

SECOND PUBLIC EXAMINATION
Honour School of Natural Science

ORGANIC CHEMISTRY IA – SAMPLE PAPER 2011

Candidates should answer *SIX* questions.

Time Allowed: 2.5h

Please begin your answer to each question in a new booklet.

The numbers in square brackets on the right of the pages indicate the approximate marks the examiners intend to assign to each part of the question.

The following abbreviations are used:

Me = CH₃

Ph = C₆H₅

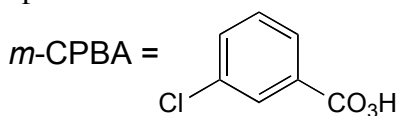
Bu = CH₃CH₂CH₂CH₂

t-Bu = (CH₃)₃C

s-Bu = CH₃CH₂CH(CH₃)

CoA = Coenzyme A

hν = photochemical irradiation



Acidic, basic or aqueous work-up conditions are assumed, with concomitant protonation or deprotonation of charged intermediates. Assume reactions are carried out at room temperature, unless otherwise indicated.

Guide to Questions

1. Aromatic and Heterocyclic Chemistry
2. Reactivity
3. Reactive Intermediates
4. Biological chemistry

5. Conformation and Stereoselectivity
6. Heteroatom chemistry
7. Physical Organic Chemistry
8. Spectroscopy

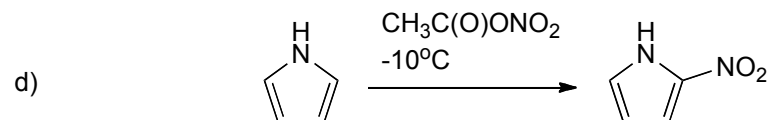
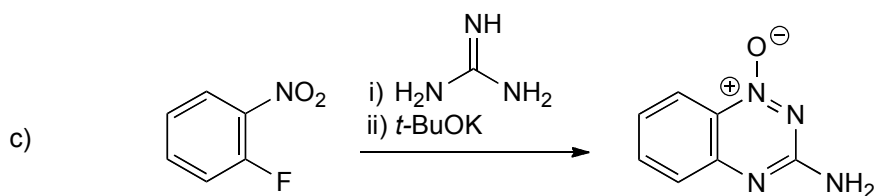
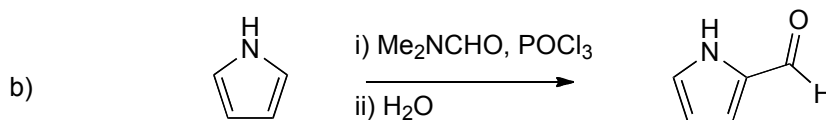
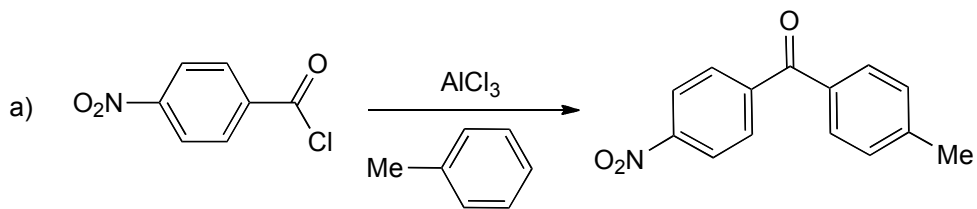
Do not turn over the page until told you may do so.

This is a mock exam paper, designed to illustrate the possible *style* of questions for Part 1A 2011, but not necessarily the exact content. The titles in the Guide to Questions will not necessarily be conserved from one year to the next.

1. Answer Parts A and B.

Part A.

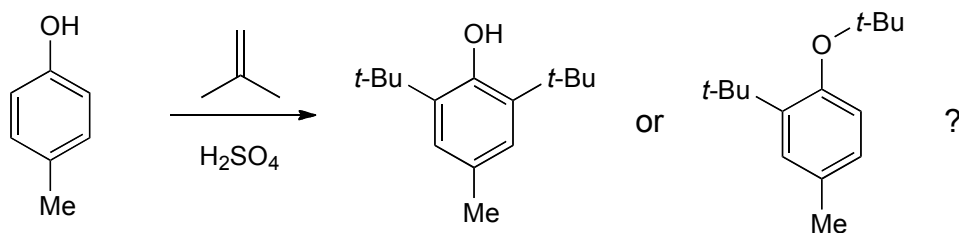
Suggest mechanisms for *three* of the following.



[3 × 5]

Part B.

Describe a spectroscopic method that would enable determination of the structure of the product in the following reaction. Justify your choice.

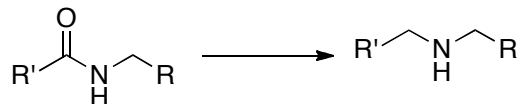


[5]

2. Answer Parts A, B and C.

Part A.

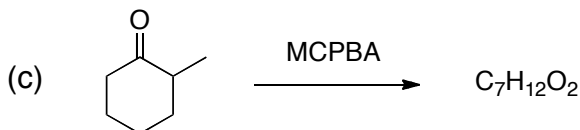
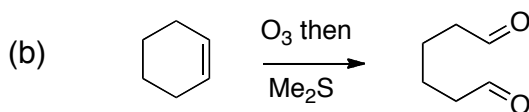
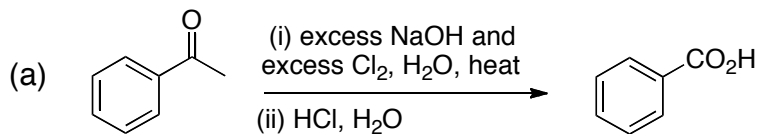
Suggest reagents and reaction conditions that could be used to achieve *either* of the indicated conversions below, giving a mechanistic rationale for your choice (more than one step may be necessary).



[4]

Part B.

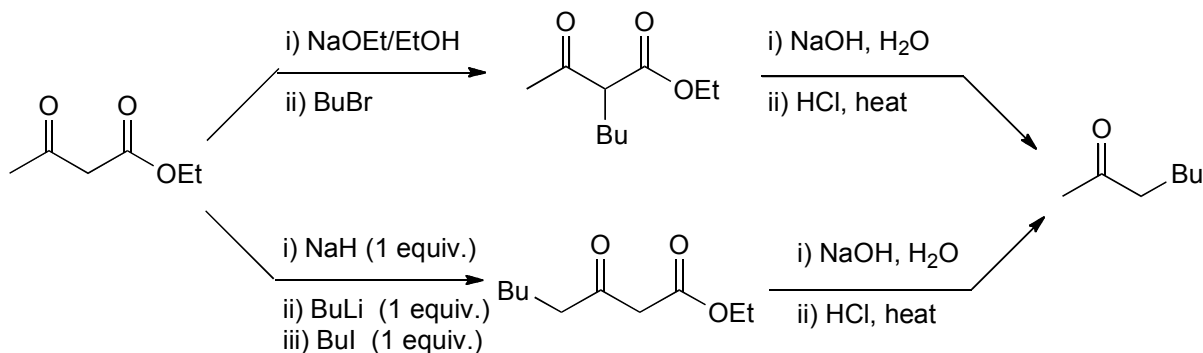
Provide explanations for *two* of the following.



[2 × 4]

Part C.

Provide an explanation for the following sequence.

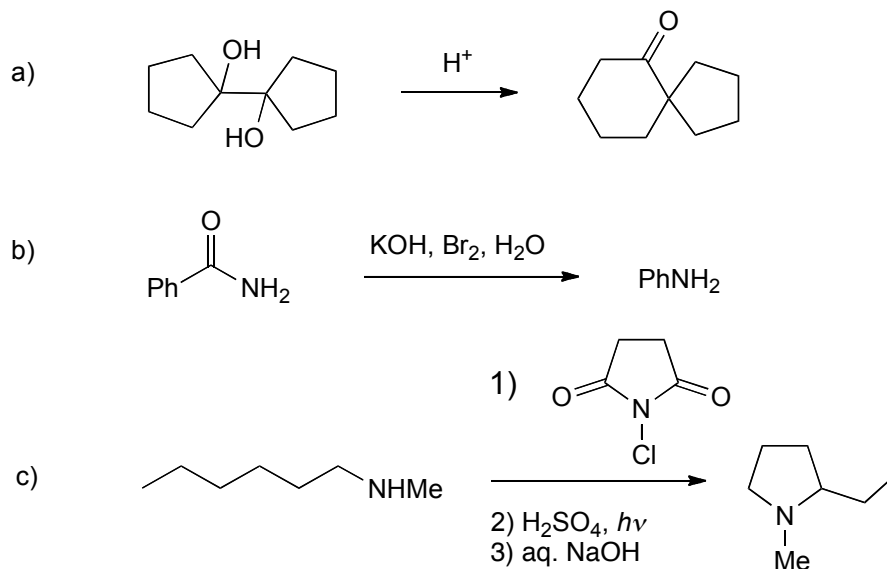


[8]

3. Answer Parts A, B and C.

Part A.

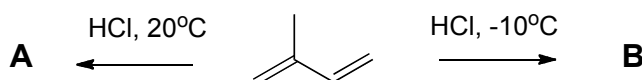
Suggest mechanisms for *two* of the following reactions.



[2 × 5]

Part B.

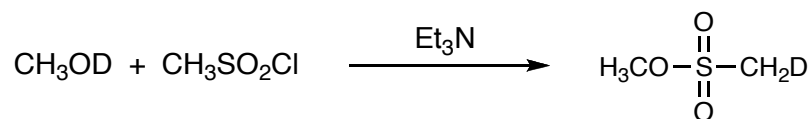
Identify the isomeric products **A** and **B** (C_5H_9Cl) in the following sequence, and provide an explanation for their formation.



[5]

Part C.

When the following reaction is carried out with deuterated methanol (CH_3OD), one deuterium is incorporated in the sulfonate ester product as shown. Explain this observation.

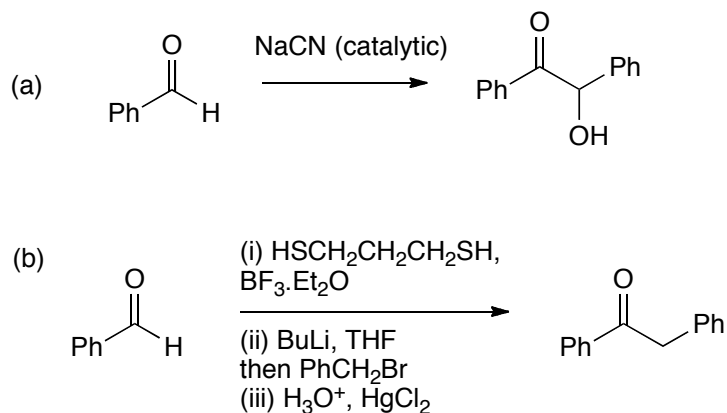


[5]

4. Answer Parts A and B.

Part A.

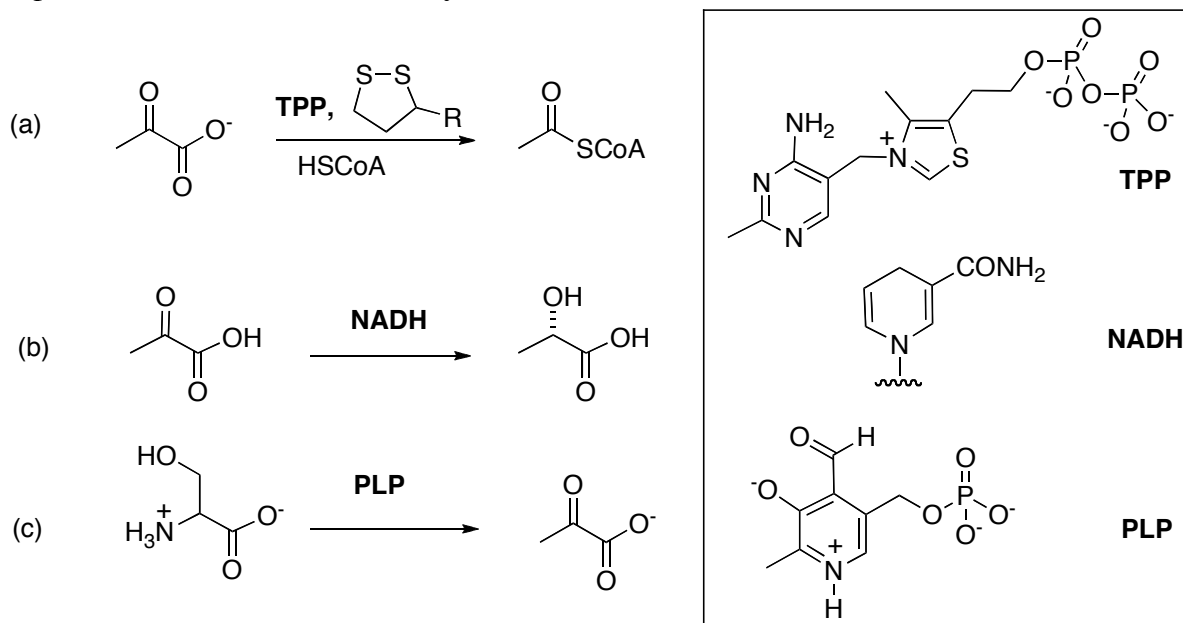
Provide mechanisms for **both** of the following reactions, and use your answer to illustrate the use of the term “*umpolung*” (reversal of reactivity) in organic chemistry.



[2 × 7]

Part B.

Suggest reaction mechanisms and explain as fully as possible *one* of the following. You are not expected to describe details of enzyme active sites.

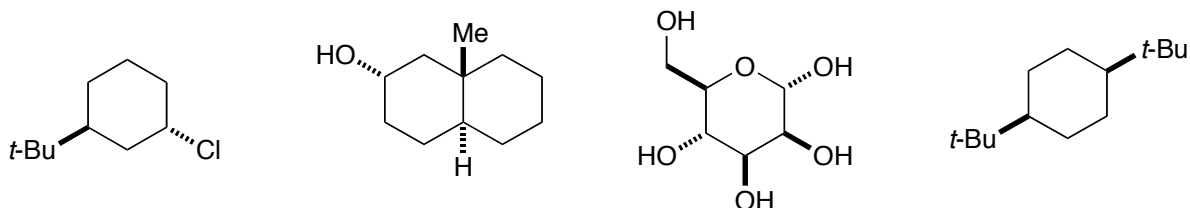


[6]

5. Answer both Parts A and B.

Part A.

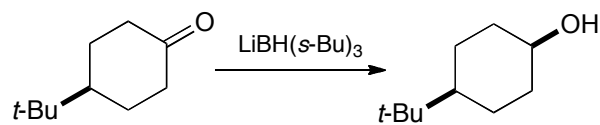
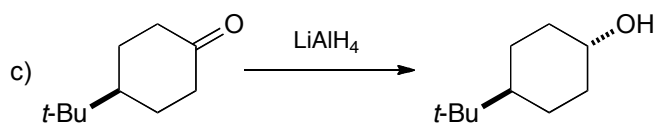
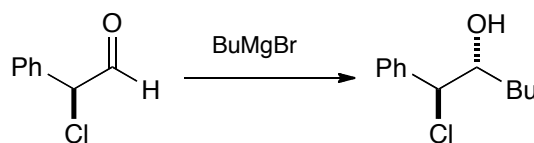
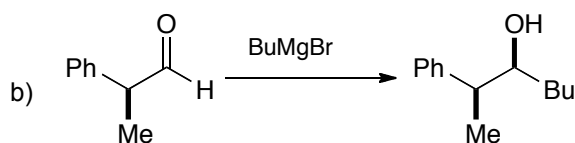
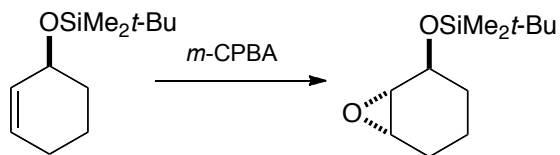
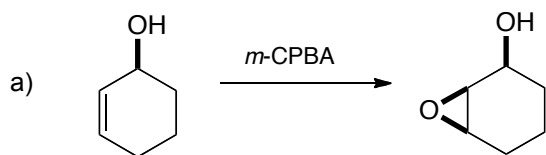
Discuss the factors which affect the preferred conformations of six-membered rings. You may wish to refer to some or all of the following molecules to illustrate your answer, or provide examples of your own.



[8]

Part B.

Contrast and explain the outcomes of **two** of the following pairs of reactions; in each case only the major product diastereomer is shown.



[2 × 6]

6. Answer *both* Parts A and B.

Part A

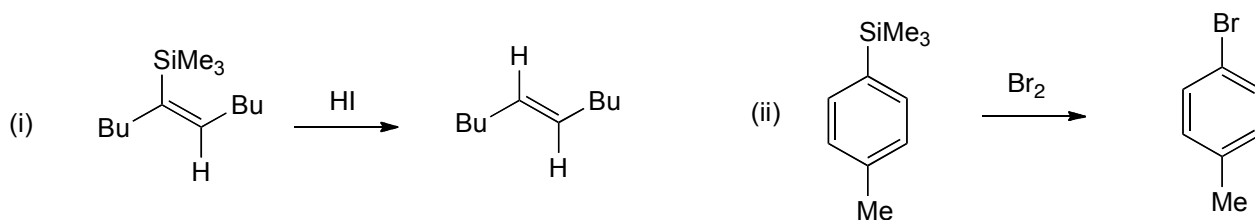
Describe one method for the preparation of aldehydes from primary alcohols using dimethyl sulfoxide (Me_2SO) as a reagent. Your answer should include a mechanism for the reaction. Why is Jones' reagent (CrO_3 , aq H_2SO_4 , acetone) not efficient for this purpose?

[6]

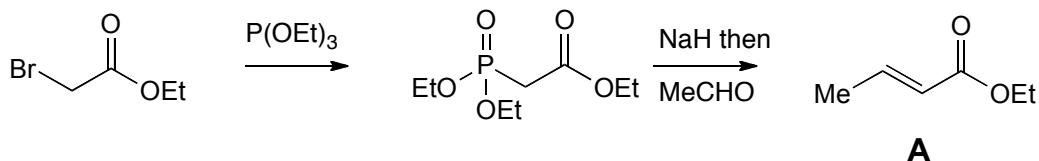
Part B.

Provide explanations for *two* of the following.

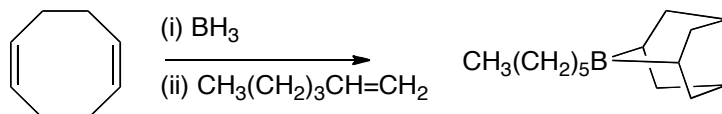
(a) Write mechanisms for the following two reactions. Account for the stereochemistry of the product in (i).



(b) Write mechanisms for the following two reactions. How could ^1H NMR spectroscopy be used to confirm the stereochemistry of compound A?



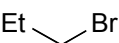
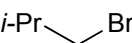
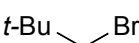
(c) Write mechanisms for the two steps of the following sequence.



[2 × 7]

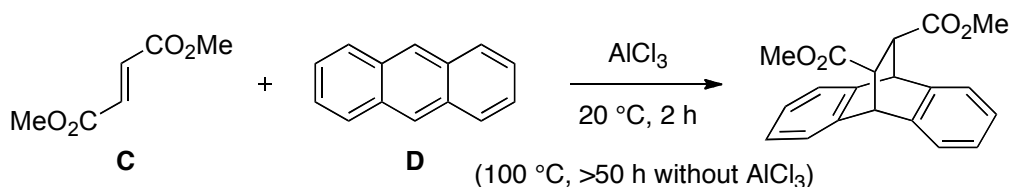
7. Provide explanations for *four* of the following.

(a) The relative rate constants (k_{rel}) for the S_N2 reaction (NaOEt, EtOH, 55°C) of the primary alkyl bromides decrease as shown below.

			
k_{rel}	1.0	0.11	1.5×10^{-5}

(b) The relative basicities of simple amines, determined in aqueous solution, increases in the order shown by series **A**: $\text{NH}_3 < \text{MeNH}_2 < \text{Me}_3\text{N} < \text{Me}_2\text{NH}$ whereas, in the gas phase, the order is shown by series **B**: $\text{NH}_3 < \text{MeNH}_2 < \text{Me}_2\text{NH} < \text{Me}_3\text{N}$.

(c) The rate of reaction of dimethyl fumarate **C** with anthracene **D** to give the indicated product is markedly increased by the addition of AlCl_3 .



(d) The thermal ring-opening of cyclobutene diesters **E** and **F** gives different stereoisomers of the product (that is, the processes are stereospecific).



(e) The thermodynamic parameters for the dissociation of simple carboxylic acids **G** in aqueous solution, tabulated below. [T = 298 K]

Acid G	$\text{p}K_{\text{a}}$	$\Delta H / \text{kJ mol}^{-1}$	$T\Delta S / \text{kJ mol}^{-1}$
$\text{CH}_3\text{CO}_2\text{H}$	4.8	-0.4	-27.4
HCO_2H	3.8	-0.3	-22.0

[4 × 5]

8. Answer *all* of Parts A, B, C and D.

Part A

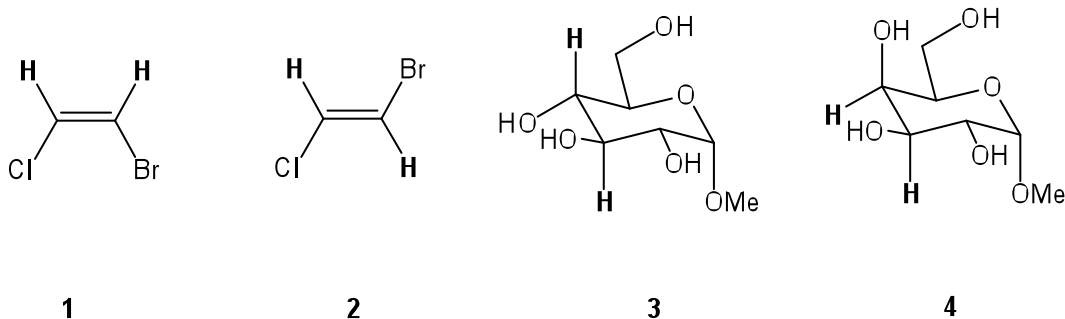
Sketch the form of the “Karplus curve” that depicts the general dependence of the ^1H - ^1H coupling constant $^3J_{\text{HH}}$ and the dihedral angle ϕ between adjacent (vicinal HC-CH) protons. What is significant about $\phi = 90^\circ$?

[3]

Part B

Which of structures **1** and **2** has the greater 3-bond ^1H - ^1H coupling constant between the hydrogen atoms shown in bold? Likewise, which of structures **3** and **4** has the greater 3-bond ^1H - ^1H coupling constant between the hydrogen atoms shown in bold? Give your reasoning.

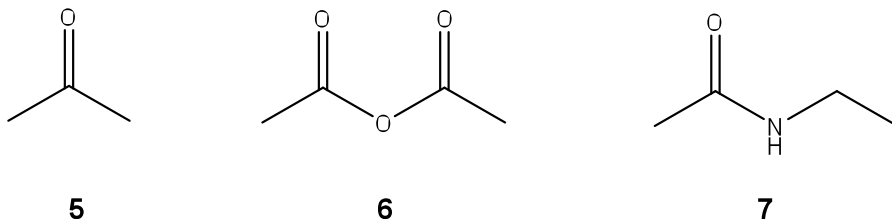
[3]



Part C

Indicate how the compounds **5**, **6** and **7** could be distinguished by infra-red spectroscopy, giving a brief explanation of the basis for their different behaviour.

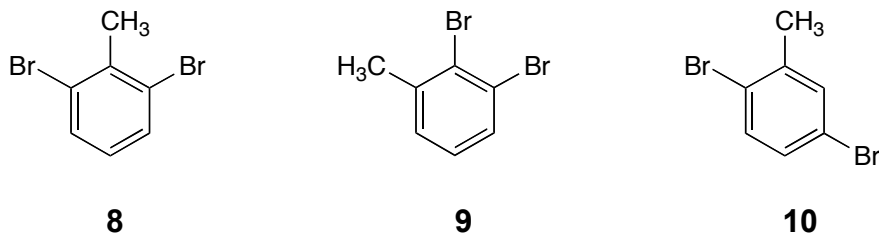
[4]



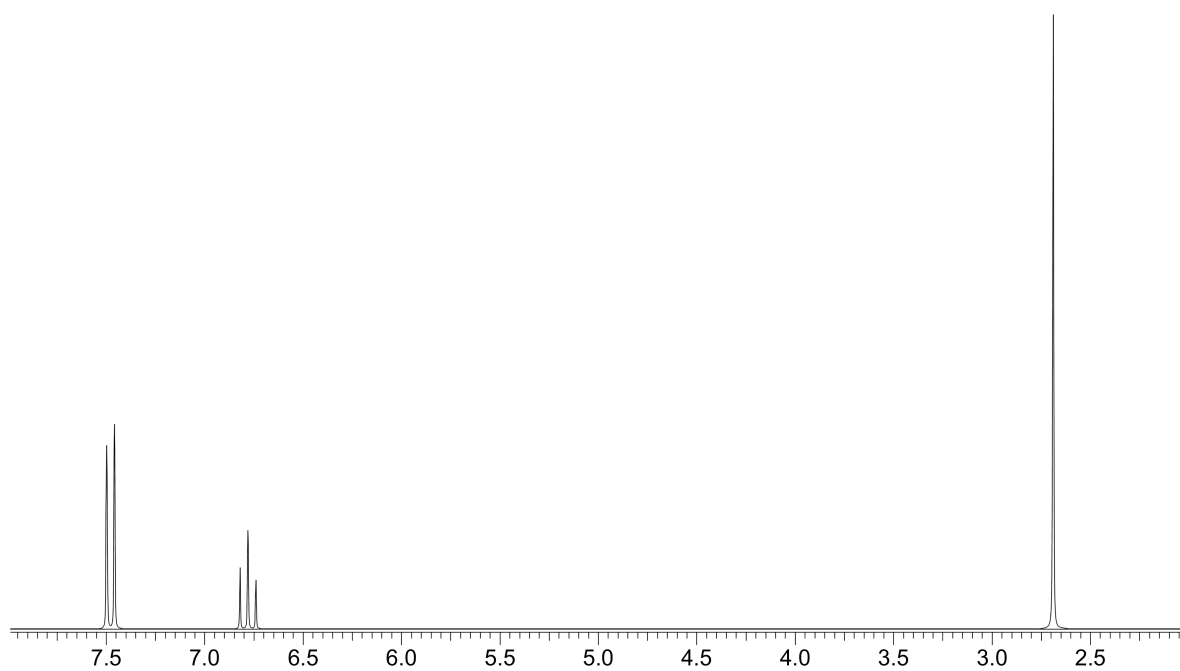
Part D

Assign with reasoning the ^1H NMR spectra I-III (all recorded in CDCl_3) to each of the following isomers **8-10**, explaining the observed chemical shift and spin coupling patterns.

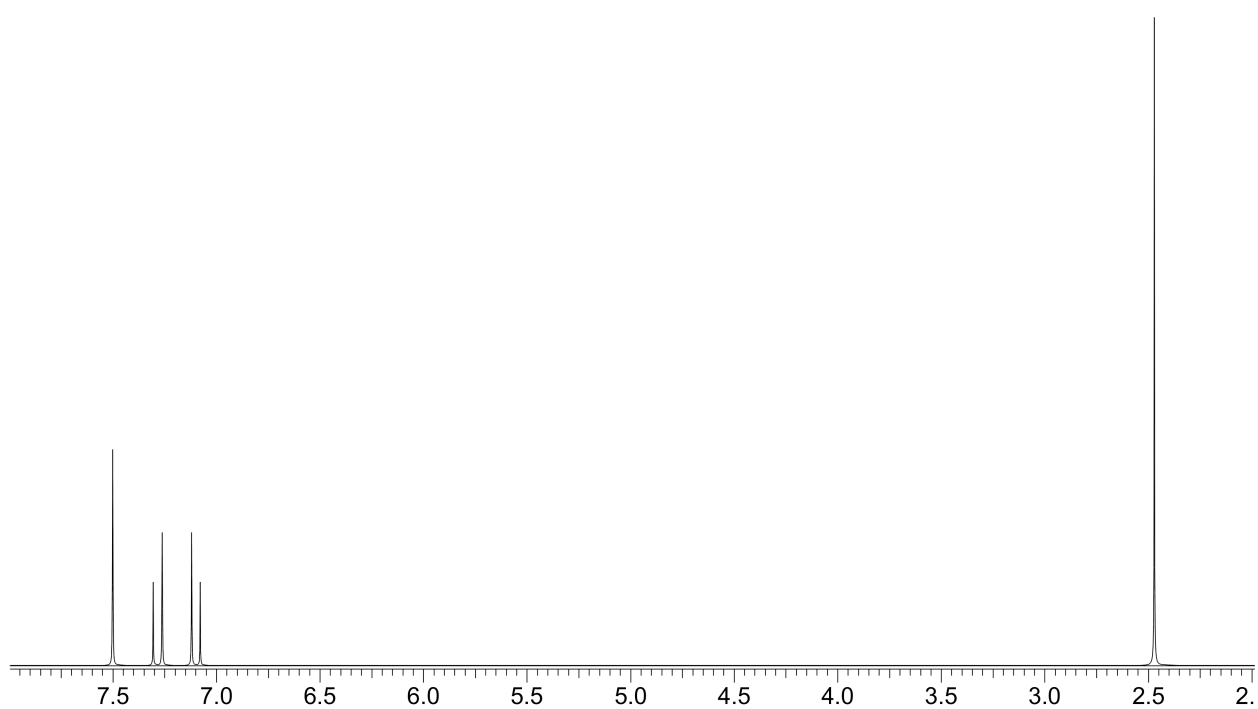
[10]



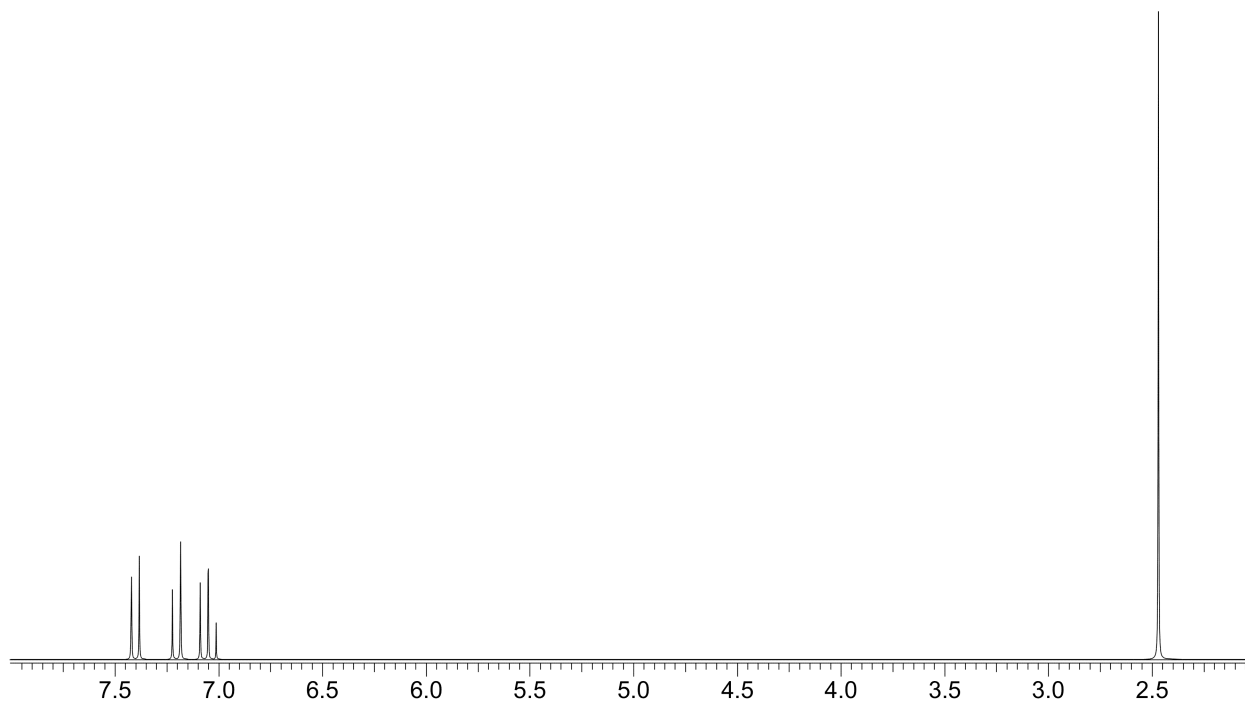
Spectrum I



Spectrum II



Spectrum III



END OF PAPER