**Name:** _____

**CHEM 633: Advance Organic Chemistry**
**Midterm 1**

Please answer the following questions clearly and concisely.

You may write your answers in the space provided and/or on additional pages.

Please write your initials on each page you wish to turn in.

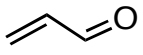
There are 10 total pages to this exam. Please be sure your copy has 10 pages before you begin.

Molecular models are allowed.

Calculators are unnecessary and prohibited.

| Problem | Points |
|---|---|
| 1 | _____/10 |
| 2 | _____/10 |
| 3 | _____/10 |
| 4 | _____/10 |
| 5 | _____/10 |
| 6 | _____/10 |
| 7 | _____/10 |
| 8 | _____/10 |
| 9 | _____/10 |
| 10 | _____/10 |
| **TOTAL** | **_____/100** |

1. (10 points) Please draw the specified orbital for the following molecules (Think FMO).

a. LUMO of 

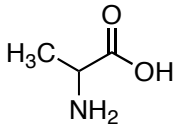

b. HOMO of $NMe_3$

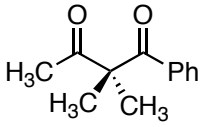
c. LUMO of allyl cation

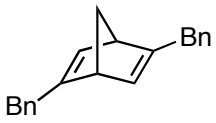
d. HOMO of 1,3-butadiene

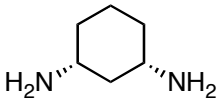
e. HOMO of ethylene

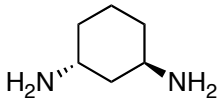
2. (10 points) Please label the following molecules as chiral or achiral. No explanation is necessary.

a. 


b. 


c. 

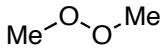

d. 


e. 

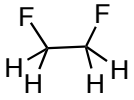
3. (10 points) For each of the following molecules, stereoelectronic, rather than steric factors, dictate the geometry of the structure. Draw the most stable conformation and clearly label the dominant stereoelectronic interactions that either stabilize the preferred conformation or destabilize the higher energy conformation.

a.


b.

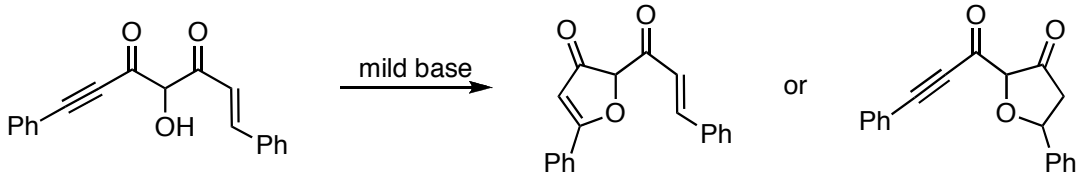



c.

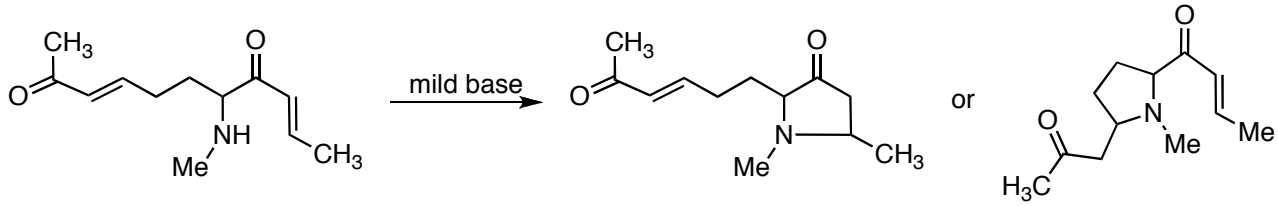


4. (10 points) Please predict and circle the major product in each the following reactions and briefly state the reason behind your choice.

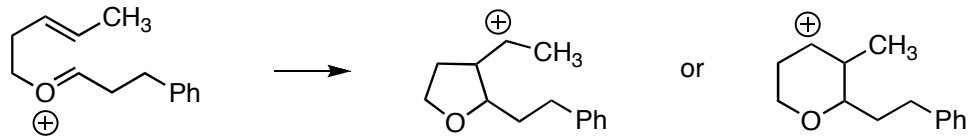
a.



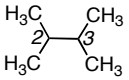

b.



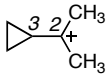

c.



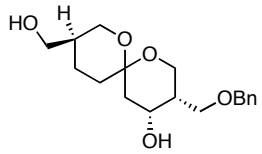
5. (10 points) Please draw a torsional energy diagram illustrating the barrier to rotation around the C2–C3 bond of 2,3-dimethylbutane, clearly labeling the relative energy and geometry of each conformation.



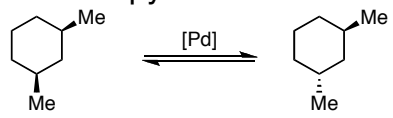

6. (10 points) Please explain the unusually high energy barrier to rotation about the C2–C3 bond of the following cation.



7. (10 points) Please draw the most stable conformation of the following dioxospiran. Please point out the features that make your proposed conformation lower in energy than the other possibilities.



8. (10 points) Consider the *cis–trans* isomerization of 1,3-dimethylcyclohexane, which may be easily isomerized under a variety of conditions using a palladium catalyst. You may assume that both isomers are observable by spectroscopy.




*cis* *trans*

a. Please predict which isomer (*cis* or *trans*) is more stable, and clearly illustrate the rationale behind your prediction.

b. Explain how one can experimentally determine $\Delta H°$ and $\Delta S°$ of this process. Include all equations and graphs that are necessary for analyzing the data.

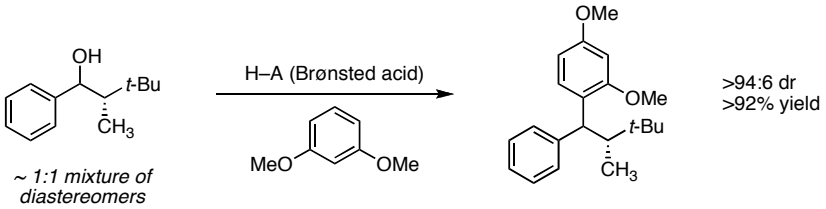
c. The experimentally determined enthalpy and entropy of isomerization are given below. Provide an explanation of the magnitudes and signs of enthalpy and entropy.

$\Delta H° = 1.97$ kcal/mol

$\Delta S° = 1.6$ eu

d. Using the experimental data, explain how the equilibrium constant for this reaction varies as a function of temperature.

9. (10 points) Bach showed that stereocenters adjacent to a benzylic hydroxy group can dictate the facial preference for the following acid-promoted Friedel–Crafts reaction (*JACS* **2005**, *127*, 9348).




a. Please propose an arrow-pushing mechanism for this transformation.

b. Predict the stereochemistry of the major product. Please rationalize your prediction by clearly illustrating all relevant stereoelectronic and steric interactions. (HINT: The diastereoselectivity of this reaction does NOT depend on the relative stabilities of the diastereomeric products.)

10. (10 points) Propose an arrow-pushing mechanism for the following transformation (Fukuyama et al. *ACIE* **2000**, *39*, 4073). Do not concern yourself with stereochemistry.