

Spectroscopies Worksheet #1

This is an exercise to give you more experience with interpretation of spectral data.

- It is a 73 point exercise that I am asking you to turn in at lecture time on Tuesday, October 22.
- So why distribute it now if it isn't due for 4 weeks? Because if you can get a head start with it, you will learn some things that will make writing your lab Report #2 easier and better. I encourage you to work on this exercise, at least some, before writing up that lab report. That is, the sooner you work through this worksheet, the more it will help you with report writing.
- The goal is to have everyone score 73 points! You may (*in fact, you should*) work together, but each of you must turn in your own set of final answers. Print this file, place your hand-written answers on that printed version, and turn that in as your finished worksheet.
- Most importantly, this exercise is meant to be a learning tool (not an annoying homework assignment) so that all of you can improve your ability to interpret spectral data. Use textbooks and TA's as resources. The TA's will not tell you the answers. They will answer specific and thoughtful questions, though, provided you have put some effort into the issue at hand.
- You will learn things from this exercise that will enhance your ability to interpret the spectral data you are collecting for each new compound that you make.

Technical Notes:

- Pay attention to the spectrometer frequency that was used to record each spectrum. It is either 300 or 500 MHz, and this is indicated in the text in the upper left corner of each spectrum. This is necessary for you to know as you deduce the value of the coupling constants (i.e., convert ppm values to Hz).
- The last two pages (pp 20, 21) of this PDF contain some chemical shift effects of different substituents on aromatic (benzene) rings that you will find useful in answering some of the questions and some ranges of typical J values (in hertz, Hz) for some common H-H relationships.

Full file:

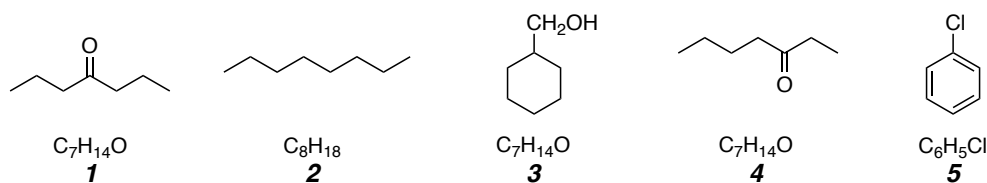
- Please find and print the (21 pages of the) worksheet from the course website under "Spectroscopies Worksheet #1 (posted 9-24-24)" (the PDF is named "2312 Spectroscopies Worksheet F24.pdf").

Part I.

The three mass spectra (A-C) for this problem are located on page 4. The three compounds giving rise to these spectra are *among* the five shown below (1-5). Give the structure of the ion responsible for each of the peaks labeled with the number of its mass on each of the mass spectra (draw your structures directly on each mass spectrum).

- Label the structure responsible for spectrum A with "A"
- Label the structure responsible for spectrum B with "B"
- Label the structure responsible for spectrum C with "C"

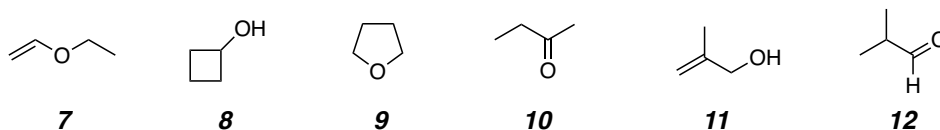
(Leave the remaining two structures blank)



Part II.

The three infrared spectra (D-F) for this problem are located on page 5. The three compounds giving rise to these spectra are *among* the six shown below (7-12).

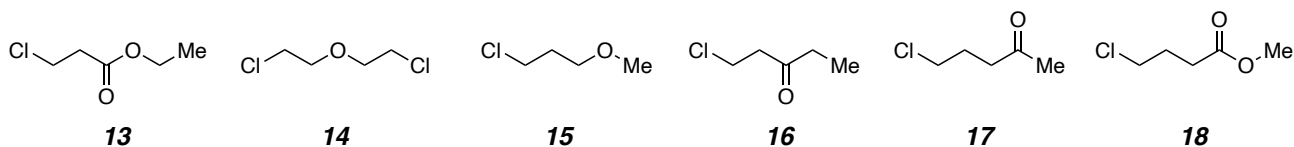
- Label the structure responsible for spectrum D with "D"
 - Label the structure responsible for spectrum E with "E"
 - Label the structure responsible for spectrum F with "F"
- (Leave the remaining three structures blank)



Part III.

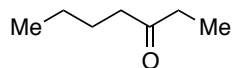
The three proton NMR spectra (G-I) for this problem are located on page 6. The three compounds giving rise to these spectra are *among* the six shown below (13-18). I have labeled each resonance with the *relative* intensity of the peaks (i.e., the integral) and, where necessary for clarity, the multiplicity.

- Label the structure responsible for spectrum G with "G"
 - Label the structure responsible for spectrum H with "H"
 - Label the structure responsible for spectrum I with "I"
- (Leave the remaining three structures blank)



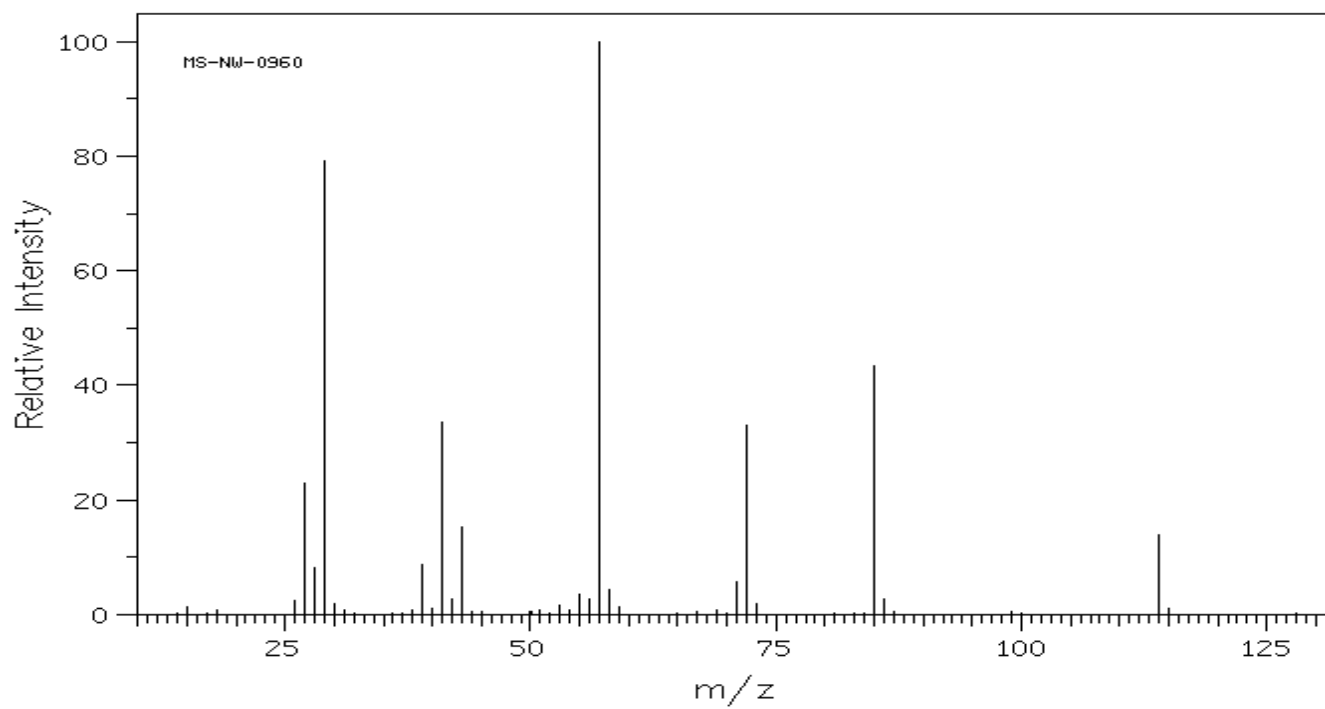
Part IV

The mass spectrum below is that of 3-heptanone (**19**). Indicate the structure of the ion responsible for the peak at each of the following five masses (m/z).



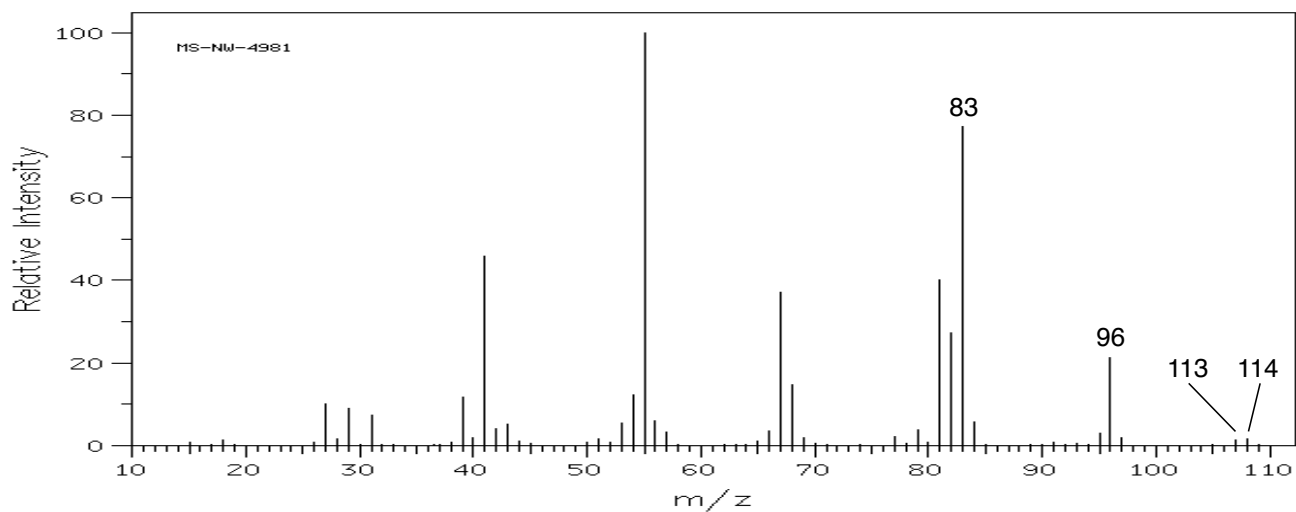
19

$m/z = 29$	$m/z = 72$	$m/z = 115$	$m/z = 57$	$m/z = 85$
------------	------------	-------------	------------	------------

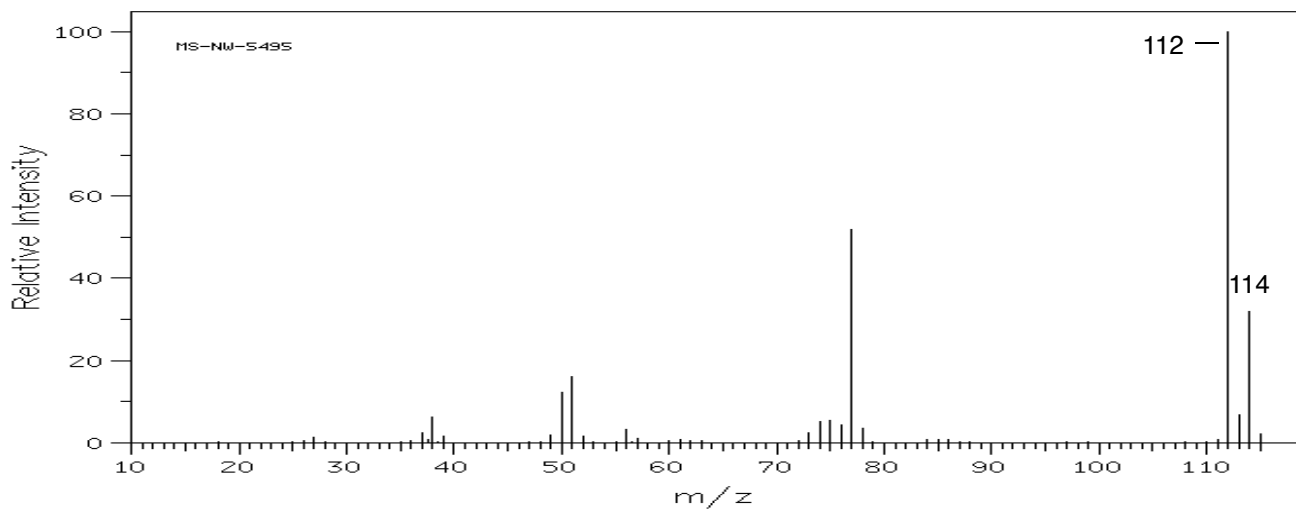


Mass Spectra for Part I

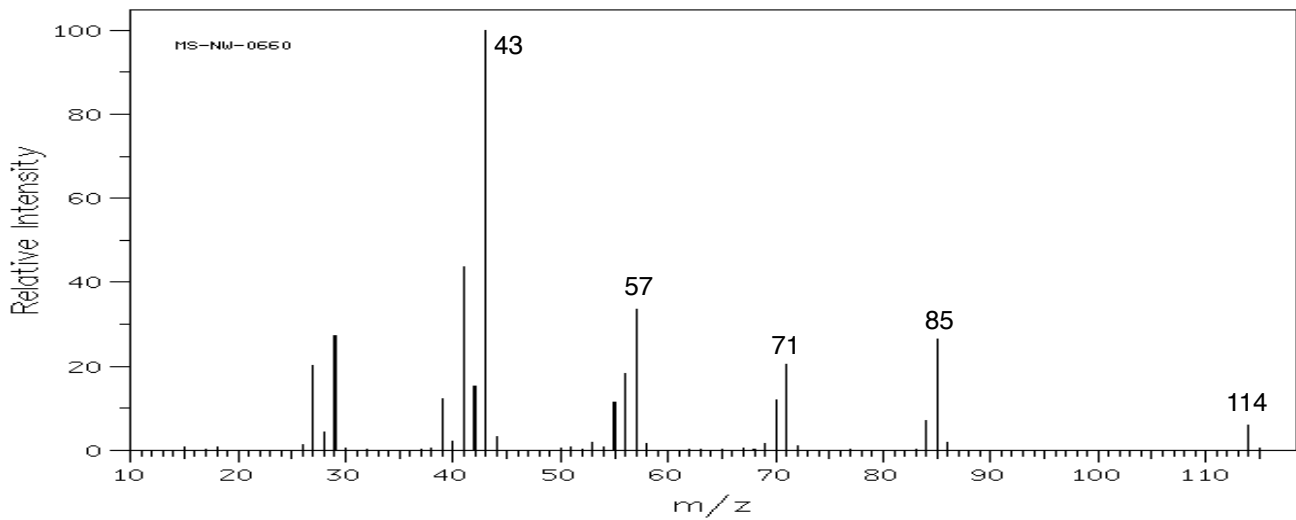
Spectrum A



Spectrum B

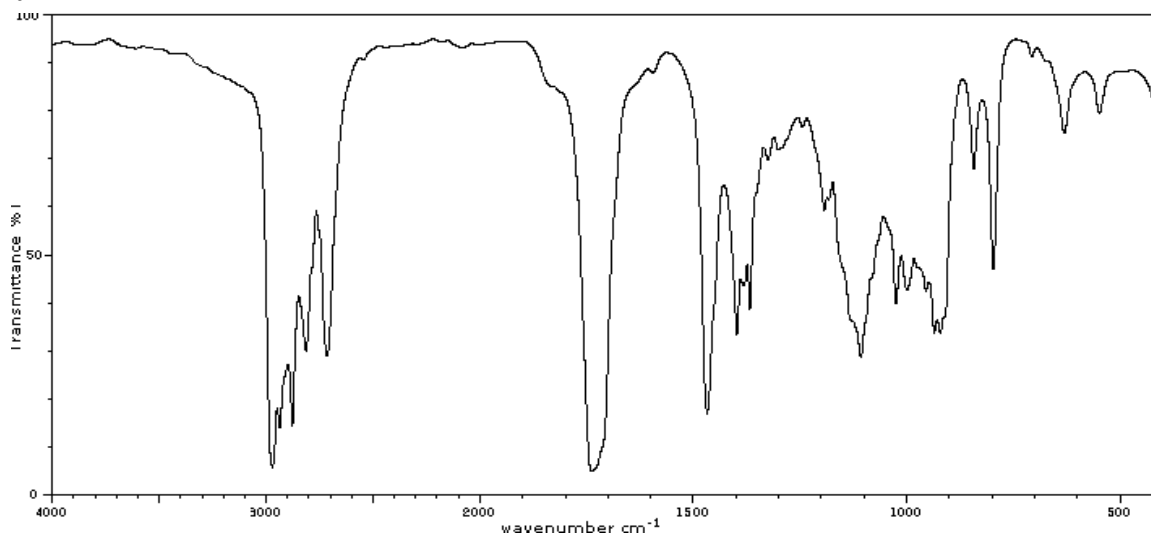


Spectrum C

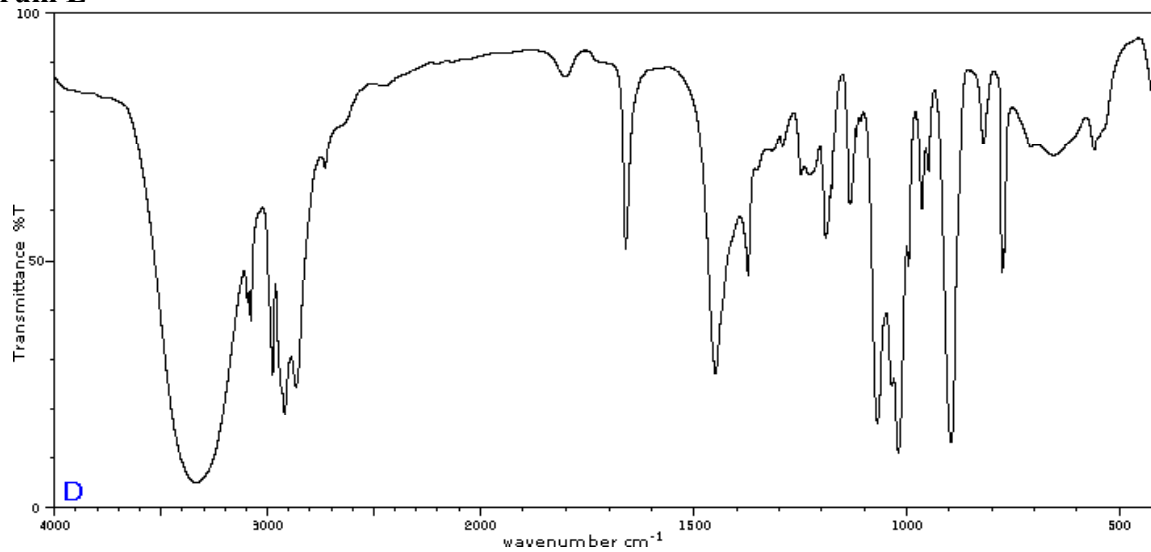


Infrared Spectra for Part II

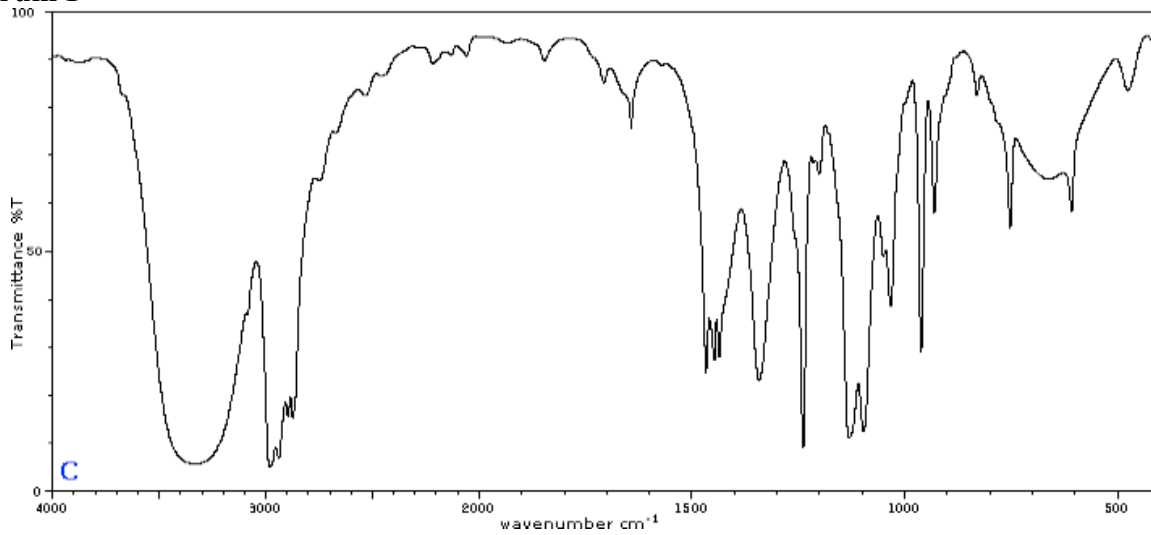
Spectrum D



Spectrum E

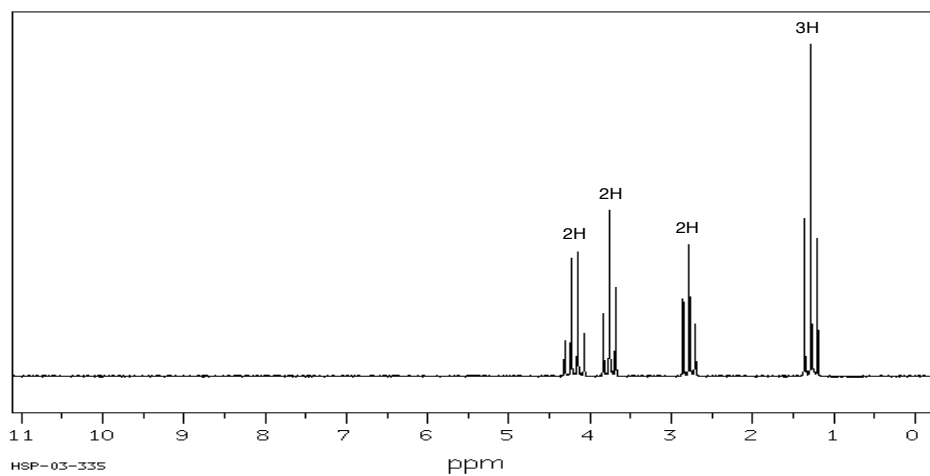


Spectrum F

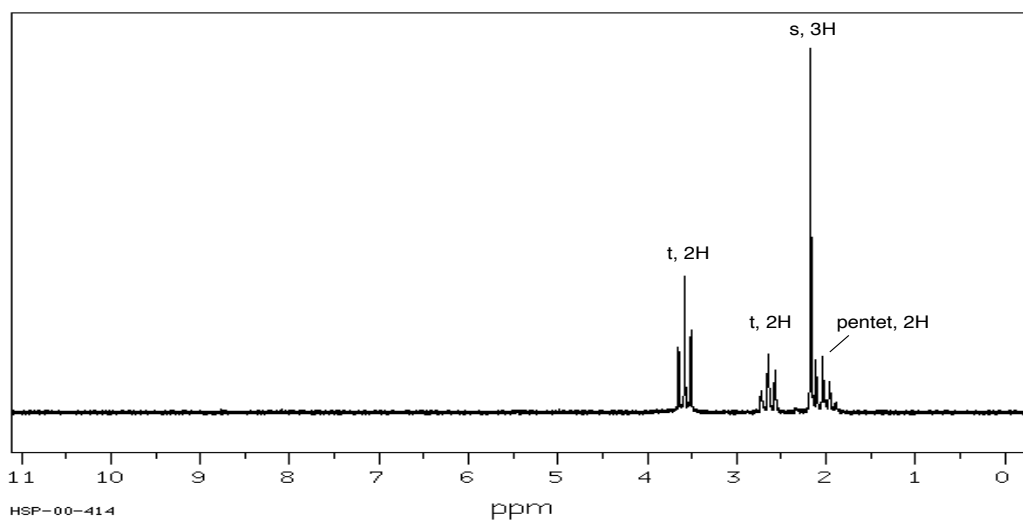


Proton NMR Spectra for Part III

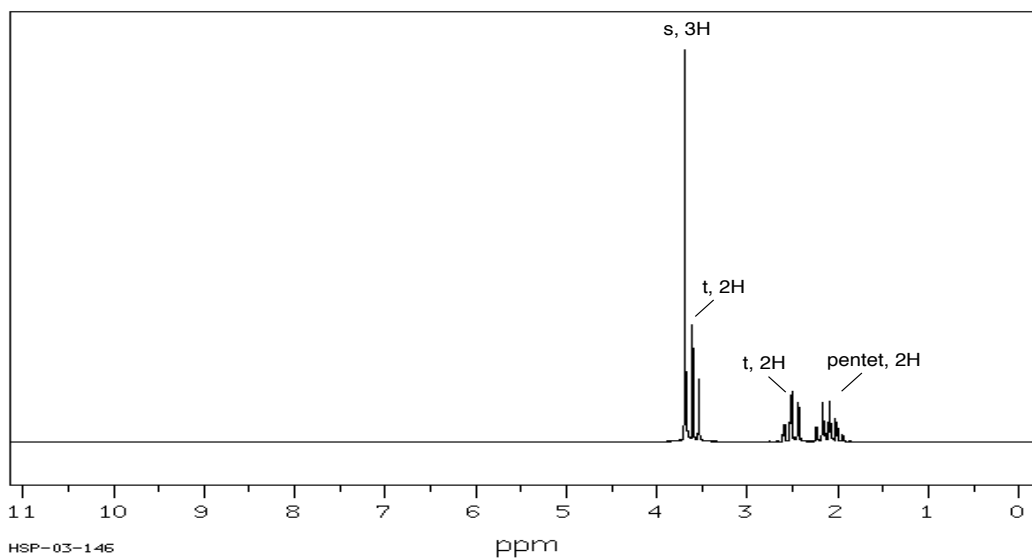
Spectrum G



Spectrum H



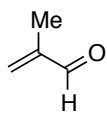
Spectrum I



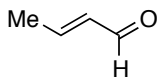
Part V.

On the following three pages (pp 8-10) are eight nmr, ir, and/or mass spectra labeled **Spectrum 1** through **Spectrum 8**. Each is of one of the sixteen structures listed below (**A-P**). All of these possible answers have the same molecular formula (i.e., C_4H_6O). All of your answers for this problem should appear in the boxes on the bottom of this page.

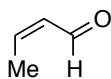
Assign the correct structure to each **Spectrum #** by adding the appropriate letter to the box beside each **Spectrum #** at the bottom of this page. Note: it is possible that the same structure (i.e., letter) could be the correct answer for more than one **Spectrum #**.



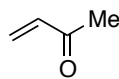
A



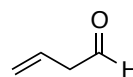
B



C



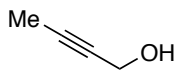
D



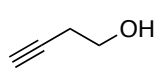
E



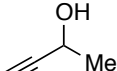
F



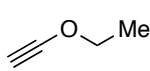
G



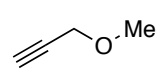
H



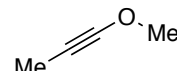
I



J



K



L



M



N



O



P

Spectrum 1

Spectrum 5

Spectrum 2

Spectrum 6

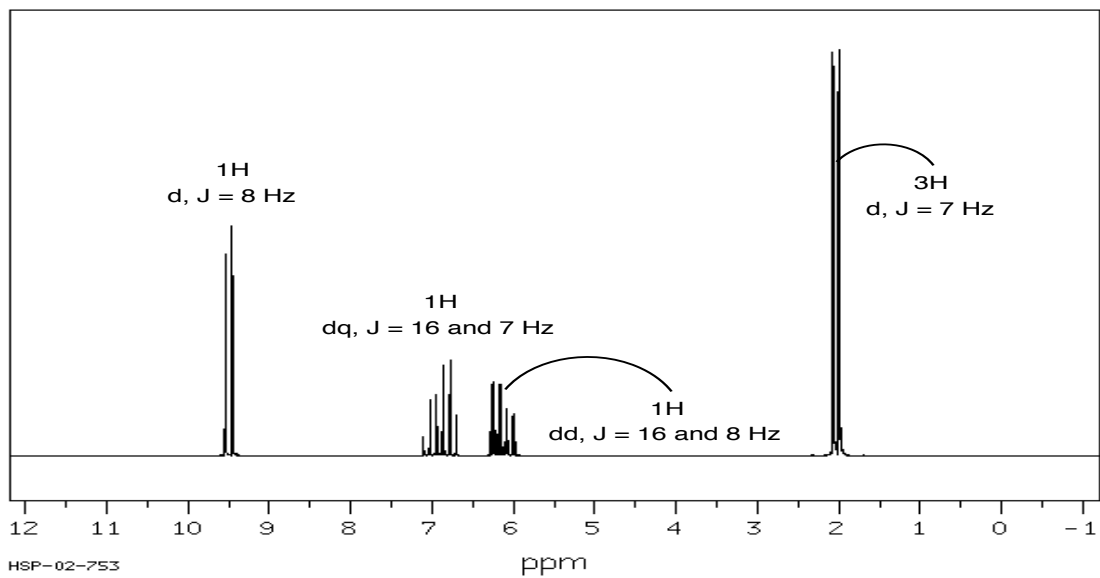
Spectrum 3

Spectrum 7

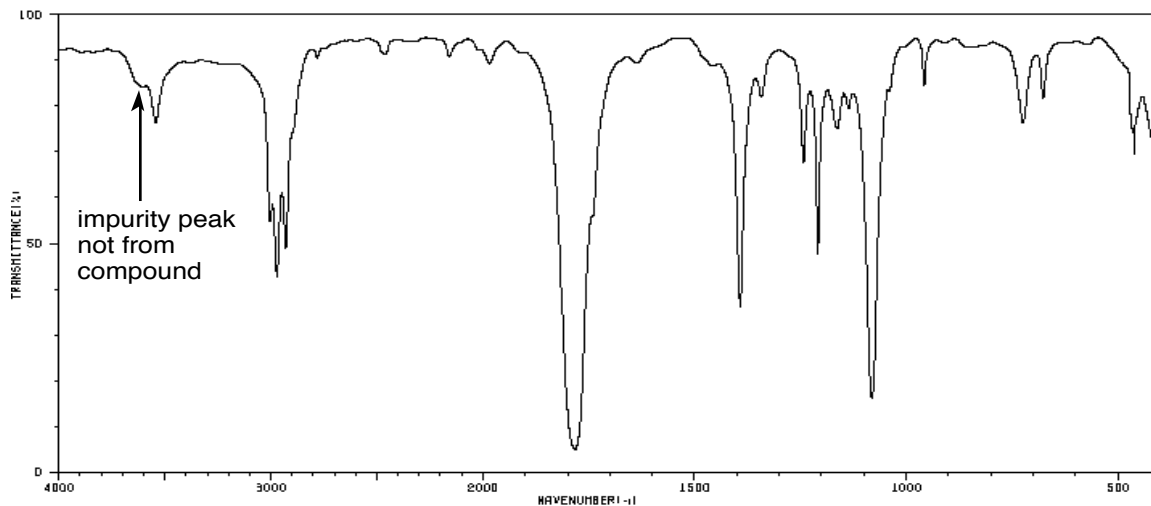
Spectrum 4

Spectrum 8

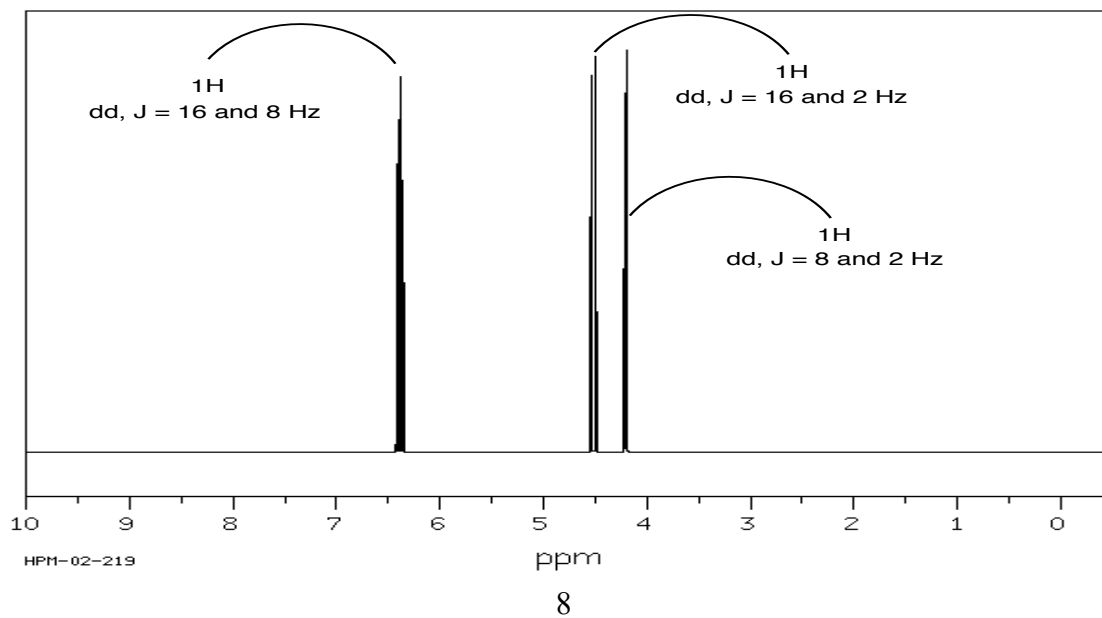
Spectrum 1



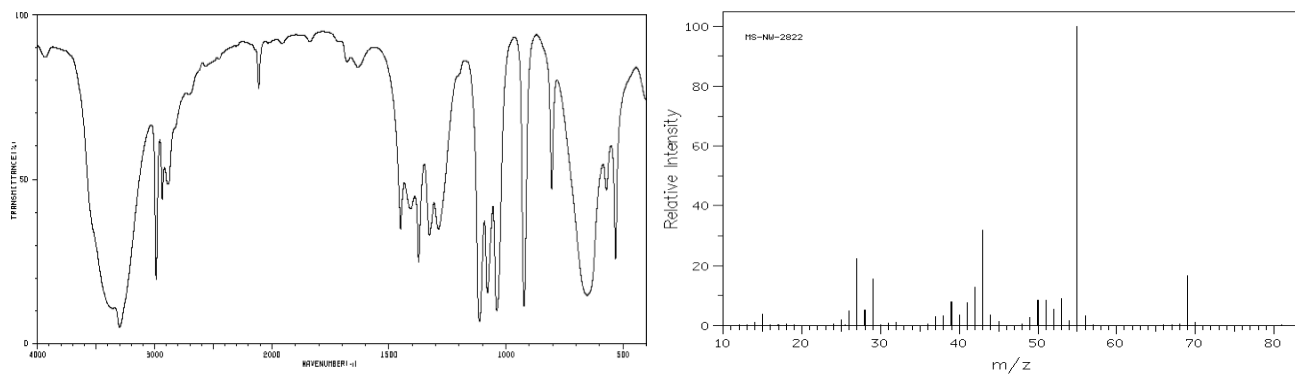
Spectrum 2



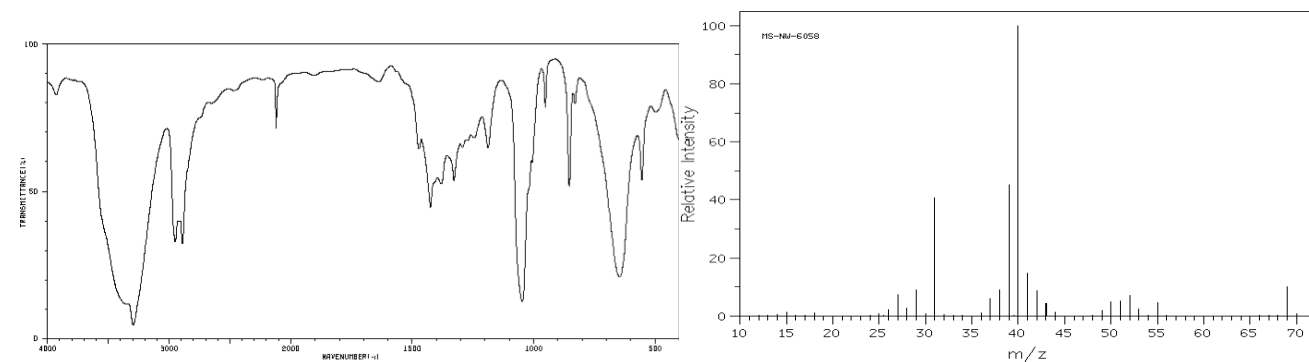
Spectrum 3



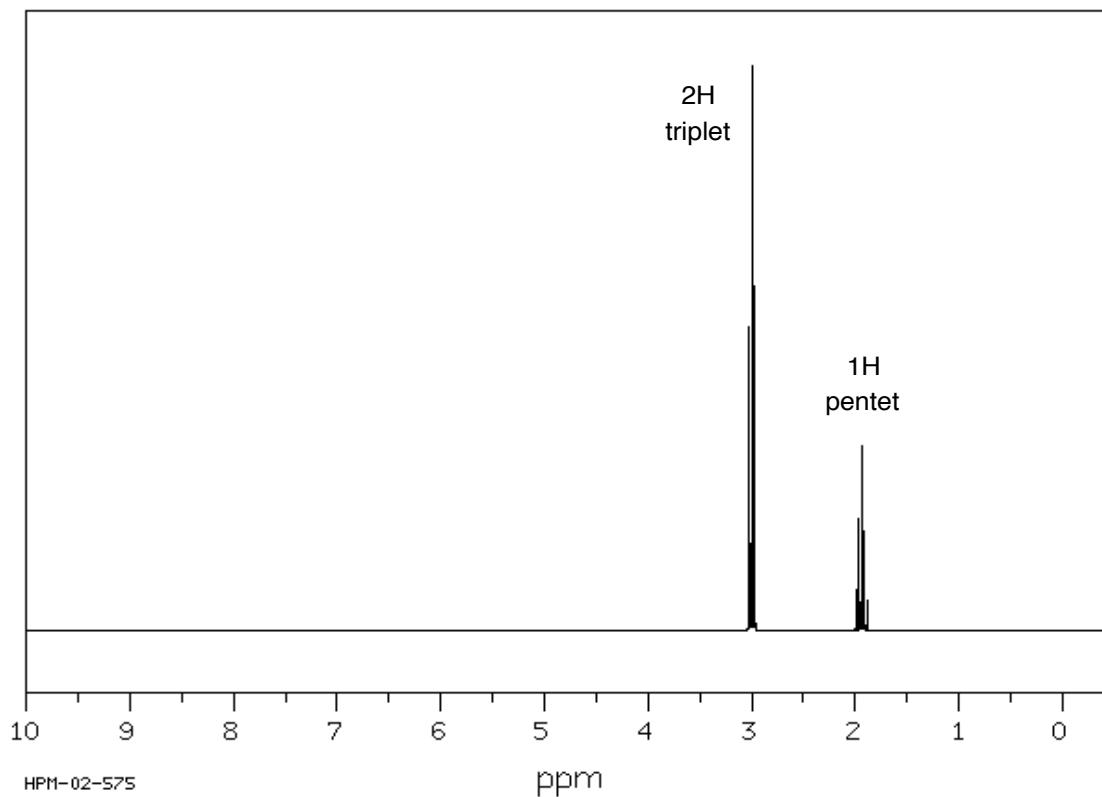
Spectrum 4 (these IR and mass spectra are both of the same compound)



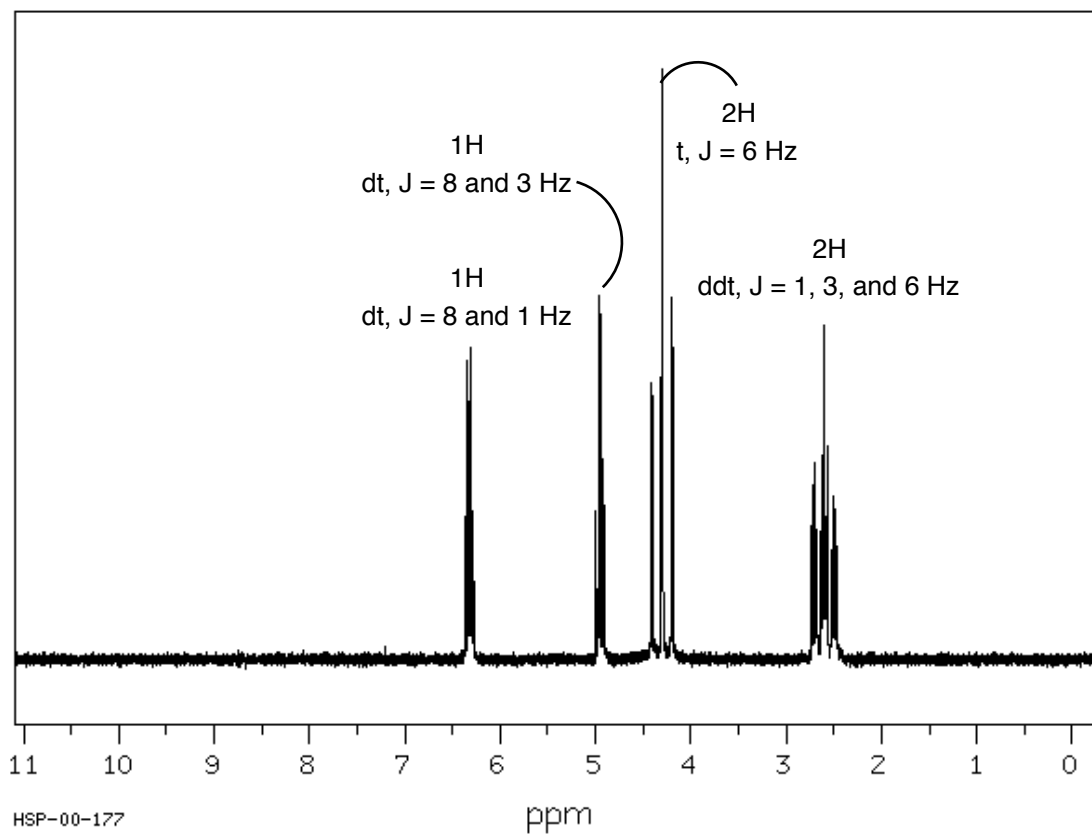
Spectrum 5 (these IR and mass spectra are both of the same compound)



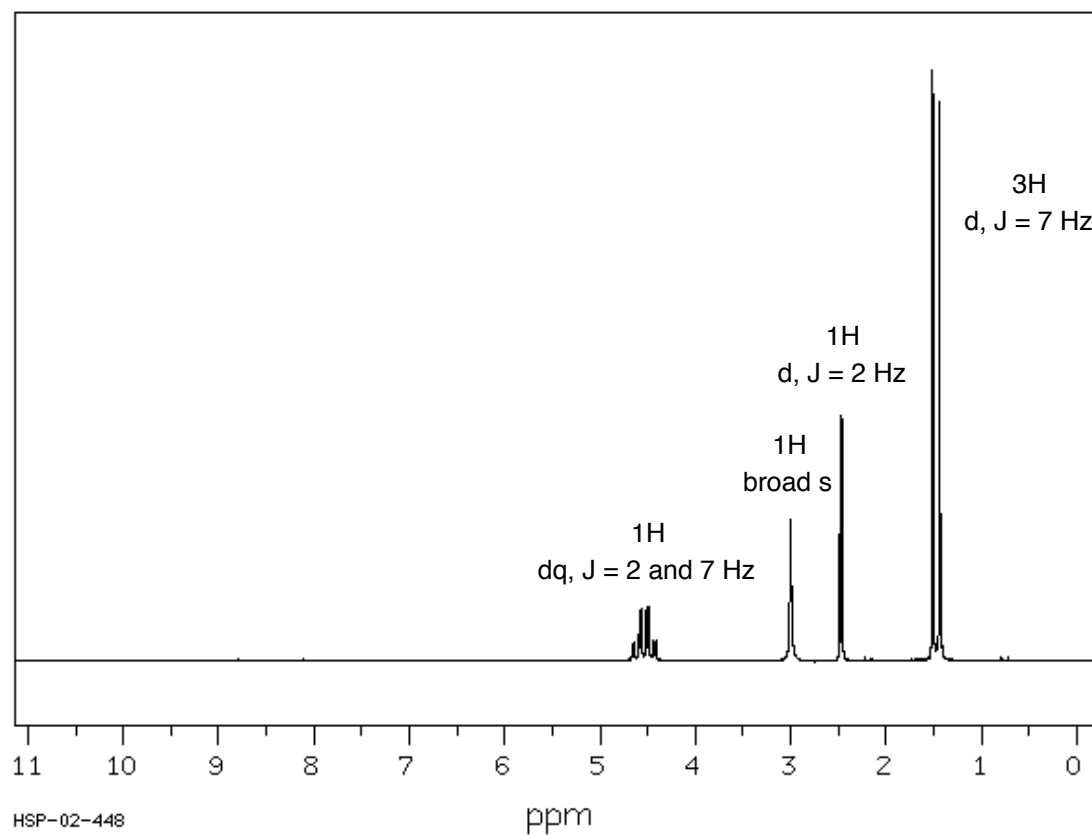
Spectrum 6



Spectrum 7



Spectrum 8



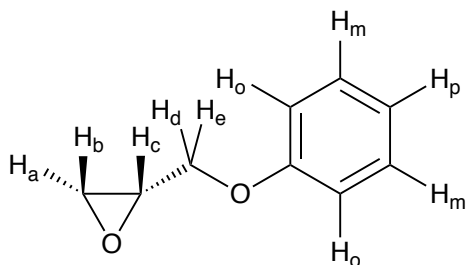
Part VI.

I have uploaded two NMR (zipped) folders to the website. These are ^1H spectra that a former TA recorded in CDCl_3 at 500 MHz. They are named:

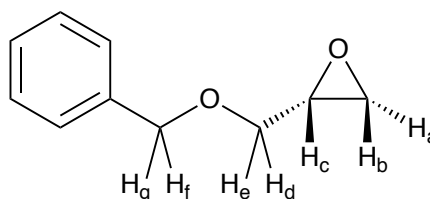
"Epoxyphenoxypropane-161014"

"Benzyl glycidyl ether-161014"

Assign all resonances to each of the protons in each of these two compounds; indicate this by writing the approximate chemical shift beside each proton in each of the two structures. It will not be possible to assign which of the diastereomeric protons is H_d vs. H_e (or H_f vs. H_g). To distinguish (and assign) H_a vs. H_b , you need to know that vicinal protons on an epoxide ring typically have a coupling constant between 4-5 Hz if they are cis to one another and 2-3 Hz if they are trans.



2-(phenoxymethyl)oxirane
[1,2-epoxy-3-phenoxypropane]



2-((benzyloxy)methyl)oxirane
[benzyl glycidyl ether]

The aliphatic protons are well-resolved, first-order multiplets. Determine the coupling constants between each of the following pairs of protons in benzyl glycidyl ether:

$$J_{ab} =$$

$$J_{ac} =$$

$$J_{bc} =$$

$$J_{cd} =$$

$$J_{ce} =$$

$$J_{de} =$$

$$J_{gf} =$$

Determine the coupling constants of the aromatic protons in "epoxyphenoxypropane." You will notice some "funny business" at the base of each of these resonances. This is a result of a phenomenon called magnetic inequivalence, which we will discuss some in lecture. You can still determine the magnitude of the principal coupling constants from the most intense lines.

$$J_{o,m} =$$

$$J_{m,p} =$$

$$J_{o,p} =$$

Problem VII.

Compounds **A** and **B** are disubstituted benzene derivatives, and compound **C** is a trisubstituted benzene derivative. The molecular formulas are as follows: **A**, C_6H_5BrO ; **B**, C_6H_5ClO ; **C**, $C_6H_4Cl_2O$. Complete Table I (next page) by entering the requested data for each compound and then answer the following questions. Note: The spectral data for all of these compounds were recorded at 300 MHz and are found on six pages following Table I. To be consistent, label each set of resonances as a, b, c, d, etc. starting with the most downfield (largest δ) resonance.

- 1) How will an electron donating group (EDG) on an aromatic ring affect the chemical shifts of the aromatic protons (vs. the “parent” hydrogen atom substituent) and why? What about an electron withdrawing group (EWG)?
- 2) Which positions will be affected most dramatically by a conjugated EWG and EDG (*ortho*, *meta*, and/or *para*)? Draw resonance structures of benzaldehyde and anisole (methoxybenzene) to show this.
- 3) Based on your answers (coupling constants, integration, chemical shifts) to questions 1) and 2), determine the structures of compounds **A** and **B** and assign each proton to a peak on the spectrum (letter each proton on the structure you draw according to the letter of its resonance, as labeled on each spectrum). Notice how well the incremental chemical shift parameters listed in Table 3.10 correlate with the actual chemical shifts of compound **A**. Use these parameters to help you assign each of the four resonances for the aromatic protons in compound **B**.
- 4) Draw the six possible structures for compound **C**? Which ones of these six possible structures can easily be eliminated based on the spin-spin coupling information? (Recall that ortho protons have large, meta have much smaller, and para tiny to non-observable coupling constant values.) Assign the correct isomer by considering the chemical shift and coupling constant data. There are two possible candidate structures that are very hard to distinguish because the incremental chemical shift effects become less accurate for multiply substituted benzene derivatives. That is, their additivity is imperfect.

Table IA. Compound A

ID	Chemical Shift	Integration	Multiplicity	J values (Hz)	J(n,m)
a					
b					

Table IB. Compound B

ID	Chemical Shift	Integration	Multiplicity	J values (Hz)	J(n,m)
a	7.30	1H	dd	7.8 1.5	J(a,d) J(a,b)
b					
c					
d					

Table IC. Compound C

ID	Chemical Shift	Integration	Multiplicity	J values (Hz)	J(n,m)
a					
b					
c					

0.000

1A

4.952

6.707
6.715
6.730
6.736
6.737
7.318
7.319
7.325
7.340
7.346
7.347

Pulse Sequence: s2pu1
 User:
 Date: Sep. 25, 2001
 Solvent: CDC13
 File:
 Starting Time: 12:33:22
 Completion Time: 12:33:38
 Total acq. time 1 minute
 UNITYplus-500 "spectrum"
 Ambient temperature
 PULSE SEQUENCE
 Relax. delay 1.500 sec
 Pulse 90.0 degrees
 Acq. time 1.999 sec
 Width 6003.3 Hz
 Single scan
 OBSERVE H1, 300.1683401 MHZ
 DATA PROCESSING
 Line broadening 0.1 Hz
 F: size 131072

ppm
1
2
3
4
5
6
7
8

20.88

38.30
40.82

Pulse Sequence: s2pu1

User: [REDACTED]

Date: Sep. 25, 2001

Solvent: CDCl3

File: [REDACTED]

Starting Time: 12:33:22

Completion Time: 12:33:38

Total acq. time 1 minute

UNITYplus-500 "spectrum"

Ambient temperature

PULSE SEQUENCE

Relax. delay 1.500 sec

Pulse 90.0 degrees

Acq. time 1.999 sec

Width 6093.3 Hz

Single scan

OBSERVE H1, 300.1683401 MHZ

DATA PROCESSING

Line broadening 0.1 Hz

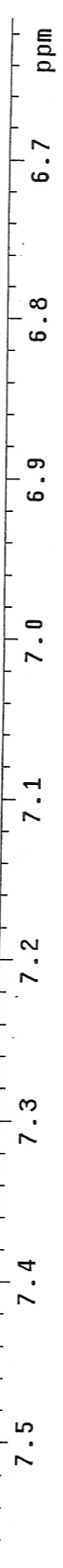
FT size 131072

1A

EXPANSION

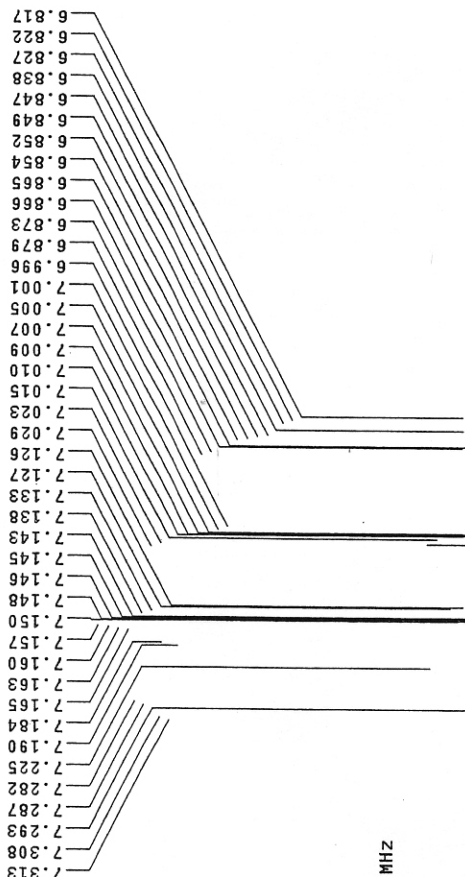
7.358
7.351
7.347
7.346
7.340
7.325
7.323
7.319
7.318
7.314
7.307
7.257

6.748
6.741
6.737
6.736
6.730
6.715
6.707
6.697

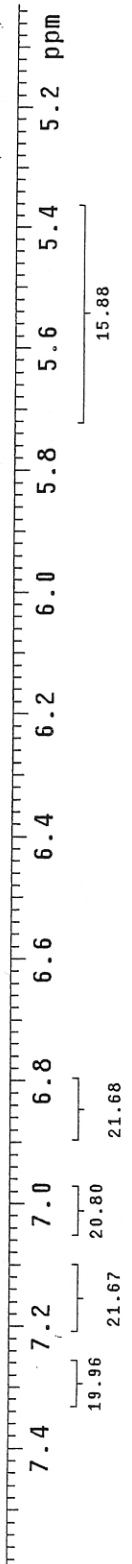
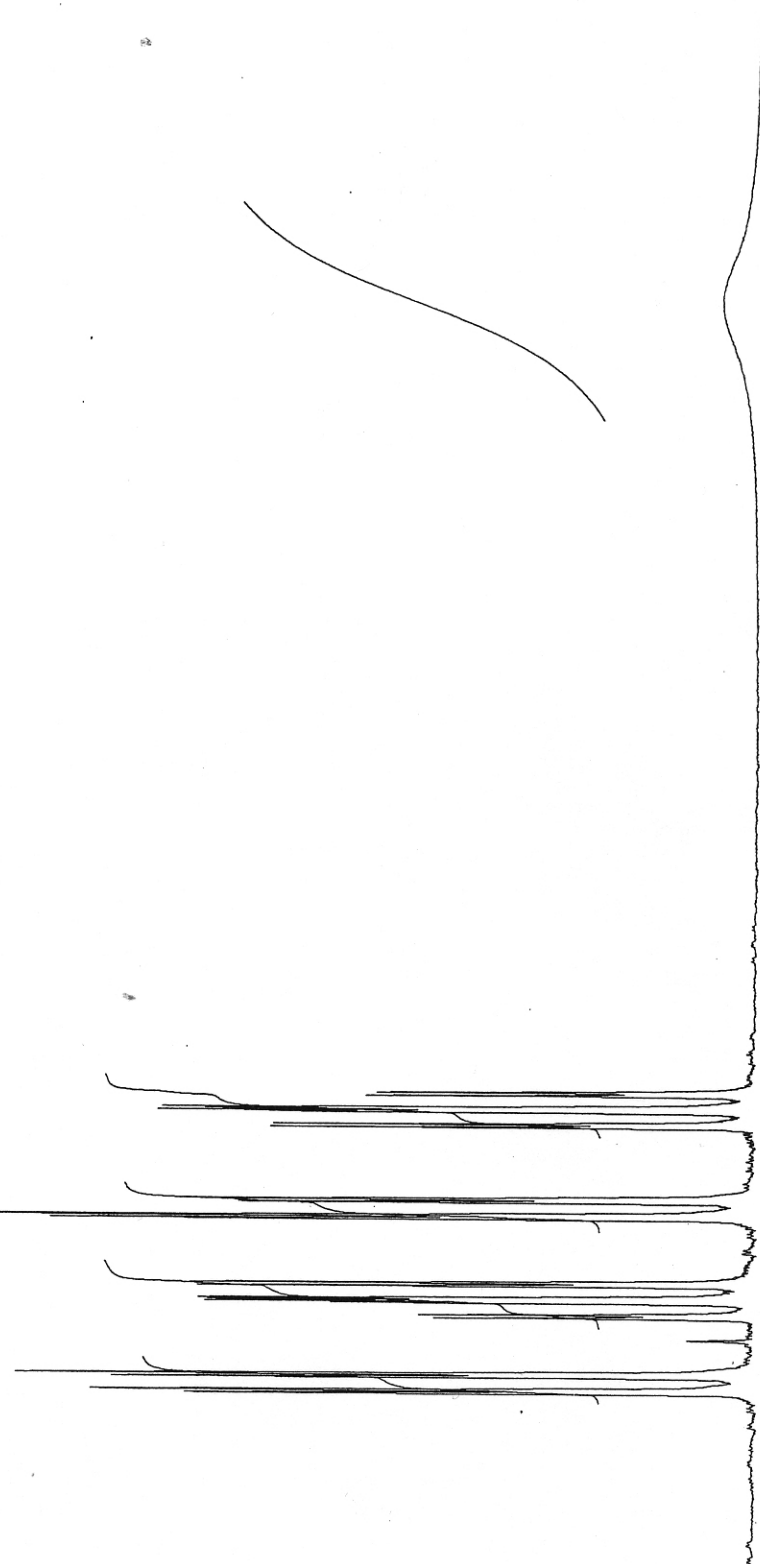
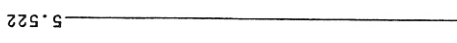


STANDARD 1H OBSERVE

Pulse Sequence: s2pu1
User: ██████████
Date: Sep. 25, 2001
Solvent: CDC13
File: ██████████
Starting Time: 12:22:25
Completion Time: 12:22:37
Total acq. time 1 minute
UNITYplus-500 "spectrum"
Ambient temperature
PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 1.999 sec
Width 6003.3 Hz
Single scan
OBSERVE H1, 300.1683496 MHZ
DATA PROCESSING
Line broadening 0.1 Hz
FT size 131072



1B



STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

User: [REDACTED]

Date: Sep. 25, 2001

Solvent: CDCl3

File: [REDACTED]

Starting Time: 12:22:25

Completion Time: 12:22:37

Total acq. time 1 minute

UNITYplus-500 "spectrum"

Ambient temperature

PULSE SEQUENCE

Relax. delay 1.500 sec

Pulse 90.0 degrees

Acq. time 1.999 sec

Width 6003.3 Hz

Single scan

OBSERVE H1, 300.1683496 MHZ

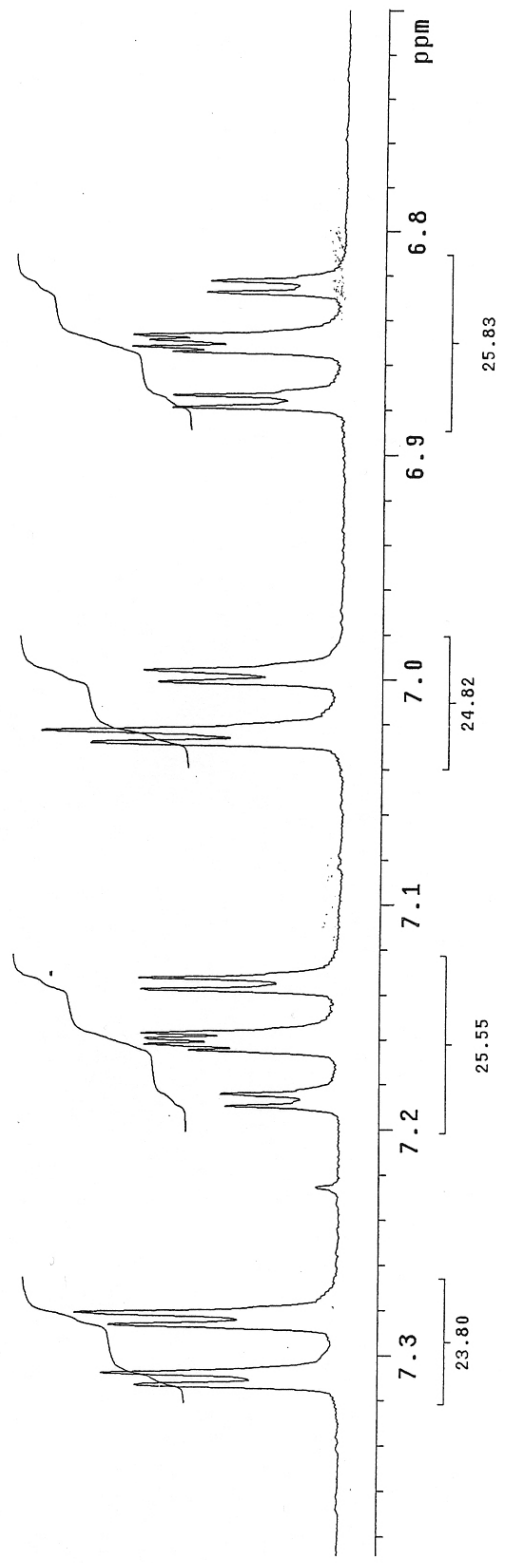
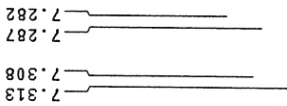
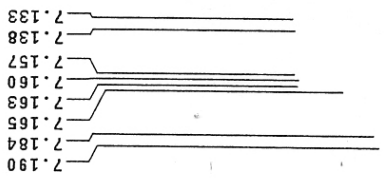
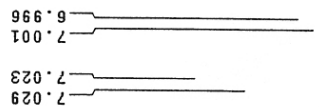
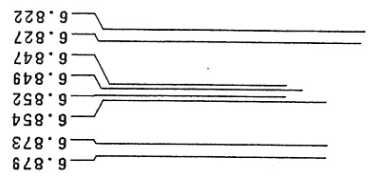
DATA PROCESSING

Line broadening 0.1 Hz

FT size 131072

1B

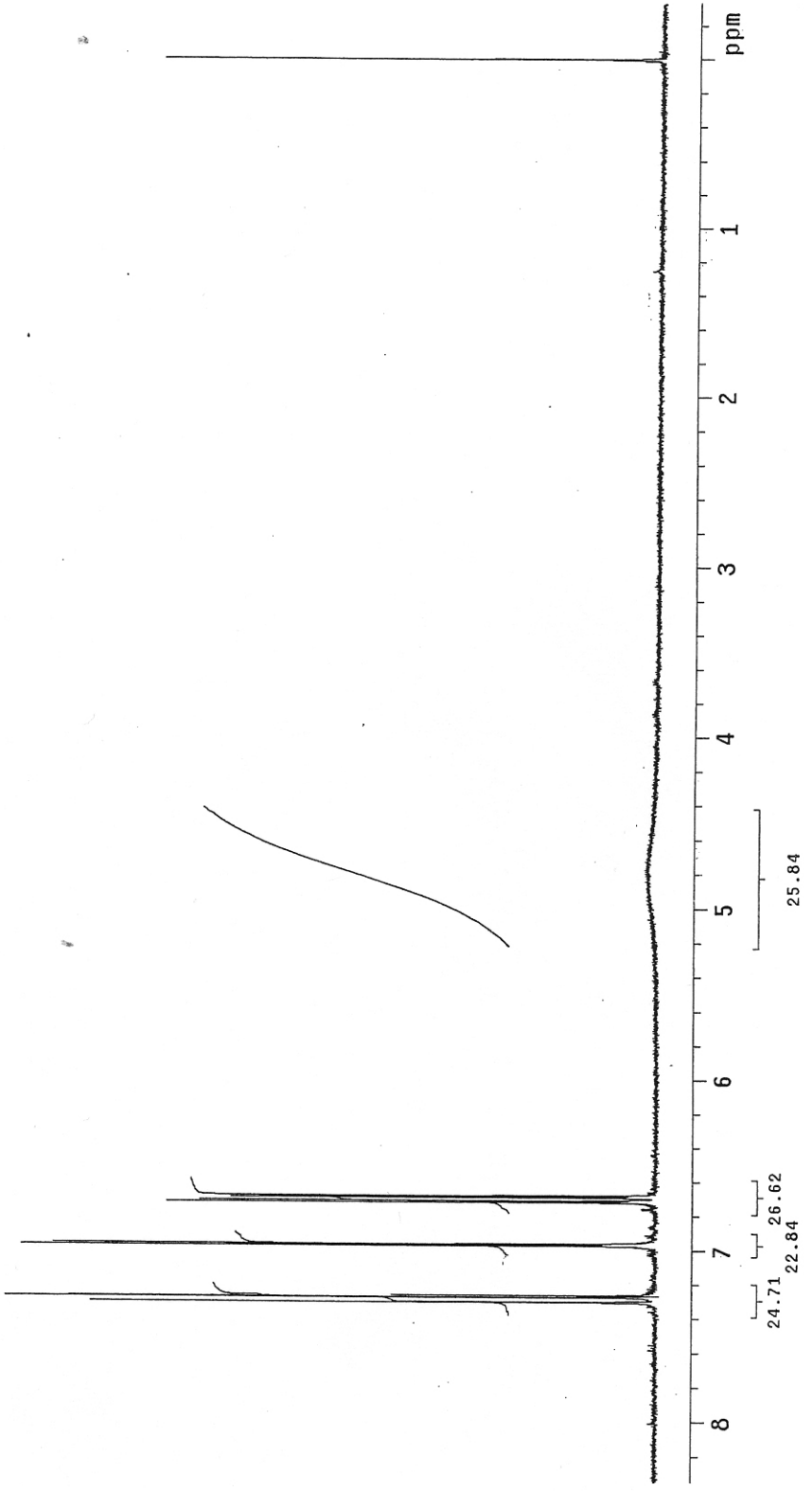
EXPANSION



7.906
7.277
7.265
6.972
6.963
6.723
6.721
6.713
6.711
6.692
6.682

Pulse Sequence: s2pul
 User: ██████████
 Date: Sep. 25, 2001
 Solvent: CDC13
 File: ██████████
 Starting Time: 12:29:26
 Completion Time: 12:29:38
 Total acq. time 1 minute
 UNITYplus-500 "spectrum"
 Ambient temperature
 PULSE SEQUENCE
 Relax. delay 1.500 sec
 Pulse 90.0 degrees
 Acq. time 1.999 sec
 Width 6003.3 Hz
 Single scan
 OBSERVE H1, 300.1683379 MHZ
 DATA PROCESSING
 Line broadening 0.1 Hz
 FT size 131072

1C



Pulse Sequence: s2pu1

User: [REDACTED]

Date: Sep. 25, 2001

Solvent: CDC13

File: [REDACTED]

Starting Time: 12:29:26

Completion Time: 12:29:38

Total acq. time 1 minute

UNITYplus-500 "spectrum"

Ambient temperature

PULSE SEQUENCE

Relax. delay 1.500 sec

Pulse 90.0 degrees

Acq. time 1.999 sec

Width 6003.3 Hz

Single scan

OBSERVE H1, 300.1683379 MHz

DATA PROCESSING

Line broadening 0.1 Hz

FT size 131072

1C

EXPANSION

6.721
6.711
6.692
6.682

6.972
6.963

7.306
7.277

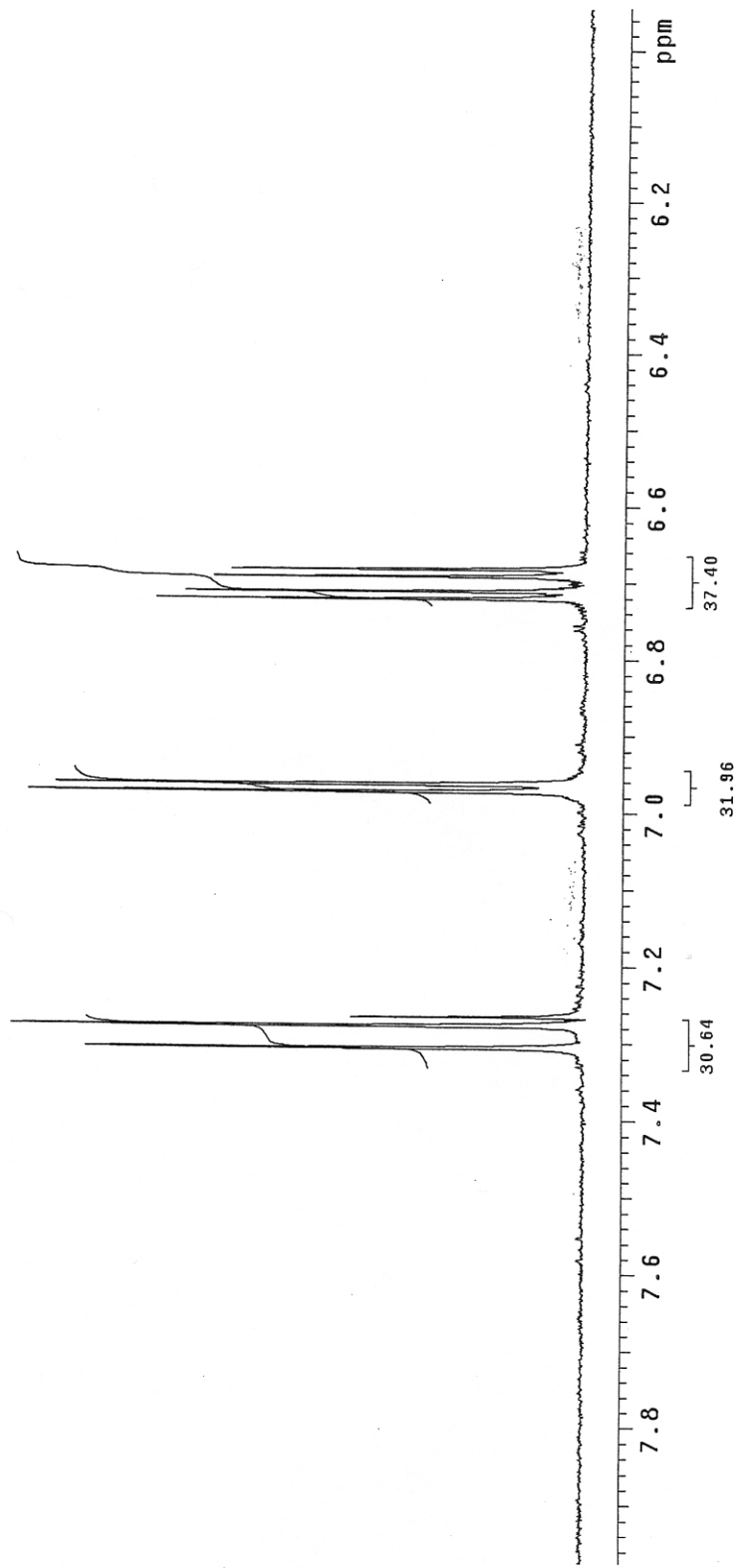
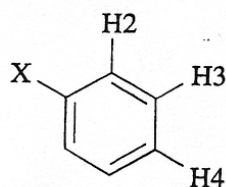


TABLE 3.10 ^1H NMR Benzene Shift Increment Values (ppm)

Substituent X	H2	H3	H4
<i>H</i> (base value)	7.26	7.26	7.26
CH ₃	-0.20	-0.12	-0.22
C ₂ H ₅	-0.14	-0.06	-0.17
CH(CH ₃) ₂	-0.13	-0.08	-0.18
C(CH ₃) ₃	0.02	-0.08	-0.21
C ₆ H ₅	0.37	0.20	0.10
CH=CH ₂	0.06	-0.03	-0.10
C≡CH	0.15	-0.02	-0.01
CN	0.36	0.18	0.28
CHO	0.56	0.22	0.29
COCH ₃	0.62	0.14	0.21
COC ₆ H ₅	0.47	0.13	0.22
COOH	0.85	0.18	0.21
COCl	0.84	0.22	0.36
COOCH ₃	0.71	0.11	0.21
COOPh	0.90	0.17	0.27
CONH ₂	0.61	0.10	0.17
OH	-0.56	-0.12	-0.45
OCH ₃	-0.48	-0.09	-0.44
OC ₆ H ₅	-0.29	-0.05	-0.23
OCOCH ₃	-0.25	0.03	-0.13
CH ₂ OH	-0.07	-0.07	-0.07
NH ₂	-0.75	-0.25	-0.65
NH(CH ₃)	-0.80	-0.22	-0.68
N(CH ₃) ₂	-0.66	-0.18	-0.67
NO ₂	0.95	0.26	0.38
F	-0.26	0.00	-0.20
Cl	0.03	-0.02	-0.09
CH ₂ Cl	0.00	0.00	0.00
Br	0.18	-0.08	-0.04
I	0.39	-0.21	0.00

from
 "ORGANIC STRUCTURE
 ANALYSIS" BY
 CREWS, P.;
 RODRIGUEZ, J.; and
 JASPERS, M.
 OXFORD
 1998.

P. L. Corio, B. P. Dailey, *J. Am. Chem. Soc.* **1956**, 78, 3043.

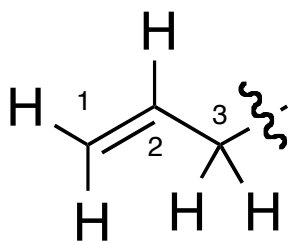
different. However, as will be seen in the following, much more definitive results can be obtained from examining ^{13}C shifts.

Aromatic Carbons of Benzenoid and Nonbenzenoid Rings. Resonances of the normal and the heteroatom-containing compounds of this class occur over a broad region, from δ 100 to 160, depending upon the substituents present. Examples are collected in Chart 3.1f; they illustrate the wide variability of shifts possible for aromatic compounds. The lack of a benzene ring current effect on carbon chemical shifts can be observed for methyl

Typical Coupling Constant (*J*) Values

Convention: ^{*i*}*J* means an *i*-bond coupling (i.e., there are *i* intervening bonds between the two coupled protons). Three-bond coupling is the most common.

J(n,m)

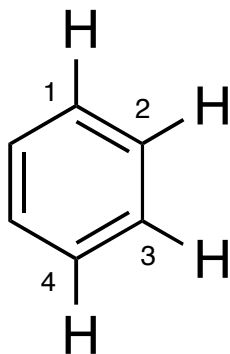


²*J*(1,1) 0-3 Hz (geminal)

³*J*(1,2) 15-18 Hz (*trans*)

³*J*(1,2) 10-12 Hz (*cis*)

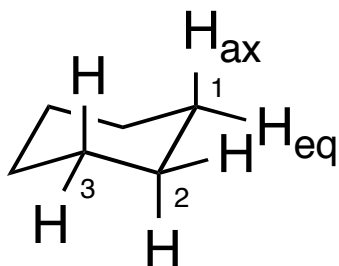
⁴*J*(1,3) 0-3 Hz (allylic)



³*J*(1,2) 7-9 Hz (*ortho*)

⁴*J*(1,3) 1-3 Hz (*meta*)

⁵*J*(1,4) 0-1 Hz (*para*)



²*J*(1,1) 12-16 Hz (geminal)

³*J*(1_{ax},2_{ax}) 12-14 Hz (diaxial)

³*J*(1_{ax},2_{eq}) 2-4 Hz (axial-equatorial)

³*J*(1_{eq},2_{eq}) 3-5 Hz (diequatorial)

⁴*J*(1_{eq},3_{eq}) 0-2 Hz ("W")