

NAME _____



Hey! Be an electron? I'd rather be a proton.

Really!

I'm *Positive!*

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

Problem 1 12 pts _____

Problem 2 6 pts _____

Problem 3 20 pts _____

Problem 4 10 pts _____

Problem 5 24 pts _____

Problem 6 15 pts _____

Problem 7 30 pts _____

Problem 8 21 pts _____

Problem 9 16 pts _____

Problem 10 20 pts _____

Problem 11 25 pts _____

given 1 pt **1** _____

TOTAL _____

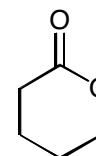
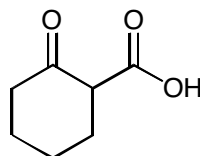
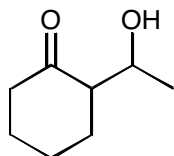
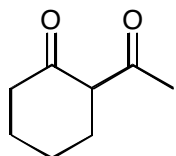
**RELAX! Don't get Overwhelmed.
 Think about what you know.**

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

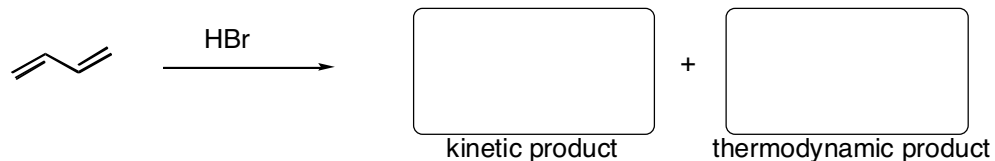
In the multiple step reaction sequences, look at what kind of reaction takes place in the second step to give you clues on what functional group you need to have after the first step.

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

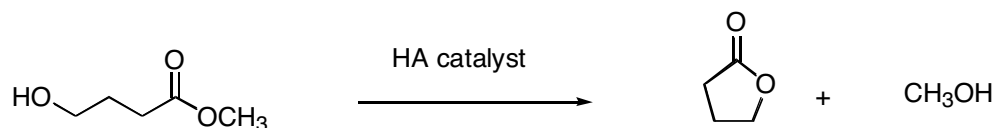
1. Identify the most acidic hydrogens in the following molecules. (12 pts)



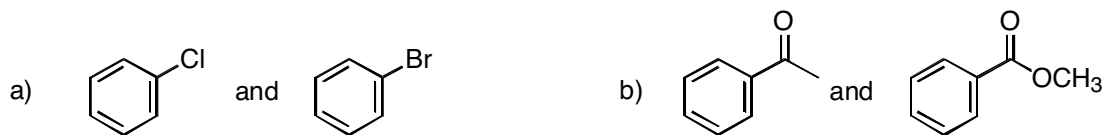
2. The addition of 1 equivalent of HBr to 1,3-butadiene results in two products. The major product changes if the reaction is carried out at low temperature (kinetic) or high temperature (thermodynamic). Write the structure of these products. (6 pts)



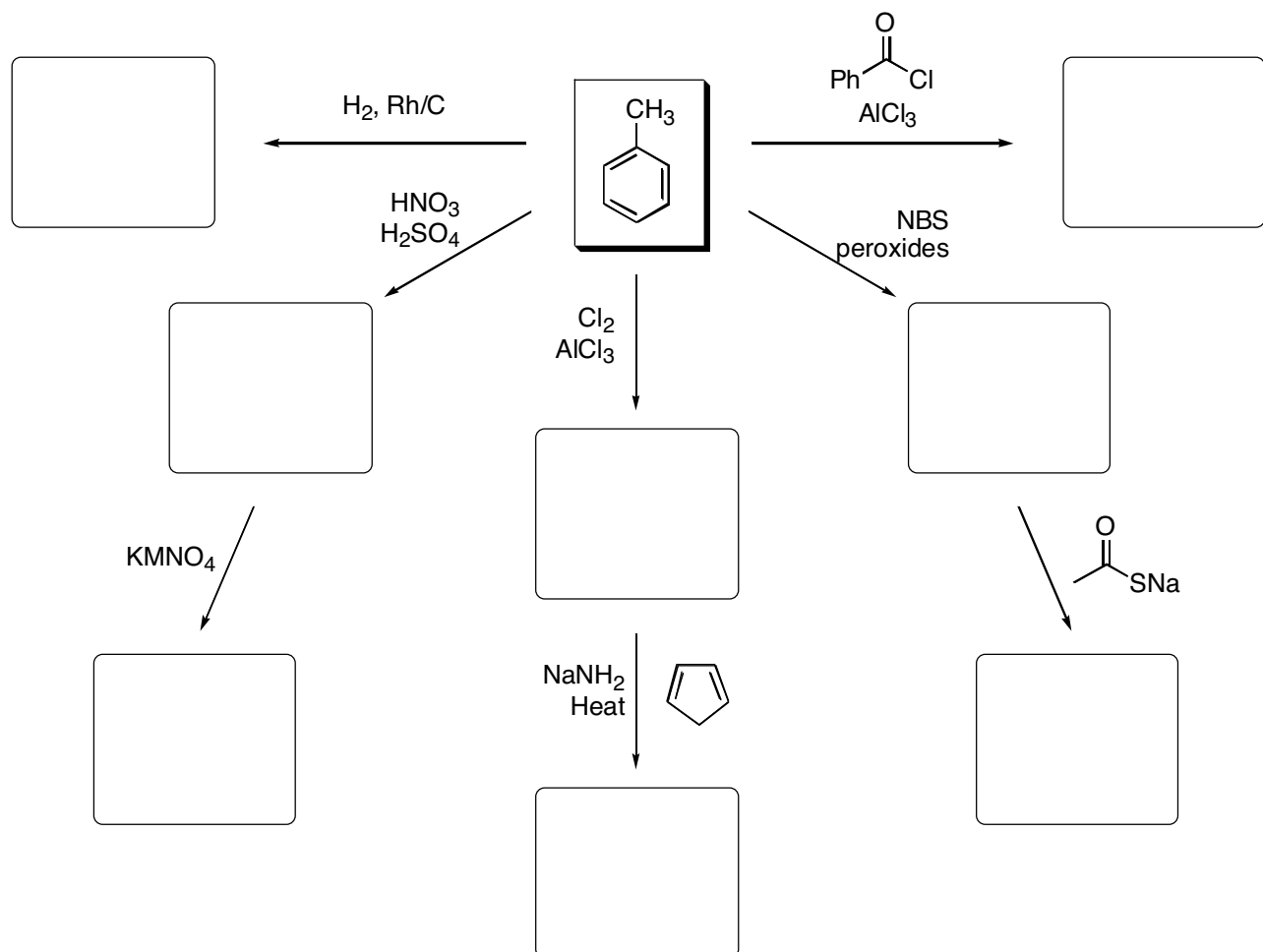
3. When methyl 4-hydroxybutanoate is treated with an acid catalyst a transesterification takes place to yield a lactone. The mechanism is identical to a Fischer esterification except methanol is the leaving group instead of water. Write out the complete mechanism showing all intermediates and arrows indicating electron flow. (20 pts)



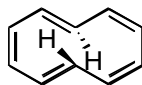
4. Describe how you would distinguish between the following molecules using NMR, IR, or Mass Spectrometry. (eg. What technique and what would you observe as the difference) (10 pts)



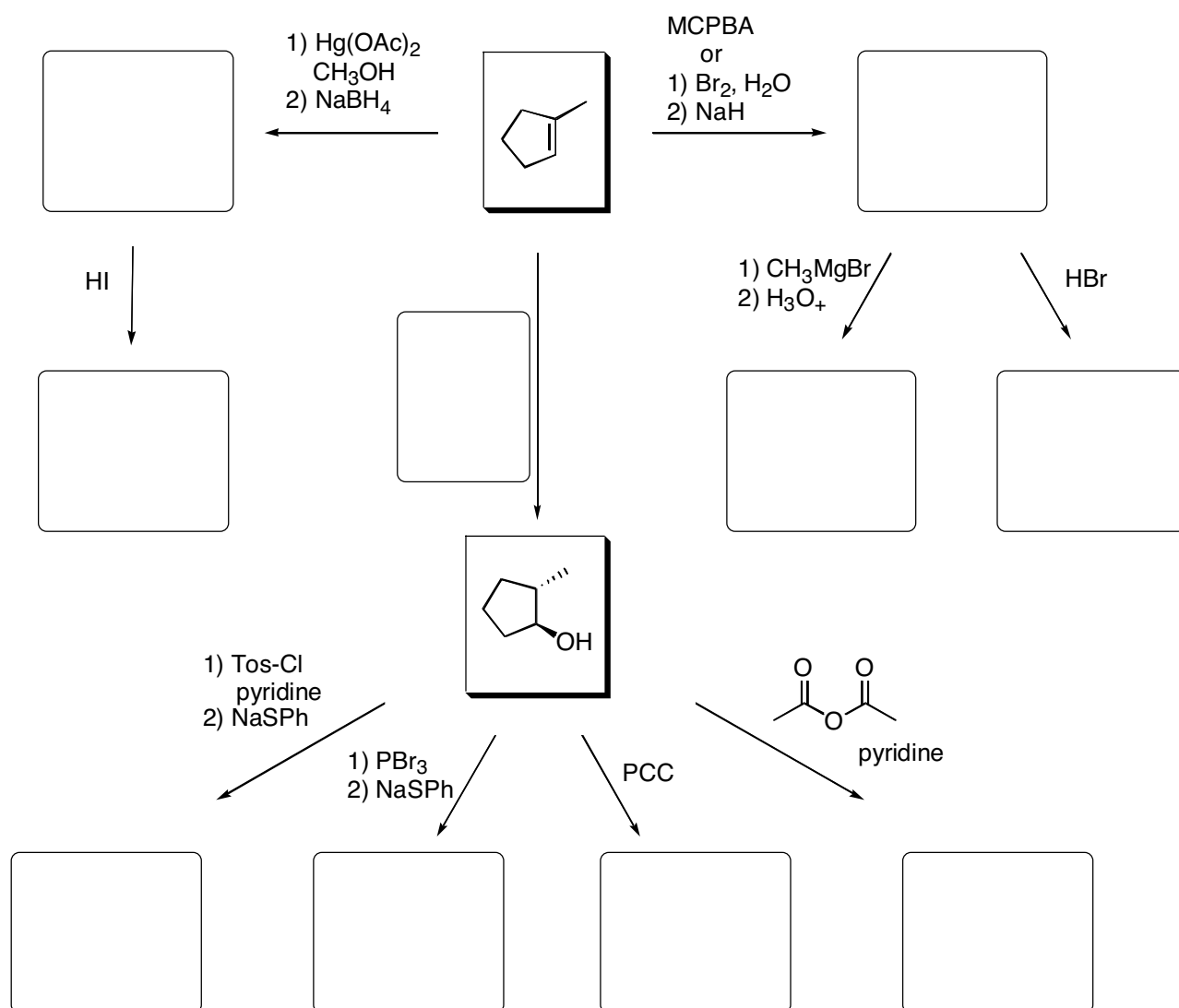
5. Provide the major product for the reactions below. For ortho-para directors you need only show the para product. (24 pts)



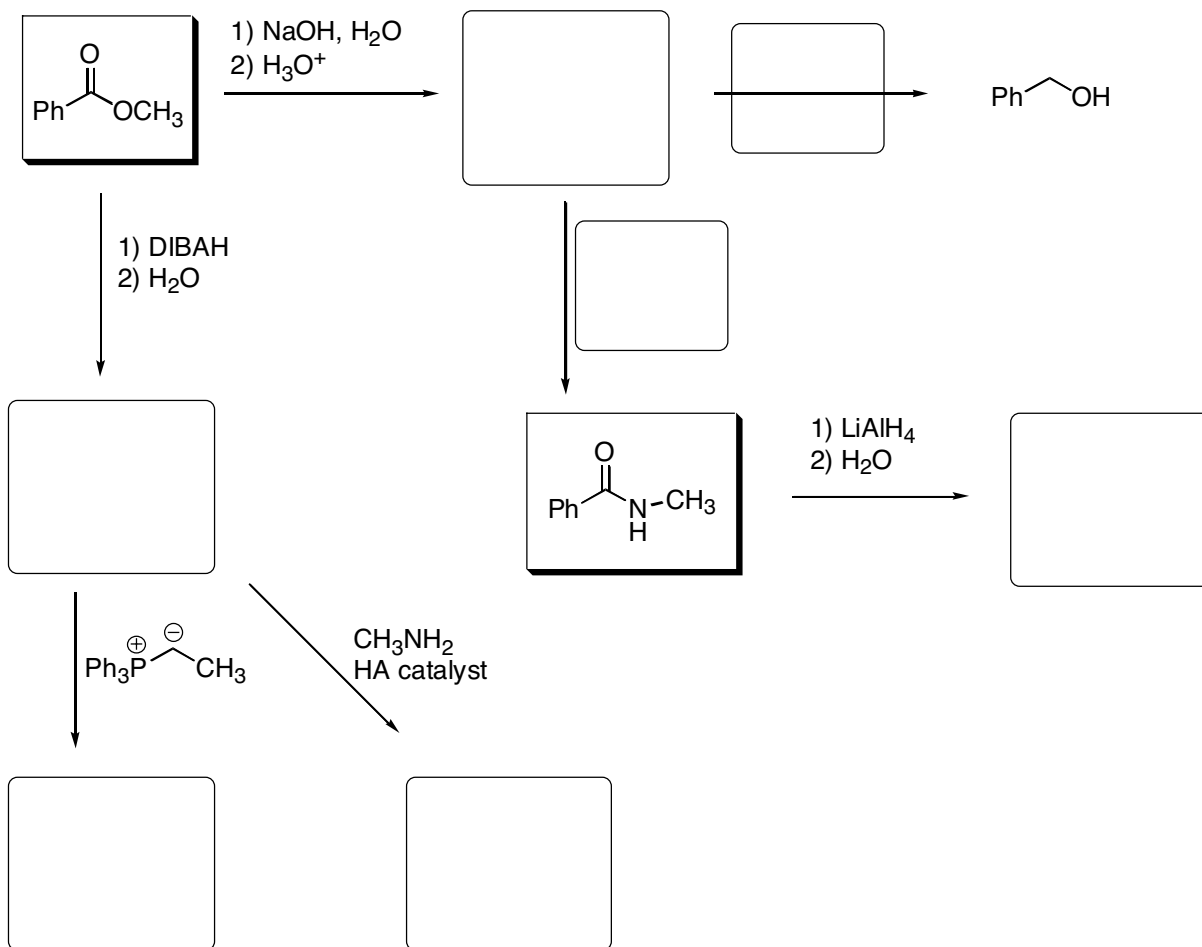
6. Which of the following molecules are **NOT** aromatic. Briefly explain why. (15 pts)



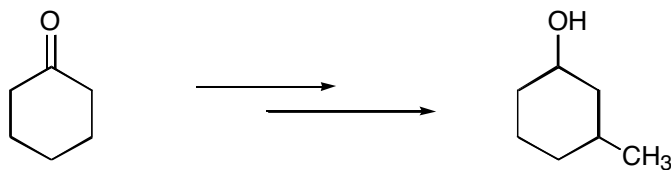
7. Provide the missing major products or reagents for the following. (30 pts)



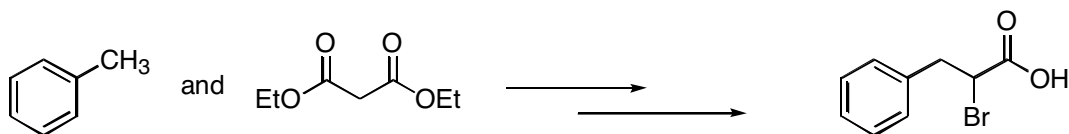
8. Provide the missing major products or reagents for the following. (21 pts)



9. Show how you would synthesize 3-methylcyclohexanol from cyclohexanone. Hint: This can be done in 4 steps. (5 counting an H₂O workup step) (16 pts)



10. Show how you would synthesize the following bromoacid starting from toluene and diethylmalonate. Hint: This can be done in 5 steps counting a hydrolysis and uses a Hell-Volhard-Zelinskii reaction. (20 pts)



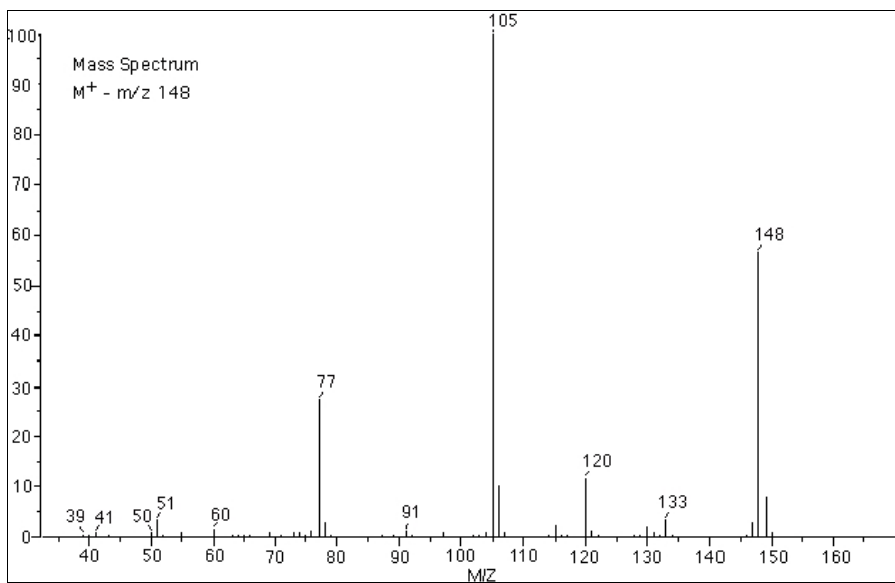
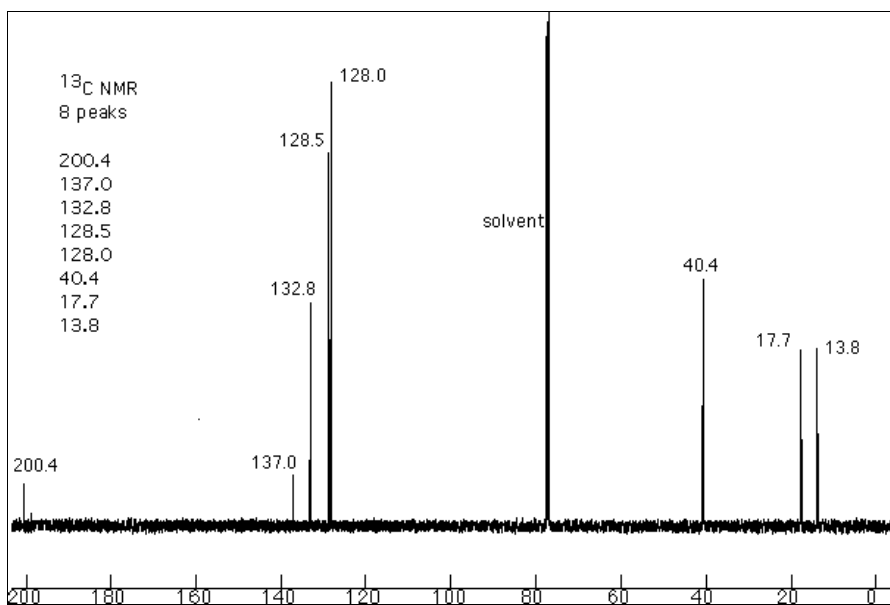
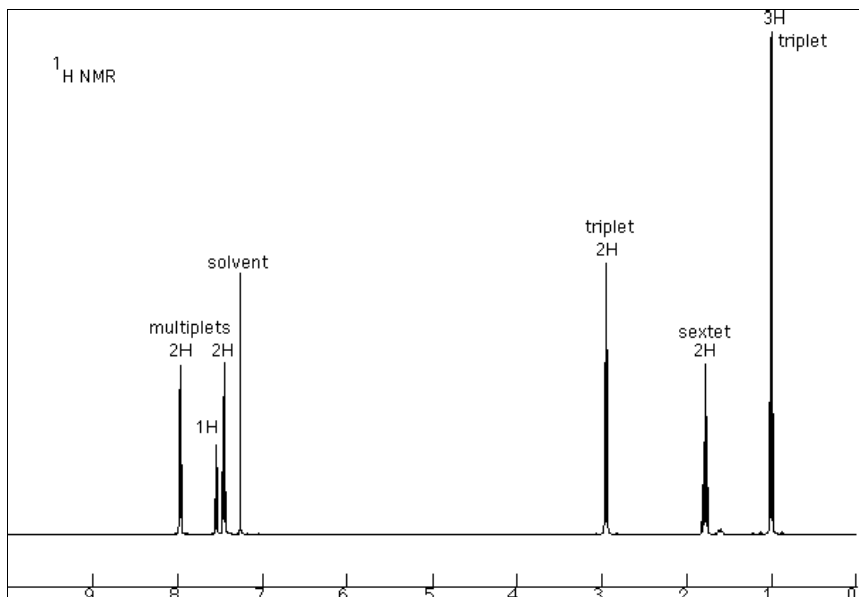
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11. Answer the following questions about an unknown molecule with a molecular formula of $C_{10}H_{12}O$. The IR spectra shows a strong absorbance at 1680 cm^{-1} . The ^1H NMR, ^{13}C NMR, and mass spectrum for this unknown are shown on the following page. (25 points)

How many degrees of unsaturation does the molecule possess?

What type of functional group does the carbon resonance at 200 ppm represent?

What is the structure of the unknown molecule?

In the Mass Spectrum, what does the base peak correspond to (draw a structure)?



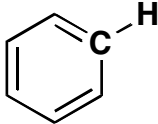
Infrared Stretching Absorptions

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
$\begin{array}{l} -\text{C}\equiv\text{C}- \\ -\text{C}\equiv\text{N} \\ \text{O}=\text{C}=\text{O} \end{array} \quad \left. \vphantom{\begin{array}{l} -\text{C}\equiv\text{C}- \\ -\text{C}\equiv\text{N} \\ \text{O}=\text{C}=\text{O} \end{array}} \right\}$	2100-2260	medium	
$\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$	1680-1750	strong	
$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$	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