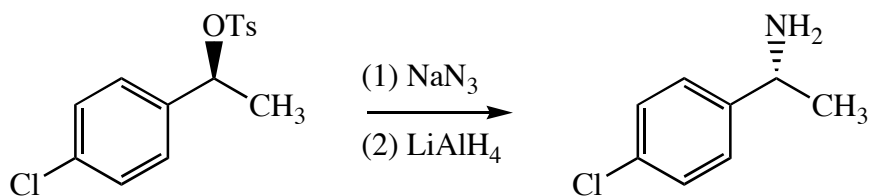
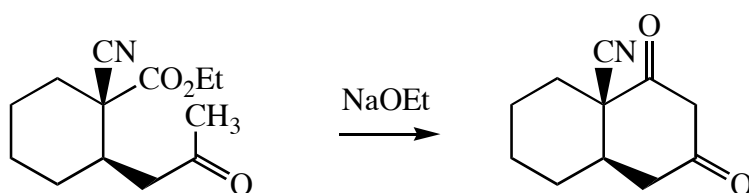


1. (4 pts. each, 32 pts. total.) Draw the *major* product of each of the following reactions, including the stereochemistry, if appropriate. **Do not draw mechanisms!**

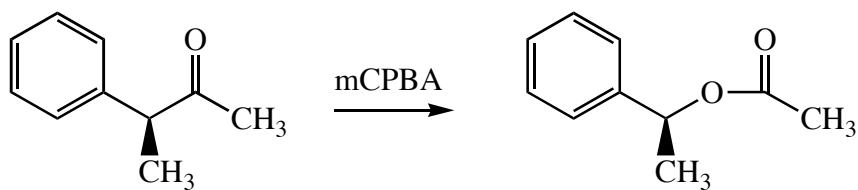
(a)



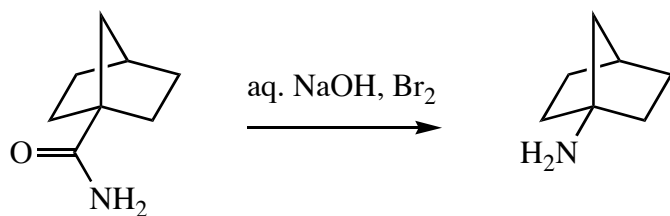
(b)



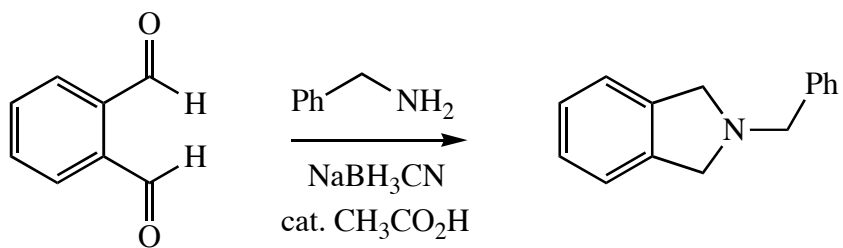
(c)



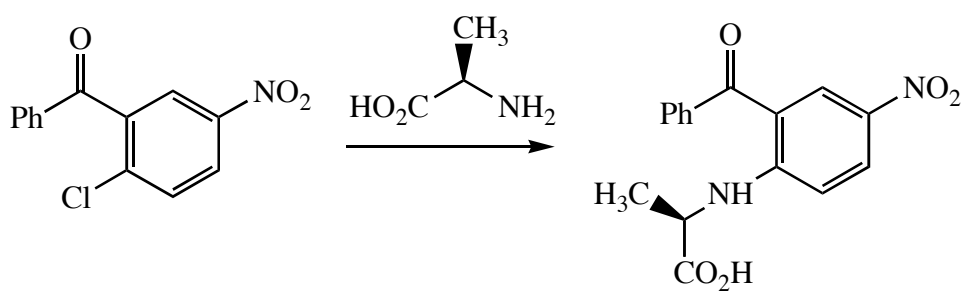
(d)



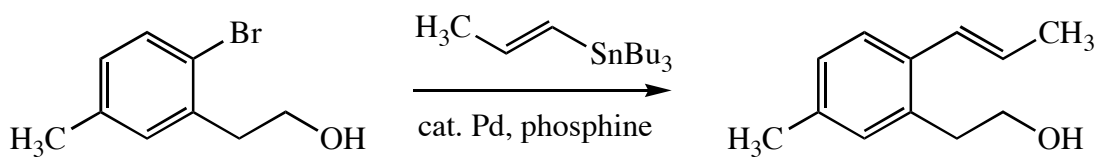
(e)



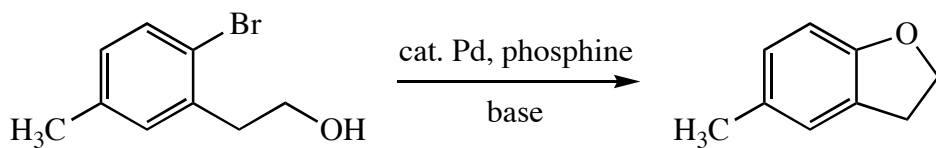
(f)



(g)

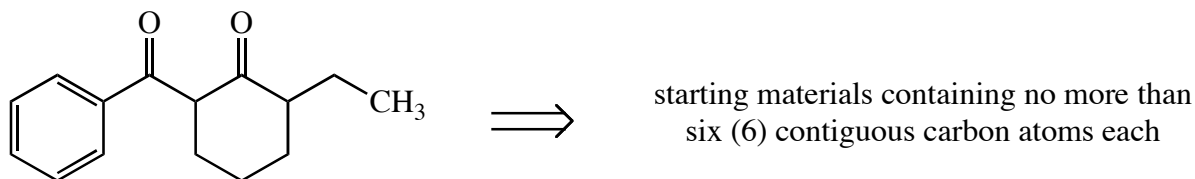


(h)

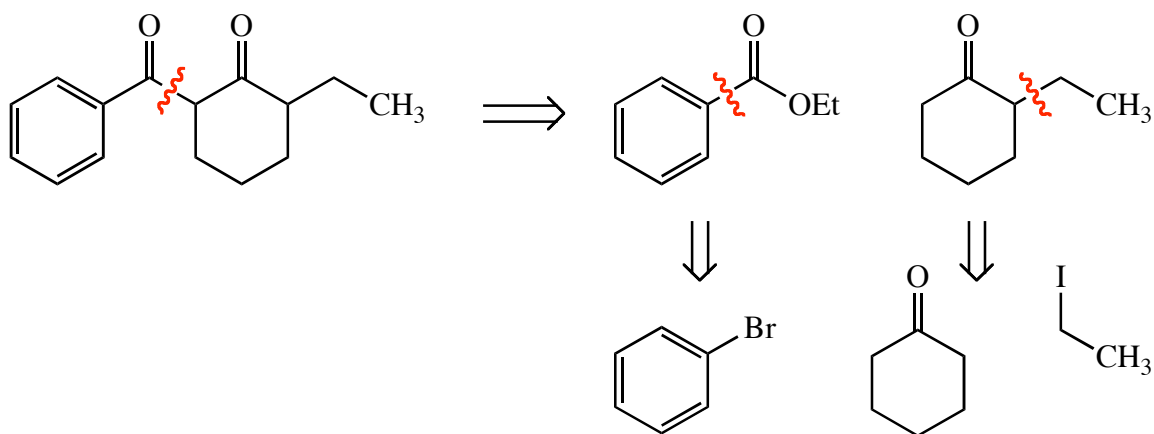


2. (16 pts. each, 32 pts. total.) Design a synthesis of each of the following compounds from the given starting materials. Each synthesis will require more than one step. Show each intermediate compound and all reagents you will need for each step. (Don't panic if you can't remember the reagents for a particular step; partial credit will be given.) There may be more than one correct answer. **Do not show mechanisms. You are strongly advised to do a retrosynthetic analysis before drawing the synthetic sequence in the forward direction.**

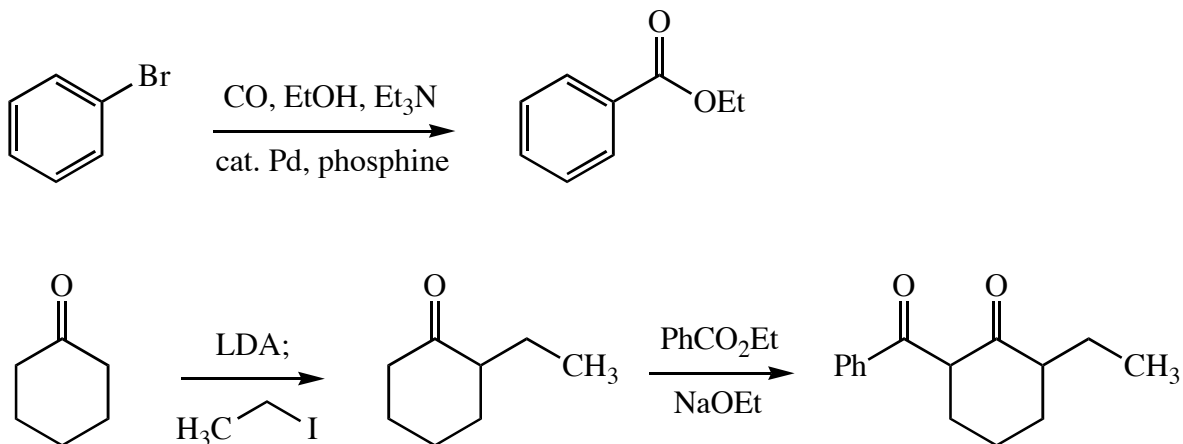
(a) (16 pts.)



Retro:

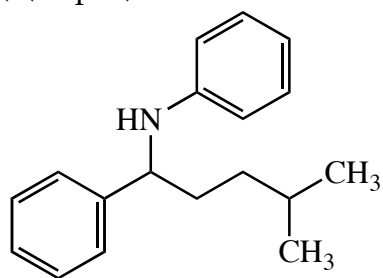


Forward:



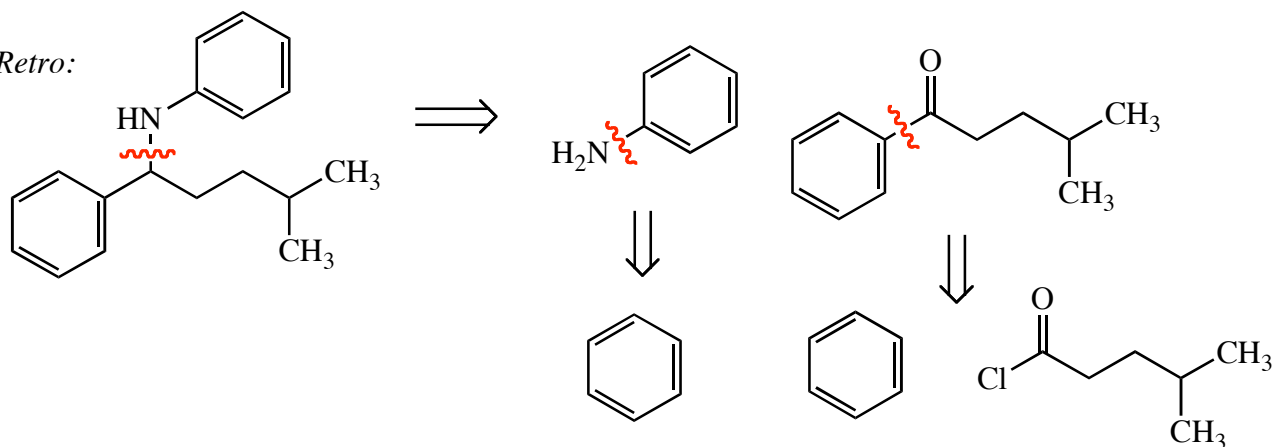
As always in retrosynthesis problems, there are many other correct answers.

(b) (16 pts.)

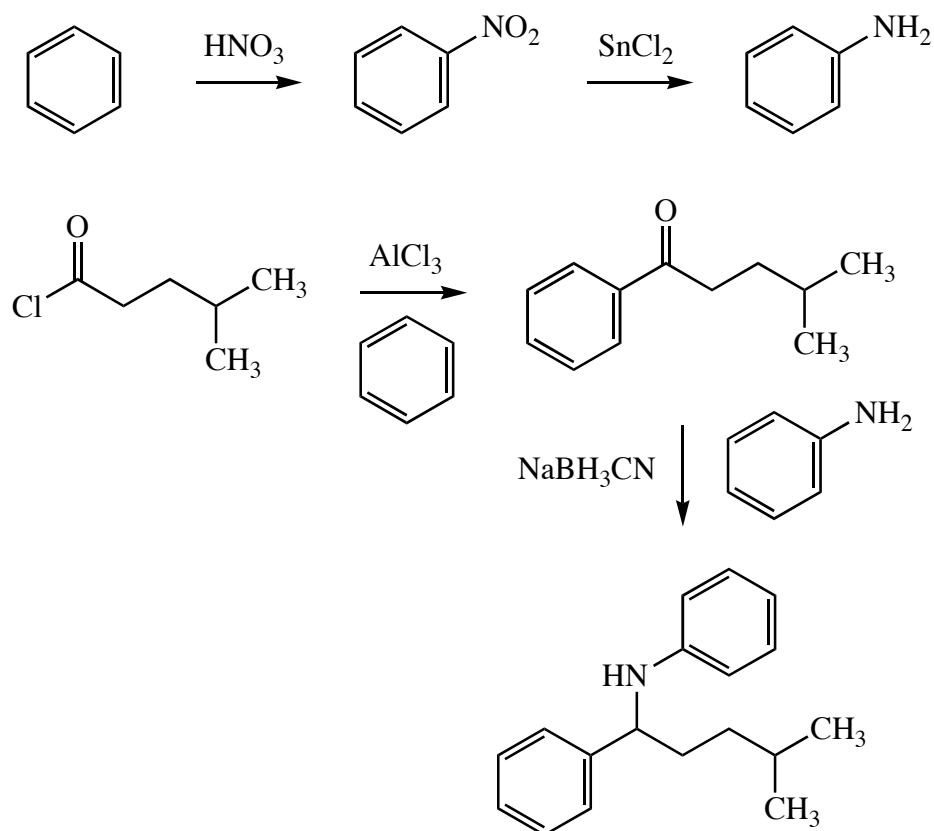


starting materials containing no more than six (6) contiguous carbon atoms each AND that do NOT contain EITHER of the C-N bonds that are present in the product

Retro:

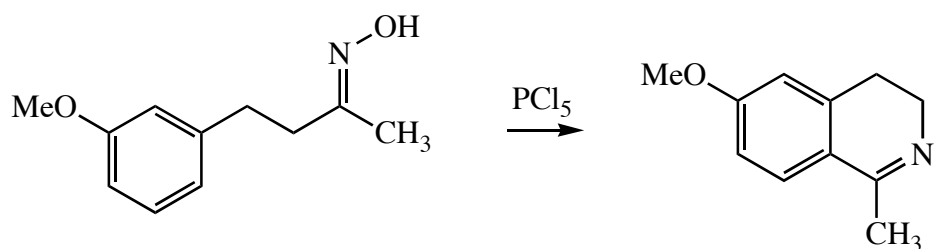


Forward:

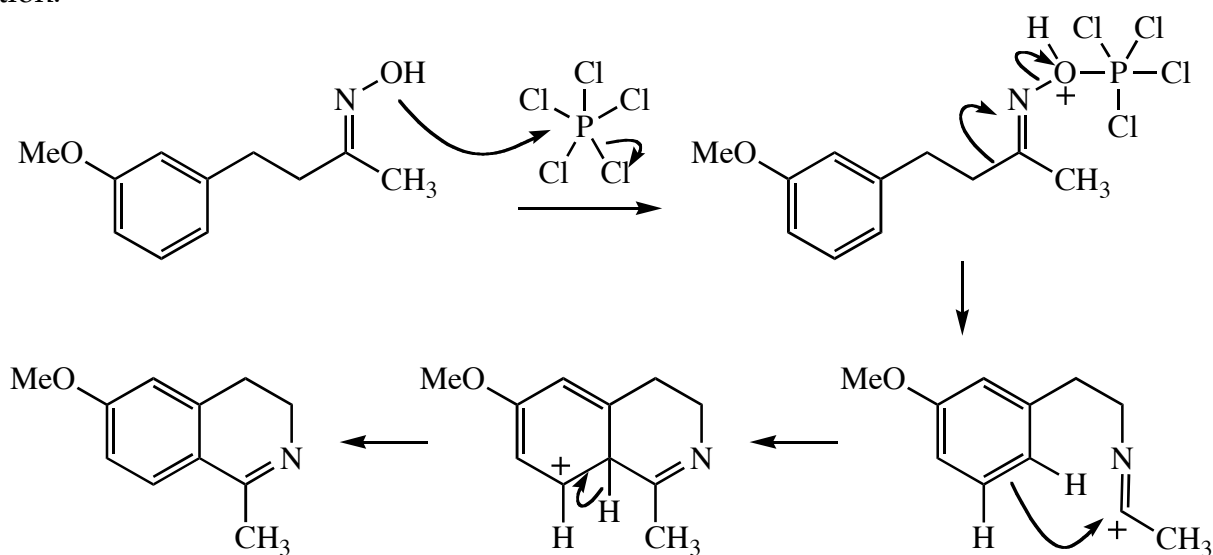


3. (20 pts. each, 40 pts. total.) Draw a reasonable mechanism for each of the following reactions. Use the conventional curved arrows to show the movement of electrons in each step. **You are strongly advised to obey Grossman's rule and to number your atoms.**

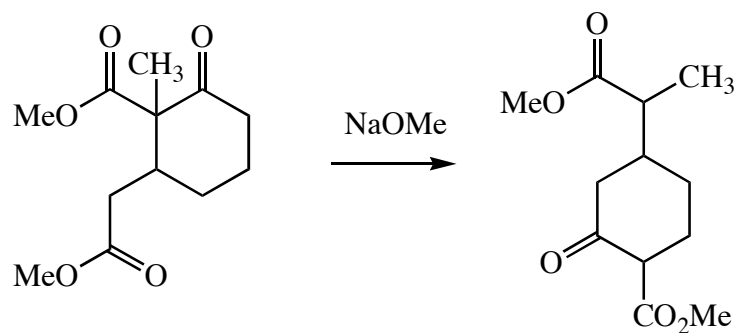
(a) (20 pts.)



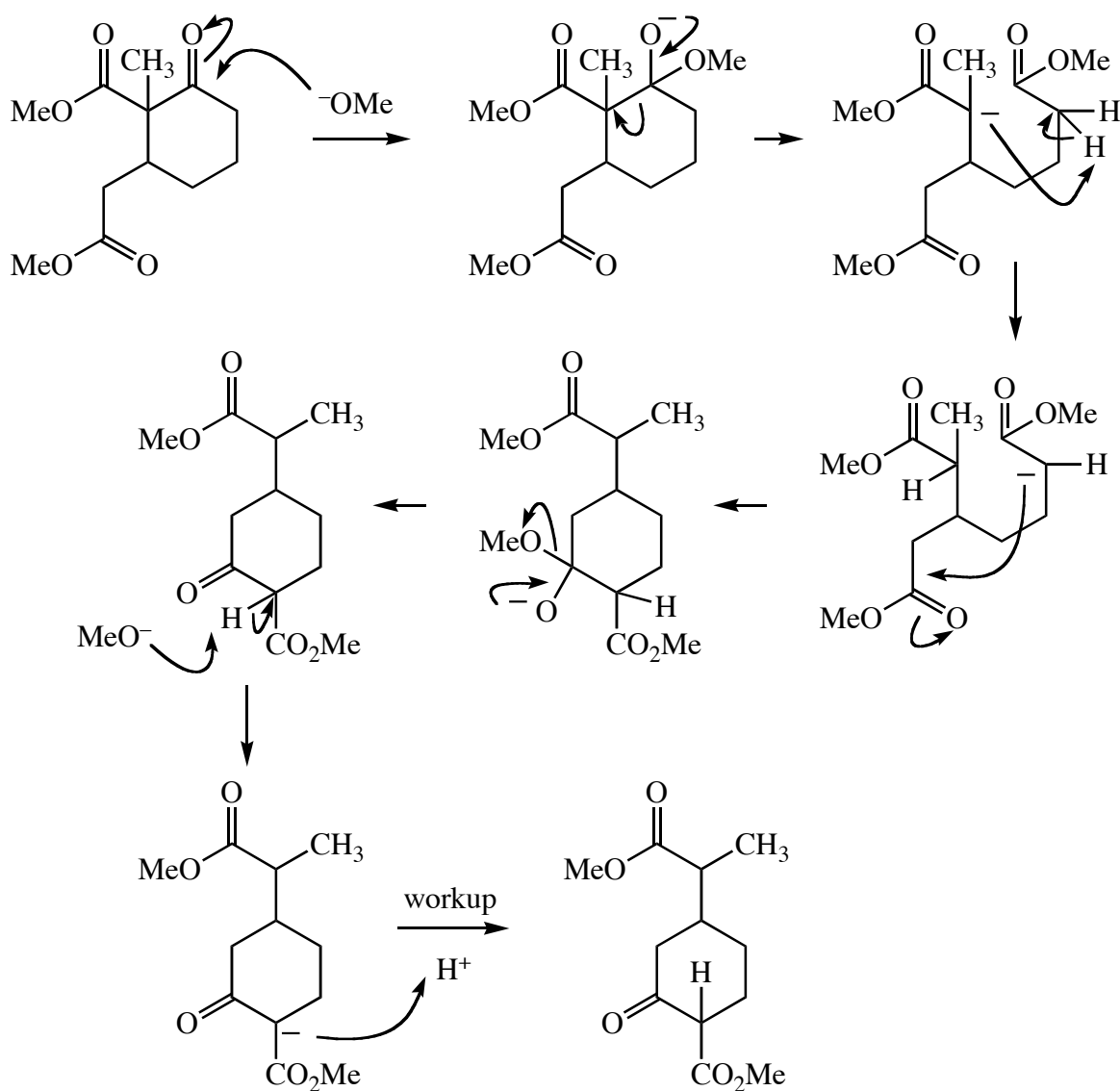
Begins with a Beckmann rearrangement and finishes with an intramolecular Friedel-Crafts reaction.



(b) (20 pts.)



A retro-Dieckmann reaction followed by a Dieckmann reaction.



4. (4 pts. each, 24 pts. total.) Clearly explain each of the following observations in one or two grammatically correct English sentences and as many structural drawings as you need.

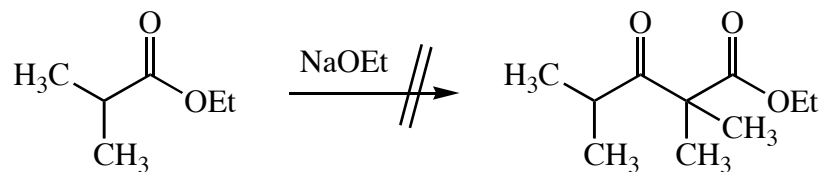
(a) The ^1H NMR spectrum of benzyl fluoride, PhCH_2F , shows a *doublet* for the CH_2 group, whereas the ^1H NMR spectra of benzyl chloride and benzyl bromide show *singlets* for their CH_2 groups.

The most abundant isotope of the F atom has a spin of $\pm 1/2$, just like the H atom, so the H atoms in the CH_2 group in PhCH_2F are split into a doublet. The most abundant isotopes of the Cl and Br atoms have spins of 0, so they do not split the resonances of the H atoms in the CH_2 groups of PhCH_2Cl and PhCH_2Br .

(b) It is easy to tell whether an IR absorbance at 3300 cm^{-1} is due to an NH or a $\text{C}(\text{sp})\text{-H}$.

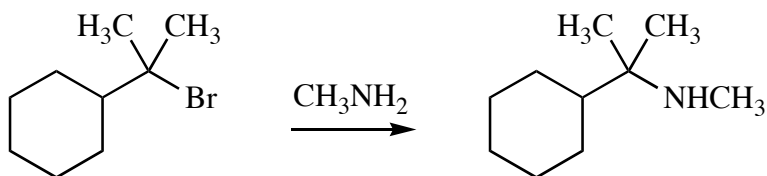
If it's due to a $\text{C}(\text{sp})\text{-H}$, then there will be a moderate $\text{C}\equiv\text{C}$ stretch at about 2200 cm^{-1} also.

(c) Claisen condensations do not proceed well when the ester has only one acidic H atom.



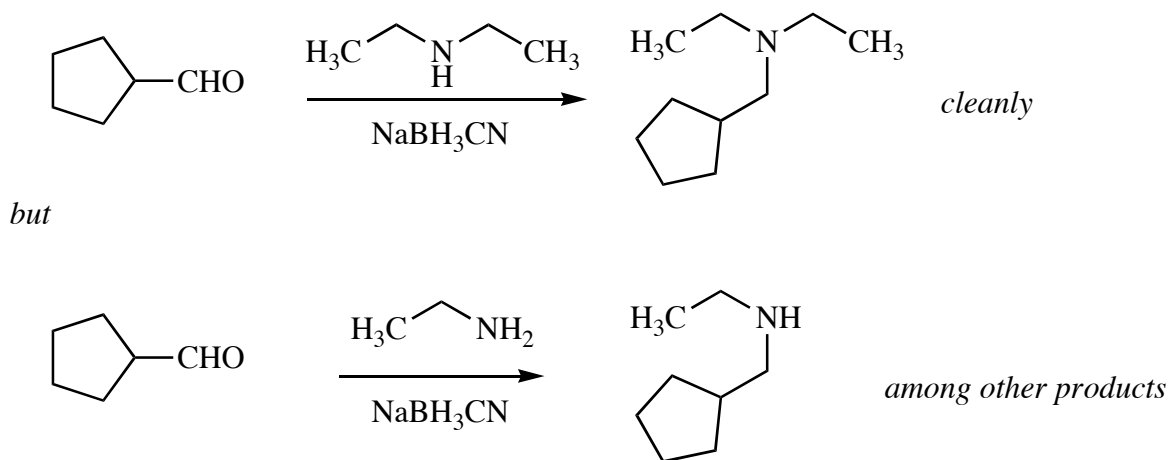
The Claisen condensation is thermodynamically driven by deprotonation of the very acidic C atom between the two carbonyl groups in the product. If there is no H atom on this C atom, then the retro-Claisen reaction occurs, returning the product to starting materials.

(d) The following reaction is *NOT* a good way to prepare the target compound.



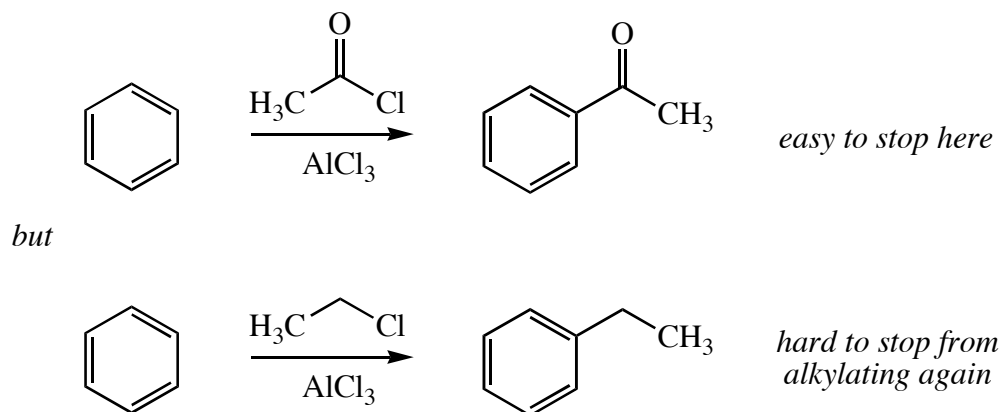
A substitution reaction at C(sp³) can proceed by the S_N2 or S_N1 mechanism. The S_N2 mechanism proceeds very poorly when the electrophile is a 3° alkyl halide. The S_N1 mechanism requires acidic conditions, under which the basic N atom will be protonated, rendering it nonnucleophilic.

(e) The reductive amination of secondary amines with aldehydes to give tertiary amines, works very well, but the reductive amination of primary amines with aldehydes to give secondary amines does not often give the product cleanly.



In the second reaction, the 2° amine product can undergo a second reductive amination, giving a 3° amine. In the first reaction the 3° amine product cannot undergo a second reductive amination because the reaction requires that an iminium ion form, and 3° amines can't form iminium ions.

(f) It is easy to stop a Friedel–Crafts *acylation* after one substitution, but it is difficult to stop a Friedel–Crafts *alkylation* after one substitution.



Acyl groups are electron-withdrawing, deactivating groups in Friedel–Crafts reactions, so the product of the first reaction is less reactive than the starting material. Alkyl groups are electron-donating, activating groups in Friedel–Crafts reactions, so the product of the second reaction is more reactive than the starting material.

5. (22 pts. total.) The last three pages of this exam show the MS, IR, and ^1H NMR spectra of an organic compound. Answer the following questions using these spectra.

(a) (4 pts.) What does the mass spectrum indicate about the number of N, Cl, and Br atoms in this compound?

The M^+ peak is odd, so there is an odd number of N atoms. There is an $\text{M}+2$ peak $1/3$ the height of the M^+ peak, so there is one Cl atom.

(b) (4 pts.) Based on the mass and NMR spectra, propose a reasonable formula for this compound.

Assume one N. $169 - 35 - 14 = 120$. The maximum number of C atoms in 120 is 10, so that gives a formula of C_{10}NCl — hardly likely. A more likely formula is $\text{C}_9\text{H}_{12}\text{NCl}$. But the NMR spectra shows there are 8 H atoms. Replace CH_4 with O. The best answer is $\text{C}_8\text{H}_8\text{NOCl}$.

(c) (4 pts.) Name a functional group whose presence in this compound is indicated by the IR spectrum, and briefly describe the spectral features that lead to this conclusion. *Be specific.*

A secondary carboxamide is indicated by the absorbance at 1666 cm^{-1} and the N–H stretch at 3304 cm^{-1} .

(d) (4 pts.) What group do the ^1H NMR resonances at 7–8 ppm suggest is present in this compound? *Be specific.*

A para-disubstituted benzene ring.

(e) (6 pts.) Draw a structure consistent with all three spectra and your answers to (a–d).

The 3H singlet at 2.0 ppm indicates a CH_3 group adjacent to a π bond. The fragments and the assembled compound are:

