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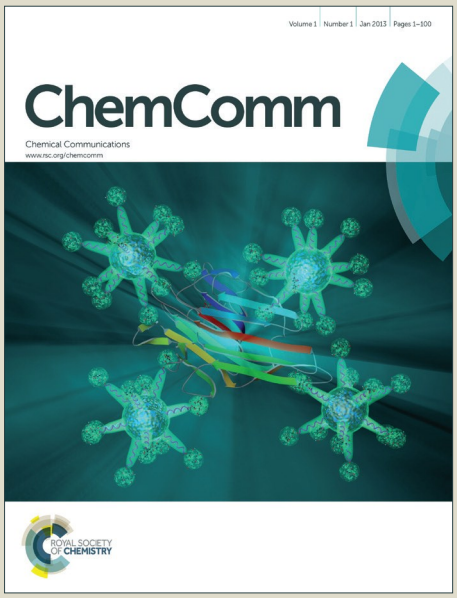

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Ligand-Controlled Gold-Catalyzed Cycloisomerization of 1,n-Enyne Esters toward Synthesis of Dihydronaphthalene

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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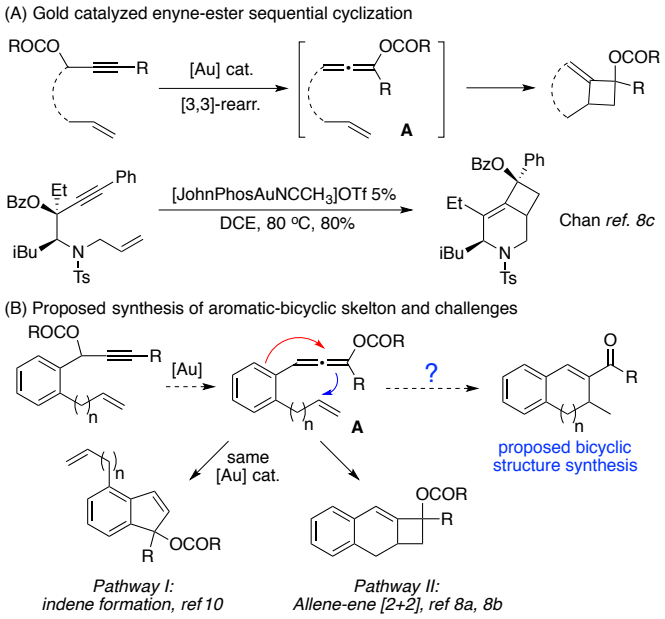
We describe herein a gold-catalyzed rearrangement of propargyl esters followed by allene-ene cyclization to afford substituted bicyclic [4.4.0] dihydronaphtalene compounds. This method is also applied to vinylethers and vinylamines of 1,7-enyne esters to form dihydroquinoline and dihydrobenzopyrane structures. The basis of this transformation is the ligand-controlled preferential activation of the alkene over the allene, affording the desired aromatic bicyclic structures in moderate to excellent yields.

Dihydronaphthalene,[1] hydroquinoline[2] and dihydrobenzo pyrane[3] are important building blocks in chemical and biological research. Their syntheses are often achieved through intramolecular cyclization. However, preparation of these aromatic bicyclic structures has relied on C-C and C-X bond formation strategies with limited functional group tolerance.[4] Due to these limitations, the development of divergent strategies to access these bicycles are of significant interest.

Catalysis employing gold complexes have been used in recent years to facilitate the synthesis of complex molecules.[5] One of these reactions is the gold-catalyzed cycloisomerization of 1,n-enyes. This reaction is a hallmark method for the efficient and atom economical single-step synthesis of complex molecules.[6] Among these reported systems, those involving an enyne bearing a propargyl ester exhibit special reactivity.[7] As shown in **Scheme 1A**, upon treatment with a gold catalyst, allene intermediate **A** forms[8] via a propargyl ester [3,3]-rearrangement. Sequential [2+2] cycloaddition involving the allene and alkene produces a cyclobutane product.[9] Later, Chen and coworkers reported several new transformations using this general strategy to yield 4 and 6-membered bicycles with excellent synthetic efficiency.[10] Our initial idea was to achieve the synthesis of aromatic bicyclic structures by modifying this scheme to favor the enyne cyclization reaction over the [2+2] cyloaddition. (**Scheme 1B**).



Scheme 1. Gold-catalyzed enyne-ester rearrangement

However, this synthetic route has not been utilized in the past to form the desired bicyclic compounds. This is mainly due to the possible formation of the undesirable indene

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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DOI: 10.1039/C6CC03032G
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product via a benzene addition to the Au-activated allene intermediate (**Scheme 1B**).[11]

Typical gold catalysts will activate both alkyne and allene with approximately equal selectivity. Thus, there arises a problem of how to achieve the selective alkyne and alkene activation in the presence of the allene intermediate.

Currently, our group is exploring the applications of 1,2,3-triazoles as ligands for the formation of new transition metal complexes. These efforts have led to the discovery of 1,2,3-triazole gold complexes, TA-Au, that exhibit significantly improved catalyst stability.[12] One interesting discovery of the TA-Au catalyst was its considerable chemoselectivity; the catalyst selectively activates alkynes over allenes.[13] Thus, we postulated whether it is possible to use triazole gold catalysts to realize the proposed transformation by selectively avoiding allene activation. To test this hypothesis, enyne ester **1a** was prepared and charged with $PPh_3Au(TA)OTf$ (TA=benzotriazole) catalyst. Reactions with $PPh_3Au(TA)OTf$ afforded allene **2a** in nearly quantitative yields, while those with PPh_3AuNTf_2 gave exclusively the indene product **4a** (**Figure 1**).

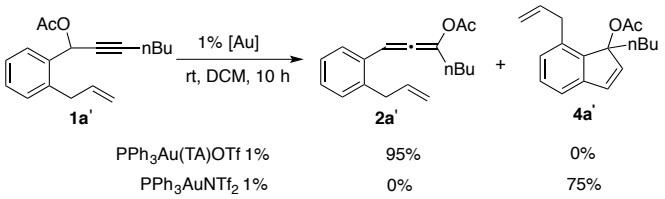
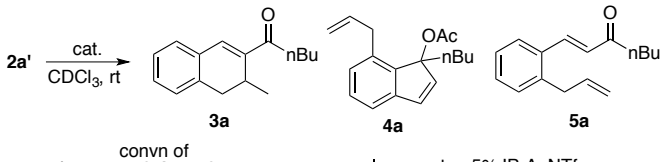


Figure 1. Gold-catalyzed enyne-ester rearrangement

In accordance with our previous report, TA-Au exhibited excellent chemoselectivity in the preferential activation of the alkyne over the allene. However, this catalyst was not suitable for alkene activation. To evaluate the reaction between the allene and alkene, we isolated allene **2a'** and charged it with various Lewis acids. As shown in **Figure 2**, typical Lewis acids, including HOTf, $Sc(OTf)_3$ and $Bi(OTf)_3$, activated allene over alkene, with no desired cyclization product **3a**. Because allene **2a** should theoretically possess a higher electron density than the simple alkene, differentiation between these two functional groups based solely on electronic effects is not viable.



cat.	convn of 2a'	3a	4a	5a
2% TfOH	100%	0%	nd	nd
2% $Sc(OTf)_3$	60%	0%	20%	40%
2% $Bi(OTf)_3$	100%	0%	55%	45%

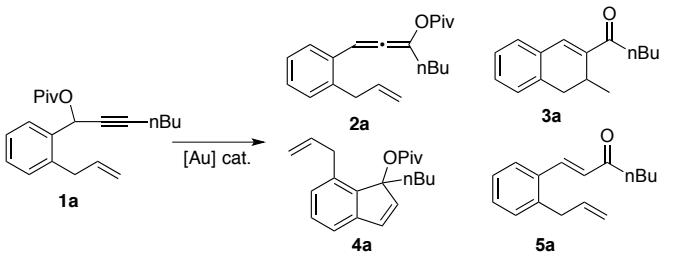
cat. = 5% $IPrAuNTf_2$

convn of 2a'	3a	4a	5a
73%	11%	35%	8%

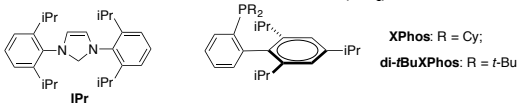
Figure 2. Gold catalyzed allene-ene cycloisomerization

With this concern, we focused our attention on the steric factors that may cause the two functional groups to have different reactivity. In comparison with the alkene, the allene moiety of **2a** is more sterically hindered due to its three substituents. Thus, it may be possible to hinder allene activation by using a sterically bulky catalyst. To explore this idea, a more stable OPiv propargyl ester **2a** was prepared (instead of OAc **2a'**) and charged with 5% $IPrAuNTf_2$ catalyst at rt. As expected, the desired cyclization product **3a** was observed, albeit in low yield. Starting with this initial result, we investigated the reaction of **1a** with various gold complexes bearing bulky primary ligands. The results are summarized in **Table 1**.

Table 1. Screening of reaction conditions[a,b]



Entry	cat.	temp	solvent	additive	yield (%) 2	3	4	5
1	5% PPh_3AuNTf_2	rt	CH_2Cl_2	-	0	0	75	20
2	5% $IPrAuNTf_2$	rt	CH_2Cl_2	-	27	11	35	8
3	5% XPhosAu(TA)OTf	rt	CH_2Cl_2	-	80	0	0	0
4	5% XPhosAu(ACN)SbF_6	rt	CH_2Cl_2	-	42	48	0	0
5	5% $^tBu_3PAuNTf_2$	rt	CH_2Cl_2	-	52	10	23	6
7	5% di-^{t}BuXPhosAuNTf$_2$	rt	CH_2Cl_2	-	0	65	<5	<5
8	5% di-^{t}BuXPhosAuNTf$_2$	rt	Tol	-	0	74	trace	trace
9	5% di-^{t}BuXPhosAuNTf$_2$	rt	Tol	H_2O (3 eq)	0	83	trace	trace
10	**2% di-^{t}BuXPhosAuNTf$_2$**	**50 °C**	**Tol**	**H_2O (3 eq)**	**0**	**89**	**trace**	**trace**



[a] Reaction condition: To a solution of **1a** (1 mmol) and additive in toluene (0.2 M) catalyst was added and stirred for 12 hours. [b] ^{1}H-NMR yields by 1,3,5-trimethoxybenzene as internal standard are shown.

We started screening with PPh_3AuNTf_2 and it gave no desired product **3a** (entry 1). While switching the ligand to IPr gave 11% of the desired product with 27% of the unconverted allene-ene (entry 2). XPhosAu(TA)OTf failed to activate allene-ene **2a** to yield any of the cyclization products due to the lower reactivity of catalyst (entry 3). Gratifyingly, XPhosAu(ACN)OTf gave 48% of the desire product **3a** (entry 4). Improving on this result, using 5 mol % Di-^{t}BuXphosAuNTf$_2$ formed the desired product in high yields.[14] This result is likely based on the hypothesis that a bulkier catalyst would favour the alkene activation over the sterically-hindered allene. Solvent screening revealed that toluene was the best solvent for the reaction system. Additionally, using water as an additive enhanced reaction yields. Finally, reducing the catalyst loading to 2 mol % and increasing the temperature to 50°C, afforded 89% of the final product **3a** with trace indene **4a** formed. Encouraged by these results, we explored the substrate scope of the transformation (**Table 2**). Notably, OAc substrate **1a'** gave the similar reaction with general 10-15% lower yields of the desired product **3**.

Reaction of **1** with 3 equivalent D_2O was performed to explore the reaction mechanism. As expected, the fully deuterium labelled compound **3h'** was obtained (>99% ^{2}D). This result provides direct evidence of gold promoted alkene activation as the key step in the cyclization as discussed above. The proposed reaction mechanism is shown in **Figure 3**.

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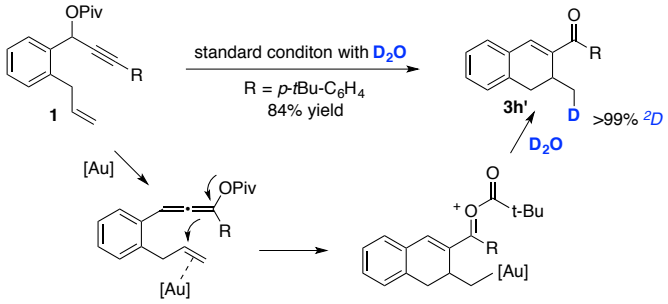
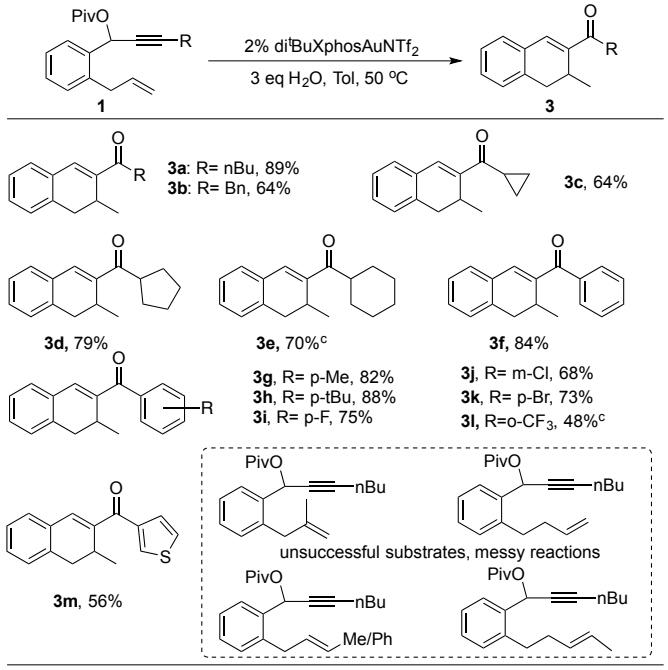
Figure 3. Plausible mechanism of the cyclization reaction.



This reaction proved to tolerate substrates bearing a wide range of functionalities. Aliphatic linear (**3a**, **3b**), cyclic alkynes (**3c**-**3e**), and aromatic alkynes (**3f**) gave moderate to excellent yields. Electron-donating and electron-withdrawing substituented arenes were also tolerated (**3g**-**3l**). Most notably, thiophene-substituted substrates gave the desired bicycle with a moderate yield (**3n**). However, our methodology was not compatible with di- or tri-substituted alkenes and internal alkenes, as desired products were not formed. This result may arise from the steric hindrance of the substituted alkenes. Overall, we developed a new methodology for the synthesis of substituted dihydronaphtalenes with good substrate tolerability and good yields.

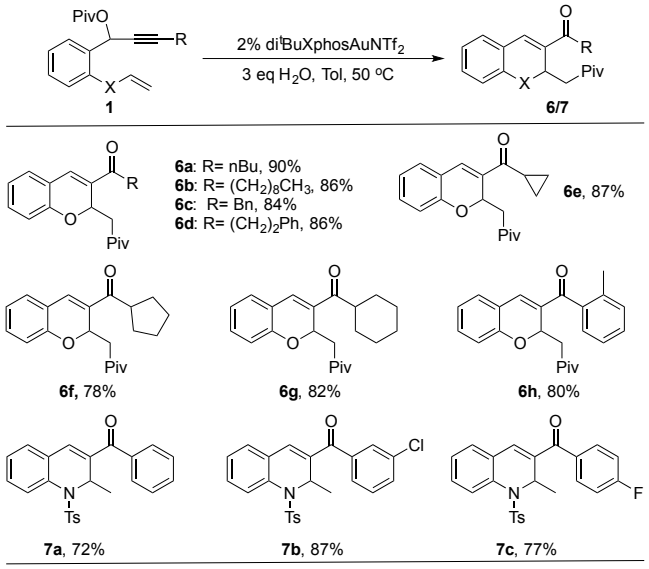
Table 2. Substrate scope of dihydronaphtalene[a,b,c]



[a] Reaction condition: To a solution of **1a** (1 mmol) and water (3 mmol) in toluene (0.2 M di^{t}BuXPhosAuNTf$_2$ was added and stirred for 12 hours at 50 °C. [b] Isolated yield. [c] ^{1}H-NMR yields.

Encouraged by our success, we focused next on the evaluation of substrates containing O and N heteroatoms. The corresponding substrates were prepared and subjected to our optimized conditions. As expected, hydrobenzopyrane **7** and hydroquinoline **8** derivatives were observed. The reaction scope is shown in **Table 3**.

Table 3. Extended substrate scope for hydrobenzopyrane[a,b]



[a] Reaction condition: To a solution of **1a** (1 mmol) and water (3 mmol) in toluene (0.2 M ditBuXPhosAuNTf$_2$ was added and stirred for 12 hours at 50 °C. [b] Isolated yield.

The functional group tolerance of our gold-catalyzed cyclization facilitates the synthesis of substituted hydrobenzopyranes. Both aliphatic and aromatic groups can be incorporated while sustaining the high yield of the product (**6a**-**6h**). This expanded methodology provided a route to hydrobenzopyranes and hydroqunolines, valuable synthons present in a variety of natural products.

One interesting observation of this reaction was the migration of the Piv group during formation of the final product by displacing the carbon-gold bond. This result was synthetically valuable because it gave us the possibility of installing different groups on the methyl group of the pyrane ring. However, this phenomenon did not occur when using nitrogen-containing substrates (**7a**-**7c**).

Considering that the double bonds of vinyl ethers are more reactive due to high electron density, we questioned whether they could be used to facilitate the formation of the 7 and 8-membered ring. The starting materials were prepared according to literature procedure.[15] However, subjecting the substrate to the optimized conditions (gold catalyst with 3 eq. H_2O) gave significant amounts of vinyl ether hydration product. Thus, anhydrous conditions were used to avoid this side reaction. Under these anhydrous conditions, the desired cyclization product **8** was observed along with a traces amount of the [2+2] product (**Figure 4**). Notably, formation of 8-membered rings gave low yield.

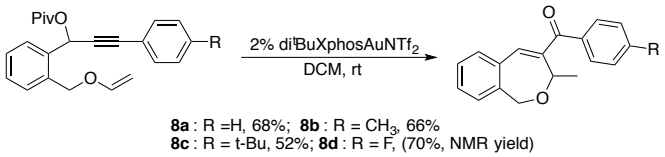


Figure 4. Substrate extension to seven-membered ring systems

Surprisingly, in contrast to the formation of hydrobenzopyran, there was no Piv migration observed. While this reaction proceeds with aromatic alkynes, the use of aliphatic alkynes resulted in slower reactions and the formation of unidentified products.

Herein we report a chemoselective Au-catalyzed activation

facilitated by the steric hindrance. This chemoselective activation enabled us develop a methodology to synthesize dihydronapthalene, dihydrobenzopyrane, and hydroquinoline derivatives with excellent functional group tolerance.

We thank the NSF (CHE-1362057) and NSFC (21228204) for financial support.

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