

## **Infra-Red (IR)- Nuclear Magnetic Resonance (NMR)** **Exercises In Molecular Spectroscopy- Structural Determination**

**Purpose :** to determine the structure of organic compounds

**Discussion :**

Unknown compounds may be isolated from natural sources or may be the result of laboratory synthesis. In determining their structure, physical properties such as boiling point and density are collected. Such data are useful for comparing the unknown to known compound but contain little definitive structural information. Qualitative chemical tests may be carried out to obtain structural information. For example, you carried out the bromine and Baeyer tests to characterize the double bond of cyclohexene. Qualitative chemical tests are not unambiguous. More than one functional group may give the same positive test. Bromine and potassium permanganate react with other functional groups in addition to reacting with the double bond. An addition, qualitative chemical tests are destructive. The unknown cannot be recovered after the test. This is a great disadvantage if only a limited amount of the unknown is available.

Spectroscopy – Spectroscopic methods provide useful information about the structure of organic compound. In absorption spectroscopy, we study the interaction of molecules with electromagnetic radiation. Frequently, absorption at a particular frequency indicates the presence of a specific structural unit within the molecule. Spectroscopy is advantageous because it is rapid and non-destructive. The sample may be recovered after study. Usually only a small quantity is required and much structural information is present in each spectrum. Spectra that are routinely used to obtain structural information by organic chemists are ultraviolet, UV; infrared, IR; and nuclear magnetic resonance, NMR. In this experiment you become familiar with the characteristic absorption bands of several common functional groups.

**Directions:**

Study text or any other organic text to identify the structure of each compound using the following spectrums. Please write your answers clearly in space provided.

**IR Spectrum:**

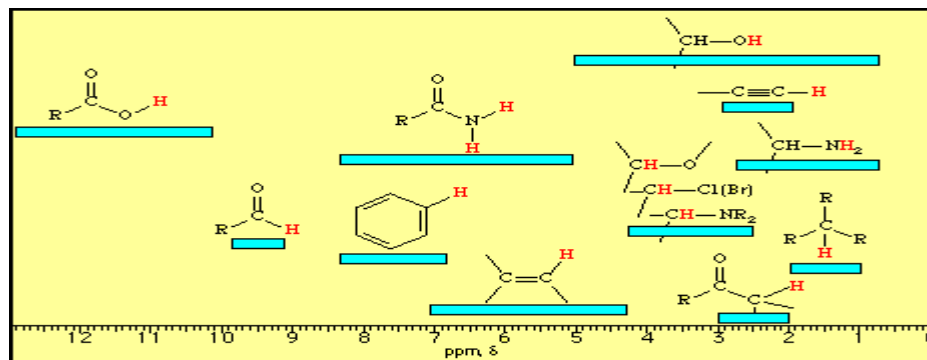
- I. Learn and locate the wavelength of maximum of each IR band
- II. Learn to study each IR spectrum and identify functional group present such as hydroxyl group, carbonyl group, carboxylic group, .....

**NMR Spectrum:**

- I. Learn to locate the  $^1\text{H}$  NMR chemical shift of each type in the spectrum.
- II. Learn to interpret the integration signals and how to interpret the splitting of coupled protons.
- III. Study each spectrum and deduce the molecular structure by proton NMR (PMR) spectra.

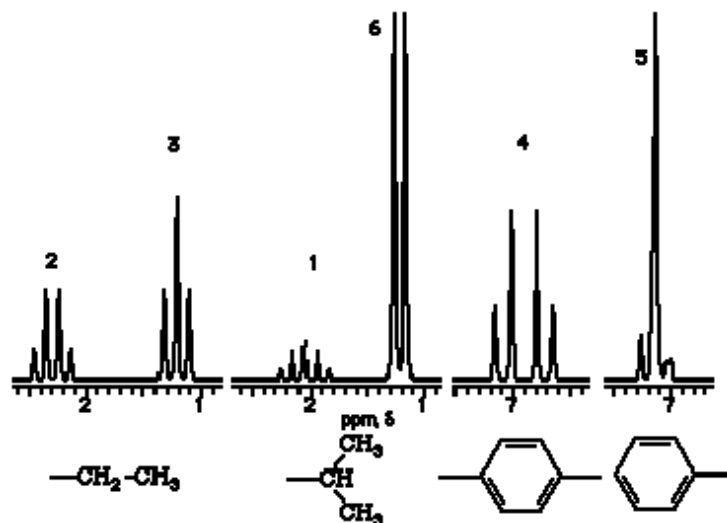
## Helpful information

### Proton NMR Chemical Shifts



- Electronegative groups are "deshielding" and tend to move NMR signals from neighboring protons further "downfield" (to higher ppm values).
- Protons on oxygen or nitrogen have highly variable chemical shifts which are sensitive to concentration, solvent, temperature, etc.
- The  $\pi$ -system of alkenes, aromatic compounds and carbonyls strongly deshield attached protons and move them "downfield" to higher ppm values.

### Common $^1\text{H}$ NMR Splitting Patterns



The examples given above represent only the simplest and most common coupling patterns seen in the  $^1\text{H}$  NMR.

- I. A simple ethyl group displays a quartet and a triplet in the ratio 2:3; the chemical shift of the  $\text{CH}_2$  group is sensitive to the attached substituent and typically varies between  $\delta \approx 4$  (for oxygen) to  $\delta \approx 2$  (for a carbonyl).
- II. An isopropyl group displays a septet (7 peaks) and a doublet in the ratio 1:6; again, the chemical shift of the  $\text{CH}_2$  group is sensitive to the attached substituent and typically varies between  $\delta \approx 4$  (for oxygen) to  $\delta \approx 2$  (for a carbonyl).
- III. A 1,4-disubstituted aromatic compound displays two doublets in the ratio of 1:1, typically in the region around  $\delta \approx 7$ .
- IV. In spite of the fact that there are three different types of hydrogens in a monosubstituted aromatic compound, the  $^1\text{H}$  NMR typically displays a single peak in the region around  $\delta \approx 7$ . This is because the differences in chemical shift are typically small, as are the coupling constants.

**REPORT FORM**

Name \_\_\_\_\_

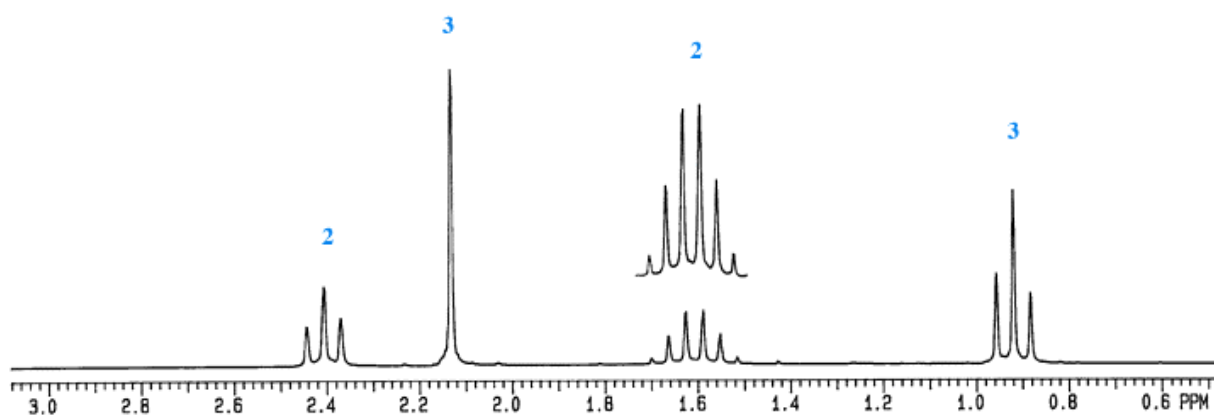
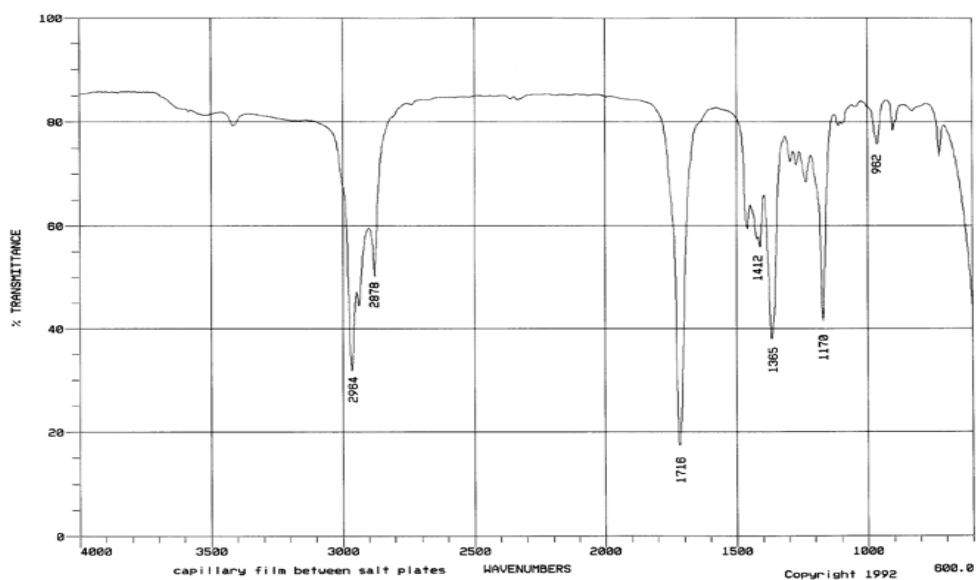
Instructor \_\_\_\_\_

Date \_\_\_\_\_

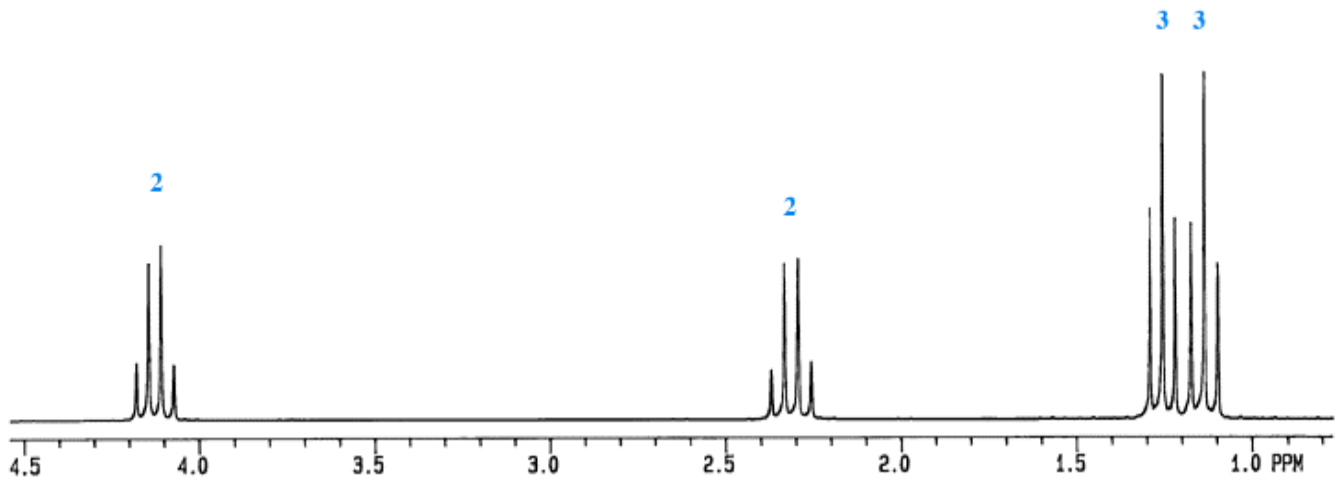
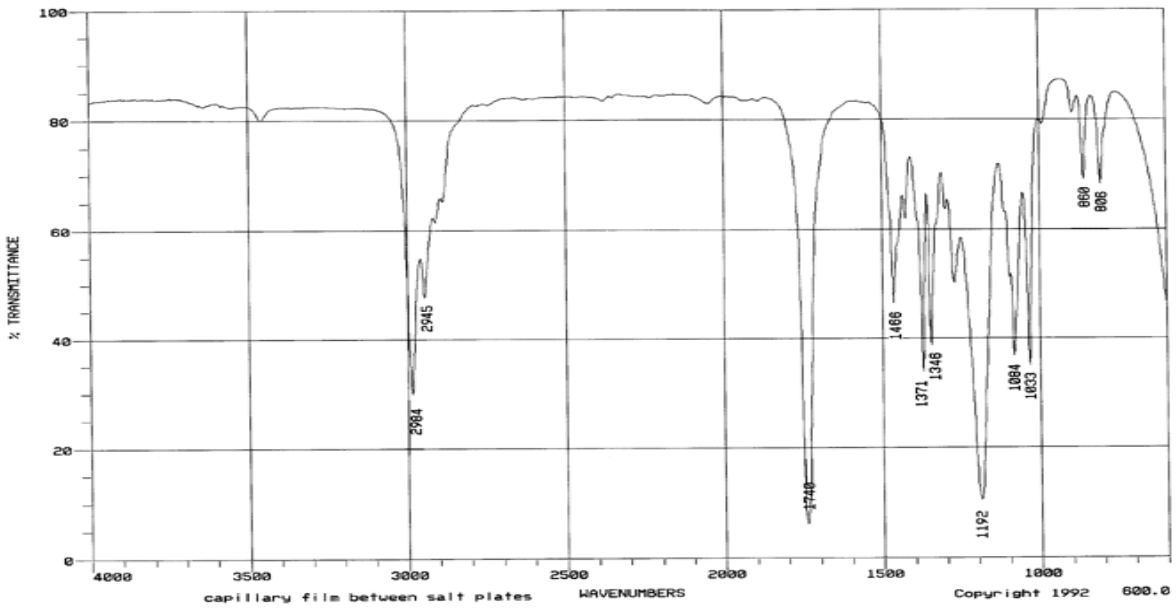
**Questions**

1. How could you tell if an unknown is an alcohol by examining its IR spectrum?
  
  
  
  
  
  
  
  
  
  
2. How could you distinguish between cyclohexane and cyclohexene using IR?
  
  
  
  
  
  
  
  
  
  
3. In general how could you identify a compound as an alkane, alkene, alkyne, or arene using IR?
  
  
  
  
  
  
  
  
  
  
4. An unknown has the following physical data:  
Molecular formula of  $C_3H_8O$   
IR: 3400, 2950, 1460, 1385, 1365, 1100  $cm^{-1}$   
Draw the structures consistent with the analysis. Which one is consistent with the IR data? Assign absorption to support your answer.
  
  
  
  
  
  
  
  
  
  
5. Give absorption frequency range ( in  $cm^{-1}$ ) for each of the following.  
-O-H stretch \_\_\_\_\_ -CO- stretch \_\_\_\_\_ -C-H stretch \_\_\_\_\_  
  
 $\equiv C-H$  stretch \_\_\_\_\_  $= C-H$  \_\_\_\_\_

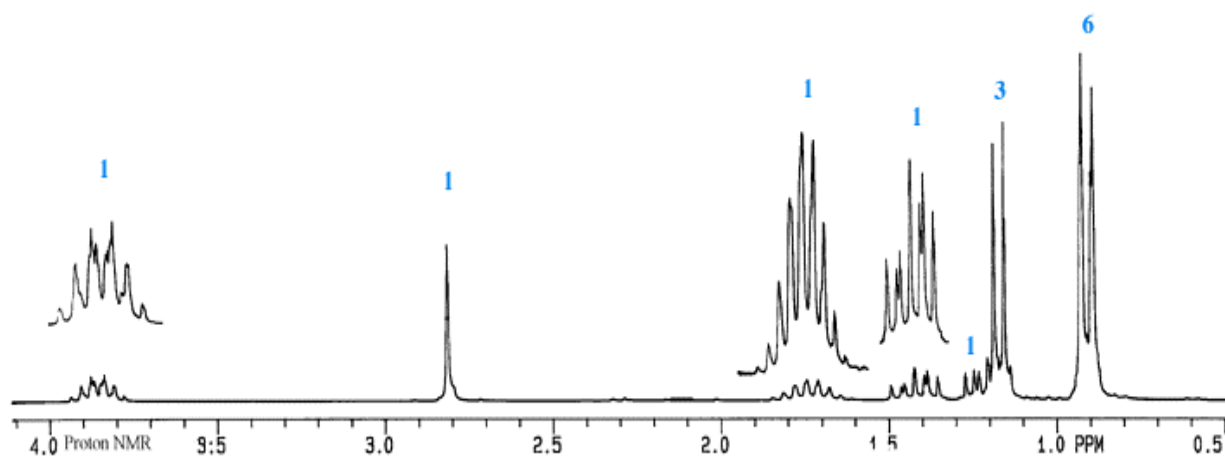
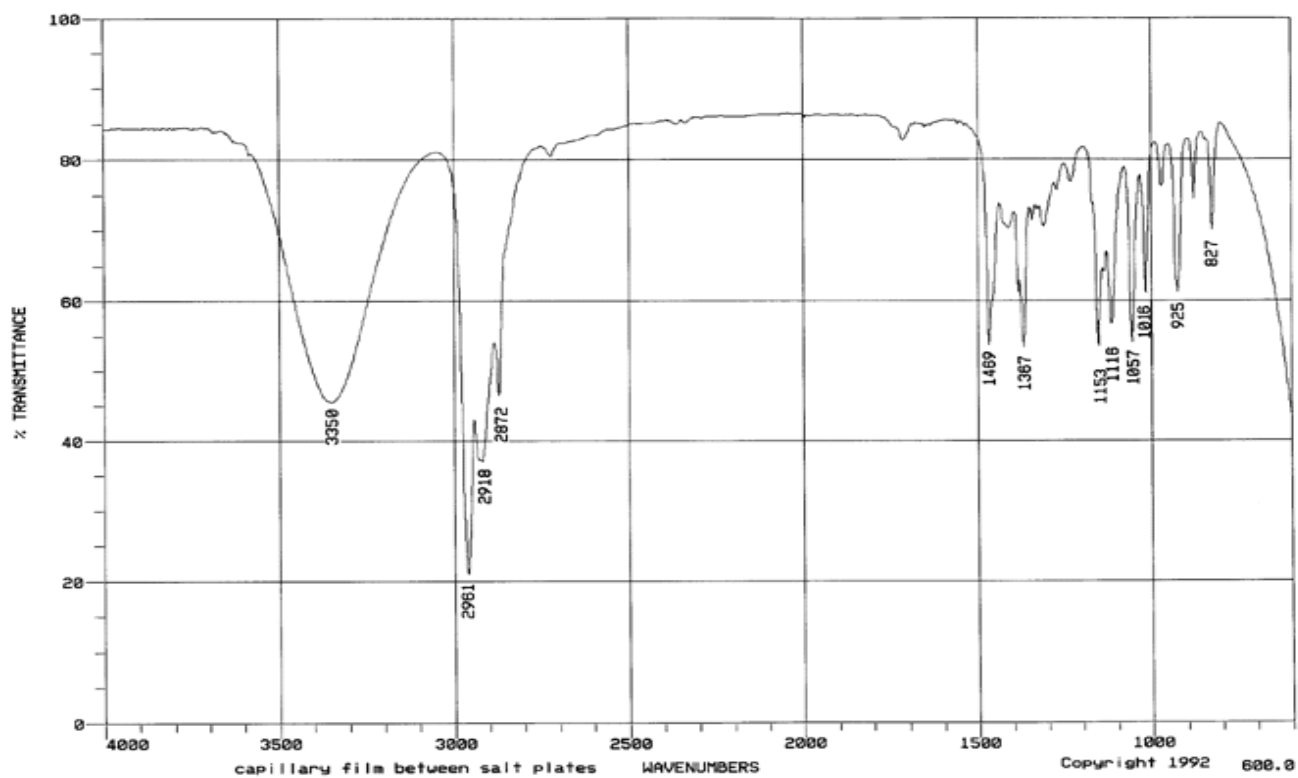
# Problem 1 – C<sub>5</sub>H<sub>10</sub>O



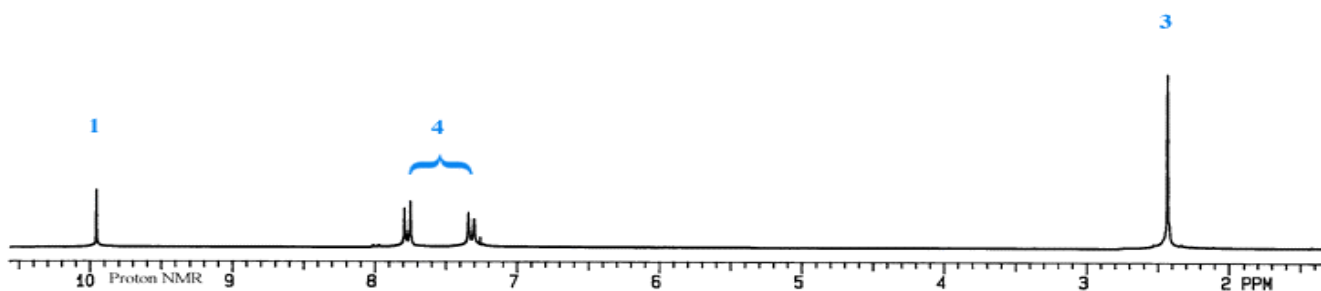
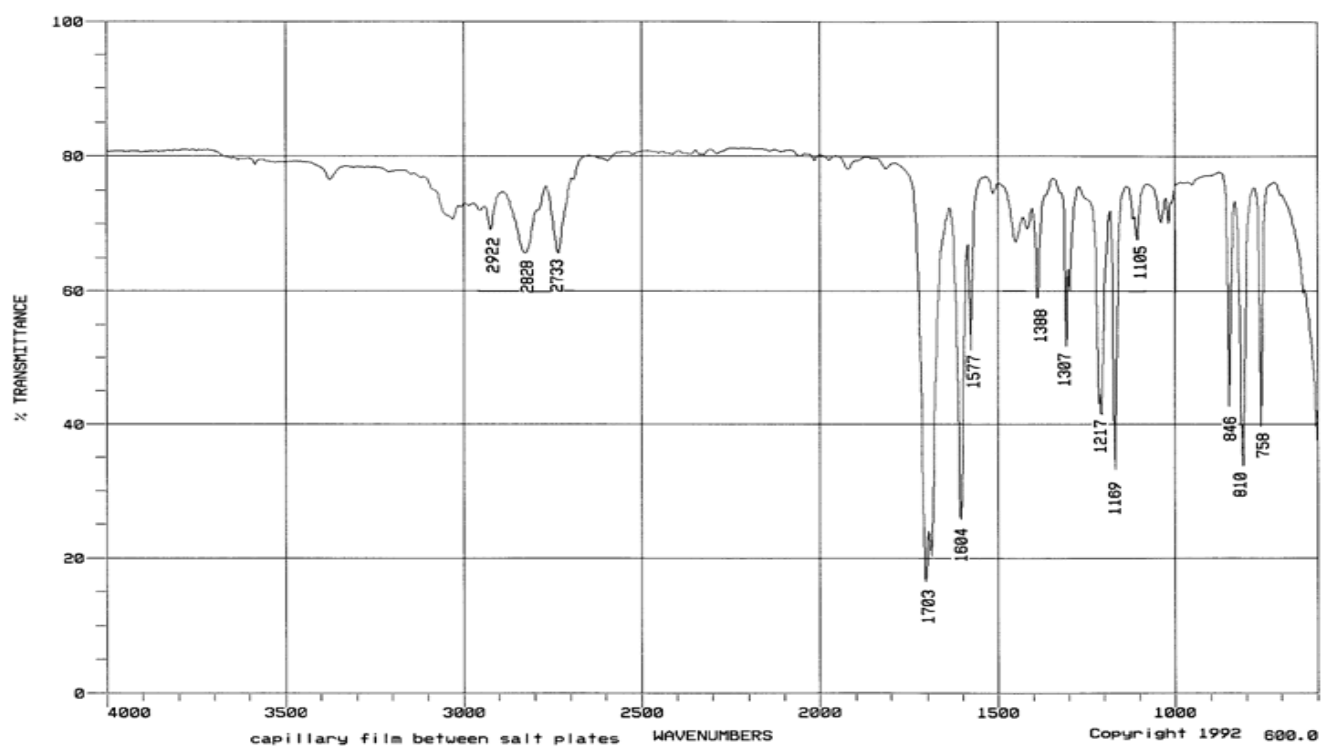
# Problem 2 - C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>



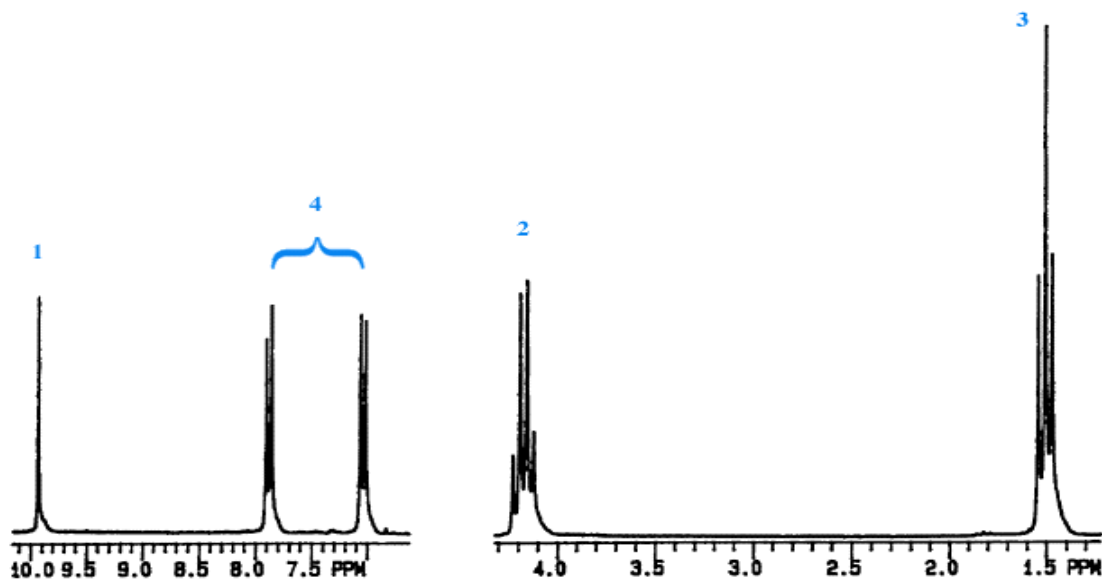
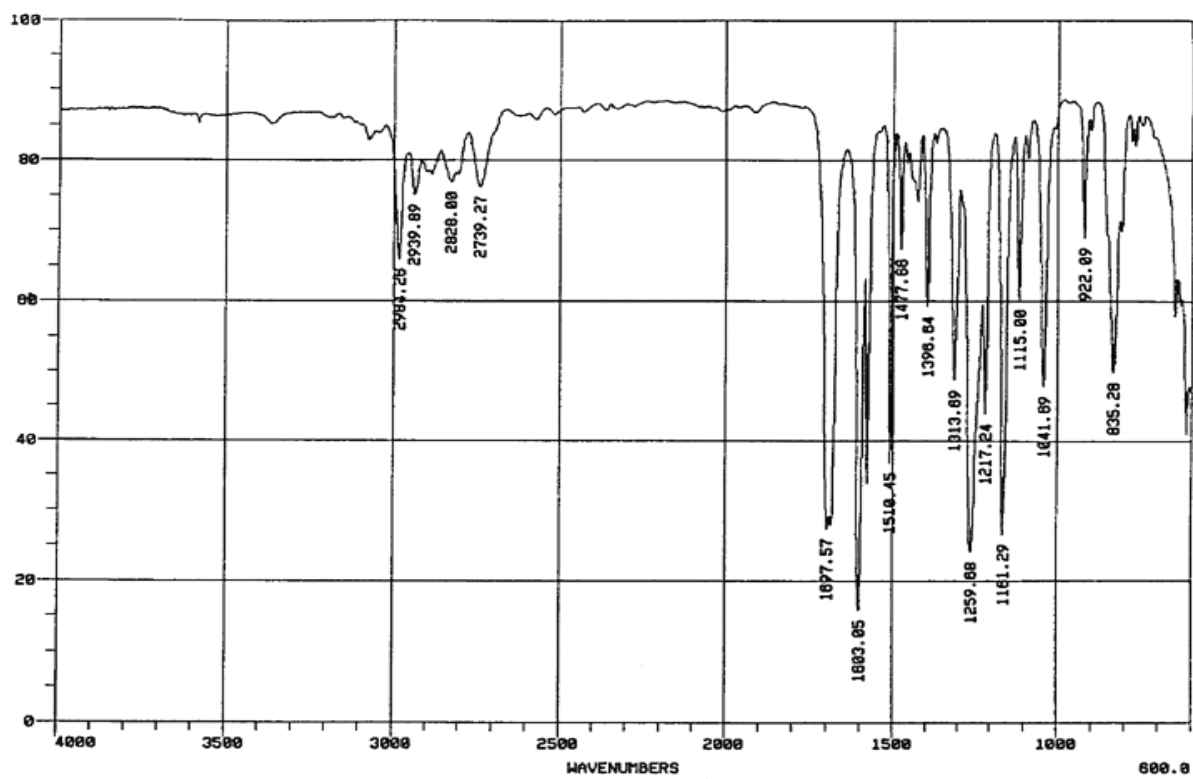
# Problem 3 – C<sub>6</sub>H<sub>14</sub>O



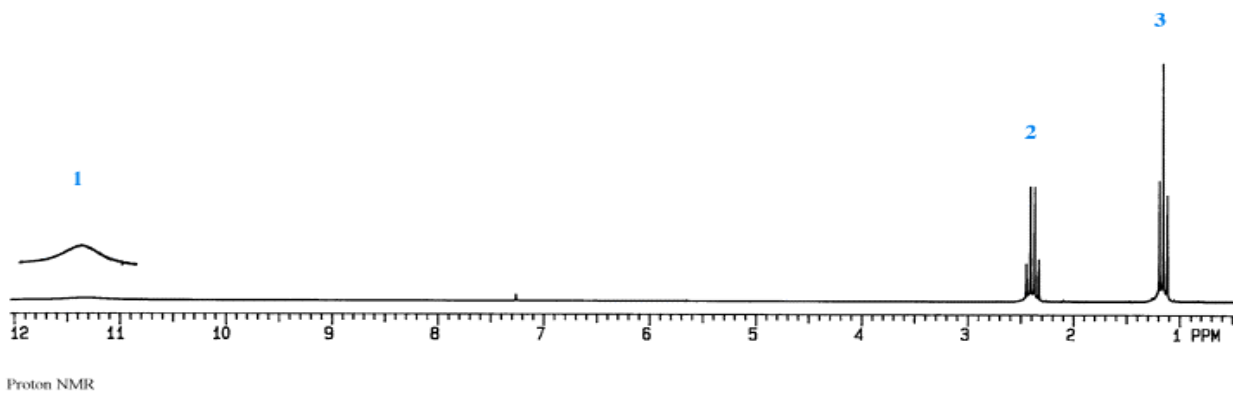
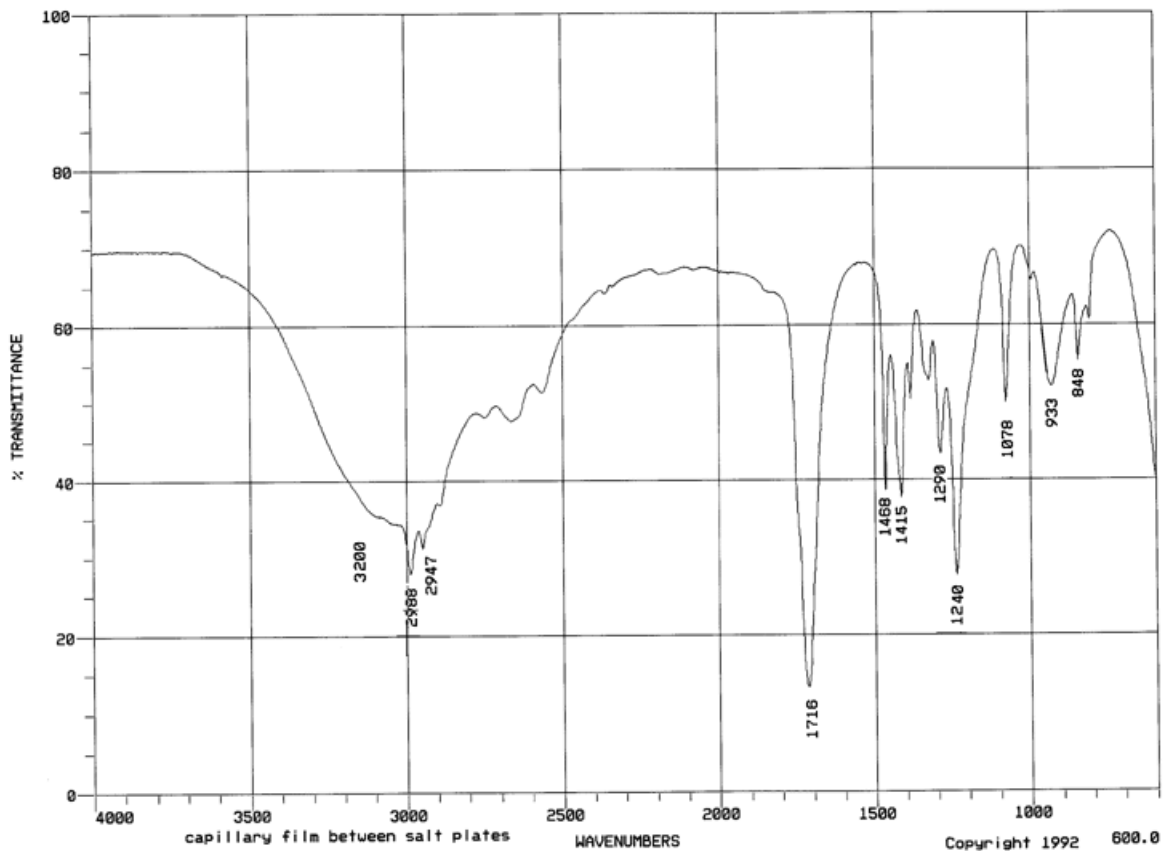
## Problem 4 – C<sub>8</sub>H<sub>8</sub>O



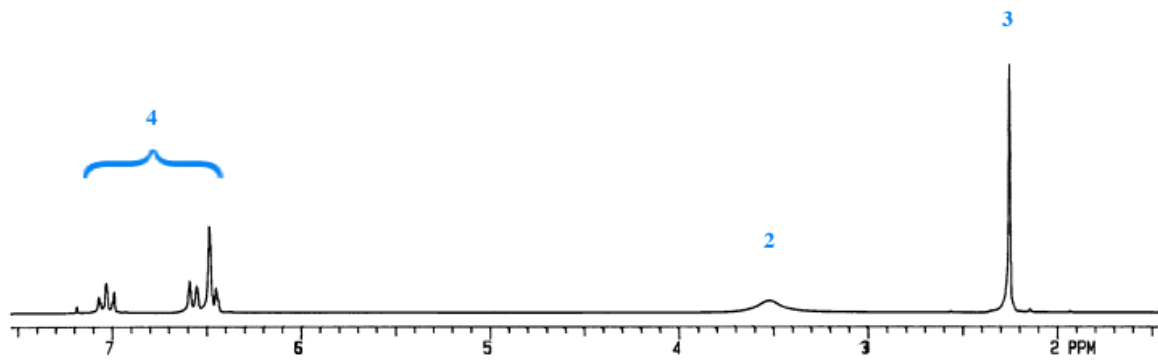
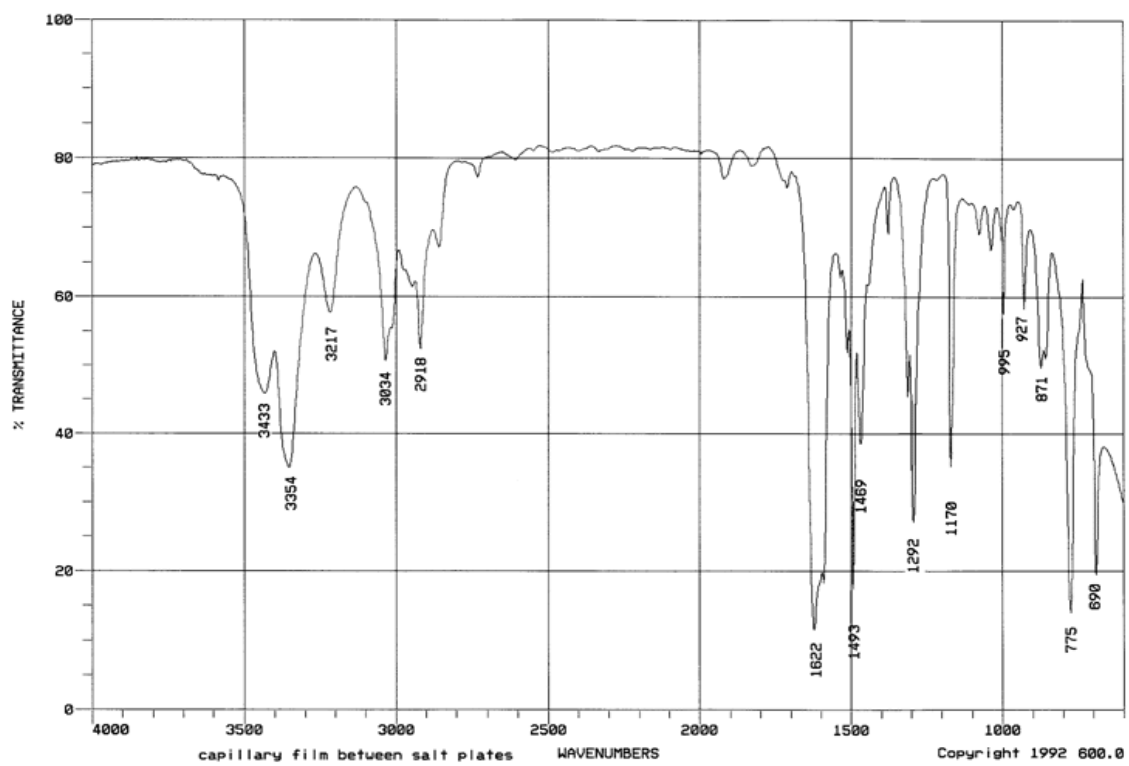
## Problem 5 – C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>



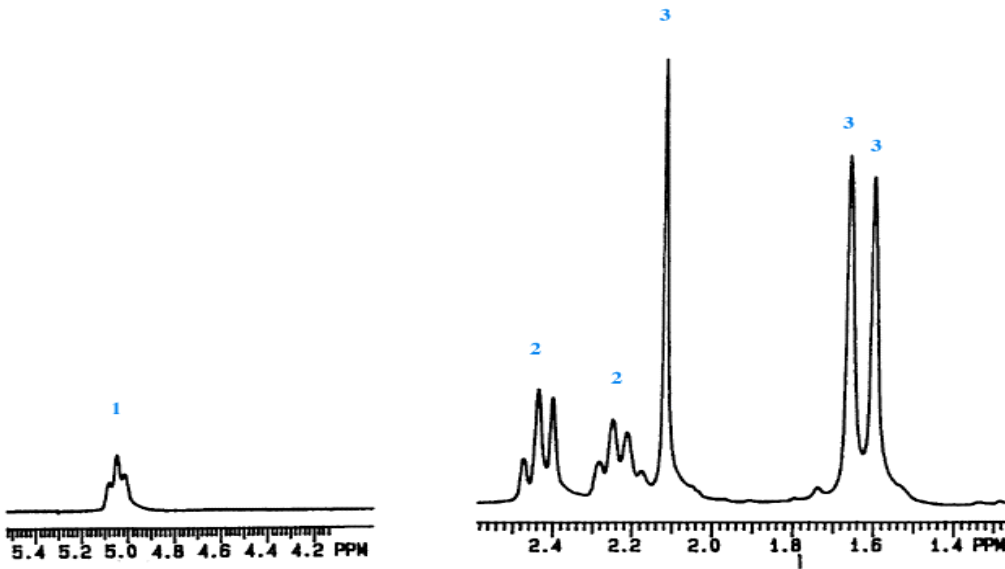
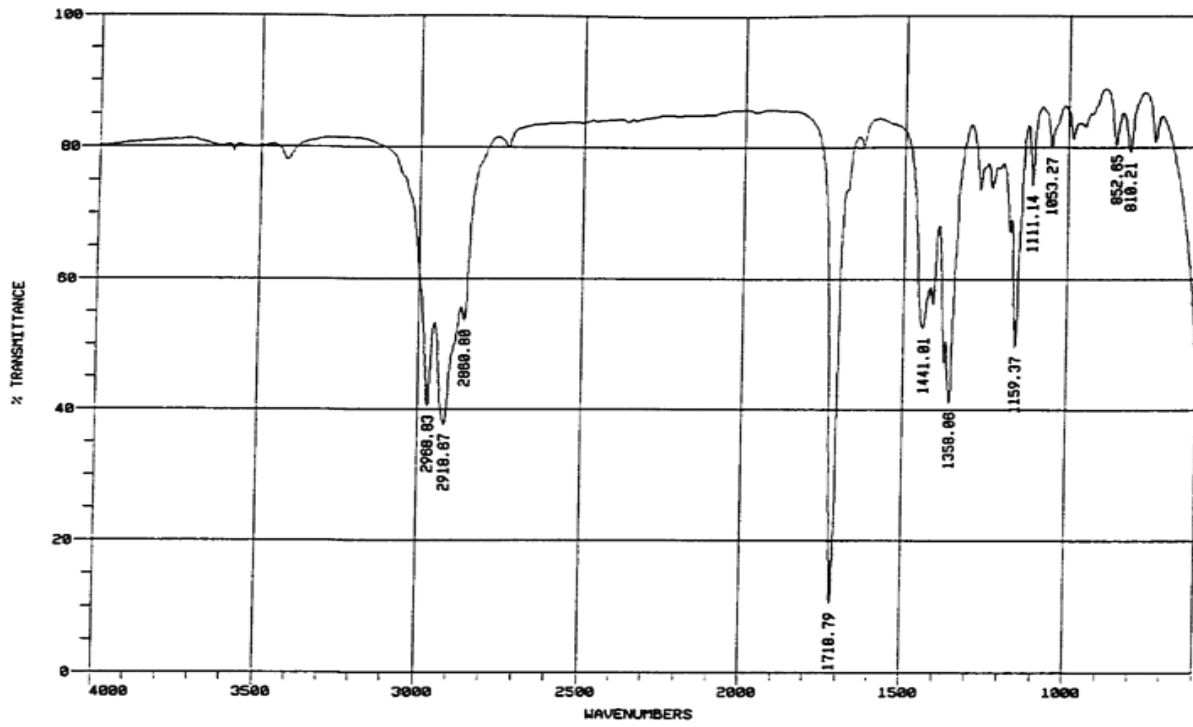
# Problem 6 – C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>



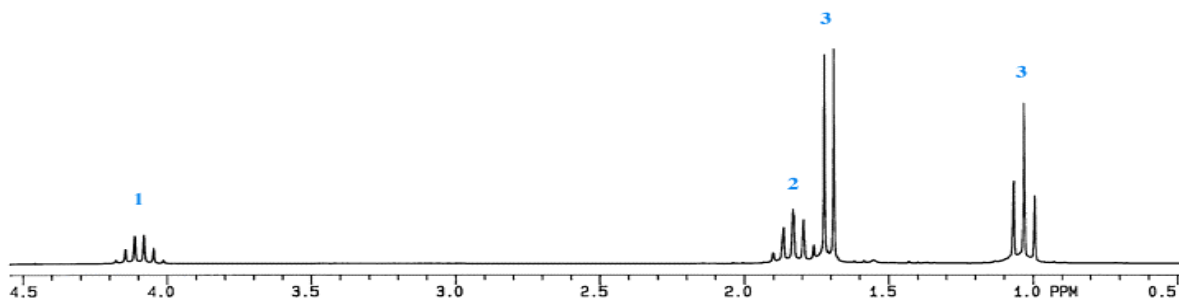
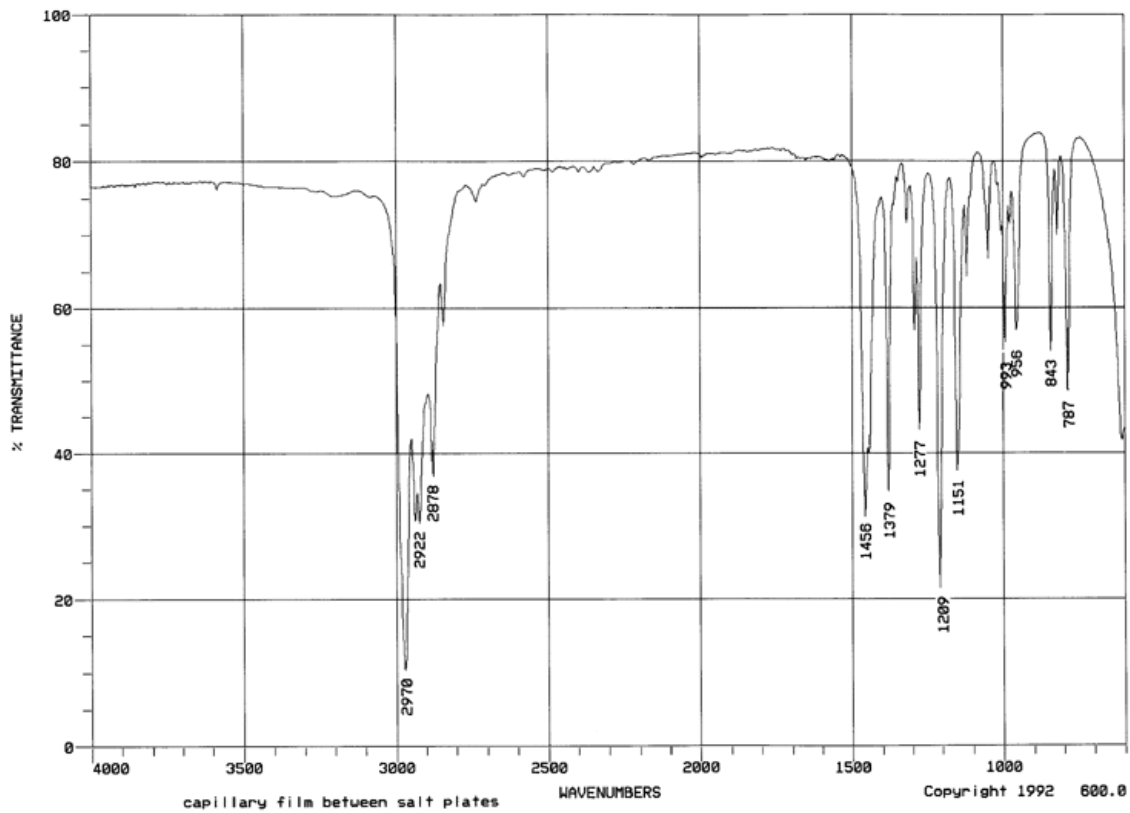
# Problem 7 – C<sub>7</sub>H<sub>9</sub>N



# Problem 8 – C<sub>8</sub>H<sub>14</sub>O



# Problem 9 – C<sub>4</sub>H<sub>9</sub>Br



# Problem 10 – C<sub>10</sub>H<sub>14</sub>O

