Gold-Catalyzed Assembly of Heterobicyclic Systems

Liming Zhang and Sergey A. Kozmin*

Department of Chemistry, University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

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Au (Gold)
79
197.97

Preconceived Opinion: Expensive and Inert

Au: 1 g $133.50	**$AuCl_3$: 1 g $115.00**
Pd: 1 g $ 70.50	**AuCl: 1 g $132.50**
Ru: 1 g $ 43.40	**$PdCl_2$: 1 g $ 78.30**

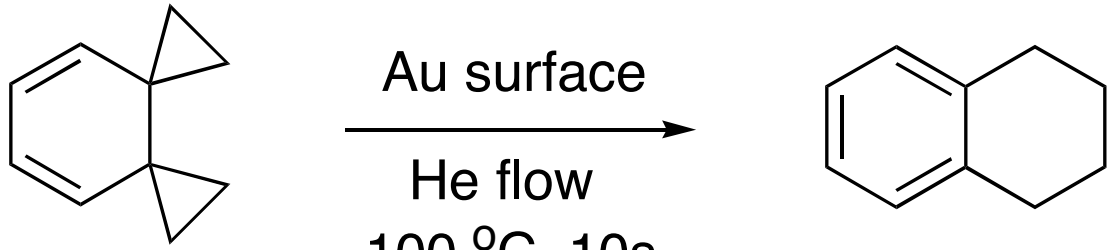
99.99%

Aldrich 2005-2006 Catalog

Inert?-- Heterogeneous Catalyst

--Hydrochlorination of ethyne
--Oxidation of CO
--Oxidative decomposition of halogenated hydrocarbons
--Reduction of NO with CO to N_2 and CO_2

--Gold can also catalyze rearrangements of hydrocarbons

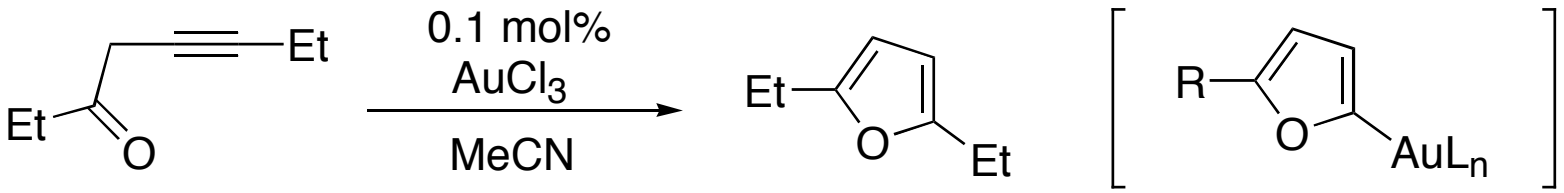


90%

Meyer and Meijere. *TL*, 1976, 497.

Gold Salts --An Eldorado for Homogeneous Catalysis?

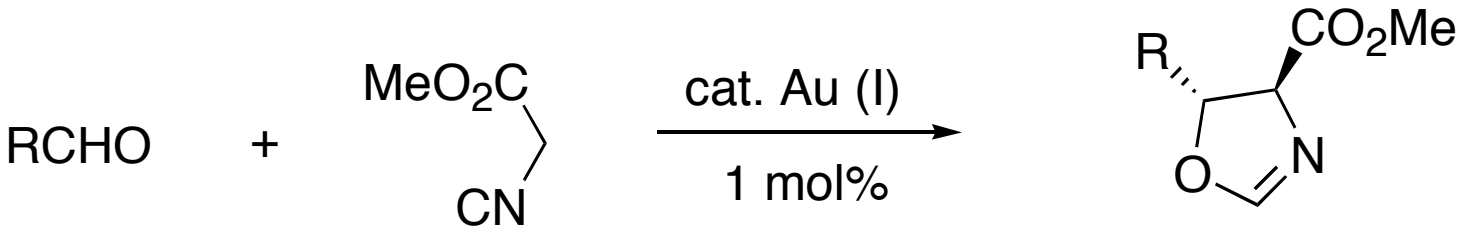
--First Gold chloride catalyzed *C-C* and *C-O* coupling by Hashmi.



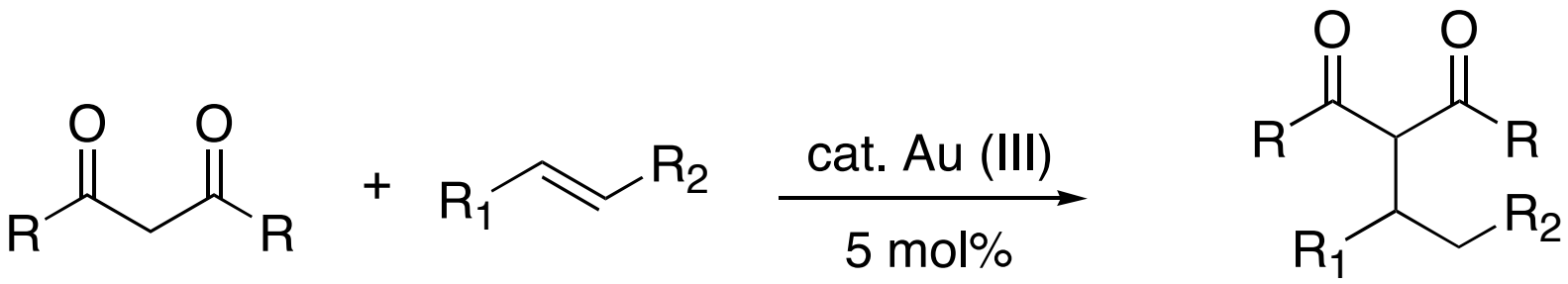
Hashmi et al. *ACIE*, 2000, *39*, 2285.
Highlighted by: Dyker *ACIE*, 2000, *39*, 4237.

--In 2004, more than a dozen Gold salts catalyzed reactions were published only in JACS as Communications.

Gold Catalyzed Methylene C-H Activation

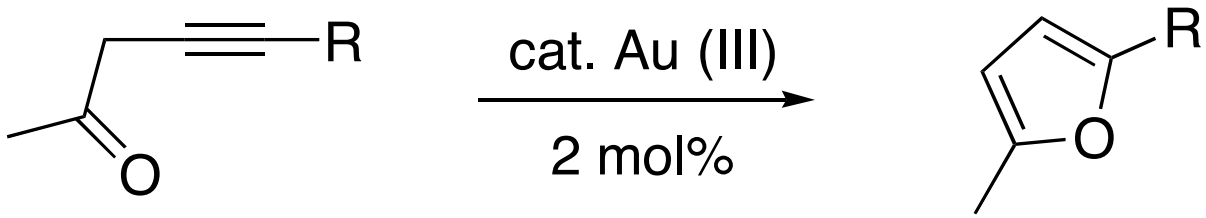


Hayashi et al. *JACS*, 1986, *108*, 6405.

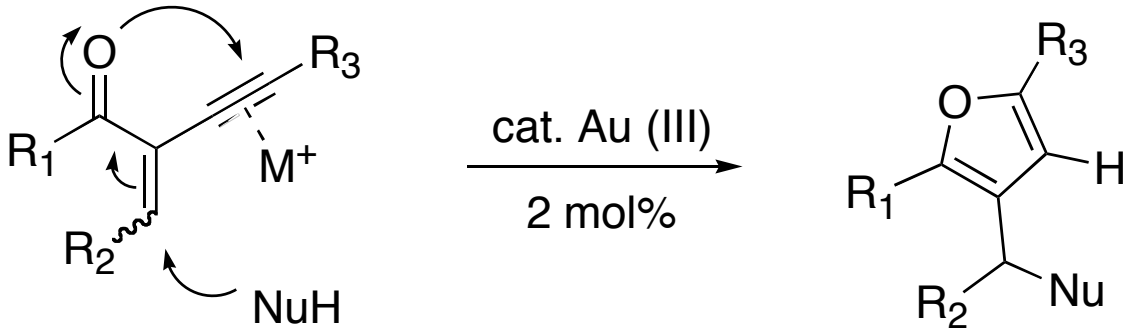


Li et al. *JACS*, 2004, *126*, 6884.

Gold Catalyzed Furan Ring Synthesis

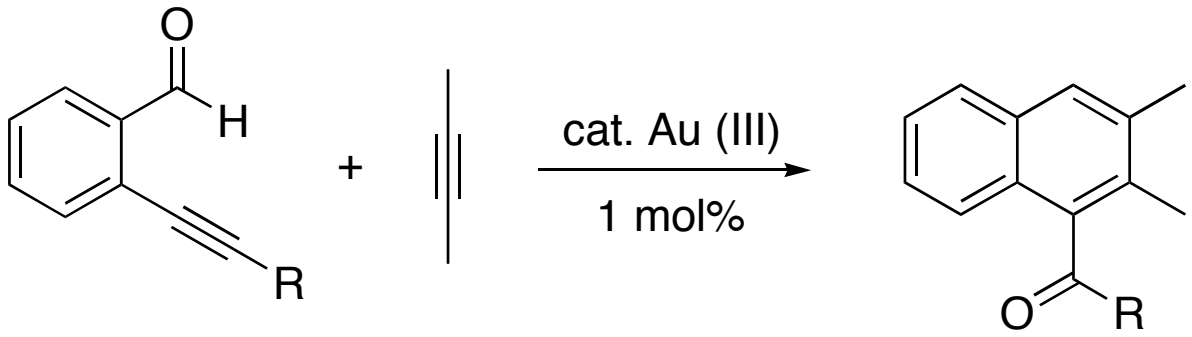


Hashmi et al. *ACIE*, 2000, *39*, 2285.
Hashmi et al. *JACS*, 2000, *122*, 11553.

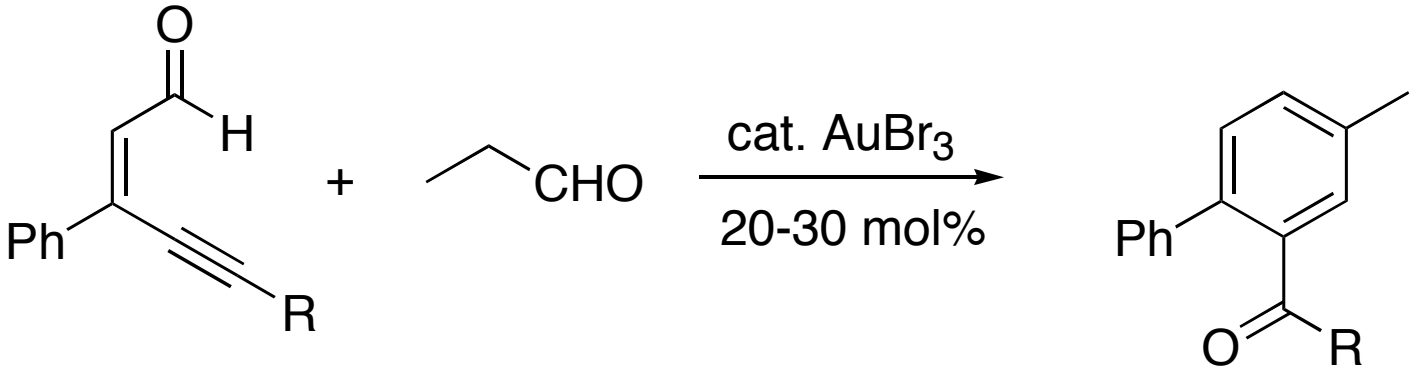


Larock et al. *JACS*, 2004, *126*, 11164.

Gold Catalyzed Benzannulation

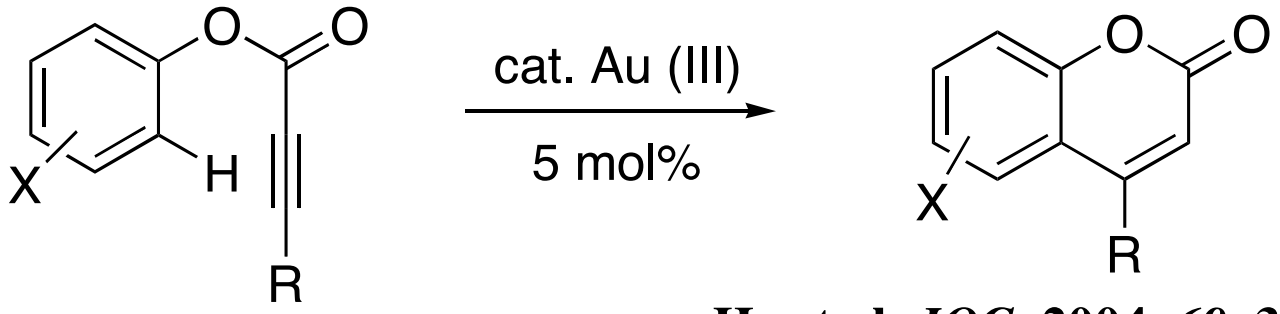


Yamamoto et al. *JACS*, 2002, *124*, 12650.



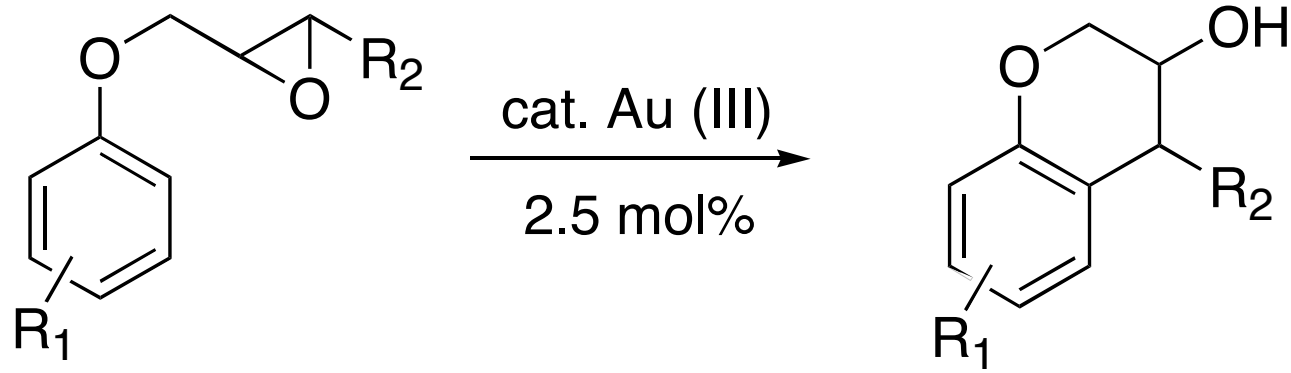
Yamamoto et al. *JACS*, 2004, *126*, 7458.

Gold Catalyzed Functionalization of Aromatic C-H Bond



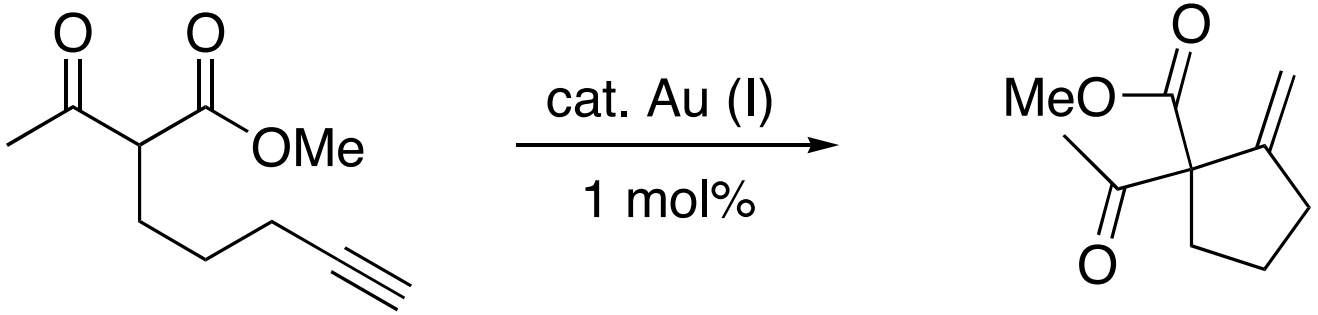
He et al. *JOC*, 2004, *69*, 3669.

For amines: Echavarren et al. *ACIE*, 2004, *43*, 2402.
For Intermolecular reactions: Reetz et al. *EJOC*, 2003, 3485.

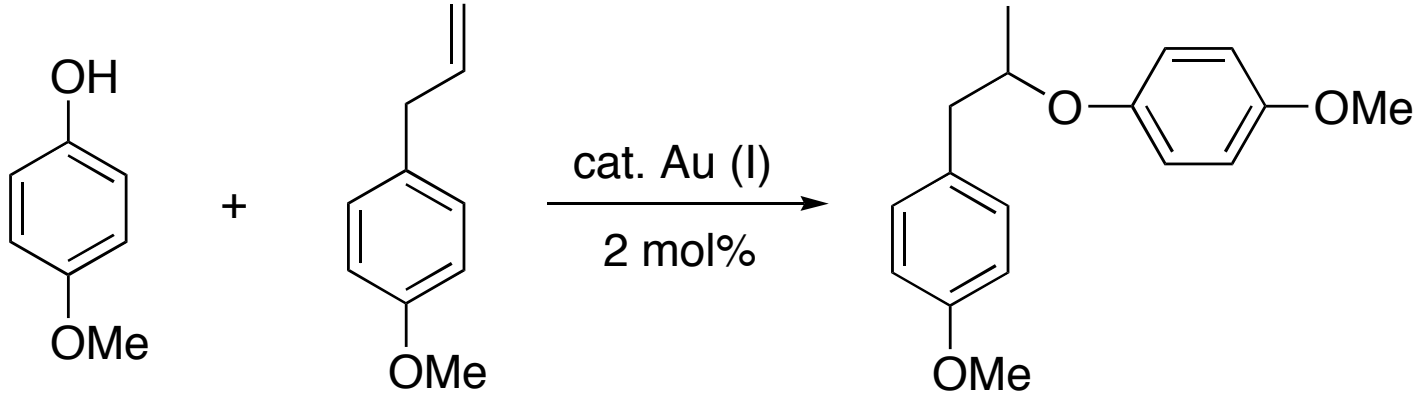


He et al. *JACS*, 2004, *126*, 5964.

Other Gold Catalyzed Reactions



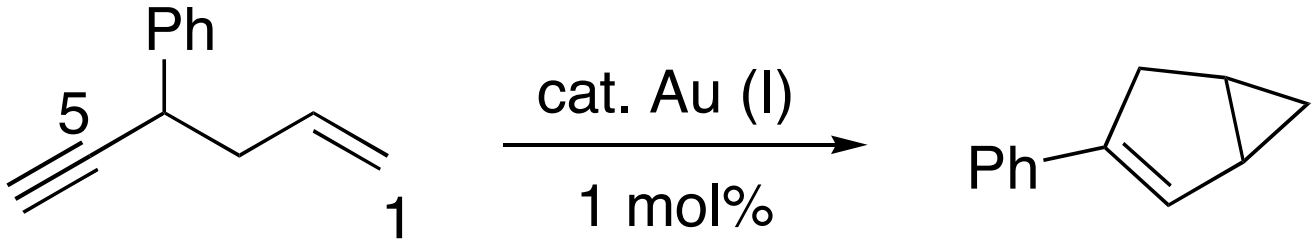
Toste et al. *JACS*, 2004, *126*, 4526.



First example of activation of alkenes

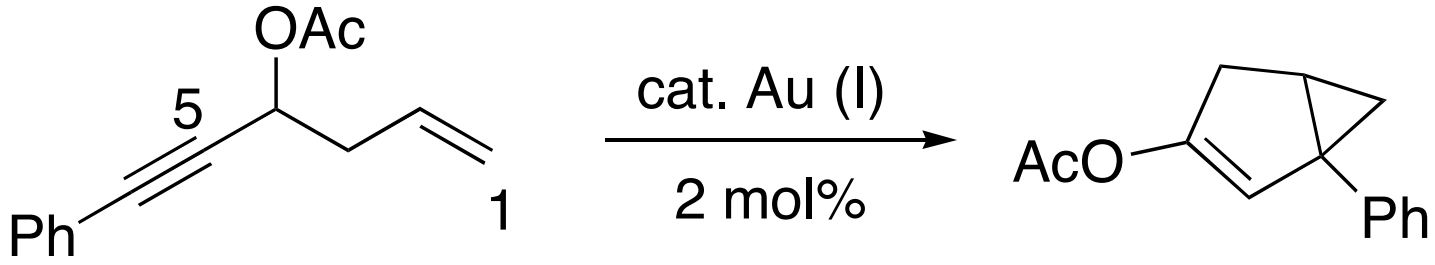
He et al. *JACS*, 2005, *ASAP*.

Gold Catalyzed Reactions on 1, 5-Enynes I



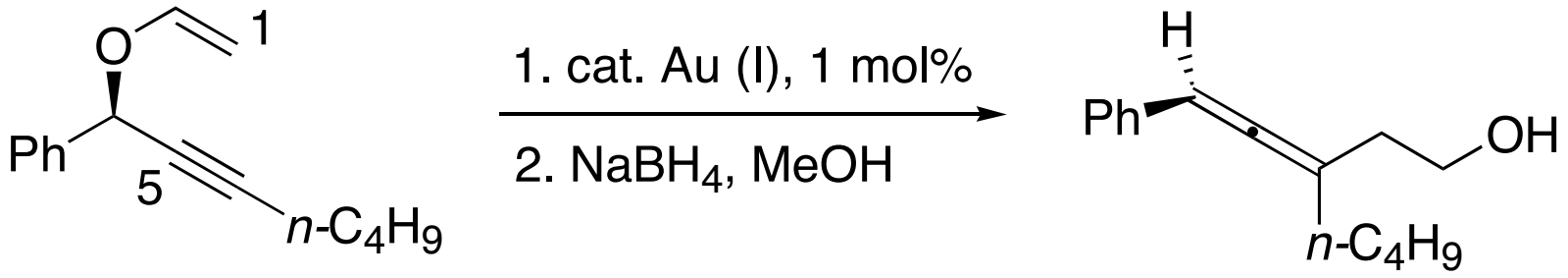
Bicyclo[3.1.0]hexenes

Toste et al. *JACS*, 2004, *126*, 10858.

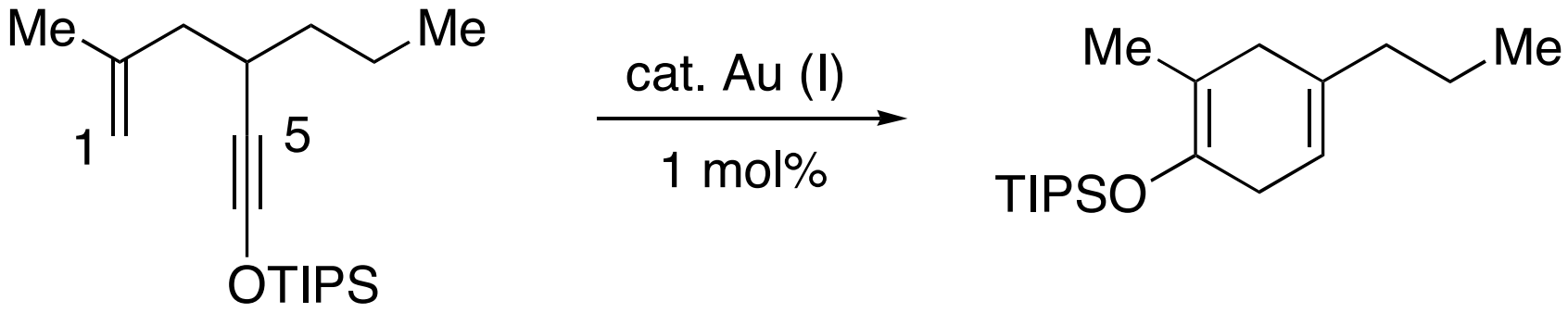


Furstner et al. *JACS*, 2004, *126*, *8654*.

Gold Catalyzed Reactions on 1, 5-Enynes II

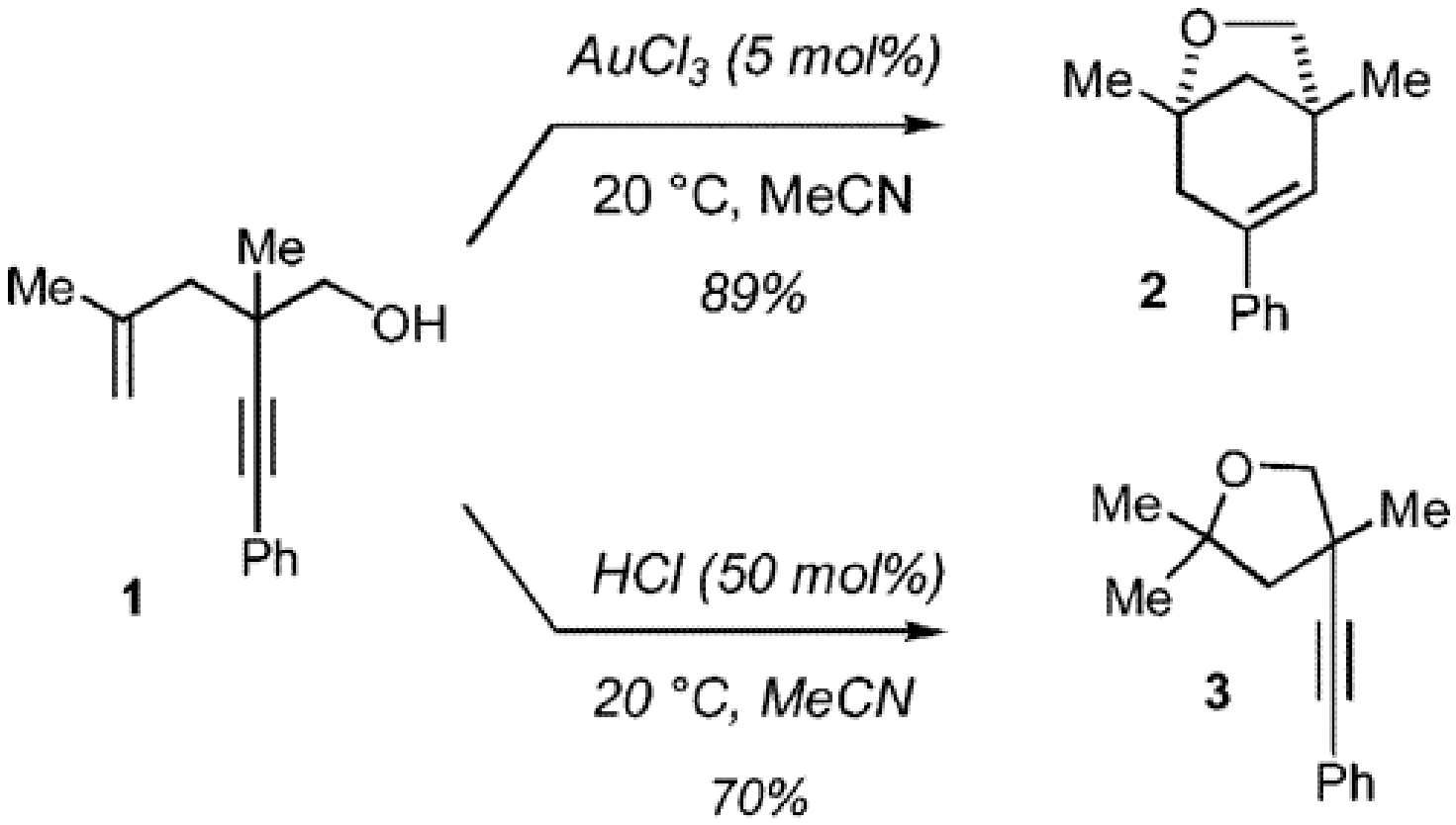


Toste et al. *JACS*, 2004, *126*, 15978.



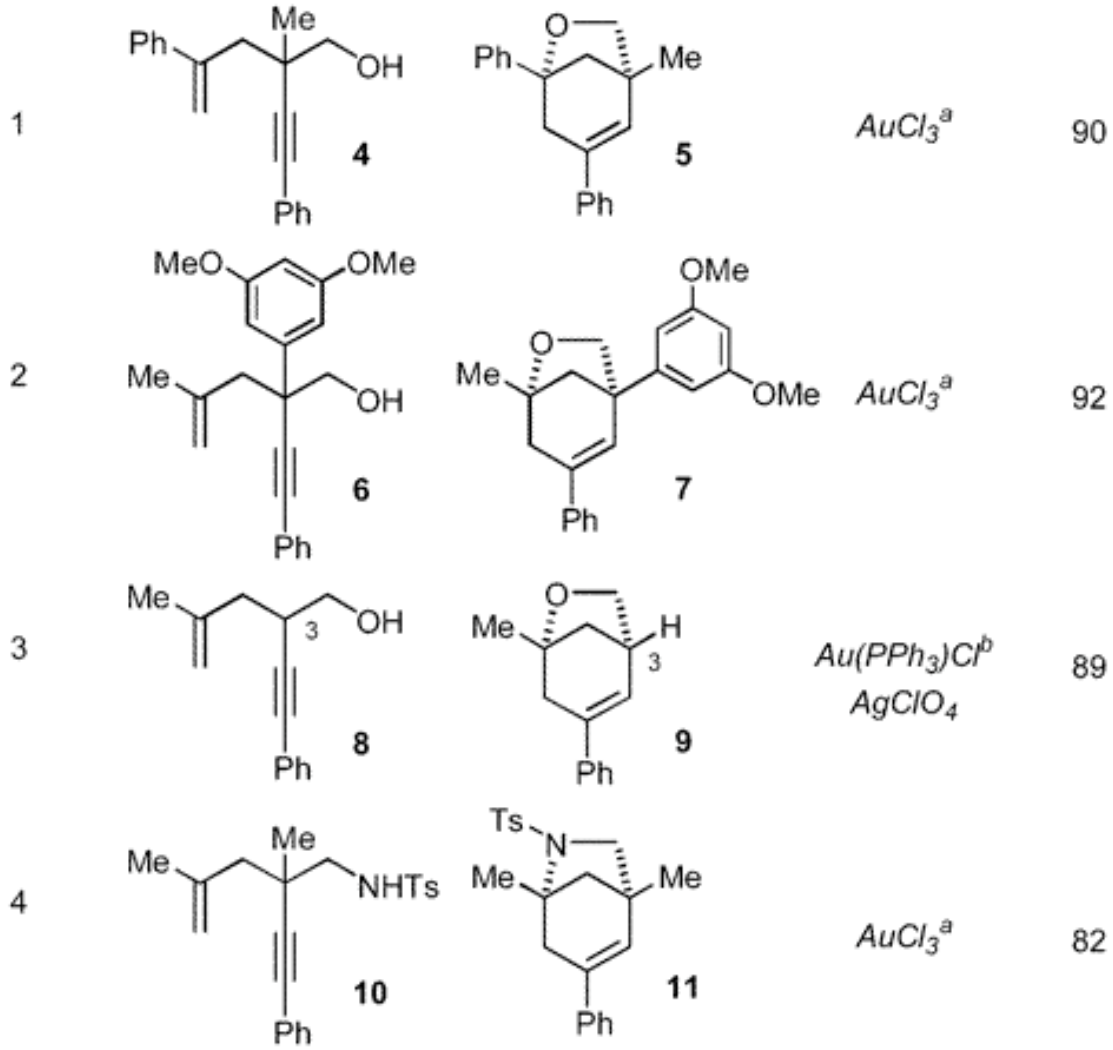
Kozmin et al. *JACS*, 2004, *126*, *11806*.

Gold Catalyzed Reactions on 1, 5-Enynes III: Assembly of Heterobicyclic Systems



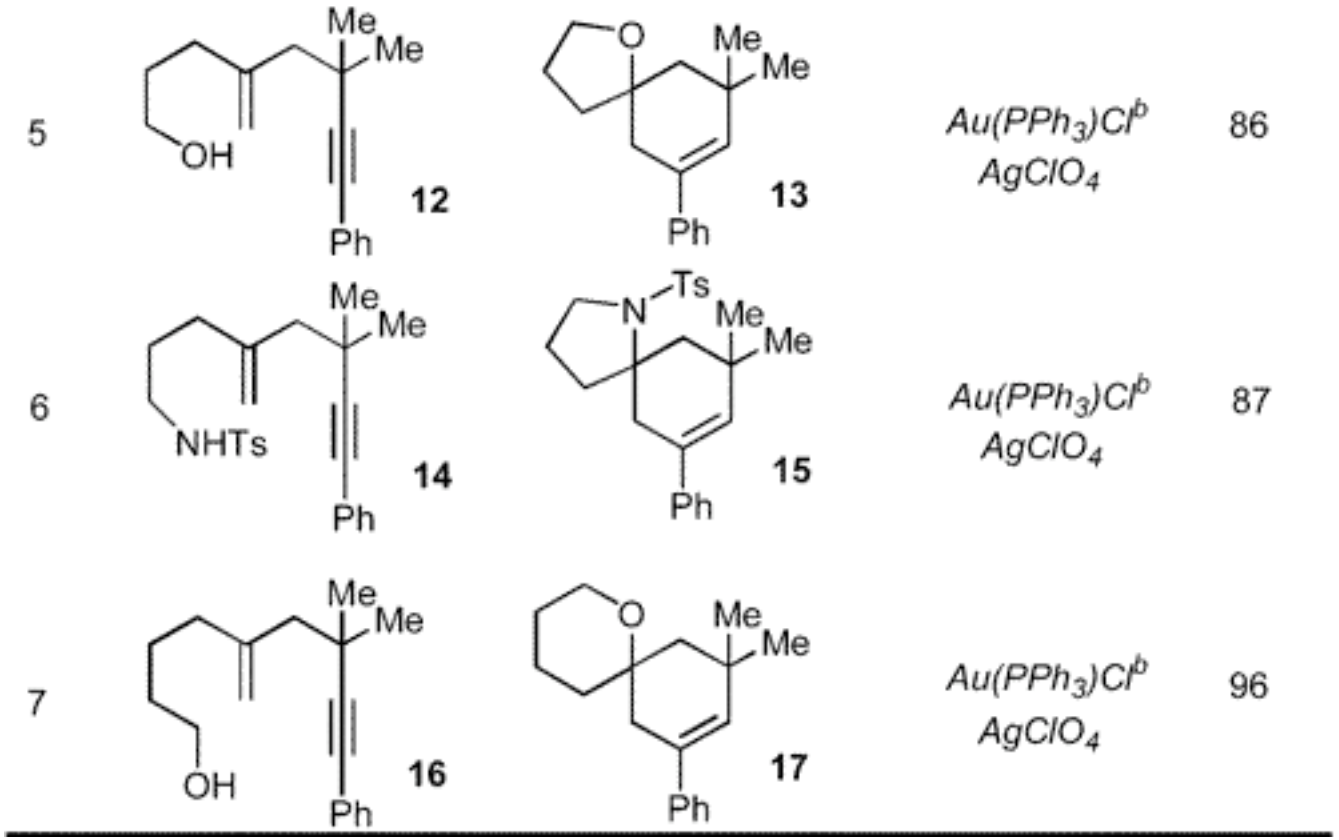
Kozmin et al. *JACS*, 2005, *127*, *ASAP*.

Gold Catalyzed Synthesis of Oxa- or Azabicyclic[3.2.1]octene



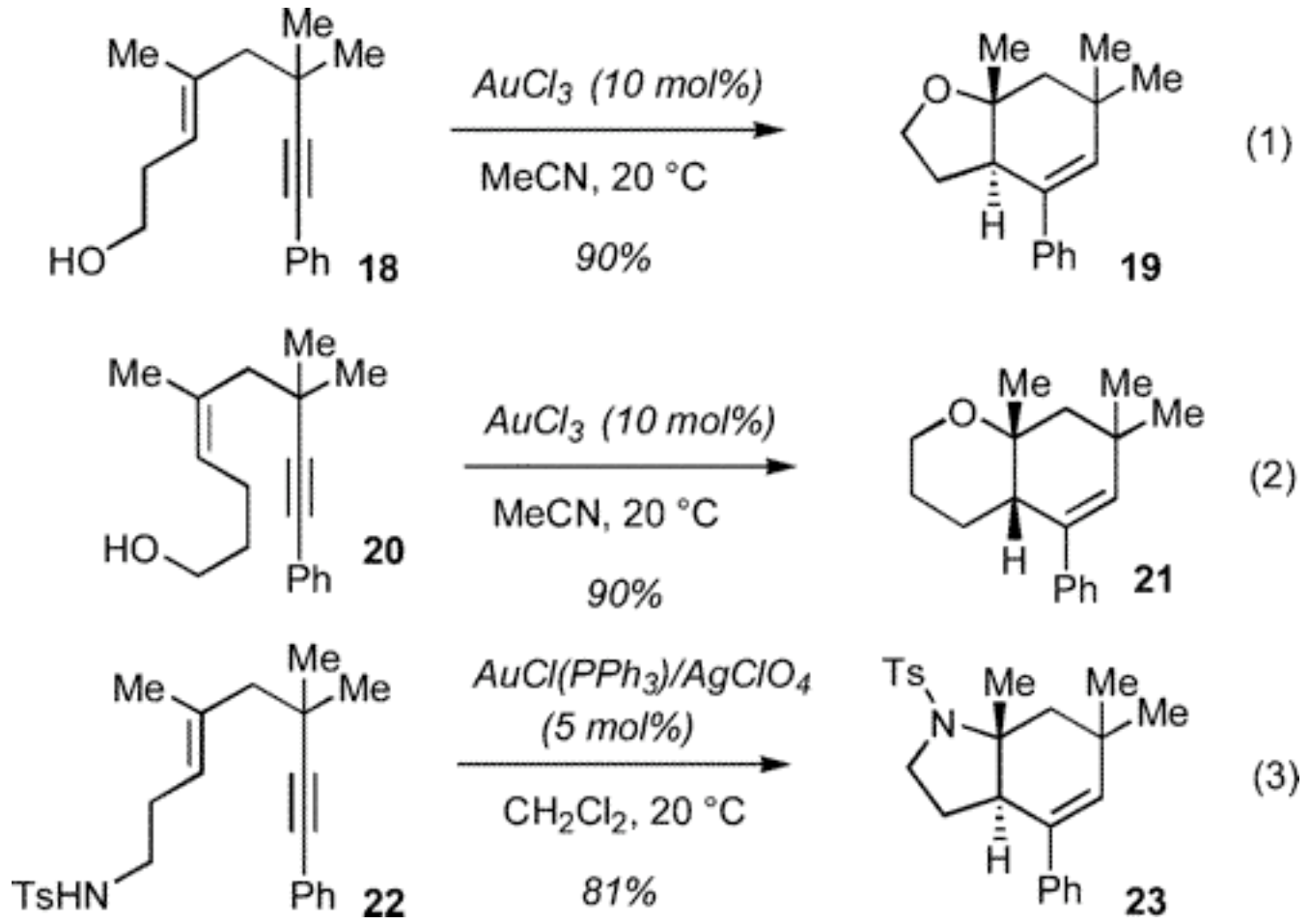
Kozmin et al. *JACS*, 2005, *127*, *ASAP*.

Gold Catalyzed Synthesis of Oxa- or Azaspirocyclic Compounds



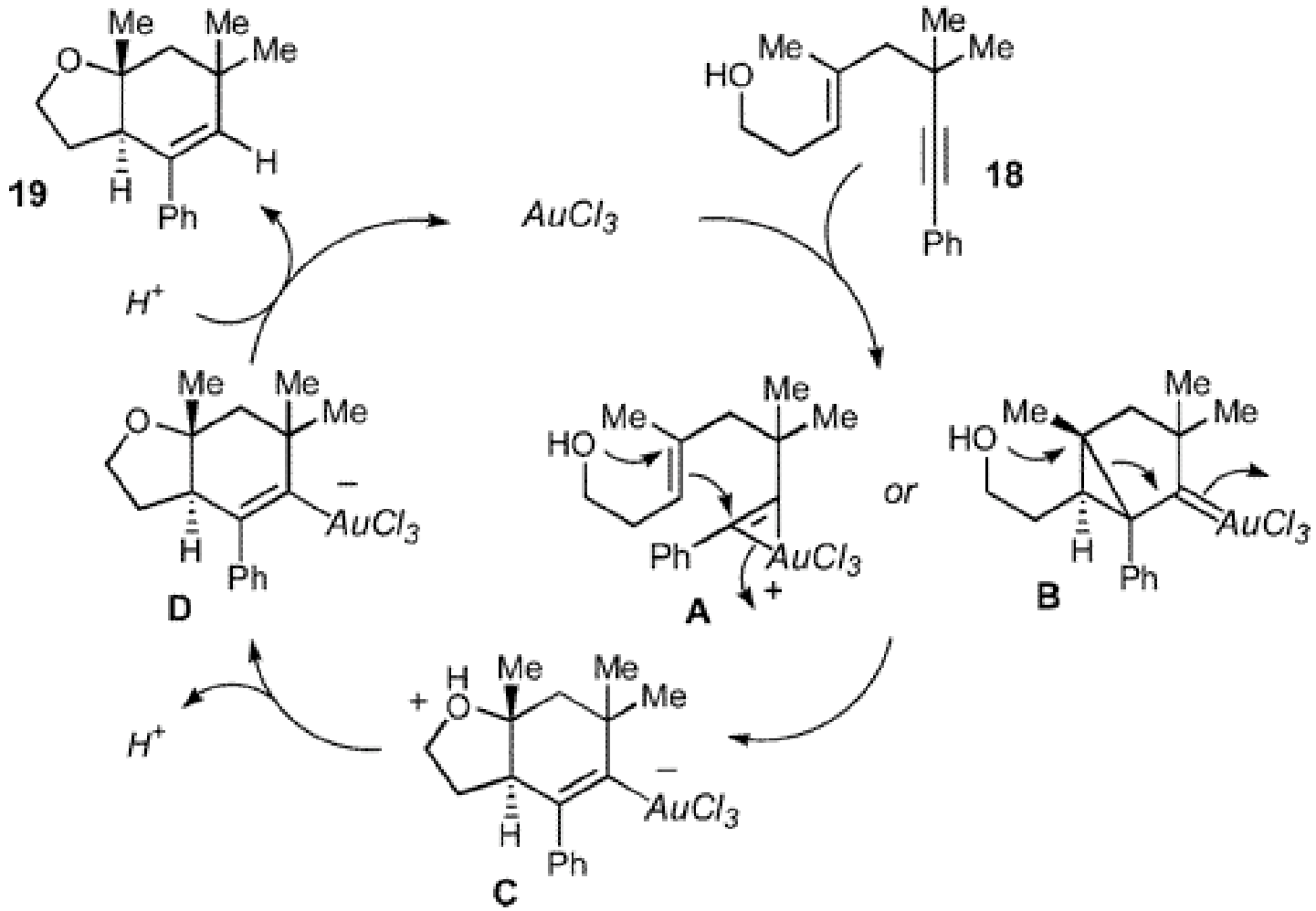
Kozmin et al. *JACS*, 2005, *127*, *ASAP*.

Gold Catalyzed Synthesis of Fused Heterobicycloalkenes



Kozmin et al. *JACS*, 2005, *127*, *ASAP*.

Gold Catalyzed Synthesis of Heterobicyclic Systems



Chemoselective gold-based alkyne activation, carbocyclization, intramolecular nucleophilic addition, followed by protodemetalation.

Kozmin et al. *JACS*, 2005, *127*, *ASAP*.

Conclusions

1. Developed an efficient gold-catalyzed double cyclization of simple 1,5-enynes with oxygen- or nitrogen-based nucleophiles.

2. A convergent approach to oxa and azabicyclic alkenes with bridged, fused, and spirocyclic structure.

3. The assembly procedure proceeds diastereospecifically.

4. Develop the chiral gold catalysts?

5. Chemoselectivity between alkenes and alkynes.