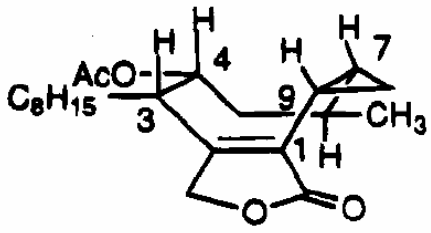
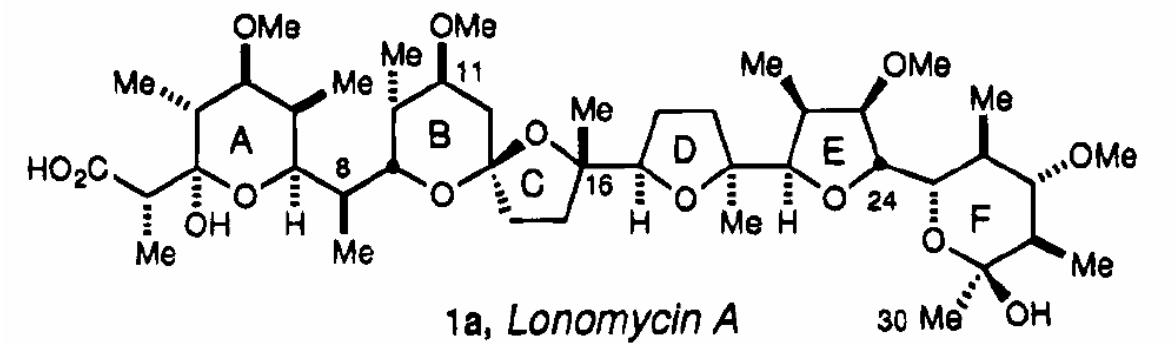
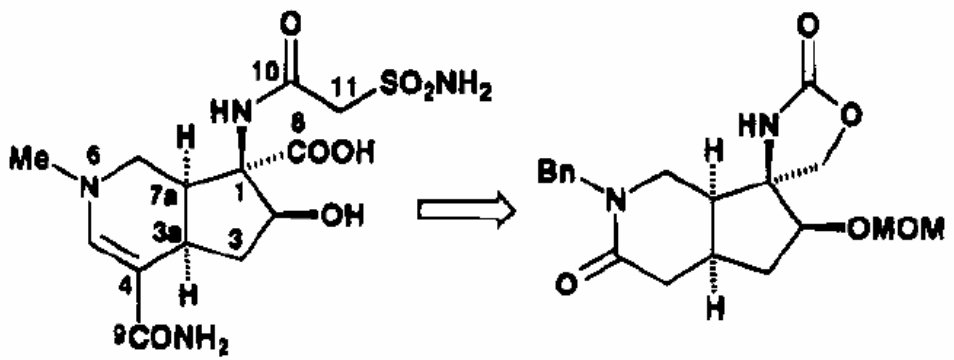
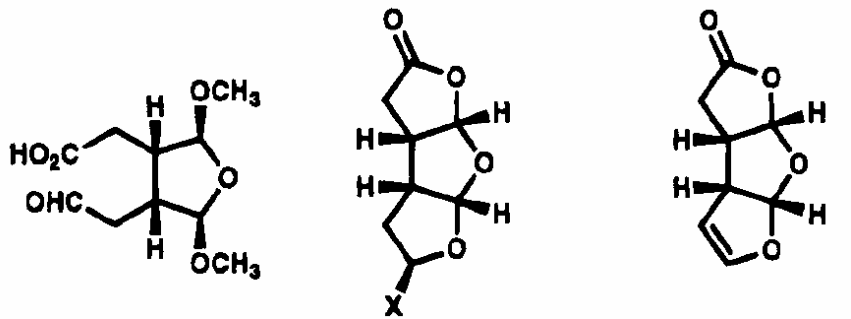
JACS 1995
Year In Review









1995 Stat Sheet:

- Number of papers published in *J. Am. Chem. Soc.* in 1995: **2,172**

- Most cited paper: **3295** citations!
  Cornell, WD, Cieplak, P, Bayly, CI, et. al., *J. Am. Chem. Soc.* **1995**, *117*, 5179
  "A 2nd Generation Force-Field For The Simulation Of Proteins, Nucleic Acids And Organic Molecules."

- Top 10 most prolific authors of 1995:
  1. Nicolaou (13)
  2. Bergman (11)
     Trost, B. M. (11)
  4. Adam, W. (10)
     Danishefsky (10)
     Houk (10)
     Rheingold, A.L. (10)
     Shaeffer, H.F. (10)
     Smith, A.B. (10)
  10. Turro, N.J. (9)
      Solomon, E.I. (9)

- Constant Themes:
  - DNA Cleavage (Enediynes, etc)
  - Monolayers

Prominent Total Syntheses NOT Discussed:

Nicolaou – Taxol (In Classics)

Nicolaou – Brevetoxin B (In Classics)

J.D. White – Avermectin B_1, 1908 (Good Story. >30 pages!)

Overman – Strychnine, 5776 (Full Paper)

Carreira – Zaragozic Acid, 8106 (w/ Du Bois)

Pancratistatin – Hudlicky (3643), Keck (7289), Trost (10143)

Macbecin – Panek, 10587 (Not very 'efficient' use of methodology..)

A.B. Smith – Discodermolide, 12011 (Communication)

Syntheses Discussed:

Paquette – Acetoxycrenulide

Kende – Altemicidin, Lankacidin

Evans – Lonomycin A

White – Euonyminol

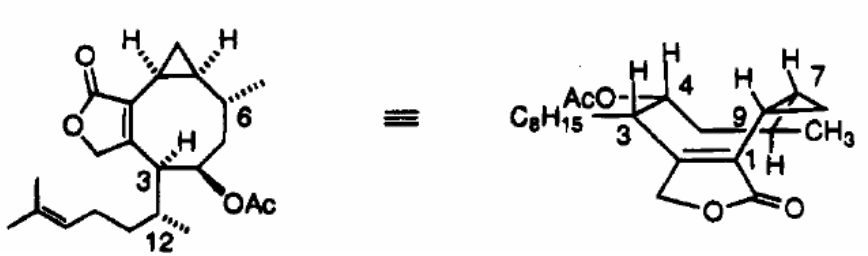
Corey – Gracilin

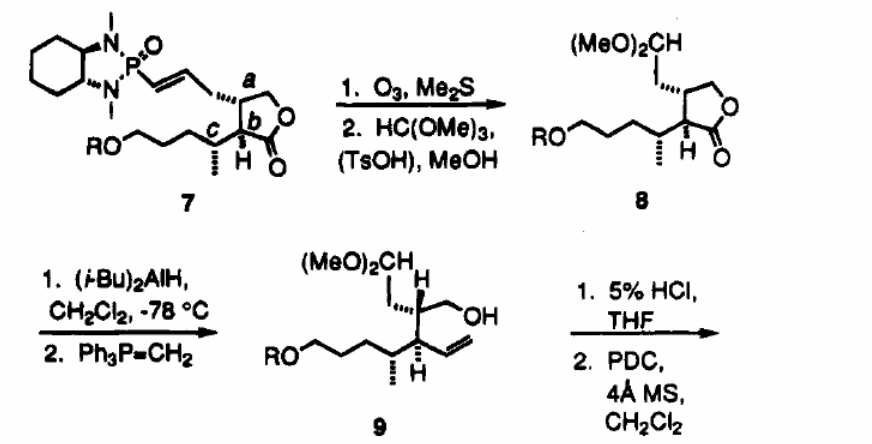
Carreira – Trehazolin

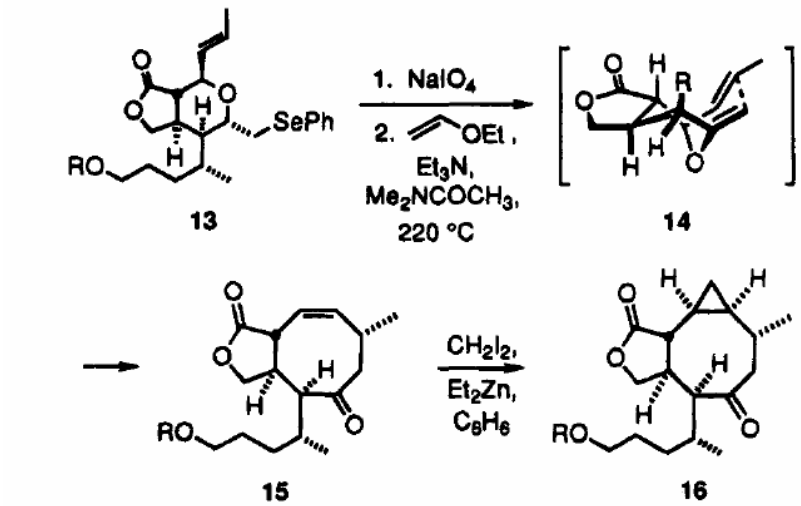
Hoveyda – Sch 38516

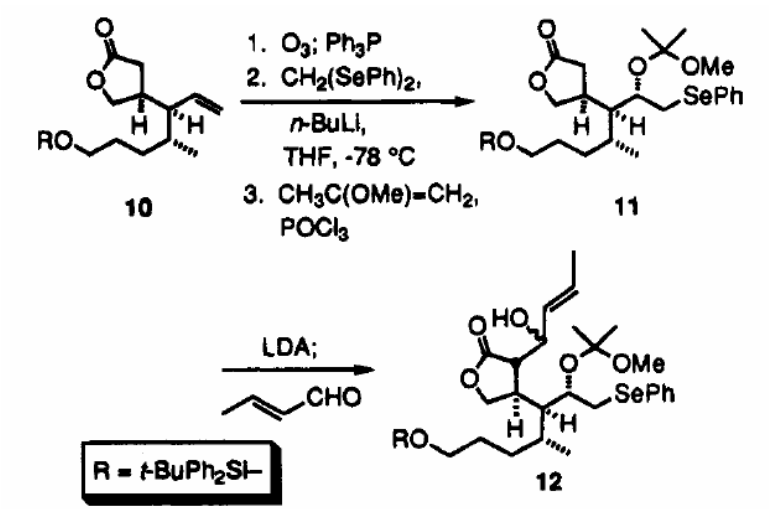
Paquette, Acetoxycrenulide, 1455

(Communication)









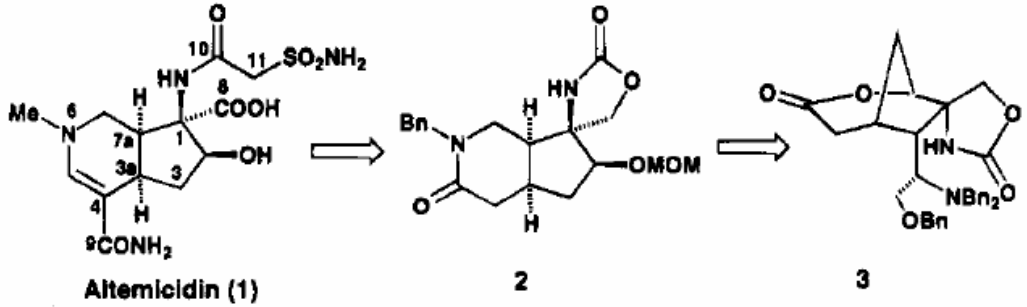
Highlights-

1: Hanessian Allylation (7 easily accessed from R-Citronellol) to install a,b stereocenters

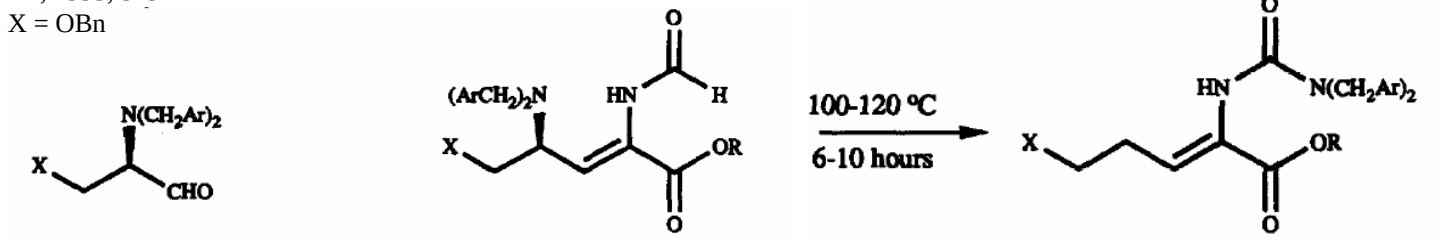
2: Ox. Cleavage → Claisen → Simmons-Smith

Kende, Altemicidin, 10597

(Communication)

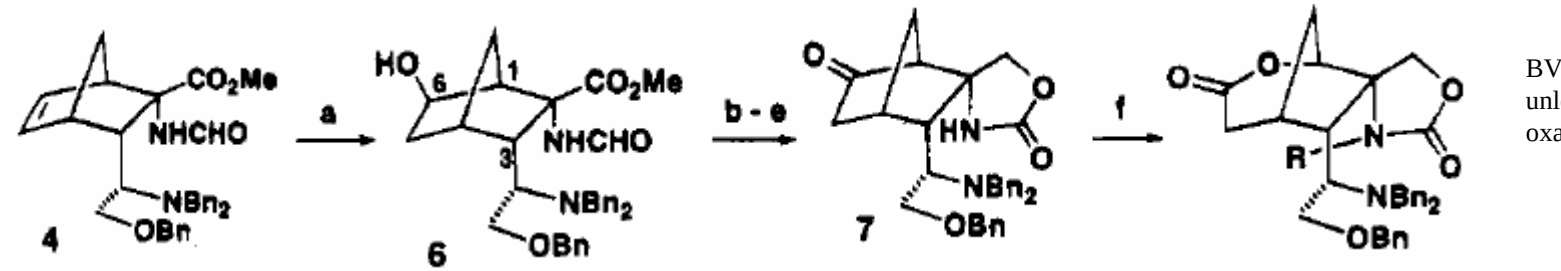


Dienophile from (D)-Alanine:
TL, 1993, 579
X = OBn



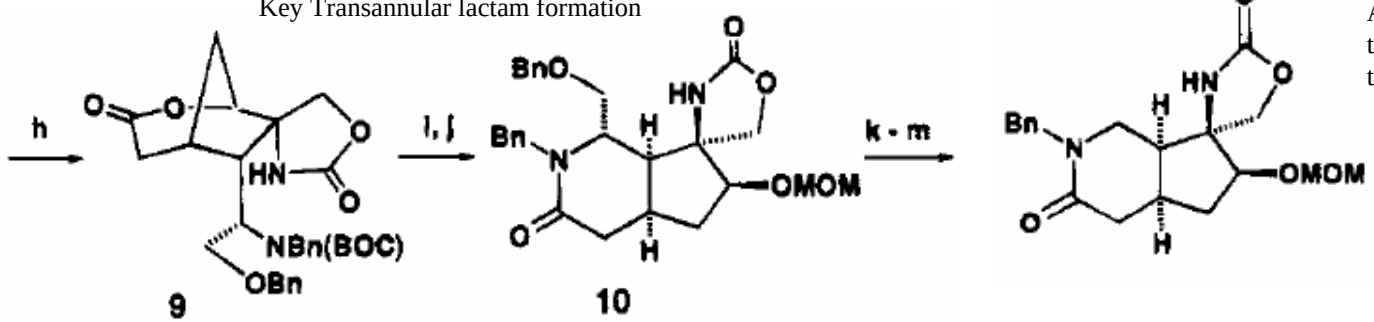
Unprecedented Rearrangement!!

Mech??



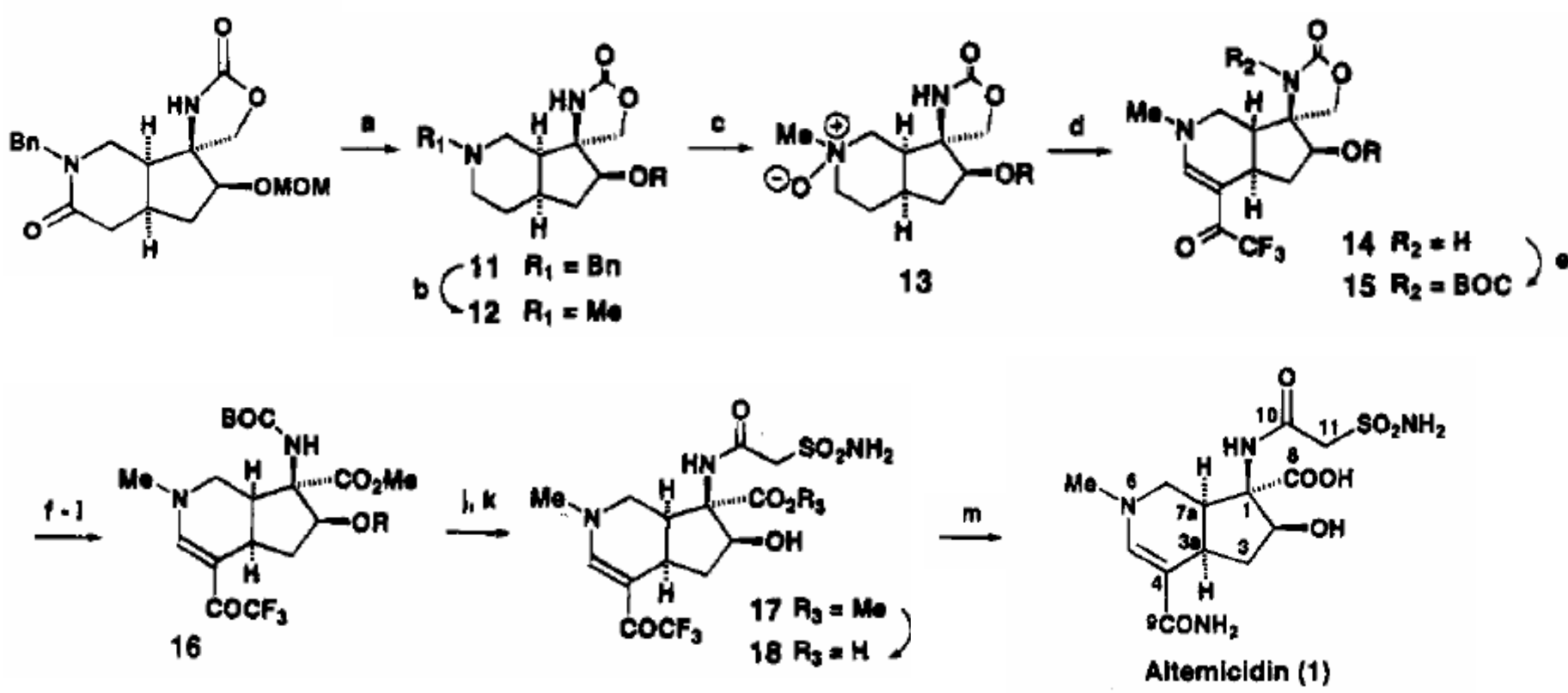
BV gave wrong regio unless protected as oxazolidinone

Key Transannular lactam formation



Alanine OBn directs hydroboration then removed later via oxidation to aldehyde then Wilkinson's cat.

Kende, Altemicidin (cont)

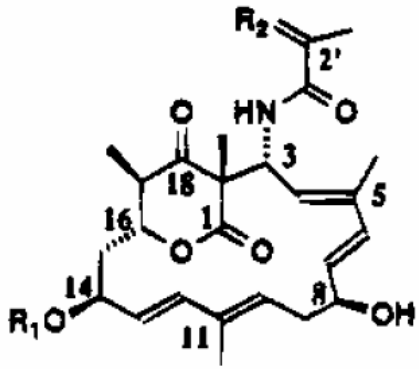


Highlights:

1- Diastereoselective DA with cyclopentadiene and enantiopure dieneophile
2- OBn-directed hydroboration
3- Transannular lactam formation
4- Potier-Polonovski Rearrangement
5- LOTS of N,O PG chemistry in this paper

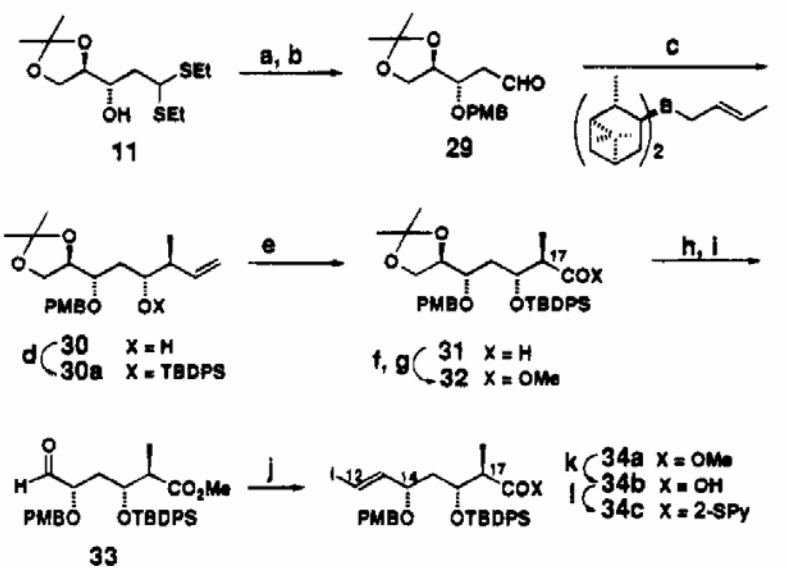
Kende, Lankacidin C, 8258

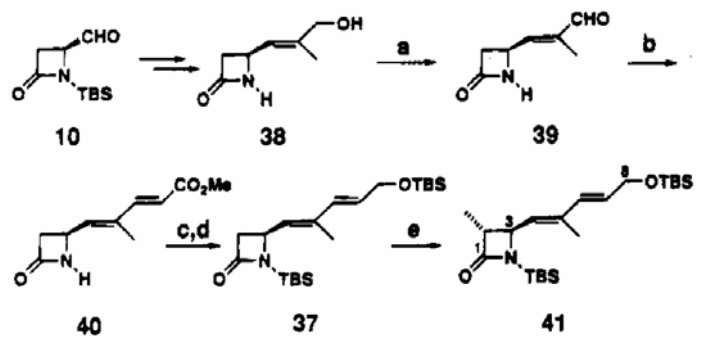
(Full Paper)

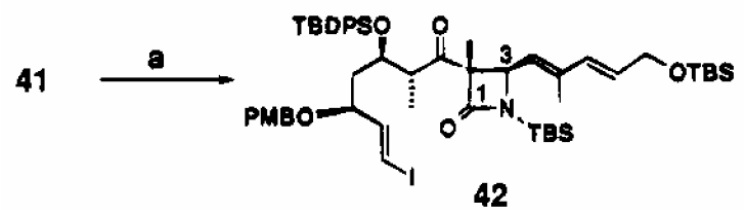


R_1	R_2	Compound
H	O	Lankacidin C (1)
$COCH_3$	O	Lankacidin A
H	H, OH	Lankacidinol
$COCH_3$	H, OH	Lankacidinol A

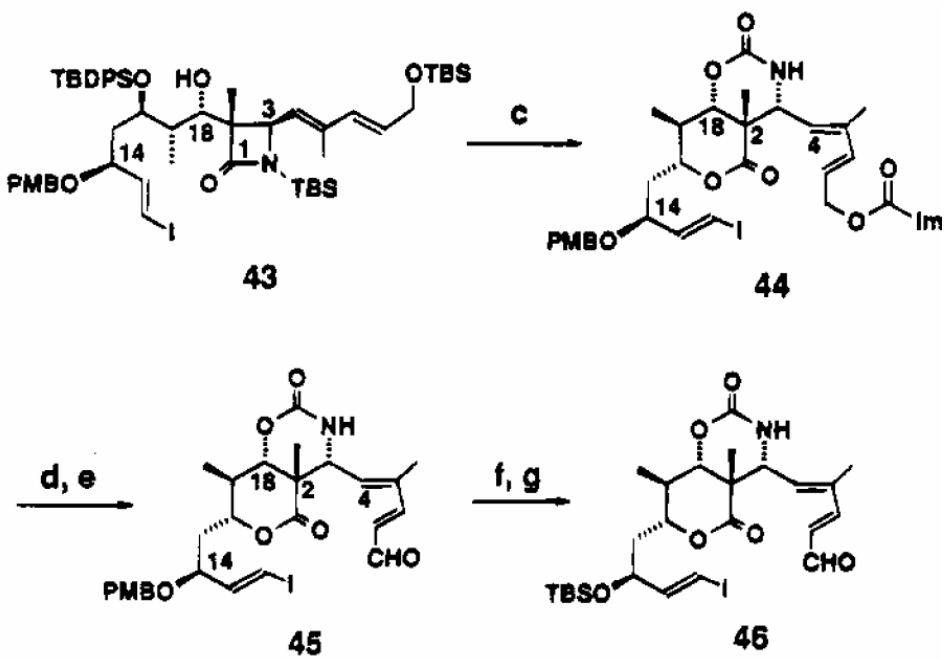
11 readily derived from D-arabinose
10 derived from L-aspartic acid

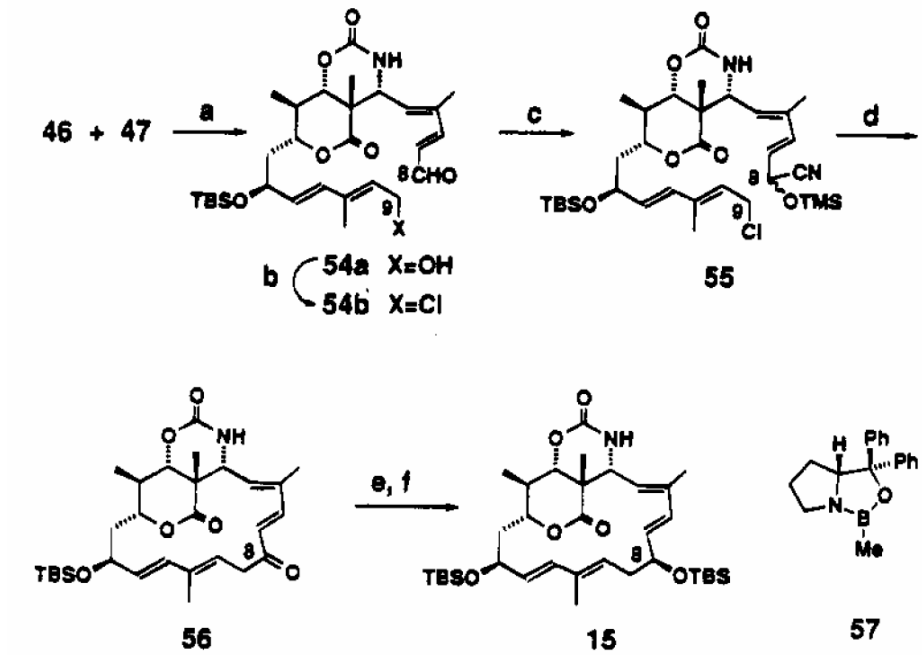


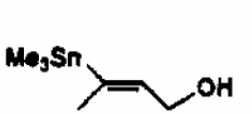




Kende, Lankacidin C (cont)







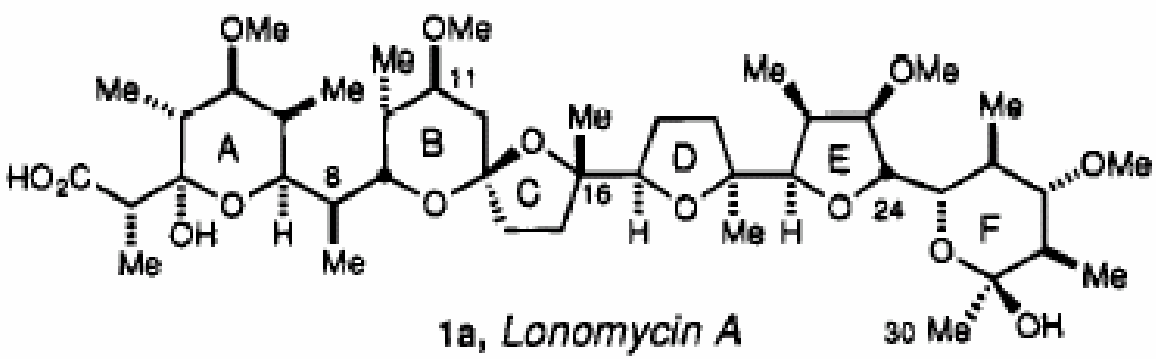
47

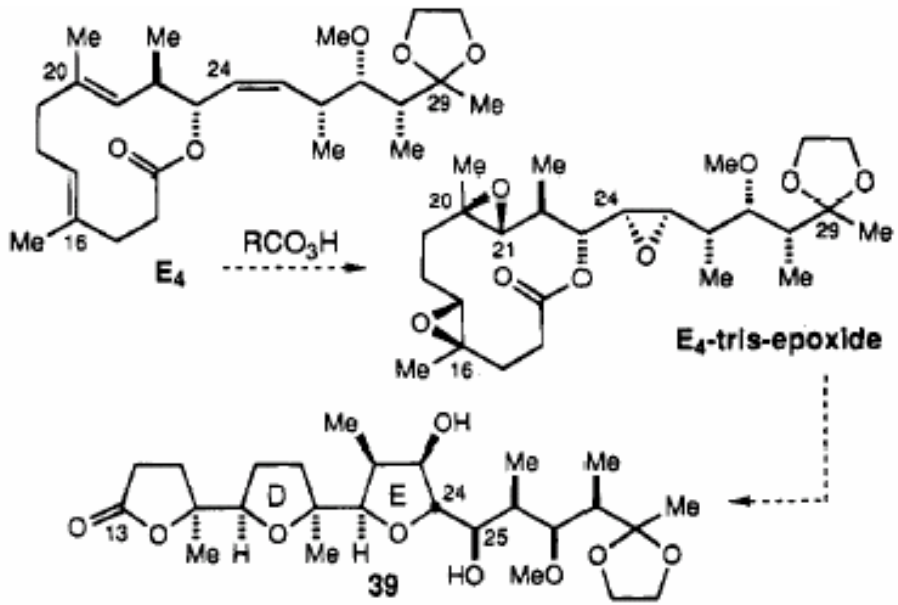
Highlights:

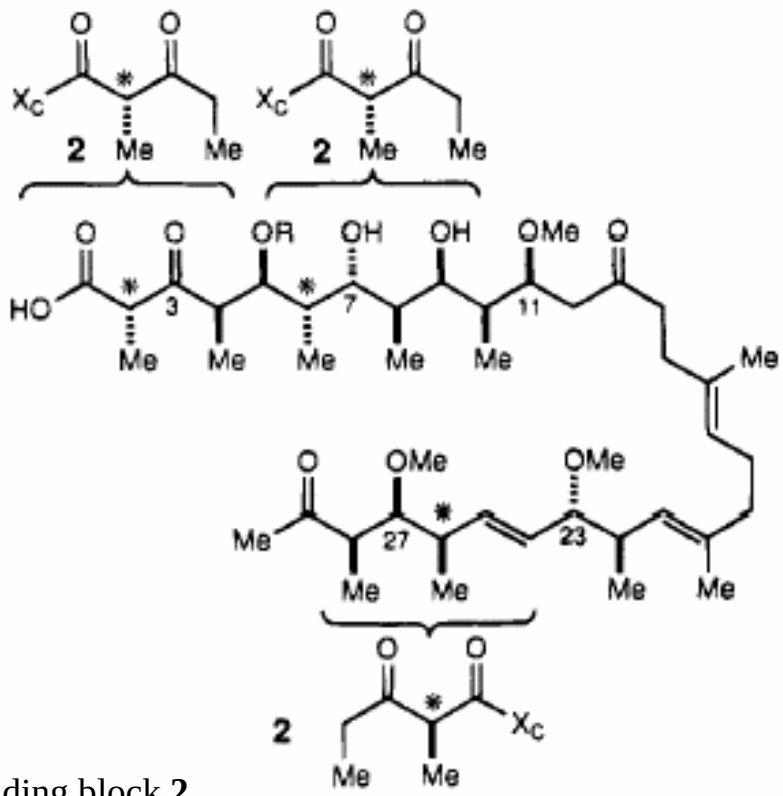
1- Highly convergent and stereoselective
2- N → O acyl transfer to make lactone **44** from lactam **43**
3- Stork-Takahashi cyanohydrin methodology for macrocyclization
4- **15** was a relay compound due to instability of natural product to acid and base
5- Very good chemistry

Evans, Lonomycin A, 3448

(Full Paper)







Highlights:

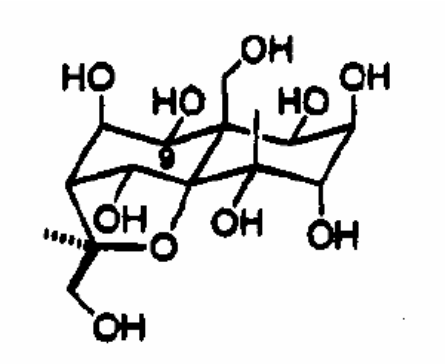
1- Lots of Aldol chemistry

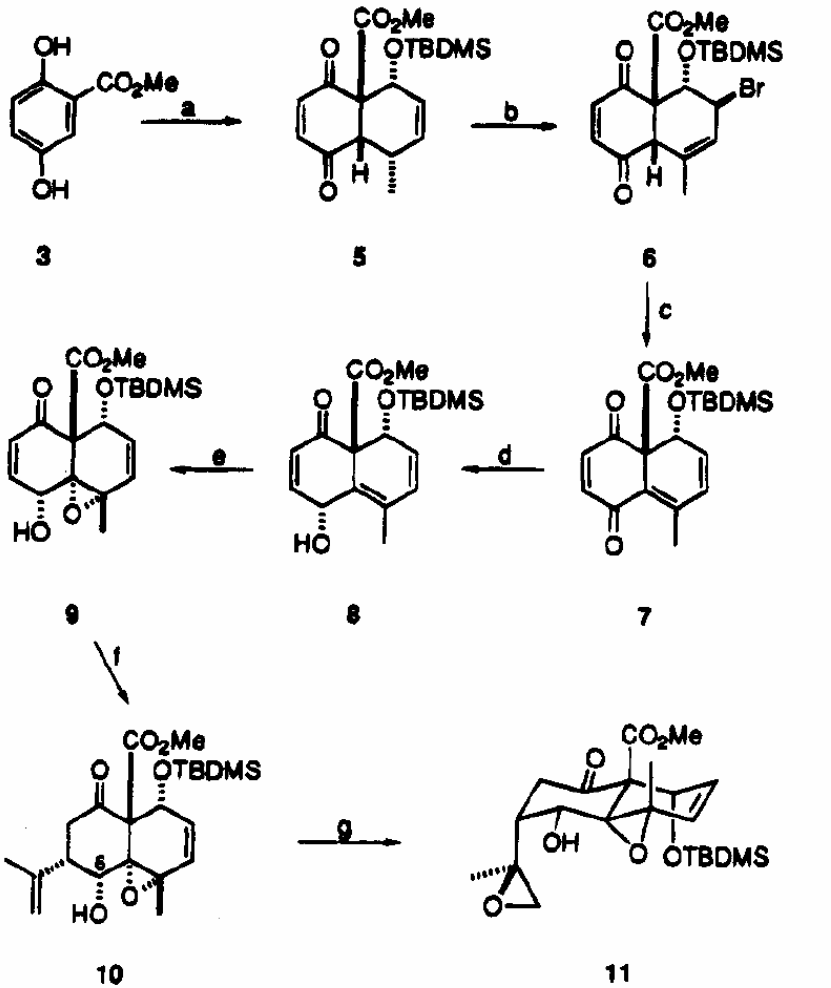
2- Leighton worked on the beta-keto imide building block **2**

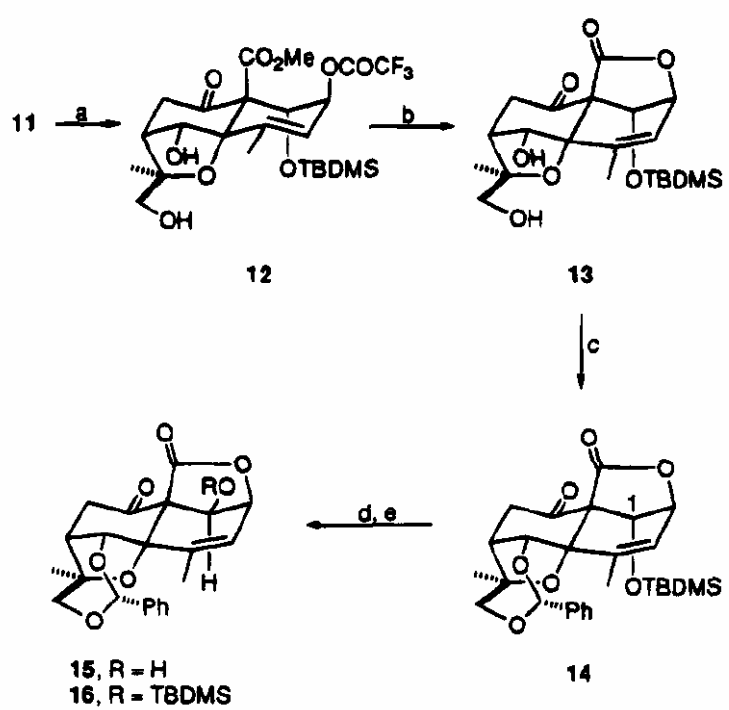
3- Good read

White, Euonyminol, 9780

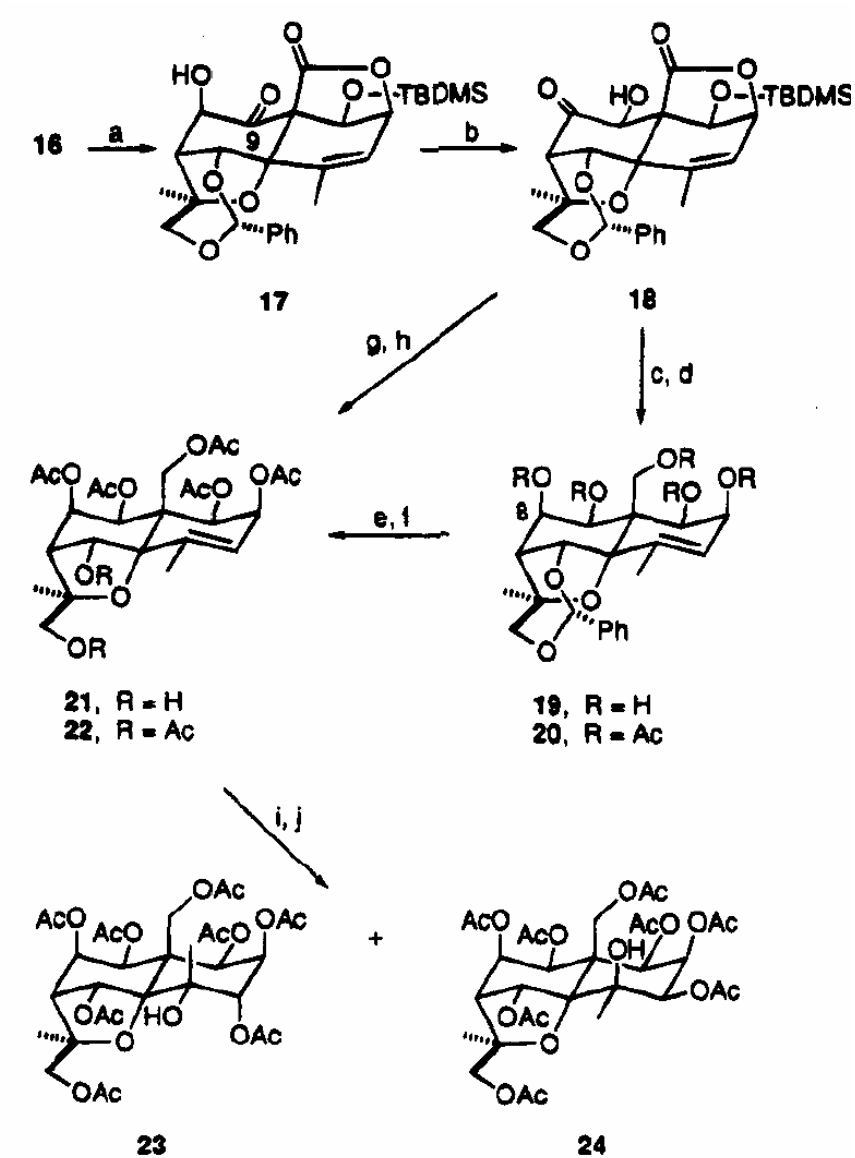
(Communication)







White, Euonyminol (cont)

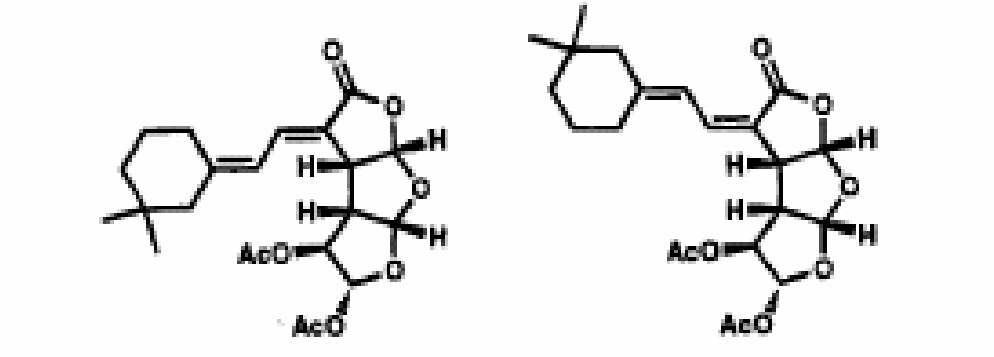


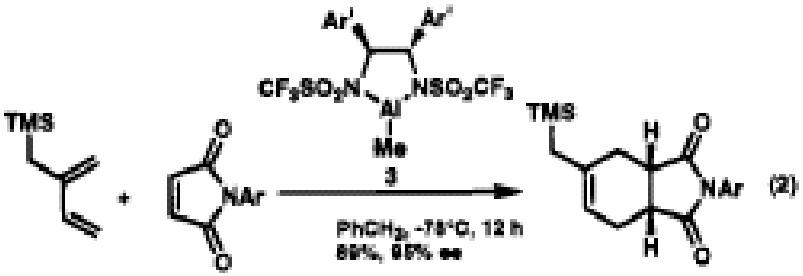
Highlights:

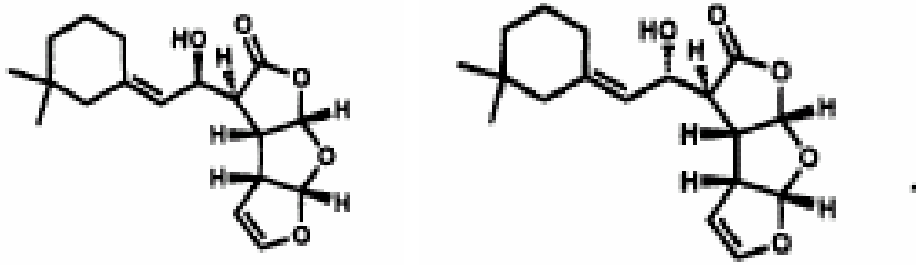
1- Rapid assembly of polyhydroxylated framework
2- Michael addn of isopropenyl Grignard-ate complex
3- TFA cascade epoxide opening (**11** → **12)**
4- Lobry de Brun-Alberda van Eckstein transformation
5- Only a 1:8 ratio of **23** (desired) to **24** ☹

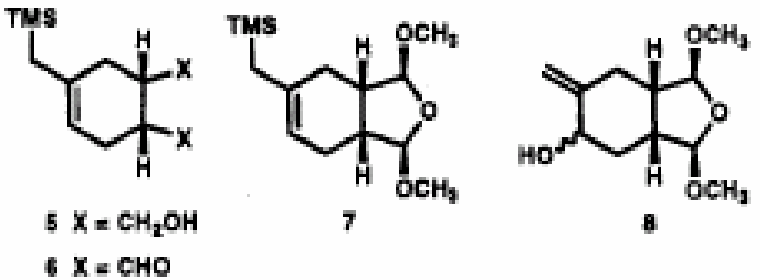
Corey, Gracilin B and C, 9616

(Communication)







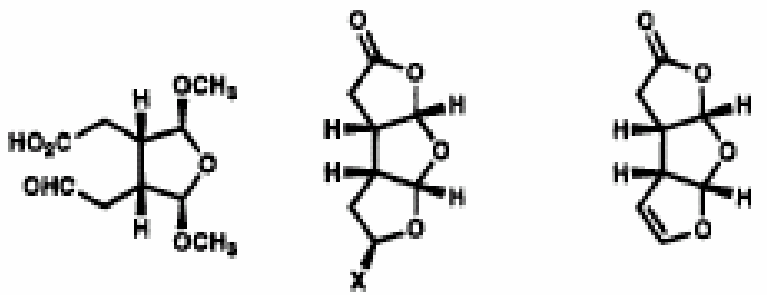


Highlights:

1- Allylsilane → epoxide → direct ox. Cleavage

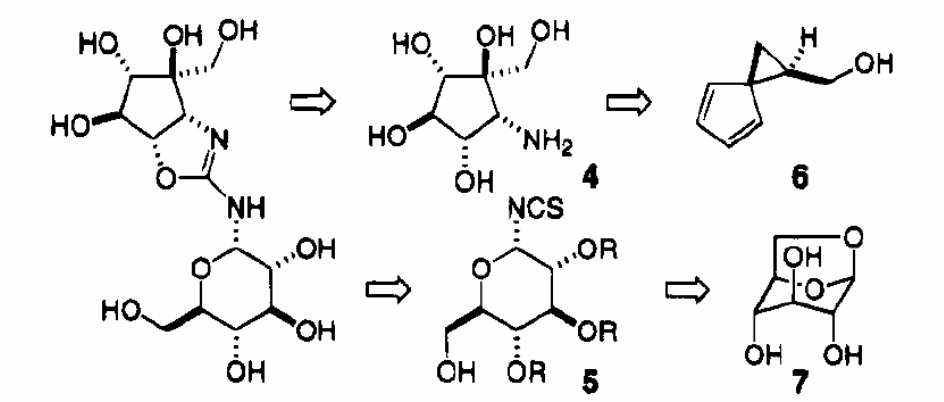
2- Both natural products available through aldol

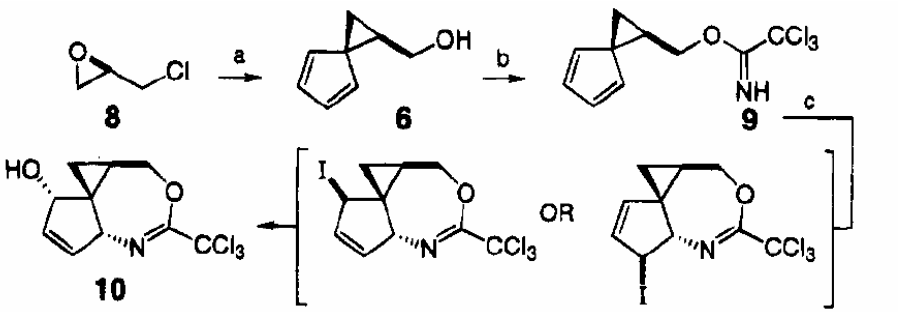
3- Reduction of succinimide a little clumsy at first

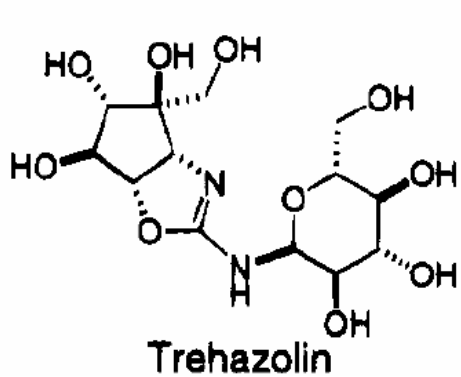


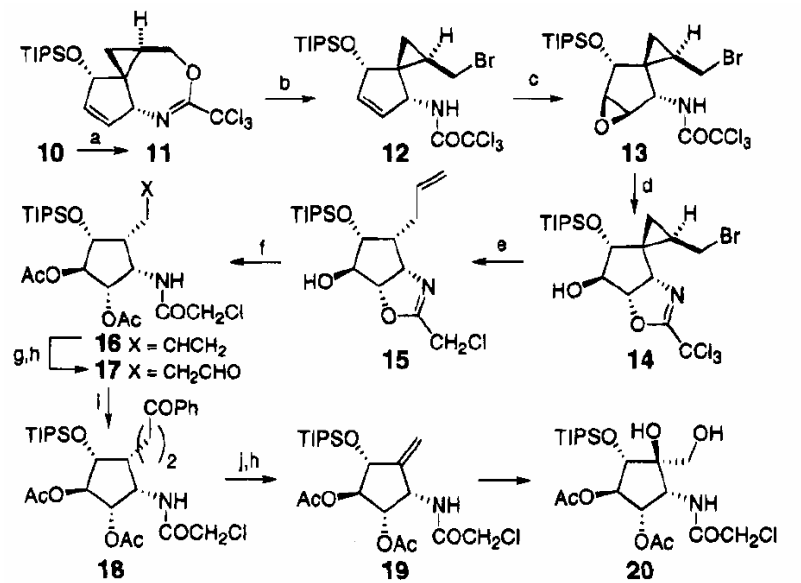
Carreira, Trehazolin, 11811

(Communication)









Highlights:

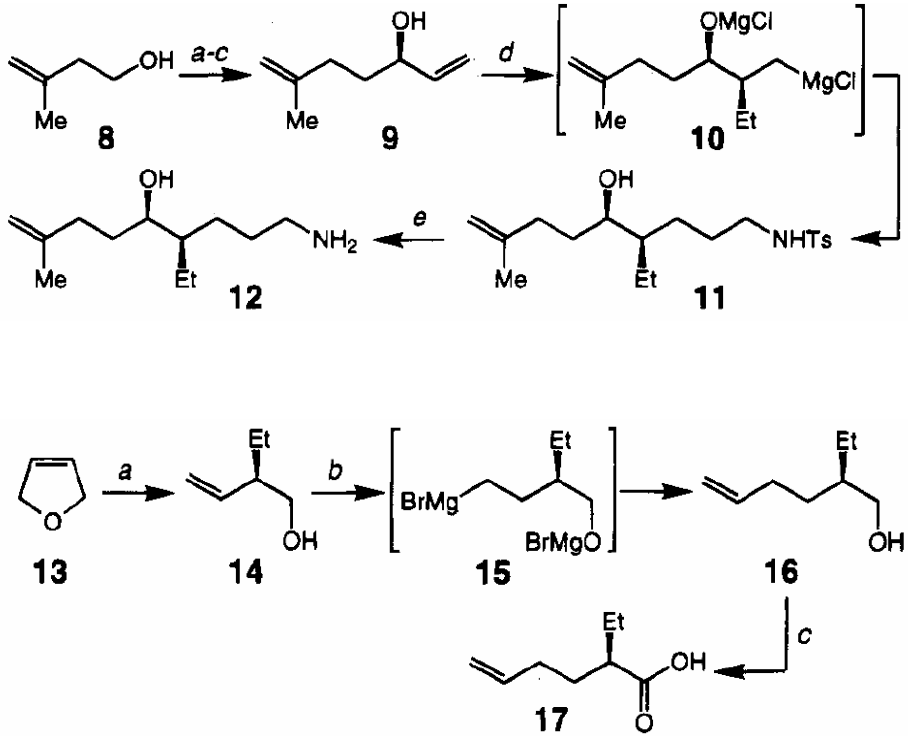
1- Previously unknown chiral Cp cyclopropane

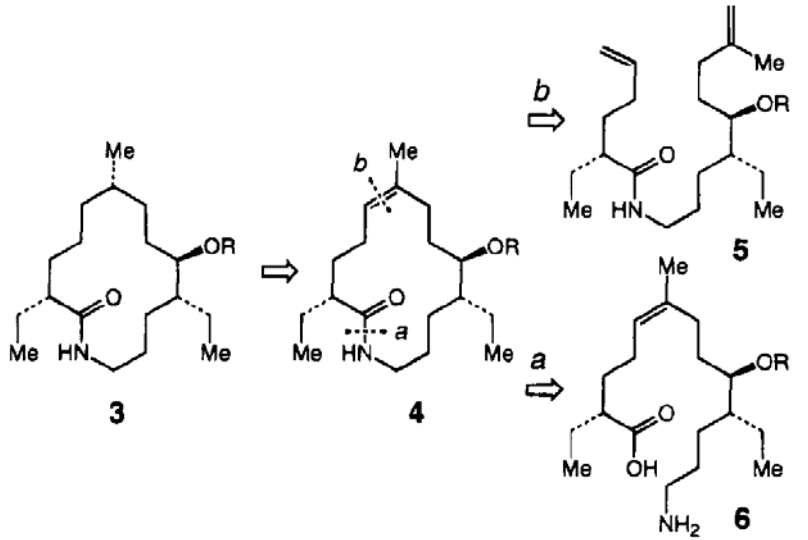
2- Polyfunctionalized chiral cyclopentane methods

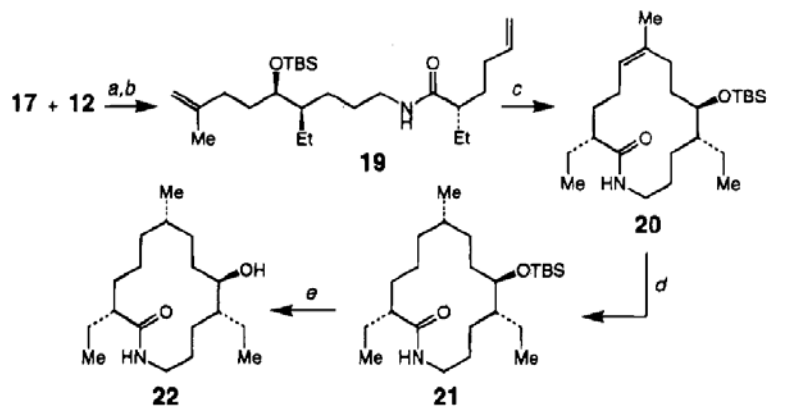
3- Unique bromination of **11** → allyl → ketone → exo-methylene via Norrish cleavage!

Hoveyda, Sch 38516, 2943

(Communication)







Highlights:

1- First RCM in natural product synthesis!!!

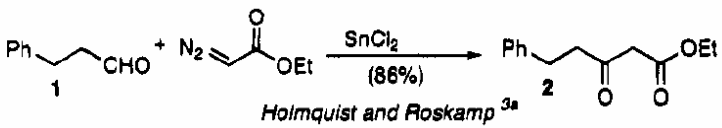
2- Unbelievably fast and enantioselective

3- Fantastic discussion of carbomagnesation reactions on page 7097

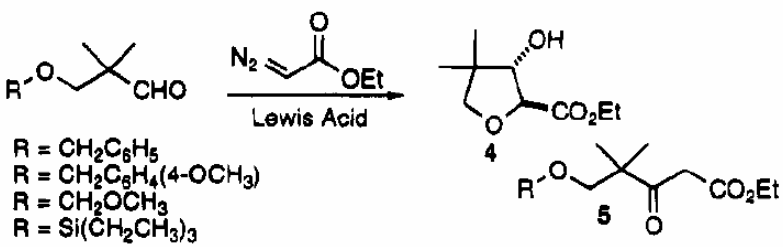
Angle (UC Riverside), 8041

Denmark, 2100

Stereoselective Synthesis of Tetrahydrofurans *via* the Lewis Acid Promoted Reaction of β-Benzyloxy Aldehydes and Ethyl Diazoacetate



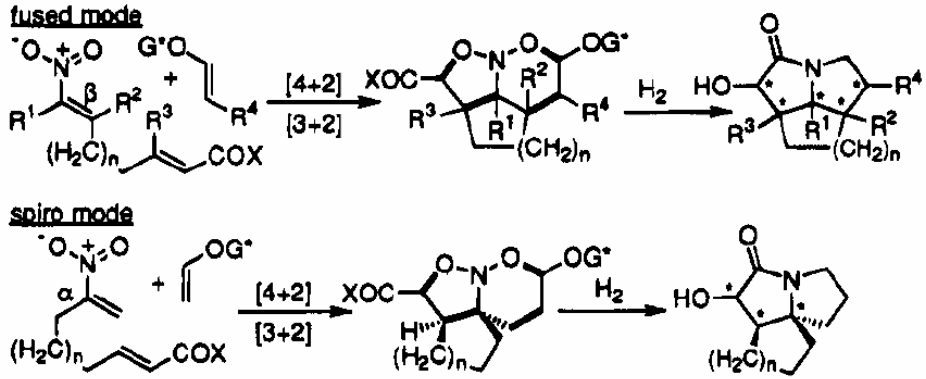
Holmquist and Roskamp [3a]



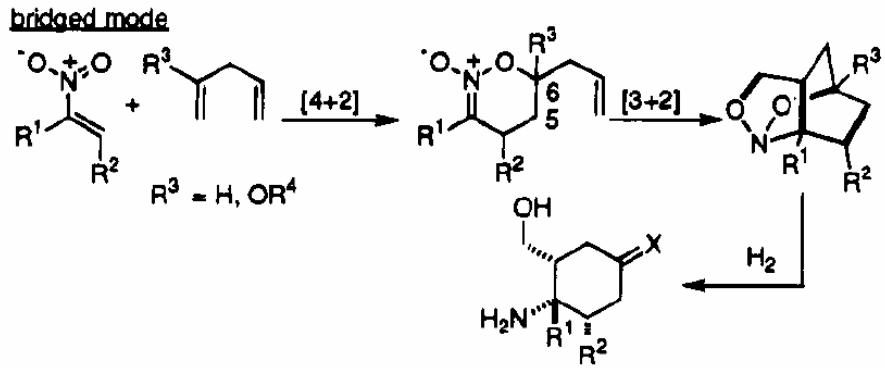
3a R = $CH_2C_6H_5$
3b R = $CH_2C_6H_4(4\text{-}OCH_3)$
3c R = CH_2OCH_3
3d R = $Si(CH_2CH_3)_3$

Tandem Inter [4 + 2]/Intra [3 + 2] Cycloadditions. 6. The Bridged Mode†

Scheme 1

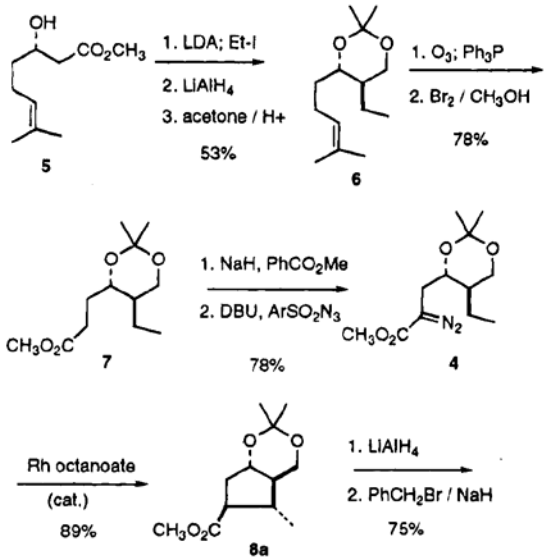


Scheme 2



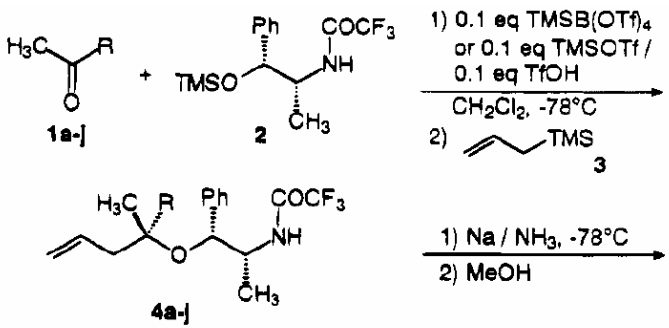
Taber, 5757

Highly Diastereoselective Cyclopentane Construction: Enantioselective Synthesis of the Dendrobatid Alkaloid 251F



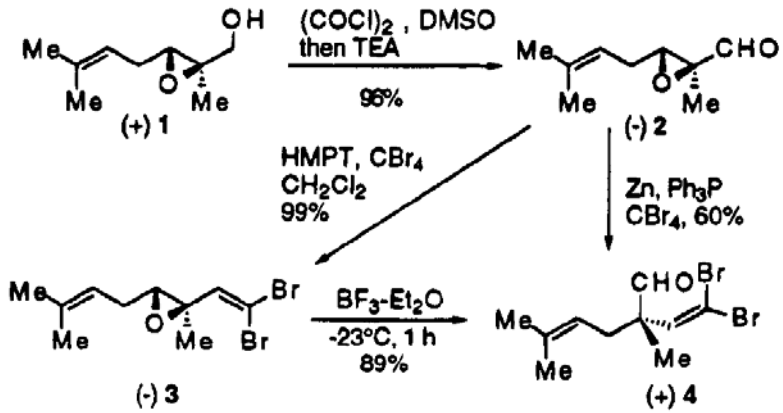
Tietze, 5851

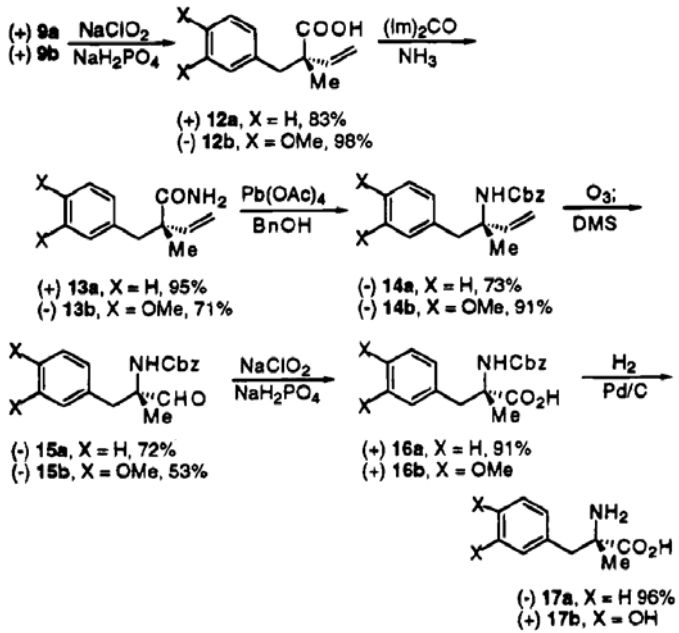
Enantioselective Synthesis of Tertiary Homoallylic Alcohols via Diastereoselective Addition of Allylsilanes to Ketones



Jung, 7379

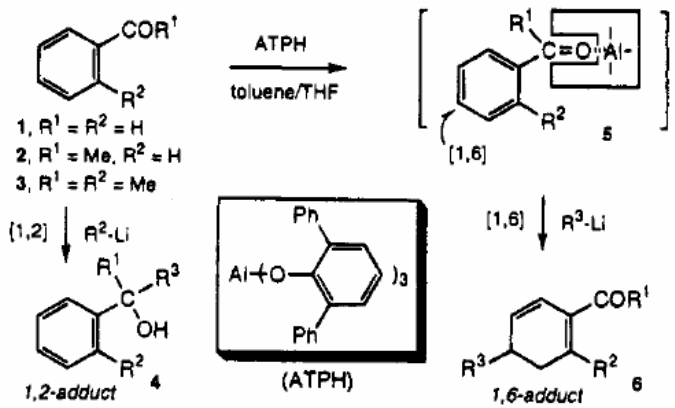
Stereospecific Rearrangement of Optically Active Tertiary Allylic Epoxides To Give Optically Active Quaternary Aldehydes: Synthesis of α-Alkyl Amino Aldehydes and Acids

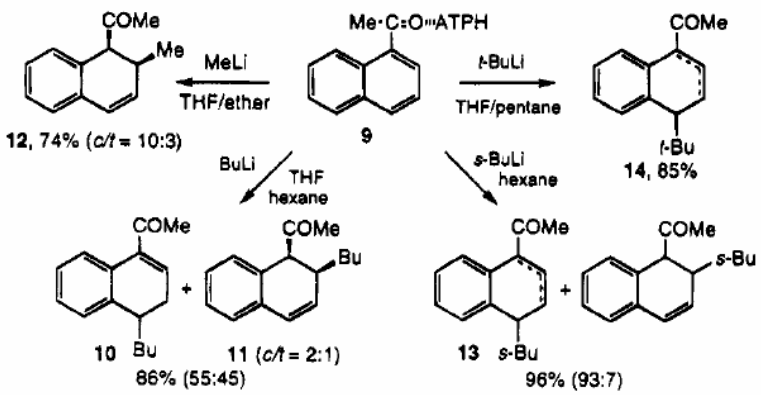




Yamamoto, 9091

Unprecedented Nucleophilic Addition of Organolithiums to Aromatic Aldehydes and Ketones by Complexation with Aluminum Tris(2,6-diphenylphenoxide)





Trost, 5371

Elaboration of Conjugated Alkenes Initiated by Insertion into a Vinylic C−H Bond