

COMPLETE THIS SECTION : Up to TWO POINTS will be removed for incorrect/missing information!

PRINTED **FIRST NAME** \_\_\_\_\_ *Answer Key* PRINTED **LAST NAME** \_\_\_\_\_

Person on your **LEFT** (or **Empty** or **Aisle**) \_\_\_\_\_

Person on your **RIGHT** (or **Empty** or **Aisle**) \_\_\_\_\_

Class you are REGISTERED FOR (onground or hybrid) \_\_\_\_\_

The room where most students will take the test for your class, i.e. LS A-191 for onground and PS H-152 for hybrid) \_\_\_\_\_

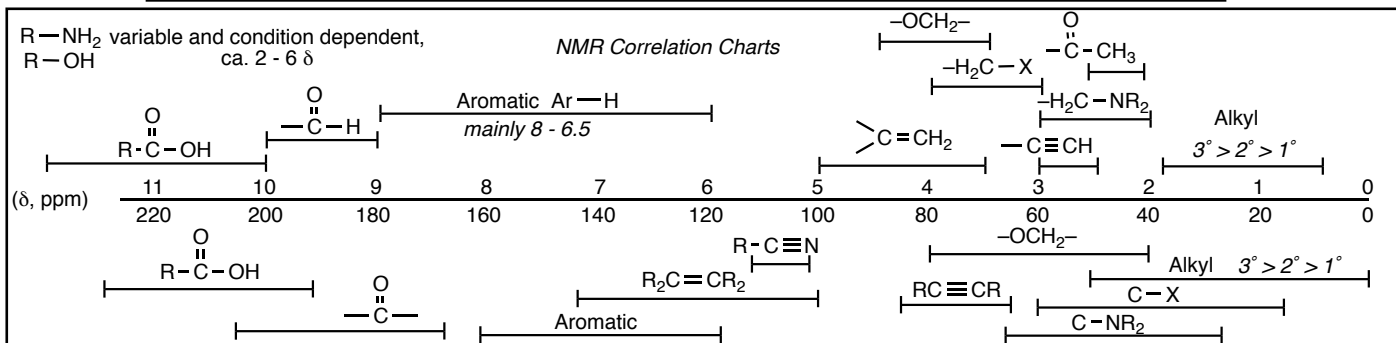
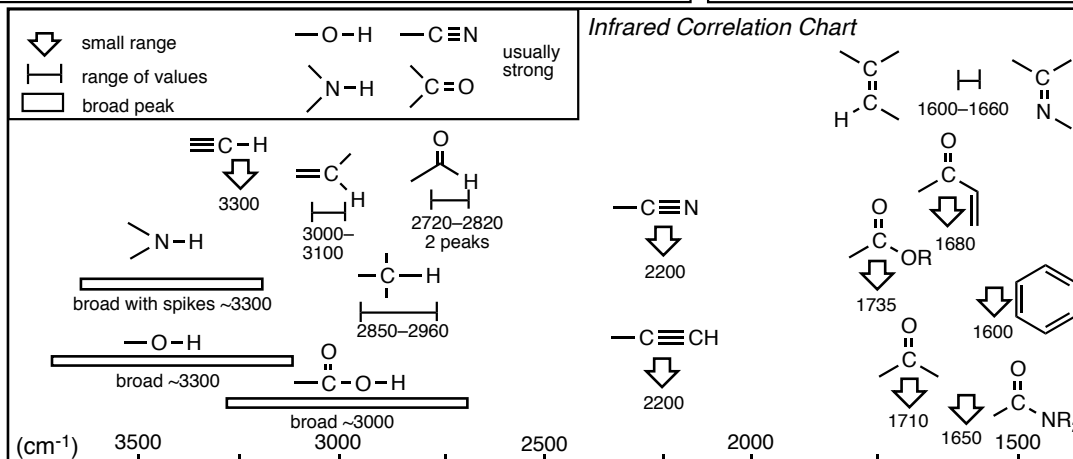
**\*\*YOU ARE NOT ALLOWED TO TAKE SPARE COPIES OF THIS EXAM FROM THE TESTING ROOM\*\***

- |   |                                  |
|---|----------------------------------|
| • PRINT YOUR NAME ON EACH PAGE!           | • WRITE CLEARLY!                 |
| • READ THE DIRECTIONS CAREFULLY!          | • MOLECULAR MODELS ARE ALLOWED   |
| • USE BLANK PAGES AS SCRATCH PAPER        | • DO NOT USE RED INK             |
| work on blank pages will not be graded... | • DON'T CHEAT, USE COMMON SENSE! |

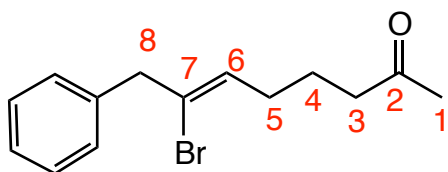
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

### Interaction Energies, kcal/mol

	Eclipsing		Gauche
H/H	-1.0	Me/Me	-0.9
H/Me	-1.4	Et/Me	-0.95
Me/Me	-2.6	i-Pr/Me	-1.1
Et/Et	-3.1	t-Bu/Me	-2.7



Question 1 (13 pts.) Provide a IUPAC name for the following structure, do not forget to use E/Z and R/S as appropriate.



7-bromo-8-phenyloct-(6Z)-en-2-one

Question 2 (24 pts.) On each side of the following equilibrium:

a) IDENTIFY THE CIRCLED FUNCTIONAL GROUPS

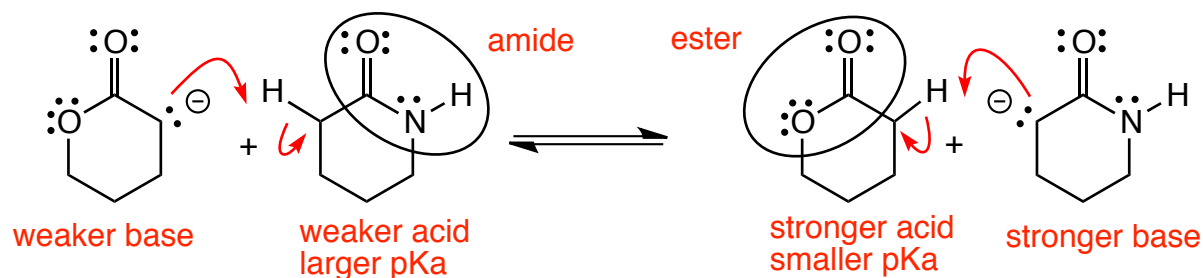
b) add the curved arrow pushing in both directions

c) identify the stronger and weaker acid and base on each side

d) indicate which acid would have the LOWER pKa

e) indicate which side the equilibrium would lie

f) Give a brief explanation for your choices of strong and weak acids and bases

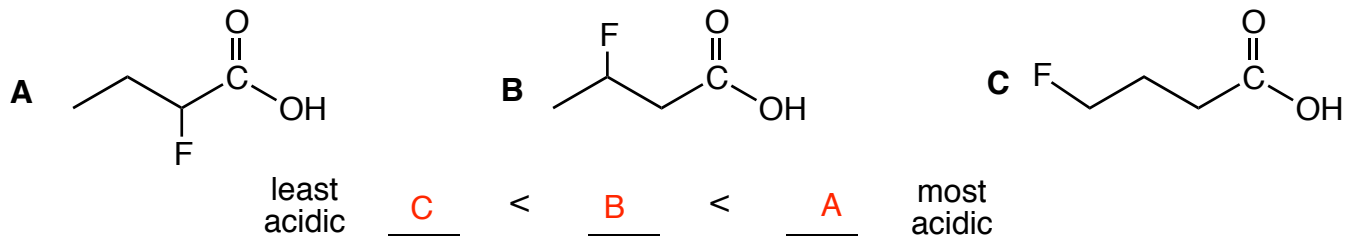


equilibrium on THIS side

The second pair of nonbonding electrons on the deprotonated amide are stabilized by conjugation into the C=O bond, lowering their energy and stabilizing the anion. This ion is thus the weaker base, corresponding to the stronger acid.

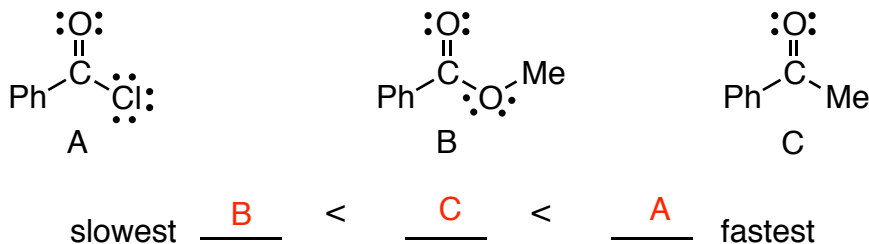
the stronger base is stronger because of the presence of the nitrogen that acts as a stronger donating group to destabilize the enolate anion, compared to the weaker oxygen donating group in the ester

Question 3 (12 pts.) Rank the following three structures in order of increasing Bronsted acidity. Give a BRIEF explanation.



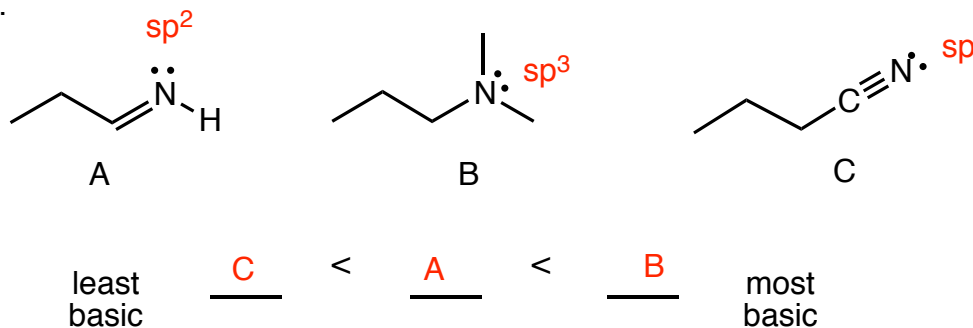
the carboxylate is stabilized by the fluorines via the inductive effect, the further the F from the anion, the weaker the inductive effect

Question 4 (16 pts.) Rank in order of increasing rate of reaction with a Grignard reagent, give a BRIEF explanation that includes the terms Lewis acid/electrophile and Lewis base/nucleophile



The Grignard is a nucleophile/Lewis base, the carbonyls are the electrophiles/Lewis acids, the electrophilic atom is the C of the C=O, in A the electrophilic Cl activates this carbon towards nucleophilic attack and in B the -OMe is resonance electron donating and deactivates this carbon towards nucleophilic attack

Question 5 (12 pts.) Rank the following in order of increasing basicity, give a BRIEF explanation.

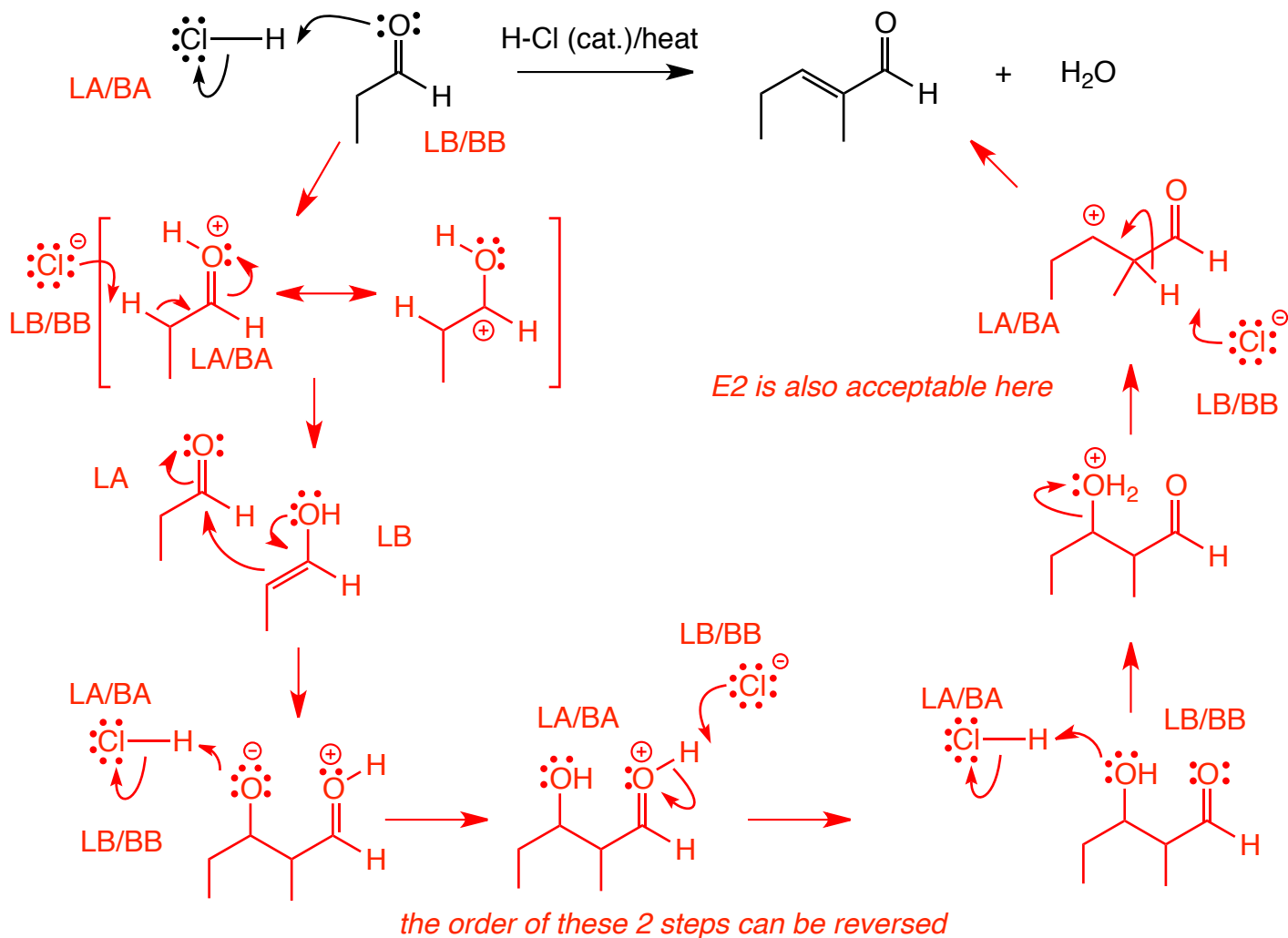


non-bonding electrons are lower in energy the more s-character the A.O., lower in energy means less reactive, less basic

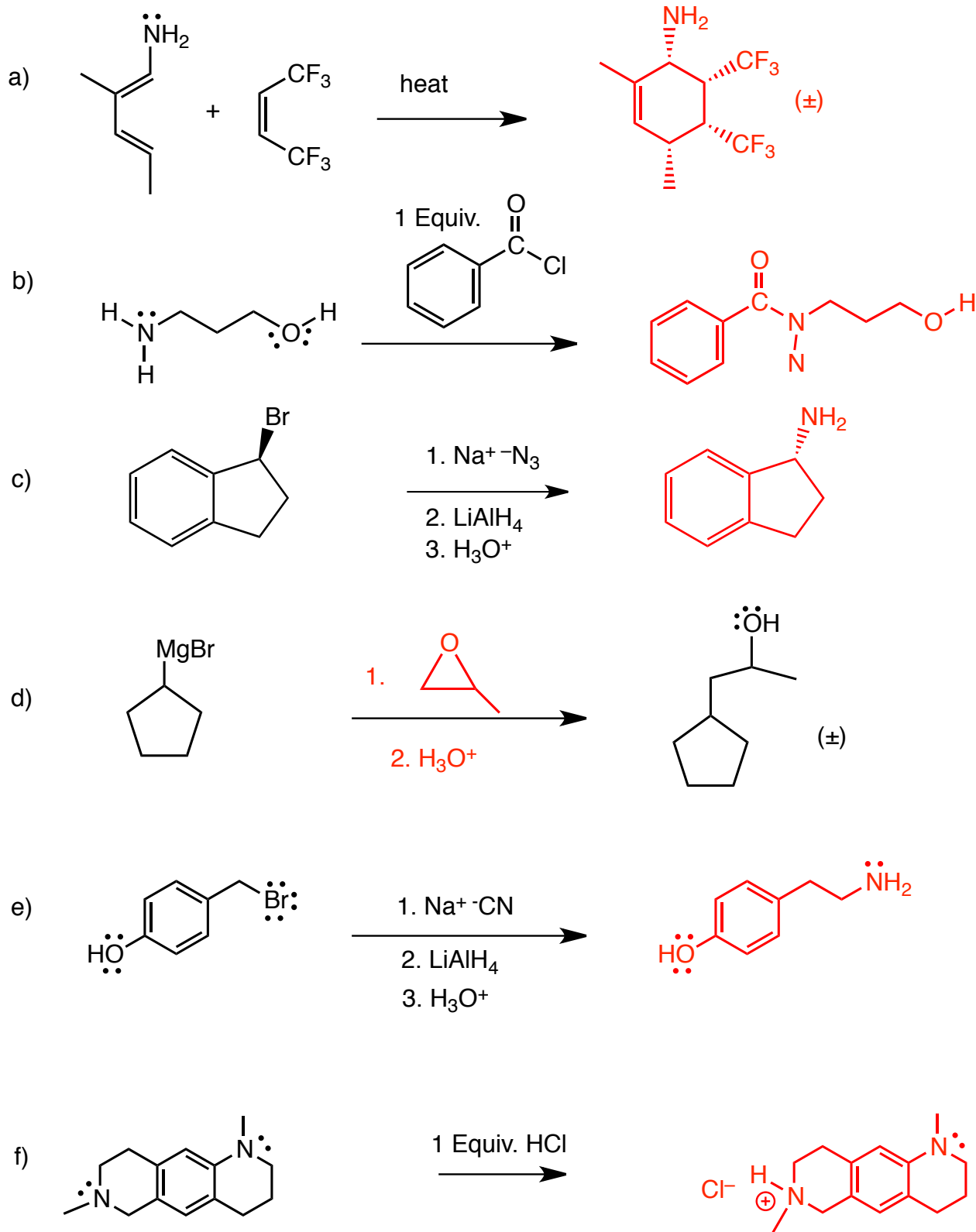
Question 6 (26 pts) Give a curved arrow pushing mechanism for the following reaction

• For each INTERMOLECULAR step, indicate the Lewis acid and base (LA or LB) and whether they are also Bronsted acids and bases (BA or BB) as appropriate

• You MUST show where every proton comes from and goes to, no abbreviated  $+H^+/-H^+$  notation  
*you do NOT need to show resonance contributor for the intermediates in this case!*

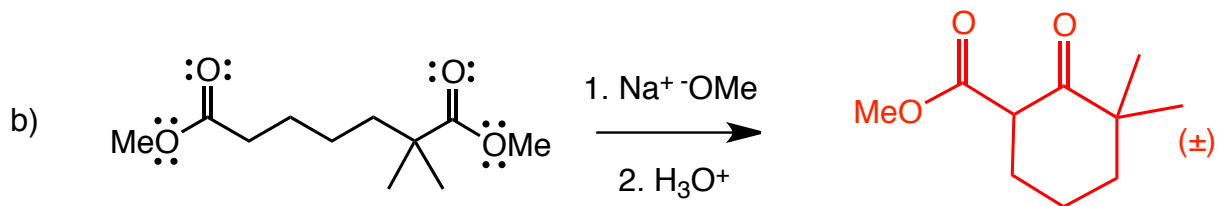
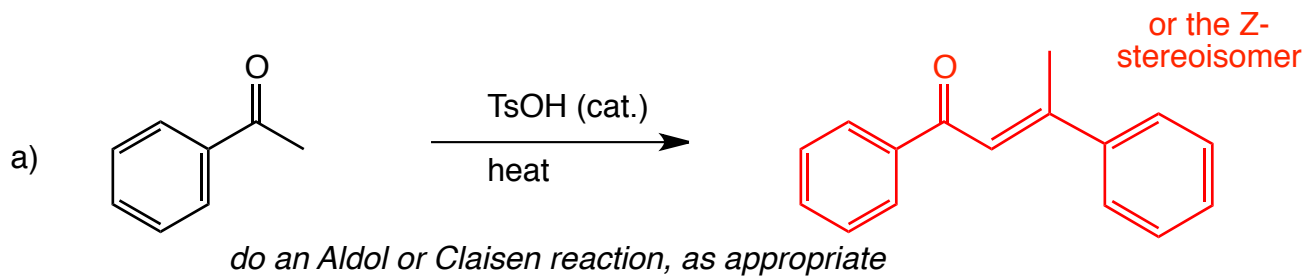


Question 7 (48 pts) Provide the missing major organic products or reagents/conditions for the following reactions. **Do not forget to include stereochemistry as appropriate** and INDICATE ANY RACEMIC MIXTURES.



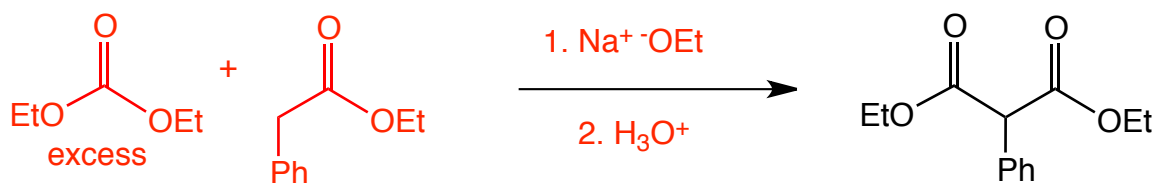
don't panic, this is a simple Brønsted acid/base reaction, all it is asking is where the proton would go  
IGNORE STEREOCHEMISTRY/Racemic mixtures for this problem

Question 8 (16 pts.) Provide the missing major organic products for the following reactions. **Do not forget to include stereochemistry as appropriate** and INDICATE ANY RACEMIC MIXTURES. These two reactions are either Aldol or Claisen reactions.

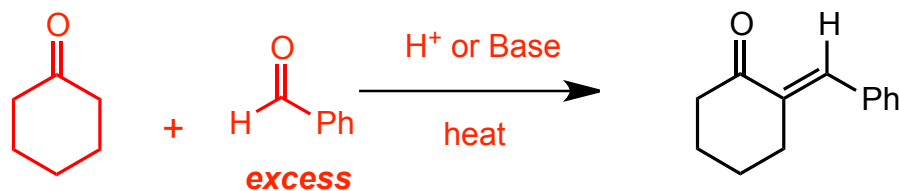


Question 9 (16 pts)

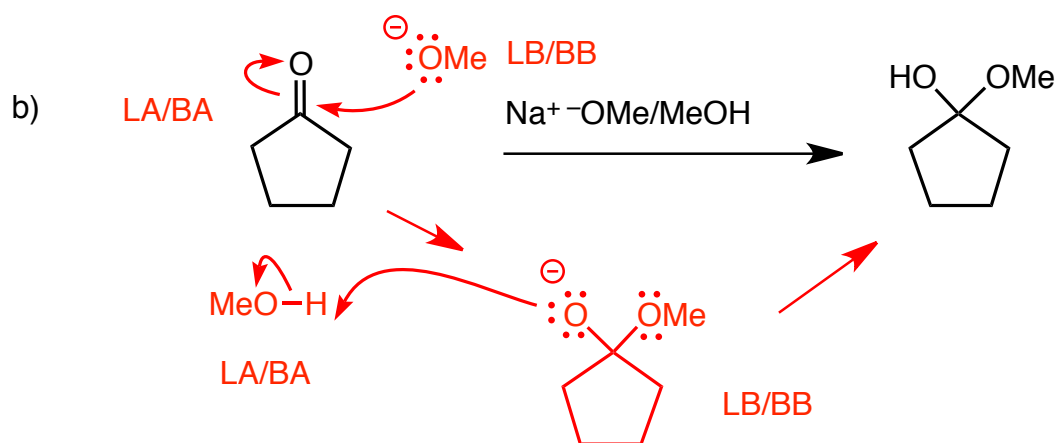
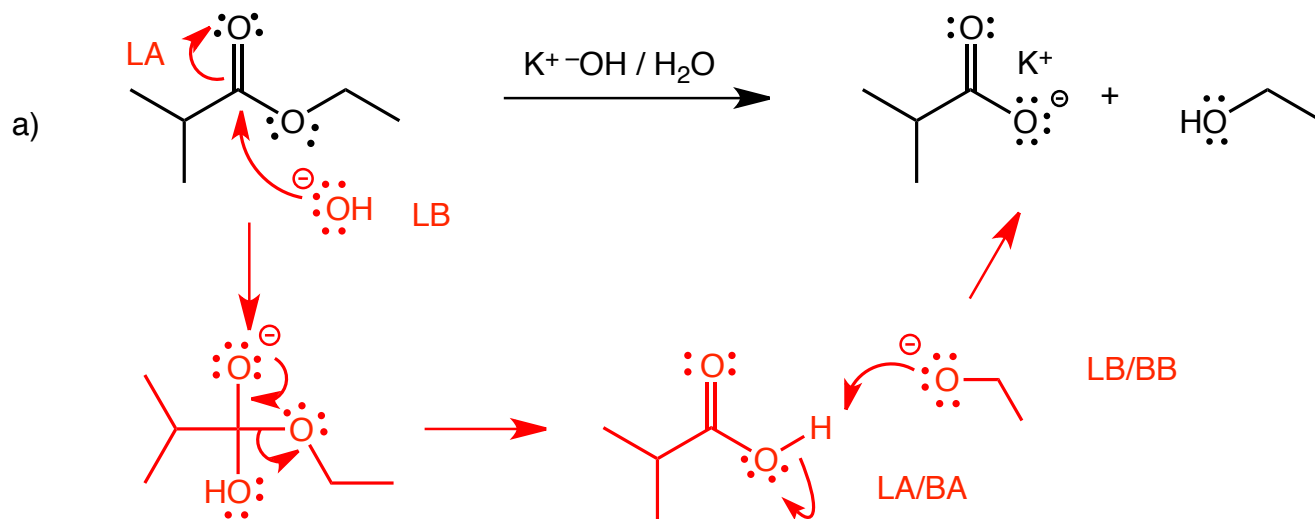
a) Give the reactants AND reagents/conditions that would allow you to synthesize the provided structure in a Claisen reaction



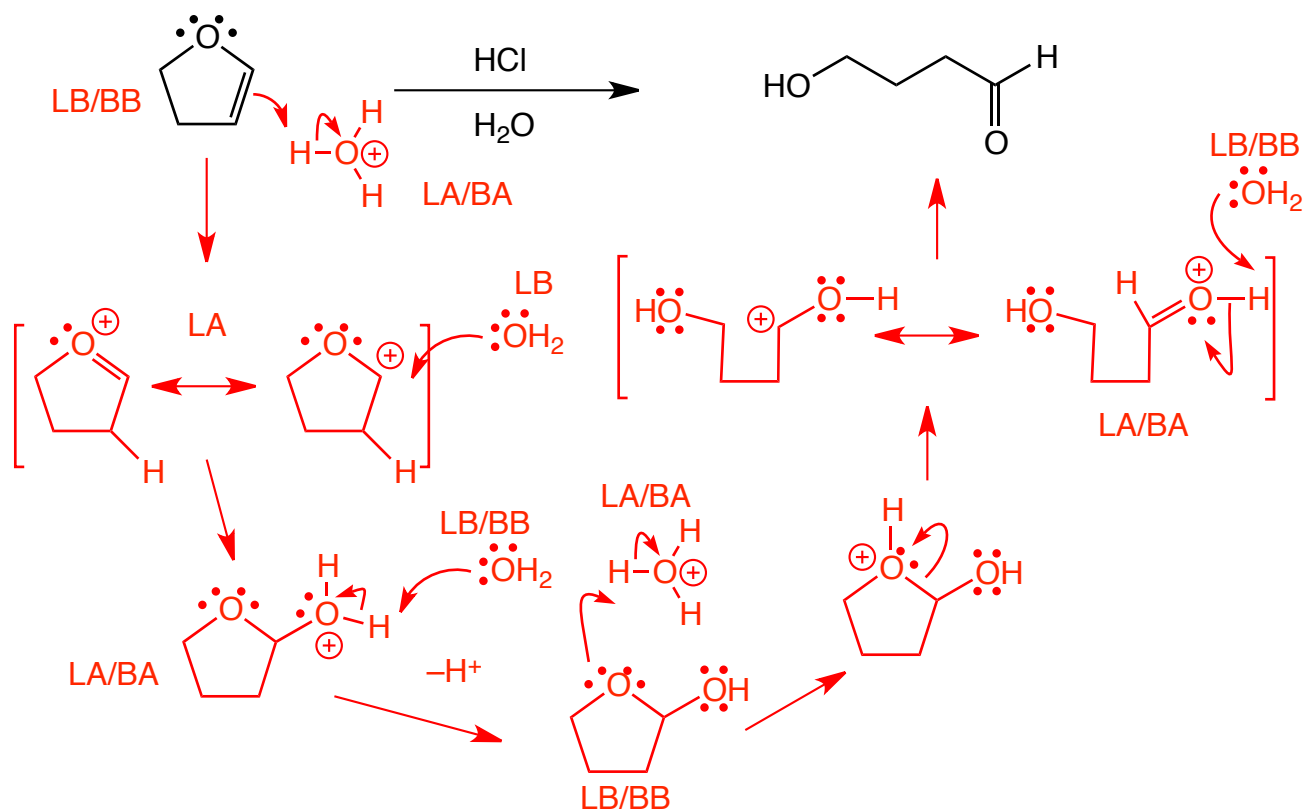
b) Give the reactants AND reagents/conditions that would allow you to synthesize the following structure in an Aldol condensation.



Question 10 (36 pts.) Give a curved arrow-pushing mechanism for the following two reactions  
 • **SHOW WHERE EVERY PROTON COMES FROM AND GOES TO**  
 • **Indicate the Lewis acid and base (LA or LB) at each INTERMOLECULAR step and whether they are also Brønsted acids and bases (LA/BA or BA/BB)**



- Question 11 ( 28 pts.) Give a curved arrow-pushing mechanism for the following reaction
- **SHOW WHERE EVERY PROTON COMES FROM AND GOES TO (no  $+H^+$  or  $-H^+$ )**
  - **DRAW ALL RESONANCE CONTRIBUTORS** for the intermediates
  - **Add C–H bonds as necessary**
  - **At each INTERMOLECULAR step, INDICATE THE Lewis acid and base (LA or LB) and whether they are also Bronsted acids and bases (BA or BB) as appropriate**



Extra Credit Question (5 pts). Which functional group formed the basis of the "two-electron sensitizer" molecule that enhances the speed of motion picture film?

amine

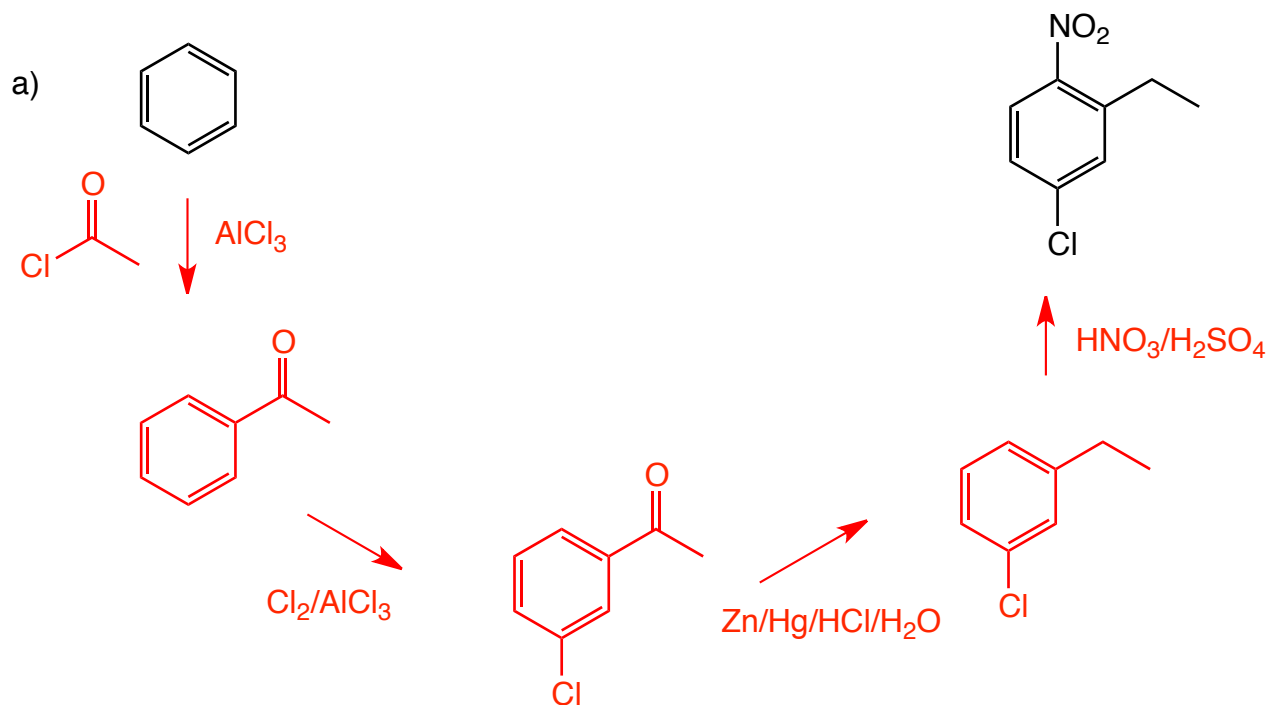
ester

amide

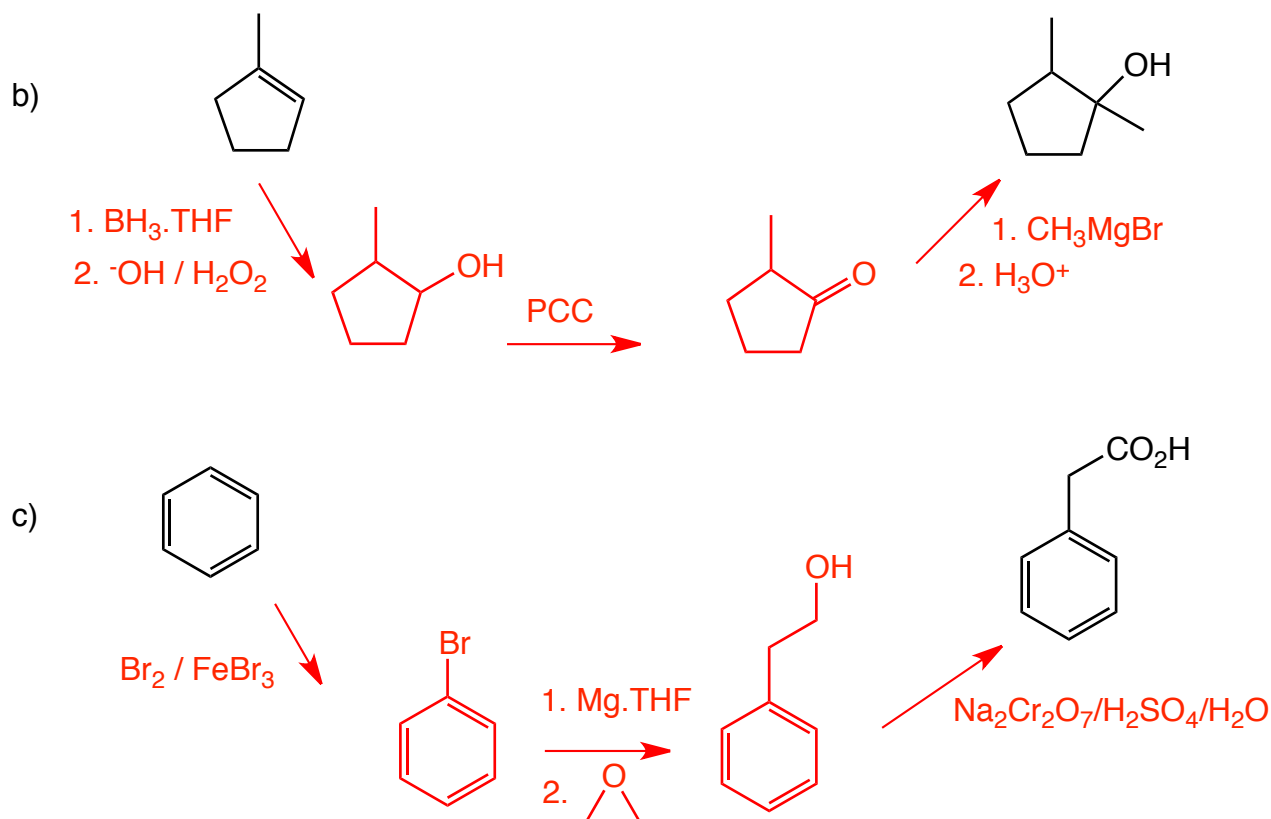
aldehyde



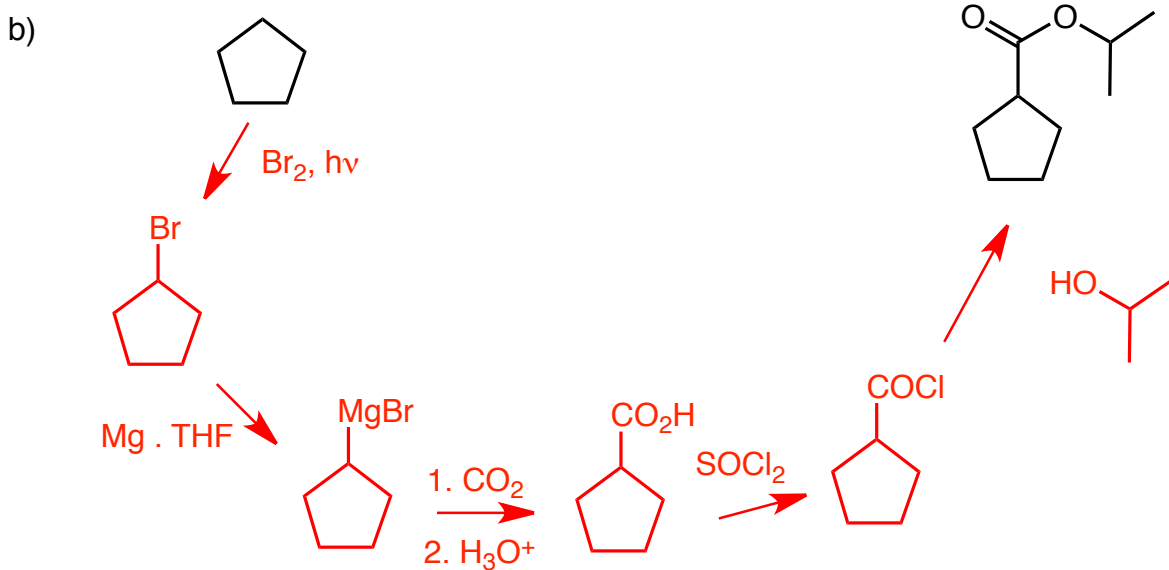
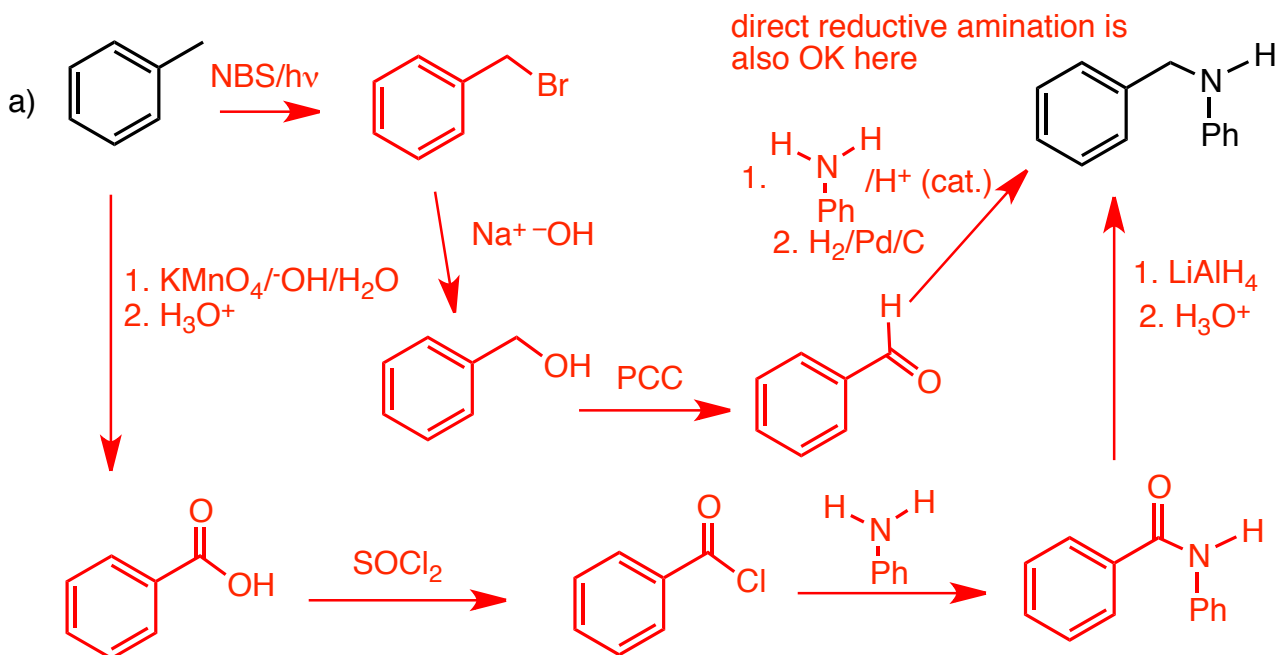
Question 12 (50 pts.) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. For question a) you must indicate steps that require separation of isomers.



THE NEXT TWO SYNTHESIS PROBLEMS, b) and c), USE MAINLY REACTIONS FROM THE "MINIMAL SET OF REACTIONS" PROVIDED RECENTLY ON THE CLASS WEB PAGE!

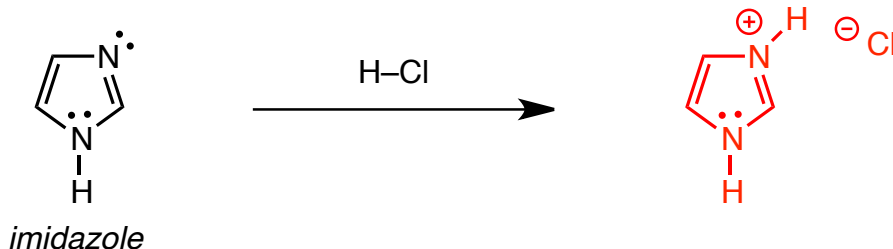


Question 13 (40 pts.) Synthesize the (target) molecule on the right from the starting molecule the left. this can not be done in one reaction. Give reagents and conditions and the intermediate molecules at each step. Do not show any mechanisms or transient intermediates.

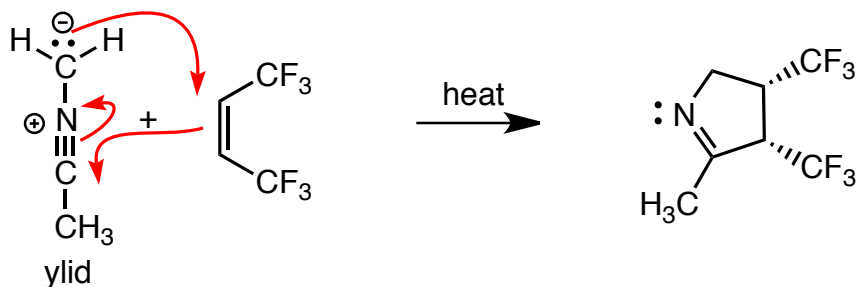


Question 14 (14 pts.)

- a) Is imidazole (shown below) aromatic, non-aromatic or antiaromatic? **aromatic**
- b) Give the product of the reaction of imidazole with H-Cl, i.w., where will the proton go?



Question 15 (24 pts.) There are several kinds of ylids in organic chemistry, we only looked at one in our course, i.e. the phosphonium ylid. When I did postdoctoral work at Columbia, I studied the reactions of nitrile ylids, such as the one shown below.



- a) Draw the curved arrows that describe the bond making and making in this reaction.
- b) How many electrons are involved in the transition state of this reaction? **6**
- c) For an allowed reaction, should this number of electrons be in a Hückel or a Möbius transition state? **Hückel**
- d) Draw the HOMO of the ylid and the LUMO of the alkene on TOP of the structures that are re-drawn for you below.



- e) Does the reaction shown above proceed via a Hückel or a Möbius transition state? **Hückel**
- f) Is the reaction shown above allowed or forbidden? **Allowed**