive oxidant, *N*-fluorobenzenesulfonimide (NFSI) reacts readily with Cu(I) complexes to afford Cu(III)-imide species **45** that is in equilibrium with Cu(II)-stabilized sulfonimide radical **46** (Scheme 43). Thus, this nitrogen-centered radical derived from NFSI and Cu(I) complexes could initiate aminofunctionalization of alkenes.

For example, Zhang reported regioselective aminofluorination of styrenes with NFSI under CuBr/bathocuproine-catalyzed reaction conditions (Scheme 44).[65] The use of bis(pinacolato)-diborone (B_2pin_2) and AgF as additives was crucial to facilitate the aminofluorination. The DFT calculations suggested that the C–F bond formation is likely enabled by F-radical abstraction from NFSI. This process concurrently generates the sulfonimide radical that can maintain the radical chain for aminofluorination.

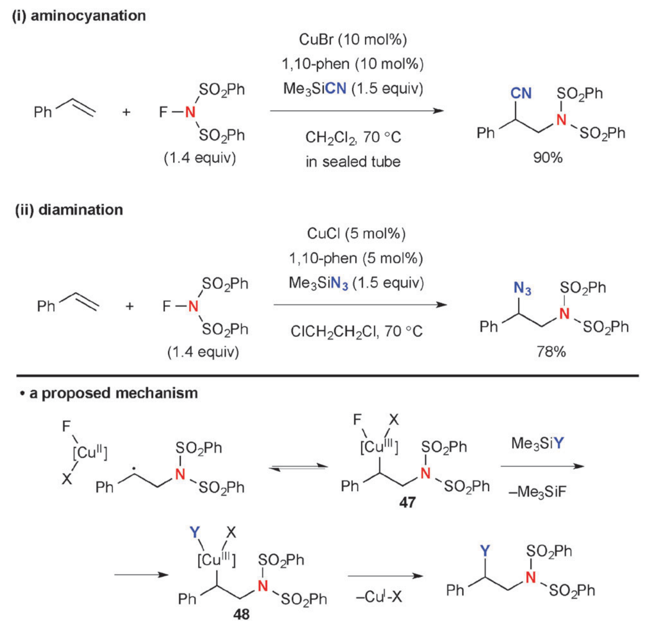
In place of fluorine incorporation, cyano, amido, and azido moieties could be installed by Cu-catalyzed radical aminofunctionalization with NFSI. Xiong/Li/Zhang revealed that the reaction of styrene with NFSI and TMSCN under the CuBr-1,10-phen catalytic system gives an aminocyanation product (Scheme 45-i).[66] Similarly, aminoazidation was developed by Studer using $TMSN_3$ (Scheme 45-ii).[67] The C–CN and C–N_3 bond formation is mediated *via* radical recombination presumably through formation of organo-Cu(III) intermediate **47** followed by ligand exchange with TMSCN or $TMSN_3$ to afford another organo-Cu(III) species **48** and subsequent C–CN or C–N_3 reductive elimination. The driving force of the ligand exchange could



Scheme 43 The reaction of NFSI with Cu(I) complexes for aminofunctionalization of alkenes.



Scheme 44 Cu(I)-Catalyzed aminofluorination of styrene with NFSI.



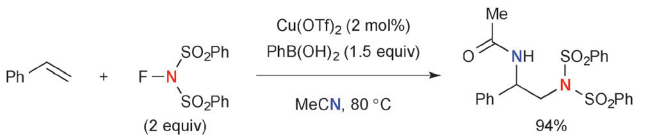
Scheme 45 Cu(I)-catalyzed aminocyanation and diamination of styrene with NFSI.

be preferential elimination of TMSF due to the strong affinity between Si and F atoms.

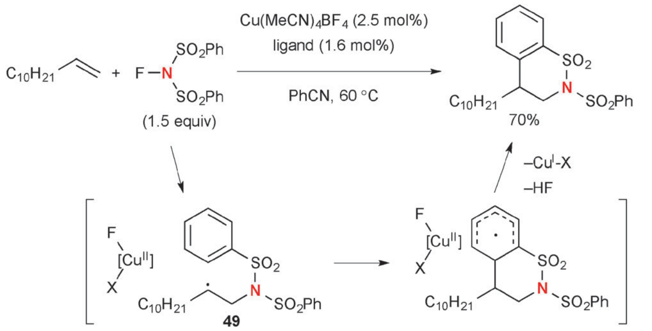
Interestingly, when the Cu-catalyzed reaction of styrene with NFSI was conducted in the presence of $PhB(OH)_2$ in acetonitrile, a diamination product was formed through incorporation of acetonitrile by the Ritter-type reaction (Scheme 46).[67]

On the other hand, the Cu(I)-catalyzed reactions of aliphatic alkenes with NFSI provide non-stabilized secondary radicals **49**, which undergo intramolecular radical addition to the phenylsulfonyl moiety to afford sultams (Scheme 47).[68]

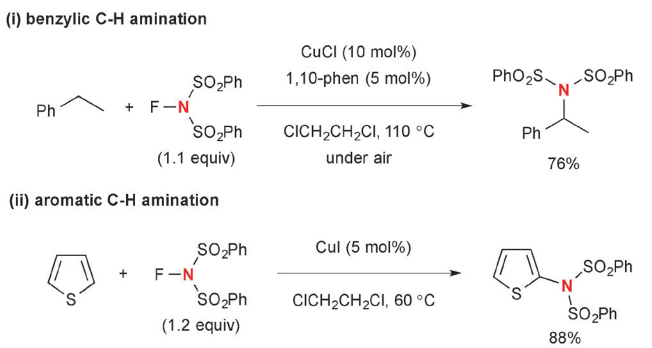
The combination of the Cu(I)-catalyst and NFSI is also capable of functionalizing benzylic sp^3 C–H bonds (Scheme 48-i)[69] as well as sp^2 C–H bonds (Scheme 48-ii)[70] on 5-membered-aromatic heterocycles such as thiophene and furan through the radical mechanism with the transient sulfonimide radical.



Scheme 46 Cu(OTf)$_2$-catalyzed diamination of styrene with NFSI and acetonitrile.



Scheme 47 Synthesis of sultams by the Cu(I)-catalyzed reaction of aliphatic alkenes with NFSI.

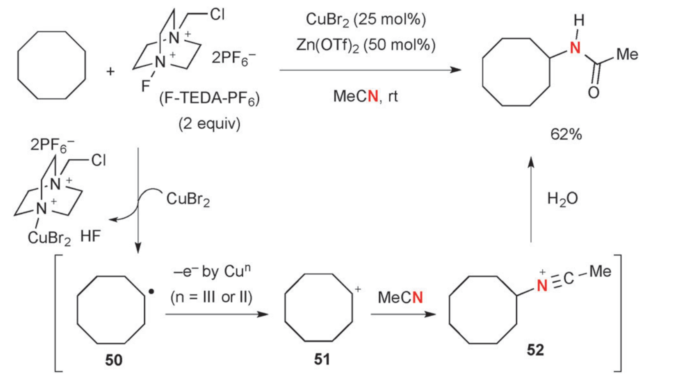


Scheme 48 Cu(I)-catalyzed C–H amination with NFSI.

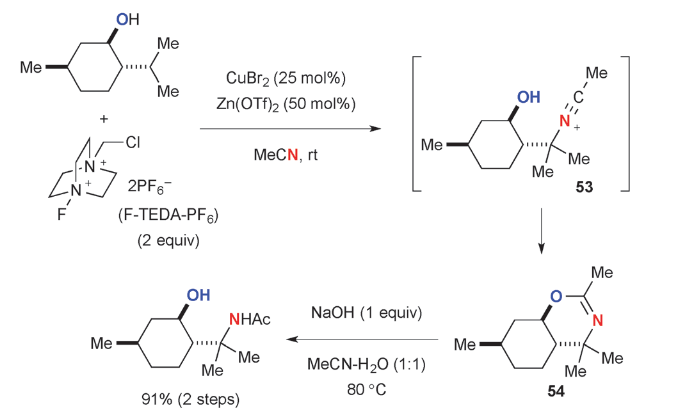
7.2. With Selectfluor® and its derivatives (F-TEDA-X)

Selectfluor® [1-chloromethyl-4-fluoro-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate] and its derivatives (known as F-TEDA-X reagents, where X stands for their counter anions) have been used as versatile fluorination reagents in organic synthesis,[71] while these reagents could be utilized as strong oxidants of Cu(II) and Cu(I) complexes to generate highly reactive Cu(III) species that can abstract the H-radical from sp^3 hybridized carbons. The combination of Cu catalysts and F-TEDA-X reagents is thus capable of oxidizing unactivated aliphatic C–H bonds. For example, Baran developed Cu-catalyzed Ritter-type aliphatic C–H amination with acetonitrile in the presence of F-TEDA-PF$_6$ (Scheme 49).[72,73] The C–H amination is likely enabled by a stepwise sequence involving (1) H-radical abstraction; (2) SET oxidation of the resulting C-radical **50** to carbocation **51**; (3) Ritter-type amination by solvent acetonitrile. Nitrilium ion **52** is finally hydrolyzed to give acetamide products.

Interestingly, substrates having hydroxyl or carbonyl groups rendered the C–H amination process more chemo-selective and efficient presumably by their chelation effect. For example, the



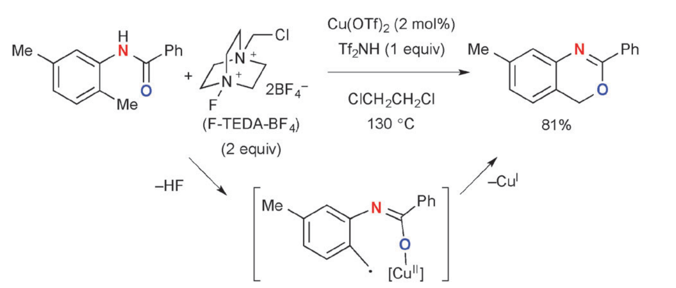
Scheme 49 CuBr$_2$-catalyzed C–H amination of cyclooctane with F-TEDA-PF$_6$.



Scheme 50 CuBr$_2$-catalyzed C–H amination of menthol with F-TEDA-PF$_6$.

CuBr$_2$-catalyzed reaction of (−)-menthol with F-TEDA-PF$_6$ afforded the chemo-selective C–H amination product dihydrooxazine in very high yield through intramolecular trap of the transient nitrilium ion **53** by the hydroxyl group (Scheme 50). Dihydrooxazine moiety **54** could be easily hydrolyzed into the corresponding 1,3-aminoalcohol.

A similar directing effect in chemo-selective aliphatic C–H oxygenation was observed in the reactions of *N*-(2-alkylphenyl)-benzamides in the presence of Cu(OTf)$_2$ as the catalyst and F-TEDA-BF$_4$ (Selectfluor®) for synthesis of 4*H*-3,1-benzoxazines through *ortho*-aliphatic C–H oxygenation (Scheme 51).[74] The reactions selectively functionalize the *ortho*-alkyl group presumably *via* H-radical abstraction by the amide–Cu chelate intermediate,



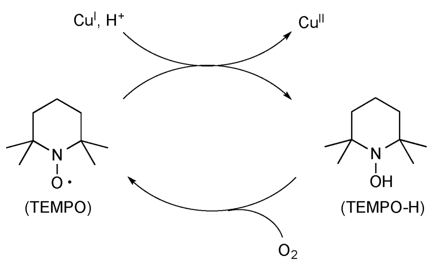
Scheme 51 Cu(OTf)$_2$-catalyzed C–H oxygenation with F-TEDA-BF$_4$.

whereby aliphatic C–H bonds in the other positions (*e.g. meta*-methyl group) are kept intact.

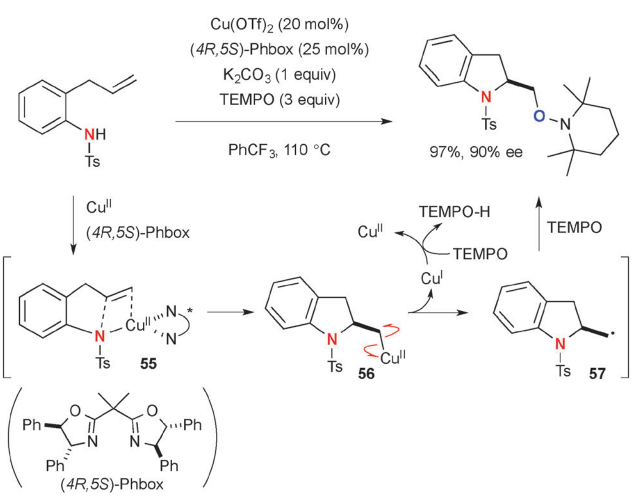
8. With 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)

A persistent radical, TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), has been utilized for Cu-catalyzed oxidative C–O bond forming reactions. The unique feature of TEMPO is that it works as an oxidant of Cu(I) species to generate Cu(II) species and its reduced form TEMPO-H could be reoxidized by molecular O_2 to regenerate TEMPO (Scheme 52).[75]

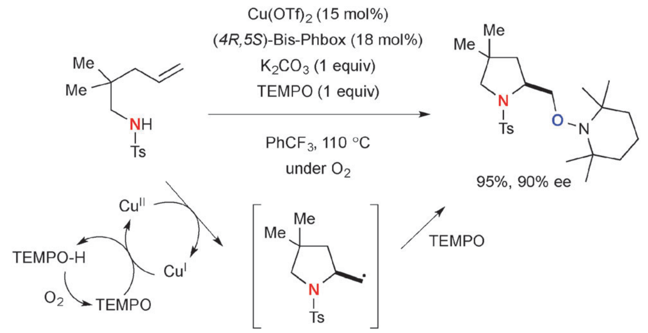
Chemler developed Cu-catalyzed enantioselective intra/intermolecular aminooxygenation of alkenyl *N*-sulfonamides with TEMPO for synthesis of indoline and pyrrolidine derivatives (Scheme 53), in which TEMPO plays two roles as the external oxygen source and stoichiometric oxidant to realize catalytic turnover.[76] The detailed mechanistic analyses in experimental and theoretical manners revealed that the process is initiated by concerted *syn*-aminocupration of alkenes by Cu(II)-amido species **55** to construct heterocyclic frameworks having organocopper(II) moiety **56**.[77] Subsequent C–Cu(II) bond homolysis results in formation of C-radical **57** that is trapped by TEMPO to afford the aminooxygenation product. The resulting lower valent Cu(I) species is reoxidized to the Cu(II) complex by TEMPO.



Scheme 52 Oxidation of Cu(I) species to Cu(II) species by TEMPO.



Scheme 53 Cu-Catalyzed aminooxygenation of alkenes with TEMPO.



Scheme 54 Cu-Catalyzed aminooxygenation of alkenes with TEMPO under an oxygen atmosphere.

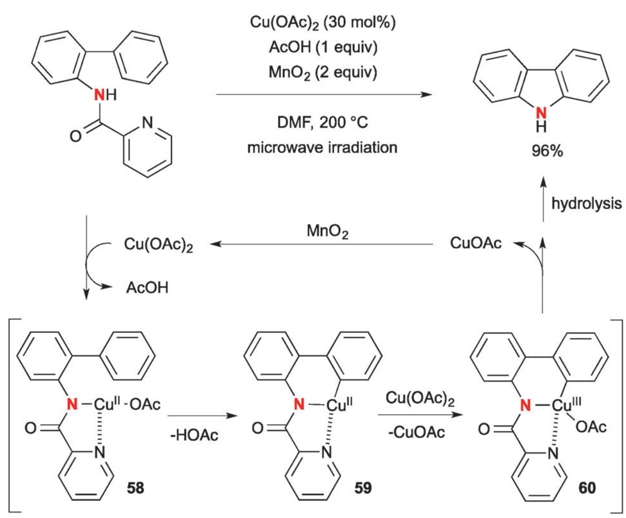
In some cases especially when *N*-pentenylsulfonamides were employed, the use of molecular oxygen as an atmosphere could make the aminooxygenation process more efficient (Scheme 54). The TEMPO loading could be reduced to 1.5 equiv. as molecular oxygen serves as an oxidant to reoxidize TEMPO-H to TEMPO.

9. With metallic oxidants

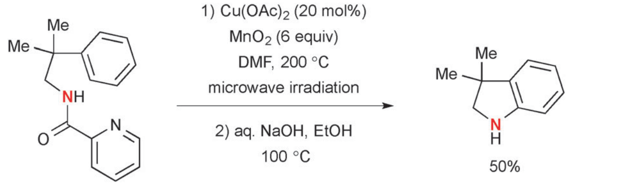
Mild and cost-economical metallic oxidants have been employed as the terminal stoichiometric oxidants to regenerate higher valent active Cu species to realize catalytic turnover for the Cu-mediated oxidative molecular transformation.

9.1. MnO_2

Hirano/Miura reported $Cu(OAc)_2$-catalyzed intramolecular aromatic C–H amination of biaryl-2-picolinamide for synthesis of carbazoles with MnO_2 as the stoichiometric terminal oxidant to realize the catalytic turnover (Scheme 55).[78] The reaction is initiated by aromatic C–H cupration by copper(II)–picolinamide chelate complex **58** to afford organo-Cu(II) intermediate **59**. Further redox disproportionation with $Cu(OAc)_2$ forms copper(III) intermediate **60** and subsequent C–N bond



Scheme 55 Cu-Catalyzed-MnO_2-mediated aromatic C–H amination for synthesis of carbazoles.



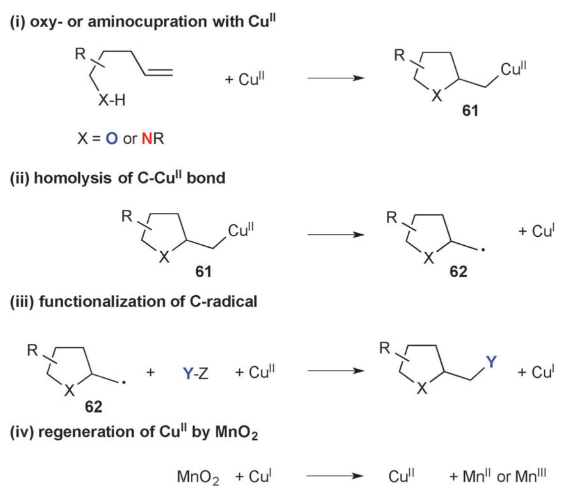
Scheme 56 Cu-Catalyzed-MnO_2-mediated aromatic C–H amination for synthesis of indolines.

reductive elimination establishes formation of the carbazole product along with generation of a lower valent Cu(I) species that is oxidized by MnO_2 to regenerate the Cu(II) catalyst.

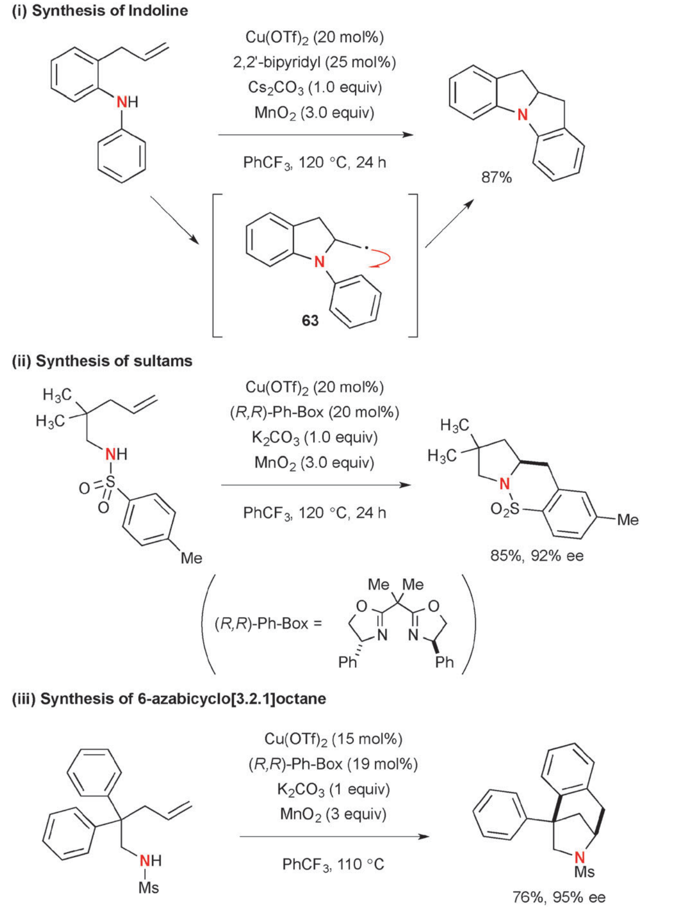
The analogous Cu-catalyzed-MnO_2-mediated C–H amination strategy with picolinamides was applied for synthesis of indolines (Scheme 56).[79]

Using MnO_2 as the terminal oxidant, Chemler developed a series of Cu(II)-catalyzed amino- and oxy-functionalization of alkenes with alkenylsulfonamides, -anilines, and -alcohols for synthesis of the corresponding heterocycles. As shown in Scheme 57, the process is composed of a multi-step sequence involving (i) amino- or oxy-cupration of alkenes to form five-membered ring organocopper(II) intermediates **61**; (ii) C–Cu(II) bond homolysis to generate C-radical **62** and Cu(I) species; (iii) radical recombination with various internal/external carbon or heteroatom sources to provide difunctionalized final products; (iv) regeneration of the higher valent Cu(II) species by oxidation of the lower valent Cu(I) species by MnO_2.

For example, treatment of *N*-aryl-2-allylaniline with 20 mol% of $Cu(OTf)_2$ in the presence of Cs_2CO_3 and MnO_2 afforded indoline derivative through intramolecular carboamination of alkenes (Scheme 58).[80] In this process, the resulting C-radical **63** was added directly to the intramolecular benzene ring to construct the new C–C bond (Scheme 58-i). Enantioselective carboamination of *N*-pentenyl(*p*-tolyl)sulfonamides was enabled by using the (*R*,*R*)-Ph-Box ligand for the $Cu(OTf)_2$ catalyst, delivering optically active bicyclic sultams (Scheme 58-ii).



Scheme 57 Cu-Catalyzed-MnO_2-mediated oxy- and amino-functionalization of alkenes.



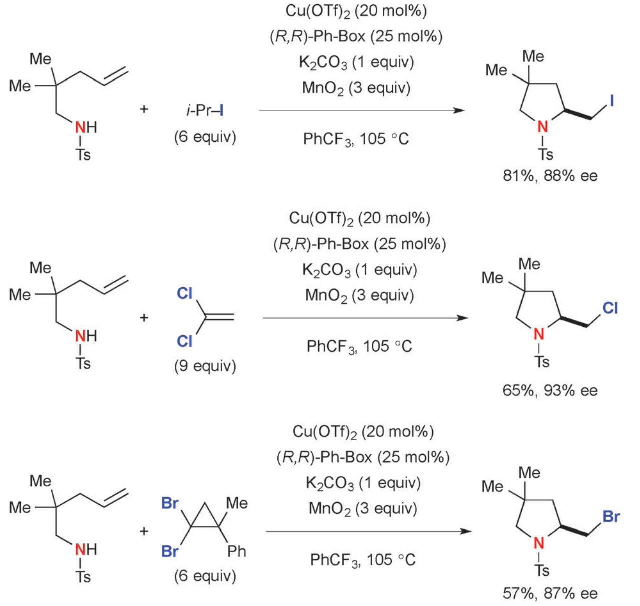
Scheme 58 Cu-Catalyzed-MnO_2-mediated carboamination of alkenes.

On the other hand, the reactions of *N*-mesyl-4-pentenylamines having the geminal diaryl moiety at the C2 position under the $Cu(OTf)_2$-(*R*,*R*)-Ph-Box catalytic system in the presence of MnO_2 provided 6-azabicyclo[3.2.1]octane in high enantioselectivity through carboamination of alkenes (Scheme 58-iii).[81]

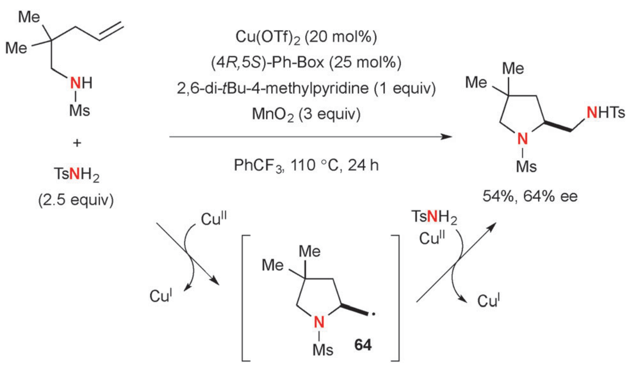
The transient C-radicals generated *via* aminocupration of *N*-sulfonyl alkenylamines could undergo an iodine transfer reaction with isopropyl iodide to form the corresponding 2-iodomethyl indolines and pyrrolidines (Scheme 59).[82] Similarly, chlorination and bromination reactions were achieved in moderate yields using 1,1-dichloroethylene and (2,2-dibromo-1-methylcyclopropyl)benzene.

Cu-Catalyzed diamination of *N*-sulfonyl-alkenylamines was developed using tosylamide ($TsNH_2$) as the external nitrogen source (Scheme 60).[83] In this case, the second C–N bond formation was enabled by radical recombination of C-radical **64** with $TsNH_2$ and Cu(II) species.

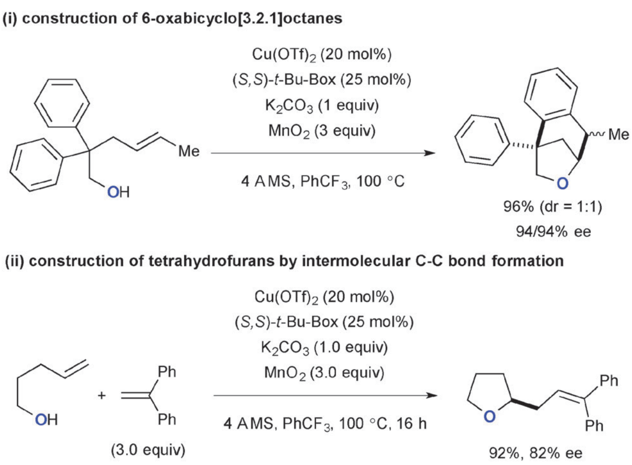
The $Cu(OTf)_2$-catalyzed-MnO_2-mediated reaction conditions were amenable to carboetherification of alkenyl alcohols, in which the second C–C bond formation was possible both in intra- and intermolecular fashions (Scheme 61).[84] Construction of 6-oxabicyclo[3.2.1]octanes was carried out using 4-pentenyl-alcohol with a geminal diaryl moiety at the C2 position *via* oxycupration of alkenes followed by intramolecular radical



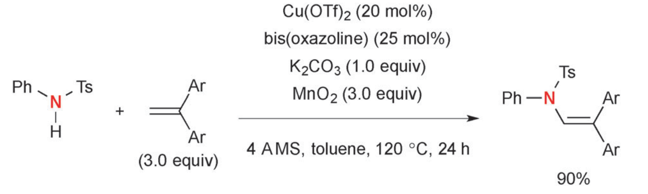
Scheme 59 Cu-Catalyzed-MnO_2-mediated-aminohalogenation of alkenes.



Scheme 60 Cu-Catalyzed-MnO_2-mediated diamination of alkenes.



Scheme 61 Cu-Catalyzed-MnO_2-mediated carboetherification of alkenes.



Scheme 62 Cu-Catalyzed-MnO_2-mediated intermolecular amination of 1,1-disubstituted alkenes.

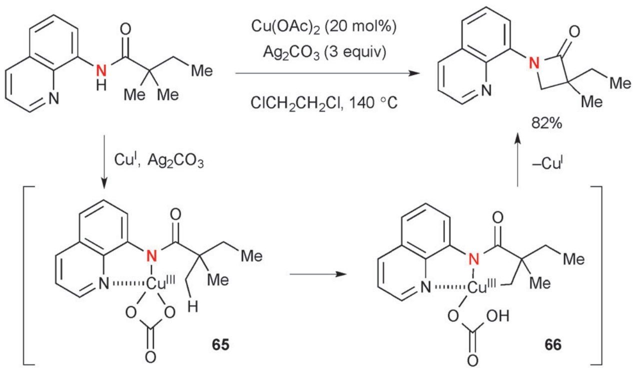
cyclization on the aryl group (Scheme 61-i). Intermolecular C–C bond formation was also realized with aryl alkenes, in which the transient C-radical underwent the oxidative Heck-type coupling with aryl alkenes to deliver 2-allyltetrahydrofurans (Scheme 61-ii).

Chemler also reported Cu-catalyzed intermolecular amination of 1,1-disubstited alkenes with *N*-arylsulfonamides in the presence of MnO_2 as a terminal oxidant (Scheme 62).[85] The reactions uniquely afforded *N*-aryl enamide products in an *anti*-Markovnikov fashion.

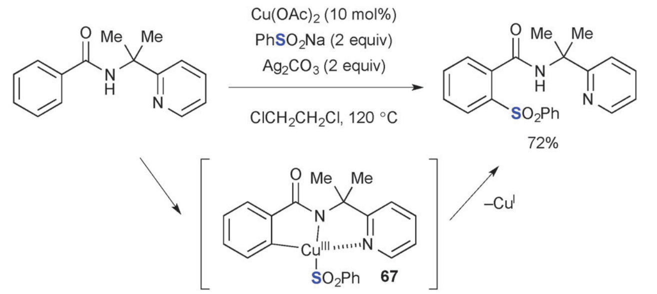
9.2. Ag_2CO_3

Ag_2CO_3 has been specifically employed as the stoichiometric oxidant for Cu-catalyzed aliphatic and aromatic C–H oxidation. Kuninobu/Kanai reported synthesis of β-lactams by Cu-catalyzed intramolecular sp^3 C–H amidation of *N*-(8-quinolinyl)amides in the presence of Ag_2CO_3 (Scheme 63).[86,87] Installation of the *N*-8-quinolinyl moiety is crucial on the amide substituent to allow it to serve as the bidentate directing group. The C–H functionalization is mediated by the transient amide–Cu(III) complex **65** through concerted metalation–deprotonation on sp^3-C–H bonds with the acetate or carbonate counter ions (the reaction with the carbonate counter ion is shown below) on the copper to provide metallacycle intermediate **66**. Finally, C–N bond forming reductive elimination affords β-lactam along with a lower valent Cu^I species that reacts further with amide and Ag_2CO_3 to regenerate the amide–Cu(III) complex to maintain the catalytic turnover.

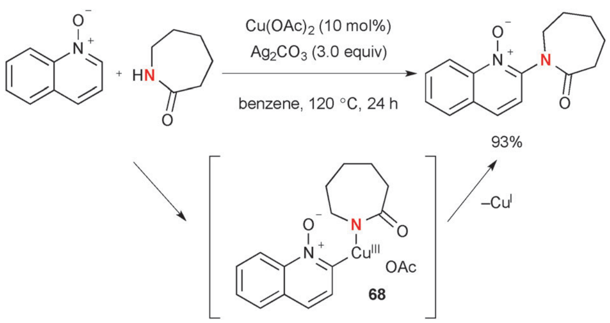
The $Cu(OAc)_2$–Ag_2CO_3 reaction system was also utilized for aromatic C–H functionalization of benzamides having a 2-pyridylmethyl moiety on the amide nitrogen through directed



Scheme 63 Cu-Catalyzed-Ag_2CO_3-mediated directed sp^3 C–H amidation.



Scheme 64 Cu-Catalyzed-Ag_2CO_3-mediated directed sp^2 C–H sulfonylation.



Scheme 65 Cu-Catalyzed-Ag_2CO_3-mediated sp^2 C–H amidation.

concerted metalation–deprotonation. Shi demonstrated Cu-catalyzed *ortho*-aromatic C–H sulfonylation of benzamides using sodium sulfinate as the sulfonylation reagent (Scheme 64).[88] The C–S bond forming reductive elimination from the transient Cu(III) metallacycle **67** furnishes the sulfonylation product.

Intermolecular sp^2 C–H amidation/amination of quinoline *N*-oxides was also reported under the $Cu(OAc)_2$–Ag_2CO_3 reaction system (Scheme 65).[89] Various lactams/cyclic amines are incorporated into the key organocopper(III) intermediate **68** prior to its C–N bond reductive elimination to deliver the final products.

10. Information of the oxidants: their commercial availability and preparation methods

Among the terminal oxidants for the Cu-catalyzed oxidative carbon–heteroatom bond formation discussed in this review, the price of the commercially available ones from Sigma-Aldrich is summarized in Table 1. Togni reagent II[90] (entry 4) and peroxides (entries 5–7) are potentially explosive, so the reactions with these reagents should need special care with proper protecting shields.

The typical preparation methods of non-commercialized oxidants such as vinyl(aryl)iodonium triflate (Section 2.2.), *O*-benzoyl-*N*,*N*-dialkylhydroxylamines (Section 4), oxaziridines (Section 5), and diaziridinones (Section 6) are illustrated in Schemes 66–69, respectively.

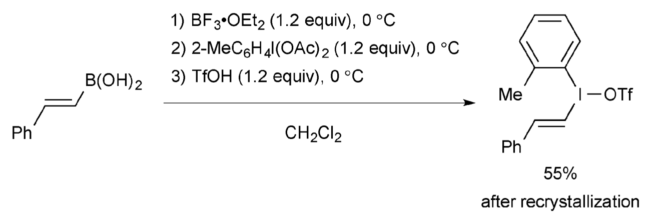
Vinyl(aryl)iodonium triflate is readily prepared from the sequential treatment of the corresponding alkenylboronic acids with $BF_3{\cdot}OEt_2$, 2-iodotoluene diacetate, and TfOH (Scheme 66).[91]

Table 1 A price list of commercially available oxidants

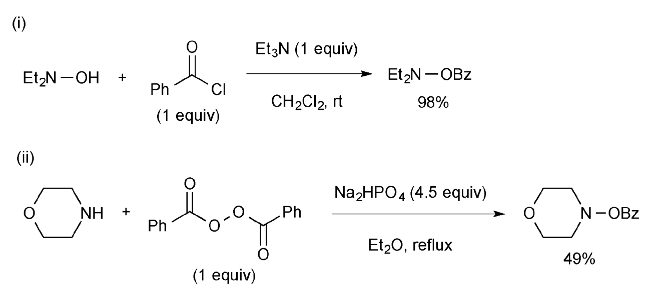
Entry	Oxidant	Price (US$)^a	CAS no.
1	$PhI(OAc)_2$	21.6/5 g	3240-34-4
2	Ph_2IOTf	114/1 g	66003-76-7
3	Togni reagent I	66.4/250 mg	887144-97-0
4	Togni reagent II	50.6/250 mg	887144-94-7
5	*t*-BuOO*t*-Bu	48.1/250 mL	110-05-4
6	*t*-BuOOH (5–6 M in decane)	151/100 mL	75-91-2
7	$(PhCO_2)_2$	43.5/50 g	94-36-0
8	$(PhSO_2)_2NF$ (NFSI)	77.2/5 g	133745-75-2
9	Selectfluor®	34.1/5 g	140681-55-6
10	TEMPO	44.9/5 g	2564-83-2
11	MnO_2 (>99%)	49.4/100 g	1313-13-9
12	Ag_2CO_3 (>99%)	34.9/5 g	534-16-7

^{a} http://www.sigmaaldrich.com/united-states.html.

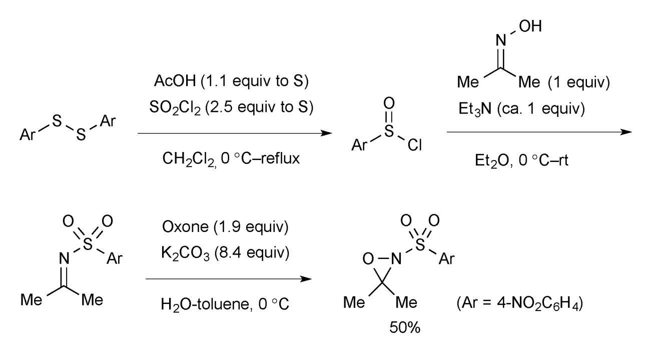
Preparation of *O*-benzoyl-*N*,*N*-dialkylhydroxylamines is conducted either by benzoylation of *N*,*N*-dialkylhydroxylamines with benzoyl chloride (Scheme 67-i) or by nucleophilic substitution reactions of dibenzoyl peroxide with the corresponding secondary amines (Scheme 67-ii).[92] *O*-Benzoyl-*N*,*N*-dialkylhydroxylamines should be stored in the freezer.



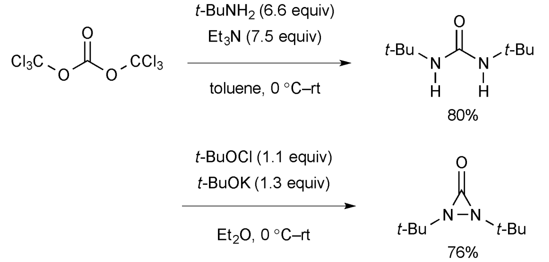
Scheme 66 Preparation of *N*-noxyl-3,3-dimethyloxaziridine.



Scheme 67 Preparation of *O*-benzoyl-*N*,*N*-dialkylhydroxylamines.



Scheme 68 Preparation of *N*-noxyl-3,3-dimethyloxaziridine.



Scheme 69 Preparation of *N*,*N*-di-*t*-butyldiaziridinone.

Oxaziridines are synthesized by oxidation of the corresponding imines with Oxone®. The scalable procedure for synthesis of *N*-nosyl-3,3-dimethyloxaziridine reported by Yoon is shown in Scheme 68.[54,93]

The synthetic procedure of *N*,*N*-di-*t*-butyldiaziridinone includes a sequence of preparation of di-*t*-butylurea and oxidative intramolecular N–N bond formation (Scheme 69).[94] *N*,*N*-di-*t*-butyldiaziridinone should be stored in the dark.

11. Conclusions

This review highlighted up-to-date developments in copper-catalyzed (anaerobic) oxidative formation of carbon–heteroatom bonds on C–H bonds and alkenes. Various combinations of copper catalysts and readily available stoichiometric oxidants have been devised to enable unique and unprecedented oxidative molecular transformations. Unlike other transition metals, the reaction modes enabled by the copper species are multifarious. For example, many of the carbon–heteroatom bond-forming processes in Cu-catalyzed oxidative molecular transformations include organocopper (C–Cu) species as the key intermediates. The chemical reactivity of the organocopper species is uniquely diverse depending on the oxidation state of the copper moiety. Higher valent C–Cu^{III} species undergo substitution reactions with heteroatom nucleophiles or reductive elimination of the C–heteroatom bond, whereas lower valent C–Cu^{I} species exhibit a nucleophilic character to react with heteroatom electrophiles such as *O*-benzoyl-*N*,*N*-dialkylhydroxylamines. On the other hand, C–Cu^{II} species undergo homolysis to generate C-radicals that could be further functionalized with radical trapping reagents such as TEMPO or heteroatom nucleophiles through radical recombination pathways with the aid of Cu^{II} species. More challenges and opportunities still remain for elucidation of the detailed reaction mechanisms and identification of active Cu-species that control the course of the reaction and improve catalytic turnovers and overall process efficiency. We anticipate that copper complexes have inexhaustible potential as catalysts to enhance our synthetic capability further.

Acknowledgements

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