Experiment 2

NMR Spectroscopy: Determination of Molecular Structures

Reading: Handbook for Organic Chemistry Lab, chapters on NMR Spectroscopy (Chapter 18) and Identification of Compounds (Chapter 20). Organic Chemistry, Marc Loudon, 6th ed., pp. 611-653 (13.1-13.7); pp. 662-667 (13.10-13.11). Organic Chemistry by Jonathan Clayden, Nick Greeves, and Stuart Warren, 2nd ed., pp. 43-79 (Ch. 3); pp. 269-301 (Ch. 13).

Nuclear Magnetic Resonance, or NMR, involves examining the electronic environment around different nuclei in a molecule. Proton NMR, or ^{1}H NMR, is among the most powerful tools available to synthetic chemists today. This experiment will introduce you to the interpretation of ^{1}H NMR spectra, and then give you practice with combining multiple sources of information – ^{1}H NMR, IR, and molecular formula – to deduce the structure of an organic compound.

There is no prelab or lab report for this experiment. Instead, it consists of three parts, split over two lab meetings:

1) During today's lab meeting, your TA will present a tutorial on how to use NMR spectra to determine the structure of a compound. You will work on a **spectroscopy worksheet** and turn it in before you leave. The worksheet is contained in your experiment manual, in the following pages, but you can also print a copy from the course website if you need to.
2) A **spectroscopy homework** is available in PDF format, linked from the course website. You only need to do ten of the problems in this homework; your TA will give you more details about whether to do problems A, B, or C. (This also means that you do not have to print the entire homework packet, only the pages that you need.) This homework is due the following week.
3) Immediately after you turn in the homework, you will take an **NMR quiz**. The problems on this quiz are similar in format to the homework problems, except there are only two of them. The back cover of your handbook contains an NMR reference sheet that you will be allowed to use during the quiz.

For the homework and the quiz, you will need to remember the key IR frequencies you were expected to memorize during the IR Spectroscopy lab.

NMR spectroscopy is a significant portion of your grade for the semester, so be sure to get enough practice that you can solve these problems in a reasonable amount of time.

Name_____

NMR In-Class Exercise

Part 1 (6 pts)

Given the molecular formula, calculate the degree of unsaturation for the following compounds. Suggest at least three possible structures consistent with the degree of unsaturation for each compound. (Special case: A nitro group, $-NO_2$, has one degree of unsaturation. This information doesn't matter when you are calculating the degree of unsaturation, but it might matter when you start drawing structures.)

1) $C_7H_{14}O_2$

2) $C_4H_{10}O$

3) $C_9H_{10}O$

4) $C_8H_9NO_3$

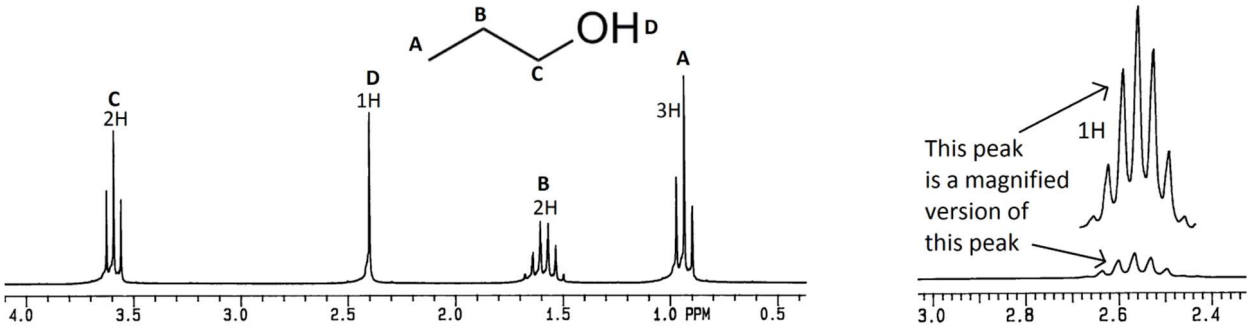
5) $C_4H_6O_2$

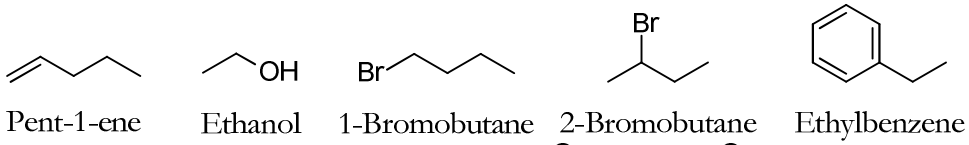
6) $C_7H_{10}Cl_2$

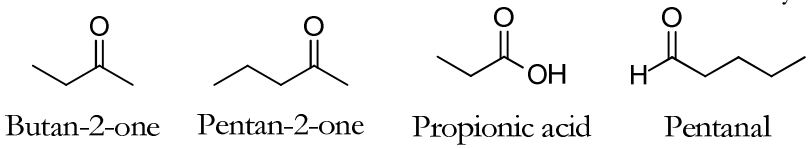
Part 2 (9 pts)

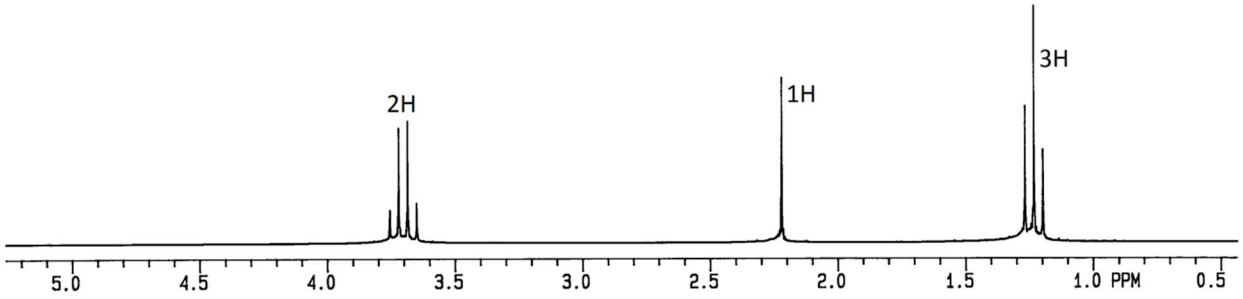
Nine compounds are drawn below. The NMR spectrum for each is among the nine spectra on the following 3 pages.

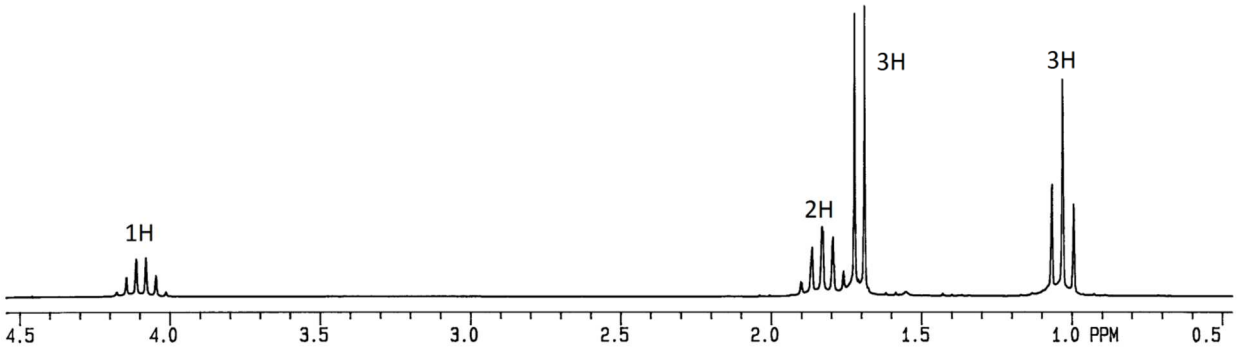
1) Match each compound with its NMR.
2) Draw the structure above the corresponding spectrum.
3) Label each type of proton in the structure with a letter, and put the same letter over the corresponding peak on the NMR spectrum (see example below). Some NMR spectra show a peak hovering above the baseline. This is a magnified view of one of the actual peaks, to allow you to see splitting more clearly.
4) Write down one or two bands which you would look for in the IR spectrum of the compound to verify your assignment.

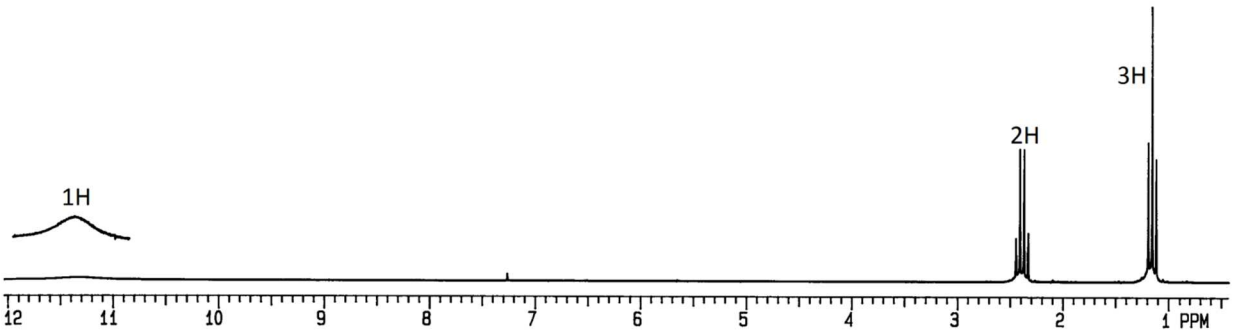


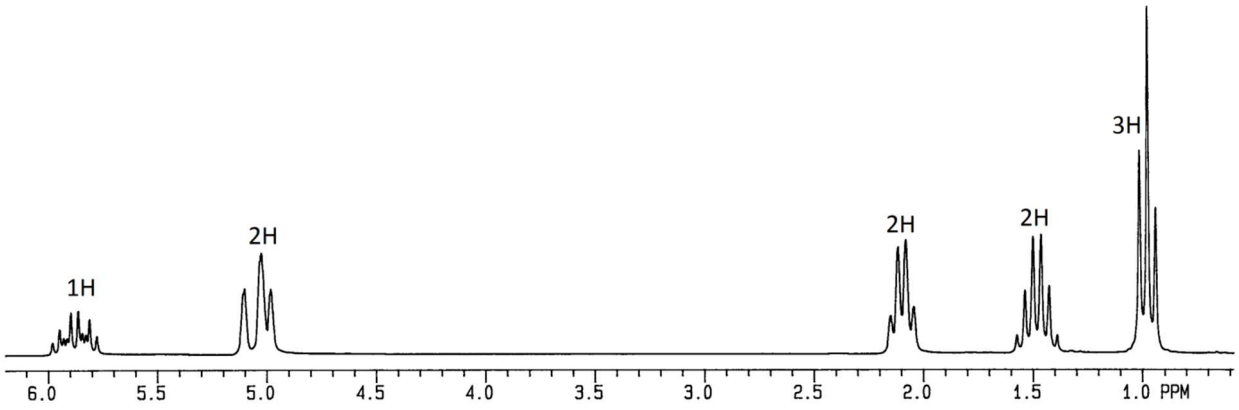


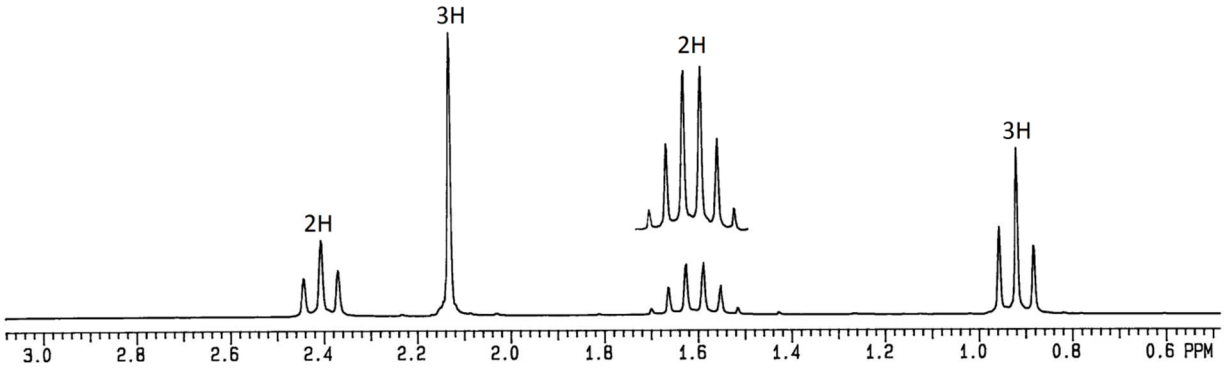





1H
2H
3H
3H
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0 PPM
0.5


1H
2H
3H
12
11
10
9
8
7
6
5
4
3
2
1 PPM


1H
2H
2H
2H
3H
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0 PPM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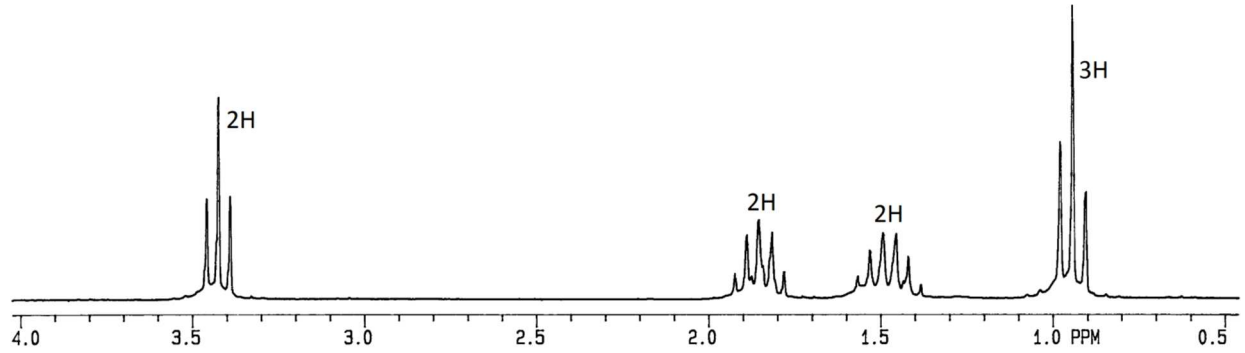
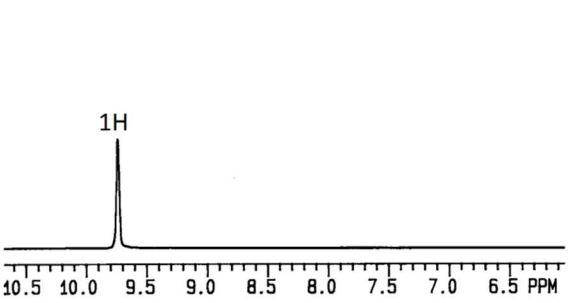
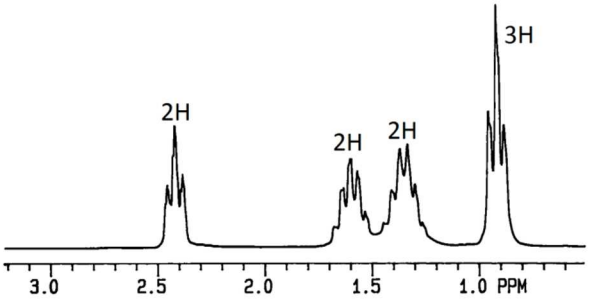
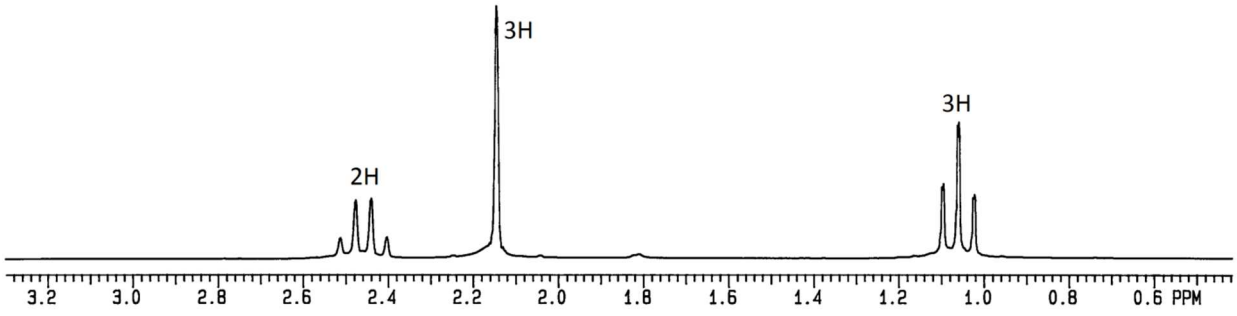
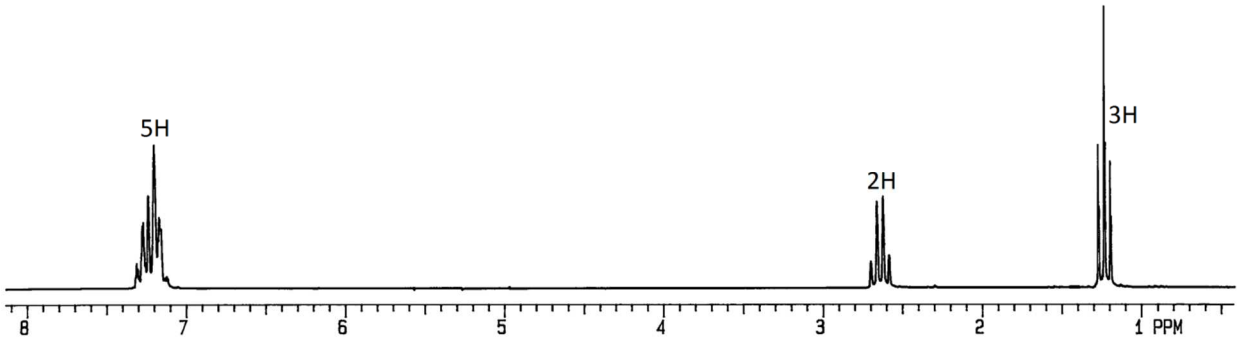
3H
2H
3H
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6 PPM


2H
2H
2H
3H
4.0
3.5
3.0
2.5
2.0
1.5
1.0 PPM
0.5


1H
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5 PPM


2H
2H
2H
3H
3.0
2.5
2.0
1.5
1.0 PPM

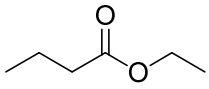

2H
3H
3H
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6 PPM


5H
2H
3H
8
7
6
5
4
3
2
1 PPM

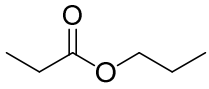
Part 3 (2 pts)

The structures of ethyl butanoate and propyl butanoate are drawn below. Note how each has an ethyl group and a propyl group; the only difference is how they are orientated around the ester functional group. The way to distinguish between the carbons on either side of the ester group is by chemical shift: the carbon next to the oxygen will usually have a shift of 3-4 ppm, while the carbon next to the carbonyl will usually have a shift of 2-3 ppm.

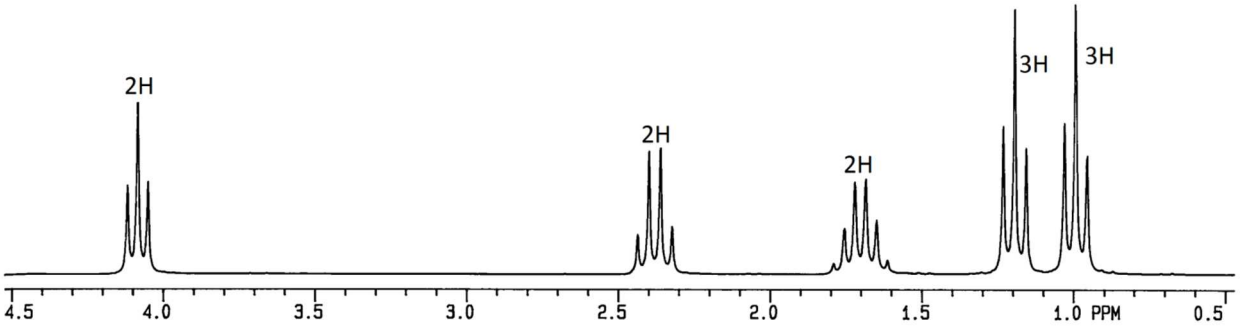
1) Match each compound with its NMR.
2) Draw the structure above the corresponding spectrum.
3) Label each type of proton in the structure with a letter, and put the same letter over the corresponding peak on the NMR spectrum.

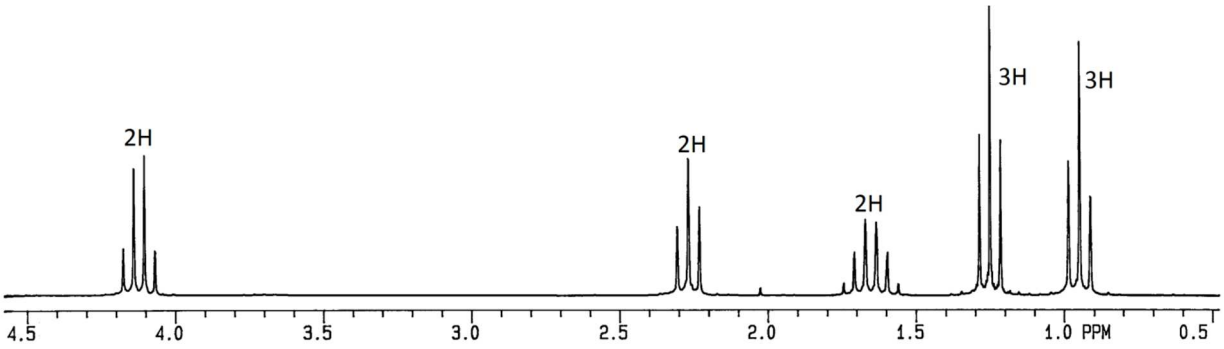


Ethyl butanoate

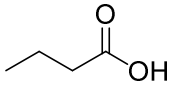


Propyl propanoate p

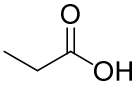




Note: Esters are named from their parent carboxylic acid. For example, ethyl butanoate is derived from butanoic acid and propyl propanoate is derived from propanoic acid.



Butanoic acid

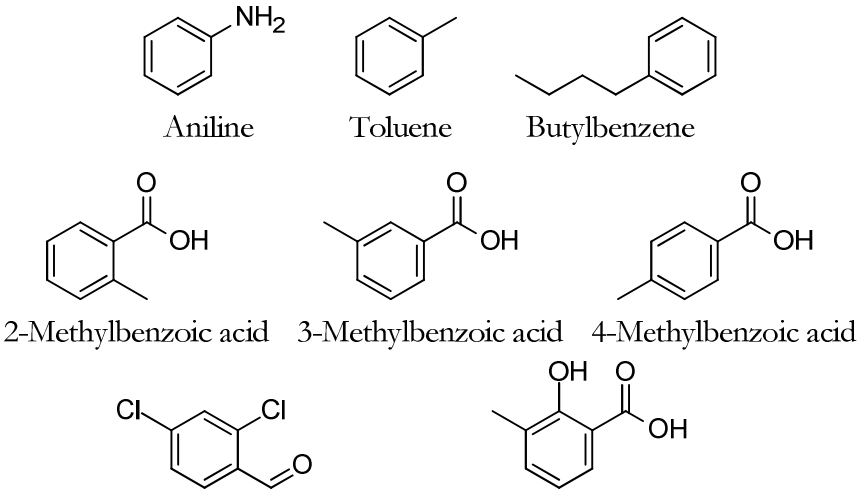


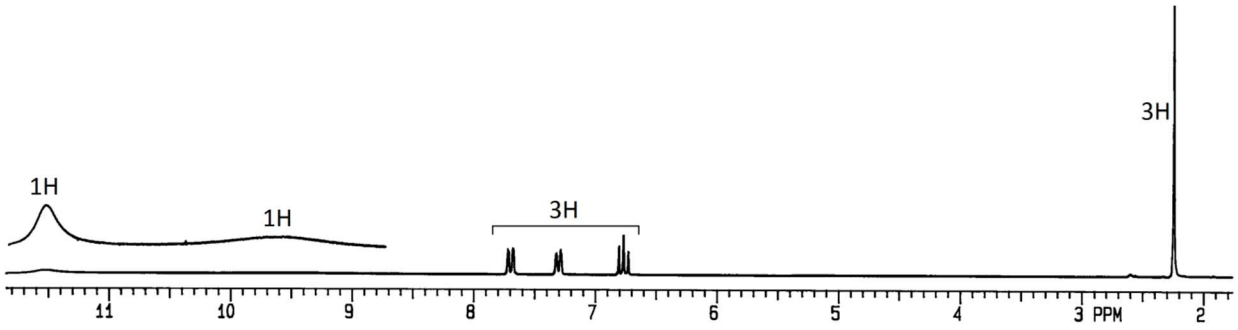
Propanoic acid

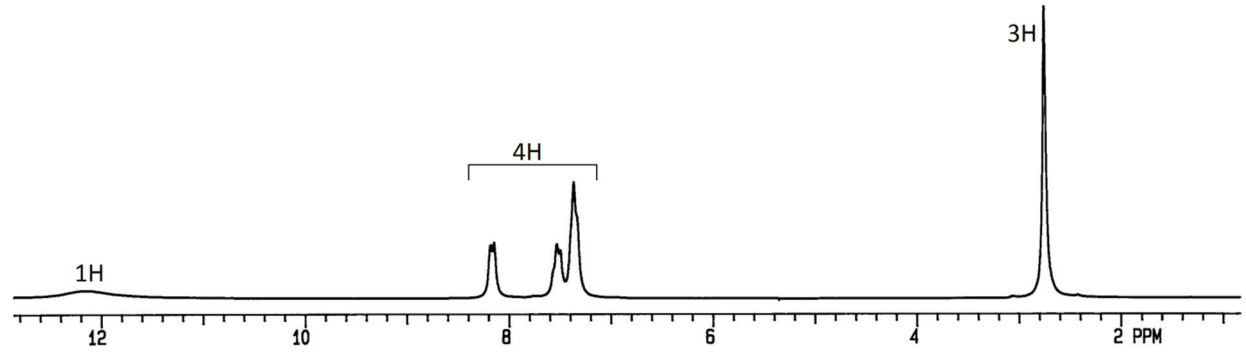
Part 4 (8 pts)

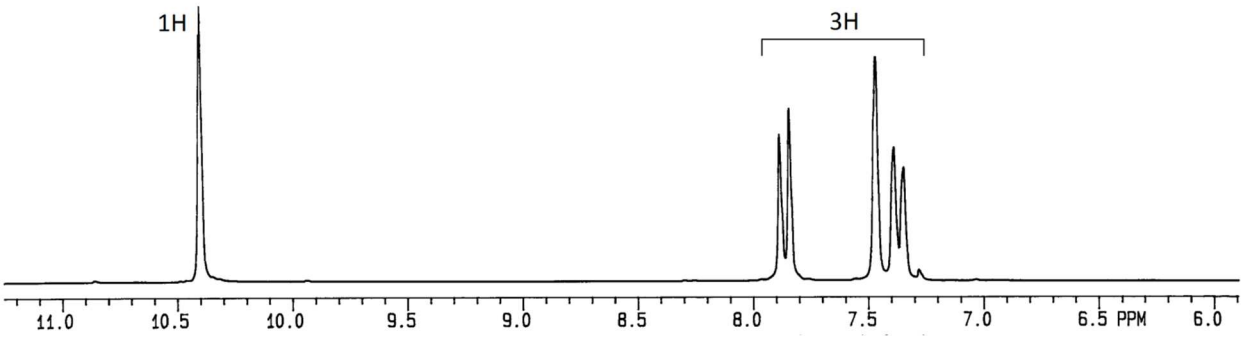
The eight spectra on the following pages represent mono, di, and trisubstituted aromatic compounds. An example of each type of disubstituted compounds is represented: ortho, meta, and para subsituted. The structures of the compounds which correspond to the eight spectra are drawn below.

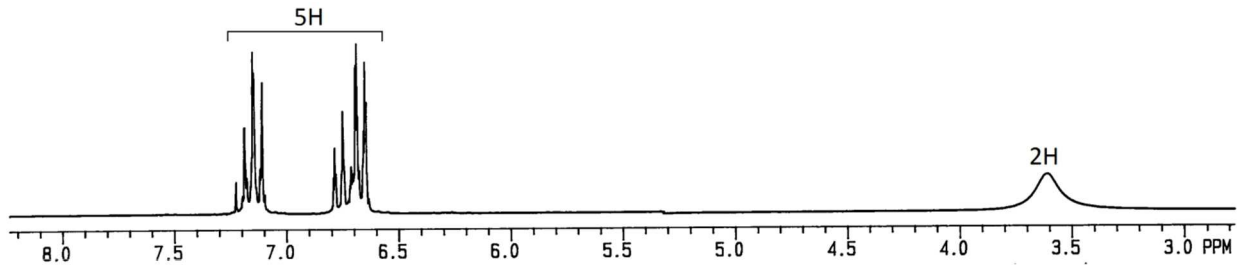
1) Match each compound with its NMR. You probably will not be able to tell an ortho from a meta substituted compound; you will not be marked off if you have these wrong. You *will* be marked off if you mix up a para with an ortho or meta substituted compound. Remember, para compounds are distinguished by their symmetric pair of doublets in the aromatic region.
2) Draw the structure above the spectrum and indicate which proton(s) correspond to which NMR peak. You do not have to assign each proton on the aromatic ring to a specific peak in the NMR aromatic region—simply indicate that they are somewhere in the aromatic grouping of NMR peaks.

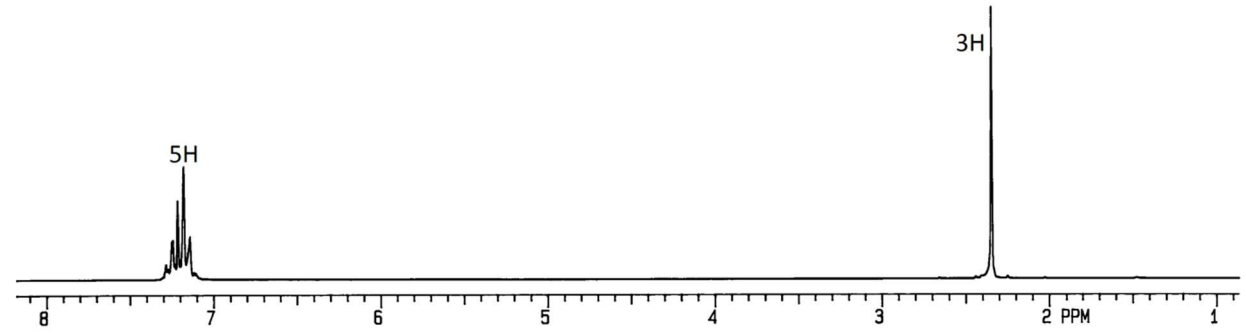


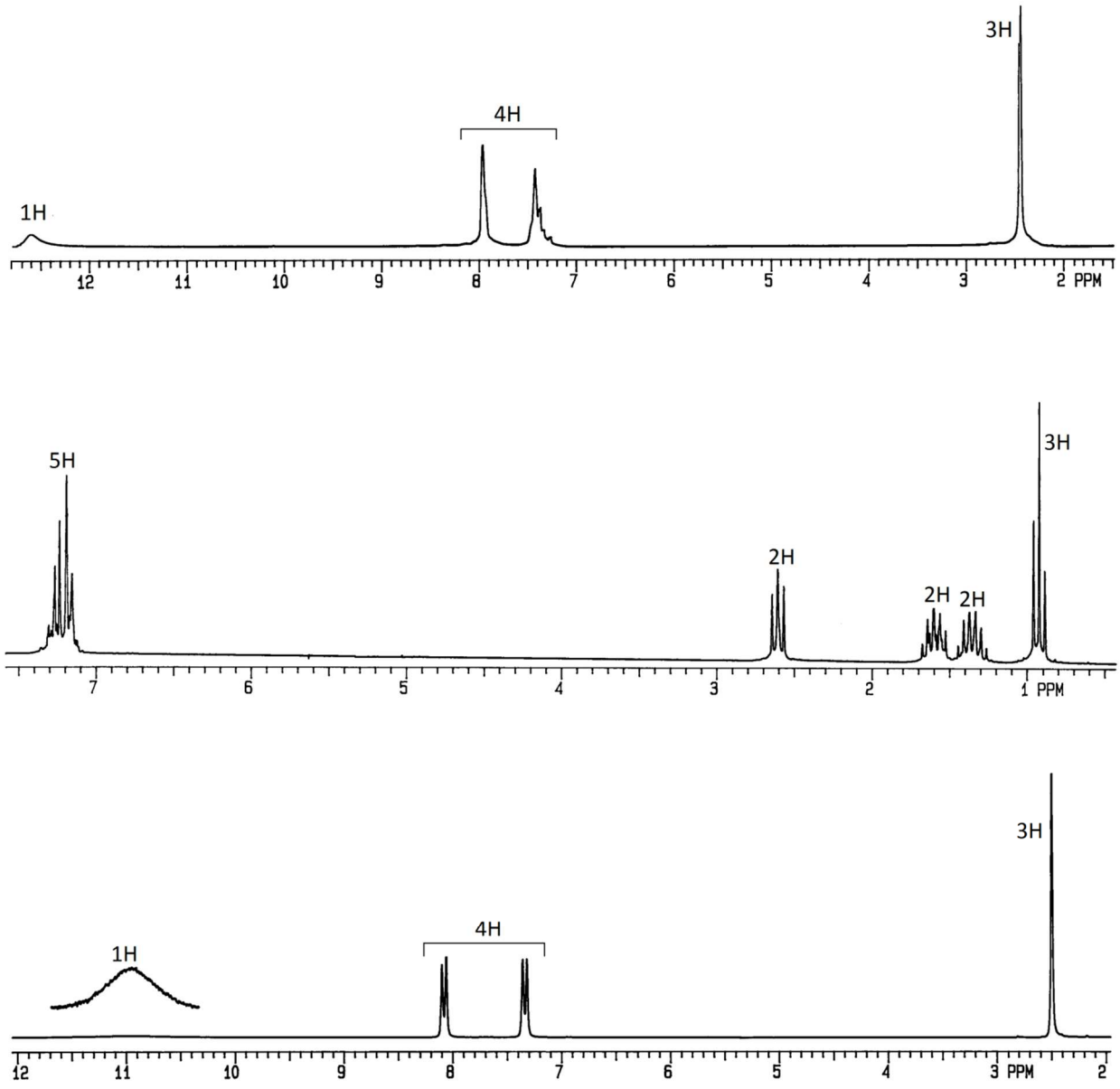



3H
4H
1H
12
10
8
6
4
2 PPM


1H
3H
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5 PPM
6.0


5H
2H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0 PPM


3H
5H
8
7
6
5
4
3
2 PPM
1


3H
4H
1H
12
11
10
9
8
7
6
5
4
3
2 PPM
5H
2H
2H
2H
3H
7
6
5
4
3
2
1 PPM
3H
4H
1H
12
11
10
9
8
7
6
5
4
3 PPM
2