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# Gold(III)-Catalyzed Regioselective Oxidation/Cycloisomerization of Diynes: An Approach to Fused Furan Derivatives

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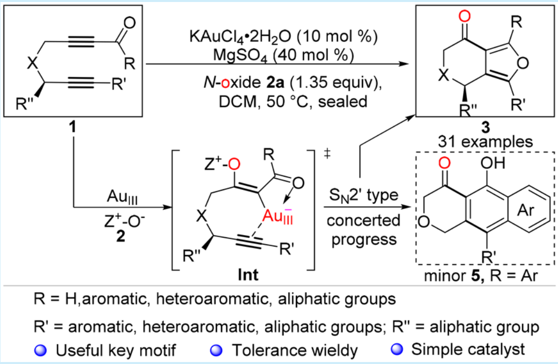
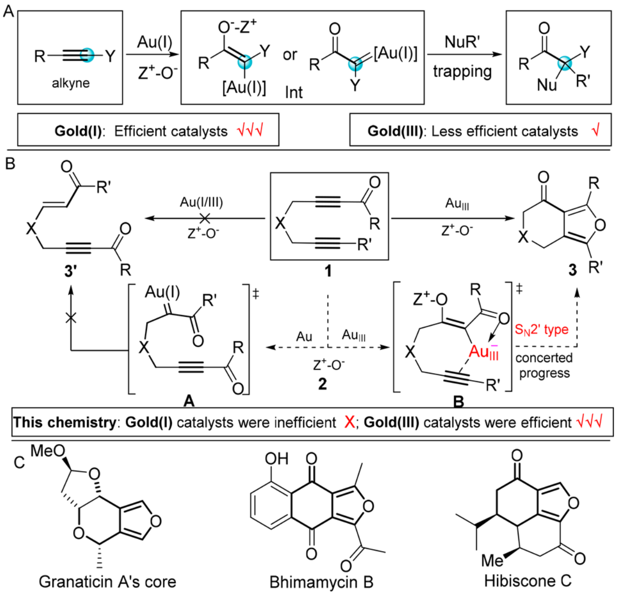
Ⓢ *Supporting Information*

**ABSTRACT:** The first gold(III)-catalyzed regioselective oxidation/cycloisomerization of diynes **1** with pyridine *N*-oxide as the oxidant was developed, providing a range of synthetically valuable and useful fused furan derivatives **3** in moderate to good yields. Control experiments and the confirmation structure of minor products **5** suggest that this chemistry was a concerted gold(III)-catalyzed oxidation/$S_N2'$-type addition/cyclization process via a *β*-gold vinyloxypyridinium intermediate and a putative vinyl cation intermediate.



The oxidation of alkynes by using intermolecular pyridine/quinoline *N*-oxides[1] as oxidants has become a valuable synthetic strategy owing to the efficient and expedient access to *α*-oxo gold carbene/carbenoid intermediates in the presence of a gold(I) catalyst.[2] Due to the strong *π*-philicity nature of gold(I), a range of functional structures of significant synthetic methods have been developed.[3−9] To date, most of the reactions reported have been proposed to proceed by the intra-[4] or intermolecular[5] trapping of the *α*-oxo gold carbene intermediates (Scheme 1A). However, in the oxidation of alkynes using *N*-oxide as the oxidant, gold(III) is a less efficient catalyst, because of their strong oxophilicity nature. For a more useful oxidation of alkynes approach and the development of a gold catalyst, as shown in Scheme 1B, our design anticipated that with alkyne−ynone substrates **1** and the *π*-philicity/oxophilicity nature of gold(III) as the catalyst, a novel noncarbene model of *β*-gold(III) vinyloxypyridinium **B** could be site selectively generated upon oxidation of the ynone C−C triple bond. Subsequently, the *β*-gold(III) vinyloxypyridinium **B** would be attacked by an appropriately tethered internal alkyne via concerted $S_N2'$ type addition[3h,4f,h,10] and cycloisomerization to afford furan derivatives **3**, which is an important motif in natural products,[11] such as Granaticin A,[11a] Bhimamycin B,[11b] and Hibiscone C[11c] (Scheme 1C). Interestingly, the easier oxidation process[12] with a simple C−C triple bond by using gold(I) catalysts was regioselectively limited in this alkyne−ynone system (Scheme 1B). As part of our ongoing work in the field of gold catalysis,[4j−l,7] we reported herein the first gold(III)-catalyzed regioselective oxidtion/cycloisomerization of diynes[6−8] to fused furan derivatives from more flexible and readily accessible systems (Scheme 1B).

Scheme 1. (A) Gold(I)-Catalyzed Selective Oxidation of Alkynes; (B) Our Design: Gold(III)-Catalyzed Regioselective Oxidation and Cycloisomerization of Alkyne−Ynone; (C) Natural Products Containing the Motif of Fused-Furan Core



Notably the reaction, if developed, would offer novel and rapid access to valuable fused cyclic products.

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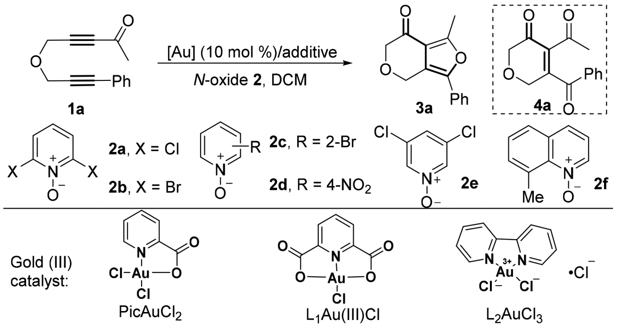
**Table 1. Initial Discovery of Gold(III)-Catalyzed Selective Oxidation/Cycloisomerization of Diyne 1a and Screening of Reaction Conditions**[a]



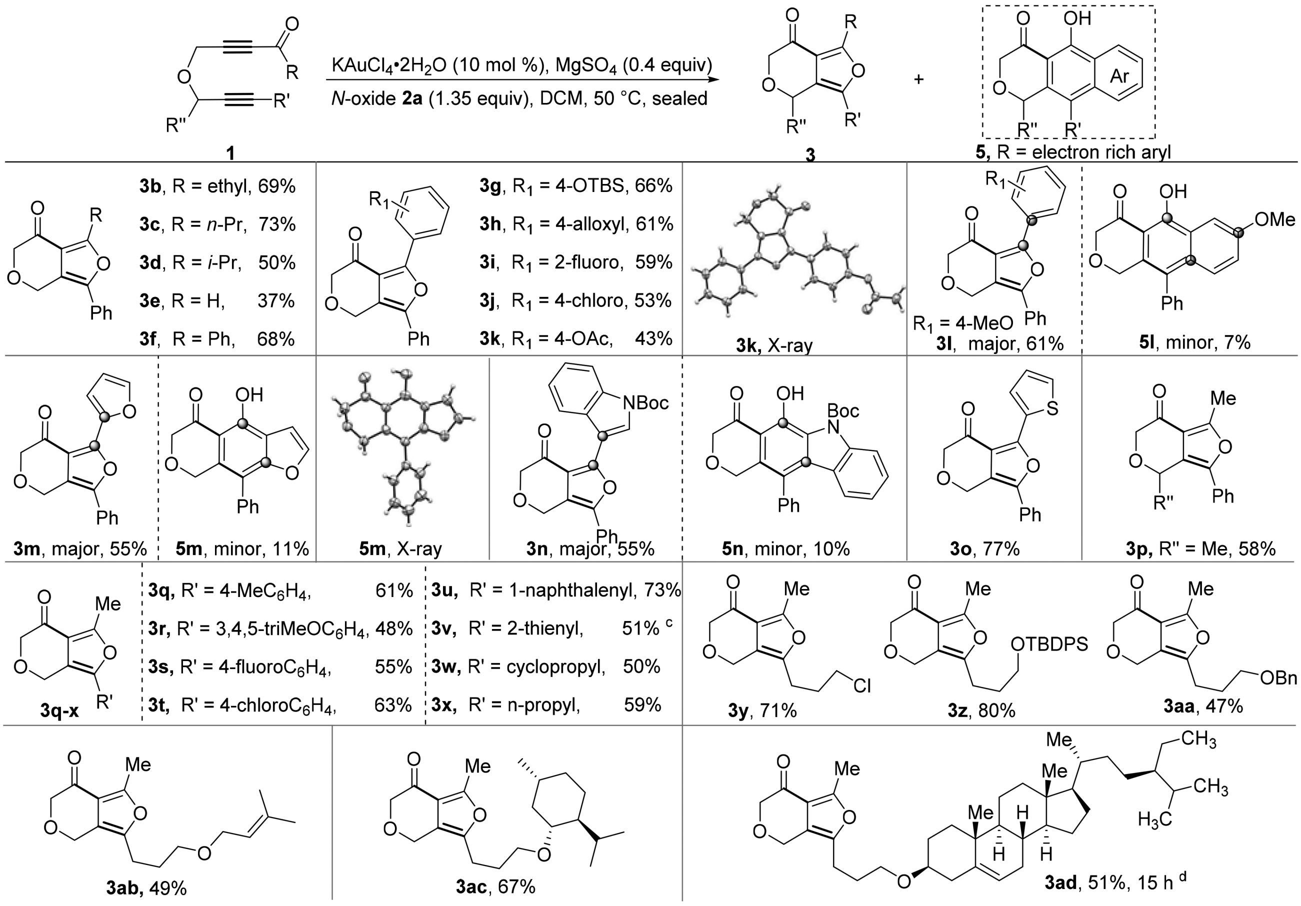
| entry | 2 | catalyst | additive (equiv) | temp (°C) | *t* (h) | yield (%)[b] |
|---|---|---|---|---|---|---|
| 1 | **2a** | $KAuCl_4{\cdot}2H_2O$ | – | rt | 6.5 | 57 |
| 2 | **2b** | $KAuCl_4{\cdot}2H_2O$ | – | rt | 6.5 | 36 |
| 3 | **2c** | $KAuCl_4{\cdot}2H_2O$ | – | rt | 6.5 | 24 |
| 4 | **2d** | $KAuCl_4{\cdot}2H_2O$ | – | rt | 6.5 | messy |
| 5 | **2e** | $KAuCl_4{\cdot}2H_2O$ | – | rt | 6.5 | 22 |
| 6 | **2f** | $KAuCl_4{\cdot}2H_2O$ | – | rt | 6.5 | messy |
| 7 | **2a** | $AuCl_3$ | – | rt | 48 | 43 |
| 8 | **2a** | $PicAuCl_2$ | – | rt | 48 | 22 |
| 9 | **2a** | $L_1Au(III)Cl$ | – | rt | 48 | 40 |
| 10 | **2a** | $L_2Au(III)Cl_3$ | – | rt | 48 | trace |
| 11 | **2a** | $IPrAuNTf_2$[c] | – | rt | 6.5 | NR |
| 12 | **2a** | $KAuCl_4{\cdot}2H_2O$ | – | 50 | 3.5 | 64 |
| ***13*** | ***2a***[d] | ***$KAuCl_4{\cdot}2H_2O$*** | ***$MgSO_4$ (0.4)*** | ***50*** | ***3.5*** | ***74***[e] |
| 14 | **2a**[d] | $KAuCl_4{\cdot}2H_2O$ | $MgSO_4$ (0.4) | 50 | 3.5 | 62[f] |
| 15 | **2a**[d] | $KAuCl_4{\cdot}2H_2O$ | $MgSO_4$ (0.4) | 50 | 3.5 | 63[g] |
| 16 | **2a**[d] | $KAuCl_4{\cdot}2H_2O$ | $MgSO_4$ (0.4) | 50 | 3.5 | 58[h] |

[a] Reaction condition: [**1a**] = 0.05 M and 1.2 equiv of the oxidant **2**. [b] Estimated by $^1H$ NMR spectroscopy using diethyl phthalate as the internal reference. [c] 5 mol % catalyst. [d] 1.35 equiv of oxidant **2a**. [e] Reactions performed on 0.2 mmol scale; 66% isolated yield of **3a** after purification by column chromatography. [f] 1,2-Dichloromethane as the solvent, [**1a**] = 0.1 M. [g] Chlorobenzene as the solvent. [h] Toluene as the solvent.

At the outset, we employed the tethered alkyne–ynone **1a**, for reaction discovery and condition optimization, some results of which are shown in Table 1. Initially, hydrated $KAuCl_4$ (10 mol %) was chosen as the catalyst, and 2,6-dichloropyridine *N*-oxide (**2a**, 1.2 equiv), as the oxidant; the reaction was carried out in dichloromethane (DCM) at room temperature for 6.5 h. To our delight, the desired tetrahydropyranone-fused furan **3a** was indeed formed in 57% NMR yield (entry 1). Screening of various other pyridine/quinoline *N*-oxides (entries 2–6) revealed that sterically hindered oxidants derived from the electron-deficient pyridine ring, i.e., 2,6-dibromopyridine *N*-oxide (**2b**, entry 2), was effective, but was still substantially inferior to even more electron-deficient 2,6-dichloropyridine *N*-oxide **2a**. A range of other gold catalysts such as $AuCl_3$ (entry 7), $PicAuCl_2$ (entry 8), $L_1AuCl$ (entry 9), and $L_2AuCl_2$ (entry 10) were invetigated, affording less than 45% yield of **3a**, even after a longer time. Gold(I) catalysts were also investigated, and the electron-rich IPr carbene was employed as the ligand, as it was previously proven to be highly effective in promoting cyclopropanation of α-oxo gold(I) carbenes, which were generated from ynones, to C–C double bonds.[4f] With $AgNTf_2$ (5 mol %) as the chloride scanvenger and **2a** (1.2 equiv) and other *N*-oxides as the oxidants (for details, see Supporting Information (SI)), the reaction was carried out in dichloromethane (DCM) at room temperature for 6.5 h. Unfortunately, no reaction was observed from crude NMR without consuming **1a** (entry 11). Screening of other cationic gold(I) complexes derived from typical ligands such as $Ph_3P$, $Cy_3P$, Phosphite, X-Phos, and $Me_4{}^tBuXPhos$ revealed that these cationic gold(I) complexes were ineffective, which indicated that the reaction required stronger Lewis acidity regarding Au(III)[13] as a smooth trigger by activating the ynone group (for details, see SI). With $KAuCl_4$ (10 mol %), the reaction was carried out at 50 °C in a sealed tube for 3.5 h, and a slightly higher yield was obtained, along with gold precipitation (entry 12). $MgSO_4$ (0.4 equiv) was chosen as an additive to increase the desired product **3a** to 74% yield without observing double oxidation product 4-acetyl-5-benzoylpyranone **4a**, which indicated that the selective oxidation–cycloisomerization was a concerted process (entry 13). Other additives, such as molecular sieves, bases, and Lewis acids were ineffective (for details, see SI). The effect of the solvents, such as, 1, 2-dichloroethane, PhCl, and toluene, were also considered, but no better results were observed (entries 14–16). Other oxidants, such as triphenylphosphine oxide and diphenyl sulfoxide, were also tested, but no good results were observed (for details, see SI).

With the optimal conditions (Table 1, entry 13) in hand, the reaction scope was examined. As shown in Scheme 2, tethered alkyne–ynones **1b–1d** possessing an aliphatic R group at the end of the carbonyl group reacted as expected, despite exhibiting moderate yields. Furthermore, the aldehyde substrate, such as **1e** with a hydrogen R group, proceeded smoothly to provide corresponding product **3e** in an acceptable yield.[14] Aromatic R groups were also investigated, such as **1f–1k**; various electron-donating and -withdrawing

Scheme 2. Reaction Scope[a,b]

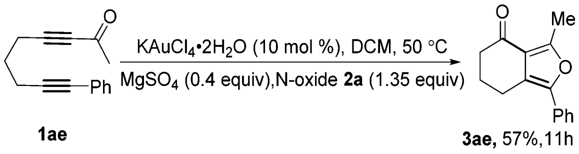


[a] The reactions were run in a sealed tube at 50 °C in DCM, and the substrate concentration was 0.05 M. [b] Yields of isolated products are reported. [c] 15% catalyst was used. [d] [M] = 0.1 M; 12% catalyst was used.

groups installed on benzene ring were also readily tolerated. The relative configuration of the product **3k** was unambiguously assigned by X-ray crystallography (CCDC 1816724).[15] Moreover, an interesting case with a *para*-OMe substituted benzene R group was transferred to afford the desired **3l** in 57% yield, along with 7% of 5-hydroxy-7-methoxy-10-phenyl-1*H*-benzo[*g*]isochromen-4(3*H*)-one **5l**. This phenomenon was also observed with a furan and indole R groups, such as substrates **1m** and **1n**; moderate yields of major tetrahydropyranone-fused furans **3m–n** were obtained separately, and around 10% yields of minor products **5m–n** were also accessed. The relative configuration of the minor product **5m** was unambiguously assigned by X-ray crystallography (CCDC 1816725), which suggested that the minor products **5** might be formed via a selective oxidation/Friedel–Crafts cycloisomerization and rearrangement process, implying the existence of a putative vinyl cation intermediate.[7] Tethered alkyne–ynone **1o** possessing a heteroaromatic R group, such as 2-thienyl, proceeded smoothly to provide corresponding product **3o** in 77% yield. The steric effect of the R″ group was also considered, such as **1p**; a methyl was readily tolerated at the propargyl position. Other tethered alkyne–ynones **1q–1x** by installing a methyl R group at the end of carbonyl group, possessing R′ groups at the end of terminal alkyne, worked well. The reaction was tolerant of various electron-rich and -deficient aromatic, heteroaromatic, and aliphatic R′ groups.

Moreover, considering synthetically useful transformations, tethered alkyne–ynones such as **1y–1ad** with different aliphatic substitutions were also investigated and afforded the desired products **3y–3ad** in moderate to good yield. A benzyl and an allyl group were tolerated, and their $\pi$ bonds did not noticeably interfere with the desired cycloisomerization, likely due to the formation of larger rings and, hence, slower cyclization kinetics. On the other hand, a simple chloro, OTBDPS substituted and chiral L-menthol and bulky $\beta$-sitosterol substituted aliphatic linker led to desired products **3y–3z** and **3ac–3ad** in good yield.

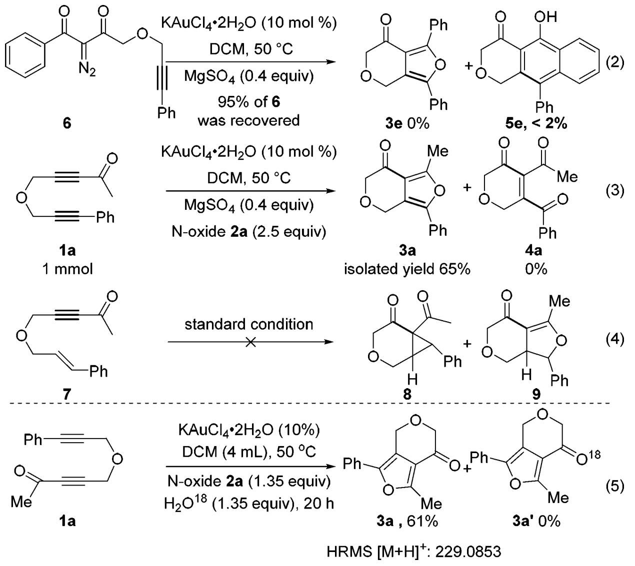
Furthermore, we attempted to extend the chemistry to the all-carbon counterpart of **1a**, i.e., 9-phenylnona-3,8-diyn-2-one **1ae**. As shown in eq 1, the desired cyclohexanone-fused furan **3ae** was formed in 57% yield after 11 h and 23% yield of **1ae** was recovered, indicating that all-carbon substrate **1ae** is less reactive than the oxygen-containing substrate **1a**.[15]



(1)

In order to gather additional experimental evidence for the mechanism, we examined the gold(III)-catalyzed reaction of the authentic diazo carbonyl species **6**[4f] as shown in Scheme 3,

### Scheme 3. Control Experiments

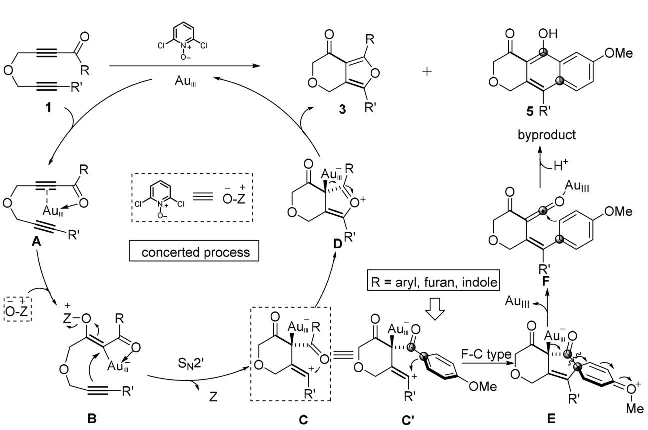


where the desired tetrahydropyranone-fused furan **3e** was not observed and only trace amount (<2%) of **5e** was observed. We also carried out **3a** at a large scale (1 mmol) with an excess of *N*-oxide **2a** (2.5 equiv), where the double oxidation product **4a**[7] was not observed and the desired **3a** was isolated in 65% yield. 5-(Cinnamyloxy)pent-3-yn-2-one **7**[4f,16] was also tested under standard conditions, but no desired gold carbenecyclopropanation product **8** and cycloisomerization product **9** was observed.

These control experiments implied that the pure $\alpha$-oxo gold carbene might not be the true reactive intermediate in the reaction, indicating that the $\beta$-gold(III)vinyloxypyridinium **B** was the more reasonable intermediate. Moreover, we also carried out the reaction in the presence of $H_2O$ without adding *N*-oxide **2a**; however, no reaction was observed. The reaction was also attempted in the presence of $H_2O^{18}$, and no $O^{18}$ labeled product **3a′** was detected from HRMS, indicating that the new oxygen of **3a** was from the *N*-oxidant **2a** (for more details, see SI-7.2).

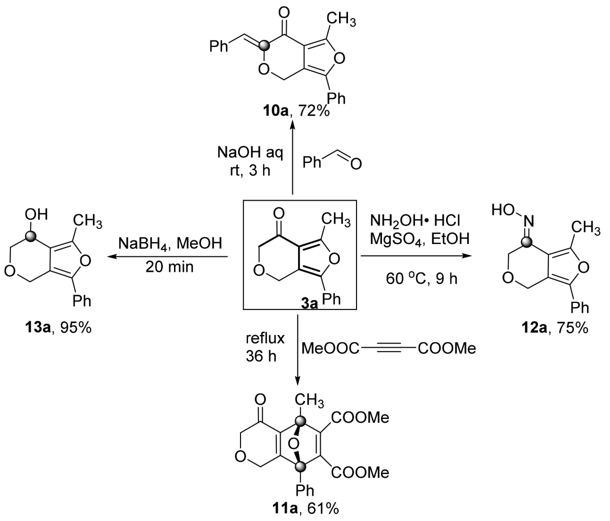
On the basis of the above observations, we propose the following plausible mechanisms for this transformation (Scheme 4). (i) Gold(III) first coordinates selectively with C−C triple bonds and the carbonyl group[13c] in the alkyne−ynone system, where the *N*-oxide site selectively attacks the distal end of ynone to give $\beta$-gold(III) vinyloxypyridinium **B**. (ii) The internal tethered alkyne group as a $\pi$-electron nucleophile attacks $\beta$-gold(III) vinyloxypyridinium **B** intermediate to drive the 2,6-dichloropydine away via $S_N2'$-type addition, resulting in the formation of a putative vinyl cation intermediate **C**. (iii) Then, the active vinyl cation intermediate **C** is trapped by the internal carbonyl group to give a more stable oxygenium-bridged intermediate **D**, which is rapidly isomerized to furan derivative **3** and releases the gold complex. (iv) Alternatively, if R groups are electron-rich aryl groups like *p*-methoxybenzene, furan, and indole, the active vinyl cation intermediate **C′** may be trapped by a rich electron site of aryl groups to give the spiro-oxonium intermediate **E**. (v) The spiro-oxonium intermediate **E** is then transferred to ethenone intermediate **F**, where a gold complex promotes the cleavage of the C−C bond between the carbonyl and spiro carbon, and then ethenone intermediate **F** is isomerized to 5-hydroxy-1*H*-benzo[*g*]isochromen-4(3*H*)-one **5** via gold-promoted Friedel−Crafts cyclization.

### Scheme 4. Proposed Mechanism



The synthetic utility of the tetrahydropyranone-fused furan products were examined by using **3a** as an illustrative example. Under standard aldol-condensation conditions, it is transferred to enone product **10a** in 72% yield (Scheme 5). Its condensation with hydramine leads to **12a** in good yield. The tetrahydropyranone-fused furan **3a** can be easily functionalized to construct **11a** and **13a** in moderate to excellent yield via a [4 + 2] cycloaddition with the C−C triple bond and reduction with $NaBH_4$.

### Scheme 5. Transformations of 3a



We have realized the first example of gold(III)-catalyzed tandem selective oxidation−cycloisomerization of diynes **1** with external pyridine *N*-oxide via a novel noncarbene model to synthesize tetrahydropyranone-fused furans **3**. The reaction tolerates hydrogen atom as well as aryl and aliphatic substitutions, and reasonable yields of **3** are obtained in these instances. Moreover, the chemistry also extends to the all-carbon counterpart of **1a**, and the desired cyclohexanone-fused furan **3ae** was obtained in moderate yield. Control experiments and the confirmation structure of minor products **5** suggest that this chemistry is a concerted gold(III)-catalyzed oxidation/$S_N2'$-type addition/cyclization process via a $\beta$-gold(III) vinyloxypyridinium intermediate and a putative vinyl cation intermediate. Meanwhile, the tetrahydropyranone-fused furan products can be prepared in large scale and readily undergo further transformations, substantially broadening the scope of accessible furan products and therefore notably enhancing the synthetic utility of these tandem reactions.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01915.

Detailed condition investigations, experimental procedures, compound characterization, and X-ray diffraction data for **3k** and **5m** (PDF)

### Accession Codes

CCDC 1816724−1816725 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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(14) The aldehyde **1e** is a very reactive substrate and the recovery yield of aldehyde **1e** was less than 80% under the gold(III) system, indicating that **1e** is not stable in the reaction system.

(15) Yield was based on the conversion; 23% of **1ae** was recovered.

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