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Copper-Catalyzed Three-Component Carboamination of Arynes: Expeditious Synthesis of *o*-Alkynyl Anilines and *o*-Benzoxazolyl Anilines

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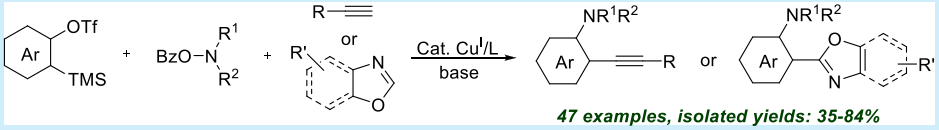
Supporting Information



ABSTRACT: A copper-catalyzed three-component reaction of in situ formed arynes, terminal alkynes, and *O*-benzoylhydroxylamines has been developed. By adjusting reaction conditions, the nucleophiles in this transformation can be extended from terminal alkynes to benzoxazoles. These procedures provide a modular and facile approach to *o*-alkynyl anilines and *o*-benzoxazolyl anilines from easily available substrates in only one step.

Anilines exist widely in biologically active natural products, valuable pharmaceuticals, and significant synthetic building blocks.[1,2] Although numerous powerful methodologies toward formation of C(sp^2)−N bonds have been developed recently,[3−5] the general and practical routes to access *ortho*-substituted anilines have still been limited. Traditional methods usually make use of coupling reactions of 1,2-dihaloarenes or *o*-iodoanilines to achieve this goal. However, it is not easy to regulate the stepwise coupling reactions and the approaches are restricted to the availability of the starting materials. As an umpolung strategy of traditional cross-couplings, electrophilic amination has been a significant tool for constructing C−N bonds.[6] By merging the electrophilic amination and Catellani reaction, *o*-alkynyl anilines can be easily prepared via the Pd-catalyzed multicomponent reaction of *ortho*-substituted aryl iodides, electrophilic aminating agents, and alkyne precursors (Figure 1A).[7] Nevertheless, when aryl iodides bearing no *ortho* substituent were used, two amino groups were introduced at the adjacent positions to iodine through C−H bond activation. And terminal alkynes cannot be directly used in this reaction.

Simultaneously, transition-metal-catalyzed aryne chemistry has become a powerful platform for 1,2-difunctionalization of arenes.[8−10] In this field, Greaney et al. developed a Cu-catalyzed one-pot reaction of arynes, heteronucleophiles, and *O*-benzoylhydroxylamines affording 1,2-dihetero-functionalized arenes in high yields (Figure 1B).[10t] Xu et al. reported a Cu-catalyzed multicomponent reaction of arynes, terminal alkynes, and electrophilic sulfenylating reagents to synthesize *o*-alkynyl arylsulfides (Figure 1C).[10v] From the perspective of mechanism, the fundamental mode of these reactions can be described as nucleophilic addition to arynes and successive electrophilic trap tandem reactions. In contrast with the strategy of precious-metal-catalyzed C−H activation, these

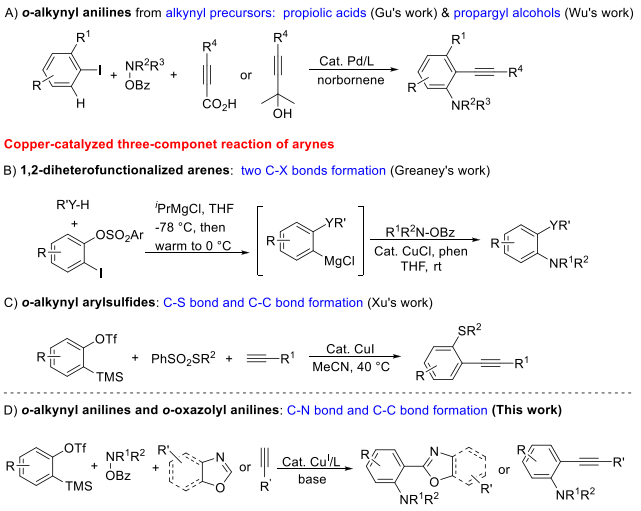


Figure 1. Strategies to synthesize *ortho*-substituted anilines using electrophilic aminating reagents.

transformations can be realized with non-noble copper catalysts.

In this context, we conceived that the copper-catalyzed three-component reaction of in situ formed benzynes, carbon nucleophiles, and electrophilic aminating reagents would provide a modular and facile synthetic approach to *ortho*-substituted anilines (Figure 2). Although the design of this reaction is relatively mature, there are still several challenges to overcome: (1) the direct amination of *int*-**I** to generate byproduct **5** through *path A*;[11] (2) the direct protonation of

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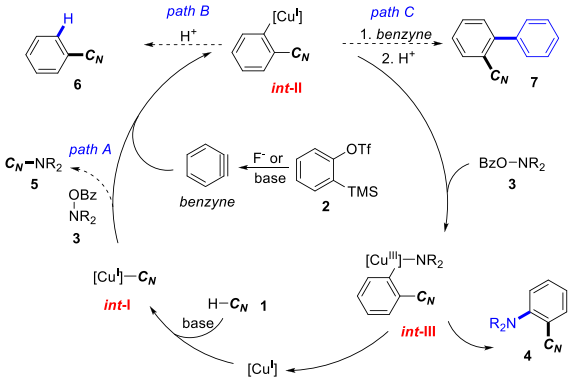
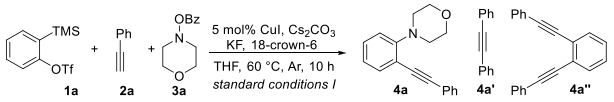


Figure 2. Proposed mechanism of the copper-catalyzed carboamination of benzynes to *ortho*-substituted anilines.

int- **II** to generate byproduct **6** through *path B*;[10e] (3) the insertion of another benzyne into the C−Cu bond of *int*-**II** and sequential protonation to generate byproduct **7** through *Path C*.[10f,g] To avoid these undesirable side reactions in our transformation, it is essential to select reactivity-matched carbon nucleophiles, seek appropriate catalysts and ligands, and control the benzyne formation rate by using suitable fluorides and bases. In continuation of our interest in transition-metal-catalyzed benzyne chemistry,[12] we herein report our preliminary results in this issue: a copper(I)-catalyzed multi component reaction of Kobayashi reagents, terminal alkynes/benzoxazoles, and *O*-benzoylhydroxylamines to afford *ortho*-substituted anilines (Figure 1D).

First, we optimized the conditions of the model reaction of *Kobayashi* reagent **1a**, alkyne **2a**, and *O*-benzoylhydroxylamine **3a** (Table 1). The 5 mol % CuI catalyzed process at 60 °C in tetrahydrofuran (THF) in the presence of KF, Cs_2CO_3, and 18-crown-6 furnished *o*-alkynyl aniline **4a** in 82% isolated yield (entry 1). Control experiments established the importance of

Table 1. Reaction Condition Optimization I



entry	variation of the *standard conditions I*	isolated yield (%)[b] **4a**/**4a′**/**4a′′**
1	none[a]	**82**/**<5**/**<5**
2	CsF instead of KF	60/11/16
3	without 18-crown-6, CsF instead of KF	44/9/31
4	K_2CO_3 instead of Cs_2CO_3	66/11/21
5	DBU instead of Cs_2CO_3	trace/47/19
6	DIPEA instead of Cs_2CO_3	67/9/19
7	toluene instead of THF	24/8/17[c]
8	$Cl_2CHCHCl_2$ instead of THF	18/10/11[d]
9	room temperature instead of 60 °C	58/9/11[e]
10	volume of THF was changed to 4.0 mL	65/11/16
11	volume of THF was changed to 2.0 mL	61/5/5

[a]0.26 mmol of **1a**, 0.26 mmol of **2a** and 0.20 mmol of **3a** in 2.5 mL of THF in the presence of 0.40 mmol of Cs_2CO_3, 0.40 mmol of KF, 0.40 mmol of 18-crown-6, and 0.01 mmol of CuI. [b]The yield of **4a** was calculated on the basis of **3a**. The yields of **4a′** and **4a′′** were calculated on the basis of **2a**. [c]37% **3a** was recovered. [d]51% **3a** was recovered. [e]19% **3a** was recovered.

the fluorine resource and base in our reaction (entries 2−6). The solvent, temperature, and concentration of substrates also have significant impact to this transformation. When the THF was replaced with toluene or 1,2-dichloroethane, the yield of **4a** decreased greatly (entries 7, 8). The reaction was also enabled at room temperature, but in a low yield (entry 9). A specific substrate concentration is necessary for the reaction (entries 10, 11). We believe that all these factors affect the formation rate of benzyne and the concentration of various active intermediates, thus affecting the efficiency and selectivity of the reaction. The unexpected byproduct **4a′′** might be produced from the attack of terminal alkynes on *int*-**III**. In this side reaction, electrophilic amination reagents only act as oxidants.

Then, we proceeded to study the scope of the substrates (Figure 3). Substituent phenyl alkynes with either an electron-donating or electron-withdrawing group on the *ortho*-, *meta*-, and *para*-position of the benzene ring were able to undergo the three-component reaction to generate the corresponding products in good to excellent yields (**4b**−**4i**). Vinyl and alkyl alkynes have also proven to be useful starting materials for the efficient construction of *o*-alkynyl anilines (**4j**−**4o**). Besides,

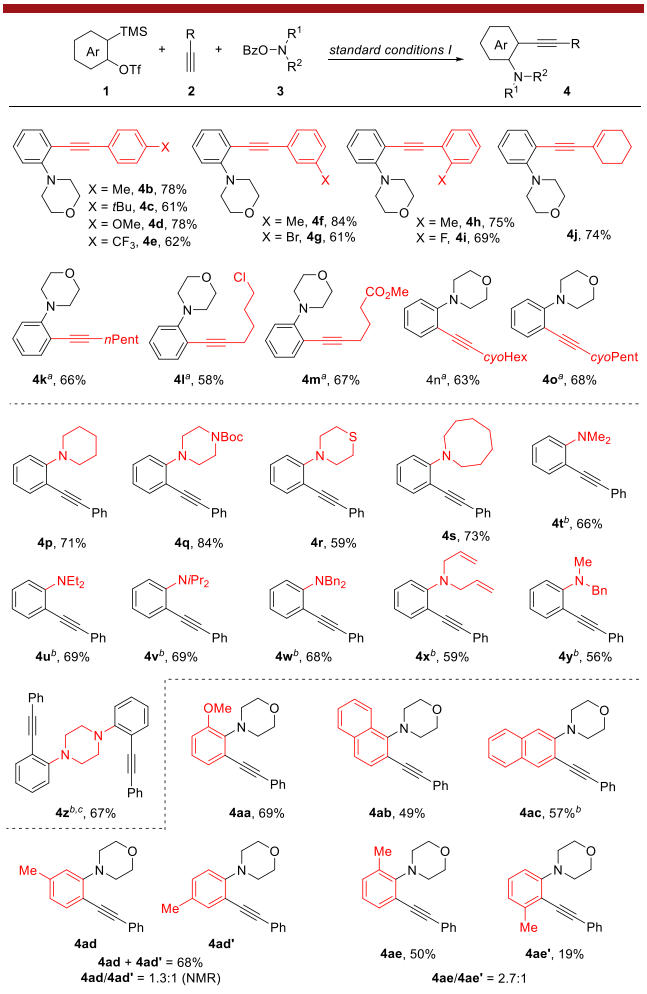


Figure 3. Scope of the three-component reaction of benzyne precursors, terminal alkynes, and *O*-benzoylhydroxylamines. Unless otherwise noted, all the reactions were carried out under the *standard conditions I* in Table 1. [a] 5 mol % CuI/dppb was used as catalyst. [b] 10 mol % CuI/dppb was used as catalyst. [c] 0.52 mmol of **1a**, 0.52 mmol of **2a**, and 0.20 mmol of **3l** in 8 mL of THF.

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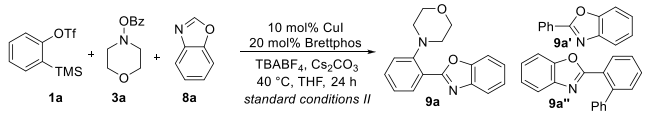
the reaction conditions were compatible with alkyl, bromide, chloride, fluoride, methoxy, ester, and trifluoromethyl groups. Further exploration demonstrated that the reaction proceeded successfully with a variety of *N*,*N*-disubstituted *O*-benzoylhydroxylamines (**4p**−**4z**). Remarkably, the allyl or benzyl substituted amine products (**4w**−**4y**) can be easily converted to corresponding primary or secondary amines. Gratifyingly, the electrophilic aminating reagent with two active sites prepared from piperazine can also participate in this reaction smoothly, producing highly symmetrical *o*-alkynyl aniline (**4z**). Various aryne precursors can also be effectively used in this reaction (**4aa**−**4ae**). Only one regioisomer (**4aa**) could be efficiently generated from 3-methoxyl substituted silylphenyl triflate.[13] Additionally, *o*-alkynyl naphthylamine **4ab** or **4ac** could be obtained from the corresponding silylnaphthyl triflate in a moderate yield. The 4-methyl substituted silylphenyl triflate gave a 1.3:1 mixture of inseparable **4ad** and **4ad′** in a 68% overall isolated yield. When 3-methyl substituted silylphenyl triflate was used, **4ae** and **4ae′** were isolated in 50% and 19% yields, respectively.

Encouraged by these results, we were devoted to searching for other carbon nucleophiles to further expand the range of substrates for the transformation. As already known, the acidity of the active hydrogen of benzoxazole is slightly weaker than that of the terminal alkyne. Therefore, electron-deficient heterocyclic arenes such as benzoxazoles are carbon nucleophiles similar to terminal alkynes under alkaline conditions in the precence of a transition-metal catalyst. Based on this inference, we designed a copper-catalyzed model reaction of benzyne precursor **1a**, *O*-benzoylhydroxylamine **3a**, and benzoxazole **5a** and optimized the reaction conditions (Table 2). We found the ligand used in this reaction was critical. When other ligands were utilized instead of Brettphos, the yield of **9a** was greatly reduced (entries 3−12). Different from the common practice, this reaction did not need a fluoride source[14] and the phase transfer regent was tetrabutyl ammonium tetrafluoroborate (entries 13−15). Next, the substrate range for the three-component reactions involving benzoxazoles was investigated (Figure 4). A series of *o*-benzoxazolyl anilines which are difficult to prepare by other means were efficiently produced in satisfactory yields from the combinations of various benzoxazoles, electrophilic aminating reagents, and benzyne precursors. It is worth noting that the **9m** and **9n** are both unique isomers in their reactions. Besides, the structure of **9p** (CCDC 1906945) was confirmed by X-ray crystallography. Although the yield was low, oxazole can also participate in this reaction to afford product **9i**. We also tried benzothiazoles, but no corresponding product was obtained under the reaction conditions. It may be due to the relatively weak nucleophilicity of benzothiazoles compared with benzoxazoles.

Finally, further transformations of the generated *o*-alkynyl aniline **4a** were investigated (Figure 5). 3-Aroyl oxazino[4,3-*a*]indole **10** could be achieved from **4a** through an efficient Cu(I)-catalyzed oxidative reaction.[15a] And in the presence of iodine, **4a** could be converted into 3-iodo indole **11** in an excellent yield.[15b]

In summary, based on the understanding of the benzyne difunctionalization mechanism, we have developed a copper-catalyzed three-component reaction of aryne precursors, terminal alkynes/benzoxazoles, and electrophilic aminating reagents. It provides an efficient and modular approach to *o*-alkynyl anilines and *o*-benzoxazolyl anilines which are otherwise difficult to prepare. These reactions show excellent functional group compatibility and can be realized from readily available starting materials in only one step. We believed that

Table 2. Reaction Condition Optimization II



entry	variation of the *standard conditions II*	isolated yield (%)[b] **9a**/**9a′**/**9a′′**
1	none[a]	**62**/−/**9**
2	$Cu(MeCN)_4BF_4$ instead of CuI	21/17/−
3	*t*BuBrettphos instead of Brettphos	40/−/21
4	Xphos instead of Brettphos	48/−/15
5	*t*BuXphos instead of Brettphos	trace/−/−[c]
6	Sphos instead of Brettphos	34/−/15
7	*i*PrSphos instead of Brettphos	32/−/11
8	Johnphos instead of Brettphos	23/8/11
9	Xantphos instead of Brettphos	trace/17/12
10	10 mol % dppb instead of Brettphos	37/11/−
11	PPh_3 instead of Brettphos	17/12/−
12	Without Brettphos	0/0/0[d]
13	18-crown-6 instead of $TBABF_4$	29/10/−
14	TBAF instead of $TBABF_4$	trace/<5/−[c]
15	CsF instead of Cs_2CO_3	12/25/11

[a]0. 60 mmol of **1a**, 0.20 mmol of **3a**, and 0.26 mmol of **8a** in 3.0 mL of THF in the presence of 0.80 mmol of Cs_2CO_3, 0.80 mmol of $TBABF_4$, 0.04 mmol of Brettphos, and 0.02 mmol of CuI. [b]The yield of **9a** was calculated on the basis of **3a**. The yields of **9a′** and **9a′′** were based on **8a**. [c]Complex mixtures. [d]95% **8a** was recovered.

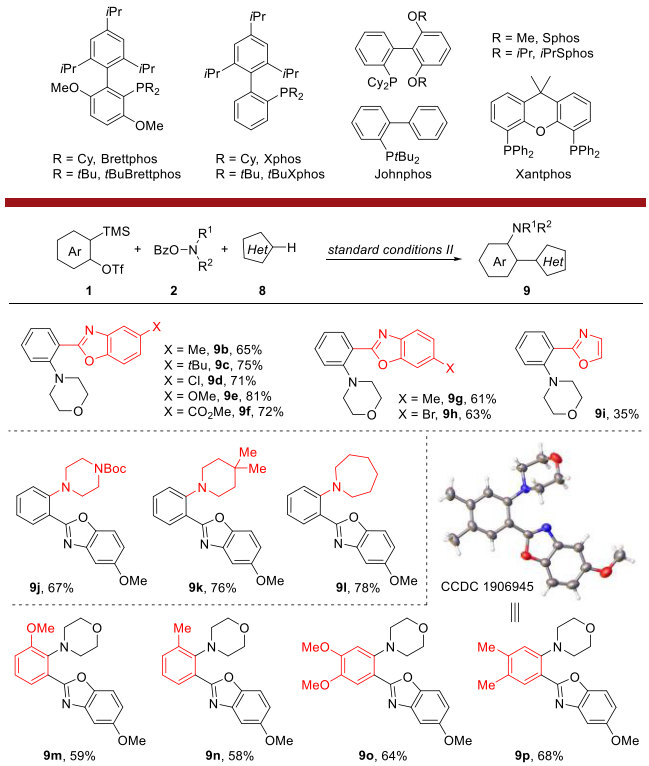


Figure 4. Scope of the three-component reaction of benzyne precursors, benzoxazoles, and *O*-benzoylhydroxylamines. Unless otherwise noted, all the reactions were carried out under the *standard conditions II* in Table 2.

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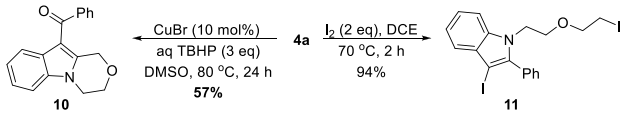

Figure 5. Further transformations of *o*-alkynyl aniline **4a**.

the scope of carbon nucleophiles used in this transformation can be continuously enlarged in future research.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01427.

Detailed experimental procedures, characterization data, and copies of the ^{1}H and ^{13}C NMR spectra for all previously unknown products (PDF)

Accession Codes

CCDC 1906945 contains 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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