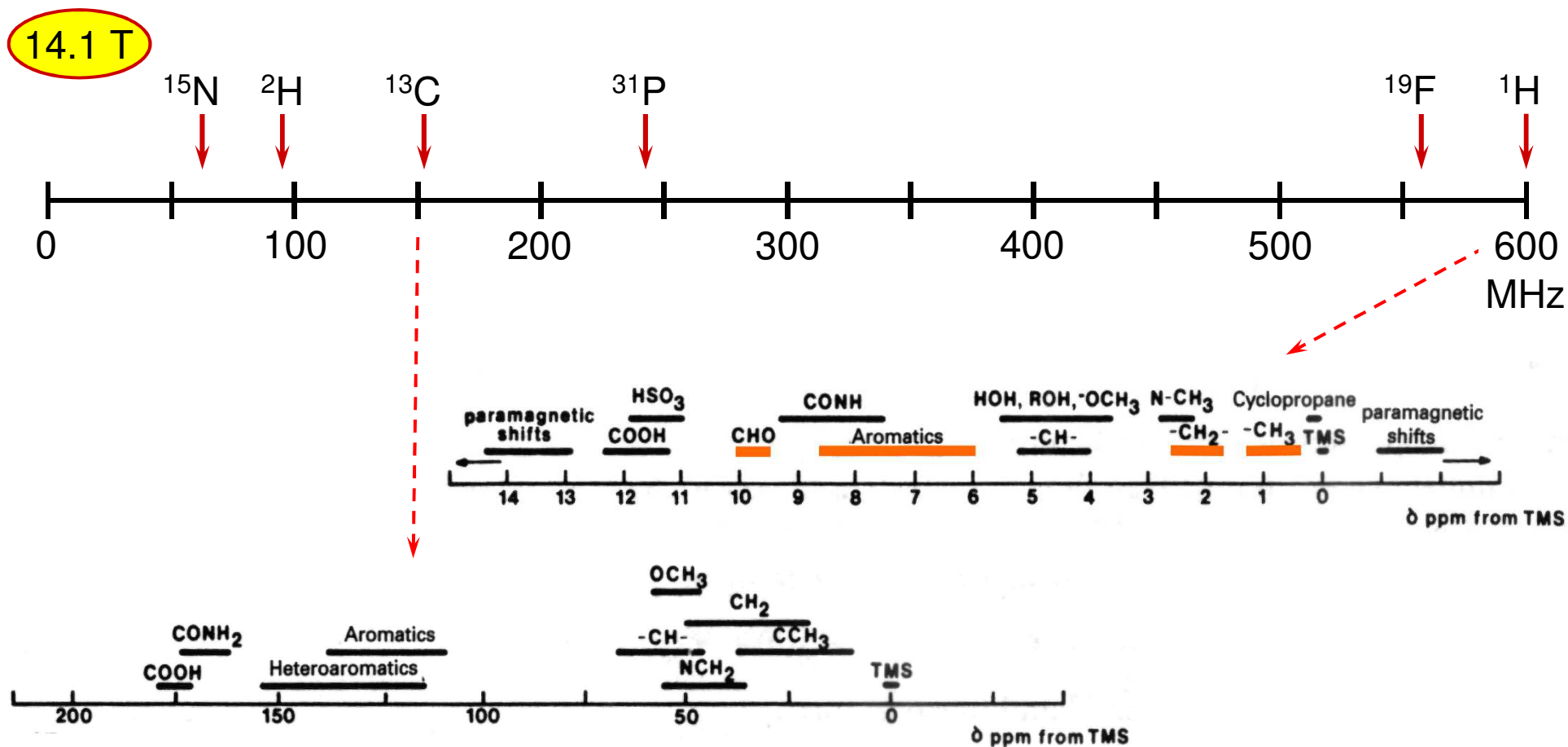


# Chemický posun

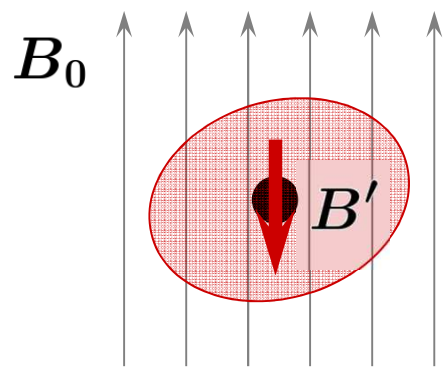
# Které spektrum měříme



Velké rozdíly v rezonančních frekvencích

vždy sledujeme jedno jádro

# Chemický posun



Stínění jádra elektrony

lokální magnetické pole

$$B = B_0 - B' = B_0(1 - \sigma)$$

↪ pozměněná frekvence precese

$$\nu = \frac{\gamma}{2\pi} B_0(1 - \sigma)$$

$$\delta = 10^6 \frac{\nu - \nu_{ref}}{\nu_{ref}}$$

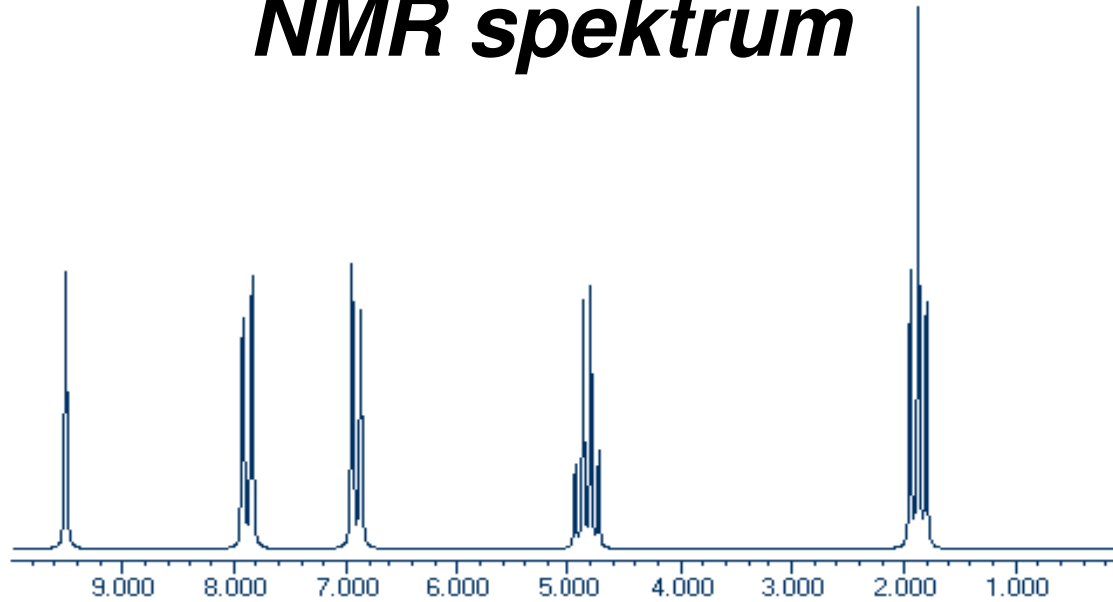
ppm

*parts per million*

## Příklad pro <sup>1</sup>H

TMS	500 000 000 Hz	0 ppm	300 000 000 Hz
MeOH	500 001 650 Hz	3.3 ppm	300 000 990 Hz
Benzen	500 003 635 Hz	7.27 ppm	300 002 181 Hz
	$B_0 = 11.7 \text{ T}$		$B_0 = 7.1 \text{ T}$

# *NMR spektrum*



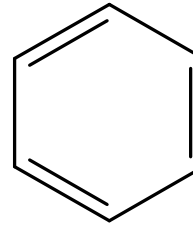
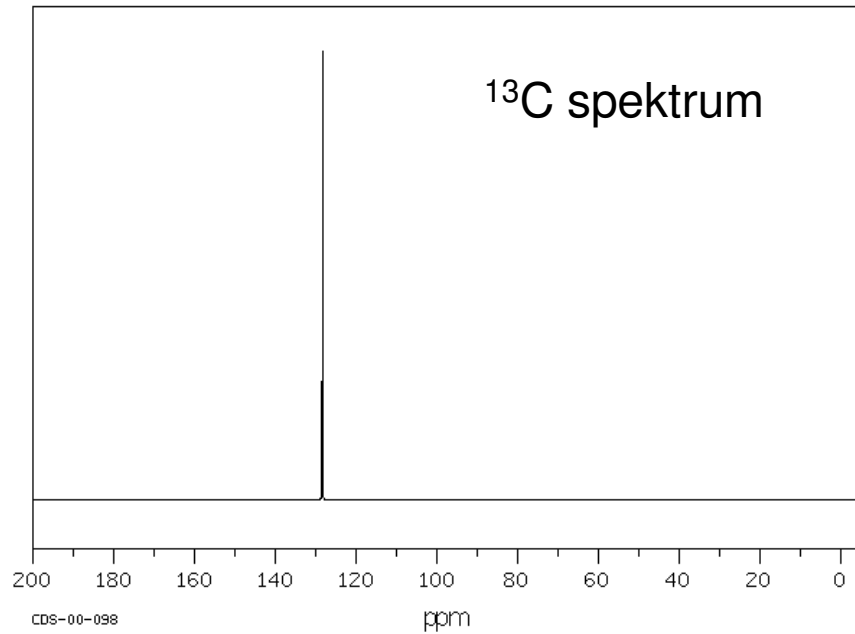
← ppm, frekvence →

→ stínění elektrony ←

high  $\delta$   
low field  
downfield  
paramagnetic shift  
deshielding

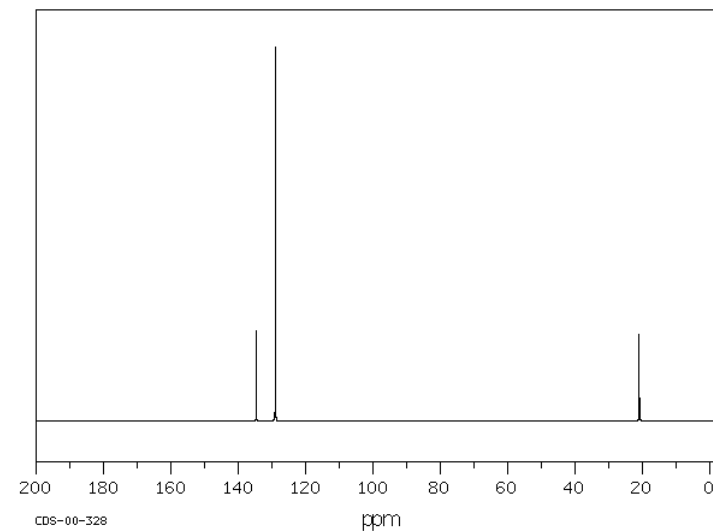
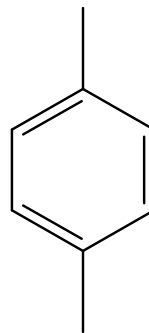
low  $\delta$   
high field  
upfield  
diamagnetic shift  
shielding

# Symetrie a chemický posun

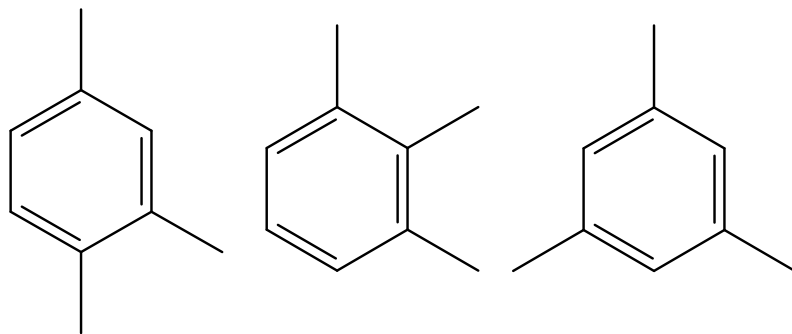


*stejně chemické okolí*  
=  
*stejně stínění elektrony*

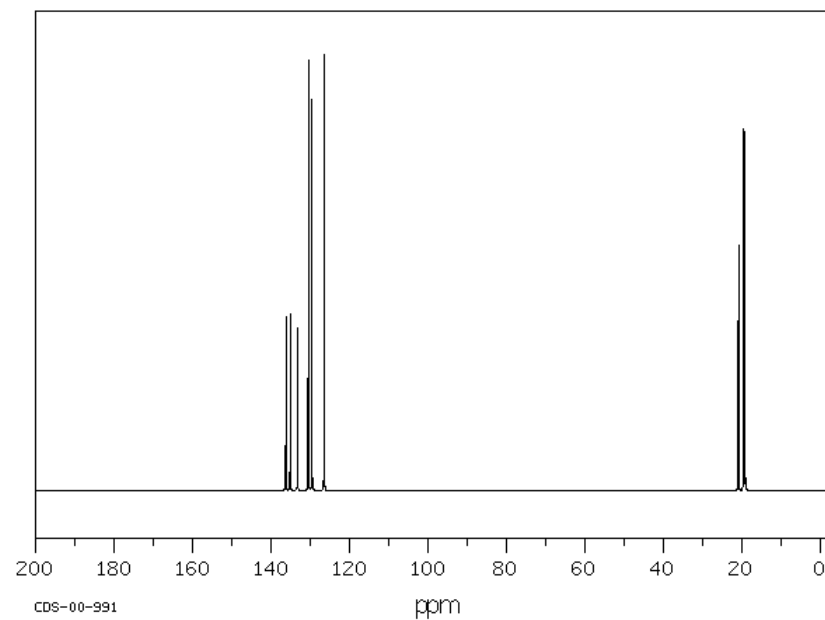
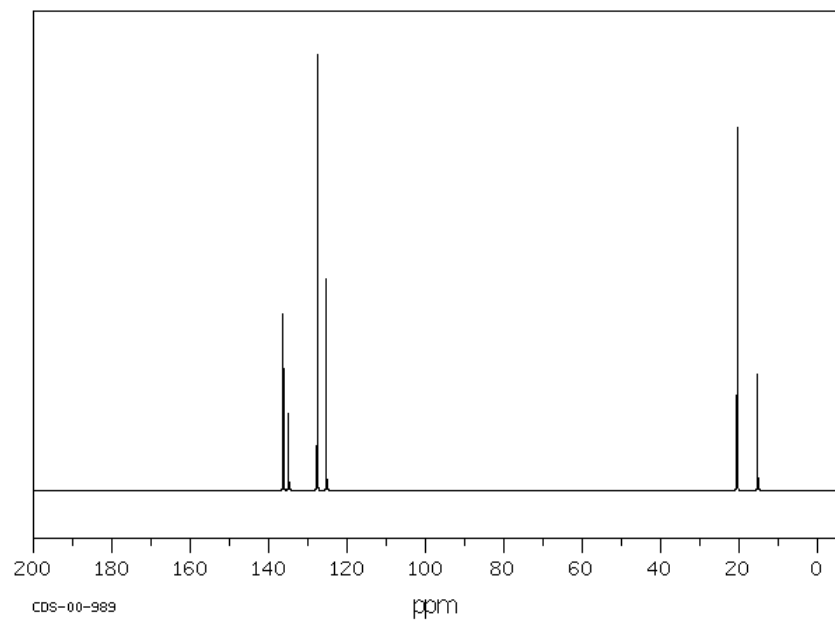
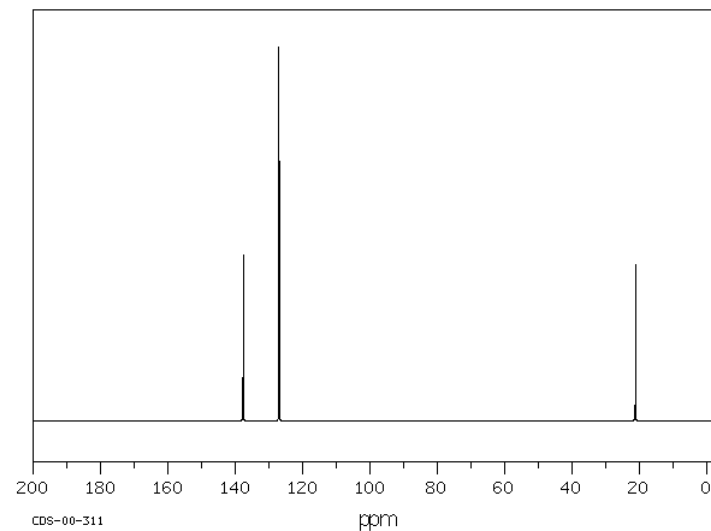
*počet signálů*  
=  
*počet neekvivalentních jader*



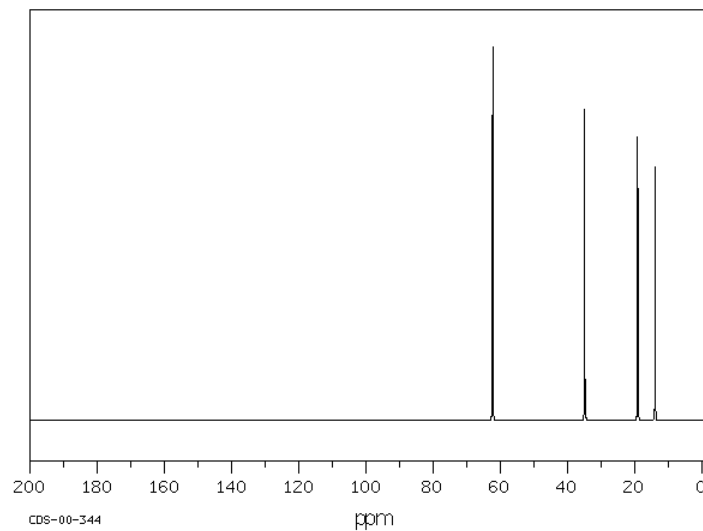
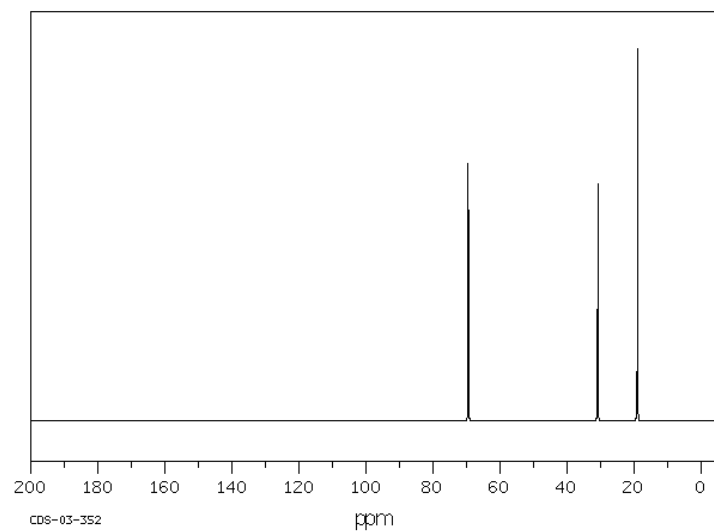
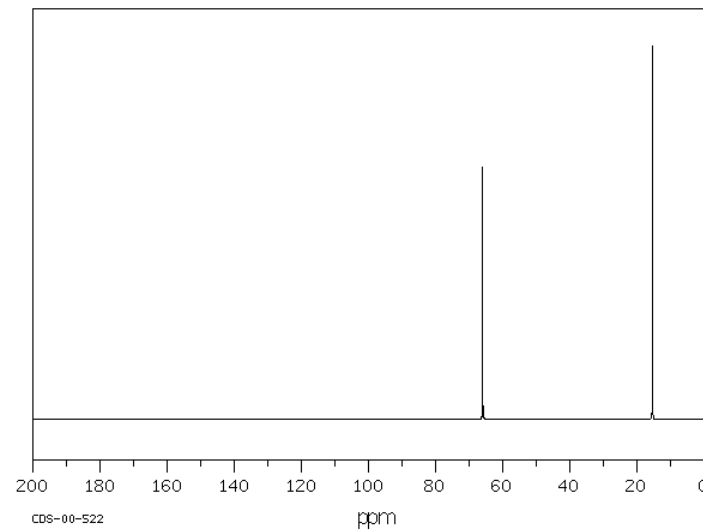
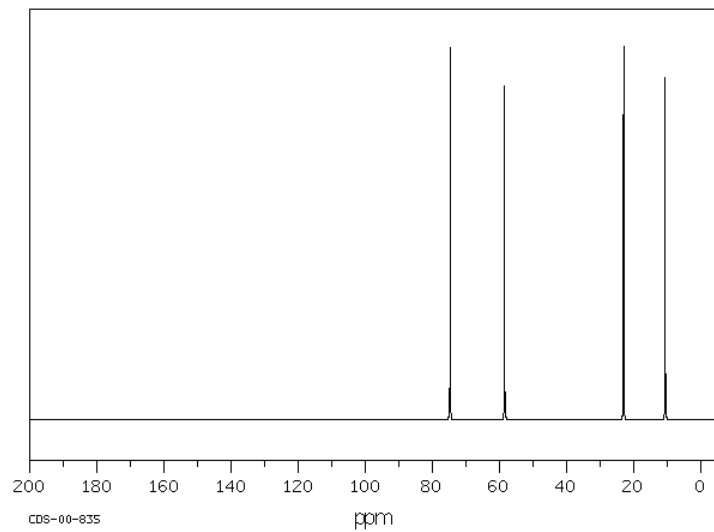
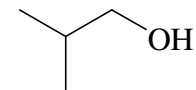
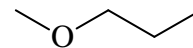
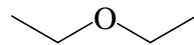
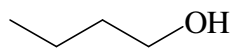
# Cvičení



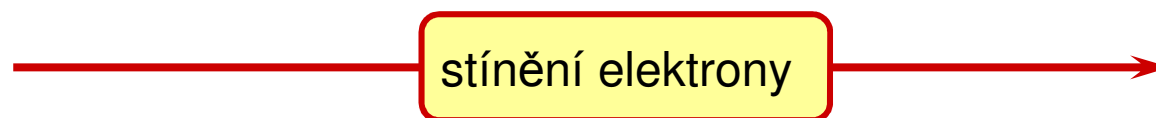
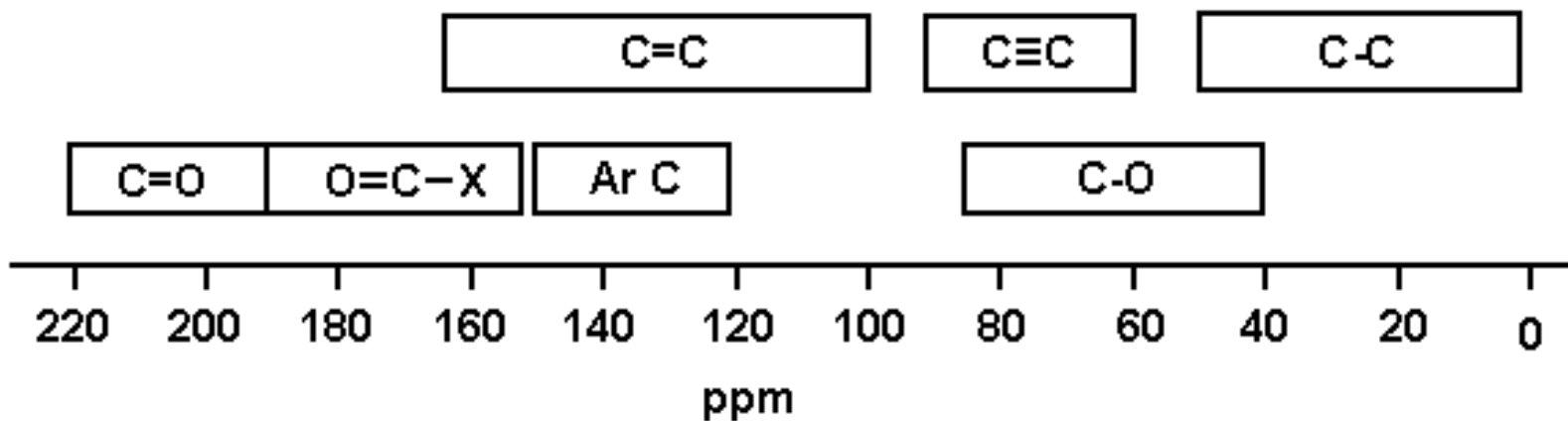
Přiřaďte  $^{13}\text{C}$  spektra těmto molekulám



4 izomery  $C_4H_{10}O$



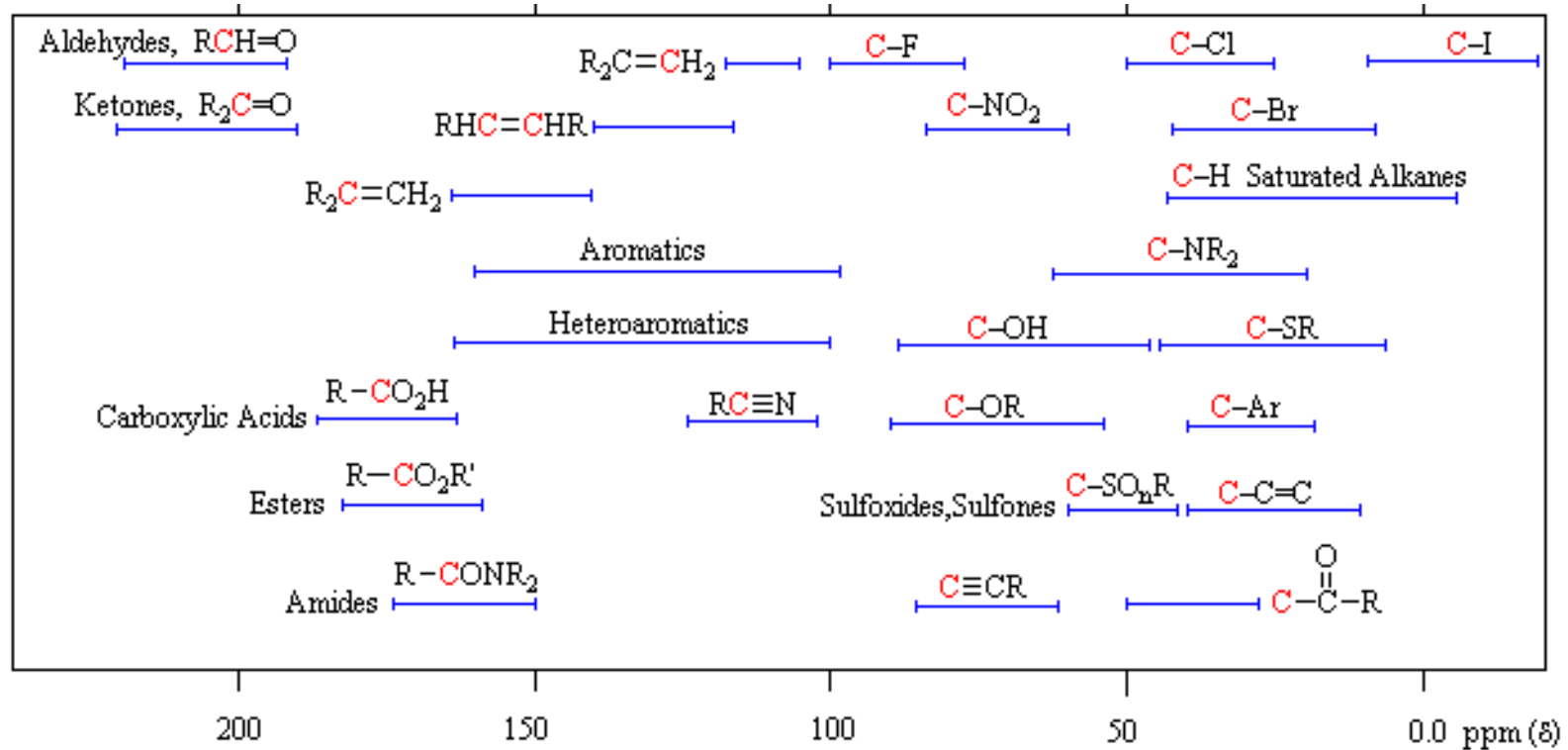
# Chemické posuny $^{13}\text{C}$



Obecný princip: *více elektronů kolem jádra = nižší  $\delta$*



# Chemické posuny $^{13}\text{C}$



- elektronegativita
- hybridizace
- indukční a rezonanční efekt
- vliv substituentů
- efekt těžkého atomu,  $\gamma$  efekt, ...

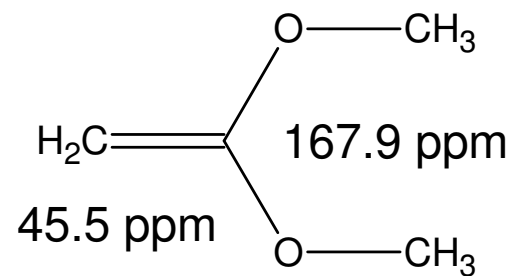
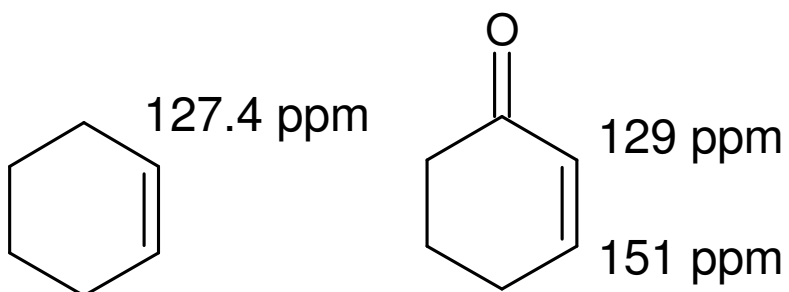
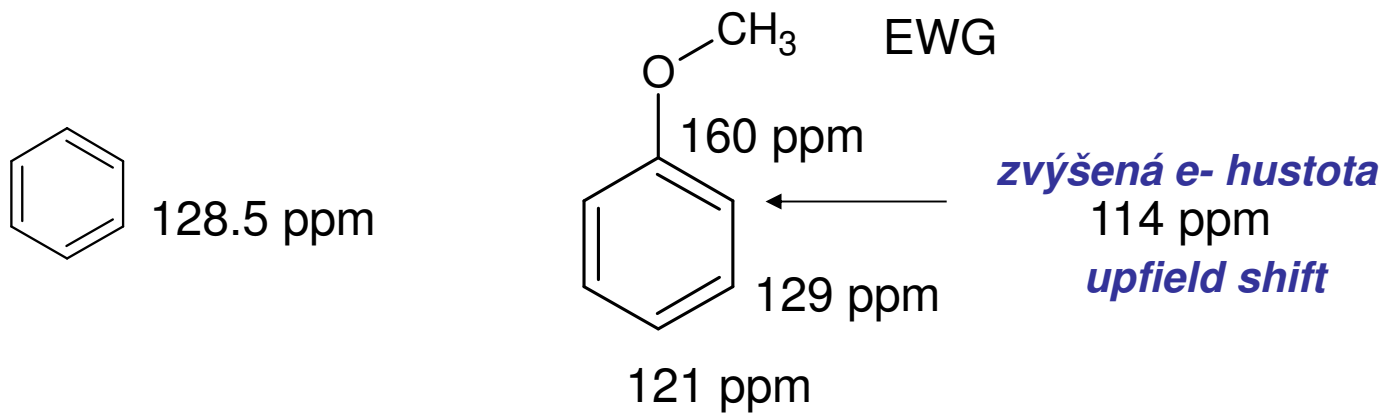
# ***Elektronegativita***

CH<sub>4</sub> -2.4 ppm

	CH <sub>3</sub> X	CH <sub>2</sub> X <sub>2</sub>	CHX <sub>3</sub>	CX <sub>4</sub>
Cl	25 ppm	54 ppm	77 ppm	96 ppm
Br	10 ppm	21 ppm	12 ppm	-29 ppm
I	-21 ppm	-54 ppm	-140 ppm	-292 ppm

***Efekt těžkého atomu***

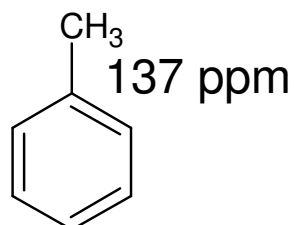
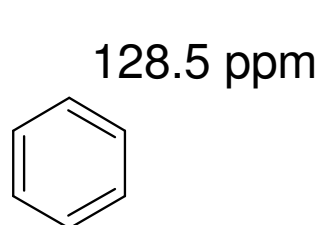
# Indukční a rezonanční efekt



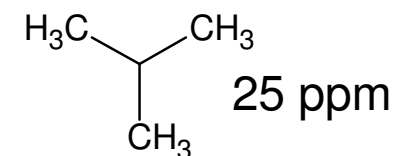
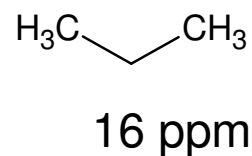
*velký přesun elektronů*

# Vliv substituentů

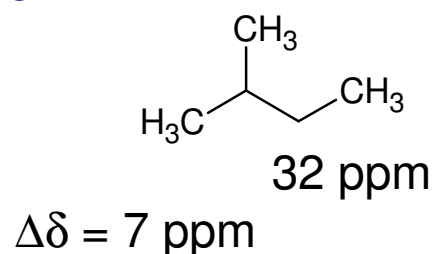
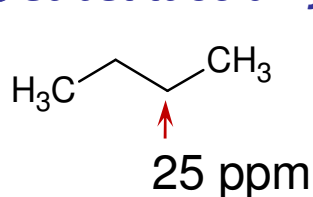
## $\alpha$ substituce alkylem



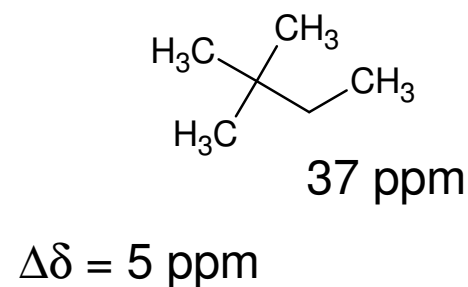
*downfield*  
 $\Delta\delta = 9$  ppm



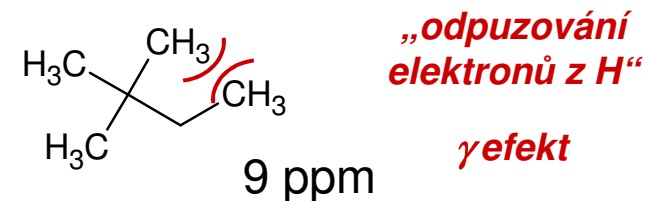
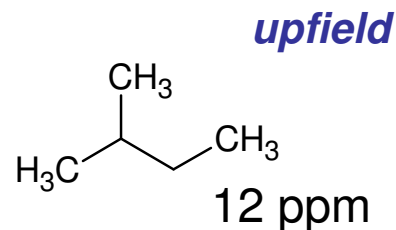
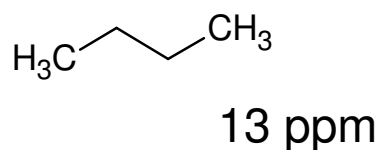
## $\beta$ substituce alkylem



*downfield*

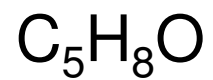


## $\gamma$ substituce alkylem

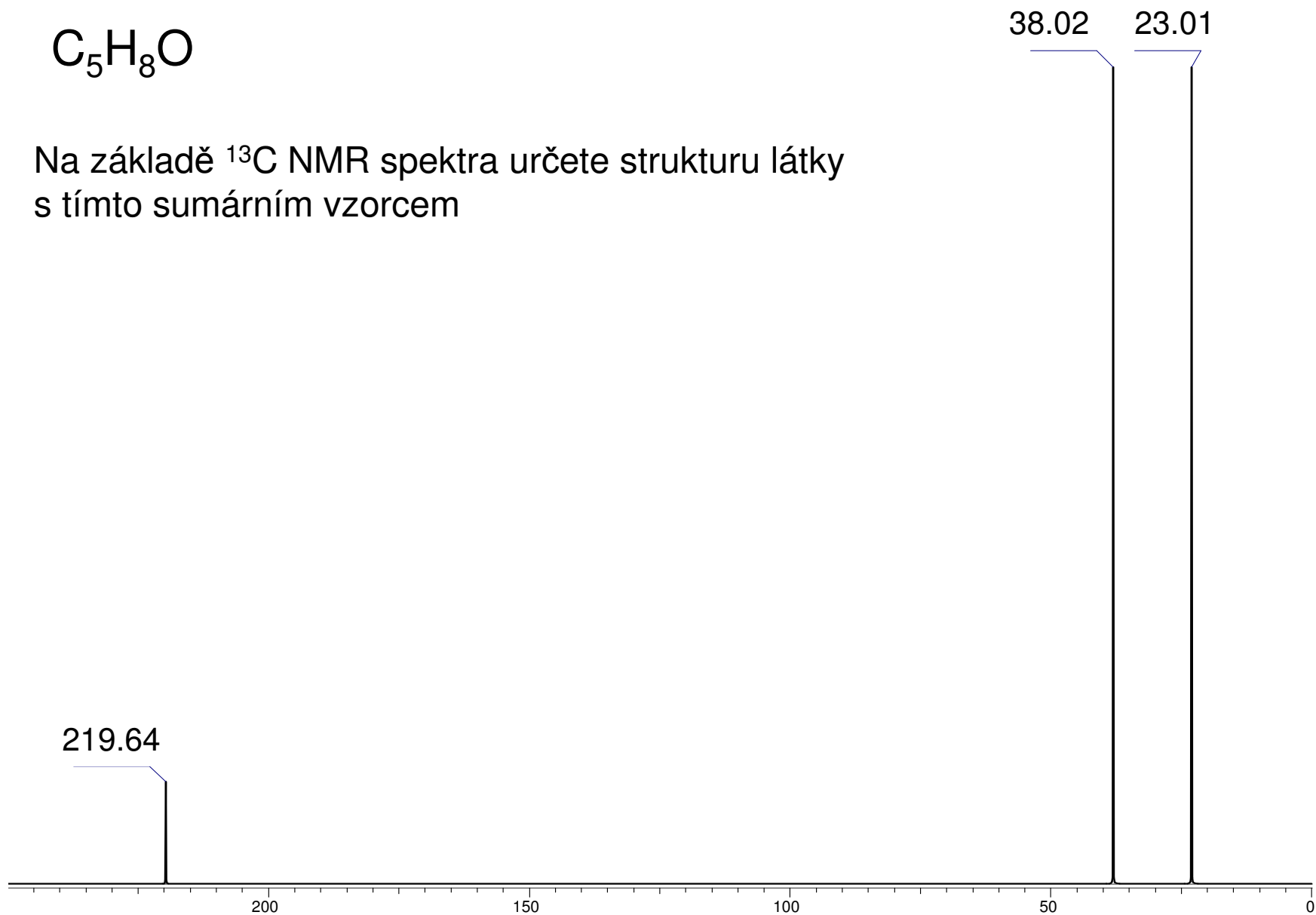


Vliv na chem. posun „rozumně“ aditivní – empirická pravidla predikce

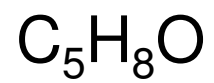
# Cvičení



Na základě  $^{13}\text{C}$  NMR spektra určete strukturu látky s tímto sumárním vzorcem



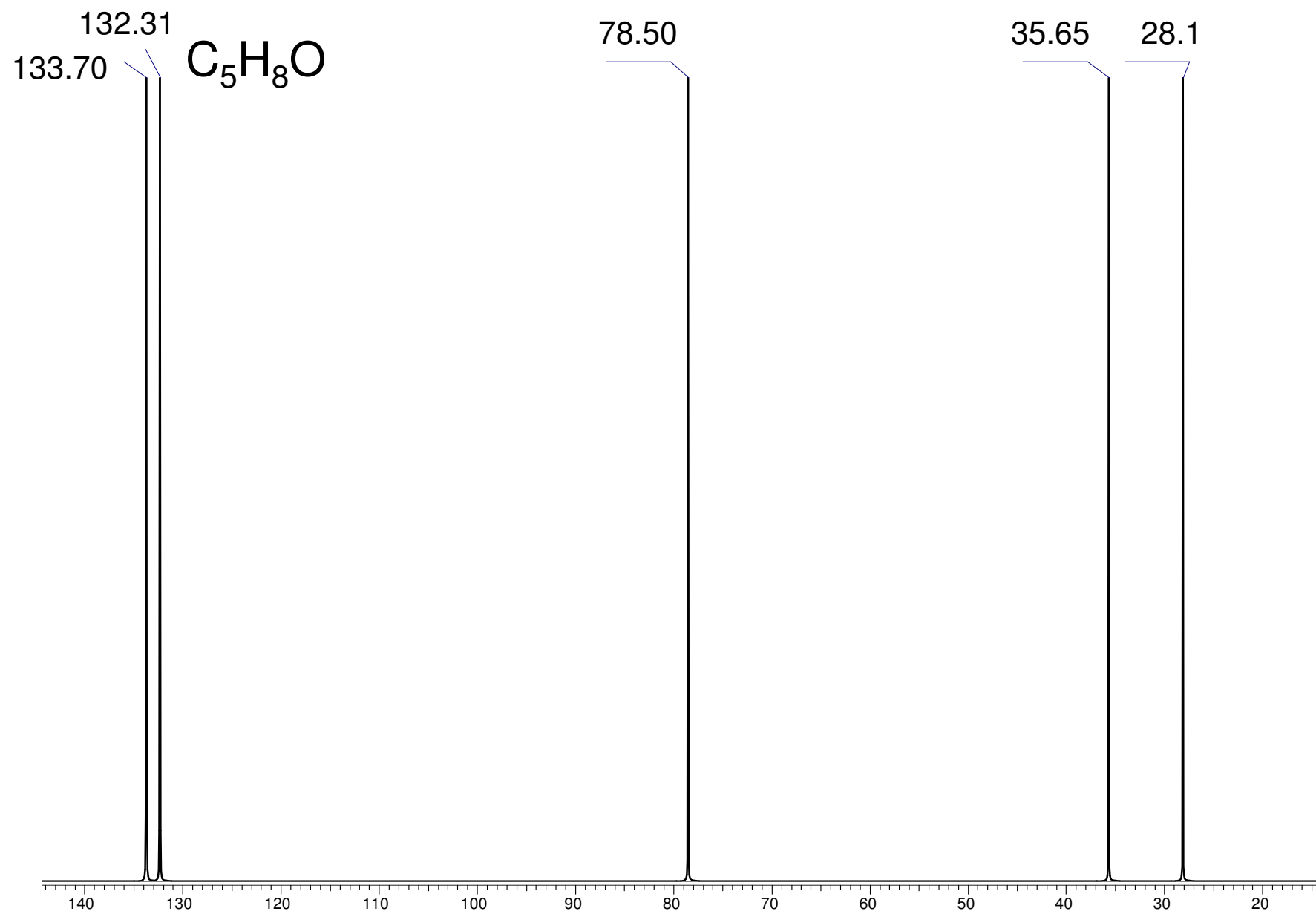
128.38

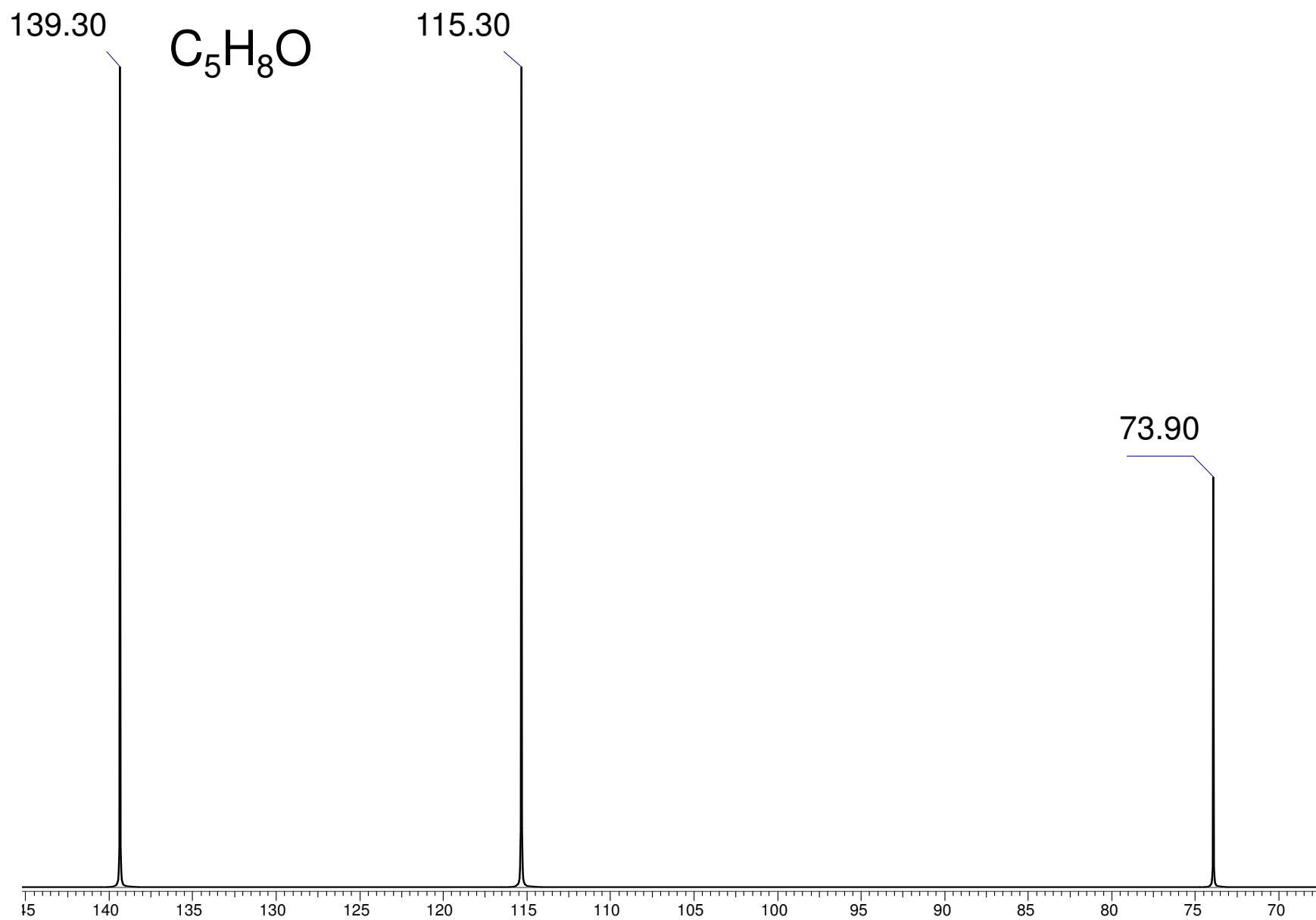


42.50

71.20

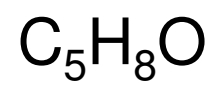








139.07 133.85 130.99 118.53



62.80

