NMR Spectroscopy: ^{13}C and DEPT-135

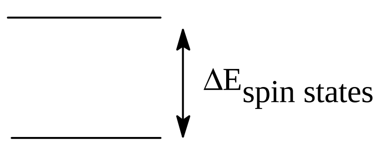
Introduction

This laboratory will serve as an introduction to Nuclear Magnetic Resonance Spectroscopy (NMR). NMR is the most useful method for determining the structure of an organic compound. During this laboratory period, you will work problems that will help you develop the skills needed to interpret ^{13}C NMR data. While you are working on these questions, your instructor will take groups of students to run an unknown sample on the NMR spectrometer. Based upon the NMR spectra you will collect for the unknown compound, you will identify it as one of eight possible unknowns.

Background

Nuclear magnetic resonance is the basis for an important medical tissue-imaging instrument (MRI). It is also the most powerful technique available for determining molecular structure. Although there are many types of NMR experiments, they all give information regarding the environment of atomic nuclei. This module is designed to introduce you to two of these structure-determination techniques and demonstrate how structural information is extracted from the NMR spectra that are produced. Both of these experiments give information regarding the carbon nuclei in a sample.

Ninety-nine percent of the carbon atoms in organic molecules are ^{12}C while the remaining one percent are ^{13}C. Only the ^{13}C atoms are observed by NMR. The nuclei of the ^{13}C atoms have two ways that they can spin (spin states). If the molecules containing these are placed in a strong magnetic field, the two spin states become different in energy and more nuclei occupy the lower energy state. One characteristic of the spinning nuclei is that they wobble as they spin with a frequency called the Larmor frequency. It turns out that the difference in the energies of the spin states is related to this Larmor frequency.



$$\Delta E_{spin\ states} = h\,\nu_{Larmor}$$

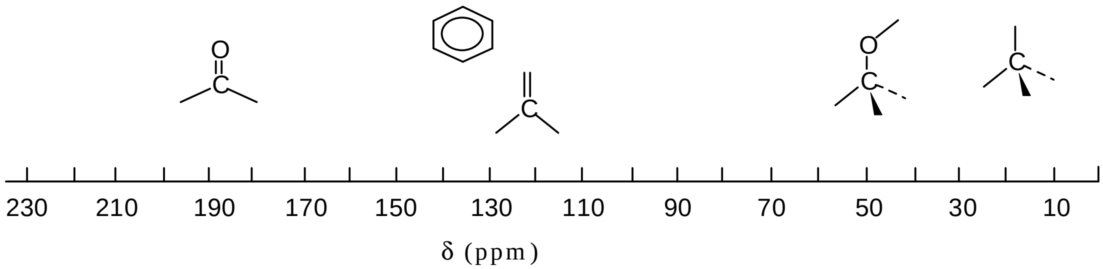
$$\Delta E_{light} = h\,\nu_{light}$$

resonance occurs when $\nu_{Larmor} = \nu_{light}$

If an amount of light energy equal to the difference in energy of the spin states is absorbed, a nucleus will change from one spin state to the other. This "resonance" event occurs when the frequency of the light is the same as the Larmor frequency. The energy difference is small and the light is in the radio frequency range (60 – 500 MHz).

What makes this useful to us is that the Larmor frequency of a nucleus is influenced by its molecular environment, specifically, the electron density in its vicinity. Thus a unique NMR signal is produced for each carbon atom that is in a unique molecular environment. That is, each different kind of carbon atom in a molecule produces a different ^{13}C NMR signal. These signals are displayed as peaks on a graph in which the horizontal axis is the fractional difference in Larmor frequency compared to a reference. This difference is called "chemical shift" and has the units of parts per million (ppm).

There is a correlation chart of chemical shifts on page 533 of Smith's text and in your lab notebook. What you really need to know is that aliphatic (*sp*^{3}) carbons absorb between 0 and 80 ppm and carbon atoms close to an electronegative atom (N or O) are on the high end of this range. You also should know that *sp*^{2} hybridized carbons in alkenes and benzene rings absorb between 100 and 150 ppm and carbonyl carbon atoms (C=O) between 160 and 220. The carbonyl carbons of aldehydes and ketones are in the high part (200-220) of this range and the carbonyl carbons of acid derivatives such as esters are on the low end (170-180) of the range.



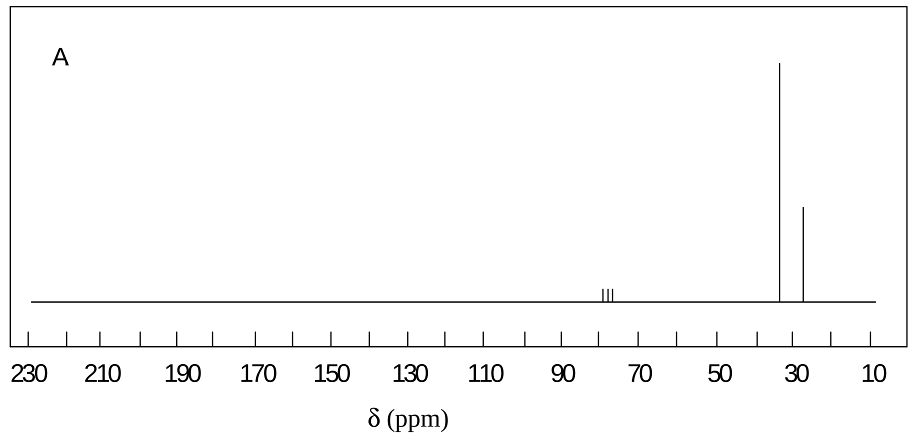
The information that the spectrum provides regarding molecular structure is obtained from the number of signals in the spectrum and the position of each signal on the chemical shift scale. You do have to exercise some care since occasionally two different signals fall at the same chemical shift position and appear to be only one peak. The information provided by ^{13}C NMR is seldom sufficient by itself to completely characterize the structure of a complex organic molecule. The technique is most powerful when used in conjunction with other molecular probes such as infrared spectroscopy, proton NMR, and DEPT. Proton NMR will be covered in CHEM 3411. DEPT is covered later in this module.

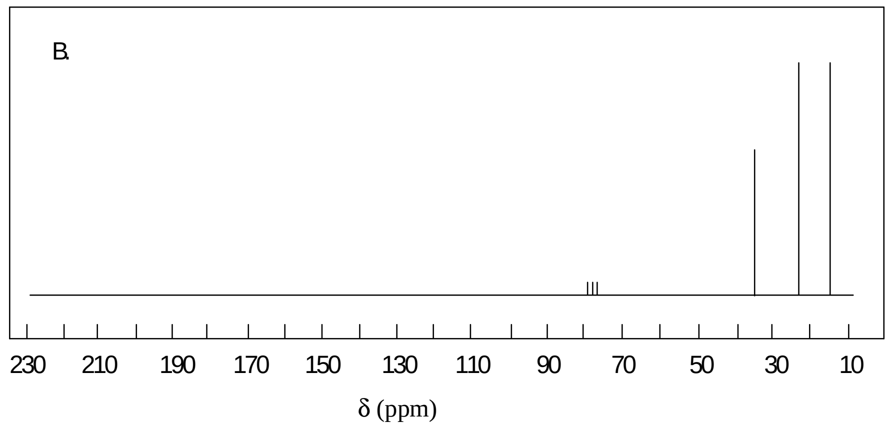
^{13}C NMR Problems

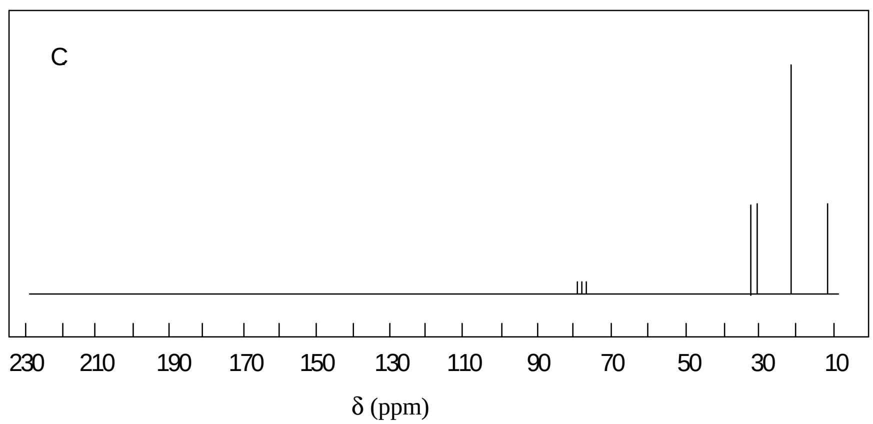
1. There are three isomeric pentanes with a molecular formula of C_5H_{12}.

    A. Draw structural formulas for each of these compounds, name them, and determine the number of unique carbon atoms in each.

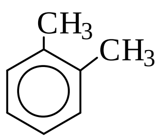
B. Below are ^{13}C NMR spectra for each of the isomeric pentanes you drew in part A. Match the correct spectrum with each of the structural formula that you drew. The three peak signal at 78 ppm is due to the deuterochloroform solvent.

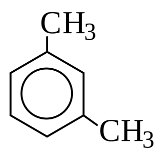


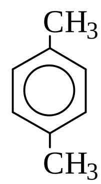


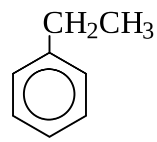


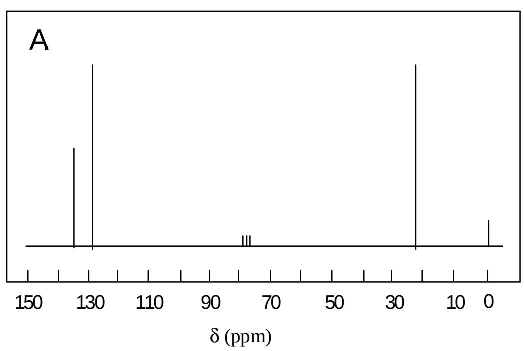
2. Below are the structures of four compounds with molecular formulas of C_8H_{10} that contain benzene rings. The ^{13}C NMR spectra for these compounds are shown below. Draw planes of symmetry for each structure and use them to assist you in determining the number of unique carbon atoms, then match each compound with its spectrum. Note that the peaks are in two regions of the spectrum: benzene carbons from 100 to 140 ppm and aliphatic carbon atoms from 10 to 50 ppm. The signal at 0 ppm in each case is the tetramethylsilane (TMS) reference and the three peak signal at about 78 ppm is due to the deuterochloroform solvent. These can be disregarded.

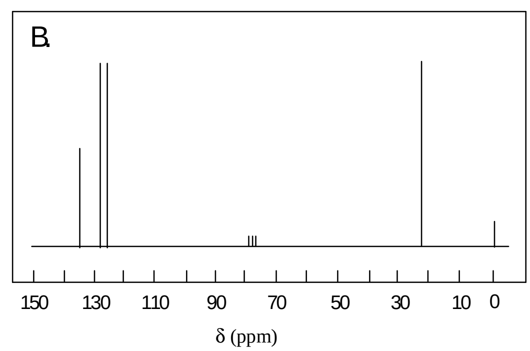


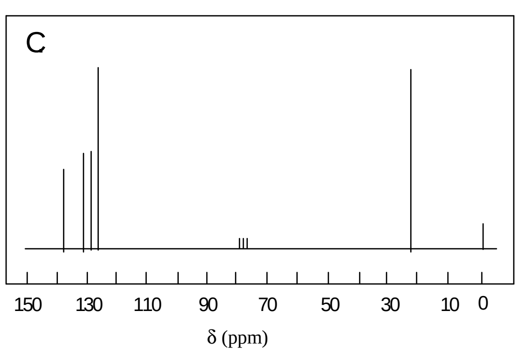


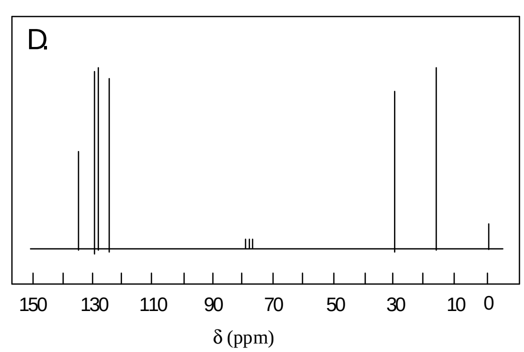




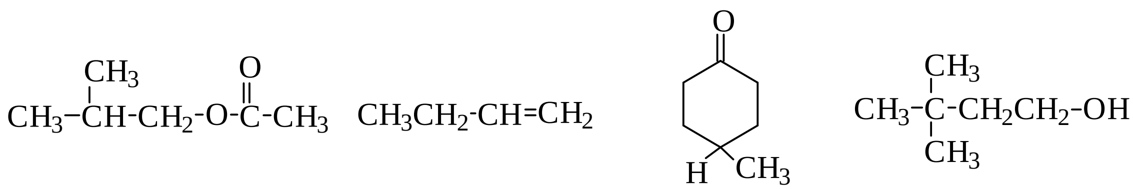


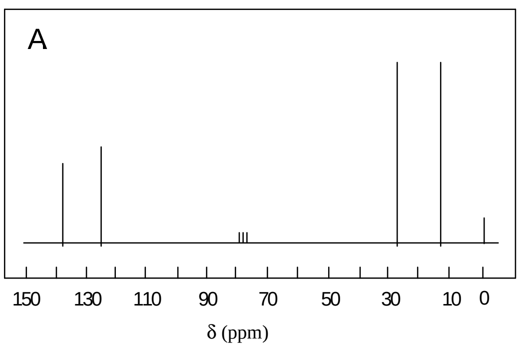


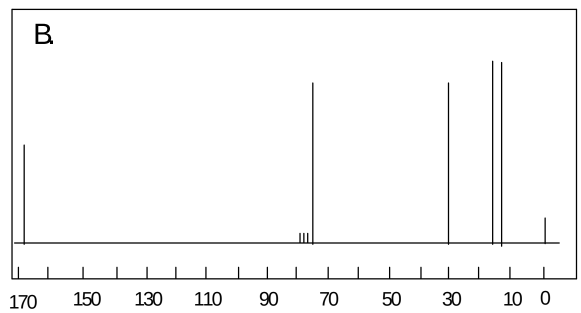


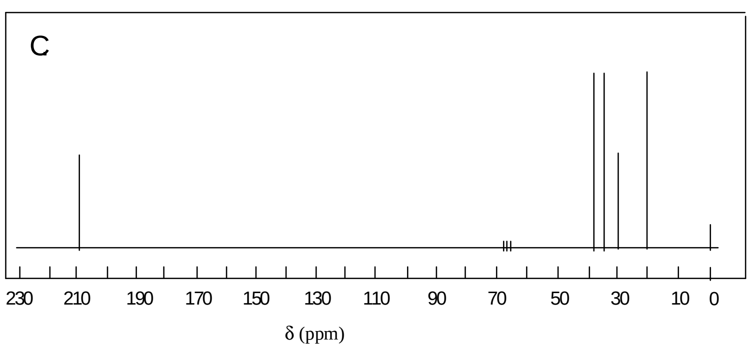


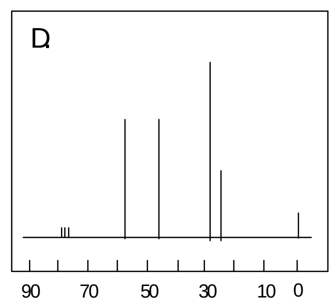
3. Here are the structures of compounds with various functional groups. Select the structure of the compound that produces each of the ^{13}C NMR spectra shown below. Use the chemical shift information from page 2.



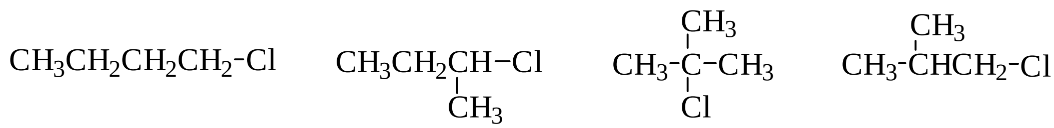


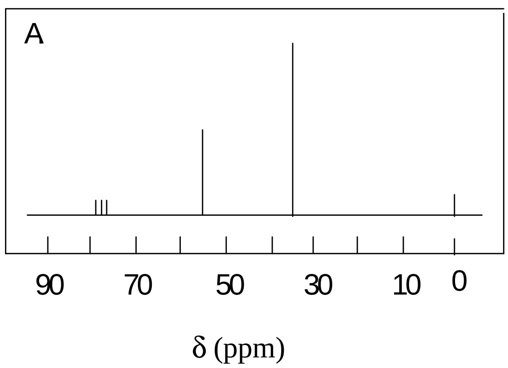


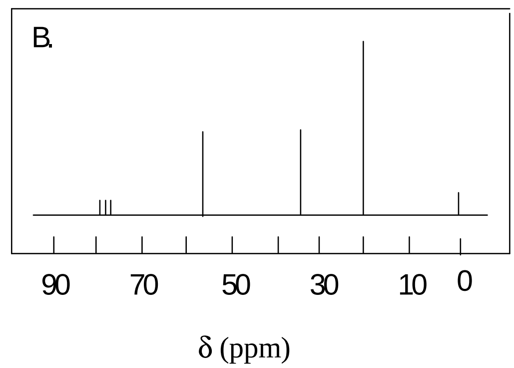


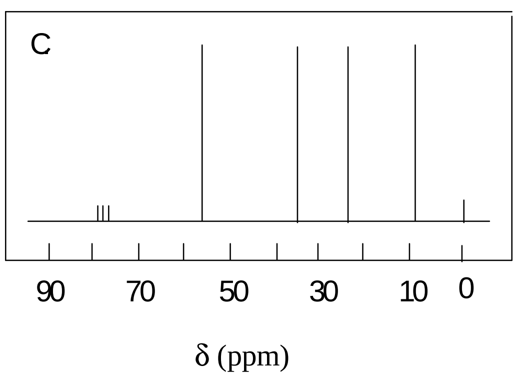


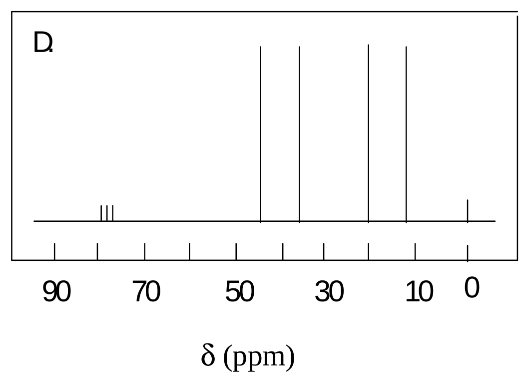
4. Below are the structures of the four isomers of C_4H_9Cl and their ^{13}C NMR spectra. Two of the spectra can be unequivocally matched with the correct structure. Make this identification and assign each signal in the spectrum to the carbon atom in the molecule that produces that signal.











It is impossible to assign the correct structure to two of the spectra above in an unequivocal fashion. Why is that? In such cases chemists perform additional experiments. The next page describes the DEPT experiment, a technique that enables differentiation of these two compounds.

Distortionless Enhancement By Polarization Transfer (DEPT)

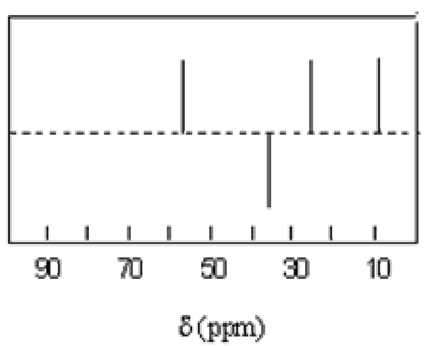
Modern NMR spectrometers come equipped with computer controlled radio frequency transmitters that can be used to manipulate nuclei in ways that create new types of spectra containing additional structural information. One of these techniques is referred to as DEPT. The DEPT technique produces different effects depending on the number of hydrogen atoms bonded to a carbon atom. By doing a series of spectra it is possible to identify the number of hydrogen atoms attached to the carbon atom producing each of the signals in a ^{13}C NMR spectrum. This is valuable information for identifying which carbon atom in a molecule produces which signal in the NMR, a process that is essential to verifying a proposed structural formula.

Although there are a number of different DEPT experiments, the most common is the DEPT-135. This experiment shows positive signals for all CH and CH_3 carbon atoms in the molecule. Conversely, CH_2 carbon atoms show as negative signals. Signals for carbon atoms with no attached hydrogen atoms are not present in this spectrum.

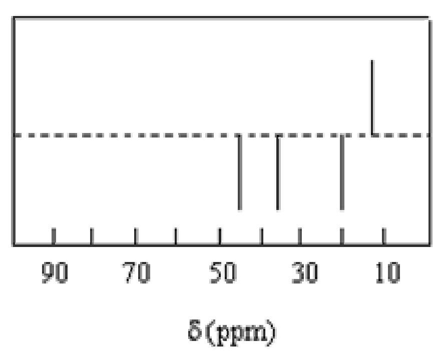
The DEPT-135 and the normal ^{13}C spectrum can be used together to determine the number of hydrogen atoms attached to the carbon atom producing each signal in the spectrum. This is very useful information that aids in structural determination.

5. In problem 4 it was impossible to correlate structures with spectra C and D with absolute certainty. Below are the DEPT-135 spectra for those two compounds. Use these along with the normal ^{13}C spectra given in problem 4 to make those correlations and assign each NMR signal to a specific carbon atom.

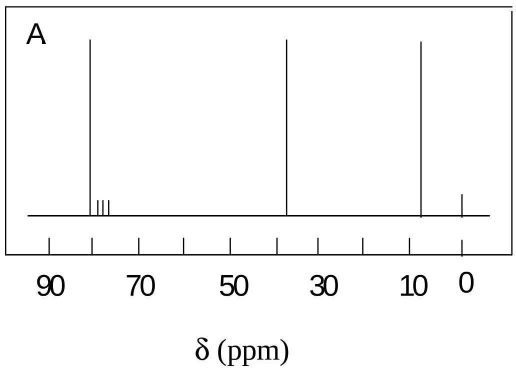
Compound C- DEPT 135

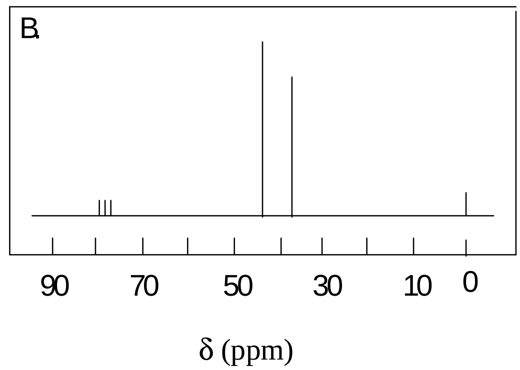


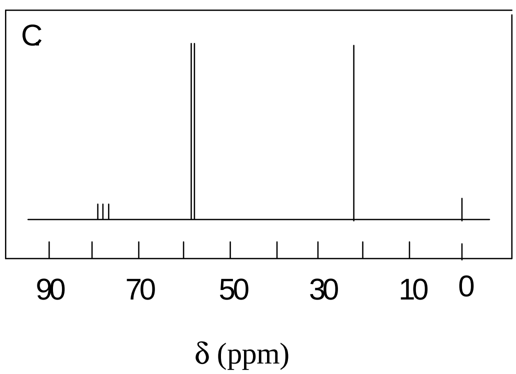
Compound D – DEPT 135

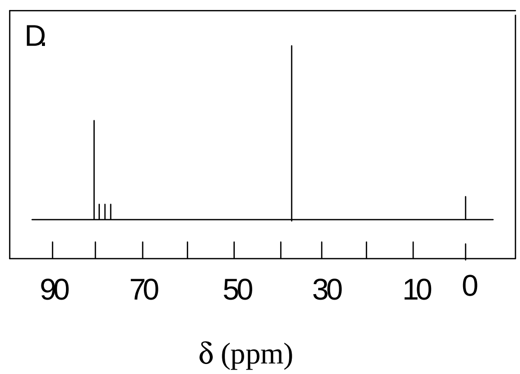


6. Below are the structures of four compounds with molecular formulas of $C_3H_6Cl_2$ and their ^{13}C NMR spectra. Match each compound with its spectrum. A DEPT-135 spectrum for compound C is provided.

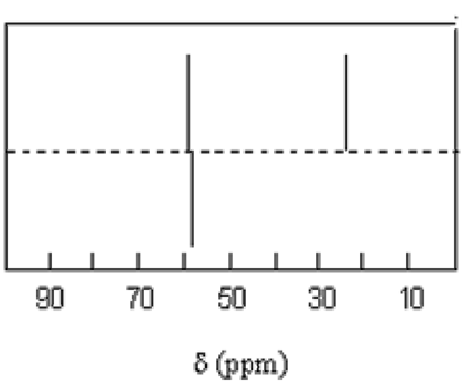






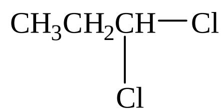


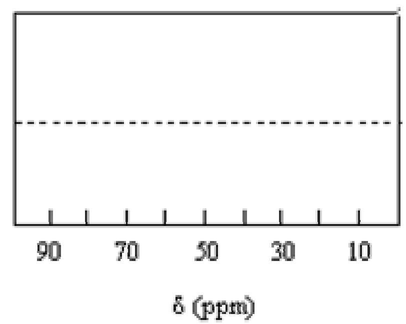
Compound C – DEPT 135

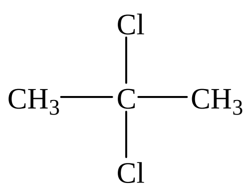


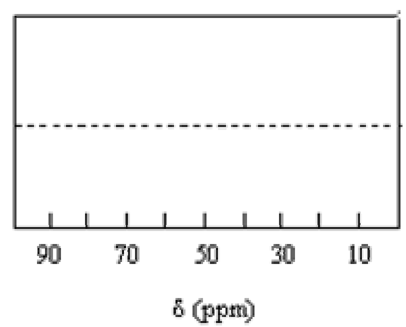
7. Use the blank axes below to draw the DEPT-135 spectrum for each of the compounds in question 6 above. You will need to refer to the ^{13}C NMR spectra provided in question 6.

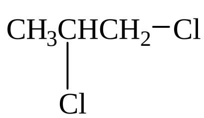
<u>Structure</u> | <u>Predicted DEPT-135</u>

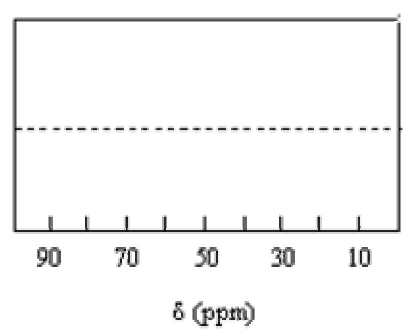




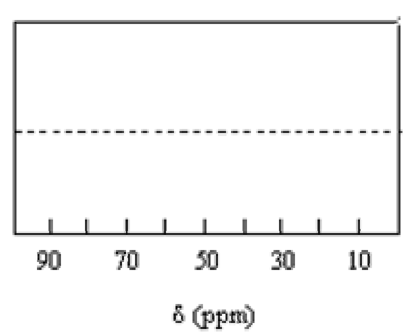








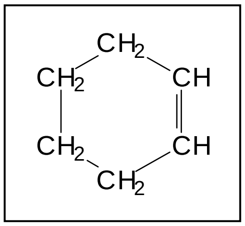
$Cl-CH_2CH_2CH_2-Cl$



^{13}C NMR Unknowns

The following eight compounds have been selected as unknowns for ^{13}C analysis. You will select an unknown at random, obtain its ^{13}C and its DEPT-135 spectra and identify your unknown from the list. Answer the questions about each before proceeding with the analysis of your spectra.

A. Cyclohexene:



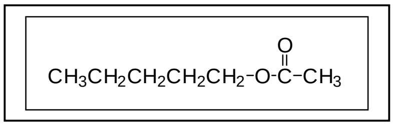
How many signals will appear in its ^{13}C spectrum? ________

How many signals in its DEPT-135 spectrum will point up? ______

How many signals in its DEPT-135 spectrum will point down? __________

How many signals in its ^{13}C spectrum will not be present in its DEPT-135? _________

B. Amyl acetate:



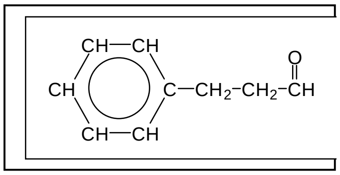
How many signals will appear in its ^{13}C spectrum? ________

How many signals in its DEPT-135 spectrum will point up? __________

How many signals in its DEPT-135 spectrum will point down? __________

How many signals in its ^{13}C spectrum will not be present in its DEPT-135? _________

C. Hydrocinnamaldehyde:



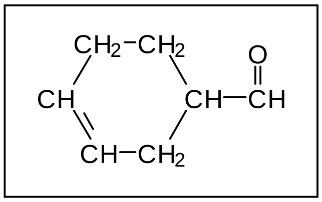
How many signals will appear in its ^{13}C spectrum? ________

How many signals in its DEPT-135 spectrum will point up? __________

How many signals in its DEPT-135 spectrum will point down? __________

How many signals in its ^{13}C spectrum will not be present in its DEPT-135? _________

D. 3-cyclohexene-carbaldehyde:



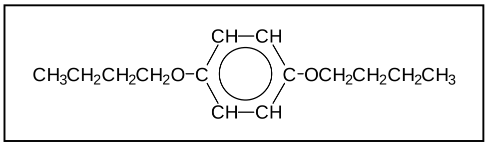
How many signals will appear in its ^{13}C spectrum? ________

How many signals in its DEPT-135 spectrum will point up? __________

How many signals in its DEPT-135 spectrum will point down? __________

How many signals in its ^{13}C spectrum will not be present in its DEPT-135? _________

E. p-dibutoxybenzene



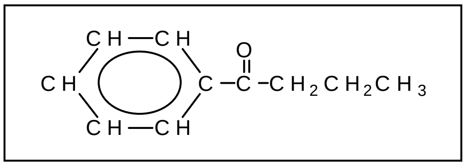
How many signals will appear in its ^{13}C spectrum? ________

How many signals in its DEPT-135 spectrum will point up? __________

How many signals in its DEPT-135 spectrum will point down? __________

How many signals in its ^{13}C spectrum will not be present in its DEPT-135? _________

F. butyrophenone:



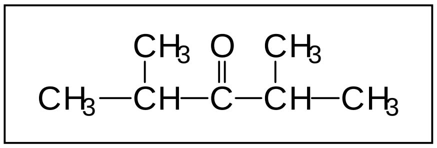
How many signals will appear in its ^{13}C spectrum? ________

How many signals in its DEPT-135 spectrum will point up? __________

How many signals in its DEPT-135 spectrum will point down? __________

How many signals in its ^{13}C spectrum will not be present in its DEPT-135? _________

G. 2,4-dimethyl-3-pentanone



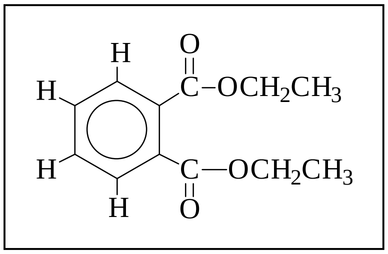
How many signals will appear in its ^{13}C spectrum? ________

How many signals in its DEPT-135 spectrum will point up? __________

How many signals in its DEPT-135 spectrum will point down? __________

How many signals in its ^{13}C spectrum will not be present in its DEPT-135? _________

H. diethylphthalate:



How many signals will appear in its ^{13}C spectrum? ________

How many signals in its DEPT-135 spectrum will point up? __________

How many signals in its DEPT-135 spectrum will point down? __________

How many signals in its ^{13}C spectrum will not be present in its DEPT-135? _________

Analysis of ^{13}C and DEPT-135 spectra of an unknown:

1) What is the identifying code for your unknown? ___________

2) How many signals are present in the ^{13}C spectrum of your unknown? _____________

3) How many signals in your DEPT-135 spectrum point up? ________

4) How many signals in your DEPT-135 spectrum point down? ________

5) How many signals in its ^{13}C spectrum are not present in its DEPT-135? ________

6) Compare the results from the spectra of your unknown with the behavior that you predicted for each of the eight compounds and determine which compound you have.

Name of unknown Structure of unknown

7. Label each of the unique carbon atoms (a, b, c, etc) in the molecule and, to the degree that you can, assign each of them to a signal in your ^{13}C NMR spectrum

Signal (ppm)	Assignment
_______	_______
_______	_______
_______	_______
_______	_______
_______	_______
_______	_______
_______	_______
_______	_______
_______	_______
_______	_______