

Advanced Organic Chemistry (CHE 311/511)
Final Examination
Dec. 17-21, 2007
Prof. W. P. Malachowski

Name: _____

Read each question carefully before answering. Be certain you understand everything the question is requesting. Do the easy questions first. If questions appear confusing or exceedingly complex, then you may need to rethink the question. Keep in mind the intended examination topics. The exam has a total of nine pages and seven questions.

In organic chemistry, hand-drawn pictures convey specific information. Be sure the drawing you have made conveys the essential information required to answer the question. Make certain that three-dimensional pictures display the correct atom arrangements. Don't forget to include formal charges when appropriate.

You may use models to assist in determining answers. You may use scrap paper to work out problems before entering your final answer on the exam sheets. In addition, feel free to use the back side of the exam sheets for scrap. If necessary, you may enter exam answers on the back side of the exam sheets, however you must clearly indicate which problems are located on the back of the exam pages.

Graduate students:

Complete 12 of 16 boxes in question 1 (4 pts. each)

Complete questions 2 and 3. (54 pts.)

Complete six of eight parts in questions 4 and 5. (12 pts. each)

Total points: 174

Undergraduate students:

Complete 10 of 16 boxes in question 1 (4 pts. each)

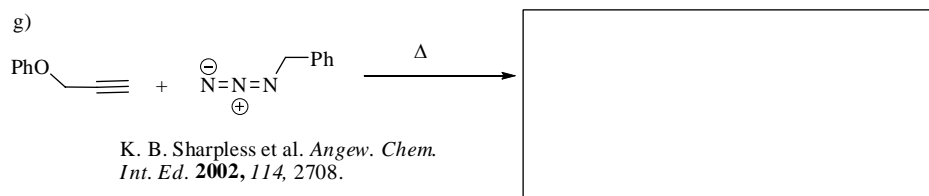
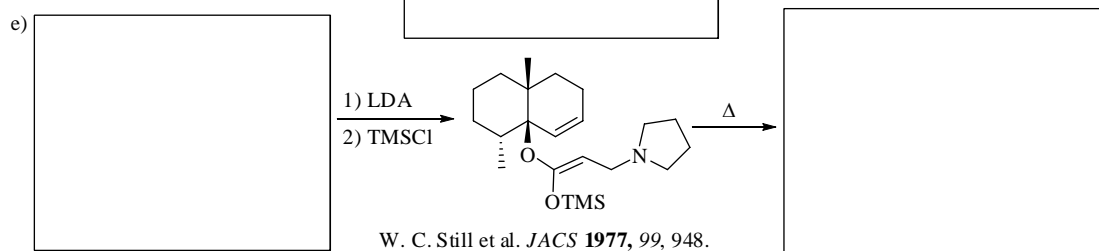
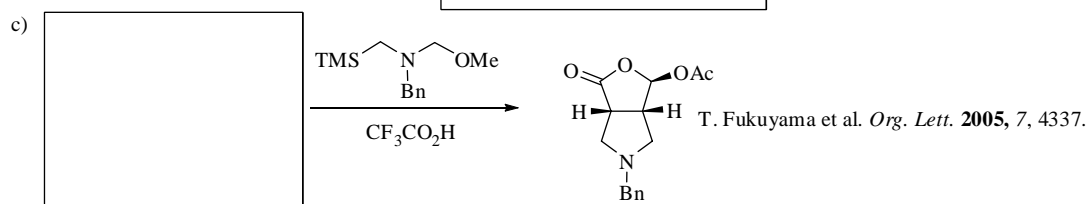
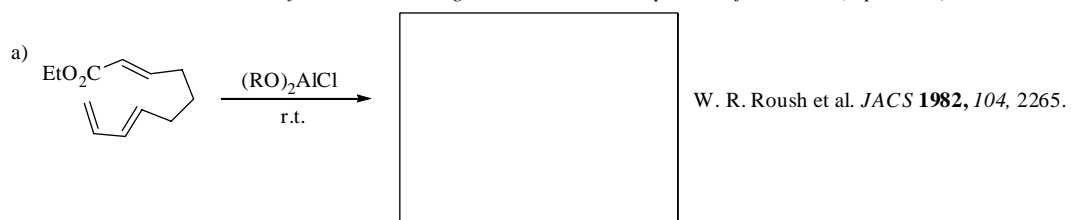
Complete questions 2 and 3. (54 pts.)

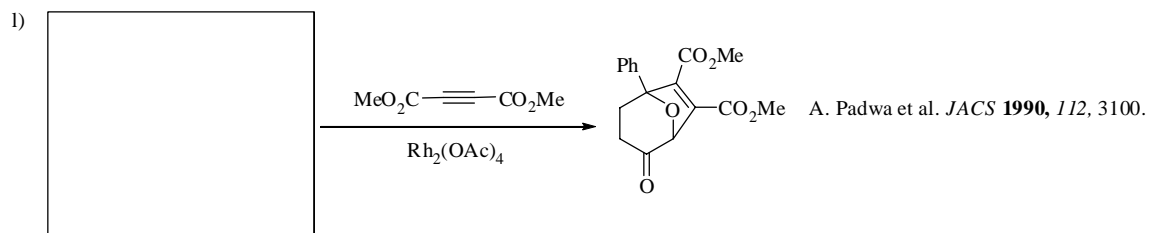
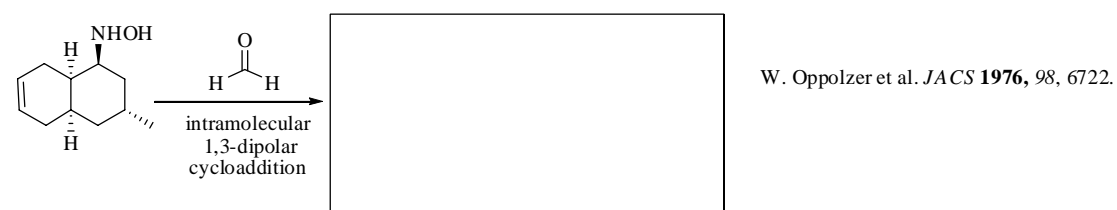
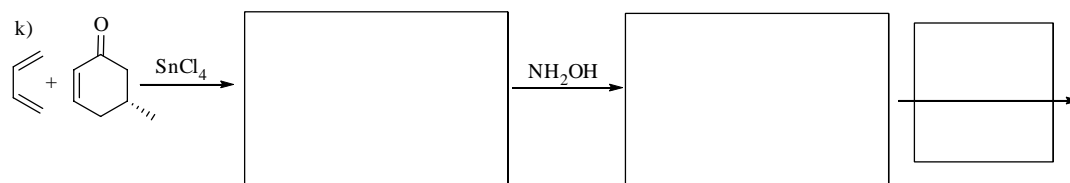
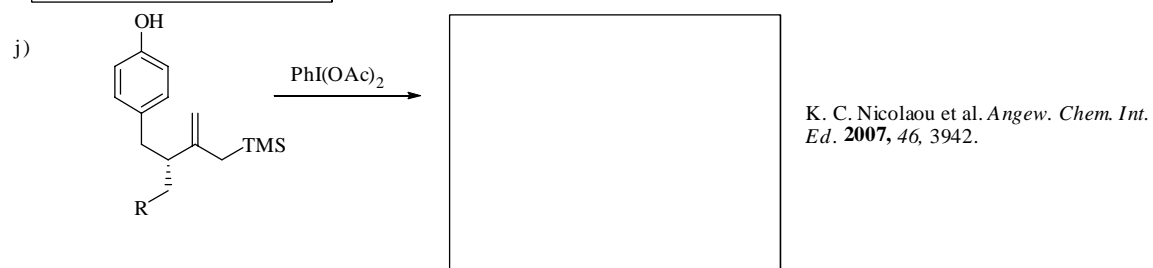
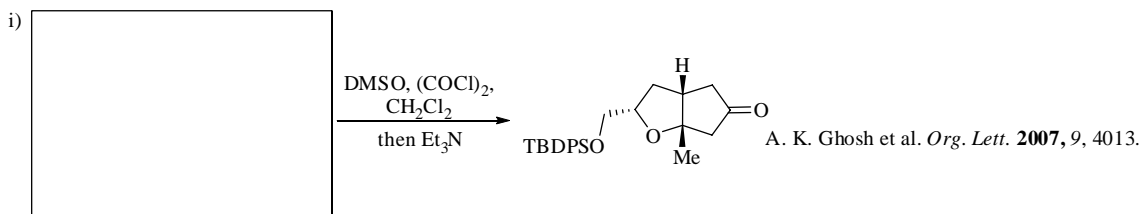
Complete five of eight parts in questions 4 and 5. (12 pts. each)

Total points: 154

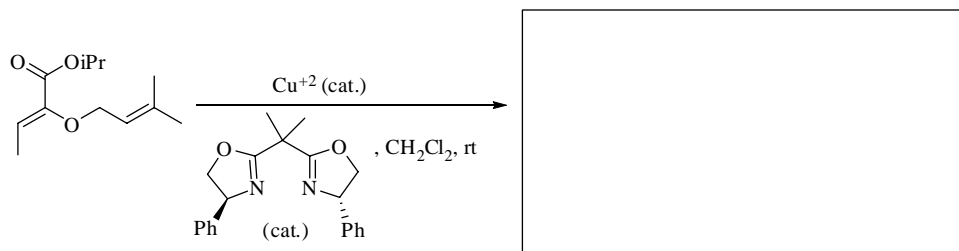
Bonus points: *If my meds are working when I grade the exam, there will be up to 10 bonus points be awarded for additional correct answers.*

1. Provide the necessary information (product, reagent or starting material) to complete the following reactions.
 Graduate students must do 12 of 16 boxes. Undergraduates need to complete 10 of 16 boxes. (4 pts. each)





2. Unfortunately, we didn't have time to talk about catalytic enantioselective [3,3]-sigmatropic rearrangements, but it's your lucky day! I'm going to give you an opportunity to answer a question about the subject on the final exam. A few years ago Martin Hiebermann and co-workers reported the first example of a catalytic enantioselective sigmatropic rearrangement in *Angewandte Chemie International Edition* (2001, 40, 4700). Based on your knowledge of related subjects answer the following questions.



- a) Draw the product of the reaction in the box to the right. The new stereocenter in the major product of the reaction has an S configuration. Make sure your product reflects this outcome. (6 pts.)
- b) Draw the transition state of the reaction in the space below. Keep in mind this should be the thermodynamically most favorable transition state. FOR THIS QUESTION YOU CAN IGNORE THE CATALYST. (6 pts.)

- c) On the transition state drawn above, draw the electron flow arrows to convert your transition state to your product. (3 pts.)
- d) What is the common name given to this type of [3,3]-sigmatropic rearrangement? (2 pts.)
- e) This reaction is thermodynamically favorable. Why? (2 pts.)

f) Based on our discussions of similar enantioselective catalysts, propose a catalyst interaction with the transition state structure drawn above. Hint: use the most electron rich sterically accessible Lewis basic sites on the substrate to coordinate the Lewis acid reagent. (5 pts.)

3. Throughout the course, we discussed examples of chemo-, regio- and stereoselective reactions. Show one example of each type of reaction and briefly describe why the process is selective. You do not need an exact literature example, but you should show a structure that illustrates your point. You should show the reagents and draw the product. (30 pts.)

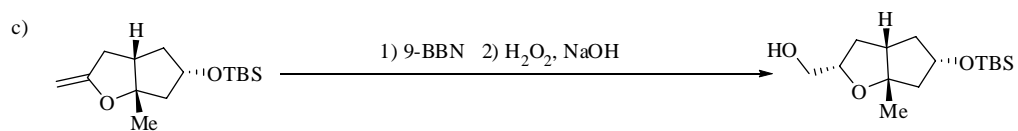
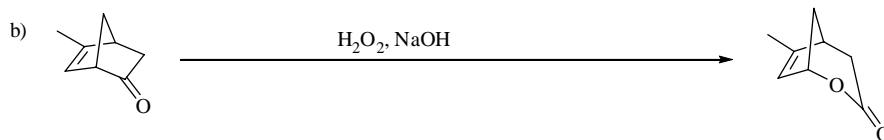
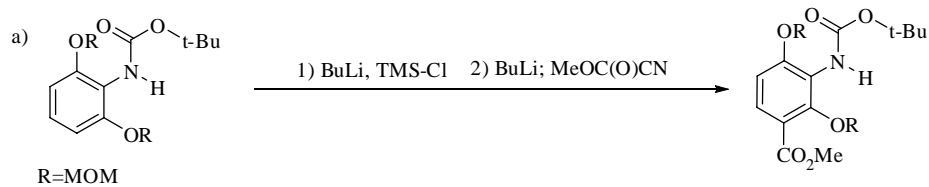
1) Example of a chemoselective reaction

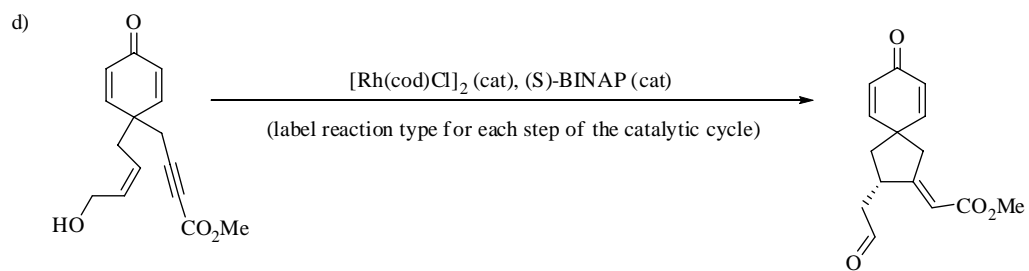
2) Example of a regioselective reaction

3) Example of a stereoselective reaction

The following two questions, 4 and 5, have four parts each. Undergraduate students must answer five of the eight parts and at least two from each section. Graduate students must answer six of eight parts. (12 pts. each)

4. Propose a mechanism for the following reactions.





5. Provide a series of synthetic reactions to transform the starting material to the product shown.

