

CHEM 330

Exam 2

November 18, 2013

ANSWERS

Your name: _____

This document consists of 7 pages

This a closed-notes, closed-book exam

You may use your set of molecular models

Time: 1.5 h

1. _____ / 10

2. _____ / 15

3. _____ / 15

4. _____ / 20

5. _____ / 20

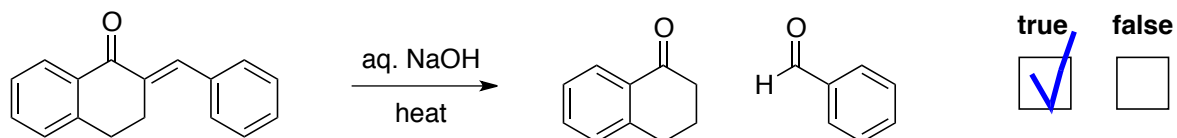
6. _____ / 20

TOTAL _____ / 100

This exam counts for 25% of your CHEM 330 final grade

1. (10 pts.) Check the appropriate box to indicate whether the following statements are true or false:

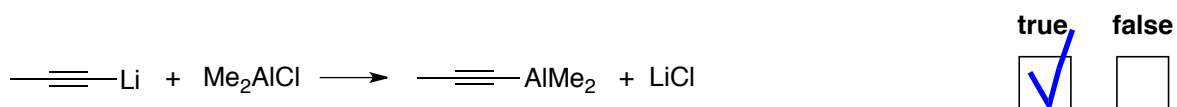
a. The process shown below is a reverse aldol-dehydration reaction:



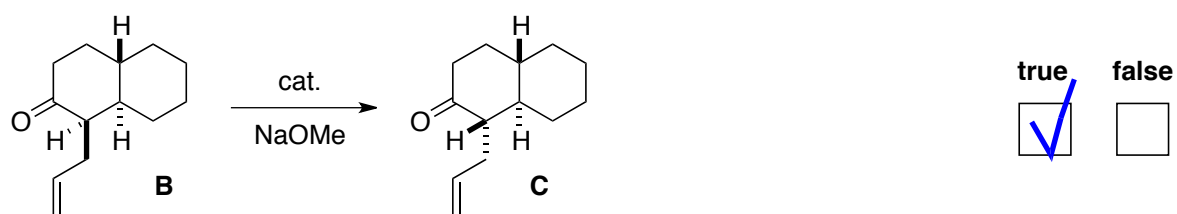
b. Compound **A** may be prepared as shown below:



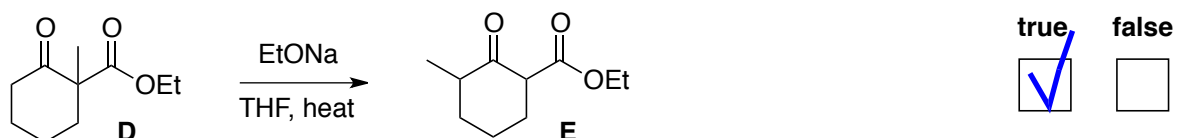
c. The following is a transmetallation reaction:



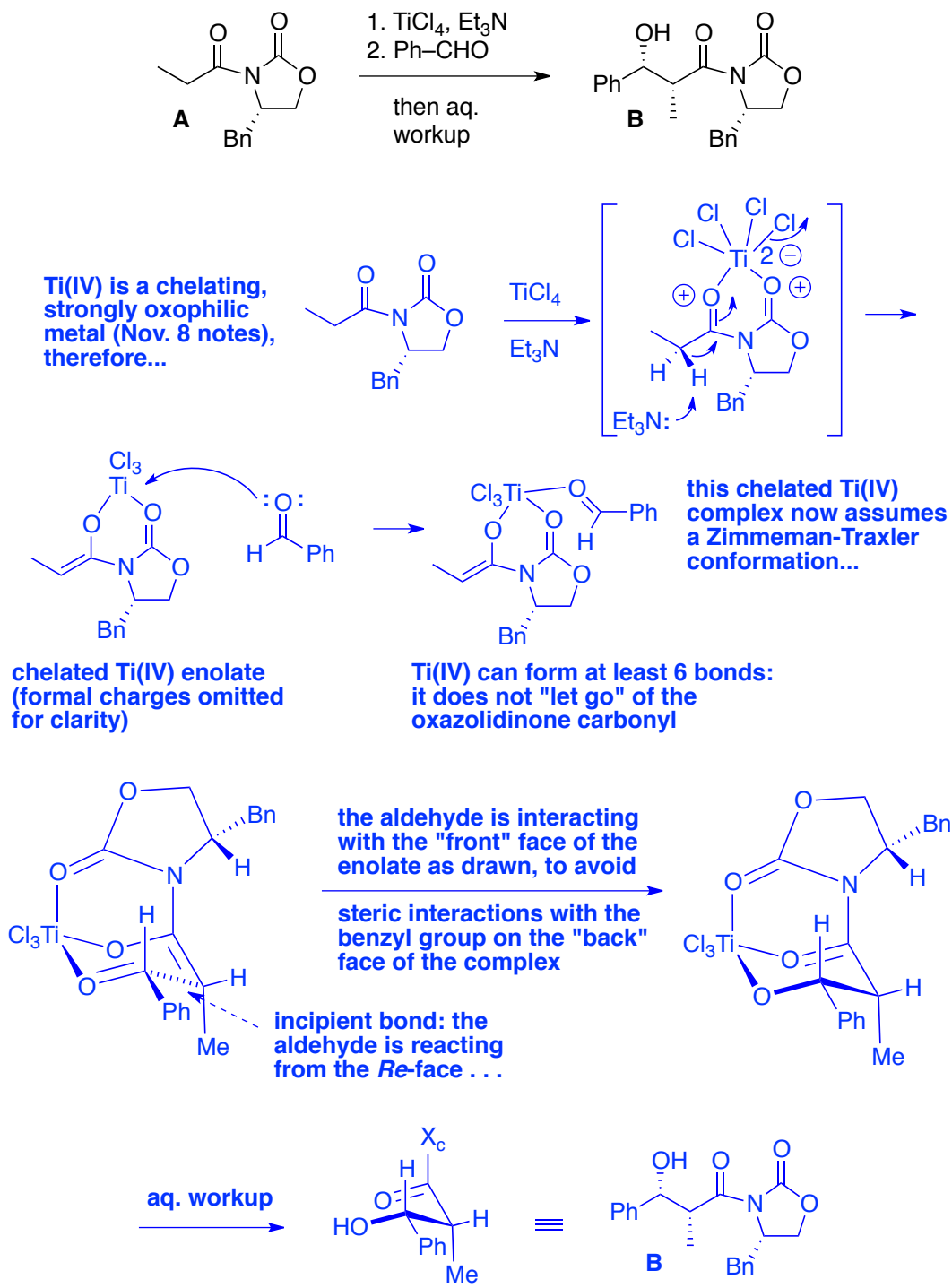
d. Treatment of **B** with catalytic NaOMe will cause isomerization to **C**:



e. Heating **D** in the presence of NaOEt in THF will cause the formation of **E**:

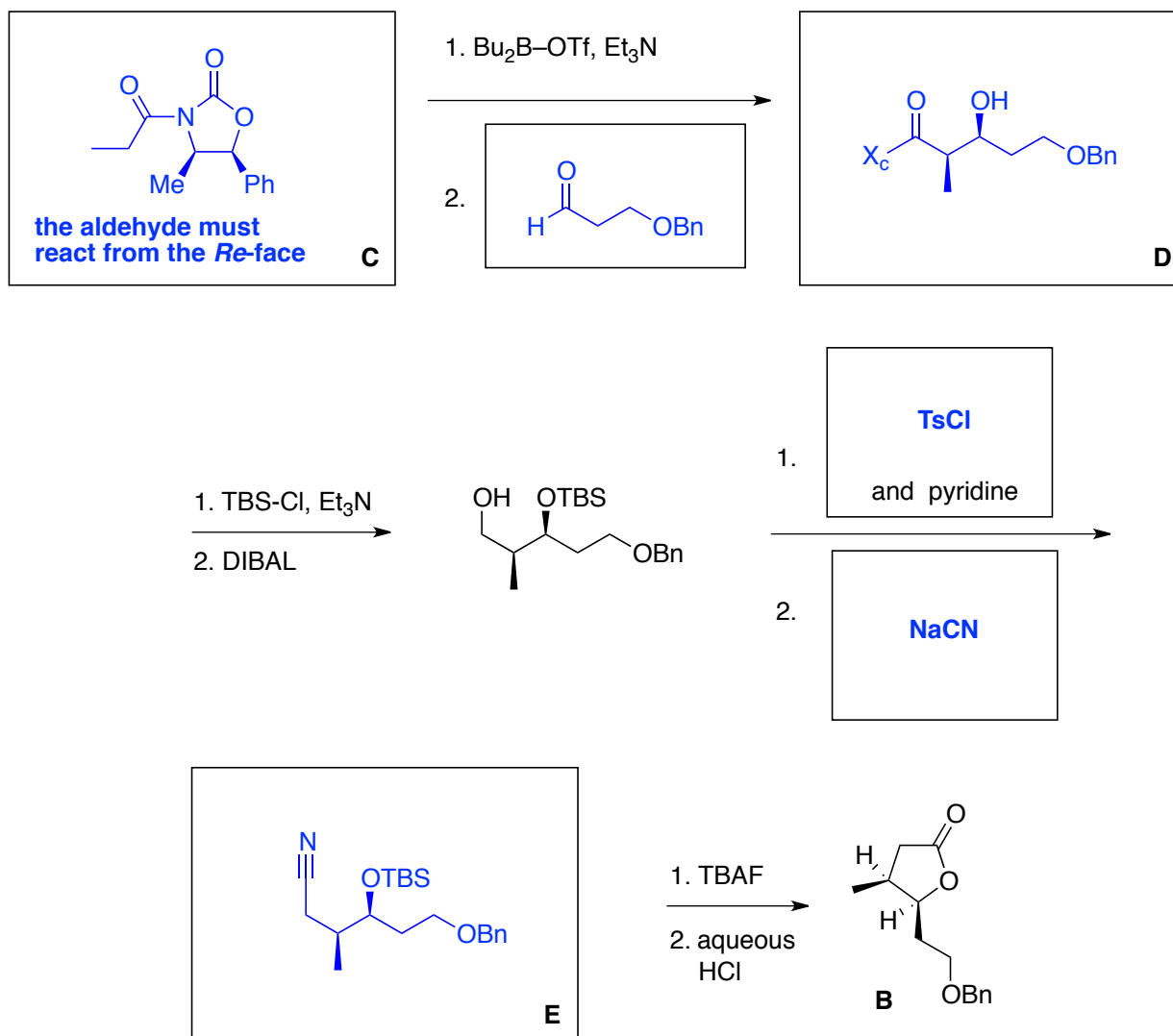
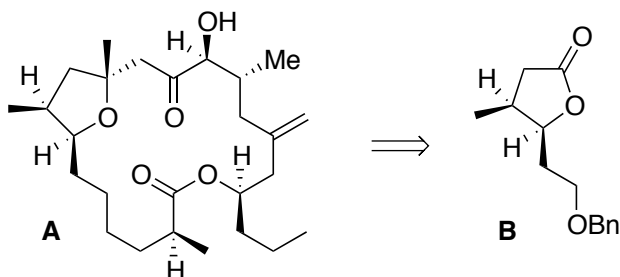


2. (15 pts.) We have seen in class that the dibutylboron enolate of Evans imide **A** will add selectively to the *Si*-face of an aldehyde. Provide a rationale for the observation that treatment of **A** with 1 equivalent each of TiCl_4 and triethylamine, followed by Ph-CHO , affords an aldol product, **B**, resulting from *Re*-face attack onto the aldehyde. Your answer must include a transition state diagram that convincingly illustrates the reason(s) for this reversal of faciality.

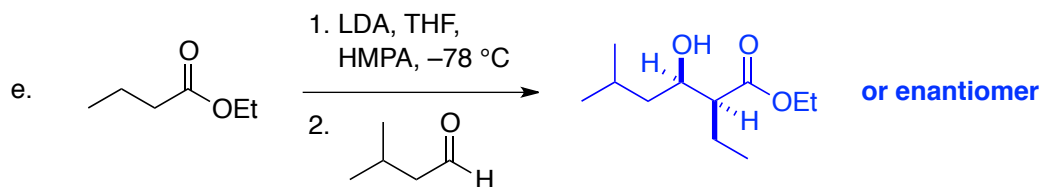
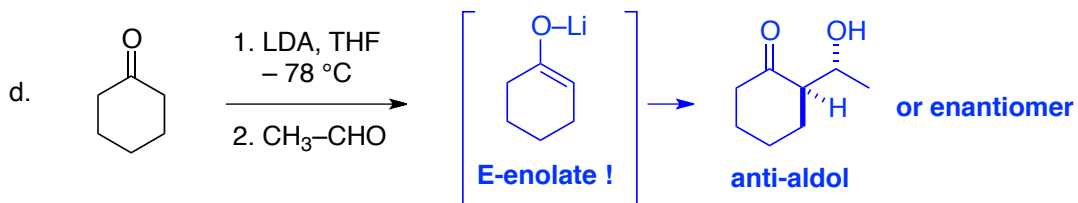
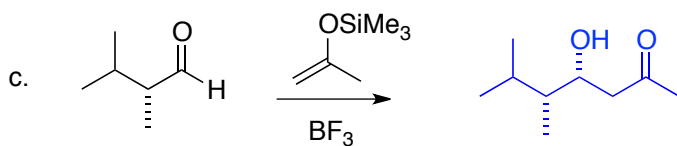
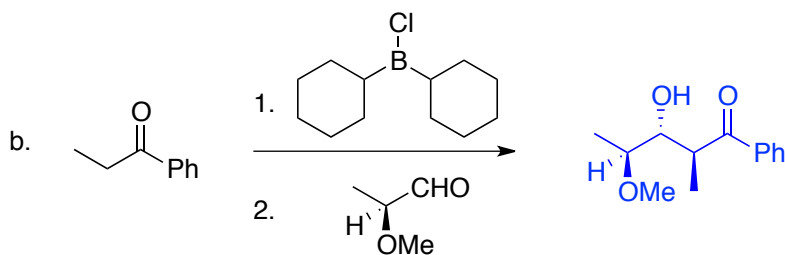
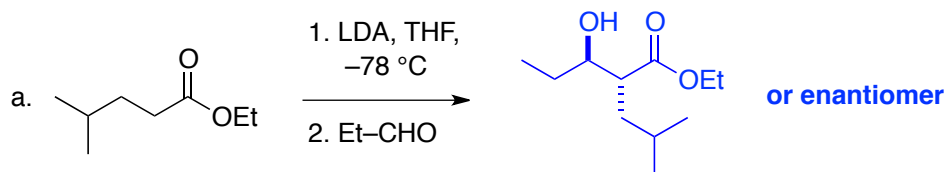


3. (15 pts.) Compound **B** is a fragment of the potent antitumor agent, amphidinolide T1, **A**. A synthesis of **B** (cf. *J. Am. Chem. Soc.* **2003**, 125, 2378) is outlined in the diagram below. Complete this diagram by indicating all missing reagents / products. Each box corresponds to **one** reagent / product.

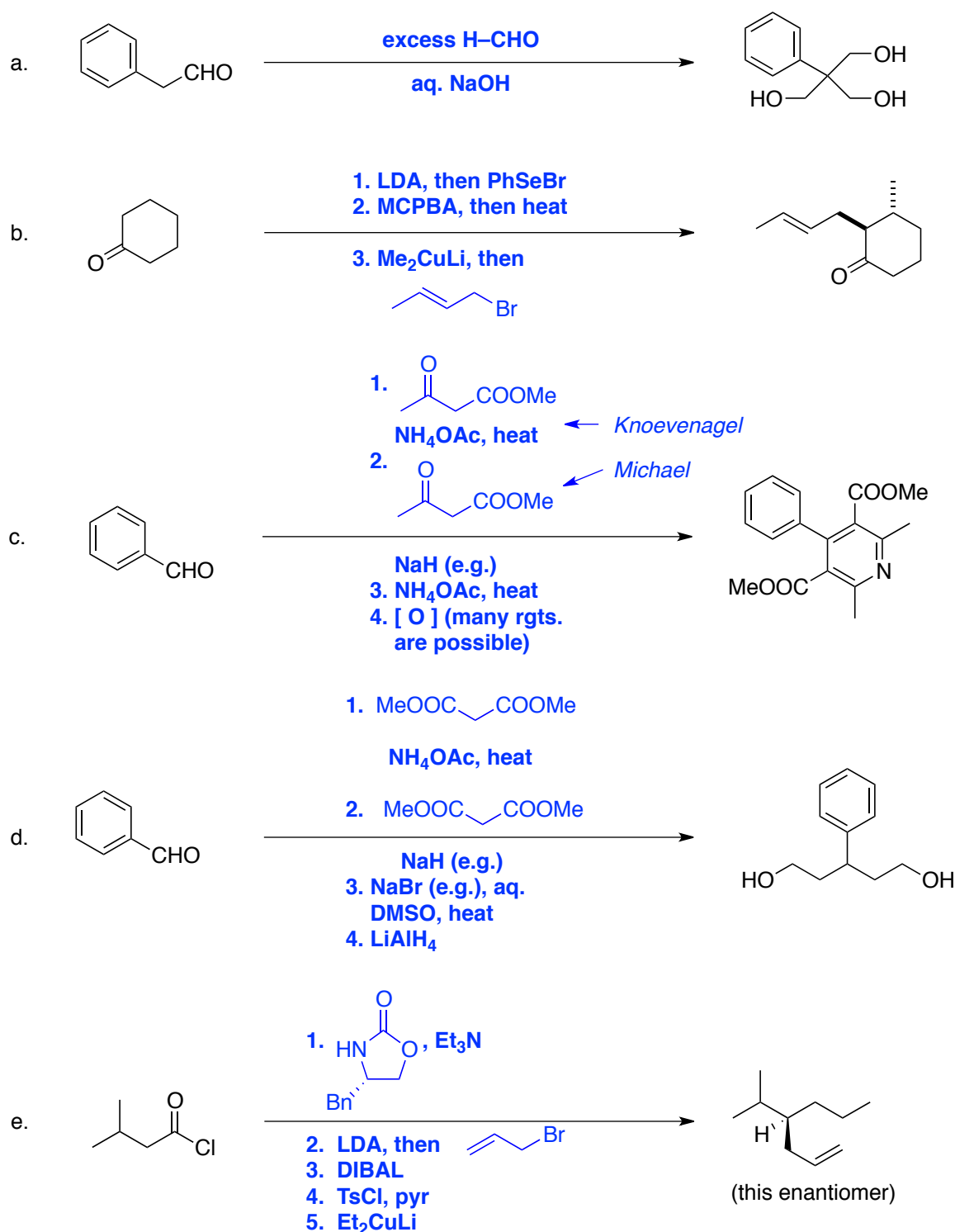
Note: aqueous workup steps are understood and are not to be included in your answers.



4. (20 pts.) Draw the structure of the major product expected from the reactions shown below.
Note: it is understood that each reaction is subject to a final aqueous workup.

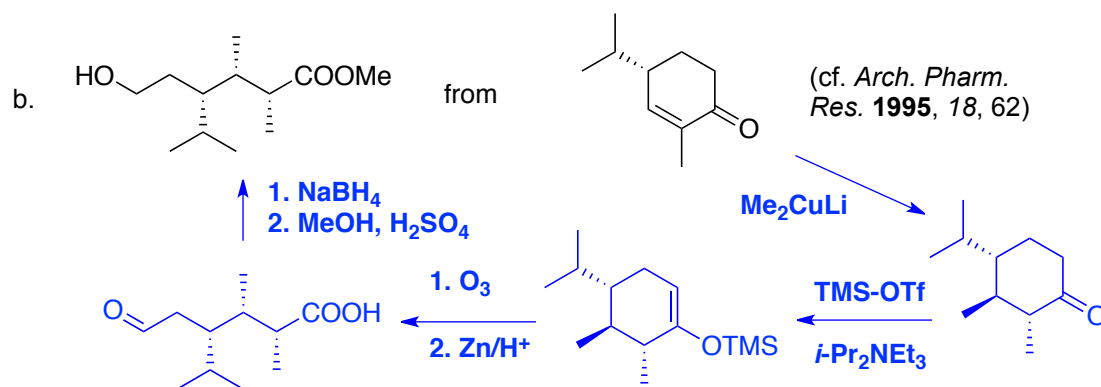
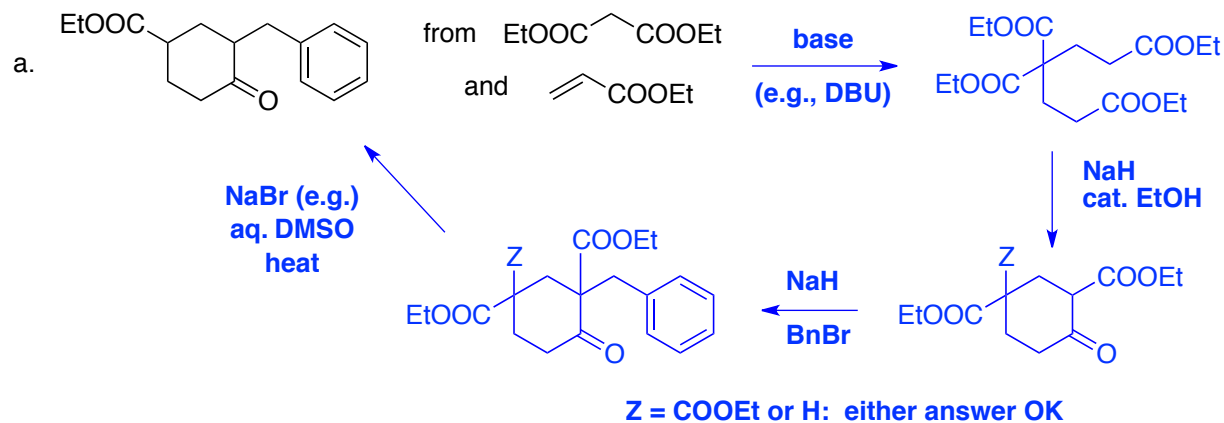


5. (20 pts.) Propose a method to achieve the transformations shown below. In each case, a multistep sequence (= not just one reaction, but several) may be required. Indicate all requisite reagents, in the correct order, as a numbered list above/below the reaction arrow. **Aqueous workups after each step are understood and there is no need to specify them.**



alternative answers may be acceptable

6. (20 pts.) Propose a method to synthesize the substances shown below from the indicated materials. Assume the availability of all reagents needed to convert the starting compound into the product (e.g., bases, alkyl halides, etc.). Present your answer as a flowchart. **It is not necessary to draw mechanisms. Also, aqueous workups after each step are understood.**



alternative answers may be acceptable