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

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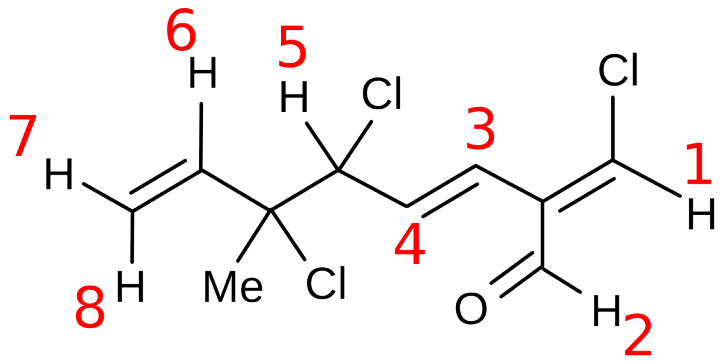
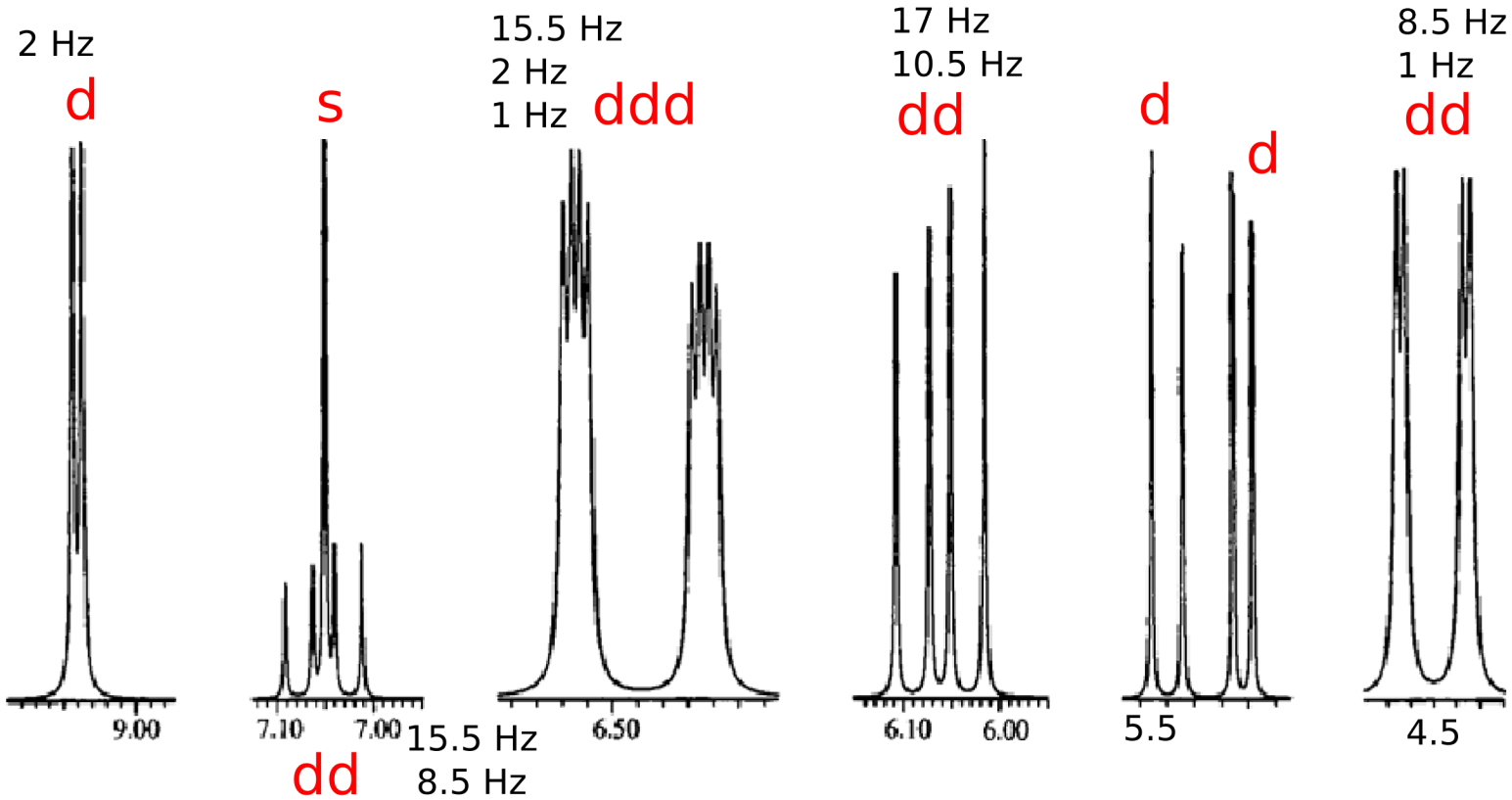
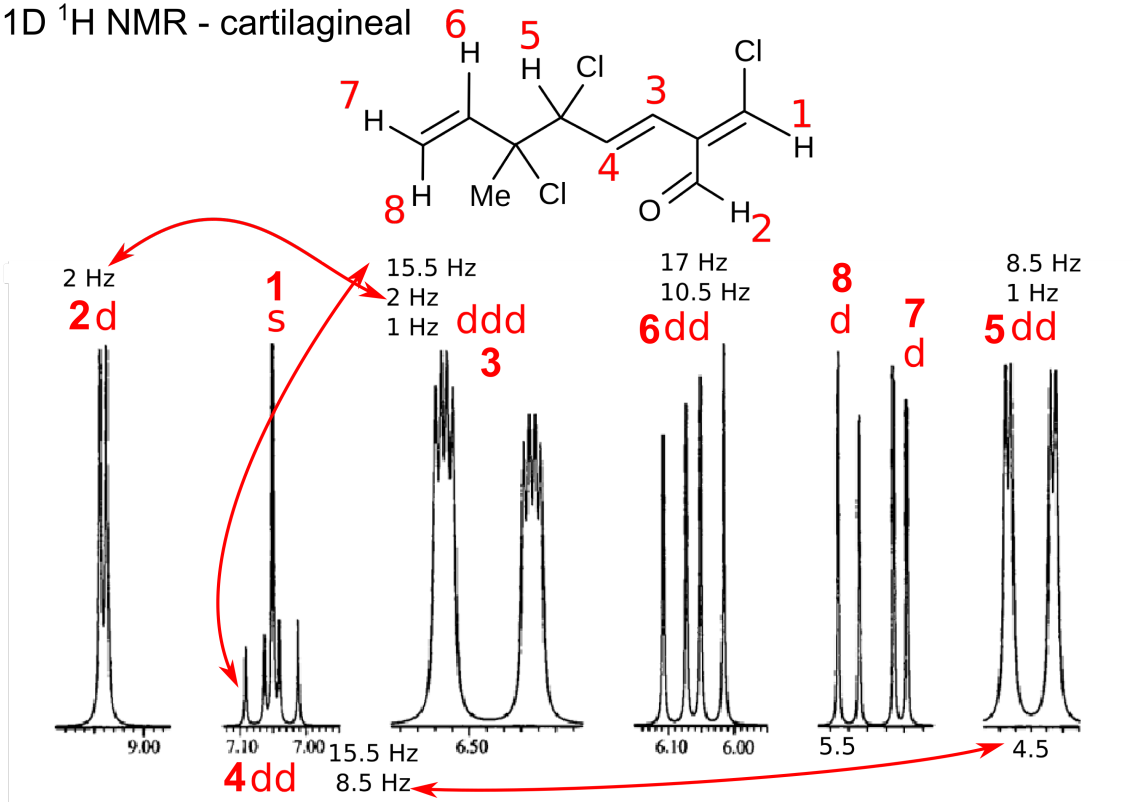
Control of 1D ^{1}H NMR spectrum of cartilagineal





Control of 1D ^{1}H NMR spectrum - cartilagineal

1D ^{1}H NMR - cartilagineal

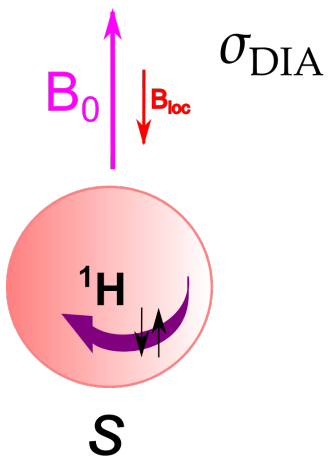


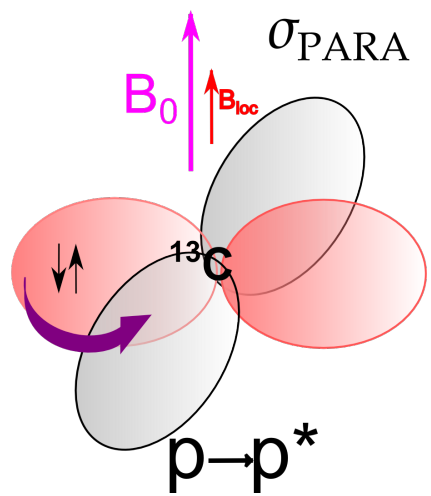
Notes:

- highest shift - **H-2** - proton of aldehydic group, splitted to doublet with J = 2 Hz (small value, interacting partner is relatively far away)
- the same J = 2 Hz belongs to doublet of doublets of doublets around 6.5 ppm, other Js: J = 1 Hz and J = 15.5 Hz - three J-constants - three partners - **H-3**
- large J-value 15.5 Hz suggests near neighbor - other signal with the same constant is doublet of doublets around 7 ppm - **H-4**
- last constant of multiplet at 6.5 ppm - J = 1 Hz - partner distant from H-3: either H-1 or H-5, the same J- constant belongs to doublet of doublets at 4,5 ppm - two constants, two partners which is not the case for H-1 - therefore signal at 4,5 ppm belongs to **H-5**
- just for check: both multiplets H-4 and H-5 are coupled with H-3 and with each other as well (J = 8.5 Hz)
- the only singlet in the spectrum is isolated **H-1**
- last unasigned doublet of doublets (6,1 ppm) must be **H-6** because it is the only proton from the trio H-6, H-7, H-8 with two unequivalent neighbors - larger coupling comes from interaction with **H-8** in *trans* position, smaller coupling comes from interaction with *cis* oriented **H-7**
- signal of the methyl group is not present in this spectrum

^{1}H vs ^{13}C NMR

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





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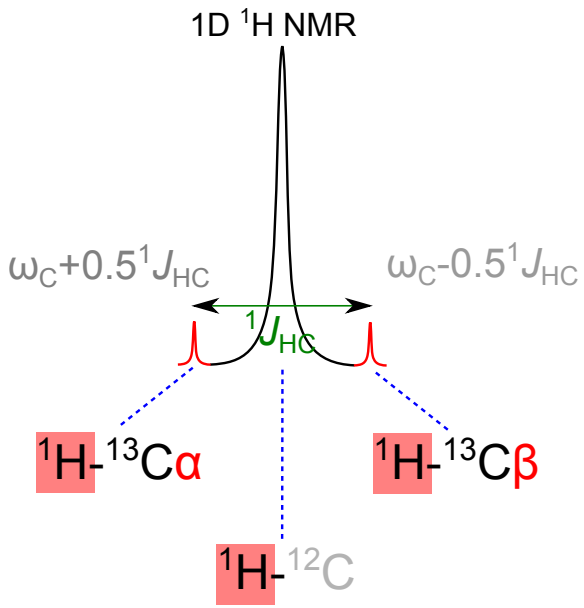
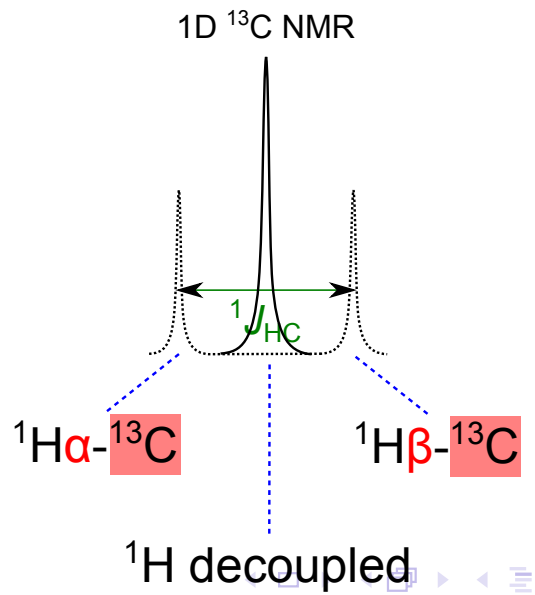
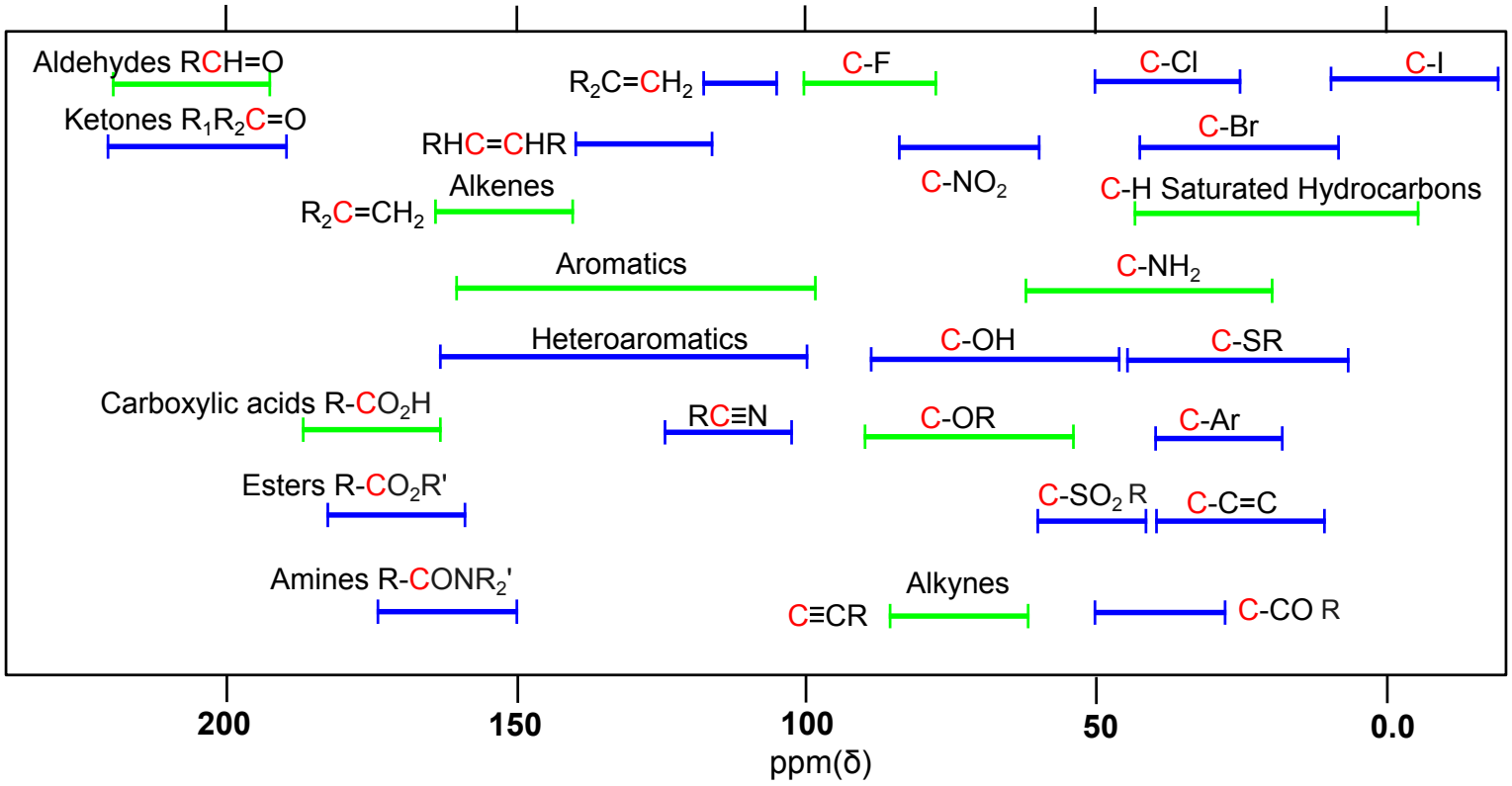




Important regions of ^{13}C chemical shifts



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

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

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

- often not observable

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

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

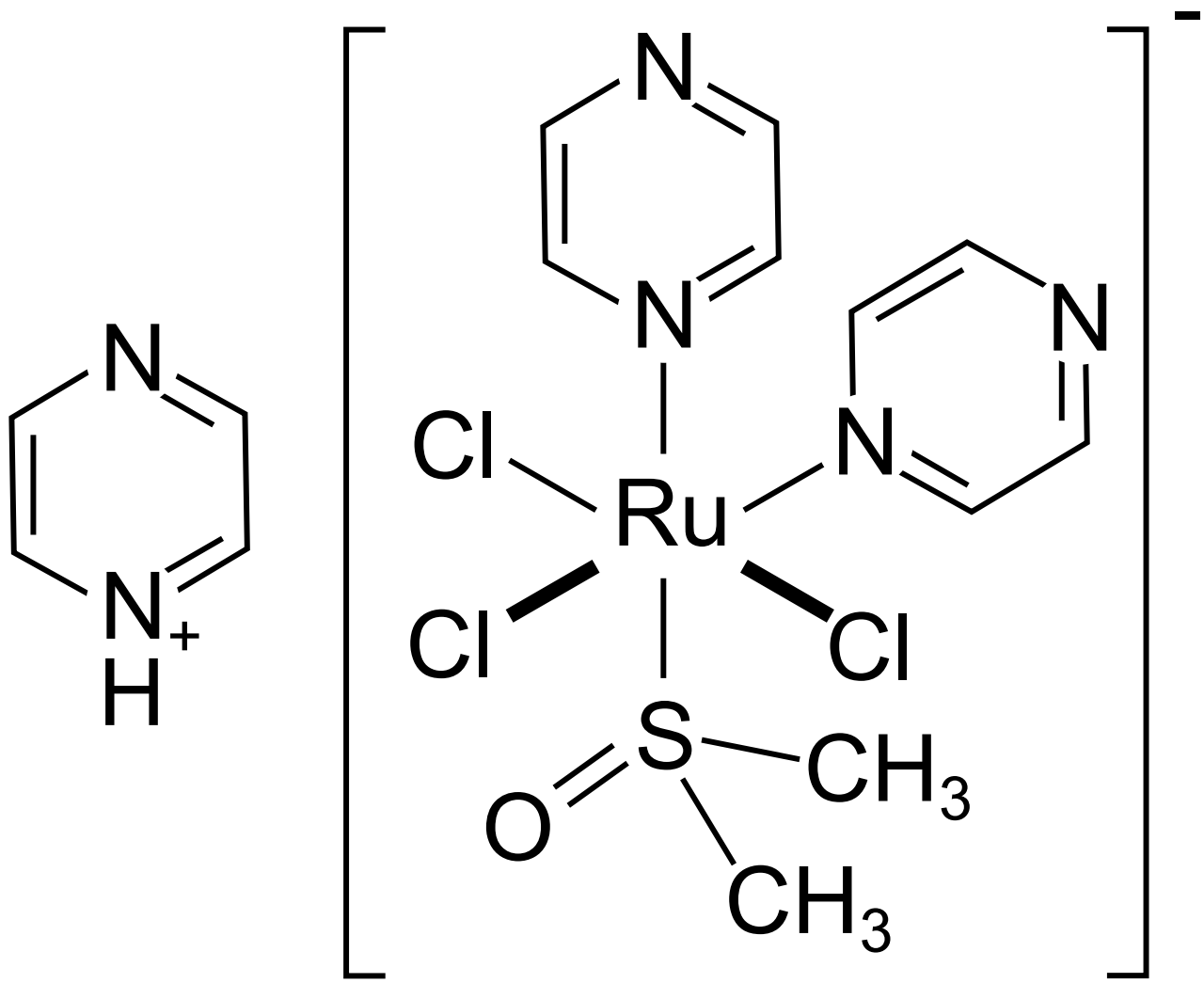
Values of chemical shift of important solvents

Abbr.	Formula	^{1}H	^{13}C
ACN	CH_3CN	1.9	118
Benzene	C_6H_6	7.2	128
	$CHCl_3$	7.2	77
DCM	CH_2Cl_2	5.3	54
DMF	$(CH_3)_2NCHO$	2.9, 8.0	32, 163
DMSO	$(CH_3)_2SO$	2.5	40
MeOH	CH_3OH	3.3, 4.8	49
Water	H_2O	**4.8**	-

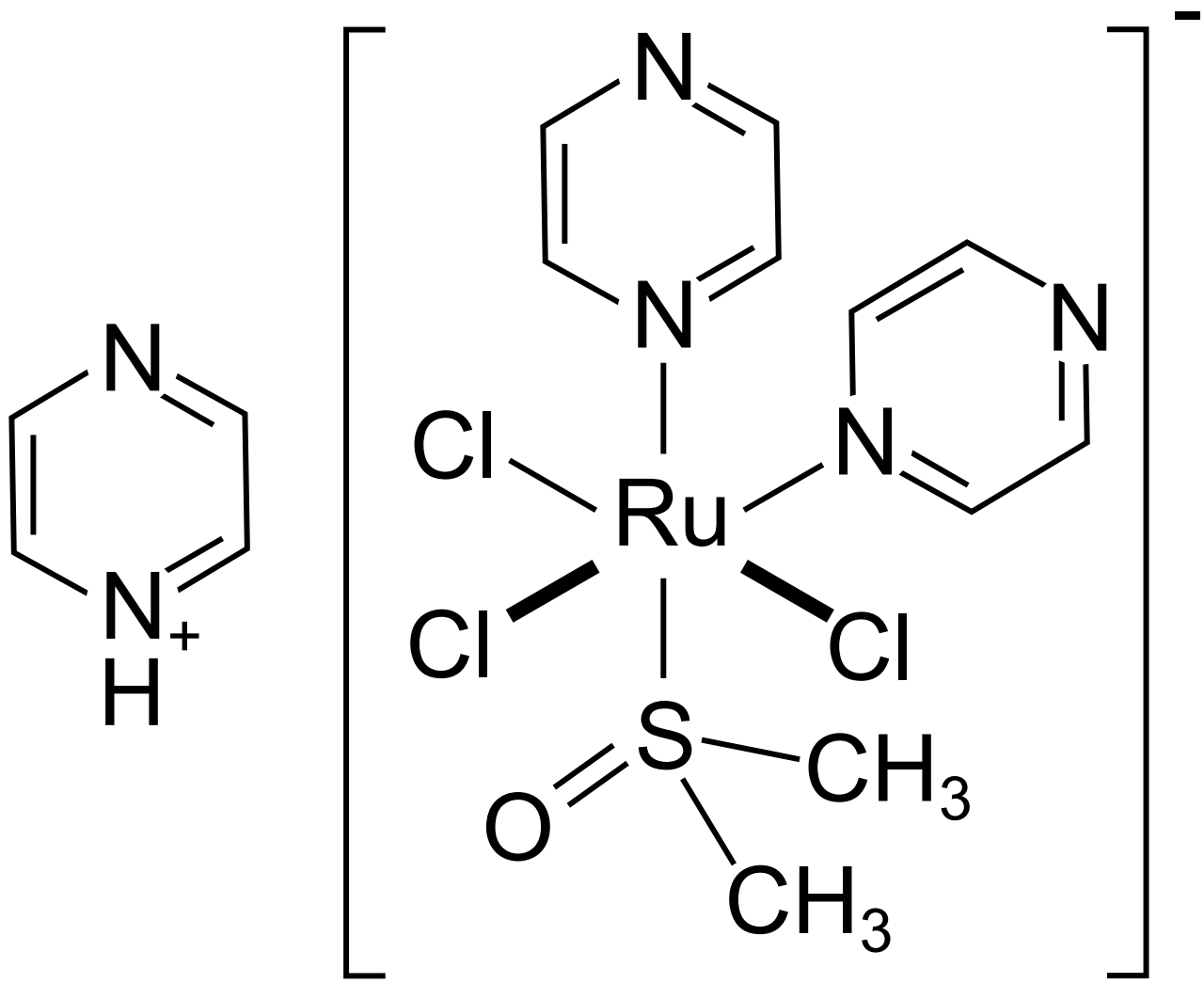
EXPLAIN effect of solvent on the position of residual ^{1}H water signal:

$CHCl_3$ - **1.6**, ACN - **2.1**, DMSO - **3.3**, MeOH - **4.9**

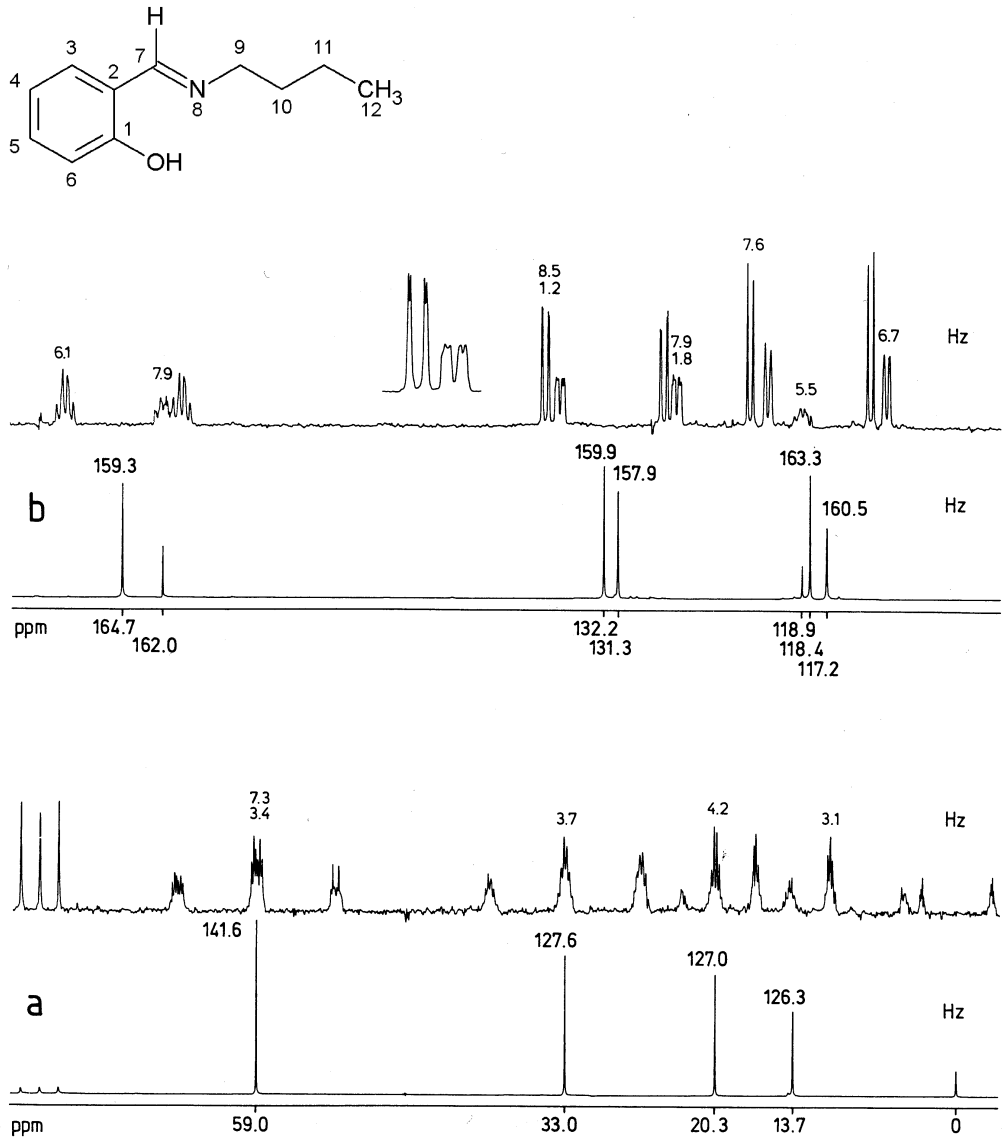
How many ^{13}C signal would you expect in the NMR spectrum?



How many ^{13}C signal would you expect in the NMR spectrum? **7**



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



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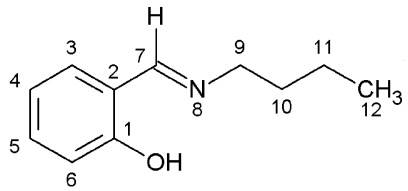
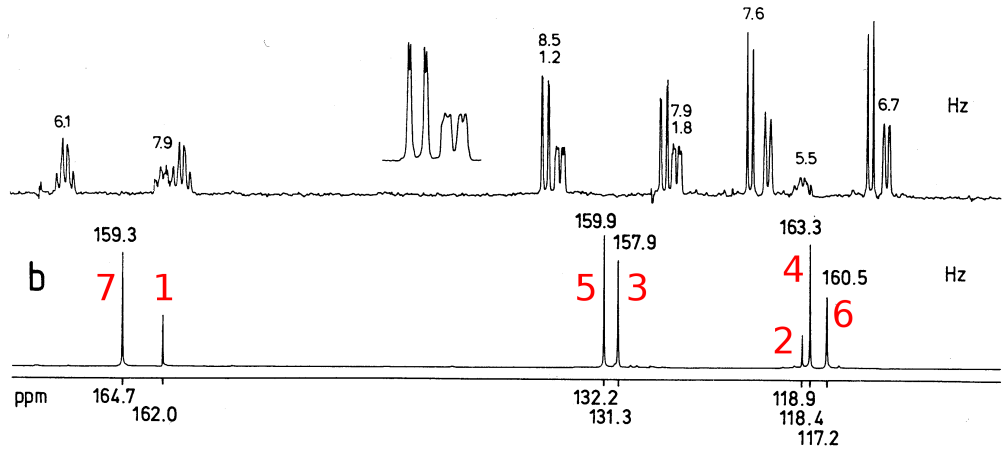
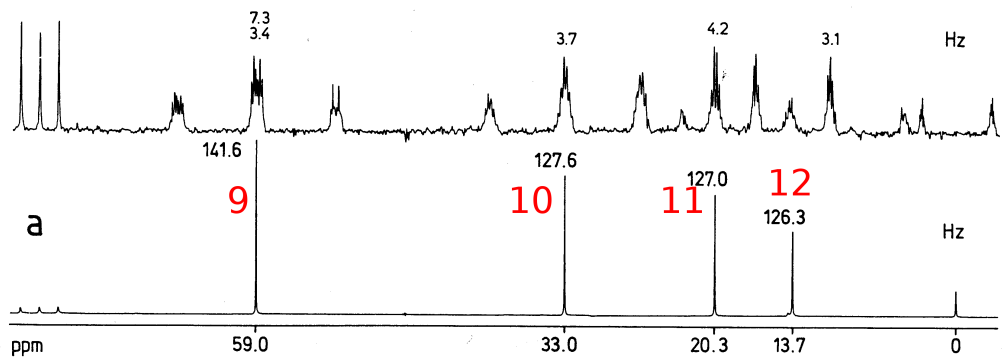


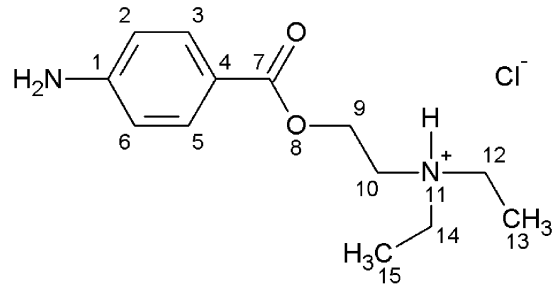


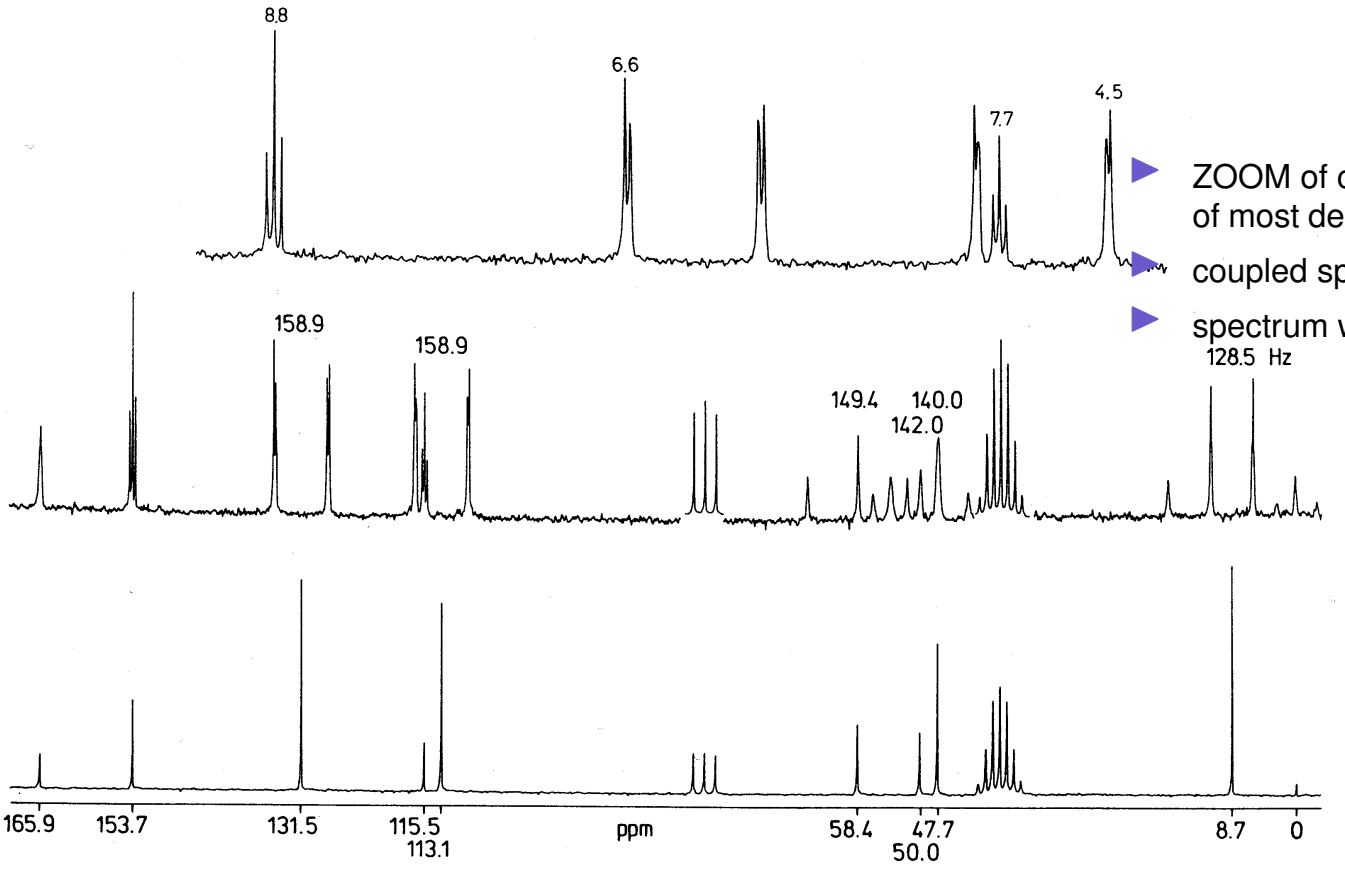


Notes:

- 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**$\rightarrow$**C12**: decaying effect of N8

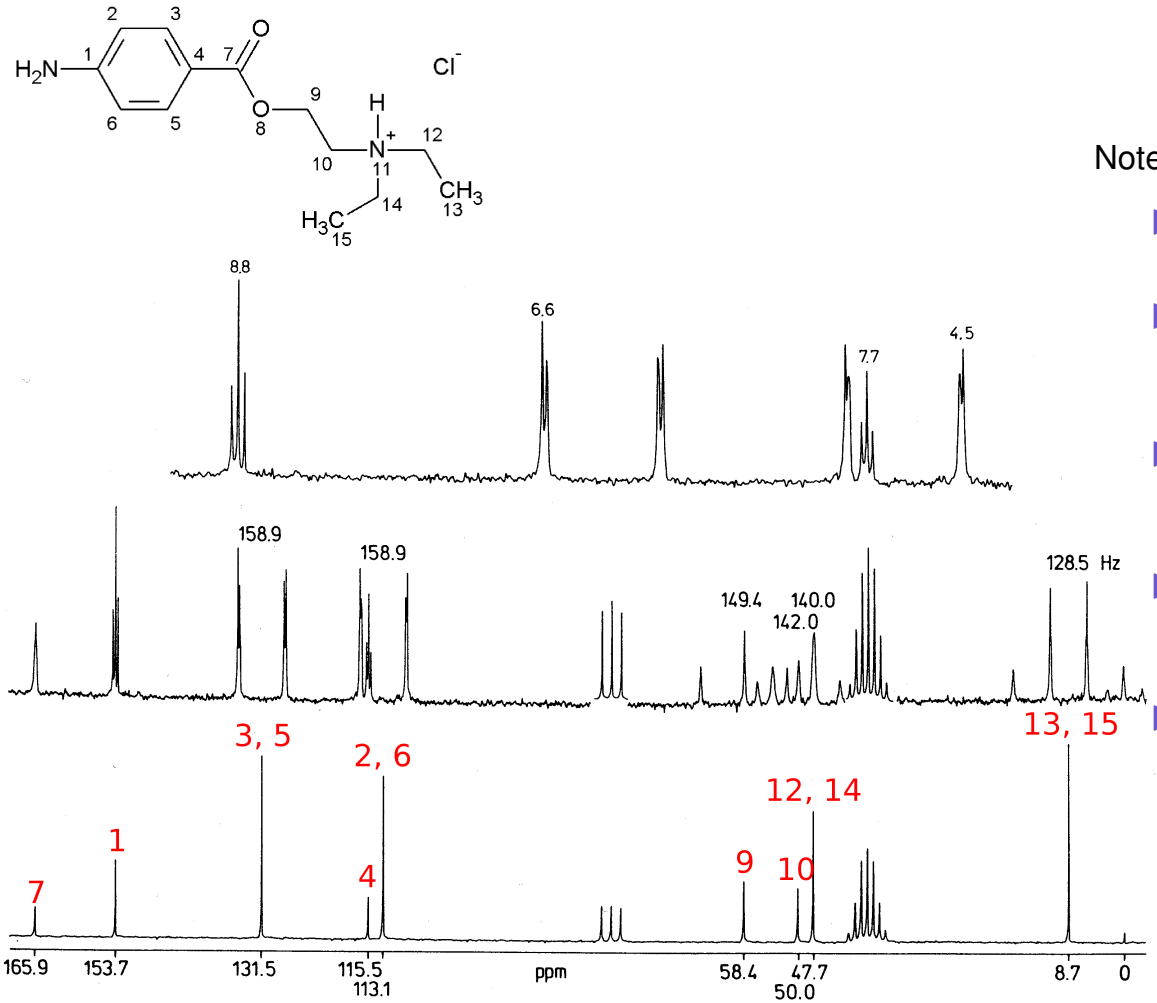
1D ^{13}C-NMR 2





- ZOOM of coupled region of most deshielded signals
- coupled spectrum
- spectrum with decoupling

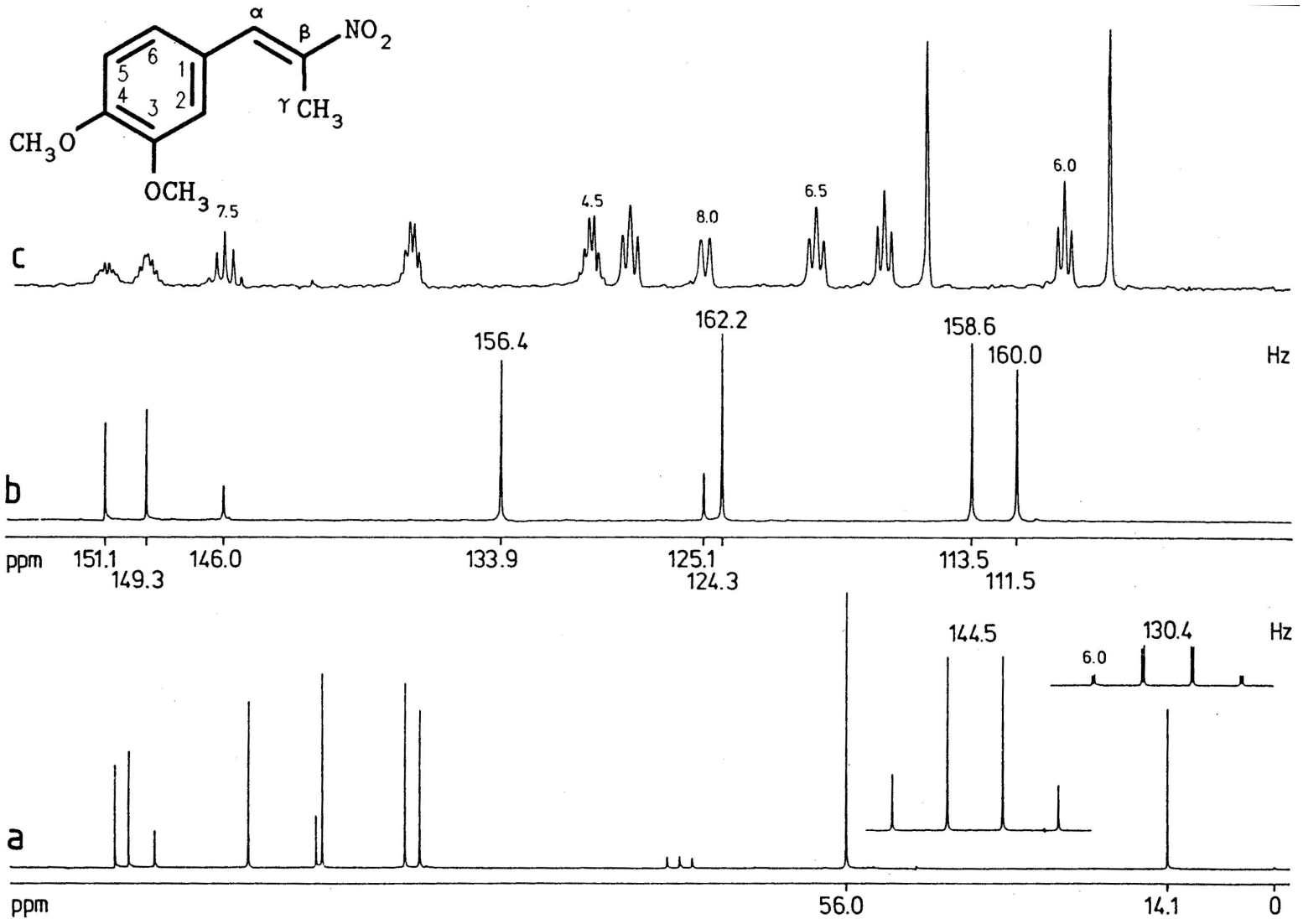
1D ^{13}C-NMR 2



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



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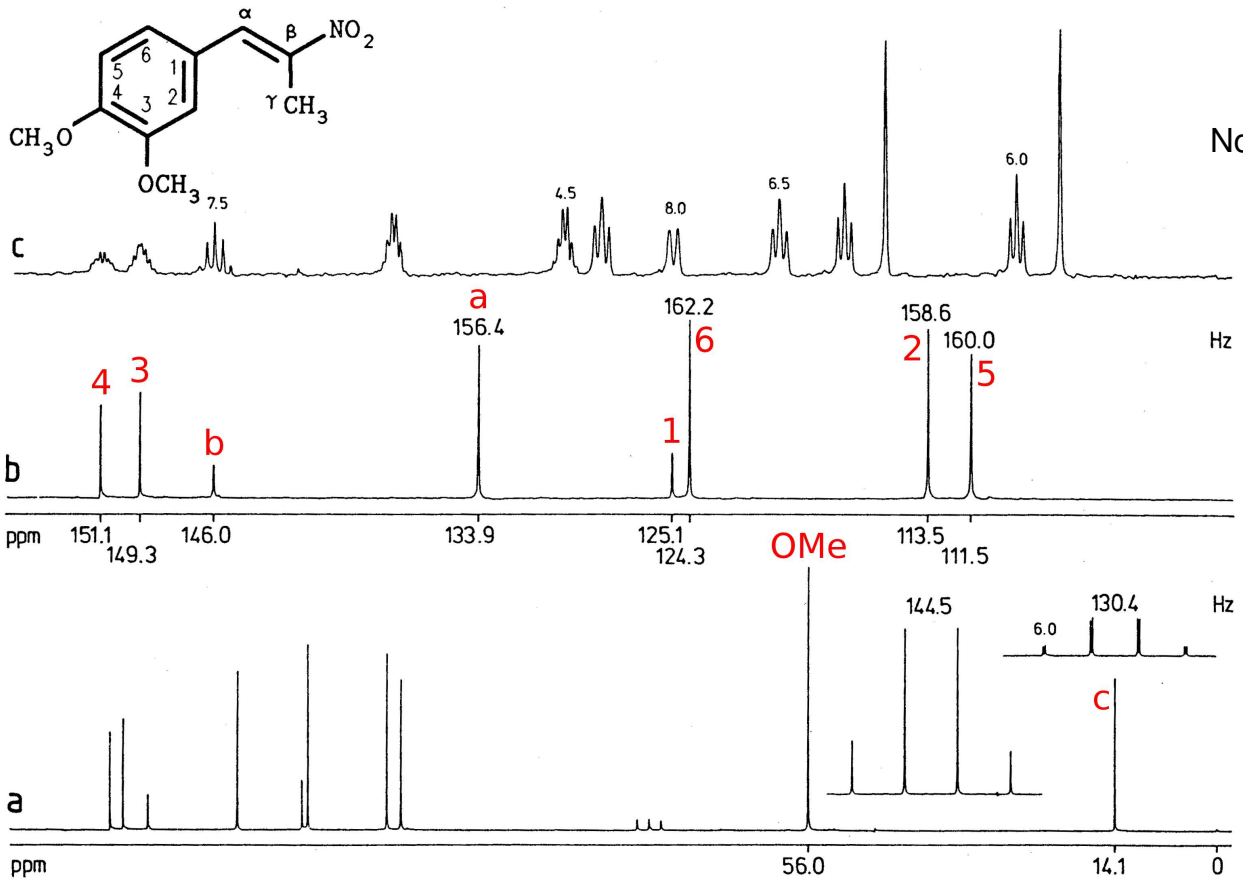
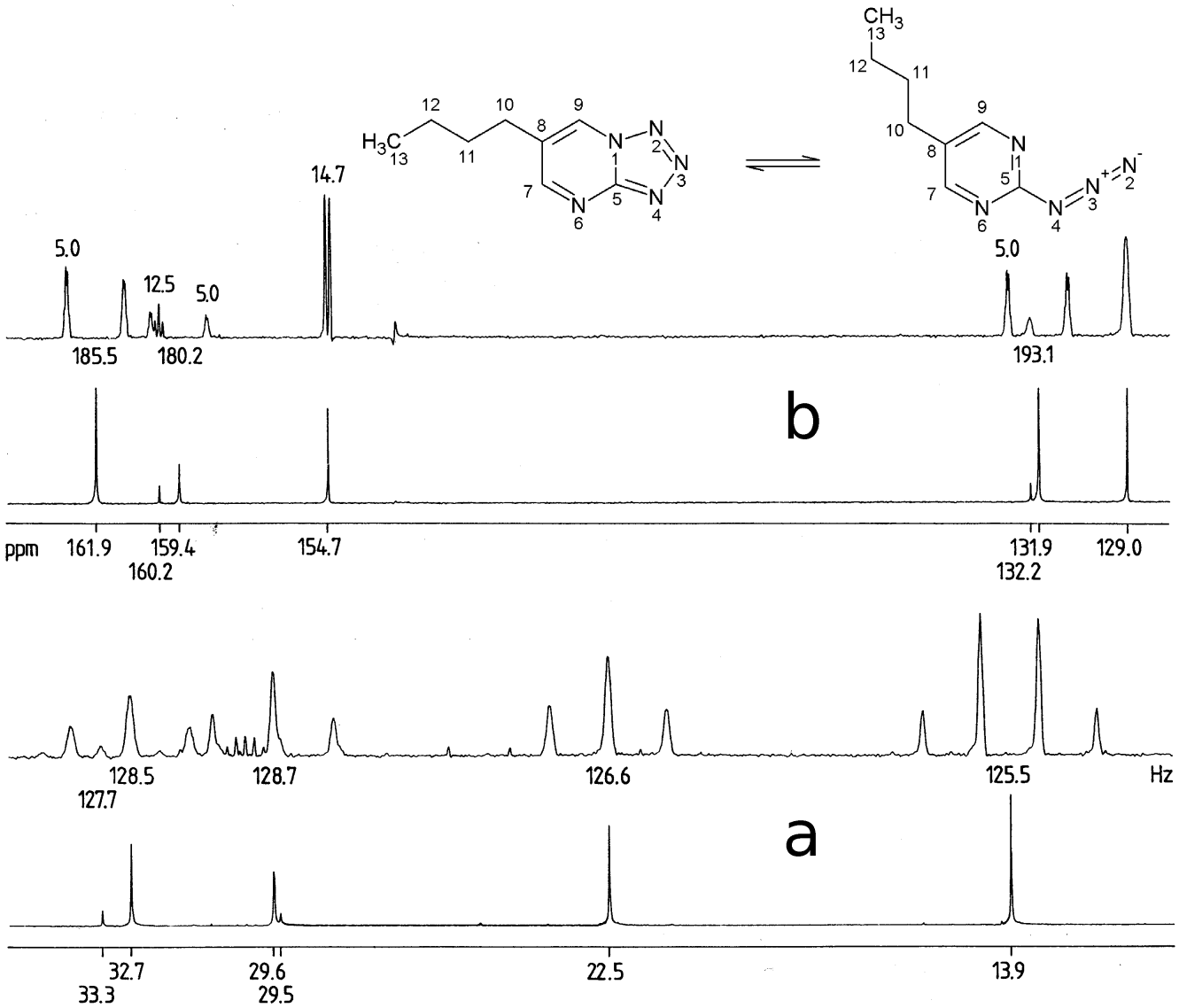


Notes:

- **C3**/**C4** quaternary aromatic deshielded by O, **C**β quaternary coupled by CH_3 and CαH
- **C**α deshielded by NO_2
- **C1** last quaternary aromatic signal
- **C2**/**C6** coupled mutually and with Cα, **C5** isolated (contraintuitive)
- quartets **OMe**, **C**γ

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



Which form dominates and why?

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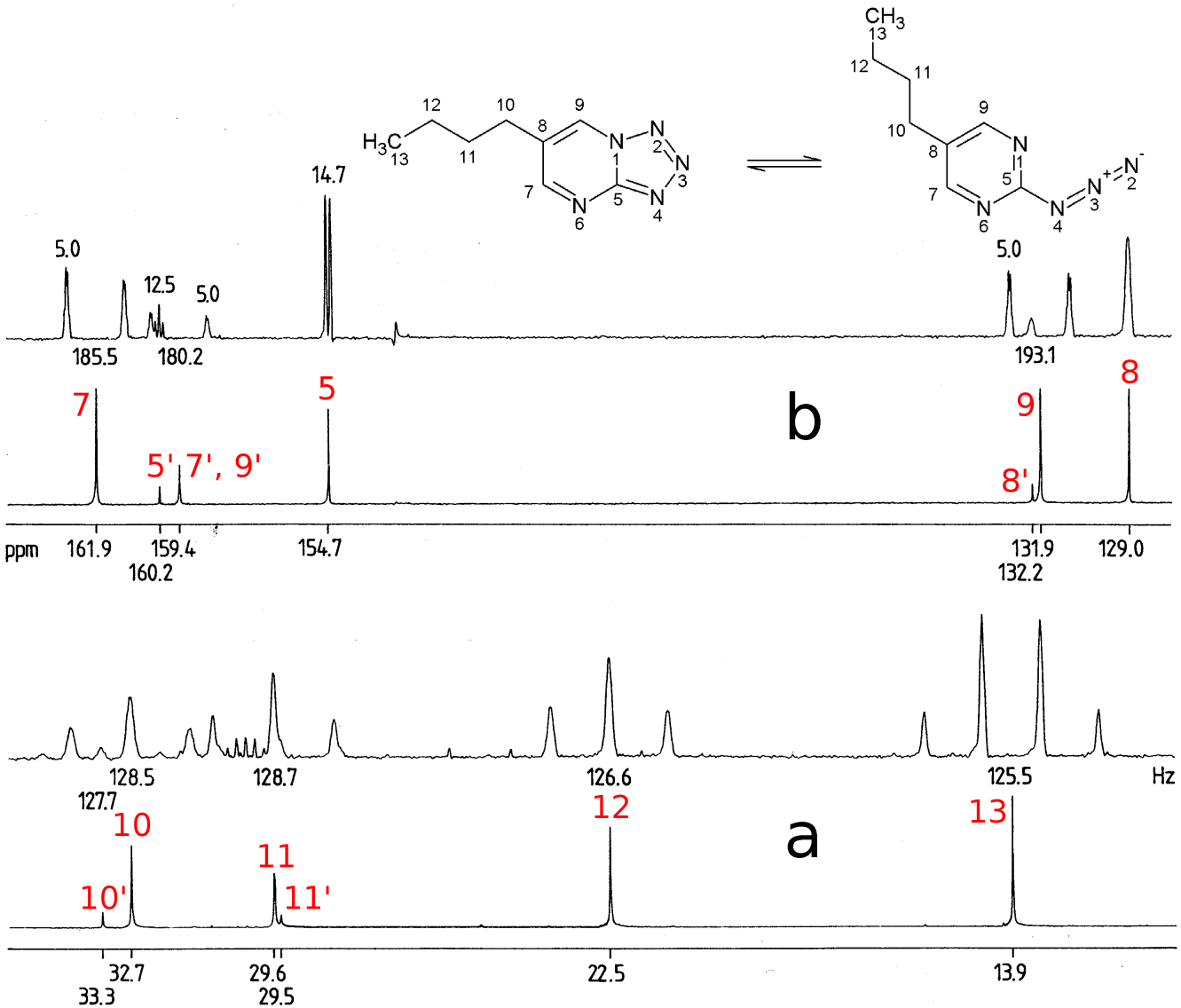

Which form dominates and why?

Next topic

Vector Model + 13C APT experiment