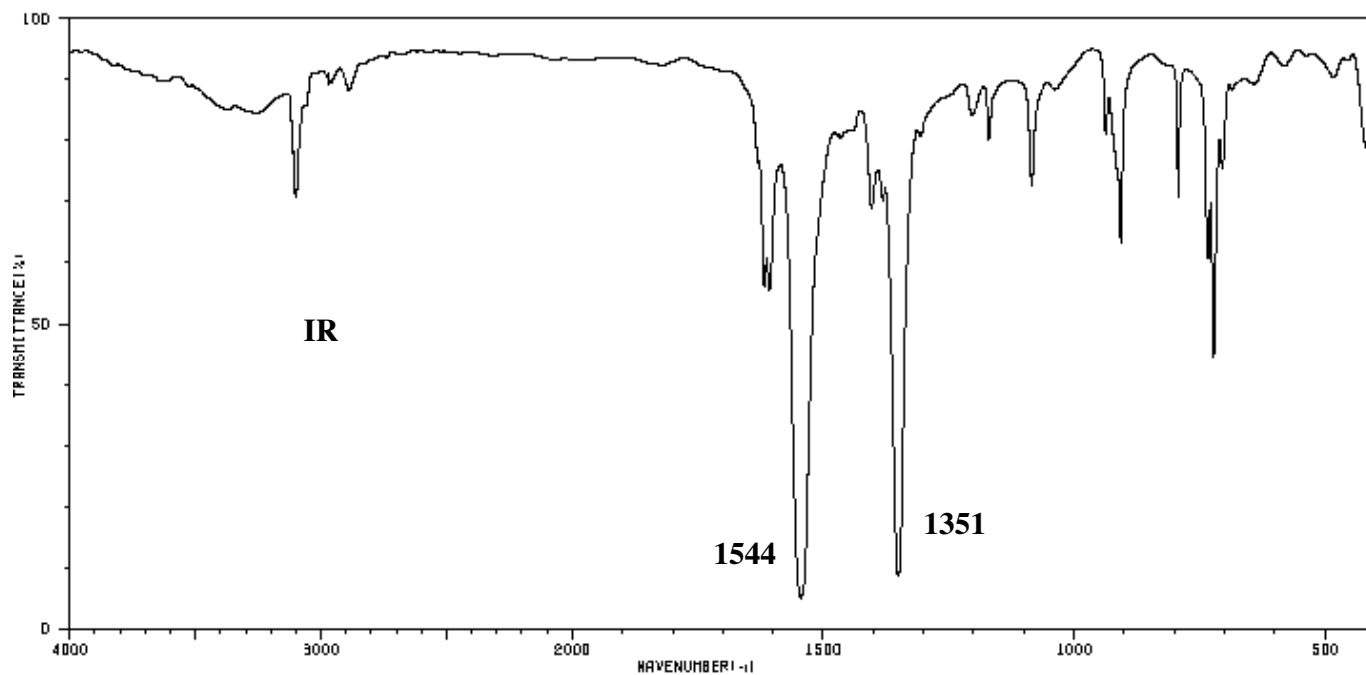
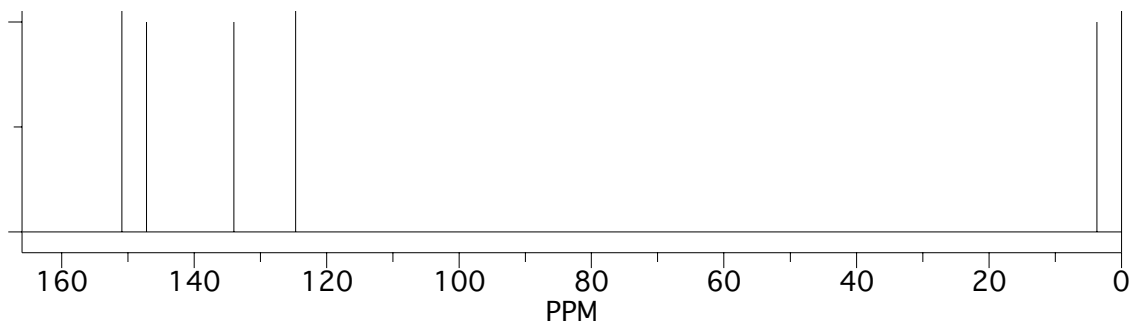


1. (36 points total) Use the information provided below and the IR and NMR spectra on the next page to answer the following questions.
- a. (10 points) Determine the **molecular formula** that satisfies the following data (**circle** your final answer): EA (found): C, 37.02; H, 2.22; N, 18.50; **and** $M^+ = 227$
- b. (6 points) Calculate the **Index of Hydrogen Deficiency** (IHD) for the molecule in **a**, above (**circle** your final answer).
- c. (5 points) An IR spectrum of the molecule in **a** appears on the following page. What functional group or groups correspond(s) to the **2 most intense** peaks in the spectrum? **Draw** the structure of this/these group(s), **showing all bonds** (i.e. single, double, triple).
- d. (10 points) Using the information in **a**, **b**, and **c**, above, and the ^1H NMR and ^{13}C NMR spectra on the next page, determine a structure of this unknown molecule that is consistent with **all** data. **Draw the structure of this molecule below** (**circle** your final answer).
- e. (5 points) **Provide an explanation** for the fact that the singlet at 9.4 ppm in the ^1H NMR spectrum appears so far downfield.
- f. (EXTRA CREDIT, 5 points): What is this compound, and what is its most notorious physical property?

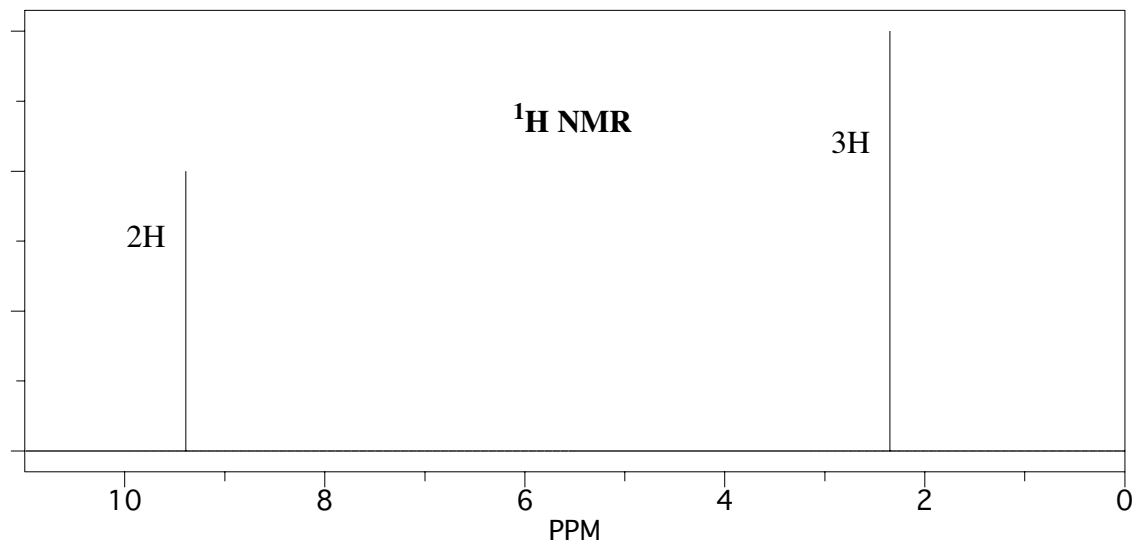
(IR, ^1H NMR and ^{13}C NMR spectra for the molecule in problem 1 on the previous page)



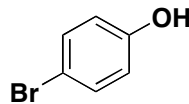
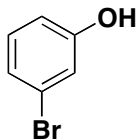
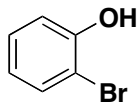
^{13}C NMR



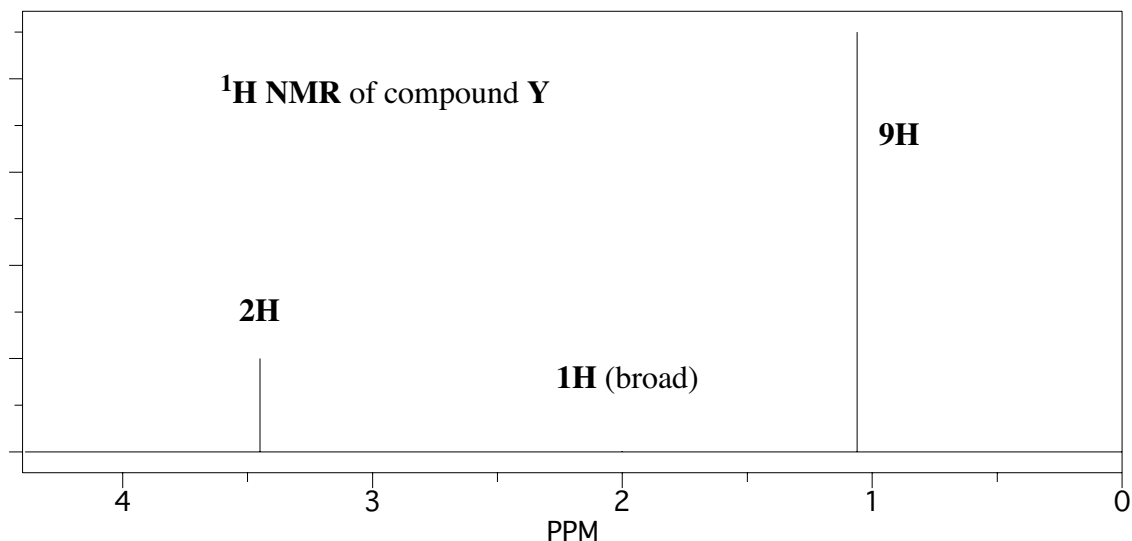
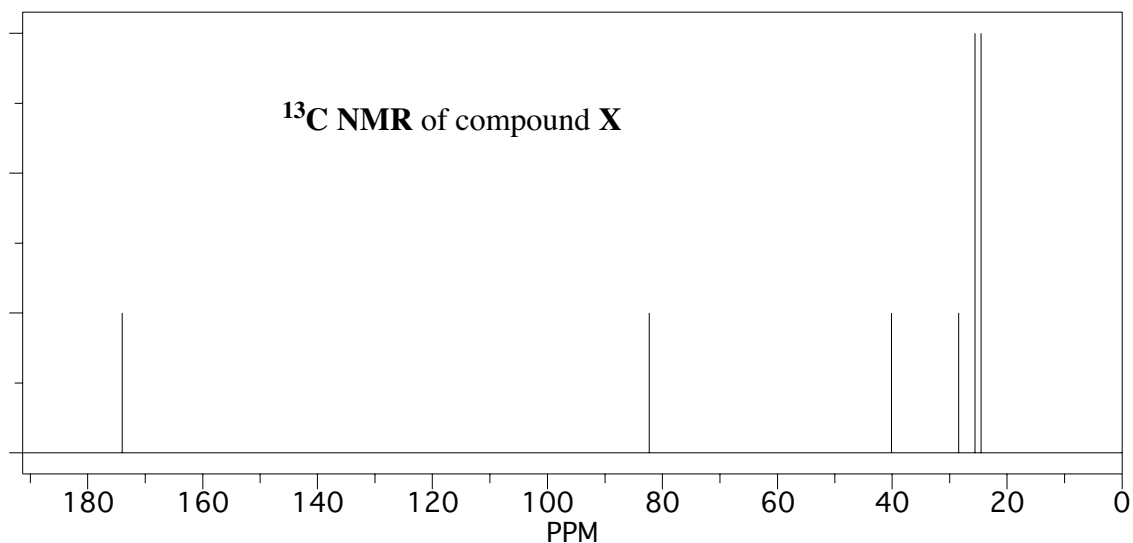
^1H NMR



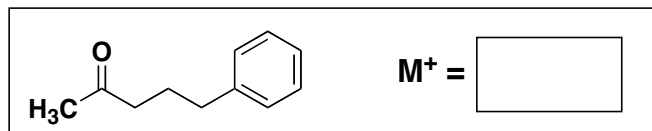
2. (20 points) Using **only** ^1H NMR spectroscopy, how would you **conclusively** distinguish between **all 3 isomers** (*ortho*, *meta*, and *para*) of bromophenol? **Be as specific as necessary in order to differentiate *ortho* from *meta*, *meta* from *para*, and *ortho* from *para*.** (Suggestion: Use chemical structures as part of your answer.)



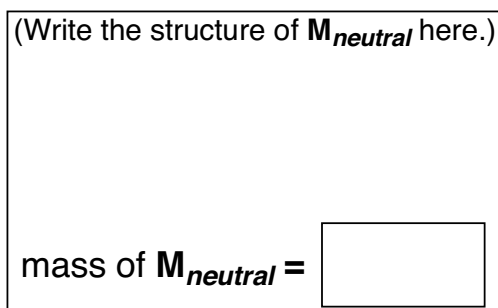
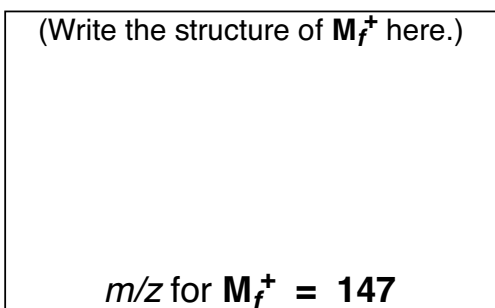
3. (20 points) An unknown compound **X** (containing **only** carbon, hydrogen, and oxygen) has $m/z = 172$ (M^+) and **115**, and its ^{13}C NMR spectrum below. When treated with lithium aluminum hydride in ether, a **single** compound **Y** is produced, and its ^1H NMR spectrum is given below. In the space below the NMR spectra at the bottom of the page, **draw the structures of X and Y**. Circle your final answers and **clearly** indicate which is compound **X** (12 points) and which is compound **Y** (8 points).



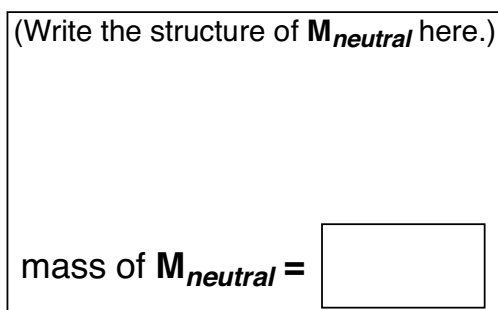
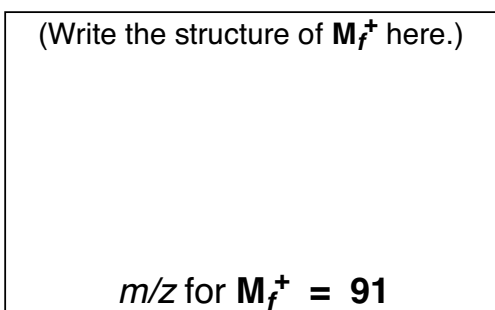
4. (24 points) Mass spectrometry was performed on 5-phenyl-2-pentanone (below), and several signals corresponding to **fragments** (M_f^+) were observed in the spectrum. Write the m/z value observed for M^+ in the box provided (3 points). In each question below the m/z value for M_f^+ is provided. **Draw the structure** of M_f^+ in the corresponding box (3 points each). Also, **write the molecular weight** of the **neutral species** ($M_{neutral}$) formed in each fragmentation in the boxes on the right (1 point each). Finally, **draw the structure** of each ($M_{neutral}$) in the boxes on the right (3 points each). **BE SURE TO INDICATE WHETHER EACH M_f^+ and EACH $M_{neutral}$ is a radical** (i.e. has an unpaired electron).



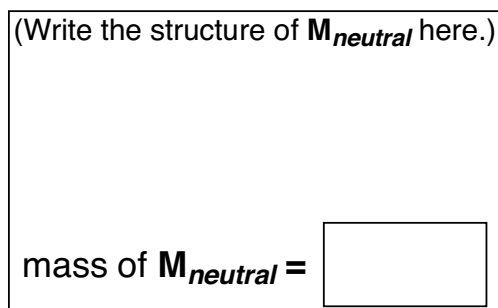
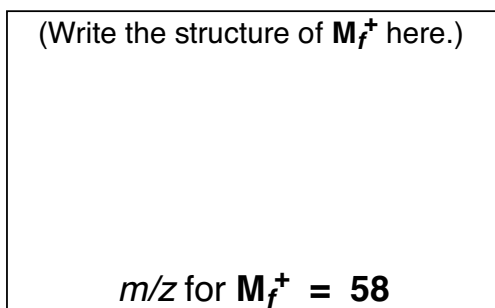
a.



b.



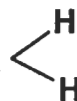
c.



¹H NMR Coupling Constants (Expanded)

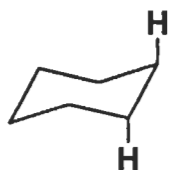


vicinal 6-8 Hz
(averaged by free rotation)

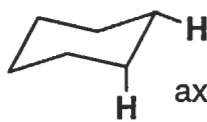


geminal 12-15 Hz
acyclic
can be 0-25 Hz in
cyclic systems

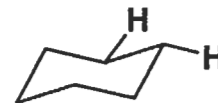
In rigid systems, vicinal coupling can range from 0 to 15 Hz. For example:



ax-ax 6-14 Hz

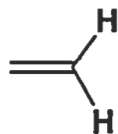


ax-eq 0-5 Hz



eq-eq 0-5 Hz

Spin-spin coupling in alkenes:



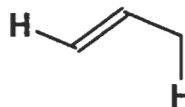
geminal 0-3 Hz



cis 6-12 Hz

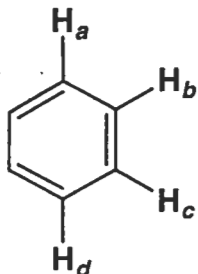


trans 12-18 Hz



allylic 0-3 Hz

Spin-spin coupling in arenes:



J_{ab} (ortho) 6-10 Hz

J_{ac} (meta) 1-3 Hz

J_{ad} (para) 0-1 Hz

Note: Structures shown above represent generic coupling situations and not the specific molecules depicted (in which the labeled protons would be chemically equivalent and would not couple).

Characteristic Functional Group Chemical Shifts in ^{13}C NMR (ppm)

Alkanes		Organohalogen	
Methyl (RCH_3)	0-30	C–F	70-80
Methylene ($\text{RCH}_2\text{R}'$)	15-55	C–Cl	25-50
Methine ($\text{RCH}(\text{R}')(\text{R}'')$)	25-55	C–Br	10-40
Quaternary ($\text{RC}(\text{R}')(\text{R}'')(\text{R}''')$)	30-40	C–I	–20-10
Alkenes	100-150	Ketones, Aldehydes	185-220
Aromatic	120-160	Carboxyl Derivatives	
Alkynes	70-90	Acids	150-185
Nitriles	110-125	Esters	155-180
Alcohols, Ethers	50-90	Amides	150-180
Amines	40-60	Carbamates	150-160