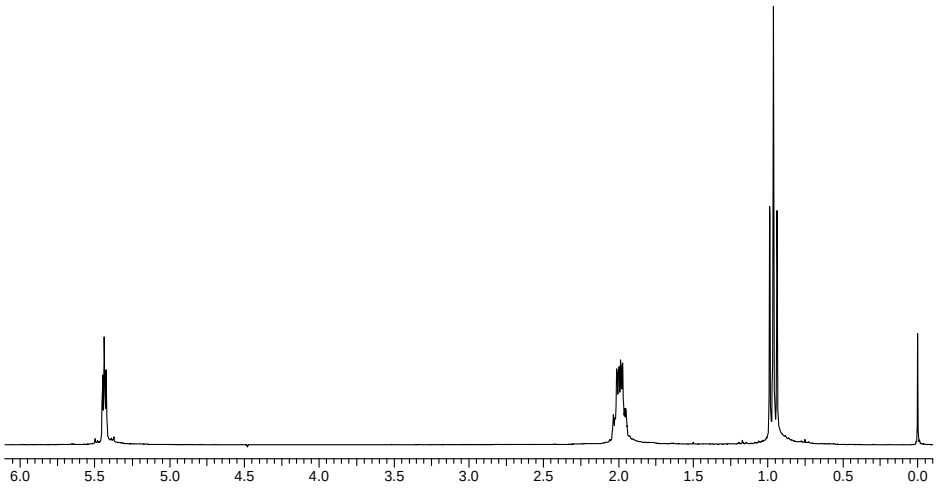
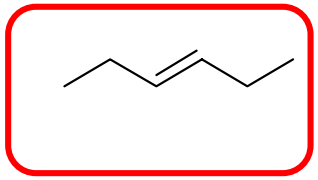
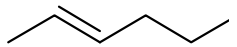
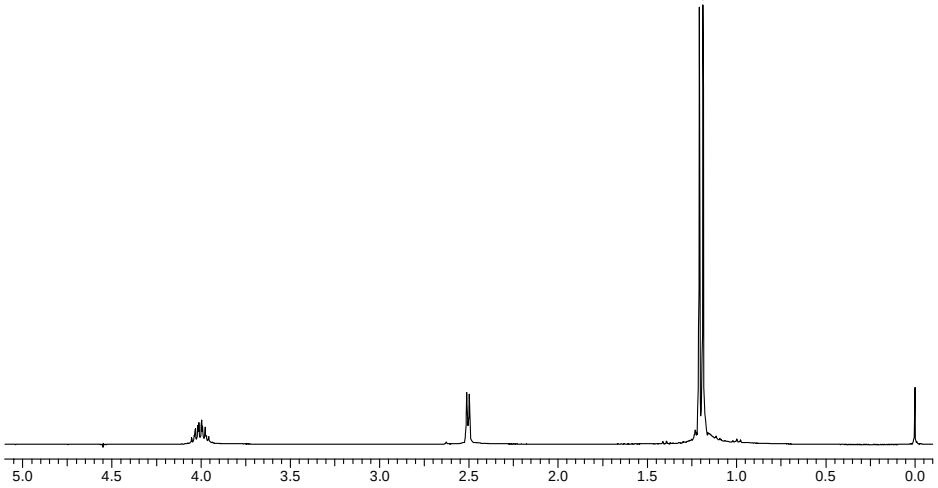
Homework

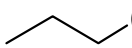




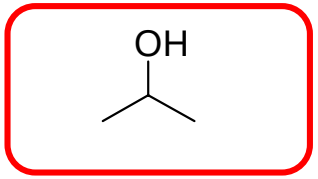
or



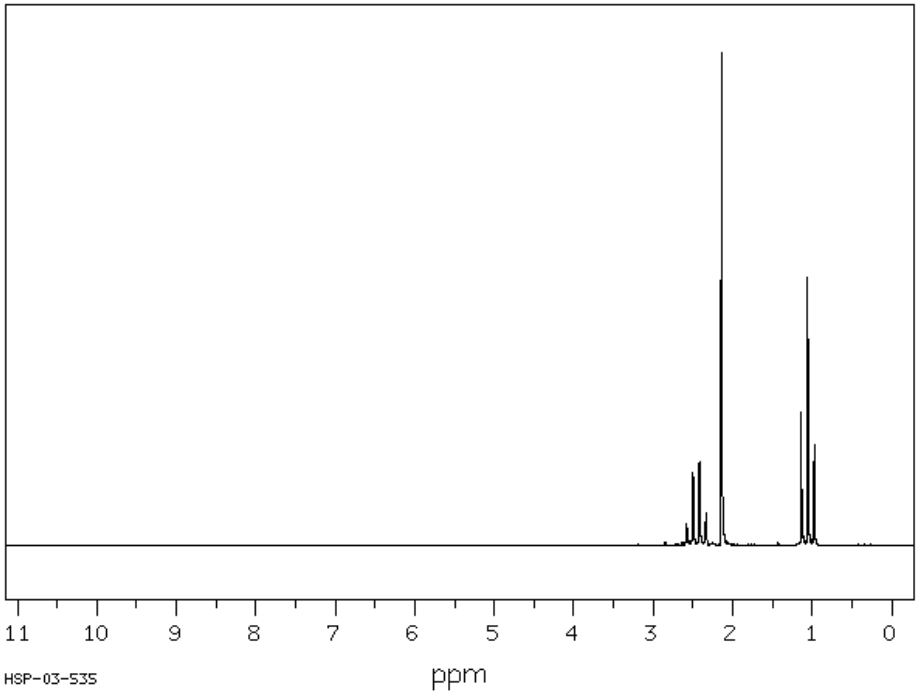


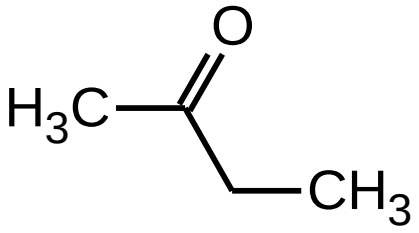


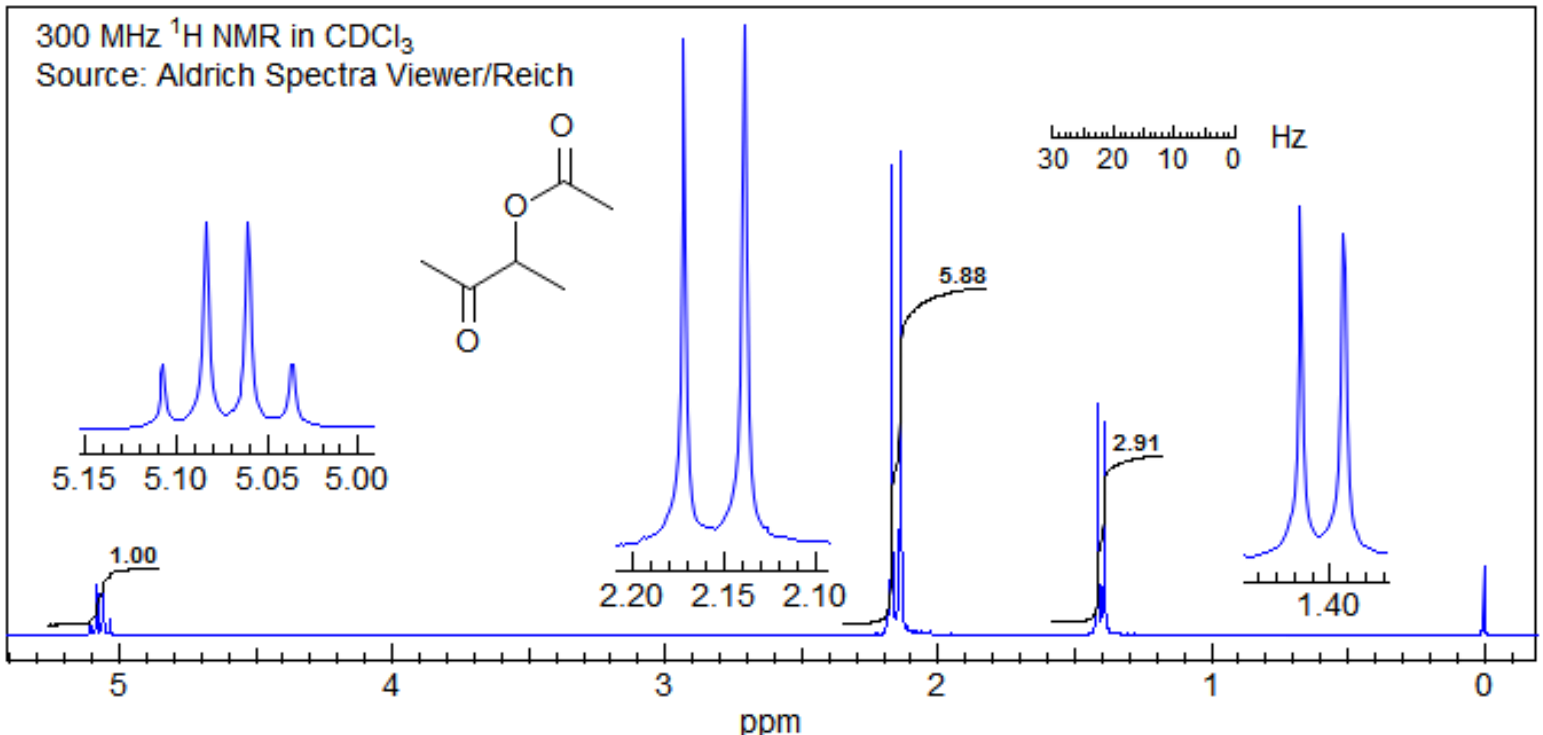
or

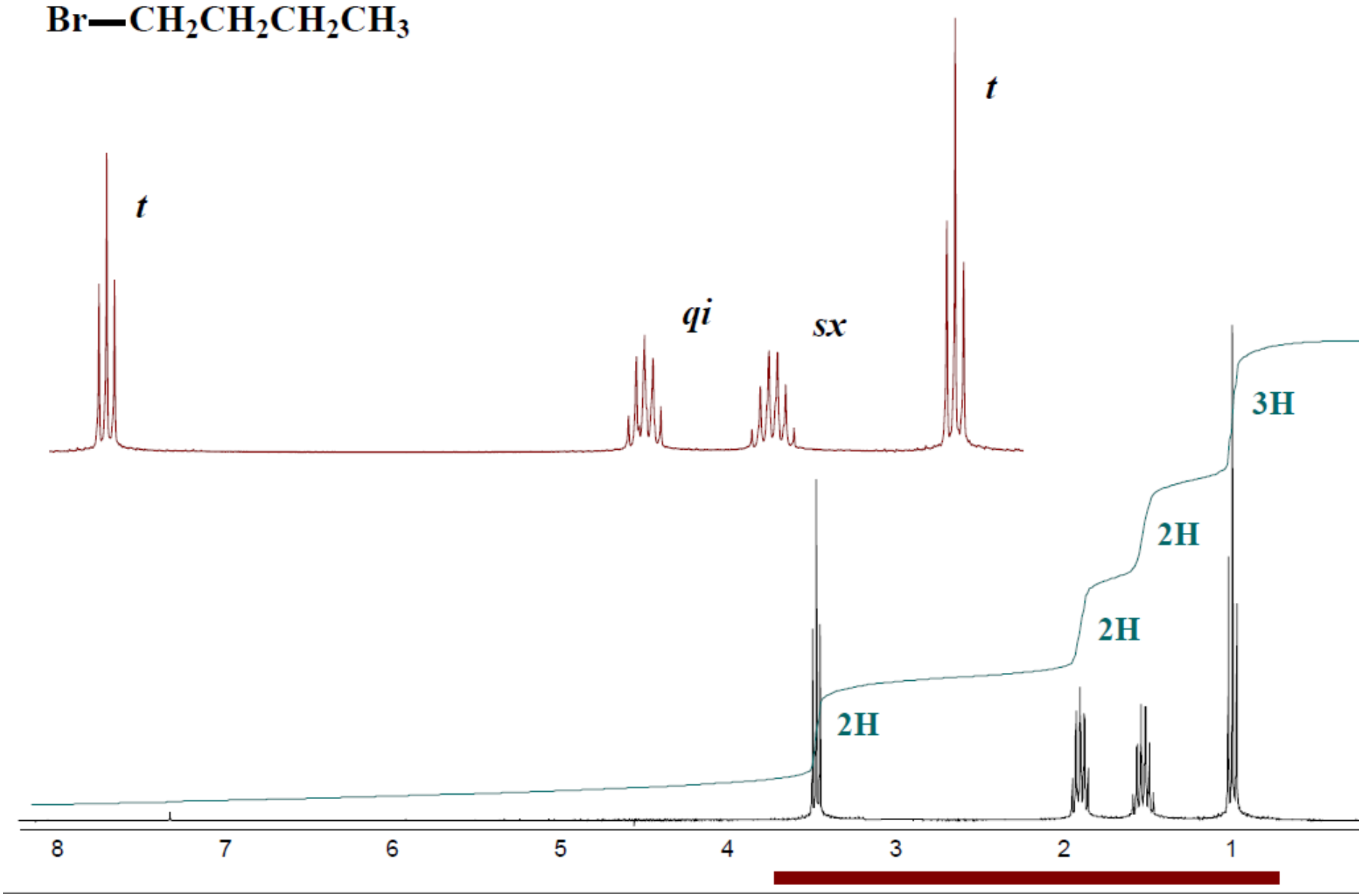


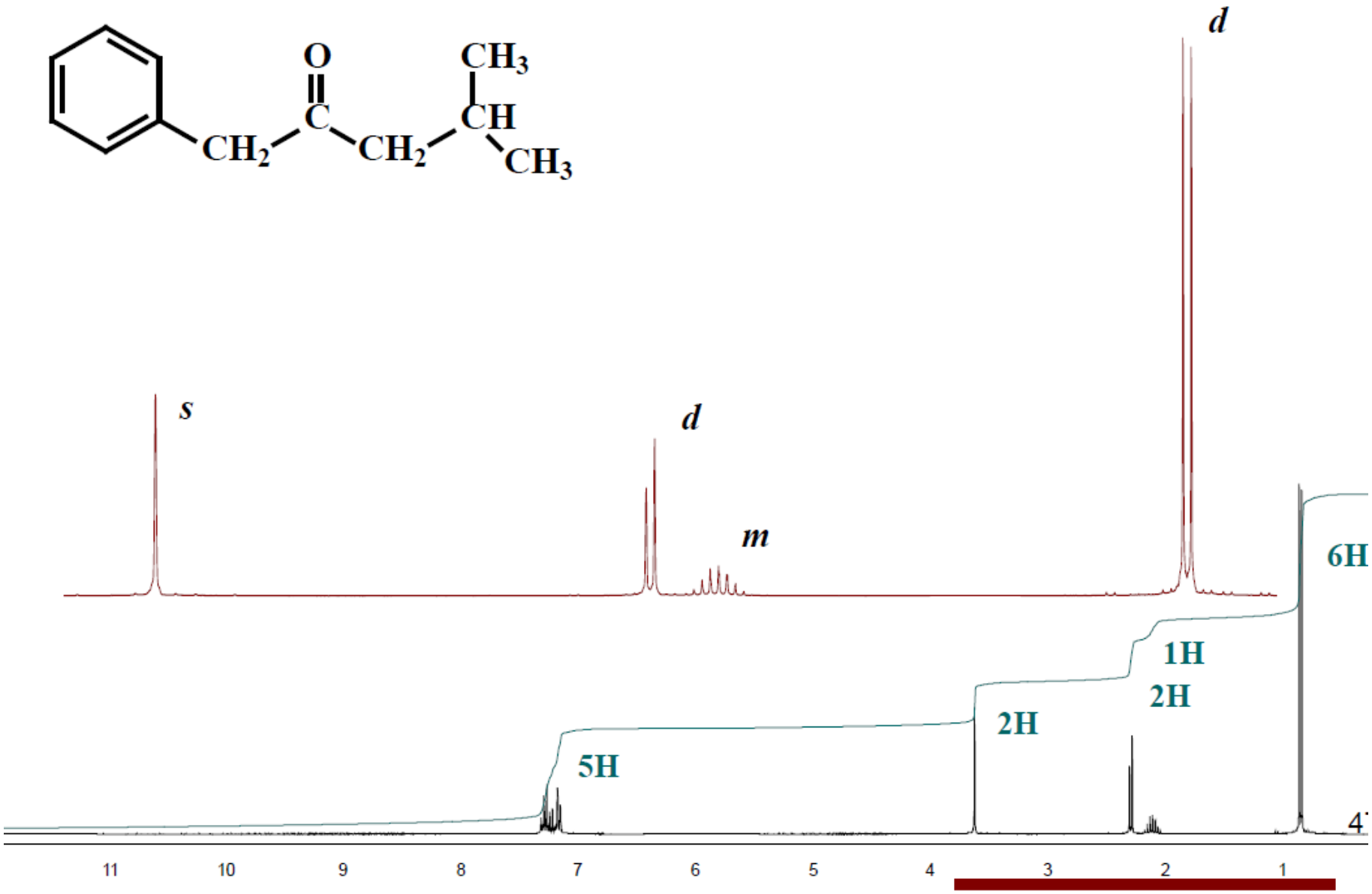
Coupling with OH is not always visible, depends on solvent

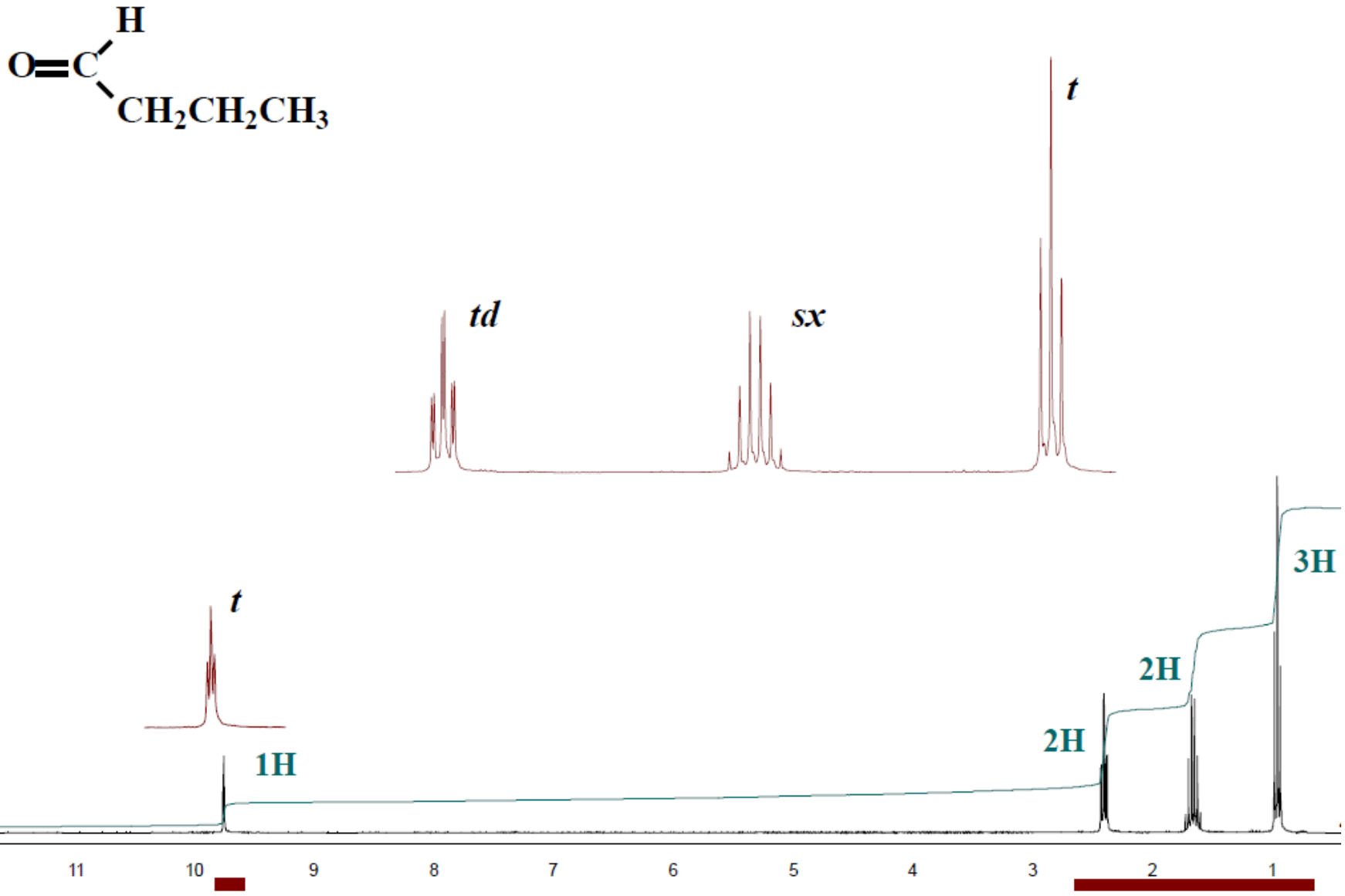

11 10 9 8 7 6 5 4 3 2 1 0
ppm
HSP-03-535


O
H3C
CH3

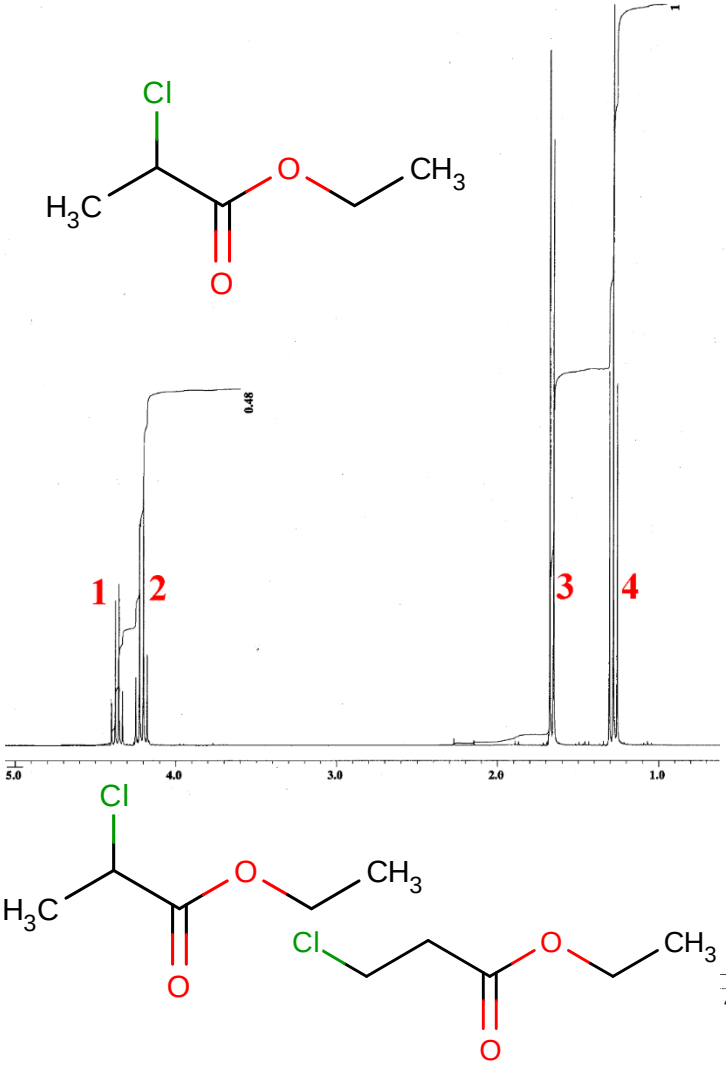

300 MHz 1H NMR in CDCl3
Source: Aldrich Spectra Viewer/Reich
O
O
O
5.15 5.10 5.05 5.00
1.00
2.20 2.15 2.10
5.88
30 20 10 0 Hz
2.91
1.40
5 4 3 2 1 0
ppm

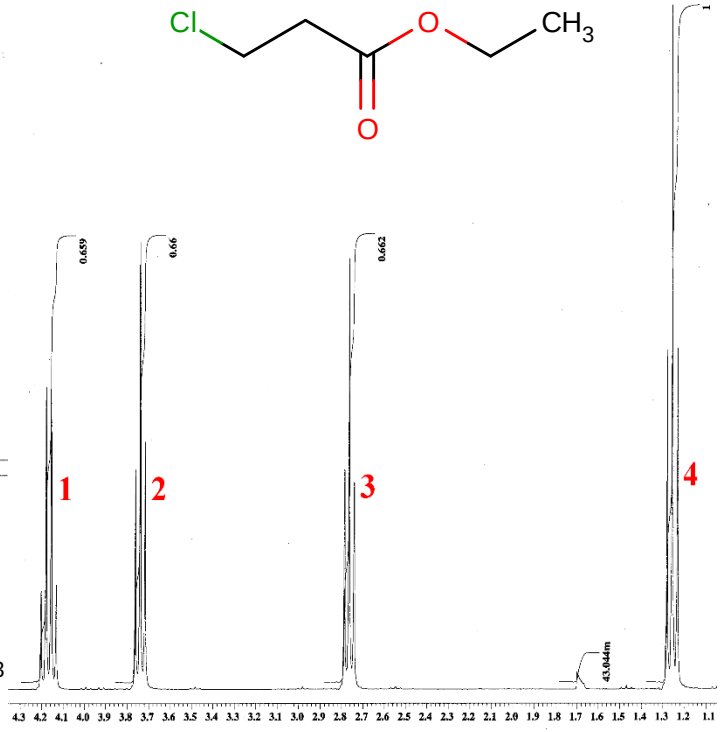

Br—CH2CH2CH2CH3
t
t
qi
sx
3H
2H
2H
2H
8
7
6
5
4
3
2
1

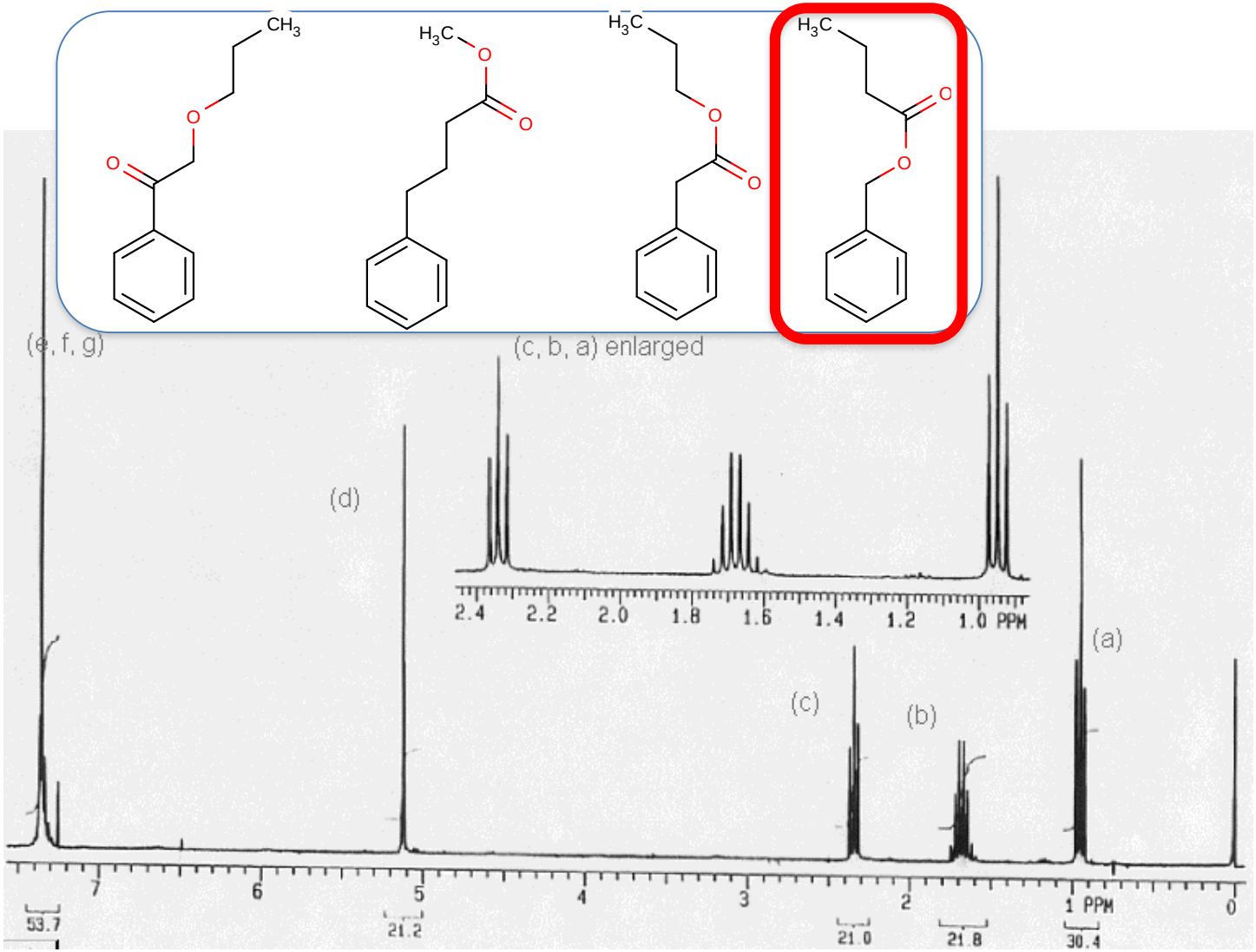

O
CH3
C
CH
CH2
CH2
CH3
d
s
d
m
6H
1H
2H
2H
5H
11
10
9
8
7
6
5
4
3
2
1


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

Ethyl chloropropionates, which is which?



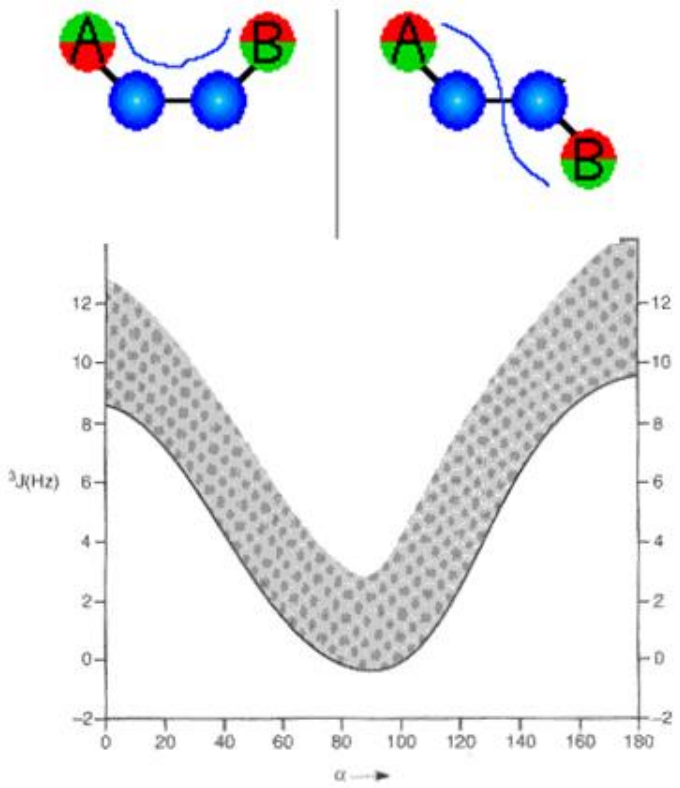



(e, f, g)
(d)
(c, b, a) enlarged
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0 PPM
(c)
(b)
(a)
7
6
5
4
3
2
1 PPM
0
53.7
21.2
21.0
21.8
30.4

Information about

1.Coupling partners → Constitution

2.Bond angle → 3D structure!!!

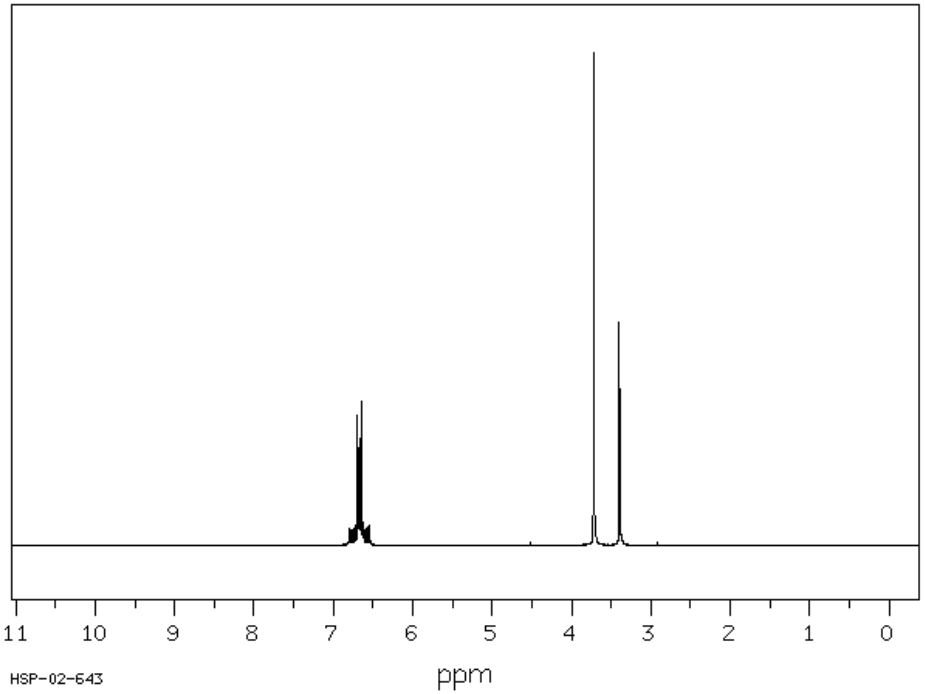


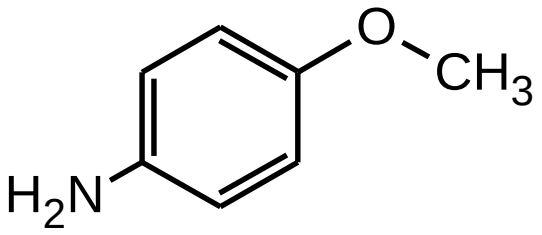
Karplus equation

Coupling constants

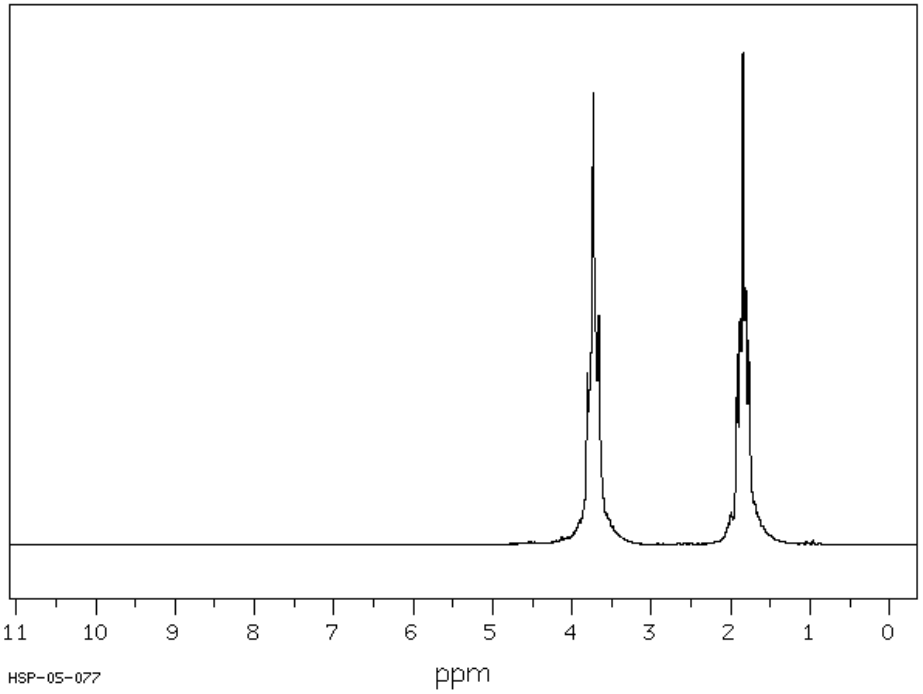
^{2}J aliphatic	10-16	cis	12
^{2}J sp^2	1-2	trans	16
^{3}J aliphatic free rotation	6-7	ortho	7-9
ax-ax	12	meta	2
ax-eq, eq-eq	2-3	para	1

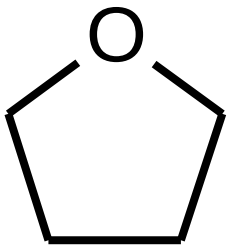
Lots of experimentally collected values can be find in tables





Non first order spectra!!!





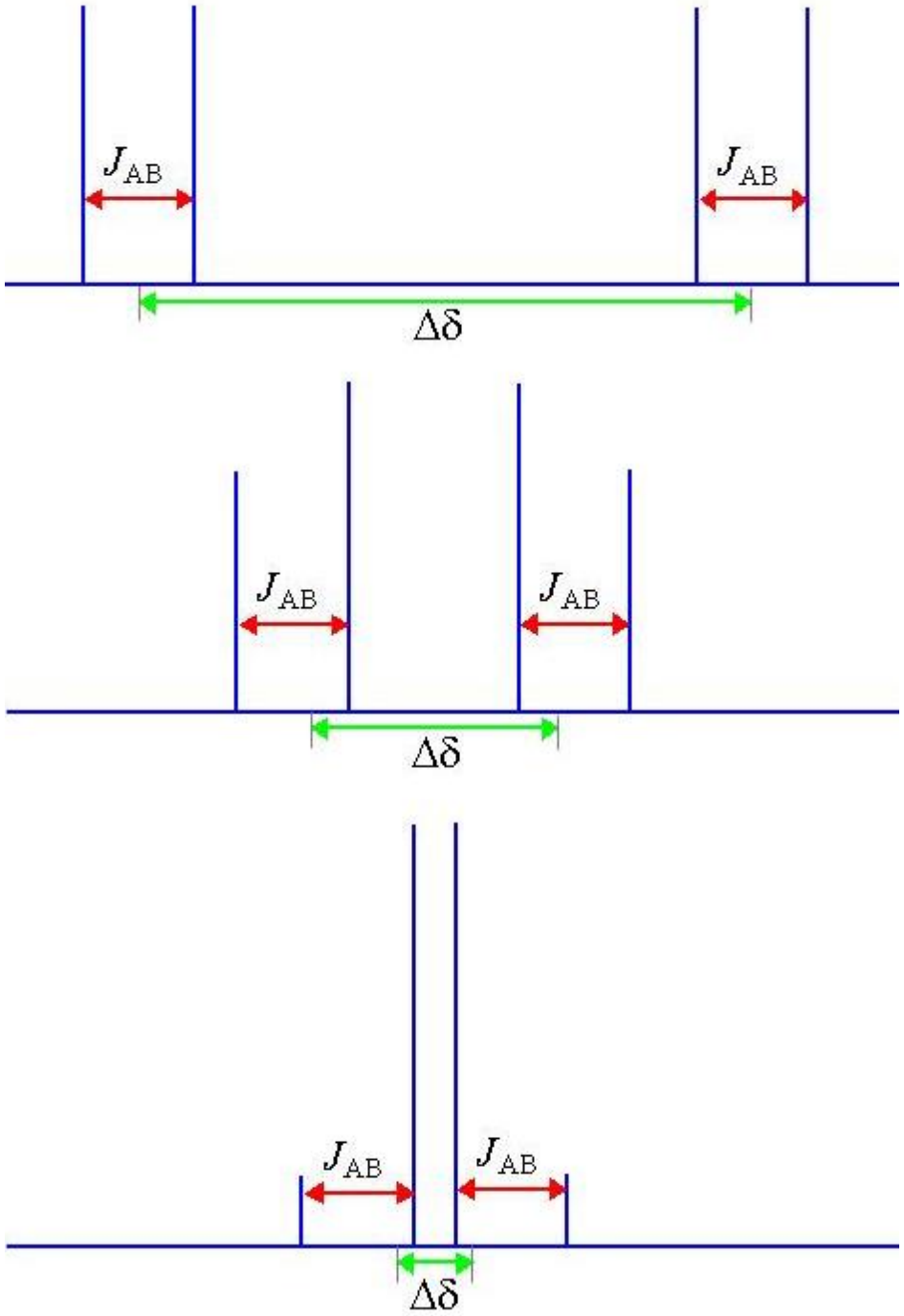
Non first order spectra

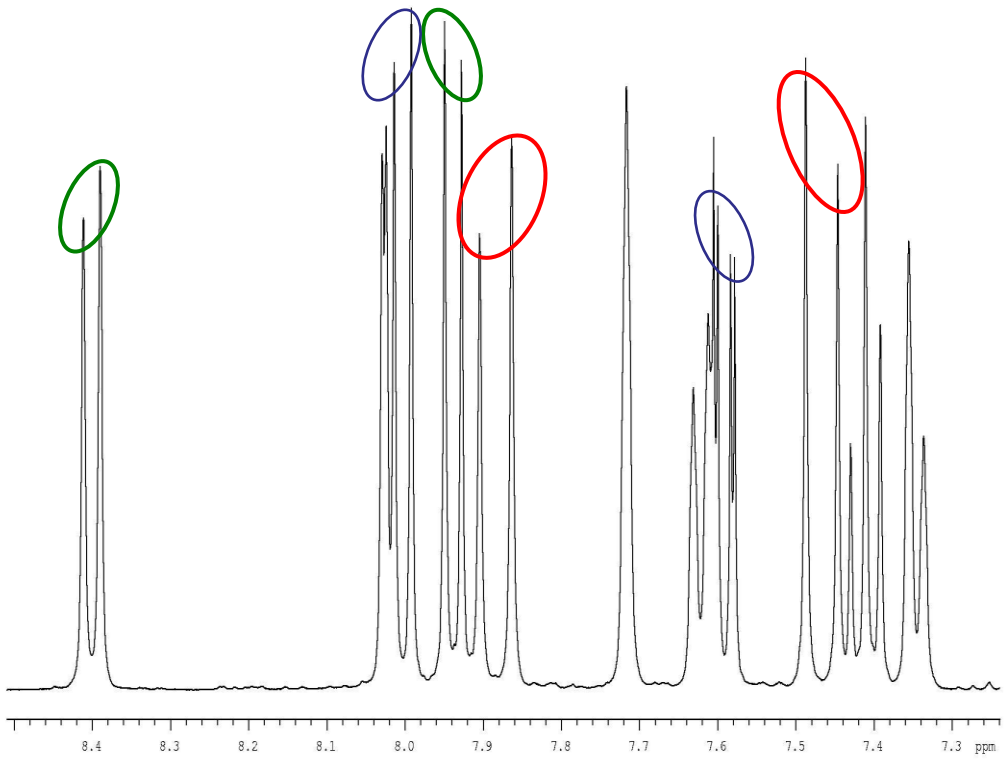
First order: $10 * J < \Delta\upsilon$

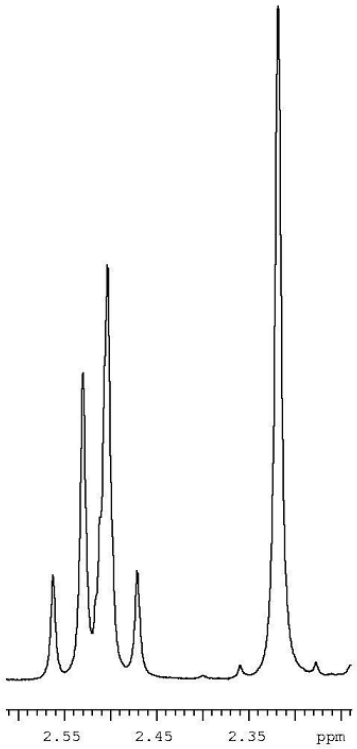
J / $\Delta\upsilon$ increasing, the spectrum <u>can change totally</u>

Spin systems named by the letters of alphabet

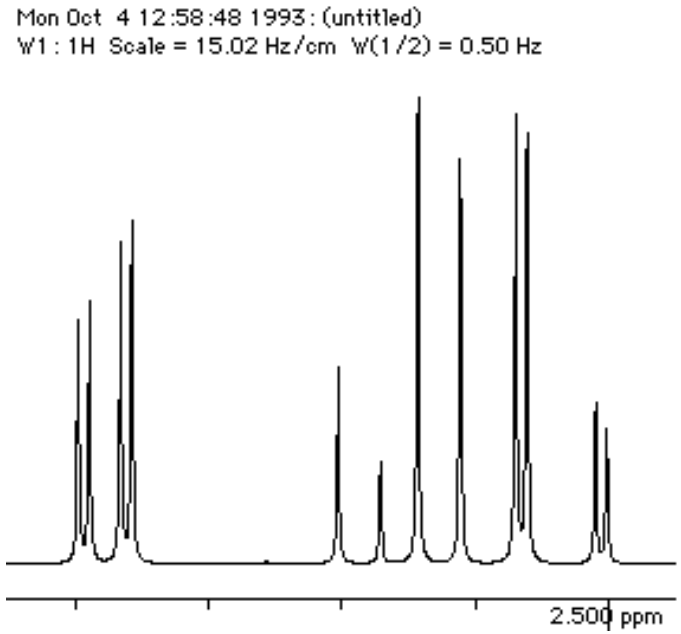
AB

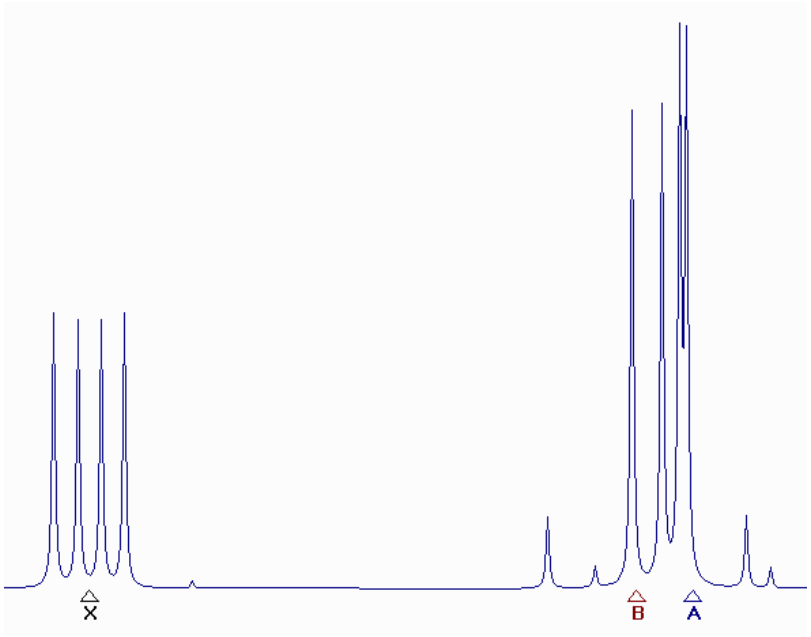


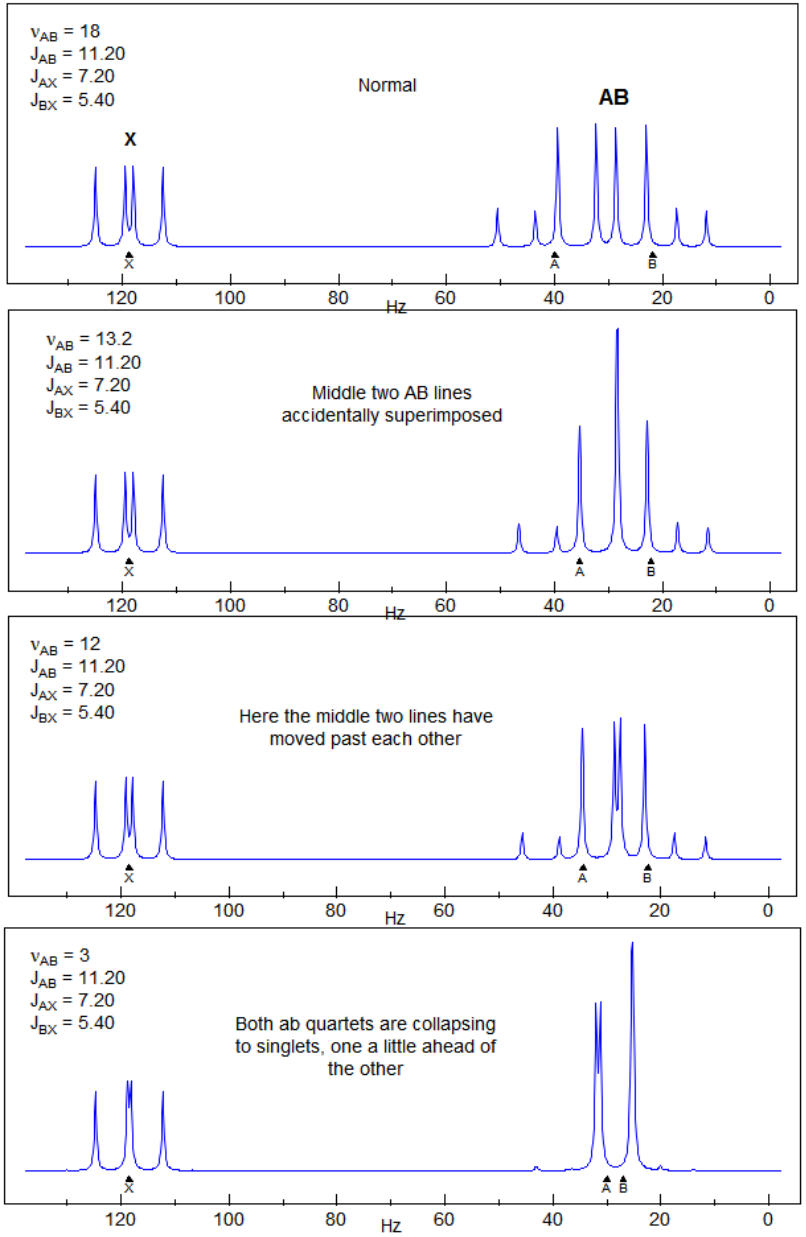

8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
ppm

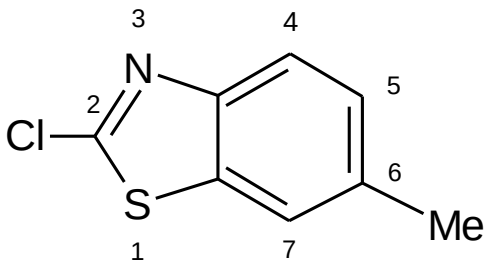

2.55
2.45
2.35
ppm

ABX

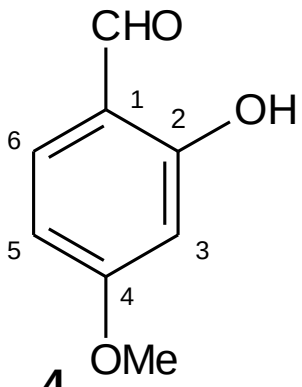

Mon Oct 4 12:58:48 1993: (untitled)
W1: 1H Scale = 15.02 Hz/cm W(1/2) = 0.50 Hz
2.500 ppm


X
B
A

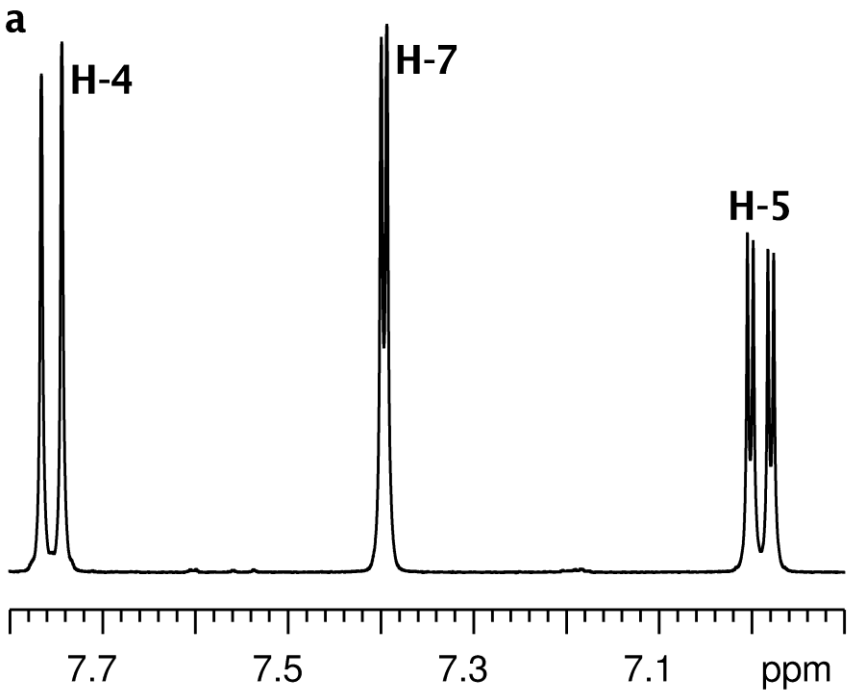

ν_{AB} = 18
J_{AB} = 11.20
J_{AX} = 7.20
J_{BX} = 5.40
Normal
X
AB
ν_{AB} = 13.2
J_{AB} = 11.20
J_{AX} = 7.20
J_{BX} = 5.40
Middle two AB lines accidentally superimposed
ν_{AB} = 12
J_{AB} = 11.20
J_{AX} = 7.20
J_{BX} = 5.40
Here the middle two lines have moved past each other
ν_{AB} = 3
J_{AB} = 11.20
J_{AX} = 7.20
J_{BX} = 5.40
Both ab quartets are collapsing to singlets, one a little ahead of the other
120 100 80 60 40 20 0
Hz

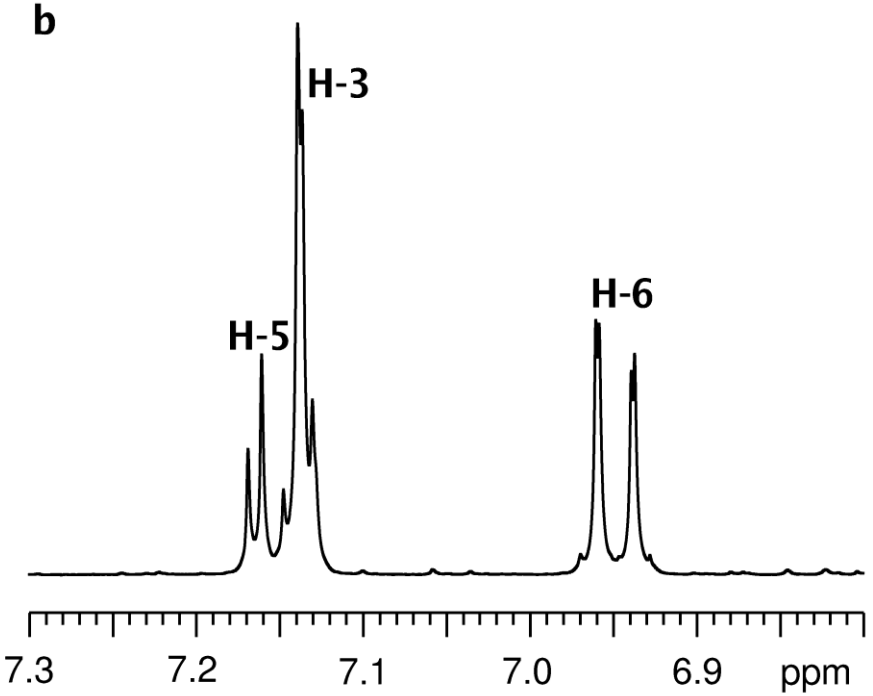

3
4
N
2
5
Cl
6
S
Me
1
7

3

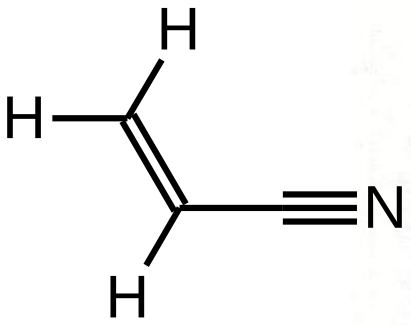

CHO
1
2
OH
6
5
3
4
OMe

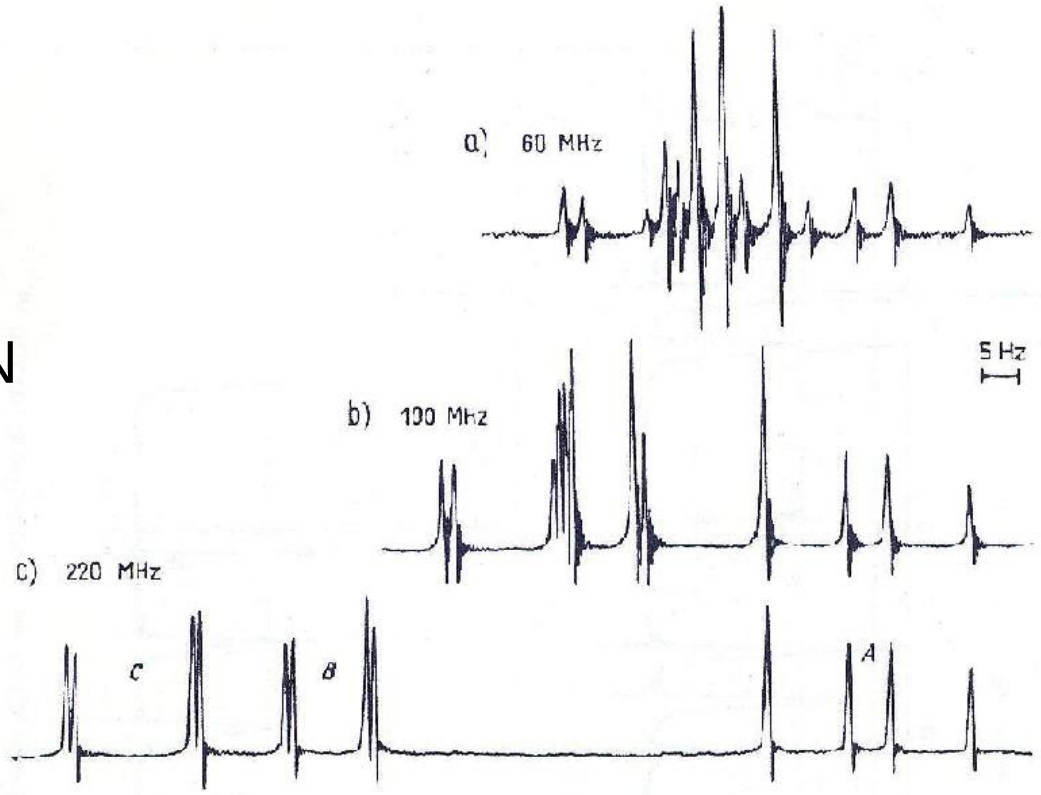
4


a
H-4
H-7
H-5
7.7
7.5
7.3
7.1
ppm


b
H-3
H-5
H-6
7.3
7.2
7.1
7.0
6.9
ppm

Acrylnitrile





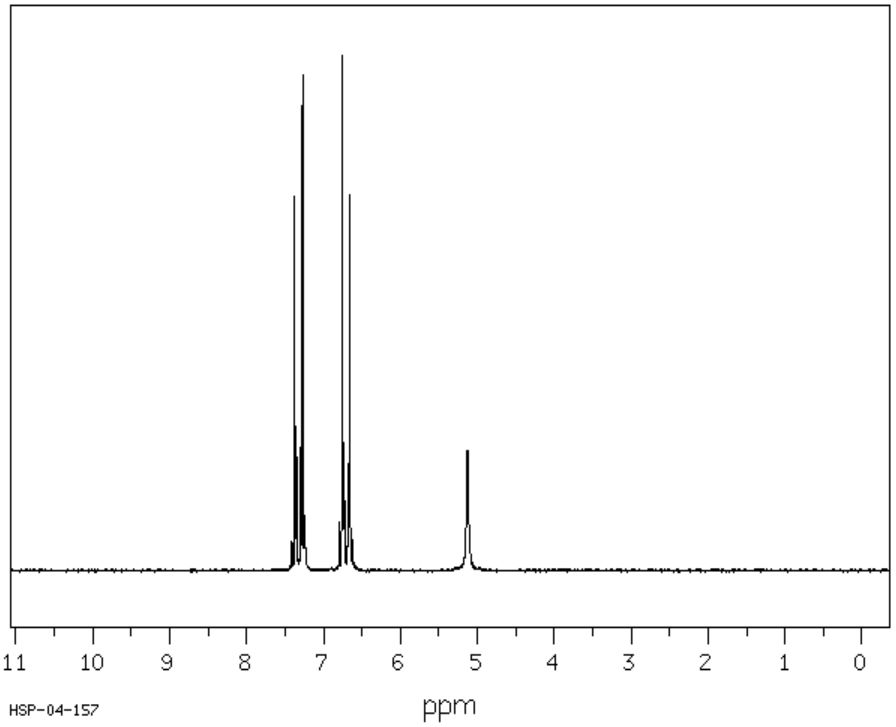
400 MHz

Increasing B_0 the spectrum gets closer to first order. Why?

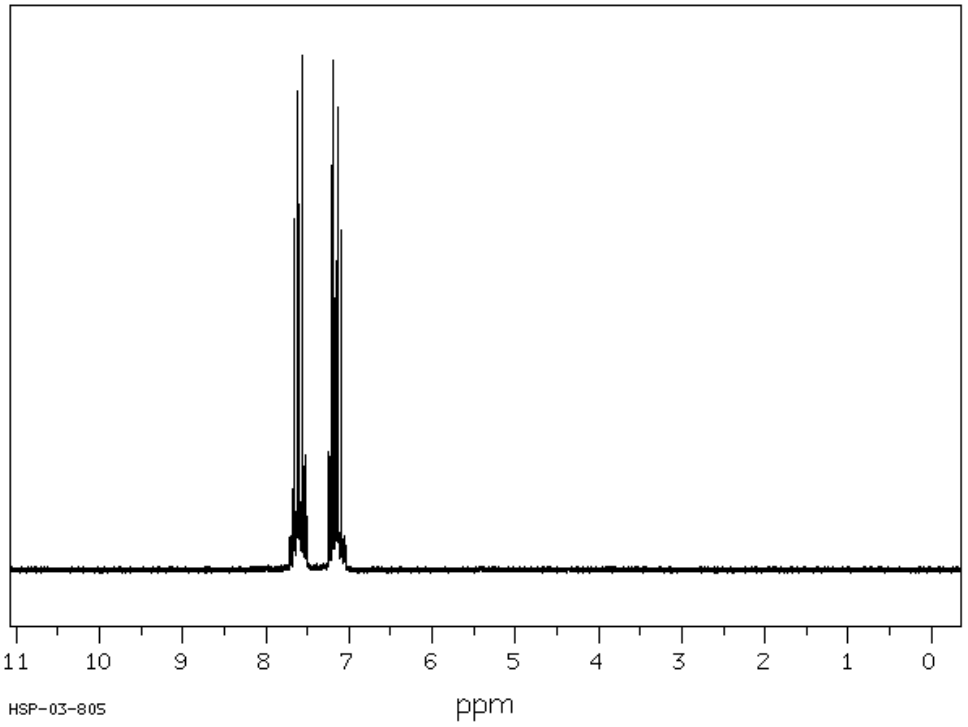
Complicated spin systems: pl. AA' BB'

p- v. *o*-disubstituted benzene (chemically equivalent but magnetically not equivalent)

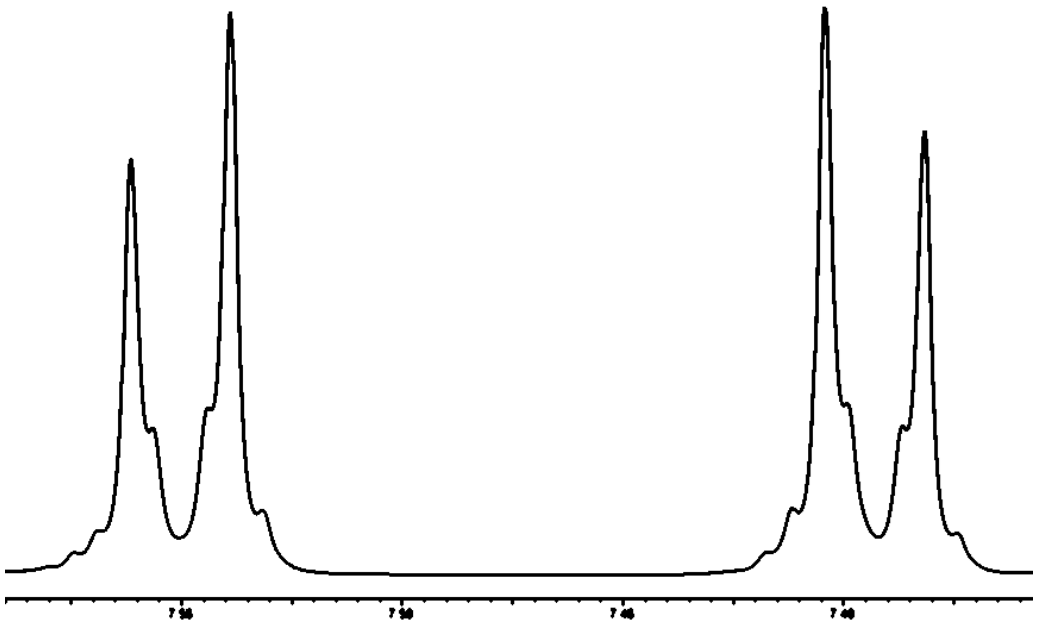
p-bromophenol



1,2-dibromobenzene



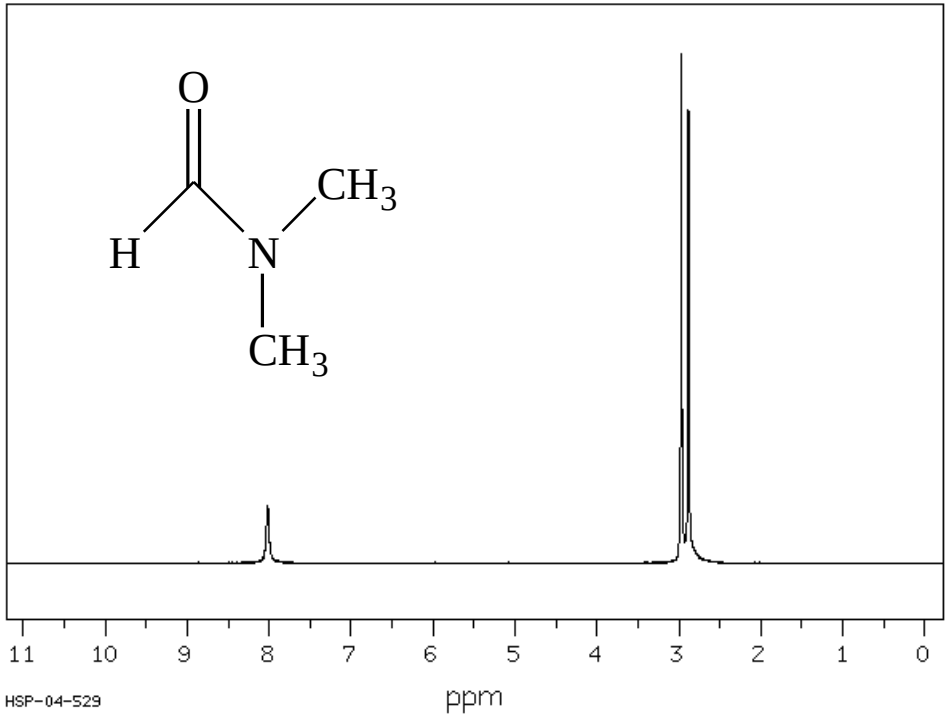
THF behaves similarly!

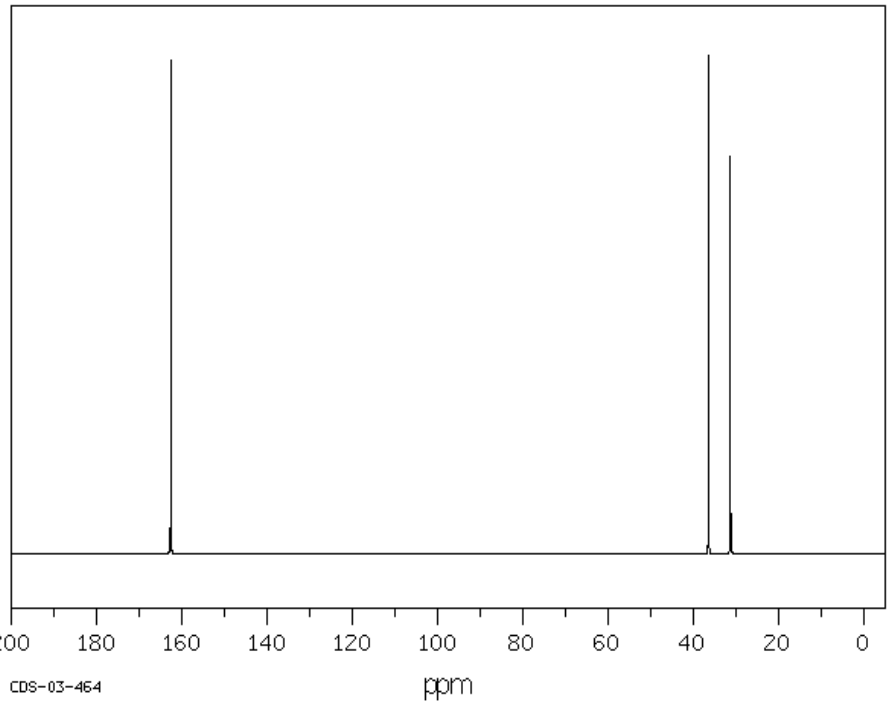

7.56
7.50
7.46
7.40

Magnetic anisotropy

Neighbouring groups have effect on chemical shift through space as well (not just through chemical bond)

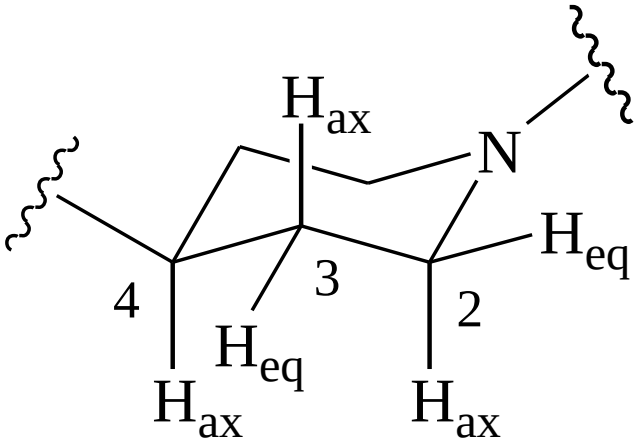
DMF





Magnetic anisotropy

Ring positions

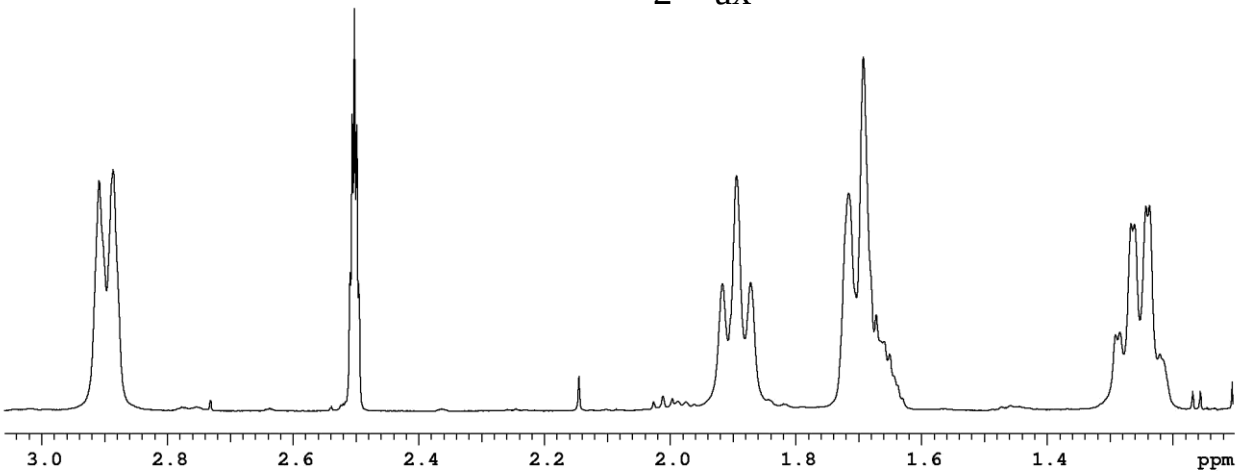


$_3H_{eq} + {}_4H$

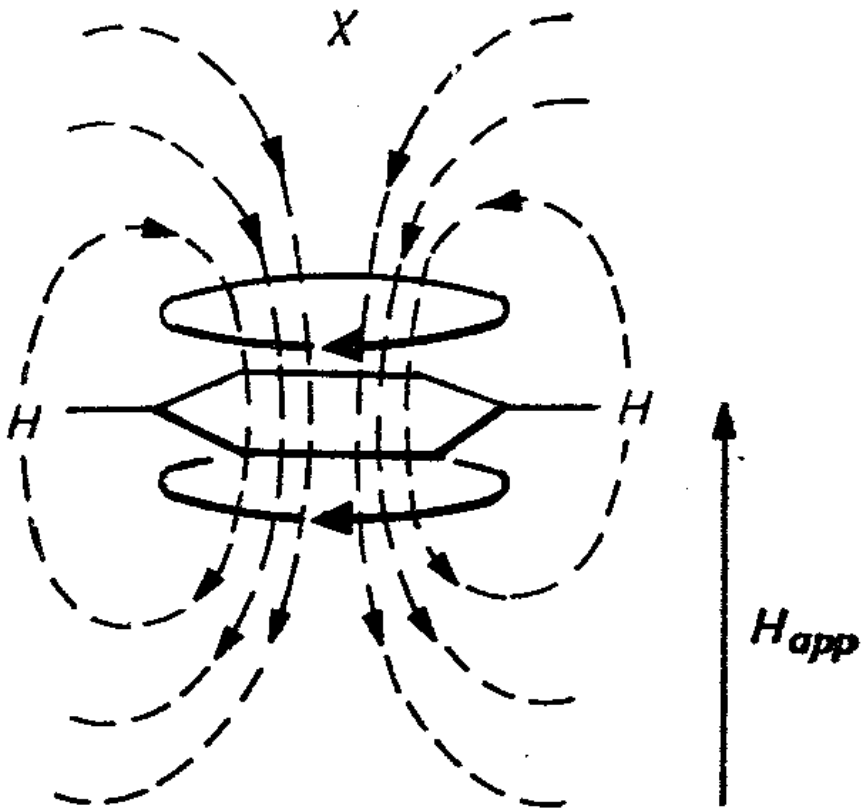
$_2H_{eq}$

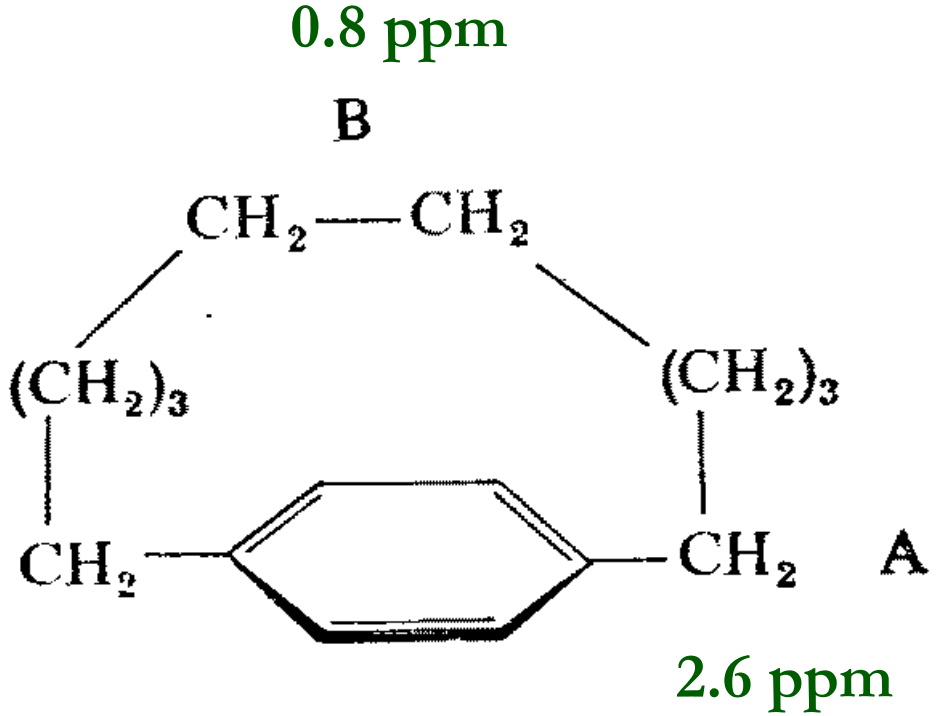
$_2H_{ax}$

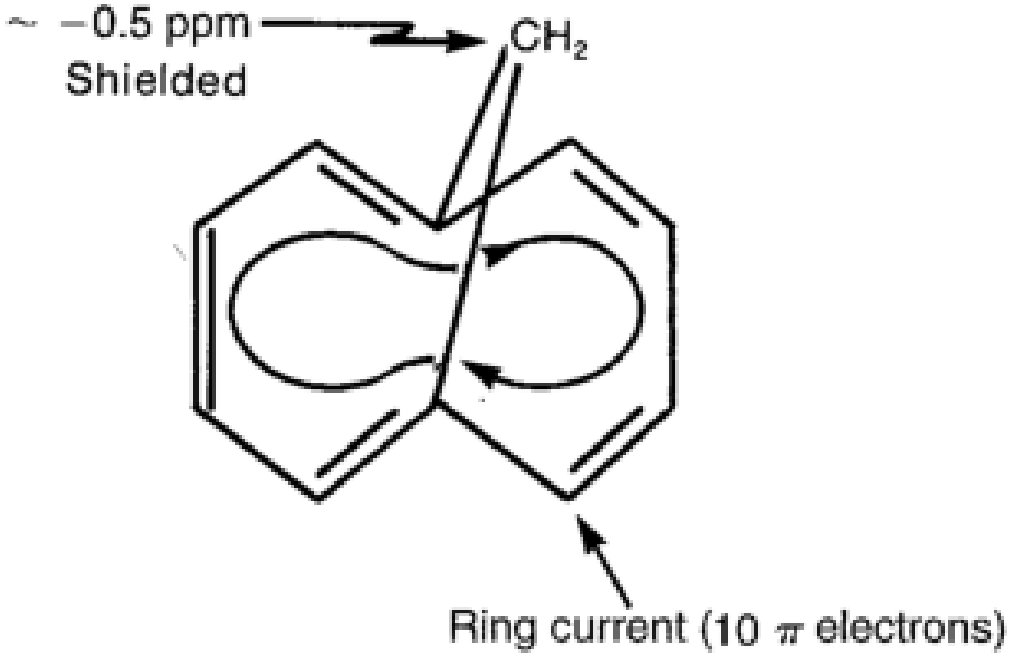
$_3H_{ax}$

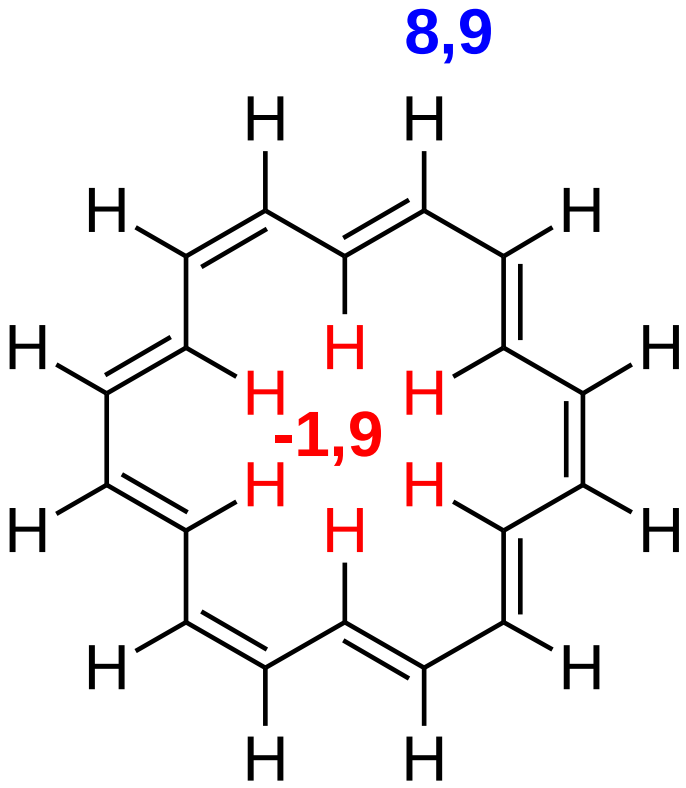


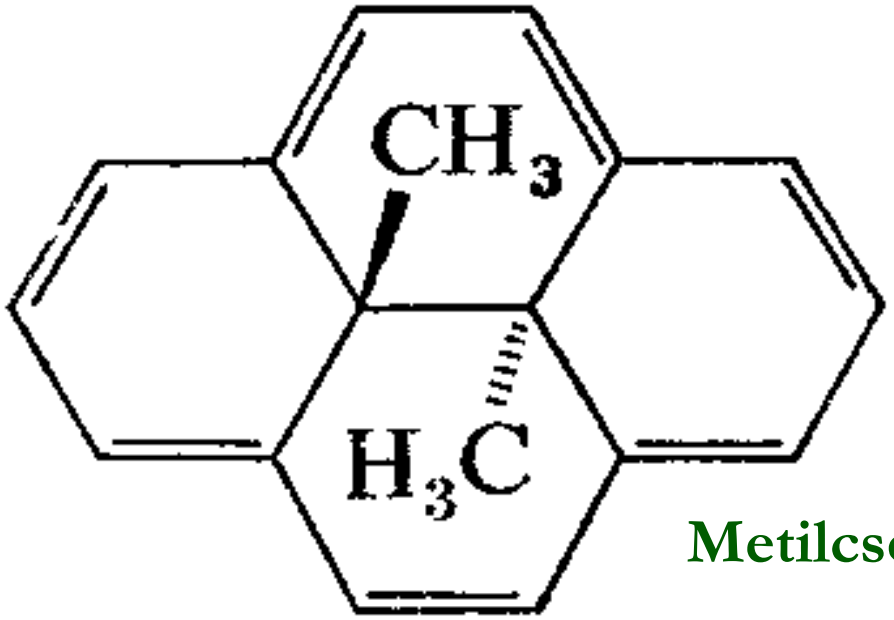
Aromatic ring currents



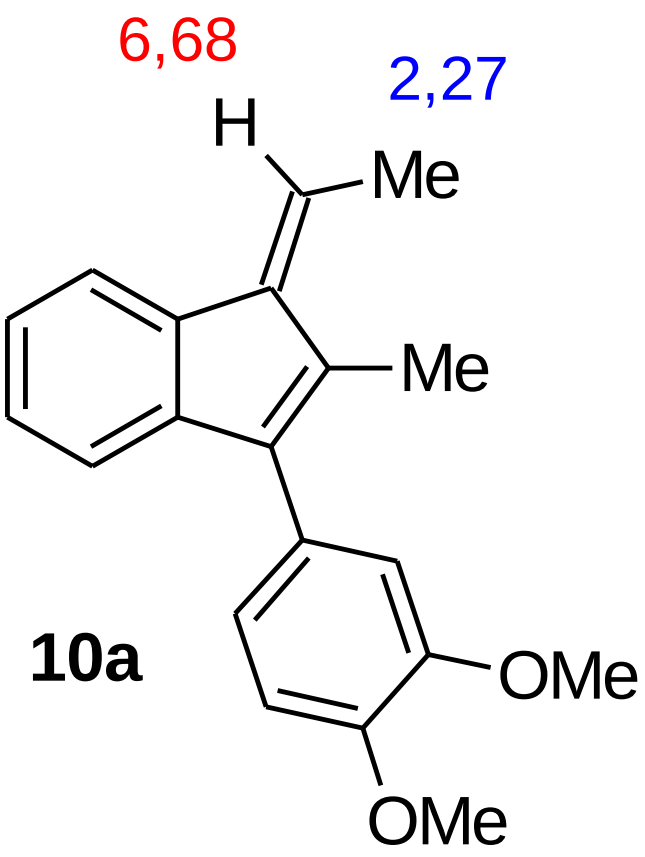




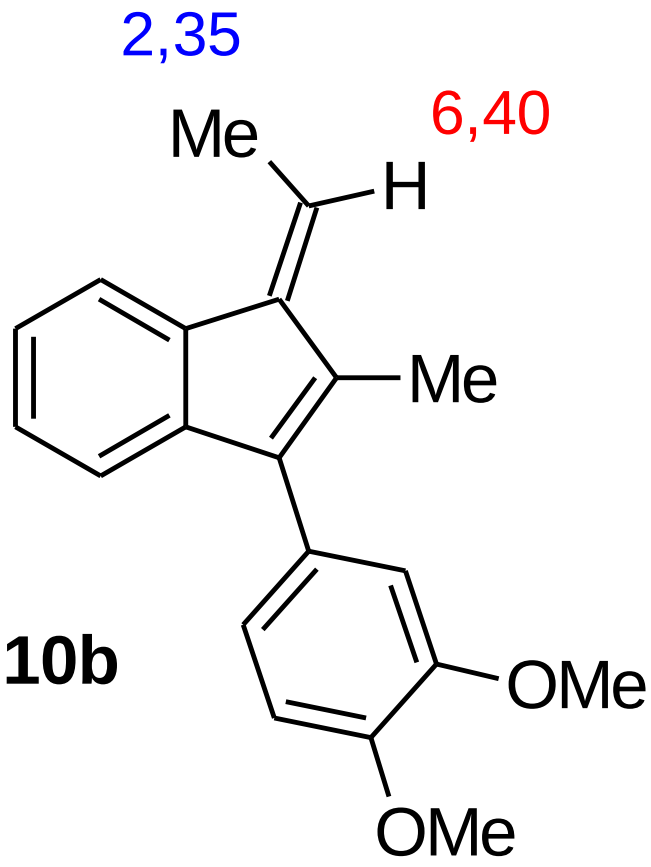




Metilcsoport: -4.2 ppm

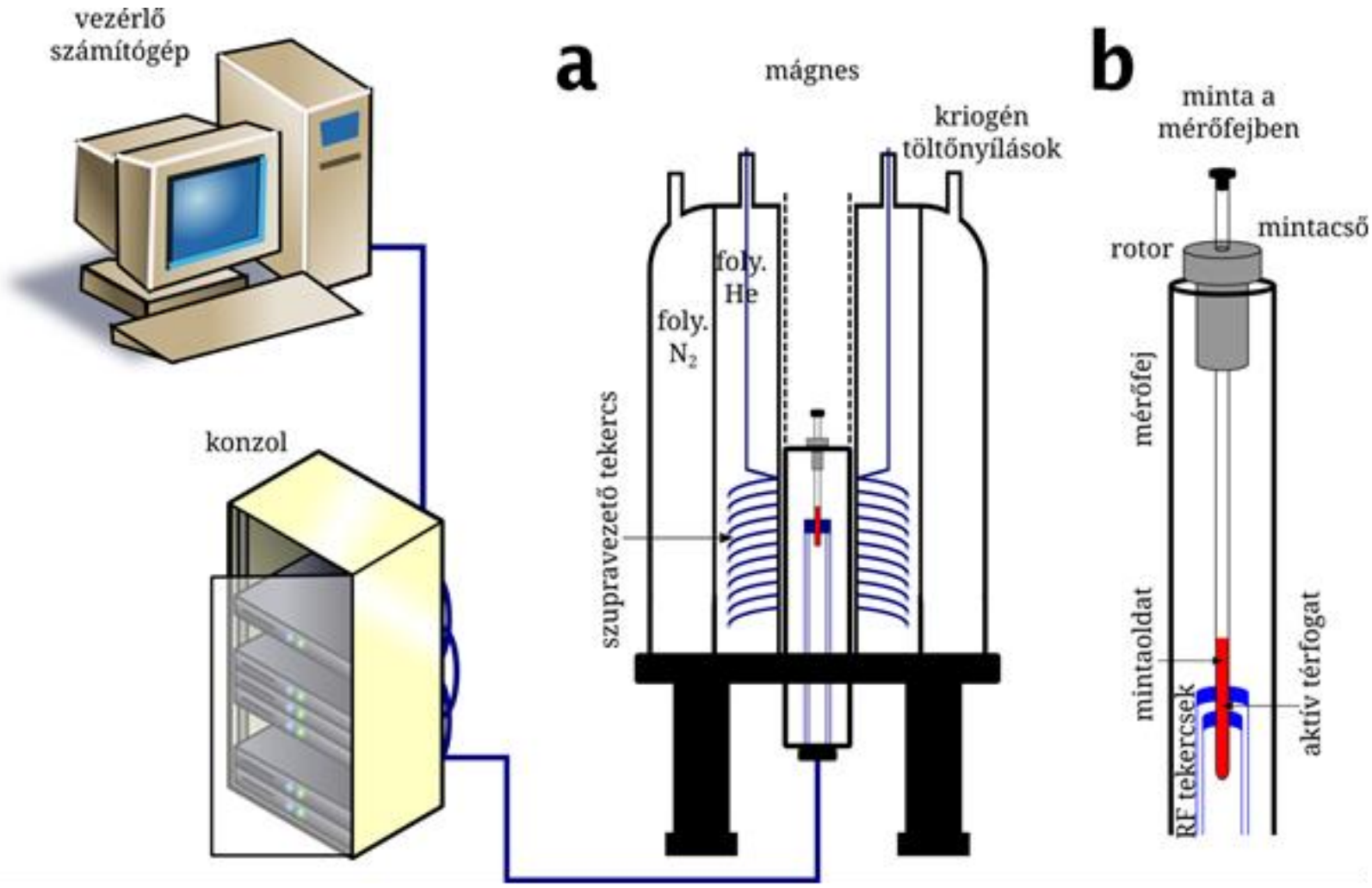


10a



10b

NMR spectrometer

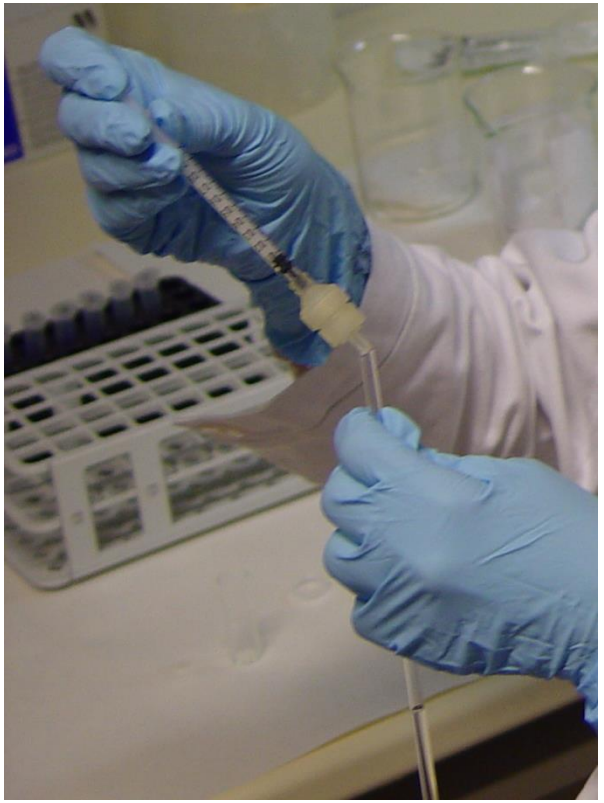


How to measure?

1. Sample preparation
    1. Solvent
    2. O_2 exemption
    3. Filtering

2. Measurement
    1. Setting the instrument: tune, lock, shim
    2. Parameters

3. Data managment
    1. FT
    2. Phase correction
    3. Baseline correction (BC)
    4. Referencing (TMS, solvent)
    5. Integral (^1H)



(…administrating…)

$$\nu = \frac{\gamma}{2\pi} \cdot B$$

Is B constant (not taking chemical shift in account)?

NO!

The coil defines **H** (magnetic field)

The magnetic induction (**B**) depends on the material in the magnetic field!!!

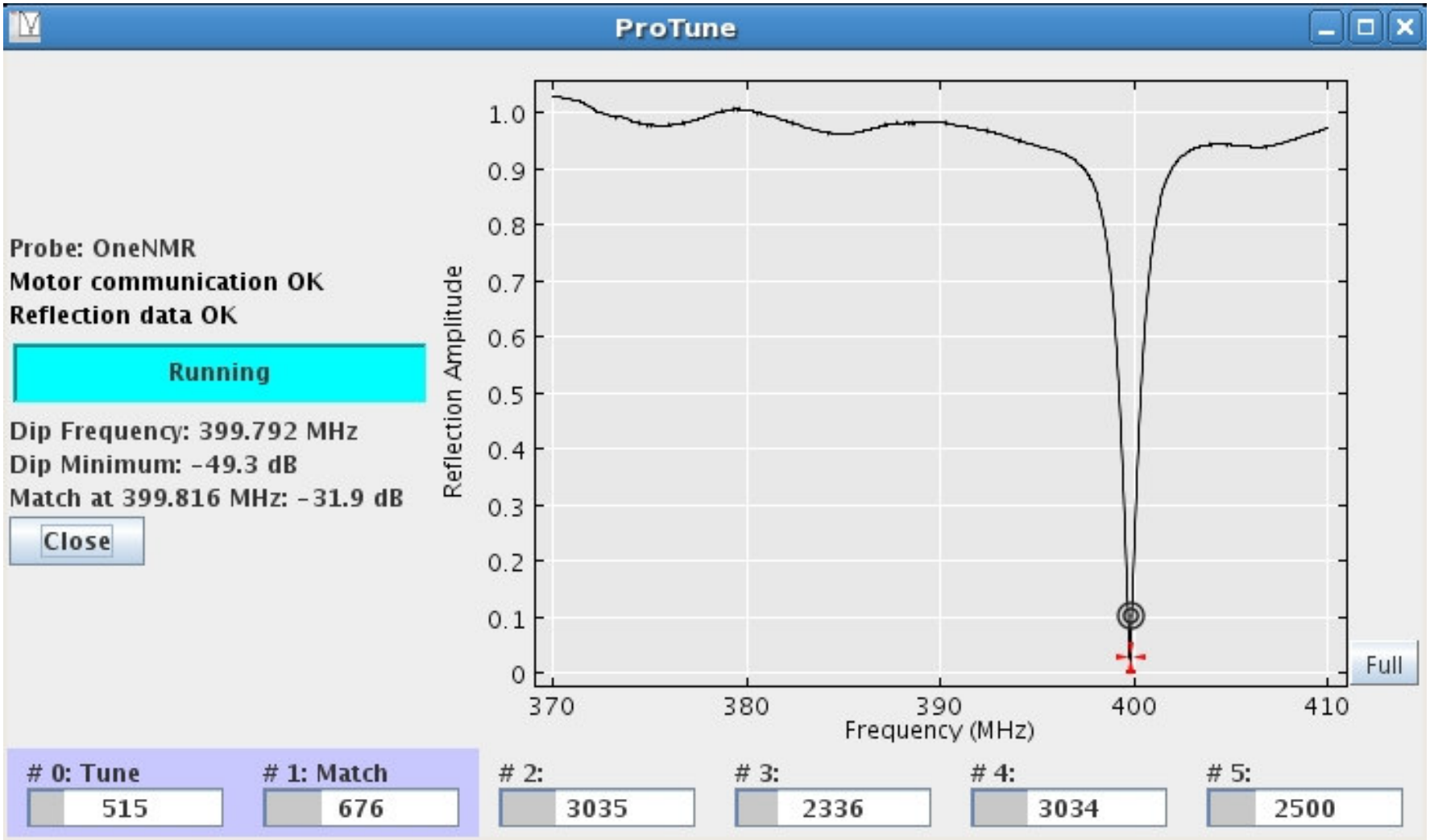
$$B = \mu H$$

Magnetic permeability

Does the material changes in the instrument???

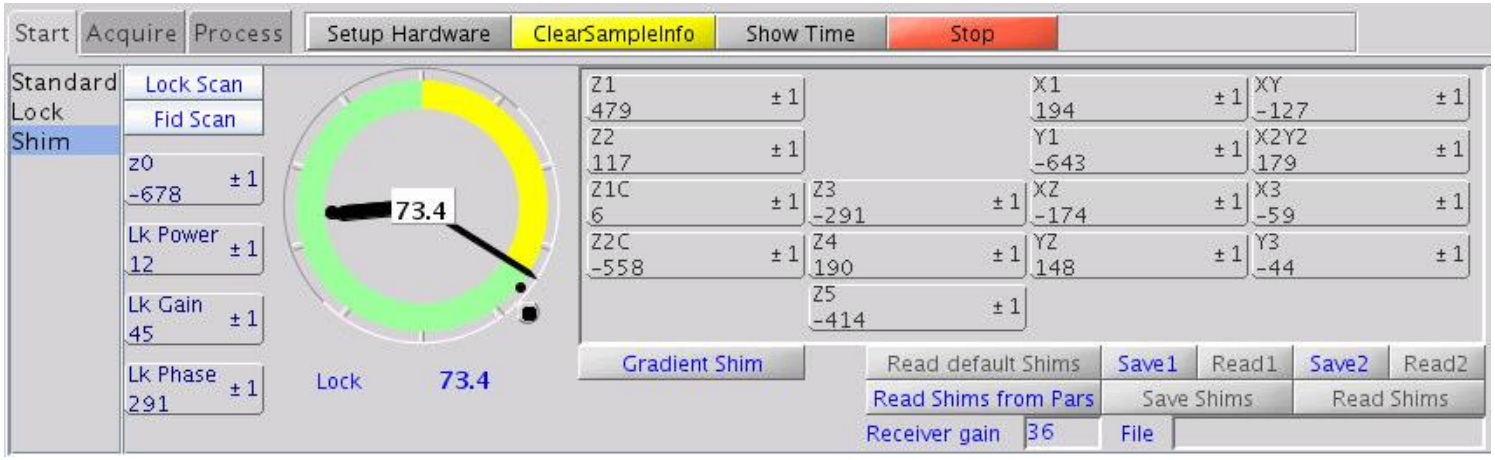
YES!!!

Tuning: RF coils parameters set depending on tube and solvent

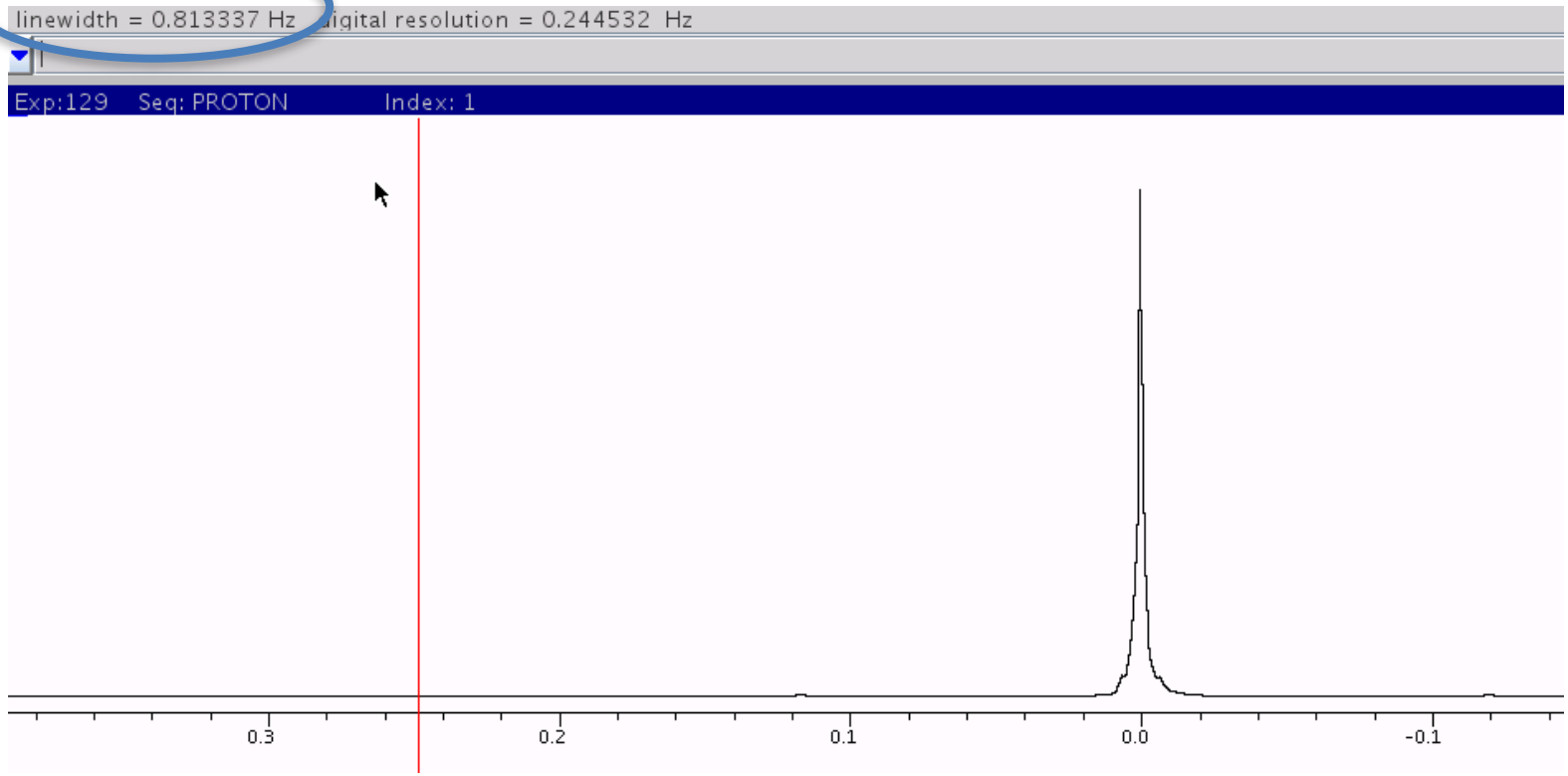


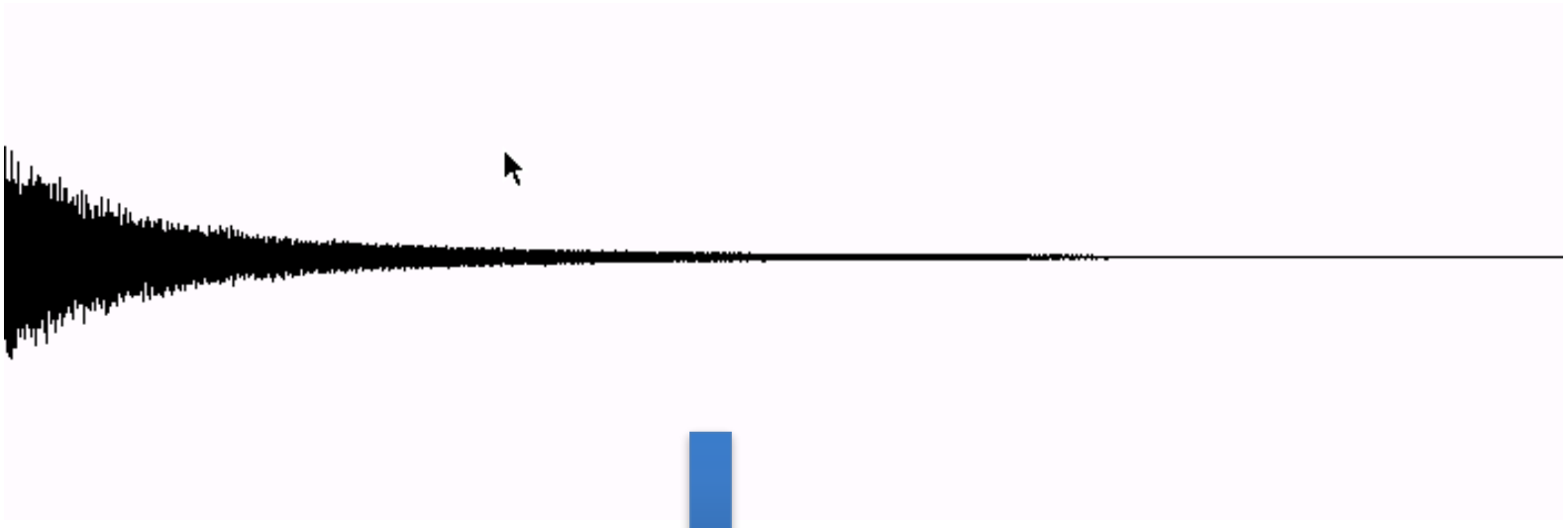
Lock: Solvent D signal to maintain B constant

Shimming: magnetic field homogenity

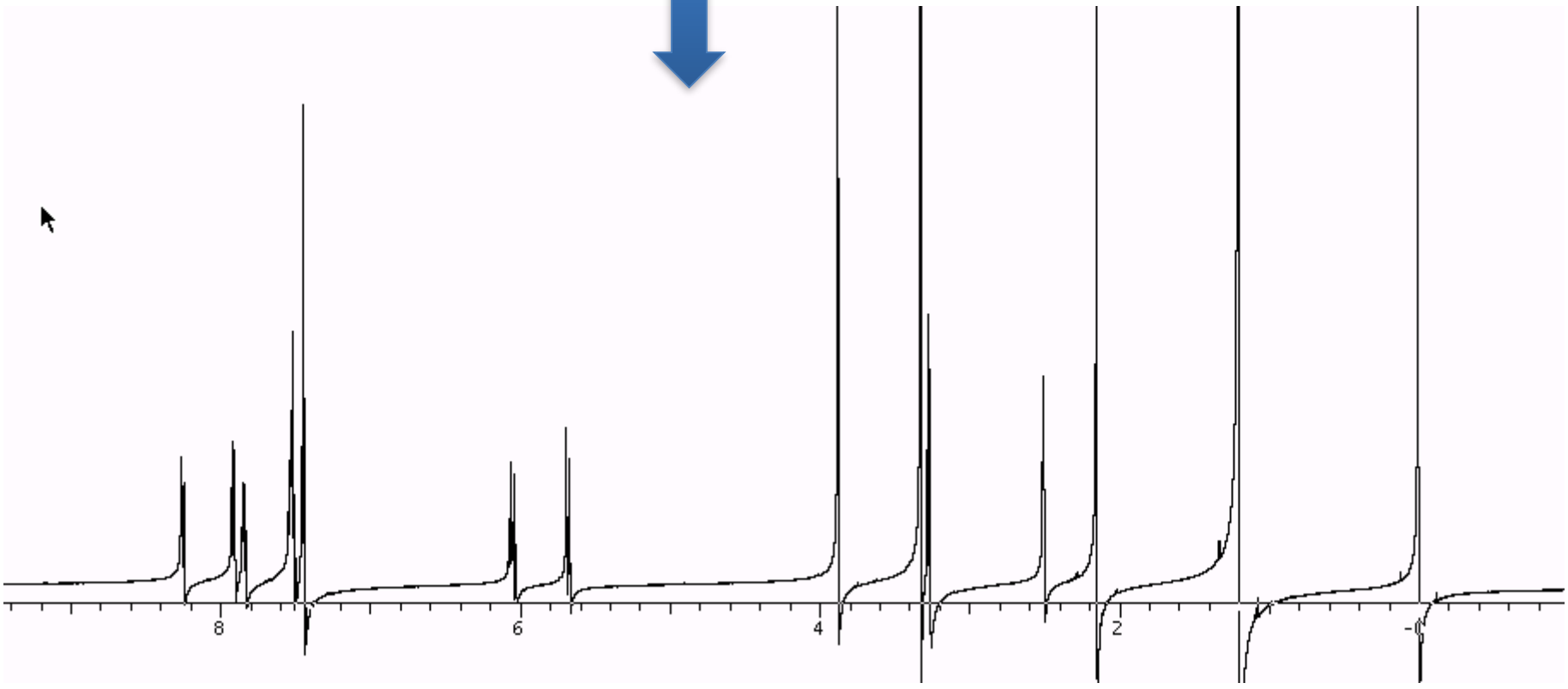


Control: singulet signal (eg. TMS) width

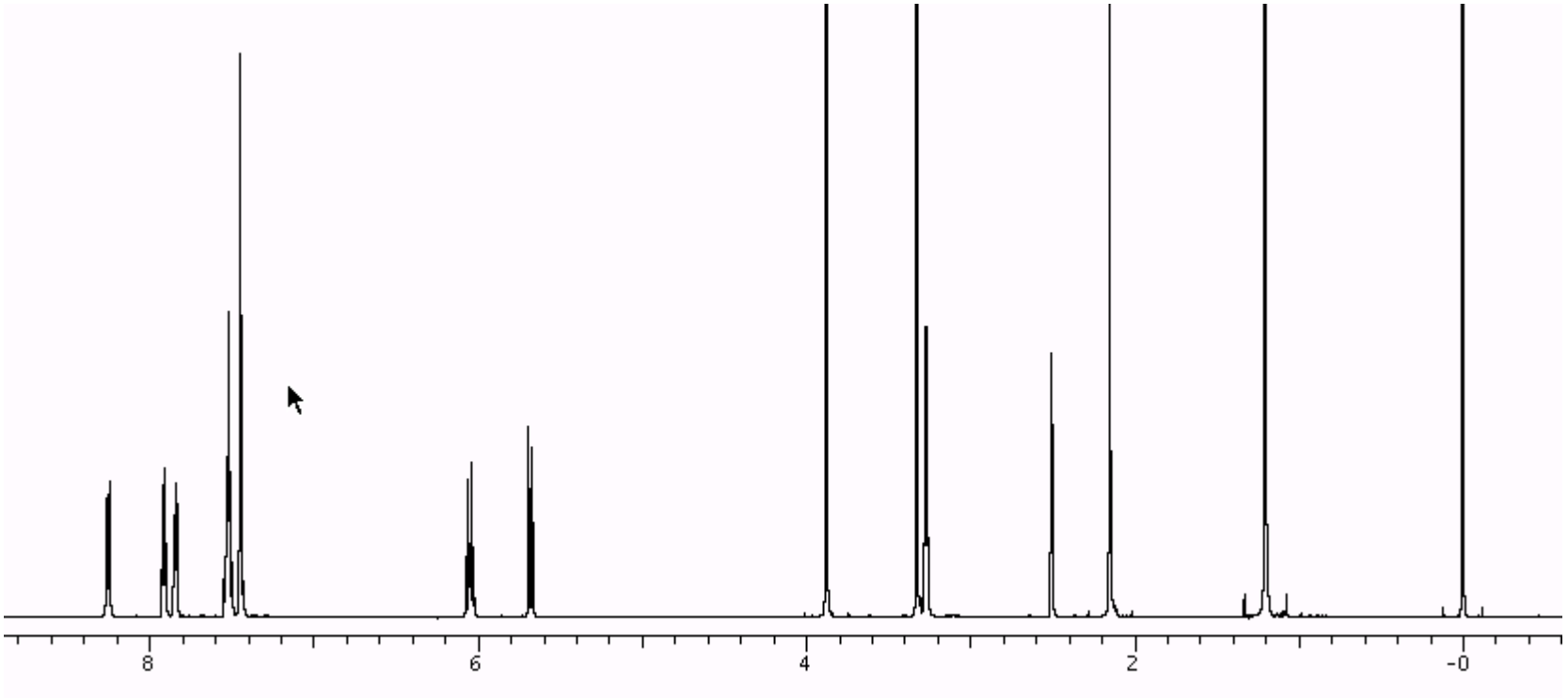


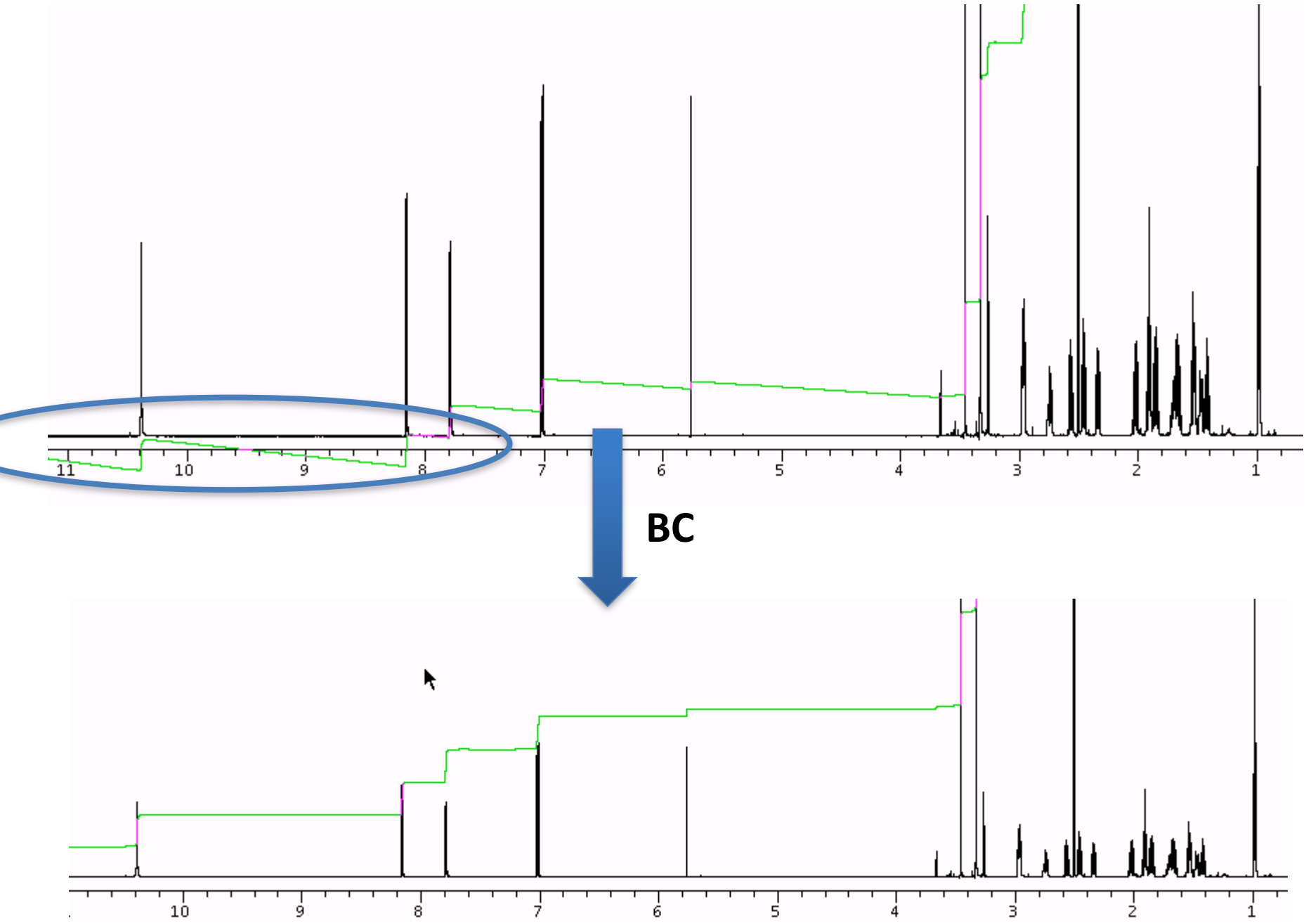


FT



Phase correction




11
10
9
8
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BC
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3
2
1

Integration