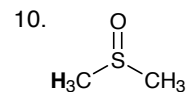
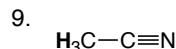
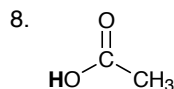
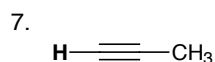
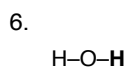
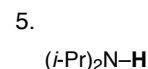
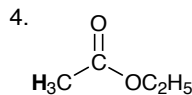
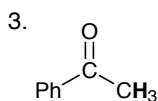
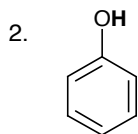
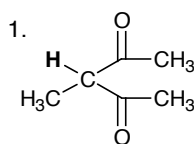


CEM 852 Final Exam

May 2, 2000

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. Good luck.

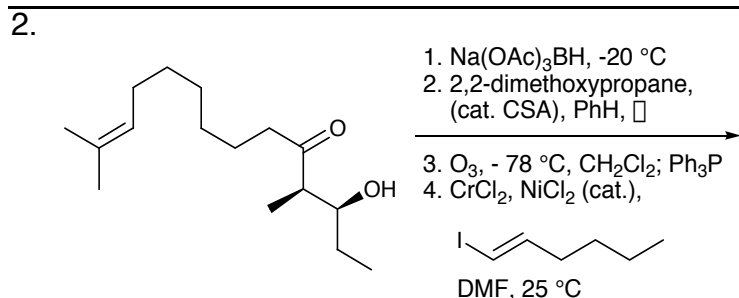
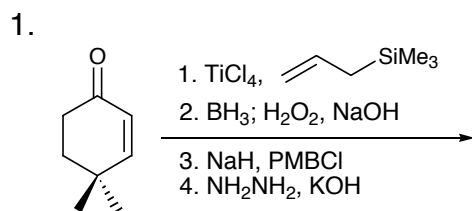
I. Provide the approximate pKa's (within 2 pKa units) of the following compounds. (10 pts)



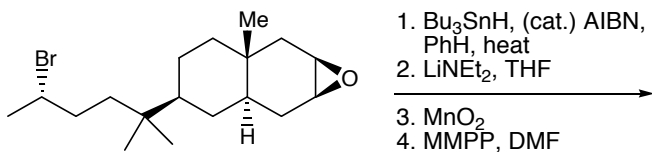
II. Provide definitions of the following terms. Feel free to define these terms through the use of chemical examples. (10 pts)

1. umpolung
2. regioselectivity
3. Zimmermann-Traxler transition structure
4. Z-(O)-enolate
5. kinetic resolution

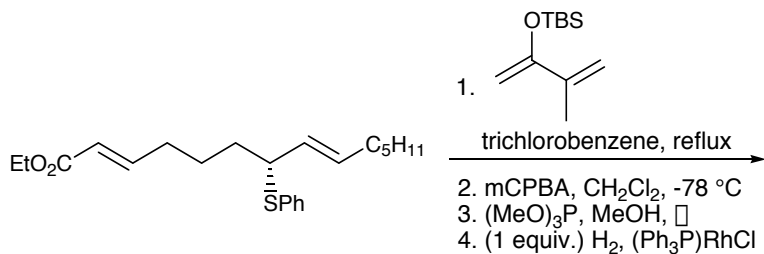
III. Provide the product or products of the reactions outlined below. Show all intermediate compounds and be sure to indicate the product's relative or absolute stereochemistry. For reactions where multiple products are possible, be sure to indicate the major and minor species. (36 pts)



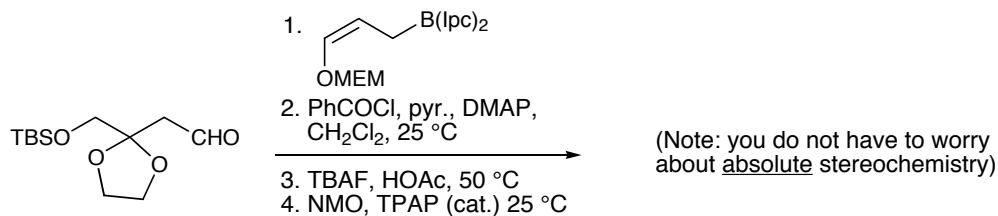
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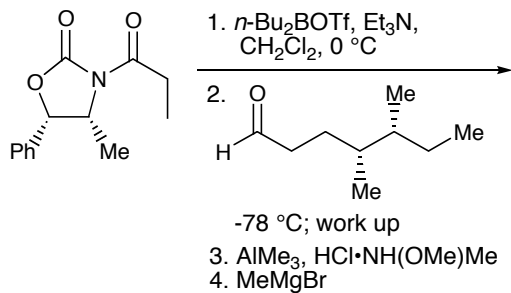
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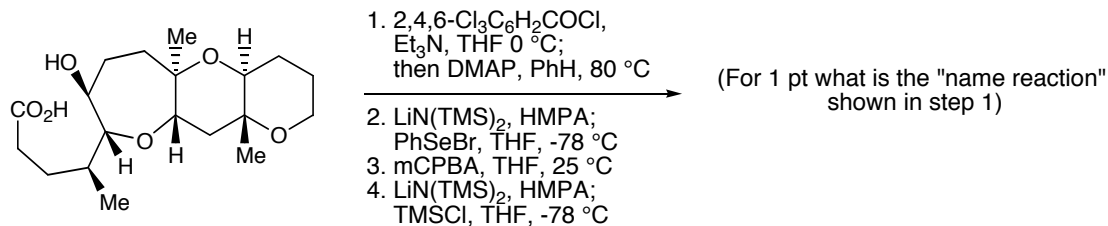
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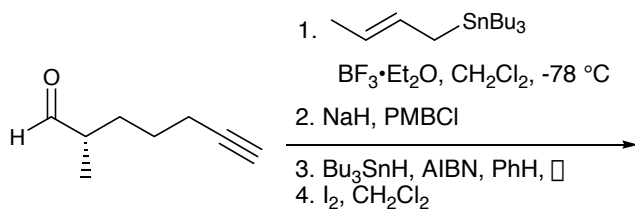
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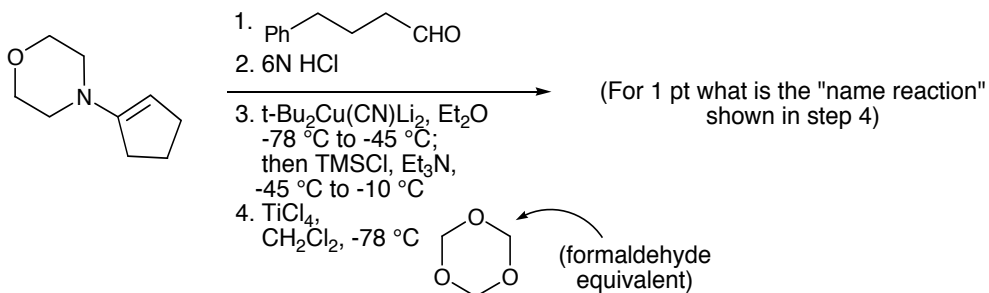
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8.

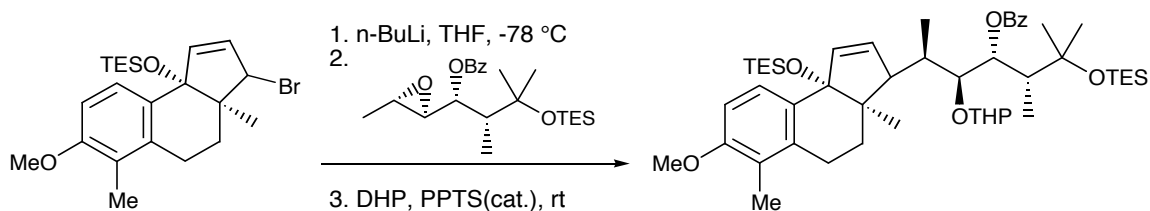


9.

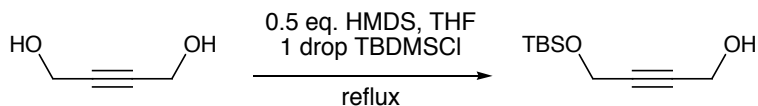


IV. Shown below are eleven reaction sequences from last week's student presentations. State at least one reason why each reaction Scheme is problematic as written. (22 pts)

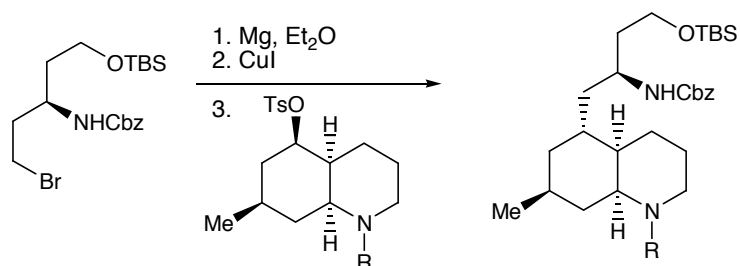
1.



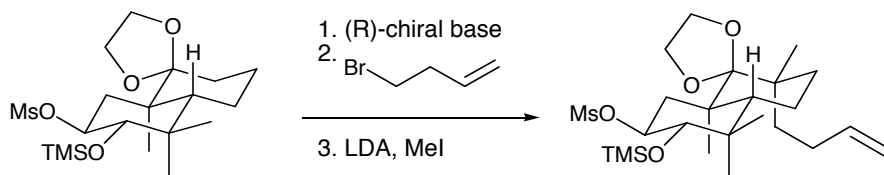
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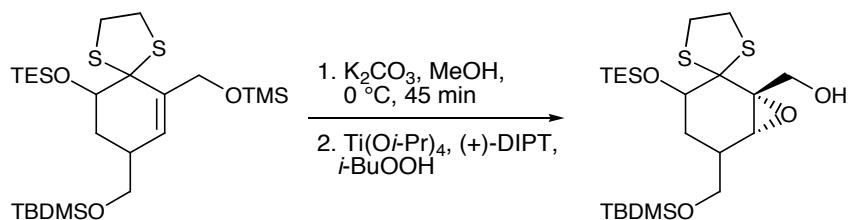
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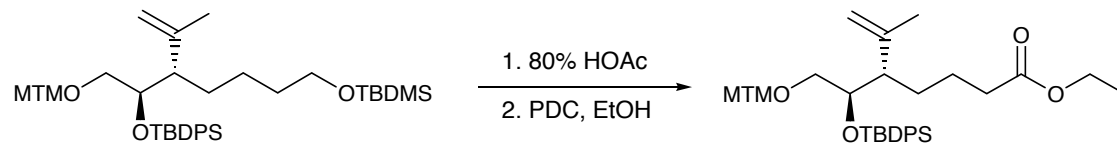
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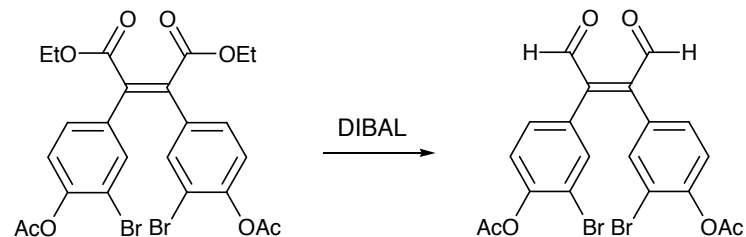
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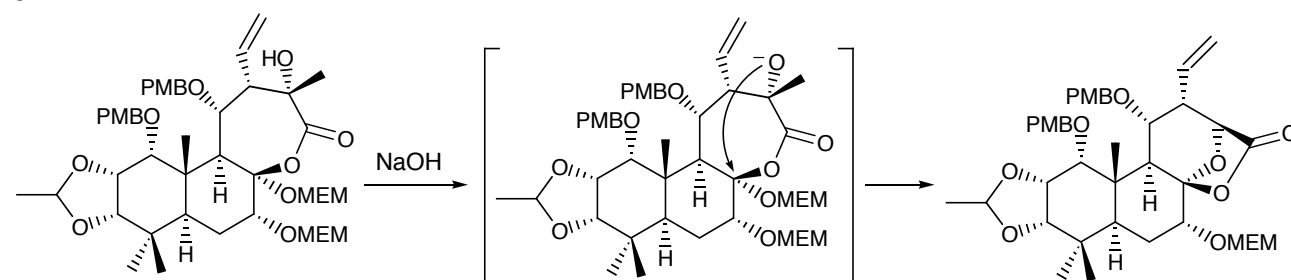
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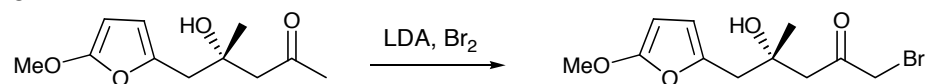
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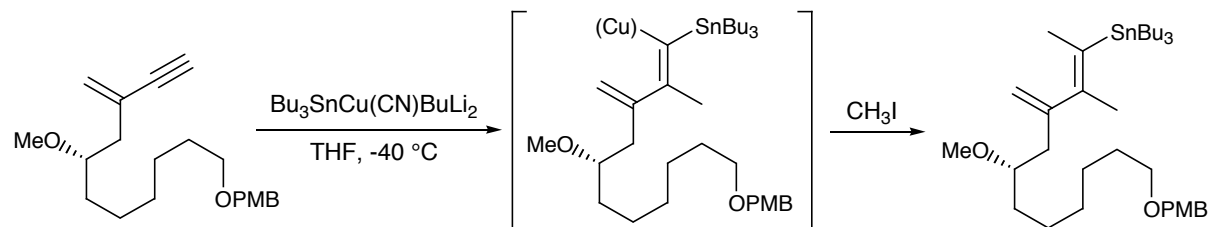
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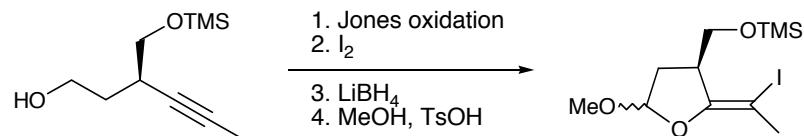
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10.

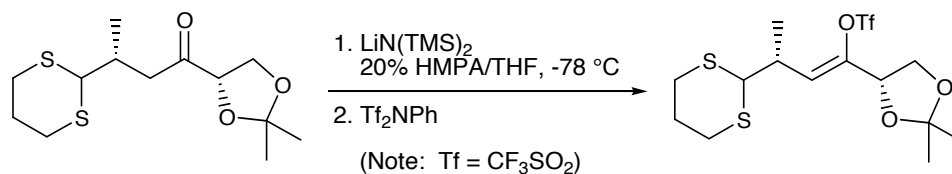


11.

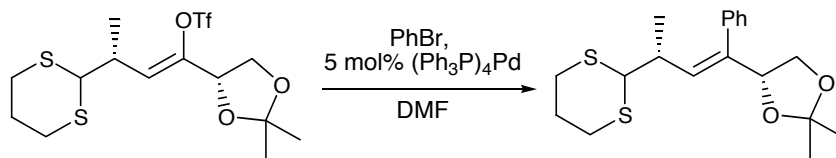


V. Provide a detailed mechanistic account of the following transformations.

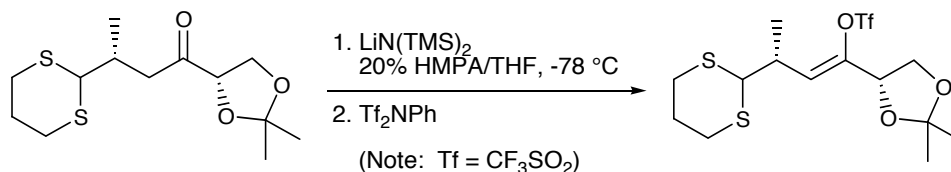
(a) (5 pts)



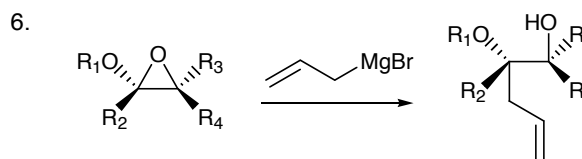
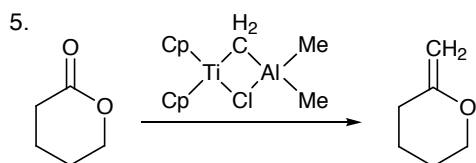
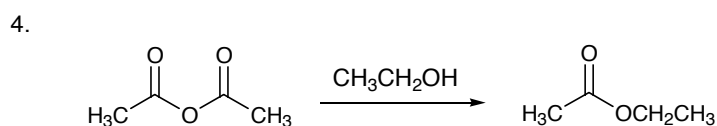
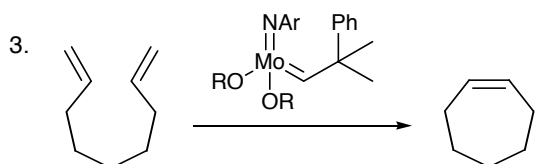
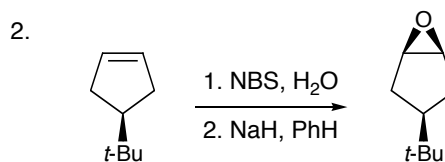
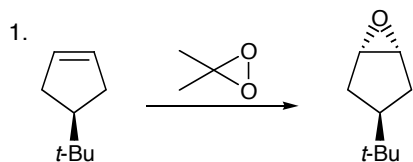
(b) (5 pts)



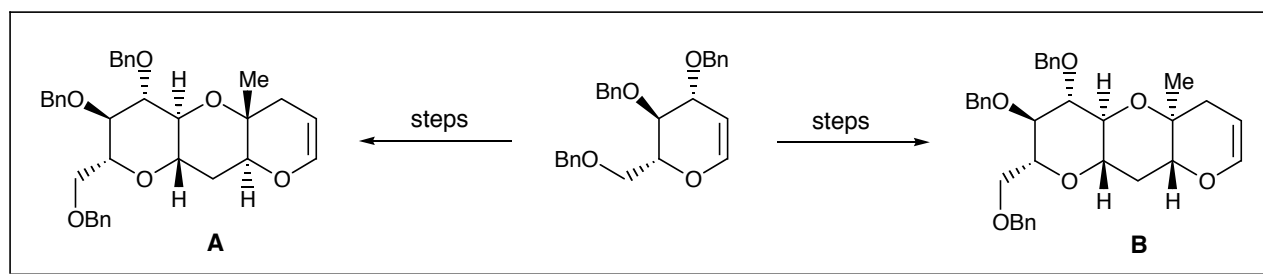
VI. In problem Va, why is 20% HMPA/THF used as solvent. With HMPA present what leads to the observed result? What result would you expect if the HMPA were left out? Why? (10 pts)



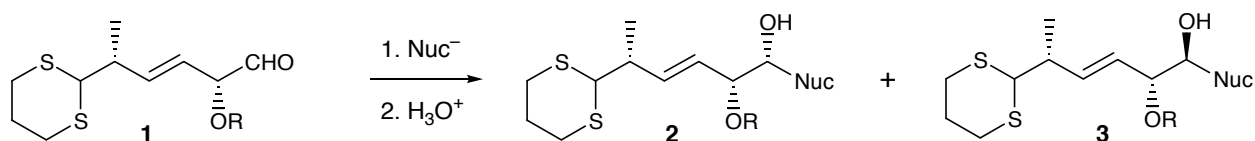
VII. Given the biological importance of molecules such as brevetoxin B, which contains repeating fused ether rings, chemists continue to develop new methods to construct such ring systems. Many of these approaches require chemistry that is no more sophisticated than what we have seen in CEM 852. Six such transformations are shown below.



Using any combination of these six transformations (you may use any of these types of reactions as many times as you wish), devise selective syntheses of **A** and **B** from tribenzyl-D-glucal. (20 pts)

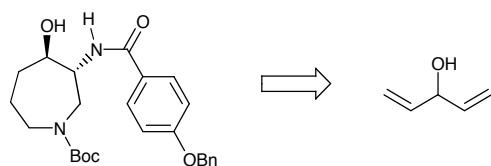
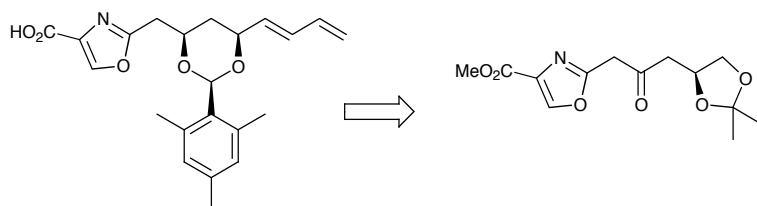
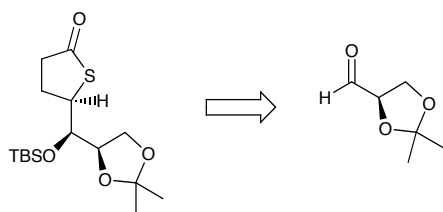


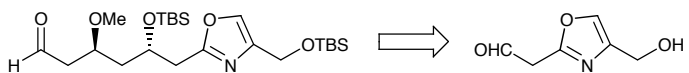
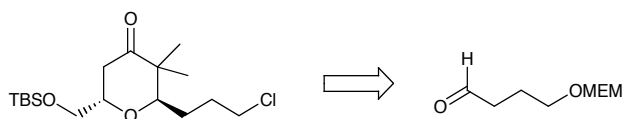
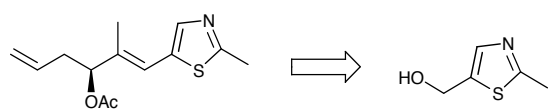
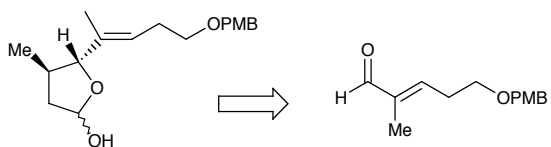
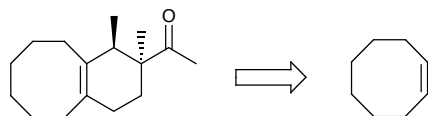
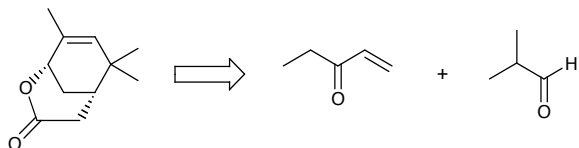
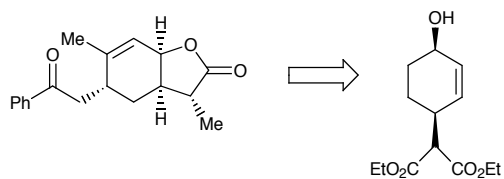
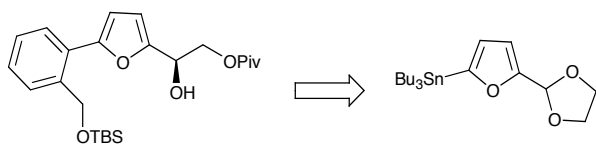
VIII. A group of chemists needed anti-alcohol **3** as part of a synthetic project. They assumed that aldehyde **1** would follow a Felkin-Ahn addition model with the TBS ether serving as the large group. However when the reaction products were analyzed, the ratio of **2** to **3** was 5:1. In an attempt to get this reaction to favor the formation of **3**, they replaced the TBS group with an even larger BPS group. However this substitution actual *decreased* the relative amount of **3** ($2/3 = >20:1$). Interestingly, when the R group was made smaller (R = MOM) that the ratio of **3** actual improved ($2/3 = 2:1$) although it remained the minor product. Explain these results. (10 pts)



R = Si(Me)₂t-Bu (TBS) then $2/3 = 5/1$
 R = Si(Ph)₂t-Bu (BPS) then $2/3 = >20/1$
 R = MOM then $2/3 = 2/1$

IX. (20 pts) Develop a *stereoselective* syntheses for **one** of the eleven molecules shown below. I would like to see the product of each step. You may employ the starting materials provided or use your own. (Any starting materials chosen by you should be available from Aldrich.)





Bonus Question: A character in the novel *The Cantor's Dilemma* is based on one of this year's seminar speakers. Which one ? (2 pts)

- Bob Grubbs
- Andy Hamilton
- Keith Ingold
- Kathy Parker
- Qifei Yang