

University of Massachusetts Boston, Department of Chemistry
Chemistry Doctoral Program, Written Qualifying Examinations

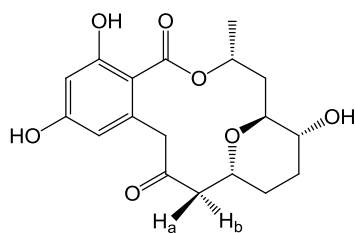
July 18, 2011

Organic Chemistry I

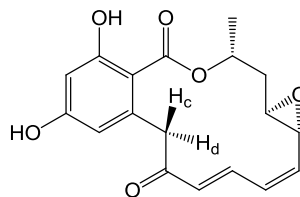
Questions are based on the following article:

Martinez-Solorio, D.; Belmore, K. A.; Jennings, M. P. "Synthesis of the Purported *ent*-Pochonin J Structure Featuring a Stereoselective Oxocarbenium Allylation" *J. Org. Chem.* **2011**, 76, 3898–3908.

1. Consider following compounds:



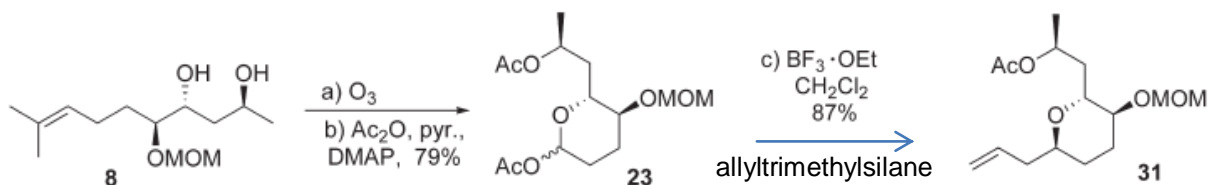
pochonin J



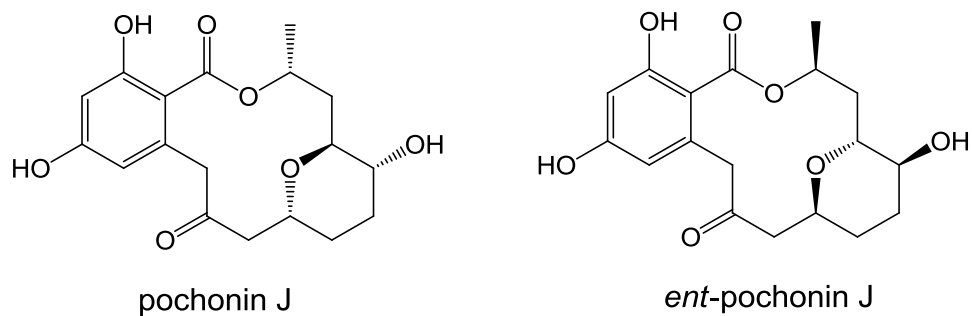
radicol

- a. (1 point) For these two molecules, identify all the stereogenic centers and determine their configurations.
- b. (1 point) What are the relationship (homotopic, heterotopic....) between H_a and H_b as well as H_c and H_d ? What are the ^1H NMR splitting patterns for H_a and H_b as well as H_c and H_d ?

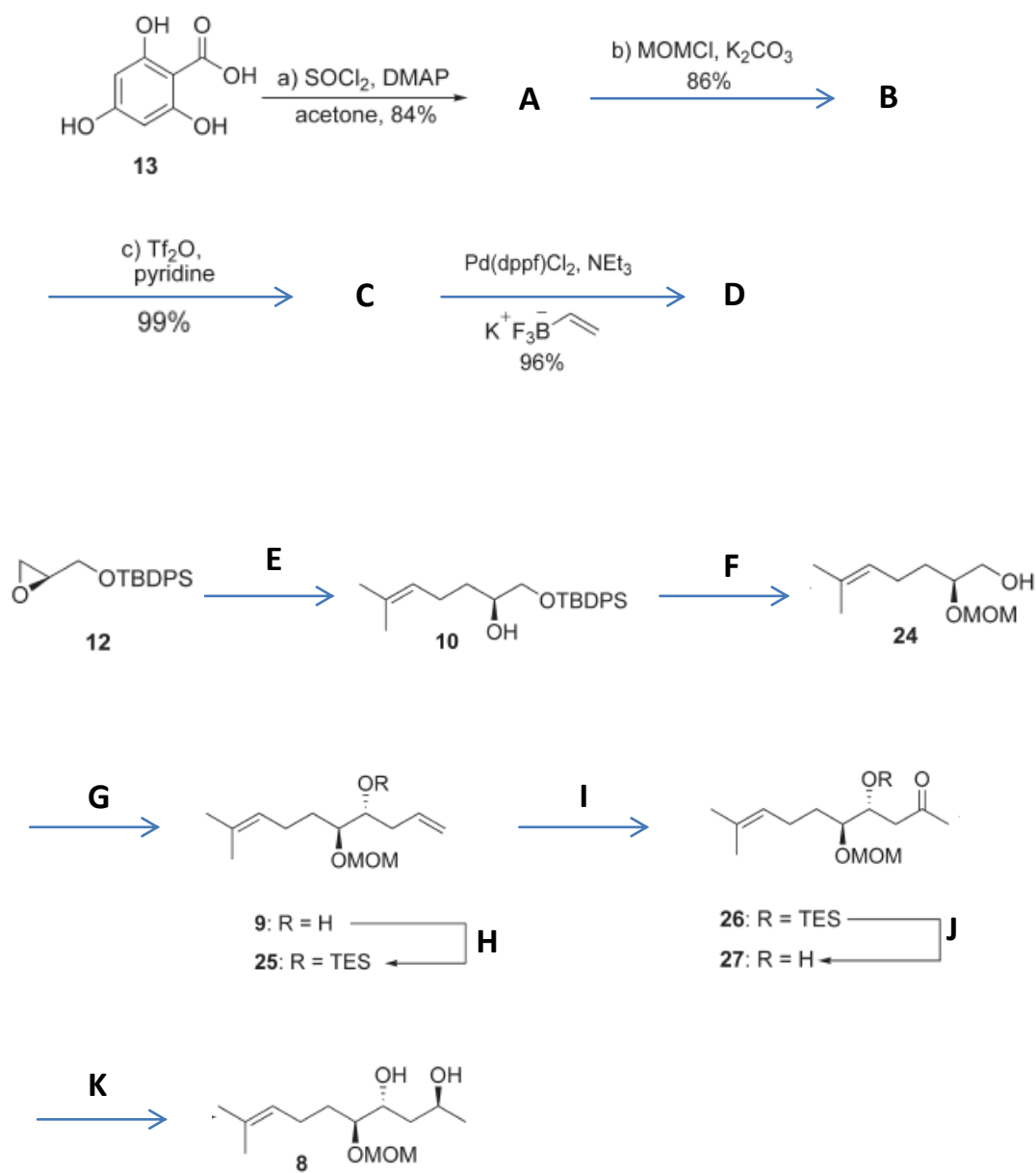
2. (2 points) Give the reaction mechanisms for converting **8** to **23** and then to **31**.



3. (0.5 points) This work discovered that the spectral (1H NMR and ^{13}C NMR) and optical rotation data of synthetic *ent*-pochonin J did not agree with the natural sample pochonin J. If the structure of *ent*-pochonin is correct. The structure proposed for natural sample pochonin J could still be right or wrong, and why?



4. Consider following transformations.



a. (2 points) Give the structures of compounds **A** to **D**.

b. (3.5 points) Give the reaction conditions **E** to **K**.

Green Chemistry Questions

1. (1 point) From a green chemistry point-of-view, comments on the major differences between “discovery chemistry” and “process chemistry”.
2. (1 point) What are the major green chemistry challenges in the total synthesis of natural products? Do you aware any examples of using green synthetic techniques to benefit the total synthesis?