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COMMUNICATION

Gold-catalyzed efficient synthesis of 2,4-disubstituted furans from aryloxy-enynes†

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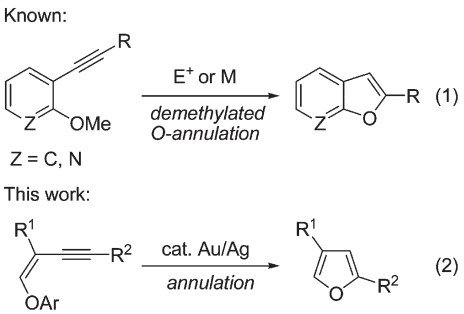
A series of (*E*)-1-aryloxy-1-en-3-ynes has been prepared by Sonogashira coupling of 2-bromo-3-aryloxypropenoates with terminal alkynes using $Pd(PPh_3)_4$ and CuI as the catalysts in Et_3N. The resulting enynyl-aryl ethers are found to be highly applicable to the synthesis of 2,4-disubstituted furans with an ester group at C-4 position through an Au/Ag-catalyzed annulation reaction under extremely mild reaction conditions.

Furans are of great importance as core structures of many natural products and pharmaceuticals.[1] They are also useful building blocks in synthetic organic chemistry.[2] Accordingly, many synthetic approaches toward the synthesis of furan rings have been disclosed.[3] Among them, the intramolecular attack of a nucleophilic oxygen atom onto a C–C triple bond offers a straightforward access to furan derivatives. Generally, these reactions include the electrophilic cyclization of functionally substituted alkynes and the transition metal-catalyzed annulation. A wide range of furans have been prepared using these strategies. The precursors employed are acetylenic compounds containing a pendant oxygen functionalities, such as enynones,[4] enynols,[5] alkynyl ketones,[6] 2-methoxypent-4-yn-1-ols,[7] γ-alkynyl ketones,[8] alkynyl ketone enolates,[9] allenyl compounds,[10] and propargyl ketones.[11] In these reactions, the carbonyl oxygen or a hydroxyl group served as a nucleophile to attack the activated triple bonds. On the other hand, the heteroannulation reaction utilizing the oxygen from an ether moiety as the nucleophile has also proved to be efficient for the construction of furan rings *via* the cleavage of a C–O bond. Most of the studies focus on the methyl ethers bearing an *ortho* alkyne for the synthesis of benzo-fused heterocycles through the demethylation reactions,[12,13] such as benzo[*b*]furans, furopyridinones, furopyrones, and furocoumarins (Scheme 1, eqn (1)). However, there is no report for the utility of aryl ethers for the preparation of furans. We assumed



Scheme 1

that the utility of aryl ethers for the preparation of furans might also be possible (Scheme 1, eqn (2)). During the course of our ongoing study on the development of heterocycle forming protocols using substrates with push-pull character,[14] we found that (*E*)-1-aryloxy-1-en-3-ynes could readily be converted to 2,4-disubstituted furans in the presence of an Au catalyst. Herein, we would like to report these results.

The requisite (*E*)-1-aryloxy-1-en-3-ynes with an ester group on C-2 (**3**) were synthesized *via* the Sonogashira coupling of the corresponding 2-bromo-3-aryloxypropenoates and terminal alkynes (Table 1). It is known that Sonogashira coupling usually was carried out using both palladium and copper as catalysts in Et_3N. In fact, when the coupling reaction of **1a** with phenylacetylene (**2a**) was performed using 5 mol% of $Pd(PPh_3)_4$ and 10 mol% of CuI in Et_3N at 70 °C, the desired product **3a** could be obtained in 88% isolated yield (Table 1, entry 1). As can be seen from Table 1, a variety of 2-halo-3-aryloxypropenoates reacted with terminal alkynes smoothly at 70 °C in Et_3N, and the corresponding (*E*)-1-aryloxy-1-en-3-ynes were produced in high yields in most cases. Aryl alkynes with both electron-donating and electron-withdrawing groups at the *para* position of the aromatic ring gave satisfactory yields (Table 1, entries 2–5). The substituents on terminal alkynes have also been expanded successfully to alkenyl (Table 1, entry 7) and alkyl groups (Table 1, entries 8–11). It is noteworthy that not only the 2-halo-3-aryloxypropenoates but also the 2-halo-3-alkyloxypropenoate derivatives (Table 1, entries 12, 14) were compatible with the reaction and gave the target products in good yields.

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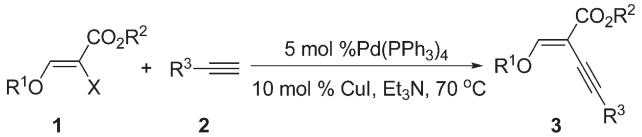
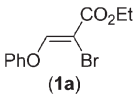
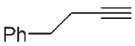
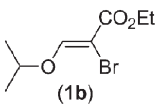
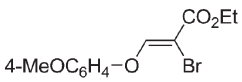
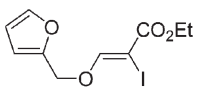
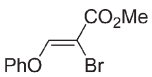
†Electronic supplementary information (ESI) available: Experimental details, spectroscopic characterization of all new compounds and X-ray crystallography of compound **3d**.[20] CCDC 850260 (**3d**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob07173h

Table 1 Synthesis of (*E*)-1-aryloxy-1-en-3-ynes



1 2 3

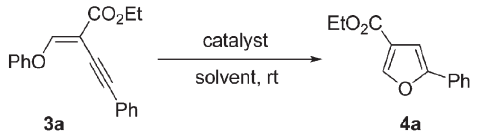
Entry	Vinyl bromide	Alkyne	Product	Yield (%)[a]
1	 (**1a**)	Ph— (**2a**)	**3a**	88
2	**1a**	4-MeC$_6$H$_4$— (**2b**)	**3b**	86
3	**1a**	4-MeOC$_6$H$_4$—	**3c**	92
4	**1a**	3,4,5 -(MeO)$_3$C$_6$H$_2$—	**3d**	92
5	**1a**	4-ClC$_6$H$_4$—	**3e**	89
6	**1a**	1-Naph—	**3f**	54[b]
7	**1a**	1-^{C}Hex—	**3g**	78[c]
8	**1a**	n-C$_4$H$_9$—	**3h**	43[d]
9	**1a**	n-C$_5$H$_{11}$—	**3i**	68[d]
10	**1a**	n-C$_6$H$_{13}$—	**3j**	60[d]
11	**1a**		**3k**	89
12	 (**1b**)	**2a**	**3l**	29[d]
13	 (**1c**)	**2b**	**3m**	71
14	 (**1d**)	**2a**	**3n**	73
15	 (**1e**)	**2a**	**3o**	94

[a] Isolated yields. Unless noted, all the reactions were carried out with the ratio of **1** : **2** = 1 : 2 at 70 °C for 2–24 h. [b] 1-Naph is 1-naphthyl. [c] 1-^{C}Hex is 1-cyclohexenyl. [d] 3.0 equiv. of alkyne was used.

In recent years, the use of gold catalysis has emerged as a powerful synthetic method for the construction of C–C and C–X bonds[15] under mild reaction conditions, especially for the C–O bond formation. Excellent work on furan formation catalyzed by gold has been reported.[4–11] We envisioned that the thus formed enynyl–aryl ethers would undergo an Au-catalyzed intramolecular C–O bond forming reaction toward furan derivatives, and the nucleophilic oxygen may either come from the carbonyl oxygen or the ether moiety. Initially, the reaction of (*E*)-1-phenoxy-1-en-3-yne with an ethyl ester group on C-2 (**3a**) was carried out using PPh$_3$AuCl (5 mol%) as the catalyst in THF at room temperature. However, no desired product was detected (Table 2, entry 1). It is interesting that when PPh$_3$AuCl (5 mol%) and AgOTf (5 mol%) were employed, the desired 2,4-disubstituted furan derivative **4a**[16] was formed in 92% yield (Table 2, entry 2). Lowering the catalyst loading to 2 mol% gave similar yield to that of 5 mol% (Table 2, entry 3). Changing the solvent to dichloromethane or toluene, **4a** were produced in 71% and 56% yields, respectively (Table 2, entries 5, 9). The use of only AgOTf (5 mol%) resulted in no reaction (Table 2, entry 4). Other Ag additives such as AgBF$_4$ or AgSbF$_6$ resulted in trace or lower yield of **4a** (Table 2, entries 6, 7). Therefore, the optimized reaction condition was to use 2 mol% of PPh$_3$AuCl and 2 mol% of AgOTf as the catalysts, THF as the solvent at room temperature.

With the optimized reaction conditions in hand, we next examined the substrate scope of this catalytic method for the synthesis of 2,4-disubstituted furans using a variety of (*E*)-1-aryloxy-1-en-3-ynes (Table 3). Firstly, we investigated the electronic effects of the aromatic substituents on triple bond. It was

Table 2 Optimization studies for the formation of furan **4a**



Entry	Catalyst (mol%)	Solvent	Time (h)	Yield[a]
1	PPh_3AuCl (5)	THF	7	N.R.
2	$PPh_3AuCl/AgOTf$ (5)	THF	6	92%
3	$PPh_3AuCl/AgOTf$ (2)	THF	7	91%
4	AgOTf (5)	THF	7	N.R.
5	$PPh_3AuCl/AgOTf$ (2)	DCM	7	71%
6	$PPh_3AuCl/AgBF_4$ (2)	THF	24	Trace
7	$PPh_3AuCl/AgSbF_6$ (2)	THF	8	68%
8	PPh_3AuNTf_2 (2)	THF	8	69%
9	PPh_3AuNTf_2 (2)	Toluene	24	56%

[a] Isolated yield.

found that electron-donating aryl groups such as –Me or –OMe afforded the corresponding products **4b**, **4c** in 77% and 85% yields, respectively (Table 3, entries 2, 3). The trimethoxyl aryl substitute also gave the desired **4d** in 72% yield (Table 3, entry 4). An electron-withdrawing (–Cl) aryl group afforded the corresponding furan **4e** in 84% yield (Table 3, entry 5). The naphthyl substituted one (**3f**) gave a good result (Table 3, entry 6). The cyclohexenyl substituted precursor worked nicely, producing the corresponding furan **4g** in 44% yield (Table 3, entry 7). The substituents on the triple bond could also be alkyl groups, such as n-butyl (**3h**), n-pentyl (**3i**), and n-hexyl (**3j**), furnishing **4h**, **4i**[17] and **4j** in 76%, 87% and 90% yields, respectively (Table 3, entries 8–10). **3k** with a phenylethyl group on the triple bond reacted successfully under the optimal conditions, leading to the corresponding **4k** in 82% yield (Table 3, entry 11). When the 4-methoxyphenoxyl substituted enynyl ether **3m** was employed, it furnished **4b** in 85% yield (Table 3, entry 13). It is noteworthy that the aryloxyl substituent of **3** can be changed to alkyloxyl

Table 3 Synthesis of various of 2,4-disubstituted furans

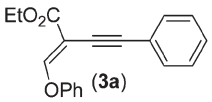
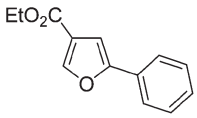
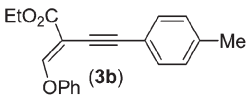
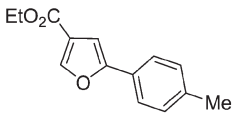
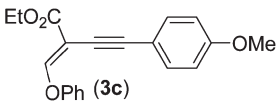
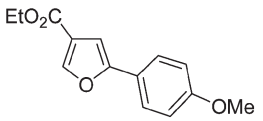
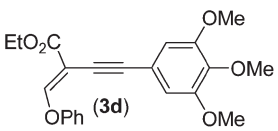
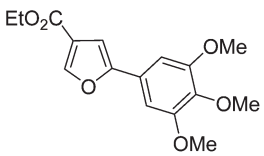
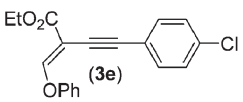
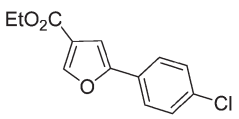
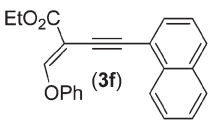
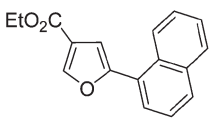
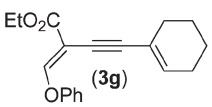
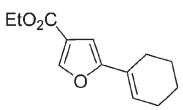
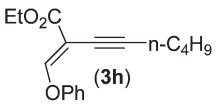
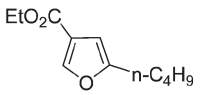
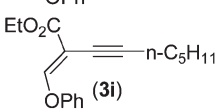
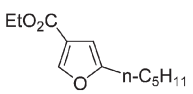
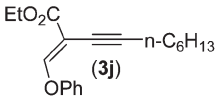
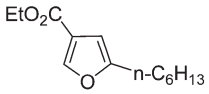
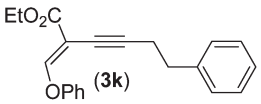
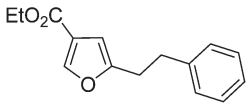
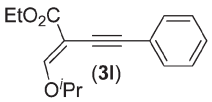
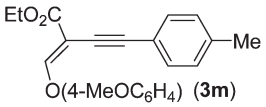
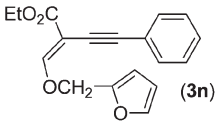
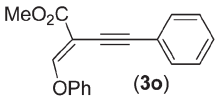
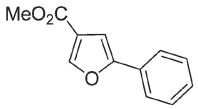
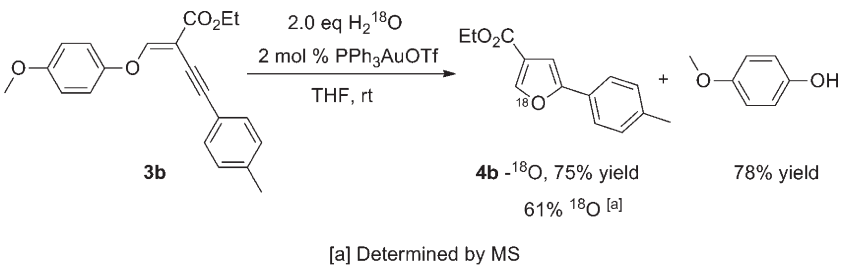
Entry	Enynyl ether	Time (h)	Product		Yield (%)[a]
1		7		**4a**	91
2		4		**4b**	77
3		3		**4c**	85
4		5		**4d**	72
5		7		**4e**	84
6		12		**4f**	71[b]
7		10		**4g**	44
8		3		**4h**	76
9		7		**4i**	87

Table 3 *(Contd.)*

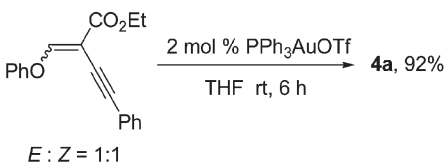
Entry	Enynyl ether	Time (h)	Product		Yield (%)[a]
10	 (**3j**)	7		**4j**	90[c]
11	 (**3k**)	6		**4k**	82
12	 (**3l**)	21		**4a**	60
13	 (**3m**)	4		**4b**	85
14	 (**3n**)	6		**4a**	88
15	 (**3o**)	4		**4l**	90

[a] Isolated yields. Unless noted, all the reactions were carried out using 2 mol% of PPh_3AuCl and AgOTf in THF. [b] 5 mol% of PPh_3AuCl and AgOTf were used. [c] Along with 42% of phenol were obtained.



Scheme 2 Isotopic experiment.

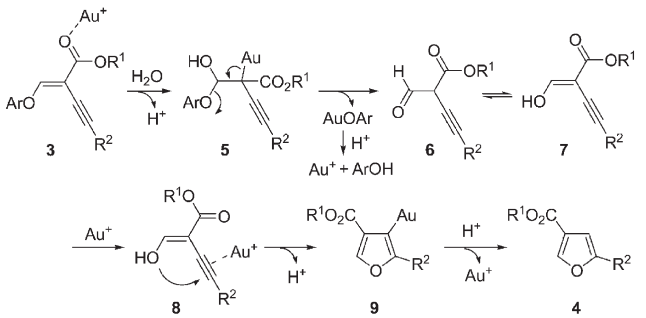
groups, providing the desired **4a** in good to high yields (Table 3, entries 12, 14). The ester group on C-2 could also be methyl ester, and the corresponding furan **4l** was produced in 90% yield (Table 3, entry 15). Very interestingly, a mixture of **3a** (*E* : *Z* = 1 : 1) could also afford the desired **4a** in high yield under the optimal conditions (eqn (1)). This result may further broaden the substrate scope of this method.



(1)

In order to understand the reaction mechanism, we examined the reaction of (*E*)-ethyl 2-(phenoxymethylene)dec-3-ynoate (**3j**) under the optimal conditions carefully. It was found that not only the desired furan **4j** was obtained in 90% yield after 7 h, phenol was also isolated in a yield of 42% (Table 3, entry 10). One possibility is that a dearylated *O*-annulation process occurs, and the aryl part of the vinyl–aryl ether moiety is transformed to phenol. Another possibility is that the aryl–enol–ether is hydrolyzed to the corresponding carbonyl group by H_2O, which may come from the air, and then undergo an *O*-cyclization. It is noteworthy that when H_2O (1–3 equiv.) was added to the reaction mixture of **3a**, the desired **4a** could be obtained in around 80% yield. More H_2O resulted in a much lower yield. The addition of 4 Å MS gave only a trace amount of the desired product. It indicated that certain amount of H_2O may play an important role in the reaction. To prove this point, we carried out an isotopic labeling experiment using **3b** with 2 equiv. of $H_2{}^{18}O$, and found that 61% of ^{18}O was incorporated in the final furan ring, whereas, phenol was formed without clear ^{18}O incorporation (Scheme 2).

On the basis of the above observations, a possible reaction mechanism is proposed in Scheme 3. First, coordination of C═O double bond of compound **3** to Au^+ facilitates the



Scheme 3 A proposed reaction pathway.

nucleophilic attack of H_2O to the C=C double bond to give **5**. Next, elimination of AuOAr produces **6** or **7**. Then **7** is activated by the subsequent coordination of the alkynyl moiety to Au^+ which enhances the electrophilicity of the triple bond,[18] and facilitates an intramolecular cyclization of the enol oxygen onto the alkyne to afford **9**. Protonation[19] of **9** with regeneration of the Au^+ catalyst furnishes the desired furan **4**.

In conclusion, we have shown that (*E*)-1-aryloxy-1-en-3-ynes can be efficiently prepared by the Sonogashira coupling reaction using 2-bromo-3-aryloxypropenoates and terminal alkynes. The resulting (*E*)-1-aryloxy-1-en-3-ynes are successfully applied to the synthesis of 2,4-disubstituted furans with an ester group at C-4 position through Au/Ag-catalyzed annulation reaction. Aryl, alkenyl and alkyl substituents on the acetylene terminus are compatible in the annulation reaction, furnishing the desired furans in good to high yields. In this procedure, Au catalyzed two reactions in one-pot, one is the hydrolysis reaction of (*E*)-1-aryloxy-1-en-3-ynes, and the other is the subsequent *O*-cyclization reaction. Further studies of these interesting (*E*)-1-aryloxy-1-en-3-ynes to extend the synthetic utility in organic chemistry are in progress in our group.

Experimental section

A typical procedure for the Au-catalyzed formation of ethyl 5-phenylfuran-3-carboxylate

(*E*)-Ethyl 2-(phenoxymethylene)-4-phenylbut-3-ynoate (58 mg, 0.2 mmol), THF (2 mL), PPh_3AuCl (2.0 mg, 2 mol%), AgOTf (0.1 mL, 0.04 M in THF, 2 mol%) are added to a Schlenk tube. The resulted solution was stirred at room temperature. After the reaction was complete as monitored by thin-layer chromatography, the solvent was evaporated under the reduced pressure and the residue was purified by chromatography on silica gel to afford the 2,4-disubstituted furan derivatives **4a** (33 mg, 76%) as a yellow solid; m.p. 45 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 1.36 (t, J = 6.8 Hz, 3H), 4.33 (q, J = 7.2 Hz, 2H), 6.97 (s, 1H), 7.30–7.32 (m, 1H), 7.37–7.41 (m, 2H), 7.66–7.68 (m, 2H), 8.02 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 14.28, 60.49, 104.44, 121.24, 123.97, 128.09, 128.73, 129.82, 146.67, 155.08, 163.10; HRMS (EI) for $C_{13}H_{12}O_3$: calcd 216.0786, found 216.0787.

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20 CCDC 850260 (**3d**) contains the supplementary crystallographic data for this paper.