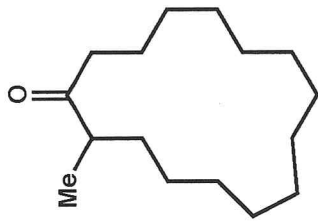
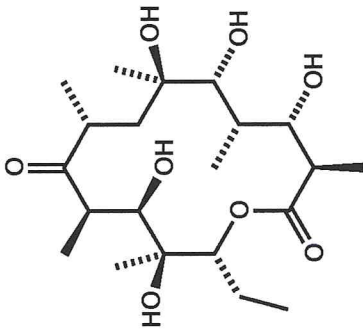


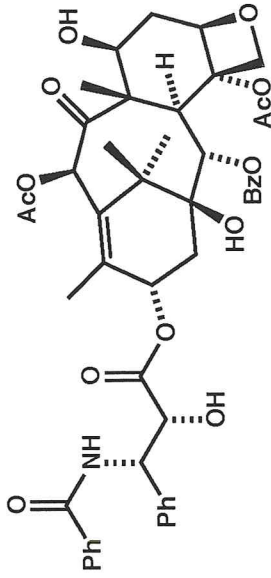
LARGE RINGS



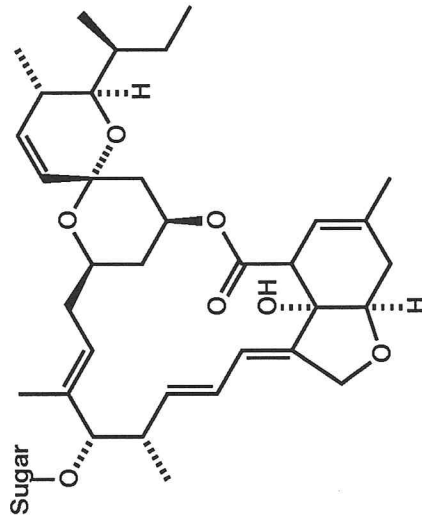
Muscone



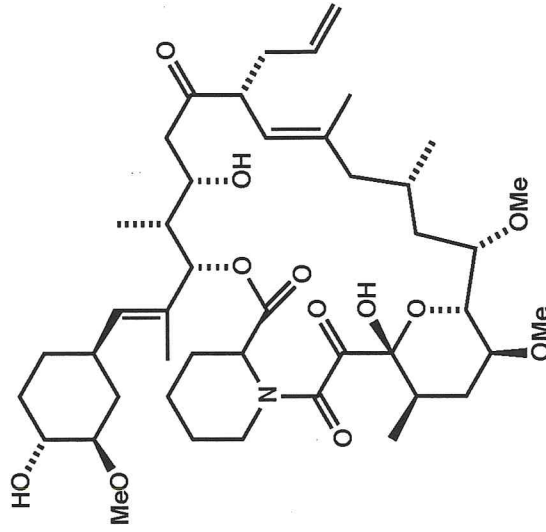
Erythronolide A



Taxol

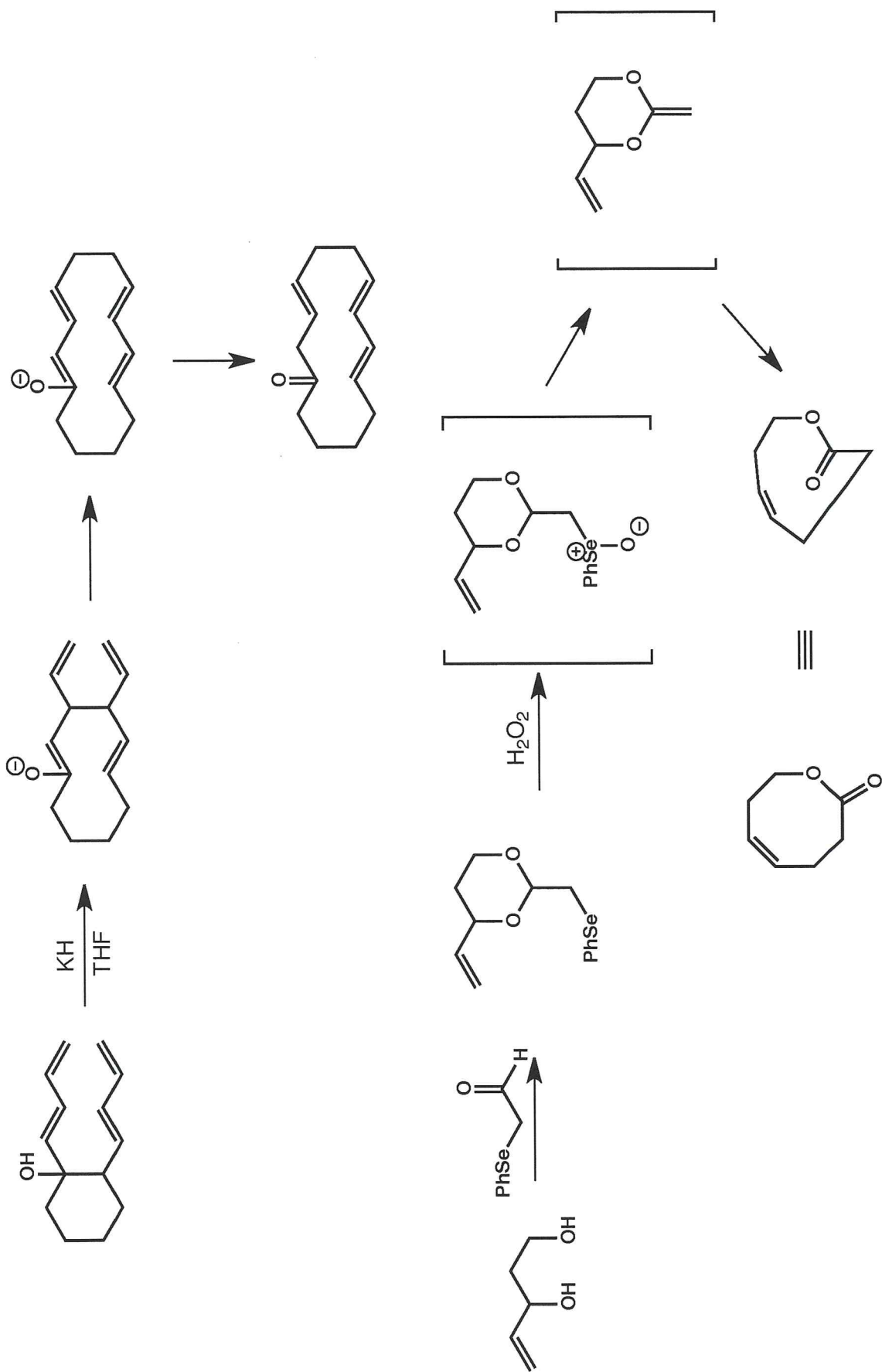


Avermectin

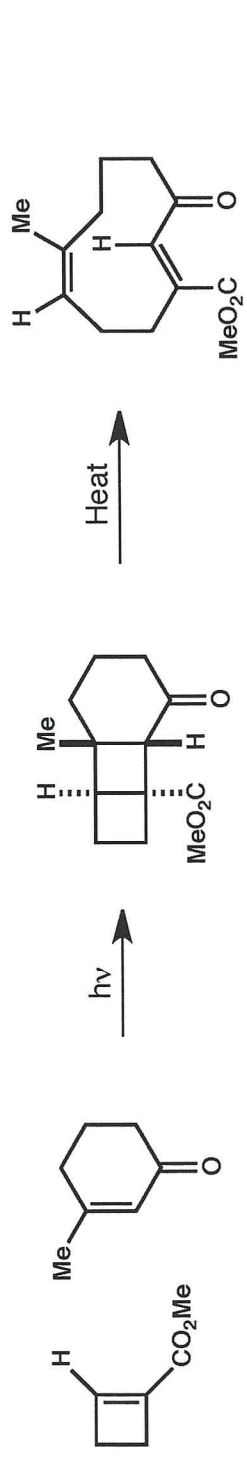


FK-506

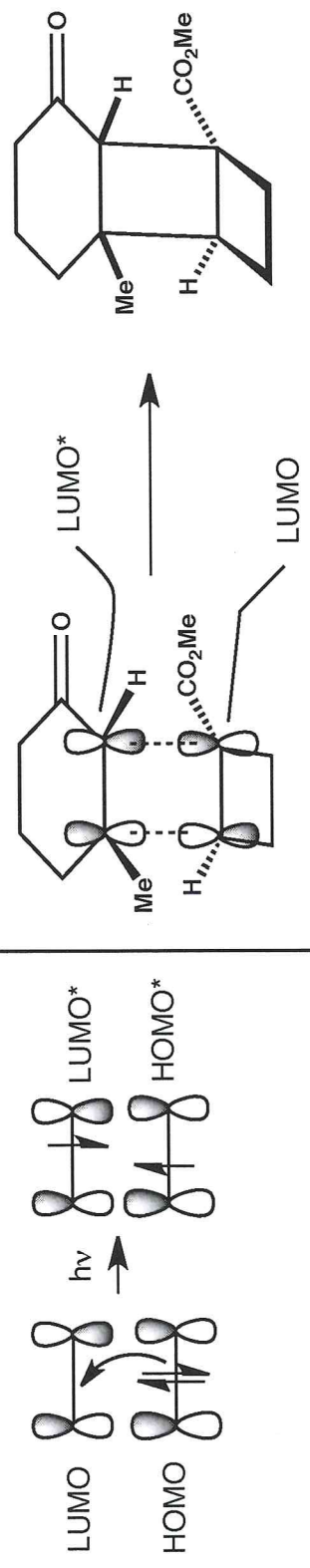
FORMATION OF LARGE RINGS 1: SIGMATROPIC REARRANGEMENTS



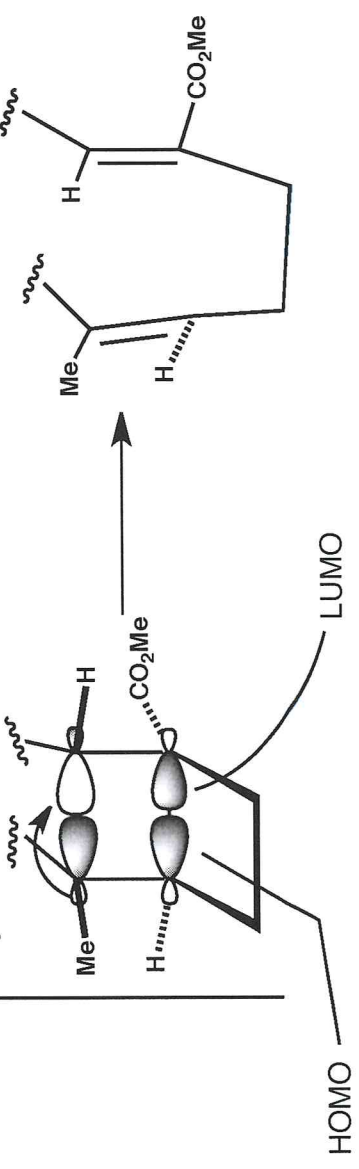
# LARGE RINGS 2:[2+2]-Cycloaddition /Cycloreversion



Cycloaddition: Photochemical process

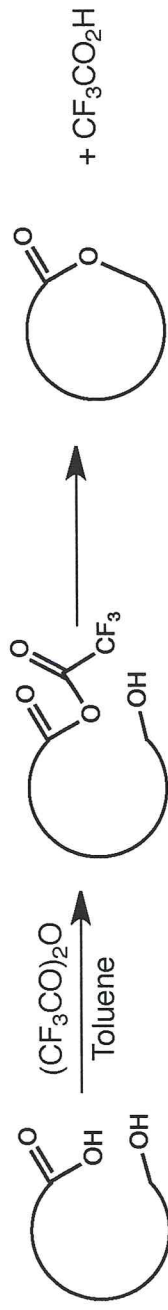


Cycloreversion: Thermal Process, HOMO - bonding, LUMO - antibonding.

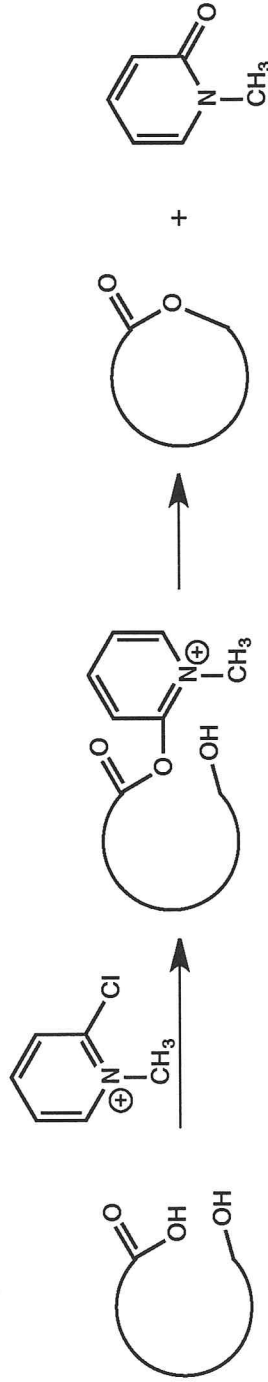


# MACROLACTONIZATION 1

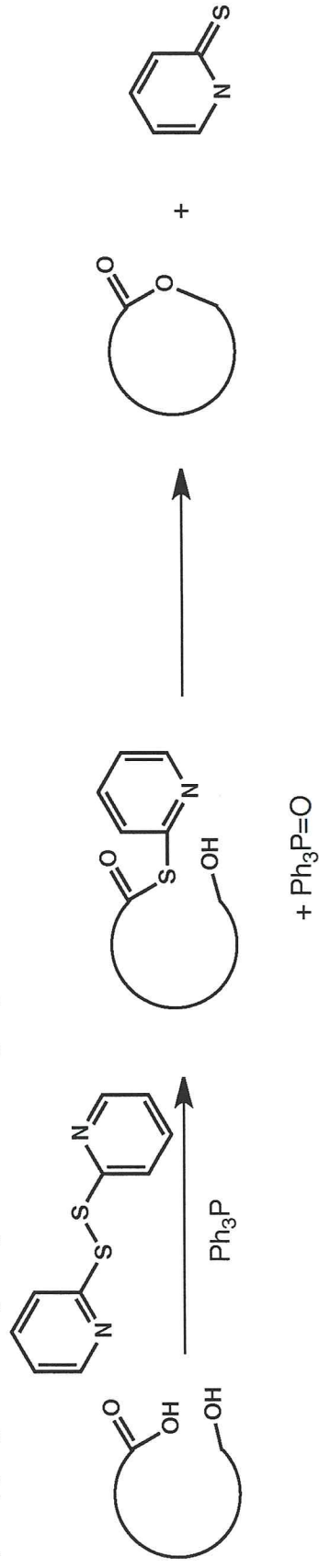
1) Mixed Anhydrides



2) Mukaiyama's Reagent

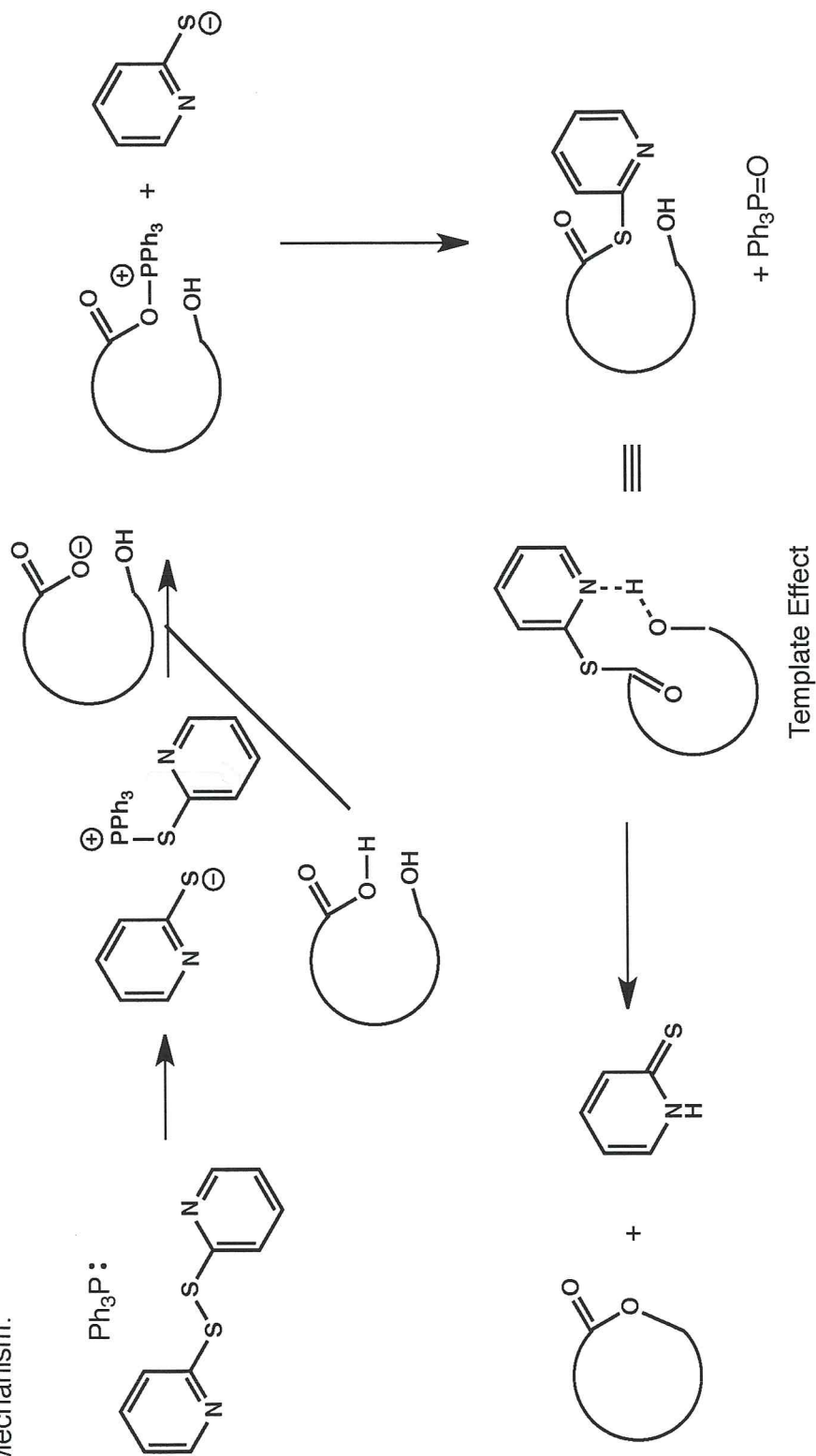


3) 2,2'-dipyridyldisulfide (Corey-Nicolaou Reagent)

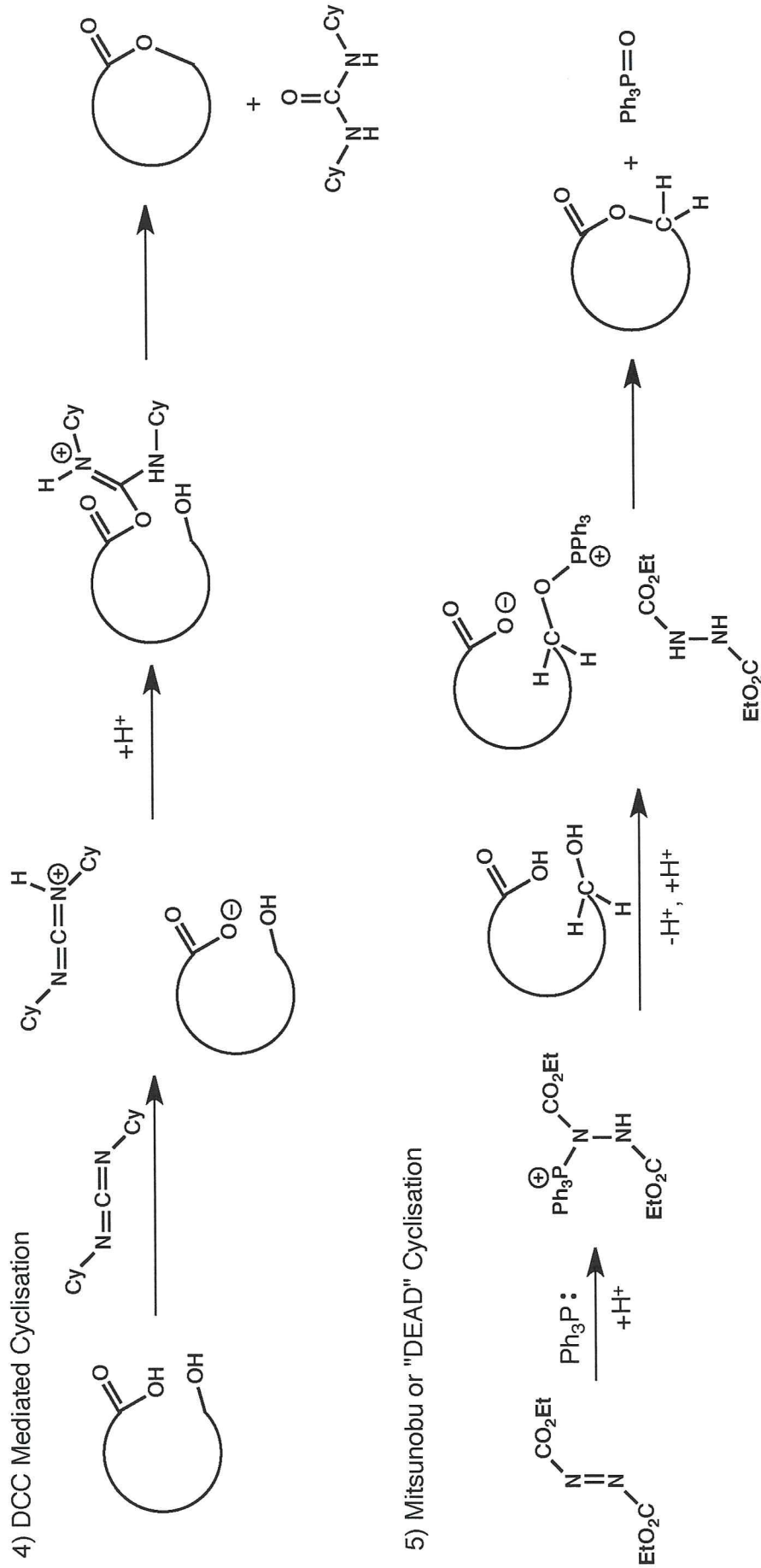


# COREY-NICOLAOU MACROLACTONIZATION

Mechanism:

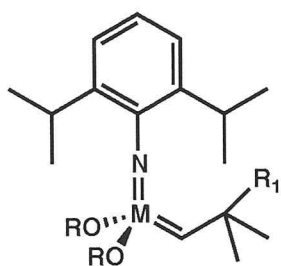


## MACROLACTONIZATIONS 2

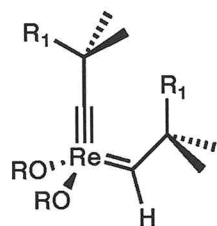


Here we have activation of the hydroxyl group.  
 This is an  $S_N2$  reaction with inversion of configuration at this original hydroxyl centre.

## OLEFIN METATHESIS

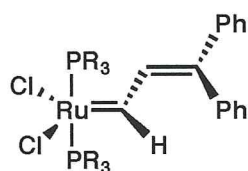


M = Mo, W

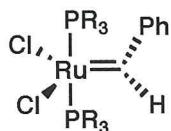


SCHROCK catalysts

R = alkyl, aryl  
R<sub>1</sub> = Me, Ph

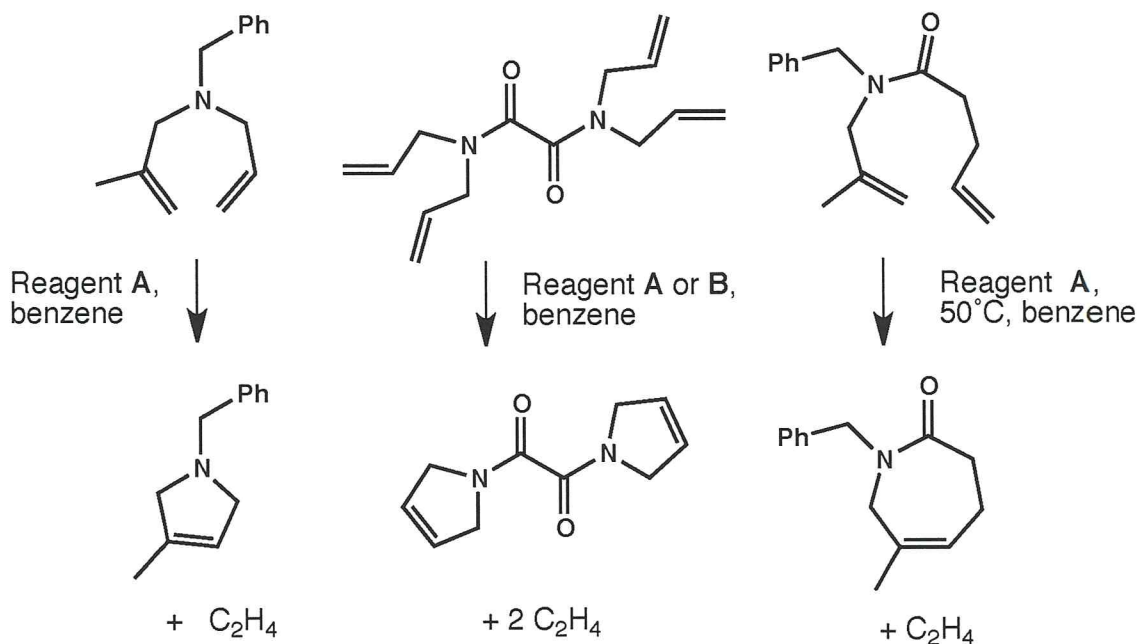


or



GRUBBS catalysts

R = Ph or

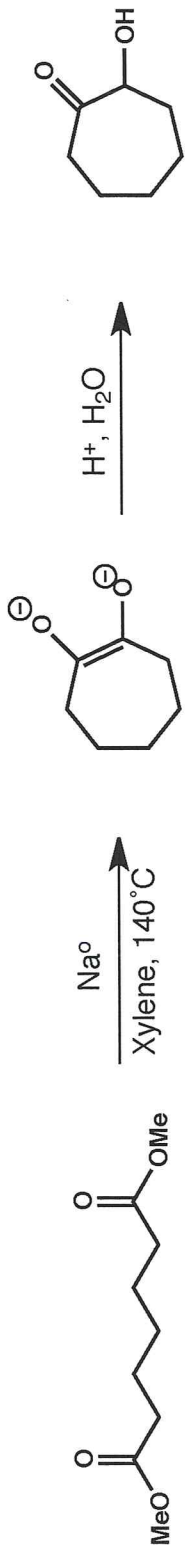


Reagent A: Mo(CHCMe<sub>2</sub>Ph)(NAr)(OCMe(CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub> (Ar=2,6-(i-Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) SCHROCK

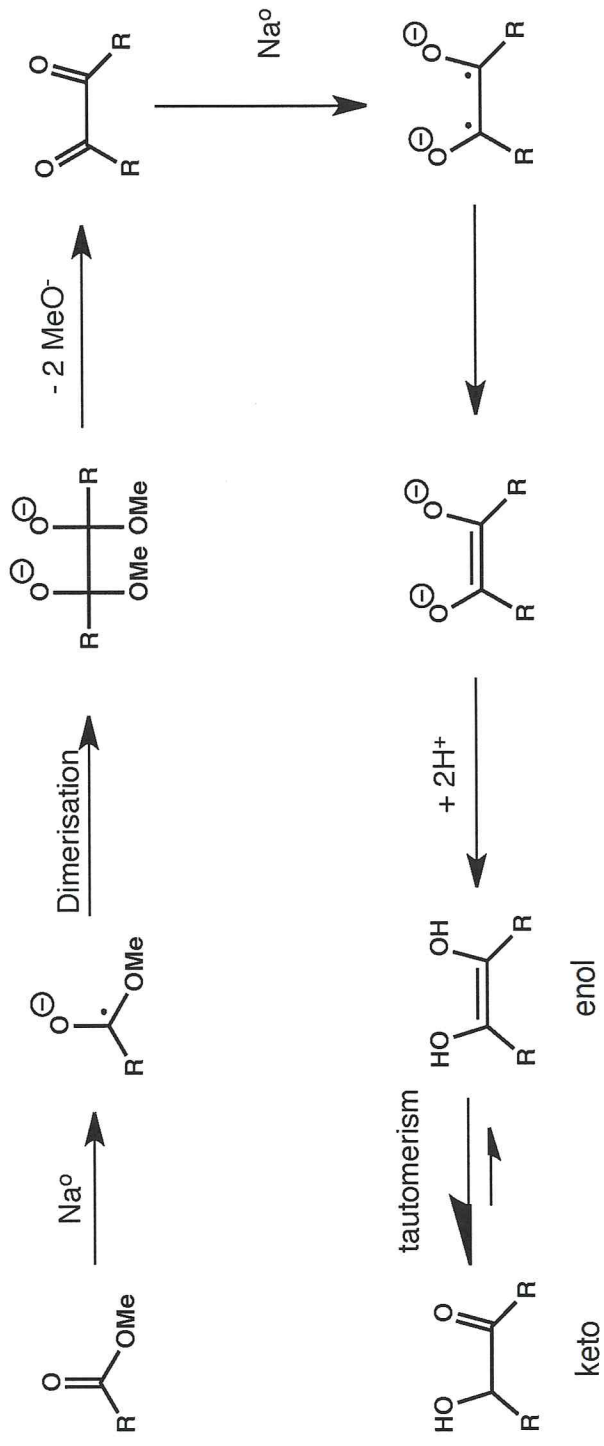
Reagent B: Cl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>Ru=CHCH=(Ph)<sub>2</sub>

GRUBBS

## ACYLOIN CONDENSATION



Mechanism





# McMURRY COUPLING

