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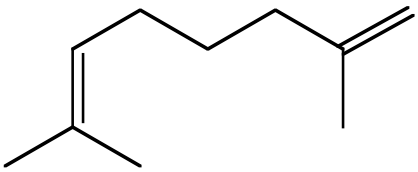
Exam II – Principles of Organic Chemistry II – CH 212
April 18th 2003 – 7:30 AM to 9:00 AM

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) Consider the following reaction schemes:

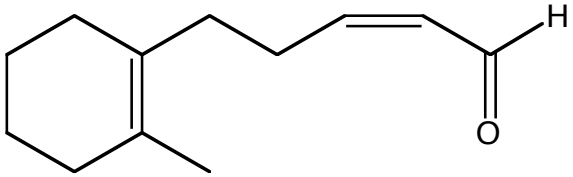
1)



i) mCPBA (1 eq.), CH_2Cl_2
ii) BH_3, ether / H_2O_2 / NaOH
iv) PBr_3, ether
v) Mg, THF / H_2O
vi) H_2SO_4,Δ

→ **$C_{10}H_{18}$**

2)



i)  **OMe , Δ**
ii) $NaBH_4$, EtOH
iii) PBr_3, ether
iv) HCCLi, ehter / H_2O
v) mCPBA (1 eq.), CH_2Cl_2
vi) n-BuLi, ehter / H_2O
vii) H_2SO_4, Δ

→ **$C_{18}H_{24}O$**

a) Provide the structures of all the intermediates and products.

b) Write detailed reaction mechanisms for the steps highlighted with bold/oversized letters.

Part **2** is a bear. You may want to know that the final compound is a tricyclic fused ring system, with ring sizes 6, 9, and 6…

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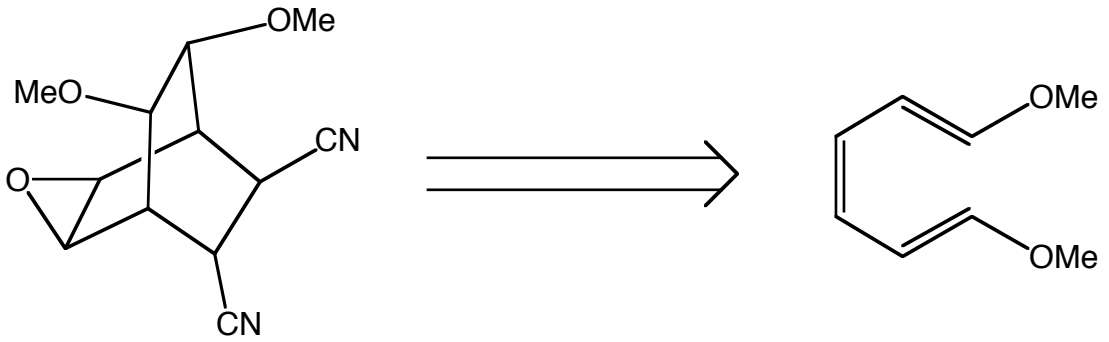
2) (20 points) Compound **A** can be prepared in three steps starting from compound **B**:



A B

You only need two reagents, one of which is a dienophile with structure $C_4H_2N_2$.

a) Propose the synthetic approach you would follow to obtain **A** starting from **B**, including detailed mechanisms for the three reactions.

b) Can this synthesis give you other stereoisomers of **A**? If so, present the structure of one of them, and justify your answer based on reaction mechanisms.

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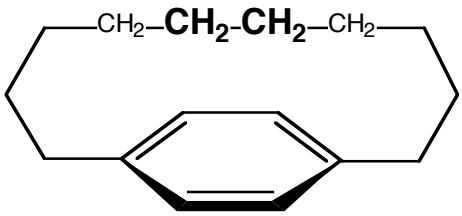
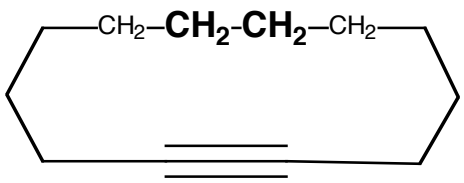
3) (20 points) Once again you found yourself with too much time in your hands, so you decided to prepare the following two, completely useless, molecules:

A) 

B) 

Once you finished, you took ^{1}H-NMR spectra of both compounds. For **A**, the chemical shift of the bolded protons is -1.50 ppm, while the corresponding protons in **B** have a chemical shift of +3.00 ppm.

Taking into account that the chemical shift for similar protons in straight-chain alkanes is approximately 1.50 ppm, explain the observations presented above.

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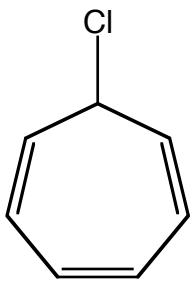
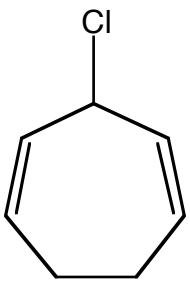
4) (20 points) You studied the kinetics of the solvolysis reaction in EtOH of the following two compounds:

A) 

B) 

a) Write the mechanism of solvolysis for both compounds in EtOH.

b) You measured the rate of solvolysis for both compounds, and found that compound **A** reacts with the solvent 10,000 times faster than compound **B**. Explain this observation based on the structure of the two compounds and the mechanism of the solvolysis reaction.

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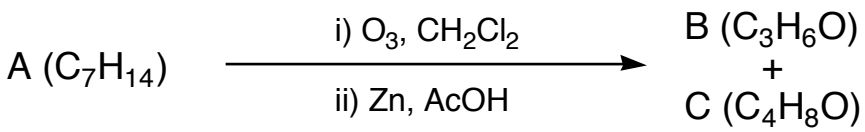
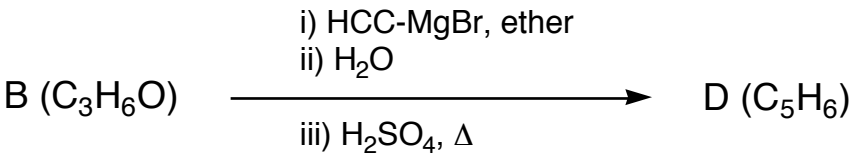
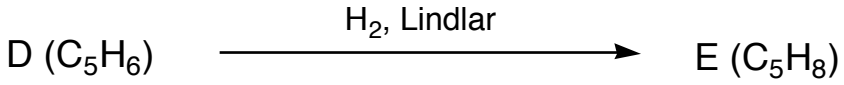
5) (30 points) A certain compound **A** (C_7H_{14}) is subjected to the following reactions:



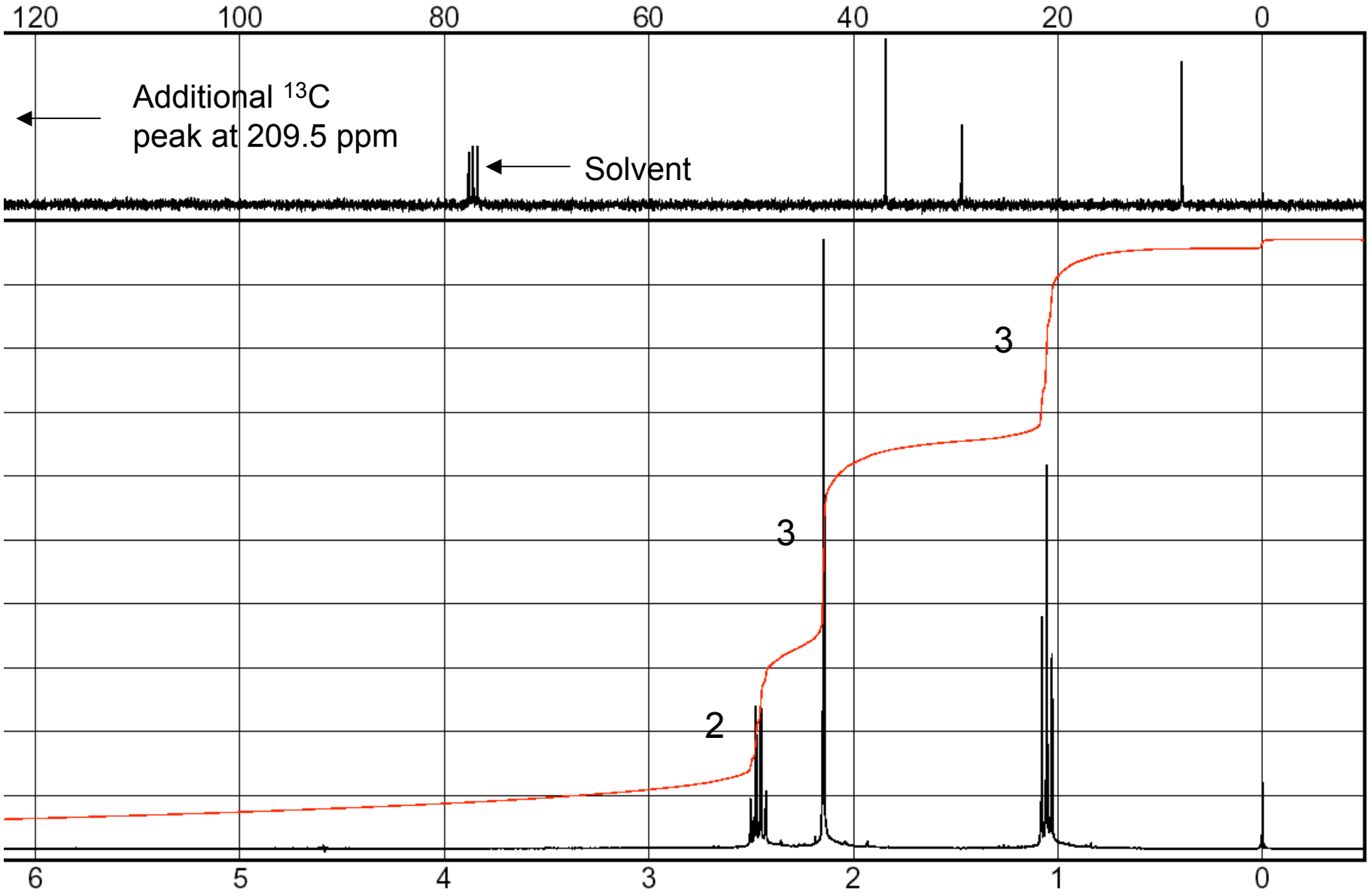




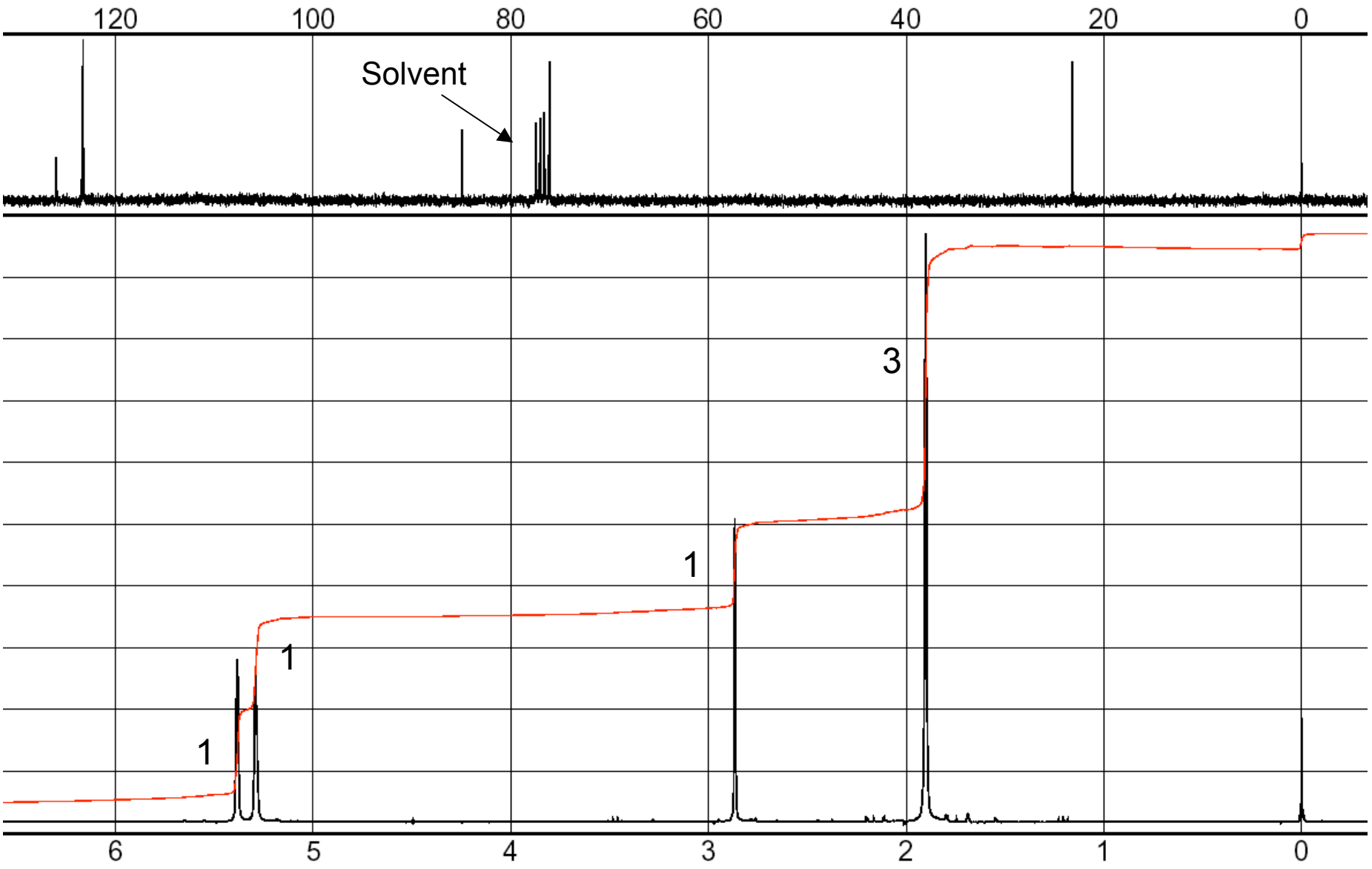
In addition to the information provided above, you recorded NMR and IR spectra for compounds **C** (NMR), **D** (NMR, IR), and **E** (NMR, IR), which is provided in the following pages.

With all these data, elucidate the structures of compounds **A** through **E**. You do not need to write detailed mechanisms for the reactions or present extensive spectral assignments. However, it would help if you draw the molecules in the spectra and draw arrows from the protons/carbons to the signals.

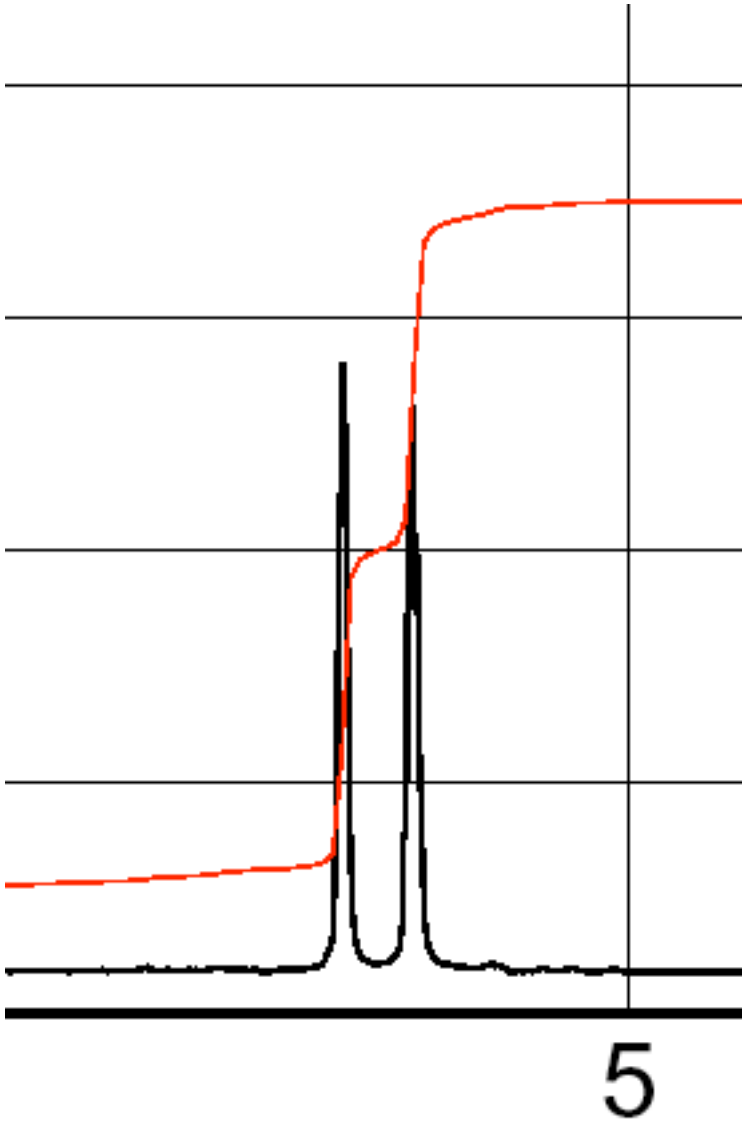
Problem 5 - Compound C NMR

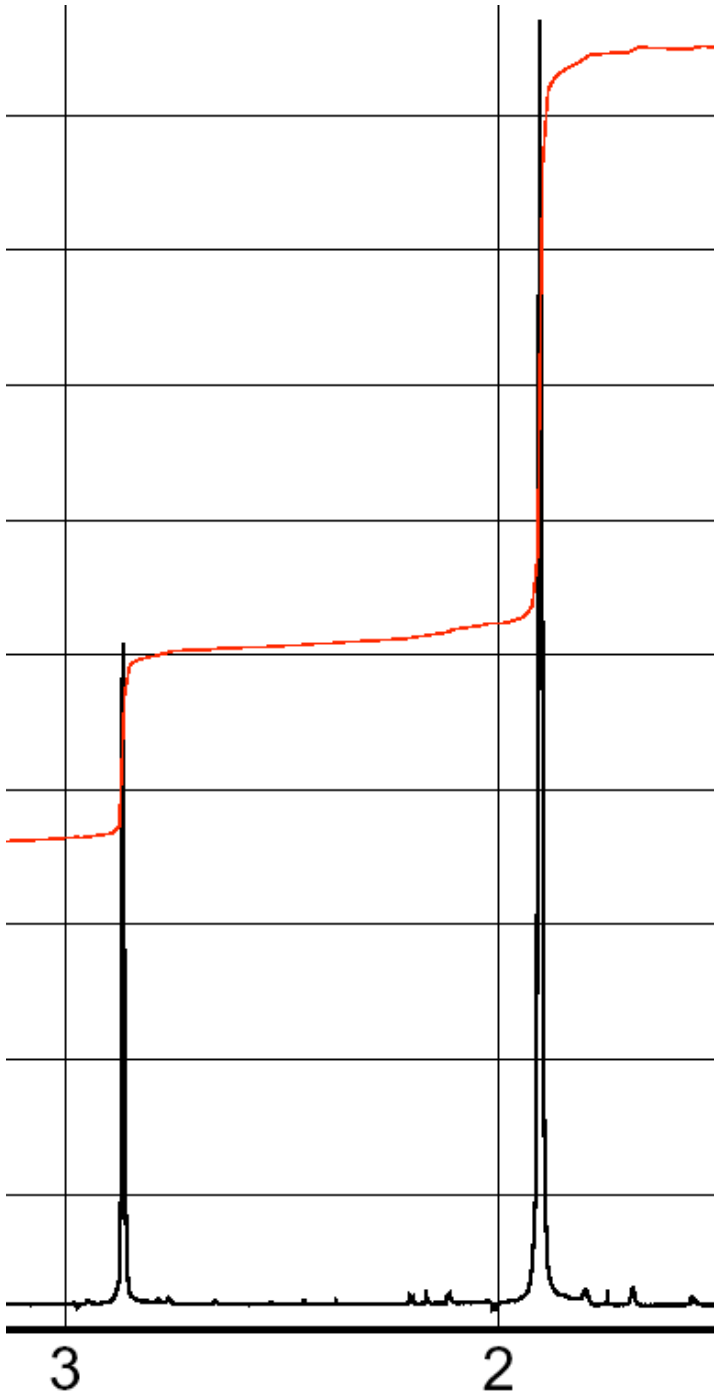


Problem 5 - Compound D NMR

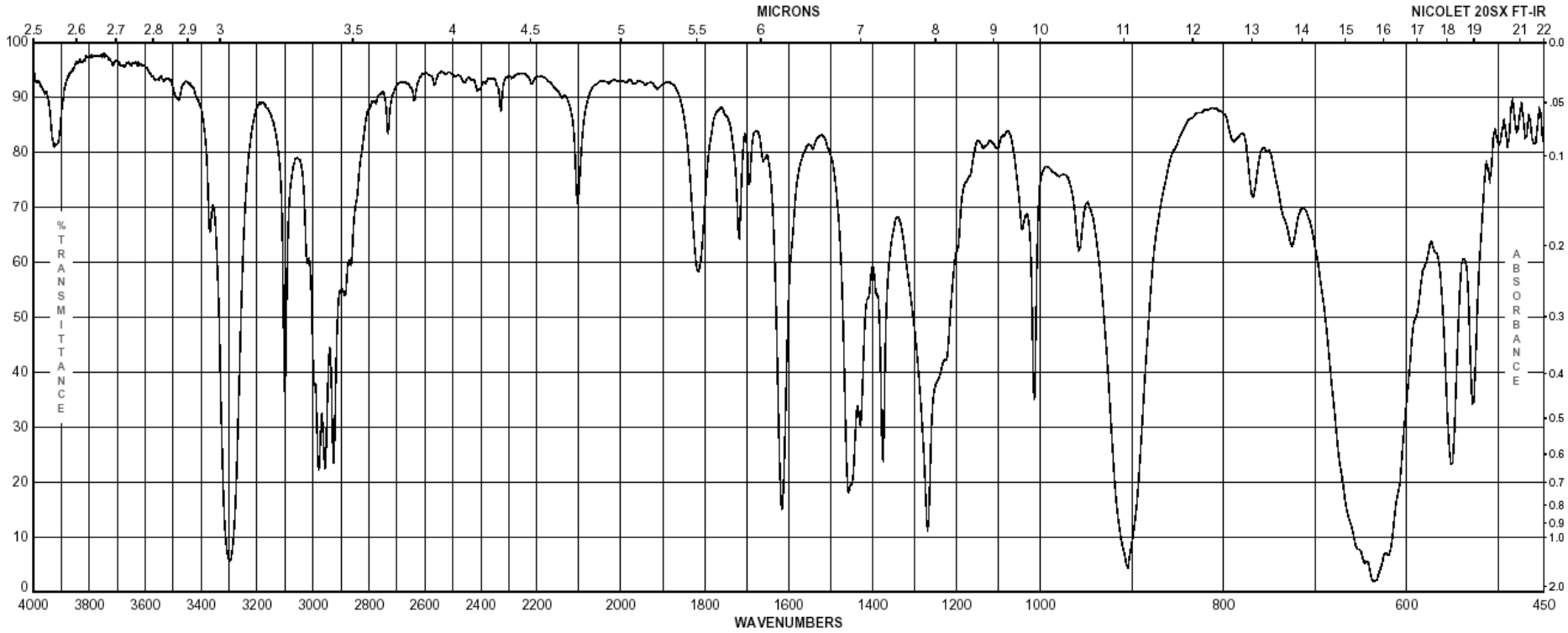


Problem 5 - Compound D NMR (expansion)

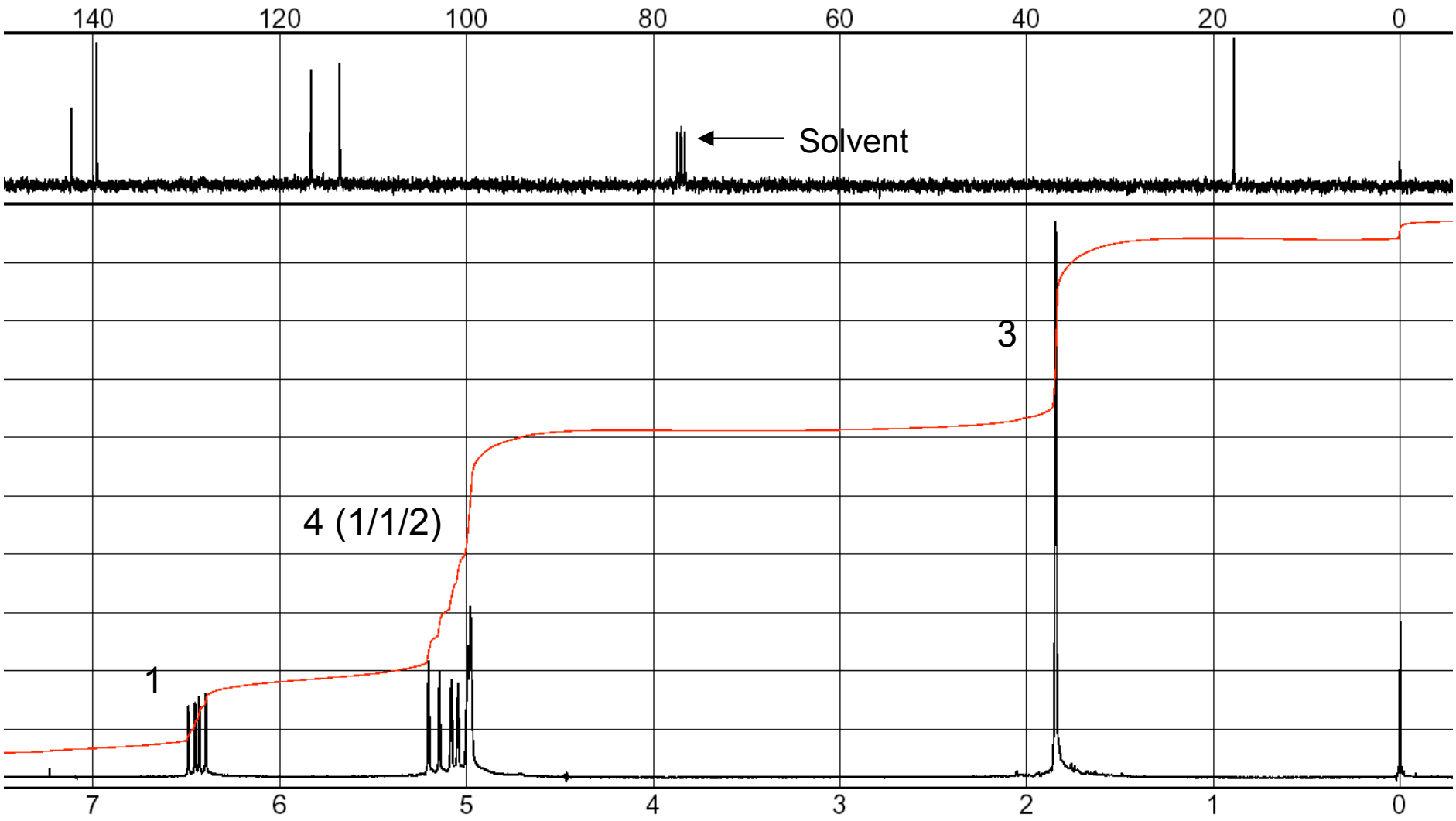




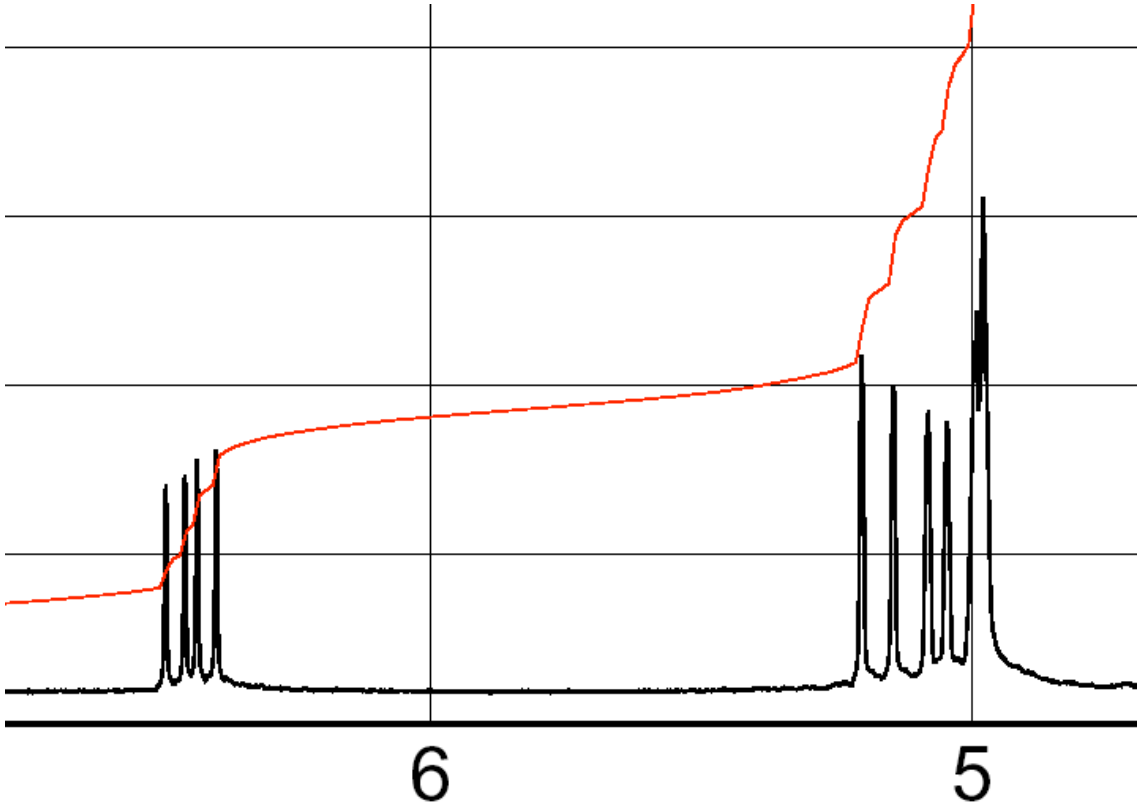
Problem 5 - Compound D IR



Problem 5 - Compound E NMR



Problem 5 - Compound E NMR (expansions)



Problem 5 - Compound E IR