Asymmetric Total Synthesis and Biosynthetic Implications of Perovskones, Hydrangenone, and Hydrangenone B

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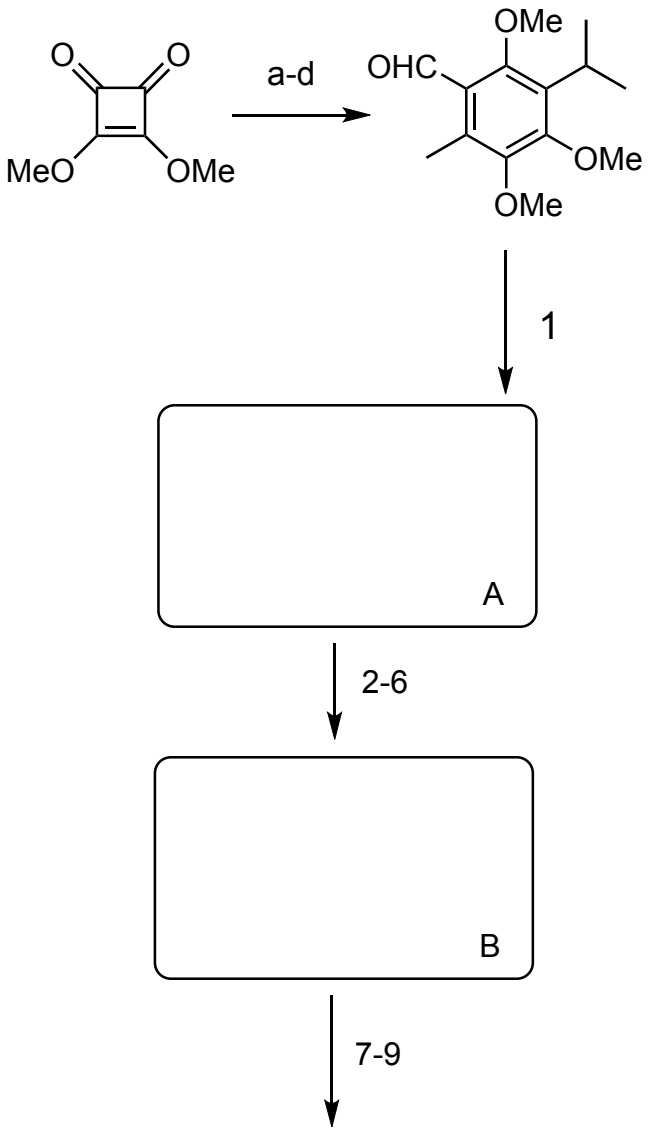
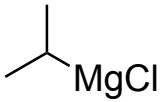
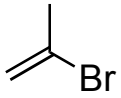
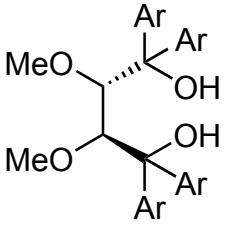


a.  then TFAA

b. *t*-BuLi  *then* toluene, 70 °C

c. NaH, MeI

d. $SnCl_4$, Cl_2CHOMe



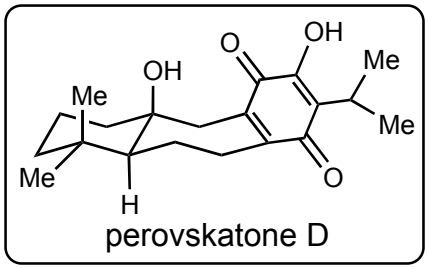
Ligand **1**

1. *hv* (366 nm), Ti(O*i*-Pr)$_4$, Ligand **1**
2. IBX
3. $PdCl_2$, H_2
4. $Li(tBuO)_3AlH$
5. PhP_3, I_2, quinoline
6. AIBN, Bu_3SnH
7. Li, NH_3/THF
8. DDQ
9. AgO, dioxane/HNO_3

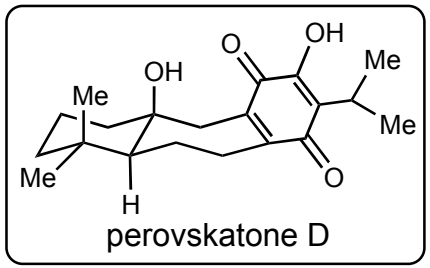
Step 1:
Draw A with correct stereochemistry
Hint:
This reaction is called "photoenolization/Diels−Alder".
Check the natural product for the stereochemistry outcome of this reaction

Step 4:
hint: It's a bulky reducing agent

Step 5: Name the reaction



perovskatone D



perovskatone D

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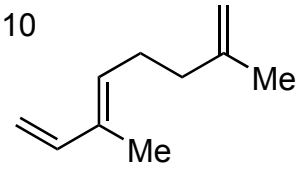
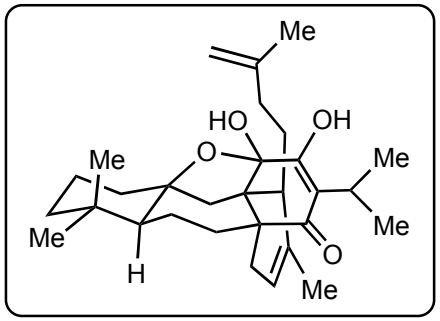


10. $Eu(fod)_3$

Step 10:
Endo or exo?
This is a biomimetic reaction, suggest any other reaction conditions you may want to try when you do this reaction?



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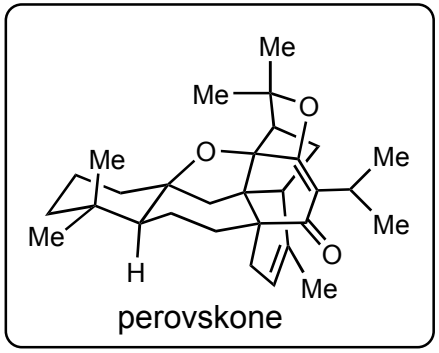
11. $Cu(OTf)_2$

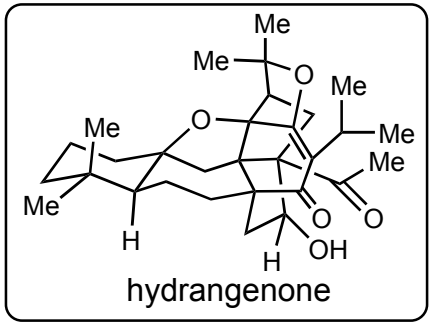
12. O_3, Me_2S
13. pyrrolidine, AcOH

Step 11:
This is also a biomimetic reaction, the mechanism? Which named reaction it would possibly be?



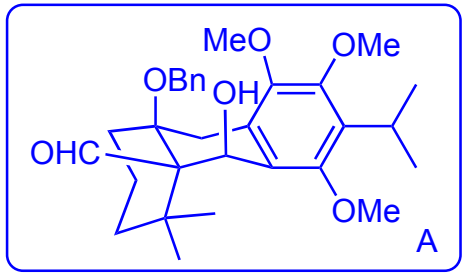
perovskone

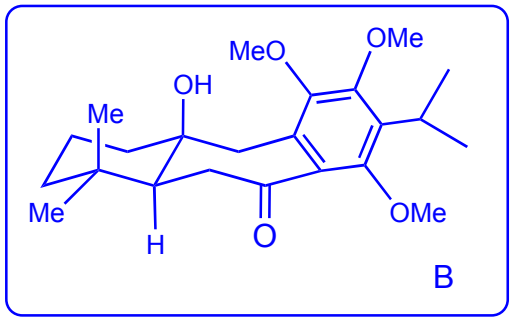
12-13



hydrangenone

step b: Moore rearrangement





Step 5: Appel reaction

Step 10: *endo*

Most of the biomimetic DA reaction are *endo* selectivity.

Other conditions: heating in toluene or xylene or neat, high pressure, heating in aqueous $LiClO_4$

Step 11

Prins reaction