

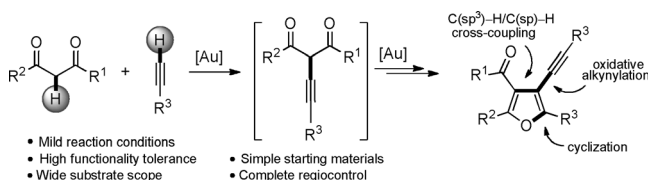
Gold-Catalyzed C(sp³)–H/C(sp)–H Coupling/Cyclization/Oxidative Alkynylation Sequence: A Powerful Strategy for the Synthesis of 3-Alkynyl Polysubstituted Furans**

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Abstract: In sharp contrast to the gold-catalyzed reactions of alkynes/allenes with nucleophiles, gold-catalyzed oxidative cross-couplings and especially C–H/C–H cross-coupling have been under represented. By taking advantage of the unique redox property and carbophilic π acidity of gold, this work realizes the first gold-catalyzed direct C(sp³)–H alkynylation of 1,3-dicarbonyl compounds with terminal alkynes under mild reaction conditions, with subsequent cyclization and in situ oxidative alkynylation. A variety of terminal alkynes including aryl, heteroaryl, alkenyl, alkynyl, alkyl, and cyclopropyl alkynes all successfully participate in the domino reaction. The protocol offers a simple and region-defined approach to 3-alkynyl polysubstituted furans.

The homogeneous gold-catalyzed reactions of alkynes/allenes with nucleophiles have been recognized as one of the most powerful and useful tools in organic synthesis.^[1] The oxidation state of gold rarely changes in these transformations. In contrast, the gold-catalyzed oxidative cross-coupling reactions remain a great challenge because of the relatively high redox potential of the Au^I/Au^{III} couple ($E^0 = +1.41$ V).^[2] Recent research has demonstrated that the use of gold catalysts goes beyond the simple substitution of the conventional palladium, rhodium, and ruthenium catalysts in oxidative cross-coupling.^[3] The representative work of Ball, Lloyd-Jones, and Russell,^[4] and de Haro and Nevado^[5] have clearly shown the great potential of gold catalysis in oxidative C–H activation/C–C cross-coupling. Despite significant progress, the promising oxidative C–H/C–H cross-coupling reactions which obviate the prefunctionalization of both coupling partners have been largely under developed. To the best of our knowledge, only the gold-catalyzed oxidative C(sp²)–H/C(sp²)–H homocoupling,^[6] C(sp³)–H/C(sp³)–H^[7] cross-coupling, and C(sp²)–H/C(sp)–H cross-coupling^[5] have been realized, and the C(sp³)–H/C(sp)–H cross-coupling still remains unexplored. Following our work in C(sp³)–H func-

tionalization,^[8] we were interested in the gold-catalyzed direct C(sp³)–H alkynylation.^[9] In combination with the unique ability of gold to act as a mild carbophilic π acid, we envisioned that the resulting acetylene-containing molecules could encounter a one-pot intramolecular cyclization reaction which enables rapid access to intricate cyclic scaffolds from basic chemicals. As a proof of concept, we herein report the first gold-catalyzed C(sp³)–H/C(sp)–H cross-coupling/cyclization/oxidative alkynylation sequence of 1,3-dicarbonyl compounds with terminal alkynes to afford 3-alkynyl polysubstituted furans under mild reaction conditions (Scheme 1).



Scheme 1. The gold-catalyzed C(sp³)–H/C(sp)–H coupling/cyclization/oxidative alkynylation sequence.

Polysubstituted furans are widely distributed in naturally occurring products, bioactive molecules, and pharmaceuticals, and are also important building blocks in organic synthesis.^[10] Consequently, a large number of methods have been established for the synthesis of such molecules,^[11] and they mainly rely on the intramolecular cyclization of complex acyclic precursors which may suffer from tedious multistep synthesis and purification. Undoubtedly, new protocols that can assemble the furan ring from simple chemicals are highly desirable. Moreover, the installation of additional functional groups during the formation of the furan ring is more attractive from the viewpoint of synthetic efficiency. 3-Alkynyl furans are among the most important functionalized furans because the acetylene groups allow a broad range of transformations including oxidation, reduction, addition, cyclization, metathesis, etc. However, owing to the inherent low reactivity of the furan C3-position, the general and efficient synthesis of 3-alkynyl polysubstituted furans has been a challenge.^[12] The methodology described herein represents a simple and region-defined approach to 3-alkynyl polysubstituted furans.

To realize the cascade reaction, several obstacles have to be overcome, including: 1) the identification of a robust catalyst system that allows the smooth occurrence of all distinct reactions and avoids mutual interference between different types of reactions, 2) the realization of the unpre-

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Table 1: Optimization of the reaction conditions.^[a]

	1a	2a	3a
			L1
			L2
Entry	Catalyst	Ligand	Yield [%] ^[b]
1	4 mol % Ph ₃ PAuCl	none	trace
2	4 mol % Ph ₃ PAuCl/AgOTf	none	0
3	4 mol % AuCl ₃	none	trace
4	4 mol % PicAuCl ₂	none	17
5	4 mol % [AuCl ₂ (bipy)]Cl	none	44
6	4 mol % HAuCl ₄ ·xH ₂ O	10 mol % bipy	33
7	4 mol % HAuCl ₄ ·xH ₂ O	10 mol % L1	25
8	4 mol % HAuCl ₄ ·xH ₂ O	10 mol % L2	22
9	4 mol % AuCl ₃	10 mol % bipy	21
10	4 mol % AuBr ₃	10 mol % bipy	16
11	4 mol % HAuCl ₄ ·xH ₂ O	30 mol % bipy	70
12	3 mol % HAuCl ₄ ·xH ₂ O	30 mol % bipy	66
13	2 mol % HAuCl ₄ ·xH ₂ O	30 mol % bipy	37

[a] Reaction conditions: ethyl acetoacetate (**1a**; 1.0 mmol), phenylacetylene (**2a**; 0.5 mmol), gold catalyst, ligand, KOAc (2.0 equiv), and PhI(OAc)₂ (2.0 equiv) in toluene (5.0 mL) under N₂ at 40 °C for 24 h.

[b] Yield of isolated product.

cedented gold-catalyzed oxidative C(sp³)-H alkylation with terminal alkynes, 3) the suppression of the homocoupling reaction of terminal alkynes, and 4) the inhibition of the protodeauration of the gold furyl intermediates. Thus, we first devoted much effort to optimizing the reaction conditions of ethyl acetoacetate (**1a**) and phenylacetylene (**2a**; Table 1). It was found that Ph₃PAuCl, Ph₃PAuCl/AgOTf, AuCl₃, and PicAuCl₂ all gave poor results (Table 1, entries 1–4). To our delight, the desired furan **3a** was obtained in 44 % yield when [AuCl₂(bipy)]Cl was used as the catalyst (Table 1, entry 5). This promising result encouraged us to explore the catalysts generated in situ from commercially available gold(III) sources (e.g., AuCl₃, AuBr₃, and HAuCl₄·xH₂O) and ligands (e.g. bipy, L1, and L2). After screening various parameters (see Table S1 in the Supporting Information), 3 mol % of HAuCl₄·xH₂O as the catalyst, 30 mol % of bipy as the ligand, 2.0 equivalents of PhI(OAc)₂ as the oxidant, and 2.0 equivalents of KOAc as the base in toluene at 40 °C were chosen as the optimal reaction conditions (Table 1, entry 12). Under these reaction conditions, **3a** was obtained in 66 % yield, and the protodeaured product of the gold 3-furyl intermediate was not observed in the reaction system.

With the optimal reaction conditions in hand, we started to explore the scope of the 1,3-dicarbonyl compounds (Table 2). It was found that ethyl, methyl, *tert*-butyl, benzyl, and allyl acetoacetates (**1a–e**) all reacted with **2a** to afford the furans **3a–e** in 55–66 % yields (Table 2, entries 1–5). The sterically more hindered **1f** also smoothly underwent the domino reaction (Table 2, entry 6). However, the reaction of the α -aryl-substituted 1,3-dicarbonyl compounds **1g–j** furnished the desired products **3g–j** in slightly lower yields than

Table 2: The scope of 1,3-dicarbonyl compounds.^[a]

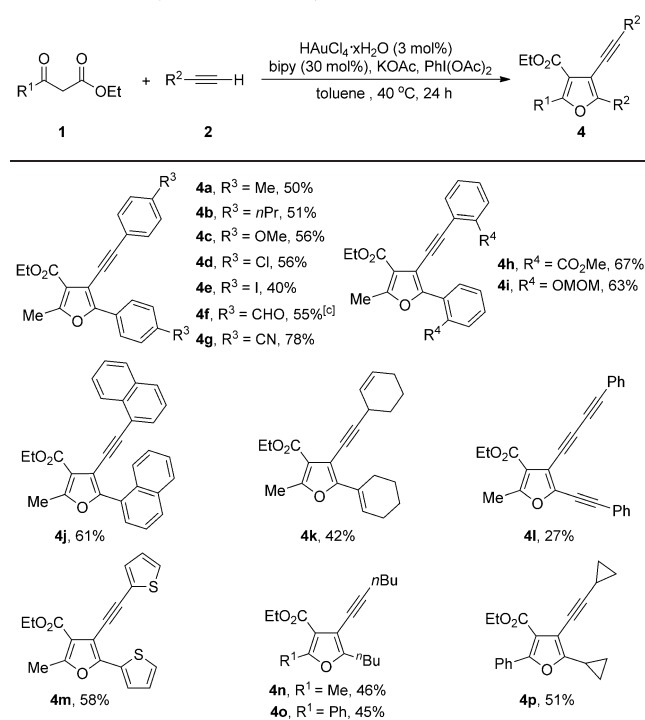
	1	2a	3
Entry	1	Product 3	Yield [%] ^[b]
1			66
2			57
3			55
4			61
5			56
6			60
7			59 ^[c]
8			59 ^[c]
9			50
10			52 ^[c]
11			66
12			54
13			70 ^[c]
14			54

[a] Reaction conditions: **1** (2.0 equiv), **2a** (0.5 mmol), HAuCl₄·xH₂O (3 mol %), bipy (30 mol %), KOAc (2.0 equiv), PhI(OAc)₂ (2.0 equiv), and toluene (5.0 mL) under N₂ at 40 °C for 24 h. [b] Yield of the isolated product. [c] At 80 °C.

the corresponding α -alkyl-substituted substrates. In these cases, better yields were generally obtained when the reactions were performed at an elevated temperature of 80 °C (Table 2, entries 7–10). β -Ketoamides and 1,3-diketones were also suitable substrates and showed reactivities comparable to that of β -ketoesters (Table 2, entries 11–14). The structure of the product **3l** was confirmed by single-crystal X-ray analysis.^[13] Remarkably, when the unsymmetrical 1,3-diketone **1n** was subjected to the standard reaction conditions, the cyclization of the carbonyl group adjacent to the methyl moiety occurred selectively to afford the 2-methyl-substituted furan **3n** (Table 2, entry 14). It should be emphasized that the yields obtained in these reactions were pretty good considering that three different types of reactions occurred successively in one pot.

Next, the scope of terminal alkynes was evaluated (Table 3). It was found that the current protocol tolerated a wide range of functional groups (e.g., alkyl, methoxy, methoxymethoxy (MOMO), chloro, iodo, cyano, ester, and aldehyde) on the phenyl ring of aryl alkynes (**4a–i**), and offer the opportunity for further organic transformations. The compatibility of the iodo group is especially attractive considering its high reactivity towards Sonogashira coupling (**4e**). Besides aryl alkynes, other alkynes including alkyl, alkenyl, heteroaryl, cyclopropyl, and bulky naphthalenyl alkynes also underwent the reaction to deliver the desired furans in moderate to good yields (**4j**, **4k**, and **4m–p**). However, when the terminal 1,3-diyne **2m** [1-(buta-1,3-diynyl)benzene] was employed, the product **4l** was obtained in a low yield of 27 %, probably because of the low stability of **2m**. These 3-alkynyl furan-based π -conjugated materials (**4**) and their derivatives such as the poly(hetero)aryl compound **8** (discussed below) could be expected to exhibit interesting

Table 3: The scope of terminal alkynes.^[a,b]

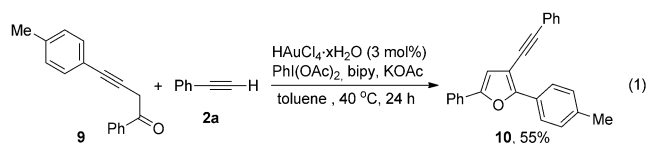


[a] Reaction conditions: **1** (2.0 equiv), **2** (0.5 mmol), $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ (3 mol%), bipy (30 mol%), KOAc (2.0 equiv), $\text{PhI}(\text{OAc})_2$ (2.0 equiv) and toluene (5.0 mL) under N_2 at 40 °C for 24 h. [b] Yield of the isolated product. [c] At 80 °C.

photophysical properties and find potential applications in materials science.

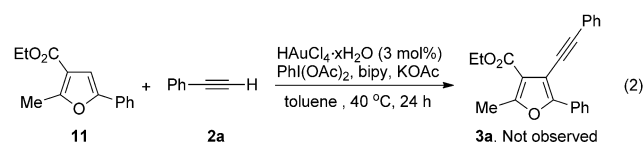
The synthetic usefulness of this protocol was subsequently illustrated (see the Supporting Information). The 3-alkynyl furan **3a** could be readily hydrogenated to afford the corresponding 3-alkyl furan **5** (ethyl 2-methyl-4-phenethyl-5-phenylfuran-3-carboxylate) [Eq. (S1)], and especially the (*Z*)-3-alkenyl furan **6** ((*Z*)-ethyl 2-methyl-5-phenyl-4-styryl-furan-3-carboxylate) which was not easy to access by traditional methods such as Heck coupling or Wittig reaction [Eq. (S2)]. In addition, the poly(hetero)aryl compound **8** (ethyl 4-(benzofuran-2-yl)-5-(2-hydroxyphenyl)-2-methylfuran-3-carboxylate) was easily synthesized from **4i** through the removal of the MOM group and subsequent palladium-catalyzed cyclization of the resulting **7** (ethyl 5-(2-hydroxyphenyl)-4-((2-hydroxyphenyl)ethynyl)-2-methylfuran-3-carboxylate) [Eq. (S3)].^[14,15]

We then moved on to study the mechanism of this cascade reaction. It was found that the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) had a negligible effect on the reaction of **1a** with **2a**, thus ruling out the possibility of a radical pathway (see Table S2 in the Supporting Information).^[16] The reaction of diphenylacetylene with **1a** did not occur under the standard reaction conditions, thus indicating the critical role of the acetylenic proton [see Eq. (S4) in the Supporting Information]. Moreover, the reaction of β -alkynyl ketone **9** with **2a** afforded the desired furan **10** in 55 % yield [Eq. (1)]. These observations demon-



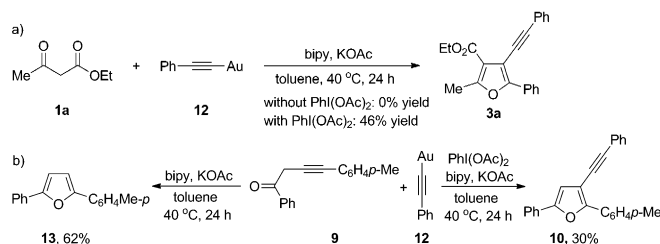
strated that the domino reaction first underwent the $\text{C}(\text{sp}^3)\text{--H/C}(\text{sp})\text{--H}$ cross-coupling, although many attempts to isolate the coupled 2-alkynyl-1,3-dicarbonyl compound failed.

It is well-documented that gold intermediates are easily quenched by protonation.^[1] However, the exposure of the C3-unsubstituted furan **11** and **2a** to the standard reaction conditions failed to deliver any **3a** [Eq. (2)], thus suggesting



that the protodeauration of the gold 3-furyl complex could not be involved in this cascade process. Therefore, the alkynyl moiety might be integrated into the furan ring through the in situ oxidative alkynylation of the gold 3-furyl intermediate.^[12a,17]

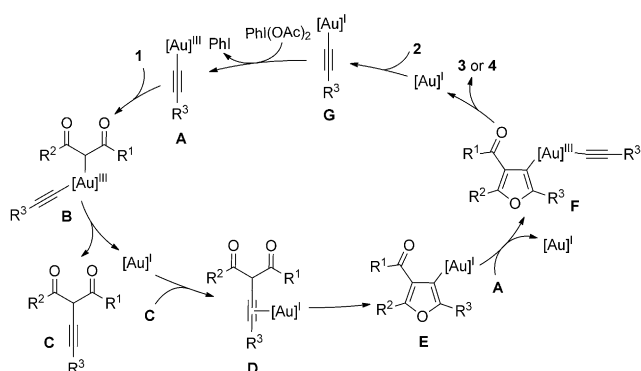
To get some insight into the mechanism, the stoichiometric reactions of the gold(I)-acetylide **12** with **1a** and **9** were investigated individually (Scheme 2). It was found that the



Scheme 2. Stoichiometric reactions of gold(I) acetylide.

reaction of **1a** with **12** could not deliver any products in the absence of $\text{PhI}(\text{OAc})_2$. However, **3a** was obtained in 46 % yield with the addition of 2.0 equivalents of $\text{PhI}(\text{OAc})_2$ (Scheme 2a). Treatment of **9** with **12** in the absence or presence of $\text{PhI}(\text{OAc})_2$ afforded the cyclization product **13** and cyclization/alkynylation product **10** in 62 and 30 % yields, respectively (Scheme 2b). Based on these results, three scenarios can be envisaged: 1) The gold(III) alkynyl intermediate may serve as a reactive species; 2) both the $\text{C}(\text{sp}^3)\text{--H/C}(\text{sp})\text{--H}$ coupling and the in situ oxidative alkynylation involve $\text{Au}^{\text{I}}/\text{Au}^{\text{III}}$ redox cycle; and 3) the transmetalation between the gold acetylide and gold furan complex is possible since there is no free acetylene in this reaction mixture.

On the basis of these observations, a tentative mechanism was proposed (Scheme 3).^[5,17] The domino reaction starts with the reaction of gold(III) precatalyst and the terminal alkyne **2** to generate the gold(III) acetylide **A**. The reaction of **A** with **1** and subsequent reductive elimination delivers the 2-



Scheme 3. Proposed mechanism.

alkynyl-1,3-dicarbonyl **C** and a gold(I) species. The alkynyl moiety of **C** then coordinates with gold(I) to induce the intramolecular nucleophilic attack of oxygen atom onto alkyne to afford the gold(I) complex **E**. Transmetalation from **E** to **A** leads to the formation of **F**. The gold(III)-catalyzed cyclization of **C** and subsequent transmetalation between **A** and the resulting gold(III) intermediate is also a possible pathway to **F**. Upon reductive elimination of **F**, the desired product **3** or **4** is formed. The reaction of the released gold(I) complex with terminal alkyne **2** and subsequent oxidation by $\text{PhI}(\text{OAc})_2$ lead to the regeneration of **A**.

In summary, by taking advantage of the unique redox property and carbophilic π acidity of gold, we have achieved for the first time the gold-catalyzed oxidative $\text{C}(\text{sp}^3)\text{-H}/\text{C}(\text{sp})\text{-H}$ cross-coupling of 1,3-dicarbonyl compounds with terminal alkynes, a step which is followed by cyclization and in situ oxidative alkylation in a cascade process. The protocol offers an unusually simple approach to 3-alkynyl polysubstituted furans, and features mild reaction conditions, readily available starting materials, complete regiocontrol, wide substrate scope, and high functional-group tolerance. It is worth noting that the previously reported gold-catalyzed C-H alkylation reactions are only applicable to $\text{C}(\text{sp}^2)\text{-H}$ bonds and employ either electron-deficient terminal alkynes^[5] or alkynyl hypervalent iodine reagents^[12a,18] as the alkynyl source. In the current protocol, a variety of terminal alkynes including aryl, heteroaryl, alkenyl, alkynyl, alkyl, and cyclopropyl alkynes all successfully participate in the domino reaction. This strategy would broaden the chemistry of gold and hold great potential in the concise synthesis of complex molecules.

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from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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