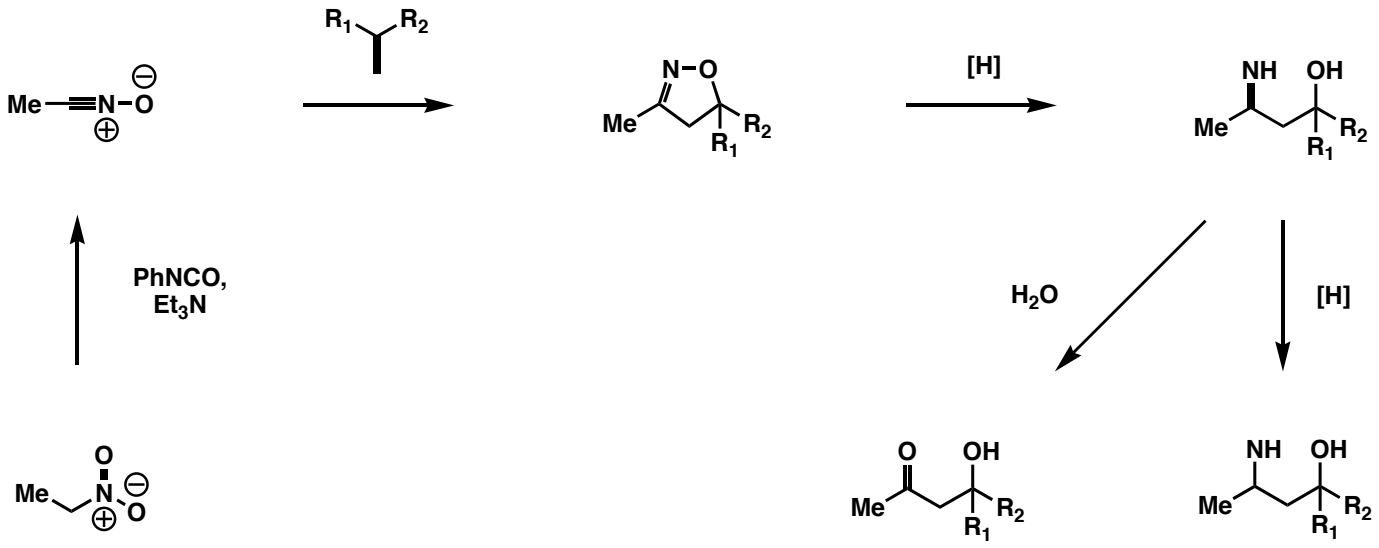
JACS 1982:
A Survey of Papers with a Focus on Synthetic Organic Chemistry

Baran Lab Group Meeting

15 October 2003

Carlos A. Guerrero

Reagents and Methods



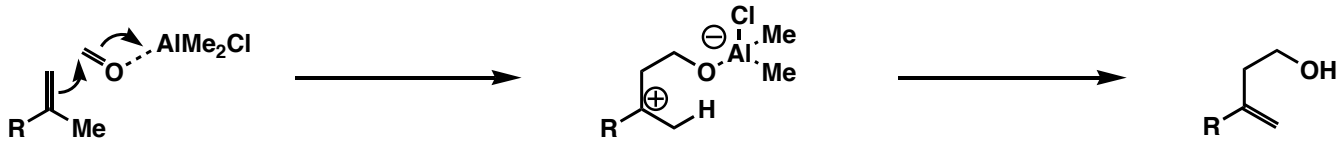
By 1982, the [3 + 2] cycloaddition of alkenes and nitrile *N*-oxides was well known. However, this chemistry had never been applied to the synthesis of β-hydroxy ketones.

The major obstacle to implementing this reaction as an aldol equivalent is over-reduction to give the β-amino alcohol.

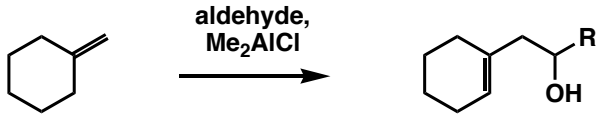
Curran found that catalytic Rany nickel under an H_2 atmosphere and addition of a buffer cleanly give imino alcohols that readily hydrolyze to give the desired compounds. Syn and anti ratios are never a problem because 1) the cycloaddition is syn and 2) the alkene geometry is fixed.

Reagents and Methods

Me_2AlCl mediated heteroene reactions of aldehydes and alkenes:



The reaction of methylenecyclohexane with certain aldehydes demonstrates the utility of this reaction:



R = Me (91), R = *i*-Bu (74), R = Ph (69), R = H (80), R= *t*-Bu (93)

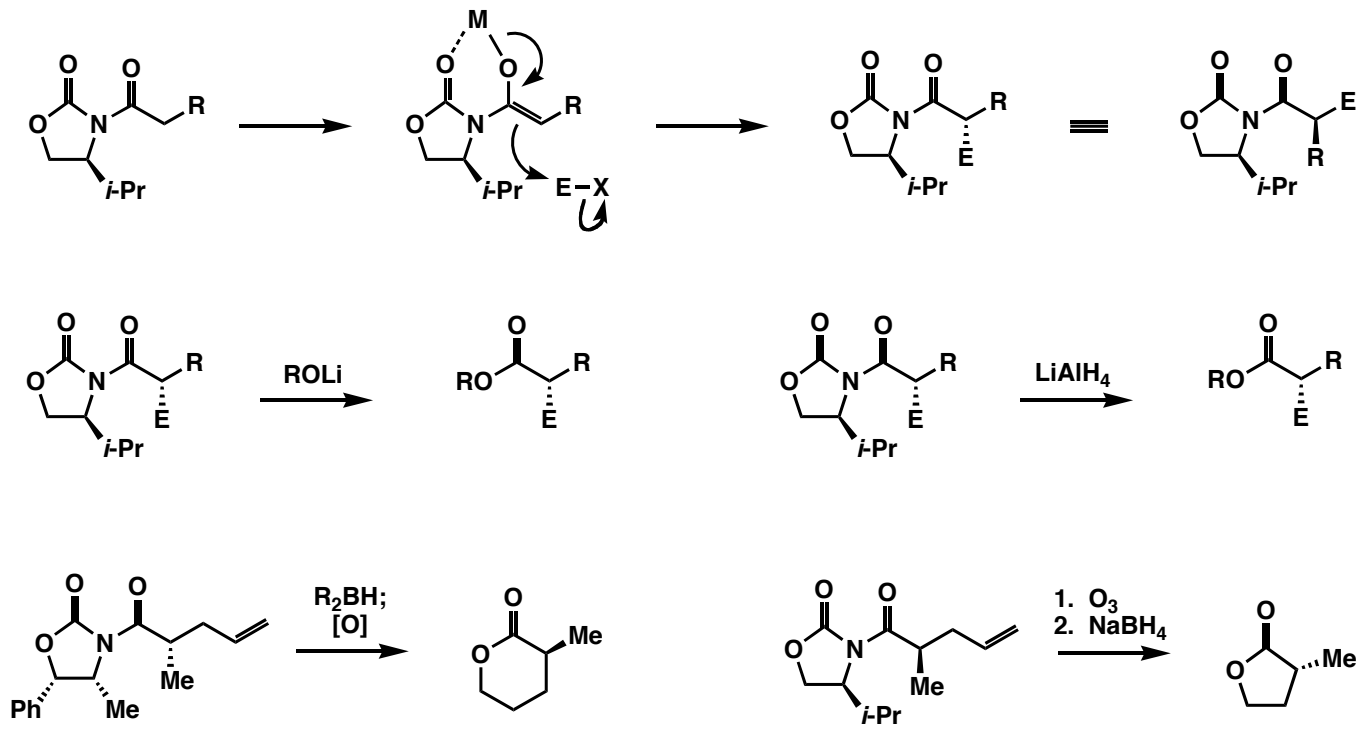
The moderate to high yields obtained highlight the mild nature of this transformation. Other protic or Lewis acids usually isomerize the alkene.

1, 1-disubstituted alkenes are most reactive. Ene reactions with tri- and tetrasubstituted alkenes also occur readily, but due to their slower rates, two competing reactions may take place. The first, methyl addition to the aldehyde, occurs with hindered and aromatic aldehydes. The second, aldol reaction, occurs with some aliphatic aldehydes. Alkenes which would give a secondary carbocation do not react with aldehydes other than formaldehyde.

B. B. Snider, D. J. Rodini, T. C. Kirk, R. Cordova. 555.

Reagents and Methods

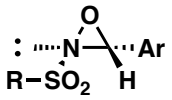
The Evans asymmetric alkylation reaction was discovered in 1980. The focus of his paper in 1982 was transformations of the imides that resulted after the reaction.



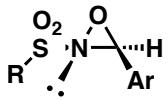
D. A. Evans, M. D. Ennis, D. J. Mathre. 1737.

Reagents and Methods

Davis oxaziridines: reagents that serve as chiral sources of electrophilic oxygen:

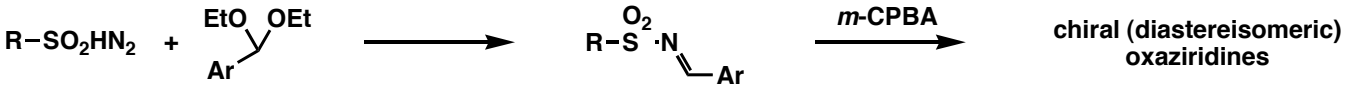


R, R



S, S

The oxaziridines are made in the following way:

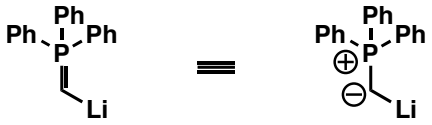


ee's for sulfide oxidations are modest (maximum of 46%). However, the reagents have been applied to asymmetric hydroxylation of enolates. In the case of a chiral enolate (Evans imide), the R group does not need to be chiral.

F. A. Davis, R. H. Jenkins Jr., S. B. Awad, O. D. Stringer, W. H. Watson, J. Galloy. 5412.

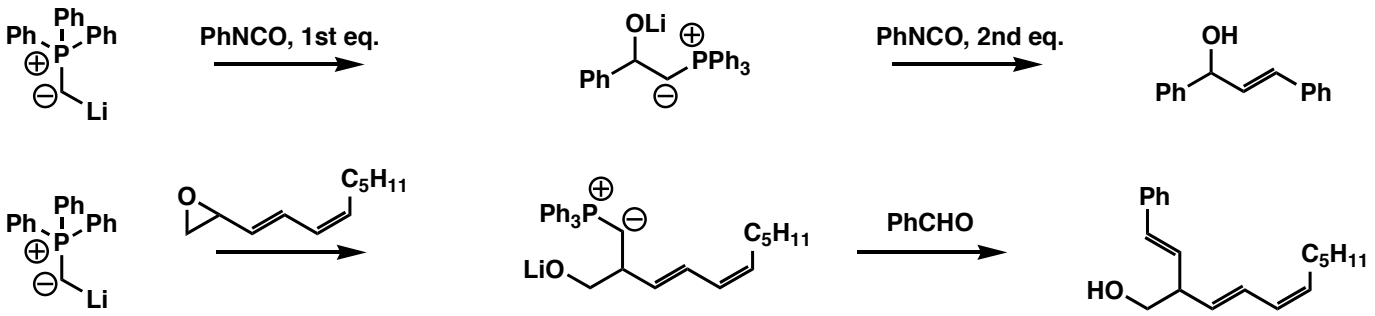
Reagents and Methods

-Lithiomethylenetriphenylphosphorane, a Highly Reactive Ylide Equivalent



The reagent is generated by treating methyltriphenylphosphonium bromide with 2 eq. of *s*-BuLi or by treating methylene-triphenylphosphorane with 1 eq. *t*-BuLi.

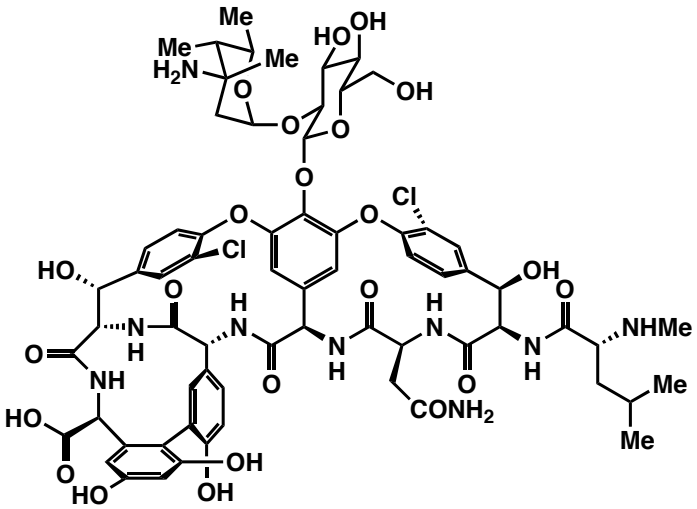
Reactivity:



E. J. Corey, J. Kang. 4293.

Structure Determinations

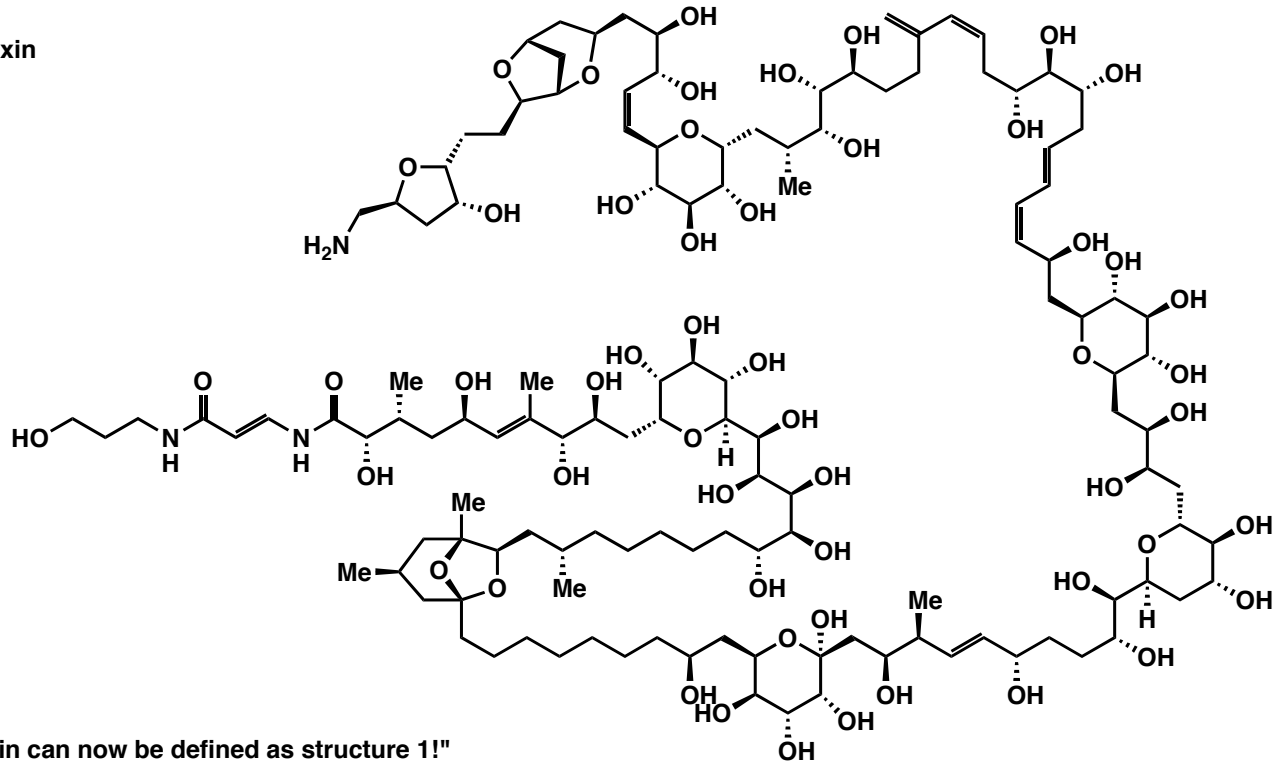
Vancomyin:



C. M. Harris, T. M. Harris. 4293.

Structure Determinations

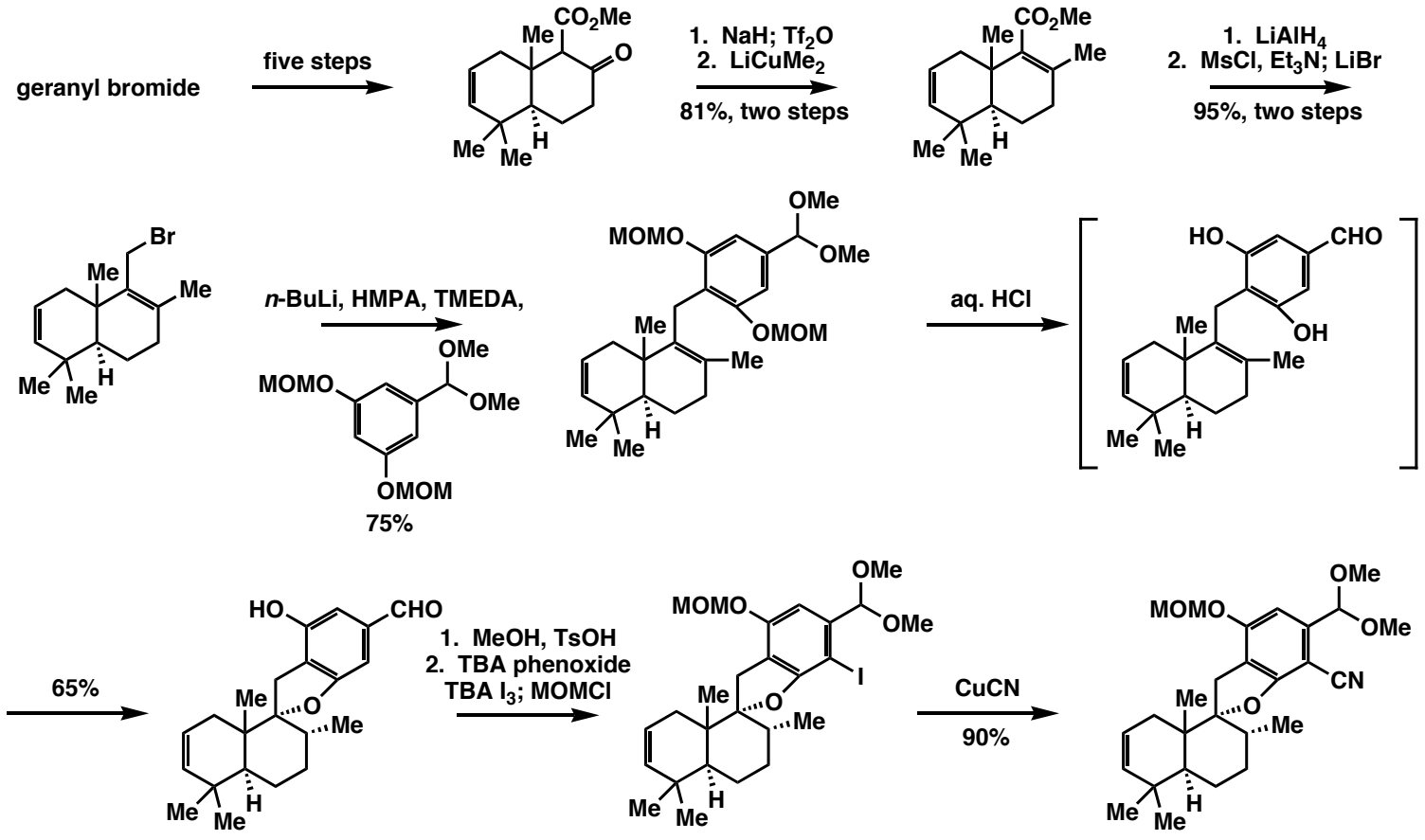
1: palytoxin



"Palytoxin can now be defined as structure 1!"

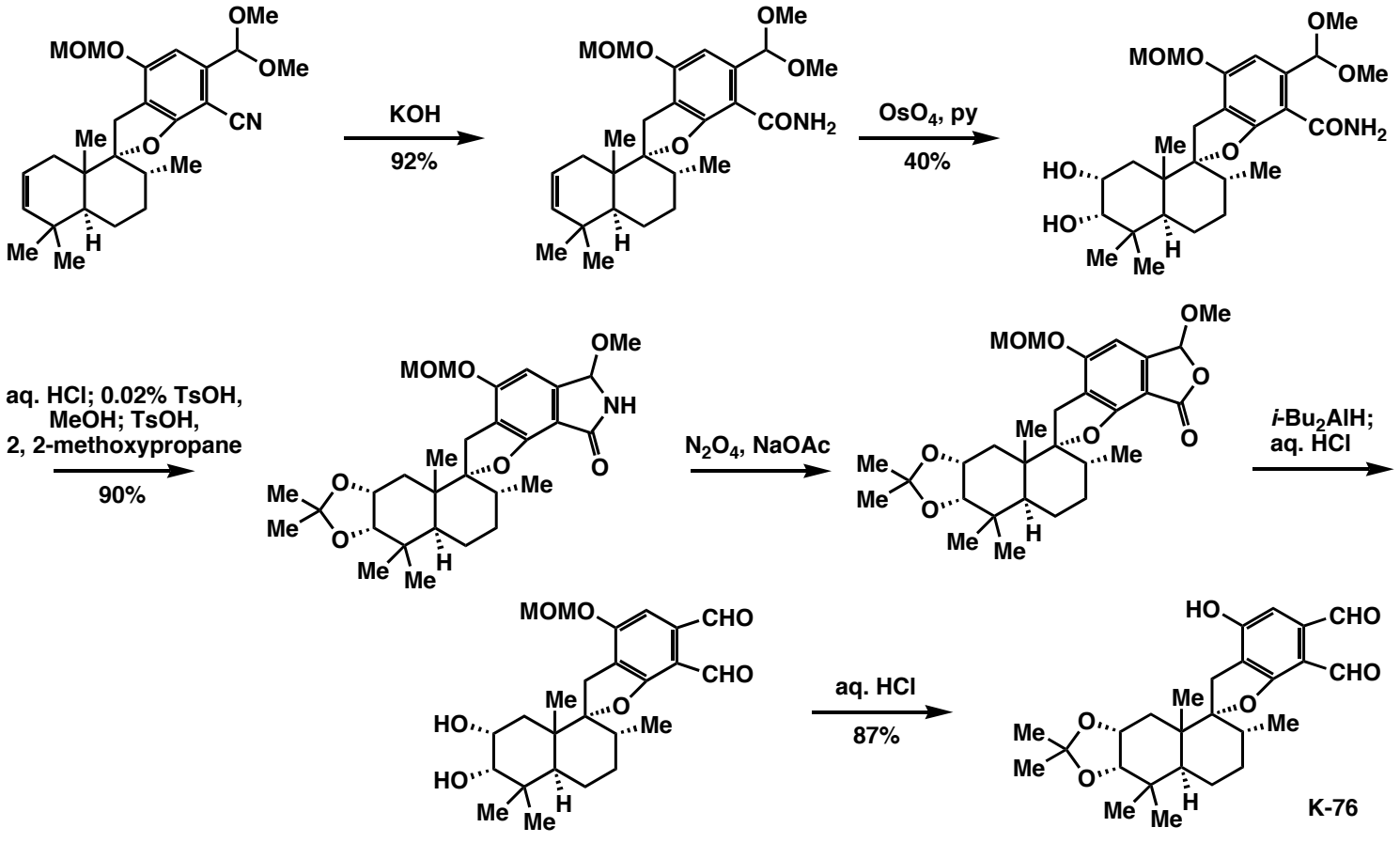
Y. Kishi, D. Uemura, Y. Hirata, *et al.* 7369.

Total Syntheses



E. J. Corey, J, Das. 5551.

Total Syntheses



E. J. Corey, J, Das. 5551.

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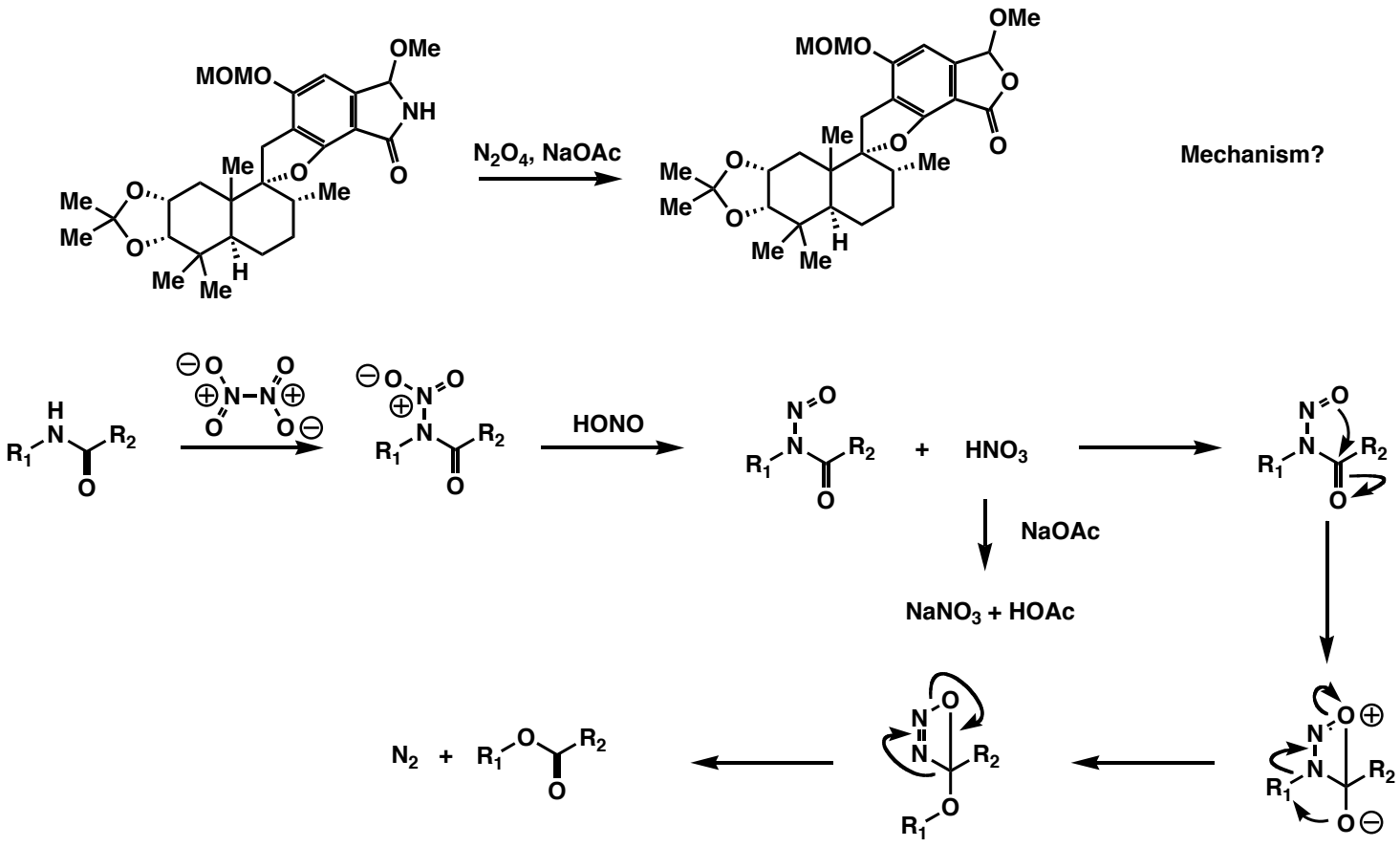

E. J. Corey, J, Das. 5551.

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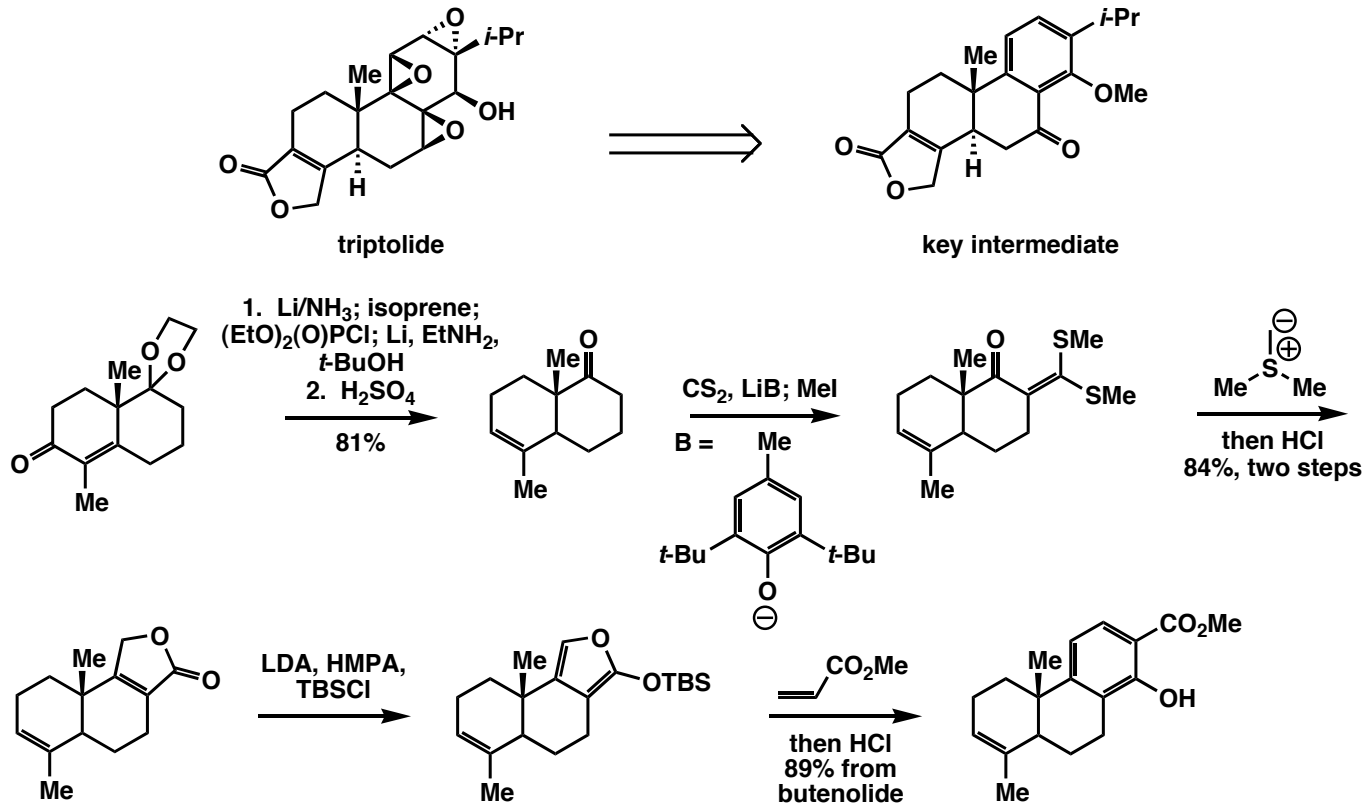

L. C. Grover, E. E. van Tamelen. 867.

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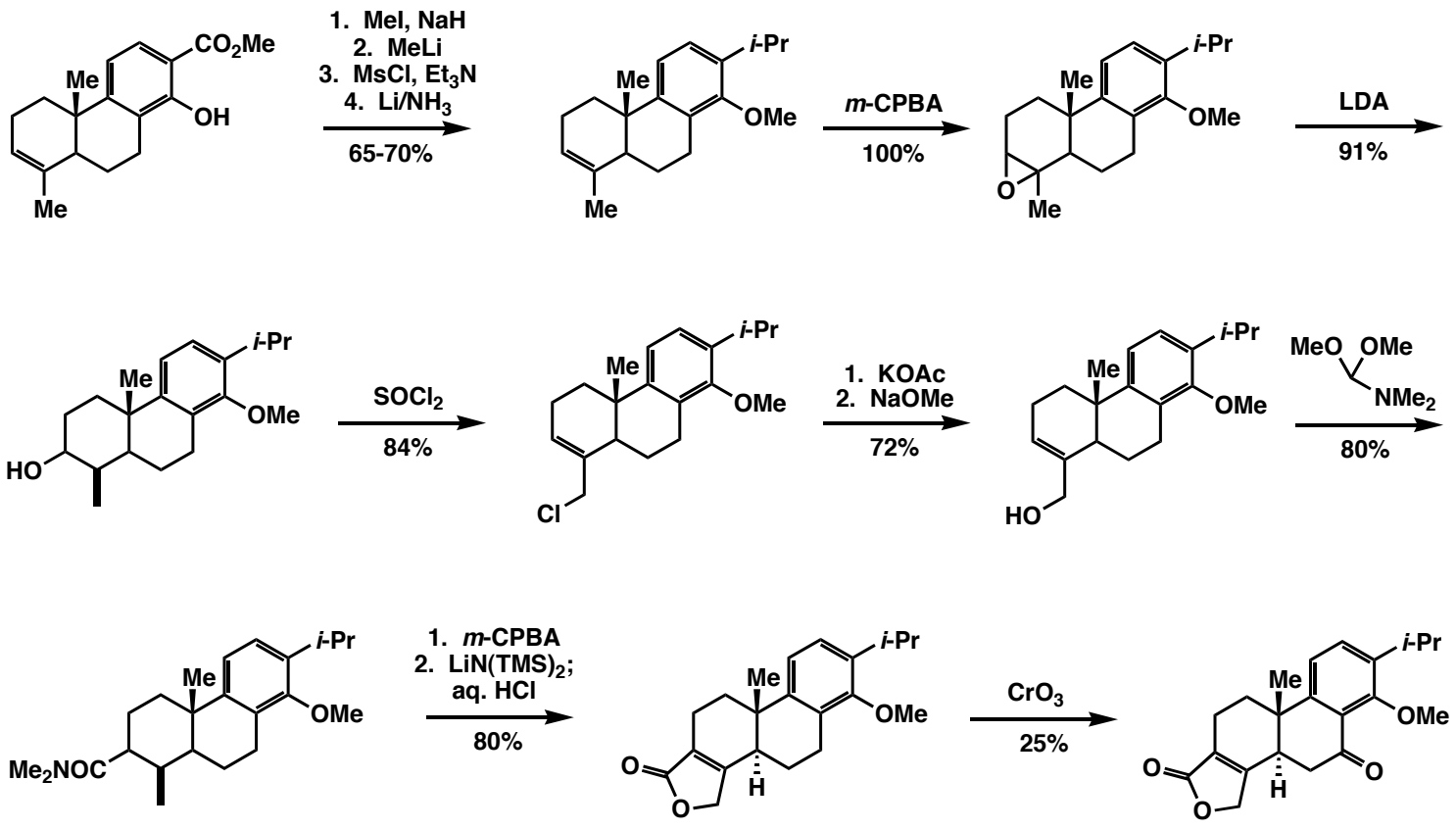

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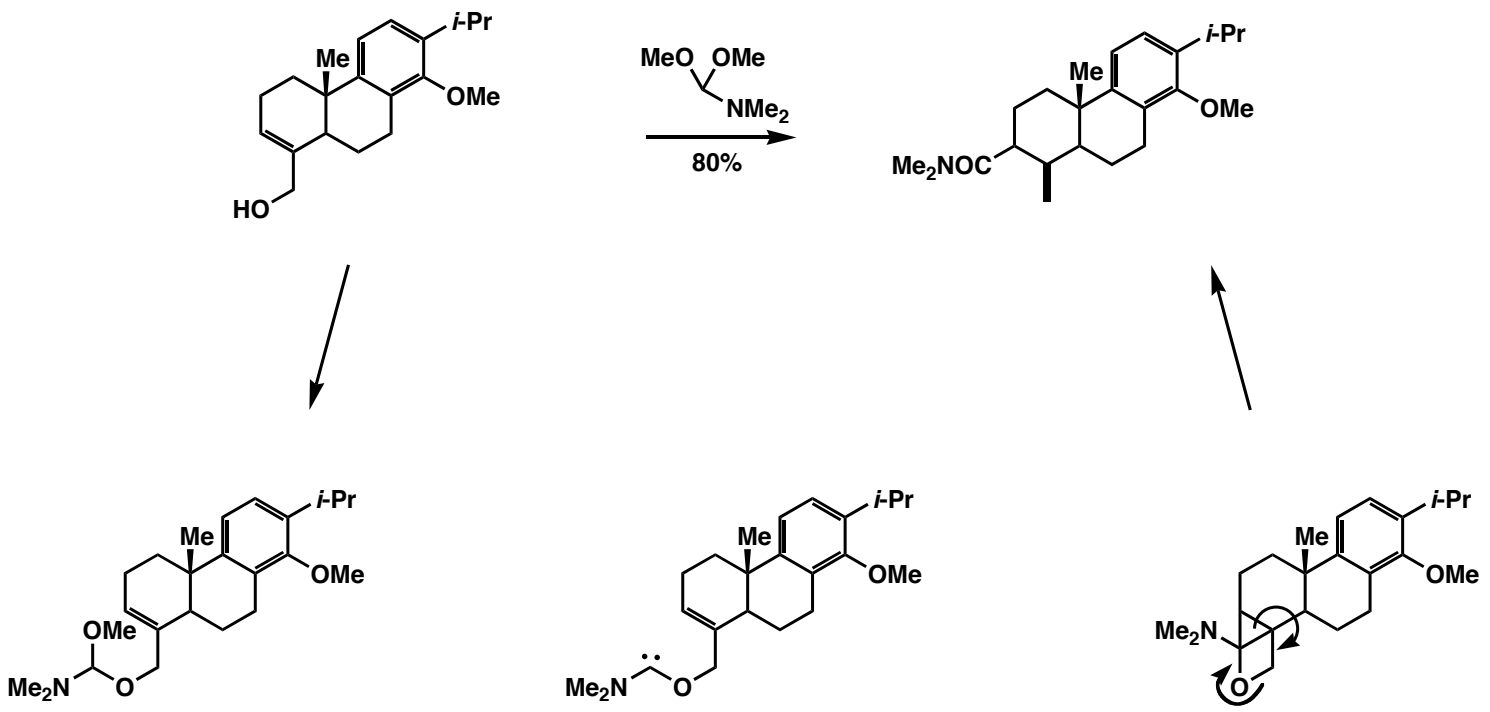

L. C. Grover, E. E. van Tamelen. 867.

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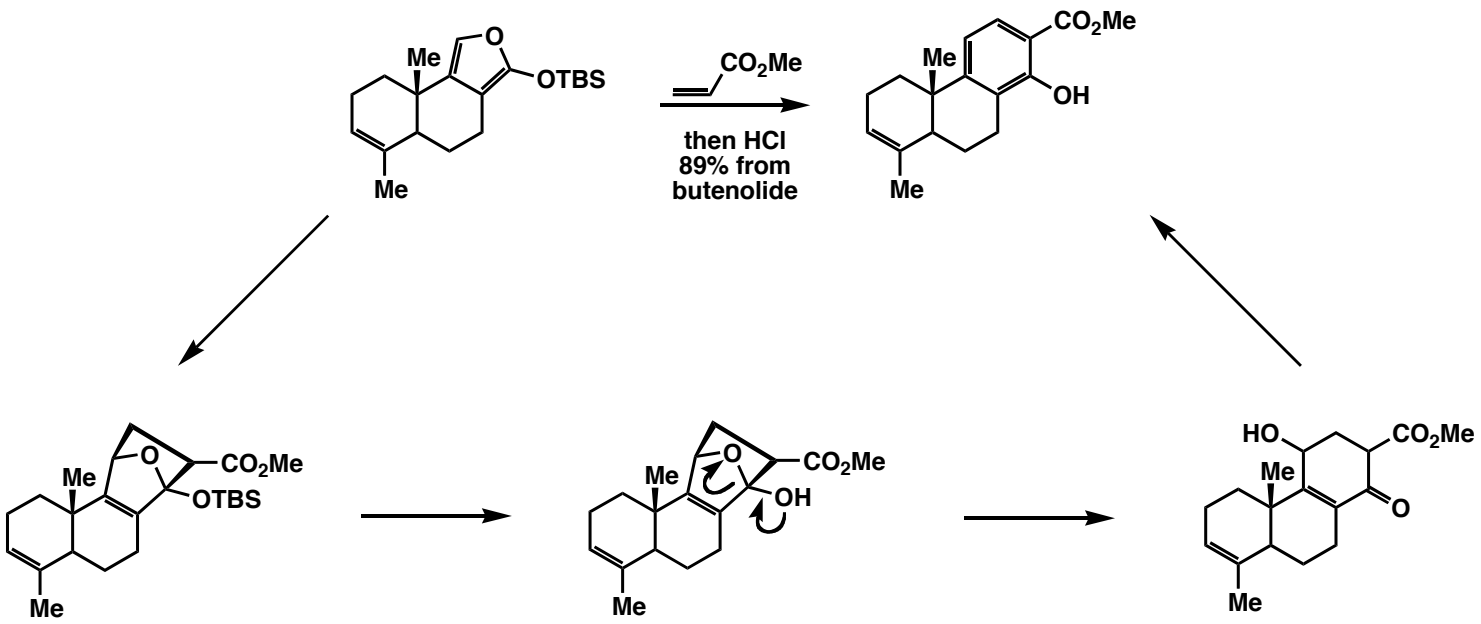

L. C. Grover, E. E. van Tamelen. 867.

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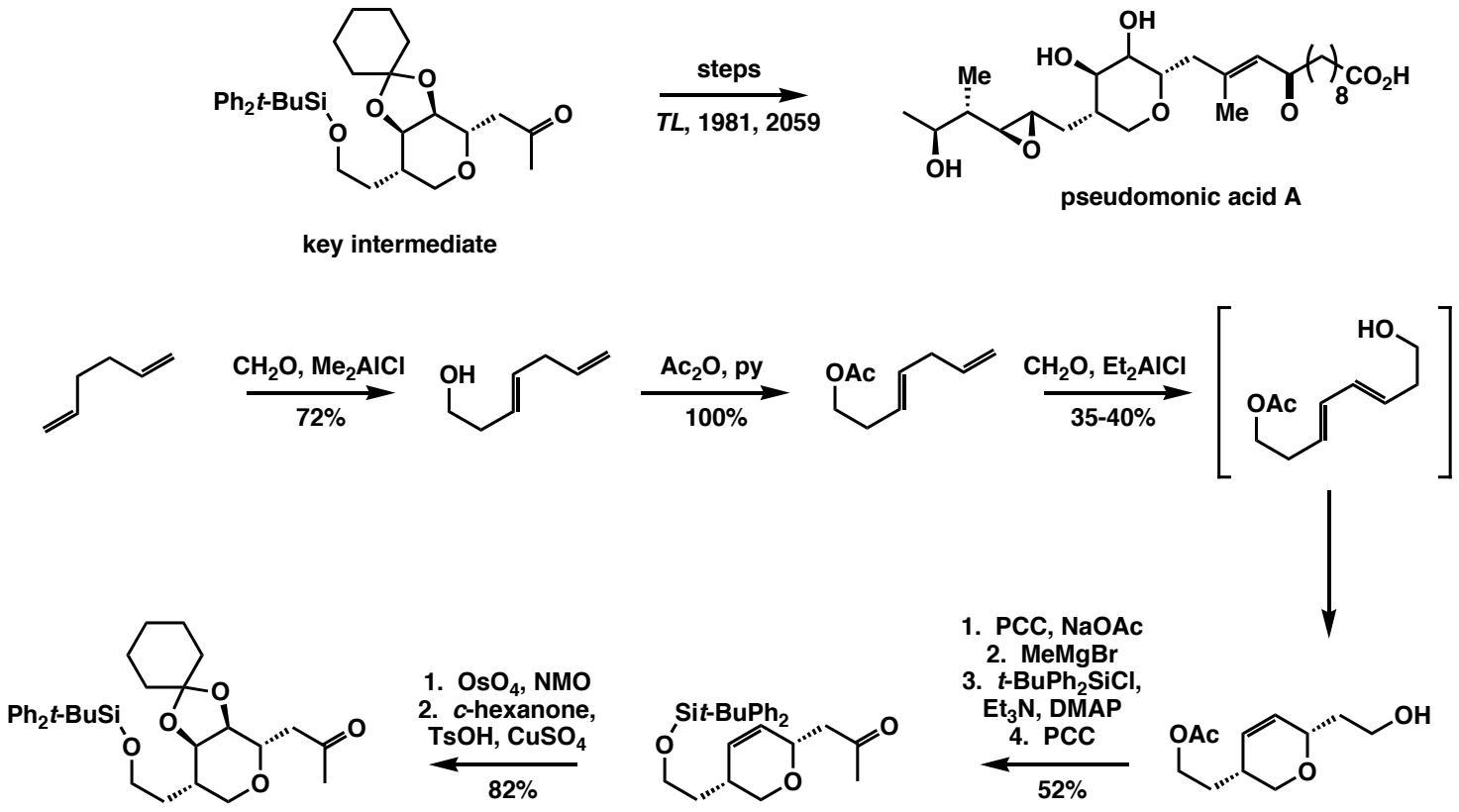
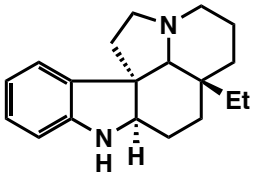
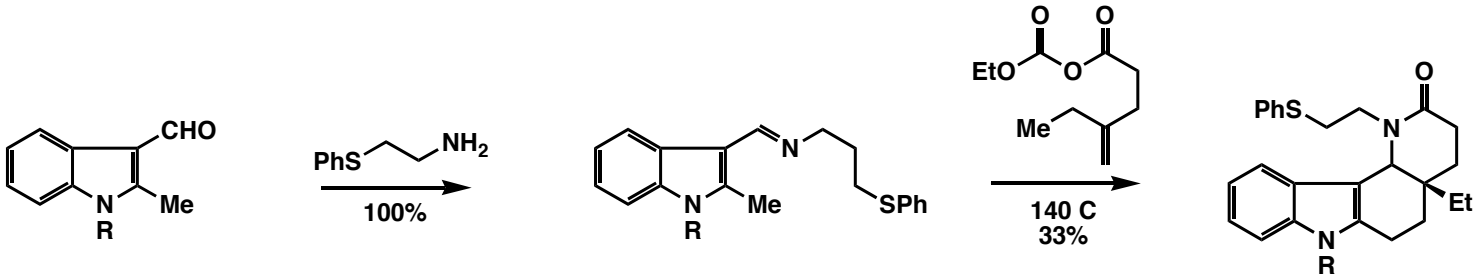


B. B. Snider, G. B. Phillips. 1113.

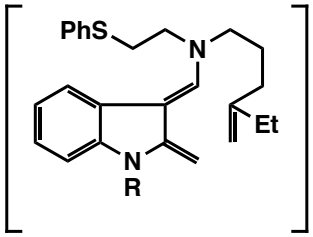
Total Syntheses



dl-aspidospermidine

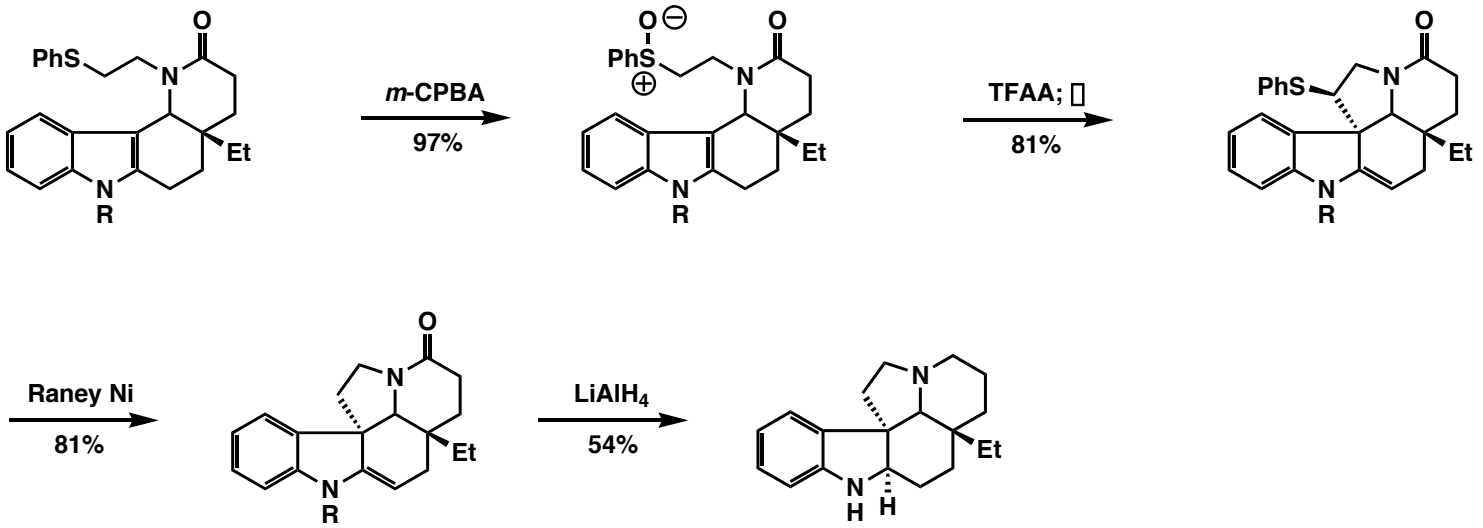


R= $MeOC_6H_4SO_2$



T. Gallager, P. Magnus, J. C. Huffman. 1140.

Total Syntheses



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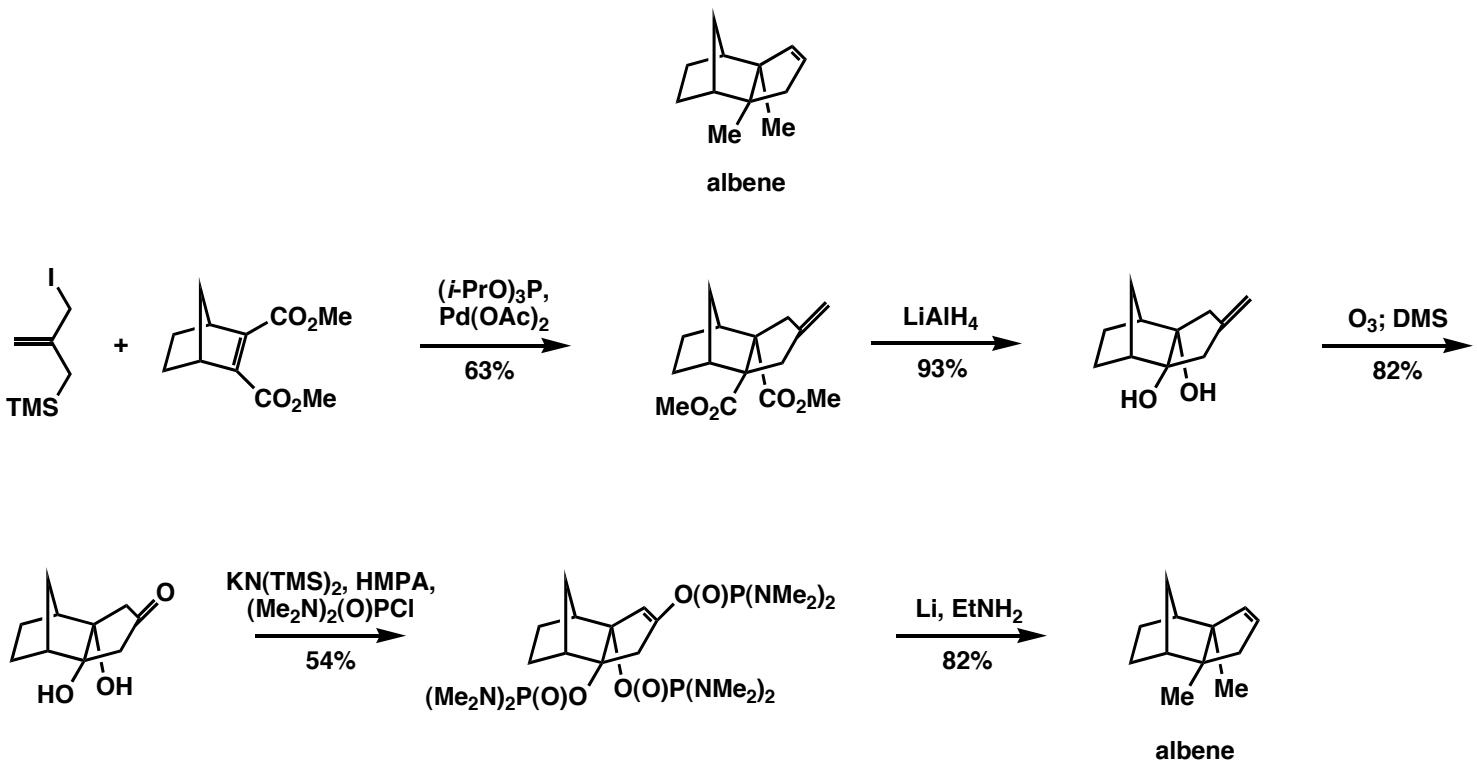
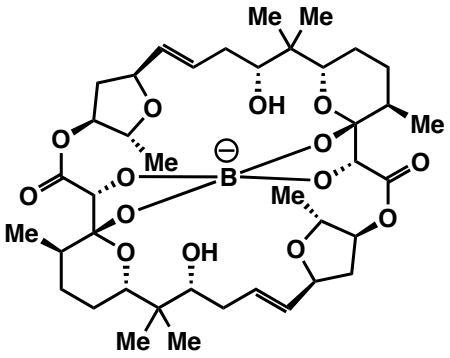
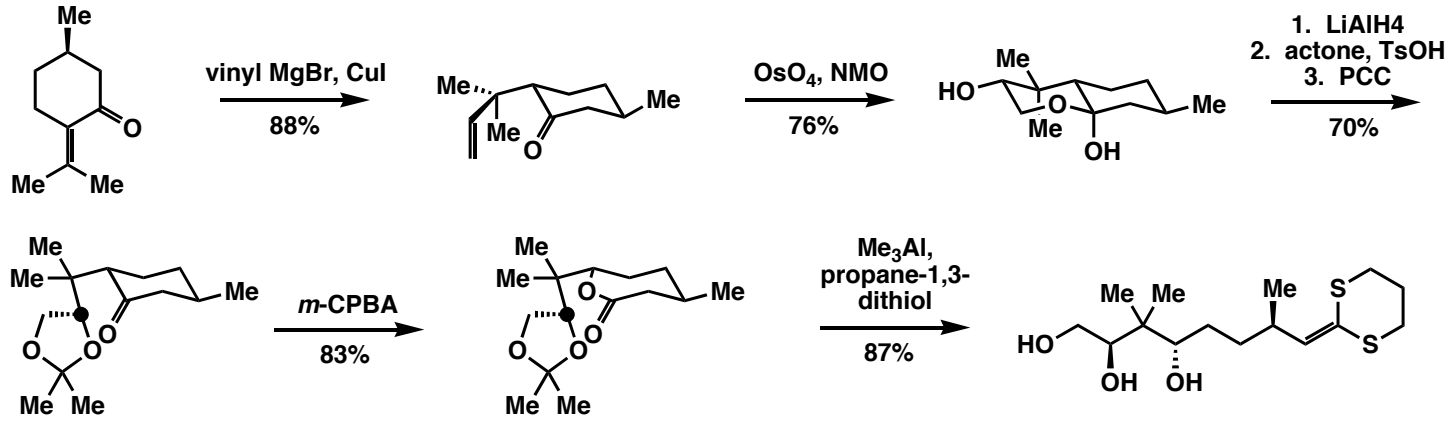


B. M. Trost, P. Renaut. 6668.

Total Syntheses

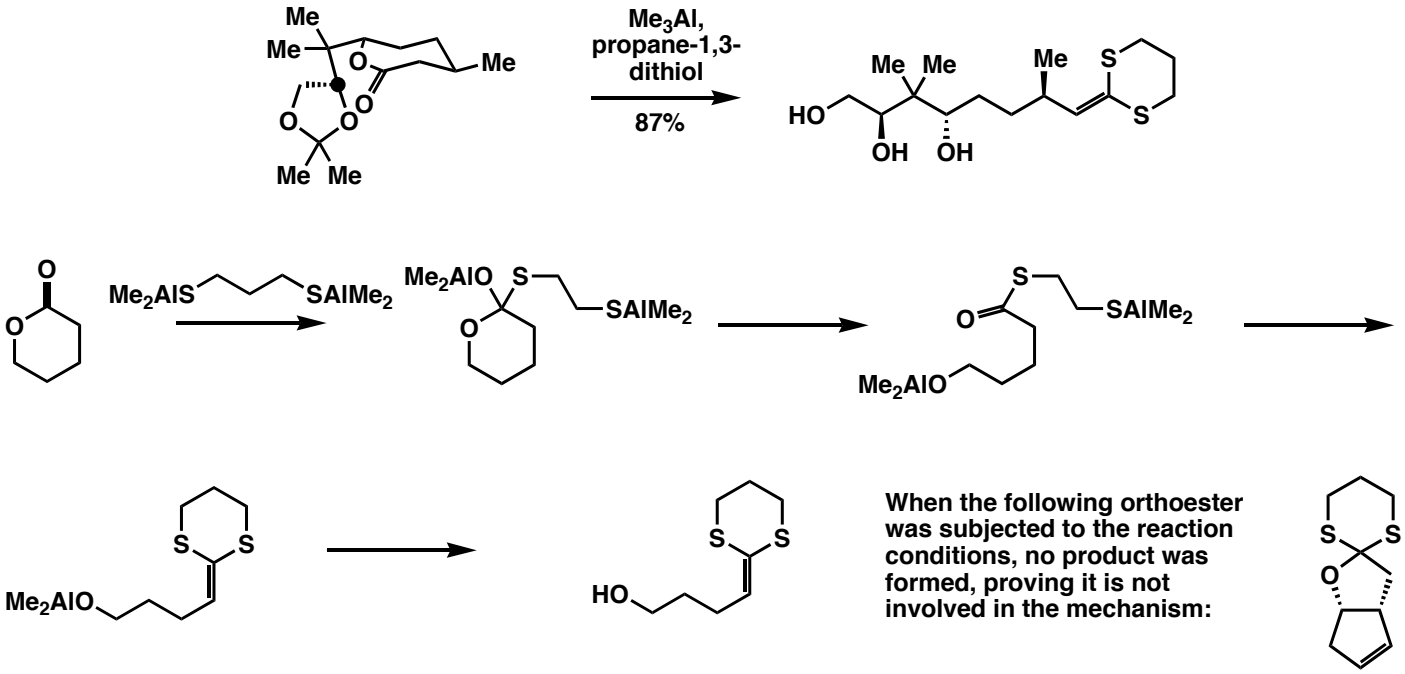


aplasmomycin



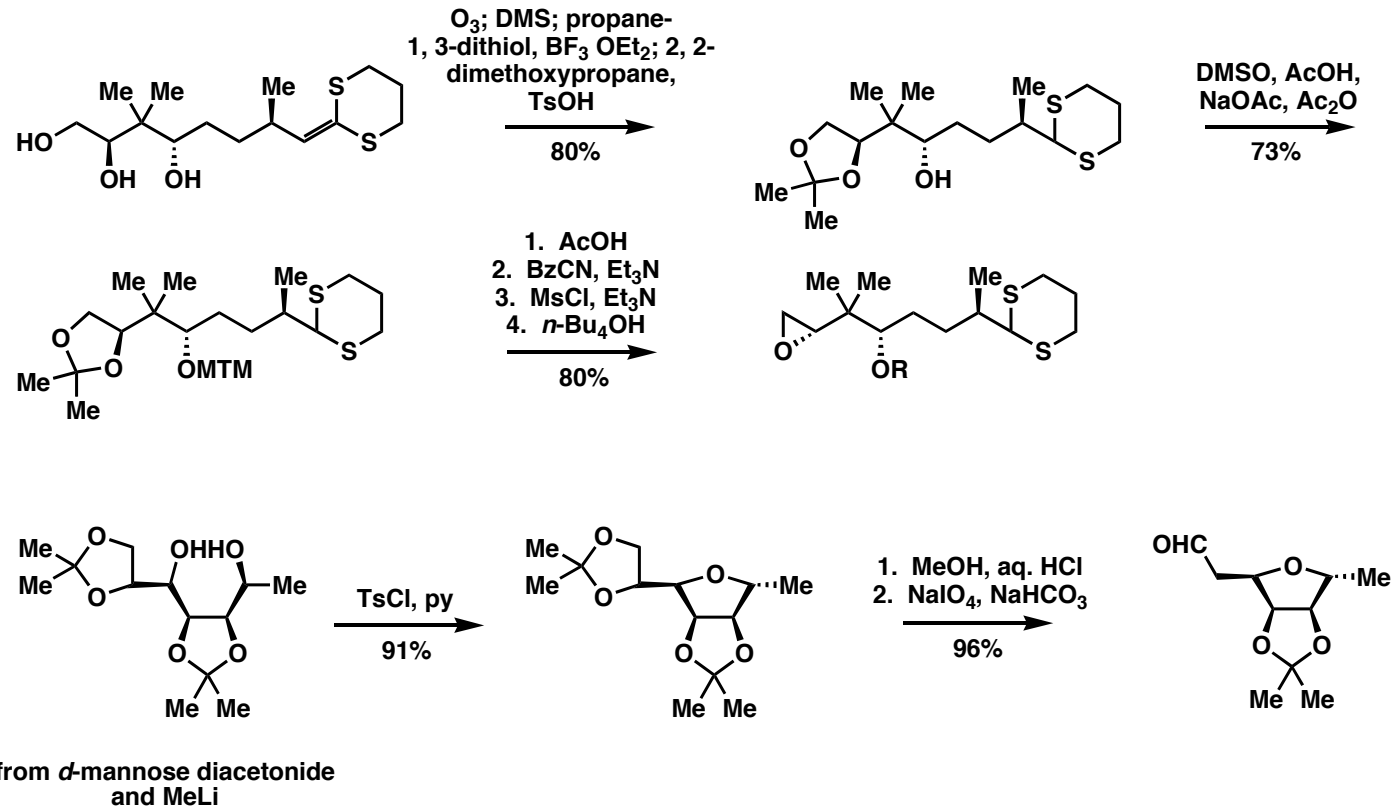
E. J. Corey, B. C. Pan, D. H. Hua, D. R. Deardorff. 6816.

Total Syntheses



E. J. Corey, B. C. Pan, D. H. Hua, D. R. Deardorff. 6816.

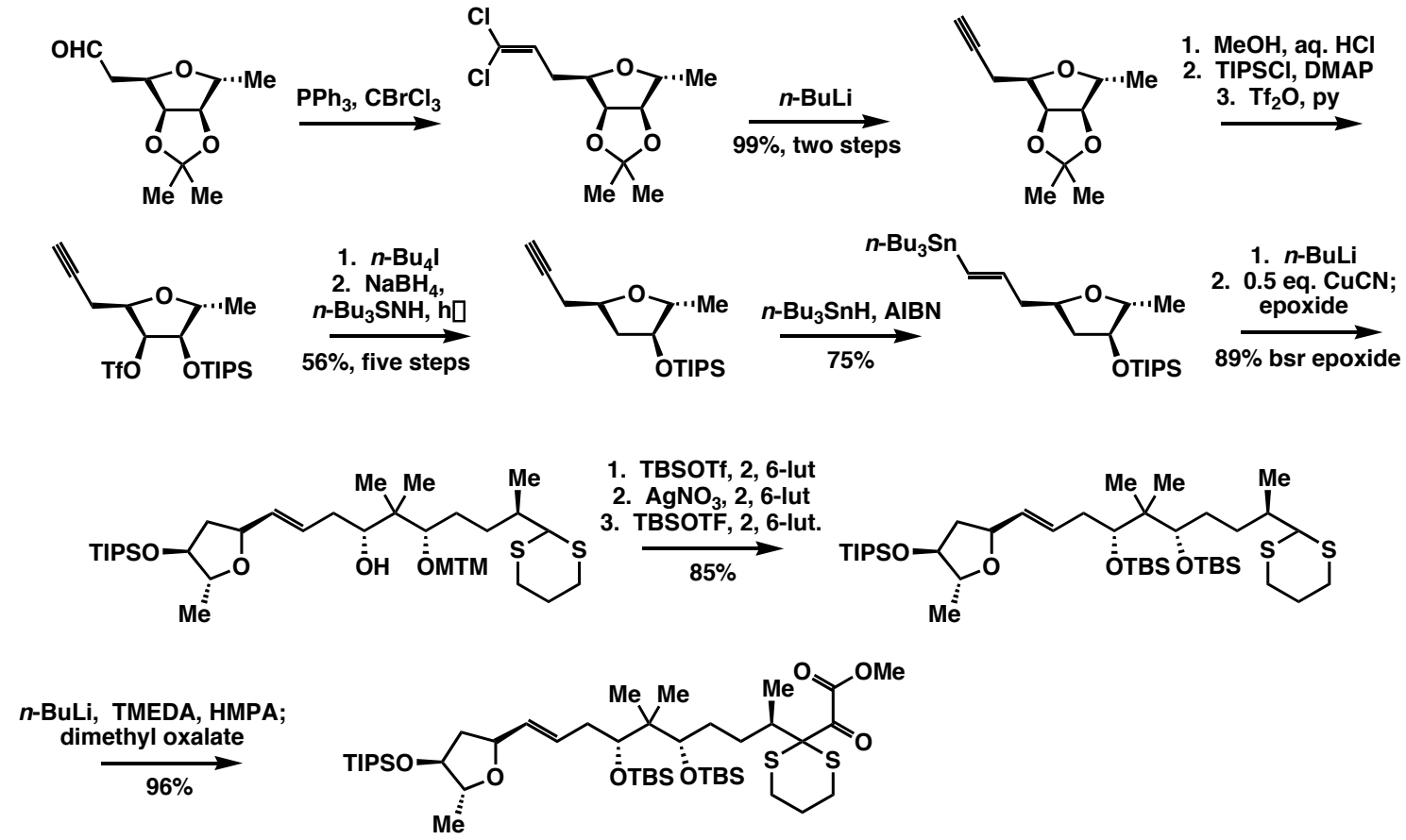
Total Syntheses



from *d*-mannose diacetonide and MeLi

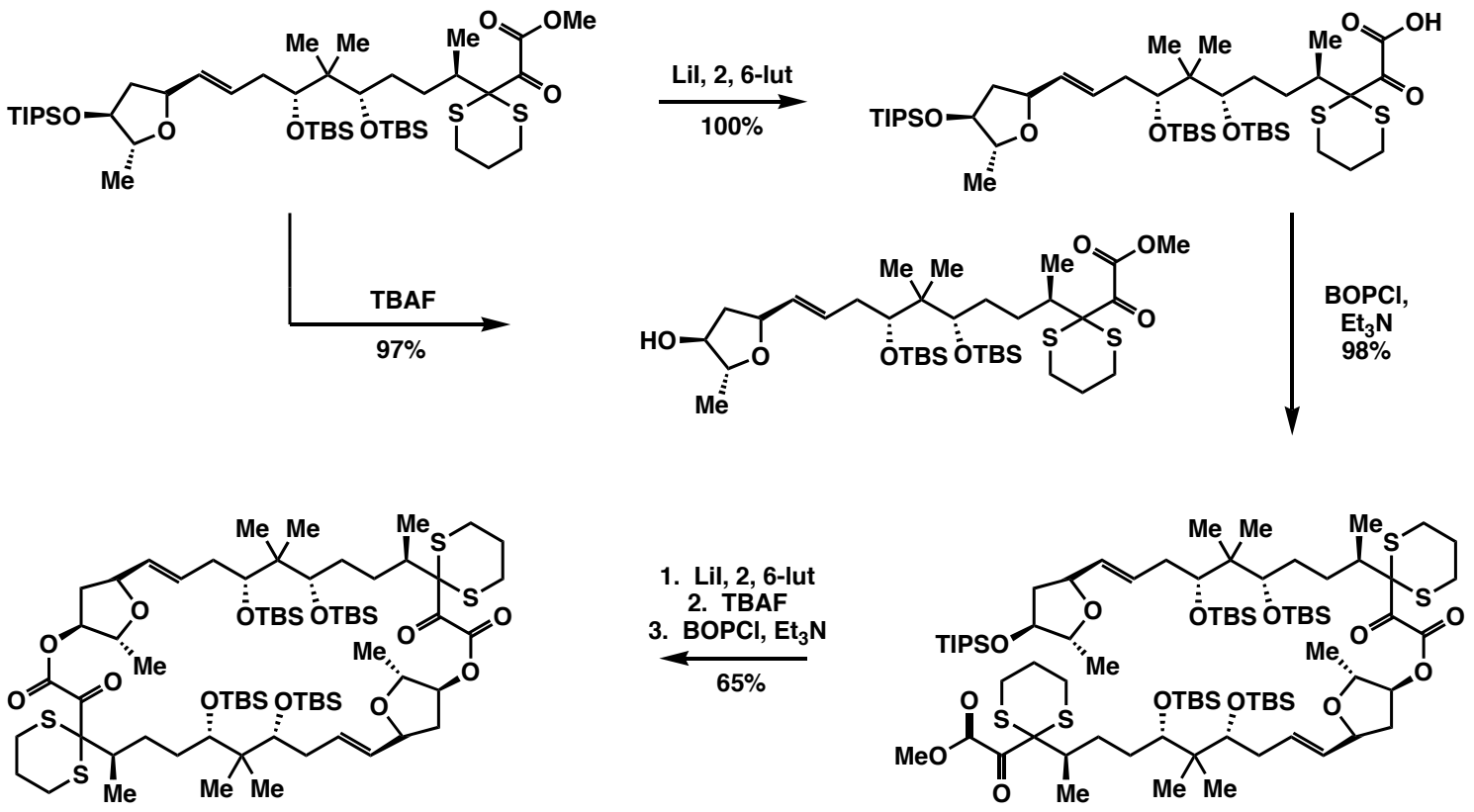
E. J. Corey, B. C. Pan, D. H. Hua, D. R. Deardorff. 6816.

Total Syntheses



E. J. Corey, B. C. Pan, D. H. Hua, D. R. Deardorff. 6816. E. J. Corey, D. H. Hua, B. C. Pan, S. P. Seitz. 6818.

Total Syntheses



E. J. Corey, D. H. Hua, B. C. Pan, S. P. Seitz. 6818.

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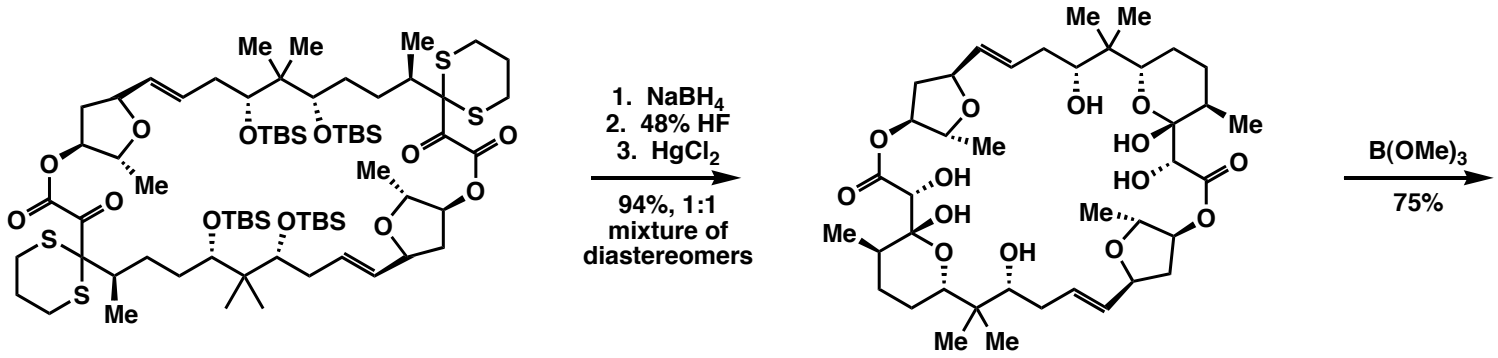

aplasmomycin

E. J. Corey, D. H. Hua, B. C. Pan, S. P. Seitz. 6818.