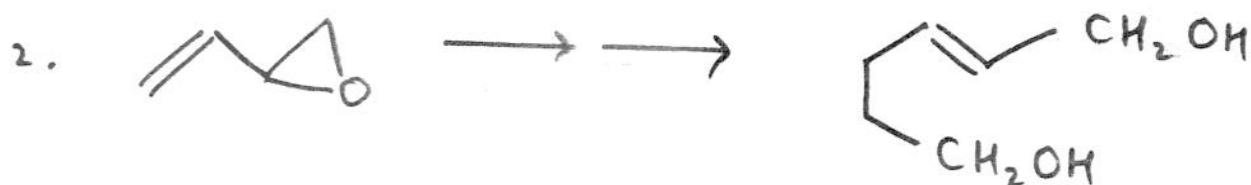
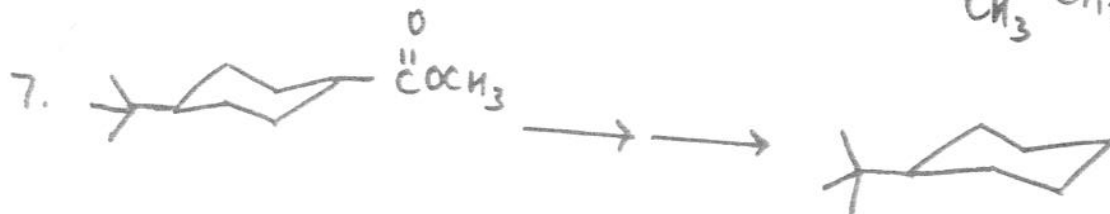
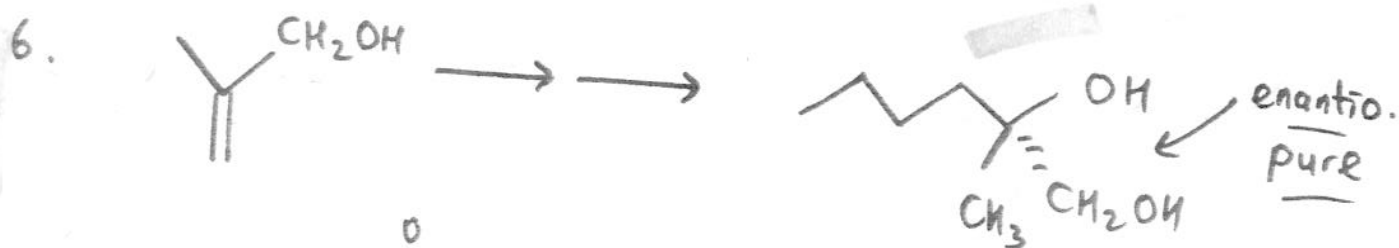
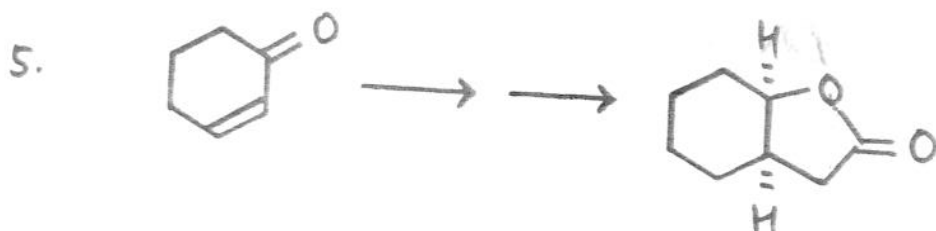
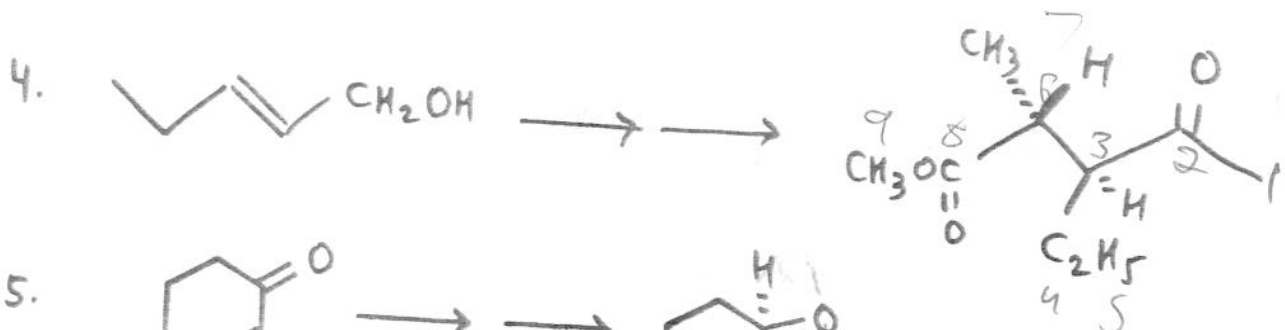


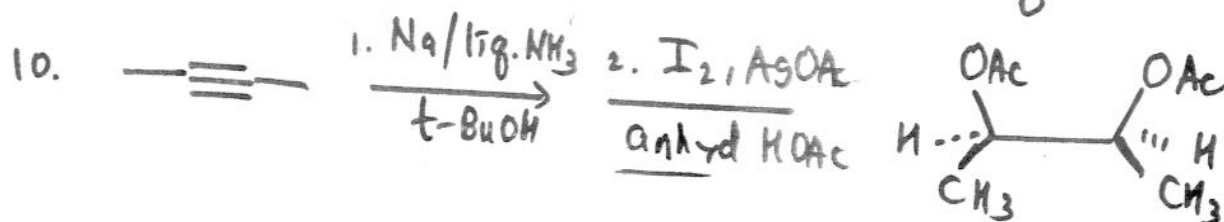
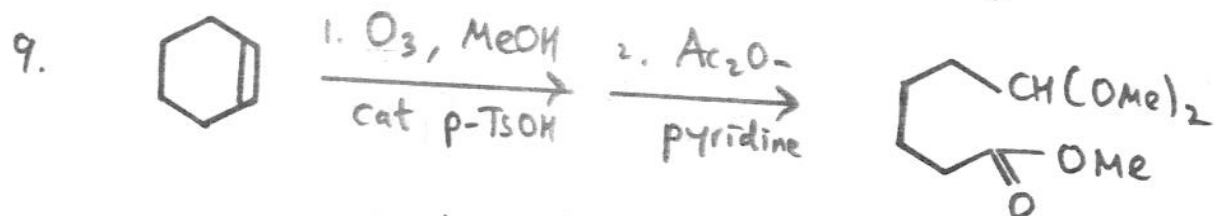
Write your answers in the normal numerical sequence in your bluebook. Don't forget to put your name on the bluebook; do not turn in the exam sheet or scratchpaper. You may use molecular models for this exam.

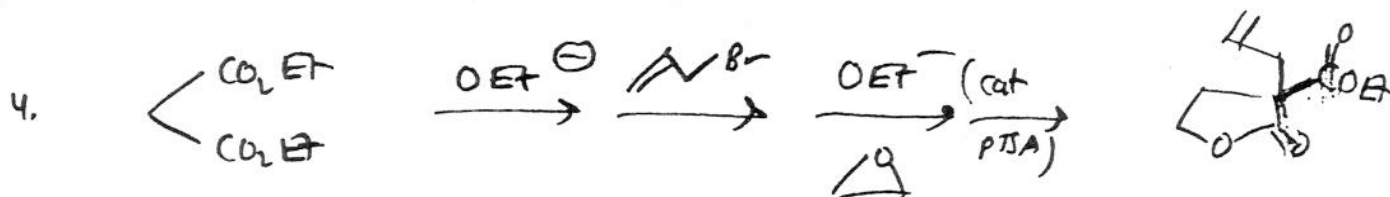
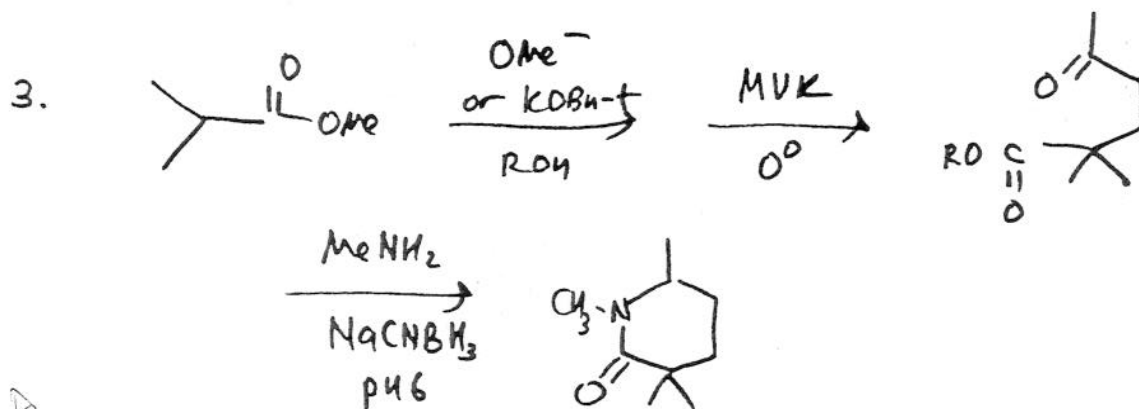
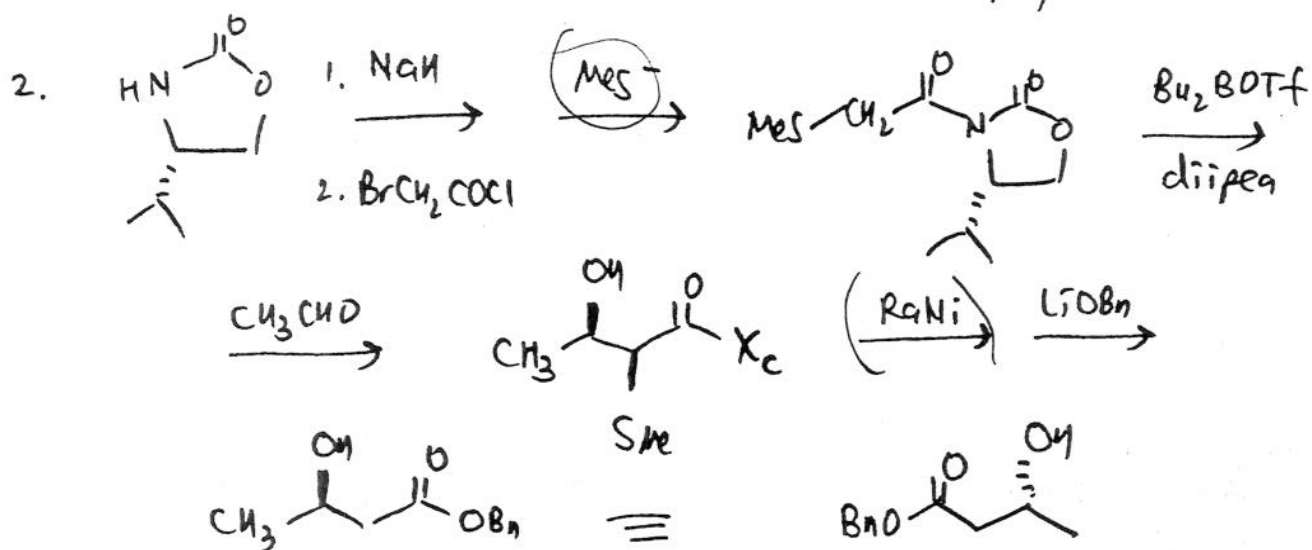
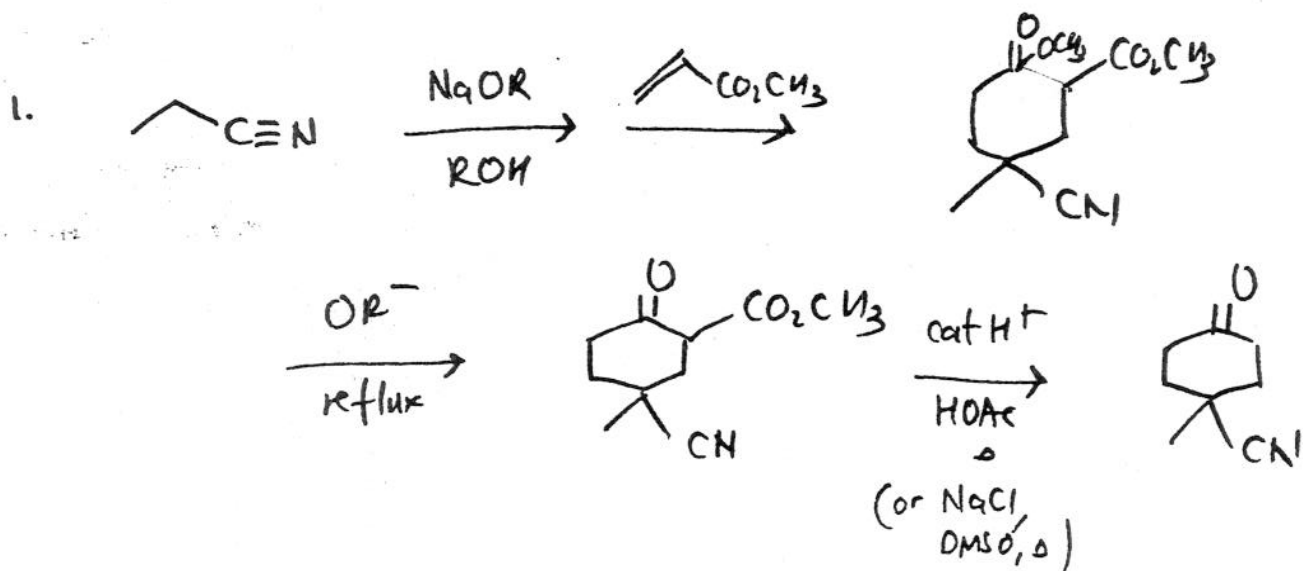
Part A: Propose an efficient, sterecontrolled sequence from each starting material to product, specifying any necessary catalysts, normal reagents or "Aldrich" intermediates. Assume all products are racemic unless otherwise stated; do not give mechanisms. Each problem is 10 points.





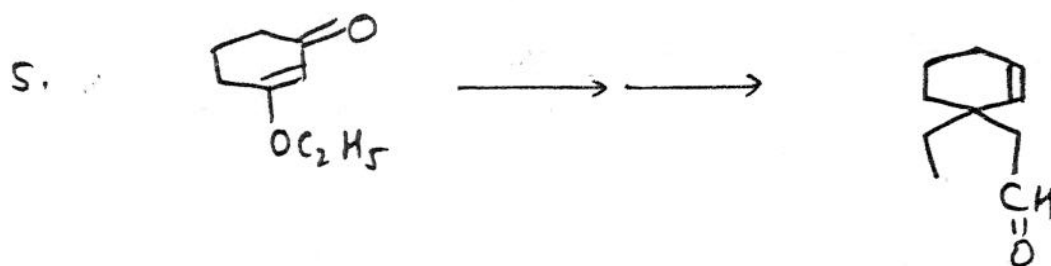
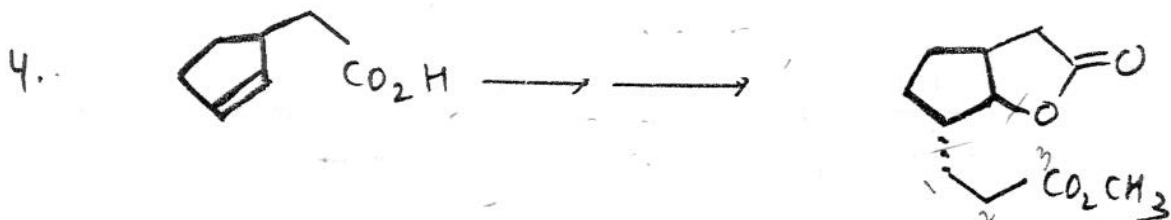
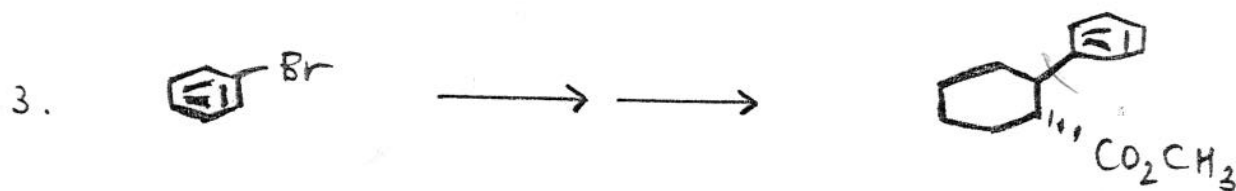
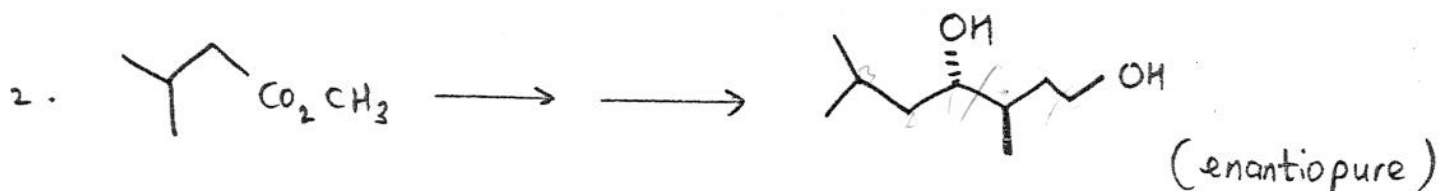
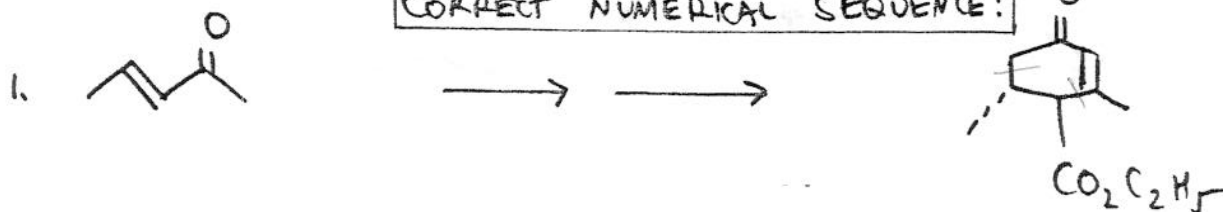
Part B: The following two problems are 10 points each.
Write a mechanism for each of the sequences below.



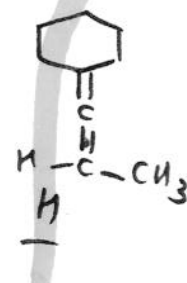
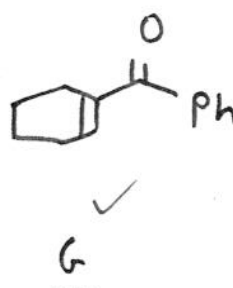
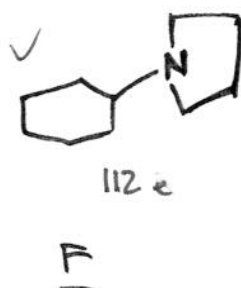
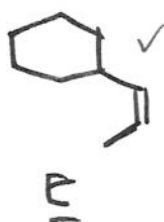
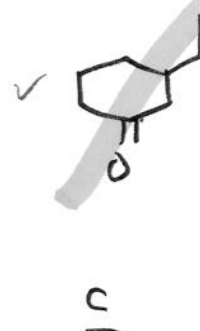
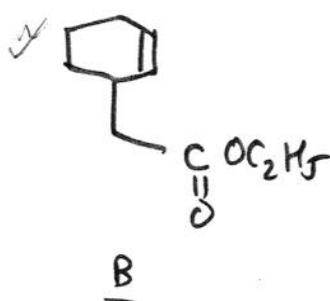
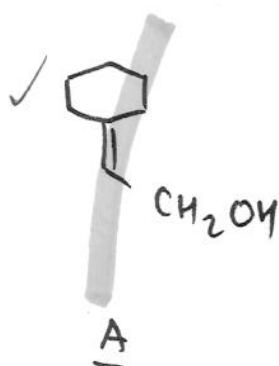


(molecular models may be used in this examination)

PROPOSE DIRECT, SHORT AND STEREOCONTROLLED ROUTES TO EACH TARGET COMPOUND, SPECIFYING ANY STANDARD REAGENTS OR "ALDRICH" CHEMICALS REQUIRED. TARGETS ARE RACEMIC EXCEPT AS NOTED. PLACE BLUEBOOK ANSWERS IN THE CORRECT NUMERICAL SEQUENCE!



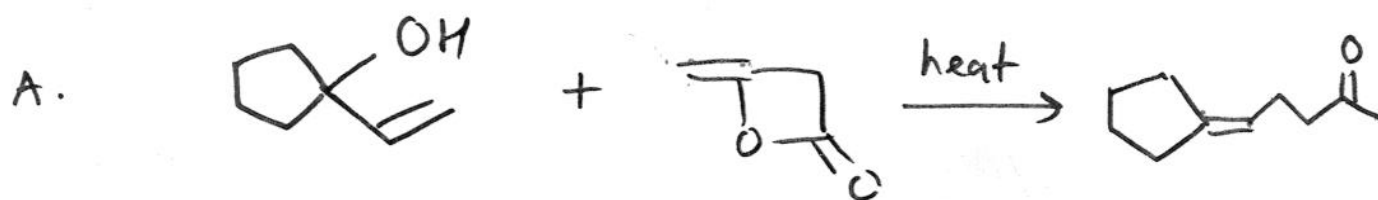
1. Starting from cyclohexanone or 2-cyclohexenone, devise a simple and reliable synthesis of each of the following compounds

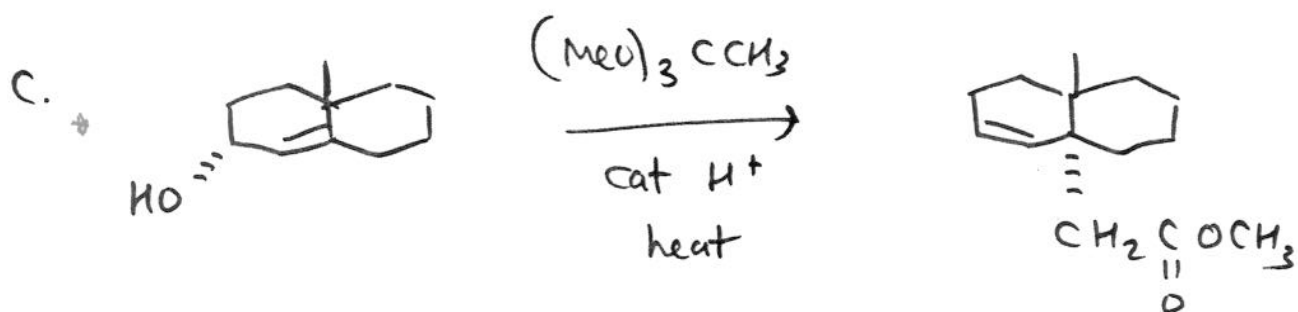
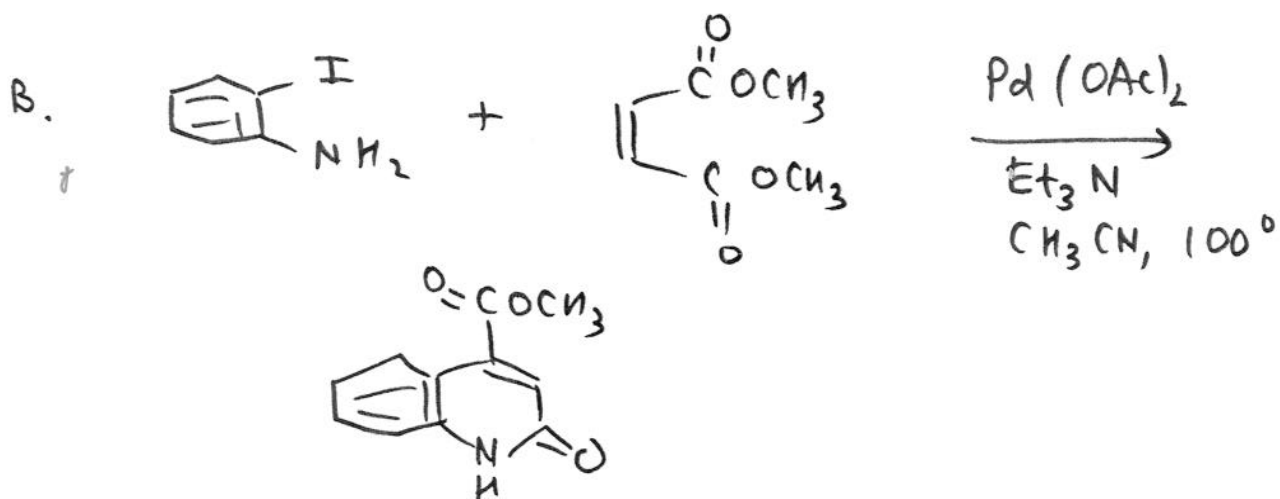


23.9798
23.8668

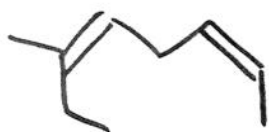
11/2 e
Kag

2. Show a detailed mechanism for each step of the following reactions, using electron-pushing where practical.

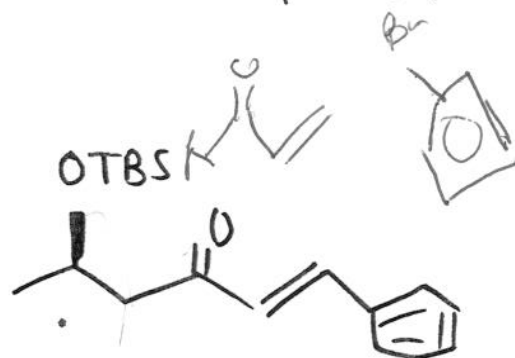




3. Starting with Aldrich precursors and using at least one acetylenic intermediate, propose stereoccontrolled syntheses of the following compounds.



A

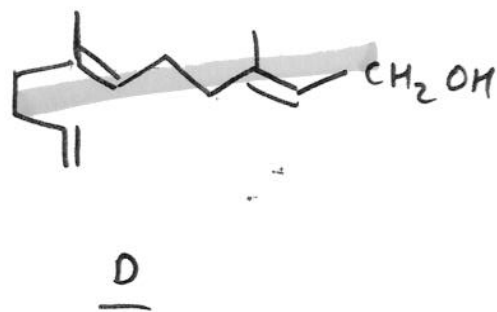
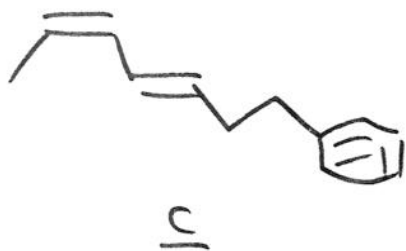


B

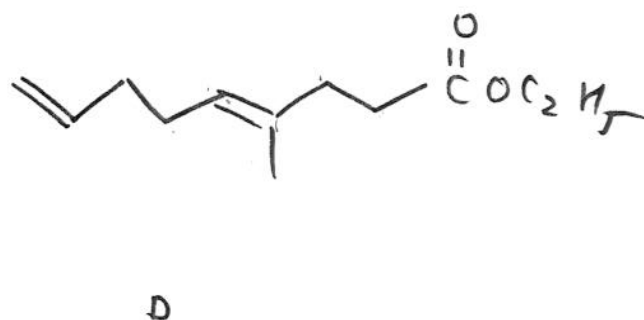
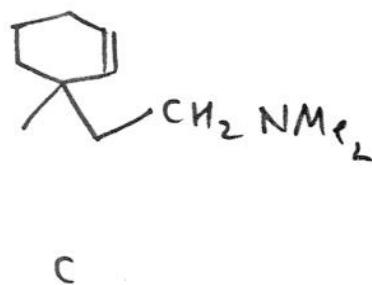
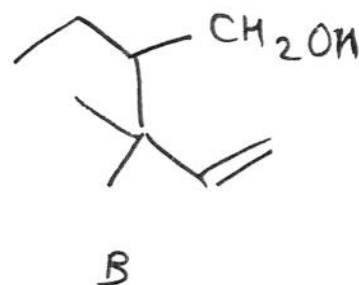
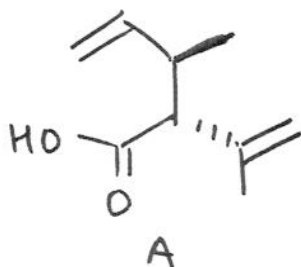
SET 1

Kenney's method

(p. 3)



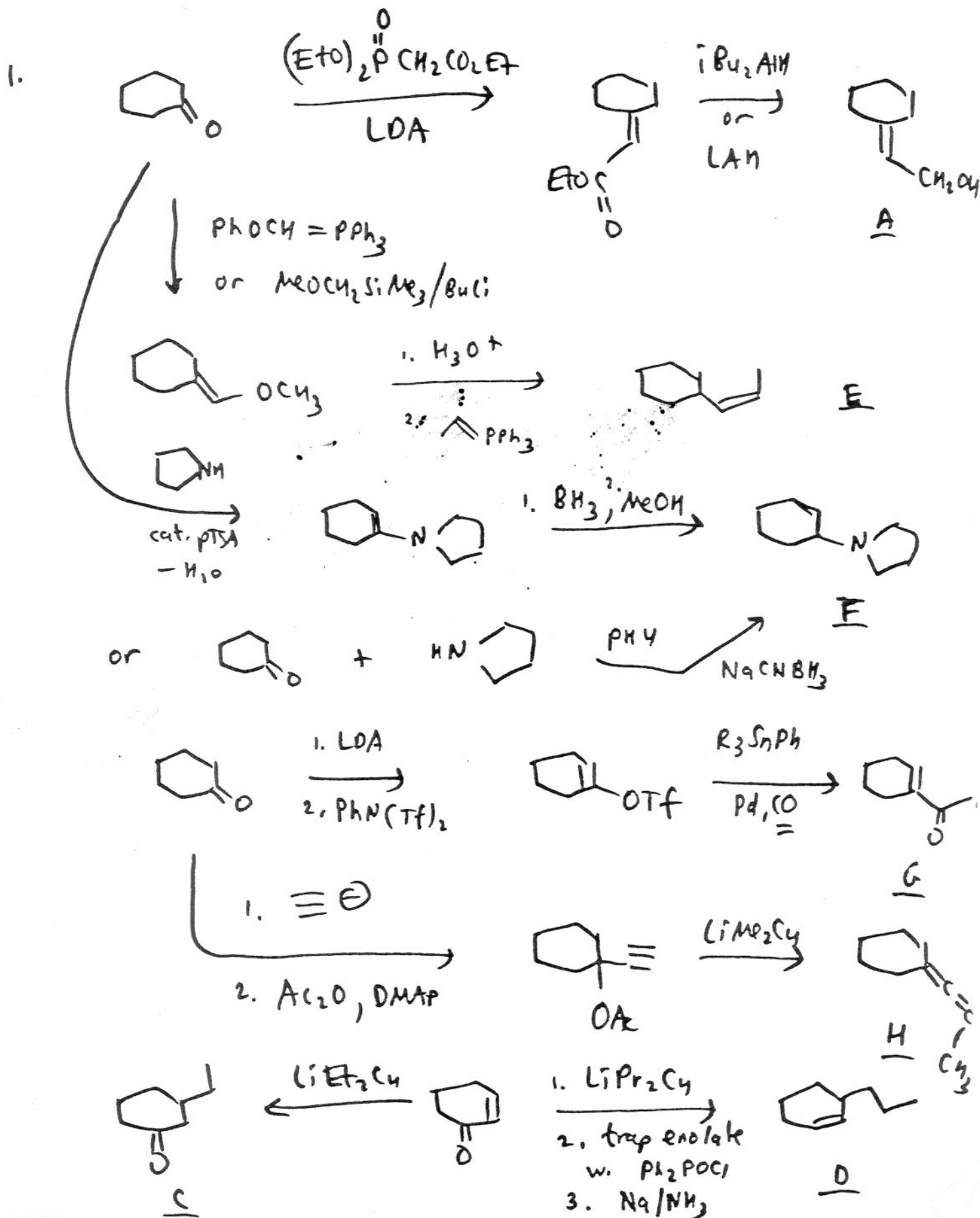
4. Using Claisen-type (or related) rearrangement, and Aldrich starting materials, devise an efficient stereocontrolled route to each of the following targets.



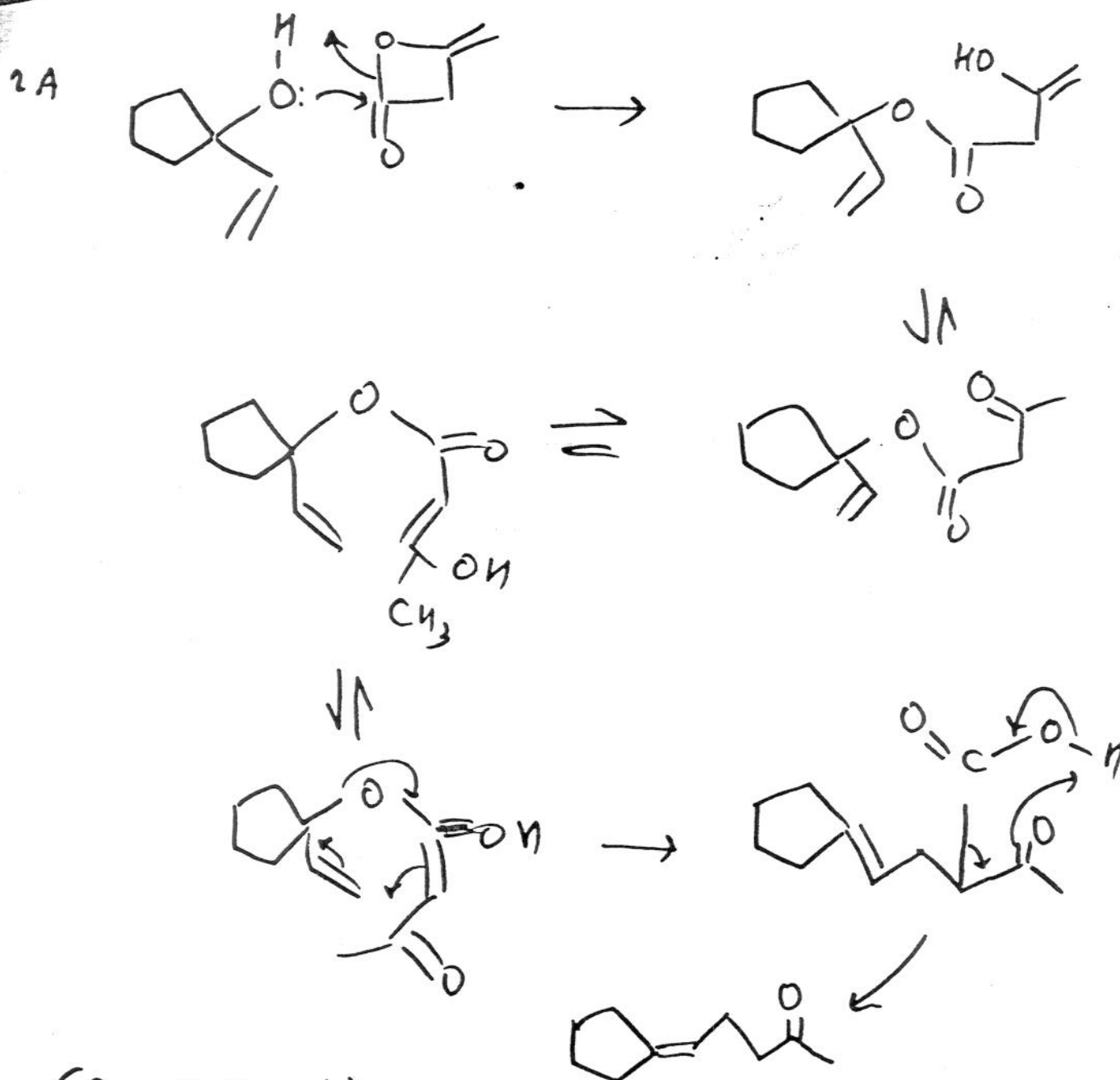
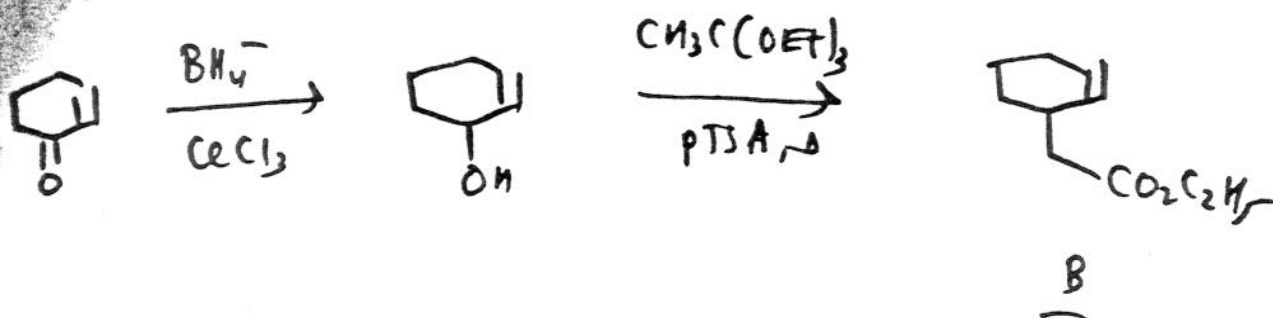
CHM 435

SET 1 - POSSIBLE

Solder 285
ANSWERS

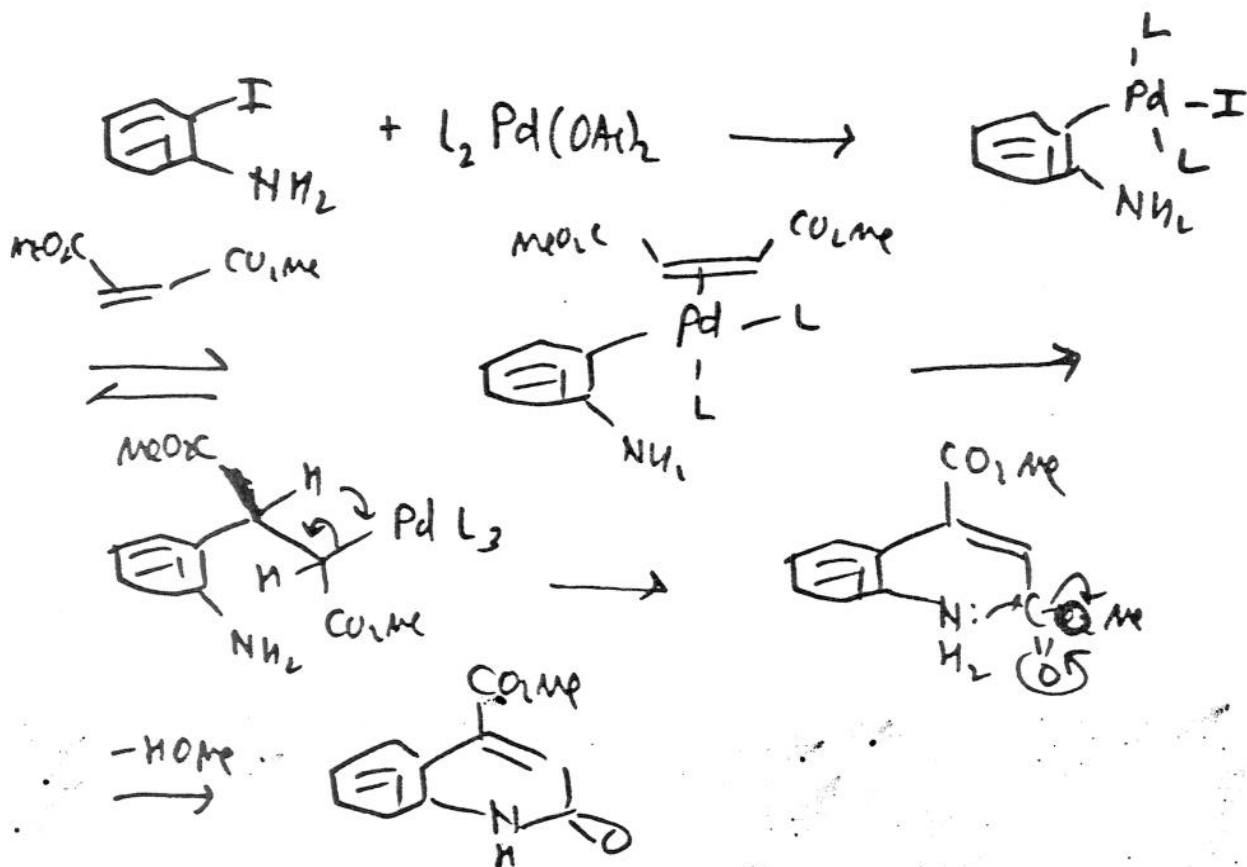


(SET 1)

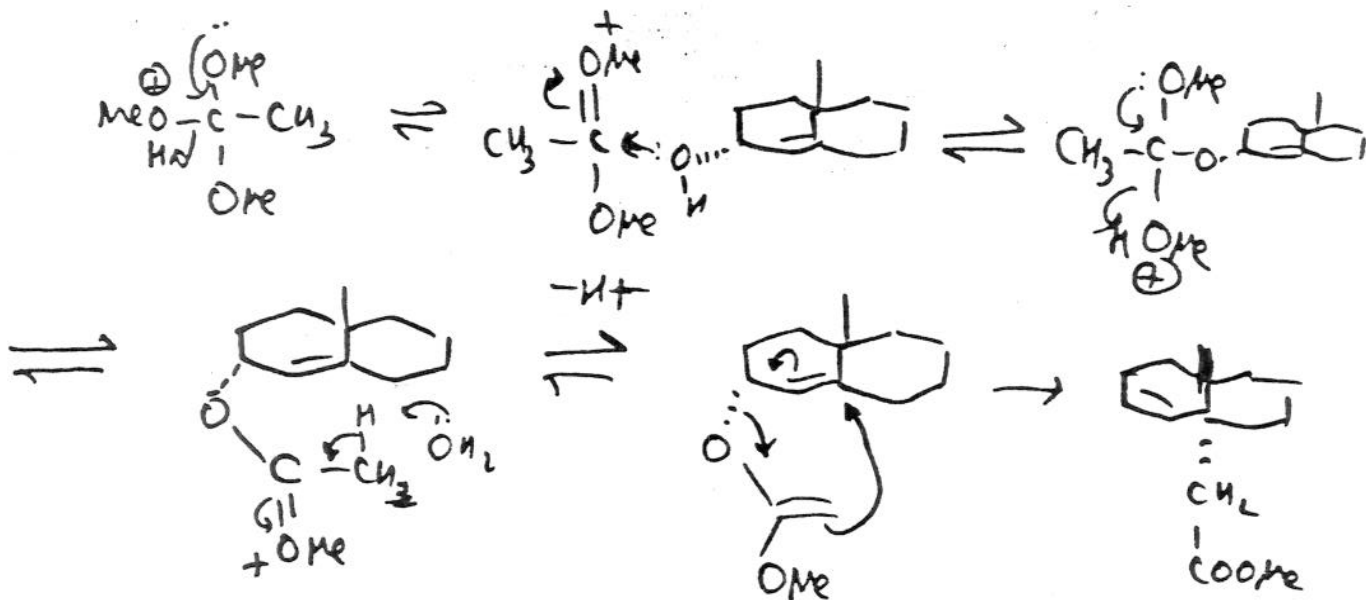


(Carroll Rearr.)

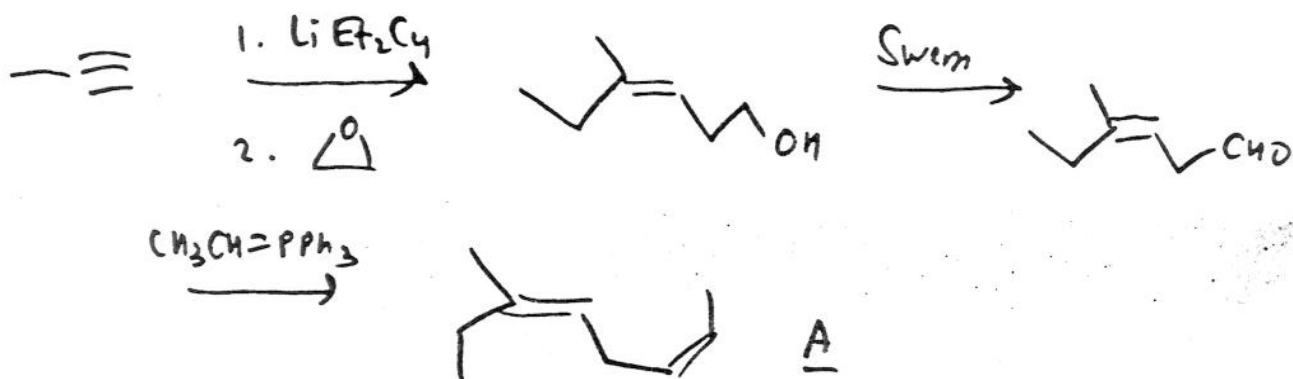
2B



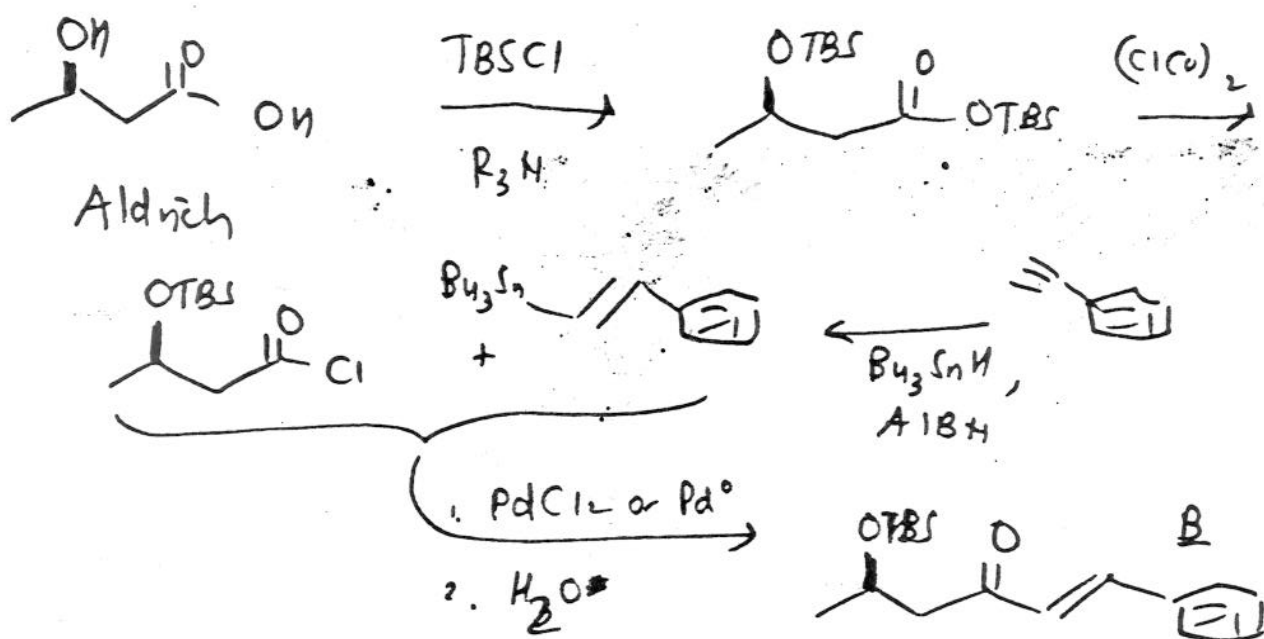
2c



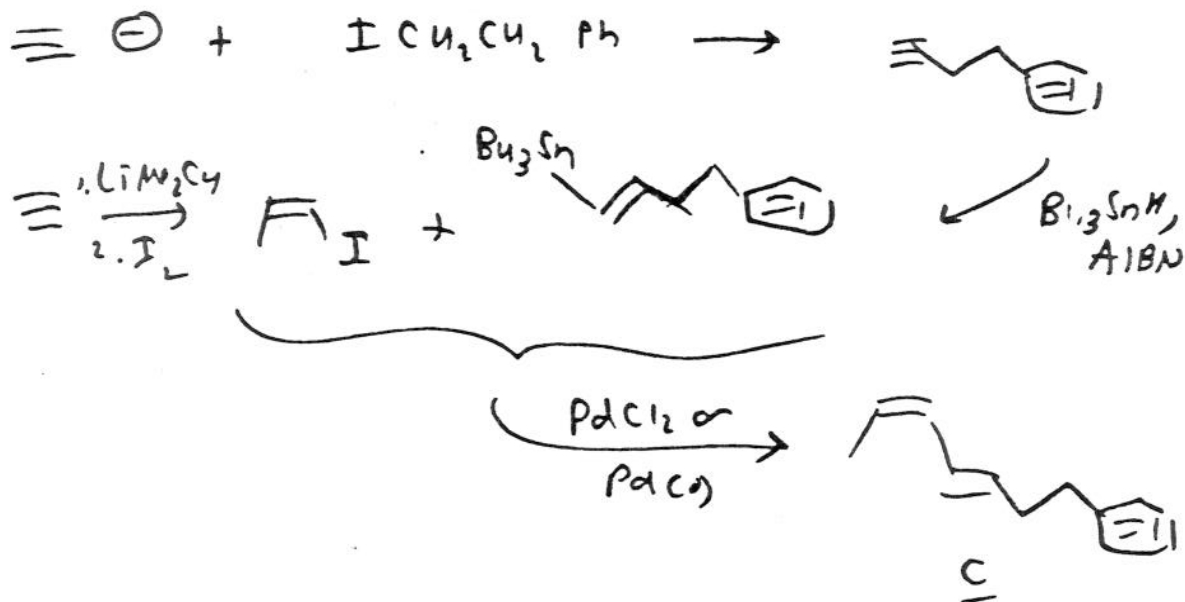
3A



3B



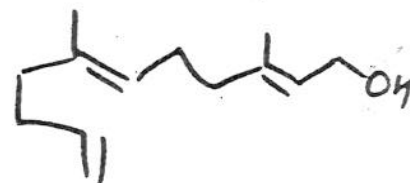
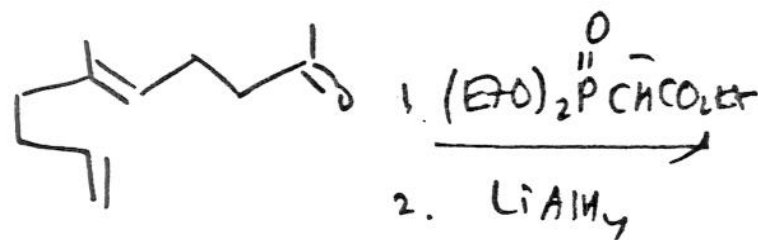
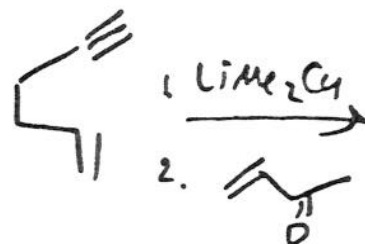
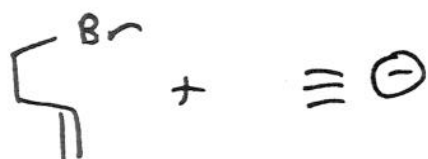
3C



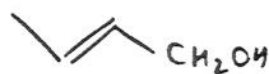
(Set 1)

p.5

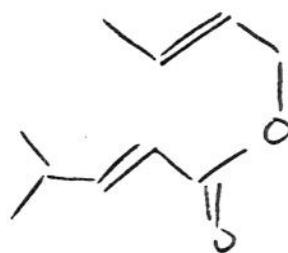
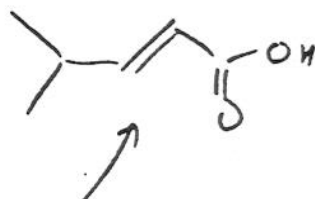
3D



4A

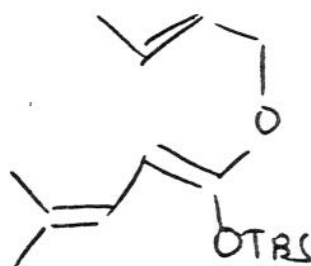


couple via DCC
or acid chloride



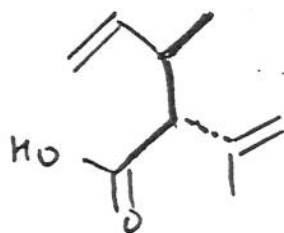
Can make from >CHO
+ Ph3P=CHCO2Et

1. LDA
HMPA
TBSCl



transcort
chain

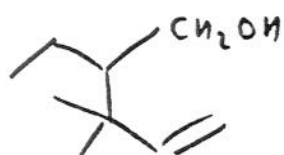
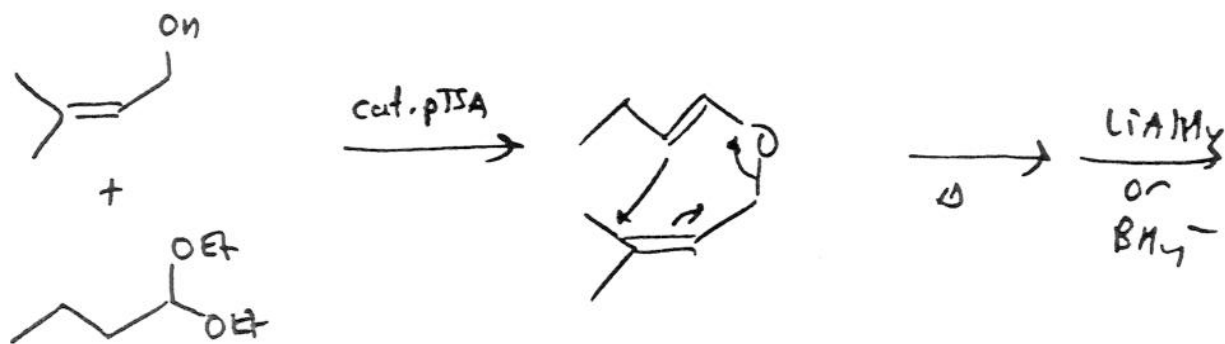
60°
1. chair
Ireland
rearrst,
1. H₂O



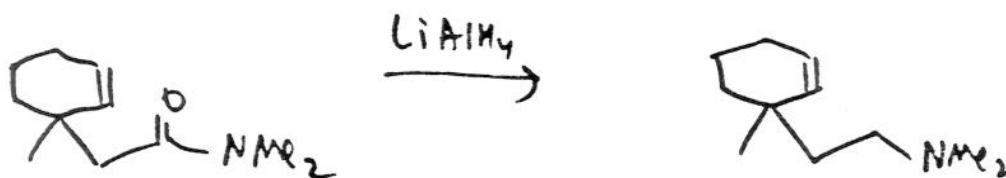
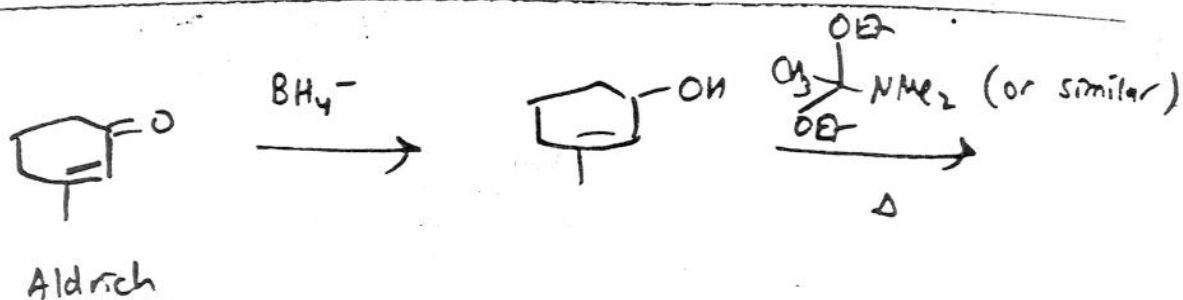
(Set 1)

4B

p.6



4C.



4D.

