

JACS Year in Review: 1984

Laura Schacherer

July 14th, 2006

Statistics for *JACS* 1984

Total Number of Papers: 2,215

Most Cited Paper: p.765 (cited 3,531x!) “ A New Force Field for Molecular Mechanical Simulation of Nucleic Acids and Proteins.”

Top 25 Authors:

22: Smith PA

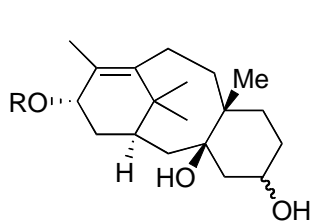
15: Huffman JC, Paquette LA (14), Cotton FA(13), Dewar MJ(12),
Freiser BS(10), Gray HB (10), Lippard SJ(10), Scaiano JC(10)

9: Corey EJ

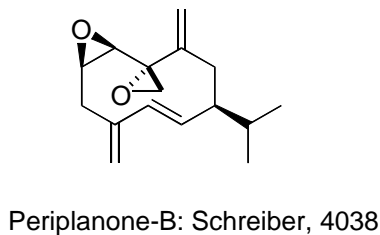
8: Clardy J, Lamar GN, Marks TJ, Trost BM, Whittle RR

7: Brown HC, Bruice TC, Chisholm MH, Cram DJ, Fendler JH,
Gassman, PG, Hawthorne MF, Houk KN, Ingold KU.

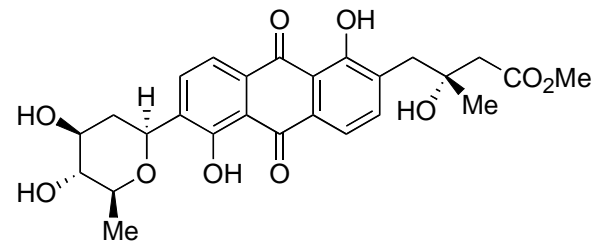
Some Synthetic Achievements in 1984:



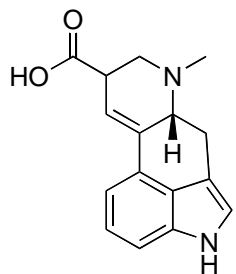
Taxane: Holton, 5731



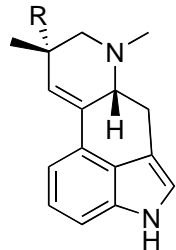
Periplanone-B: Schreiber, 4038



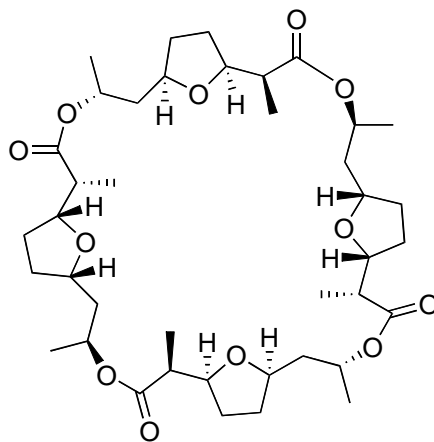
Vineomycin B2 aglycon: Danishefsky, 2453



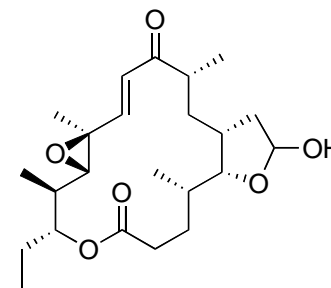
Lysergic Acid



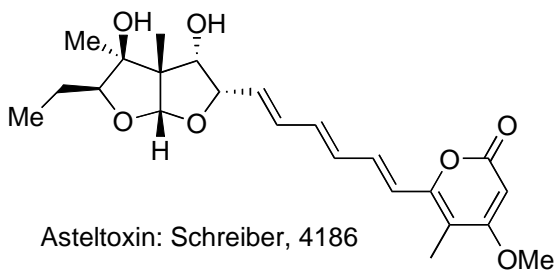
R=H, Lysergine
R=OH: Setoclavine
Rebek, 1813



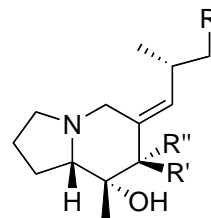
Nonactin: Bartlett, 5304



3-Deoxyrosaranolide: W.Clark Still, 1148

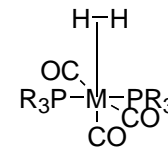


Asteltoxin: Schreiber, 4186



Allopumiliotoxin A alkaloids: Overman, 5360

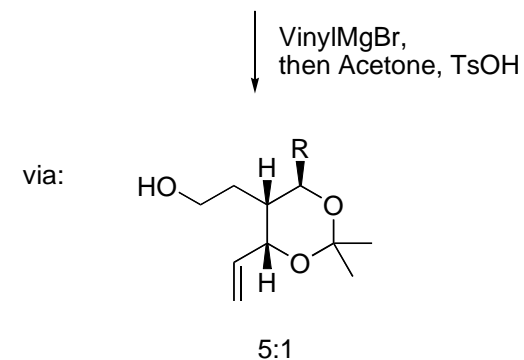
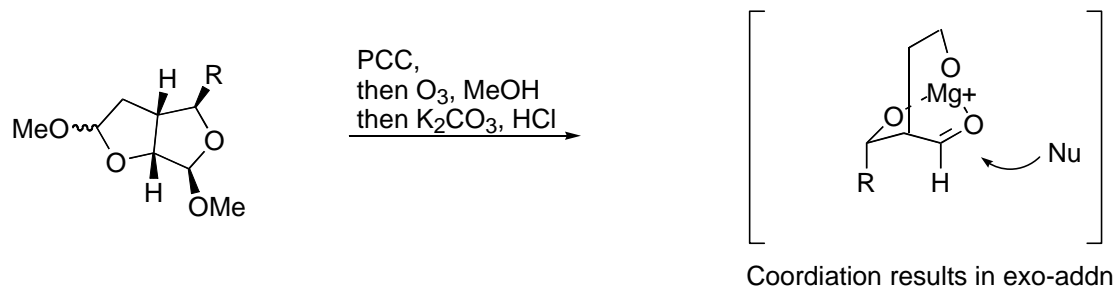
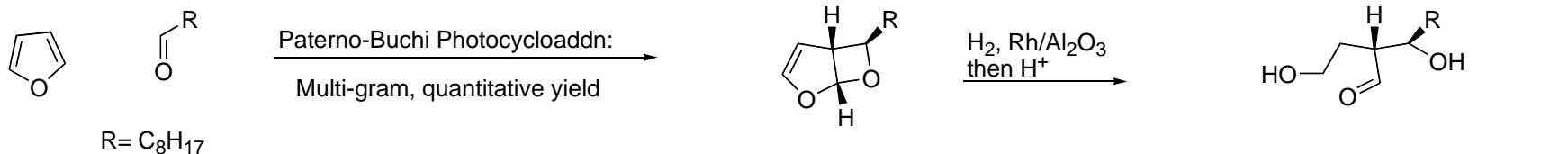
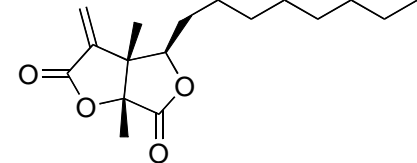
Pumiliotoxin A alkaloids, R'=R''=H: 4192



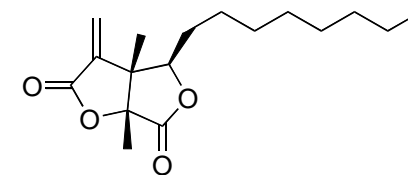
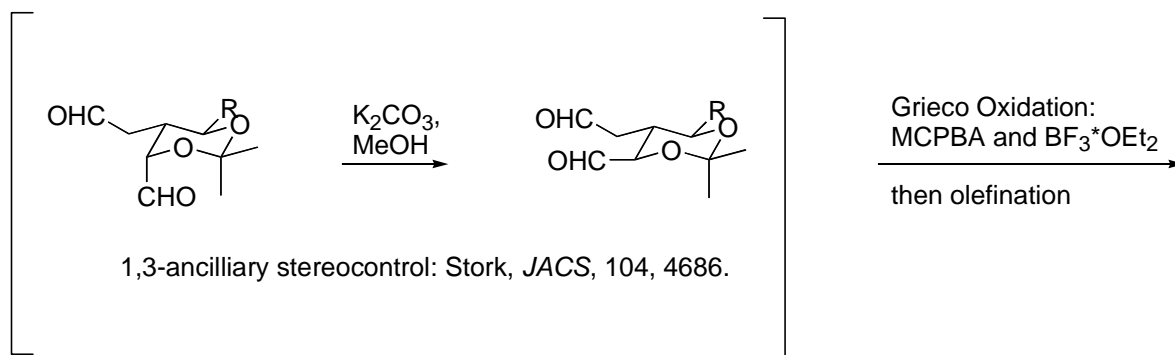
M=Mo, W

First Crystal Structure of Agostic H₂ Complex: 451

Avenaciolide: Schreiber, p.7200

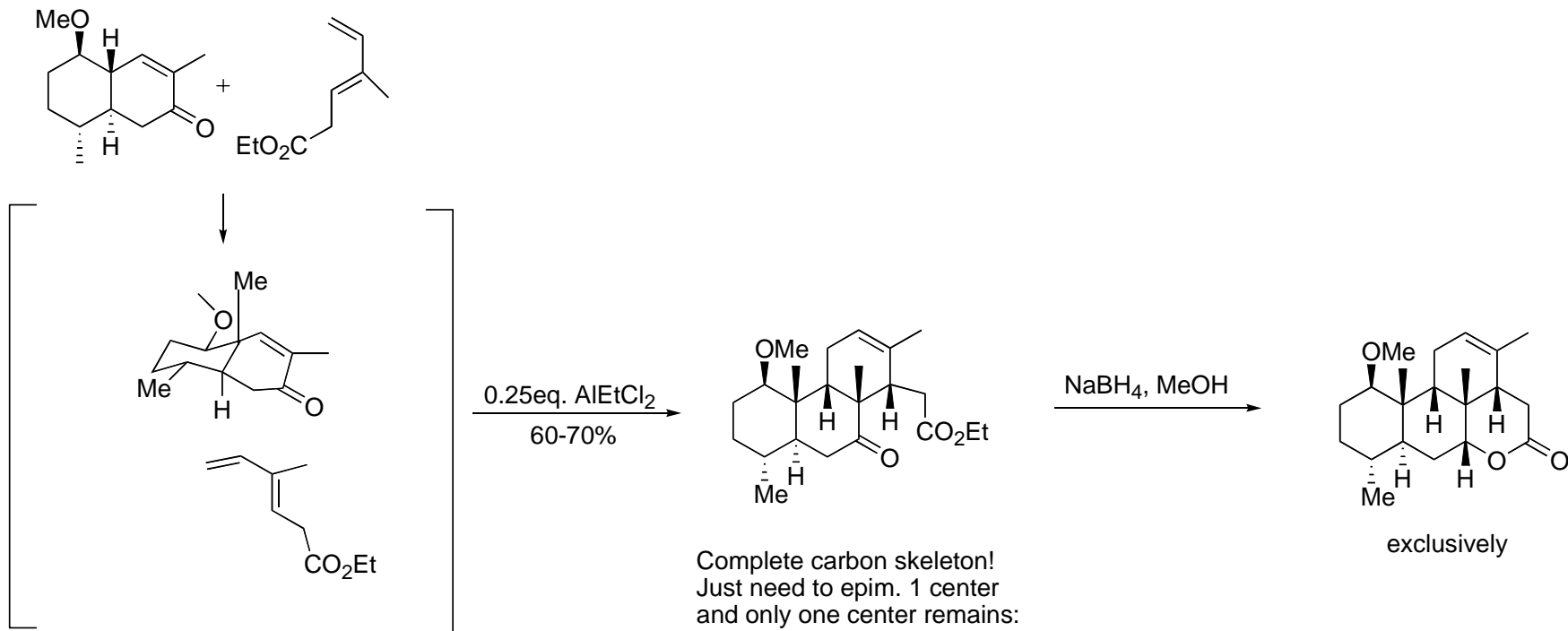
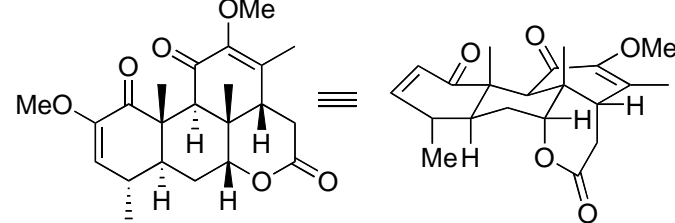


via:



10 Steps, 14.3% yield

Quassin: Grieco, p.3539

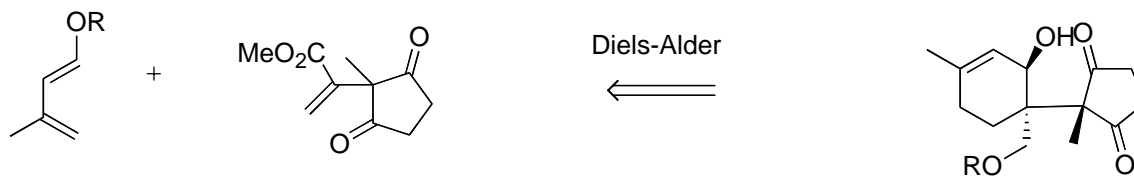
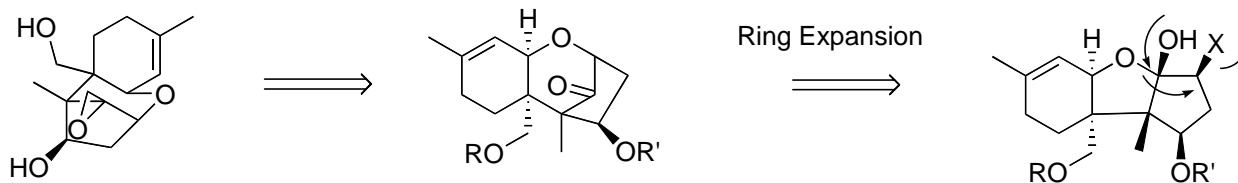
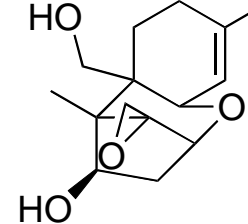


Desired adduct from ENDO approach to the alpha face of the enone

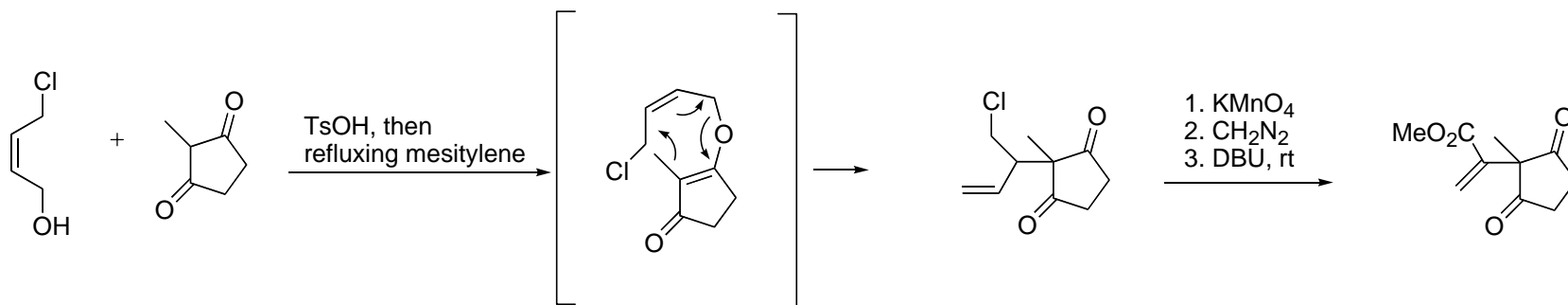
Complete carbon skeleton!
Just need to epim. 1 center
and only one center remains:

exclusively

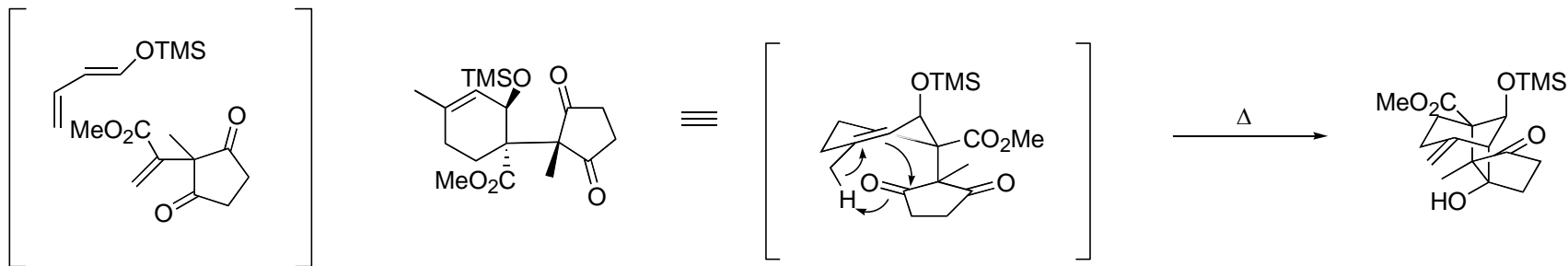
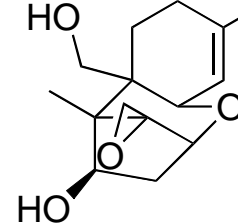
Verrucarol: Trost, p.383 (retrosynthesis)



To access dienophile:

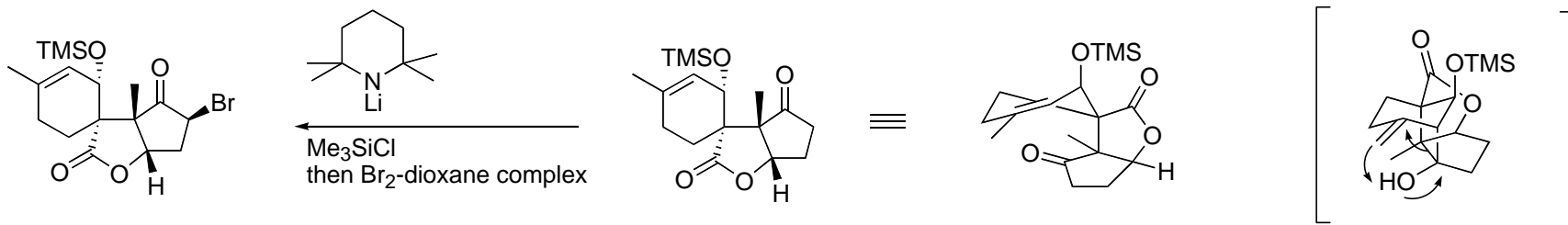


Verrucarol: Trost, p.383 (Diels-Alder)



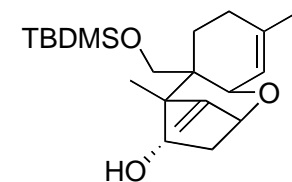
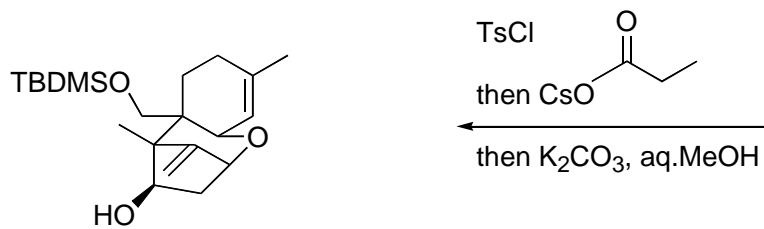
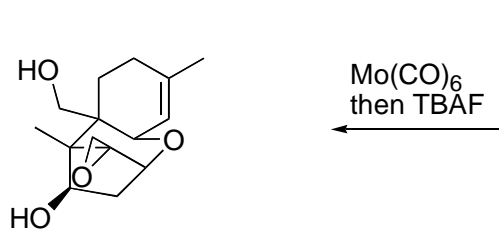
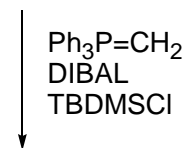
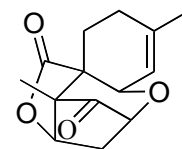
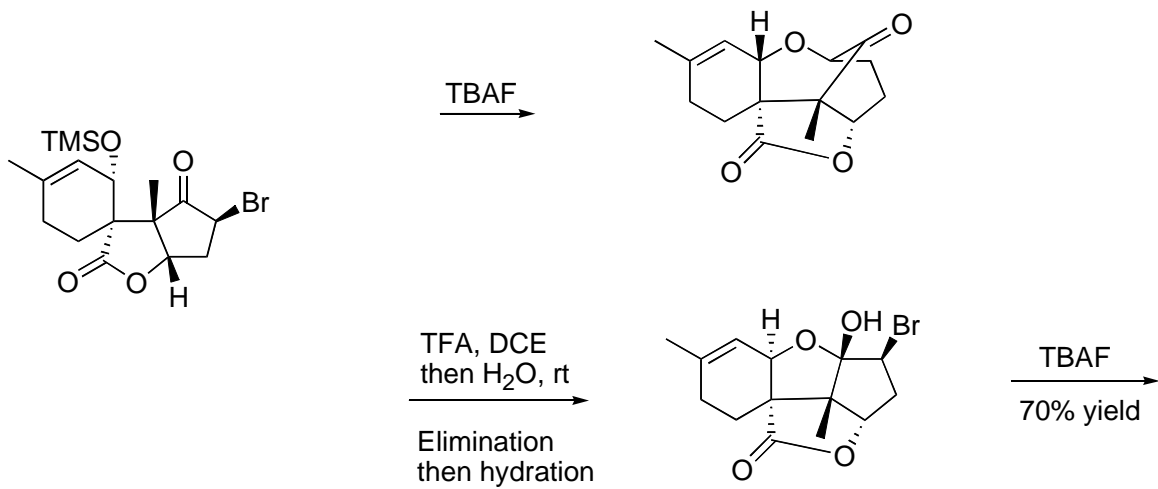
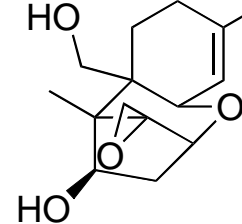
Undesired tandem D-A then ene reaction.
But a convenient way to differentiate
carbonyls

NaBH₄, then Collins Ox as wkup
then FVT retro-ene

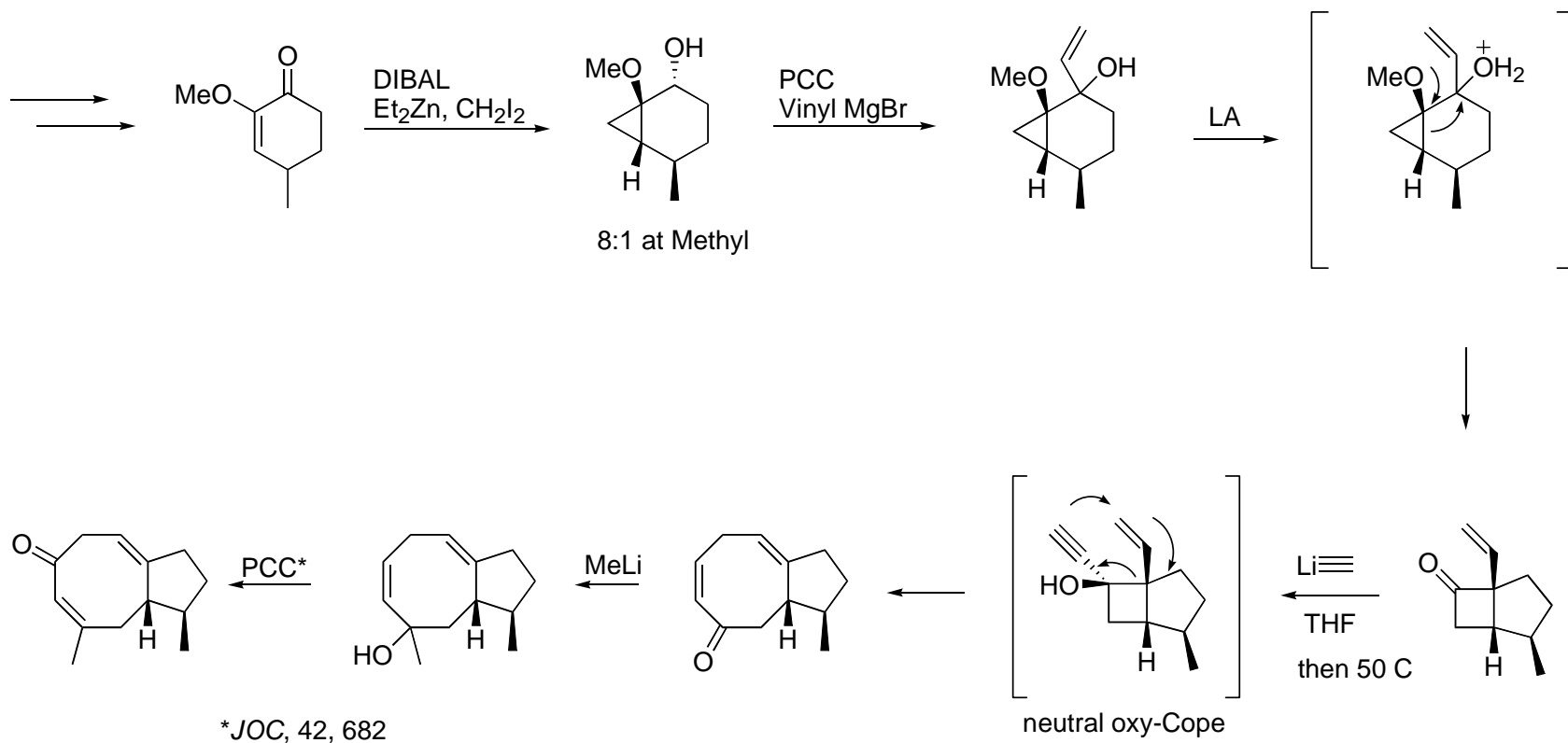
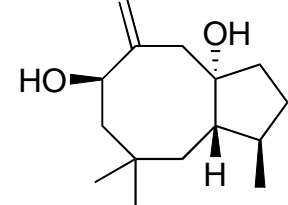


What remains? Epimerization of OTMS and ring contraction

Verrucarol: Trost, p.383 (key step)

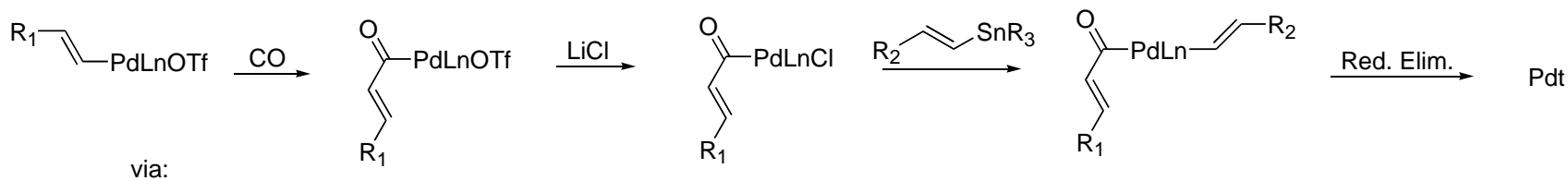
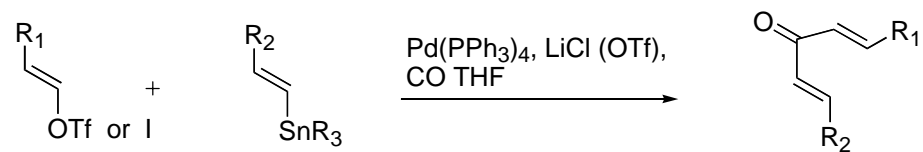
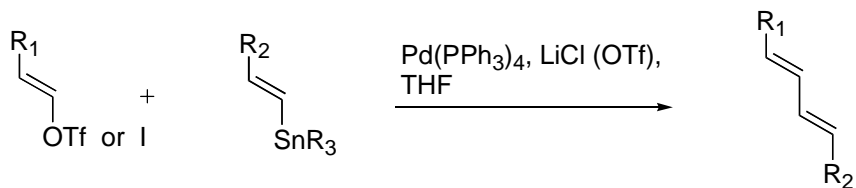


Poitediol: Gadwood, p.3869

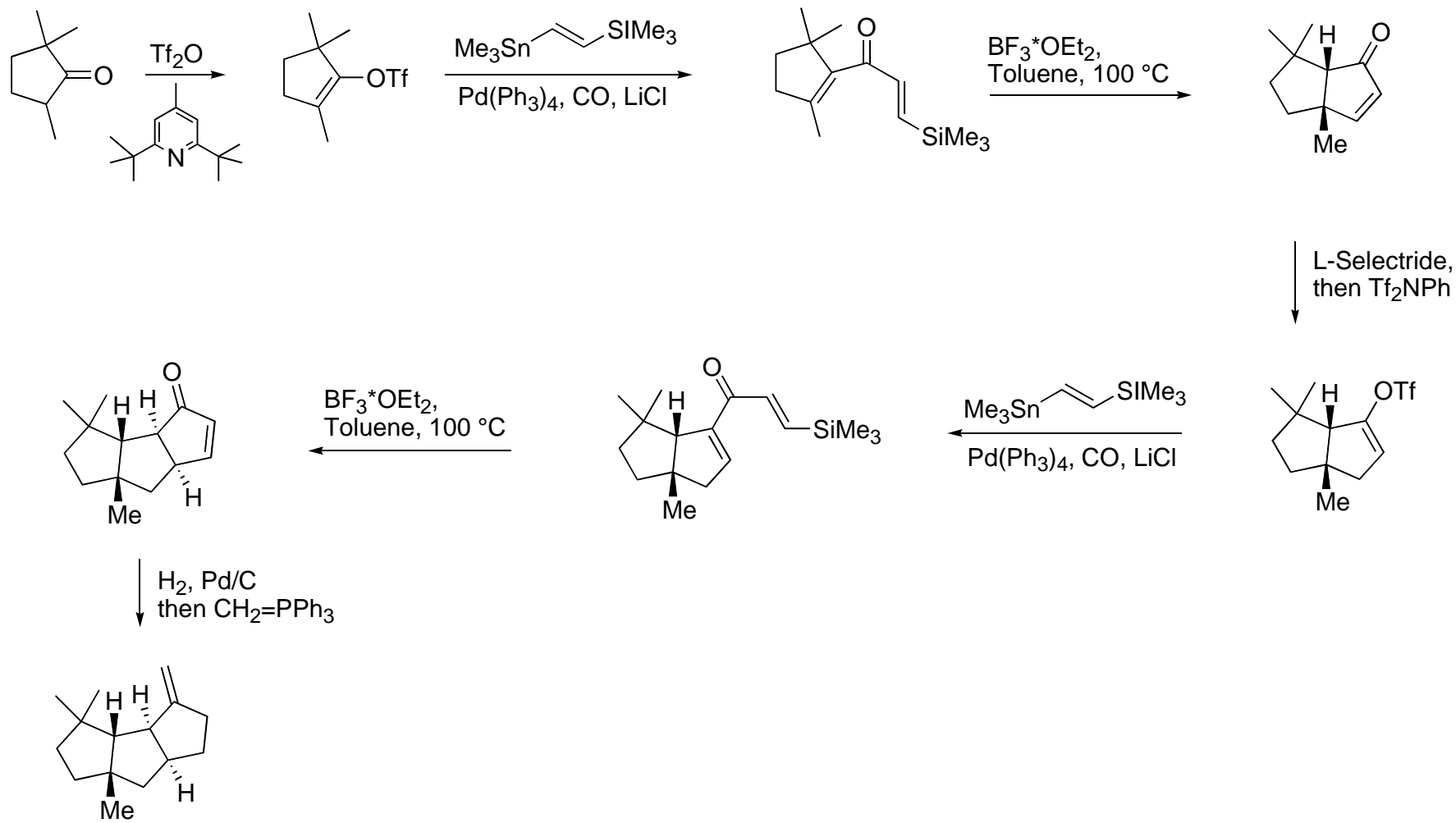
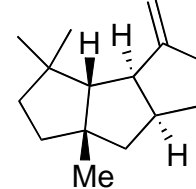


Methodology: Stille

Stille Coupling: 4630, 7500 (OTf)
4833, 6417 (Iodides)

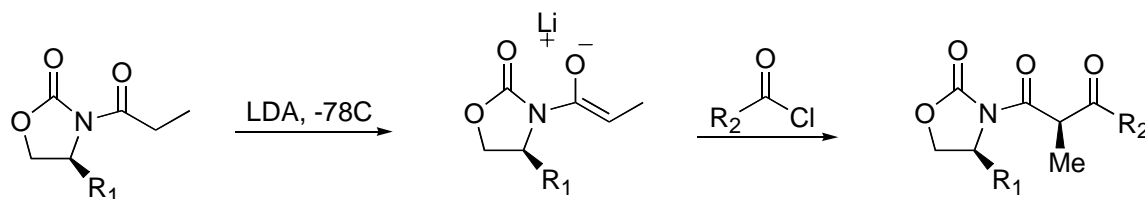


Δ -Capnellene: Stille, p.7500



Methodology: Evans

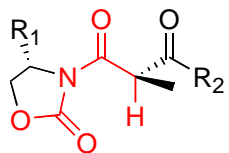
Evans Asymmetric Acylation: 1154



R₂=Me, Et, Ph

yields: 55, 83-95%

diastereomeric ratios >95:5



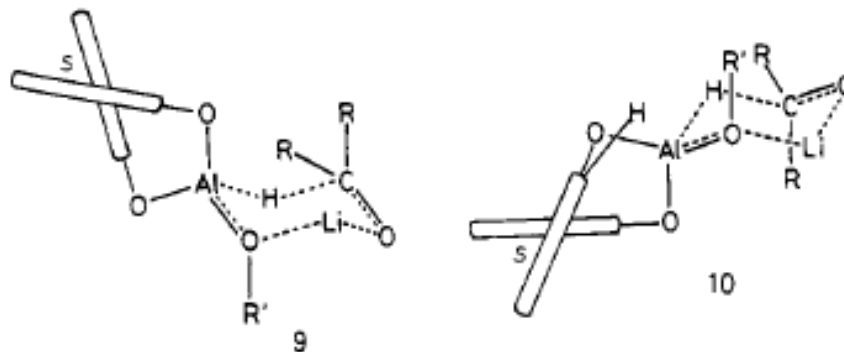
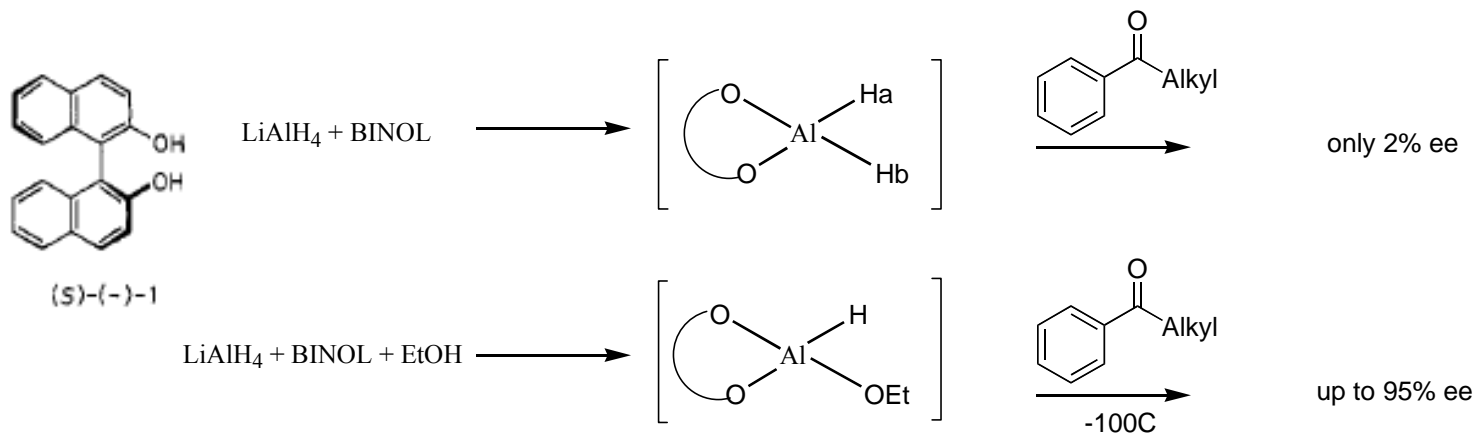
How can this be, with an epimerizable center?

Due to A(1,3) strain-like interaction the hydrogen is orthogonal to the carbamate carbonyl

One of the first examples of chiral β-dicarbonyls

Methodology: Noyori

Noyori: Enantioselective Binaphthol-Modified LAH Reagents, 6709,6717

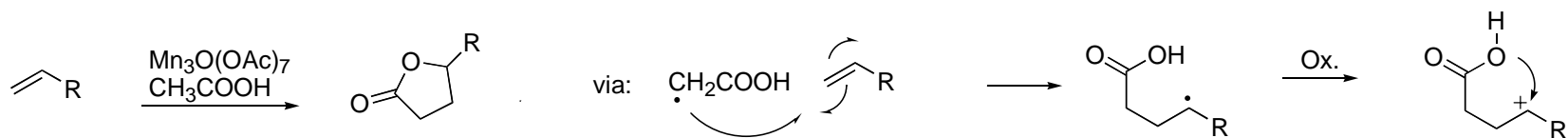


Scope includes aryl, acetylenic and alpha,beta-unsaturated ketones

Methodology: Corey

Corey: Polycyclic Lactone Synthesis, 5384

It was known that:



Perhaps this reaction could be made more useful in an intramolecular sense?

