CEM 852 Final Exam

May 6, 2010

This exam consists of 7 pages. Please make certain that your exam has all of the necessary pages. Total points possible for this exam are 150. In answering your questions, please write legibly and draw all structures clearly. Write all your answers in the exam booklets. Good luck.

I. For the following compounds provide their pKa's within 2 pKa units. (5 pts)

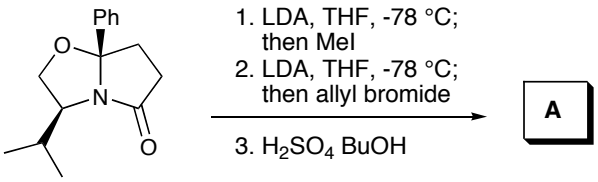
1. DMSO
2. C**H**$_3$CO$_2$Et
3. CH$_3$COC**H**$_2$CO$_2$Et
4. C**H**$_3$CH=CH$_3$
5. CH$_3$C**H**$_2$NO$_2$

II. Explain, describe, or illustrate each of the following chemical processes. (15 pts)

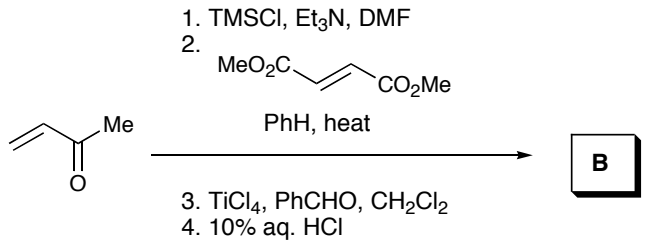
1. dynamic kinetic resolution
2. a type III crotylation
3. a catalytic asymmetric desymmetrization
4. a reaction that proceeds with double diastereodifferentiation
5. organocatalysis

III. Provide the product or products of the reactions outlined below. Show all intermediate compounds and be sure to indicate the product's relative or absolute stereochemistry. For reactions where multiple products are possible, be sure to indicate the major and minor species. (30 pts)

1.

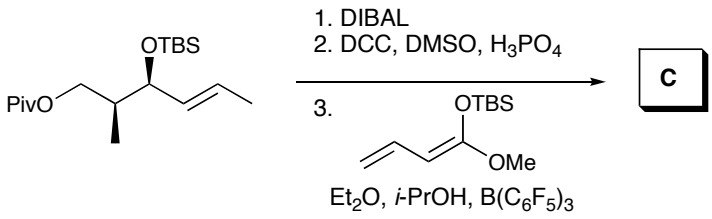


2.



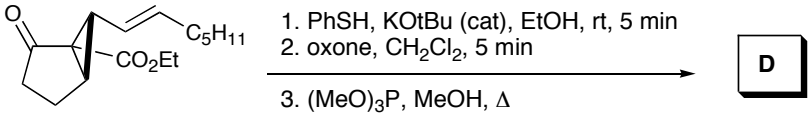
(hint: the last step eliminates water)

3.



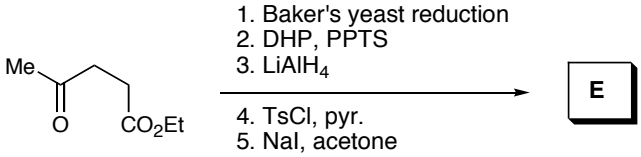
(hint: this is NOT a [4+2] cyclization)

4.

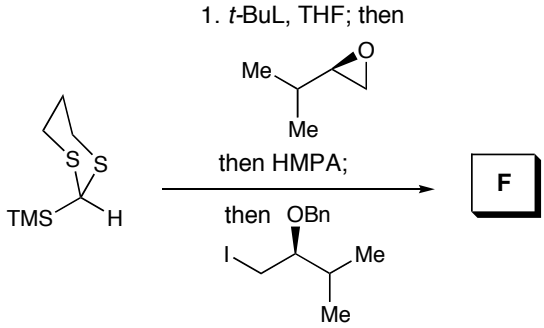


(hint: the first step opens the cyclopropyl ring)

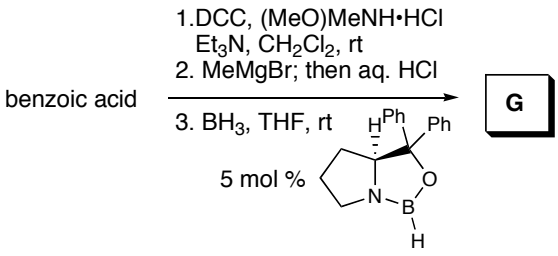
5.



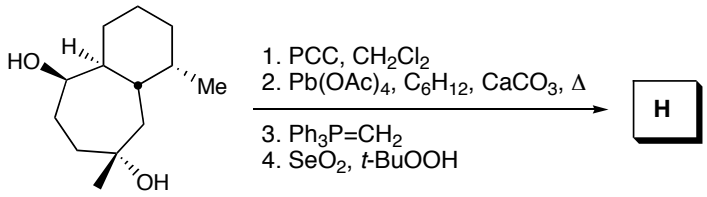
6.



7.



8.



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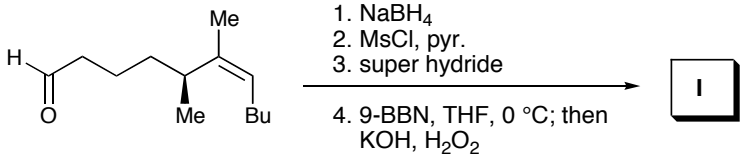
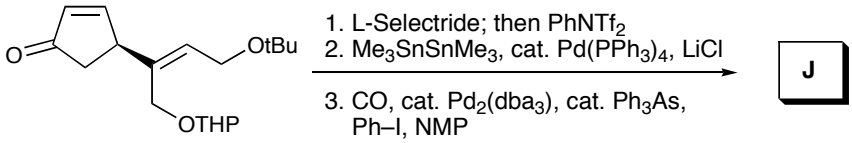
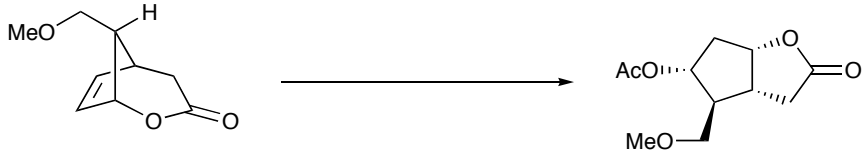


10.



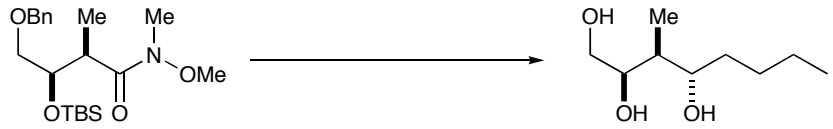
IV. Provide conditions that will effect the transformations outlined below. Some of these conversions will require more than one reaction, so be sure to show all intermediate compounds. (30 pts)

1.

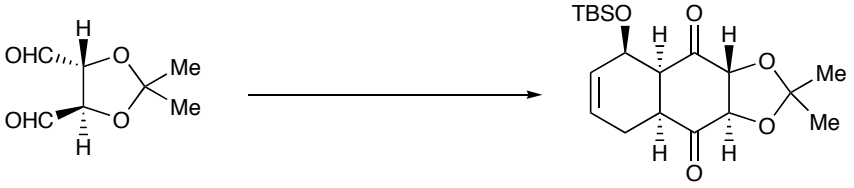


2.

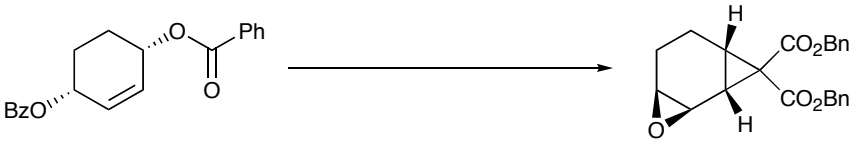
3.



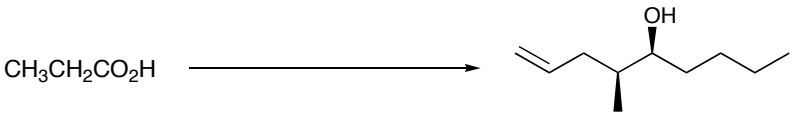
4.



5.



6.



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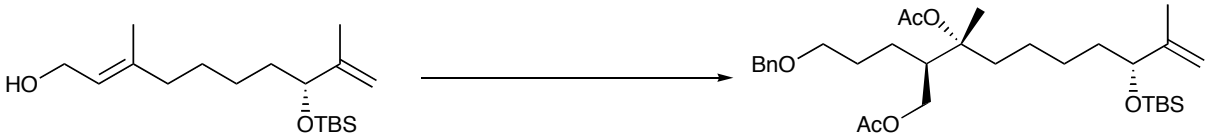

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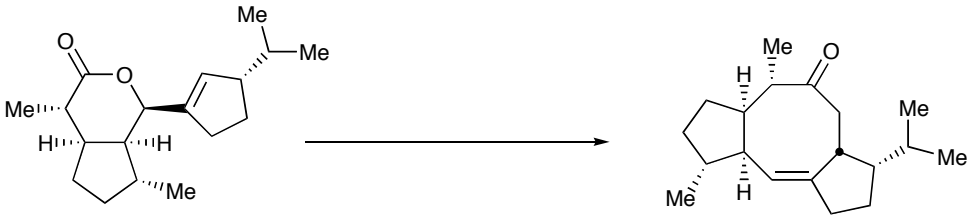
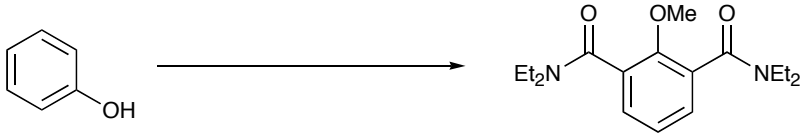
9.

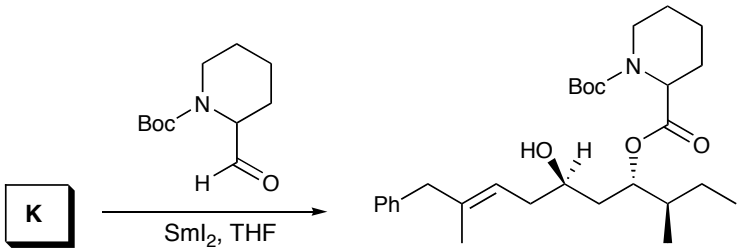


10.

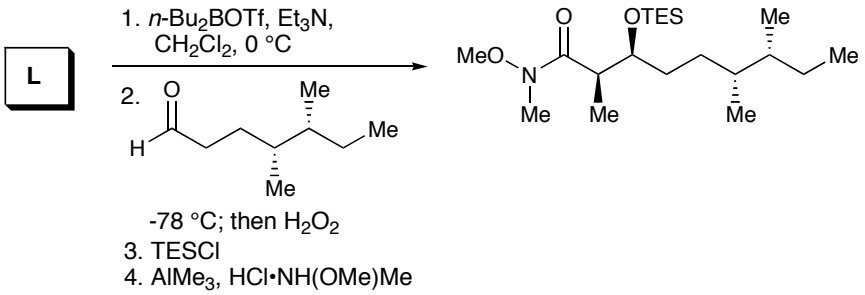


V. Provide the starting substrate for the reactions outlined below. (18 pts)

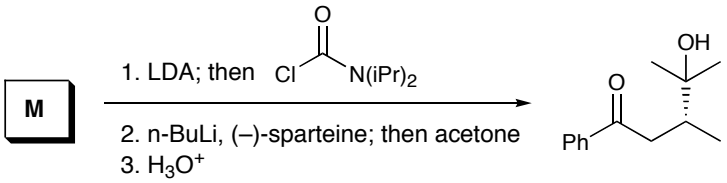
1.


K
Boc
N
H
O
SmI2, THF
Boc
N
HO
H
O
O
Ph

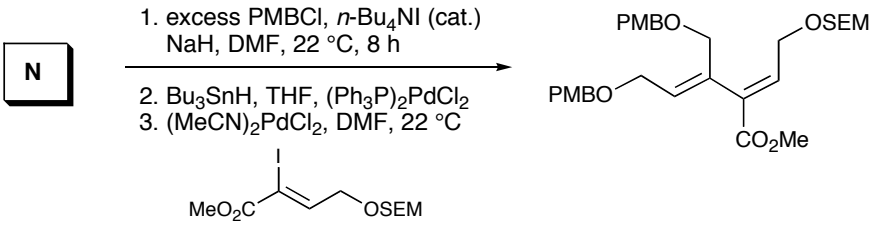
2.


L
1. n-Bu2BOTf, Et3N,
CH2Cl2, 0 °C
2.
O
H
Me
Me
Me
-78 °C; then H2O2
3. TESCl
4. AlMe3, HCl•NH(OMe)Me
O
OTES
Me
MeO
N
Me
Me
Me
Me

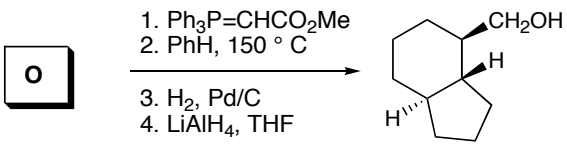
3.


M
1. LDA; then
O
Cl
N(iPr)2
2. n-BuLi, (–)-sparteine; then acetone
3. H3O+
OH
O
Ph

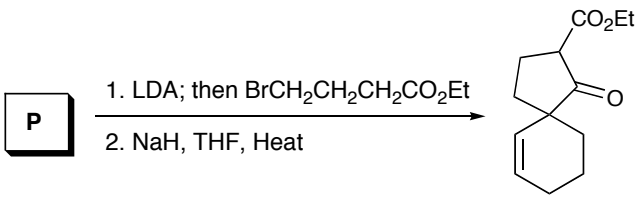
4.


N
1. excess PMBCl, n-Bu4NI (cat.)
NaH, DMF, 22 °C, 8 h
2. Bu3SnH, THF, (Ph3P)2PdCl2
3. (MeCN)2PdCl2, DMF, 22 °C
I
MeO2C
OSEM
PMBO
OSEM
PMBO
CO2Me

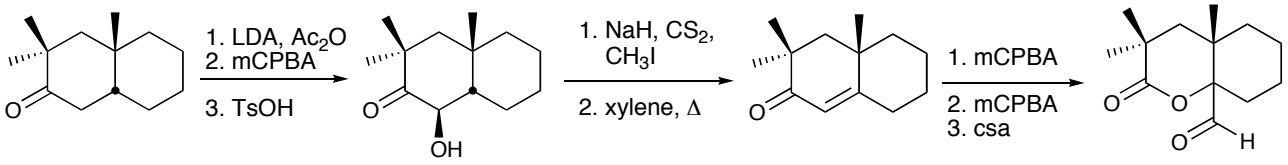
5.


O
1. Ph3P=CHCO2Me
2. PhH, 150 ° C
3. H2, Pd/C
4. LiAlH4, THF
CH2OH
H
H

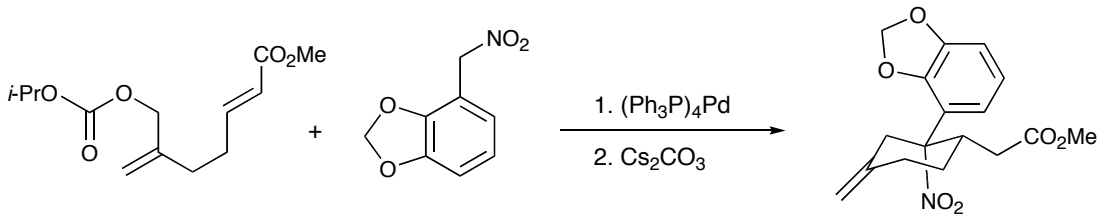
6.


P
1. LDA; then BrCH2CH2CH2CO2Et
2. NaH, THF, Heat
CO2Et
O

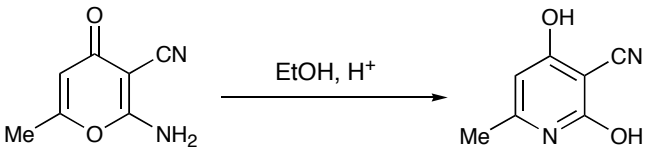
VI. Provide complete arrow (electron) pushing mechanisms for the transformations shown. (12 pts)



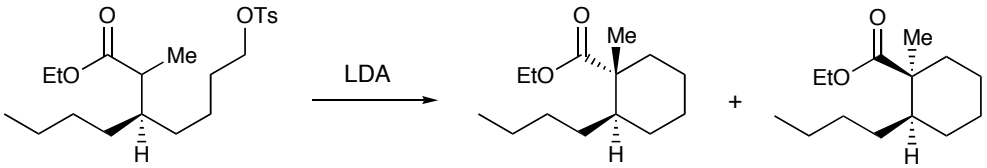
VII. Provide complete arrow (electron) pushing mechanisms for the transformations shown. (6 pts)



VIII. Provide a complete arrow (electron) pushing mechanism for the transformation shown. (6 pts)

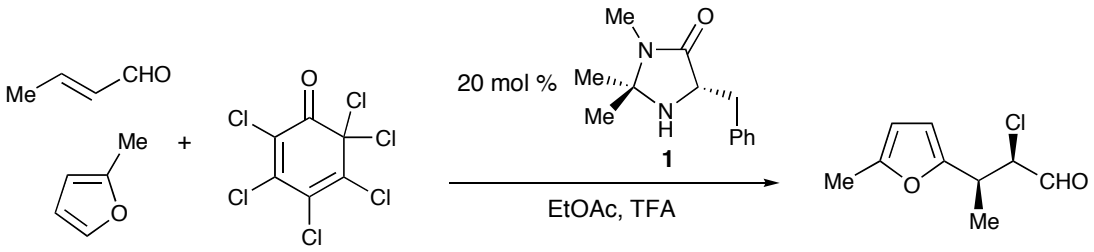


IX. For the reaction shown below explain the stereochemical outcome. (6 pts)



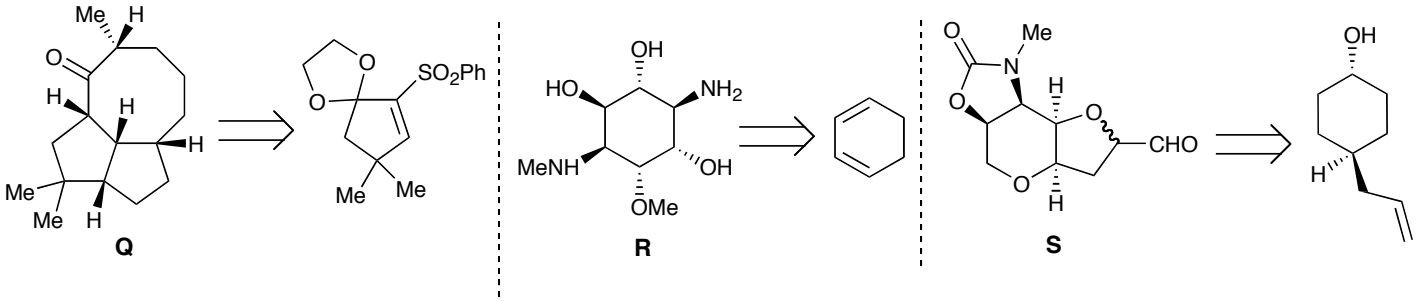
98 : 2

X. In class we saw examples of MacMillan's organocatalytic reactions with imidazolidinone catalysts (e.g. **1**). Among his clever uses for this catalyst is his development of a merged iminium-enamine cascade. An example of this process is shown below.



In this reaction scheme, the enal reacts with **1** to generate an activated iminium species that can enantioselectively intercept a wide variety of nucleophiles (e.g. 2-methylfuran). The conjugate addition adduct is an enamine, which in turn can react with a wide array of electrophiles (e.g. the chlorinated quinone). Subsequent hydrolysis affords the product and regenerates the catalyst. Illustrate this catalytic cycle and show the mechanistic steps involving the nucleophile addition and electrophile capture. (Note: You do not have to explain the stereochemistry.) (10 pts)

XI. Provide a stereoselective (relative stereochemistry only) synthesis of ONE of the compounds shown below, beginning with the indicated starting material (12 pts).



Bonus Question: Which compound was found in the paint of all red Ferrari's built from 2000–2004?