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Gold Catalysis

Gold(I)-Catalyzed Intramolecular Cycloisomerization of Propargylic Esters with Furan Rings

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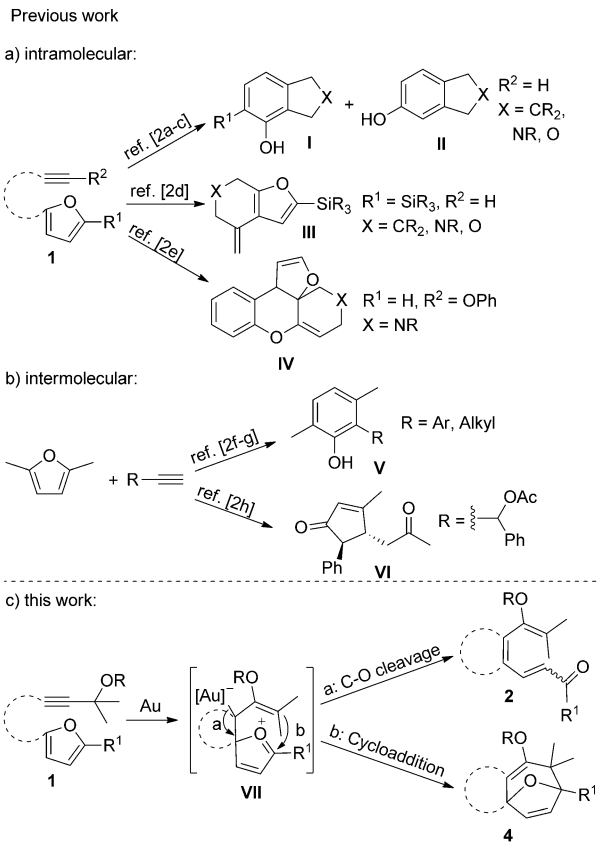
Abstract: A gold-catalyzed intramolecular cycloisomerization of α-yne-furans **1** is described in this contribution. A variety of cyclic α,β-unsaturated aldehyde or ketone derivatives and nitrogen-containing tricyclic adducts were obtained selectively in moderate to excellent yields under mild conditions by varying the substituents on the standard substrates.

Over the past decade, homogeneous gold catalysis has witnessed rapid growth for C–C, C–O or C–N bond-forming reactions mainly due to the soft carbophilic Lewis acid properties of gold complexes toward C–C multiple bonds.[1] In comparison to other transition-metal catalysts, gold complexes can efficiently catalyze reactions under very mild conditions that are tolerant of air or moisture to give excellent chemoselectivity and wide functional group compatibility. In particular, gold-catalyzed cycloisomerizations of α-yne-furans have attracted much attention owing to the efficient synthesis of anellated carbo- or heterocyclic compounds.[2] In 2000 and 2001, the pioneering work on the intramolecular alkyne/furan cyclization reactions catalyzed by Au^{III}[2a] or Pt^{II}[2b,c] to afford phenols **I** and **II** was reported by Hashmi, Echavarren and their co-workers (Scheme 1a), respectively. Afterwards, the group of Hashmi discovered several new reaction patterns by varying the substituents on α-yne-furans **1**: In the case of silyl substituents at the 5-position of furan rings, gold-catalyzed reactions led to the formation of anellated furans **III**, presumably through a hydroarylation reaction pathway;[2d] When there is an aryloxy substituent at the terminal position of the alkyne moiety, the chiral, polycyclic compound **IV** could be obtained.[2e] As for the intermolecular reaction of a furan with an alkyne, the synthesis of phenols **V** (Scheme 1b) has been realized by the elegant work of Hashmi[2f] and Echavarren[2g] as well.



Scheme 1. Previous and our work on the cyclization of α-yne furan.

On the other hand, propargylic esters are very important feedstocks in organic synthesis.[3] In the presence of gold,[4–10] platinum[11] or rhodium[12] catalysts, propargylic esters have versatile reactivities to undergo 1,2- or 1,3-acyloxy migration,[4–12] leading to the formation of a metal–carbene or an allenic intermediate that is allowed further transformation to diversified substances. As a part of our ongoing interest on the transition-metal-catalyzed or mediated reactions of propargylic esters, we have already reported several interesting transformations of propargylic ester derivatives.[13] Very recently, Echavarren discovered intermolecular reactions of propargylic esters with furans to afford the corresponding cyclized products in good yields (Scheme 1b).[2h] Based on these findings contributed by Hashmi and Echavarren, we envisaged that α-yne-furans bearing propargylic esters might undergo very interesting cycloiso-

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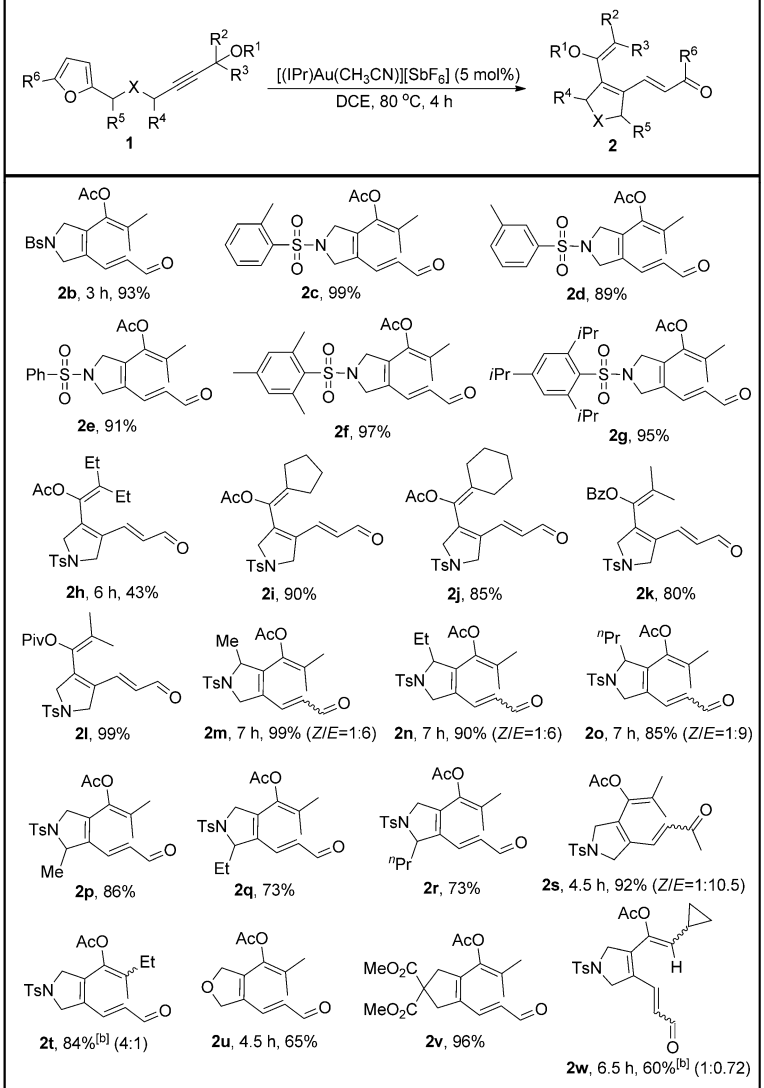
merizations if catalyzed by a gold complex. To our great delight, upon treatment of substrate **1** with a gold catalyst, the key spirointermediate **VII** was formed from a gold–carbene species, leading to switchable synthesis of α,β-unsaturated aldehydes/ketones **2** or [4C+3C] cycloadducts **4**, respectively (Scheme 1c).

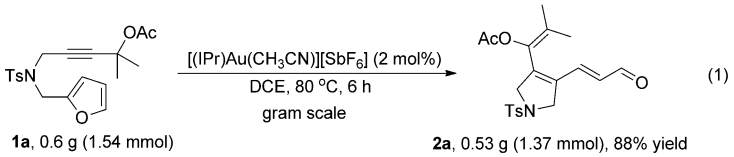
We commenced our study with α-yne-furan **1a** as the standard substrate. After extensive optimization (see the Supporting Information for details), we found that treatment of **1a** with 5 mol% [(IPr)Au(CH$_3$CN)][SbF$_6$] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) in dry 1,2-dichloroethane at 80 °C gave the desired product α,β-unsaturated aldehyde **2a** in 88% yield. The structure of **2a** has been unequivocally confirmed by X-ray diffraction.[14] With the optimized conditions in hand, we turned our attention to determine the scope and limitations of the reaction. As summarized in Table 1, all of the reactions proceeded smoothly to afford the corresponding products **2b–g** in 89–99% yields when the sulfonyl group was *p*-bromobenzenesulfonyl (Bs), *o*-methylbenzenesulfonyl, *m*-methylbenzenesulfonyl, benzenesulfonyl, mesitylenesulfonyl (Mes) and 2,4,6-triisopropylbenzenesulfonyl, which indicated that the electronic properties and steric effect of sulfonyl group did not have significant impact on the reaction outcome. Next, the scope of this transformation with respect to the substituent of the propargylic esters was examined. When both R^2 and R^3 were an ethyl group (**2h**), the chemical yield of the desired product was only 43%. However, to our delight, cycloalkyl groups gave much better results (**2i,j**). Reactions of starting materials with a pendant benzoyl (Bz, **1k**) or pivaloyl (Piv, **1l**) group instead of an acyl (Ac) migrating group were found to be well-tolerated under the standard conditions, furnishing the desired products **2k,l** in 80 and 99% yields, respectively. We further tested the effect of substituents at R^4. Similarly, substrates **1m–o** underwent the cycloisomerization smoothly to give the corresponding products but as *Z*- and *E*-isomeric mixtures. Furthermore, to expand the scope of this reaction, we also investigated the effect of the substituent at R^5. We were pleased to find that **1p–r** gave much better results. Substituted furan **1s** also produced the corresponding α,β-unsaturated methyl ketone[15] **2s** in 92% yield as approximately 10:1 (*E*/*Z*) isomers. Substrates **1t** and **1w** bearing different substituents on the propargyl esters were also suitable for this reaction, giving the corresponding cyclized products as isomeric mixtures in reasonable yields. Moreover, the oxygen- or carbon-tethered substrates **1u** and **1v** were also suitable for this cycloisomerization, providing the desired aldehydes in 65 and 96% yields, respectively. Thus, this reaction scope was highly general with respect to the R^1–R^6 groups. Notably, the catalyst loading could be reduced to 2 mol%, and the synthesis of **2a** was also possible on a gram scale [Eq. (1)], highlighting the good reproducibility and practicability of this cycloisomerization reaction.

Table 1. Substrate scope of gold-catalyzed cycloisomerization of **1**.[a]



[a] Reaction conditions: **1** (0.2 mmol); [(IPr)Au(CH$_3$CN)][SbF$_6$] (5 mol%); anhydrous DCE (1.0 mL). Yields are those of the isolated products. [b] Mixture of *Z*/*E* isomers.

To determine more precisely the influence of the substitution, we prepared the substrate **3a** with two carbon atoms in the tether between the propargylic ester and the furan subunit and treated it with the gold catalyst. To our surprise, a nitrogen-containing tricyclic adduct **4a** was obtained in 69% yield



(1)

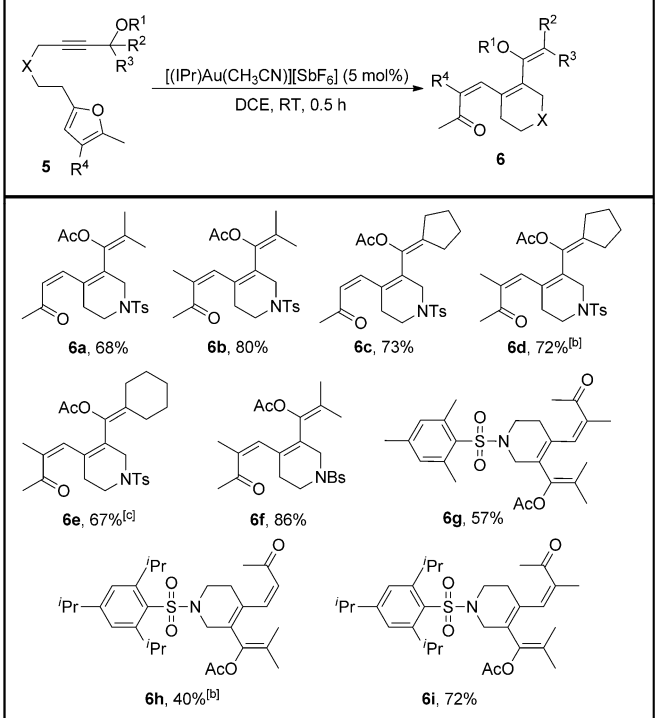
instead of the expected product α,β-unsaturated aldehyde. This might be due to an increase of the steric flexibility with a longer tether that will be favored for the formal [4C+3C] cycloaddition pathway.[16] The structure of **4a** has been unequivocally confirmed by X-ray diffraction.[14] We then performed the reaction at room temperature to synthesize tricyclic products **4** and the results are summarized in Table 2. As can be seen from Table 2, substrates **3b** and **3c** bearing benzenesulfonyl or mesitylenesulfonyl (Mes) gave the desired products **4b** and **4c** in respective yields of 68 and 54%. Meanwhile, substrates in which the methyl groups on the acetate carbon center were replaced with a more sterically demanding cyclobutane (**3d**,**e**), cyclopentane (**3f**) or cyclohexane (**3g**) were also found to undergo the reaction smoothly, giving the corresponding spirotetracyclic adducts **4d**–**g** in 38–94% yields. Furthermore, starting material **3h** with a pendant benzoyl (Bz) group instead of an acyl (Ac) migrating group was also suitable for this reaction, giving the corresponding tricyclized product in a reasonable yield. Only when both R^2 and R^3 were propyl moieties (**3i**), the desired product could not be obtained (see Supporting Information).

It is worth noting that when substrate with a α-methyl group on furan ring was treated with gold catalyst, the α,β-unsaturated methyl ketone **6a** was obtained in 68% yield in the same pathway as shown in Table 1. Due to the steric hindrance of the methyl group, the formal [4C+3C] cycloaddition was blocked out, which might be able to account for the formation of **6**. We next examined the generality of the reactions with respect to various substrates **5** under the optimized conditions and the results are shown in Table 3. The substrate **5b** (R^4 = Me), containing another methyl group at the β-position of furan ring, also underwent the reaction smoothly to give the corresponding product **6b** in 80% yield. Pleasingly, substrates with a more sterically demanding cyclopentane (**5c**,**d**) or cyclohexane (**5e**) instead of the methyl groups were also found to undergo this reaction very well, affording the corresponding nitrogen-containing cyclohexene adducts **6c**–**e** in 67–73% yields. Meanwhile, all of the reactions proceeded smoothly to afford the corresponding products **6f**–**i**[17] in 40–86% yields when the sulfonyl group was *p*-bromobenzenesulfonyl (Bs), mesitylenesulfonyl (Mes) and 2,4,6-triisopropylbenzenesulfonyl. When both R^2 and R^3 were ethyl moieties (**5j**), the 1,3-acyloxy migration allene product were exclusively formed instead of the desired α,β-unsaturated ketone (see the Supporting Information).

Moreover, the reaction could also be extended to the alkyl-substituted alkynes[18] and the results are summarized in Table 4. Substrates bearing methyl, isopropyl and cyclopropyl groups could produce the desired α,β-unsaturated aldehydes **8a**–**c** in moderate yields. When a more sterically large cycloalkane such as cyclopentane (**7d**) or cyclohexane (**7e**) was introduced to the substrate, we found that the reaction was inefficient under the standard conditions. However, changing the gold catalyst into sterically bulky phosphine coordinated gold catalyst **A** and increasing the reaction time gave better results (Table 4).

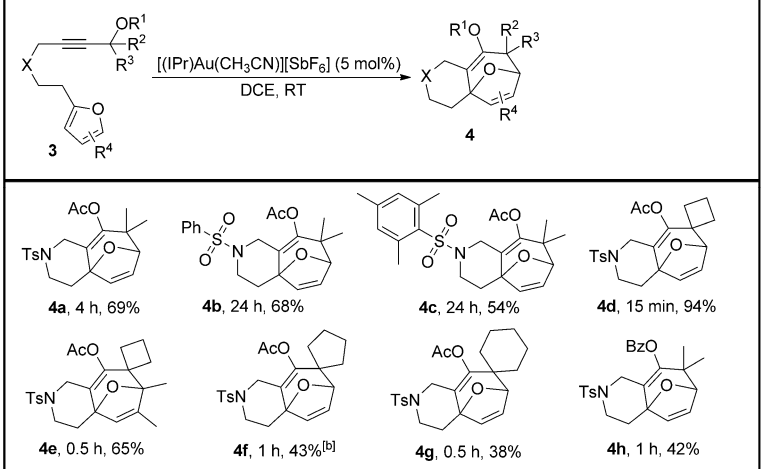
To verify the reaction pathway of the nitrogen-containing tricyclic adducts **4**, the control experiment has been performed by treating **3a** with the sterically bulky phosphine coordinated

Table 3. Substrate scope of gold-catalyzed cycloisomerization of **5**.[a]



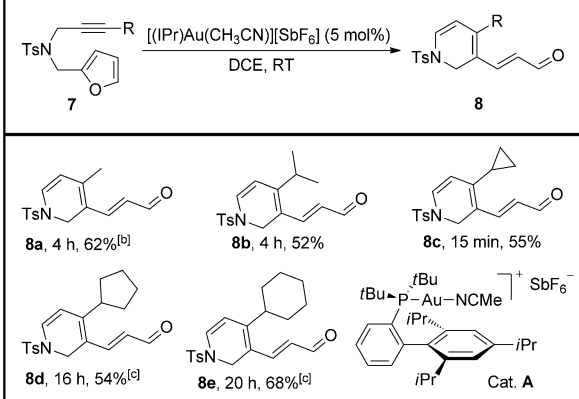
[a] Reaction conditions: **5** (0.1–0.2 mmol); [(IPr)Au(CH$_3$CN)][SbF$_6$] (5 mol%); anhydrous DCE (1.0 mL). Yields are those of the isolated products. [b] Reaction time: 1 h. [c] Reaction time: 2 h.

Table 2. Substrate scope of gold-catalyzed cycloisomerization of **3**.[a]



[a] Reaction conditions: **3** (0.1–0.2 mmol); [(IPr)Au(CH$_3$CN)][SbF$_6$] (5 mol%); anhydrous DCE (1.0 mL). Yields are those of the isolated products. [b] Reaction performed at 80 °C.

Table 4. Substrate scope of gold-catalyzed cycloisomerization of **7**.[a]



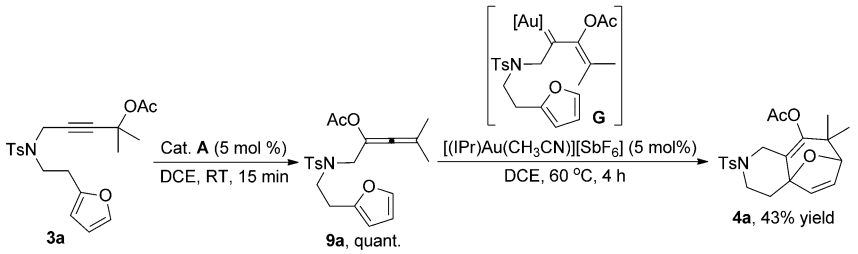
[a] Reaction conditions: **7** (0.1 mmol); [(IPr)Au(CH$_3$CN)][SbF$_6$] (5 mol%); anhydrous DCE (1.0 mL). Yields are those of the isolated products. [b] Reaction performed at 80 °C. [c] Cat. **A** was used.

gold catalyst **A** in dry DCE[13d] and it was found that the 1,3-acyloxy migration product **9a** could be obtained in quantitative yield after 15 min. When using **9a** as the starting material and subjecting it to the standard conditions, **4a** was formed in 43% yield, thus indicating that the acyloxy-substituted allene **9a** was the plausible intermediate of this reaction to generate the key intermediate **G** for the cycloisomerization (Scheme 2).

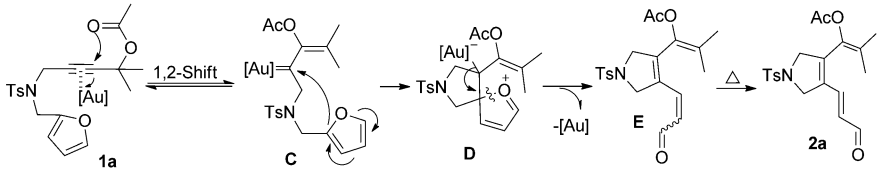
A possible mechanism[19] to account for the above experimental results is shown in Scheme 3. Gold(I) activation of the triple bond in **1a** promotes the formation of the gold–carbene intermediate **C** through a reversible 1,2-acyloxy migration. A nucleophilic attack of the α-position of furan results in the formation of the spirointermediate **D**, which undergoes a C–O cleavage to produce intermediate **E** as *Z*/*E* isomeric mixture. Finally, the thermodynamically more stable product **2a** is formed upon heating.[20]

As for the [4C+3C] cycloaddition pathway, based on the control experiments and previous literature,[16] the mechanistic working hypothesis (Scheme 4) consists of an initial activation of the propargylic ester **3a** to generate the gold carbene intermediate **F** through a reversible 1,2-acyloxy migration. Notably, the gold–carbene intermediate **F** can be also obtained from an allenic ester **9a** through a reversible 1,2-acyloxy migration, which is initially formed from **3a** through a reversible 1,3-acyloxy migration in the presence of gold catalyst.[7d,f] A nucleophilic attack of the α-position of furan results in the formation of the spirointermediate **G**,[21] which then undergoes a cyclization process to give product **4a** and regenerates the gold catalyst.

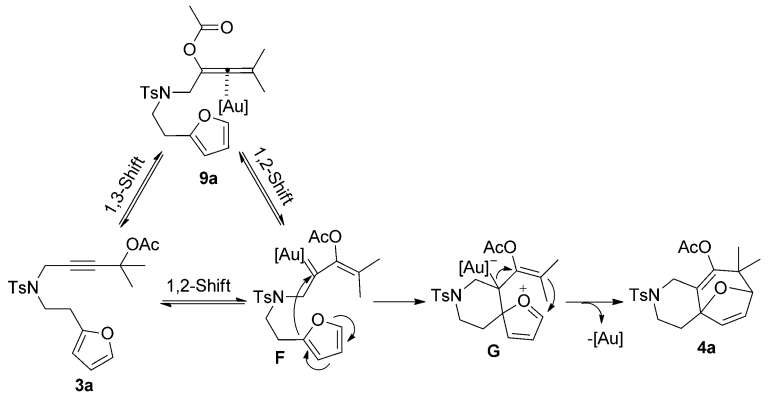
The synthetic utility of these products is shown in Scheme 5 by further transformations into other valuable products. For instance, compound **2a** was readily converted into the conjugated tetraene **12a** in 54% yield by Wittig reaction.[22] Furthermore, the tricyclic products **4a** and **4c** could be smoothly hydrolyzed under mild basic conditions with potassium carbonate in methanol, thus yielding the corresponding ketones **10a** and **10c** in 70 and 72% yields, respectively. Subsequently treatment of **10a** with 3.0 equivalent of *meta*-chloroperbenzoic



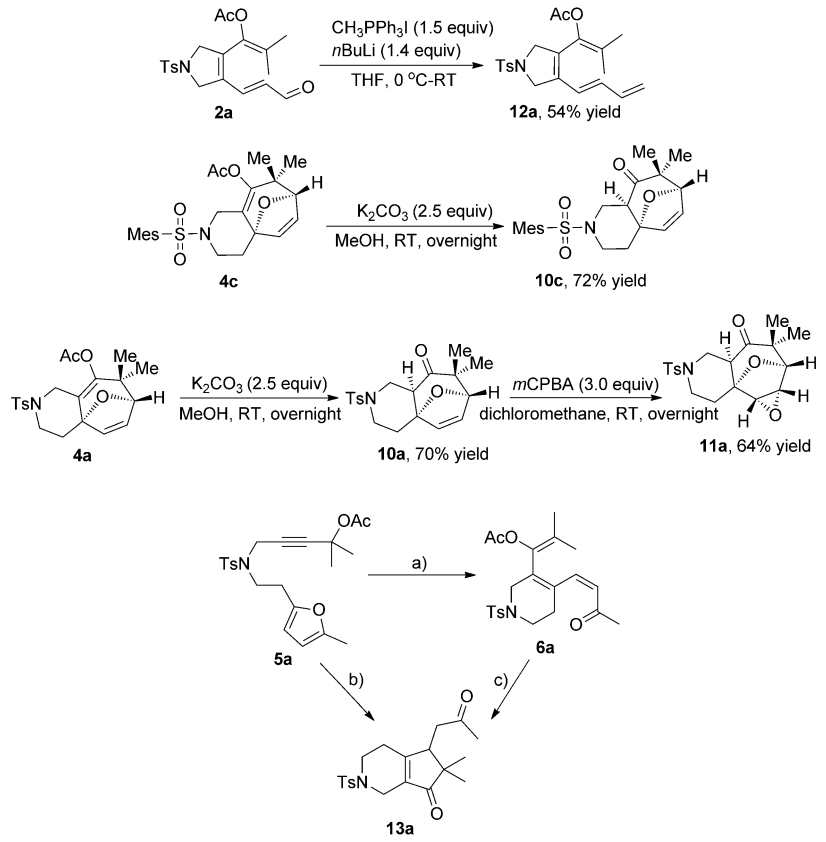
Scheme 2. Control experiment of **3a**.



Scheme 3. A plausible reaction mechanism for the formation of **2a**.



Scheme 4. A plausible reaction mechanism for the formation of **4a**.



Scheme 5. Transformations of products **2a**, **4c**, **4a** and **6a**. a) [(IPr)Au(CH_3CN)][SbF_6] (5 mol%), DCE, RT, 0.5 h, 68%; b) [(IPr)Au(CH_3CN)][SbF_6] (5 mol%), DCE, RT, 0.5 h; then HOTf (1.0 equiv), RT, 2 h, 80%; c) HOTf (1.0 equiv), dichloromethane, RT, 2 h, 82%.

acid (*m*CPBA) gave the corresponding epoxide product **11a** in 64% yield. Moreover, the nitrogen-containing bicyclic adduct **13a** could be obtained in 82% yield by treatment of **6a** with 1.0 equivalent of HOTf (Scheme 5). The structures of compounds **11a** and **13a** were confirmed by use of NMR spectroscopic data and X-ray diffraction analyses.[14] The bicyclic product **13a** could be also afforded in the yield of 80% in a one-pot manner using **5a** as the starting materials through gold catalysis and the subsequent treatment with 1.0 equivalent of HOTf (Scheme 5).

In conclusion, we have developed a highly efficient and accessible gold-catalyzed intramolecular cycloisomerization of propargylic esters with furan rings. By varying the substituents on the substrates, we could obtain two different types of cyclized products in moderate to excellent yields under mild conditions. The reaction mechanism is proposed on the basis of the control experiments and previous literature, and some interesting transformations of the products are also disclosed. Further applications of this chemistry and more detailed mechanistic investigations are underway in our laboratory.

Acknowledgements

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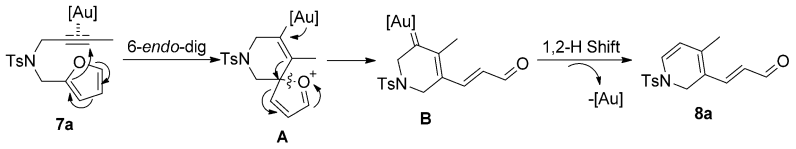

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Gold Catalysis

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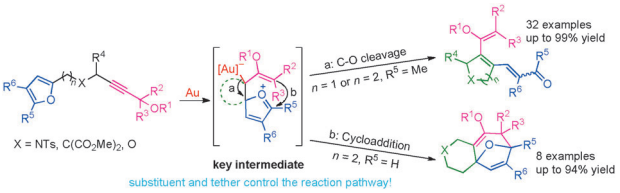
Gold(I)-Catalyzed Intramolecular Cycloisomerization of Propargylic Esters with Furan Rings



Going for gold: A variety of cyclic α,β-unsaturated aldehyde or ketone derivatives and tricyclic adducts were obtained selectively through a gold-catalyzed intramolecular reaction of propargylic esters with furan rings (see scheme). Several interesting transformations of the products are also reported.