

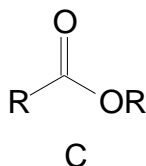
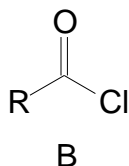
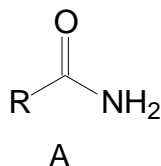
## ORGANIC CHEMISTRY 3 (CETOTA3): PAPER B

**SECTION A** (Answer this section on a separate examination answer script)

### QUESTION 1

1.1 Calculate the energy for a 600 nm photon? (6)

1.2 Carbonyls absorb IR irradiation between 1700 - 1800  $\text{cm}^{-1}$  and the exact position is dependent on the strength of the C=O bond. Match the following carboxylic acid derivatives with their predicted IR absorption frequency provided in the block on the right. (6)



1800  $\text{cm}^{-1}$

1750  $\text{cm}^{-1}$

1695  $\text{cm}^{-1}$

1.3 The acronyms below describe various analytical techniques. What do they stand for?

1.3.1  $^1\text{H}$ -NMR (1)

1.3.2 MS (1)

1.3.3 IR (1)

1.3.4 UV/Vis (1)

1.4 What analytical technique produces the "fingerprint" of a compound? (1)

1.5 Which subatomic particle is affected in all the analytical techniques mentioned in question 1.3? (1)

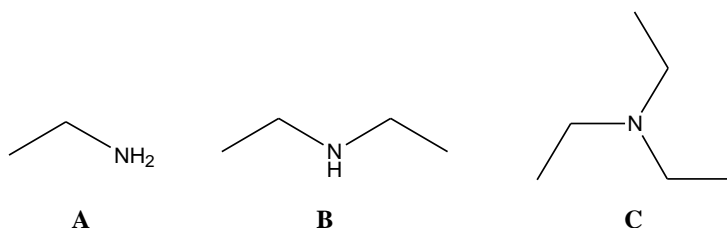
1.6 Which analytical technique functions by the following reaction sequence? (1)



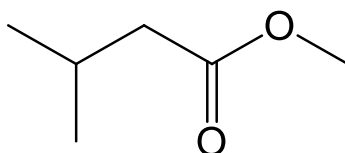
[19]

**QUESTION 2**

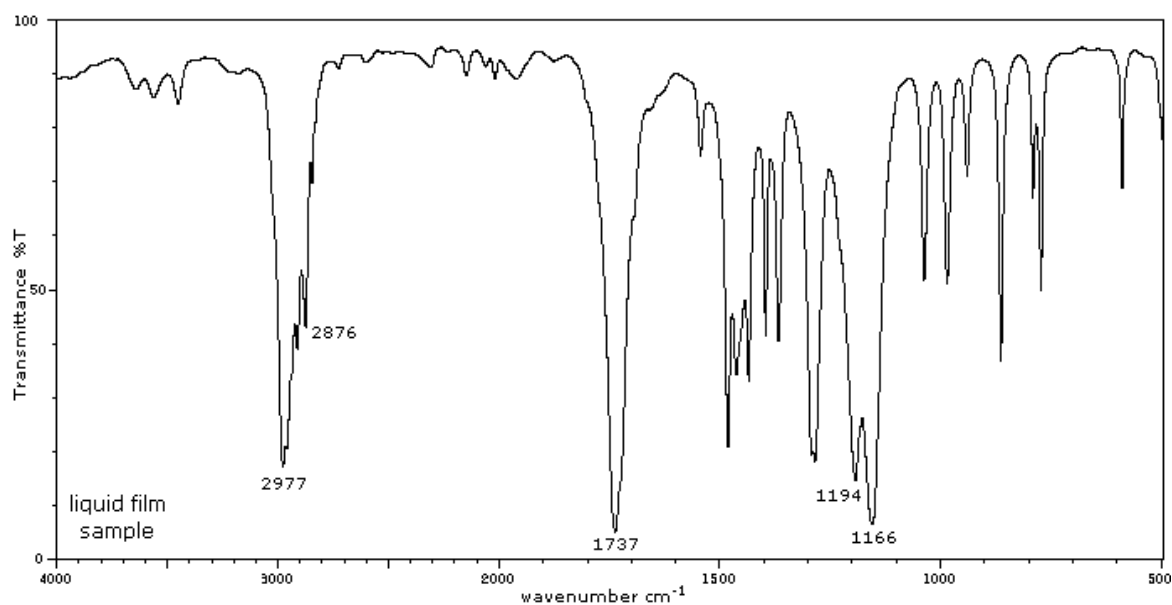
2.1 Explain how IR spectroscopy could be used to distinguish between the following compounds: (6)



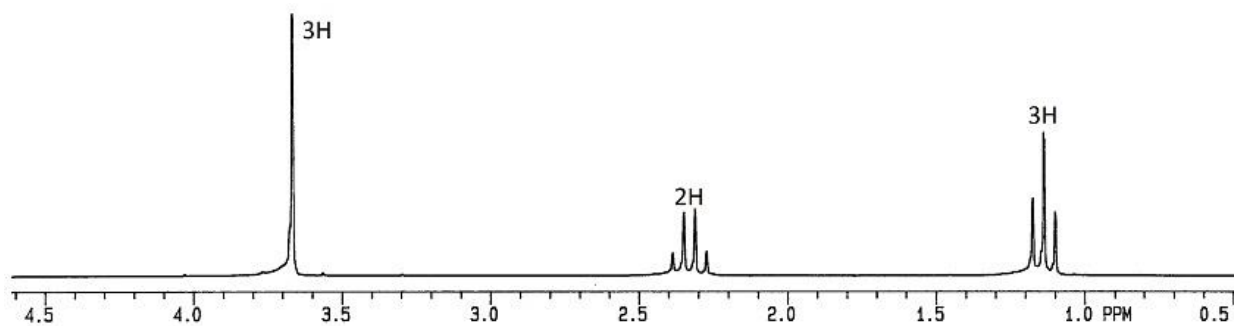
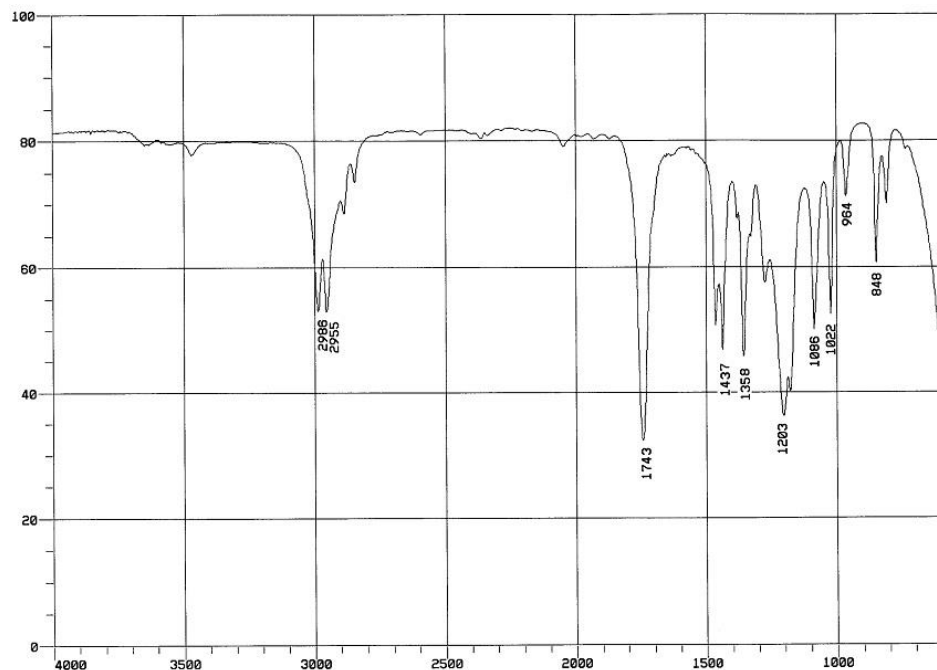
2.2 Determine the multiplicity of each signal for the compound below. You can use arrows to label the multiplicity of each signal. (2)



2.3 A student was analyzing a sample of a sweet-smelling liquid which was found to have a boiling point at 101°C. The infrared spectrum obtained for this sample is given below. Assign the most probable functional groups present in the sample. (6)



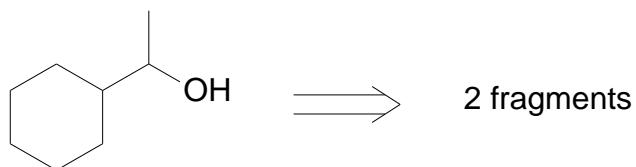
2.4 Identify the following unknown structure ( $C_4H_8O_2$ ) based on the spectroscopic data provided on the following pages. Partial marks will be allocated for your reasoning. (13)



[27]

**QUESTION 3**

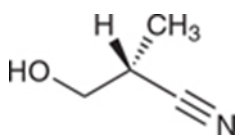
Show the first step in the retrosynthesis of the following molecules. Use the number of fragments provided below as your guide to answer the question.



(4)

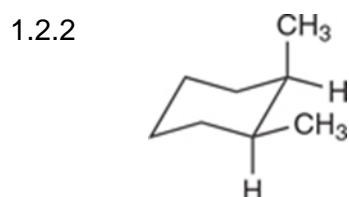
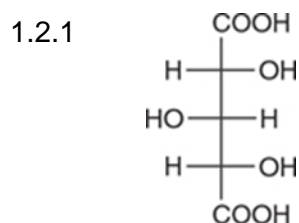
**SECTION B** (*Answer this section on a separate examination answer script*)**QUESTION 1**

- 1.1 What is the configuration of the stereocenter in the following compound? (2)

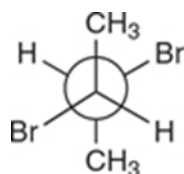


- 1.1.1 R  
1.1.2 S  
1.1.3 Z  
1.1.4 Depends on T

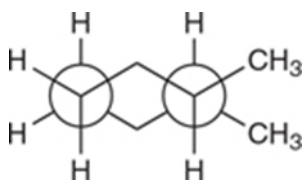
- 1.2 Which of these compounds is expected to be optically active at room temperature? (2)



1.2.3

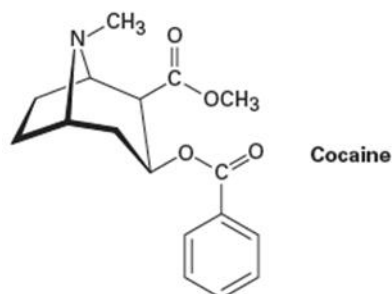


1.2.4



1.3 Describe using equations how you would resolve a racemic mixture of (R) and (S) 2-hydroxypropanoic acid using (R) 1-phenylethylamine. (6)

1.4 A 1.20 g sample of cocaine [ $\alpha$ ]<sub>D</sub> = -16, was dissolved in 7.50 mL of chloroform and placed in a tube having a path length of 5.00 cm.



1.4.1 Calculate the observed rotation? (2)

1.4.2 Is cocaine dextrorotatory or levorotatory based on your answer in 1.4.1? (1)

1.5 *cis*-1,2-Dimethylcyclopropane has more strain than *trans*-1,2 – dimethylcyclopropane. How can you account for this difference? (2)

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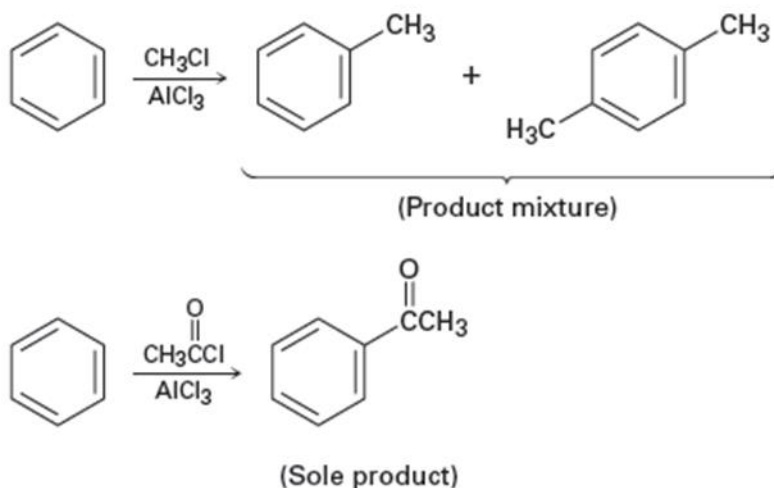
**[15]**

**QUESTION 2**

- 2.1 The relative energy levels of the five  $\pi$  molecular orbitals of the cyclopentadienyl system are similar to those in benzene. Draw an energy level molecular orbital diagram illustrating the five orbitals occupied by cyclopentadienyl anion. (2)
- 2.2 Thiophene, is a sulphur-containing heterocycle, undergoes typical aromatic substitution reactions rather than addition reactions. Why is thiophene aromatic? (2)

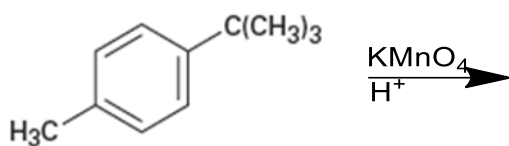


- 2.3 Using the reaction scheme below, provide an explanation why Friedel-Crafts alkylation often give polysubstitution but Friedel-Crafts acylation not. (2)

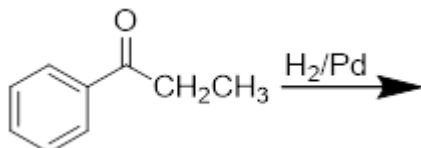


- 2.4 Provide a synthesis scheme of **4-bromo-2-nitrotoluene** from benzene (5)
- 2.5 Write the name of the product (major) you would expect from the following reactions: (4)

2.5.1

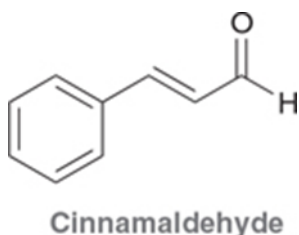


2.5.2

**[15]****QUESTION 3**

3.1 Trimethylacetaldehyde does not undergo an aldol reaction when treated with a base. Explain why not. (2)

3.2 Cinnamaldehyde is one of the primary constituents of cinnamon oil and contributes significantly to the odor of cinnamon. Starting with benzaldehyde and using any other necessary reagents, show how you might prepare cinnamaldehyde. (4)



3.3 Fill in the blanks – write **only** the missing word corresponding to the blank, not the complete sentence – of the statements associated with organic reactions. (10)

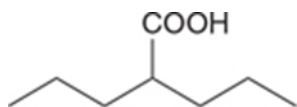
In acidic conditions, an aldehyde or ketone will react with a secondary amine to form an 3.3.1. In the Wolff-Kishner reduction, a hydrazone is reduced to an 3.3.2 under strongly basic conditions. 3.3.3 of acetals, imines, and enamines under acidic conditions produces ketones or aldehydes.

In acidic conditions, an aldehyde or ketone will react with two equivalents of a thiol to form a 3.3.4. When treated with Raney nickel, thioacetals undergo desulfurization to yield a 3.3.5 group.

When treated with a hydride reducing agent, such as lithium aluminum hydride ( $\text{LiAlH}_4$ ) or sodium borohydride ( $\text{NaBH}_4$ ), aldehydes and ketones are reduced to 3.3.6. When treated with hydrogen cyanide ( $\text{HCN}$ ), aldehydes and ketones are converted into 3.3.7.

The Wittig reaction can be used to convert a ketone to an 3.3.8. A Baeyer-Villiger oxidation converts a ketone to an ester by inserting 3.3.9 next to the carbonyl group. Cyclic ketones produce cyclic esters called 3.3.10.

- 3.4 Show how you would use the malonic ester synthesis to prepare the compound below (4)



**[20]**

**SECTION C** (Answer this section on a separate examination answer script)

**QUESTION 1**

- 1.1 Using DFT methods, how would you investigate the reactivity of two organic chemicals? How would you conclude which chemical is more reactive than the other using DFT approaches? (3)
- 1.2 State one advantage and one disadvantage of density functional theory? (2)
- 1.3 Define linear density approximation (LDA) functionals. Explain their major limitation when modelling organic reactions. (3)
- 1.4 In terms of applications and limitations, outline the differences between Semi Empirical methods and Ab Initio methods. (4)
- 1.5 State three areas of application for Molecular Mechanics (MM) methods as applied in computational chemistry. (3)



1.6 State two applications of computational chemistry in each of the following

1.6.1 Medicinal chemistry (2)

1.6.2 Analytical chemistry (2)

1.6.3 Forensic chemistry (1)

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**[20]**

**TOTAL MARKS: 120**

**DATA:**

$$h = 6.6262 \times 10^{-34} \text{ Js}$$

$$c = 3 \times 10^8 \text{ m/s}$$

## pKa Table

X	pK <sub>a</sub>
I	-10
Br	-9.0
Cl	-7.0
F	3.2

R	pK <sub>a</sub>
CF <sub>3</sub>	-14
OH	-9.0
Me	-1.2
Ph	-0.6

R	pK <sub>a</sub>
CF <sub>3</sub>	-0.25
H	3.8
Me	4.8
t-Bu	5.0
OH	6.4

R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	pK <sub>a</sub>
H	H	NO <sub>2</sub>	7.1
H	H	NO <sub>2</sub>	8.4
H	H	H	9.9
H	H	OMe	10.2

R <sub>1</sub>	R <sub>2</sub>	pK <sub>a</sub>
Me	Me	9.0
OEt	Me	11
OMe	OMe	13
OEt	OEt	13.3

R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	pK <sub>a</sub>
Me	Me	Me	18.0
Me	Me	H	16.5
Me	H	H	16.0
H	H	H	15.5
CF <sub>3</sub>	H	H	12.5
CF <sub>3</sub>	CF <sub>3</sub>	H	9.3

R	pK <sub>a</sub>
t-Bu	24.5
Et	25.0

R <sub>1</sub>	R <sub>2</sub>	pK <sub>a</sub>
H	H	38
Et	H	38
Et	Et	40

R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	pK <sub>a</sub>
Ph	H	H	41
CH=CH <sub>2</sub>	H	H	43
H	H	H	48
Me	H	H	50
Me	Me	H	51
Me	Me	Me	53

$$\text{H-X}$$

$$\text{R-S(=O)}_2\text{H}$$

$$\text{R-C(=O)OH}$$

$$\text{R}_1\text{C(=O)CH(R}_2\text{)C(=O)R}_3$$

$$\text{R}_1\text{C(=O)CH(R}_2\text{)C(=O)R}_3$$

$$\text{R}_1\text{C(=O)CH(R}_2\text{)C(=O)R}_3$$

$$\text{R}_1\text{C(=O)CH(R}_2\text{)C(=O)R}_3$$

$$\text{R}_1\text{N(R}_2\text{)H}$$

$$\text{R}_1\text{C(R}_2\text{)(R}_3\text{)H}$$

-10

-5

0

5

10

15

20

25

35

40

45

50

$$\text{R}_1\text{C(=O)CH(R}_2\text{)C(=O)R}_3$$

$$\text{R}_1\text{C(=O)CH(R}_2\text{)C(=O)R}_3$$

$$\text{R}_1\text{C(=O)CH(R}_2\text{)C(=O)R}_3$$

$$\text{H-F (3.2)}$$

$$\text{H-F (3.2)}$$

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$$\text{H-F (3.2)}$$

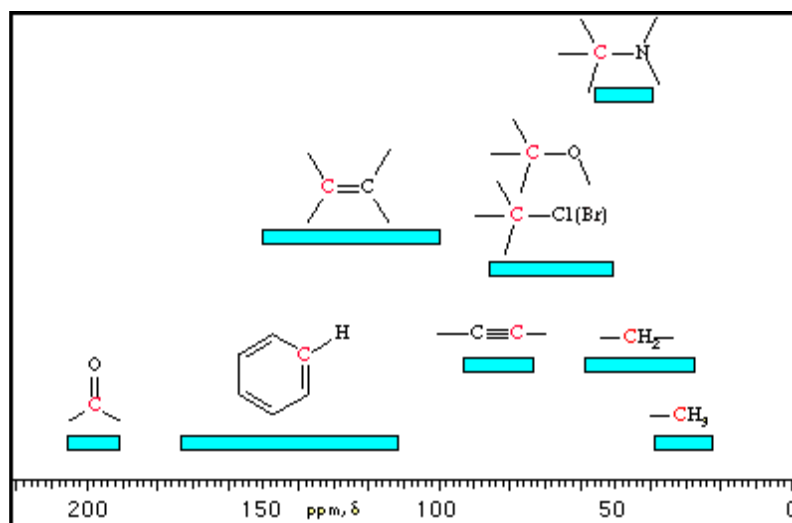
R <sub>1</sub>	R <sub>2</sub>	pK <sub>a</sub>
Me	H	-8.0
Me	Me	-7.3
Me	OMe	-6.5
Me	Ph	-6.2
Me	OH	-6.1

R <sub>1</sub>	R <sub>2</sub>	pK <sub>a</sub>
Me	Me	-3.8
Et	Et	-3.6
Et	H	-2.4
Me	H	-2.2
H	H	-1.7

R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	pK <sub>a</sub>
H	H	H	9.2
Me	H	H	10.5
Me	Me	H	10.6
Me	Me	Me	10.6
Et	Et	Et	10.8
Pr	Pr	H	11.1

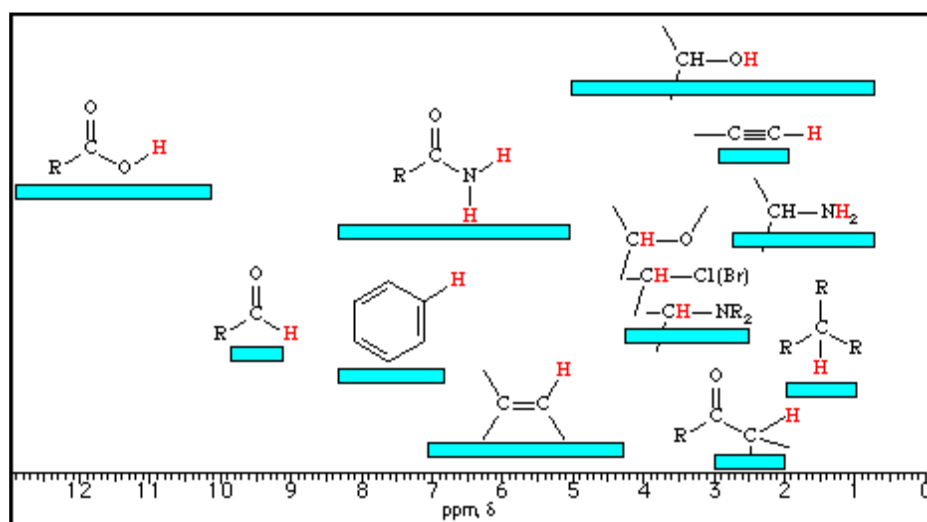
R	pK <sub>a</sub>
Ph	16.0
H	17.0
Me	19.2

R	pK <sub>a</sub>
Ph	23
H	25

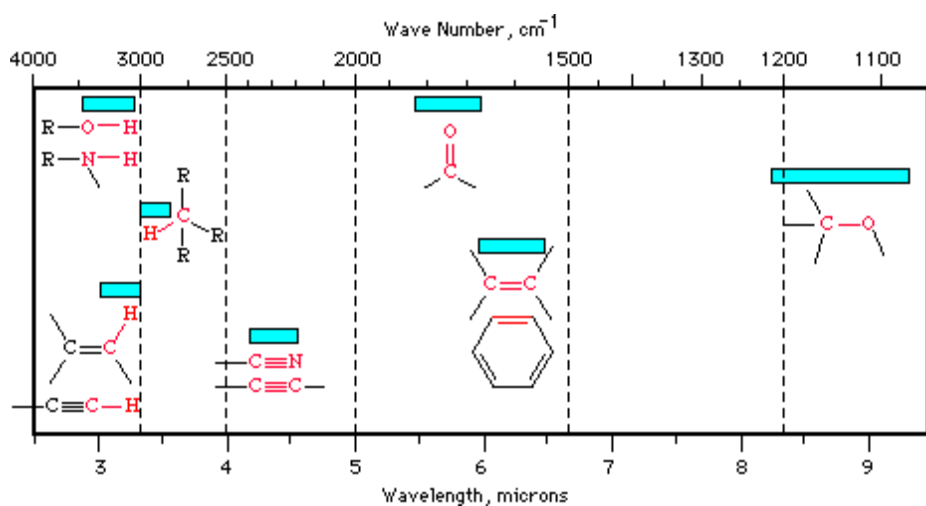


**<sup>13</sup>C NMR  
Correlation Chart**

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UNIVERSITY OF  
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**<sup>1</sup>H NMR  
Correlation Chart**



**IR  
Correlation Chart**