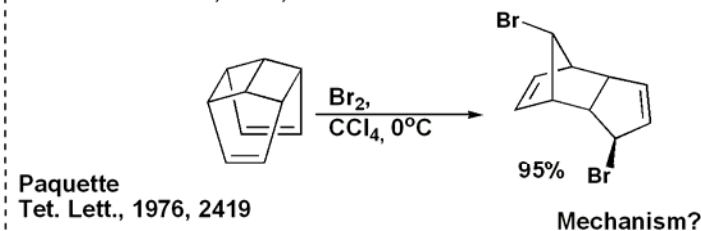
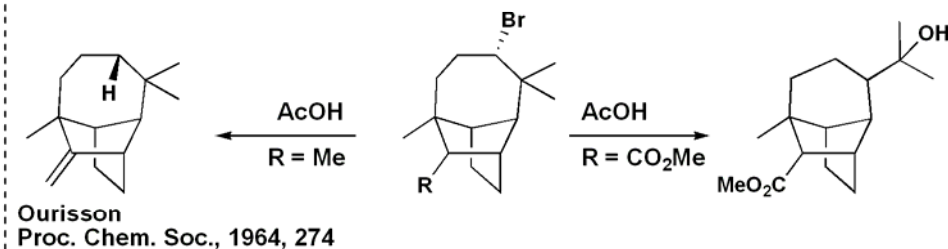
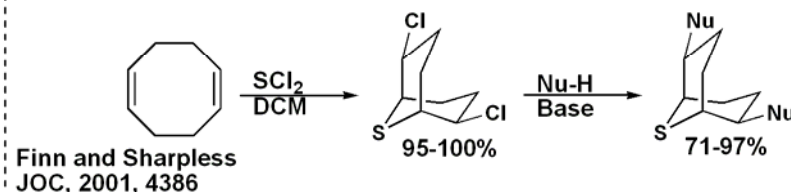
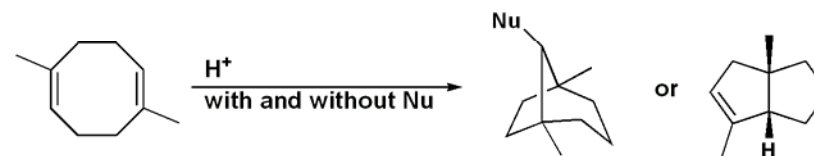
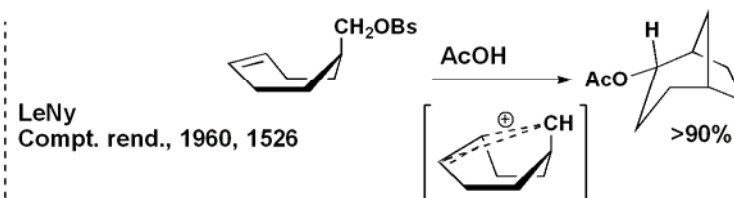
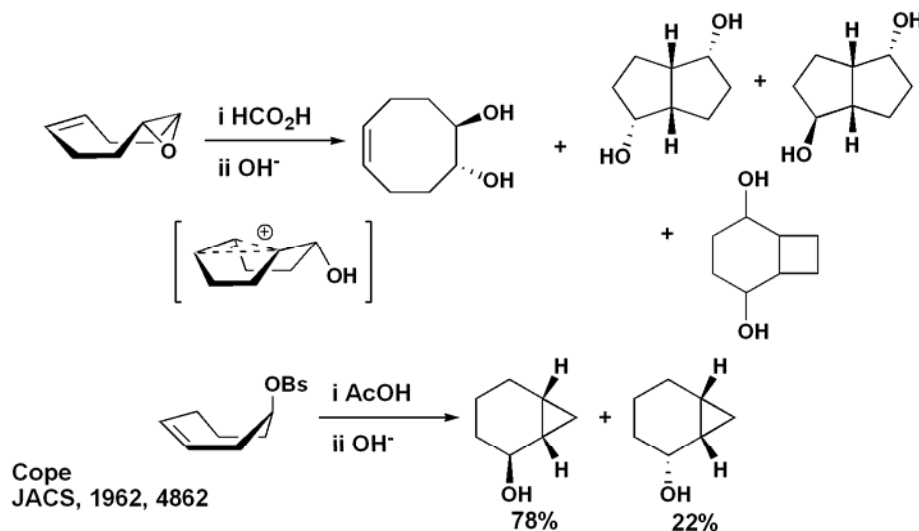
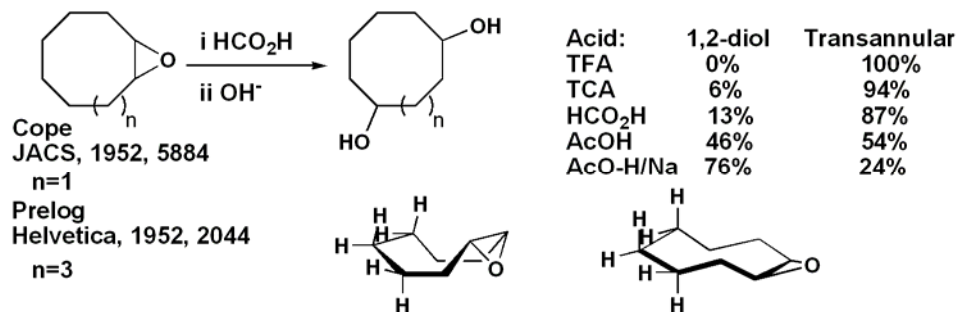


Transannular = across the ring  
 Defined as those reactions which leads to the formation of a covalent bond between atoms on opposite sides of a ring compound

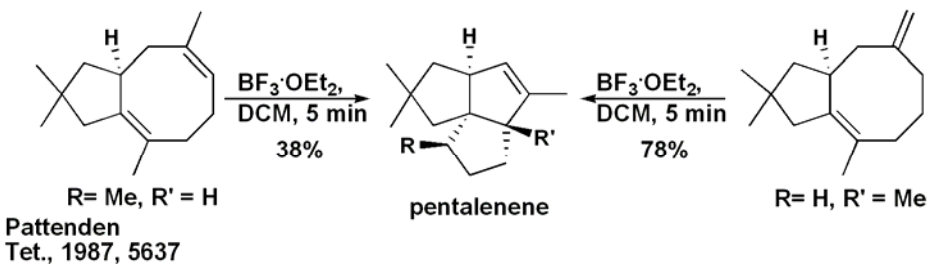
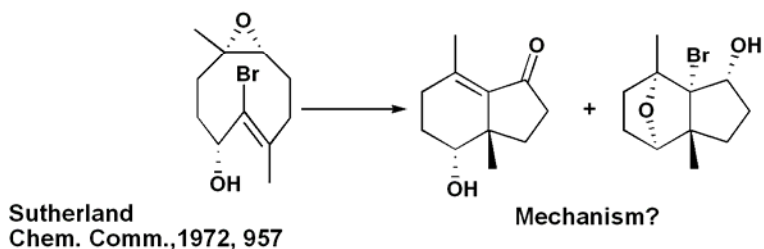
Initial transannular work:  
 Cope used 8-membered rings and  
 Prelog 10-membered rings

Scifinder: Transannular 3800,  
 Transannular reactions 160/1000

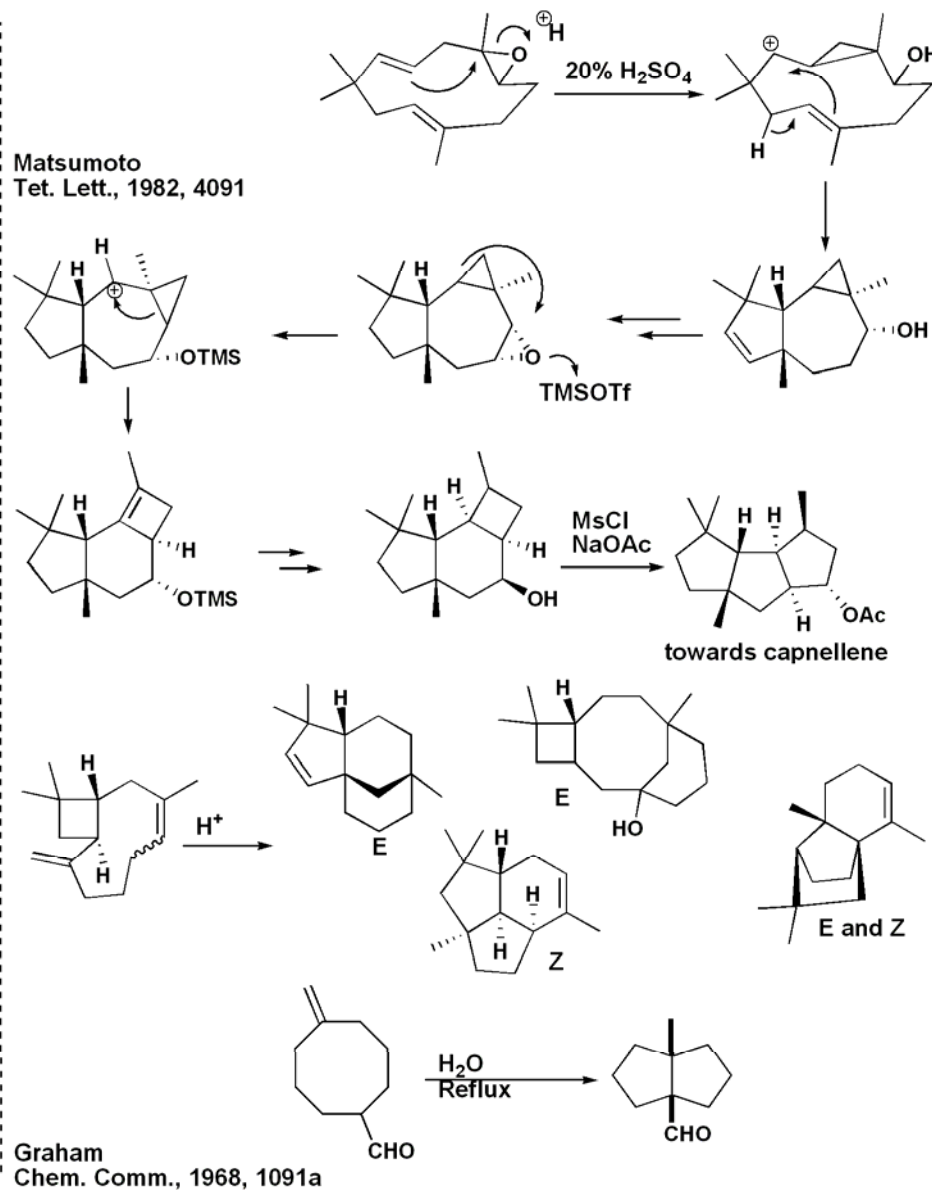
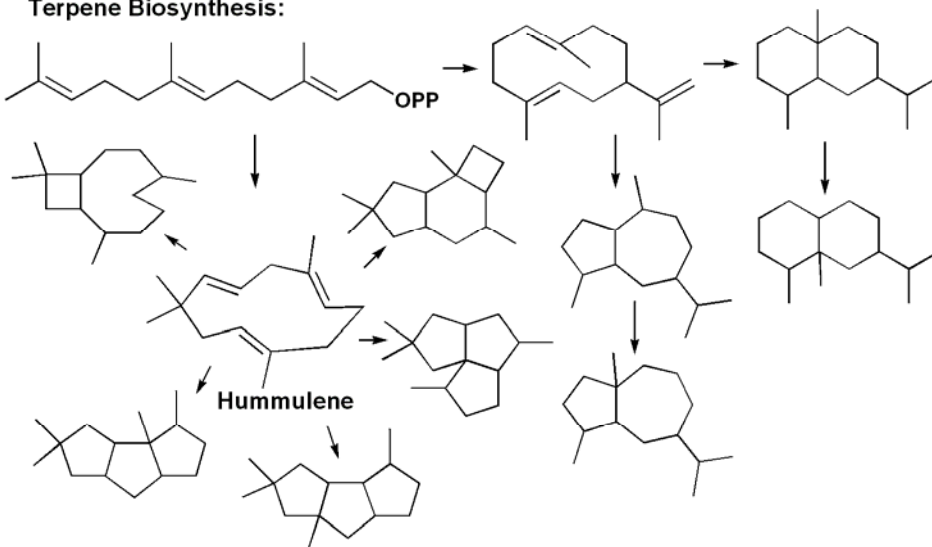
Cope: Kind of neighboring group effect  
 for which the confirmation of the ring is responsible.

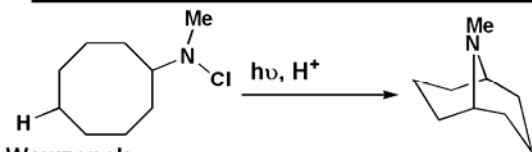


# Transannular reactions

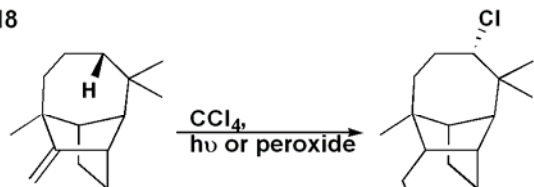


Terpene Biosynthesis:

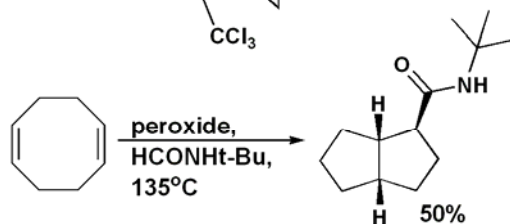




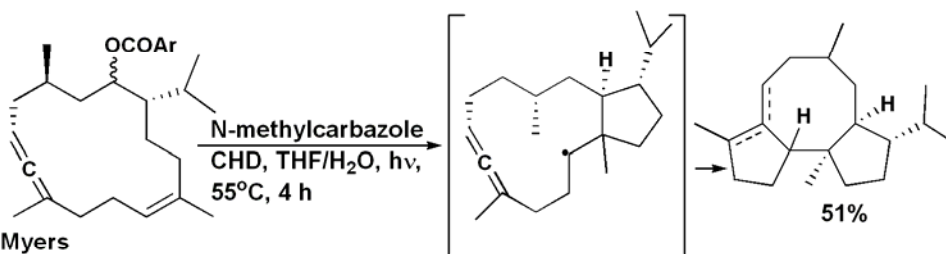
Wawzonek  
JACS, 1950, 2118



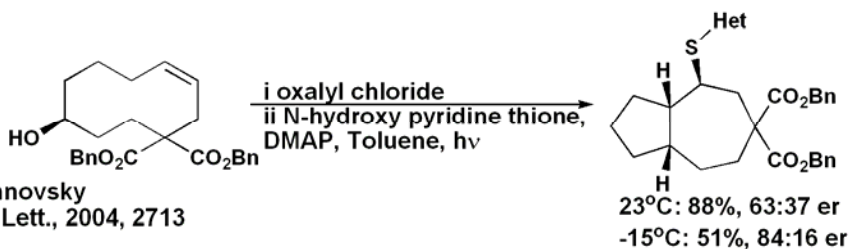
Ourisson  
Proc. Chem. Soc., 1964, 274



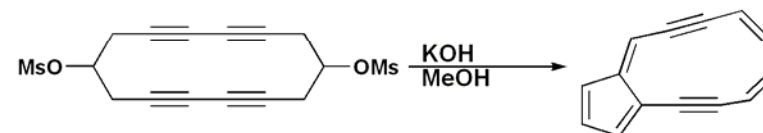
Dowbenko  
JACS, 1965, 946



Myers  
JACS, 1995, 3057

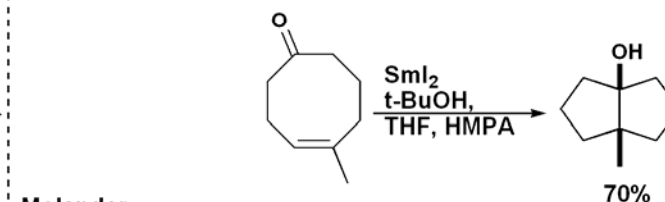
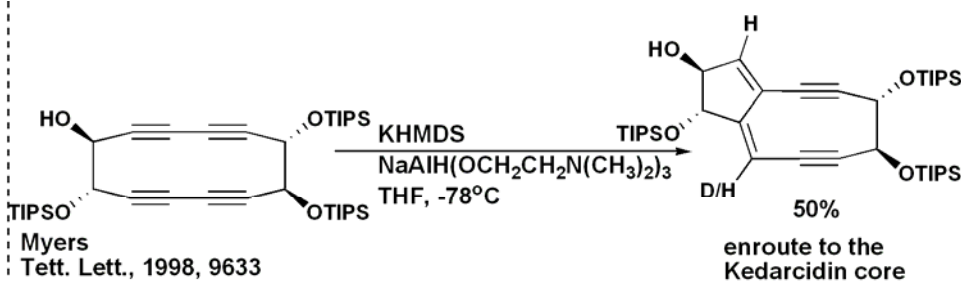


Rychnovsky  
Org. Lett., 2004, 2713

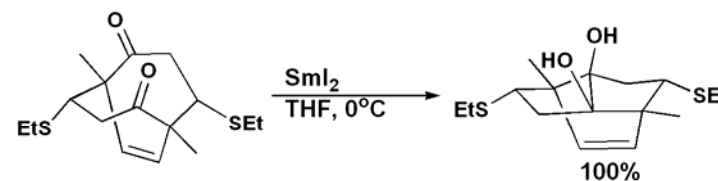


Mayer and Sondheimer  
JACS, 1966, 602

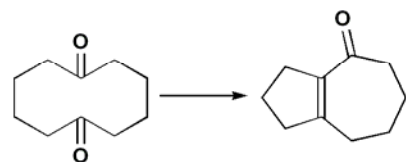
Mechanism?



Molander  
JOC, 2007, 1755

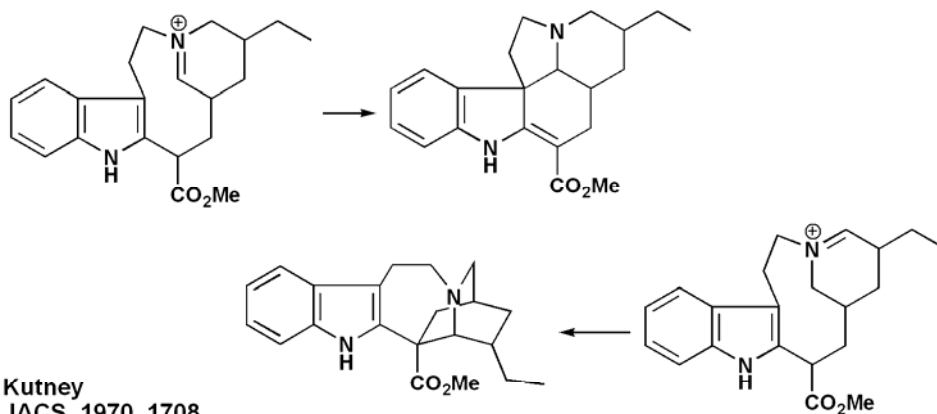


Inoue  
Tet. Lett., 2009, 1035

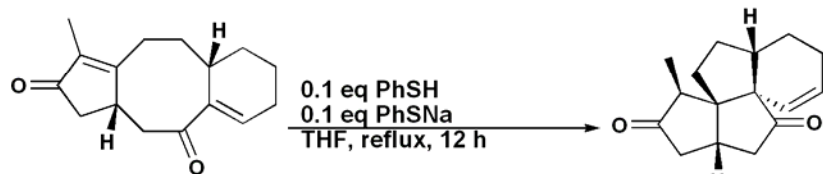


"trivial" transannular reaction?

Vinca and Iboga alkaloids:



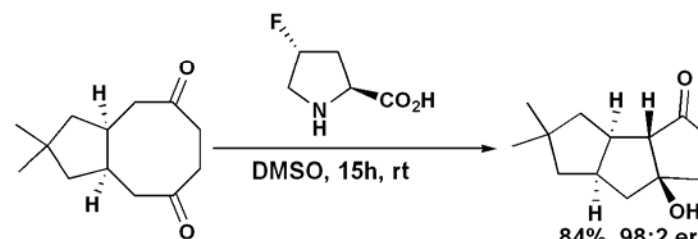
Kutney  
JACS, 1970, 1708



Moore  
Org. Lett., 1999, 375

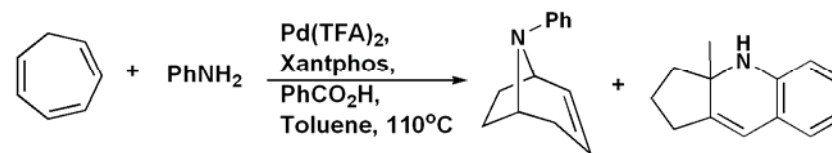
Carbonskeleton of waihoesene

Mechanism?

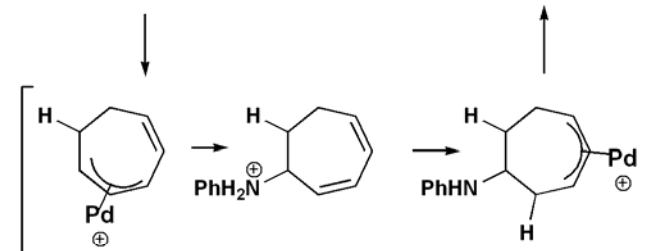


List  
JACS, 2008, 6737

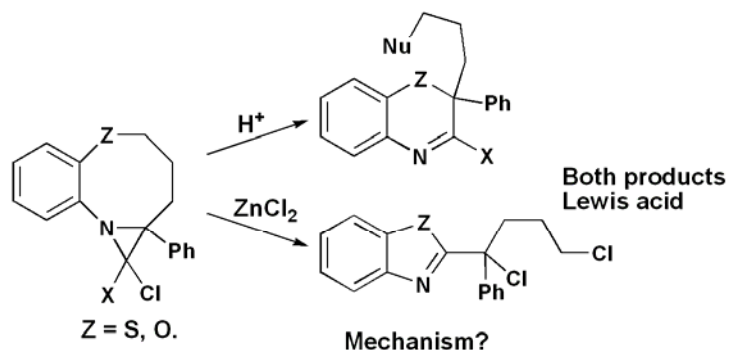
84%, 98:2 er  
enroute to (+)-hirsutene



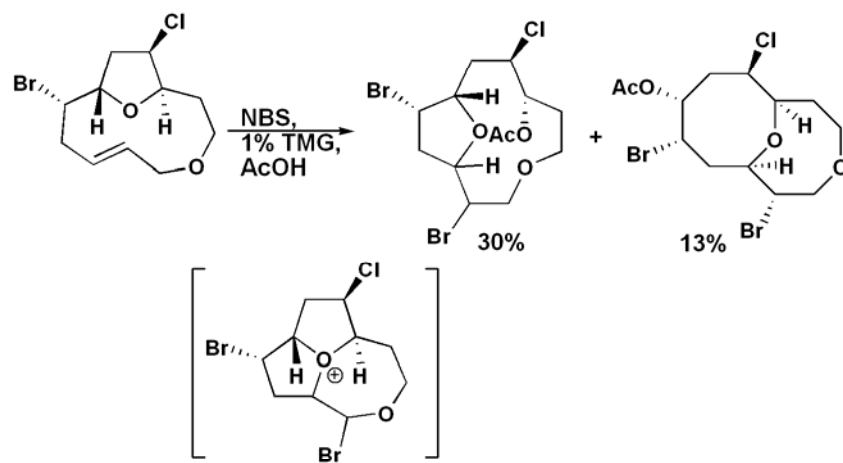
Mechanism for biproduct?



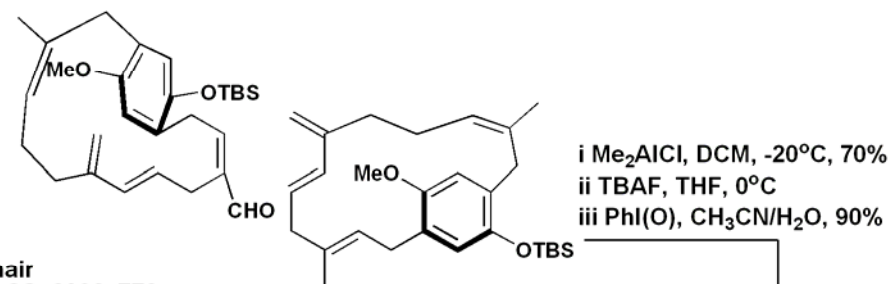
Hartwig  
JACS, 2006, 8134



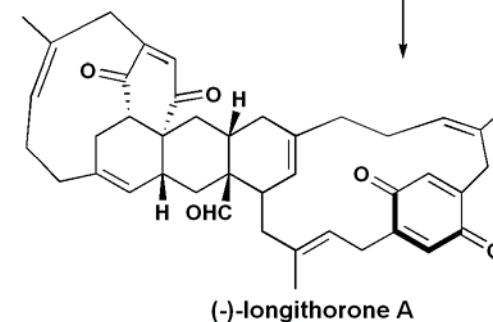
Khlebnikov  
Russian JOC, 2007, 1071



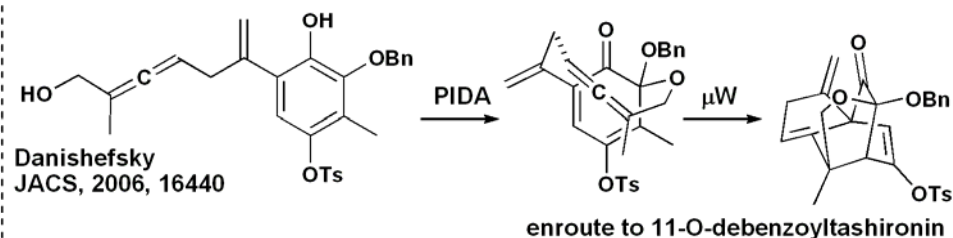
Braddock  
JOC, 2009, 1835



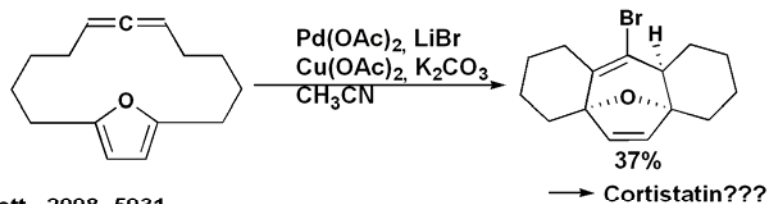
Shair  
JACS, 2002, 773



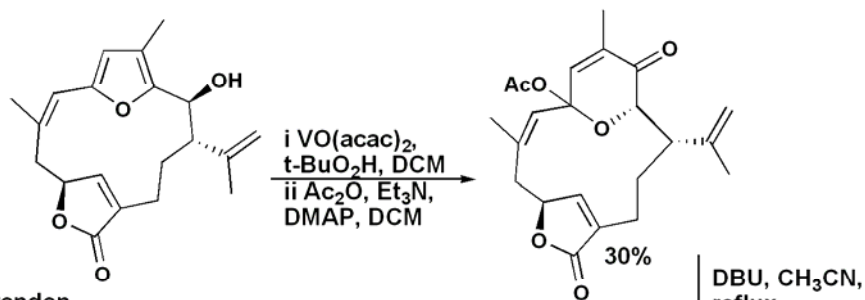
Deslongchamps: The complexity and power of the transannular Diels-Alder (TADA) strategy arises from a judicious choice of substituents that will govern the conformation adopted by the macrocycle at the transition state level, via transannular steric repulsion and electronic interactions



Danishefsky  
JACS, 2006, 16440



Gung  
 Tet. Lett., 2008, 5931



Pattenden  
 Tet. Lett., 2006, 6401

