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Copper-catalyzed, silver-mediated formal [3+2] cycloaddition of simple alkynes with β-ketoesters through propargylic C(sp^3)–H functionalization†

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A copper-catalyzed propargylic [3+2] cycloaddition of simple alkynes with β-ketoesters through the propargylic C(sp^3)–H functionalization has been realized. Under catalysis by CuI in combination with 1,10-phenanthroline hydrate as the ligand and Ag_2CO_3 as a bifunctional reagent (oxidant and base), the reaction proceeds smoothly with a broad substrate scope, thus providing a variety of highly functionalized furans in moderate to high yields. This represents the first successful example of the catalytic propargylic cycloaddition of simple alkynes with bisnucleophiles based on the propargylic C(sp^3)–H functionalization strategy.

Catalytic propargylic cycloadditions featuring metal–allenylidene complexes as key intermediates have been well established recently as powerful tools for the construction of various carbocyclic and heterocyclic frameworks.[1] In these reactions, an allenylidene fragment is typically obtained from alkynes bearing propargylic leaving groups, thus allowing the transformation of propargylic compounds through a redox-neutral event (Scheme 1, II). One more efficient and attractive alternative would be the direct oxidative propargylic C–H functionalization of readily available simple alkynes to perform analogous propargylic cycloadditions (Scheme 1, II). Moreover, the use of a propargylic hydrogen atom as a leaving group also eliminates the need to install the propargylic esters, carbonates, and halides necessary for traditional propargylic cycloadditions. Indeed, some transformations of simple alkynes involving propargylic hydrogen atoms through the assistance of transition metals have been disclosed recently.[2] Except some propargylic oxidations,[3] however, the use of a propargylic C(sp^3)–H functionalization strategy that allows simple alkynes to participate directly in the propargylic transformation appears to be rather limited and highly challenging. Schomaker and coworkers reported an intramolecular propargylic C–H amination of homopropargylic carbamates or sulfamates catalyzed by $[Rh_2(esp)_2]$ in combination with $PhI(OAc)_2$ or AgOTf with PhIO (Scheme 1, Ia).[4] Lu and Zhang *et al.* elegantly developed a Co-catalyzed intramolecular amination of the propargylic C–H bonds of *N*-bishomopropargylic sulfamoyl azides (Scheme 1, Ib).[5] To the best of our knowledge, no catalytic intermolecular propargylic cycloaddition of readily available simple alkynes with bisnucleophiles, which proceeds through a propargylic C(sp^3)–H functionalization strategy, has been realized to date. Our recent success in the copper-catalyzed propargylic cycloaddition with propargylic esters[6] as biselectrophiles led us to consider using readily available simple alkynes as the surrogate for propargylic esters. The key to realize this new cyclization strategy should be in search of a suitable catalytic and oxidative system that enables the generation of bis-electrophilic Cu–allenylidene complexes **A** from simple alkynes efficiently. Herein we describe the first example of Cu-catalyzed propargylic [3+2] cycloaddition of simple alkynes with β-ketoesters on the basis of the propargylic C(sp^3)–H activation strategy, thus leading to a variety of highly functionalized furans in good yields (Scheme 1, III).

In searching for suitable cross-partners for this unprecedented cycloaddition of simple alkynes, we were particularly attracted to β-ketoester due to its availability and demonstrated reactivity as the *C*,*O*-bisnucleophile for various cycloadditions.[7] We initiated our investigation with the reaction of 1-phenyl-2-propyne **1a** with ethyl 3-oxo-3-phenylpropanoate **2a** in the presence of various copper precursors, N,N-ligands and oxidants (Table 1). Initial attempts using $Cu(OTf)_2$ and 1,10-phenanthroline hydrate in combination with a range of organic oxidants were really disappointing. Either no conversion or a complex mixture was obtained (entries 1–3). After extensively screening diverse types of oxidants, we were excited to observe the formation of expected [3+2] cycloadducts with $AgNO_3$ as the oxidant, albeit as a mixture of furan **3aa** and 2,3-dihydrofuran **3aa′** in low yields. By the addition of DBU to the reaction mixture, 2,3-dihydrofuran **3aa′** could be readily and fully converted into furan **3aa**. Consequently, the [3+2] cycloadduct **3aa** was isolated in 36% yield in this case (entry 4).

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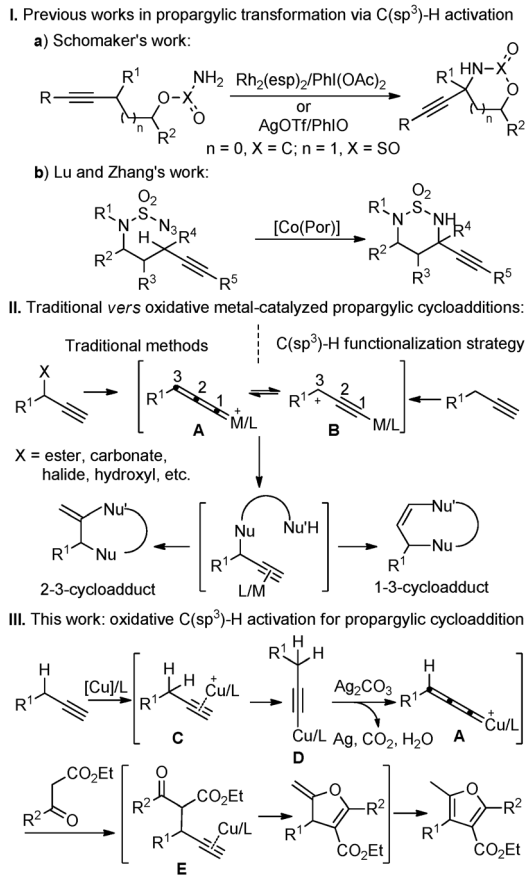
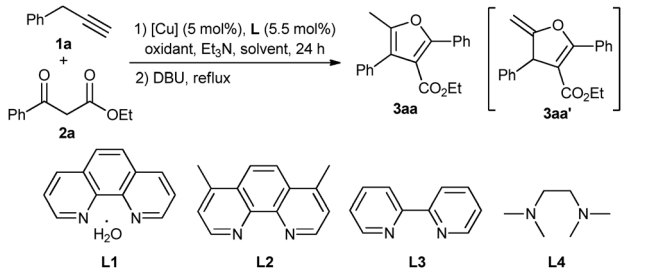


Scheme 1 Catalytic propargylic transformation of simple alkynes *via* propargylic C(sp^3)–H activation.

Further screening of silver salts identified Ag_2CO_3 as the optimal oxidant, which led to the formation of **3aa** in a good yield of 73% (entry 6). Subsequent ligand screening did not improve the reaction outcome (entries 6–9). Copper salts showed some influence on the reactivity (entries 10–12), and CuI was demonstrated to be the best choice in terms of yield (entry 12). When a series of solvents were examined, a significant difference was observed. The reaction performed in THF, PhMe or DMSO led to the decreased yields (entries 13–15). EtOH was proven to be the most suitable solvent, in which 91% yield of **3aa** was obtained (entry 16). An additional base additive was not necessary as a slightly improved result was achieved in its absence (entry 17). This result suggested that Ag_2CO_3 should act as a bifunctional reagent (oxidant and base). Both CuI and Ag_2CO_3 were essential for the reaction, and the absence of any one of them would inhibit the reaction completely (entries 18 and 19).

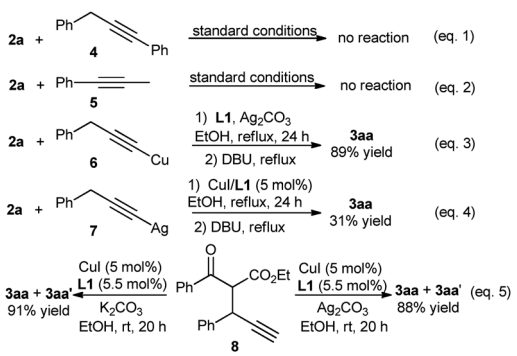
Some control experiments were carried out to examine the proposed mechanism in Scheme 1, III. Internal alkynes **4** and **5** did not work in the cycloaddition (eqn (1) and (2), Scheme 2), which indicated that the formation of copper acetylide **D** should be necessary to initiate the reaction as the traditional propargylic transformation.[1] Cu- and Ag-acetylides **6** and **7** were prepared, respectively, and subjected to the reaction under standard conditions.[8] As expected, Cu-acetylide **6** proceeded smoothly to give **3aa** in 89% (eqn (3)), while Ag-acetylide **7** led to **3aa** in 31% yield (eqn (4)). This result suggested that Cu-acetylide **D** may be directly generated from the alkynes by deprotonation. However, the formation of Cu-acetylide **D** from Ag-acetylide *via* transmetalation could not be ruled out. The supposed intermediate **8** was prepared and subjected to the reaction under the standard conditions and with K_2CO_3 instead of Ag_2CO_3 (eqn (5)). In both cases, the reaction gave the expected **3aa** and **3aa′** in similar yields, suggesting that the reaction should proceed through intermediate **E** with Ag_2CO_3 just as a

Table 1 Screening of the reaction conditions[a]



Entry	[Cu]	L	Oxidant	Solvent	Yield[b] (%)
1	$Cu(OTf)_2$	**L1**	2,6-DMBQ	CH_2Cl_2	—
2	$Cu(OTf)_2$	**L1**	$PhI(OAc)_2$	CH_2Cl_2	—
3	$Cu(OTf)_2$	**L1**	TBHP	CH_2Cl_2	—
4	$Cu(OTf)_2$	**L1**	$AgNO_3$	CH_2Cl_2	36
5	$Cu(OTf)_2$	**L1**	AgOAc	CH_2Cl_2	29
6	$Cu(OTf)_2$	**L1**	Ag_2CO_3	CH_2Cl_2	73
7	$Cu(OTf)_2$	**L2**	Ag_2CO_3	CH_2Cl_2	51
8	$Cu(OTf)_2$	**L3**	Ag_2CO_3	CH_2Cl_2	64
9	$Cu(OTf)_2$	**L4**	Ag_2CO_3	CH_2Cl_2	41
10	$Cu(OAc)_2 \cdot H_2O$	**L1**	Ag_2CO_3	CH_2Cl_2	64
11	CuCl	**L1**	Ag_2CO_3	CH_2Cl_2	80
12	CuI	**L1**	Ag_2CO_3	CH_2Cl_2	88
13	CuI	**L1**	Ag_2CO_3	THF	73
14	CuI	**L1**	Ag_2CO_3	PhMe	54
15	CuI	**L1**	Ag_2CO_3	DMSO	59
16	CuI	**L1**	Ag_2CO_3	EtOH	91
17[c]	CuI	**L1**	Ag_2CO_3	EtOH	93
18[c]	—	**L1**	Ag_2CO_3	EtOH	—
19[c]	CuI	**L1**	—	EtOH	—

[a] Reaction conditions: **1a** (0.44 mmol), **2a** (0.2 mmol), [Cu] (0.01 mmol, 5 mol%), **L** (0.011 mmol, 5.5 mol%), Et_3N (0.24 mmol) and oxidant (0.24 mmol, 1.2 equiv.) in 3 mL of an anhydrous solvent under N_2 in a Schlenk tube at refluxing temperature for 24 h, then DBU (0.24 mmol, 1.2 equiv.) was added and monitored by TLC, unless otherwise noted. [b] Isolated yield of **3aa**. [c] No addition of Et_3N in the reaction.



Scheme 2 Control experiments.

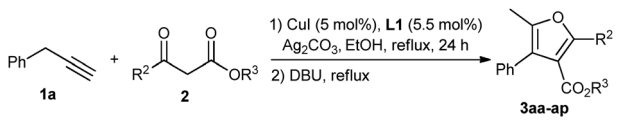
base in the cyclization step. These experiments, combined with the same cycloadduct obtained as in the traditional propargylic cycloaddition, support the supposed mechanism in Scheme 1.

With the optimal reaction conditions in hand, we set out to explore the generality of this catalytic system. The scope with respect to various β-ketoesters was investigated. As shown in Table 2, the reaction was highly sensitive to the substitution pattern on the phenyl ring. Thus, both 4-Cl and 3-Cl-substituted substrates (**2c** or **2d**, respectively) gave the cycloadducts in high yields (entries 3 and 4), while substrate **2b** bearing a 2-Cl substituent led to a substantive decrease in the yield (entry 2). The substituent at the *para* position of the phenyl ring was well tolerated, and β-ketoesters bearing either electron-donating (Me, OMe and CH_3CONH) or electron-withdrawing (CN, F, Br, and Cl) groups gave good to high yields, besides 4-OH substituted β-ketoester **2j** that gave **3aj** in only 31% yield (entries 4–11). 2-Naphthyl-substituted substrate **2l** underwent the cycloaddition well, furnishing the desired cycloadduct **3al** in 89% yield (entry 12). Heteroaromatic substrate **2m** also proceeded with excellent reactivity to generate the corresponding cycloadduct **3am** in 94% yield (entry 13). Notably, aliphatic β-ketoesters were also well-tolerated in the cycloaddition. For example, ethyl acetoacetate **2n** reacted smoothly with **1a** to afford the furan product **3an** in 92% yield (entry 14). Even with the sterically hindered β-ketoester **2o**, the reaction gave the desired cycloadduct **3ao** in a good yield of 81% (entry 15). Methyl benzoylacetate **2p** also served well in the reaction, providing the cycloadduct **3ap** in 91% yield albeit contaminated with a small amount of transesterification product **3aa** (entry 16). The structure of the cycloadduct was unambiguously confirmed by the single-crystal X-ray diffraction analysis of **3ap**.[9]

Next, the scope of propargylic derivatives was evaluated under the same set of reaction conditions. A series of propargylic derivatives (**1a–k**) reacted with **2a** smoothly and furnished the corresponding cycloadducts **3aa–ka** in moderate to excellent yields (Table 3). The electronic properties of the substituent at the *para*-position of the phenyl ring showed a significant effect on the reaction performance (entries 2–7). Thus, 4-amino substituted substrate **1e** showed a very low conversion (entry 5), whereas **1g** with a 4-F group led to the cycloadduct **3ga** in up to 96% yield (entry 7). The low reactivity of **1e** may be due to the nucleophilic ability of the amino group, which competitively suppressed the nucleophilic attack of the β-ketoester at the initial propargylic alkylation step. Increased steric bulk (**1h**) at the *ortho*-position of the phenyl ring was tolerated, but led to somewhat diminished conversions (entry 8). 2-Thienyl substrates (**1j**) also worked in this reaction, but the yield of the cycloadduct was not so satisfactory (entry 10). Pent-4-yn-1-ylbenzene **1k** could also undergo this cycloaddition, and give the desired cycloadduct **3ka** in 60% yield although in this case 10 mol% of catalyst was required (entry 11).

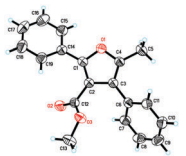
To illustrate the utility of the developed method in the construction of structurally diverse and fully substituted furans, we attempted to further elaborate the cycloadducts by converting the ester group into an aryl substituent *via* catalytic decarboxylative coupling. Although the decarboxylative

Table 2 Scope of the [3+2] cycloaddition with respect to β-ketoesters[a]



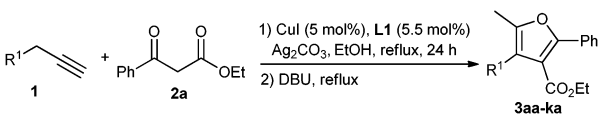
Entry	**2** (R^2, R^3)	Product (**3**)	Yield[b] (%)
1	**2a** (Ph, Et)	**3aa**	93
2	**2b** (2-ClC_6H_4, Et)	**3ab**	53
3	**2c** (3-ClC_6H_4, Et)	**3ac**	91
4	**2d** (4-ClC_6H_4, Et)	**3ad**	90
5	**2e** (4-FC_6H_4, Et)	**3ae**	89
6	**2f** (4-BrC_6H_4, Et)	**3af**	82
7	**2g** (4-CN, Et)	**3ag**	60
8	**2h** (4-MeC_6H_4, Et)	**3ah**	94
9	**2i** (4-$MeOC_6H_4$, Et)	**3ai**	88
10[c]	**2j** (4-HOC_6H_4, Et)	**3aj**	31
11	**2k** (4-CH_3CONH, Et)	**3ak**	89
12	**2l** (2-naphthyl, Et)	**3al**	89
13	**2m** (2-thienyl, Et)	**3am**	94
14[d]	**2n** (Me, Et)	**3an**	92
15[d]	**2o** (^{i}Pr, Et)	**3ao**	81
16	**2p** (Ph, Me)	**3ap**	91 (45)[e]

[a] Reaction conditions: **1a** (0.44 mmol), **2** (0.2 mmol), CuI (0.01 mmol, 5 mol%), 1,10-phenanthroline hydrate (0.011 mmol, 5.5 mol%), Ag_2CO_3 (0.24 mmol, 1.2 equiv.) in 3 mL of EtOH in a Schlenk tube at refluxing temperature for 24 h, then DBU (0.24 mmol, 1.2 equiv.) was added and monitored by TLC. [b] Isolated yield of **3**. [c] 10 mol% CuI was used. [d] 0.72 mmol DBU was used. [e] Yield in parentheses was obtained with MeOH as the solvent.



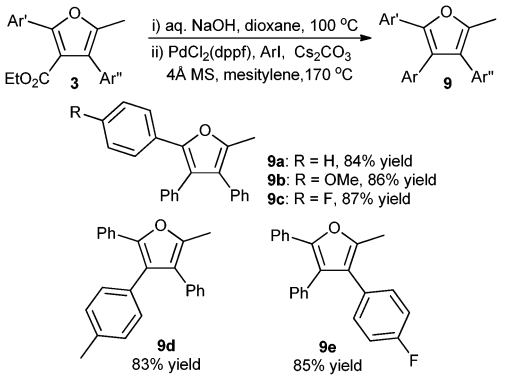
3ap

Table 3 Scope of the [3+2] cycloaddition with respect to alkynes[a]



Entry	**1** (R^1)	Product (**3**)	Yield[b] (%)
1	**1a** (Ph)	**3aa**	93
2	**1b** (4-MeC_6H_4)	**3ba**	55
3	**1c** (4-$MeOC_6H_4$)	**3ca**	72
4	**1d** (4-HOC_6H_4)	**3da**	59
5	**1e** (4-$H_2NC_6H_4$)	**3ea**	—
6	**1f** (4-$CF_3C_6H_4$)	**3fa**	53
7	**1g** (4-FC_6H_4)	**3ga**	96
8	**1h** (2-FC_6H_4)	**3ha**	86
9	**1i** (3-FC_6H_4)	**3ia**	94
10[c]	**1j** (2-thienyl)	**3ja**	40
11[d]	**1k** ($PhCH_2CH_2$)	**3ka**	60

[a] Reaction conditions: **1** (0.44 mmol), **2a** (0.2 mmol), CuI (0.01 mmol, 5 mol%), 1,10-phenanthroline hydrate (0.011 mmol, 5.5 mol%), Ag_2CO_3 (0.24 mmol, 1.2 equiv.) in 3 mL of EtOH in a Schlenk tube at refluxing temperature for 24 h, then DBU (0.24 mmol, 1.2 equiv.) was added and monitored by TLC. [b] Isolated yield of **3**. [c] The reaction was performed in CH_2Cl_2 under catalysis by $CuBr_2$. [d] 10 mol% CuI and 0.72 mmol DBU were used.



Scheme 3 Transformation of cycloadducts *via* catalytic decarboxylative coupling.

coupling has been well established in the past decade, it remains highly challenging and less investigated with sterically congested heteroaromatic acids.[10] It has been found that the hydrolytic products of **3** could readily undergo decarboxylative coupling with aryl iodides under catalysis by $Pd(dppf)Cl_2$, thus providing various 2-methyl-3,4,5-triaryl furans in high yields (Scheme 3).

In summary, we have developed a novel copper-catalyzed oxidative propargylic [3+2] cycloaddition of readily available simple alkynes with β-ketoesters *via* a propargylic C–H bond cleavage. The use of CuI as the catalyst precursor and Ag_2CO_3 as the bifunctional oxidant and base additive was crucial for the success of realizing this cycloaddition. This protocol displayed a broad substrate scope, and then provided a variety of highly functionalized furans in moderate to high yields. This represents the first successful example of the employment of a propargylic C(sp^3)–H functionalization strategy in catalytic propargylic cycloaddition with bis-nucleophiles. We believe that this propargylic C(sp^3)–H functionalization strategy will find widespread applications in the catalytic propargylic transformation, and further advance the research in this field. Detailed mechanistic studies and further application of the present catalytic system to other propargylic transformation reactions are currently underway in our laboratory.

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Conflicts of interest

There are no conflicts to declare.

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