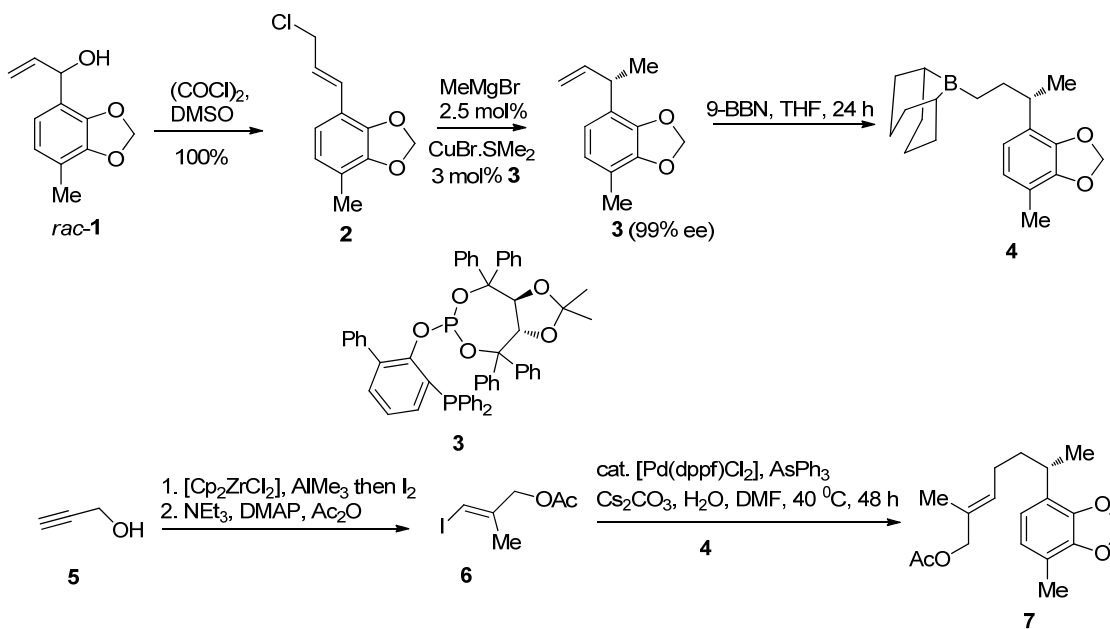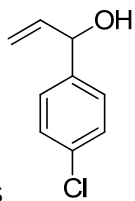Submitted by Gong XU

# From **"An enantioselective total synthesis of helioporins C and E"**

## *Problems:*



1. Explain the formation of the Cinnamyl Chloride **2** from Allylic alcohol **1**.
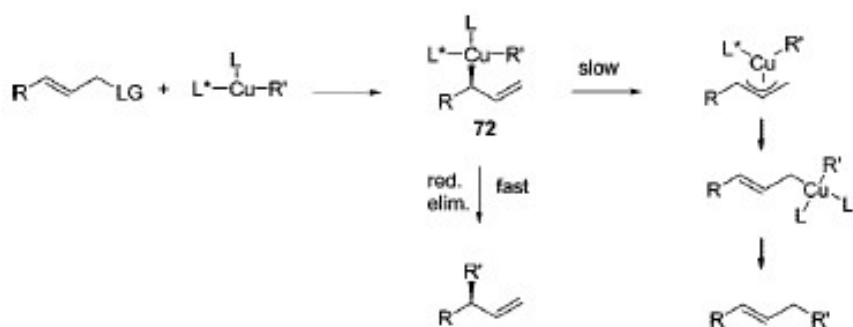   How is the reacton with the substrate having electron-poor aromatic rings,

   

   such as , under the same conditions?

2. Propose a intermediate during the copper-catalyzed asymmetric alllylic substitutions.

3. Give the mechanism of the reaction from **5** to **6**.

# Solutions:

1. Aryl allylic alcohols are converted to halogenated unsaturated ketones or allylic halides using excess Moffatt-Swern reagent. Electron-poor aromatic rings favor formation of the halogenated ketone, while electron-donating substituents in the ortho or para positions favor formation of the allylic halide.
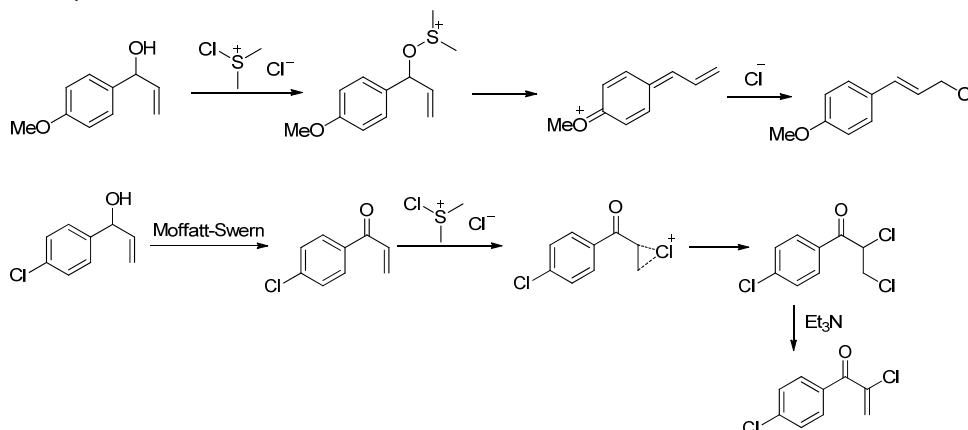


2. The copper-catalyzed asymmetric allylic substitutions most likely proceed through a **CuIII intermediate**. Oxidative addition of the allylic substrate to the organocopper(I) complex leads to CuIII intermediate. If the CuIII intermediate is formed from a monoalkylcopper(I) species, there will be only one R′ group on copper and a fast reductive elimination takes place. Electron-withdrawing ligands will increase the rate of reductive elimination, whereas electrondonating ligands slow the reductive elimination. Rearrangement to allyl- and finally primary σ-allylcopper should be slow compared to reductive elimination. With two R′ groups on copper, reductive elimination from CuIII intermediate is slowed and rearrangement to the primary σ-allylcopper species is favored.



3.



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$Me_3Al$ + $Cl_2ZrCp_2$ ⇌ $Me_2Al$⟨Me, Cl⟩$ZrCp_2$(Cl) ⇌ $Me_2Al$⟨Cl, Cl⟩$ZrCp_2$(Me)

$\xrightarrow{RC\equiv CH}$ $Me-ZrCp_2$⋯Cl⋯$AlMe_2Cl$ (RC≡CH) ⟶ (R)(Me)C=C(H)(ZrCp_2)⟨Cl, Cl⟩AlMe_2

⟶ (R)(Me)C=C(H)(AlMe_2)⟨Cl, Cl⟩ZrCp_2 ⇌ (R)(Me)C=C(H)(AlMe_2) + $Cl_2ZrCp_2$



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