



**MASINDE MULIRO UNIVERSITY OF  
SCIENCE AND TECHNOLOGY  
(MMUST)**

**MAIN CAMPUS**

**UNIVERSITY EXAMINATIONS  
2021/2022 ACADEMIC YEAR**

**FIRST YEAR SECOND SEMESTER EXAMINATIONS  
MAIN EXAM**

**FOR THE DEGREE  
OF  
MASTERS OF SCIENCE (CHEMISTRY)**

**COURSE CODE: SCH 830**

**COURSE TITLE: ADVANCED ORGANIC SPECTROSCOPY**

**DATE: 02/08/2022**

**TIME: 8.00-10.00 AM**

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**INSTRUCTIONS TO CANDIDATES**

1. Answer all questions
2. Find IR chart and characteristic NMR chemical shifts tables attached to the question paper

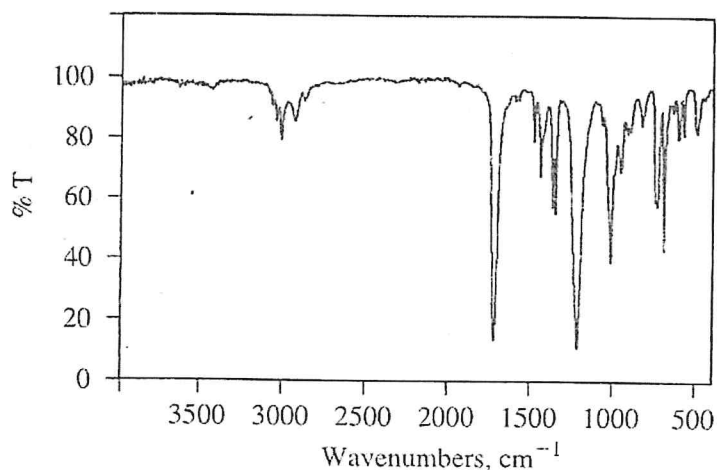
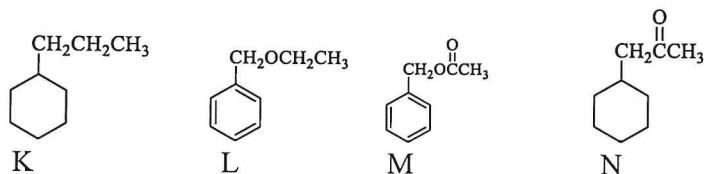
TIME: 3 Hours

MMUST observes ZERO tolerance to examination cheating

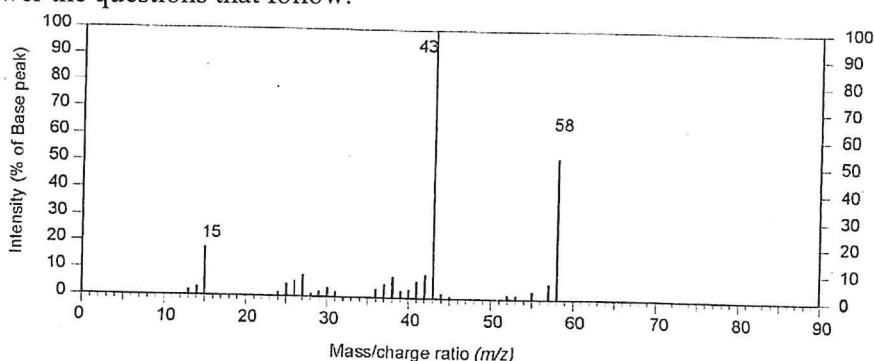
This Paper Consists of 12 Printed Pages. Please Turn Over. 

**QUESTION 1 (17 Marks)**

- a) Explain the following observations
- Unlike  $^{13}\text{C}$  NMR, most  $^{13}\text{C}$  NMR spectra appear as a series of singlets 1 mark
  - In some cases, the  $^{13}\text{C}$  spectrum can appear as multiplets. Why and how is this solved? 2 marks
- b) Cyclohexane protons exist in two different environments as either axial or equatorial. However, The NMR spectrum of cyclohexane, however, shows only a single sharp peak at 1.4 ppm. Explain 2 marks
- c) Give three reasons why not all bands are observed in an IR spectrum. 3 marks
- d) Which of the following compounds is the most likely structure of the compound characterized by the IR spectrum shown below? Explain your reasoning. 4 marks



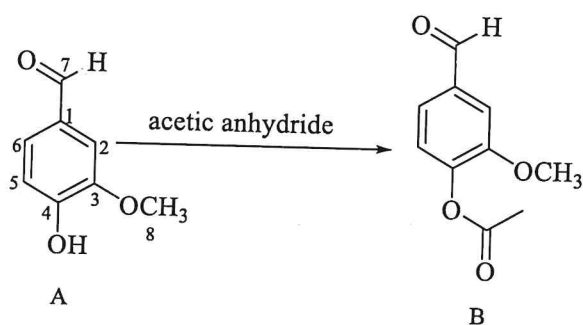
- e) A compound X having molecular formula  $\text{C}_3\text{H}_6\text{O}$  shows the following mass spectrum. Study it and answer the questions that follow.



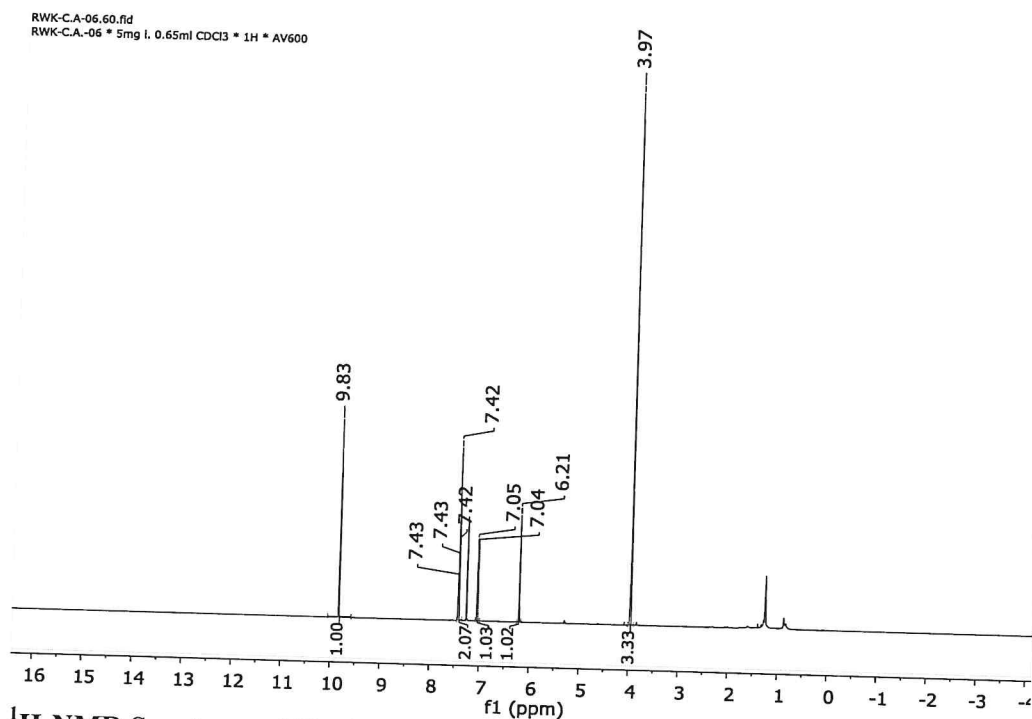
- By use of explanation, identify the molecular ion peak and base peak 2 marks
- Using chemical formulae explain the origin of peaks at  $m/z$  43 and 15. 3 marks

**Question Two 19 marks**

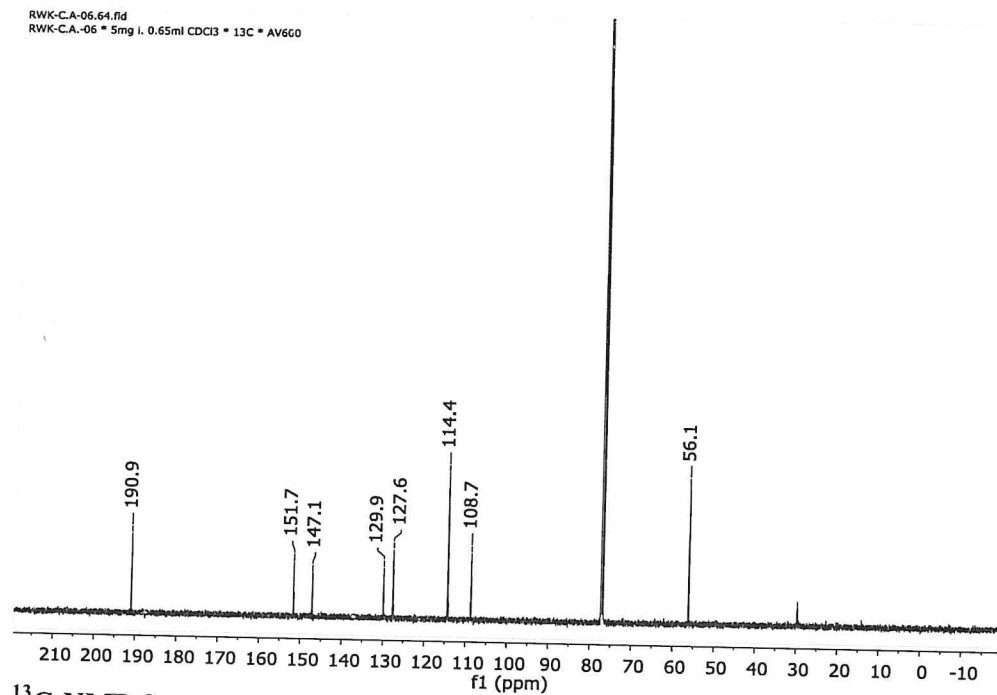
- a) A postgraduate student isolated Vanillin (A) from the root bark of medicinal plant *Cordia africana* as a light-yellow solid. She later performed acetylation of the compound to yield its acetylated product B.



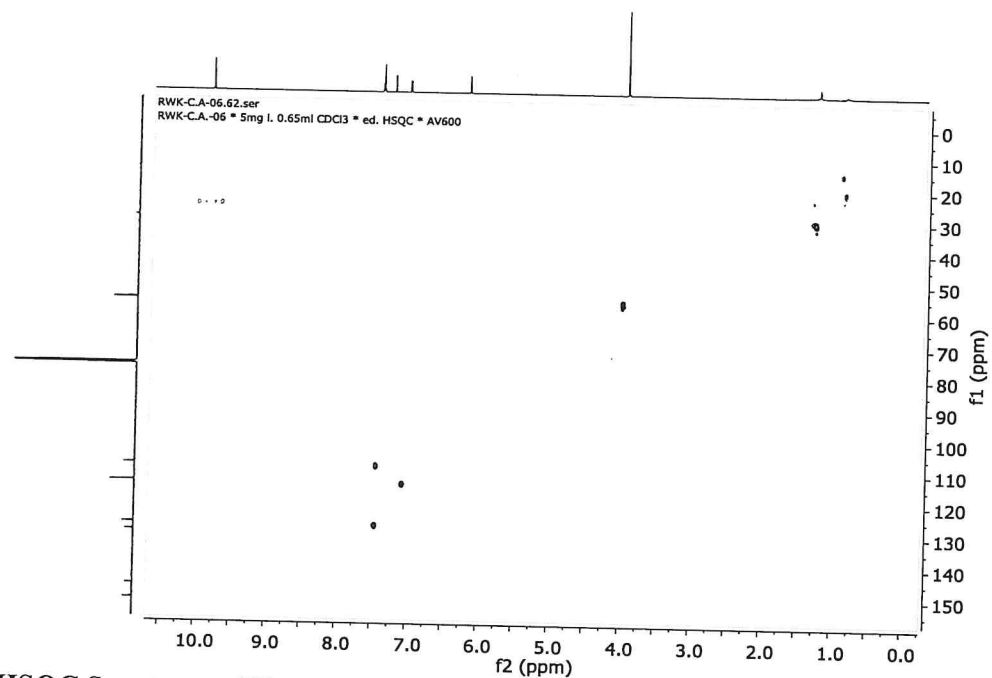
- i) Explain why the compound A would appear coloured 1 mark
- ii) Study  $^1\text{H-NMR}$  spectrum of compound A and assign all the protons. 6 Marks
- iii) Study  $^{13}\text{C-NMR}$  spectrum of compound A and assign all the carbons. Justify the aromatic region assignment using the table for increment system for aromatic carbons 8 Marks
- iv) How would the student use  $^1\text{H-NMR}$  data to confirm conversion of A to B 2 Marks
- v) What two main differences does the student expect between the  $^{13}\text{C-NMR}$  spectra of compounds A and B? 2 Marks



$^1\text{H-NMR}$  Spectrum of Vanillin (A)



<sup>13</sup>C-NMR Spectrum of Vanillin (A)



HSQC Spectrum of Vanillin (A)

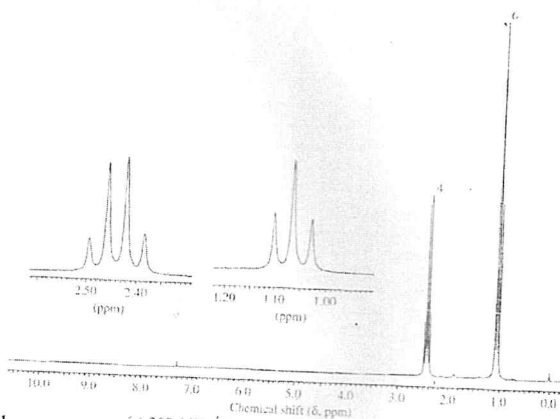
### QUESTION 3 (12 Marks)

- a) An unknown organic compound showed a molecular ion peak at  $m/z$  86 in its mass spectrum from which a molecular formula of  $C_5H_{10}O$  was established. It was observed to be a colourless liquid slightly soluble in water. The infrared 200- MHz <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra are provided for the compound.

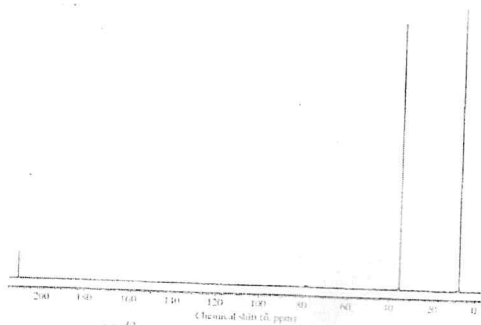
- i. Determine the Index of Hydrogen Deficiency of the compound 2 marks
- ii. What functional groups can be obtained the IR spectrum? 2 marks
- iii. Considering the chemical shift integration and splitting patterns in  $^1\text{H-NMR}$  spectrum establish the types of protons present in the compound 2 marks
- iv. What further information can be obtained from  $^{13}\text{C-NMR}$  spectrum? 1 mark
- v. From the information above propose a structure for the compound 1 mark



IR spectrum of compound P

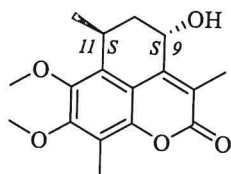


$^1\text{H-NMR}$  spectrum of compound P



$^{13}\text{C-NMR}$  spectrum of compound P

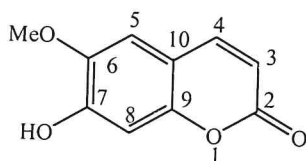
Interpretation of NOESY spectrum of coumarin derivative whose structure is given below showed that 9-OH and 14-CH<sub>3</sub> were on the opposite side.



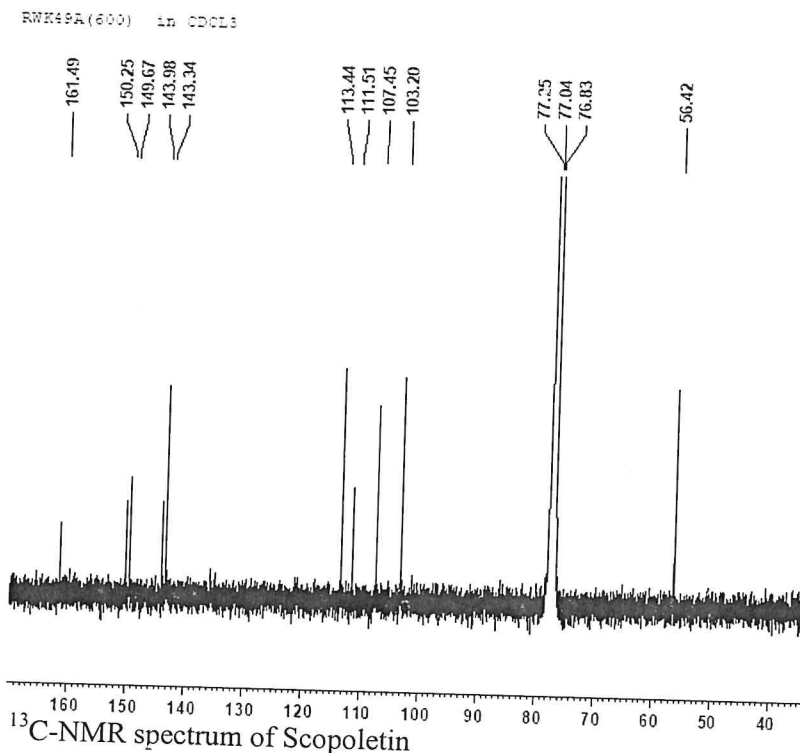
- Explain the obvious correlation obtained from NOESY data, and how it resolved the relative configuration of the compound 2 marks
- Explain how absolute configuration of the compound above would be established 2 marks

**Question Four 12 marks**

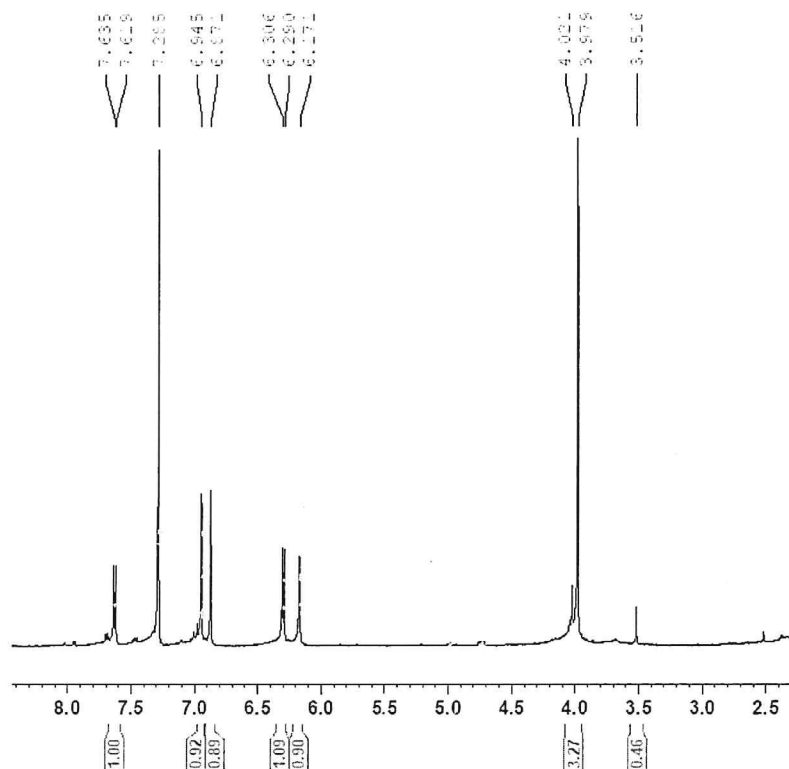
- Study the structure and <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of Scopoletin given below then answer the questions that follow.



Scopoletin

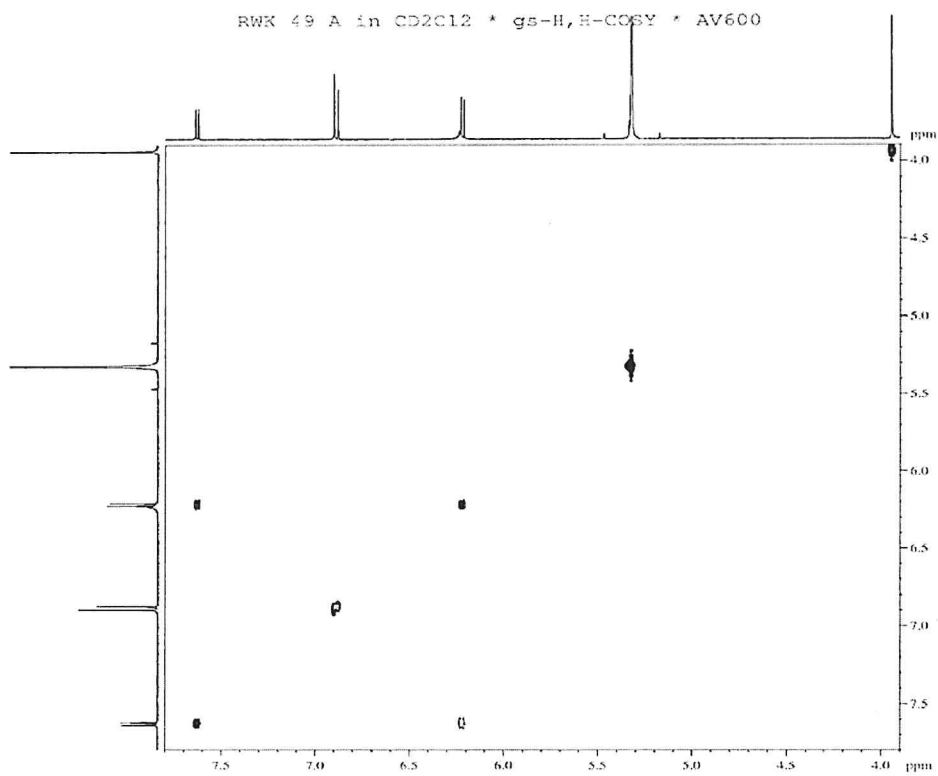


RW49A(600) in CDCl3

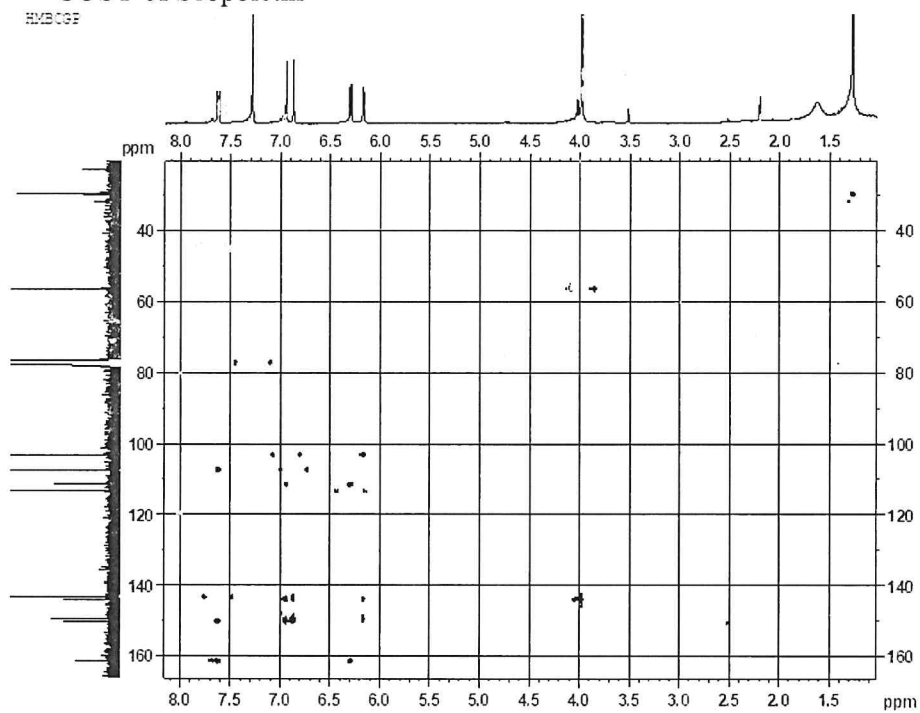


<sup>1</sup>H-NMR spectrum of Scopoletin

- Assign the carbons C-2 and C-7 of the structure 2 marks
- Identify the solvent peak from the <sup>1</sup>H-NMR spectrum 1 mark
- Which proton(s) does the peak at 3.98 represent? Explain 2 marks
- Calculate and comment on the coupling constants (J) of the doublets observed in the <sup>1</sup>H-NMR spectrum. 2 marks
- Assign the doublets in the structure. Explain 1 mark
- Describe how the COSY and HMBC spectra below for Scopoletin would support the assignment given in a (v) above 4 marks



COSY of Scopoletin



HMBC of Scopoletin

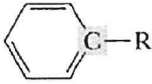






## Table of Characteristic IR Absorptions

<i>frequency, cm<sup>-1</sup></i>	<i>bond</i>	<i>functional group</i>
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H-bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β-unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β-unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in-ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in-ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH <sub>2</sub> X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H “oop”	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

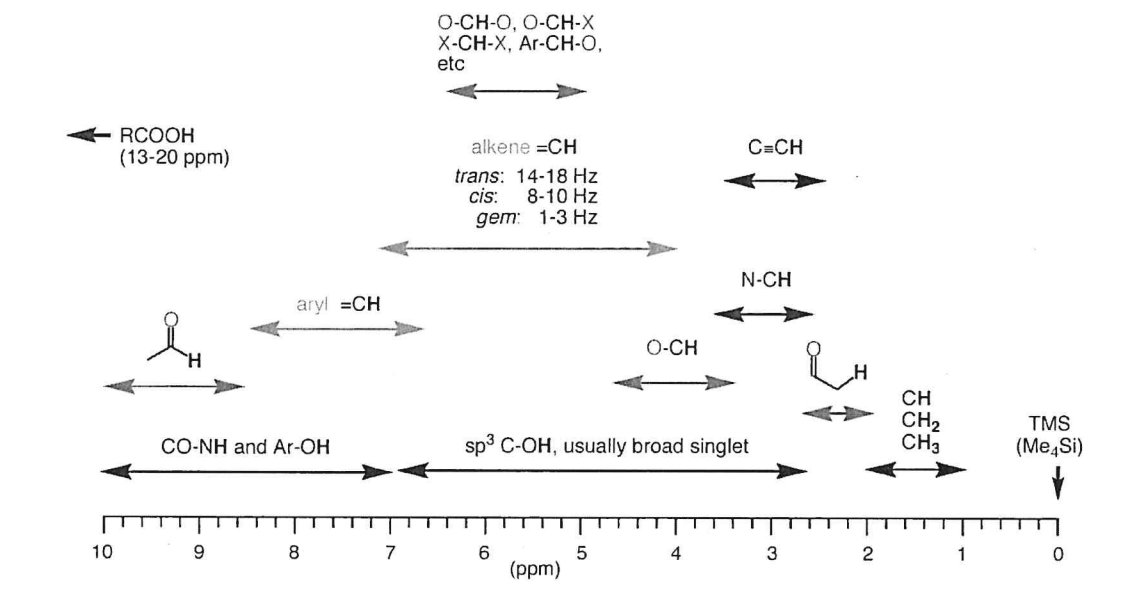
m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

## Characteristic $^{13}\text{C}$ -NMR Chemical Shifts

Type of Carbon	Chemical Shift ( $\delta$ )	Type of Carbon	Chemical Shift ( $\delta$ )
$\text{RCH}_3$	0-40		110-160
$\text{RCH}_2\text{R}$	15-55		160-180
$\text{R}_3\text{CH}$	20-60		165-180
$\text{RCH}_2\text{I}$	0-40		175-185
$\text{RCH}_2\text{Br}$	25-65		180-210
$\text{RCH}_2\text{Cl}$	35-80		
$\text{R}_3\text{COH}$	40-80		
$\text{R}_3\text{COR}$	40-80		
$\text{RC}\equiv\text{CR}$	65-85		
$\text{R}_2\text{C}=\text{CR}_2$	100-150		

### CHEM 30C, COMMON $^1\text{H}$ NMR CHEMICAL SHIFT RANGES

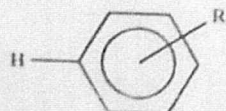
Common NMR solvents:  
 $\text{CDCl}_3$ ,  $\text{D}_3\text{C-SO-CD}_3$ ,  $\text{D}_2\text{O}$   
 $\text{CD}_3\text{OD}$



### CHEM 30B, COMMON $^{13}\text{C}$ NMR CHEMICAL SHIFT RANGES

# Increment system for estimation of chemical shifts of benzene protons

Formula:  $\delta = 7.26 + \Sigma I$

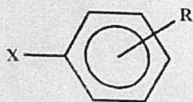


Substituent	$I_{ortho}$	$I_{meta}$	$I_{para}$	group
-H	0	0	0	
-CH <sub>3</sub>	-0.18	-0.10	-0.20	methyl
-CH <sub>2</sub> CH <sub>3</sub>	-0.15	-0.06	-0.18	ethyl
-CH(CH <sub>3</sub> ) <sub>2</sub>	-0.13	-0.08	-0.18	isopropyl
-C(CH <sub>3</sub> ) <sub>3</sub>	0.02	-0.09	-0.22	tert-butyl
-CH <sub>2</sub> Cl	0.00	0.01	0.00	
-CH <sub>2</sub> OH	-0.07	-0.07	-0.07	
-CH <sub>2</sub> NH <sub>2</sub>	0.01	0.01	0.01	
-CH=CH <sub>2</sub>	0.06	-0.03	-0.10	vinyl
-CCH	0.15	-0.02	-0.01	alkyne
-C <sub>6</sub> H <sub>5</sub>	0.30	0.12	0.12	phenyl
-CHO	0.56	0.22	0.29	aldehyde
-COCH <sub>3</sub>	0.62	0.14	0.21	Me-ketone
-COCH <sub>2</sub> CH <sub>3</sub>	0.63	0.13	0.20	
-CO-C <sub>6</sub> H <sub>5</sub>	0.47	0.13	0.22	
-COOH	0.85	0.18	0.25	acid
-COOCH <sub>3</sub>	0.71	0.11	0.21	Me-ester
-COOC <sub>6</sub> H <sub>5</sub>	0.90	0.17	0.27	
-CONH <sub>2</sub>	0.61	0.10	0.17	amide
-COCl	0.84	0.20	0.36	acid chloride
-CN	0.36	0.18	0.28	nitrile

-NH <sub>2</sub>	-0.75	-0.25	-0.65	amino
-NH(CH <sub>3</sub> )	-0.80	-0.22	-0.68	Me-amine
-N(CH <sub>3</sub> ) <sub>2</sub>	-0.66	-0.18	-0.67	Di-Me-amin
-N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> Γ	0.69	0.36	0.31	Ammonium
-NHCOCH <sub>3</sub>	0.12	-0.07	-0.28	Amido
-NO	0.58	0.31	0.37	nitroso
-NO <sub>2</sub>	0.95	0.26	0.38	nitro
-SH	-0.08	-0.16	-0.22	thiol
-SCH <sub>3</sub>	-0.08	-0.10	-0.24	Me-thioether
-SC <sub>6</sub> H <sub>5</sub>	0.06	-0.09	-0.15	
-SO <sub>2</sub> OH	0.64	0.26	0.36	sulfon
SO <sub>2</sub> NH <sub>2</sub>	0.66	0.26	0.36	sulfonamide
-OH	-0.56	-0.12	-0.45	phenol
-OCH <sub>3</sub>	-0.48	-0.09	-0.44	Me-ether
-OCH <sub>2</sub> CH <sub>3</sub>	-0.46	-0.10	-0.43	
-OC <sub>6</sub> H <sub>5</sub>	-0.29	-0.05	-0.23	
-OOCCH <sub>3</sub>	-0.25	0.03	-0.13	acetate
-OOC <sub>6</sub> H <sub>5</sub>	-0.09	0.09	-0.08	benzoate
-F	-0.26	0.00	-0.20	fluoro-
-Cl	0.03	-0.02	-0.09	chloro-
-Br	0.18	-0.08	-0.04	bromo-
-I	0.39	-0.21	-0.03	iodo-

# Increment system for estimation of chemical shifts of benzene carbons

Formula:  $\delta = 128.5 + \Sigma I$



Substituent	ipso	ortho	meta	para
-H	0	0	0	0
-CH <sub>3</sub>	9.3	0.6	0	-3.1
-C <sub>2</sub> H <sub>5</sub>	15.7	-0.6	-0.1	-2.8
-CH(CH <sub>3</sub> ) <sub>2</sub>	20.1	-2.0	0	-2.5
-C(CH <sub>3</sub> ) <sub>3</sub>	22.1	-3.4	-0.4	-3.1
-CH=CH <sub>2</sub>	7.6	-1.8	-1.8	-3.5
-CCH (alkyne)	-6.1	3.8	0.4	-0.2
-C <sub>6</sub> H <sub>5</sub>	13.0	-1.1	0.5	-1.0
-CF <sub>3</sub>	2.6	-2.6	-0.3	-3.2
-CH <sub>2</sub> Cl	9.1	0	0.2	-0.2
-CH <sub>2</sub> Br	9.2	0.1	0.4	-0.3
-CH <sub>2</sub> OR	13.0	-1.5	0	-1.0
-CH <sub>2</sub> NR <sub>2</sub>	15.0	-1.5	-0.2	-2.0
-CHO	7.5	0.7	-0.5	5.4
-COCH <sub>3</sub>	9.3	0.2	0.2	4.2
-COOH	2.4	1.6	-0.1	4.8
-COOR	2.0	1.0	0	4.5
-CONR <sub>2</sub>	5.5	-0.5	-1.0	5.0

-NH <sub>2</sub>	19.2	-12.4	1.3	-9.5
-NR <sub>2</sub>	21.0	-16.0	0.7	-12.0
-NHCOCH <sub>3</sub>	11.1	-9.9	0.2	-5.6
-N=N-C <sub>6</sub> H <sub>5</sub>	24.0	-5.8	0.3	2.2
-N=C=O	5.7	-3.6	1.2	-2.8
-NO <sub>2</sub>	19.6	-5.3	0.8	6.0
-SH	2.2	0.7	0.4	-3.1
-SCH <sub>3</sub>	10.1	-1.6	0.2	-3.5
-SC <sub>6</sub> H <sub>5</sub>	6.8	0.5	2.2	-1.6
-SO <sub>3</sub> H	15.0	-2.2	1.3	3.8
-F	35.1	-14.3	0.9	-4.4
-Cl	6.4	0.2	1.0	-2.0
-Br	-5.4	3.3	2.2	-1.0
-I	-32.3	9.9	2.6	-0.4