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MAIN EXAMINATION

JANUARY – APRIL 2019 TRIMESTER

FACULTY OF SCIENCE

DEPARTMENT OF NATURAL SCIENCE (CHEMISTRY)

REGULAR PROGRAMME

CHEM 305: ORGANIC SPECTROSCOPY

Date: APRIL 2019	**Duration: 2 Hours**
INSTRUCTIONS: Answer Question ONE and ANY OTHER TWO Questions	

Q1. a) Explain the following terms as used in the study of organic spectroscopy. Use appropriate examples. **(5 Marks)**

i) Chromophores
ii) IR stretches and bends
iii) Chemical shift
iv) Molecular ion

b) i) Explain the working principle of a UVvis spectrophotometer **(3 marks)**

ii) Given that, the correlations of conjugated diene according to Woodward-Feiser rules are as follows:

i) Base value for homoannulardiene = 253 nm
ii) Base value for heteroannulardiene = 214 nm
iii) Alkyl substituent or Ring residue attached to the parent diene = 5 nm
iv) Double bond extending conjugation = 30 nm
v) Exocyclic double bonds = 5 nm
vi) Polar groups: -OAc = 0 nm
-OAlkyl = 6 nm
-Cl, -Br = 5 nm

Calculate the absorption maximum for 1-methylcyclohexa-1,3-diene . **(2 marks)**

c) i) A sample of an organic compound with a mass of 1.224 g was completely burned in oxygen and found to produce 2.340 g of carbon (IV) oxide and 1.433 g of water only. The molecular mass of the compound was 46.0 a.m.u.

i) Calculate the empirical and molecular formula of the organic compound. **(3 marks)**

ii) Propose possible functional isomers of the compound. **(2 marks)**

ii) Consider the mass spectrum of benzoic acid **(Figure 1)** and identify the ions responsible for the major peaks. **(2 marks)**

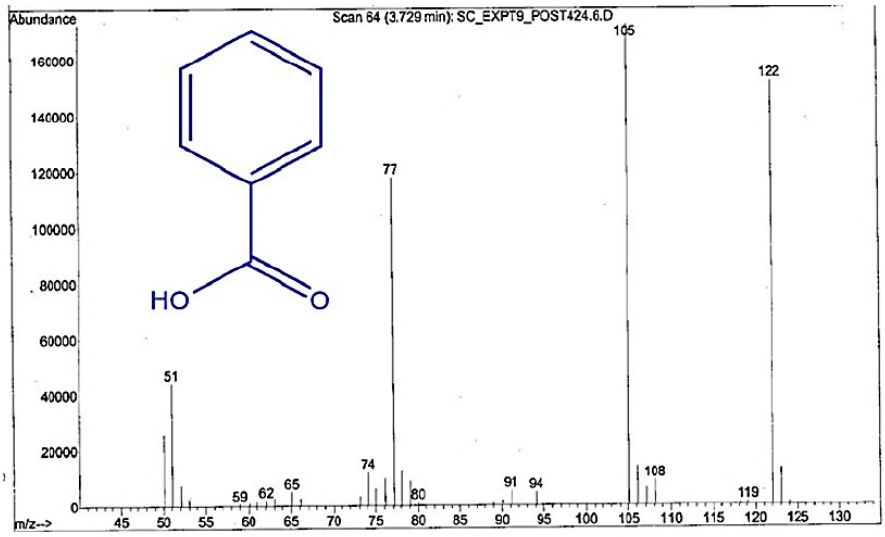


Figure 1

d) The IR spectra in **Figure 2 and 3** are of ethanol and ethanoic acid. Draw the full structural formula for both compounds, and then determine giving reasons, which spectrum is due to which compound. **(4 marks)**

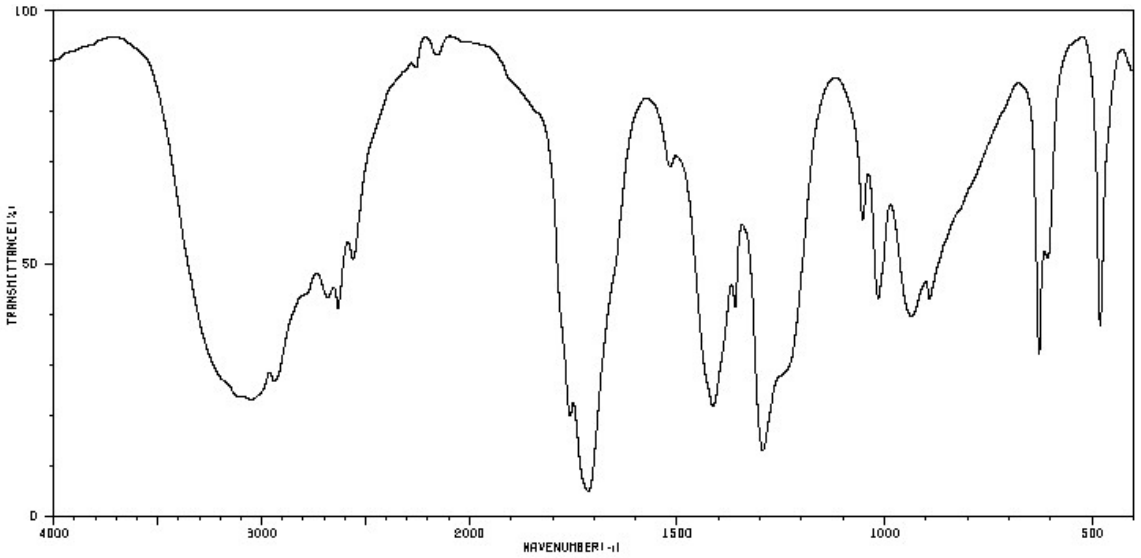


Figure 2

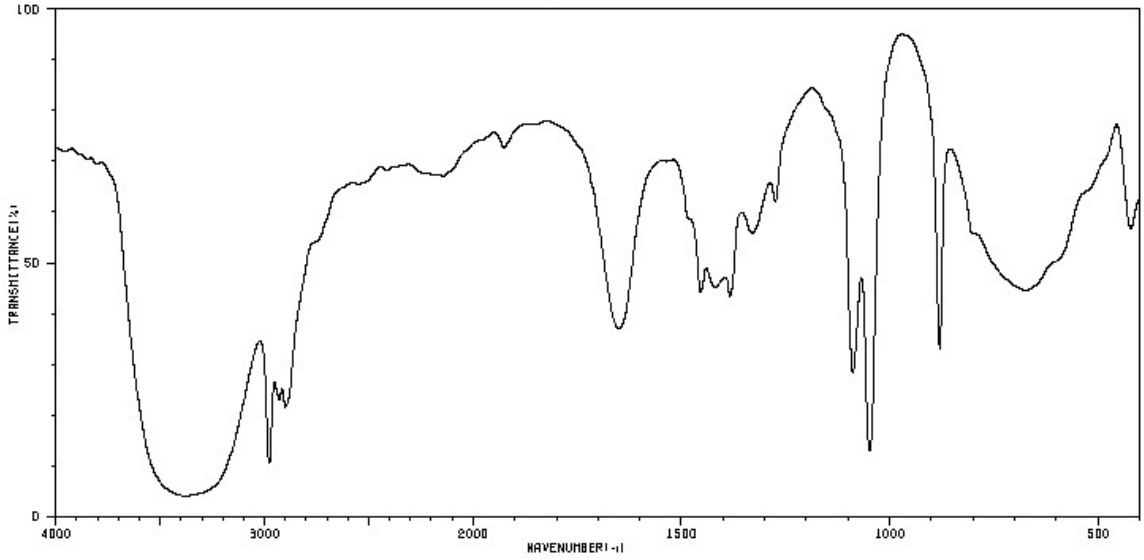


Figure 3

e) Predict the multiplicities of the signals in the proton NMR spectra of the following compounds. **(5 Marks)**

i) $CH_3CH(Cl)CH_2CH_2Cl$

ii) $CH_3CO_2CH(CH_3)CH_2CH_3$

f) The following is data from IR **(Figure 4a)** and ^1H NMR spectra (300 MHz) **(Figure 4b)** of a compound A. The molecular formula of compound A is $C_4H_8O_2$ and it contains one unsaturation. **(4 marks)**

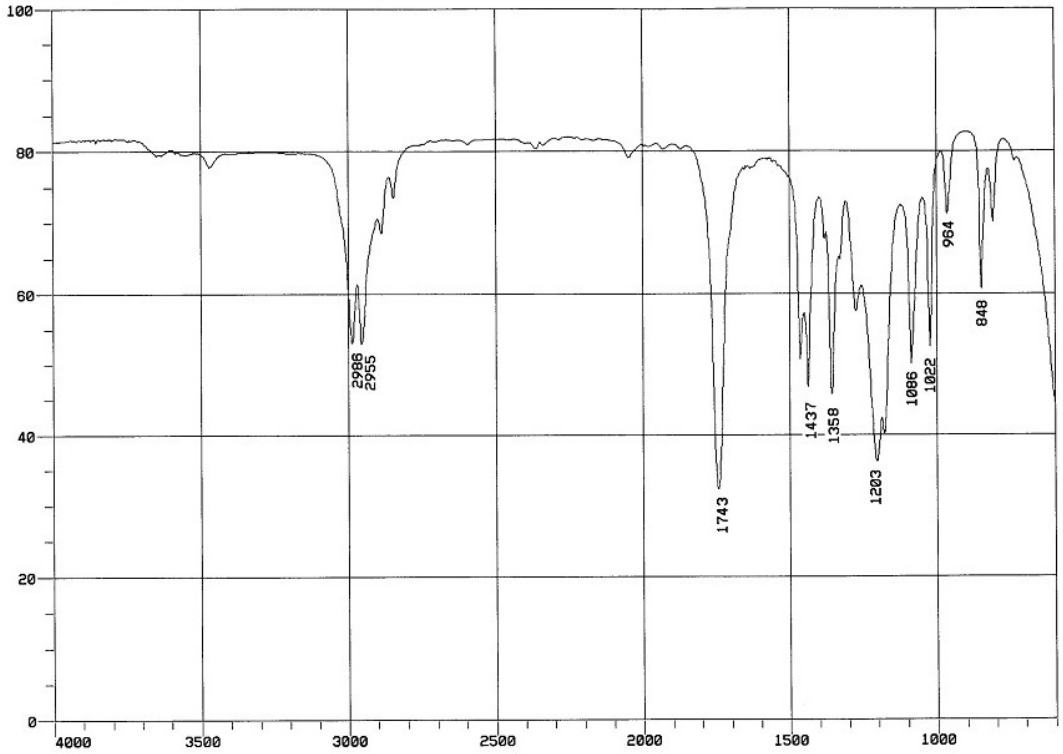


Figure 4a

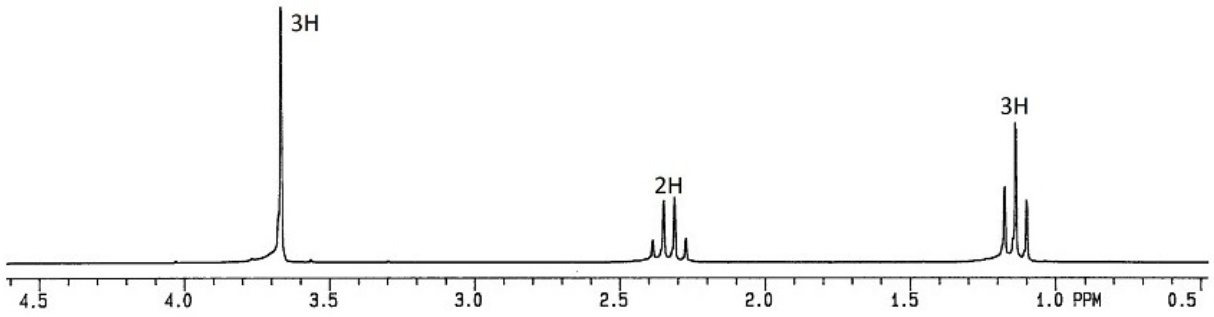


Figure 4b

Q2. a) The spectra provided below **(Figure 5 a – d)** were obtained when a molecules was analyzed. Use the spectra to provide a structure that is consistent with the data. (Give your reasoning). **(10 marks)**

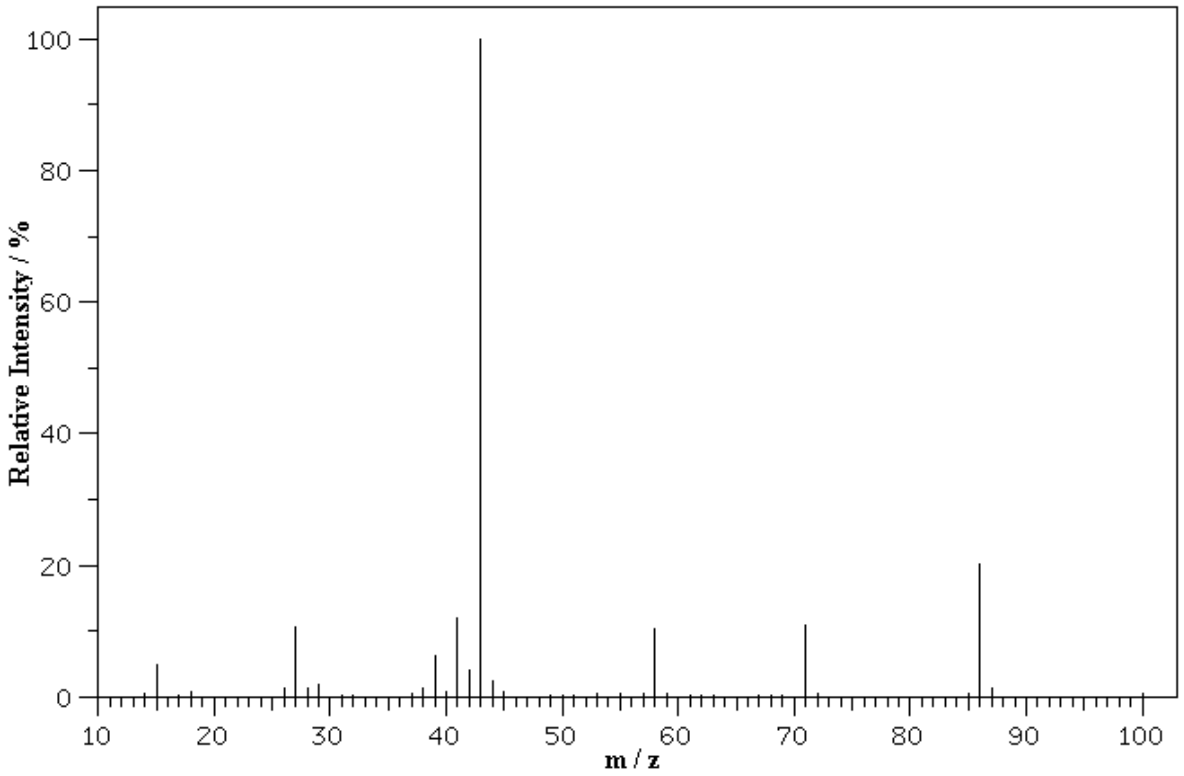


Figure 5a

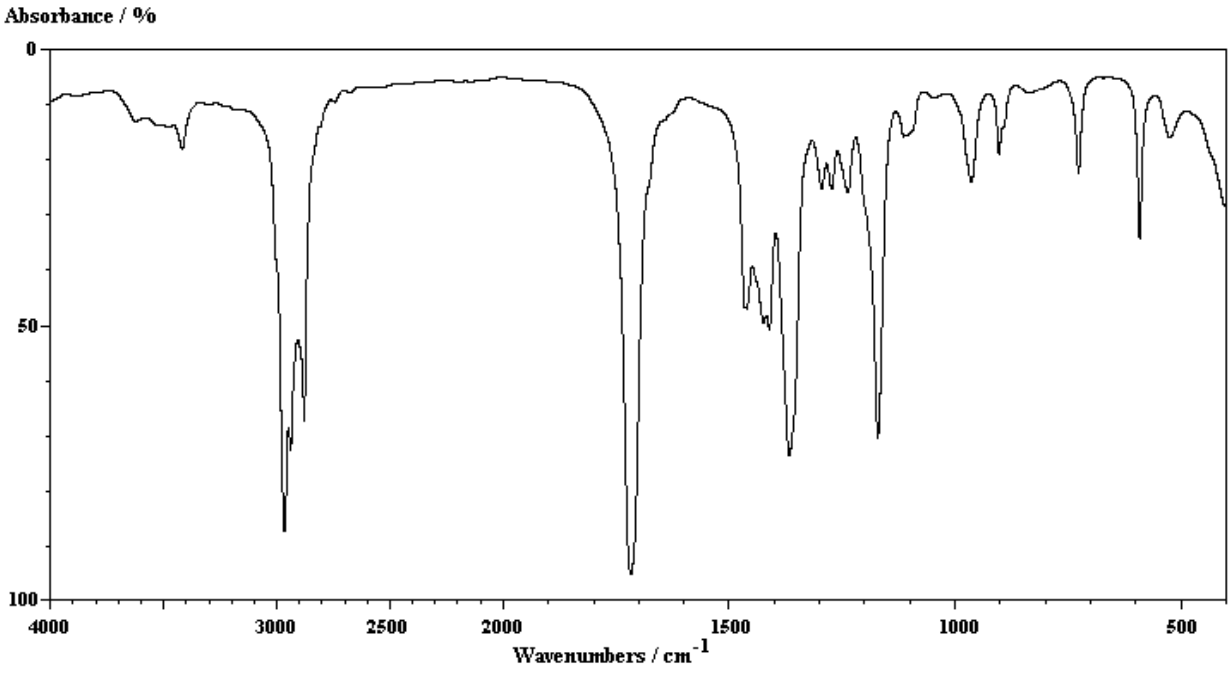

Absorbance / %
0
50
100
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1

Figure 5b

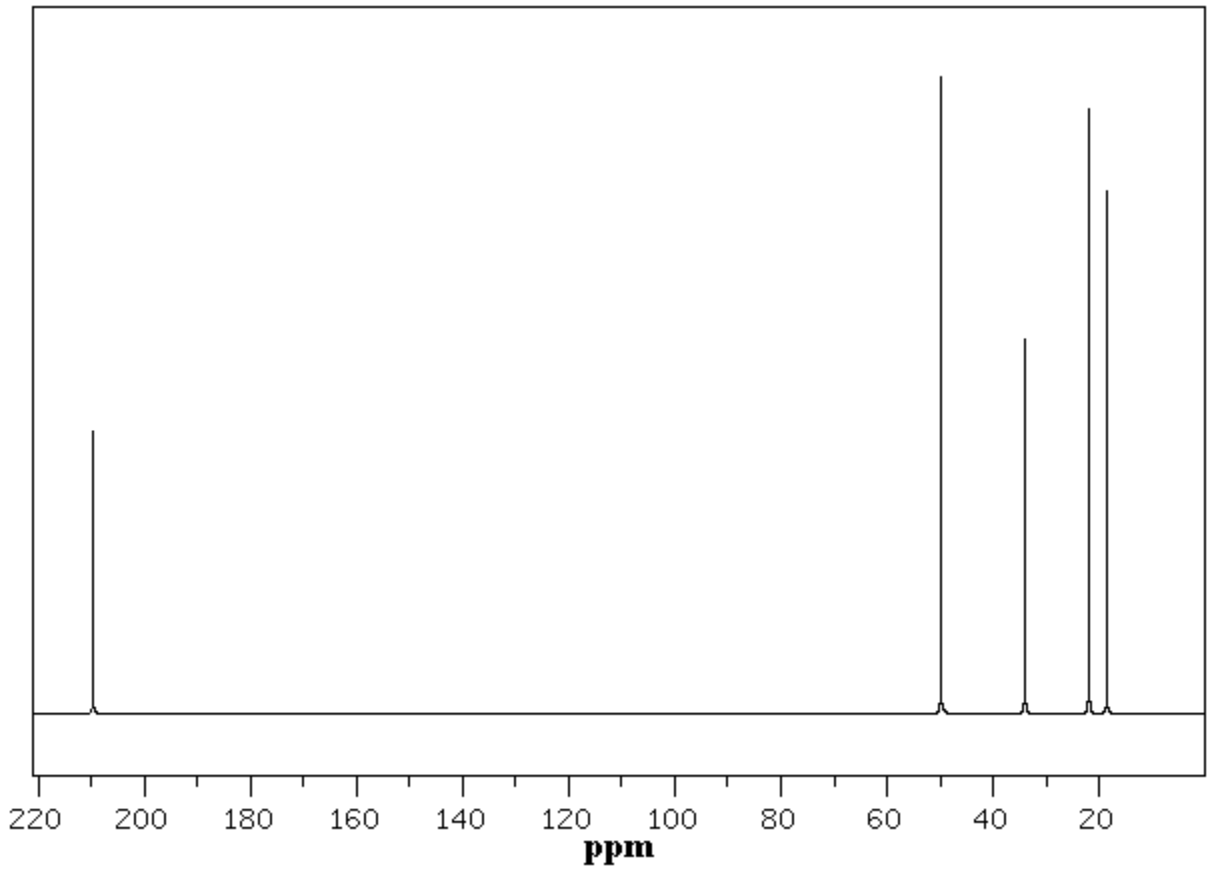


Figure 5c

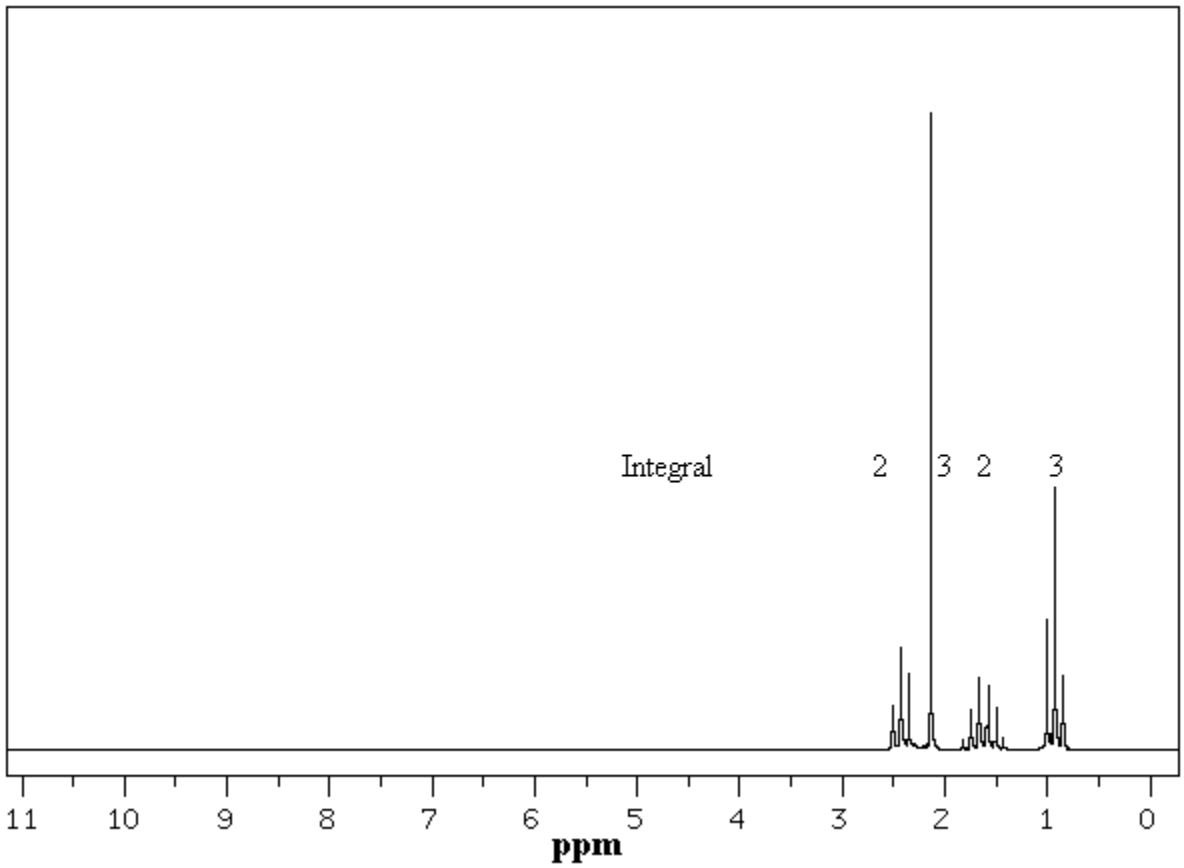


Figure 5d

b) Give structure(s) consistent with each of the following sets of NMR data:

i) $C_9H_{11}Br$: δ 2.15 (2H quintet), δ 2.75 (2H, singlet), 3.38 (2H, triplet) and δ 7.22 (5H, singlet) **(5 marks)**

ii) C_6H_{10}: triplet δ 22.9, triplet δ 25.3 and doublet δ 134.2 **(5 marks)**

Q3. a) The most intense peak in the mass spectrum of 2,2-dimethylbutene occur at m/z 29 and 86. Account for the peaks and show the carbocations associated with the peaks **(4 Marks)**

b). i) Two isomeric compounds J and K with the same molecular formula $C_6H_{12}O_2$ have the following ^1H NMR peaks.
J: δ 1.44 (9H, singlet) and 1.95 (3H, singlet)
K: δ 1.20 (9H, singlet) and 3.67 (3H, singlet)

ii) Compounds J and K have IR peaks at 1715 – 1750 cm^{-1}
Suggest the structures of J and K, and assign the chemical shift values to the hydrogen atoms in the respective structure.

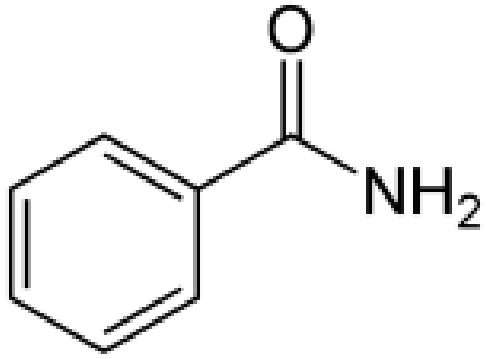
(6 marks)

Q4. a) Listed below are some spectra and molecular formulae of some organic molecules. Propose with reasons, a structure that is consistent with each set of data.

i) MF: C_4H_8O; IR: 1720 cm-1, ^{1}H NMR δ 1.05 (3H, t), 2.13 (3H,s)

ii) MF: C_7H_8O; IR: 3550 - 3200 cm-1, ^{1}H NMR δ 2.43 (1H, s), 4.58 (2H,s) and 7.28 (5H,m) **(10 marks)**

b) Predict the main IR absorption peaks one would expect in the spectrum of benzamide. **(5 marks)**



Benzamide

c) Predict the ^{13}C and ^{1}H NMR peaks that one would expect in the spectrum of benzamide. Show your reasoning. **(5 marks)**

Q5. a) The spectra provided below (Figure 6 a- d) were obtained when a molecules C_7H_8O was analyzed. Use the spectra to identify the molecule (Give your reasoning). Hint: the compound is aromatic. **(10 marks)**

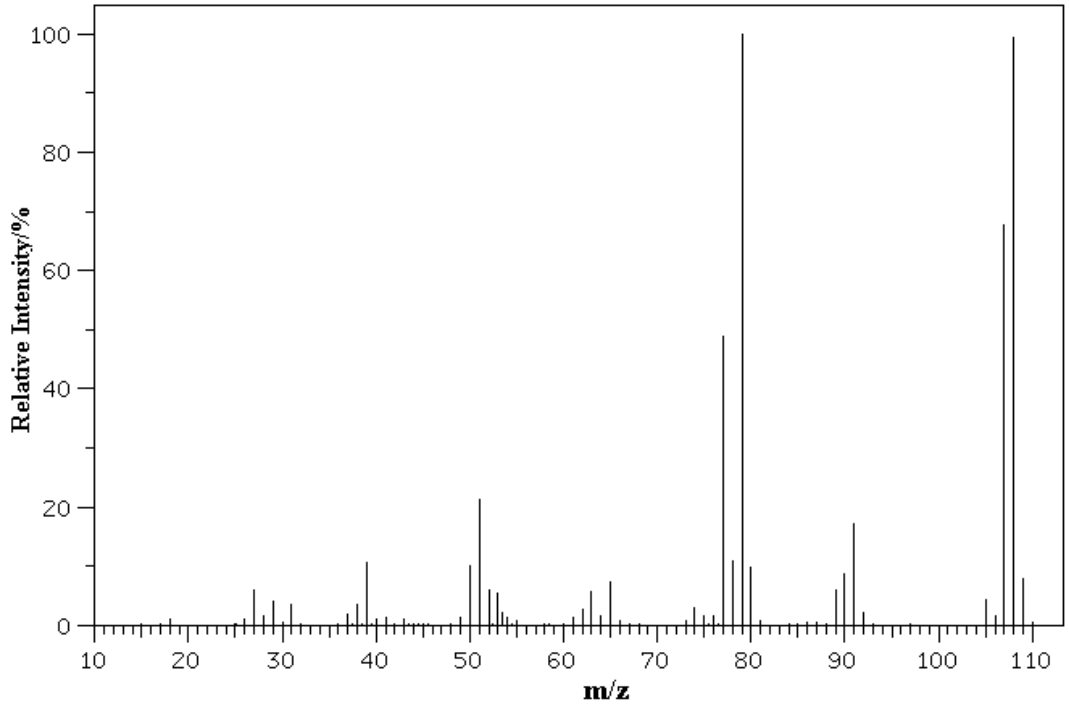


Figure 6a

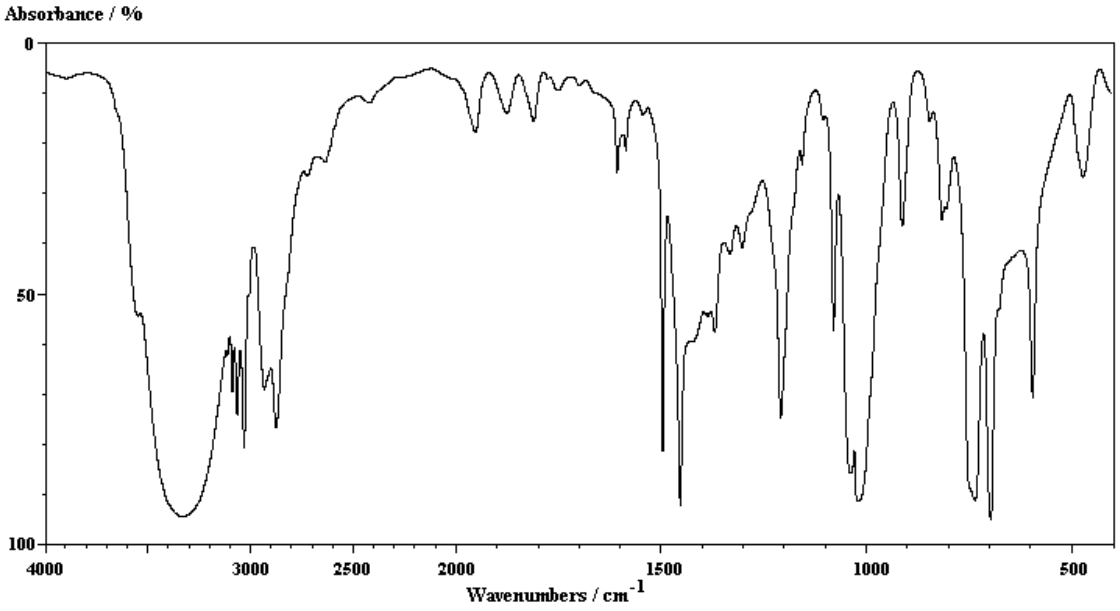


Figure 6b

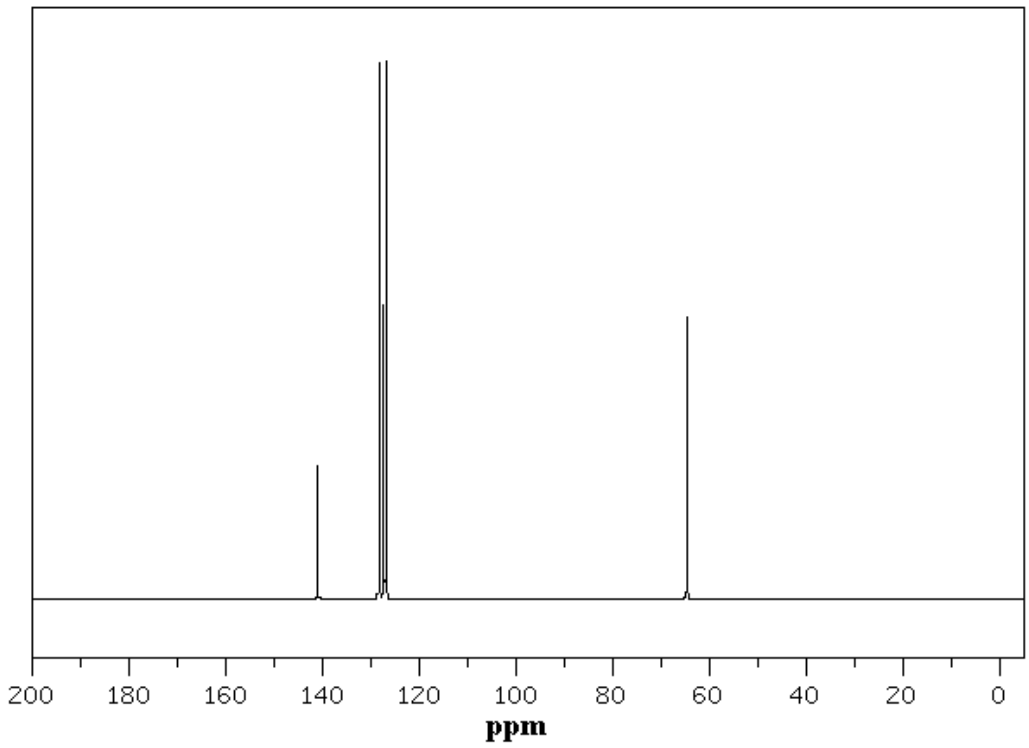


Figure 6c

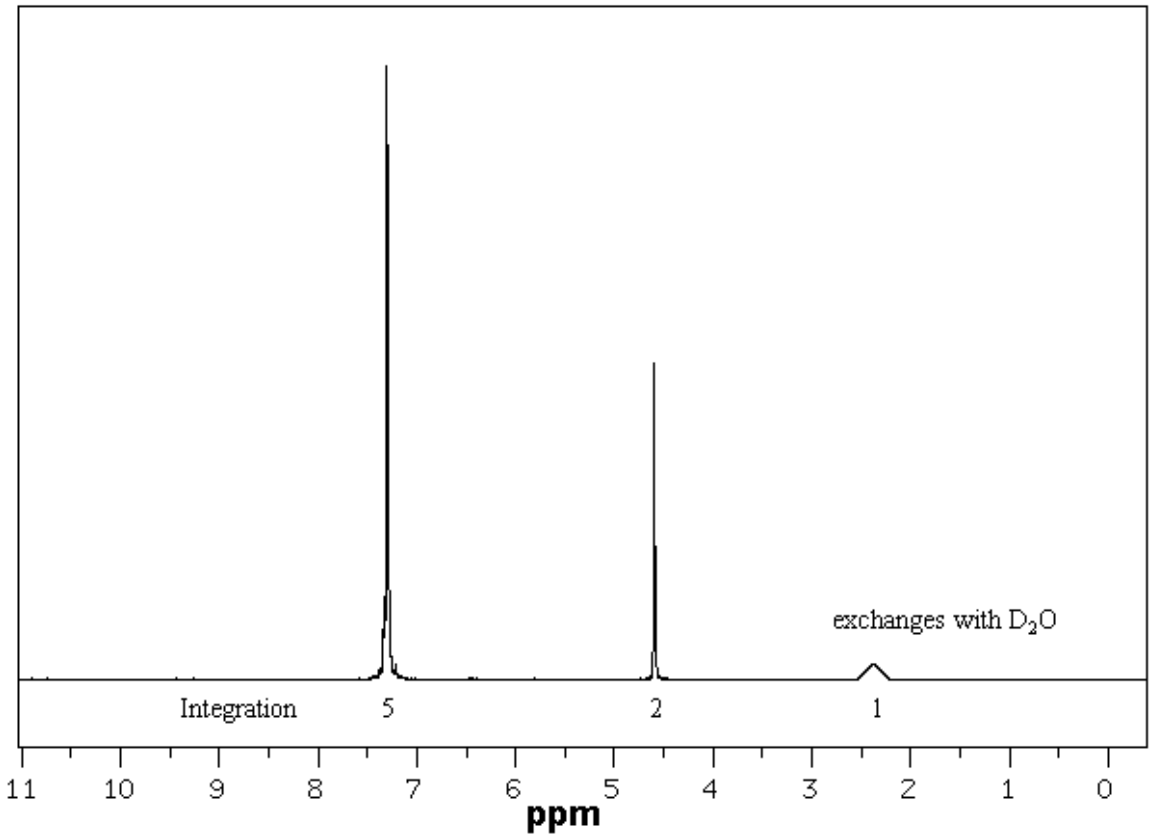


Figure 6d

b) i) Draw block diagrams of a Mass Spectrophotometer (MS). **(4 marks)**

ii) Explain the function of each part of the MS and explain how it is used to obtain spectra **(6 marks)**

END