MCGILL UNIVERSITY
FACULTY OF SCIENCE

DEPARTMENT OF CHEMISTRY

Version 1

Room: _____

Seat: _____

CHEMISTRY 222/234 – Midterm 1

October 10th, 2017, 6:15 – 8:30 pm

LAST NAME **FIRST NAME** **last 4 ID numbers**

EXAMINER: Dr Dmitrii Perepichka

INSTRUCTIONS:

1. Fill in your full name, student number and "check-bit" on the provided scantron answer sheet.

2. Answer all **24** questions in Part A on the scantron sheet (**60** marks); answer all **4** questions in Part B directly on the exam provided (**40** marks).

3. Make dark marks for your answer only when you are sure of your response. Pens or pencils are ok but do not remark your answer (no X) if you use pen.

4. Put your name and last 4 digits of your student ID on the first page of the exam as well as on the section B and hand it in along with the answer sheet at the end of the exam. ***There must be an answer sheet and an exam for each student.***

5. Exam results will be posted on myCourses in several days.

6. Simple calculators are permitted- no memory. NMR and IR spectroscopy charts are provided at the end of the exam booklet. For students who use English as a second language, translation dictionaries are permitted. Molecular models are permitted.

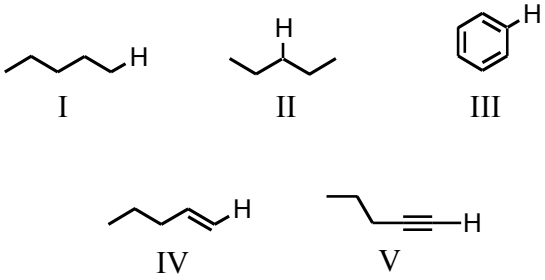
7. **PLEASE DO NOT ASK QUESTIONS OF THE INVIGILATORS ABOUT INTERPRETATIONS OF THE EXAM QUESTIONS. IF YOU HAVE A QUERY OF SIGNIFICANCE, PLEASE SUMMARIZE IN ON THE FRONT OF THE EXAM AND IT WILL BE EVALUATED**.

8. THE EXAMINATION SECURITY MONITOR PROGRAM DETECTS PAIRS OF STUDENTS WITH UNUSUALLY SIMILAR ANSWER PATTERNS ON MULTIPLE-CHOICE EXAMS. DATA GENERATED BY THIS PROGRAM CAN BE USED AS ADMISSIBLE EVIDENCE, EITHER TO INITIATE OR CORRROBORATE AN INVESTIGATION OR CHARGE OF CHEATING UNDER SECTION 16 OF THE CODE OF STUDENT CONDUCT AND DISCIPLINARY PROCEDURES.

INVIGILATORS: AT THE END OF THE EXAM, PLEASE MAKE A SEPARATE PILE OF THE ANSWER SHEETS. THANK YOU

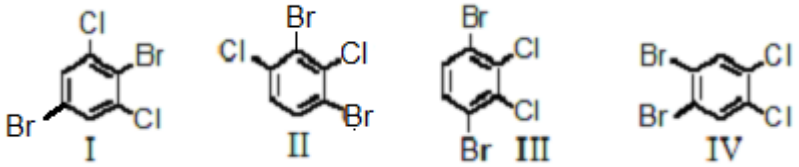
Part A: Multiple Choice (24 questions – 2.5 marks each, 60 marks total)
Choose the one alternative that best completes the statement or answers the question

1. Which carbon-hydrogen bond have the highest frequency IR absorption?



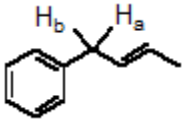
A) I
B) II
C) III
D) IV
E) V

2. A dibromodichlorobenzene which gives four signals in the broadband proton-decoupled ^{13}C spectrum could be:



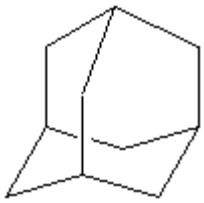
A) I
B) II
C) III
D) IV
E) More than one of these

3. In the structure shown, H_a and H_b are classified as:



A) homotopic protons.
B) vicinal protons.
C) enantiotopic protons.
D) diastereotopic protons.
E) isomeric protons.

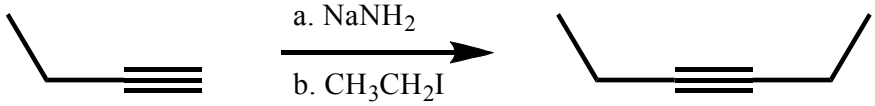
4. For the shown compound, how many different signals would you see in the ^{13}C NMR? (Assume that you can see them all.)



A) 1
B) 2
C) 4
D) 8
E) None of these choices.

5. Gasoline is a mixture of >100 different isomers of hydrocarbons consisting from ~6 to >20 carbon atoms. What method would be most suitable for separation of these individual components for analysis:
A) Distillation
B) Recrystallization
C) Extraction
D) Gas chromatography (GC)
E) High-pressure liquid chromatography (HPLC)

6. For the following reaction sequence (it is not necessary to understand the chemistry) what significant change(s) would be expected by IR (ignoring C-H absorptions)?



A) A peak around 1710 cm^{-1} would disappear.
B) A peak around 1710 cm^{-1} would appear.
C) A peak around 2150 cm^{-1} would disappear.
D) A peak around 2150cm^{-1} would appear.
E) No change would be observed.

7. For the methylene group *b* in 1-bromopropane, the maximum theoretical multiplicity in the ^1H NMR spectrum, presuming that J_{ab} is sufficiently different from J_{bc}, is which of these?

$CH_3-CH_2-CH_2-Br$

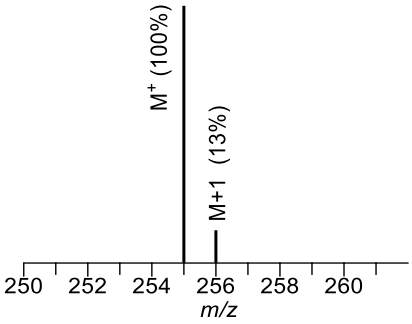
c b a

A) 3
B) 5
C) 7
D) 9
E) 12

8. Which of these isotopes is NMR active?
   A) ^{12}C
   B) ^{16}O
   C) ^{19}F
   D) ^{28}Si
   E) ^{32}S

9. Mikhail Tswett is credited with invention of
   A) X-ray crystallography
   B) Atomic Force Microscopy
   C) Chromatography
   D) Nuclear Magnetic Resonance spectroscopy
   E) Mass-spectrometry

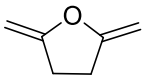
10. A molecular ion with the shown isotope pattern is most likely to contain:



   A) 10 carbons, 3 chlorines
   B) 12 carbons, 1 nitrogen
   C) 12 carbons, 4 sulfurs
   D) 13 carbons, no nitrogens, no bromines
   E) 18 carbons, 1 oxygen and 23 hydrogens

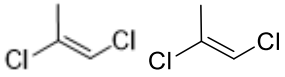
11. 1H and 13C NMR signals are not observed together in the same spectrum because
   A) The natural abundance of magnetic ^{13}C nucleus is only 1.1%
   B) Signals of protons are intentionally removed form of ^{13}C NMR via broad-band proton decoupling
   C) 1H nuclei have four time larger gyromagnetic ratio and resonate at much higher frequency than 13C nuclei
   D) 1H nuclei have four time smaller gyromagnetic ratio and resonate at much lower frequency than 13C nuclei
   E) 13C nucleus is heavier than 1H and appears at ~13 times higher frequency than 1H.

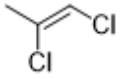
12. Consider the expected ^{1}H NMR spectrum of 2,4-dimethyl-1,4-pentadiene. Which of the following is likely to be observed?



A) 8 signals: all singlets
B) 4 signals: two doublets, two triplets
C) 3 signals: all singlets
D) 3 signals: one singlet, 2 doublets
E) 2 signals: all singlets

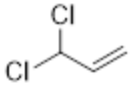
13. Which of the compounds below can have the following 1H NMR spectrum : δ = 6.35 (1H, d, J = 12 Hz), 6.09 (1H, dd, J = 12 and 6 Hz), 4.09 (2H, d, J = 6 Hz)

A) 

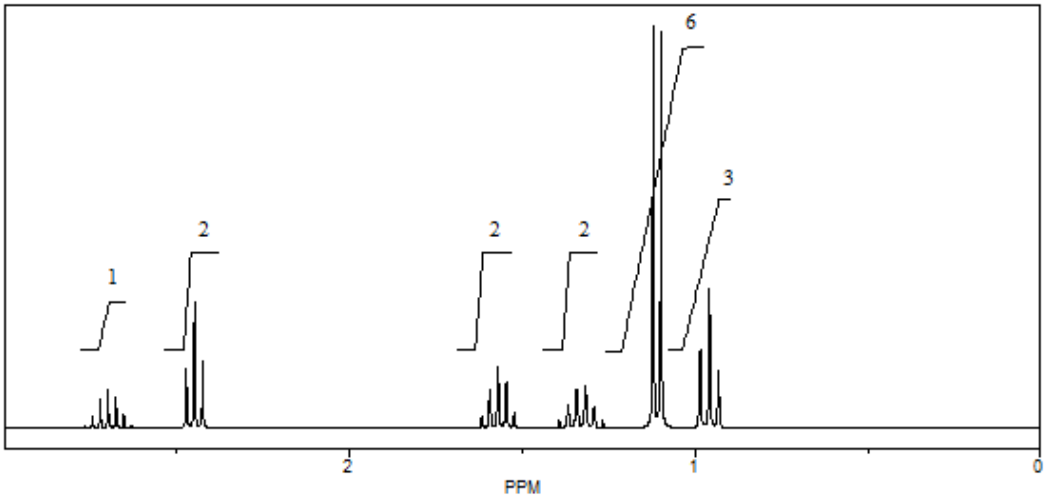
B) 

C) 

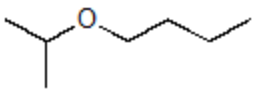
D) 

E) 

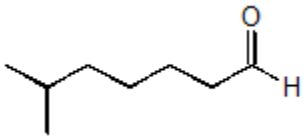
14. What is the structure of the compound in the following ^{1}H-NMR spectrum with the molecular formula $C_8H_{16}O$? Relative integration is shown.



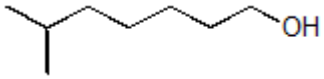
A)



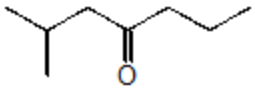
B)



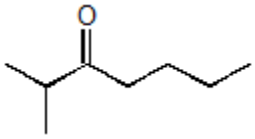
C)



D)



E)

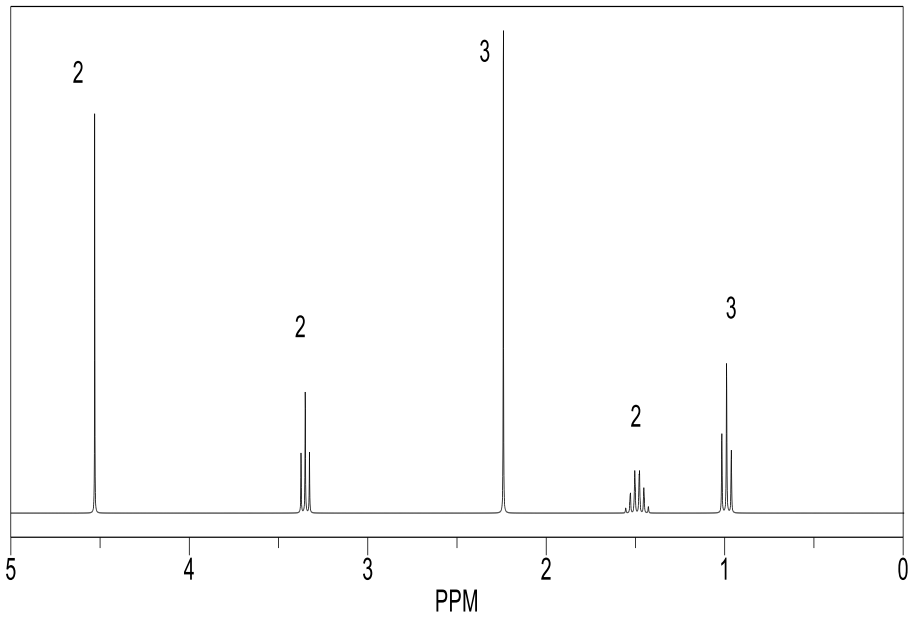


15. The data below from the molecular ion region of the mass spectrum of a halogen-containing compound are consistent with the presence of what halogen(s) in the original compound?

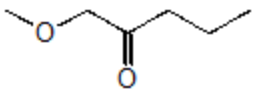
M^+ (51%)
M+2 (100%)
M +4 (49%)

A) One Br
B) One Cl
C) One Br and one Cl
D) Two Br
E) Two Cl

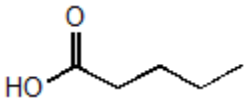
16. What is the structure of the compound in the following ^{1}H-NMR spectrum ? Relative integration is shown.



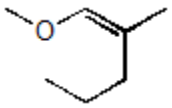
A)



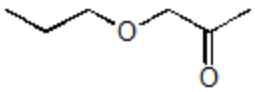
B)



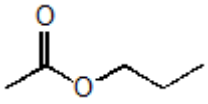
C)



D)

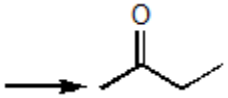


E)



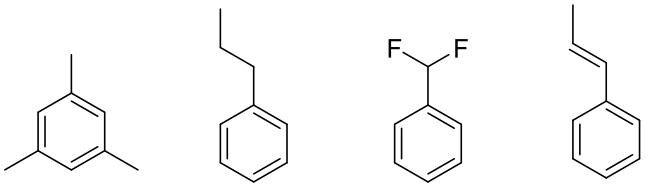
17. Predict the base peak for 2-methyl-2-propanol,
    A) m/z 15
    B) m/z 17
    C) m/z 43
    D) m/z 57
    E) m/z 59

18. Which one of the following best represents the predicted approximate chemical shift and coupling for the hydrogen(s) indicated with the arrow?



A) 1.00 ppm, singlet
B) 2.10 ppm, singlet
C) 2.10 ppm, triplet
D) 3.10 ppm, singlet
E) 3.10 ppm, triplet

19. Which of the following compounds would be expected to have the base peak m/z = 91 in its mass spectrum?

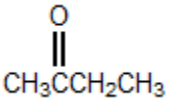


I **II** **III** **IV**

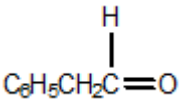
A) I
B) II
C) III
D) IV
E) more than one of these

20. A downfield (δ 9-10) doublet is observed in the ^{1}H NMR spectrum of:

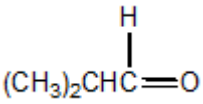
A)



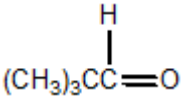
B)



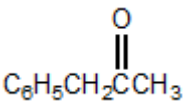
C)



D)



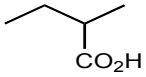
E)



21. A compound $C_5H_{11}Cl$ which exhibits only two singlets in the ^1H NMR spectrum must be:
    A) 1-Chloropentane
    B) 1-Chloro-2,2-dimethylpropane
    C) 1-Chloro-2-methylbutane
    D) 3-Chloropentane
    E) 1-Chloro-3-methylbutane

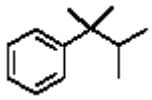
22. The IR stretching frequency occurs at the lowest frequency for which of these bonds?
    A) C-H
    B) C-C
    C) C-N
    D) C-O
    E) C-Br

23. For the functional group(s) on the following molecule, what characteristic IR absorption(s) would be expected (ignoring C-H absorptions)?



    A) peaks around 1700 and 1650 cm^{-1}
    B) a strong broad peak over 3600 to 2500 and around 1710 cm^{-1}
    C) peaks around 1650 and 3300 cm^{-1}
    D) peaks around 3300 and 1710 cm^{-1}
    E) none of these choices.

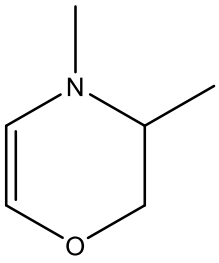
24. Predict the number of signals in proton-decoupled ^{13}C NMR of 2,3-dimethyl-2-phenylbutane.



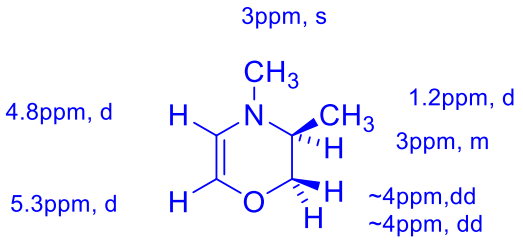
    A) Six
    B) Eight
    C) Ten
    D) Eleven
    E) Twelve

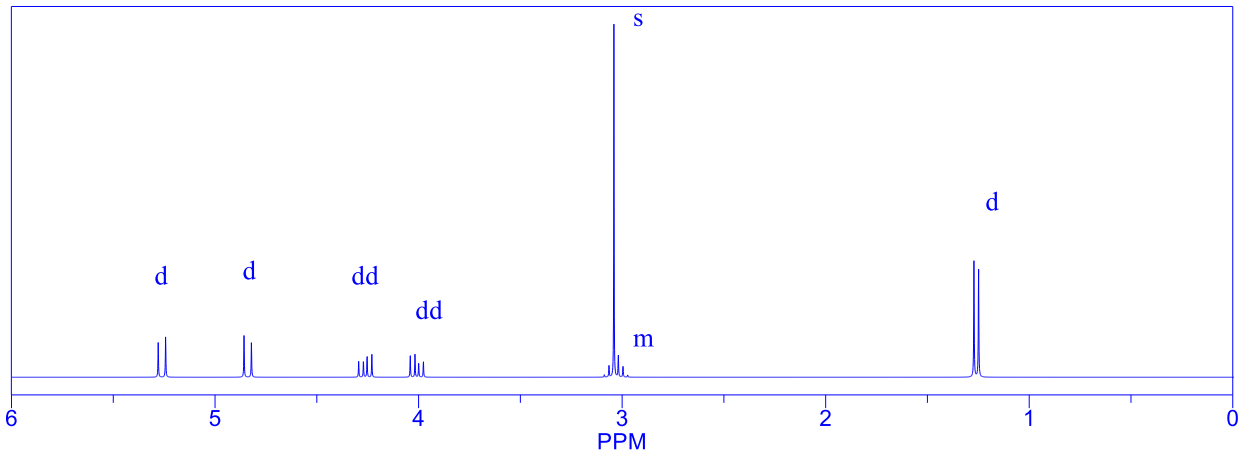
Part B (out of 40)

1) (**10 marks**) Draw the expected ^{1}H NMR spectrum of compound **A**, attributing all inequivalent protons and showing their approximate chemical shift (δ, ppm) in the expected order and splitting pattern (multiplicity). Indicate the position of tetramethylsilane (TMS) reference on the spectrum.



A

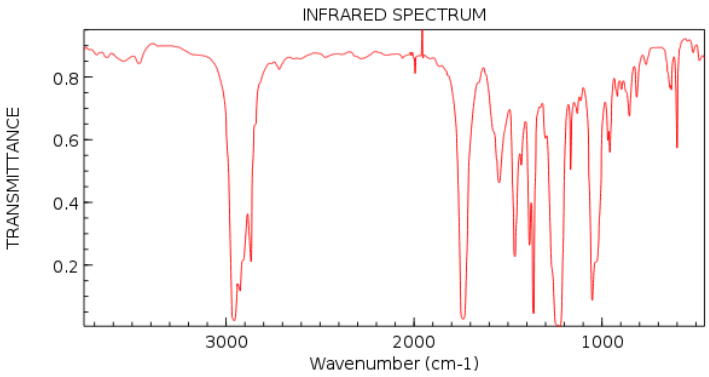


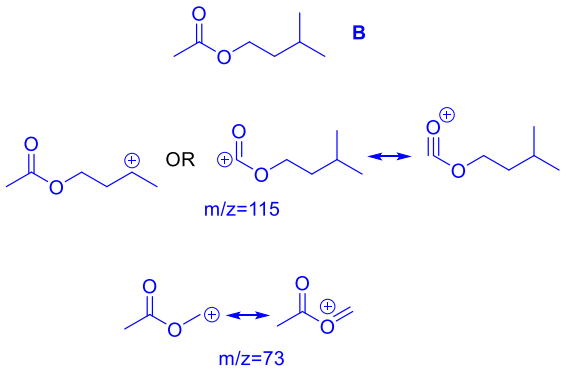


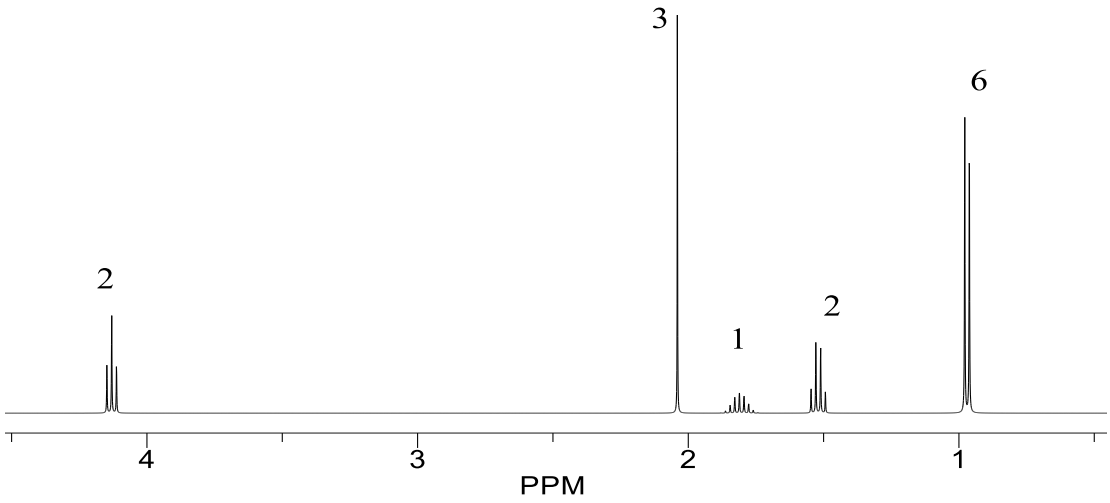
* tertiary CH at ~3ppm appears as a multiplet (m). Sextet and doublet of doublet of tripletsare also acceptable answers.

** NCH3 singlet overlaps with CH multiplet, but any location ~3-3.5 would be acceptable for both signals.

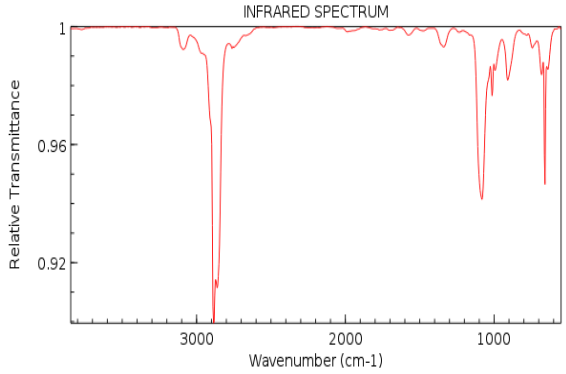
2) **(10 marks) B** is an essential component of pear and banana oils. Its HR-MS shows a molecular ion at 130.0992 Da which corresponds to $C_7H_{14}O_2$ and two most abandon fragments at 115.0755 Da and 73.0283 Da. It has the following IR and ^1H NMR spectra (with integrations shown above each peak) and shows 6 peaks in proton-decoupled ^{13}C NMR. Show the structure of this compound attributing each NMR peak. Show the structure of the two fragments detected in positive mode HRMS.

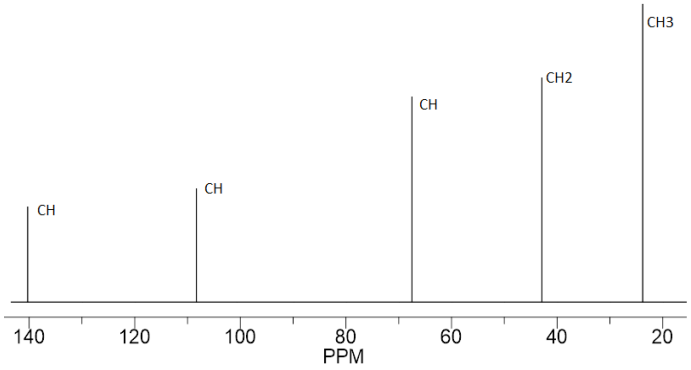


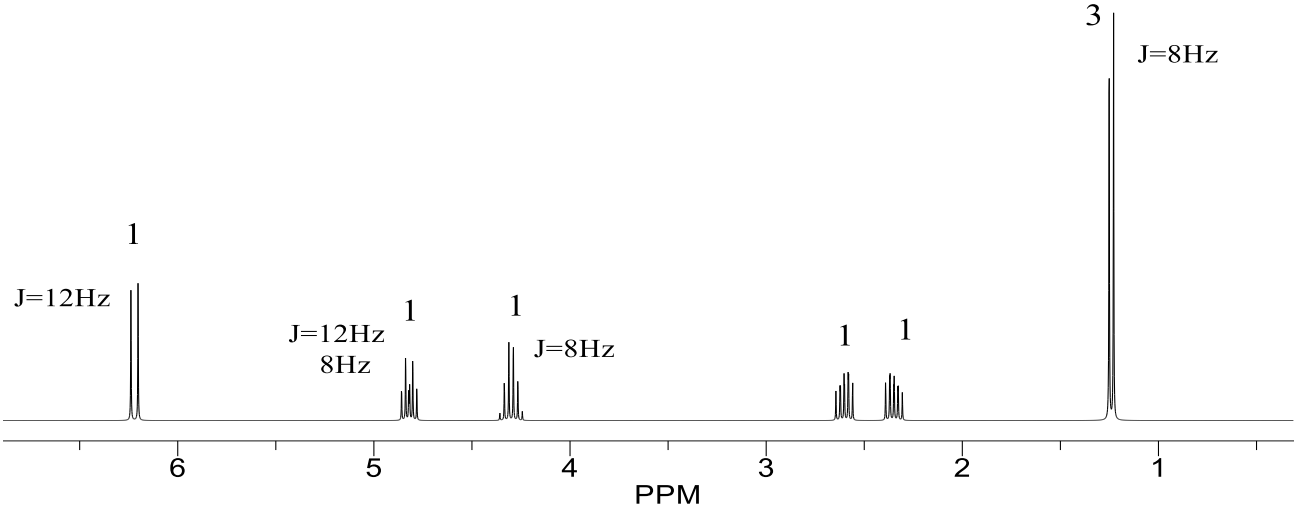


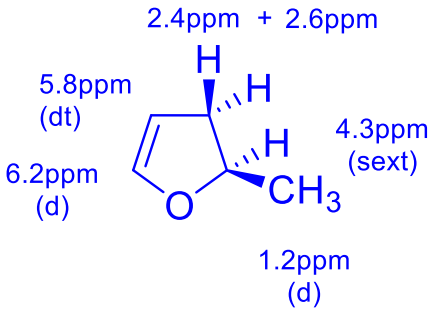


3) (**12 marks**) Propose the structure of compound **C** (C_5H_8O) based on its IR, ^{13}C NMR (DEPT data provided) and ^{1}H NMR (relative integration and some splitting constants are shown) spectra below. Assign all ^{1}H NMR peaks and explain the splitting pattern of protons appearing near 2.5ppm.



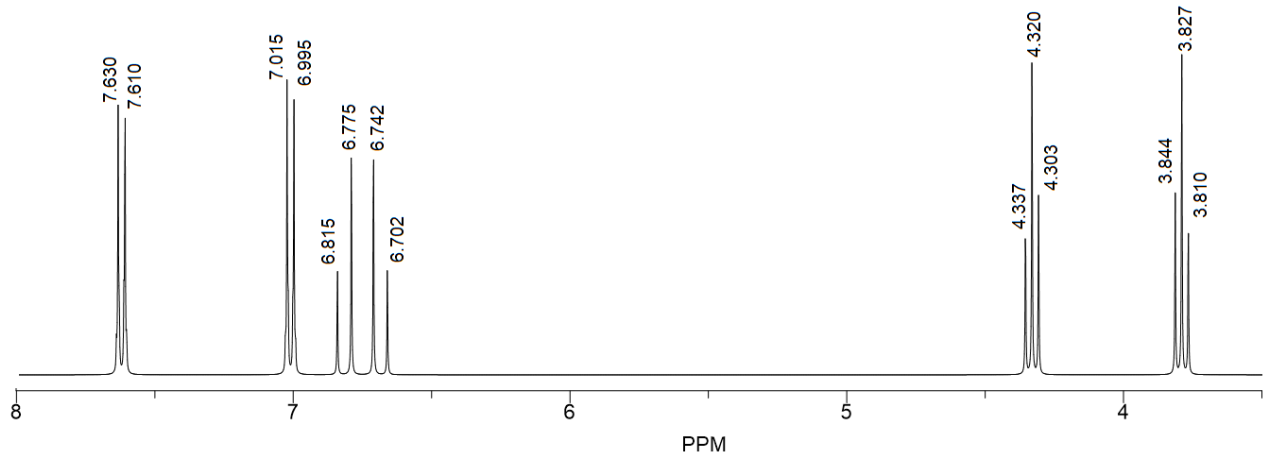






Two multiplets at 2.4 and 2.6ppm are due to diastereotopic protons on the CH2. Each of them should have a theoretical ddd multiplicity. They appear as mutliplets with 5 lines due to overlap.

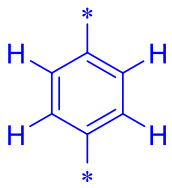
4) (**8 marks**) The 1H NMR spectrum below was recorded on 9.4 Tesla / 400 MHz instrument. (i) Show multiplicity (*s* for singlet, *d* for doublet, *t* for triplet, *q* for quartet) of each inequivalent groups of protons on the spectrum, (ii) determine the corresponding splitting constants (in Hz) and indicate which groups of protons interact with each other. (iii) What structural fragments are most likely present in the analyzed compound? (iv) What explains the different intensity of the peaks in 6.50 – 6.90 region of the spectrum.

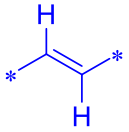


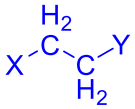
(i, ii) δ (ppm) = 7.62 (d, 8.0 Hz), 7.01 (d, 8.0 Hz), 6.79 (d, 16.0 Hz), 6.72 (d, 16.0 Hz), 4.32 (t, 6.8 Hz), 3.29 (t, 6.8 Hz). Splitting pairs: two doublets with J=8Hz; two doublets with J=16Hz; two triplets with J=6.8Hz

(iii)

Two doublets 7-8 ppm; two doublets at 6.6-6.8ppm; two triplets at 3.7-4.4ppm







X,Y - very electronegative atoms (O, Cl, N)

(iv) 'roof effect' (two multiplets due to interacting protons show increased relative intensity of the "inner" lines – i.e. those close to each other).