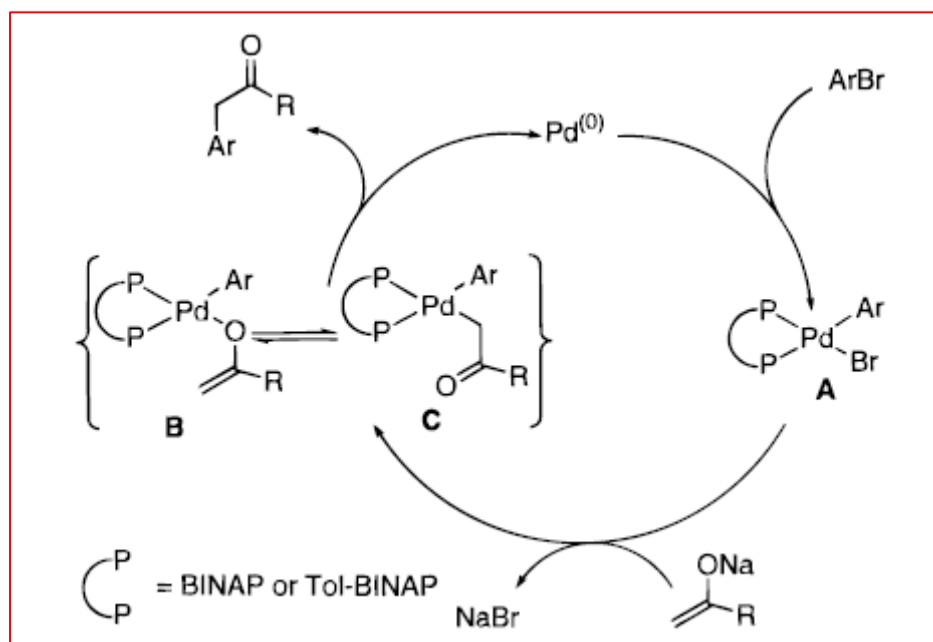
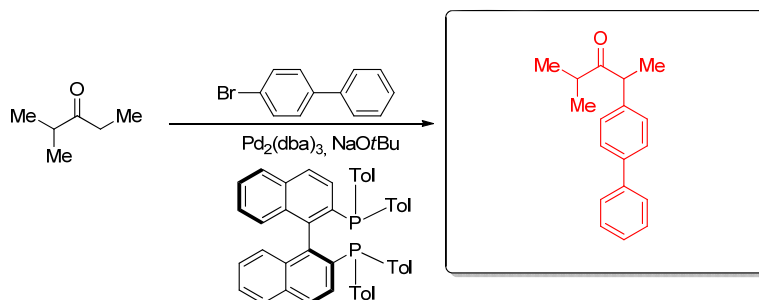




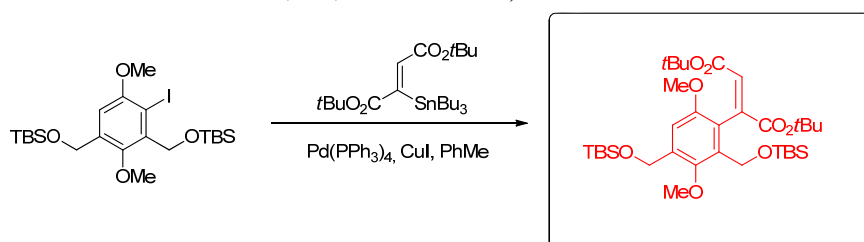
Problem Set No. 7 Key

1. Provide the following product and a potential catalytic cycle. The resting state is predicted to be a Pd(0) species?



Buchwald et al. J. Am. Chem. Soc. 1997, 119, 11108-11109

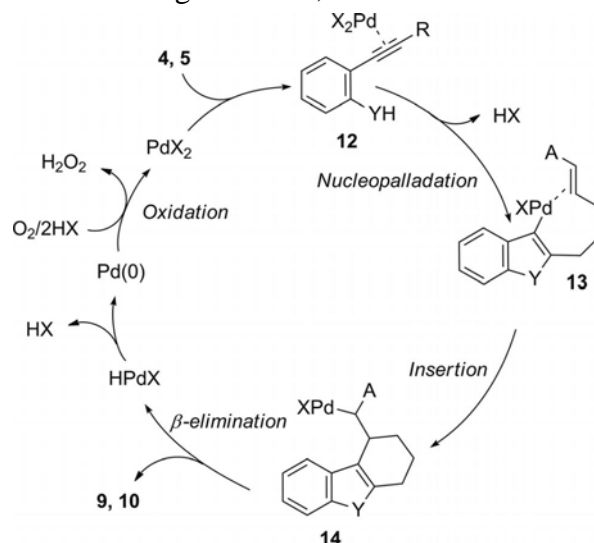
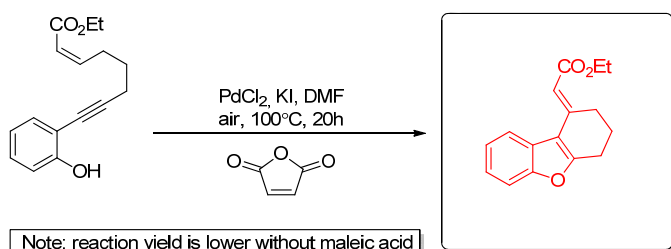
2. Provide the product. What is the name of this reaction? What role does CuI play (see Angew. Chem. Int. Ed. 2004, 43, 4704 – 4734)



“The effect of CuI is to mitigate the “autoretardation” by free L of the rate determining associative transmetalation.”

See Eur. J. Org. Chem. 2012, 107–113

3. Based on the catalytic cycle, predict the products of the following reactions;

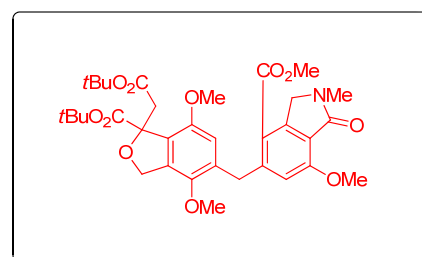
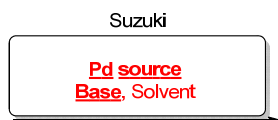
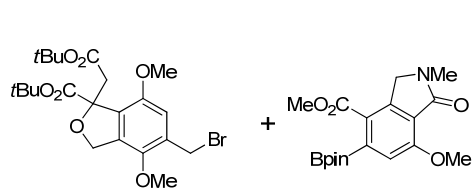


Based on the catalytic cycle, what role(s) do you think maleic acid plays?

The maleic acid most likely scavenges both the HX and H₂O₂ formed.

See *Eur. J. Org. Chem.* **2012**, 99–106

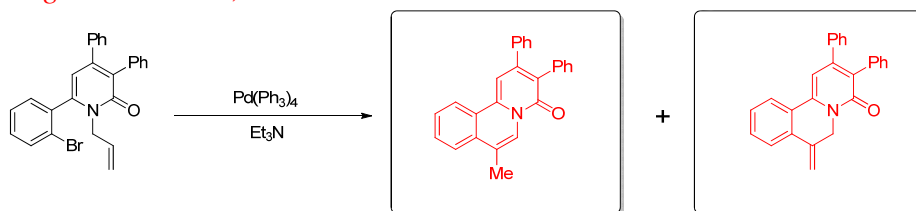
4. Draw the product and provide the reagents.



Eur. J. Org. Chem. **2012**, 107–113

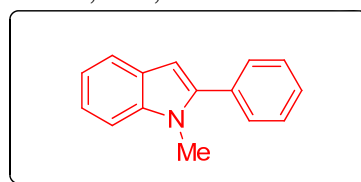
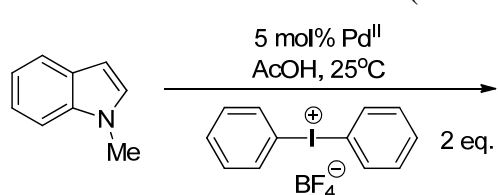
5. Provide the products

Eur. J. Org. Chem. **2012**, 275–280



Both are tricyclic

6 Provide the product. What is significant about this reaction? What is the structure of the IMes ligand? Why do the two catalyst provide different results? What is significant about the new mechanism that is offered (see *JACS* **2006**, 128, 4972-4973)



Pd(OAc)₂ 49%, 5 min
IMesPd(OAc)₂ 86%, 18 h

The reaction is a room temp C-H activation. IMes = NHC carbene ligand. The Pd(OAc)₂ appears to decompose leaving SM behind. The IMes ligand stabilizes the catalytic intermediate better. Pd(II)→Pd(IV).