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Copper-Catalyzed C−H Oxidative Radical Functionalization and Annulation of Aniline-Linked 1,7-Enynes: Evidence for a 1,5-Hydride Shift Mechanism

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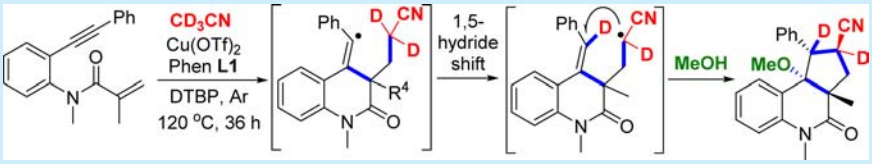
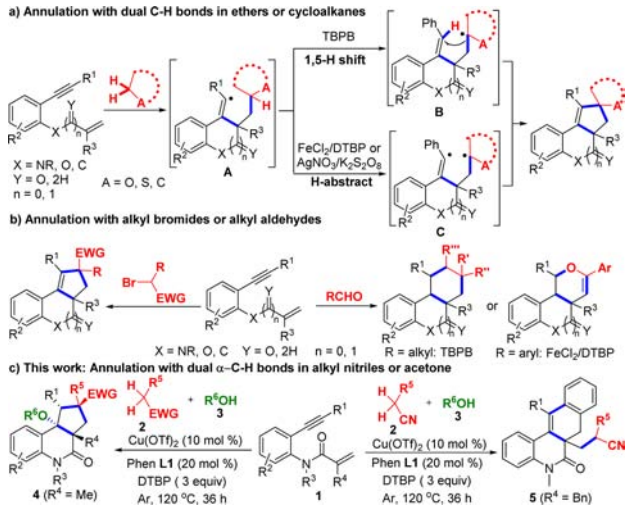
Supporting Information



ABSTRACT: A new copper-catalyzed tandem C−H oxidative radical functionalization and annulation of aniline-linked 1,7-enynes with alkyl nitriles or acetone is described. This reaction allows the selective construction of 1*H*-cyclopenta[*c*]quinolines and benzo[*j*]phenanthridin-6(5*H*)-ones which rely on the substitution effect at the 2-position of the acrylamide moiety. The mechanism involving a 1,5-hydride shift process is proposed according to the control deuterium-labeled experiment.

The 1,*n*-enyne annulation reaction represents one of the most powerful and straightforward methods for the construction of diverse cyclic compounds in organic synthesis and medicinal chemistry.[1−3] In this field, attractive approaches include the [2 + 2 + m] annulation of 1,*n*-enynes with the m-unit reagents, which provide a practical shortcut to building valuable polycyclic molecules.[2,3] Particularly, the [2 + 2 + 1] carbocyclization reactions of 1,*n*-enynes have been well developed to access five-membered carbocycle-fused polycycles, but the majority focus on transition-metal catalyzed Pauson−Khand-type reactions and the radical-mediated version remains a great challenge.[1−3] Thus, development of a conceptually new 1,*n*-enyne [2 + 2 + 1] carbocyclization strategy is interesting and mandatory. Recently, an oxidative radical-mediated strategy has proven to be appealing for the [2 + 2 + 1] carbocyclization of 1,*n*-enynes.[4−7] The Jiang/Tu/Li group[4] and our group[5a] have independently reported the first [2 + 2 + 1] oxidative annulation of 1,*n*-enynes with the dual C−H bonds on the identical carbon atom (Scheme 1a). Subsequently, our group[5b−d] and the other groups[5e,f] have extended the m-unit reagents to alkyl bromides or alkyl aldehydes for the 1,*n*-enyne [2 + 2 + m] carbocyclization transformations (Scheme 1b). However, the mechanism for the [2 + 2 + 1] carbocyclization of 1,*n*-enynes requires further investigation because two possible pathways were proposed during the reaction terminated by the C−H bond process (Scheme 1a): one is the hydride transfer followed by radical addition,[5a] and the other involves direct hydrogen abstraction by peroxides which subsequently undergoes coupling between two radicals.[4] (***CAUTION***: Peroxides may explode at high temperature at larger scale!) Further, to our knowledge, methods for the [2 + 2 + 1] annulation of 1,*n*-enynes with dual *α*−C-H bonds in alkyl nitriles have never been reported although the nitrile group is a versatile functional group precursor in synthesis.[8]

Scheme 1. Oxidative Radical Annulation of 1,*n*-Enynes



Herein, we report a new copper-catalyzed C−H oxidative radical functionalization and annulation of aniline-linked 1,7-enynes with alkyl nitriles or acetone;[7] this tandem reaction provides a selective shortcut to 1*H*-cyclopenta[*c*]quinolines and benzo[*j*]-phenanthridin-6(5*H*)-ones relying on the substitution nature of the acrylamide moiety (Scheme 1c). Notably, such

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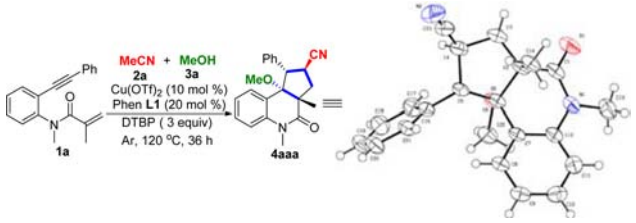
polycyclic compounds are the structural motifs of numerous natural products and pharmaceuticals.[9]

We initially chose *N*-methyl-*N*-(2-(phenylethynyl)phenyl)-methacrylamide (**1a**) as a model substrate for the designed oxidative tandem C−H radical functionalization/annulation protocol (Table 1). Gratifyingly, enyne **1a** treated with MeCN (**2a**), MeOH (**3aa**), $Cu(OTf)_2$, 1,10-phenanthroline **L1** (Phen), and di-*tert*-butyl peroxide (DTBP) at 120 °C afforded the desired product **4aaa** in 67% yield (entry 1). However, the reaction could not occur without Cu catalysts (entry 2). We found that a higher amount of $Cu(OTf)_2$ had no impact on the yield (entry 3). Further, other catalysts, such as $CuCl_2$, $Cu(acac)_2$, $Fe(OTf)_3$, $Cu(OAc)_2$, and CuOTf, were less effective than $Cu(OTf)_2$ (entries 4−6). The results indicated that the effect of ligands played an important role in the reaction (entries 7−9). Note that the reaction without Phen **L1** delivered **4aaa** in a lower yield (entry 7). Although other ligands, including 2,2′-bipyridine **L2** and 4-dimethylaminopyridine (DMAP) **L3**, had a positive effect (entries 8 and 9), they were less efficient than Phen **L1**. A screen of the amount of DTBP revealed the use of 3 equiv of DTBP as the best choice (entries 1 and 10−12). While the use of dicumyl peroxide (DCP) furnished product **4aaa** in 45% yield (entry 13), other oxidants, including TBHP and $PhI(OAc)_2$, had no reactivity (entry 14). A lower reaction temperature (100 °C) resulted in the formation of **4aaa** with a diminishing yield (entry 15). Among the ratios of MeCN and MeOH examined, the 1:1 ratio was preferred (entries 1 and 16−17). Enyne **1a** was decomposed without MeOH (entry 18). Pleasingly, the standard conditions were applicable to the scale of enyne **1a** up to 1 mmol (entry 19).

We next turned our attention to explore the scope of this carbocyclization protocol with respect to enynes **1**, nitriles **2**, and alcohols **3** under the standard conditions (Schemes 2 and 3). We found that enyne **1b** with a free N−H bond was inert for the reaction (**4baa**). Gratifyingly, a wide range of substituents, including aryl, heteroaryl, and alkyl, at the terminal alkyne were perfectly tolerated (**4caa**−**laa**). For aryl alkynes **1c**−**h**, several substituents, including Me, MeO, Br, Cl, F, and CN, on the aryl ring were well consistent, and the electronic nature slightly affect the reactivity (**4caa**−**haa**). In the case of naphthalen-1-yl-, pyridin-3-yl-, or thiophen-2-yl-substituted alkynes **1i**−**k**, the reaction furnished **4iaa**−**kaa** in 53%, 64%, and 69% yields, respectively. Aliphatic alkyne **1l** was suitable for assembling **4laa** in good yield. The electronic nature of the substituents on the phenyl ring of the aniline moiety affected the reaction: While using enynes **1m**−**n** bearing an electron-donating group, Me or

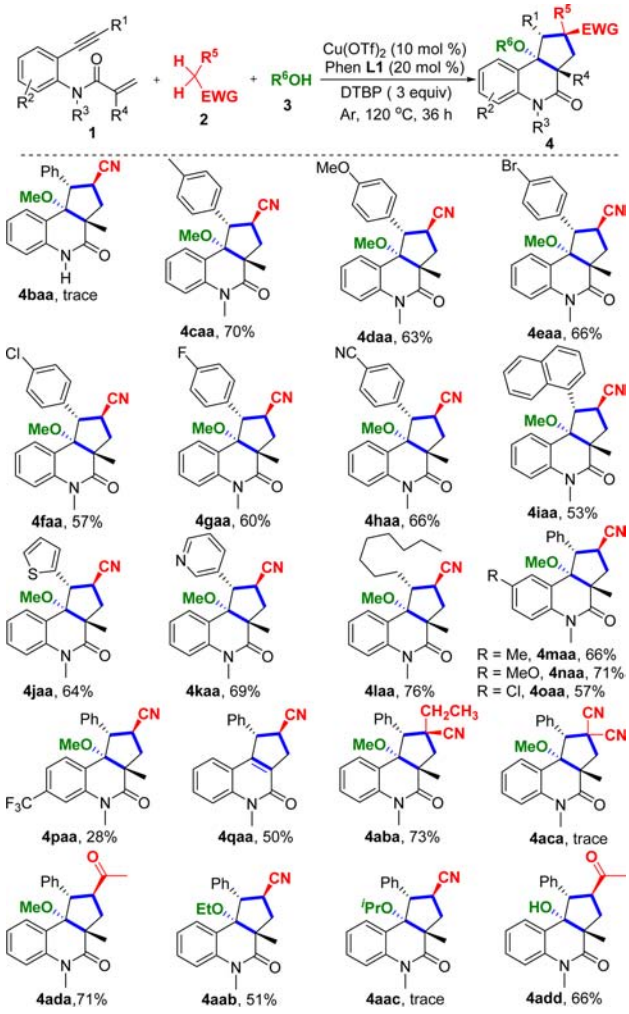
Table 1. Optimization of the Reaction Conditions[a]



entry	variation from the standard conditions	yield (%)
1	none	67
2	without $Cu(OTf)_2$	0
3	$Cu(OTf)_2$ (20 mol %)	67
4	$CuCl_2$, $Cu(acac)_2$, or $Fe(OTf)_3$ instead of $Cu(OTf)_2$	19 to 21
5	$Cu(OAc)_2$ instead of $Cu(OTf)_2$	36
6	CuOTf instead of $Cu(OTf)_2$	52
7	without Phen **L1**	6
8	2,2′-bipyridine **L2** instead of Phen **L1**	35
9	DMAP **L3** instead of Phen **L1**	20
10	without DTBP	0
11	DTBP (2 equiv)	58
12	DTBP (4 equiv)	69
13	DCP instead of DTBP	45
14	TBHP or $PhI(OAc)_2$ instead of DTBP	trace
15	100 °C	51
16	MeCN/MeOH (4:1; 2 mL)	65
17	MeCN/MeOH (1:4; 2 mL)	45
18[b]	without MeOH	trace
19[c]	none	62

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1 mL), **3a** (1 mL), $Cu(OTf)_2$ (10 mol %), Phen **L1** (20 mol %), argon, 120 °C and 36 h. The dr value is >20:1, as determined by ^1H NMR analysis of the crude product. Some side-products from decomposition of **1a** via the C−N bond cleavage were determined by GC-MS analysis. [b]Most of **1a** was decomposed. [c]**1a** (1 mmol) for 48 h.

Scheme 2. [2 + 2 + 1] Carbocyclization of 1,7-Enynes[a]



[a]Reaction conditions: **1** (0.2 mmol), **2** (1 mL), **3** (1 mL), $Cu(OTf)_2$ (10 mol %), Phen **L1** (20 mol %), argon, 120 °C and 36 h. The. dr value of all the products **4** is >20:1, as determined by ^1H NMR analysis of the crude product.

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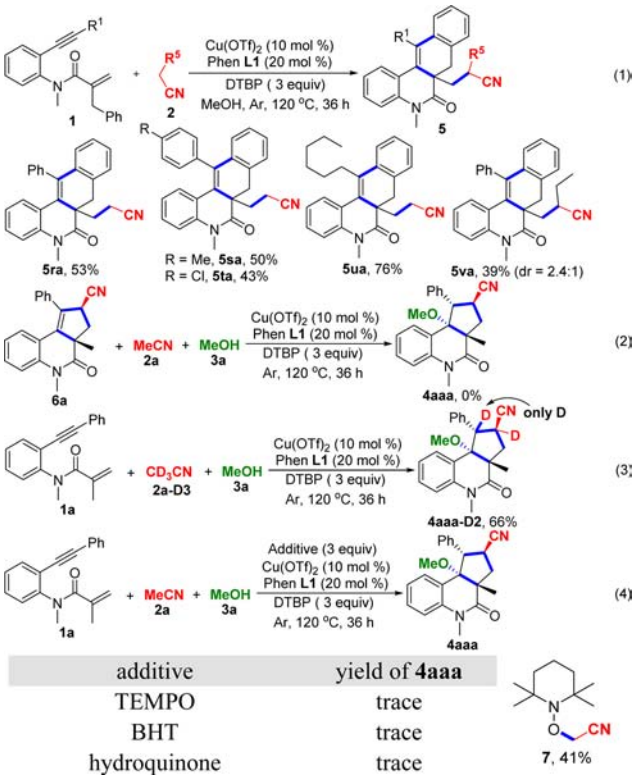
Scheme 3. Other Enynes and Control Experiments



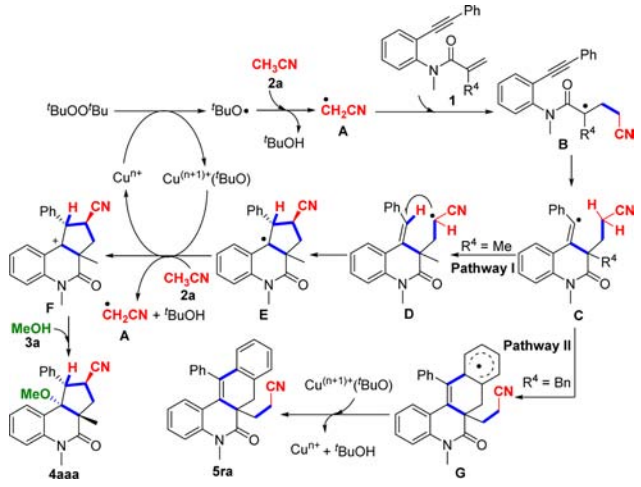
additive	yield of **4aaa**
TEMPO	trace
BHT	trace
hydroquinone	trace

MeO, afforded **4maa**–**naa** in good yields, enynes **1m**–**n** with an electron-withdrawing group, Cl or CF_3, assembled **4oaa**–**paa** in 57% and 28% yields, respectively. Notably, enyne **1q** without a substituent at the 2-position of the acrylamide moiety provided the other non-MeO-substituted product **4qaa**. We were pleased to find that both butyronitrile (**2b**) and acetone (**2d**) were viable substrates leading to **4aba** and **4ada** in high yields. However, malononitrile (**2c**) had a rather lower reactivity (**4aca**) due to the strong electron-withdrawing nature. A series of *O*-nucleophiles **3b**–**d**, namely EtOH, *i*-PrOH, and H_2O, were subsequently examined. While EtOH was a suitable substrate as the desired product **4aab** was furnished in 51% yield, *i*-PrOH (**3c**) had no reactivity for the reaction (**4aac**). Interestingly, the use of H_2O (**3d**) resulted in the formation of the hydroxyl-containing product **4aad** in 66% yield. However, ethanethiol (**3e**) had no reactivity for the reaction.

For enynes **1r**–**v** with a Bn group at the 2-position of the acrylamide moiety, the reaction delivered benzo[*j*]-phenanthridin-6(5*H*)-ones **5ra**–**va**, not the expected 1*H*-cyclopenta[*c*]quinolines **4** (eq 1; Scheme 3). For example, treatment of enyne **1v** with MeCN (**2a**) or *n*-PrCN (**2b**) afforded the corresponding intramolecular annulation products **5ra** and **5va** in moderate yields. The control experiment showed that the product **4aaa** was not formed from substrate **6a** by a simple addition reaction (eq 2). The deuterium-labeled results in eq 3 suggest a 1,5-hydride shift process. We found that the reaction was completely suppressed when using a stoichiometric amount of radical scavenger, such as TEMPO, 2,6-di-*tert*-butyl-4-methylphenol (BHT), and hydroquinone. Further, 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acetonitrile (**7**) was obtained in 41% yield (eq 4). These results imply the reaction via a radical process.

The plausible mechanism of the carbocyclization protocol was proposed (Scheme 4).[3−7] DTBP is readily converted into the

Scheme 4. Possible Mechanisms



^{t}BuO· radical and the $Cu^{(n+1)+}(^t$BuO) species[7] under heating with the aid of a Cu catalyst, followed by single-electron transfer (SET) which affords the alkyl radical **A**. Addition of the alkyl radical **A** across the C−C double bond in enyne **1** gives the radical intermediate **B**, which sequentially reacts with the C−C triple bond to offer the intermediate **C**. Two pathways for the reaction of the intermediate **C** take place on the basis of the substitution effect (R^4). One pathway involves the hydride transfer of intermediate **C** to form the alkyl radical intermediate **D**, and then annulation delivers the intermediate **E** when the R^4 group is the methyl group. Single-electron transfer (SET) between the intermediate **E** and MeCN with the aid of the $Cu^{(n+1)+}(^t$BuO) species gives the cation intermediate **F**, which undergoes the nucleophilic reaction with MeOH to generate the product **4aaa**. The other pathway is direct addition of the intermediate **C** to the aromatic ring leading to the intermediate **G** when the R^4 group is the phenyl group. Finally, hydrogen abstraction of the intermediate **G** by the $Cu^{(n+1)+}(^t$BuO) species occurs leading to the product **5ra**.

In summary, we have developed a new radical-mediated route to produce 1*H*-cyclopenta[*c*]quinolines and benzo[*j*]-phenanthridin-6(5*H*)-ones via copper-catalyzed oxidative tandem C−H radical functionalization/annulation of aniline-linked 1,7-enynes with alkyl nitriles or acetone. The control deuterium-labeled experiment provides true evidence for the occurrence of a 1,5-hydride shift. Furthermore, the reaction provides a straightforward and practical access to polycyclic rings with excellent functional group tolerance and high selectivity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03352.

Detailed experimental procedures, characterization data of the products and the CIF information (PDF)
Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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