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** $M^+ = 227$

   $C_7H_5N_3O_6$

   b. (6 points) Calculate the **Index of Hydrogen Deficiency** (IHD) for the molecule in **a**, above (**circle** your final answer).

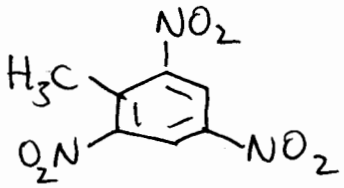
   7

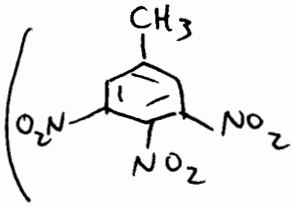
   c. (5 points) An IR spectrum of the molecule in **a** appears on the following page. What functional group or groups correspond(s) to the **2 most intense** peaks in the spectrum? **Draw** the structure of this/these group(s), **showing all bonds** (i.e. single, double, triple).

   NITRO GROUPS

   d. (10 points) Using the information in **a**, **b**, and **c**, above, and the ^{1}H 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).

   ALSO SATISFACTORY

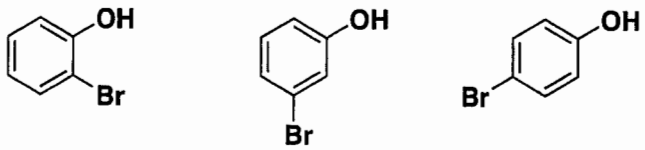
   e. (5 points) **Provide an explanation** for the fact that the singlet at 9.4 ppm in the ^{1}H NMR spectrum appears so far downfield.

   2 NO_2 (e^--WITHDRAWING) DESHIELD PROTONS ON AROMATIC RING SIGNIFICANTLY.

   f. (EXTRA CREDIT, 5 points): What is this compound, and what is its most notorious physical property?

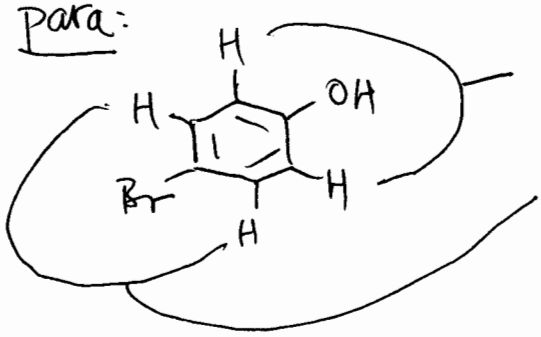
   (2,4,6)-TRINITROTOLUENE (TNT). EXPLOSIVE.

2. **(20 points)** Using **only ^{1}H 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.)



SPIN-SPIN COUPLING CAN DIFFERENTIATE ALL 3 FROM ONE ANOTHER

para:

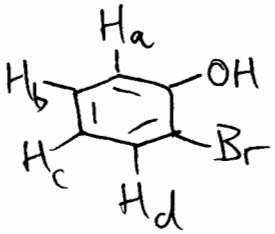


each 2H, d (or dd, J = 7-8, 2) (meta coupling)

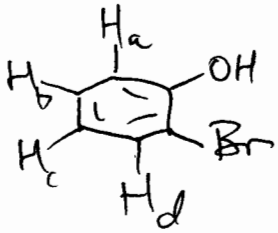
J = 7-8

↑ DEPENDING ON STRENGTH OF MAGNET USED, THIS COUPLING MAY OR MAY NOT BE EVIDENT IN ^{1}H NMR SPECTRUM.

ortho:



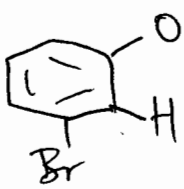
or



- J_{Ha-Hb} : 7-8 Hz } Ha : d
- J_{Hb-Hc} : 7-8 Hz
  J_{Hb-Hc} : 7-8 Hz } Hb : dd
- Hc : SAME PATTERN AS Hb : dd
- Hd : " " " Ha : d

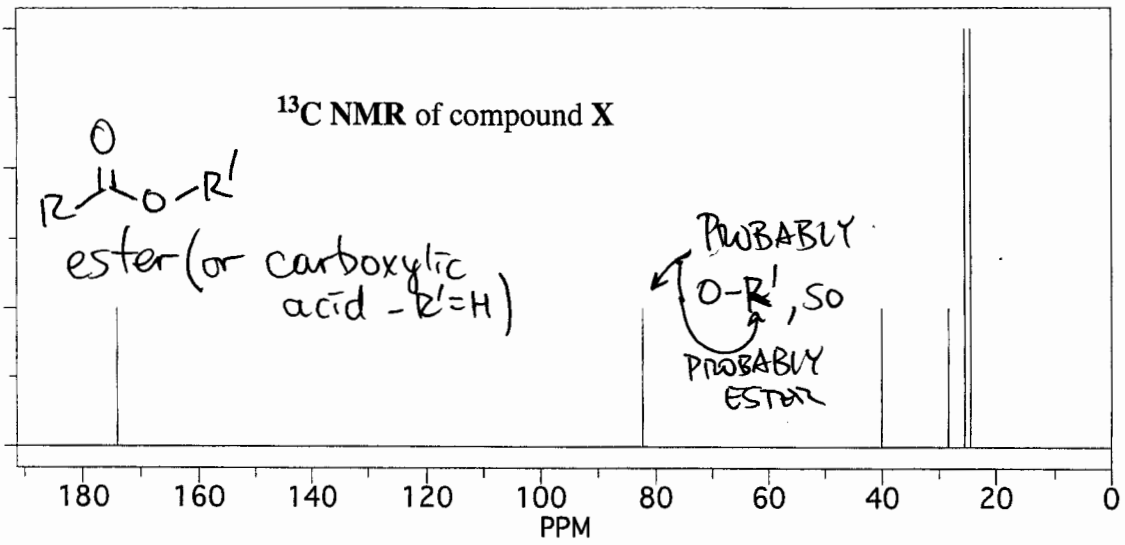
IF META COUPLINGS DETECTABLE, THEN EACH PROTON HAS 1 ADDITIONAL 2 Hz-COUPLING, i.e. J_{Ha-Hc}, J_{Hb-Hd}, etc.

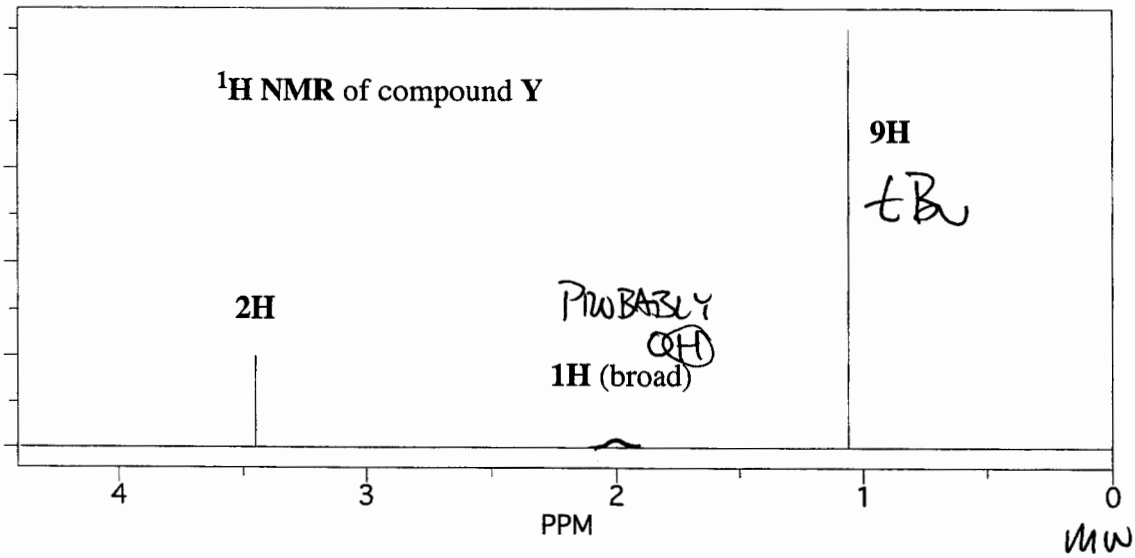
meta:



WILL BE SINGLET (ONLY ONE 4) (OR dd or t, J ≈ 2, 2 IF MAGNET OF HIGH ENOUGH FIELD)

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 **^{1}H 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).





DOUBLE-CHECK:

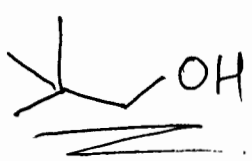
$C_{10}H_{20}O_2$

MW = 172

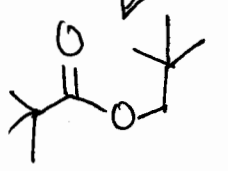
SO:

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R' \xrightarrow{LiAlH_4} RCH_2OH + R'OH$$

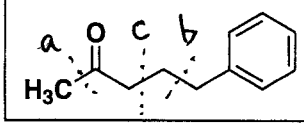
BUT $RCH_2 = R'$, BECAUSE BOTH ALCOHOLS ARE "Y"

$\therefore$ Y = RCH_2OH = 

tBu (9H), $2H_s$, 1H

X = 

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).



M^+ = 162

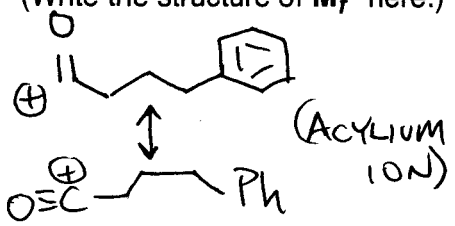
$C_{11}H_{14}O$

MW = 162

M^+ = 162

a.

(Write the structure of M_f^+ here.)



(Acylium ion)

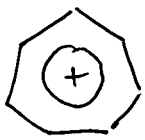
m/z for M_f^+ = **147**

(Write the structure of $M_{neutral}$ here.)

mass of $M_{neutral}$ = 15

b.

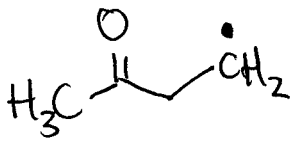
(Write the structure of M_f^+ here.)



(tropylium ion)

m/z for M_f^+ = **91**

(Write the structure of $M_{neutral}$ here.)



mass of $M_{neutral}$ = 71

c.

McLAFFERTY REARRANGEMENT

(Write the structure of M_f^+ here.)

(radical cation)

m/z for M_f^+ = **58**

(Write the structure of $M_{neutral}$ here.)

mass of $M_{neutral}$ = 104