^{1}H NMR Spectroscopy

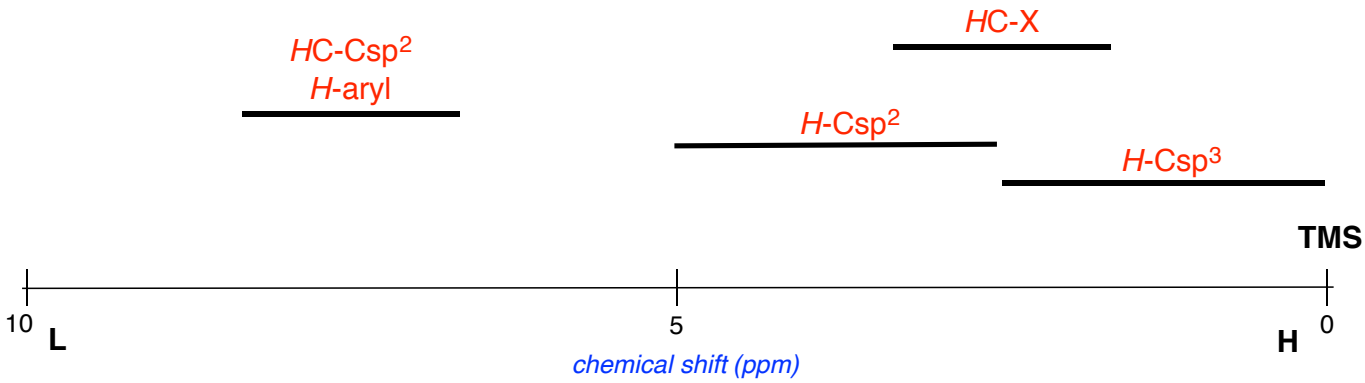
from chapter _____ in the recommended text

A. Introduction

.

B. Chemical Shifts In ^{1}H Spectra

smaller

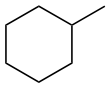


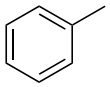
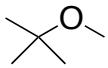
high field region
low field region from 5 – 6.5 ppm

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

higher

lower

$H_2C{=}CH_2$

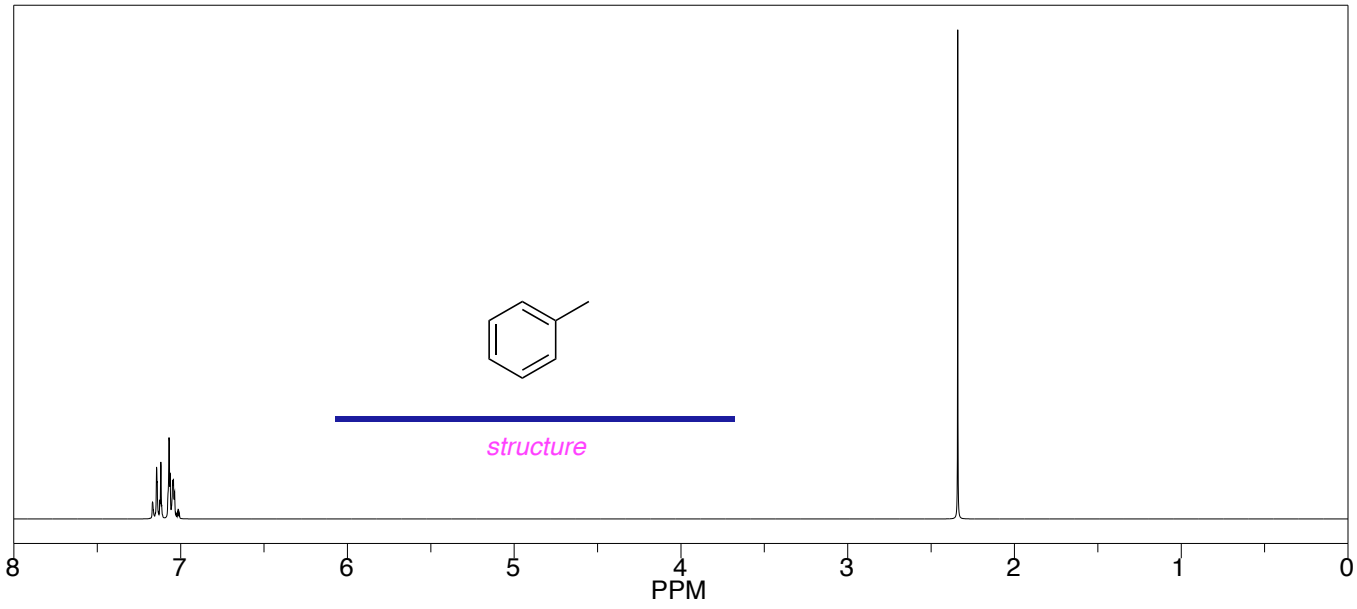
1.4 - 1.2 | 1.4 - 1.2 and 0.9 | 7.5 | 7.5 and 2.3 | 3.5 and 1.4 - 1.2 | 0.9 | 5.2

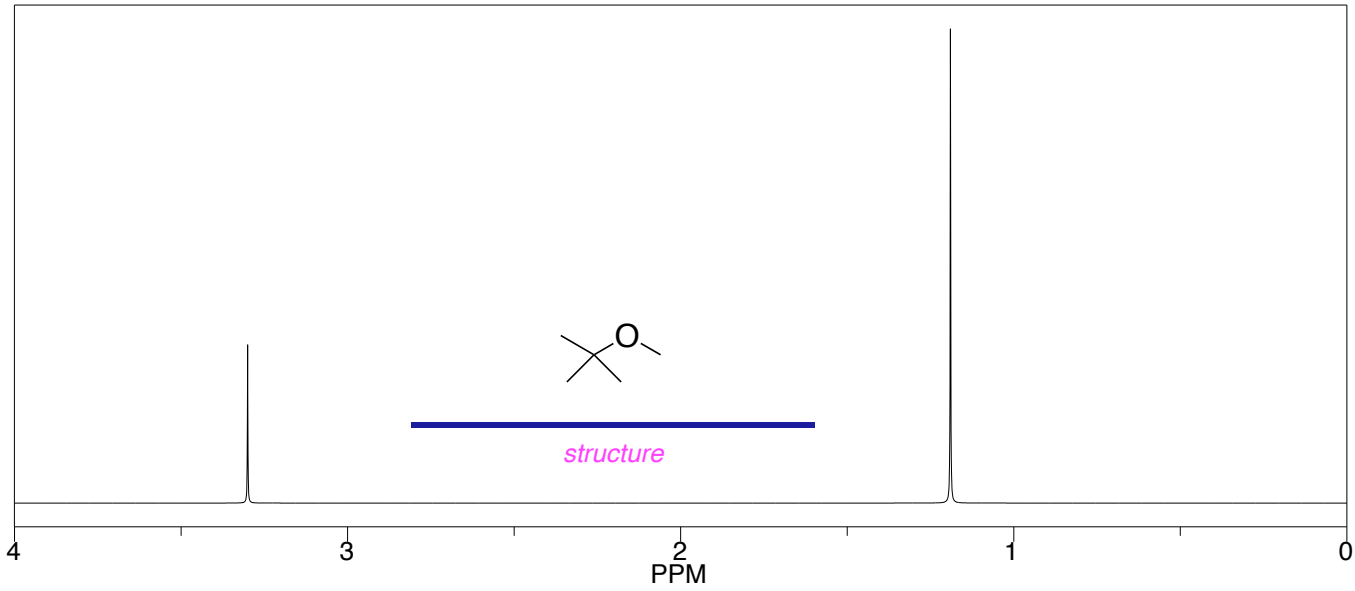
select from δ = 7.5, 5.2, 3.5, 2.3, 1.4 - 1.2, and, or 0.9

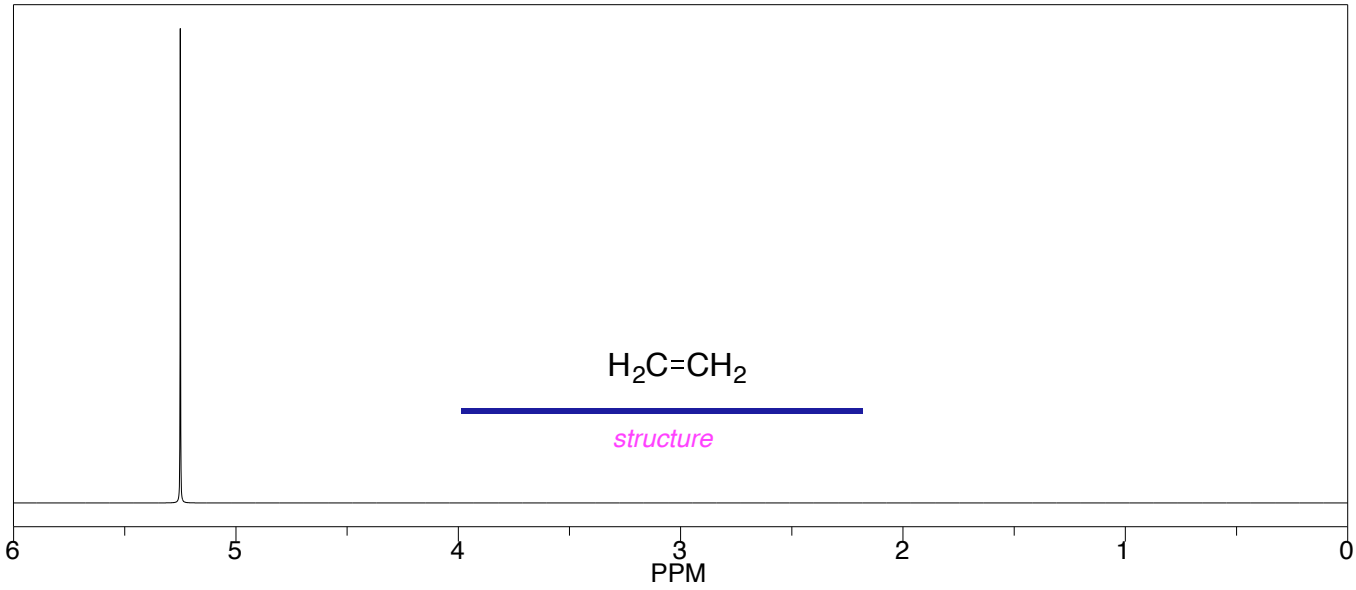
__1__ __5__ __1__ __4__ __2__ __1__ __1__

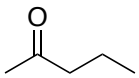
indicate number of H environments

x.



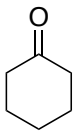

O
structure
4
3
2
1
0
PPM


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



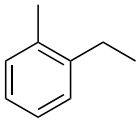
__4___
inequivalent H

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



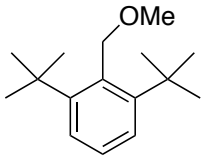
__3___
inequivalent H

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



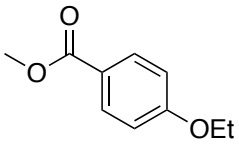
___7__
inequivalent H

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



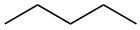
__5___
inequivalent H

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



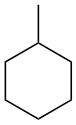
___5__
inequivalent H

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



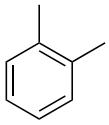
__3___
inequivalent H

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



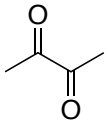
___8__
inequivalent H

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



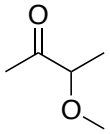
___3__
inequivalent H

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



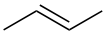
___1__
inequivalent H

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



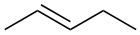
___4__
inequivalent H

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



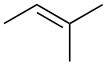
___2__
inequivalent H

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



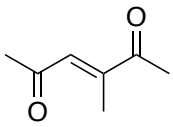
___5__
inequivalent H

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



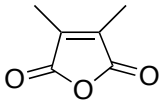
__4___
inequivalent H

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

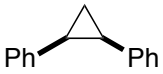
number of resonances (ppm):
0 - 2 __0__
2 - 3 __1__
3 - 4 __0__
4 - 7 __0__
7 - 9__0__

___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_

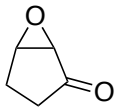


__6___
inequivalent H

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

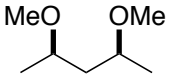
___5__
inequivalent H

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



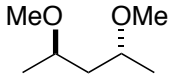
__6___
inequivalent H

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



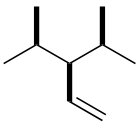
__5___
inequivalent H

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



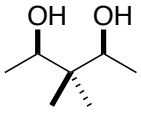
__4__
inequivalent H

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



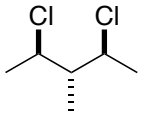
__6___
inequivalent H

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



__5___
inequivalent H

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

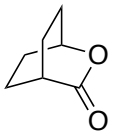


___4__
inequivalent H

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_

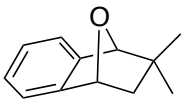


___6__
inequivalent H

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_

___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).

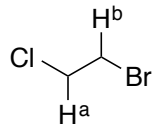
hetero-

Homonuclear ^{1}H Coupling

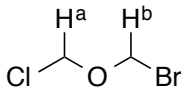
is not removed

2 and 3 bond *homo*nuclear couplings.

ie *4* bond homonuclear



A



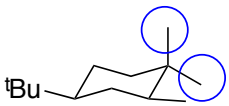
B

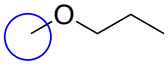
3 bonds and *do*

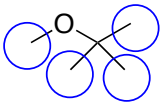
4 bonds between them and *do not*

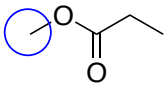
do not appear to be split.

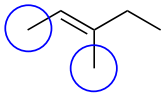
singlets.

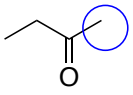


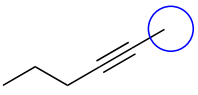


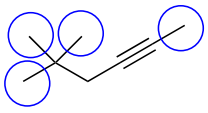


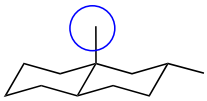


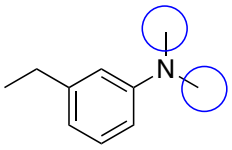


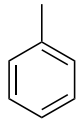




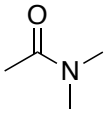








molecule 1



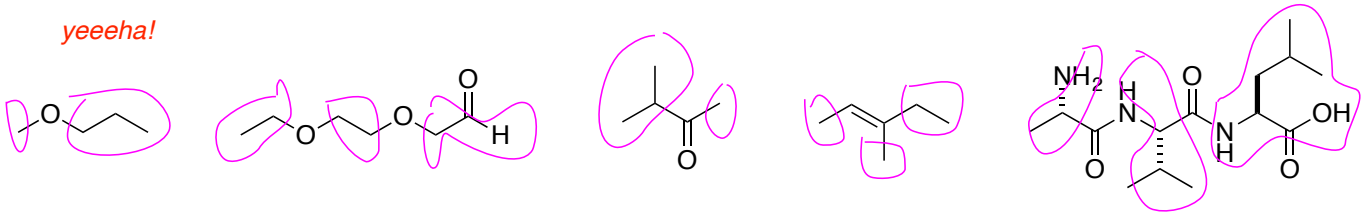
molecule 2

molecule 3

Spin Systems

any number >1 NMR

yeeeha!



n + 1

does not

follows Pascal's triangle.

H^a-C-H^b Spin Systems

will not

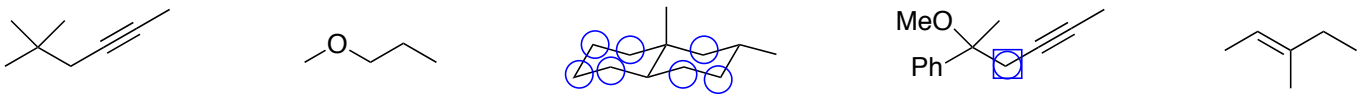
doublet.

sometimes

will

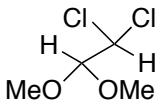
will

appear as a *doublet*.

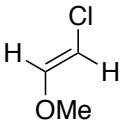


H^a-C-C-H^b Spin Systems

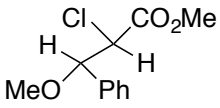
smaller than



isolated H^aCCH^b



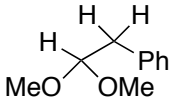
molecule 1



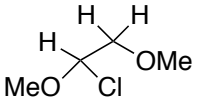
molecule 2

will
triplet
doublet

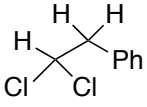
$H^aC\text{-}CH^b_2$ Spin Systems



isolated $H^aCCH^b_2$



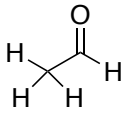
molecule 1



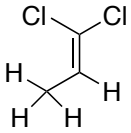
molecule 2

$H^aC\text{-}CH^b_3$ Spin Systems

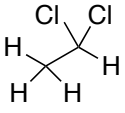
will
quartet, and H^b appears as a *doublet*.



isolated $H^aCCH^b_3$



molecule 1



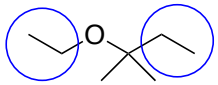
molecule 2

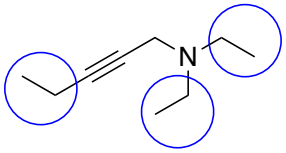
$H^a_2C\text{-}CH^b_3$ Spin Systems (Isolated Ethyl Groups)

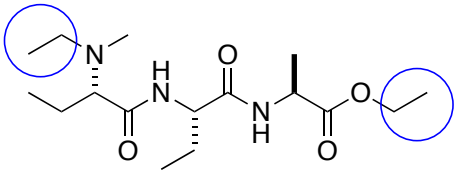
does not

do not

triplet, and the methylene is a *quartet*.



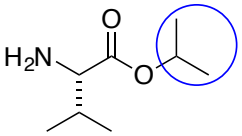


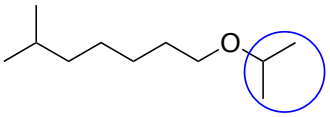


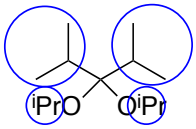
$(H^a_3C)_2CH^b$ Spin Systems (Isolated ^{i}Pr Groups)

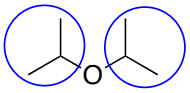
heptet with a relative intensity of _1:6:15:20:15:6:1

doublets.

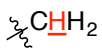








Common Splitting Patterns In Organic Molecules

A 

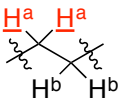
s

B 

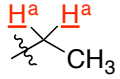
s

C 

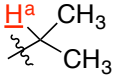
d

D 

t

E 

q

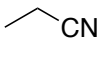
F 

hept

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

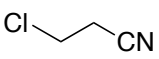
methyl	methylene	methylene	ethylene	ethyl	iso-propyl

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



E

3



D

4

F

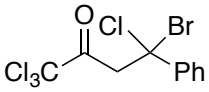
5

A

2

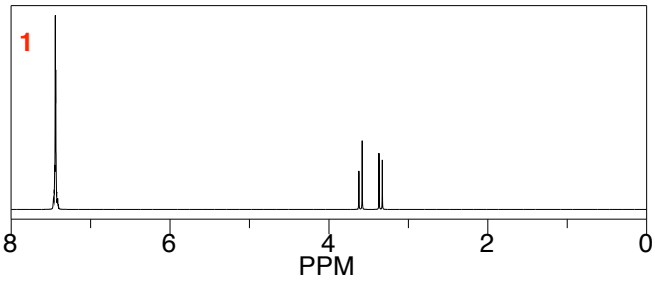
B

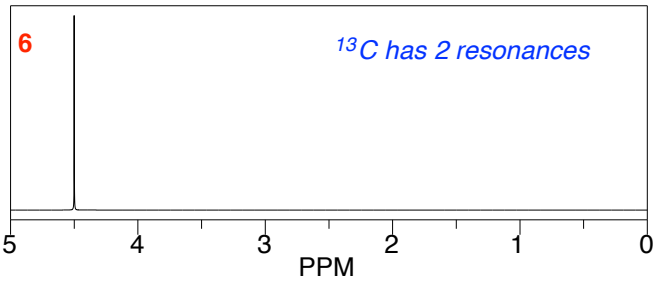
6

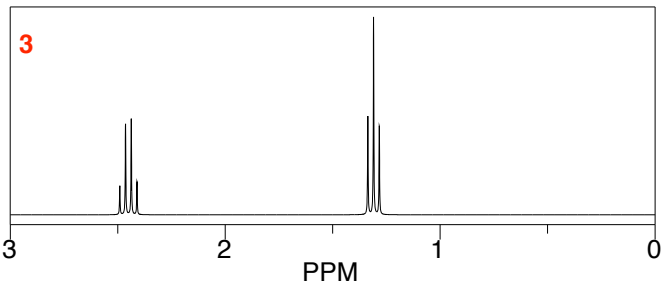


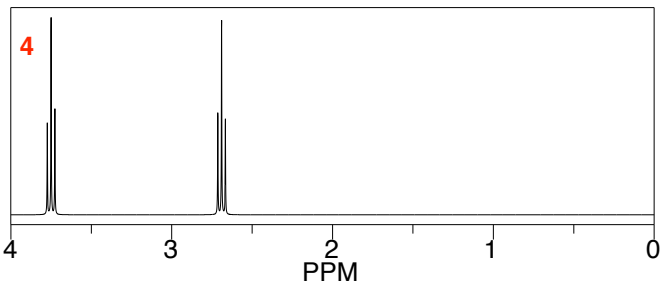
C

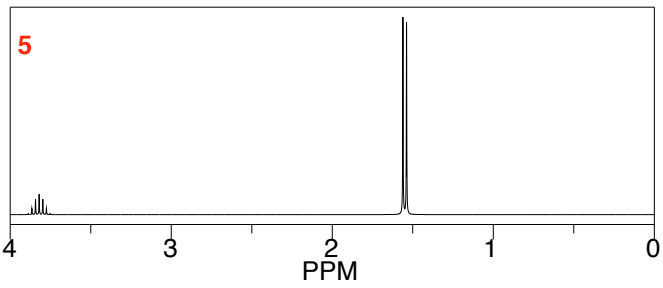
1

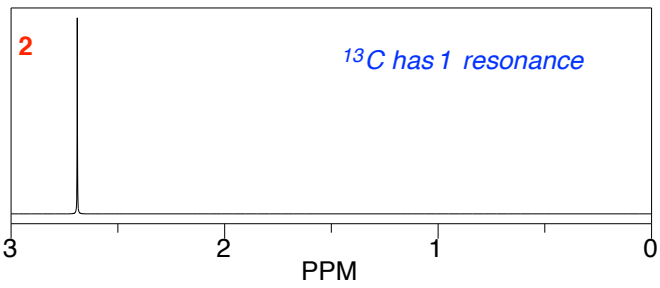


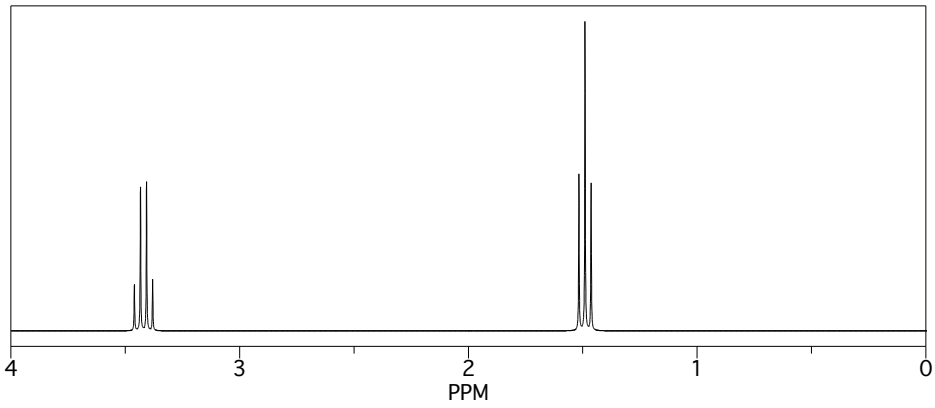


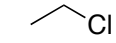




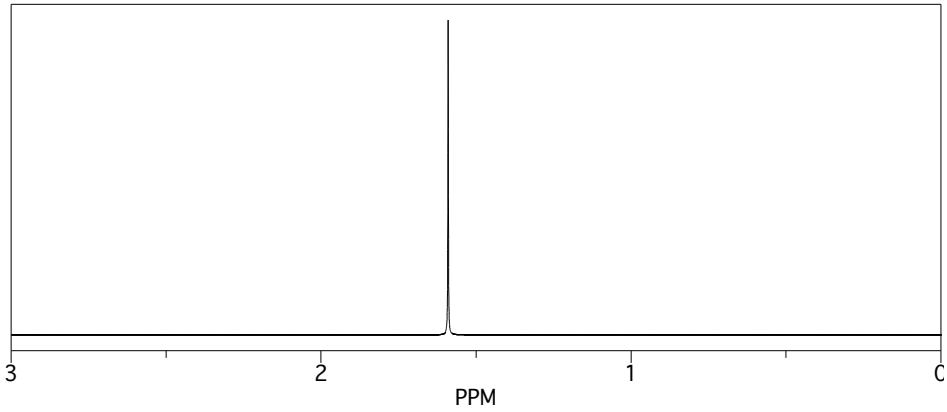




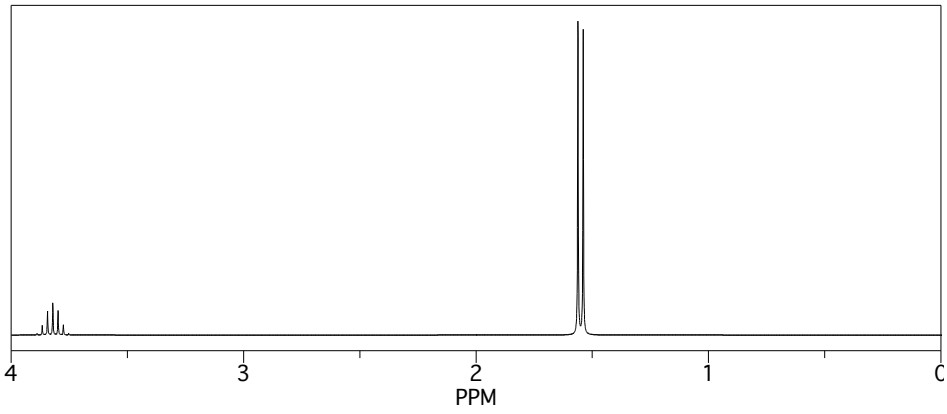




structure

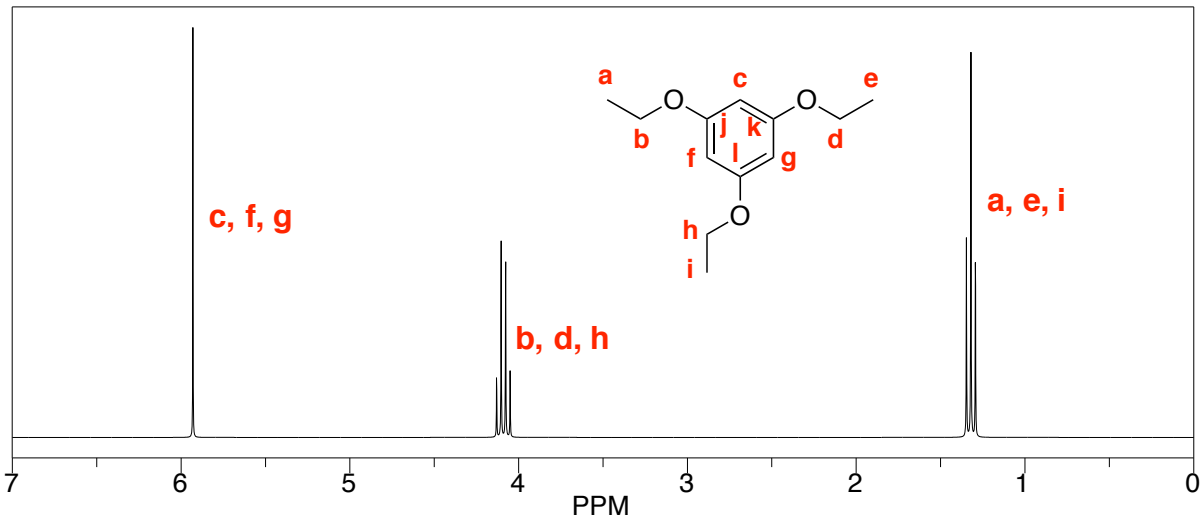


structure

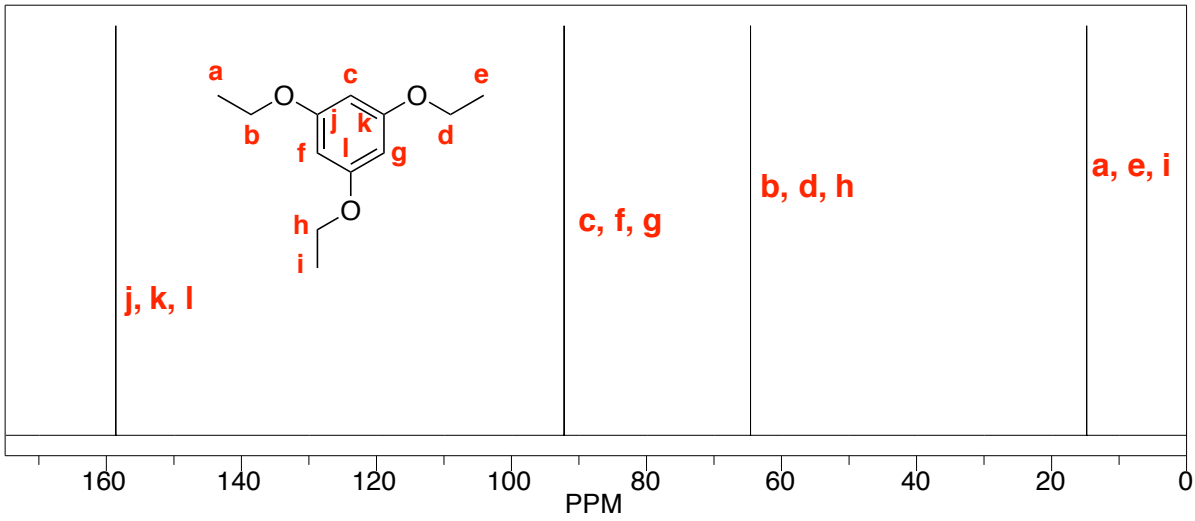


structure

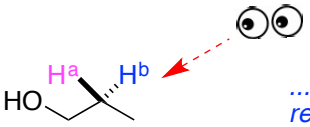
^{1}H NMR



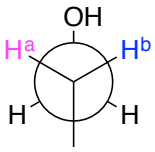
^{13}C NMR



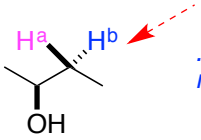
D. Diastereotopic Protons



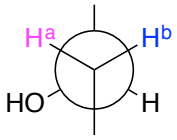
..... can be represented as



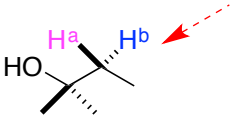
where Ha and Hb are equivalent



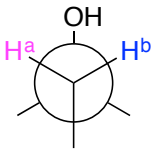
..... can be represented as



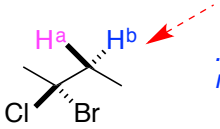
where Ha and Hb are not equivalent



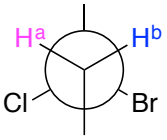
..... can be represented as



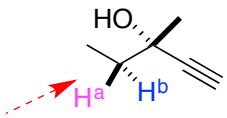
where Ha and Hb are equivalent



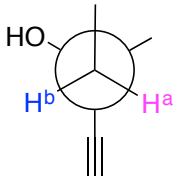
..... can be represented as



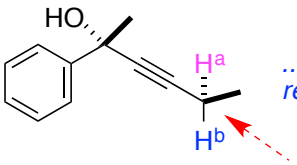
where Ha and Hb are not equivalent



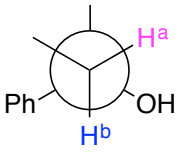
..... can be represented as



where Ha and Hb are not equivalent

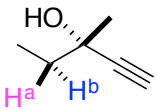


..... can be represented as

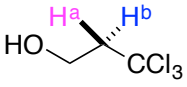


where Ha and Hb are not equivalent

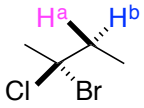
inequivalent



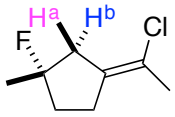
Ha: __quintet__
Hb: __quintet__



Ha: __triplet__
Hb: __triplet__

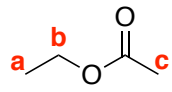


Ha: __quintet__
Hb: __quintet__

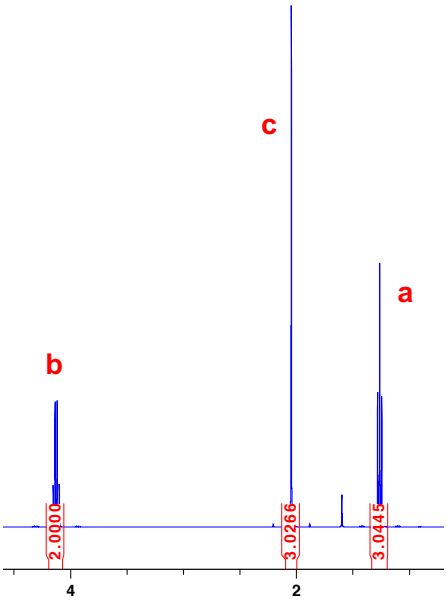


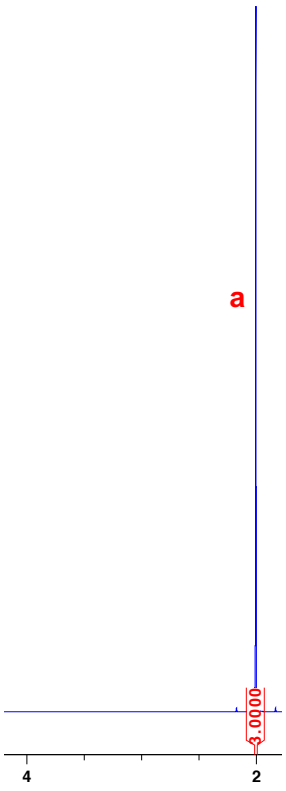
Ha: __triplet___
Hb: __triplet___

E. Some Problems Involving Spectral Interpretation

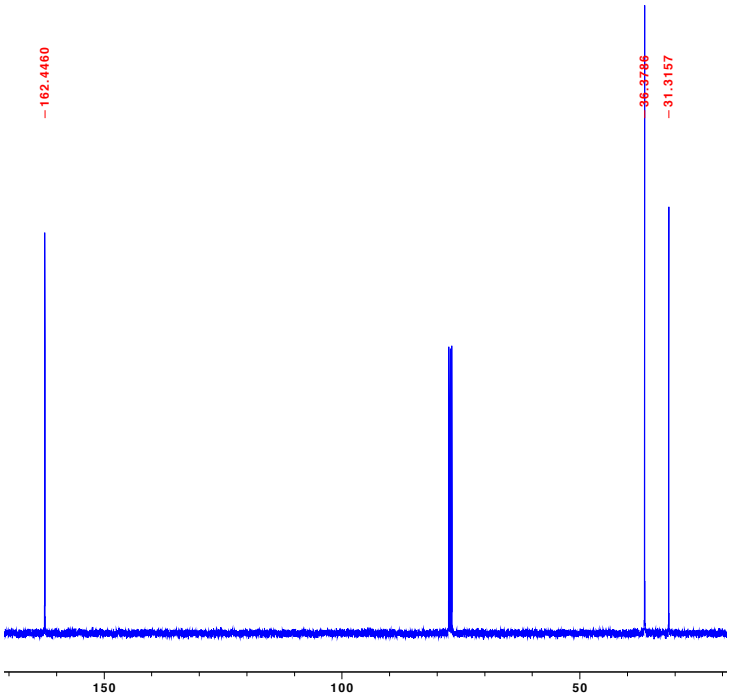


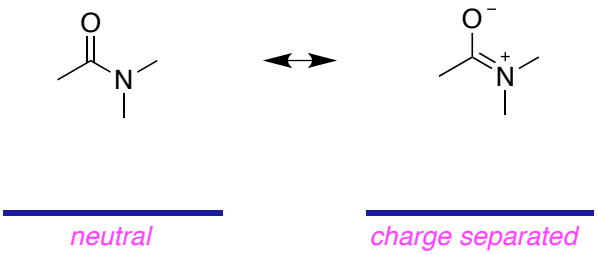
structure





structure

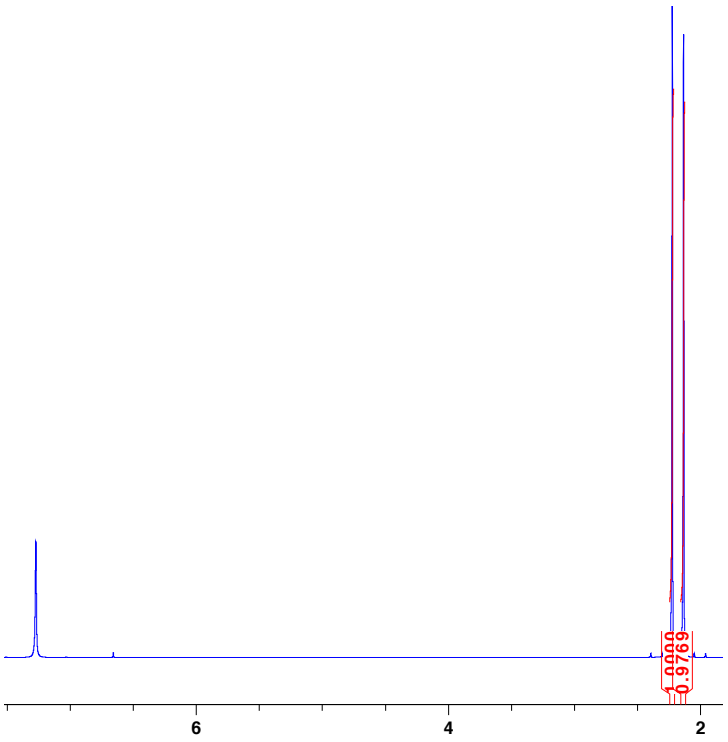


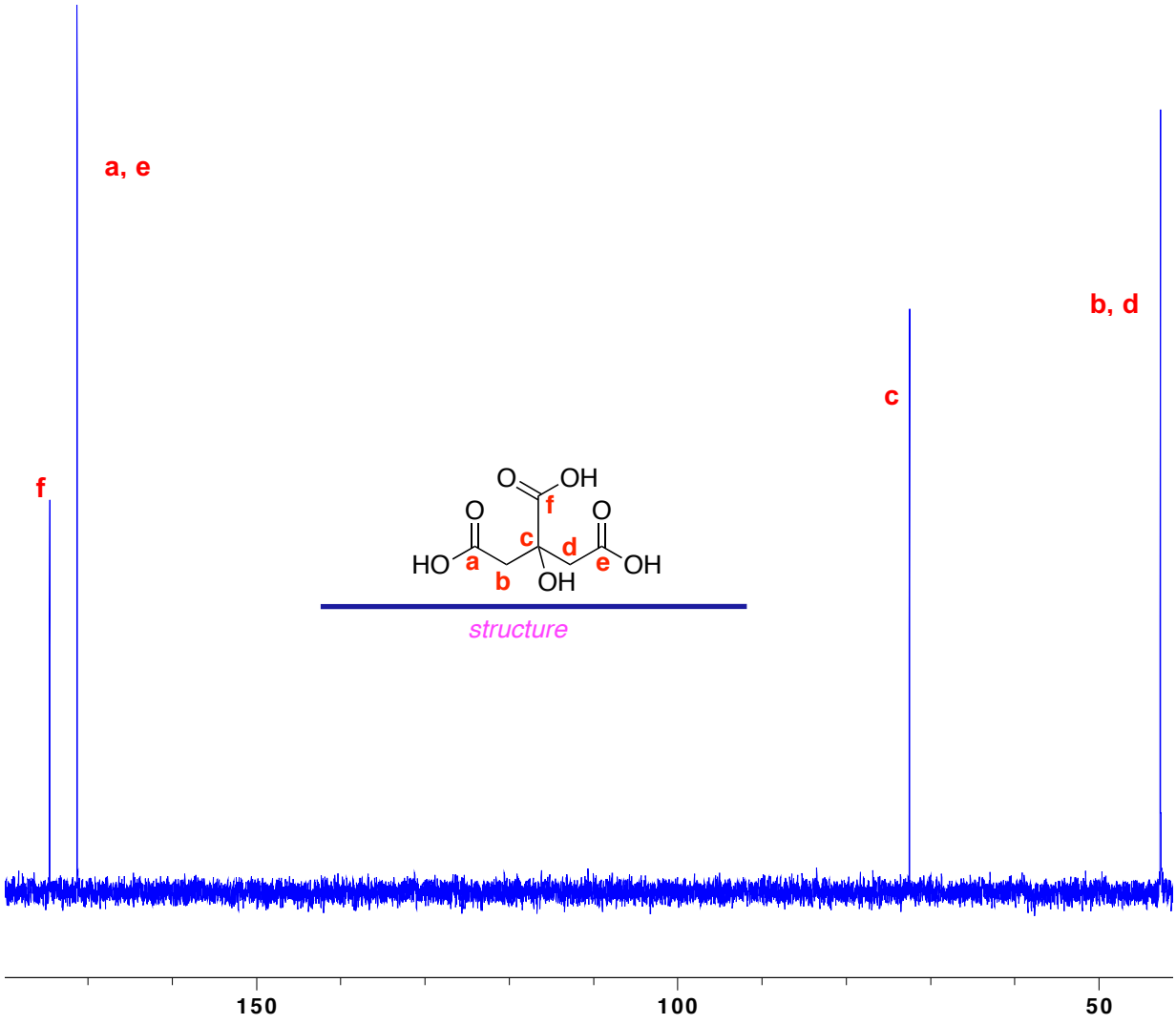


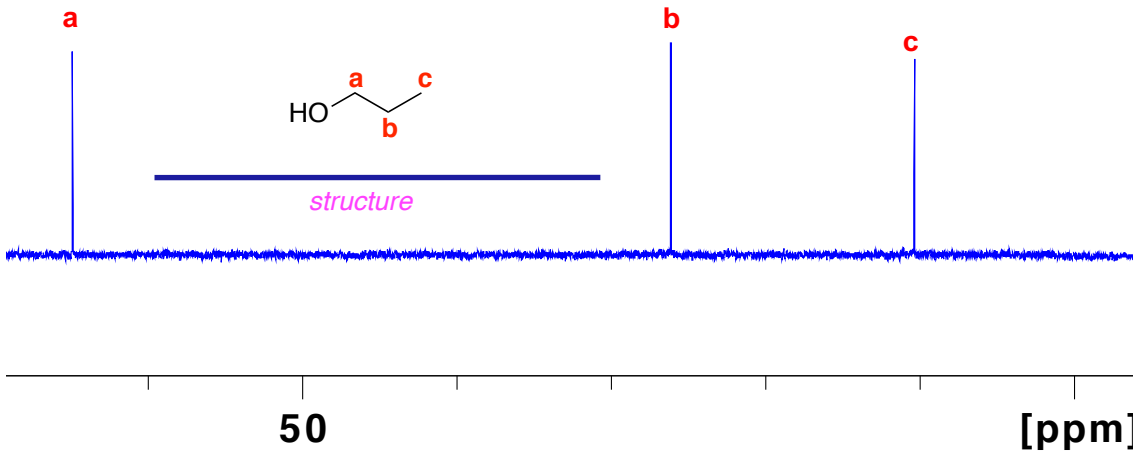
neutral *charge separated*

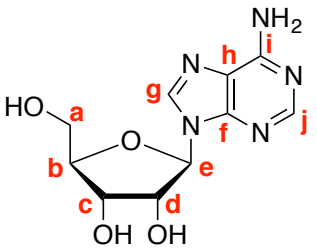
Explain why *two* methyl resonances are seen in each spectrum:

___The resonance structures create different environments around methyl groups

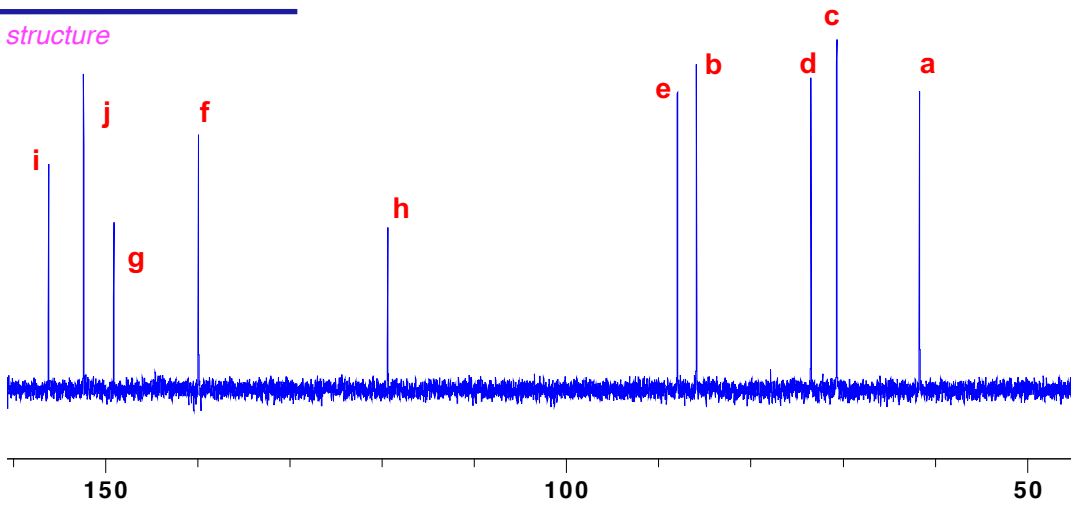


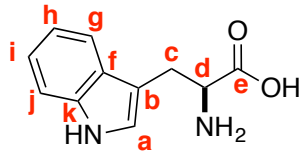

a, e
f
c
b, d
O
OH
f
O
O
c
d
HO
a
b
OH
e
OH
structure
150
100
50


a
b
c
a
c
HO
b
structure
50
[ppm]

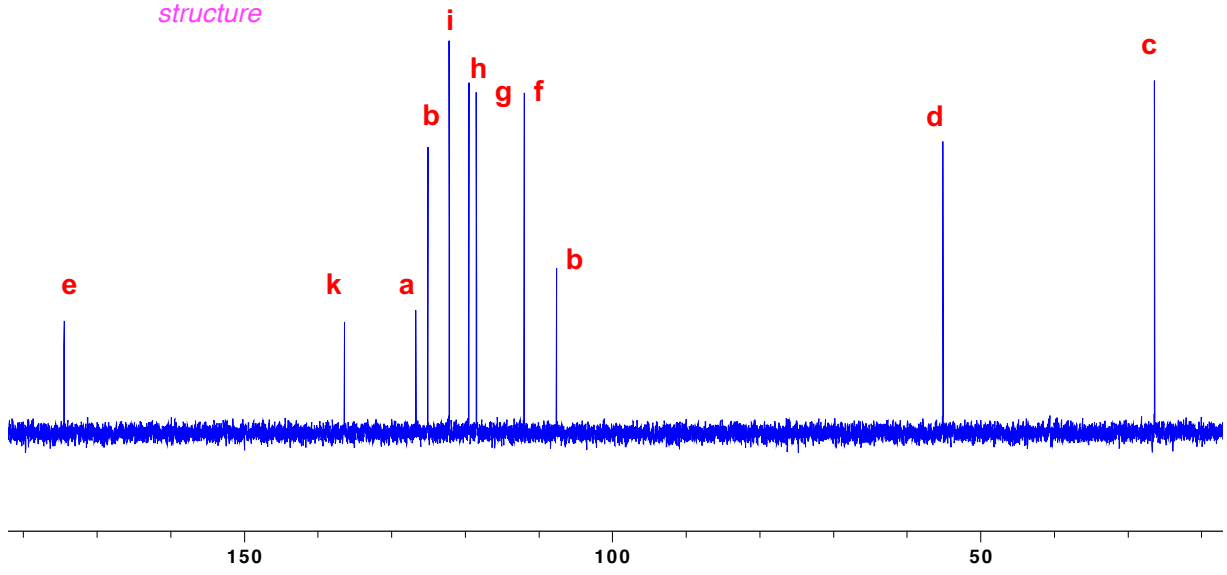


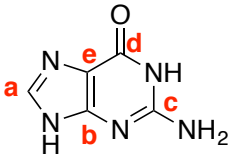
structure



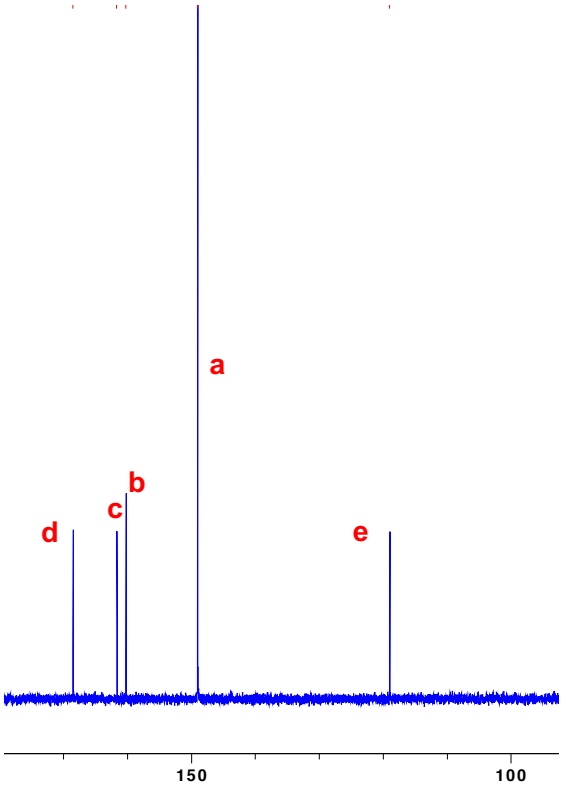


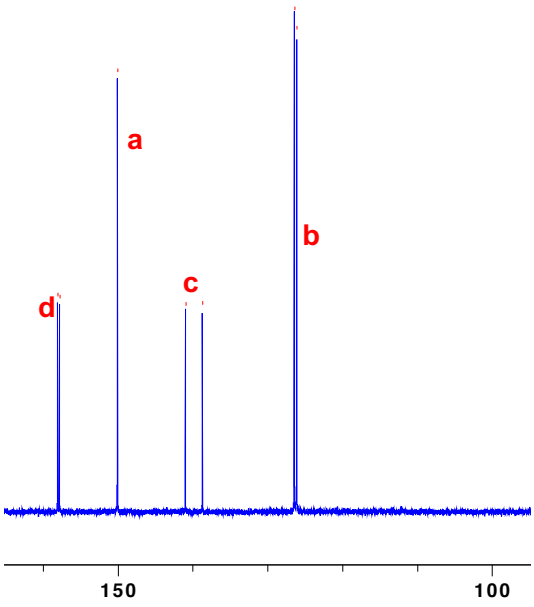
structure

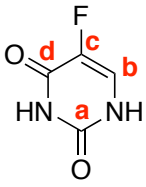




structure







structure