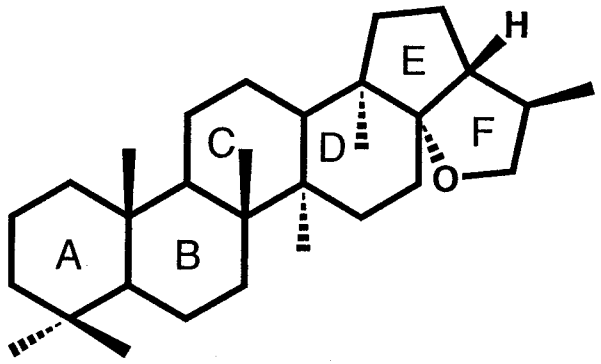
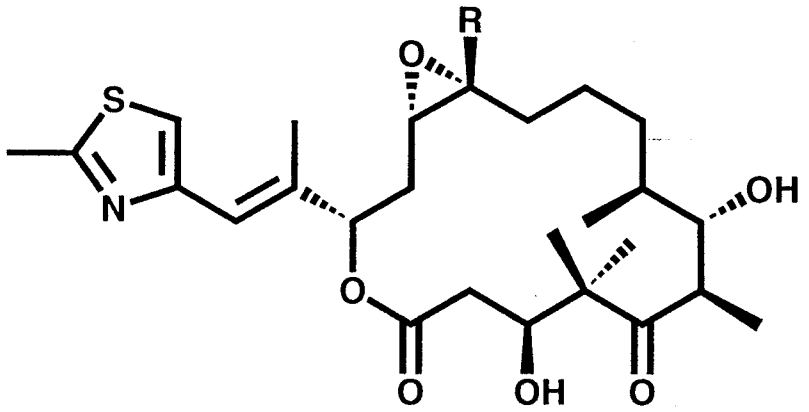
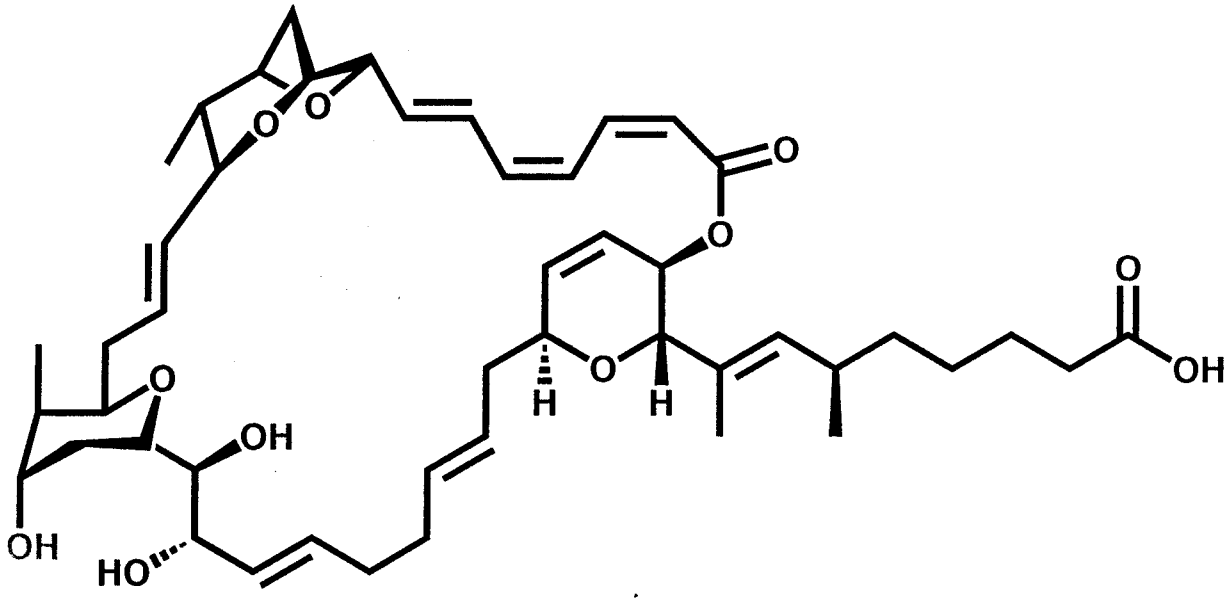
Biologically Active Natural Products from Different Sources:



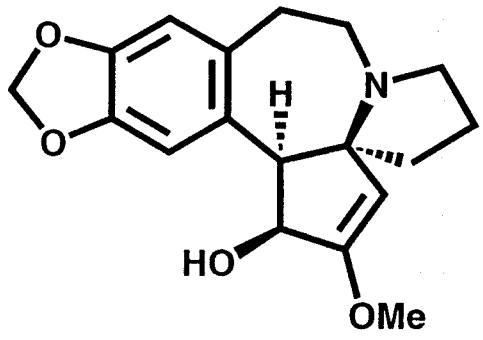
Hopane Oxide



Epothilone A: R = H
Epothilone B: R = Me

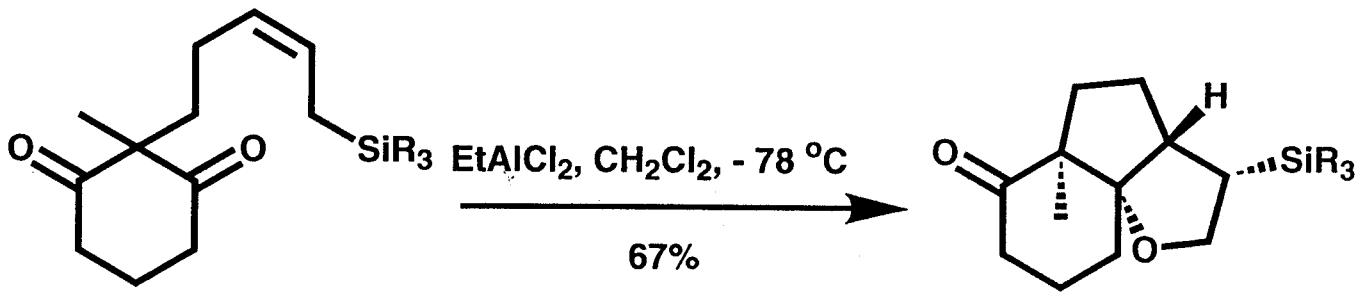


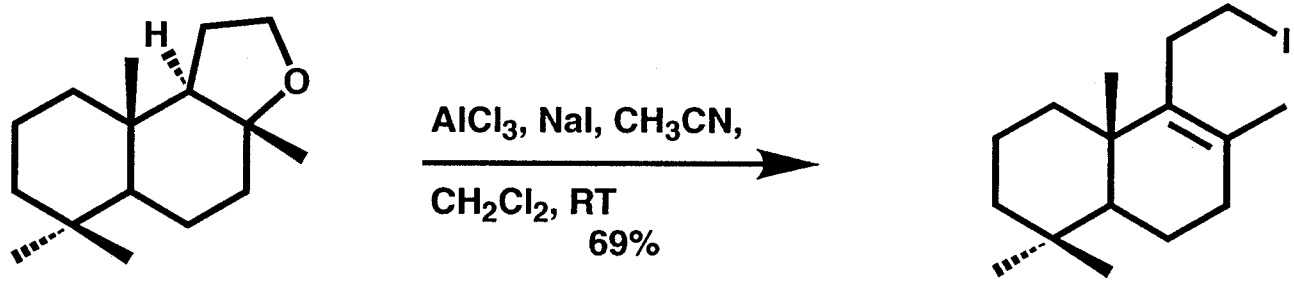
Sorangicin A



Cephalotaxine

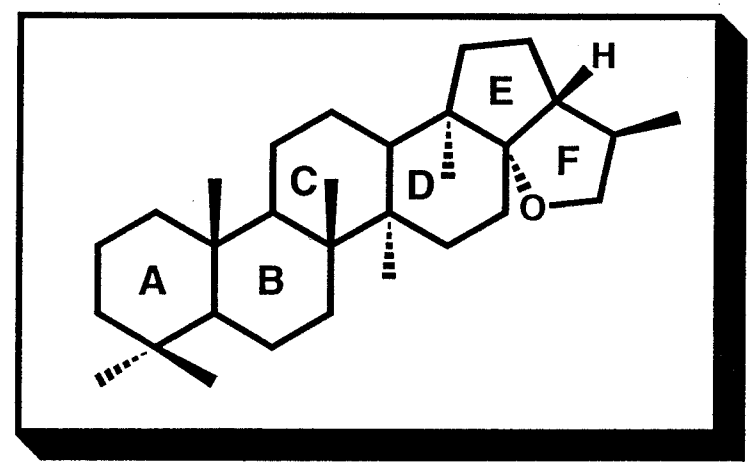
Syntheses of the AB- and DEF-Fragments of Hopanes:



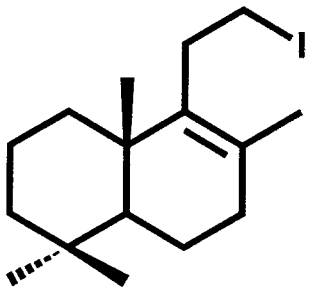


(-)-Ambroxide

$R_3 = Ph_2t\text{-}Bu$

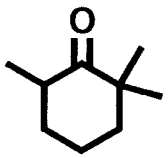


Model Study for Final Ring Closure:

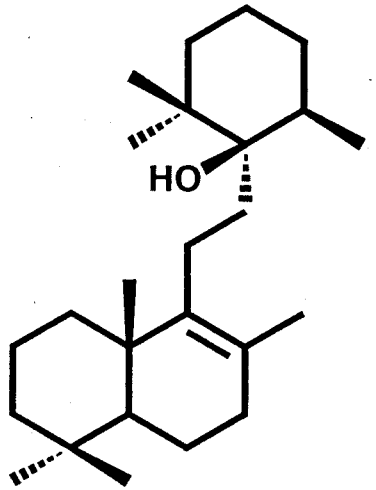


1. *t*-BuLi, Et_2O, 20 min

2.



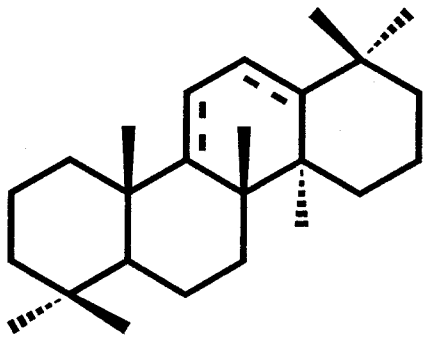
64%

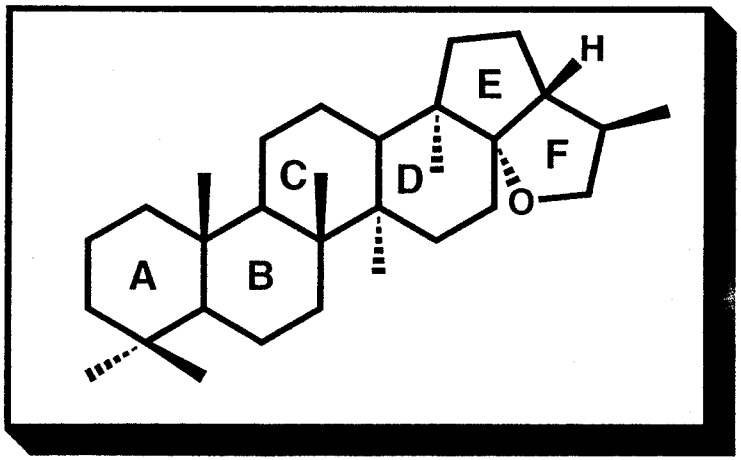


1 : 1 Mixture

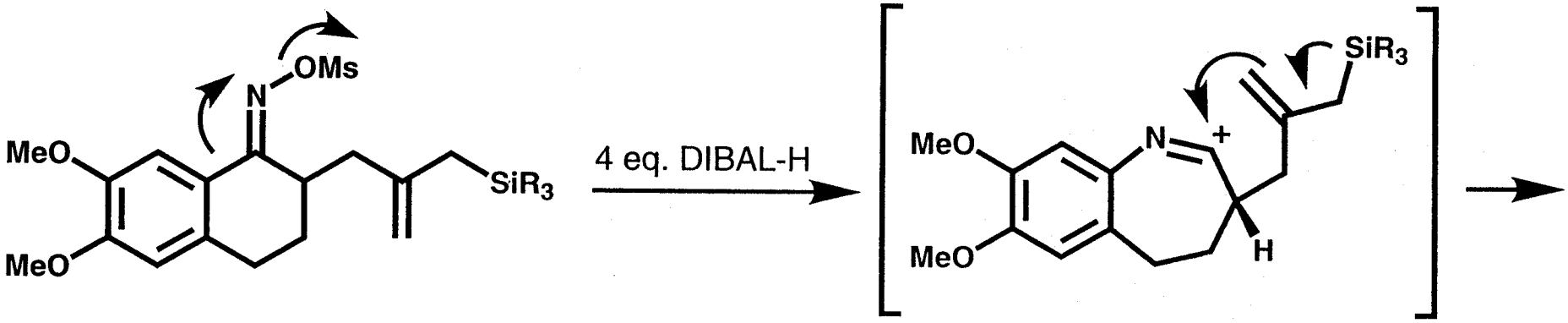
$SnCl_4$, CH_2Cl_2, - 78 °C

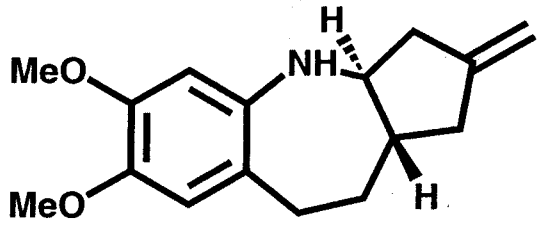
50%



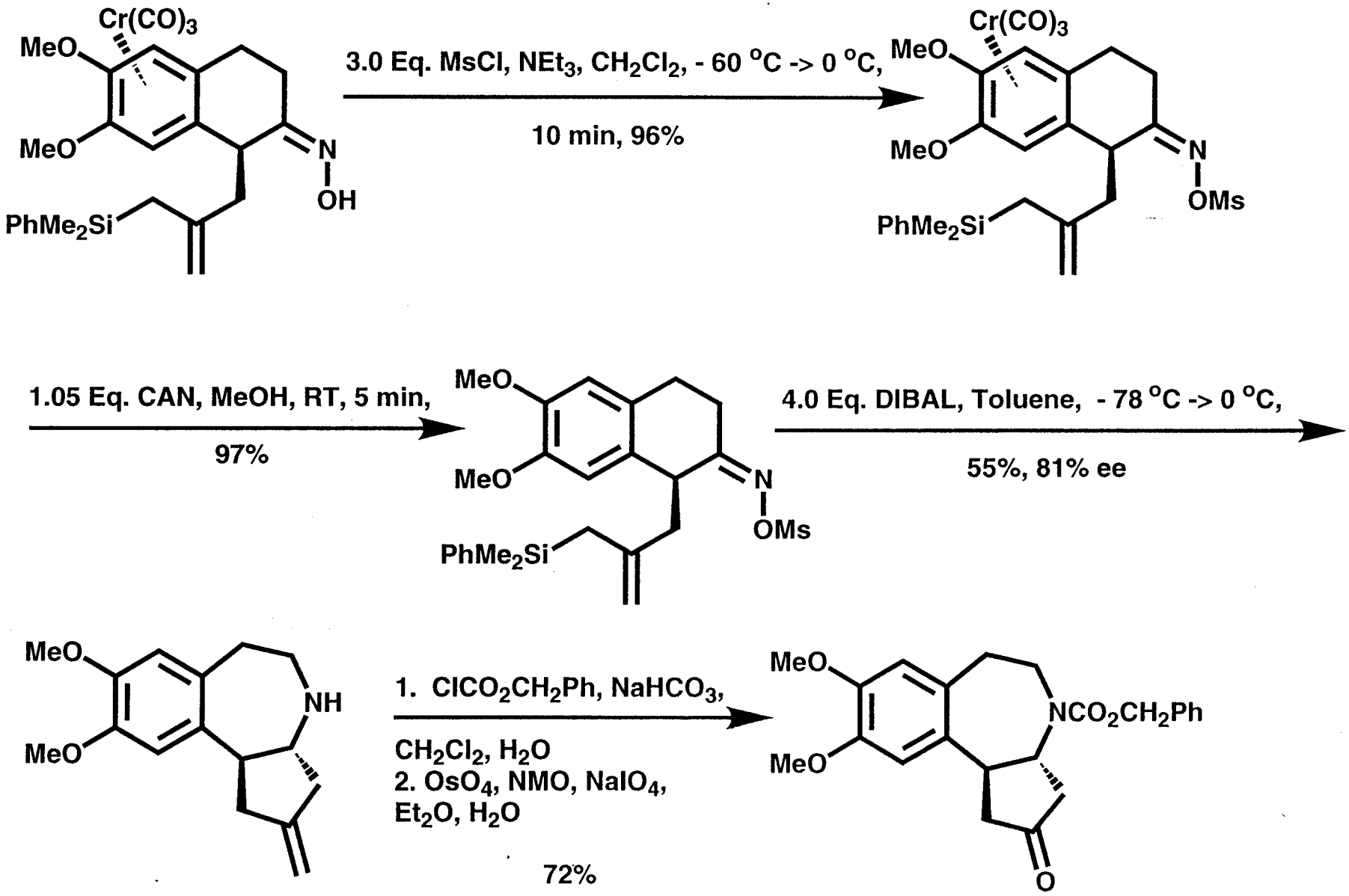


Proposed Mechanism for the Beckmann Rearrangement/Allylsilane Cyclization:

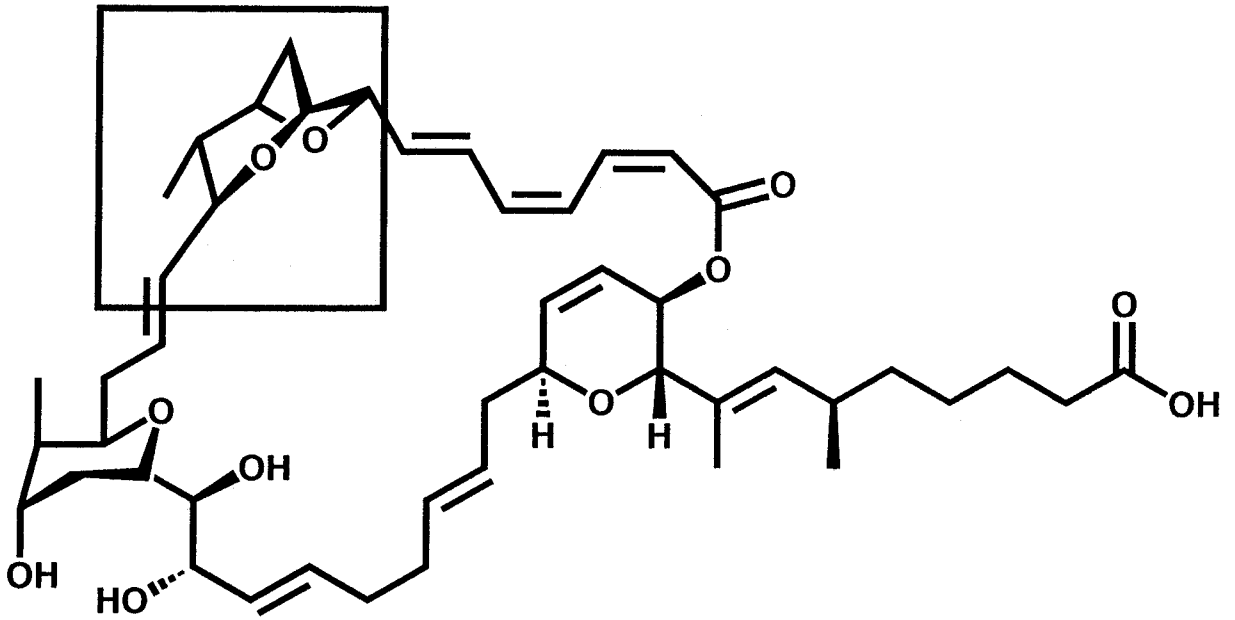




Asymmetric Synthesis of the Cephalotaxine Framework:

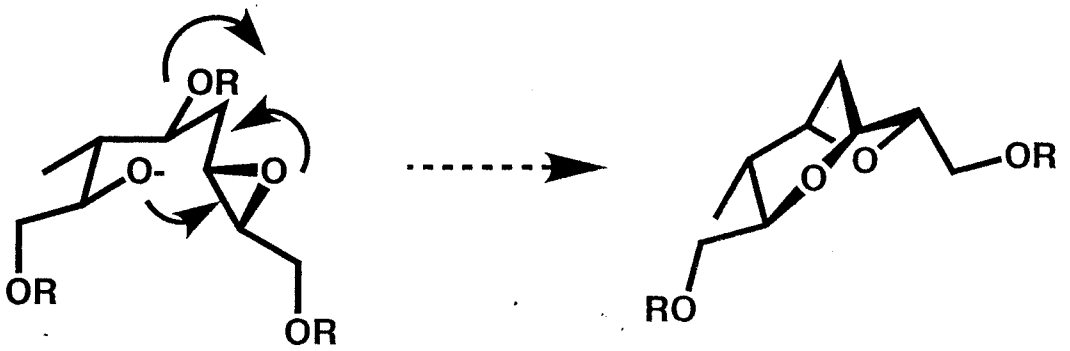


Total Synthesis of Sorangicin A: Approach to the Bicyclic Ether

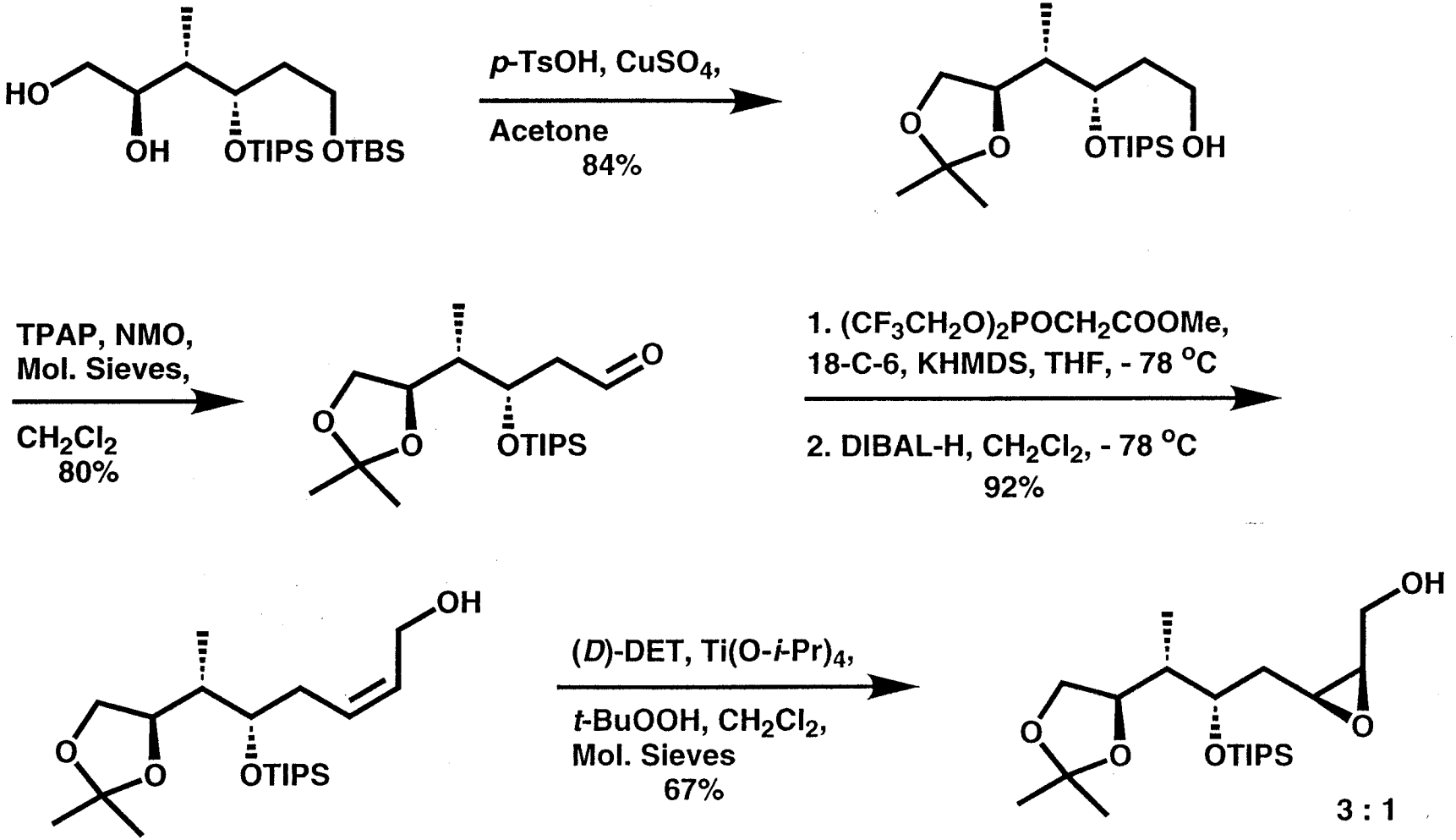


Sorangicin A

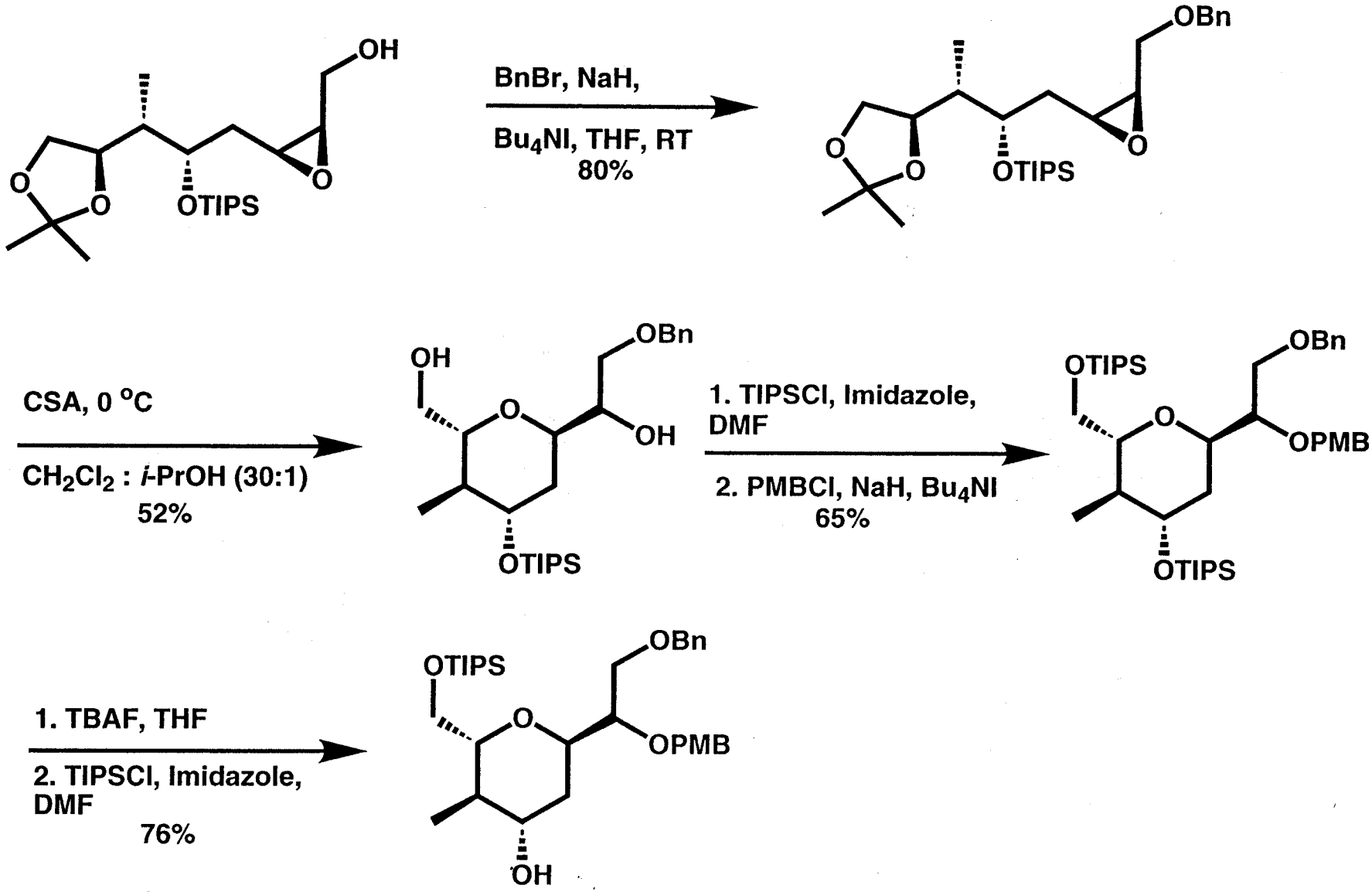
Tandem Fashion:



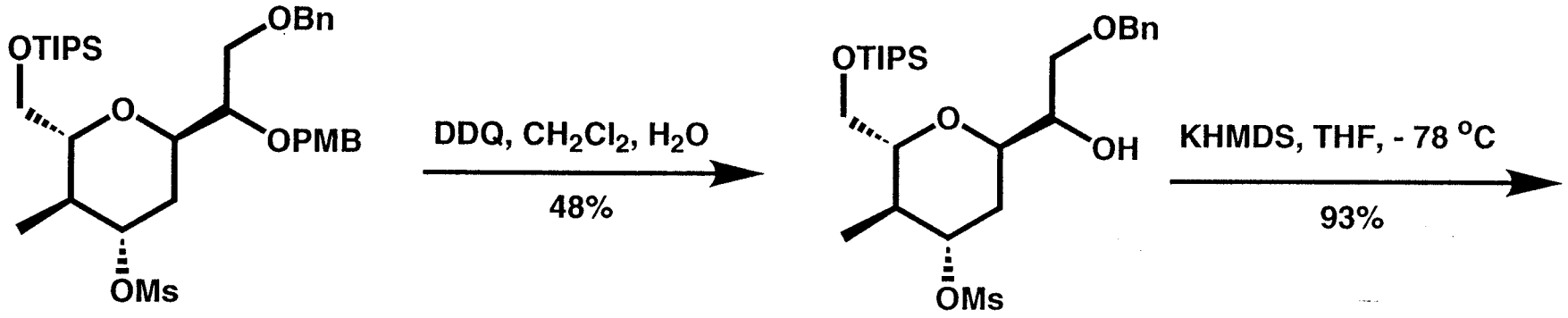
Total Synthesis of Sorangicin A: Approach to the Bicyclic Ether

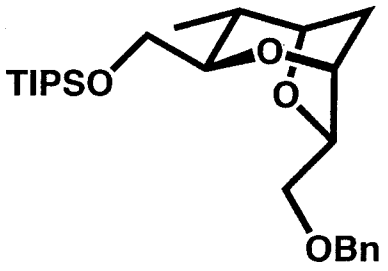


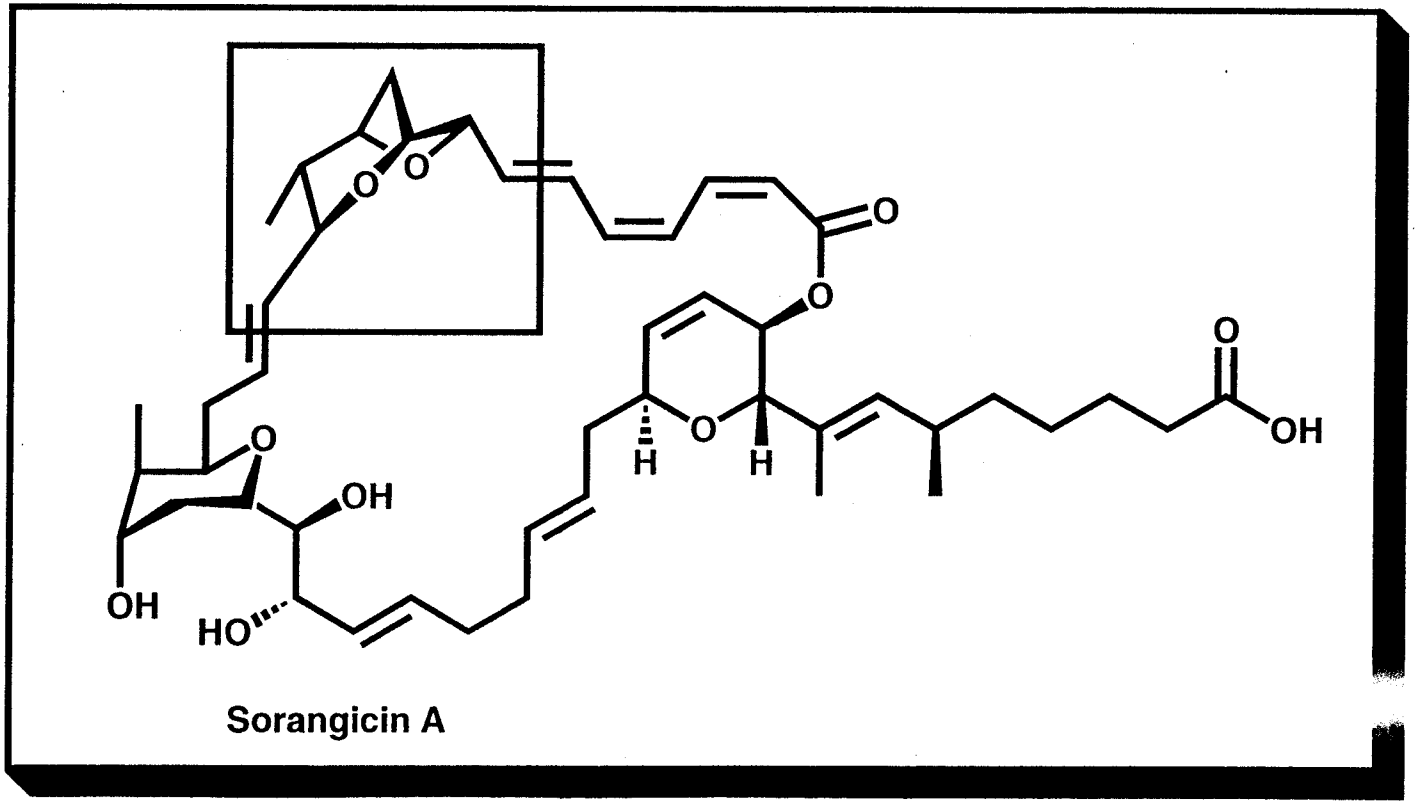
Total Synthesis of Sorangicin A: Approach to the Bicyclic Ether



Total Synthesis of Sorangicin A: Approach to the Bicyclic Ether

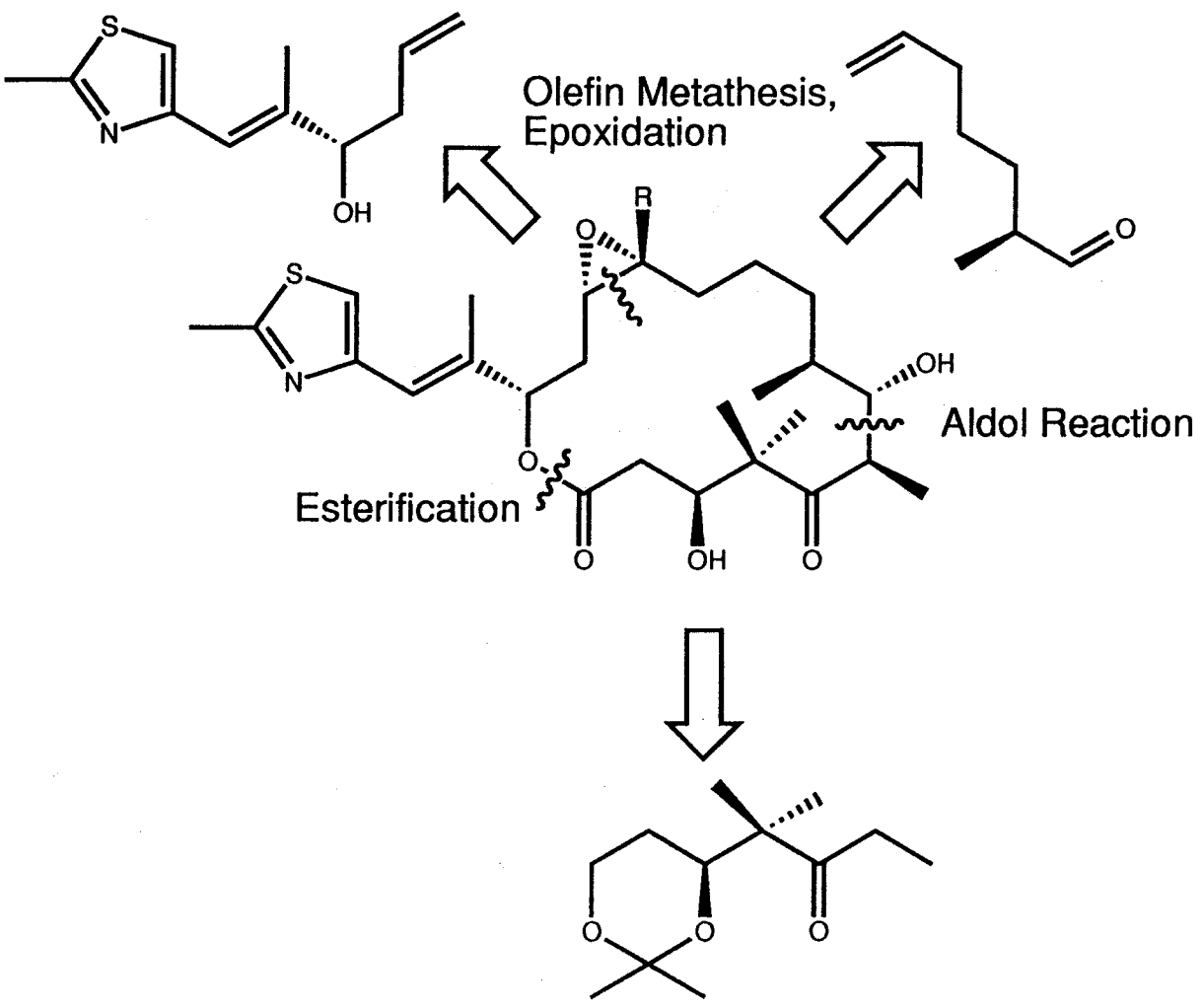




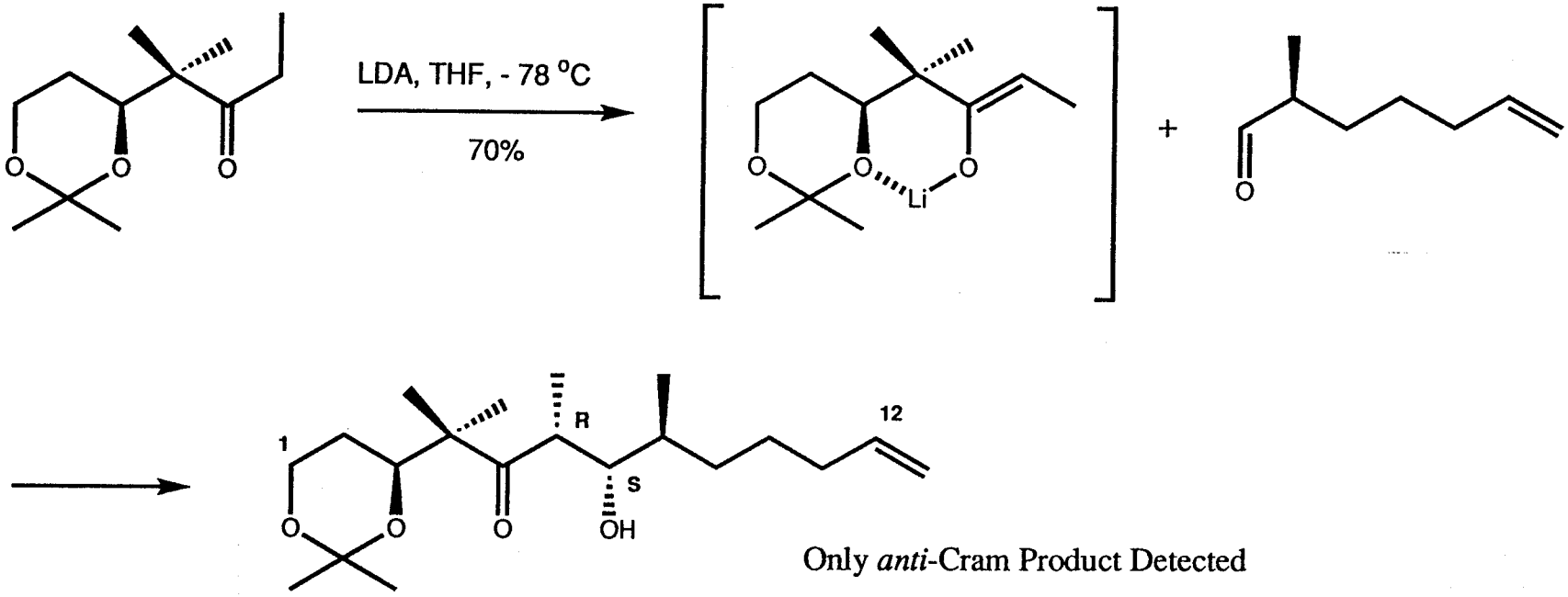


Sorangicin A

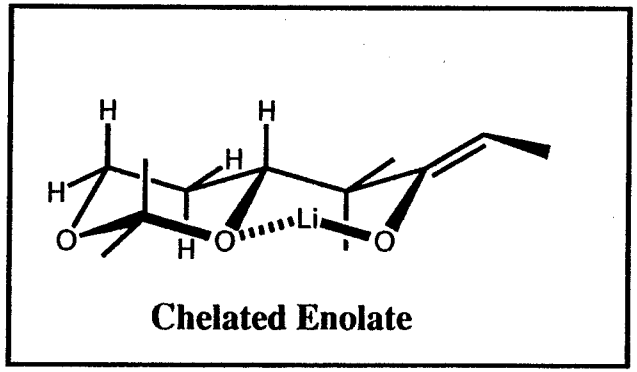
Strategy:


Olefin Metathesis,
Epoxidation
Aldol Reaction
Esterification

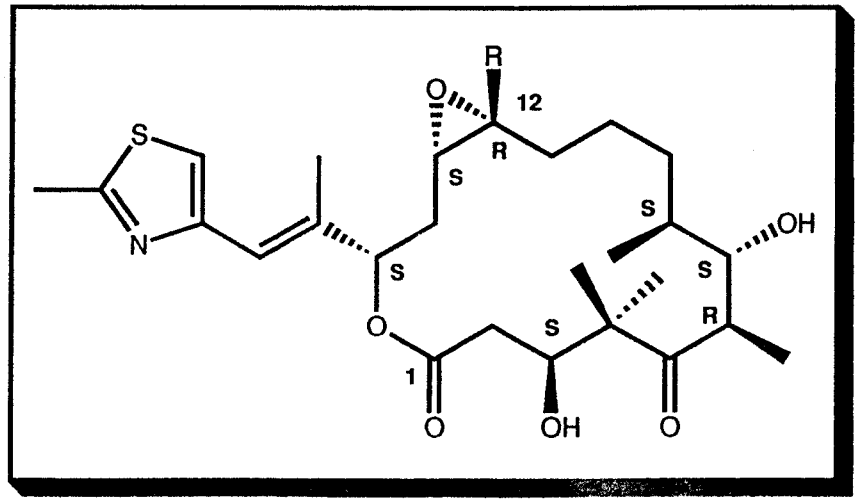
Synthesis of Subunit C1-C12 by Aldol Reaction:



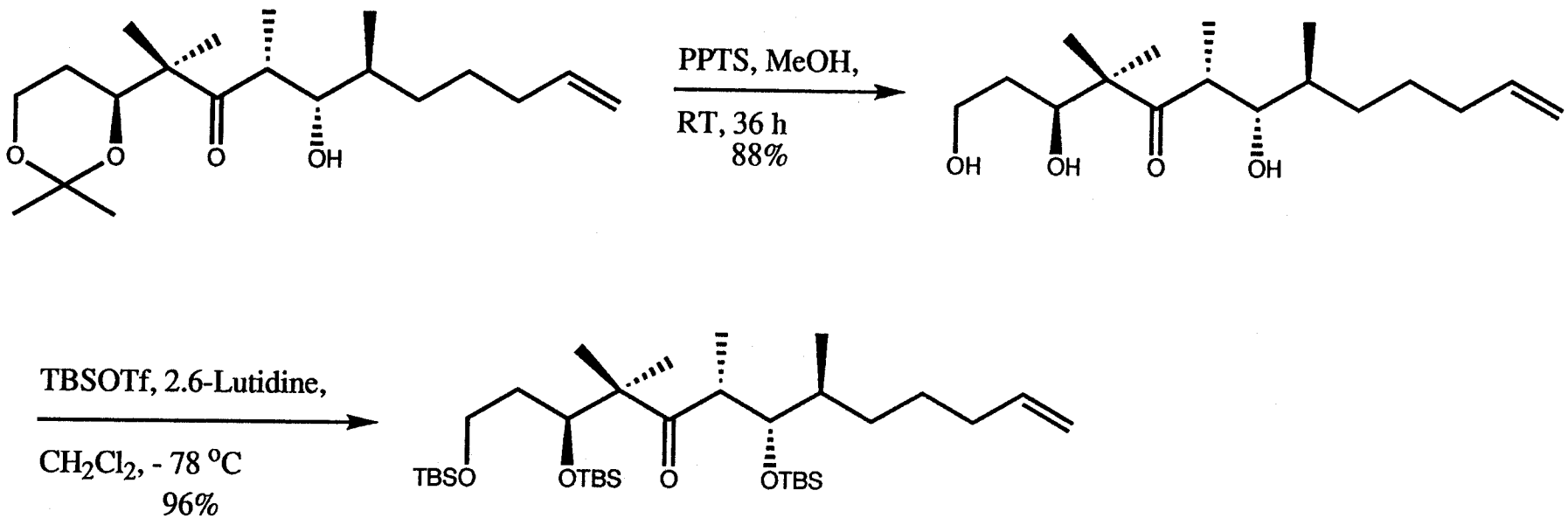
Only *anti*-Cram Product Detected

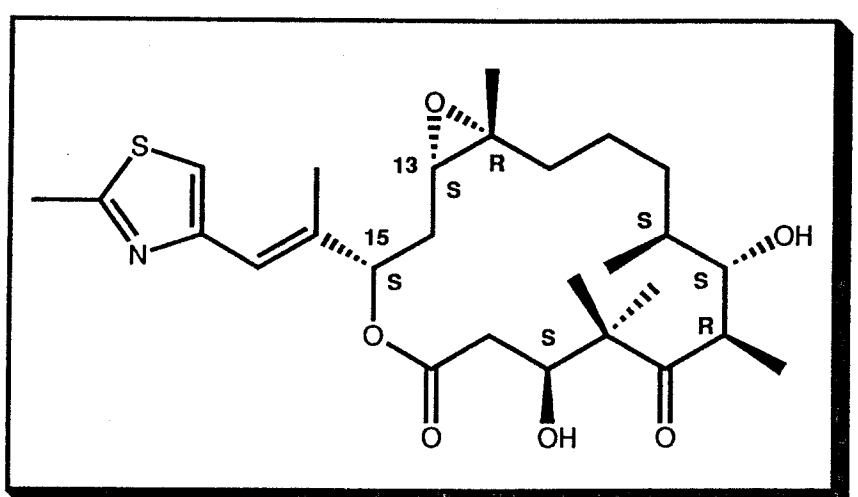


Chelated Enolate

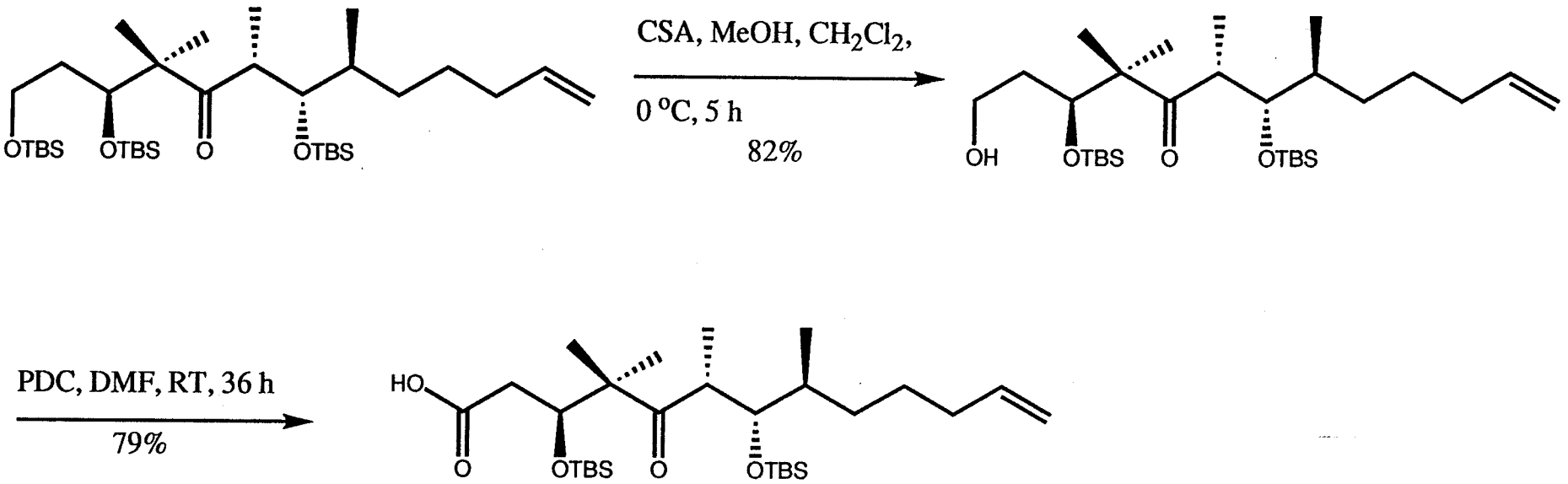


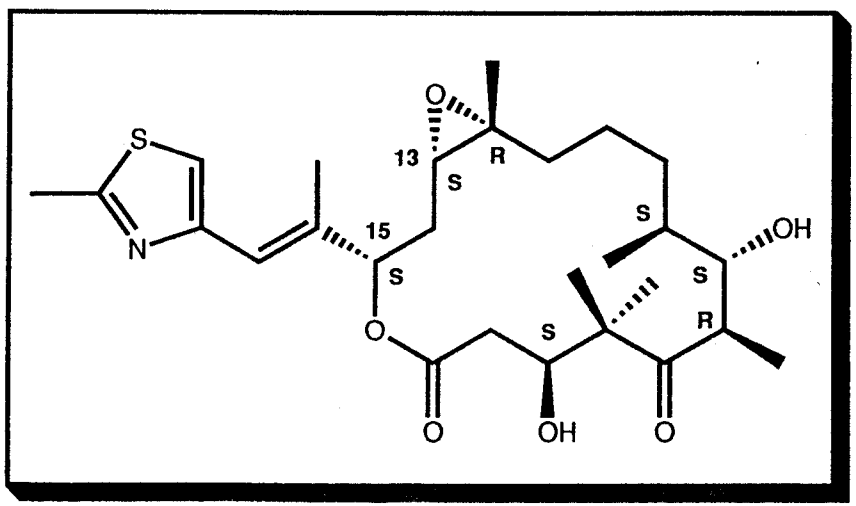
Transformation to Acid:



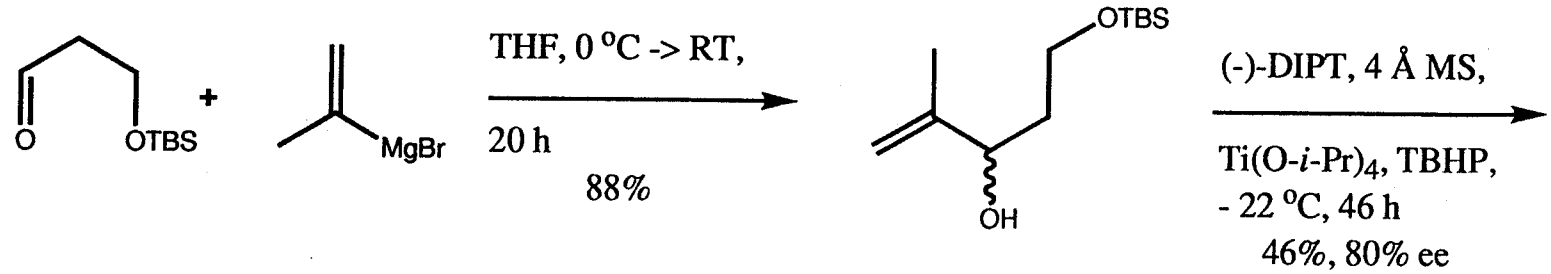


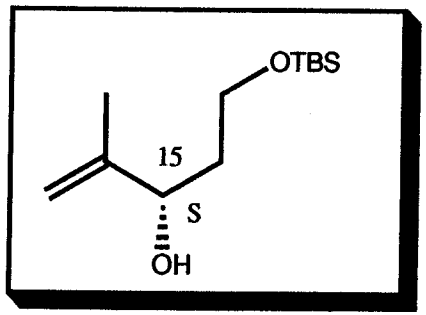
Transformation to Acid:

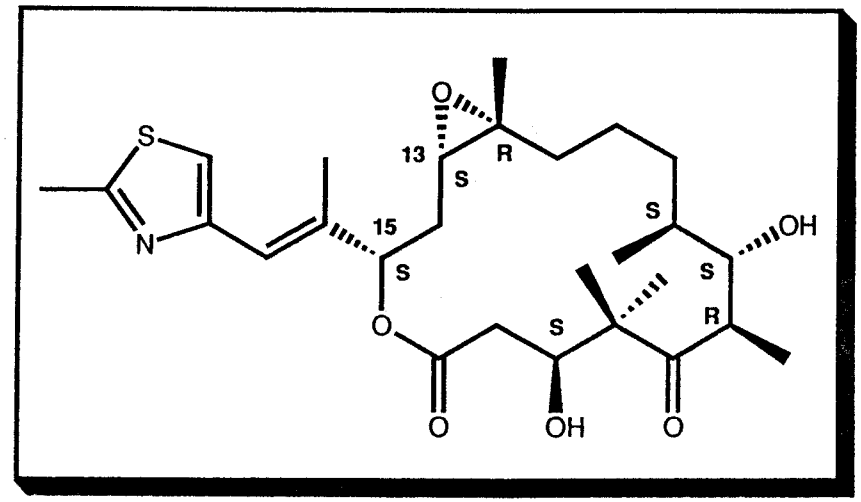




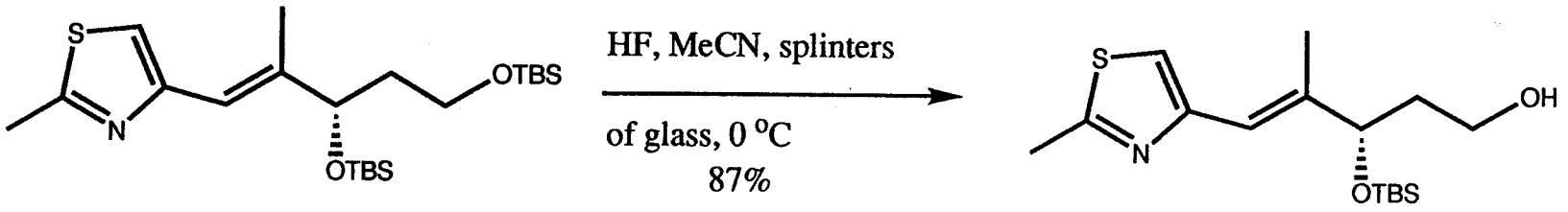
Sharpless Resolution:

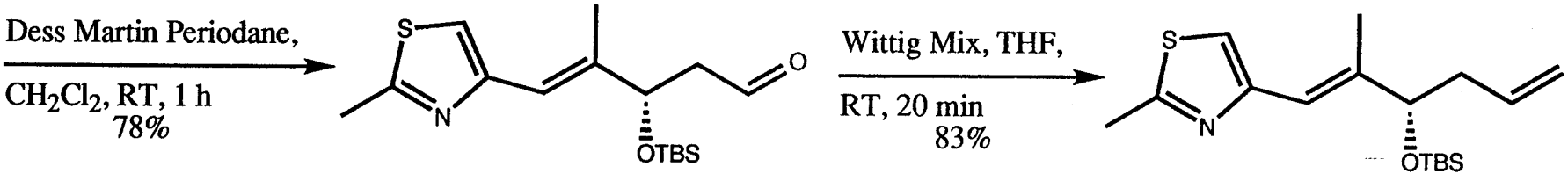


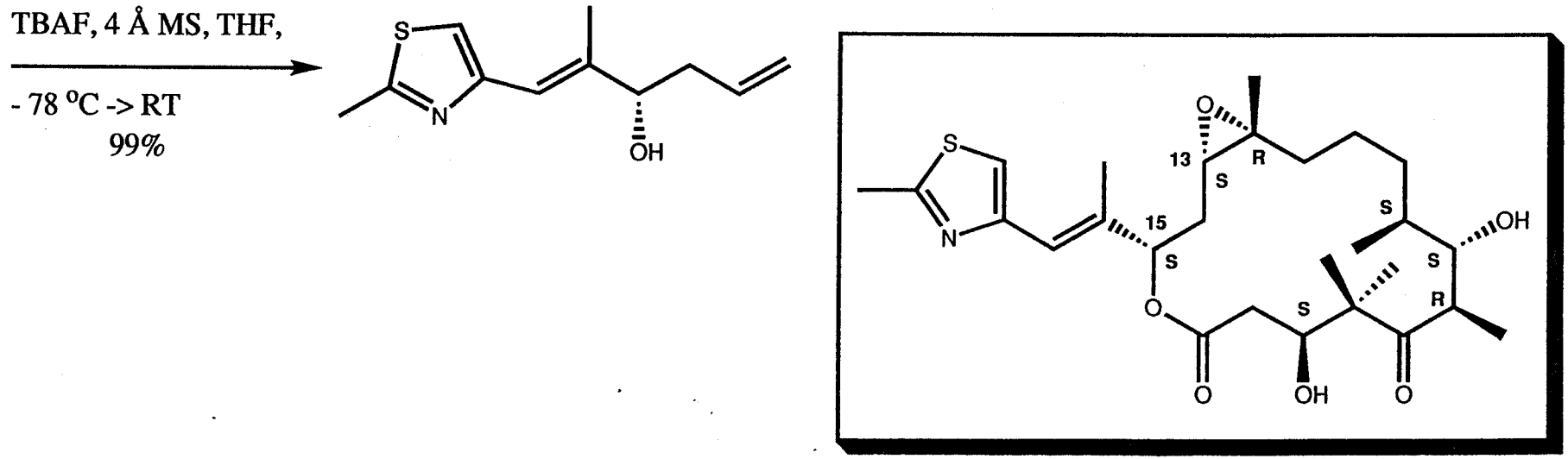




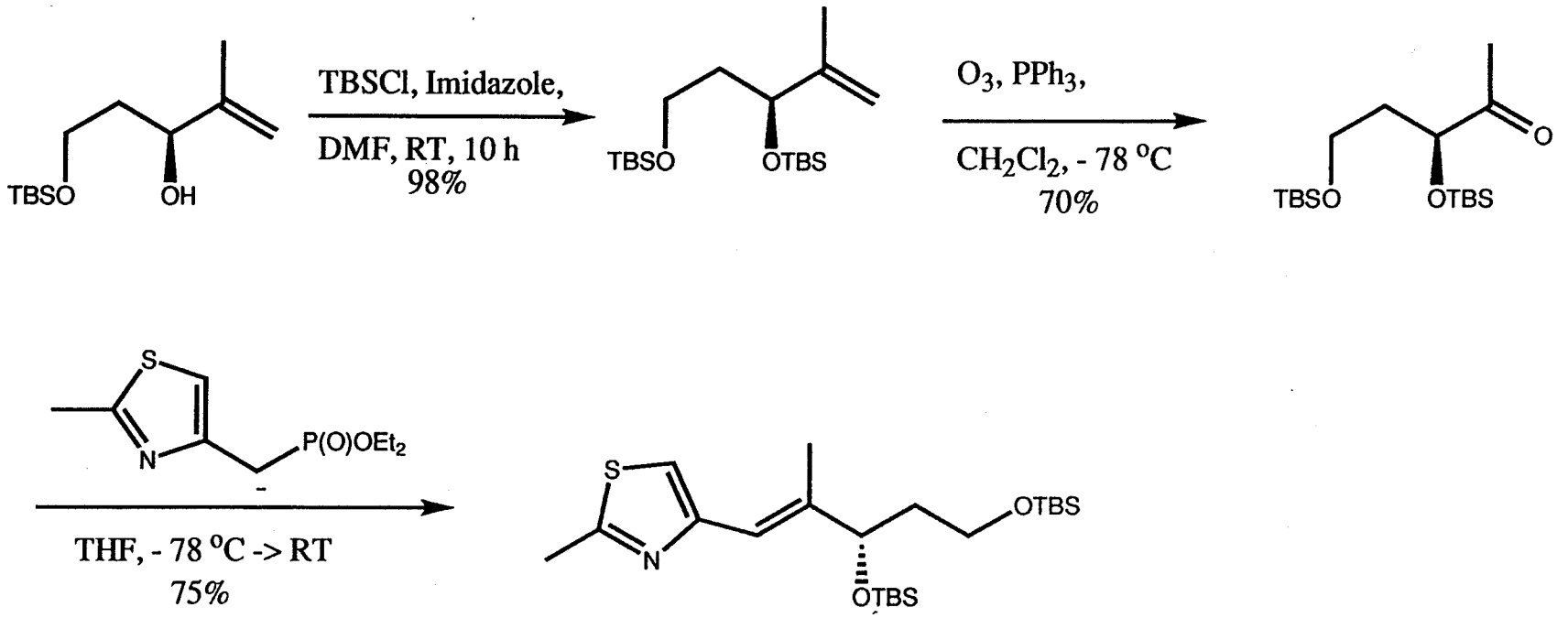
Synthesis of the Thiazole Fragment:

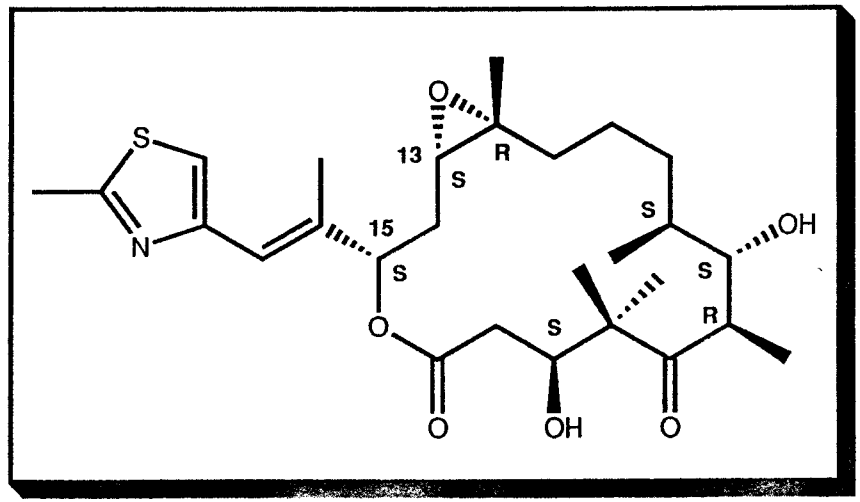




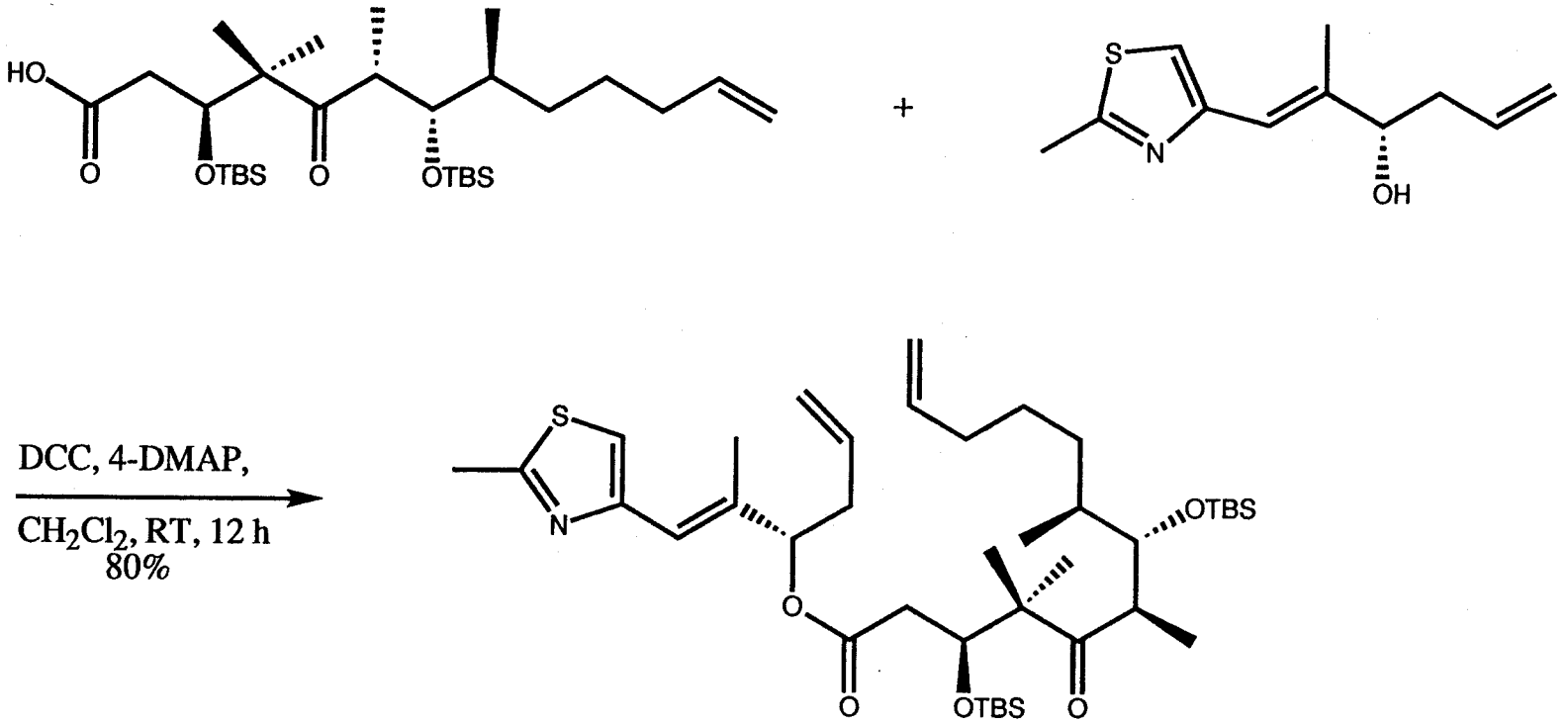


Synthesis of the Thiazole Fragment:

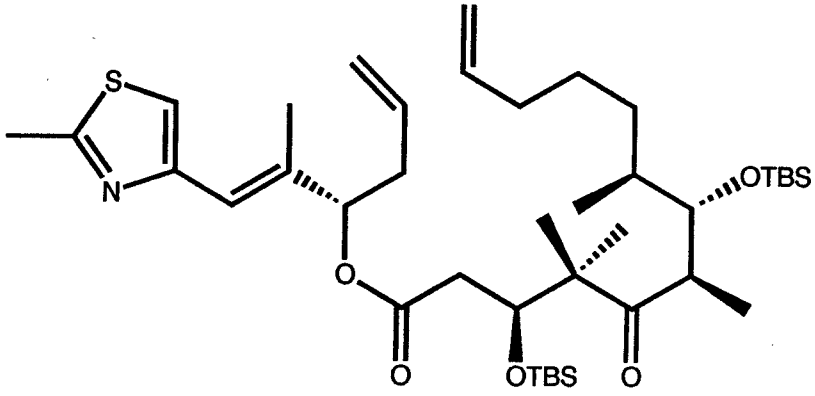




Esterification:



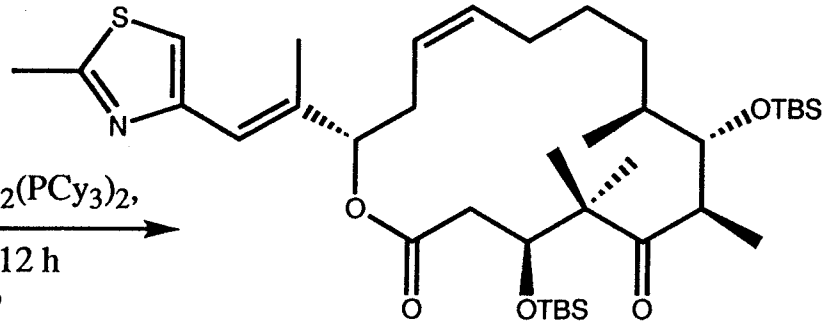
Ring Closing Metathesis:



$[RuCHPh]Cl_2(PCy_3)_2$,

CH_2Cl_2, RT 12 h

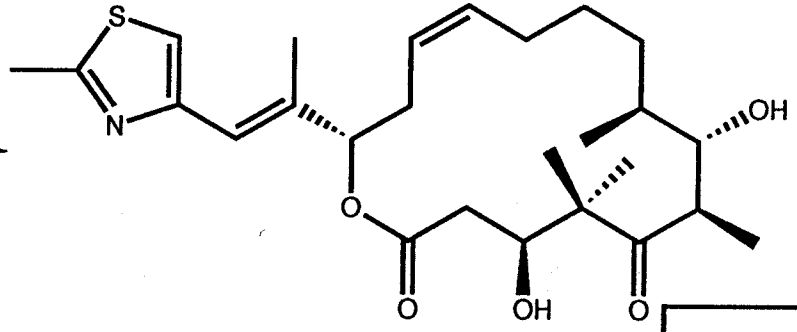
94%



HF, MeCN, Et_2O,

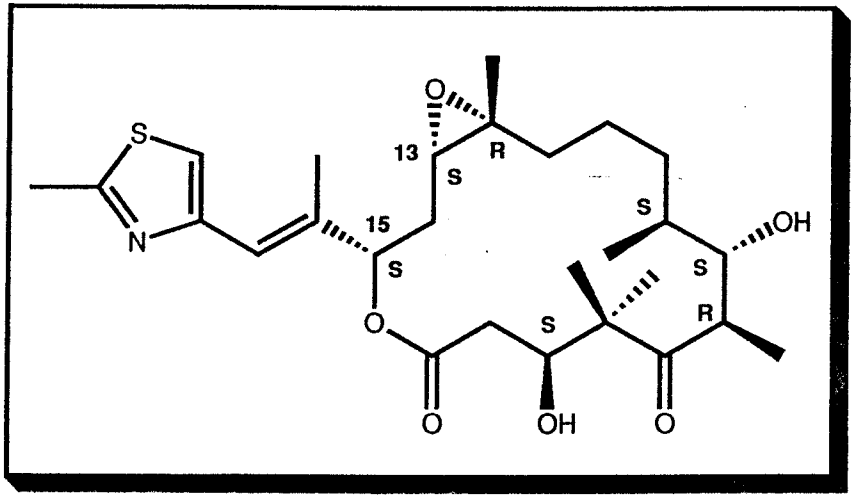
RT, 12 h

65%

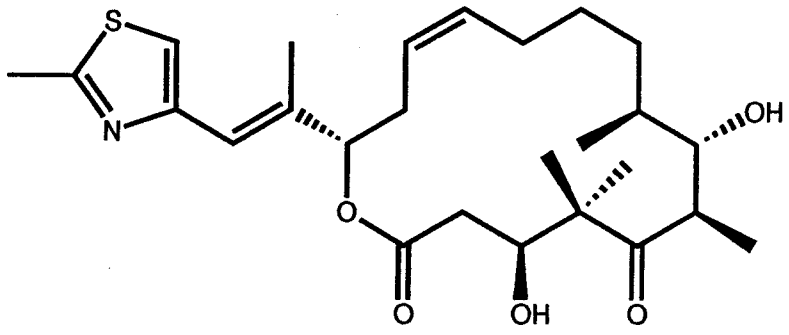


$Z : E = 1 : 1$

Epothilone C



Regio- and Stereoselective Epoxidation:

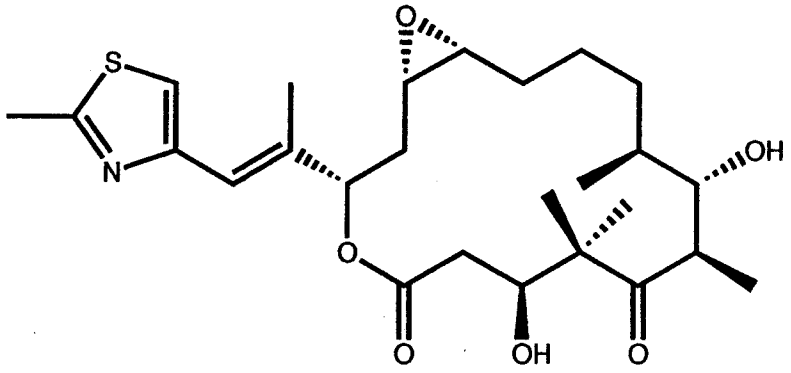


$Z : E = 1 : 1$

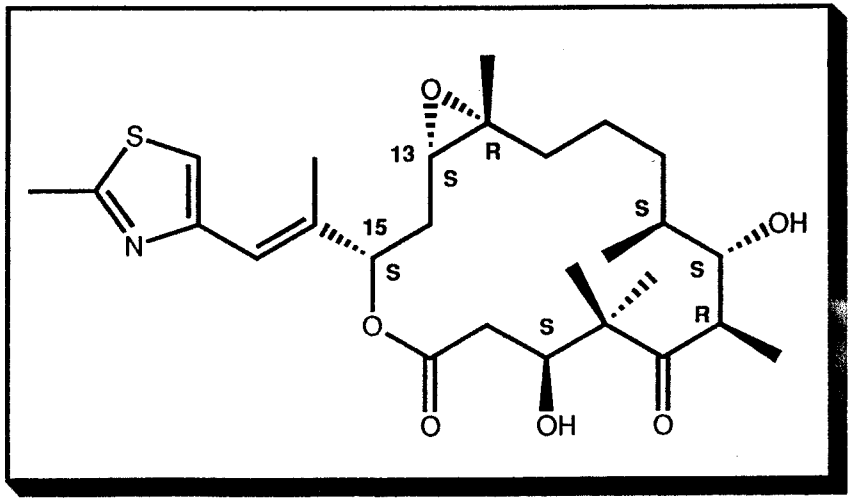
Dimethyl Dioxirane, CH_2Cl_2,

- 35 °C, 2 h

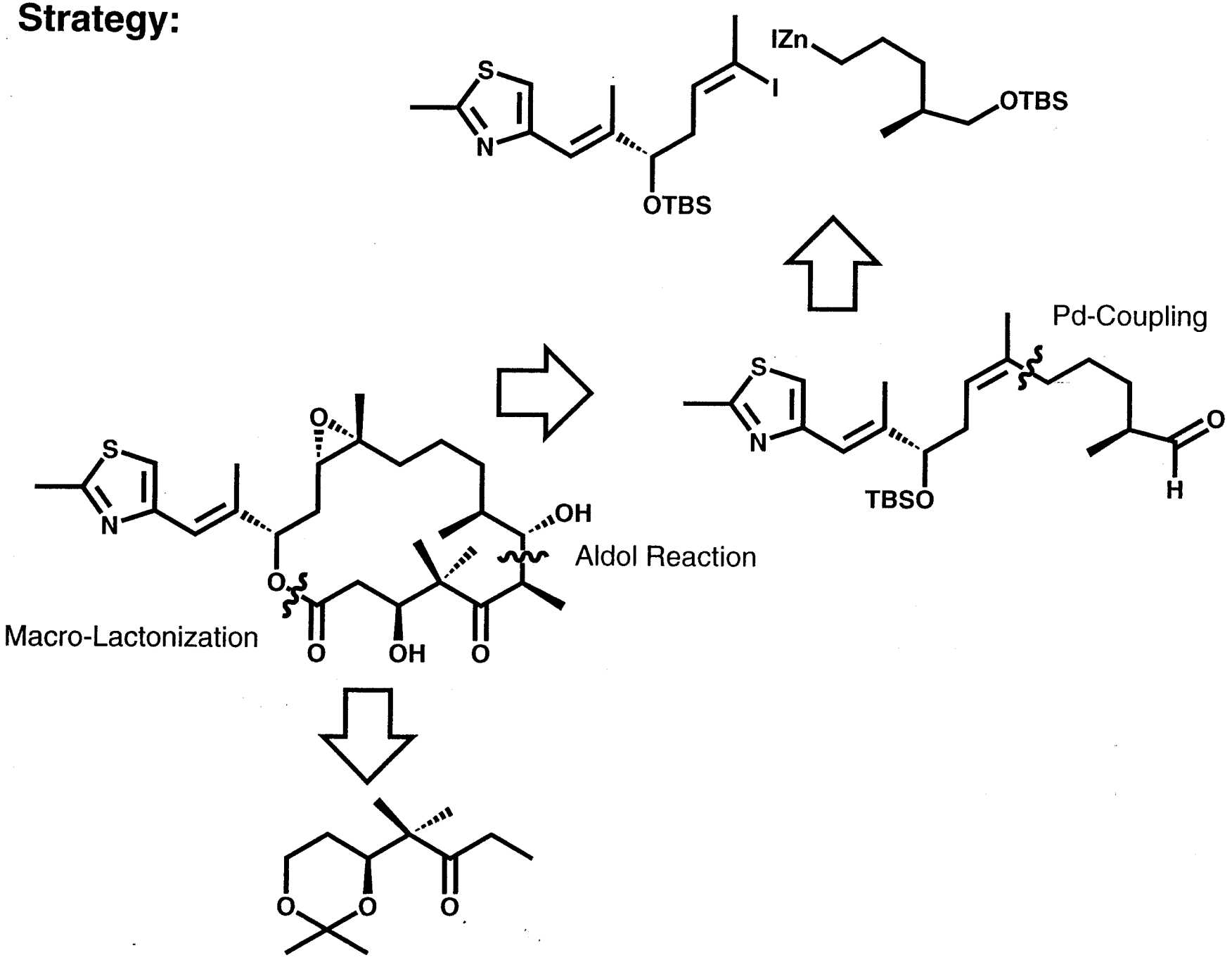
48%



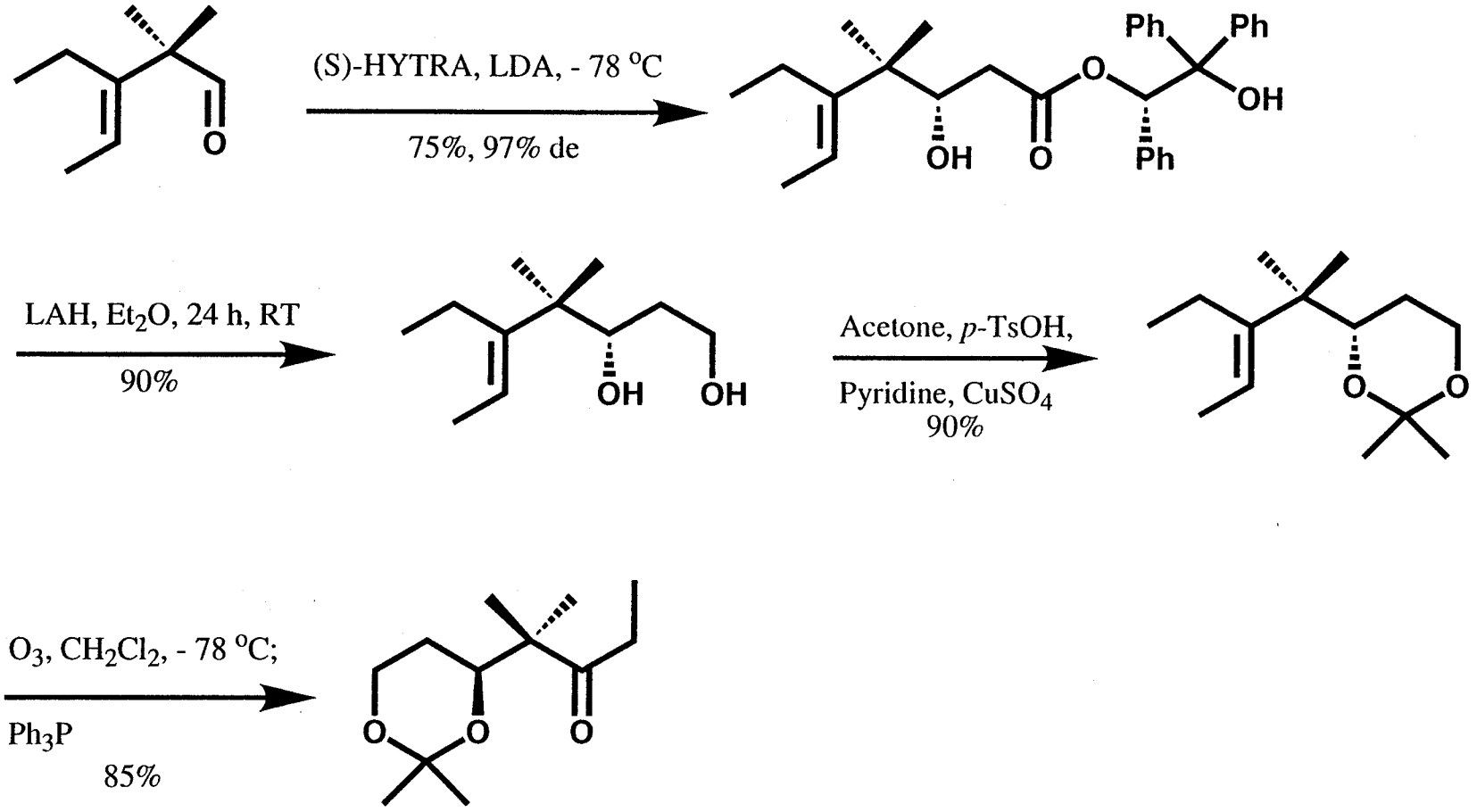
(-)-Epothilone A



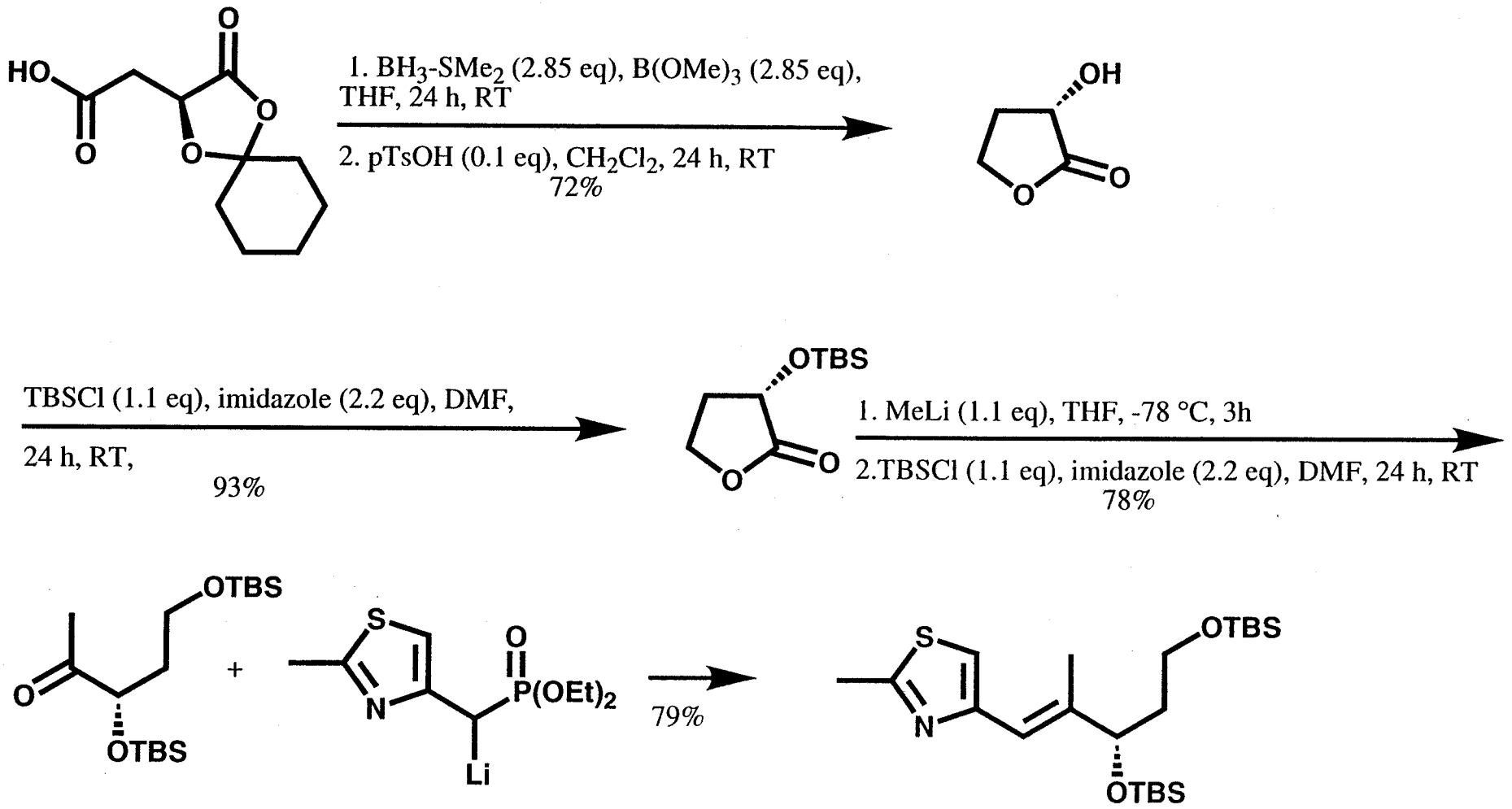
Strategy:


IZn
I
S
N
OTBS
OTBS
Pd-Coupling
TBSO
H
O
OH
Aldol Reaction
Macro-Lactonization
O
OH
O

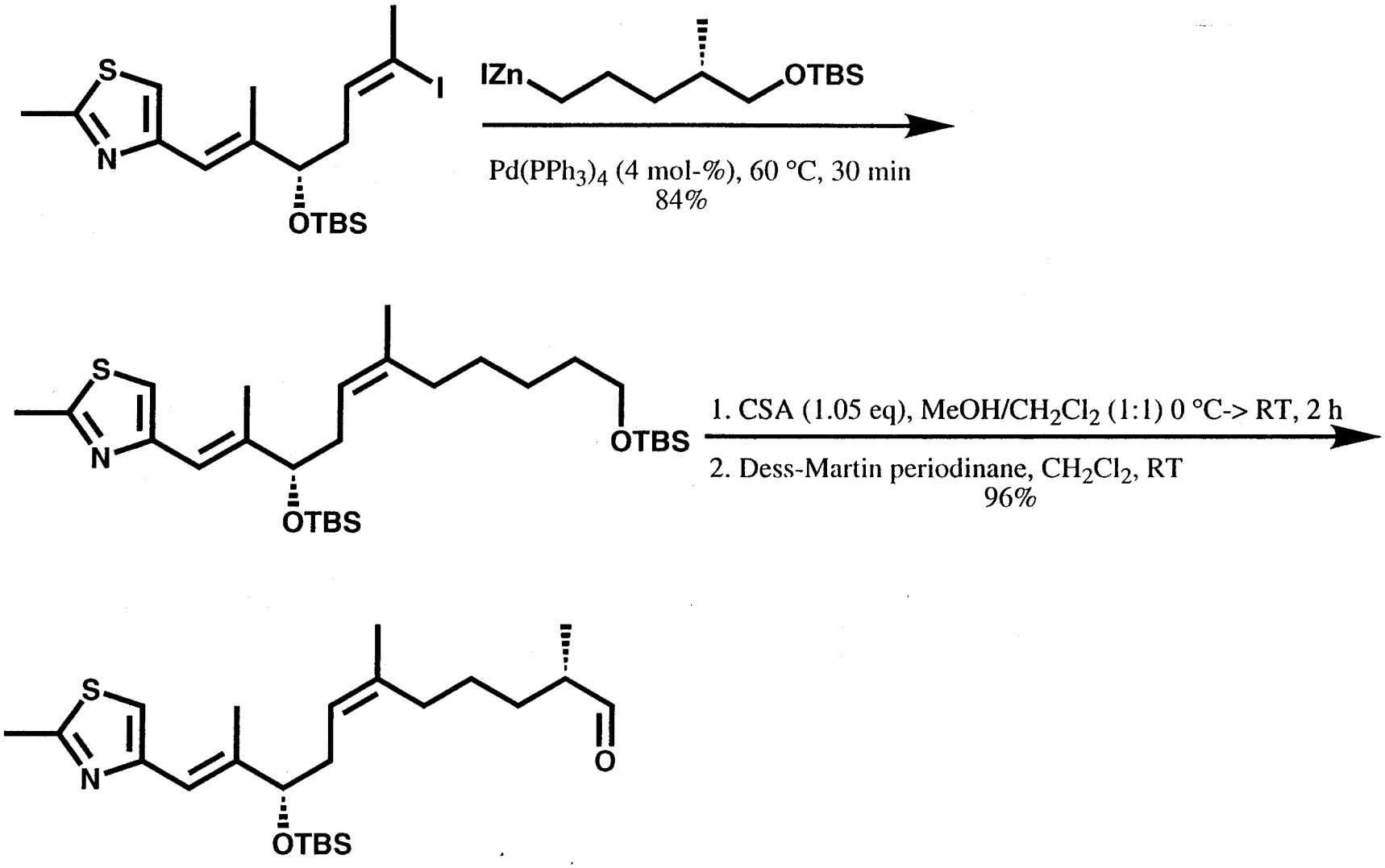
HYTRA-Route to Functionalized Ketone:



(*S*)-Malic Acid Approach for Thiazole Fragment



Palladium-Mediated Coupling:



Key Aldol Reaction to Synthesize Epothilone B: