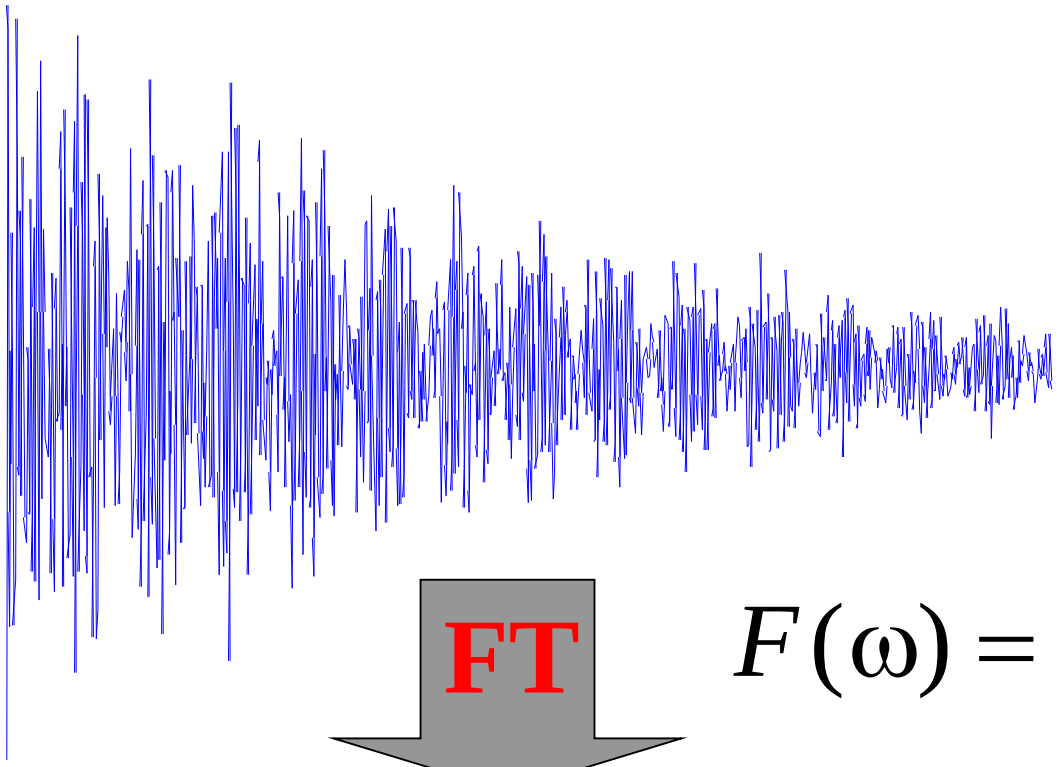
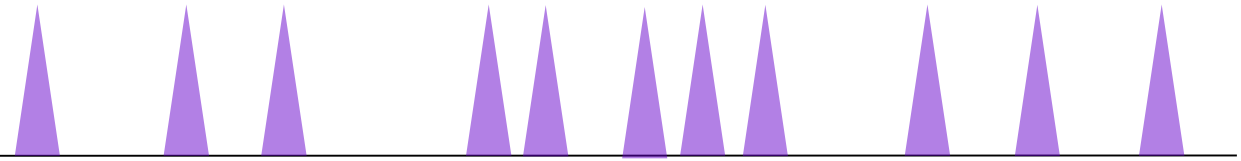
FID= Free Induction Decay



f(t)

FT

$$F(\omega) = \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt$$



F(ω)

MOST important NMR active nuclei

$I \neq 0$ Spin quantum number

	^{1}H	^{13}C	^{15}N	^{14}N	D	^{19}F	^{31}P
Natural abundance	100 %	1%	0,4 %	99,6 %	0,01 %	100 %	100 %
spin	1/2	1/2	1/2	1	1	1/2	1/2

^{12}C, ^{16}O not NMR active!

Even mass number and even atomic number

$\Rightarrow$ ***I* = 0** (^{12}C, ^{16}O)

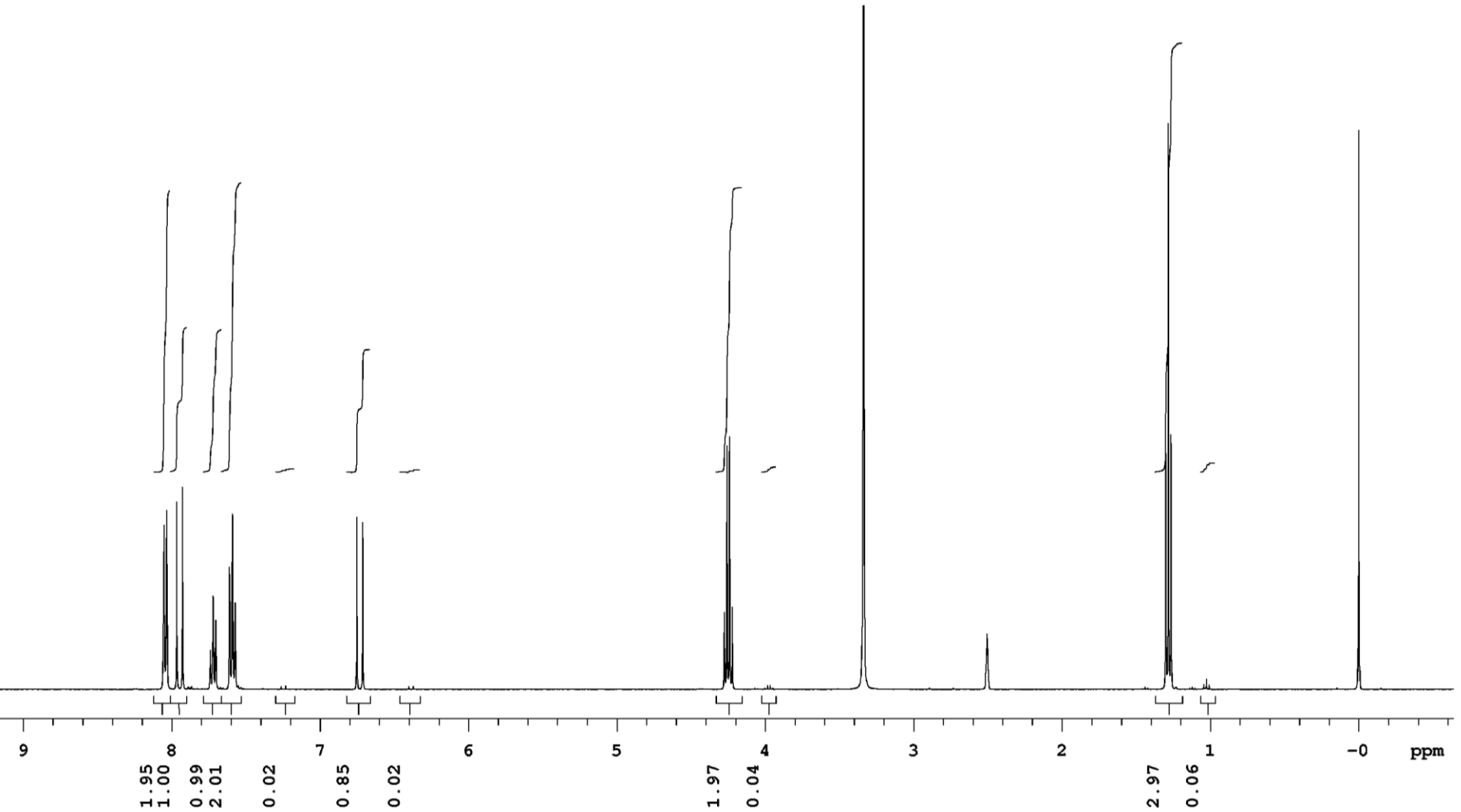
Even mass number and odd atomic number

$\Rightarrow$ ***I* = *integer*** (^{14}N, ^{2}H, ^{10}B)

Even mass number $\Rightarrow$ ***I* = *1/2, 3/2, 5/2…etc***

(^{1}H, ^{13}C, ^{15}N, ^{31}P)

NMR Spectrum → structure



Most important spectral information:

chemical shift
spin-spin coupling
area under peaks (integral)

Chemical shift

$$\nu_0 = \frac{\gamma}{2\pi} \cdot B_0$$ Gyromagnetic ratio

$$\nu_1 = \frac{\gamma}{2\pi} \cdot (1-\sigma) B_0$$ Shielding factor

V (Hz)	499840000	399950000	800130000
1	499839783	399949826	799743653
2	499839503	399949602	799743204
3	499838347	399948677	799741355
4	499838330	399948663	799741328
5	499838276	399948620	799741241
6	499838260	399948607	799741216
7	499837458	399947966	799739933

Resonance frequency is in MHz range, small difference

Dependent on B_0

Chemical Shift

Difference to a reference material, devided by field strength no field dependence any more

$$d = \frac{n - n_0}{n_0} \times 10^6$$

↓

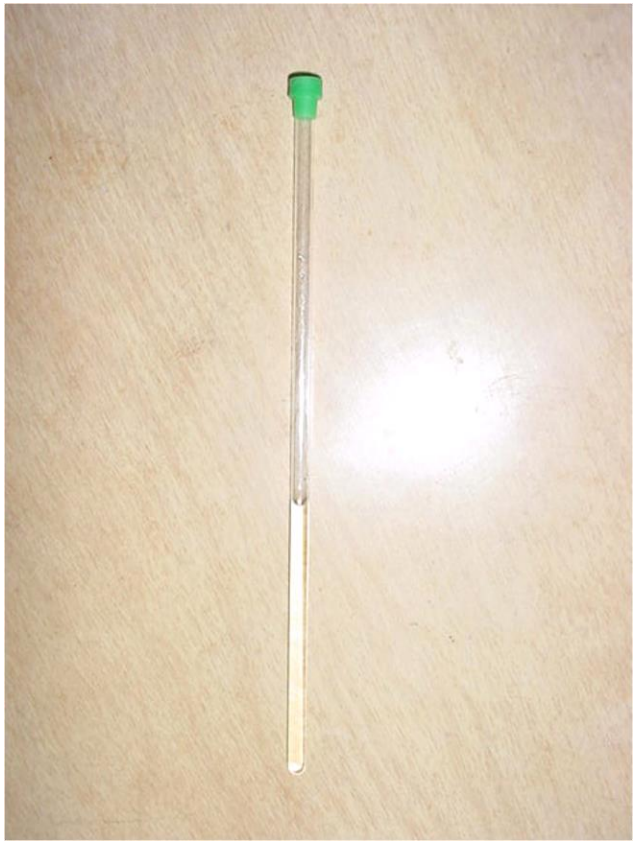
δ scale, ppm

Reference: TMS (very often) 0 ppm (cheap, inert, „nice" signal)

Solvent, temperature, pH dependent!

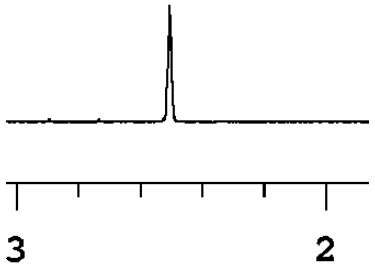
Sample

?



Solvents: should not contain H!

$CDCl_3$ 7,27
DMSO-d_6 2,50
D_2O
....



D is used for maintaining B_0 stable and constant „lock”

(Very) insensitive

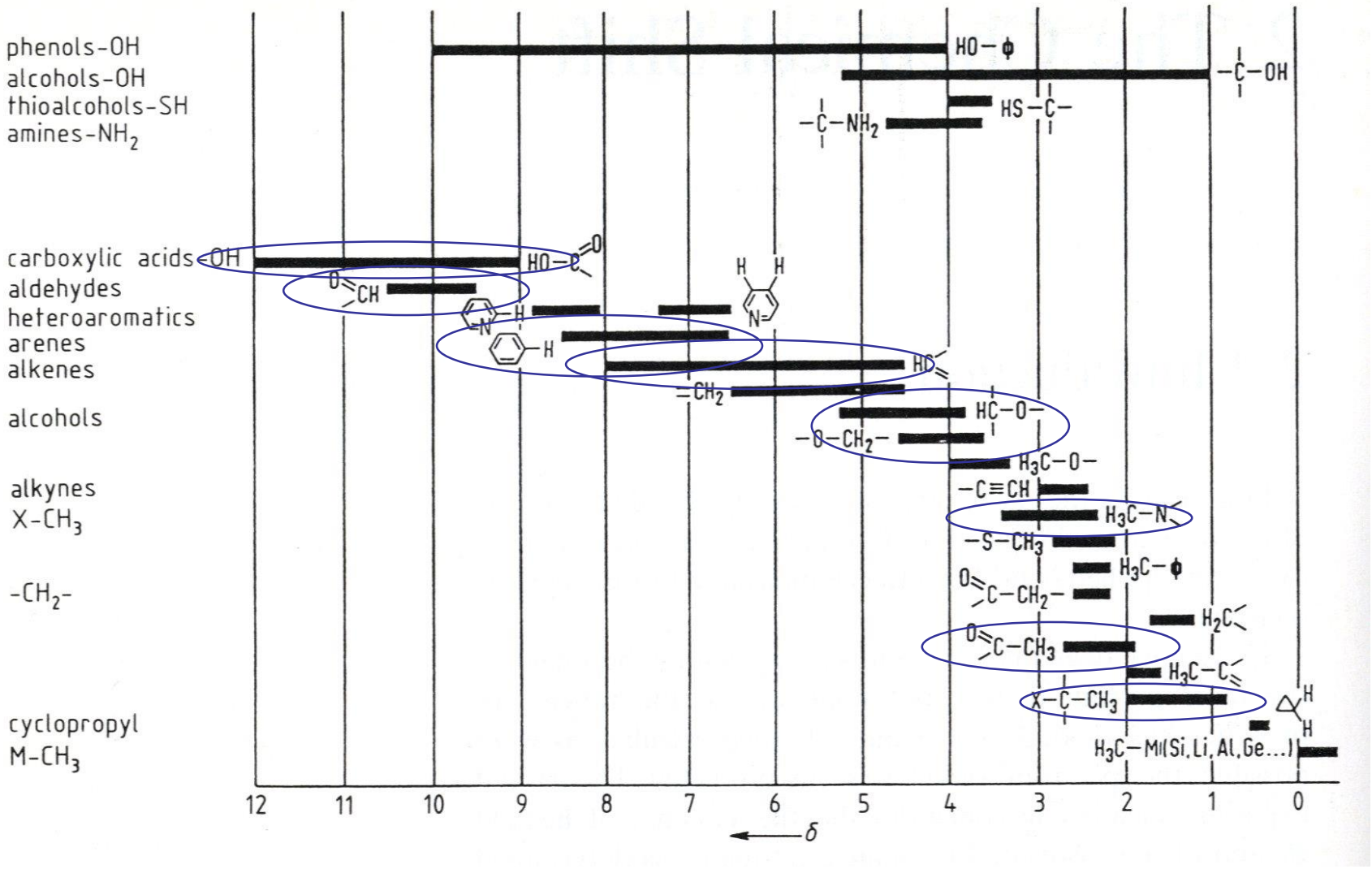
Non invasive

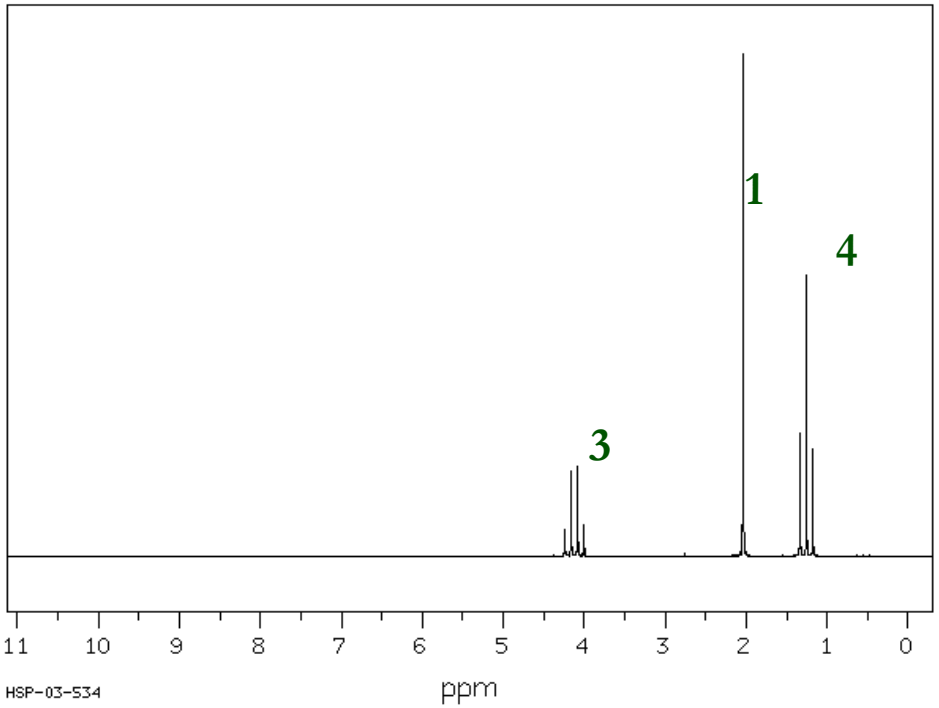
Most detailed information about structure (besides Xray)

Electron density has the biggest effect:

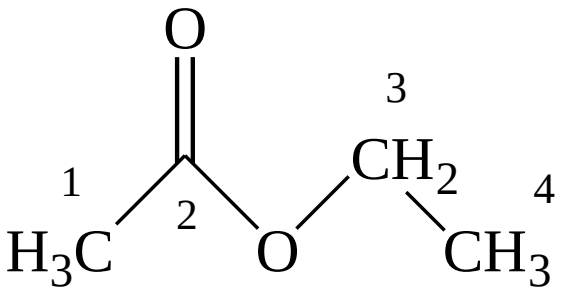
Electronwithdrawing substituent increases δ.

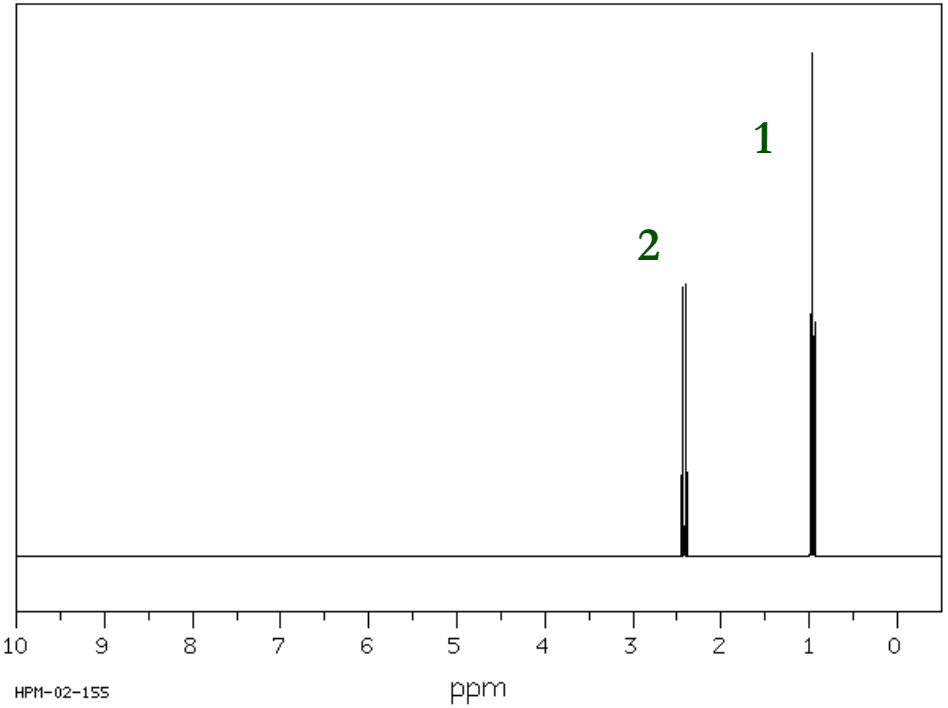
^1H



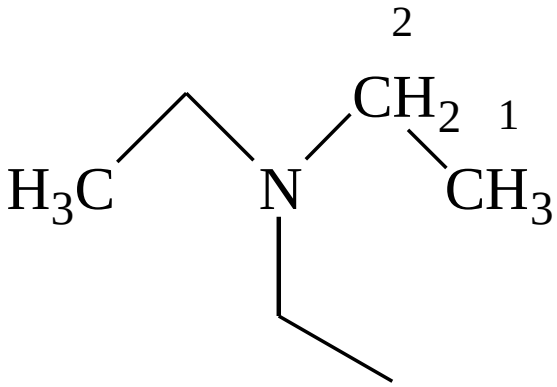


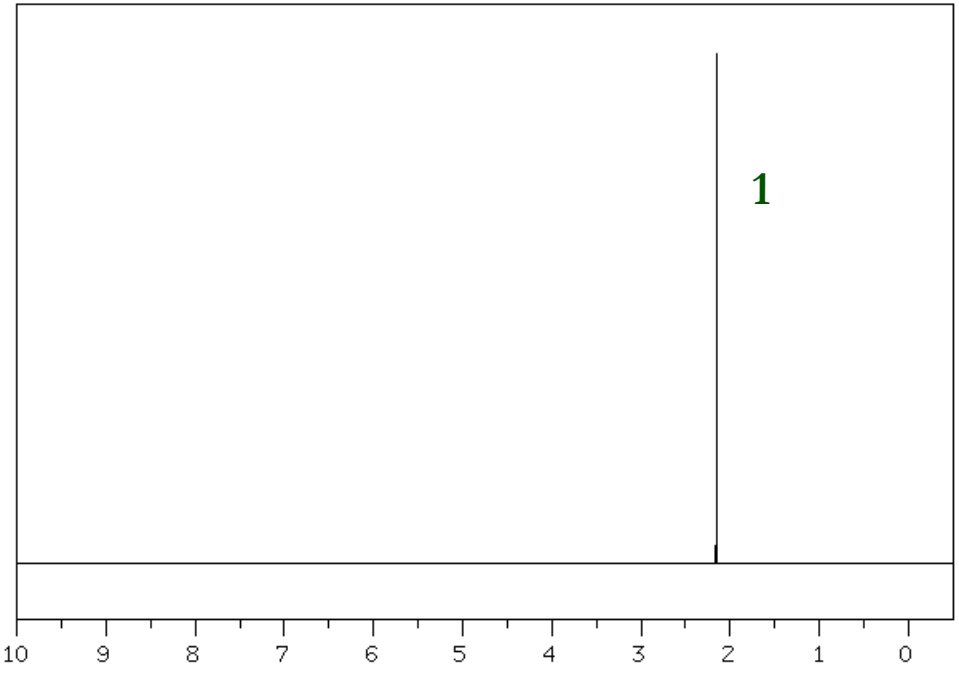
Ethyl acetate



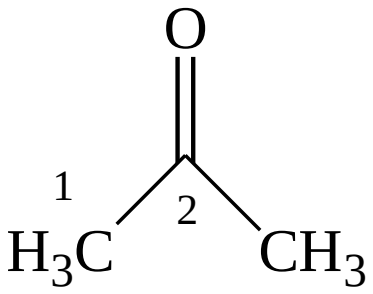


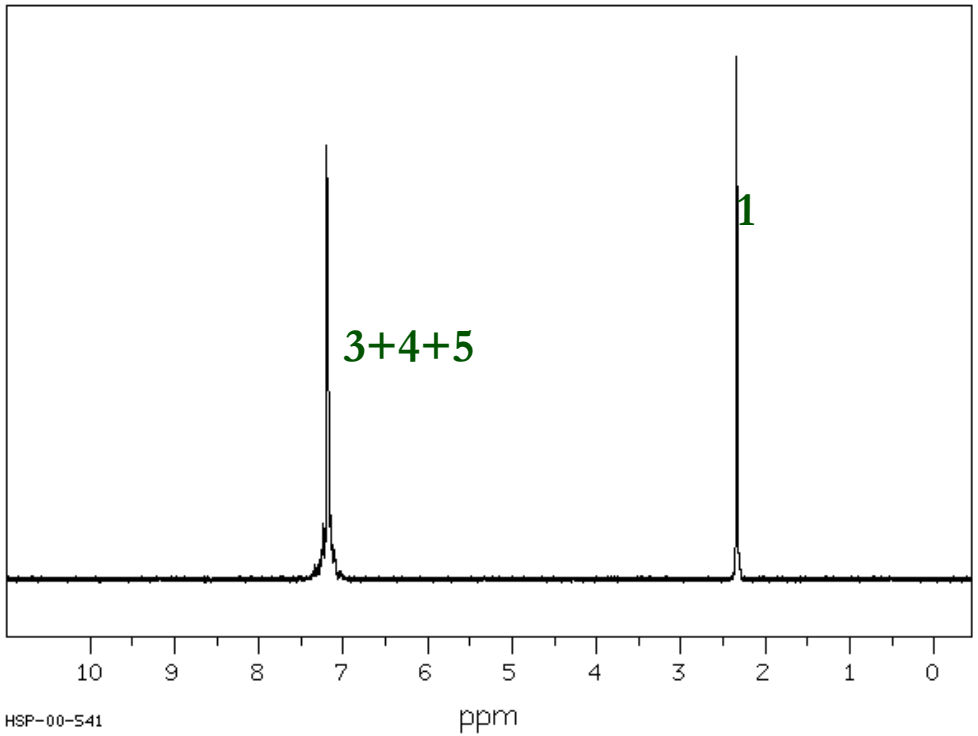
Triethyl amine



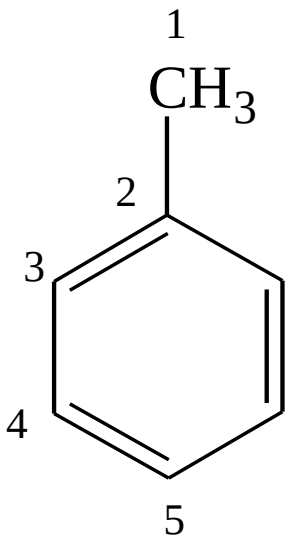


Acetone



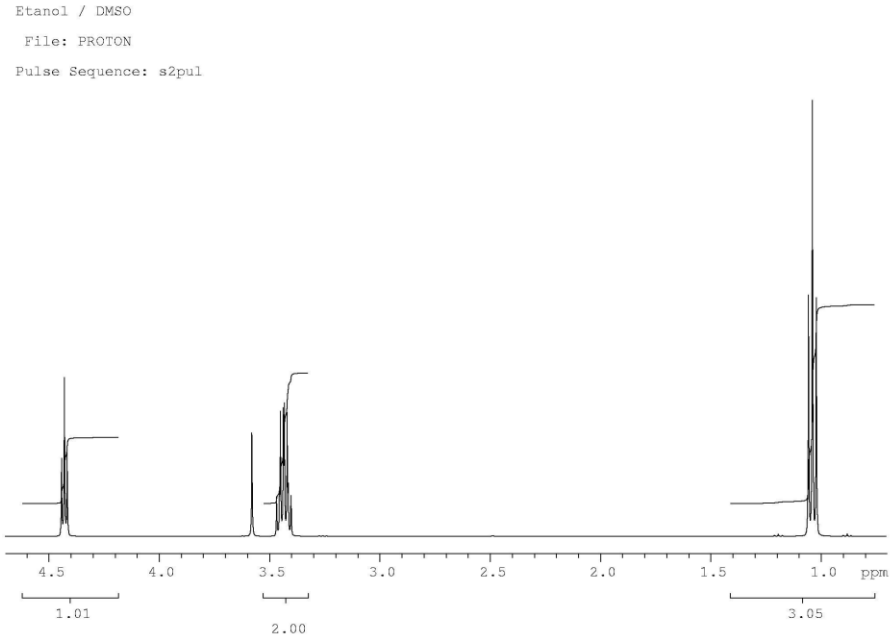


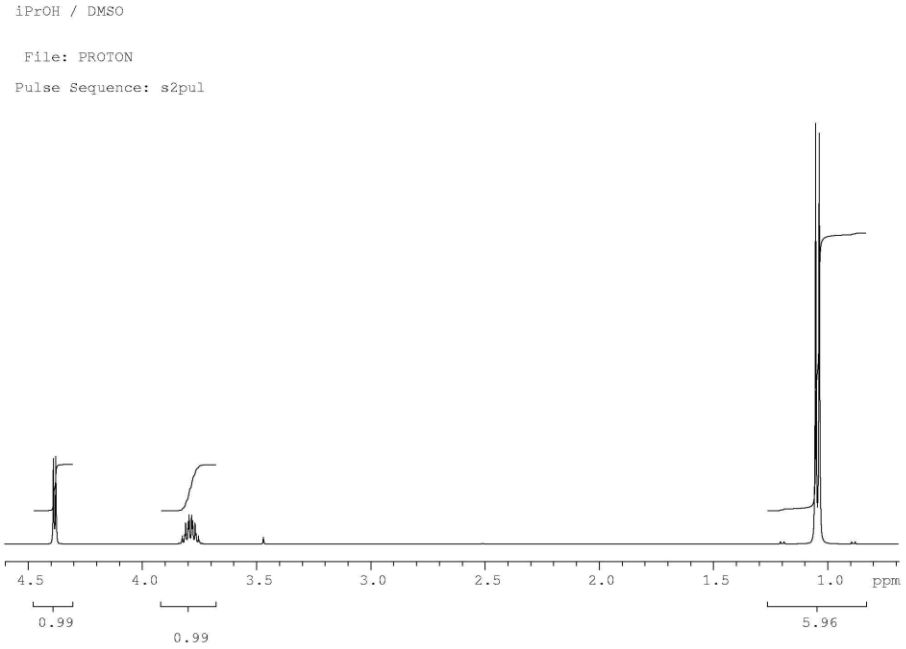
Toluene



Integral

In the ^{1}H spectrum it is proportional to the number of nuclei





Spin-spin coupling

in ^{1}**H spectrum**

Spin state of neighbouring nuclei seen through chemical bonds

Splitting of peaks

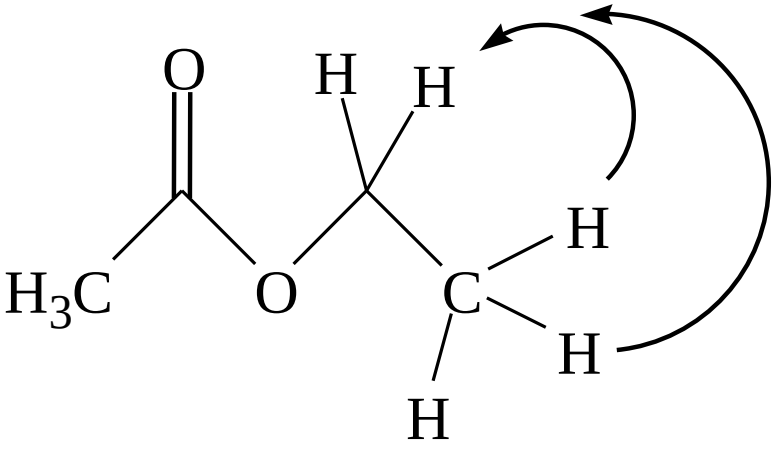
Measured in Hz, not dependent from magnetic field

Same for the coupling partners

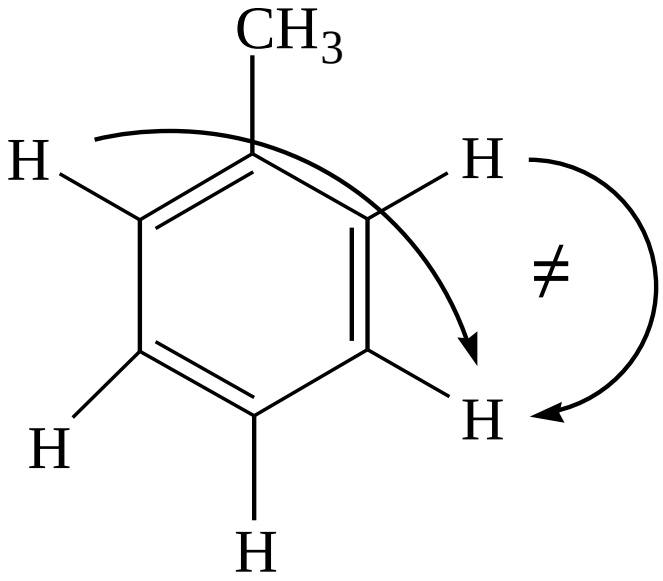
VERY dependent from bond angle (eg, and everything else)

Equivalent nuclei: chemically and magnetically equivalent:

their relationship to the remaining part of the molecule is the same



BUT!



Chemically equivalent but magnetically not!

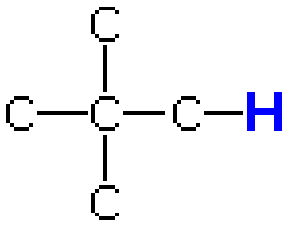
No visible coupling between equivalent nuclei, but always between nonequivalent ones!

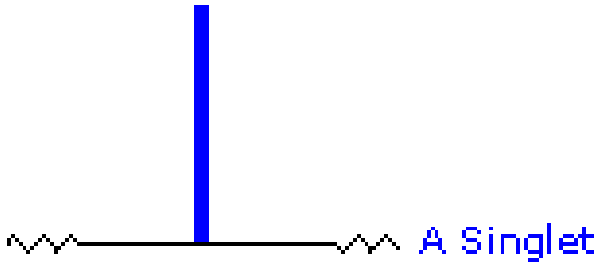
***n*+1-rule: *n* equvalent partners results in *n*+1 multiplicity**

(IF I=1/2)

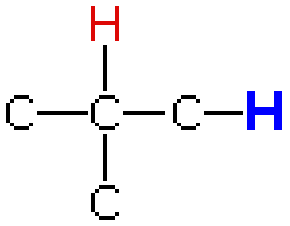
Pascal triangle

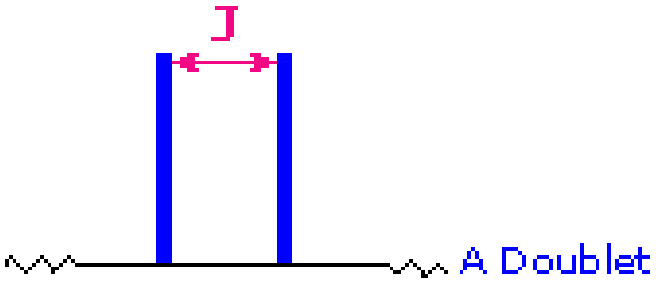
No Coupled Hydrogens



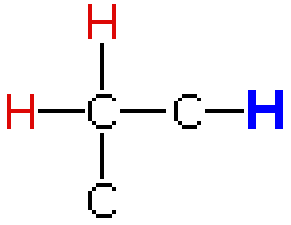


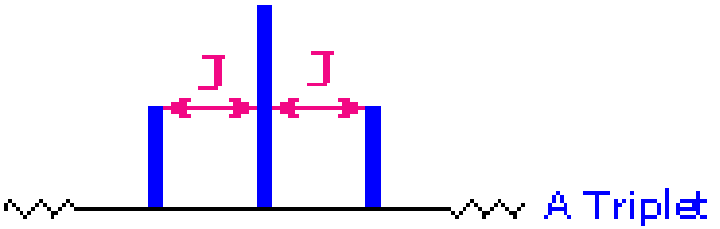
One Coupled Hydrogen



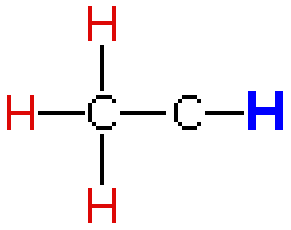


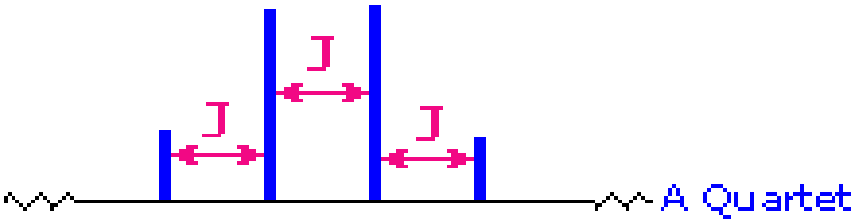
Two Coupled Hydrogens

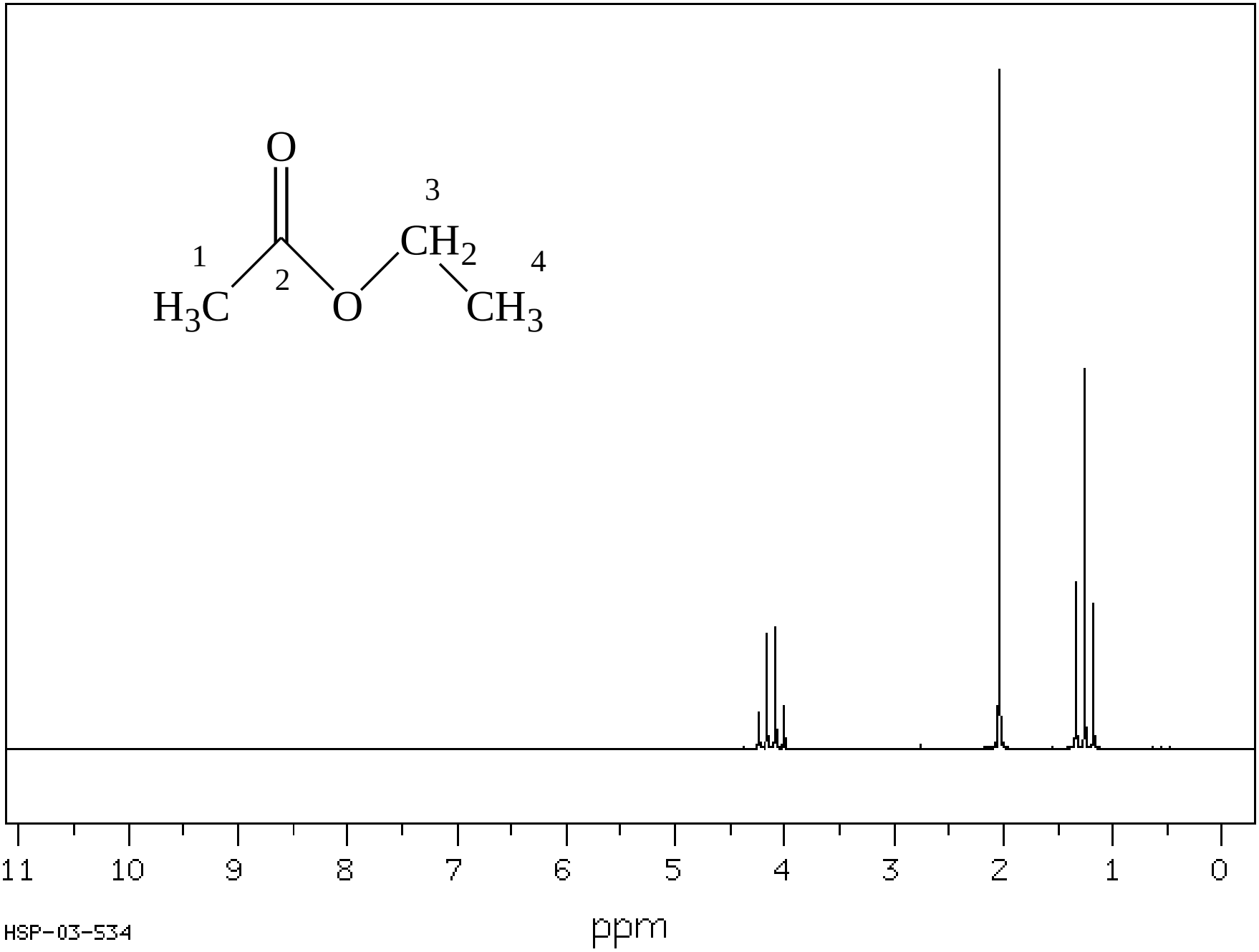




Three Coupled Hydrogens





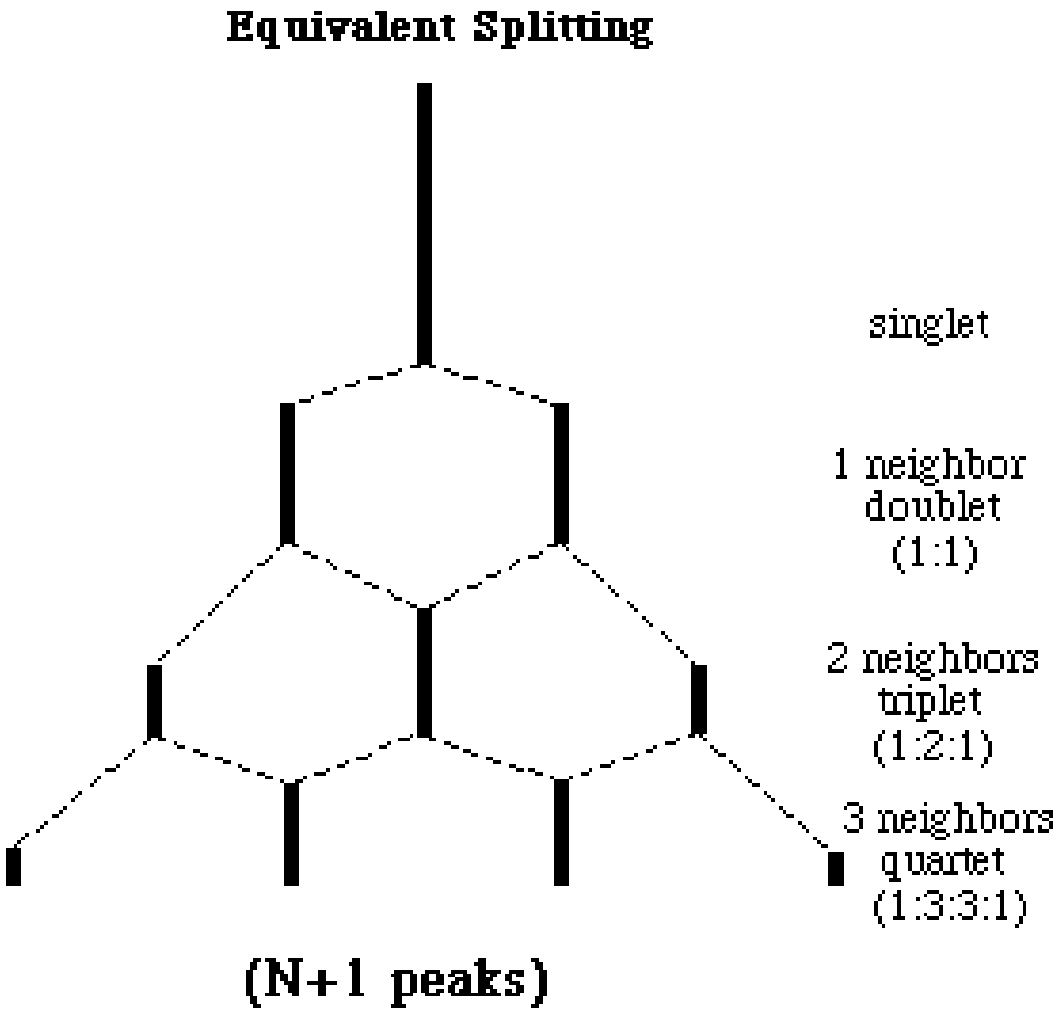

O
3
1
CH2
4
2
H3C
O
CH3
11
10
9
8
7
6
5
4
3
2
1
0
HSP-03-534
ppm

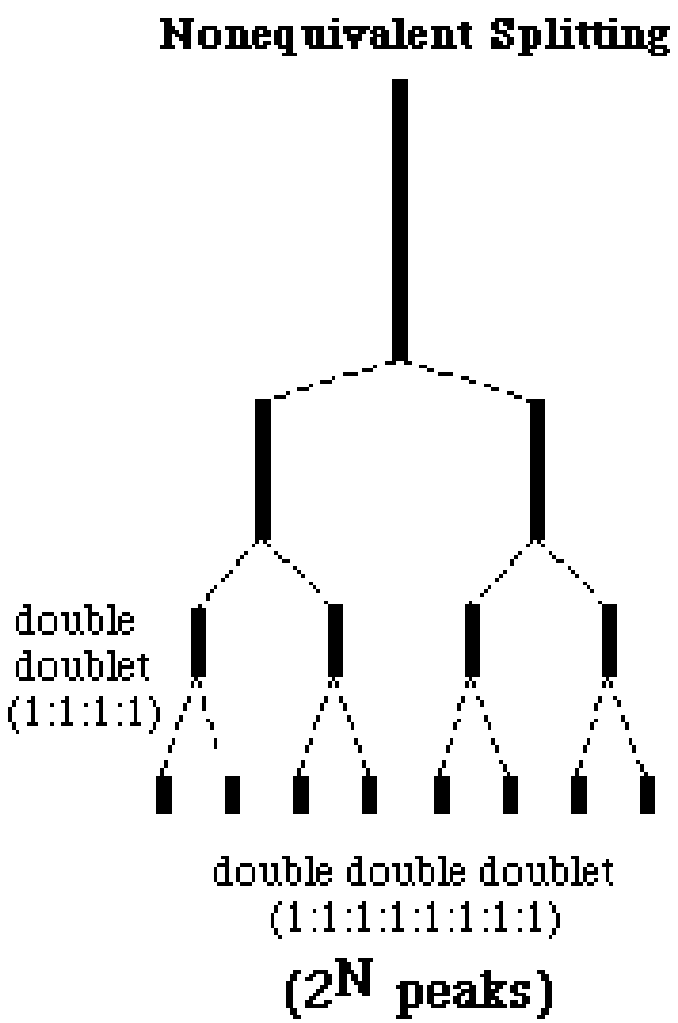
Coupling caused by different nuclei

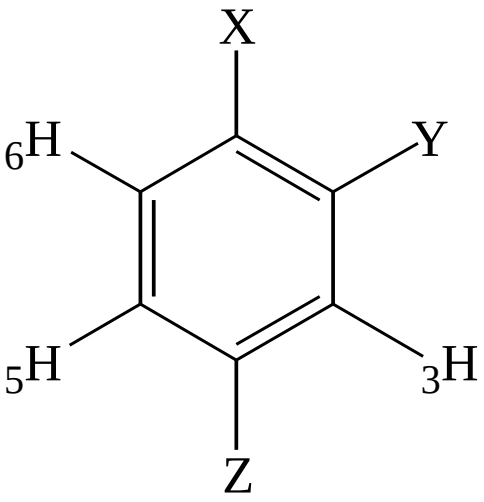
If there are more different couling partners, the couplings caused are superimposed onto each other

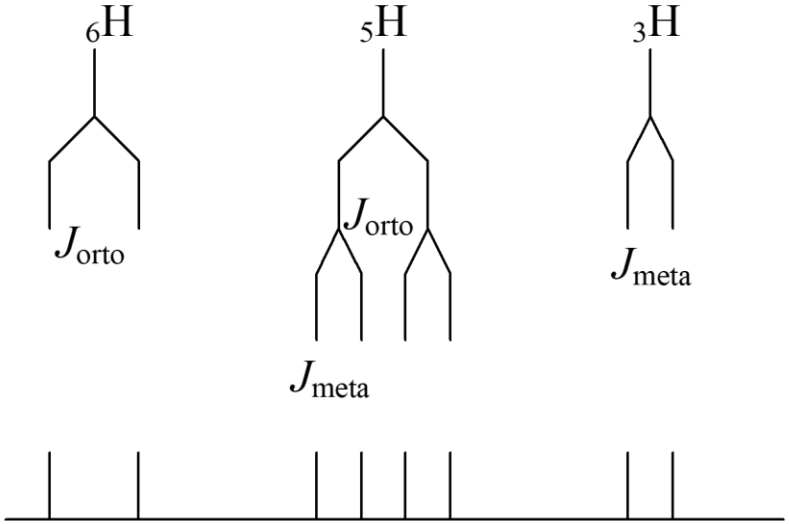
Can be derived step by step

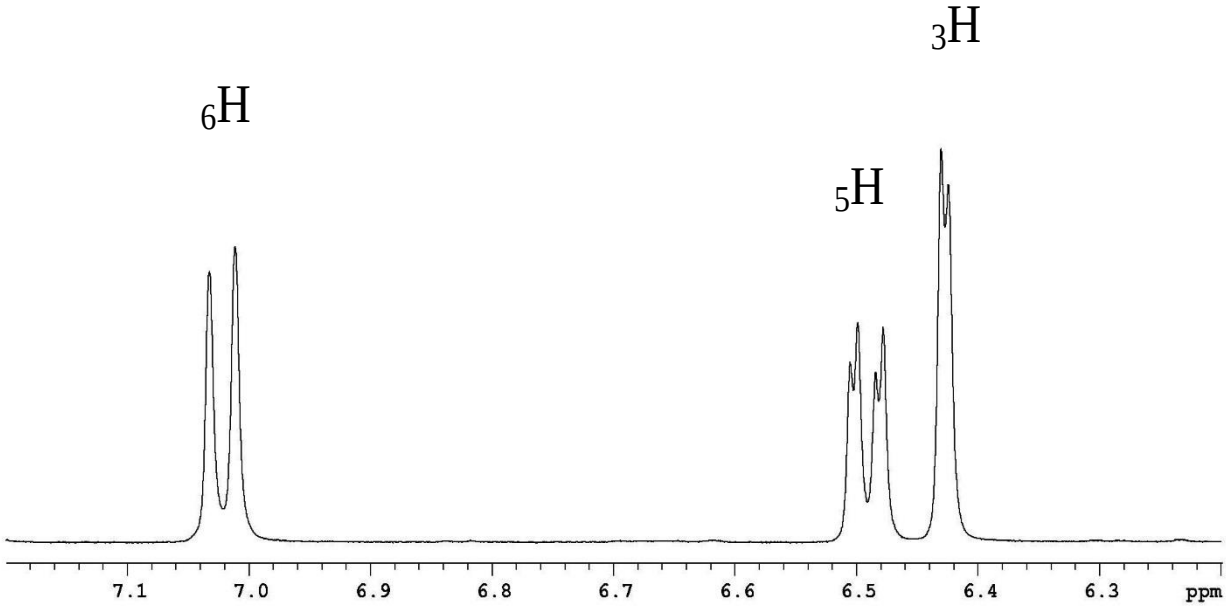
Splitting Patterns

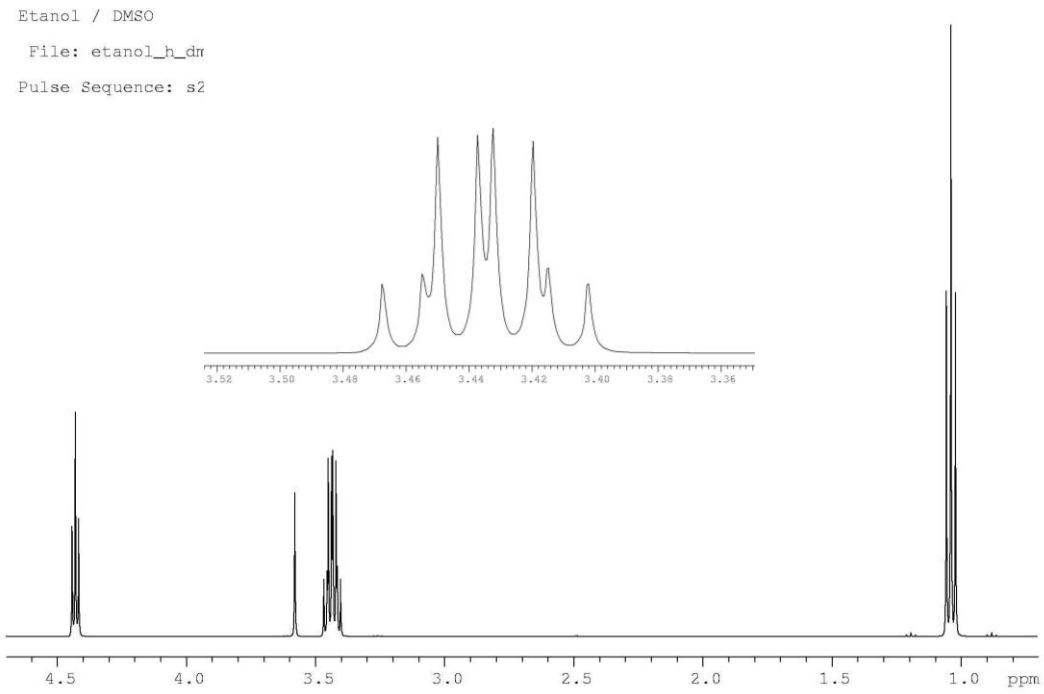


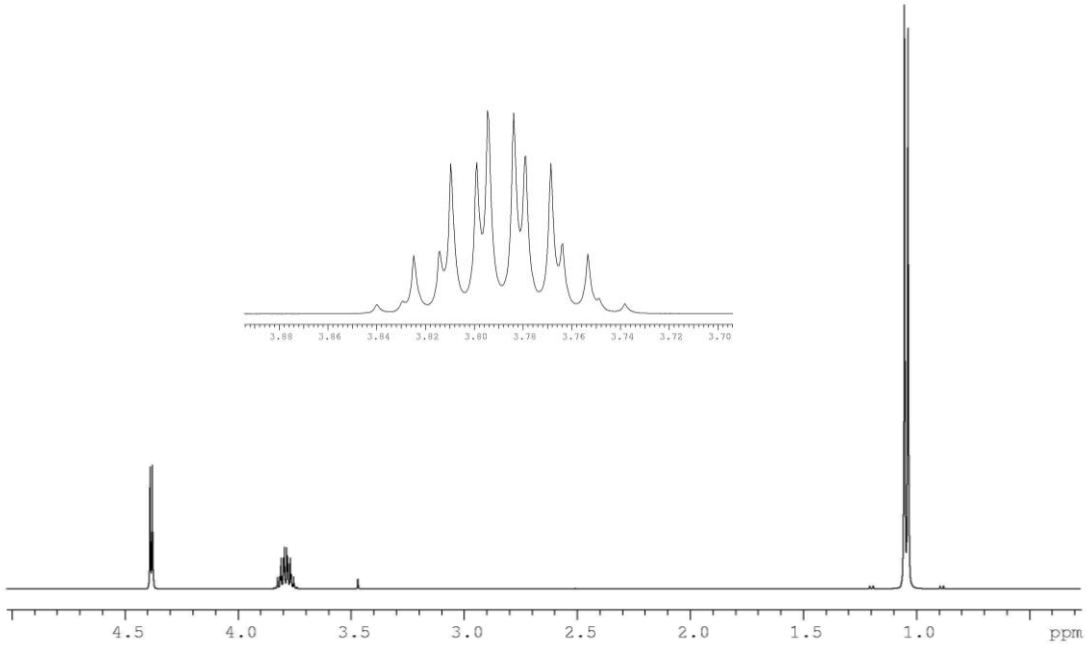


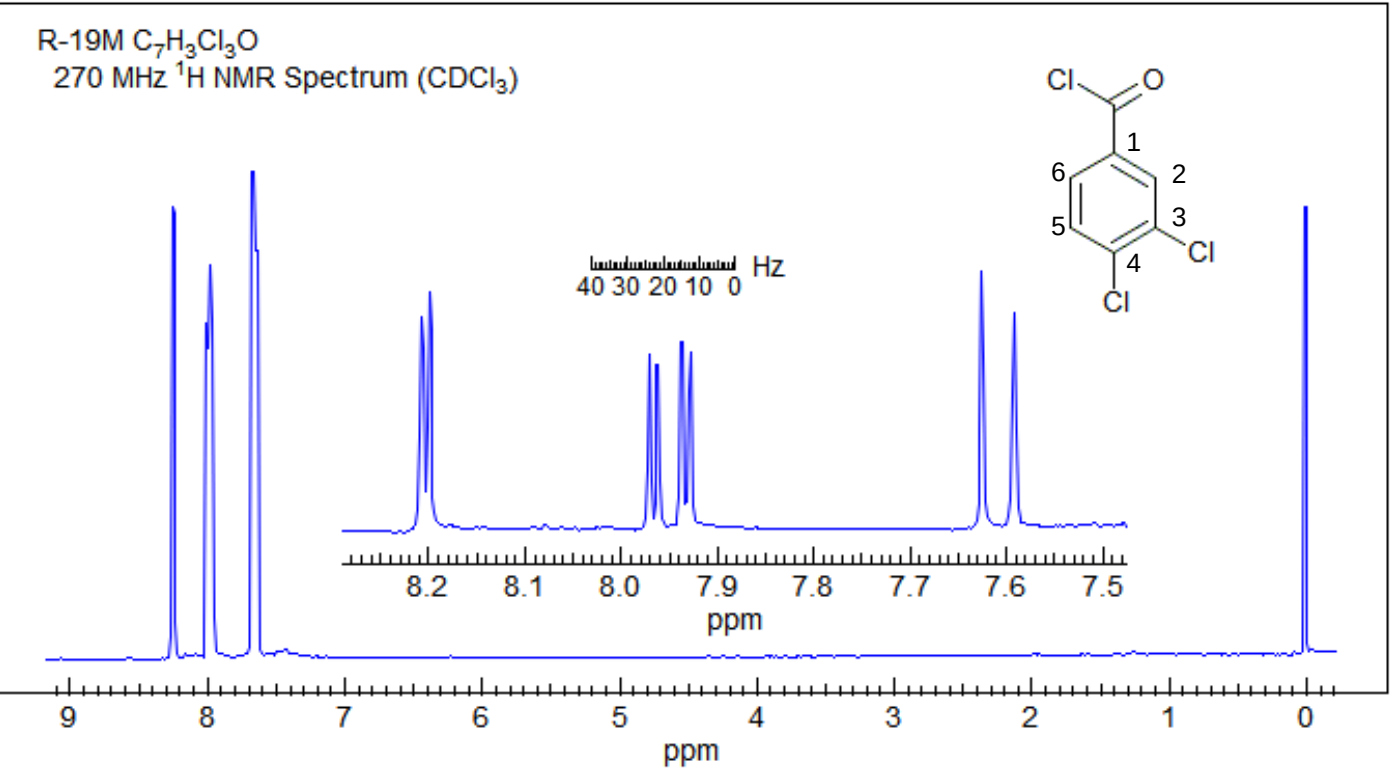

X
Y
Z
6H
5H
3H

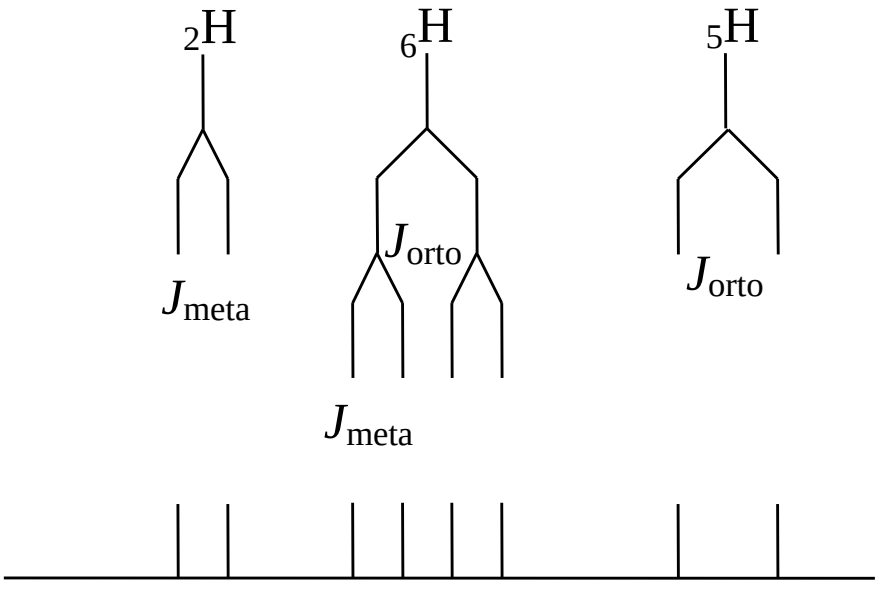

6H
5H
3H
Jorto
Jorto
Jmeta
Jmeta

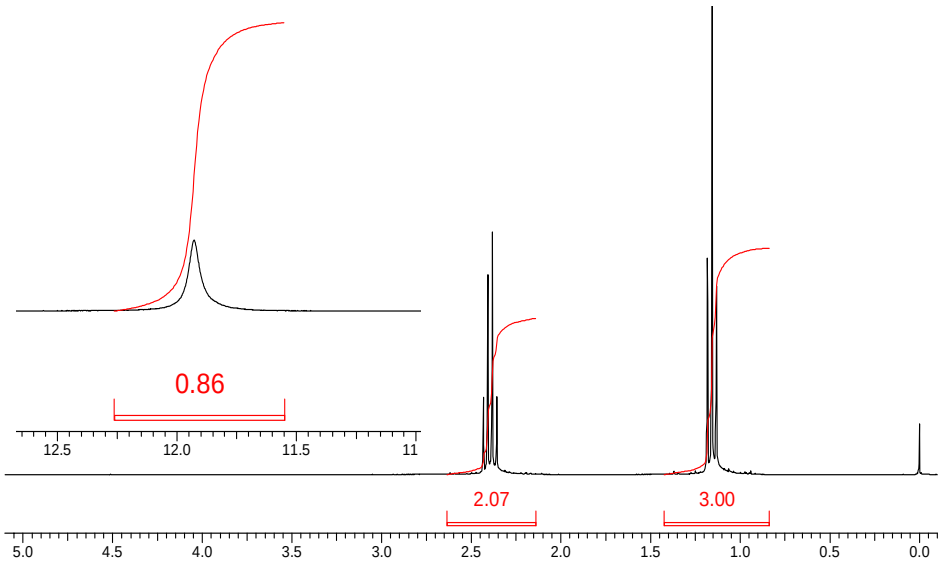

3H
6H
5H
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
ppm

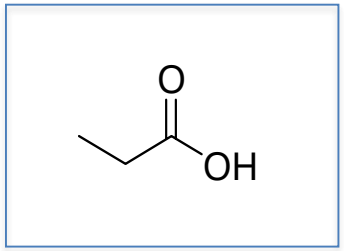

Etanol / DMSO
File: etanol_h_dm
Pulse Sequence: s2
3.52 3.50 3.48 3.46 3.44 3.42 3.40 3.38 3.36
4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm


3.88 3.86 3.84 3.82 3.80 3.78 3.76 3.74 3.72 3.70
4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

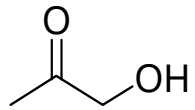

R-19M $C_7H_3Cl_3O$
270 MHz ^1H NMR Spectrum ($CDCl_3$)
Cl
O
1
2
3
Cl
4
Cl
5
6
Hz
40 30 20 10 0
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5
ppm
9 8 7 6 5 4 3 2 1 0
ppm

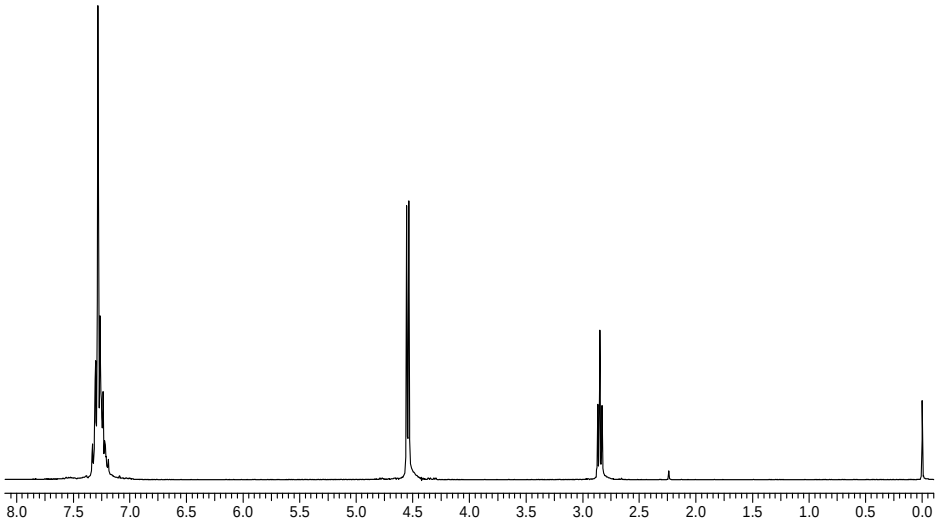

$_2H$
$_6H$
$_5H$
J_{meta}
J_{orto}
J_{orto}
J_{meta}

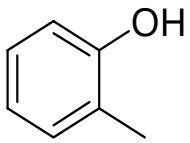

0.86
12.5
12.0
11.5
11
2.07
3.00
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


O
OH

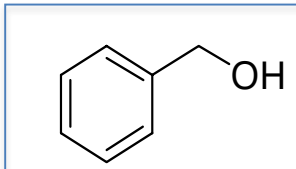
or


O
OH

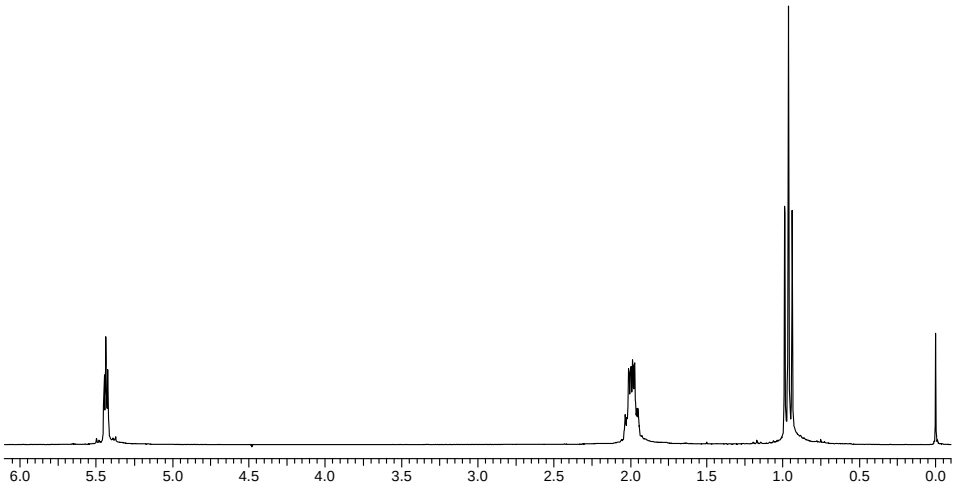

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

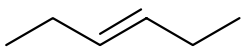

OH

or

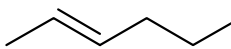

OH

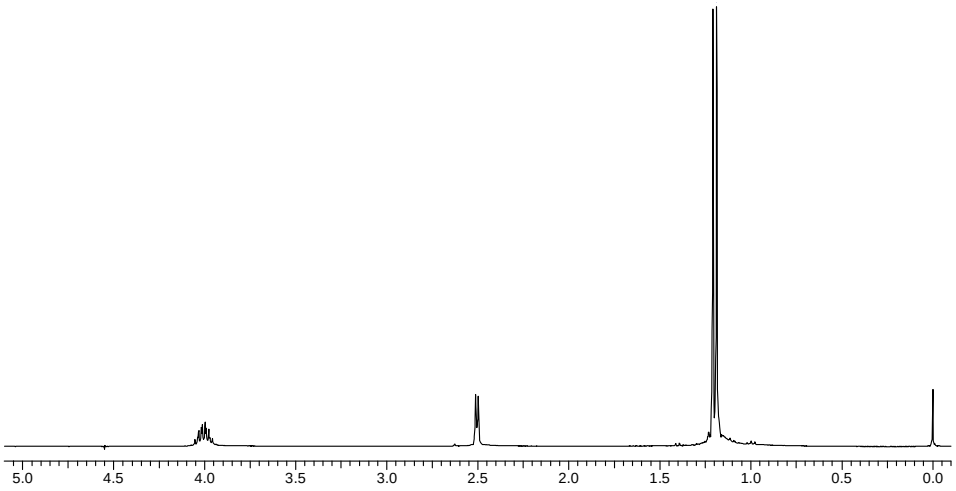
Homework

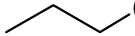




or







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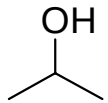
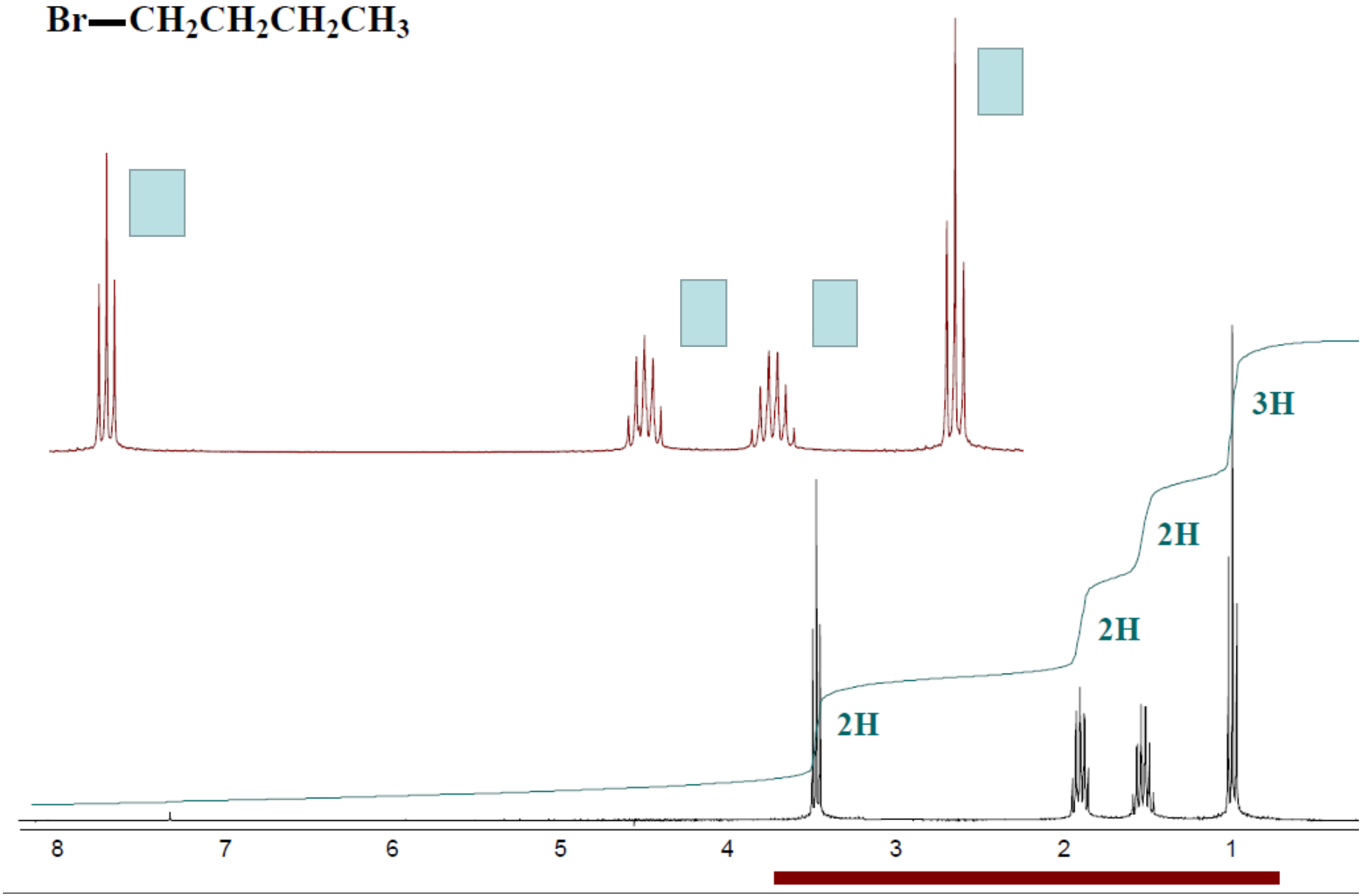
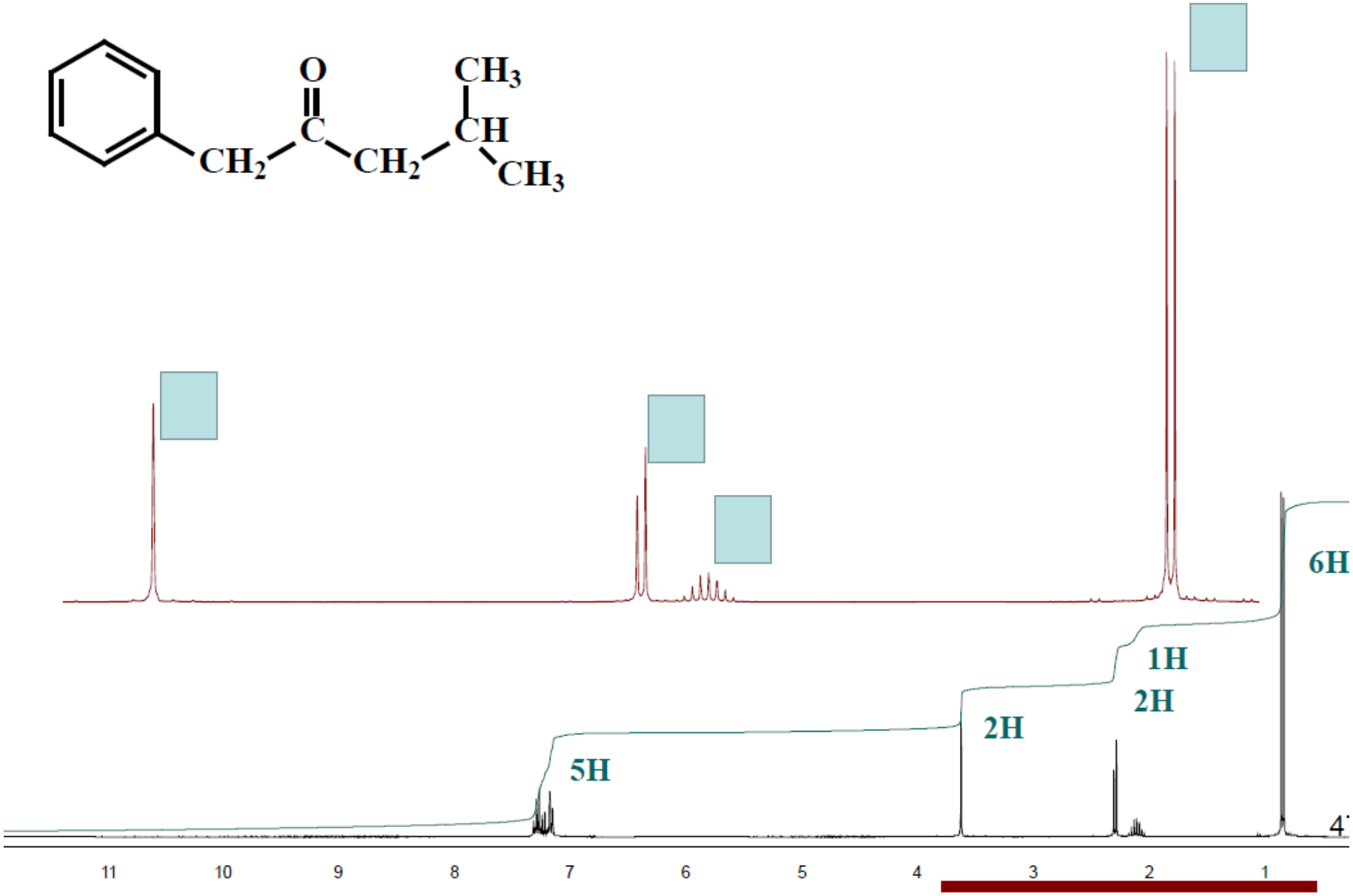
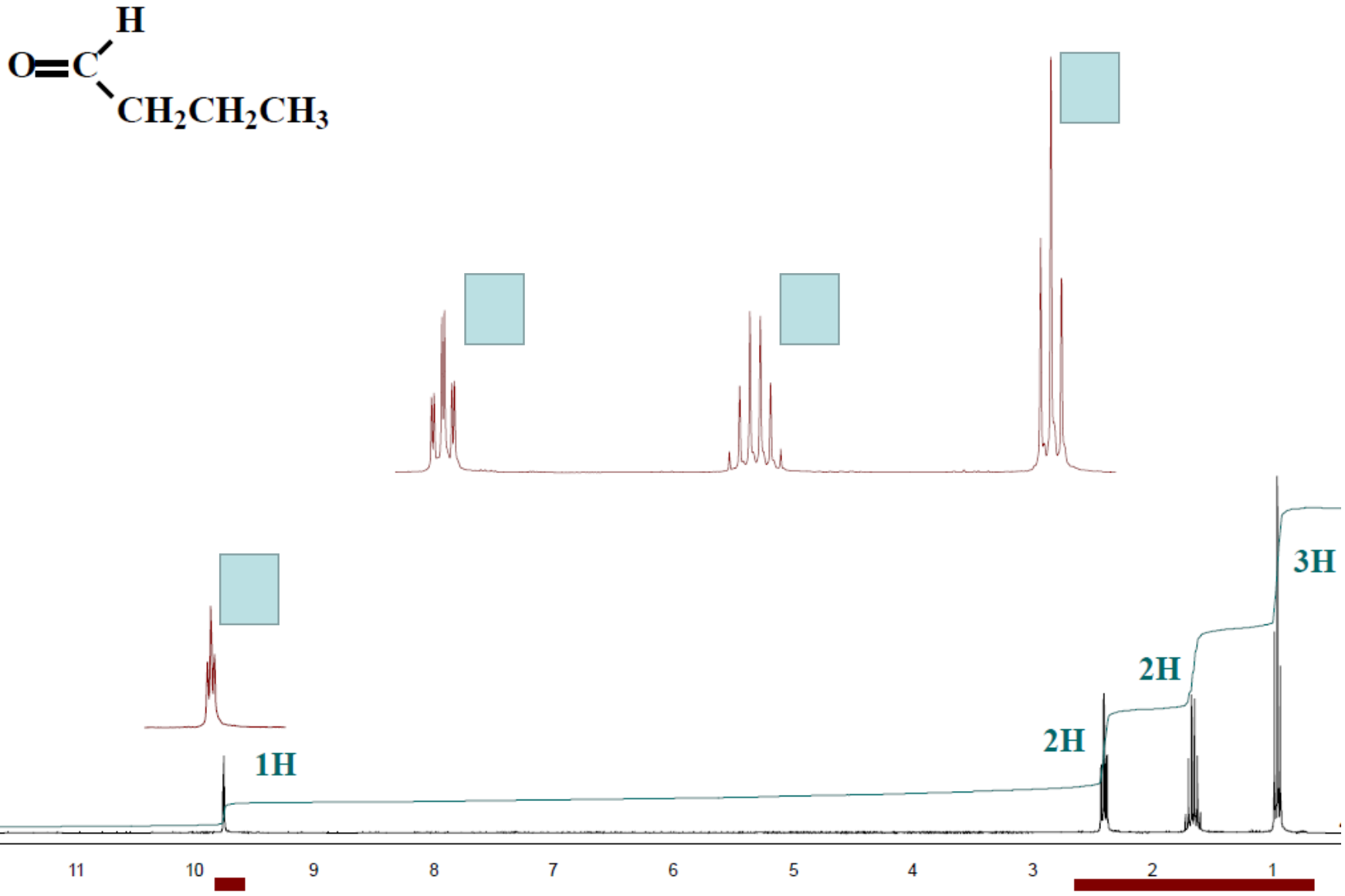
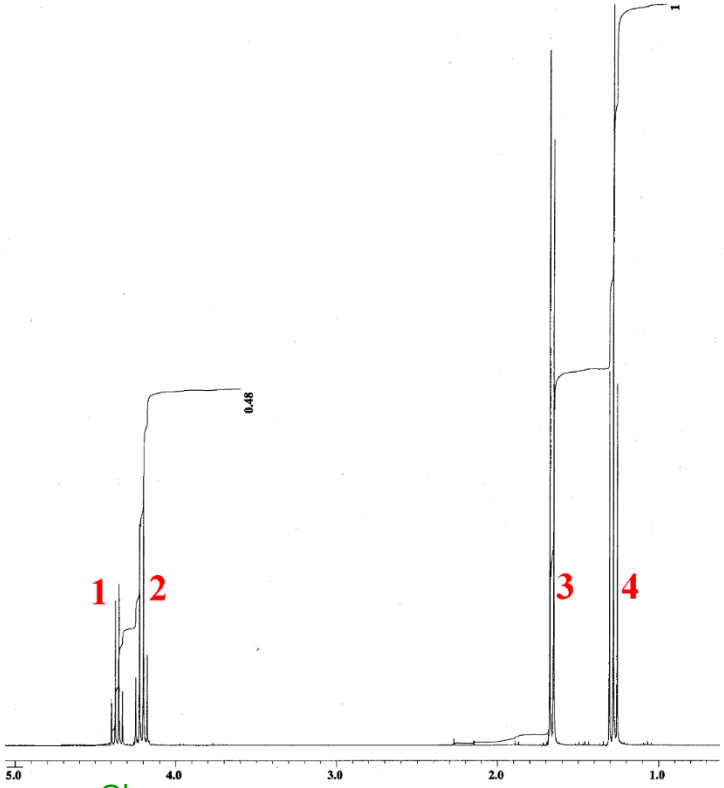


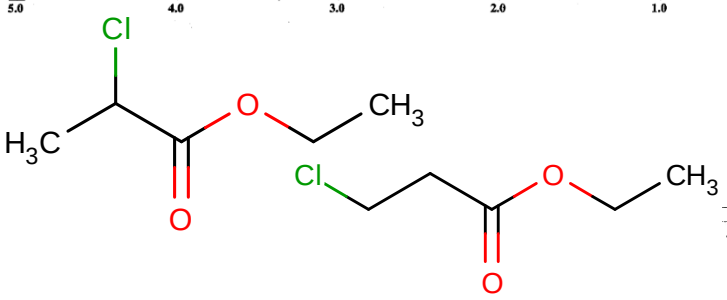

Br—CH2CH2CH2CH3
3H
2H
2H
2H
8
7
6
5
4
3
2
1

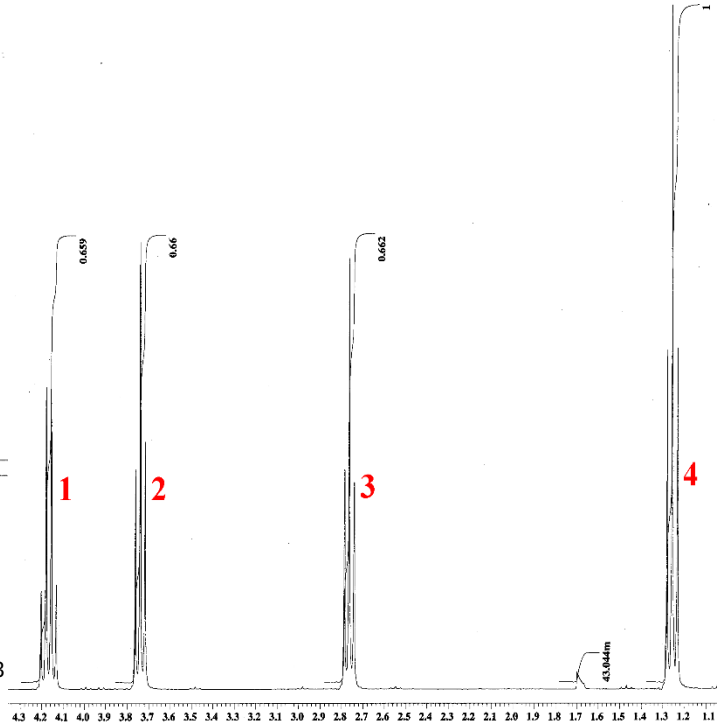

O
CH3
C
CH
CH2
CH2
CH3
6H
1H
2H
2H
5H
11
10
9
8
7
6
5
4
3
2
1

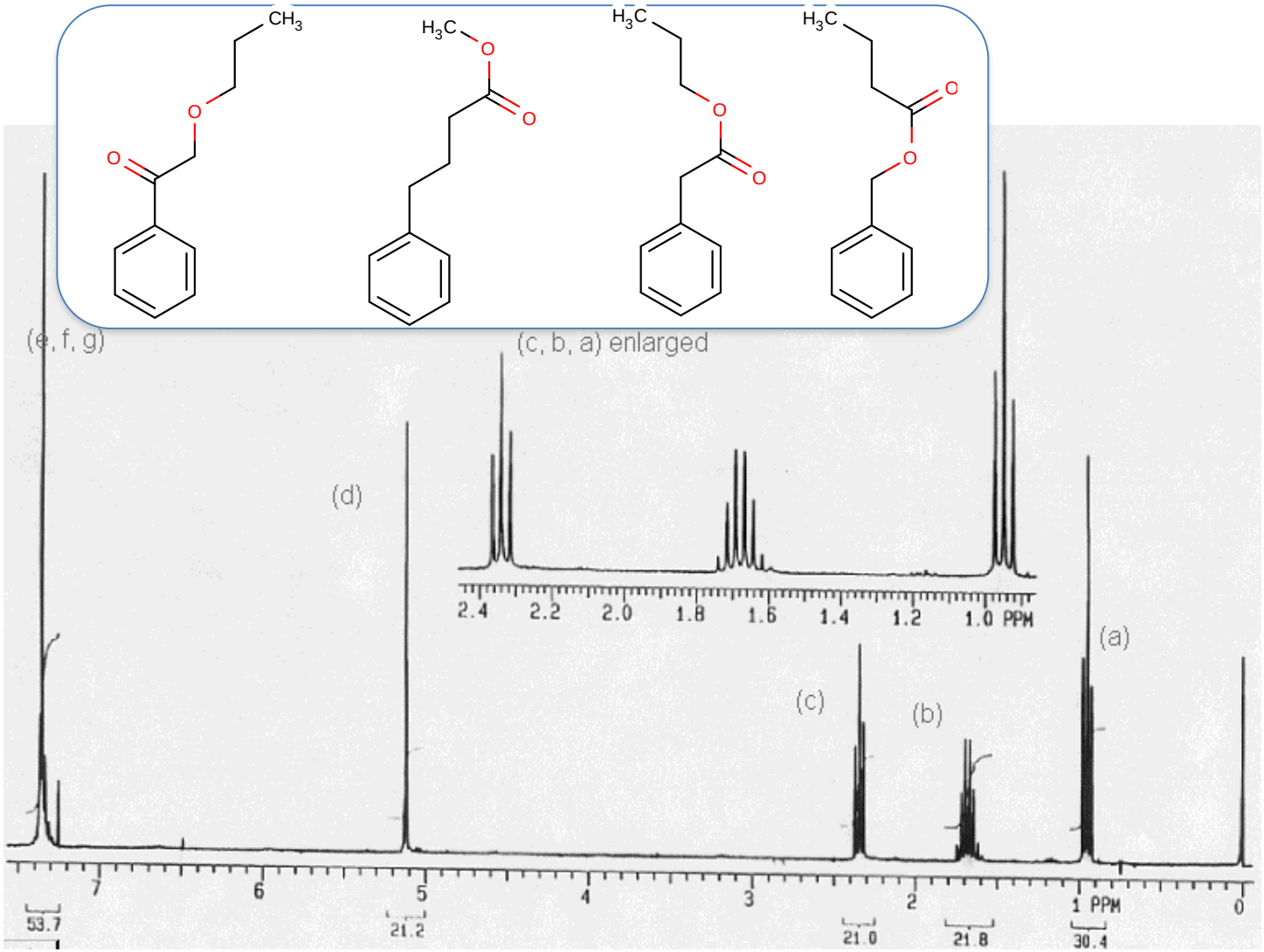

H
O
C
CH2CH2CH3
1H
2H
2H
3H
11
10
9
8
7
6
5
4
3
2
1

Ethyl chloropropionates, which is which?








(e, f, g)
(d)
(c, b, a) enlarged
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0 PPM
(c)
(b)
(a)
7
6
5
4
3
2
1 PPM
0
53.7
21.2
21.0
21.8
30.4