

# Total Synthesis and Elucidation of the Absolute Configuration of the Diterpene Tonantzitlolone<sup>†</sup>

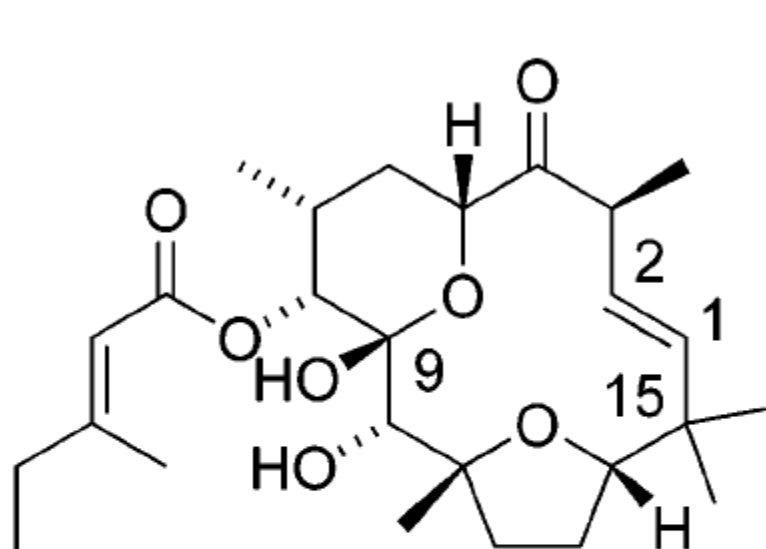
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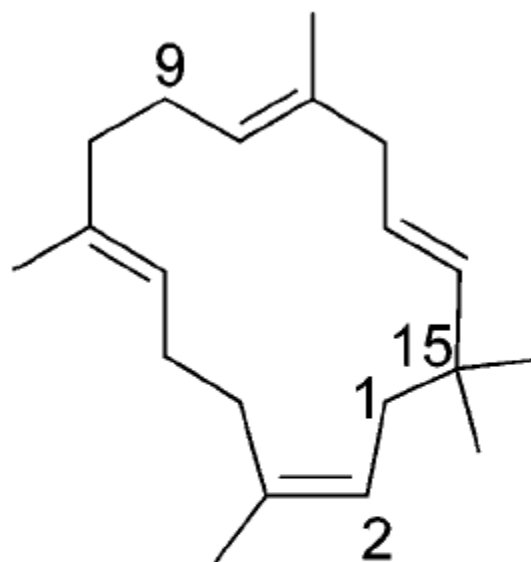
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# Naturally Occuring 15-membered Carbocyclic Ring Systems

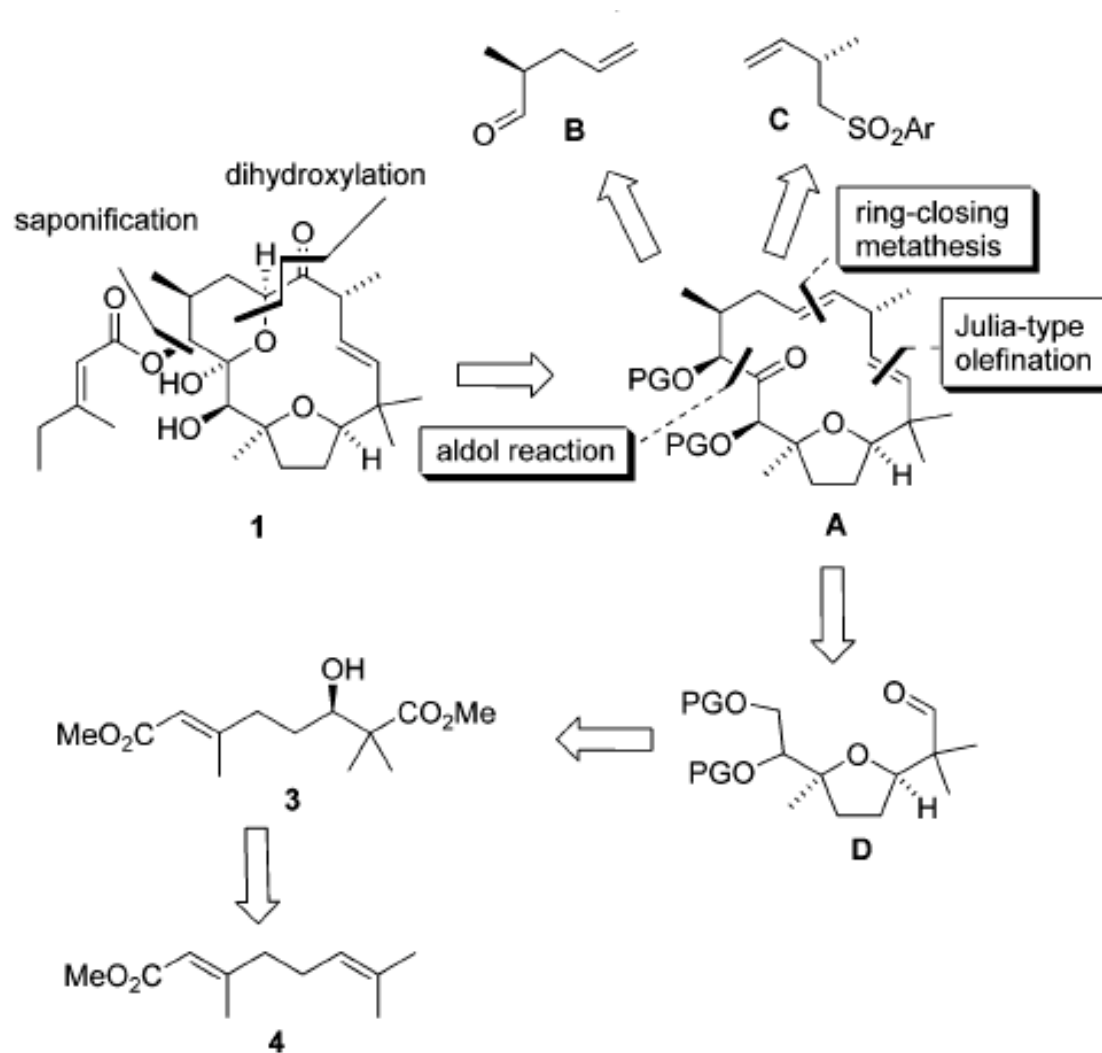


**Tonantzitlone 1**  
(as determined from  
the present work)



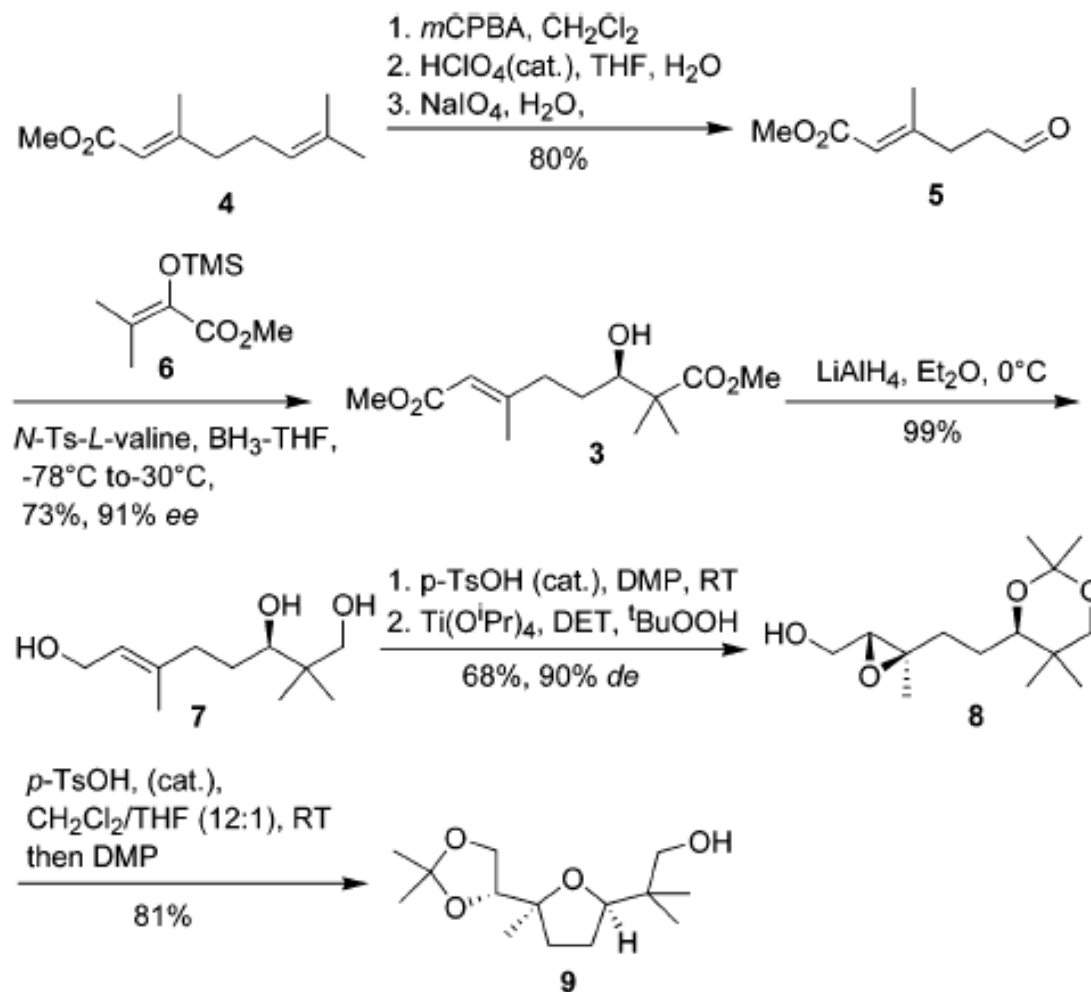
**Flexibilene 2**

# Retrosynthetic Analysis



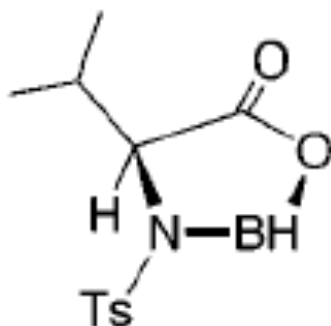
<sup>a</sup> PG = protective group. Ar = aryl.

# Synthesis of Intermediate 9 from Methyl Geranate 4

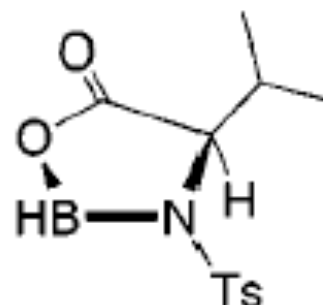


<sup>a</sup> *m*CPBA = *meta*-chloroperbenzoic acid. Ts = *p*-toluene sulfonyl. DMP = 2,2-dimethoxy propane. DET = (–)-diethyl-D-tartrate.

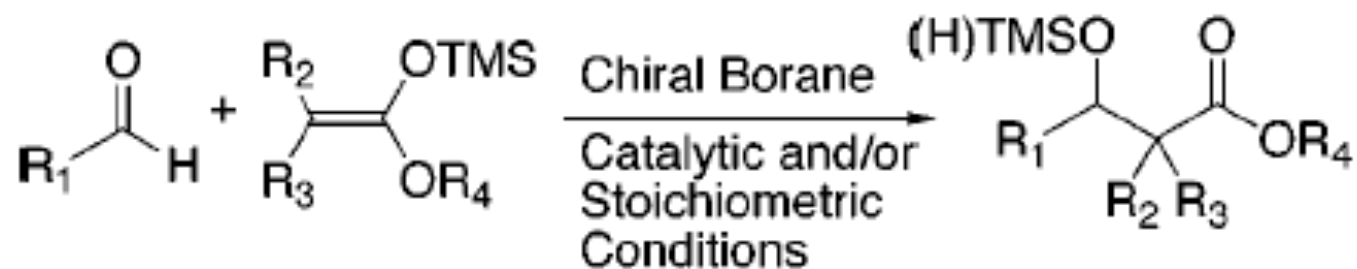
# General Feature of the Oxazaborolidinone-Promoted Asymmetric Aldol Reaction



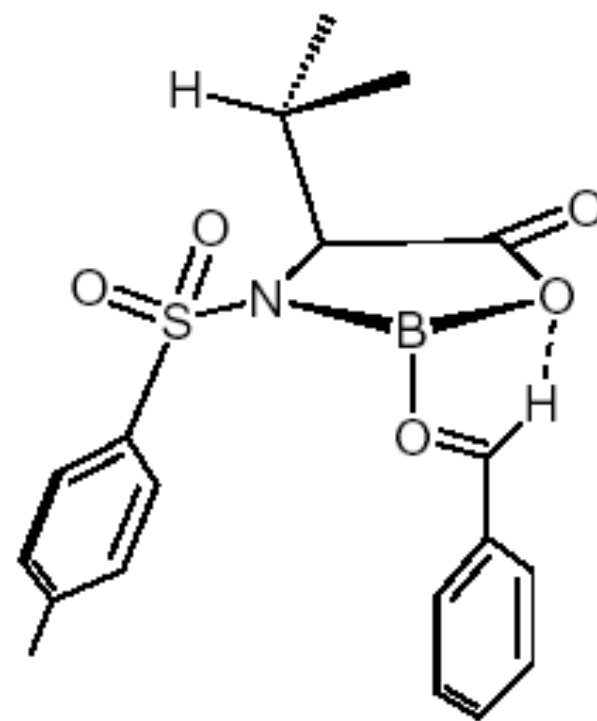
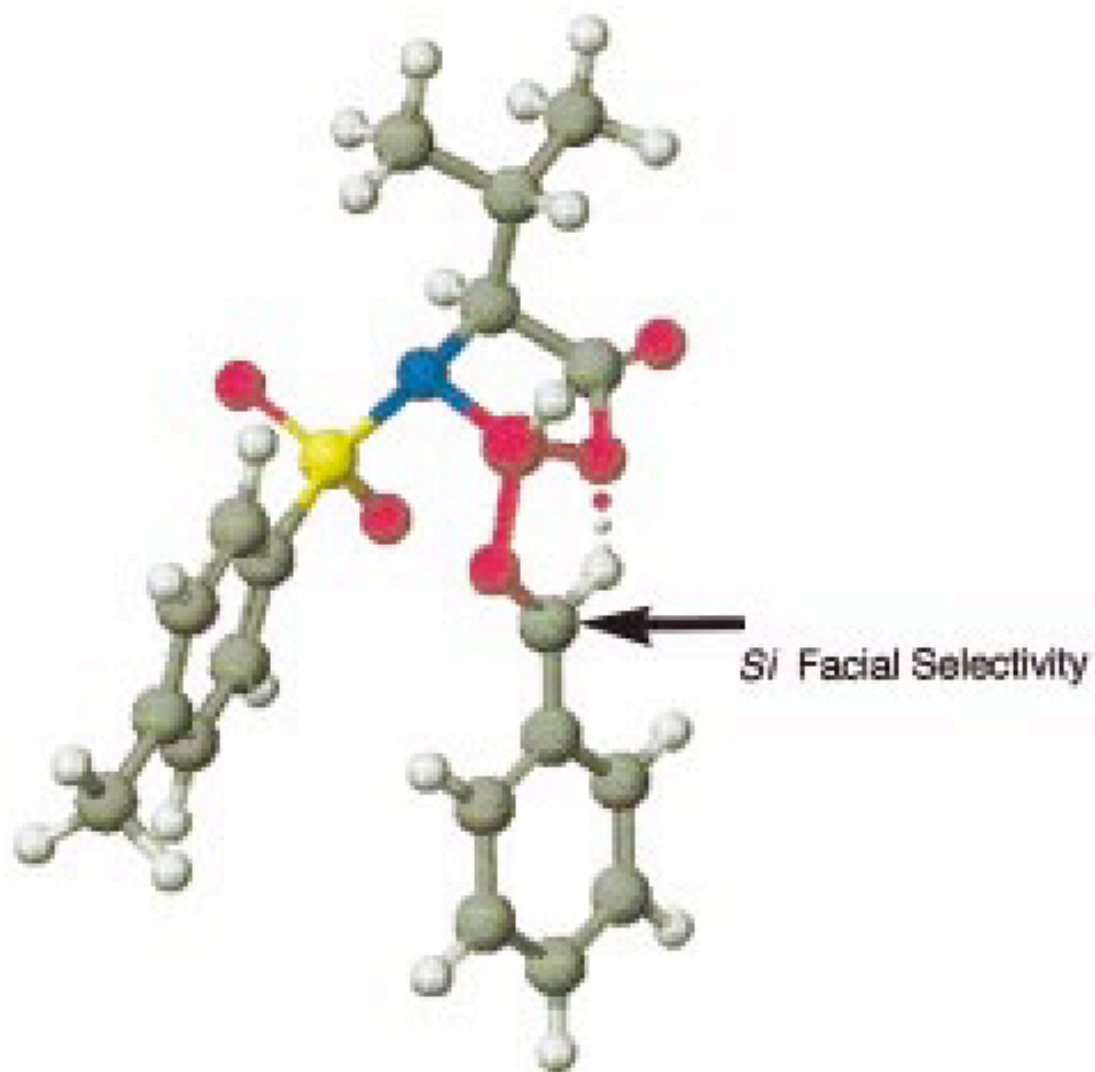
(*S*)-Oxazaborolidinone 1



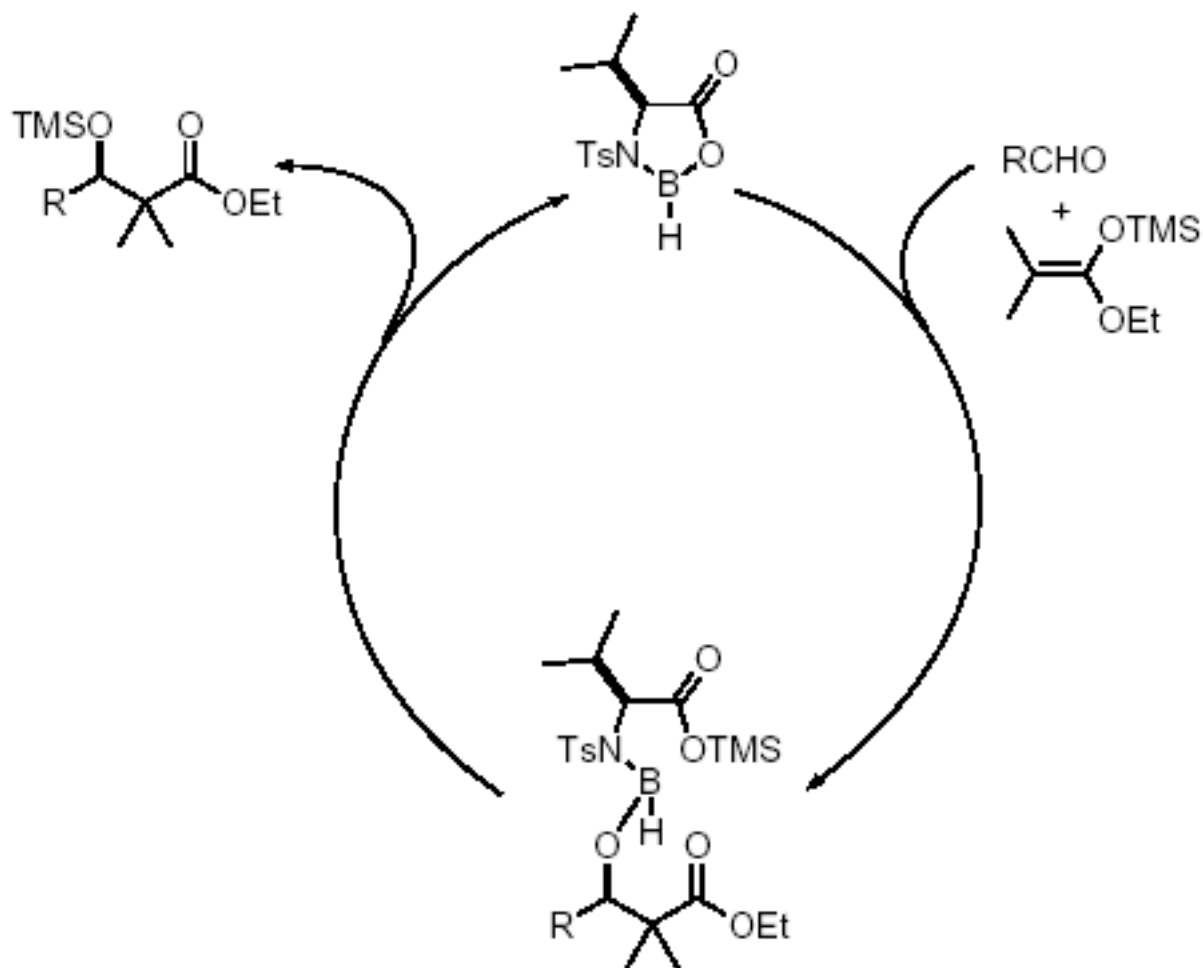
(*R*)-Oxazaborolidinone 2



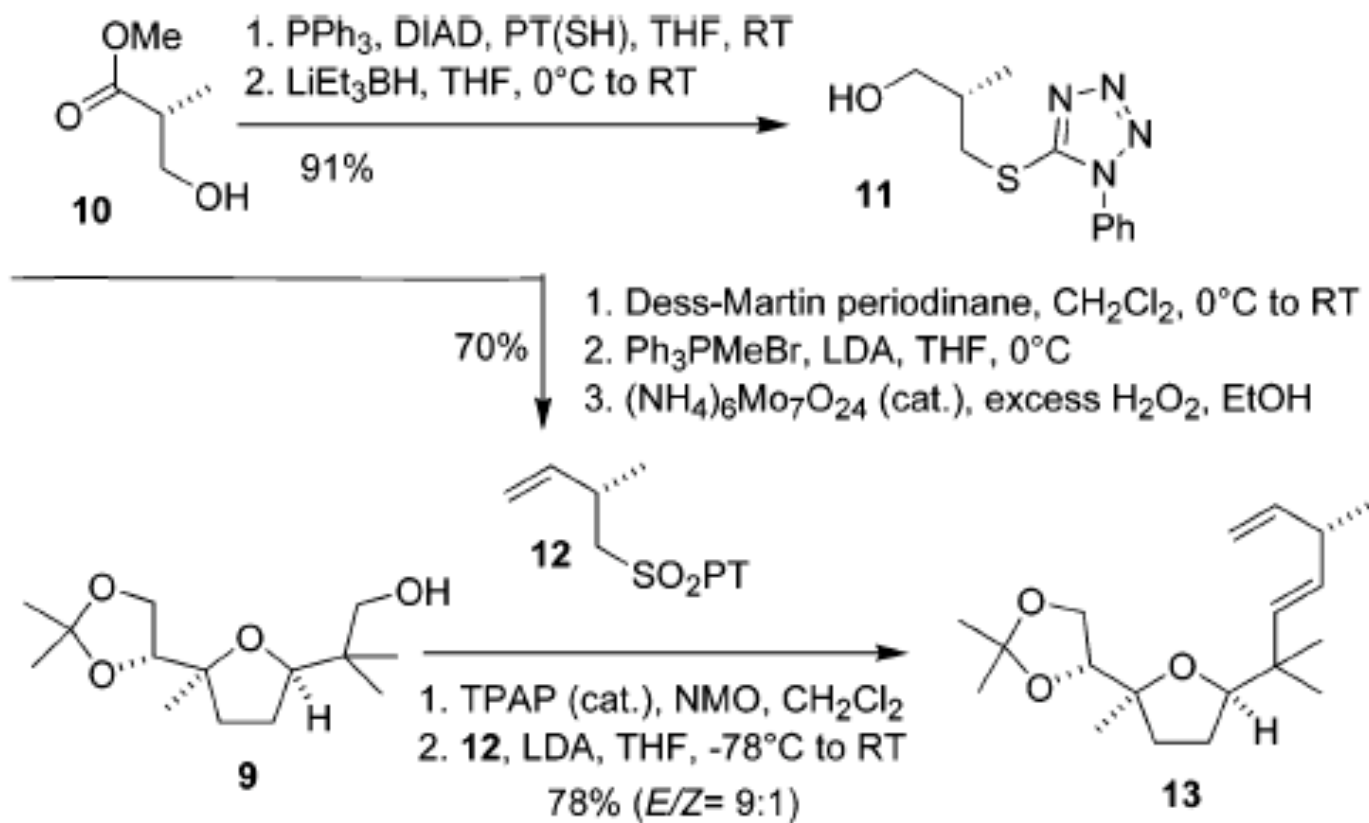
# Presumed Transition State Assembly



# Proposed Mechanism of the Oxazaborolidinone Catalyzed Aldol Reaction



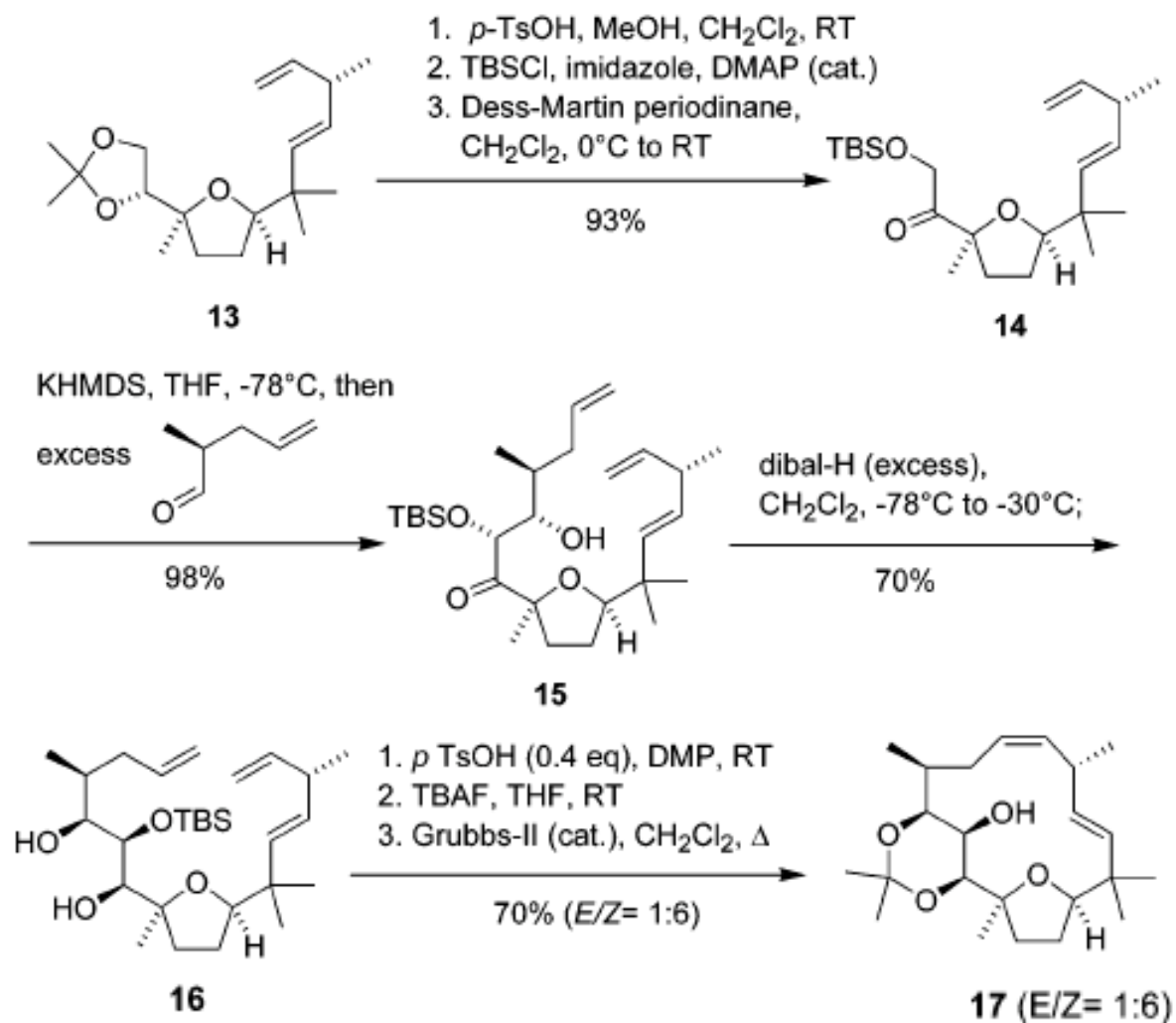
# Preparation of Fragments 12 and 13



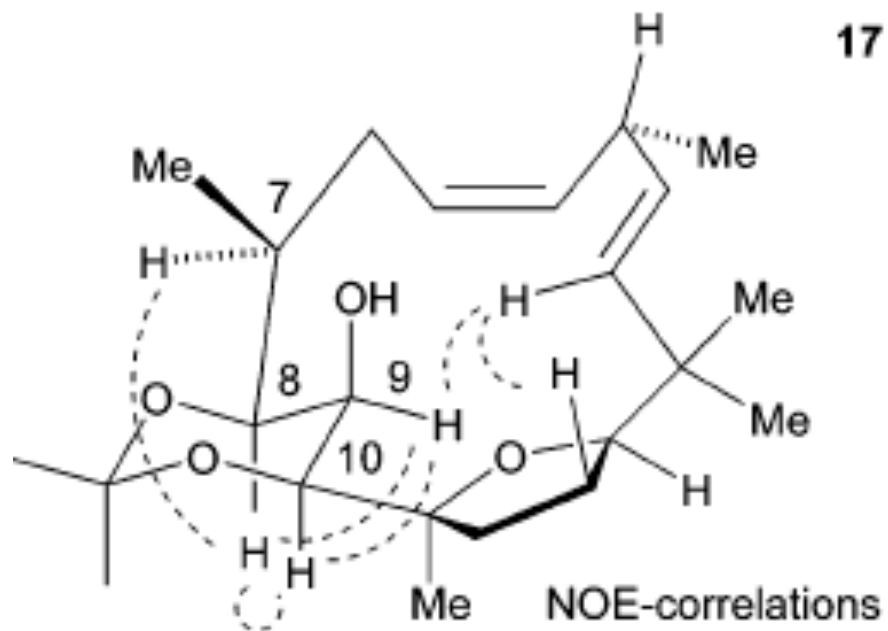
<sup>a</sup> DIAD = diisopropylazodicarboxylate. PT(SH) = phenyltetrazole (thiol). TPAP = tetra-*n*-propylammonium perruthenate. NMO = *N*-methylmorpholine-*N*-oxide. LDA = lithiumdiisopropylamide.



# Preparation of Macrocycle 17



# Evan's and Rychnovsky NOE Correlation Studies



# Completion of Total Synthesis of (ent)-1

