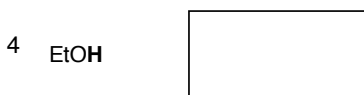
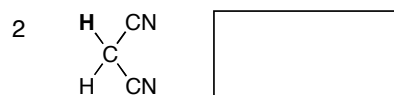
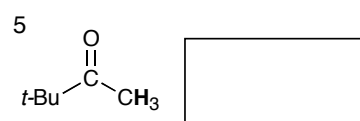
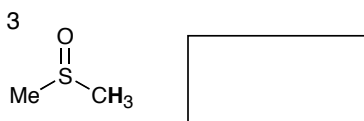
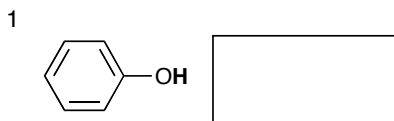


# CEM 852 Final Exam

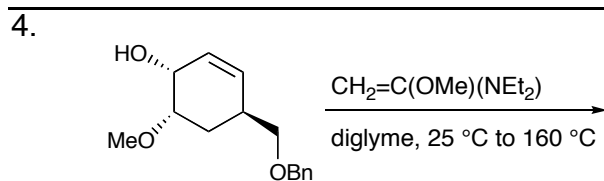
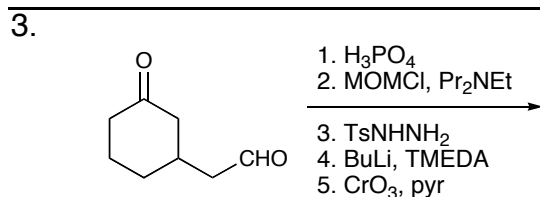
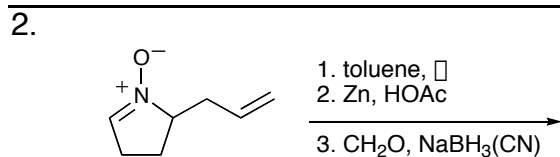
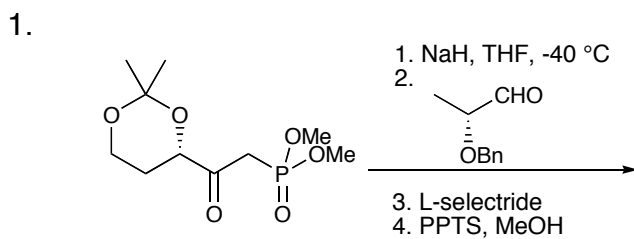
May 4, 1998

This exam consists of 5 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. Good luck.

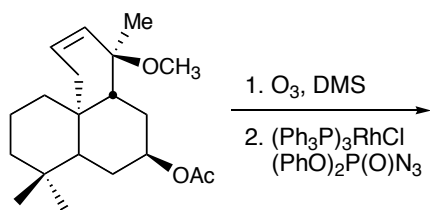
I. Provide the approximate pKa's (within 2 pKa units) of the following compounds. (5 pts)



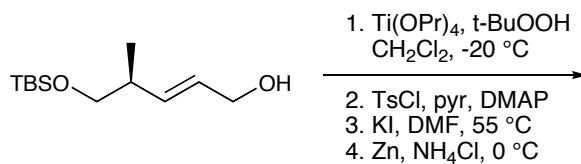
II. (30 pts) Provide the product or products of the reactions outlined below. Show all intermediate compounds and be sure to indicate the product's relative or absolute stereochemistry. For reactions where multiple products are possible, be sure to indicate the major and minor species.



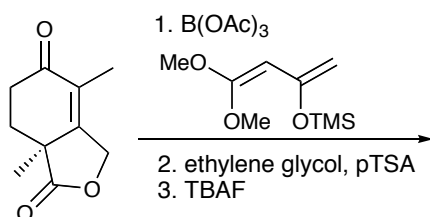
5.



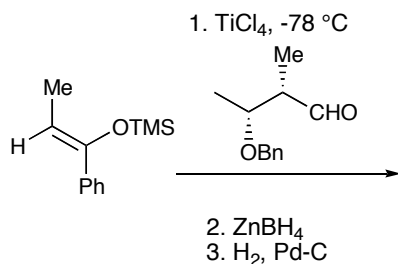
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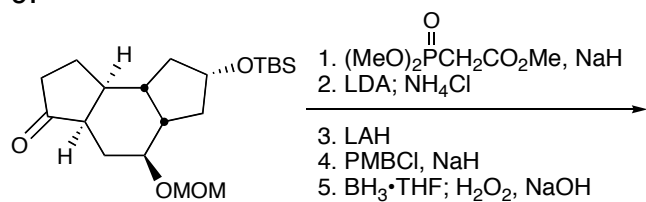
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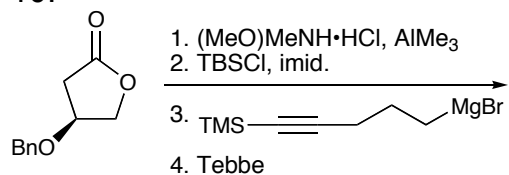
8.



9.

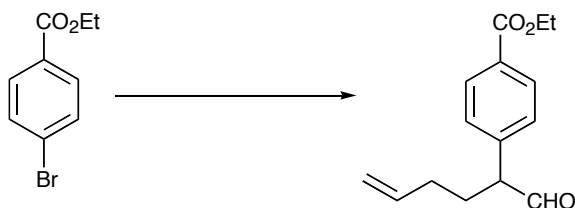


10.

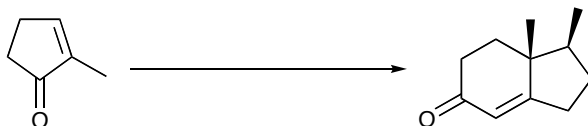


III. (15 pts) Provide conditions which will effect the transformations outlined below. Most of these conversions will require more than one reaction, so be sure to show all intermediate compounds.

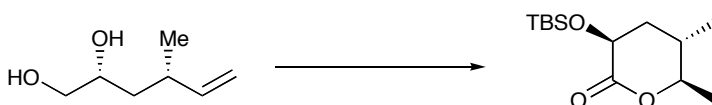
1.



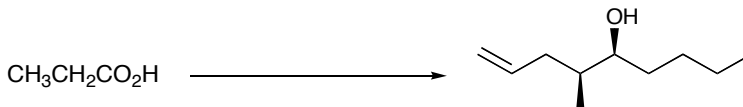
2.



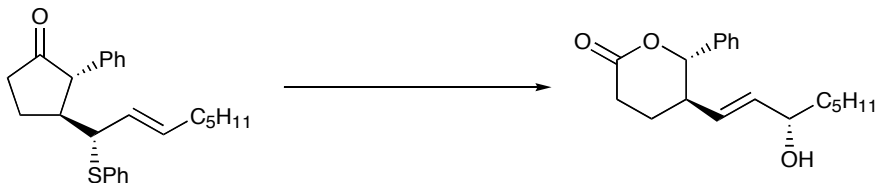
3.



4.



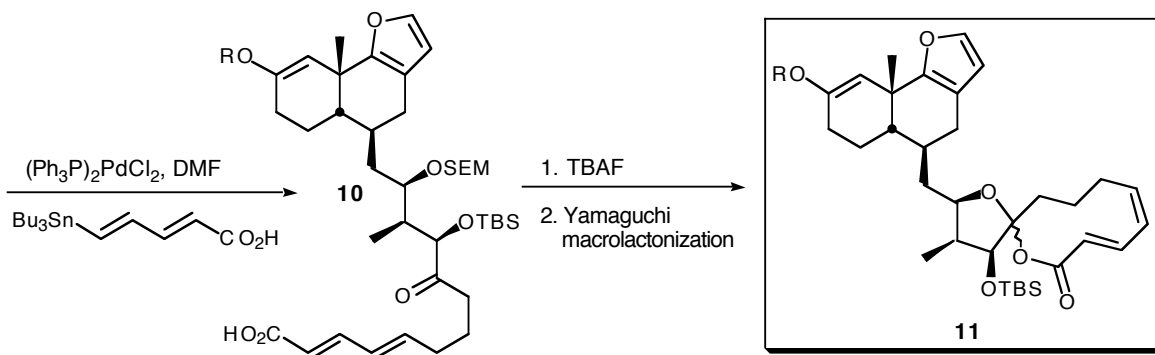
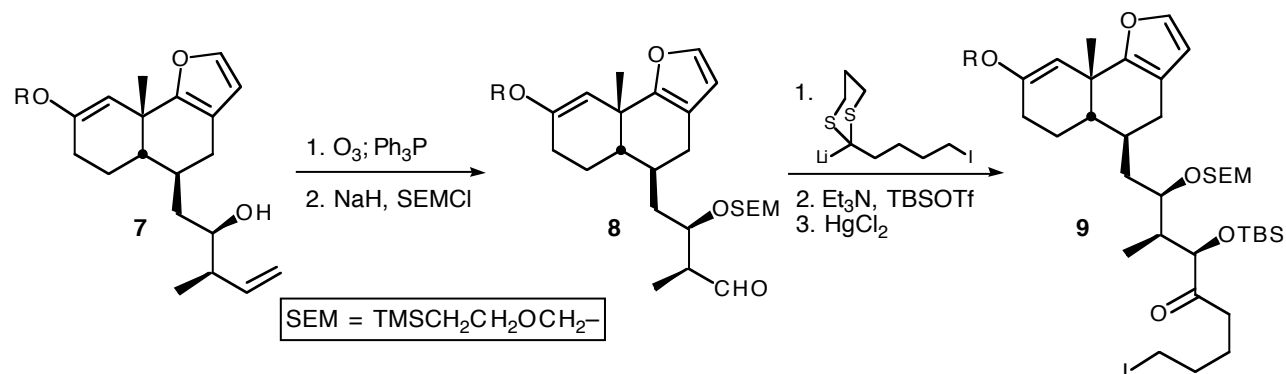
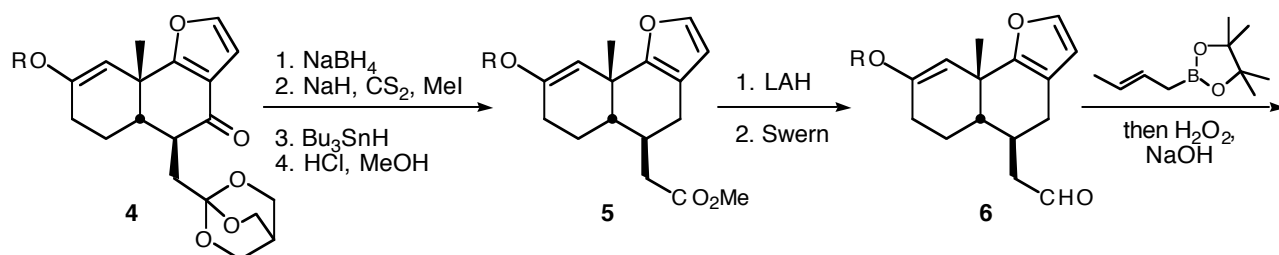
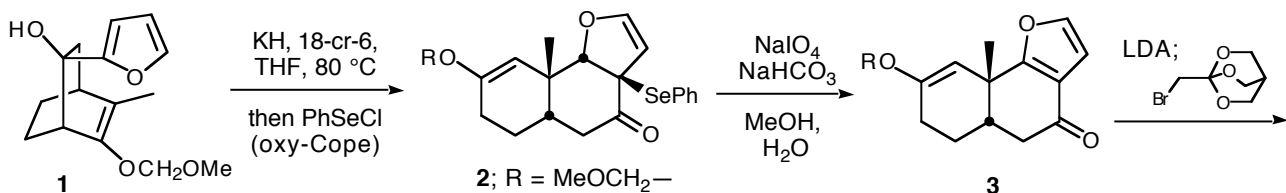
5.



IV. (5 pts) Describe one method of obtaining syn-Aldol products with defined absolute stereochemistry.

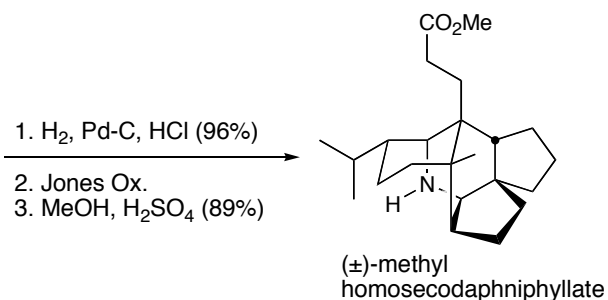
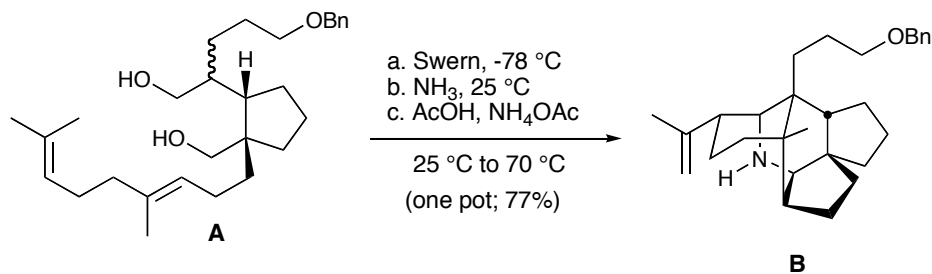
V. (5 pts) Describe one method of obtaining anti-Aldol products with defined absolute stereochemistry.

VI. (15 pts) There are at least ten steps within the following synthetic scheme have problems and will not provide the desired results. Identify five of these "problem" steps and explain the expected synthetic difficulties with those steps.



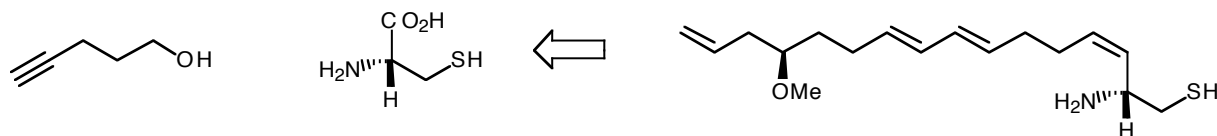
**VII.** (15 pts) In 1988, Heathcock and co-workers published the total synthesis of (±)-methyl homosecodaphniphyllate. The centerpiece of this synthesis is a remarkable one-pot protocol in which diol **A** is converted into pentacycle **B** with an overall yield of 77%. The ring forming

reactions in this sequence include an intramolecular imination, a [4+2] cycloaddition, and an intramolecular  $\alpha$ -cation cyclization. Provide a detailed mechanistic account of the transformation of **A** to **B**.



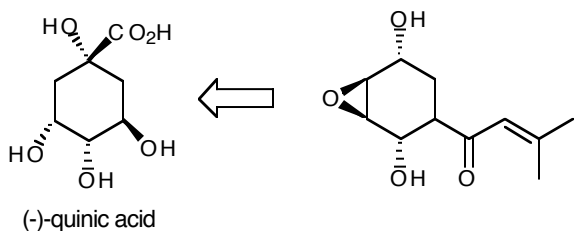
**VIII.** (60 pts) Develop *stereoselective* syntheses for **three** of the four molecules shown below. I would like to see the product of each step. You may employ the literature starting materials provide or use your own, which should also be available from Aldrich.

A.



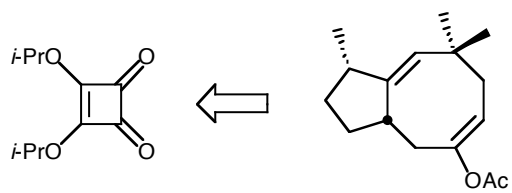
White, *JACS* **1997**, *119*, 103.

B.



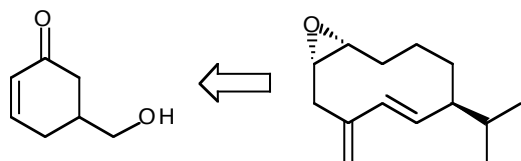
Barros, *JOC* **1997**, *62*, 3984.

C.



MacDougall, *JOC* **1997**, *62*, 3792.

D.



Still, *KCN* Chapter 13. p 215.