

Gold Catalysis in Organic Reactions

Krit Setthakarn (May Research Lab) 10/06/2015

Periodic Table of the Elements

The image shows a standard periodic table of elements. The element Gold (Au) is highlighted with a red box. The table includes element symbols, names, atomic numbers, and atomic masses. A legend at the bottom identifies various groups: Alkali Metal, Alkaline Earth, Transition Metal, Basic Metal, Semimetal, Nonmetal, Halogen, Noble Gas, Lanthanide, and Actinide.

Gold catalysts

•Au(I)

-AuCl, AuBr

-PPh₃AuX; X = Cl⁻, Br⁻, OTf⁻, NTF₂⁻, BF₄⁻

•Au(III)

-AuCl₃, AuBr₃

-Na[AuCl₄], K[AuCl₄]

Roles in transition metal catalyzed reaction

•Rarely

- Migratory Insertion
- Oxidative Addition
- Reductive Elimination
- β-Hydride Elimination

•Commonly

- Proto-demetalation

•Electron configuration : [Xe] 4f¹⁴5d¹⁰6s¹

•Oxidation states : 5,4,3,2,1,-1

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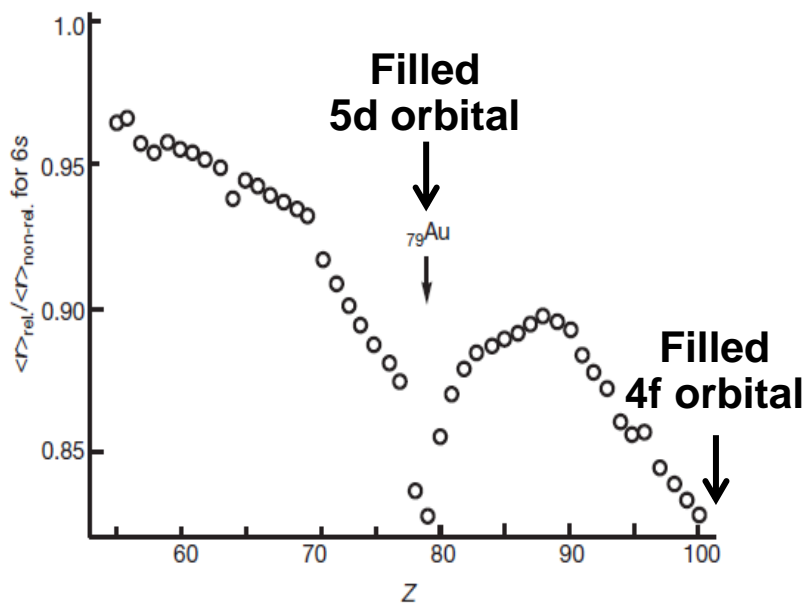
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- **Relativistic Effects**

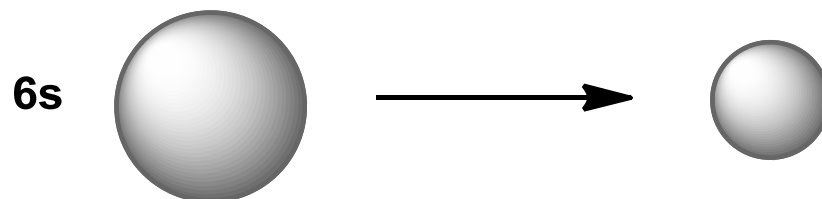
Phenomenon is resulted from the need to consider velocity as significant relative to the speed of light.

$$m = m_0 / \sqrt{1 - (v/c)^2}$$

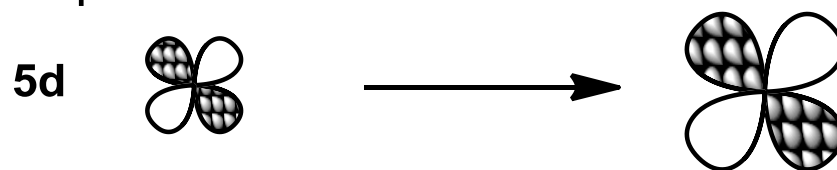
- Calculated Relativistic contraction of the 6s orbital



- Contracted 6s orbital



- Expanded 5d orbital



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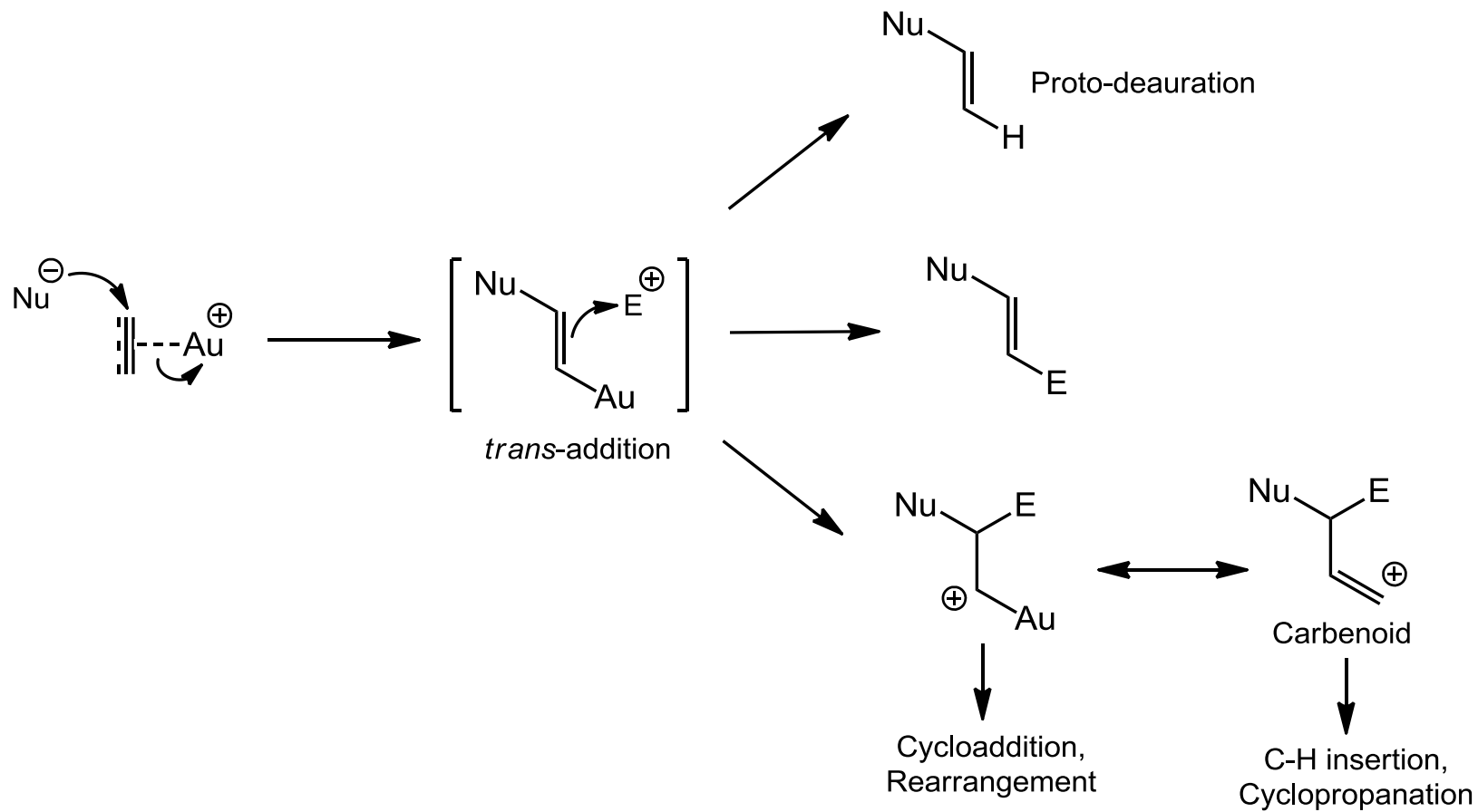
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Element	Electron affinity (EA) kJ/mol	Electronegativity (EN)
Rhodium (Rh)	109.704	2.28
Silver (Ag)	125.624	1.93
Gold (Au)	222.749	2.4

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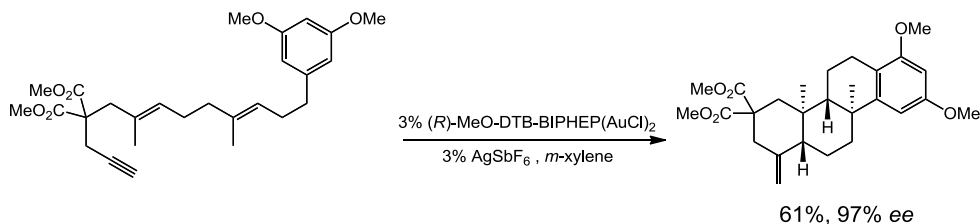
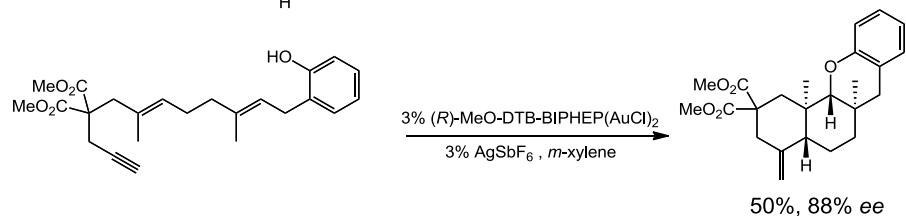
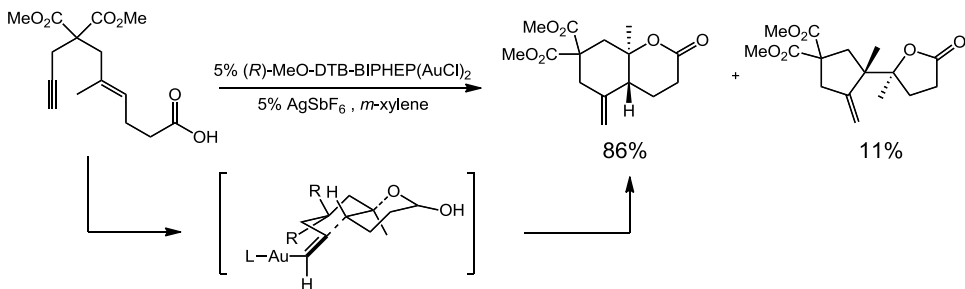
Reaction Scopes of Gold Catalysis



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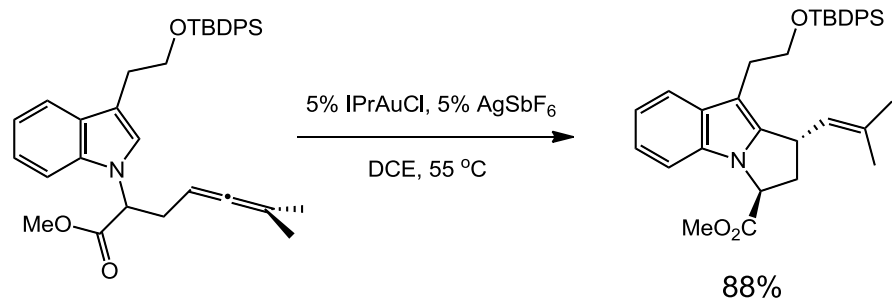
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•Oxygen Nucleophiles



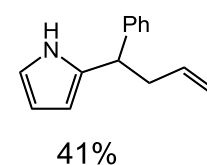
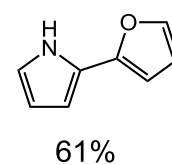
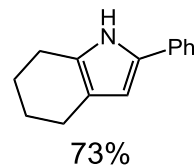
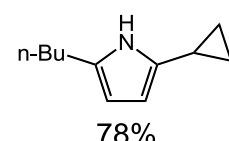
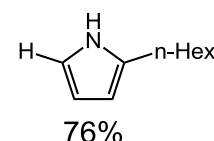
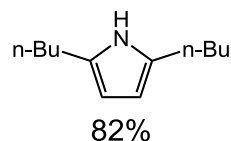
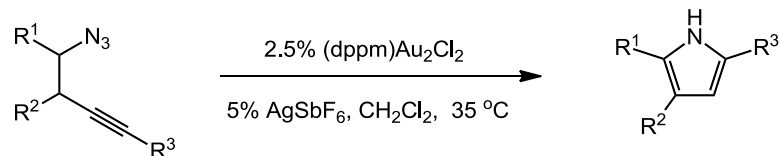
Toste, F. D. *et al. J. Am. Chem. Soc.* **2010**, *132*, 8276.

•Carbon Nucleophiles



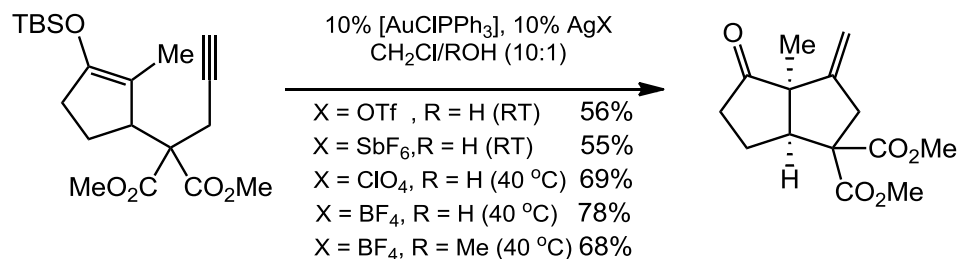
Toste, F. D. *et al. Chem. Sci.* **2011**, *2*, 1706.

•Nitrogen Nucleophiles



Toste, F. D. *et al. J. Am. Chem. Soc.* **2005**, *127*, 11260.

•Carbon Nucleophiles

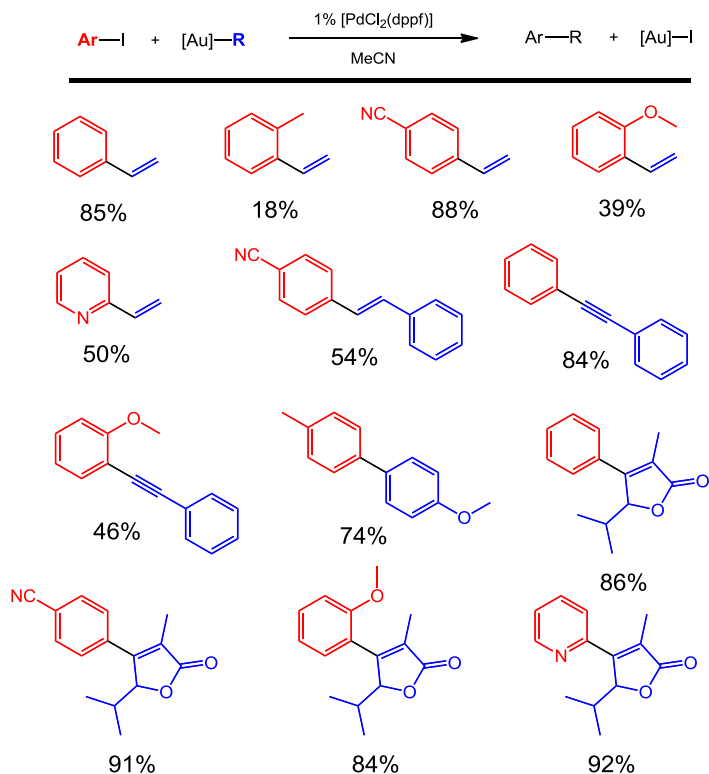


Toste, F. D. *et al. Angew. Chem. Int. Ed.* **2006**, *45*, 5991.

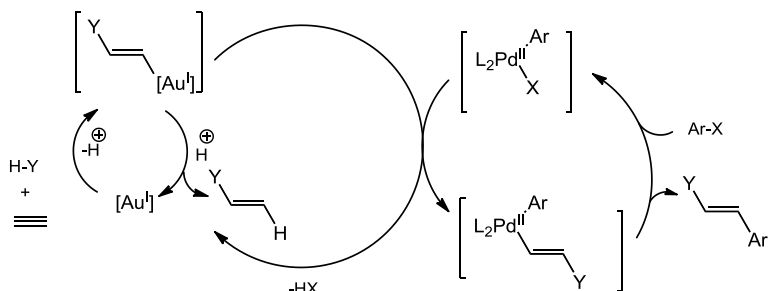
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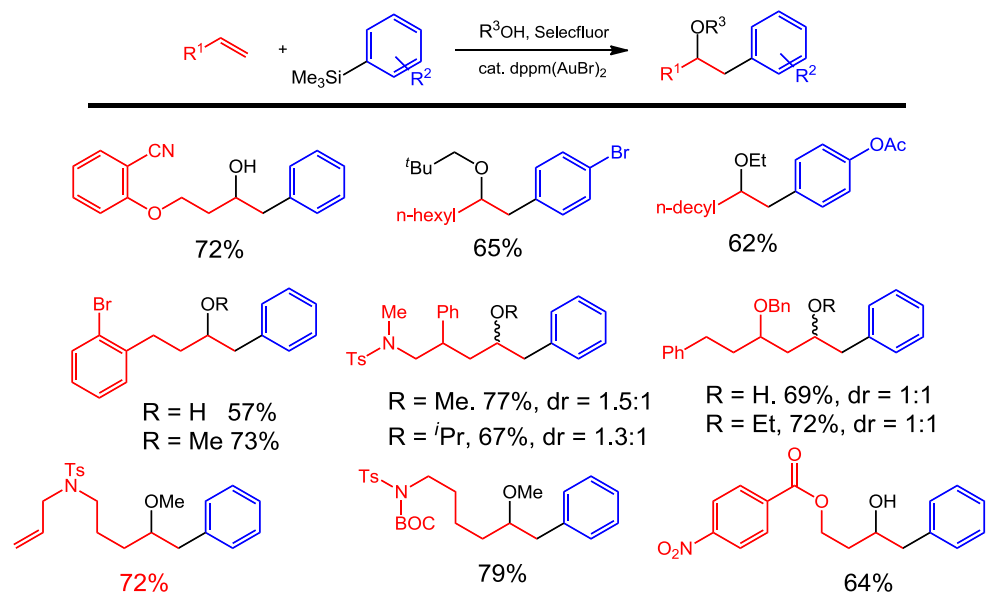
•Palladium/Gold cross coupling



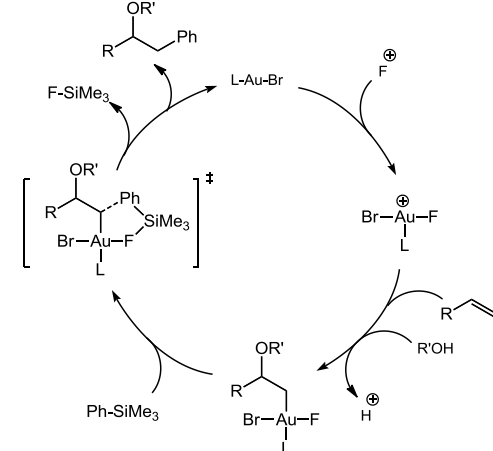
•Proposed mechanism



•Silane/Gold cross coupling



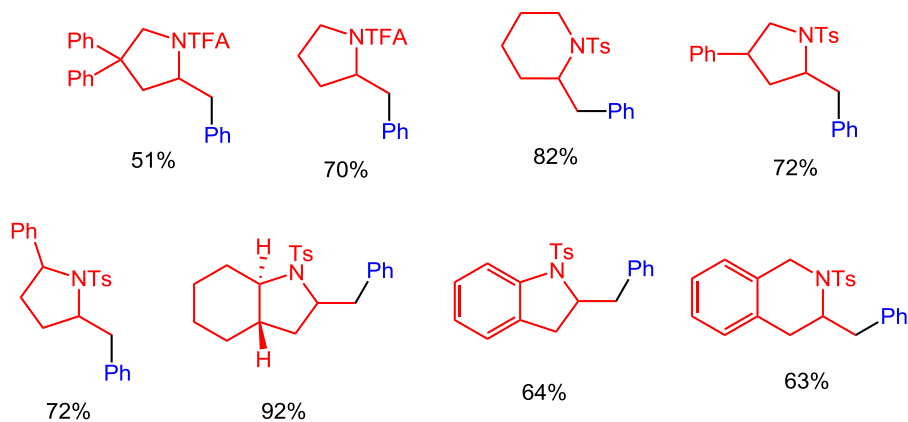
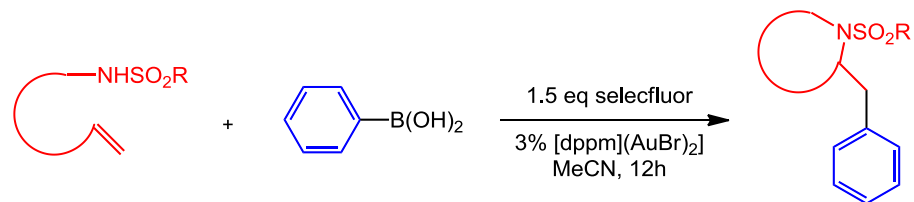
•Proposed mechanism



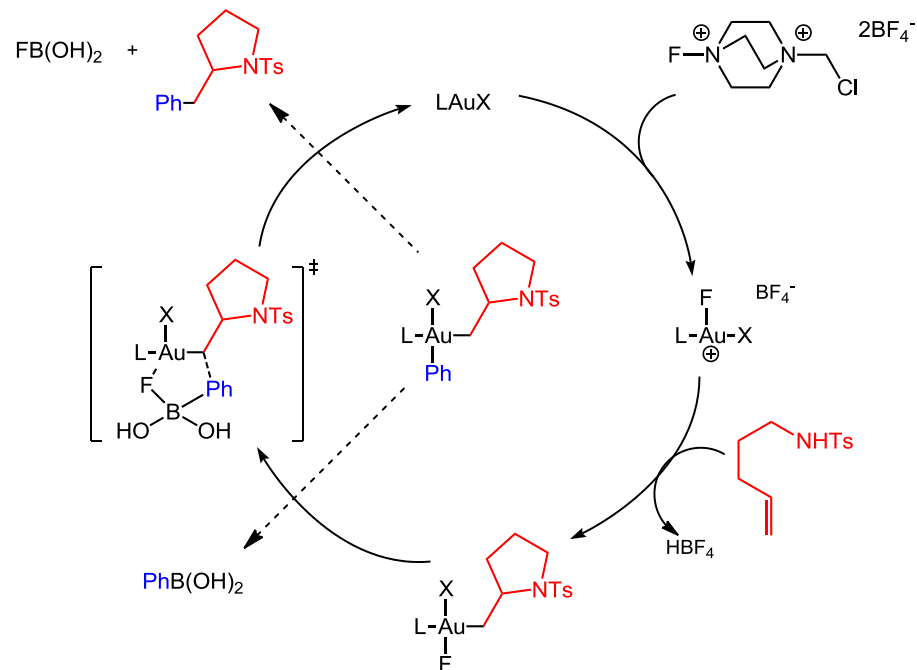
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•Boron/Gold cross coupling



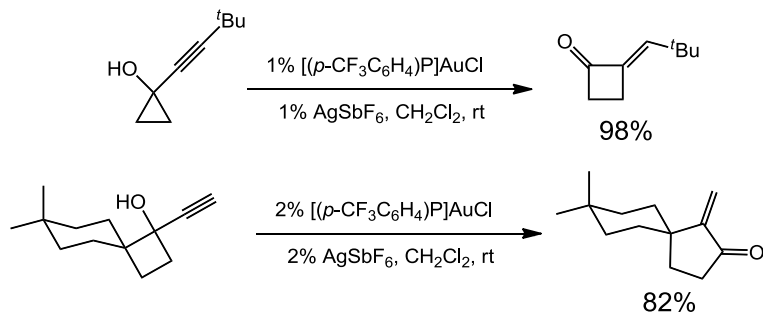
•Proposed mechanism



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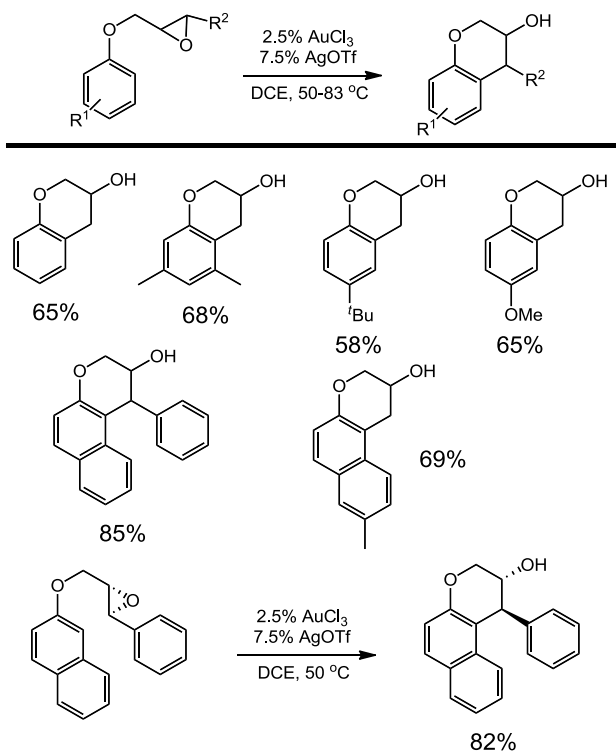
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•Ring expansion

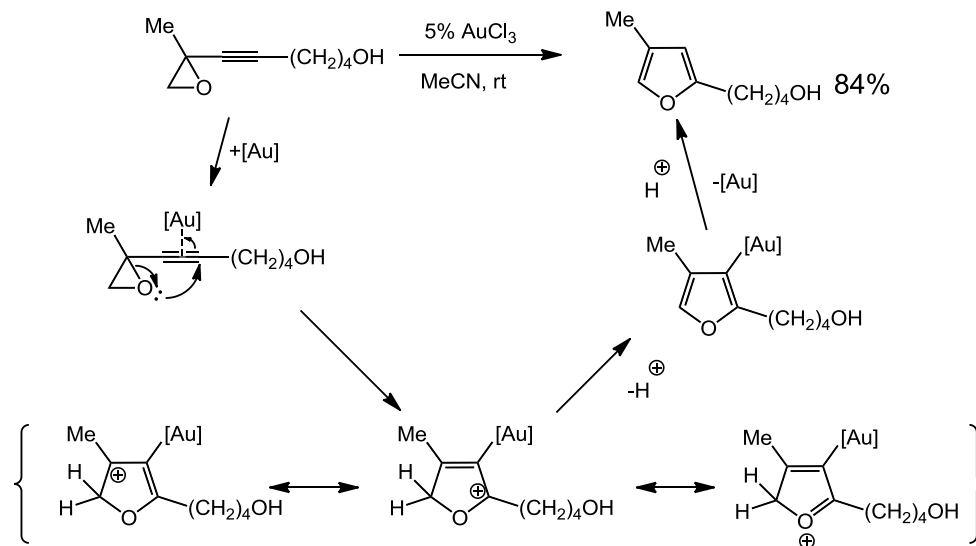


Toste, F. D. *et al. J. Am. Chem. Soc.* **2005**, *127*, 9708.

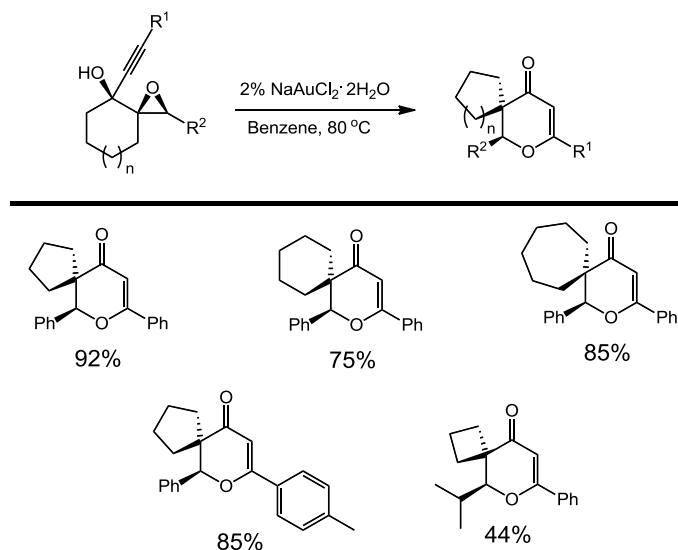
•Ring formation



Shi, Z. *et al. J. Am. Chem. Soc.* **2004**, *126*, 5964.



Hashmi, A. S. K. *et al. Adv. Synth. Catal.* **2004**, *346*, 432.

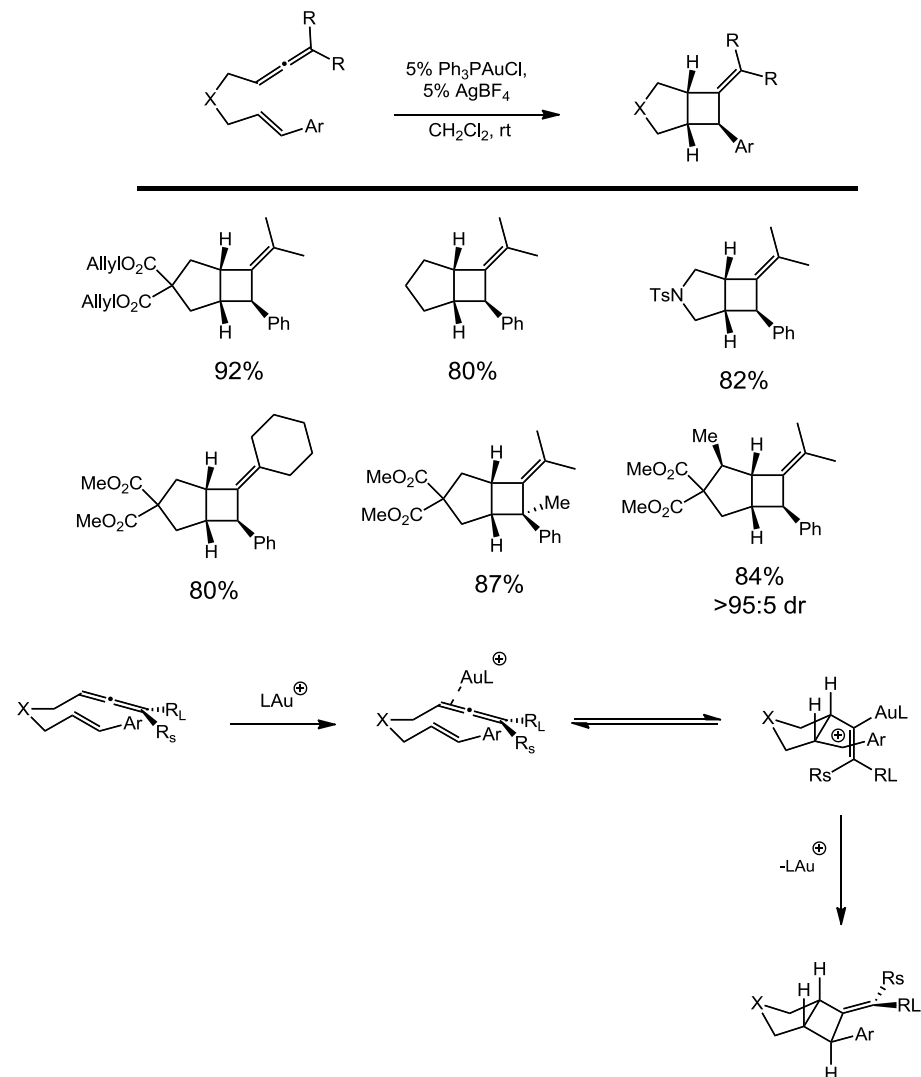
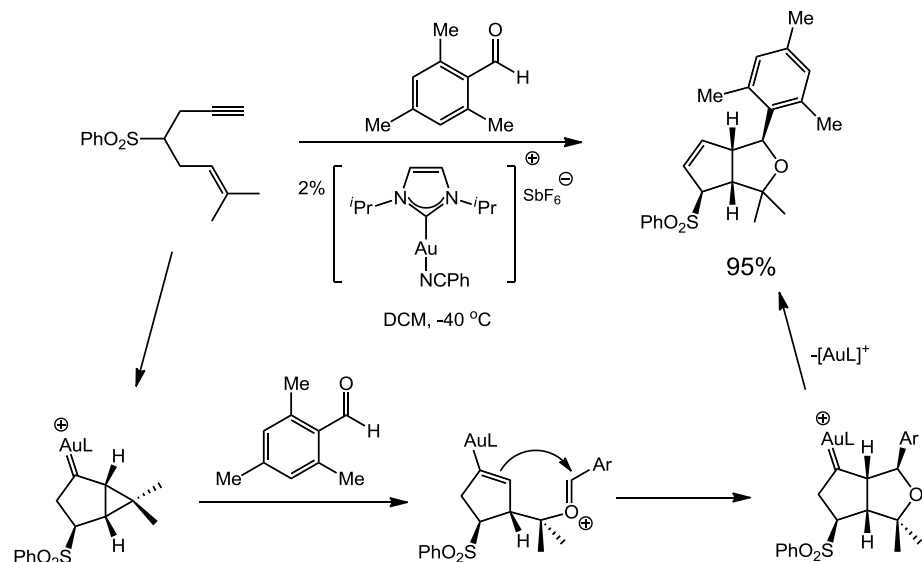


Liang, Y.-M. *et al. Chem. Eur. J.* **2008**, *14*, 5282.

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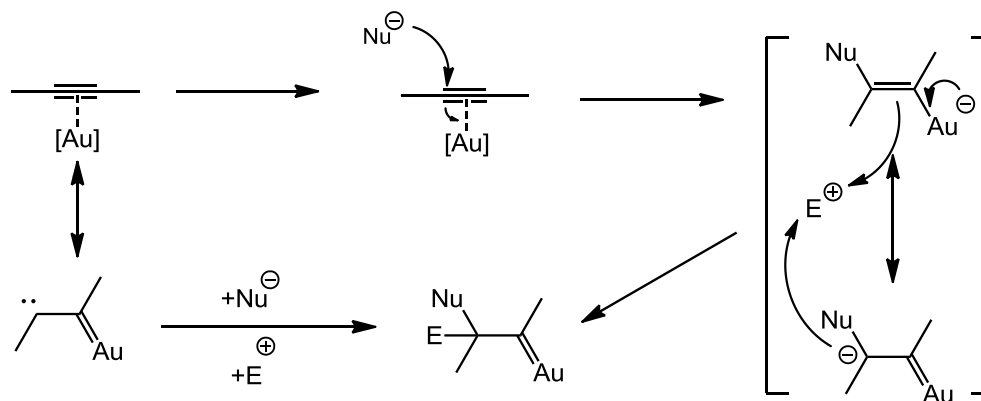
•Cycloaddition



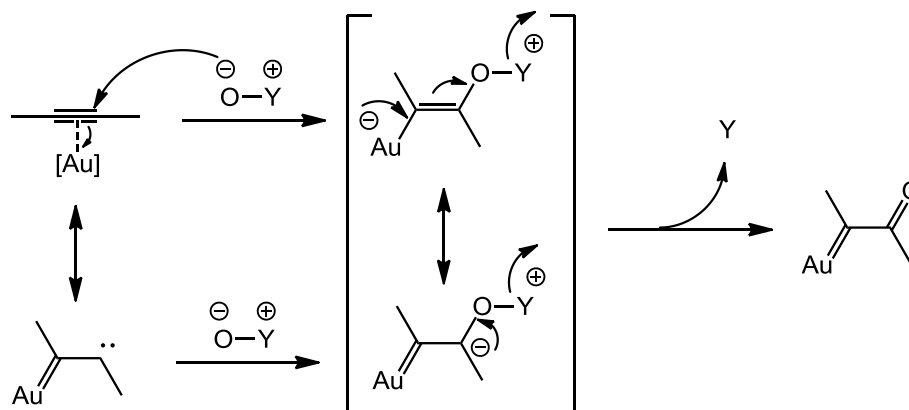
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•Nucleophilic/electrophilic reactivity of Gold-alkyne complex



•Formation of α -oxo gold carbenoid

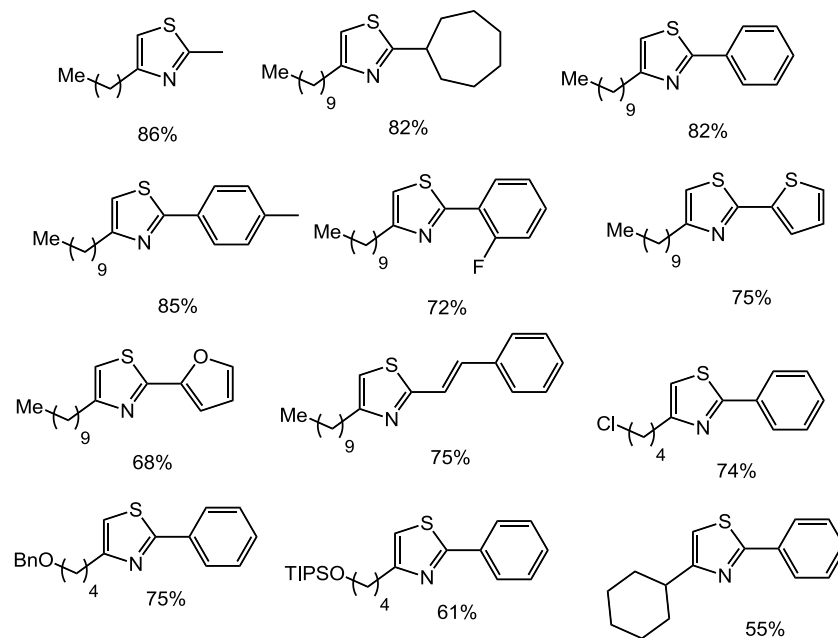
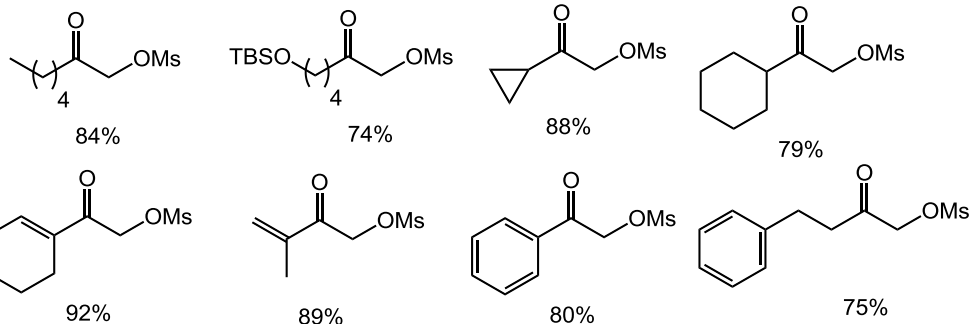
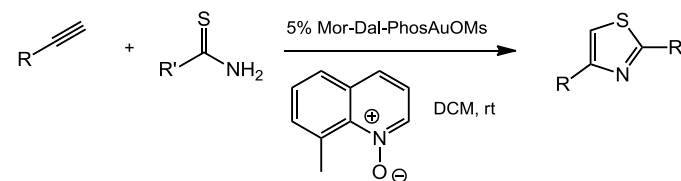
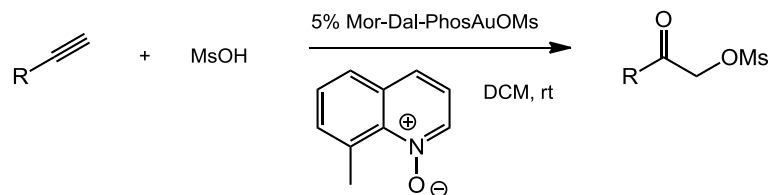


Oxidant = pyridine/quinoline N-oxides or sulfoxide

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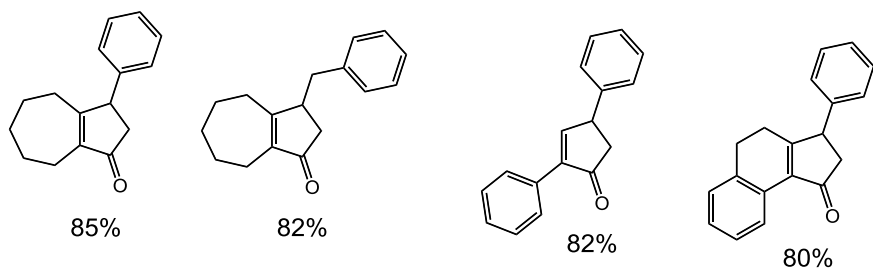
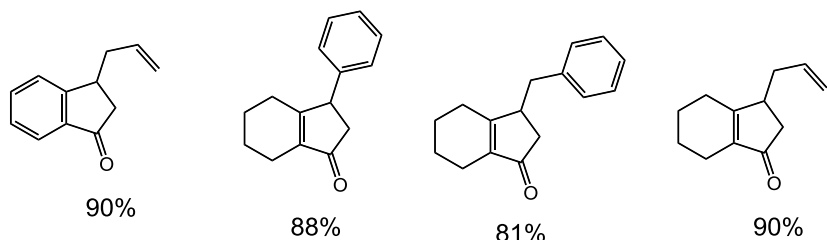
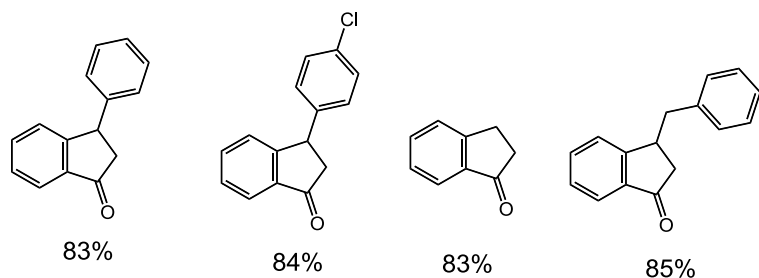
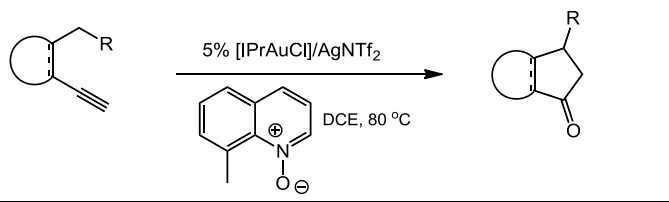
•Gold-catalyzed Oxidation of Terminal Alkynes



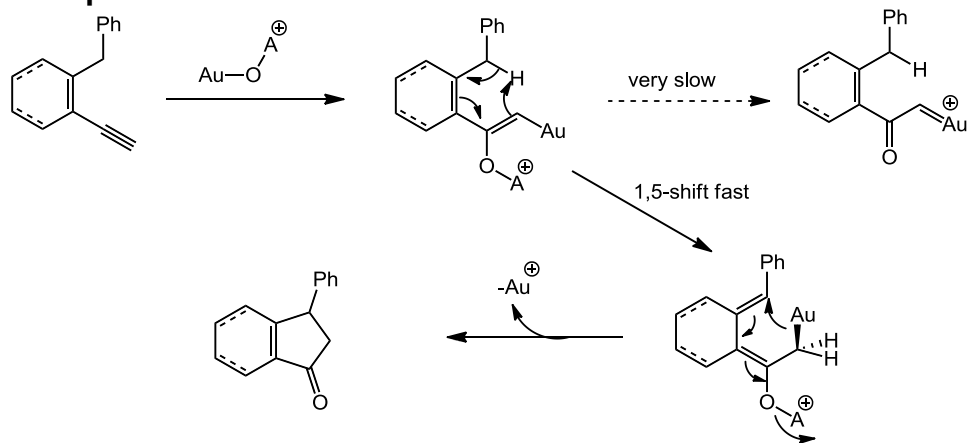
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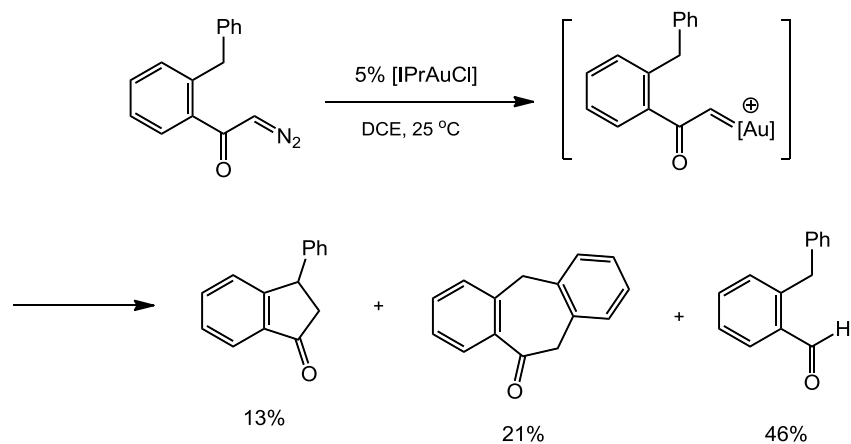
•Oxidative cyclization



•Proposed mechanism



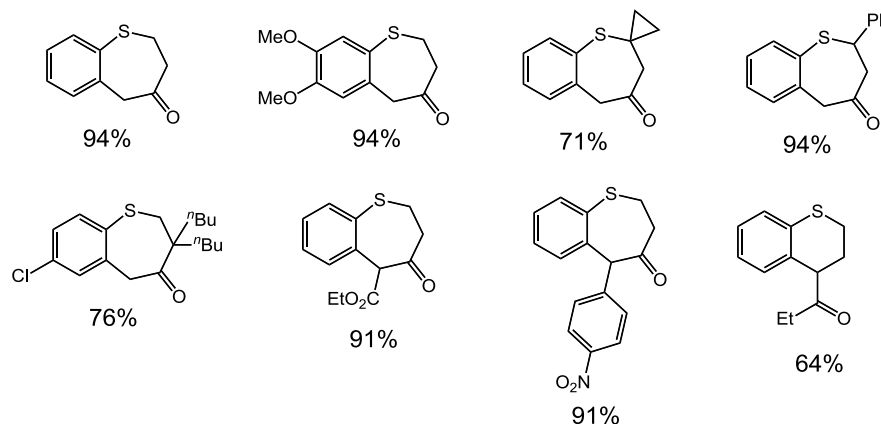
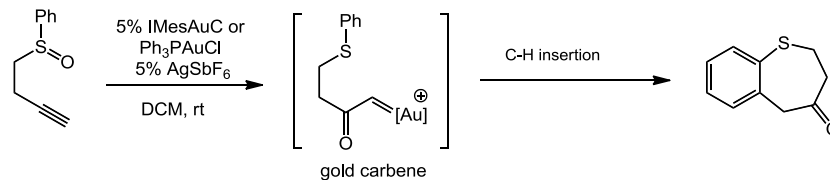
•Mechanism study



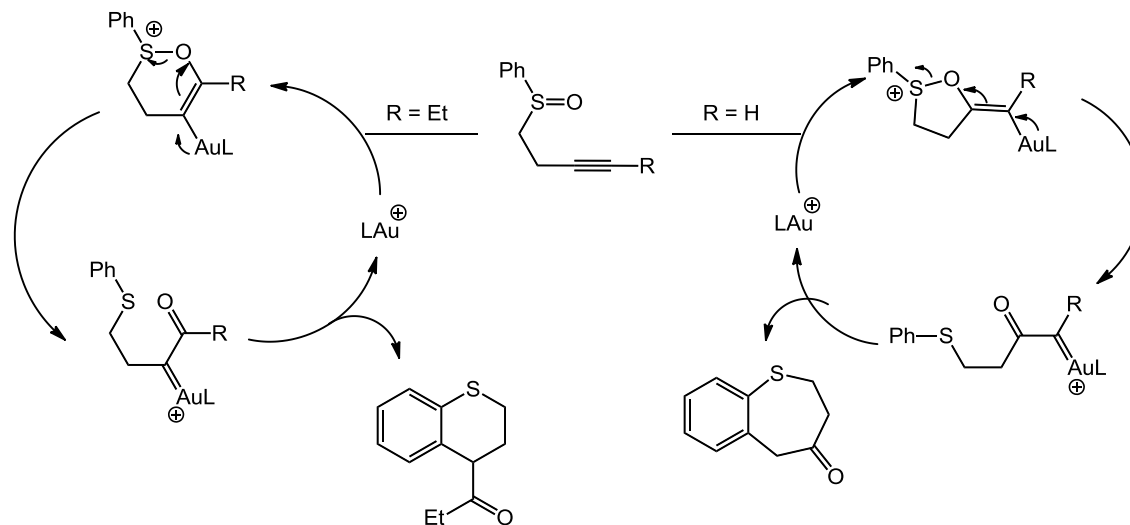
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•Proposed mechanism



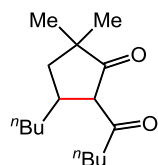
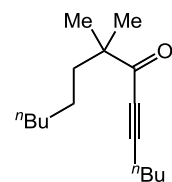
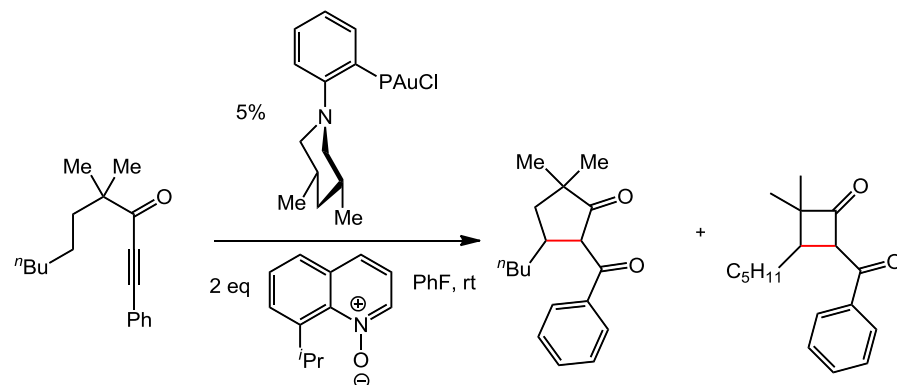
•Proposed mechanism



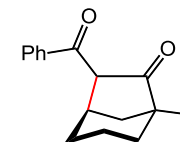
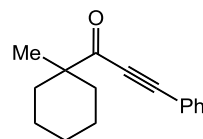
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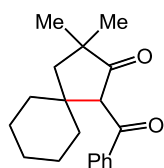
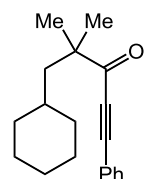
•C-H insertion



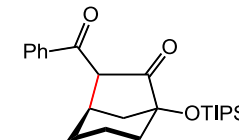
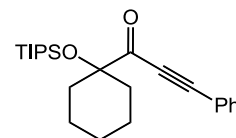
94%
(>25:1)



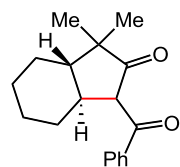
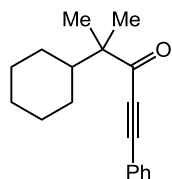
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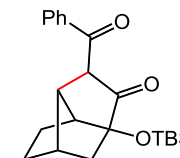
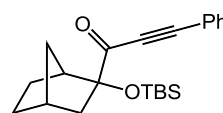
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(18.2:1)



75%



72%
trans/cis : >20:1



76%