Classics in Tetrahedron Letters

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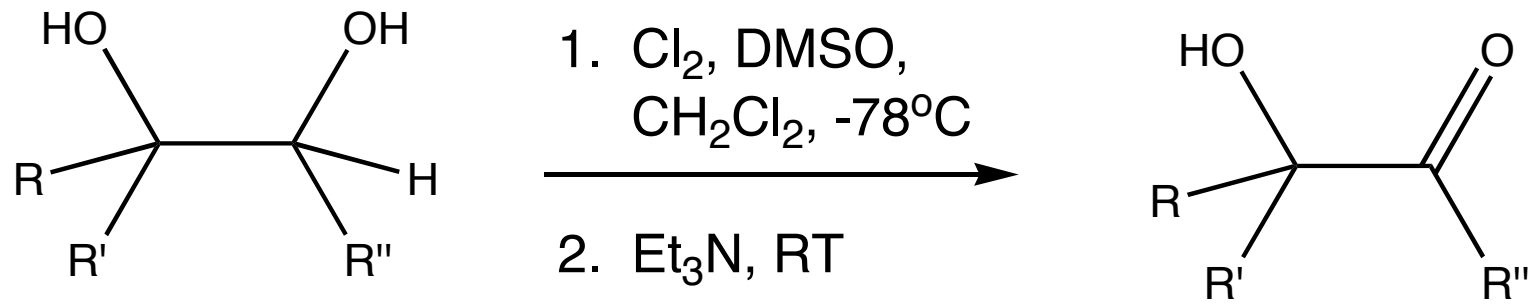
Baran Group Meeting: 9/24/03

The Plan

- Methodology
- Protecting Groups
- Natural Products
- Syntheses

Methodology

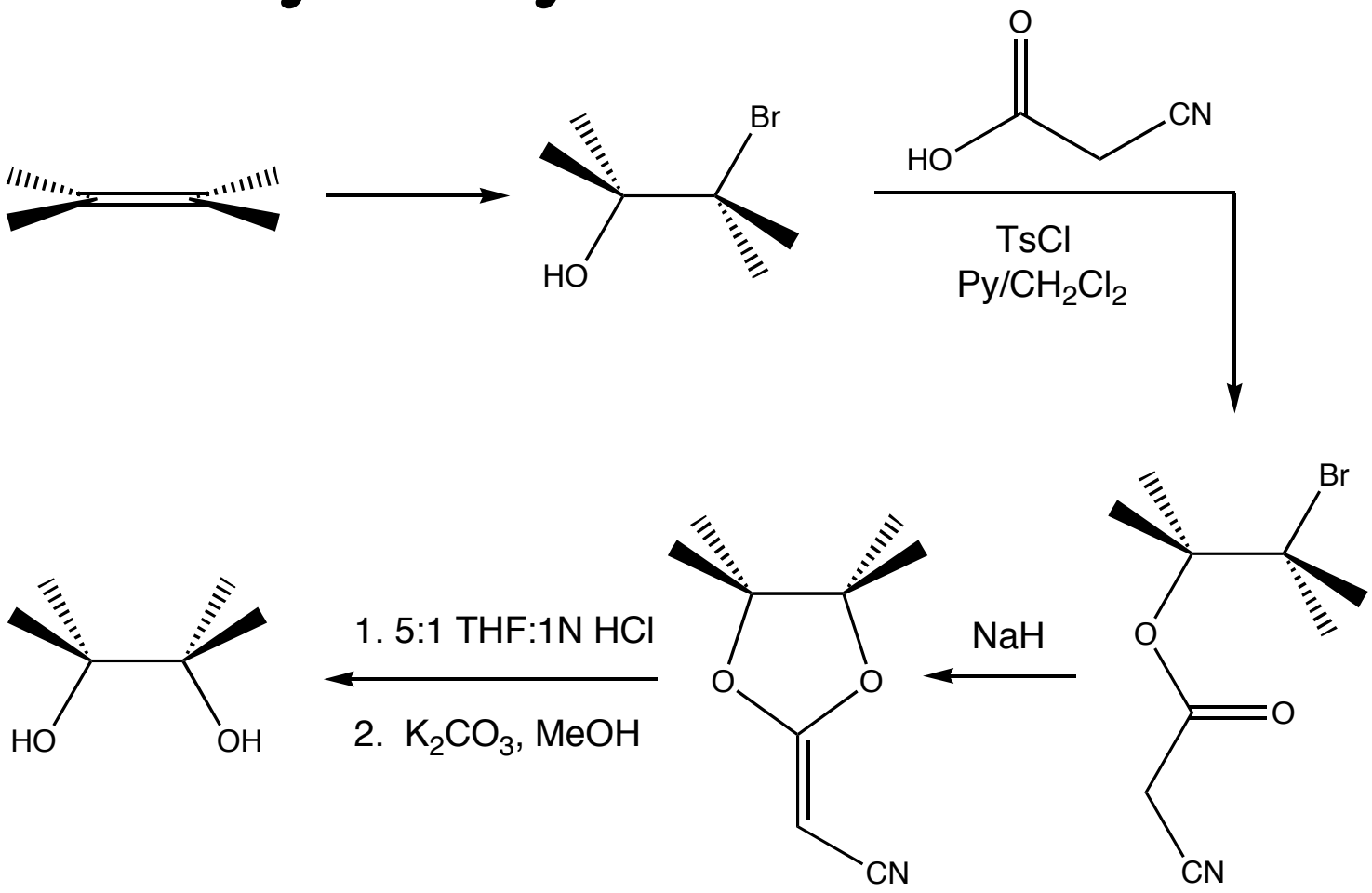
Oxidation of Vicinal Diols



Can selectively oxidize the secondary alcohol in the presence of the tertiary alcohol without cleavage.

Corey. **1974**, 287

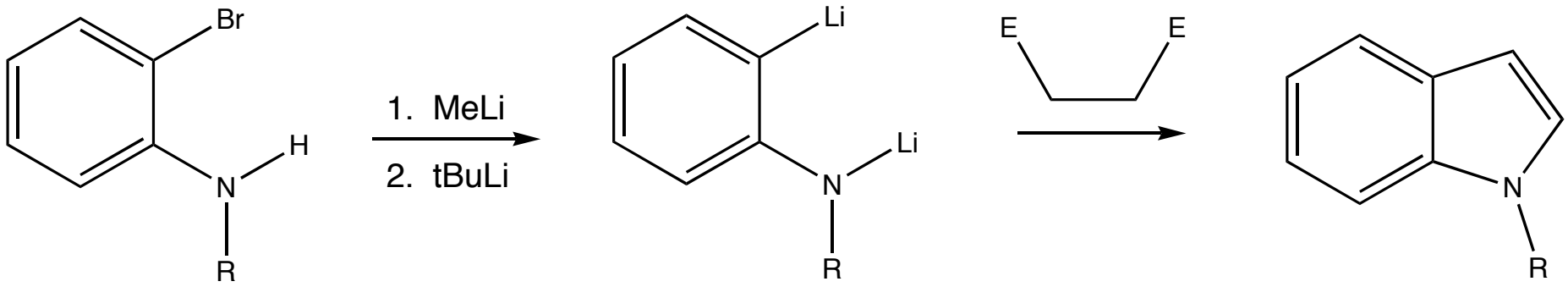
cis-Hydroxylation of alkenes



Allows selectivity during bromohydrin formation

Corey. **1982**, 4217

Indole Synthesis



Biselectrophiles used: a-chloroketones, □,□-epoxyketone (Li enolate), and enediones

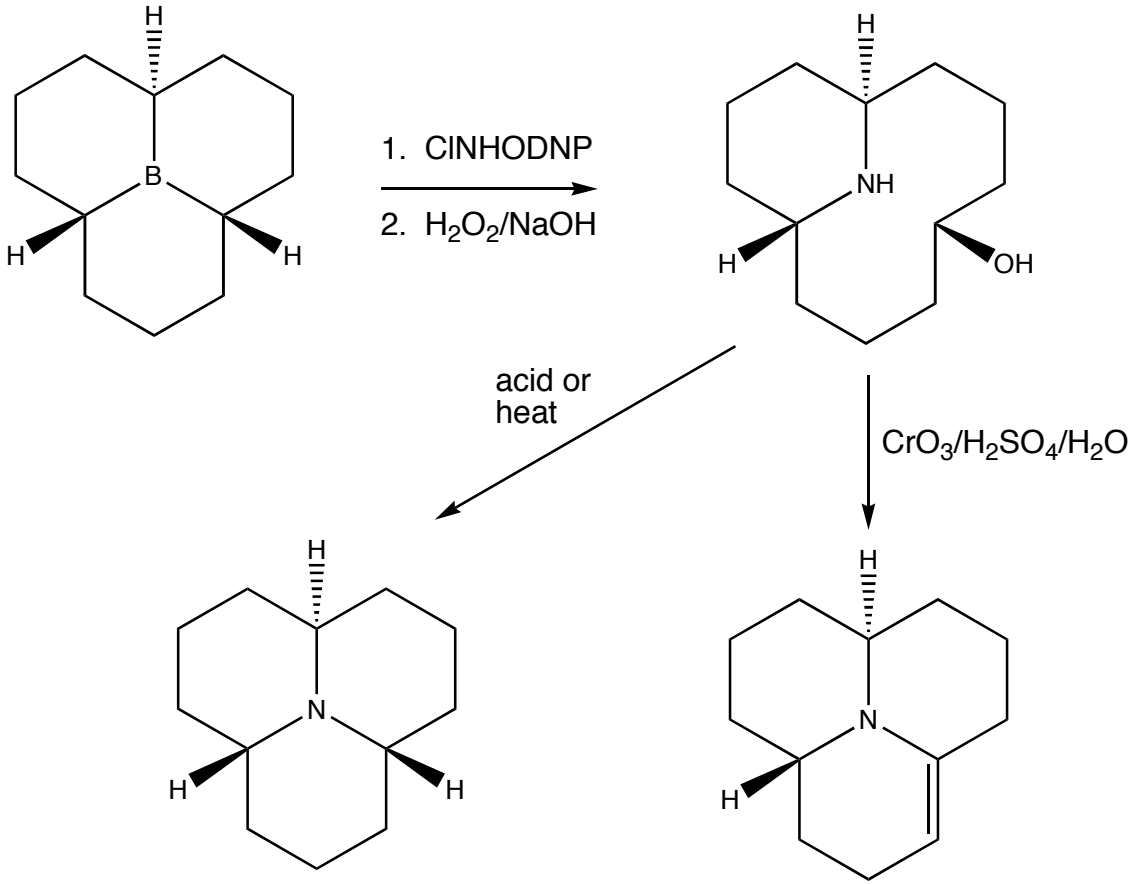
Also used 5-substituted anilines

R is a general protecting group: best results with BOC

Yields: 50-90%

Wender. **1981**, 1475

An Interesting Reaction:



Mueller. **1976**, 2925
Mueller. **1979**, 1991

Alcohol Oxidations

Collins Reagent[1]

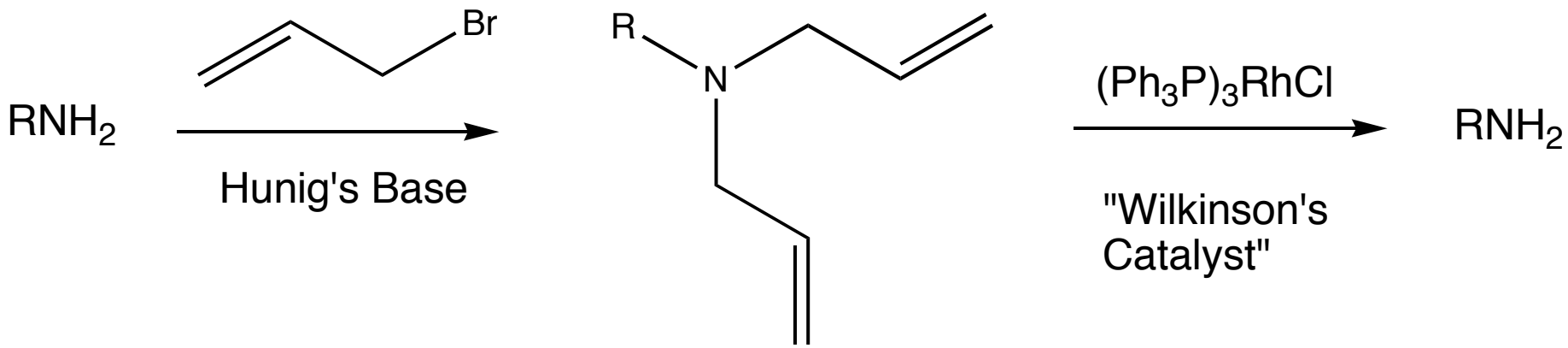
PCC[2]

PDC[3]

Collins. **1968**, 3363
Corey. **1975**, 2647
Corey. **1979**, 399

Protecting Groups

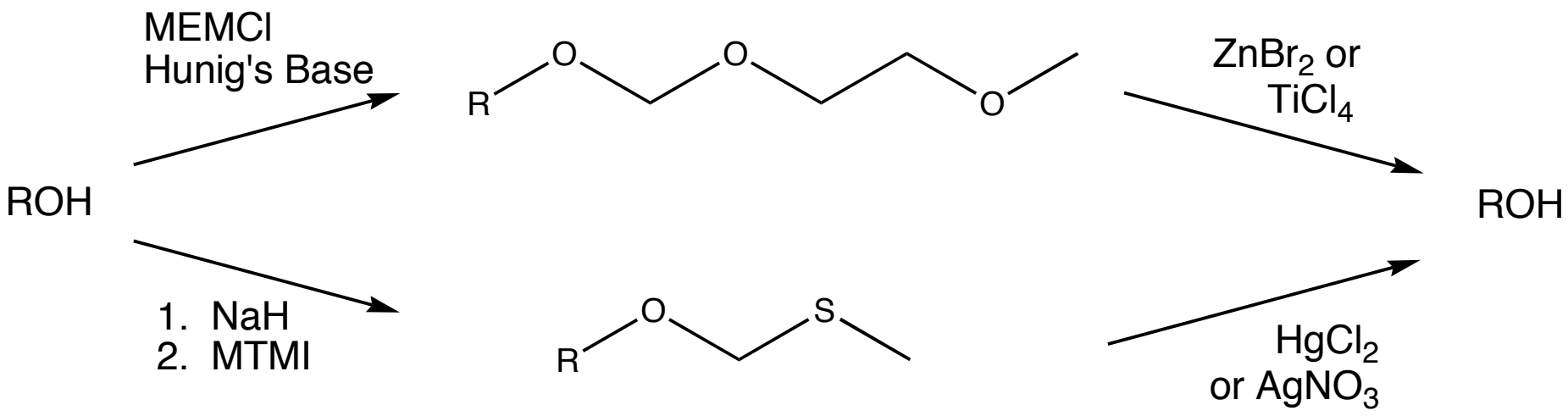
N,N-Diallyl



Acid/Base Stable and Nucleophile Inert

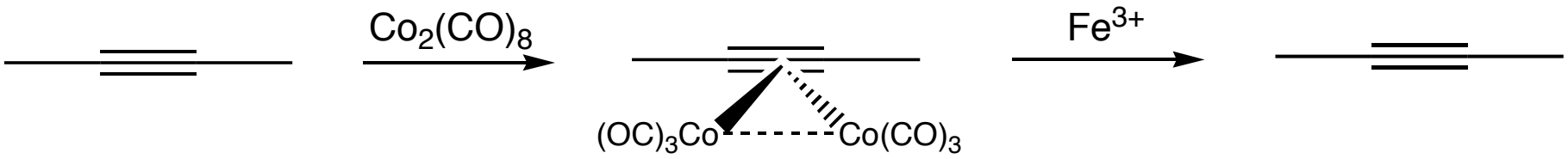
Ganem. **1981**, 1483

MEM[1] and MTM[2]



[1]Corey. **1976**, 809
[2]Corey. **1975**, 3269

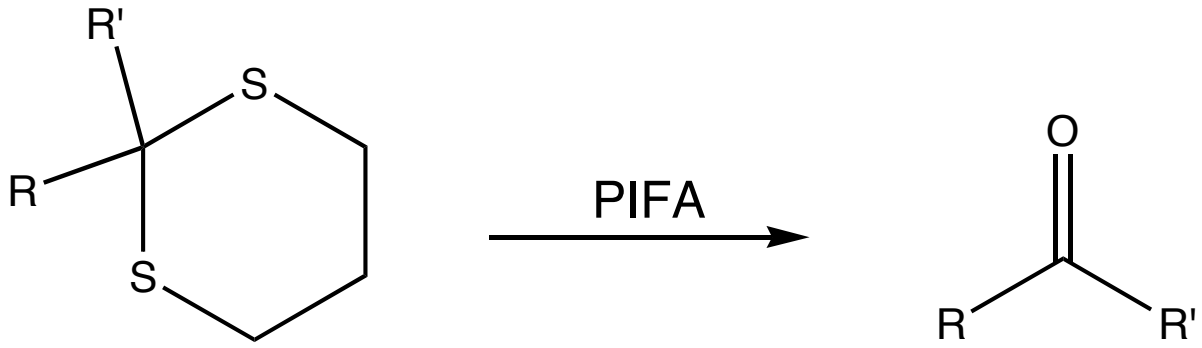
Protection for Alkynes



Alkyne now protected from reagents which can affect alkenes or alkynes.

Nicholas. **1971**, 3475

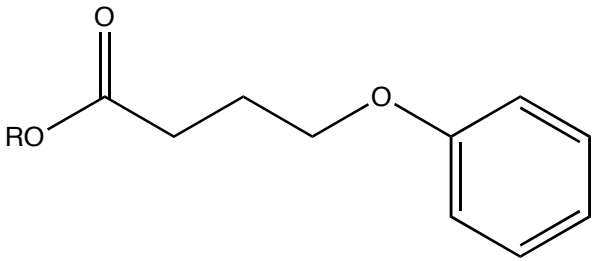
Not New, But Improved: Thioacetals



Improved method of removal which is selective for thioacetals.

Stork. **1989**, 287

BOB[1]



Protection:

1. Fisher Esterification
2. Mitsunobo Esterification
3. Jacobsen Asymmetric Epoxide Opening with Carboxylic acids, catalyzed with Co(salen)[2]

Deprotection:

1. Hydrogenolysis/lactonization:
   H_2, Pd/C then KOtBu

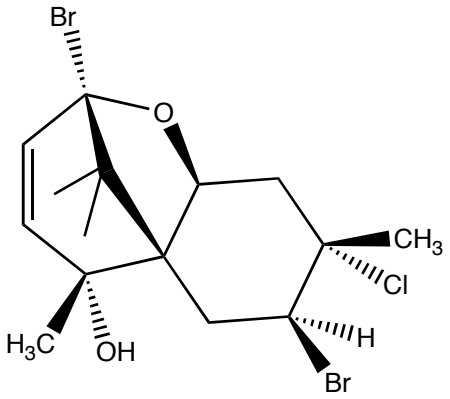
Protecting Capability:

1. Assumed similar to other esters
2. Can remove in presence of other esters

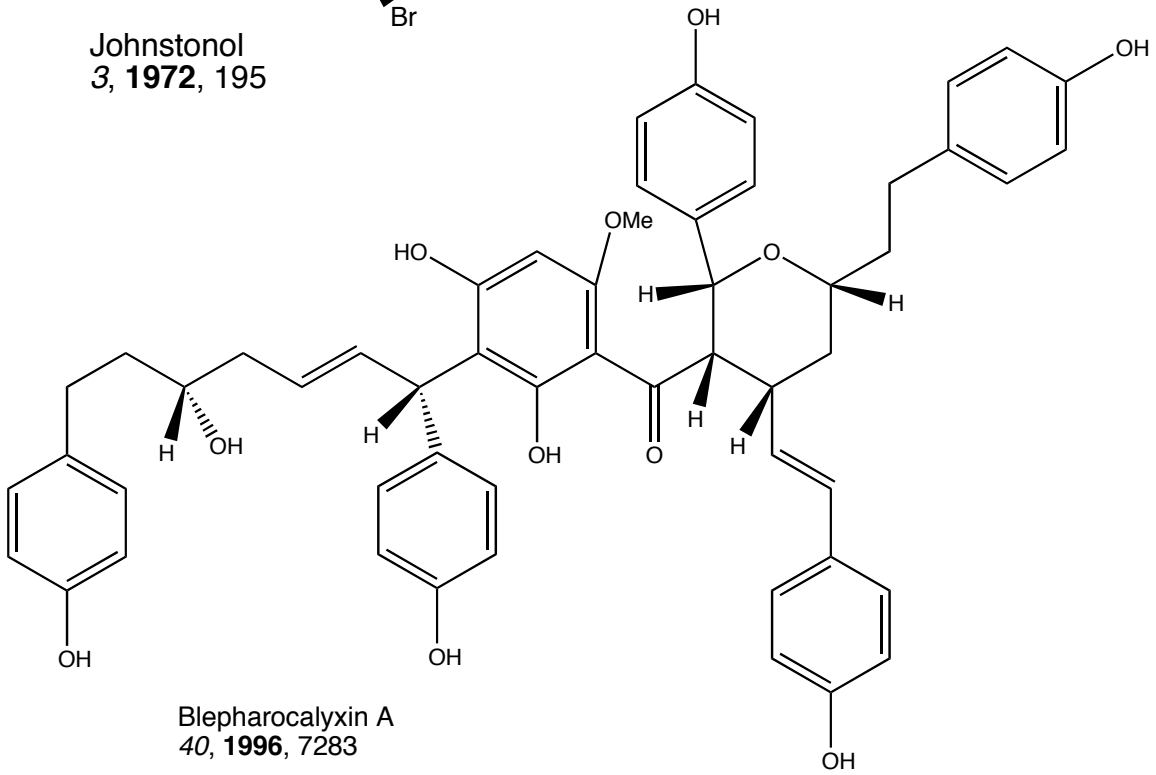
[1]Ganem. **2000**, 9523
[2]Jacobsen. **1997**, 773

Natural Products Reported in Tetrahedron Letters

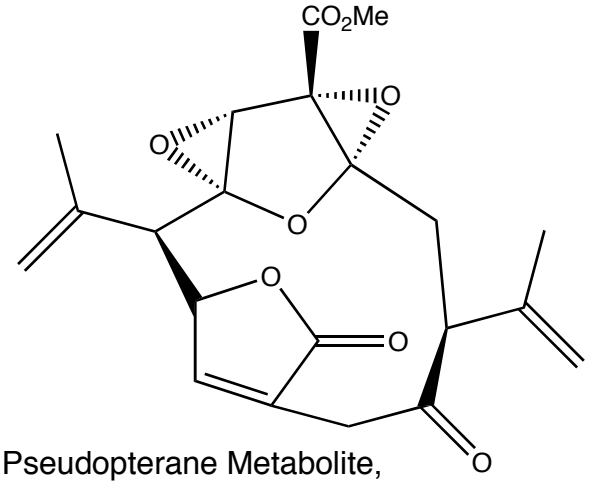
Natural Products



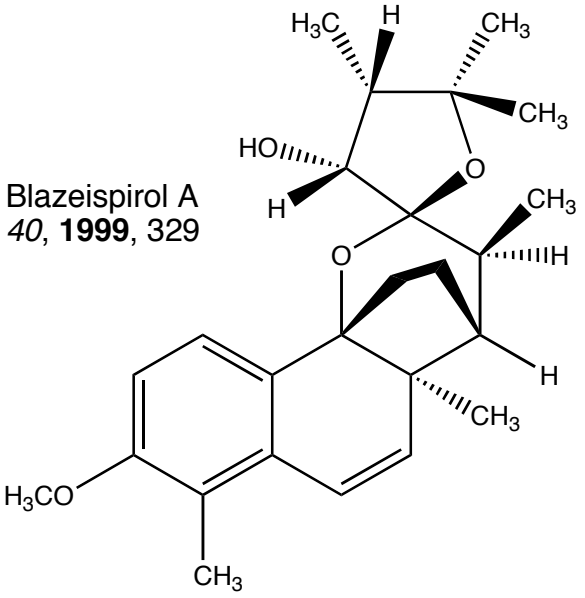
Johnstonol
3, **1972**, 195



Blepharocalyxin A
40, **1996**, 7283

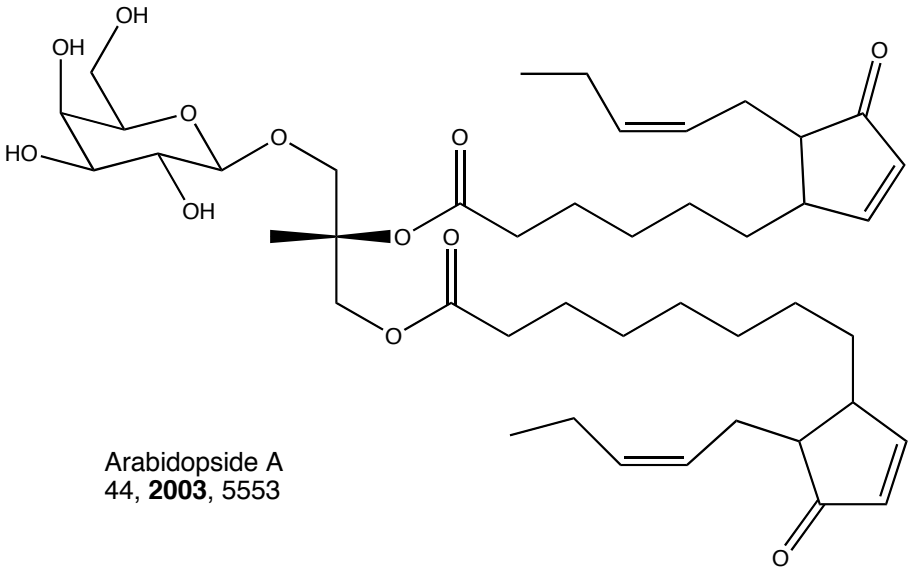


Pseudopterane Metabolite,
36, **1991**, 4661

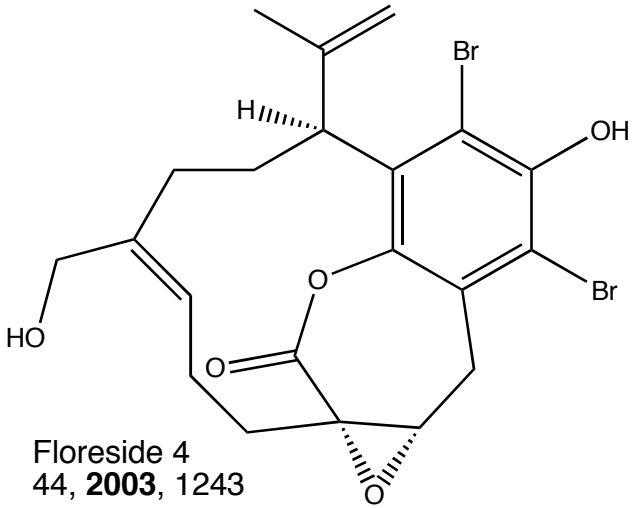


Blazeispirol A
40, **1999**, 329

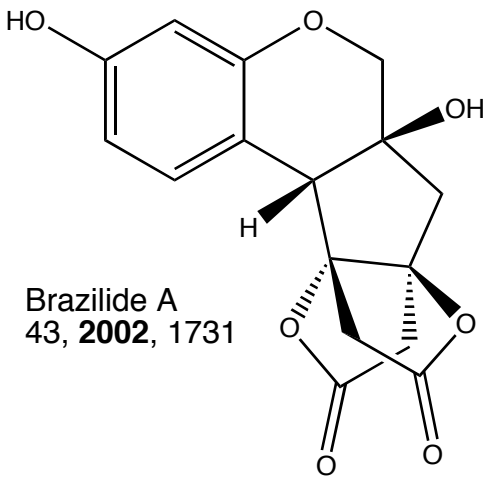
Natural Products



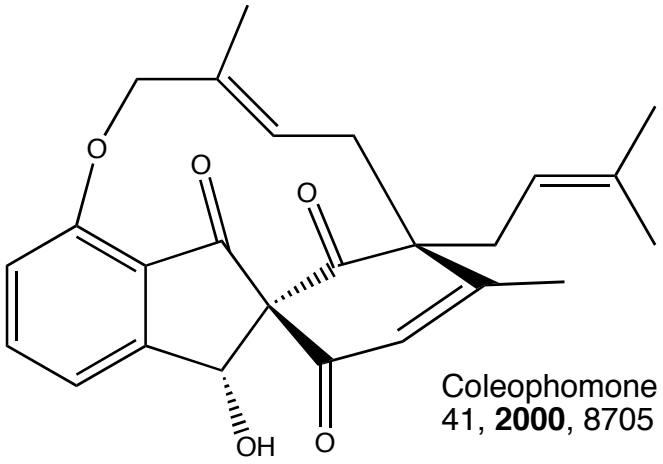
Arabidopside A
44, **2003**, 5553



Floreside 4
44, **2003**, 1243



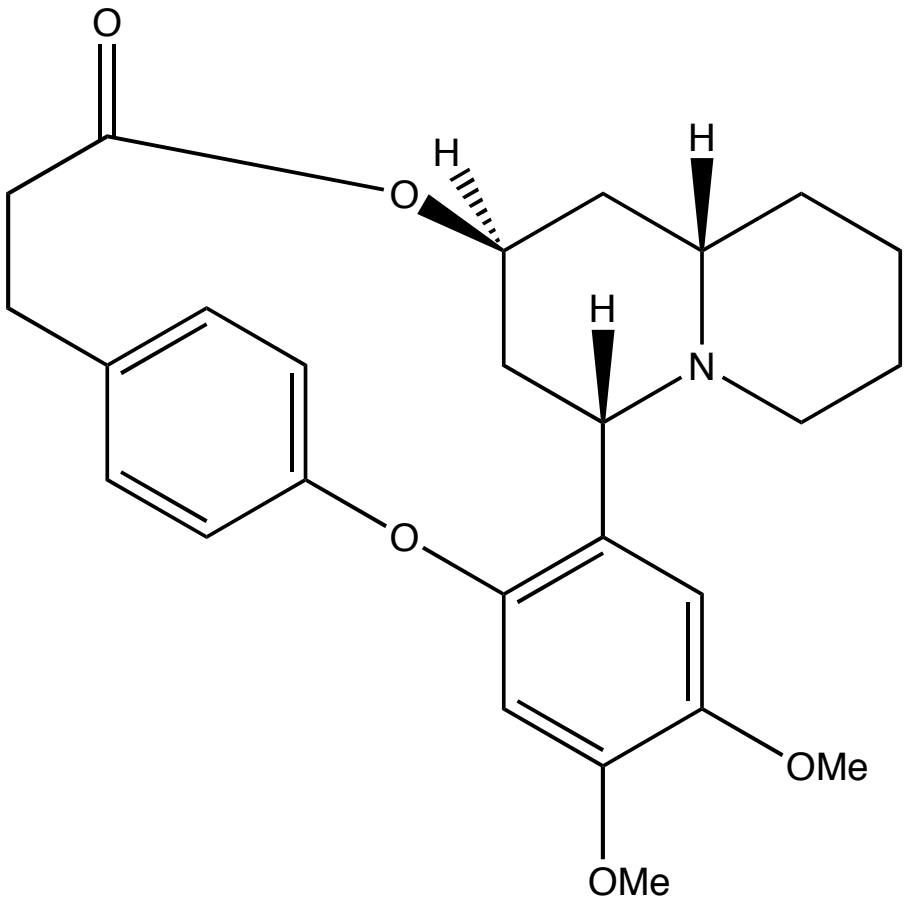
Brazilide A
43, **2002**, 1731



Coleophomone A
41, **2000**, 8705

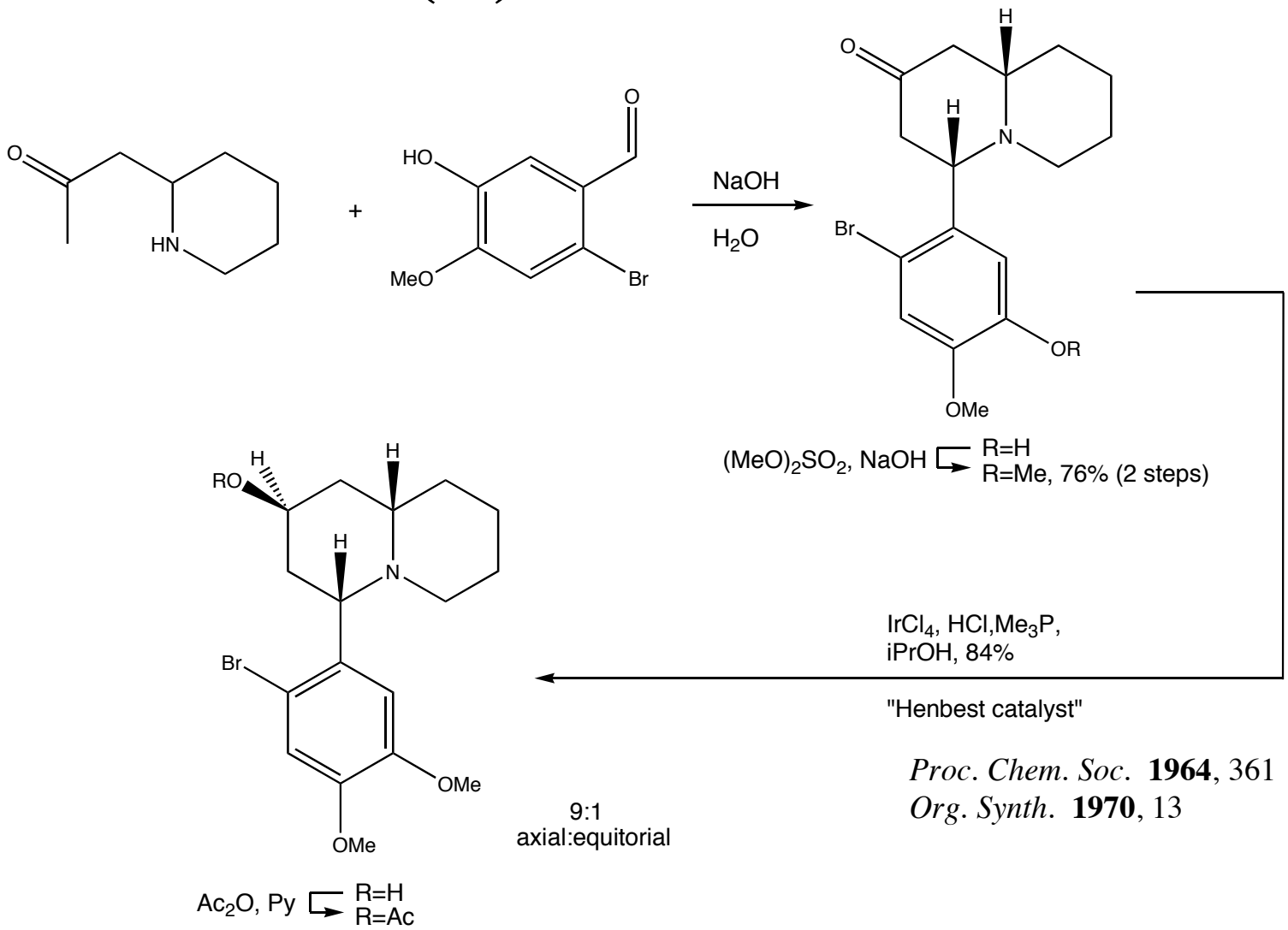
Syntheses

(±)-Decaline



Arata. **1973**, 2355

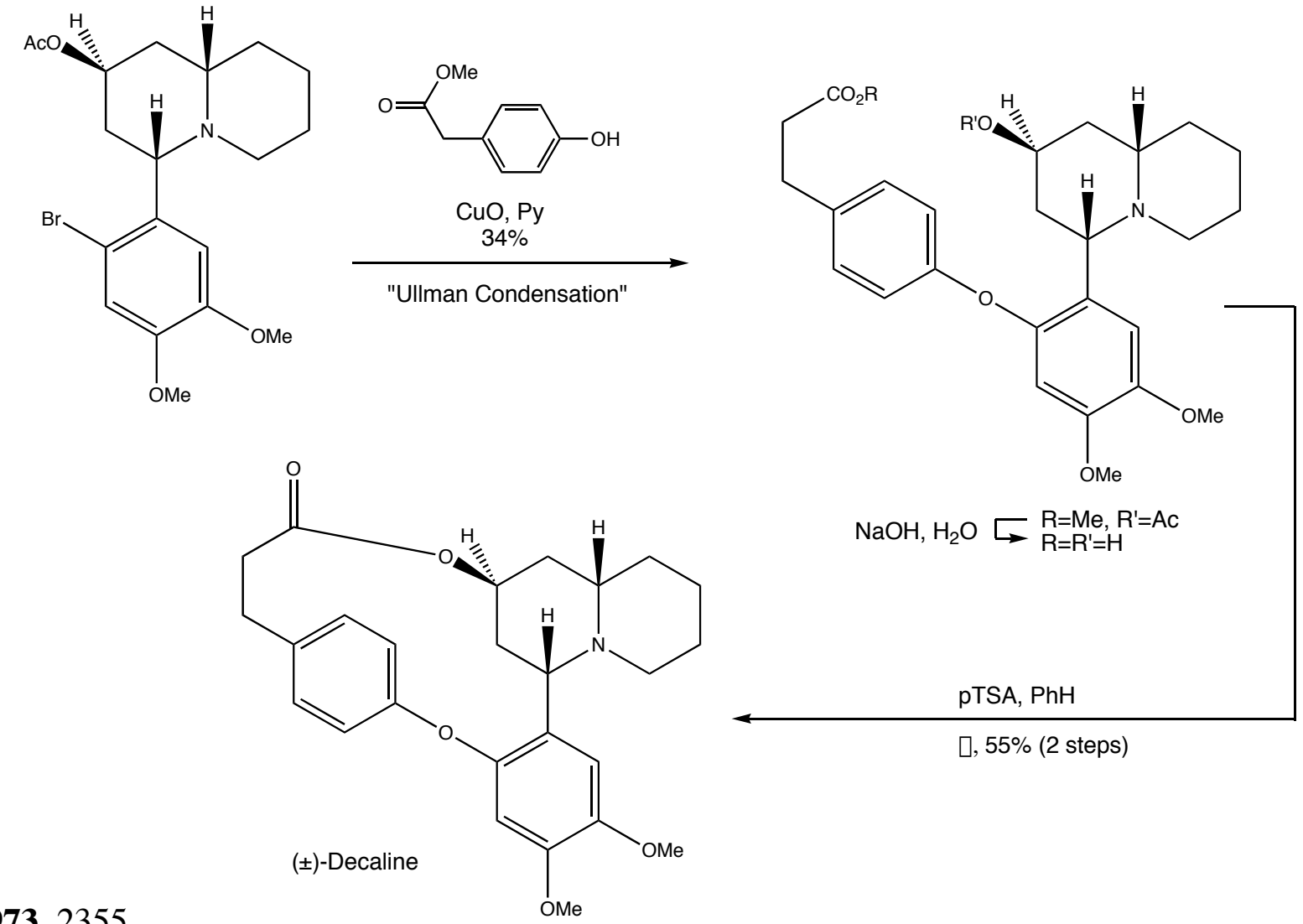
(±)-Decaline



Proc. Chem. Soc. **1964**, 361
Org. Synth. **1970**, 13

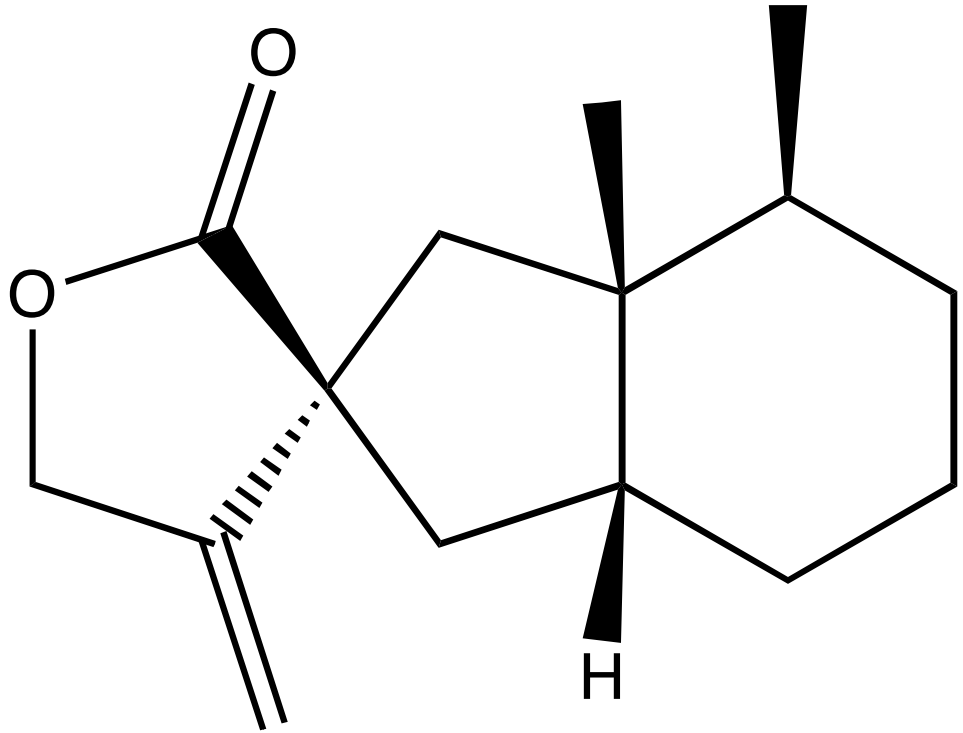
Arata. **1973**, 2355

(±)-Decaline



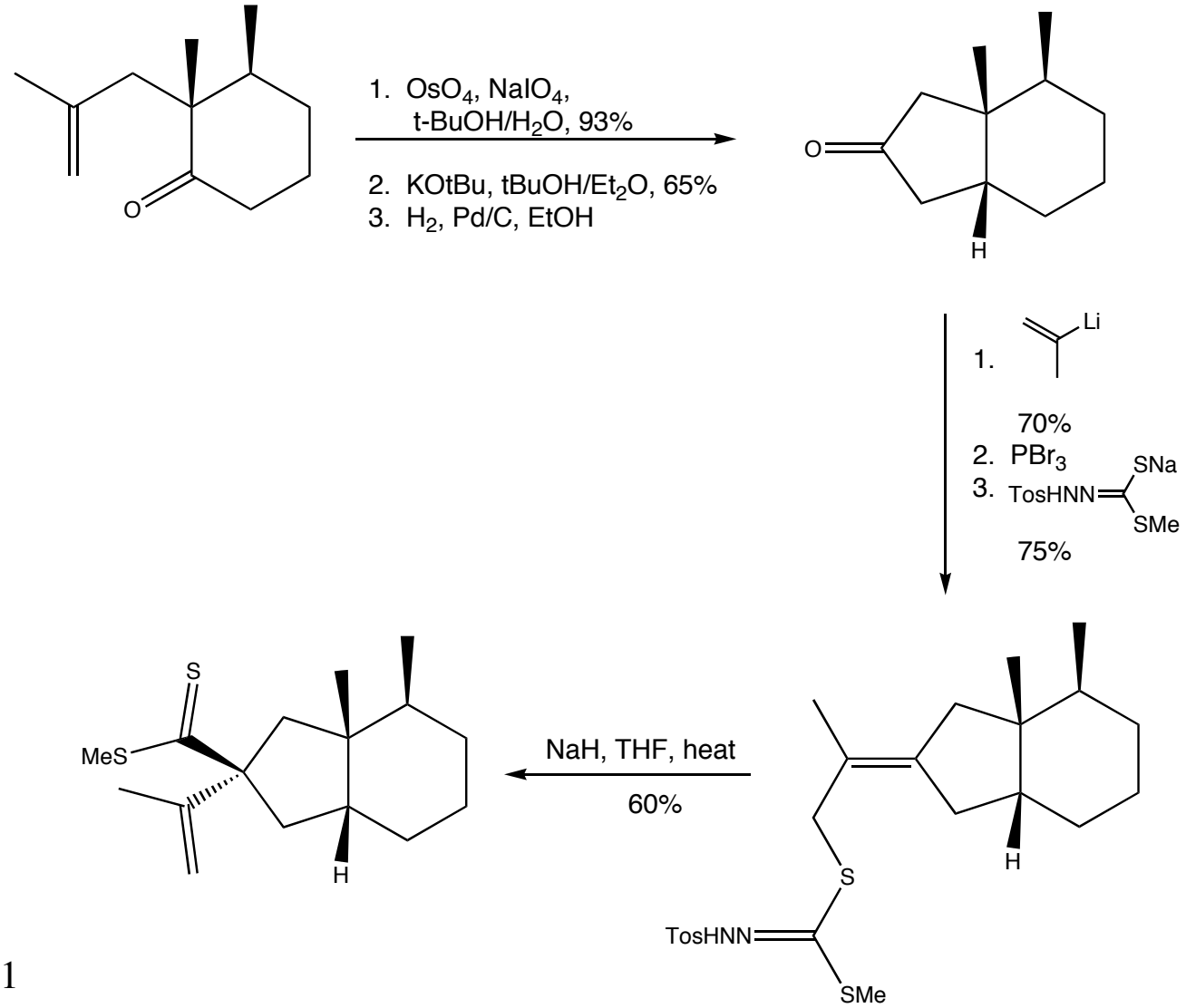
Arata. **1973**, 2355

(±)-Bakkenolide A



Evans. **1973**, 4691

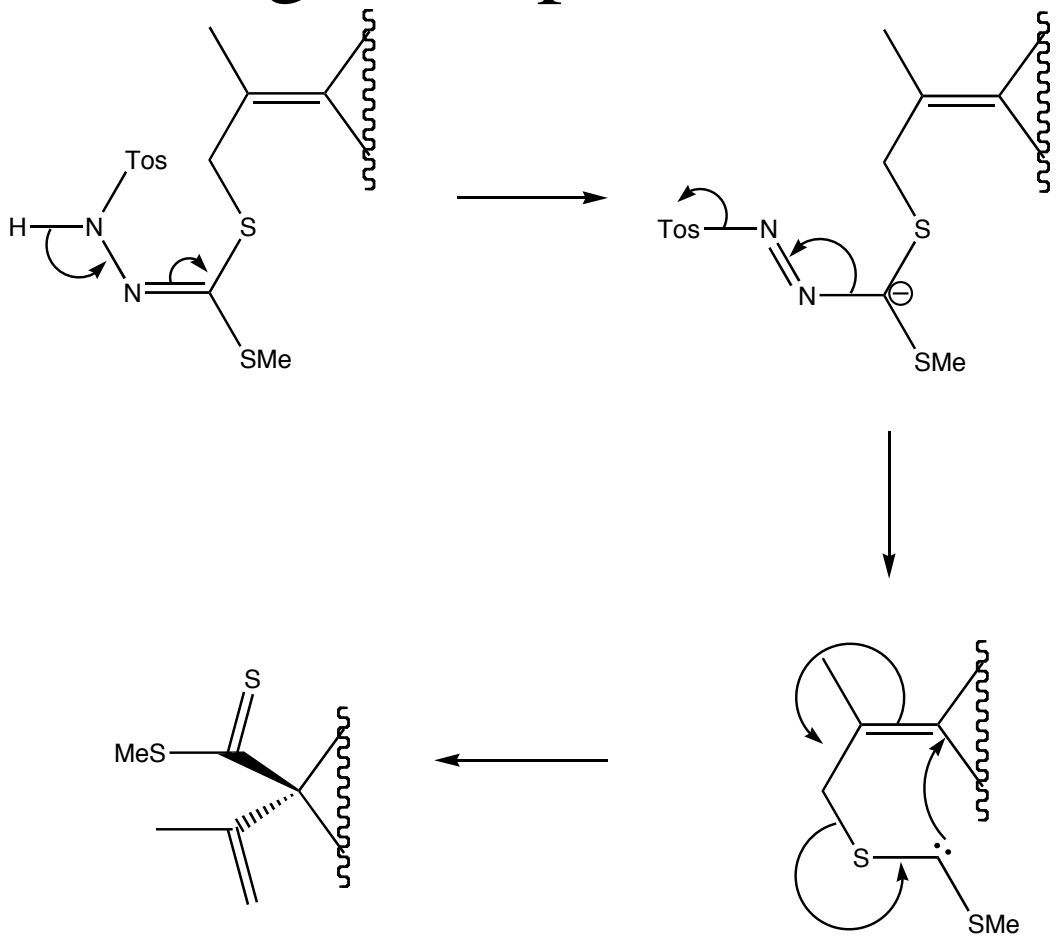
(±)-Bakkenolide A



Evans. **1973**, 4691

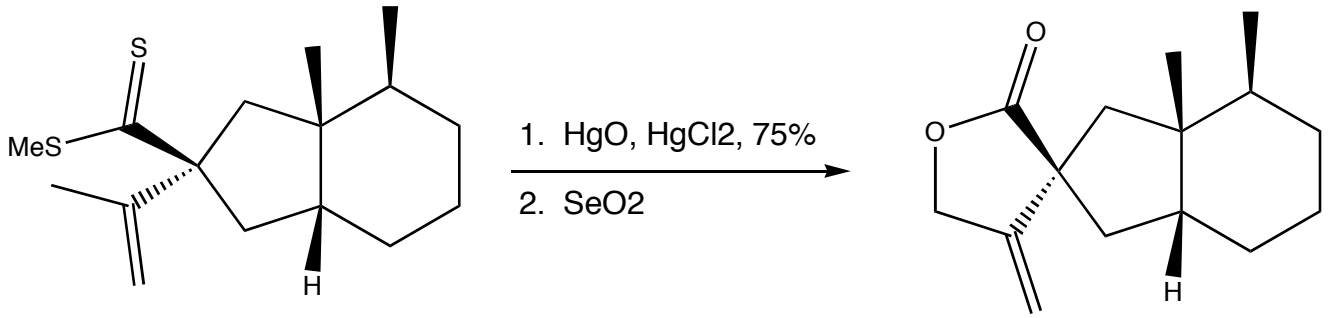
(±)-Bakkenolide A

Sigmatropic RAR



Evans. **1973**, 4691

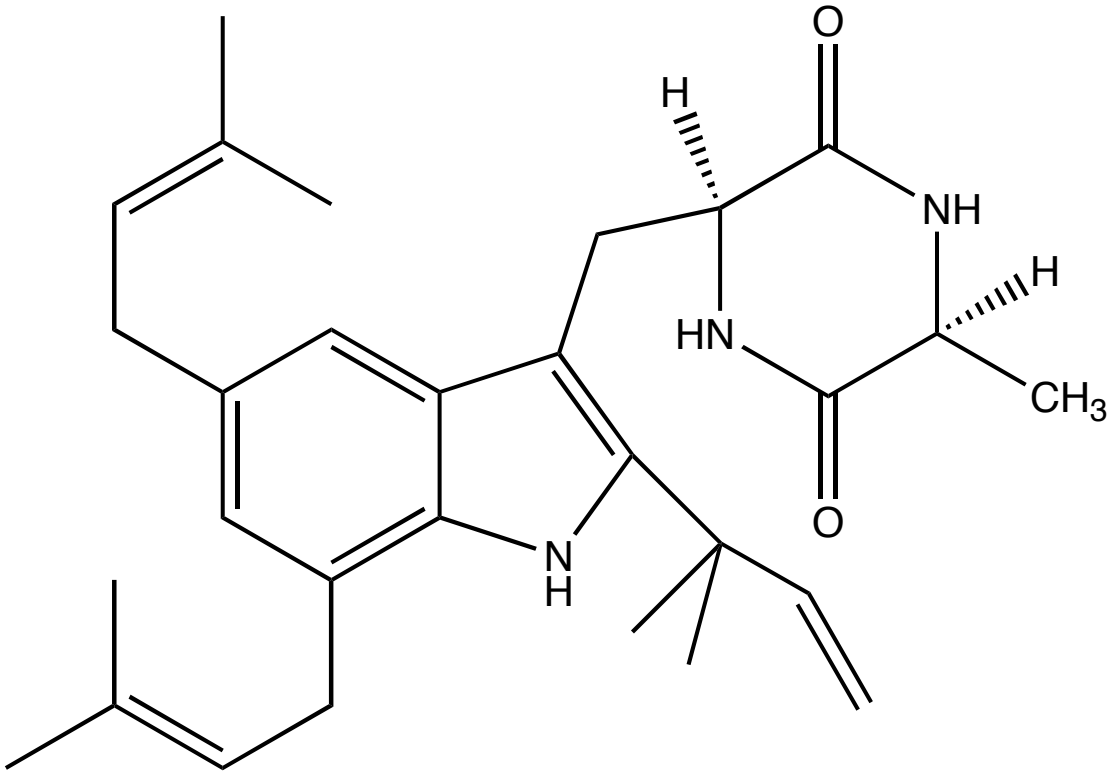
(±)-Bakkenolide A



(±)Bakkenolide A

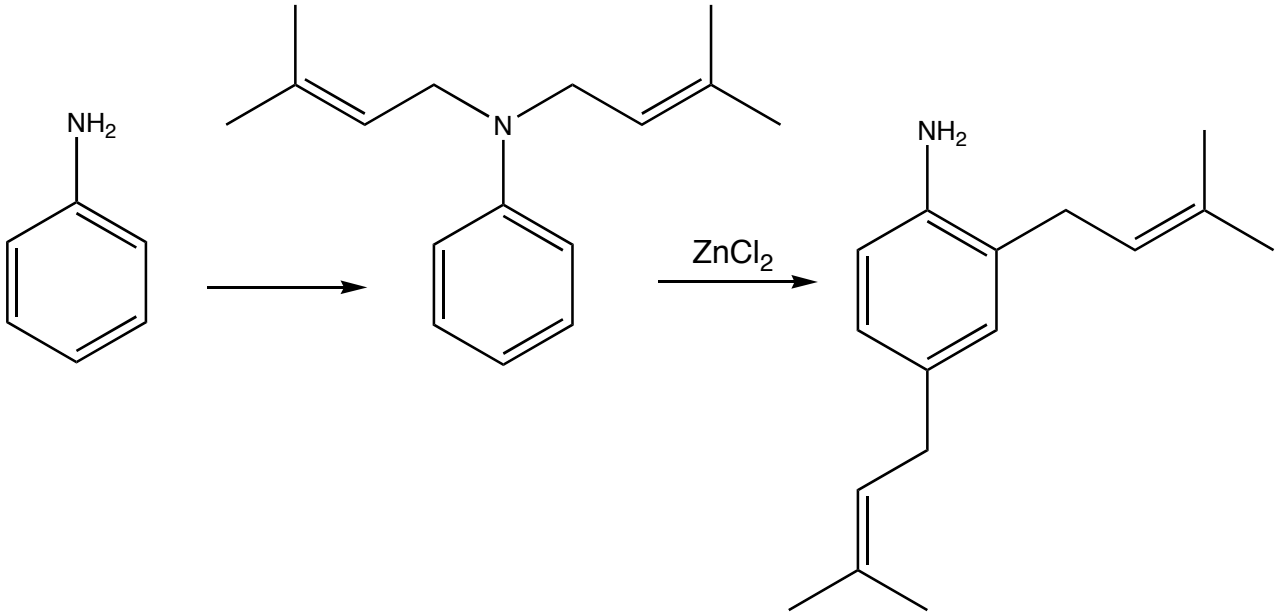
Evans. **1973**, 4691

Echinulin



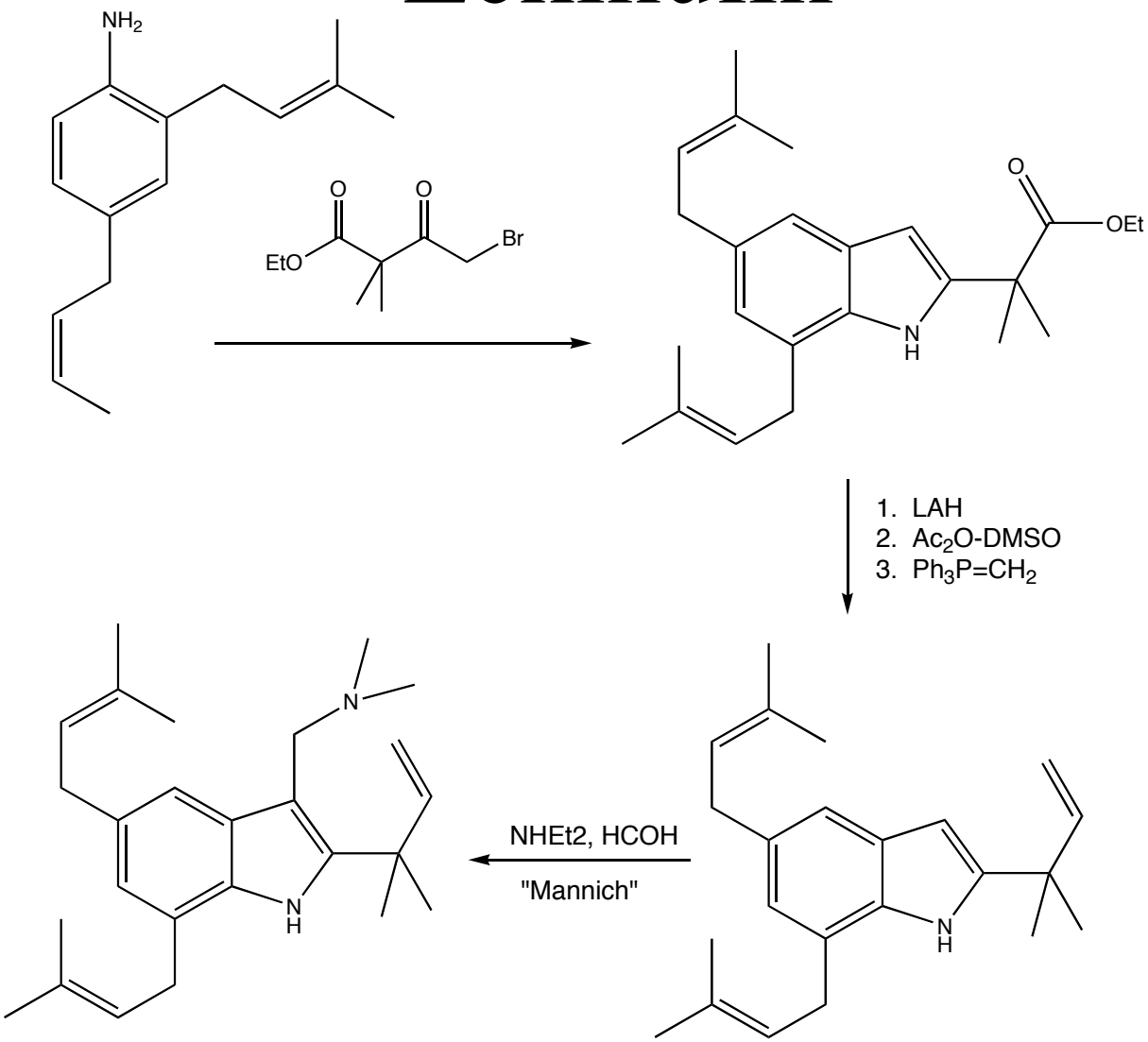
Kishi. **1971**, 4665

Echinulin



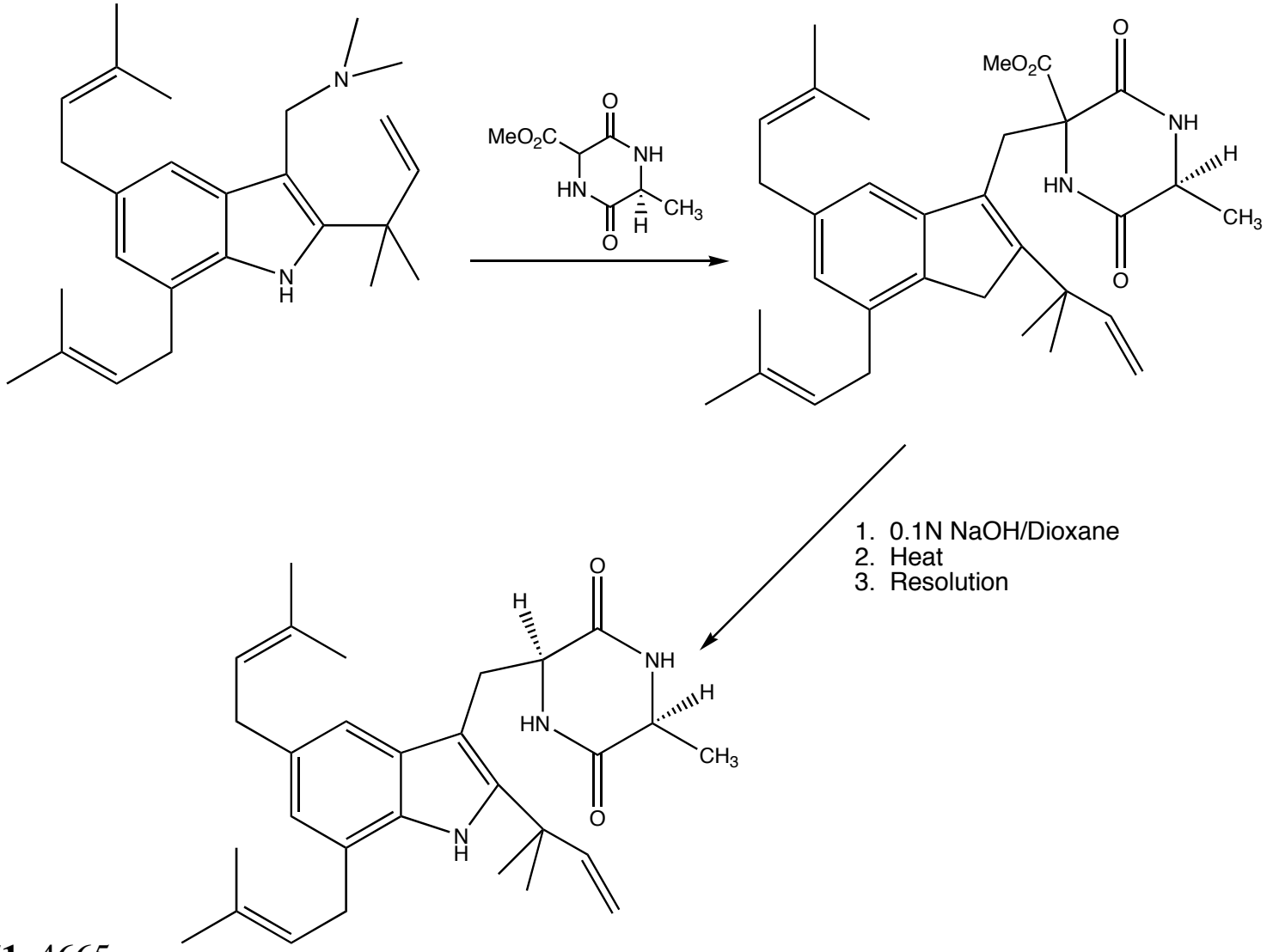
Kishi. **1971**, 4661

Echinulin



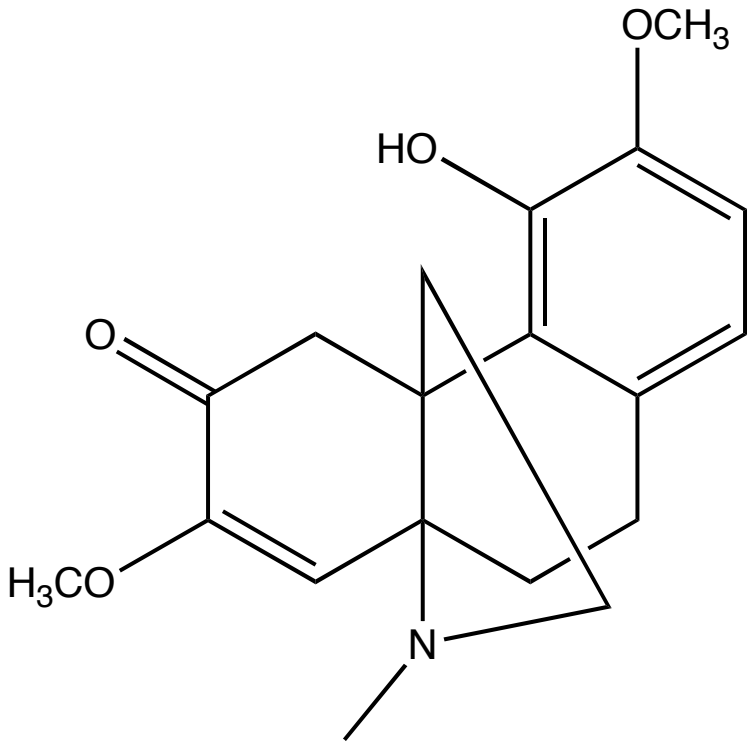
Kishi. **1971**, 4665

Echinulin



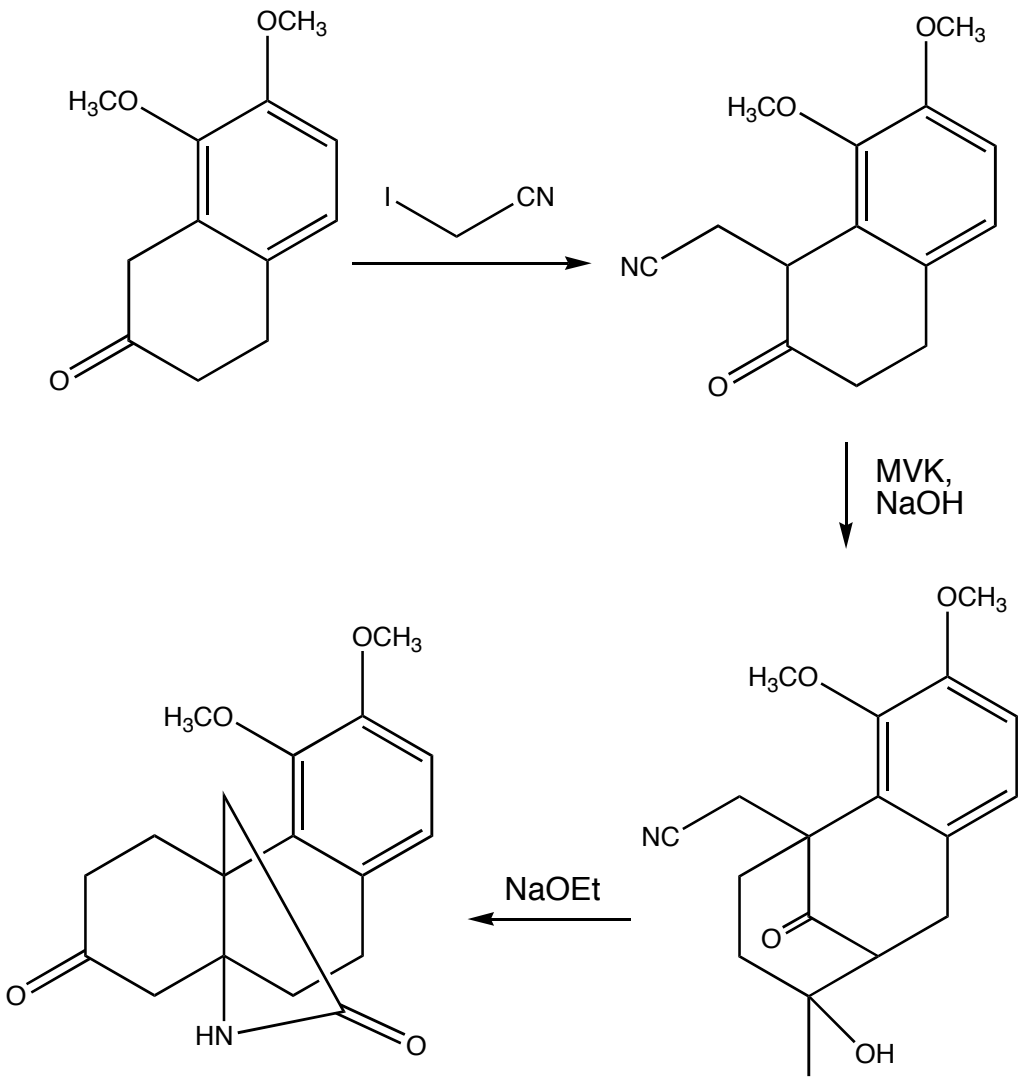
Kishi. **1971**, 4665

dl-Cepharamine



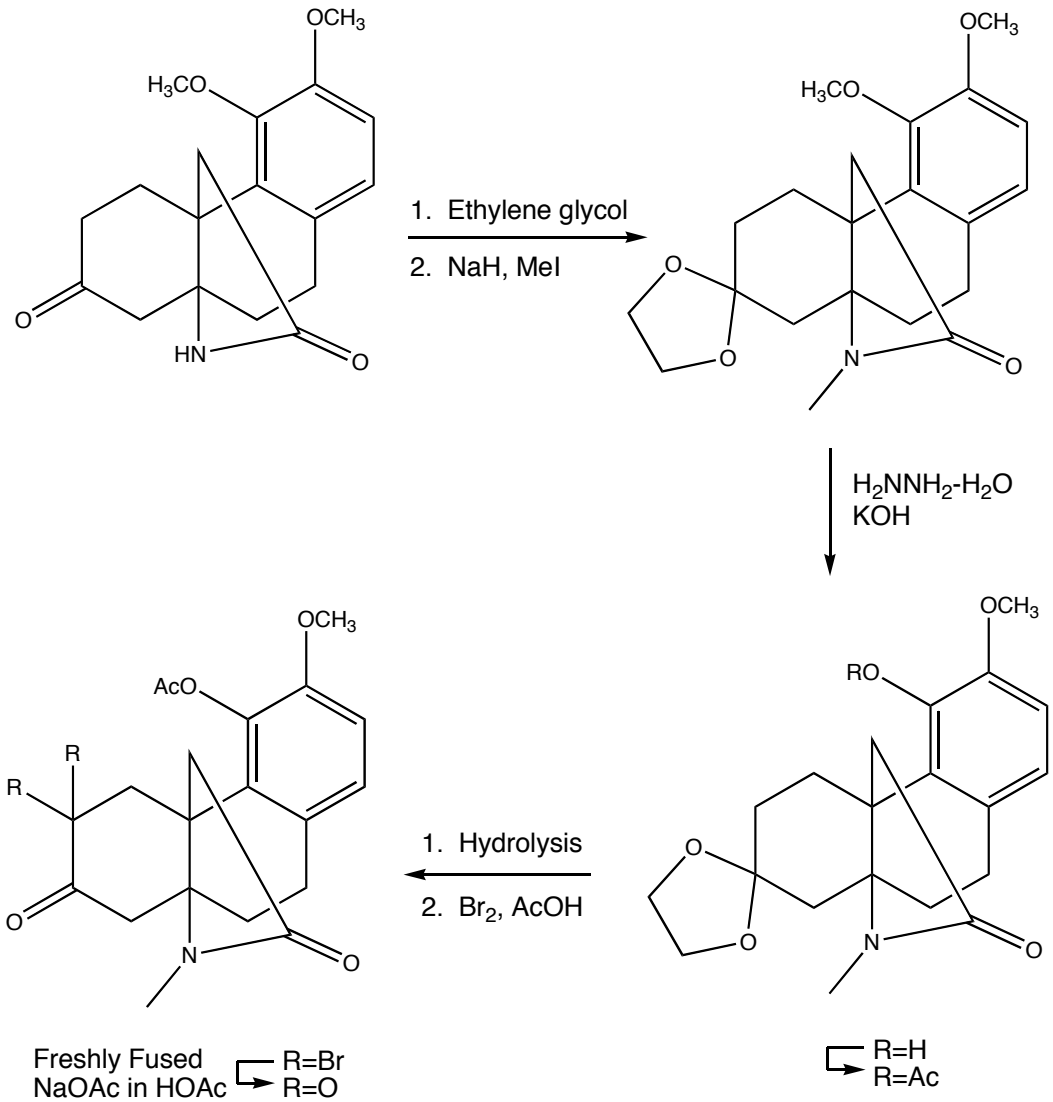
Kitano. **1969**, 1611

dl-Cepharamine



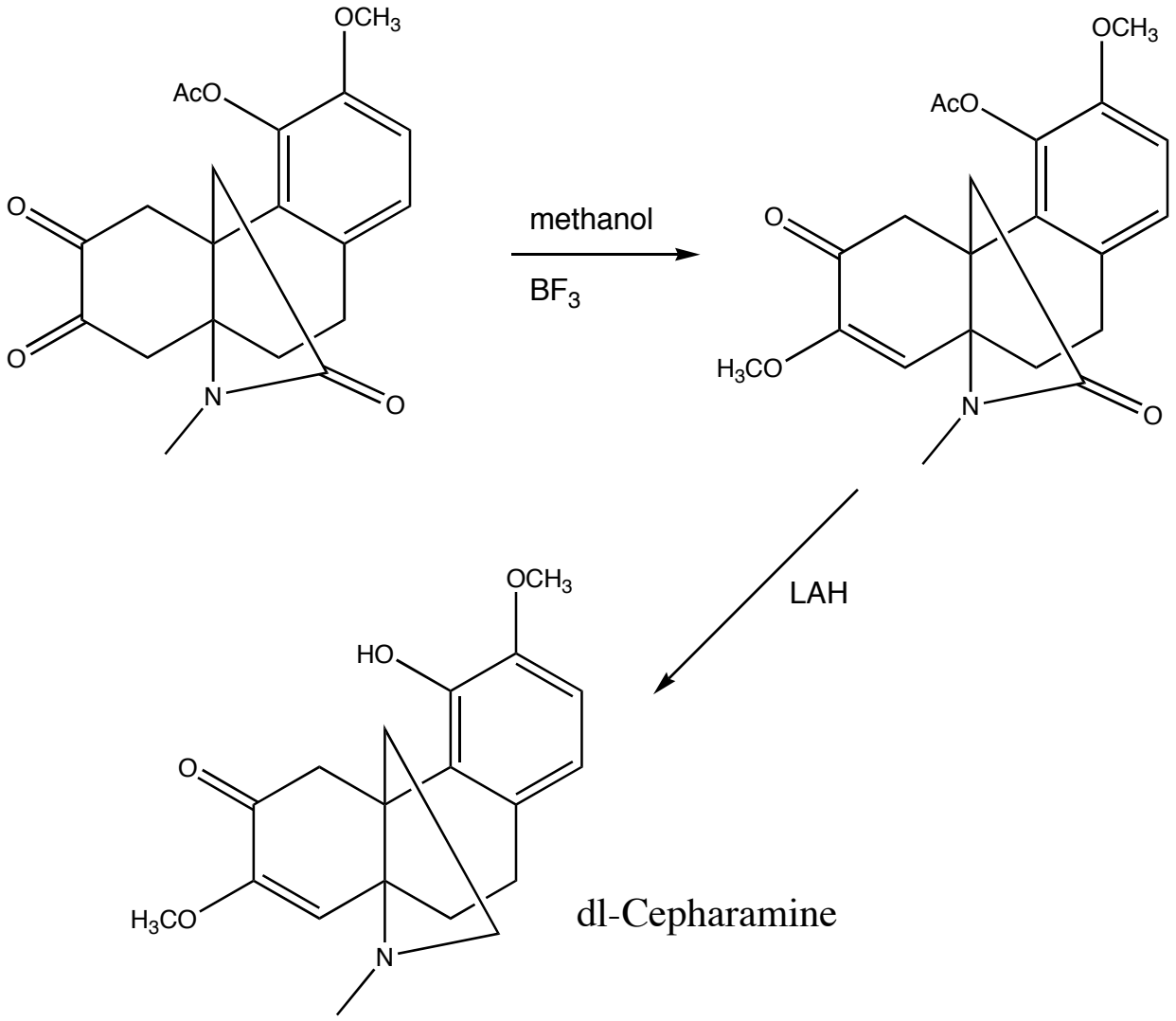
Kitano. **1969**, 1611

dl-Cepharamine



Kitano. **1969**, 1611

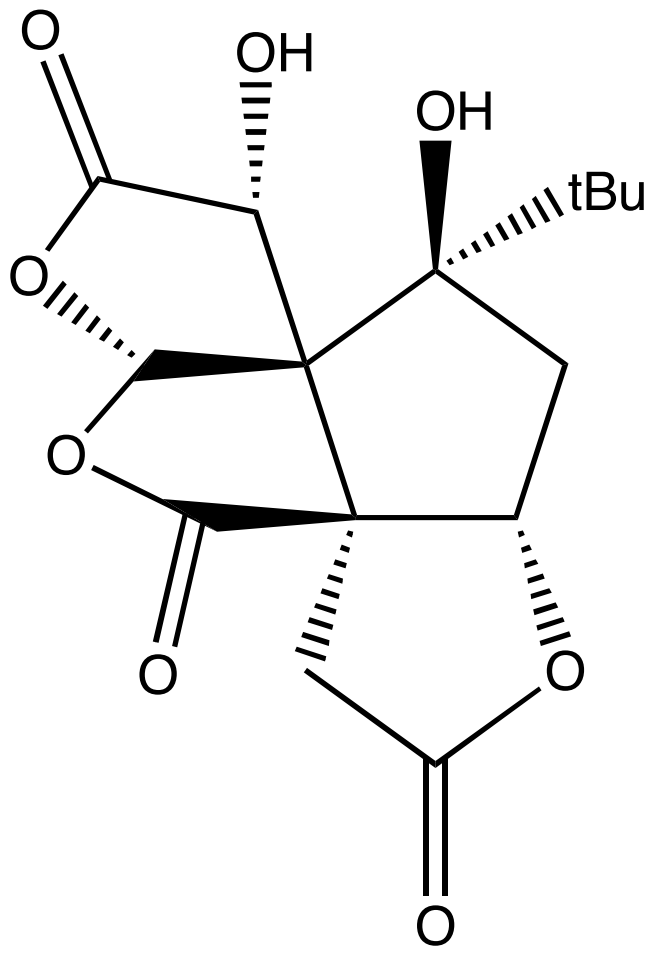
dl-Cepharamine



dl-Cepharamine

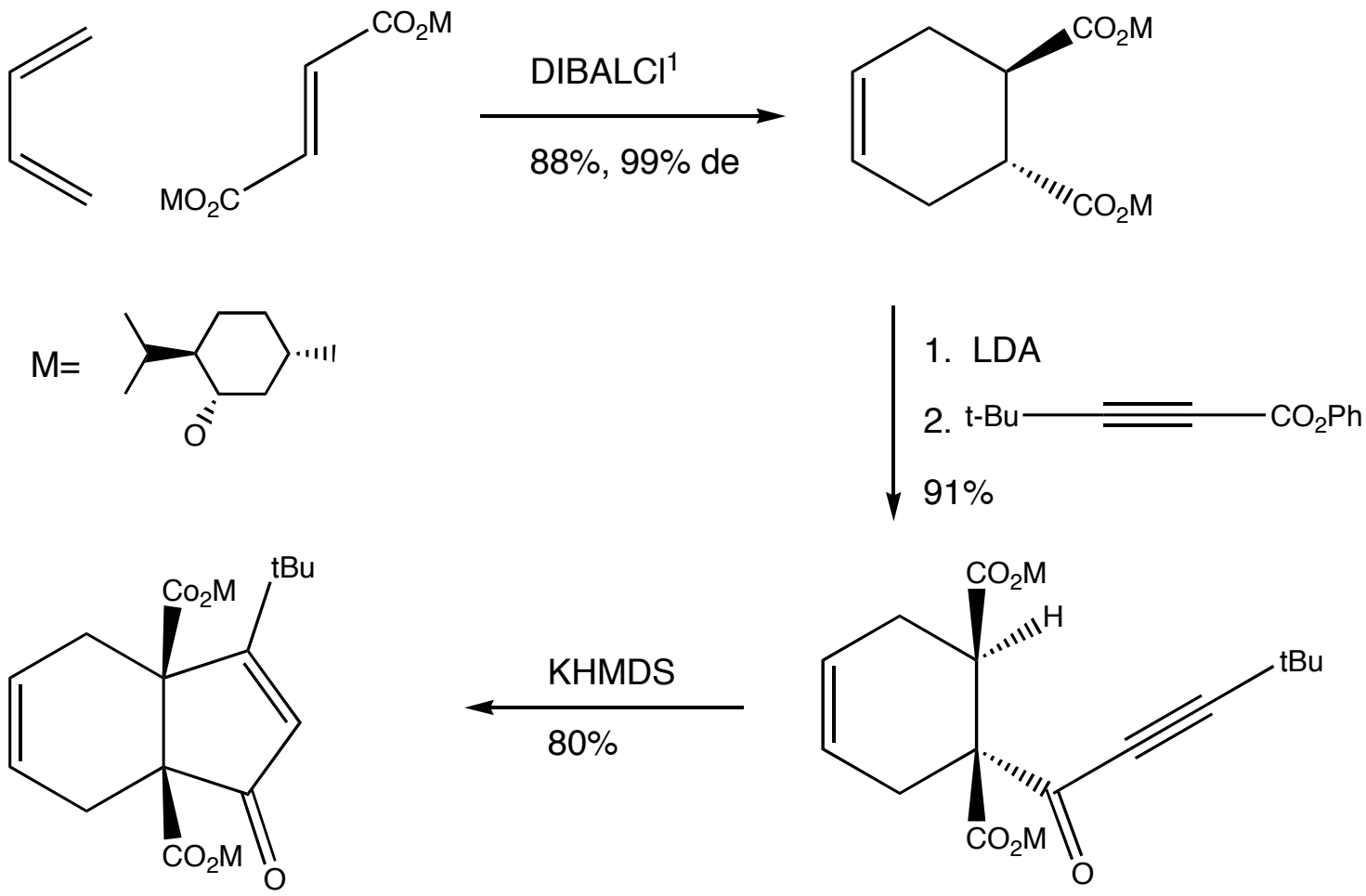
Kitano. **1969**, 1611

(-)-Bilobalide



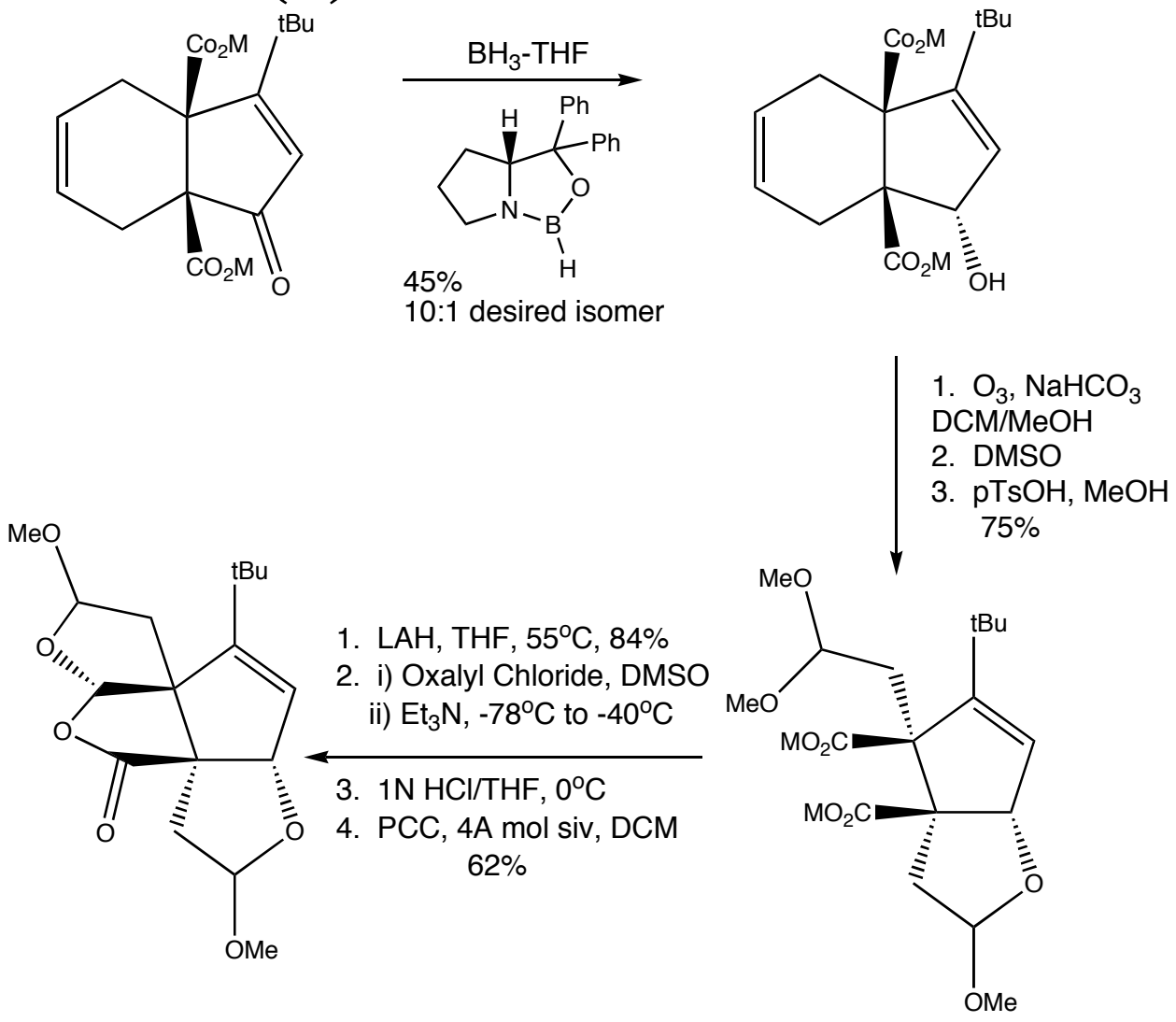
Corey. **1988**, 3423. Racemic synthesis originally presented in *J. Am. Chem. Soc.* **1987**, 7534

(-)-Bilobalide



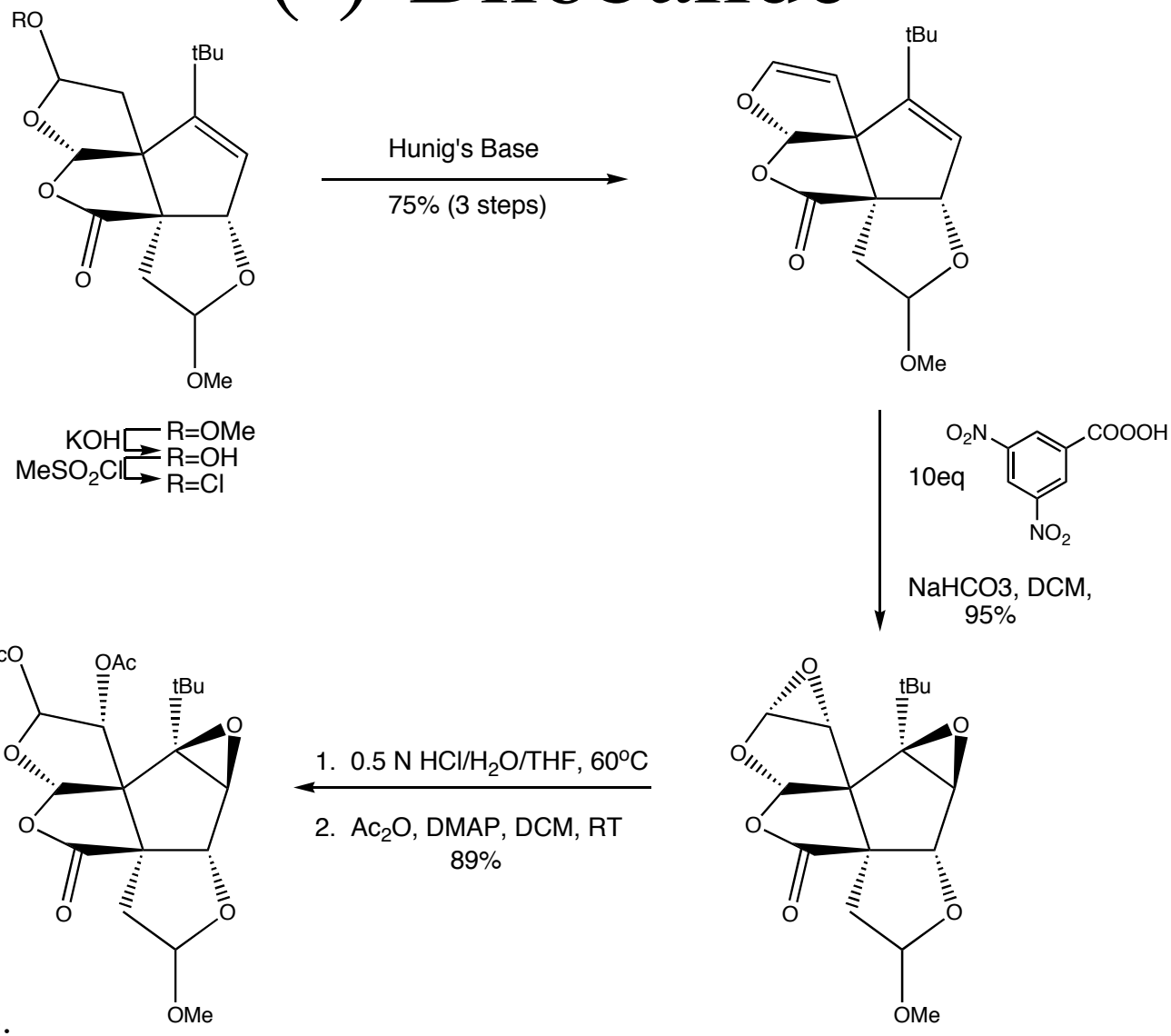
Corey. **1988**, 3423. [1]Developed by Yamamoto. **1986**, 4507

(-)-Bilobalide



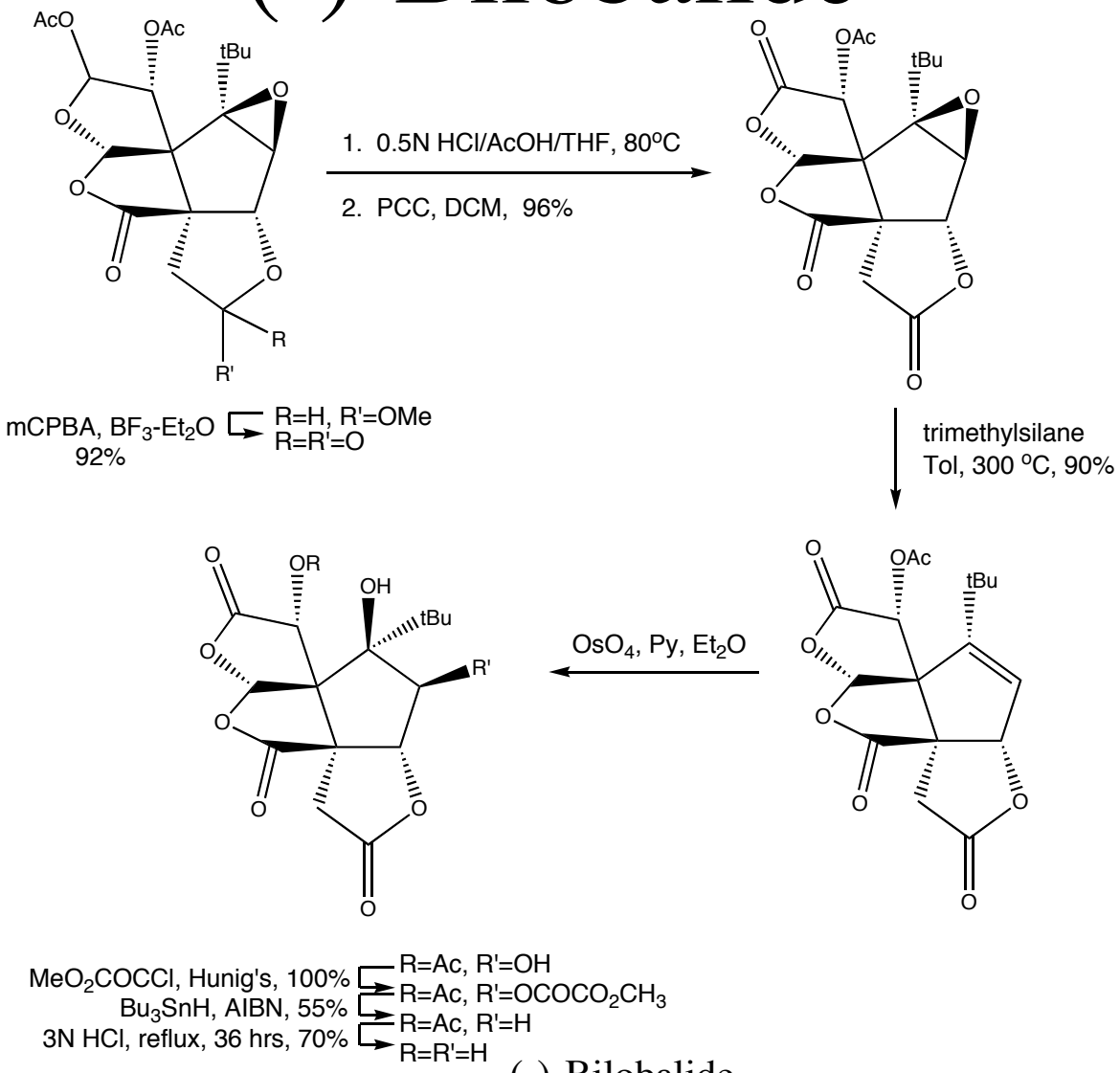
Corey. **1988**, 3423.

(-)-Bilobalide



Corey. **1988**, 3423.

(-)-Bilobalide



Corey. **1988**, 3423.

(-)-Bilobalide

Conclusions