

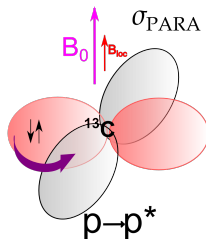
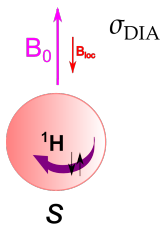
C8953
NMR structural analysis - seminar
1D ^{13}C -NMR

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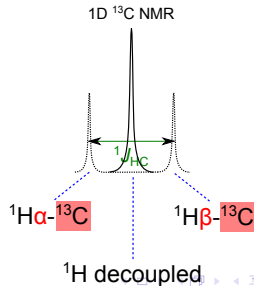
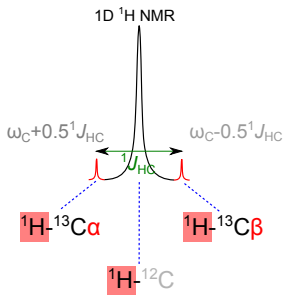
^1H vs ^{13}C NMR

	^1H	^{13}C
Spin number	$^1\text{H}: s=\frac{1}{2} \times ^2\text{H}: s=1$	$^{13}\text{C}: s=\frac{1}{2} \times ^{12}\text{C}: s=0$
Abundance [%]	99.98	1.1
Gyromagnetic ratio [$10^7 \text{ rad}\cdot\text{T}^{-1}\cdot\text{s}^{-1}$]	26.8	6.7
Chemical shift range [ppm]	0 - 15	0 - 200
Nuclear shielding	σ_{dia}	$\sigma_{\text{dia}} + \sigma_{\text{para}}$
Integration of signals	✓	✗
T_1 relaxation [s]	1-20	1-40
Homonuclear J -interaction	✓	✗
$\text{H} \leftrightarrow \text{C}$ J -interaction ($\sim 100\text{-}250 \text{ Hz}$)	carbon satellites	$(n+1)$ splitting \times decoupling

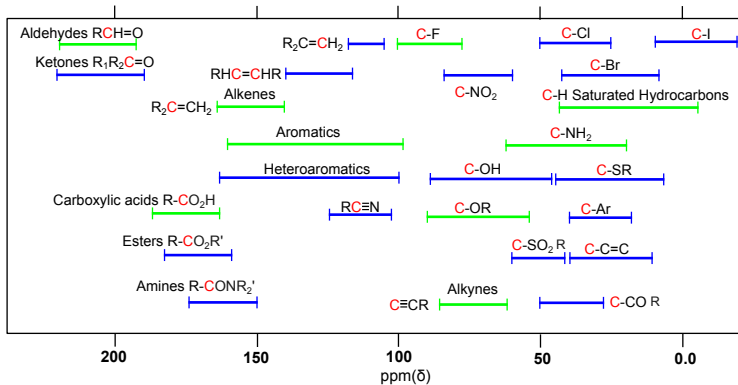


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Important regions of ^{13}C chemical shifts



$^1J_{\text{CH}}$ depends on the bond order (hybridization \Leftrightarrow s-character)

- ▶ $-\text{C}-\text{H} \quad ^1J_{\text{CH}} \approx 125 \text{ Hz}$
- ▶ $=\text{C}-\text{H} \quad ^1J_{\text{CH}} \approx 160 \text{ Hz}$
- ▶ $\equiv\text{C}-\text{H} \quad ^1J_{\text{CH}} \approx 250 \text{ Hz}$
- ▶ X-C-H
 - ▶ X = N, O, S, F, Cl, ... $^1J_{\text{CH}} \uparrow$
 - ▶ X = Li, Mg, ... $^1J_{\text{CH}} \downarrow$

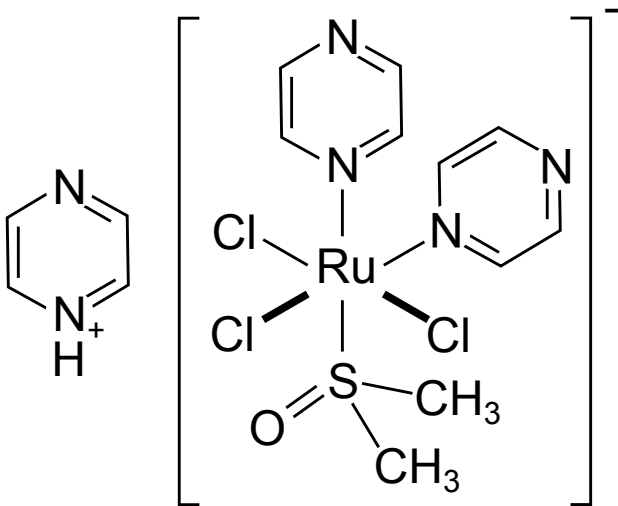
$^2J_{\text{CH}} < 0$ or close to zero ($< 3 \text{ Hz}$)

- ▶ often not observable

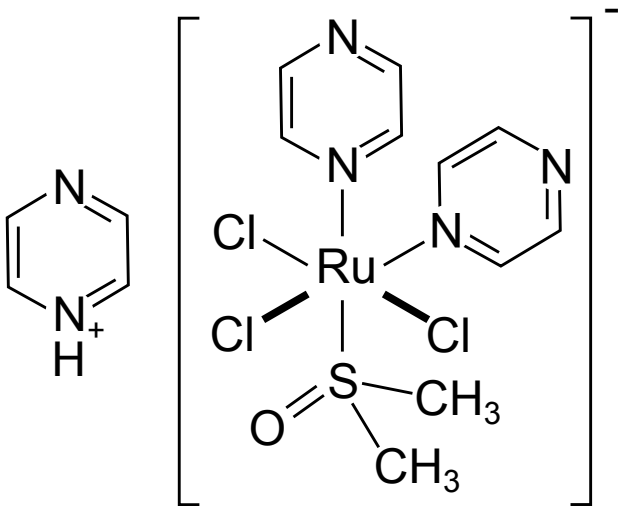
in 1D ^{13}C H-C interaction suppressed by DECOUPLING
 \Rightarrow simplification of spectra (splitting removed, sensitivity)

- ▶ saturation of ^1H energy levels during decoupling enhances relatively intensity of ^{13}C signals because of heteronuclear nOe \Rightarrow quaternary carbons usually less intensive.

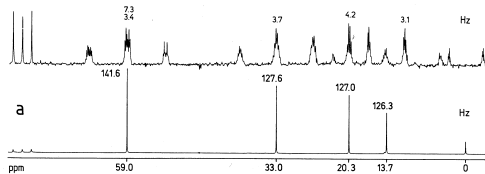
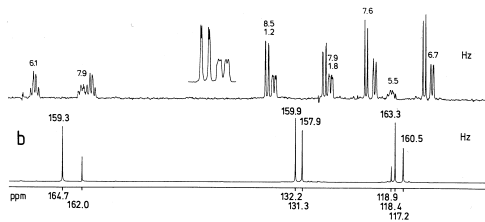
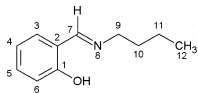
How many ^{13}C signal would you expect in the NMR spectrum?



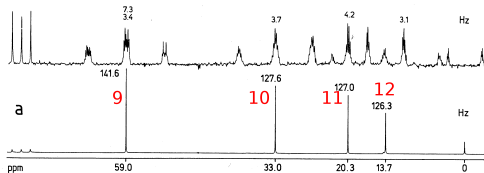
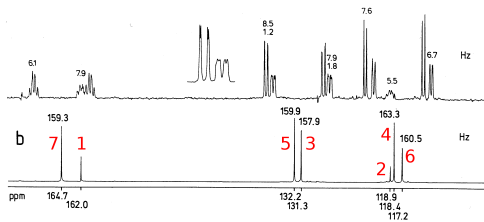
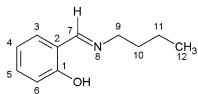
How many ^{13}C signal would you expect in the NMR spectrum? **6**



1D ^{13}C -NMR 1, bottom without CPD



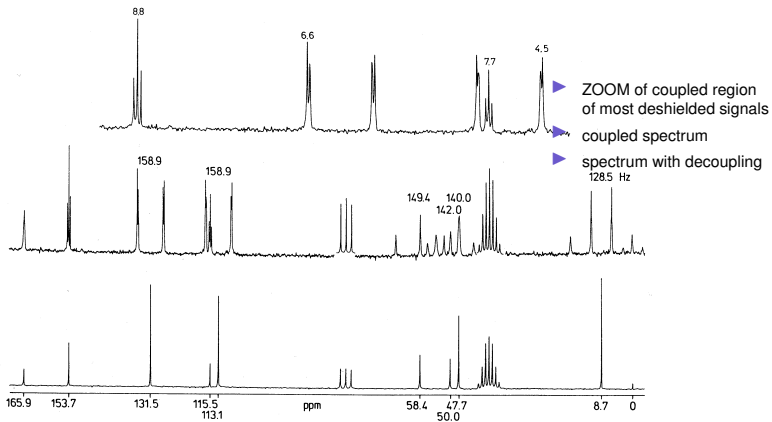
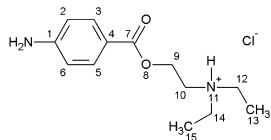
1D ^{13}C -NMR 1, bottom without CPD



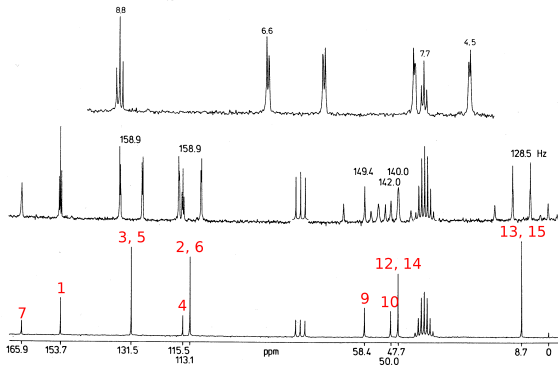
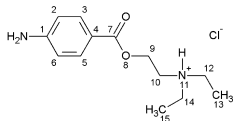
Notes:

- ▶ numbers at top of peaks refers to values J_{HC} constants
- ▶ **C1+C7** connected to electronegative groups (C1 quaternary)
- ▶ **C2** ipso aromatic, **C4+C6** shielded by M+ of OH
- ▶ **C5+C4** NOE-enhanced in bit larger extend by close H
- ▶ **C9** → **C12**: decaying effect of N8

1D ^{13}C -NMR 2



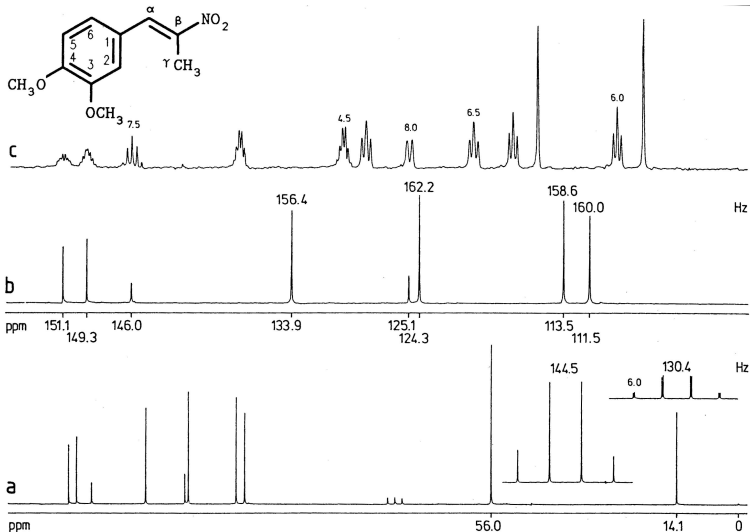
1D ^{13}C -NMR 2



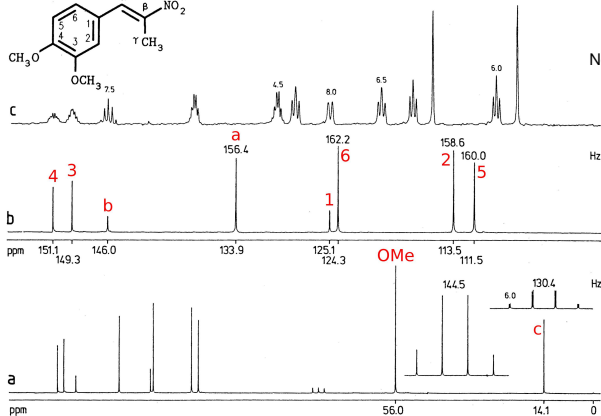
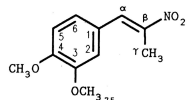
Notes:

- ▶ **C7** carbonyl, **C1** attached to N
- ▶ **C3/5** deshielded by M-CO, **C2/6** shielded by M+ of NH_2
- ▶ **C4** last quaternary aromatic signal (most isolated from H nuclei)
- ▶ **C9** effect of esteric group, ? **C10** affected by NH exchange
- ▶ **C12/C14 + C13/C15** decaying effect of N^+

1D ^{13}C -NMR 3, *b* - zoom of right region, *a* - full decoupled spectrum



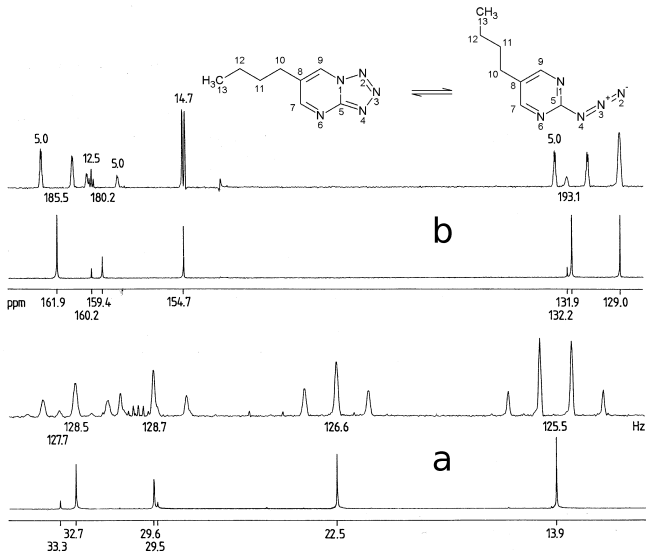
1D ¹³C-NMR 3, *b* - zoom of right region, *a* - full decoupled spectrum



Notes:

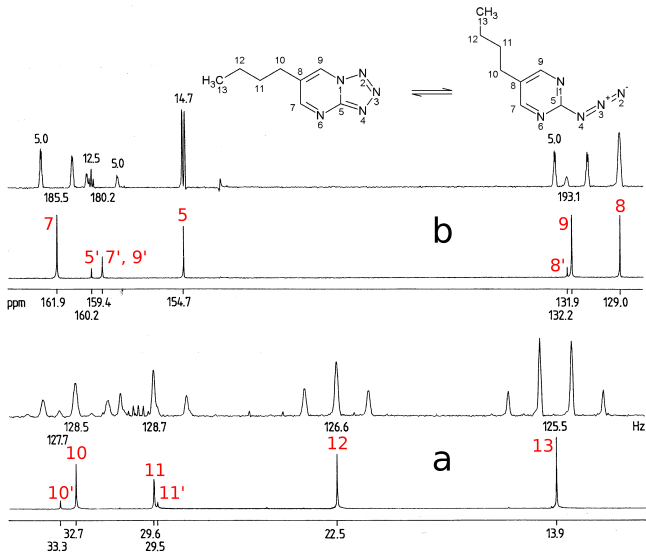
- ▶ **C3/C4** quaternary aromatic deshielded by O, **C β** quaternary coupled by CH₃ and C α H
- ▶ **C α** deshielded by NO₂
- ▶ **C1** last quaternary aromatic signal
- ▶ **C2/C6** coupled mutually and with C α , **C5** isolated (contrainuitive)
- ▶ quartets **OMe**, **C γ**

1D ^{13}C -NMR 4, consider equilibrium minor-major form



Which form dominates and why?

1D ^{13}C -NMR 4, consider equilibrium minor-major form



Which form dominates and why?

Next topic

Vector Model + ^{13}C APT experiment