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Gold(III)-catalyzed synthesis of 2,5-disubstituted furans from substituted 5-methoxyhex-3-yn-2-ols—Mechanistic outlook

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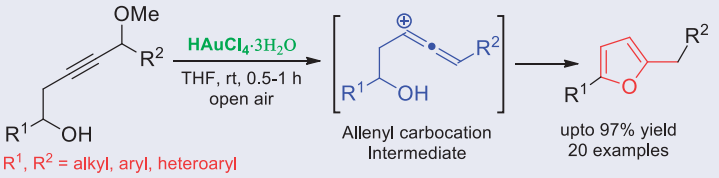
ABSTRACT

Gold(III)-catalyzed activation of alkynes has been applied for the synthesis of 2,5-disubstituted furans from substituted 5-methoxy-hex-3-yn-2-ols. Mechanistically, the reaction proceeds via an allenyl carbocation intermediate followed by *5-endo-dig* cyclization. The high-yielding, open-air, room temperature reaction conditions applied to synthesize a series of alkyl, aryl, and hetero aryl-substituted furans provide uniqueness to the strategy.

GRAPHICAL ABSTRACT



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KEYWORDS
Allenyl carbocation; *5-endo-dig*; one-pot; open-air; propargyl ether

Among the five-membered heterocyclic compounds, the substituted furans are important building blocks in many biologically active natural products, which are mostly available in plants, algae, and microorganisms.[1] Furans have also been the central core of many pharmaceutical drugs and optoelectronic materials (Figure 1).[2]

Furans are extensively used as important intermediates in industrial organic synthesis such as flavors, material sciences, agrochemicals, polymers, etc. In addition to that, furans are employed as useful building blocks for other heterocyclic, acyclic, and macromolecules as they undergo facile transformations such as concerted cycloadditions (Diels–Alder), electrophilic substitutions, metallations, or ring-opening reactions for synthesizing 1,4-dicarbonyl compounds and thus can be transformed into a variety of other functionalities.[3]

Classical approaches like Paal–Knorr synthesis, acid-catalyzed intramolecular cyclization of 1,4-dicarbonyl compounds,[4] Feist–Benary annulations[5] have been widely used in the synthesis of substituted furans. The metal-catalyzed approach offers several advantages in terms of efficiency and functional group compatibility as compared to the

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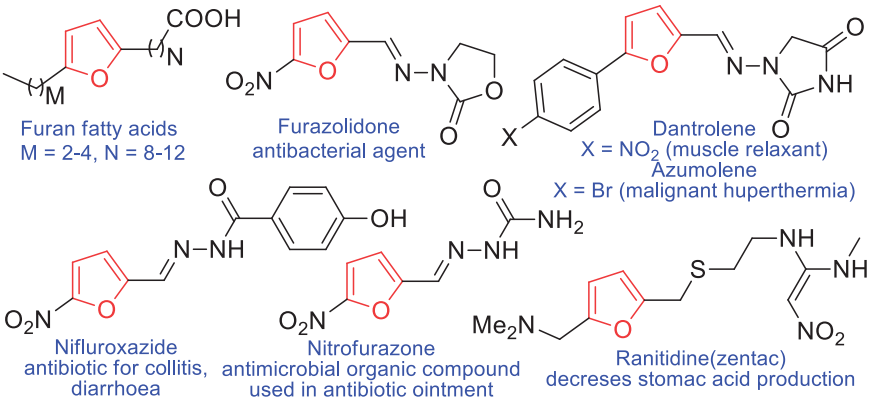


Figure 1. Substituted furans as central core in natural products and pharmaceutical drugs.

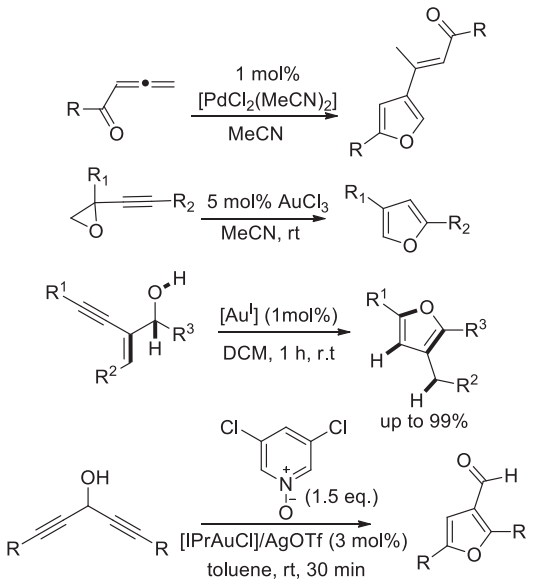
classical approach.[6] Organocatalytic approaches have also been described previously like Krische's phosphine-mediated reductive condensation of γ-acyloxy butynoates and Jørgensen's synthesis of 2-hydroxyalkyl and 2-aminoalkyl furans.[7] Being efficient Л-activators, gold catalysis is being extensively used in enormous organic transformations in the last decade.[8]

In the early 20th century, the first synthesis of furans has been disclosed by the Hashmi group from allenyl ketones in the presence of a homogenous gold catalyst.[9] The second report of furan synthesis also came up from the Hashmi group again by the reaction of gold chloride and allynyl epoxide.[10] In 2011, the Hashmi group again disclosed a new gold(I)-carbene cascade toward the synthesis of substituted furans from alkynylallyl alcohol.[11] An efficient gold(I)-catalyzed cascade reaction that leads to 3-formylfurans from symmetric and unsymmetric 1,4-diyn3-ols in the presence of an N-oxide via oxygen transfer results in 1,2-alkynyl migration is favored over a hydride shift followed by cyclization afford the desired functionalized furan core in good to excellent yield.[12] The schematic representation of furan synthesis from the Hashmi group by employing gold catalysts is explained in Scheme 1. Furans were also have been synthesized by different groups via cycloisomerization-elimination reaction cascade.[13]

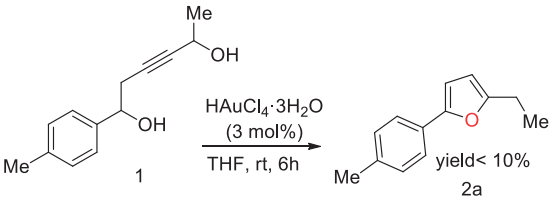
In the aforesaid reports, but-3-yn-1,2-diols as substrates were used for the synthesis of furans which resulted in limited substrate scope, also the mechanistic explanations were based on a theoretical approach. In this report, 5-methoxypent-3-yn-1-ols are employed toward the synthesis of 2-substituted furans. The present transformation has been added with mechanistic explanation and experimental evidence which attests to the formation of a 6-membered pyran ring as a side-product.

It may be highlighted that 5-methoxypent-3-yn-1-ols are easier to be synthesized as compared to the earlier used but-3-yn-1,2-diols with facile reaction conditions. Another important outlook is the mechanistic rationale and this demands an acute investigation. For instance, a typical allenyl intermediate was reported by Zhu[14] which asks for more experimental support on its generation.

Thus, we disclose an Au-catalyzed activation of substituted propargylic alcohols as an important strategy toward the synthesis of substituted furans. Generation of the dihydropyran as a minor product exemplifies the mechanistic rationale involving an allenyl carbocation.



Scheme 1. Gold catalyzed synthesis of furan core via cycloisomerization-elimination mechanism.



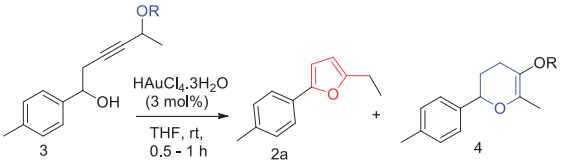
Scheme 2. Furan synthesis from propargyl alcohol.

Results and discussion

An initial experiment with propargyl alcohol (**1**) by employing 3 mol% of AuCl catalyst at room temperature was nonproductive. The same propargyl alcohol (**1**) was stirred in the presence of 3 mol% of $HAuCl_4.3H_2O$ as a catalyst in THF and delivered furan (**2a**) with low yields as in Scheme 2.

In order to achieve better yields of synthesized furan, the propargyl alcohol (1) was converted to the appropriate propargyl ether (**3**). The 5-methoxy-1-(*p*-tolyl)hex-3-yn-1-ol (**3a**) with methyl protection, delivered an impressive yield of 93% of furans (**2a**) along with the 7% pyran derivative (**4a**). However, the substituted 5-alkoxy-hex-4-yn-2-ols bearing other protecting groups result in furans with satisfactory yield along with a negligible amount of pyran (**4**) which is summarized in Scheme 3. This turned out to be important information for us, which clearly clarified the mechanism of the reaction.

The reaction conditions were optimized in the presence of various solvents, varied catalyst concentrations, and temperature. The 5-methoxy-1-(*p*-tolyl)hex-3-yn-1-ol (**3a**) was taken for standardization of reaction conditions. With 2 mol% of catalyst, in 8 h at room temperature, 74% of the yield of furan was obtained. However, increasing the



Entry	3	2a	4
1	**3a**, R = Methyl	93%	4a, 7%[a]
2	**3a**[1], R = Ethyl	91%	4b, trace
3	**3a**[2], R = Propyl	87%	4c, trace
4	**3a**[3], R = Benzyl	84%	4d, trace

[a]Isolated and confirmed by spectroscopic analysis

Scheme 3. Furan synthesis from 5-alkoxy-hex-4-yn-2-ols.

Table 1. Optimization of reaction condition.

Entry	Catalyst (X mol%)	Solvent	Temp. (°C)	Yield (%)
1	3	THF	rt	93
2	3	DCM	rt	36
3	3	MeCN	rt	10[a]
4	3	Acetone	rt	15[a]
5	3	H_2O	rt	NR
6	3	PhMe	rt	30
7	3	DMSO	rt	NR
8	2	THF	rt	74[b]
9	**5**	**THF**	**rt**	**97**
10	10	THF	rt	96
11	5	THF	0 °C	55
12	5	THF	45 °C	71

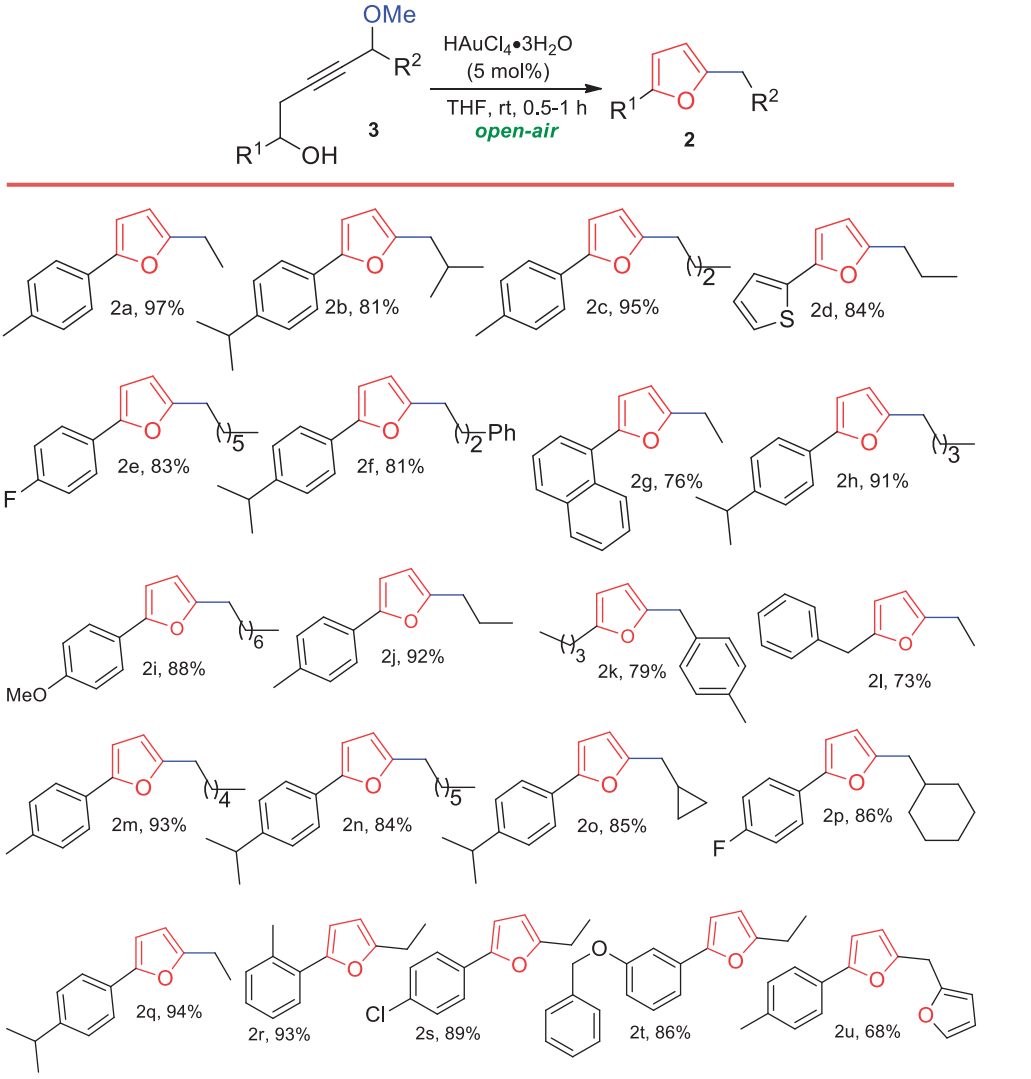
[a]After 6 h of reaction time in open-air; NR: No Reaction, Starting material was left; [b]After 8 h reaction time.

catalyst concentration to 5 mol% at room temperature delivered the furan (**2a**) with 97% of yield. With incremental addition of catalyst concentration from 5 to 10 mol%, no significant increase of yield was observed. Furthermore, with an increase of temperature to 45 °C, the yield of the reaction decreased to 71%.

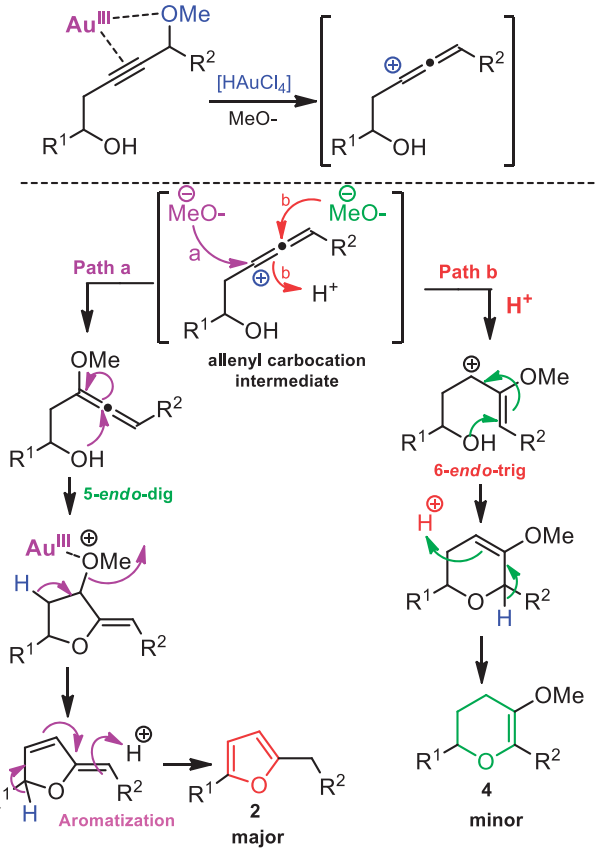
Hence, the optimal condition was maintained with a combination of 5 mol% of catalyst concentration at room temperature in THF solvent. Further, the reaction was also monitored under an inert atmosphere. It was worth noting that, the same yield was observed in both open-air and in presence of inert conditions which clearly ruled out the requirement of inert conditions for the transformation. The standard optimized condition was summarized in Table 1.

The generalizability of the methodology was checked by employing the reaction with differently substituted 5-methoxy-hex-3-yn-2-ols with standard conditions. For cyclic (**2o** and **2p**), acyclic (**2i** and **2l**), aryl (**2a**, **2b**, and **2g**), and heteroaryl (**2d** and **2u**) substituted 5-methoxy-hex-3-yn-2-ols, the methodology worked smoothly with good to excellent yields. The furan derivative **2a** was obtained with the maximum yield of 97% whereas a minimum yield of 68% of **2u** was obtained which is summarized in Table 2.

Table 2. Substrate scope of substituted furans.



It may be proposed that the reaction proceeds via a subsequent cycloisomerization-elimination pathway[15] as depicted in Scheme 1. The isolation of the minor dihydropyran (**4a**) discloses the vital mechanistic route to this transformation which was not disclosed in earlier communications by such catalysis. Based on the observation, especially the non-isolation of the dihydropyran (**4b–4d**) in Scheme 3 with non-nucleophilic alkoxides like benzyloxy (**3a**^{3}), propyloxy (**3a**^{2}), it can be articulated that the reaction proceeds through an allenyl carbocation intermediate. The two pathways (**a**) and (**b**) are mutually exclusive. The reaction pathway (**a**) proceeds through the allenyl carbocation which undergoes a 5-*endo-dig* cyclization to deliver the furan, as summarized in Scheme 4.



Scheme 4. Plausible reaction mechanism.

Experimental section

General procedure (A) for synthesis of 2,5-disubstituted furans (2a–2u)

The methoxy-protected propargylic alcohols, (**3a–3t**) in THF were taken in an "open-flask." 5 mol% of $HAuCl_4.3H_2O$ in THF was added slowly into the reaction mixture. The mixture was stirred at room temperature and the product formation was monitored by TLC. The reaction was stirred approximately for 0.5 to 1 h. After the completion, the mixture was extracted with EtOAc (2 × 3 mL) and distilled water, and the organic layer was filtered over anhydrous Na_2SO_4 and was being concentrated applying vacuum. Then, the residue was subjected to flash column chromatography using silica 200:400 mesh size. Elution with the appropriate ratio of Hexane: EtOAc, affords the corresponding 2,5-disubstituted furans, (**2a–2u**) with an excellent yield.

General procedure (B) for the synthesis of substituted 6-methoxyhept-3-yn-2-ol (3a–3u)

Diprotected propargylic alcohols, (**5a–5t**) were taken in THF. The solution of Tetrabutylammonium fluoride (TBAF, 1.2 equiv.) was added to the well-stirred reaction

mixture. The reaction was performed in an inert atmosphere and monitored by TLC. After 3–4 h, the reaction was completed and quenched with distilled water and washed with ethyl acetate. The organic layer was collected over anhydrous Na_2SO_4 and concentrated. The mass was subjected to column-chromatography using silica (200:400 mesh); elution with Hexane: EtOAc affords the desired mono-protected alcohols (**3a–3u**).

2-Ethyl-5-(p-tolyl)furan (2a)

According to general procedure A, 2-ethyl-5-(*p*-tolyl)furan, **2a** was synthesized with 97% of yield (65 mg, 0.34 mmol) as yellowish gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5–7.56 (m, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 6.53 (d, $J = 3.2$ Hz, 1H), 6.09–6.08 (m, 1H), 2.75 (q, $J = 7.6$ Hz, 2H), 2.39 (s, 3H), 1.32 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 152.4, 136.5, 129.3, 128.6, 123.3, 105.9, 104.9, 21.5, 21.2, 12.3. IR(neatfilm, KBr): 2961, 2845, 2349, 1651, 1454, 1247, 1033, 936, 831 cm^{-1}. HRMS (ESI) calcd. for $C_{13}H_{14}O$: $[M + H]^+$: 187.1123, Found 185.1125.

5-Methoxy-6-methyl-2-(p-tolyl)-3,4-dihydro-2H-pyran (4a)

5-methoxy-6-methyl-2-(*p*-tolyl)-3,4-dihydro-2H-pyran, **4a** was obtained by general procedure A as a side product with low yield of 7% as white semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, $J = 8$ Hz, 2H), 7.18 (d, $J = 8$ Hz, 2H), 5.14 (t, $J = 12$ Hz, 1H), 3.33 (s, 3H), 2.35–2.23 (m, 4H), 2.20 (s, 3H), 2.19–2.14 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.6, 136.2, 129.1, 126.4, 126.3, 84.3, 50.9, 33.3, 25.7, 21.1, 16.3. IR(neatfilm, KBr): 2975, 2831, 2337, 1653, 1441, 1267, 1011, 946, 851 cm^{-1}. HRMS (ESI) calcd. for $C_{14}H_{18}O_2$: $[M + H]^+$: 219.1385, Found 219.1387.

Conclusions

In summary, this report has demonstrated an efficient protocol of Gold(III)-catalyzed synthesis of 2,5-disubstituted furans from substituted 5-methoxy-hex-3-yn-2-ols via an elimination-cyclization-aromatization pathway. The substitution of the hydroxyl group with methoxy in the propargyl alcohols led to a significant improvement in the reactivity and the formation of furans in good to excellent yield. The one-pot, room temperature, and open-air reaction conditions and the isolation of side-product make this protocol highly practical and mechanistically acceptable.

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Disclosure statement

NO potential conflict of interest was reported by the author(s).

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