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Pd/Cu-catalyzed cascade Sonogashira coupling/cyclization reactions to highly substituted 3-formyl furans†

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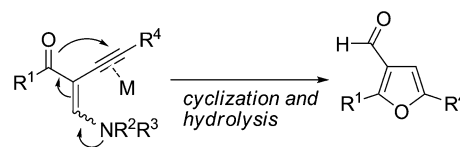
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An efficient palladium/copper-catalyzed approach to the synthesis of highly substituted 3-formyl furans from the reactions of readily available α -bromo enaminones with terminal alkynes has been developed. This methodology was realized by the cascade reactions of Sonogashira coupling and the subsequent intramolecular cyclization.

Transition metal-catalyzed cascade reactions have been proved as powerful tools for the synthesis of a variety of organic compounds in a one-pot manner.¹ These reactions allow the rapid construction of elaborate or highly functionalized organic molecules in one single operation. Polysubstituted furans are very important as core structures of many natural products and pharmaceuticals.² They are also useful building blocks in synthetic organic chemistry.³ As a result, a variety of synthetic procedures have been disclosed for furan ring formation.⁴ Among the many approaches to substituted furans, transition metal-catalyzed cyclization reactions are the most effective. The acyclic precursors involve allenyl ketones,⁵ alkynyl ketones,⁶ 2-(1-alkynyl)-2-alken-1-ones,⁷ enynols or phenols,⁸ 1,3-enynyl ketones⁹ and others.¹⁰ Although these methods are efficient for substituted furan formation, procedures for the preparation of formylated furans are rare,¹¹ and the metal mediated direct synthesis of trisubstituted furans with a C-3 or C-4 formyl group has not been reported,¹² to the best of our knowledge. 3-Formyl furan derivatives are versatile synthetic intermediates for the preparation of core structures of bioactive natural products that have shown a wide range of activities such as anticancer, antifungal and antifouling agents,¹³ for example, for the preparation of bioactive butenolides and (–)-nakadomarin A which showed cytotoxic activity against murine lymphoma L1210 cells.¹⁴ Generally, 3-formyl furans could be synthesized in two ways. First is the metalation of furan rings followed by formylation.¹⁵ This could be problematic because metalation usually occurs preferentially at the C-2 and C-5 positions. Second is the reduction of carboxylic acids or carboxylic esters¹⁶ on the furan rings obtained, for example,

from the Feist–Benary synthesis.¹⁷ This has some drawbacks such as the protection and deprotection of other functional groups on the furan ring. Therefore, the development of an efficient and direct approach for 3-formyl furan formation is highly desired. During the course of our ongoing study on the development of heterocycle forming protocols,¹⁸ we found that functionalized 1,4-dihydropyridines could be efficiently prepared from enaminones.¹⁹ Enaminones are versatile reagents that combine the ambident nucleophilicity of enamines with the ambident electrophilicity of enones. We envisioned that enaminones incorporating an alkyne moiety at the α -position might undergo transition metal-catalyzed cyclization to substituted furans with a C-3 formyl group after hydrolysis, because the inherent behavior of the push-pull-substituted enaminones may further facilitate the nucleophilic attack of the carbonyl oxygen to the triple bond (Scheme 1).



Scheme 1

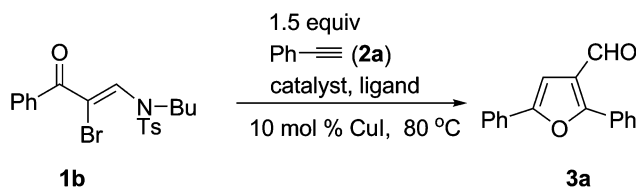
Herein, we would like to report the effective synthesis of 3-formyl trisubstituted furans through cascade Sonogashira coupling/cyclization reactions (Scheme 2).

The requisite α -bromo enaminones were synthesized *via* bromination of *N*-substituted enaminones which were readily prepared through conjugate addition of anilines or aliphatic amines with terminal alkynones or ethyl propiolate.¹⁹ The reaction of (*Z*)-2-bromo-3-(butylamino)-1-phenylprop-2-en-1-one (**1a**; Scheme 2, R² = Bu, R³ = H) bearing a secondary amine group with phenylacetylene (**2a**) was first carried out using Pd/Cu as the catalysts. However, no Sonogashira coupling product was obtained after screening a variety of reaction conditions. We thought that protected amine might be necessary for the coupling reaction. Then a *p*-toluenesulfonyl protected α -bromo enaminone of (*Z*)-*N*-(2-bromo-3-oxo-3-phenylprop-1-en-1-yl)-*N*-butyl-4-methylbenzenesulfonamide (**1b**) was prepared instead to react with **2a** (Table 1). When the reaction was carried out using Pd(PPh₃)₂Cl₂ (5 mol%) and CuI (10 mol%) as catalysts, Et₃N as the base in THF, only the Sonogashira coupling product, namely (*E*)-*N*-(2-benzoyl-4-phenylbut-1-en-3-ynyl)-*N*-butyl-4-methylbenzenesulfonamide (**4a**), was obtained in 80% yield

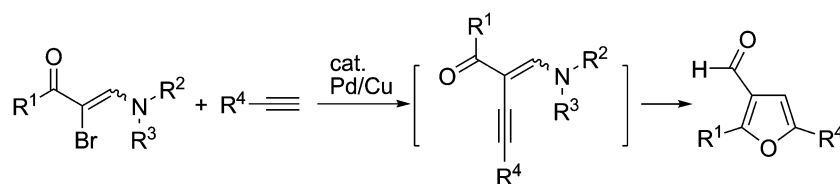
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Table 1 Optimization studies for the formation of 3-formyl furan **3a**

						
entry	catalyst (5 mol%)	ligand (10 mol%)	H ₂ O	solvent	time (h)	yield(%) ^a
1 ^b	Pd(PPh ₃) ₂ Cl ₂	—	—	THF	12	4a (80) ^c
2 ^b	Pd(PPh ₃) ₂ Cl ₂	—	—	DMF	12	trace
3 ^b	Pd(PPh ₃) ₂ Cl ₂	—	—	CH ₃ CN	12	—
4	Pd(PPh ₃) ₂ Cl ₂	—	—	^t Pr ₂ NH	14	63
5	Pd(PPh ₃) ₂ Cl ₂	—	—	Et ₃ N	24	67
6	Pd(PPh ₃) ₂ Cl ₂	—	1.0	Et ₃ N	24	64
7	Pd(PPh ₃) ₂ Cl ₂	—	10.0	Et ₃ N	16	62
8	Pd(PPh ₃) ₂ Cl ₂	—	5.0	Et ₃ N	16	81
9 ^d	Pd(PPh ₃) ₂ Cl ₂	—	5.0	Et ₃ N	17	82
10	Pd(OAc) ₂	Ph ₃ P	5.0	Et ₃ N	20	76

^a Isolated yields. ^b 3.0 equiv of Et₃N was added as the base. ^c The reaction was carried out at 50 °C. ^d 2.0 equiv of **2a** was used.

**Scheme 2**

(Table 1, entry 1). Changing the solvent to DMF gave a trace amount of 3-formyl furan **3a** (Table 1, entry 2). Other solvents such as CH₃CN gave no desired products (Table 1, entry 3). Interestingly, when ^tPr₂NH was used as the solvent, **3a** could be obtained in 63% yield (Table 1, entry 4). To our delight, Et₃N gave the desired **3a** in 67% yield after 24 h (entry 5). It is worthy to note that the addition of H₂O (5 equiv) can remarkably shorten the reaction time and give a much higher yield (81%) of the expected product (Table 1, entry 8). 2 equiv of phenylacetylene gave a similar result as that of 1.5 equiv (Table 1, entry 9). Other Pd catalysts such as Pd(OAc)₂ in the presence of PPh₃ gave a lower yield of the desired product even with a longer reaction time (Table 1, entry 10). It was clear that the optimized reaction condition was to use 5 mol% of Pd(PPh₃)₂Cl₂ and 10 mol% of CuI as the catalysts, 5 equiv of H₂O and Et₃N as the solvent at 80 °C.

With the optimized reaction conditions in hand, we next examined the substrate scope of this catalytic method for the synthesis of 3-formyl furans using a variety of α -bromo enaminones **1** and terminal alkynes **2** (Table 2). Firstly, we investigated the electronic effects of the aromatic substituents on terminal alkynes. It was found that an electron-withdrawing (-Cl) aryl group afforded the corresponding product **3b** in 76% yield (Table 2, entry 2). An electron-donating (-OMe) aryl group resulted in 83% yield with dramatically less reaction time (Table 2, entry 3). 1-Ethynynaphthalene (**2d**) gave good result (Table 2, entry 4). Alkyl substituted alkynes such as oct-1-yne (**2f**) and propargylic ether **2g** were also compatible under the reaction conditions, furnishing **3f**, **3g** in 63% and 35% yields, respectively (Table 2, entries 6, 7). The reaction proceeded smoothly with various *N*-Ts substituted α -

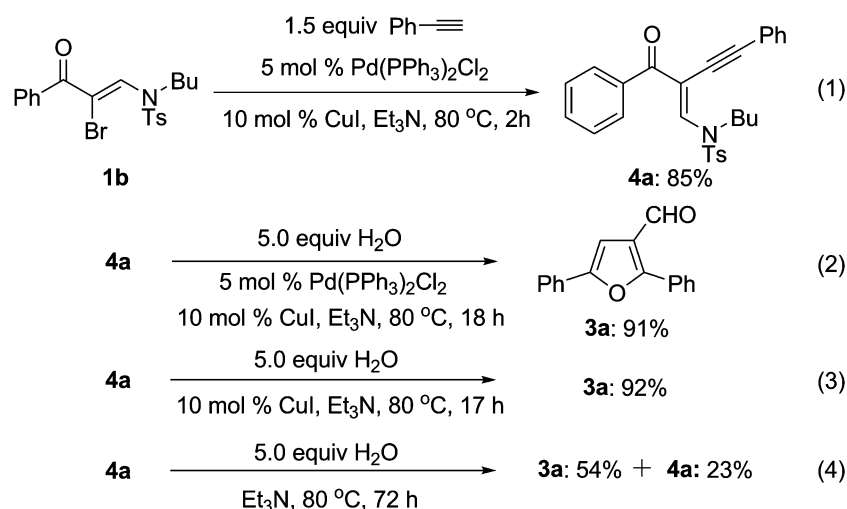
bromo enaminones to produce the desired 3-formyl trisubstituted furans in good to high yields. α -Bromo enaminone **1c** with a 4-methoxyphenyl substituent located on the carbonyl moiety led to the formation of **3h** in 80% yield (Table 2, entry 8). The substituents on carbonyl carbon could also be 4-chlorophenyl, 2-furanyl or 1-naphthyl, and the corresponding 3-formyl furans were obtained in 60–83% yields (Table 2, entries 9–11). When α -bromo enaminone with a cyclohexyl group on carbonyl carbon was employed, the reaction with phenylacetylene was completed in a much longer reaction time to give the desired product **3i** in moderate yield (Table 2, entry 12). The cyclization has also been successfully extended to the *N,N*-diisopropyl substituted α -bromo enaminone **1h**, and 62% yield of **3a** was obtained through the reaction with phenylacetylene (Table 2, entry 13). When an acetyl protected α -bromo enaminone **1i**, namely *N*-(2-bromo-3-oxo-3-phenylprop-1-en-1-yl)-*N*-(4-methoxyphenyl)acetamide, was reacted with phenylacetylene under the standard reaction conditions, **3a** was isolated in 84% yield along with *N*-(4-methoxyphenyl)acetamide in 93% yield. However, when *N,N*-diphenyl substituted α -bromo enaminone such as (*Z*)-2-bromo-3-(diphenylamino)-1-phenylprop-2-en-1-one was used to react with **2a**, only trace amount of the desired furan was detected with most of the α -bromo enaminone remaining.

To understand the reaction mechanism, we stopped the reaction of **1b** with phenylacetylene after 2 h. The coupling product **4a** was isolated in 85% yield [Scheme 3, eqn (1)]. The isolated **4a** was subjected to the standard conditions to afford **3a** in 91% yield after 18 h [Scheme 3, eqn (2)]. Without the addition of Pd(PPh₃)Cl₂, 10 mol% of CuI also furnished **3a** in 92% in 17 h [Scheme 3,

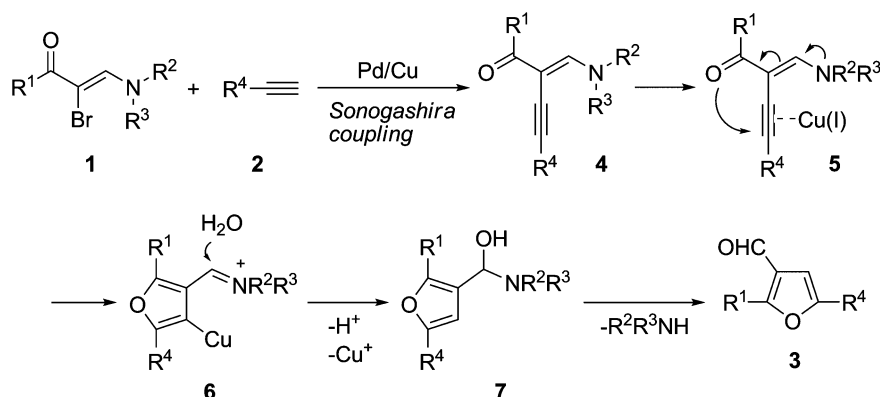
Table 2 Synthesis of various of trisubstituted 3-formyl furans

Entry	Bromoaminone	Alkyne	Time (h)	Product	Yield (%) ^a
1		Ph-C≡CH (2a)	16		81
2	1b	<i>p</i> -ClC ₆ H ₄ -C≡CH (2b)	21		76
3	1b	<i>p</i> -MeOC ₆ H ₄ -C≡CH (2c)	11		83
4	1b	Naph-C≡CH (2d)	35		73 ^b
5	1b		11		69
6	1b	Bu-C≡CH (2f)	21		63
7	1b	Ph-CH ₂ -O-CH ₂ -C≡CH (2g)	50		35
8		2a	20		80
9		2a	12		60
10		2a	14		83
11		2a	14		78
12		2a	42		41 ^c
13		2a	12	3a	62

^a Isolated yields. Unless noted, all the reactions were carried out at 80 °C with Pd(PPh₃)₂Cl₂ (5 mol%) and CuI (10 mol%) as catalysts, 1.5 equiv of alkyne and 5.0 equiv of H₂O in Et₃N. ^b Naph is 1-naphthyl. ^c Hex is cyclohexyl.



Scheme 3



Scheme 4 A proposed reaction pathway.

eqn (3)]. Surprisingly, without any metal catalysts, **3a** could also be produced in 54% yield, however, a longer reaction time of 72 h was required. Moreover, the reaction of **1b** with phenylacetylene under the optimal reaction conditions without the addition of CuI could also afford the desired **3a** in a much lower yield of 54% after 15 h. These results indicated that copper salts could accelerate the intramolecular cyclization process.

On the basis of the above observations, a possible reaction mechanism is proposed in Scheme 4. First, Sonogashira coupling of α -bromo enaminone **1** and terminal alkyne took place to give the alkynylated enaminone **4**. Then the subsequent coordination of the alkynyl moiety to the Cu(I) salt enhances the electrophilicity of the triple bond,²⁰ which facilitates an intramolecular cyclization of the carbonyl oxygen onto the alkyne to afford the iminium cation **6**. Hydrolysis of **6** and protonation with regeneration of the Cu(I) catalyst led to the desired 3-formyl furan **3**.

In conclusion, we have successfully developed an efficient method for the synthesis of trisubstituted furans with a formyl group at the C-3 position that are difficult to access by other methods, through Pd/Cu -catalyzed Sonogashira coupling/cyclization cascade reaction. Further applications of this novel Pd/Cu -catalyzed trisubstituted furan formation procedure to extend the scope of synthetic utility of the reaction are under progress in our group.

Experimental section

A typical procedure for the Pd -catalyzed one-pot synthesis of 2,5-diphenylfuran-3-carbaldehyde (**3a**)

To a solution of (*Z*)-*N*-(2-bromo-3-oxo-3-phenylprop-1-enyl)-*N*-butyl-4-methyl benzenesulfonamide (**1b**) (218 mg, 0.5 mmol) in Et_3N was added H_2O (0.045 mL, 2.5 mmol), phenylacetylene **2a** (0.082 mL, 0.75 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (18 mg, 5 mmol%) and CuI (10 mg, 10 mmol%) in this sequence. The resulting solution was stirred at 80°C for 16 h, the solvent was evaporated under reduced pressure and the residue was diluted with EtOAc and washed with satd. aq. NH_4Cl . The organic layer was separated, and the aqueous layer was extracted with EtOAc . The combined organic layers were dried over Na_2SO_4 . The solvent was evaporated under reduced pressure, and the product was isolated by chromatography on a silica gel column to give the yellow solid product 2,5-diphenylfuran-3-carbaldehyde (**3a**); 101 mg (81%); mp $84\text{--}85^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3 , Me_4Si) δ 7.04 (s, 1H), 7.28–7.32 (m, 1H), 7.37–7.51 (m, 5H), 7.69–7.77 (m, 4H), 10.10 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , Me_4Si) δ 103.85, 124.06, 124.63, 127.80, 128.33, 128.69, 128.73, 128.89, 129.18, 130.00, 153.79, 160.23, 185.42; HRMS calcd for $\text{C}_{17}\text{H}_{12}\text{O}_2$ 248.0837, found 248.0834.

Acknowledgements

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