



UNIVERSITI  
TEKNOLOGI  
PETRONAS

## FINAL EXAMINATION MAY 2024 SEMESTER

**COURSE** : YBB2093 - MOLECULAR SPECTROSCOPY  
**DATE** : 9 AUGUST 2024 (FRIDAY)  
**TIME** : 9:00 AM - 12:00 NOON (3 HOURS)

### INSTRUCTIONS TO CANDIDATES

1. Answer **ALL** questions in the Answer Booklet.
2. Begin **EACH** answer on a new page in the Answer Booklet.
3. Indicate clearly answers that are cancelled, if any.
4. Where applicable, show clearly steps taken in arriving at the solutions and indicate **ALL** assumptions, if any.
5. **DO NOT** open this Question Booklet until instructed.

**Note** :

- i. There are **TWENTY (20)** pages in this Question Booklet including the cover page .
- ii. **DOUBLE-SIDED** Question Booklet.

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1. a. Explain the information that can be acquired from vibrational and electronic spectroscopies.

[4 marks]

- b. A photon with an energy of  $5.94 \times 10^{-20}$  J is absorbed by HBr.

- i. Identify the spectral region for this absorption.

[4 marks]

- ii. Sketch an energy level for this transition.

[4 marks]

- iii. Calculate the force constant (in  $\text{Nm}^{-1}$ ) if the mass of bromine atom is  $6.0 \times 10^{-26}$  kg and mass of hydrogen atom is  $1.7 \times 10^{-27}$  kg.

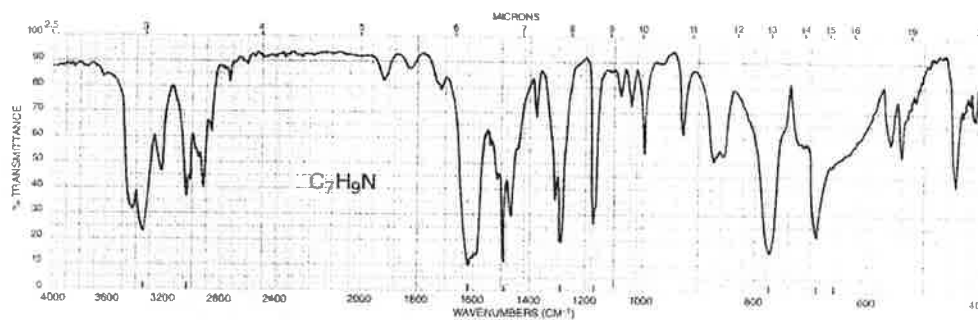
[4 marks]

- c. Illustrate the possible modes of vibration for acetylene and cyclohexane.

[4 marks]

2. a. The absorbance of a 0.01 M colorant solution in ethanol is 0.6989 in a 2-cm cell of the wavelength 500 nm. Calculate:
- Percentage transmittance  
[3 marks]
  - Molar absorption coefficient  
[4 marks]
- b. Draw any **TWO (2)** molecules that can show  $\pi \rightarrow \pi^*$  transition each.  
[6 marks]

- c. **FIGURE Q2** shows the FTIR spectrum of unknown sample with a molecular formula of  $C_7H_9N$ .



**FIGURE Q2:** FTIR spectrum.

- i. Calculate the index of hydrogen deficiency for this unknown sample.

[2 marks]

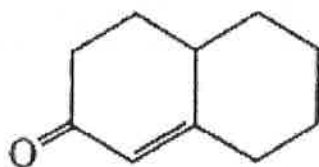
- ii. Predict the molecular structure of this unknown sample based on the index of hydrogen deficiency in **part (c)(i)** and FTIR spectrum in **FIGURE Q2**. Rationalize the predicted molecular structure.

[5 marks]

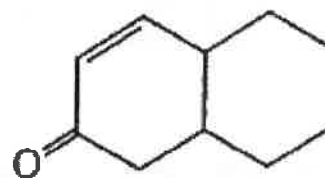
3. a. Propose a simple spectroscopic method to differentiate the isomeric dienes of 2,4-hexadiene and 2,5-hexadiene.

[5 marks]

- b. Predict the maximum wavelengths for each of the following compounds in **FIGURE Q3** using the Woodward-Fieser's Rules and justify if those compounds can be distinguished using a UV-visible spectroscopy.



Compound A



Compound B

**FIGURE Q3:** Compound A and Compound B.

[7 marks]

- c. A compound with the molecular formula of  $C_8H_8O_2$  exhibits in its proton NMR spectrum with peaks as shown in **TABLE Q3**.

**TABLE Q3:** Proton NMR peaks.

Chemical shift (ppm)	Area	Multiplicity
9.78	1.00	Singlet
7.75	2.02	Doublet
6.90	2.01	Doublet
3.77	3.17	Singlet

- i. Predict the types of hydrogen based on the values of chemical shifts given in **TABLE Q3**.

[4 marks]

- ii. Propose the molecular structure of this compound.

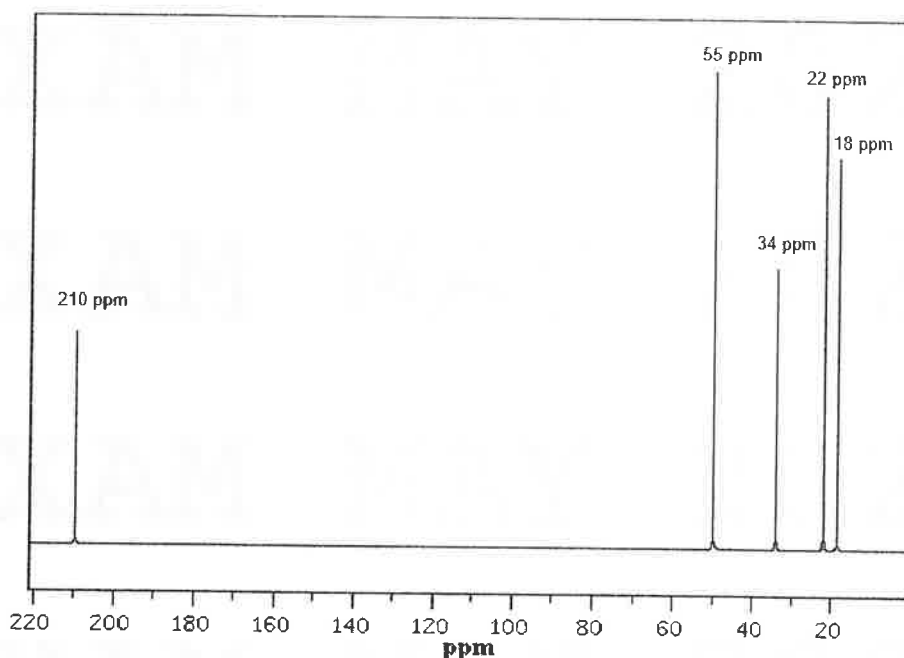
[4 marks]

4. a. Given the magnetogyric ratio for  $^{19}\text{F}$  is  $2.5181 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$ , determine the relative number of  $^{19}\text{F}$  nuclei at higher over lower magnetic states at  $25^\circ\text{C}$  in the magnetic field of 2.4 T.

[4 marks]

- b. **FIGURE Q4b** shows the carbon-13 NMR spectrum for a compound with the molecular formula of  $\text{C}_5\text{H}_{10}\text{O}$ . This compound also exhibits the following peaks in its proton NMR spectrum:

- A triplet at 0.9 ppm, integral = 3
- A hexet at 1.7 ppm, integral = 2
- A singlet at 2.1 ppm, integral = 3
- A triplet at 2.4 ppm, integral = 2

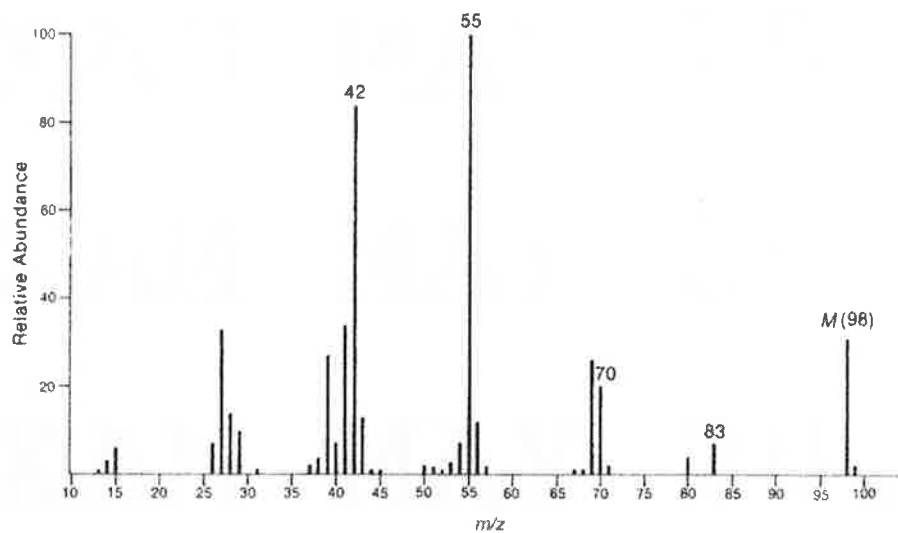


**FIGURE Q4b:** Carbon-13 NMR spectrum.

Propose the molecular structure of this compound with justification.

[8 marks]

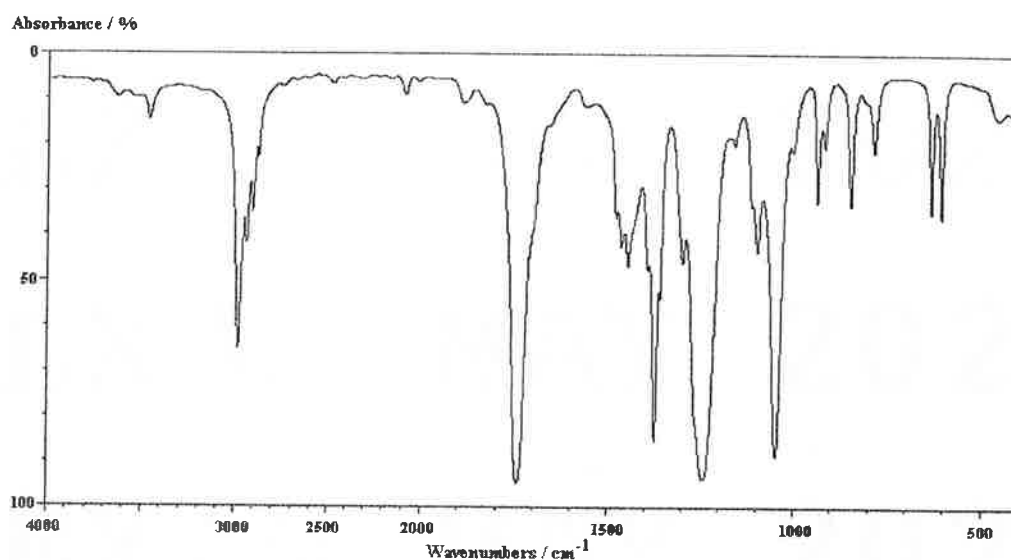
- c. **FIGURE Q4c** shows the mass spectrum of cyclohexanone. Predict the structures of molecular ions corresponding to each fragmented ion peak in this mass spectrum.



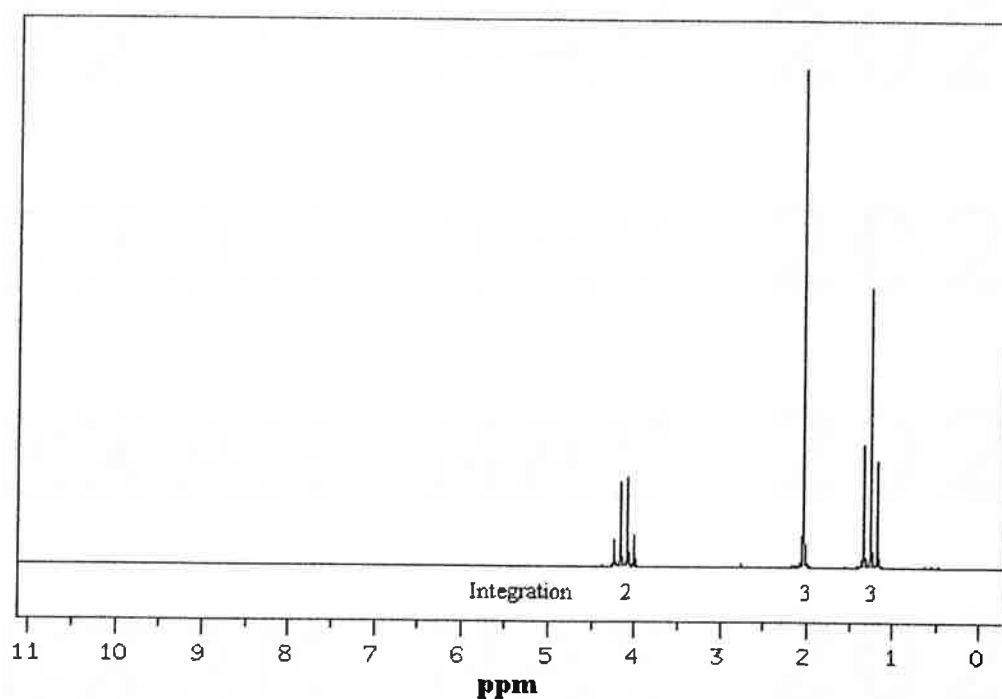
**FIGURE Q4c:** Mass spectrum of cyclohexanone.

[8 marks]

5. A chemist decided to analyse an unknown compound. The chemist obtained the following spectra for this unknown compound: FTIR spectrum in **FIGURE Q5.1**, proton NMR spectrum in **FIGURE Q5.2**, carbon-13 NMR spectrum in **FIGURE Q5.3** and mass spectrum in **FIGURE Q5.4**.



**FIGURE Q5.1:** FTIR spectrum of unknown compound.



**FIGURE Q5.2:** Proton NMR spectrum of unknown compound.



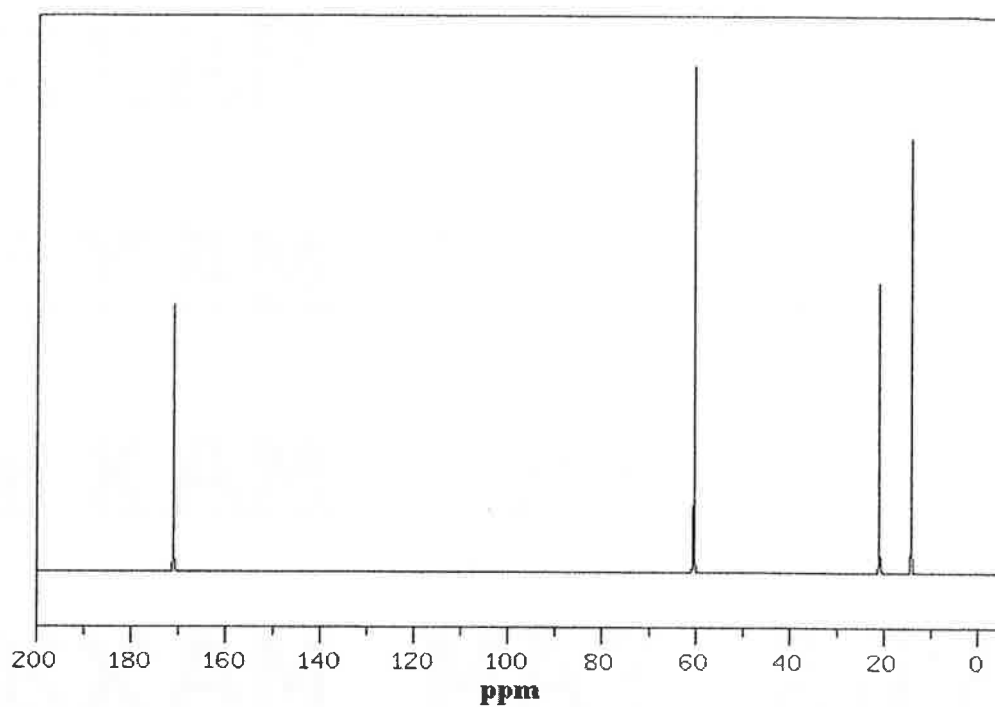


FIGURE Q5.3: Carbon-13 NMR spectrum of unknown compound.

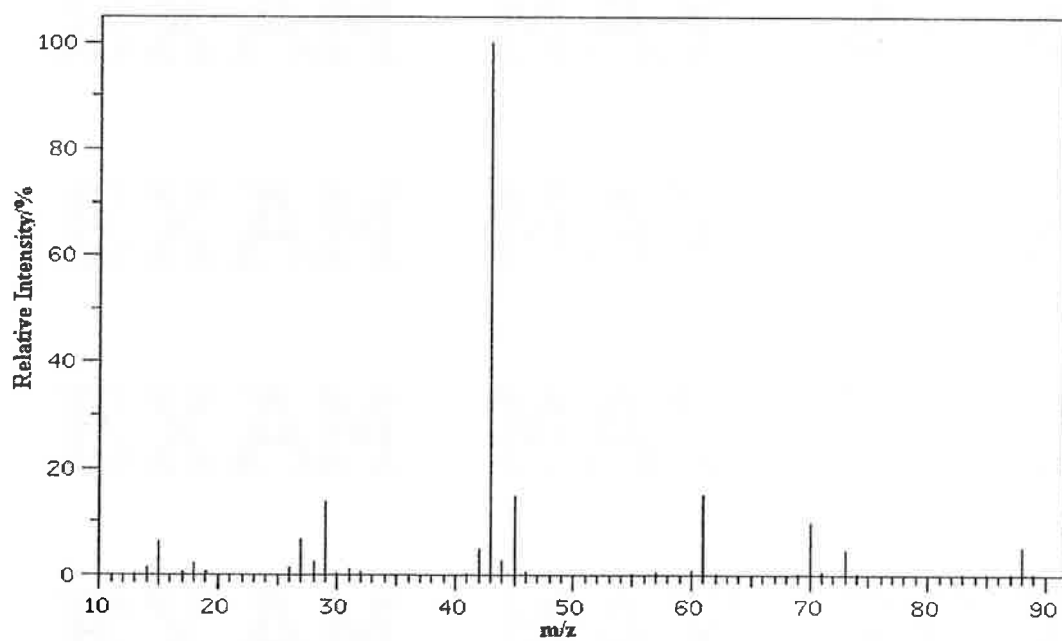


FIGURE Q5.4: Mass spectrum of unknown compound.

- a. Predict **ALL** the functional groups in FTIR spectrum (**FIGURE Q5.1**).

[3 marks]

- b. Interpret the proton NMR spectrum (**FIGURE Q5.2**) with justification.

[8 marks]

- c. Interpret the carbon-13 NMR spectrum (**FIGURE Q5.3**) with justification.

[3 marks]

- d. Interpret the mass spectrum (**FIGURE Q5.4**) with justification and propose the molecular structure of this unknown compound.

[6 marks]

- END OF PAPER -



	$= -459.67\text{ }^{\circ}\text{F}$	$1\text{ J}$	$= 0.23901\text{ cal}$
$^{\circ}\text{F}$	$= \frac{9}{5}(^{\circ}\text{C}) + 32$		$= 1\text{ C} \times 1\text{ V}$
$^{\circ}\text{C}$	$= \frac{5}{9}(^{\circ}\text{F} - 32)$	$1\text{ cal}$	$= 4.184\text{ J}$
		$1\text{ eV}$	$= 1.602 \times 10^{-19}\text{ J}$

## APPENDIX B

## PHYSICAL CONSTANTS

Atomic mass unit	1 amu	= $1.661 \times 10^{-24}$ g
	1 g	= $6.022 \times 10^{23}$ amu
Avogadro's number	$N$	= $6.022 \times 10^{23}$ / mol
Boltzmann's constant	$k$	= $1.381 \times 10^{-23}$ J/K
Electron charge	$e$	= $1.602 \times 10^{-19}$ C
Faraday's constant	$F = Ne$	= $9.649 \times 10^4$ C/mol
Gas constant	$R$	= 8.314 J/mol-K
		= 0.08206 L-atm/mol-K
Mass of electron	$m_e$	= $5.486 \times 10^{-4}$ amu
		= $9.110 \times 10^{-28}$ g
Mass of neutron	$m_n$	= 1.009 amu
		= $1.675 \times 10^{-24}$ g
Mass of proton	$m_p$	= 1.007 amu
		= $1.673 \times 10^{-24}$ g
Pi	$\pi$	= 3.142
Planck's constant	$h$	= $6.626 \times 10^{-34}$ J-s
Speed of light	$c$	= $2.998 \times 10^8$ m/s
Rydberg constant	$R_H$	= $1.097 \times 10^7$ m <sup>-1</sup>
	$hcR_H$	= $2.179 \times 10^{-18}$ J

## APPENDIX C

## ATOMIC MASSES OF THE ELEMENTS

Symbol	Element	Atomic Number	Atomic Mass	Symbol	Element	Atomic Number	Atomic Mass
Ac	Actinium	89	227.03*	Hg	Mercury	80	200.59
Al	Aluminum	13	26.981539	Mo	Molybdenum	42	95.94
Am	Americium	95	241.06*	Nd	Neodymium	60	144.24
Sb	Antimony	51	121.757	Ne	Neon	10	20.1797
Ar	Argon	18	39.948	Np	Neptunium	93	237.05
As	Arsenic	33	74.92159	Ni	Nickel	28	58.6934
At	Astatine	85	209.99*	Nb	Niobium	41	92.90638
Ba	Barium	56	137.327	N	Nitrogen	7	14.00674
Bk	Berkelium	97	249.08*	No	Nobelium	102	259.10*
Be	Beryllium	4	9.012182	Os	Osmium	76	190.2
Bi	Bismuth	83	208.98037	O	Oxygen	8	15.9994
B	Boron	5	10.811	Pd	Palladium	46	106.42
Br	Bromine	35	79.904	P	Phosphorus	15	30.973762
Cd	Cadmium	48	112.411	Pt	Platinum	78	195.08
Ca	Calcium	20	40.078	Pu	Plutonium	94	239.05*
Cf	Californium	98	252.08*	Po	Polonium	84	209.98*
C	Carbon	6	12.01115	K	Potassium	19	39.0983
Ce	Cerium	58	140.115	Pr	Praseodymium	59	140.90765
Cs	Cesium	55	132.90543	Pm	Promethium	61	146.92*
Cl	Chlorine	17	35.4527	Pa	Protactinium	91	231.03588
Cr	Chromium	24	51.9961	Ra	Radium	88	226.03
Co	Cobalt	27	58.93320	Rn	Radon	86	222.02*
Cu	Copper	29	63.546	Re	Rhenium	75	186.207
Cm	Curium	96	244.06*	Rh	Rhodium	45	102.90550
Dy	Dysprosium	66	162.50	Rb	Rubidium	37	85.4678
Es	Einsteinium	99	252.08*	Ru	Ruthenium	44	101.07
Er	Erbium	68	167.26	Sm	Samarium	62	150.36
Eu	Europium	63	151.965	Sc	Scandium	21	44.955910
Fm	Fermium	100	257.10*	Se	Selenium	34	78.96
F	Fluorine	9	18.9984032	Si	Silicon	14	28.0855
Fr	Francium	87	223.02*	Ag	Silver	47	107.8662
Gd	Gadolinium	64	157.25	Na	Sodium	11	22.989768
Ga	Gallium	31	69.723	Sr	Strontium	38	87.62
Ge	Germanium	32	72.61	S	Sulfur	16	32.066
Au	Gold	79	196.96654	Ta	Tantalum	73	180.9479
Hf	Hafnium	72	178.49	Tc	Technetium	43	98.906
He	Helium	2	4.002602	Te	Tellurium	52	127.60
Ho	Holmium	67	164.93032	Tb	Terbium	65	158.92534
H	Hydrogen	1	1.00794	Tl	Thallium	81	204.3833
In	Indium	49	114.82	Th	Thorium	90	232.0381
I	Iodine	53	126.90447	Tm	Thulium	69	168.93421
Ir	Iridium	77	192.22	Sn	Tin	50	118.710
Fe	Iron	26	55.847	Ti	Titanium	22	47.88
Kr	Krypton	36	83.80	W	Tungsten	74	183.85
La	Lanthanum	57	138.9055	U	Uranium	92	238.0289
Lw	Lawrencium	103	262.11*	V	Vanadium	23	50.9415
Pb	Lead	82	207.2	Xe	Xenon	54	131.29
Li	Lithium	3	6.941	Yb	Ytterbium	70	173.04
Lu	Lutetium	71	174.967	Y	Yttrium	39	88.90585
Mg	Magnesium	12	24.3050	Zn	Zinc	30	65.39
Mn	Manganese	25	54.93805	Zr	Zirconium	40	91.224
Md	Mendelevium	101	258.10*				

\* Atomic mass of the longest-lived isotope.

## APPENDIX D

## IR CORRELATION CHART

Functional Group	Type of vibration	Characteristic absorption band (cm <sup>-1</sup> )	Intensity
Alcohol			
O-H	Stretch, H-bonded	3200 - 3600	Strong, broad
O-H	Stretch, non H-bonded	3500-3700	Strong, sharp
C-O	Stretch	1050 - 1150	Strong
Alkane			
C-H	Stretch	2850 - 3000	Strong
C-H	Bending	1350-1480	variable
Alkene			
=C-H	Stretch	3010-3100	Medium
=C-H	Bending	675-1000	Strong
C=C	Stretch	1620-1680	variable
Alkyl Halide			
C-F	Stretch	1000-1400	Strong
C-Cl	Stretch	600 - 800	Strong
C-Br	Stretch	500 - 600	Strong
C-I	Stretch	500	Strong
Alkyne			
≡C-H	Stretch	3300	Strong, sharp
-C≡C-	Stretch	2100 - 2260	Variable, not present in symmetrical alkynes
Amine			
N-H	Stretch	3300-3500	Medium (primary amines have two bands; secondary have one band, often very weak)
C-N	Stretch	1080 - 1360	Medium-weak
N-H	Bending	1600	Medium
Aromatic			
C-H	Stretch	3000-3100	Medium
C=C	Stretch	1400-1600	Strong-weak, multiple bands
C-H	bending	1000-700	strong
Carbonyl			
C=O	Stretch	1670-1820	Strong
Ether			
C-O	Stretch	1000-1300	Strong
Nitrile			
C-N	Stretch	2210-2260	medium
Nitro			
N-O	Stretch	1515-1560 & 1345	Strong, two bands

## APPENDIX E

## IR correlation chart

## IR Absorption Frequencies of Functional Groups containing a Carbonyl (C=O)

Functional Group	Type of vibration	Characteristic absorption band (cm <sup>-1</sup> )	Intensity
Carbonyl			
C=O	Stretch	1670-1820	Strong
Acid			
C=O	Stretch	1700-1725	Strong
O-H	Stretch	2500-3300	Strong, broad
C-O	Stretch	1210-1320	Strong
Aldehyde			
C=O	Stretch	1710-1720	Strong
=C-H	Stretch	2820-2850 & 2720-2750	Medium, two peaks
Amide			
C=O	Stretch	1640-1690	Strong
N-H	Stretch	3100-3500	
N-H	Bending	1550-1640	Strong
Anhydride			
C=O	Stretch	1800-1830 & 1740-1775	Two bands
Ester			
C=O	Stretch	1735-1750	Strong
C-O	Stretch	1000-1300	Two bands or more
ketone			
Acylic	Stretch	1705-1725	Strong
Cyclic	Stretch	3-membered – 1850 4-membered – 1780 5-membered – 1745 6-membered – 1715 7-membered – 1705	Strong
ab-unsaturated	Stretch	1665-1685	Strong
Aryl ketone	Stretch	1680-1700	Strong



## APPENDIX F

## EMPIRICAL RULES: WOODWARD FIESER RULES FOR DIENE

	Homoannular (cisoid)	Heteroannular (transoid)
	$\lambda$ (nm)	$\lambda$ (nm)
Parent (BASE VALUES)	253	214
INCREMENTS FOR:	30	30
Double-bond-extending conjugation		
Alkyl group or ring residue	5	5
Exocyclic double bond	5	5
-Polar groupings:		
-OCOCH <sub>3</sub>	0	0
-OR	6	6
-Cl, Br	5	5
-NR <sub>2</sub>	60	60

## Typical absorptions for chromophores

Class	$\lambda_{\max}$ (nm)	Class	$\lambda_{\max}$ (nm)
R-OH	180	R-NO <sub>2</sub>	271
R-O-R	180	R-CHO	190, 290
R-NH <sub>2</sub>	190	R <sub>2</sub> CO	180, 280
R-SH	210	RCOOH	205
R <sub>2</sub> C=CR <sub>2</sub>	175	RCOOR'	205
R <sub>2</sub> C $\equiv$ CR <sub>2</sub>	170	RCONH <sub>2</sub>	210
R-C $\equiv$ N	160		
R-N=N-R	340		

## APPENDIX G

## EMPIRICAL RULES: WOODWARD FIESER RULES FOR ENONES

	$\lambda$ (nm)
<b>BASE VALUES</b>	
Six-membered ring or acyclic parent enone	215
Five-membered ring parent enone	202
Acyclic dienone	245
<b>INCREMENTS FOR:</b>	
Double-bond-extending conjugation	30
Alkyl group or ring residue	
$\alpha$	10
$\beta$	12
$\gamma$ and higher	18
Polar groupings:	
-OH	
$\alpha$	35
$\beta$	30
$\gamma$	50
-OCOCH <sub>3</sub> $\alpha$ , $\beta$ , $\gamma$	6
-OCH <sub>3</sub>	
$\alpha$	35
$\beta$	30
$\gamma$	17
d	31
-Cl	
$\alpha$	15
$\beta$	12
-Br	
$\alpha$	25
$\beta$	30
Exocyclic double bond	5
Homocyclic diene component	39

## EMPIRICAL RULES: WOODWARD FIESER RULES FOR ALDEHYDES, ACIDS AND ESTERS

	Base value (nm)
With $\alpha$ or $\beta$ alkyl groups	208
With $\alpha$ , $\beta$ or $\beta$ , $\beta$ dialkyl groups	217
With $\alpha$ , $\beta$ , $\beta$ alkyl groups	225
For an exocyclic $\alpha$ , $\beta$ double bond	Add 5
For an endocyclic $\alpha$ , $\beta$ double bond in a five-membered or seven-membered ring	Add 5




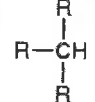
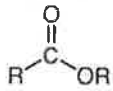
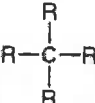
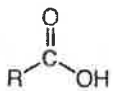

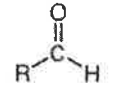
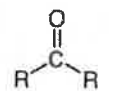
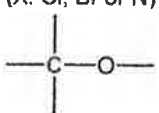
## APPENDIX H

NMR: CHEMICAL SHIFTS FOR SELECTED TYPES OF PROTONS ( $^1\text{H}$ )

Type of Hydrogen	Chemical Shift Range in ppm	Type of Hydrogen	Chemical Shift Range in ppm
$\text{R-CH}_3$	0.7 - 1.3		11.0 - 12.0
$\text{R-CH}_2\text{-R}$	1.2 - 1.4		3.5 - 4.8
$\text{R}_3\text{CH}$	1.4 - 1.7		5.0 - 9.0 <sup>a</sup>
	1.6 - 2.6		0.5 - 4.0 <sup>a</sup>
	2.1 - 2.4		2.2 - 2.9
	2.1 - 2.5		3.0 - 5.0 <sup>a</sup>
	2.1 - 3.0		4.1 - 4.3
	2.3 - 2.7		2.0 - 3.0
	4.5 - 6.5		1.0 - 4.0 <sup>a</sup>
	6.5 - 8.0		3.0
$\text{R-C}\equiv\text{C-H}$	1.7 - 2.7		4.2 - 4.8
	3.2 - 3.8		3.1 - 4.1
$\text{R-O-H}$	0.5 - 5.0 <sup>a</sup>		2.7 - 4.1
	4.0 - 12.0 <sup>a</sup>		2.0 - 4.0
	9.0 - 10.0		

## APPENDIX I

NMR: CHEMICAL SHIFTS FOR SELECTED TYPES OF CARBONS ( $^{13}\text{C}$ )

Type of Carbon	Chemical Shift (ppm)	Type of Carbon	Chemical Shift (ppm)
$\text{R}-\text{CH}_3$	0 – 35		80 – 150
	15 – 55		110 – 170
	25 – 55		165 – 175
	30 – 40		175 – 185
	10 – 65		190 – 200
(X: Cl, Br or N)			200 – 220
	50 – 90		
$\text{R}-\text{C}\equiv$	70 – 90		