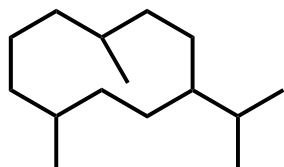


## Germacrane Skelton



Scifinder Hit: 6801 hits (journal) till 09.2011

only 1 hit in 1963, 676 hits in 2009, 729 hits in 2010

Review: "Sesquiterpenes with Ten-Membered Carbon Rings. A Review"

Sorm, F. *J. Agr. Food. Chem.* **1971**, *19*, 1081.

"Sesquiterpenoids"

Roberts, J. S.; Bryson, I. *Nat. Prod. Rep.* **1984**, 105.

"Natural Sesquiterpenoids"

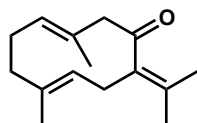
Fraga, B. M. *Nat. Prod. Rep.* 1985-2007 (ref Adio's review)

"The Synthesis of Germacrane Sesquiterpenes and Related Compounds"

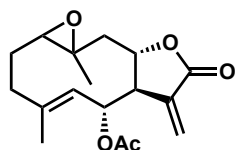
Minnard, A. J.; Wijnberg, J. B. P. A.; de Groot, A. *Tetrahedron*, **1999**, *55*, 2115.

"Germacrane A-E and related compounds: thermal, photochemical and acid induced transannular cyclizations" Adio, A. M. *Tetrahedron*, **2009**, *65*, 1533.

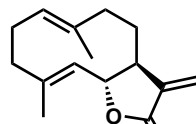
Structural establishment: **Germacrone** (Sorm, 1957). **Pyrethrosine** (Barton, 1957), **Costunolide** (Sorm, 1959, X-ray)



Germacrone



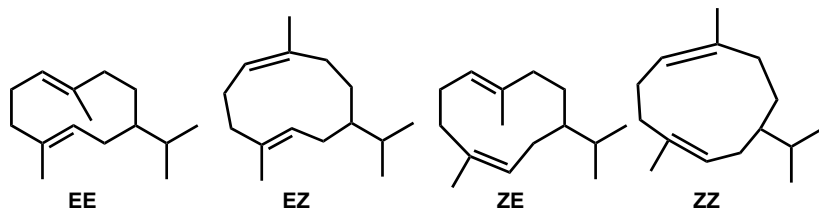
Pyrethrosine



Costunolide O

Structure:

- Two endocyclic double bond
- Two methyl group and a isopropyl group
- Cyclodecadiene consists of two isoprene
- The double bond geometry trend of natural occurrence  
(EE) > (EZ) ~ (ZE) > (ZZ)



EE

EZ

ZE

ZZ



Feverfew



Herb root



American Cockroach



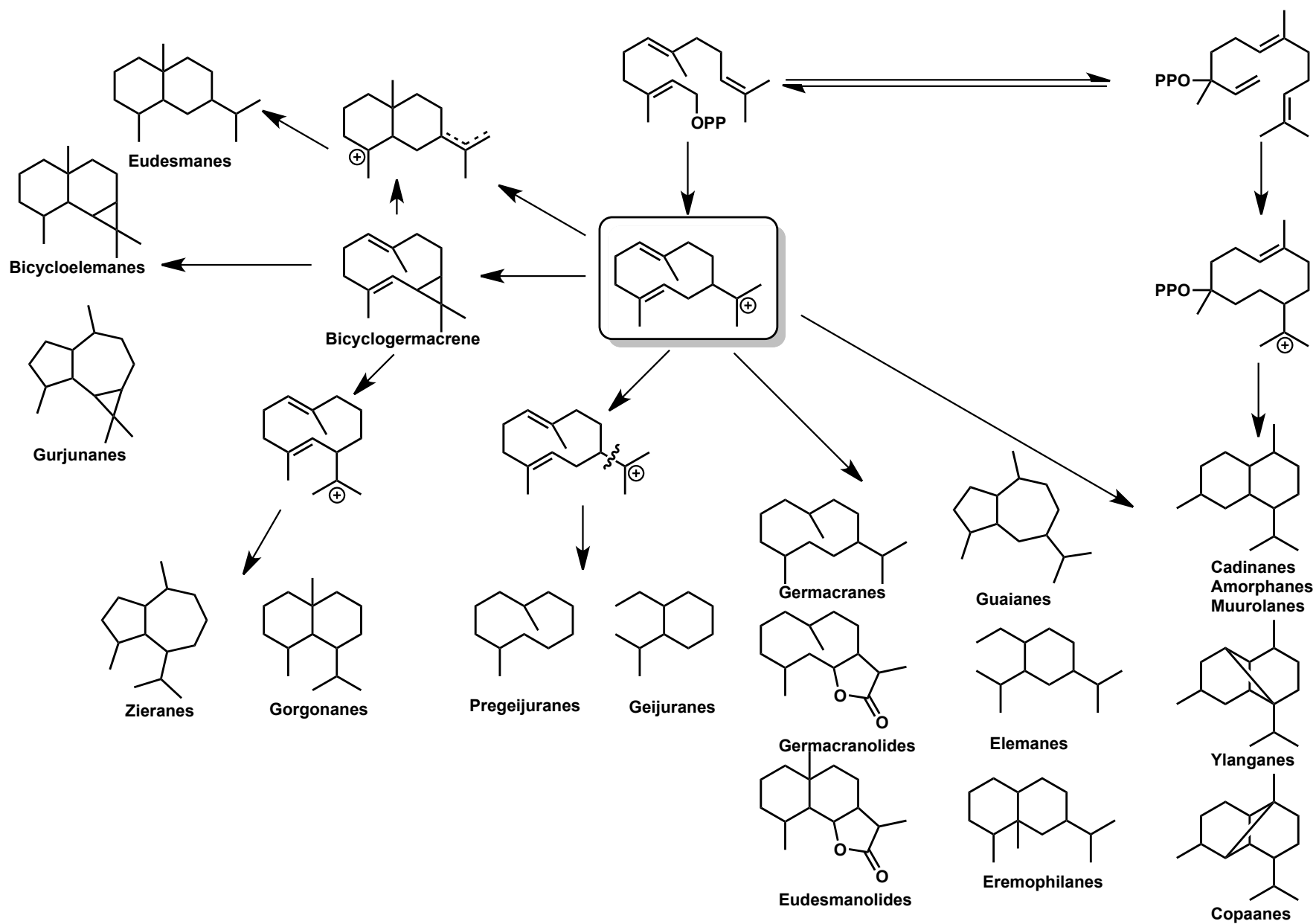
Aphid

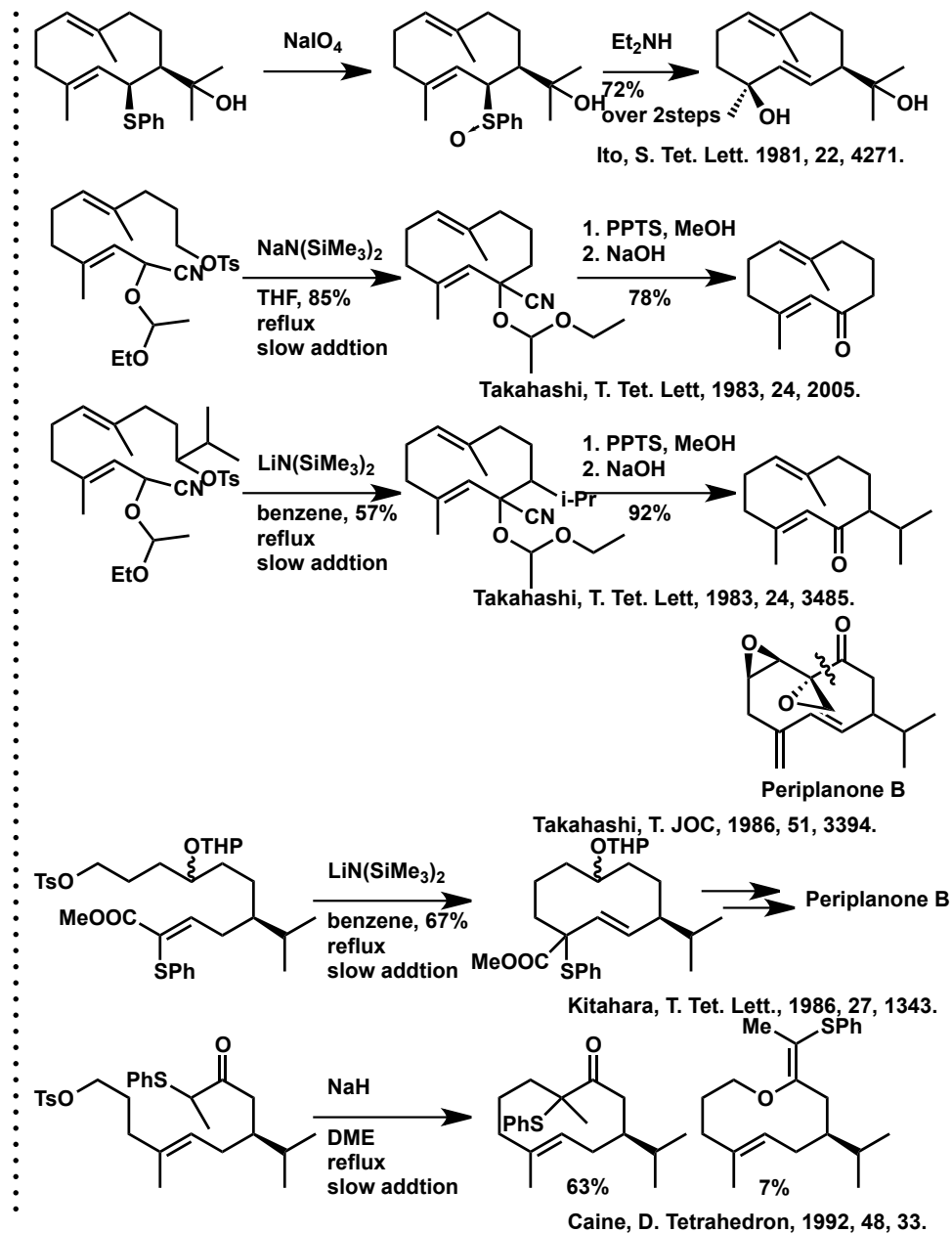
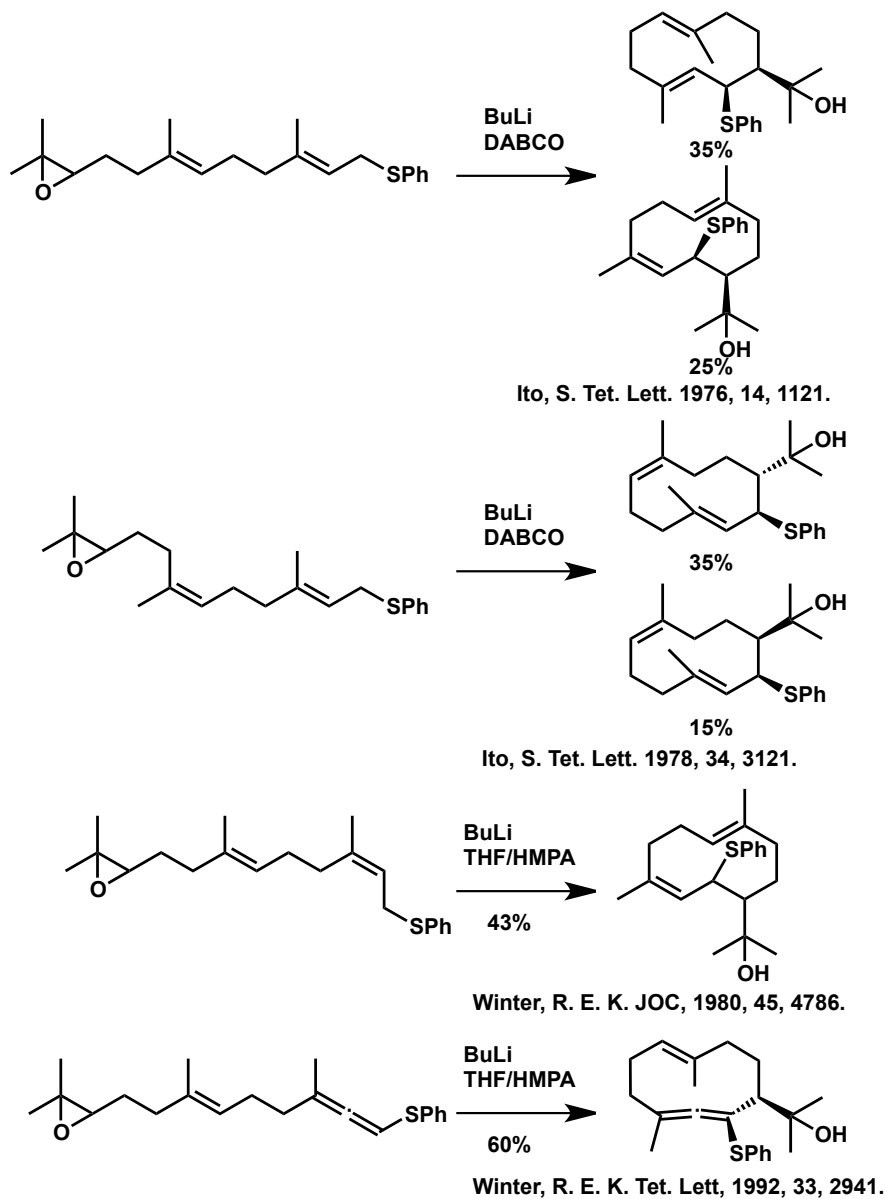


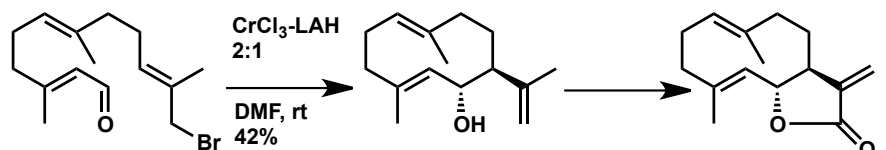
Marine Interbrate

Bioactivity:

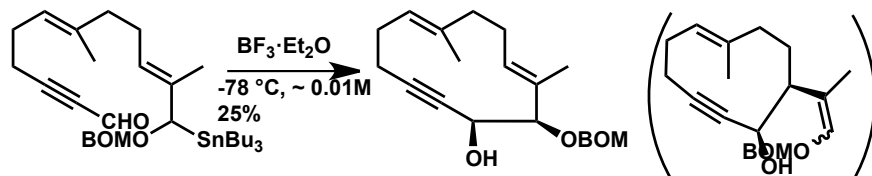
sex pheromones, alarm pheromone, anti-inflammatory activities, anti-cancer agents, antiparasitic activity, antibacterial and antifungal activities, antifeedant, tubulin inhibitor, phytotoxic activity, inhibitor of tumour necrosis and interleukin-6, PTP1B inhibitor, NF-κB inhibitors, inhibitors of preadipocyte differentiation, inhibitors of germination and seedling growth in plant species, moth antennal receptor neuron activator, nematocidal activity, cytotoxic activity, tyrosinase inhibitory activities and other various biological activities.



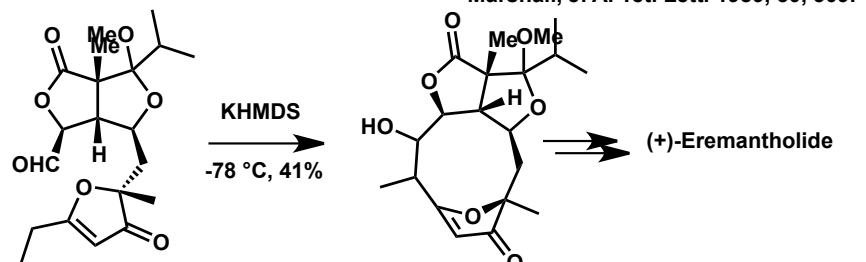




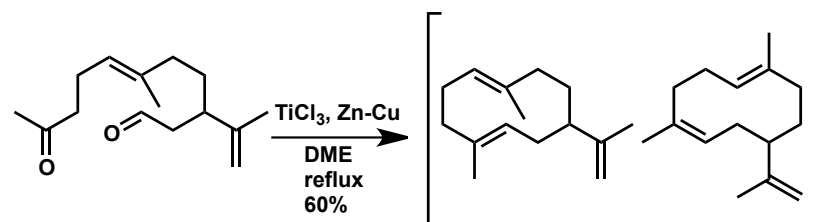
Costunolide: Kitagawa, I. Chem. Lett. 1986, 85.



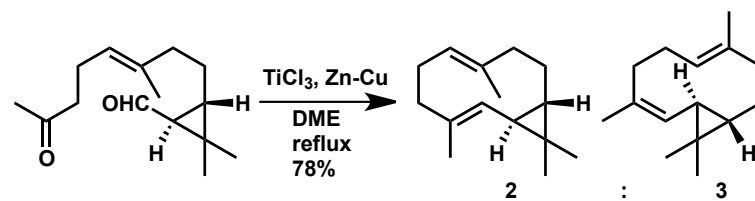
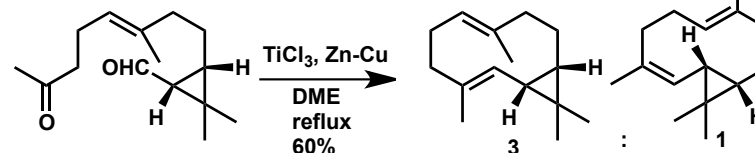
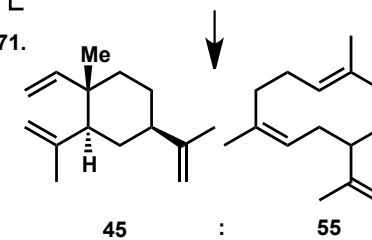
Marshall, J. A. Tet. Lett. 1989, 30, 309.



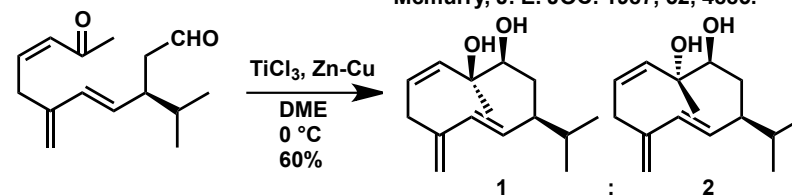
Takao, K. Tet. Lett. 1995, 36, 1487.



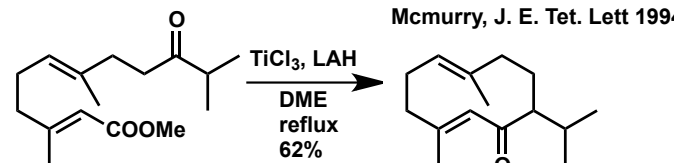
Mcmurry, J. E. Tet. Lett. 1985, 26, 2171.



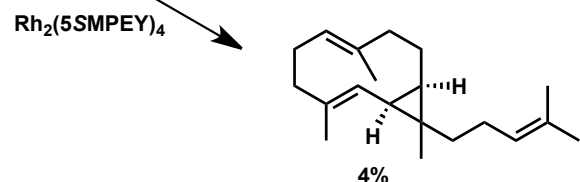
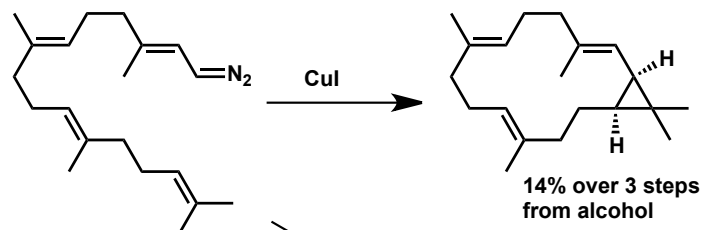
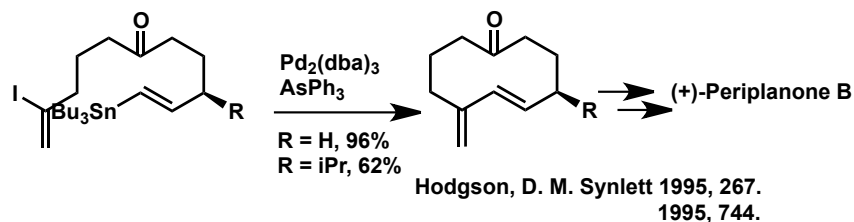
Mcmurry, J. E. JOC. 1987, 52, 4885.



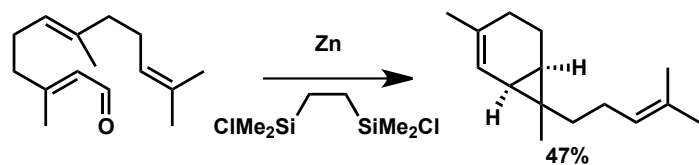
Mcmurry, J. E. Tet. Lett. 1994, 35, 4505.



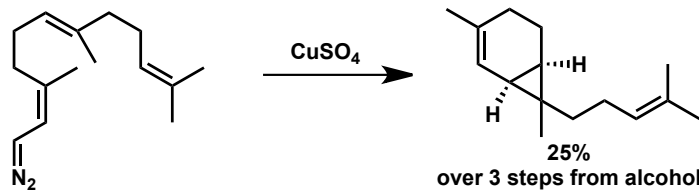
Liu, Y. Synthesis 1994, 267.



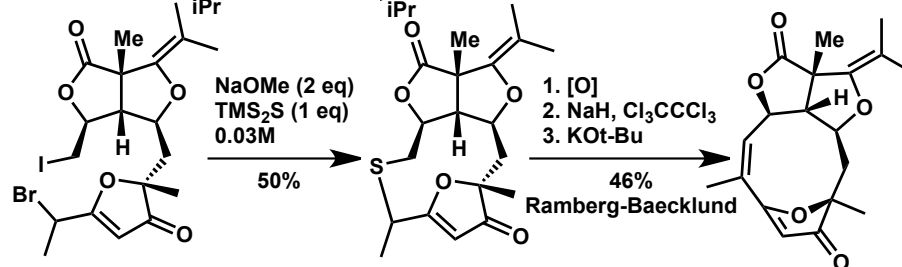
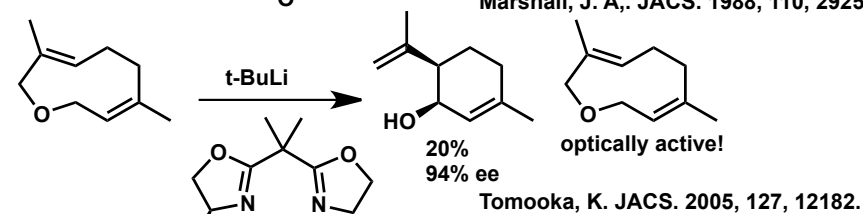
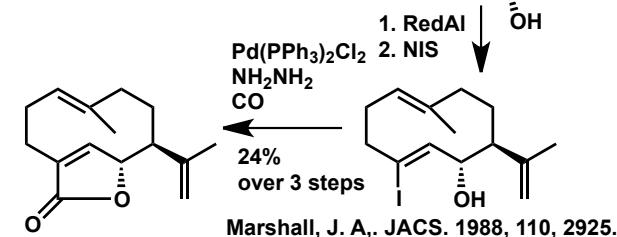
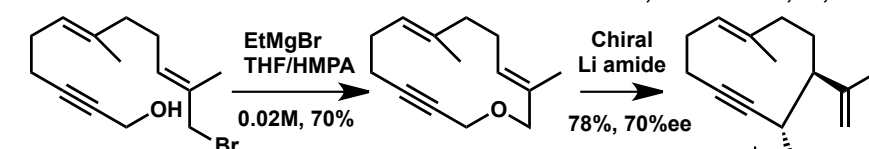
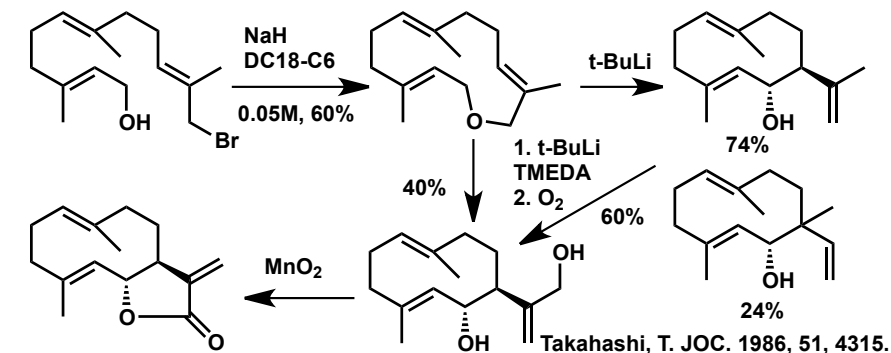
Takahashi, T. *Chem. Lett.* 1982, 863  
 Doyle, M. P. *ARKIVOC*, 2002, 180.



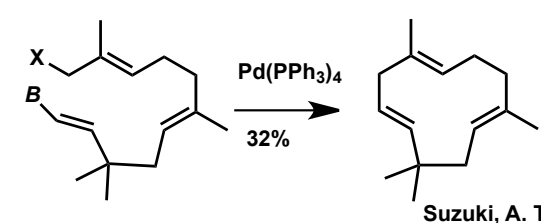
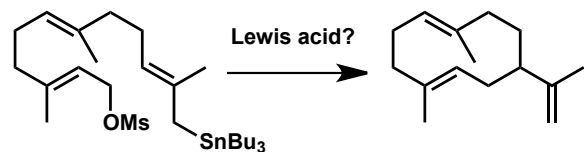
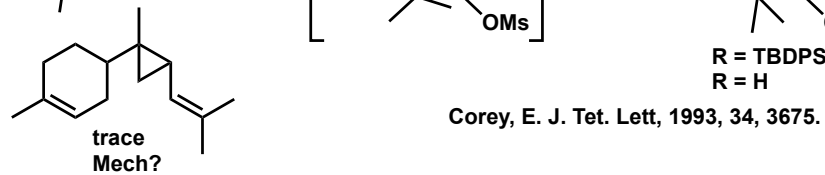
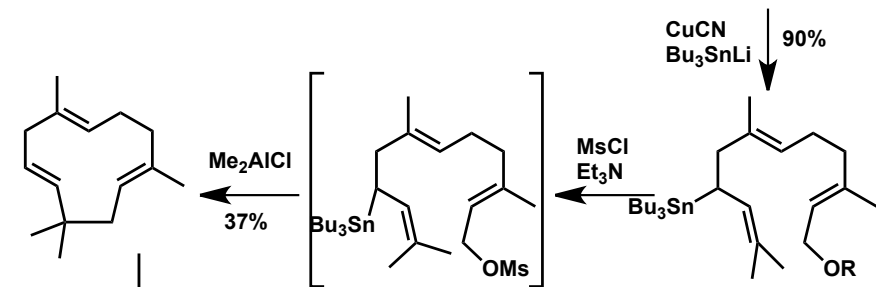
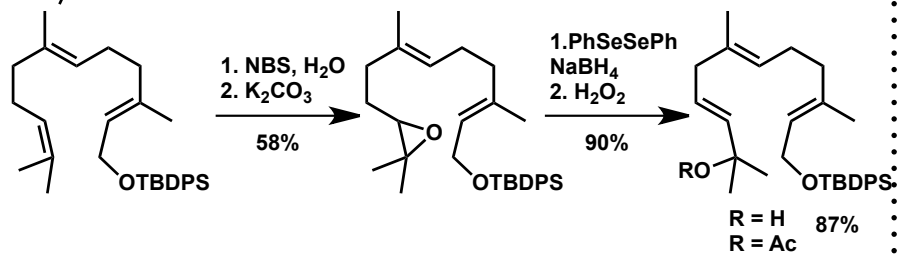
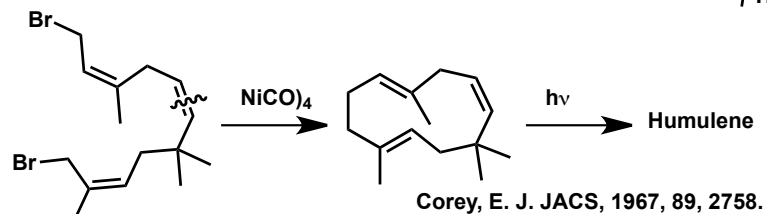
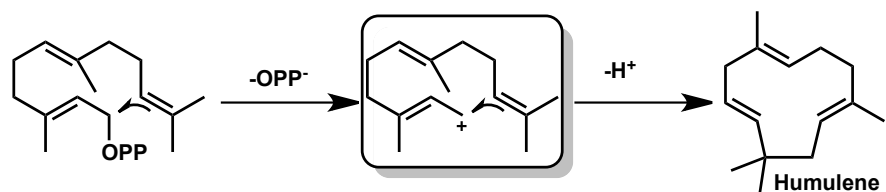
Motherwell, J. A. *Tet. Lett.* 1995, 36, 1121



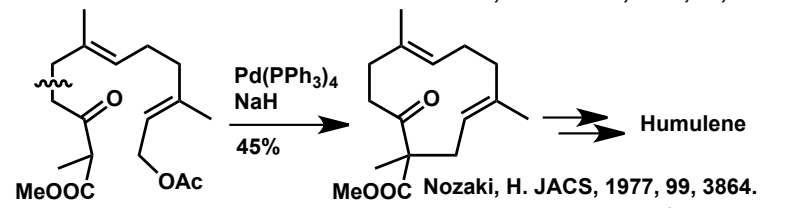
Corey, E. J. *Tet. Lett.* 1969, 38, 3257



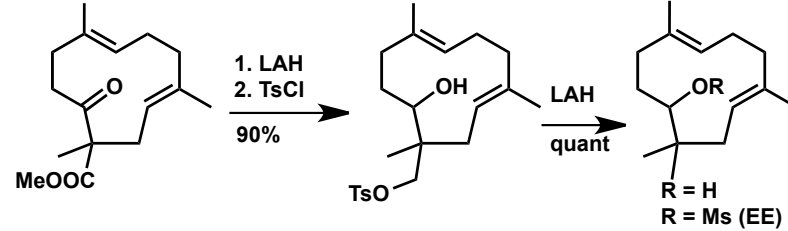
Boeckman, Jr. R. K. *JACS.* 1991, 113, 9682.



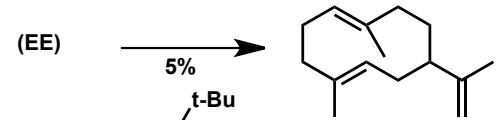
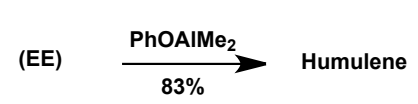
Suzuki, A. Tet. Lett., 1984, 25, 761.



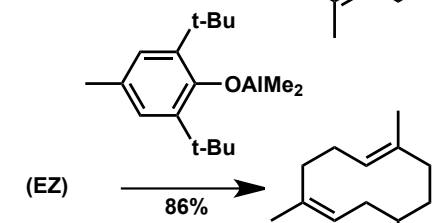
Nozaki, H. JACS, 1977, 99, 3864.



R = H  
R = Ms (EE)



EZ overall 62%



Nozaki, H. Tet. Lett., 1978, 32, 2903.

