

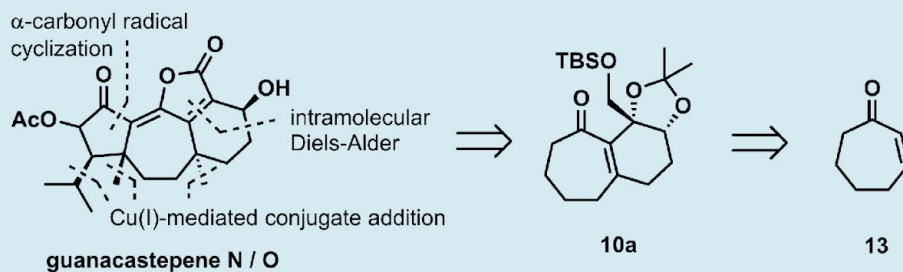
Stereoselective Total Syntheses of Guanacastepenes N and O

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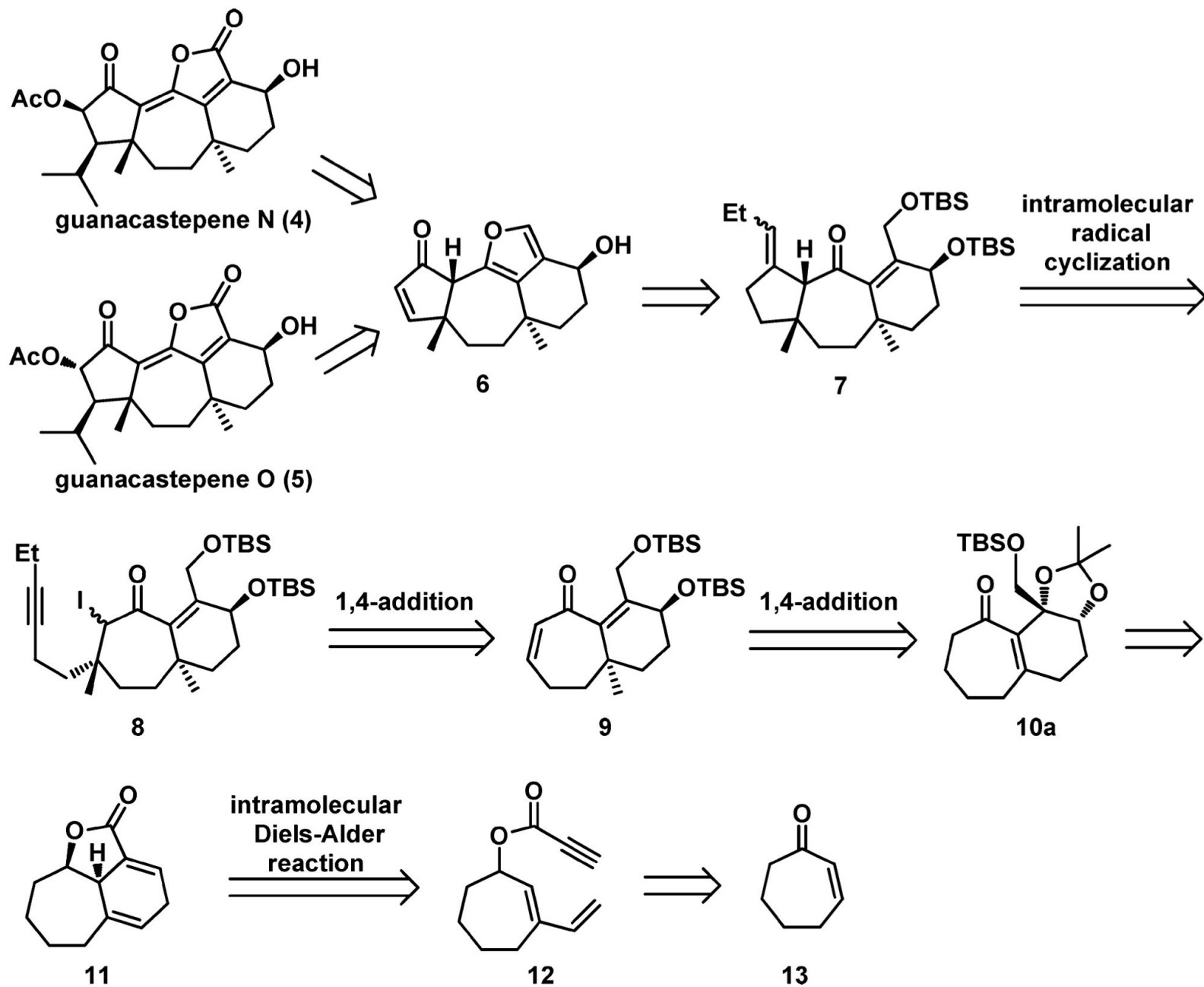
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S Supporting Information

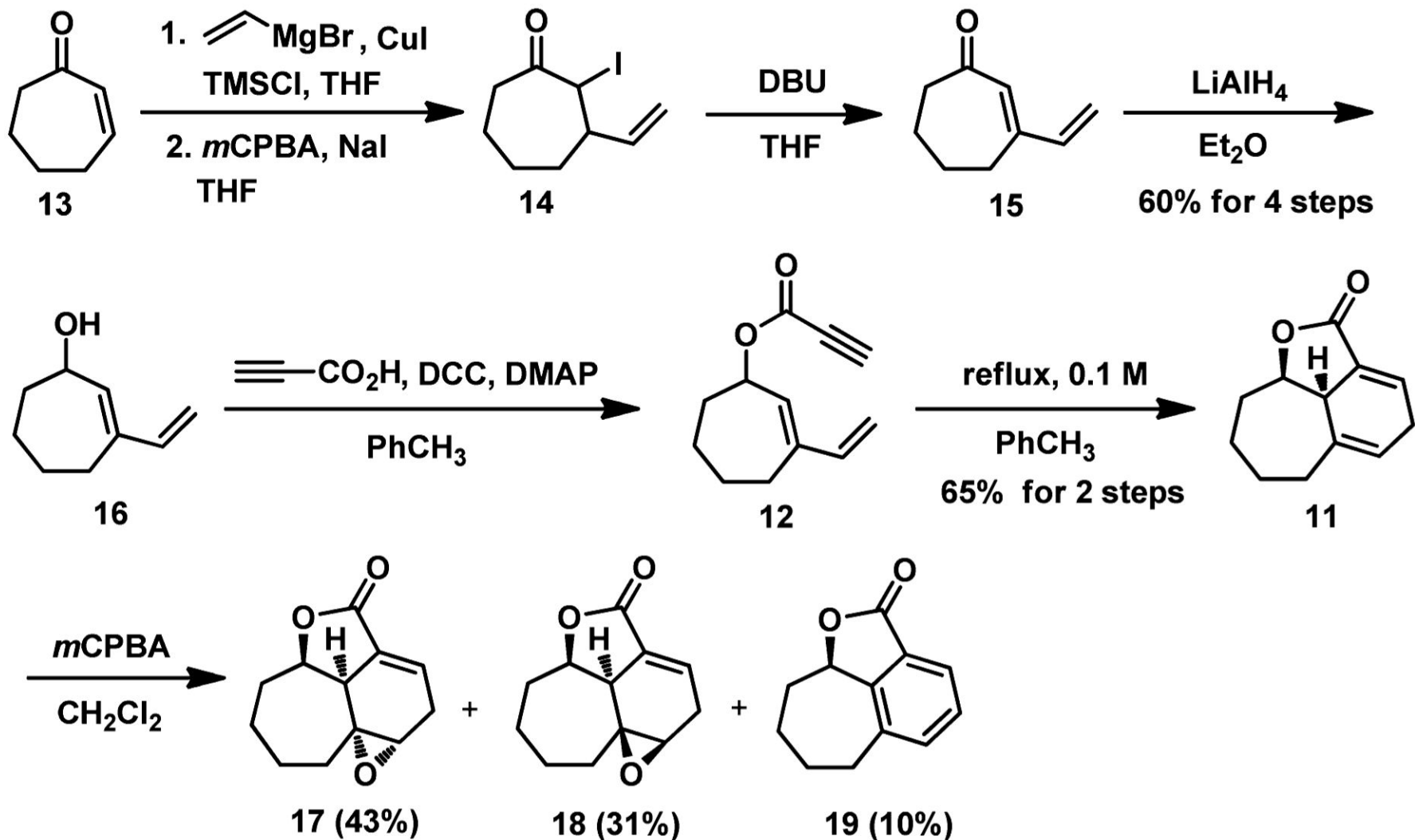
ABSTRACT: Total syntheses of (\pm)-guanacastepenes N and O were accomplished with 2-cycloheptenone as starting material. The six- and five-membered rings of the core [5, 7, 6] ring skeleton were constructed with an intramolecular Diels–Alder reaction and α -carbonyl radical cyclization. The quaternary centers and their stereochemistry were established with sequential Cu(I)-mediated conjugate additions. A sequence with dihydroxylation, conjugate addition, and β -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.



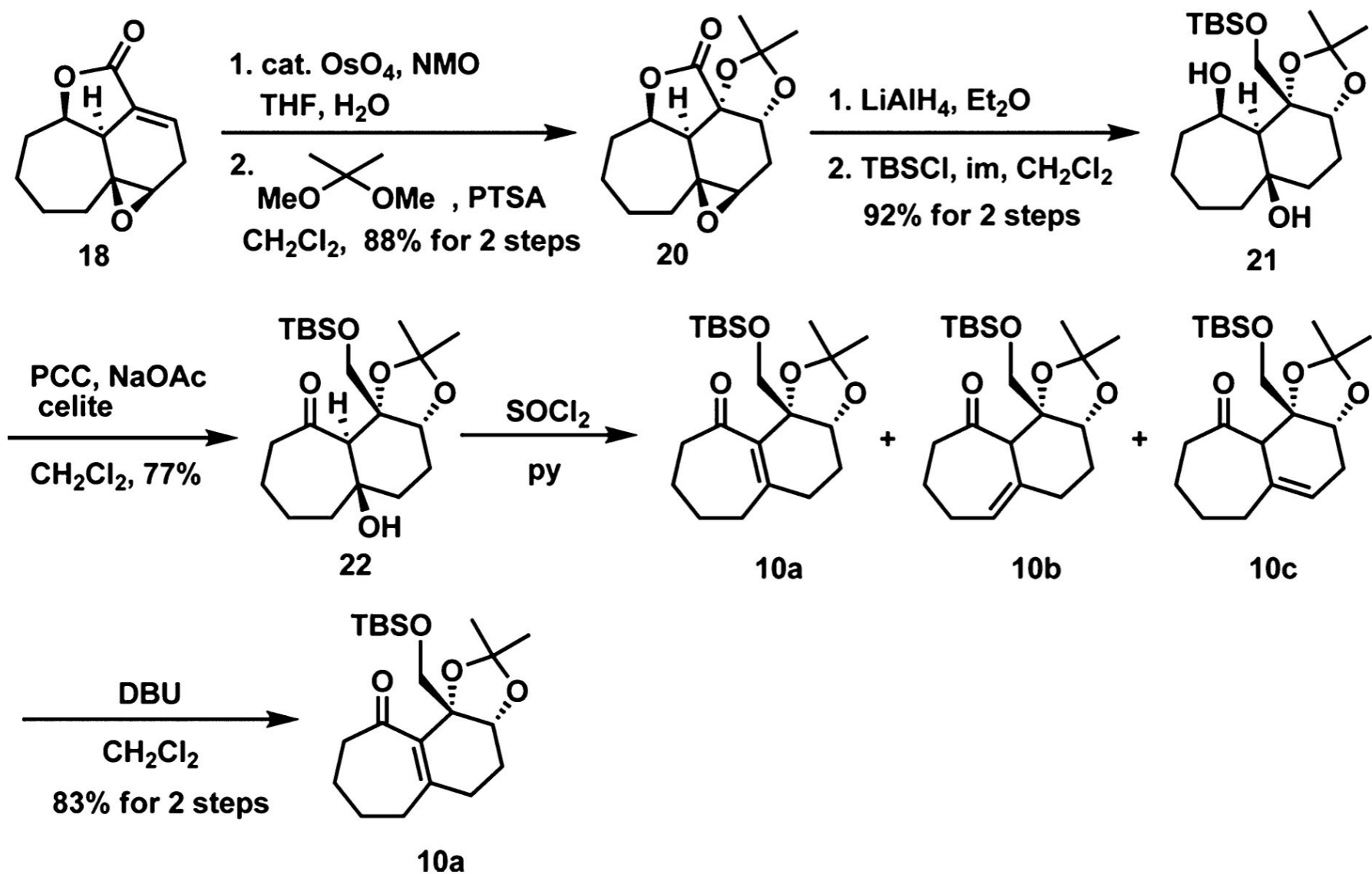
Scheme 1. Retrosynthesis of Guanacastepenes N and O



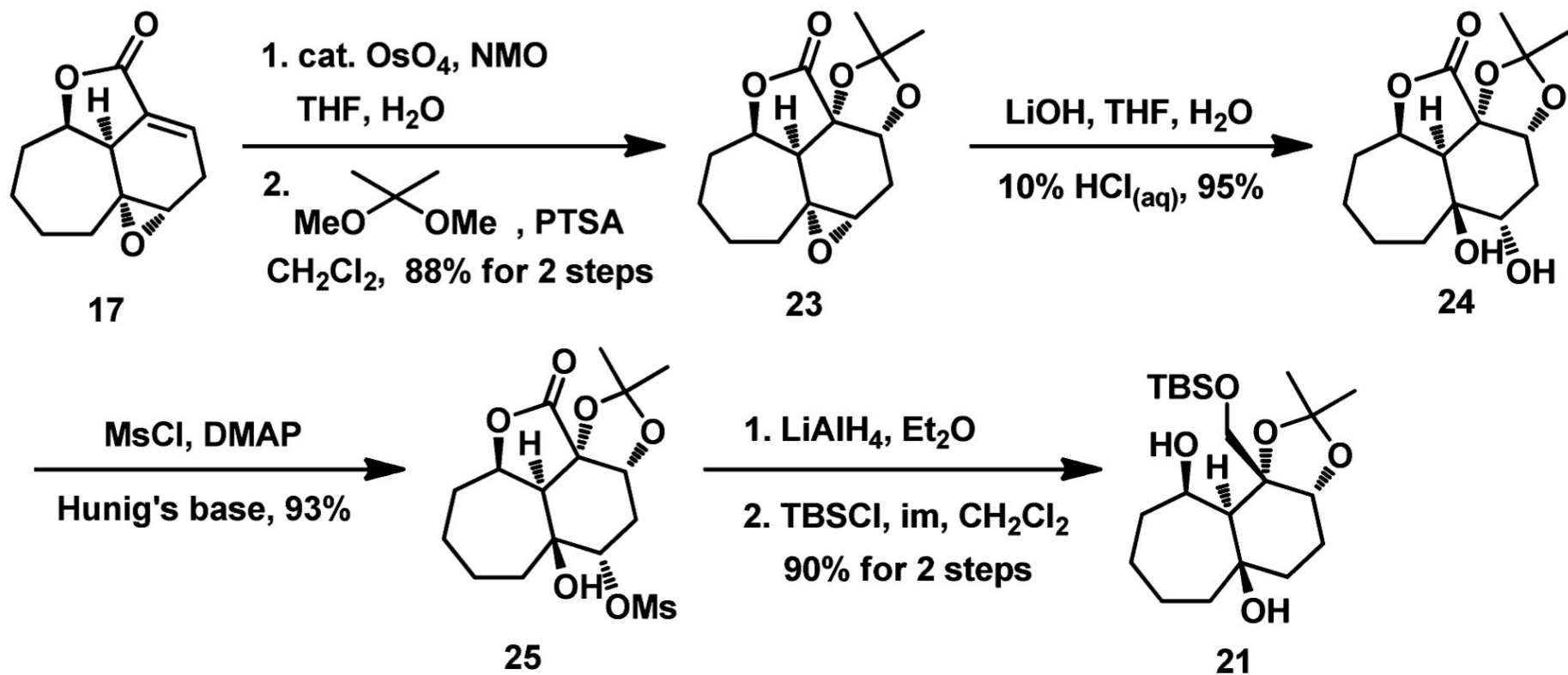
Scheme 2. Synthesis of Compounds 17 and 18



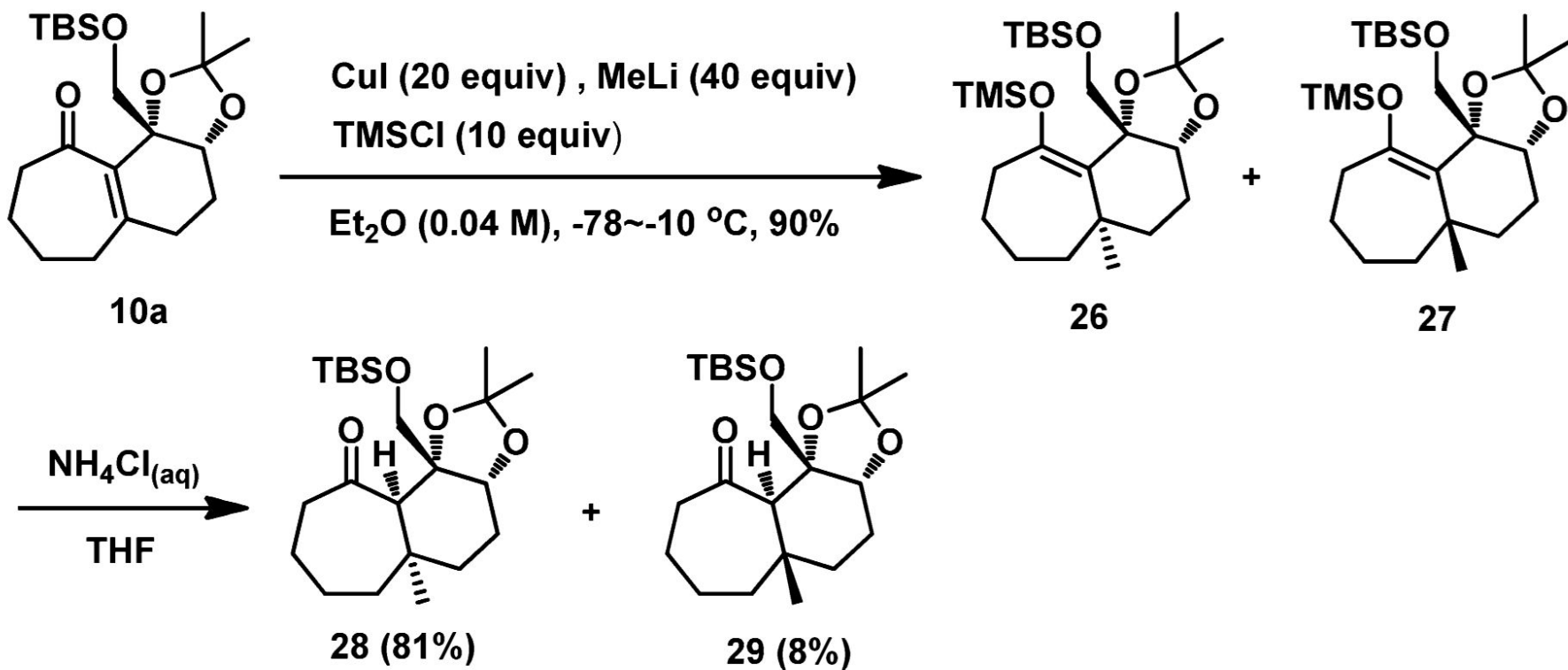
Scheme 3. Synthesis of Enone 10a



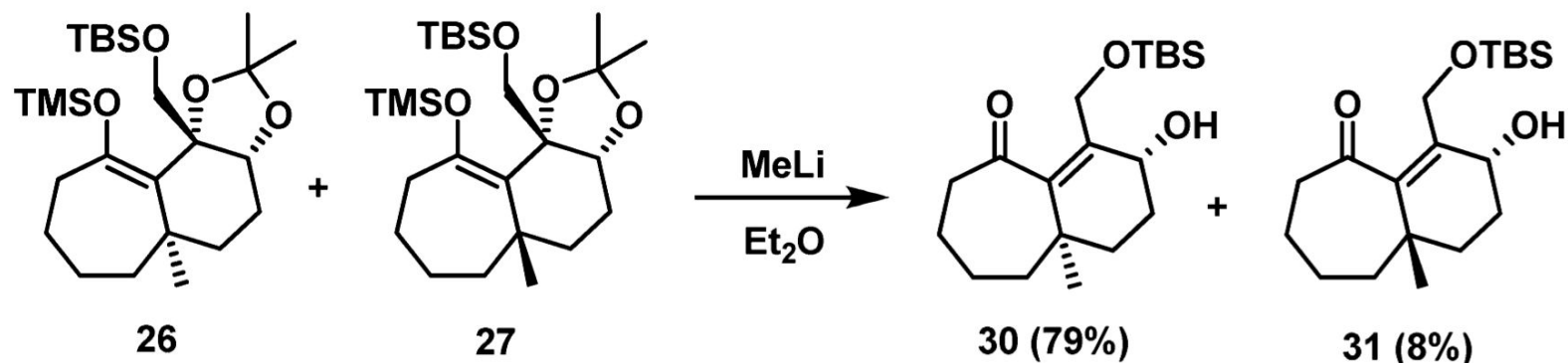
Scheme 4. Synthesis of Diol 21



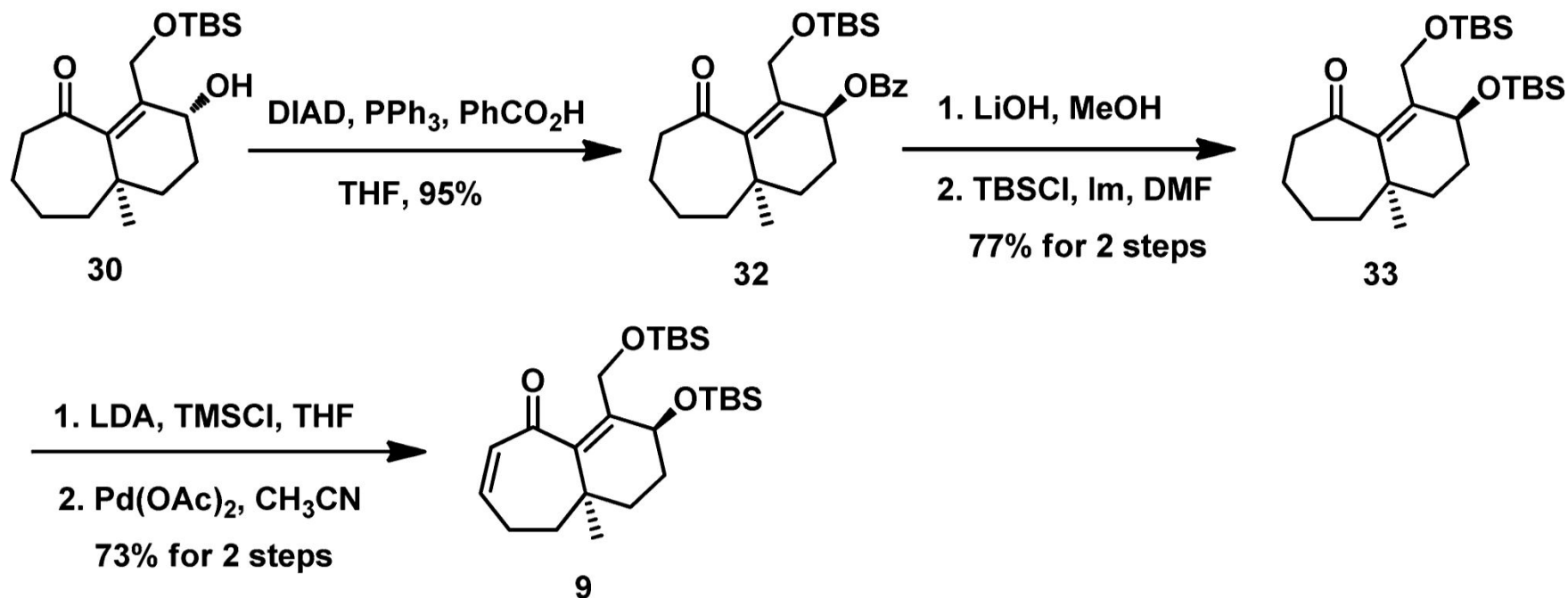
Scheme 5. Synthesis of Compounds 28 and 29



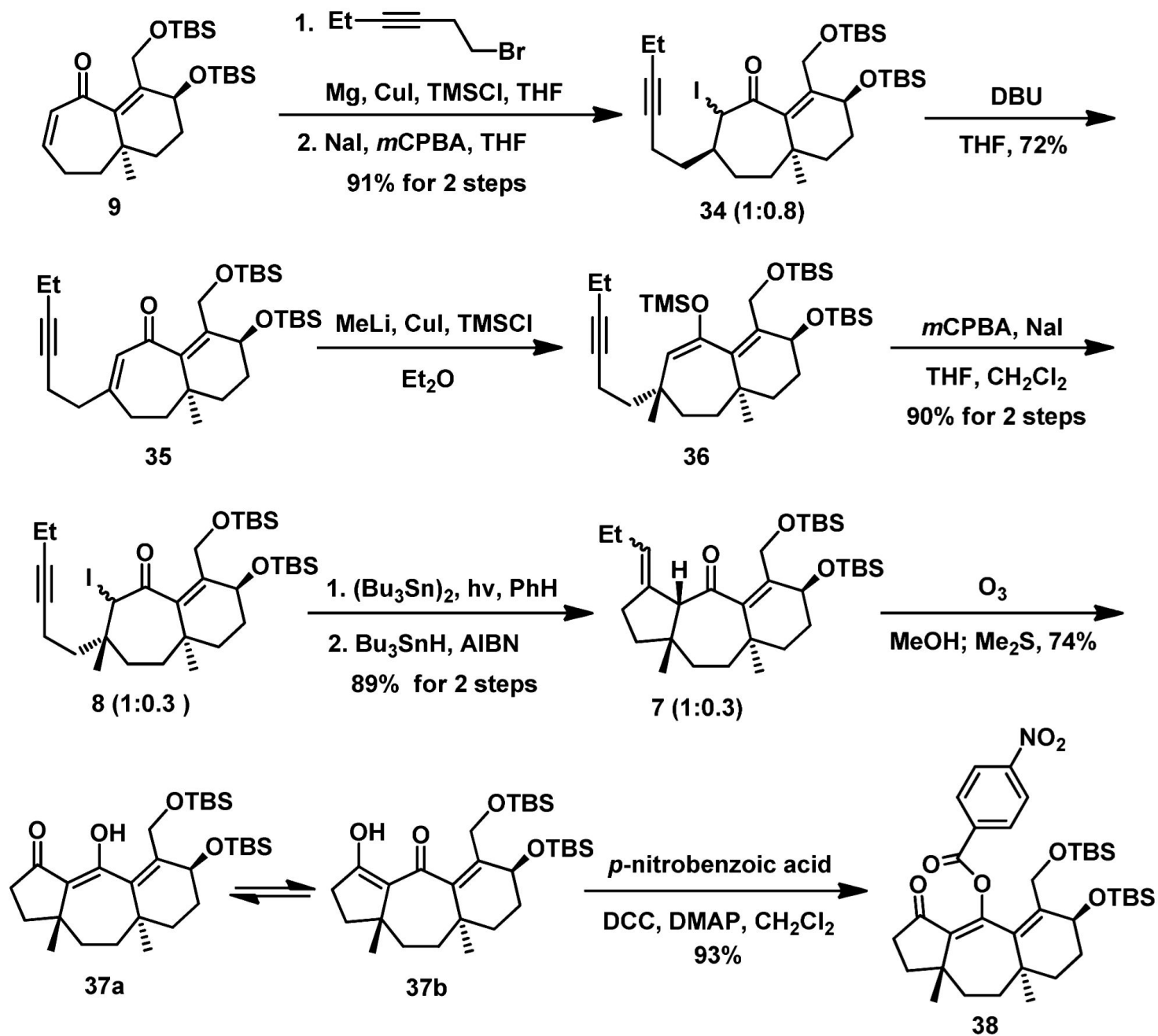
Scheme 6. Synthesis of Enones 30 and 31 via β -Elimination Reaction



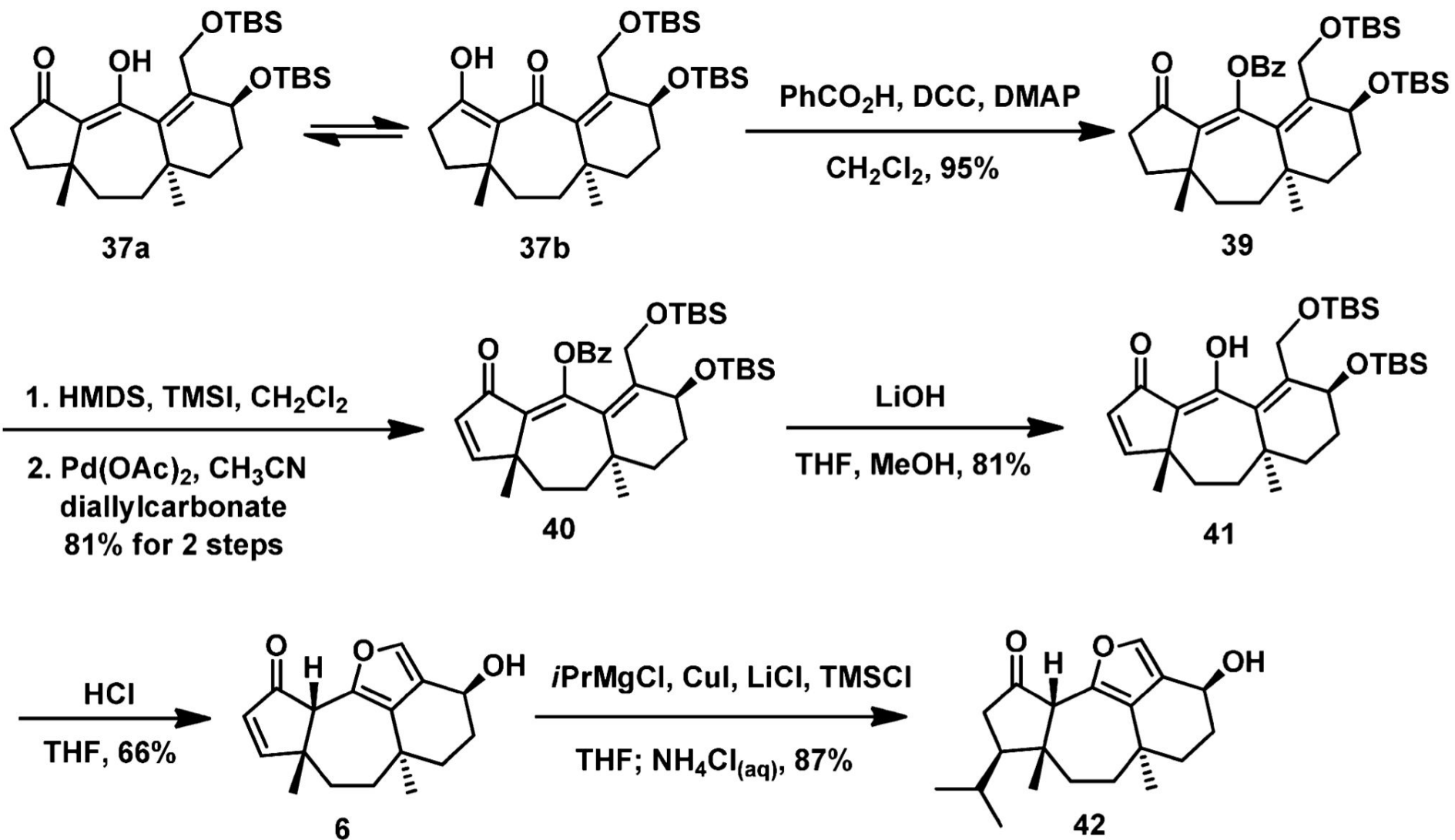
Scheme 7. Synthesis of Dienone 9



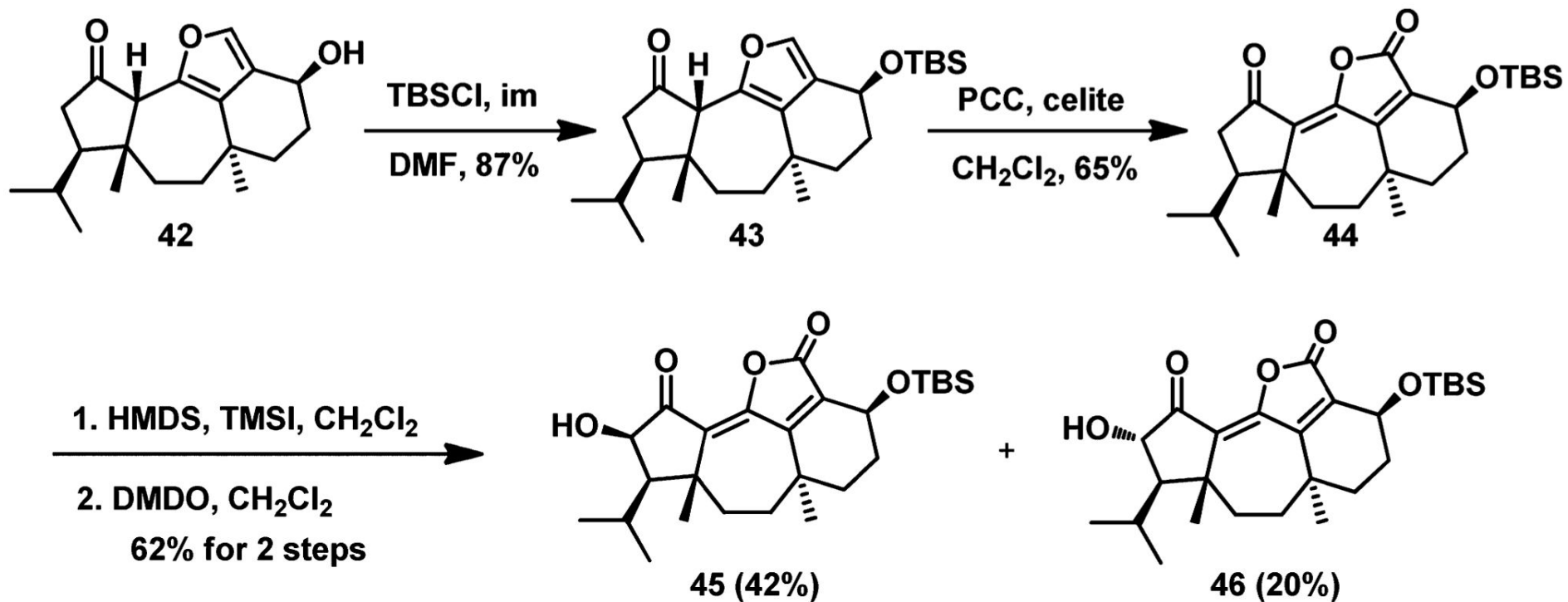
Scheme 8. Synthesis of Compounds 37a, 37b, and 38



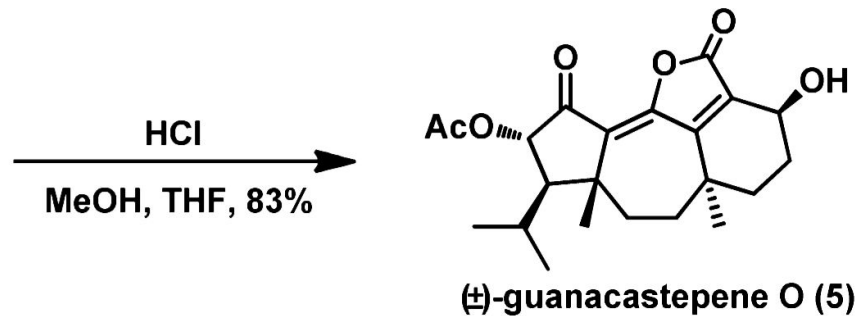
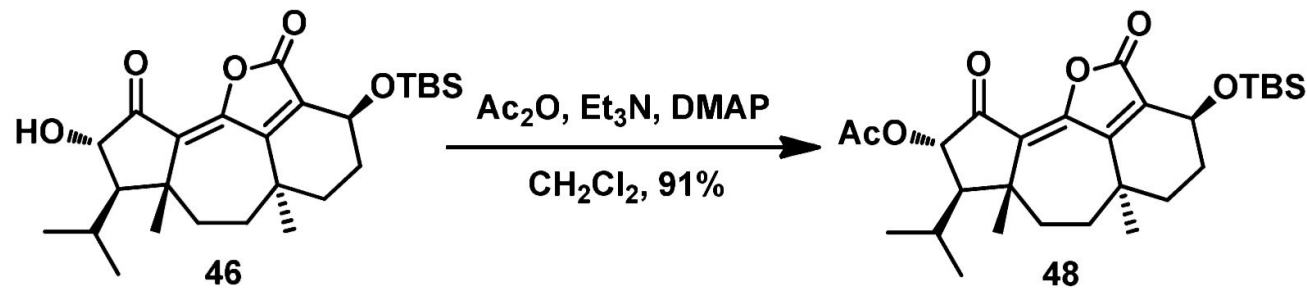
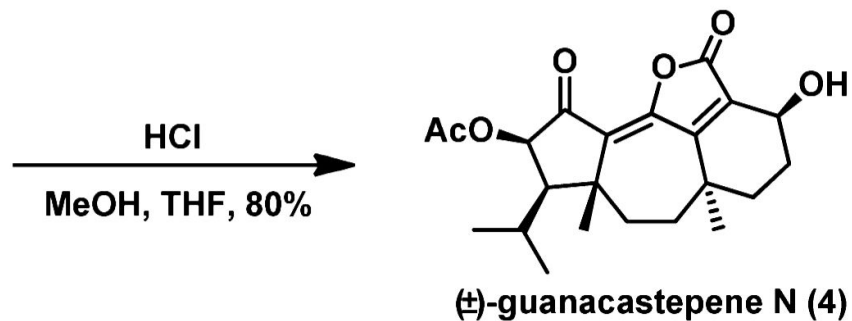
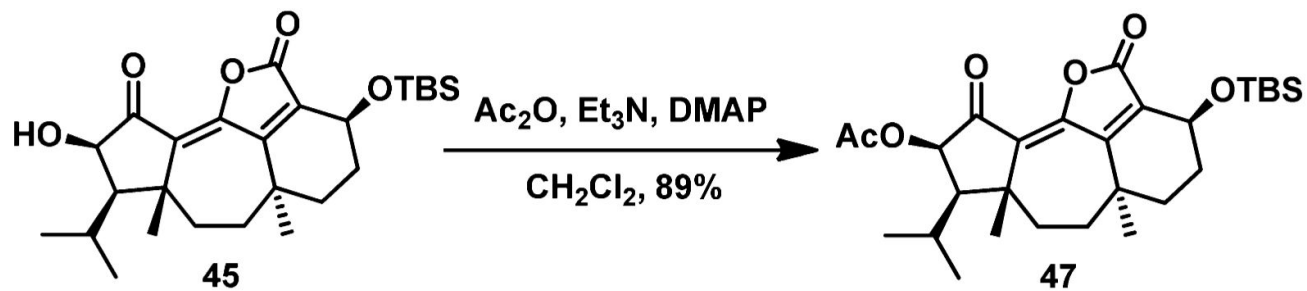
Scheme 9. Synthesis of Furan 42



Scheme 10. Synthesis of Lactones 45 and 46



Scheme 11. Synthesis of Guanacastepenes N and O



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

