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

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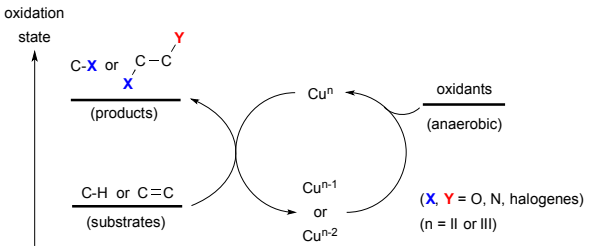
This review updates recent advances in Cu-catalyzed (anaerobic) oxidative carbon-heteroatom bond formation onto sp^3- and sp^2-C–H bonds as well as alkenes, classifying by types of the stoichiometric oxidants.

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 state into highly functionalized (oxidized) molecules in chemo- and stereo-selective manners is a long-standing goal in chemical synthesis. In this context, direct installation of carbon-heteroatom bonds onto ubiquitous C–H bonds (both sp^3- and sp^2-hybridized) is of great significance to streamline the multi-step molecular transformations needed for 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 ubiquitous nature of the C–H bonds. On the other hand, oxidative difunctionalization of alkenes provided another efficient way to address highly oxidized molecular complexity through installing two distinct functional groups in 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 unprecedented catalytic processes of their own.[3] Among such first row transition metals, copper complexes exhibit unique and versatile reactivity and good functional group tolerance.[4] A broad range of the oxidation states in copper complex (mainly from Cu^0 to Cu^{III} applied in chemical synthesis)[5,6] enables to promote redox reactions *via* either single-electron or two-electron-transfer fashion (or both in the sequential processes), depending on the reaction conditions and types of the substrates used. Variety of the 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 the hetero atoms introduced onto the products (Scheme 1).



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

This review focuses on recent advances in copper-catalyzed oxidative carbon-heteroatom bond forming reactions onto C–H bonds as well as alkenes. These reactions are classified by 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 details,[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*-

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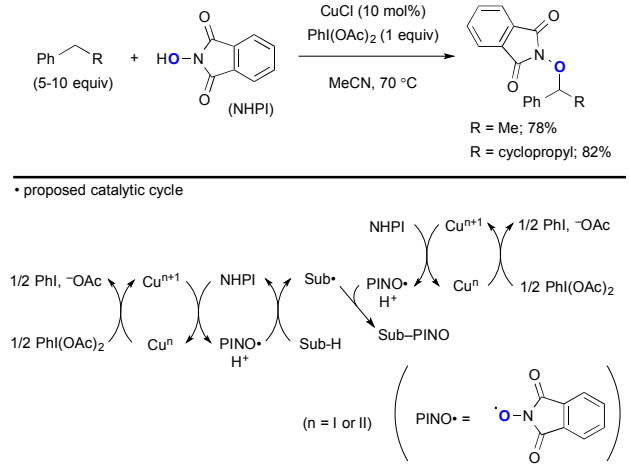
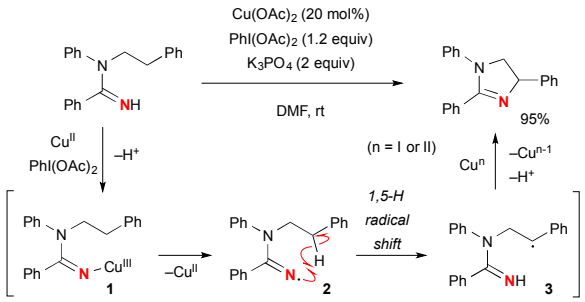
hydroxyphthalimide (NHPI) under CuCl-catalyzed-PhI(OAc)$_2$-mediated reaction conditions (Scheme 2).[8] The radical mechanism is proposed, where oxidatively formed phthalimide *N*-oxyl (PINO) radical undergoes H-radical abstraction from the substrates (Sub-H) to generate the corresponding C-radicals (Sub•). Their subsequent recombination with 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 PINO radical keeping the cyclopropyl moiety intact, indicating kinetically faster radical recombination or alternative organometallic mechanism involved.



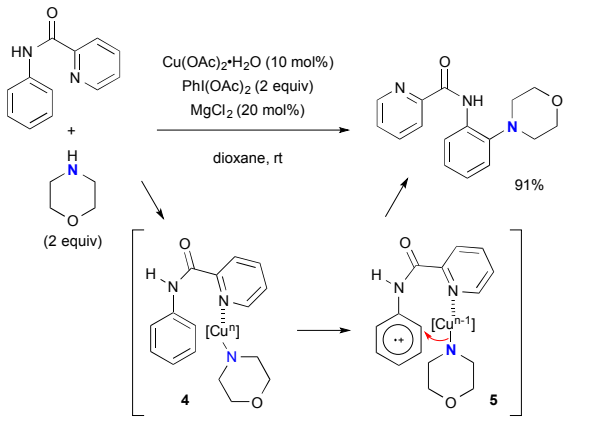
Scheme 2 Cu-catalyzed-PhI(OAc)$_2$-mediated sp^3-C–H oxygenation with NHPI.

Chiba reported that 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. 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 carbocation and subsequent C–N bond formation to furnish dihydroimidazole. Radical recombination mechanism is not ruled out for the C–N bond formation.



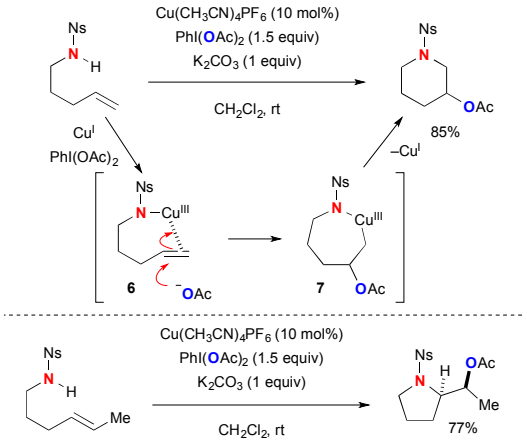
Scheme 3 Aliphatic C–H amination with amidines under Cu-catalyzed-PhI(OAc)$_2$-mediated reaction conditions.

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



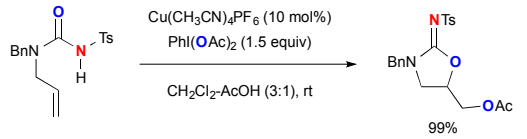
Scheme 4 Cu-catalyzed-PhI(OAc)$_2$-mediated directed sp^2-C–H amination.

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 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 the 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 alkene takes place to afford metallacycle intermediate **7**, in which more substituted carbon is preferentially acetoxylated. Reductive elimination of C–N bond finally furnishes the heterocyclic products.



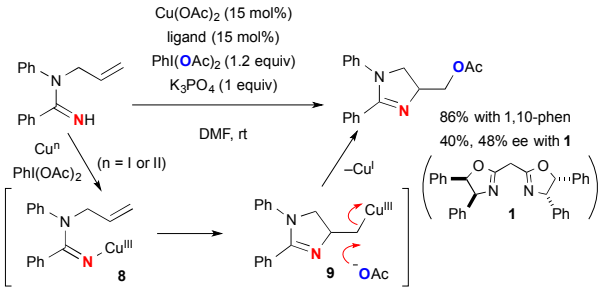
Scheme 5 Cu-catalyzed-PhI(OAc)$_2$-mediated aminoacetoxylation of alkenes.

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



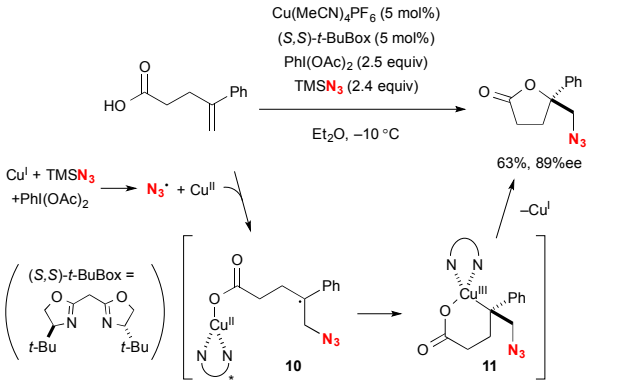
Scheme 6 Cu-catalyzed-PhI(OAc)$_2$-mediated oxyacetoxylation of alkenylureas.

On the other hand, Cu(OAc)$_2$-catalyzed-PhI(OAc)$_2$-mediated reactions of *N*-allylamidines afforded 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 was observed in aminoacetoxylation. This observation implicates that the process might involve aminocupration of alkene by the putative amidinyl copper(III) intermediate **8** *via* an organometallic pathway to form an organocopper(III) intermediate, that is unlike the aliphatic C–H amination of *N*-alkylamidines involving free radical intermediates (Scheme 3). Finally, nucleophilic displacement of the organocopper(III) moiety **9** with acetate ion to give the final product.



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

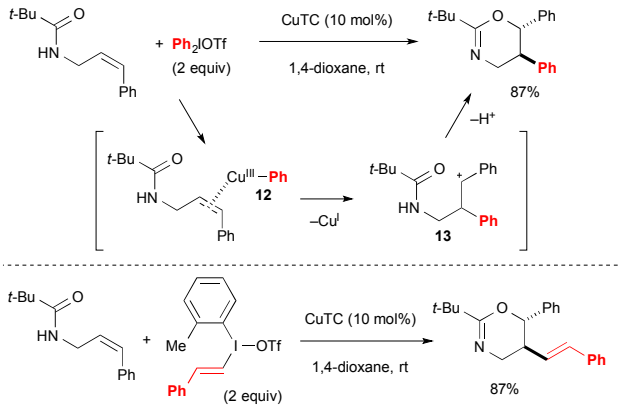
Recently, Buchwald reported Cu-catalyzed enantioselective synthesis of functionalized lactones from alkenylcarboxylic acids through oxyfunctionalization of alkenes as the key step (Scheme 8).[15] For example, oxyazidation was enabled using a catalytic amount of Cu(MeCN)$_4$PF$_6$ with TMSN$_3$ and PhI(OAc)$_2$ (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 alkene to generate tertiary radical **10**, that recombines with intramolecular Cu^{II}-carboxylate moiety in stereoselective fashion with the chiral Box ligand. Finally, C–O reductive elimination from metallacyle **11** gave the lactone product with regeneration of the Cu(I) catalyst.



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

2.2. Diaryliodonium salts [Ar$_2$IX]

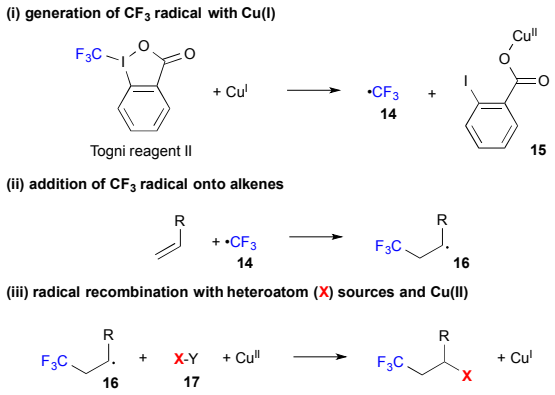
Treatment of Cu(I) complexes with diaryliodonium salts results in formation of aryl-Cu(III) species like **12** in Scheme 9, that could be used for electrophilic activation of alkenes to induce their carbo-functionalization. For example, Gaunt reported that the reaction of *N*-allylamides could afford oxyarylation products in 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]



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

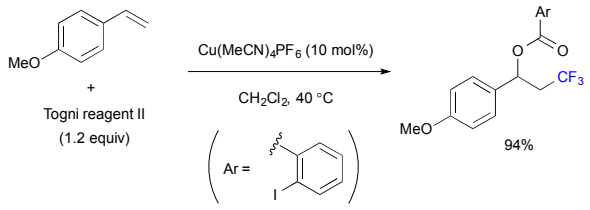
2.3. The Togni reagents

It has been shown that single-electron-reduction of 1-trifluoromethyl-1,2-benziodoxol-3(1H)-one (known as the 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.



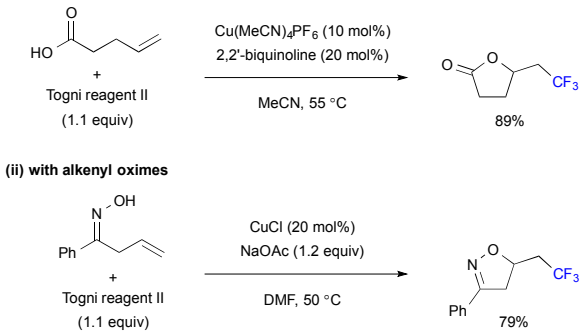
Scheme 10 Cu-catalyzed trifluoromethylation of alkenes with the Tonig reagent

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



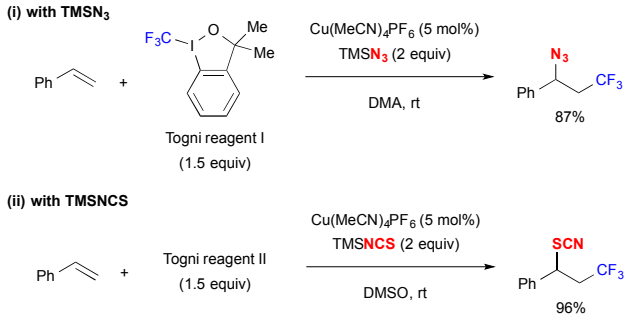
Scheme 11 Cu-catalyzed intermolecular oxytrifluoromethylation

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.



Scheme 12 Cu-catalyzed intramolecular oxytrifluoromethylation

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 the Togni reagent I) provided better yields of the desired azidation products as the reaction with 1,2-benziodoxol-3-one generates 2-iodobenzoyloxylaiton product as the side product.

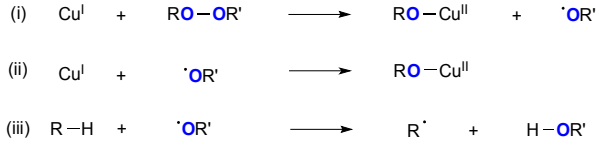


Scheme 13 Cu-catalyzed trifluoromethylazidation and trifluoromethylthiocyanation of alkenes.

3. With Peroxides

Various types of peroxides have been employed as the stoichiometric oxidants and often as the source 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.

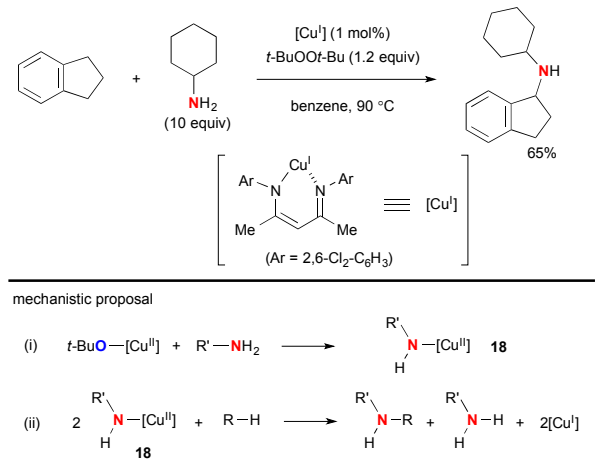
The resulting alkoxy radical could further oxidize Cu(I) species to give another Cu(II) alkoxide (path-ii) or undergo H-radical abstraction from the substrates to form C-radical (path-iii).



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

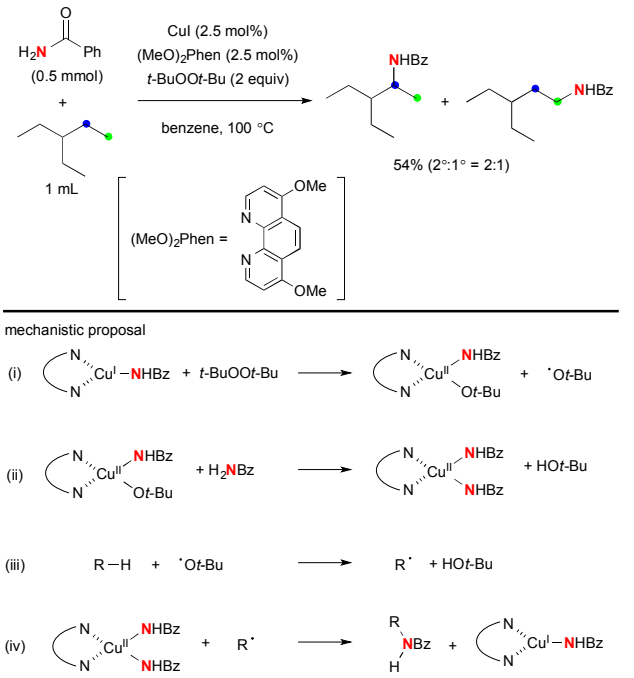
3.1. With di-*t*-butylperoxide (*t*-BuOO*t*-Bu)

Warren reported seminal works 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 its 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.



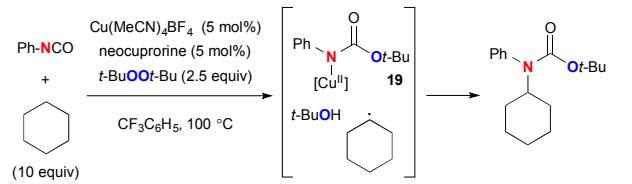
Scheme 15 Cu-catalyzed-*t*-BuOO*t*-Bu-mediated aliphatic C−H amination

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 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 *t*-butoxy radical (path-iii) and radical recombination of the resulting C-radical with transient Cu(II) amidate complexes (path-iv). An analogous ligand-free Cu-catalyzed aliphatic C−H amidation and imidation with *t*-BuOO*t*-Bu was developed independently by Huang and Yu/Cheng.[25]



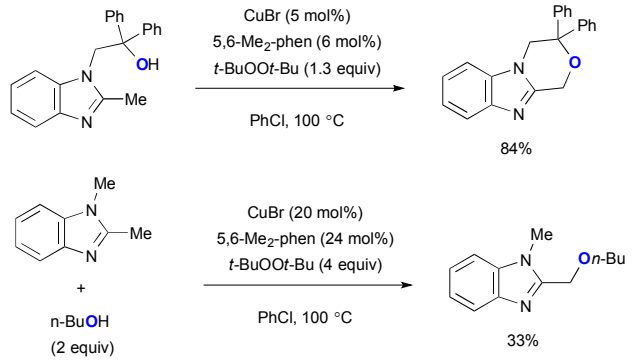
Scheme 16 Cu-catalyzed-*t*-BuOO*t*-Bu-mediated aliphatic C−H amidation

This type of Cu-catalzyed-*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 the 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.



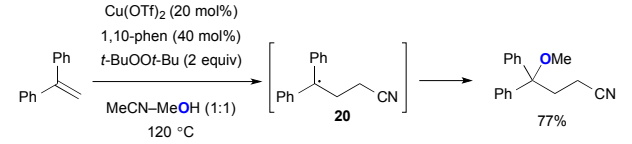
Scheme 17 Cu-catalyzed-*t*-BuOO*t*-Bu-mediated synthesis of tertiary carbamates with isocyanates as the amide source.

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 works in the same system, while the yields of the C−H alkoxylation products were moderate.



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

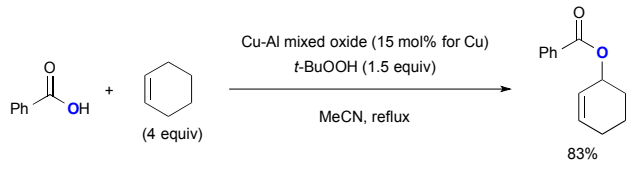
Zhu recently reported carboetherification of aryl alkenes with solvent amounts of acetonitrile and alcohol under Cu-catalzyed- *t*-BuOO*t*-Bu-mediated reaction conditions (Scheme 19).[28] The radical clock experiment implicated that the benzylic radical intermediate **20** is formed by the addition of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



Scheme 19 Cu-catalyzed carboetherification of alkenes

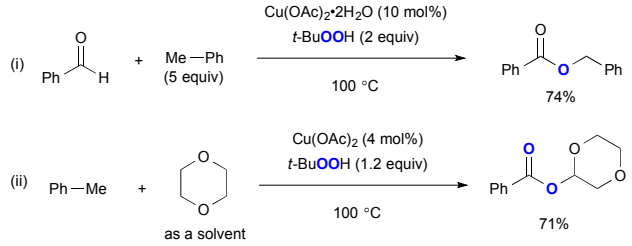
3.2. With *t*-butylhydroperoxide (*t*-BuOOH: TBHP)

t-Butylhydroperoxide (TBHP) exhibits analogous reactivity 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 Cu-Al mixed oxide could be utilized as the heterogeneous catalysis for Kharasch-Sosnovsky type allylic C–H oxygenation with TBHP as the stoichiometric oxidant.[29,30]



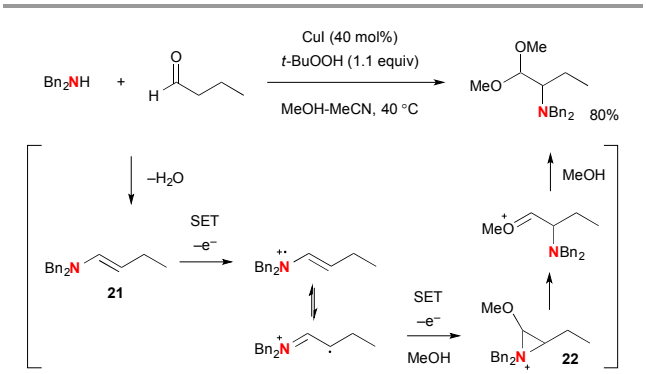
Scheme 20 Cu-catalyzed carboetherification of alkenes

In addition, TBHP uniquely serves as an oxygen source for enhancing 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 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]



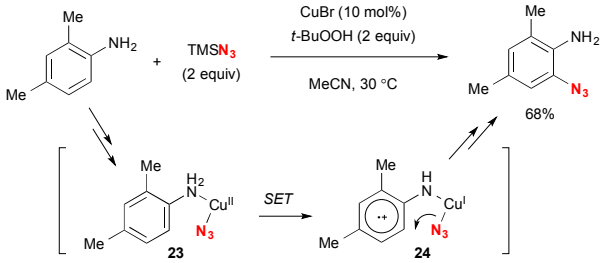
Scheme 21 Cu-catalyzed-TBHP-mediated ester synthesis

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 multi-step sequence including successive two single-electron-oxidation of the 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.



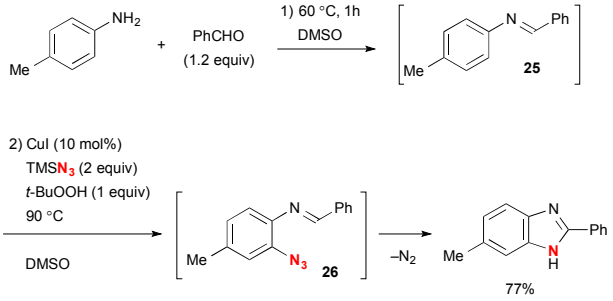
Scheme 22 Cu-catalyzed α-amination of aldehydes

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 in ambient temperature (Scheme 23).[35] The single-electron-oxidation of benzene ring by the higher valent Cu(II) species **23** adjacent to the primary amine moiety followed by azido ion transfer in the cation radical **24** is proposed for the C–H azidation. This is a rare example on the directed *ortho* C–H functionalization of anilines.



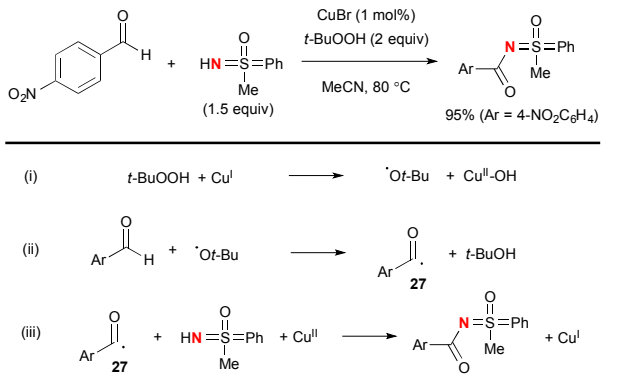
Scheme 23 Cu-catalyzed *ortho*-C–H azidation

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 for the directing group in aromatic C–H oxidation under Cu-catalyzed-TBHP-mediated reaction conditions.[37]



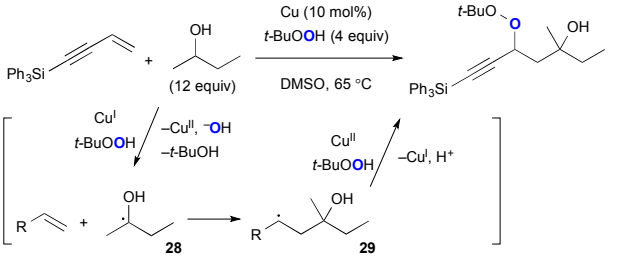
Scheme 24 Cu-catalyzed-*t*-BuOOH-mediated aromatic *ortho*-azidation

Bolm developed Cu-catalyzed oxidative *N*-acylation of sulfoximines with aldehydes (Scheme 25).[38] *t*-Butoxy radical derived from decomposition of TBHP by Cu(I) complexes (Scheme 25-i) could abstract H-radical from aldehydes to generate the corresponding acyl radicals **27** (Scheme 25-ii). The transient acyl radical **27** undergoes radical recombination with sulfoxyimines mediated by higher valent Cu(II) species to give the product along with re-generation of lower valent Cu(I) species (Scheme 25-iii).



Scheme 25 Cu-catalyzed oxidative *N*-acylation of sulfoximines

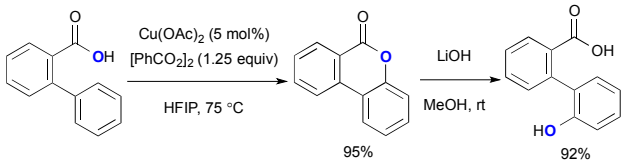
In the presence of Cu(I) complexes, TBHP can serve as the source of *t*-butoxy radical, that mediates H-radical abstraction to give C-radical, whereas TBHP itself can also be introduced as the new oxygen functionality *via* the C–O bond forming process. Loh demonstrated Cu-catalyzed three-components 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 the secondary radicals **29**, that recombine with TBHP mediated by Cu(II) species (Scheme 26).[39] Patel reported analogous Cu-catalyzed three-components coupling of electron-deficient alkenes, cycloalkanes, and TBHP.[40]



Scheme 26 Cu-catalyzed carbooxygenation of alkenes

3.3. With benzoyl peroxide (BPO)

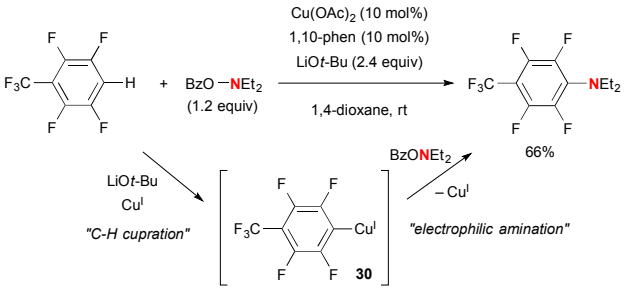
While benzoyl peroxide (BPO) has rarely been utilized as the partner with Cu-catalyzed oxidative molecular transformation, Martin recently reported Cu-catalyzed intramolecular aromatic C–H oxygenation of 2-arylbenzoic acids specifically mediated by BPO as the terminal oxidant (Scheme 27).[41] The reaction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



Scheme 27 Cu-catalyzed aromatic C–H oxygenation

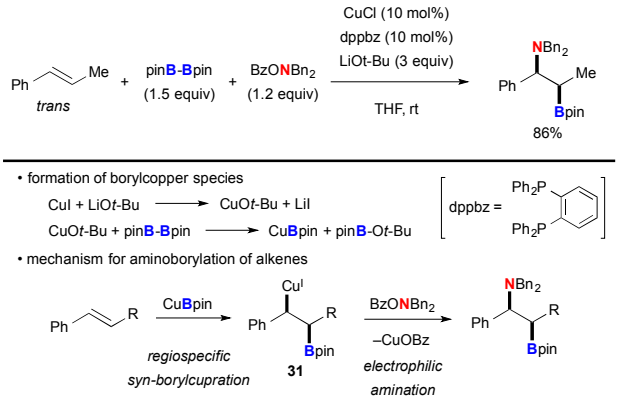
4. With *O*-benzoyl-*N*,*N*-dialkylhydroxylamines

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 could be applied for C2-amination of quinoline-*N*-oxides by Li/Wu.[44]



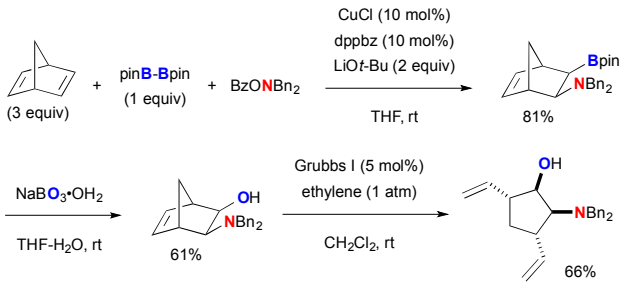
Scheme 28 Cu-catalyzed aromatic C–H amination with hydroxylamines

Hirano/Miura demonstrated the combination of boryl-cupration 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 LiO*t*-Bu resulted in formation of aminoboration product (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.



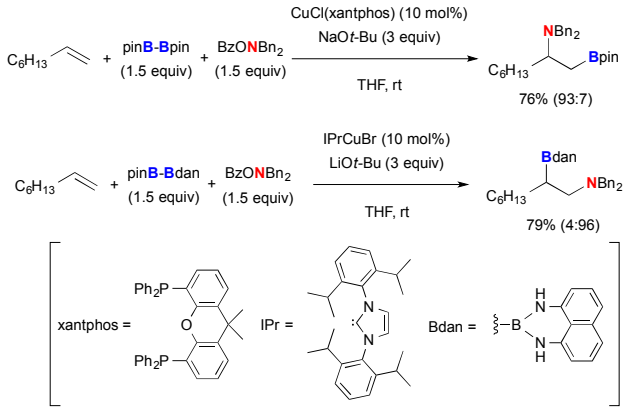
Scheme 29 Cu-catalyzed aminoboration of alkenes

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.



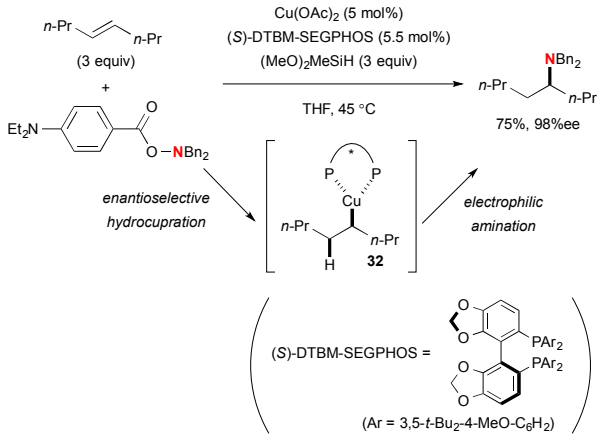
Scheme 30 Cu-catalyzed aminoboration of norbornadiene and further molecular transformation

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



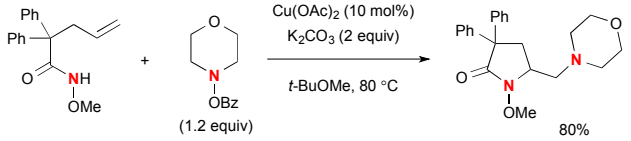
Scheme 31 Cu-catalyzed regiodivergent aminoboration of non-activated terminal alkenes

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 the ligands on copper catalysts is crucial to control the reactions (i.e. to prevent the side reactions such as hydride reduction of hydroxyl amines).



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

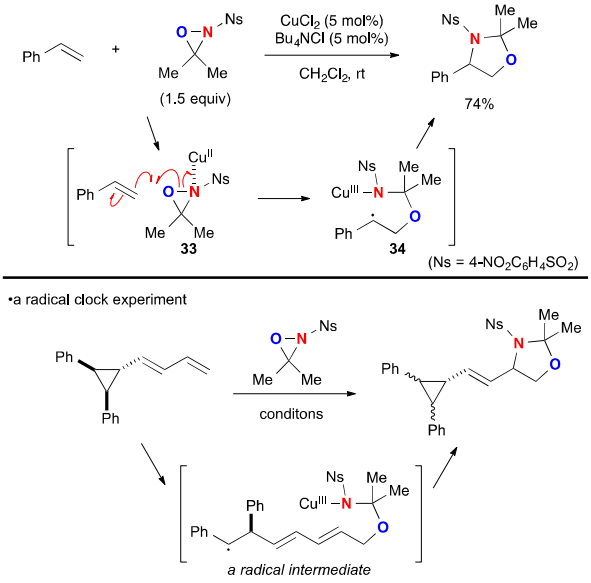
Wang recently developed Cu-catalyzed diamination of alkenes using alkenyl *O*-Me-hydroxamic acids and BzO−NR_2, that afforded functionalized nitrogen-heterocycles (Scheme 33).[53] The process is composed of intramolecular aminocupration of alkenes and subsequent electrophilic amination. As a deuterium-labeling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



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

5. With oxaziridines

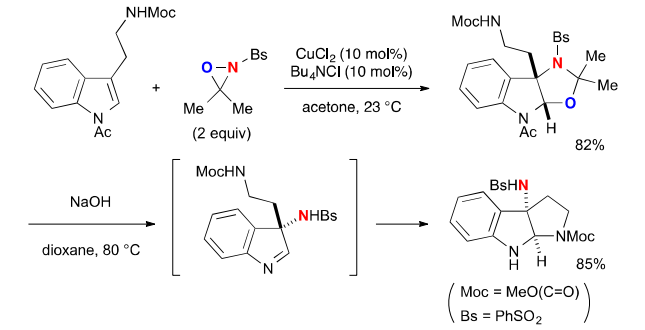
Highly strained three-membered ring oxaziridines work with copper complexes to facilitate aminooxygenation of alkenes. Yoon developed $CuCl_2$-catalyzed aminooxygenation of alkenes with *N*-sulfonyloxaziridines, that could be dramatically facilitated by chloride additives such as Bu_4NCl (Scheme 34).[54] The detailed mechanistic investigation elucidated that Cu(II)-oxaziridine complex **33** undergoes C−O bond forming radical addition onto alkene 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.



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

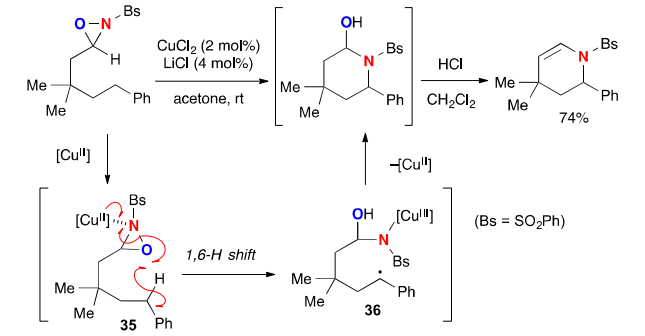
This aminooxygenation strategy with *N*-sulfonyl oxaziridines was capable of functionalizing indoles (Scheme 35).[55] It is worthy to note that the resulting aminal derived

from *N*-acyltryptamine was readily transformed to 3-aminopyrroloindoline by base treatment.



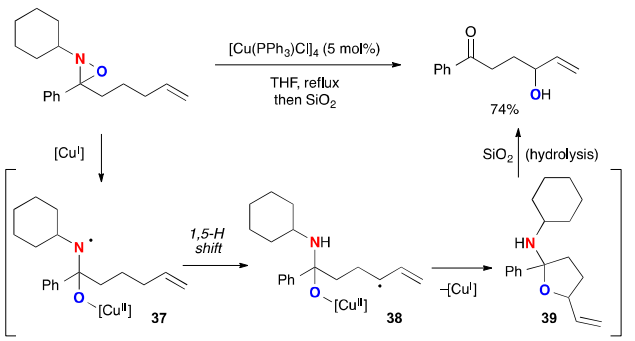
Scheme 35 Cu-catalyzed aminooxygenation of indoles with *N*-sulfonyloxaziridines

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 $CuCl_2$-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.



Scheme 36 Cu(II)-catalyzed C−H amination with N-sulfonyloxaziridines

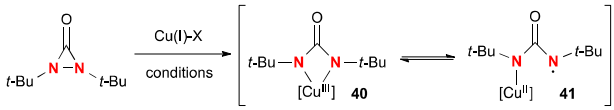
On the other hand, Aubé recently reported Cu(I)-catalyzed allylic sp^3 C−H oxygenation with *N*-alkyl oxaziridines (Scheme 37).[57] This method could oxidize the allylic position *via* the sequence of 1) formation of aminyl radical **37** having a Cu(II)-alkoxide tether through single-electron-reduction of *N*-alkyl oxaziridines by the Cu(I) complex; 2) generation of allylic radical by 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.



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

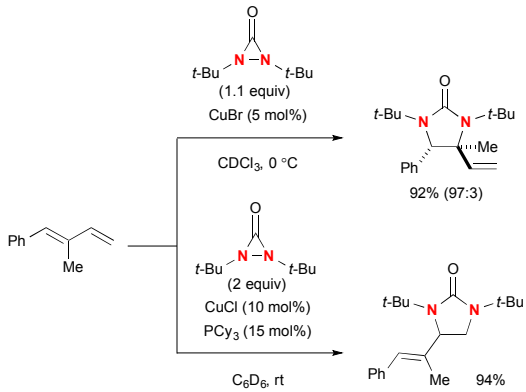
6. With diaziridinone derivatives

Similarly with 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 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).



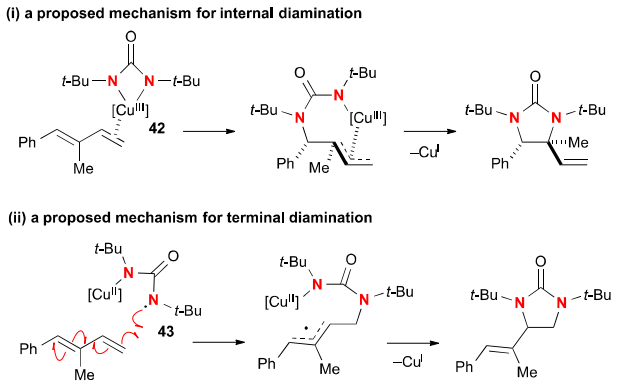
Scheme 38 The reaction of di-*t*-butyldiaziridinone with Cu(I) complexes.

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, the reactions of conjugated dienes and *N*,*N*-di-*t*-butyldiaziridinone with a catalytic amount of CuBr generally undergoes diamination of internal alkenes, whereas terminal alkenes could be functionalized under the CuCl-phosphine ligand catalytic system (Scheme 39).



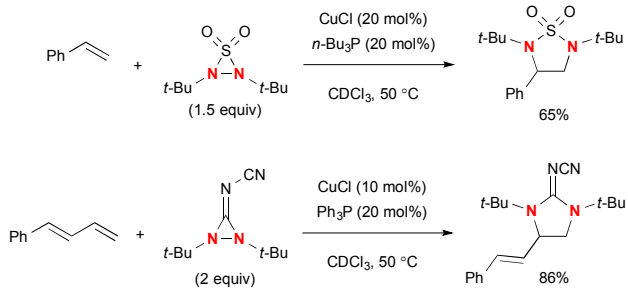
Scheme 39 Regioselectivity in Cu(I)-catalzyed diamination of conjugated dienes with *N*,*N*-di-*t*-butyldiaziridinone.

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 overall process *cis*-diamination (Scheme 40-i). On the other hand, diamination of terminal alkenes involves the 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 N-Cu(II) moiety to afford the diamination product along with regeneration of the Cu(I) catalyst (Scheme 40-ii).



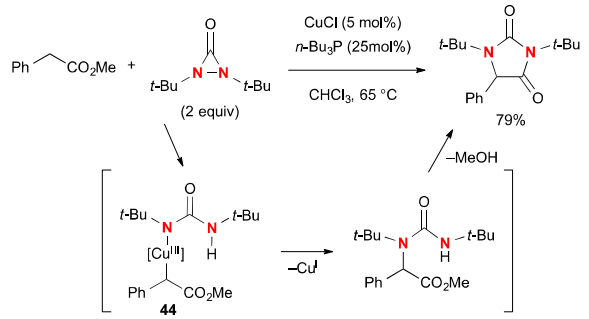
Scheme 40 The proposed reaction mechanisms for diamination

This stepwise radical-mediated diamination of alkenes with *N*,*N*-di-*t*-butyldiaziridinone by 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 were also developed by the CuCl-chiral phosphine[60] and Cu(I)-chiral phosphate systems.[61] Analogously 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).



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

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 provided 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.

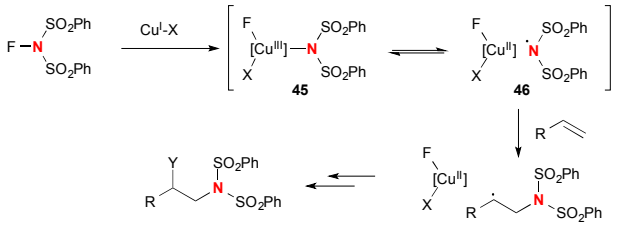


Scheme 42 Synthesis of hydantoins from esters and *N*,*N*-di-*t*-butyldiaziridinone *via* α-amination.

7. With fluoroamine derivatives

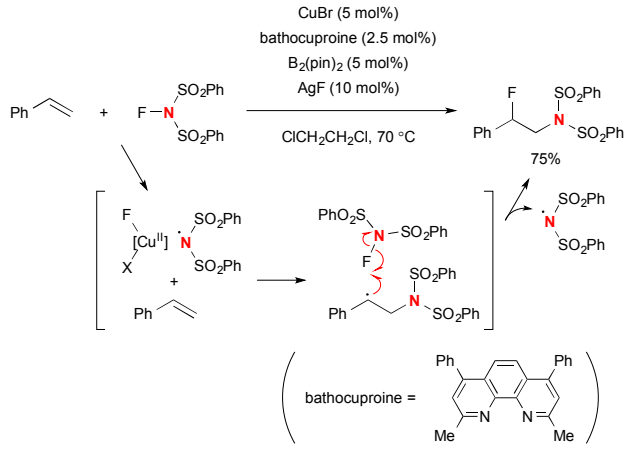
7.1. with *N*-fluorobenzenesulfonimide (NFSI)

A highly reactive oxidant, *N*-fluorobenzenesulfonimide (NFSI) reacts readily with Cu(I) complexes to afford Cu(III)-imide species **45**, that is under 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.



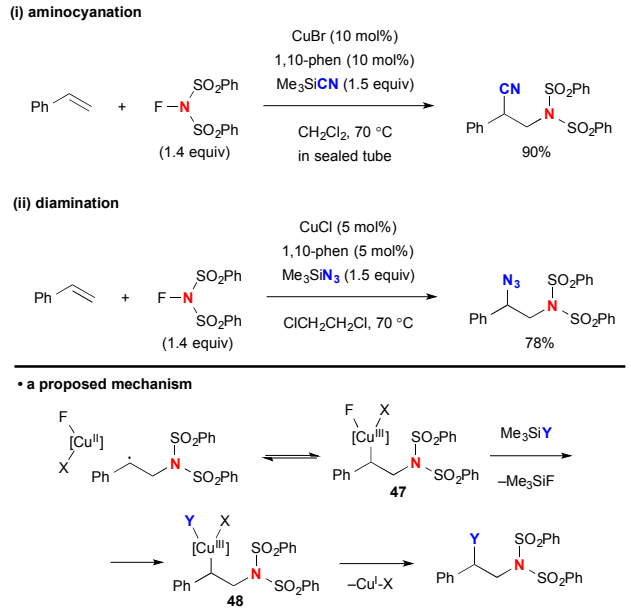
Scheme 43 The reaction of NFSI with Cu(I) complexes for aminofunctionalization of alkenes.

For example, Zhang reported regioselective aminofluorination of styrenes with NFSI under CuBr/bathocuproine-catalyzed reaction conditions (Scheme 44).[65] Use of bis(pinacolato)diborone (B_2pin_2) and AgF as additives was crucial to facilitate the aminofluorination. The DFT calculation 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.



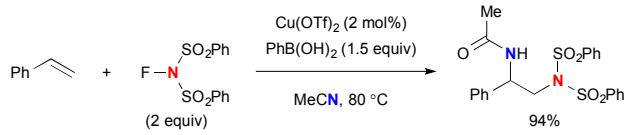
Scheme 44 The reaction of NFSI with Cu(I) complexes for aminofunctionalization of alkenes.

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



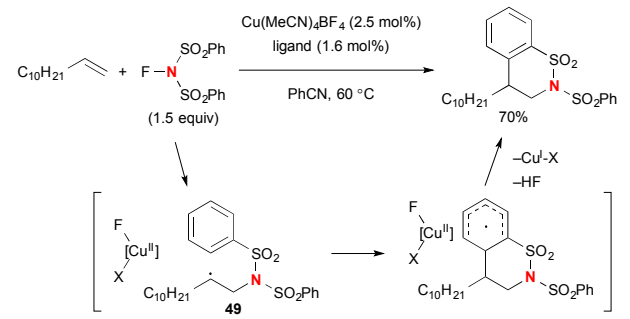
Scheme 45 Cu(I)-catalyzed aminocyanation and diamination of styrene with NFSI.

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]



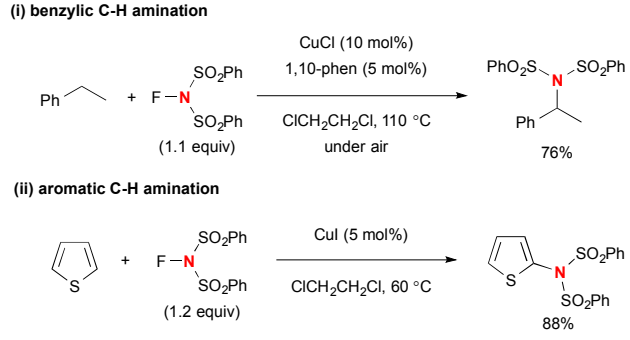
Scheme 46 $Cu(OTf)_2$-catalyzed diamination of styrene with NFSI and acetonitrile.

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]



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

The combination of Cu(I)-catalyst and NFSI is also capable for 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 radical mechanism with the transient sulfonimide radical.

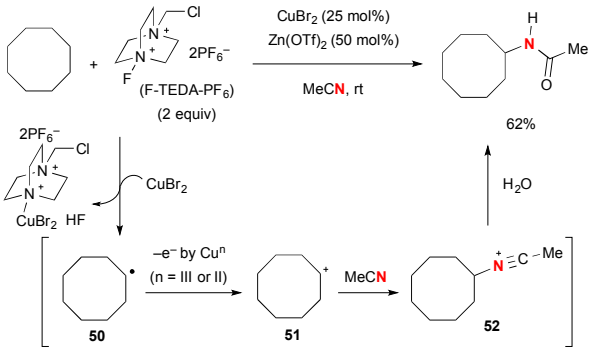


Scheme 48 Cu(I)-catalyzed C–H amination with NFSI.

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

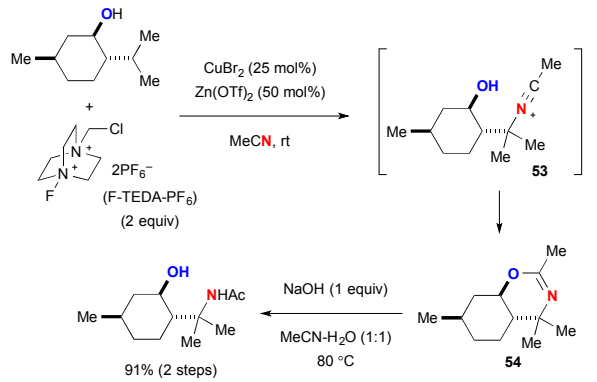
Selectfluor® [1-chloromethyl-4-fluoro-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate] and its

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] whereas these reagents could be utilized as a strong oxidant of Cu(II) and Cu(I) complexes to generate highly reactive Cu(III) species, that can abstract 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 stepwise sequence involving 1) H-radical abstraction; 2) SET oxidation of the resulting C-radical **50** to the carbocation **51**; 3) Ritter-type amination by solvent acetonitrile. The nitrilium ion **52** is finally hydrolyzed to give acetamide products.



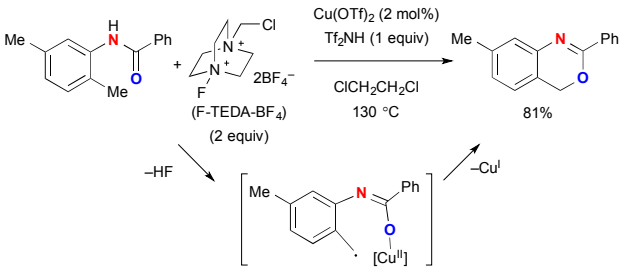
Scheme 49 $CuBr_2$-catalyzed C−H amination of cyclooctane with F-TEDA-PF_6.

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, $CuBr_2$-catalyzed reaction of (–)-menthol with F-TEDA-PF_6 afforded a chemo-selective C−H amination product as 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.



Scheme 50 $CuBr_2$-catalyzed C−H amination of menthol with F-TEDA-PF_6.

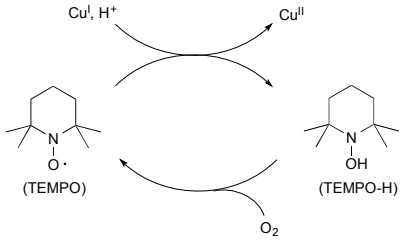
Similar directing effect in chemo-selective aliphatic C−H oxygenation was observed in the reactions of *N*-(2-alkylphenyl)benzamides in the presence of $Cu(OTf)_2$ as the catalyst and F-TEDA-BF_4 (selectfluor®) for synthesis of 4*H*-3,1-benzoxazines through *ortho*-aliphatic C−H oxygenation (Scheme 51).[74] The reactions selectively functionalize the *ortho*-alkyl group presumably *via* H-radical abstraction by the amide-Cu chelate intermediate, whereby aliphatic C−H bonds in the other positions (e.g. *meta*-methyl group) are kept intact.



Scheme 51 $Cu(OTf)_2$-catalyzed C−H oxygenation with F-TEDA-BF_4.

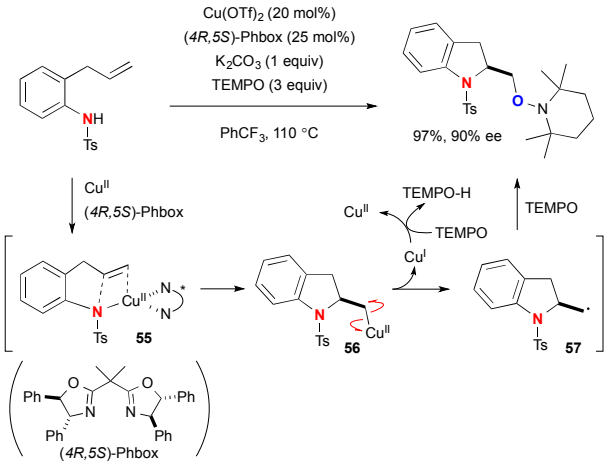
8. With 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)

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]



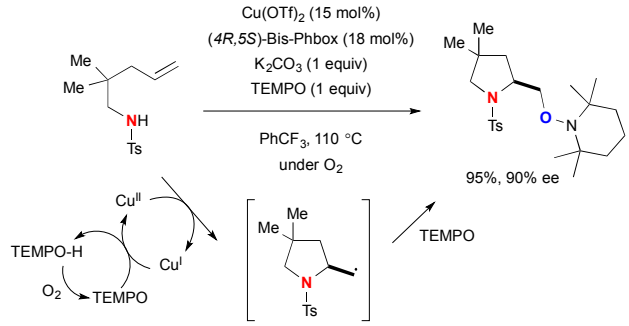
Scheme 52 Oxidation of Cu(I) species to Cu(II) species by TEMPO.

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 in two roles as the external oxygen source and stoichiometric oxidant to make 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 an 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 53 Cu-catalyzed aminooxygenation of alkenes with TEMPO.

In some cases especially when *N*-pentenylsulfonamides were employed, 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.



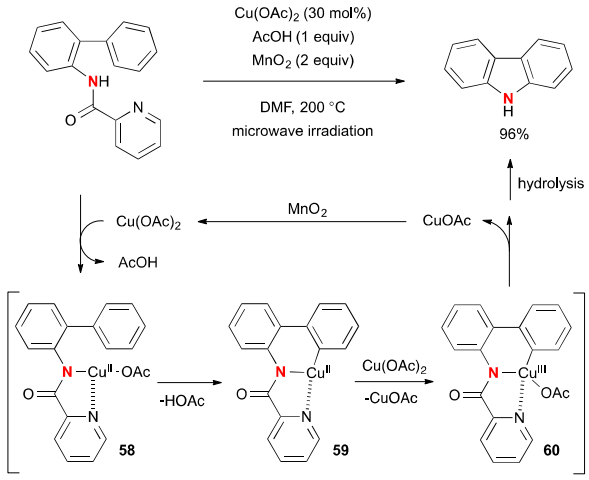
Scheme 54 Cu-catalyzed aminooxygenation of alkenes with TEMPO.

9. With metallic oxidants

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

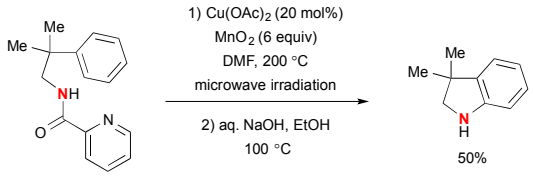
9.1. MnO_2

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 the copper(II)-picolinamide chelate complex **58** to afford organo-Cu(II) intermedaiate **59**. Further redox disproportionation with $Cu(OAc)_2$ forms copper(III) intermediate **60**, and subsequent C−N bond reductive elimination establishes formation of the carbazole product along with generation of lower valent Cu(I) species, that is oxidized by MnO_2 to regenerate Cu(II) catalyst.



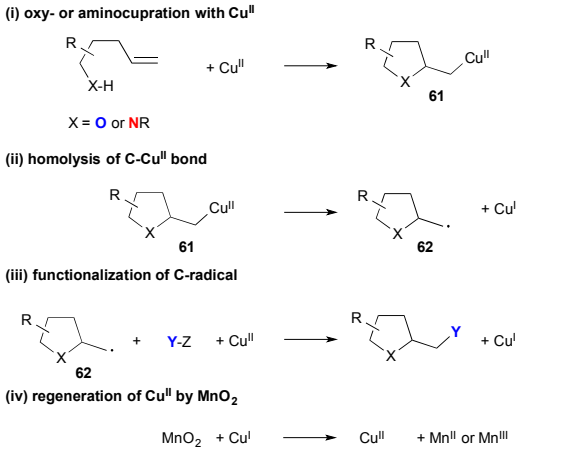
Scheme 55 Cu-catalyzed-MnO_2-mediated aromatic C−H amination.

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



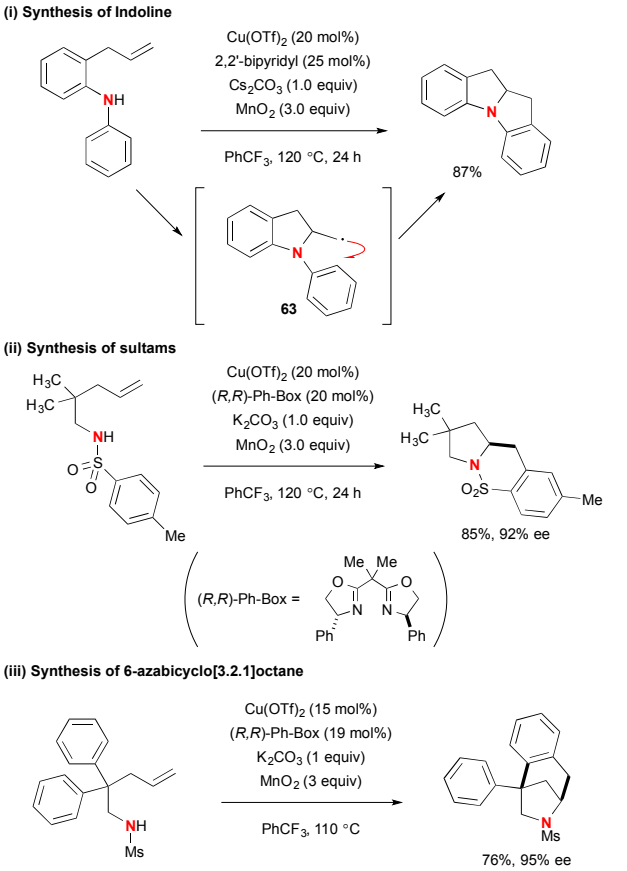
Scheme 56 Cu-catalyzed-MnO_2-mediated aromatic C−H amination.

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 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 lower valent Cu(I) species by MnO_2.



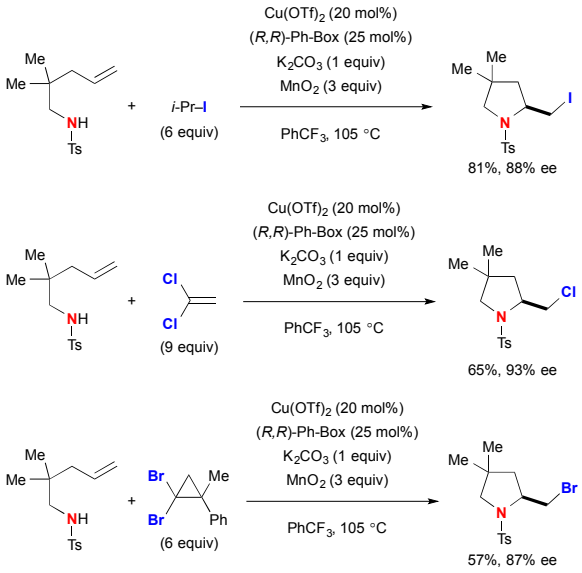
Scheme 57 Cu-catalyzed-MnO_2-mediated oxy- and amino-functionalization of alkenes.

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 alkene (Scheme 58).[80] In this process, the resulting C-radical **63** 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 (*R*,*R*)-Ph-Box ligand for the $Cu(OTf)_2$ catalyst, delivering optically active bicyclic sultams (Scheme 58-ii). On the other hand, the reactions of *N*-mesyl-4-pentenylamines having geminal diaryl moiety at the C2 position under $Cu(OTf)_2$-(*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]



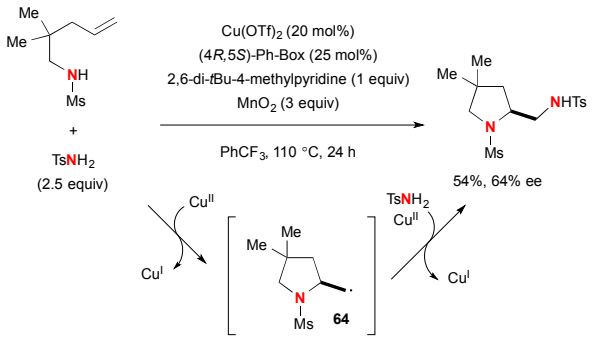
Scheme 58 Cu-catalyzed-MnO_2-mediated carboaminaion of alkenes.

The transient C-radicals generated via aminocupration of *N*-sulfonyl alkenylamines could undergo 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.



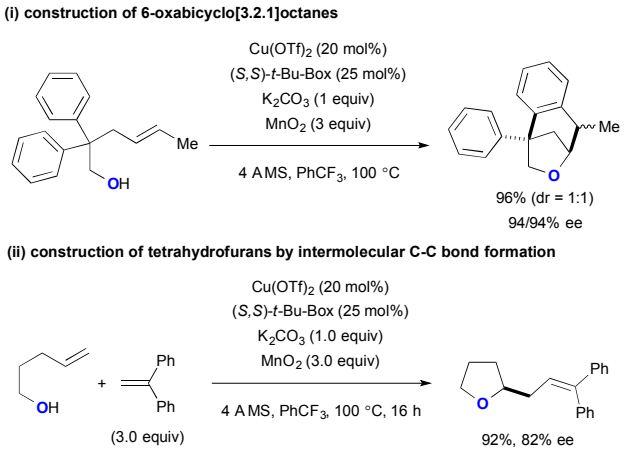
Scheme 59 Cu-catalyzed-MnO_2-mediated-aminohalogenation of alkenes.

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 is enabled by radical recombination of the C-radical **64** with $TsNH_2$ and Cu(II) species.



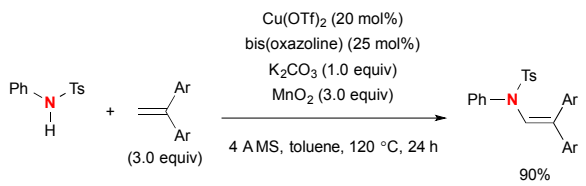
Scheme 60 Cu-catalyzed-MnO_2-mediated diamination of alkenes.

The $Cu(OTf)_2$-catalyzed-MnO_2-mediated reaction conditions are amenable to carboetherification of alkenyl alcohols, in which the second C–C bond formation is possible both in intra- and intermolecular fashion (Scheme 61).[84] Construction of 6-oxabicyclo[3.2.1]octanes was developed from 4-pentenylalcohol with a geminal diaryl moiety at the C2 position via oxycupuration of alkenes followed by intramolecular radical cyclization onto the aryl group (Scheme 61-i). Intermolecular C–C bond formation was also realized with aryl alkenes, in which the transient C-radical undergoes the oxidative Heck-type coupling with aryl alkenes to deliver 2-allyltetrahydrofurans (Scheme 61-ii).



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

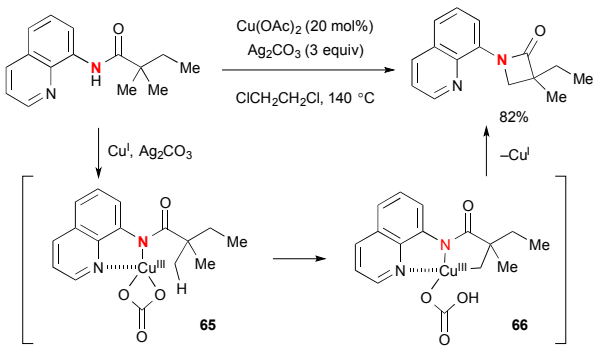
Chemler also reported Cu-catalyzed intermolecular amination of 1,1-disubstited alkenes with *N*-arylsulfonamides in the presence of MnO_2 as a terminal oxidant (Scheme 62).[85] The reactions uniquely afford *N*-aryl enamide products in the *anti*-Malkovnikov fashion.



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

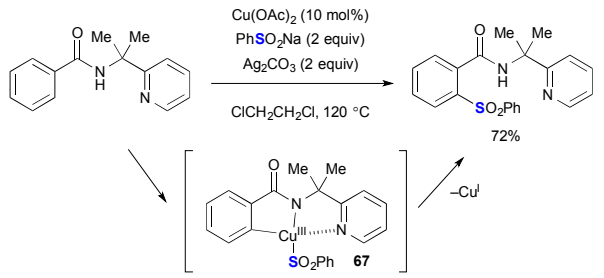
9.2. Ag_2CO_3

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 for working 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 a metallacycle intermediate **66**. Finally, C–N bond forming reductive elimination affords β-lactam along with 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.



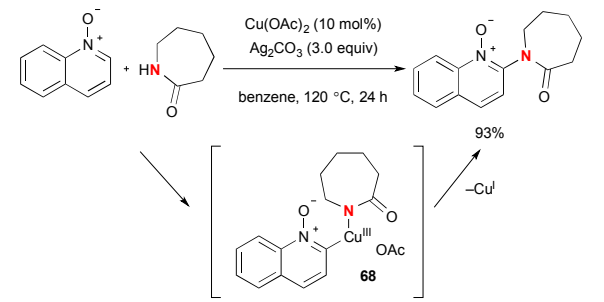
Scheme 63 Cu-catalyzed-Ag_2CO_3-mediated directed sp^3 C–H amidation.

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 concerted metallation-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.



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

Intermolecular sp^2 C−H amidation/amination of quinoline *N*-oxides were 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** in prior to its C−N bond reductive elimination to deliver the final products.



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

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. The Togni reagent II[89] (entry 4) and peroxides (entries 5-7) are potentially explosive so that the reactions with these reagents should need special cares with proper protecting shields.

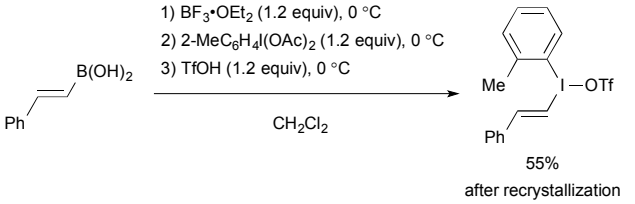
Table 1 A price list of commercially available oxidants

Entry	Oxidant	Price (US$)[a]	CAS No.
1	$PhI(OAc)_2$	21.6 / 5 g	3240-34-4
2	Ph_2IOTf	114 / 1g	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

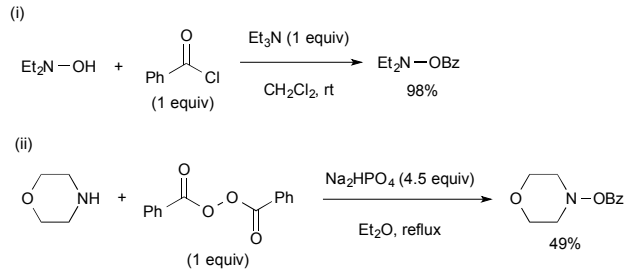
The typical preparation methods of non-commercialized oxidants such as vinyl(aryl)iodonium triflate (section 2.2.), *O*-benzoyl-*N*,*N*-dialkylhydroxylamines (section 4), oxaziridines (section 5), and diaziridinones (section 6) are illustrated in Schemes 66-69, respectively.

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



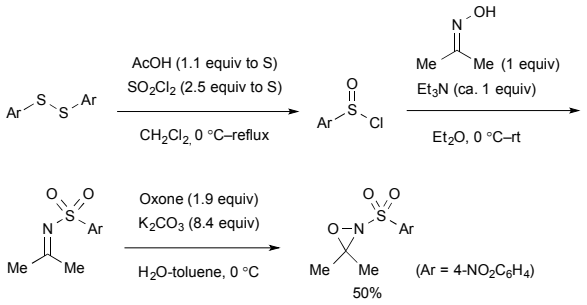
Scheme 66 Preparation of *N*-noxyl-3,3-dimethyloxaziridine.

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



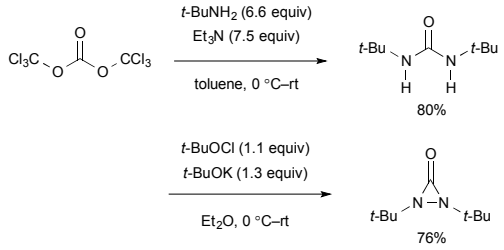
Scheme 67 Preparation of *O*-benzoyl-*N*,*N*-dialkylhydroxylamines.

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]



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

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 dark.



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

11. Conclusions

This review highlighted up-to-date developments on copper-catalyzed (anaerobic) oxidative formation of carbon-heteroatom bonds onto 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-catalzyed 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 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 controls the course of the reaction and improves catalytic turnovers and overall process efficiency. We anticipate copper complexes have inexhaustible potentials as the catalysis to enhance our synthetic capability further.

Acknowledgements

Our co-workers whose names appear in the references are gratefully acknowledged for their intellectual and experimental contributions. These works were supported by funding from Nanyang Technological University and Singapore Ministry of Education (Academic Research Fund Tier 2: MOE2010-T2-1-009 and MOE2012-T2-1-014).

Notes and references

1 For recent selected reviews on transition-metal-catalyzed C−H oxidation, see: (a) J. L. Jeffrey and R. Sarpong, *Chem. Sci*., 2013, **4**, 4092; (b) J. Yamaguchi, A. D. Yamaguchi and K. Itami, *Angew. Chem., Int. Ed.*, 2012, **51**, 8960; (c) D. Y.-K. Chen and S. W. Youn, *Chem. Eur. J.*, 2012, **18**, 9452; (d) M. C. White, *Science,* 2012, **335**, 807; (e) R. T. Gephart III, and T. H. Warren, *Organometallics,* 2012, **31**, 7728; (f) J. L. Roizen, M. E. Harvey and J. Du Bois, *Acc. Chem. Res*., 2012, **45**, 911; (g) T. A. Ramirez, B. Zhao and Y. Shi, *Chem. Soc. Rev*., 2012, **41**, 931; (h) H. M. L. Davies, J. Du Bois and J.-Q. Yu, *Chem. Soc. Rev.,* 2011, **40**, 1855; (i) T., Newhouse and P. S. Baran, *Angew. Chem., Int. Ed.,* 2011, **50**, 3362; (j) J. Du Bois, *Org. Process Res. Dev.,* 2011, **15**, 758; (k) F. Collet, C. Lescot and P. Dauban, *Chem. Soc. Rev.,* 2011, **40**, 1926; (l) T. W. Lyons and M. S. Sanford, *Chem. Rev.,* 2010, **110**, 1147; (m) F. Collet, R. H. Dodd and P. Dauban, *Chem. Commun.*, 2009, 5061; (n) M. M. Díaz-Requejo and P. J. Pérez, *Chem. Rev.*, 2008, **108**, 3379.

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