Chem 221b

Problem Set 1

Chapter 13

Due: Monday, January 24, 2005

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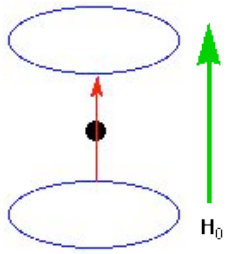
1. The Novice Level in the NMR module is an interactive exercise that will help you learn about ^{1}H and ^{13}C NMR. The estimated order of complexity is 15, 11, 12, 2, 3, 7, 1, 10, 6, 8, 4, 5, 9, 13, 16, 14, and 17-20. Try to avoid the solutions until you are truly in need. These exercises are important. I hope to do some of them in class.



An α spin nucleus precessing in a magnetic field

How do I go about solving one of these "railroad" problems? I don't have a clue. You don't have to call (Chem) 221b Baker Street for help. Try the following practice problem. Click here. A solution is provided but ple-e-e-e-e-ase don't look at the solution until you are truly stumped.

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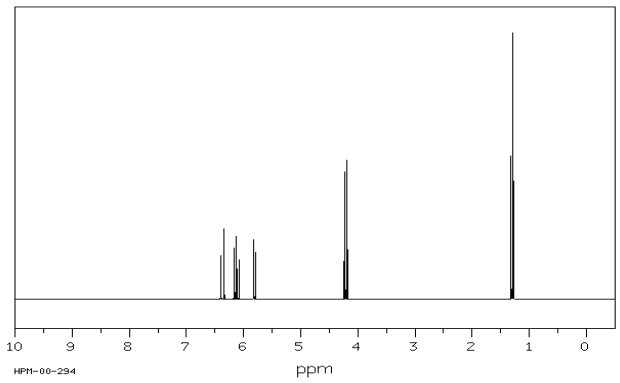
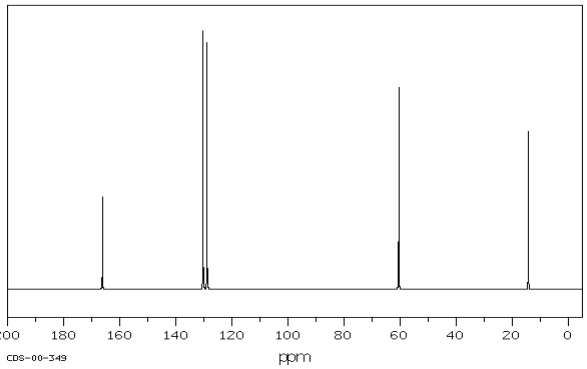
2. Draw ^{1}H NMR spectra for the three isomeric esters, ethyl acetate, methyl propionate, and n-propyl formate. Place the signals at their approximate chemical shift (the realative order should be correct), pay attention to multiplicity and area of the signals.

3. Compounds **A**, **B**, and **C** all have only an ethyl and vinyl pattern in their ^{1}H NMR spectra. The ^{13}C NMR and mass spectra are also provided. What are the structures of **A**, **B**, and **C** ? Show your reasoning?

Compound **A**:

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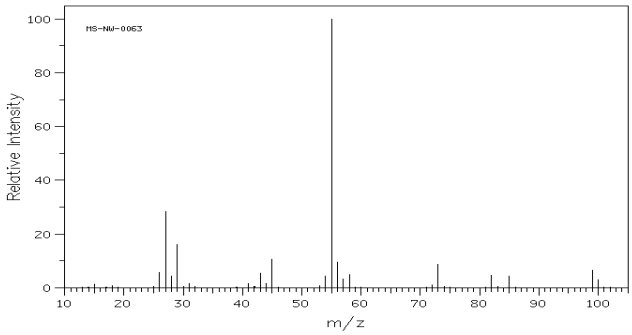
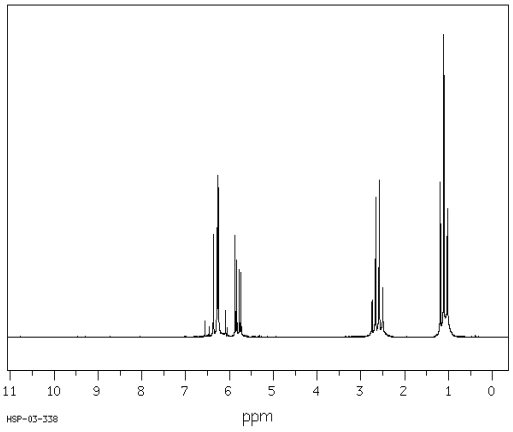
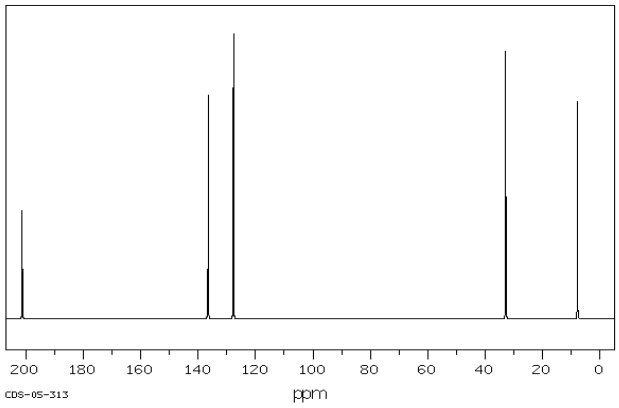
CDS-00-349
ppm


MS-NW-0063
Relative Intensity
100 80 60 40 20 0
10 20 30 40 50 60 70 80 90 100
m/z

Compound **B**:


11 10 9 8 7 6 5 4 3 2 1 0
HSP-03-338
ppm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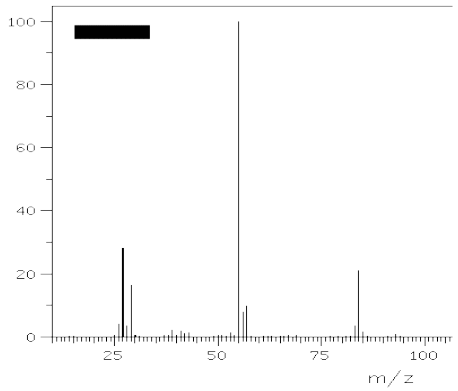
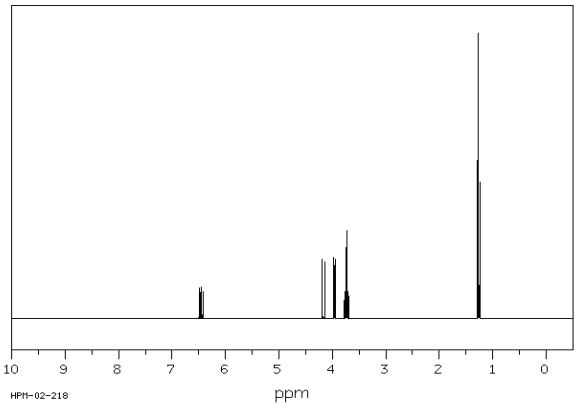
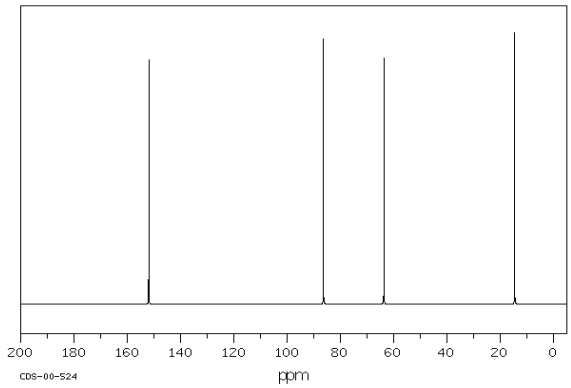
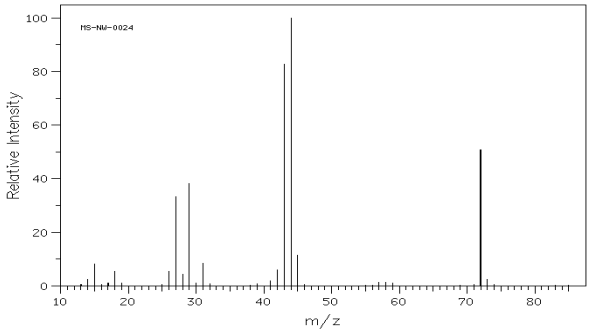
CDS-05-313
ppm



Compound **C**:







4. Treatment of compound **A** with a Grignard reagent **B** produces compound **C**. Exposure of **C** to H_2SO_4 readily provides two compounds: **D** and (*E*)**-E**. Ozonolysis and dimethyl

sulfide reduction of **D** affords **F** and **G**, while treatment of (*E*)-**E** with catalytic OsO_4/HIO_4 gives rise to **H** and **I**.

Compound **A**: ^{1}H NMR: δ 1.17 (6H, d, J=6.94 Hz), 2.56 (1H, septet, J=6.94 Hz), 3.67 (3H, s). [see Fig. 1]

Compound **F**: See Fig. 2 and the blowups, Figs. 3 and 4.

Compound **H:** ^{1}H NMR: δ 2.21 (3H, d, J=2.9 Hz), 9.79 (1H, q, J=2.9 Hz).

Compound **I:** ^{1}H NMR: δ 1.04 (3H, t, J=7.3 Hz), 1.10 (6H, d, J=6.9 Hz), 2.48 (2H, quartet, J=7.3 Hz), 2.62 (1H, septet, J=6.9 Hz) [see also Figs. 5 and 6]

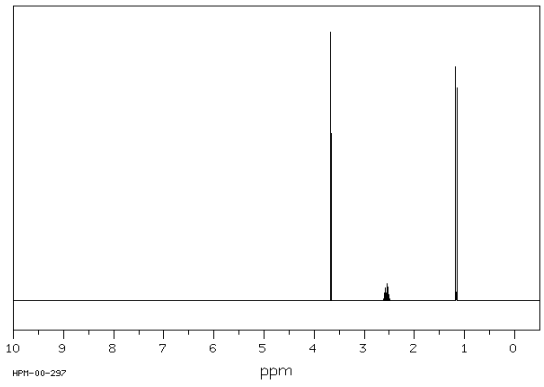


Fig. 1

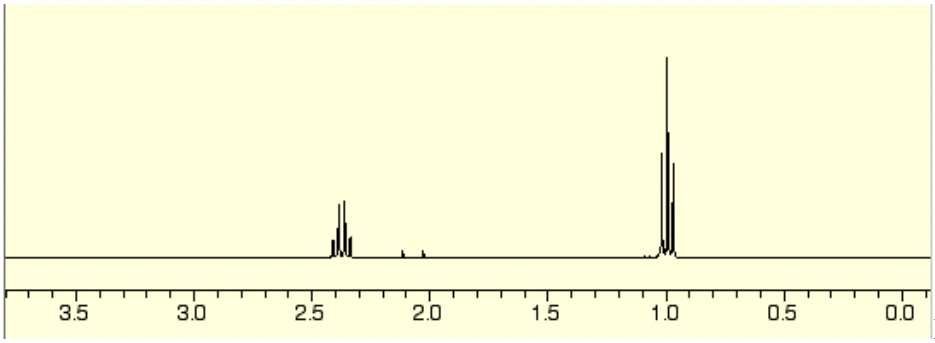


Fig. 2

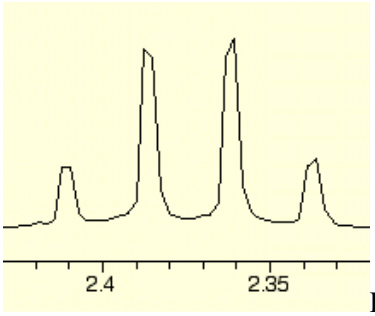


Fig. 3

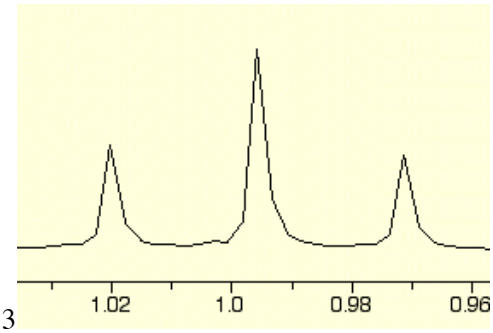


Fig. 4

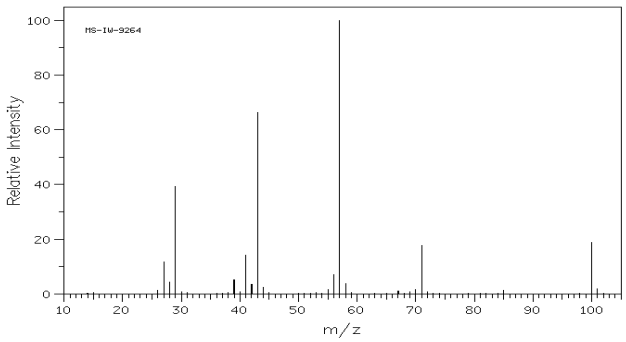


Fig.5

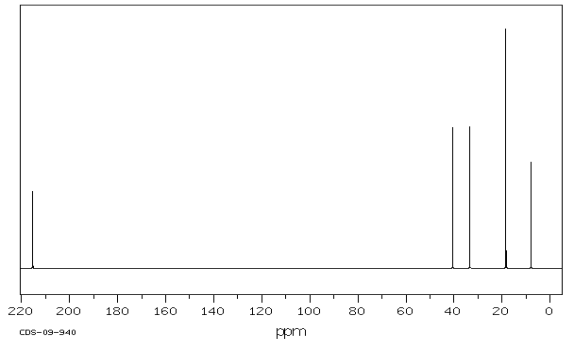


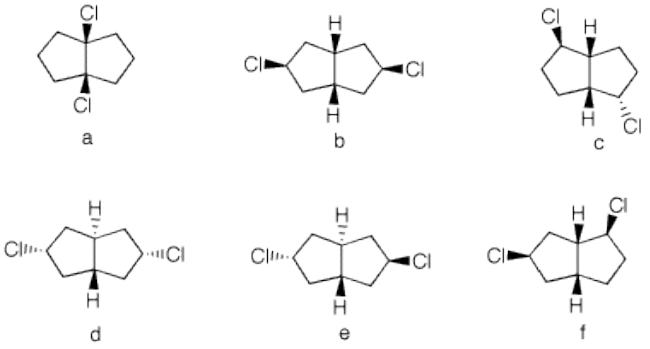
Fig. 6

a) Assign the structures to **A-I**. Show your reasoning.

b) The spectum of compound **F** in Figs. 2-4 were recorded at 300 MHz. What is the value of the coupling constant J? Show work. Confirm your answer using both Figs. 3 and 4.

c) Explain the origin of the two most intense peaks in Fig. 5.

5. Determine the number of singlets present in the broadband decoupled ^{13}C spectrum of each of the following dichlorides. Mark the identical carbons in each structure with a, b, c ...



6. In the 1997 Miramax film, Good Will Hunting, Minnie Driver's character Skylar did a considerable amount of grousing about organic chemistry in general and ^{1}H NMR spectroscopy in particular. Her complaint about interpreting the proton spectrum of ibogamine has merit. There isn't a lot of information in it. Click here.

a) Look at the downfield region of the spectrum. What is the large singlet? What are the chemical shifts of the sp^2 aromatic protons? How many of each are there?

b) What is the chemical shift, integral, and multiplicity of the highest field signal in the spectrum? Assign this signal.

c) What is the sign of the optical rotation of ibogamine shown here?

On the other hand, if her assignment had been to interpret the ^{13}C NMR spectrum of ibogamine, she may not have been so bored. It is much more informative. Click here for the ^{13}C NMR spectrum.

d) What is the strong set of signals around 77 ppm? [It is actually 3 signals (triplet) and not 4 signals as the print out at the top of the spectrum indicates.]

e) Are all of the carbons of ibogamine present in the spectrum?

f) Draw the structure of laevorotatory ibogamine.

g) What enantiomer of ibogamine is Will Hunting (Matt Damon) drawing here?

h) Assign the singlets in the region 100-150 ppm to their respective carbons.That is, assign the taller signals (mark them with an "x" in part f.) to the appropriate group of carbons and the shorter signals (mark them with a "y") to their carbons. You will not be able to make a specific assignment of individual carbons.

i) Locate the carbons that absorb at higher field than 40 ppm. Mark them with a "z". How might they be described?

j) How many carbons remain unassigned? Describe the two types of carbons that remain. How many of each are there?