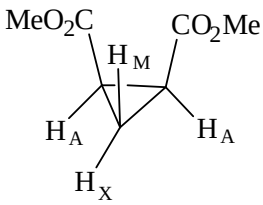
**CHEM 293**
**Sample Final**
**Dr. H.M. Muchall**

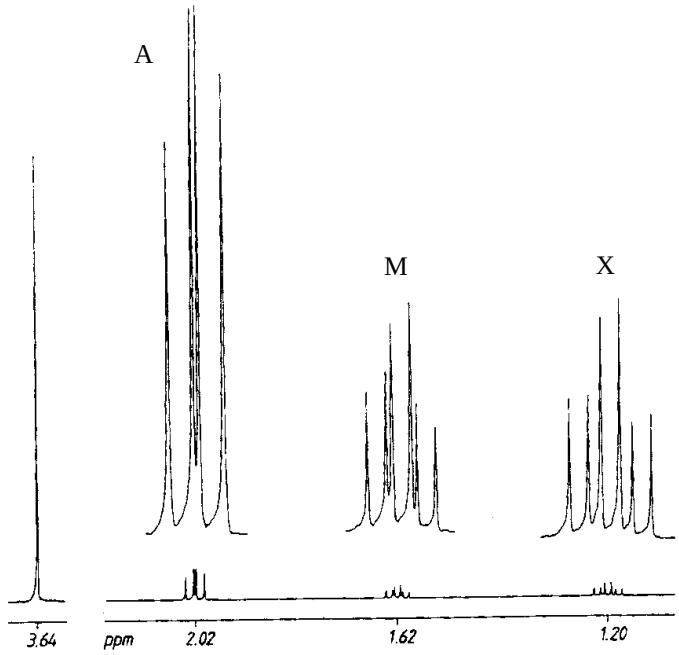
_____
**Name**

***Show all work. Remember: a point a minute! This exam is MUCH longer than the upcoming Final.***

***Textbook and calculator allowed. The textbook can be marked up, but pages must not have been added!***

1. (7.5 points) The following cyclopropane gives rise to an $A_2MX$ pattern in its $^1H$ NMR spectrum (400 MHz).




a) Identify the signals as to their multiplicities (spectroscopic notation).

A: M: X:

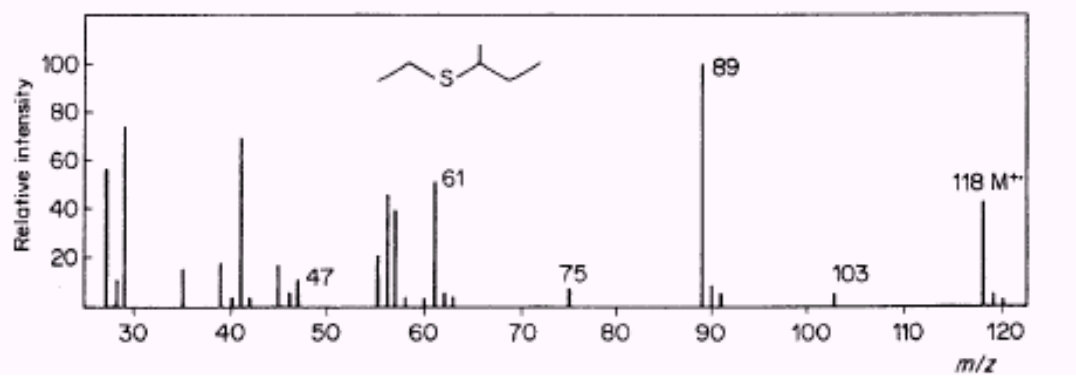
b) Determine the three coupling constants (in Hz) from the enlarged insets (1 ppm = 15.6 cm). Clearly indicate on the spectrum which lines you use.

$J_{AM}$: ____cm, ____Hz $J_{AX}$: ____cm, ____Hz $J_{MX}$: ____cm, ____Hz

c) Draw **accurate** tree diagrams for the A and X signals (10 Hz = 1 cm: use a ruler!).

A: X:

2. For the following mass spectrum,




give the species from the fragmentations below. Make sure you indicate radical cations, cations or radicals where appropriate. Include the masses of all fragments below each fragment. Also include the type of fragmentation where possible.

a) (6.5 points) m/z 118 → m/z 103 → m/z 75 (5 structures total needed here)

b) (5 points) m/z 118 → m/z 103 → m/z 47 (5 structures total needed here)

3. (16 points) Answer the following questions. **Circle** TRUE or FALSE. Give a short explanation with an example to illustrate or clarify or correct the TRUE or FALSE statement.

a) The $^{13}C$ nucleus never couples with the $^{1}H$ nucleus. TRUE/FALSE

b) In $^{1}H$ NMR spectroscopy, at a low enough field, there are no second order spectra. TRUE/FALSE

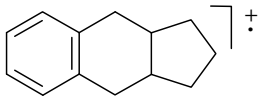
c) The chemical shift information from a proton-coupled and a proton-decoupled $^{13}C$ NMR spectrum is the same. TRUE/FALSE

d) $^{13}C$ NMR spectra are not integrated due to the fast relaxation of all $^{13}C$ nuclei. TRUE/FALSE

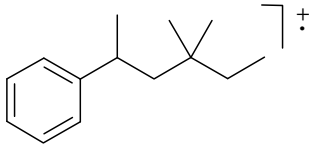
e) An ethyl radical is detected at m/z 29. TRUE/FALSE

f) An increase in conjugation leads to an increase in the energy required for a UV-Vis absorption. TRUE/FALSE

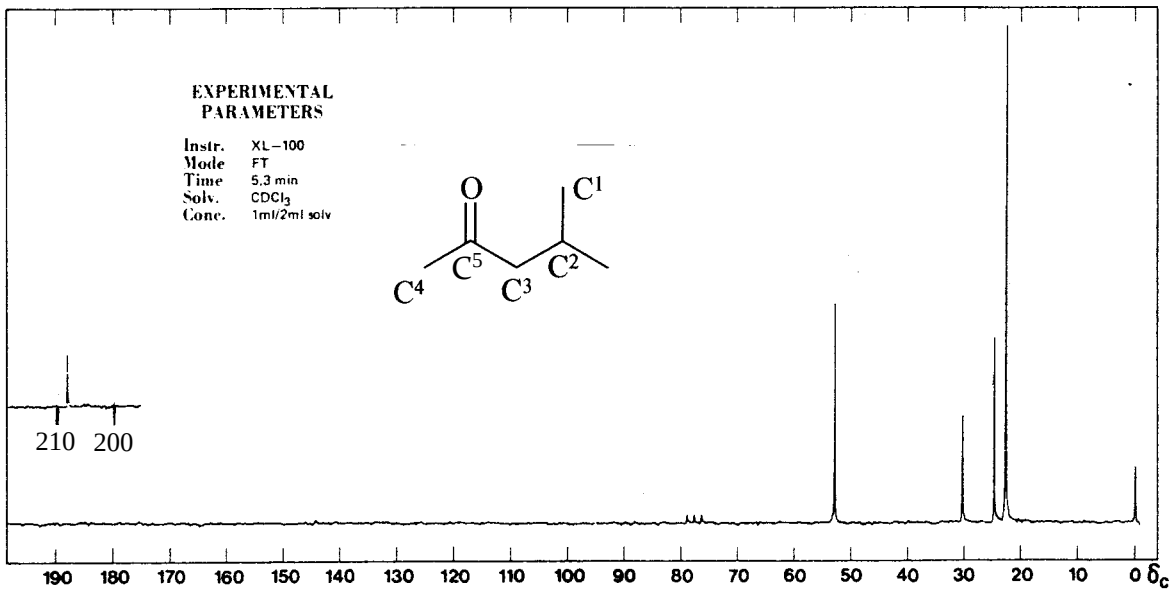
g) The following species fragments in a Retro-Diels-Alder reaction to give a strong signal at m/z 68. TRUE/FALSE



h) The following species undergoes a McLafferty-type rearrangement easily. TRUE/FALSE



4. Given below is the proton-decoupled $^{13}C$ NMR spectrum for the indicated compound.




a) (5 points) Starting with a base value of –2.3 ppm, calculate the $^{13}C$ chemical shift for $C^1$, $C^2$, $C^3$, and $C^4$. Briefly evaluate each for reliability. Give an estimate for $C^5$.

$C^1$:

$C^2$:

$C^3$:

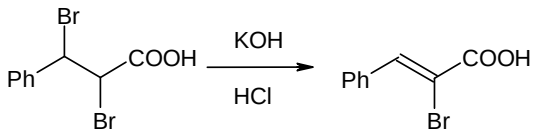
$C^4$:

$C^5$:

b) (2.5 points) With the calculated chemical shifts, on the spectrum above, label **all** signals with the multiplicity you would observe in a proton-coupled $^{13}C$ NMR spectrum.

5. (12 points) Students in an experimental organic chemistry lab ask themselves the following questions and want to gain the answers using the indicated spectroscopic methods. Use the methods indicated for both **reactant and product** and give the **most important change** that you would observe in each set of spectra in order to answer the questions (you will only provide the signal that would give the answer, not the answer itself!). Do not write sentences: supply only the **spectroscopic information** (e.g., ν(C–H) s 2900 $cm^{-1}$; q (7 Hz), 2H, 2.21 ppm). Use calculations (UV-Vis, NMR) where possible.

a) Has the elimination taken place?

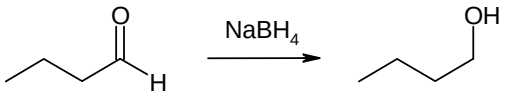



***reactant spectrum:*** ***product spectrum:***

UV-Vis:

$^{1}$H-NMR:

b) Has the reduction taken place?

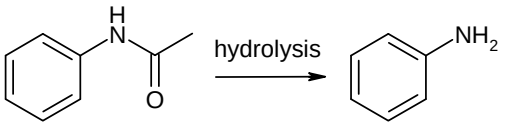



***reactant spectrum:*** ***product spectrum:***

$^{1}$H NMR:

$^{13}$C-NMR
(decoupled):

c) Is the compound in the bottle still the desired amide, or has it become useless because all or some has hydrolyzed?



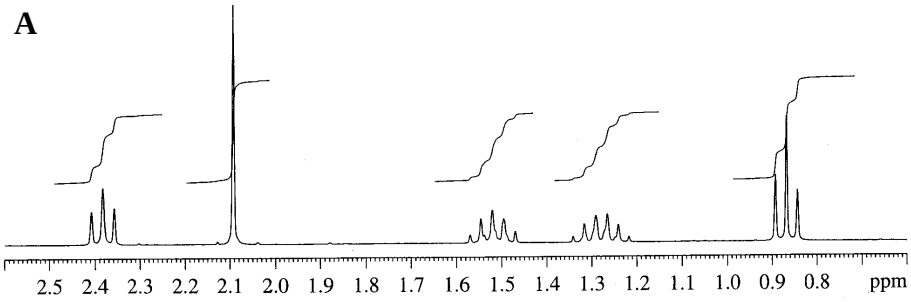

***reactant spectrum:*** ***product spectrum:***

UV-Vis:

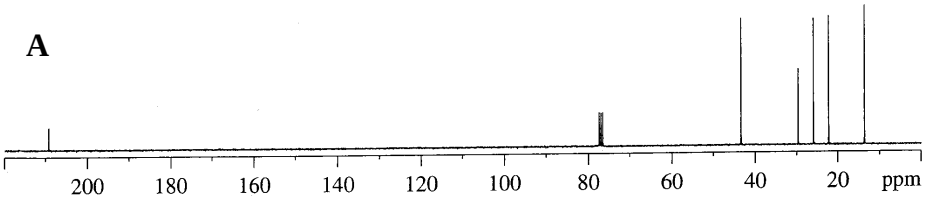
IR:

6. (10 points) The $^{1}H$ and $^{13}C$ NMR spectra of oxygen-containing compounds **A** and **B** (**A** is 100 g/mol, **B** 114 g/mol) are given below. Identify the two compounds. Remember that every signal carries certain information, and it must be labeled with that information. Some signals will give more detailed information than others.

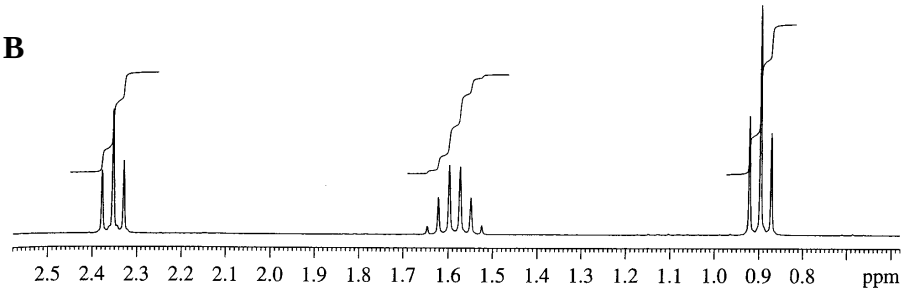
**A**



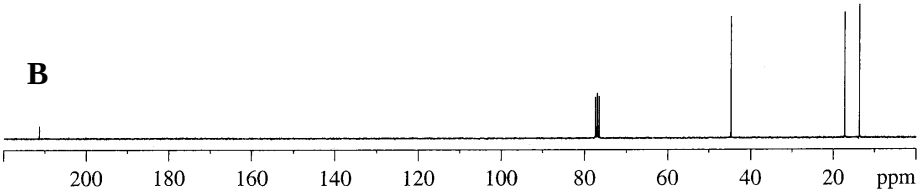

**A**



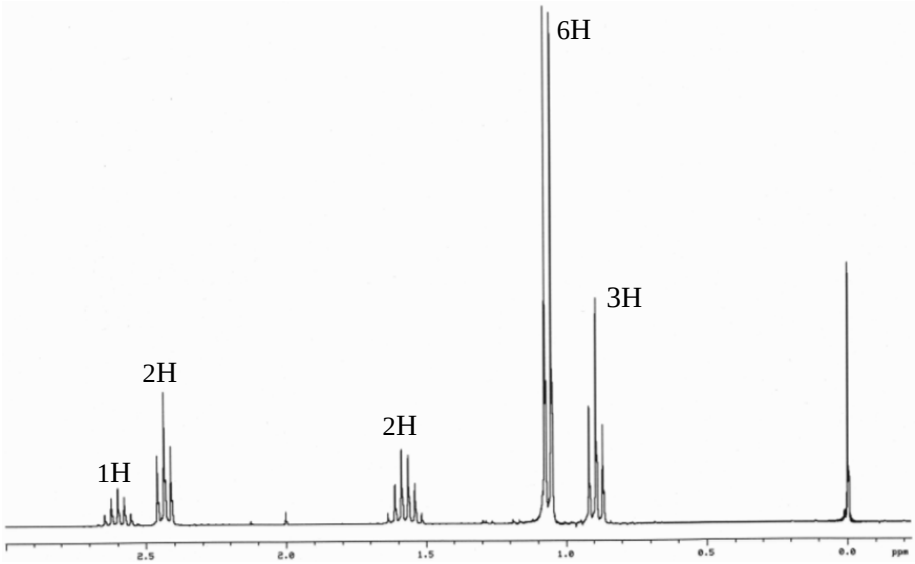

**B**

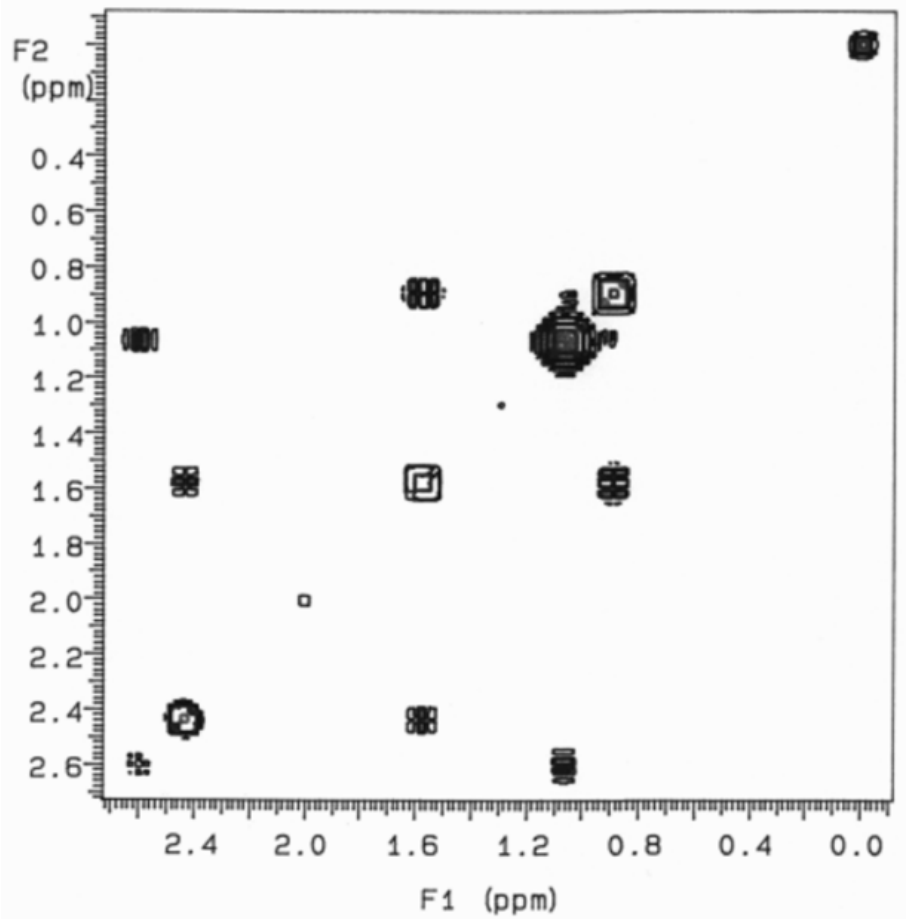



**B**



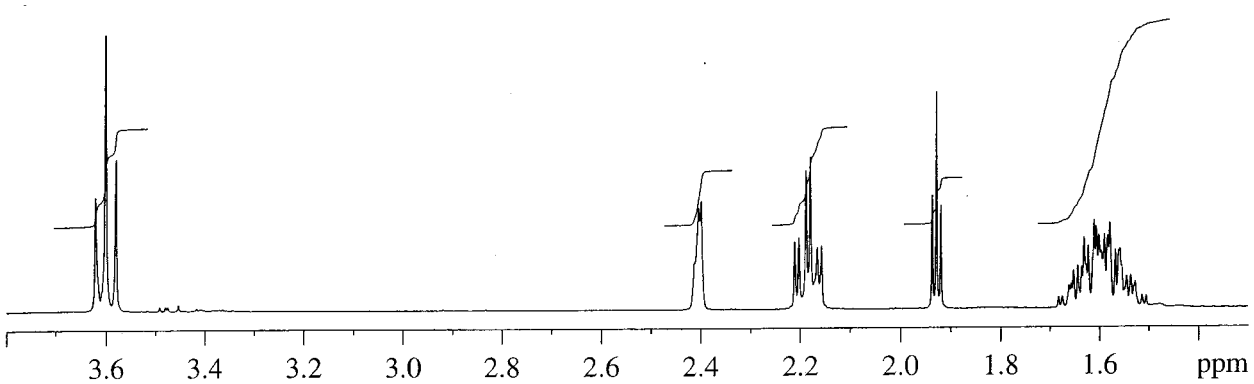
7. (6.5 points) The COSY (H/H correlation) belongs to a ketone. Identify the compound: Perform a graphical analysis, list all correlations, and give the connectivity of the coupling system(s). The $^{1}$H NMR spectrum is provided for integration purposes **only** (do **not** work with the signal multiplicity!).



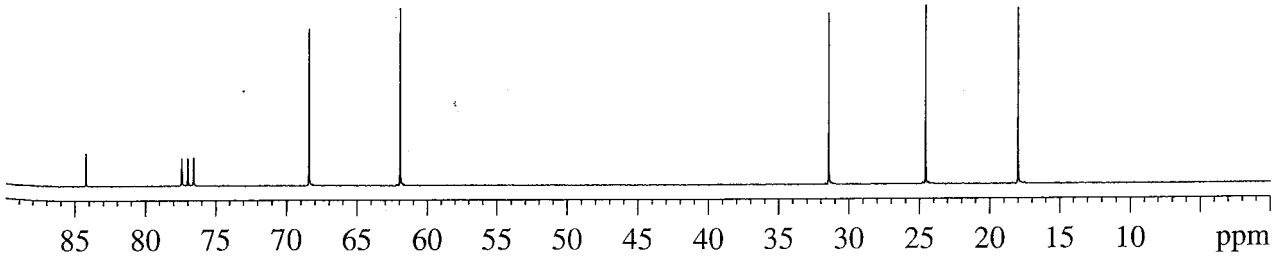



8. (20.5 points) Identify the unknown from its data on pages 8 and 9. Use all the data for your interpretation. Label all pertinent signals (spectroscopic notation!), and include partial structural information gained whenever possible **on the spectra**. Simply writing a, b, c etc. on a proposed structure and labeling spectral signals accordingly will not get you points. Cross-check data where possible (IR versus $^{1}$H NMR results, H-count, C-count, U, etc.). You do not need to calculate chemical shifts.

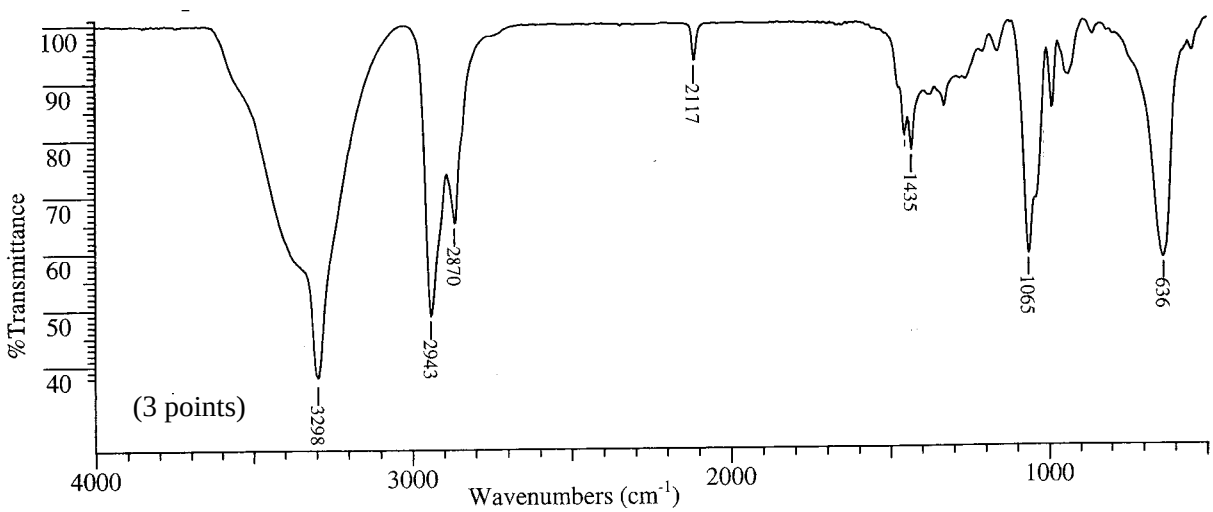
(1 point atom count, 1 point molecular formula, 1 point U, 3 points final structure)

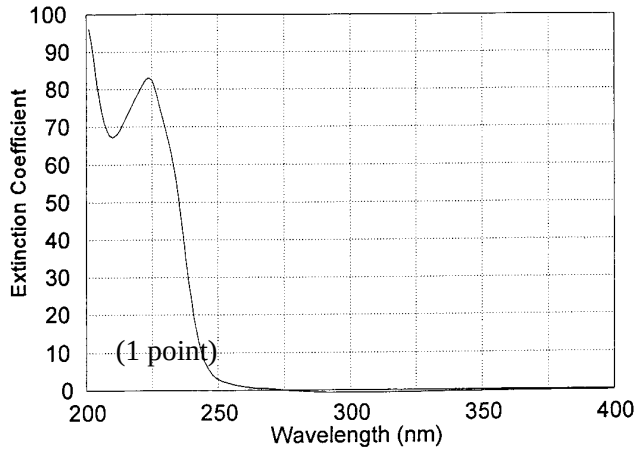


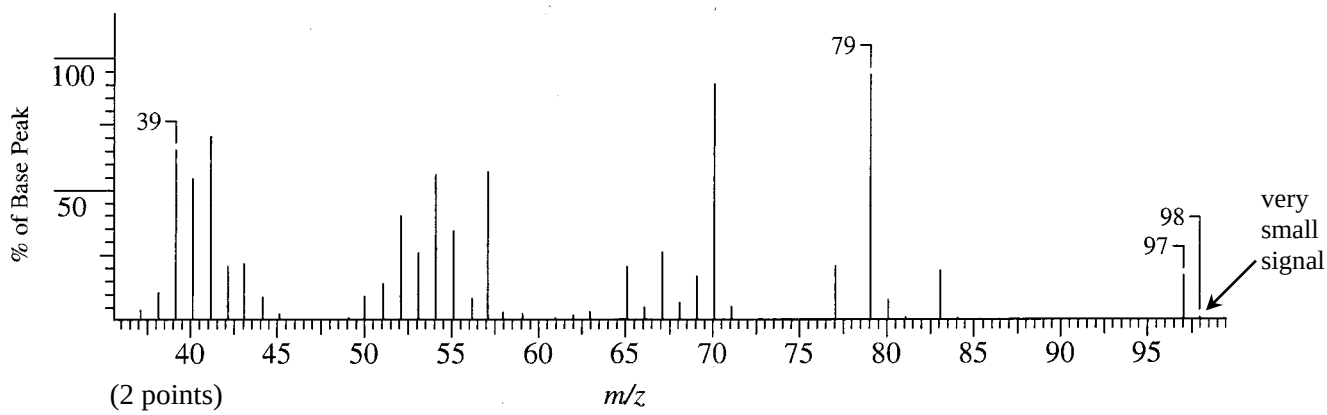

(5.5 points)




(3 points)




For the mass spectrum: Give structures for all numbered peaks.