

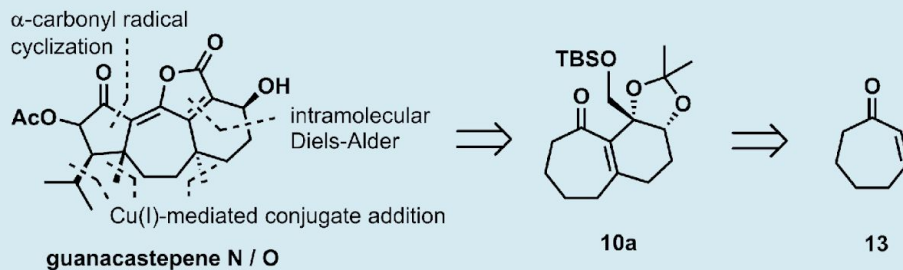
# Stereoselective Total Syntheses of Guanacastepenes N and O

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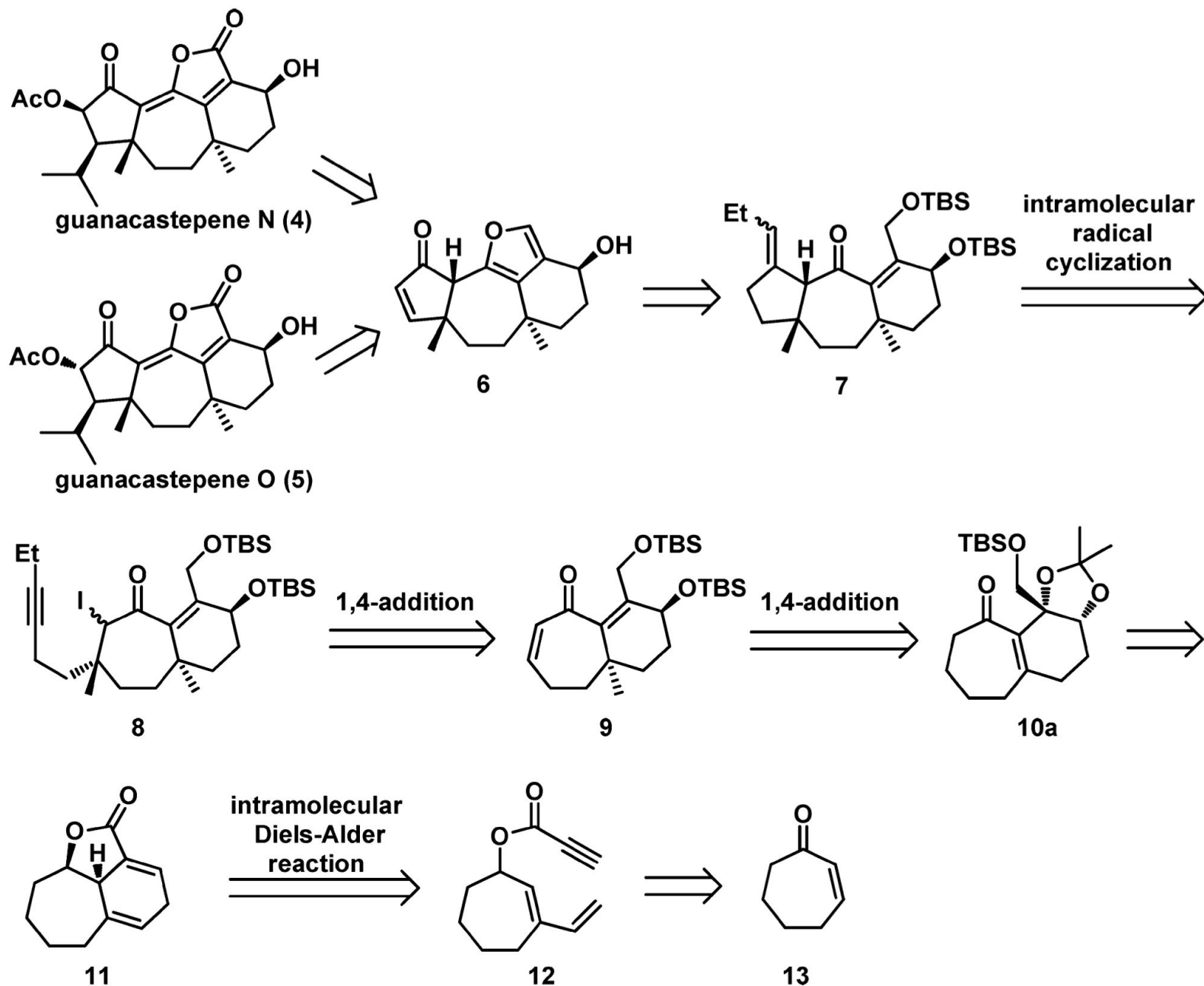
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## S Supporting Information

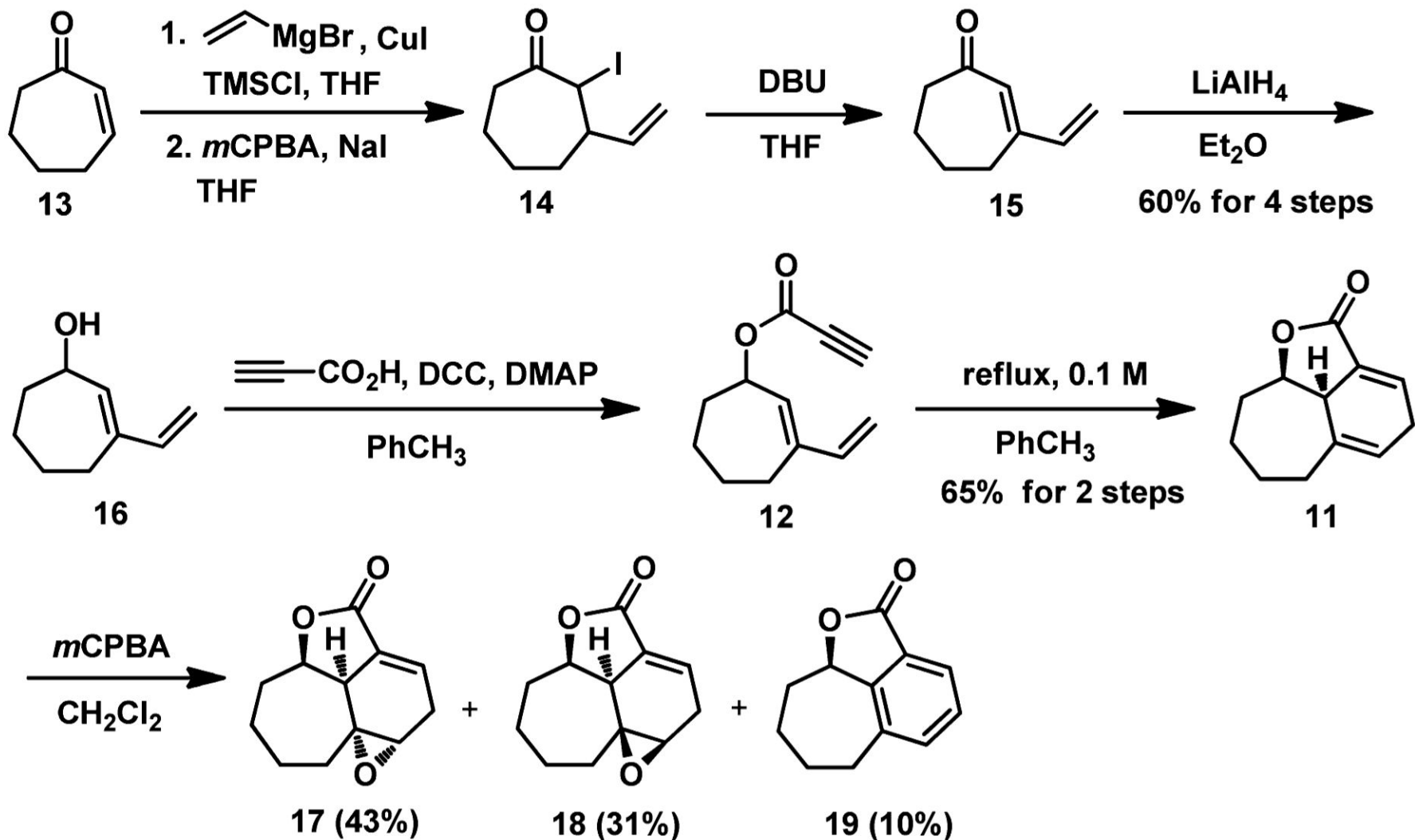
**ABSTRACT:** Total syntheses of ( $\pm$ )-guanacastepenes N and O were accomplished with 2-cycloheptenone as starting material. The six- and five-membered rings of the core [5, 7, 6] ring skeleton were constructed with an intramolecular Diels–Alder reaction and  $\alpha$ -carbonyl radical cyclization. The quaternary centers and their stereochemistry were established with sequential Cu(I)-mediated conjugate additions. A sequence with dihydroxylation, conjugate addition, and  $\beta$ -elimination was devised to incorporate all oxygen functionalities at positions. The total synthesis is adaptable for the synthesis of enantiopure guanacastepenes N and O using chiral intermediate (*R*)-3-vinyl-2-cycloheptenol obtained from lipase-catalyzed kinetic resolution.



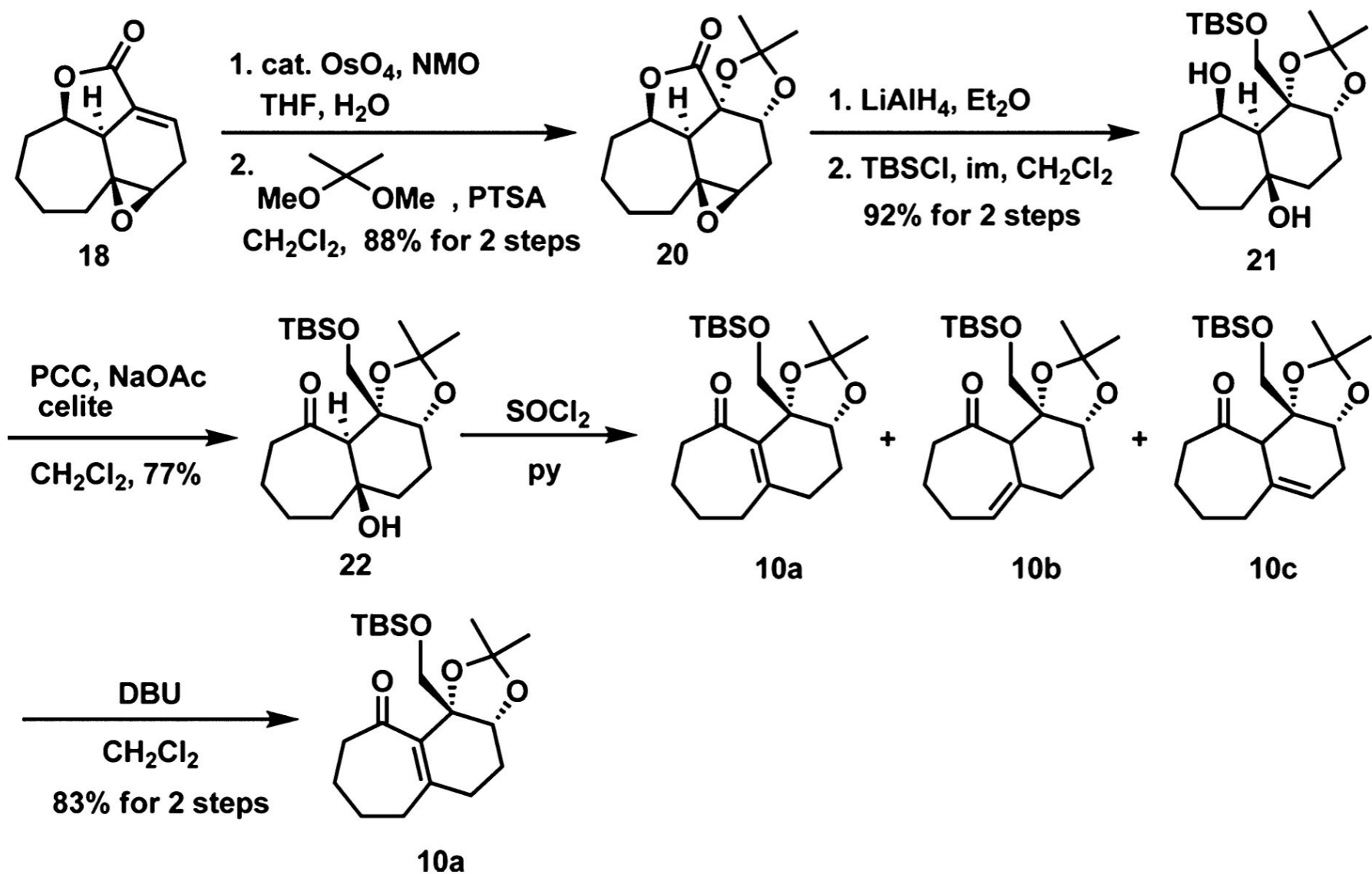
# Scheme 1. Retrosynthesis of Guanacastepenes N and O



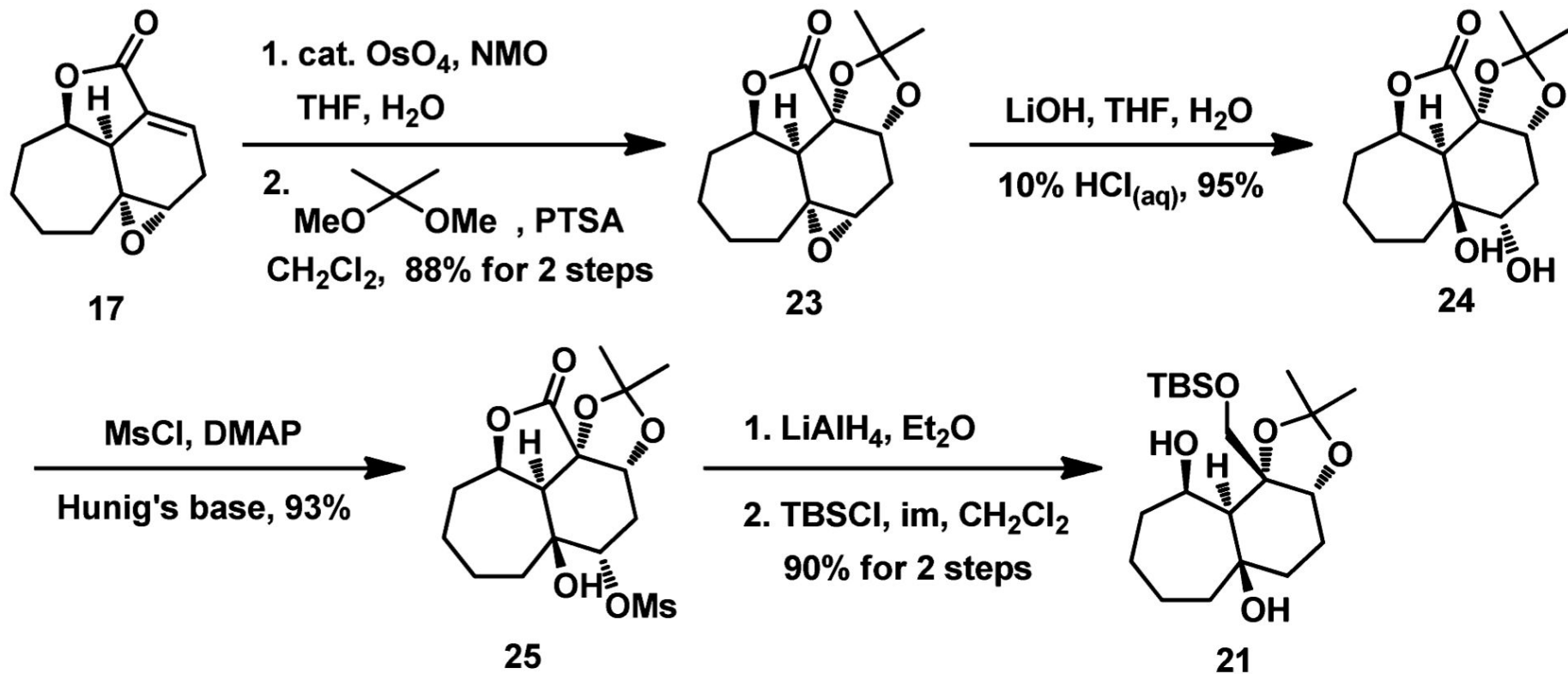
## Scheme 2. Synthesis of Compounds 17 and 18



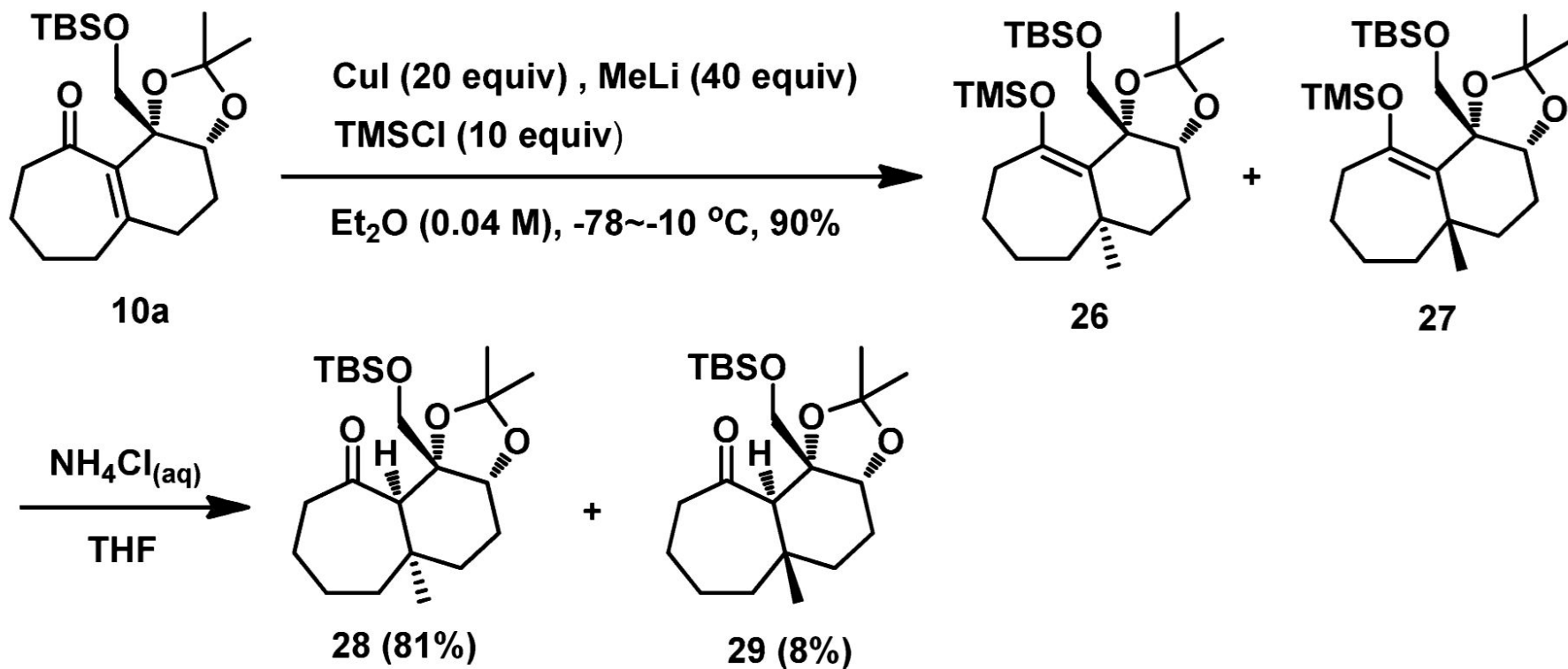
# Scheme 3. Synthesis of Enone 10a



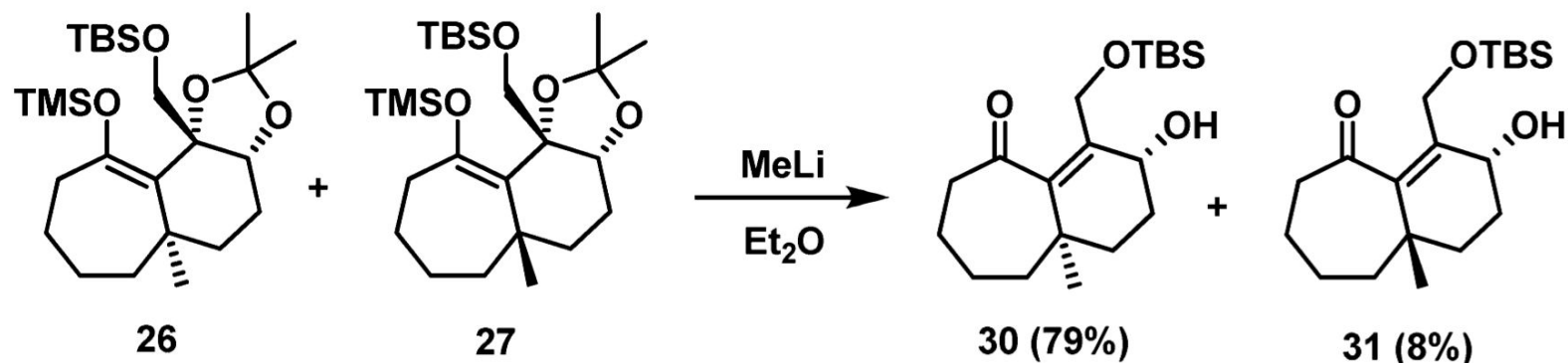
## Scheme 4. Synthesis of Diol 21



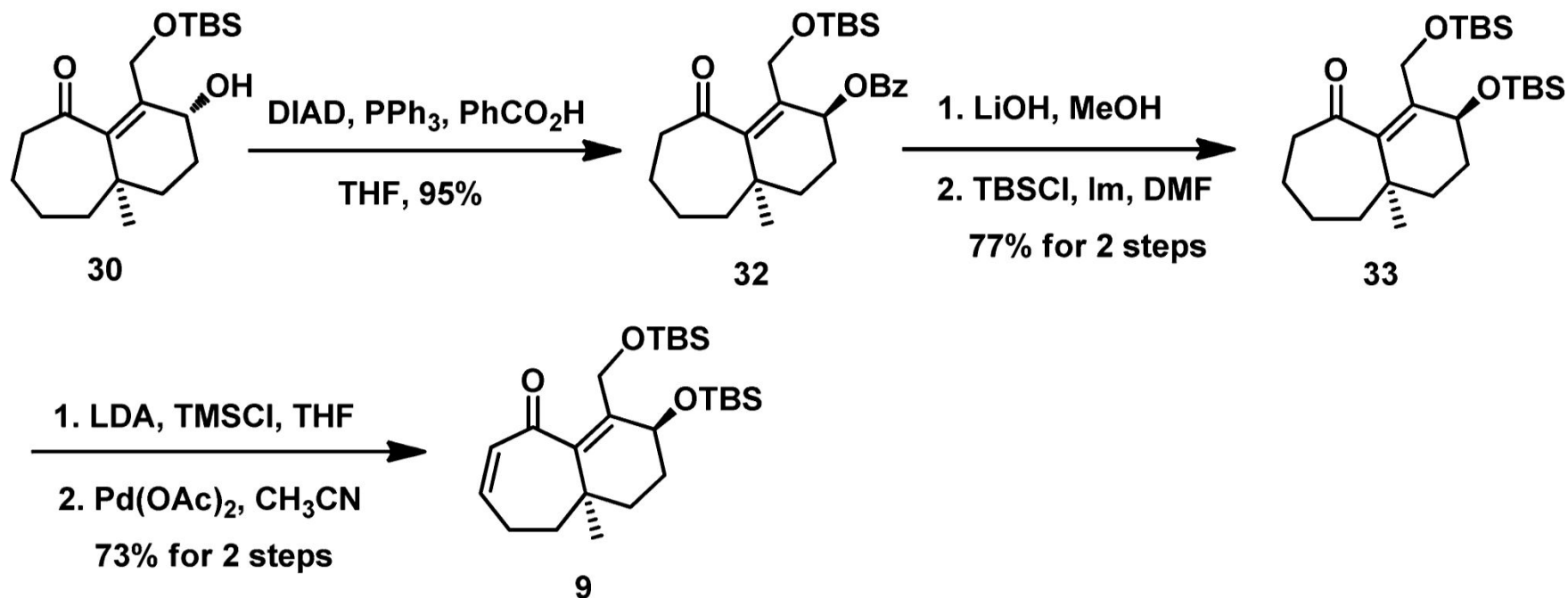
## Scheme 5. Synthesis of Compounds 28 and 29



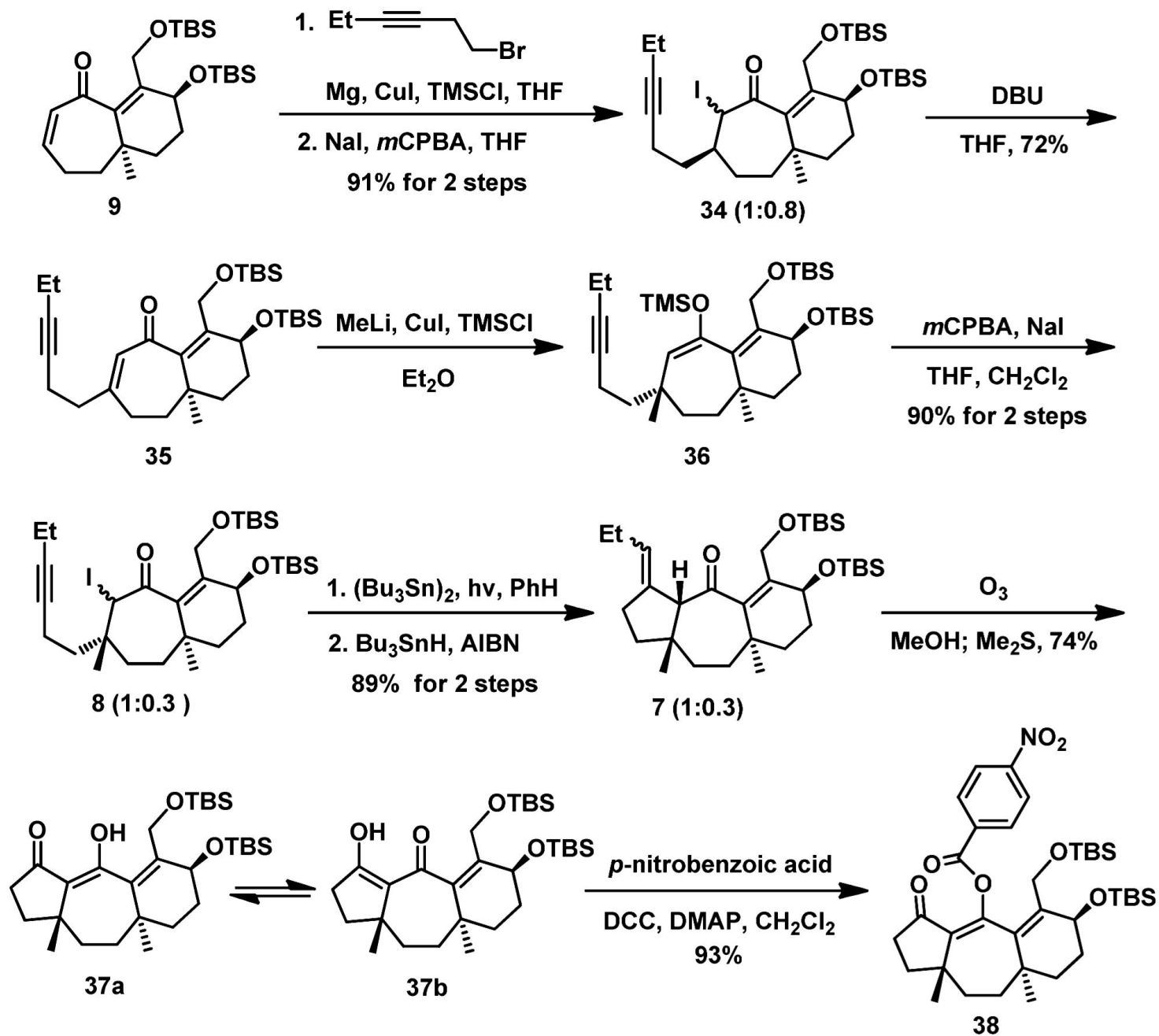
# Scheme 6. Synthesis of Enones 30 and 31 via $\beta$ -Elimination Reaction



# Scheme 7. Synthesis of Dienone 9

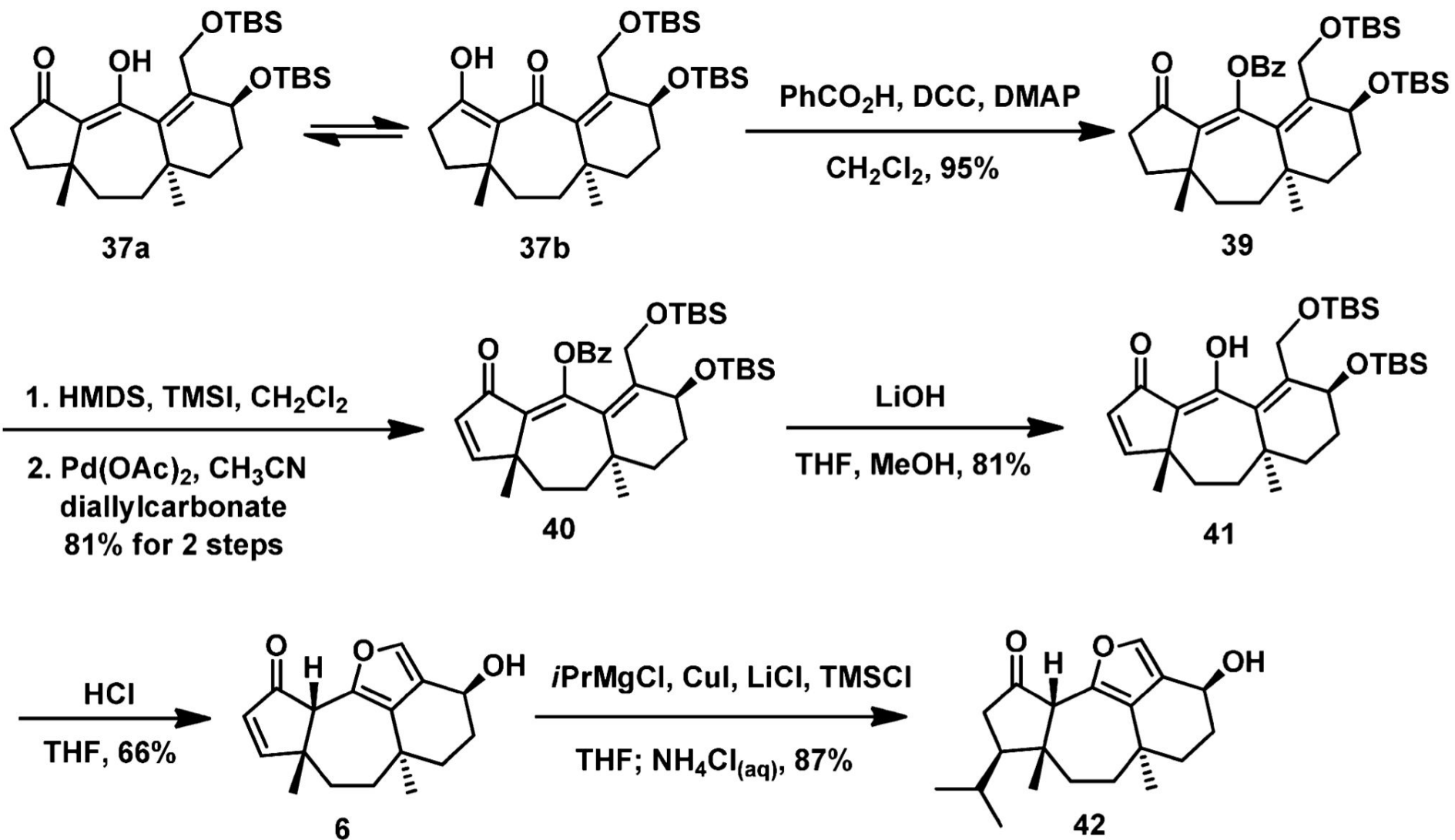


# Scheme 8. Synthesis of Compounds 37a, 37b, and 38

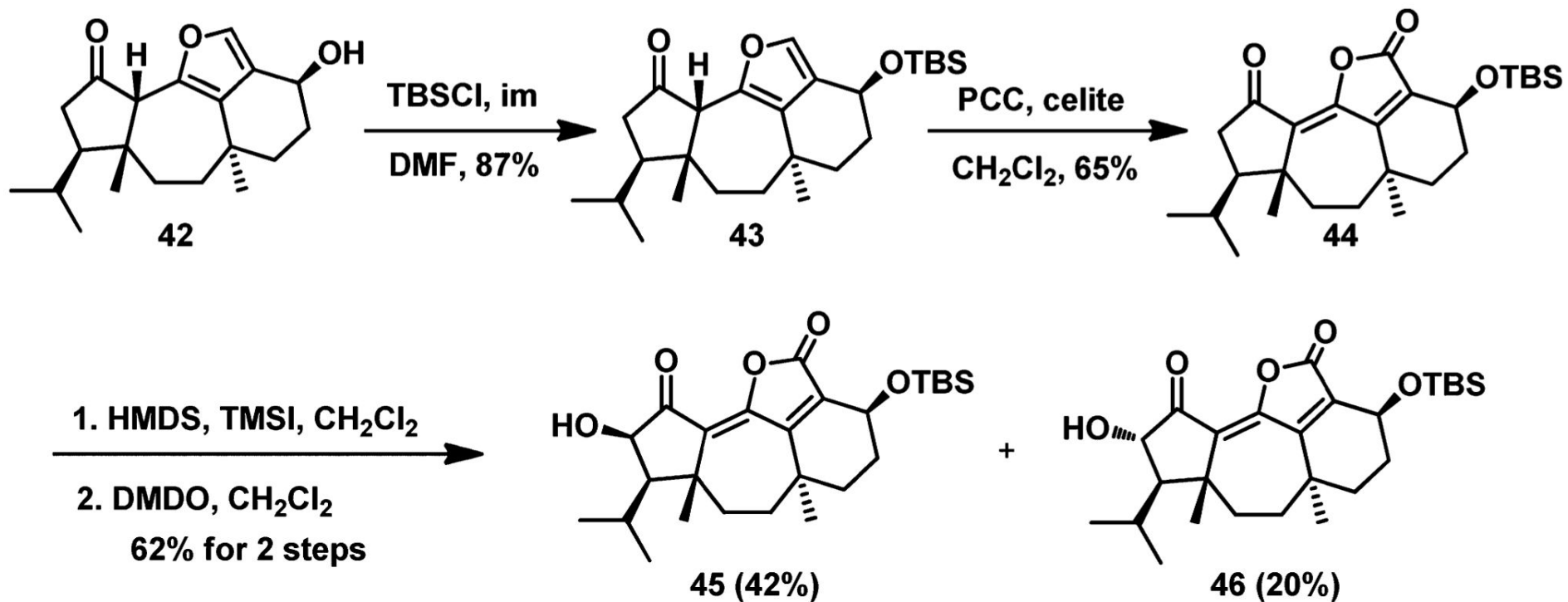




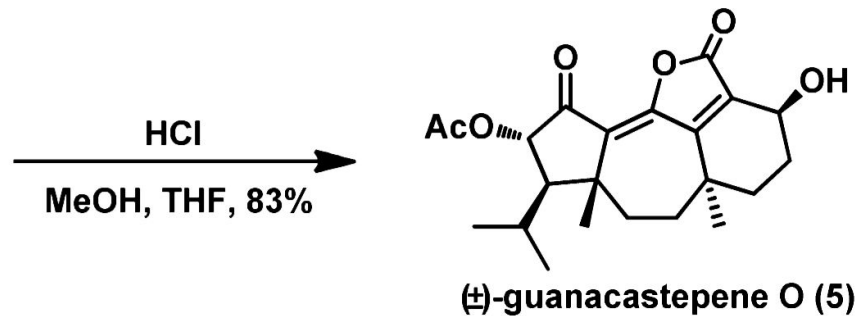
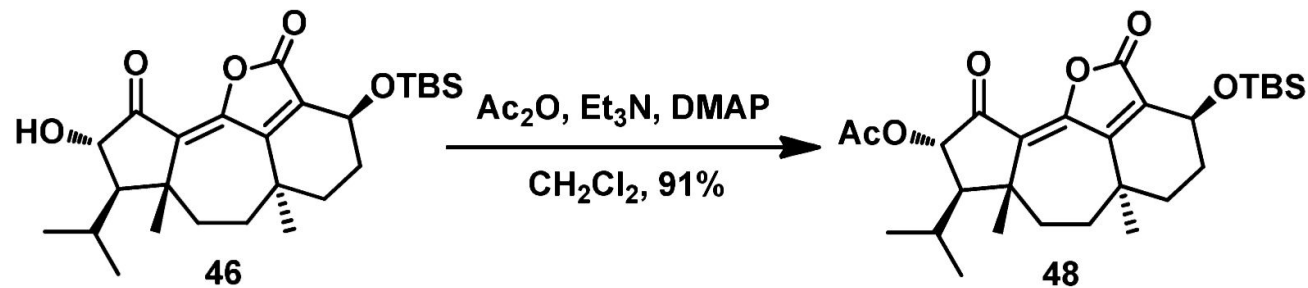
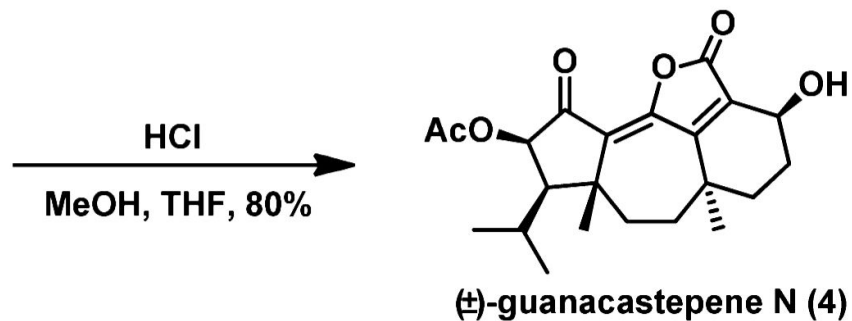
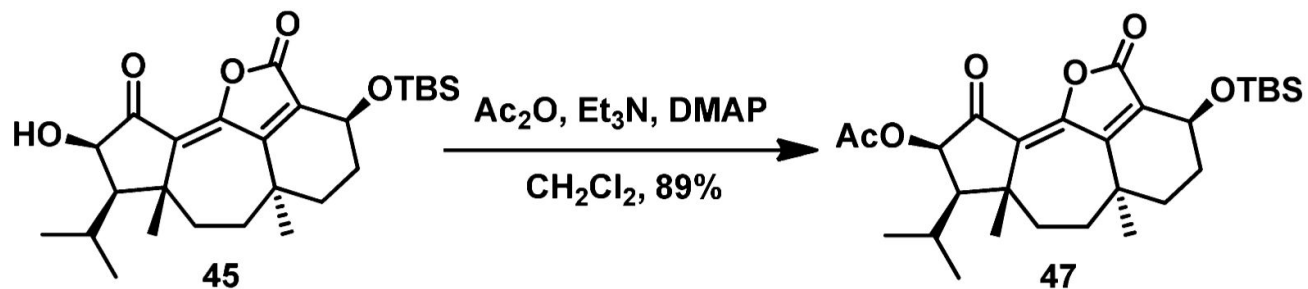
# Scheme 9. Synthesis of Furan 42



## Scheme 10. Synthesis of Lactones 45 and 46



# Scheme 11. Synthesis of Guanacastepenes N and O



## Scheme 12. Synthesis of Chiral Dienol (*R*)-16

