UNIVERSITY OF ESWATINI
FINAL EXAMINATION 2018/2019

TITLE OF PAPER	:	ORGANIC SPECTROSCOPY & STRUCTURE ELUCIDATION
COURSE NUMBER	:	CHE331
TIME	:	Three Hours
INSTRUCTIONS	:	Answer any **FOUR Questions**. Each Question carries 25 Marks.

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) Arrange the following radiations in increasing order of wavelength; UV, X-rays, Radio waves, Infrared, visible

[5]

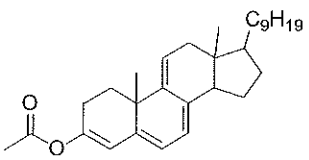
(b) A 0.01M solution of a compound transmits 20% of radiation in a container with a path length equal to 1.5 cm. Calculate the molar extinction coefficient (ε) of the compound.

[4]

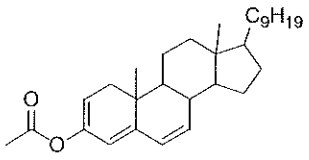
(c) Calculate the absorption maximum (λ_{max}) in the ultraviolet spectrum of 2,3 dimethylene bicycle [2, 2, 1] heptane.

[4]

(d) Calculate the absorption maximum (λ_{max}) for the three steroid structures below;



A



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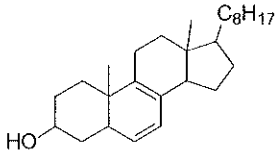
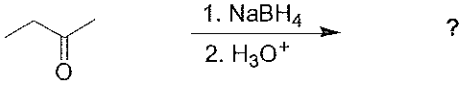


C

[6]

(e) Propose plausible IR absorption bands and *m/z* of the products.

(i)



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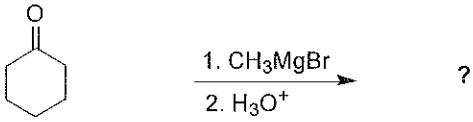

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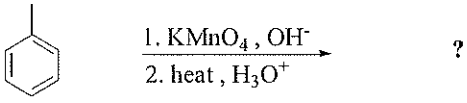


[6]

Question 2

(a) Suggest how pentan-2-one and pentan-3-one could be distinguished in a mass spectrum. Write equations to show the formation of any important fragment ions.

[6]

(b) What are mass-to-charge ratios (*m/z*) for the three biggest peaks in the mass spectrum associated with the intact, unfragmented molecular ion of dichlorobenzene?

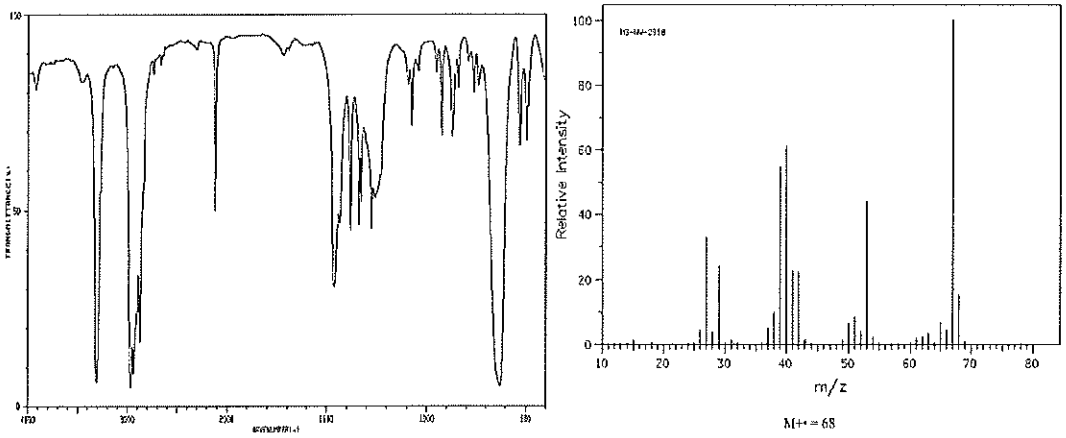
[4]

(c) Name any five applications of IR spectroscopy.

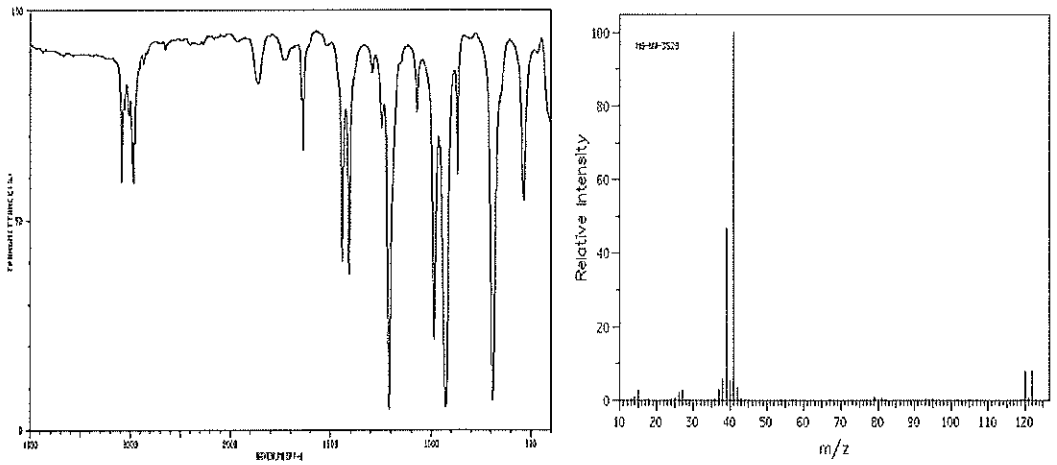
[5]

(d) Determine the molecular formula and possible structures for each unknown based on the given spectra. **[10]**

(i)



(ii)



Question 3

(a) The integrated ^{1}HNMR spectrum of a compound of formula $C_4H_{10}O$ is shown below. Examine the spectrum, interpret all signals and propose a structure. [8]

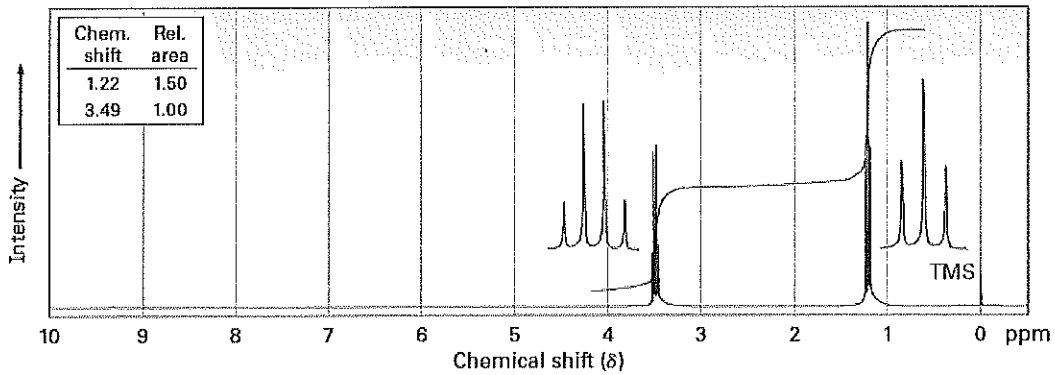


Figure X; The Intergrated ^{1}HNMR Spectrum of $C_4H_{10}O$

(b) Propose a structure for an aromatic hydrocarbon, $C_{11}H_{16}$, that has the following ^{13}C NMR spectral data:
Broadband decoupled: 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
[9]

(c) Compound **A**, $C_4H_8O_3$, has infrared absorptions at 1710 and 2500 to 3100 cm^{-1} and has the ^{1}H NMR spectrum shown below. Propose a structure for **A**.
[8]

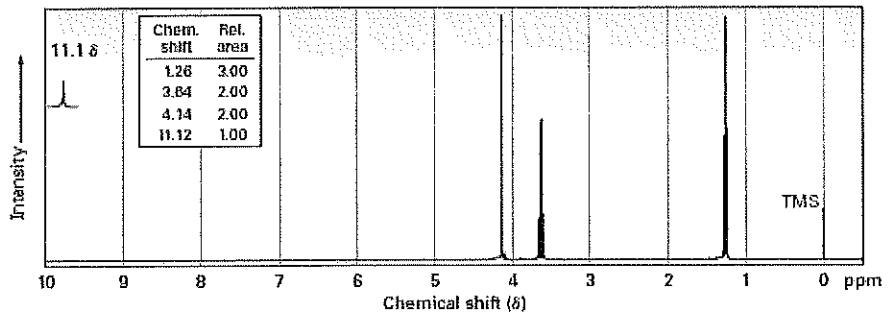


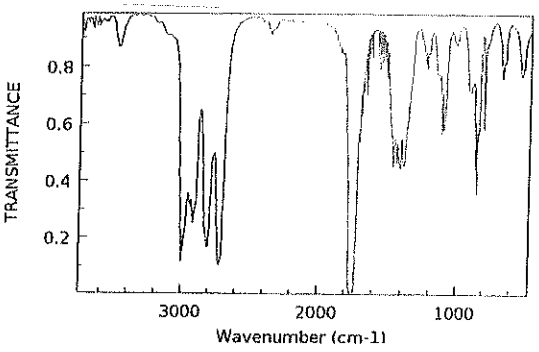
Figure X; ^{1}H NMR spectrum of $C_4H_8O_3$

Question 4

(a) The IR spectra of four (4) compounds are provided below. Match each spectrum with the correct compound.

[8]

A



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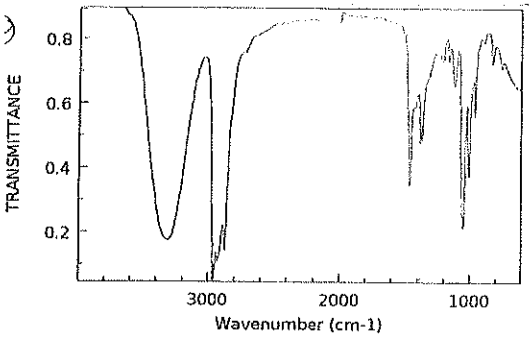
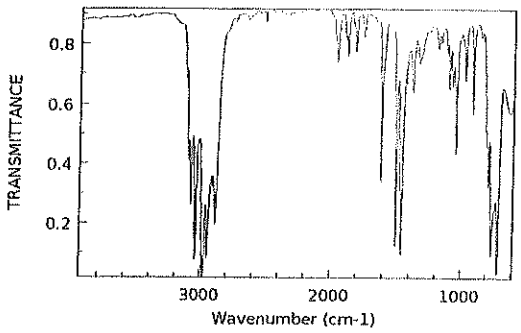
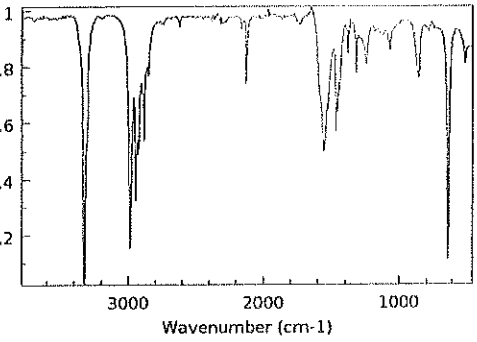
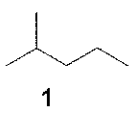


C

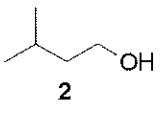


D

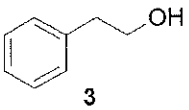




1



2



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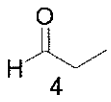

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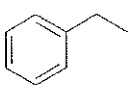

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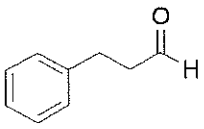

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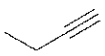


7

8

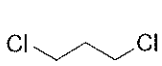
(b) A compound with the formula $C_4H_8O_2$ was subjected to mass spectrometry and found to give a base peak $m/z = 73$, In addition to a molecular ion peak at $m/z = 88$. The infra-red analysis of the molecule showed a sharp peak at 1710 cm^{-1}. ^{1}HNMR of the molecule yielded the following peaks;

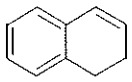
Chemical Shift	Splitting	Integrating Factor
1.10	Triplet	3
2.01	Singlet	3
4.10	Quartet	2

Deduce the structure of the molecule and account for the formation of all the peaks in the spectra.

[8]

(c) Predict the splitting patterns you would expect from each proton in the following molecules.





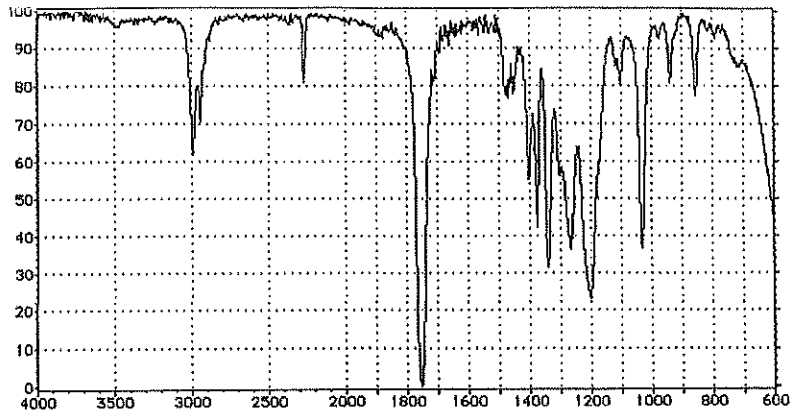
[5]

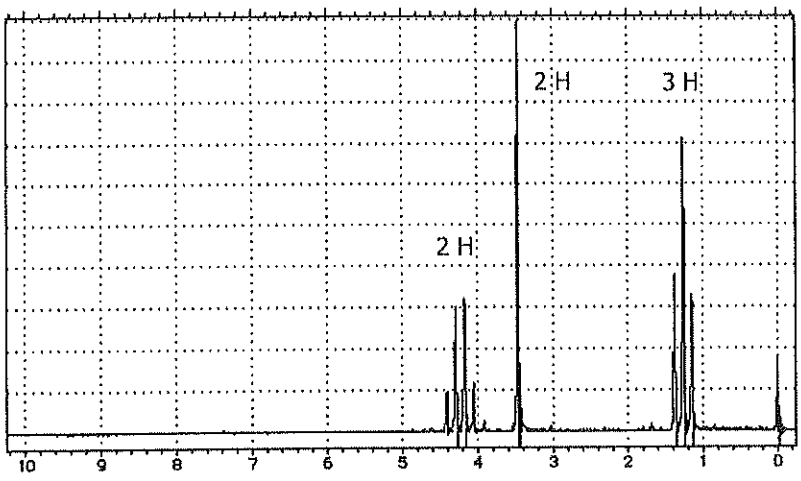
(d) Name four (4) factors that influence the chemical shift.

[4]

Question 5

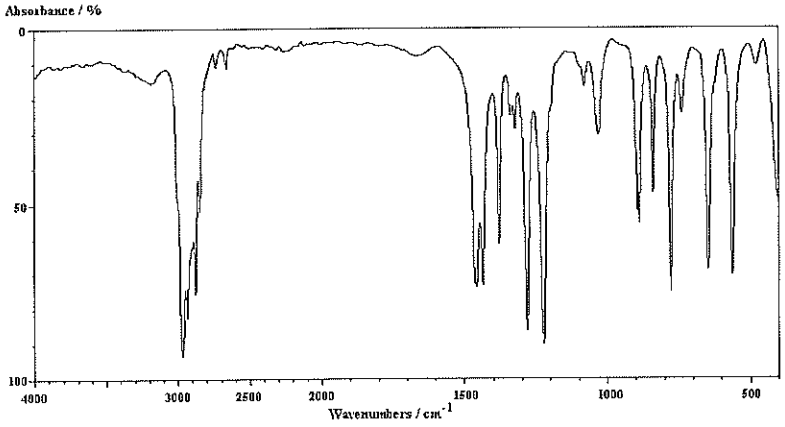
(a) Predict the structure of a compound with the formula $C_5H_7NO_2$ that best fits the IR and ^{1}HNMR spectra below;

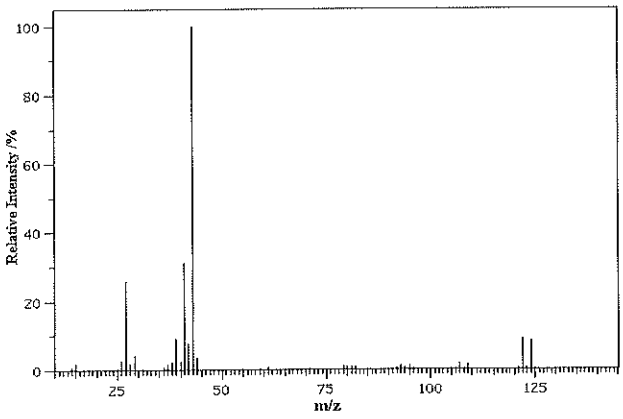


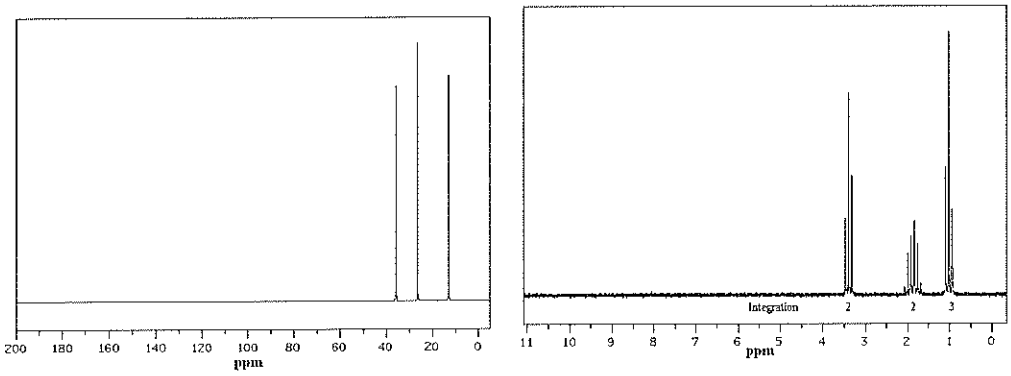


[5]

(b) Draw the structure that best fits the following spectra

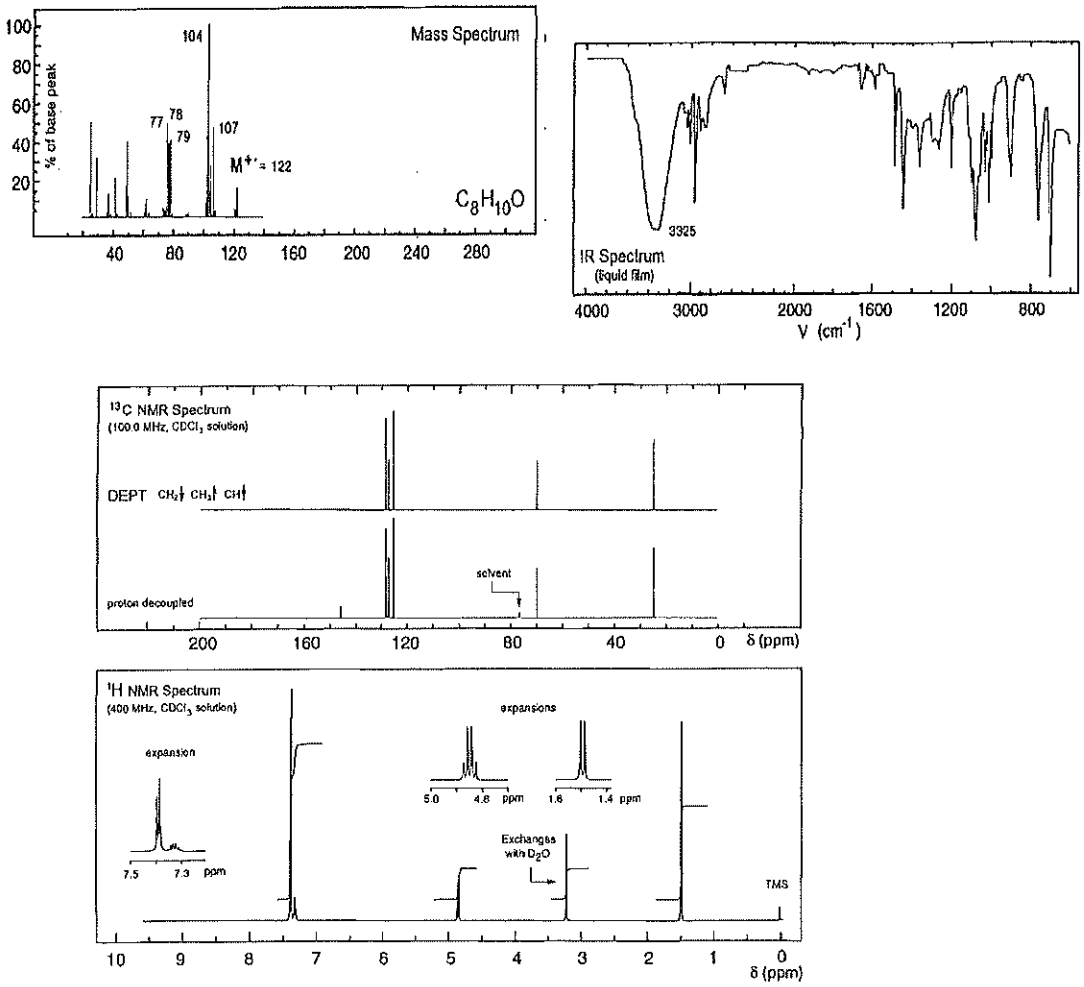






[10]

(c) Draw the structure that best fits the following spectra;

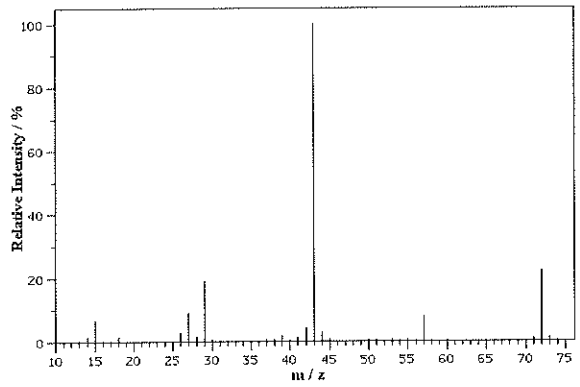


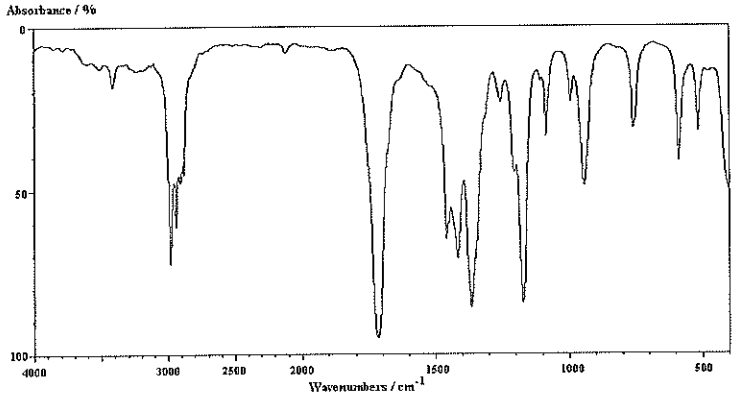
[10]

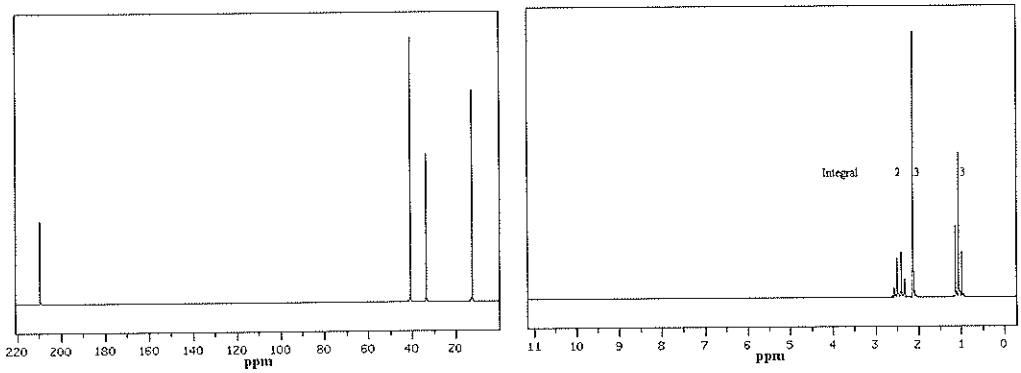
Question 6

(a) Draw the structure that best fits the following spectra

[10]







(b) Using only ^{1}H NMR spectroscopy, how would you conclusively distinguish between all 3 isomers (ortho, meta, and para) of bromophenol? Be as specific as necessary in order to differentiate ortho from meta, meta from para, and ortho from para.

[10]

(c) 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]

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)