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Copper-Catalyzed Aerobic Oxidative Cyclization of 2-Alkynylanilines with Nitrosoarenes: Synthesis of Organic Solid Mechanoluminescence Compounds of 4-Oxo-4*H*-cinnolin-2-ium-1-ide

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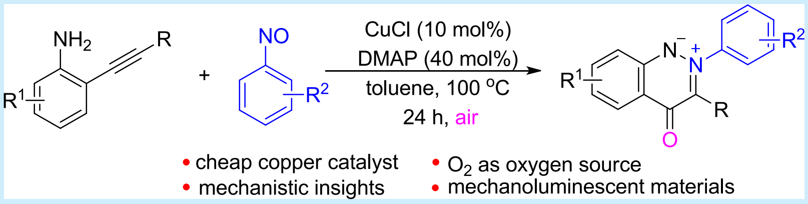

ABSTRACT: An efficient Cu(I)/DMAP/air system for the one-pot synthesis of 4-oxo-4*H*-cinnolin-2-ium-1-ides, which are often difficult to prepare by traditional routes from substituted 2-alkynylanilines and nitrosoarenes, was developed. These 4-oxo-4*H*-cinnolin-2-ium-1-ides have practical applications as mechanoluminescent materials. Preliminary mechanistic experiments were performed, and a plausible mechanism for this tandem process is proposed. The use of an inexpensive copper catalyst and molecular oxygen as the oxygen source and the oxidant make this an attractive green protocol with potential synthetic applications.

Unique chemical and biological activities have conferred quaternary ammonium salts many outstanding biofunctional properties.[1] Cinnolinium salts being an example, they have been widely used as core functional structures in desired medical and gene compounds (Figure 1).[2] The development of methods for the synthesis of cinnolinium salts has therefore attracted much attention. The classical method for synthesizing these compounds involves S_N2-type reactions of cinnolines with alkyl halides, but such a synthetic approach is hardly industrialized due to the halide pollution and less availability of reactants. Furthermore, *N*-aryl-substituted salts cannot be synthesized via this route.[3] Although Heck et al. proposed a novel approach for the synthesis of cocinnolinium salts through the palladium(II) coordinated azobenzenes (Scheme 1a),[4] this method is not catalytic and results in a relatively low yield.

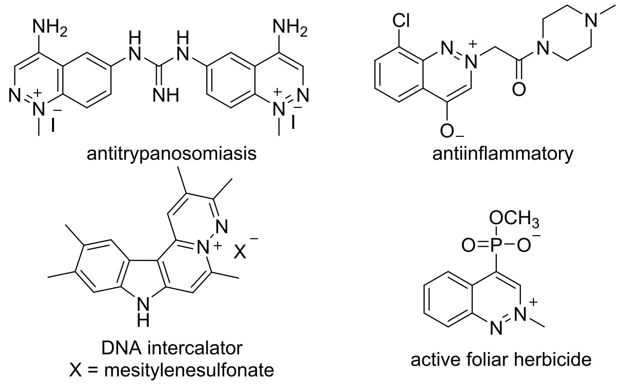

Figure 1. Representative cinnolinium salts with pharmaceutically and biologically active.

Transition-metal-catalyzed cross-coupling reactions are powerful synthetic methods for the construction of useful chemicals and extensively adopted by synthetic chemists because of their good step and atom economies.[5] Meanwhile, azobenzenes and their derivatives demonstrated superior properties due to their cis−trans transformation.[6] As a result, the synthesis of heterocyclic compounds via transition-metal-catalyzed aromatic *ortho* C−H bond activation and cyclization reactions of azobenzenes has been widely studied.[7] Cheng and You independently developed oxidative C−H activation/cyclization coupling reactions of alkynes with azo compounds affording cinnolinium salts (Scheme 1b).[8a−c] Chuang's group developed a one-pot cascade synthesis of cinnolinium salts via palladium(II)-catalyzed C−H bond activation of alkenes and 2-azobiaryl compounds (Scheme 1c).[8d] Li and co-workers used diazo compounds as effective coupling partners in rhodium-

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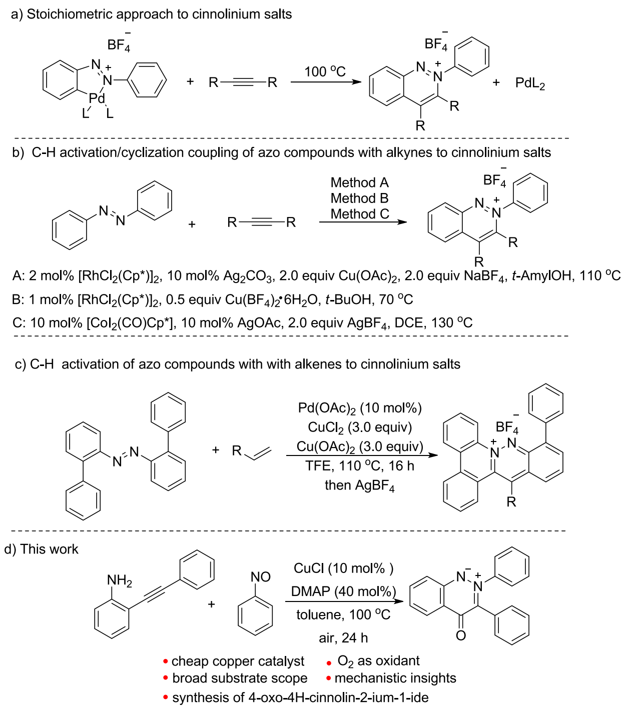
Scheme 1. Reaction Design for the Construction of 4-Oxo-4*H*-cinnolin-2-ium-1-ides

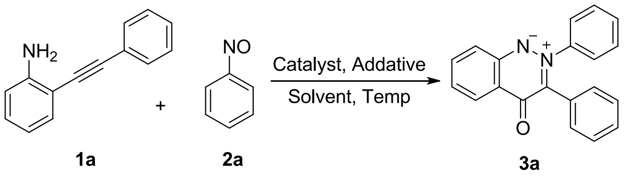


(III)-catalyzed C−H transformations to cinnolinium salts.[9] Wang's group reported Rh(III)-catalyzed oxidative coupling/cyclization reactions of Boc-arylhydrazines and alkynes to afford cinnolinium salts.[10] However, in many cases, the practicality of these methods is offset by the excessive use of strong oxidants, expensive additives, and noble-metal catalysts, the narrow reaction scope, and the laborious workups needed for side-product removal. The development of convenient, practical methods for accessing diverse cinnolinium salt skeletons from stable and easily obtained substrates is therefore important. Inspired by previous research, we envisioned that 2-alkynyl-substituted azobenzenes formed in situ from 2-alkynylanilines and aromatic nitroso compounds would undergo intramolecular electrophilic addition to yield cinnolinium salts. Here, we report a copper-catalyzed condensation/cycloaddition cascade for the synthesis of organic solid mechanoluminescence compounds of 4-oxo-4*H*-cinnolin-2-ium-1-ides from 2-alkynylanilines and aromatic nitroso compounds (Scheme 1d).

Therefore, we initiated our studies by the synthesis of 4-oxo-2,3-diphenyl-4*H*-cinnolin-2-ium-1-ide (**3a**) from 2-(phenylethynyl)aniline (**1a**) and nitrosobenzene (**2a**) for optimization experiments. First, the screening of copper sources showed that CuCl was superior in furnishing the aiming product **3a** in 66% isolated yield (Table 1, entries 1−6). The structure of **3a** was further confirmed by X-ray diffraction analysis (CCDC 2045163; Figure 2). This reaction did not work while Cu(0) such as copper powder was used (Table 1, entry 6). A series of nitrogen ligands were then screened with 4-dimethylaminopyridine (DMAP) giving the best 69% yield (Table 1, entries 7−10). A survey of solvents revealed that the solvent effect did not significantly influence the current transformation, and the use of dimethylsulfoxide (DMSO), CH_3CN, 1,4-dioxane, and hexane afforded the desired product **3a** in 58% to 63% yield (Table 1, entries 11−14). The amount of additive was next tested, and the yield increased to 86% when 0.4 equiv of DMAP was used (Table 1, entries 15−17). The reaction did not work when the ligand was absent, a significant amount of azobenzene was formed instead (Table 1, entry 18). It was found that 10 mol % of CuCl was sufficient to carry out this reaction successfully (Table 1, entries 19 and 20). However, the yield of **3a** decreased to 69% when the temperature was elevated to 120 °C (Table 1, entry 21). Therefore, the optimal reaction conditions can be summarized as follows: 0.5 mmol of 2-(phenylethynyl) aniline and 0.75 mmol of nitrosobenzene in toluene (1.5 mL) with CuCl catalyst (10 mol %), DMAP (40 mol %), at 100 °C for 24 h under an air atmosphere.

With the optimized reaction conditions in hand, the scope of this copper-catalyzeddehydration/cycloaddition cascade reaction to 4-oxo-4*H*-cinnolin-2-ium-1-ide was investigated. The scope of the R group attached to the alkyne was tested with

Table 1. Conditions Screening[a]



entry	catalyst (x mol %)	additive (x equiv)	solvent	yield[d]
1	CuCl (10)	pyridine (1.0)	toluene	66%
2	CuBr (10)	pyridine (1.0)	toluene	52%
3	CuI (10)	pyridine (1.0)	toluene	N.D.
4	$CuCl_2$ (10)	pyridine (1.0)	toluene	N.D.
5	$Cu(OAc)_2$ (10)	pyridine (1.0)	toluene	54%
6	Cu powder (10)	pyridine (1.0)	toluene	N.D.
7	CuCl (10)	*o*-phenanthroline (1.0)	toluene	37%
8	CuCl (10)	Et_3N (1.0)	toluene	61%
9	CuCl (10)	2,2′-bipyridine (1.0)	toluene	37%
10	CuCl (10)	DMAP (1.0)	toluene	69%
11	CuCl (10)	DMAP (1.0)	DMSO	62%
12	CuCl (10)	DMAP (1.0)	CH_3CN	63%
13	CuCl (10)	DMAP (1.0)	dioxane	59%
14	CuCl (10)	DMAP (1.0)	hexane	58%
15	CuCl (10)	DMAP (0.6)	toluene	74%
16	CuCl (10)	DMAP (0.4)	toluene	86%
17	CuCl (10)	DMAP (0.2)	toluene	62%
18	CuCl (10)	DMAP (0)	toluene	N.D.
19	CuCl (5)	DMAP (0.4)	toluene	28%
20	CuCl (20)	DMAP (0.4)	toluene	84%
21[b]	CuCl (10)	DMAP (0.4)	toluene	69%
21[c]	CuCl (10)	DMAP (0.4)	toluene	85%

[a] Conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), catalyst (x mol %), additive (**x** equiv), toluene (1.5 mL), air, 100 °C, 24 h. [b] 80 °C. [c] 120 °C. [d] N.D.: Not detected.

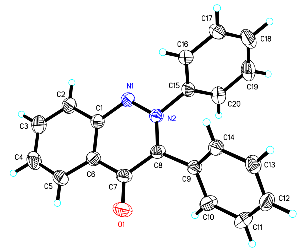
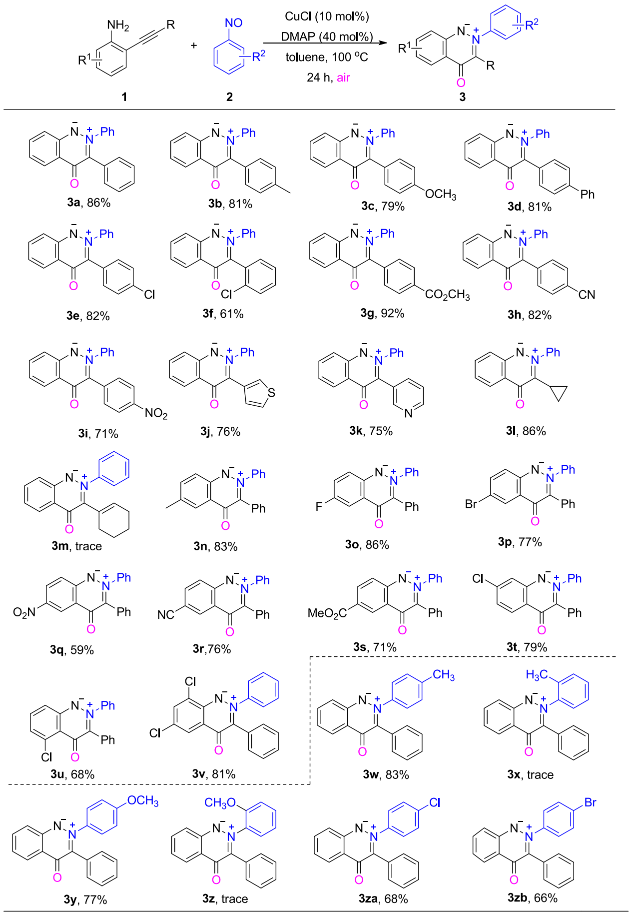


Figure 2. X-ray crystal structure of product **3a**.

aryl (**1b**−**1i**), heteroaryl (**1j**, **1k**), alkyl (**1l**), and alkenyl (**1m**) functionalities, as shown in Scheme 2. The reaction worked well with these functional groups, affording the desired products **3b**, **3c**, **3d**, **3e**, **3g**, **3h** and **3i** in 71−92% yields irrespective of the electronic properties. The structure of **3g** was confirmed by X-ray diffraction analysis (CCDC 2045166; Figure 3). The steric effect of the substituent had an obvious impact on the reaction. For example, treatment of **2a** with **1f** provided **3f** in 61% yield compared with that of **3e**. The reaction worked smoothly with heteroaryl-containing compounds such as **1j** and **1k**, affording the desired compound **3j** and **3k** in 76% and 75% yield, respectively. The current conditions gave a considerable yield of the desired product **3l** (86%) when an alkyl derivative such as cyclopropyl was performed. However, the reaction failed to deliver the desired product when an alkenyl derivative such as **1m** was used as the substrate.

Scheme 2. Substrate Scope[a]



[a] Conditions: **1** (0.5 mmol), **2** (0.75 mmol), CuCl (10 mol %), DMAP (40 mol %), toluene (1.5 mL), air, 100 °C, 24 h, isolated yield.

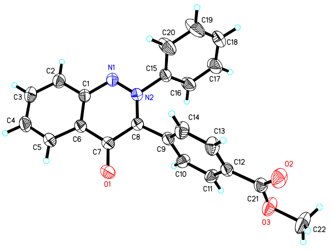


Figure 3. X-ray crystal structure of product **3g**.

Next, substrates **1n**−**1v** with a diverse substituted R^1 group of the *o*-alkynylanilines were tested. The reaction proceeded well when the aryl was attached with 4-Me, 4-F, 4-Br, 4-NO_2, 4-CN, 4-$COOCH_3$, 5-Cl, 3-Cl, and 3,5-dichloro to afford the corresponding derivatives **3n**−**3v** in 59−86% yields. Next, representative examples of substituted nitrosobenzenes **2** were examined to synthesize 4-oxo-4*H*-cinnolin-2-ium-1-ide derivatives **3w**−**3zb**. The results showed that the steric bulky nitrosobenzene such as 2-methyl and 2-methoxyl nitrosobenzene could not go through the current transformation smoothly.

We investigated the crystal structure of **3a** and found that the dihedral angles between the peripheral phenyl rings (A and B) and the central aryl ring were 50.5° and 73.0°, respectively (Figure 4a), which indicated that **3a** showed a twisted molecular conformation. Furthermore, the molecules of **3a** were found to adopt a ladder-like stacking arrangement (Figure 4b). Because of the big distance between the upper and lower molecules, no strong $\pi \cdots \pi$ stacking was observed among the molecules, indicating the loose stacking mode of **3a**. According to the previous literatures,[11] when an organic compound had a twisted molecular and loose stacking mode, this solid-state sample of this compound might exhibit the mechanoluminescence (ML) property due to the morphological change, which suggested that the fluorescence color and/or intensity changed significantly under the stimulation of external pressure. Inspired by this, we investigated the MFC activity of compound **3a** (Figure 4 and Video 1 in Supporting Information). Under the 365 nm UV light irradiation, the original solid sample of compound **3a** exhibited extremely weak blue fluorescence with a maximum emission wavelength of 461 nm. However, when the solid sample was ground with a mortar and a pestle, it showed bright blue fluorescence emission at 462 nm due to the destruction of the crystalline structure. After the external pressure was removed, the sample returned to its original state of extremely weak blue fluorescence after being exposed to air for 40 s, which might be attributed to the strong crystallization ability of compound **3a** including the C−H···O and C−H···π bonds in the crystalline state (Figure 4c). More detailed change over time of the luminescence spectra after the mechanical stimuli can be

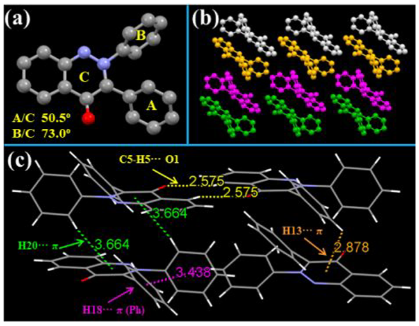
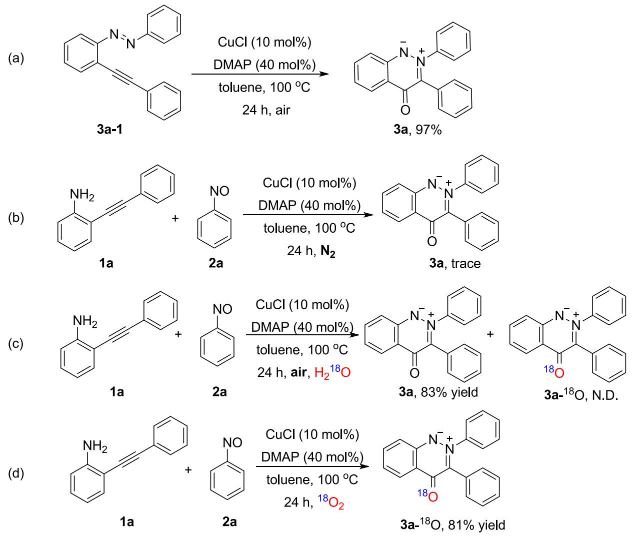


Figure 4. Single crystal of compound **3a**: (a) molecular conformation and the dihedral angles between the peripheral phenyl rings (A and B) and the central aryl ring (C); (b) stacking arrangement; (c) intermolecular interactions.

found in the Supporting Information (Figure S1). The excellent ML property of this compound provided a huge opportunity for the development of new organic fluorescent materials based on 4-oxo-4*H*-cinnolin-2-ium-1-ides.

Several control experiments were carried out to elucidate the mechanism of this electrophilic cyclization reaction, as shown in Scheme 3. According to previous reports[12] and control experiments (entry 18 in Table 1), the (*E*)-1-phenyl-2-(2-(phenylethynyl)phenyl)diazene (**3a-1**) might be an intermediate in the current transformation. The treatment of **3a-1** under standard conditions provided target compound 4-oxo-2,3-diphenyl-4*H*-cinnolin-2-ium-1-ide (**3a**) in 97% yield (Scheme 3a), indicating that the azobenzene species might be an intermediate in the current transformation. The reaction cannot work well when performed under a N_2 atmosphere (Scheme 3b). Next, the reaction was performed in the presence of 10 equiv of $^{18}OH_2$ in toluene under our standard conditions. However, no **3a**-^{18}O was detected (Scheme 3c). A labeling study with $^{18}O_2$ was further carried out, and the reaction proceeded smoothly to provide the 4-oxo-4*H*-cinnolin-2-ium-1-ide product **3a**-^{18}O containing ^{18}O in 81% yield. These results indicate that the oxygen atom of the **3a** originated from oxygen and dioxygen was essential for the transformation.

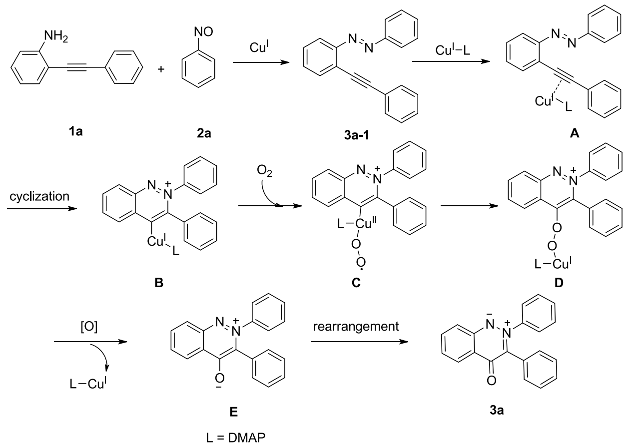
Scheme 3. Mechanistic Studies



On the basis of the above experiments and the reported literature,[13] a plausible mechanism is proposed (Scheme 4). First, condensation of 2-(phenylethynyl)aniline (**1a**) and nitrosobenzene (**2a**) gives (*E*)-1-phenyl-2-(2-(phenylethynyl)-phenyl)diazene (**3a-1**). Complexation of Cu(I) and ligand DMAP with **3a-1** yields intermediate **A**, which undergoes intramolecular cyclization to intermediate **B**. Intermediate **B** could be oxidized with oxygen in air, generating the peroxycopper **C**. Subsequent isomerization affords peroxide **D**. The O−O bond cleavage leads to intermediate **E**. Finally, rearrangement of **E** affords the desired product **3a**.

In conclusion, we have developed an efficient and mild Cu(I)/DMAP/air system for the synthesis of organic solid luminescent 4-oxo-4*H*-cinnolin-2-ium-1-ides from substituted 2-alkynylanilines and nitrosoarenes. The use of an inexpensive copper catalyst and molecular oxygen as the oxygen source and oxidant makes this an attractive green protocol with a range of potential synthetic applications. A novel catalytic cycle is proposed based on preliminary mechanistic studies. These 4-oxo-4*H*-cinnolin-2-ium-1-ides have practical applications as mechanoluminescent materials. Further studies by our group on the synthetic applications of this method are ongoing.

Scheme 4. Proposed Mechanism



■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c04186.

Experimental procedures, characterization data, NMR spectra (PDF)

MFC activity of compound **3a** (MP4)

Accession Codes

CCDC 2045163 and 2045166 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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