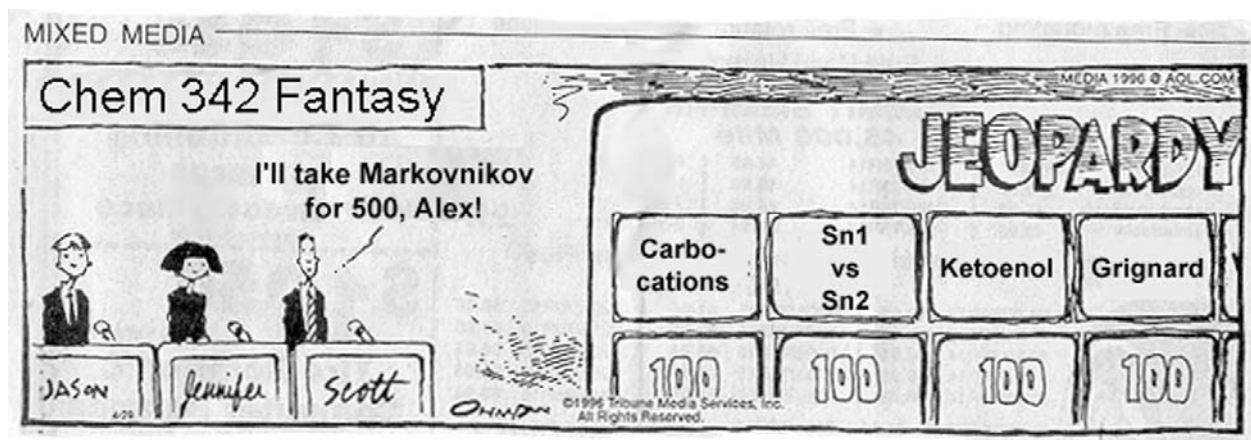


NAME _____

KEY _____



Please read through each problem carefully. Enter your answers in the spaces provided.

Problem 1 12 pts _____

Problem 2 8 pts _____

Problem 3 8 pts _____

Problem 4 24 pts _____

Problem 5 12 pts _____

Problem 6 21 pts _____

Problem 7 12 pts _____

Problem 8 34 pts _____

Problem 9 24 pts _____

Problem 10 20 pts _____

Problem 11 25 pts _____

TOTAL _____

RELAX! Think about what you know.

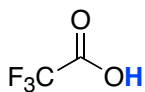
Try to answer the questions you know and can do quickly first. Then go back and tackle the problems you find more challenging.

In the multiple step reaction sequences, look at what kind of reaction takes place in the second step to give you clues on what functional group you need to have after the first step.

In synthesis problems, try to work the synthesis forwards AND backwards.

1. The following molecules all have some relatively acid proton. Match the pK_a 's that are listed below with the appropriate molecule by writing the pK_a in the boxes. (12 pts)

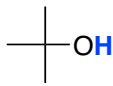
pK_a 0.2, 4, 9, 16, 20, 40



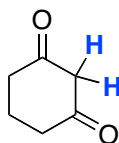
0.2



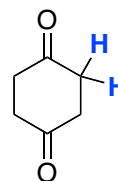
40



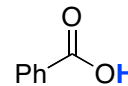
16



9

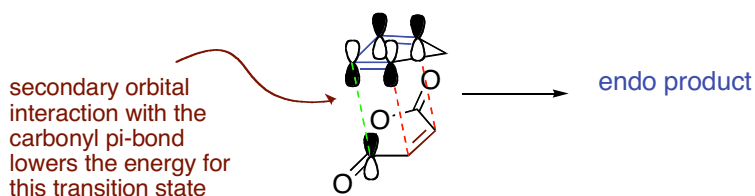
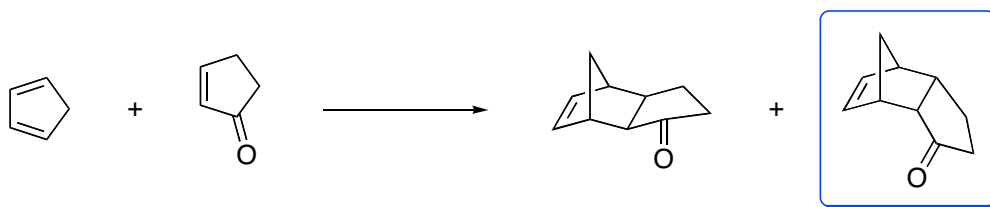


20



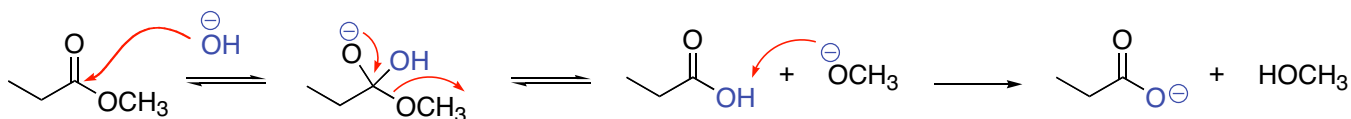
4

2. In the following Diels Alder reaction, there are two products possible. Circle the major product and briefly explain why it is formed in a larger amount. (8 pts)



3. Explain why base catalyzed hydrolysis of esters (saponification) is better than acid catalyzed hydrolysis. (8 pts)

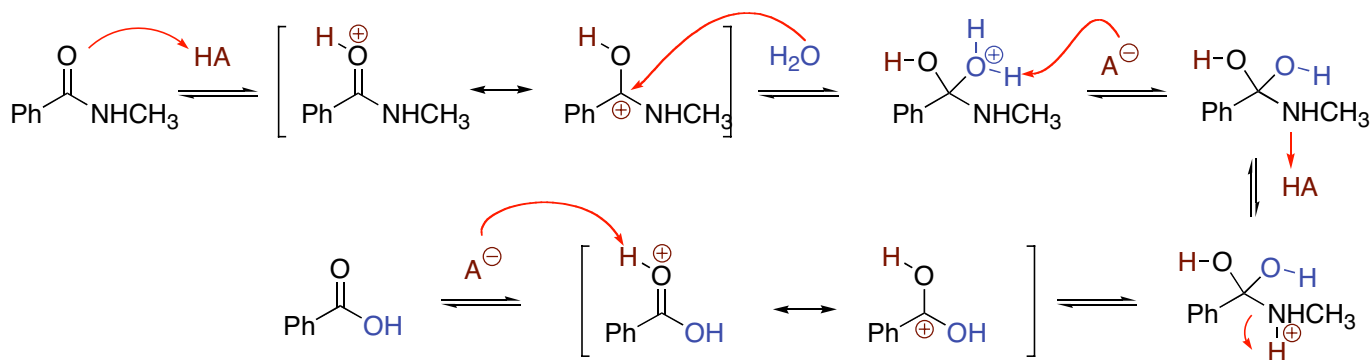
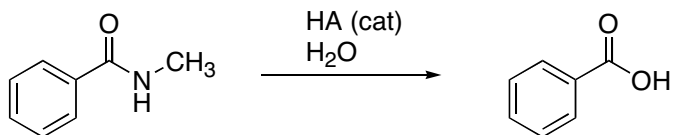
Base Catalyzed Hydrolysis (Saponification)



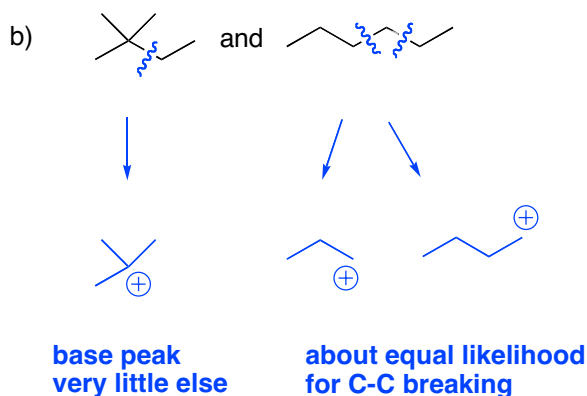
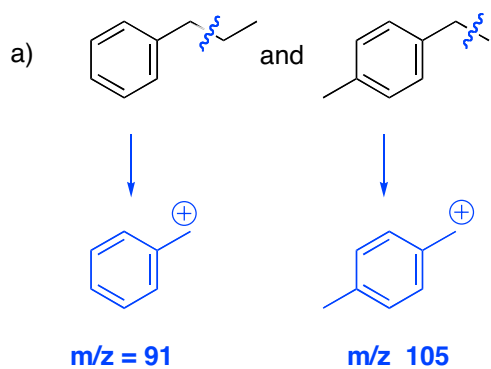
Rapid acid-base reaction takes place

Carboxylate is a thermodynamic sink and makes the reaction essentially non-reversible. To get the carboxylic acid, add acid to protonate.

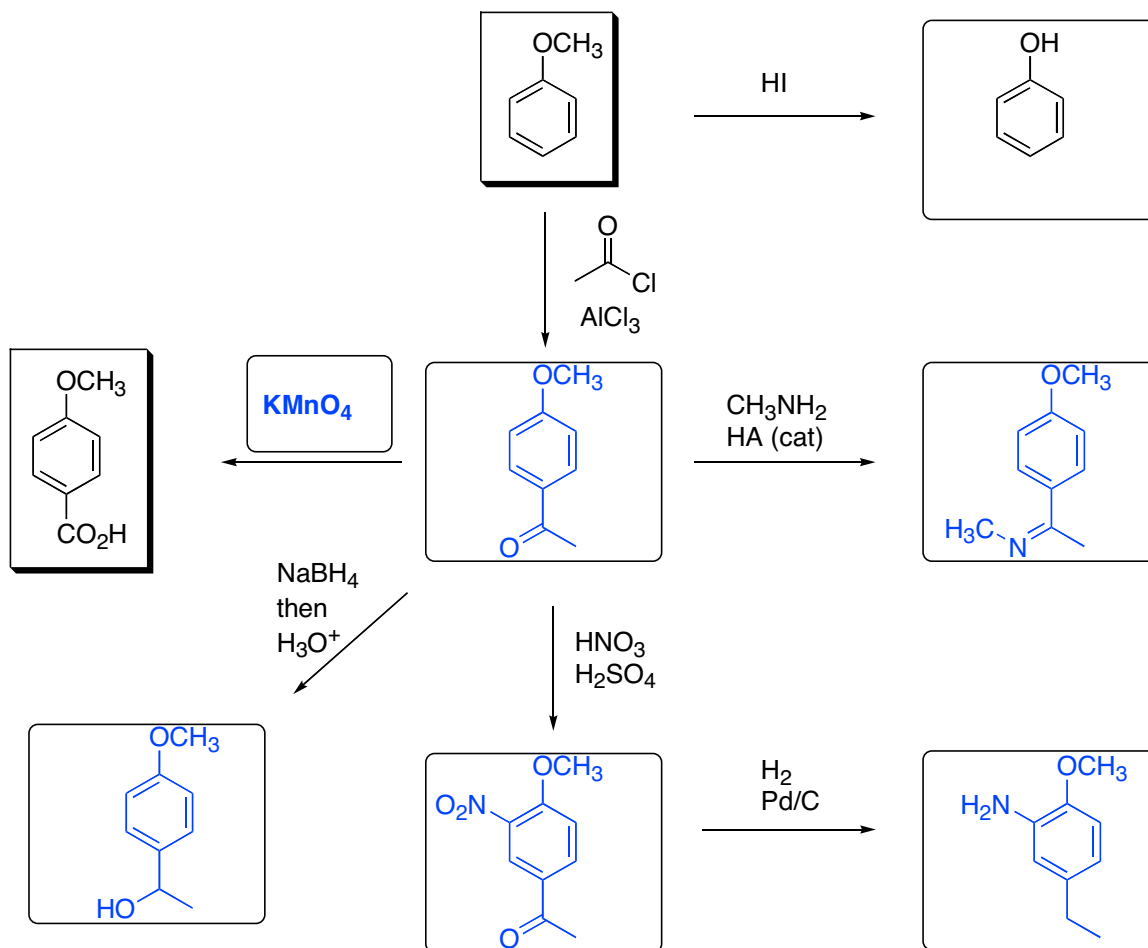
4. Write the complete mechanism for the acid catalyzed hydrolysis of *N*-methylbenzamide showing all intermediates (with appropriate resonance structures) and reaction arrows. (24 pts)



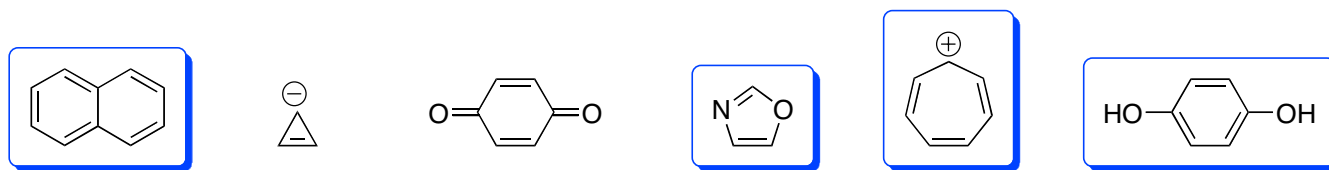
5. For each pair of molecules below, describe how the Mass Spectrum could be used to tell them apart. (12 pts)



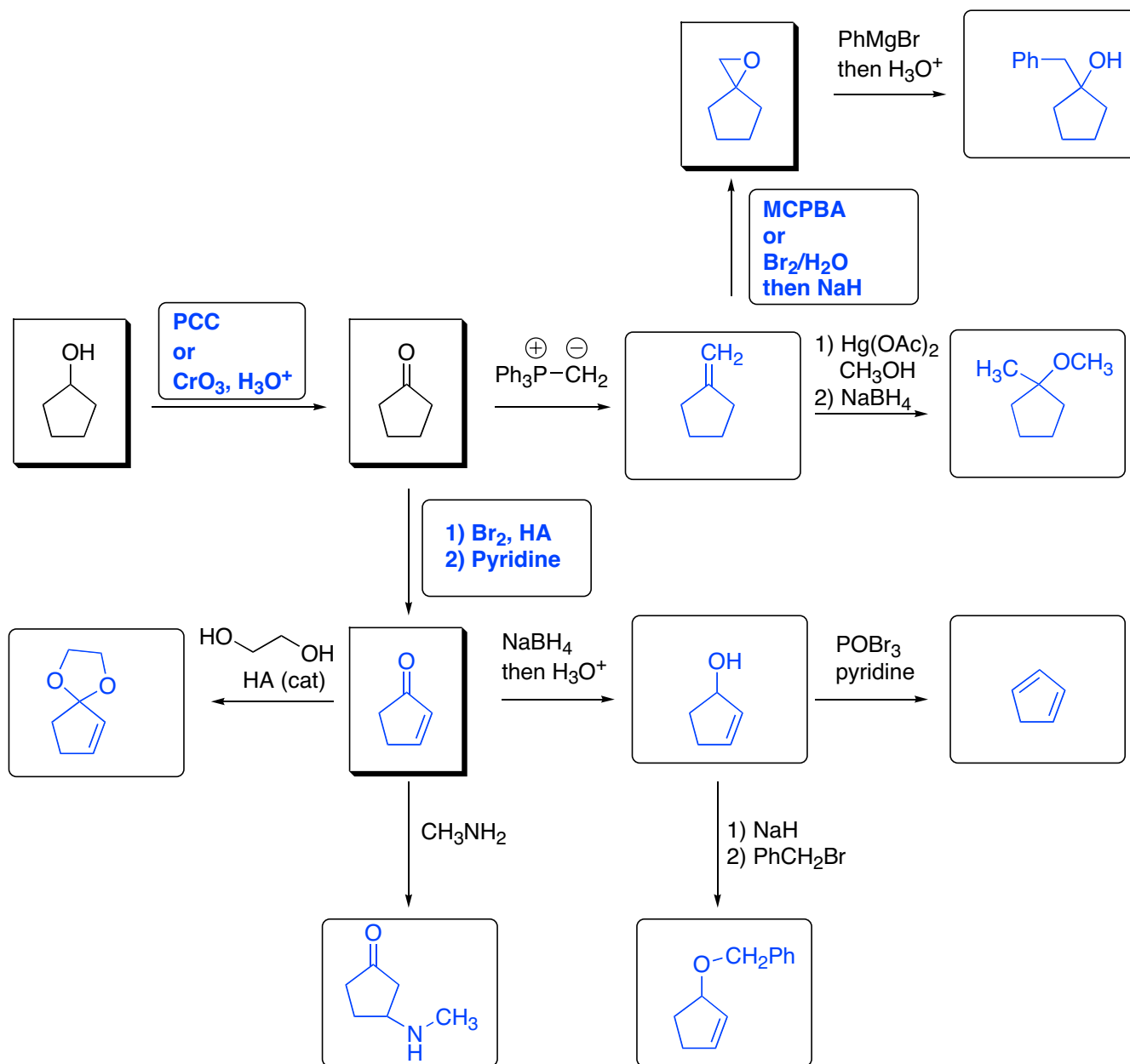
6. Provide the major product or reagent for the reactions below. For ortho-para directors you need only show the para product. (21 pts)



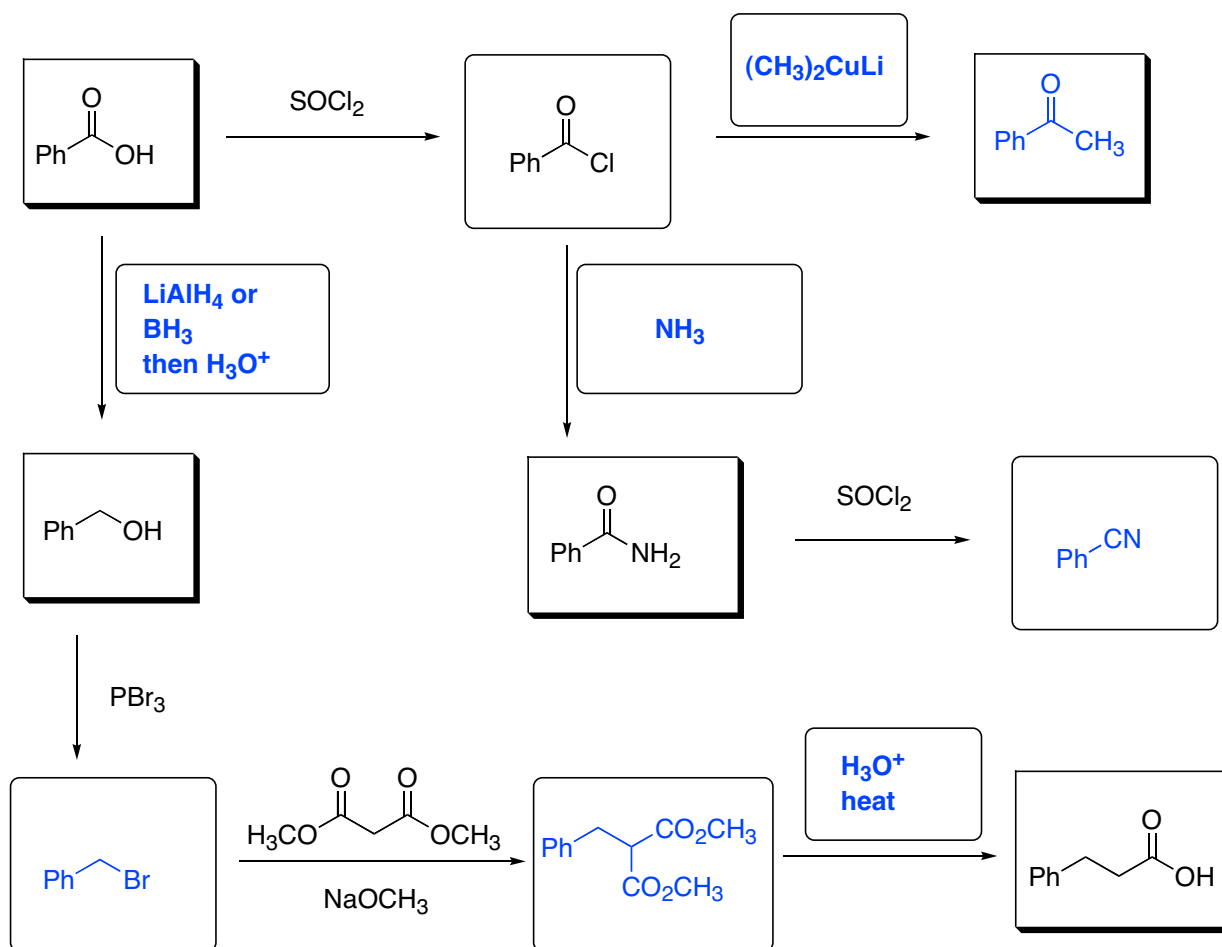
7. Indicate which of the following molecules are aromatic by circling them. (12 pts)



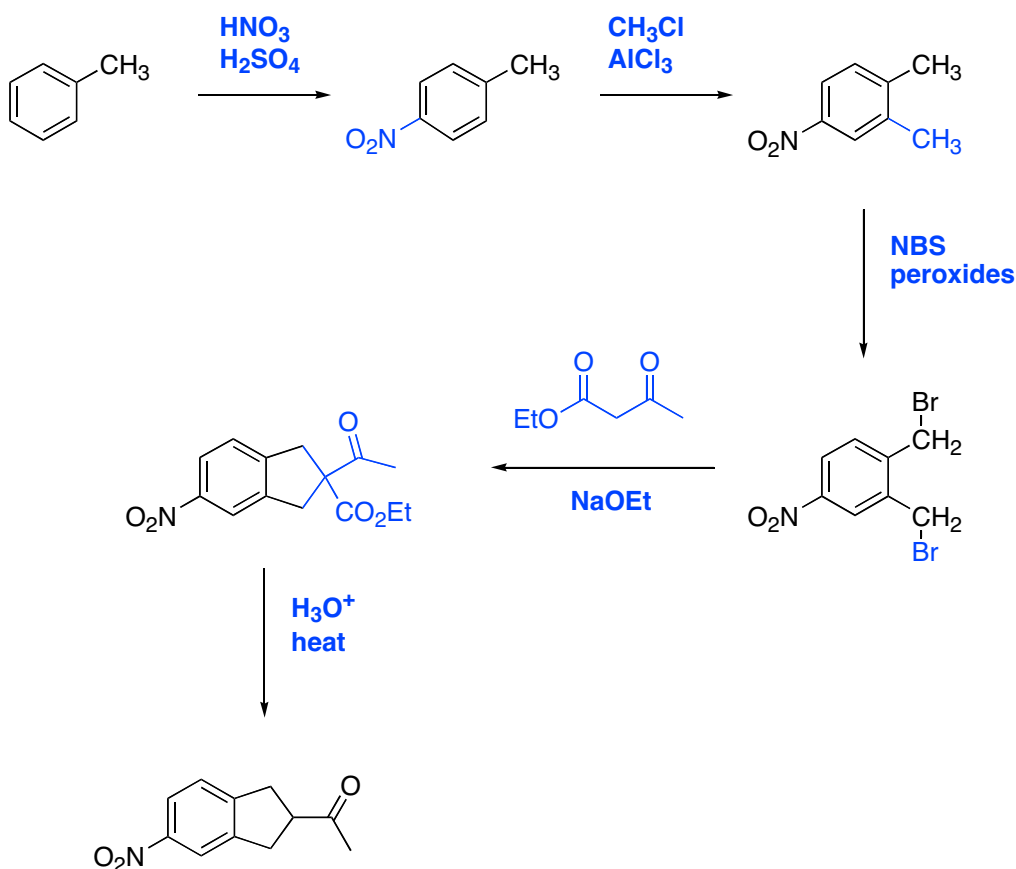
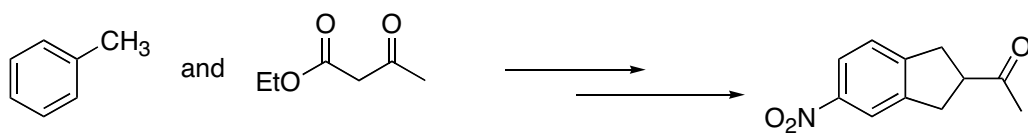
8. Provide the missing major products or reagents for the following. (34 pts)



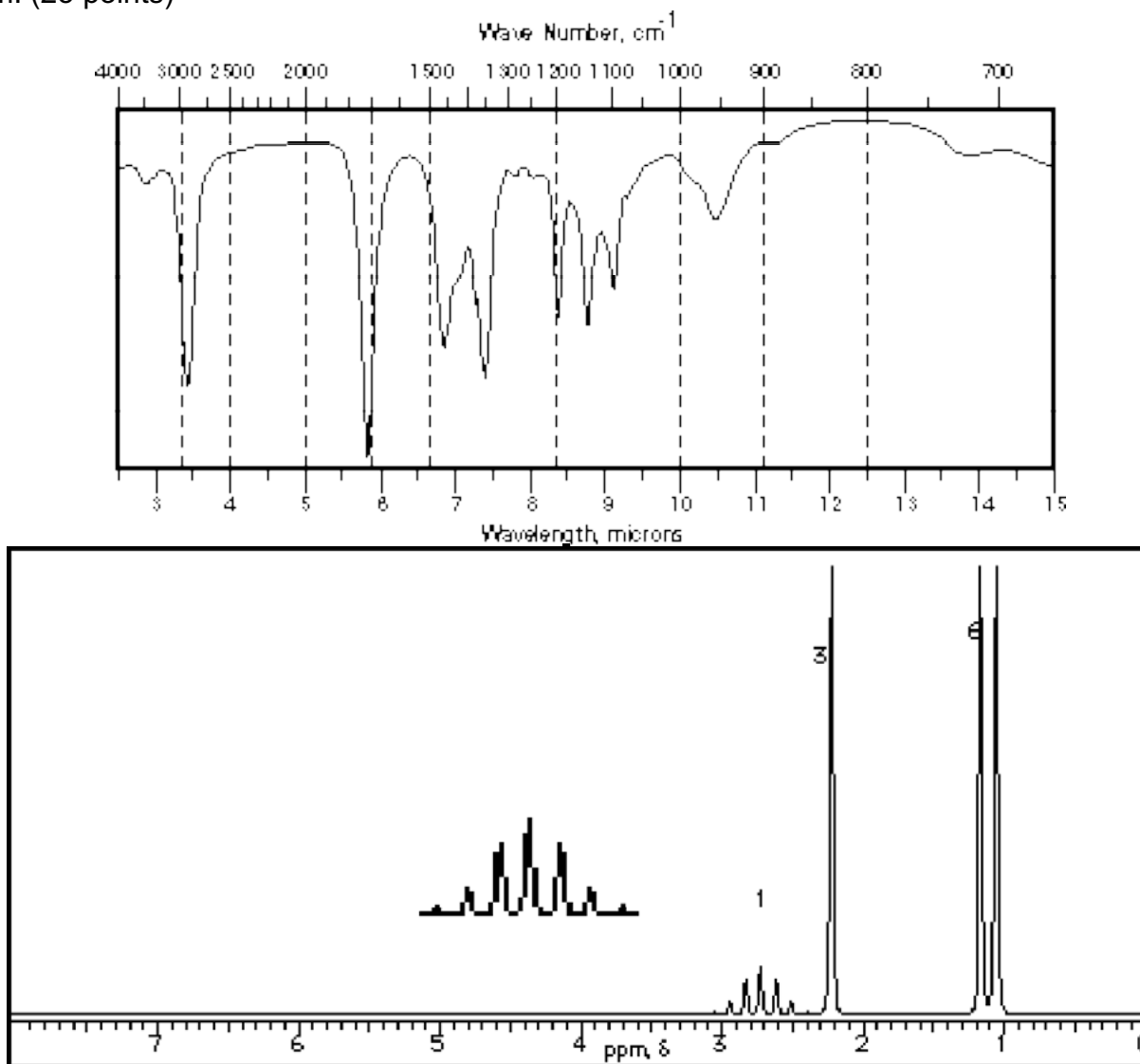
9. Provide the missing major products or reagents for the following. (24 pts)



10. Show how you would synthesize the following starting from toluene and the ketoester shown below. Hint: This can be done in 5 steps. (20 pts)



11. Answer the following questions about an unknown molecule with a molecular formula of $C_5H_{10}O$. The IR and 1H NMR are shown below. The ^{13}C NMR shows resonances at 210, 45, 22, and 16 ppm. (25 points)



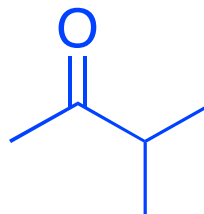
How many degrees of unsaturation does the molecule possess?

1

What type of functional group does the carbon resonance at 210 ppm represent?

KETONE

What is the structure of the unknown molecule?



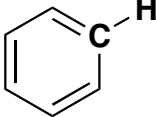
Infrared Stretching Absorptions

Functional Group	Wavenumber Range (cm ⁻¹)	Absorption Strength	notes
$\begin{array}{c} \\ -\text{C}-\text{H} \\ \end{array}$	2850-2960	medium-strong	below 3000
$\begin{array}{c} \\ =\text{C}-\text{H} \end{array}$	3020-3100	medium	above 3000
$\equiv\text{C}-\text{H}$	3300	strong	above 3000
O-H	3400-3650	broad-strong	
N-H	3300-3500	medium	#H's = #peaks
$\begin{array}{c} -\text{C}\equiv\text{C}- \\ -\text{C}\equiv\text{N} \\ \text{O}=\text{C}=\text{O} \end{array} \quad \left. \vphantom{\begin{array}{c} -\text{C}\equiv\text{C}- \\ -\text{C}\equiv\text{N} \\ \text{O}=\text{C}=\text{O} \end{array}} \right\}$	2100-2260	medium	
$\begin{array}{c} \diagdown \\ \text{C}=\text{O} \\ \diagup \end{array}$	1680-1750	strong	
$\begin{array}{c} \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \end{array}$	1640-1750	medium	
C-C	800-1300	medium	
C-O	1050-1150	medium	
C-X	<1000	strong	

Alkene out of plane bending

$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{H} \end{array}$	910 and 990	strong	$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{R} \end{array}$	700	strong
$\begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{H} \end{array}$	890	strong	$\begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{R} \end{array}$	815	strong
$\begin{array}{c} \text{H} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{H} \end{array}$	970	strong			

Typical NMR Chemical Shifts

Functional Group	Type	¹ H Chemical Shift (ppm)	¹³ C Chemical Shift (ppm)
$\begin{array}{c} \\ -\text{C}-\text{H} \\ \end{array}$	Alkane	0.7 - 1.8	10 - 60
$\begin{array}{c} \\ =\text{C}-\text{C}-\text{H} \\ \end{array}$	Allylic or next to carbonyl	1.6 - 2.4	30 - 60
$\begin{array}{c} \\ \text{X}-\text{C}-\text{H} \\ \end{array}$	next to halogen or alcohol	2.5 - 4.0	20 - 85
$\begin{array}{c} \text{O} \\ \\ \text{C}-\text{O}-\text{C}-\text{H} \\ \end{array}$	next to oxygen of an ester	4.0 - 5.0	50 - 85
$\begin{array}{c} \\ =\text{C}-\text{H} \end{array}$	vinyllic	4.5 - 6.5	110 - 150
	aromatic	6.5 - 8.0	110 - 140
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{H} \end{array}$	aldehyde	9.7 - 10.0	190 - 220
$\text{O}-\text{H}$	alcohol	varies widely will exchange with D ₂ O	N/A
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{X} \end{array}$	carbonyl of ester, amide, or carboxylic acid (X = O, N)	N/A	165 - 185
$\begin{array}{c} \text{O} \\ \\ -\text{C}- \end{array}$	carbonyl of ketone or aldehyde	N/A	190 - 220