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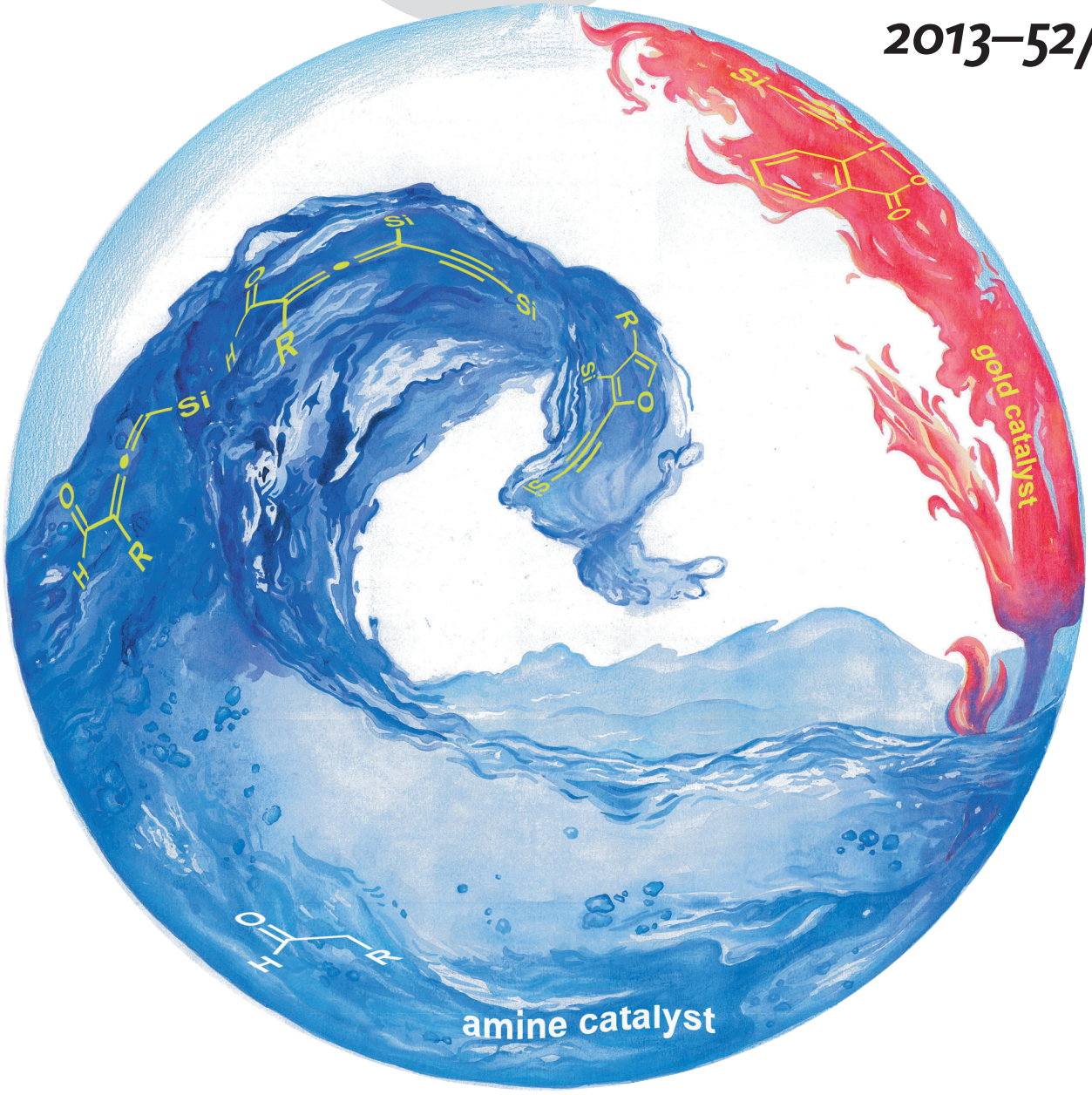


## Synergistic catalysis ...

… enables previously unattainable bond formation by activating both reaction partners orthogonally through the use of two catalysts in one pot. In their Communication on page 14219 ff., Y. Huang and co-workers describe the first direct $\alpha$-vinylidenation of aldehydes and an $\alpha$-vinylidenation/$\gamma$-functionalization cascade to access tri- and tetrasubstituted allenyl aldehydes by using synergistic catalysis with a gold catalyst and a secondary amine.

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# Direct α-Vinylidenation of Aldehydes and Subsequent Cascade: Gold and Amine Catalysts Work Synergistically**

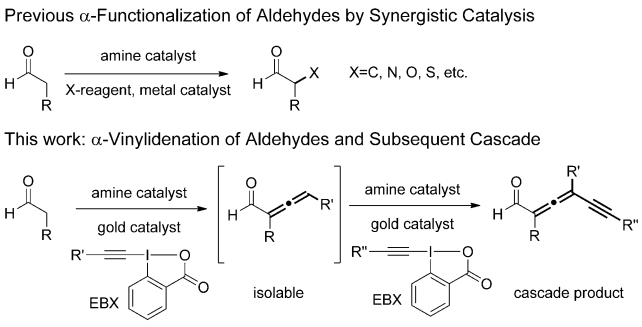
*Zhaofeng Wang, Xijian Li, and Yong Huang**

***Abstract:*** *Carbonyl-substituted allenes are highly important synthetic intermediates for a number of heterocycles and strained-ring systems. However, chemistry of allenyl aldehydes has not been explored as extensively as their ketone, ester, or amide analogues because of a lack of general synthetic methods. Described herein is the first direct α-vinylidenation of aldehydes and an α-vinylidenation/γ-functionalization cascade to access tri- and tetrasubstituted allenyl aldehydes using a combination of a gold catalyst and an secondary amine. The reactive enamine intermediate of an aldehyde reacts with the gold-activated hypervalent silylethynyl benziodoxolone to selectively generate the corresponding trisubstituted allenyl aldehyde. The allenyl aldehyde can further react with another equivalent of the alkynylation reagent or other electrophiles to afford tetrasubstituted allenes bearing an aldehyde group, an acetylene, and a halogen functionality. This method enables rapid access to polysubstituted furans from aldehydes.*

Functionalized allenes are an important class of structural motifs which possess unique chemical properties.[1,2] For the synthesis of natural products and drug molecules, allenes are of great interest because of their chemical versatility, which enables them to participate in many characteristic organic transformations.[3] Carbonyl-substituted allenes are particularly attractive as they are important synthons for a number of heterocycles and strained-ring systems.[4] However, despite being the most synthetically versatile, allenyl aldehydes have not been explored as extensively as their ketone, ester, or amide analogues because of the lack of general synthetic methods. Certain allenyl aldehydes can be made by rearrangement of a propargyl alcohol/halide or formylation of a reactive allenyl C–H, in which the starting materials require several steps to prepare.[5] Recent advances in enamine-mediated organocatalysis have delivered a number of previously unattainable direct α-functionalization reactions of aldehydes and ketones (Scheme 1).[6] This powerful amine catalysis strategy works through several orthogonal mechanistic pathways: HOMO elevation,[7] SOMO activation,[8] and visible-light photoredox.[9] Within this paradigm, synergistic (cooperative, relay) catalysis, a process utilizing two catalysts to activate both reaction partners, has recently emerged as an very attractive approach for generating chemical bonds which have high-energy barriers to form.[10,11] Among these α-functionalization reactions of carbonyls, a carbon–carbon or a carbon–heteroatom single bond is typically formed. To the best of our knowledge, there is no such reaction allowing direct conversion of the carbonyl α-carbon atom into an allene functionality, a reaction that would enable direct access to a wide variety of allenyl aldehydes, and possibly unusual α,β,γ,δ,ε-unsaturated aldehydes by a cascade reaction.

Inspired by the recent development of electrophilic alkynylation reactions using ethynyl-1,2-benziodoxol-3(1*H*)-one (EBX) reagents,[12] we envisioned that polysubstituted allenyl aldehydes might be accessed by a vinylidenation reaction between a HOMO-elevated enamine species and a gold-activated EBX.[12e–l] We proposed that in the presence of both a secondary amine and an gold(III) or gold(I) catalyst, the energy gap between the HOMO of the enamine intermediate and the LUMO of the EBX/Au complex would be sufficiently reduced to enable a smooth electrophilic alkynylation reaction to give the intermediate **C** (Scheme 2). We expect **C** could quickly isomerize to the fully conjugated ynenamine **D**. Hydrolysis of **D** would lead to two possible products: the allenyl aldehyde **2** (by γ-protonation) and the alkynylated product **3** (by α-protonation). We expected that the γ-protonation would be favored because of both steric and electronic reasons.

In our initial survey, benzenepropanal and 1-[(triisopropylsilyl)-ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX) were used as substrates. A TIPS group was introduced at the terminal acetylene in an attempt to further facilitate the




***Scheme 1.*** α-Functionalization of aldehydes by enamine/metal synergistic catalysis.

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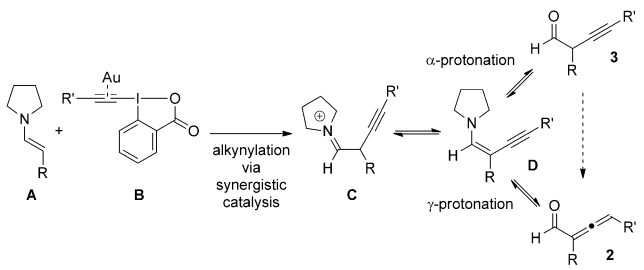



***Scheme 2.*** Proposed synergistic strategy for the α-vinylidenation of aldehydes.

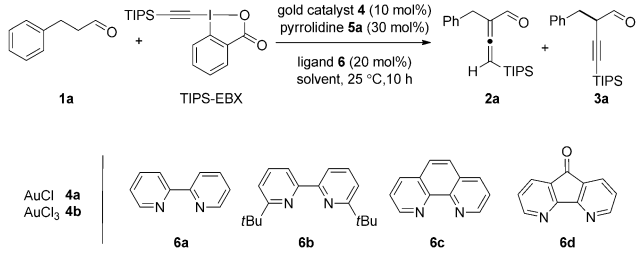
α-alkynylation step (by stabilizing the possible carbene intermediate through hyperconjugation and accelerating the 1,2-shift).[13] No allenyl or alkynylated aldehyde was observed in the absence of either the gold or amine catalysts. Gratifyingly, the combination of AuCl and pyrrolidine led to a detectable conversion into a mixture of the α-allenyl aldehyde **2a** and the α-alkynylated aldehyde **3a** in about a 6:1 ratio (Table 1, entry 1). Other metals failed to promote this transformation. Both the amines and gold species were systematically investigated. Surprisingly, the popularly used imidazolidinones and substituted prolinols were ineffective, and only the aldol dimerization product was observed, despite the fact that both types of amines are excellent HOMO-raising catalysts for various electrophiles. Acid co-catalysts did not improve the conversions. Both gold(III) and gold(I) worked well for this reaction.

The gold catalyst did not tolerate phosphine or N-heterocyclic carbene ligands (see the Supporting Information for the comprehensive reaction parameter investigation). In sharp contrast, the conversion into the allenyl aldehyde was significantly improved by chelating nitrogen ligands. In particular, 4,5-diazafluorenone resulted in a greater than 70% yield using either AuCl or $AuCl_3$ (Table 1, entries 6 and 8).[14] The competing aldol reaction was the major side reaction when the secondary amine was employed catalytically. Gratifyingly, increasing the loading of pyrrolidine to 100 mol% improved yields to greater than 90% (Table 1, entries 9 and 10). It is worth noting that the successful isolation of the allenyl aldehyde product suggests that the bulky TIPS and the amine catalyst likely inhibit the cycloisomerization of the product to the corresponding furan in situ.

The scope of the aldehydes was examined next. β-Aryl aldehydes, including various substituted phenyls and furyls, reacted in good yields with moderate to good allene/alkyne selectivities (Table 2, **2a–e** and **2k**). Straight-chain alkyl substrates, including those containing O or N heteroatoms were very effective, with allene/alkyne ratios generally higher than those obtained from their β-aryl counterparts (**2f–i**). The reactions of the β-branched aldehydes were sluggish, and the yields were somewhat low (**2j–n**). Aldehydes bearing a tertiary β-carbon atom were poor substrates. For example, 3,3-dimethylbutanal resulted in a 40% combined yield of **2o** and **3o** in a 1:2 ratio.

We envisioned that both the allene (**2**) and alkyne (**3**) products could react with the amine to generate the previous

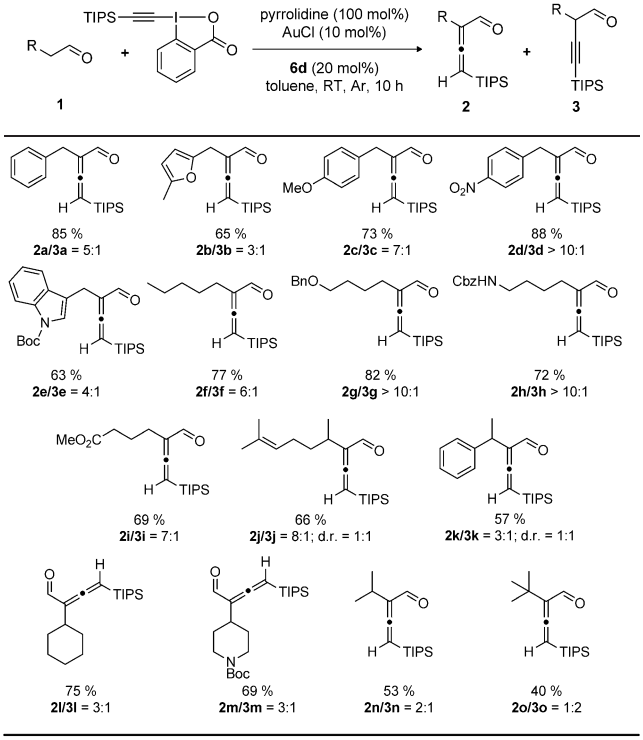
***Table 1:*** Survey of reaction conditions for the α-vinylidenation of aldehydes.[a]




| Entry | Gold | Ligand | Yield [%][b] |
|---|---|---|---|
| 1 | **4a** | none | 36 |
| 2 | **4b** | none | 31 |
| 3 | **4a** | **6a** | 42 |
| 4 | **4a** | **6b** | 38 |
| 5 | **4a** | **6c** | 49 |
| 6 | **4a** | **6d** | 77 |
| 7 | **4b** | **6c** | 37 |
| 8 | **4b** | **6d** | 74 |
| 9[c] | **4a** | **6d** | 93 |
| 10[c] | **4b** | **6d** | 91 |

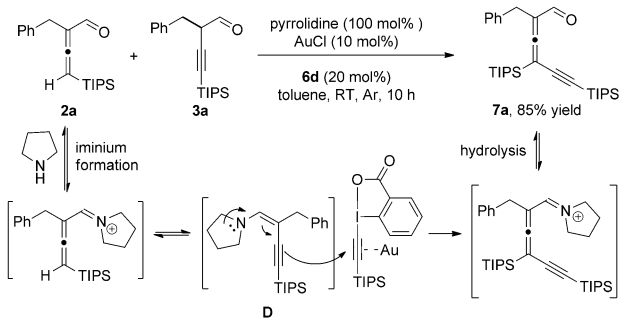
[a] Reactions were conducted with 0.1 mmol TIPS-EBX and 0.2 mmol **1a** in 1 mL solvent. [b] Combined yields for **2** and **3** were determined by GC using biphenyl as the internal standard. [c] 0.1 mmol pyrrolidine was used. TIPS = triisopropylsilyl.

***Table 2:*** Substrate scope of aldehydes for α-vinylidenation.[a]




[a] Yield (combined) of **2** and **3** upon isolation. Average of two runs. Ratio of **2**/**3** and d.r. determined by integration of the peaks in the NMR spectra the crude reaction mixture. Boc = *tert*-butoxycarbonyl, Cbz = benzyloxycarbonyl.

ynenamine intermediate **D** (Scheme 2), which would engage in a second electrophilic alkynylation with EBX, preferably at the γ-carbon atom (Scheme 3).[15] A mixture of **2a** and **3a** was

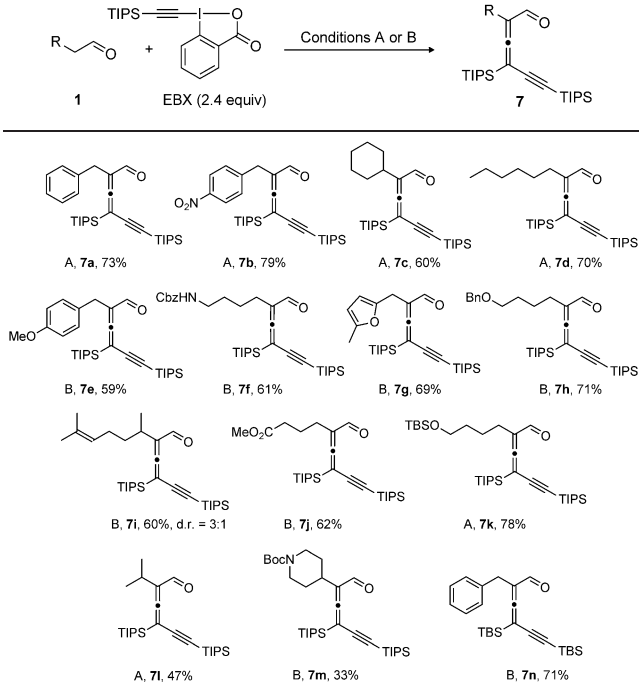



***Scheme 3.*** Second eletrophilic alkynylation.

subjected to 1.2 equivalents of TIPS-EBX under otherwise standard conditions (Table 2). To our delight, the allene-tethered alkynyl aldehyde **7a** was obtained in 85% yield upon isolation (Scheme 3).

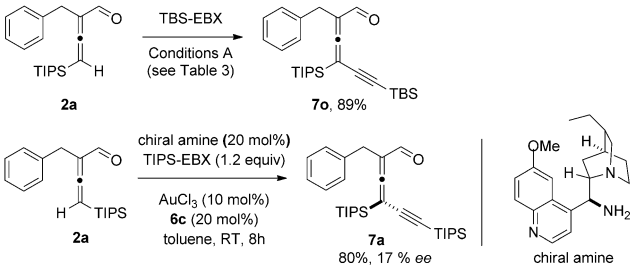
The successful alkynylation of the allenyl aldehyde **2a** prompted us to explore the one-pot cascade using a simple aldehyde and excess TIPS-EBX. AuCl and $AuCl_3$, in combination with the ligands **6a** and **6c**, respectively, were found to be crucial for the direct conversion of an aldehyde into the corresponding γ-alkynyl allenyl aldehyde (Conditions A and B, Table 3). As a result of the strong Lewis acidity of $AuCl_3$,

***Table 3:*** α-Vinylidenation/γ-alkynylation cascade by synergistic catalysis.[a]




[a] Conditions A: 20 mol% pyrrolidine, 10 mol% $AuCl_3$, 20 mol% **6c**, toluene, RT, 24 h. Conditions B: 20 mol% pyrrolidine, 10 mol% AuCl, 20 mol% **6a**, toluene, RT, 24 h. Yields are those of the isolated products. TBS = *tert*-butyldimethylsilyl.

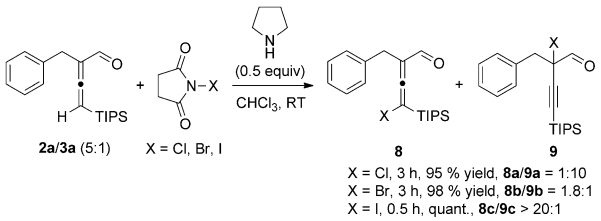
sensitive substrates resulted in complex reaction mixtures. The corresponding AuCl conditions (Conditions B) provided a milder alternative. This cascade was general for a broad scope of aldehydes (Table 3). Only silyl-EBX worked for the vinylidenation and the vinylidenation/alkynylation cascade. The corresponding Ph-EBX failed to generate any allene or alkyne products. When the TIPS-EBX-derived allenyl aldehyde **2a** was subjected to Conditions B with TBS-EBX (Scheme 4), the hybrid silylated γ-alkynyl allenyl aldehyde **7o**




***Scheme 4.*** Reaction of allenyl aldehyde **2a** with TBS-EBX and an enantioselective reaction using a chiral amine.

was obtained in 89% yield. A catalytic amount of pyrrolidine performed significantly better for the cascade reaction, while stoichiometric loading of the amine led to a complicated mixture. Notably, the reaction became less sensitive to the amount of the amine catalyst, possibly because of rapid γ-alkynylation. A number of secondary and primary amines catalyzed this cascade reaction efficiently. Several chiral amine catalysts were examined in an effort to synthesize the tetrasubstituted allenyl aldehyde **7** enantioselectively (Scheme 4). The initial results were encouraging. A chiral primary amine derived from quinine showed excellent catalytic activity with 17% *ee*.[16]

Other electrophiles were examined for the γ-functionalization of **D**. Electrophilic halogen reagents were excellent substrates using the amine catalyst alone (Scheme 5). Inter-



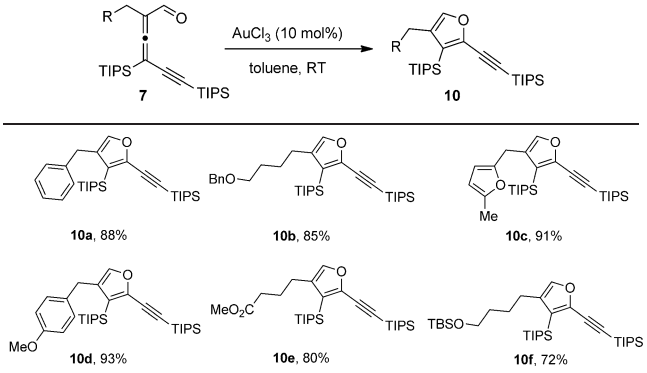

***Scheme 5.*** Halogenation of allenyl aldehyde **2a**.

estingly, the regioselectivity was strongly affected by the halogen element used. For NCS, the propargyl chloride **9a** was obtained preferentially over the corresponding allenyl chloride **8a**. The regioselectivity decreased to 1:1.8 for NBS. Complete iodination of the allene was observed when NIS was used, likely because of both steric minimization and better chemical compatibility between the soft sp-hybridized carbon nucleophile and soft electrophiles.

The seemingly unstable cascade product, γ-alkynyl allenyl aldehydes, were smoothly converted into 2-alkynyl-3-silylfurans using $AuCl_3$, thus rendering a highly efficient two-step synthesis of trisubstituted furans from aldehydes.[14b,17] In the absence of gold, the furan products started to appear when the γ-alkynyl allenyl aldehydes were stood at room temperature as neat for several days or stirred with excess TFA (5 equiv, 48% yield, 24 h). Various 4-alkyl-3-silyl-2-alkynyl furans were synthesized in high yields (Table 4), thus demonstrating the synthetic utility of the aforementioned cascade transformation. Attempts to access the heterocycles directly from the corresponding aldehydes led to low yields. The alkynyl TIPS could be selectively removed under the TBAF/THF conditions to yield the furan-substituted terminal alkyne quantitatively.

***Table 4:*** Synthesis of trisubstituted furans.[a]




[a] Yields are those of the isolated products.

The mechanistic aspect of the gold-activated electrophilic alkynylation is intriguing. Both π activation and oxidative addition pathways are plausible. Since the oxidative addition pathway requires a gold(I) species, this activation mode seems less likely as both gold(I) and gold(III) catalysts exhibited nearly identical activity. Presumably, the addition of the enamine to the gold-activated triple bond is followed by either β elimination or α elimination/1,2-shift to lead to the key ynenamine intermediate **D** (in Scheme 2) which is hydrolyzed by γ-protonation.[18]

In summary, we have developed the first direct α-vinylidenation and the α-vinylidenation/γ-alkynylation cascade of aldehydes using silyl-EBX with a synergistic gold/amine catalyst system. Functionality-rich, tri- and tetrasubstituted allenes bearing a versatile aldehyde and an acetylene functionality were prepared in a straightforward protocol. This method enables rapid access to polysubstituted furans from aldehydes. The enantioselective aspects and detailed mechanism of these reactions are currently under investigation.

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**Keywords:** allenes · enamines · gold · organocatalysis · synthetic methods

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