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Gold-Catalyzed Oxidative Cyclizations of {*o*-(Alkynyl)phenyl propargyl} Silyl Ether Derivatives Involving 1,2-Enynyl Migration: Synthesis of Functionalized 1*H*-Isochromenes and 2*H*-Pyrans

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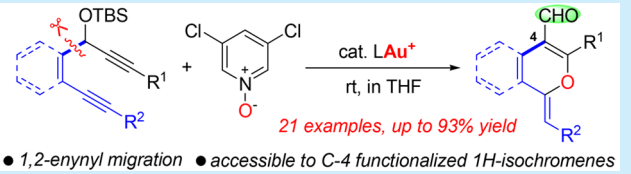
Supporting Information

ABSTRACT: A new and convenient strategy for the synthesis of functionalized 1*H*-isochromene and 2*H*-pyran derivatives based on gold-catalyzed oxidative cyclizations of *o*-(alkynyl)-phenyl propargyl ether derivatives has been developed. The reaction proceeds via gold-catalyzed highly regioselective oxidation, followed by 1,2-migration of an enynyl group and nucleophlic addition. Isocoumarins were also constructed through oxidative cleavage of the exocyclic double bond of the obtained 1*H*-isochromenes.



1*H*-Isochromene, isocoumarin, and 2*H*-pyran frameworks are not only the core structures of many natural products and pharmaceuticals, but also serve as the useful building blocks for the construction of highly complex target molecules.[1] They also display a wide range of biological activities. For example, mansonone F (**a**) exhibits antiproliferative effects and anti-MRSA activities;[2a,b] compound **b** is a potential antitumor agent against breast cancer,[2c] oosponol (**c**) exerts strong antifungal activity;[2d] vermelhotin (**d**) exhibits moderate antiplasmodial activity.[2e] (See Figure 1.) The great importance

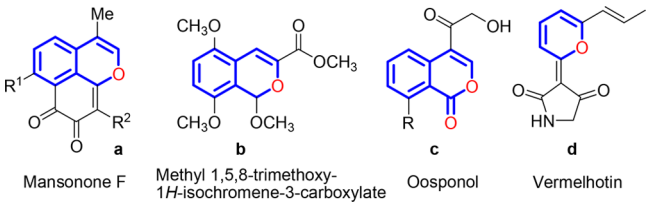
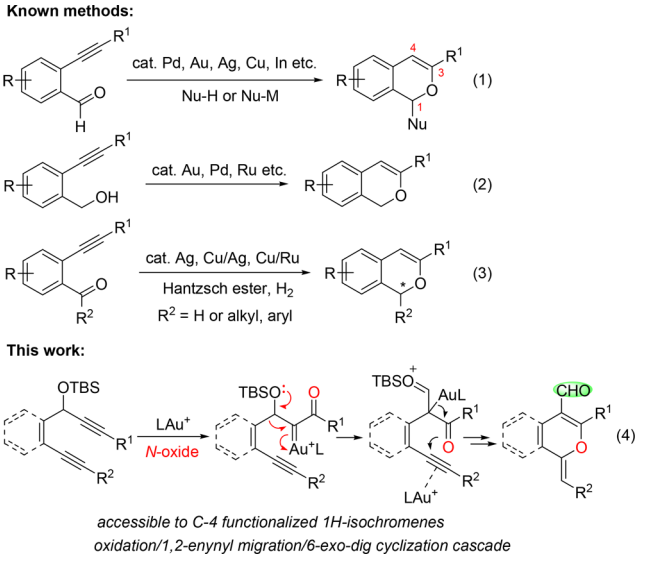


Figure 1. Bioactive 1*H*-isochromene and its derivatives.

of these compounds initiated substantial efforts on the development of efficient synthetic strategies for these heterocycles. In this regard, transition-metal-catalyzed cycloisomerizations of *ortho*-alkynylaryl aldehydes[3] in the presence of C, N, or O nucleophiles or *ortho*-alkynylbenzyl alcohols[4] represent one of the most convenient routes for the synthesis of 1*H*-isochromenes (see Scheme 1, eqs 1 and 2). Despite the two possible regioisomers (dihydroisobenzofurans vs 1*H*-isochromenes derived from *5-exo-dig* and *6-endo-dig* cyclization, respectively) that might be principally formed in these reactions, selective generation of 1*H*-isochromenes could be usually achieved under the appropriate reaction conditions using the former methods (Scheme 1, eq 1). However, the

Scheme 1. Metal-Catalyzed Cyclizations to 1*H*-Isochromenes



latter one usually suffers from the low regioselectivity of the cycloisomerization step. Recently, metal-catalyzed transformation of *ortho*-alkynylaryl aldehydes or ketones into 1*H*-isochromenes through a reduction (including enantioselective reduction) using Hantzsch ester as a hydride source[5] or asymmetric hydrogenation of the in situ-formed isochromenylium ions[6] have also been reported (Scheme 1, eq 3).

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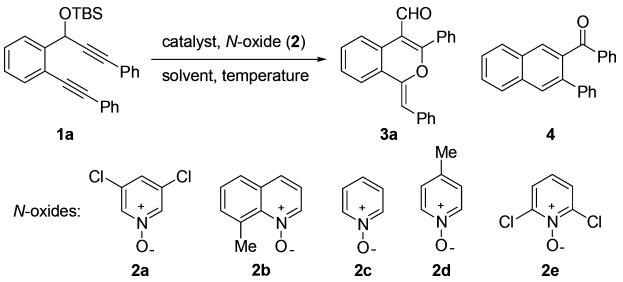
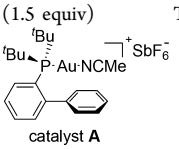
Table 1. Optimization of the Catalytic System



entry	catalyst	*N*-oxide	solvent	temperature (°C)	time (h)	yield[a] (%)
1	catalyst **A** (5 mol %)	**2a** (2 equiv)	THF	50	10	61
2	PPh_3AuNTf_2 (5 mol %)	**2a** (2 equiv)	THF	50	6	78
3	$IPrAuCl/AgBF_4$ (5 mol %)	**2a** (2 equiv)	THF	50	24	64
4	$IPrAuCl/AgPF_6$ (5 mol %)	**2a** (2 equiv)	THF	50	16	83
5	$IPrAuNTf_2$ (5 mol %)	**2a** (2 equiv)	THF	50	3	89
6	$IPrAuNTf_2$ (5 mol %)	**2a** (2 equiv)	DCE	50	5	9
7	$IPrAuNTf_2$ (5 mol %)	**2a** (2 equiv)	toluene	50	4	69
8	$IPrAuNTf_2$ (5 mol %)	**2b** (2 equiv)	THF	50	5	75
9	$IPrAuNTf_2$ (5 mol %)	**2c** (2 equiv)	THF	50	24	46
10	$IPrAuNTf_2$ (5 mol %)	**2d** (2 equiv)	THF	50	18	38
11	$IPrAuNTf_2$ (5 mol %)	**2e** (2 equiv)	THF	50	18	*b*
12	$PicAuCl_2$ (5 mol %)	**2a** (2 equiv)	THF	50	18	0 (83)
13	$PicAuCl_2$ (5 mol %)/$AgNTf_2$ (10 mol %)	**2a** (2 equiv)	THF	50	24	30
14	IPrAuCl (5 mol %)	**2a** (2 equiv)	THF	50	18	0 (90)
15	$AgNTf_2$ (5 mol %)	**2a** (2 equiv)	THF	50	12	0 (90)
16	$IPrAuNTf_2$ (5 mol %)		THF	50	19	*c*
17	$IPrAuNTf_2$ (5 mol %)	**2a** (2 equiv)	THF	rt	10	88
18	$IPrAuNTf_2$ (5 mol %)	**2a** (1.5 equiv)	THF	rt	14	87
19	$IPrAuNTf_2$ (5 mol %)	**2a** (1.0 equiv)	THF	rt	24	84
20	$IPrAuNTf_2$ (2 mol %)	**2a** (1.5 equiv)	THF	rt	24	88



[a]^{1}H NMR yields using as CH_2Br_2 as an internal standard. The yields of the recovered **1a** are shown in parentheses. [b]Complex mixture. [c]**4** was obtained in 45% yield.

However, it is still difficult to introduce a functional group at the C-4 position of 1*H*-isochromenes using these methods.[7]

Recently, transformations involving electrophilic gold carbenoids have attracted much attention, because such intermediates can trigger a diversity of valuable reactions.[8] Among these reactions, 1,2-migration of a C−C or C-X bond to the adjacent gold carbenoids serves as an efficient protocol for the construction of molecular complexity.[9] Our previous work revealed that the gold could catalyze a highly regioselective and chemoselective oxidative ring expansion of 2-alkynyl-1,2-dihydropyridines to azepines using pyridine-*N*-oxide as the oxidant, which proceeds via exclusive 1,2-migration of a vinyl or an aryl group.[9f] The competitive 1,2-hydride migration was not observed. Later, this system was extended to the synthesis of tropone and various carbocycles or heterocycles.[9g−i] During our further studies on gold-catalyzed migration reactions, we found that new heterocycles could be accessed by merging the gold-catalyzed 1,2-migration of an enynyl group with a subsequent cyclization cascade (Scheme 1, eq 4). It was noted that, in 2014, Hashmi et al. reported an elegant synthesis of highly substituted 3-formylfurans by a gold(I)-catalyzed oxidation/1,2-alkynyl migration/cyclization cascade.[9c] Herein, we report a new and convenient strategy for the synthesis of functionalized 1*H*-isochromene and 2*H*-pyran derivatives via gold-catalyzed oxidative cyclization of *o*-(alkynyl)phenyl propargyl ether derivatives involving highly selective 1,2-enynyl group migration, followed by nucleophilic addition. The exocyclic C=C bond in the obtained 1*H*-isochromenes could be selectively reduced, or cleaved to provide isocoumarins, which are also prevalent motifs in many bioactive molecules. It was noted that 1,2-enynyl migration onto a gold-carbenoid species has not yet been reported.

Our initial efforts focused on the gold-catalyzed oxidative reaction of *o*-(alkynyl)phenyl propargyl ether **1a** (Table 1). After systematic and detailed investigation on the effects of gold catalysts, ligands and *N*-oxides, we found that a 1*H*-isochromene product **3a** bearing a formyl group at the C-4 position was formed in 61% yield at 50 °C for 10 h upon treatment of **1a** with 5 mol % of Johnphos(MeCN)$AuSbF_6$ (catalyst **A**) bearing a crowded biphenyl phosphine ligand and 2.0 equiv of 3,5-dichloropyridine *N*-oxide **2a** in THF (Table 1, entry 1). The results indicate that a selective 1,2-enynyl migration might be involved during the reaction. The use of PPh_3-ligated gold catalyst PPh_3AuNTf_2 improved the yield of **3a** to 78% (Table 1, entry 2). Gold(I)-carbene complex of

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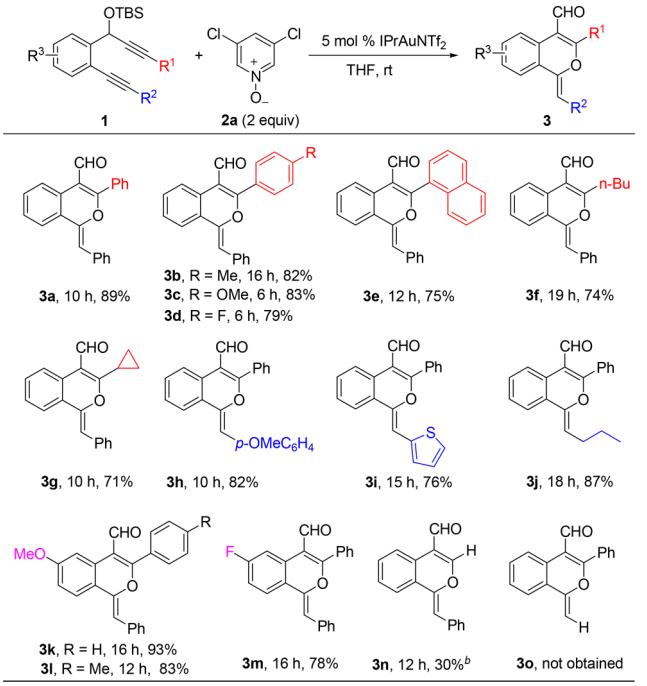
IPrAuCl/$AgBF_4$ (IPr = 2,6-bis(diisopropylphenyl)imidazol-2-ylidene) was also effective for this reaction to afford **2a** in 64% yield (Table 1, entry 3). To our delight, further screening of the catalysts revealed that changing the counterions on the gold-carbene catalysts to PF_6^- or NTf_2^- gave high yields of **3a** (Table 1, entries 4 and 5, 83%−89%). Especially, NTf_2^- was highly efficient for this transformation, leading to **3a** in 89% yield within 3 h. A complex reaction mixture was observed when the reaction was carried out in DCE, whereas in toluene, the desired product was produced in 69% yield (Table 1, entries 6 and 7). Investigation of other *N*-oxides such as **2b**−**2e** indicated that *N*-oxide **2a** gave the best results (Table 1, entries 8−11 vs entry 5). In the presence of gold(III) complex $PicAuCl_2$ (dichloro(2-pyridinecarboxylato)gold), however, the desired **3a** was not obtained (Table 1, entry 12). The addition of $AgNTf_2$ as a chloride scavenger resulted in the formation of **3a** in 30% yield (Table 1, entry 13). Control experiments with IPrAuCl or $AgNTf_2$ alone did not give the desired product (Table 1, entries 14 and 15). Without *N*-oxides, naphthyl ketone **4** was the major product (Table 1, entry 16). **4** might be formed via first formation of an allenol intermediate, followed by 6-*endo*-*dig* cyclization.[10,11] When the reaction was performed at room temperature, good results could also be obtained with the use 2.0 or 1.5 equiv of *N*-oxide **2a** (Table 1, entries 17 and 18). Further decreasing the amounts of *N*-oxide **2a** to 1.0 equiv resulted in a slightly decreased product yield (84%) and a longer reaction time (Table 1, entry 19). High yield of **3a** was also observed in the presence of 2 mol % gold catalyst (Table 1, entry 20).

We next examined the substrate scope of this novel migration reaction under the conditions shown in Table 1, entry 16. To our delight, the reaction proved to be quite general, with respect to the substitution pattern on the tethering benzene ring and the R^1 and R^2 groups on the alkyne terminus; in most cases, the desired 1*H*-isochromene products were obtained in good to high yields (Scheme 2). First, we examined the effect of substituents R^1 on the alkyne terminus. In the cases of aryl-substituted alkynes, a variety of functional groups on the aryl ring were tolerated well. For example, both electron-rich (*p*-Me, *p*-OMe) and electron-deficient (*p*-F) aryl alkynes underwent the reaction smoothly, providing the corresponding products **3b**−**3d** in high yields of 79%−83%. Sterically encumbered 1-naphthyl group was also very compatible (**3e**). The reactions of alkyl-substituted alkynes such as *n*-butyl- or cyclopropyl-substituted ones were also satisfactory, leading to **3f** and **3g** in 74% and 71% yields, respectively. Next, we examined the substituent effects on the bottom alkyne terminus (R^2). As we expected, aryl, heteroaryl (exemplified by 2-thienyl group) and alkyl groups were all compatible for this reaction (**3h**−**3j**, 76%−87% yields). The reaction was also well applicable to the substrates bearing methoxyl or fluorine groups on the tethering aryl ring (**3k**−**3m**). The reactivity of terminal alkynes on both side-arms were also examined. However, the desired products were not observed under the standard reaction conditions. After careful screening, 30% yield of the target product **3n** was isolated in acetone catalyzed by JohnphosAu(MeCN)SbF_6 in the presence of 8-methylquinoline *N*-oxide as the oxidant using **1n** bearing an upper terminal alkyne moiety as the substrate.

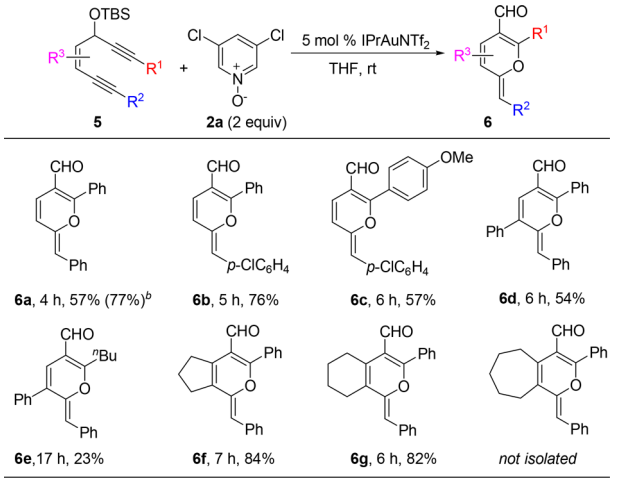
The method has also been successfully extended to enynyl propargyl ethers **5** without the tethered aromatic ring, and 2*H*-pyran derivatives **6** were synthesized accordingly (see Scheme 3). Note that these products generally have low stability;

Scheme 2. Substrate Scope of the Gold-Catalyzed Synthesis of 1*H*-Isochromenes[a]



[a]Isolated yields. [b]Reaction conditions: **1n** (0.2 mmol), 8-methylquinoline *N*-oxide (0.4 mmol) and catalyst **A** (5 mol %) in acetone at 50 °C.

Scheme 3. Substrate Scope of the Gold-Catalyzed Synthesis of 2*H*-Pyrans[a]



[a]Isolated yields. [b]8-Methylquinoline *N*-oxide was used.

therefore, an appropriate separation procedure is very important for getting pure products. After some trials, we found that separation by column chromatography on silica gel that was treated with petroleum ether: Et_3N = 1:1 and then petroleum ether before loading the sample afforded the desired products (**6**) with high purity. The oxidative cyclization of enynyl propargyl ethers **5** unsubstituted or with a phenyl substituent at the central double bond transformed to polyfunctionalized 3-formyl-2*H*-pyrans **6a**−**6d** smoothly in 54%−77% yields. Note that, in the case of **6a**, the use of 8-methylquinoline *N*-oxide afforded higher yields of the pyran

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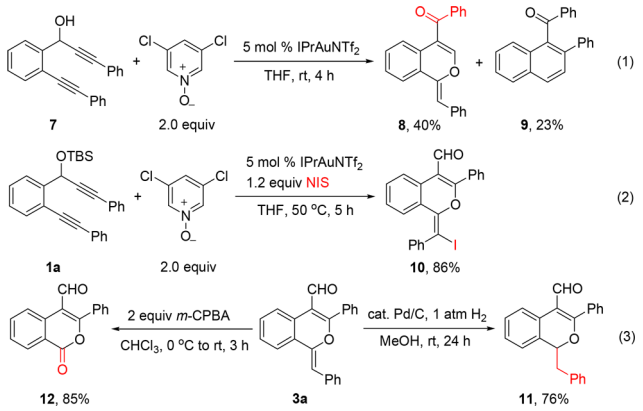
products. Substrate **5e** bearing an alkyl group led to **6e** in a low yield, along with an unknown byproduct (ca. 27%). The byproduct is likely derived through competitive 1,2-OTBS migration. 2*H*-Pyrans **6f** and **6g** fused with a five- or six-membered ring could also be synthesized in high yields via this method. However, when a substrate with a fused seven-membered ring was employed, although a major product could be observed at the early stage of the reaction, it decomposed gradually during the reaction process. Compared with the results of **5a** and **1a**, the formation of pyran **6a** occurs faster than that of **3a**. The results indicate that the migratory aptitude of an alkynyl-linked vinyl group is more favorable than an alkynyl-linked phenyl group.[9g]

We next focused on the synthesis of the related 1*H*-isochromene derivatives. Interestingly, cyclization of non-protected propargyl alcohol **7** gave 4-acyl-isochromene **8** in 40% yield, along with **9**[12] in 23% yield. **8** was formed via the attack of a formyl group instead of a keto group to the triple bond (Scheme 4, eq 1). However, the addition of NIS to the

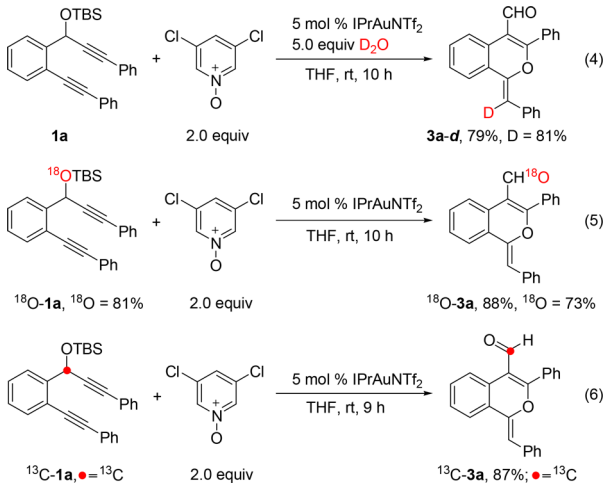
Scheme 4. Synthesis of Related Compounds



reaction mixture produced the iodinated 1*H*-isochromene **10** in high yield, in which phenyl group orients *trans*, with respect to the O atom (Scheme 4, eq 2). Possibly, double bond isomerization occurs under gold-catalyzed conditions.[11] This result also supports the formation of a vinyl gold intermediate in a domino process. Reduction of 1*H*-isochromene **3a** under the classical conditions delivered 1*H*-isochromene **11** in 76% yield, in which only the exocyclic double bond was reduced. **3a** could also be transformed to isocoumarin **12** by an oxidative cleavage reaction of the exocyclic double bond (Scheme 4, eq 3). Isocoumarin moiety is found in many natural products and biologically active molecules. Our method also provides a practical procedure for the synthesis of functionalized isocoumarins.

To validate the reaction mechanism, isotopic labeling experiments were performed. Cyclization of **1a** in the presence of 5.0 equiv of D_2O afforded **3a**–**3d** in 79% yield with 81% deuterium incorporation at the exocyclic double bond, indicating a vinyl gold intermediate is involved. The proton source in the reaction system probably comes from a trace amount of water that existed in the reaction mixture. ^{18}O- and ^{13}C-labeled substrates were also prepared, which converted to the corresponding 1*H*-isochromenes in high yields under the standard conditions. Both the ^{18}O- and ^{13}C labels were found at the formyl group in the products (see Scheme 5). The results indicate that a 1,2-enynyl migration does indeed occur in the reaction process.

Scheme 5. Isotopic Labeling Experiments



In conclusion, we have developed a concise and regioselective access to highly functionalized 1*H*-isochromene and 2*H*-pyran derivatives. Mechanistic studies revealed that an unprecedented 1,2-enynyl migration on an α-carbonyl gold carbenoid intermediate was involved as the key step for this transformation. The method offers several advantages, such as easily accessible starting materials, high efficiency, and wide functional group tolerance. Further extensions of this reaction to the synthesis of other heterocycles are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02380.

Experimental details, spectroscopic characterization of all new compounds, and X-ray crystallography of compounds **3l**, **6b**, **8**, and **10** (PDF)

Accession Codes

CCDC 1844822−1844825 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, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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