^{1}H NMR Spectroscopy

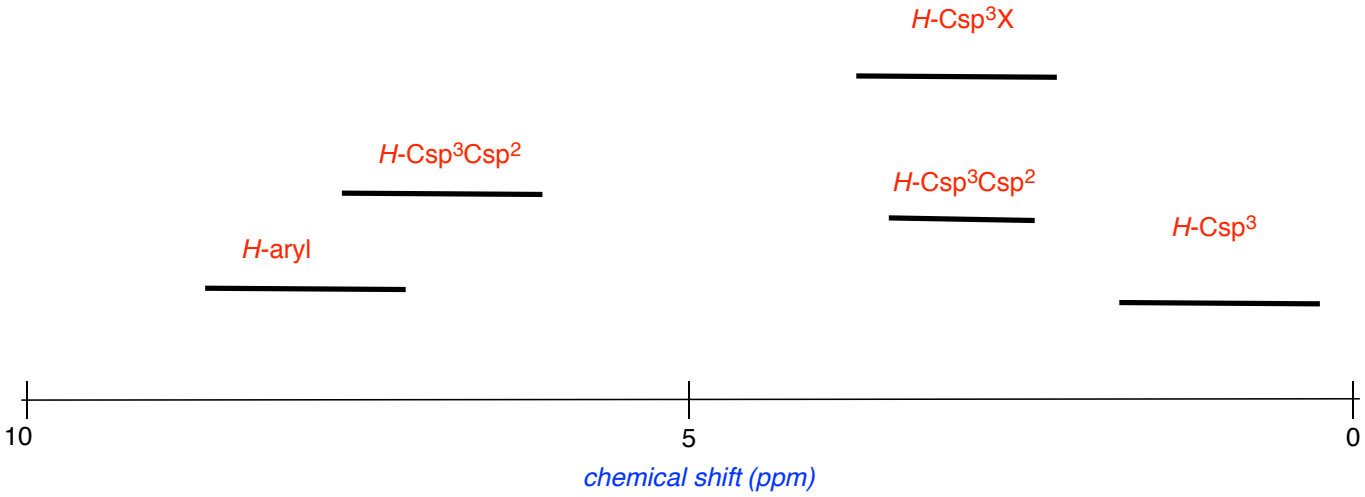
from chapter _____ in the recommended text

A. Introduction

.

B. Chemical Shifts In ^{1}H Spectra

smaller

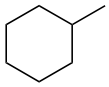


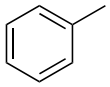
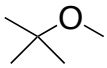
high field region
low field region from 5 – 6.5 ppm

lower field than *H*C-Csp^3 atoms
allylic and benzylic
higher chemical shifts than *H*C-Csp^3

higher

lower

$H_2C{=}CH_2$

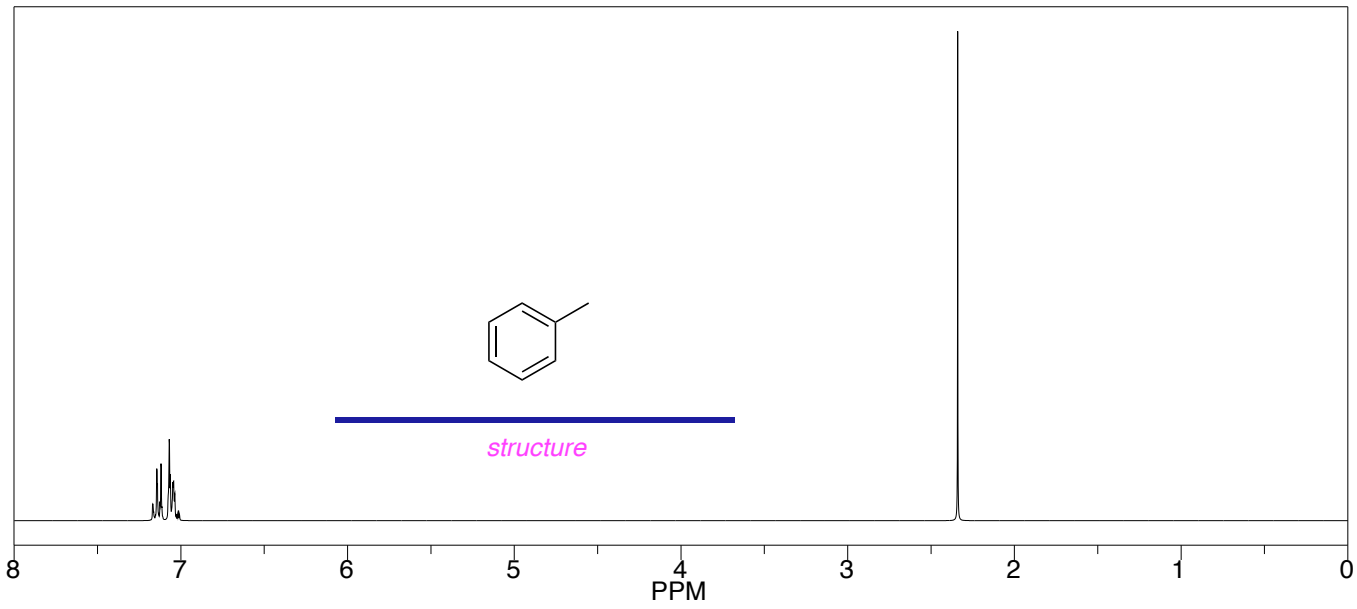
1.4 - 1.2 | 1.4 - 1.2 and 0.9 | 7.5 | 7.5 and 2.3 | 3.5 and 1.4 - 1.2 | 0.9 | 5.2

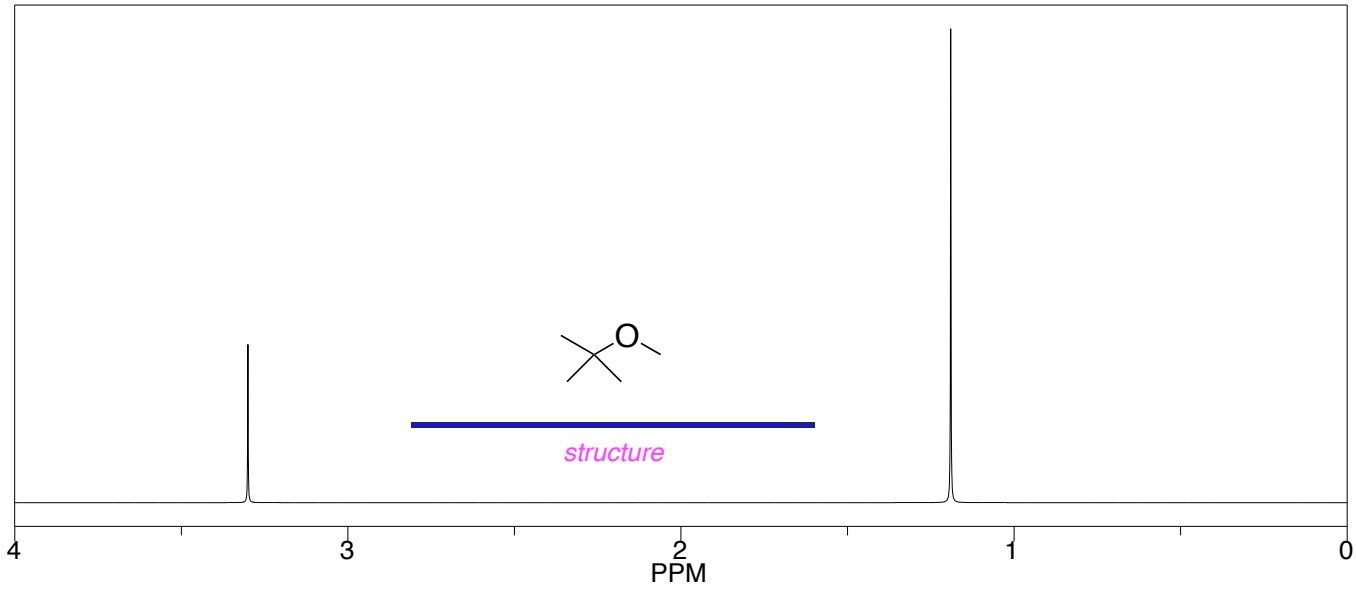
select from δ = 7.5, 5.2, 3.5, 2.3, 1.4 - 1.2, and, or 0.9

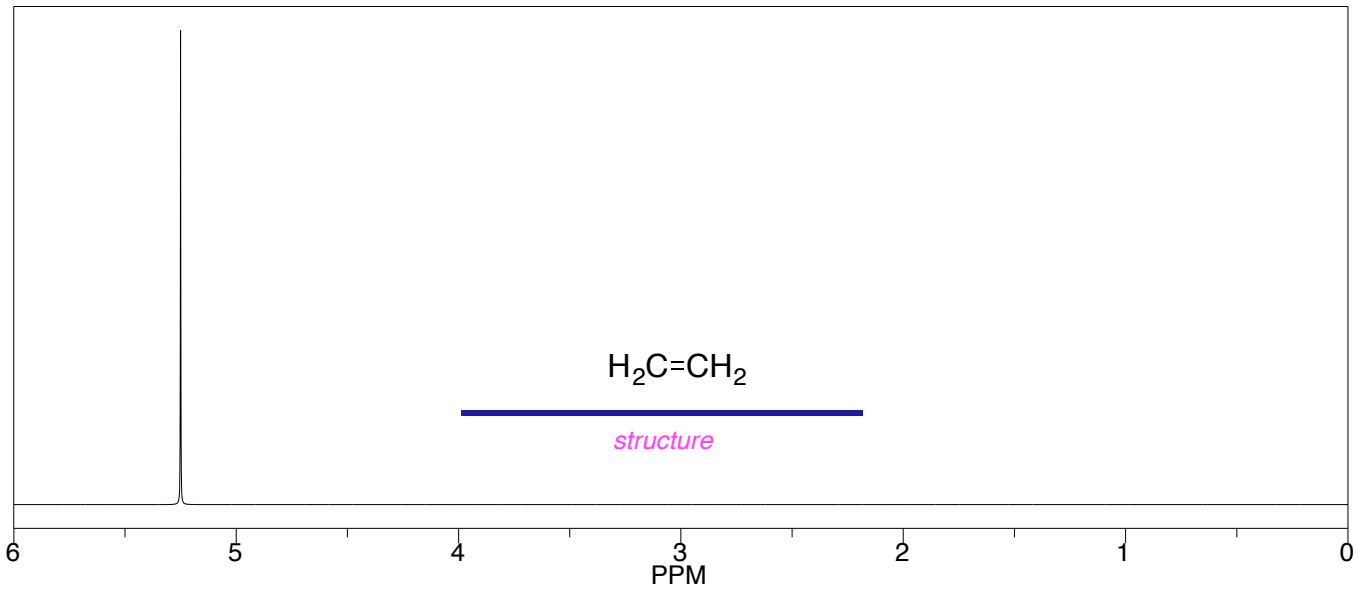
__1__ __5__ __1__ __4__ __2__ __1__ __1__

indicate number of H environments

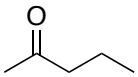
x.




O
structure
4
3
2
1
0
PPM

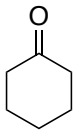

H2C=CH2
structure
6
5
4
3
2
1
0
PPM

NOTE FROM KB: it is very difficult to be sure about the chemical shift ranges for some of these protons, in other words some are borderline. When the book is re-printed I will make the ranges broader.



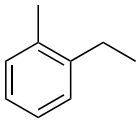
__4___
inequivalent H

number of resonances (ppm):
0 - 2 _2__
2 - 3 _2__
3 - 4 _0__
4 - 7 _0__
7 - 9 _0__



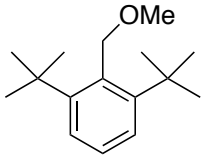
__3___
inequivalent H

number of resonances (ppm):
0 - 2 __2__
2 - 3 __1__
3 - 4 __0__
4 - 7 __0__
7 - 9__0__



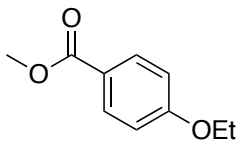
___7__
inequivalent H

number of resonances (ppm):
0 - 2 __1__
2 - 3 __2__
3 - 4 __0__
4 - 7 __0__
7 - 9___4_



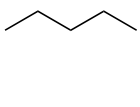
__5___
inequivalent H

number of resonances (ppm):
0 - 2 __1__
2 - 3 __0__
3 - 4 __1__
4 - 7 __1__
7 - 9___2_



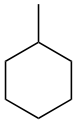
___5__
inequivalent H

number of resonances (ppm):
0 - 2 __1__
2 - 3 __0__
3 - 4 __2__
4 - 7 __0__
7 - 9__2__



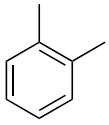
__3___
inequivalent H

number of resonances (ppm):
0 - 2 __3__
2 - 3 __0__
3 - 4 __0__
4 - 7 __0__
7 - 9__0__



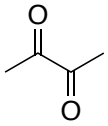
___8__
inequivalent H

number of resonances (ppm):
0 - 2 __8__
2 - 3 __0__
3 - 4 __0__
4 - 7 __0__
7 - 9__0__



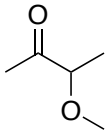
___3__
inequivalent H

number of resonances (ppm):
0 - 2 __0__
2 - 3 __1__
3 - 4 __0__
4 - 7 __0__
7 - 9___2_



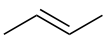
___1__
inequivalent H

number of resonances (ppm):
0 - 2 __0__
2 - 3 __1__
3 - 4 __0__
4 - 7 __0__
7 - 9___0_



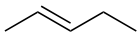
___4__
inequivalent H

number of resonances (ppm):
0 - 2 __1__
2 - 3 __1__
3 - 4 __1__
4 - 7 __1__
7 - 9__0__



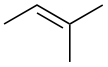
___2__
inequivalent H

number of resonances (ppm):
0 - 2 __1__
2 - 3 __0__
3 - 4 __0__
4 - 7 __1__
7 - 9___0_



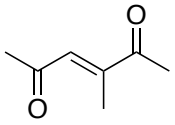
___5__
inequivalent H

number of resonances (ppm):
0 - 2 __3__
2 - 3 __0__
3 - 4 __0__
4 - 7 __2__
7 - 9___0_



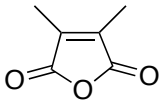
__4___
inequivalent H

number of resonances (ppm):
0 - 2 __3__
2 - 3 __0__
3 - 4 __0__
4 - 7 __1__
7 - 9___0_



__4___
inequivalent H

number of resonances (ppm):
0 - 2 __1__
2 - 3 __2__
3 - 4 __0__
4 - 7 __1__
7 - 9___0_



__1___
inequivalent H

number of resonances (ppm):
0 - 2 __0__
2 - 3 __1__
3 - 4 __0__
4 - 7 __1__
7 - 9__0__

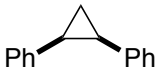
NOTE FROM KB: it is very difficult to be sure about the chemical shift ranges for some of these protons, in other words some are borderline. When the book is re-printed I will make the ranges broader.

___1__
inequivalent H

number of resonances (ppm):
0 - 2 __1__
2 - 3 __0__
3 - 4 __0__
4 - 7 __0__
7 - 9___0_

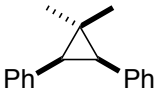
___4__
inequivalent H

number of resonances (ppm):
0 - 2 __4__
2 - 3 __0__
3 - 4 __0__
4 - 7 __0__
7 - 9___0_



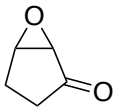
__6___
inequivalent H

number of resonances (ppm):
0 - 2 __2__
2 - 3 __1__
3 - 4 __0__
4 - 7 __0__
7 - 9___3_



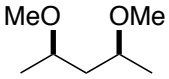
___6__
inequivalent H

number of resonances (ppm):
0 - 2 __2__
2 - 3 __1__
3 - 4 __0__
4 - 7 __0__
7 - 9___3_



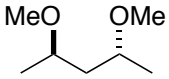
__6___
inequivalent H

number of resonances (ppm):
0 - 2 __2__
2 - 3 __2__
3 - 4 __1__
4 - 7 __1__
7 - 9__0__



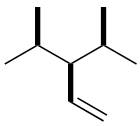
__5___
inequivalent H

number of resonances (ppm):
0 - 2 __3__
2 - 3 __0__
3 - 4 __2__
4 - 7 __0__
7 - 9___0_



__4__
inequivalent H

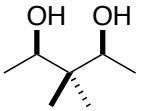
number of resonances (ppm):
0 - 2 __2__
2 - 3 __0__
3 - 4 __2__
4 - 7 __0__
7 - 9___0_



__7___
inequivalent H

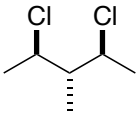
number of resonances (ppm):
0 - 2 __4__
2 - 3 __0__
3 - 4 __0__
4 - 7 __3__
7 - 9___0_

note OH resonance
chemical shift varies



__5___
inequivalent H

number of resonances (ppm):
0 - 2 __3__
2 - 3 __0__
3 - 4 __1__
4 - 7 __1__
7 - 9___0_



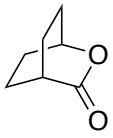
___4__
inequivalent H

number of resonances (ppm):
0 - 2 __3__
2 - 3 __0__
3 - 4 __1__
4 - 7 __0__
7 - 9__0__

__2___
inequivalent H

number of resonances (ppm):
0 - 2 __2__
2 - 3 __0__
3 - 4 __0__
4 - 7 __0__
7 - 9___0_

note plane of symmetry

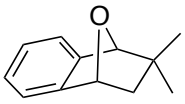


___6__
inequivalent H

number of resonances (ppm):
0 - 2 __4__
2 - 3 __1__
3 - 4 __0__
4 - 7 __1__
7 - 9___0_

__4___
inequivalent H

number of resonances (ppm):
0 - 2 __4__
2 - 3 __0__
3 - 4 __0__
4 - 7 __0__
7 - 9___0_



___10__
inequivalent H

number of resonances (ppm):
0 - 2 __4__
2 - 3 __0__
3 - 4 __0__
4 - 7 __2__
7 - 9___4_

note C2 axis

___4__
inequivalent H

number of resonances (ppm):
0 - 2 __2__
2 - 3 __1__
3 - 4 __0__
4 - 7 __1__
7 - 9___0_

C. Coupling In ^{1}H NMR

two bond couplings

Heteronuclear Coupling To ^{13}C Is Unimportant

1.11

are not

NMR silent).

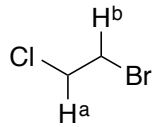
hetero-

Homonuclear ^{1}H Coupling

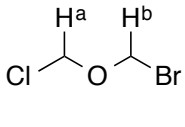
is not removed

2 and 3 bond *homo*nuclear couplings.

ie 4 bond homonuclear



A



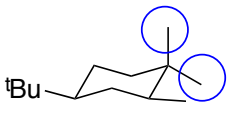
B

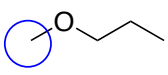
3 bonds and *do*

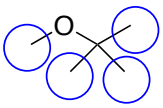
4 bonds between them and *do not*

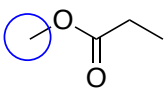
do not appear to be split.

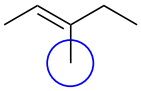
singlets.

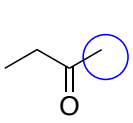


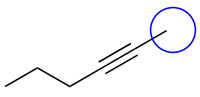


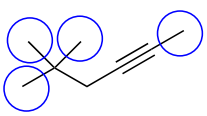


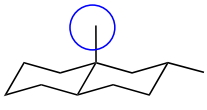


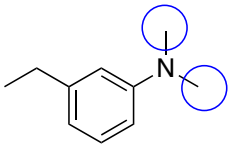


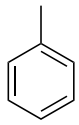




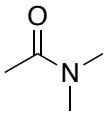








molecule 1



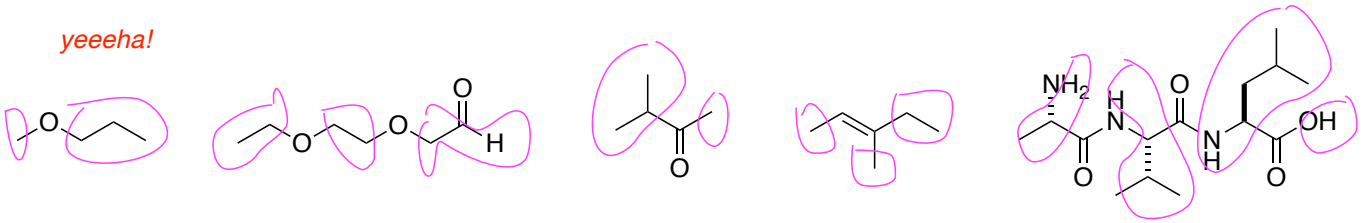
molecule 2

molecule 3

Spin Systems

any number >1 NMR

yeeeha!



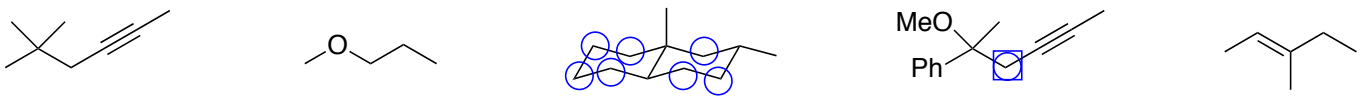
n + 1
does not
does
follows Pascal's triangle.

H^a-C-H^b Spin Systems

will
doublet.

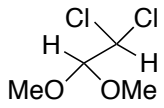
sometimes
will

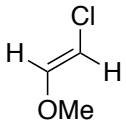
will
appear as a *doublet*.

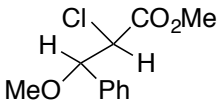


H^a-C-C-H^b Spin Systems

smaller than



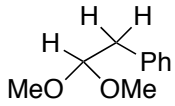


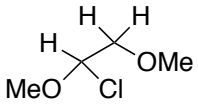


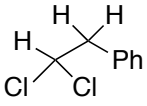
isolated H^aCCH^b | *molecule 1* | *molecule 2*

will
triplet
doublet

H^aC-CH^b_2 Spin Systems



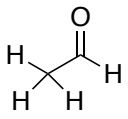


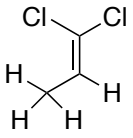


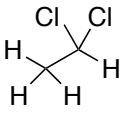
isolated $H^aCCH^b_2$ | *molecule 1* | *molecule 2*

H^aC-CH^b_3 Spin Systems

will
quartet, and *H^b* appears as a *doublet*.







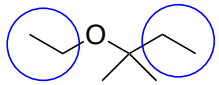
isolated $H^aCCH^b_3$ | *molecule 1* | *molecule 2*

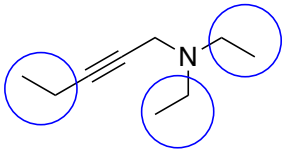
$H^a_2C\text{-}CH^b_3$ Spin Systems (Isolated Ethyl Groups)

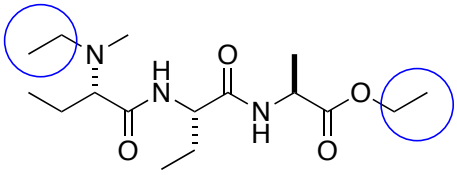
does not

do not

triplet, and the methylene is a *quartet*.



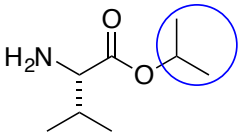


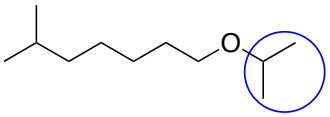


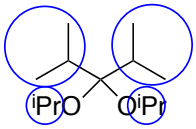
$(H^a_3C)_2CH^b$ Spin Systems (Isolated ^{i}Pr Groups)

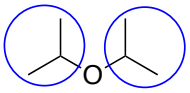
heptet with a relative intensity of _1:6:15:20:15:6:1

doublets.

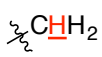








Common Splitting Patterns In Organic Molecules

A 

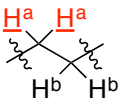
s

B 

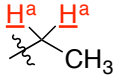
s

C 

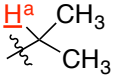
d

D 

t

E 

q

F 

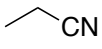
hept

s = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *quin* = quintet, *sex* = sextet, *hept* = heptet, *oct* = octet

methyl | methylene | methylene | ethylene | ethyl | iso-propyl

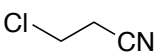
fragment name

possible fragment names: ethyl, ethylene, *iso*-propyl, methyl, methylene



E

3



D

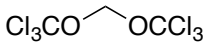
4

F

5

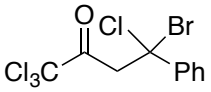
A

2



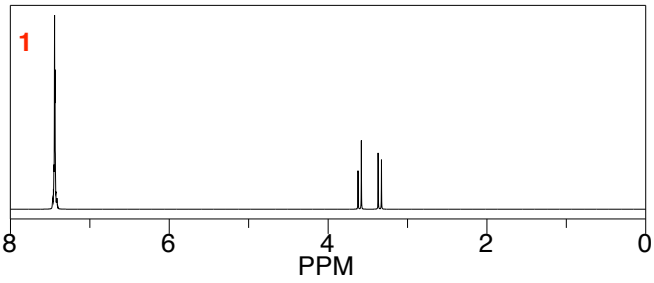
B

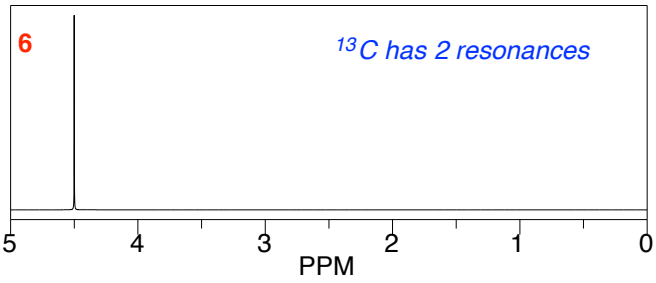
6

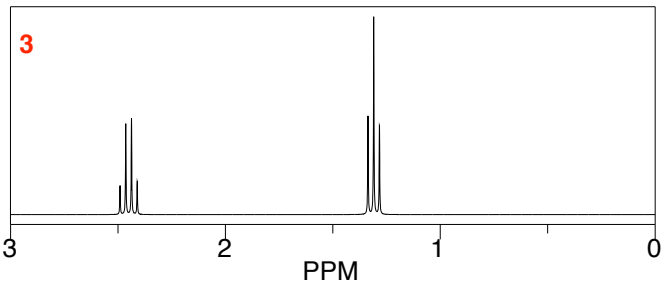


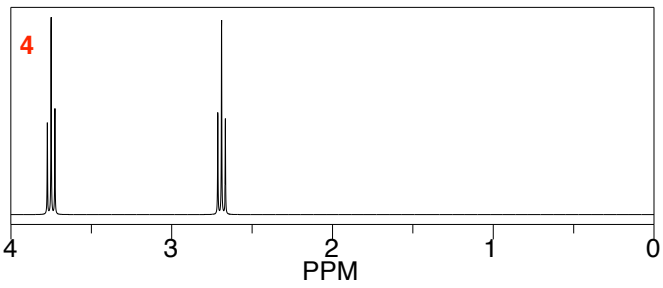
C

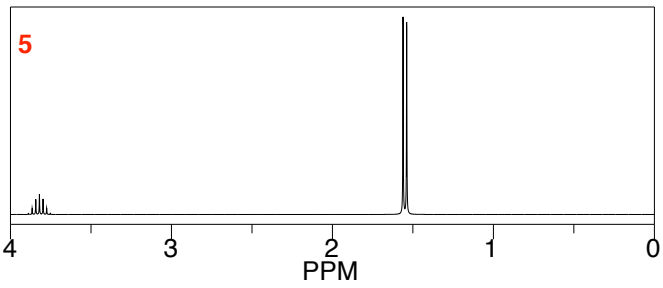
1

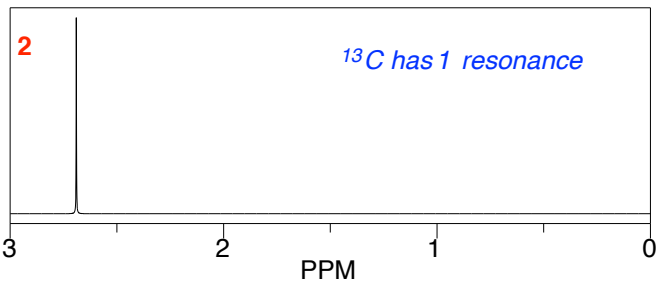


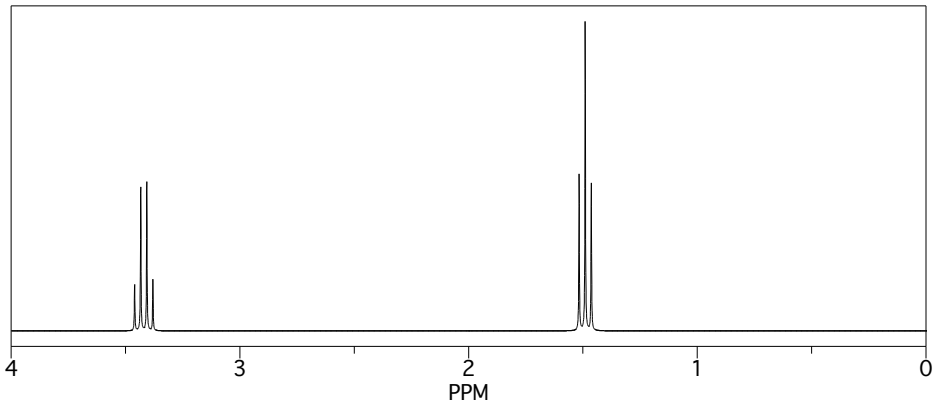


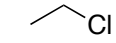




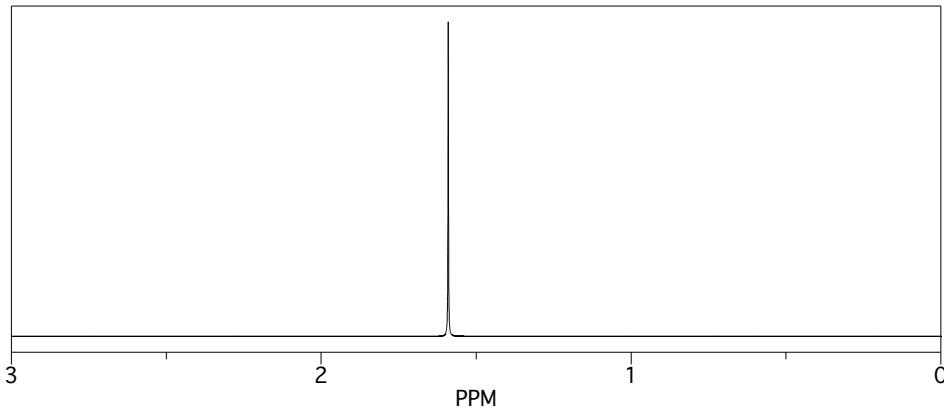




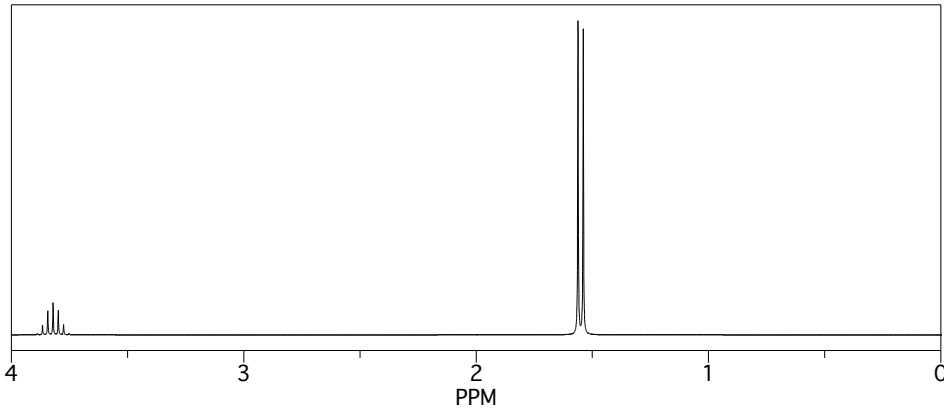




structure

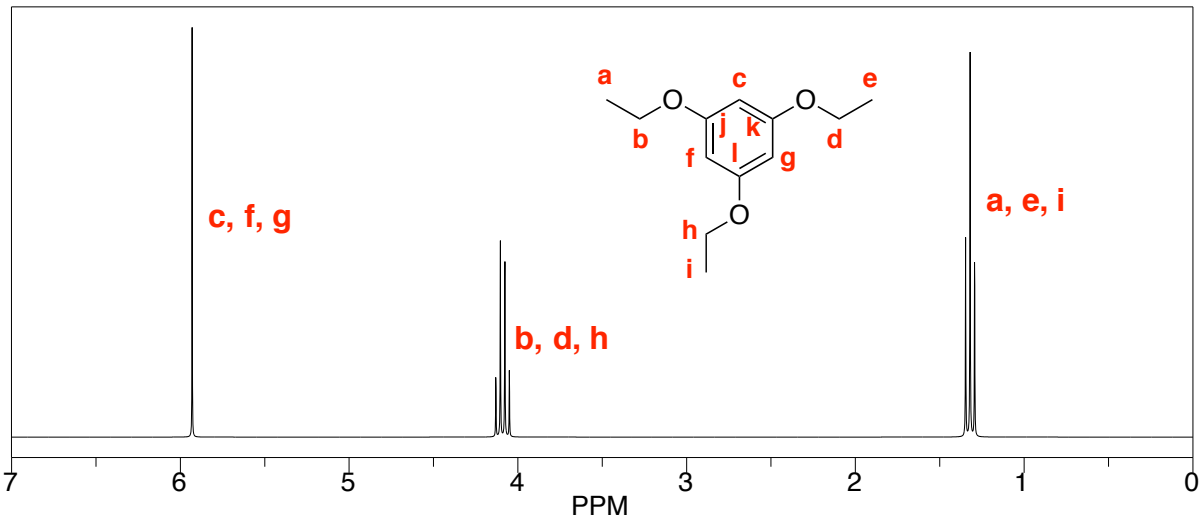


structure

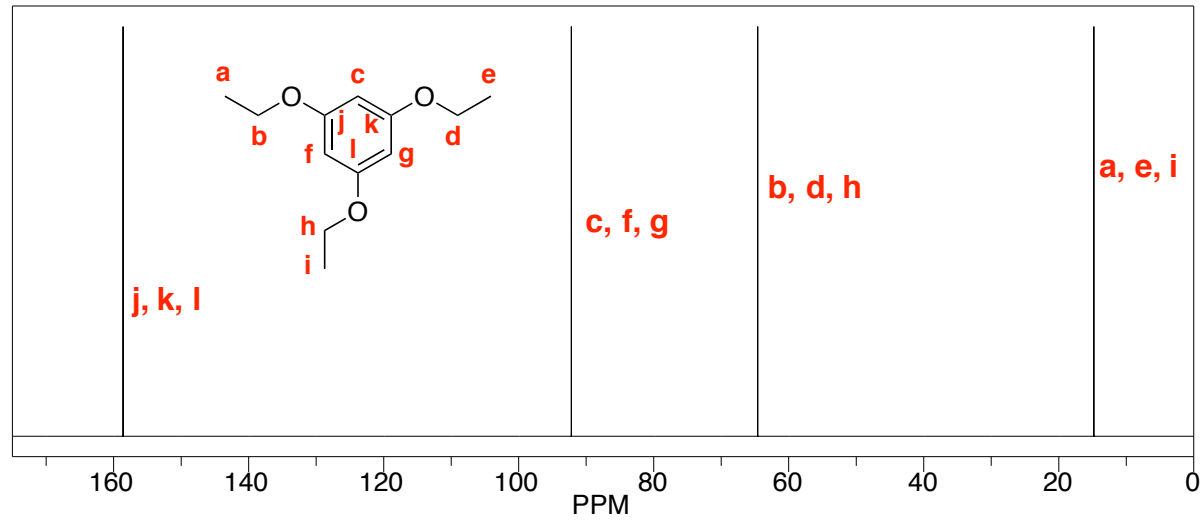


structure

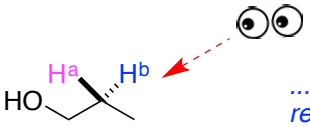
^{1}H NMR



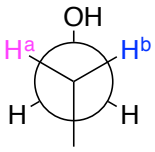
^{13}C NMR



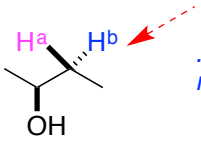
D. Diastereotopic Protons



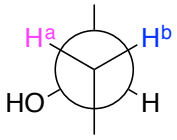
..... can be represented as



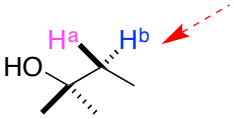
where H^a and H^b <u>are</u> equivalent



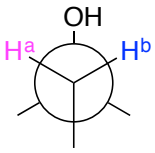
..... can be represented as



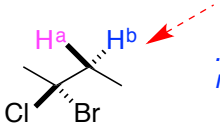
where H^a and H^b <u>are not</u> equivalent



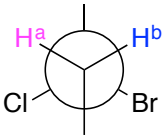
..... can be represented as



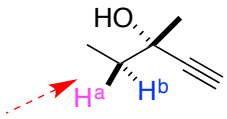
where H^a and H^b <u>are</u> equivalent



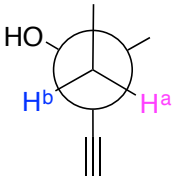
..... can be represented as



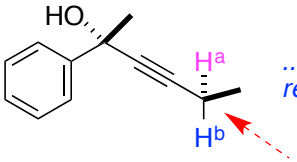
where H^a and H^b <u>are not</u> equivalent



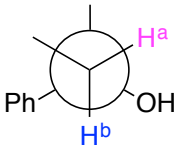
..... can be represented as



where H^a and H^b <u>are not</u> equivalent

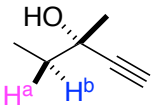


..... can be represented as

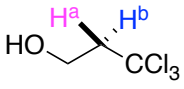


where H^a and H^b <u>are not</u> equivalent

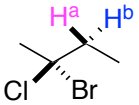
<u>inequivalent</u>



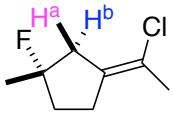
H^a: __doublet of quartets__
H^b: __doublet of quartets__



H^a: __triplet__
H^b: __triplet__

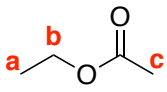


H^a: __doublet of quartets__
H^b: __doublet of quartets__

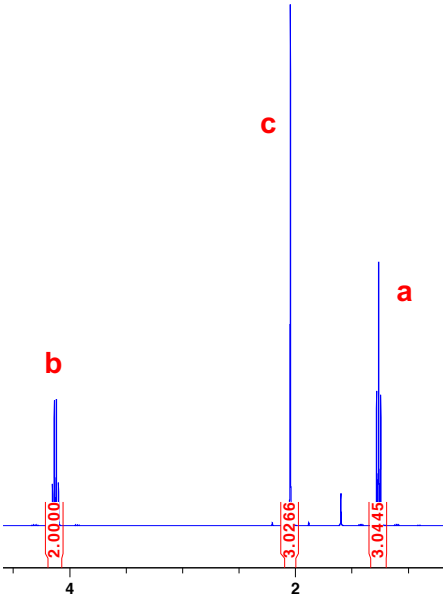


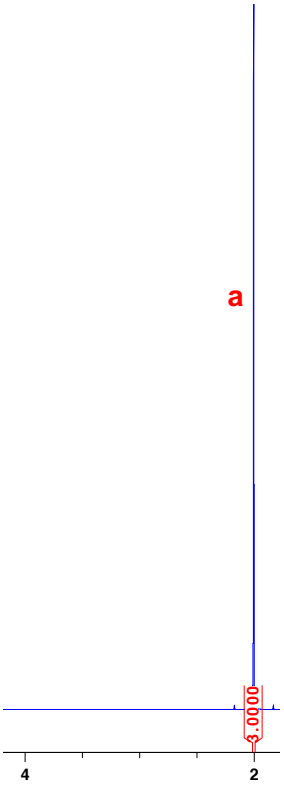
H^a: __doublet of doublets___
H^b: __doublet of doublets___

E. Some Problems Involving Spectral Interpretation



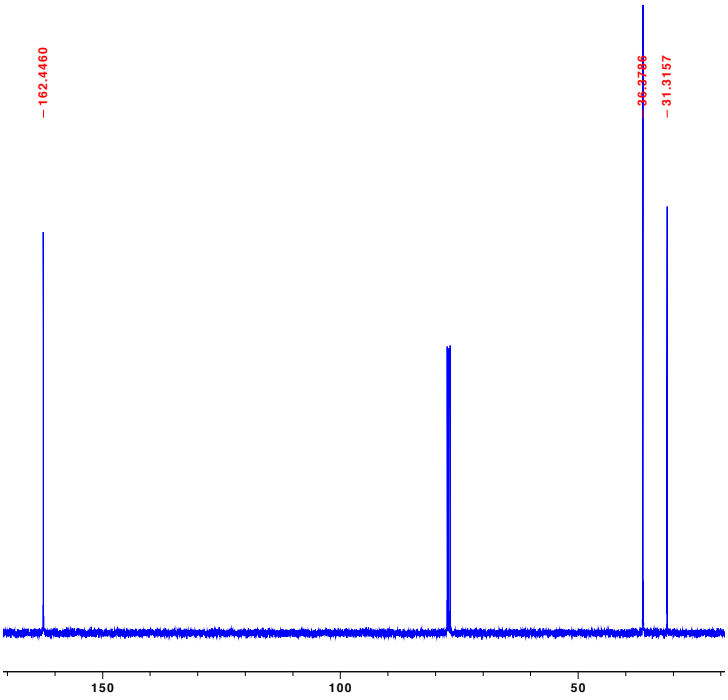
structure

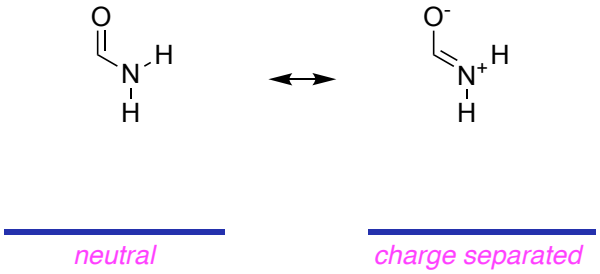




structure

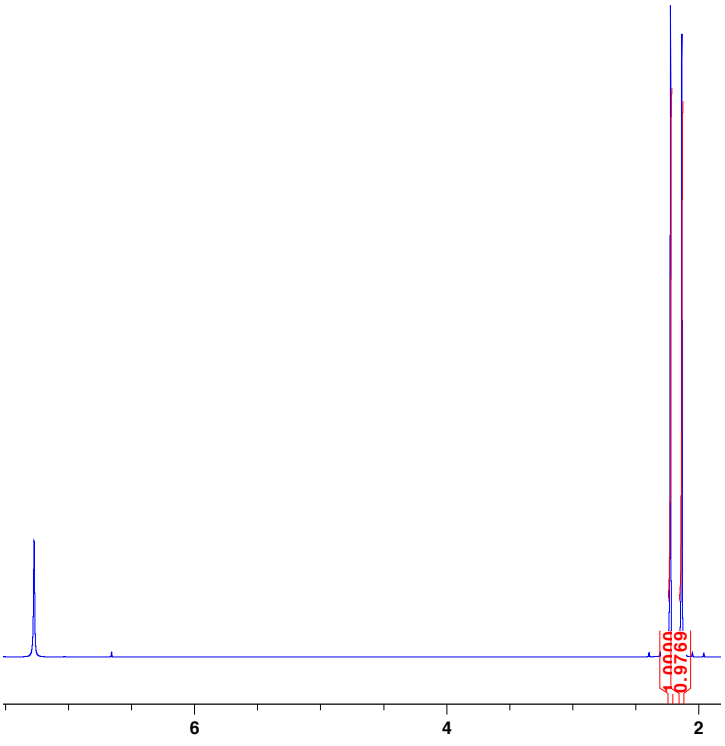
Here are the proton and carbon spectra of dimethyl formamide (DMF). Draw a resonance structure of DMF that shows a charge separation between *O* and *N*.





Explain why *two* methyl resonances are seen in each spectrum:

because rotation around the OC-N bond is slow on the NMR time scale, due to this resonance effect___



…