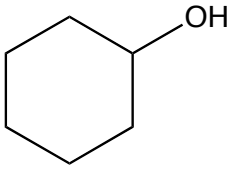
Name: _____

Exam I – Principles of Organic Chemistry II – CH 212
February 26th 2008 – 1:00 PM to 3:00 PM

Look over the whole exam and work on what you feel more comfortable FIRST! Show all your work if you want to receive partial credit. Use front and back of each page to write your answers. Be clear and concise, and use PENCIL to avoid making a big mess…

1) (30 points) Predict the structure of the products and intermediates for the following reactions sequences. Provide the mechanisms of the bolded reactions only.

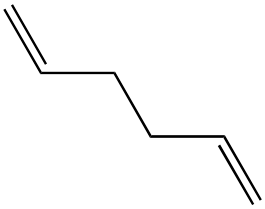
i) 

i) PBr_3
ii) $tBuO^-K^+$

C_6H_{10}

i) O_3, MeOH
ii) Zn, AcOH

$C_6H_{10}O_2$

ii) 

i) BH_3, Et_2O
ii) H_2O_2, NaOH

$C_6H_{14}O_2$

PCC, CH_2Cl_2

$C_6H_{10}O_2$

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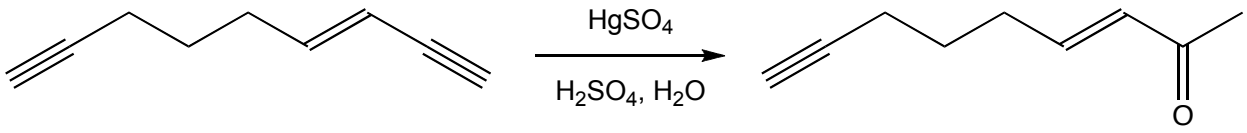
2) (30 points) Treatment of the following alkyndiene with one equivalent of $HgSO_4$ in acidic media leads exclusively to the ketone on the right:



a) Draw the structure of the mercuronium ion intermediate that will lead to the ketone drawn above.

b) Based on the structure you drew for part (**a**), explain why is the alkyne moiety on the right side of the molecule that gets hydroxylated, and not the one on the left (i.e., explain why you get the product you get…).

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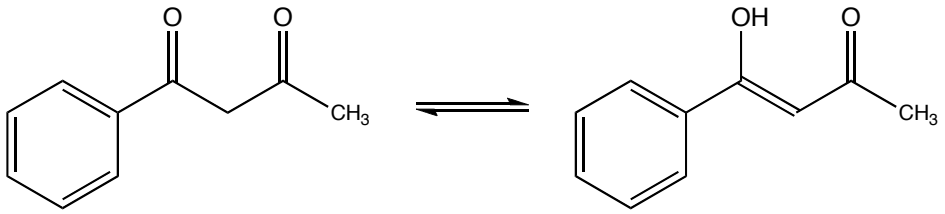
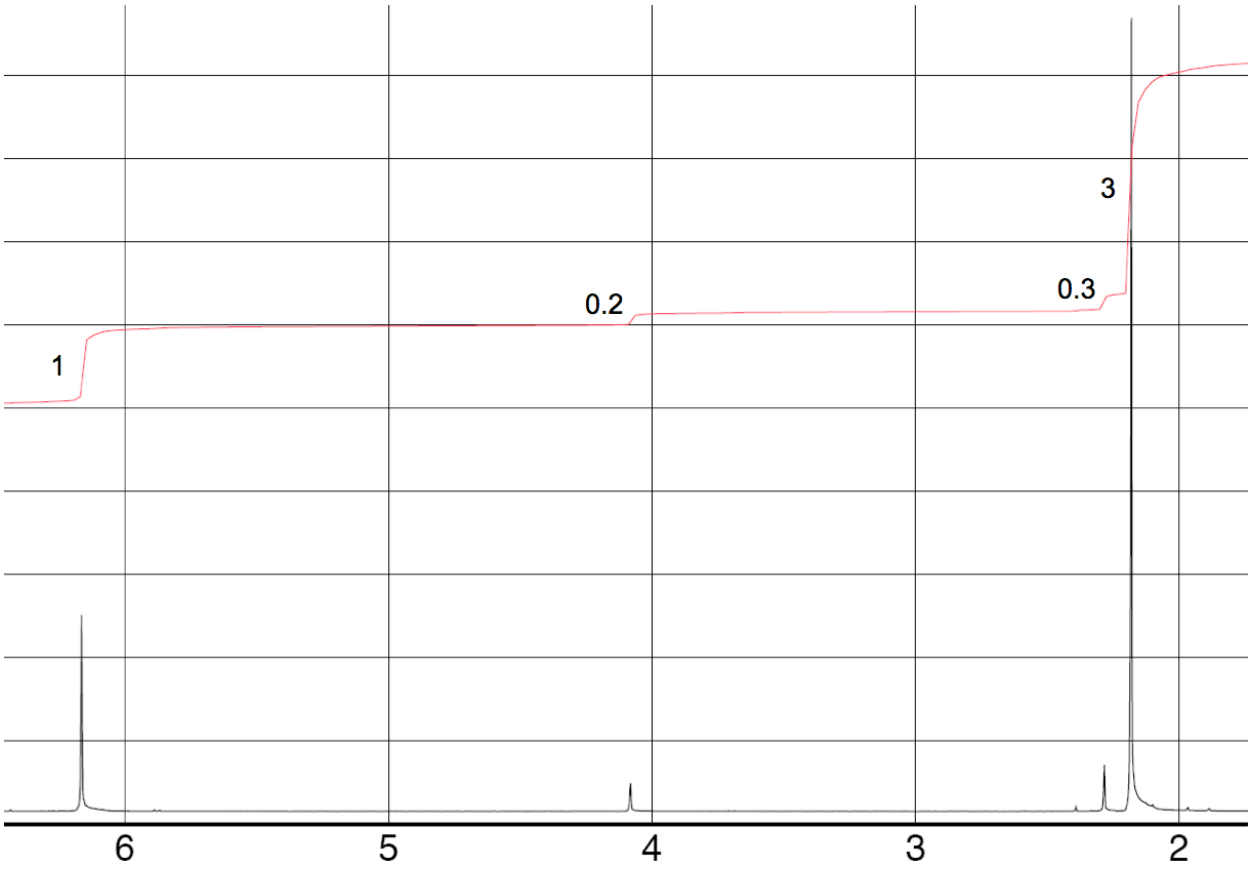
3) (30 points) Benzoyl acetone exists in rapid equilibrium between *keto* and *enol* isomers:



As a result, the high-field region of its ^{1}H NMR spectrum shows two sets of signals, one corresponding to the *keto* form, and one to the *enol* form:



a) Based on the structures of both benzoyl acetone isomers, assign which signals correspond to which form of the molecule. Pay attention to their relative intensities when you do this.

b) Using the assignments from part (**a**), determine which form is present in higher percentage. Can you explain why?

Note: The aromatic protons and the -OH proton are not shown in the spectrum…

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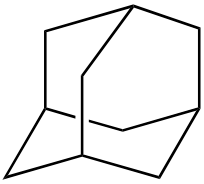
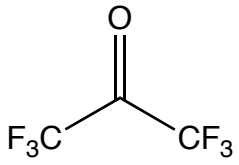
4) (30 points) For the following three compounds:

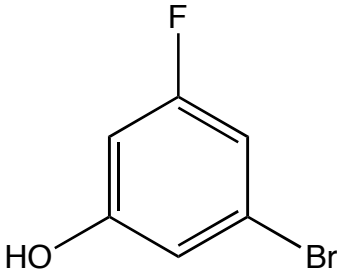
1)



2)



3)



a) Calculate their degree of unsaturation, and show in the structure what gives rise to this number (i.e., double bonds, rings, halides, etc…).

b) Determine how many ^{1}H and ^{13}C NMR signals you will find in their spectra (i.e., identify magnetically equivalent and non-equivalent nuclei).

c) For each magnetically equivalent set of protons, specify their multiplicity, assuming that all coupling constants are equal.

d) To which of the three compounds shown above do the ^{1}H and ^{13}C NMR spectra provided in the attached pages belong?

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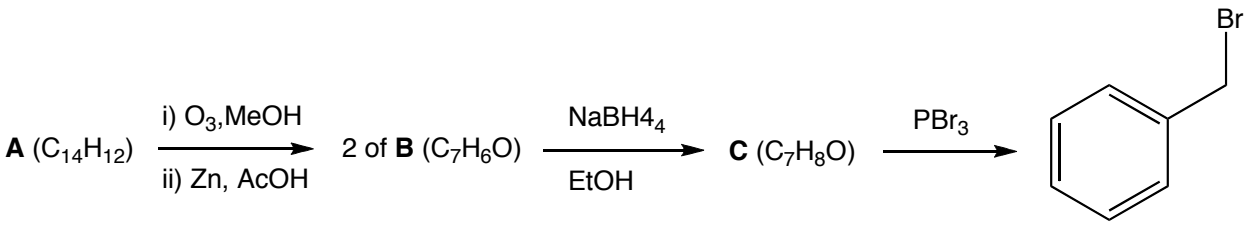
5) (30 points) You came across a symmetric aromatic alkene of molecular formula $C_{14}H_{12}$ (compound **A**) and decided to run a number of reactions to kill time:



^{1}H NMR, ^{13}C NMR, and IR data for compounds **A**, **B**, and **C** are provided in the attached pages.

Using the information provided, give the structures for compounds **A** through **C**. You do not need to write all the reaction mechanisms, but make sure to do a proper assignment of all the signals and multiplicities in the ^{1}H NMR spectra for all compounds. You can do that in the spectra if you want, but make sure to turn them in at the end of the exam.

Hint: There are not that many symmetric aromatic alkenes with molecular formula $C_{14}H_{12}$…

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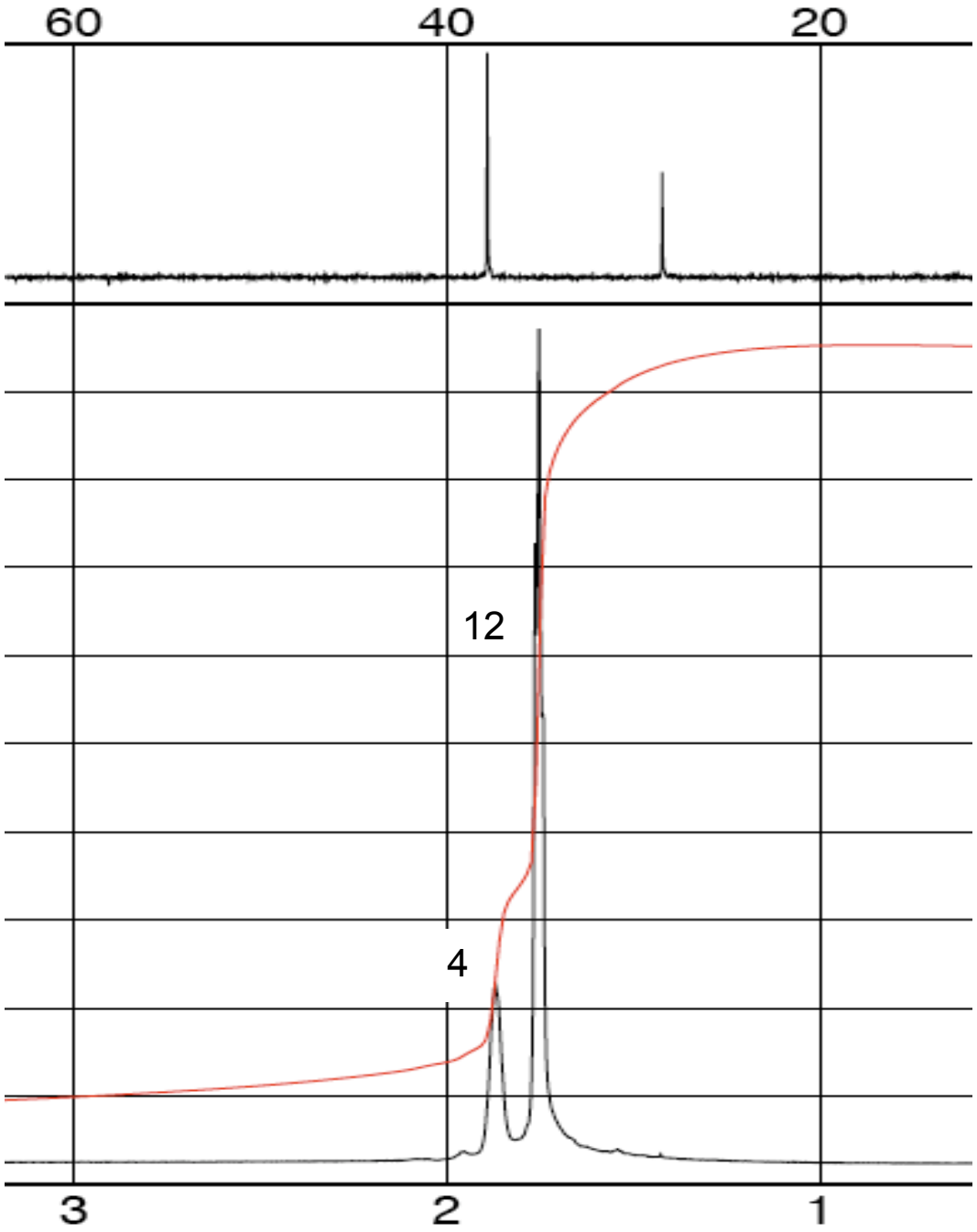
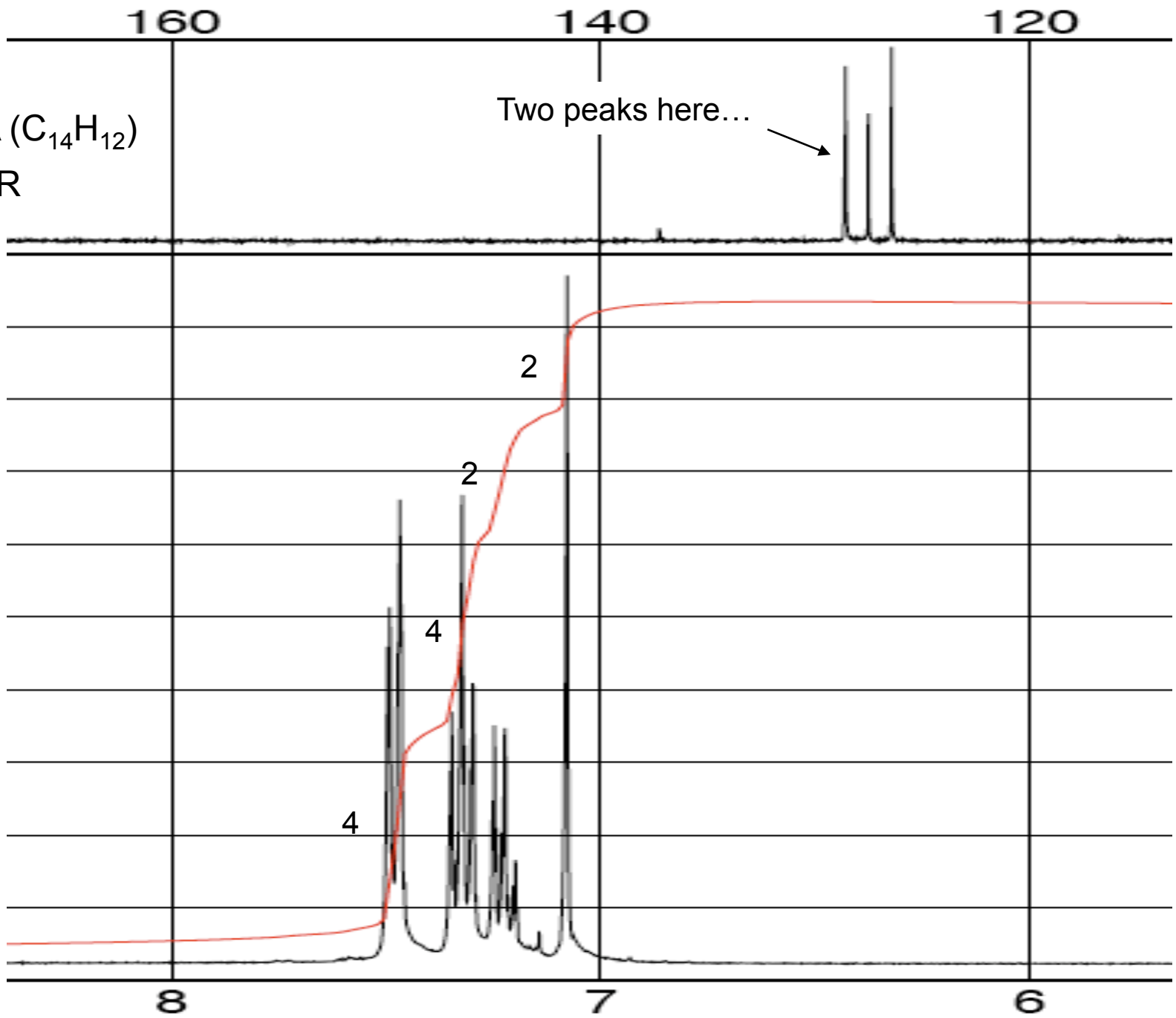
Problem 4



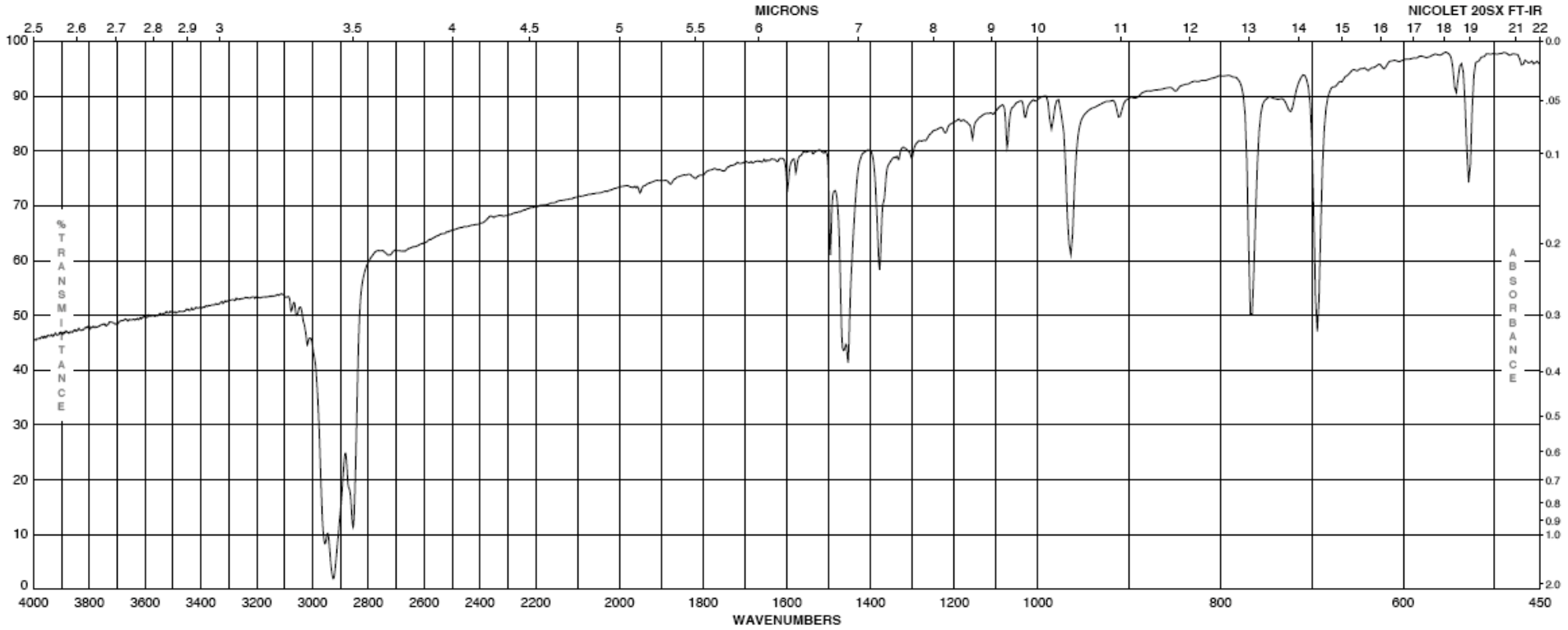
Problem 5

Compound A ($C_{14}H_{12}$)

^{1}H & ^{13}C NMR



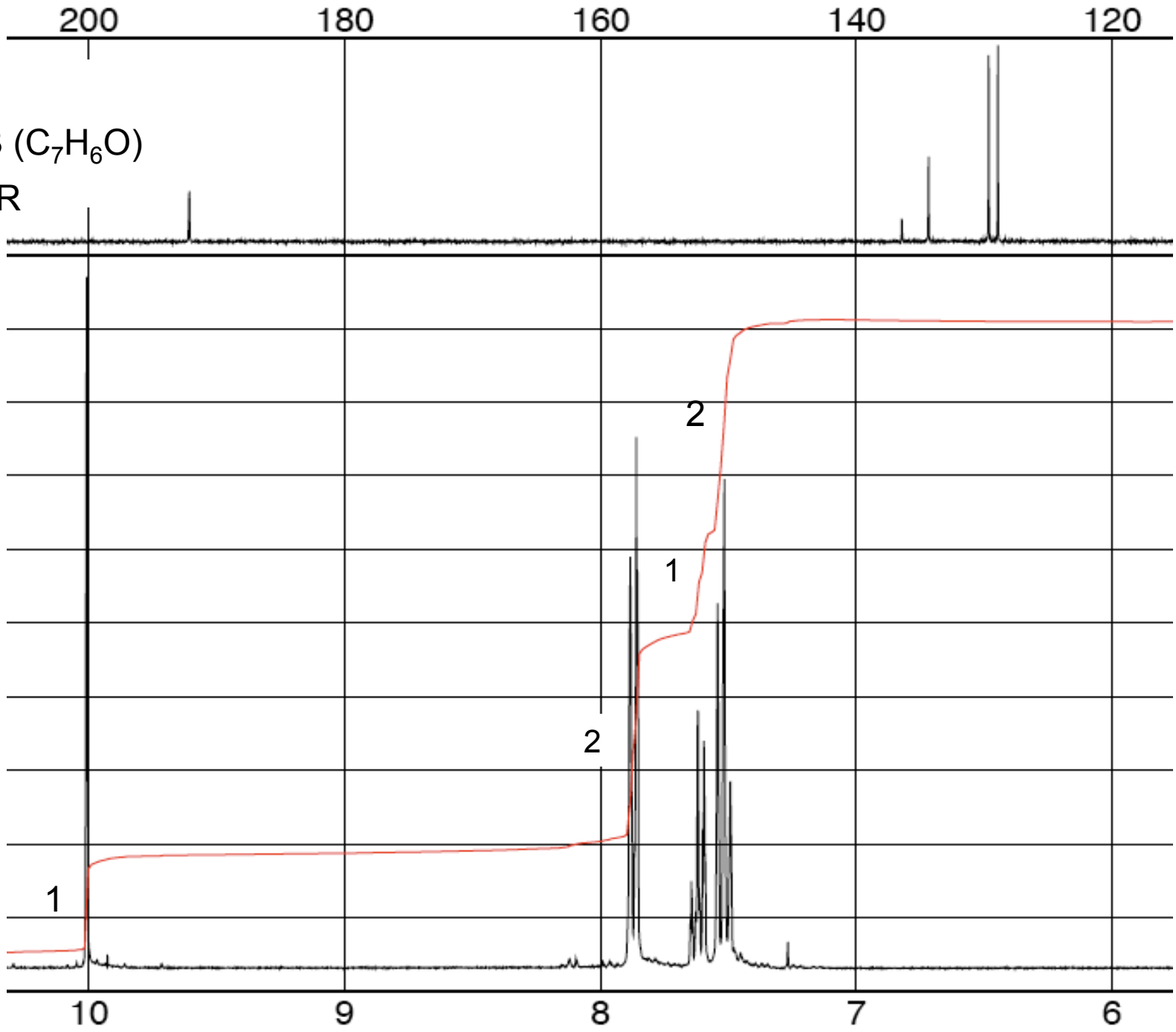
Problem 5 - Compound A ($C_{14}H_{12}$) - IR



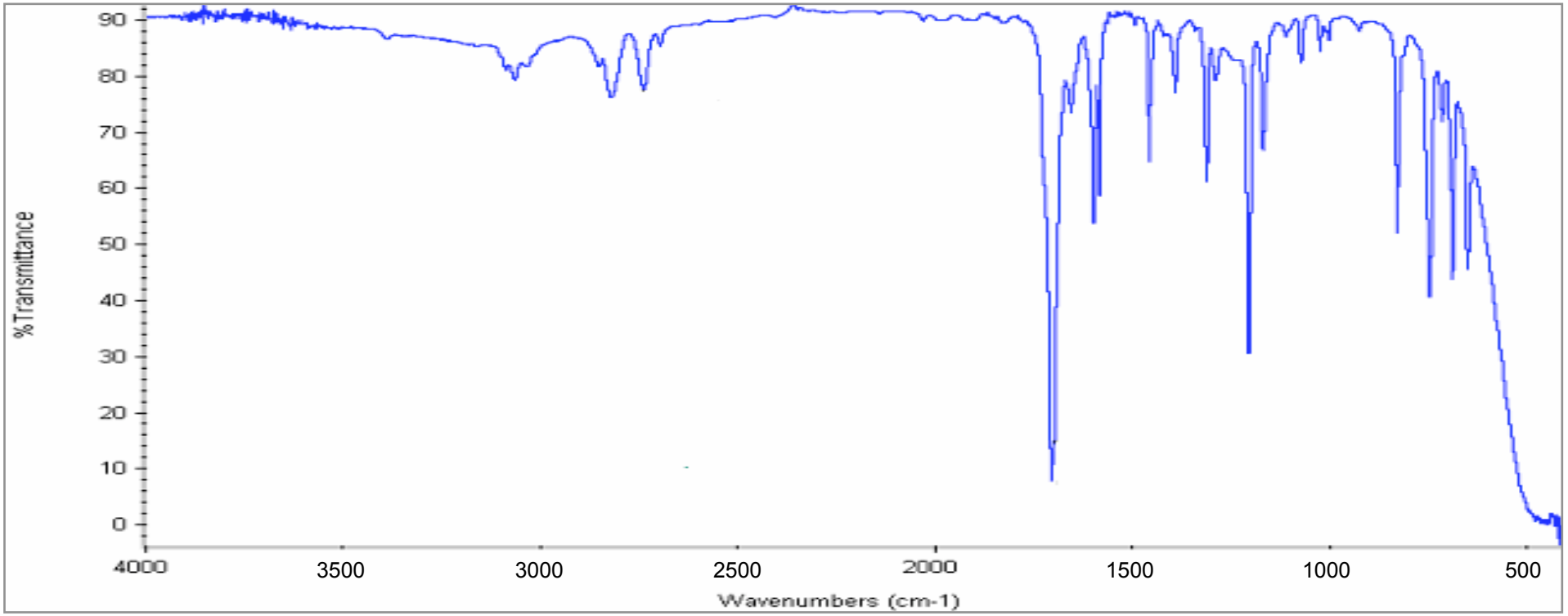
Problem 5

Compound B (C_7H_6O)

^{1}H & ^{13}C NMR



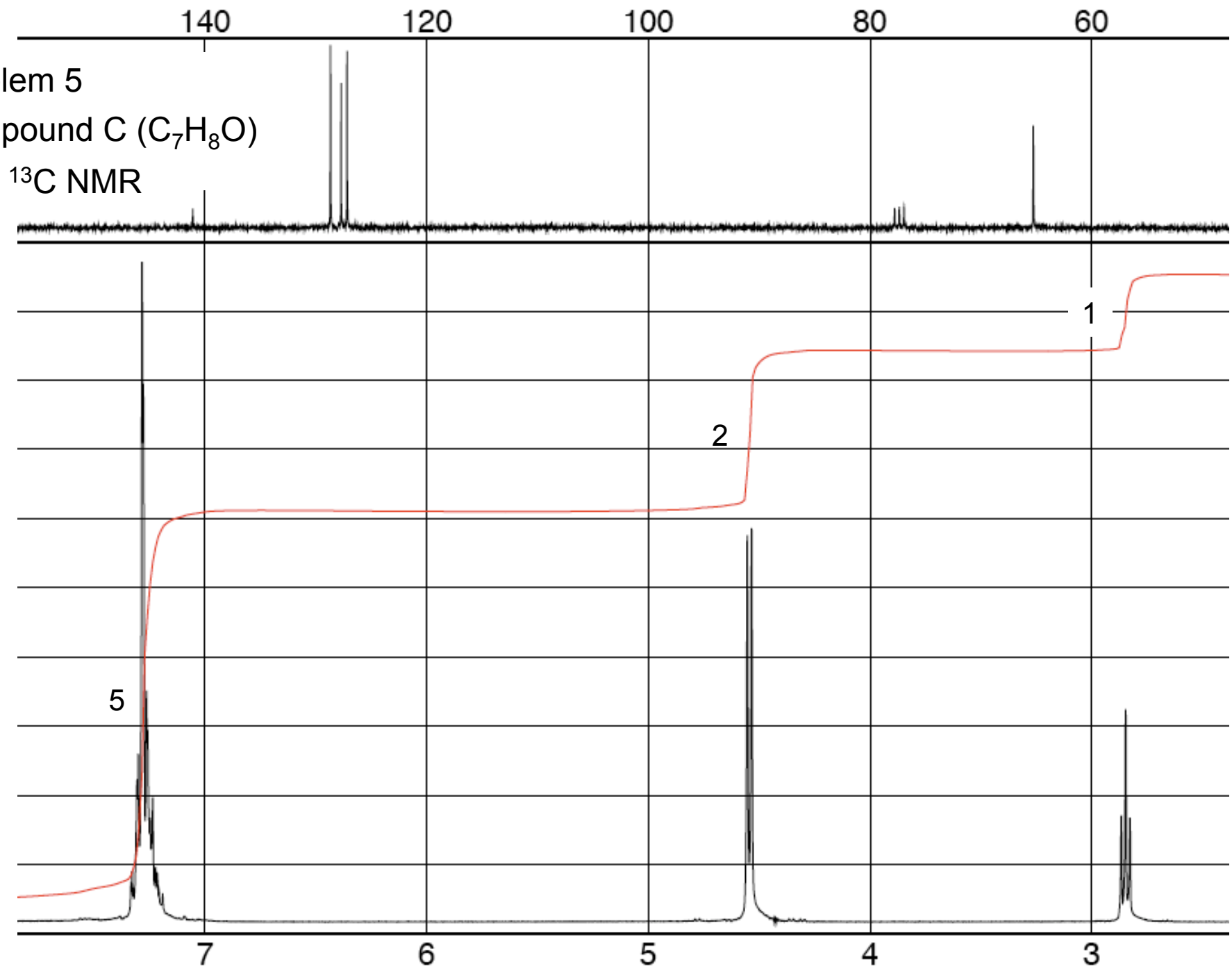
Problem 5 - Compound B (C_7H_6O) - IR



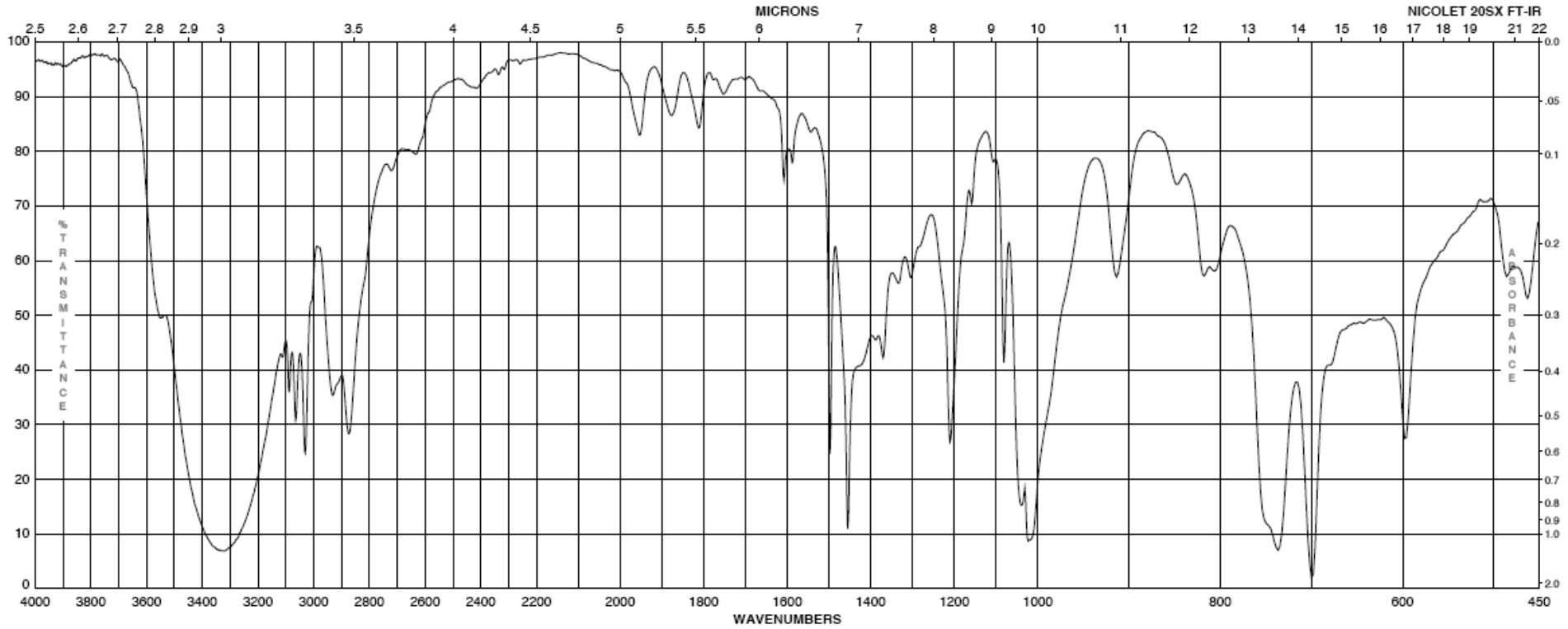
Problem 5

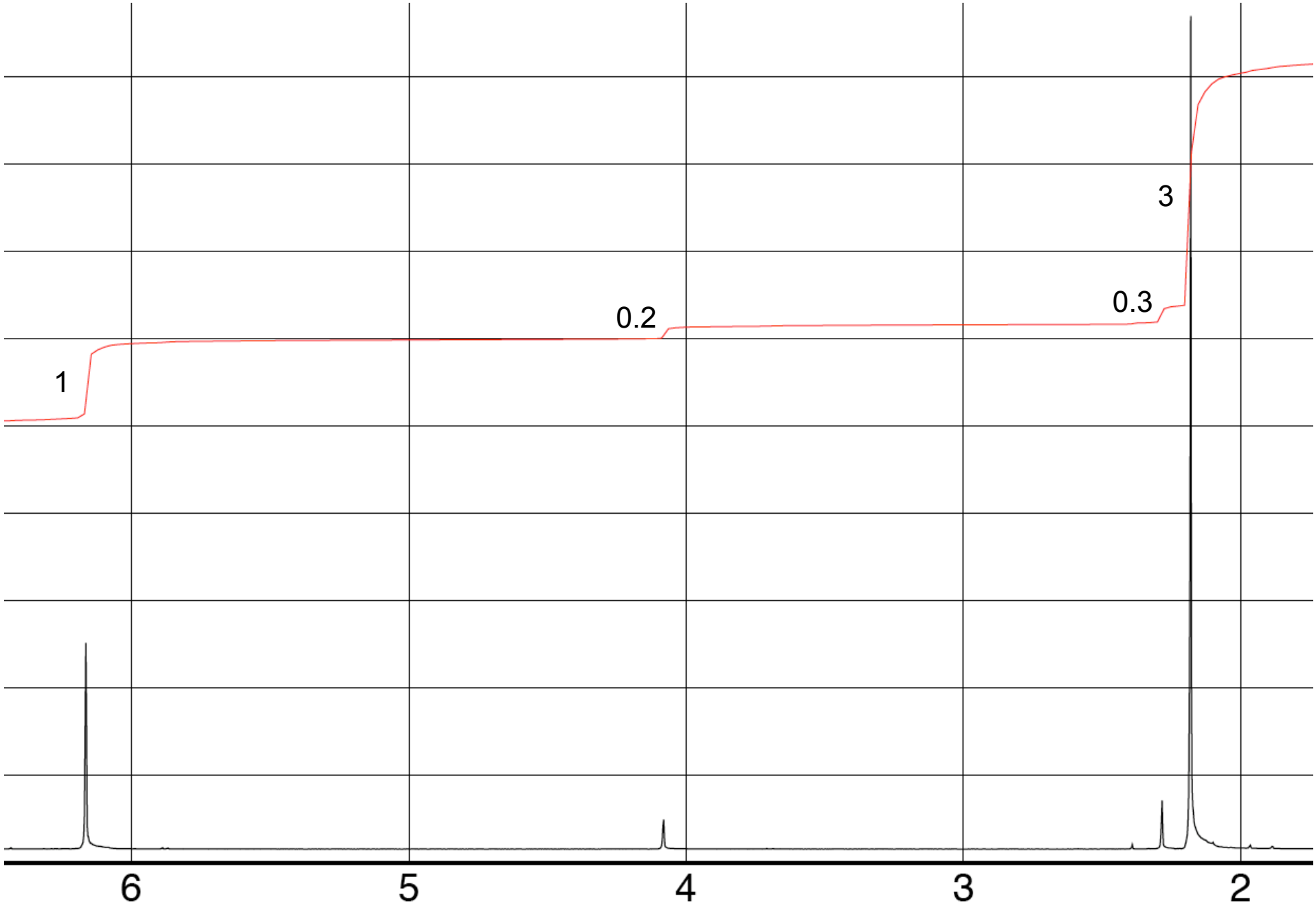
Compound C (C_7H_8O)

^1H & ^{13}C NMR



Problem 5 - Compound C (C_7H_8O) - IR




1
0.2
0.3
3
6
5
4
3
2