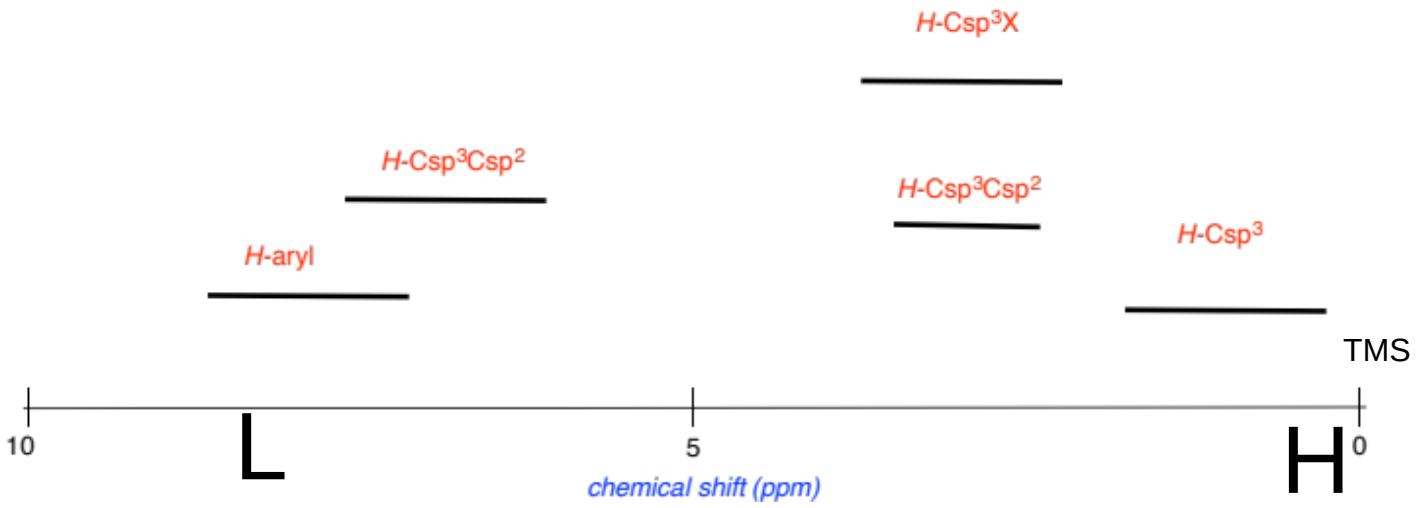
^{1}H NMR Spectroscopy

from chapter _____ in the recommended text

A. Introduction

B. Chemical Shifts In ^{1}H Spectra

chemical shift range in ^{1}H NMR is much *smaller* than in ^{13}C NMR.



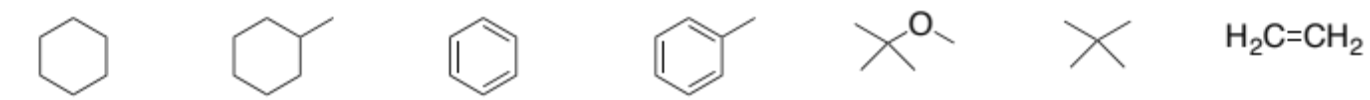
carbon atoms tend to resonate in the *high* field region from 0.5 – 2.5 ppm
sp^2-hybridized carbon atoms tend to be seen at *lower* field region from 5 – 6.5 ppm

*H*Csp^3-Csp^2 tend to be shifted to *lower* field than *H*C-Csp^3 atoms
C*H*-alkene and C*H*-aryl protons, *ie allylic and benzylic, r*espectively, tend to resonate at *higher* chemical

attached to an aromatic ring tend to resonate at *higher* chemical shifts than

shifted to significantly *lower* field than *H*C-C atoms

Chemical shifts of functional groups with relatively acidic hydrogen's (*eg* alcohols, carboxylic acids, amines) tend to vary with solvent and sample concentration due to *hydrogen* bonding.



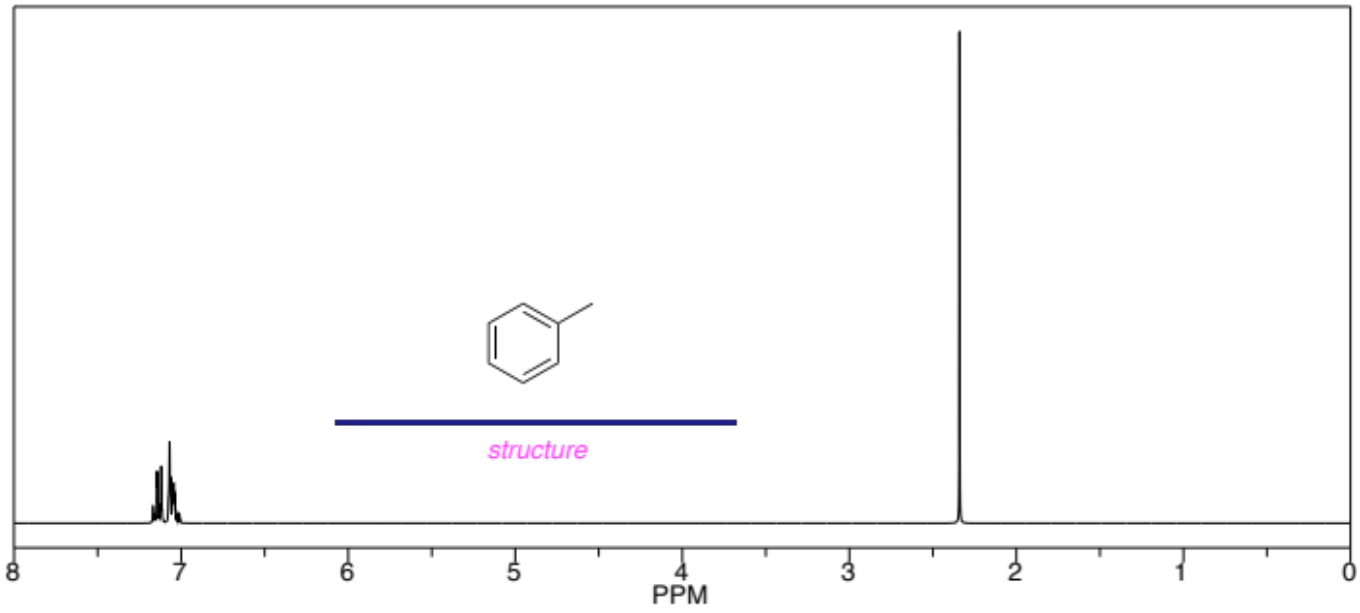
1.4 - 1.2	1.4 - 1.2 and 0.9	7.5	7.5 and 2.3	3.5 and 1.4 - 1.2	0.9	5.2

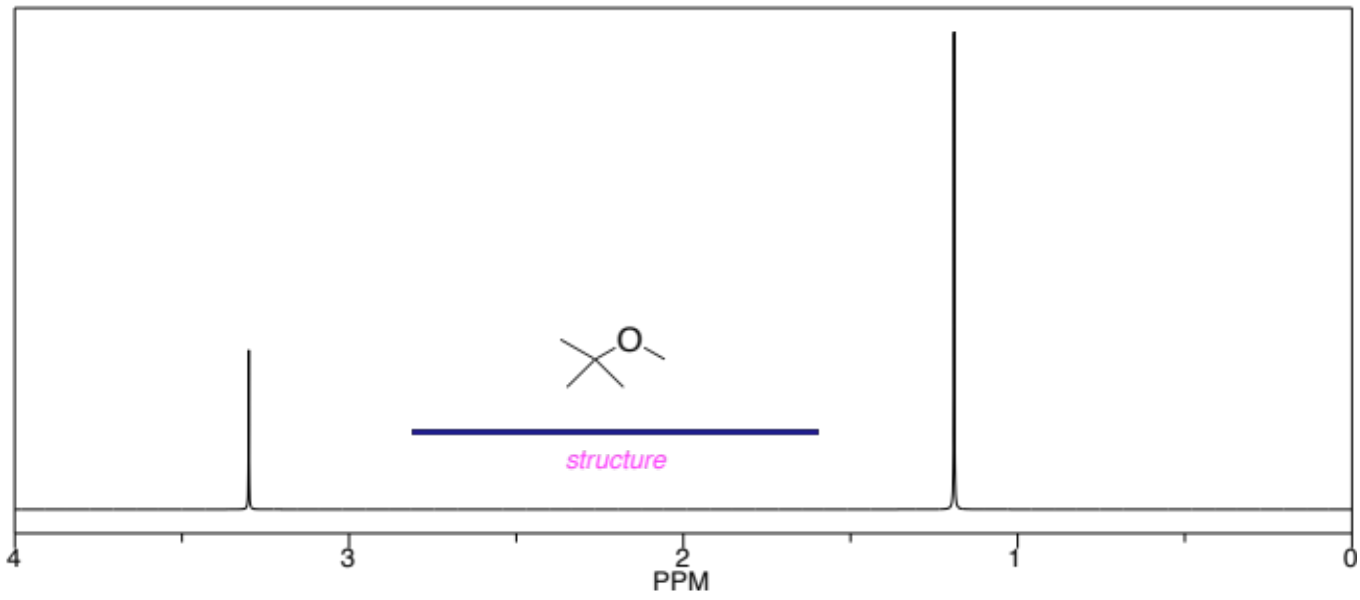
select from δ = 7.5, 5.2, 3.5, 2.3, 1.4 - 1.2, and, or 0.9

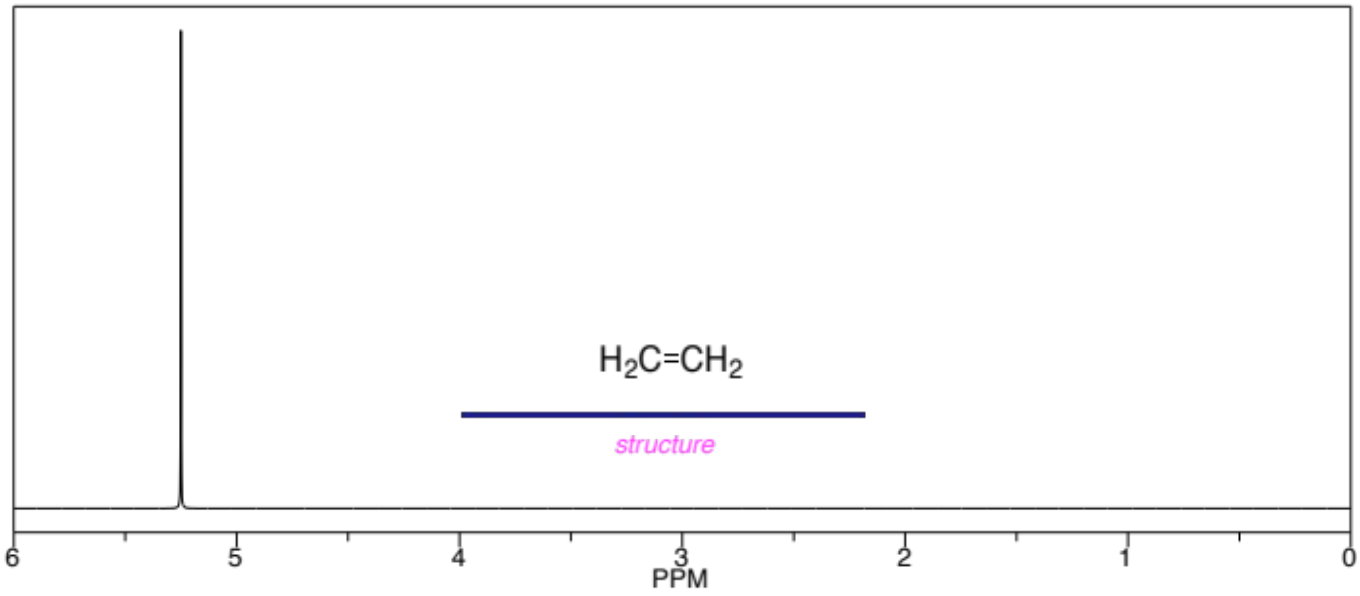
__1__	__5__	__1__	__4__	__2__	__1__	__1__

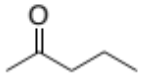
indicate number of H environments

If there are *x* unique *H* environments the number of NMR signals will be *x*.



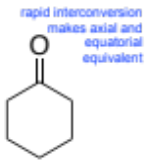

O
structure
4
3
2
1
0
PPM


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



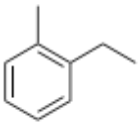
__4___
inequivalent H

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



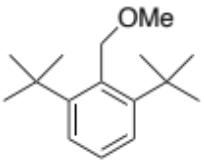
__3___
inequivalent H

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



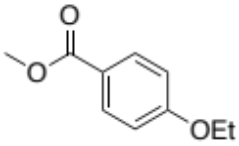
___7__
inequivalent H

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



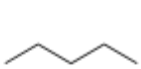
__5___
inequivalent H

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



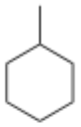
___5__
inequivalent H

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



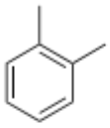
__3___
inequivalent H

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



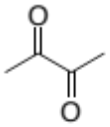
___8__
inequivalent H

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



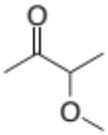
___3__
inequivalent H

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

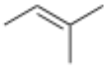
number of resonances (ppm):
0 - 2 __1__
2 - 3 __1__
3 - 4 __1__
4 - 7 __1__
7 - 9__0__

___2__
inequivalent H

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

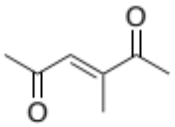
___5__
inequivalent H

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



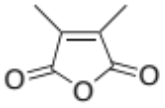
__4___
inequivalent H

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__

Note: For some hydrogens, it is quite difficult to know in which range it will resonate in, so these are educated approximations.

___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

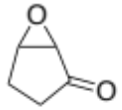
number of resonances (ppm):
0 - 2 __4__
2 - 3 __0__
3 - 4 __0__
4 - 7 __0__
7 - 9___0_

__6___
inequivalent H

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

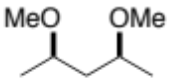
___6__
inequivalent H

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



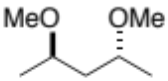
__6___
inequivalent H

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



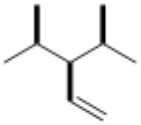
__5___
inequivalent H

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



__4__
inequivalent H

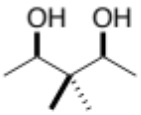
number of resonances (ppm):
0 - 2 __2__
2 - 3 __0__
3 - 4 __2__
4 - 7 __0__
7 - 9___0_



__7___
inequivalent H

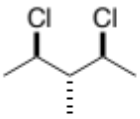
number of resonances (ppm):
0 - 2 __4__
2 - 3 __0__
3 - 4 __0__
4 - 7 __3__
7 - 9___0_

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_



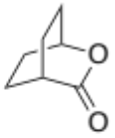
__4___
inequivalent H

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

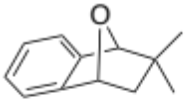


___6__
inequivalent H

number of resonances (ppm):
0 - 2 __4__
2 - 3 __0__
3 - 5 __1__
5 - 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_

Note: For some hydrogens, it is quite difficult to know in which range it will resonate in, so these are educated approximations.

C. Coupling In ^{1}H NMR

In the ^{a}C-C-^{b}H system ^{a}C may couple to ^{b}H via *two* bonds, *ie two* bond couplings.

Heteronuclear Coupling To ^{13}C Is Unimportant

The natural abundance of ^{13}C in organic molecules is *1.11* %
most protons attached to a carbon atom *are not* split by the one bond ^{13}C nuclear spins

^{12}C, does not occur because that nucleus is NMR *silent*).

Coupling between ^{13}C and ^{1}H are examples of *hetero-* nuclear couplings.

Homonuclear ^{1}H Coupling

splitting other protons, hence this *homo* -nuclear coupling information usually *is not* removed

2 and 3 bond *homo* nuclear couplings.

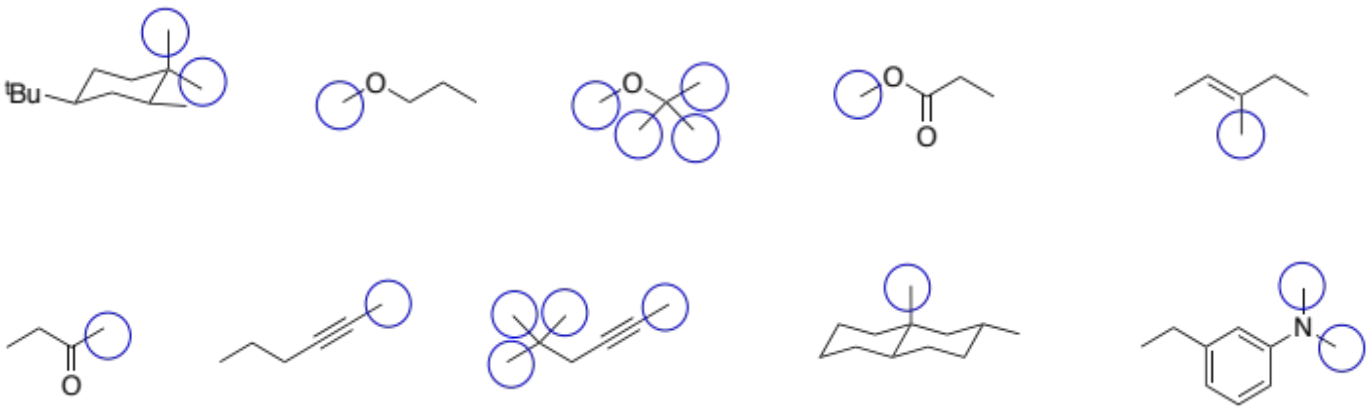
Couplings of the type H^{a}-C-C-C-H^{b}, *ie 4* bond homonuclear

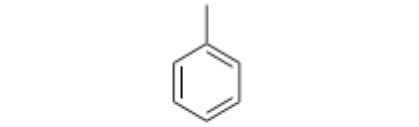
$ClCH_2CH_2Br$ **A** are separated by *3* bonds and *do* give significant couplings.

in $ClCH_2OCH_2Br$ **B** have *4* bonds between them and *do not* give significant couplings.

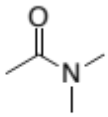
Equivalent protons in NMR spectra *do not* appear to be split.

Resonances in molecules like CMe_4, MeOMe, MeCOMe, and $MeCOCH_2Cl$ are *singlets*.





molecule 1

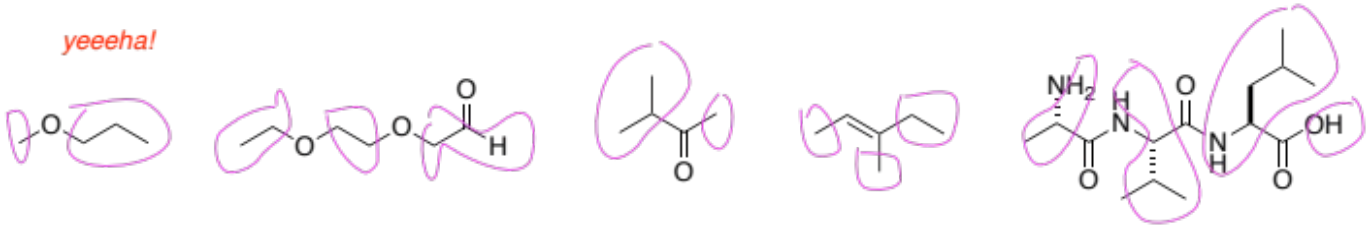


molecule 2

molecule 3

Spin Systems

They consist of *any number >1 NMR* protons.



its resonance will be split into *n + 1* signals

It *does not* matter how many protons *are being split* but it *does* matter

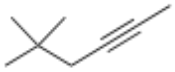
The relative intensities of the peaks in the split signal *follows Pascal's triangle*.

H^a-C-H^b Spin Systems

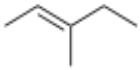
field that reaches us *will* depend on whether the spin
will appear as a *doublet*.

CH_2 group can *sometimes* be inequivalent, and if they are then the *will* appear to split each other.

then the field that reaches us *will* depend on whether the spin of H^b
appear as a *doublet*.

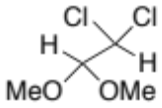




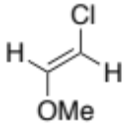


H^a-C-C-H^b Spin Systems

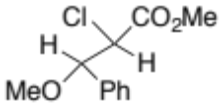
Coupling in the *H^a*-C-C*H*^{b} system will be *smaller* than in the *H^a*-C-*H*^{b} system



isolated H^aCCH^b



molecule 1



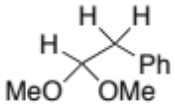
molecule 2

CH^b_2 system when a magnetic field is applied *will* depend on whether the spin of H^b is aligned or opposed

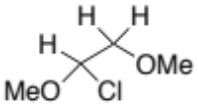
In this system, *H^a* will appear as a *triplet* due to coupling with *H^b*.

Conversely, *H^b* will appear as a *doublet* due to coupling with *H^a*.

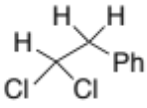
H^aC-CH^b_2 Spin Systems



isolated $H^aCCH^b_2$



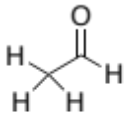
molecule 1

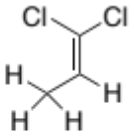


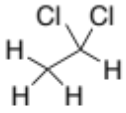
molecule 2

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

The field that reaches H^a in an $H^a\text{-}C\text{-}CH^b_3$ system *will* depend on whether the spin of H^b is
H^a will appear as a *quartet*, and H^b appears as a *doublet*.





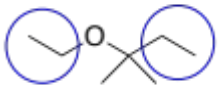


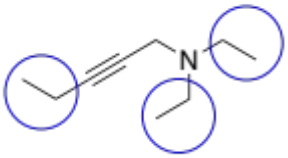
isolated $H^aCCH^b_3$ | *molecule 1* | *molecule 2*

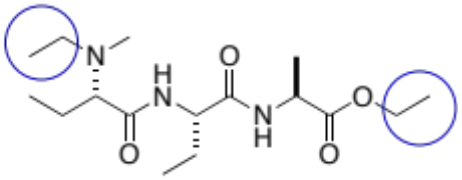
$H^a_2C\text{-}CH^b_3$ Spin Systems (Isolated Ethyl Groups)

In a $H^a_2C\text{-}CH^b_3$ system, it *does not* make any difference to the splitting
protons in NMR spectra *do not* split each other.

where the methyl part is a *triplet*, and the methylene is a *quartet*.

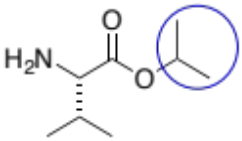


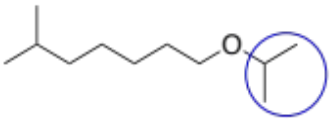


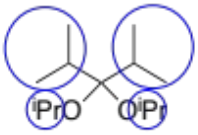


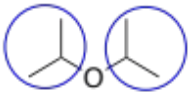
$(H^a_3C)_2CH^b$ Spin Systems (Isolated ^{i}Pr Groups)

hence H^b will appear as a *heptet* with a relative intensity of _1:6:15:20:15:6:1 whereas the methyl groups
will be split into *doublets*.

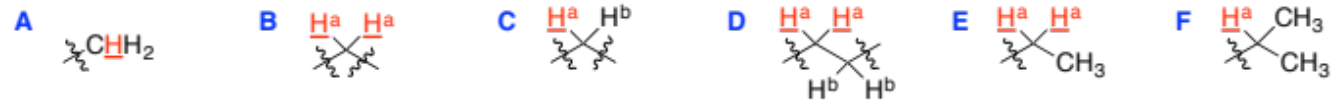








Common Splitting Patterns In Organic Molecules

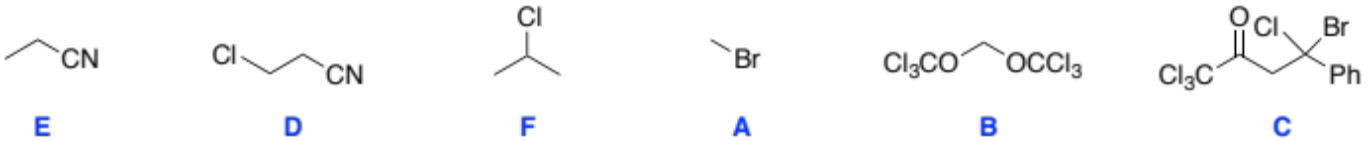


s *s* *d* *t* *q* *hept*

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

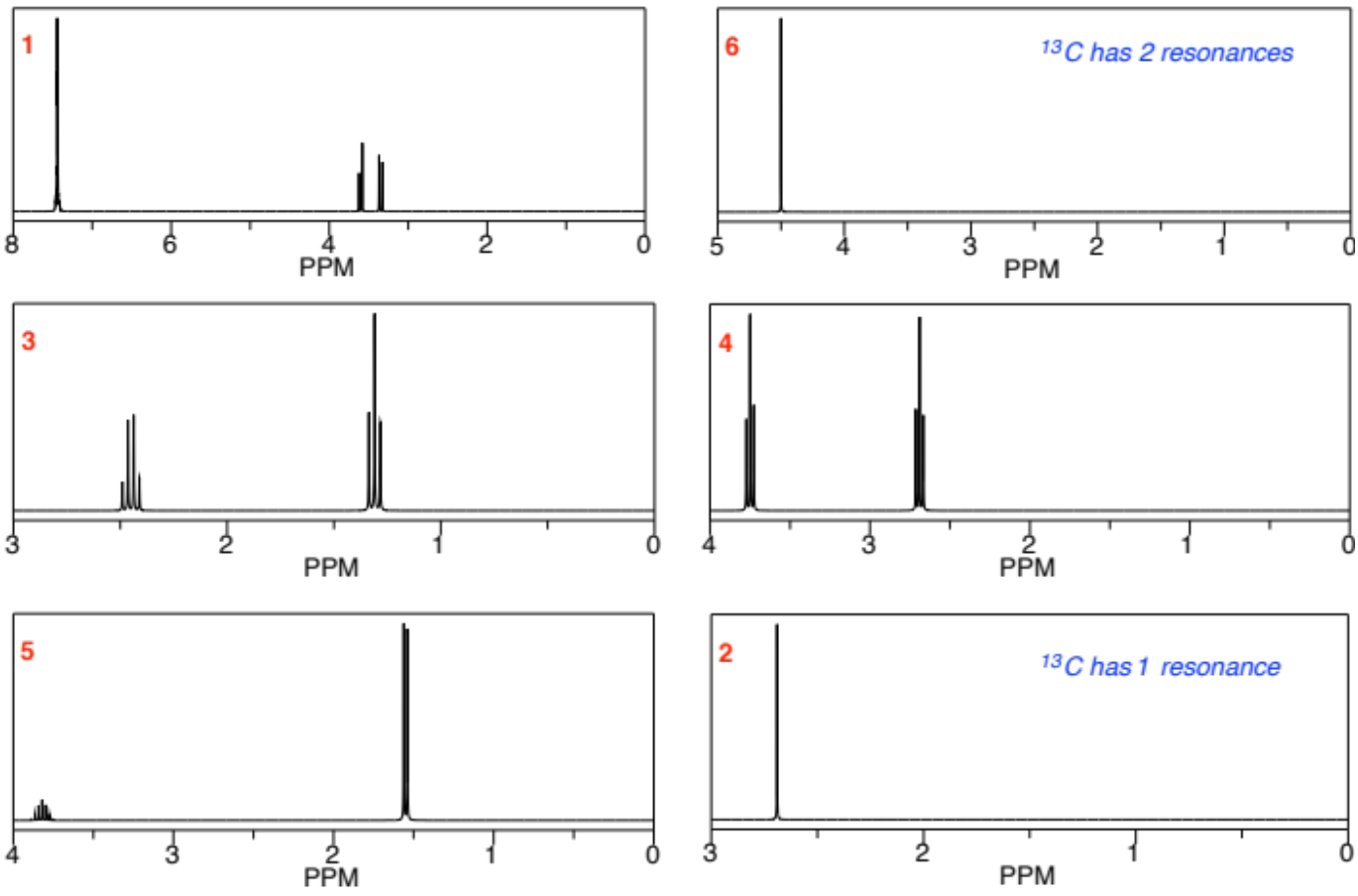
methyl | methylene | methylene | ethylene | ethyl | iso-propyl

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

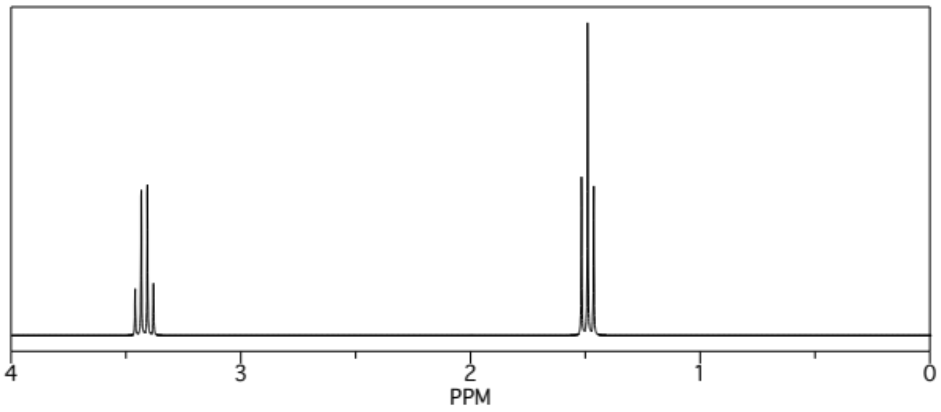


E **D** **F** **A** **B** **C**

3 **4** **5** **2** **6** **1**

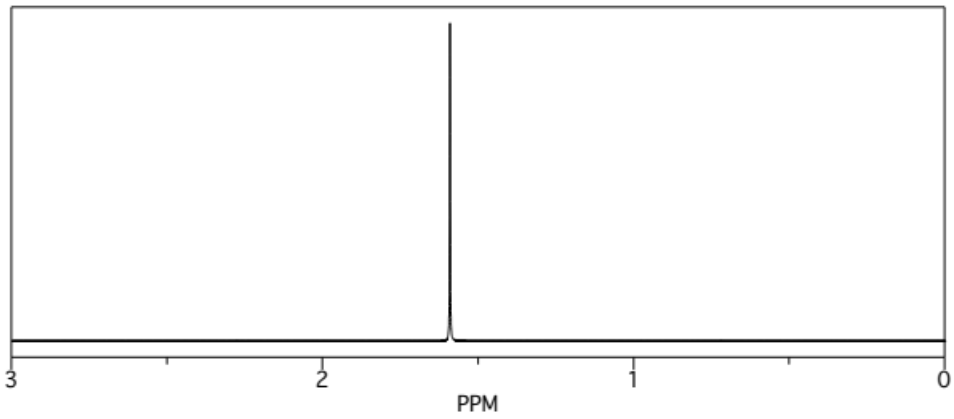


Sorry, that the positions of **2** and **6** change in the answers above.

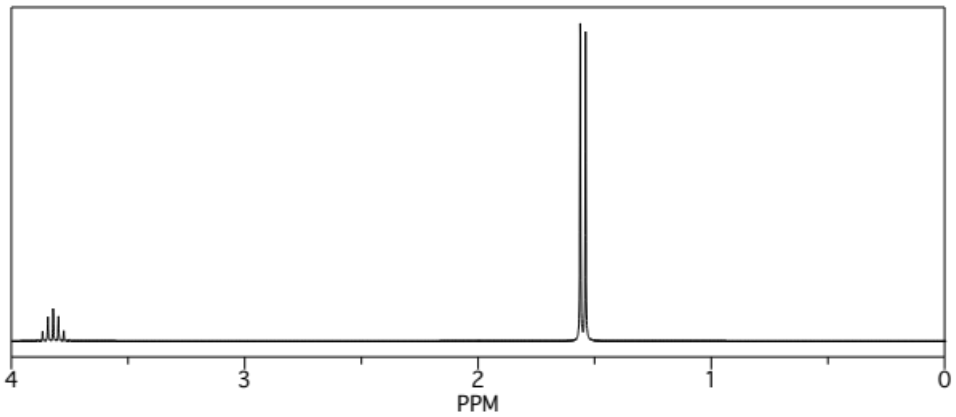


structure

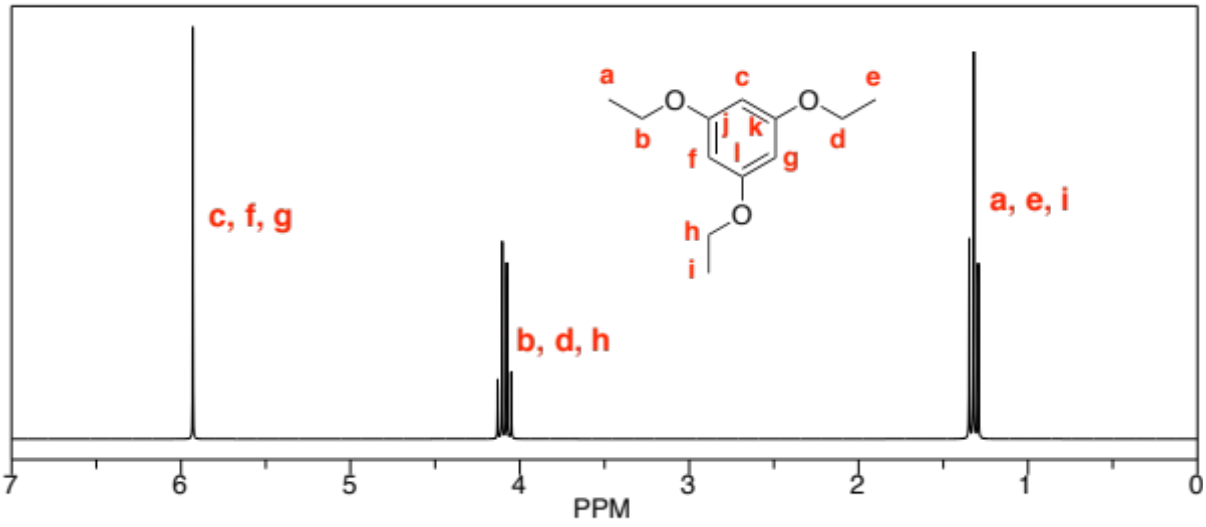
structure



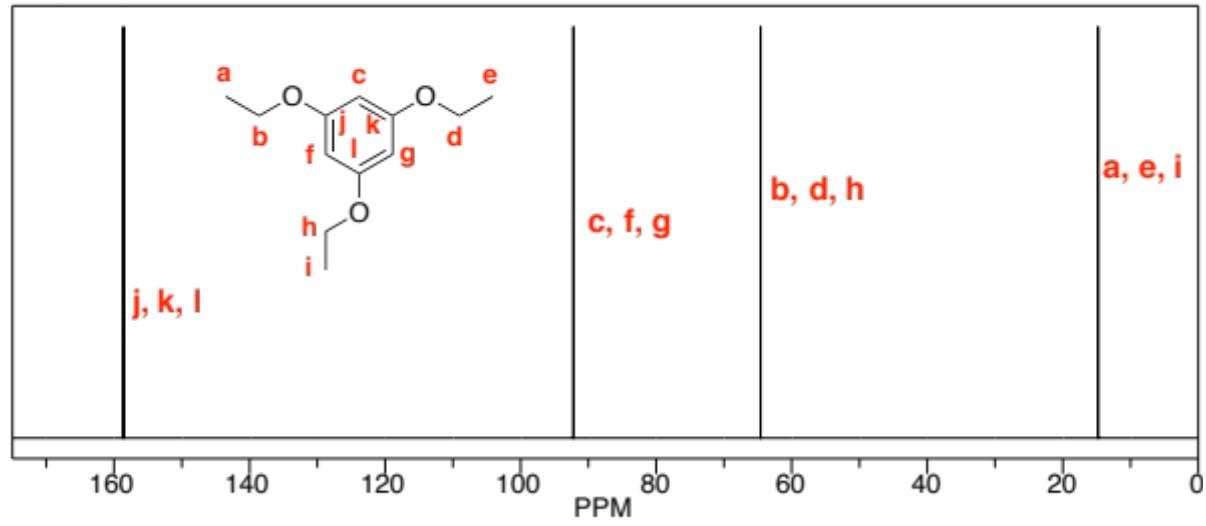
structure



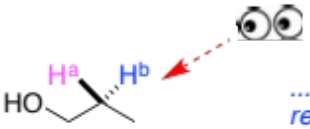
^{1}H NMR



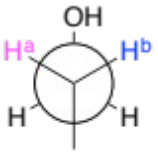
^{13}C NMR



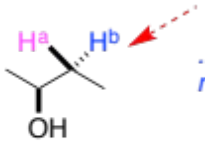
D. Diastereotopic Protons



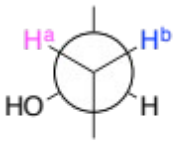
..... can be represented as



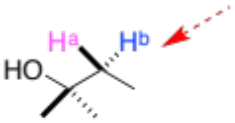
where H^a and H^b <u>are</u> equivalent



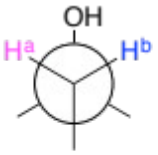
..... can be represented as



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

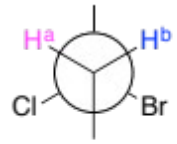


..... can be represented as

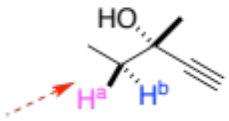


where H^a and H^b <u>are</u> equivalent

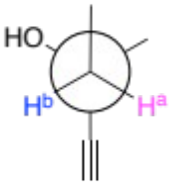
..... can be represented as



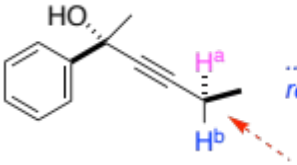
where H^a and H^b <u>are not</u> equivalent



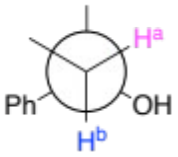
..... can be represented as



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

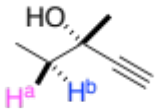


..... can be represented as

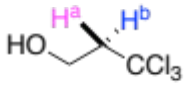


where H^a and H^b <u>are not</u> equivalent

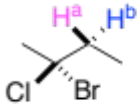
Protons on a methylene group are *inequivalent* when the methylene



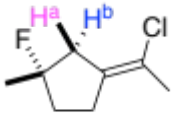
H^a: __doublet of quartets__
H^b: __doublet of quartets__



H^a: __triplet__
H^b: __triplet__

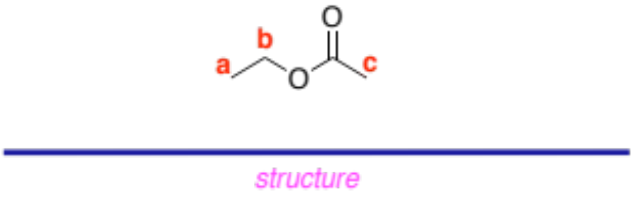


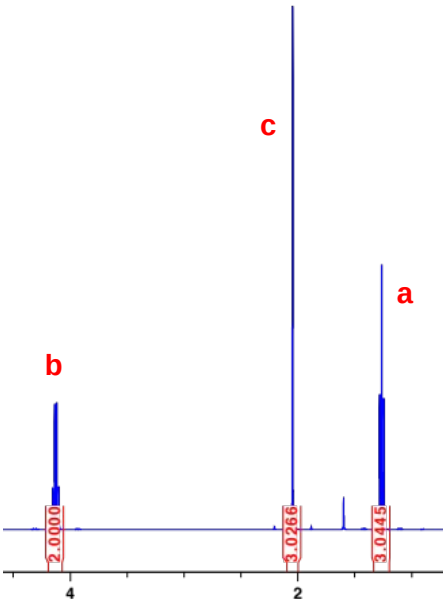
H^a: __doublet of quartets__
H^b: __doublet of quartets__

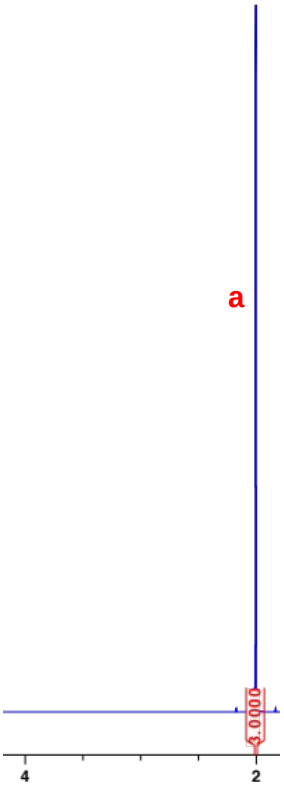


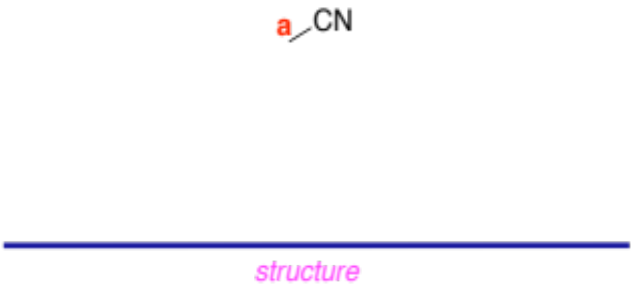
H^a: __doublet of doublets___
H^b: __doublet of doublets___

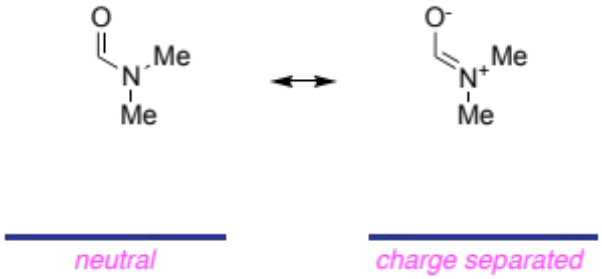
E. Some Problems Involving Spectral Interpretation





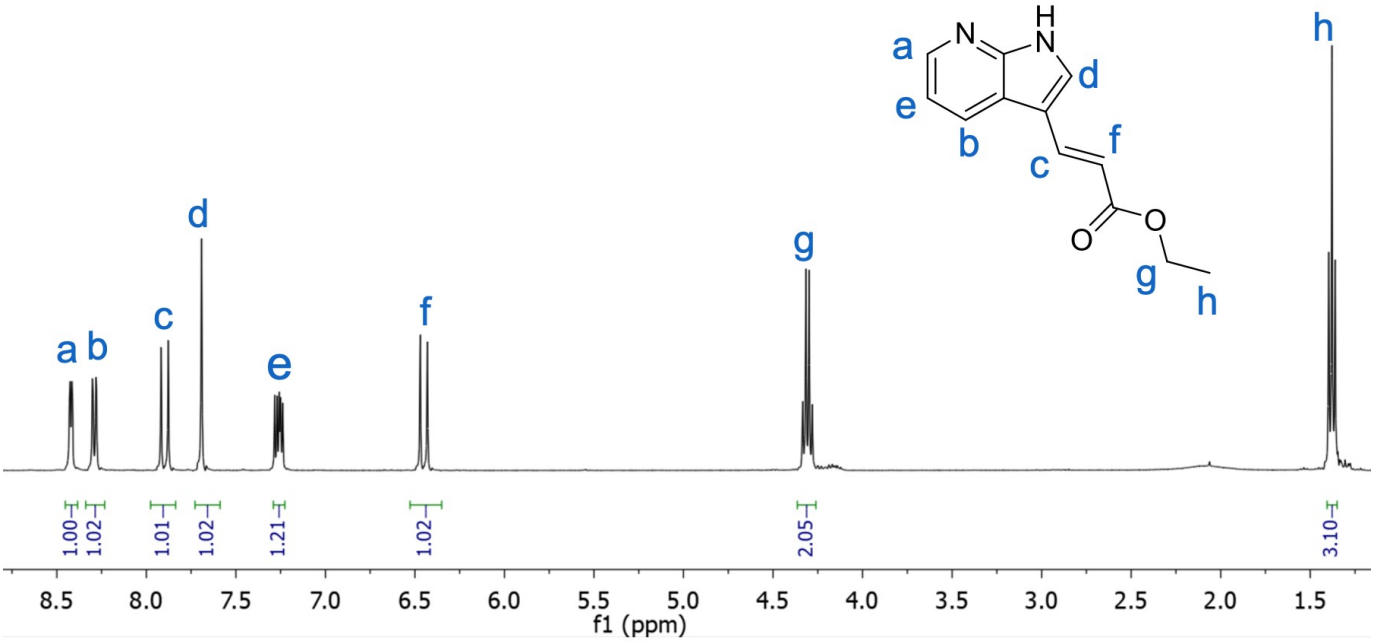


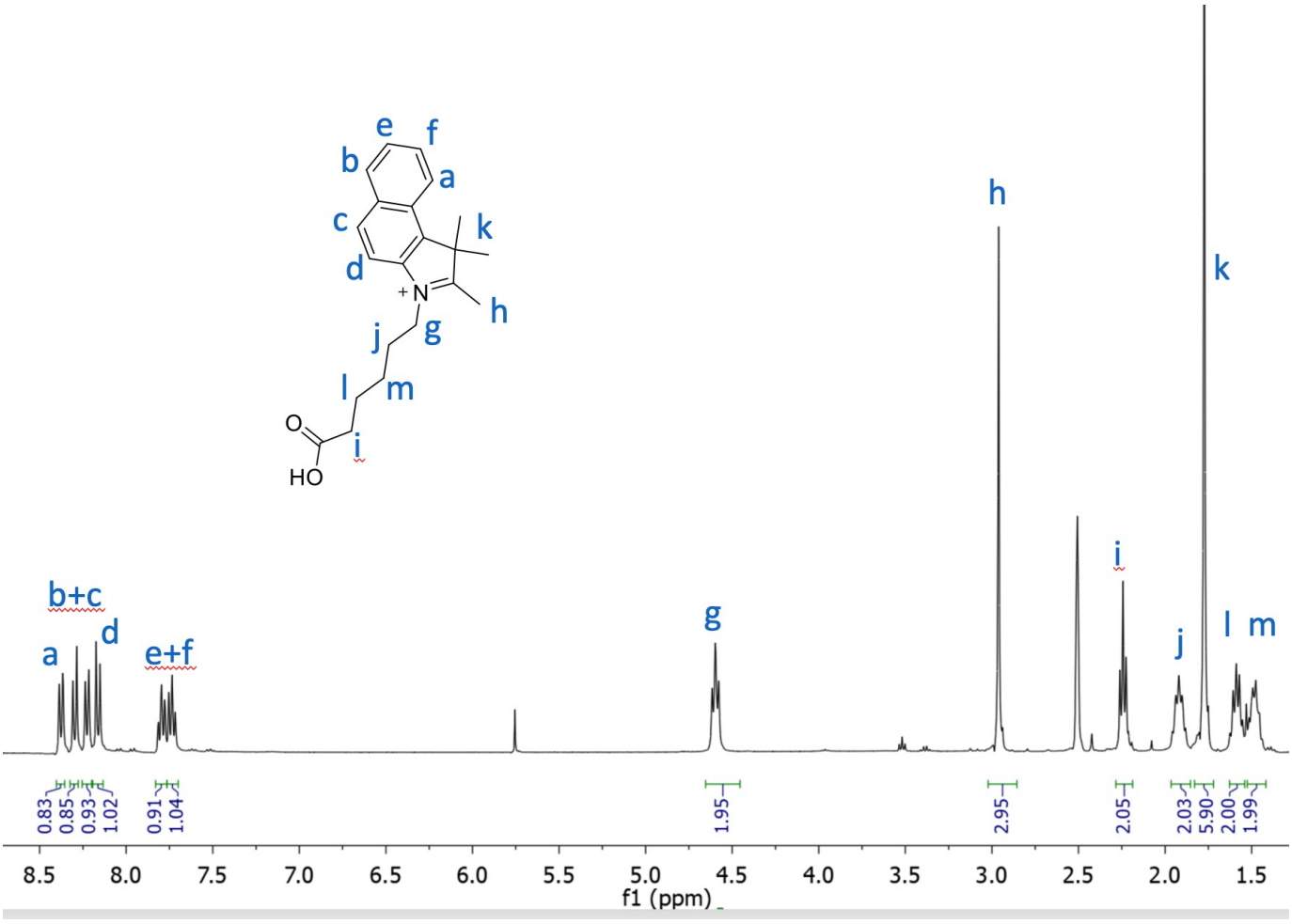


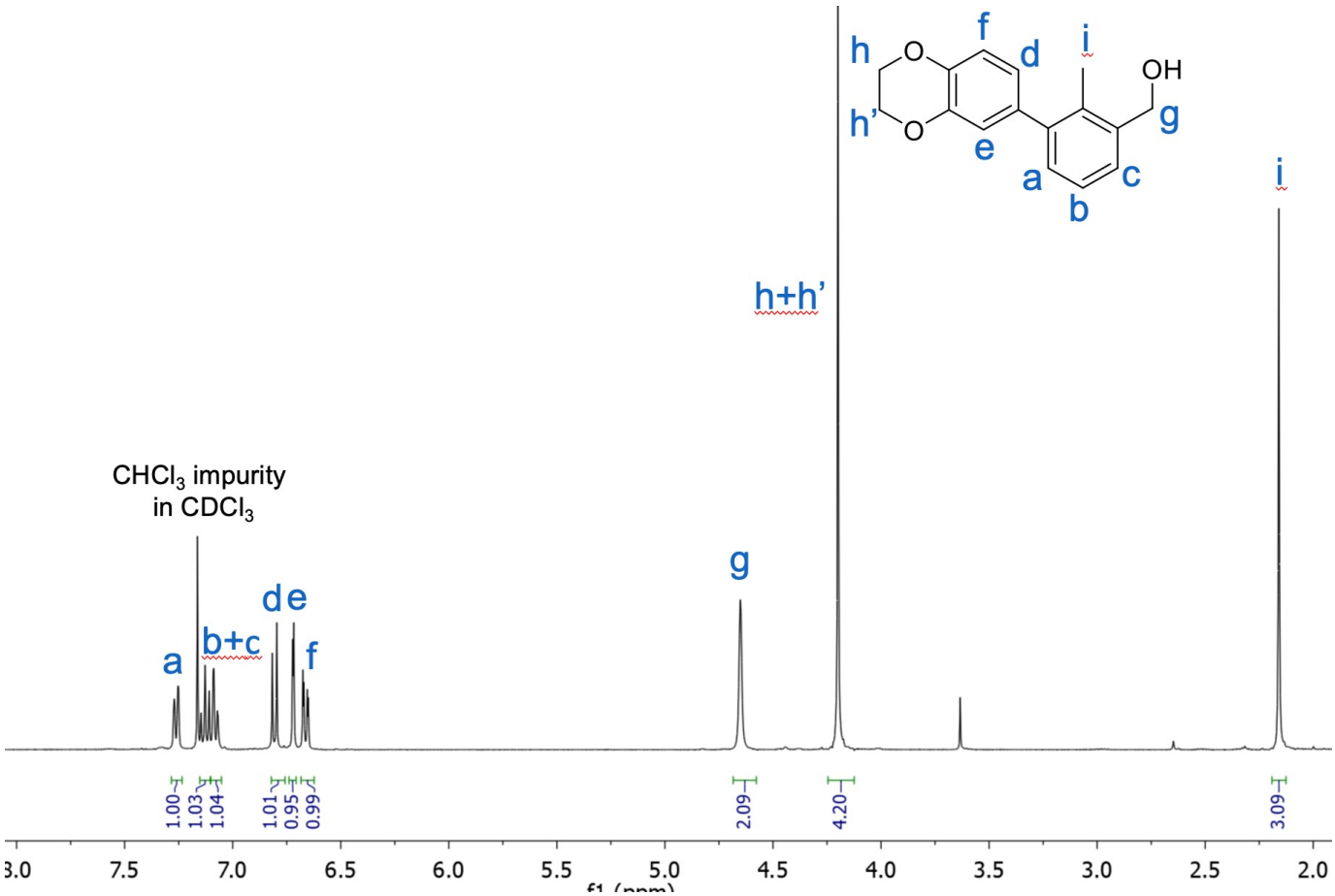


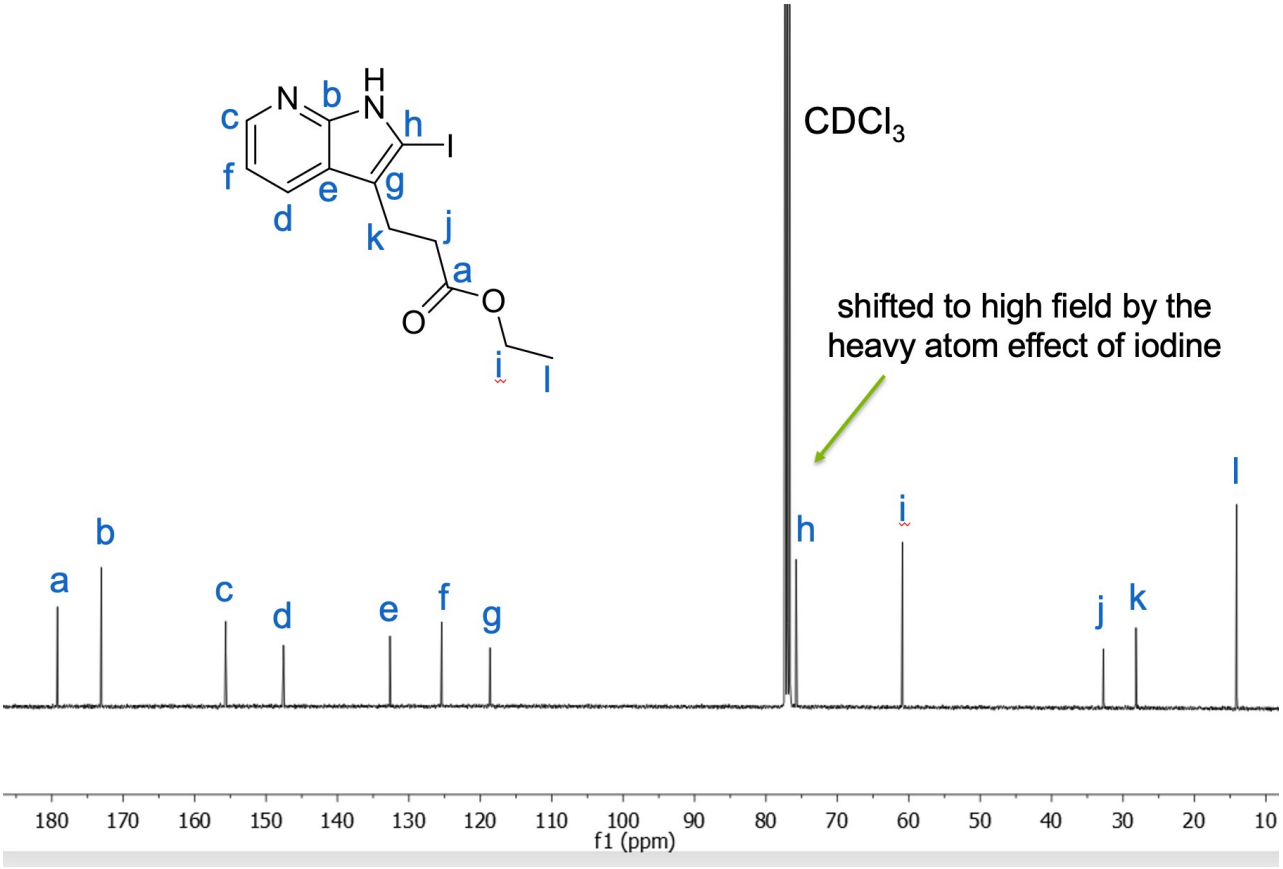
Explain why *two* methyl resonances are seen in each spectrum:

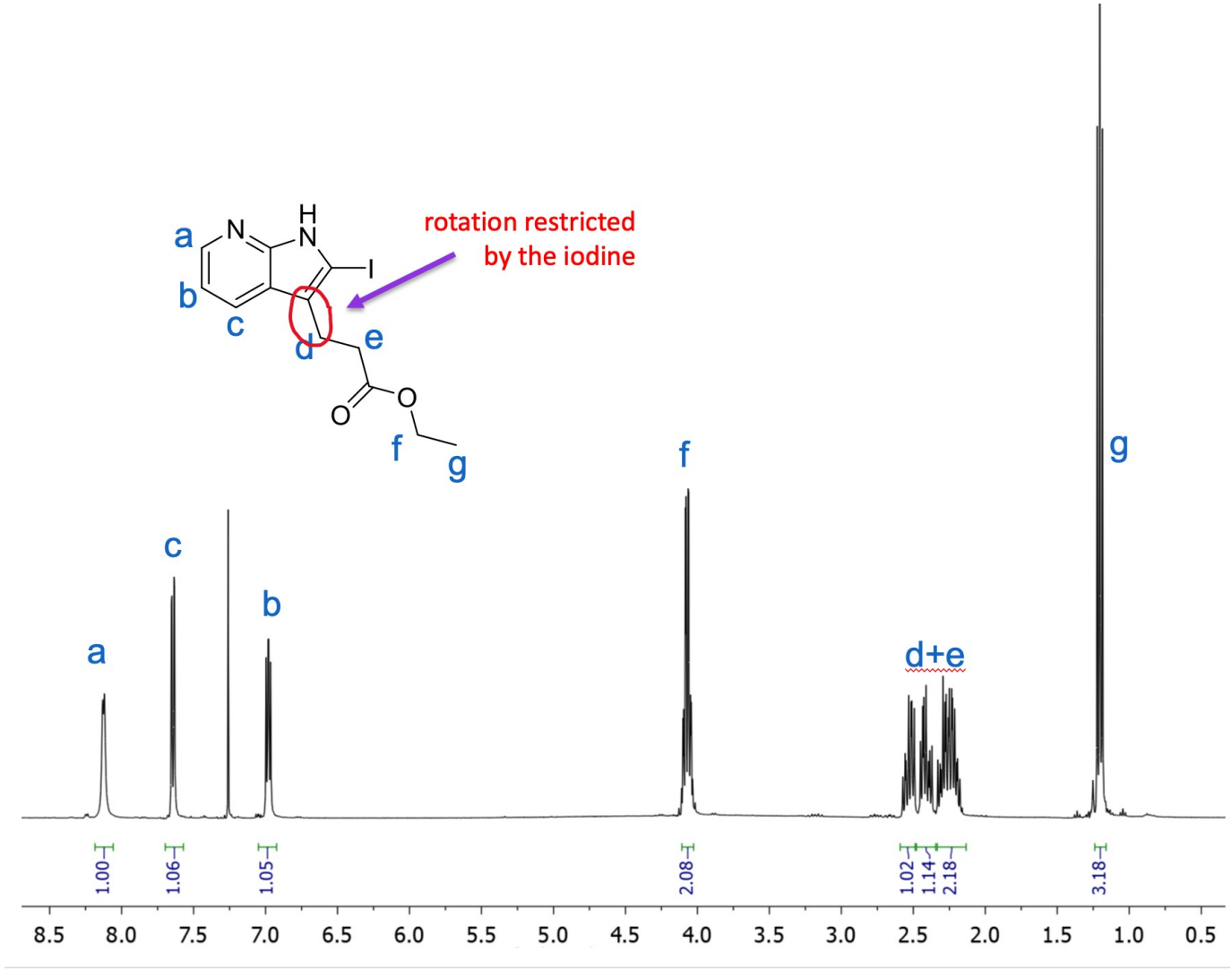
because rotation around the OC-N bond is slow on the NMR time scale, due to this resonance effect


a b c d e f g h
1.00 1.02 1.01 1.02 1.21 1.02 2.05 3.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)


b+c a d e+f g h i j k l m
0.83 0.85 0.93 1.02 0.91 1.04 1.95 2.95 2.05 2.03 5.90 2.00 1.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)


h
O
f
d
i
OH
h'
O
g
e
a
c
b
i
h+h'
CHCl3 impurity
in CDCl3
g
d e
b+c
a
f
1.00
1.03
1.04
1.01
0.95
0.99
2.09
4.20
3.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0


CDCl3
shifted to high field by the heavy atom effect of iodine
a
b
c
d
e
f
g
h
i
j
k
l
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


rotation restricted
by the iodine
a
b
c
d
e
f
g
H
N
N
I
O
O
a
c
b
f
d+e
g
1.00
1.06
1.05
2.08
1.02
1.14
2.18
3.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5