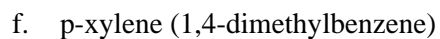
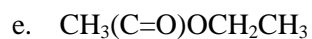
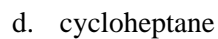
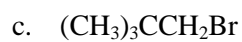
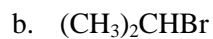


Organic Chemistry 321  
Workshop: Spectroscopy  
NMR-IR Problem Set

1. Draw an NMR spectrum for each of the following compounds. Indicate each peak by a single vertical line (for example, a quartet would be shown as 4 vertical lines whose heights are 1:3:3:1). Estimate approximate shift positions using your handout or text.



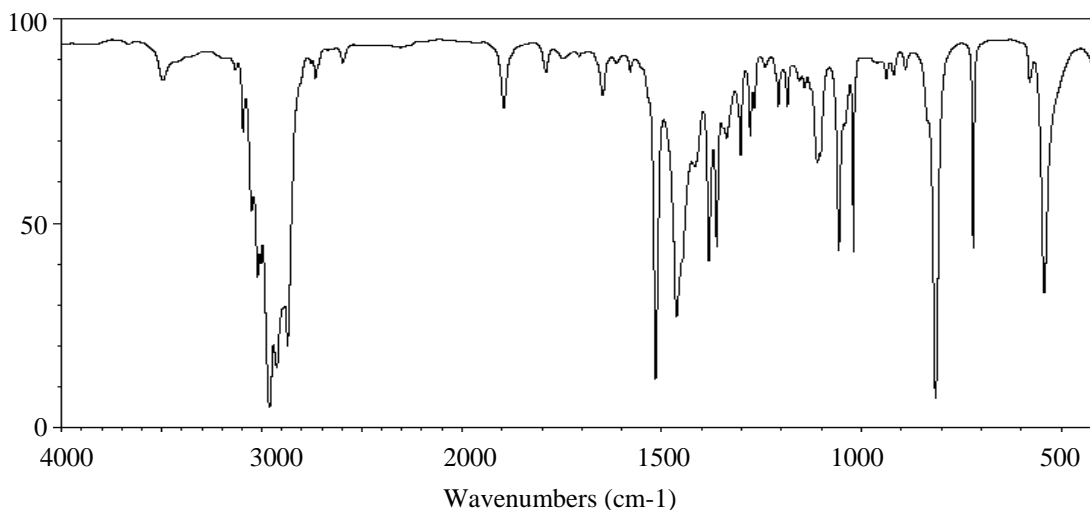
2. Listed on the next page are proton NMR absorption peaks for several compounds. In some cases characteristic infrared absorptions are given as well. Propose a structure consistent with each set of data.

**Here is a procedure for interpreting proton nmr spectra.** It is not comprehensive, but it may be a good start.

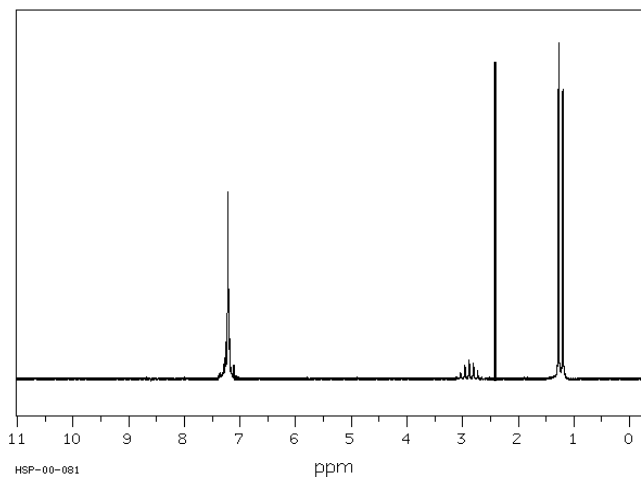
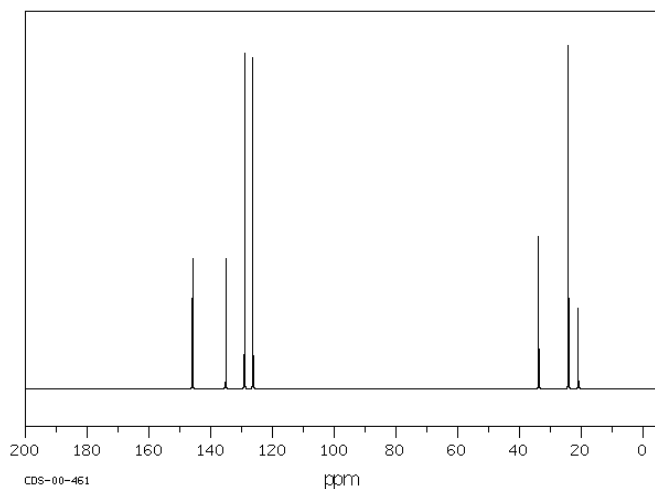
- a. Use the molecular formula to compute the Index of Hydrogen Deficiency (IHD, also known as DU). Note that each separate benzene ring (individual, not fused to another benzene ring) accounts for 4 "IHD units". Presence of ordinary (i.e. not benzene) double bonds is demonstrated by absorption of Br<sub>2</sub> or H<sub>2</sub>. Benzene does not react with either of these. Remember that "IHD units" may result from any combination of rings, double bonds, or triple bonds.
- b. Is there a signal between 6.5-9 ppm? If so there is at least one benzene ring. Subtract the #H for that signal from 6 to get the number of substituents attached to the ring. You get # of H from info about peak areas. (This does not tell you where on the ring they are located, but the <sup>13</sup>C spectrum may help – see below).
- c. Before you worry about splitting, find the # of H for each signal. It may be given directly or you may have to estimate peak areas relative to each other. The ratios will be small whole numbers. If peaks are very narrow you can use relative peak heights to estimate "area" ratios. Knowing the # of H atoms that cause each signal, plus the molecular formula, allows you to guess at the kind and number of H-bearing fragments of the molecule. Fragments must be structurally reasonable. For example, you could not have a single C with more than 3 H. Explicitly write **each** fragment down and show the number of "empty" bonds (every C must have 4 bonds, O must have 2 bonds, N must have 3 bonds). Examples (not an exhaustive list and some empty bonds not shown):
  - 1 H : CH (has 3 empty bonds) **or** -OH **or** =NH
  - 2 H : -CH<sub>2</sub>- **or** -NH<sub>2</sub> **or** two CH that are in very similar environments [if on *alkene* sp<sup>2</sup> C, δ is > 4.5]
  - 3 H : -CH<sub>3</sub>
  - 4 H : is δ < 6 ppm? write **two separate -CH<sub>2</sub>- groups**  
is δ > 6 ppm? write a **benzene** ring with two "empty bonds"
  - 6 H : **two identical -CH<sub>3</sub>** (write **two separate -CH<sub>3</sub> groups**)
- d. Write any other fragments needed by comparing the molecular formula to fragments written thus far (other fragments might be halogen atom, C without any H [alkyl/alkenyl/alkynyl/aromatic], carbonyl C, double bonded O, trisubstituted N or triple-bonded N). The complete collection of fragments that you write will help you to assemble the molecule.
- e. Consider structural implications offered by chemical shift (δ) values:
  - <3 ppm: ordinary alkyl
  - 3 - 5: the C bearing this H also has attached halogen or O
  - 4.5 - 6.9: vinylic CH (internal or terminal)
  - 6.5 - 9: aromatic CH (benzene ring) – typically wide "singlet" or multiplet
  - 8 – 10 (if very sharp or clean multiplet): aldehyde CH
  - >9: carboxylic acid OH – always a singlet
- f. Splitting patterns reveal # of H of a different class on a neighboring C. Keep in mind the symmetry of simple splits and how splitting trees caused by many different neighbors mess up the symmetry.
- g. If IR or <sup>13</sup>C spectra are available, glean what you can from these (O-H stretch? N-H stretch? C=O stretch? # of unique C?)
- h. Assemble fragments ("empty" bonds of fragments act like Velcro patches that can stick to other Velcro patches – you can "stick" fragments together in various ways). Connect fragments so that signal splitting, chemical shift and # of H for each signal predicted from your structure ALL match those in the spectrum. Make sure that you connect ALL fragments into a single molecule. <sup>13</sup>C spectra normally reveal all unique carbon atoms (there are rare exceptions) and can help you decide where to connect multiple substituents on benzene rings (ortho, meta or para).

<u>Compound</u>	<u>NMR Spectrum</u>	<u>IR Spectrum</u>	<u>IHD</u>	<u>proposed structure</u>
a. C <sub>7</sub> H <sub>8</sub> O	singlet, δ2.43 (1H) singlet, δ4.58 (2H) multiplet, δ7.28 (5H)	broad peak 3200-3550 cm <sup>-1</sup>		
b. C <sub>15</sub> H <sub>14</sub> O	singlet, δ2.40 (3H) singlet, δ5.08 (1H) multiplet, δ7.25 (10H)	strong peak 1720 cm <sup>-1</sup>		
c. C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	singlet, δ3.25 (6H) singlet, δ3.45 (4H)			
d. C <sub>8</sub> H <sub>9</sub> Br	doublet, δ2.00 (3H) quartet, δ5.15 (1H) multiplet, δ7.35 (5H)			
e. C <sub>3</sub> H <sub>5</sub> Cl <sub>3</sub>	singlet, δ2.20 (3H) singlet, δ4.02 (2H)			
f. C <sub>4</sub> H <sub>9</sub> Br	doublet, δ1.04 (6H) multiplet, δ1.95 (1H) doublet, δ3.33 (2H)			
g. C <sub>10</sub> H <sub>12</sub> <i>**Is this an alkene or not? Note δ values!</i>	multiplet, δ0.65 (2H) multiplet, δ0.81 (2H) singlet, δ1.37 (3H) multiplet, δ7.17 (5H)			
h. C <sub>9</sub> H <sub>11</sub> Br	messy quintet, δ2.15 (2H) triplet, δ2.75 (2H) triplet, δ3.38 (2H) multiplet, δ7.22 (5H)			

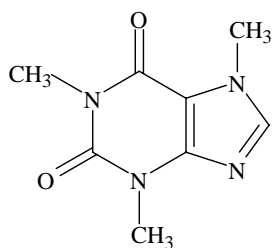
3. Give a molecular structure for  $C_{10}H_{14}$  that is consistent with the IR,  $^1H$ -NMR and  $^{13}C$ -NMR spectra below. *Hints: start with the  $^1H$  spectrum. Since no numbers of H are associated with peaks, you have to estimate. Begin with the smallest signal, which is probably caused by one H. If all of its little spikes were piled one on top of the other, about how high would the resulting single line be? By what factor is the neighboring singlet higher? How many H does it represent? Continue this procedure to estimate the number of H causing each signal. Don't forget that you know the molecular formula (above). Many of the other spectra in this exercise can be approached the same way. The  $^{13}C$  spectrum can be used to guess connectivity to benzene rings – compare number of unique carbons in your structure to the number of lines in the  $^{13}C$  spectrum. Consider each mark as a single line unless specifically noted otherwise.*



(The  $^{13}C$  spectrum below has 7 lines.)



4. How many peaks would you expect to find in the proton NMR spectrum of caffeine (structure below)?



5. When dissolved in  $\text{CDCl}_3$ , a compound whose molecular formula is  $\text{C}_4\text{H}_8\text{O}_2$  gives a proton NMR spectrum that consists of a doublet at  $\delta 1.35$ , a singlet at  $\delta 2.15$ , a broad singlet at  $\delta 3.75$  (1H), and a quartet at  $\delta 4.25$  (1H). When  $\text{D}_2\text{O}$  is added, the compound gives a similar proton spectrum except that the signal at  $\delta 3.75$  has disappeared. The infrared spectrum of the compound shows a strong absorption peak near  $1720\text{ cm}^{-1}$ . Propose a structure for the compound and explain why the signal at  $\delta 3.75$  disappears upon addition of  $\text{D}_2\text{O}$ .

6. Propose a structure for a compound with molecular formula  $\text{C}_9\text{H}_{10}$  which decolorizes bromine in carbon tetrachloride and whose proton NMR spectrum consists of the following peaks:

doublet	$\delta 3.1$ (2H)
multiplet	$\delta 4.8$
multiplet	$\delta 5.1$
multiplet	$\delta 5.8$
multiplet	$\delta 7.1$ (5H)

7. After catalytic hydrogenation, a compound whose molecular formula is  $\text{C}_5\text{H}_8$  gave a dimethylcyclopropane as the sole product.

a) Four structures are possible for the compound (ignoring enantiomers). What are they?

b) The hydrogenated product was found to be exclusively *cis*-1,2-dimethylcyclopropane. The  $^1\text{H-NMR}$  spectrum of the compound shows signals at  $\delta 1.04$  and  $\delta 2.22$  which integrate to a ratio of 1 to 3. Which of the possible structures is consistent with all of the above information?

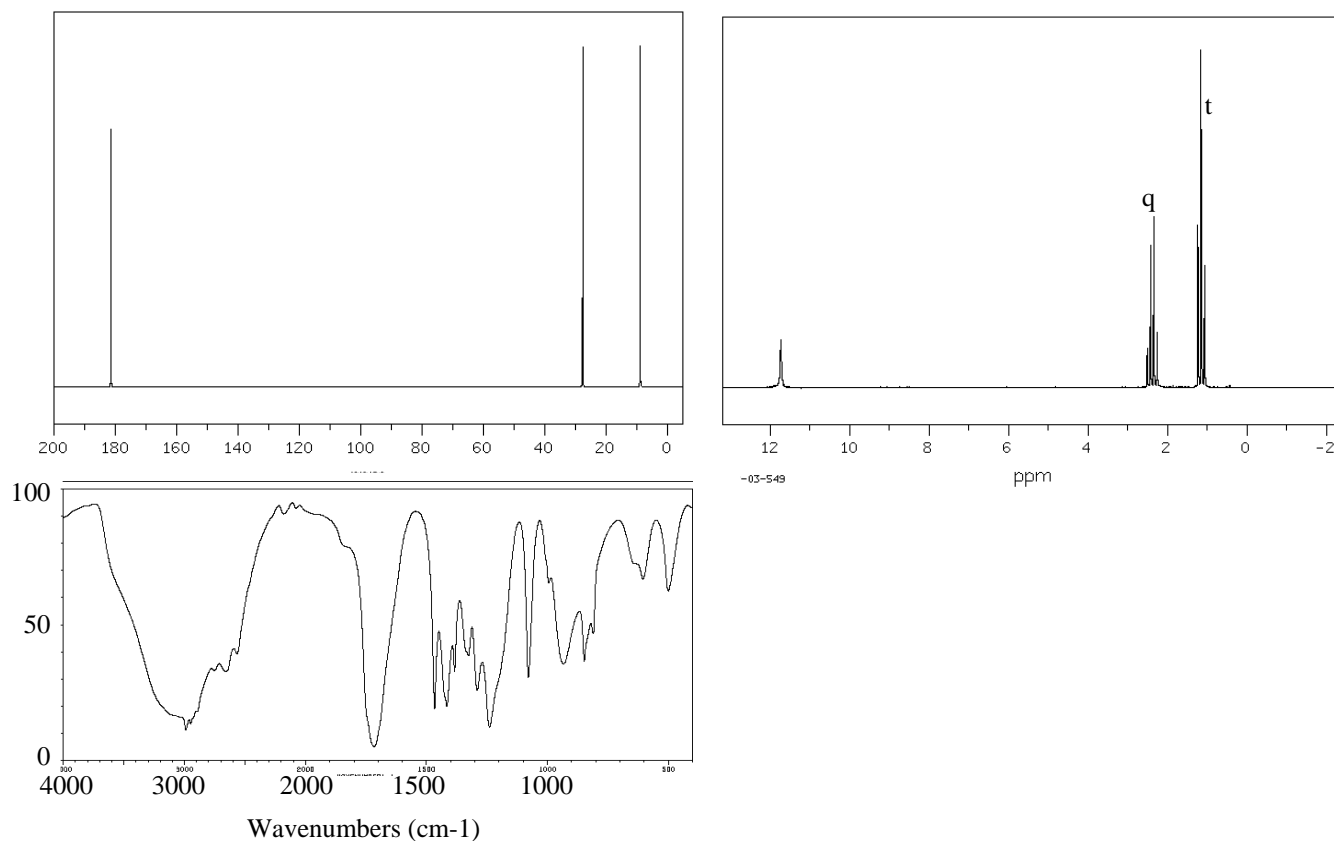
8. The  $^1\text{H}$ -NMR spectrum of bromocyclohexane shows a downfield multiplet (1H) at  $\delta 4.16$ . At  $-75^\circ\text{C}$ , this multiplet separates into two multiplets of unequal area that together integrate to 1H. The multiplets are at  $\delta 3.97$  and  $\delta 4.64$  in the ratio 4.6 to 1.0 relative to each other.

a) How do you account for the separation of the multiplets when temperature is lowered?

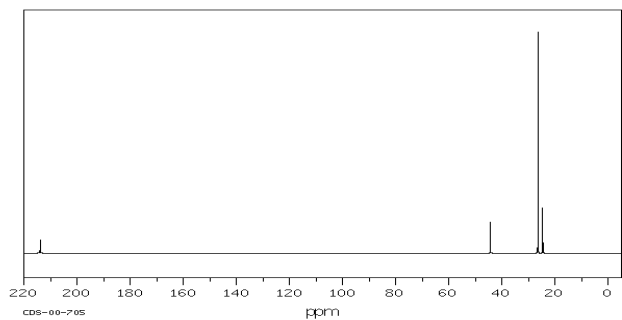
b. Which conformation of the molecule predominates at  $-75^\circ\text{C}$ , and what percentage of all the molecules are in this conformation at a given instant? (hint: use the ratios)

9. Show the structures of the compounds with the following spectra.

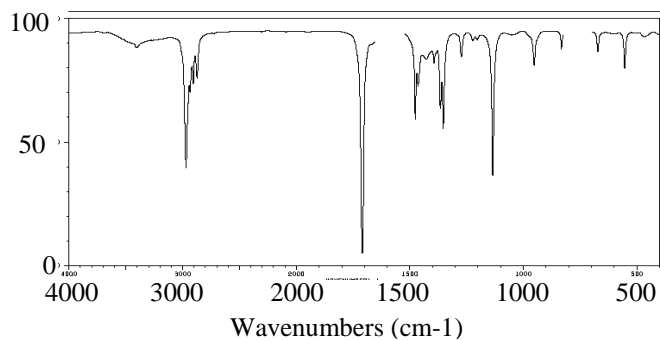
a)  $\text{C}_3\text{H}_6\text{O}_2$  ( $^{13}\text{C}$  has 3 lines)



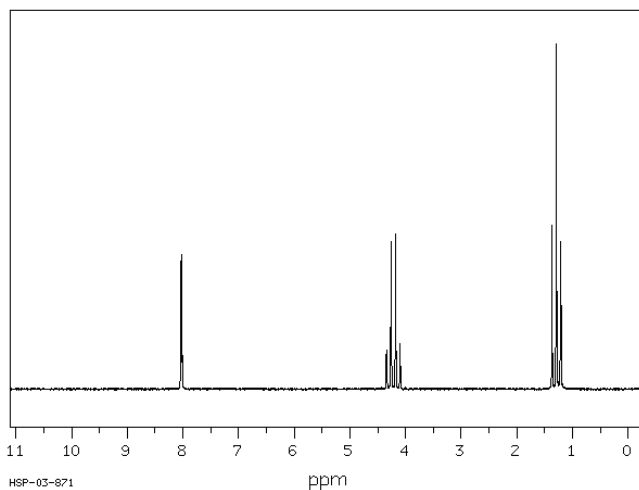
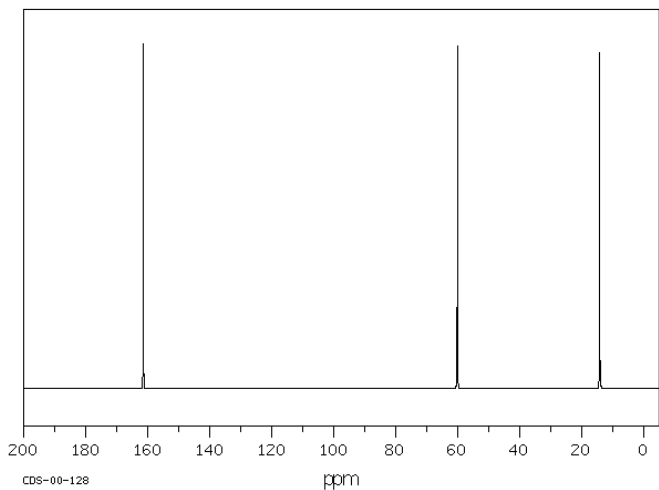
b)  $C_6H_{12}O$  ( $^{13}C$  has 4 lines)



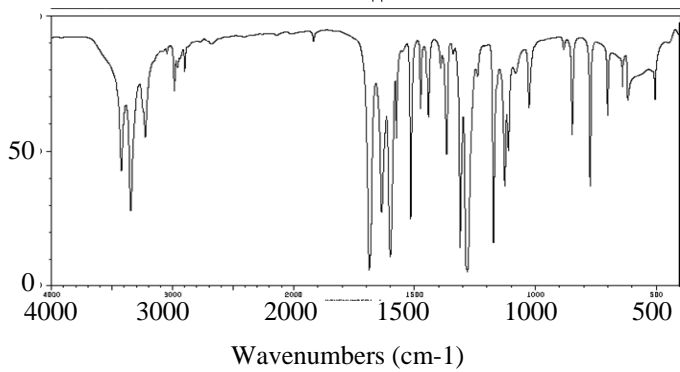
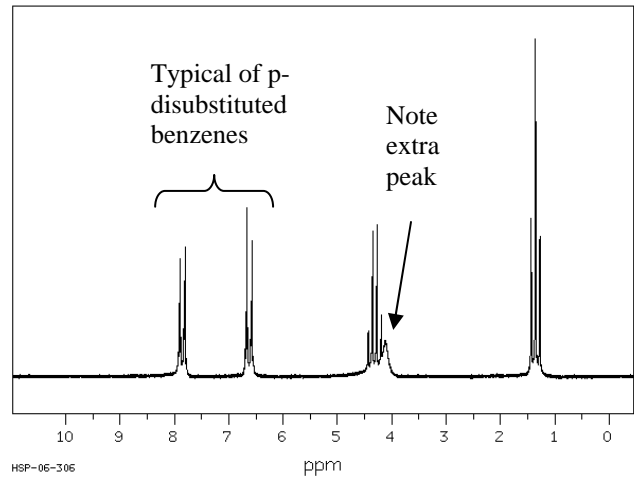
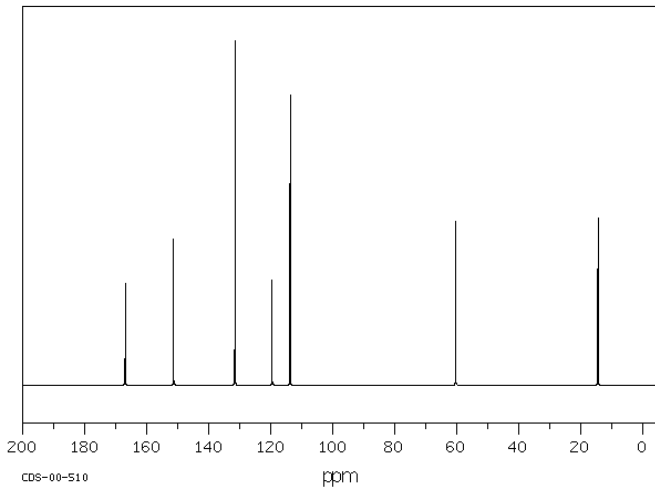
$^1H$  spectrum has a singlet (a) at about 1 ppm and another singlet (b) at about 3.3 ppm. Area ratio of (a)/(b) = 3.



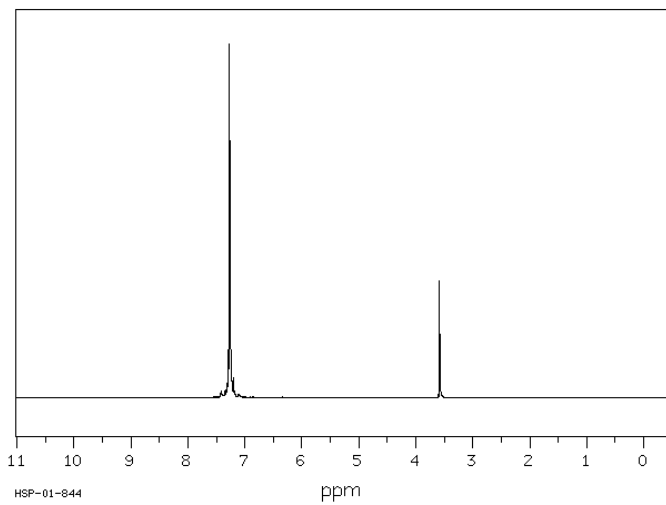
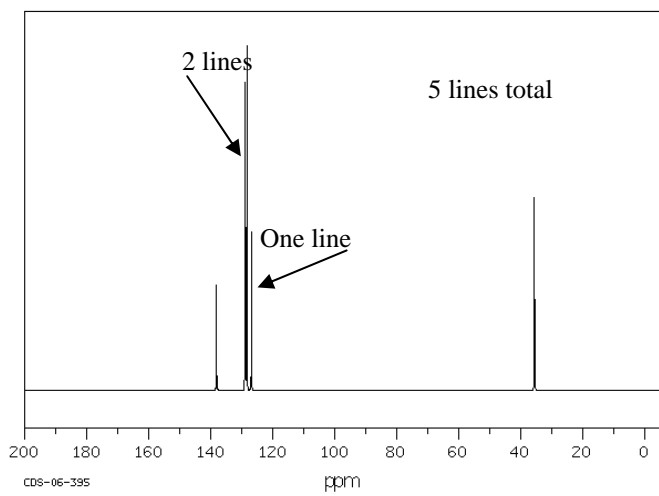
c.  $C_3H_6O_2$  ( $^{13}C$  has 3 lines)



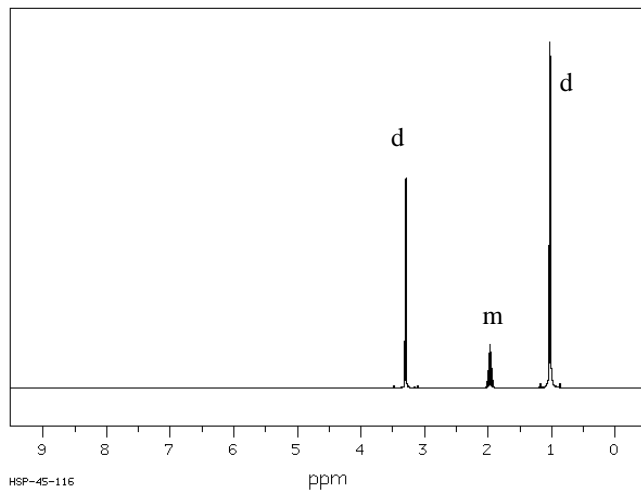
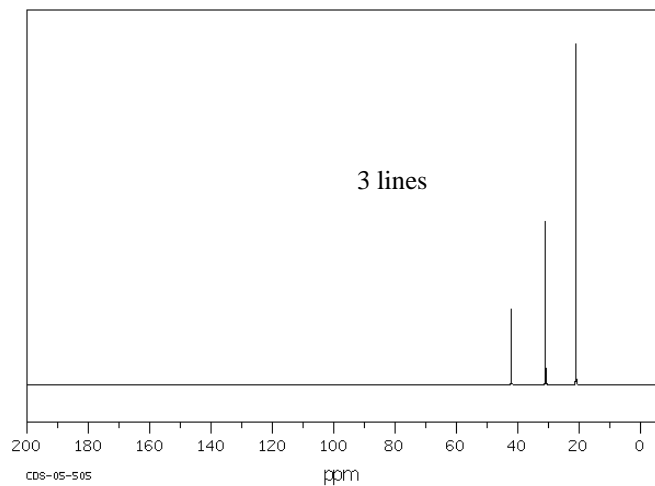
d.  $C_9H_{11}NO_2$  ( $^{13}C$  has 7 lines)



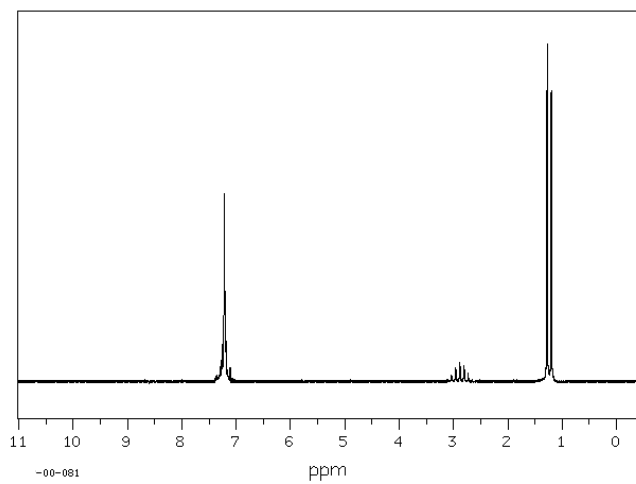
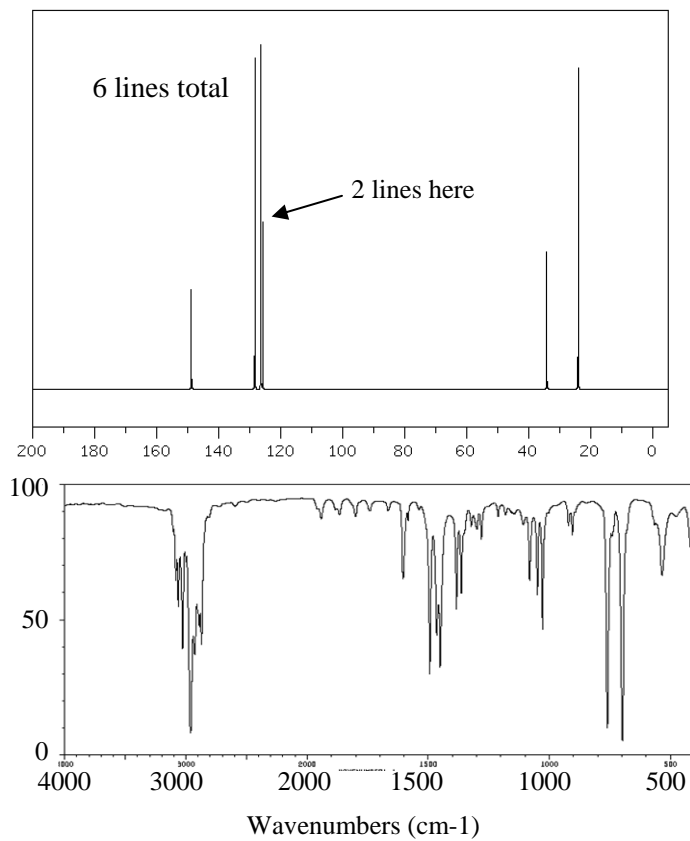
e.  $C_{14}H_{14}S$



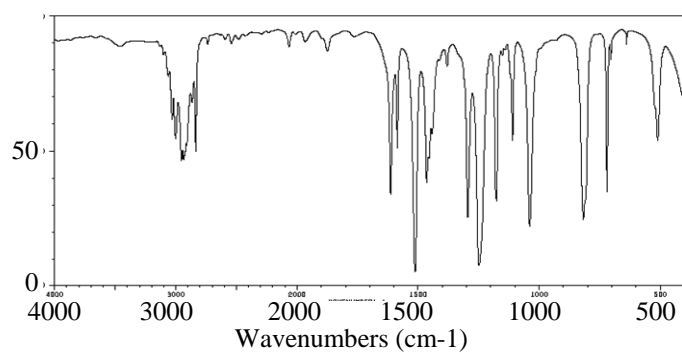
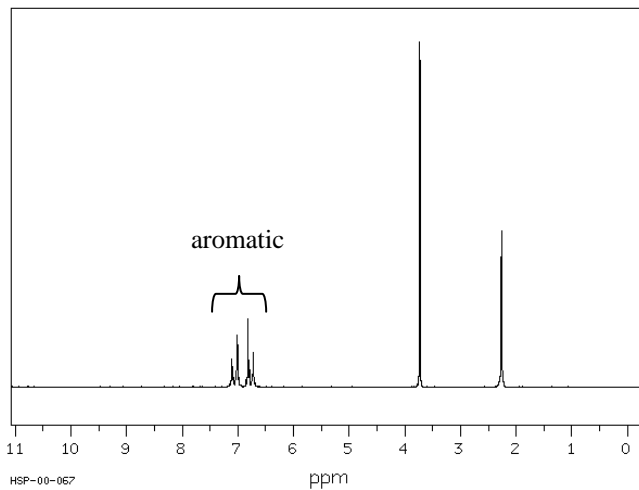
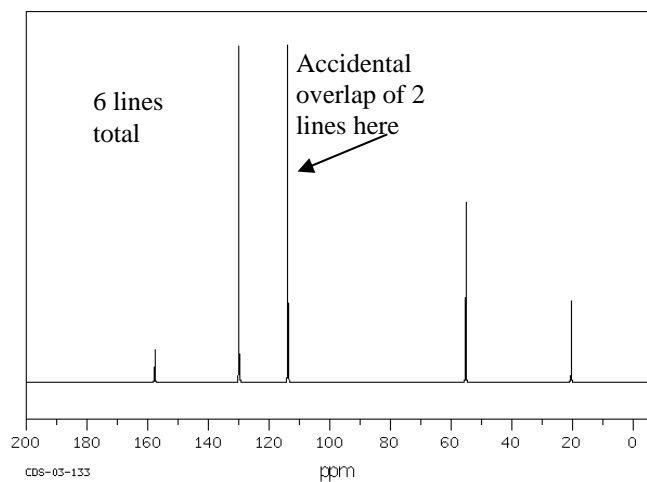
f.  $C_4H_9Br$



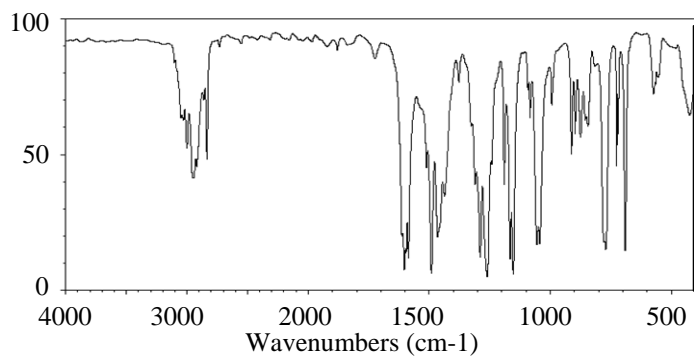
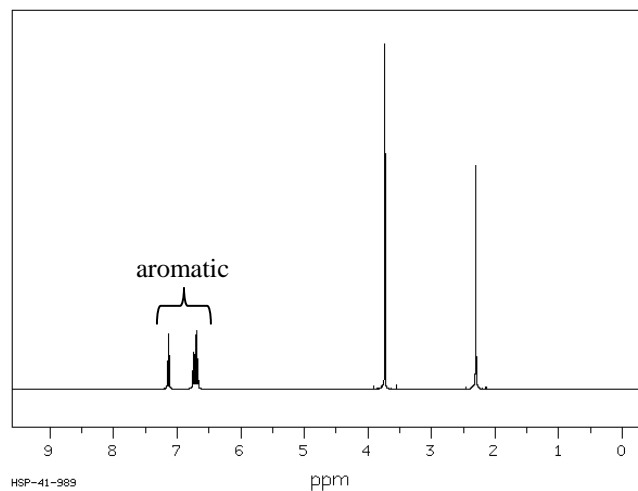
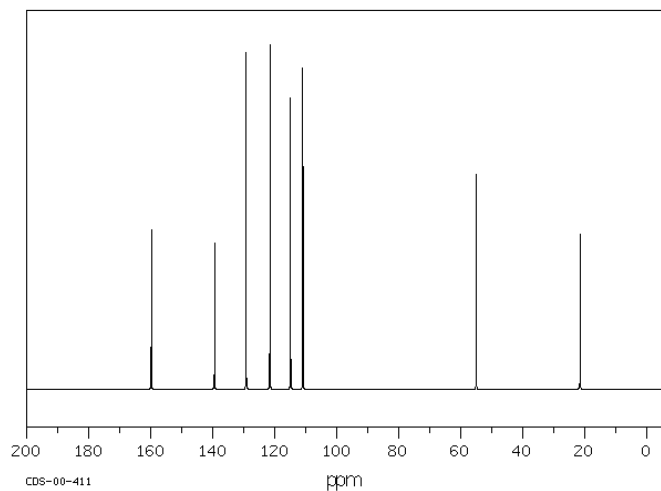
g.  $C_9H_{12}$  ( $^{13}C$  has)



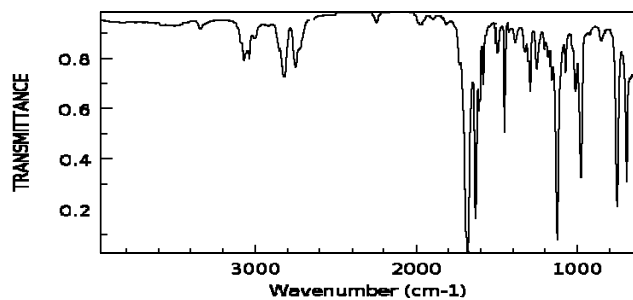
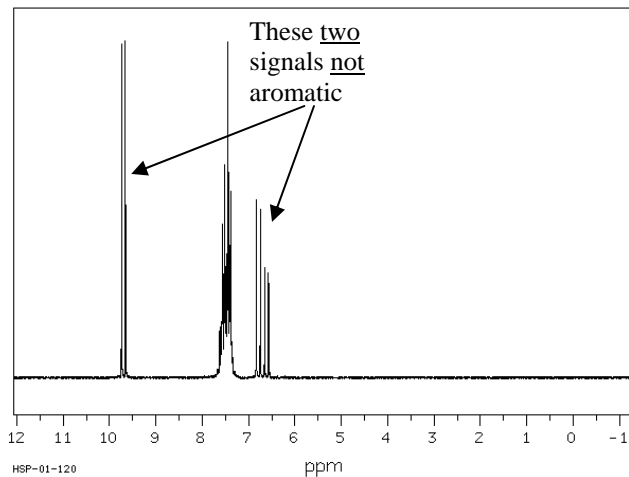
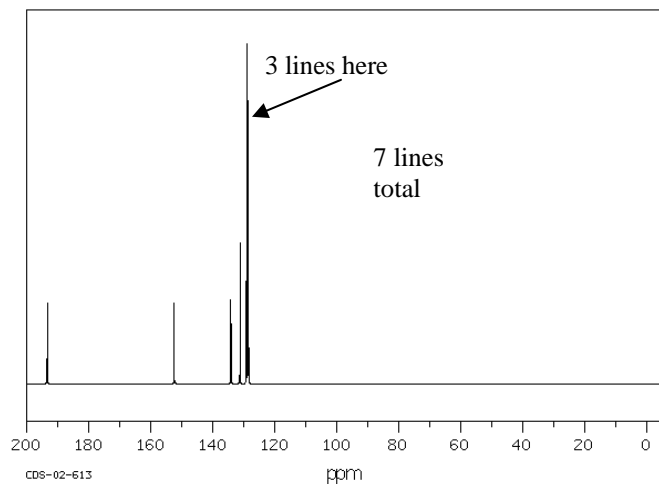
h.  $C_8H_{10}O$



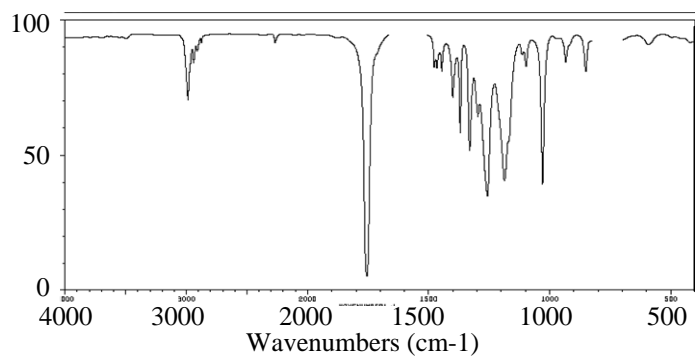
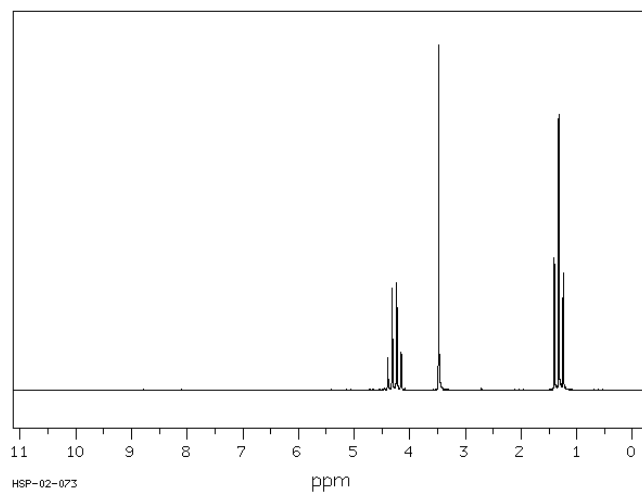
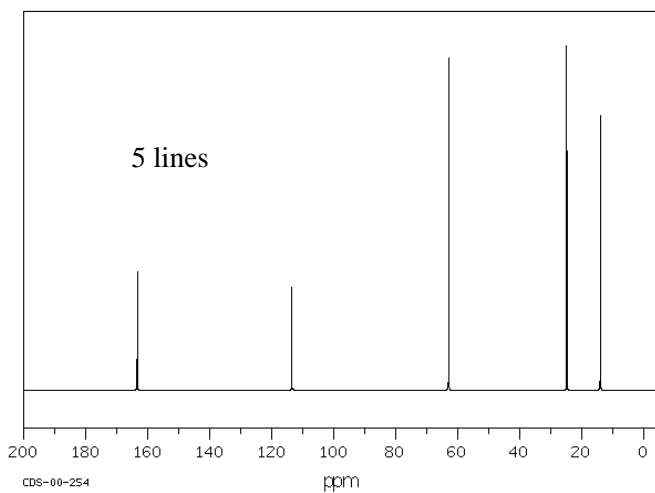
i.  $C_8H_{10}O$  ( $^{13}C$  has 8 lines)



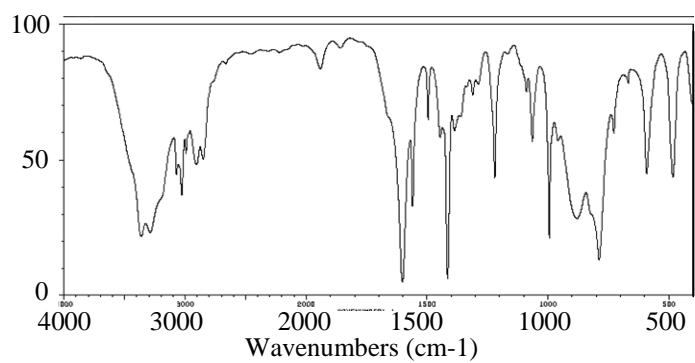
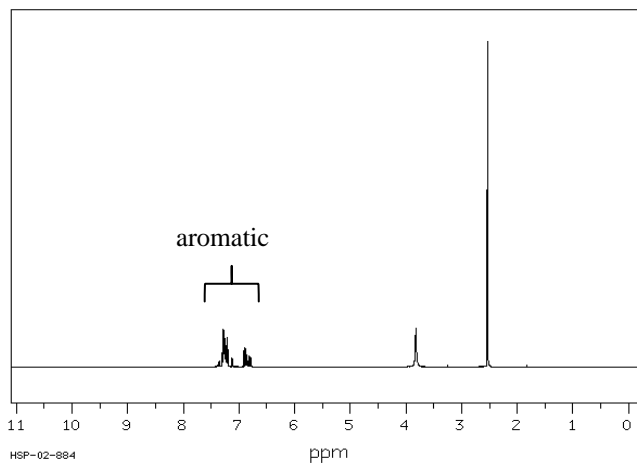
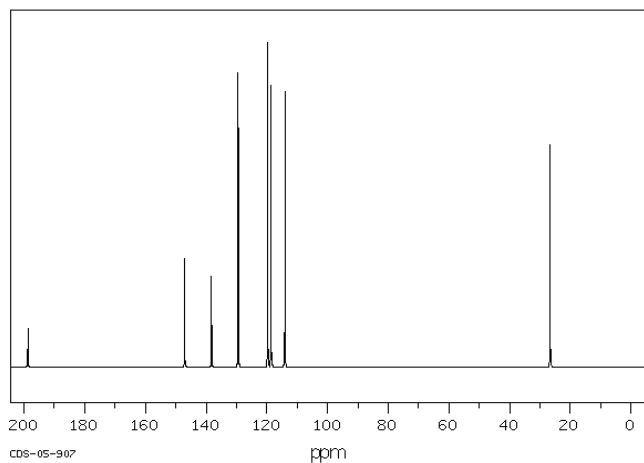
j.  $C_9H_8O$



k.  $C_5H_7NO_2$  (hint: an important clue is in the IR spectrum)



l.  $C_8H_9NO$  ( $^{13}C$  has 8 lines)



m.  $C_{10}H_{10}O$

