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### Title

Gold Catalyzed Ring Enlargement

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### Publication Date

2021



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## Reflective essay

Ziguang Yang *College of Creative Studies UC Santa Barbara*

I have been researching gold catalysis in Zhang group since my freshman year; My research project was gold catalyzed ring expansion reactions. During the epidemic period, I tried to find some ways to develop research ideas. My graduate tutor noticed my enthusiasm for this research and suggested that I took literature research as a form of remote research. The literature review was an important part of the research project, even more, important than the actual work. By doing a literature review project on gold-catalyzed ring extension reaction, I have developed solid skills in literature research and benefited a lot from it.

Our research project on synthesizing chiral cyclopentadienyl esters was meaningful, while the cyclopentadienyl group played an critical role in polyester, resin, plastic flame retardants, drugs, spices, and other materials. An efficient synthesis method of chiral cyclopentanone can help people better optimizing the total synthesis path. And gold-catalyzed asymmetric synthesis of chiral cyclopentanone was a subset of gold-catalyzed ring extension reactions.

To carry out my review project in a more effective and disciplined way, I decided to begin with some reviews in this field. The review articles provide me with an excellent point to deploy my search with refined materials relative to the gold-catalyzed ring expansion reactions. The problem became how do I find those review papers and how do I get access to it? Fortunately, with the courtesy of UCSB library, I have my SciFinder account established with the help of our librarian Mr. Chuck Huber. With the help of the powerful search engine SciFinder, I found four review articles about the gold-catalyzed transformations of the strained rings with the largest citations. After reading these four review papers thoroughly, I got a general idea of the

major reaction modes of the highly strained rings with the gold catalysts. Then, I tried to categorize those relevant reactions with my understanding: the ring expansion pathway and the ring-opening pathway, which has set the primary structure of my review, and then I elaborated on each of the two major categories with some small sections, such as the different gold intermediate and different substrates motifs. I then marked all those references that would fit with the categories of my review. With the full text available via UCSB proxy server provide by our library, I could get access to those related articles in a planned way with questioning how they designed the reactions and they optimized their conditions, and they proposed their mechanisms. More importantly, I could learn about all the drawbacks of those methodologies, which would rarely be discussed in their abstract parts. After incorporating all those articles into the corresponding sections of my review project, my mentor Ke suggested that I should be careful that I may have missed some recently published works after those review articles. However, finding those newly published articles seemed to be difficult and tedious. Luckily, I have figured out how to effectively locate those new works utilizing the citation map of the SciFinder. Since those review papers have contained lots of previous work on the gold-catalyzed ring expansion processes, most of the newly published works will cite those reviews. Therefore by clicking the "cited by" button, I could instantly discover any related work published after those reviews and add them to my review project. Finally, I did extra proofreading by checking the supporting information of selected articles as well as checking the recent publications of those well-known groups that were doing gold catalysis, such as Professor Dean Toste at UC Berkeley, Professor Liming Zhang at UC Santa Barbara, Professor Antonio M. Echavarren at ICIQ and Professor Seunghoon Shin at Hanyang University.

By doing this literature review project about the gold-catalyzed ring expansion reactions, I understood the gold catalysis on highly strained substrates. I also concluded some useful ideas about the new reactivity mode, which may be further applied to our ongoing research project. Moreover, the review project provides me lots of practical experience of the literature search that would make me more proficient in future literature studies. Lastly, viewing all the works in a particular research topic was an interesting thing to do as I could see how the methodologies developed as time passed. It was a great pleasure to appreciate all those ingenious designs and speculations by those excellent researchers all over the world.

# Gold Catalyzed Ring Enlargement



College of Creative Studies

Presented by Ziguang Yang  
Supervised by Ke Zhao and Dr. Liming Zhang

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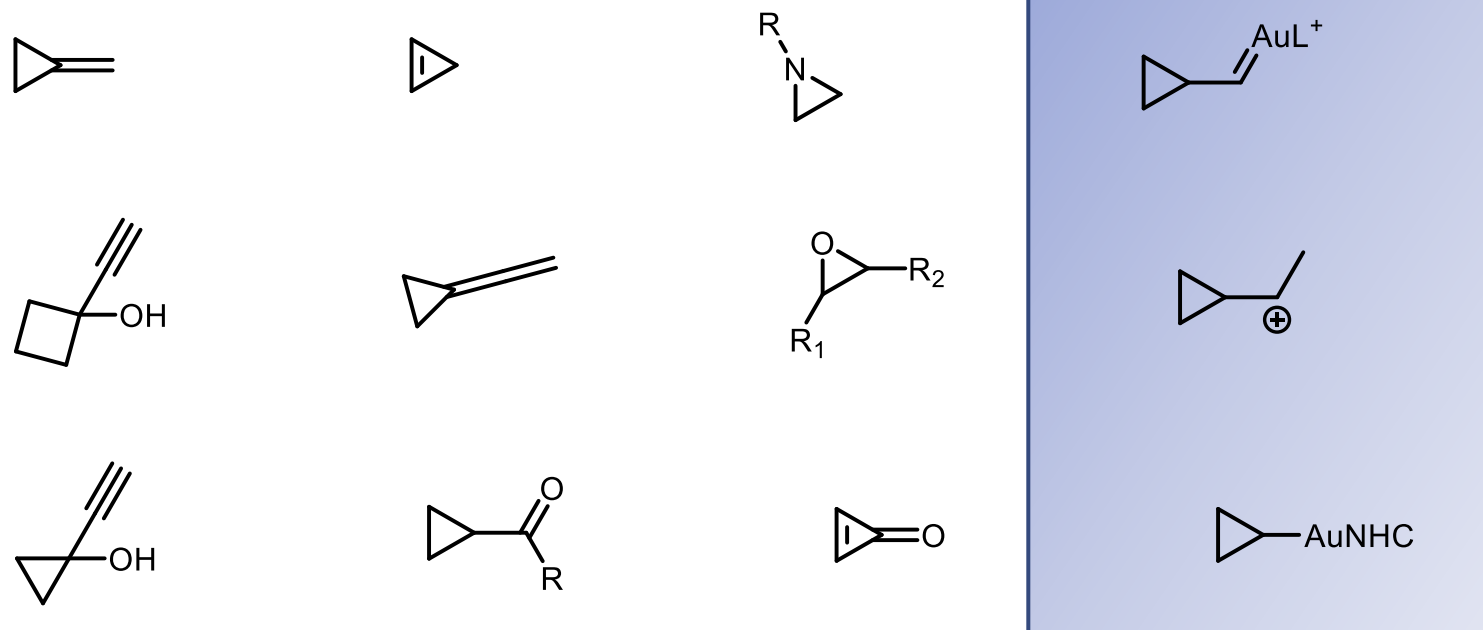
## ▶ Part II ring opening mechanism

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# Background information of the substrates

- ▶ The strained rings (usually the three-membered or four-membered ring)

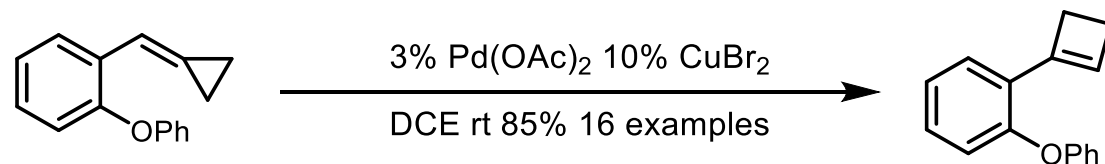




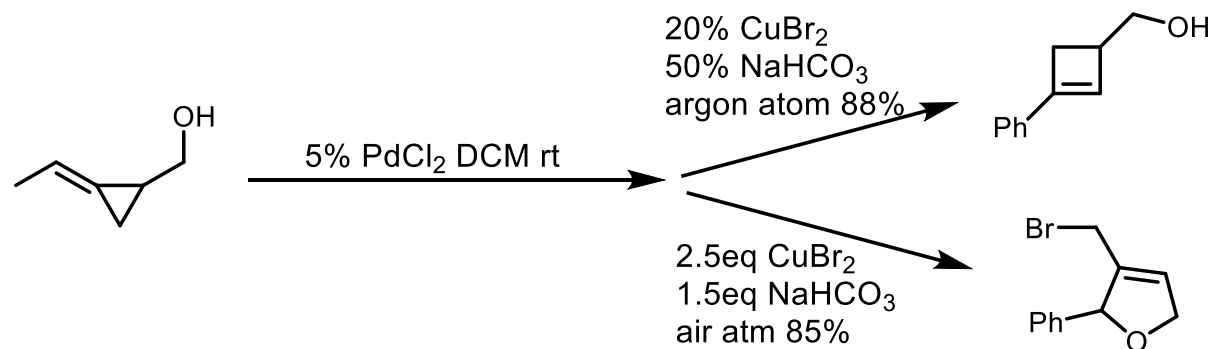
# Background information of the metal catalyzed ring expansion reactions

- ▶ Many metal catalyst are able to catalyze the ring-expansion reactions

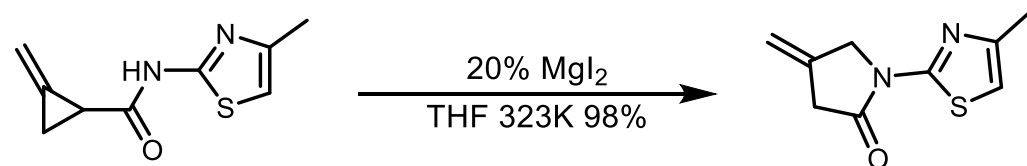
Shi, M.; Liu, L.-P.; Tang, J. J. Am. Chem. Soc. 2006, 128, 7430-7431



Tian, G.-Q.; Yuan, Z.-L.; Zhu, Z.-B.; Shi, M. Chem. Commun. 2008, 2668-2670

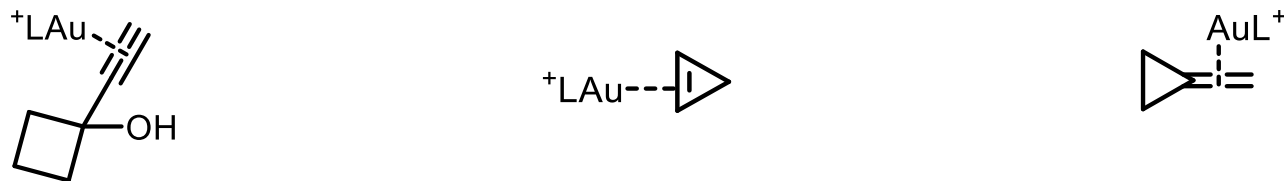


Scott, M. E.; Schwarz, C. A.; Lautens, M. Org. Lett. 2006, 8, 552 - 5524

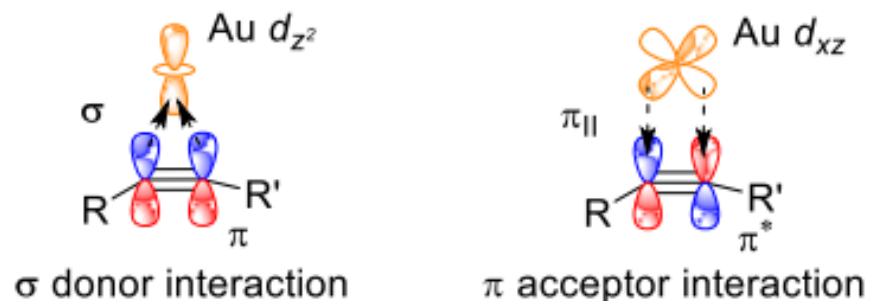


# Background information: Why bother gold?

- ▶ The  $\pi$  electron rich moiety in the highly strained ring substrates can be readily activated by the gold catalyst to initiate a cascade reaction.



- ▶ The activation pattern of both  $\sigma$  donor and  $\pi$  acceptor interactions. And the dual activation mode make the triple bond very weak and easy to break.



- ▶ The versatile potential following up transformations for gold catalysis.

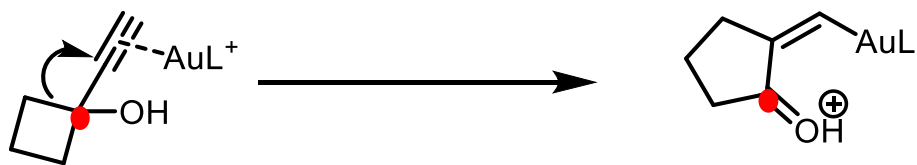
Nazarov cyclization

3,3-sigmatropic rearrangement

gold carbene formation

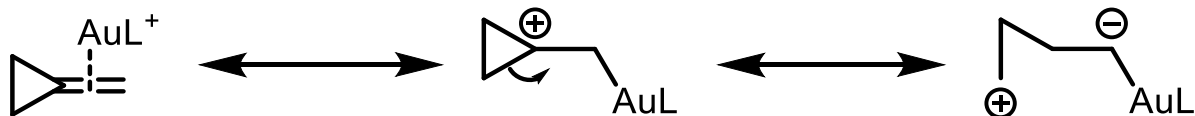
# Two major pattern observed

- ▶ The ring expansion process: one of the bond from the original ring migrate to the position nearby while maintaining the ring structure. (concerted mechanism)



Usually happens with a electron donating group at the **red position** to resolve the positive charge

- ▶ The ring opening process: one of the bond from of original ring breaks and forming a double bond with the nearby electron deficient carbon and yield a (linear) shape intermediate that usually characterized as 1,4 carbon dipole species. (stepwise mechanism)



Usually occurs in the bicyclic system and the cyclopropene system and need electron donating group to stabilize the 1,n-dipole

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- ▶ The gold carbene system

- ▶ **Part II ring opening mechanism**

- ▶ The bicyclic system

- ▶ The 1,n-dipole system

- ▶ The cyclopropene and its derivative system

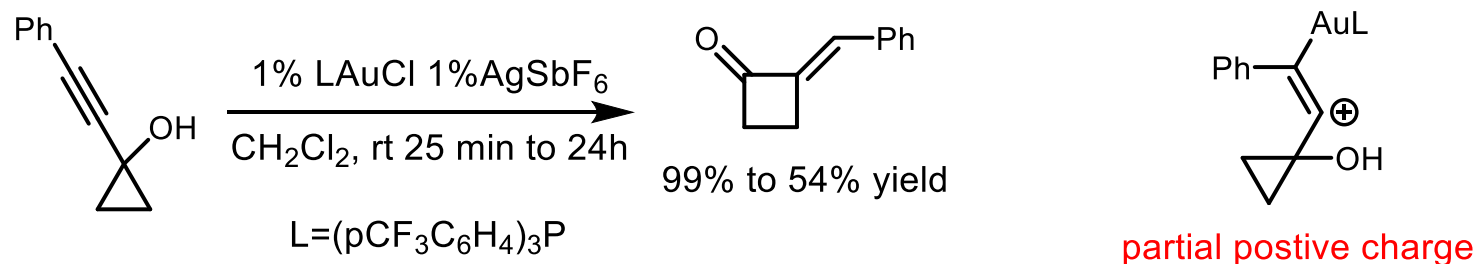
- ▶ The heterocycle system

- ▶ **Conclusion**

The gold activated unsaturated bond usually contain the substrates of the alkynyl-cyclopropanol or cyclobutanols. The gold will activate the triple bond and make it readily to accept the electrons from the highly strained rings next to it. Then the protodeauration process quickly followed and terminate the reaction and sometimes followed up reactions may happen if there was no proton source in the system. This chemistry was first explored by Professor F. D. Toste at UC Berkeley and followed up by Professor Shi Min at Shanghai Institute of Organic Chemistry.

# The cyclopropanol and alkyne(allene) system

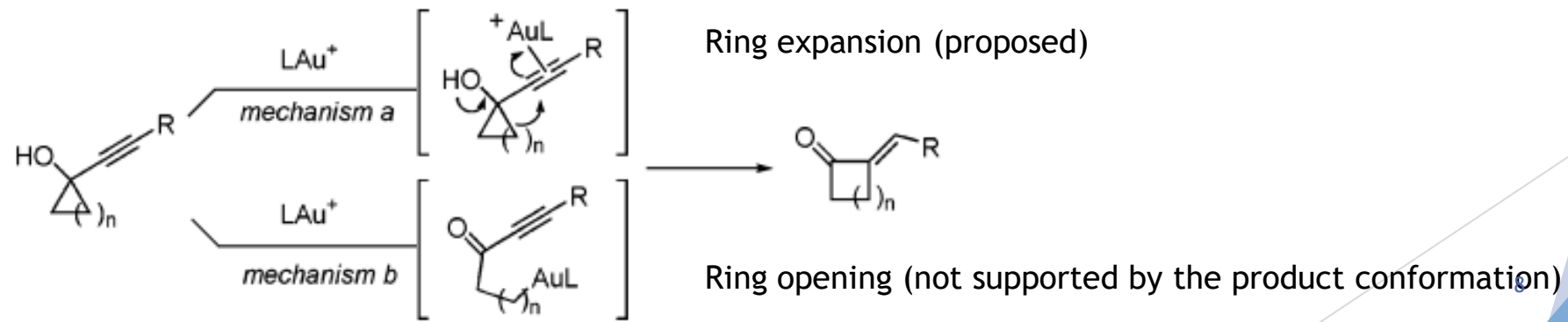
- ▶ Gold catalyzed ring expansion of cyclopropanols (Toste 2005)



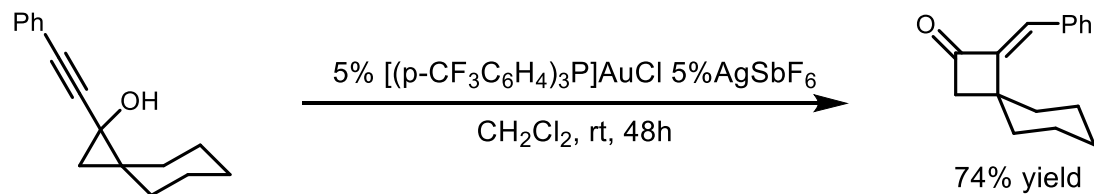
The **electron-deficient** ligand is more favorable

Indicated that the ring expansion is motivated by the **partial positive charge** next to the ring

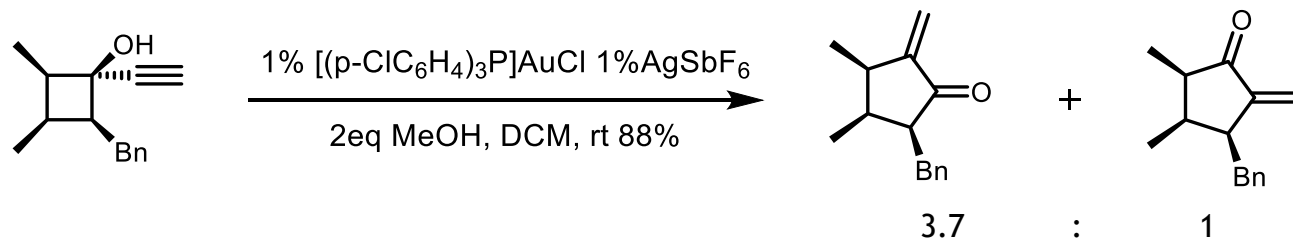
The mechanism proposed was somewhat primitive as at that time the characterization method cannot determine where would the gold catalyst coordinate to.



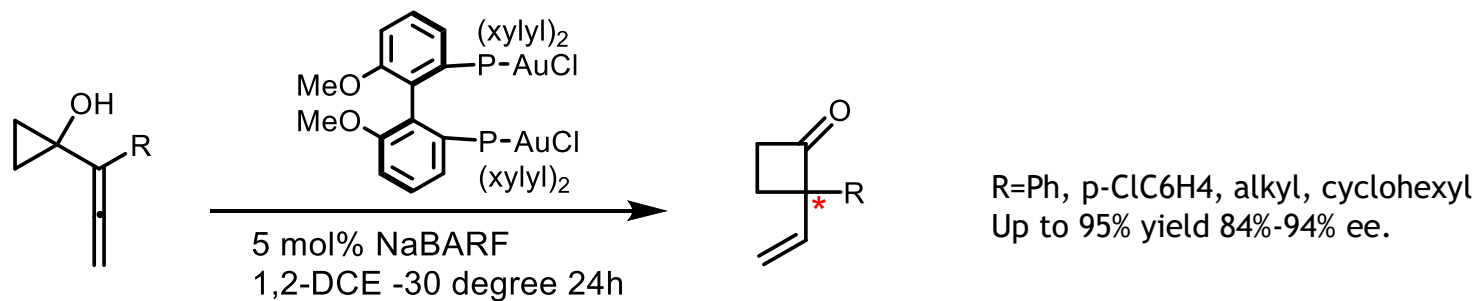
- ▶ The cationic gold catalyst preferentially migrate the more substituted chain.



- ▶ The substrate scope also include cyclobutanols.

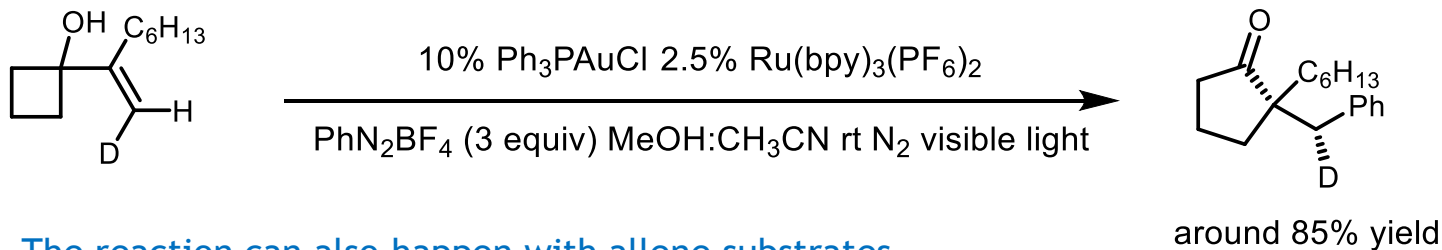


- ▶ The similar reactivity is observed for the [allene & cyclopropanol system](#). (Toste 2009)

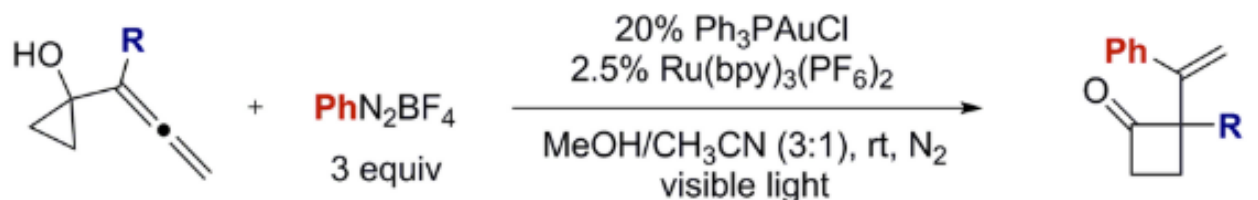


Generation of a quaternary chiral center

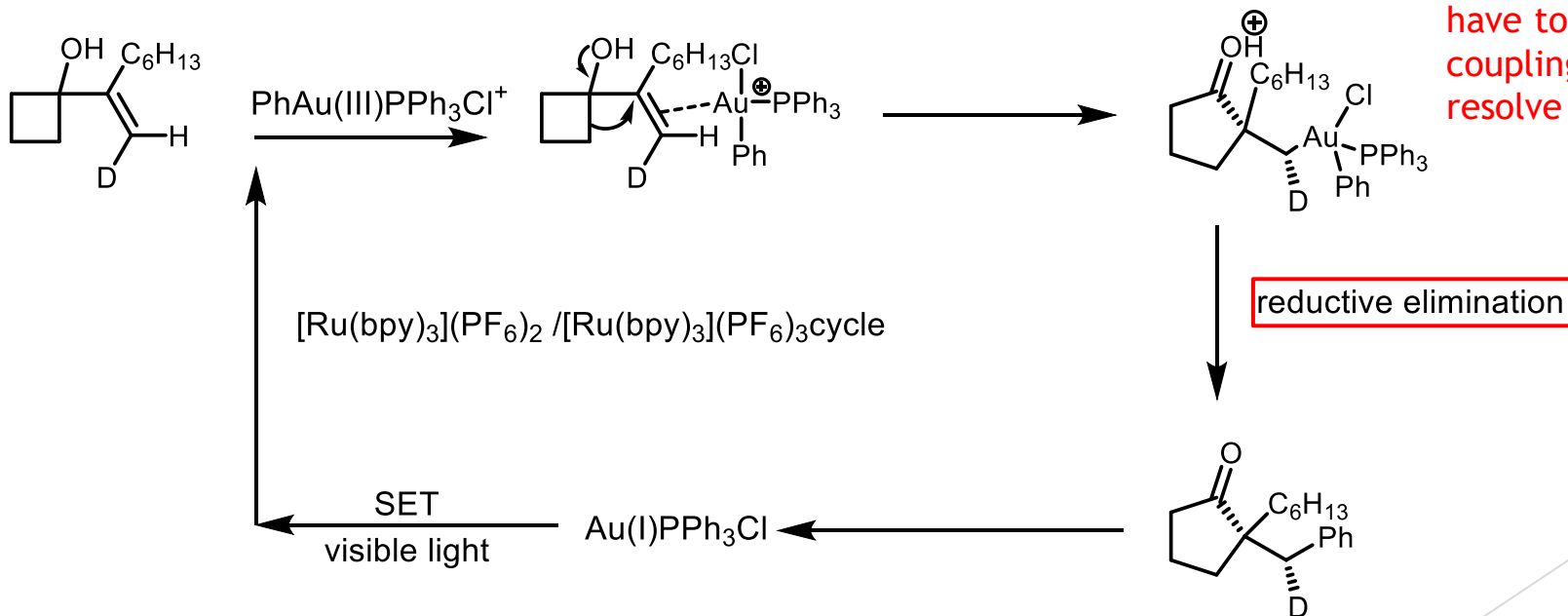
- ▶ The alkene group can also coordinated to the Au(III) catalyst to have the similar reactivity (Toste 2014)



The reaction can also happen with allene substrates

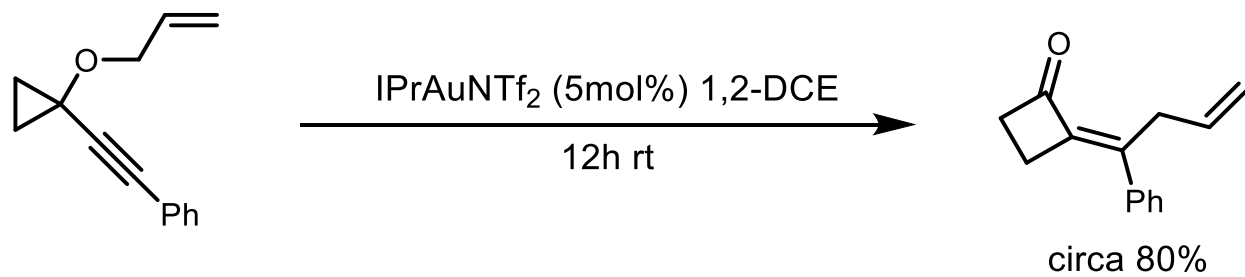


Mechanism:

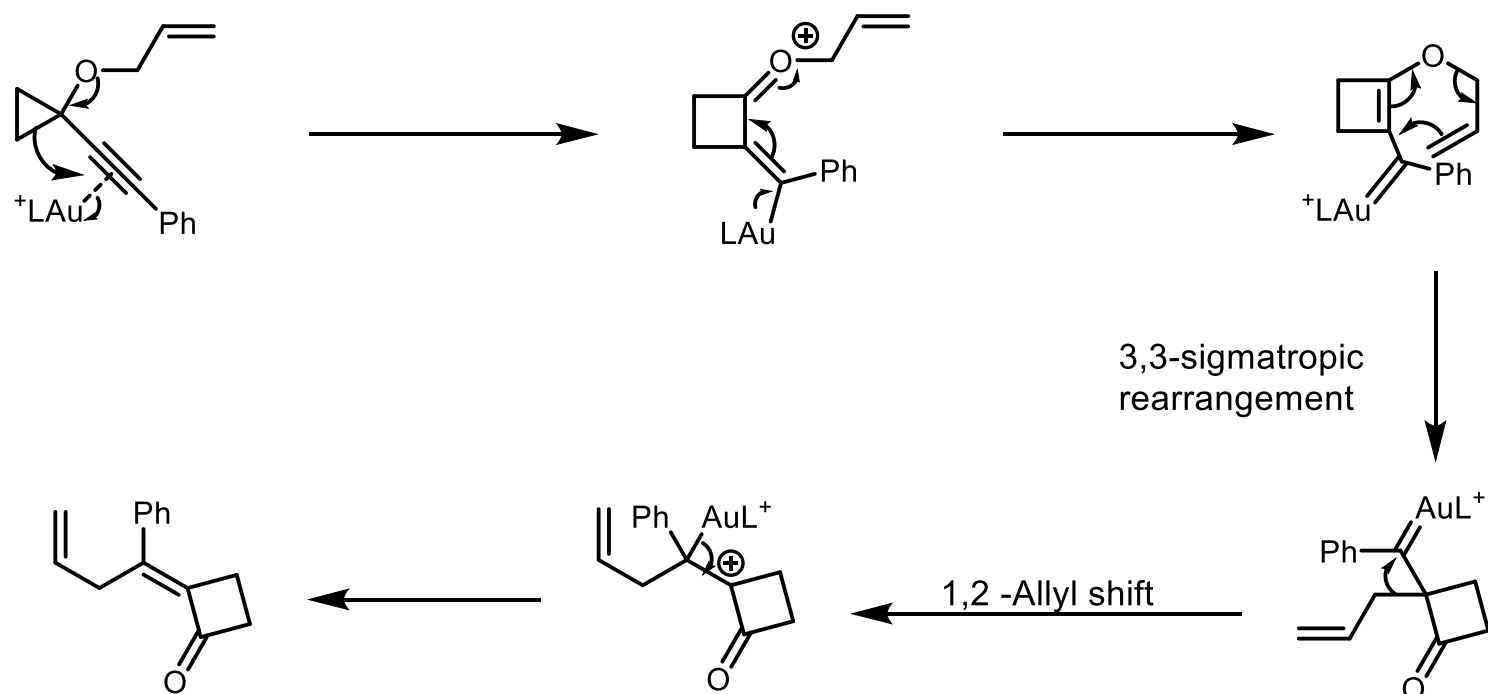


The reason to use a photo-redox catalysis here was due to the fact that the protodeauration process for  $\text{sp}^3$  gold-carbon bond was problematic and they have to design a reductive coupling reaction to resolve for this problem.

- The ether substrate followed with 3,3-sigmatropic rearrangement. (Shi Min 2019)



- Mechanism studies:





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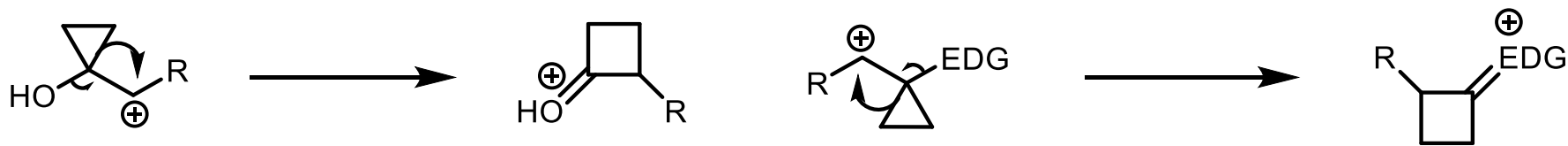
- ▶ The bicyclic system
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- ▶ The cyclopropene and its derivative system
- ▶ The heterocycle system

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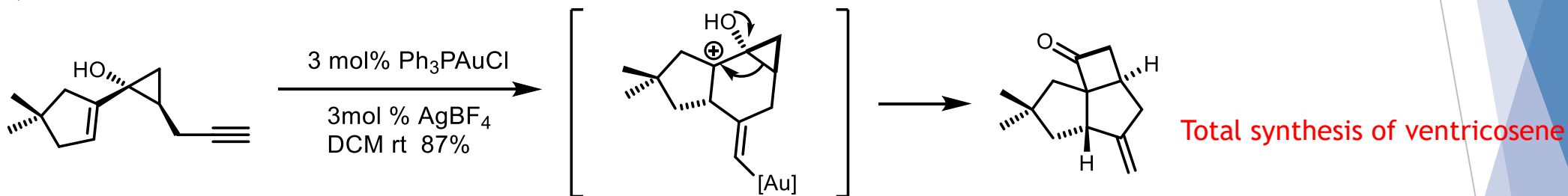
The carbocation system was relative simple for its reactivities, first there will be one carbocation generated at the alpha position of the strained ring, then the ring will migrate to quench the positive charge. The generation of the positive charge was the most challenging part of the whole reaction, and it was usually generated via the acyl rearrangement. However, Professor A.M. Echavarren has developed a effective method to get access to the carbocation intermediate via his cycloisomerization 1,6-enyne system.

# The cyclopropane(ol) and carbocation system

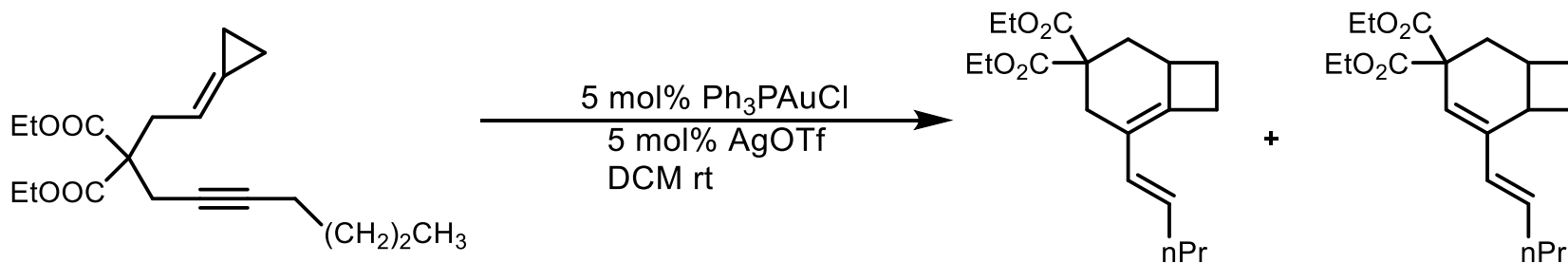
- ▶ The general model of the system was a carbocation next to the strained ring.



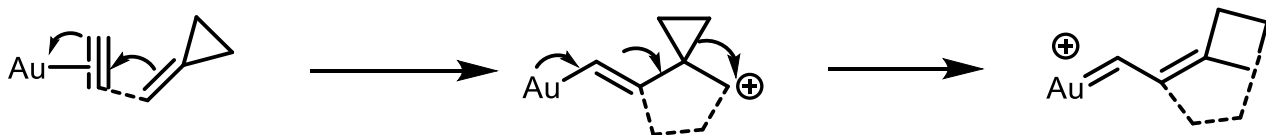
- ▶ Work of Toste in 2008



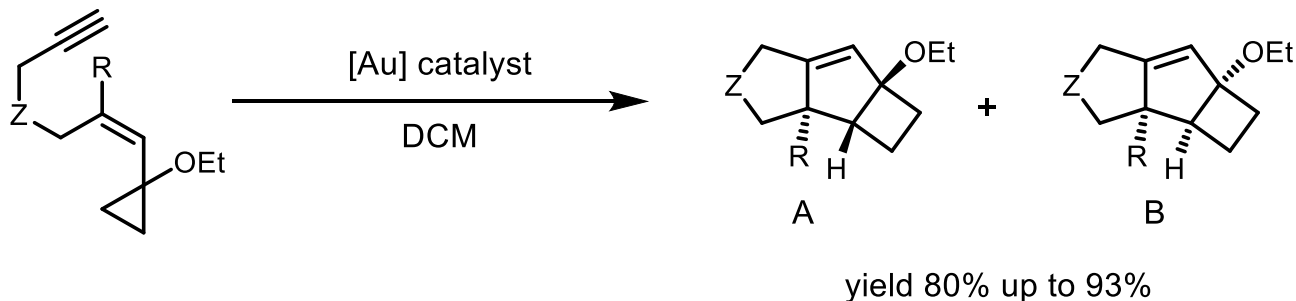
Application:



Mechanism:

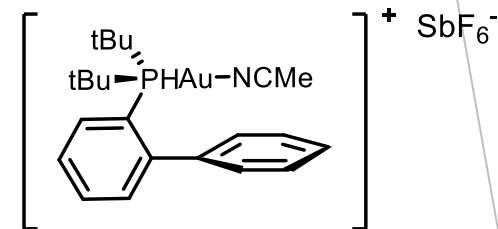


- ▶ Another carbocation intermediate generated from the gold catalyzed cycloisomerization reactions (Echavarren 2006)



Au catalyst:

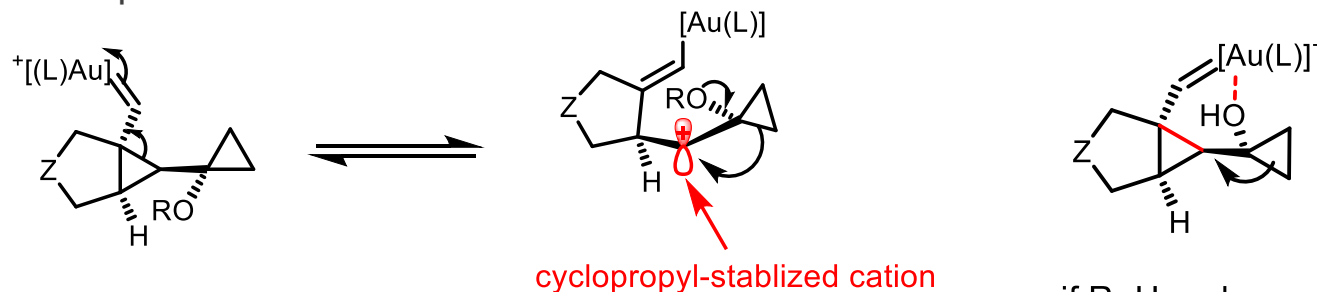
1. favor both product



AuCl favor for the formation of product A (> 12:1 ratio)

Conditions: 3% to 5% mol H<sub>2</sub>O and cationic catalyst significantly speed up the reaction.

- ▶ Mechanism: Cyclopropyl-stabilized cation form the initial cycloisomerization. Then followed by the ring expansion.



only the bond trans to the red bond can migrate?

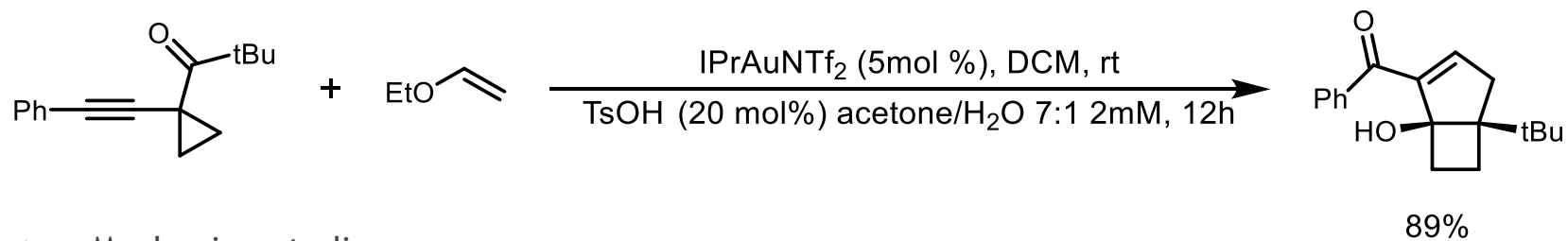
concerted mechanism  
preferred with AuCl as catalyst

stepwise mechanism  
preferred with cationic gold catalyst

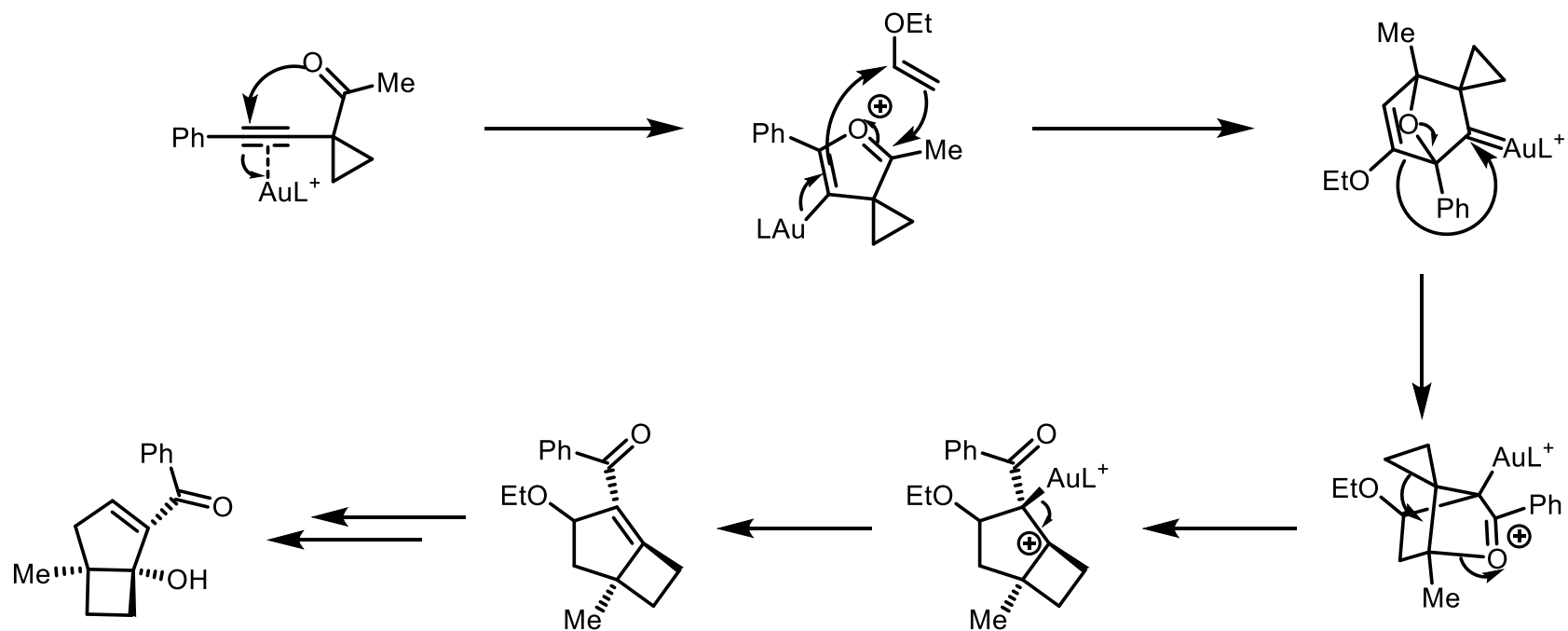
if R=H and somehow we can have a hydrogen bond formed with the gold catalyst, the OR will be locked as the same side with the gold catalyst

what may happen if we want to selective migrate the group on the cyclopropane ring?

► (Liming Zhang 2008) (Similar system with the 1,4 dipole system)



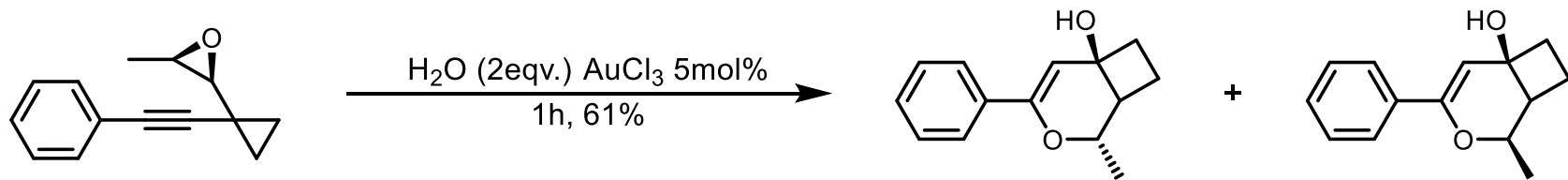
► Mechanism studies:



Actually a stepwise process with a carbocation

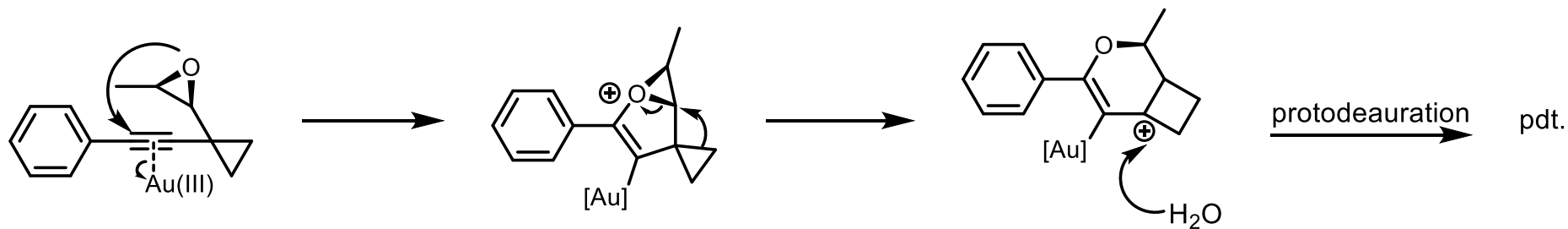
# The epoxy-ring generates the carbocation

- ▶ Work of Rai-Shung Liu in 2010.

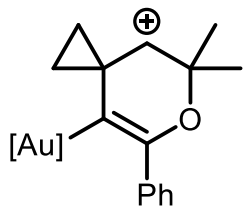


circa 90% yield and dr > 10:1

- ▶ Mechanism studies:



- ▶ For chiral enriched substrates, the loss of the ee value is observed and can be attributed to the generation of the dimethyl-stabilized carbocation.



dimethyl-stabilized carbocation

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- ▶ The heterocycle system

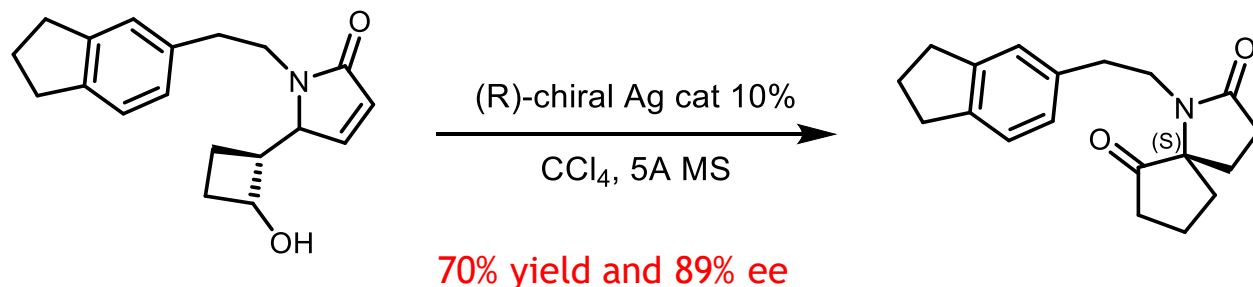
## ▶ Conclusion

The electron deficient conjugation system was very similar to the carbocation system and it was actually a remote carbocation from the ring and connected to the ring with the conjugate system. In this class of reactions, the gold catalyst usually present a dual activation model by acting as the Lewis acid to activate the conjugate system as well as a initiation tool for the expansion of the strained rings. This chemistry was extensively studied by Professor Yongqiang Tu from China and Professor Seunghoon Shin from South Korea. Now there might be chance to achieve the asymmetric version via the chiral ligands

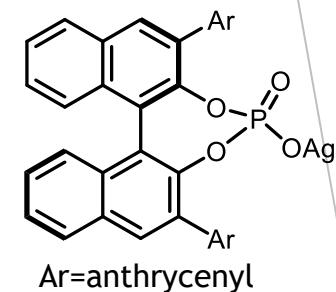
# The early work with chiral silver catalyst

- Synthesis of (-)-Cephalotaxine via tandem semipinacol rearrangement reaction

(Yong-Qiang Tu 2012)

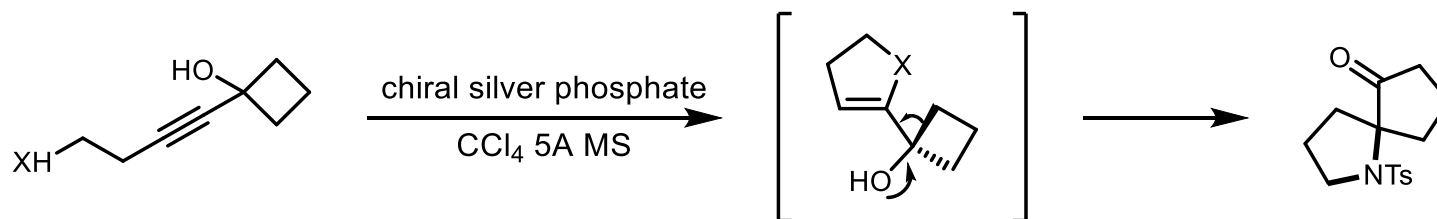


catalyst



- chiral silver catalyst seemed to be able to control the stereochemistry of the heterocyclic ring, the gold catalyst [Ph<sub>3</sub>PAuOTf]/p-TsOH is also tried with 90% yield

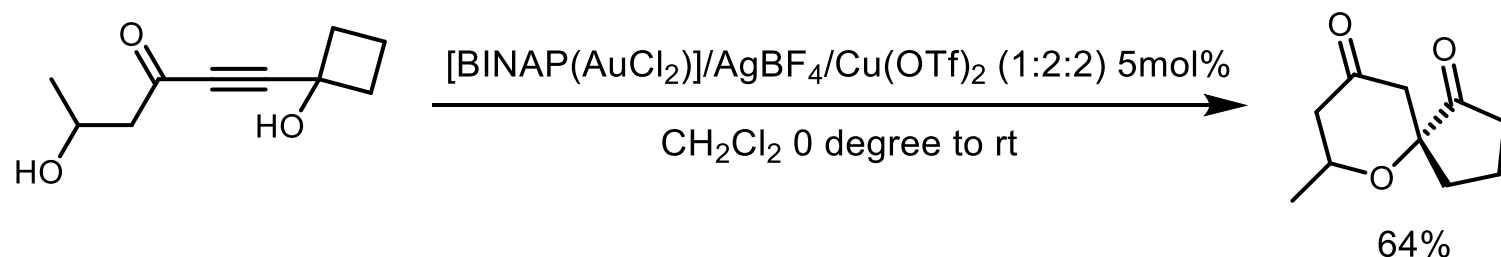
- Mechanism:



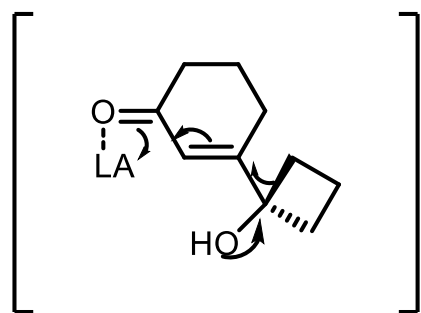
- Drawbacks: The method is only effective for the synthesis of the aza-spiro[4.4]nonane skeleton, and the attempts for the construction of another important type of spiro skeleton 6-aza/oxa-spiro[4.5] decane failed.

# Expanded scope with gold catalyst

- ▶ This work can build six membered rings as well as the five membered rings. (Shuyu-Zhang 2015)



- ▶ The activation mode is similar to the previous work, but it is a dual activation.



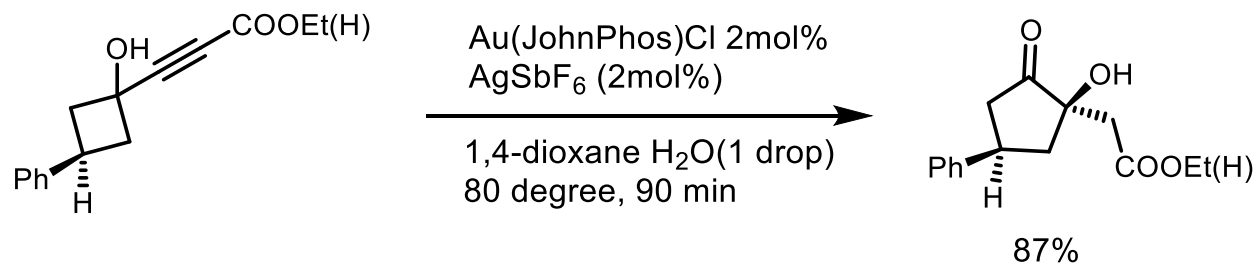
dual activation which described the design that the gold would both act as a Lewis acid as well as the initiator of the ring migration.

- ▶ Special note: this work was not enantioselective, but it should have the potential if the chiral gold catalyst is applied.



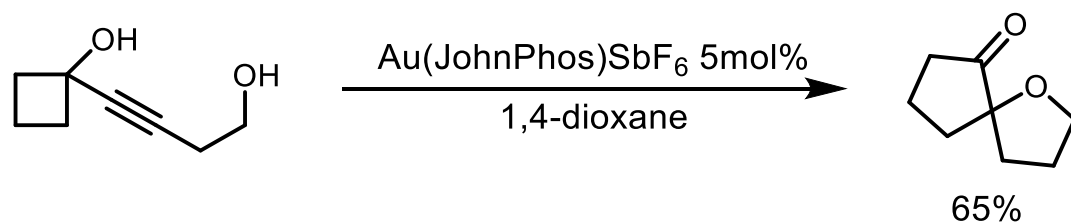
# The positive carbonyl carbon as the EWG

- ▶ Initial work of Seunghoon Shin in 2012 inspired by F. D. Toste

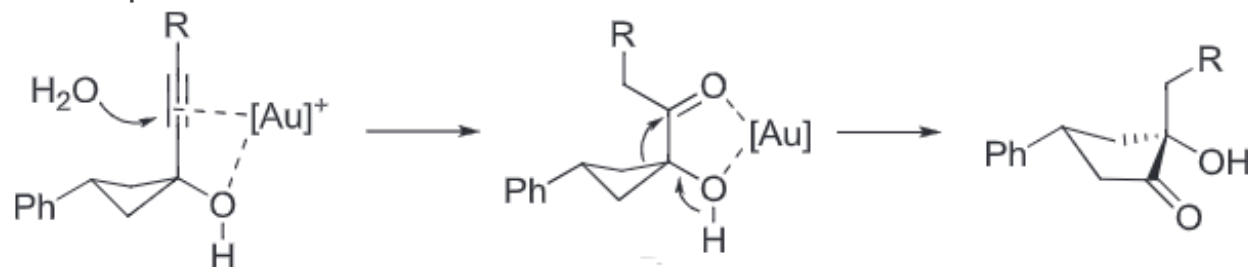


Single diastereomer observed

- ▶ Synthesis of spirocyclic ethers via tandem ring-expansion reaction



- ▶ Important intermediate

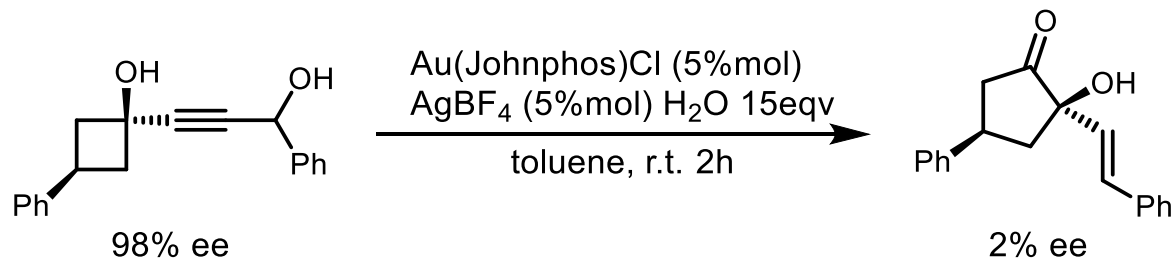


- ▶ The drawbacks of this system

The reaction can only happen with the terminal alkyne and the COOEt substituents.

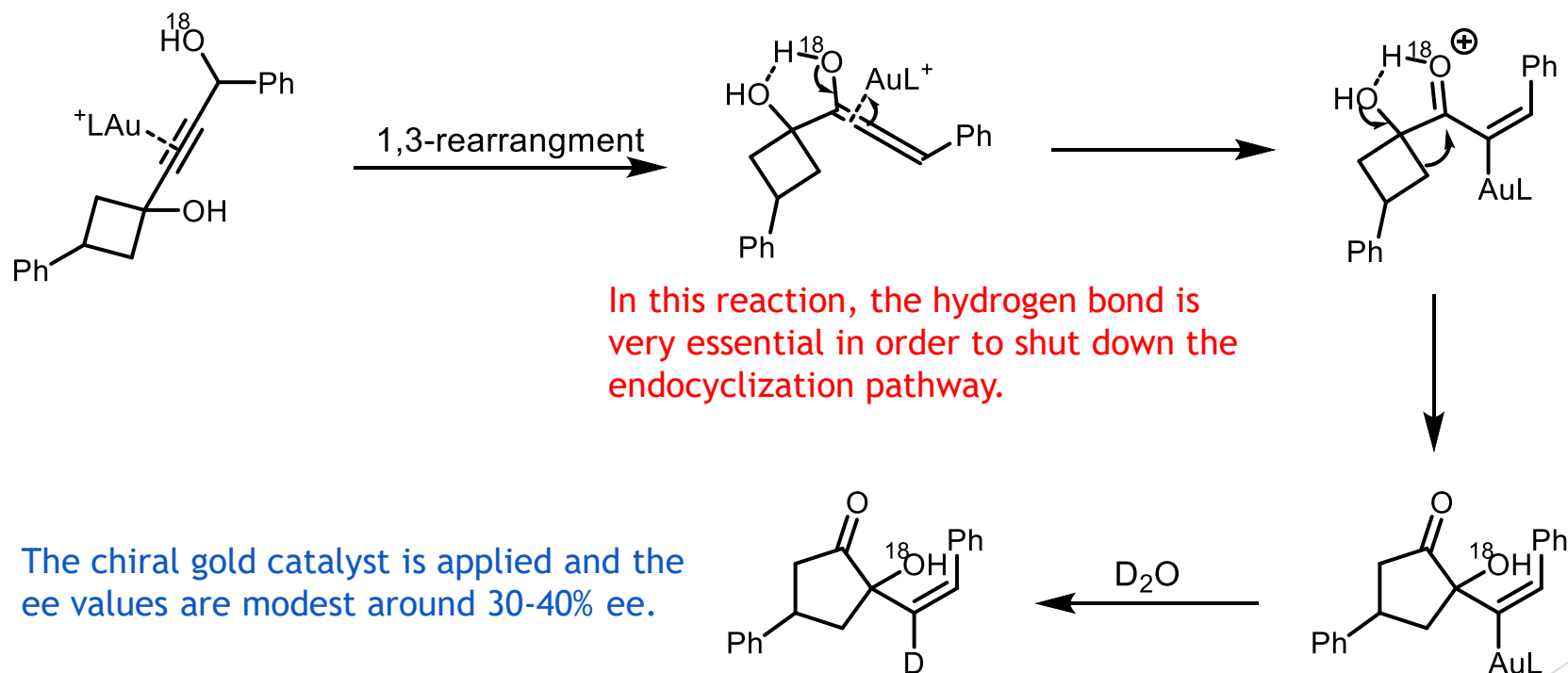
► The continuing work of Seunghoon Shin (2014).

► The regioselective synthesis of hydroxy cyclopentanones.



The loss of chirality indicates the allene intermediate

► Mechanism studies:



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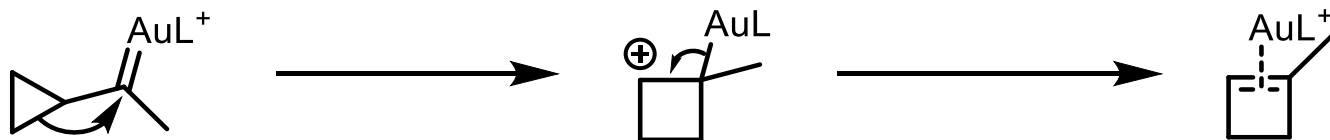
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## ▶ Conclusion

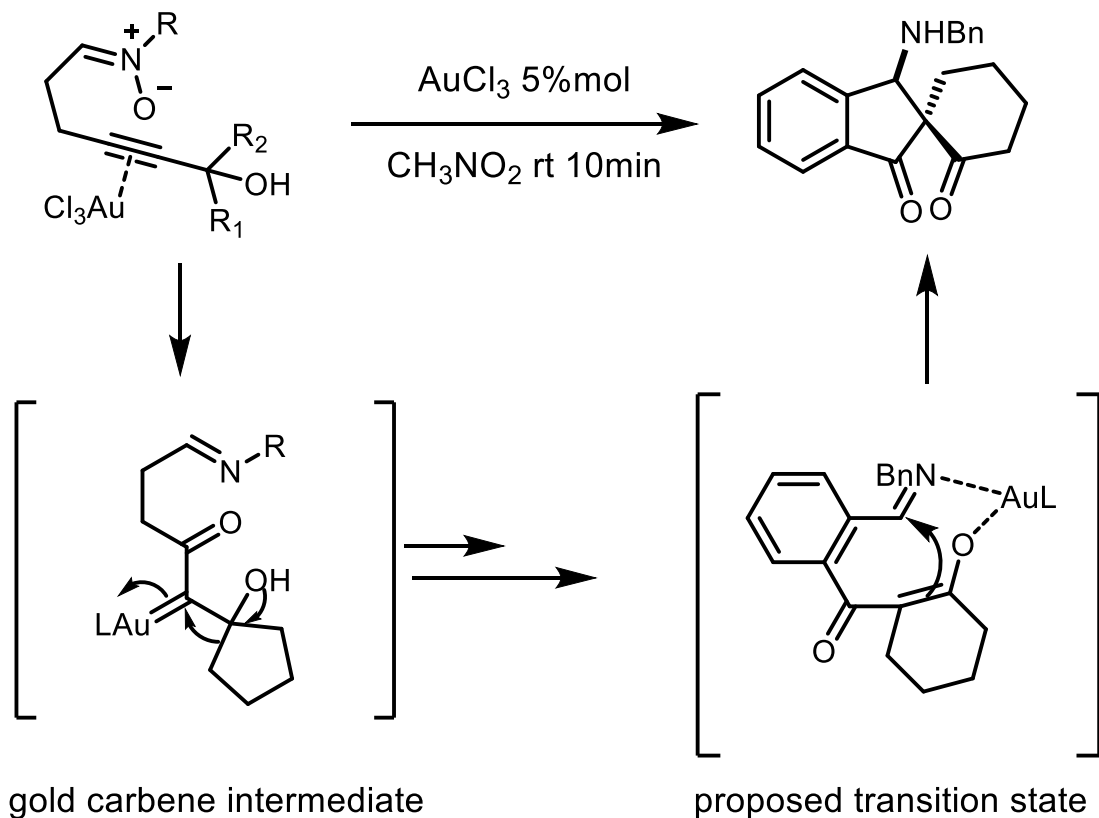
The gold carbene was a relatively new concept compared to classical metal carbenes. In the gold catalyzed ring expansion reactions, the gold carbene can be considered a electron deficient center that can accept a pair of electrons from the highly strained ring. The gold carbene can be easily generated from the cycloisomerization of enyne systems. One key feature of this chemistry was the complicated following up reactions for the gold carbene intermediate, it could readily be eliminated to generate a double bond, or it could slide back to generate carbocations giving this system tremendous opportunities waiting for researchers to exploit.

# The gold carbene intermediate system

- ▶ The model of the gold carbene system



- ▶ The work of Seunghoon Shin

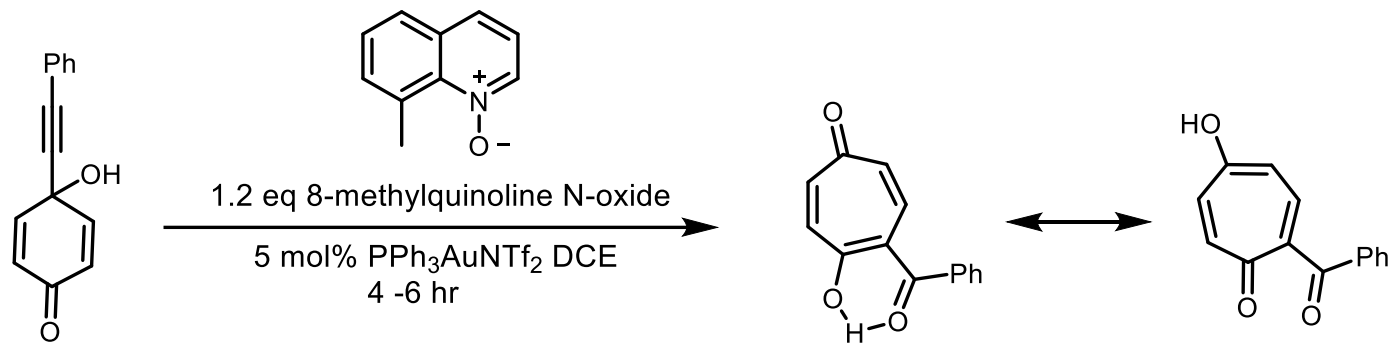


The reaction temperature is rt to 60 degree and the time is around 1h, the substituent of the benzene ring does not have a significant impact on the rate and yield of the reaction, however, **the relative size of the R1 and R2 group decided the migration rate.**

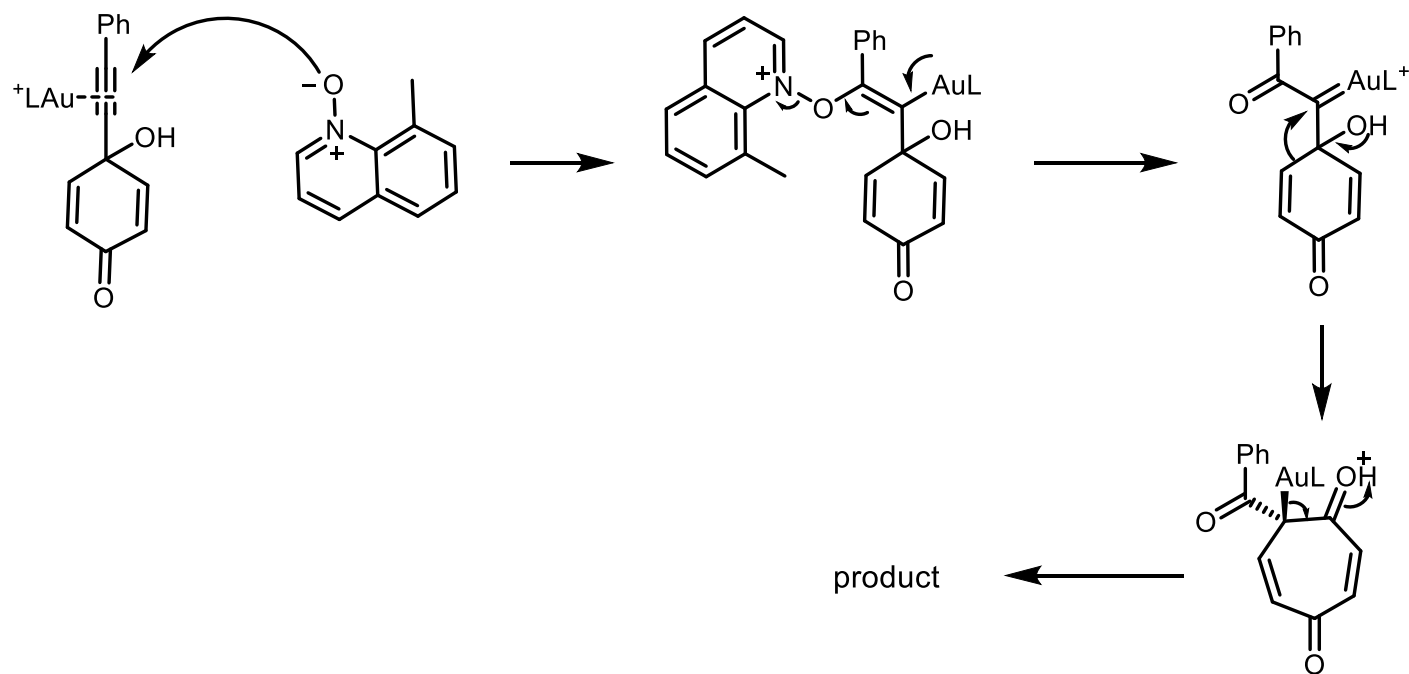
‡ Only observed a single diastereomer of the product in the  $^1\text{H}$  NMR spectrum of the crude mixture (d.r. > 20:1). At the same time, the control of the chirality is predicted to be hard given the planar character of the gold carbene intermediates.

► Work of Yuanhong Liu & Shi Li 2015

Similar activation mode of the reaction with pyridine-N-oxide

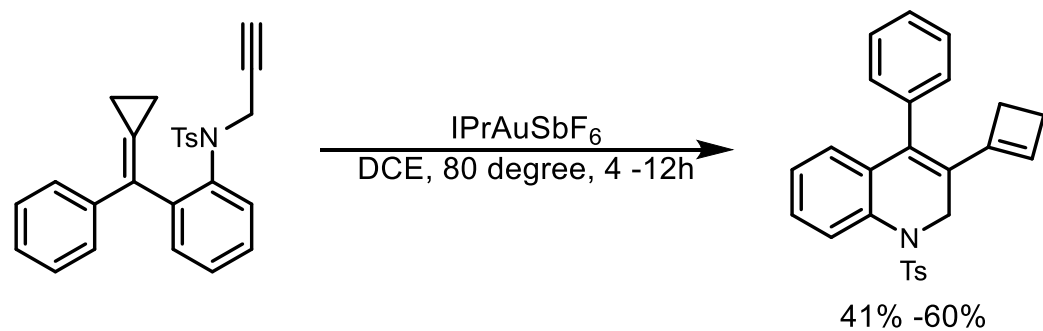


► Mechanism studies:

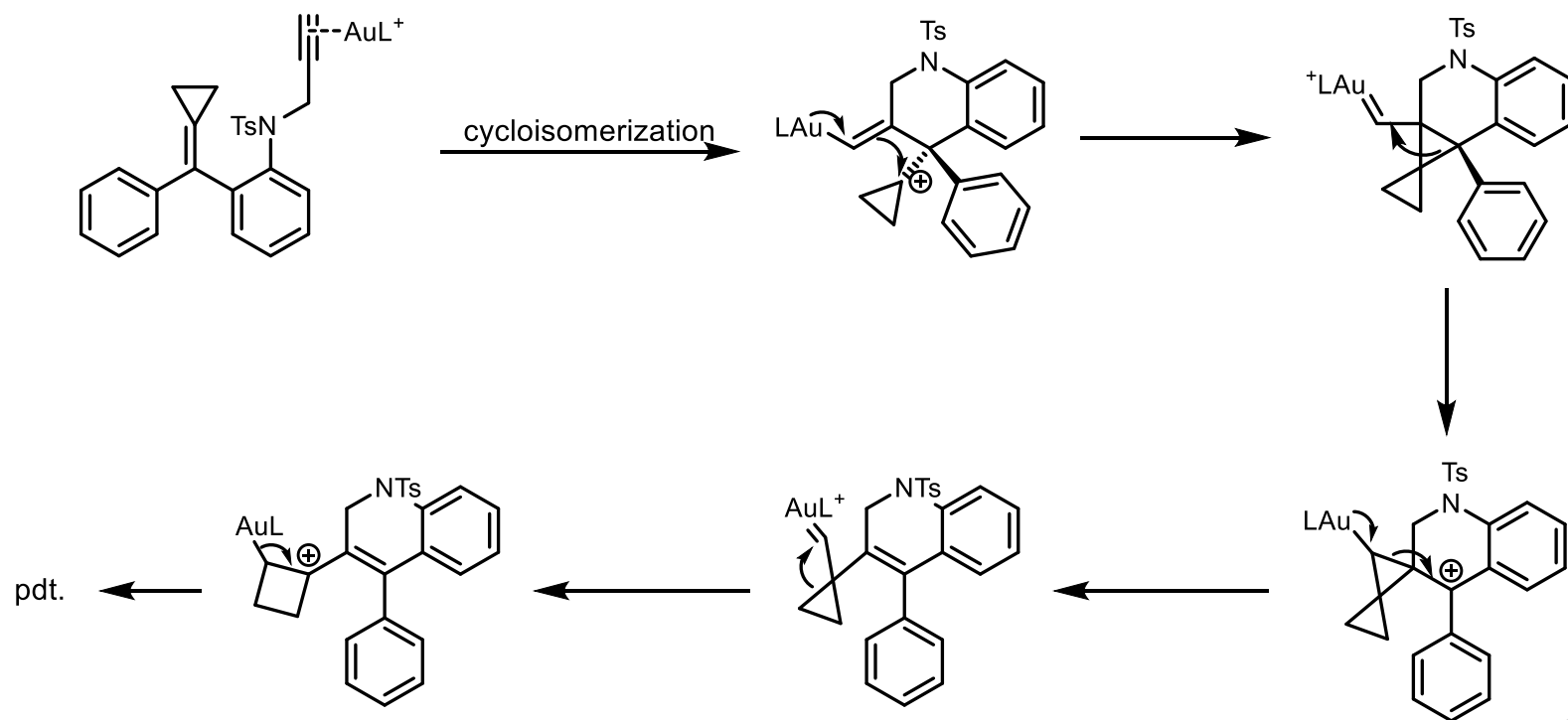


► The work of Shi Min in 2018.

(gold carbene generated by the cycloisomerization reaction)

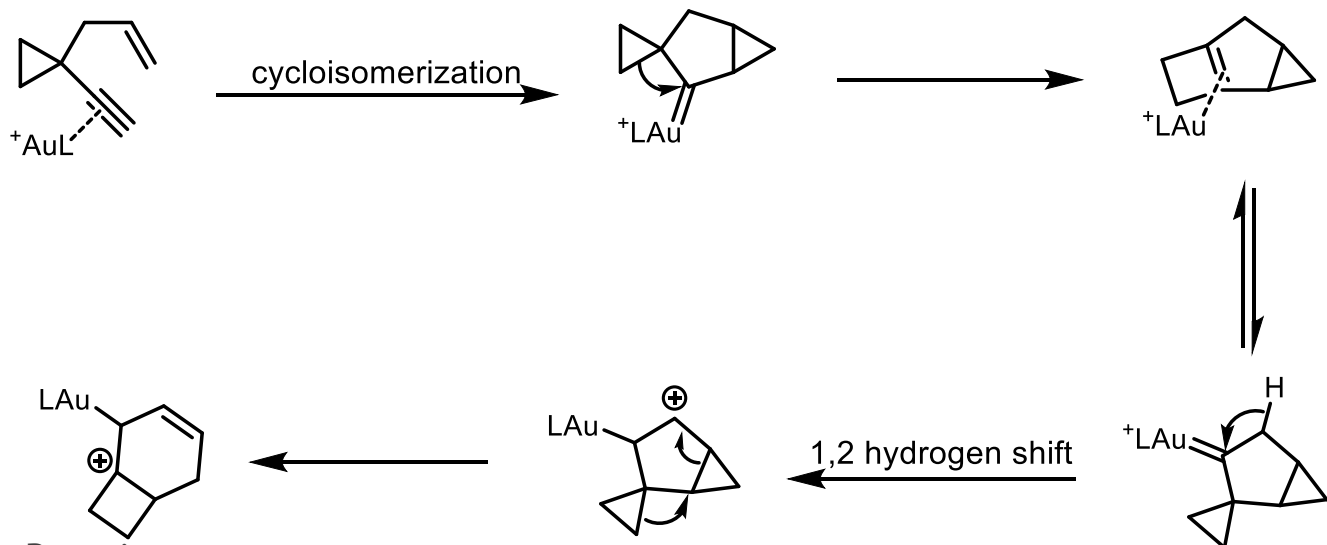


► Mechanism:

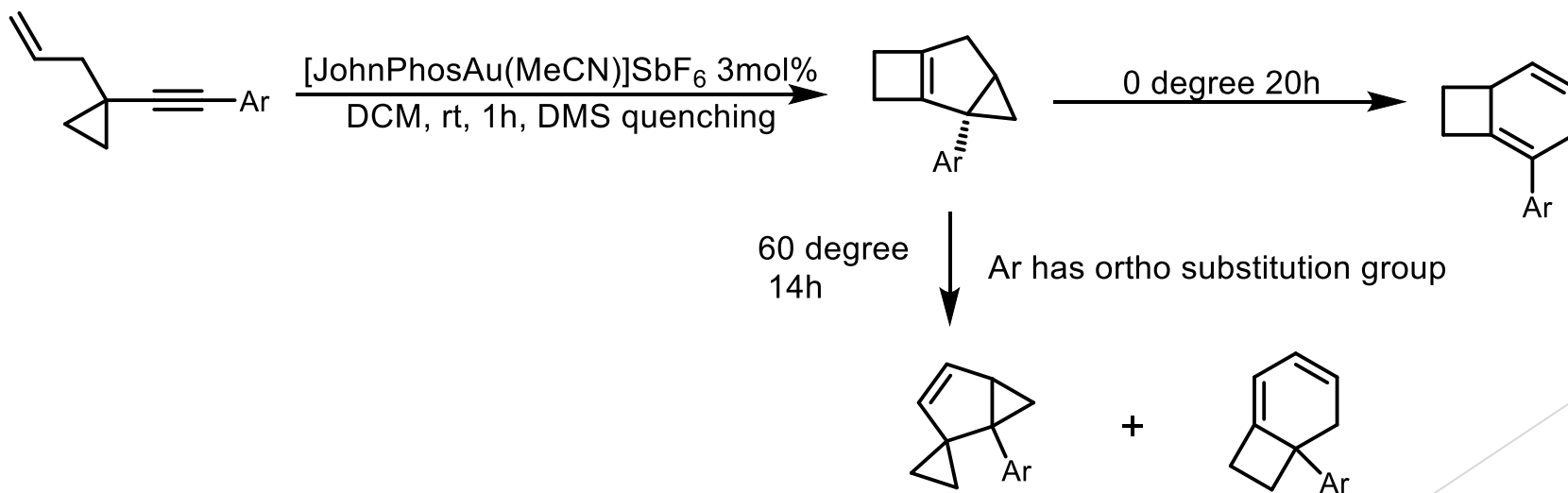


# Complications of gold carbene intermediates

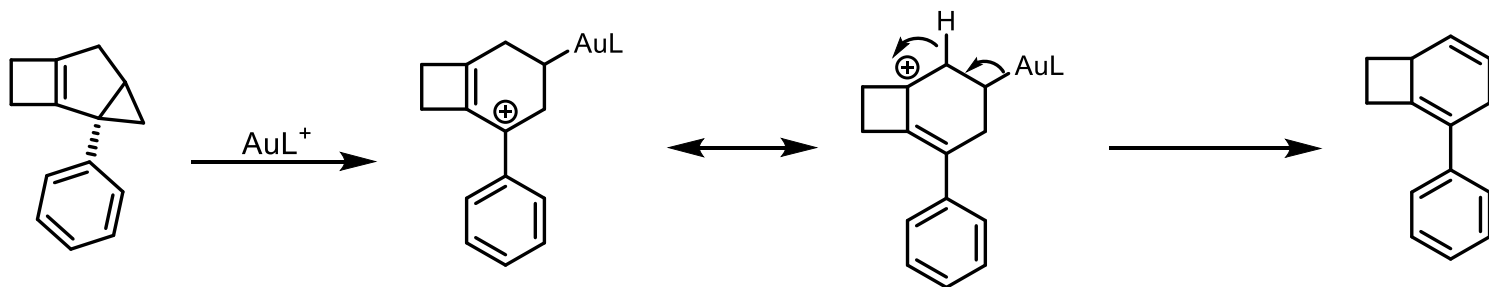
- ▶ The complications of the cyclobutene system as the direct product of gold carbene intermediate via ring expansion. (Work of Shi Min and Tang Xiang-Ying 2016)



- ▶ Reaction scope:



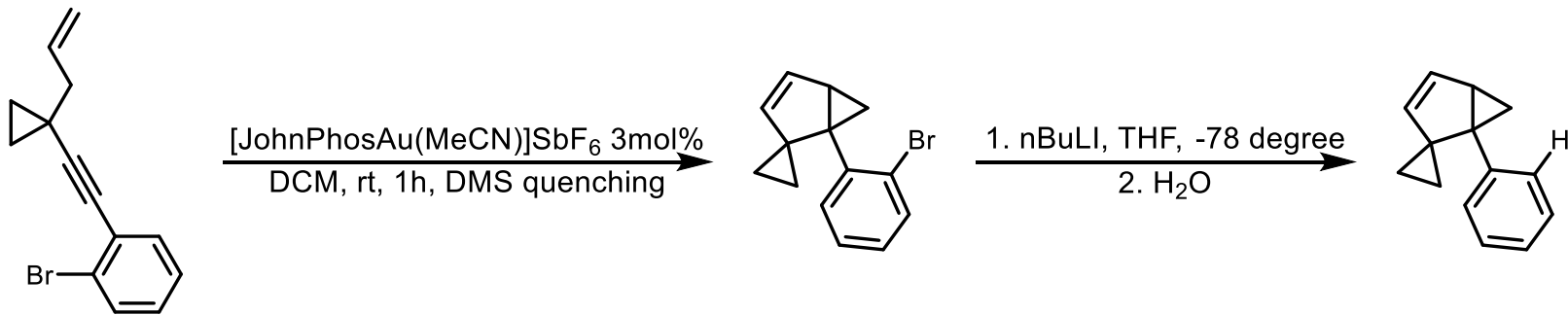
► The ortho-substituent effect.



The carbocation structure is not stable when there is a substituents at the ortho position

► The application of the ortho-substituent effect.

► The removable Br control the reaction outcome.





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## ▶ Part I ring expansion mechanism

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- ▶ The electron deficient conjugation system
- ▶ The gold carbene system

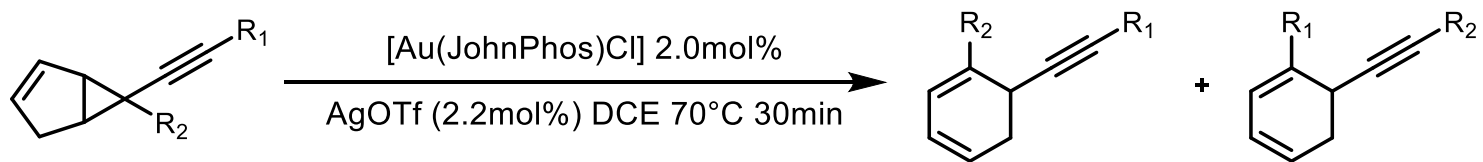
## ▶ Part II ring opening mechanism

- ▶ The bicyclic system
- ▶ The 1,n-dipole system
- ▶ The cyclopropene and its derivative system
- ▶ The heterocycle system

## ▶ Conclusion

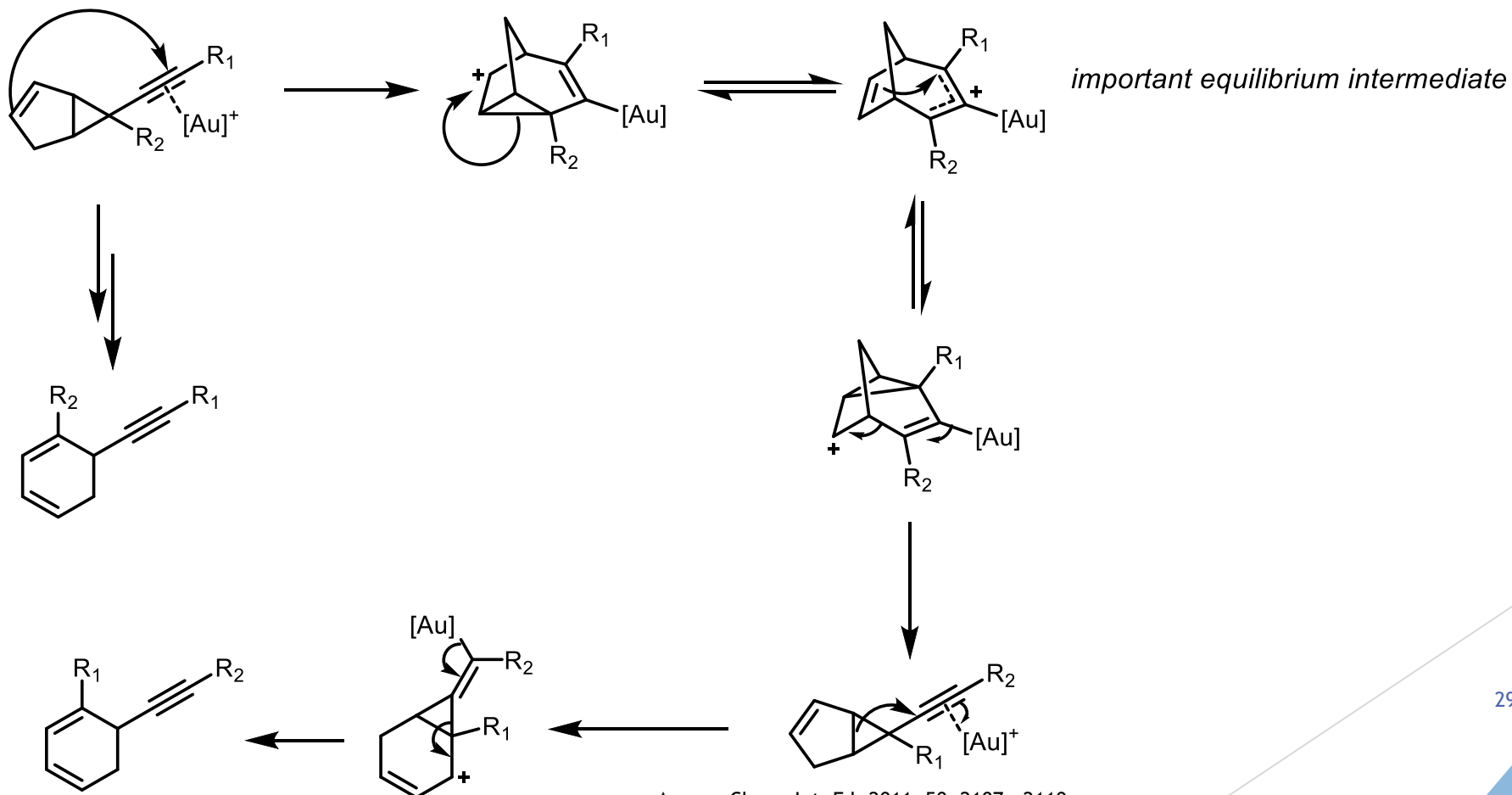
Because the single ring system usually go with the ring expansion system rather than forming the unstablized 1,n-dipoles, the ring opening pathway were rare for cyclic-aplihatic substrates. However, when there was another ring present, the ring opening of one ring will generate a larger ring instead of 1,n-dioples. Thus, the bicyclic system usually go by ring opening pathways and quickly afford the enlarged ring.

► Rearrangement of 1-alkenyl-2-alkynylcyclopropane substrates. (J Barluenga 2011)

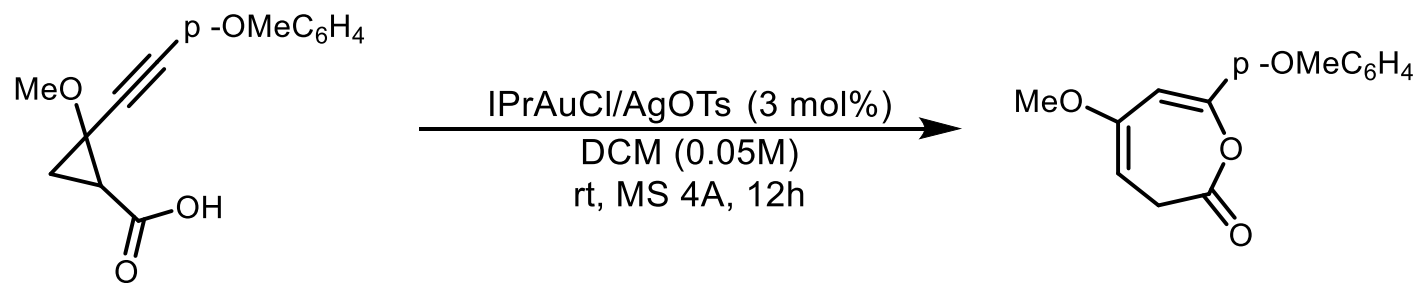


$\text{R}_1 = \text{Ph}, p\text{-ClC}_6\text{H}_4, \text{PMeOC}_6\text{H}_4$  (aromatic)  
 $\text{R}_2 = \text{Ph}, c\text{-Pr}, t\text{Bu}$  (can be aromatic or alkyl)

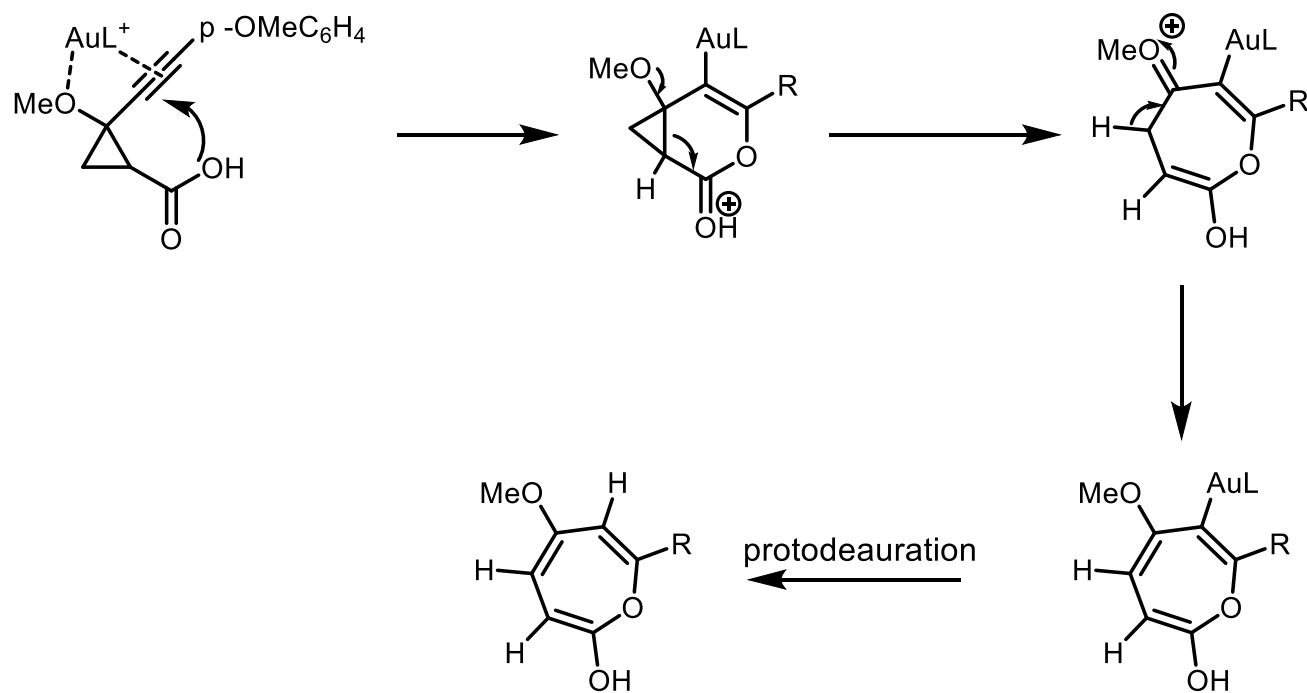
► Mechanism studies:



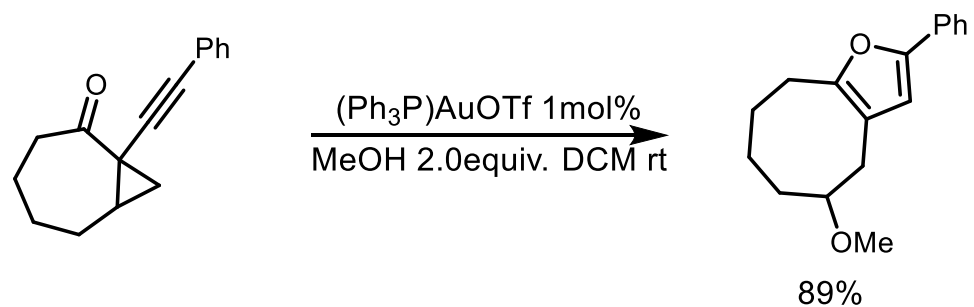
► The work of Enrique Aguilar in 2013.



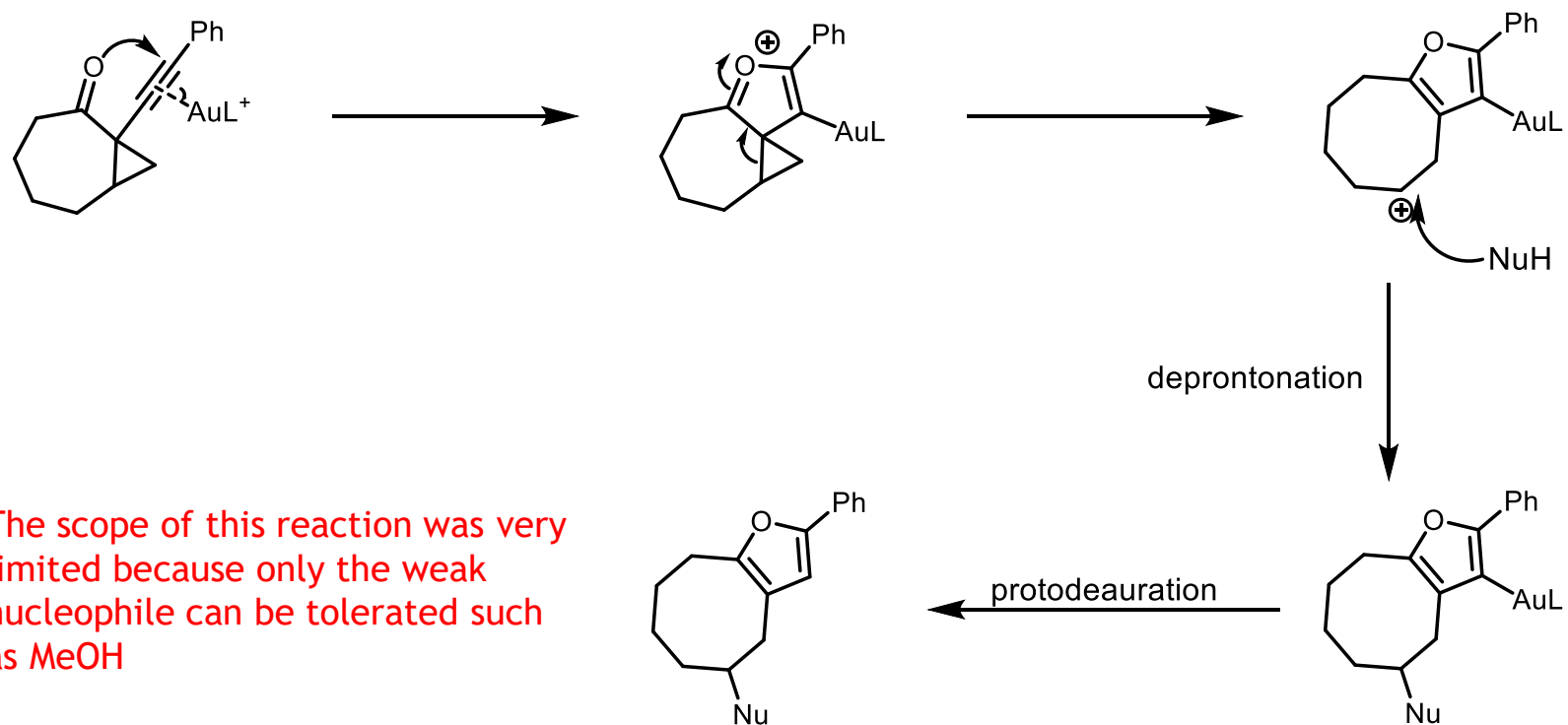
► Mechanism studies:



► The ring opening process in the generation of furan. (Schmalz 2006)



► Mechanism studies:



The scope of this reaction was very limited because only the weak nucleophile can be tolerated such as MeOH

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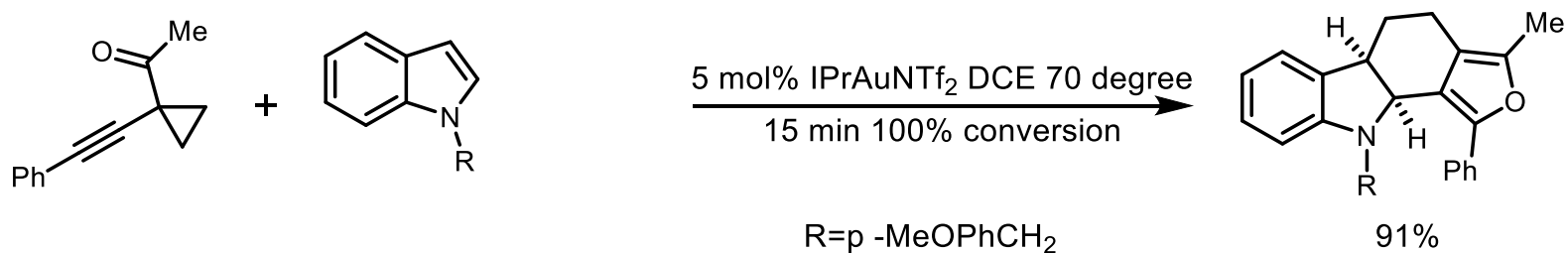
## ▶ Conclusion

As mentioned before, the 1,n-dipole system was not a very stable intermediate in the reaction. However, with the specially designed electron withdrawing ligands placed onto the gold catalyst, the gold catalyst can serve as a stabilizing group for the carbonanion. Also, due to the fact that the protodeauration process of sp<sup>3</sup> C-H bond was problematic, the 1,n-dipole usually cannot quenched by proton, the addition with other dipole species such as indole and cycloheptanones can resolve the problem. This chemistry was relatively less studied. However, Professor Liming Zhang from UC Santa Barbara has done some pioneer work in this field.

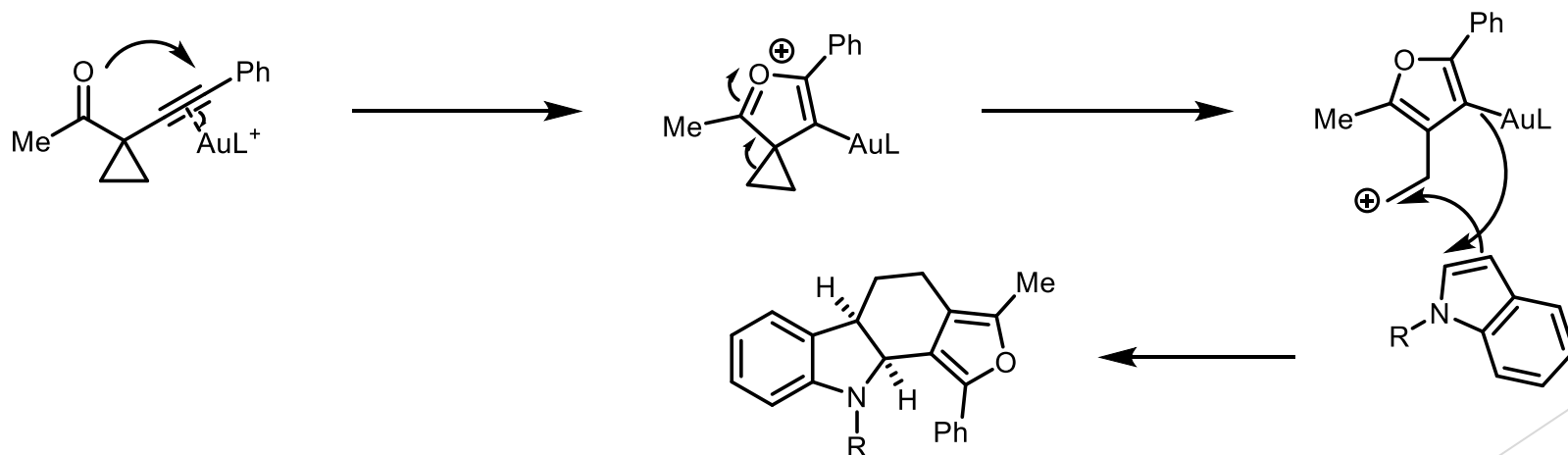
# The stabilized 1,n-dipole system

- ▶ The general mode of 1,n-dipole system

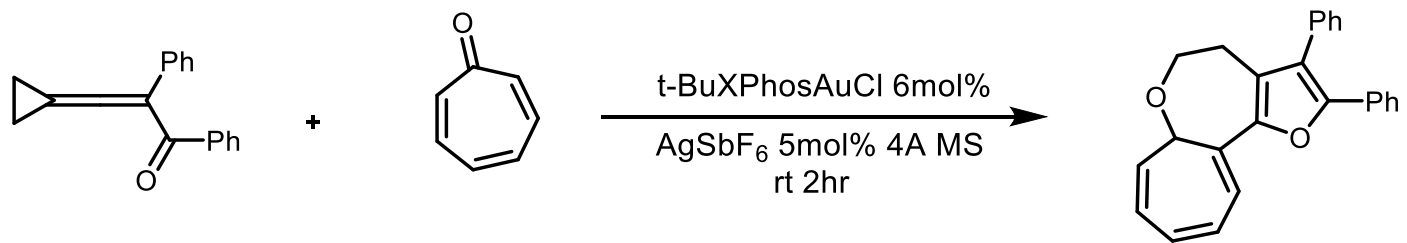
- ▶ The work of Liming Zhang in 2008



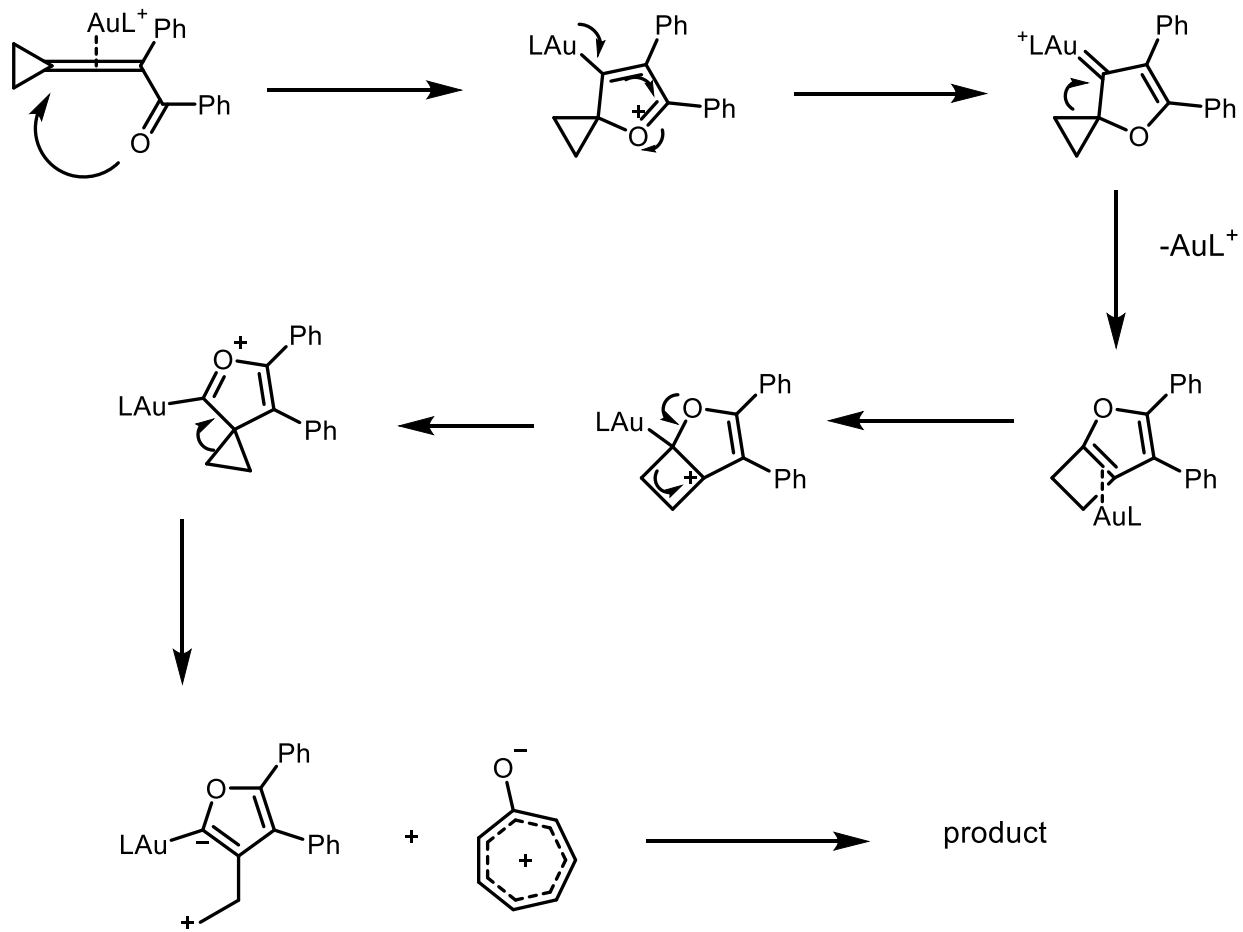
- ▶ Mechanism studies:



► The work of Reng Hongjun in 2020.



► Mechanism studies:



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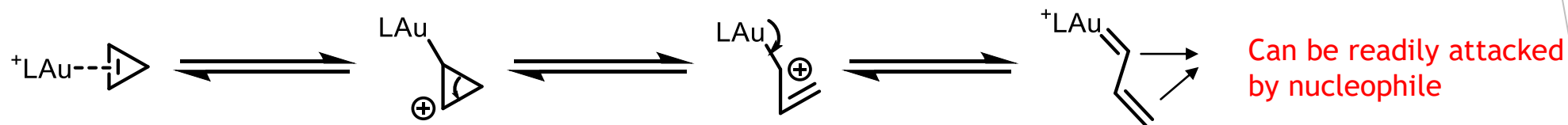
- ▶ Introduction and background information
- ▶ Part I ring expansion mechanism
  - ▶ The gold-activated unsaturated bond system
  - ▶ The carbocation system
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  - ▶ The bicyclic system
  - ▶ The 1,n-dipole system
  - ▶ The cyclopropene and its derivative system
  - ▶ The heterocycle system
- ▶ Conclusion

The cyclopropene can first use its double bond to act as a neutral ligand to coordinate to the gold catalyst. Then, under the activation of gold, the equilibrium of its opened ring form will be established and the ring opened form contained a electron deficient conjugate system as well as a gold carbene that were ready for incoming nucleophilic attack and to go through a series of followed up reactions. In this field, Professor Min Shi from Shanghai Institute of Organic Chemistry and Professor Liming Zhang from UC Santa Barbara played significant roles using the indole as a mild nucleophile.

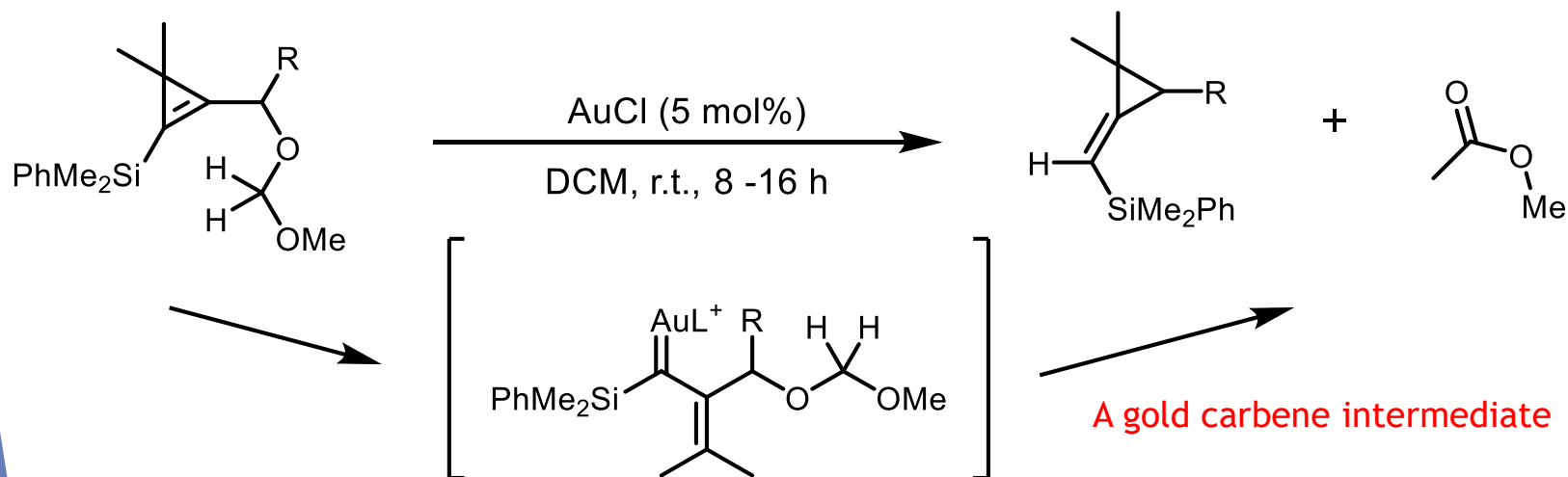


# The cyclopropene system

- ▶ Model of the cyclopropene system.

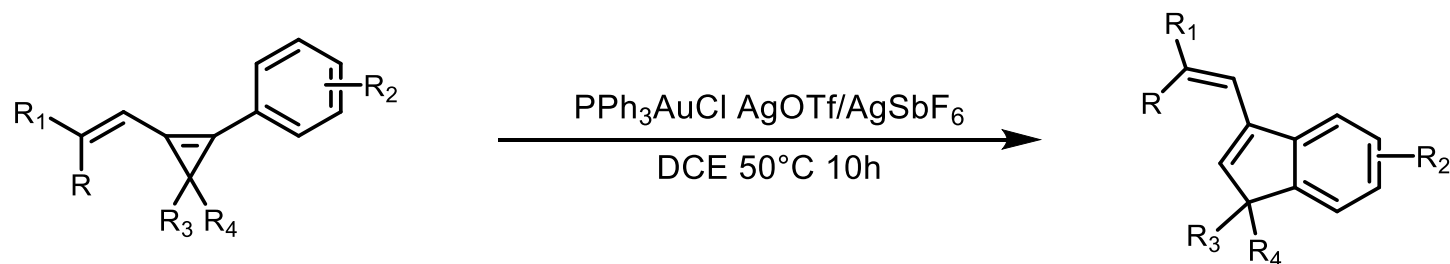


- ▶ The simple dissociation system (J. Cossy 2016)

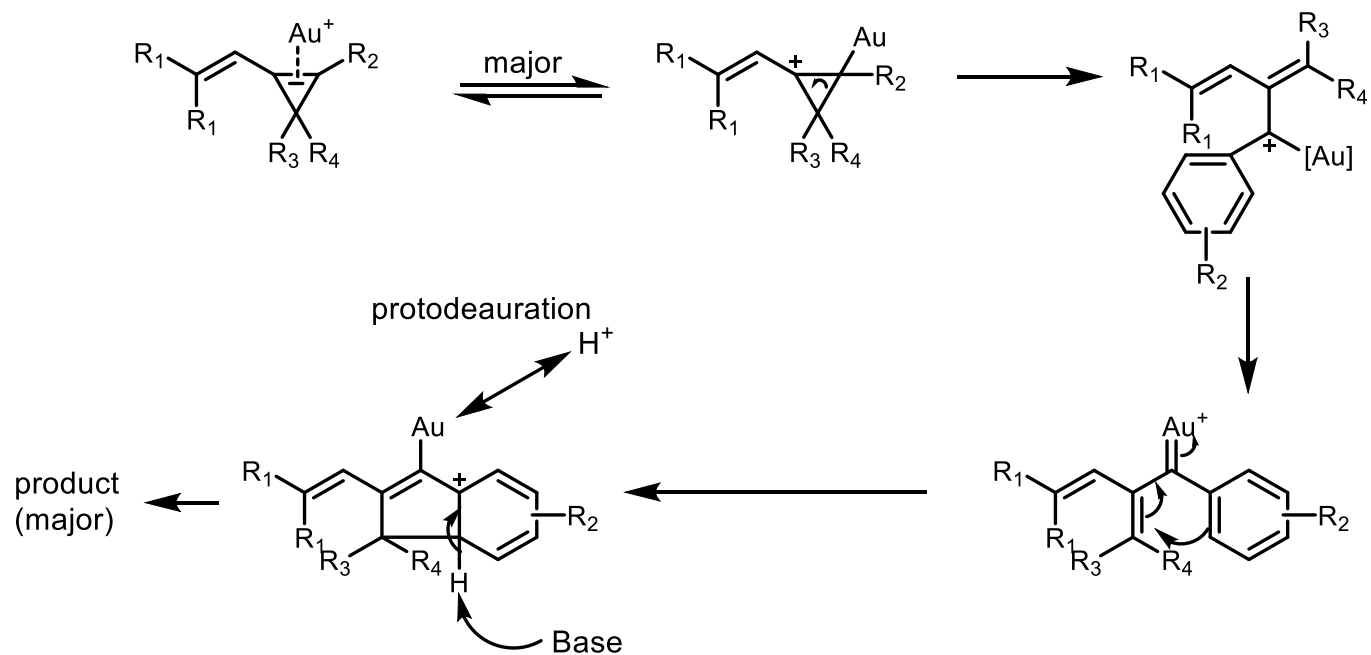


# The opening of cyclopropane ring

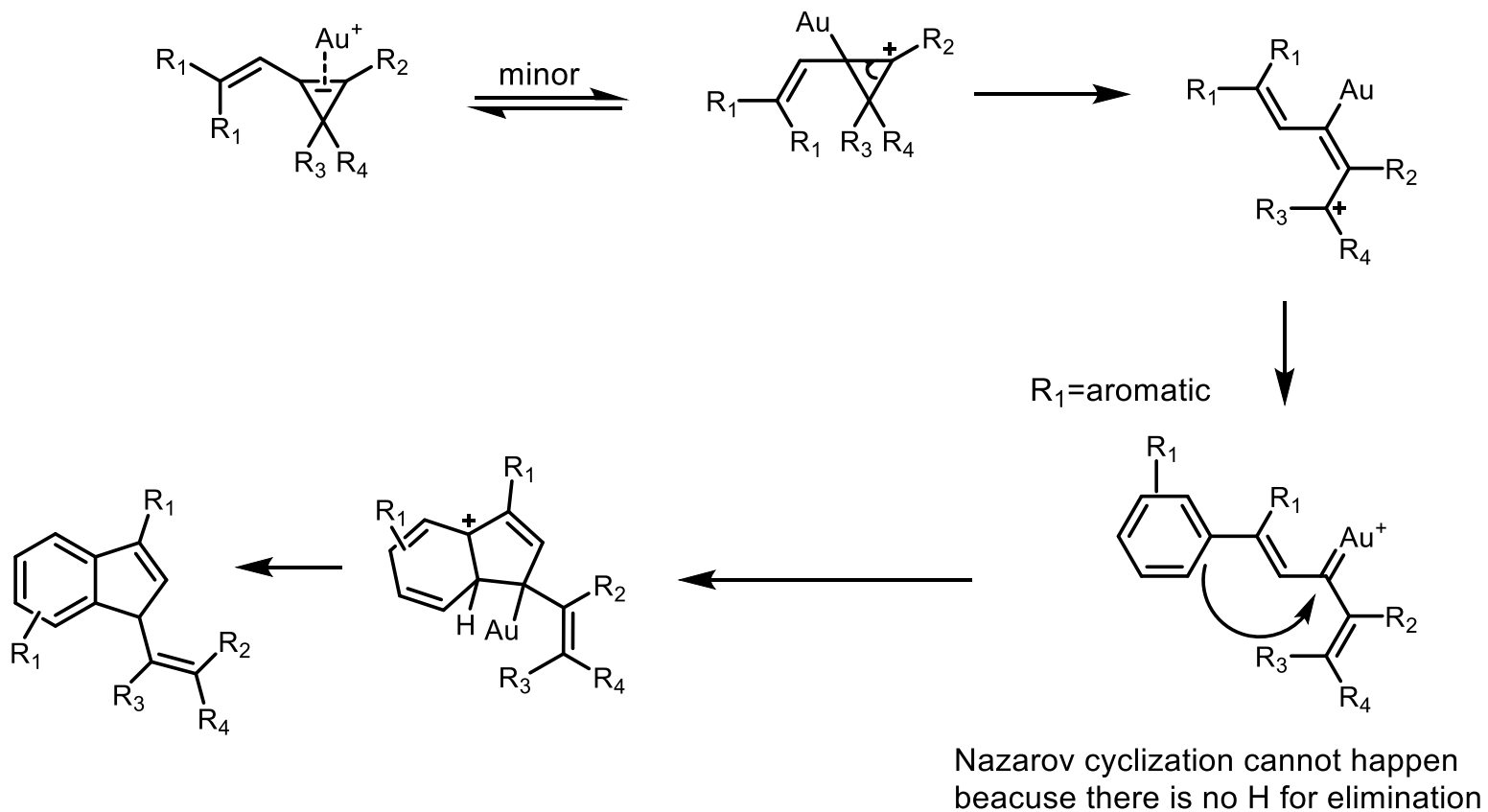
- ▶ Another opening of the ring followed by the Nazarov cyclization reaction.
- ▶ Work of Shi Min in 2008.



- ▶ Mechanism studies:



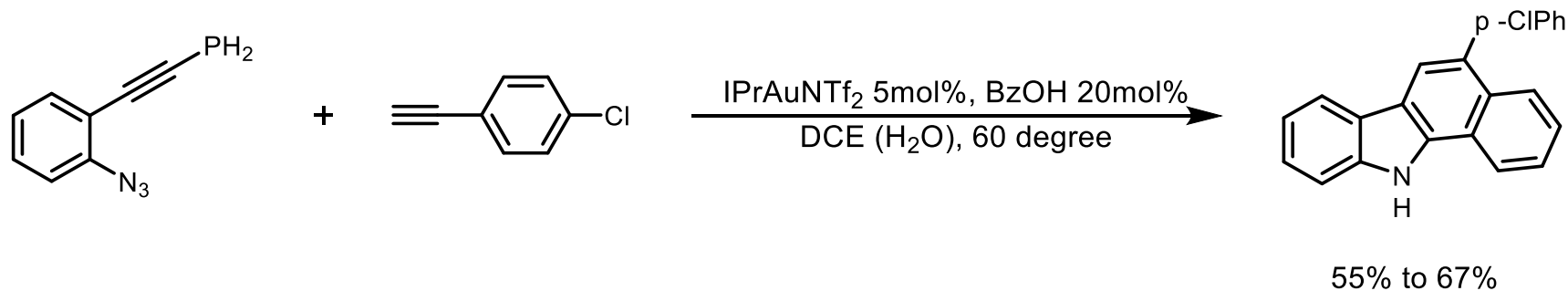
- ▶ An alternative side of the ring opening can also occur.



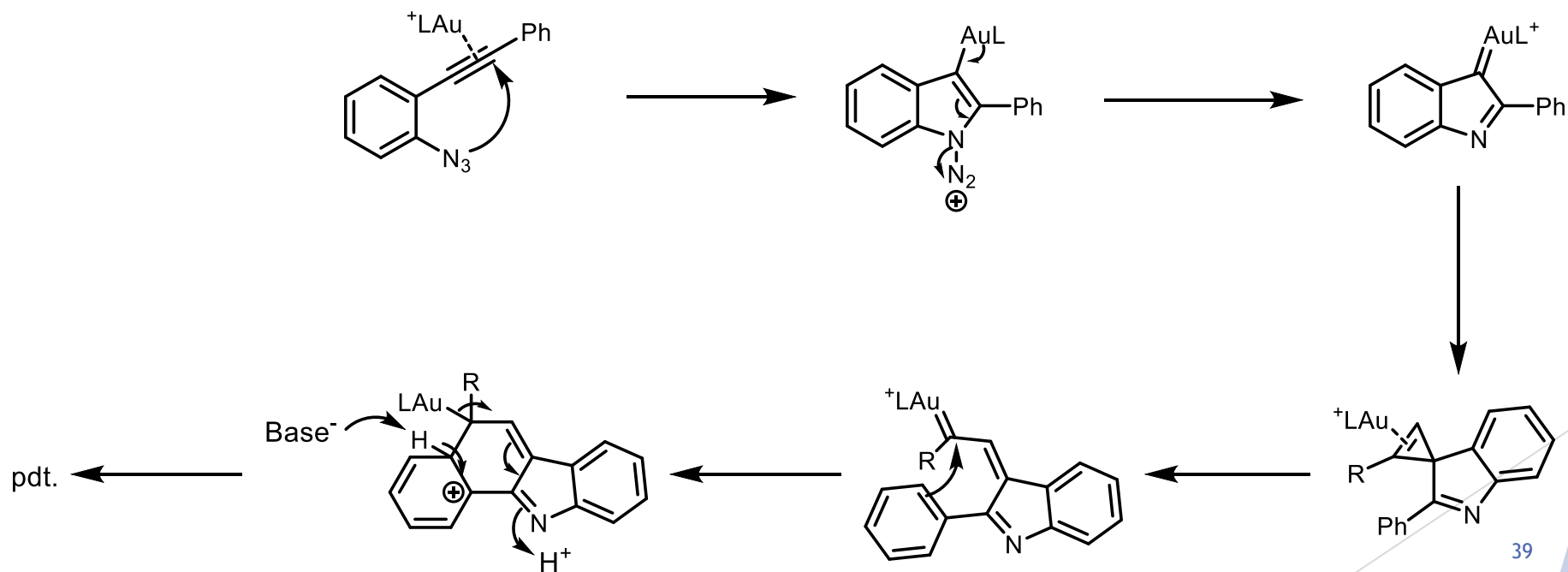
When the base is a **weak base** such as MeOH, Et<sub>3</sub>N, and CH<sub>3</sub>CO<sub>2</sub>H there are mixed products when the base is DBU 100% major observed and when **the mole percentage of DBU decrease from 50% to 20%** the minor product is observed again.

# Cyclopropane can be generated in situ

- ▶ Work of Gong-Liu Zhu and Liming Zhang in 2016.



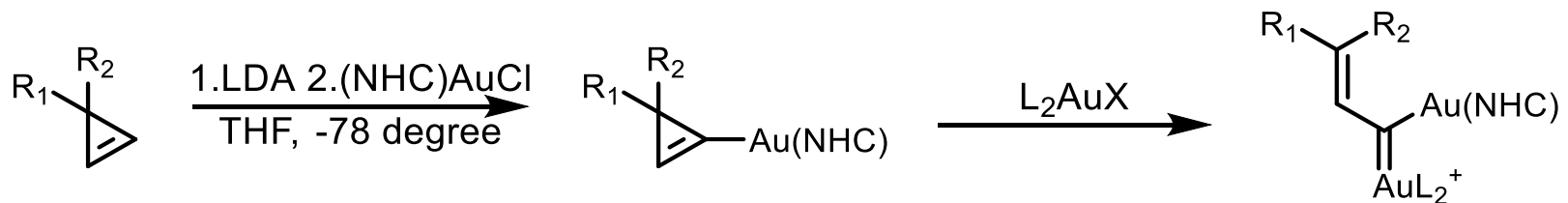
- ▶ Mechanism studies:



Proton tautomerization

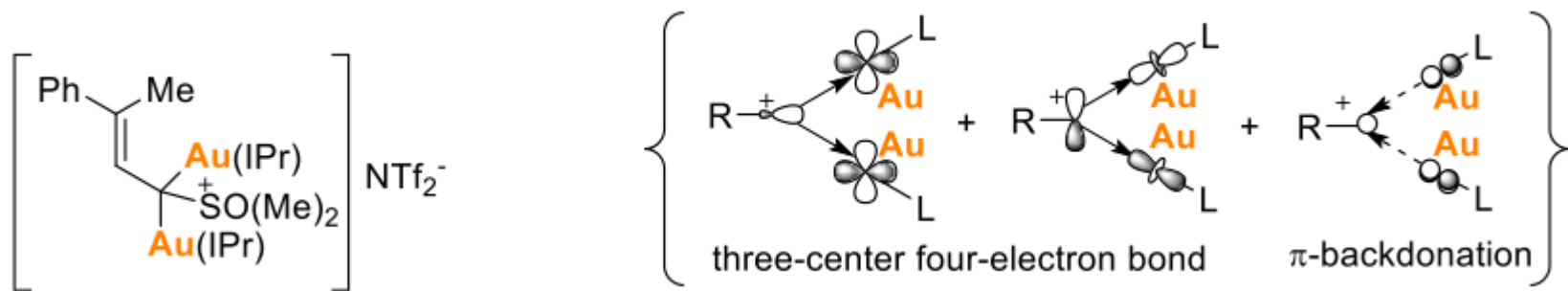
# Rare NHC Gold(I) Complexes

- ▶ General model of the NHC gold(I) complex.



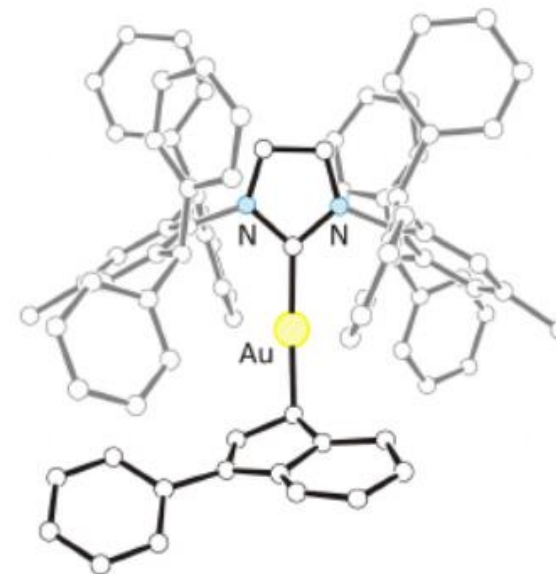
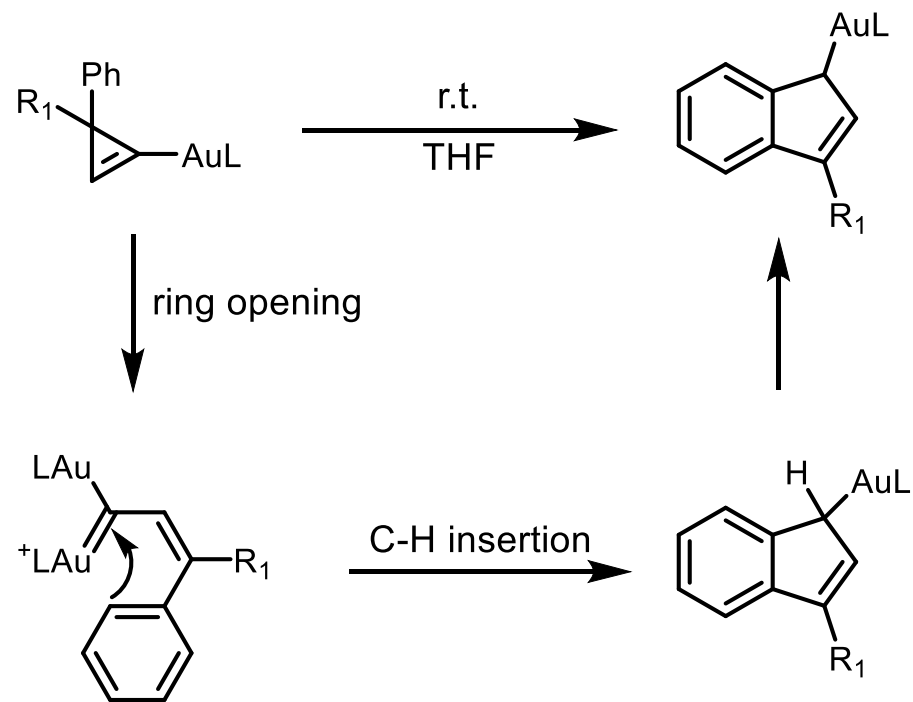
Note: the NHC can be *i*Pr for example.

- ▶ The DFT calculations for the bonding pictures of NHC gold(I) complex.



The gold catalyst served as a dual activation forming the gold carbene intermediate and the terminal gold complexes

- ▶ The pioneer work of Professor Stephen K. Hashmi
- ▶ R<sub>1</sub> can be methyl group or phenyl group and yield was between 70% to 99%.



The solid structure of the NHC gold carbene intermediate

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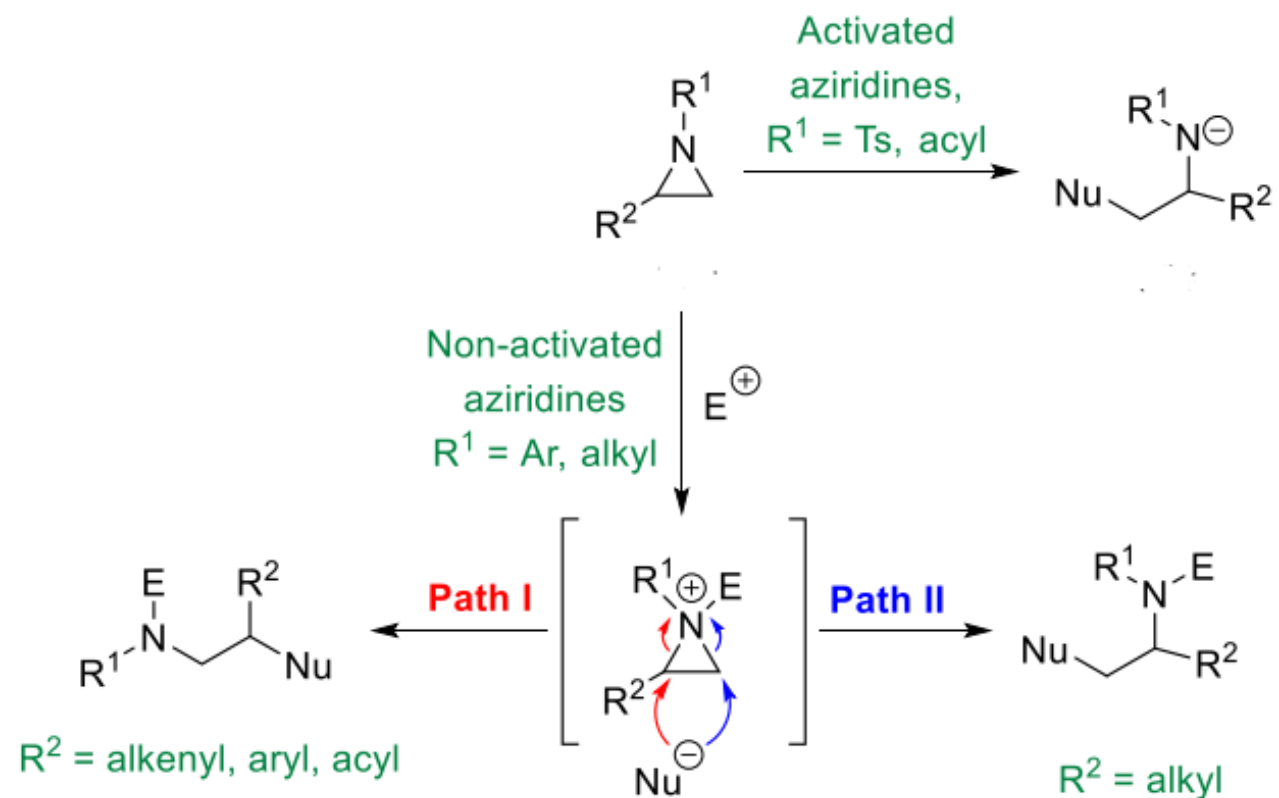
- ▶ The bicyclic system
- ▶ The 1,n-dipole system
- ▶ The cyclopropene and its derivative system
- ▶ The heterocycle system

## ▶ Conclusion

The heterocycles systems usually refer to the aziridines and epoxides. Because the heterocycles were already polarized, and usually heteroatoms such as nitrogen or oxygen that were more electronegative than carbon, so that they were very good at stabilizing the negative charge after the ring opening. Therefore, this kind of systems were readily attacked by nucleophiles and the gold catalyst oftentimes just initiate the ring opening process and then become a bystander in the following up conversions.

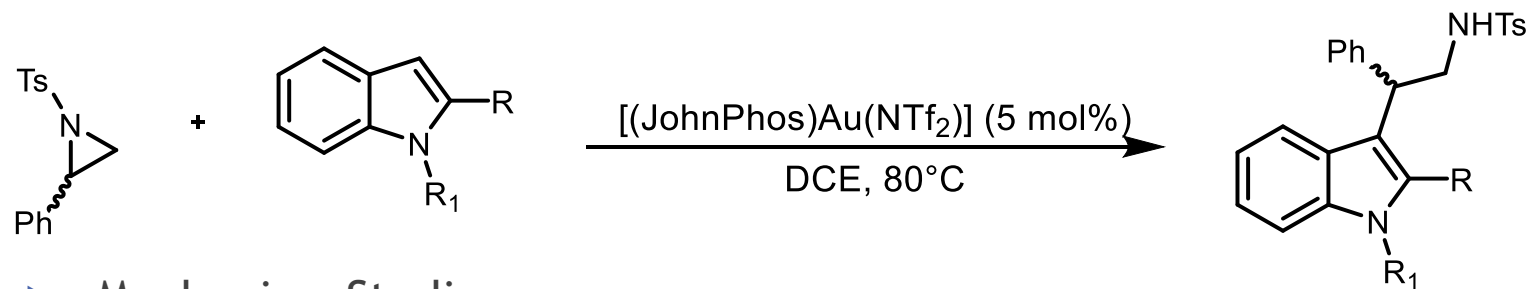
# The heterocycle is already polarized

- ▶ The general model for the aziridines.

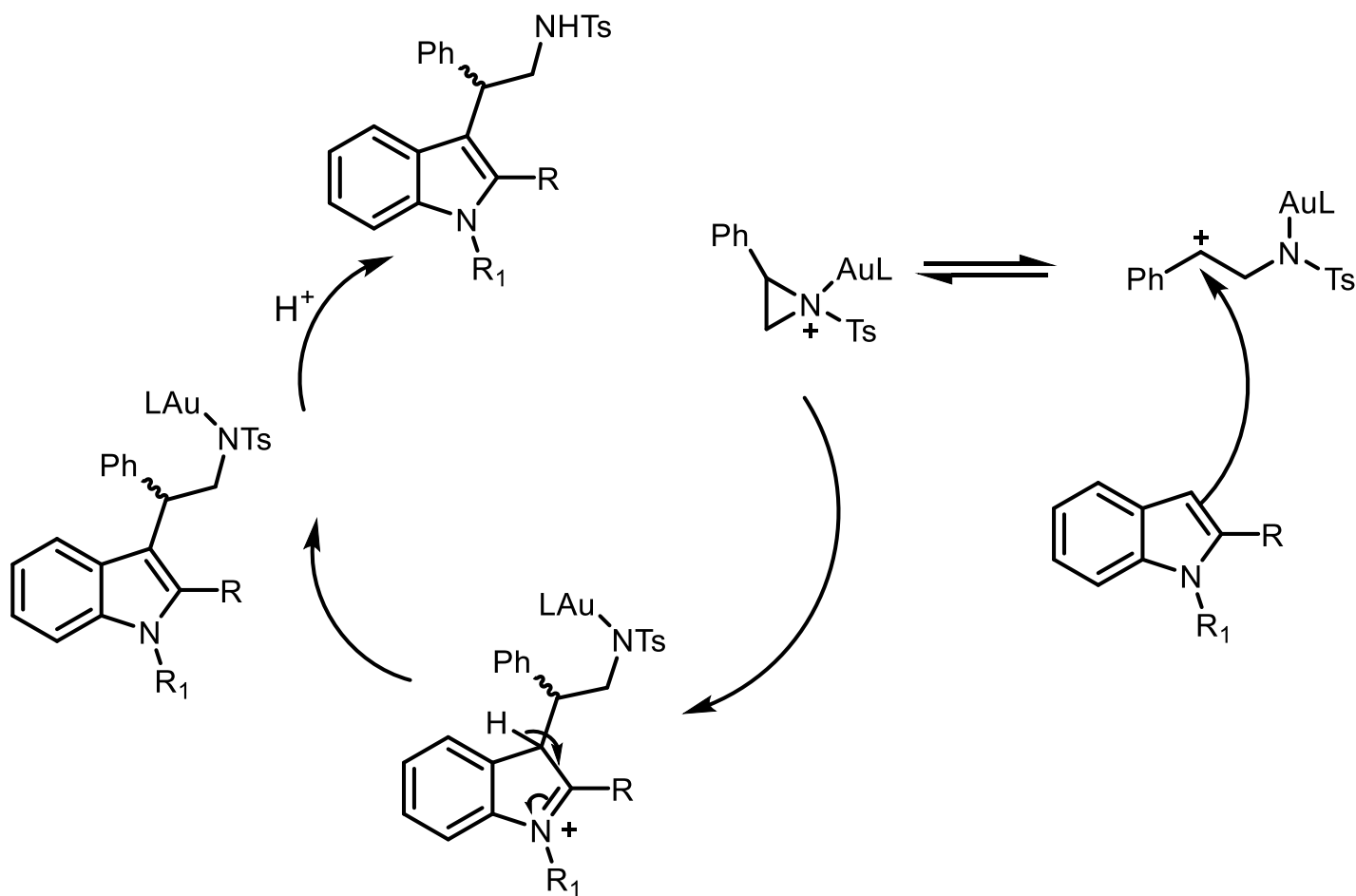




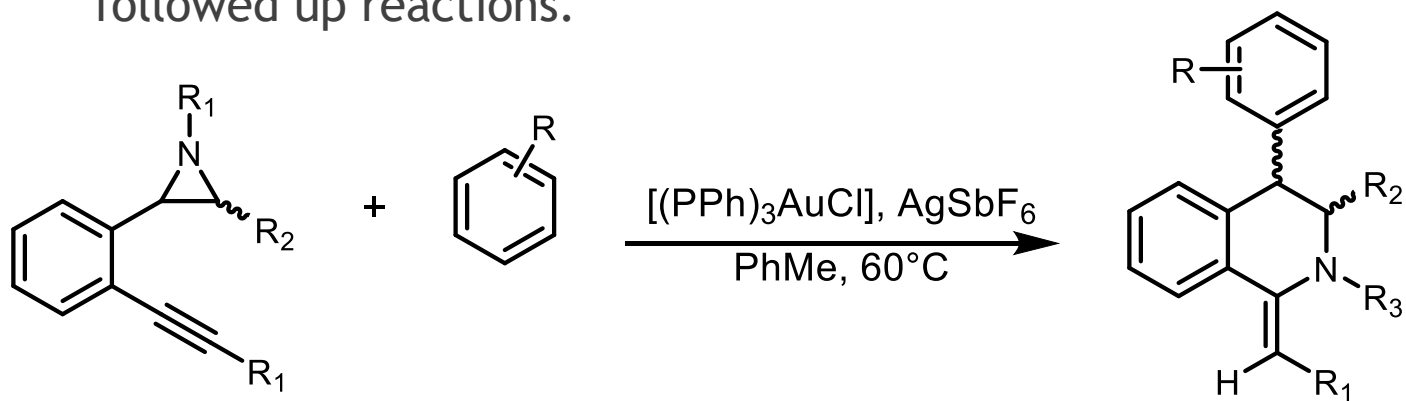
► The typical work of indole as a nucleophile. (Elisabetta Rossi 2016)



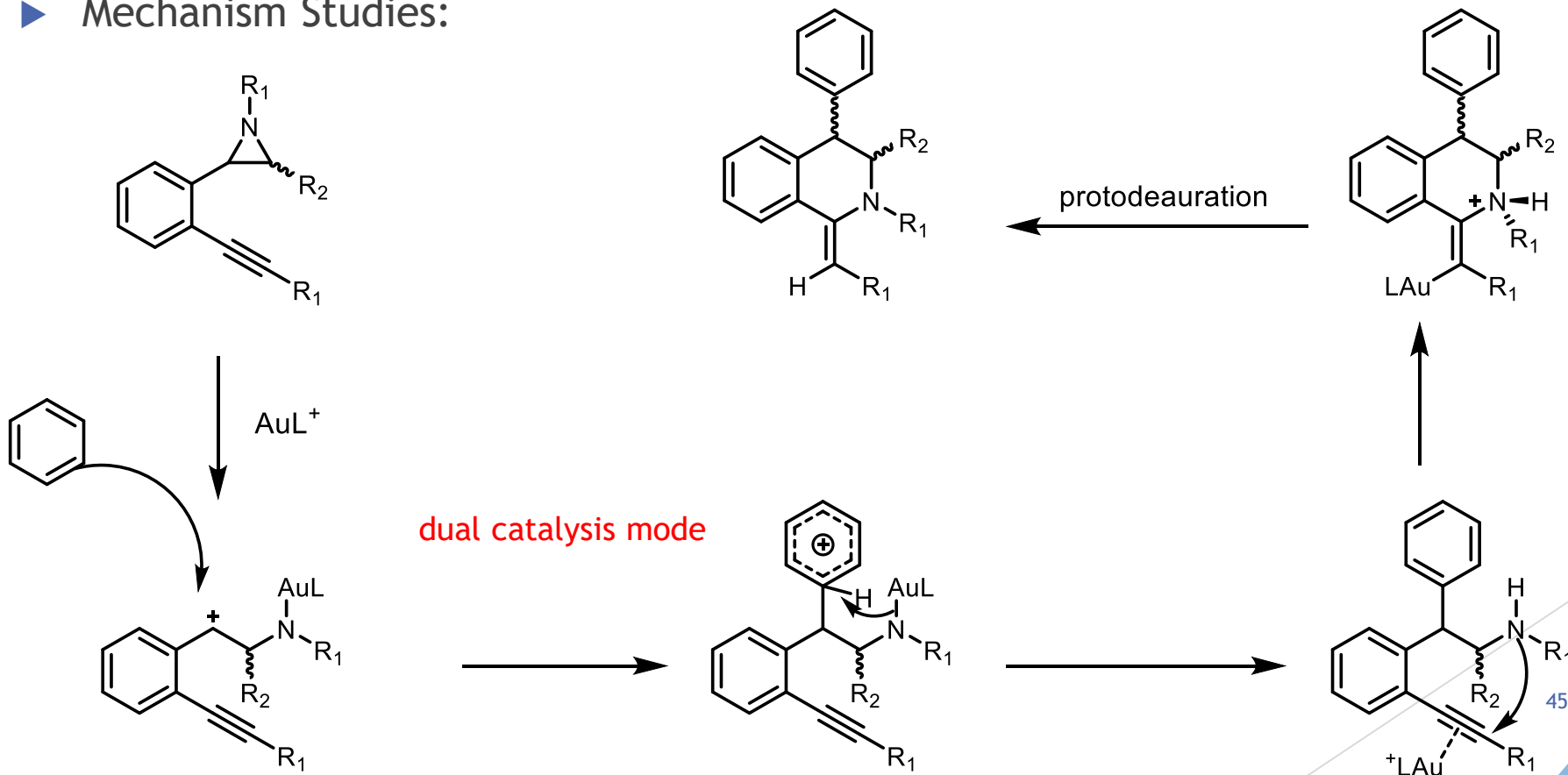
► Mechanism Studies:



- ▶ The opened ring can act as an **intramolecular nucleophile** to launch secondary followed up reactions.



- ▶ Mechanism Studies:



# Conclusion and future outlook.

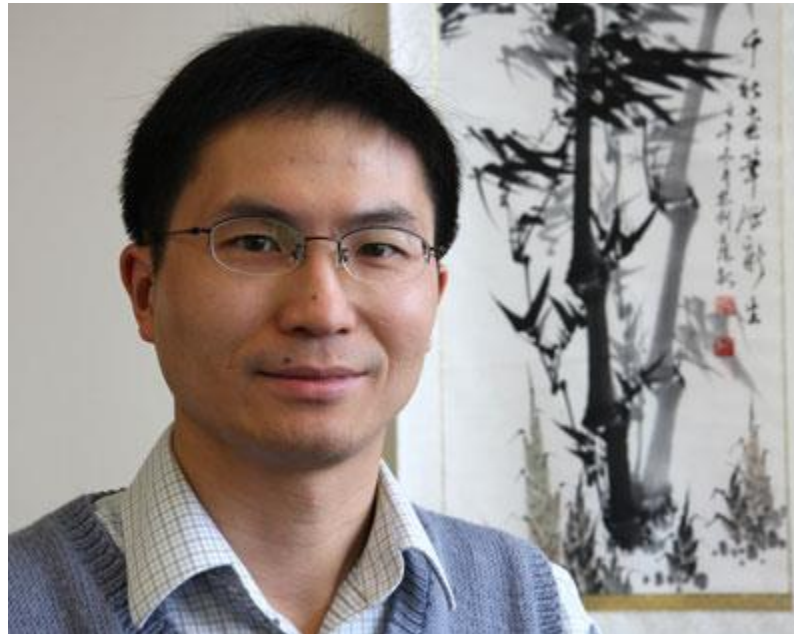
- ▶ The gold catalyzed ring expansion reactions have broad substrate scope and incorporate complicated transformations. Two main categories of the reactions including ring expansion pathway and ring opening pathway were discussed accordingly. The limit of this kind of transformation was the relatively limited substrate scope, only certain kind of small rings can react and the condition usually need to be free of strong nucleophiles. One potential for these kind of reactions was the asymmetric version of the gold catalyzed ring-expansion reactions utilizing the chiral ligands. It has been studied extensively in recent years but so far there has only a few examples of high enantioselectivity reported. Thus, developing efficient chiral ligands for the gold catalyzed ring expansion reaction seemed to be critical in the future prosperity of this field.

# The end, thanks for your patience.

- ▶ Special thanks to:
- ▶ Doctor candidate Ke Zhao



Dr. Liming Zhang



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### Citation Format: ACS(American Chemical Society)

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