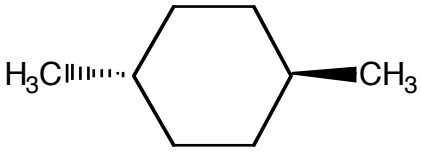
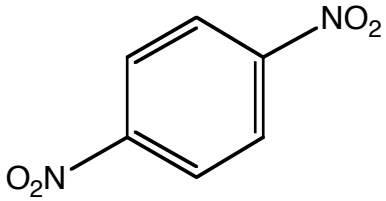
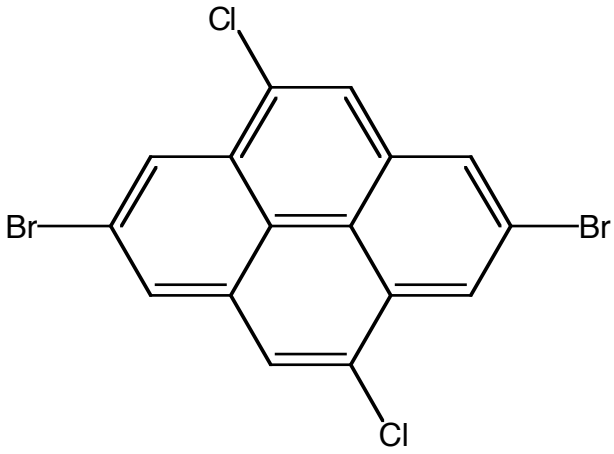
Chemistry 212 – Problem set 2 – Due Friday 30th at 5:00 PM

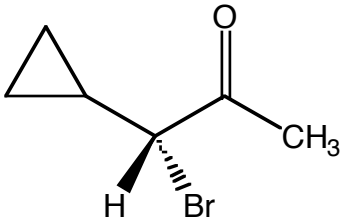
Note: An additional file, psetII_spectra.pdf, has all the spectra needed for problems **3** and **4** at higher resolution, so you can download it and expand them for easier analysis.

1) (20 points) For the following compounds:





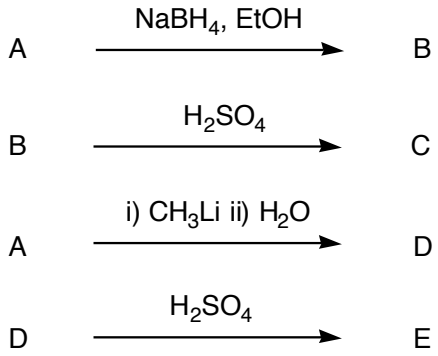




a) Determine how many ^{1}H- and ^{13}C-NMR signals you will find in their spectra (i.e., identify magnetically equivalent and non-equivalent nuclei).
b) Predict the approximate chemical shift of each ^{1}H signal using chemical shift tables (you can find these on the www).
c) For each magnetically equivalent set of protons, specify their multiplicity, assuming that all coupling constants are equal and considering only ^{3}J's.

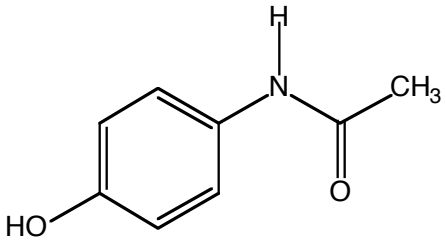
2) (20 points) A certain sample shows two (unrelated) doublets at 1.20 and 1.30 ppm, each integrating to one proton. The doublet at lower field has a coupling of 12 Hz, and the other one of 15 Hz. Draw a 'stick-spectrum' of the signal you would see if you take the spectrum using a 60 MHz (1.4 Tesla) instrument. Repeat this, but using a 400 MHz (9.4 Tesla) instrument. Can you tell me what is one of the purposes of buying a big NMR from your results?

3) (30 points) As part of a research project, you were given a linear alkylaldehyde (compound **A**), which has the ^{1}H-NMR spectrum show in the next page (spectrum **a**). In order to identify the compound, you did the following reactions:

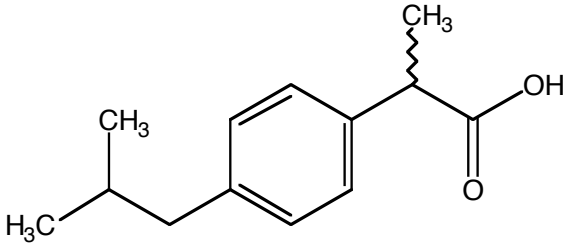


Spectra for the compounds obtained after each reaction are also provided in the next pages (spectra **b**-**e**). With this information, determine the structure of compounds **A**, **B**, **C**, **D**, and **E**, and provide the mechanism for the formation of each one of them. Make sure to explain the integrals and multiplicities of all the signals observed in the spectra provided.

4) (30 points) Unfortunately, we all had to use the two following molecules at one time or another. They are acetaminophen (**a**) and ibuprofen (**b**), whose structures are drawn below.



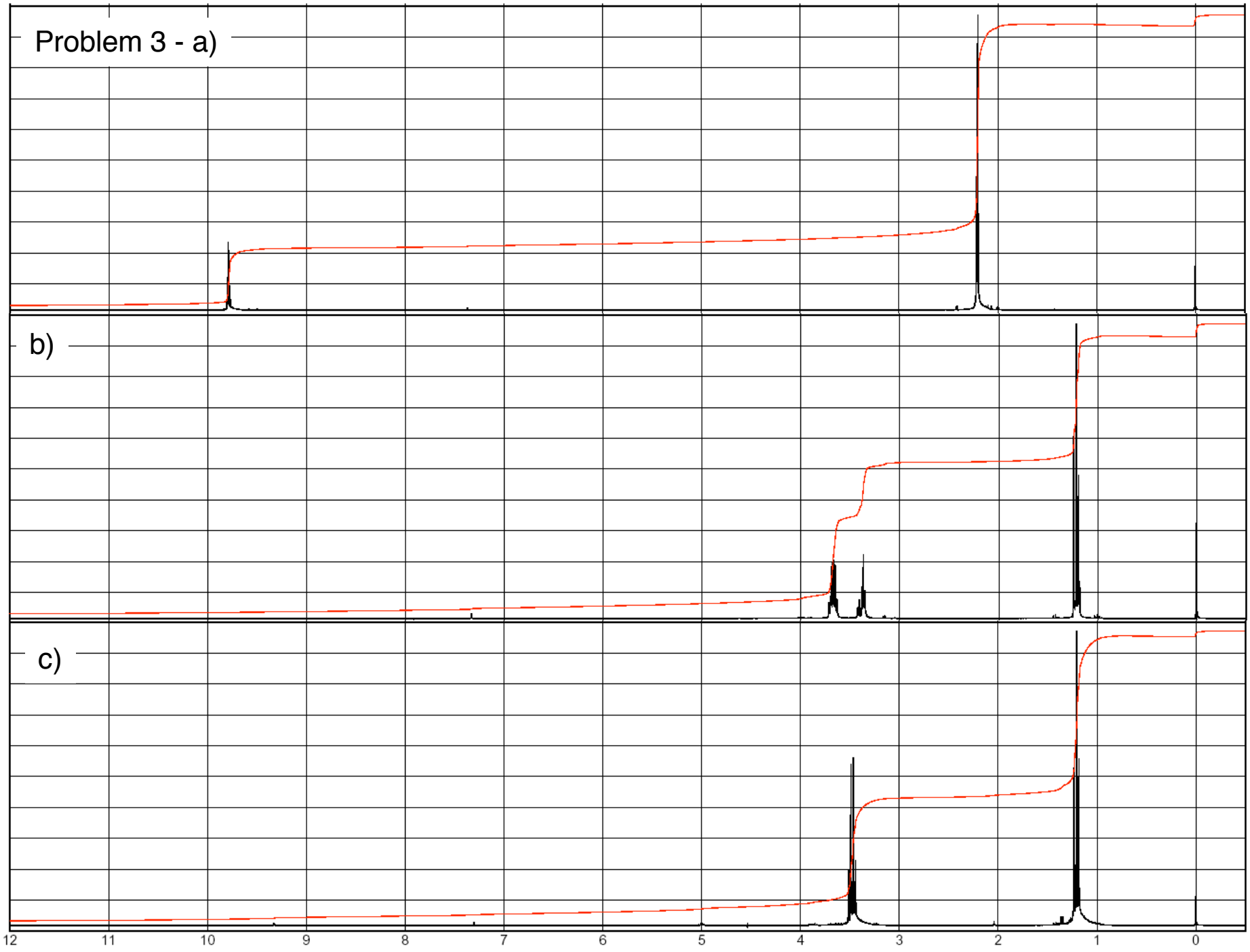
Acetaminophen (a)

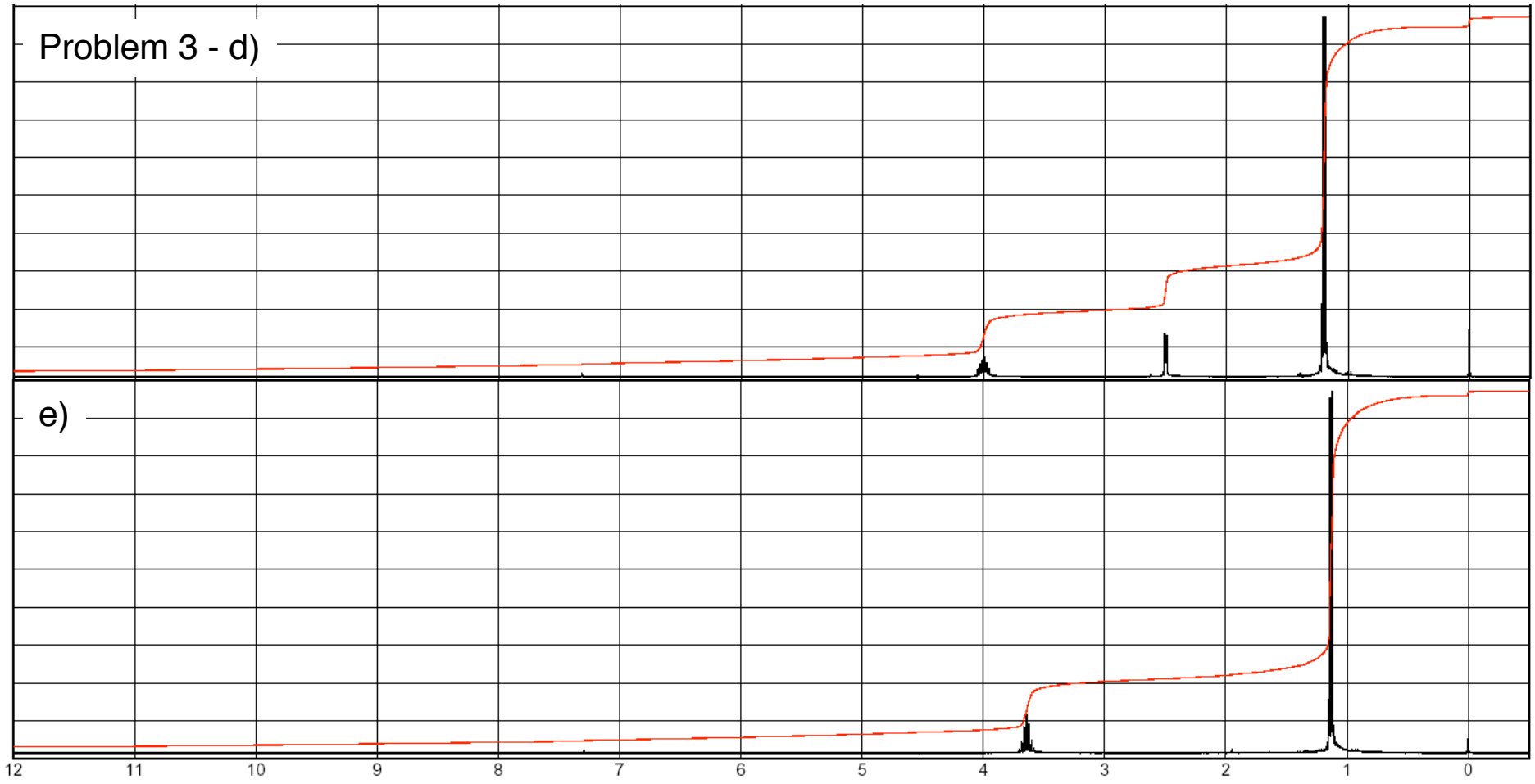


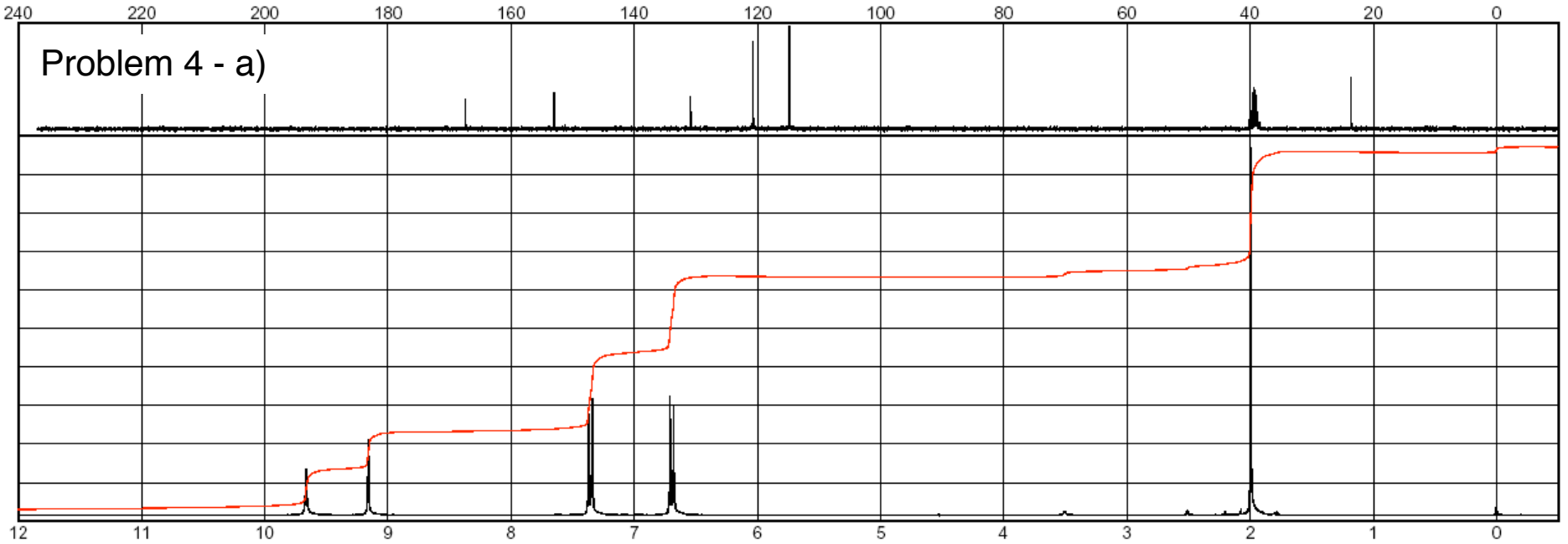
Ibuprofen (b)

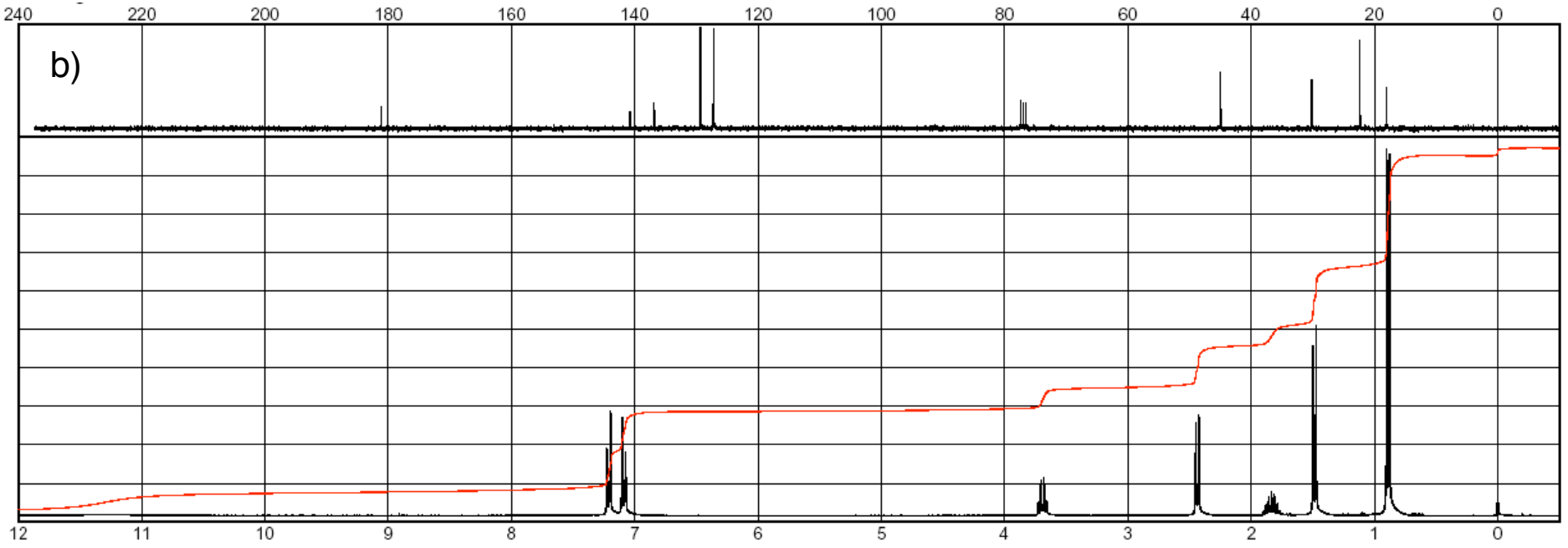
In the next page, I give you ^{1}H- and ^{13}C-NMR spectra of both molecules, but I forgot to label which set is which. Thus:

a) Assign the proper set of spectra to each drug.
b) Once you are done with (**a**), do your best to assign each signal in the spectra to their corresponding protons and carbons in the molecule.
c) Explain the integration of all signals.
d) Identify all the multiplets in the spectra as doublets, triplets, etc., explaining why each signal gives rise to that multiplicity.


Problem 3 - a)
b)
c)
12
11
10
9
8
7
6
5
4
3
2
1
0


Problem 3 - d)
e)
12
11
10
9
8
7
6
5
4
3
2
1
0


Problem 4 - a)
240 220 200 180 160 140 120 100 80 60 40 20 0
12 11 10 9 8 7 6 5 4 3 2 1 0


b)
240 220 200 180 160 140 120 100 80 60 40 20 0
12 11 10 9 8 7 6 5 4 3 2 1 0