

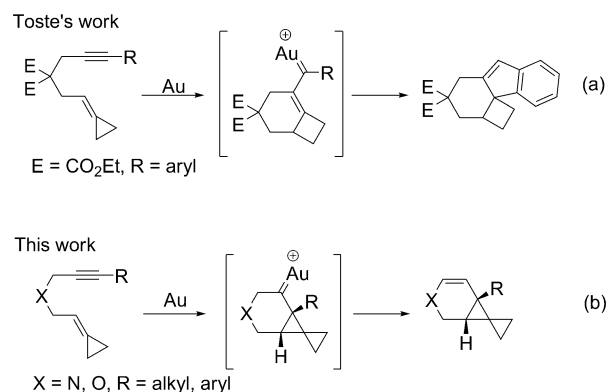
Gold(I)-Catalyzed Cycloisomerization of Nitrogen- and Oxygen-Tethered Alkylidenecyclopropanes to Tricyclic Compounds

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Homogeneous catalysis by gold complexes has received considerable attention in recent years.^[1] Among these interesting reactions, gold-catalyzed cycloisomerization of 1,6-enynes is one of the most important strategies for the construction of functionalized cyclic structures.^[2] Nitrogen- and oxygen-bridged enynes are useful starting materials for the preparation of heterocyclic building blocks. Since Blum et al. first reported the PtCl₄-catalyzed cycloisomerization of allyl propynyl ether to 3-oxabicyclo[4.1.0]heptenes in 1995,^[3a] this type of 6-*endo-dig* cycloisomerization has been developed by the use of transition-metal catalysts, such as platinum,^[3] rhodium,^[4] gold^[5] and iridium.^[6] For example, Chung and co-workers reported the gold-catalyzed cyclization of enynes containing an olefinic cycle to give azabicyclo[4.1.0]heptenes under mild conditions.^[5c] Similar oxygen heterocycles with high diastereoselectivities have been reported by Michelet's and Chen's groups.^[5f,h]

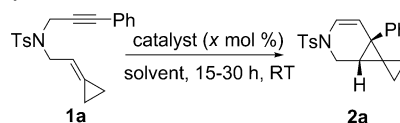
Alkylidenecyclopropanes (ACPs) containing a coordinating double bond and a strained carbocycle can undergo a number of interesting metal-assisted cycloadditions when tethered by alkenes or alkynes.^[7] In this aspect, Toste's group reported a new gold-catalyzed ring-expanding enyne cycloisomerization reaction that allows for rapid preparation of complex polycyclic ring systems (Scheme 1a).^[2j] Herein, we report a new construction of tricyclic compounds along with cycloisomerization from alkylidenecyclopropanes toward six-membered heterocyclic rings (Scheme 1b).

Initial studies by using alkylidenecyclopropane **1a** (0.2 mmol) as the substrate were aimed to determine the reaction outcome and subsequently optimize the reaction conditions. The results are summarized in Table 1. We found that an interesting tricyclic product **2a** was formed in 69% yield by using [(PPh₃)AuCl]/AgOTf as the catalyst



Scheme 1. Gold-catalyzed cycloisomerization of alkylidenecyclopropanes tethered by alkynes.

Table 1. Optimization of the reaction conditions for gold(I)-catalyzed intramolecular cyclization.



Entry ^[a]	Catalyst [x mol %]	Solvent	Yield [%], ^[b] 2a
1	[(PPh ₃)AuCl]/AgOTf (5)	DCE	69
2 ^[c]	PtCl ₂ (5)	DCE	45
3 ^[c]	RhCl(CO)(PPh ₃) ₂ /AgSbF ₆ (5)	DCE	Complex
4	[(PPh ₃)AuCl] (5)	DCM	NR
5	AgOTf (5)	DCM	NR
6	[(PPh ₃)AuCl]/AgOTf (5)	toluene	20
7	[(PPh ₃)AuCl]/AgOTf (5)	MeCN	NR
8	[(PPh ₃)AuCl]/AgOTf (5)	1,4-dioxane	37
9	[(PPh ₃)AuCl]/AgOTf (5)	CHCl ₃	87
10	[(PPh ₃)AuCl]/AgOTf (5)	DCM	90
11	[(PPh ₃)AuCl]/AgOTf (10)	DCM	44
12	[(PPh ₃)AuCl]/AgSbF ₆ (5)	DCM	42
13	[(PPh ₃)AuCl]/AgBF ₄ (5)	DCM	39
14	[(PMe ₃)AuCl]/AgOTf (5)	DCM	47
15	[(tBu ₃ P)AuCl]/AgOTf (5)	DCM	90
16	[AuCl ₃]/AgOTf (5)	DCM	3
17	[(IPr)AuCl]/AgOTf (5)	DCM	58
18	[(tBuXPhos)Au(NCMe)]SbF ₆ (5)	DCM	94

[a] All reactions were carried out by using **1a** (0.2 mmol) in the presence of catalyst (x mol %) in various solvents (2.0 mL) unless otherwise specified. [b] Yield of isolated product. [c] At 80 °C. NR = no reaction.

(5 mol %) in 1,2-dichloroethane (DCE) at room temperature (20 °C) (Table 1, entry 1). The structure of compound

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201200978>. Experimental procedures and spectral data for all new compounds. X-ray crystal structures and data for **2a**, **3p** and **4n**. This material is available free of charge via the Internet at [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1521-3765](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1521-3765).

2a was confirmed by NMR spectroscopic data and X-ray diffraction analysis (see the Supporting Information).^[8] Carrying out the reaction in the presence of PtCl_2 or $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]/[\text{AgSbF}_6]$ (5 mol %), which were effective catalysts in other similar reactions, afforded the desired product **2a** in lower yield or complex product mixtures, respectively (Table 1, entries 2 and 3).^[3b–h,j,m,4d] Control experiments indicated that by using $[(\text{PPh}_3)\text{AuCl}]$ or AgOTf alone as the catalyst did not promote the reaction (Table 1, entries 4 and 5). Further examination of solvent effects revealed that dichloromethane (DCM) was the solvent of choice, and **2a** was formed in lower yield in other organic solvents, such as toluene, MeCN, 1,4-dioxane, or CHCl_3 (Table 1, entries 6–10). Moreover, adding $[(\text{PPh}_3)\text{AuCl}]/\text{AgOTf}$ (10 mol %) afforded **2a** in 44 % yield (Table 1, entry 11). Changing silver salt to AgSbF_6 or AgBF_4 did not improve the reaction outcomes (Table 1, entries 12 and 13). By using $[(\text{PMe}_3)\text{AuCl}]$ or $[(t\text{Bu}_3\text{P})\text{AuCl}]$ instead of $[(\text{PPh}_3)\text{AuCl}]$ as the gold catalyst gave **2a** in 47 and 90 % yields, respectively, and $[(\text{IPr})\text{AuCl}]$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) as well as AuCl_3 were not effective gold catalysts in this reaction (Table 1, entries 14–17). In the presence of $[(t\text{BuXPhos})\text{Au}(\text{NCMe})]\text{SbF}_6$

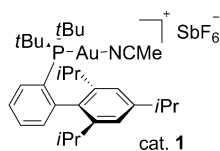


Figure 1. Structure of $[(t\text{BuXPhos})\text{Au}(\text{NCMe})]\text{SbF}_6$.

(Figure 1, cat. **1**), **2a** could be obtained in 94 % yield under otherwise identical conditions (Table 1, entry 18). Therefore, the optimal reaction conditions have been identified to carry out the reaction in DCM at room temperature by using $[(t\text{BuXPhos})\text{Au}(\text{NCMe})]\text{SbF}_6$ (5 mol %) as the catalyst.

We next examined the substrate generality of the reaction under the optimized conditions, and the results are shown in Table 2. As can be seen, for nitrogen-tethered substrates **1b–d** with an electron-donating group on the benzene ring, such as MeO and Me groups, the reactions proceeded smoothly to give the desired products **2b–d** in 87–99 % yields (Table 2, entries 1–3). When the electron-withdrawing groups, Br or Cl, were introduced on the benzene ring (substrates **1e** and **1f**), the corresponding products **2e** and **2f** were obtained in 98 and 99 % yields, respectively (Table 2, entries 4 and 5). The aromatic group of **1** could also be a naphthyl group (substrate **1g**), giving the cycloisomerized compound **2g** in 99 % yield (Table 2, entry 6). As for substrates **1h** ($\text{R} = \text{Me}$) and **1i** ($\text{R} = \text{Et}$) with an alkyl group at the terminal of alkyne moiety, tricyclic compounds **2h** and **2i** could be formed in 73 and 87 % yields, respectively (Table 2, entries 7 and 8). In the case of other N-sulfonated amines ($\text{X} = \text{NNs}$ or NBs), the reaction also proceeded smoothly to give the desired products **2j** and **2k** in 88–99 % yields, indicating a broad substrate scope of this reaction (Table 2, entries 9 and 10). For oxygen-tethered alkylidene-cyclopropanes, such as substrates **1l** and **1m**, the reactions produced **2l** and **2m** in 71 and 80 % yields, respectively (Table 2, entries 11 and 12). Further examination of sub-

Table 2. Substrate scope of the gold(I)-catalyzed cycloisomerization.

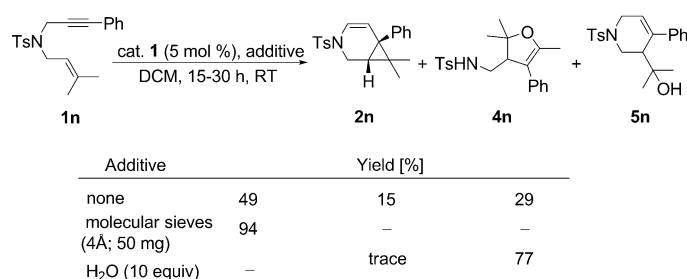
Entry ^[a]	1	X	R	Yield [%], ^[b] 2
1	1b	NTs	4-MeOPh	2b , 87
2	1c	NTs	4-MePh	2c , 95
3	1d	NTs	3-MePh	2d , 90
4	1e	NTs	2-BrPh	2e , 98
5	1f	NTs	4-ClPh	2f , 99
6	1g	NTs	1-naphthyl	2g , 99
7	1h	NTs	Me	2h , 73
8	1i	NTs	Et	2i , 87
9	1j	NNs	Ph	2j , 88
10	1k	NBs	Ph	2k , 99
11	1l	O	Ph	2l , 71
12	1m	O	4-ClPh	2m , 80
13 ^[c]	1n			2n , 94
14	1o			NR
15	1p			3p , 71

[a] All reactions were carried out by using **1** (0.2 mmol) in the presence of cat. **1** (5 mol %) in DCM (2.0 mL) at RT for 15–30 h. [b] Yield of isolated product. [c] Molecular sieves (4 Å, 50 mg) was added. Ts = 4-toluenesulfonyl; Ns = 4-nitrobenzenesulfonyl; Bs = 4-bromobenzenesulfonyl; NR = no reaction.

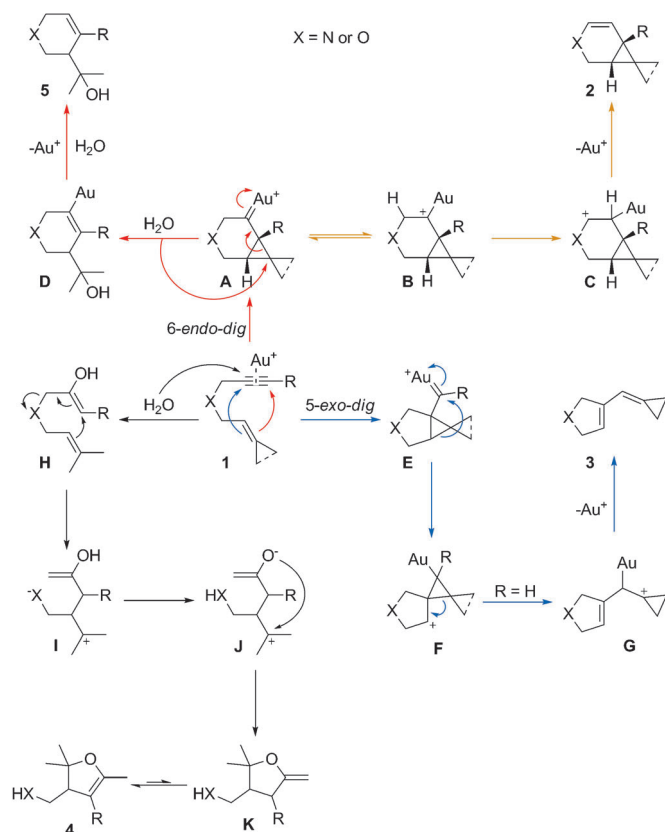
strate **1n** revealed that the azabicyclo[4.1.0]heptene derivative **2n** could be obtained in 94 % yield, when 4 Å molecular sieves was added (Table 2, entry 13). As for 1,7-enyne **1o**, no reaction occurred under the standard conditions (Table 2, entry 14). When the terminal of alkyne moiety is a hydrogen atom (substrate **1p**), the corresponding 1,3-diene **3p** could be obtained in 71 % yield rather than the tricyclic product (Table 2, entry 15).^[9] The product structures of **2b–n** were determined by NMR spectroscopic data, MS, and HRMS. The structure of compound **3p** was confirmed by NMR spectroscopic data and X-ray diffraction analysis (see the Supporting Information).^[10]

On the other hand, in the case of 1,6-enyne **1n**, under the standard conditions, the reactions produced **2n**, **4n**, and **5n**^[11] in 49, 15, and 29 % yields, respectively. Then, adding molecular sieves (4 Å, 50 mg) into the reaction system, azabicyclo[4.1.0]heptene derivative **2n** could be obtained in 94 % yield as the sole product. Alcohol derivative **5n** was formed in 77 % yield along with a trace amount of 2,3-dihydrofuran derivative **4n**, when H_2O (10 equiv) was added, suggesting that products **4n** and **5n** are derived from adventitious water (Scheme 2). The structure of compound **4n** was confirmed by NMR spectroscopic data and X-ray diffraction analysis (see the Supporting Information).^[12]

Plausible mechanisms for these reactions are outlined in Scheme 3 on the basis of above results. Coordination of Au^{I} complex to the alkyne forms intermediate **1**, which evolves



Scheme 2. Gold(I)-catalyzed cycloisomerization of **1n** by using different conditions.



Scheme 3. A plausible reaction mechanism.

to give the cyclopropyl Au–carbene intermediate **A** (via 6-*endo-dig* cyclization) or **E** (via 5-*exo-dig* cyclization), which are often observed in gold-catalyzed cycloisomerizations of 1,6-enynes. It should be also mentioned here that we did not observe any product via 6-*exo-dig* cyclization as reported by Toste and co-workers.^[2j] There might be an equilibrium between the intermediates **A** and **B**, intermediate **B** is expected to undergo a facile [1,2]hydride shift to generate intermediate **C**, followed by elimination of Au^I complex to give product **2** (orange arrow).^[5f] Alternatively, nucleophilic attack of water on the cyclopropyl moiety of intermediate **A** gives intermediate **D**, which undergoes hydrolysis to produce alcohol derivative **5** (red arrow).^[5b] On the other hand,

carbenoid **E** can undergo a rearrangement to give a spiro intermediate **F**.^[4b,9a] Depending on the substitution pattern, when R = H, the spiro intermediate **F** undergoes fragmentation to produce the carbocation **G**, followed by elimination of Au^I complex to give 1,3-diene **3** (blue arrow). As depicted by black arrows, activation of the alkyne moiety by Au^I complex induces a nucleophilic attack of water to give intermediate **H**. Skeletal reorganization of intermediate **H** produces enol **I**, followed by intramolecular proton transfer to form the oxo-anion intermediate **J**. Intermediate **J** undergoes intramolecular nucleophilic attack to produce tetrahydrofuran **K**, which can also further tautomerize to the corresponding 2,3-dihydrofuran derivative **4**.

In conclusion, we have developed a new gold(I)-catalyzed cycloisomerization of nitrogen and oxygen-tethered alkydenecyclopropanes to provide an easy access to tricyclic compounds or bicyclo[4.1.0]heptene derivatives in high yields under very mild conditions. Further applications of this air- or moisture-tolerant reaction of a gold-catalyzed tandem system and more detailed mechanistic investigation are underway in our laboratory.

Experimental Section

General procedure for gold(I)-catalyzed cycloisomerization of alkydenecyclopropanes under the standard reaction conditions: Under ambient atmosphere, an alkydenecyclopropanes **1** (0.2 mmol, 1.0 equiv) was dissolved in DCM (2.0 mL) in an Schlenk tube, and [(*t*BuXPhos)Au(NCMe)]SbF₆ (5 mol %) was added. Then, the reaction mixture was stirred at RT until the reaction was completed. The solvent was removed under reduced pressure, and the residue was purified by a flash-column chromatography (SiO₂) to give the corresponding product **2** in moderate-to-excellent yields.

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Keywords: cyclization • cyclotrimerization • homogeneous catalysis • heterocycles • gold

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