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Copper-Catalyzed Radical [2 + 2 + 1] Annulation of Benzene-Linked 1,*n*-Enynes with Azide: Fused Pyrroline Compounds

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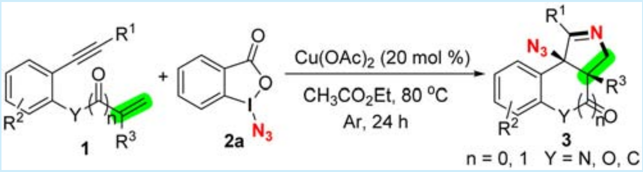
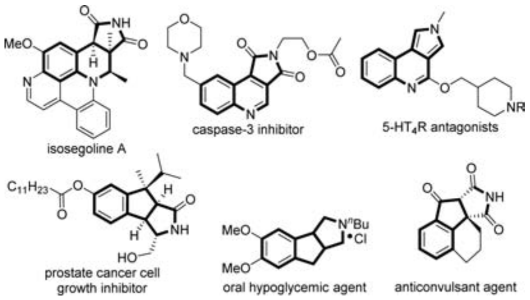
S *Supporting Information*

ABSTRACT: A novel selective copper-catalyzed radical [2 + 2 + 1] annulation of benzene-linked 1,*n*-enynes with azido-benziodoxolone to access fused pyrroline compounds, including 3*H*-pyrrolo[3,4-*c*]quinolin-4(3*aH*)-ones, chromeno-[3,4-*c*]pyrrol-4(9*bH*)-one, and indeno[1,2-*c*]pyrroline, has been developed, which proceeds via the addition of the azide radical to the alkene, annualtion, and azidation cascade.



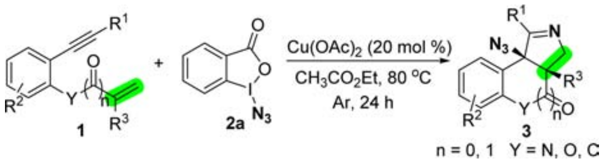
Straightforward assembly of fused polycyclic heteroarene hydrocarbons is important and continues to attract the attention of synthetic chemists due to the unique inherent characteristics and wide applications of these compounds[1] such as fused pyrrole molecules (Scheme 1),[2] which are prevalent structural motifs in various natural products, pharmaceuticals, and functional materials. Despite their importance, the available synthetic methods to access these fused pyrroline frameworks often require several steps and/or the use of unavailable starting materials.[2,3] Thus, a strongly desirable alternative for assembling these scaffolds would involve a one-step approach, but obstacles such as functional-group tolerance and selectivity issues make this strategy formidably challenging.

Scheme 1. Important Examples of Nitrogen-Containing Five-Membered-Cyclic-Ring-Fused Molecules



The [2 + 2 + 1] annulation reaction has emerged as a powerful and straightforward means to build five-membered cyclic systems.[4−6] There have been remarkable advances in terms of selectivity and molecular complexity construction in this reaction. While assembly of diverse fused five-membered carbocyclic compounds is permitted through the [2 + 2 + 1] annulation of 1,*n*-enynes with a one-carbon unit (CO,[5] ethers,[6a] cycloalkanes,[6b] etc.), no examples of a catalytic 1,*n*-enyne [2 + 2 + 1] annulation for the construction of fused pyrroline scaffolds have been reported. Azides are recognized as one of the most common nitrogen resources for the synthesis of nitrogen-containing compounds, including nitrogen-containing cyclic molecules.[7−9] In this context, the azide radical-mediated strategy is particularly attractive for the functionalization of alkenes.[8] On this basis, we envisioned that the 1,*n*-enyne [2 + 2 + 1] annulation might be triggered by the addition of the azide radical to the alkene moiety, in which the azide is used as a one-nitrogen unit. Herein, we report a novel copper-catalyzed, azide radical-mediated, [2 + 2 + 1] annulation/azidation of benzene-linked 1,*n*-enynes (*n* = 6, 7) with azido-benziodoxolone, which enables the one-step synthesis of various fused pyrroline molecules, including 3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-ones, chromeno[3,4-*c*]pyrrol-4(9b*H*)-one, and indeno[1,2-*c*]-pyrroline (Scheme 2).

Scheme 2. [2 + 2 + 1] Annulation/Azidation of 1,*n*-Enynes with Azide



Our investigation started with the [2 + 2 + 1] annulation of *N*-methyl-*N*-(2-(phenylethynyl)phenyl)methacrylamide (**1a**) with azido-benziodoxolone (**2a**) for reaction condition optimization (Table 1). Gratifyingly, when 1,7-enyne **1a** was treated with 3 equiv of azido-benziodoxolone (**2a**) and 20 mol % $Cu(OAc)_2$ in CH_3CO_2Et at 80 °C for 24 h, it afforded the desired 9*b*-azido-5,9*b*-dihydro-3*H*-pyrrolo[3,4-*c*]quinolin-4-

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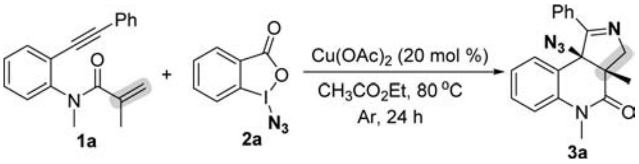
Table 1. Screening of Optimal Conditions[a]



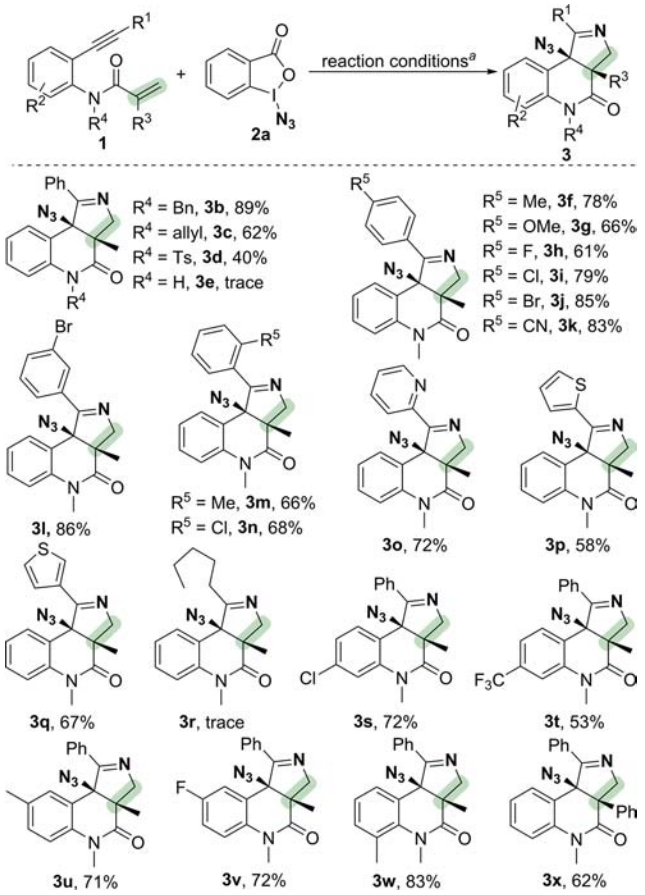
entry	variation from the standard conditions	yield (%)[c]
1	none	75
2	**2a** (2 equiv) for 36 h	61
3	**2a** (2.5 equiv) for 36 h	67
4	$TMSN_3$ or NaN_3 instead of **2a**	0
5	$CuCl_2$ instead of $Cu(OAc)_2$	60
6	$CuBr_2$ instead of $Cu(OAc)_2$	55
7	$Cu(acac)_2$ instead of $Cu(OAc)_2$	48
8	CuOAc instead of $Cu(OAc)_2$	50
9	$Cu(OAc)_2$ (10 mol %)	58
10	without $Cu(OAc)_2$	trace
11	1,4-dioxane instead of CH_3CO_2Et	57
12	DMF instead of CH_3CO_2Et	42
13	CH_2ClCH_2Cl instead of CH_3CO_2Et	55
14	100 °C	73
15	50 °C	32
16[b]	none	71

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (3 equiv), $Cu(OAc)_2$ (20 mol %), CH_3CO_2Et (3 mL), argon, 80 °C, and 24 h. Only cis (9*b*-azido/3*a*-methyl)-isomer was observed as determined by ^1H NMR spectroscopic analysis of the crude product. [b]**1a** (1 g, 3.64 mmol) for 48 h. [c]Isolated yield.

(3*aH*)-one (**3a**)[11] in the highest yield (75%; entry 1). Further screening revealed that lowering the amount of azidobenziodoxolone (**2a**) led to a decrease in yield (entries 2−3). However, no desired product **3a** was observed when using $TMSN_3$ or when NaN_3 replaced azidobenziodoxolone (**2a**) (entry 4). A series of other Cu salts, such as $CuCl_2$, $CuBr_2$, $Cu(acac)_2$, and CuOAc, were subsequently examined (entries 5−8): they displayed high catalytic activity for the annulation but were less efficient than $Cu(OAc)_2$. It was noted that the absence of Cu catalysts led to no formation of the desired product **3a** (entry 10). Other solvents, such as 1,4-dioxane, DMF, and CH_2ClCH_2Cl, were found to be less effective than CH_3CO_2Et (entries 11−13 versus entry 1). While at 100 °C the product **3a** was afforded in the same yield as at 80 °C (entry 14), the temperature at 50 °C sharply decreased the yield to 32% (entry 15). Notably, the standard conditions were applicable to the gram-scale synthesis of **3a** in 71% yield (entry 16).

With the standard conditions, the scope of this copper-catalyzed [2 + 2 + 1] annulation of benzene-linked 1,*n*-enynes was examined in the presence of azido-benziodoxolone (**2a**) (Schemes 3 and 4). Initially, the substitution effect of the nitrogen atom was investigated (**3b−e**; Scheme 3): Whereas 1,7-enynes **1b−d**, bearing a benzyl group, an allyl group, or a tosyl group on the nitrogen atom, are viable to construct 3*H*-pyrrolo[3,4-*c*]quinolin-4(3*aH*)-ones **3b−d** in moderate to good yields, 1,7-enyne **1e** with a free *N*-H group was inert and resulted in no formation of **3e**. Gratifyingly, several substituents, namely Me, MeO, F, Cl, Br and CN, on the aromatic ring at the terminal alkyne were well tolerated (**3f−n**). For example, *p*-Me- or *o*-Me-substituted 1,7-enynes **1f** and **1m** successfully furnished **3f** and **3m** in 78% and 66% yields, respectively. Halogen groups, F, Cl, and Br, were also

Scheme 3. Variation of the 1,7-Enynes[a]



[a]Reaction conditions: **1** (0.3 mmol), **2a** (3 equiv), $Cu(OAc)_2$ (20 mol %), CH_3CO_2Et (3 mL), argon, 80 °C and 24 h. Only cis (9*b*-azido/3*a*-substituent)-isomer was observed as determined by ^1H NMR spectroscopic analysis of the crude product.

compatible with the optimal conditions (**3h−j**, **3l**, **3s**, and **3v**), which will enable subsequent modifications at the halogenated positions. In the case of the pyridin-2-yl-, thiophen-2-yl-, and thiophen-3-yl-containing alkynes **1o−q**, the corresponding heteroaryl-containing products **3o−q** were constructed in 58−72% yields. However, aliphatic alkyne **1r** had no reactivity for the formation of **3r**. The standard conditions were found to be compatible with a number of substituents, including Cl, CF_3, Me, and F, on the aromatic ring of the aniline moiety (**3s−w**). Using 5-Cl- or 5-CF_3-substituted 1,7-enynes **1s** and **1t**, the reaction achieved moderate to high yields (**3s−t**). 1,7-Enynes **1u** and **1v** with a Me group or a F group at the 4 position were converted to **3u** and **3v** in good yields. Because the bulky 6-Me-substituted 1,7-enyne **1w** showed good reactivity, the product **3w** was obtained in 83% yield. Interestingly, the standard conditions were applicable to the synthesis of **3x** in 62% yield when starting from 1,7-enyne **1x** with a Ph group on the 2 position of the acrylamide moiety.

As shown in Scheme 4, chromeno[3,4-*c*]pyrrol-4(9*bH*)-one **3y** was successfully constructed from phenol-linked 1,7-enyne **1y** under the standard conditions with 1.5:1 dr because the electronegativity oxygen was larger than that of nitrogen (eq 1). Interestingly, this [2 + 2 + 1] annulation reaction could be extended to benzene-linked 1,6-enyne, giving the indeno[1,2-*c*]pyrroline **3z** in 55% yield (eq 2). Unfortunately, *N*-methyl-*N*-(2-(phenylethynyl)phenyl)cinnamamide **1aa** was not a suitable

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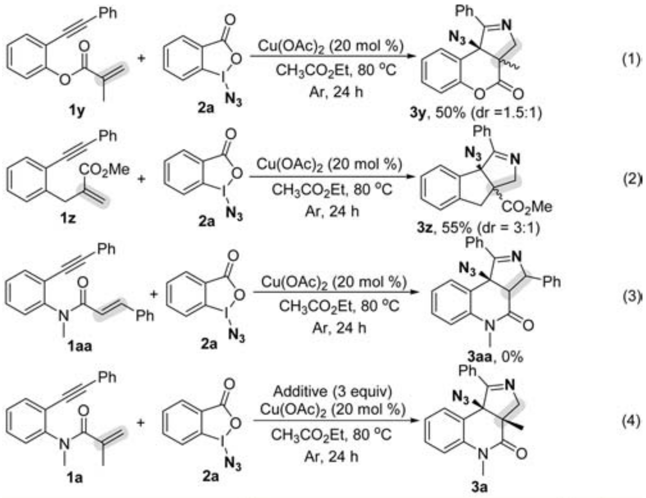
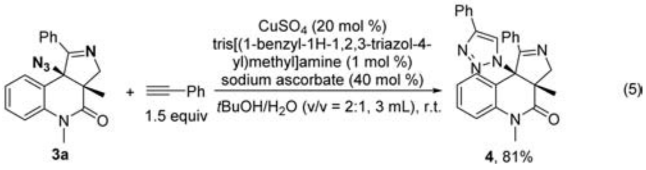
Scheme 4. Control Experiments and Utilization of Product 3a



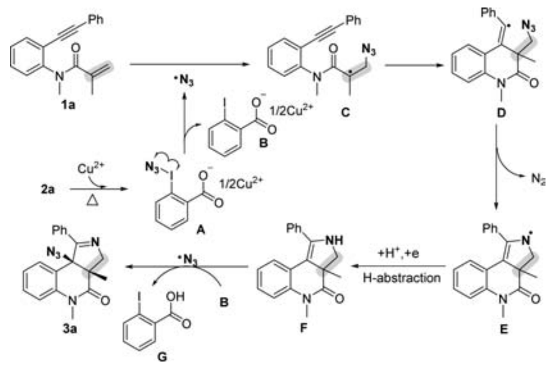
additive	yield of **3a**
TEMPO	trace
hydroquinone	trace
2,6-di-tert-butyl-4-methylphenol (BHT)	trace



substrate (eq 3). The reaction of 1,7-enyne **1a** with azido-benziodoxolone (**2a**) was completely suppressed by a stoichiometric amount of radical inhibitors, including TEMPO, hydroquinone, and BHT (eq 4), implying that this reaction includes a radical process[9] (the radical intermediates could not be isolated according to the reported papers[9d]). Interestingly, treatment of product **3a** with 1.5 equiv of ethynylbenzene, CuSO$_4$, tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)-methyl]amine (TBTA), sodium ascorbate, and a mixture of *t*BuOH and H$_2$O delivered 3*a*,5-dimethyl-1-phenyl-9*b*-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-3,3*a*,5,9*b*-tetrahydro-4*H*-pyrrolo-[3,4-*c*]quinolin-4-one **4** in 81% yield (eq 5, Scheme 4).[10]

Based on the present results and the literature studies, the possible mechanism for this [2 + 2 + 1] annulation reaction is shown in Scheme 5.[6−8,10] Initially, an azide radical is generated from azido-benziodoxolone **2a** with the aid of the active Cu^{2+} species under heating and forms N$_3$-containing 2-iodo-benzoate **A**. Decomposition of **A** gives copper(II) salt **B**, with simultaneous release of a relatively stable azide radical. Subsequently, the addition of the azide radical to the alkene moiety of enyne **1a** affords alkyl radical intermediate **C**. The intermediate **C** readily undergoes cyclization with the alkyne moiety to give vinyl radical intermediate **D**, and then an aminyl radical **E** forms, through intramolecular addition of an vinyl radical to an azido group, followed by the loss of N$_2$. Radical **E** is transformed into intermediate **F** via H-abstraction or a reduction−protonation sequence. Finally, the addition of another azide radical to the alkene moiety of intermediate **F** and deprotonation by 2-iodobenzoate **B** furnish the desired product **3a** and 2-iodobenzoic acid **G**.

Scheme 5. Possible Mechanisms



In summary, we have developed the first method toward highly important fused pyrroline molecules, including 3*H*-pyrrolo[3,4-*c*]quinolin-4(3a*H*)-ones, chromeno[3,4-*c*]pyrrol-4-(9*bH*)-one, and indeno[1,2-*c*]pyrroline, by using copper-catalyzed azide radical-mediated [2 + 2 + 1] annulation/azidation of benzene-linked 1,*n*-enynes (*n* = 6, 7) with azido-benziodoxolone. This method provides an efficient and practical avenue to incorporate a nitrogen atom from azido-benziodoxolone into the five-membered cyclic system. Moreover, an azido group was also introduced into the products, thus providing the potential for additional modification of the product. Further studies on the mechanism and applications of this [2 + 2 + 1] annulation method are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03040.

Descriptions of experimental procedures for compounds and analytical characterization (PDF)

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Notes

The authors declare no competing financial interest.

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(11) CCDC 1413636 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3a