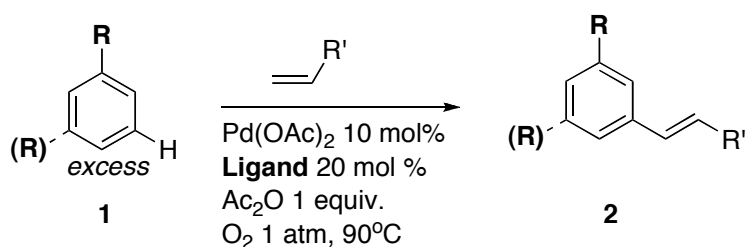


# Cumulative Examination Organic Chemistry

By: Vladimir Gevorgyan  
(February 4, 2010)

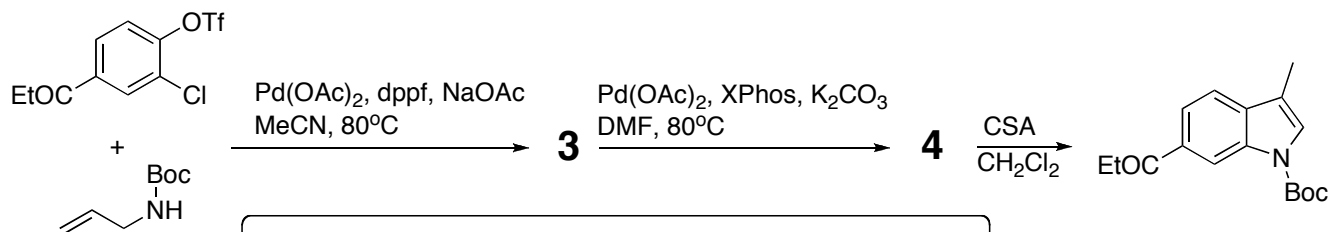
Try to answer all questions. Partial credits will be given for incomplete answers.  
Extra credits will be given for detailed answers.

- (I) **30 pts.** During his very recent seminar at UIC, Prof. Jin-Quan Yu (Scripps) described development of the *meta*-selective olefination reaction of aromatic compounds proceeding via a C-H activation pathway [*J. Am. Chem. Soc.* **2009**, *131*, 5072].



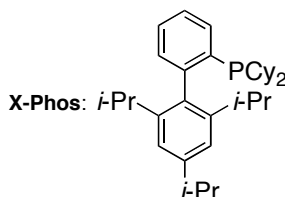
- (1) **10 pts.** Explain the role of **R group(s)**, give at least two examples of **R** employed in this reaction;
- (2) **10 pts.** Draw the structure of pyridine-based **Ligand**, successfully employed in this reaction, and provide the author's reasoning for it;
- (3) **10 pts.** Draw the reasonable detailed mechanism for transformation **1** to **2**;

- (II) **20 pts.** Draw intermediates **3** and **4** (**8 pts.**). Provide reasonable mechanisms for all three steps (**12 pts.**). [Baxter *et al*, *Org. Lett.* **2010**, ASAP, DOI:10.1021/ol902636v]

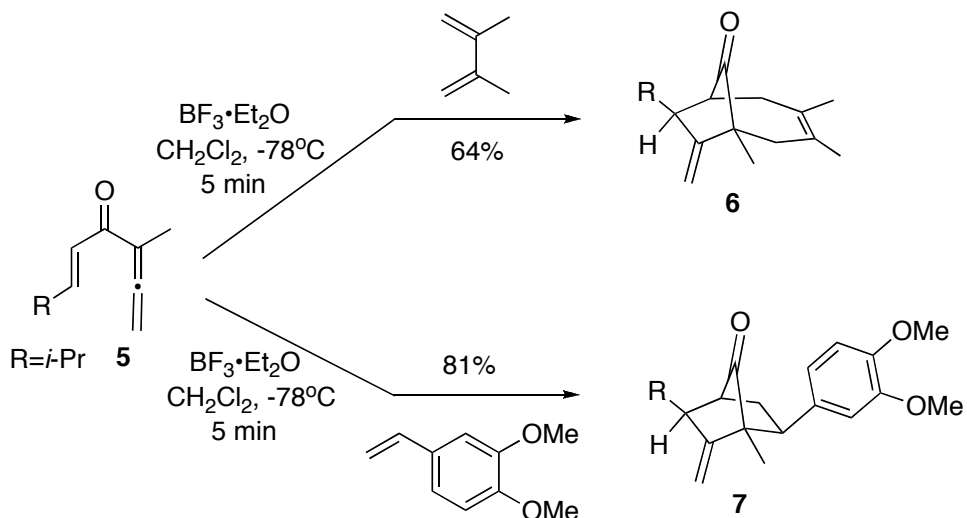


**Hints**

**CSA:** Camphorsulfonic acid  
**dppf:** 1,1'-Bis(diphenylphosphino)ferrocene  
**Boc:** *tert*-Butoxycarbonyl

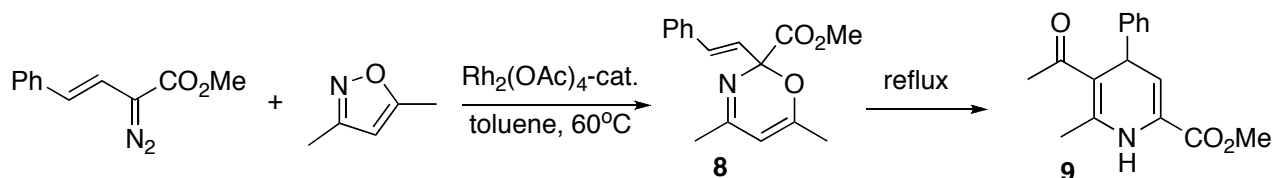


(III) **20 pts.** [Burnell *et al*, *J. Am. Chem. Soc.* **2010**, 132, 1685]. Provide mechanism for the interrupted Nazarov cyclization of allenyl vinyl ketone **5** into bicyclic structures **6** and **7** (**2 x 10 pts.**).



Questions from past exams

(IV) **20 pts.** [Davies *et al*, *J. Am. Chem. Soc.* **2008**, 130, 8602]. Propose **detailed** mechanism for the formation of **5** and **6** (**2 x 10 pts.**).



(V) **10 pts.** [Wang *et al*, *Adv. Synth. Catal.* **2008**, 350, 2359]. Draw the structures for intermediates **10** and **11** (**2 x 5 pts.**).

