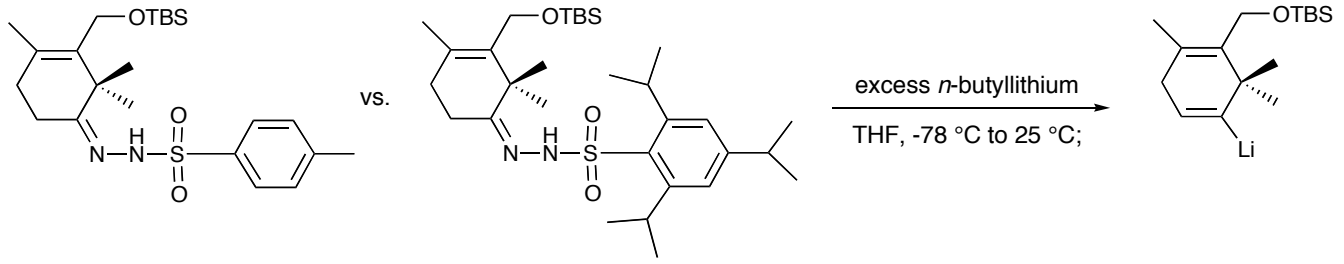
CEM 852 Final Exam Key

May 5, 1999

This exam consists of 6 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. What advantage do 2,4,6-triisopropylbenzenesulfonylhydrazones offer over the more traditional tosylhydrazones in Shapiro reactions? (3 pts)

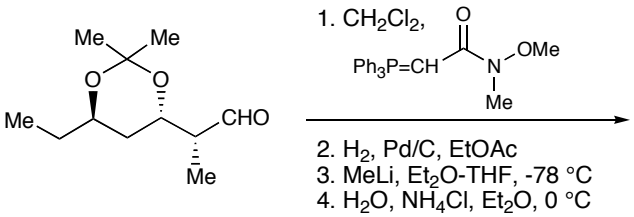


II. Provide definitions of the following terms. Feel free to define these terms through the use of chemical examples. (12 pts)

1. stereospecific:
2. % diastereomeric excess (%de)
3. synthon
4. (1,3)-allylic strain ($A_{(1,3)}$ strain
5. double asymmetric induction
6. Bürgi-Dunitz trajectory

III. (24 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.

1.



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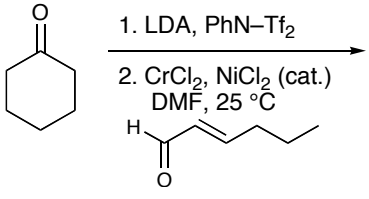

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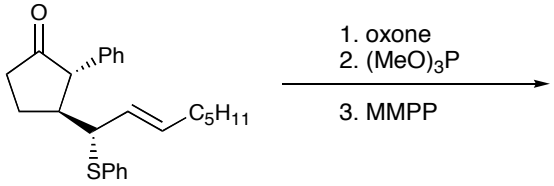

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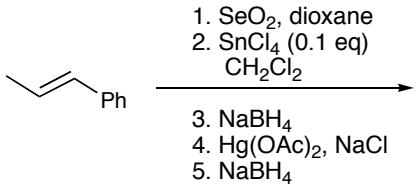

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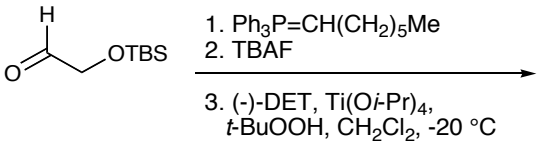

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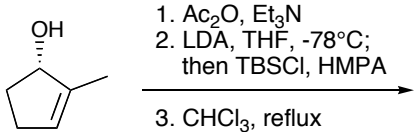

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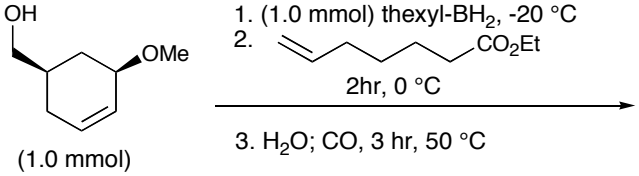

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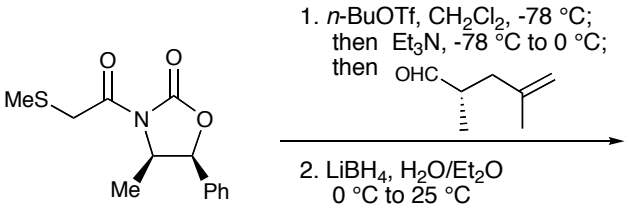
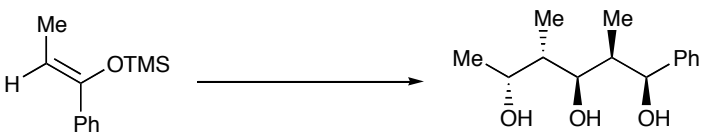


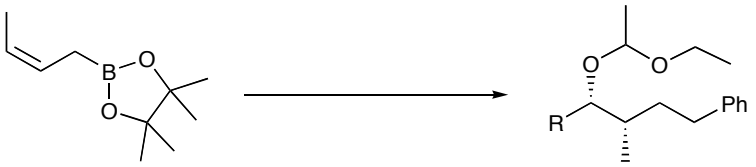
III. (15 pts) Provide conditions which will effect the transformations outlined below. Most of these conversions will require more than one reaction, so be sure to show all intermediate compounds.

1.



2.

3.



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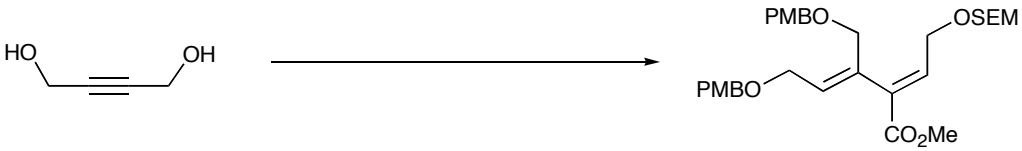

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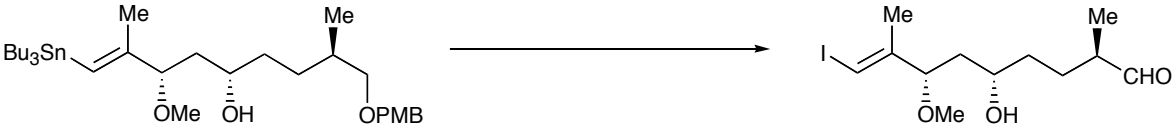
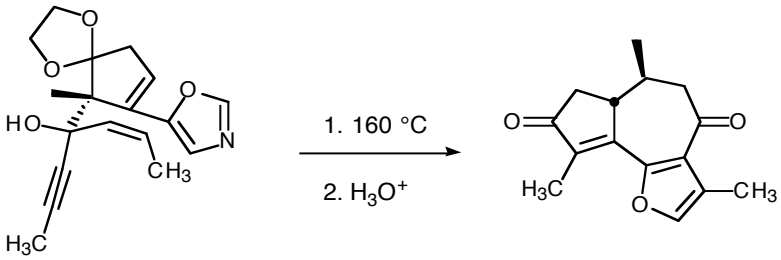
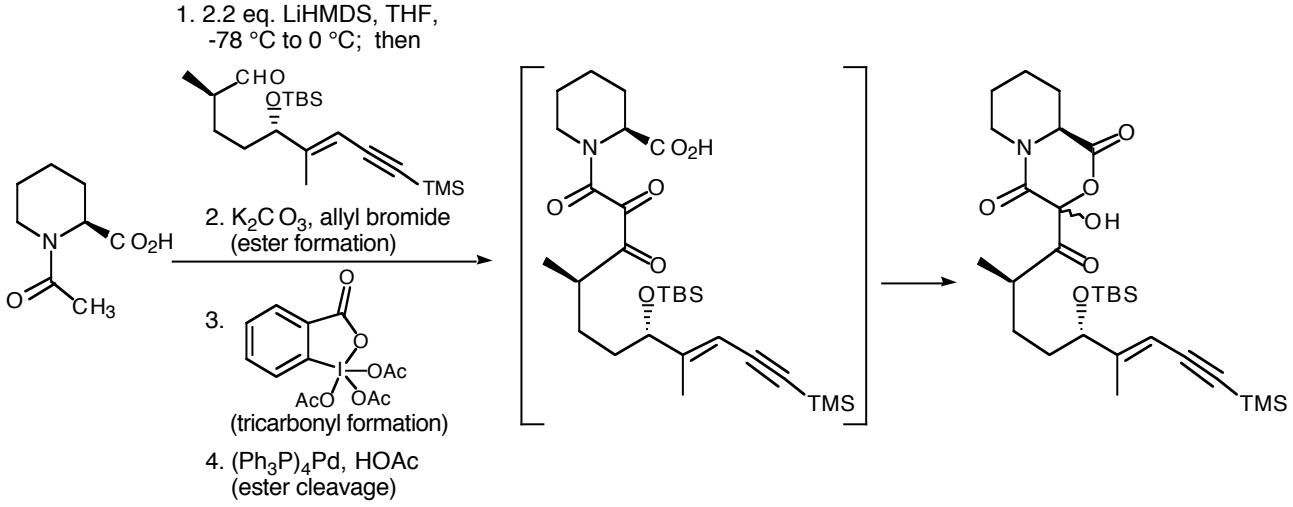


IV. Provide a detailed arrow pushing mechanistic account of the following transformations.

1. (10 pts)

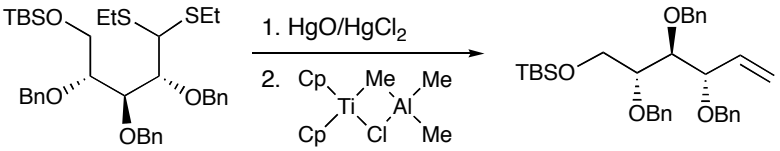


2. (15 pts)



V. A "synthetic approach" to (+)-epi-cyclophellitol is shown below. For each scheme state if the reaction conditions indicated will *or* will not provide the indicated product. For the schemes that will not provide the indicated product, specifically describe the problem with the scheme as shown. Hint: four out of the five reaction schemes shown will NOT provide the indicated product. (15 pts)

1.



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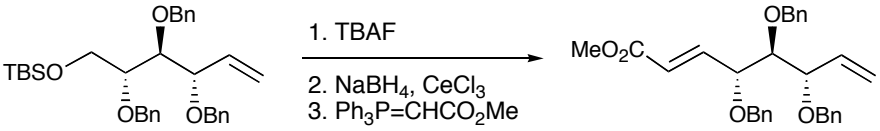

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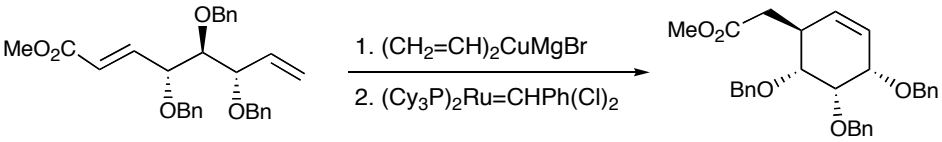

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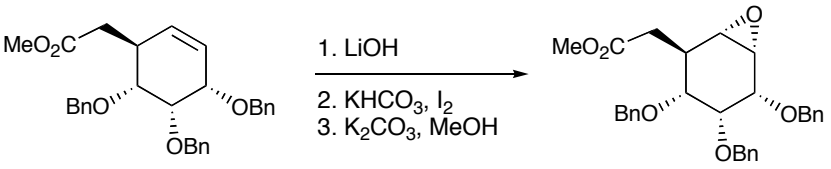

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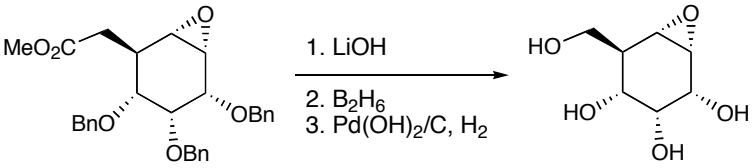
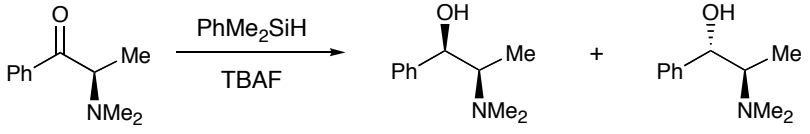
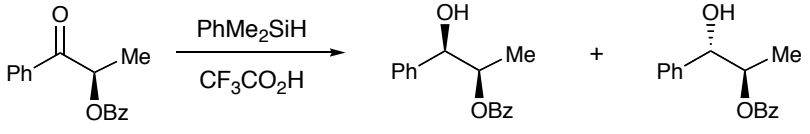


VI. Using Newman projections explain the stereoselectivity of the reactions shown below. (10 pts)

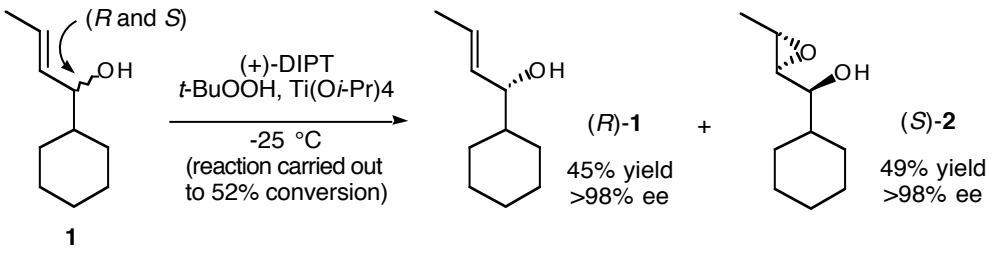


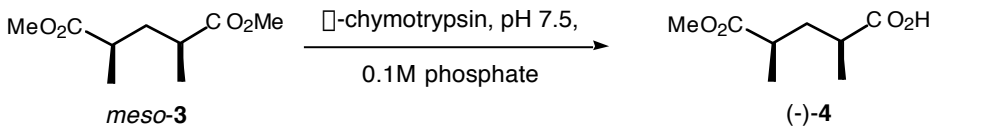
Diastereoselection > 99 : 1

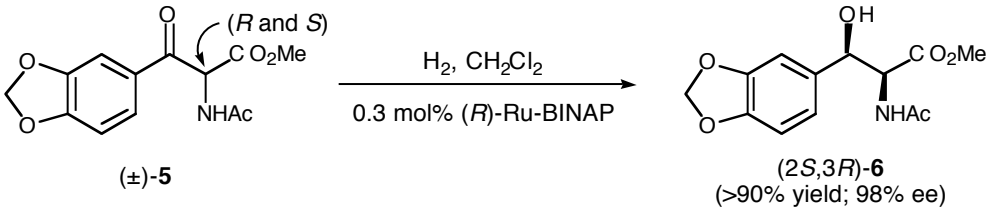


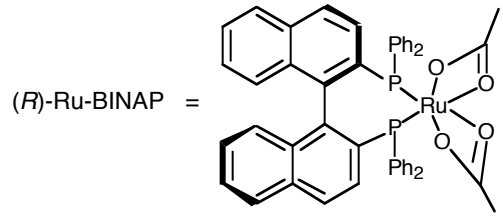
Diastereoselection > 3 : 97

VII. Typically the kinetic resolution of a racemic mixture of enantiomers will afford a maximum yield of 50%. For example at 52% conversion, the Sharpless epoxidation of a mixture of *R* and *S* **1** will afford a 45% yield of (*R*)-**1** in >98% ee along with the (*S*)-epoxide (**2**). One way to get around this 50% limitation is to employ meso starting materials. Thus the enzymatic desymmetrization of *meso*-diester (**3**) can afford (-)-**4** in 94% yield with 96% ee.





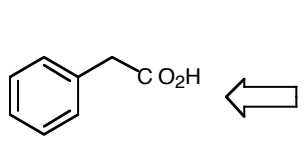




Several years ago Noyori developed another way in which the 50% limitation could be overcome. Starting with *racemic* mixtures of enantiomers such as (±)-**5** Noyori showed he could carry out stereoselective hydrogenations to 100% completion, yet produce a single isomer in high yield and in high %ee. How? (15 pts)

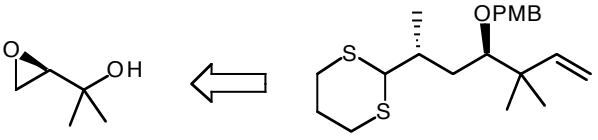
VIII. (30 pts) Develop *stereoselective* syntheses for **two** of the three molecules shown below. I would like to see the product of each step. You may employ the literature starting materials provide or use your own, which should also be available from Aldrich.

1.



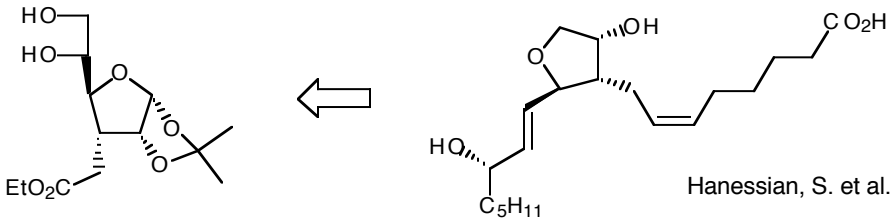
Prashad, M. et al. *J. Org. Chem.* **1999**, *64*, 1750-1753

2.



D'Auria, M.V. et al. *J. Org. Chem.* **1998**, *63*, 7382-7388

3.



Hanessian, S. et al. *Acc. Chem. Res.* **1979**, *12*, 159.