
Literature Report 2013-10-09

Huang, W.-X. checker: Wu, B.

Au-Catalyzed Carboalkoxylation of Alkynes

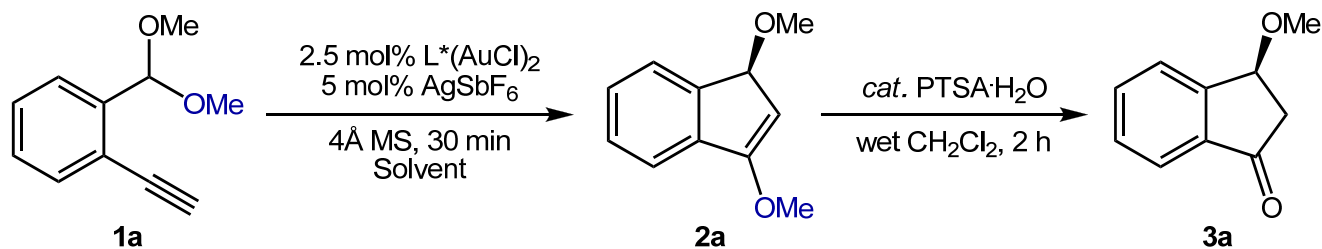
Toste, F. D. *et al.*

J. Am. Chem. Soc. **2013**, *135*, 12600–12603.

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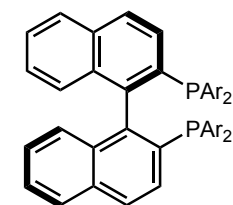
- 1. Au-Catalyzed Enantioselective Carboalkoxylation of Alkynes**
- 2. Toste Group's Previous Work**
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Table 1. Optimization of the Reaction Conditions

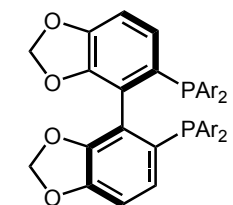


entry	L*	solvent	yield (%)	ee (%)
1	L1	CH ₂ Cl ₂	75	8
2	L2	CH ₂ Cl ₂	77	2
3	L3	CH ₂ Cl ₂	71	5
4	L4	CH ₂ Cl ₂	74	24
5	L4	CCl ₄	74	94
6	L4	benzene	80	89
7	L4	toluene	88	94
8 ^a	L4	toluene	92	95

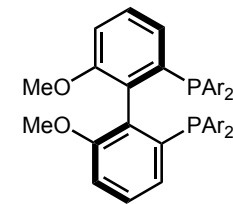
^a2.5 mol % AgSbF₆ was used.



Ar = Ph L1
Ar = 3,5-(t-Bu)₂-4-(MeO)C₆H₂ L2



Ar = 3,5-(t-Bu)₂-4-(MeO)C₆H₂ L3



Ar = 3,5-(t-Bu)₂-4-(MeO)C₆H₂ L4

Table 2. Substrate Scope of Aryl Acetylenes

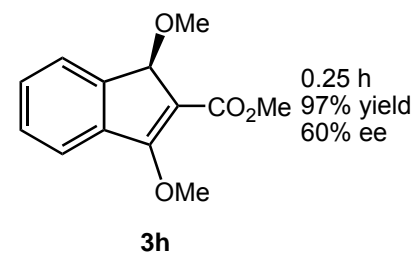
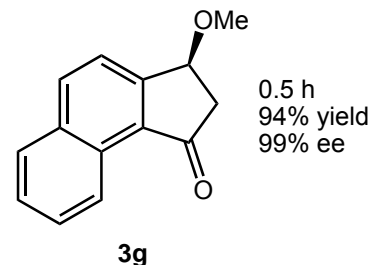
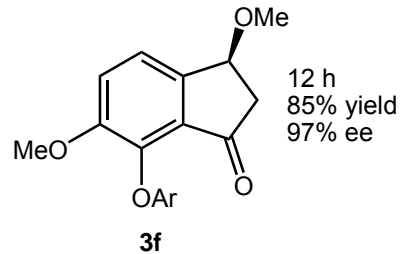
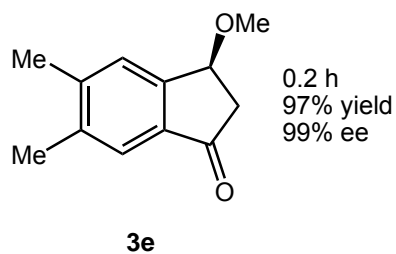
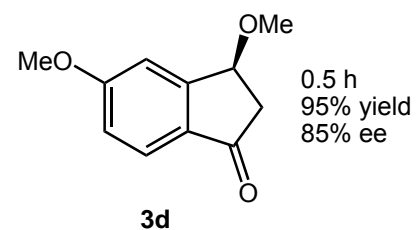
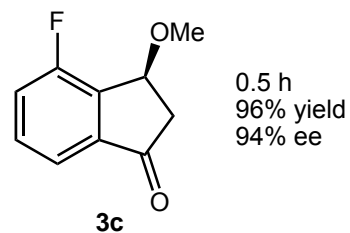
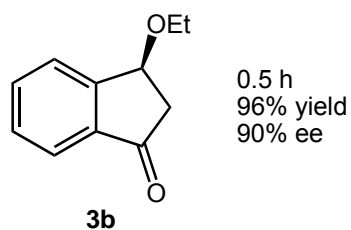
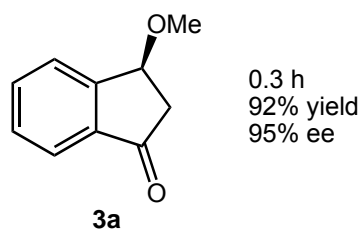
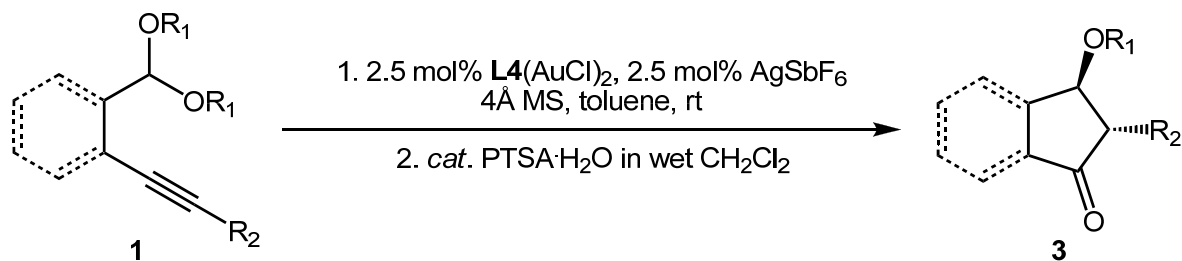
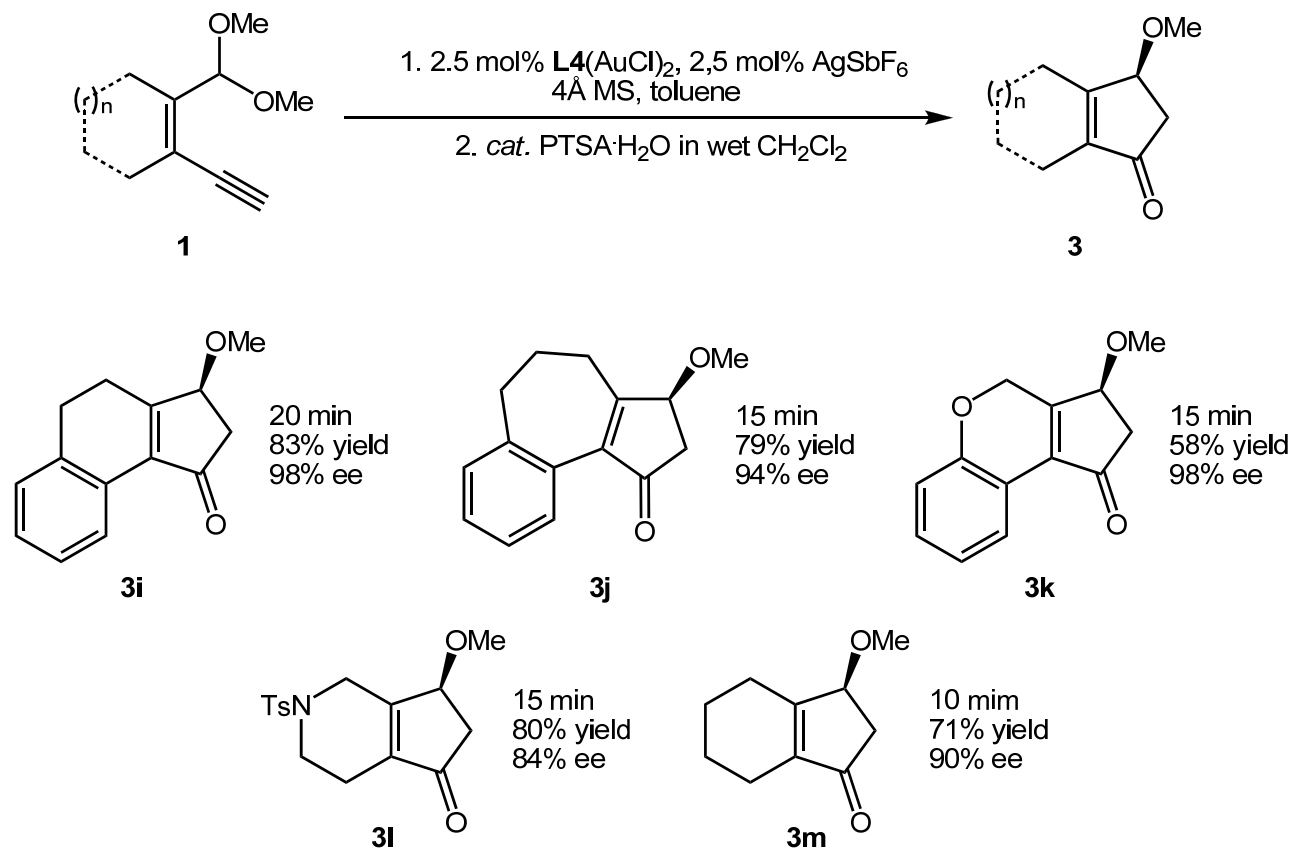
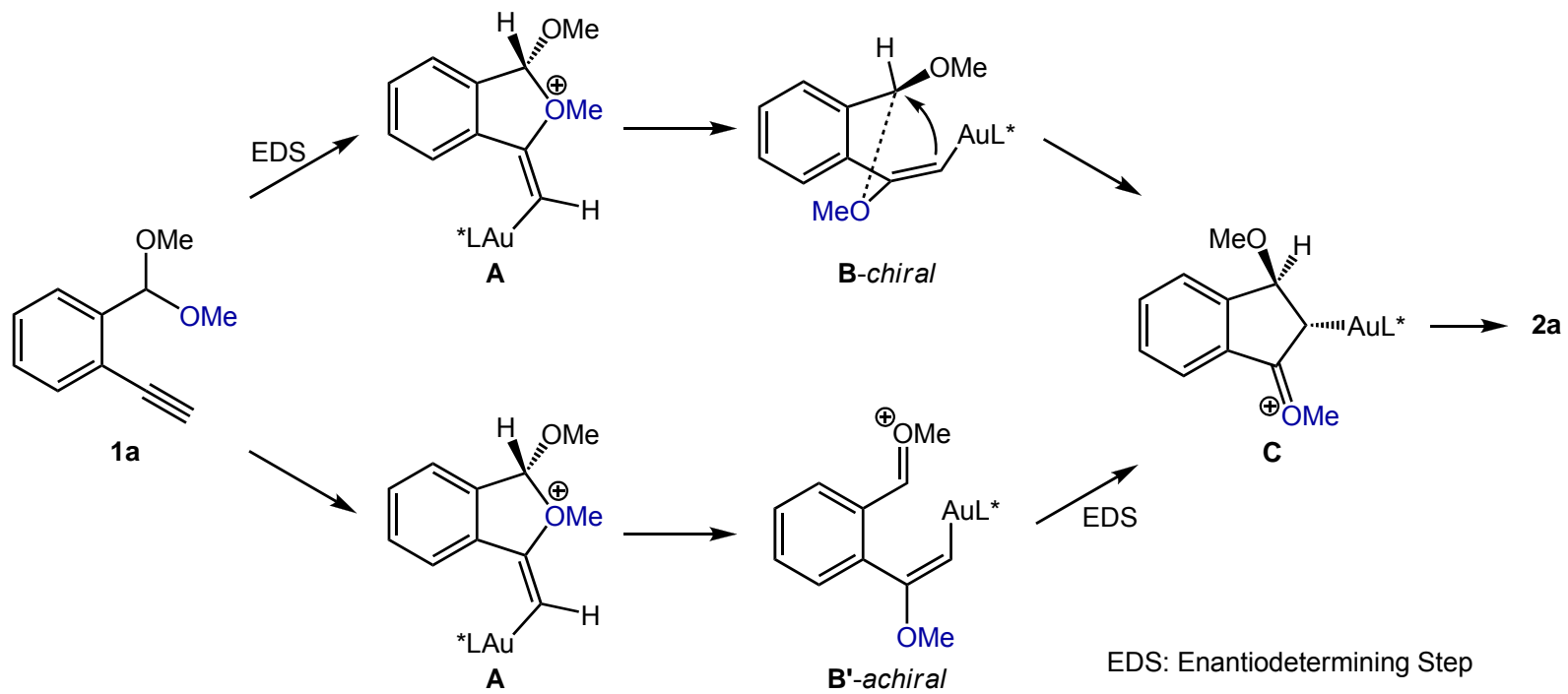


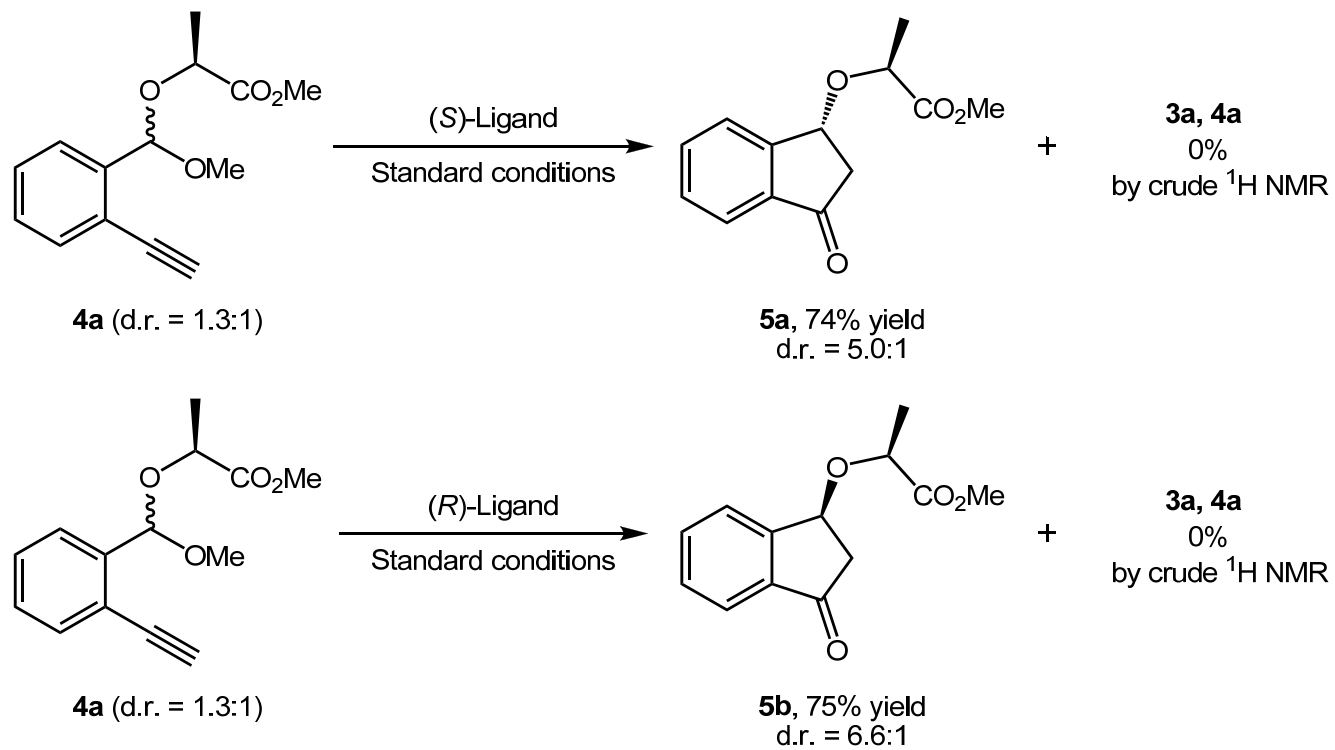
Table 3. Substrate Scope of Vinyl Acetylenes



Scheme 1. Two Possible Pathways

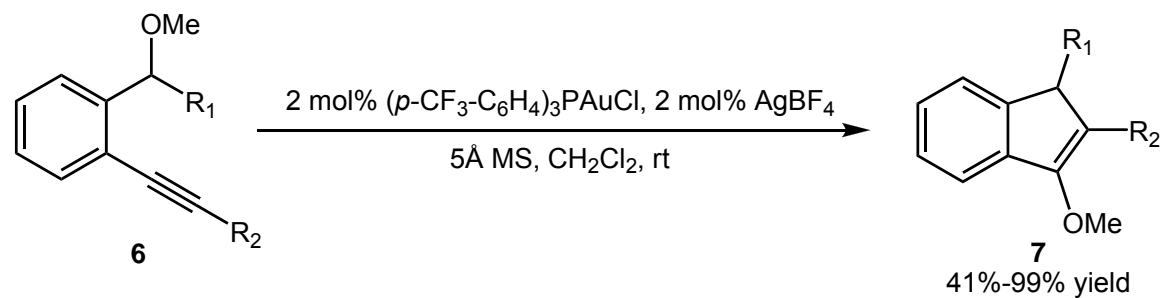


Scheme 2. Mixed Acetal Study

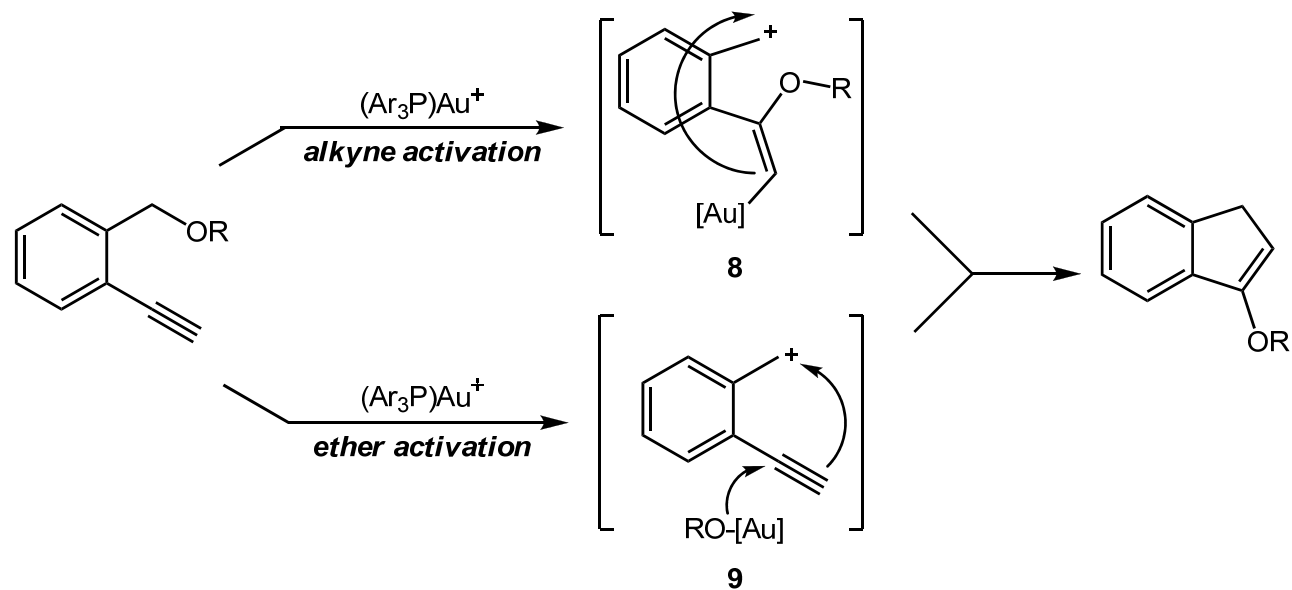


2. Toste Group's Previous Work

Scheme 1. Synthesis of Indenyl Ethers

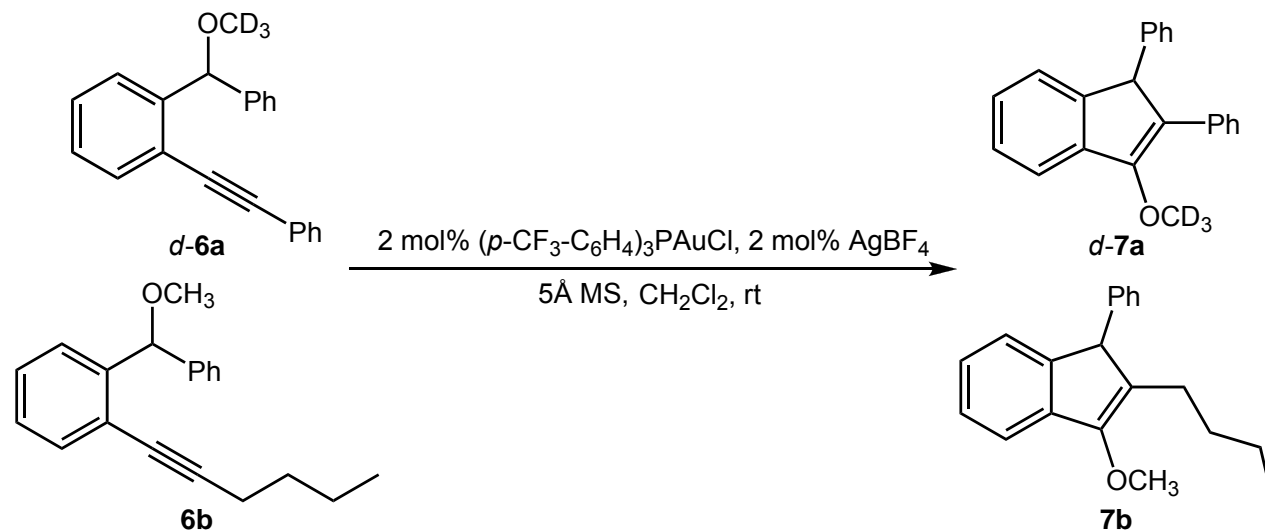


Scheme 2. Two Possible Pathways



Toste, F. D. et al. *J. Am. Chem. Soc.* **2006**, *128*, 12062.

Scheme 3. A Double Label Crossover Experiment



6c $R^1 = \text{Ph}$, $R^2 = \text{CO}_2\text{CH}_3$, $R^3 = \text{CH}_3$ (82% ee)

ent-6d $R^1 = \text{H}$, $R^2 = \text{Ph}$, $R^3 = \text{CH}_3$ (99% ee)

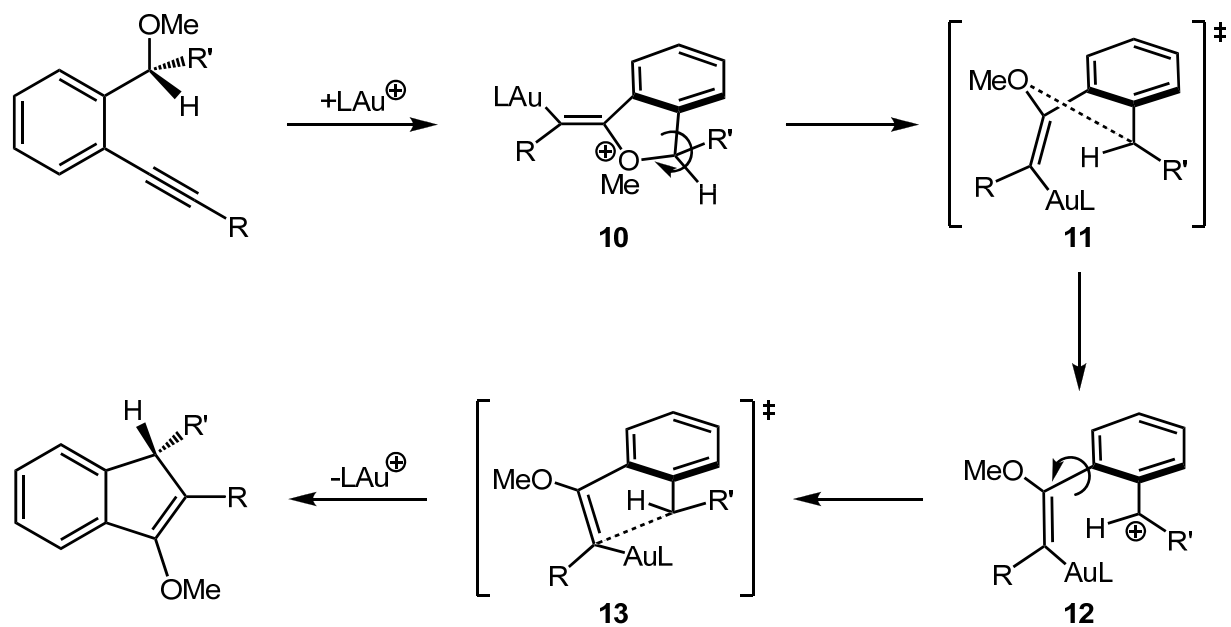
6e $R^1 = \text{Ph}$, $R^2 = \text{CO}_2\text{CH}_3$, $R^3 = \text{allyl}$ (73% ee)

7c (99%, 81% ee)

ent-7d (92%, 95% ee)

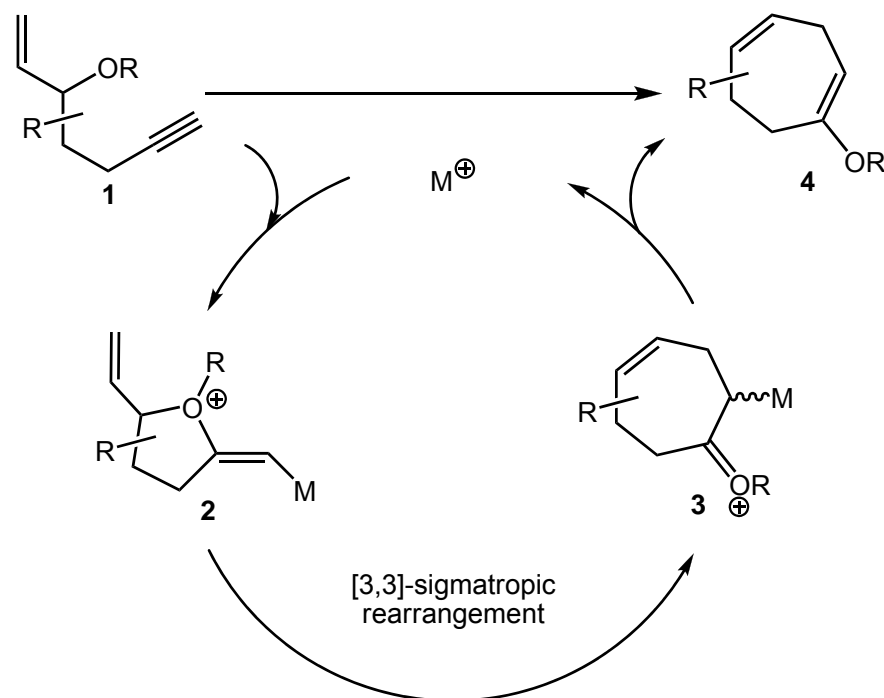
7e (92%, 59% ee)

Scheme 4. Proposed Mechanism



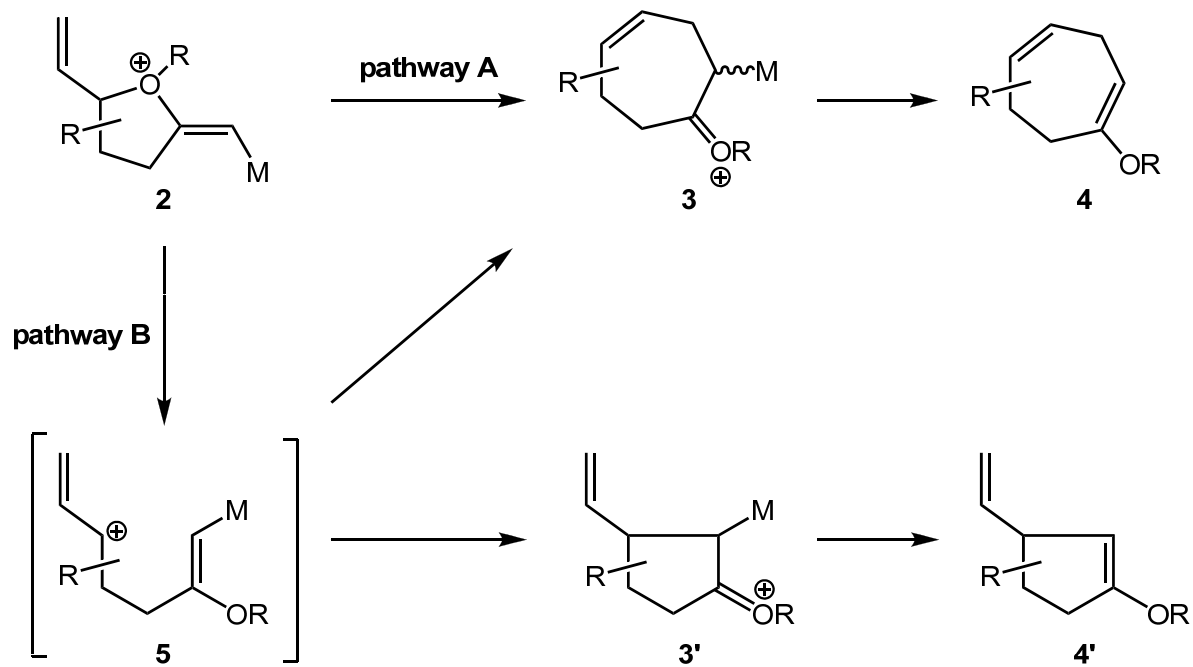
3. Rhee Group's Work

Scheme 1. Proposed Mechanism for the Gold(I)-Catalyzed Cycloisomerization of 3-Alkoxy-1,6-enynes.

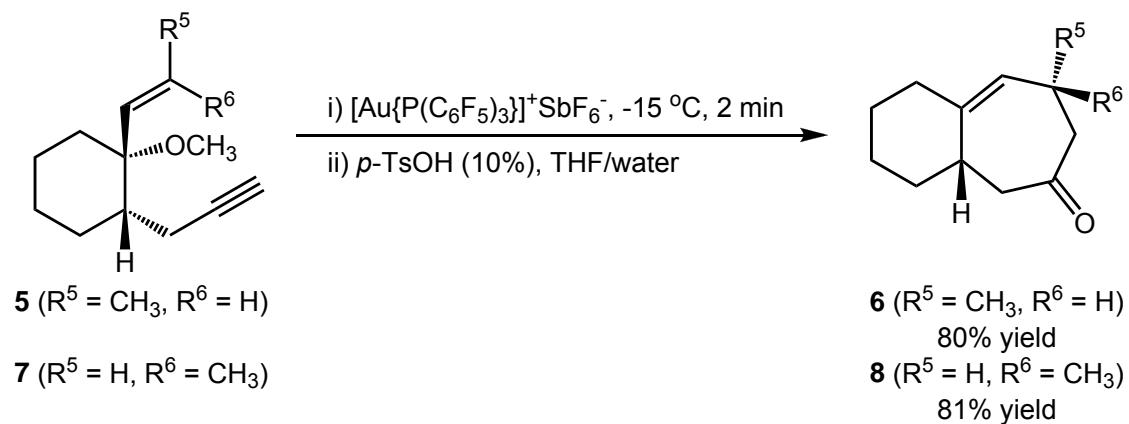
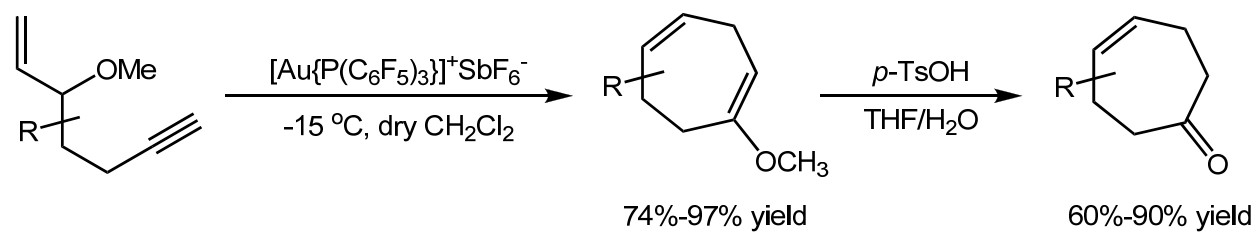


Rhee, Y. H. *et al. Angew. Chem. Int. Ed.* **2008**, *47*, 2263.

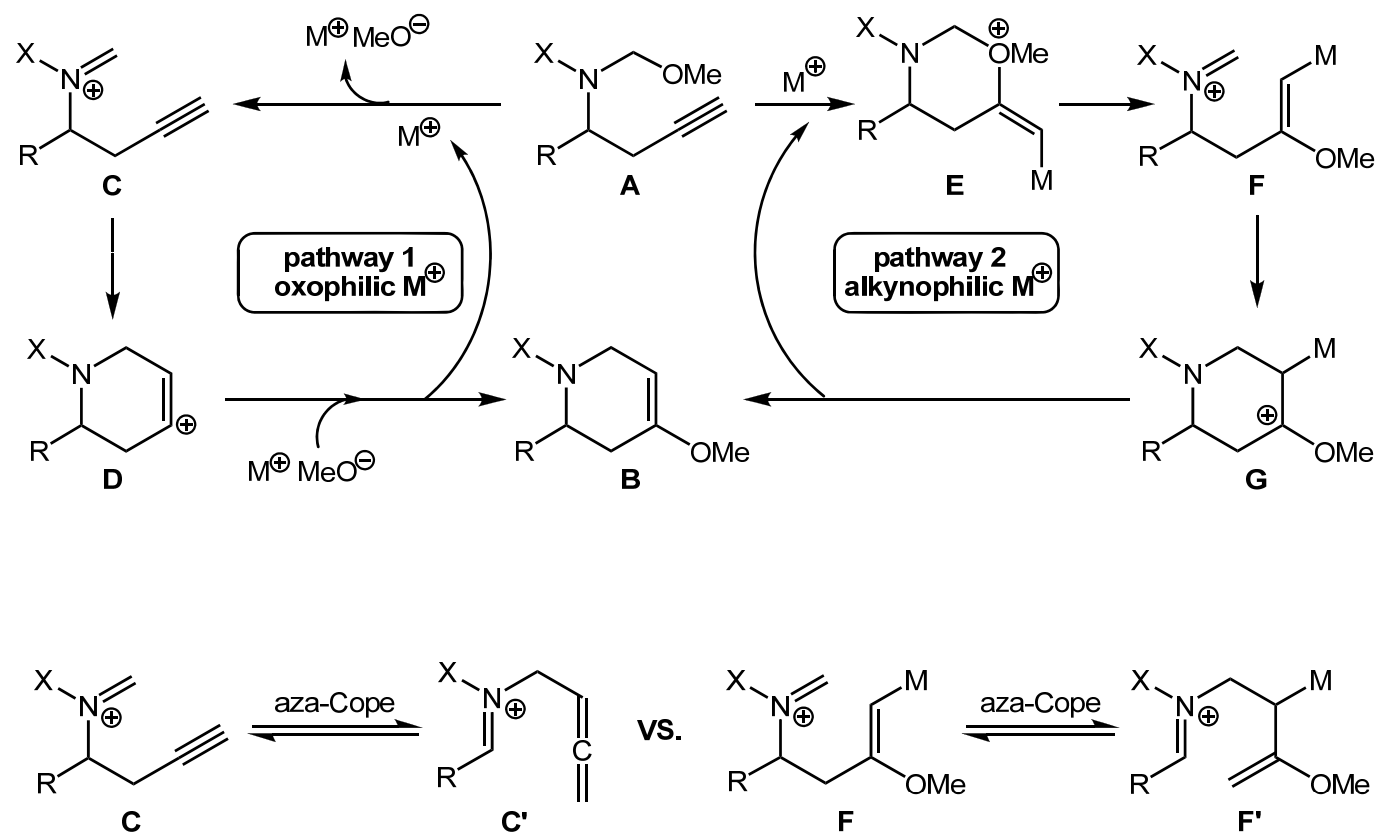
Scheme 2. Sigmatropic Rearrangement (pathway A) versus Carboalkoxylation (pathway B)



Scheme 3. Scope of the Gold(I)-Catalyzed Cycloisomerization of 3-Methoxy-1,6-enynes

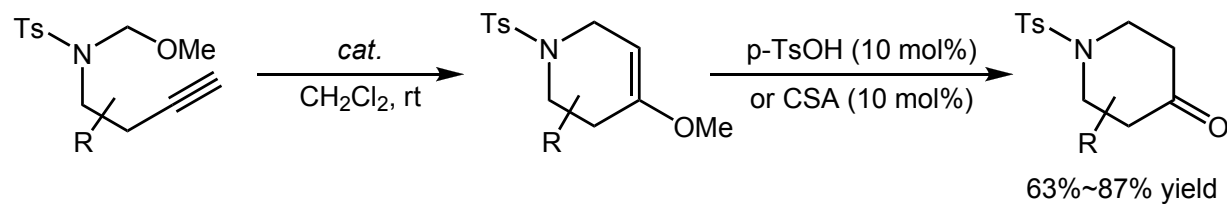


Scheme 1. Two Pathways for the Cycloisomerization of A

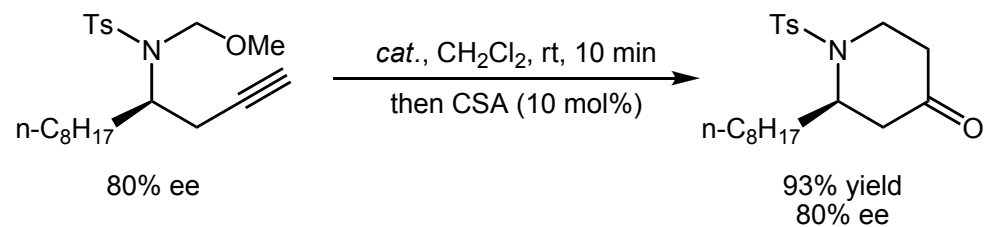


Rhee, Y. H. *et al.* *J. Am. Chem. Soc.* **2009**, *131*, 14660.

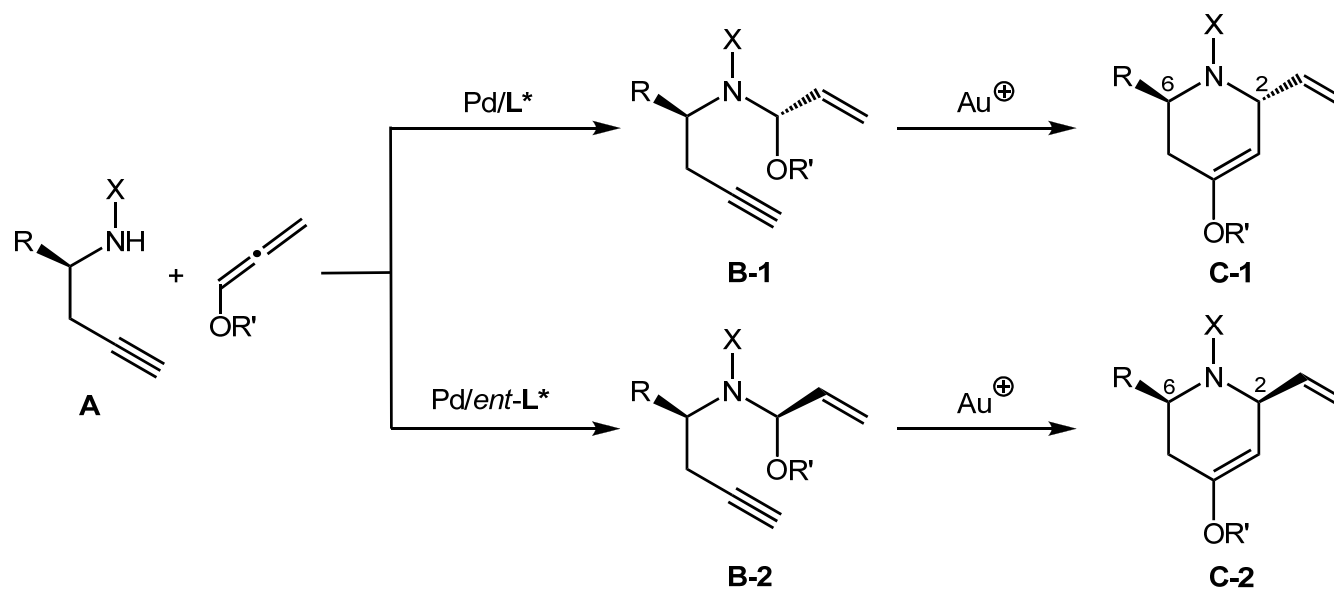
Scheme 2. Scope of the Gold(I)-Catalyzed Cycloisomerization



cat.: Au[P(C₆F₅)₃]SbF₅ (5 mol%) / 2,6-di-*tert*-butylpyridine (4 mol%)

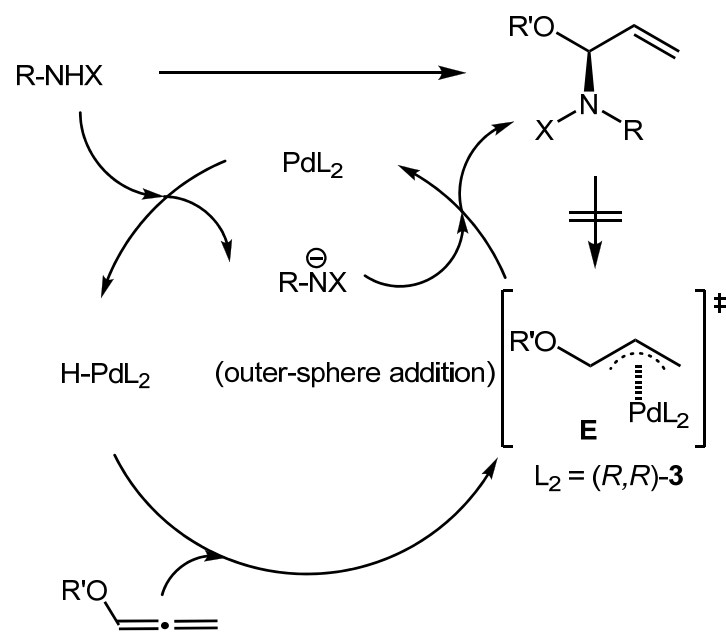
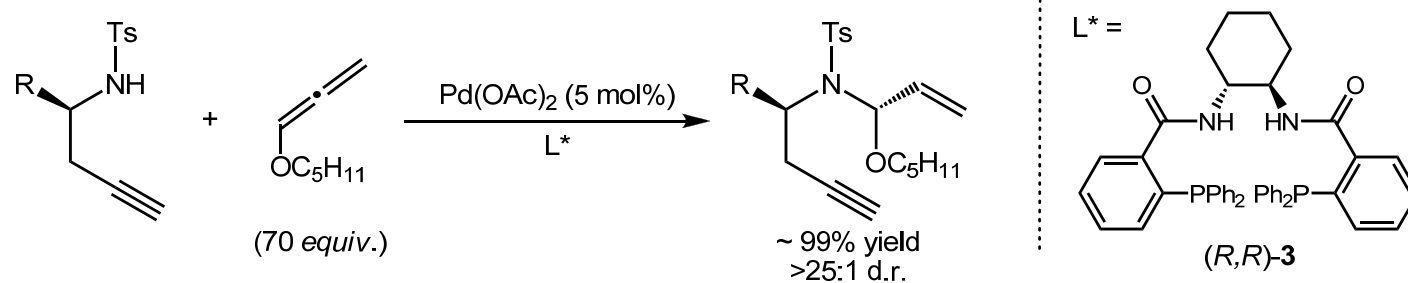


Scheme 1. Synthesis of Stereodefined *N,O*-Acetal and Application

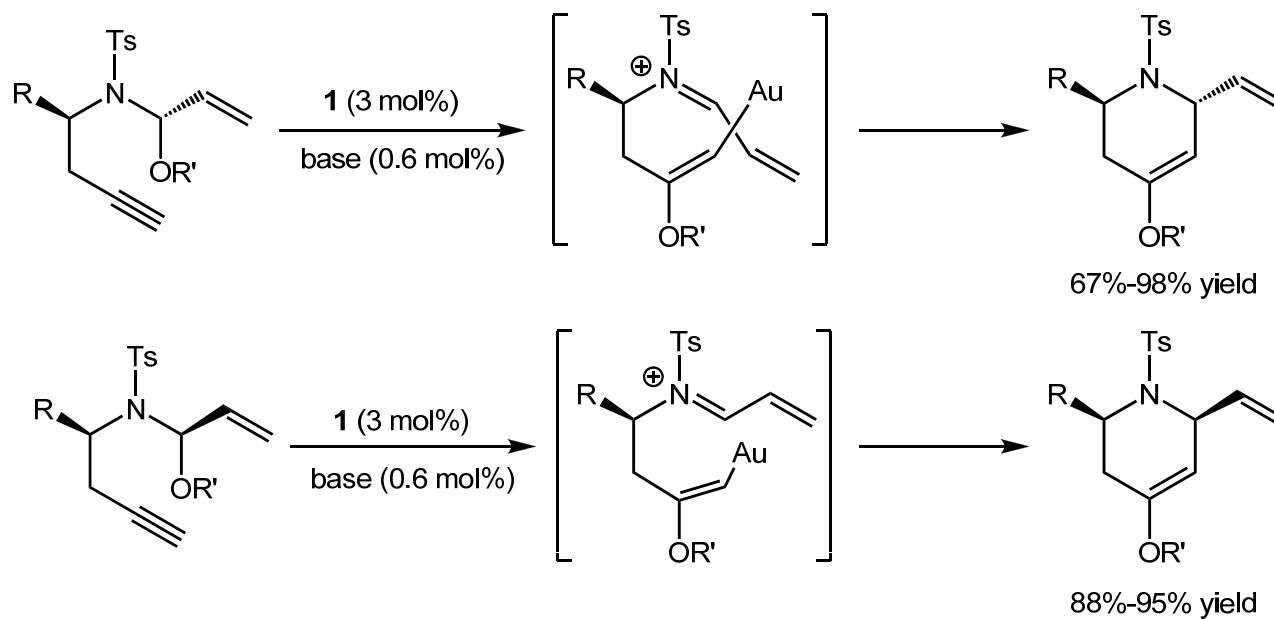


Rhee, Y. H. *et al.* *J. Am. Chem. Soc.* **2012**, *134*, 4011.

Scheme 2. Scope and Mechanism of the Hydroamination



Scheme 2. Gold-Catalyzed Cycloisomerization

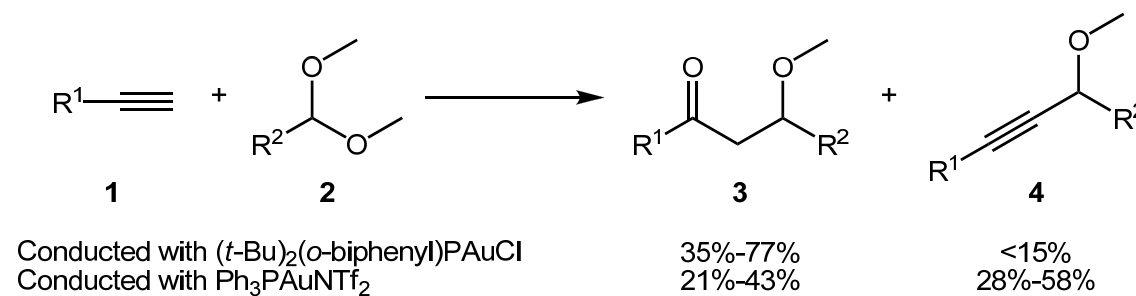


(R' = *n*-C₅H₁₁)

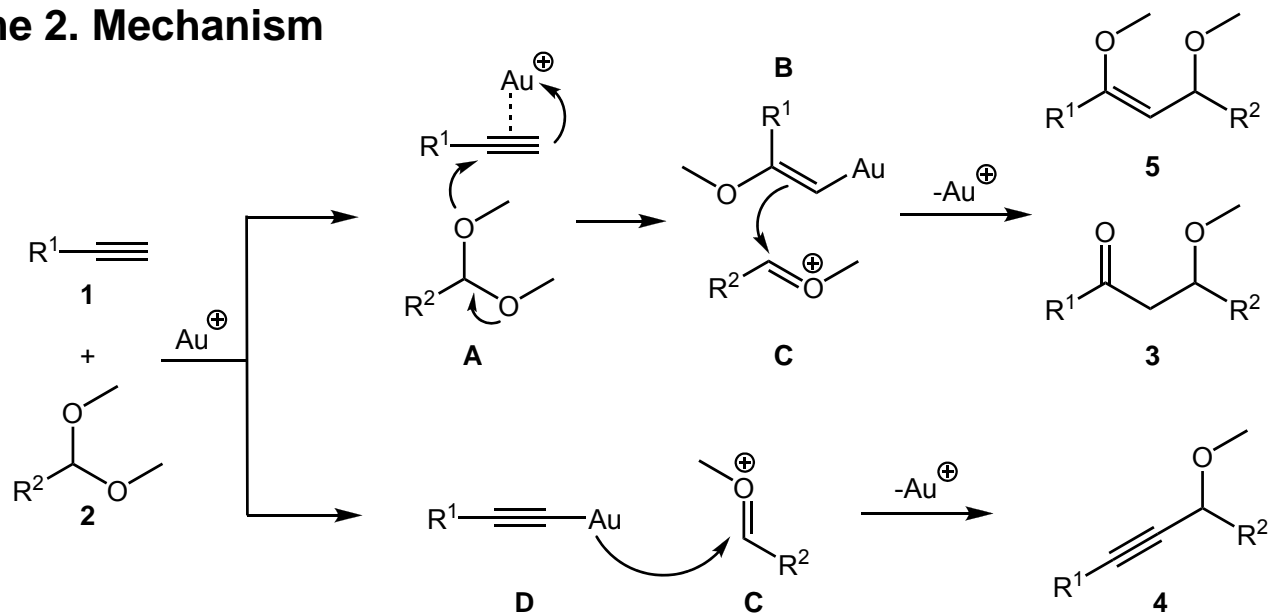
1: Au[P(*t*-Bu)₂(*o*-Ph)Ph]⁺(CH₃CN)SbPF₆⁻
base = 2,6-di-*tert*-butylpyridine

4. Other groups' work

Scheme 1. Gold-Catalyzed Intermolecular Alkyne Carboalkoxylation

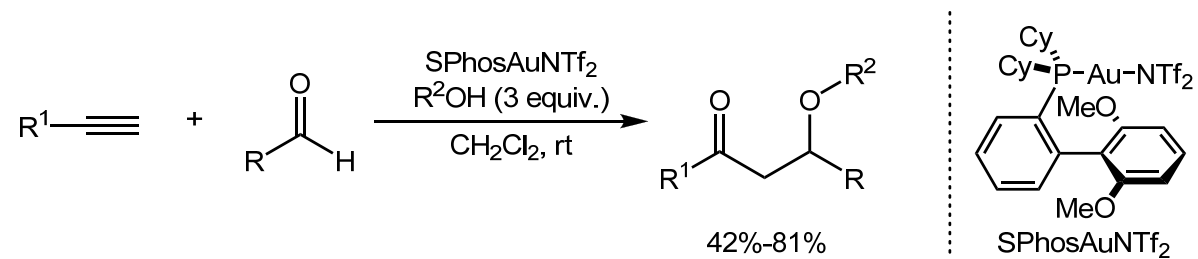


Scheme 2. Mechanism

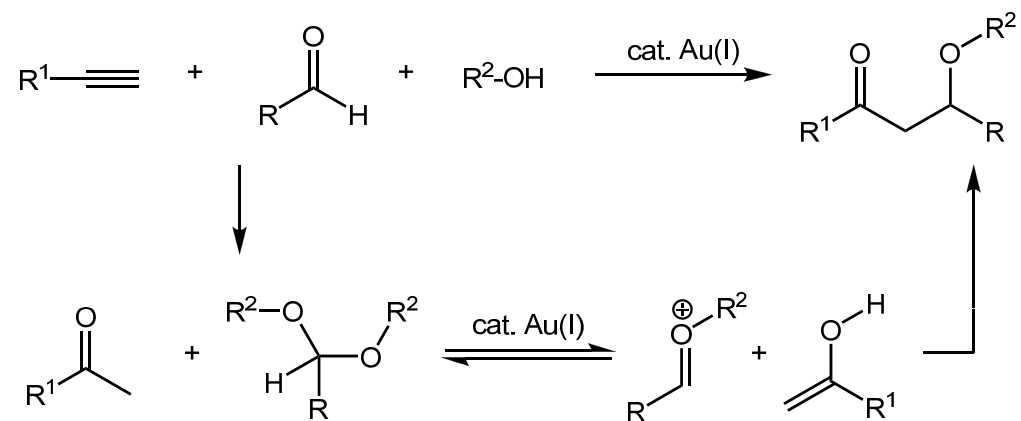


Hu, X. *et al. Adv. Synth. Catal.* **2012**, 354, 981.

Scheme 3. Gold-Catalyzed Intermolecular Alkyne Carboalkoxylation



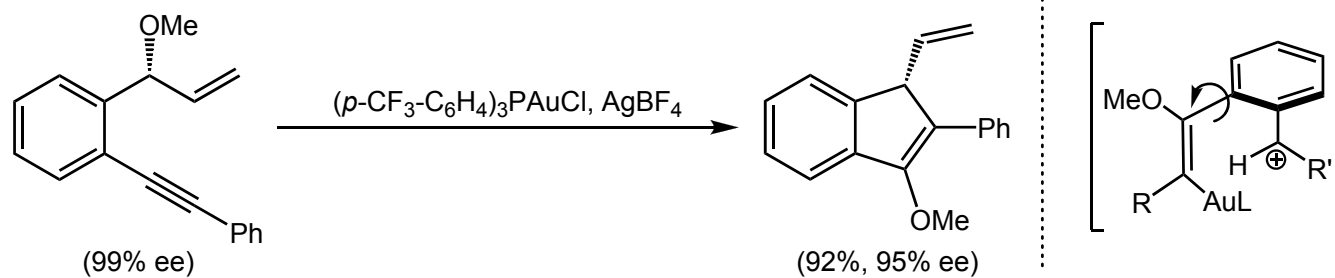
Scheme 4. Mechanism



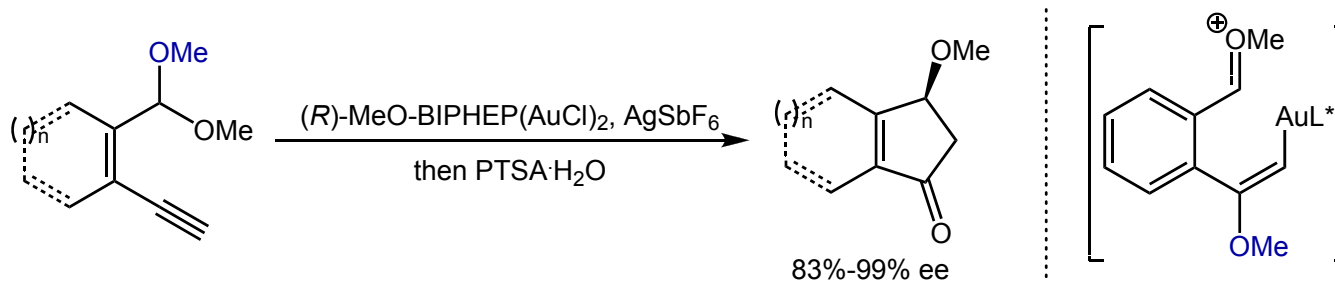
Wolfe, J. P. *et al. Adv. Synth. Catal.* **2012**, 354, 3451.

5. Summary

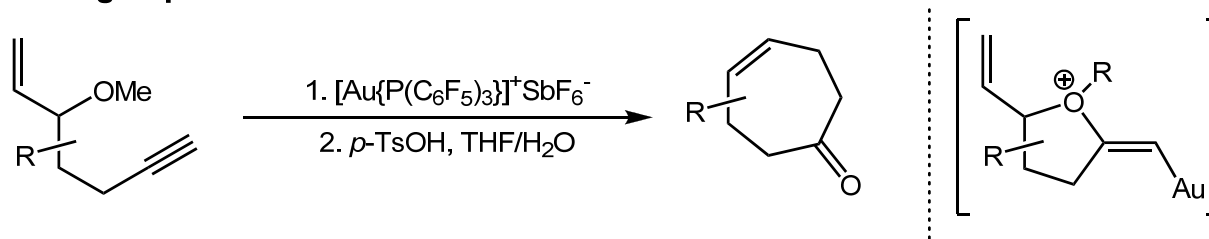
Toste group in 2008



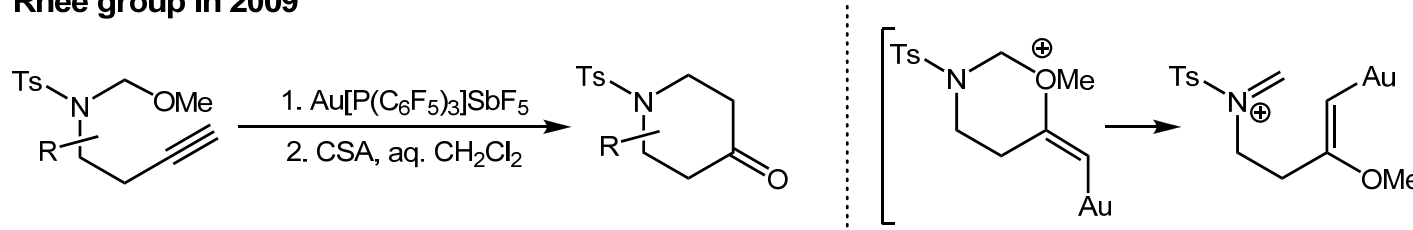
Toste group in 2013



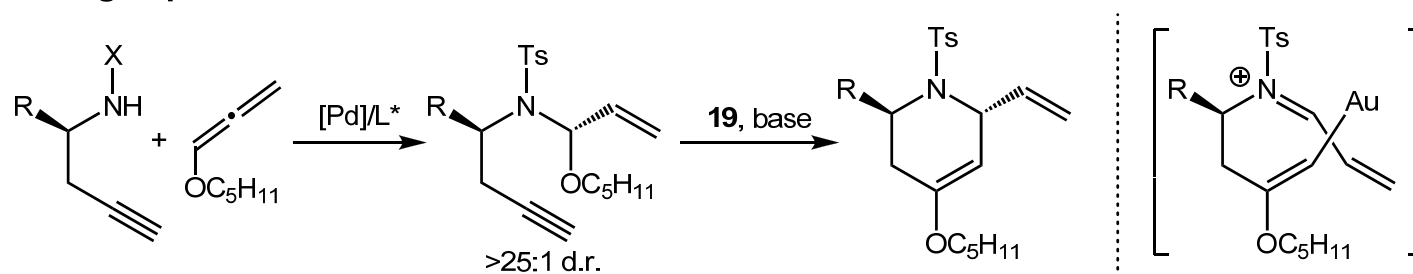
Rhee group in 2008



Rhee group in 2009



Rhee group in 2012



19: $\text{Au}[\text{P}(t\text{-Bu})_2(o\text{-Ph})\text{Ph}]^+(\text{CH}_3\text{CN})\text{SbPF}_6^-$
base = 2,6-di-*tert*-butylpyridine

Gold(I)-catalyzed carboalkoxylation of alkynes affords a direct and atom-economical synthetic approach to diversified cyclic enol ethers bearing stereogenic centers at the β position. We and Rhee reported that carboalkoxylation occurs with efficient chirality transfer from enantio-enriched benzylic ethers and *N,O*-acetals, respectively. Despite the intensive development of homogeneous gold(I)-catalyzed enantio-selective reactions, enantioselective carboalkoxylation of alkynes has posed an unsolved challenge. This could be attributed in part to the low reactivity of the ether C–O bond, which necessitates the use of highly electrophilic catalytic systems and precludes many others developed for enantioselective gold catalysis. In addition, our group's previous work pertaining to chirality transfer suggested that initial desymmetrization of sterically modest ether linkages might be required.

In conclusion, we have developed the first gold-catalyzed enantioselective carboalkoxylation of alkynes, including phenyl acetylenes and vinyl acetylenes, which allowed a variety of highly enantioenriched 3-methoxyindanones and cyclopentenones to be prepared. **Mechanistic studies suggested that a vinylgold species and a prochiral oxocarbenium ion are involved in the enantioselectivity-determining cyclization.** Despite the prevalence of vinylgold intermediates in gold-catalyzed reactions of allenes and alkynes, this reaction constitutes a rare example of enantioselective carbon-carbon bond formation from this organometallic species.

谢谢大家，请多批评指正！
