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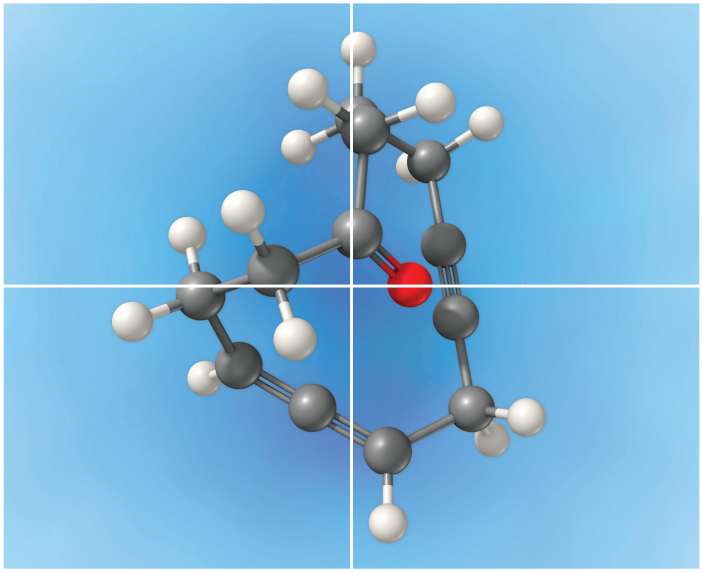

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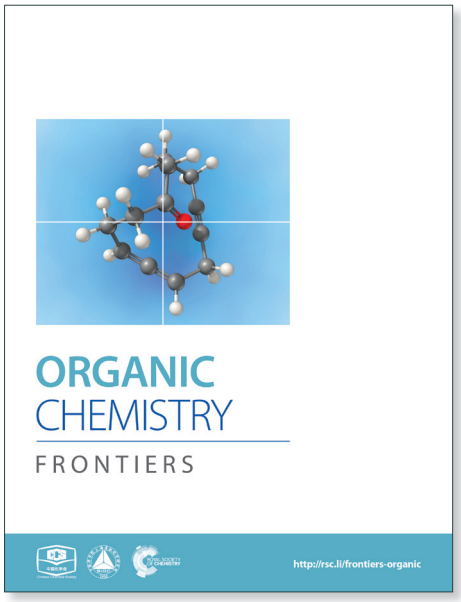

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Cu-Catalyzed sp^3 C–H Bonds Oxidative Functionalization of Alkylazaarenes and Substituted Ethanones: An Efficient Approach to Isoxazoline Derivatives

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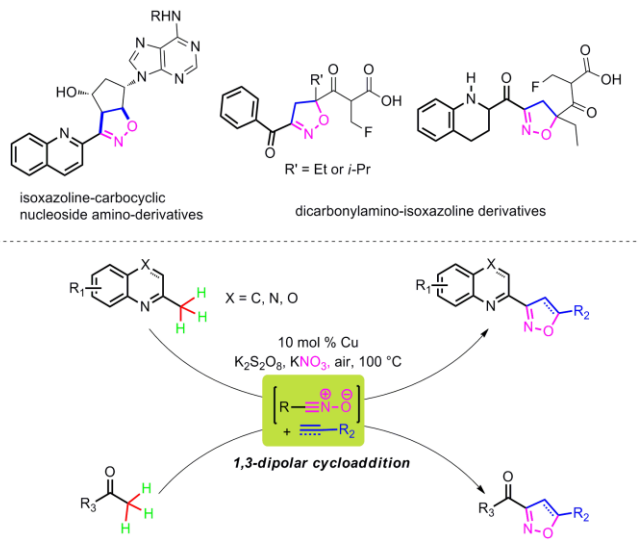
Cu-catalyzed sp^3 C–H bonds oxidative functionalization of alkylazaarenes and substituted ethanones to different kinds of isoxazoline derivatives by 1, 3-dipolar cycloaddition is reported. Cheap sources of nitro, commercially available substrates, as well as a variety of alkenes (alkynes) are applied in this transformation.

Isoxazoline derivatives display an array of significant biological properties including antiviral, antidiabetic, antitubulin, as well as antineoplastic activity. [1] Currently, drugs containing the isoxazoline moiety have already been used in common clinical treatment, and some representative molecules are shown in Scheme 1.[2] Meanwhile, isoxazoline derivatives are useful ligands[3] and valuable synthetic intermediates for the construction of 1,3-diketones, β-hydroxyketones, and γ-amino alcohols.[4] As a result, great efforts have been devoted in order to develop synthetic methods for isoxazoline derivatives during the past century.[5] The classic, well-established approach of 1,3-dipolar cycloaddition of dipolarophiles with nitrile oxides has shown great advances in the synthesis of isoxazolines. However, as the nitrile oxides need to be prepared in situ from specific substrates, such as hydroximinoyl chlorides, aldoximes, and primary nitro compounds with certain reagants,[4b],[5] the development of alternative methods for the formation of nitrile oxides from stable, cheap, and readily accessible precursors as well as identifying convenient catalytic systems is still particularly challenging and highly attractive.

Expanding the applicability and exploring simple catalytic systems for metal-catalyzed sp^3 C–H bond functionalizations have been ambitious goals for chemists during the past decade.[6] Among them, the metal-catalyzed sp^3 C–H bond nitration reaction is still an unresolved task.[7] Herein, we used Cu-catalyzed sp^3 C–H bond nitration to form the nitrile oxides and subsequently to go through 1,3-dipolar cycloadditions with alkenes or alkynes in order to obtain isoxazoline derivatives. The sp^3 C–H bonds of the methylazaarenes and substituted ethanones were successfully converted into the oxidative products combined with various alkenes. Generally, by using a cheap nitro source (KNO_3) and commercially available substrates, this method provided an efficient and concise approach to isoxazoline derivatives, which might possess great potential applications in the design of ligands as well as in tests of biological activity (Scheme 1).

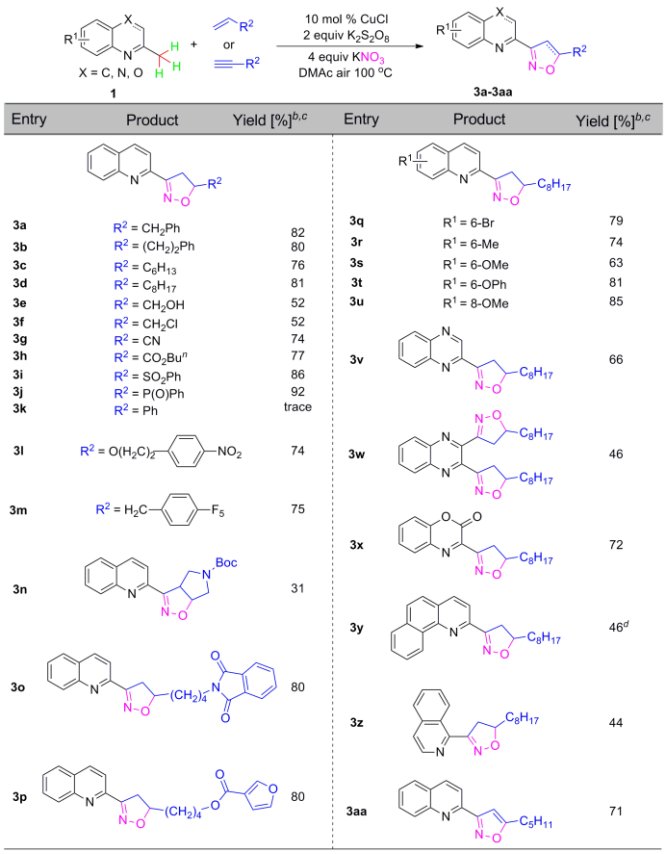


Scheme 1. Cu-catalyzed different types of sp^3 C–H bonds oxidative functionalzation to synthesis isoxazolines.

Metal-catalyzed oxidation of the benzylic sp^3 C–H bond of the methylazaarenes has stimulated great research efforts during the last decade,[8] so we chose 2-methylquinoline **1a** as the standard substrate to react with allylbenzene **2a** in order to perform this sp^3 C–H oxidative functionalization reaction. After a series of screens on different catalysts, oxidants, solvents, and nitro sources, we settled

on the following reaction conditions: 10 mol % of CuCl as catalysts, 2 equiv of $K_2S_2O_8$ as oxidant, 4 equiv of KNO_3 as nitro source, and DMAc as a solvent at 100 °C for 12 hr under air atmosphere. The desired 1, 3-dipolar cycloaddition product **3a** was obtained in 82% yield combined with a trace amount of quinoline-2-carbaldehyde as the byproduct (see Supporting Information).

Table 1. Substrate scope: methyl azzarenes, alkenes and alkyne. [a]

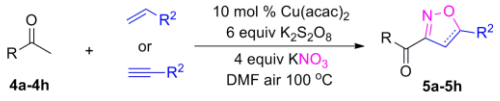


Entry	Product	Yield [%][b,c]	Entry	Product	Yield [%][b,c]
3a	R^2 = CH_2Ph	82	3q	R^1 = 6-Br	79
3b	R^2 = $(CH_2)_2Ph$	80	3r	R^1 = 6-Me	74
3c	R^2 = C_6H_{13}	76	3s	R^1 = 6-OMe	63
3d	R^2 = C_8H_{17}	81	3t	R^1 = 6-OPh	81
3e	R^2 = CH_2OH	52	3u	R^1 = 8-OMe	85
3f	R^2 = CH_2Cl	52			
3g	R^2 = CN	74			
3h	R^2 = CO_2Bu^n	77			
3i	R^2 = SO_2Ph	86			
3j	R^2 = P(O)Ph	92			
3k	R^2 = Ph	trace			
3l	R^2 = $O(H_2C)_2$–NO_2	74	3v		66
3m	R^2 = H_2C–F_5	75	3w		46
3n		31	3x		72
3o		80	3y		46[d]
3p		80	3z		44
			3aa		71

[a] Reaction was carried out with CuCl (10 mol %), $K_2S_2O_8$ (2.0 equiv), KNO_3 (4.0 equiv), 2-methyl azaarenes (0.30 mmol), alkenes or alkyne (0.9 mmol) in DMAc (3.0 mL) at 100 °C for 12 h under air. [b] Isolated yield. [c] All the reaction systems produced trace amounts of corresponding quinoline-2-carbaldehyde as byproduct. [d] Mixed with trace amount of impurities.

With optimized conditions in hand, we explored the substrate scope. First, a variety of alkenes were tested. In general, all these terminal alkenes with either electron- donating or electron-withdrawing substituents afforded the corresponding isoxazoline products in moderate to excellent yields (Table 1). For example, alkenes bearing useful functional groups, such as free alcohol, cyano, ester, phenylsulfinyl, and nitro led to the desired product in moderate to good yields (**3e**, **3g**, **3h**, **3i**, **3l**). Diphenyl(vinyl)phosphine oxide produced the product in an excellent yield of 92% (**3j**). Aliphatic alkenes were shown to be compatible with the optimized conditions (**3a**, **3c**, **3d**, **3o**, **3p**). When styrene was applied in the reaction, only a trace amount of product was achieved (**3k**). Besides terminal alkenes, a cycloolefin was also a suitable substrate, although a low yield was achieved (**3n**). Next, substituted 2-methylquinoline was tested, wherein electronically disparate substituents on the aromatic ring had limited influence on the reaction process, and the corresponding products were obtained in moderate to good yields (**3q**-**3u**). We also used 3-methylquinoline and 4-methylquinoline as substrates to performed this reaction, however, 3-methylquinoline could only provide a trace amount of desired product and 4-methylquinoline failed to provide any corresponding product. Different 2-methyl azaarenes were also applied into the catalytic system, and 2-methylbenzo[*f*]quinoxaline, 2-methylquinoxaline, 1-methylisoquinoline, and substituted benzoxainones all gave the desire product in moderate to good yields (**3v**-**3z**), but 2-methylpyridine failed to give the desired product. An alkyne also served as a good dipolarphile under this catalytic system and 1-heptyne provided the desired product in 71% yield (**3aa**). But phenylacetylene was not a suitable substrate for this transformation. When 2-ethylquinoline was used as substrate under the standard condition, a cascade sp^3 C–H bond oxidative functionalization was achieved to access the different isoxazoline derivatives.[9]

Table 2. Substrates scope: acetophenone. [a]

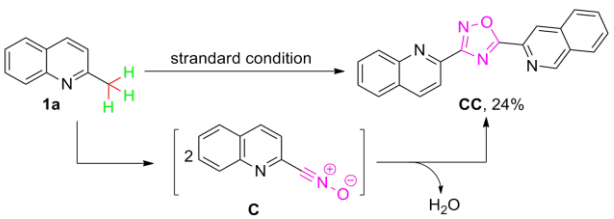


Entry	Ketone	Alkene or Alkyne	Product	Yield [%][b]
4a	R^3 = 4-Cl	2d	5a	23%[c]
4b	R^3 = 4-CN		5b	53%
4c	R^3 = 4-CF_3		5c	50%[c]
4d	R^3 = 4-NO_2		5d	63%
4e	R^3 = 4-OMe		5e	trace
4f	R^3 = 2-F		5f	27%
4g			5g	67%
4h			5h	62%

[a] The reaction was carried out with $Cu(acac)_2$ (10 mol %), $K_2S_2O_8$ (6.0 equiv), KNO_3 (4.0 equiv), acetophenone (0.30 mmol), alkenes or alkynes (0.9 mmol) in DMF (3.0 mL) at 100 °C for 12 h under air. [b] Isolated yield. [c] Mixed with trace amount of impurities.

a) Radical trapping experiment

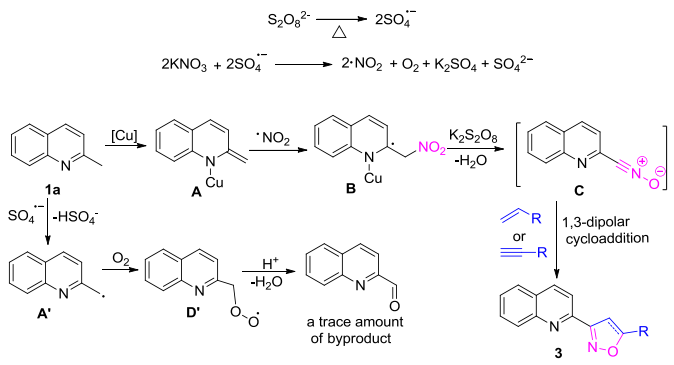
b) Oxidative dimerization reaction of 1a



Scheme 2. Control experiments

The functionalization of the α-C–H bond of carbonyl compounds has long been valued as a fundamental transformation in organic chemistry.[10] Based on this transformation, Horiuchi and Roy developed approaches to isoxazolines[11] by using acetone (or acetophenone) as substrate and solvent combined with iron salts or ammonium cerium nitrate (CAN). These achievements, however elegant, could only provide a limited substrate scope. Different acetophenones were therefore tested in order to test the applicability of our transformation. We found that with a slightly changed catalytic system, acetophenones with electron-withdrawing groups substituted on the aromatic ring could provide corresponding products in low to moderate yields, and a higher yield was achieved for more electron-deficient substrates (Table 2, 5a-5f). When 1-(quinolin-2-yl) ethanone was used as substrates, 5g and 5h were formed in 67% and 62% yield, respectively. Other ketones, propiophenone and acetone for example, failed to give the desired product.

To gain insight into the mechanism, several control experiments were carried out by using 2-methylquinoline **1a** as substrate (Scheme 2). When a radical scavenger 1,1-diphenylet-hylene (1 equiv) was added into the reaction, the desired product was not observed at all, but **AA** and **BB** were produced in yields of 29% and 14%, respectively. This result implied that the reaction might involve generation of a nitro radical and oxygen.[12] When **1a** was applied to the reaction system in the absence of alkenes or alkynes, oxadiazole **CC** was achieved in a 24% yield. This result indicates that nitrile oxide could be the key intermediate for this reaction.[5o]



Scheme 3. Proposed mechanism

On the basis of the above results and previous literature,[13],[14] we proposed a tentative pathway for this transformation (Scheme 3). Decomposition of the potassium peroxydisulphate may initially occur in order to generate the sulfate radical anion, which subsequently reacted with KNO_3 in order to form a nitrogen dioxide radical as well as oxygen.[13a-d] Meanwhile, **1a** reacted with CuCl to produce the active metal enamide species **A**,[14] and **A** was attacked by NO_2 radical in order to obtain the intermediate **B**, which provided the nitrile oxide **C** through the processes of oxidation and dehydration.[7d],[8],[13e-f] The nitrile oxide **C** then reacted with alkenes or alkynes through 1, 3-dipolar cycloaddition reaction, and the final isoxazolines **3** were achieved.[5o],[8]At the same time, **1a** could also be converted into a radical intermediate **A'** through a single electron transfer (SET) process,[7d] then **A'** reacted with oxygen to provide the byproduct quinoline-2-carbaldehyde in a trace amount (see Supporting Information).[12] When substituted acetophenone **4** was used to provide the corresponding isoxazoline derivatives **5**, a similar mechanism could be applied (active metal enol species was formed instead of enamide species **A**[10]) in the reaction course.

Conclusions

In conclusion, by using Cu-catalyzed sp^3 C–H bond nitration to generate the nitrile oxides in situ and subsequently go through 1, 3-dipolar cycloaddition with alkenes or alkynes, we developed an efficient and concise approach to isoxazoline derivatives. When an inexpensive nitro source (KNO_3) and commercially available substrates are the starting point, the sp^3 C–H bonds of methylazaarenes and substituted ethanones can be successfully functionalized with the assistance of different alkenes and alkynes. Current work is ongoing toward the application of these isoxazoline derivatives to biological activity tests.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI:10.1039/c000000x/
[§] These aouthers contributed equally to this work.

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