

C8953

NMR structural analysis seminar

Information about classes + 1D ^1H -NMR

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Information about classes

Credit:

- ▶ Max. 2 unexcused absences
- ▶ 2 successfully solved tests (midterm and final)

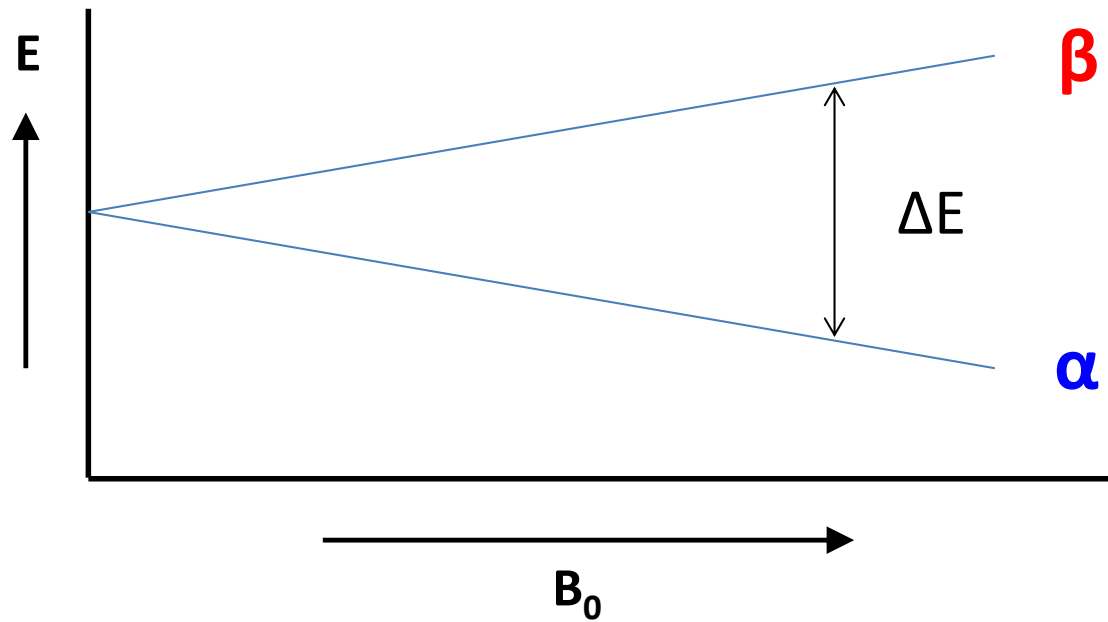
Study materials:

<https://is.muni.cz/auth/el/1431/jaro2019/C8953/um>

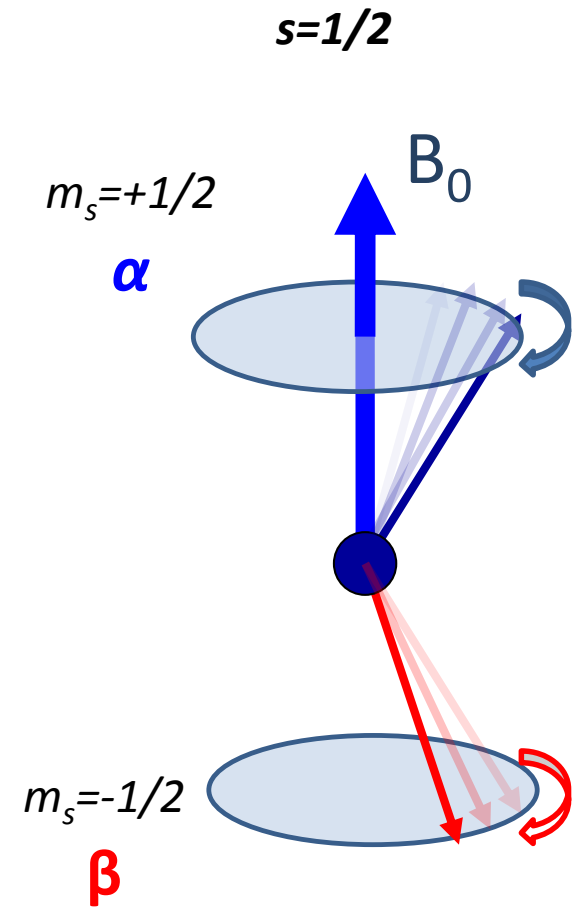
E-tests:

<https://is.muni.cz/auth/el/1431/jaro2019/C8953/odp>

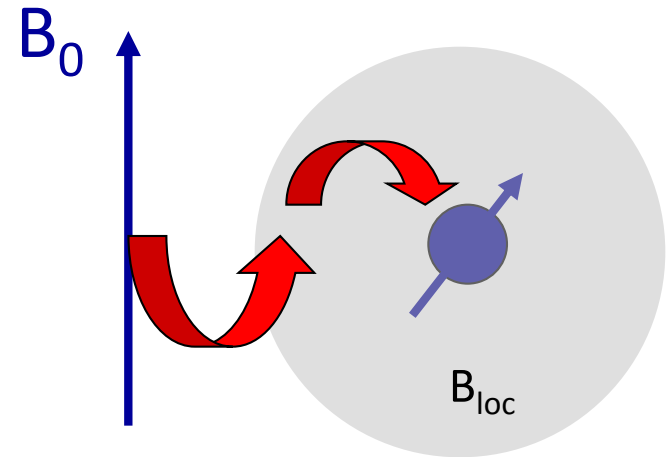
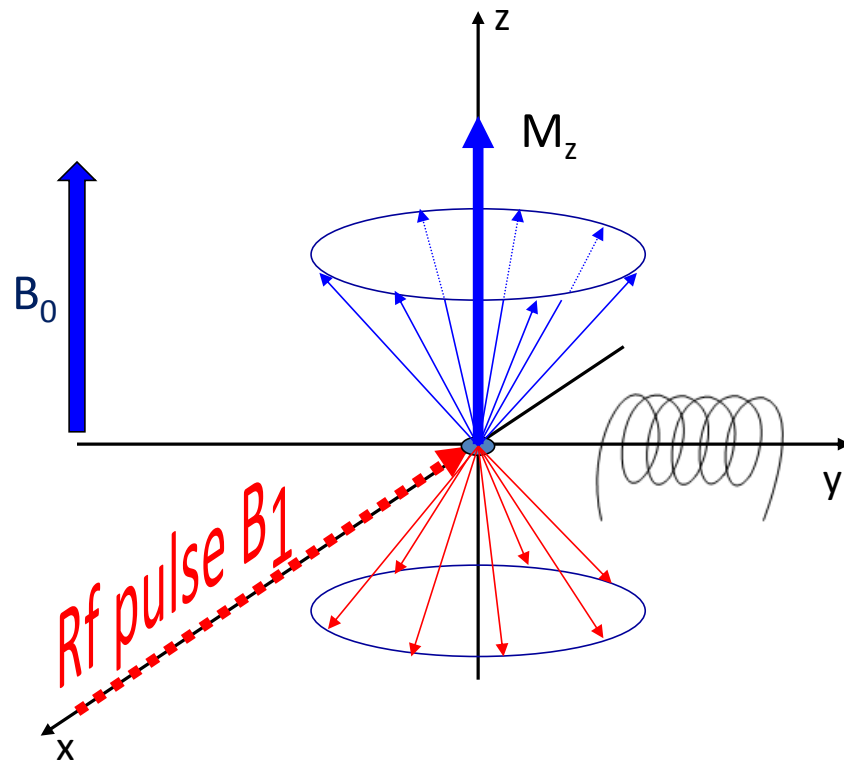
Energy levels splitting



$$N_\alpha > N_\beta$$



Behavior of nuclear spin after irradiation by RF pulse



B_0 induces local mag. field B_{loc} , which affects against B_0

↓
Nuclear shielding

Precession frequency:

Precession frequency affected by nuclear shielding:

Chemical shift:

Definition of the relative scale of the chemical shift:

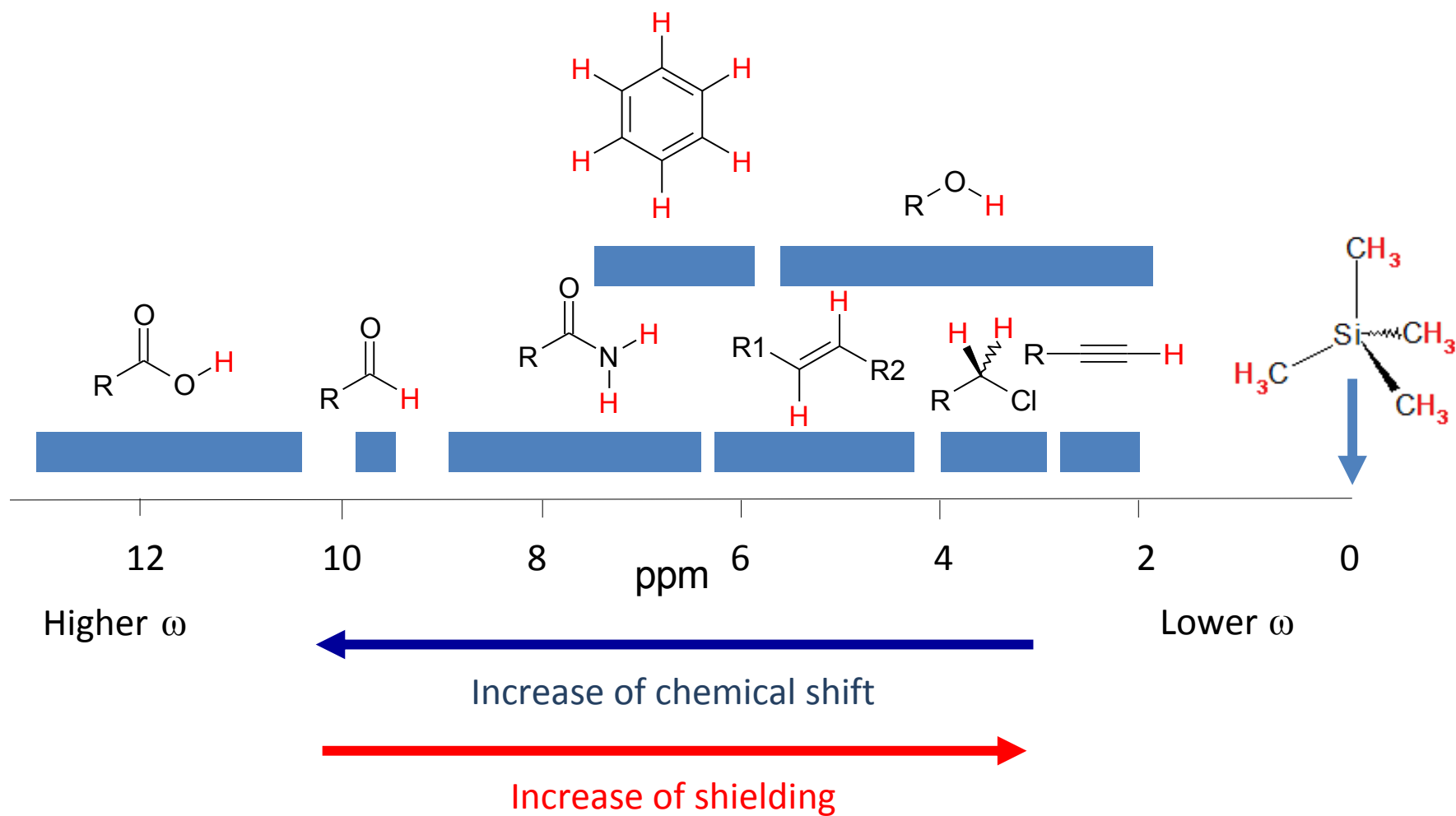
$$\omega = -\gamma B_0$$

$$\omega = -(1+\sigma)B_0$$

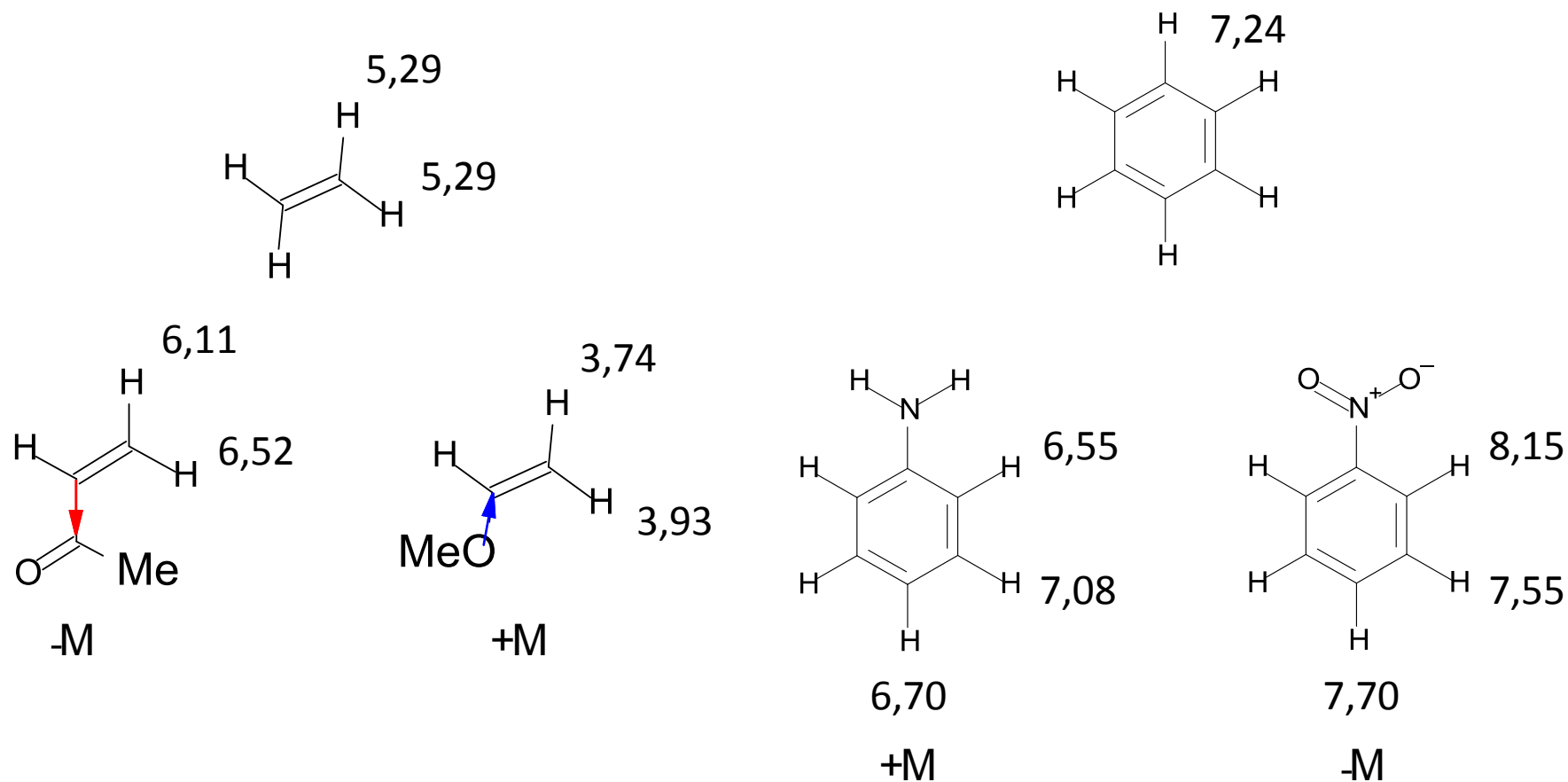
$$\delta = \omega - \omega_{ref}$$

$$\delta = (\omega - \omega_{ref})/\omega_{ref} \cdot 10^6 \text{ ppm}$$

Characteristic intervals of chemical shifts values



Mesomeric effect



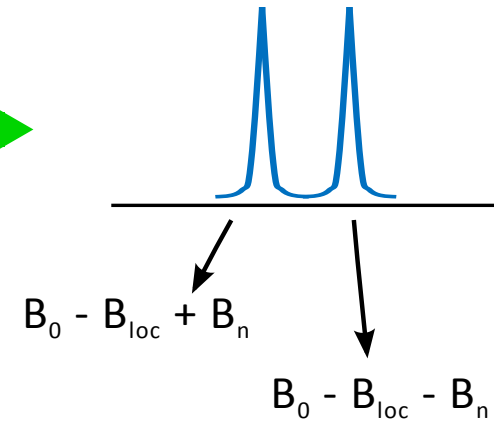
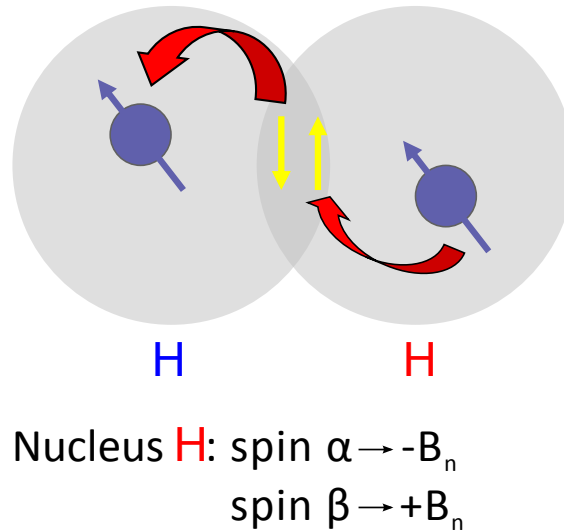
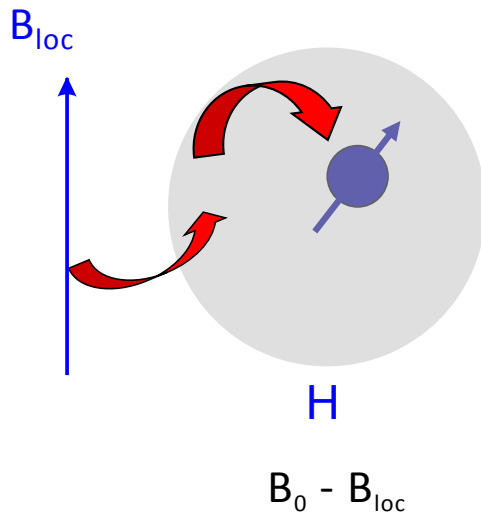
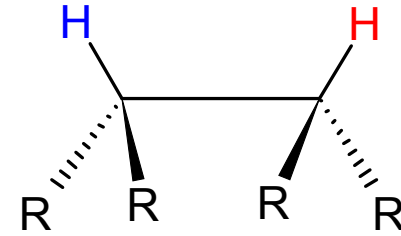
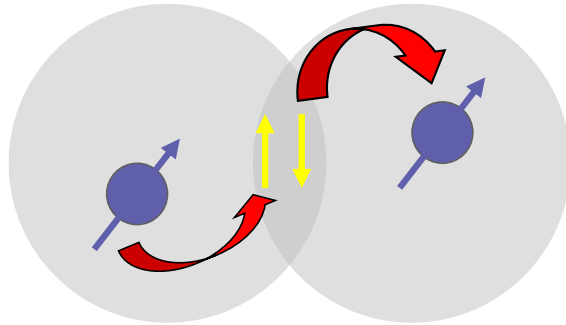
Substituents with -M effects

-F, -Cl, -Br, -I, -OH, -OR, -NH₂, -NHR, -NR₂, -SH, -SR

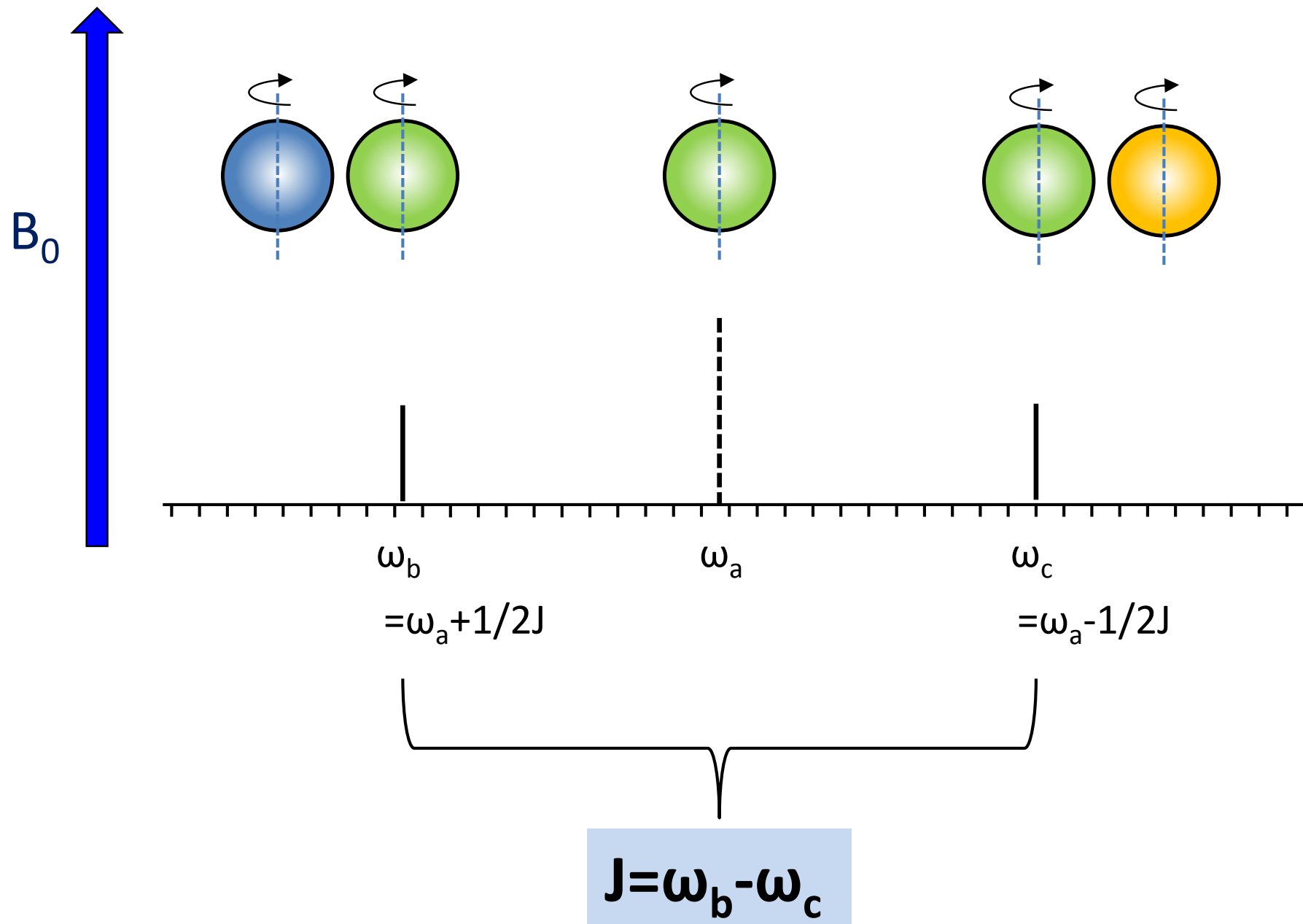
Substituents with +M effect

-CH=O, -RC=O, -C(OH)=O, -C(OR)=O, -C(NH₂)=O, -NO₂, -SO₃H, -C≡N

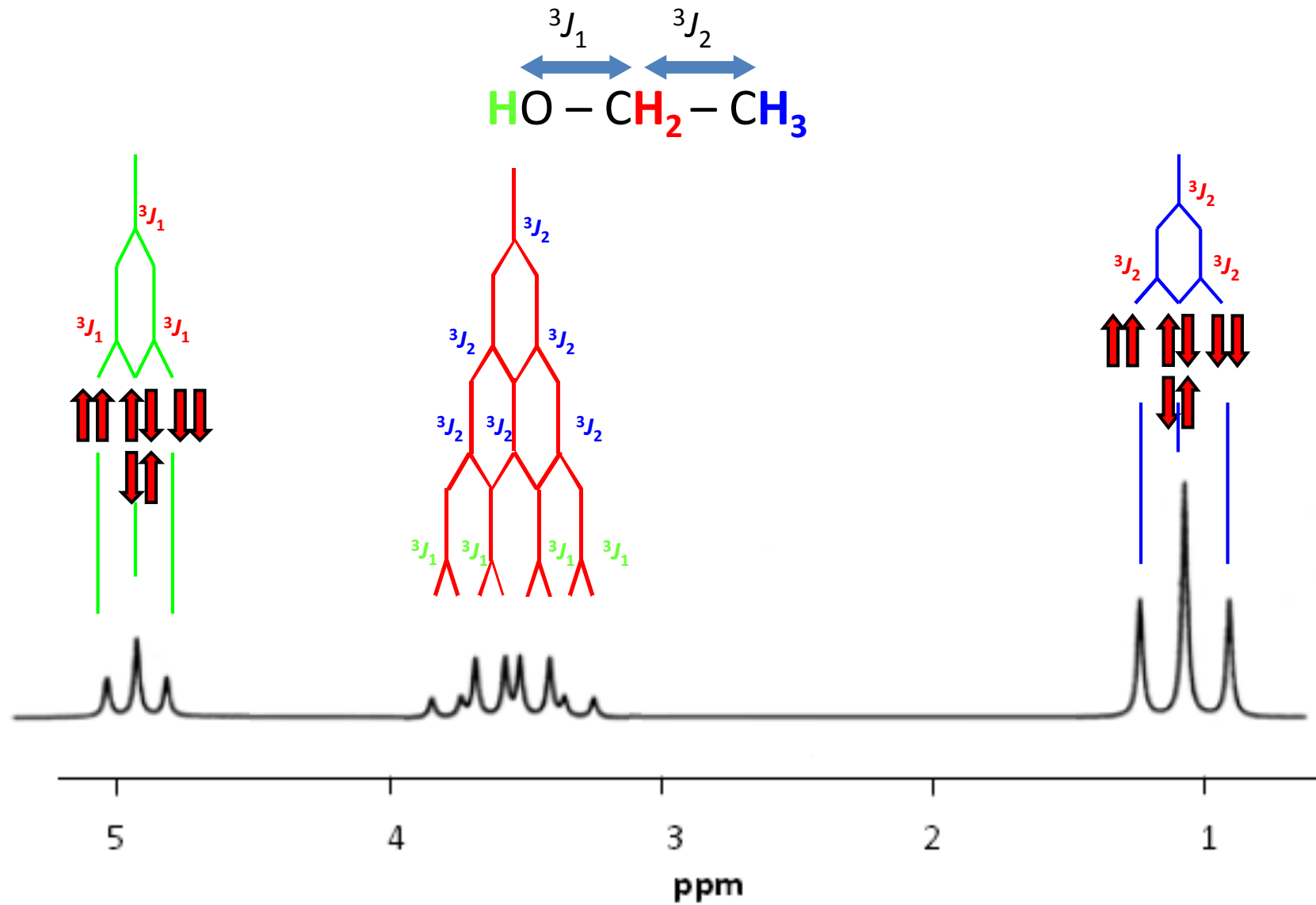
Spin-spin interaction, J -coupling



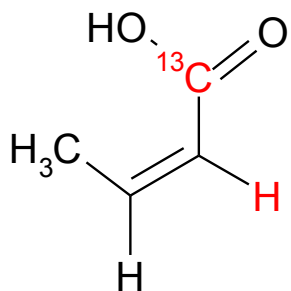
Interaction constant J



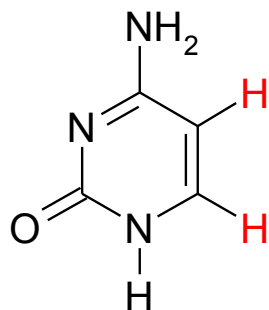
1D ^1H NMR spectrum



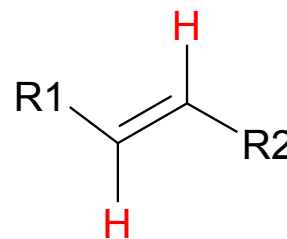
Values of J -constants - trends



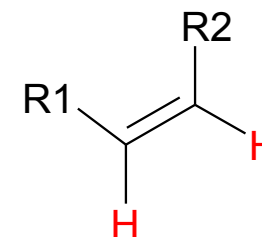
$${}^2J_{\text{CH}} = 3.1 \text{ Hz}$$



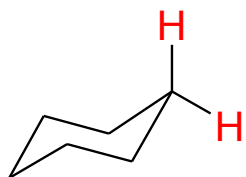
$${}^3J_{\text{HH}} = 12 \text{ Hz}$$



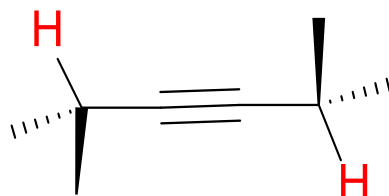
$${}^3J_{\text{HH}} = 13 - 18 \text{ Hz}$$



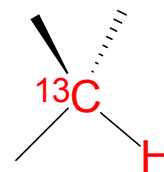
$${}^5J_{\text{HH}} = 7 - 12 \text{ Hz}$$



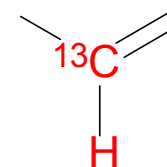
$${}^2J_{\text{HH}} = -12,5 \text{ Hz}$$



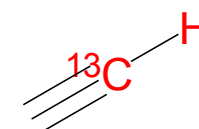
$${}^5J_{\text{HH}} = 2 - 3 \text{ Hz}$$



$${}^1J_{\text{CH}} = 125 \text{ Hz}$$

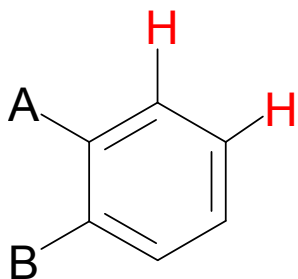


$${}^1J_{\text{CH}} = 160 \text{ Hz}$$

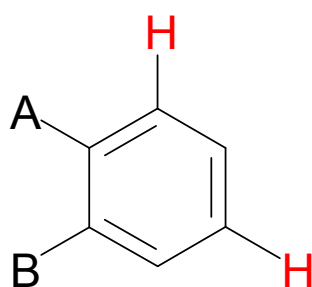


$${}^1J_{\text{CH}} = 250 \text{ Hz}$$

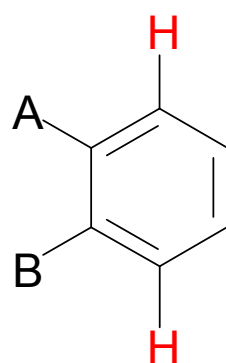
Values of J -constants - trends



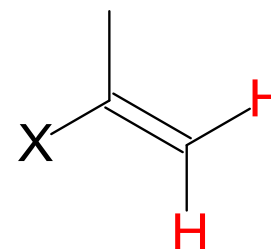
$${}^3J_{HH} = 7,5 \text{ Hz}$$



$${}^4J_{HH} = 1,5 \text{ Hz}$$



$${}^5J_{HH} = 0,7 \text{ Hz}$$



X=	Li	H	Cl	OMe	F
${}^2J_{HH}$ (Hz)	7,1	2,5	-1,4	-2,0	-3,2

1D ^1H NMR spectroscopy

- ▶ the fastest measuring, the highest sensitivity
- ▶ complicated interpretation in case of more complex systems

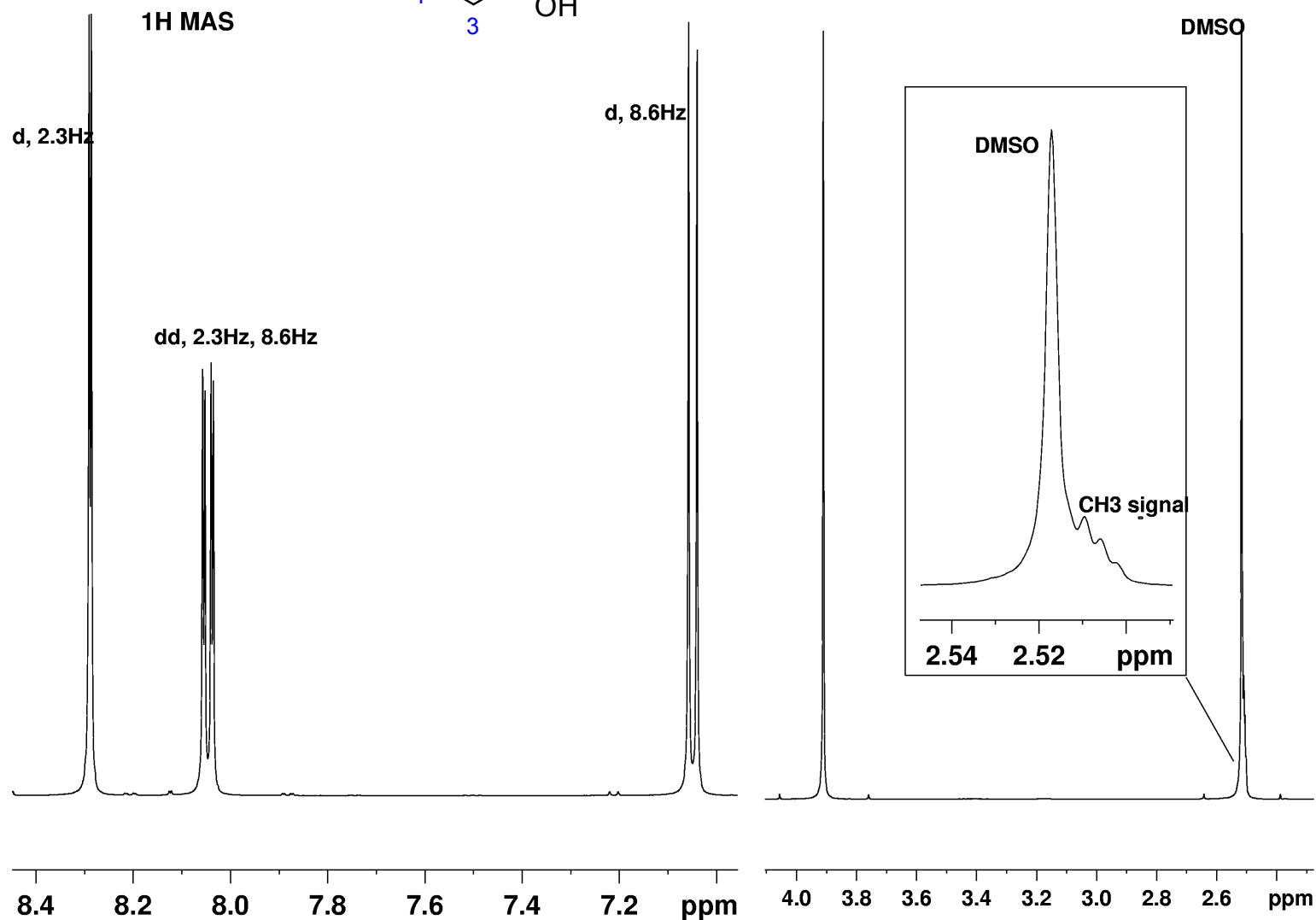
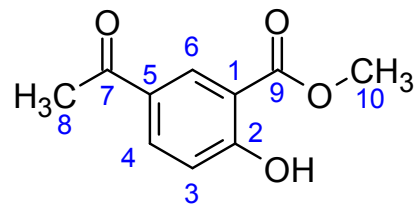
We are looking for:

- ▶ position of the signal (ppm)
- ▶ multiplicity (2J , 3J , 4J)
- ▶ intensity (integral)
- ▶ halfwidth

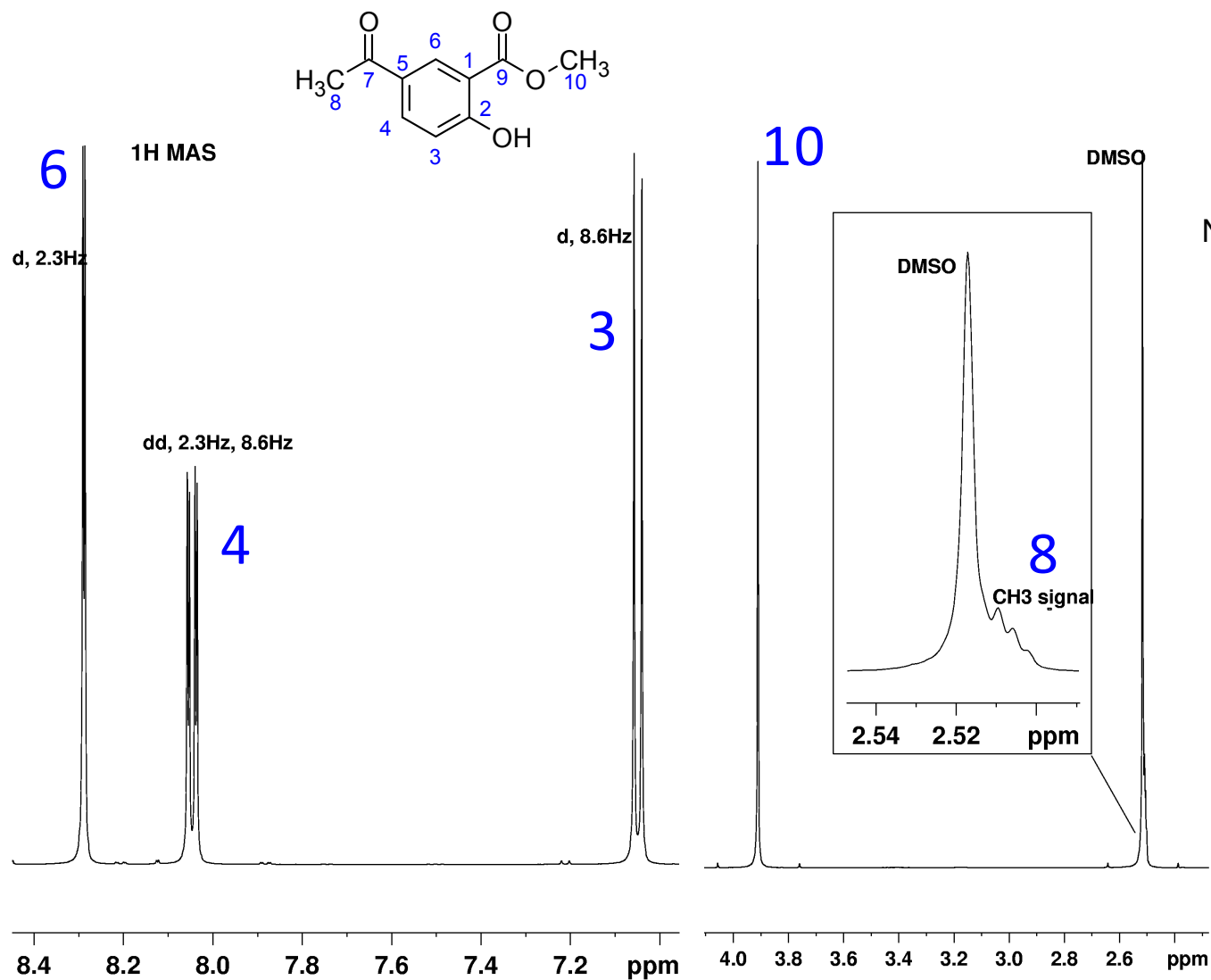
We are considering:

- ▶ chemical/magnetic equivalence
- ▶ enantiotopicity/diastereotopicity
- ▶ averaging of signals (dynamics, chemical exchange)

1D ^1H NMR spectrum of methyl-5-acetylsalicylate



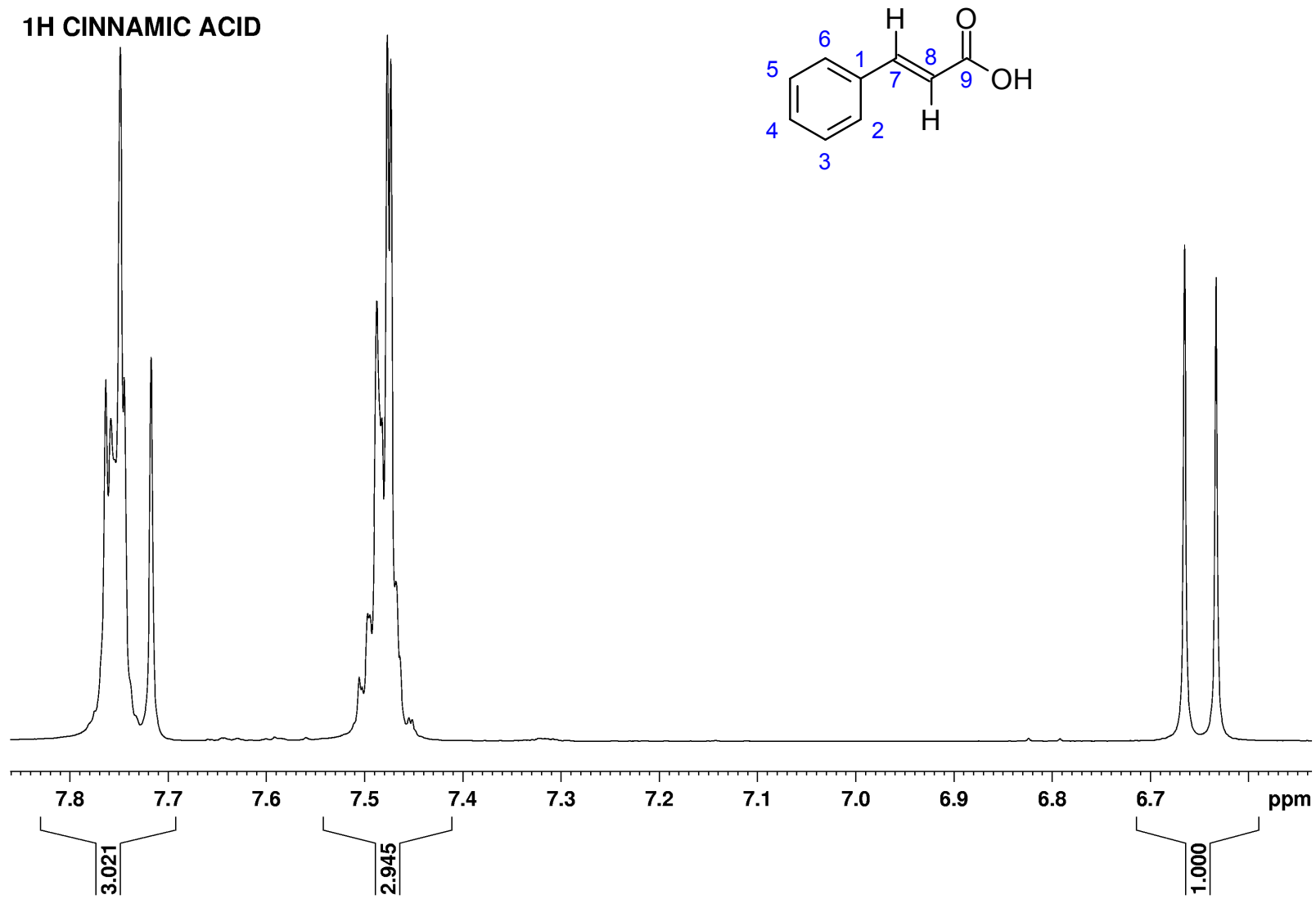
1D ^1H NMR spectrum of methyl-5-acetylsalicylate



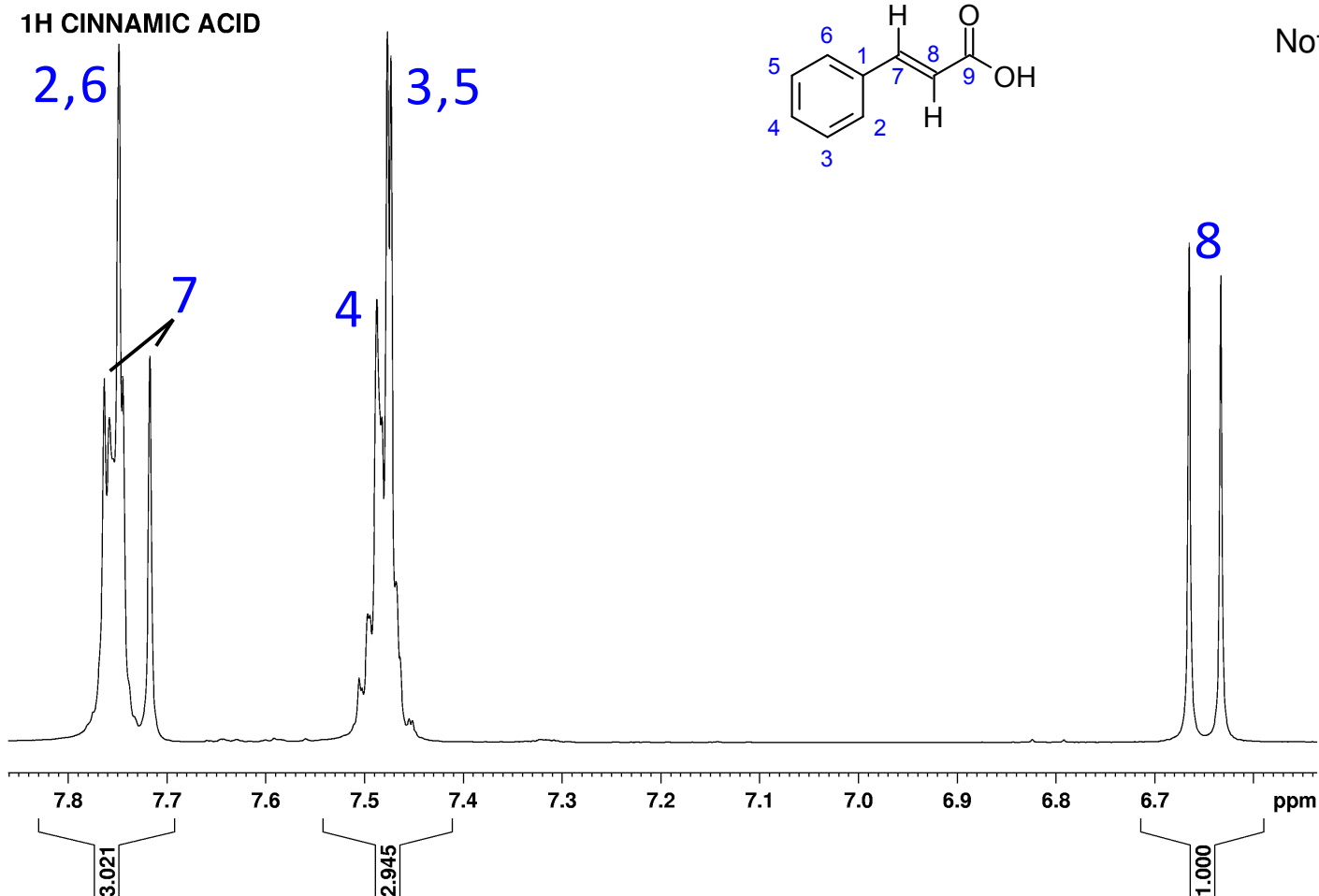
Notes:

- ▶ two singlets in the spectrum - two isolated groups in the structure - CH_3 groups; **Met-8** neighboring carbonyl has lowest shift than ester **Met-10**
- ▶ doublet of doublets (cca 8.0 ppm) - proton signal splitted by two neighbors - **H-4**
- ▶ two doublets in interaction with H-4 - based on the J -interaction: doublet with larger J -constant belongs to close proton - **H-3**, smaller J -constant - more distant proton - **H-6**

1D ^1H NMR spectrum of cinnamic acid



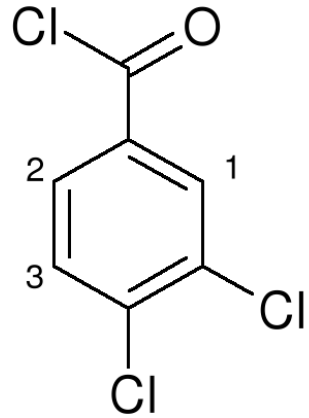
1D ^1H NMR spectrum of cinnamic acid



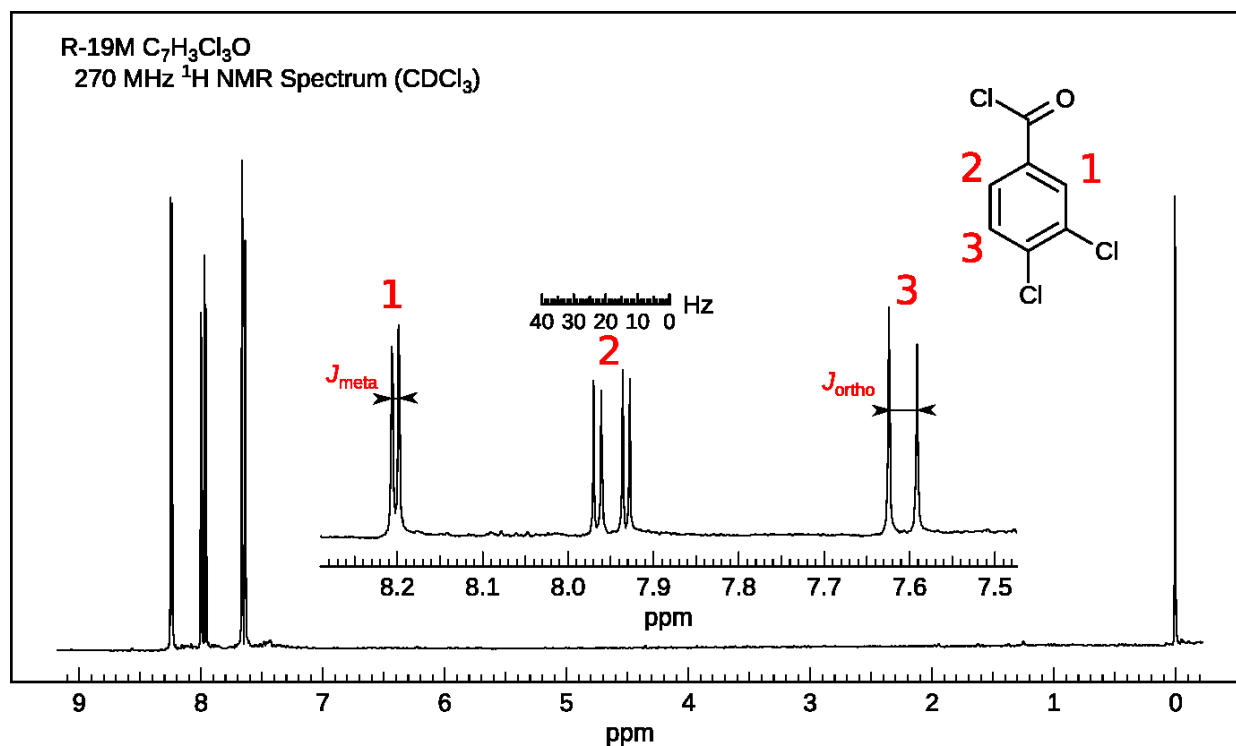
Notes:

- ▶ **H-8** - doublet with large coupling, in range of shifts of protons on double bond, integral = 1
- ▶ **H-7** - doublet with the same coupling like doublet H-8, deshielded due to -M effect of carboxyl and due to nearby aromatic ring
- ▶ more intensive signal between 7.7 and 7.8 ppm has integral: 3-1=2 protons - **H-2,6**, symmetrical, highest shift due to -M effect of substituent in *ortho* position on aromatic ring
- ▶ signal with integral = 3 around 7.5 ppm - less intensive signal - only one proton, highest shift due to -M effect of substituent in *para* position - **H-4**; more intensive signal with highest shift - **H-3,5**

Draw approximate 1D ^1H NMR spectrum of the following compound



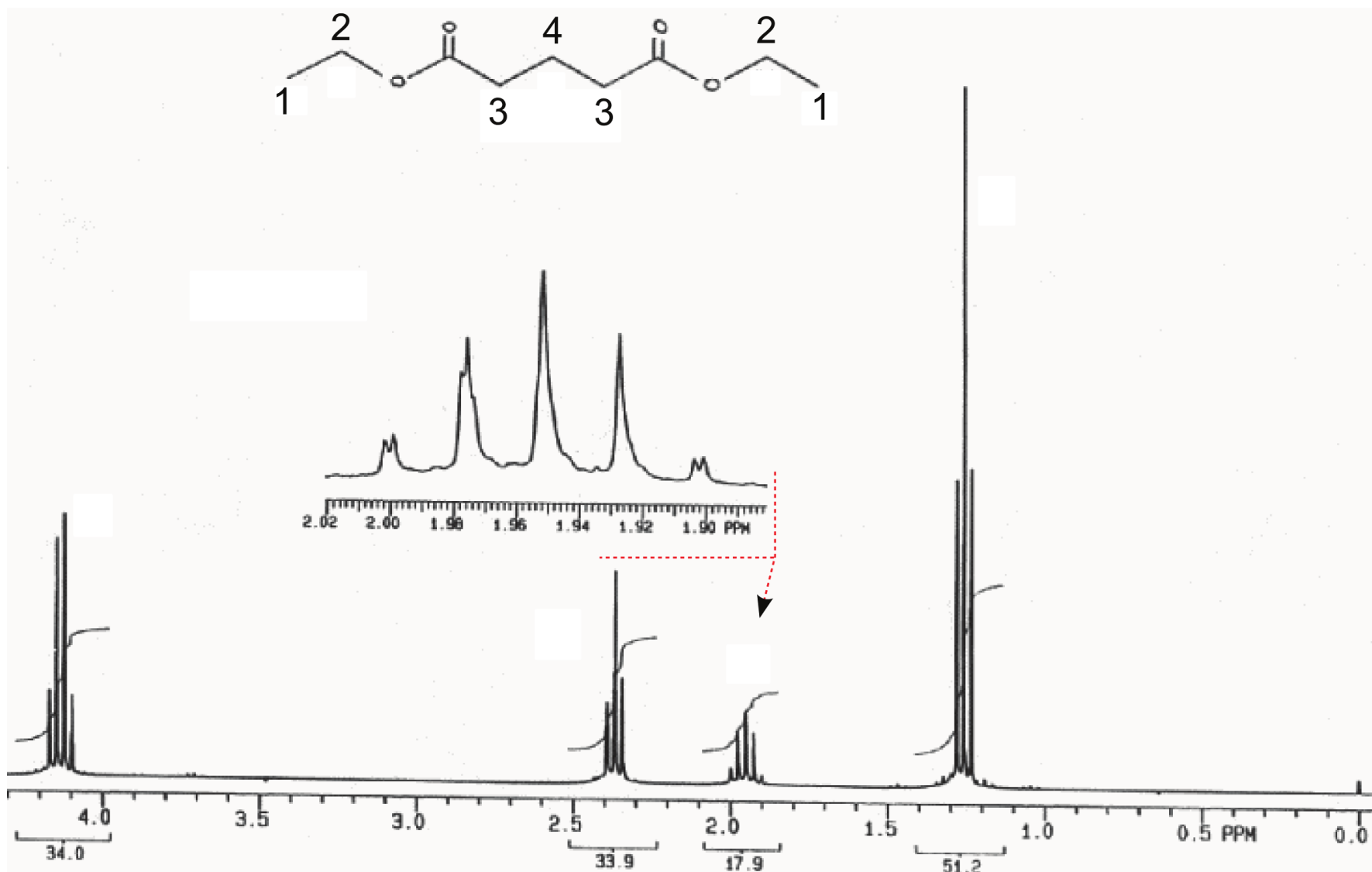
Draw approximate 1D ^1H NMR spectrum of the following compound



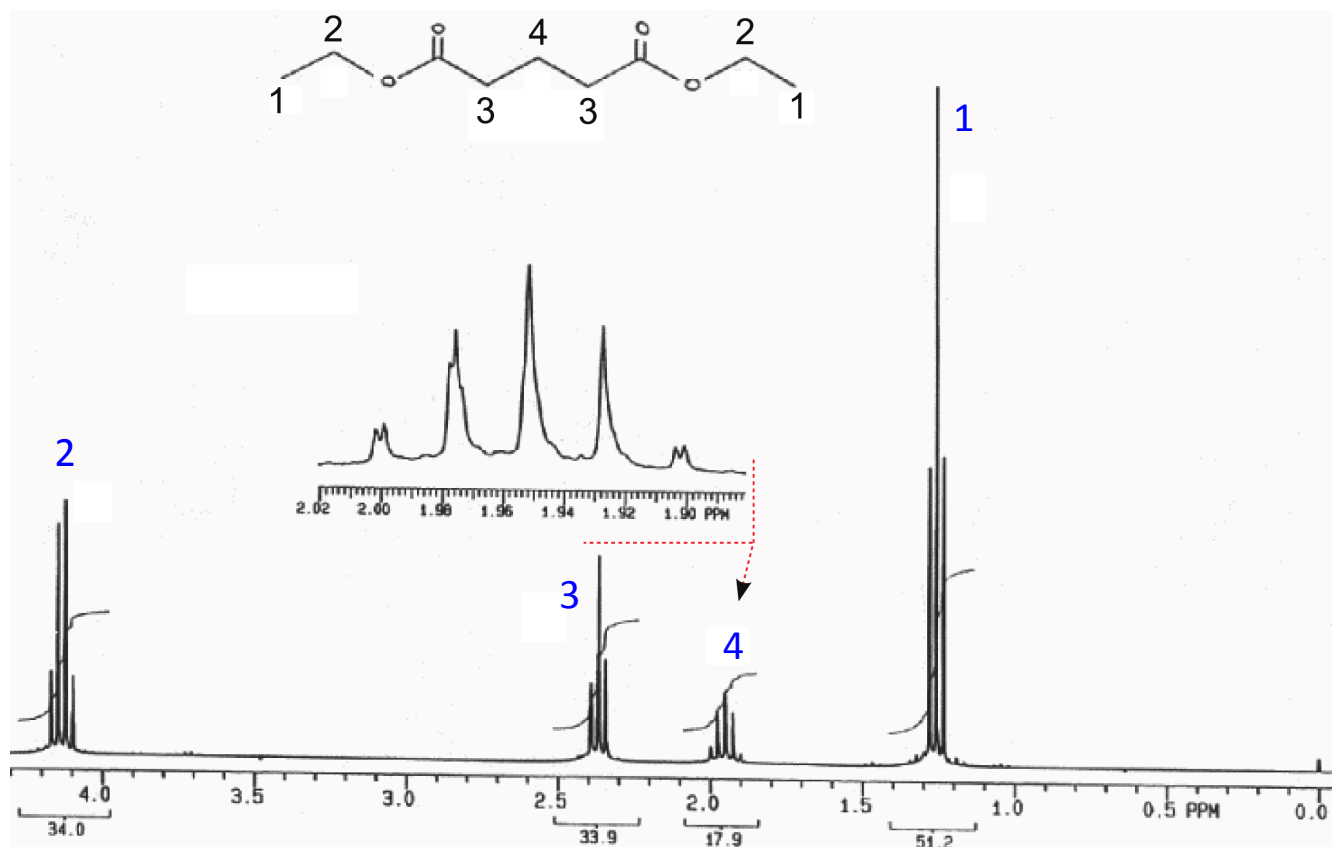
Notes:

- ▶ **H-2** - *meta*- and *ortho*- interaction with H-1 a H-3 - doublet of doublets
- ▶ **H-1** - only *meta*- interaction with H-2 - smaller coupling than **H-3** in *ortho*-interaction with H-2
- ▶ chemical shifts are result of overall effects of substituents on the aromatic ring

1D ^1H NMR spectrum of ethyl glutarate



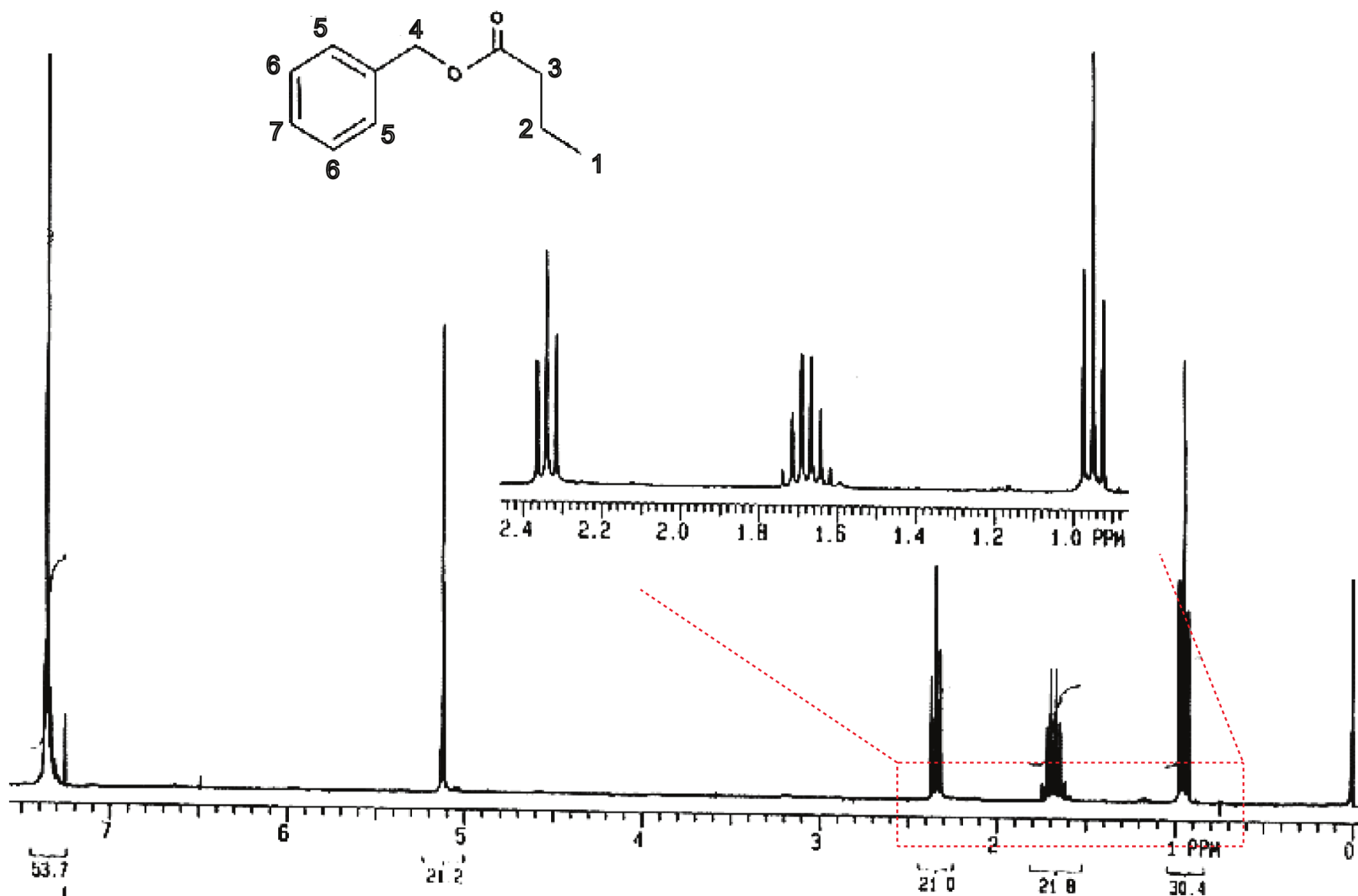
1D ^1H spectrum of ethyl glutarate



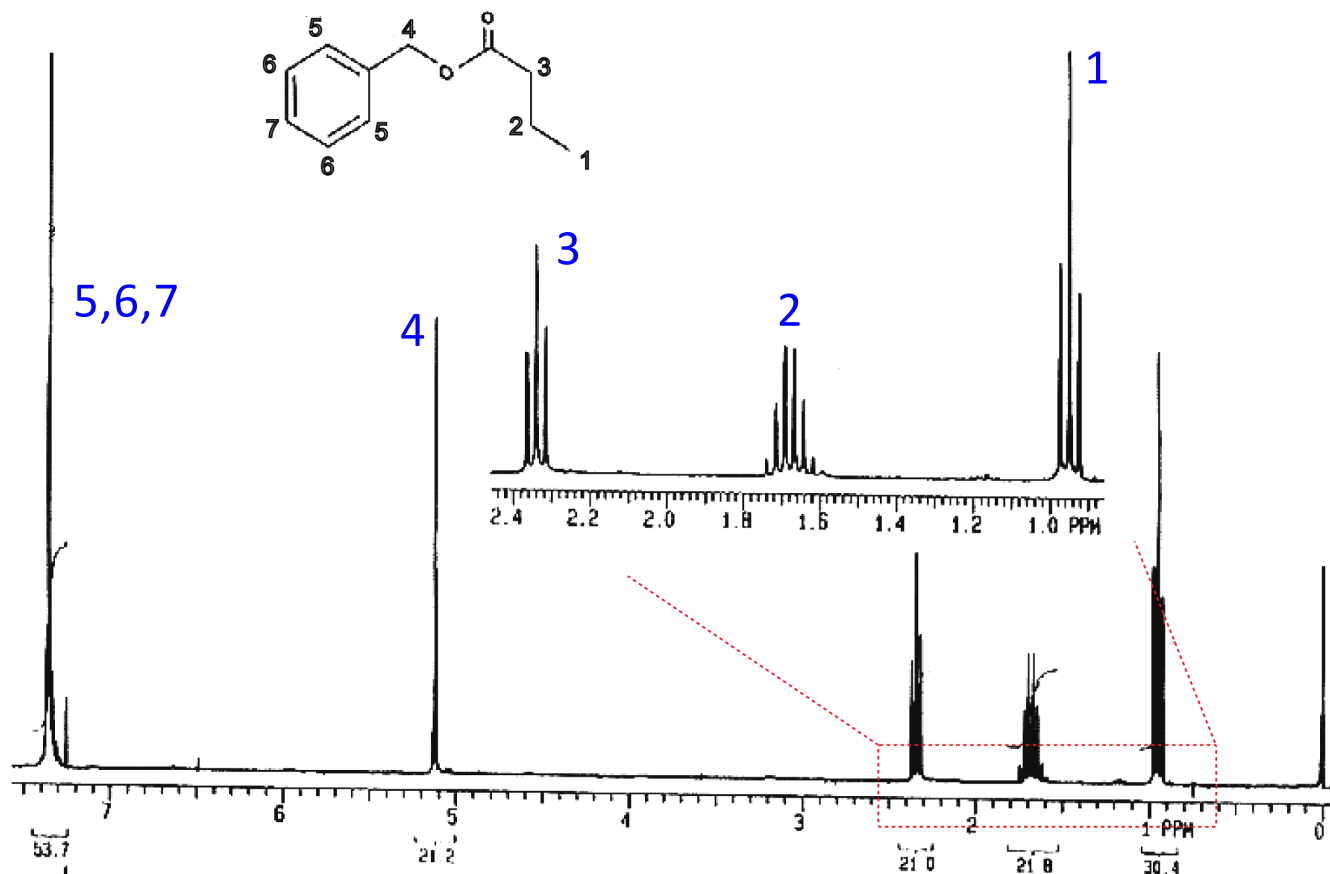
Notes:

- ▶ symmetrical molecule - equivalent groups will give rise to only one signal
- ▶ splitting corresponds to $n+1$ rule
- ▶ signal integrals correspond to number of protons in groups
H-1:H-2:H-3:H-4 in the ratio 6:4:4:2
- ▶ chemical shifts depend on chemical environment of atoms

1D ^1H NMR spectrum of benzyl butyrate



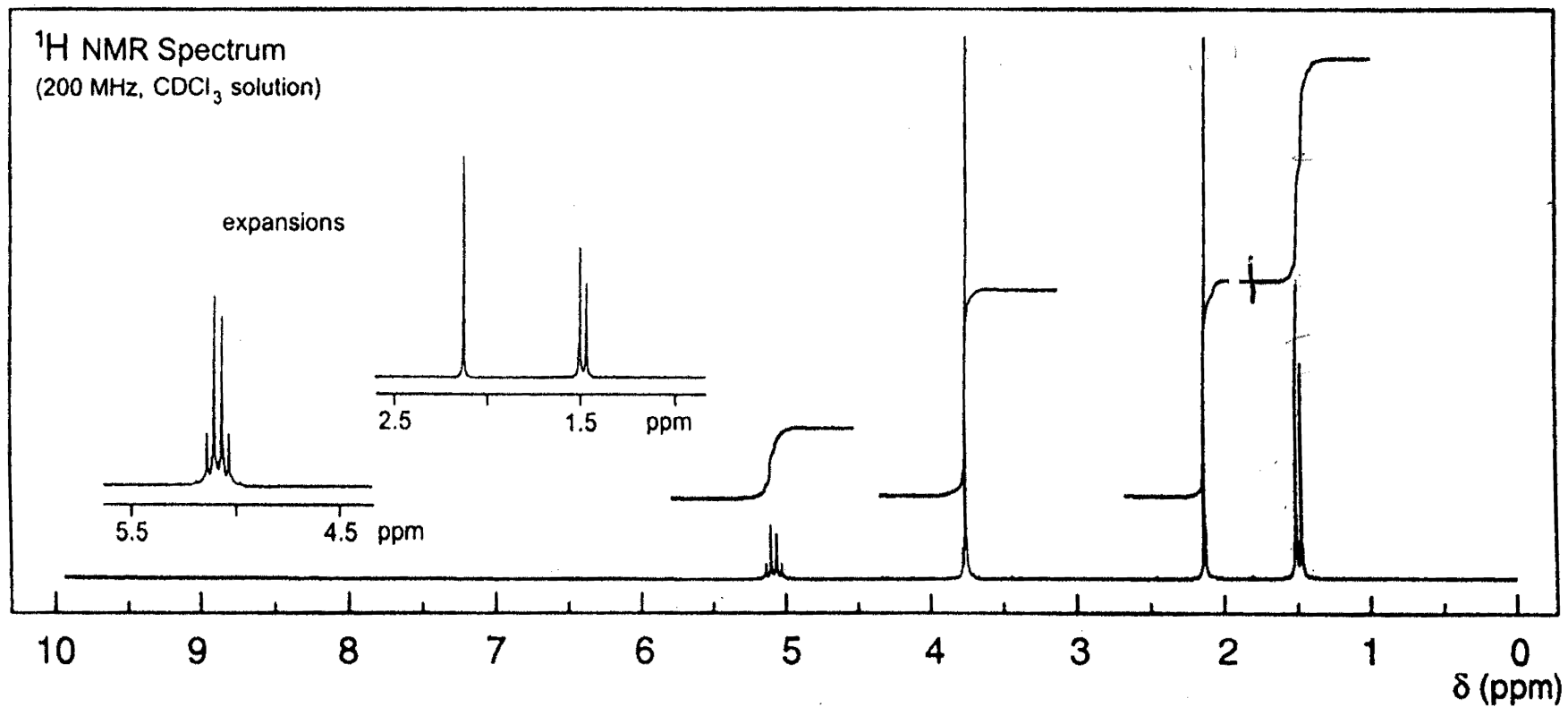
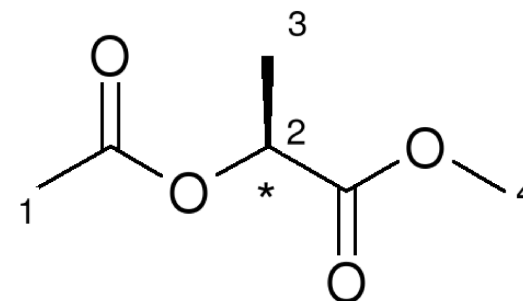
1D ^1H NMR spektrum benzylobutyrate



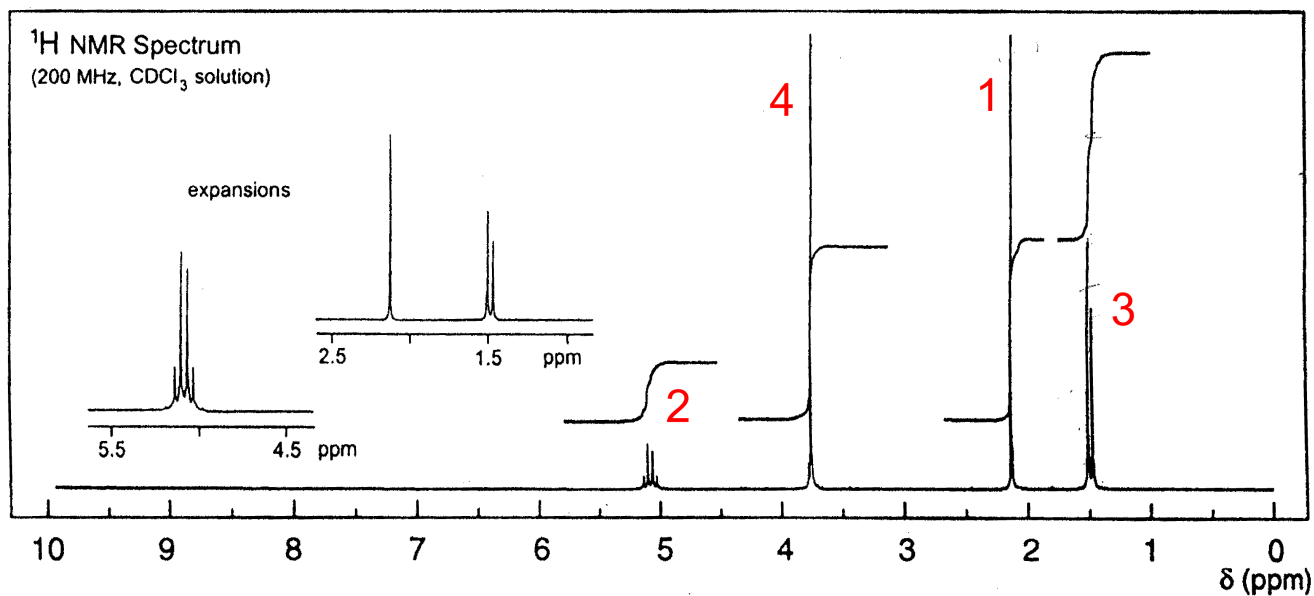
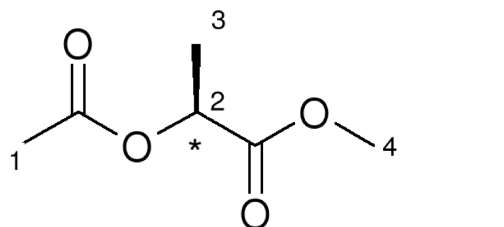
Notes

- ▶ highest shift - aromatic ring, which is flexible - **H-5, H-6, H-7** are under one signal, integral value corresponds to five protons
- ▶ lowest shifts - aliphatic chain H-1, H-2 a H-3: **H-1** - integral equals to three protons, splitted only by H-2 to triplet; **H-2** - integral equals to two protons, splitted by both H-1 and H-3 to triplet of quartets, which is due to similar J -coupling values fused into sextet; **H-3** - integral equals to two protons, splitted by H-2 to triplet
- ▶ **H-4** - integral equals to two protons, isolated signal - singlet, highest shift among all aliphatic protons due to neighboring carboxyl and aromatic ring

1D ^1H NMR - methyl 2-acetoxy propanoate

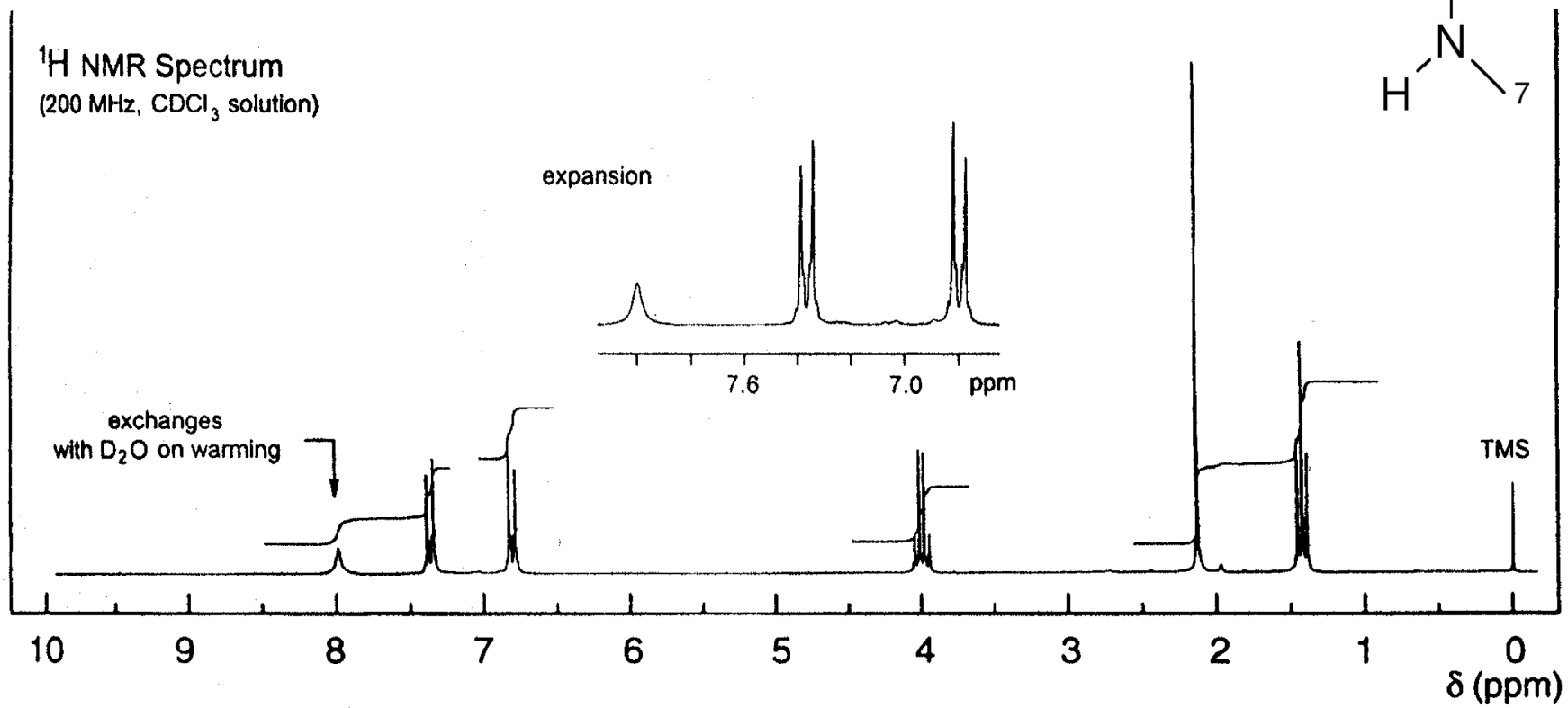
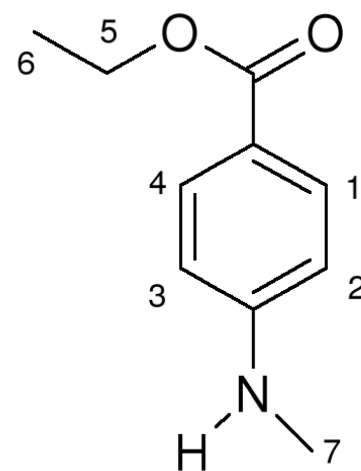


1D ¹H NMR - metyl 2-acetoxypropanoát

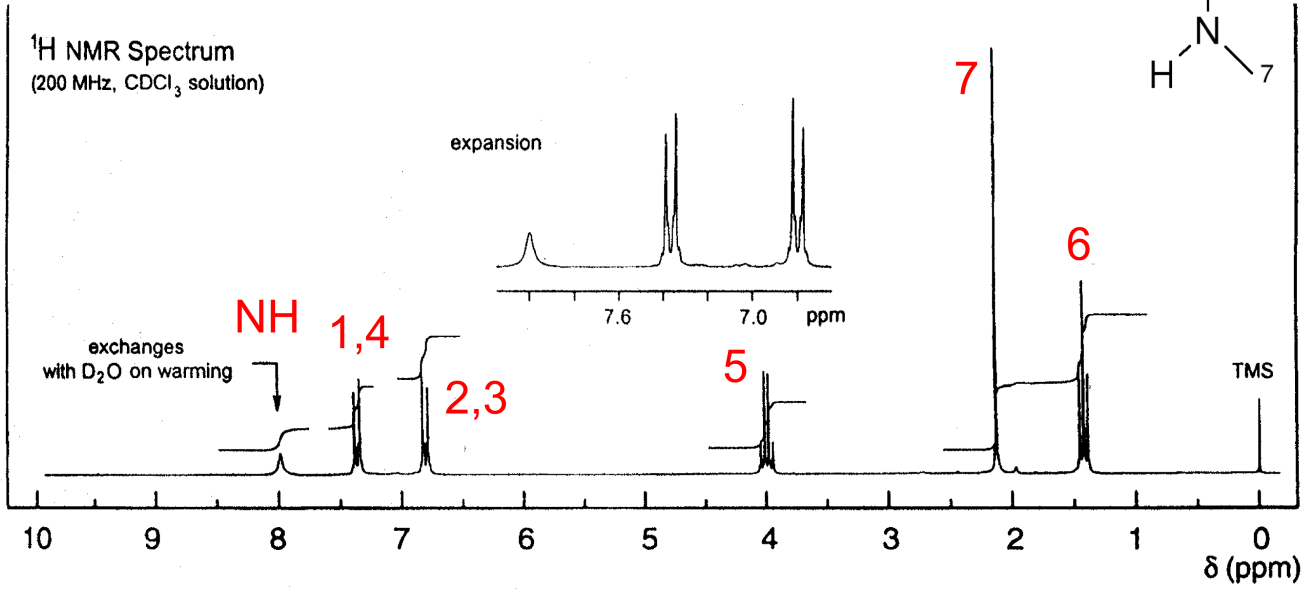
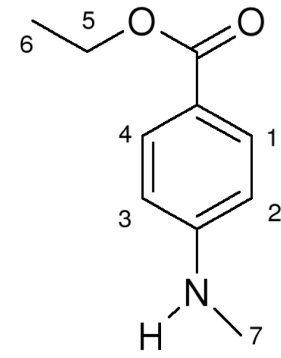


- ▶ lowest shift - methyl **H-3**, splitted due to neighboring stereogenic center C-2
- ▶ last splitted signal - **H-2** - splitted by H-3 to quartet, highest shift due to neighboring carboxyl groups
- ▶ two singlets - highest shift **H-4** next to carboxylic oxygen; lowest shift - **H-1** next to carboxylic carbon
- ▶ integrals corresponds to number of protons

1D ^1H NMR - ethyl 4-(methylamino)benzoate



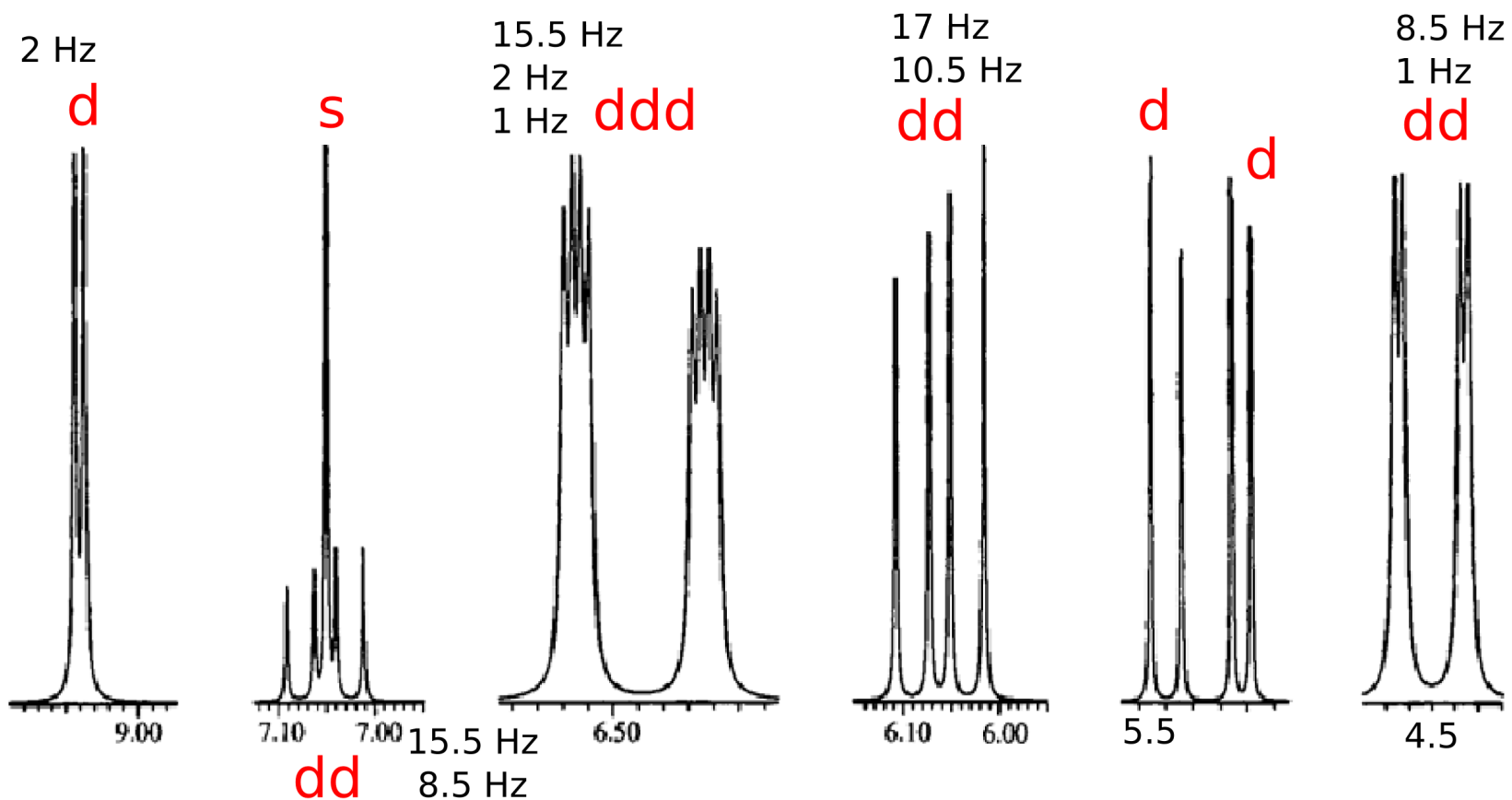
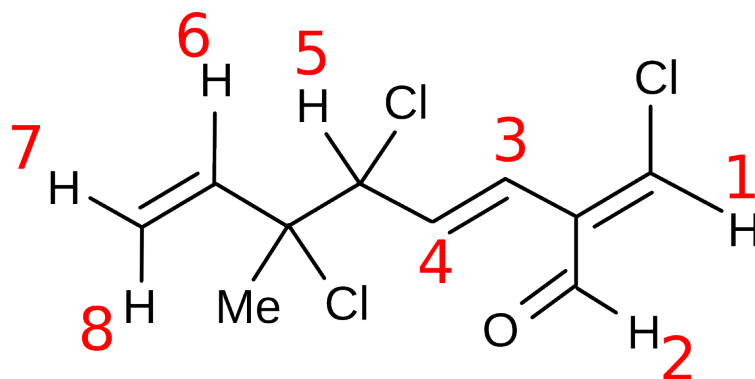
1D ¹H NMR - etyl 4-(methylamino)benzoát



Notes:

- ▶ highest shift - **NH**, least intensive and broad signal because there is dynamical exchange of the proton with the solvent, it is visible in the spectrum thanks to CDCl₃ used as solvent
- ▶ lowest shifts - alifatics - signal at 1.5 ppm splitted to triplet - methyl **H-6** splitted by H-5; singlet around 2 ppm - methyl **H-7** - isolated, highest shift than H-6 thanks to nitrogen; quartet at 4 ppm - **H-5** - splitted by methyl H-6, highest shift thanks to oxygen
- ▶ two doublets in aromatic region around 7 ppm - **H-1,4** a **H-2,3** - symmetrical, shifts are resulting from effects of both substituents on aromatic ring

1D ^1H NMR spectrum of cartilagineal



Next session:

1D ^{13}C -NMR spectra