CHEM 330

Final Exam
December 13, 2013

Your name: _____

This a closed-notes, closed-book exam

The use of molecular models is allowed

This exam consists of 11 pages

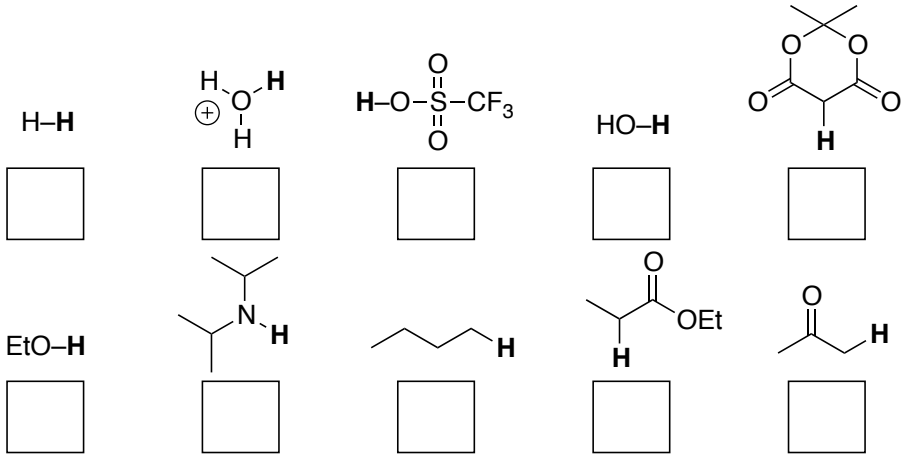
Time: 2h 30 min

1. _____ / 30
2. _____ / 30
3. _____ / 30
4. _____ / 40
5. _____ / 40
6. _____ / 40
7. _____ / 40

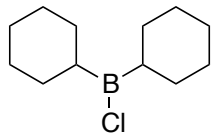
TOTAL _____ / 250 = _____ / 100

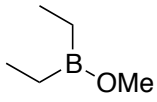
This exam counts for 50% of your CHEM 330 final grade

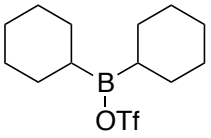
1. (30 pts.) Indicate the approximate pKa for the dissociation of the H in boldface in the substances shown below:

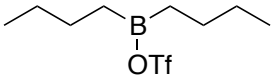


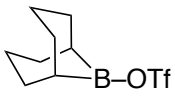
2. (30 pts.) Write a chemical equation to show an example of a reaction that involves the use of the following boron-based reagents (**do not** write mechanisms – just the reactions):

a. 

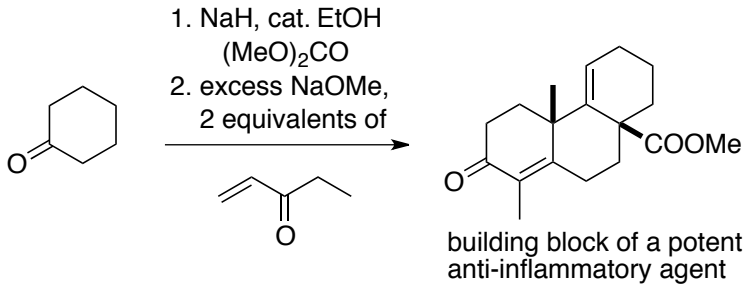
b. 

c. 

d. 

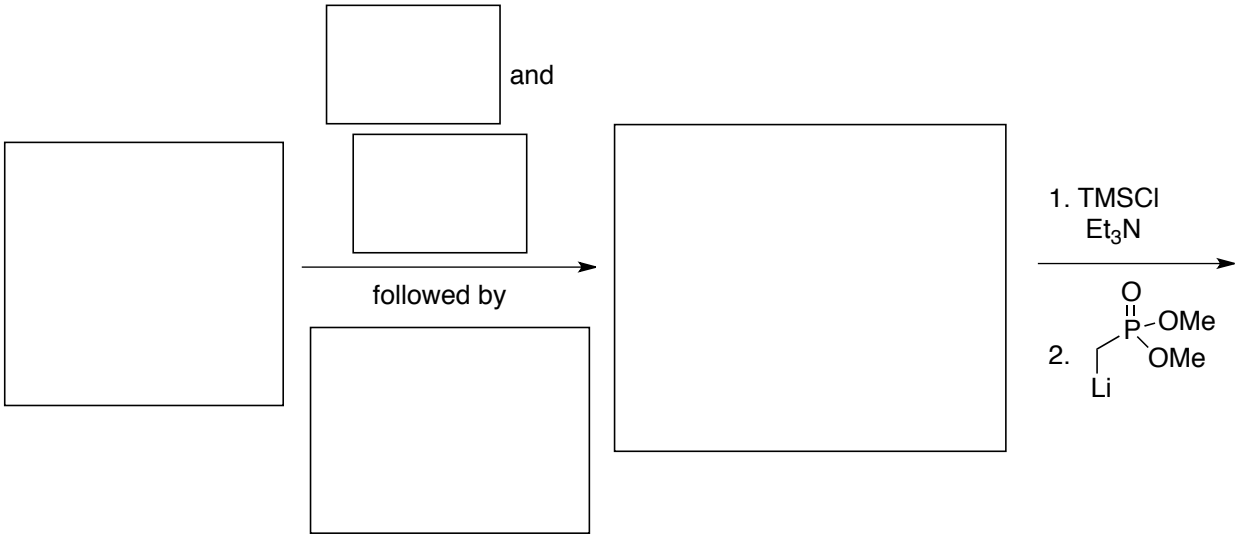
e. 

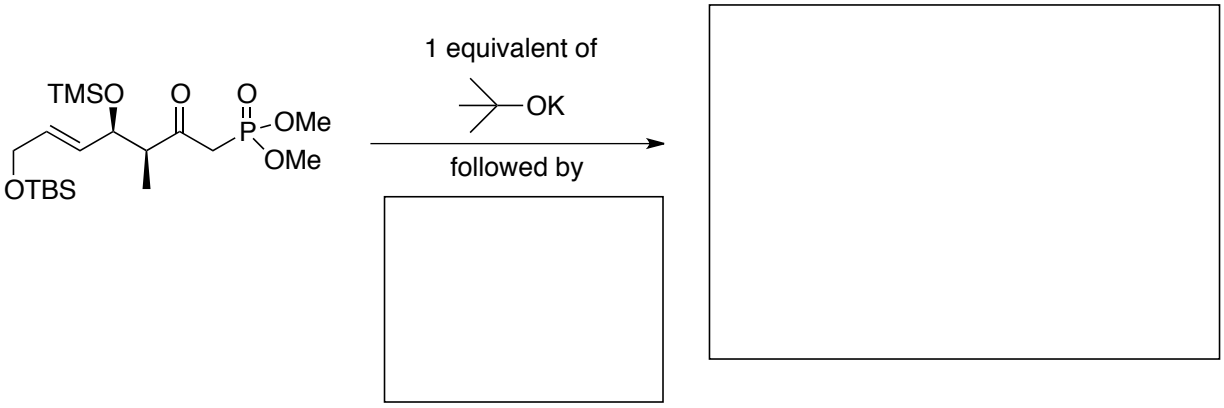
3. (30 pts.) Write an accurate mechanism for the formation of the product obtained from the following sequence (cf. *Synthesis.* **2013**, *45*, 3251):

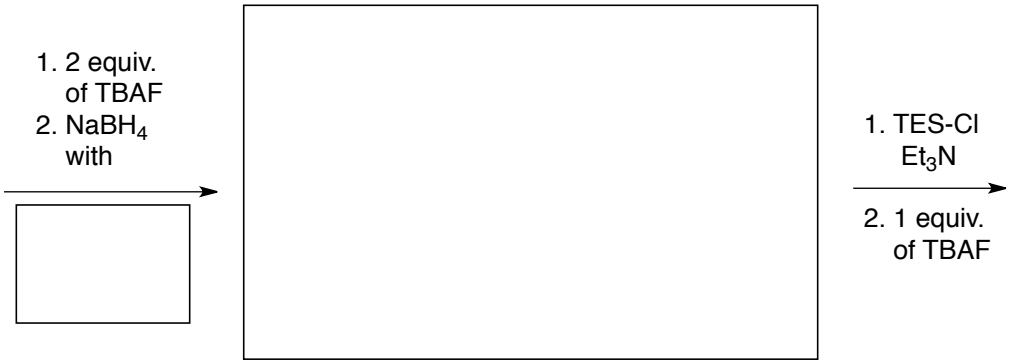


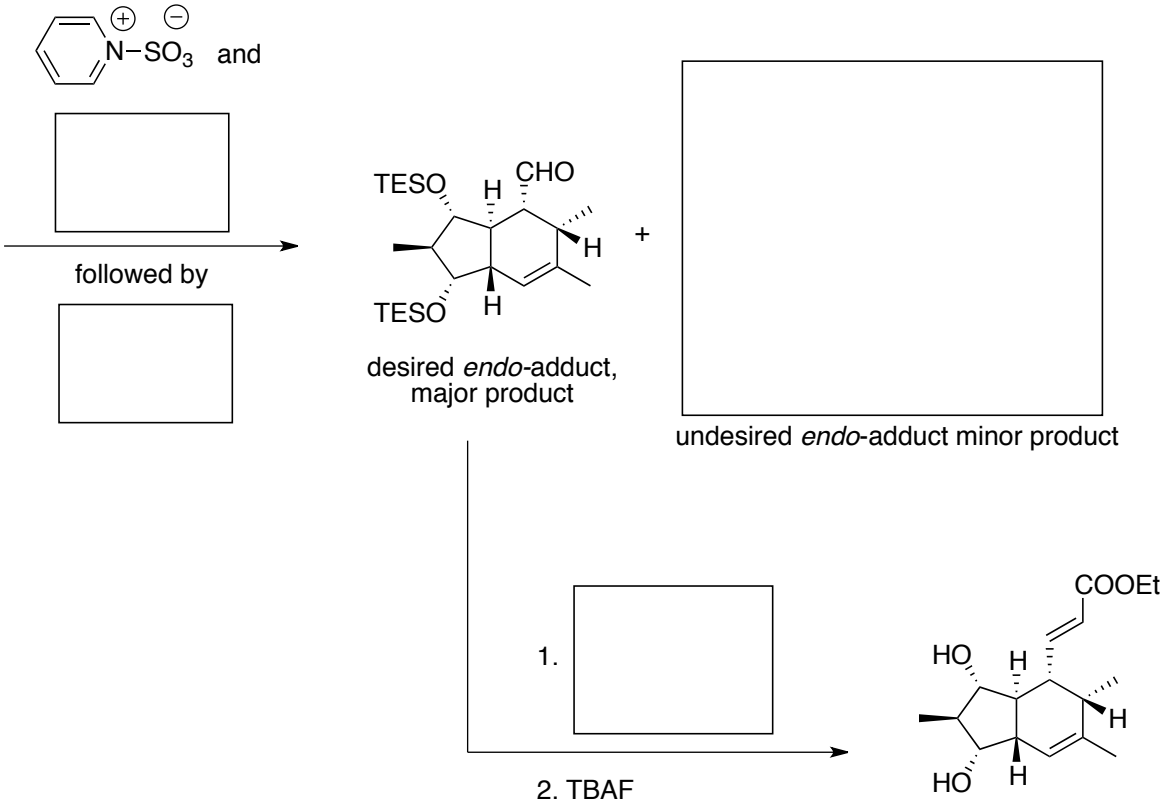
building block of a potent anti-inflammatory agent

4. (40 pts.) The following sequence is inspired by synthetic study toward the anticancer agent, FR-182877 (*Org. Lett.* **2001**, *3*, 4307). Complete this diagram by writing all the missing reagents / products in the appropriate boxes. **Important**: (i) aqueous workups are understood; (ii) compounds must be drawn with the correct configuration.



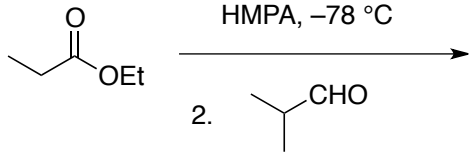




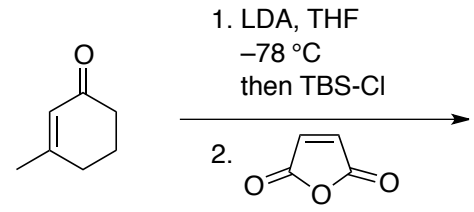

N–SO3
and
followed by
TESO
H
CHO
H
TESO
H
desired endo-adduct, major product
+
undesired endo-adduct minor product
1.
2. TBAF
COOEt
HO
H
H
HO
H

5. (40 pts.) Predict the structure of the major product expected from the following reactions. Notes: **(i) it is not necessary to draw mechanisms; (ii) aqueous workups at appropriate stages are understood.**

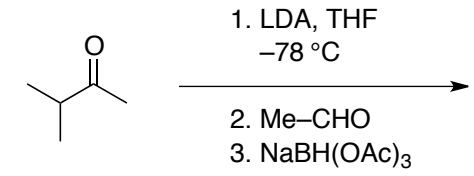
a.



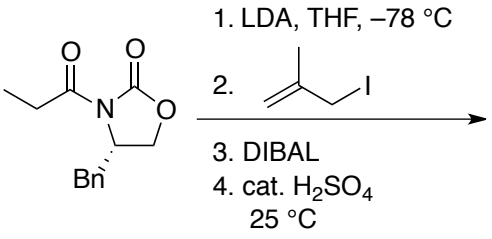
b.



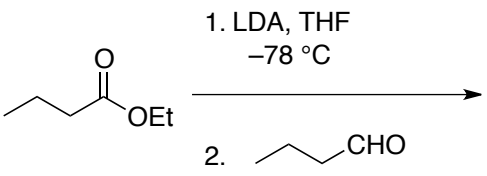
c.

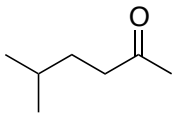


d.

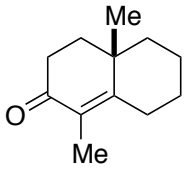


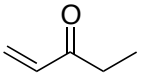
e.

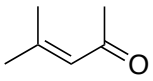


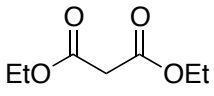
f. 

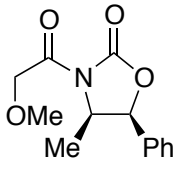
1. NaH, cat. EtOH
   EtO-CHO
2. H_2N-NH_2

g. 

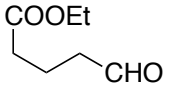
1. Li, liq. NH_3
   then 
2. *tert*-BuOK
3. Li, liq. NH_3, then
   mild H_3O^+

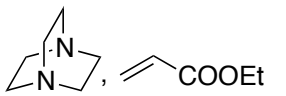
h. 

1. 
   EtONa
2. NaI, aq. DMSO
   heat
3. NaH, cat. EtOH

i. 

1. Bu_2BOTf, Et_3N, then
   OHC 
2. TBS-Cl, Et_3N
3. DIBAL
4. Pyr-SO_3, DMSO
   then Et_3N

j. 



then cat. H^+, heat

6. (40 pts.) Complete the following equations by indicating all the reagents that are necessary to effect the transformations shown. Provide your answers as a numbered list of reagents, in the correct order, written over/under the reaction arrows.

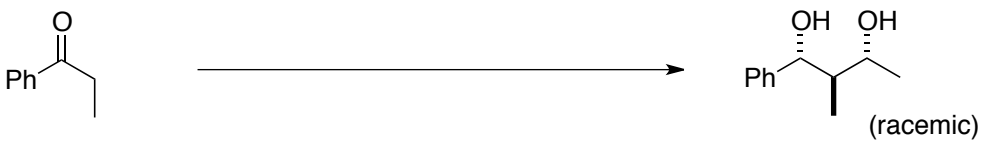
Note: aqueous workups are understood and do not need to be included in your answers.

a. 

b. 

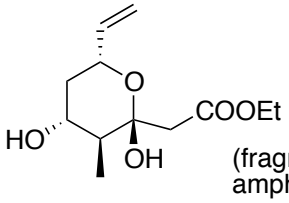
c. 

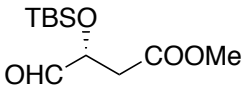
d. 

e. 

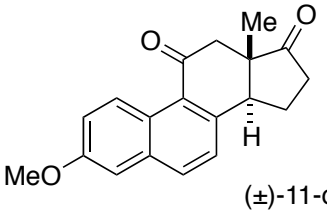
7. (40 pts.) Propose a method to achieve the enantioselective synthesis of the molecules shown below starting with the suggested building blocks. Be careful about protecting groups and configurations of stereocenters. Assume the availability of all needed reagents, auxiliaries, etc. Present your answer as a **clear** flowchart.

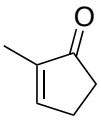
It is not necessary to draw mechanisms or to indicate aqueous workups.

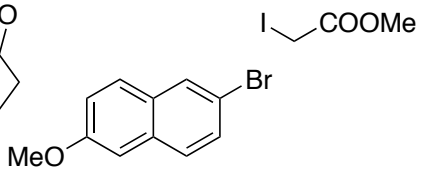
a. 

starting with: 

(fragment of the potent antitumor agent, amphidinolide P: *Org. Lett.* **2013**, *15*, 3318)

b. 

starting with 



(±)-11-oxoequilenin Me ether
(*J. Org. Chem.* **1979**, *21*, 3661)

Happy Holidays !