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Copper-Catalyzed Selective *ortho*-C−H/N−H Annulation of Benzamides with Arynes: Synthesis of Phenanthridinone Alkaloids

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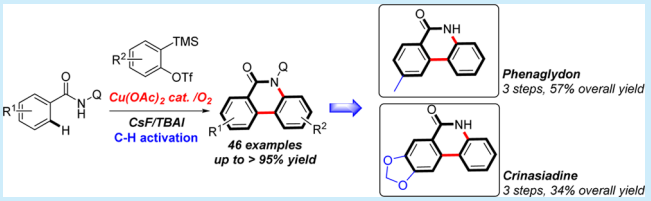
Supporting Information

ABSTRACT: An efficient and convenient copper-catalyzed method has been developed to achieve direct *ortho*-C−H/N-H annulation to synthesize phenanthridinones with arynes. This method highlights an emerging strategy to transform inert C−H bonds into versatile functional groups in organic synthesis and provides a new way to synthesize phenanthridinone alkaloids efficiently.



Phenanthridinones are very important core structural units and occur widely in a variety of alkaloids and biologically active pharmaceutical agents (Figure 1).[1] While many classical transformations have been established to form phenanthridinone skeletons, the development of more efficient and novel formation methods continues to be intensively investigated in synthetic chemistry.

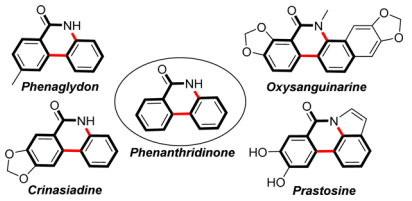
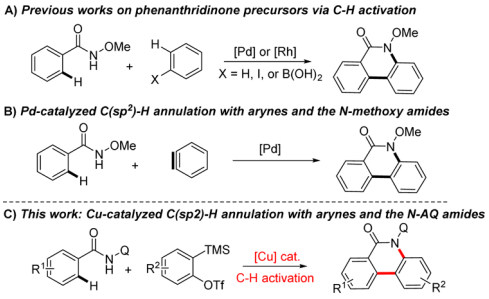


Figure 1. Alkaloids containing phenanthridinone skeletons.

Transition-metal-catalyzed direct selective conversion of unactivated C−H bonds has emerged as an attractive and arguably ideal new strategy to synthesize heterocyclic molecules.[2] The use of an intramolecular dehydrogenative annulation strategy to form phenanthridinones has been significantly developed in recent decades.[3] In 2011, a challenging intermolecular cascade using Pd- or Rh-catalyzed C−H/N−H activation and cyclization to build both C−N and C−C bonds in one pot was achieved by the Wang[4a] and Cheng[4b,c] groups as an important and more efficient new approach to the synthesis of phenanthridinones (Scheme 1A). In addition, Pd-catalyzed synthesis of phenanthridinones via oxidative carbonylation of *o*-arylanilines with CO has also been documented.[5] More recently, the Jiao group reported a Pd-catalyzed domino process employing arylcarbamic chlorides and aryl iodides for phenanthridinone derivatives.[6a] An overview of the synthetic strategy toward phenanthridinones, in particular, the use of highly reactive arynes[7,8] as a component in the one-pot synthesis of phenanthridinones, has attracted interest because of its high efficiency and directness.[9] In 2014, the Jeganmohan[9a] and Xu[9b] groups independently reported a Pd-catalyzed intermolecular *ortho*-C(sp^2)−H activation with arynes and *N*-methoxyamide to synthesize phenanthridinones (Scheme 1B).

Scheme 1. Approaches for the Synthesis of Phenanthridinones via C−H Activation



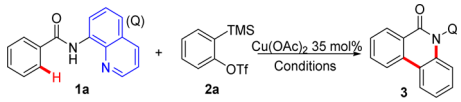
However, although Pd-catalyzed aryne annulation via C−H activation has been significantly advanced,[9−11] to date, ligand-controlled, Cu-catalyzed,[12] intermolecular unactivated direct C(sp^2)−H annulation processes with arynes to synthesize phenanthridinones have not yet been discovered. From our continuing interest and effort in developing efficient and selective unactivated C−H functionalizations and applying them in the synthesis of natural biological products,[13] we describe herein the first copper-catalyzed selective *ortho*-C−H/N−H annulation to synthesize the tricyclic core with arynes under mild conditions (Scheme 1C). This method offers a practical and environmentally friendly strategy for the rapid synthesis of phenanthridinones from simple starting materials.

Received: February 22, 2017

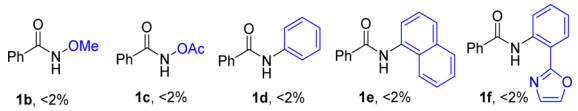
DOI: 10.1021/acs.orglett.7b00442
Org. Lett. XXXX, XXX, XXX−XXX

Our initial attempt was the intermolecular annulation of the model substrate *N*-quinolylbenzamide **1a**[14] with Kobayashi benzyne precursor **2a** (Table 1).[15] After an initial screening of

Table 1. Optimization of the Cu-Catalyzed Annulation[a]



entry	reagents (equiv)	solvents	yield of **3**[b] (%)
1	CsF (1.2), TBAB (0.5), O_2, 80 °C	dioxane	24
2	CsF (1.2), TBAB (0.5), O_2, 80 °C	DMF(**D**)	33
3	CsF (1.2), TBAB (0.5), O_2, 80 °C	MeCN(**M**)	50
4	CsF (1.2), TBAB (0.5), O_2, 80 °C	**D**:**M** (1:1)	64
5	KF (1.2), TBAB (0.5), O_2, 80 °C	**D**:**M** (1:1)	60
6	NaF (1.2), TBAB (0.5), O_2, 80 °C	**D**:**M** (1:1)	<5
7	CsF (2.4), TBAB (0.5), O_2, 80 °C	**D**:**M** (1:1)	46
8	CsF (1.2), TBAI (0.5), O_2, 80 °C	**D**:**M** (1:1)	87(83)[c]
9	CsF (1.2), TBAI (0.5), Ar, 80 °C	**D**:**M** (1:1)	21
10	CsF (1.2), TBAI (0.5), O_2, 110 °C	**D**:**M** (1:1)	65
11	CsF (1.2), TBAI (0.5), O_2, 40 °C	**D**:**M** (1:1)	18
12[d]	CsF (1.2), TBAI (0.5), O_2, 80 °C	**D**:**M** (1:1)	58

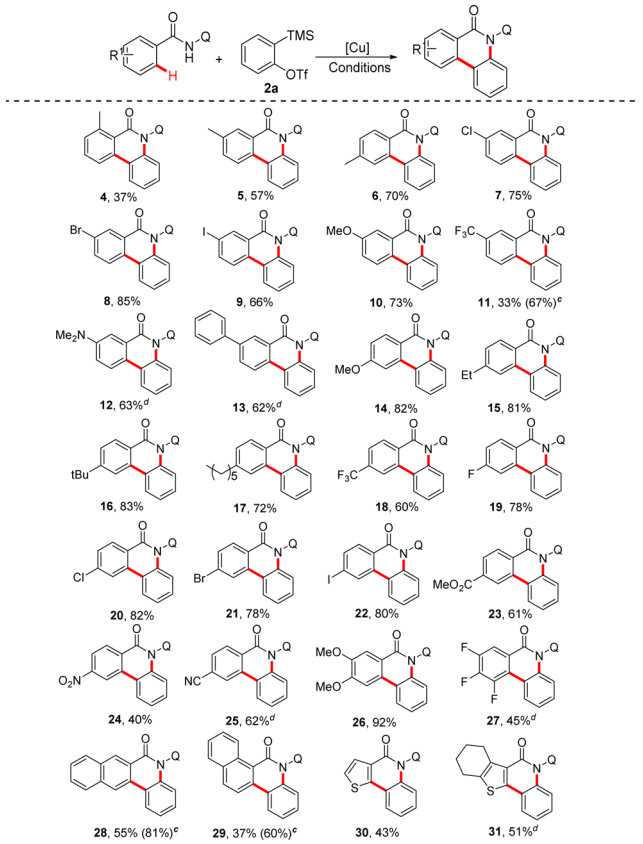


[a]All screening reactions were carried out in a 10 mL glass vial with a PTFE-lined cap on a 0.2 mmol scale. [b]Yields are based on ^{1}HNMR analysis. [c]Isolated yield in parentheses. [d]20 mol % $Cu(OAc)_2$ was used. See the Supporting Information for more reaction conditions.

the copper-catalyzed system, promising results demonstrated the feasibility of this reaction. The desired phenanthridinone product **3** was obtained in a 24% yield by using catalytic amounts of $Cu(OAc)_2$, CsF (1.2 equiv), and TBAB (0.5 equiv) at 80 °C in dioxane under O_2 as oxidant for 12 h (Table 1, entry 1). A detailed screening of various solvents revealed that the reaction could achieve higher conversions using DMF/MeCN (1:1) as the mixture solvent (entry 4). To promote the circulation of this reaction system, further studies surveyed a series of fluoride sources and additives (entries **5**–**8**). We were delighted to find that an 83% isolated yield of **3** was obtained under the optimized reaction conditions: $Cu(OAc)_2$ (35 mmol %), CsF (1.2 equiv), and TBAI (0.5 equiv) at 80 °C in DMF/MeCN (1:1) under O_2 for 12 h (entry **8**). Interestingly, O_2, as a clean and green oxidant, appeared to significantly improve the copper catalysis cycle.[13d] In comparison, when argon was used instead of O_2, the desired reaction was inhibited, resulting in a diminished 21% yield (entry 9).

With an optimized set of conditions in hand, we then probed the substrate scope of *N*-quinolylbenzamides to survey their general reactions. As shown in Scheme 2, benzamides substituted with a variety of functional groups such as alkyl, aryl, ether, ester, halogens, CF_3, NO_2, CN, and NMe_2 were well tolerated under the copper-catalyzed system and gave the phenanthridinone derivative annulation products in good to

Scheme 2. Substrate Scope of Benzamides[a,b]



[a]Reaction conditions: benzamide (0.2 mmol), **2a** (0.4 mmol), $Cu(OAc)_2$ (35 mol %), CsF (0.24 mmol), and TBAI (0.1 mmol) in DMF/MeCN (1:1, 2 mL) at 80 °C under O_2 for 12 h. [b]Isolated yields. [c]2 equiv of $Cu(OAc)_2$ was used under air for 12 h. [d]1 equiv of TBAI was used; see the Supporting Information for more reaction conditions.

excellent yields. Subsequently, the *o*-, *m*-, and *p*-methyl-substituted benzamine substrates (**4a**, **5a**, and **6a**) were used to examine the effects of sterics (**4**–**6**). It is clear that the lower steric hindrance of the *para*-substituted *N*-quinolylbenzamides (**6a**) gave the best yield. The *meta*-substituted substrates (**7a**–**13a**) demonstrated that this approach has high regioselectivity, and only the less hindered *ortho*-C–H bond could be activated to give the desired phenanthridinone products **7**–**13** without regioisomers. The regioselectivity of the annulation product was confirmed by X-ray crystallography of compound **11**. Moreover, the effect of electron-donating and electron-withdrawing groups on the benzamides was further studied. It was found that benzamides with electron-donating groups (alkyl, OMe, etc.) or weakly electron-withdrawing groups (Cl, Br, I, etc.) produced the corresponding products in good to excellent yields. Comparatively, the benzamides with strong electron-withdrawing groups (CF_3, NO_2, etc.) could be utilized to afford the annulation products in moderate to good yield (**11**, **18**, and **24**). To our delight, the yield could be increased by using more copper in the reaction system. Multisubstituted benzamides also reacted efficiently to furnish the sterically favored polysubstituted phenanthridinones **26** and **27**. In addition, the interesting polycyclic or poly heterocyclic compounds **28**–**31** could be synthesized in the copper-catalyzed system. For **28** and **29**, the annulation demonstrated a high regioselectivity but only achieved 55% and 37% yields

DOI: 10.1021/acs.orglett.7b00442
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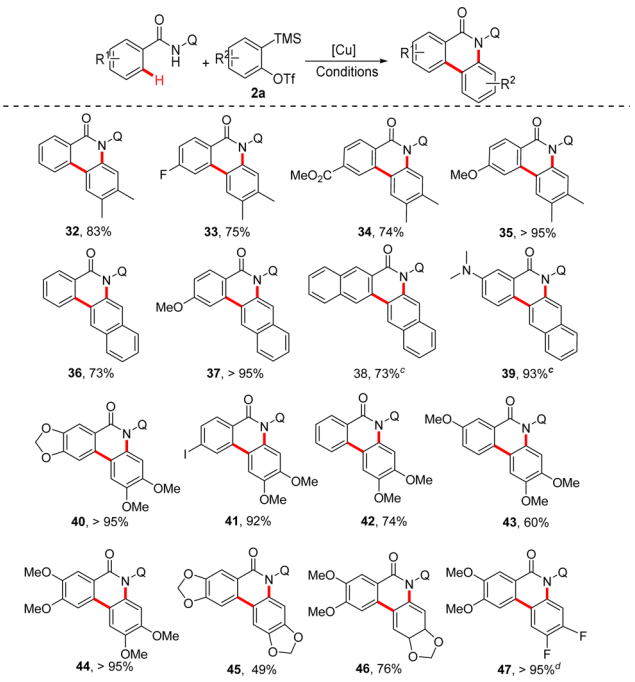
due to steric and electronic effects. The annulation efficiency could also be improved to 81% and 60% yields under the use of 2 equiv of $Cu(OAc)_2$.

We next examined the scope of functionalized aryne precursors as the general annulation partner for this reaction. As shown in Scheme 3, a variety of substituted benzamide

Scheme 3. Substrate Scope of Benzamides and Arynes[a,b]

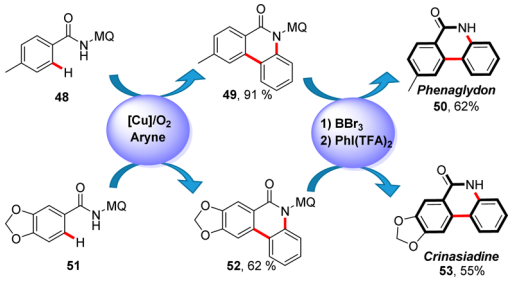


[a]Reaction conditions: benzamide (0.2 mmol), aryne precursors (0.4 mmol), $Cu(OAc)_2$ (35 mol %), CsF (0.24 mmol), and TBAI (0.1 mmol) in DMF/MeCN (1:1, 2 mL) at 80 °C under O_2 for 12 h. [b]Isolated yields. [c]2 equiv of $Cu(OAc)_2$ was used under air for 12 h. [d]50% of $Cu(OAc)_2$ and 1 equiv of TBAI were used.

substrates were reacted with electron-donating or electron-withdrawing arynes (2,3-naphthalyne precursor (**2c**), 4,5-dimethoxybenzyne precursor (**2d**), 4,5-methylenedioxybenzyne precursor (**2e**), and 4,5-difluorobenzyne precursor (**2f**)) and gave good to excellent annulation yields (**32**–**47**). Interestingly, many of the annulation products, such as **6**, **26**, **42**, and **44**, are important subunits in biologically and pharmaceutically active phenanthridinone alkaloids or their analogues.[16] To demonstrate the application of our non-noble metal copper-catalyzed *ortho*-C–H/N–H annulation method, two phenanthridinone alkaloids phenaglydon and crinasiadine were synthesized under these mild conditions (Scheme 4). Previous work has reported that the 8-amino-5-methoxyquinoline (MQ) can be used instead of 8-aminoquinoline for its easy extraction property.[17a] The *N*-MQ amides **48** and **51** first gave rise to **49** in 91% and **52** in 62% yield under the general conditions. The phenaglydon **50** and crinasiadine **53** alkaloids could then be synthesized under simple conditions[17b] in 62% and 55% isolation yields, respectively.

Since C–H activation is involved in this reaction to form the annulation products, a primary intermolecular kinetic isotope effect experiment was conducted. A KIE value of 5.7 was observed. This value suggested that the Cu-catalyzed C–H activation step is the rate-determining step.[18] In addition, a radical-trapping experiment was performed. The reaction was

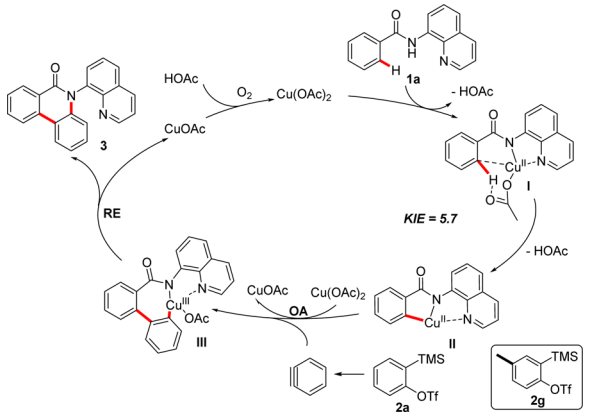
Scheme 4. Applications of Copper-Catalyzed *ortho*-C–H/N–H Annulation in the Alkaloid Synthesis of Phenaglydon and Crinasiadine



not inhibited by the addition of 2 equiv of the radical scavenger TEMPO, and **1a** still gave product **3** in 76% isolated yield. This experiment suggested that a SET was unlikely involved in this reaction. A Cu(III) intermediate was proposed for the *ortho*-C–H annulation.[19]

On the basis of the above experiments and literature precedents,[13,18,19] a plausible mechanism for this annulation reaction with arynes is proposed below in Scheme 5. First,

Scheme 5. Proposed Reaction Pathway



coordination of the amide **1a** reacted with the $Cu(OAc)_2$ generated anionic complex **I** ligated by an *N*,*N*-bidentate directing group. Subsequently, complex **I** underwent an acetate-assisted intramolecular C–H concerted metalation–deprotonation to give the key five-membered complex **II**, which then underwent carbocupration with the aryne generated from the silyl triflate to give rise to intermediate **III**. An experiment was conducted here; when unsymmetrical aryne **2g** was used in this reaction, two regioisomers were obtained with a ratio of approximately 1.2:1, which also indicated the formation of aryne intermediates in this reaction. Finally, reductive elimination of **III** afforded the desired annulation production **3**, and the copper catalyst could be regenerated by oxygen for the next cycle.

In summary, we have developed the first copper-catalyzed intermolecular *ortho*-C–H/N–H annulation of benzamides with arynes. These reactions are operationally simple and robust, avoiding the use of sensitive and expensive noble metals. The reaction also demonstrated broad substrate scope for both benzamides and arynes. The directing group can be easily removed under simple conditions, granting an efficient and straightforward strategy for the synthesis of phenanthridinone alkaloids such as phenaglydon and crinasiadine.

DOI: 10.1021/acs.orglett.7b00442
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Furthermore, applications of this C−H annulation methodology in the synthesis of more complex natural alkaloids are currently under investigation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00442.

Experimental procedures, NMR spectra, and X-ray and analytical data for all new compounds (PDF)
X-ray data for compounds **6** (CIF)
X-ray data for compounds **11** (CIF)
X-ray data for compounds **29** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the "Thousand Youth Talents Plan", NSFC (21672145), the Shuguang program from the Shanghai Education Development Foundation and the Shanghai Municipal Education Commission, and startup funds from Shanghai Jiao Tong University. We thank Prof. Gong Chen (Nankai University) for helpful suggestions and comments on this manuscript.

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