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Gold-catalyzed tandem cycloisomerization/Petasis-Ferrier rearrangement: a direct route to 3-alkoxyindanones from enynals and alcohols

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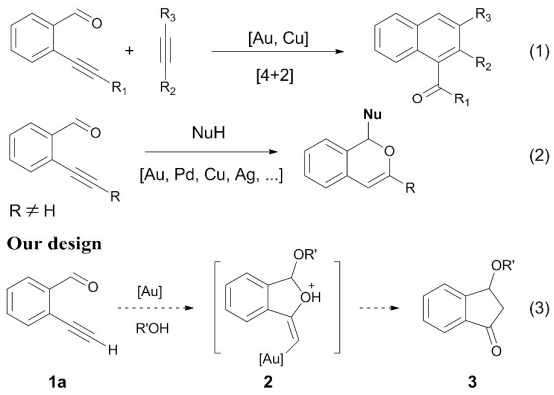
A method to prepare 3-alkoxyindanones efficiently by gold-catalyzed tandem cycloisomerization/Petasis-Ferrier rearrangement from *ortho*-ethynylarylaldehydes with alcohols is described. The reaction was accomplished in moderate to excellent yields under mild reaction conditions and also offers a convenient synthetic route to 3-alkoxycyclopentenones.

Homogeneous gold catalysis have emerged in the past few years as one of the most powerful methods for the formation of cyclic compounds through the cycloisomerization reactions and skeleton reassembly.[1,2] Among them, the cyclization processes involving with carbonyl-yne motif have been thoroughly studied to afford versatile products.[3] Particularly, *ortho*-alkynylarylaldehydes as substrates could be converted to a variety of organic molecules.[4] For example, Yamamoto et al.[5] reported the synthesis of the naphthyl ketone derivatives from *ortho*-alkynylarylaldehydes and alkynes by gold catalysis (Scheme 1, eq 1). Dyker and other groups extended this methodology for the synthesis of other naphthalene derivatives.[6] In addition, *ortho*-alkynylarylaldehydes could react with a series of nucleophiles to generate 1*H*-isochromene derivatives[4,7] (Scheme 1, eq 2) or complex polycyclic molecules rapidly under mild reaction conditions.[4,8] Following our ongoing interest in the development of gold-catalyzed tandem reactions,[9] and encouraged by these pioneering works, we intended to explore new transformations of *ortho*-alkynylarylaldehydes.

We envisioned that *o*-ethynylbenzaldehyde **1a** which proceeded through hemiacetalization/5-exo-dig cycloisomerization to give cyclic intermediate **2** under gold catalysis with alcohols would afford the skeleton rearrangement product **3** (Scheme 1, eq 3). In a related study, Toste and co-workers reported gold-catalyzed carboalkoxylation of pre-installed acetals with an alkyne motif for the synthesis of 3-alkoxyindanones.[10] In addition, Chan group reported gold-catalyzed intramolecular tandem heterocyclization/Petasis-Ferrier rearrangement with the *O*- or *N*-linked aldehyde and alkyne as substrates.[11] Furthermore, the intermolecular rearrangements of aldehydes or acetals with terminal alkynes were also reported.[12]



Scheme 1 Metal-catalyzed tandem processes of *ortho*-alkynylbenzaldehydes.

Based on these precedents, we anticipated that the designed tandem process would be possible (Scheme 1, eq 3). And the major challenges were to enable 5-exo-dig cycloisomerization with slow protodeauration and Petasis-Ferrier rearrangement to take place. Thus we utilized *ortho*-ethynylarylaldehydes with terminal alkynes as substrates to develop a gold catalyzed tandem reaction, which involves cycloisomerization/Petasis-Ferrier rearrangement sequence. Herein, we provide a method for the direct gold-catalyzed synthesis of 3-alkoxyindanones from *ortho*-

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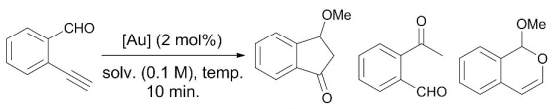
ethynylarylaldehydes and alcohols. Notably, these new strategies also offer a practical and efficient way to synthesize indanone derivatives, which are very important building blocks in natural products and biological research.[13]

First, we tested the reaction of readily available *o*-ethynylbenzaldehyde **1a** in different solvents by a variety of catalysts to establish the reaction conditions (Table 1). This revealed treating a solution of reaction containing **1a** (0.1 mmol) and methanol (1 mL, 0.1 M) with 2 mol % of $Ph_3PAuNTf_2$ at 80 °C for 10 min gave **3a** in 76% yield. In this reaction, the hydrolytic product **4** and 6-endo-dig cyclized product **5** as side products detected by ^1H NMR spectroscopy were obtained in 5% and 6% yields, respectively (Table 1, entry 1). It is worth mentioning that the substrate **1a** was consumed completely in 10 minutes without any protection. In an attempt to improve the yield of **3a**, several gold catalysts were screened (Table 1, entries 2-7). When inorganic gold salt $NaAuCl_4{\cdot}2H_2O$ was used as the catalyst, the desired product **3a** could be obtained in 88% yield after isolation, which was the best reaction conditions (Table 1, entry 7). Other catalysts such as $PtCl_2$ can also afford the desired compound **3a** in 35% yield (Table 1, entry 8). However, neither $AgNTf_2$ nor $HNTf_2$ as the catalyst could deliver the expected product **3a**. (Table 1, entries 9-10). In addition, both decreasing the reaction temperature and changing the solvents couldn't improve the yield of **3a** (Table 1, entries 11-13). Finally, lower product yield would be obtained when the catalyst loading of **6** was reduced to 1 mol% (Table 1, entry 14).

Table 1 Optimization of the reaction conditions [a]

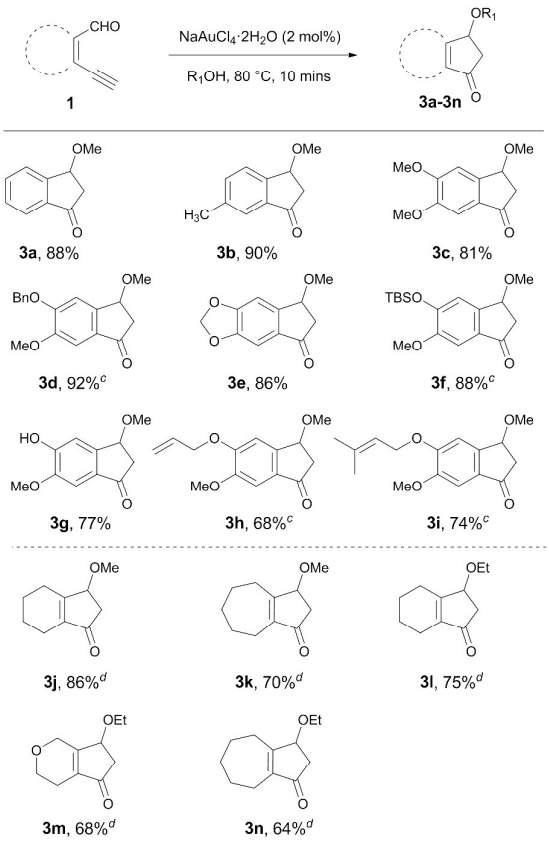


1a 3a 4 5

Entry	Cat.	Solv.	Temp. (°C)	Yield (**3a**, %)[b]
1	$Ph_3PAuNTf_2$	MeOH	80	76 [c]
2	$Cy_3PAuNTf_2$	MeOH	80	15
3	(2,4-*t*Bu_2-$C_6H_3O)_3PAuNTf_2$	MeOH	80	10
4	$AuCl{\cdot}Me_2S$	MeOH	80	50
5	$AuCl_3$	MeOH	80	83
6	$NaAuCl_4{\cdot}2H_2O$ (**6**)	MeOH	80	89
7 [d]	**6**	MeOH	80	95 (88)
8	$PtCl_2$	MeOH	80	35
9	$AgNTf_2$	MeOH	80	0
10	$HNTf_2$	MeOH	80	0
11 [d]	**6**	MeOH	60	73
12	**6**	Toluene/ MeOH(10/1)	100	85
13	**6**	DCE/ MeOH(10/1)	80	50
14 [e]	**6**	MeOH	80	82

[a] Reaction conditions: substrate **1a** (0.1 mmol), catalyst (2 mol%), and solvent (0.1 M) in air unless otherwise specified. [b] Yields determined by ^1H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. Yields of isolated product given within parentheses. [c] **4** and **5** were detected as minor side products. [d] See Table 2, footnote a. [e] 1 mol% catalyst was used.

Table 2 Substrate scope of enynals. [a, b]



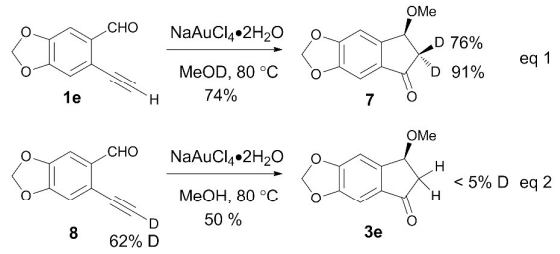
[a] Typical reaction conditions: a solution of **1** (0.1 mmol) in the solvent (0.6 mL) was added to a solution of the catalyst (2 mol%) in the solvent (0.4 mL) via a syringe pump in 5 mins at 80 °C and the mixture was stirred for another 5 mins. [b] Isolated yields are shown. [c] At 50 °C. [d] Using $Ph_3PAuNTf_2$ as a catalyst at 50 °C.

Having established the optimized reaction conditions, the substrate scope was investigated with a variety of *ortho*-ethynylarylaldehydes. As shown in Table 2, substrates containing substituted groups such as alkyl, ethers, silyl ethers, and hydroxyl group on the aromatic ring were well-tolerated under the reaction conditions (**3a-3g**). Furthermore, the reaction of the substrates with allyl ether proceeded smoothly in good yields (**3h-3i**). Unfortunately, 2-Ethynyl-5-methoxybenzaldehyde and 2-ethynyl-5-fluorobenzaldehyde were not good substrates for the formation of desired products, which resulted in complex mixture. Under the standard conditions, the other alcohols such as ethanol, allyl alcohol and cyclohexanol were not suitable for this transformation.

Surprisingly, reactions of nonaromatic enynals (**1j-1k**) catalyzed by $NaAuCl_4{\cdot}2H_2O$ gave a mixture of side products

that could not be identified by ^{1}H NMR analysis. When $Ph_3PAuNTf_2$ was used as a catalyst, the desired bicyclic compounds **3j-3n** were afforded in 64-86% yields (Table 2). Other gold catalysts were also examined, which could not improve the result.[14] Notably, ethanol was also a suitable nucleophile for this transformation, which gave the corresponding cyclic products efficiently (**3l**-**3n**).

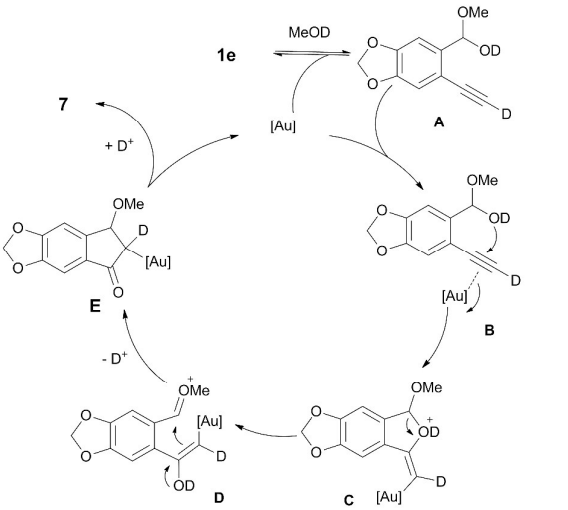
To obtain a more detailed insight into the reaction mechanism, the deuterium-labelled methanol was utilized under the standard reaction condition (Table 1, entry 7). The ^{1}H NMR analysis of the crude product obtained from the reaction of **1e** in CH_3OD under gold catalysis revealed that incorporation of deuterium has occurred at the α position of the carbonyl group (Scheme 2, eq 1 and 2). Speculatively, it would be quite likely to have deuterium exchange with the



Scheme 2 Mechanistic investigations.

hydrogen of the terminal alkyne via the intermediate gold (I) acetylide.[15,16]

Based on the above studies, we tentatively propose the following mechanism for gold-catalyzed tandem cycloisomerization/Petasis-Ferrier rearrangement reaction (Scheme 3).[11,17] The hemiacetalization of the substrate **1e** in MeOD under gold catalyst forms intermediate **A**, accompanying with the H/D exchange of the terminal alkyne.



Scheme 3 Proposed reaction mechanism.

Subsequently, coordination of the intermediate **A** to gold catalyst leads to the gold-alkyne complex **B**, followed by 5-exo-dig cycloisomerization reaction to give the vinyl gold species **C**. The intermediate **D** would be formed after C-O bond cleavage and isomerization of **C**, which is further transformed to the aurated complex **E** via Petasis-Ferrier rearrangement[18]. Finally, the protodeauration of **E** provides the desired product **7**, along with the regeneration of catalyst for the next cycle.

It is important to note that gold-catalyzed rearrangement of *ortho*-ethynylarylaldehydes and alcohols undergoes a 5-exo-dig cyclization, which is an interesting regioselective nucleophilic addition, and only a few cases were reported using other metal catalysts.[19]

In summary, we have developed a gold-catalyzed tandem cycloisomerization/Petasis-Ferrier rearrangement process for the synthesis of 3-alkoxyindanones and 4-alkoxycyclopentenones from easily accessible *ortho*-ethynylarylaldehydes or nonaromatic enynals substrates. This efficient transformation represents a novel reaction cascade to the previously reported strategies. A further study on the detailed reaction mechanism is currently underway in our laboratories.

Acknowledgements

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Graphical Abstracts

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