University of Massachusetts Boston, Department of Chemistry

Chemistry Doctoral Program, Written Qualifying Examinations

June. 16, 2009

**Organic Chemistry I**

Questions are based on the following article:

J. Craig Ruble, Alexander R. Hurd,Timothy A. Johnson,Debra A. Sherry, Michael R. Barbachyn, Peter L. Toogood, Gordon L. Bundy, David R. Graber, and Gregg M. Kamilar “Synthesis of (-)-PNU-286607 by Asymmetric Cyclization of Alkylidene Barbiturates” *J. Am. Chem. Soc.* **2009**, *131*, 3991-3997.

1. Consider following reaction (starting material **16** is nonracemic).



a. (1 point) From compounds **17** and **18,** identify all thestereogenic centers and determine their configurations.

b. (2 points) Show detail mechanisms for the formation of compounds **17** and **18.**

c. (1 point) What conclusions have been made from this experiment?

2. Consider following reaction.









a. (0.5 point) What’s the stereochemistry relationship between compounds **(+)-20** and **(-)-1**?

b. (0.5 point) What’s that “>99:1 er” mean? If use “ee”, what’s the number will be?

c. (1 point) Give a mechanism for the conversion of **(+)-20** to **(-)-1.**

d. (1 point) Which compound is more stable? Use conformational analysis to explain why.

3. Consider following transformations.

****

****



****

****

****

****

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

b. (1 point) Indicate what kind of reaction (e.g. oxidation, substitution, Suzuki coupling….) for each step of those five transformations.

**Green Chemistry Question (2 points)**

From the green chemistry point of view, comment on the synthesis of compound **16** shown in Question 3 and give your suggestions for improvement.