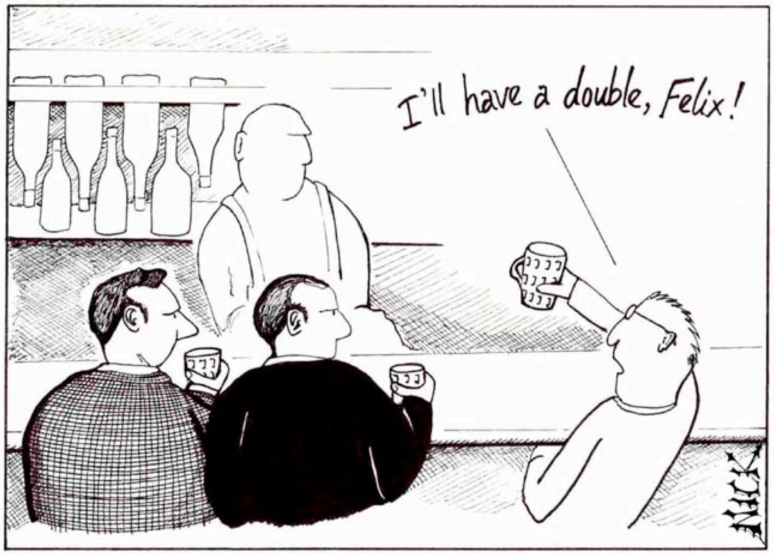
Chem 342

FINAL EXAM - KEY
14 May 2004

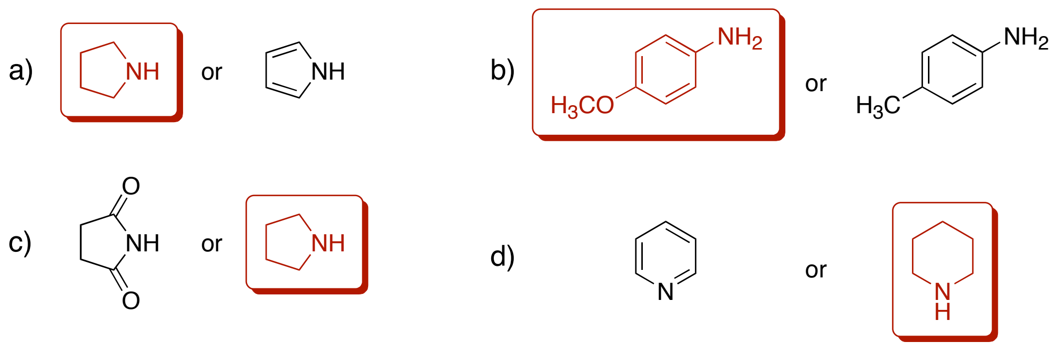
NAME____



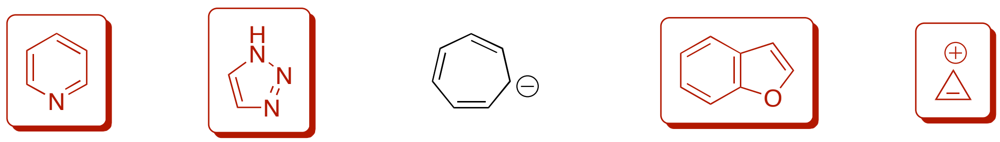
Cambridge, 1953. Shortly before discovering the structure of DNA, Watson and Crick, depressed by their lack of progress, visit the local pub.

Problem 1	12 pts	________
Problem 2	15 pts	________
Problem 3	10 pts	________
Problem 4	15 pts	________
Problem 5	10 pts	________
Problem 6	20 pts	________
Problem 7	12 pts	________
Problem 8	12 pts	________
Problem 9	30 pts	________
Problem 10	24 pts	________
Problem 11	10 pts	________
Problem 12	8 pts	________
Problem 13	8 pts	________
Problem 14	15 pts	________
TOTAL	100 pts	________

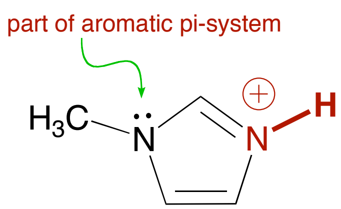
1. For each pair of molecules below, circle the one that would be the STRONGEST base. (12 pts)



2. Circle all of the following compounds that are AROMATIC. (15 pts)

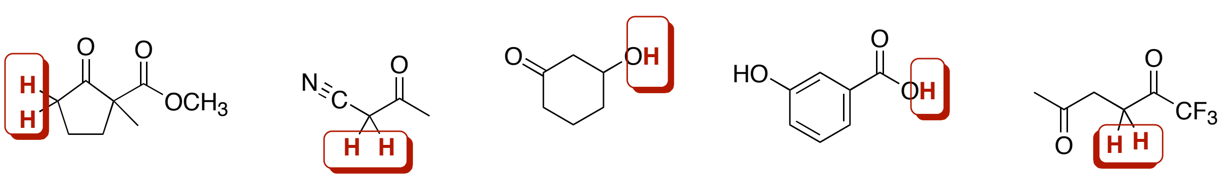


3. *N*-Methylimidazole is an aromatic heterocycle that contains two nitrogens. Upon treatment with acid, one of these nitrogens is preferentially protonated. On the structure below, draw the protonated form (eg. where does the proton go) and briefly explain why the proton adds selectively to one of the nitrogens. (9 pts)



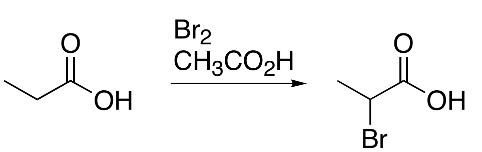
N-Methylimidazole will be protonated on the nitrogen shown. The lone pair of electrons on this nitrogen are perpendicular to the aromatic pi-system. The lone pair on the N-methyl nitrogen is not available for protonation as it is delocalized in the pi-system.

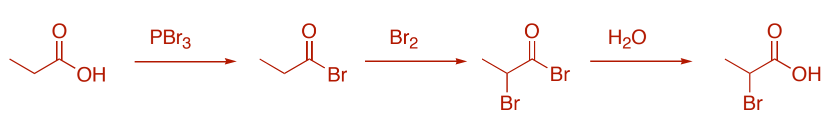
4. Identify the most acidic hydrogens in each of the following compounds. (15 pts)



5. Briefly explain why the following reaction will not work as shown. What reagents do you need to make the Hell-Vollhard-Zelinskii reaction proceed? (10 pts)

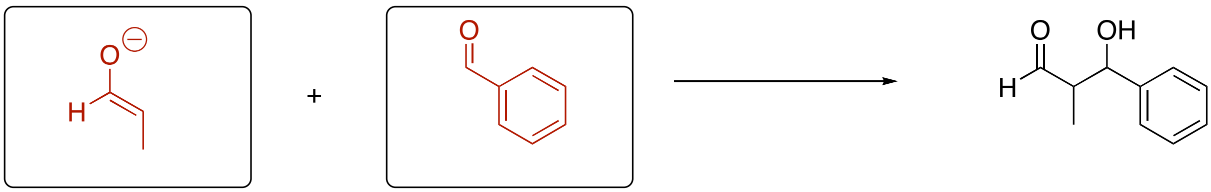
A carboxylic acid cannot enolize because the OH is the more acidic proton. Thus, you need to treat it with PBr_3 and Br_2 followed by water. This will generate an acid bromide intermediate that can be enolized and brominated on the alpha position.

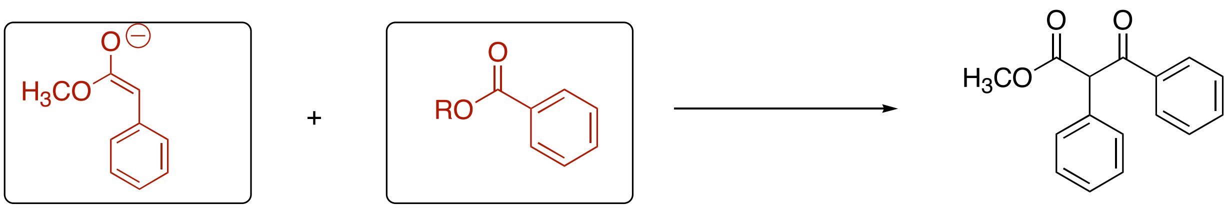




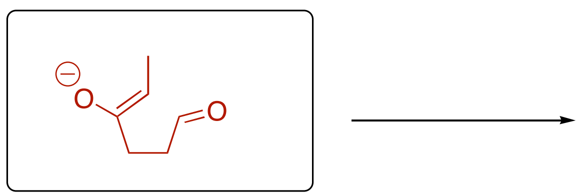
6. Carbonyl condensation reactions can occur between different kinds of carbonyl compounds. The products of three mixed condensation reactions are shown below. Draw the structures of the carbonyl compounds that react to form these products. Make sure to draw the ENOLATE form of the nucleophile and the CARBONYL form of the electrophile. (20 pts)

Enolate of Carbonyl Nucleophile | Carbonyl attacked by enolate

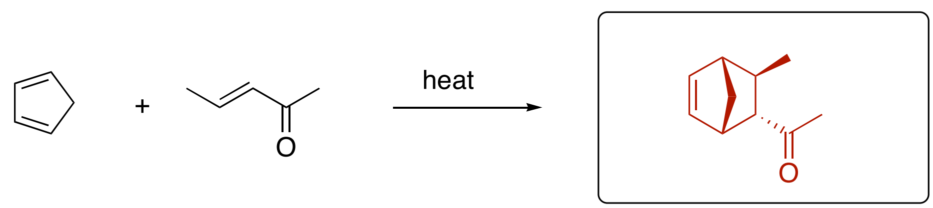
a) 

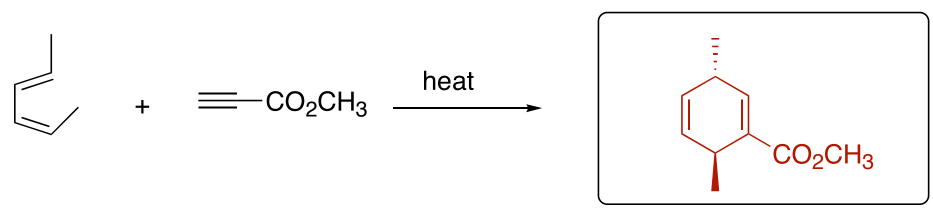
b) 

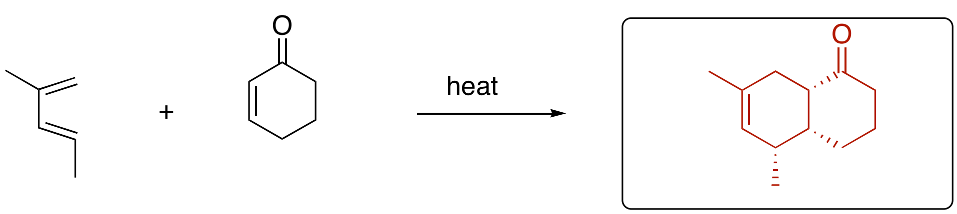
c) (both enolate and carbonyl in the same molecule - a Cyclization reaction)



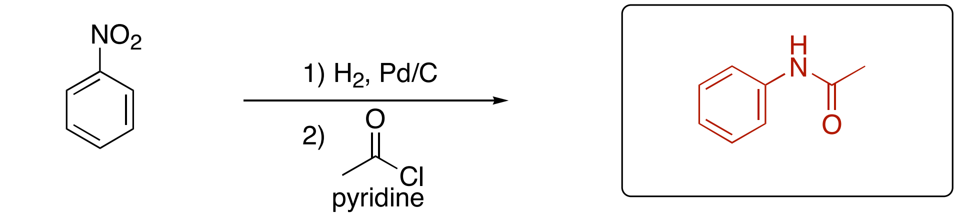
7. Draw the major product of the following Diels-Alder reactions. (12 pts)

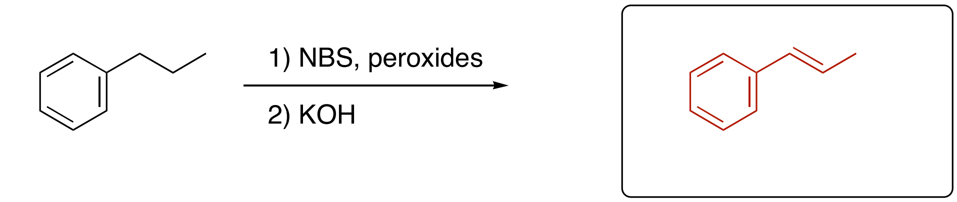
a) 

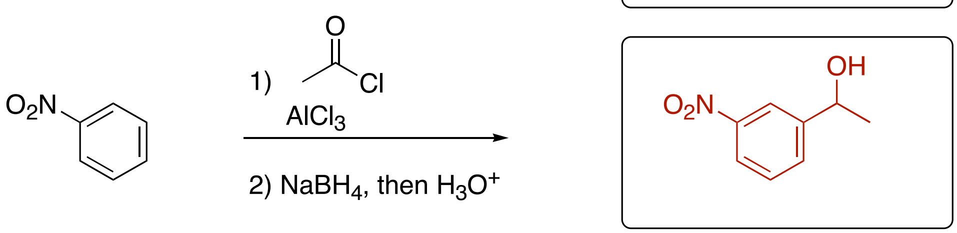
b) 

c) 

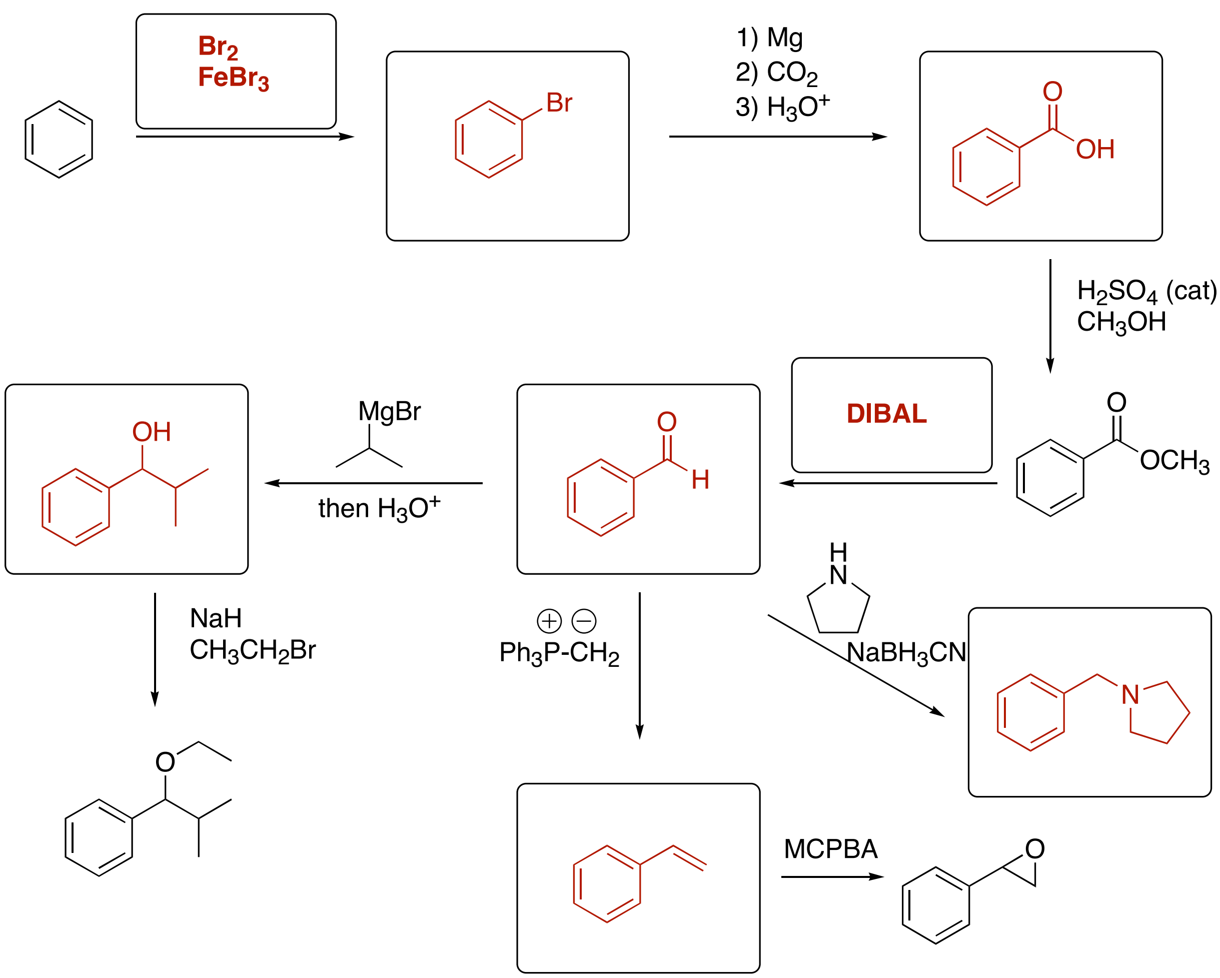
8. Provide the major product of the following reaction sequences. (12 pts)

a) 

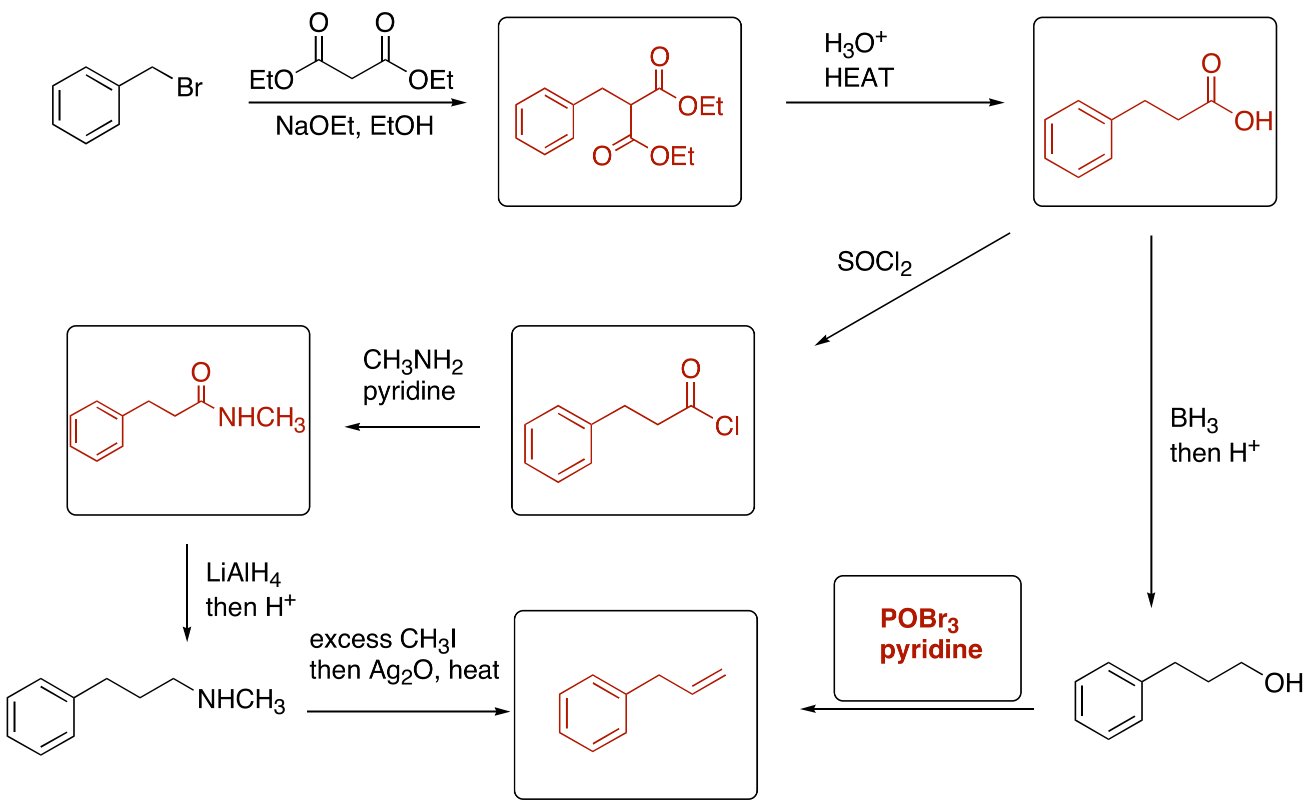
b) 

c) 

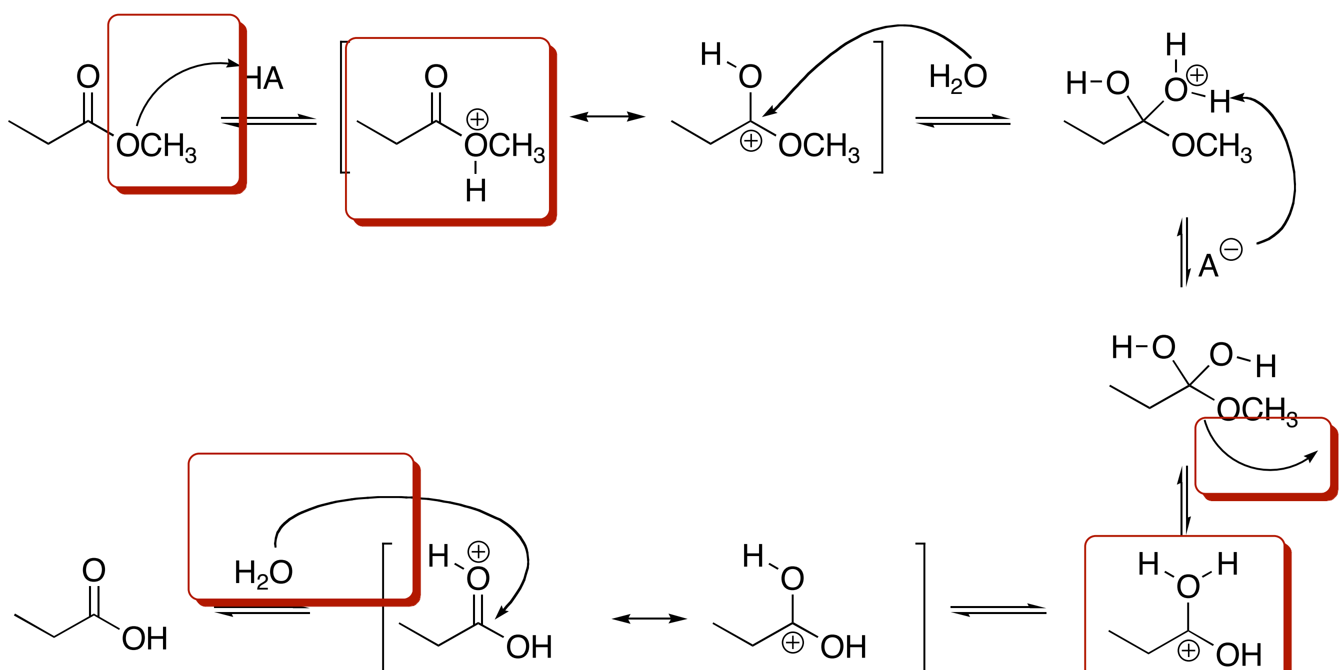
9. Fill in the missing reagents and structures in the following synthetic sequences. (30 pts)



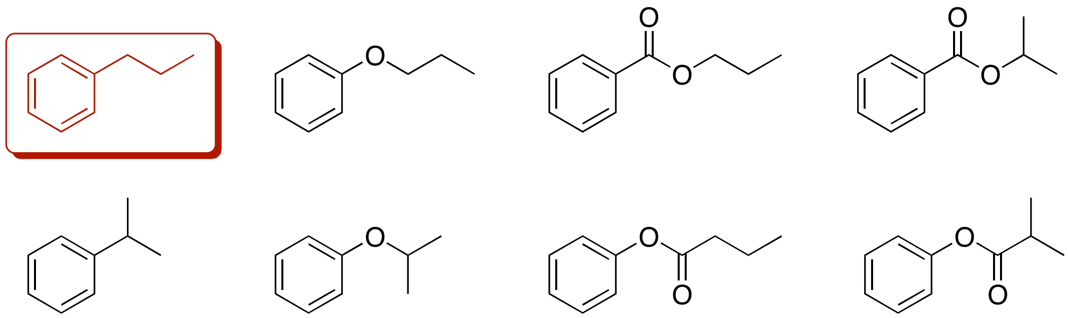
10. Fill in the missing reagents and structures in the following synthetic sequences. (24 pts)

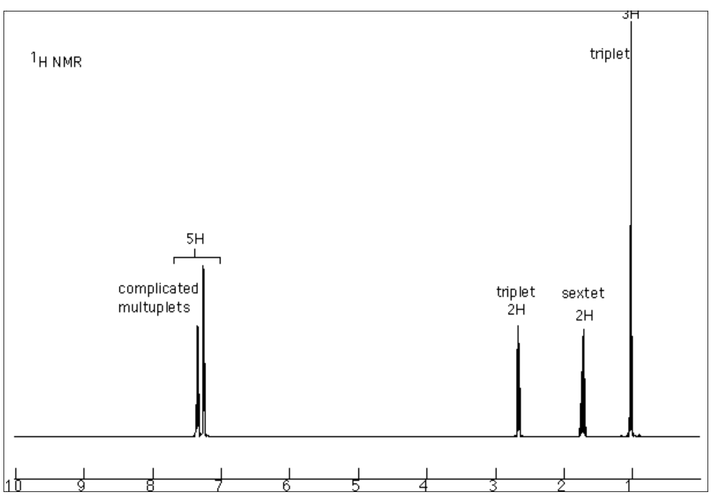


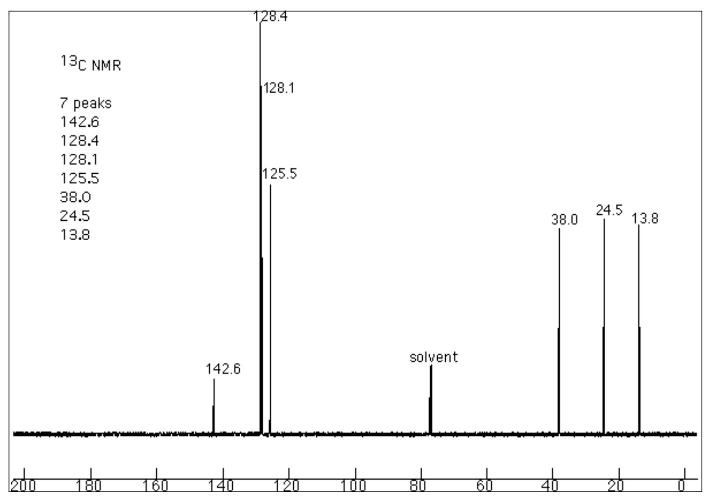
11. The mechanism for the acid catalyzed hydrolysis of esters shown below has several errors in it. Identify them by circling all incorrect ARROWS and STRUCTURES. (10 pts)



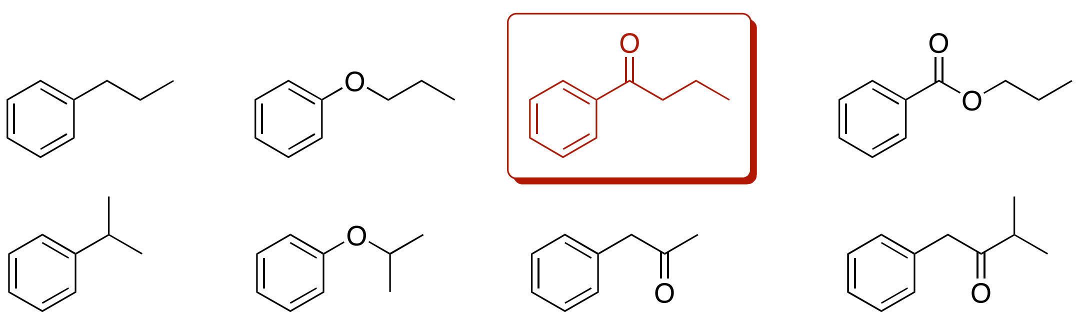
12. Circle the structure that matches the following proton and C13 NMR Data. (8 pts)

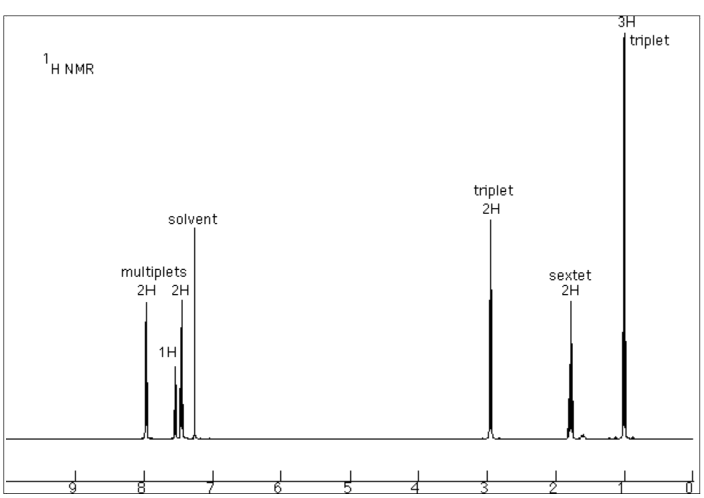


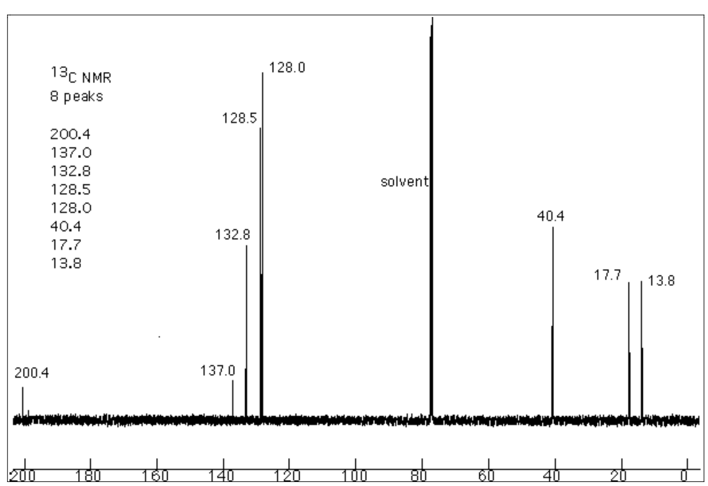




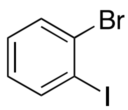
13. Circle the structure that matches the following proton and C13 NMR Data. (8 pts)



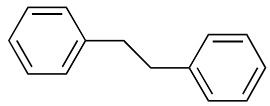




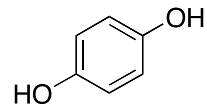
14. The three compounds shown below have very different ^{13}C NMR spectra. Match the structures with the correct spectra by placing the letter of the compound in the appropriate box. (15 points)



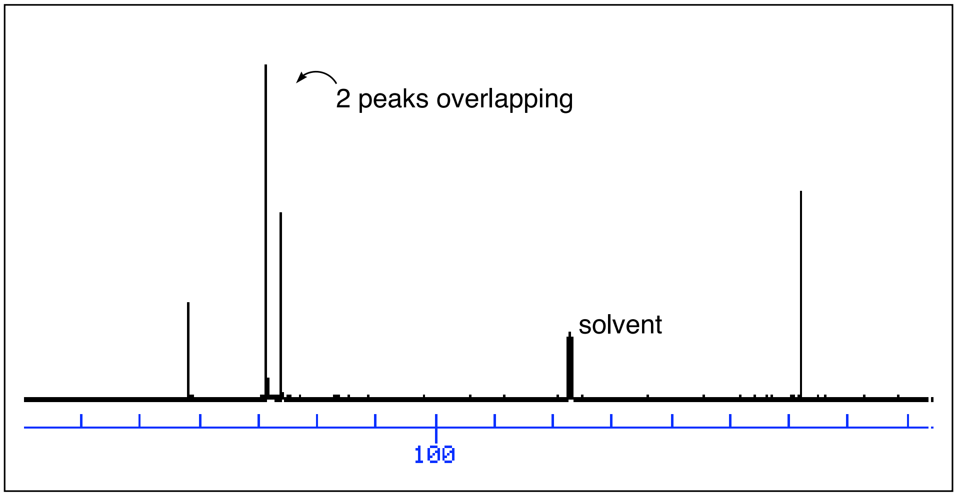
A



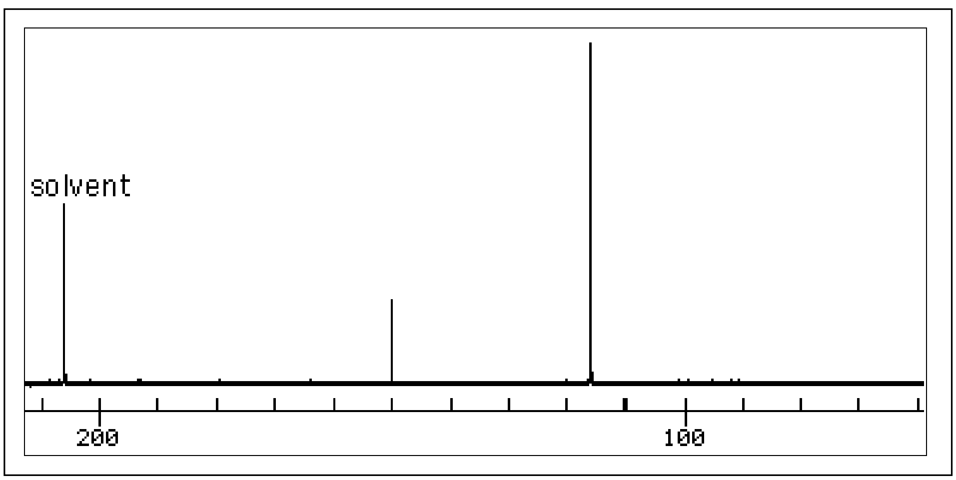
B



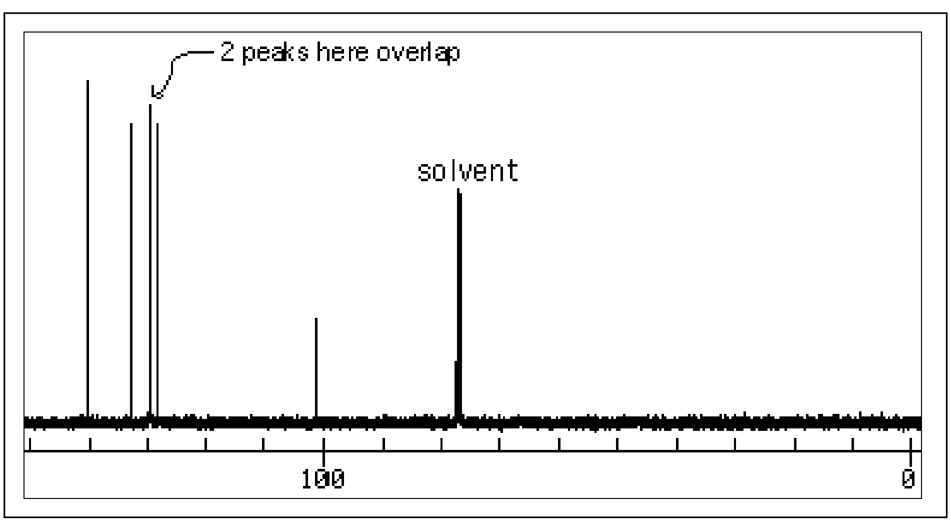
C



B



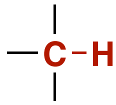
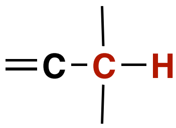
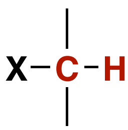
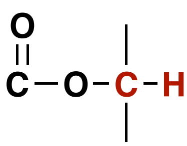
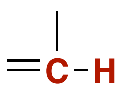
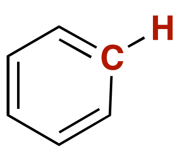
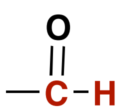
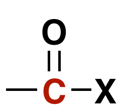
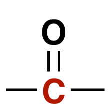
C



A

Typical NMR Chemical Shifts

(Note - these are approximate and sometimes peaks can show up outside of these ranges).

Functional Group	Type	^{1}H Chemical Shift (ppm)	^{13}C Chemical Shift (ppm)
	Alkane	0.7 -1.8	10 - 60
	Allylic or next to carbonyl	1.6 - 3.0	30 - 60
	next to halogen or alcohol	2.5 - 4.0	20 - 85
	next to oxygen of an ester	4.0 - 5.0	50 - 85
	vinylic	4.5 - 6.5	110 - 150
	aromatic	6.5 - 8.0	110 - 140
	aldehyde	9.7 - 10.0	190 - 220
O–H	alcohol	varies widely will exchange with D_2O	N/A
	carbonyl of ester, amide, or carboxylic acid (X = O, N)	N/A	165 - 185
	carbonyl of ketone or aldehyde	N/A	190 - 220