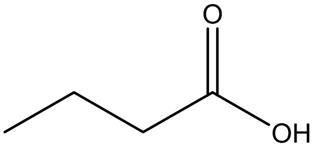
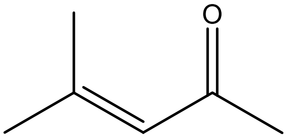
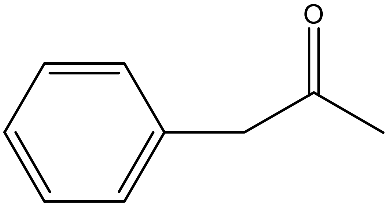
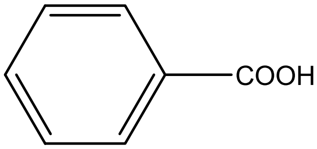
CHEM 303
Organic Chemistry II
Problem Set IV
Chapter 15
Answers

1) The following IR spectra correspond to the four compounds listed below. Match each spectrum with the correct structure and briefly justify your reasoning. (*Hint*: this means list and identify the pertinent peaks.)

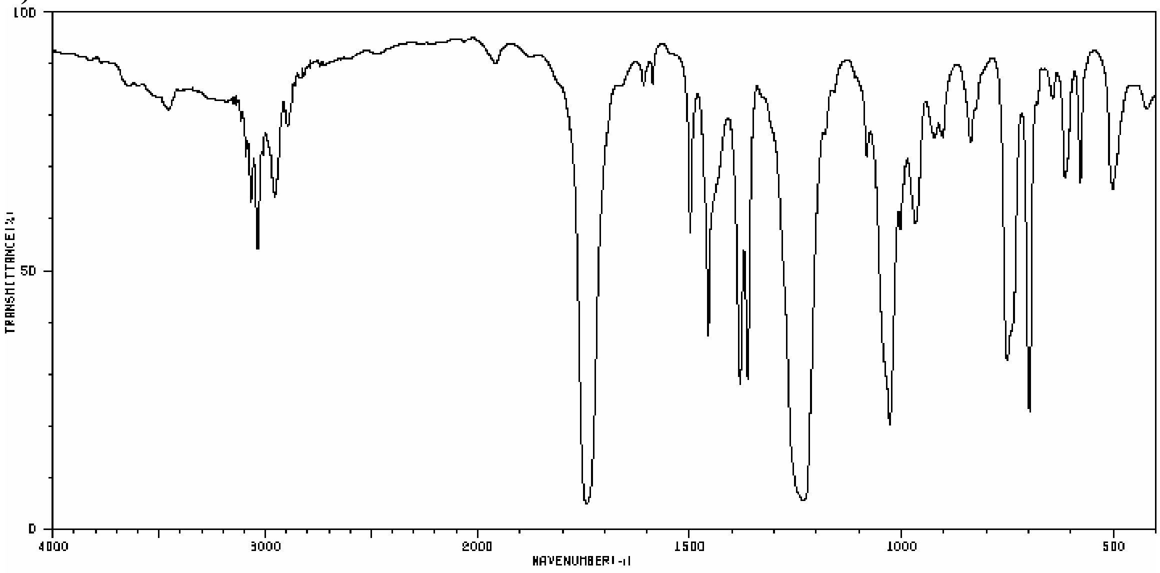




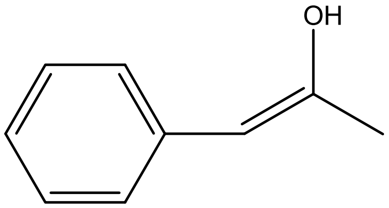




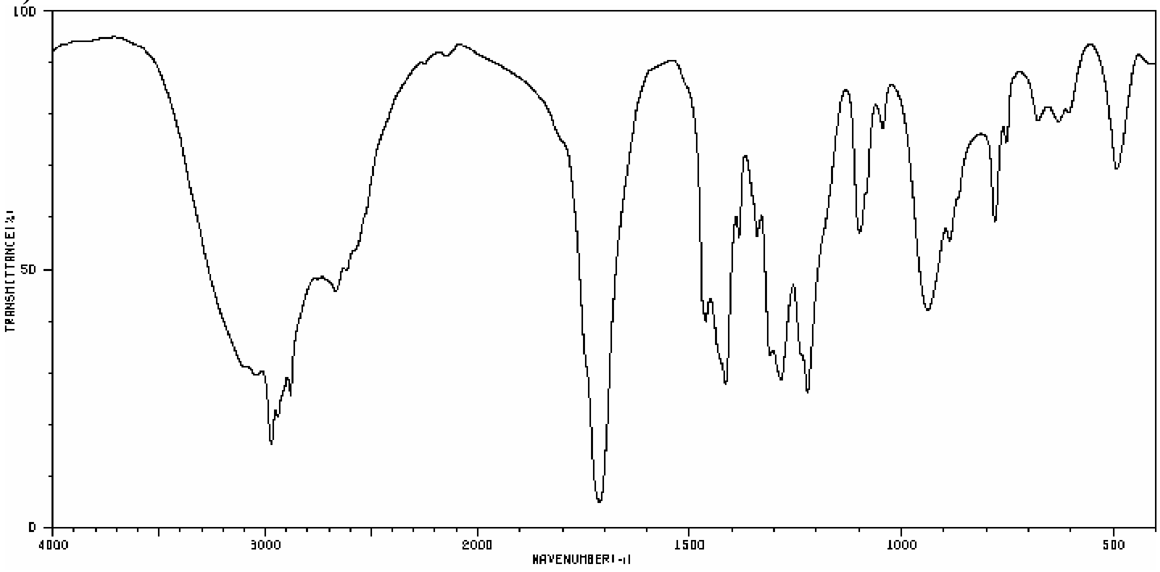
a)



There is not much to go on here, but what we do have is valuable. There is a conspicuous absence of any –OH stretching band (above 3100 cm^{-1}) which would be expected to be quite broad. Thus we have a ketone (given our four possibilities.) Were this ketone conjugated, it would be expected to have the C=O stretch moved to lower wavenumbers (longer wavelength—it's hard to get used to that idea!); since it isn't moved, we must have a non-conjugated ketone. The only ketone we are given which is non-conjugated is **phenylacetone, $PhCH_2C(O)CH_3$.** We can add to this the beginning of a weak –OH bond around the C-H stretching area—this arises from the somewhat more stable enol, shown below. This enol would also be expected to give rise to what may well be a strong C-O band at 1220 cm^{-1}, as well as the band at *ca.* 1030 cm^{-1} or so.

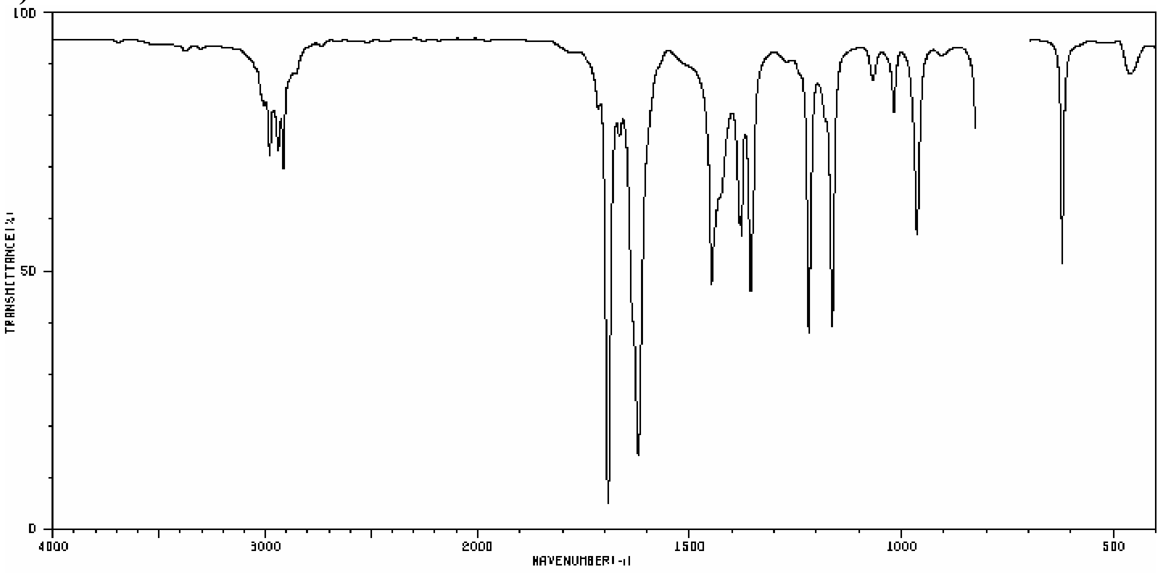


b)

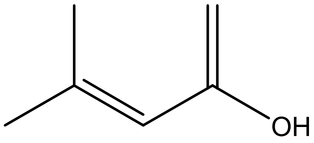


Here we have a large "associated" –OH stretching band in addition to our carbonyl. The carbonyl band is right on for a non-conjugated carbonyl, so I would say here we have **butanoic acid, $CH_3CH_2CH_2COOH$**. These are really the only peaks on which we have to go; it is the absence of other absorptions which makes this assignment possible.

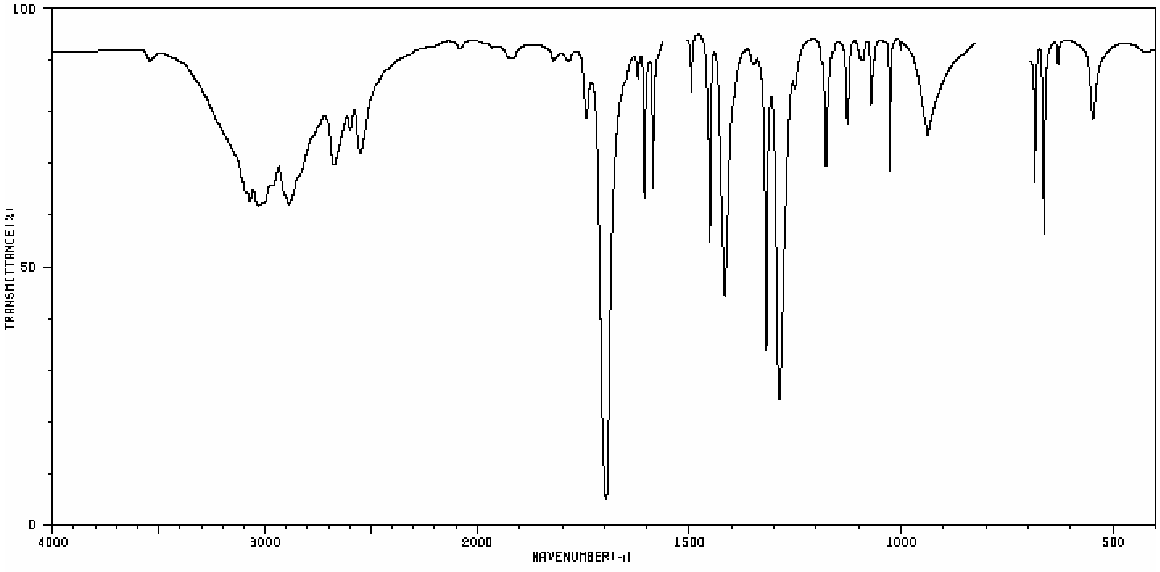
c)



Here, like the first one, there is a conspicuous absence of an –OH stretching mode, so we do not have the other acid possible. That leaves only **4-methyl-3-penten-2-one, $(CH_3)_2CH{=}CHC(O)CH_3$**. The carbonyl is moved to lower wavenumbers by conjugation (*ca.* 1695 cm^{-1}), there is a good C=C stretch around 1600 cm^{-1}, and mostly aliphatic C-H stretching around 3000-2900 cm^{-1}. There may be a bit of a contribution from the conjugated enol form, shown below, but I would suspect not much.

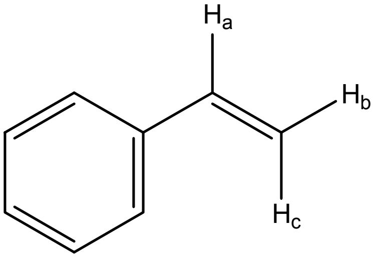


d)

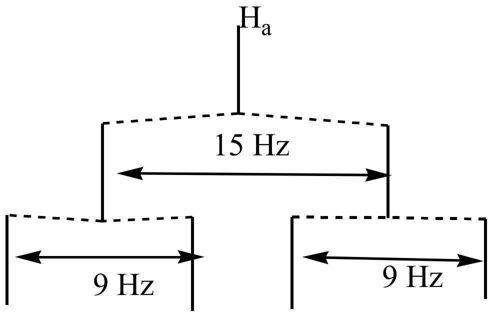


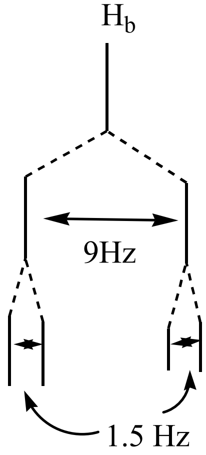
You couldn't ask for a better spectrum of a conjugated, aromatic acid. The carbonyl is moved to smaller wavenumbers (*ca.* 1695 cm^{-1}), and the necessary aromatic ring breathing modes are present (1600, 1450 cm^{-1} [sometimes the 1500 cm^{-1} is absent]), albeit weak. I would have to say that this is **benzoic acid, PhCOOH**.

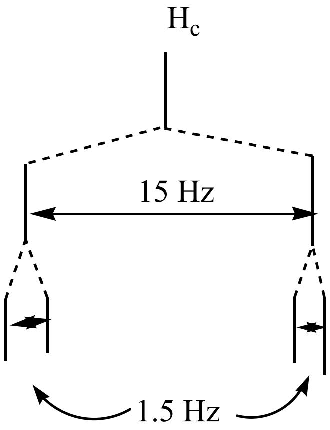
2) Describe the spin-spin splitting pattern expected for protons a, b, and c of the following compound: (*Hint*: build a tree diagram)



Let us collect our coupling constants data. ^3J (trans) = 12-18 Hz; ^3J (cis) = 6-12 Hz; ^2J (gem) = 0-3 Hz. To make our lives easier, let's take the average of each of the ranges given, and use that as our coupling constant. This yields ^3J (trans) = 15 Hz; ^3J (cis) = 9 Hz; ^2J (gem) = 1.5 Hz. Given all that, here is the tree diagram, hopefully somewhat to scale:



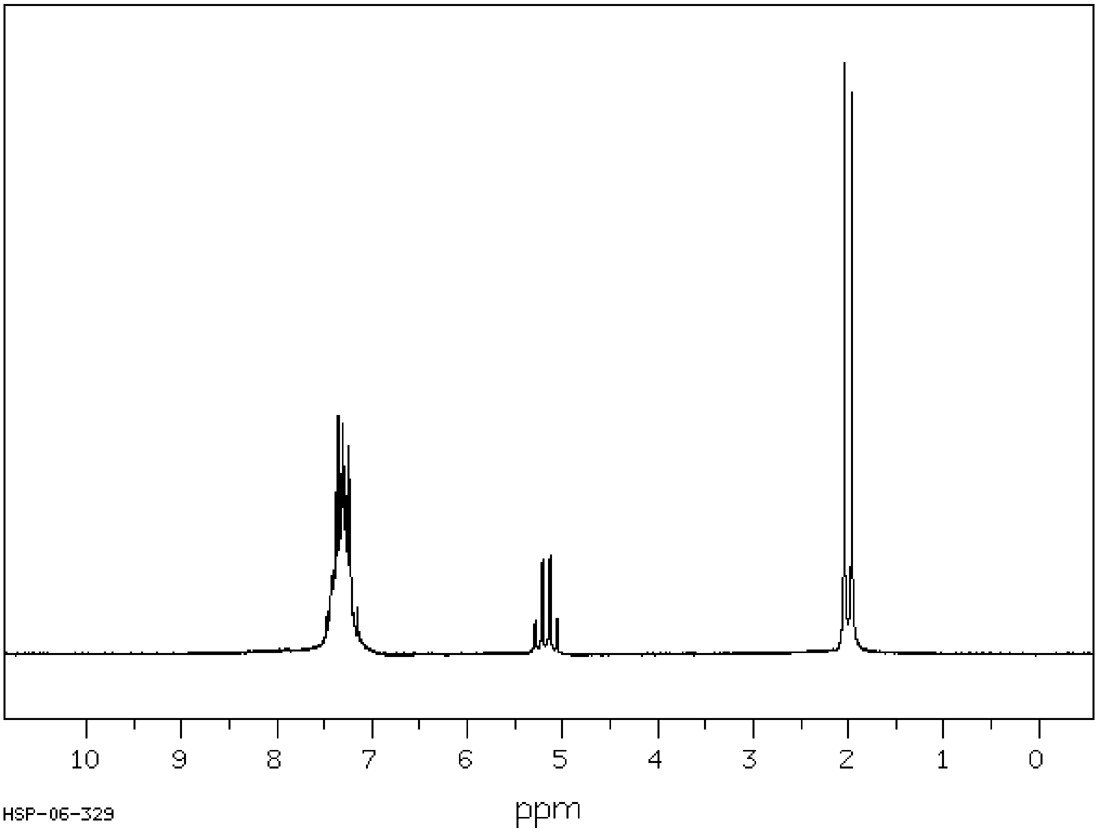




(From a separate source [and you didn't need to do this!!], the chemical shifts anticipated for these hydrogens are: H_a: δ 6.6; H_b: δ5.15; H_c: δ5.62 so depending on the strength of the field, these signals may or may not overlap!) Here is a 90 MHz spectrum of that region, which show no overlap of these signals:

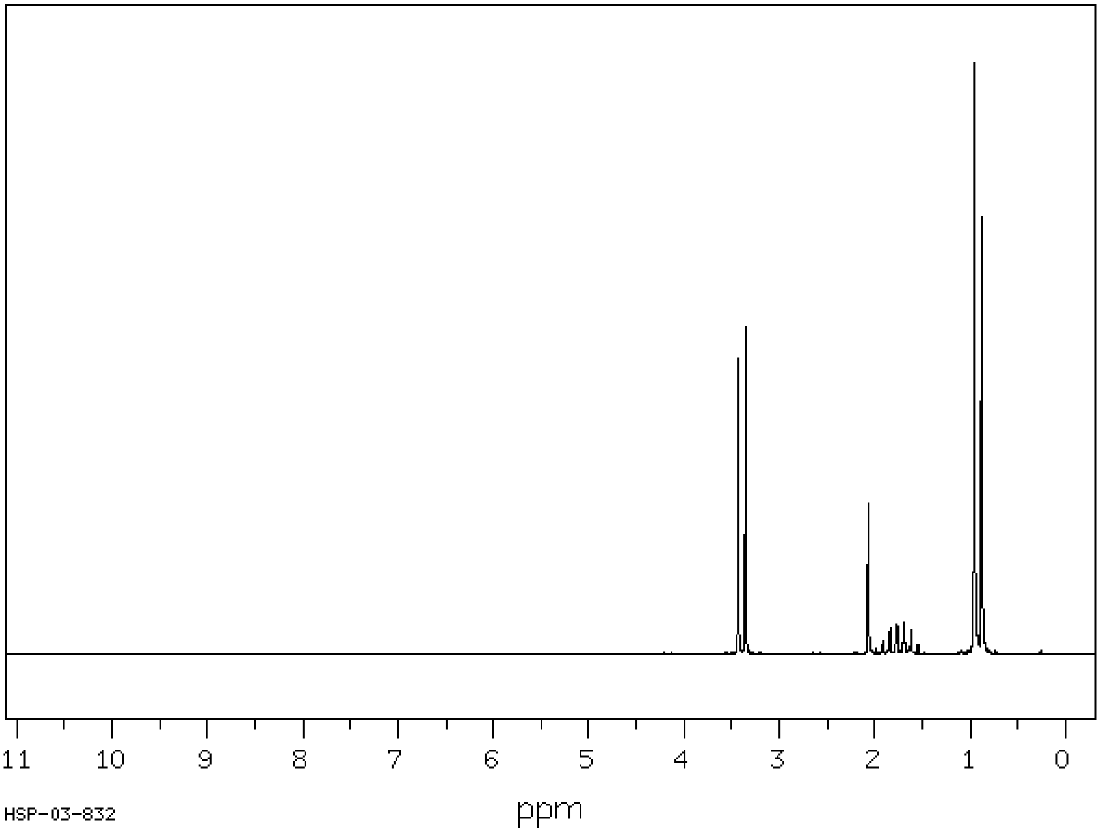
3) Propose structures consistent with each of the following ^{1}H-NMR spectra

a)
C_8H_9Br



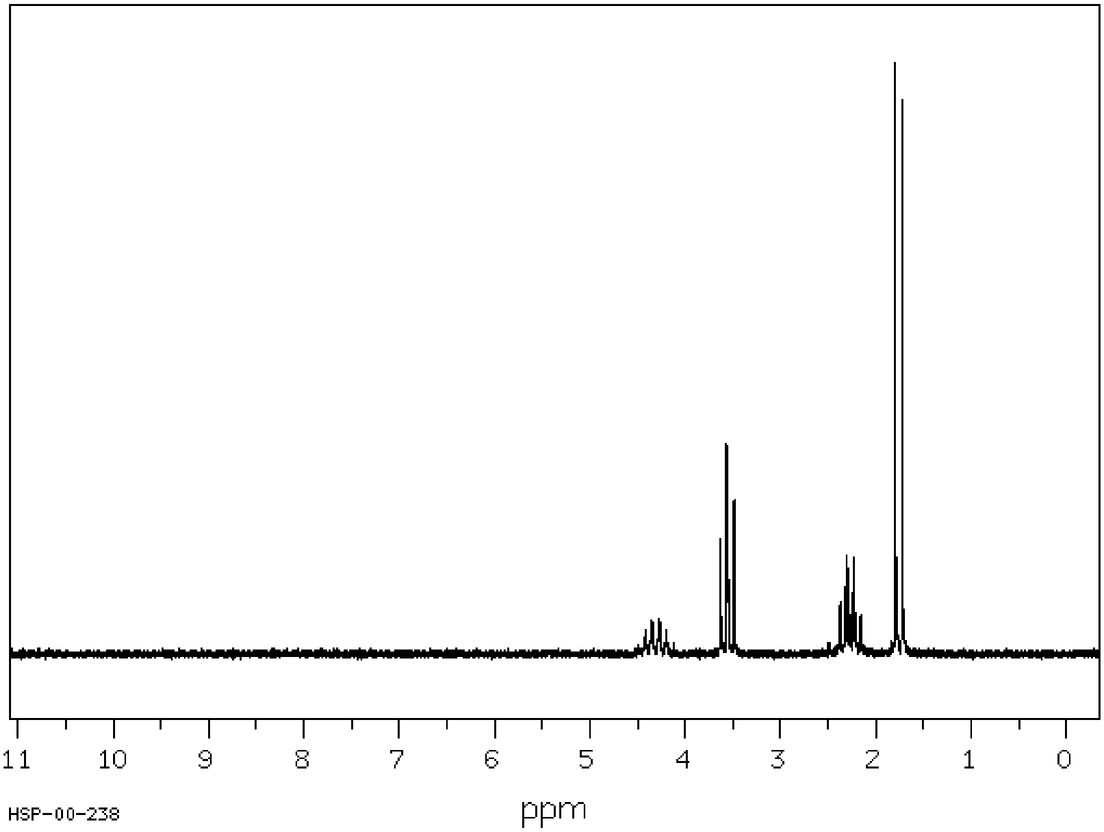
This one is a pretty easy one to start off with. There are the aromatic protons as a multiplet around $\delta7.2$, a nice quartet at $\delta5.2$, and a nice doublet (with the same coupling constant as the quartet) at $\delta1.9$ or so. The aromatic ring uses C_6H_5, leaving C_2H_4Br. The splitting and coupling tell us we have a C**H**-CH_3 and a CH-C**H_3** grouping respectively for the downfield and upfield signals (ignoring the aromatic signals.) The quartet at $\delta5.2$ is quite far downfield—further, in fact, that would be expected for CH's next to a benzene ring alone. To move a signal this far downfield needs something in addition to the benzene ring, like an halogen (which we have). Putting all this together, this is the ^{1}H-NMR for **α-bromoethylbenzene, $PhCHBrCH_3$**.

b)
$C_4H_{10}O$



The signals I see are: a doublet at δ0.9, a mulitplet at δ1.7 (or so), a sharp singlet at δ2.1, and a second doublet at δ3.4. Our formula tells us that we have a saturated compound (an alkane) so, given the oxygen, we must have an *alcohol*. Now the question is: where is the alcohol? The doublet at δ0.9 suggests a $(C\mathbf{H}_3)_2CH$ grouping (using three carbons). A doublet <u>with the same coupling constant</u> at δ3.4 suggests a group next to an electronegative element, such as the oxygen we have here *i.e.* something like $CHC\mathbf{H}_nOH$. Since we are saturated, and have accounted for 8 of our 10 hydrogens, we must have a methylene group here, and the compound is **isobutanol, $(CH_3)_2CHCH_2OH$**. The –O**H** gives rise to the sharp singlet at δ2.0. (Remember what was said about the alcohol proton being variable, and that a scrupulously dry sample (or one that just didn't dissolve water to begin with) would give a nice clean OH signal.

c)
$C_4H_8Br_2$



Again, our formula tells us we are saturated, and therefore we have some sort of dibromoalkane. I see a doublet at δ1.5, a multiplet at δ2.25 or so, a fairly clean triplet at δ3.5, and what might be a septet (not sure) at δ4.4. Let's take things in order. The most upfield doublet is probably a methyl group next to a methine bearing an electronegative element (like bromine) or C**H_3**CHBr; the multiplet next downfield may well be a methylene flanked by two different carbon groups bearing electronegative substituents *i.e.* $BrCH_nC\mathbf{H_2}CHBr$. The next downfield triplet could well be a the $BrCH_n$ group shown just before, and the furthest downfield the CHBr group. Putting everything together, I believe we have here the ^{1}H-NMR spectrum of **1,3-dibromobutane, $BrCH_2CH_2CHBrCH_3$**.

4) On the basis of the ^{1}H-NMR and IR data provided, propose consistent structures for each of the following compounds. (Note that s = singlet, d = doublet, t = triplet, q = quartet)

a) C_6H_6ClN

^{1}H-NMR: δ 3.60 (s, 2H), 6.57 (d, 2H), 7.05 (d. 2H
IR: 3400 (broad), 3250 (broad), 1590, 820 cm^{-1}

This one is fairly straightforward. The IR data strongly suggest an NH_2 group, (3400, 3250 cm^{-1}, both broad), plus an aromatic ring (1590 cm^{-1}—first part of the "1600, 1500, 1450 cm^{-1}" combination for an aromatic ring.) The NMR data confirms all of this (N**H_2** at δ3.6, C_6**H_4** at δ6.57 and 7.05) plus gives us a clue as to the substitution pattern. Two aromatic peaks split into doublet suggest two unique sets of hydrogens; the only substitution pattern which would give us this is *para*, so we have here data consistent with ***p*-chloroaniline, 4-$ClC_6H_4NH_2$**.

b) $C_2H_3Cl_3$

^{1}H-NMR: δ 3.95 (d, 2H), 5.77 (t, 1H)
IR: 2950, and several peaks below 850 cm^{-1}

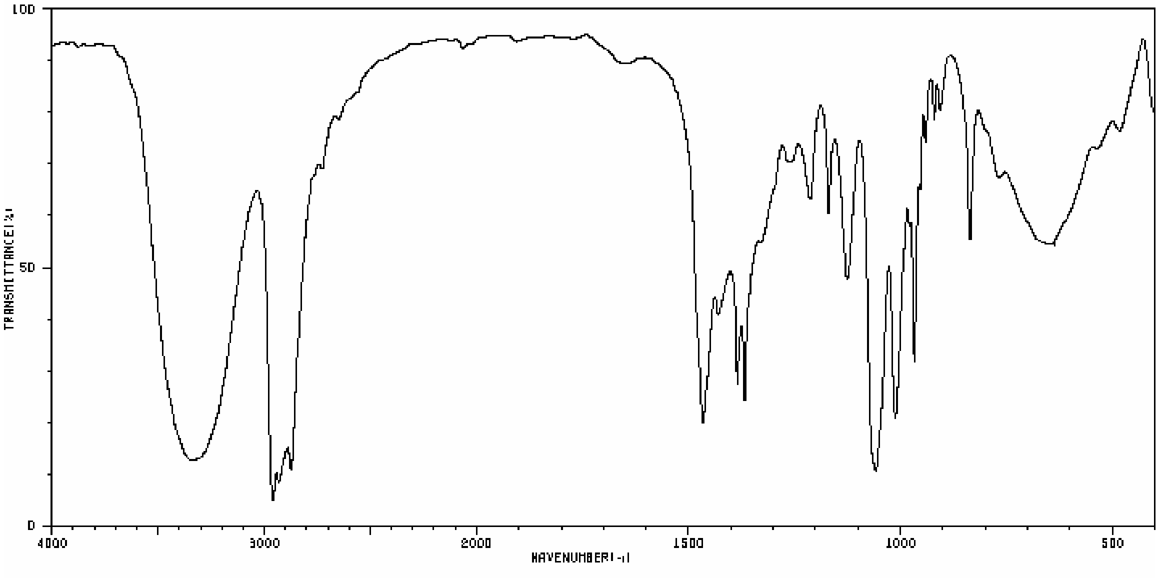
There isn't much here, but we can make a good assignment anyway. The IR data is pretty non-descript, and tells us what we kinda already knew—we have a polychlorinated alkane. The pattern of the NMR signals gives our biggest clue to our structure. We have one hydrogen strongly deshielded and next to two equivalent hydrogens, plus two equivalent hydrogens next to a single hydrogen. Given our formula, the only structure which fits is **1,1,2-trichloroethane, Cl_2CHCH_2Cl**.

c) C_3H_7ClO

^{1}H-NMR: δ 2.00 (pentet, 2H), 2.80 (s, 1H), 3.70 (t, 2H), 3.80 (t, 2H)
IR: 3200 (broad), and several peaks below 850 cm^{-1}

Starting with the IR data, we have an chloroalkyl alcohol. (The 3200 cm^{-1} peak which is broad tells us that.) In the NMR, a pentet arises from 4 equivalent adjacent hydrogens,, and we have (nearly so) just that. The signal for this pentet is upfield, so it can't be too near a strongly electronegative center, but could be β to it. The peak at δ2.80 is probably the –OH peak, and everything else is a methylene. Putting all this together, we have data consistent with **3-chloropropanol-1, $ClCH_2CH_2CH_2OH$**.

5) Compound A contains C, H, O, and its molecular weight was found to be 88 (by MS). The ^{13}C-NMR of A shows four resonances: 23, 25, 42, and 61 ppm, and its ^{1}H-NMR exhibits the following signals: δ 0.9 (d, 6H), 1.5 (six lines, 2H), 1.6 (s, 1H), 1.7 (multiplet, 1H), 3.7 (t, 2H). The IR of A is shown below. Given the spectral information provided, suggest a structure for compound A.



Starting with the IR spectrum, we see that we have an –OH stretch at 3320 cm^{-1}, complemented by a C-O stretch around 1050 cm^{-1}. Also a bunch of aliphatic C-H stretching modes between 2850 and 2970 cm^{-1}. That's about it for the IR.

Given at least one oxygen, our CH combination has to make up 72 mass units. This mass is exactly 6 carbons, which we know is impossible (we have an –OH, remember?) so let's try 5 carbons. That gives us 60 mass units in carbon, with 12 left over for hydrogen, which just perfectly fits a $C_5H_{12}O$, or a saturated alkyl alcohol.

Now to the NMR data. The ^{13}C tells us we have four distinct types of carbon, which, coupled with a 6H doublet at δ0.9 ppm, suggests a *gem*-dimethyl compound (the 1H multiplet helps confirm this fact). We now know we have $(CH_3)_2CH$, and –OH. The downfield triplet at δ3.7 fits with $–CH_2OH$. These fragments account for 4 of our 5 carbons; all that's left is a CH_2 group, and we are done. These spectral data correspond quite well with **3-methyl-1-butanol, $(CH_3)_2CHCH_2CH_2OH$**.