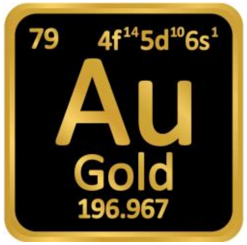
Outline:

1. Hydro-alkoxylation/amination/arylation
2. Ketalisation
3. Glycosylation
4. Conia-Ene Reaction
5. Enyne Cycloisomerization
6. 1,2-Acyloxy Migration
7. 1,3-Acyloxy Migration



9/12/2022
Au: \$55.33/gram
Pd: \$74.40/gram
Rh: \$479.05/gram

Key reactivity: Gold complexes are strong π-Lewis acids and act as “large” protons. Protodeauration is very facile.

Echavarren, A. M. *Chem. Rev.* **2015**, *1155*, 9028. https://doi.org/10.1021/cr500691k

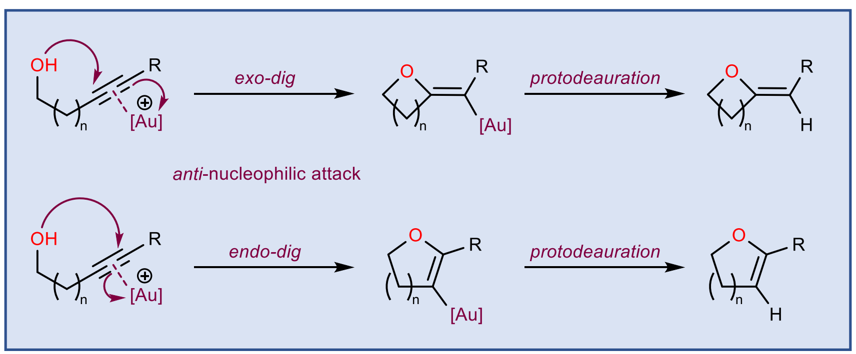
Hashmi, A. S. K. *Chem. Soc. Rev.* **2016**, *45*, 1331. **https://doi.org/10.1039/C5CS00721F**

Hashmi, A. S. K. *Chem. Soc. Rev.* **2011**, *41*, 2448. **https://doi.org/10.1039/C1CS15279C**

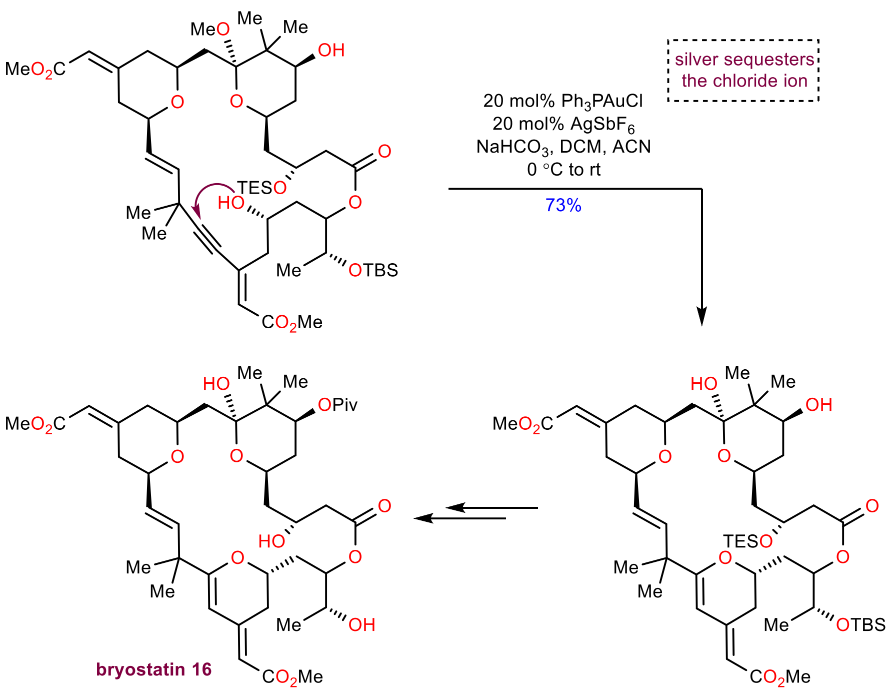
Hashmi, A. S. K. *Chem. Soc. Rev.* **2008**, *37*, 1766. **https://doi.org/10.1039/B615629K**

1. Hydro-alkoxylation/amination/arylation

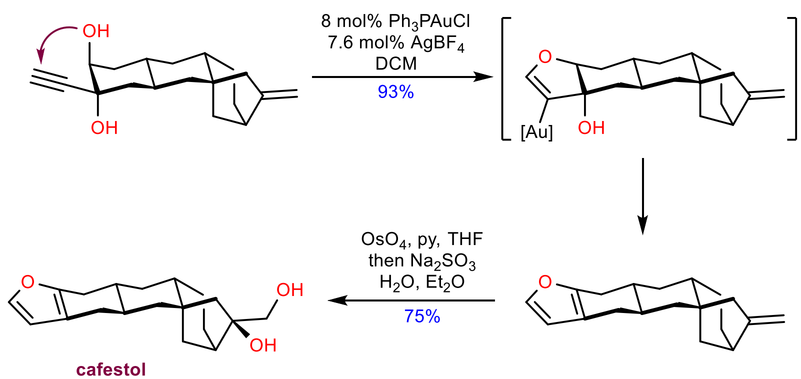
a) Hydroalkoxylation



Great replacement for toxic mercury



Trost, B. M. *Nature* **2008**, *456*, 485. https://doi.org/10.1038/nature07543



Hong. R. *Org. Lett.* **2014**, *16*, 2162. https://doi.org/10.1021/ol500623w

Gold-Catalyzed Transformations in Total Synthesis

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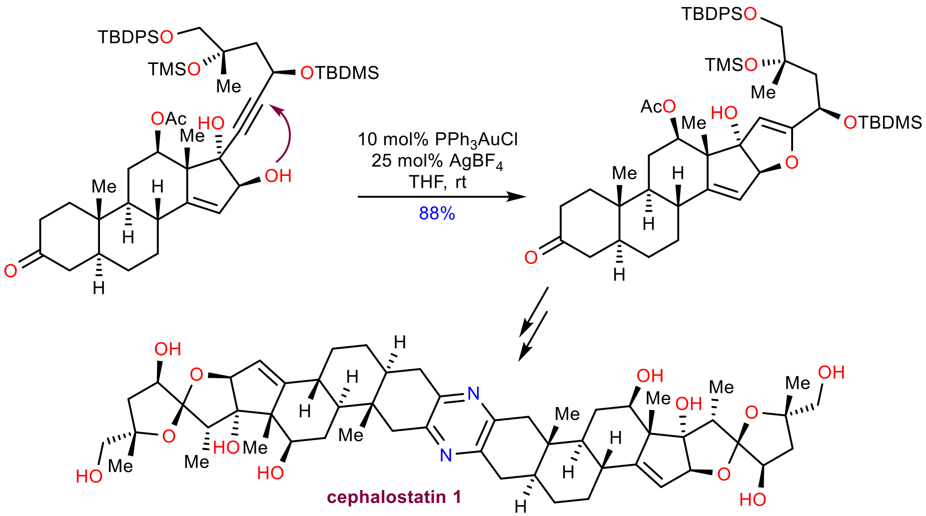
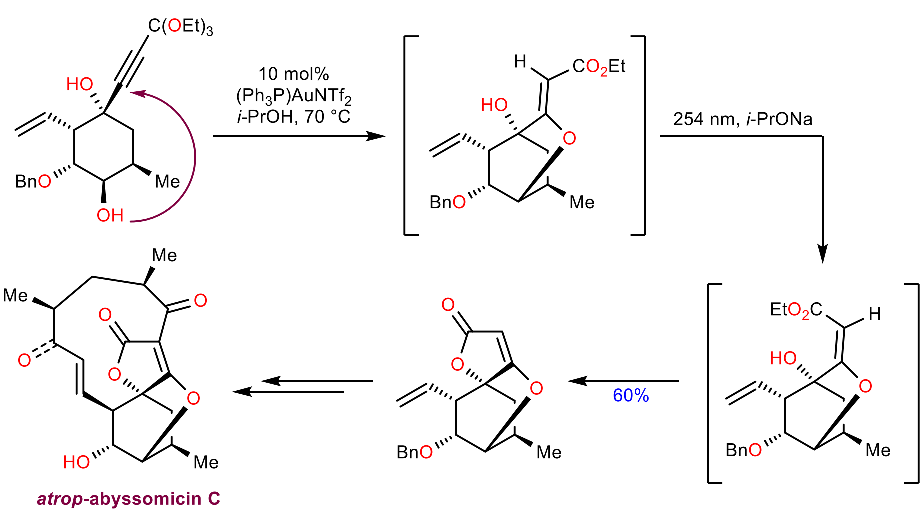
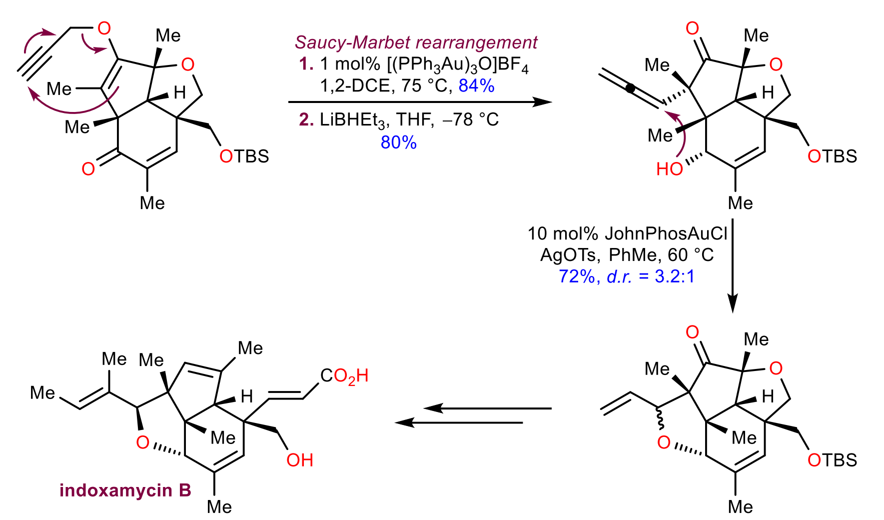


Shair, M. D. *J. Am. Chem. Soc.* **2010**, *132*, 275. https://doi.org/10.1021/ja906996c



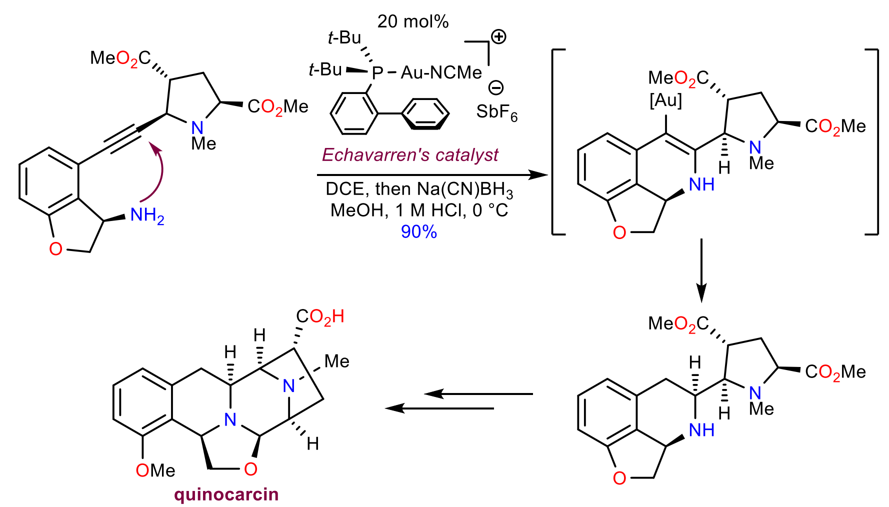
Saicic, R. *Angew. Chem. Int. Ed.* **2012**, *51*, 5687. https://doi.org/10.1002/anie.201108223

b) Hydroalkoxylation of allenes

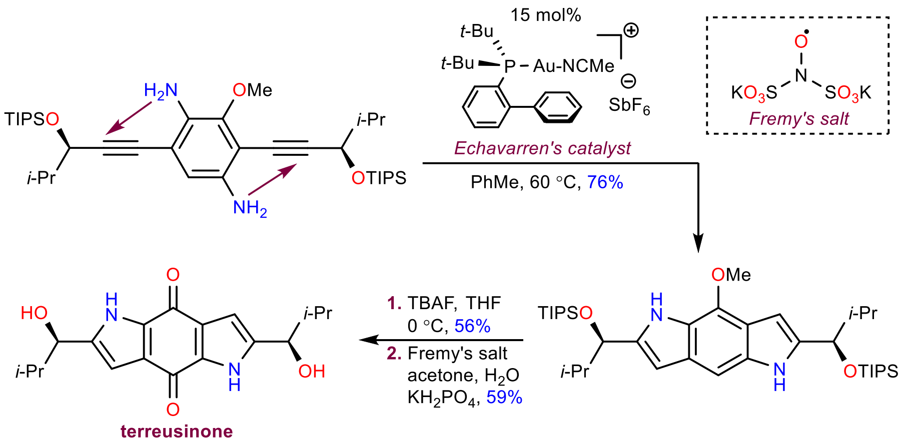


Carreira, E. M. *Angew. Chem. Int. Ed.* **2012**, *51*, 3474. https://doi.org/10.1002/anie.201109175

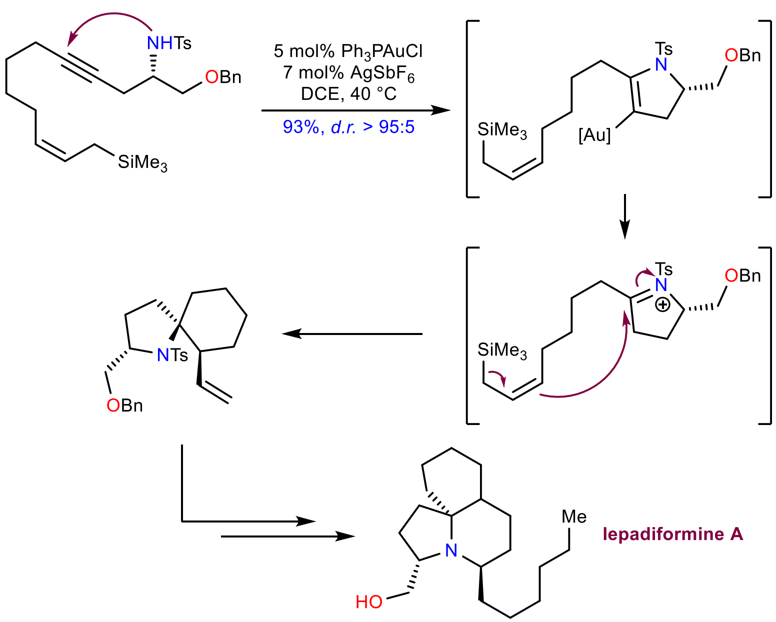
c) Hydroamination



Ohno, H. *Angew. Chem. Int. Ed.* **2012**, *51*, 9169. https://doi.org/10.1002/anie.201205106

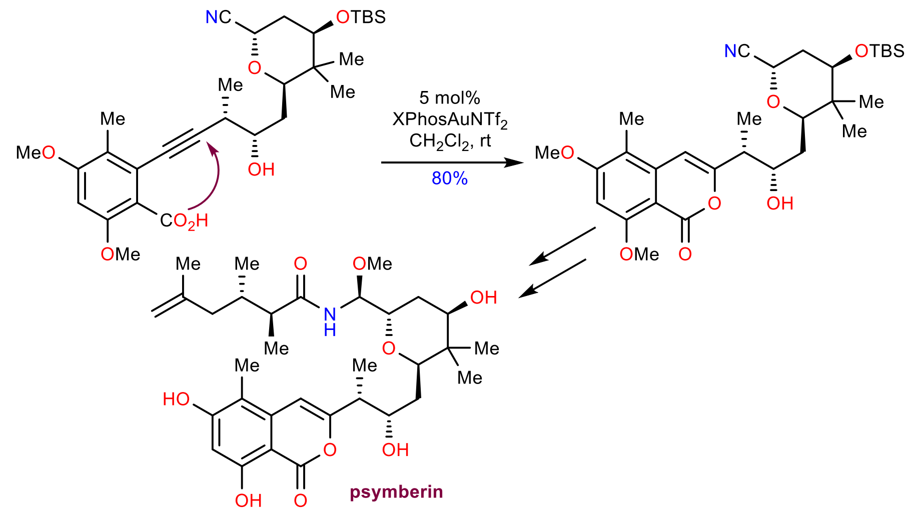


Sperry, J. *Tetrahedron* **2013**, *69*, 4563. https://doi.org/10.1016/j.tet.2013.04.025

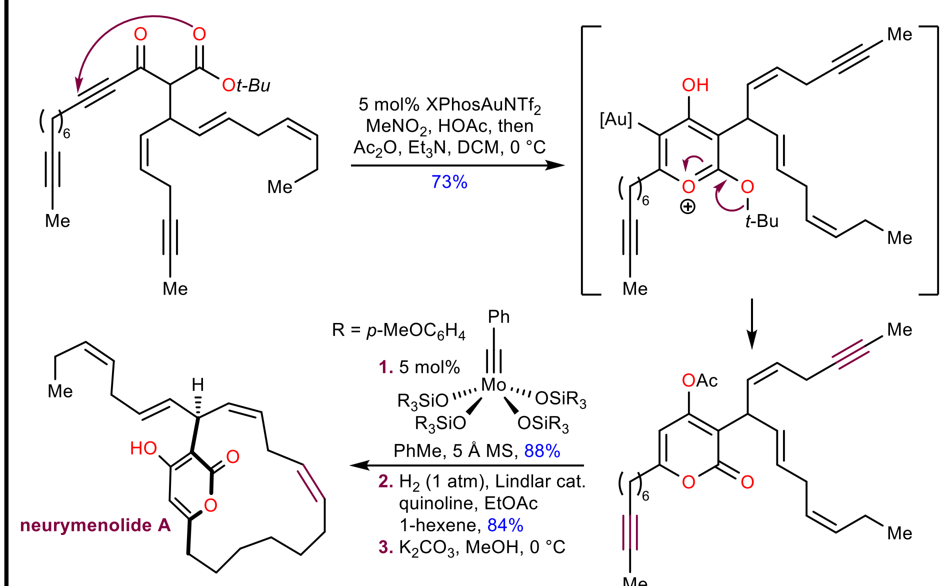


Fuwa, H. *Org. Lett.* **2022**, *24*, 6237. https://doi.org/10.1021/acs.orglett.2c02007

d) Hydrocarboxylation

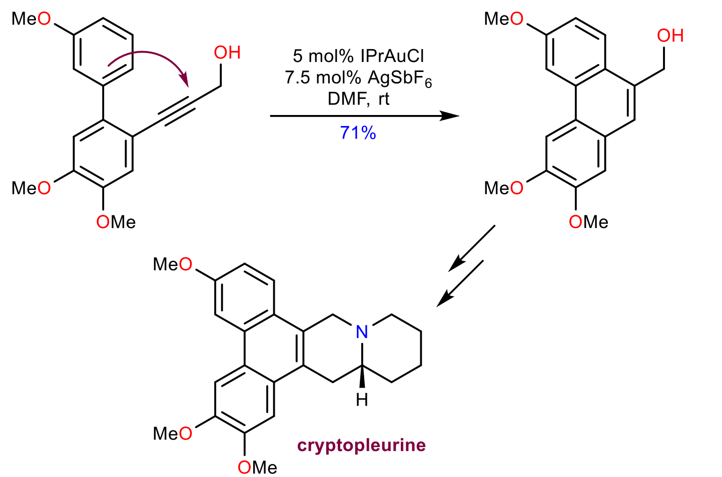


De Brabander, *J. Am. Chem. Soc.* **2012**, *134*, 17083. https://doi.org/10.1021/ja3057612

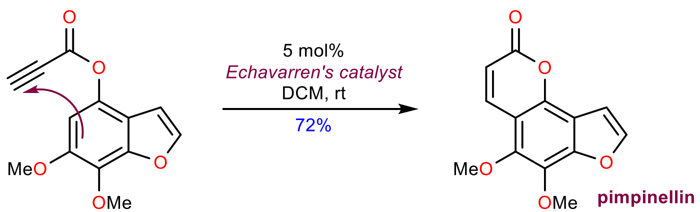


Furstner, A. *Angew. Chem. Int .Ed.* **2012**, *51*, 6929. https://doi.org/10.1002/anie.201203180

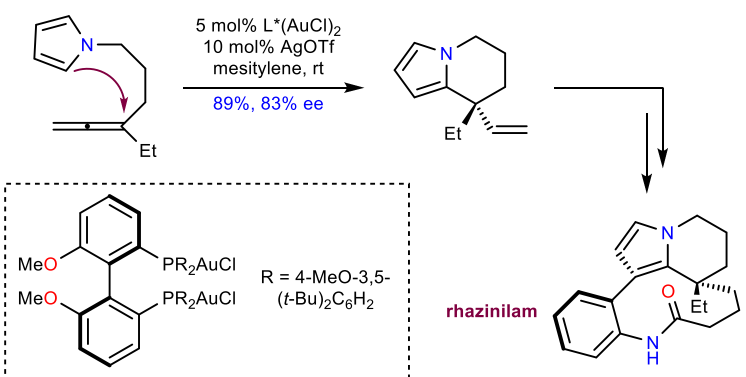
e) Hydroarylation



Shair, M. D. *J. Am. Chem. Soc.* **2010**, *132*, 275. https://doi.org/10.1021/ja906996c

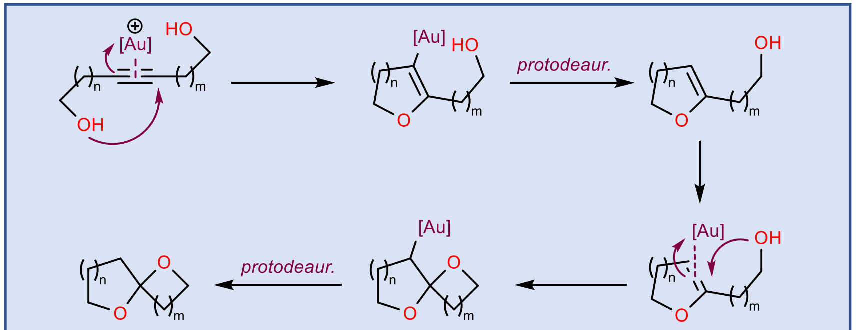


Banwell, M. G. *J. Org. Chem.* **2013**, *78*, 9876. https://doi.org/10.1021/jo401583q

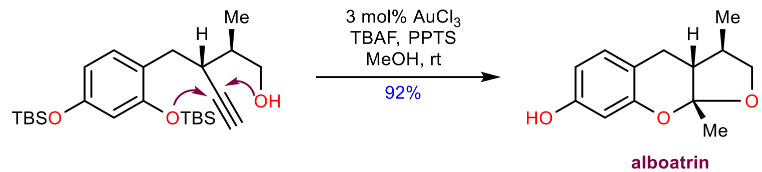


Voituriez, A. *Org. Lett.* **2017**, *19*, 4794. https://doi.org/10.1021/acs.orglett.7b02210

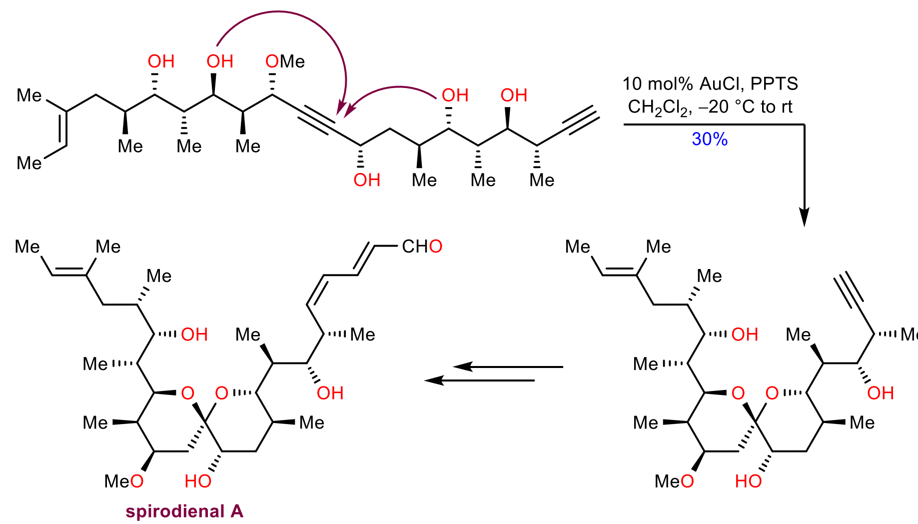
2. Ketalisation



Additional acid is often required to promote the second cyclization step.



Sarkar, T. K. *J. Org. Chem.* **2013**, *78*, 2413. https://doi.org/10.1021/jo302545n



Ley, S. V. *Angew. Chem. Int. Ed.* **2014**, *53*, 4915. https://doi.org/10.1002/anie.201402056

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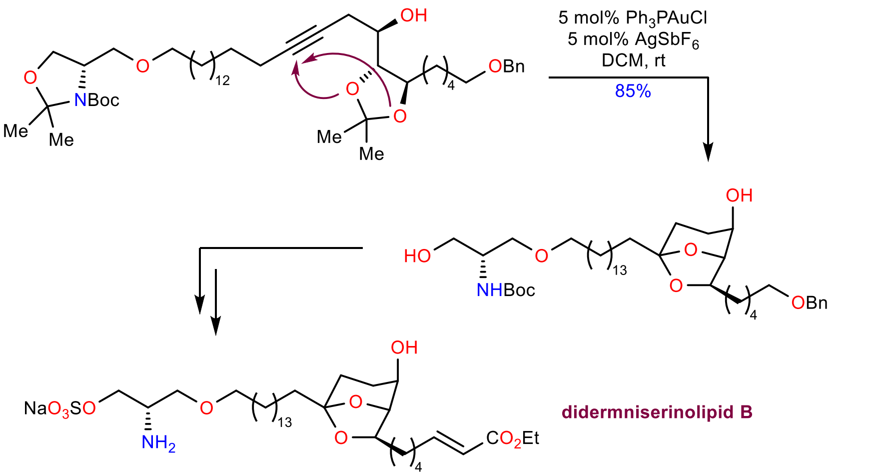
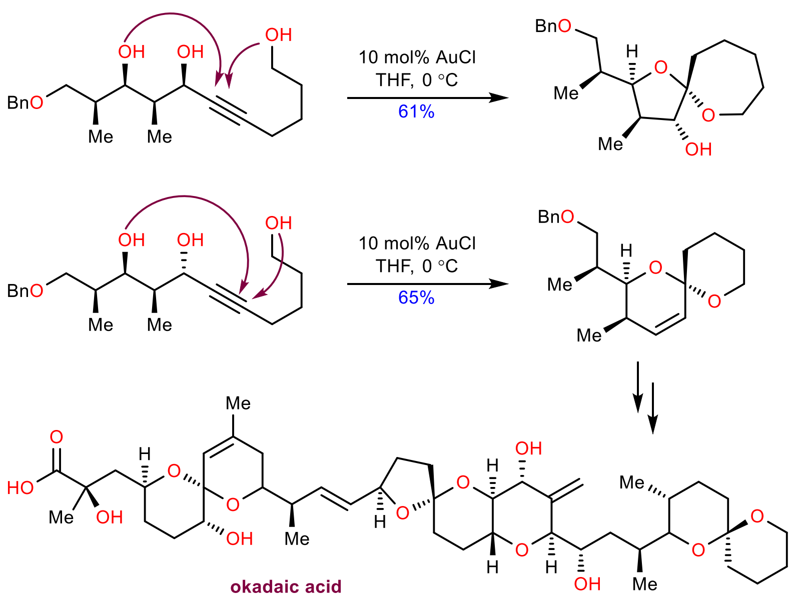
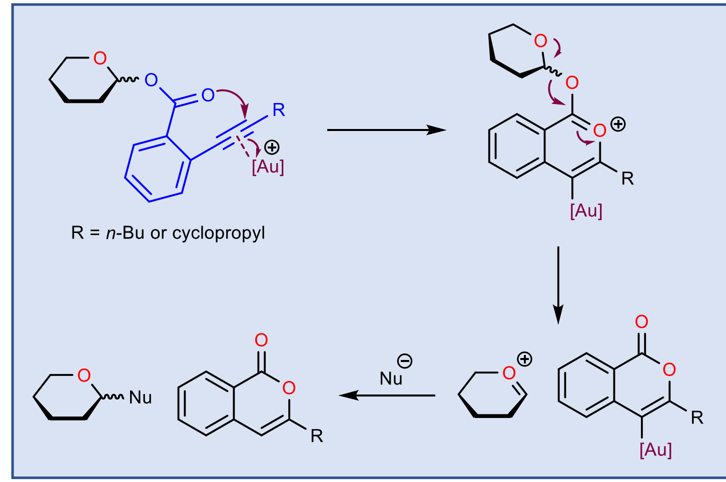


Ramana, C. V. *Tetrahedron* **2013**, *69*, 1881. https://doi.org/10.1016/j.tet.2012.12.045

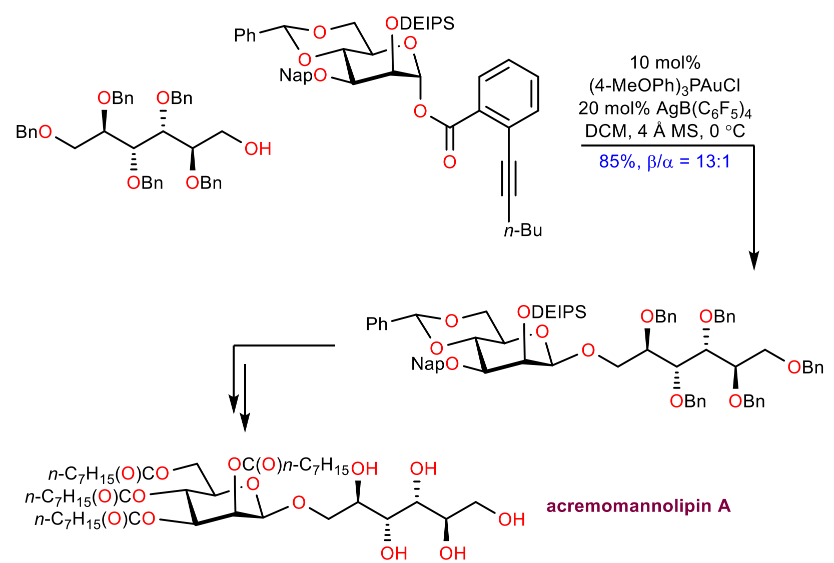


Forsyth, C. J. *Org. Lett.* **2010**, *12*, 4528. https://doi.org/10.1021/ol101833h

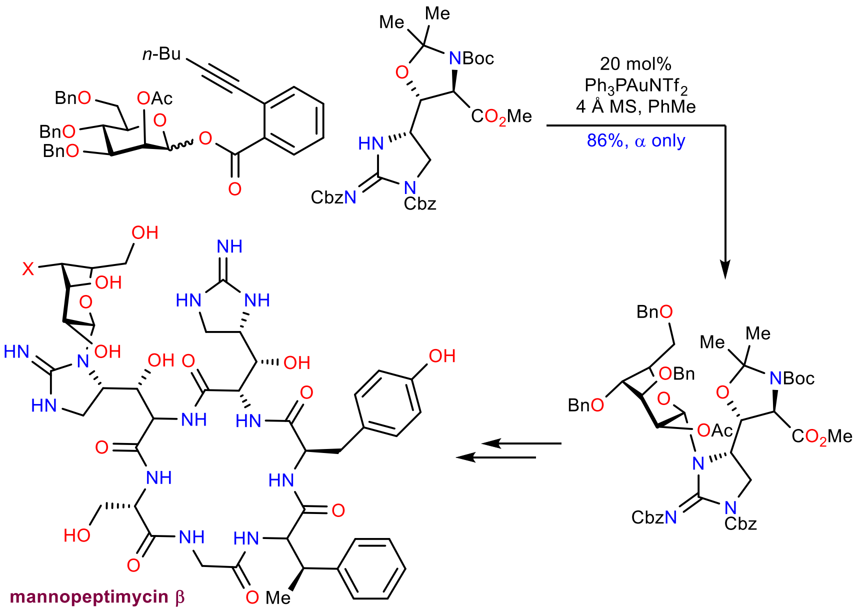
3. Glycosylation



Yu, B. *Tetrahedron Letters* **2008**, *49*, 3604. https://doi.org/10.1016/j.tetlet.2008.04.017
Yu, B. *Chem. Eur. J.* **2010**, *16*, 1871. https://doi.org/10.1002/chem.200902548
Yu, B. *Acc. Chem. Res.* **2018**, *51*, 507. https://doi.org/10.1021/acs.accounts.7b00573



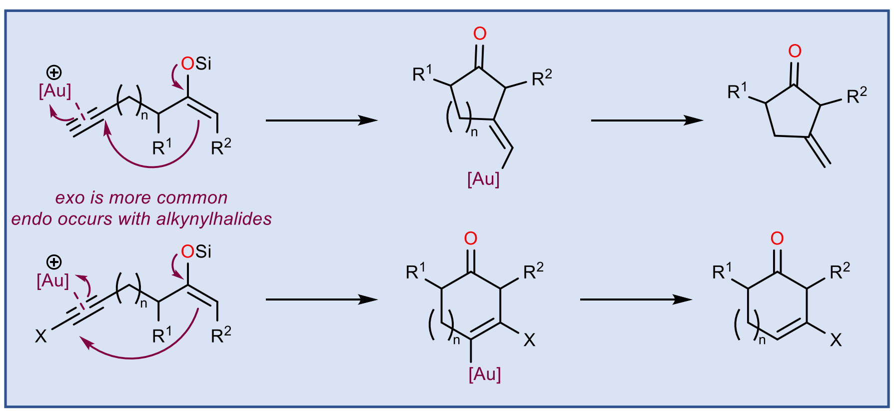
Li, M. *J. Org. Chem.* **2015**, *80*, 4164. https://doi.org/10.1021/acs.joc.5b00140

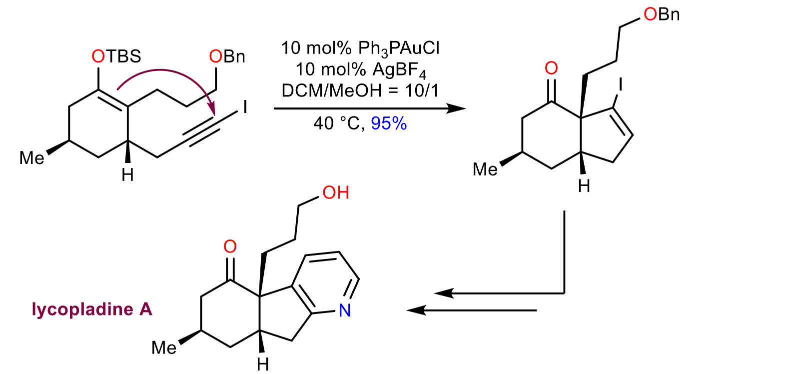


Chen, G. *J. Am. Chem. Soc.* **2016**, *138*, 3926. https://doi.org/10.1021/jacs.6b01384

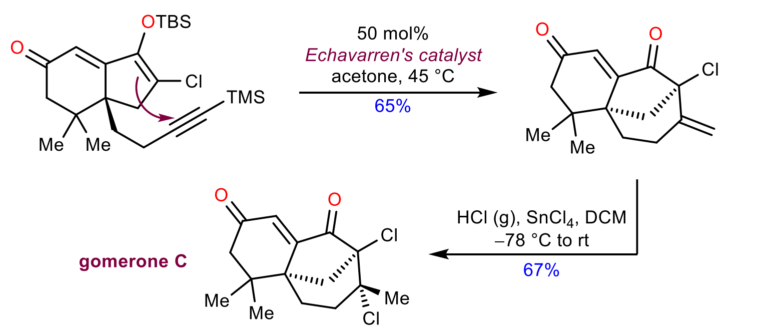
For many more examples, see: Yu, B. *Chem. Soc. Rev.* **2018**, *47*, 7954. https://doi.org/10.1039/C8CS00209F

4. Conia-Ene Reaction

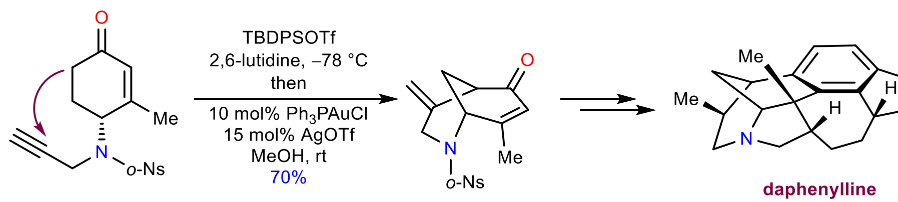




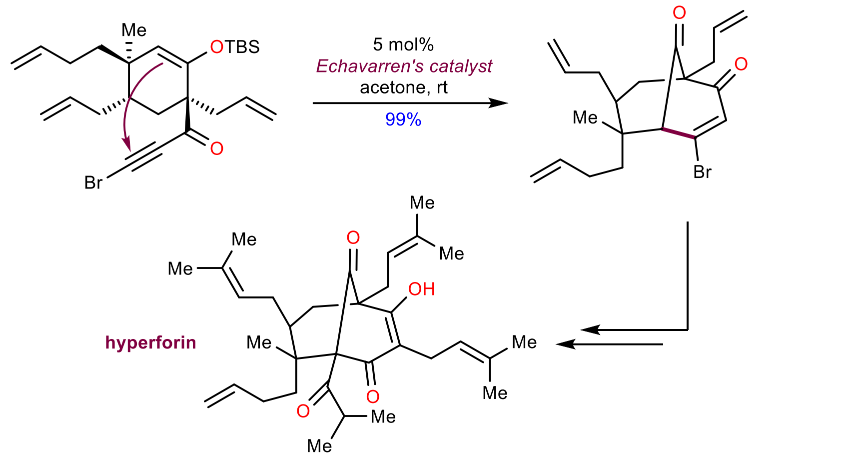
Toste, D. F. *Angew. Chem. Int. Ed.* **2006**, *45*, 5991. https://doi.org/10.1002/anie.200602035



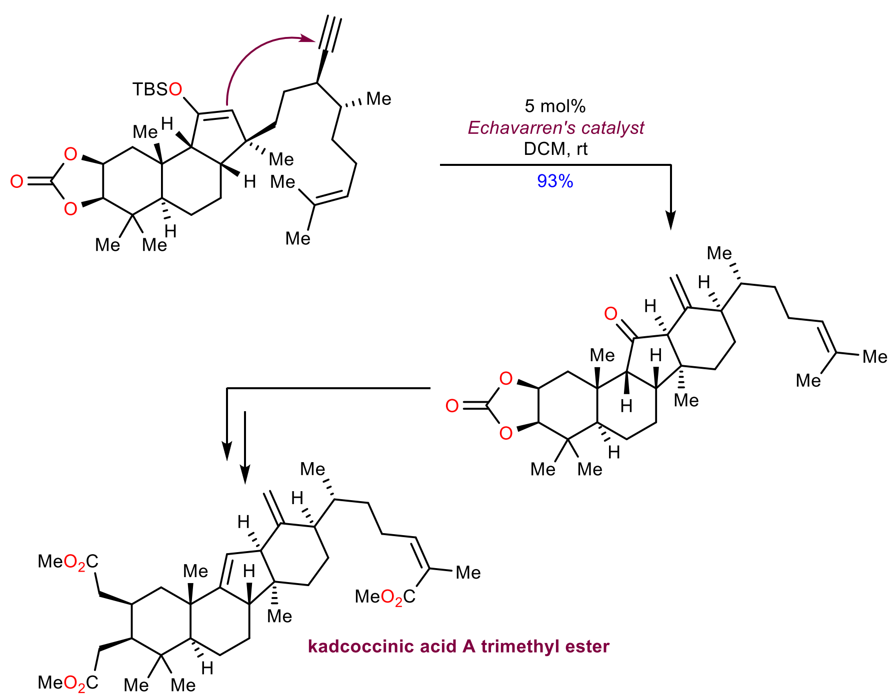
Carreira, E. M. *Angew. Chem. Int. Ed.* **2012**, *51*, 13066. https://doi.org/10.1002/anie.201207203



Li, A. *Nature Chem. Int. Ed.* **2013**, *5*, 679. https://doi.org/10.1038/nchem.1694

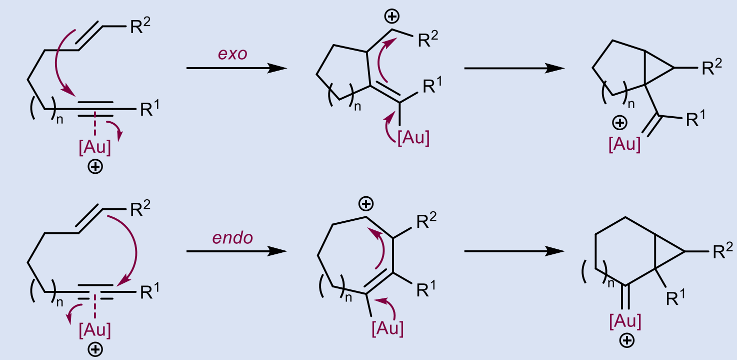


Barriault, L. *Angew. Chem. Int. Ed.* **2014**, *53*, 6701. https://doi.org/10.1002/anie.201403939

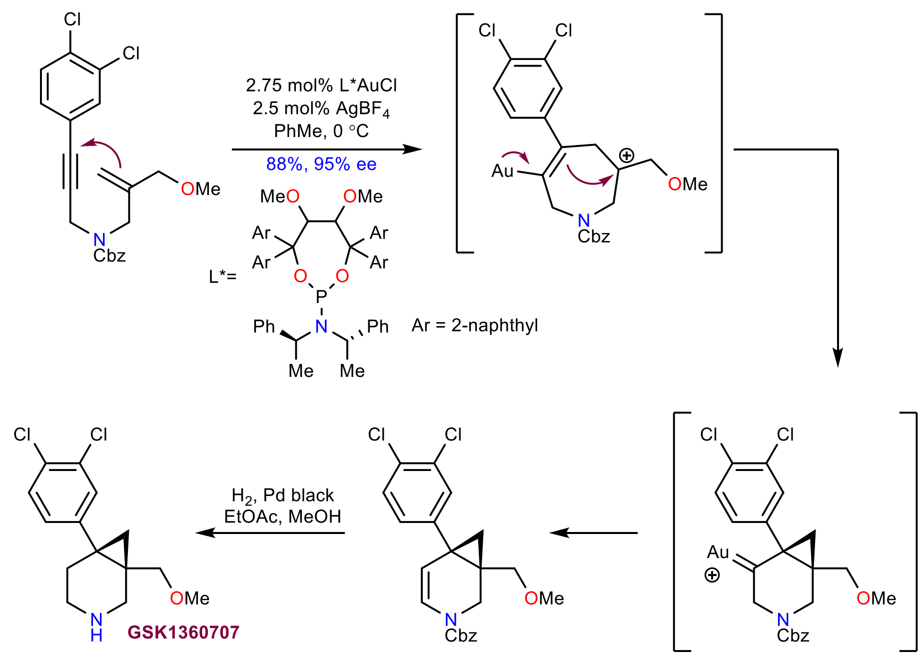


Trost, B. M. *J. Am. Chem. Soc.* **2021**, *143*, 12286. https://doi.org/10.1021/jacs.1c05521

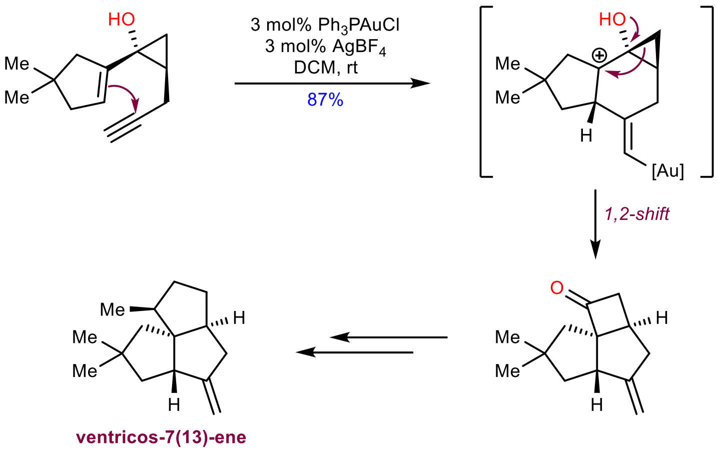
5. Enyne Cycloisomerization



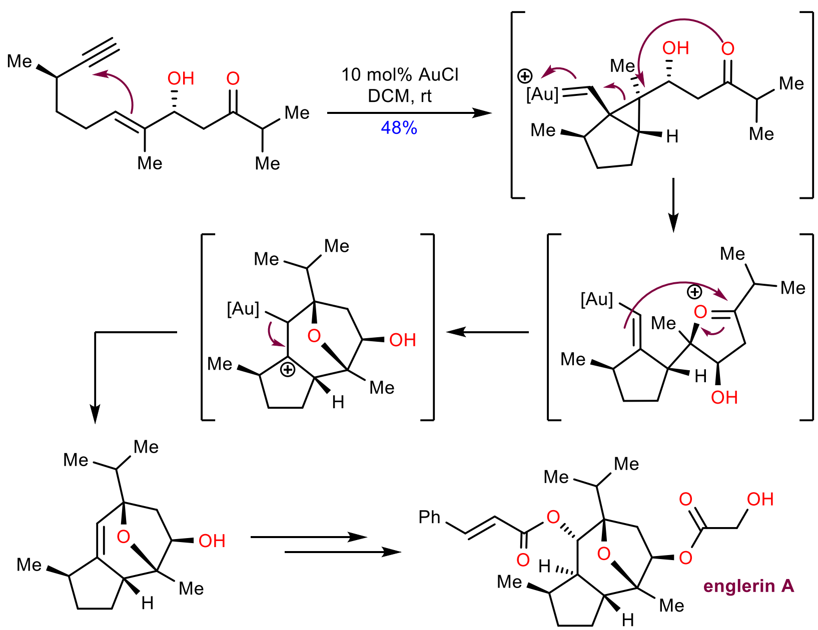
The obtained gold-carbenoid species can participate in a variety of different transformations.



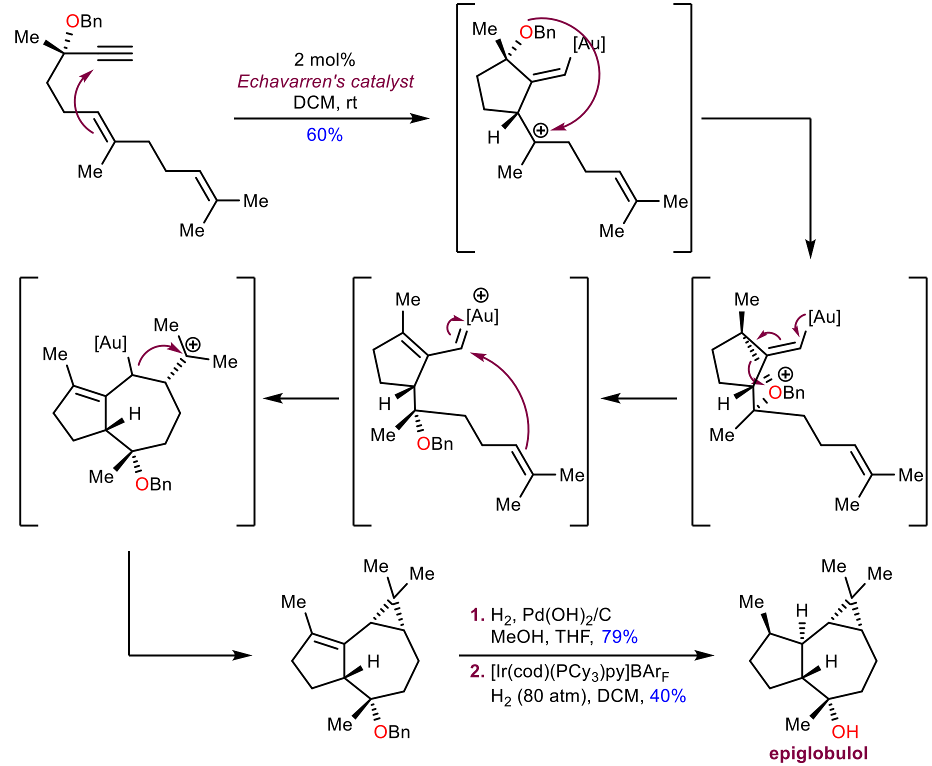
Furstner, A. *Chem. Eur. J.* **2011**, *17*, 7764. https://doi.org/10.1002/chem.201101346



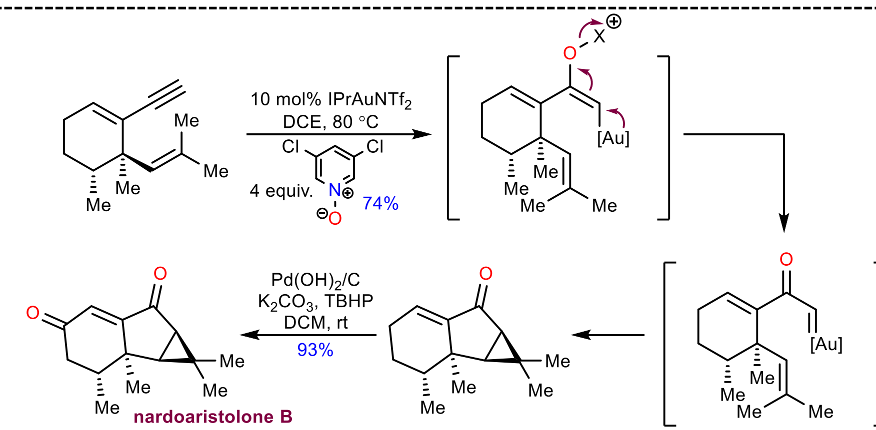
Toste, D. F. *Org. Lett.* **2008**, *10*, 4315. https://doi.org/10.1021/ol801760w



Ma, D. *Angew. Chem. Int. Ed.* **2010**, *49*, 3513. https://doi.org/10.1002/anie.201000888

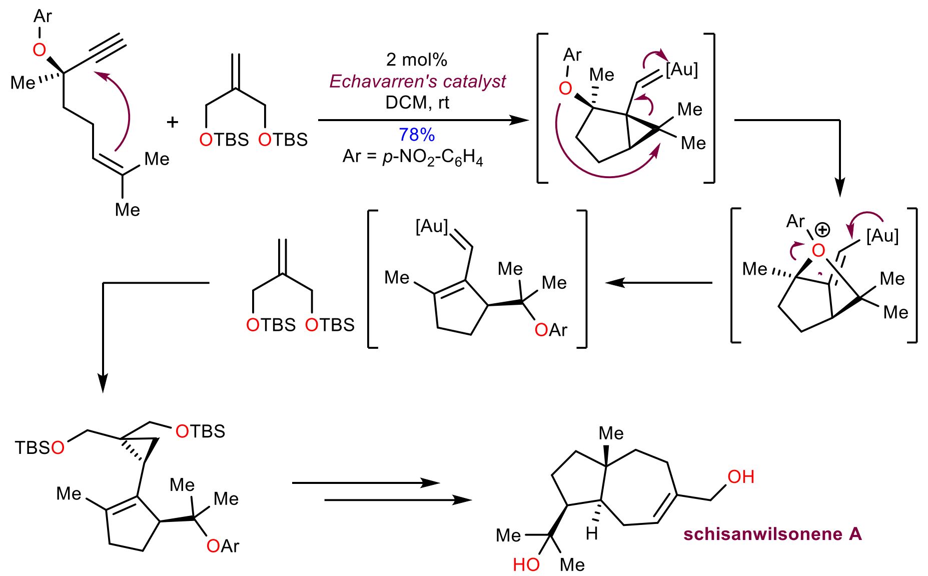


Echavarren, A. M. *Angew. Chem. Int. Ed.* **2014**, *53*, 4896. https://doi.org/10.1002/anie.201402044

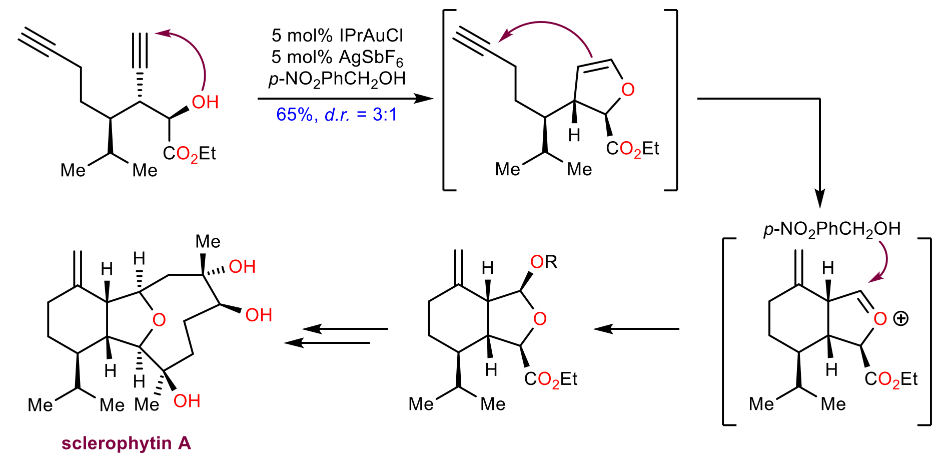


Echavarren, A. M. *Org. Lett.* **2015**, *17*, 461. https://doi.org/10.1021/ol503531n

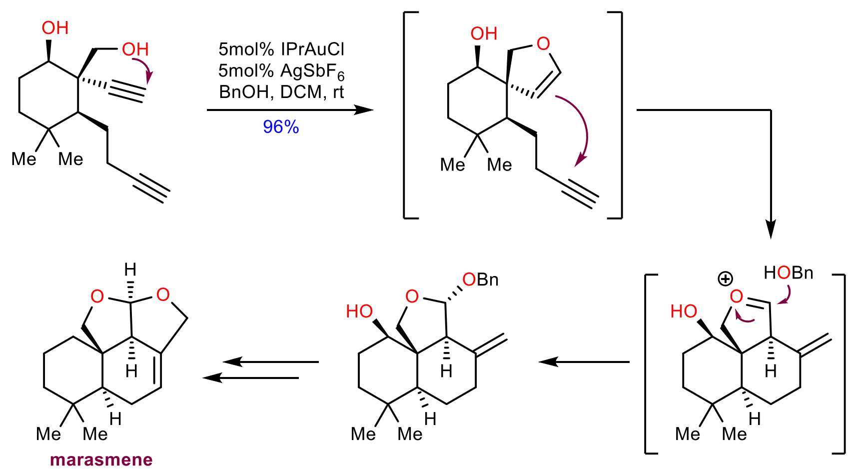
Gold-Catalyzed Transformations in Total Synthesis



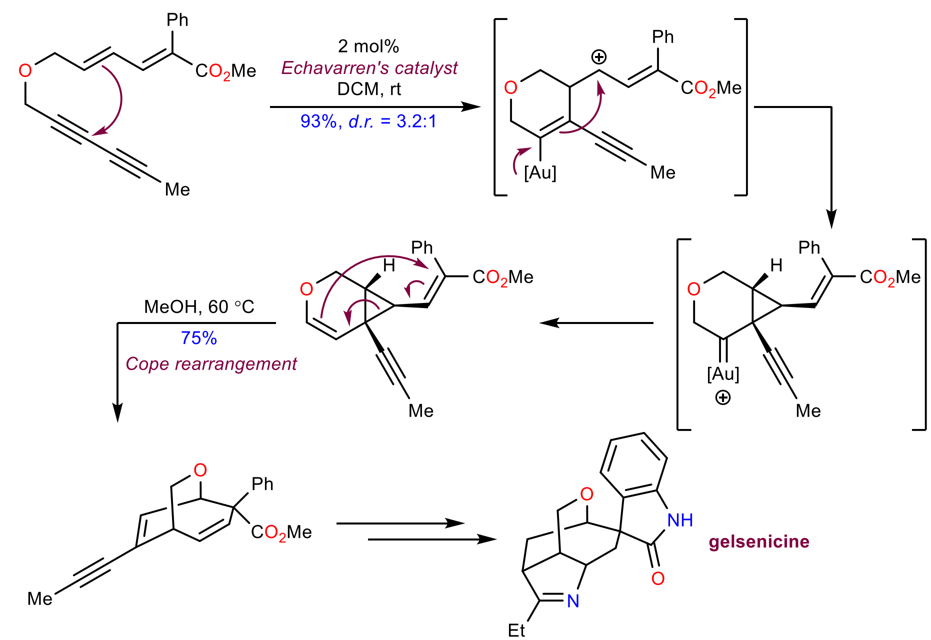
Echavarren, A. M. *Angew. Chem. Int. Ed.* **2013**, *52*, 6396. https://doi.org/10.1002/anie.201302411



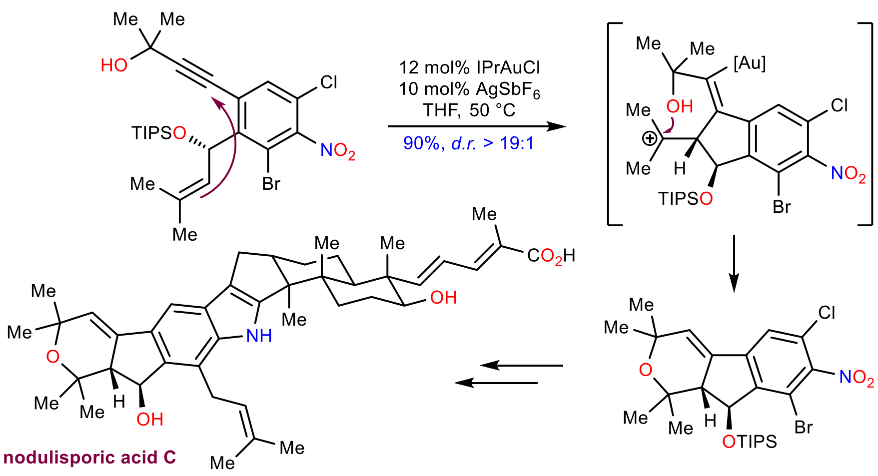
Luo, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 1837. https://doi.org/10.1002/anie.201309449



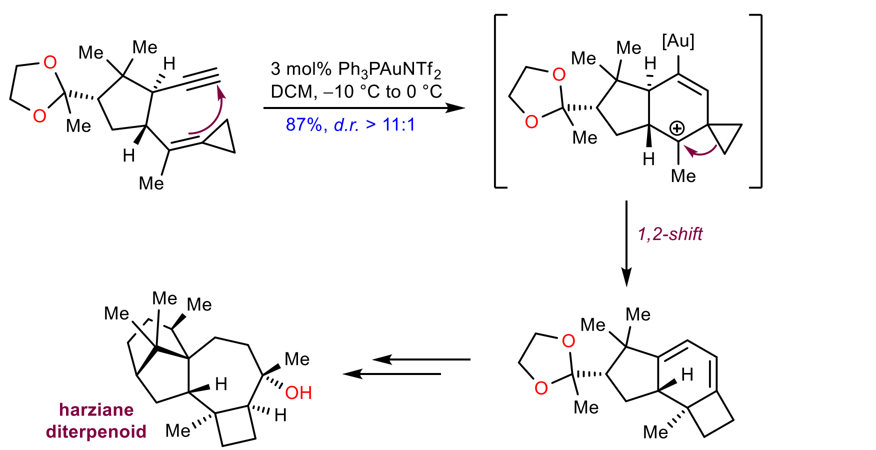
Yang, Z. *J. Am. Chem. Soc.* **2011**, *1333*, 14944. https://doi.org/10.1021/ja206837j



Ferreira, E. M. *J. Am. Chem. Soc.* **2016**, *138*, 108. https://doi.org/10.1021/jacs.5b12263

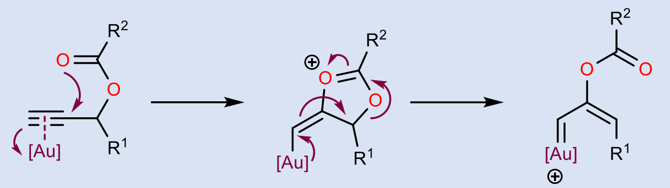


Pronin, S. *J. Am. Chem. Soc.* **2018**, *140*, 12770. https://doi.org/10.1021/jacs.8b09965



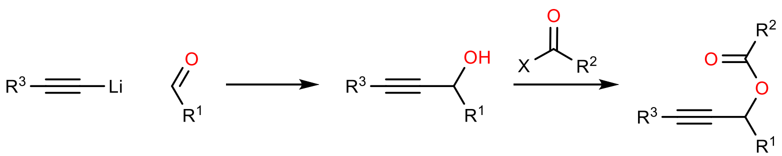
Carreira, E. M. *Angew. Chem. Int. Ed.* **2019**, *132*, 1208. https://doi.org/10.1002/ange.201912982

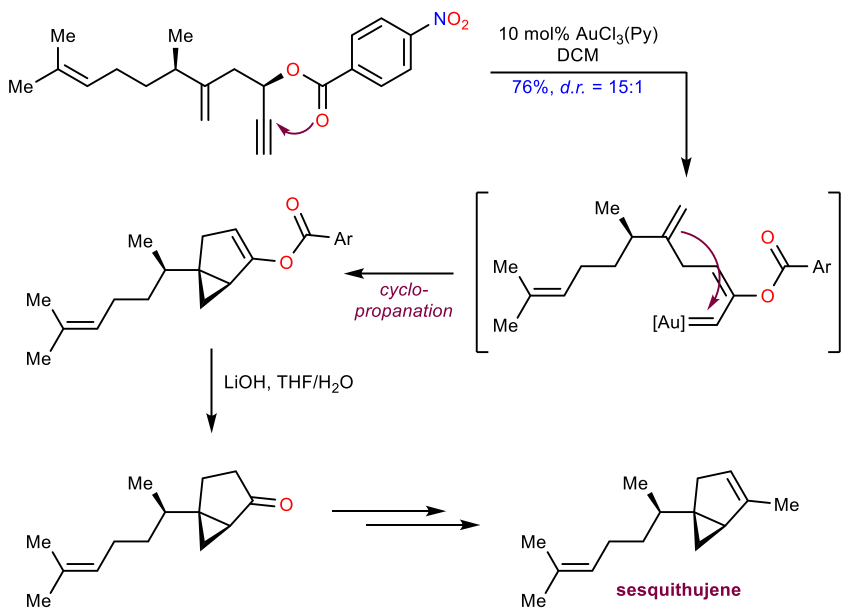
6. 1,2-Acyloxy Migration



The 1,2-shift is used to initiate different cascade reactions.

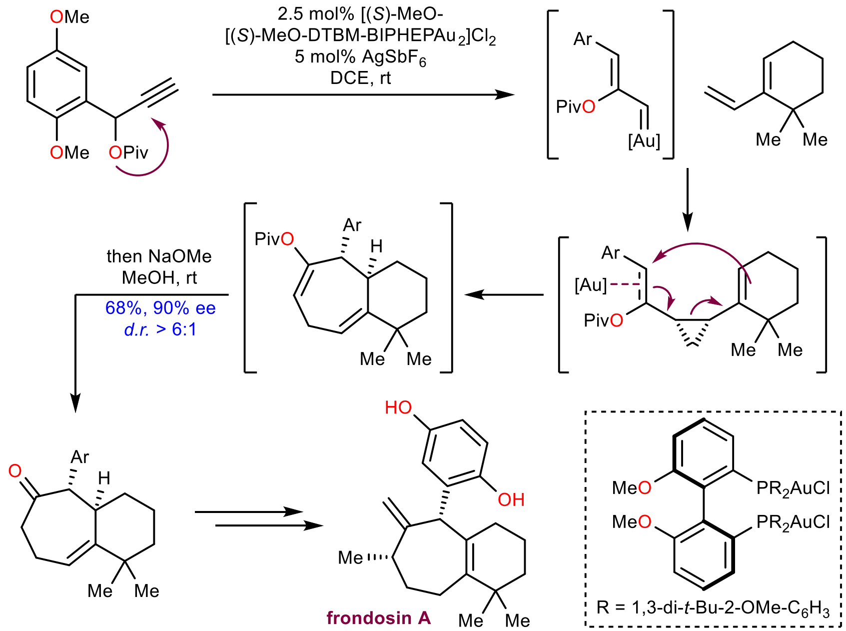
Common way of making the substrate:





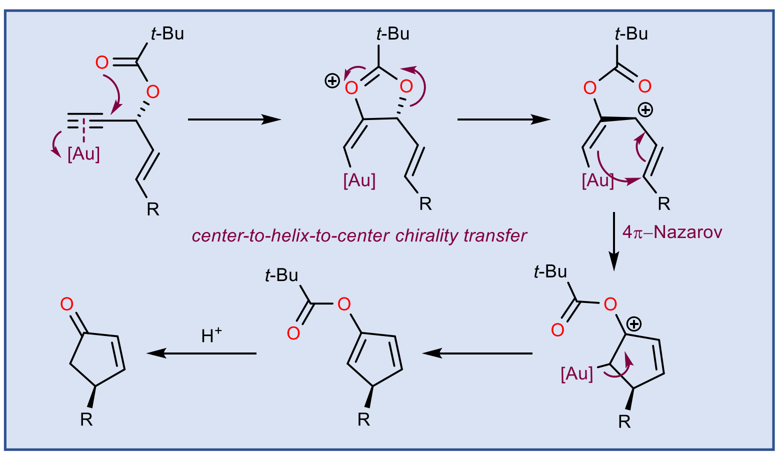
Furstner, A. *Chem. Eur. J.* **2008**, *14*, 9181. https://doi.org/10.1002/chem.200801382

Gold-Catalyzed Transformations in Total Synthesis



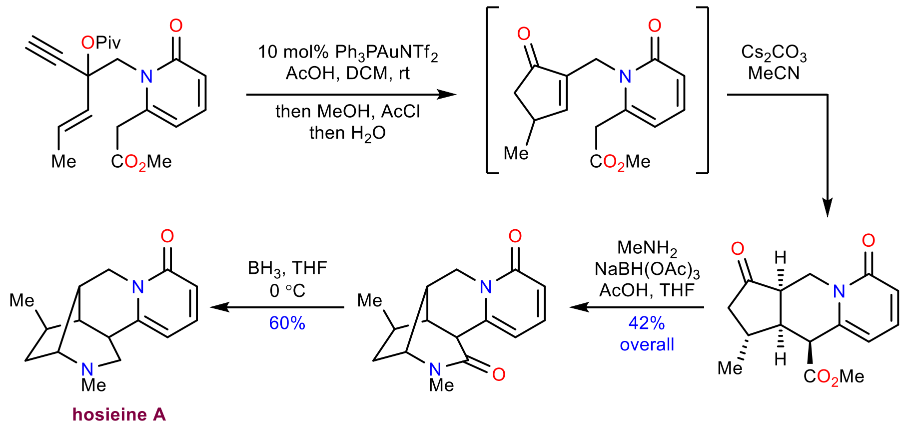
Nevado, C. *Angew. Chem. Int. Ed.* **2010**, *50*, 911. https://doi.org/10.1002/anie.201006105

Rautenstrauch Rearrangement

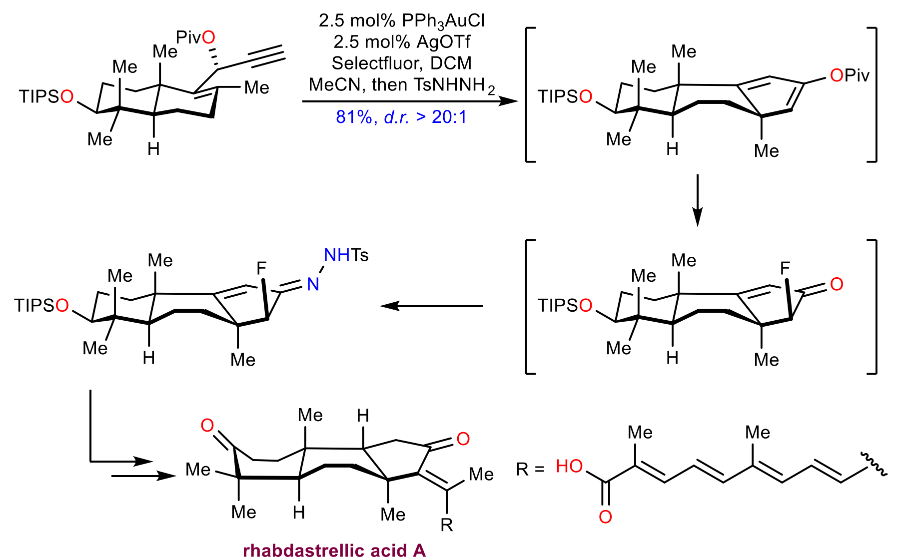


Toste, D. *J. Am. Chem. Soc.* **2005**, *127*, 5802. https://doi.org/10.1021/ja051689g

de Lera, A. R. *J. Am. Chem. Soc.* **2006**, *128*, 2434. https://doi.org/10.1021/ja057127e



Wood, J. L. *Angew. Chem. Int. Ed.* **2018**, *57*, 7664. https://doi.org/10.1002/anie.201804076



Sarlah, D. *J. Am. Chem. Soc.* **2019**, *141*, 14131. https://doi.org/10.1021/jacs.9b08487

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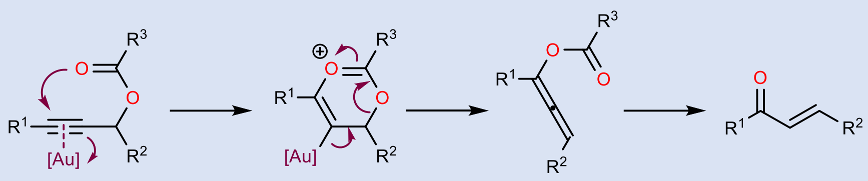
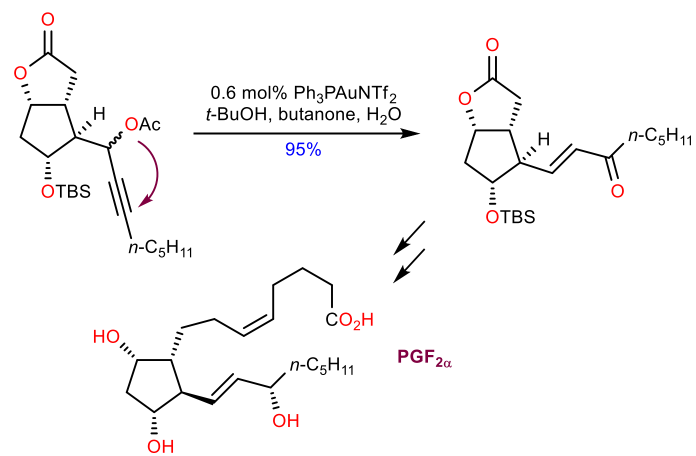
7. 1,3-Acyloxy Migration

Meyer-Schuster Rearrangement

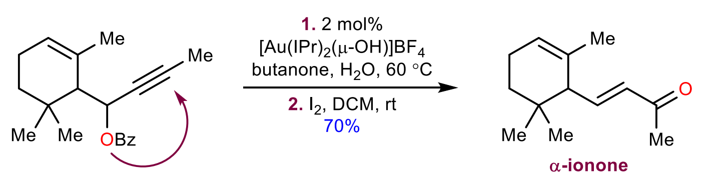


[Au] can activate the allene to initiate a cascade.

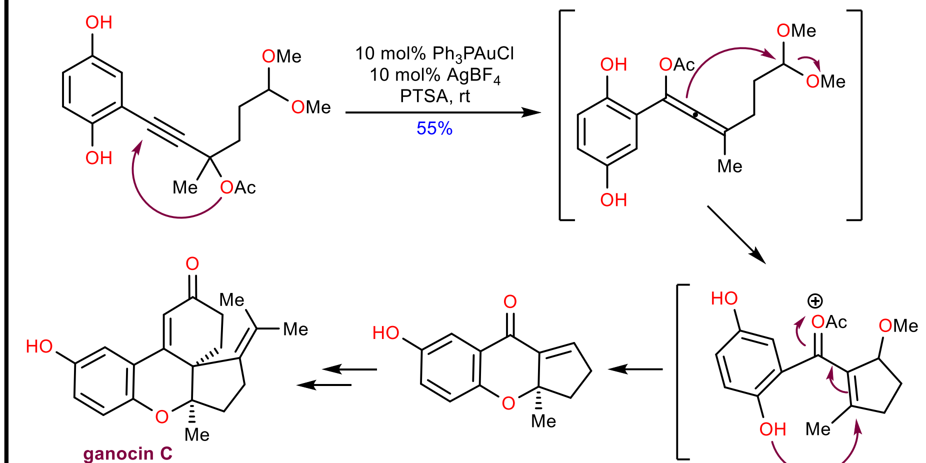
Piv-carboxylates and terminal alkynes favor 1,2-shifts while
Ac-carboxylates and internal alkynes favor 1,3-shifts.



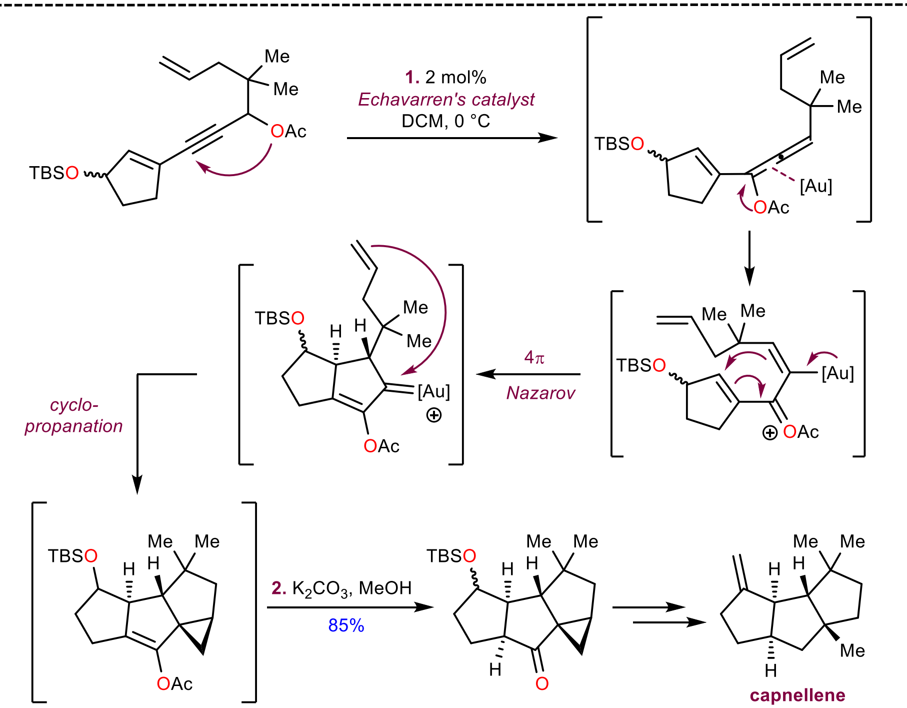
Vidari, G. *Tetrahedron* **2010**, *66*, 7472. https://doi.org/10.1016/j.tet.2010.07.069



Nolan, S. P. *Tetrahedron Letters* **2011**, *52*, 1124. https://doi.org/10.1016/j.tetlet.2011.01.010



Wang, H. *Org. Biomol. Chem.* **2016**, *14*, 10362. https://doi.org/10.1039/C6OB02049F



Malacria, M. *J. Am. Chem. Soc.* **2009**, *131*, 2993. https://doi.org/10.1021/ja808872u

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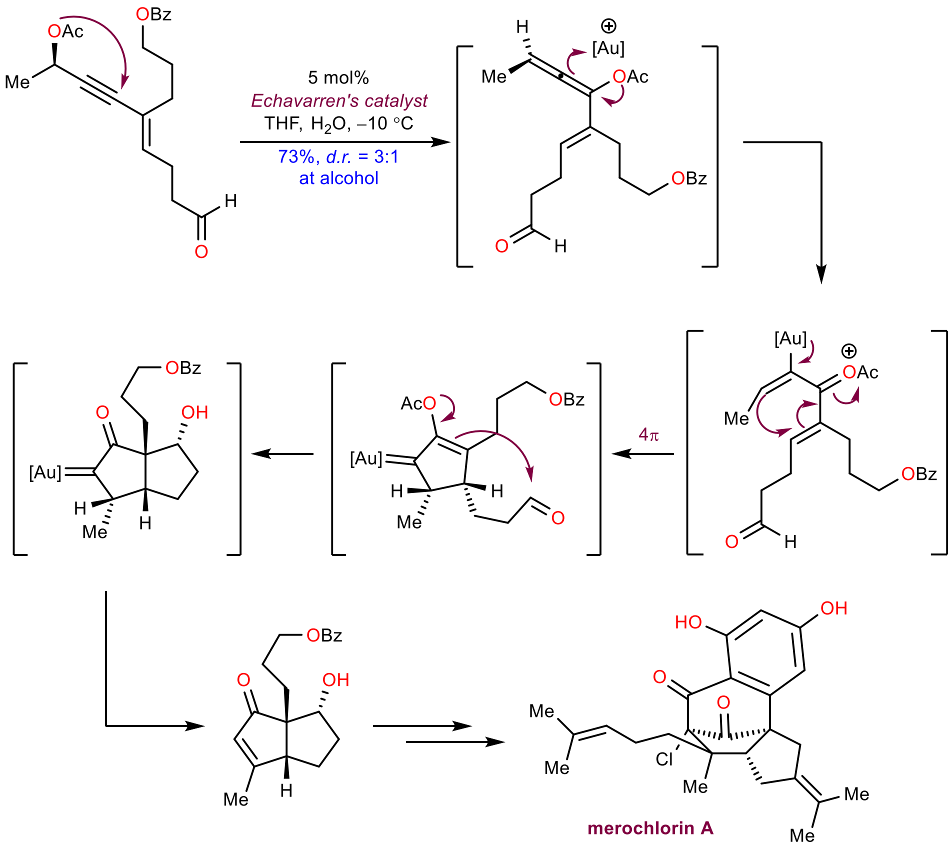

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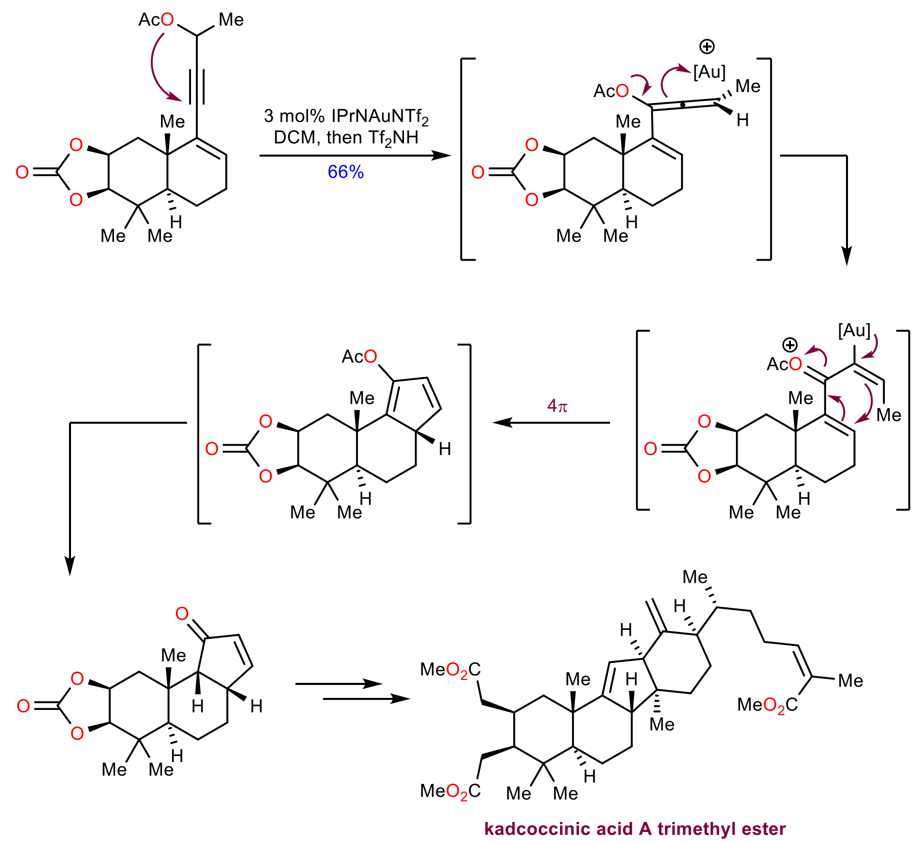

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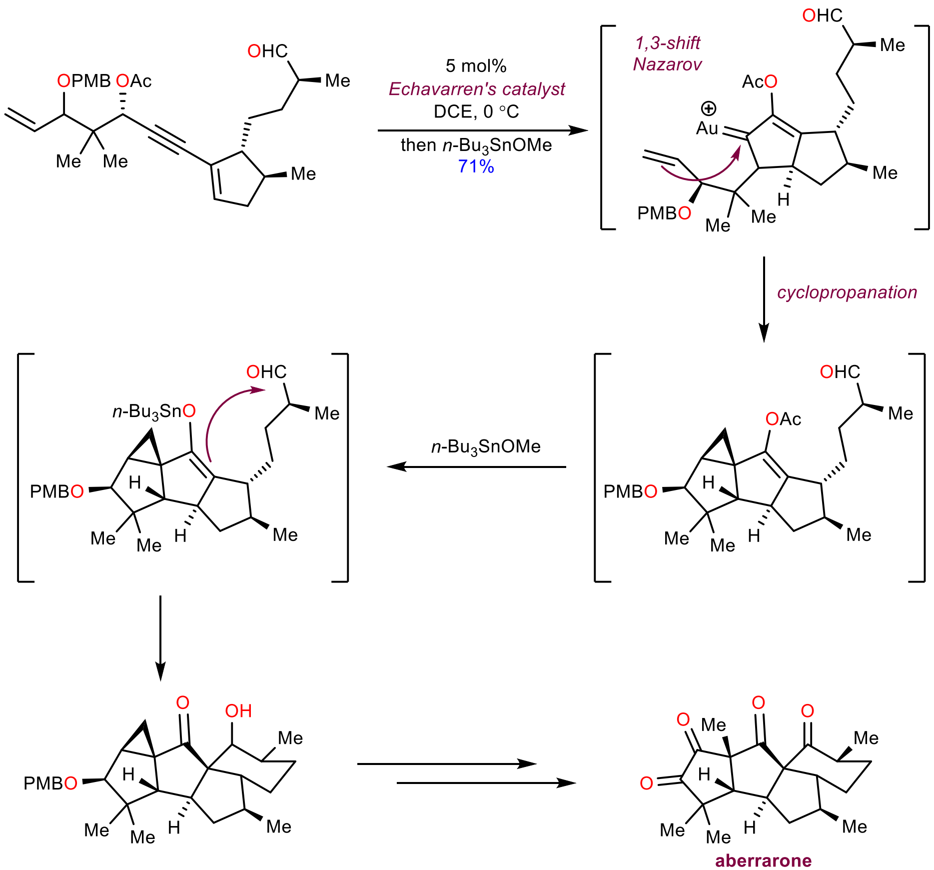

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