

C8953
NMR strukturní analýza
seminář

Informace o výuce + 1D ^1H -NMR

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2. března 2016

Informace o výuce

Zápočet:

- ▶ Max. 2 neomluvené neúčasti
- ▶ Úspěšně napsaná půlsestrální písemná práce (spektra+teorie)
- ▶ Úspěšně odevzdaný projekt
- ▶ Úspěšně vyřešená spektra závěrečné úlohy

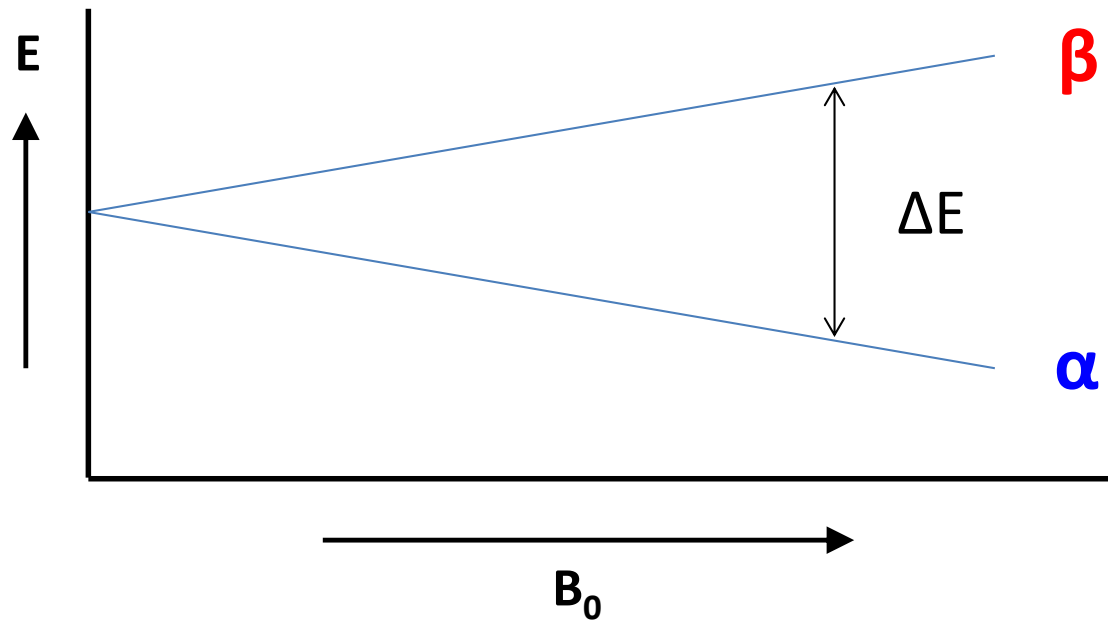
Studijní materiály:

<https://is.muni.cz/auth/el/1431/jaro2016/C8953/um>

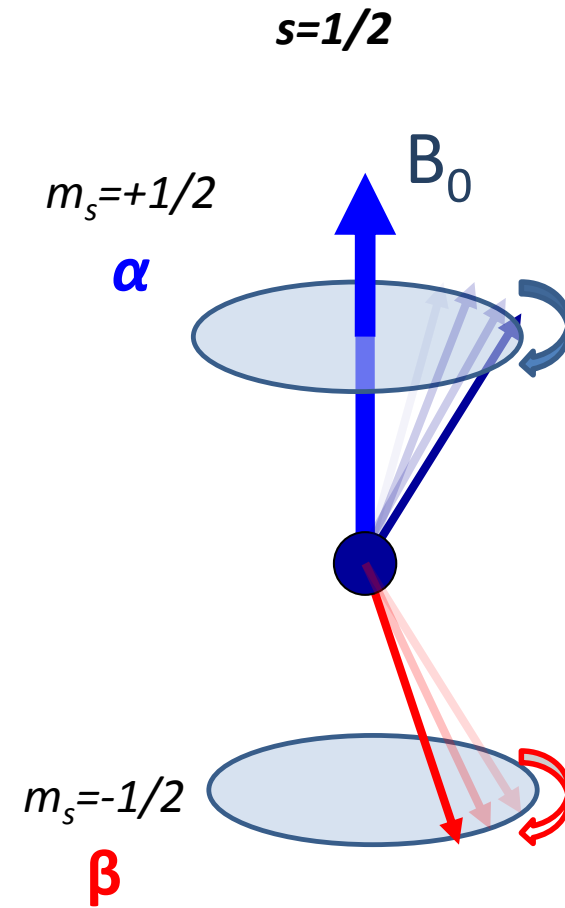
Odpovědníky:

<https://is.muni.cz/auth/el/1431/jaro2016/C8953/odp>

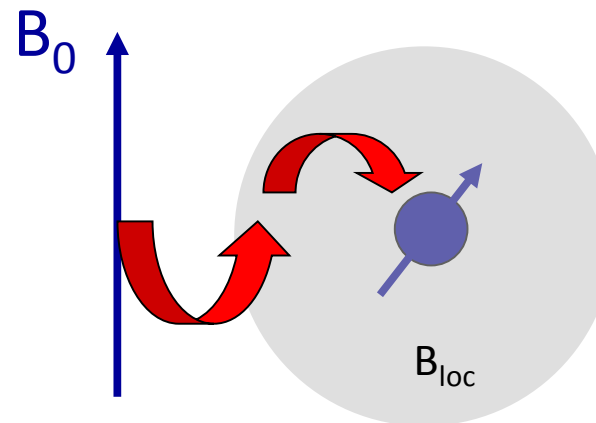
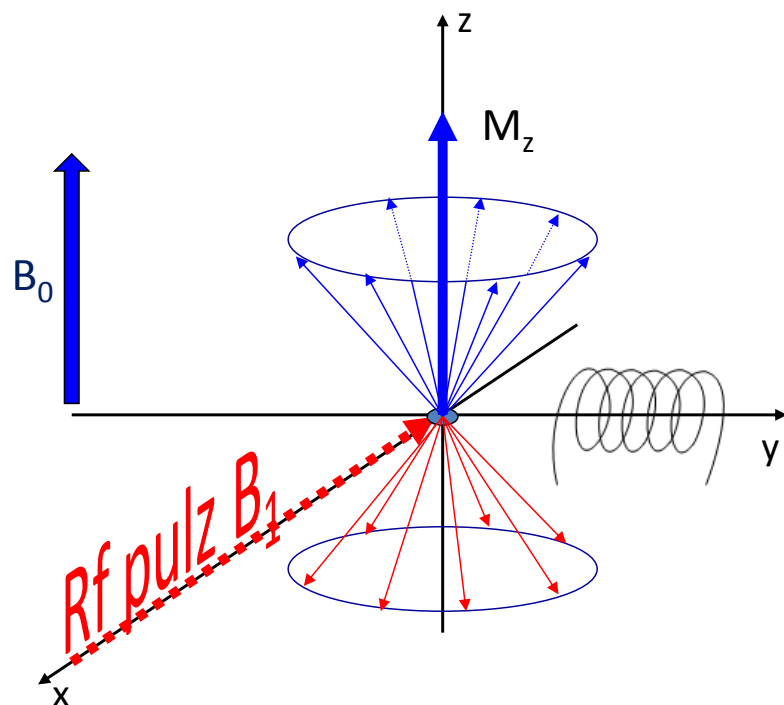
Rozštěpení energetických hladin



$$N_\alpha > N_\beta$$



Chování jaderného spinu po iradiaci RF pulzem



B_0 indukuje lokální mag. pole B_{loc} , které působí proti B_0

Jaderné stínění

Precesní frekvence:

Precesní frekvence ovlivněna stíněním jádra:

Chemický posun:

Definice relativní škály chemického posunu:

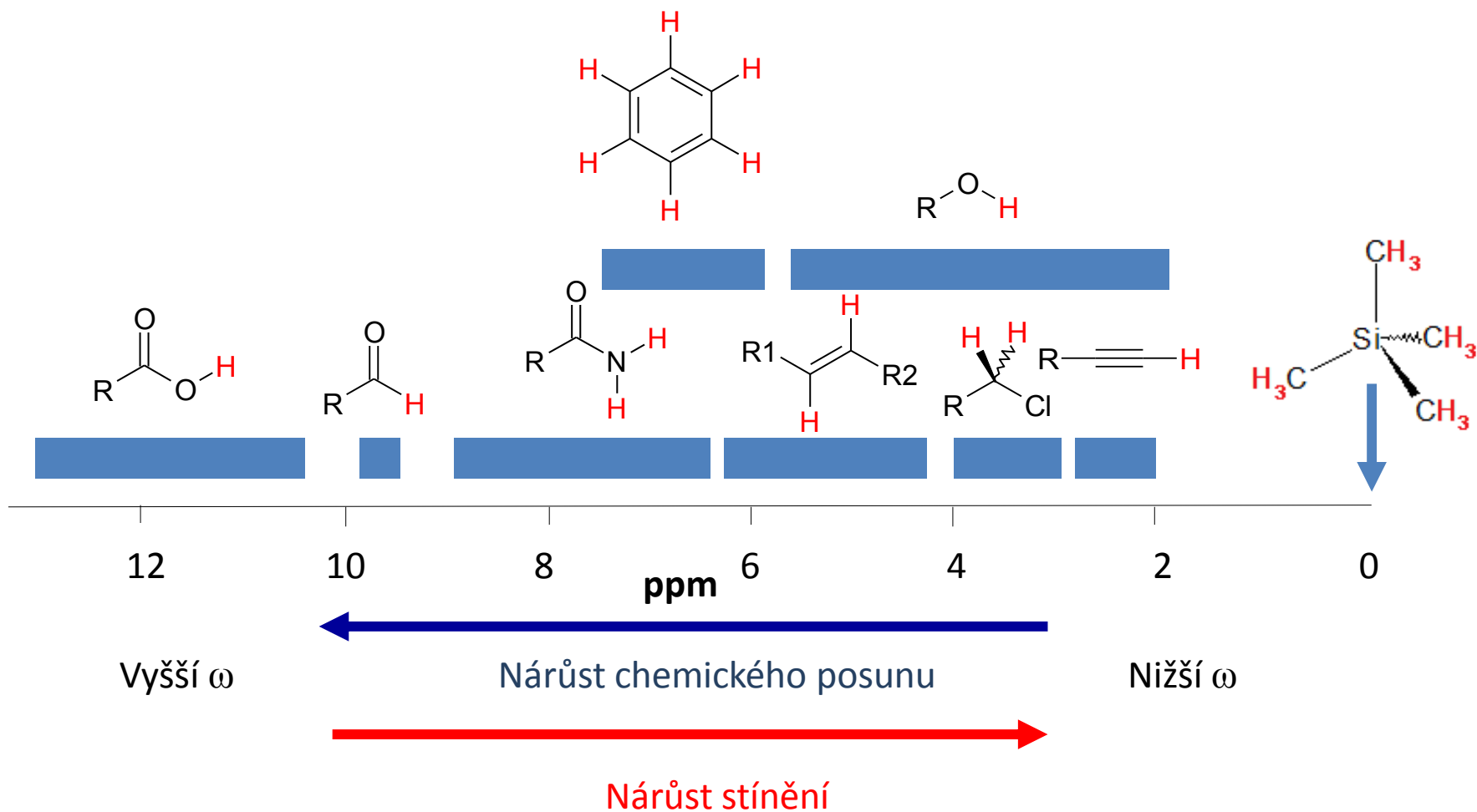
$$\omega = -\gamma B_0$$

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

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

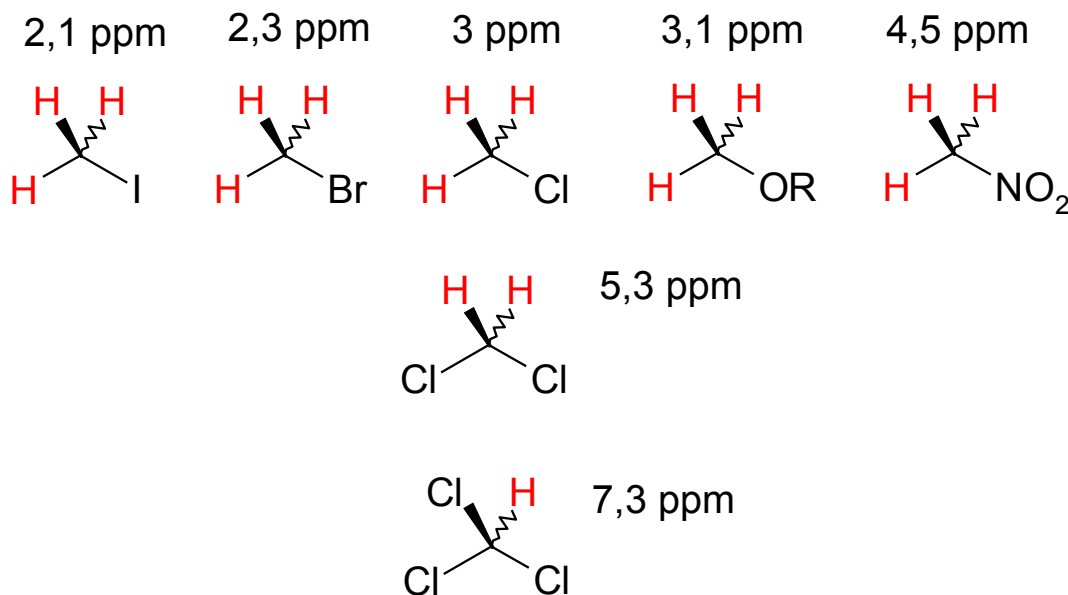
$$\delta = (\omega - \omega_{ref})/\omega_{ref} \cdot 10^6 \text{ ppm}$$

Charakteristické intervaly hodnot chemických posunů



Trendy v posunech

- ▶ Elektronegativita, indukční a mezomerní efekty substituentů
- ▶ Hybridizace
- ▶ Relativní pozice vůči kruhu, dvojité vazbě



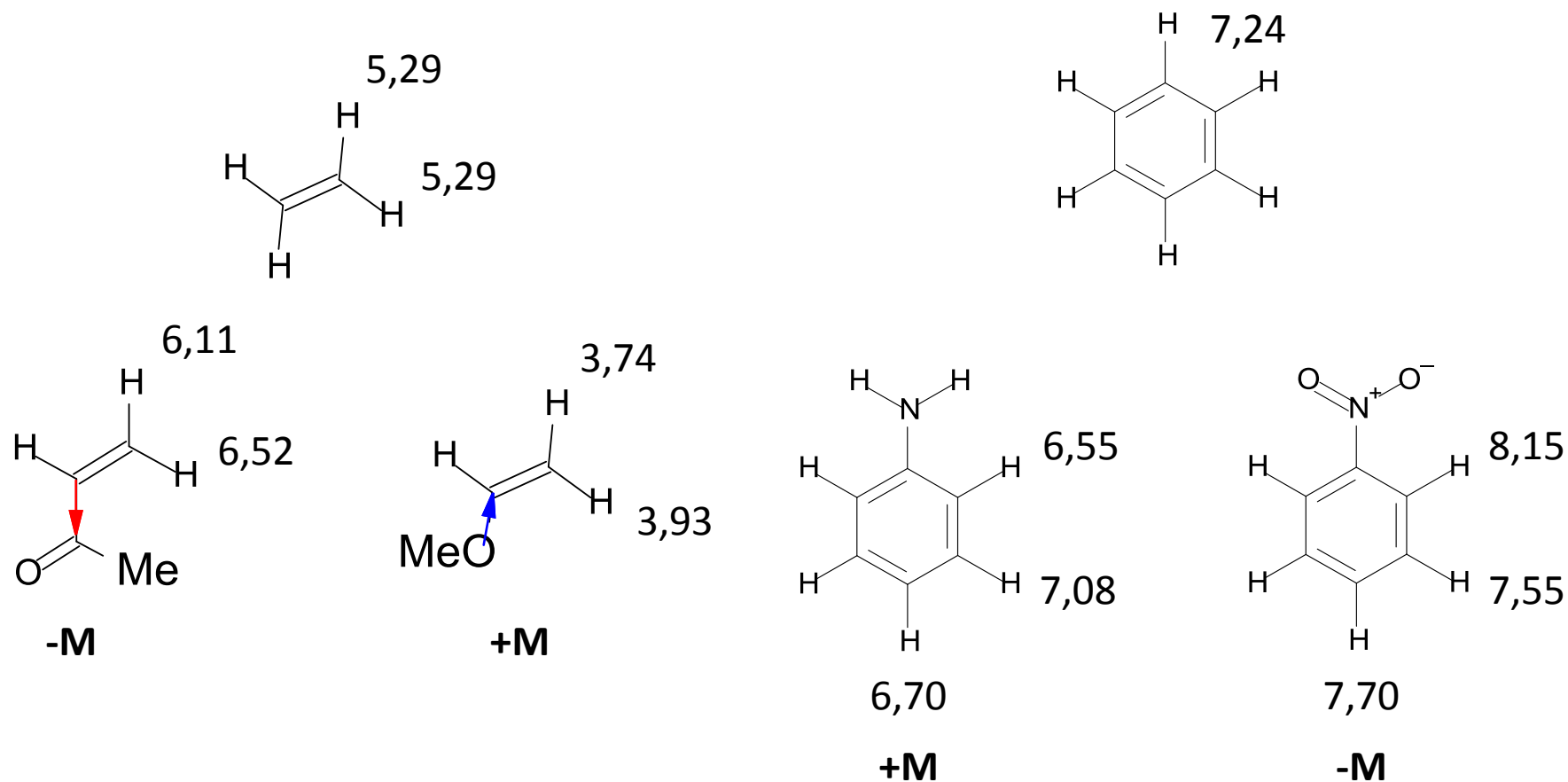
Substituenty s -I efektem

$=N^+R_2 > -N^+R_3 > -NO_2 > -NR_2$
 $-SO_2R > -SO_3 > -SOR > -SR$
 $-F > -OR > -NR_2 > -CR_3$
 $-F > -Cl > -Br > -I$
 $\equiv N > =NR > -NR_2$
 $-C\equiv CH > -CH=CH_2 > -CH_2-CH_3$

Substituenty s +I efektem

$-N-R > -O->S-$
 $-C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3 > -CH_3$
kovy

Mezomerní efekt



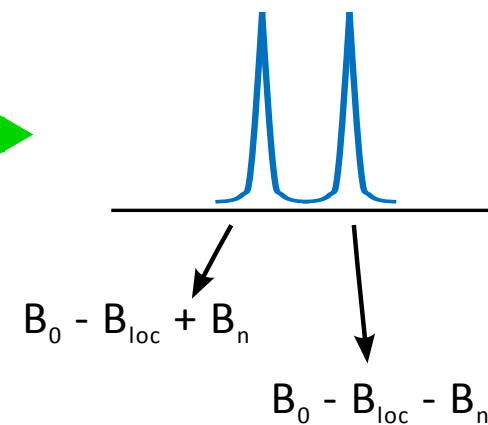
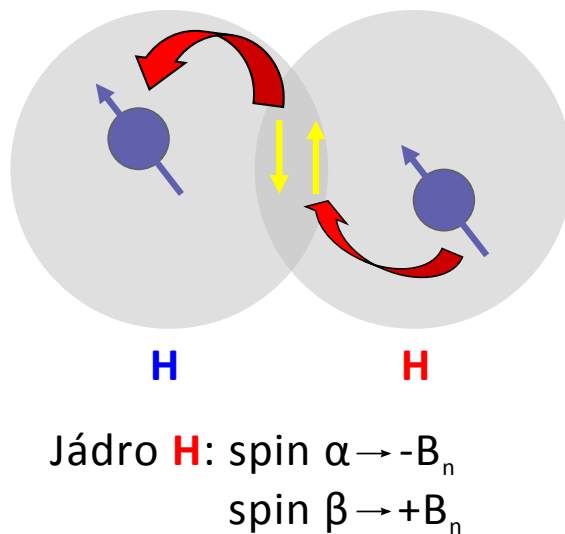
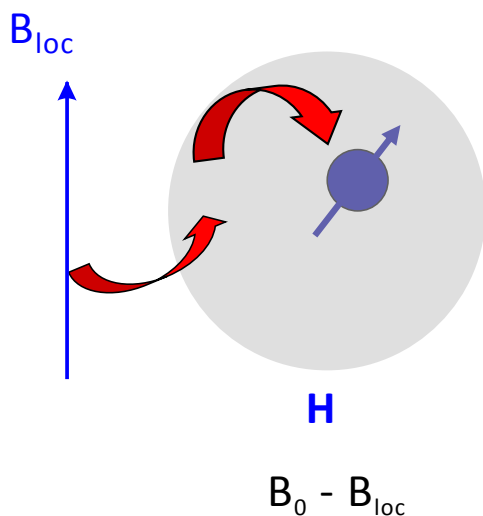
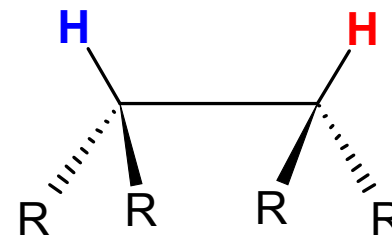
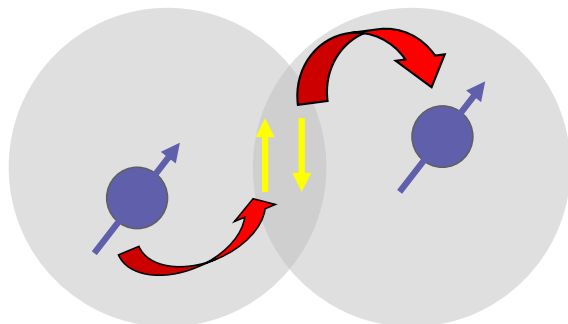
Substituenty s +M efektem:

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

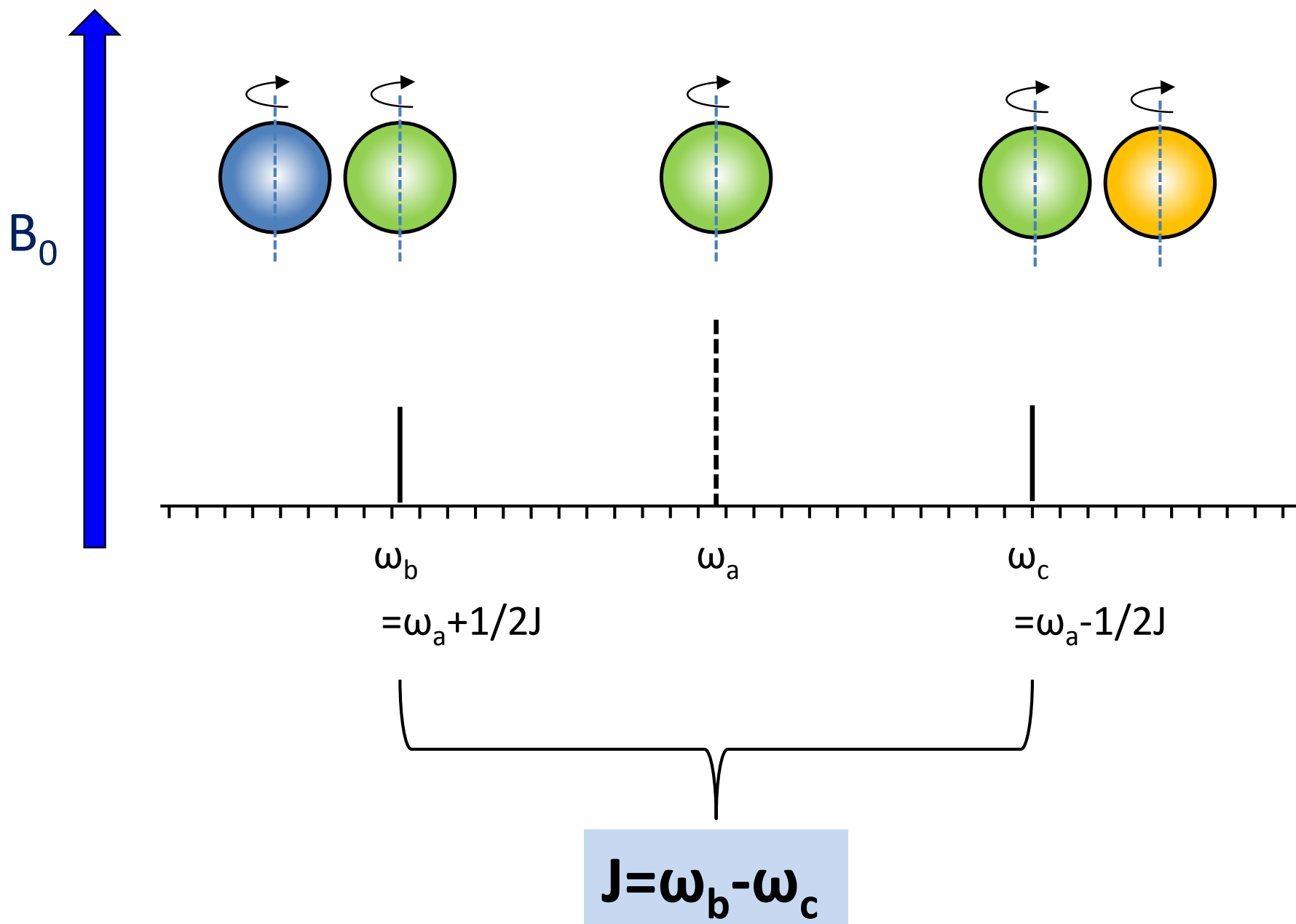
Substituenty s -M efektem:

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

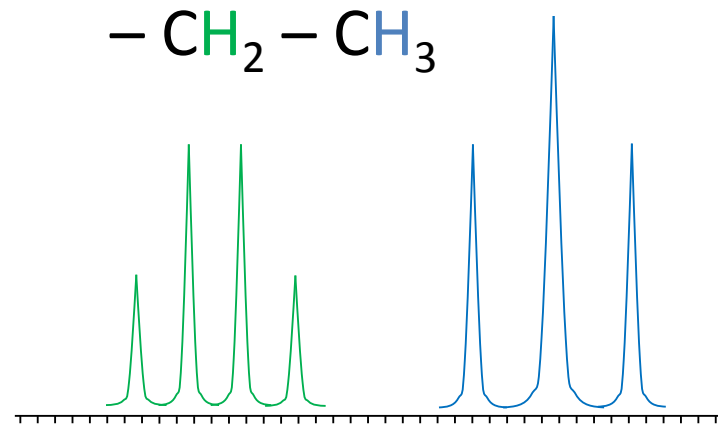
Spin-spinová interakce, J -coupling



Interakční konstanta J



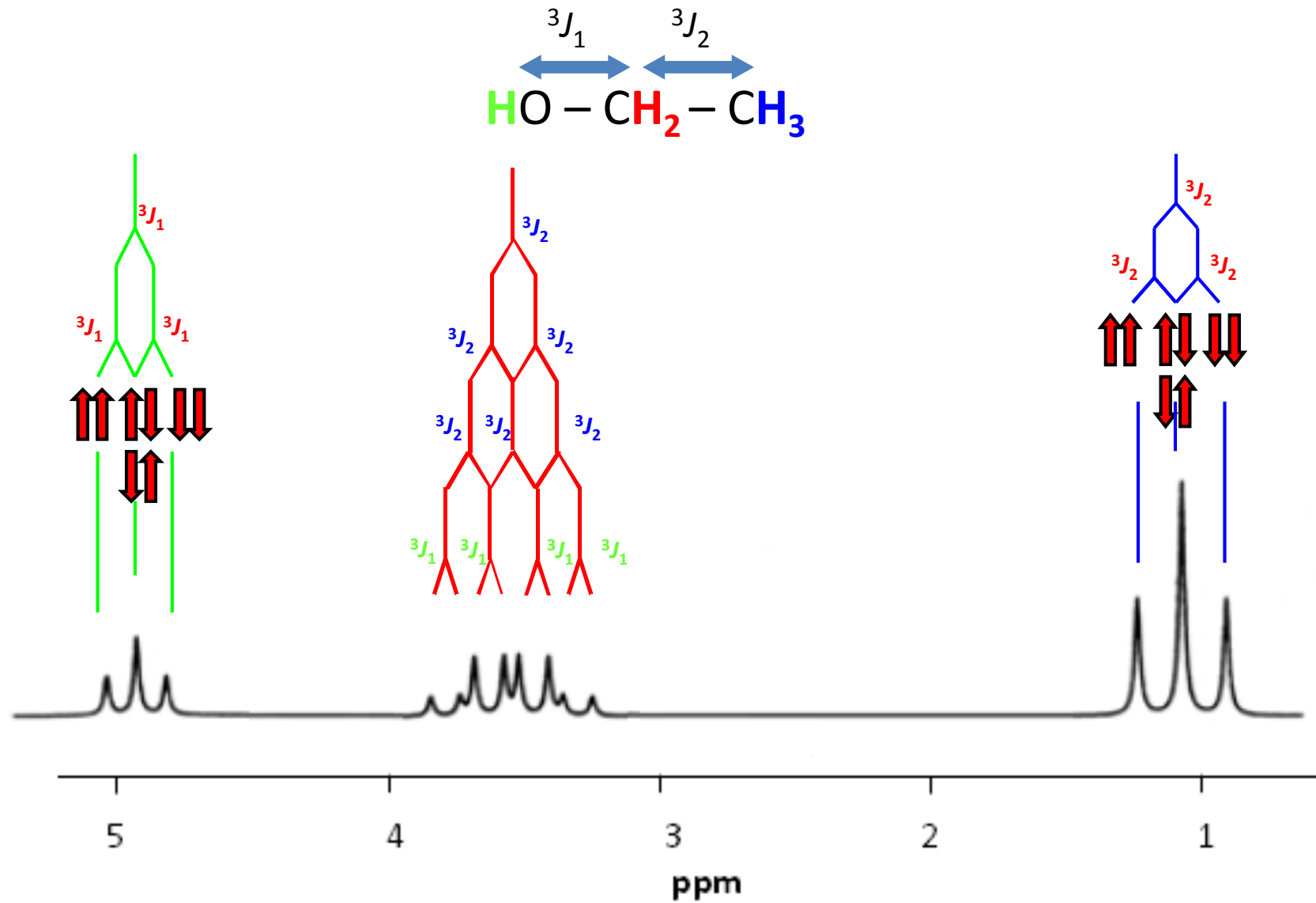
Interakční konstanta J



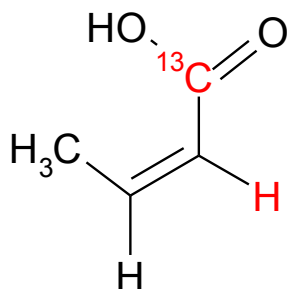
- ▶ Pro multiplicitu signálu jádra I se spinem $1/2$ platí:
 $m = n + 1$, $n =$ počet interagujících jader s jádrem I
- ▶ Intenzita čar multipletu se řídí Pascalovým trojúhelníkem

			1				
		1		1			
	1		2		1		
	1	3		3		1	
1	4		6		4	1	
1	5	10		10		5	1

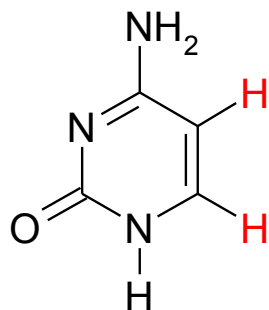
1D ^1H NMR spektrum



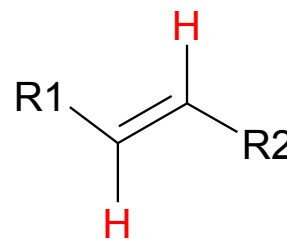
Hodnoty J -interakčních konstant



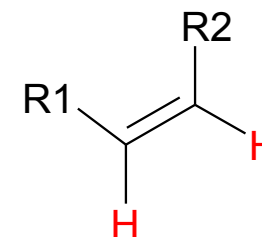
$${}^2J_{CH} = 3.1 \text{ Hz}$$



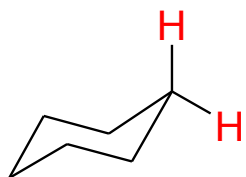
$${}^3J_{HH} = 12 \text{ Hz}$$



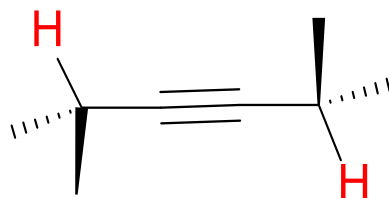
$${}^3J_{HH} = 13 - 18 \text{ Hz}$$



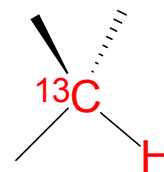
$${}^5J_{HH} = 7 - 12 \text{ Hz}$$



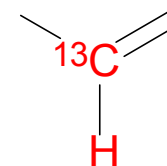
$${}^2J_{HH} = -12,5 \text{ Hz}$$



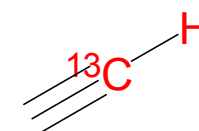
$${}^5J_{HH} = 2 - 3 \text{ Hz}$$



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

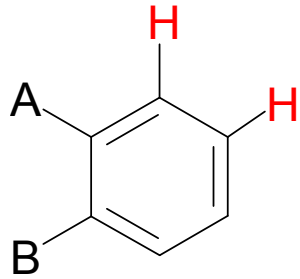


$${}^1J_{CH} = 160 \text{ Hz}$$

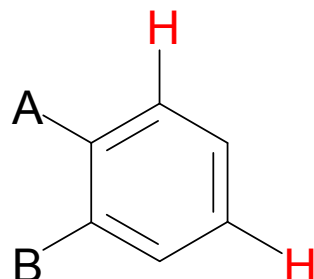


$${}^1J_{CH} = 250 \text{ Hz}$$

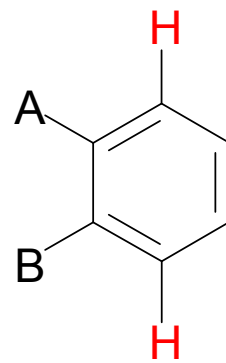
Hodnoty J -konstant - trendy



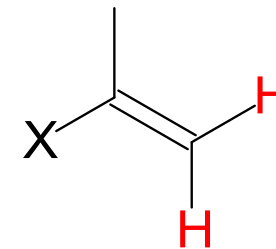
$${}^3J_{HH} = 7,5 \text{ Hz}$$



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



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



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

1D ^1H NMR spektroskopie

- ▶ nejrychleji naměřené, nejvyšší citlivost
- ▶ u komplikovanějších systémů obtížná interpretace

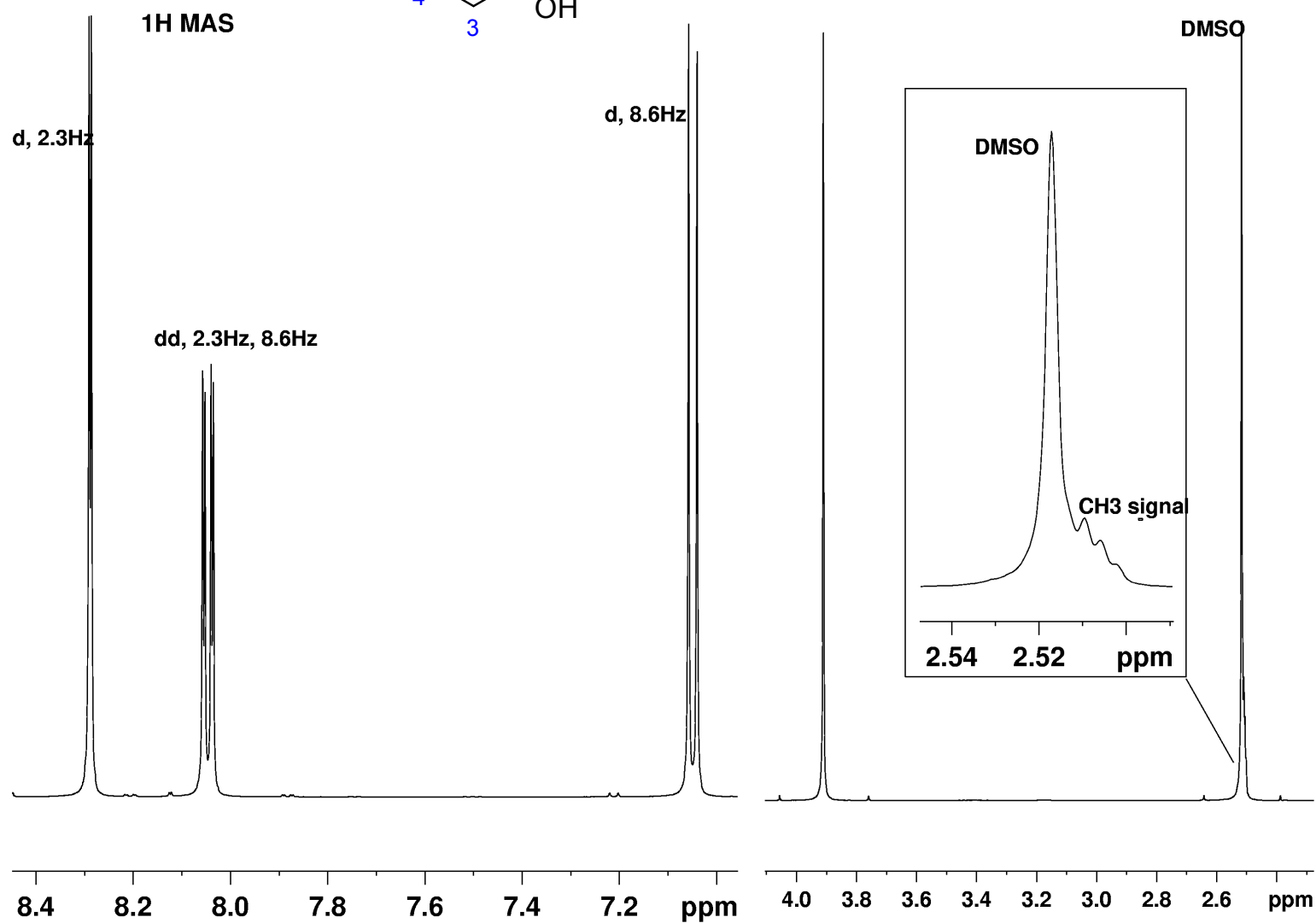
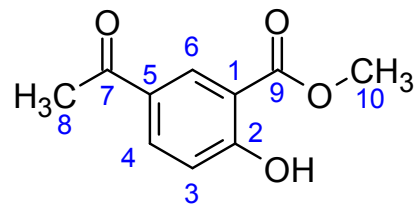
Všímáme si:

- ▶ polohy signálu (ppm)
- ▶ multiplicity (2J , 3J , 4J)
- ▶ intenzity (integrálu)
- ▶ pološířky

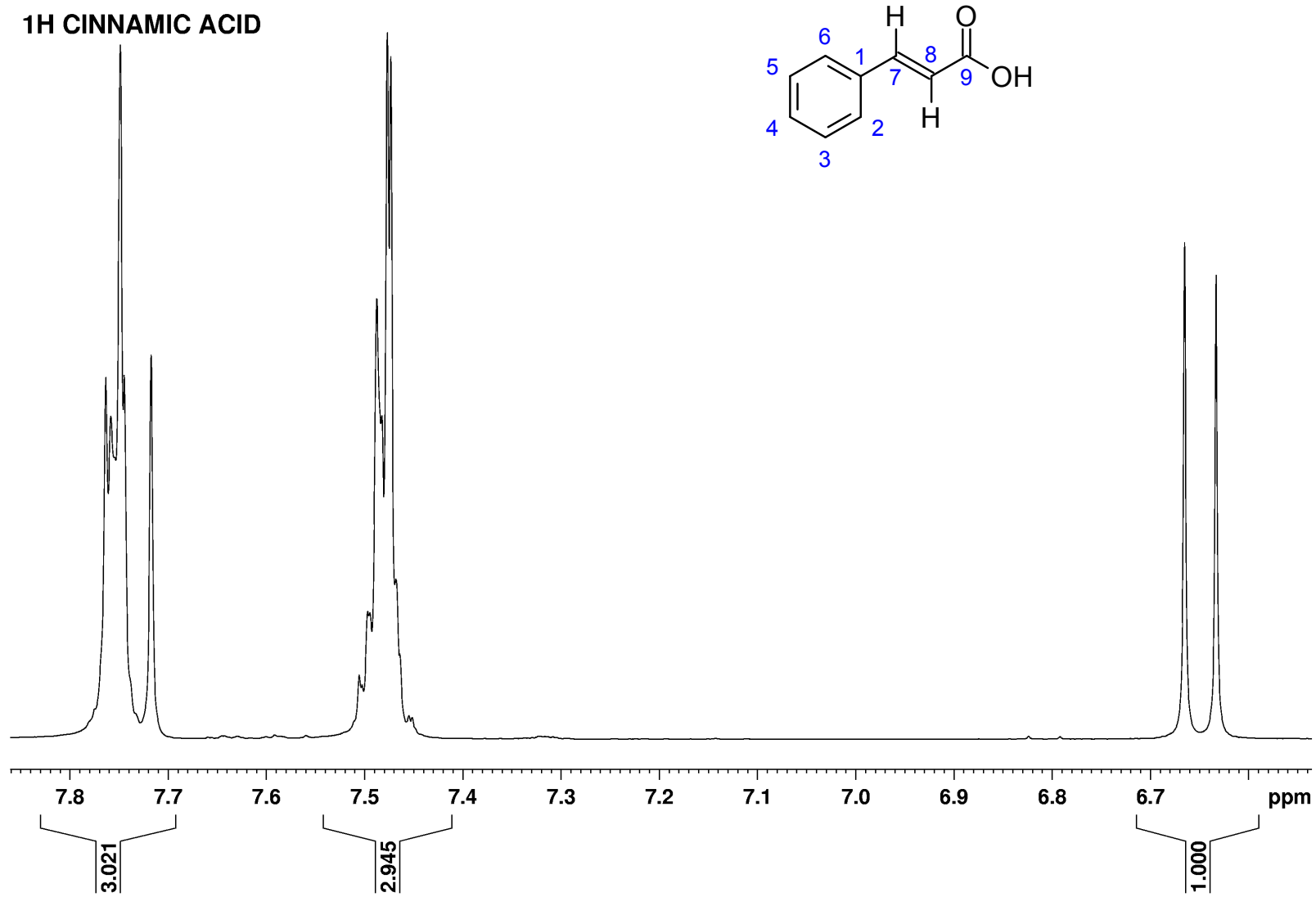
Bereme do úvahy:

- ▶ chemickou/magnetickou ekvivalenci
- ▶ enantiotopicitu/diastereotopicitu
- ▶ průměrování signálů (pohyb, chemická výměna)

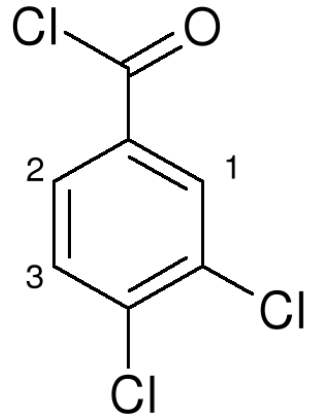
1D ^1H NMR spektrum methyl-5-acetylsalicylátu



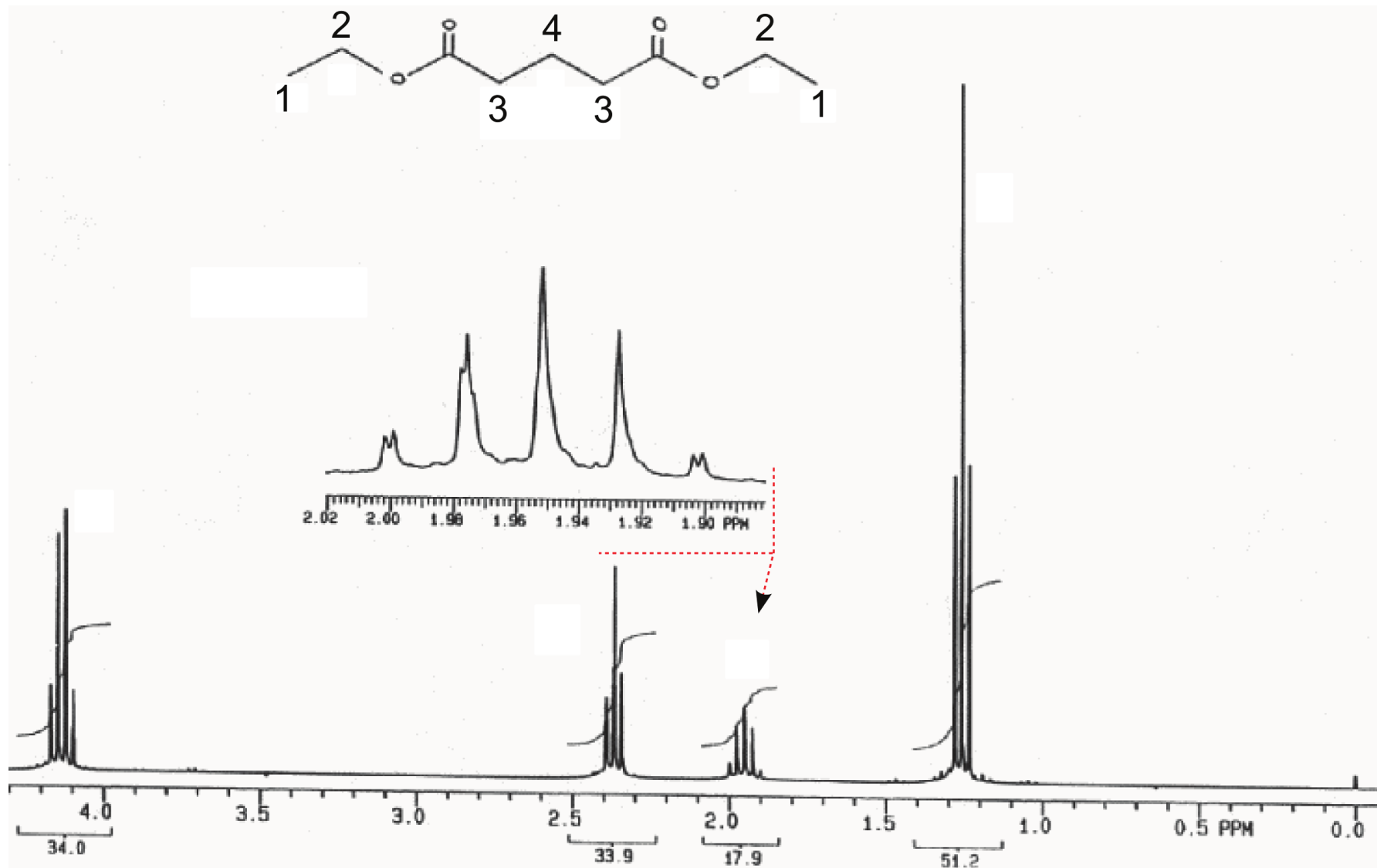
1D ^1H NMR spektrum kyseliny skořicové



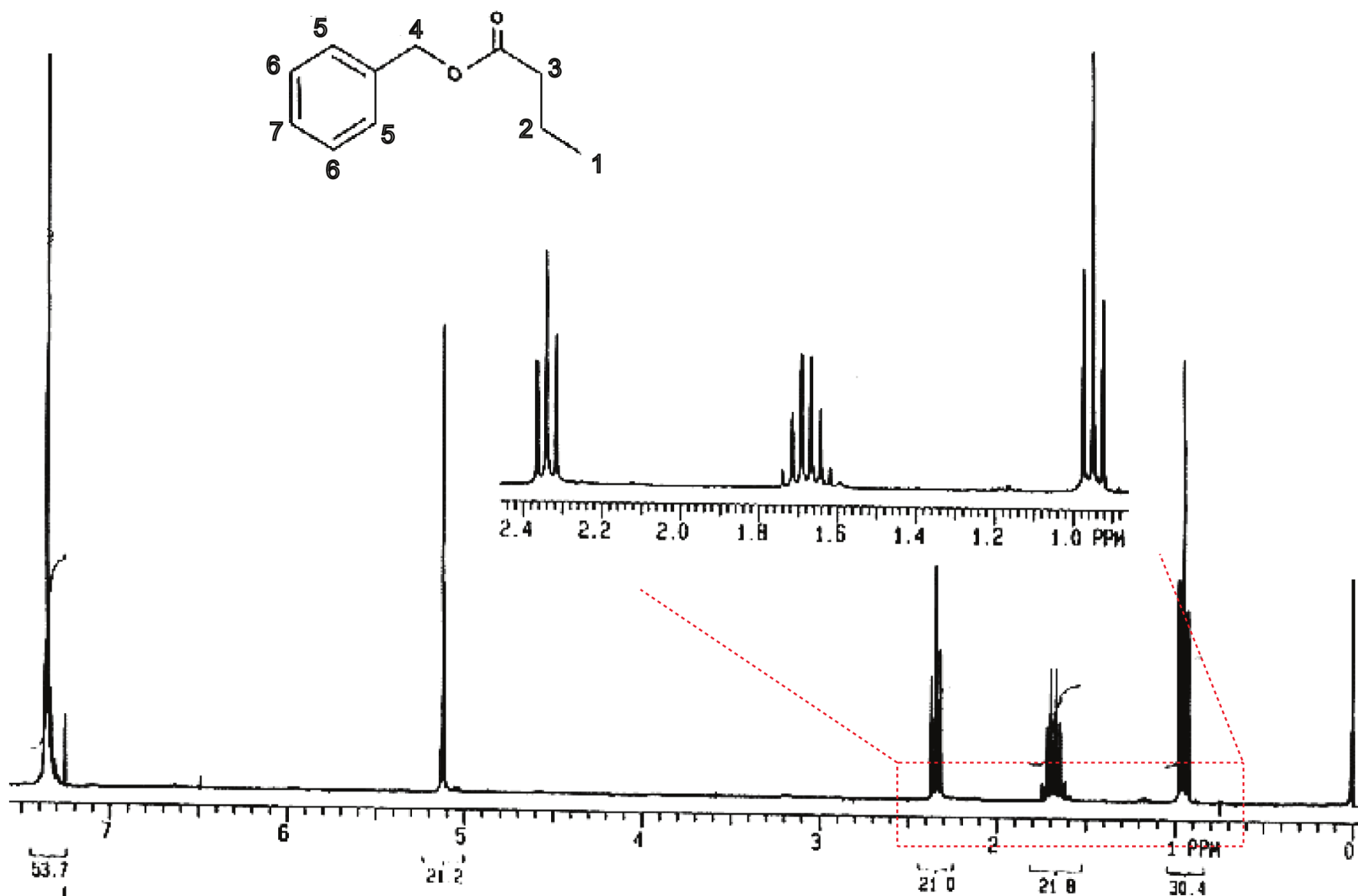
Načrtněte přibližnou podobu 1D ^1H NMR spektra následující molekuly



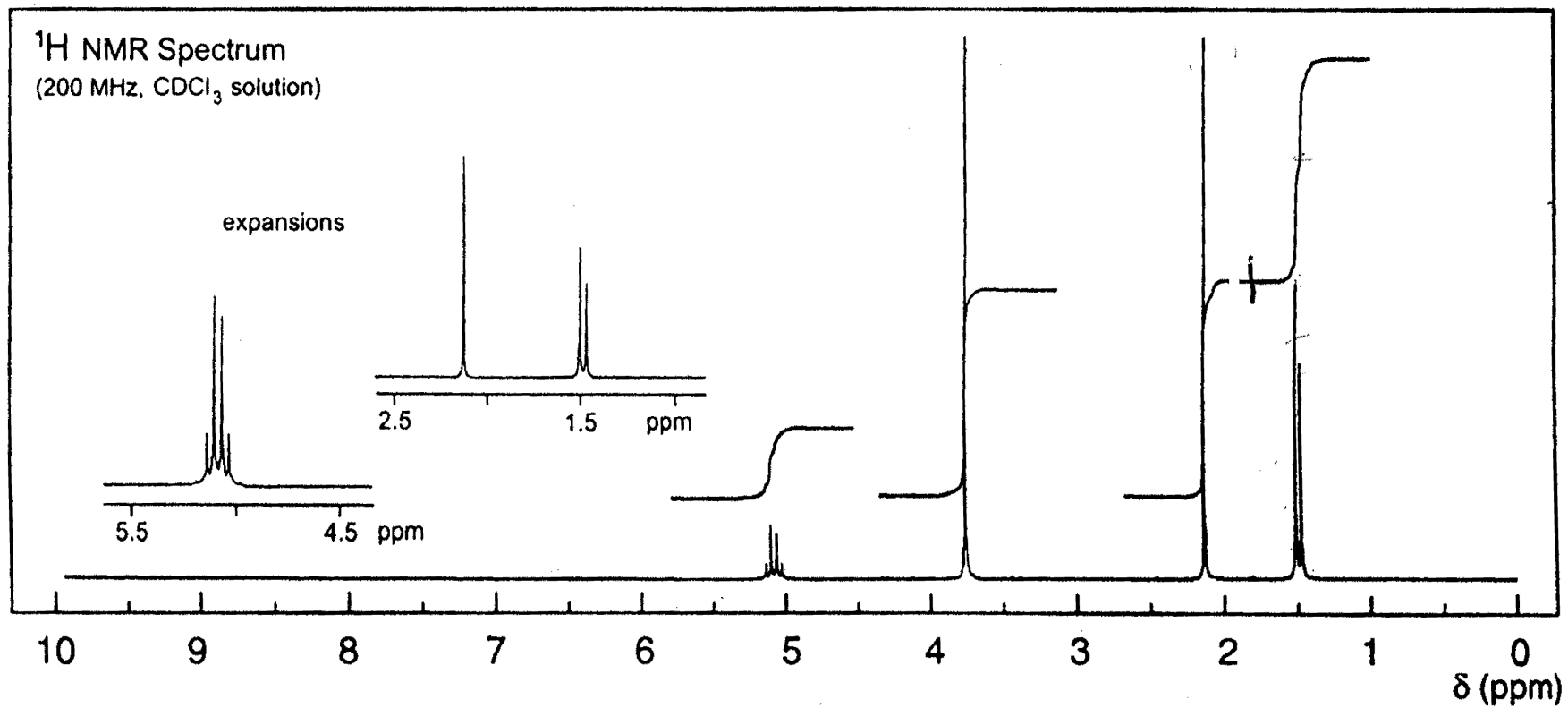
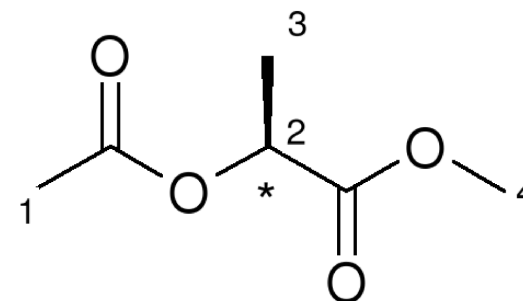
1D ^1H NMR spektrum etylglutarátu



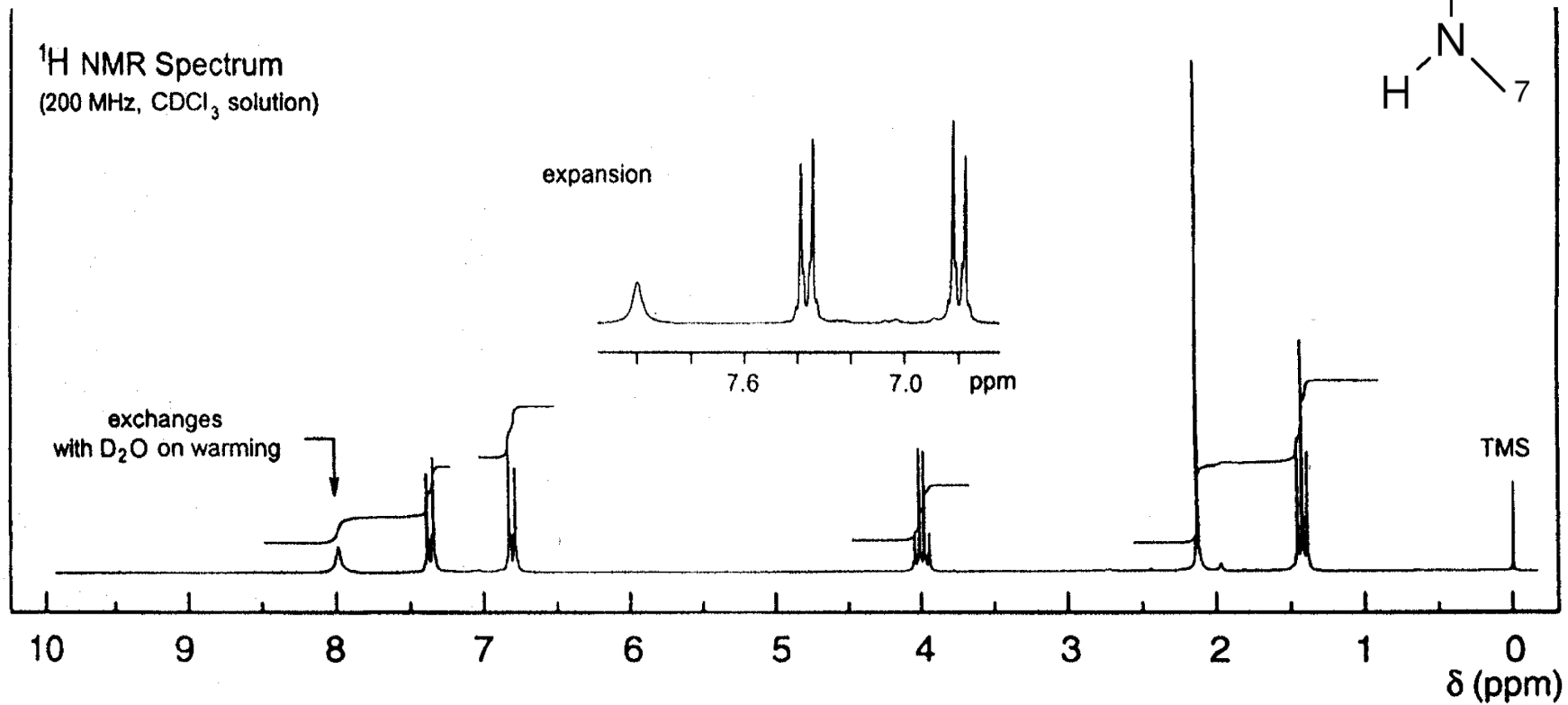
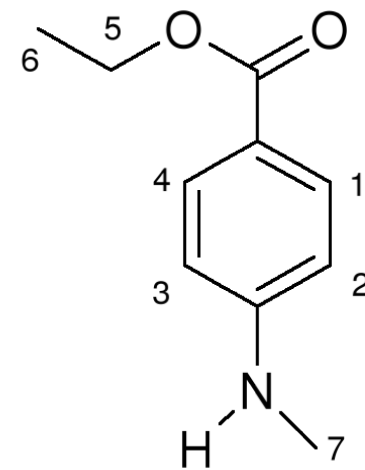
1D ^1H NMR spektrum benzylbutyrátu



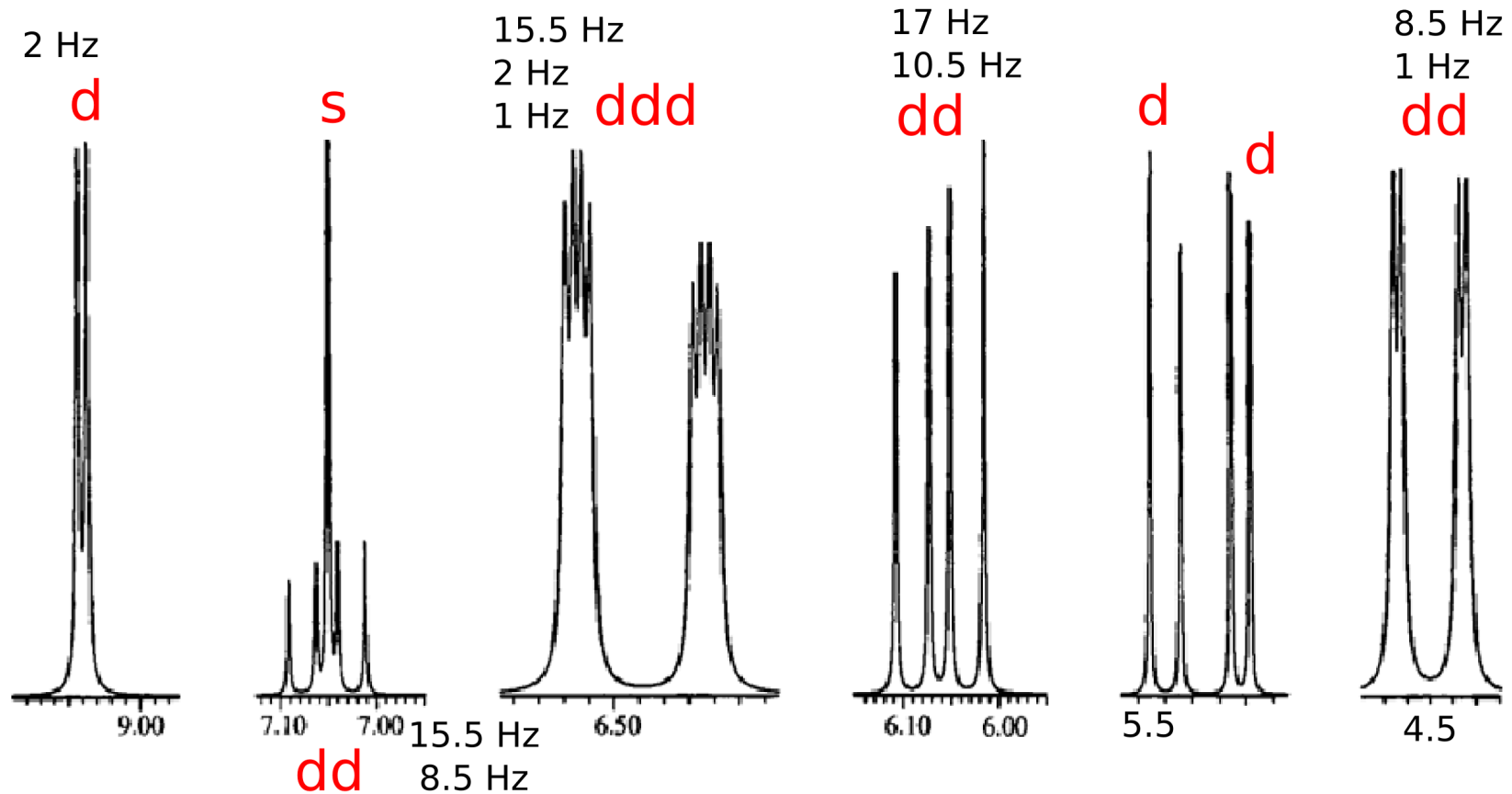
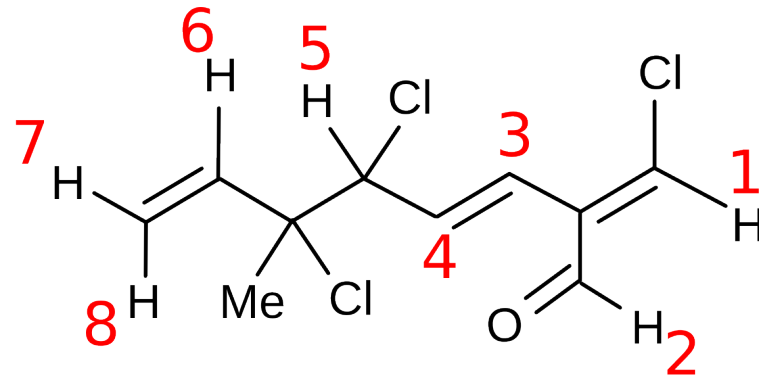
1D ^1H NMR - metyl 2-acetoxipropanoát



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



1D ^1H NMR spektrum - cartilagineal



Příště:

1D ^{13}C -NMR spektra