You are allowed to have scratch paper and a simple model set. You do not need a calculator.

Read each question carefully so that you answer properly.

Please have your ID visible on the adjacent seat.

Make sure answers are clear to receive maximum credit.

In cases where you are asked to answer only part of the problems, answering more will not count as extra credit. However, your best answers will be counted.

Do not second-guess yourself.
1. (20 points) The following MS and IR are to be used to solve this problem. Values in parentheses are the relative intensities. 4 pts for each answer.

1(a) What is the molecular mass of this compound (the molecular ion)?

On this type of problem, I will only give MS where you can find the molecular ion: you should choose the left-most (the one with all the base isotope masses) and usually largest peak within the highest mass cluster. In real life, this is not necessarily true. So you should be prepared in other types of problems to explain why the molecular ion is not visible, or is weaker, relative to other peaks.

Molecular ion is 171. Beware!!! The mass of the compound that you would calculate is actually 172 (the 171 is for one $^{79}$Br, the 173 peak is for this compound with one $^{81}$Br). To calculate the mass of the compound, you use a mass of 80 for "Br" because that is the average mass of all bromine.

1(b) What heteroatoms are present and state how you know this from the MS?

One bromine is present. Because two peaks of approximately equal height and separated by 2 mass units ($^{79}$Br and $^{81}$Br) within the molecular ion cluster of peaks.

No chlorine, as this would have made [M+2]/[M] ~ 0.33, or this effect would have been additive to the effect already seen if there was Br present.

Odd number of nitrogen atoms present, because the molecular ion has odd mass.

1(c) How many carbons are present? Show calculation. You shouldn’t need a calculator for this one.

$(6.6/100)/0.011 = 6$ carbons present. This one comes out perfect. Prepare to round off numbers if necessary.

1(d) Now you should be able to propose a molecular formula. What is it?

Formula mass is 172. So far you have C$_6$BrN$_n$, where "n" is odd. For $n = 1$, this is 166. For $n = 3$, this is too much, so must be one nitrogen present. This leaves only 6 mass units. Formula must be C$_6$H$_6$BrN.

It would be good at this point to calculate degrees of unsaturation. Expect C$_6$H$_{14}$ for fully saturated hydrocarbon. Subtract one "H" because of "Br", add one "H" because of "N".

$DU = (14-6)/2 = 4$. Immediately think that benzene is possible.

1(e) Draw a structure which is consistent with all the above. Isomers are possible. Don’t worry about that.

Check out the IR. There are no aliphatic C-H stretches, so probably is indeed a benzene. Can see weak stretch at 3191, which is probably sp$^2$ C-H stretch.

Two peaks around 3400, probably primary amine. You can get much more info from the peaks below 1700, to confirm (i.e. C=C stretch, C-N stretch, etc), but at this point, it must be a benzene with a NH$_2$ group and Br attached. Think about what you would expect from $^{13}$C and $^1$H NMR to confirm this, and which isomer it really is!!! Also, how would you confirm it is not the compound on the right.

\[ \text{not} \]
2. (10 points) Please provide a mechanism for the following conversion (ketone to acetal).

$$\text{ketone} \xrightleftharpoons{\text{EtOH, } \text{H}^+} \text{acetal} + \text{H}_2\text{O}$$

See section 16.9 of the textbook.

3. (10 points) Draw in all the protons in the following compound. Label with small letters all of the different types of protons. Next to each different type of proton, write the multiplicity you would expect in a $^1$H NMR spectrum.

Actually would be easier to make a table than to squeeze in the labels for multiplicity. Note that you have a chiral center, and therefore b and c are diastereoptic protons. This does not hold for methyl groups next to a chiral center, so protons “e” are equivalent.

<table>
<thead>
<tr>
<th>Proton</th>
<th>Multiplicity</th>
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<tbody>
<tr>
<td>a</td>
<td>s</td>
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<tr>
<td>b</td>
<td>dd</td>
</tr>
<tr>
<td>c</td>
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<td>d</td>
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<tr>
<td>e</td>
<td>d</td>
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<tr>
<td>f</td>
<td>d</td>
</tr>
</tbody>
</table>
4. (20 points) Match each of the following compounds with the appropriate $^{13}$C NMR spectrum. Write the letter of each compound in the center of the correct spectrum. It will help if you first label all different carbons within each compound. Recall that you cannot trust the intensities of peaks in $^{13}$C NMR. Spectra not all on same scale!

This one could have been solved simply by process of elimination (too easy). The top two spectra are the only ones with signals in the region for carbons within benzene rings or olefins. The top one has only two of these signals, and so must have high symmetry like the para-substituted “A”. The bottom two spectra have to be for “B” and “C”, because they are the ones which have signals in the region for C=O. You can then choose between them based on the number of signals. As for any homework problems, you should make an attempt to label all the peaks, just for practice.
5. (20 points) Match each of the following compounds with the appropriate IR spectrum. **Write the letter of each compound in the lower left corner of the correct spectrum.** One compound will be omitted.

A. \( -\text{COH} \)  
B. \( \text{C} \equiv \text{N} \)  
C. \( -\text{OH} \)  
D. \( -\text{CHO} \)

Again, can be solved very rapidly by process of elimination. Two of the spectra have C=O stretches, and only one of these has the very broad OH stretch of a carboxylic acid. The sharp peak in the top IR spectra is in a region which must be nitrile or alkyne, but too far to the right to be SH. In any case, you only have nitrile to choose from. Done!
6. (20 points) Match each of the following compounds with the appropriate $^1$H NMR spectrum. **Write the letter of each compound in the center of the correct spectrum.** Two compounds will be omitted. It will help if you first label all different protons within each compound and predict multiplicity.

You have to be able to label all different protons, predict multiplicity, and regions of the spectra where they will give rise to signals. Also understand that you may not be able to clearly see predicted multiplicities (e.g., the peak labeled “multi,” instead of the predicted $\text{tq}$ within the spectrum for compound “C”). If resolution is not good enough, or if the spectrum is not first order, then the multiplets are not well-defined. However, you can still distinguish between compounds by chemical shift, number of different signals, and integrations.

Unless an alcohol is ultra-pure and free of acidic or basic impurities, the alcohol proton does not couple cleanly to protons on adjacent atoms. Thus the broad OH proton singlet, and the methine proton is a pentet, not doublet of pentets. Do not confuse with problem #3 where you should just follow the rules for assigning multiplicity.

A  Br
B  Br
C  O
D  OH
E  \( \text{Ph} \) OH