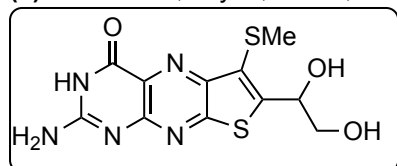
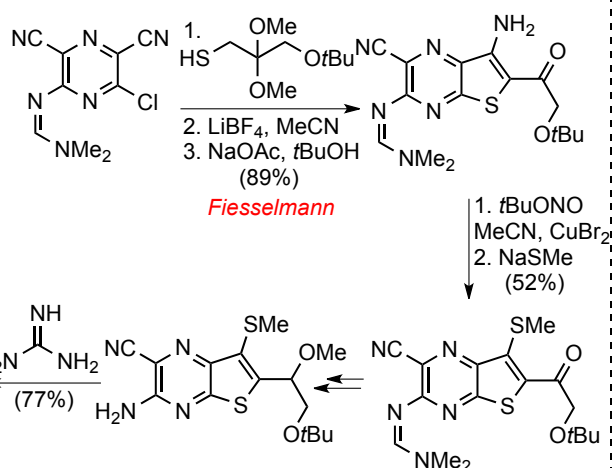
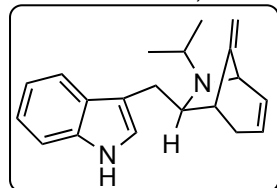


**1989** - Year of the Snake*"deep, say little and possess great wisdom"*

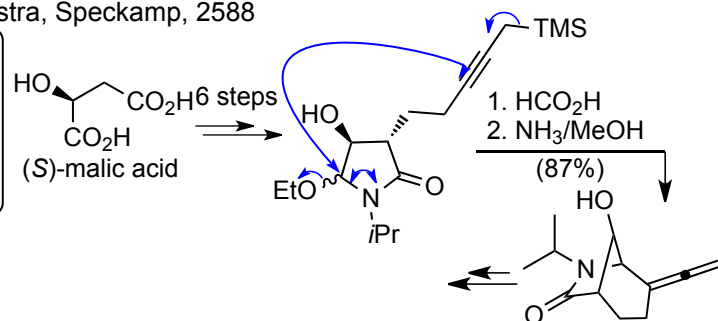
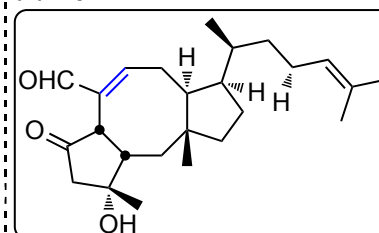
- Random Facts: Nobel Prize Chemistry Sidney Altman, Thomas R. Cech  
George H.W. Bush as 41st President of USA  
Exxon Valdez oil spill  
Soviet War in Afghan.  
Romanian Revolution

**Total Syntheses** (by page number)**(±)-Urothione**, Taylor, Reiter, 285

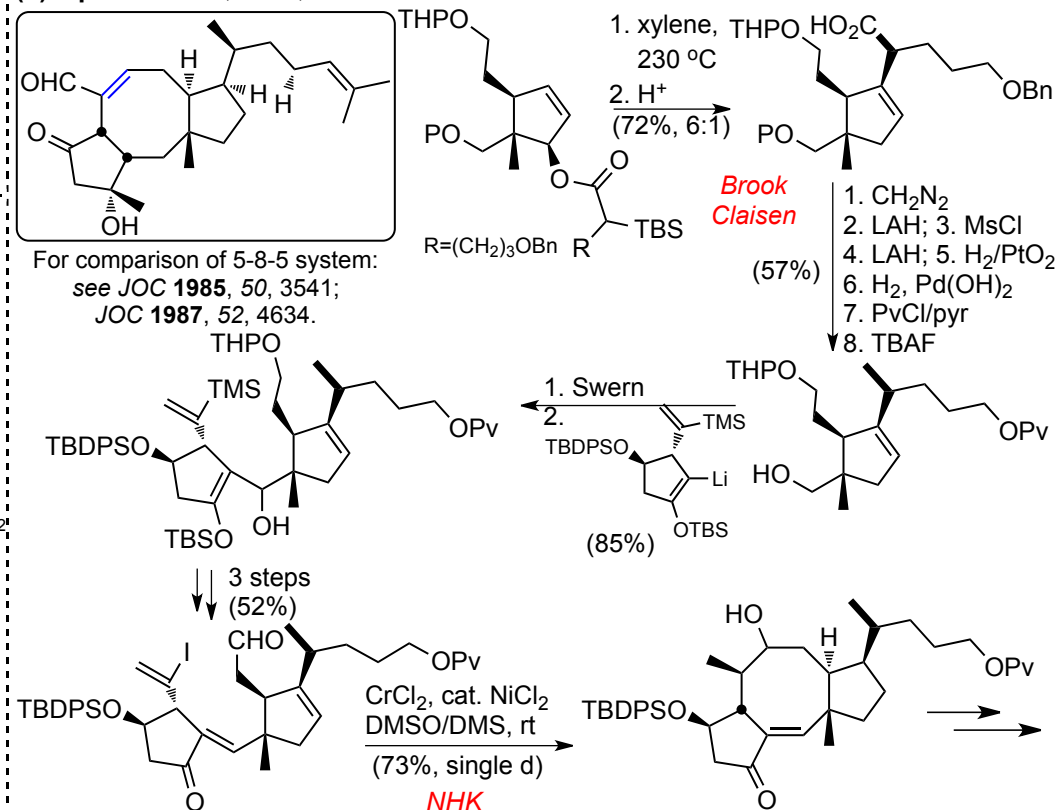
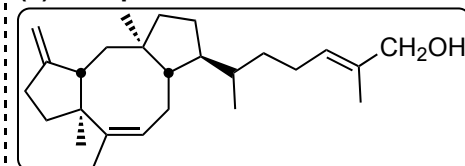
"Isolation of a very small amount of this material from large quantities of urine" and "He was, however, rated by extreme difficulties in obtaining sufficient amounts"

**Peduncularine**, Hiemstra, Speckamp, 2588

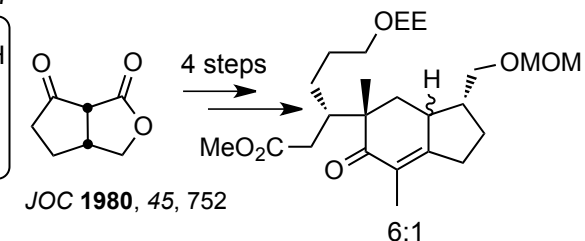
more recent synthesis  
Woerpel, JACS 2002,  
124, 11342

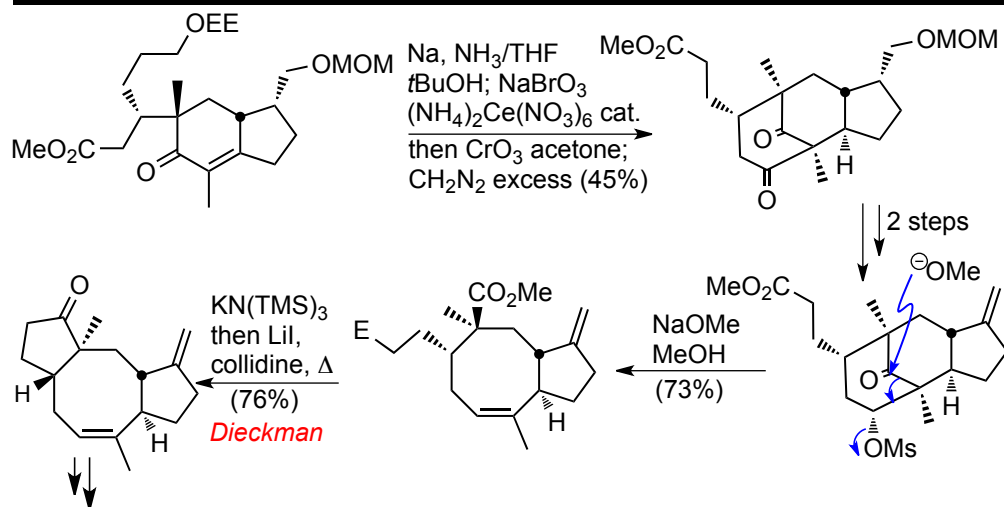
**(+)-Ophiobolin C**, Kishi, 2735

For comparison of 5-8-5 system:  
see JOC 1985, 50, 3541;  
JOC 1987, 52, 4634.

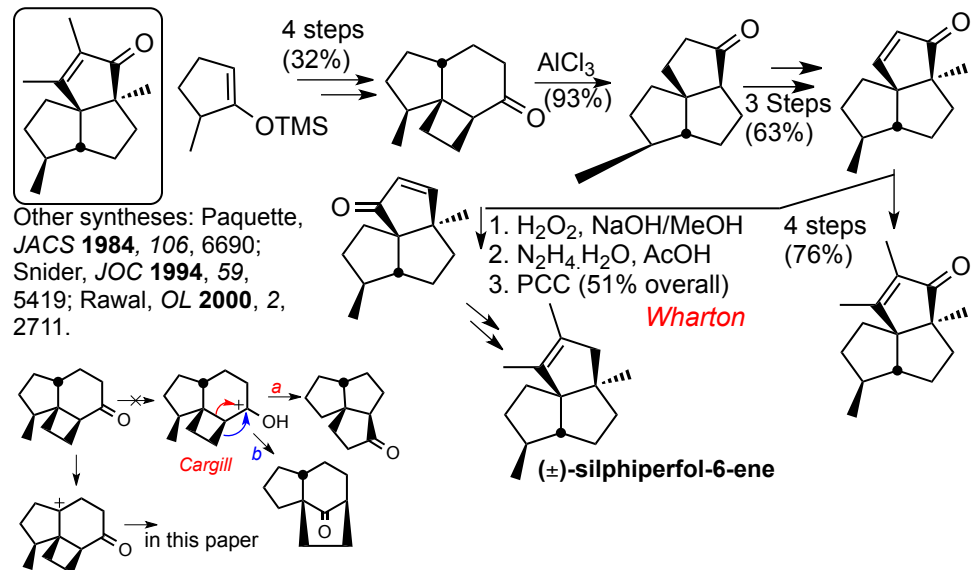
**(±)-Ceroplastol I**, Boeckman Jr., 2737

Past synthesis: Kato, JCS CC 1988, 354.

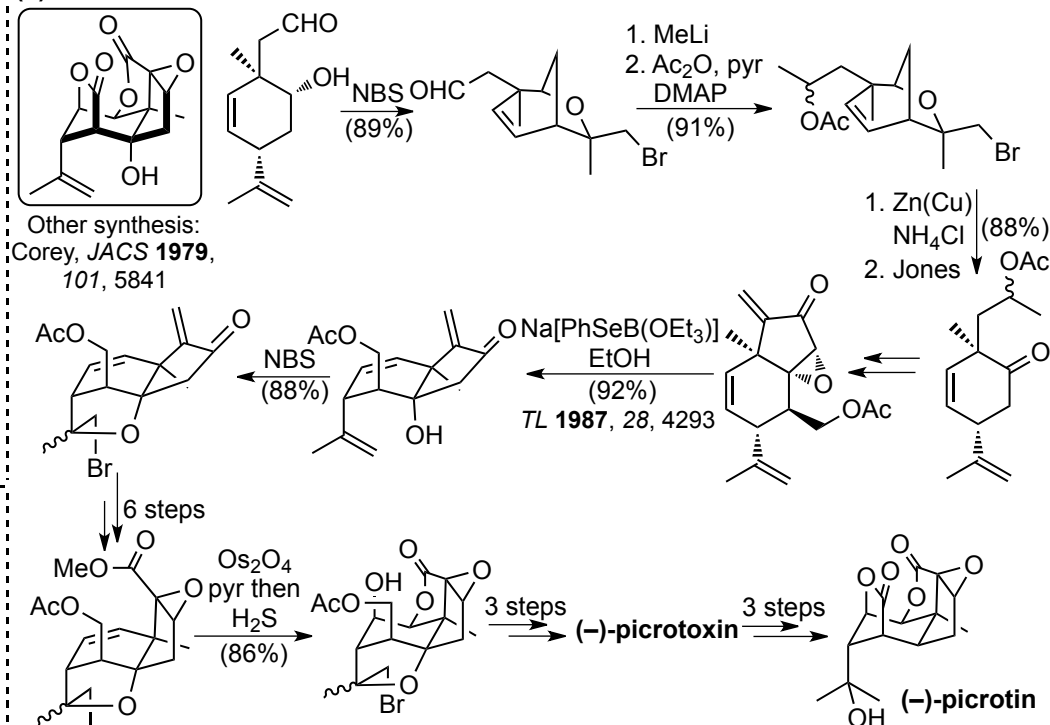




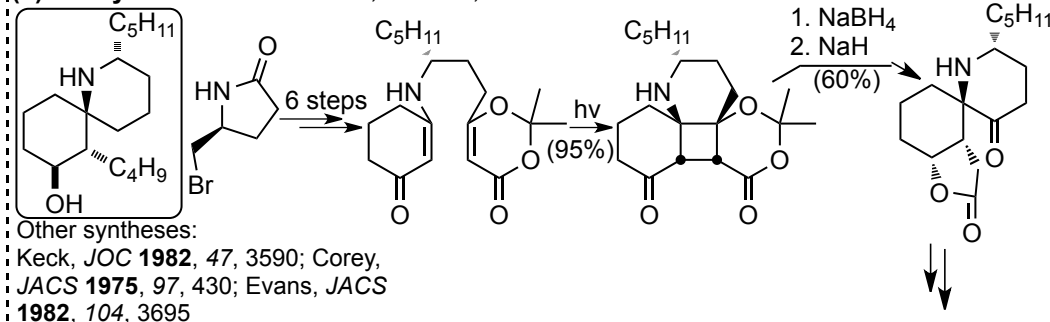
**(±)-Oxosilphiperfol-6-ene**, Kakiuchi, 3707

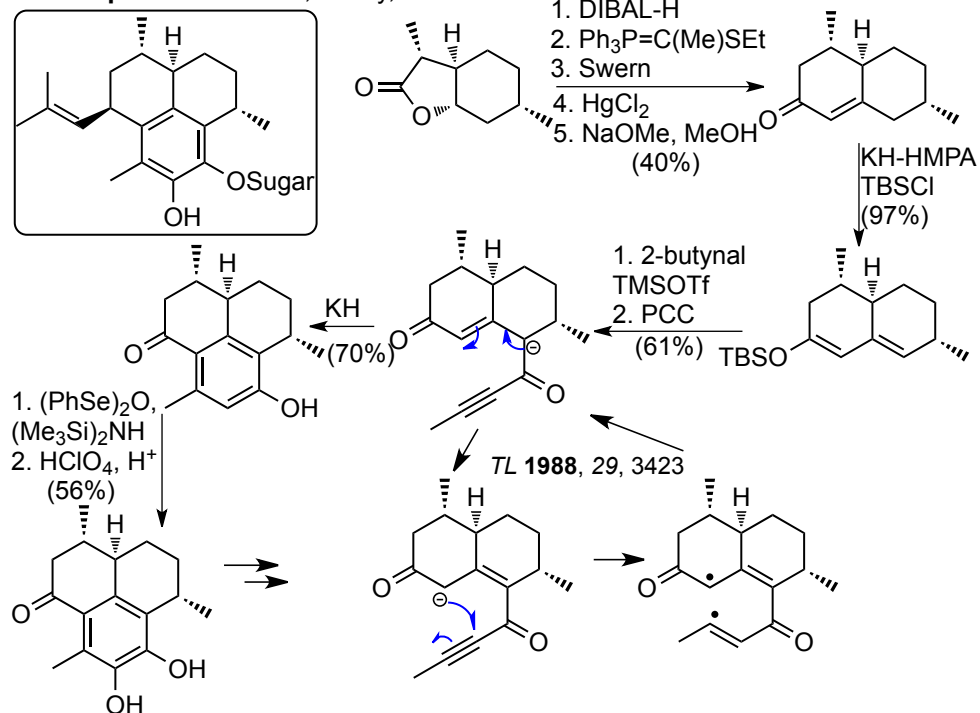
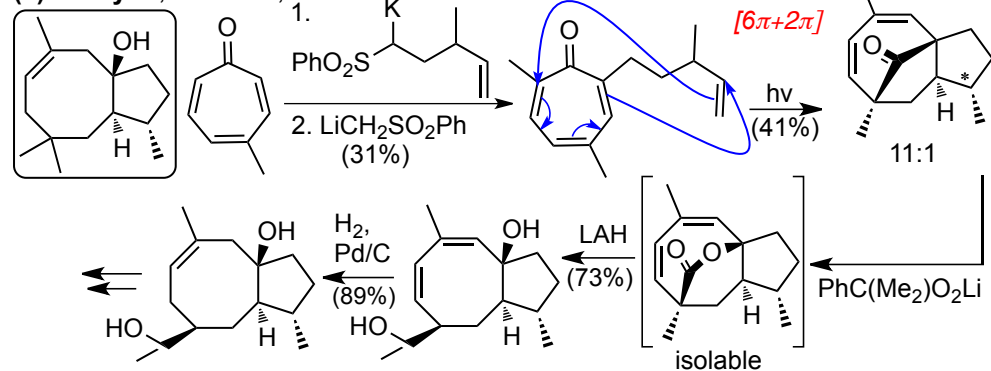
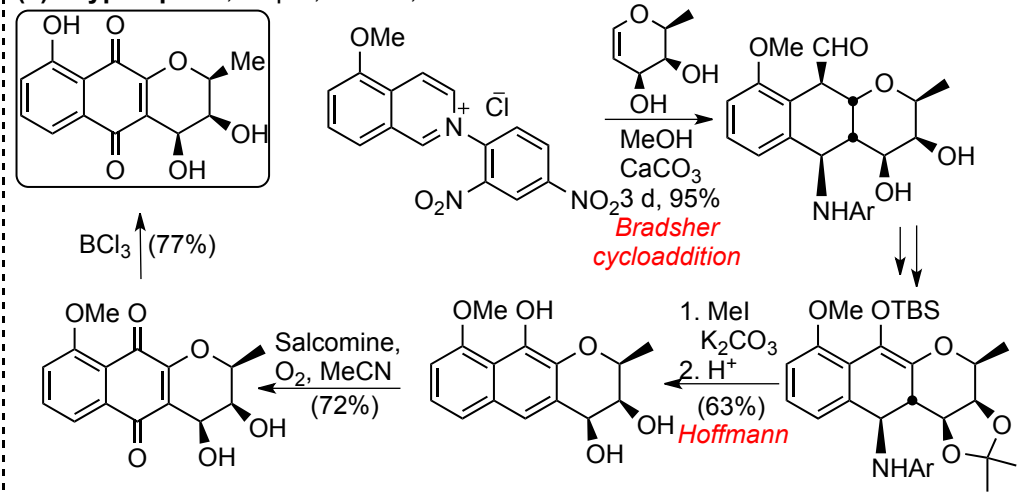
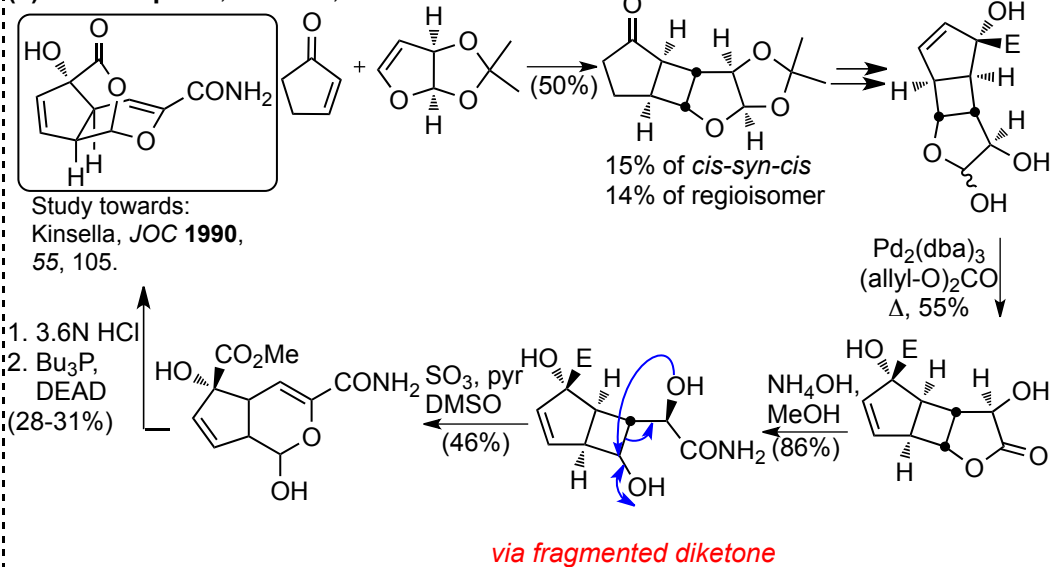


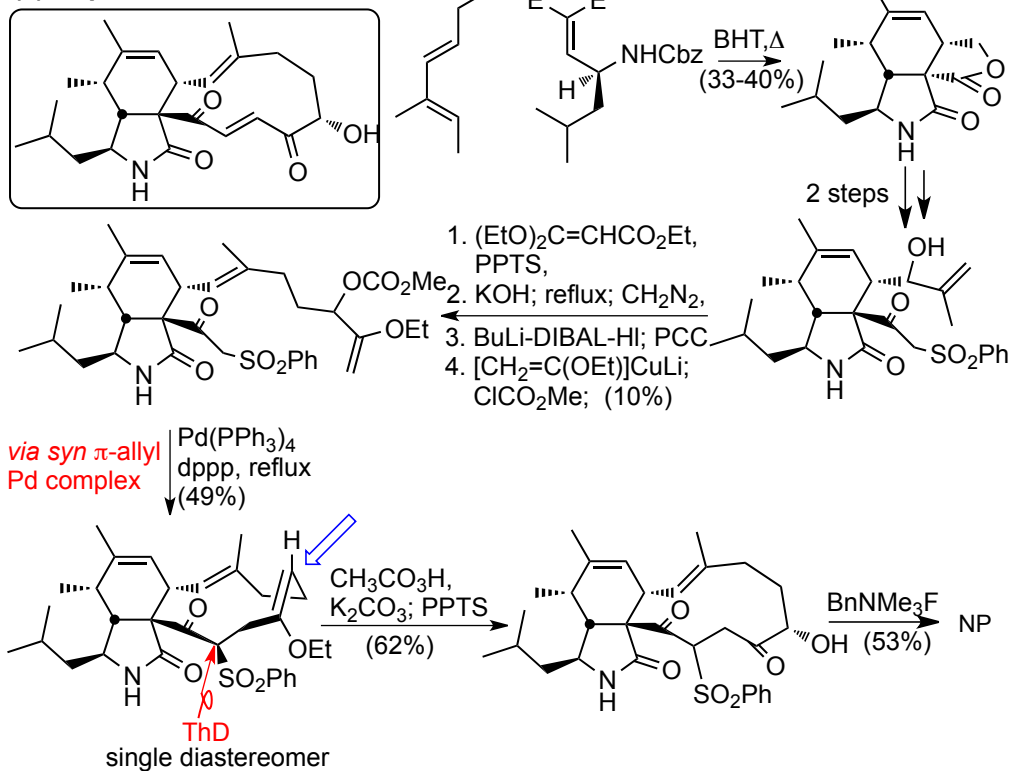
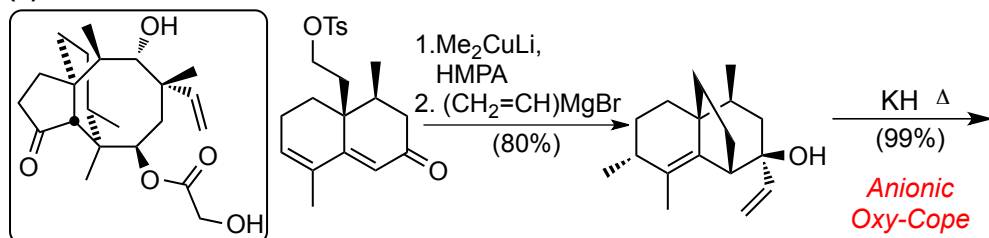
**(-)-Picrotoxin**, Yoshikoshi, 3728



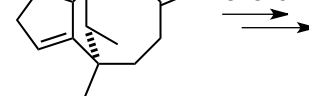
**(-)-Perhydrohistrionicotoxin**, Winkler, 4852



**Pseudopterosins A & E**, Corey, 5472**(±)-Dactylool**, Feldman, 6457**(-)-Cryptosporin**, Gupta, Franck, 7668**(-)-Echinospirin**, Smith III, 8039

**(-)-Aspochalasin B**, Trost, 8281**( $\pm$ )-Pleuromutilin**, Boeckman Jr., 8284

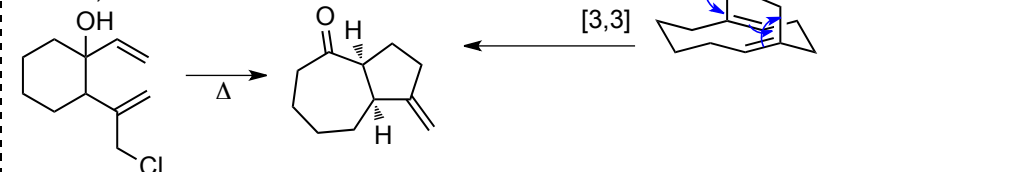
17 steps for required oxidation level and 3 more side chain Cs.



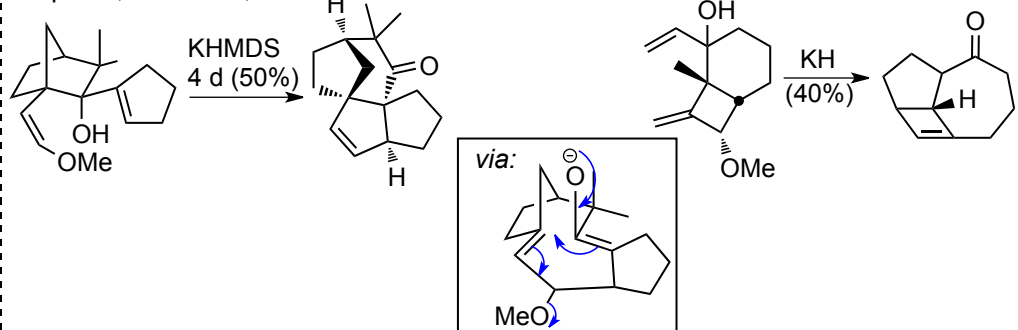
**RCM to the rescue!!!**

**Methodology: Invention and Study** via:**(Unexpected) Outcomes in Methodology**

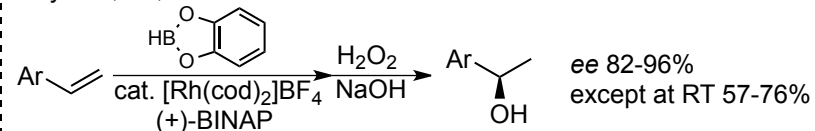
Swirin, 1815



Paquette, Schreiber, 2331

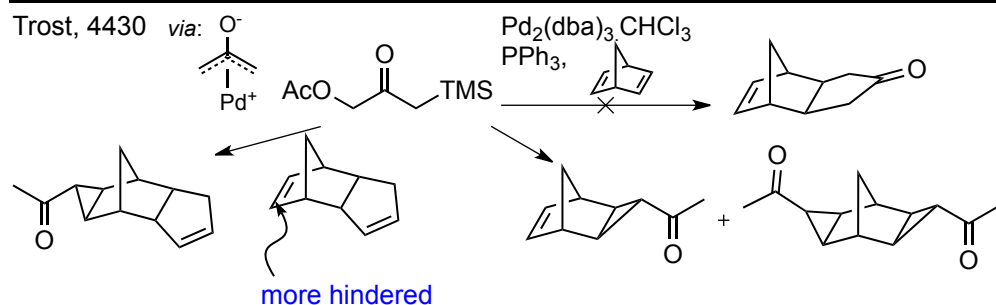


Hayashi, Ito, 3426

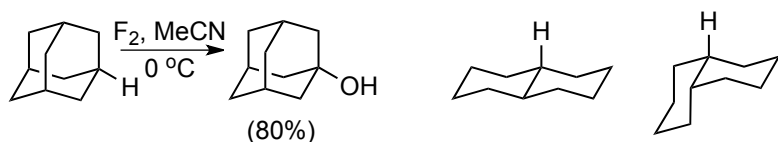


-complements normal hydroboration regioselectivity

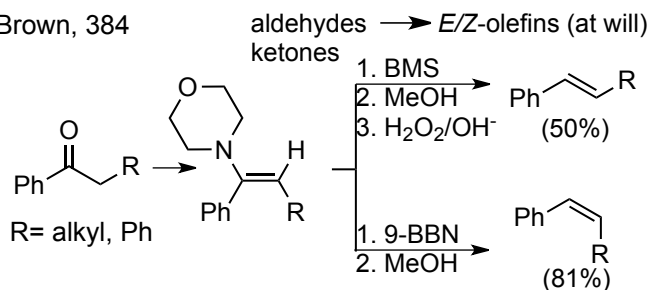
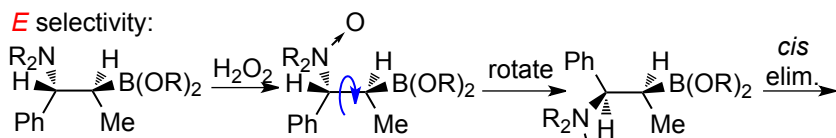
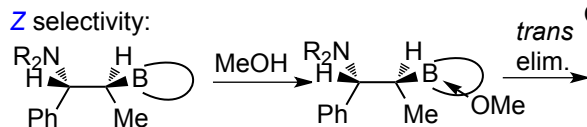
-only applicable to Rh cat. with  $3^\circ$  phosphine L and net + charge on Rh



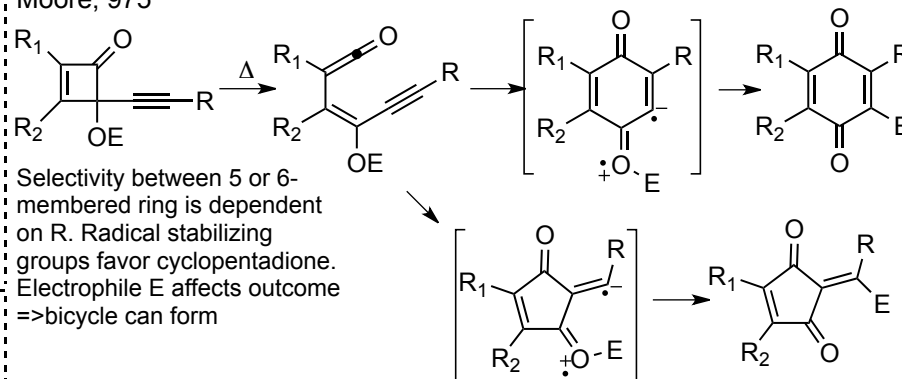
Rozen, 8325

**(Interesting) Selectivity Issues in Methodology**

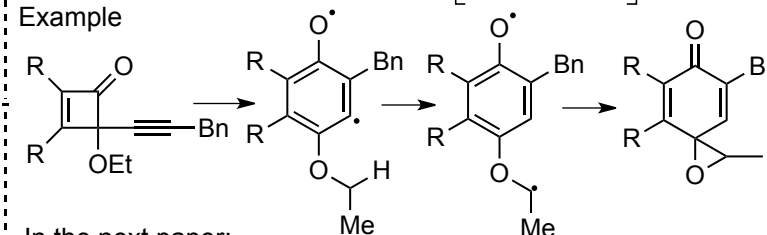
Brown, 384

*E* selectivity:*Z* selectivity:

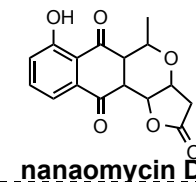
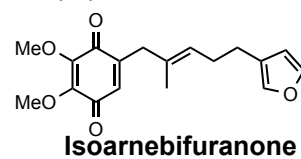
Moore, 975



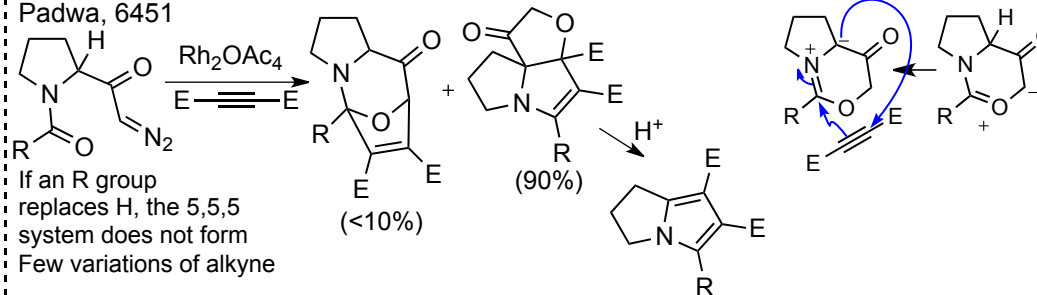
Example



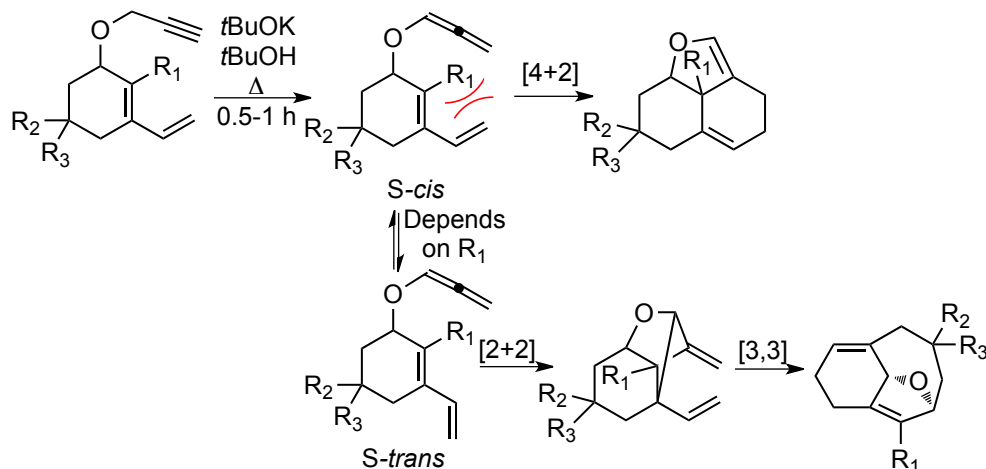
In the next paper:



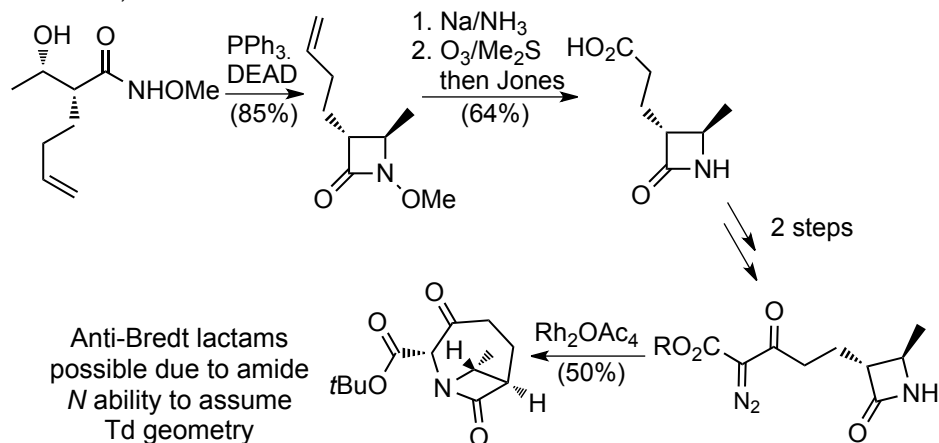
Padwa, 6451



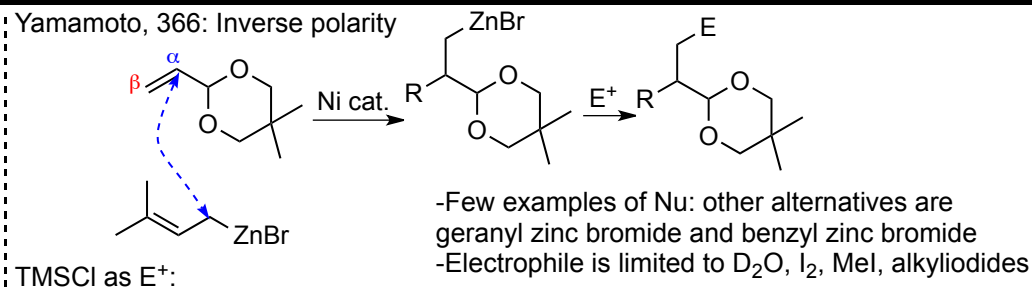
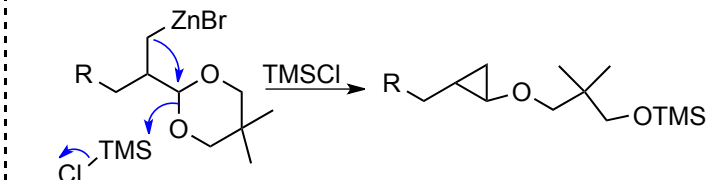
Kanematsu, 5312

**"Counter-intuitive"-chemistry in Methodology:**

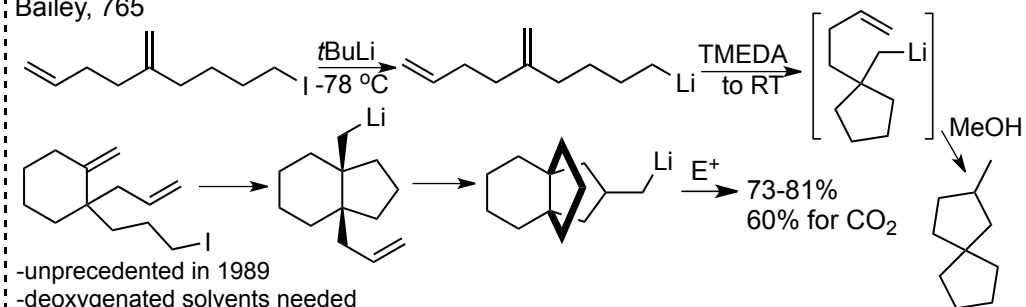
Williams, 1073: "Anti-Bredt lactam"



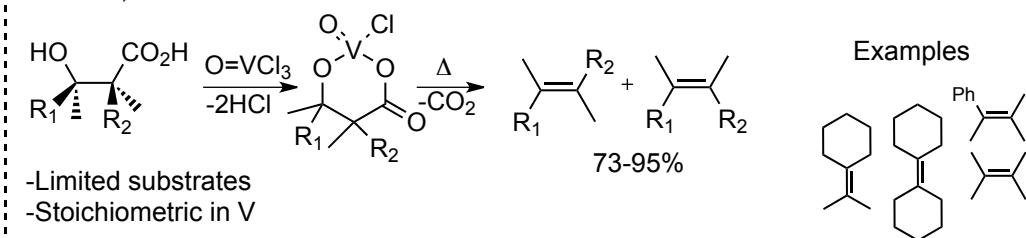
Yamamoto, 366: Inverse polarity

TMSCl as  $\text{E}^+$ :**Other Methodology:**

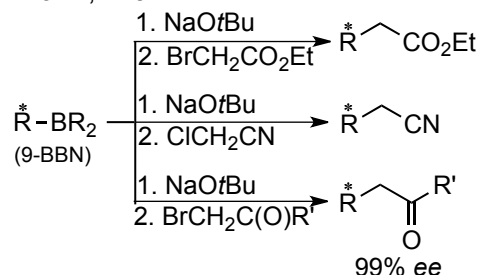
Bailey, 765



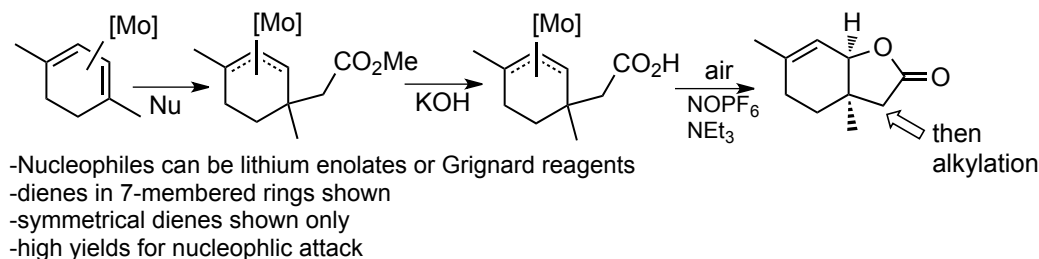
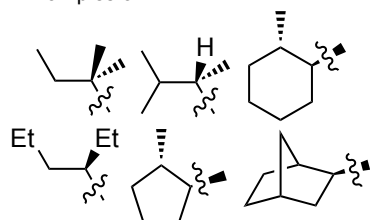
Schwartz, 3069



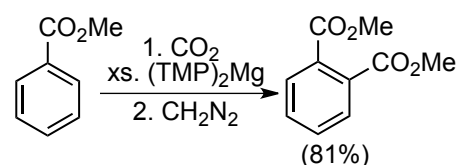
Brown, 1754



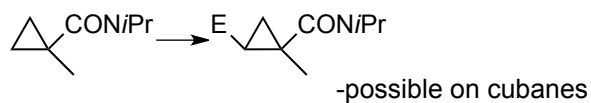
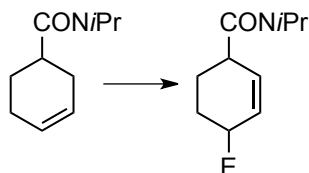
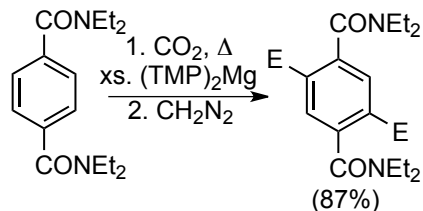
Examples of R:



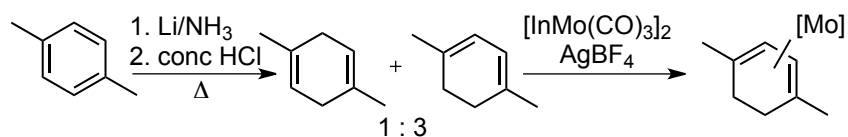
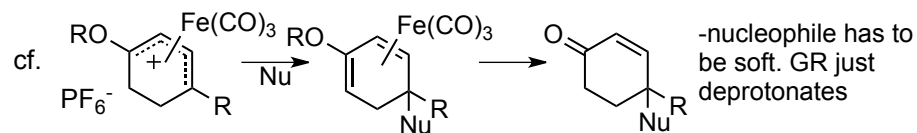
Eaton, 8016



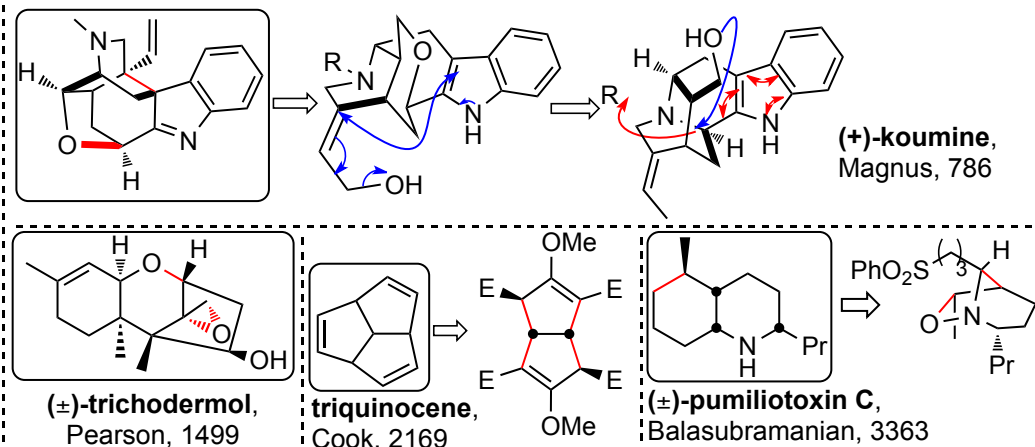
-ortho-lithiation not suitable with methyl ester  
 -double ortho-lithiation not common  
 -not limited to aromatic systems



Pearson, 6778

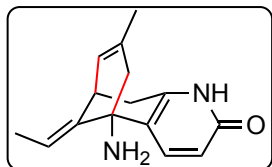
**Methodologies (not covered)**

- Buchwald Zr chemistry: Pages 776 and 2870 (see Maimone GM)
- Pd cat. cross-coupling: Negishi, 3089; 3336; 3454; 8018
- SmI<sub>2</sub> promoted reductive coupling: Molander, 8236
- TFDO oxidation: Curci, 6749
- Diels-Alder related: eg. Corey 5493
- Sharpless Dihydroxylation related
- Trost Pd-TMM related: eg. 7487.
- Nicolaou Brevetoxin B related: eg. 5321, 5330, 5335...
- Stryker's reagent-conjugate reduction, 8818.
- Aldol related

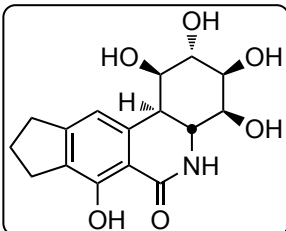
**Total Syntheses (not covered)**



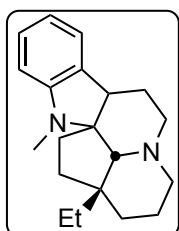
## Total Syntheses (not covered) cont'd



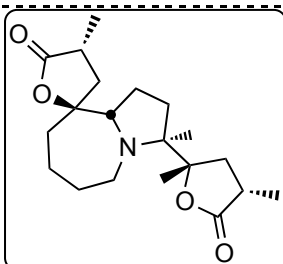
**Huperzine A,**  
Kozikowski, 4116



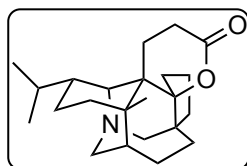
**Pancratistatin,**  
Danishefsky, 4829



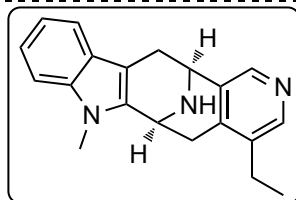
**Vallesamidine,**  
Heathcock, 1528



**(+)-croomine,** Williams,  
1923



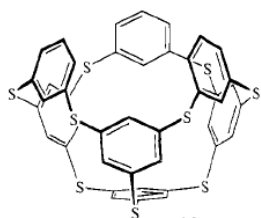
**Daphnilactone A,**  
Heathcock, 1530



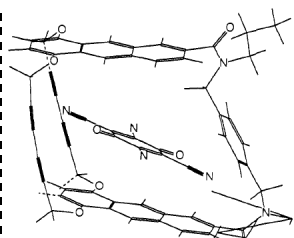
**(±)-Suaveoline,**  
Cook, 7504

and many more...

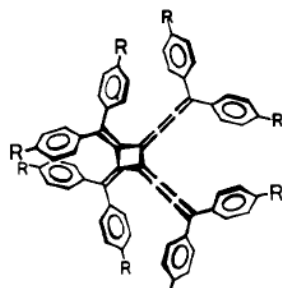
## Interesting Structures



**Large molecular bowl,**  
Pascal Jr., 6846



**Cyclophane hosts,**  
Whitlock Jr., 692



**[4]Radialene system,**  
Iyoda, 3761