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

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**OMe**

**OMe**

**OMe**

**OMe**

**a-d**

**OMe**

**OMe**

**OMe**

**OMe**

**a. MgCl then TFAA**

**b. t-BuLi then toluene, 70 °C**

**c. NaH, Mel**

**d. SnCl₄, Cl₂CHOME**

**Ar**

**Ar**

**OH**

**Ar**

**OH**

**Ar**

**OH**

**Ligand 1**

1. *hv* (366 nm), Ti(O-i-Pr)₄, Ligand 1
2. IBX
3. PdCl₂, H₂
4. Li(tBuO)₃AlH
5. PhP₃, I₂, quinoline
6. AIBN, Bu₃SnH
7. Li, NH₃/THF
8. DDQ
9. AgO, dioxane/HNO₃

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
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?

Step 11: 
This is also a biomimetic reaction, the mechanism? Which named reaction it would possibly be?
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 LiClO₄

Step 11
Prins reaction