UNIVERSITY OF ESWATINI
RE-SIT EXAMINATION 2018/2019

TITLE OF PAPER	:	ORGANIC SPECTROSCOPY & STRUCTURE ELUCIDATION
COURSE NUMBER	:	CHE 331
TIME	:	Three Hours
INSTRUCTIONS	:	Answer any **FOUR Questions**

This Paper contains 11 printed pages

You must not open this paper until the Chief Invigilator so has granted permission to do.

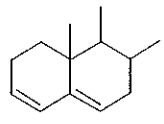
Question 1

(a)Calculate the Index of Hydrogen deficiency of the following compounds.

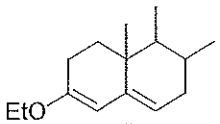
(i) $C_6H_6N_2O$
(ii) $C_{29}H_{50}O$
(iii) C_4H_3IS
(iv) $C_9H_{11}IN_2O_6$
(v) $C_{11}H_{12}Cl_2N_2O_5$

[5]

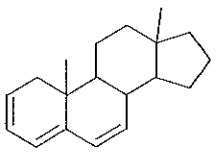
(b) Use the Woodward-Fieser rules to calculate λmax for the following compounds.



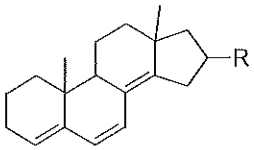
A



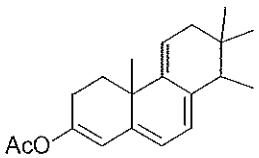
B



C



D



E

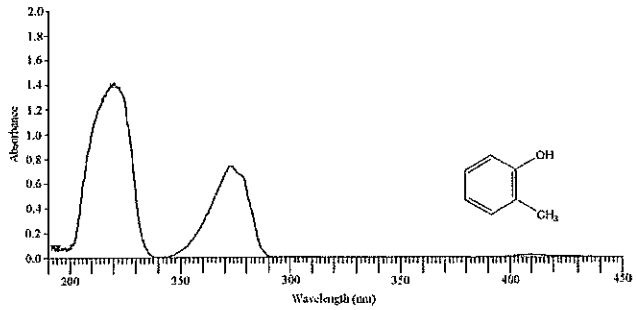
[15]

(c) Define using examples;

(i) exo double bond
(ii) endo double bond. [2]

(d) The spectrum shown below was obtained from a solution of 4.60 mg of *O*-cresol in 100 ml of ethanol and was recorded using a 1cm cell. For the peak at 273 nm the absorbance is 0.75, calculate the molar extinction coefficient ε.

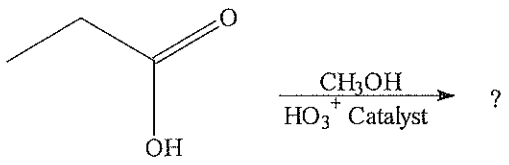
[3]



Question 2

(a) Carboxylic acids (RCOOH) react with alcohols (R^1OH) in the presence of an acid catalyst. The reaction product of propanoic acid with methanol has the following MS, IR, and NMR data. Propose a structure for this product.?

[8]



MS $M^+ = 88$

IR 1735 cm^{-1}

^1H 1011 δ (3H, triplet, J = 7 Hz); 2.32 δ (2H, quarted, J = 7 Hz); 3.65 δ (3 H, singlet)

Broadband – decoupled 13C NMR: 9.3, 27.6, 51.4, 174 δ

(b) Propose a structure for a compound $C_5H_{12}O$ that fits the following: (3H, triplet J = 7 Hz); 1.2 δ (6 H, singlet); 1.50 δ (2H, quartet J = 7 Hz); 1.64 δ (1 H, broad singlet)

[9]

(c) Propose a structure for the alcohol $C_4H_{10}O$ that has the following :

^{13}C NMR spectral data:

Broadband – decoupled ^{13}C NMR
19.0, 31.7, 69.5 δ
Dept – 90: 31.7 δ
Dept – 135 positive peak at 19.0 δ, negative peak at 69.5 δ

[8]

Question 3

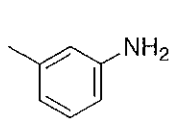
(a) Propose a structure for an aromatic hydrocarbon $C_{11}H_{16}$, that has the following ^{13}C NMR data.

Broadband decoupled C NMR: 29.5, 31.8, 50.2, 125.5, 127.5, 130.3, 139.8 δ

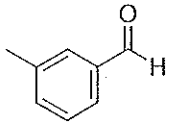
DEPT -90: 125.5, 127.5, 130.3 δ
DEPT -135: Positive Peaks at 29.5, 125.5, 127.5, 130.3 δ Negative Peak at 50.2 δ

[10]

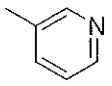
(b) Each of the following IR spectra is associated with one of the aromatic compounds below. Identify the compound associated with each spectrum. [15]



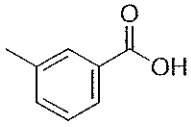
m-toluidine



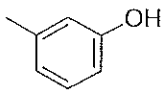
m-tolualdehyde



3-methylpyridine

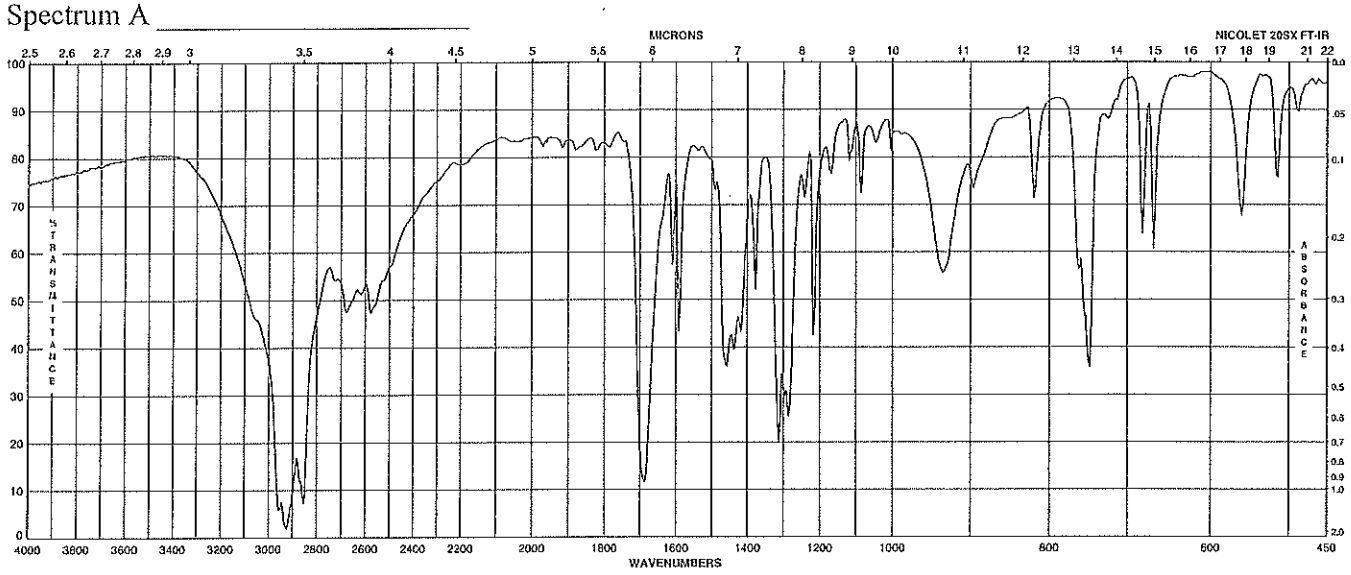


m-toluic acid

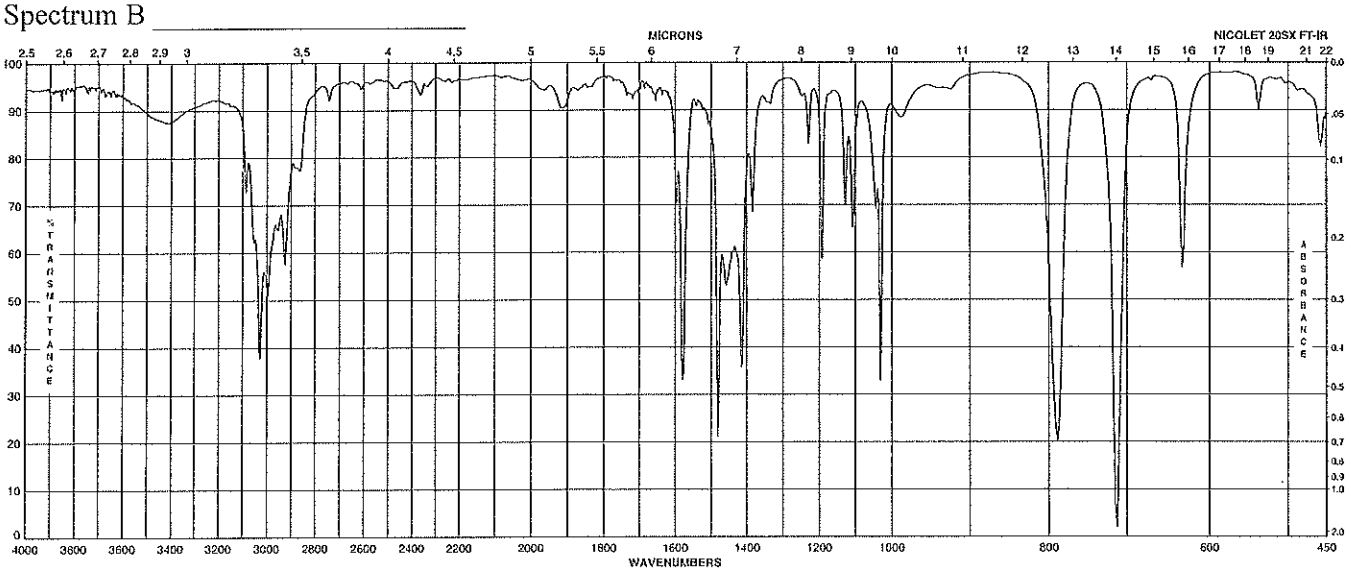


m-cresol

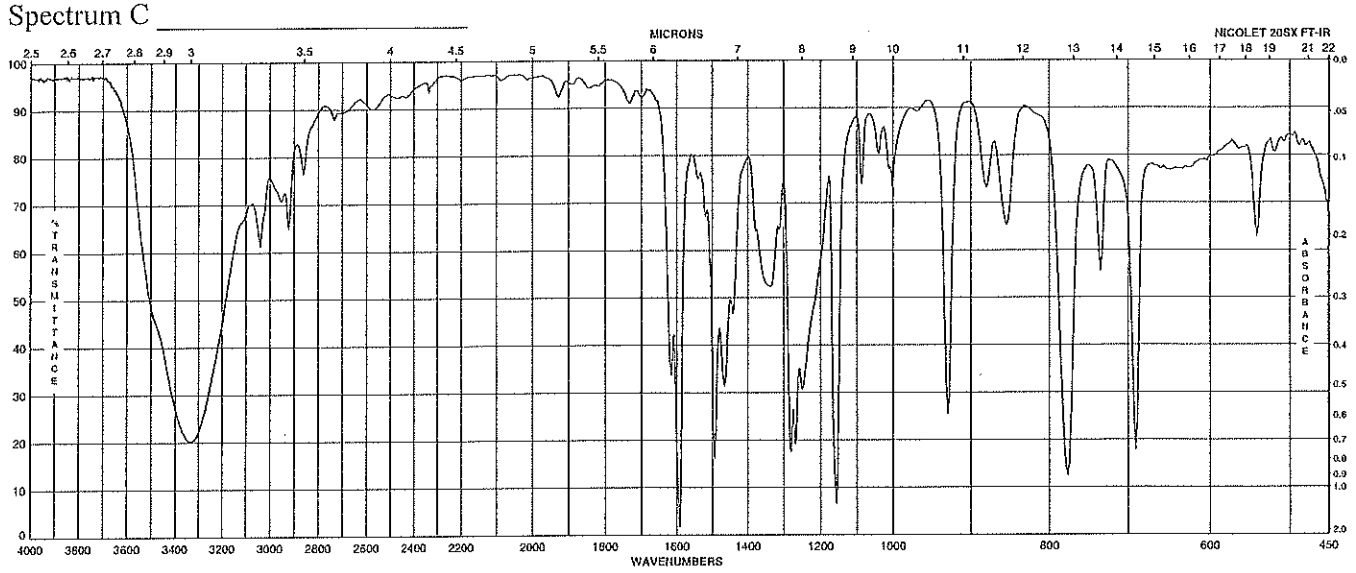
Spectrum A _____



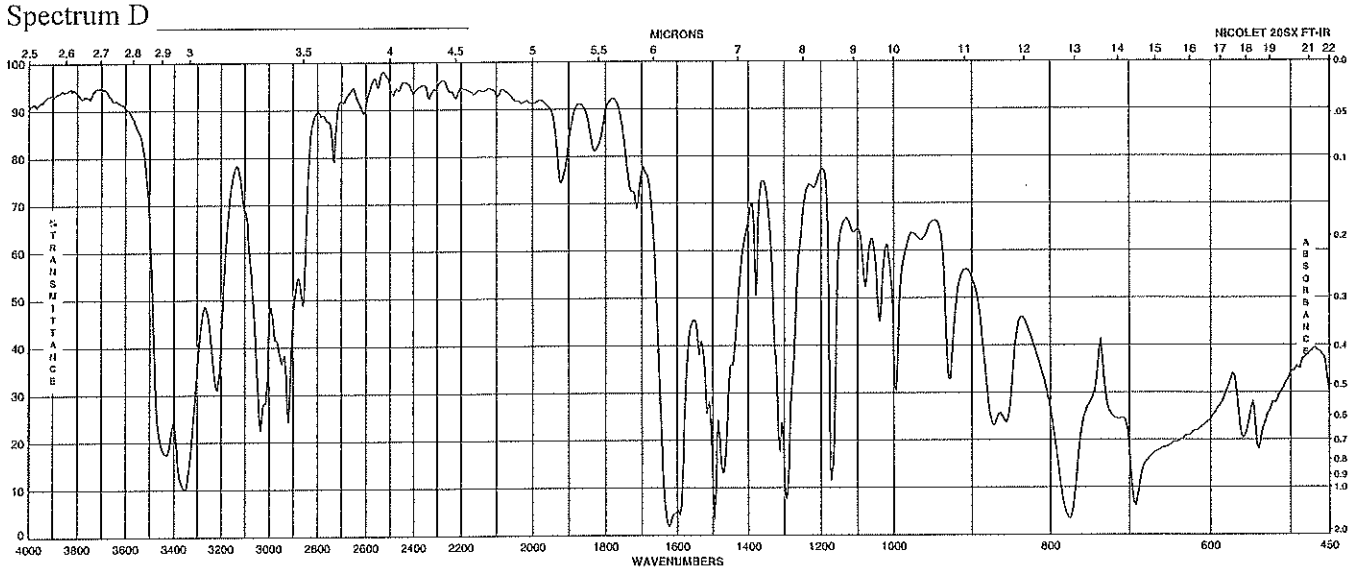
Spectrum B _____



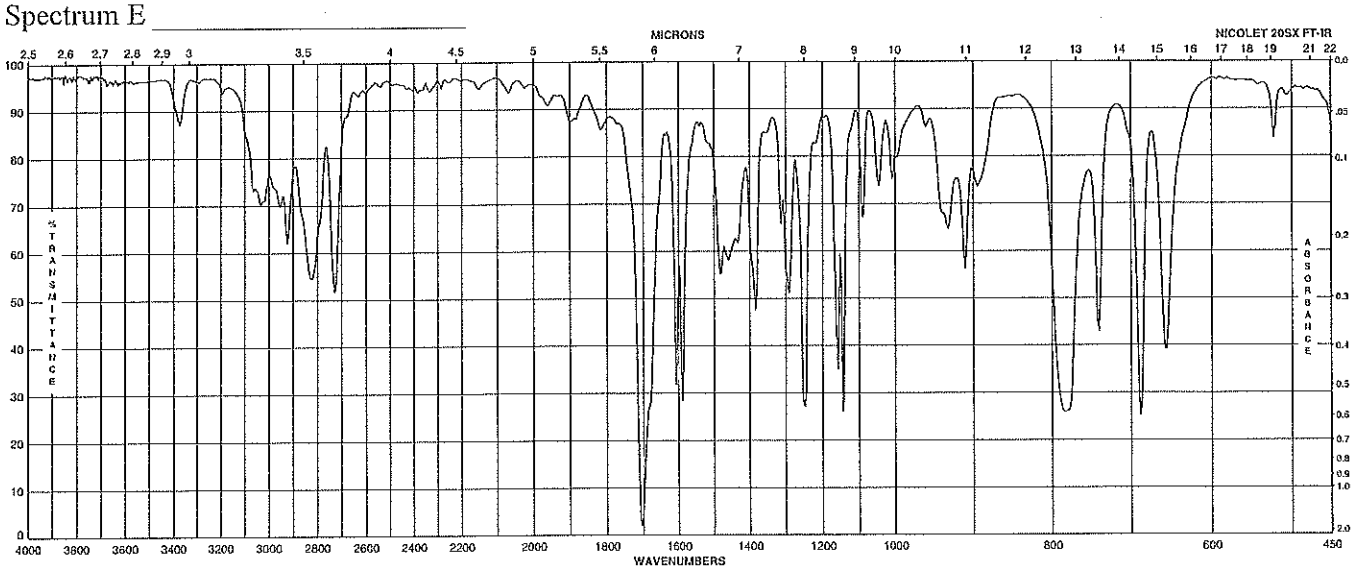
Spectrum C



Spectrum D

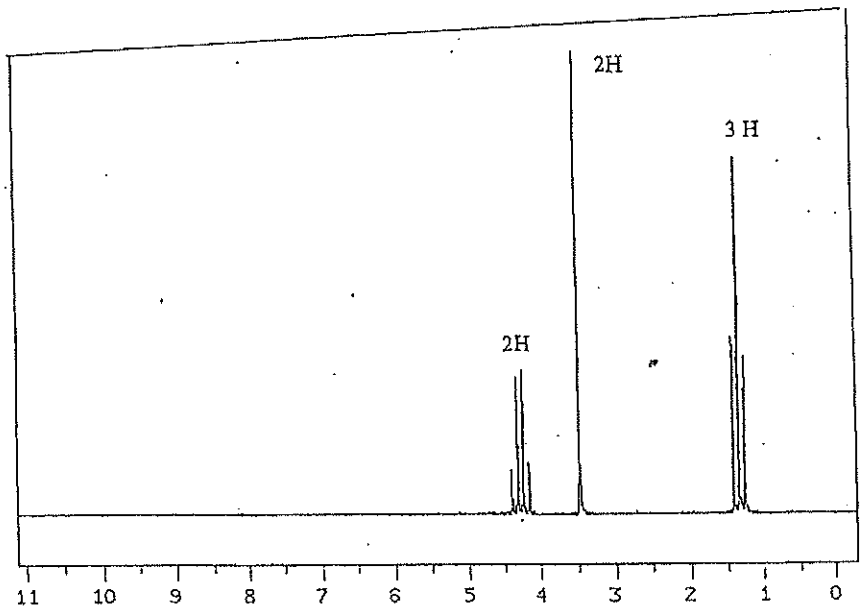


Spectrum E



Question 4

(a) To answer the following questions, consider the data and ^{1}HNMR spectrum below. The mass spectrum of this compound shows a molecular ion at $m/z = 113$, the IR spectrum has characteristic absorptions at 2270 and 1735 cm^{-1}, and the ^{13}CNMR spectrum has five (5) signals.



(a) Based on the mass spectral data and the IR data, what functional groups are present in this compound? [4]

(b) How many types of non-equivalent protons are there in this molecule? [4]

(c) Comment or describe the signal at 3.5 δ in terms of its integration, splitting pattern and chemical shift. [4]

(d) Describe the signals at 4.35 δ and 1.3 δ in terms of their integration splitting and chemical shift. [4]

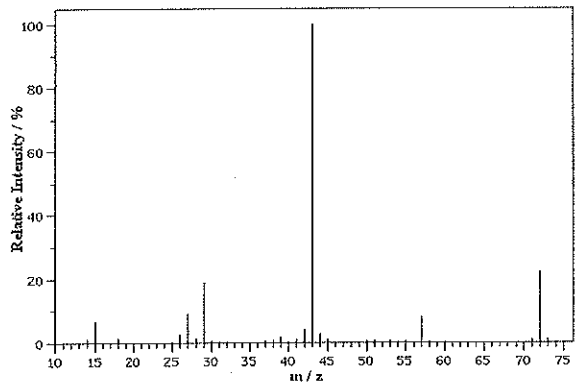
(e) What is the significance of ^{13}C NMR data? [4]

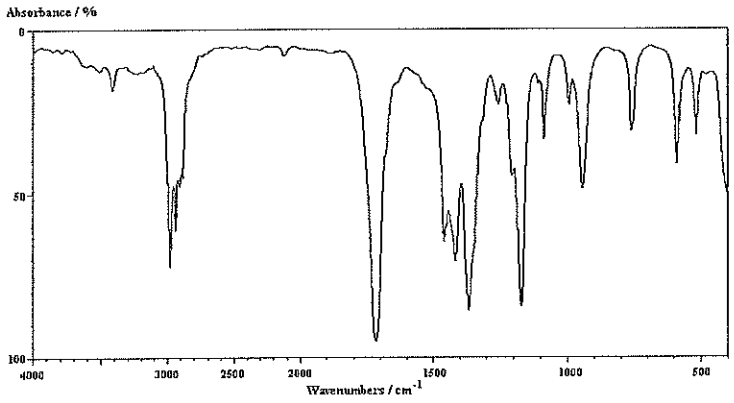
(f) Analyze all the information deduced from the data provided and then propose a structure for this compound? [5]

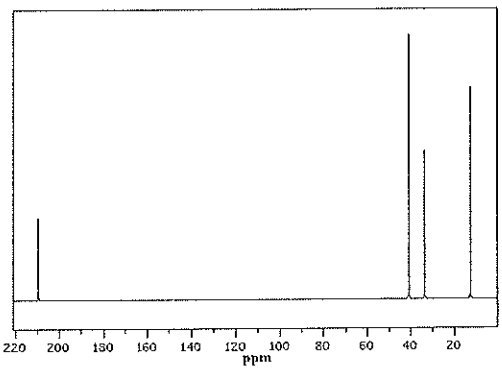
Question 5

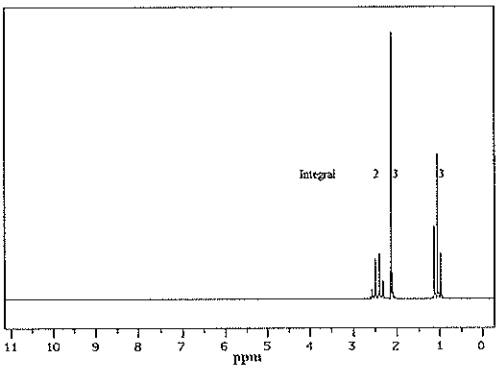
(a) The following spectral data (mass spectrum, infra-red, ^{13}C-nmr and H-nmr) is provided for an unknown compound. You are required to deduce the **structure** of the unknown compound that is consistent with all the data provided. **[20]**

(i)

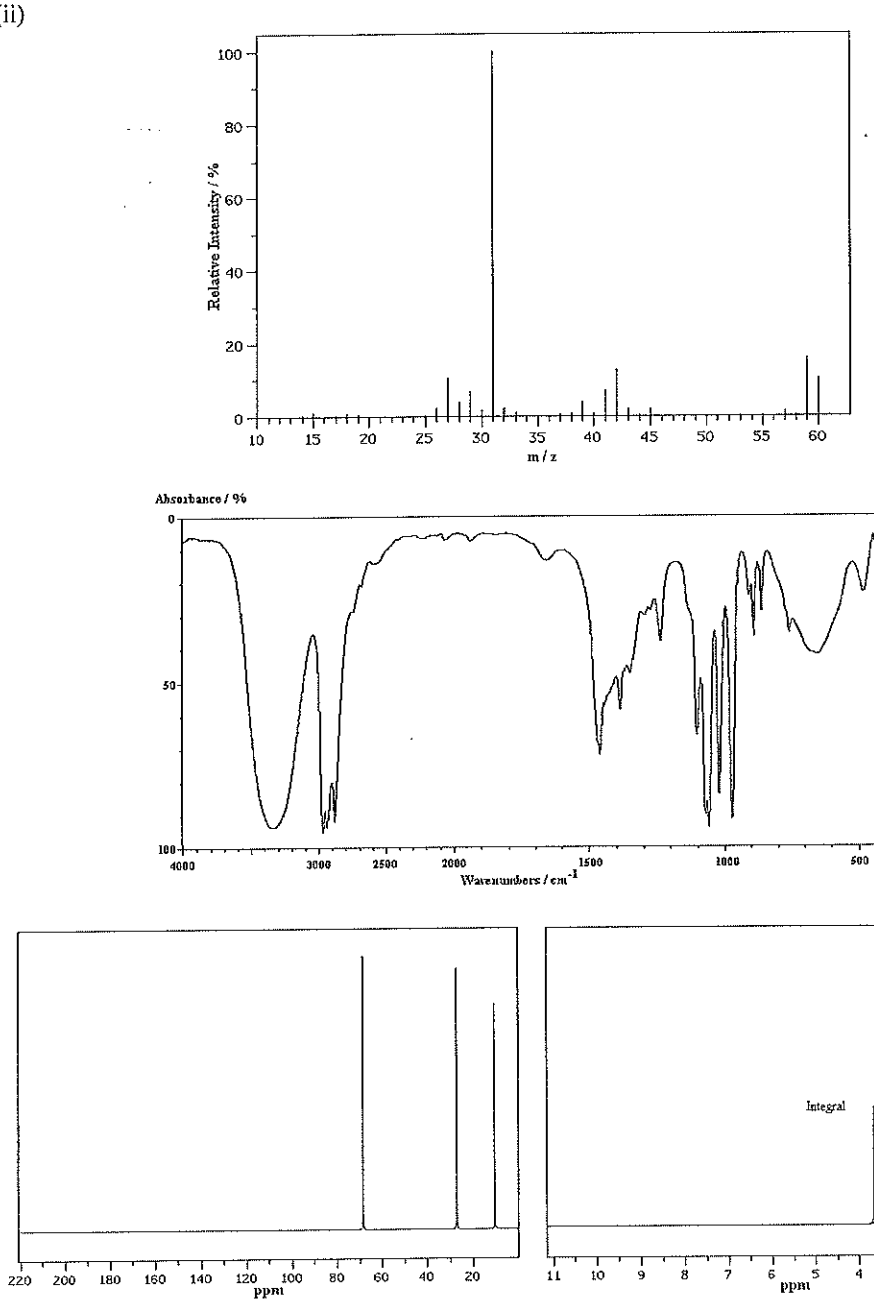








(ii)



(b) When the ^{1}H NMR spectrum of acetone, CH_3COCH_3, is recorded on an instrument operating at 200 MHz, a single sharp resonance at 2.1 δ is seen.

(i) How many hertz downfield from TMS does the acetone resonance correspond to?

(ii) If the ^{1}H NMR spectrum of acetone were recorded at 500 MHz, what would the position of the absorption be in δ units?

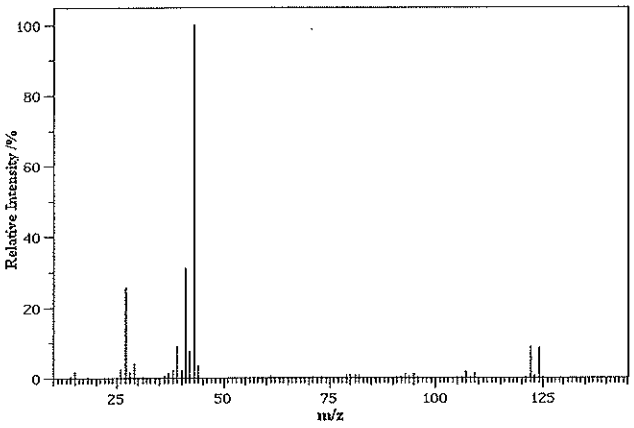
(iii) How many hertz from TMS does this 500 MHz resonance correspond to?

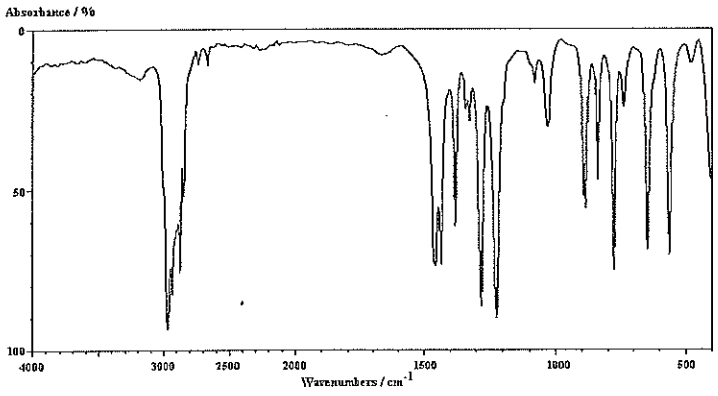
[5]

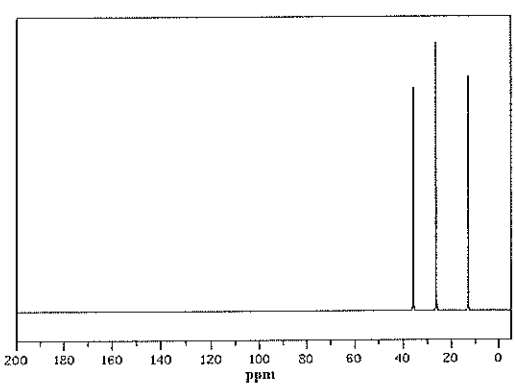
Question 6

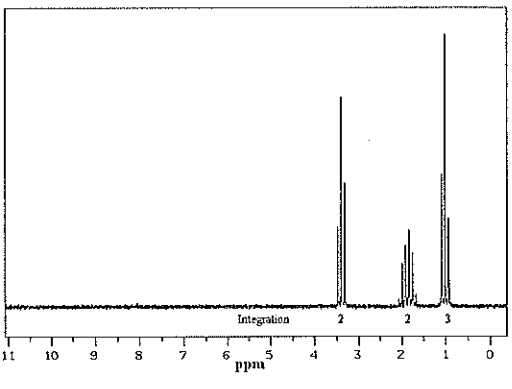
(a) The following spectral data (mass spectrum, infra-red, ^{13}C-nmr and H-nmr) is provided for an unknown compound. You are required to deduce the **structure** of the unknown compound that is consistent with all the data provided. **[20]**

(i)

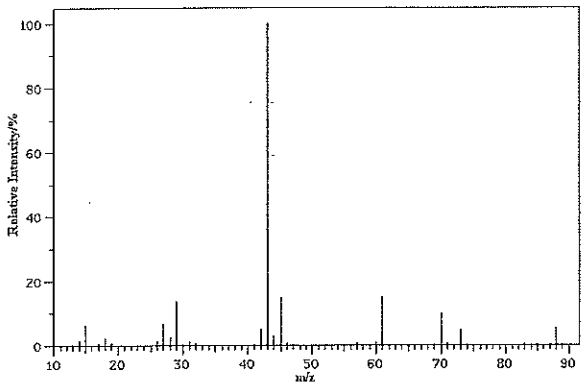


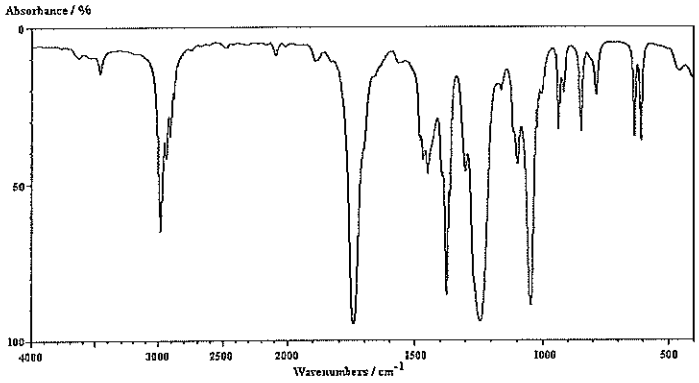


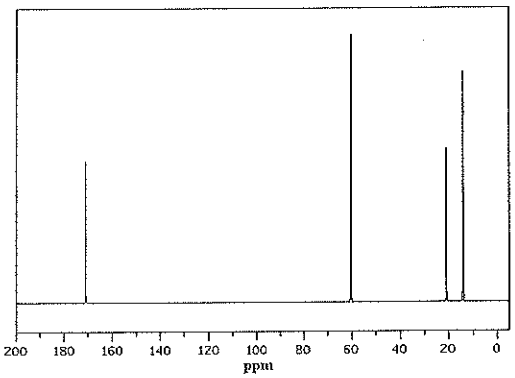


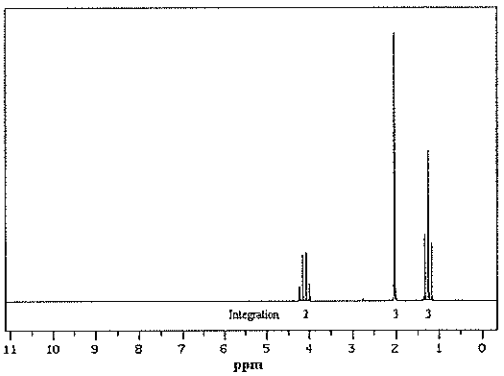


(ii)

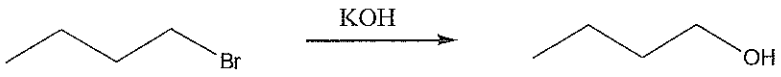








(b) Assume you are carrying out the conversion of 1-bromobutane to 1-butanol. Explain how you would use IR spectroscopy and Mass spectrometry to determine weather the reaction is complete.



[5]

TABLE 1.3 Relative Isotope Abundances of Common Elements.

Elements	Isotope	Relative Abundance	Isotope	Relative Abundance	Isotope	Relative Abundance
Carbon	^{12}C	100	^{13}C	1.11		
Hydrogen	^{1}H	100	^{2}H	0.016		
Nitrogen	^{14}N	100	^{15}N	0.38		
Oxygen	^{16}O	100	^{17}O	0.04	^{18}O	0.2
Fluorine	^{19}F	100				
Silicon	^{28}Si	100	^{29}Si	5.1	^{30}Si	3.35
Phosphorus	^{31}P	100				
Sulfur	^{32}S	100	^{33}S	0.78	^{34}S	4.4
Chlorine	^{35}Cl	100			^{37}Cl	32.5
Bromine	^{79}Br	100			^{81}Br	98
Iodine	^{127}I	100				

1												13	14	15	16	17	18
1 H 1.008	2																2 He 4.0026
3 Li 6.94	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305	3	4	5	6	7	8	9	10	11	12	13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.45	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.630	33 As 74.922	34 Se 78.97	35 Br 79.904	36 Kr 83.798
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.95	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71 *	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 #	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Nh (286)	114 Fl (289)	115 Mc (289)	116 Lv (293)	117 Ts (294)	118 Og (294)

* Lanthanide series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
# Actinide series	89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)