

# Mid-Term

## Chemistry 531

### Survey of Organic Reactions

Wednesday October 31, 2007

Name: \_\_\_\_\_.

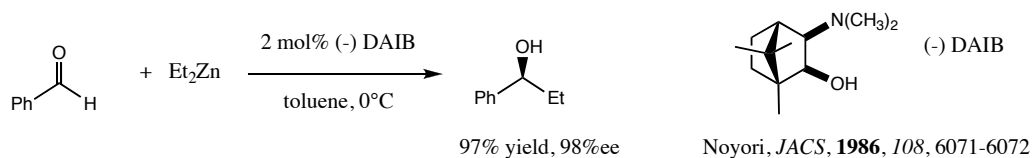
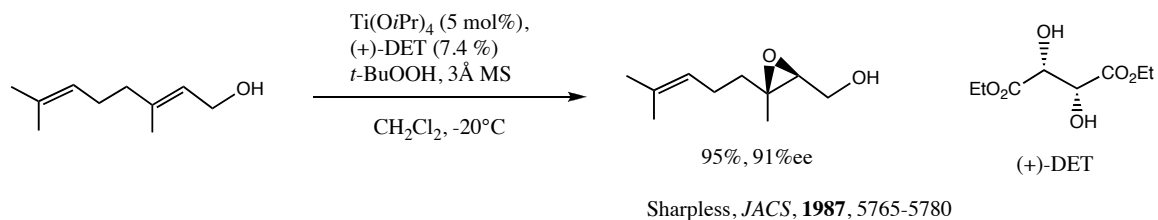
**The exam is worth a total of 150 points; answer six out of the following seven questions. Please show all work to receive full credit for an answer.**

**By putting your name on this exam, you agree to abide by California State University, Northridge policies of academic honesty and integrity**

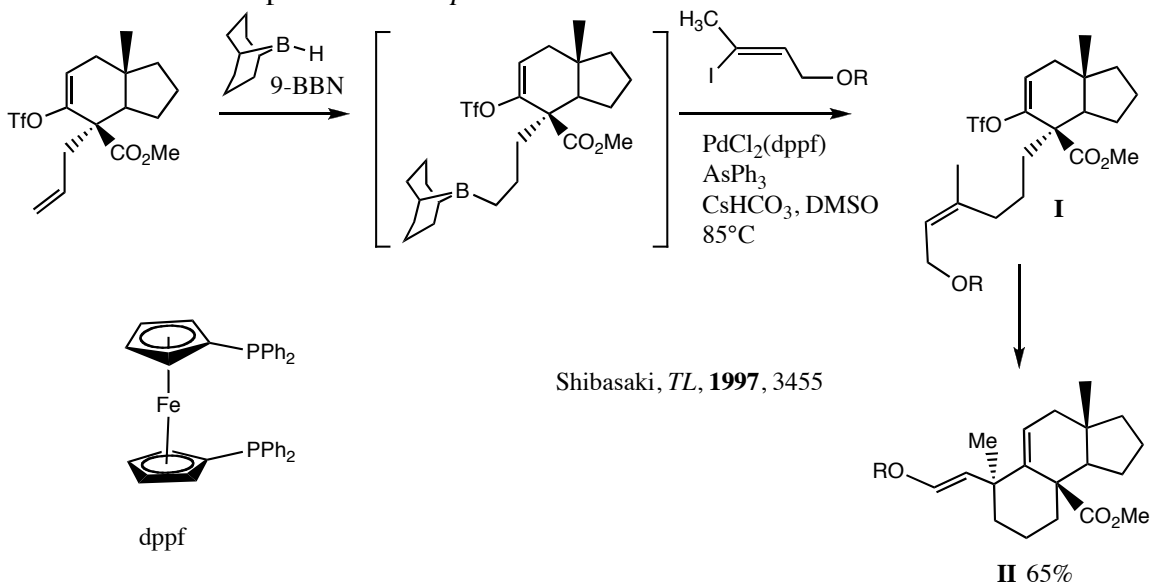
**Molecular models are allowed for this exam. Calculators are not needed.**

**Good Luck!**

1. Utilizing the following examples, explain in detail what is meant by the term “ligand accelerated catalysis”. What would be the result in the absence of the “ligand”, in terms of yield, reaction rate, and/or enantioselectivity? Choose *one* example below and depict how the ligand-metal complex interacts with the substrate(s) in the bond-forming step. *25 points*



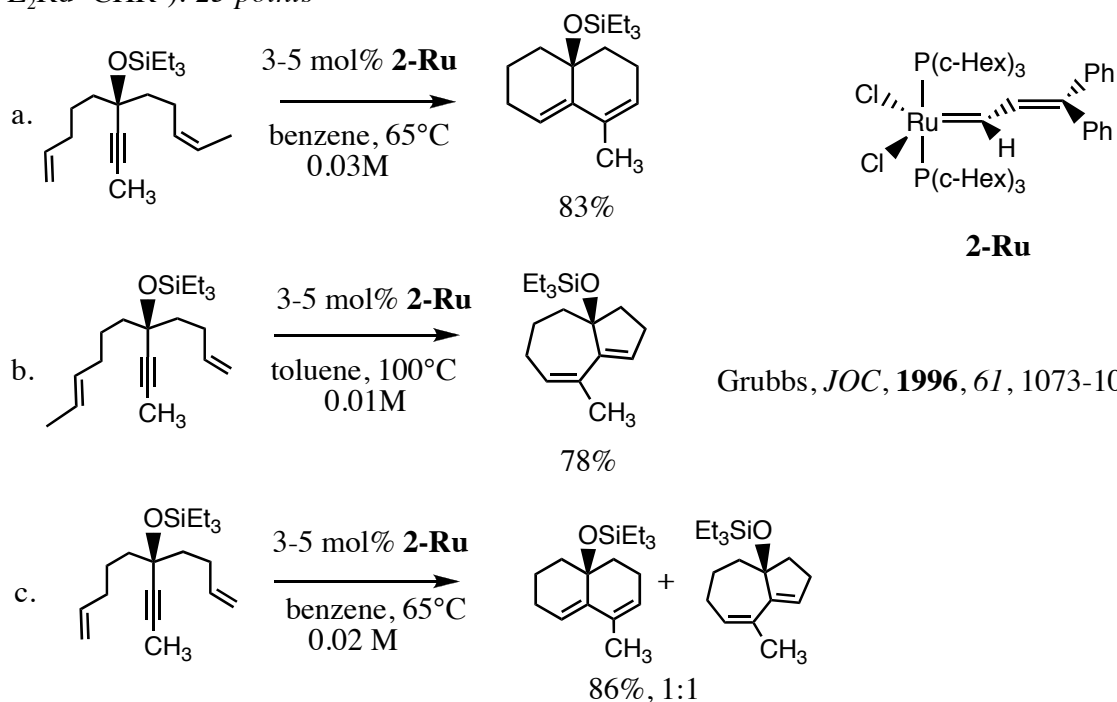
2. The following scheme represents an example of a tandem Suzuki-Heck reaction. For the Suzuki process, an alkyl borane is cross-coupled with a vinyl iodide to give intermediate **I**, which subsequently undergoes an intramolecular Heck reaction to form product **II**. 25 points



- Briefly outline a general catalytic cycle for the Suzuki reaction, using  $R^{sp^2}-I$  for the unsaturated halide,  $R'CH_2CH_2BX_2$  for the borane, and  $PdL_2$  for the catalyst. Indicate why the catalyst  $PdCl_2(dppf)$  is needed for this particular Suzuki reaction (i.e., what potential side reaction may occur if the standard catalyst  $Pd(PPh_3)_4$  is employed?). What is the purpose of adding base (in this case  $CsHCO_3$ ; in other cases  $TIOH$  or aqueous  $K_2CO_3$ ) to Suzuki reactions?
- Briefly outline a general catalytic cycle for the Heck reaction, using  $R^{sp^2}-OTf$  for the unsaturated triflate,  $(R')_2C=CHCH_2OR$  for the alkene component, and  $PdL_2$  for the catalyst. Why is base also needed for Heck reactions? How do silver salts (such as  $Ag_2CO_3$ ) facilitate the Heck reaction?

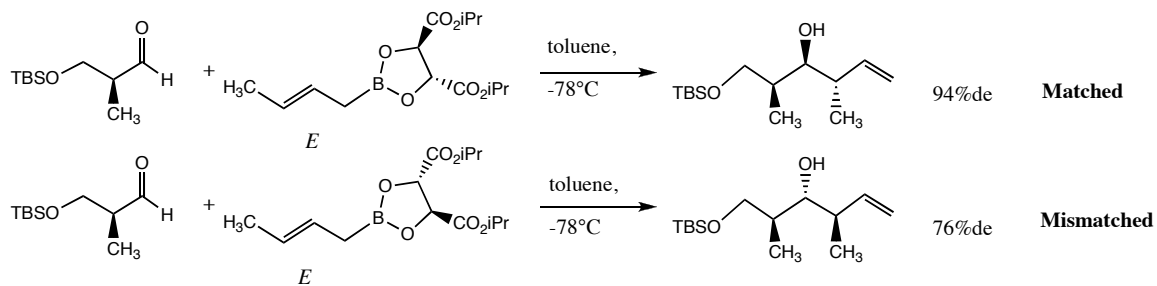


3. Briefly outline the mechanism of the catalytic ring-closing metathesis reaction for **one** of the following diene starting materials (abbreviate the catalyst as  $L_2Ru=CHR'$ ): 25 points



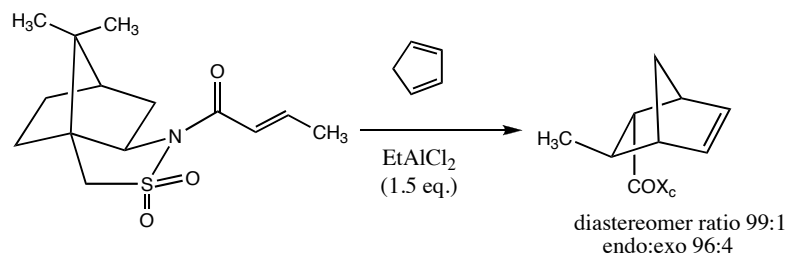
Discuss how regiochemical control is obtained in the first two cases (a and b), while the last case (c) lacks regiocontrol.

4. In the following example, explain what is meant by the terms “matched” and “mismatched”, and draw an appropriate transition state assembly which rationalizes the stereochemical outcome in each case: 25 points

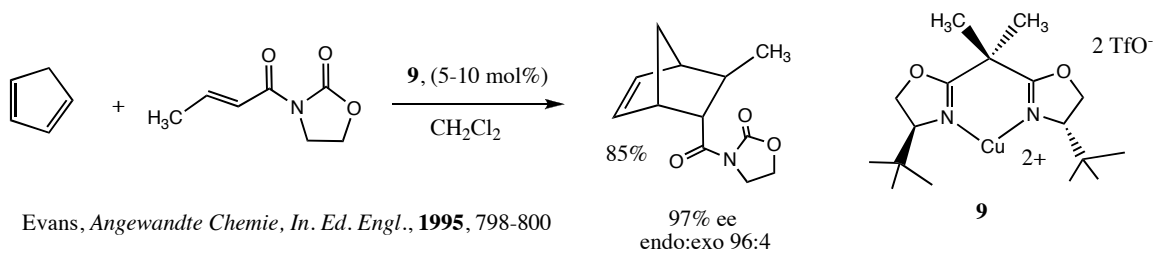


Roush, *JACS*, **1985**, *107*, 8186-8190  
 Roush, *JOC*, **1987**, *52*, 316-318

5. The transformations below represent two different strategies for obtaining enantio-enriched products in the Diels-Alder reaction. Define and differentiate between chiral-auxiliary mediated asymmetric Diels-Alder reactions and catalytic asymmetric Diels-Alder reactions. What are the advantages and drawbacks of each strategy? In each case, diagram the transition state assembly showing how  $\pi$ -facial discrimination is achieved. Why do the *dienophiles* prefer the *s-cis* form in each case? 25 points



Oppolzer, *Helv. Chim. Acta*, **1989**, 123.



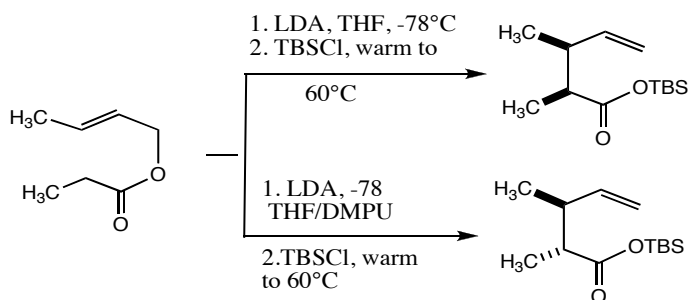
Evans, *Angewandte Chemie, In. Ed. Engl.*, **1995**, 798-800





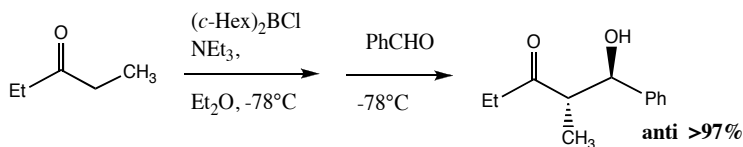
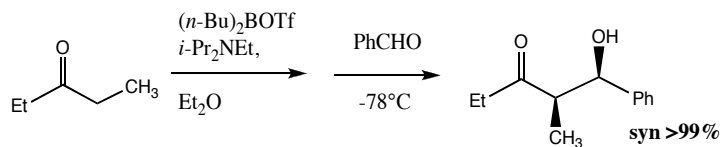
6. Enolate/Enol geometry can be a crucial factor in determining the stereochemical outcome of a given transformation. This is true in both the Ireland-Claisen rearrangement and the aldol reaction. Select *either* the Claisen or aldol process shown below, and show the geometry of the enolate formed in **each** separate case, and then draw appropriate transition state structures that rationalize the stereochemical outcome in **each** case: 25 points

**Ireland-Claisen:**



Ireland, *JOC*, **1991**, 650.

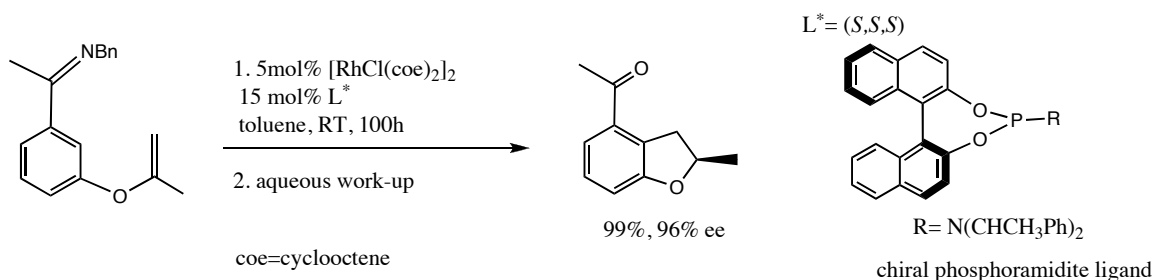
**Aldol:**



*JACS*, **1979**, 6120  
*JACS*, **1989**, 3441



7. The following reaction is an example of an enantioselective C-H activation process recently reported by Ellman and Bergman: *JOC*, **2004**, 7192-7193. 25 points



Draw a likely mechanistic scenario for this process, and address the following questions:

- Why is it important to have the imine functional group in order for this reaction to take place?
- What is the propensity for C-H insertion by metals in terms of the hybridization of the carbon atom ( $sp$ ,  $sp^2$ ,  $sp^3$ ) of the C-H bond? What is the effect of nearby heteroatoms (such as O and N) on the site of C-H insertion?
- What is the stereodefining step in the mechanism?



Congratulations!

Score:

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Page 2. \_\_\_\_\_ /25

Page 3. \_\_\_\_\_ /25

Page 4. \_\_\_\_\_ /25

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