Problem 8: Compound confusion

Curriculum links;
analytical methods, empirical formulae

Practical skills;
spectral analysis, melting point determination

The students are contacted by the data collection manager for SpectraSchool. There has been a flood and the labels have come off a number of bottles. The students are to analyse various spectra (IR, mass spec, ^{1}H and ^{13}C NMR) and use these, together with melting point determination, to identify the six unknowns.

Pre-Lab questions
(Remember to give full references for any information beyond A-level that you find out)

1. Give the structures and the melting points of the following six compounds:

- caffeine
- benzoic acid
- paracetamol
- methyl ethanoate
- 2-hydroxybenzoic acid
- propanoic acid

2. The melting point of a pure compound is known to be 95-96 ◦C. How would the melting point differ if this compound is contaminated with 5% of an impurity?

3. Carboxylic acids are weak acids but they are stronger than carbonic acid. Therefore carbon dioxide is released when they are reacted with carbonates or hydrogen carbonates (bicarbonates).

Decide which of the compounds in question 1 would release carbon dioxide from carbonates or hydrogen carbonates and write equations to represent any chemical reactions which would occur.

4. Two common solvents in NMR are deuterated chloroform ($CDCl_3$) and deuterated dimethyl sulfoxide, DMSO [$(CD_3)_2SO_2$].

a) What is a deuterium atom?
b) In their pure form, both of these solvents are invisible in ^{1}H NMR. However it is common to see residual solvent peaks in the ^{1}H NMR at δ_H 7.27 ppm for $CDCl_3$ and 2.5 ppm for DMSO. Explain why?
c) As both of these solvents contain a carbon atom, residual solvent peaks are usually evident when these solvents are used when measuring ^{13}C NMR spectra. Find the chemical shifts and multiplicity (splitting pattern) for the residual solvent peaks observed for each solvent.

5. In the mass spectrometer, fragmentation of the molecular ion of paracetamol produces a peak with m/z 43. Identify the fragment responsible for the peak, and write an equation for the fragmentation process.

SpectraSchool

Royal Society of Chemistry, Cambridge
Thomas Graham House (290),
Science Park,
Milton Road,
Cambridge
CB4 0WF

Dear scientist,

My name is John Day and I am the data collection manager for the SpectraSchool website. For each of the compounds on the database, we keep a sample of the compound in the chemical storeroom and the ^{1}H, ^{13}C, IR, mass spec and UV-visible data is held on a server in the basement. Unfortunately, overnight we have had a flood in our chemical store room which has washed the labels off all our sample bottles. We have managed to identify all the compounds bar six which by a process of elimination we know must be caffeine, benzoic acid, paracetamol, methyl ethanoate, 2-hydroxybenzoic acid and propanoic acid. In addition, water got into the server and corrupted some of the data files. Therefore for each of the compounds A-E, we can only find the data below;

Compounds A and B – IR spectra
Compounds C and D – mass spectra
Compounds E and F – elemental analysis
The ^{1}H and ^{13}C NMR files are also available but are unlabelled.

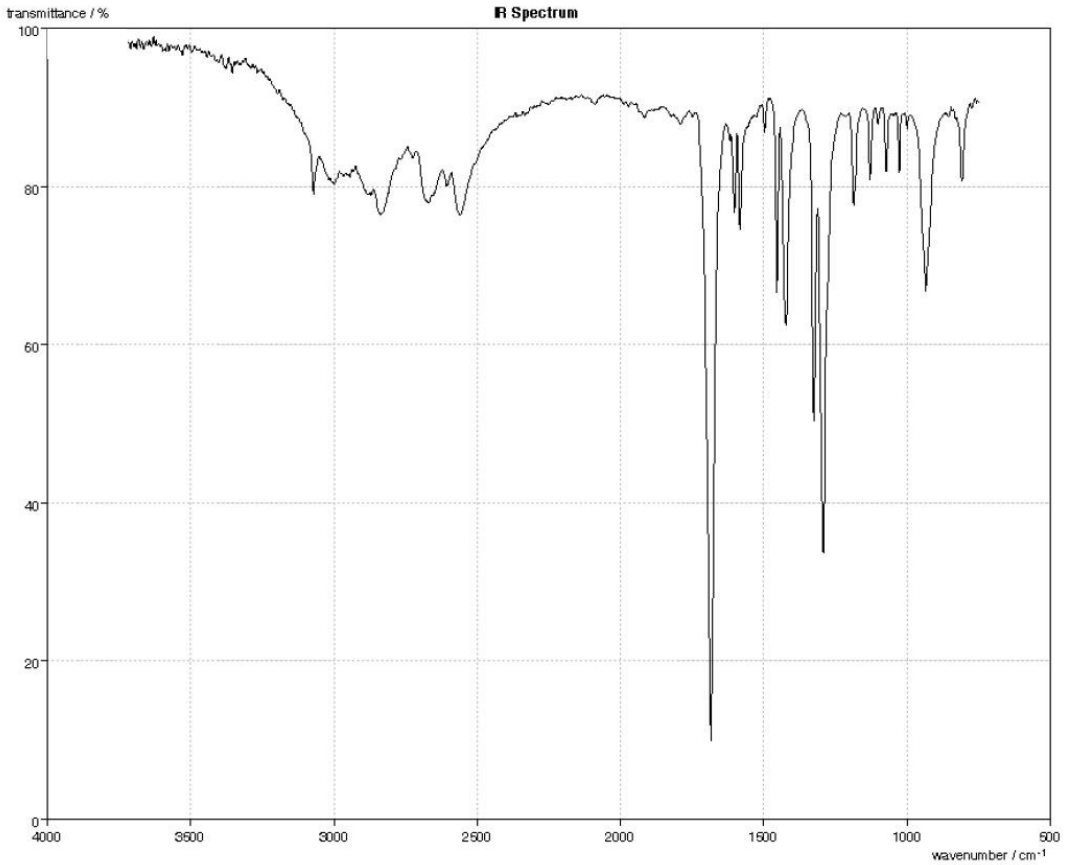
We therefore need your help in identifying samples A - F from our six unknowns and matching up the ^{1}H and ^{13}C NMR data to each compound. We have provided you with all the information we have, together with a small sample of each compound for any chemical tests you may wish to perform.

Please provide the results of your work in as succinct a format as you feel will provide us with the information we require. For verification purposes, we will need full analysis of all spectra.

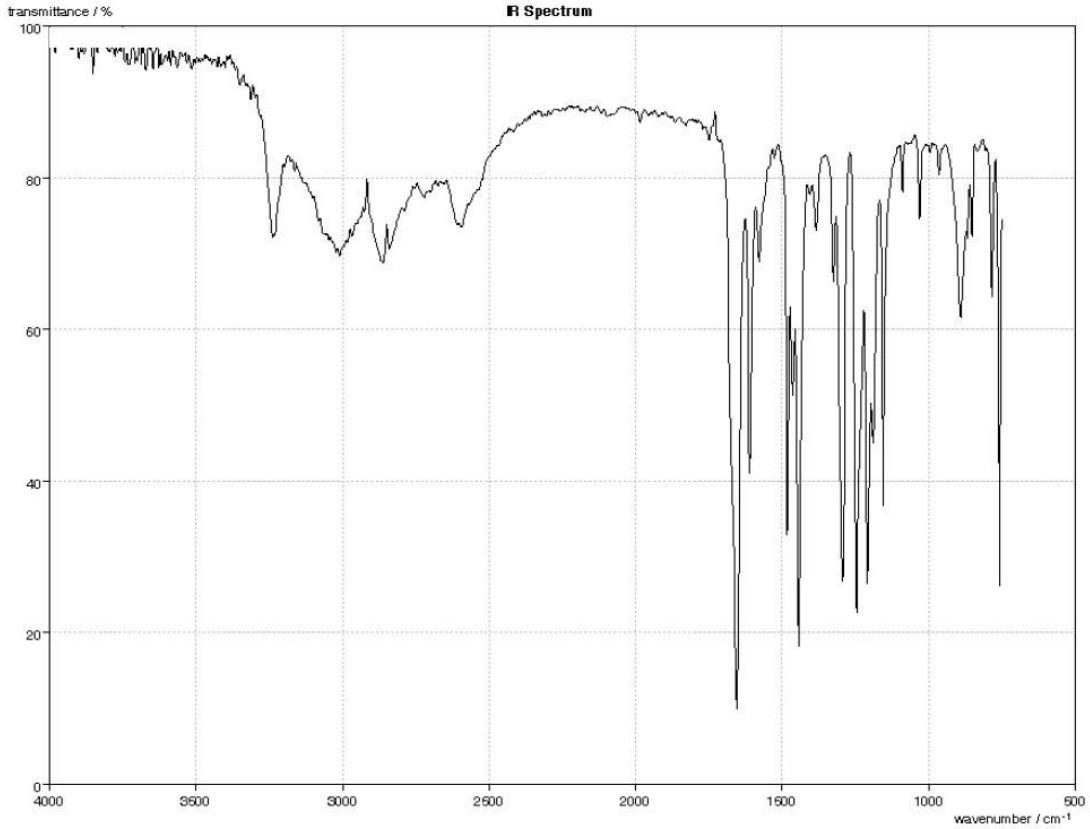
Many thanks for your support,

John Day

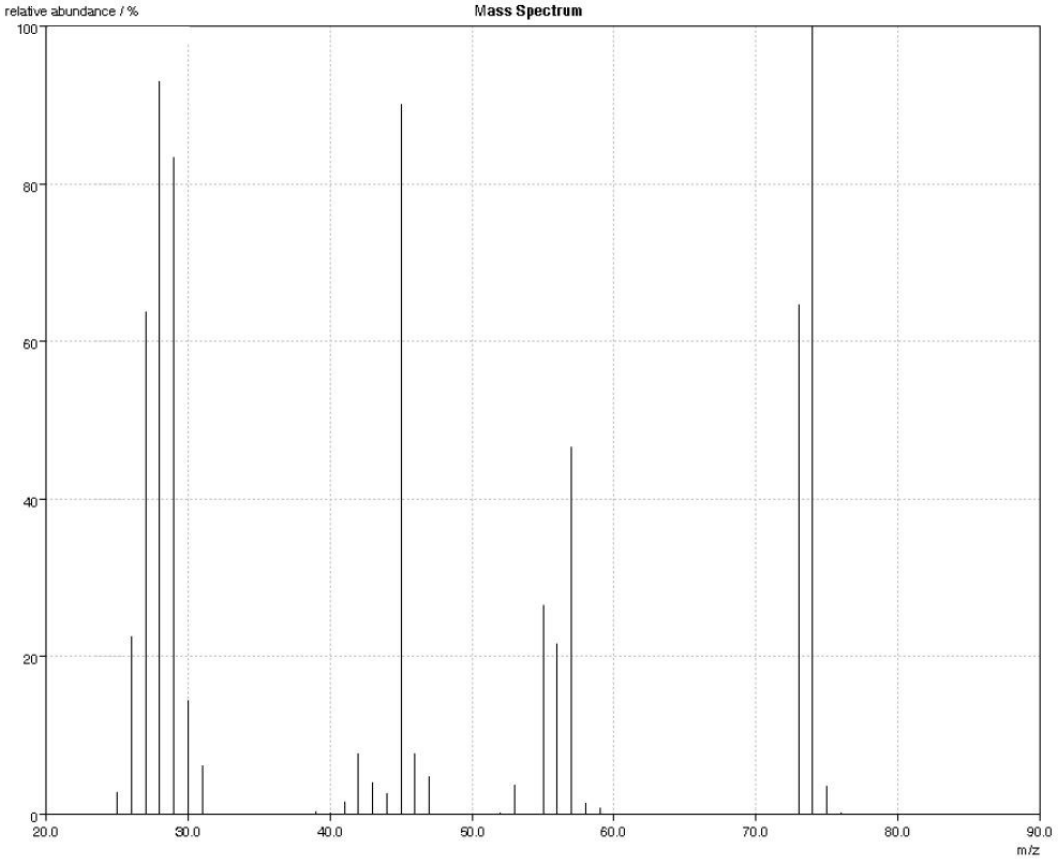
Sample A



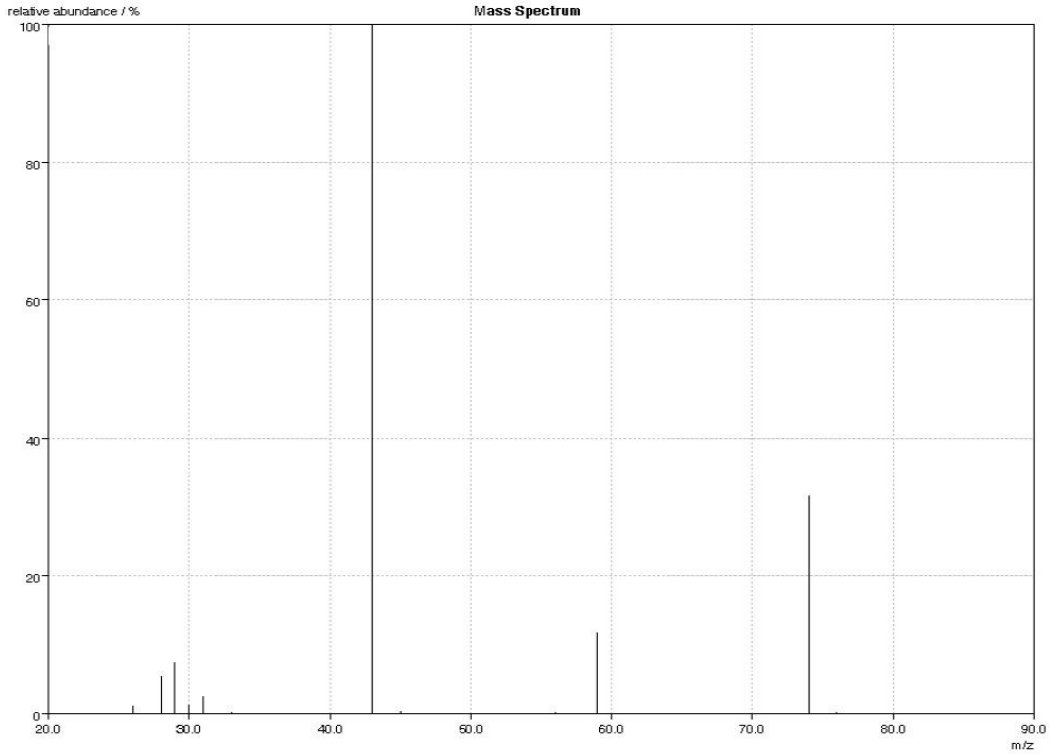
Sample B



Sample C



Sample D

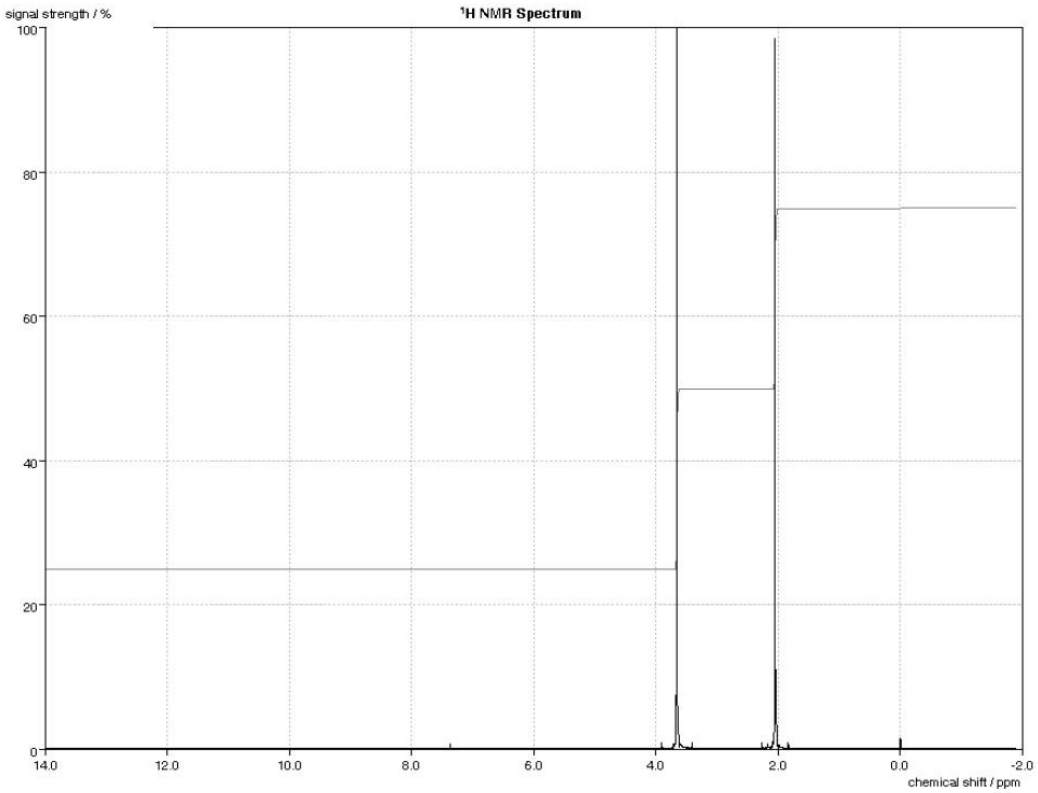


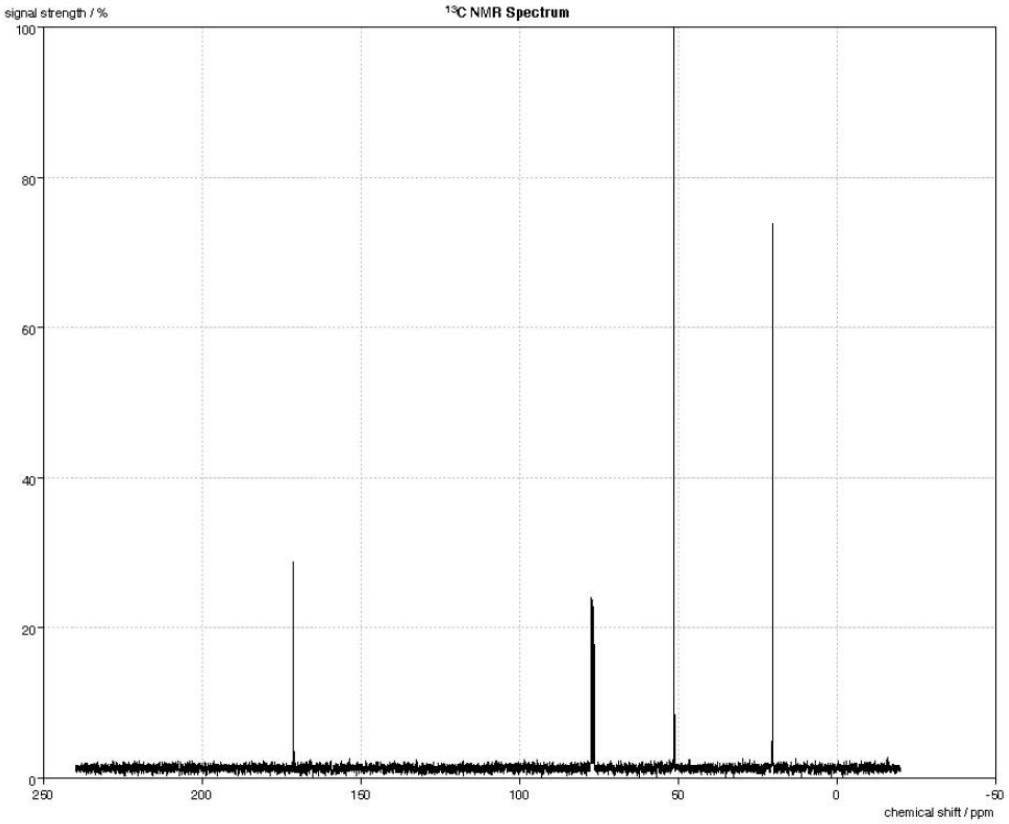
Sample E
C 63.58%; H 5.96%; O 21.19%; N 9.27%

Sample F
C 49.48%; H 5.15%; O 16.49%; N 28.87%

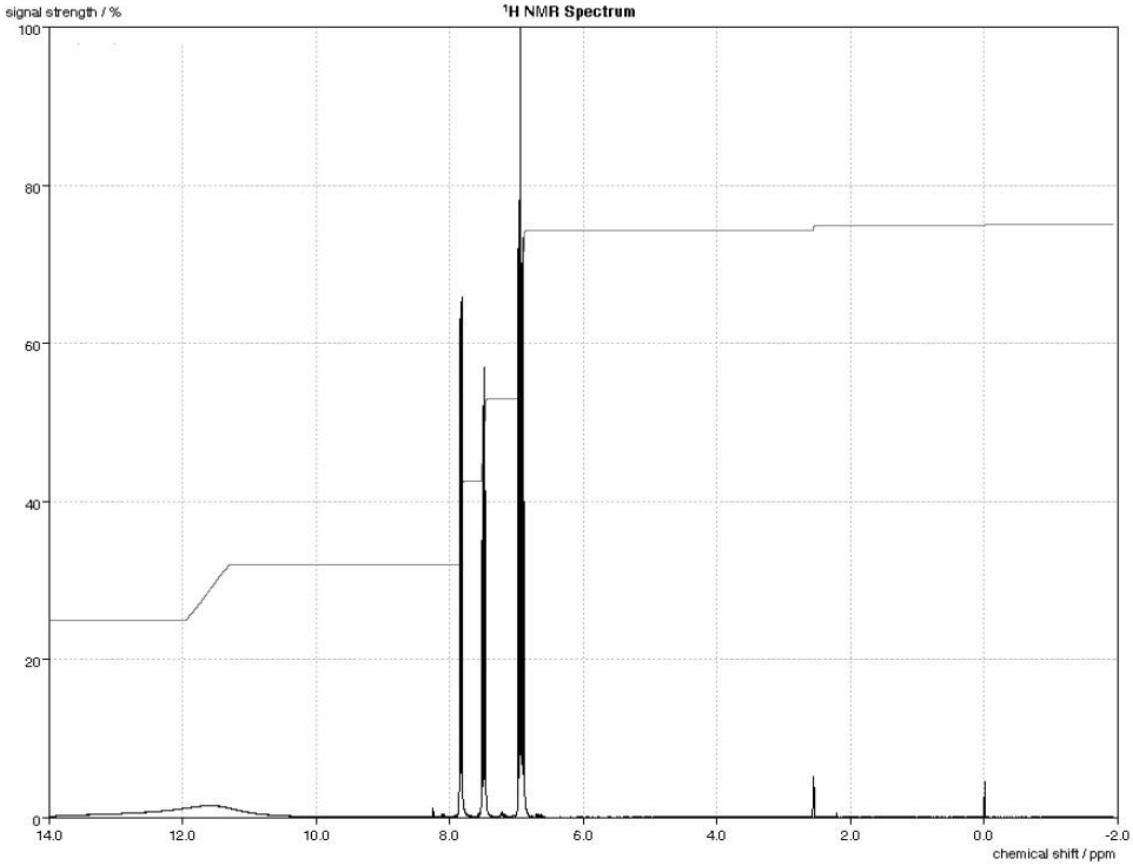
^{1}H and ^{13}C NMR data for each of the unknowns A - F. Labelled Spectra Set 1-6

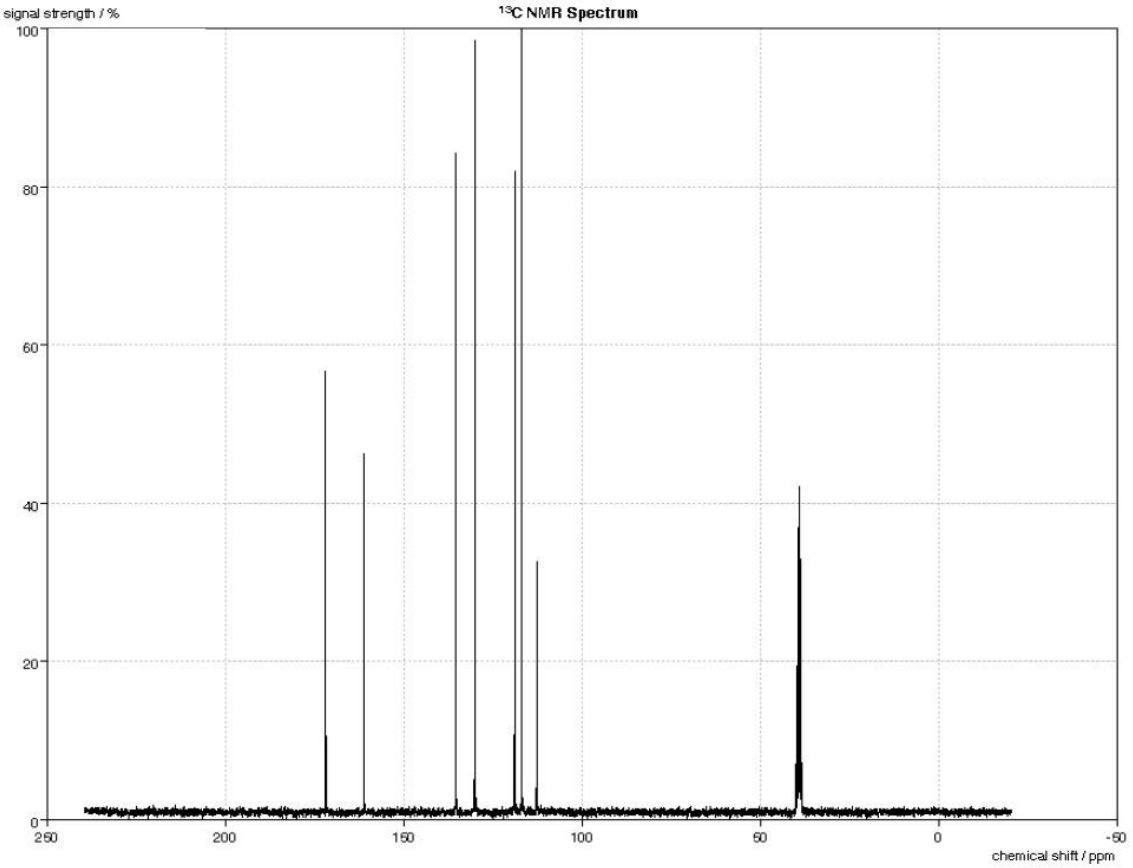
Spectral set 1



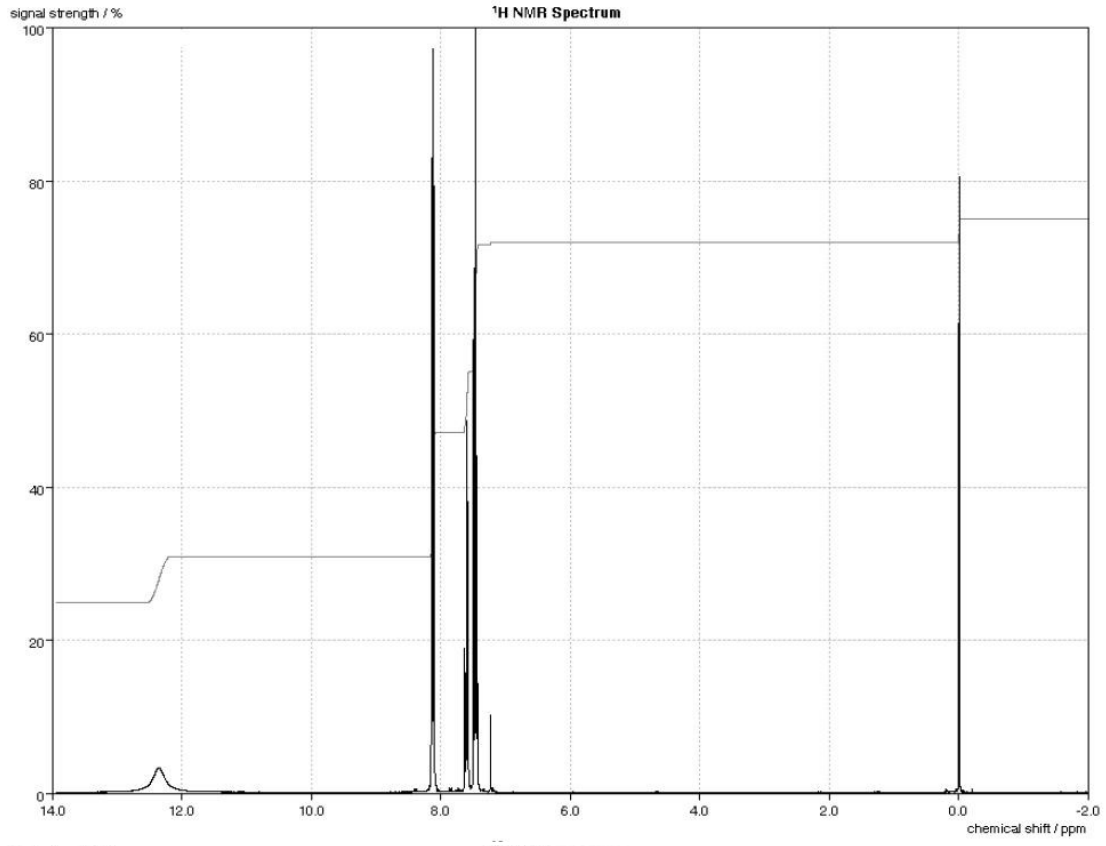


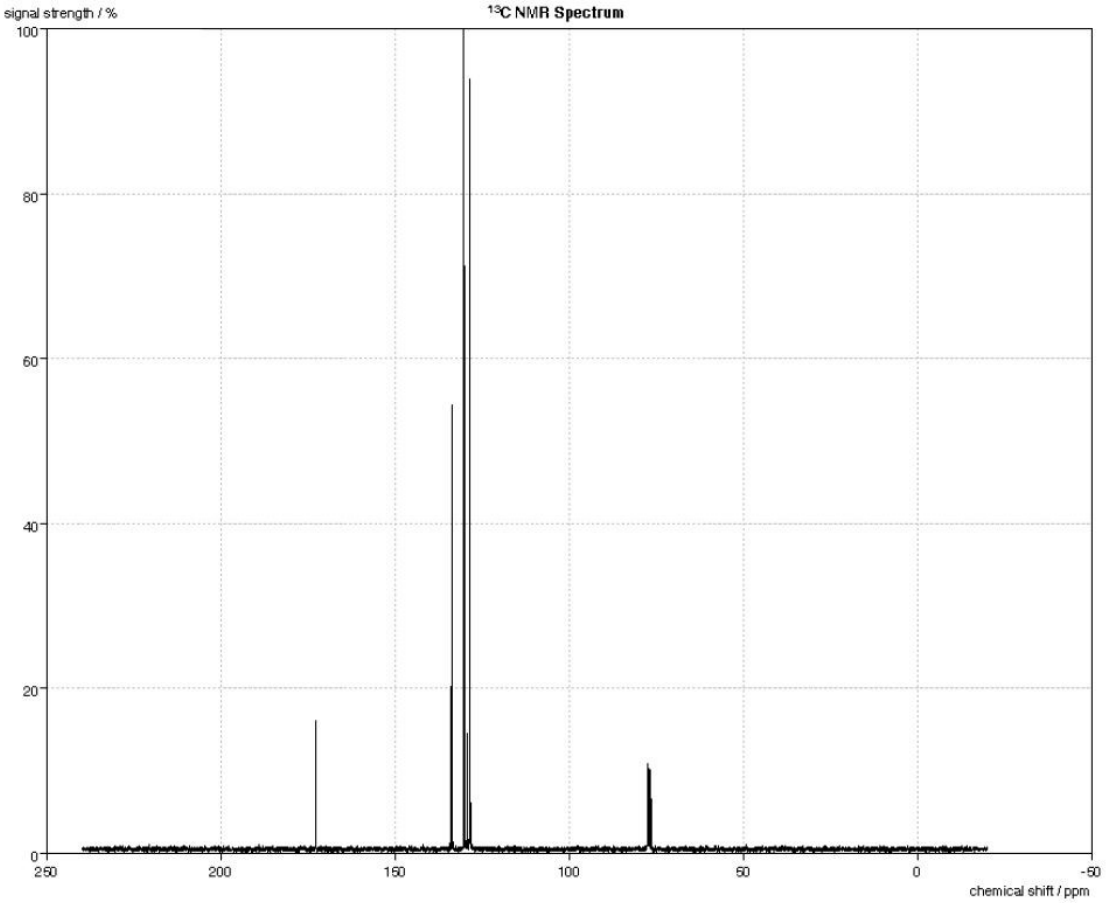
Spectral set 2



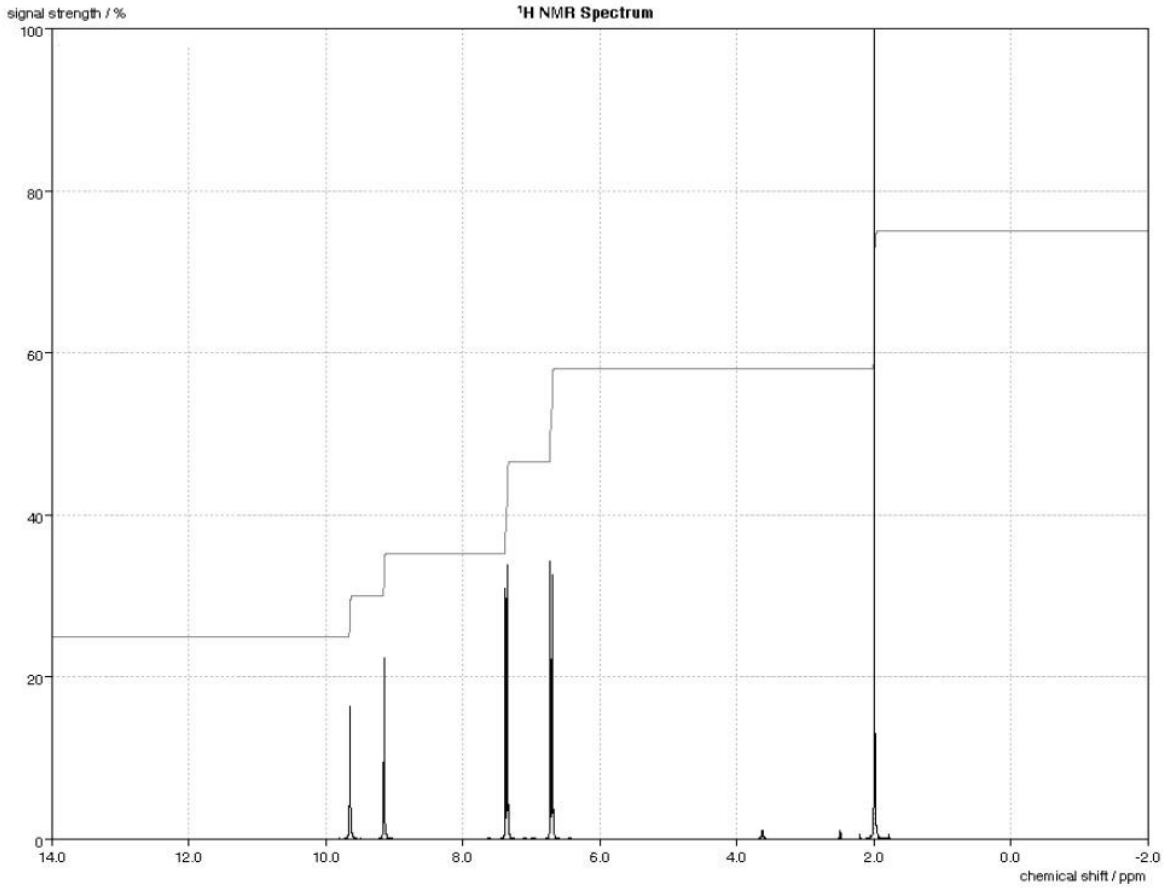


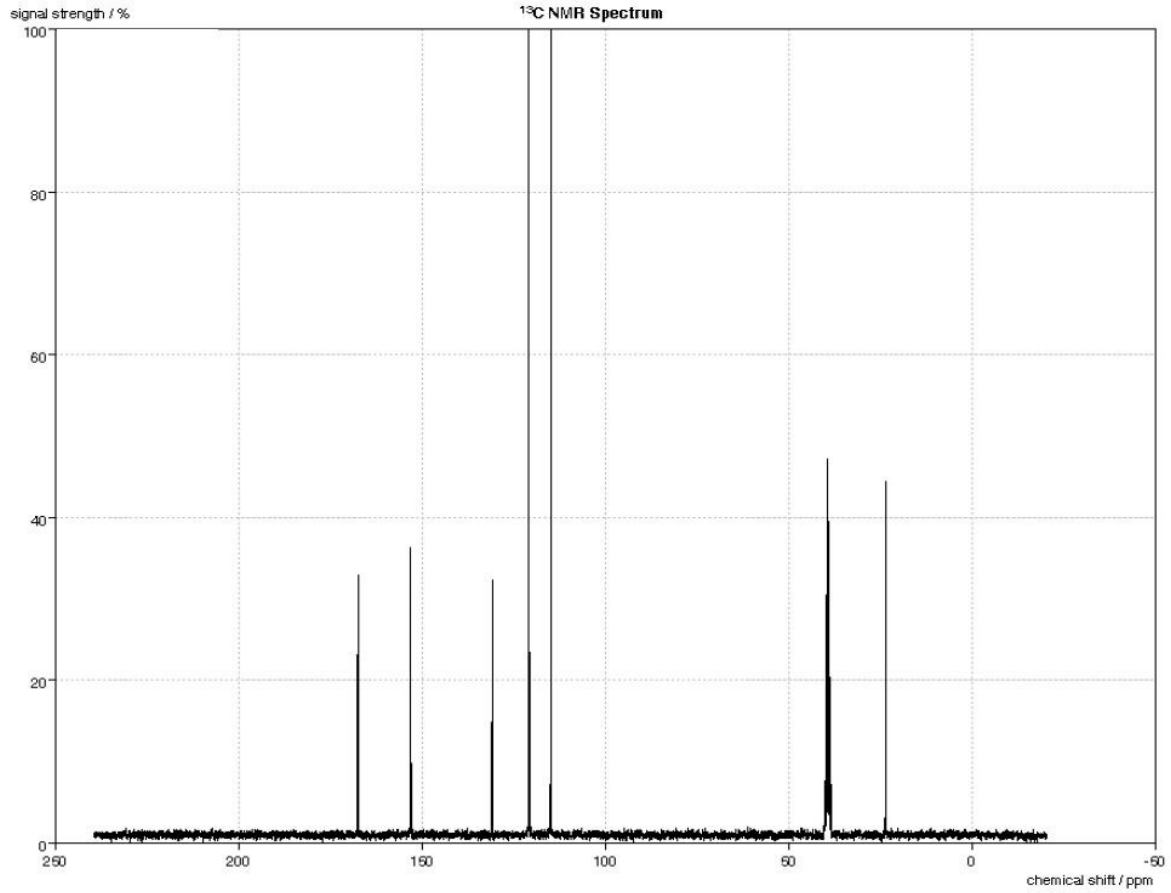
Spectral set 3



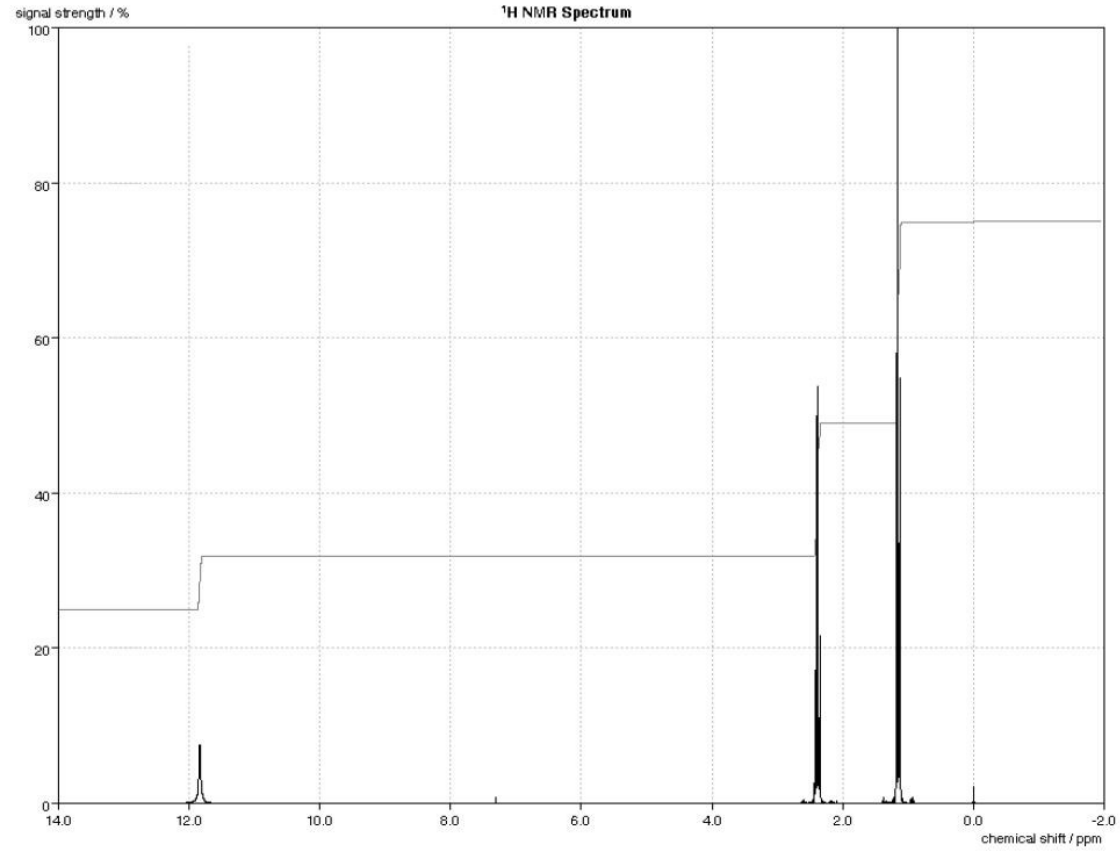


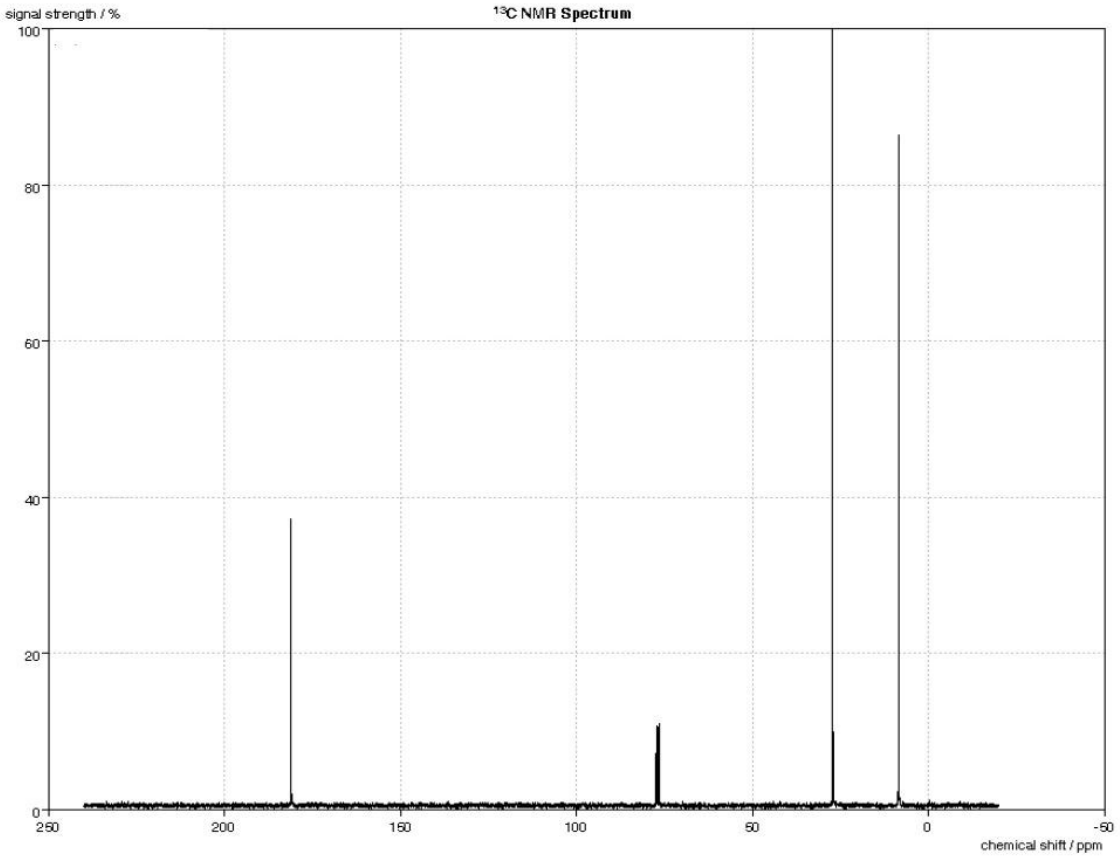
Spectral set 4





Spectral set 5





Spectral set 6