Copper(II) Triflate in Organic Synthesis

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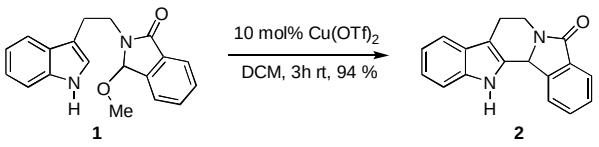
In contemporary organic synthesis, Lewis acid catalyzed reactions have gained increasing interest because of the unique reactivity and selectivity that can be achieved under mild conditions [1]. During the past few years, the outstanding potential of a variety of metal triflates (trifluoromethylsulfonates) has been discovered, thus triggering much research endeavour. The triflate anion is both weakly nucleophilic and coordinating, rendering the metal counter ion more cationic and thus a stronger Lewis acid. In many cases, solely exchanging the anion from a halide to a triflate makes it possible to promote the desired reaction or improve turnover, reaction time and yield. In addition, the solubility of catalyst may also be enhanced. Among the various metal triflates, copper(II) triflate [$Cu(OTf)_2$] plays an indispensable role in the discovery of novel and improved reaction processes. $Cu(OTf)_2$, has long been known to promote elimination reactions, oxidative coupling reactions, and reactions of diazo compounds [2], but its full synthetic capacity has long remained unveiled. Recently, copper(II) triflate has been used in a battery of extended applications, including numerous examples where $Cu(OTf)_2$ overcomes the limitations of other *en vogue* metal triflates such as $Sc(OTf)_3$ and $Yb(OTf)_3$ [3]. Readily handled on the benchtop, $Cu(OTf)_2$ may also be an *in situ* catalyst precursor for use with a variety of chiral ligands, offering a great potential for asymmetric catalysis. In addition, a salient feature of copper(II) triflate is its inherent stability in aqueous solvents, which opens the door to environmentally chemistry. In this review, the unique properties of copper(II) triflate and some copper(II) triflate derived asymmetric catalysts shall be highlighted.

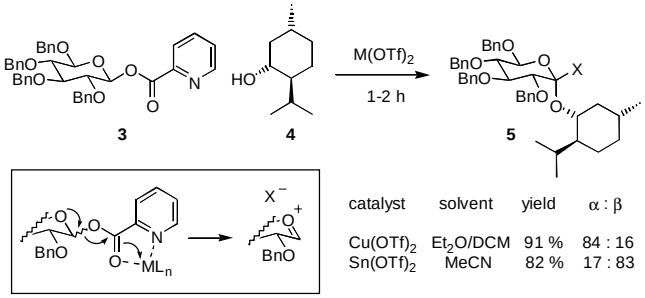
1. Alkylations and Acylations

Numerous Lewis acids are known that effectively catalyze Friedel-Crafts and related reactions, however a shortcoming of most reagents is associated with quenching the reaction; catalysts cannot be reused, causing problems with waste disposal. Like many rare earth salts, copper(II) triflate has the advantage of being recyclable from aqueous solutions after acylation and alkylation reactions. When compared with other Lewis acids, it was found to be the most successful catalyst for generating acyliminium ions in acylaminoalkylation reactions. As an example, in the presence of a catalytic amount of $Cu(OTf)_2$, α-methoxyisoindolone **1** gave β-carboline derivative **2** in 94% yield at ambient temperatures [4]. Singh *et al*. reported that $Cu(OTf)_2$ is also a highly efficient catalyst (2 mol%) for acylation of alcohols, thiols and amines using acetic anhydride/acetate at room temperature. Even hindered substrates and secondary alcohols can be efficiently acylated, albeit at slightly elevated temperatures [5].



Scheme 1 Copper(II) triflate mediated acylaminoalkylation

Copper(II) triflate mediated alkylations have also been successfully applied in carbohydrate chemistry. Promoted by $Cu(OTf)_2$, a variety of alcohols and sugars have been glycosylated with glycosyl 2-pyridinecarboxylate **3**. The reaction mechanism is based on remote activation, initiated by a bidentate coordination of the pyridine moiety of **3** to Cu(II), which results in a generation of a reactive oxonium species. While copper(II) triflate generally afford products with high α-selectivity, $Sn(OTf)_2$ complements the reaction by providing a route to β-glycosides (Scheme 2) [6].



Scheme 2 Remote activation for glycosylation

Copper(II) triflate catalyzed ring opening of epoxides, such as **6**, with amines gives rise to β-amino alcohols, an important class of organic compounds, especially in medicinal

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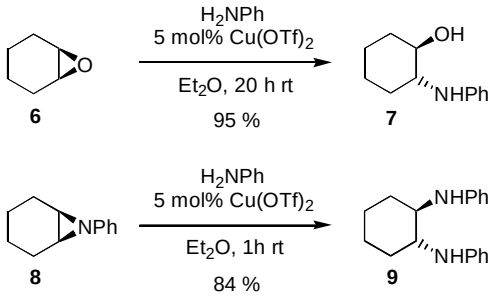
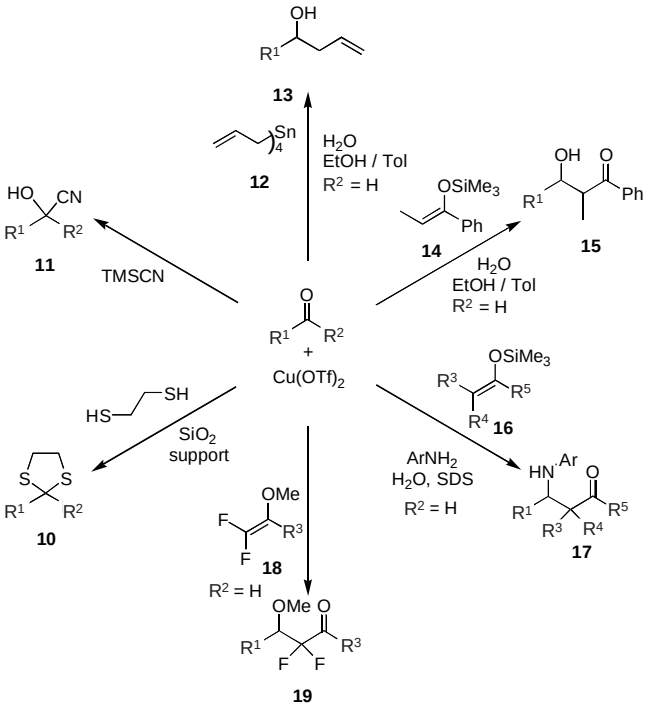
chemistry. The use of $Cu(OTf)_2$ not only provides good to excellent yields, but also overcomes the limitations of previously known catalysts that failed to promote ring opening with deactivated aromatic amines [7]. Likewise it has been reported that in the presence of 5 mol% $Cu(OTf)_2$, even unactivated aziridines, such as **8**, could be opened with aromatic amines under very mild conditions (Scheme 3) [8]. With suitable ligands, an asymmetric version of the reaction is targeted, providing valuable nonracemic amino alcohols and diamines. Interestingly, as a result of the azaphilic properties of $Cu(OTf)_2$, *N*-acylaziridines undergo oxazoline rearrangement giving access to *syn*-configurated amino alcohols [9].



Scheme 3 Ring-opening of epoxides and aziridines

2. Carbonyl Reactions and Michael Additions

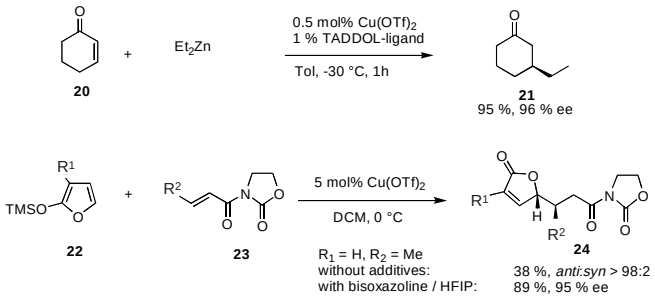
Recently, copper(II) triflate has found a variety of highly useful applications in carbonyl chemistry, as displayed in scheme 4. Singh *et al*. reported an unprecedented method for thioacetylation of aldehydes and ketones in a solvent free condition. Simple mixing of the carbonyl compound with ethanedithiol and SiO_2 – supported $Cu(OTf)_2$ at ambient temperatures provided the corresponding thioacetal in excellent yields (75–98%) [10]. Copper(II) triflate was also found to effectively catalyze trimethylsilyl cyanide addition to aromatic and aliphatic aldehydes and even aromatic ketones. Although a variety of Lewis acids are known for cyanohydrin formation, $Cu(OTf)_2$ is more versatile and moreover has great potential for extension into an asymmetric version of this reaction [11]. In this context, Yamamoto *et al*. explored a new catalytic enantio- and diastereoselective Mukayama aldol reaction with tin enolates and aldehydes using a chiral pybox copper triflate complex [12]. Several unique properties of copper(II) triflate in aldol and allylation reactions in aqueous media were found by Kobayashi *et al*. Good *syn* selectivity was observed when the reaction of silyl enol ether **14** with aldehydes was carried out in toluene–ethanol-water, and the catalyst could be recovered quantitatively. In addition, it was observed that aldehydes are allylated with tetraallyltin **12** in the presence of a catalytic amount (5–20 mol%) of $Cu(OTf)_2$ in toluene–ethanol-water [13]. An amazing example of this transformation is the copper(II) triflate mediated allylation of unprotected 2-deoxy-*D*-ribose in aqueous medium, yielding 75% of the alkylated product [13]. Copper(II) triflate catalysis also offers an environmentally friendly version of the Mannich reaction, one of the most useful methods for the synthesis of β-amino ketones and esters **17**, which could be carried out in water without using any organic solvents. The reaction takes place in hydrophobic micellar systems formed by SDS in water, in which copper triflate (5–10 mol%) catalyzes the imination of aldehydes, prior to alkylation of the resulting imines with hydrophobic silyl enolates **16** (76–86%). With a wide range of substrates the three component coupling proceeds without side reactions, while similar reactions in organic solvents sometimes tend to form deamination products [14]. For the preparation of α-amino ketones, copper(II) triflate and azo diester compounds may be used to aminate silyl enol ethers [15]. α,α-Difluoro carbonyls **19** represent valuable compounds in medicinal chemistry due to their unique properties, but their synthesis is often hampered by the *in situ* generation of unstable intermediates such as fluorinated metal enolates or silyl enol ethers. Difluorovinyl methyl ethers **18**, however, are readily obtainable and stable, but less reactive in carbonyl reactions. With copper(II) triflate as Lewis catalyst, this drawback can be circumvented and *O*-alkylated aldol-type products **19** are readily obtained [16].



Scheme 4 Copper(II) triflate catalyzed reactions of carbonyl compounds

Much effort has been devoted to the asymmetric conjugate addition of organocopper reagents, derived from Grignard or diorgano zinc reagents, to enones. Although for a long time CuI was used as a source of the reactive organocopper intermediate, it was found that $Cu(OTf)_2$ is a superior catalyst, and that addition of trivalent phosphorous ligands had an accelerating effect [17]. Alexakis *et al*. revealed that 0.5% of copper catalyst and 1% of TADDOL phosphorous ligand were sufficient for obtaining conjugate adduct **21** in high yield (95%) with excellent enantiomeric excess (96% *ee*) [18]. The chiral organocopper approach using copper(II) triflate *in situ* has found many applications [19], culminating in an unprecedented asymmetric Michael addition of zincorganyls to α,β–

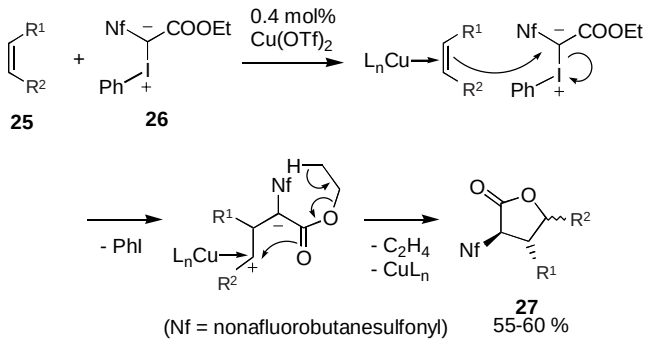
unsaturated lactones and esters [20]. Copper(II) triflate was also used in the first enantioselective Michael addition of 2-trimethylsilyloxyfuranes **22** to oxazolidinone enoates **23**, providing *anti*-**24** in 89% yield and 95% *ee*. As demonstrated by Katsuki and coworkers, this elegant conjugate addition is a convenient pathway to butenolides such as **24**, which exist as subunits of a series of natural products (Scheme 5) [21].



Scheme 5 Asymmetric Michael reactions

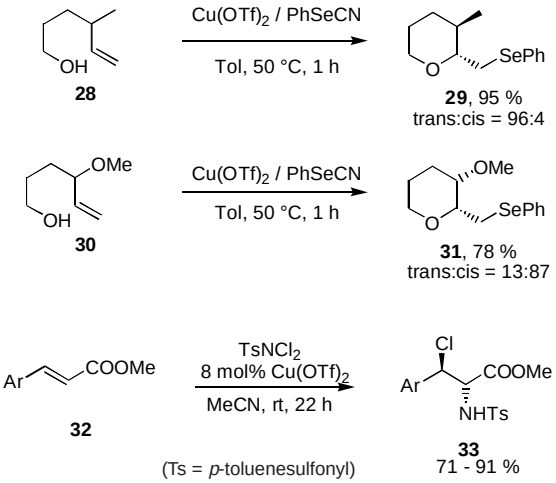
3. Electrophilic Additions

Besides being an excellent catalyst for reactions of carbonyls, copper(II) triflate is also well suited for activation of olefins. The soft Lewis acid catalyst forms electron rich Cu(I)-olefin-π-complexes that profoundly enhance the nucleophilic property of olefins. Hanack *et al*. reported that nonaflyl sulfonium ylide **26** readily attacks a preformed complex of alkene **25** and $Cu(OTf)_2$ with elimination of iodobenzene. The carbonyl oxygen substitutes the copper catalyst upon lactonization and subsequent elimination of ethene from the ethyl ester moiety (Scheme 6). The α-substituted γ-lactones **27** yielded are important intermediates in the synthesis of natural compounds [22].



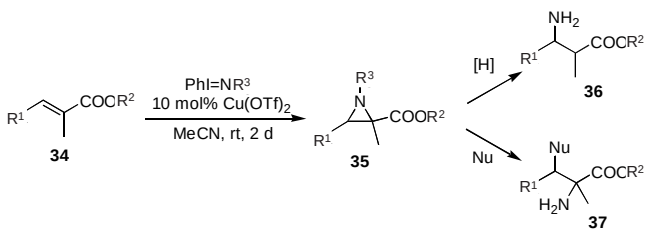
Scheme 6 Olefin activation by means of copper(II) triflate; synthesis of γ-lactones

In contrast, seleniumorganyls can be activated by $Cu(OTf)_2$ to form highly electrophilic organoselenium copper complexes that easily undergo electrophilic additions to double bonds. A reagent derived from phenyl selenocyanate and $Cu(OTf)_2$ has been successfully applied to a regio- and stereoselective cyclization of unsaturated alcohols **28** and **30**, giving cyclic ethers **29** and **31**, respectively. The stereochemical outcome is dominated by steric repulsion (*trans*-**29** predominating) or electronic attraction (*cis*-**31** predominating) between the allylic substituent and Se in cationic seleniranium intermediates (Scheme 7) [23]. Accordingly, a bridged chloronium ion is anticipated in a $Cu(OTf)_2$ catalyzed aminochlorination process. With *N*,*N*-dichloro-4-toluenesulfonamide as an oxidative nitrogen source, cinnamate esters **32** are regio- and stereoselectively aminated, leading to versatile *trans*-haloamine building blocks **33** in good to excellent yields (Scheme 7). An asymmetric process is under investigation [24].



Scheme 7 Copper(II) triflate promoted electrophilic additions to olefins

It is well known that copper-catalysis is advantageous for the preparation of cyclopropyl key structures of organic compounds. Numerous protocols for asymmetric cyclopropanation using copper catalysts with chiral and achiral nitrogen ligands have been published over the last two decades [25]. While Cu(I) catalysts are most abundantly employed, the use of $Cu(OTf)_2$ in the presence of a reducing activator such as phenyl hydrazine offers advantages, such as benchtop handling [25]. Evans and coworkers discovered that $Cu(OTf)_2$ is an efficient catalyst for the analogous olefin aziridination, and determined the oxidation state of the active catalyst as Cu(II). With catalytic copper(II) triflate and tosylated phenyliodinanes as nitrene precursors, aziridines are conveniently prepared in high yield, leading to valuable precursors for a variety of nitrogen compounds (*vide supra*) [26]. Recently, the Evans aziridination has been accomplished with substituted cinnamates **34**. The aziridine carboxylates **35** obtained may be trans-

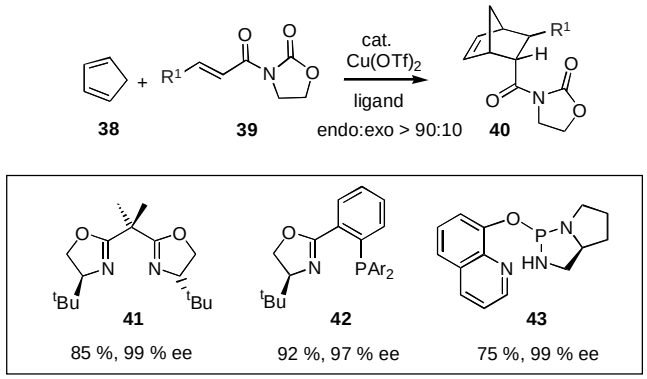


Scheme 8 Copper(II) triflate catalyzed aziridination

formed into α-substituted β-amino acids **36** and α,α-disubstituted amino acids **37**, respectively (Scheme 8) [27]. The latter serve as valuable source of intermediates especially for making amides resistant to enzymatic degradation. It should be mentioned that the copper(II) triflate catalyzed reaction of imines with ethyl diazoacetate is an optional route for the synthesis of aziridines [28].

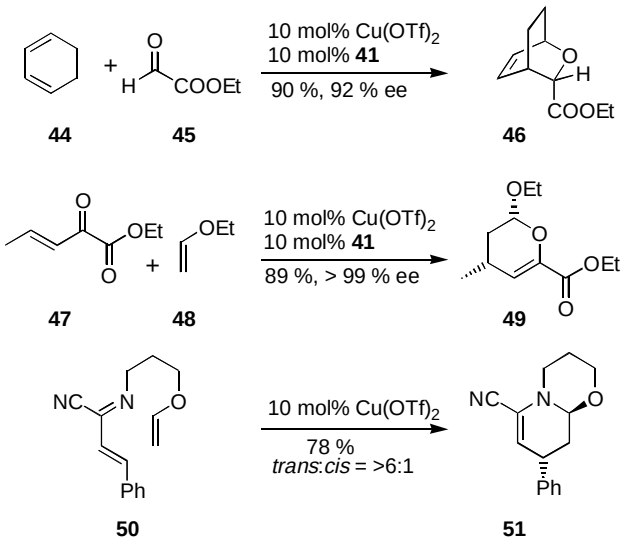
4. Cycloadditions

The Diels–Alder reaction is one of the most fundamental reactions for the preparation of both carbo- and heterocycles. This utility is unambiguously enhanced by the use of Lewis acid catalysts such as copper(II) triflate and its complexes, which both render these cycloadditions possible at lower temperatures and with shorter reaction times. In addition, both regio- and stereoselectivity may be significantly improved. For example, $Cu(OTf)_2$ complexes of C_2-symmetric bisoxazoline **41** (Evans *et al*.) [29], phosphino-oxazoline ligand **42** (Helmchen and Sagasser) [30] and quinoline-phosphine ligand **43** (Buono *et al*.) [31] are effective chiral Lewis acids that catalyze Diels–Alder additions of 3-acryloyl-1,3-oxazolidinones (**39**) with cyclopentadiene (**38**) to give adduct **40** in very good yields (75–92%) and with excellent enantioselectivities (up to 99% *ee*, scheme 9) [32–34].



Scheme 9 Asymmetric Diels–Alder reaction

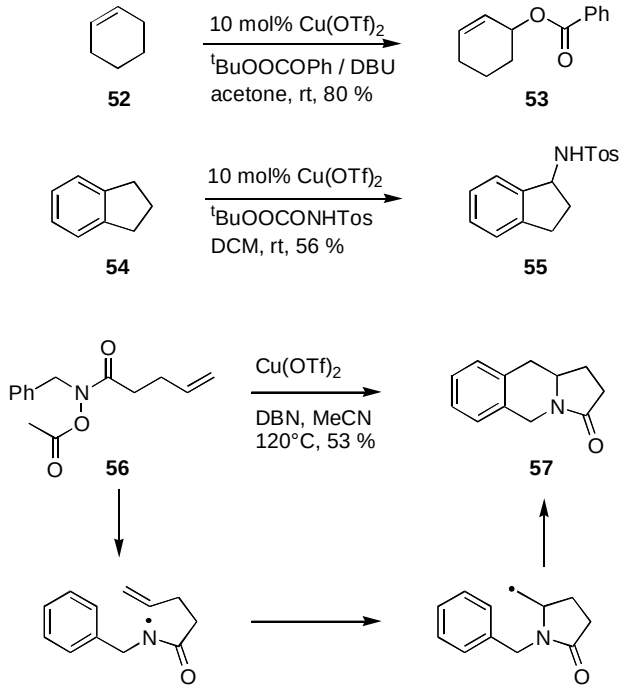
The great synthetic potential of the Diels–Alder reaction is augmented by employing hetero dienes and dienophiles, which provide a direct and convergent strategy for the construction of a variety of heterocyclic compounds. Jorgensen and coworkers have explored copper(II) triflate catalyzed asymmetric *oxa* Diels–Alder reactions utilizing chiral bisoxazoline ligands. For example, cyclohexa-1,3-diene (**44**) reacts with ethyl glyoxylate **45** to give adduct **46**, which can be easily transformed into a useful chiral lactone building block [32]. In a similar $Cu(OTf)_2$ catalyzed [4+2] cycloaddition with inverse electron demand, adducts of α,β-unsaturated α-keto esters **47** and electron rich alkenes **48** are obtained in excellent yield and optical purity (> 99 % *ee*). Substituted dihydropyrans such as **49** are appreciated as excellent precursors for synthesis of carbohydrates [35]. Asymmetric copper(II) catalyzed aza and *thia* Diels–Alder reactions also proved to be synthetically useful, giving convenient access to *N*- and *S*-heterocyclic compounds [36, 37]. The intramolecular cycloaddition of 2-cyano-1-azadiene **50** represents an unprecedented example of a metal catalyzed 1-azadiene Diels–Alder reaction. While under thermal conditions partial degradation of the fragile system was observed, with $Cu(OTf)_2$, the highly versatile compound **51** for the construction of a wide range of alkaloids was readily accomplished (Scheme 10) [38]. Copper(II) triflate/bisoxazoline complexes have also been successfully applied to 1,3-dipolar cycloadditions forming isoazolidine adducts [39].



Scheme 10 Hetero Diels–Alder reactions catalytic in $Cu(OTf)_2$

5. Radical Reactions

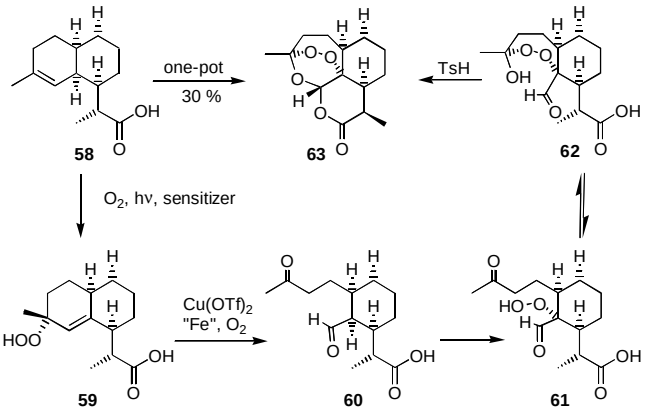
With both the ability of expanding its coordination sphere by one and promoting single electron transfers, the use of copper(II) triflate in radical reactions is an attractive option. $Cu(OTf)_2$ proves to be beneficial for atom transfer radical polymerization [40], and many applications in organic synthesis have been established. For example, in the Kharash reaction allylic C–H bonds are functionalized by means of peroxyesters and a catalytic amount of Cu(I) salts. As a drawback, this highly useful transformation is sluggish and requires activation temperatures of around 80–120 °C. Singh *et al*. found that the treatment of cyclic olefins with *tert*-butyl perbenzoate in the presence of a complex of copper(II) triflate and DBU or DBN (10 mol%) made the reaction feasible at ambient temperatures, providing allylic benzoates **53** in up to 80% yield [41]. In view of the importance of homochiral allylic alcohols in asymmetric synthesis, a variety of chiral chelating ligands have been explored [42]. For cyclic olefins, copper (II) triflate in the presence of a chiral trisoxazoline ligand developed by Katsuki *et al*., turned out to be most successful, giving enantioselectivities up to 93% *ee* [43]. As an extension of this method, benzylic amination with *tert*-butyl *N*-tosyl peroxycarbamate has also been explored, but unfortunately the enantioselectivity of the asymmetric amination was poor (Scheme 11) [45].



Scheme 11 Copper(II) triflate mediated radical reactions

Besides being capable of catalyzing allylic oxidations, the $Cu(OTf)_2$/DBN system was also found to promote a tandem cyclization of amidyl radicals derived from hydroxamic acid derivatives **56**. In a single step a tricyclic framework **57**, prevalent in the lycorane family of alkaloids was furnished (Scheme 11) [45]. Other synthetically useful applications include the $Cu(OTf)_2$ promoted photooxidative cleavage of cyclic olefins providing ω-cyano ketones [46]. Fatty acid hydroperoxides are converted into hydroperoxydioxolanes with oxygen and $Cu(OTf)_2$ [47]. As a highlight, copper(II) triflate played a crucial role in the semisynthesis of trioxane qinghaosu **63**, which is known as highly active antimalarial compound for treatment of chloroquine-resistant falciparium malaria. Haynes, Vonwiller and coworkers demonstrated that treatment of hydroperoxide **59**, obtained by photooxidation of naturally occurring qinghao acid **58**, with catalytic $Cu(OTf)_2$ under an oxygen atmosphere results in a novel cleavage-oxygenation process, providing an equilibrium mixture of the ketoaldehyde **61** and peroxyhemiacetal **62**. This mixture is cleanly convertable into qinghaosu **63**. Under optimized conditions, qinghaosu **63** and a variety of structurally related compounds were prepared in a one-pot, biomimetic process in >30% directly from qinghao acid **58** (Scheme 12) [47].

In conclusion, it is obvious that copper(II) triflate is a significant and versatile reagent in contemporary organic chemistry. Mild, efficient and easy to carry out procedures with this unique Lewis acid provide some remarkable new chemistry. Due to its stability in aqueous media, $Cu(OTf)_2$ contributes to efficient catalyst recycling and thus to the evolution of benign chemistry. The most fundamentally import aspect of $Cu(OTf)_2$ chemistry is the ability to incorporate the reagent into chiral catalysts, in which $Cu(OTf)_2$ remains an integral component of the active complex, permitting entry to a multitude of asymmetric reaction processes. Since the full potential of copper(II) triflate in organic synthesis still remains to be explored, further investigations should yield many exciting contributions to this field.



Scheme 12 One-pot synthesis of qinghaosu

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