

Palladium/Copper-Catalyzed Aerobic Intermolecular Cyclization of Eneidyne Compounds and Alkynes: Interrupting Cycloaromatization for (4 + 2) Cross-Benzannulation

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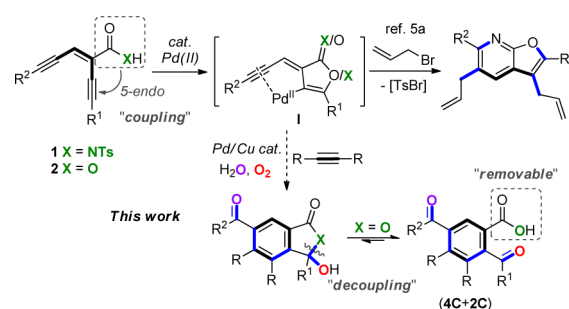
S Supporting Information

ABSTRACT: A tandem coupling–ketoxyoxygenation reaction of readily accessible eneidyne–carboxylic compounds with inner alkynes has been developed that utilizes the PdCl₂/CuBr₂ catalytic system under an O₂ atmosphere and assembles a class of isoindolinones and *o*-acylbenzoic acids. The two oxygen atoms are regioselectively incorporated into eneidyne units at the 1- and 6-positions from atmospheric molecular oxygen and H₂O, respectively, during the present process. This study uncovered a formal [4C + 2C] benzannulation–diketonization of eneidyne and alkynes via a *coupling* and *decoupling* strategy.

Since the discovery of natural eneidyne antibiotics, the cycloaromatization of (*Z*)-hexa-1,5-diyne-3-enes has emerged as an attractive approach for the preparation of versatile aromatic compounds.¹ In this area, pioneered by the studies of Wang and Finn^{2a} and Ohe, Uemura, and co-workers,^{2b} recent advances have remarkably uncovered the unique cyclization reactivity of acyclic eneidyne scaffolds in the presence of various transition-metal catalysts, such as Ru, Pt, Au, Pd, and Cu salts.² O'Connor et al.^{2c} disclosed that the cycloaromatization of eneidyne could be achieved at ambient temperature by the generation of metal complexes. Liu and co-workers notably found that Ru-catalyzed aromatization of eneidyne can involve nucleophilic addition of O-, N-, and C-centered nucleophiles to eneidyne to form functionalized aromatics.^{2d} Meanwhile, variations in substitution at the terminal alkyne carbons have revealed new reactivity trends in consecutive intramolecular cyclization.^{2e–i} In addition, fascinating cascade cyclizations of benzenoid eneidyne upon dual gold catalysis^{1g} were independently reported by the groups of Hashmi^{2j} and Zhang^{2k} in 2012. Despite these advances, the self-cyclization tendency of eneidyne units in turn causes problems in developing transition-metal-catalyzed intermolecular carbocyclization reactions,³ which have been rarely addressed despite their apparent merits in greatly expanding the scope of potential applications.⁴

We recently developed an efficient single-step procedure to synthesize eneidyne–imides **1**, which can undergo Pd(II)-catalyzed branching cycloisomerization–allylation to give allylfuro[2,3]pyridines via vinylpalladium intermediates **I** (Scheme 1).⁵ Encouraged by this result, we envisaged that an alternative insertion of external alkynes into species **I** followed by subsequent annulation might be achieved through a judicious choice of catalytic system. Herein we report a palladium/copper-catalyzed aerobic cross-coupling–ketoxyoxygenation of eneidyne

Scheme 1. Moiety-Directed Annulations of Acyclic Eneidyne Skeletons




compounds (**1** and **2**) with inner alkynes, leading to isoindolinone and *o*-acylbenzoic acid scaffolds.⁶ As a complement to the Pd(0)-catalyzed highly regioselective enyne–alkyne [4 + 2] cross-benzannulation⁷ established by Gevorgyan and Yamamoto,^{7e–h} this research discloses a formal [4C + 2C] benzannulation–diketonization of eneidyne units and alkynes by a *coupling* and *decoupling* strategy⁸ to override the innate cyclization reactivity of eneidyne.

The initial assays were carried out with eneidyne–imide **1a** and hex-3-yne (**3a**) in DMF at 35 °C (Table 1). While Pd(PPh₃)₄ was ineffective, we found that PdCl₂ (10 mol %) enabled a cross-coupling–oxygenation reaction between **1a** and **3a**, producing 3-hydroxyisoindolinone **4aa** in 45% isolated yield after 12 h (entries 1 and 2). Similar yields of **4aa** indeed were obtained with either high-purity PdCl₂ or Pd(OAc)₂ instead under an air atmosphere (entries 3 and 4).⁹ A stoichiometric amount of PdCl₂ resulted in rapid consumption of **1a** (0.5 h), but no increase in product yield was observed (entry 5). We envisioned that a radical process was possibly involved and that Cu salts might be used as cocatalysts to facilitate this Pd(II)-catalyzed aerobic transformation.¹⁰ Gratifyingly, under air or O₂ (1 atm), addition of 20 mol % CuBr₂ accelerated this reaction, affording **4aa** in 81% and 93% yield, respectively (entries 6 and 7). Switching CuBr₂ to other copper salts did not improve the yield (entries 8 and 9). Although increasing the ratio of **1a** to **3a** would lead to some undetermined byproducts, the use of 2 equiv of alkyne **3a** still gave **4aa** in good yield (entry 10). Further exploration showed that performing the reaction in an aqueous solvent system (10:1 DMF/H₂O) or decreasing the loading of PdCl₂ to 5 mol % had

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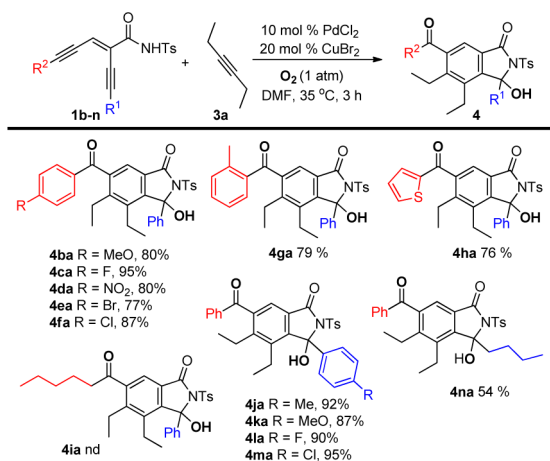
Table 1. Optimization of the Reaction Conditions^a


entry	Pd cat. (mol %)	additive	t (h)	air/O ₂	yield (%) ^b
1	Pd(PPh ₃) ₄	—	12	air	—
2	PdCl ₂	—	12	air	45
3 ^c	PdCl ₂	—	12	air	42
4	Pd(OAc) ₂	—	12	air	41
5	PdCl ₂ (100)	—	0.5	air	44
6	PdCl ₂	CuBr ₂	1.5	air	81
7	PdCl ₂	CuBr ₂	1.5	O ₂	93
8	PdCl ₂	CuI	1.5	O ₂	69
9	PdCl ₂	CuCl ₂	1.5	O ₂	82
10 ^d	PdCl ₂	CuBr ₂	2.0	O ₂	75
11 ^e	PdCl ₂	CuBr ₂	1.5	O ₂	91
12	PdCl ₂ (5)	CuBr ₂	2.0	O ₂	88
13	—	CuBr ₂	12	O ₂	—
14 ^f	PdCl ₂	CuBr ₂	12	—	<5

^aUnless otherwise noted, reactions were conducted at 35 °C on a 0.2 mmol scale of **1a** with **3a** (1.0 mmol), Pd catalyst (10 mol %), and additive (20 mol %) in DMF (1.6 mL) in air or under 1 atm O₂. ^bIsolated yields. ^cPdCl₂ (99.999% purity) was used. ^d0.4 mmol of **3a** was used. ^eIn 10:1 DMF/H₂O. ^fUnder N₂.

little influence on the reaction outcome (entries 11 and 12). In contrast, no desired product was detected in the absence of Pd catalyst, and only a trace of **4aa** was observed under N₂ (entries 13 and 14). These blank tests clearly indicated that both Pd(II) catalyst and O₂ are required for this reaction.

The scope of this reaction was then explored with a range of substituted enediyne–imides **1** (Scheme 2). Variation of R¹ and

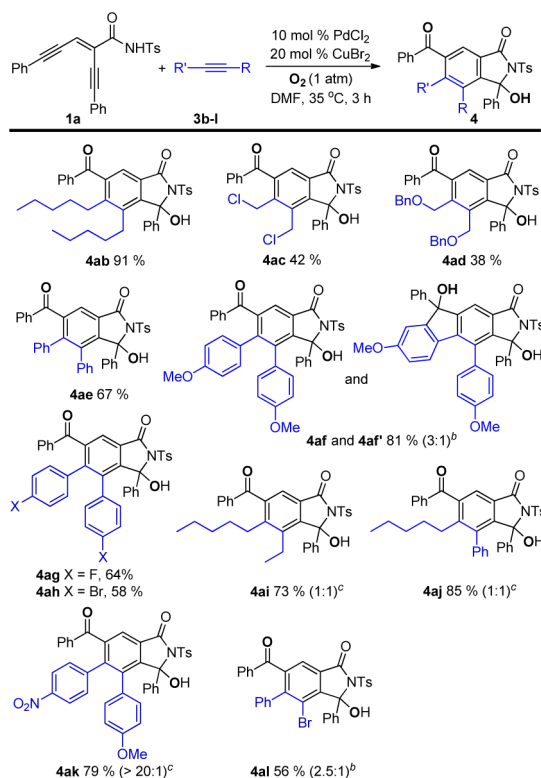
Scheme 2. Reactions of **1** and Alkyne **3a**^a

^aEnediyne **1** (0.2 mmol) and **3a** (1.0 mmol) in DMF (1.6 mL) for 3 h. nd = not detected. The yields are of the isolated products.

R² showed that benzene rings with an electron-donating group (–OMe) or an electron-withdrawing group (–F or –NO₂) as well as *o*-methyl were tolerated, leading to the corresponding products in 79–95% yield. The reaction conditions are compatible with Br and Cl, which are convenient handles for further functionalization (**4ea**, **4fa**, and **4ma**). Moreover, a heteroaromatic ring (2-thienyl) could be used in this reaction to

give **4ha** in 76% yield. It was found that employing an aryl group as R² is critical for this reaction. For example, while **1i** (R¹ = Ph, R² = *n*-C₅H₁₁) resulted in a complex transformation without any detectable **4ia**, enediyne **1n** (R¹ = *n*-Bu, R² = Ph) was a suitable substrate to afford **4na**, albeit in relatively low yield.

Next, the scope of this reaction with respect to alkynes **3** was studied (Scheme 3). Symmetrical alkynes bearing alkyl

Scheme 3. Reactions of **1a** and Alkynes **3a**^a

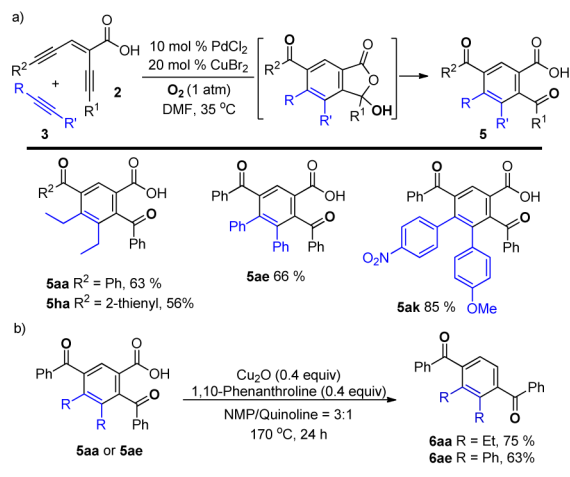
^aEnediyne **1a** (0.2 mmol) and **3** (1.0 mmol) in DMF (1.6 mL) for 3 h. ^bDetermined from the isolated yields. ^cDetermined by ¹H NMR analysis. The yields are of the isolated products.

substituents, including α -heteroatom-substituted compounds **3c** and **3d**, could participate in the process, although the yields of the corresponding products **4ac** and **4ad** were lower than that of **4ab**. Diaryl-substituted alkynes, some with electron-withdrawing and -donating groups, reacted smoothly to give **4ae**–**4ah** in decent yields. When 1,2-bis(4-methoxyphenyl)ethyne (**3f**) was used as the coupling partner, an intramolecular hydroarylation occurred, affording alcohol **4af'** as a pair of diastereoisomers in addition to the targeted product **4af**. Nonsymmetrical dialkyl and aryl alkyl alkynes provided **4ai** and **4aj**, respectively, with nearly 1:1 regioselectivity in good yield. Pleasingly, captodative diarylethyne **3k** having strong electron-biased groups (–OMe and –NO₂) at the para positions of the phenyl rings was converted to **4ak** with >20:1 regioselectivity in 79% yield. The challenging (bromoethynyl)-benzene (**3l**) still successfully underwent this coupling–oxygenation reaction, affording **4al** in 56% yield with 2.5:1 regioselectivity.

Intriguingly, a set of enediyne–carboxylic acids **2** derived from **1** or their ester precursors¹¹ smoothly underwent the cross-coupling–oxygenation with **3a** without any modification to the standard conditions for **1**, giving diketones **5aa** and **5ha** instead of the corresponding 3-hydroxyphthalide products because of

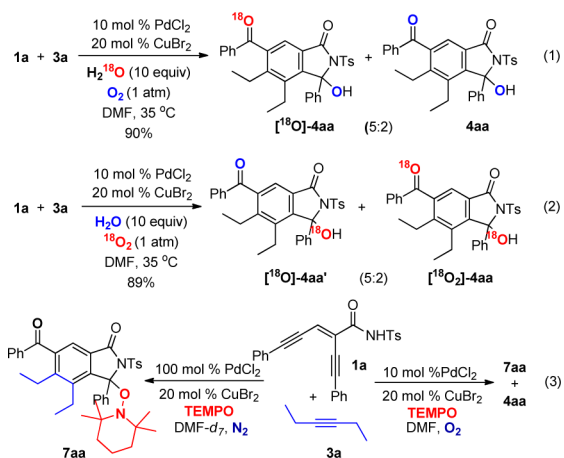
ring–chain tautomerism (Scheme 4a).^{12,6} 1,2-Diphenylethyne (3e) was also compatible with this reaction, delivering 5ae in

Scheme 4. Cyclization of Eneidyne–Carboxylic Acids 2 and Alkynes 3 and Protodecarboxylation of 5



66% yield. As expected, subsection of 2a to the pull–push alkyne 3k afforded Sak with excellent regioselectivity (>20:1) in 85% yield. Subsequent removal of the CO₂H group of 5 by Cu-catalyzed protodecarboxylation¹³ provided an efficient approach for the regioselective preparation of 1,4-diacylbenzenes 6aa and 6ae, which would be difficult to prepare by conventional methods (Scheme 4b).

To gain insight into the reaction mechanism, control experiments with ¹⁸O₂ and/or H₂¹⁸O isotopic labeling were performed. Exposure of 4aa to 10 equiv of H₂¹⁸O under the standard conditions did not form any obvious ¹⁸O-labeled products after 12 h, as detected by HRMS. The reaction in the presence of H₂¹⁸O under ¹⁶O₂ afforded [¹⁸O]4aa and 4aa (5:2) in 90% combined yield (eq 1). In contrast, [¹⁸O]4aa' and [¹⁸O₂]

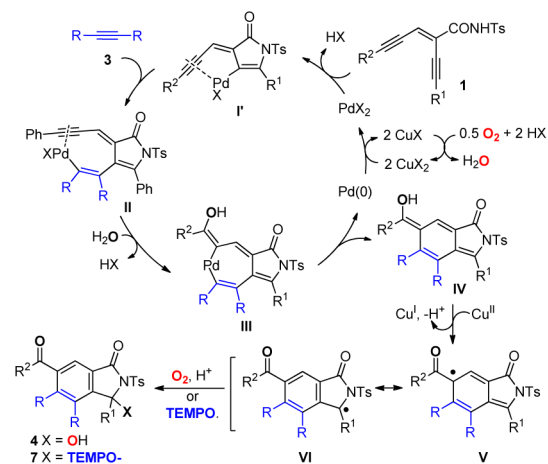


4aa (5:2) were obtained when ¹⁸O₂ (1 atm) and H₂¹⁶O were used (eq 2). These isotopic labeling results clearly indicated that the oxygen atom in the hydroxyl group of 4aa is wholly from O₂ while the ketonic oxygen comes from H₂O, presumably via a Wacker-type oxidation reaction of the alkyne.¹⁴ Incomplete incorporation of the ¹⁸O label into the ketone group was likely due to the competing attack of both adventitious water and in situ-generated water arising from catalyst regeneration with O₂ as the terminal oxidant.

Furthermore, in the presence of stoichiometric 2,2,6,6-tetramethyl-1-piperidine-1-oxyl (TEMPO), the reaction of 1a and 3a upon treatment with PdCl₂ (100 mol %) and CuBr₂ (20 mol %) in DMF-*d*₇ under N₂ cleanly yielded TEMPO adduct 7aa after 0.5 h,¹⁵ while the standard conditions provided a mixture of 4aa and 7aa (eq 3). These results hinted that a benzyl radical is generated in this process and would be responsible for the subsequent O₂ activation.

On the basis of the above observations, a proposed reaction pathway is depicted in Scheme 5. Initial 5-endo cyclization of 1a

Scheme 5. Proposed Reaction Pathway



through an intramolecular anti aminopalladation would provide vinylpalladium species I',¹⁶ which may carry out a syn carbopalladation onto external alkyne 3 to afford intermediate II. Presumably because of electronic effects of the remote conjugated carbonyl group, the regioselective nucleophilic attack of H₂O on the triple bond of II followed by reductive elimination would release enol IV and a Pd(0) species, which could be oxidized to the Pd(II) catalyst using O₂ as the terminal oxidant.¹⁷ Subsequent one-electron oxidation¹⁸ of the enol moiety of IV facilitated by Cu(II) species would afford benzyl radical VI, probably via putative radical V in favor of aromatization. Thereafter, VI would react with O₂ to afford product 4, presumably through Fenton-type fragmentation of intermediate superoxo radicals.¹⁹ On the other hand, trapping of radical VI with TEMPO would give adduct 7.

In conclusion, we have presented a palladium/copper-catalyzed aerobic cross-coupling–ketoxyoxygenation of enediyne–carboxylic compounds and inner alkynes involving O₂ activation at room temperature. Upon combination of the [4 + 2] cross-cyclization with aromatization, this process simultaneously enables the formation of benzene rings and the regioselective incorporation of two oxygen atoms from atmospheric molecular oxygen and H₂O, respectively. This study discloses the feasibility of using a *coupling* and *decoupling* strategy to override the self-cyclization reactivity of enediyne skeletons for intermolecular cyclization.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data for 4ea, 4ak, and 5aa (CIF), experimental procedures, and characterization data for new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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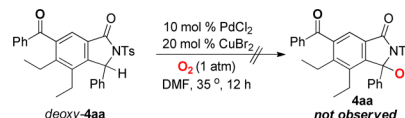
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