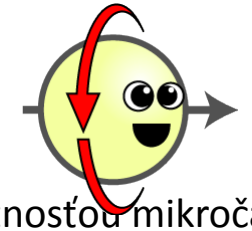
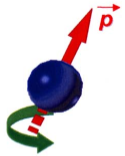
# NMR

Wiley, Organic chemistry 2ND Edition,
David Klein

# Nukleárna magnetická rezonancia

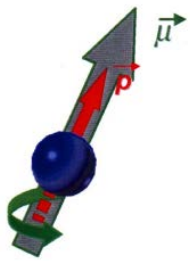


- **Spin**
  - forma uhlového momentu, ktorá je vnútornou vlastnosťou mikročastíc (nevzniká rotáciou)
  - **uhlový moment $\vec{p}$** je vektor rovnobežný s osou rotácie
  - veľkosť uhlového momentu popísaná spinovým kvantovým číslom I
  - protón a neutrón majú spin podobne jako elektrón
  - jadro má spin daný kombináciou spinov protónov a neutrónov



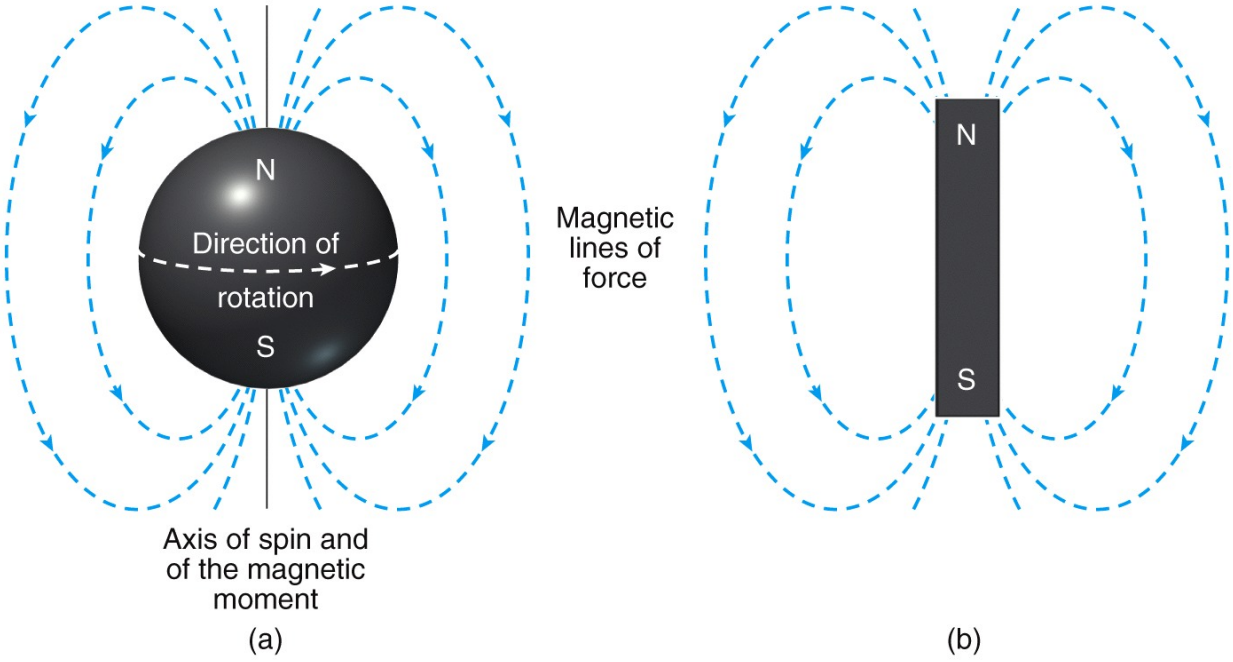

$$p = h/2\pi * \sqrt{I(I+1)}$$

- **Jadrový magnetický moment $\vec{\mu}$**
  - dôsledok spinu a náboja atómového jadra (rotujúca nabitá častica generuje dipolárny magnetický moment)
- **Gyromagnetický pomer $\gamma$**
  - konštanta úmernosti daná magnetickými vlastnosťami jadra
  - pre každé jadro charakteristický




$$\vec{\mu} = \gamma \vec{p}$$

# Jadrový magnetický moment $^{1}H$ (protónu)

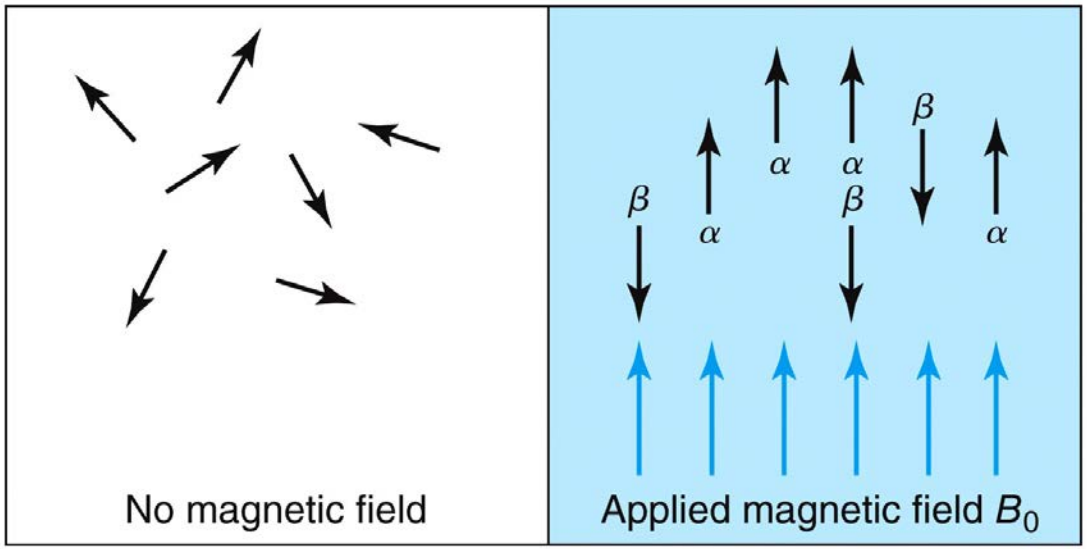


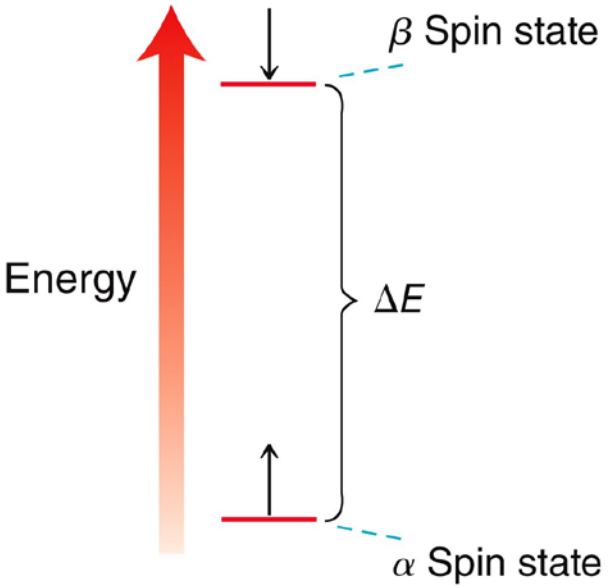

- jadro s lichým počtom protónov a/alebo lichým počtom neutrónov má spin (spin. kvant. č. **I**) a nenulový magnetický moment $\vec{\mu}$, ktorý môže byť skúmaný NMR spektrometrom

1. Úloha: Označte, ktoré jadro bude ,,NMR aktívne“:

1) $^{16}O$
2) $^{17}O$
3) $^{2}H$
4) $^{7}Li$
5) $^{32}S$
6) $^{12}C$
7) $^{13}C$
8) $^{14}N$

# Orientace mag. momentov protónov a ich energia

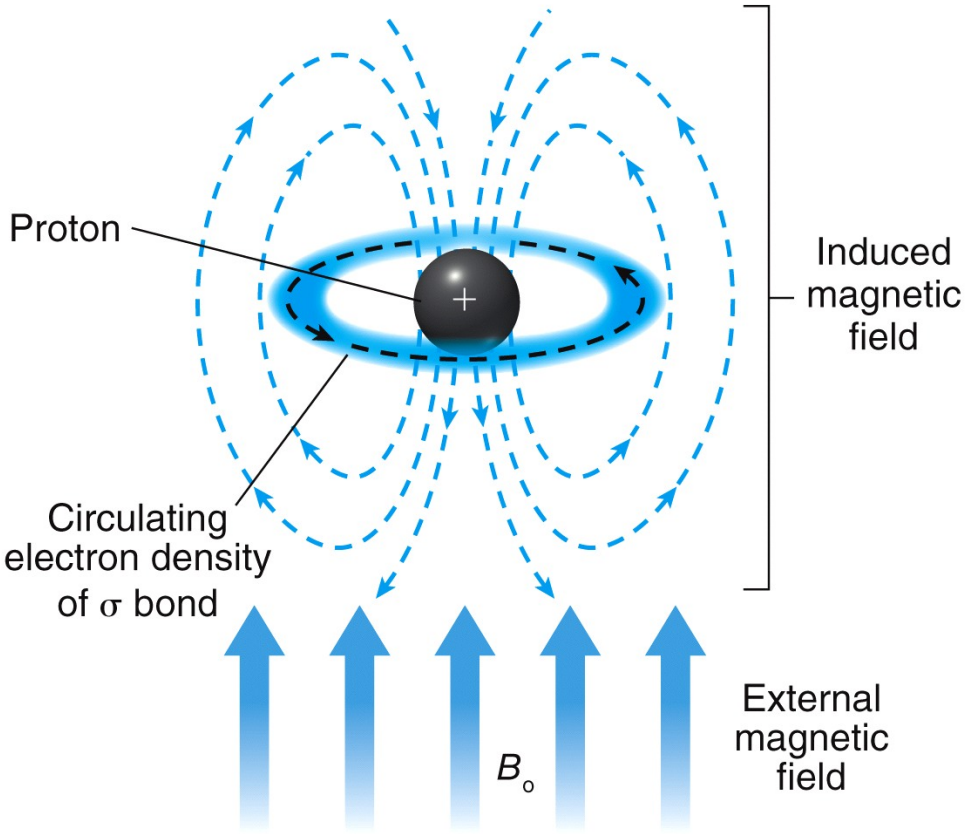



$$\Delta E = h\nu = h\gamma B_0/2\pi$$

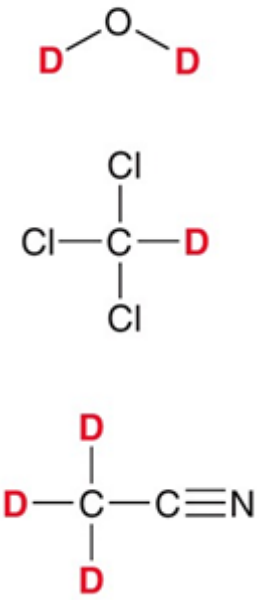
$$\nu = \gamma B_0/2\pi$$

# Indukované magnetické pole



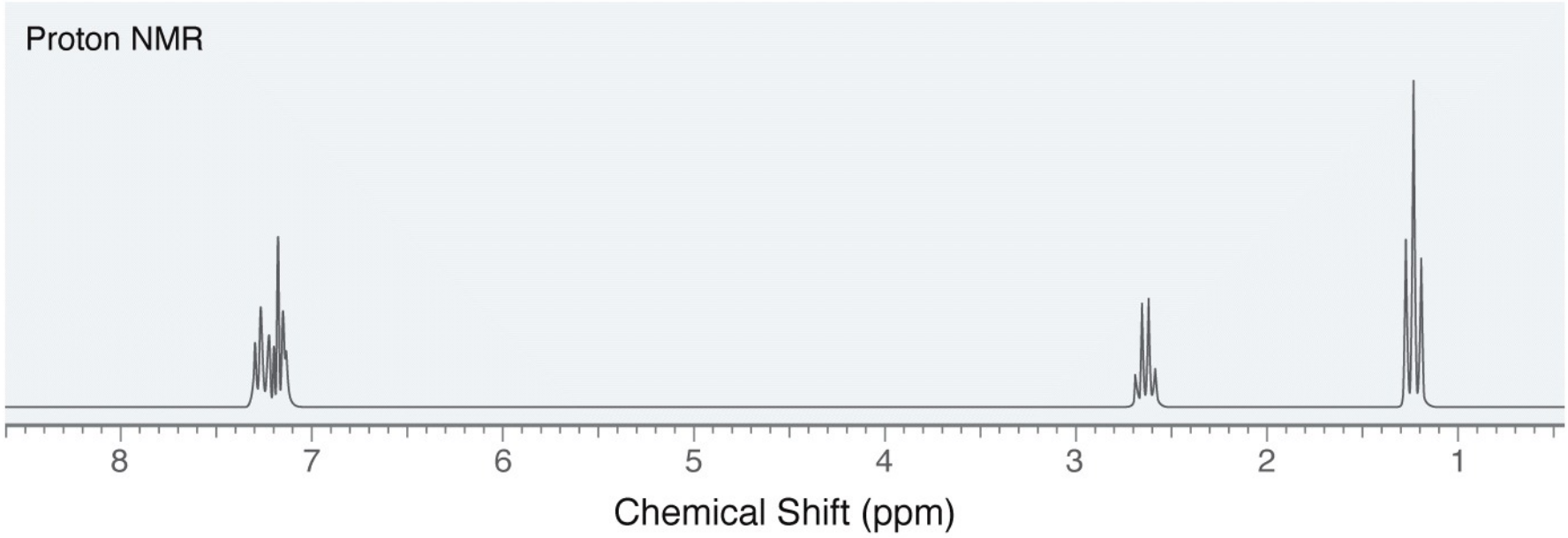

- indukované magnetické pole sa vytvára ako dôsledok pohybu elektrónovej hustoty v okolí jadra (diamagnetizmus) → jadrá sa nachádzajú v rôznom okolí (tienené/odtienené)→ líši sa $\Delta E$ medzi $\alpha$ a $\beta$ hladinami → dostávame užitočné informácie pomocou NMR spektroskopie

# Meranie NMR spektier




- deuterované rozpúšťadlá alebo neobsahujúce protón ($CCl_4$)
- ! D je taktiež ,,NMR aktívne“

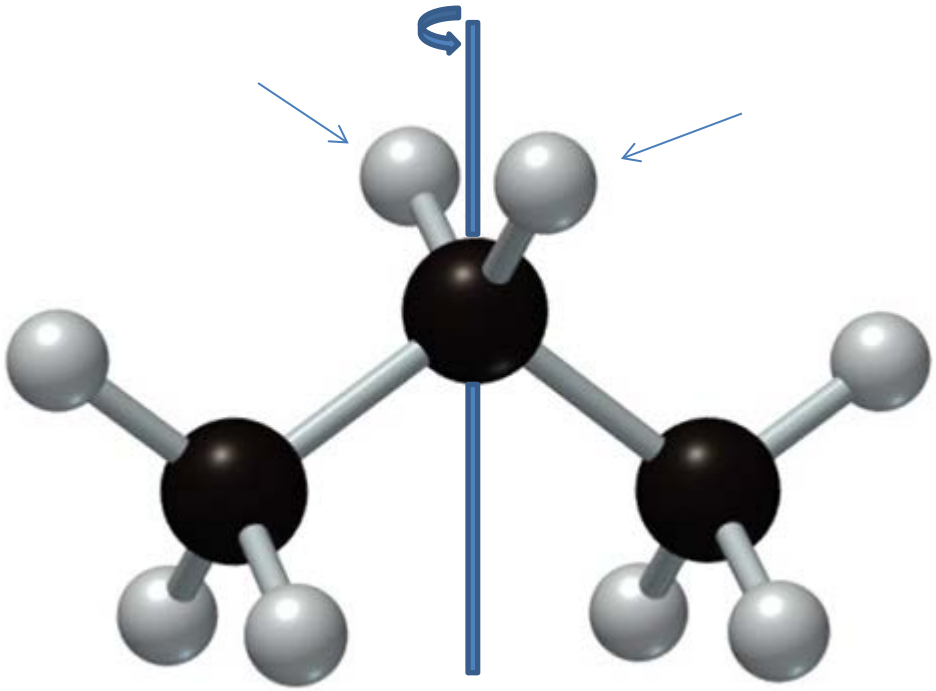
# $^{1}$H NMR (alebo protónové) spektrum




- Pozícia signálu – okolie protónu
- Plocha pod každým signálom – počet protónov
- Tvar signálu – počet susedných protónov

# Počet signálov

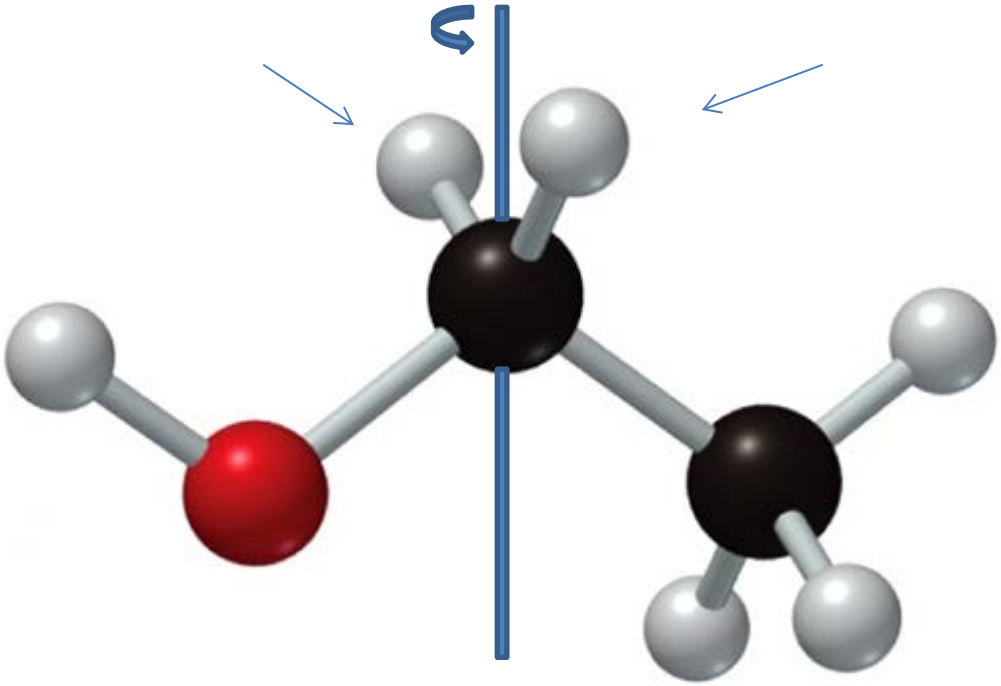
- Chemická ekvivalencia



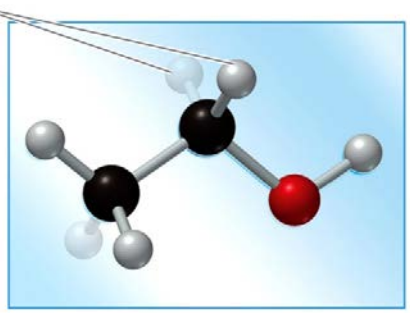
**homotopické protóny**

# Počet signálov

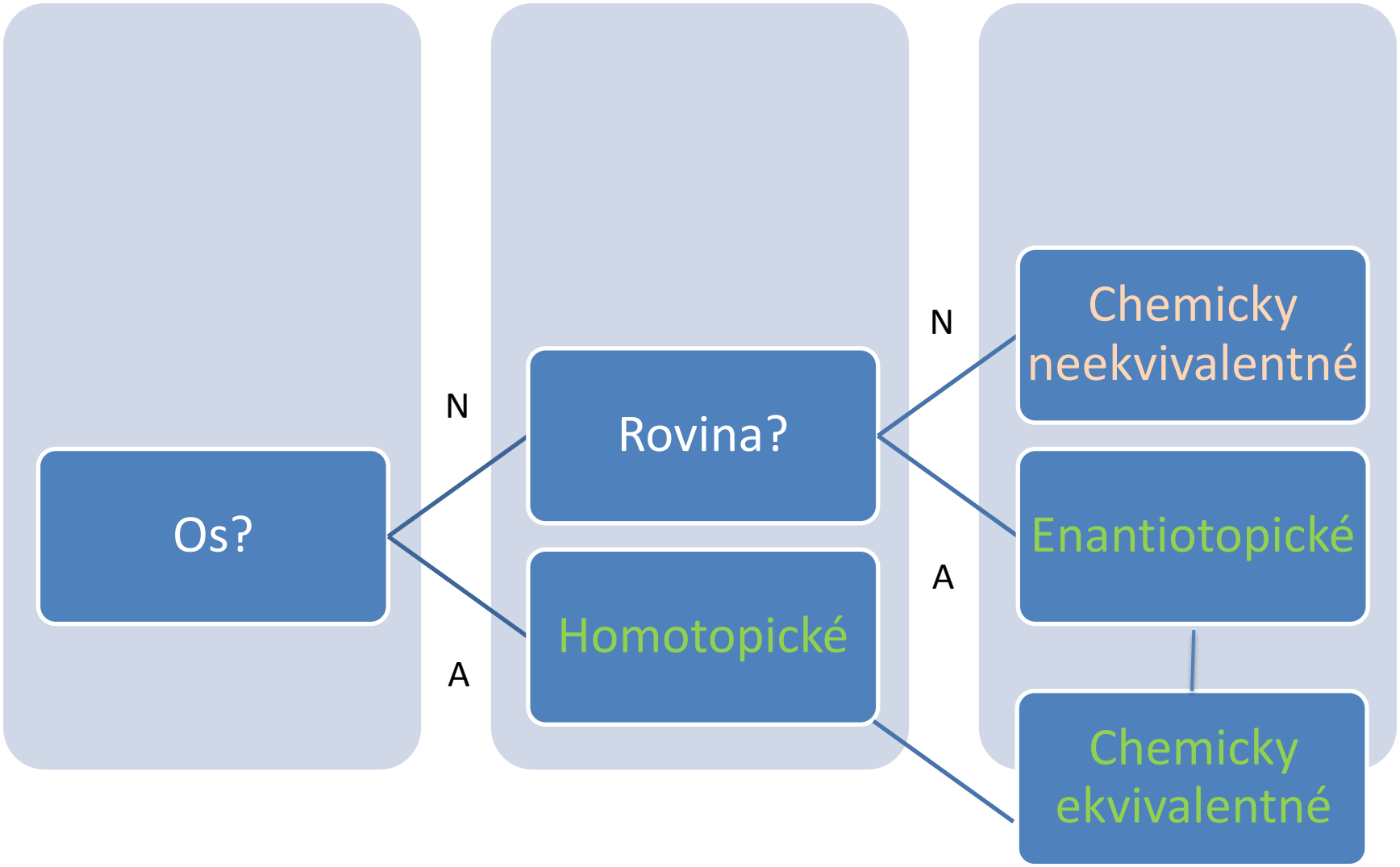
- Chemická ekvivalencia



**enantiotopické protóny**

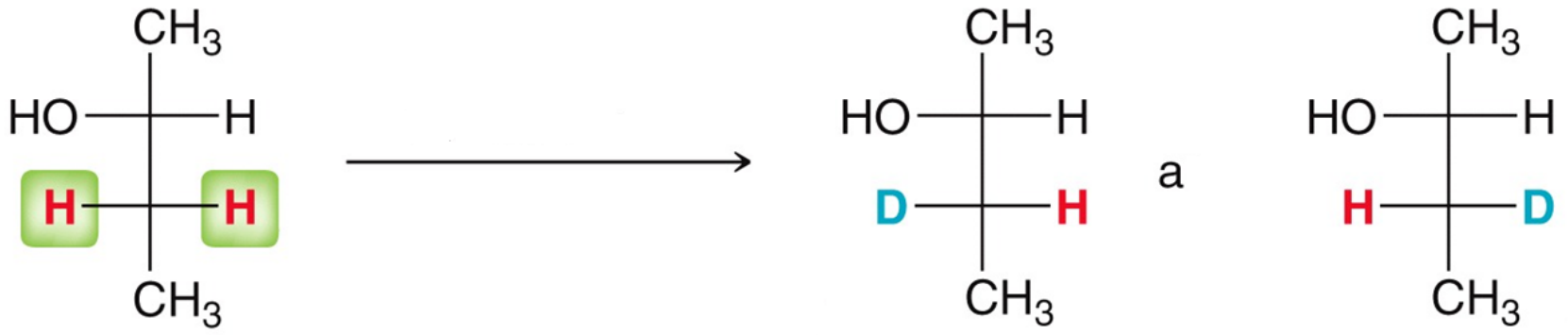


# Počet signálov



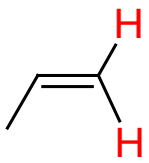
# Počet signálov

- Chemická neekvivalencia

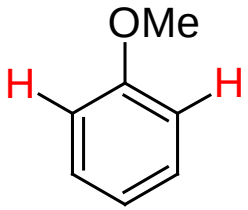



- nahradením H za D vidíme, že 2 štruktúry sú navzájom nestotožniteľné – diastereomery, preto H označené zelenou sú **diastereotopické**

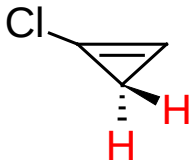
# 2. Úloha: Označte, či vyznačené protóny budú homo-, enantio- alebo diastereo- topické




1




2

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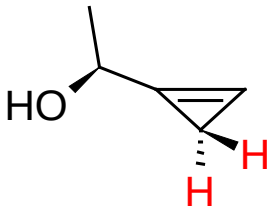


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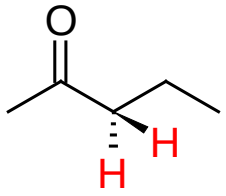


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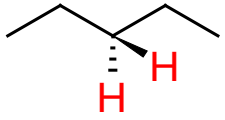


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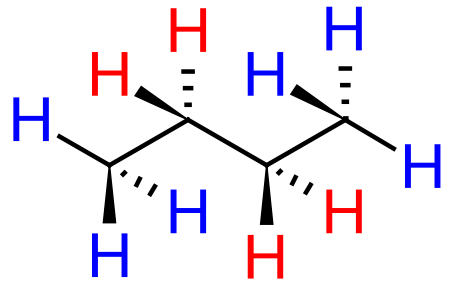
# Úloha 3:

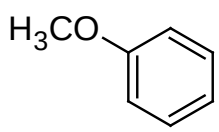



Bután má v $^{1}H$ NMR spektre 2 rôzne sady protónov (modré a červené). Vysvetli:

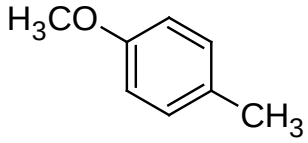
- prečo sú červené protóny chemicky ekvivalentné?
- prečo sú modré protóny ekvivalentné?
- koľko rôznych protónov má pentan (v NMR-spektre?)
- koľko rôznych protónov má hexan (v NMR-spektre?)
- koľko rôznych protónov má 1-chlorhexan (v NMR-spektre?)

# Úloha 4: Identifikácia počtu signálov

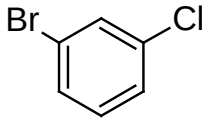
Identifikuj počet signálov očakávaných v $^{1}H$ NMR-spektre pre molekuly




1




2

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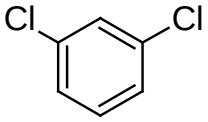


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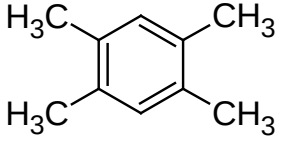


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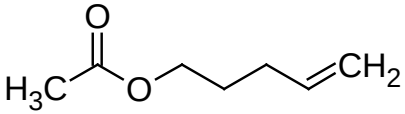
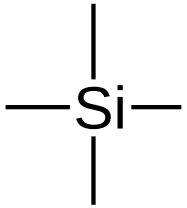



6

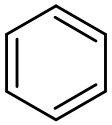
# Chemický posun

- $\delta$ – definovaný k referencii TMS



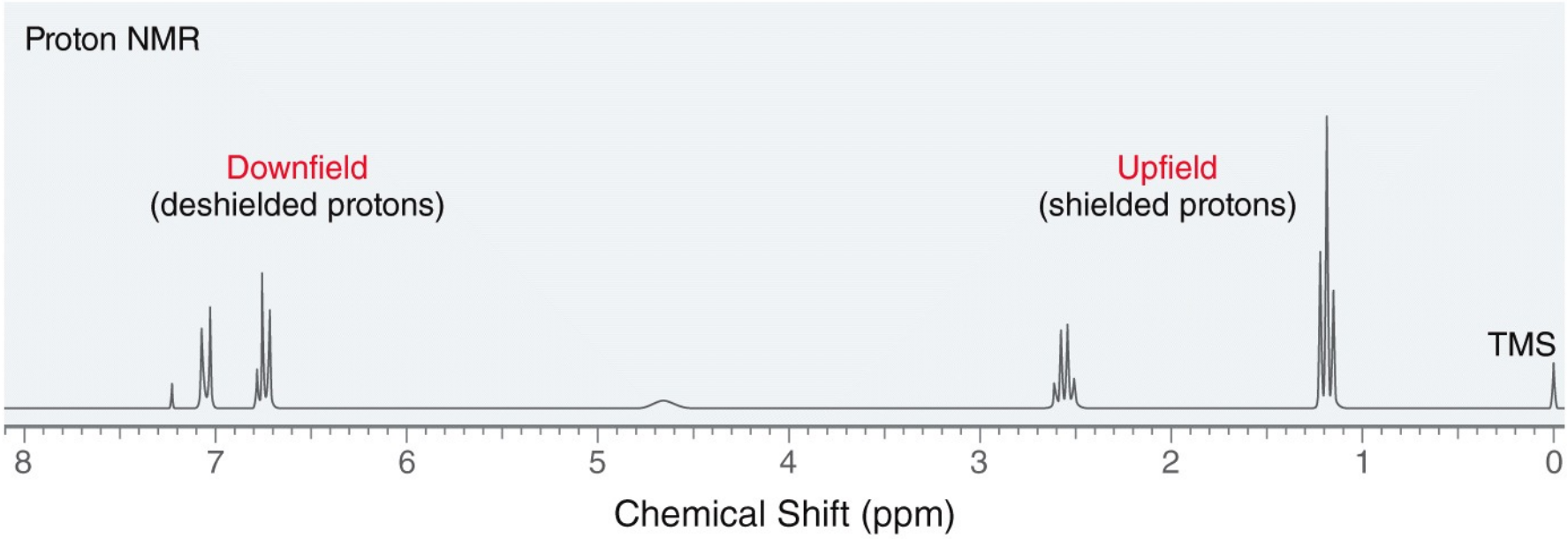

$$\delta = \frac{\text{pozorovaný posun z TMS (Hz)}}{\text{operačná frekvencia prístroja (Hz)}}$$

$$\delta = \frac{2181\ (\text{Hz})}{300\ 000\ 000\ (\text{Hz})} = 7{,}27 \cdot 10^{-6}$$

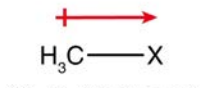


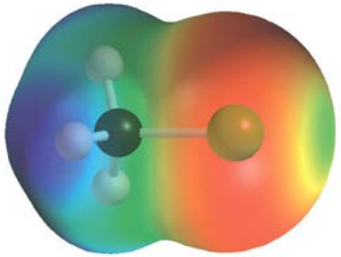
7,27 ppm

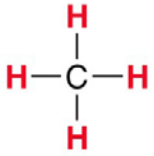
# Chemický posun



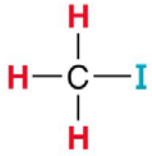
# Indukčný efekt a chemický posun



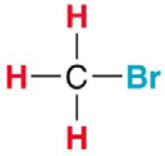





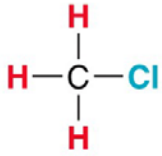
1.0 ppm



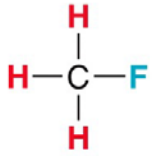
2.2 ppm



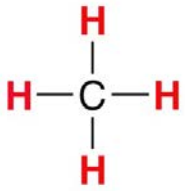
2.7 ppm



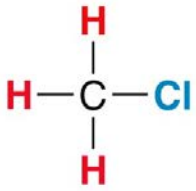
3.1 ppm



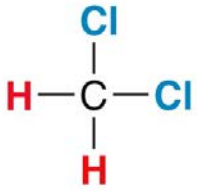
4.3 ppm



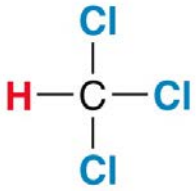
1.0 ppm



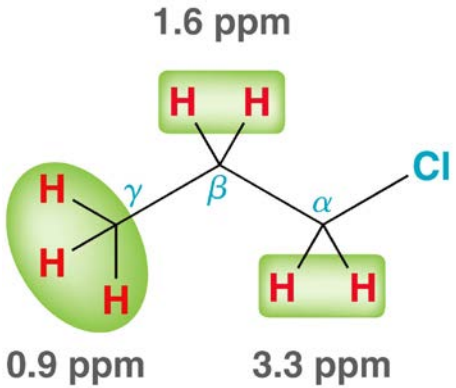
3.1 ppm



5.3 ppm



7.3 ppm



# Predpoveď chemického posunu

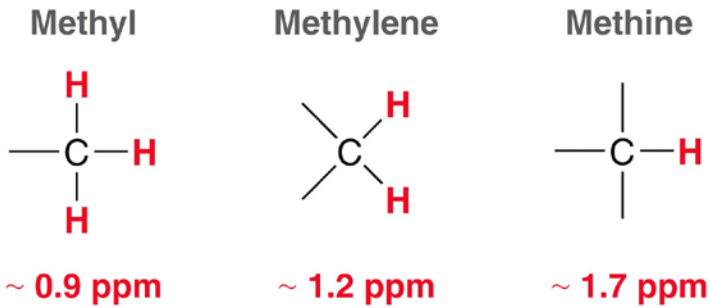
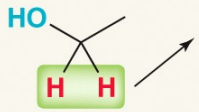
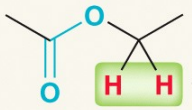
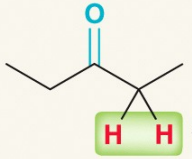
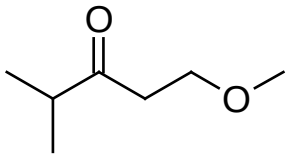



**TABLE 16.1 THE EFFECT OF NEIGHBORING FUNCTIONAL GROUPS ON CHEMICAL SHIFT**

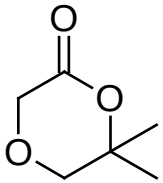
| FUNCTIONAL GROUP | EFFECT ON ALPHA PROTONS | EXAMPLE |
|---|---|---|
| **Oxygen** of an alcohol or ether | +2.5 |  Methylene group ($CH_2$) = 1.2 ppm<br>Next to oxygen = +2.5 ppm<br>3.7 ppm<br>Actual chemical shift = 3.7 ppm |
| **Oxygen** of an ester | +3 |  Methylene group ($CH_2$) = 1.2 ppm<br>Next to oxygen = +3.0 ppm<br>4.2 ppm<br>Actual chemical shift = 4.1 ppm |
| **Carbonyl group** (C=O) All carbonyl groups, including ketones, aldehydes, esters, etc. | +1 |  Methylene group ($CH_2$) = 1.2 ppm<br>Next to carbonyl group = +1.0 ppm<br>2.2 ppm<br>Actual chemical shift = 2.4 ppm |

# Úloha 5

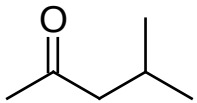
Určite chemický posun v $^{1}H$ NMR spektre molekúl:



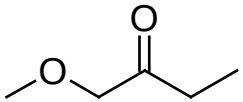

1



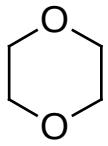

2



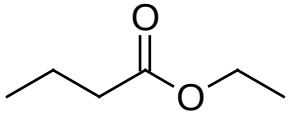

3




4

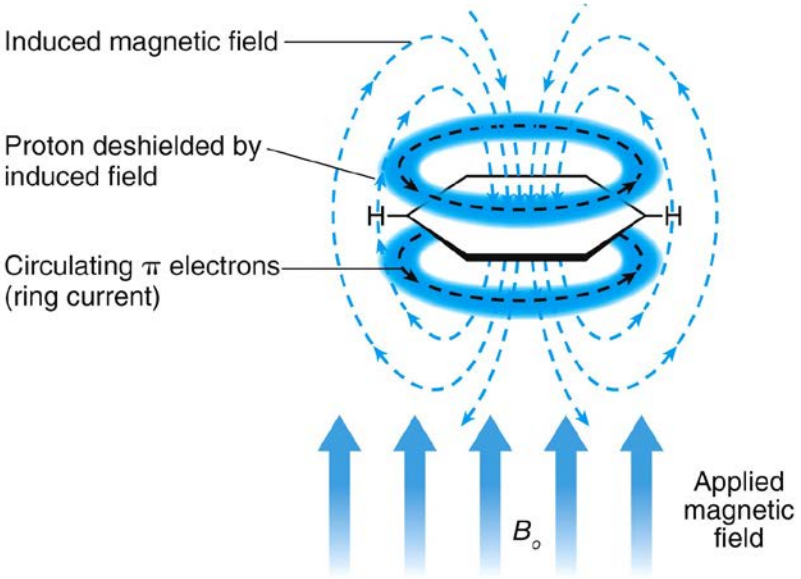


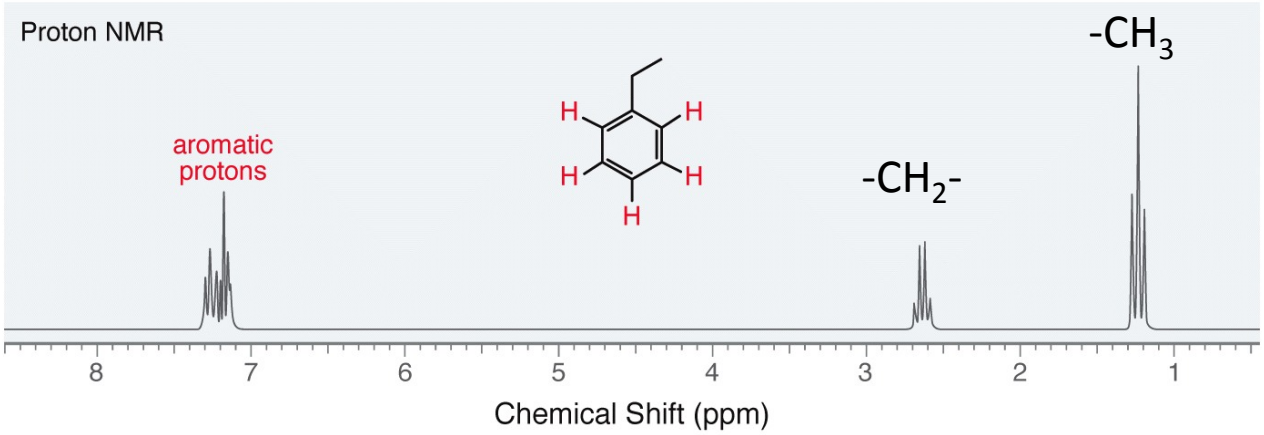

5




6

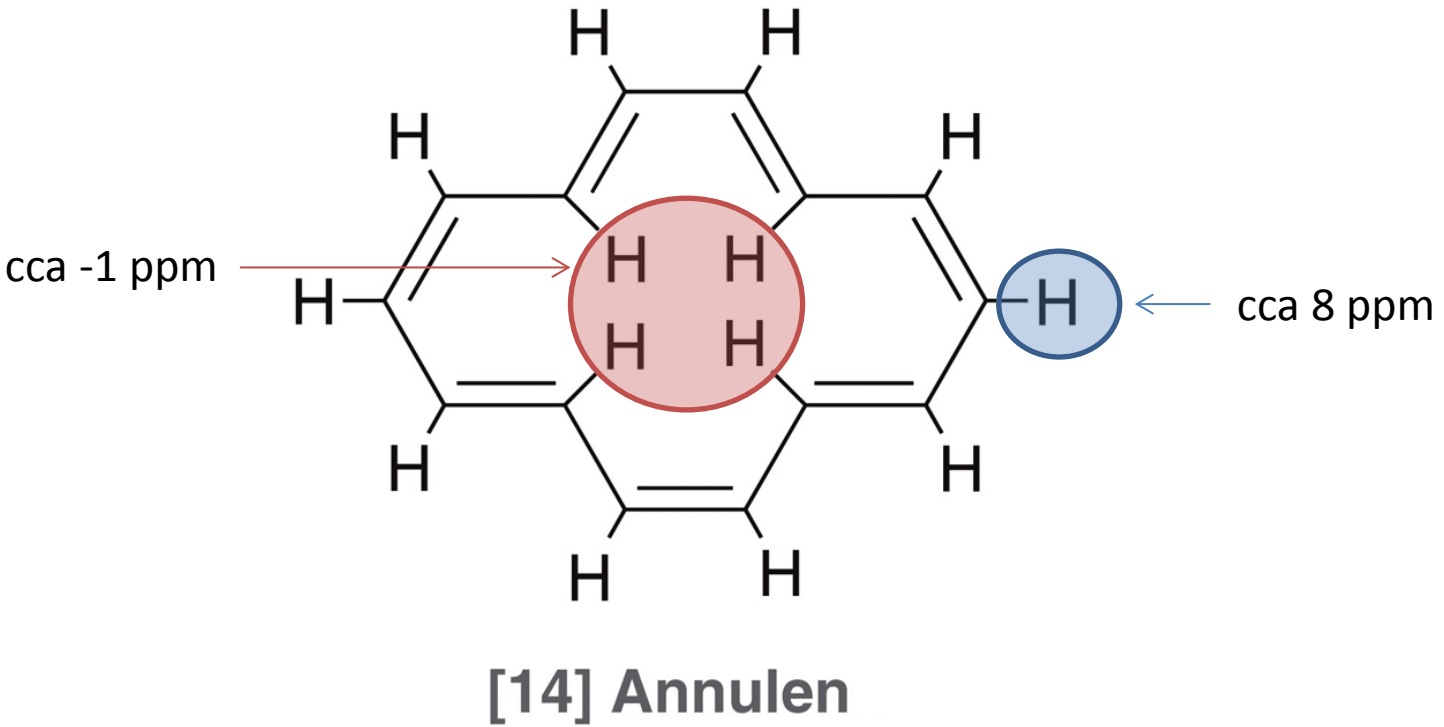
# Anizotropický efekt



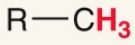
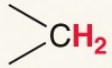
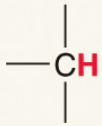
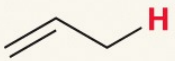
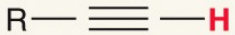
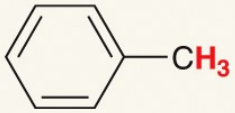
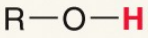
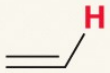
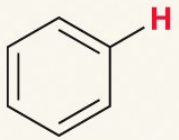
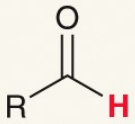
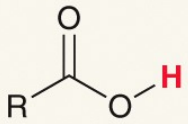
# Úloha 6

Určite, aký posun očakávate u vonkajších a vnútorných protónov [14] annulenu.



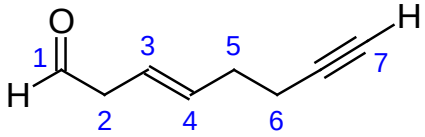
# Anizotropický efekt

**TABLE 16.2 CHEMICAL SHIFTS FOR PROTONS IN DIFFERENT ELECTRONIC ENVIRONMENTS**

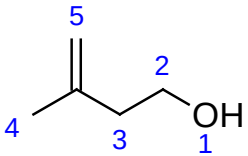
| TYPE OF PROTON | | CHEMICAL SHIFT (δ) |
|---|---|---|
| Methyl |  | ~0.9 |
| Methylene |  | ~1.2 |
| Methine |  | ~1.7 |
| Allylic |  | ~2 |
| Alkynyl |  | ~2.5 |
| Aromatic methyl |  | ~2.5 |
| Alkyl halide |  | 2–4 |
| Alcohol |  | 2–5 |
| Vinylic |  | 4.5–6.5 |
| Aryl |  | 6.5–8 |
| Aldehyde |  | ~10 |
| Carboxylic acid |  | ~12 |

# Úloha 7

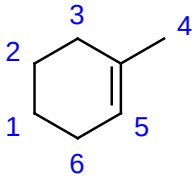
Určite teoretický očakávaný chemický posun u molekúl
(číslovanie nerešpektuje IUPAC-nomenklatúru)



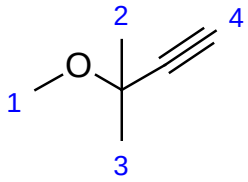

1




2



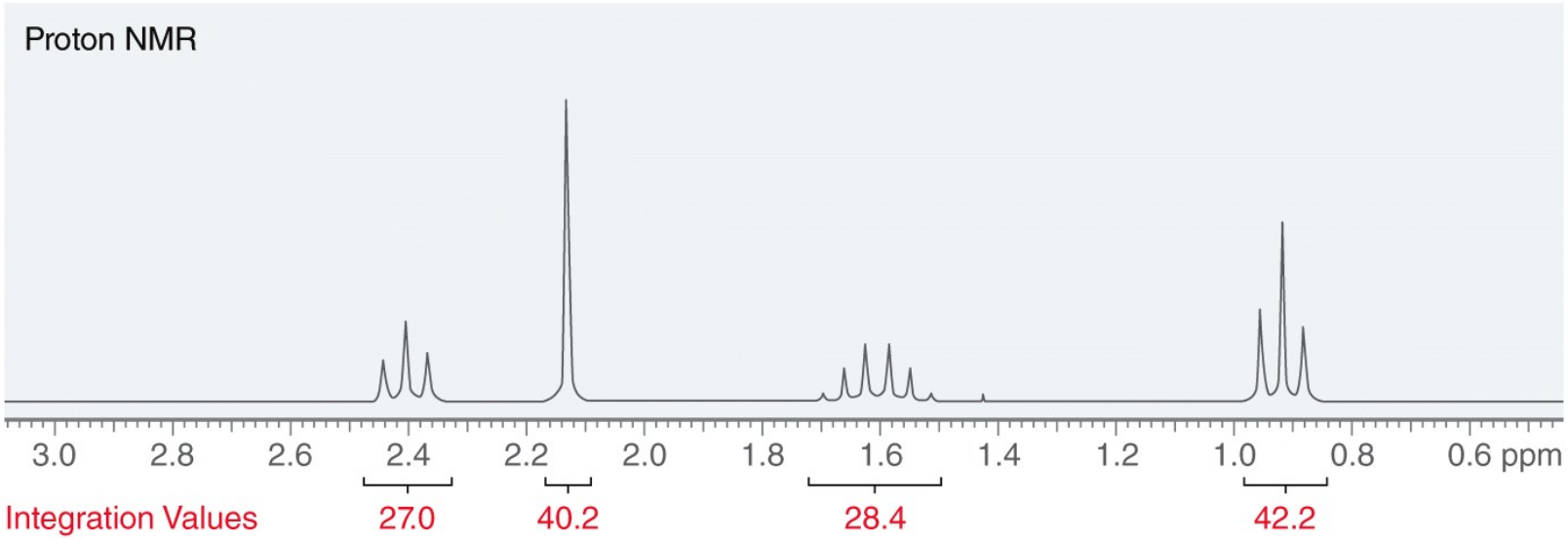

3




4

# Integrácia

- = plocha pod signálom, počet protónov poskytujúcich daný signál




- pri vyhodnocovaní – **pomer**

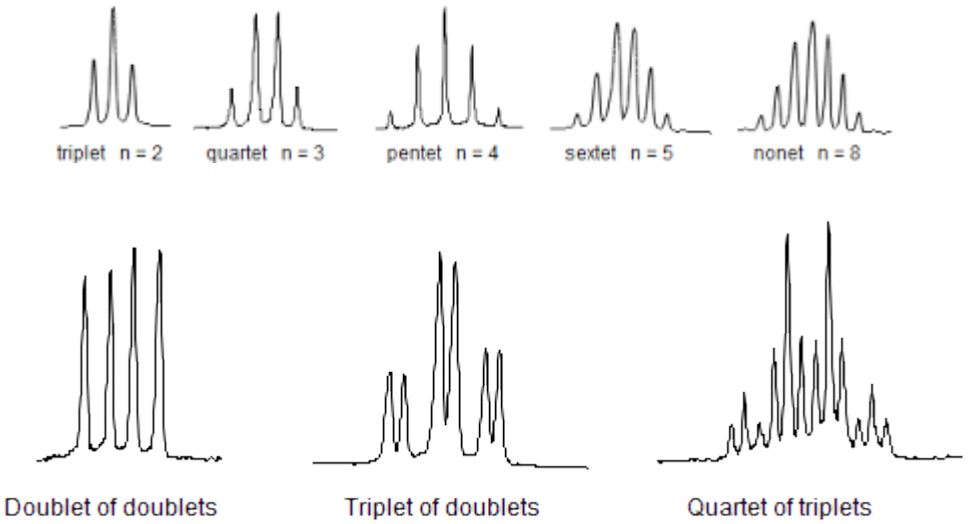
$$\frac{27}{27} = 1 \qquad \frac{40{,}2}{27} = 1{,}49 \qquad \frac{28{,}4}{27} = 1{,}05 \qquad \frac{42{,}2}{27} = 1{,}56$$

# Úloha 8

$^{1}$H NMR spektrum zlúčeniny so sumárnym molekulovým vzorcom $C_7H_{15}Cl$ vykazuje 2 signály s relatívnym pomerom integrálov 2:3. Určite štruktúru.

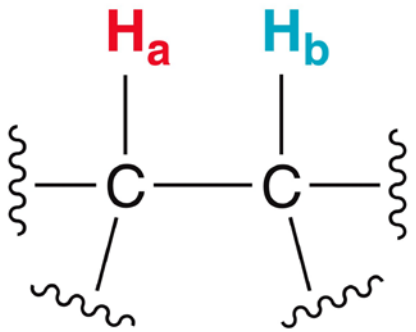
# Multiplicita

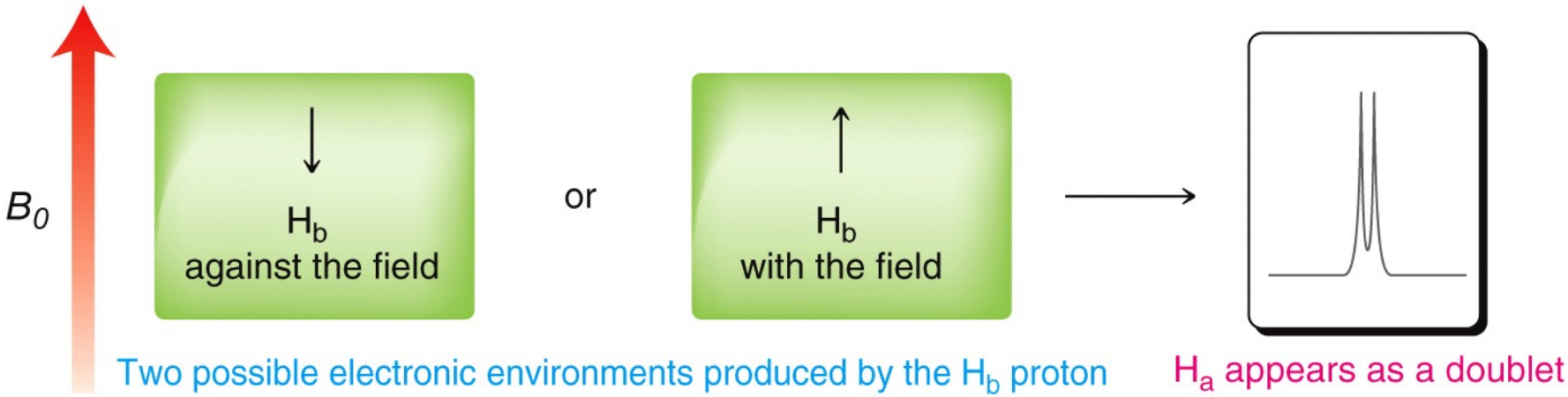
- = počet píkov v danom signále (singlet, dublet, triplet, kvartet, kvintet,…, ale aj dublet dubletu, triplet dubletu, kvartet tripletu,…)



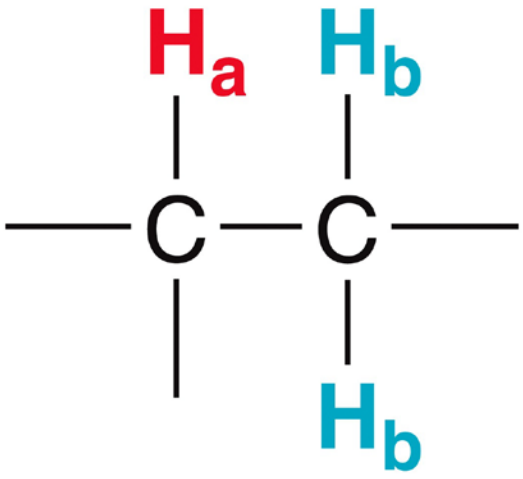
# Multiplicita

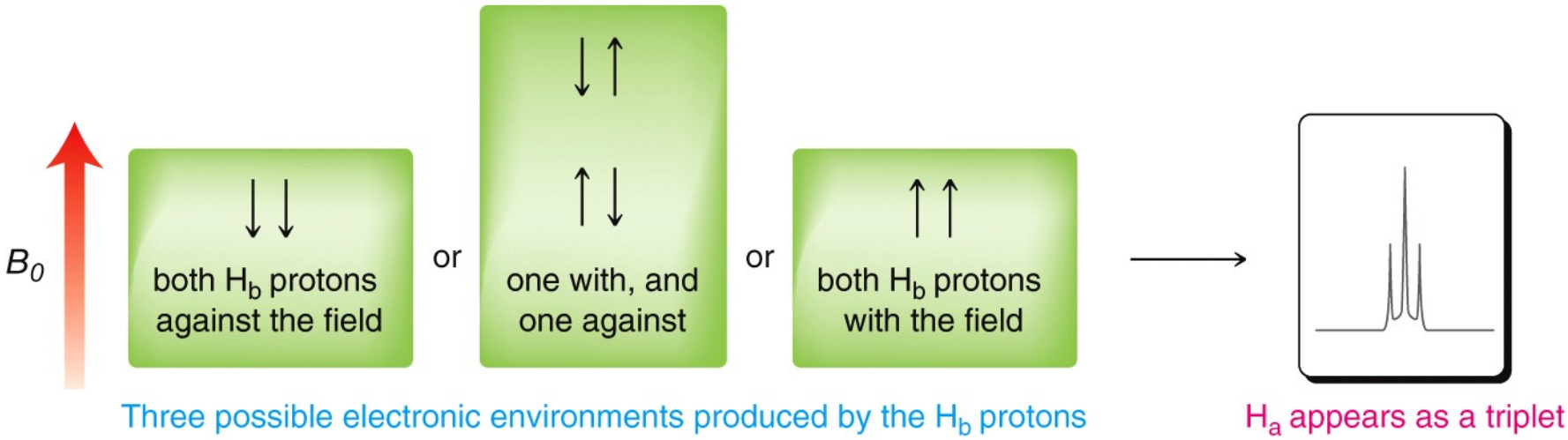
- = počet susediacich protónov
- $H_a$ a $H_b$ sú neekvivalentné
- **coupling, spin-spinové štiepenie**



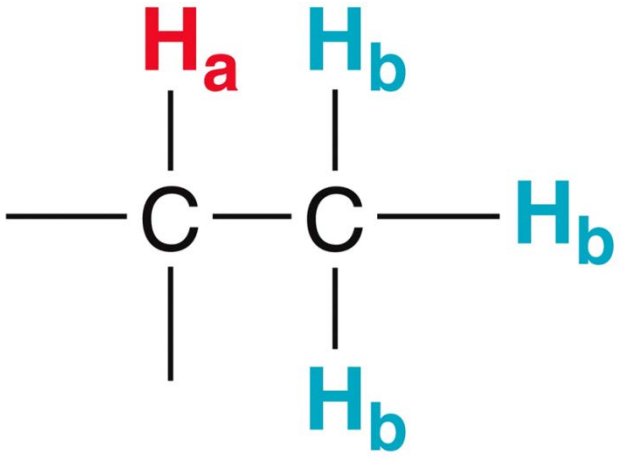



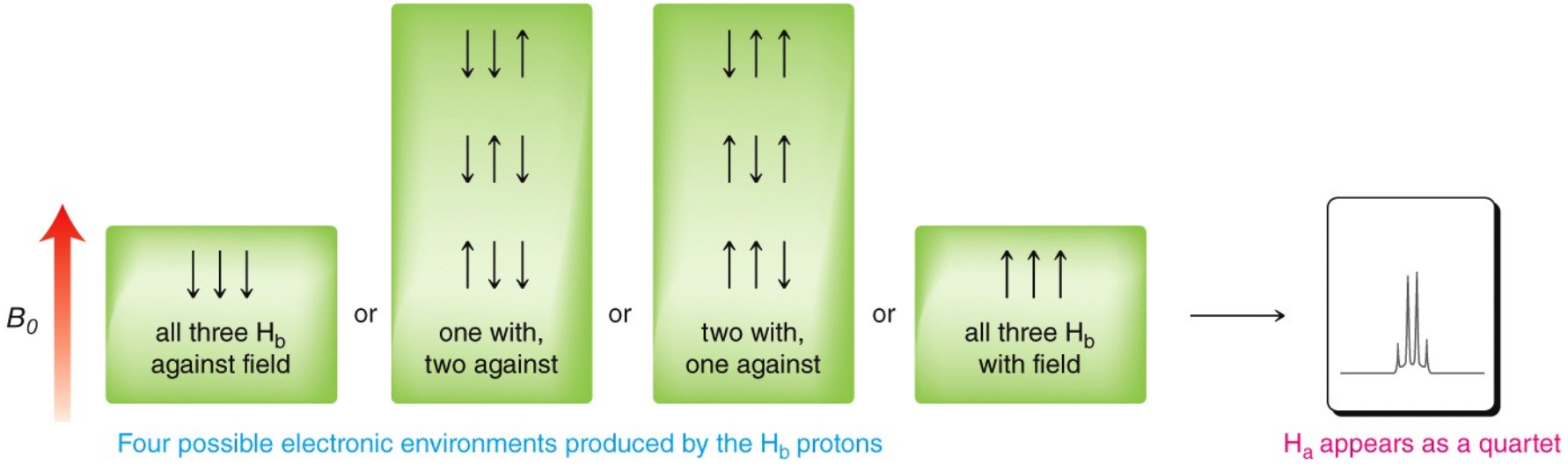
# Multiplicita



# Multiplicita



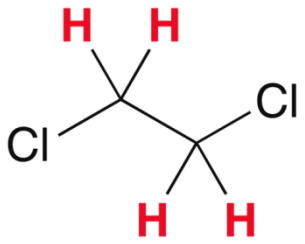
# Multiplicita

**TABLE 16.3 MULTIPLICITY INDICATES THE NUMBER OF NEIGHBORING PROTONS**

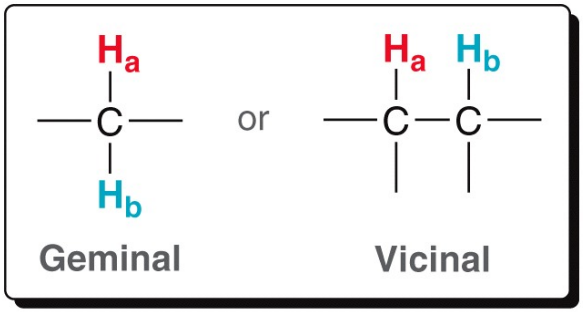
| NUMBER OF NEIGHBORS | MULTIPLICITY | RELATIVE INTENSITIES OF INDIVIDUAL PEAKS |
|---|---|---|
| 1 | Doublet | 1:1 |
| 2 | Triplet | 1:2:1 |
| 3 | Quartet | 1:3:3:1 |
| 4 | Quintet | 1:4:6:4:1 |
| 5 | Sextet | 1:5:10:10:5:1 |
| 6 | Septet | 1:6:15:20:15:6:1 |

# Faktory ovplyvňujúce štiepenie

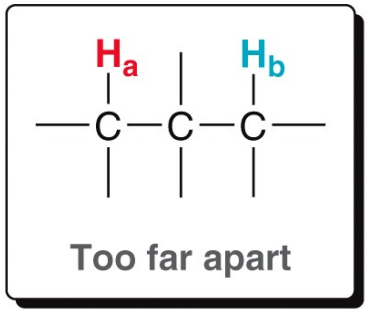
- Ekvivalentné protóny sa neštiepia




- Štiepenie môže nastať, ak sú protóny oddelené max. 2 – 3 σ väzbami (špeciálny prípad sú rigídne, napr. bicyklické alebo allylické molekuly, kde sa môže vyskytnúť štiepenie vzdialenejších protónov > 3 σ)



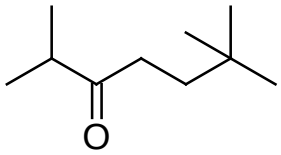

Splitting is observed



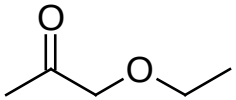

Splitting is generally not observed

# Úloha 9

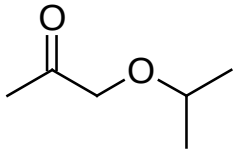
Určite multiplicitu každého signálu očakávaného v $^{1}H$ NMR spektre u nassledujúcich molekúl:



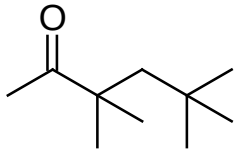

1



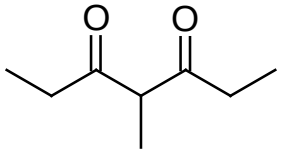

2




3



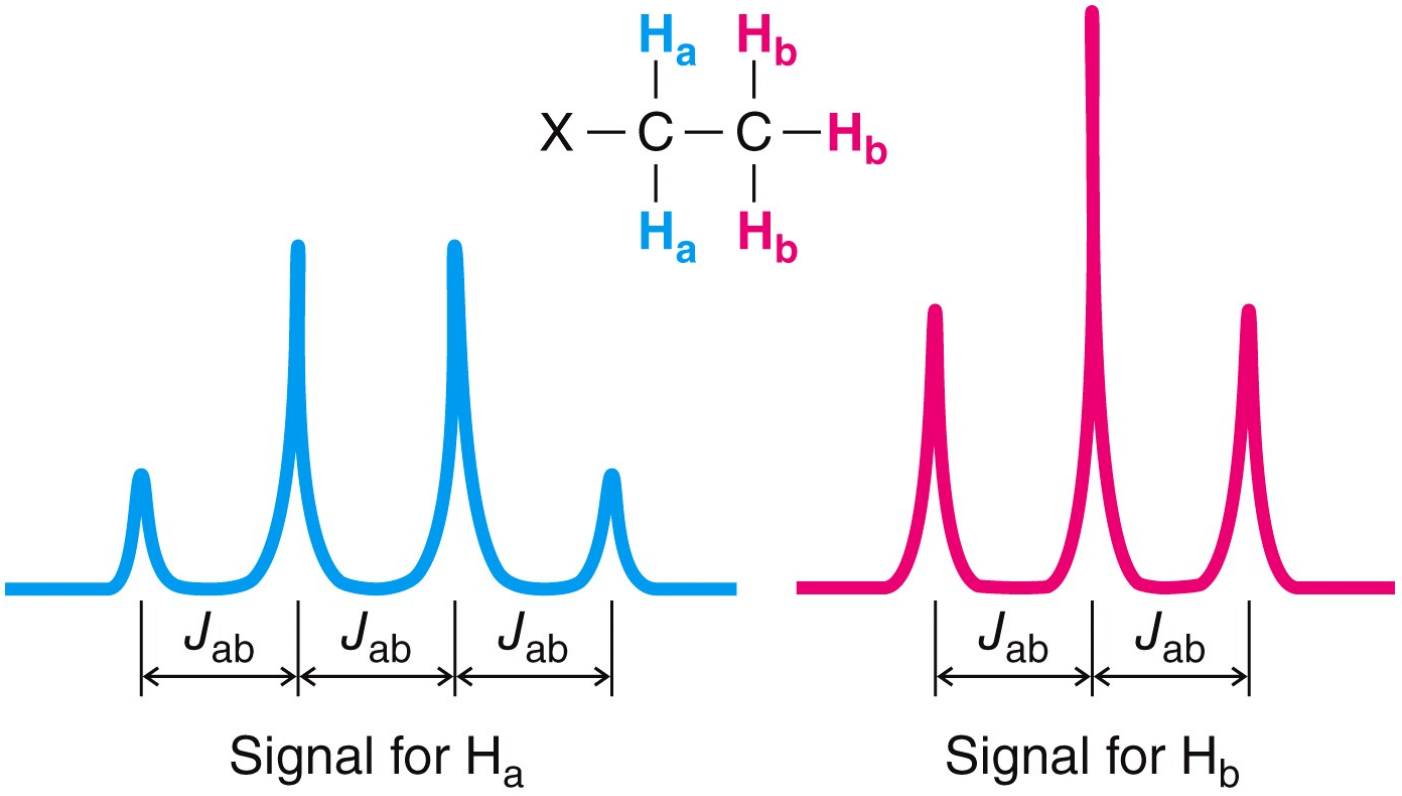

4



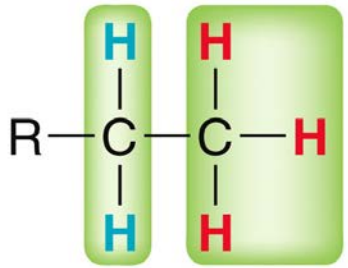

5

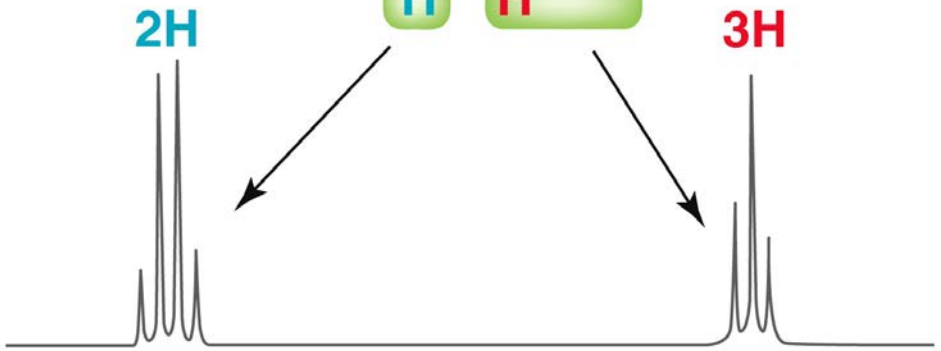
# Interakčná konštanta J

- = vzdialenosť medzi píkmi v multiplete (Hz)

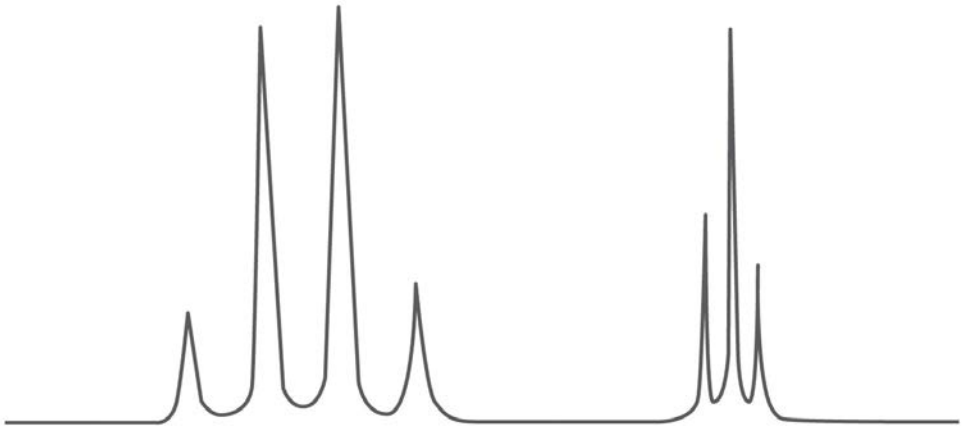


# Interakčná konštanta J



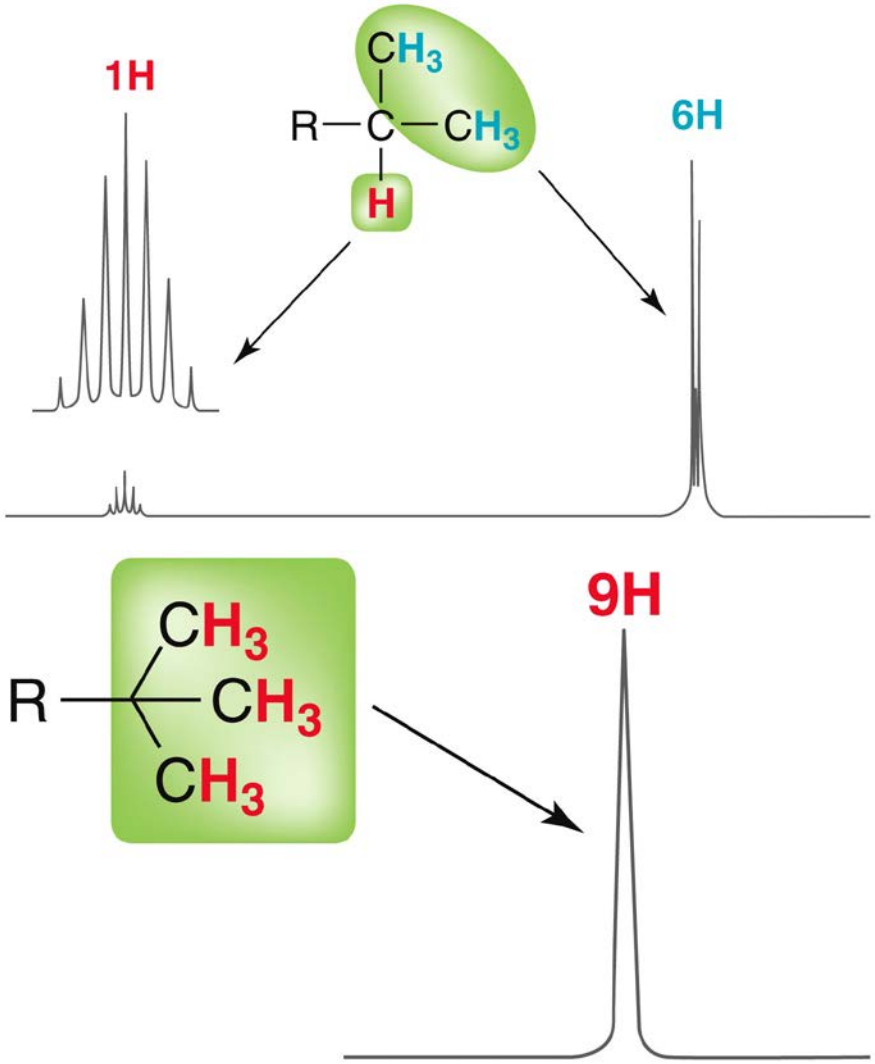

1. -$CH_2CH_3$ má rovnakú J



2. J nie je rovnaká

**Not an ethyl group**

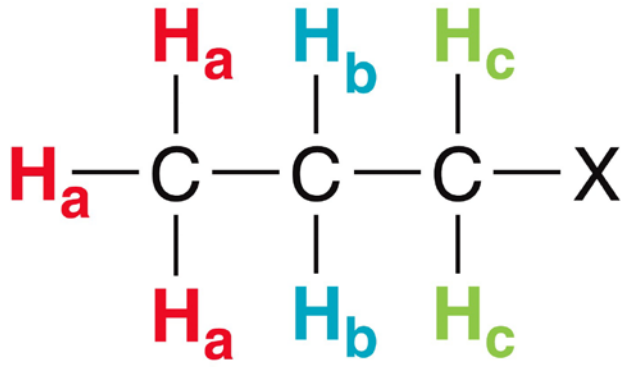
# Interakčná konštanta J



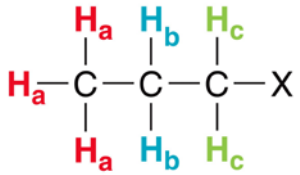
# Komplexné štiepenie

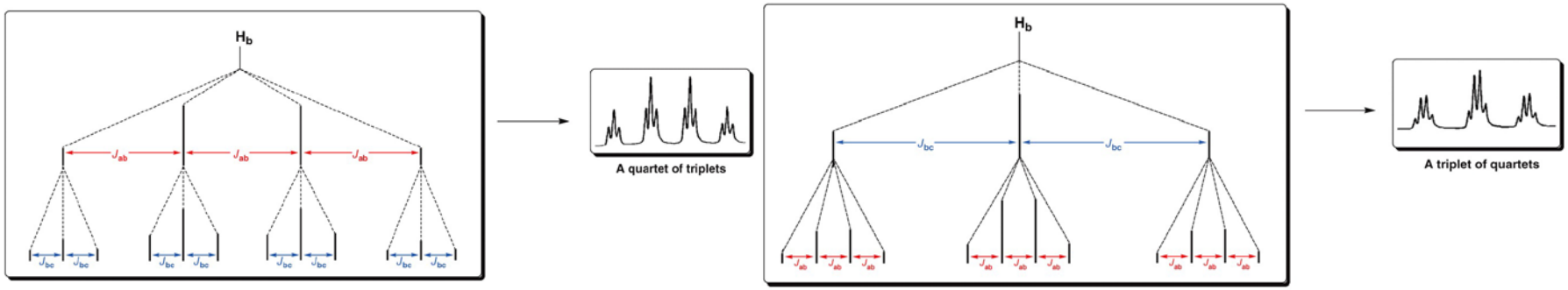
- Keď protón susedí s 2 neekvivalentnými skupinami, napr. $H_b$

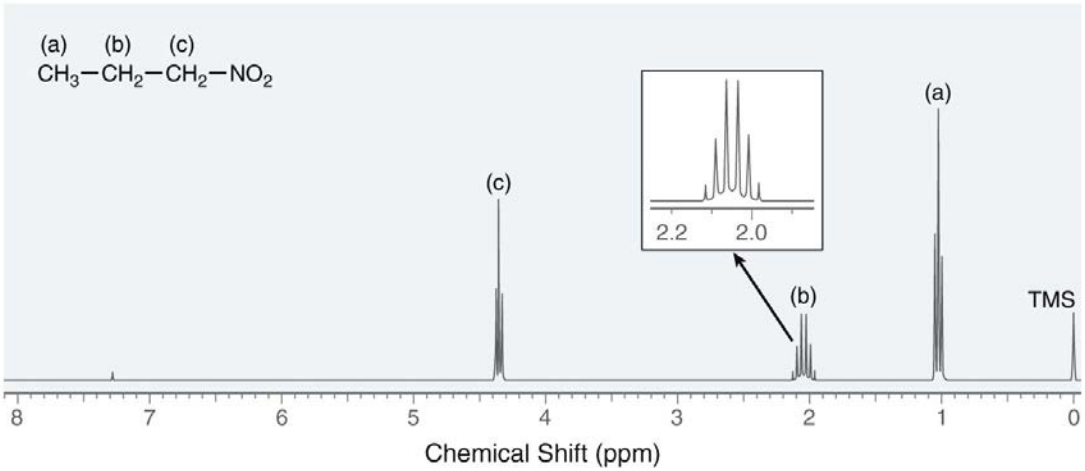
...protóny $H_a$ štiepia $H_b$ na kvartet, $H_c$ na triplet – výsledkom je **multiplet**



# 1 - nitropropan

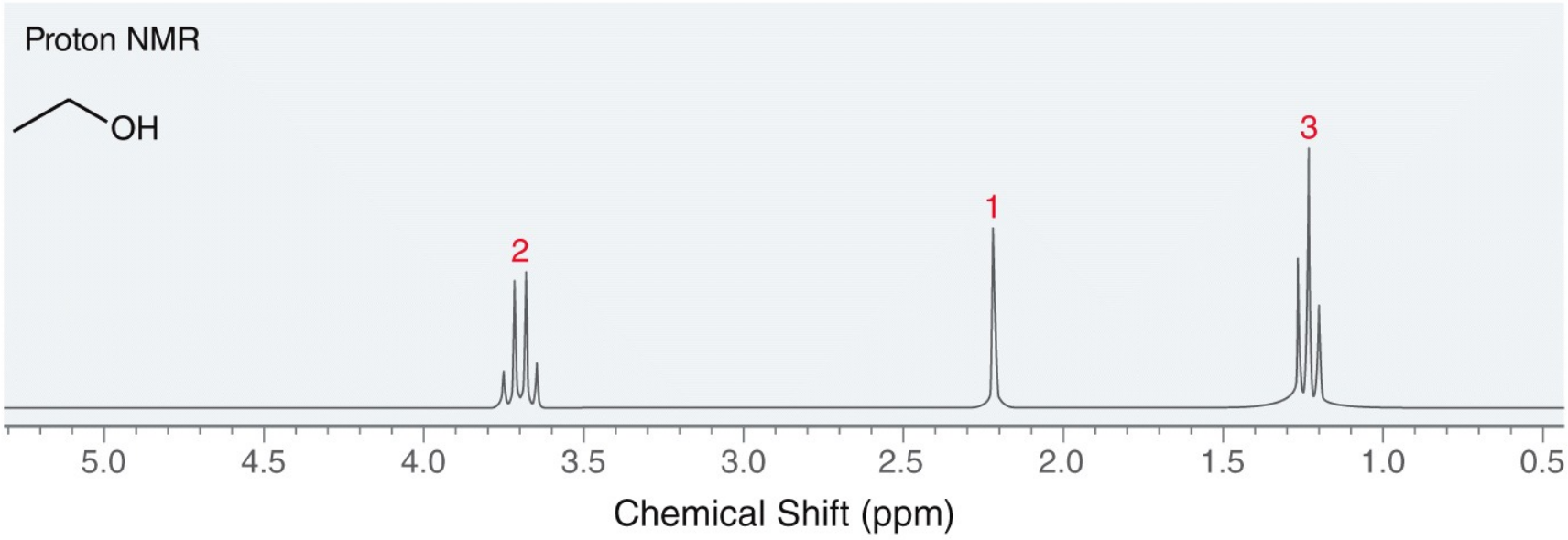


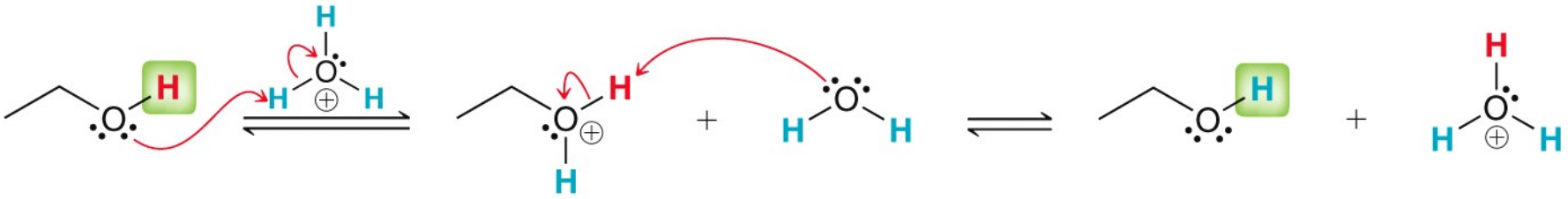




- špeciálny prípad, keď sú hodnoty $J_{ab}$ a $J_{ac}$ natoľko blízke (Hz), že sa v spektre javia akoby boli chemicky ekvivalentné

# Protóny bez J

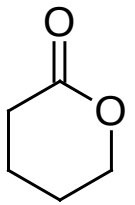



- OH- skupina je **singlet,** v prítomnosti stopových množstiev kyseliny/báze nie je štiepená susednou – $CH_2$- sk. (typicky sú hydroxylové sk. medzi 2 – 5 ppm, ale je ťažké presne odhadnúť ich pozíciu)

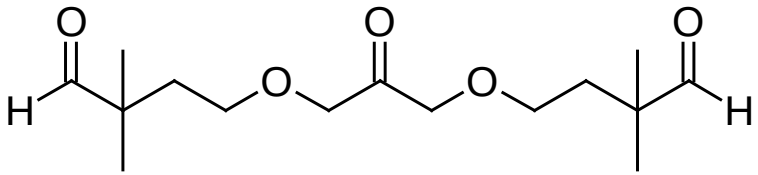


# Úloha 10

Nakreslite teoretické $^{1}H$ NMR spektrum:




1

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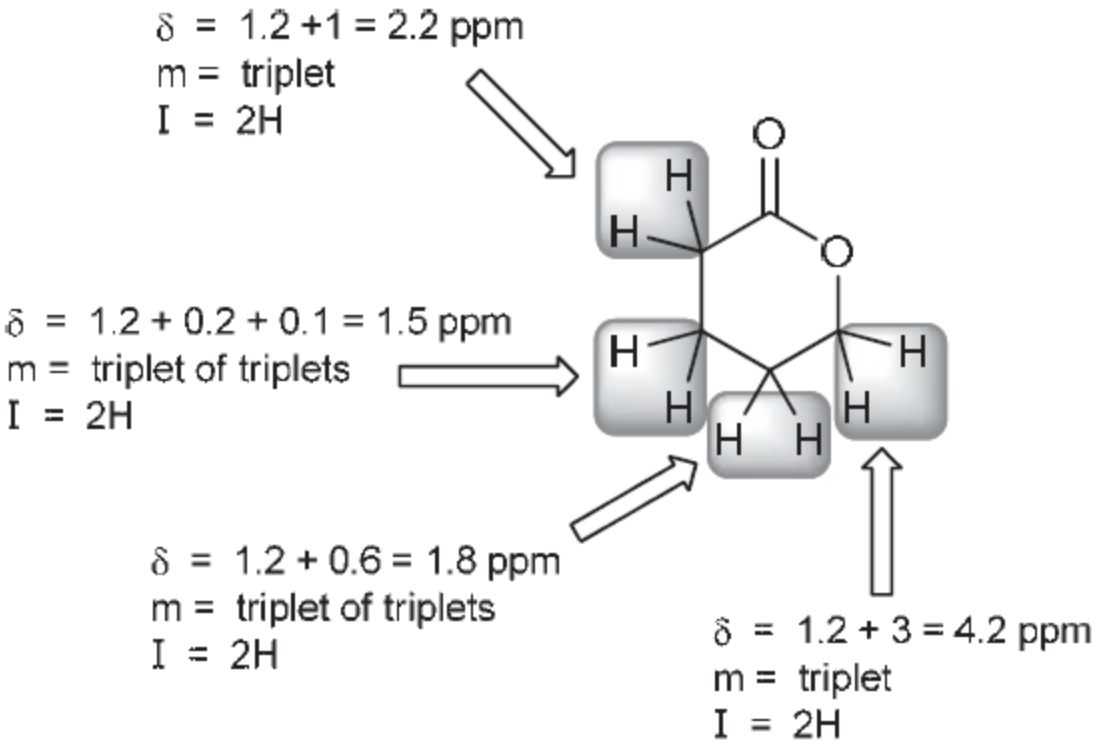
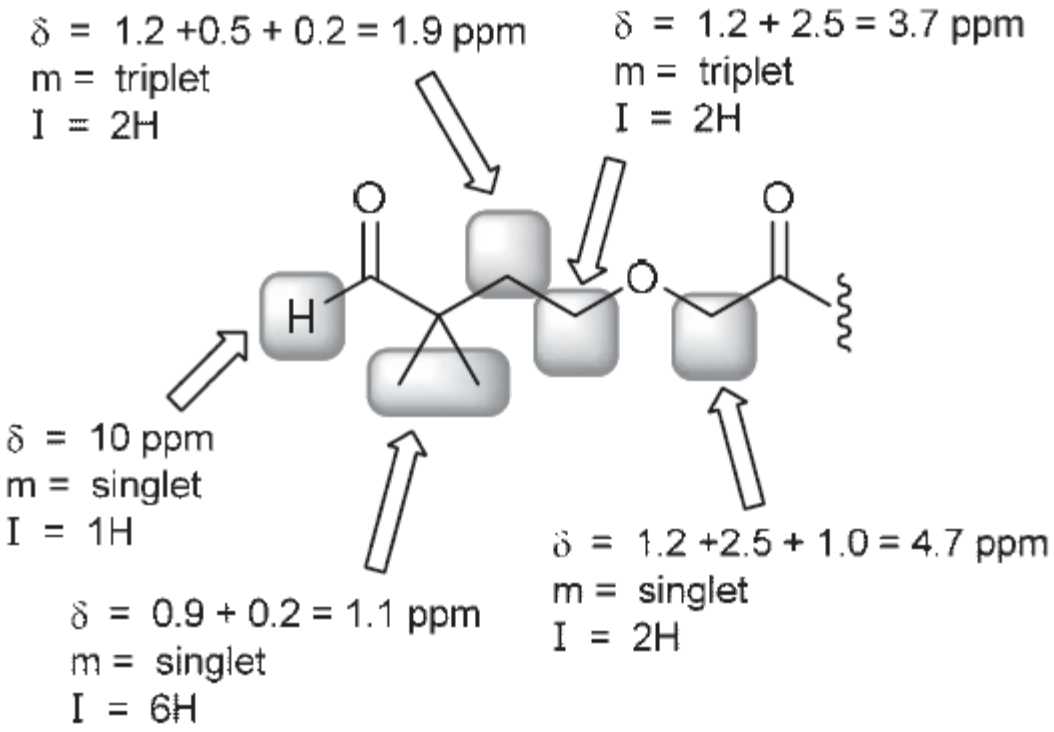
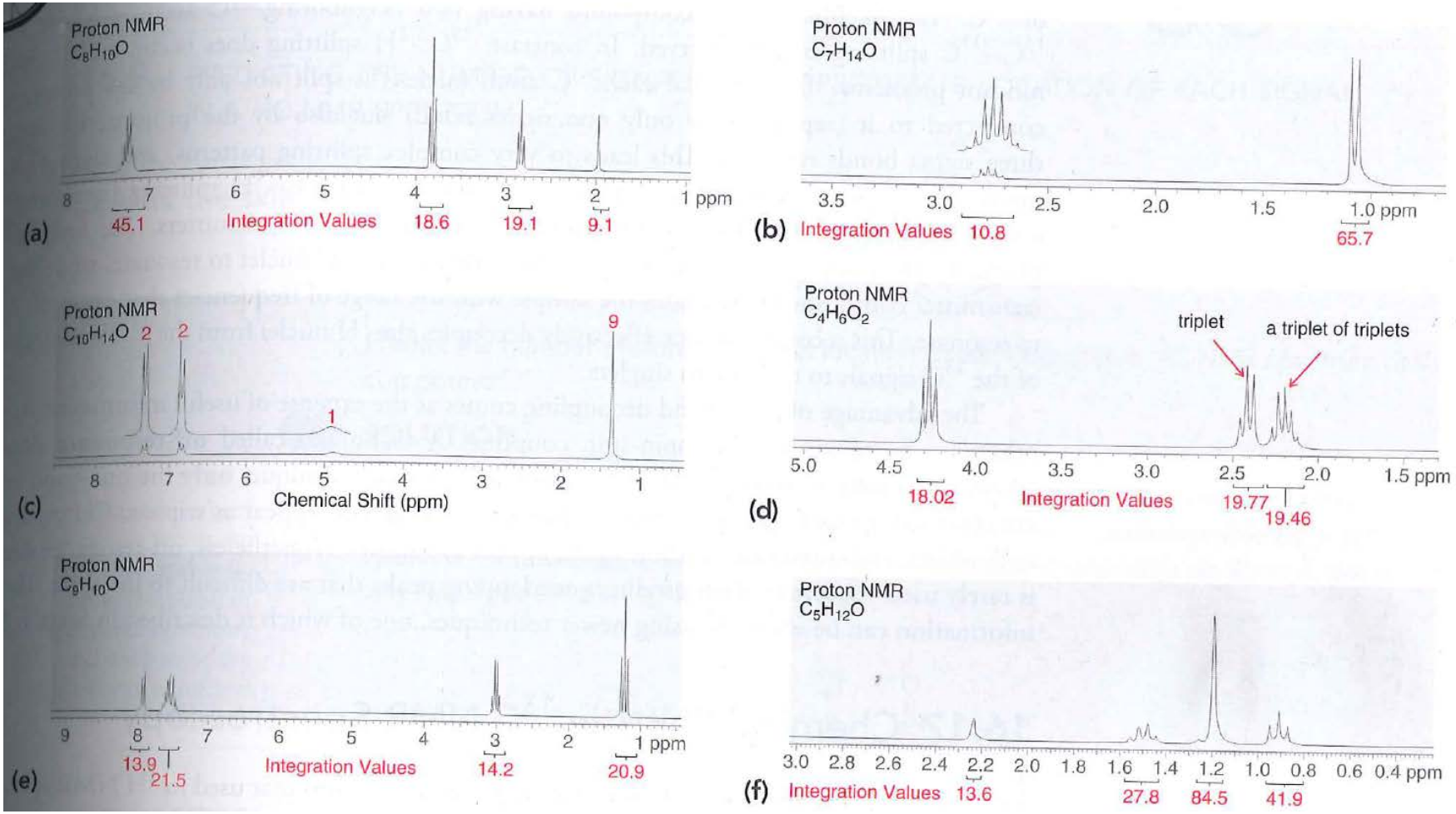

δ = 1.2 +1 = 2.2 ppm
m = triplet
I = 2H
δ = 1.2 + 0.2 + 0.1 = 1.5 ppm
m = triplet of triplets
I = 2H
δ = 1.2 + 0.6 = 1.8 ppm
m = triplet of triplets
I = 2H
δ = 1.2 + 3 = 4.2 ppm
m = triplet
I = 2H
O
O
H
H
H
H
H
H
H
H
H


δ = 1.2 +0.5 + 0.2 = 1.9 ppm
m = triplet
I = 2H
δ = 1.2 + 2.5 = 3.7 ppm
m = triplet
I = 2H
O
O
O
H
δ = 10 ppm
m = singlet
I = 1H
δ = 1.2 +2.5 + 1.0 = 4.7 ppm
m = singlet
I = 2H
δ = 0.9 + 0.2 = 1.1 ppm
m = singlet
I = 6H

# Úloha 11

- Určite štruktúru látok z nasledujúcich informácií:



# Správne odpovede

1. Úloha:

NMR aktívne budú nasledujúce jadrá:

$^{17}O$, $^{2}H$, $^{7}Li$, $^{13}C$, $^{14}N$

(jadrá s lichým počtom protónov a/alebo lichým počtom neutrónov)

# Správne odpovede

- 2.Úloha:

1. diastereotopické,
2. homotopické,
3. enantiotopické,
4. diastereotopické,
5. enantiotopické,
6. homotopické

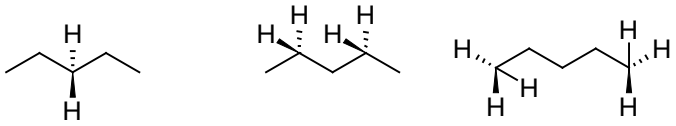
# Správne odpovede

- 3. Úloha:

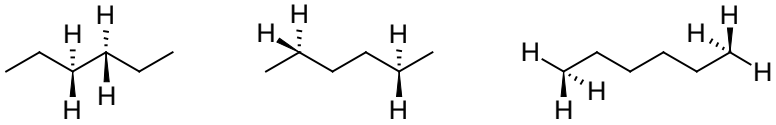
a) červené sú chemicky ekvivalentné, pretože sú navzájom nerozoznateľné po prevedení rotácie alebo zrkadlenia

b) modré sú chemicky ekvivalentné, pretože môžeme previesť rotáciu, ktorá stotožní všetky protóny

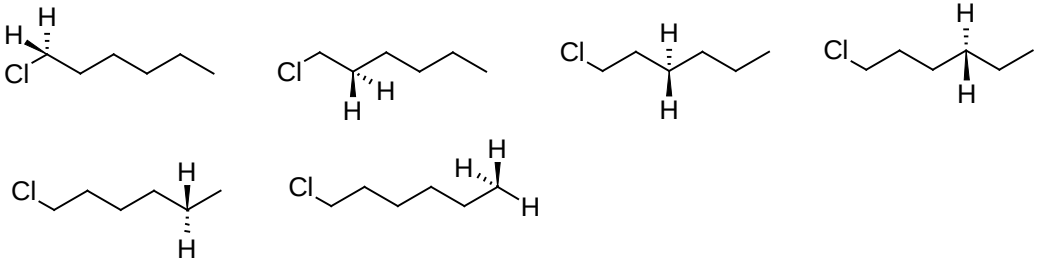
c) 3 rôzne signály líšiace sa v chemickom posune (ppm)



d) 3 rôzne signály



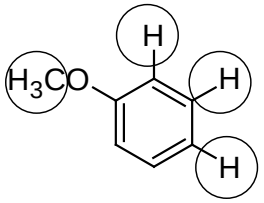
e) 6 rôznych signálov



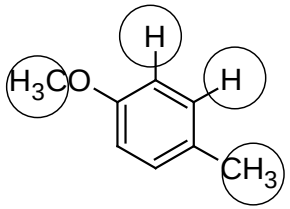
# Správne odpovede

- 4. Úloha:

1. 4 signály,
2. 4 signály,
3. 4 signály,
4. 3 signály,
5. 2 signály,
6. 7 signálov



1



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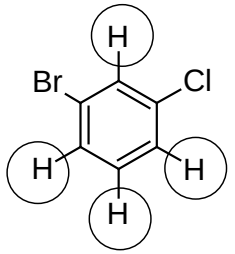

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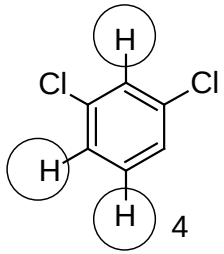

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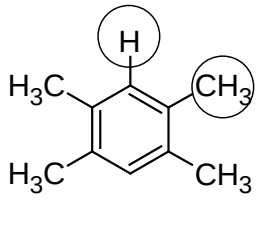

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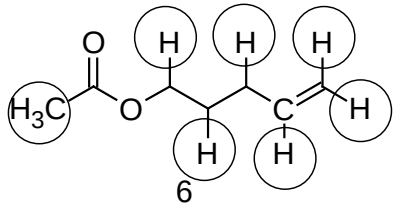
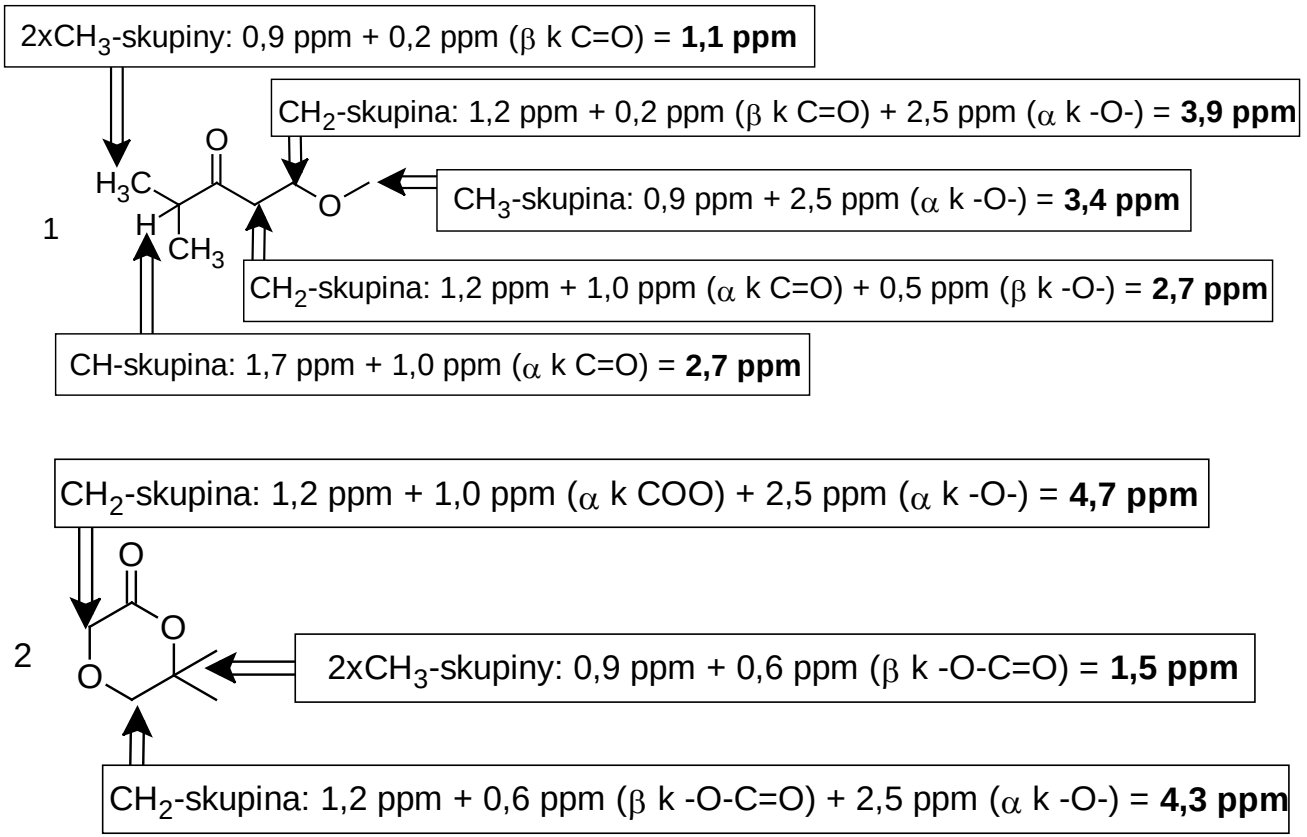


6

# Správne odpovede

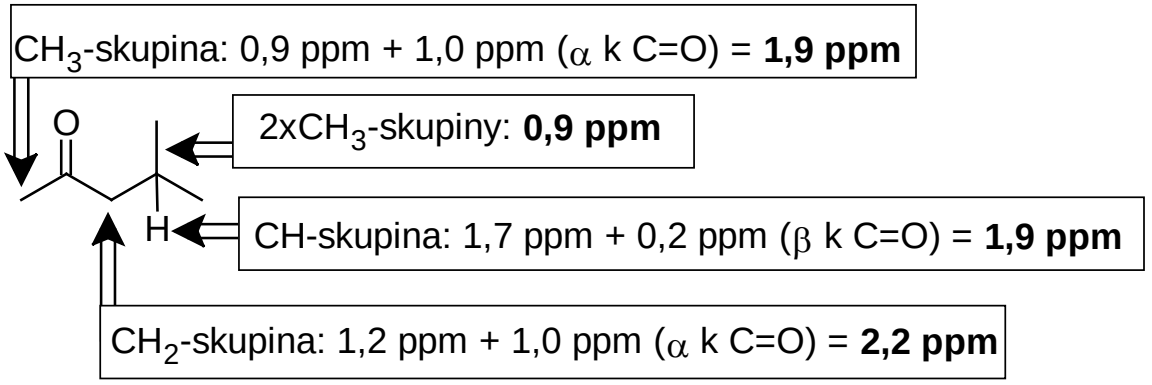
- Úloha 5:



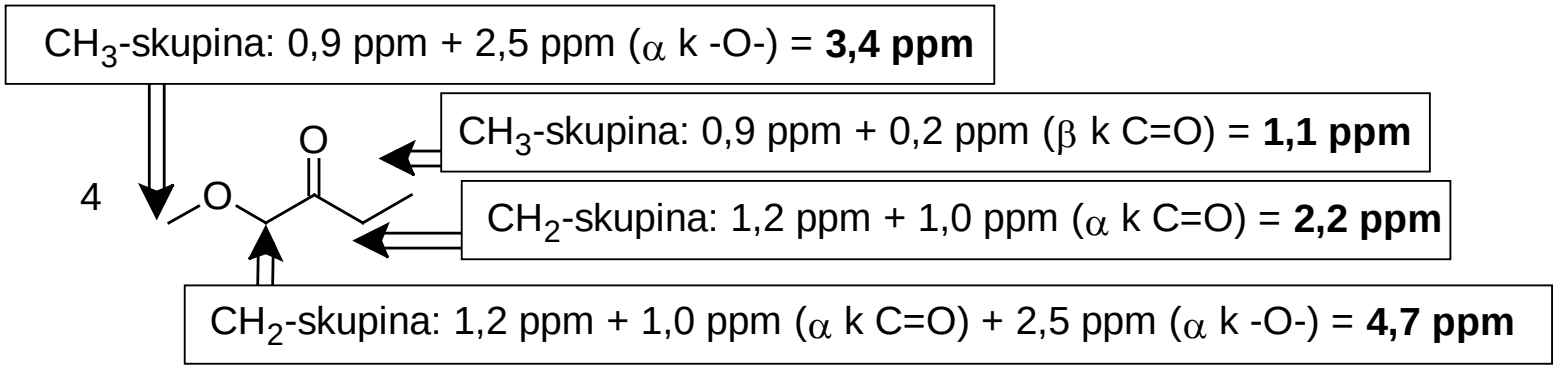
# Správne odpovede

- Úloha 5:

3



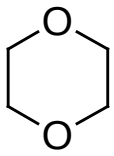

4



# Správne odpovede

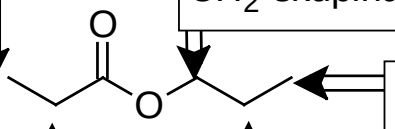
- Úloha 5:

5



4x$CH_2$-skupina: 1,2 ppm + 2,5 ppm ($\alpha$ k -O-) + 0,5 ppm ($\beta$ k -O-) = **4**,**2 ppm**

6



$CH_3$-skupina: 0,9 ppm + 0,2 ppm ($\beta$ k COO) = **1,1 ppm**

$CH_2$-skupina: 1,2 ppm + 2,5 ppm ($\alpha$ k -O-C=O) = **3,7 ppm**

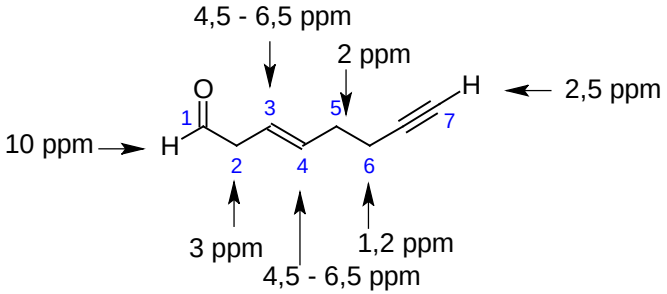
$CH_3$-skupina: **0,9 ppm**

$CH_2$-skupina: 1,2 ppm + 0,6 ppm ($\beta$ k -O-C=O) = **1,8 ppm**

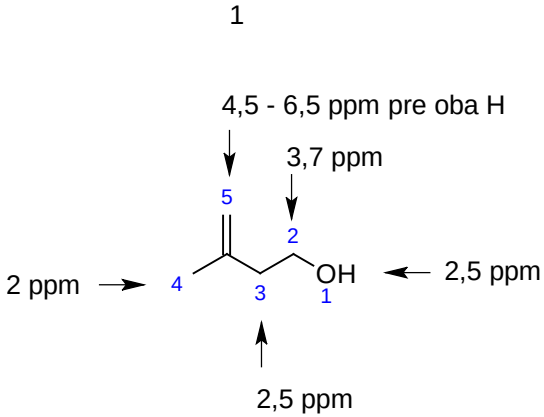
$CH_2$-skupina: 1,2 ppm + 1,0 ppm ($\alpha$ k COO) = **2,2 ppm**

# Správne odpovede

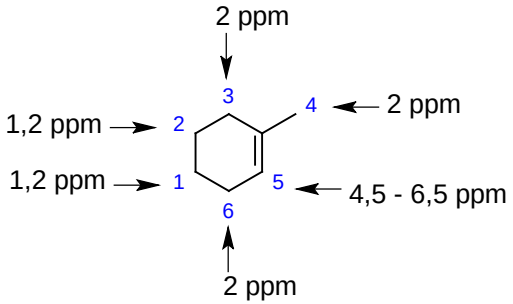
- Úloha 7:



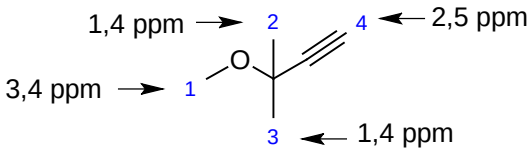

1




2



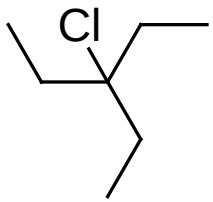

3




4

# Správne odpovede

- Úloha 8:

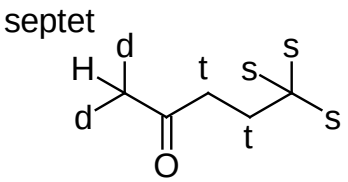



$3xCH_3 = 9$, $3xCH_2 = 6$, len 2 signály s pomerom intenzít 3:2

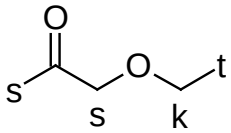
celkove 15 protónov

# Správne odpovede

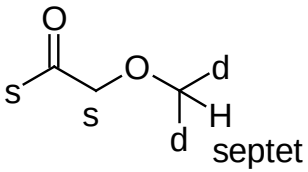
- Úloha 9: s – singlet, d- dublet, t-triplet, k - kvartet



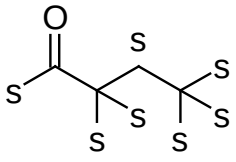

1



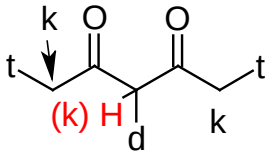

2




3



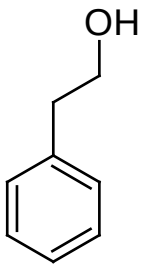

4



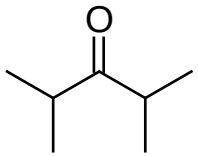

5

# Správne odpovede

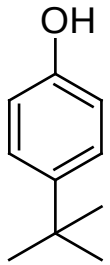
- Úloha 11:



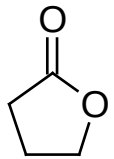

a



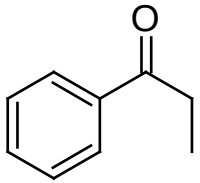

b



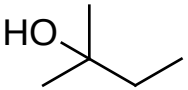

c




d




e




f