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Gold/Copper-Co-catalyzed Tandem Reactions of 2-Alkynylanilines: A Synthetic Strategy for the C2-Quaternary Indolin-3-ones

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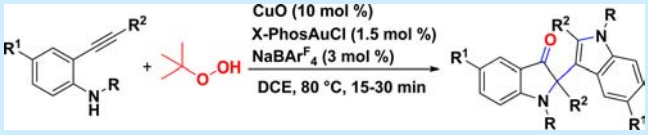
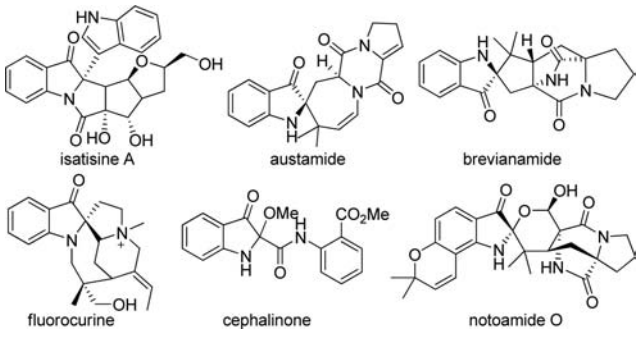
Supporting Information

ABSTRACT: A new strategy for direct and highly efficient synthesis of 2,3′-bisindolin-3-ones has been developed via a gold/copper-co-catalyzed tandem reactions of 2-alkynylanilines using TBHP as the terminal oxidant and oxygen-atom source. The single-step process involves a novel tandem intermolecular nucleophilic addition, intramolecular cyclization/oxidative cross-dehydrogenative coupling where up to four new bonds and two indole rings were created simultaneously in one-pot manner. The reaction features a broad substrate scope, good functional group tolerance, and high atom-economy.



2,2-Disubstituted indolin-3-ones are one of the privileged structural units found in many natural products such as isatisine A, austamide, brevianamide, fluorocurine, cephalinone, and notoamide O (Scheme 1) and biologically active products.[1] In addition, apart from their use as intermediates in the construction of various natural products,[2] in recent years, indol-3-one derivatives have also found wide applications in the areas of fluorescence dyeing and in solar cell applications.[3] Accordingly, the development of novel and efficient synthetic methods for 2,2-disubstituted indolin-3-one derivatives has been a major topic in synthetic organic chemistry.[1−8] For the construction of the 2,2-disubstituted indolin-3-one framework, the predominant strategy is direct transformation of indoles,[4] 3*H*-indol-3-ones,[5] and indolin-3-ones.[6] In stark contrast, reports on the direct and efficient synthesis of 2,2-disubstituted indolin-3-one derivatives from easily available acyclic starting materials in a single step are considerably rare.[7,8] The Smalley cyclization reaction of α-azidoaryl *sec*-alkyl ketones is an efficient and classical route to 2,2-disubstituted indolin-3-ones.[7] Recently, three elegant methods for the synthesis of 2,2-disubstituted indolin-3-ones have been reported via the transition-metal-catalyzed tandem transformation of acyclic alkynes; however, the reactions are severely limited to 1-nitroarylalkynes, 2-alkynyl arylazides and 1-(2-(allylamino)phenyl-4-hydroxybut-2-yn-1-ones.[8] To the best of our knowledge, direct methods for one-pot synthesis of 2,2-disubstituted indolin-3-ones from simple 2-alkynylanilines have never been reported. Herein, we report a new synthetic strategy for the direct, one-pot synthesis of 2,2-disubstituted indolin-3-ones via gold/copper-co-catalyzed tandem reactions of simple 2-alkynylanilines employing TBHP as the terminal oxidant and oxygen-atom source.

Scheme 1. Representative Natural Products with a 2,2-Disubstituted Indolin-3-one Skeleton



As part of our endeavors on carbon−carbon and carbon−heteroatom bond-forming reactions,[9] we recently disclosed several routes for the synthesis of 1,2,3-triazoles,[10a] α-amino-cyclopentenones,[10b] dihydrotriazinones,[10c] and dihydropyridazinones[10c] starting from easily accessible α-amino carbonyl derivatives. These results and our interests in the synthetic applications of functionalized alkynes[11] prompted us to investigate the cyclization reaction of *N*-substituted 2-(2-(ethynyl)arylamino)acetamides **1a**. As a result, we found that the tandem reaction of **1a** (0.2 mmol) proceeded smoothly to give 2-phenyl-2,3′-biindolin-3-one **2a** in 70% yield in the presence of X-PhosAuCl (1.5 mol %), NaBAr$^F_4$ (3.0 mol %), CuO (10 mol %), and *tert*-butyl hydroperoxide (1.5 equiv) in DCE (1.0 mL) at 80 °C for 15 min along with 1*H*-indole **3a** in 9% yield (Table 1, entry 5).[12] Decreasing the amount of CuO, X-PhosAuCl, and NaBAr$^F_4$ led to comparatively lower yields of **2a** (Table 1, entries 1−4). Other copper catalysts, such as CuOAc·H_2O and CuBr, were less effective (Table 1, entry 9) or ineffective (Table 1, entry 10). Different oxidants were also screened; however, no product **2a** was obtained when 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and *tert*-butyl-peroxybenzoate (TBPB) were used as the oxidants (Table 1, entries 11 and 12). In addition, when the reaction was carried out

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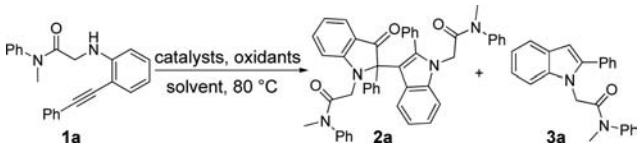
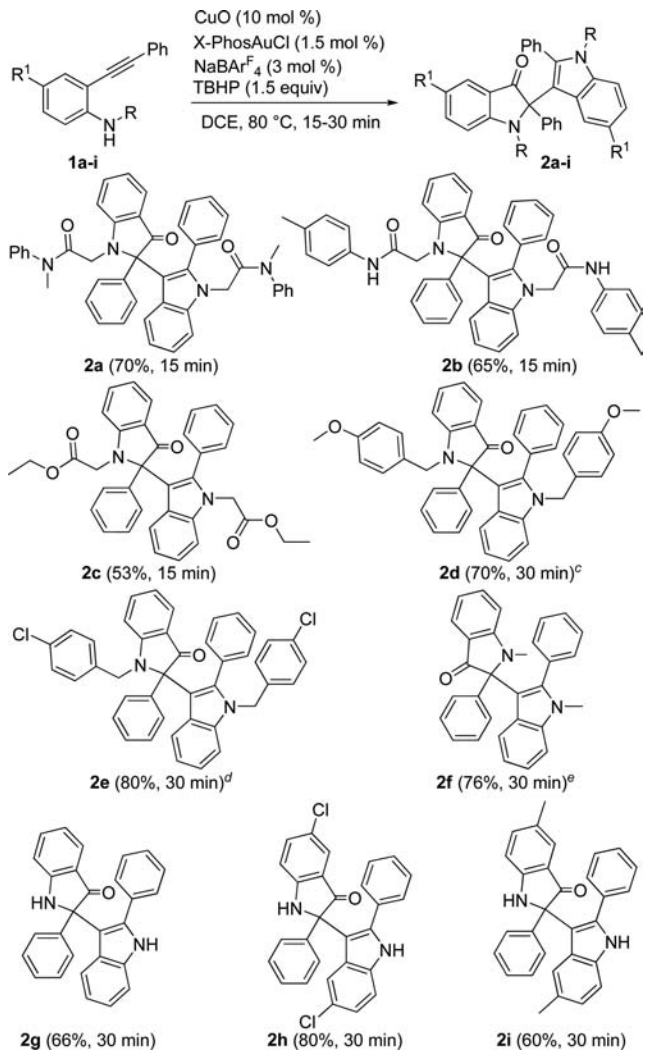
Table 1. Optimization of Reaction Conditions[a]



entry	catalyst (mol %)	oxidant (equiv)	solvent	yield[b] (%) 2a	yield[b] (%) 3a
1	CuO (5)/X-PhosAuCl (1)/$NaBAr^F_4$ (2)	TBHP (1.5)	DCE	51	28
2	CuO (10)/X-PhosAuCl (1)/$NaBAr^F_4$ (2)	TBHP (1.5)	DCE	59	28
3	CuO (15)/X-PhosAuCl (1)/$NaBAr^F_4$ (2)	TBHP (1.5)	DCE	61	30
4	CuO (10)/X-PhosAuCl (1.5)/$NaBAr^F_4$ (2)	TBHP (1.5)	DCE	64	20
5	CuO (10)/X-PhosAuCl (1.5)/$NaBAr^F_4$ (3)	TBHP (1.5)	DCE	70[c]	9[c]
6	CuO (15)/X-PhosAuCl (1.5)/$NaBAr^F_4$ (3)	TBHP (1.5)	DCE	69	9
7	CuO (10)/X-PhosAuCl (2)/$NaBAr^F_4$ (3)	TBHP (1.5)	DCE	70	10
8	CuO (10)/X-PhosAuCl (1.5)/$NaBAr^F_4$ (3)	TBHP (2.0)	DCE	69	10
9	$Cu(OAc)_2H_2O$ (10) /X-PhosAuCl (1.5) /$NaBAr^F_4$ (3)	TBHP (1.5)	DCE	49	42
10	CuBr (10)/X-PhosAuCl (1.5)/$NaBAr^F_4$ (3)	TBHP (1.5)	DCE		trace
11	CuO (15)/X-PhosAuCl (1.5)/$NaBAr^F_4$ (3)	DDQ (1.5)	DCE		
12	CuO (15)/X-PhosAuCl (1.5)/$NaBAr^F_4$ (3)	TBPB (1.5)	DCE		
13	CuO (10)/X-PhosAuCl (1.5)/$NaBAr^F_4$ (3)	TBHP (1.5)	toluene	trace	95
14	CuO (10)/X-PhosAuCl (1.5)/$NaBAr^F_4$ (3)	TBHP (1.5)	DMF	trace	36

[a]Reaction conditions: **1a** (0.2 mmol), CuO (0.01−0.03 mmol), X-PhosAuCl (0.002−0.004 mmol), $NaBAr^F_4$ (0.004−0.006 mmol), solvent (1.0 mL), at 80 °C for 15−30 min. X-Phos =2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl, $NaBAr^F_4$ = sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, TBHP = *tert*-butyl hydroperoxide, TBPB = *tert*-butylperoxybenzoate, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. [b]Estimated by ^1H NMR spectroscopy using dimethyl phthalate as an internal standard. [c]Isolated yield.

Scheme 2. Synthesis of 2,2′-Diphenyl-2,3′-biindolin-3-ones 2a−i[a,b]



[a]Reaction conditions: **1** (0.4 mmol), CuO (0.04 mmol), X-PhosAuCl (0.006 mmol), $NaBAr^F_4$ (0.012 mmol), DCE (2.0 mL), TBHP (0.6 mmol), at 80 °C for 15−30 min. [b]Isolated yield. [c]2.0 equiv of TBHP was used. [d]0.1 equiv of $Cu(OAc)_2·H_2O$ and 4.0 equiv of TBHP were used. [e]0.1 equiv of $Cu(OAc)_2·H_2O$ was used.

in toluene or DMF (Table 1, entries 13 and 14), only a trace amount of **2a** was observed (TLC).

Under the optimal reaction conditions (Table 1, entry 5), the scope and generality of the reaction were examined, and the results are summarized in Scheme 2. It is obvious that the tandem reaction showed broad tolerance for various R substituents at the nitrogen. All selected 2-(phenylethynyl)anilines **1a−f**, bearing various alkyl and benzyl R groups, could efficiently undergo the tandem reaction to give the corresponding 2,2′-diphenyl-2,3′-biindolin-3-ones **2a−f** in good to high yields. More importantly, in the case of *N*-unprotected 2-(phenylethynyl)aniline **1g**, the tandem reaction also worked well, yielding the desired product **2g** in 66% yield. In addition, substrates **1h** and **1i** possessing electron-withdrawing and electron-donating R^1 groups on the aminophenyl ring produced the desired 2,2′-diphenyl-2,3′-biindolin-3-ones **2h** and **2i** in 80% and 60% yields, respectively. In addition, it should be noted that this tandem reaction is easy to scale-up. A gram-scale reaction of 1.55 g of **1g** was carried out under the optimal conditions, furnishing 1.03 g of the desired product **2g** in 64% isolated yield.

Next, we turned to extending the scope of the reaction by varying the substituents on the alkyne moiety of 2-alkynylanilines **1**. As shown in Scheme 3, all selected substrates **1j−n**, bearing electron-rich and electron-deficient aryl, heteroaryl, and alkyl R^2 groups at the alkyne terminus, could provide the desired 2,3′-diindolin-3-ones **2j−n** in good to high yields. Similarly, the desired 2,3′-diindolin-3-ones **2o−r** were obtained in good to high yields from the substrates **1o−r** with different substituents on the alkyne and aryl moieties.

To further probe the mechanisms for formation **2**, some control experiments were designed and investigated. When **1g** was treated with CuO (10 mol %) under otherwise identical conditions but in the absence of X-PhosAuCl and $NaBAr^F_4$, no desired product **2g** was produced and only coupling product **4g** was generated in 35% yield along with the recovery of **1g** in 55% yield (Scheme 4, a), which demonstrates that X-PhosAuCl and

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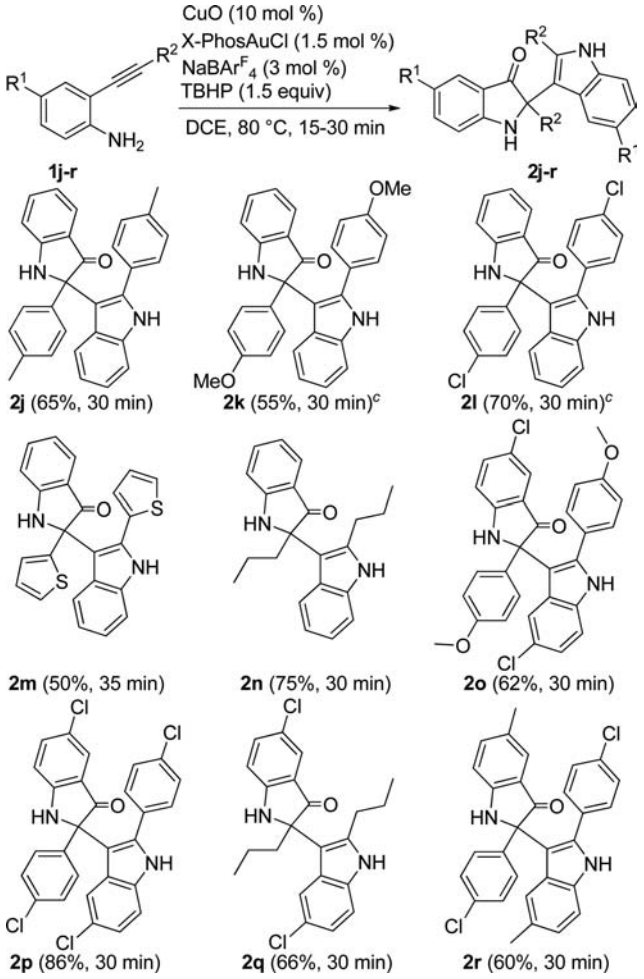
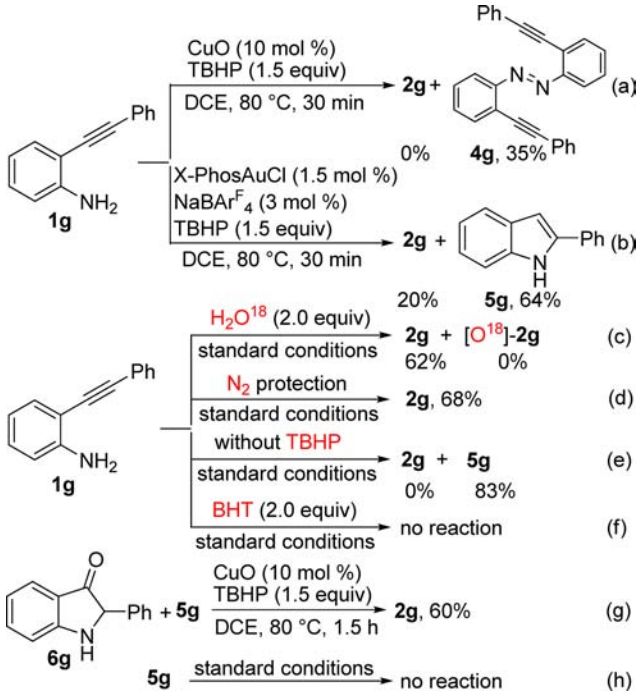
Scheme 3. Synthesis of 2,3′-Diindolin-3-ones 2j−r[a,b]



[a]Reaction conditions: **1** (0.4 mmol), CuO (0.04 mmol), X-PhosAuCl (0.006 mmol), NaBAr$^F_4$ (0.012 mmol), DCE (2.0 mL), TBHP (0.6 mmol), at 80 °C for 30−35 min. [b]Isolated yield. [c]2.0 equiv of TBHP was used.

NaBAr$^F_4$ play an important role for the cyclization transformation. The desired product **2g** was obtained in 20% yield along with the formation of indole **5g** in 64% yield under otherwise identical conditions but in the absence of CuO (Scheme 4, b). In addition, the reaction of **1g** in dry DCE did not provide [^{18}O]-**2g** in the presence of $H_2{}^{18}O$ (2.0 equiv) under otherwise identical conditions (Scheme 4, c). When the reaction was carried out under an atmosphere of nitrogen, the desired product **2g** was produced in 68% yield (Scheme 4, d). However, no desired product **2g** was generated, and only indole **5g** was obtained in 83% yield when the reaction was performed under otherwise identical conditions but in the absence of TBHP (Scheme 4, e). These results indicate that H_2O and O_2 atmospheres are not involved in the tandem reaction and TBHP participated in the transformation as the oxidant source. The formation of product **2g** was suppressed under the optimized conditions in the presence of 2.0 equiv of 2,6-di-*tert*-butyl-4-methylphenol (BHT) as a radical inhibitor (Scheme 4, f), indicating that a radical process was involved in the reaction. In addition, the reaction of **6g** (0.2 mmol) and **5g** (0.2 mmol) proceeded smoothly to give the desired product **2g** in 60% yield in the presence of CuO (10 mol %) and TBHP (1.5 equiv) in DCE (1.0 mL) at 80 °C for 1.5 h (Scheme 4, g). No reaction was

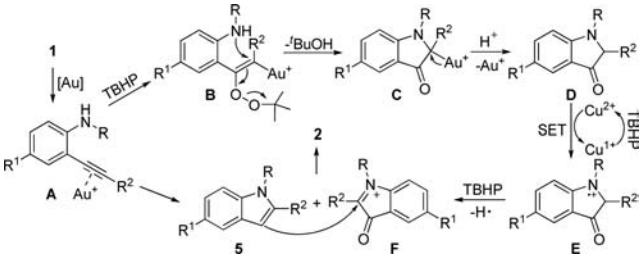
Scheme 4. Control Experiments for Mechanistic Studies



observed when indole **5g** was used as a partner under the optimal reaction conditions (Scheme 4, h).

On the basis of the above experimental results together with related reports,[13,14] a possible mechanism for the formation of **2** is proposed in Scheme 5. Initially, the attack of the hydroxy group

Scheme 5. Proposed Mechanisms for the Formation of 2



of TBHP on the electrophilic π-alkyne moiety of gold complex **A** generates intermediate **B**,[13] which undergoes an intramolecular amination cyclization reaction in a 5-*endo-dig* fashion, followed by elimination of *t*-BuOH and protonation to give intermediate **D**.[13] Immediately, intermediate **D** is oxidized by CuO through a single-electron transfer (SET) process to generate the ammoniumyl radical cation intermediate **E**, which undergoes hydrogen radical transfer to form iminium salt intermediate **F**.[14] Finally, indole **5**, generated in situ via gold-catalyzed intramolecular cyclization of **1**,[13] undergoes nucleophilic addition with iminium salt intermediate **F**, followed by loss of a proton to produce the corresponding indolin-3-ones **2** (Scheme 5).

In conclusion, we have developed a new strategy for the direct and highly efficient synthesis of 2,3′-bisindolin-3-ones via a gold/copper-cocatalyzed tandem reactions of simple 2-alkynylanilines using TBHP as the terminal oxidant and oxygen-atom source. The single-step process involves a novel tandem intermolecular nucleophilic addition, intramolecular cyclization/oxidative cross-dehydrogenative coupling where up to four new bonds and two

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indole rings were created simutaneously in a one-pot manner. The reaction features broad substrate scope, good functional group tolerance, operational simplicity, and high atom-economy. Further work on the applications and extension of the present catalytic system is currently under investigation 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.7b00200.

Experimental procedures, characterization of data for all new compounds, and X-ray crystallographic data for **2a** (PDF)

X-ray crystallographic data for **2a** (CIF)

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Notes

The authors declare no competing financial interest.

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