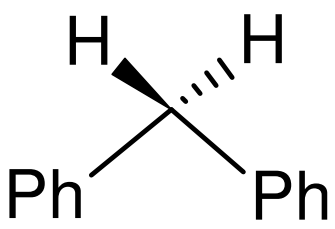
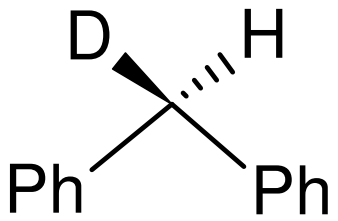
^{1}H NMR spektroskopie

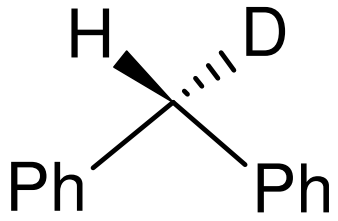
Ekvivalence, chiralita, spinové systémy,
J konstanta, řád spektra

Chemická ekvivalence

- Jádra jsou chemicky ekvivalentní, pokud existuje operace symetrie, která je na sebe převádí
- CH_3 vodíky jsou ekvivalentní díky rychlé rotaci
- Chemicky ekvivalentní jádra mají stejný chemický posun

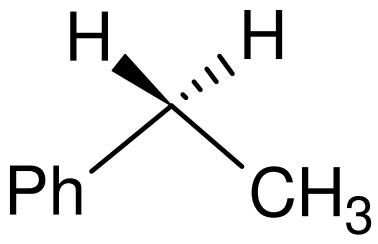


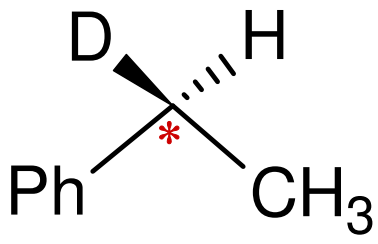


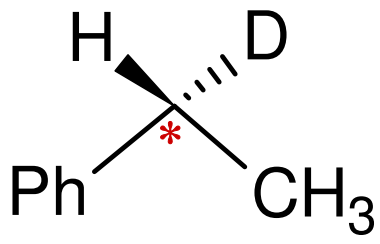


vodíky jsou homotopické

Chemická ekvivalence





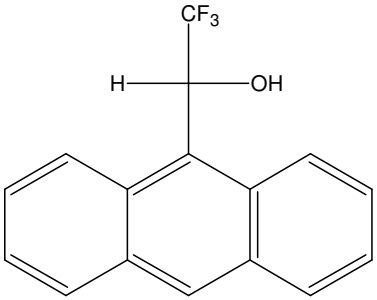


vodíky jsou enantiotopické

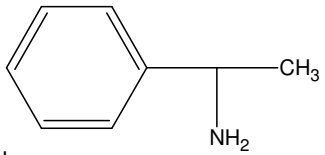
jsou chemicky ekvivalentní

<u>Možnosti rozlišení v NMR:</u>

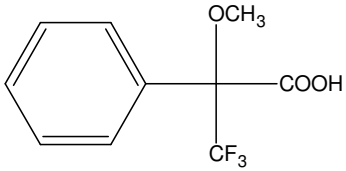
- chirální posunová činidla (2,2,2-trifluor-1-anthrylethanol)



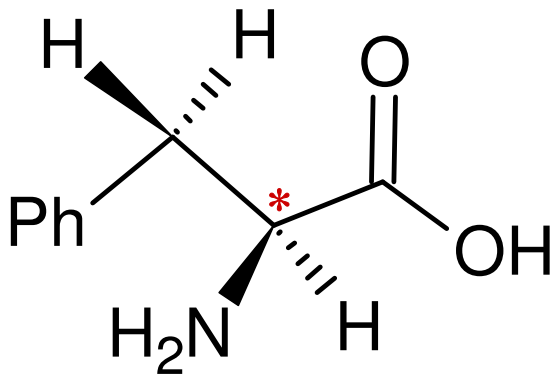
- chirální rozpouštědlo (1-fenylethanamin)

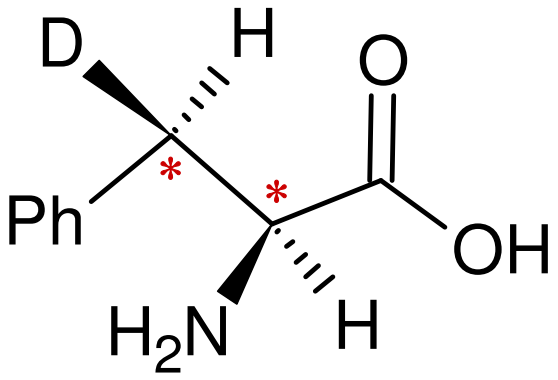


- derivatizace (Mosherova kyselina)



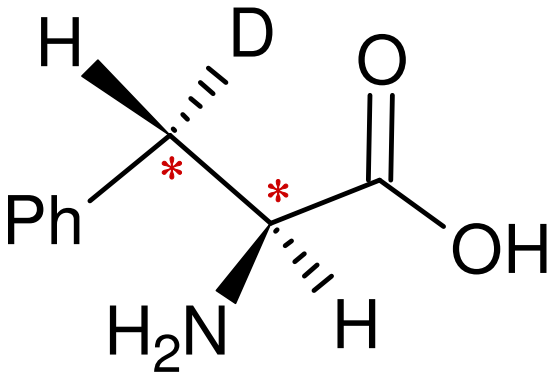
Chemická ekvivalence



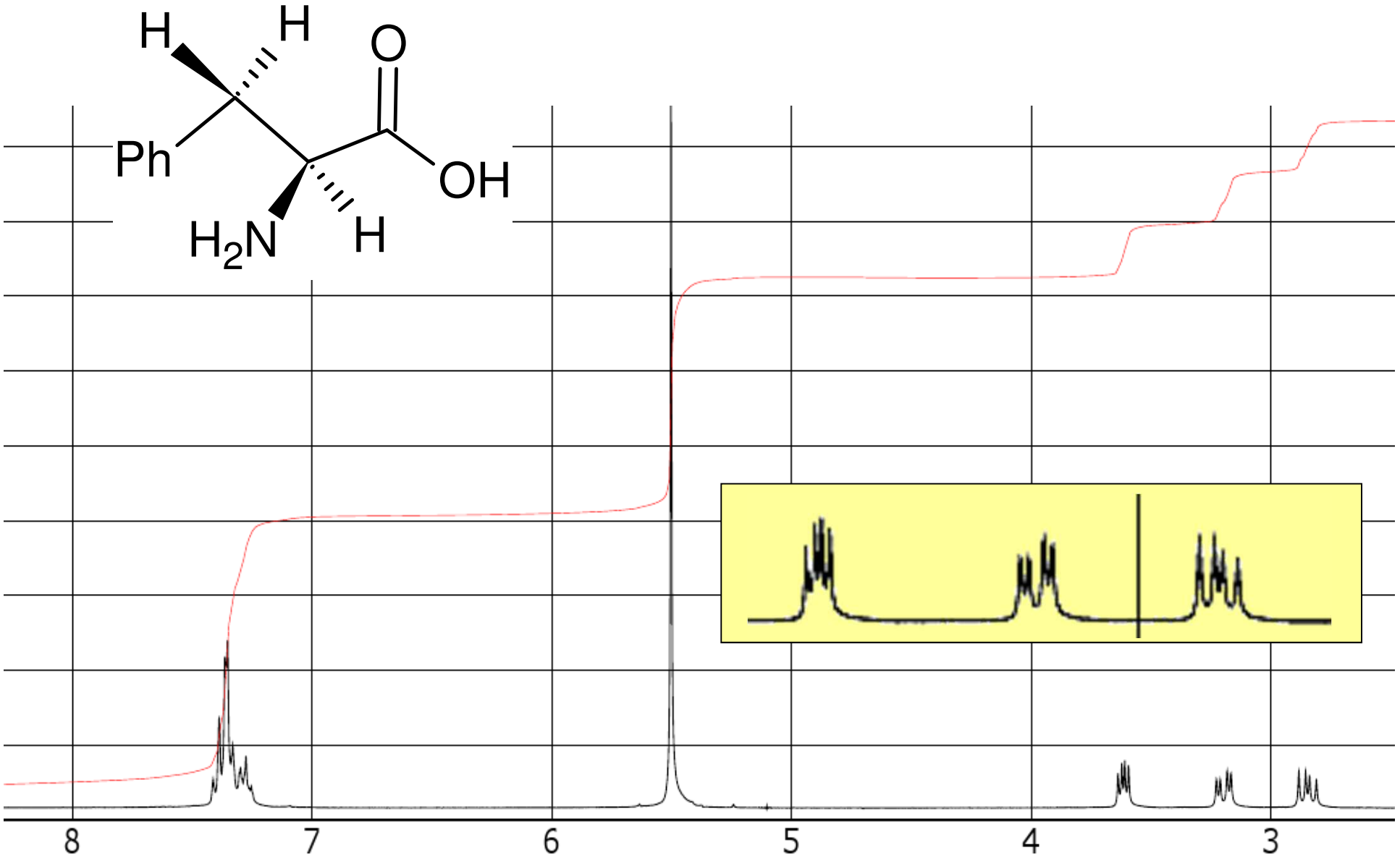


vodíky jsou diastereotopické

nejsou chemicky ekvivalentní

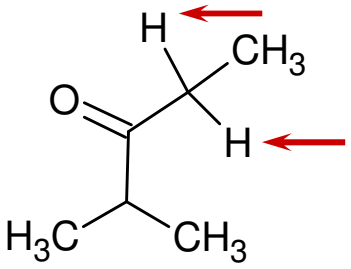


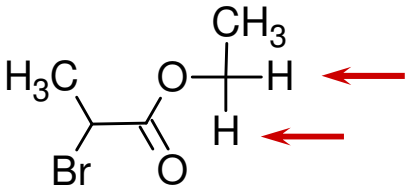
Chemická ekvivalence

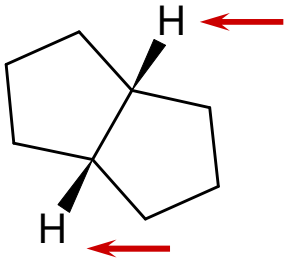


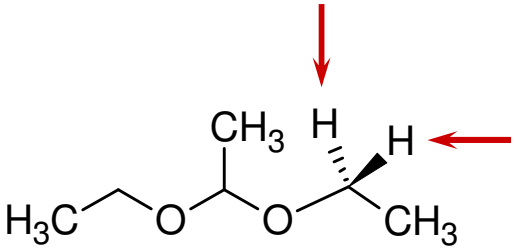
Chemická ekvivalence

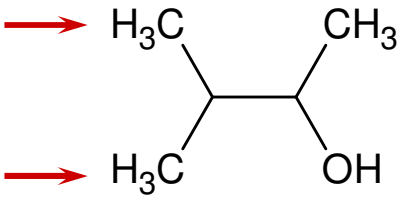
Homotopické, enantiotopické nebo diastereotopické?



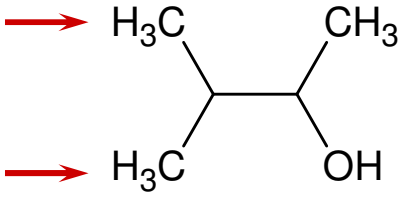








Chemická ekvivalence



3-methyl-2-butanol

diastereotopické

^{1}H NMR 300 MHz

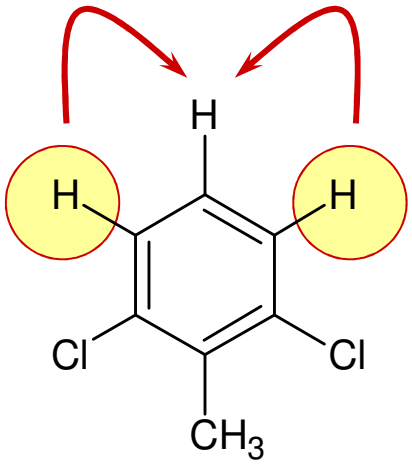
Magnetická ekvivalence

Jádra jsou magneticky ekvivalentní, pokud

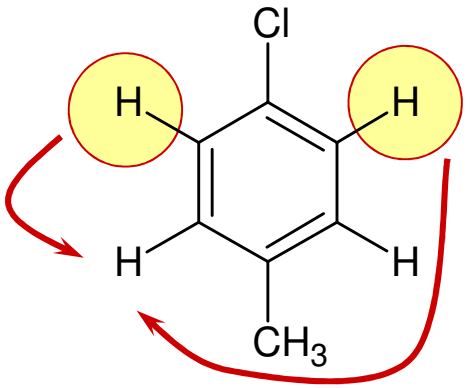
- jsou chemicky ekvivalentní

a zároveň

- mají stejné geometrické postavení k ostatním NMR aktivním jádrům (mají s nimi stejnou J vazbu)

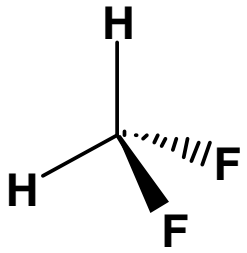


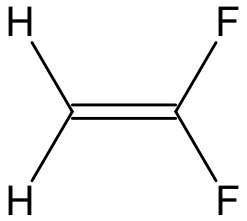
mezi magneticky ekvivalentními jádry se ve spektru neprojevuje J vazba

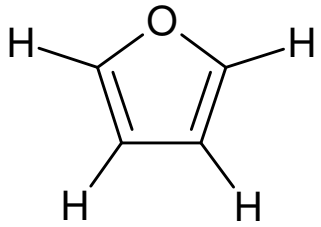


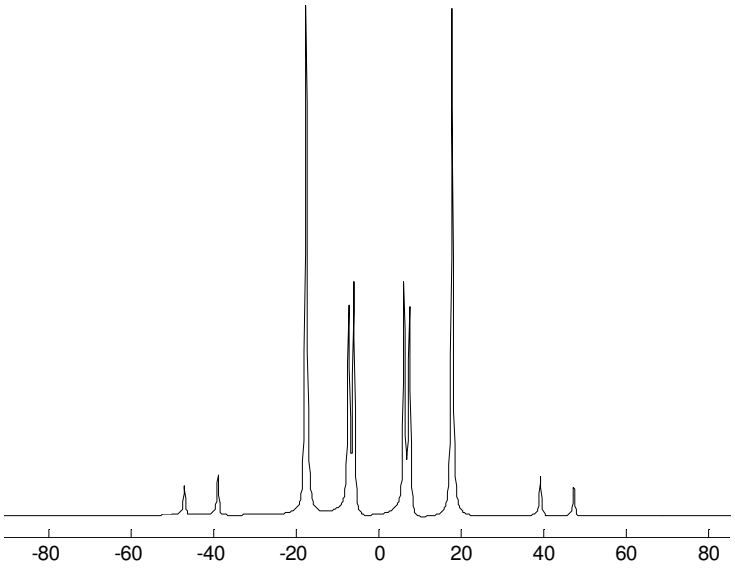
spektra chemicky ekvivalentních, přitom magneticky neekvivalentních jader nelze analyzovat dle pravidel 1. řádu

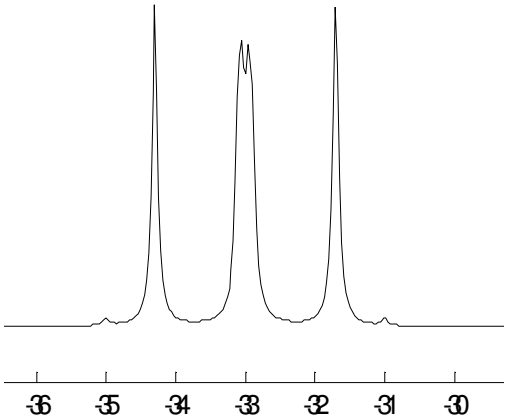
Magnetická ekvivalence





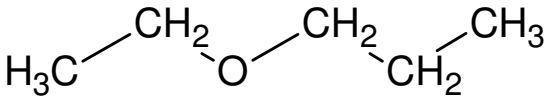


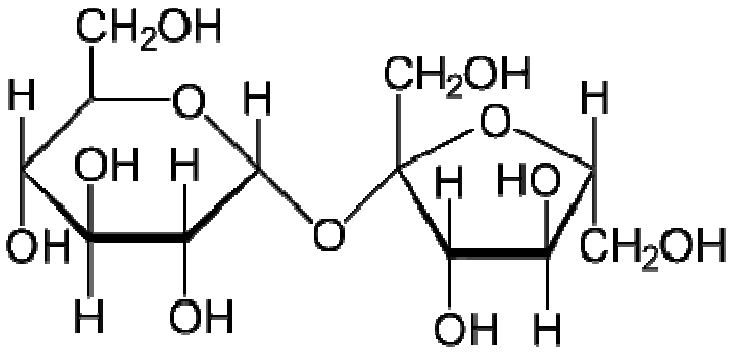


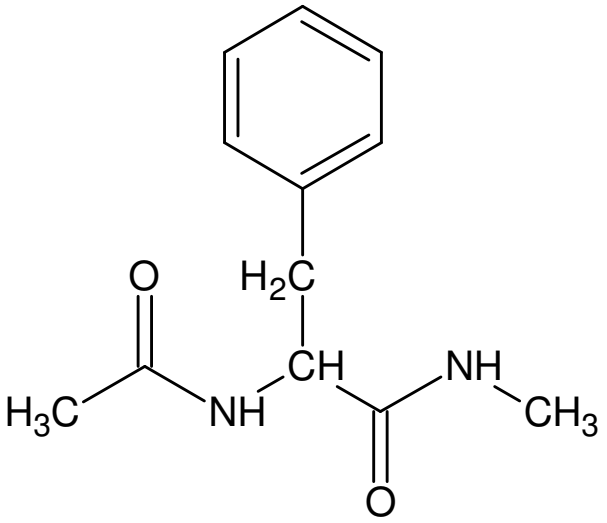


Spinový systém

úplná množina NMR aktivních jader, ve které jsou členové provázáni J-interakcemi

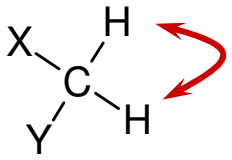




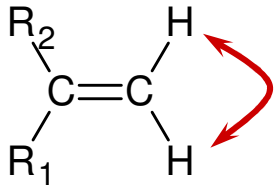


J vazba

Geminální $^{2}J_{HH}$

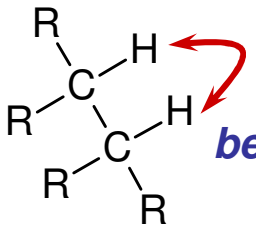


5 – 20 Hz



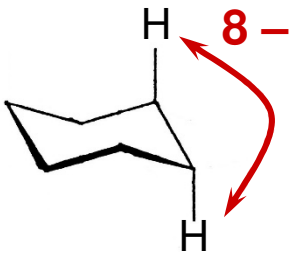
0 – 2 Hz

Vicinální $^{3}J_{HH}$

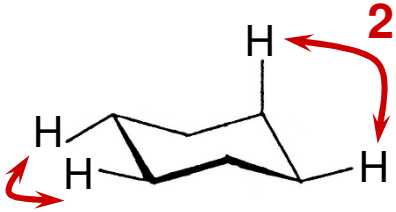


6 – 8 Hz

bez konformační preference



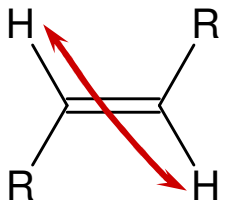
8 – 10 Hz



2 – 3 Hz

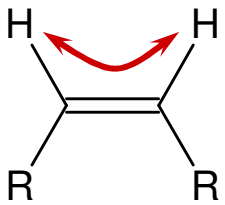
2 – 3 Hz

trans



14 – 18 Hz

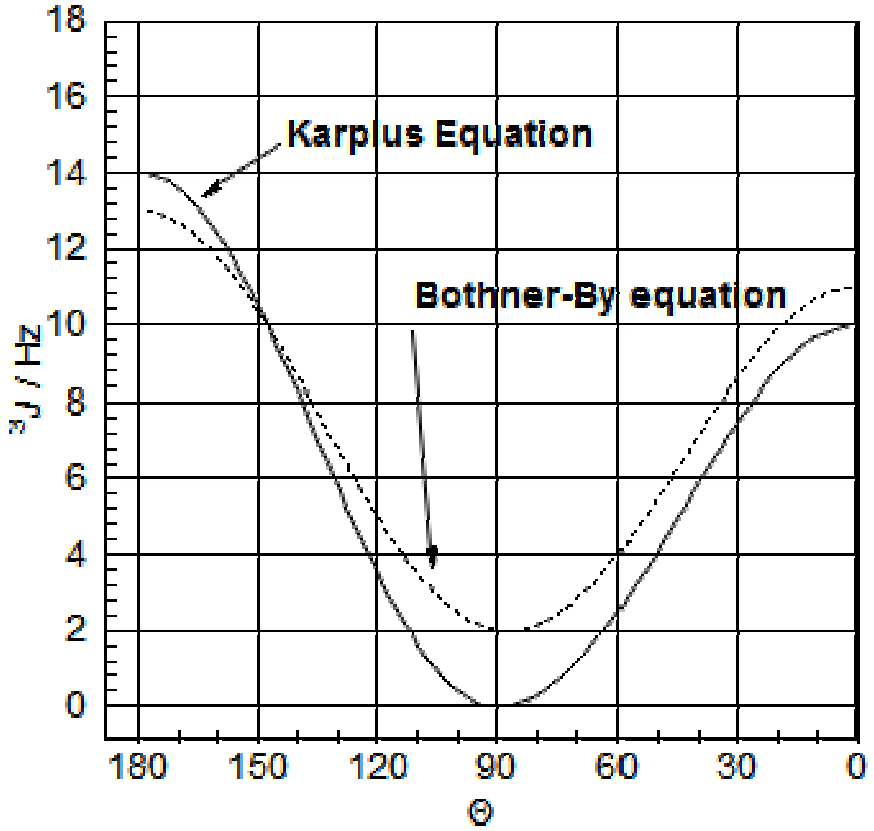
cis

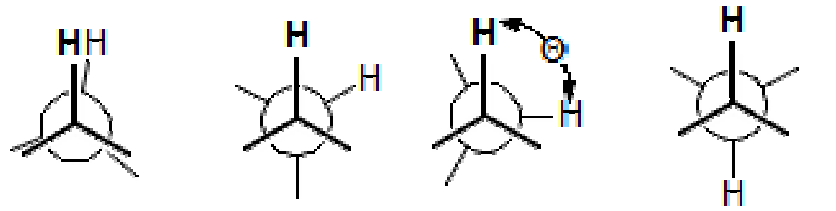


7 – 12 Hz

Karplusova křivka

závislost $^3J_{HH}$ na dihedrálním úhlu





Θ = 0° ^3J = 7-11 Hz

Θ = 60° ^3J = 2-5 Hz

Θ = 90° ^3J = 0-2 Hz

Θ = 180° ^3J = 8-15 Hz

Karplus Equation

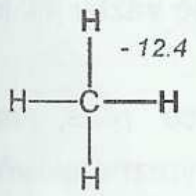
$^3J_{HH} = J_o \cdot \cos^2\Theta - K$

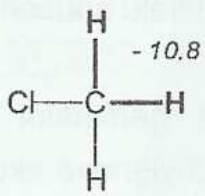
J_o = 14 (90-180°), J_o = 10 (0-90°), K = 0

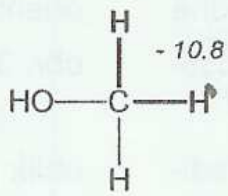
Bothner-By equation

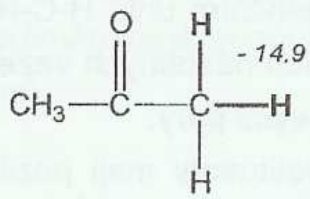
$^3J_{HH} = 7 - \cos\Theta + 5 \cdot \cos 2\Theta$

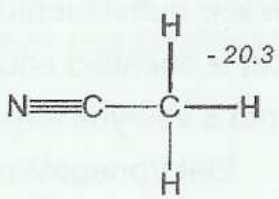
$^2J(H,H)$

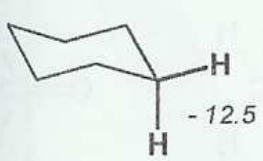


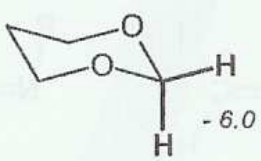


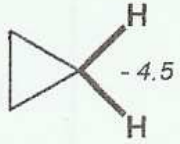


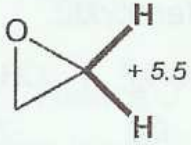


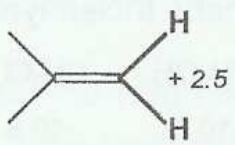


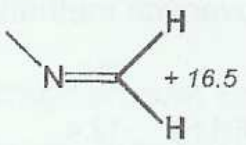




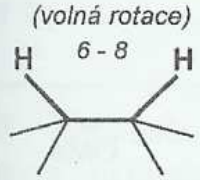


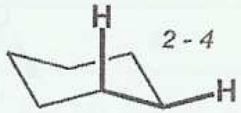


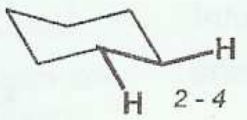


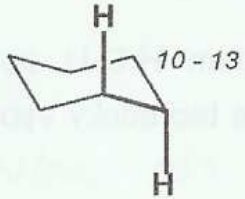


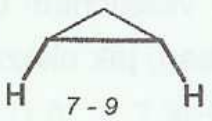
$^3J(H,H)$

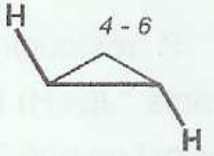


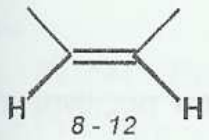


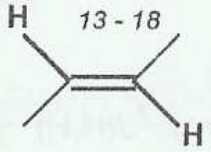


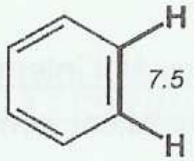


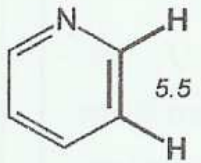


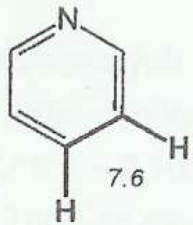


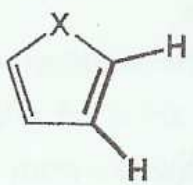


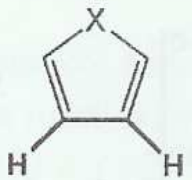






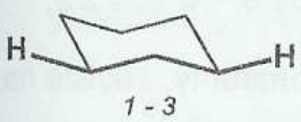


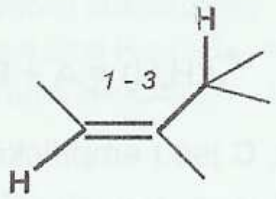


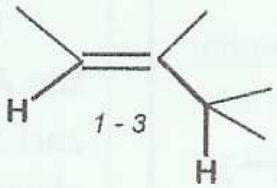


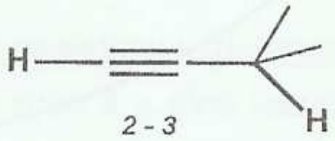
X		
1.8	O	3.4
2.6	NH	3.5
4.8	S	3.5

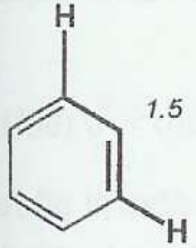
$^4J(H,H)$

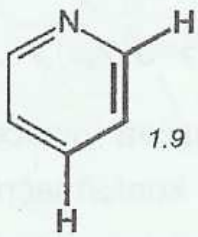


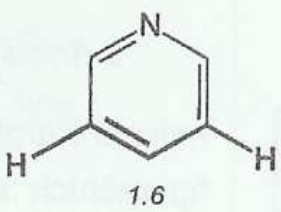


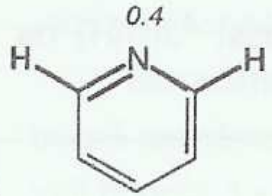


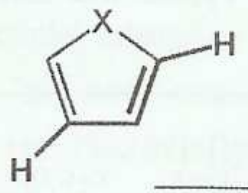




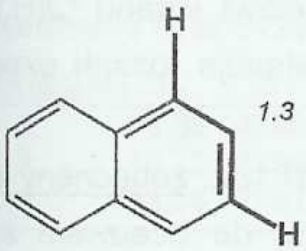


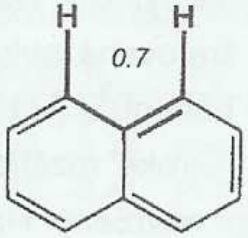




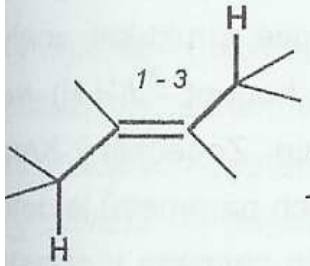


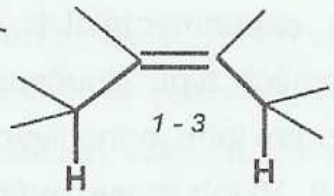
X		
0.9	O	1.5
1.3	NH	2.1
1.0	S	2.8

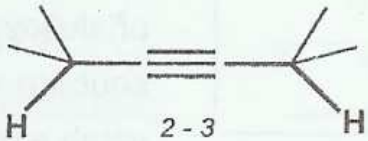


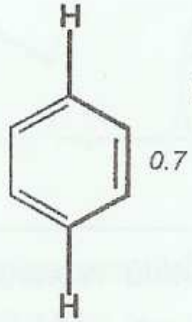


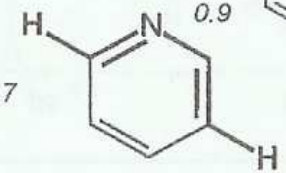
$^5J(H,H)$

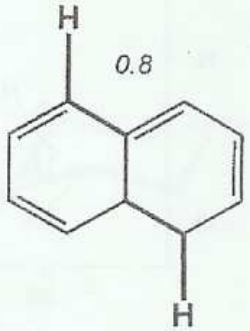




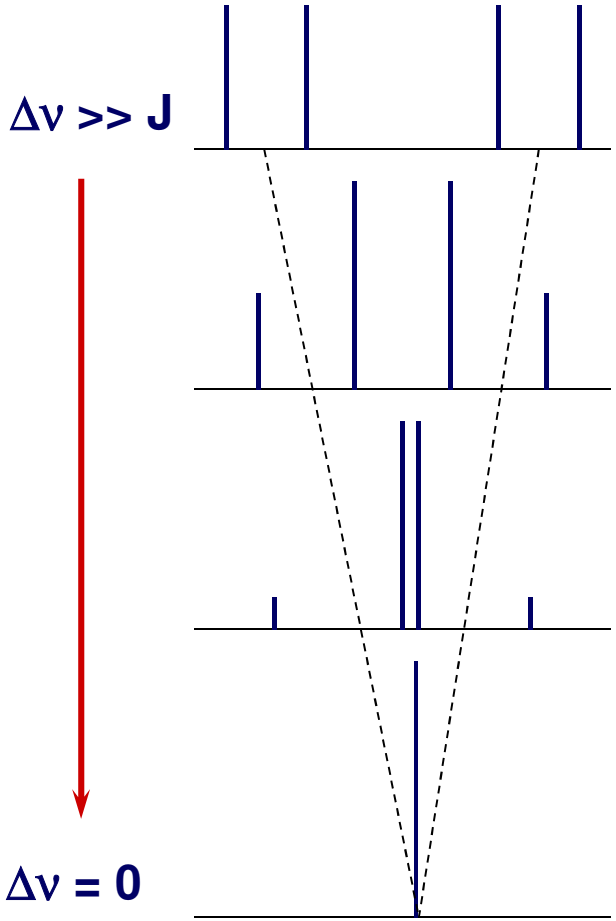








Řád spektra



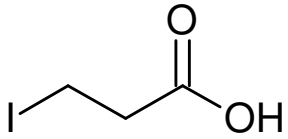
spektrum 1. řádu

„pseudo-první řád“

spektrum vyššího řádu

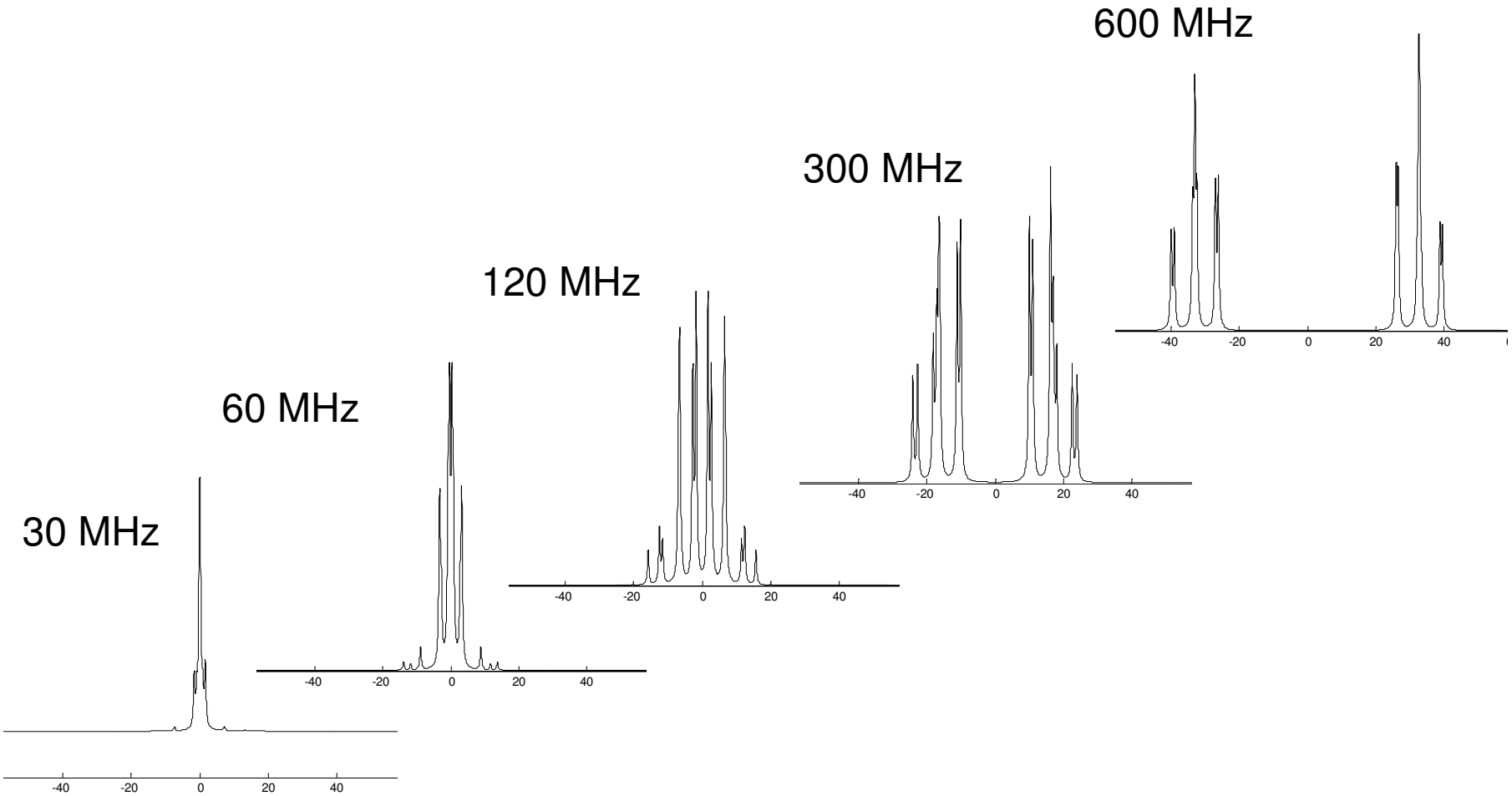
střískový efekt

Řád spektra

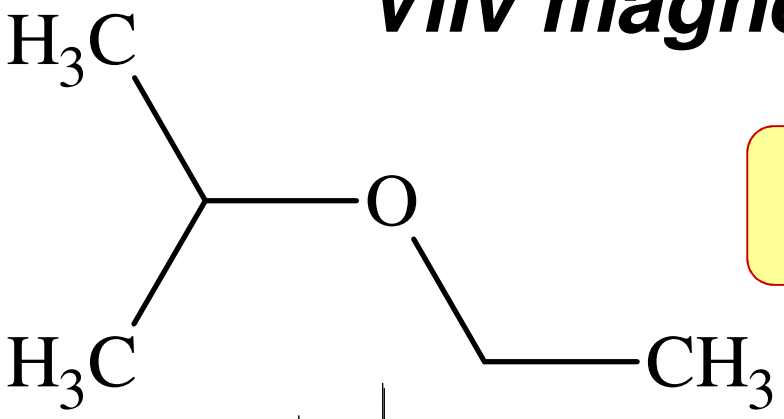


rozdíl chem. posunů 0.11 ppm

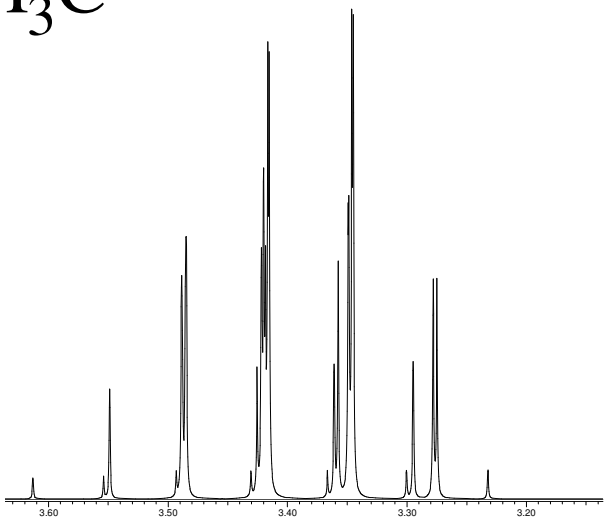
J vazba 7 Hz



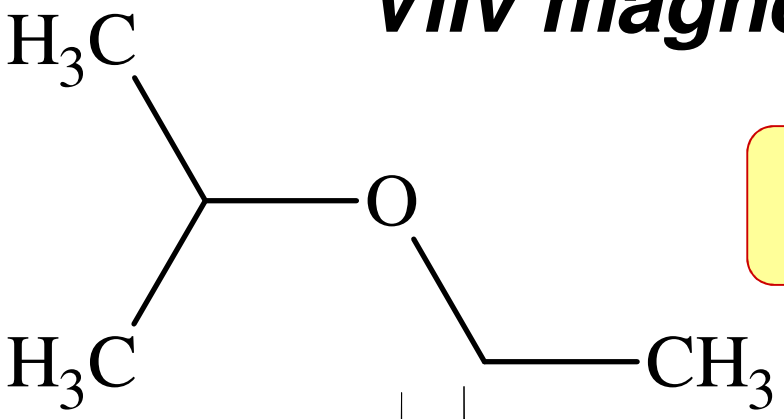
Vliv magnetického pole



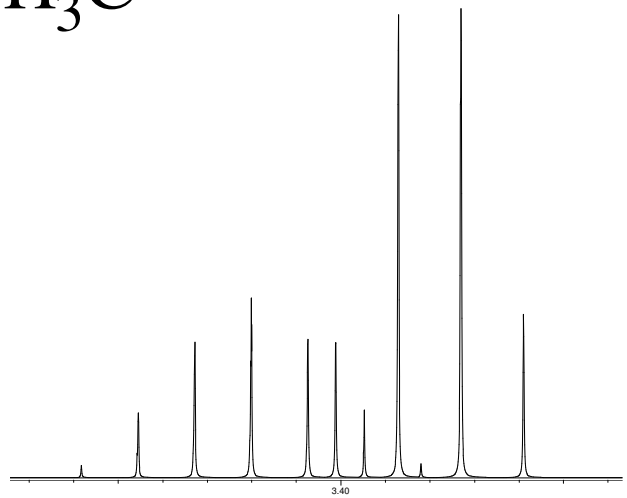
100 MHz

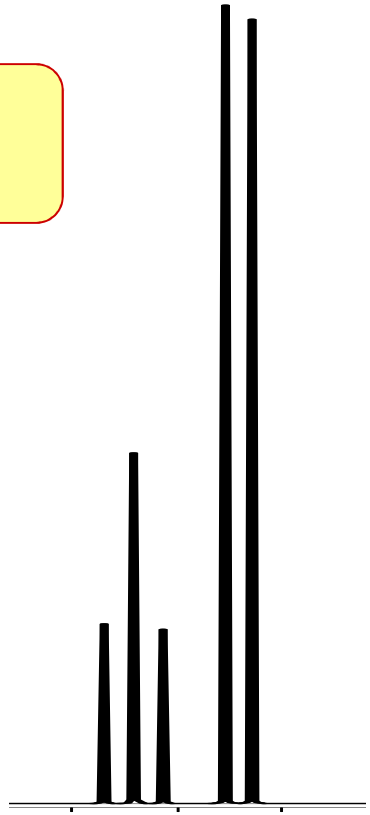


Vliv magnetického pole



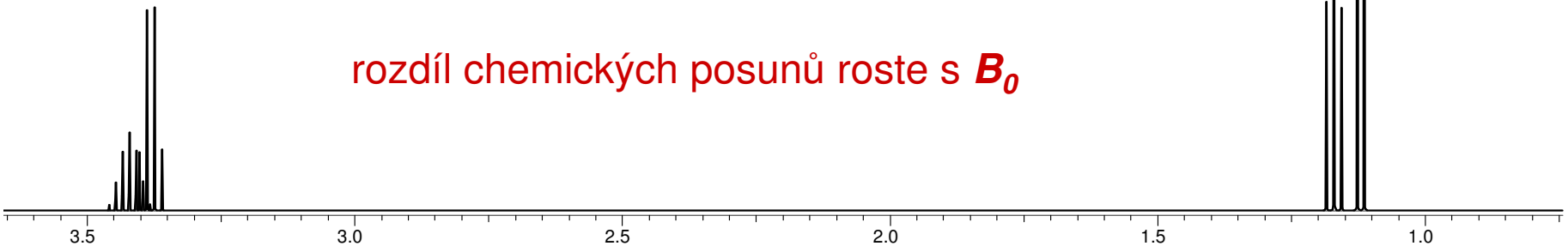
500 MHz



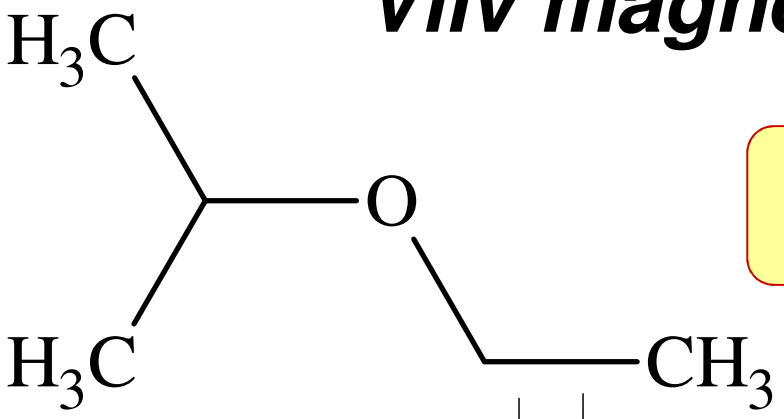


J vazba – velikost štěpení nezávisí na B_0

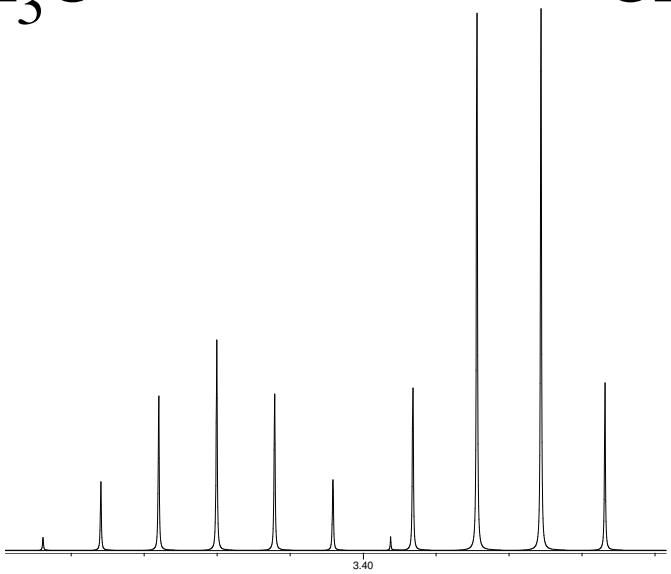
rozdíl chemických posunů roste s B_0



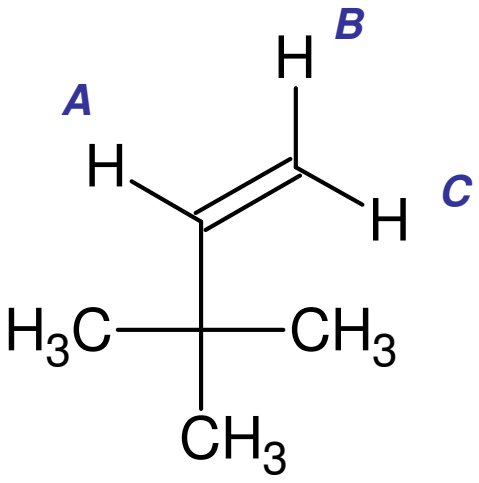
Vliv magnetického pole



800 MHz



Analýza štěpení

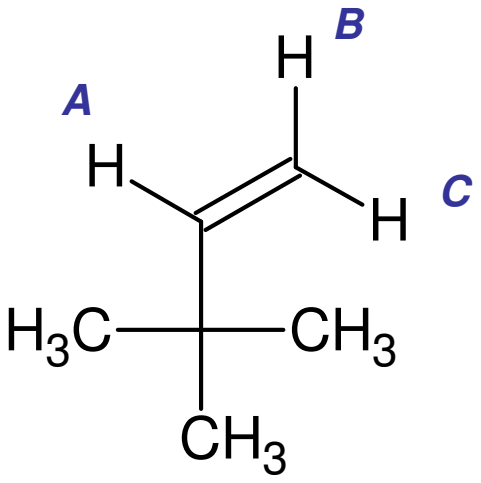


J_{AB} = J_{AC} = J_{BC} =

Jak vypadají signály?

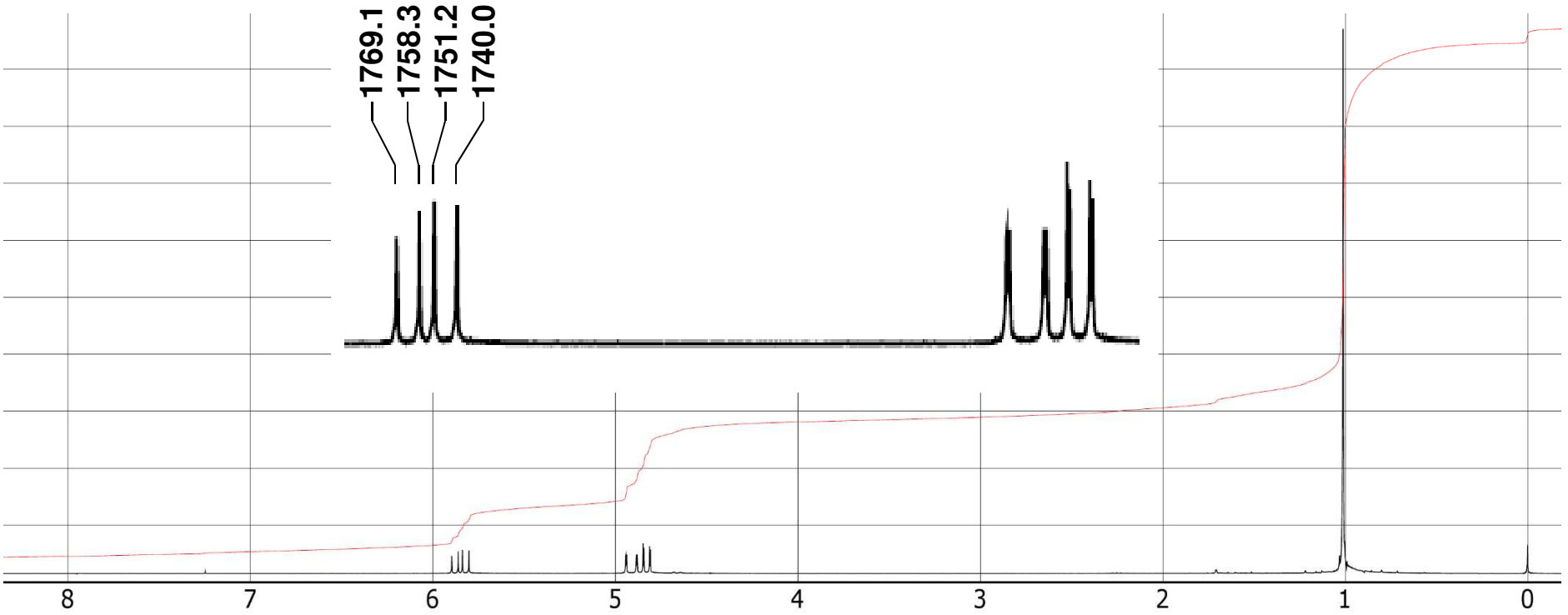
H *A* H *B* H *C*

Analýza štěpení



J_{AB} = ? J_{AC} = ? J_{BC} = ?

zápis:



Analýza štěpení

Určete strukturu a konformaci, zapište spektrum