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

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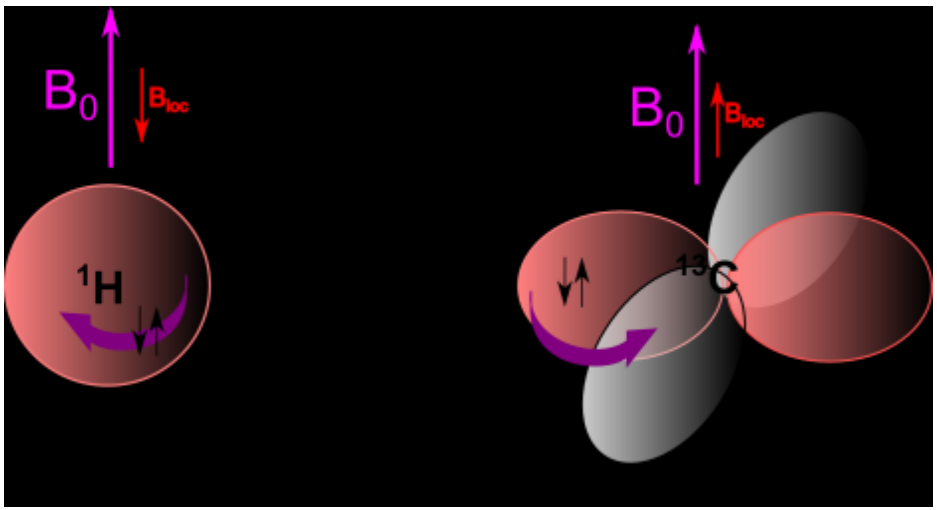
# $^{1}H$ vs $^{13}C$ NMR

| | $^{1}H$ | $^{13}C$ |
|---|---|---|
| Spin number | **$^{1}H$: s=$\frac{1}{2}$** $^{2}H$: s=1 | **$^{13}C$: s=$\frac{1}{2}$** $^{12}C$: 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 | $\sigma_{dia}$ | $\sigma_{dia}$ + $\sigma_{para}$ |
| Integration of signals | C | |
| $T_1$ relaxation [s] | 1-20 | 1-40 |
| Homonuclear *J*-interaction | C | |
| H↔C *J*-interaction (~ 100-250 Hz) | carbon satellites | (*n* + 1) splitting decoupling |



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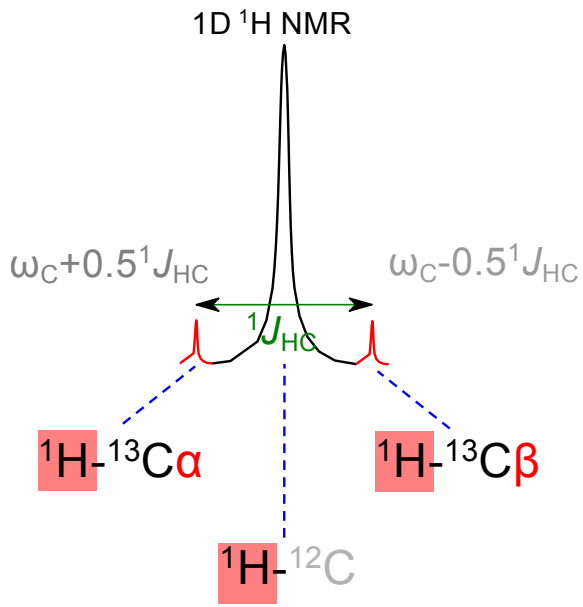
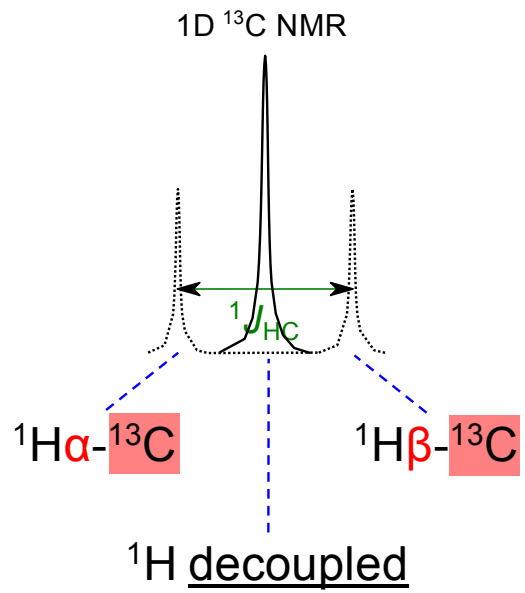
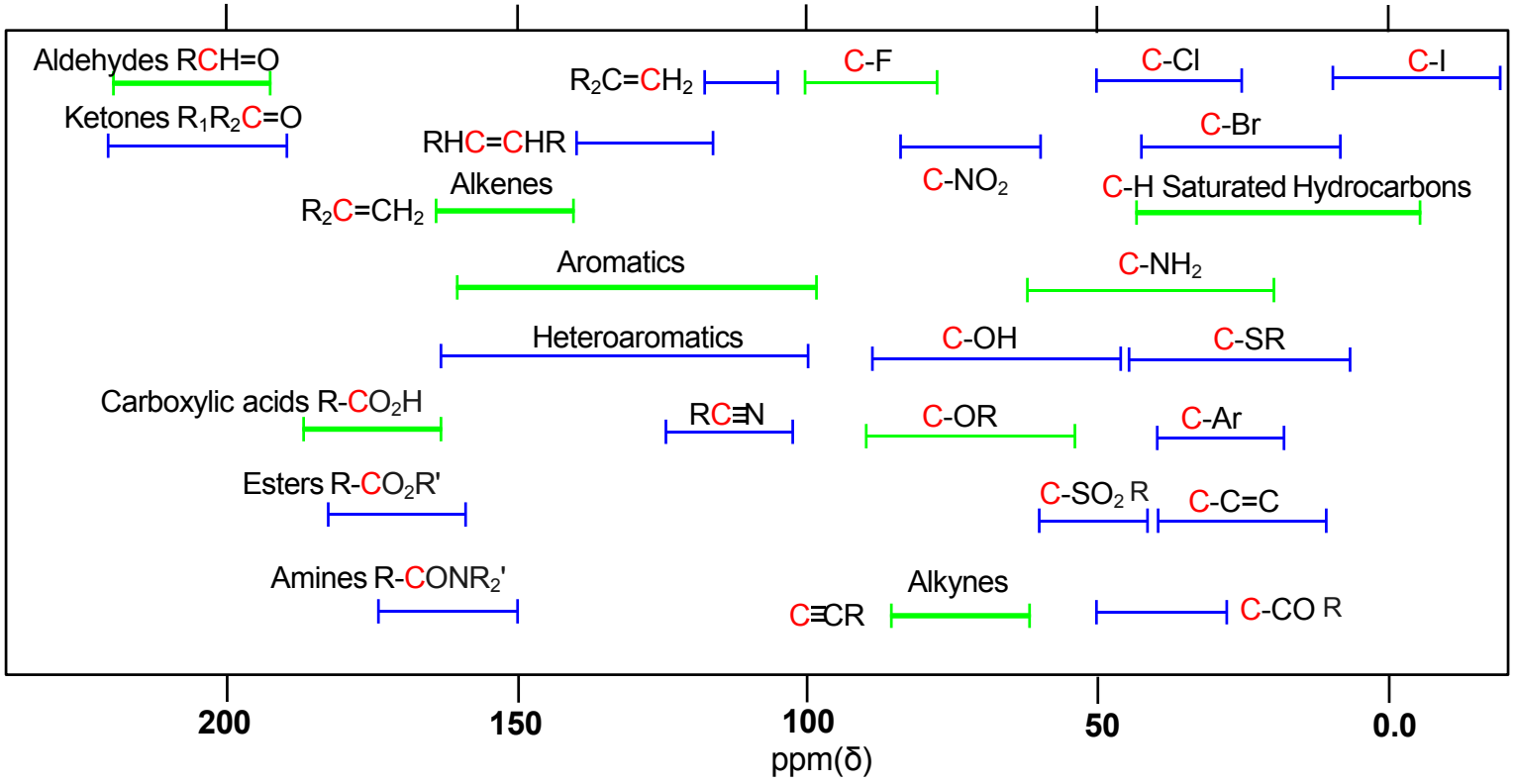


# Important regions of $^{13}C$ chemical shifts



## $^1J_{CH}$ depends on the bond order ( hybridization $\Leftrightarrow$ c. haracter )

- -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.

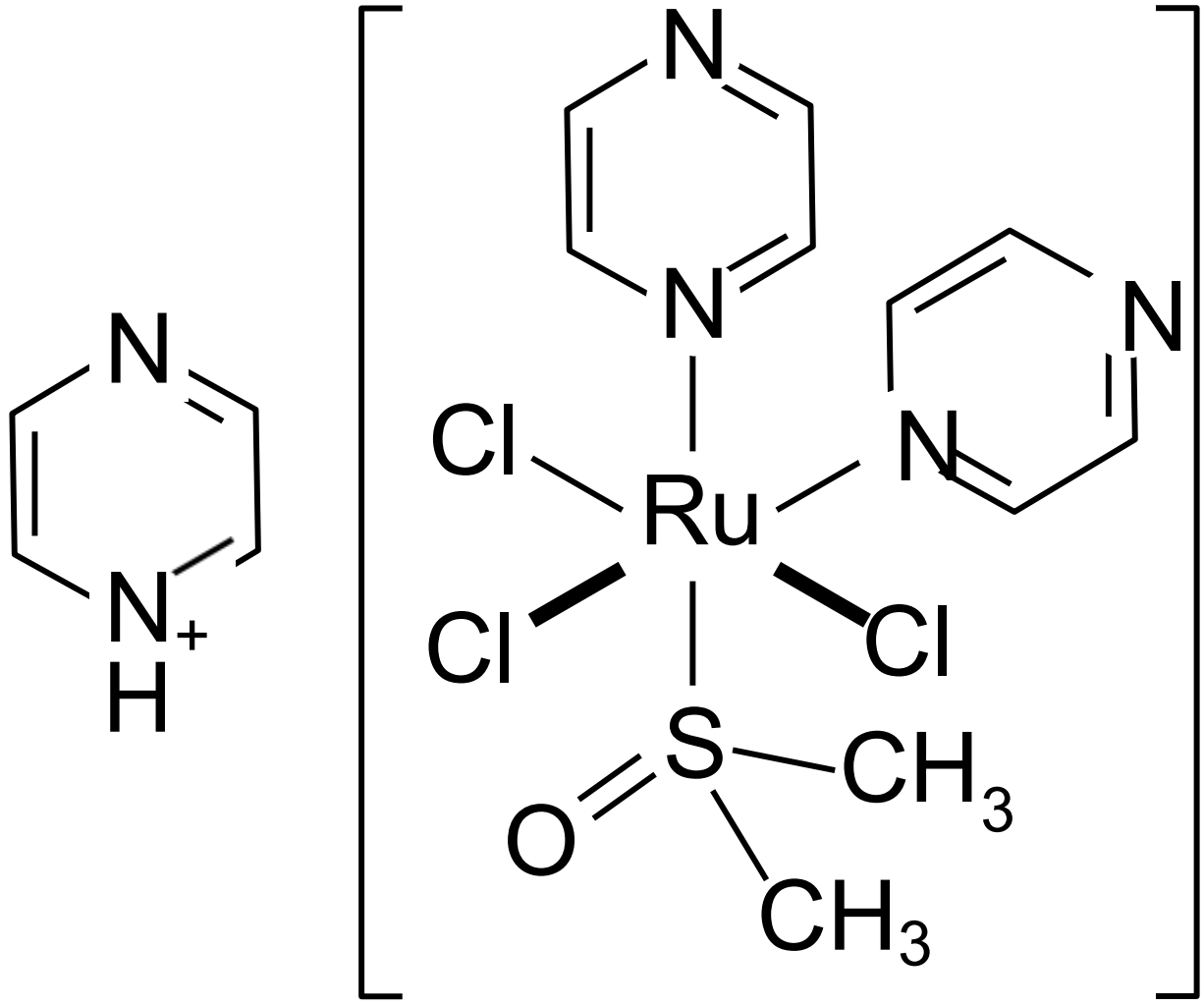
# Values of chemical shift of important solvents

| **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** | - |

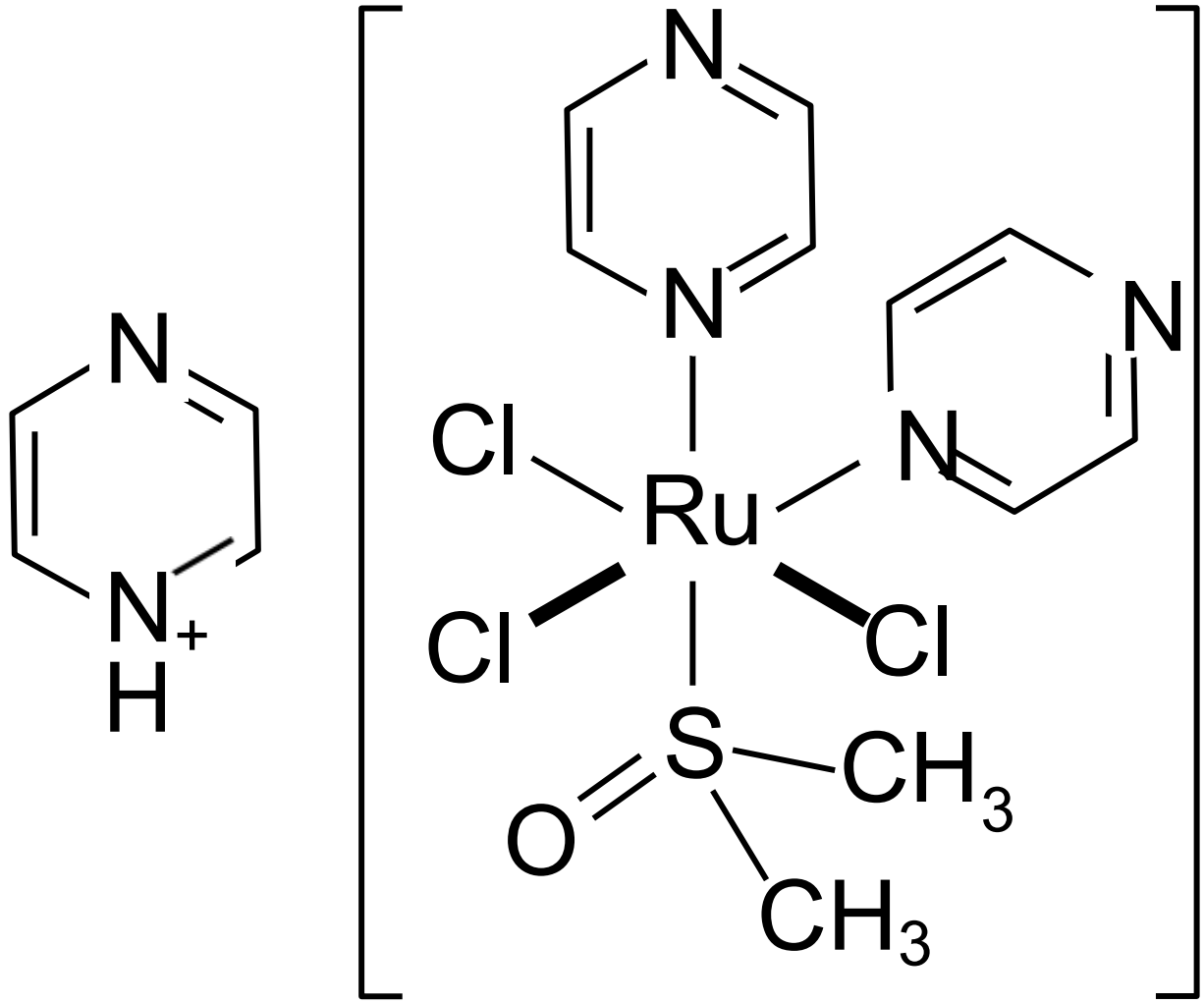
EXPLAIN effect of solvent on the position of residual $^{1}H$ water signal:

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

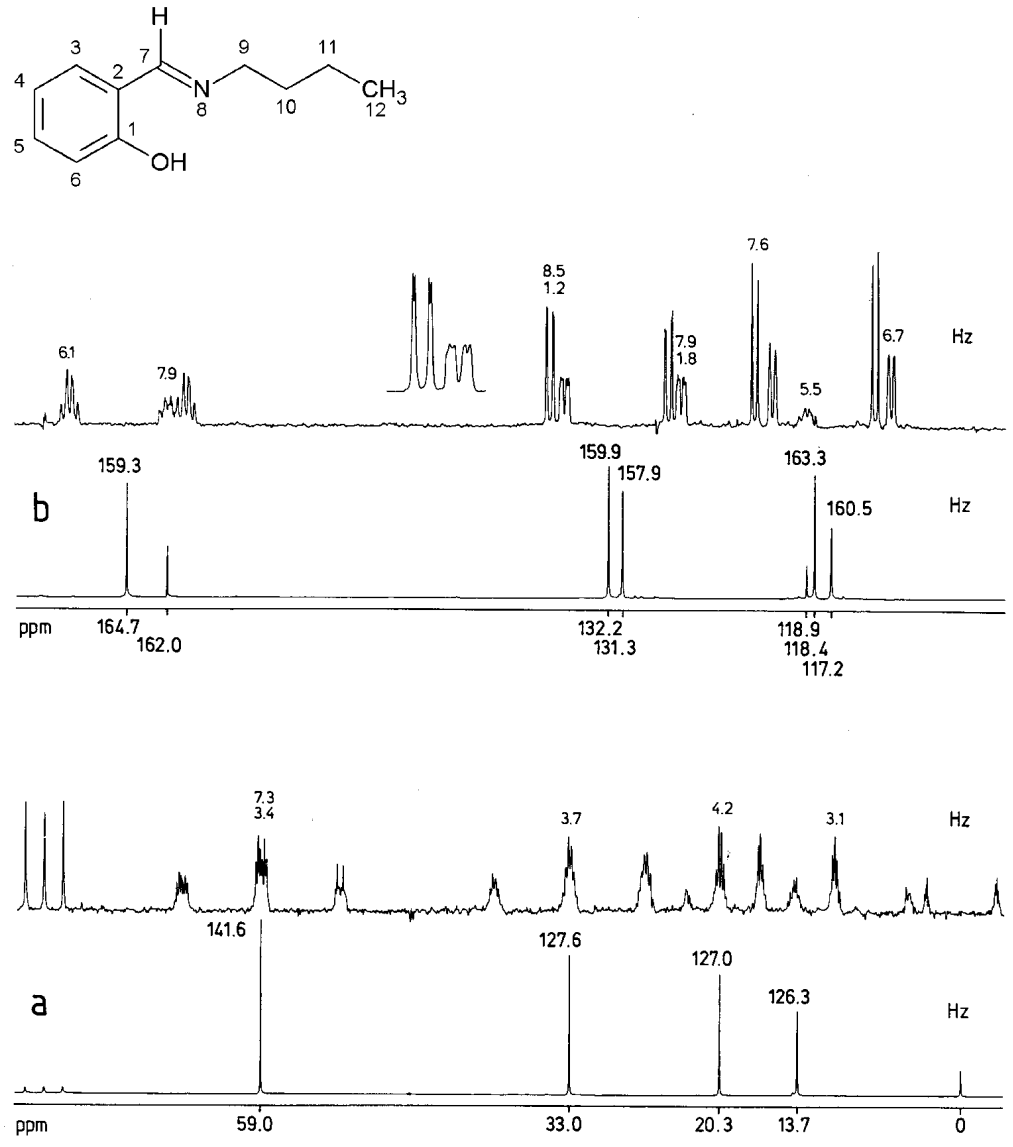
# How many $^{13}C$ signal would you expect in the NMR spectrum?



# 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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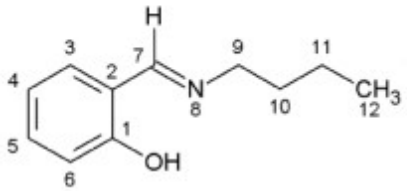
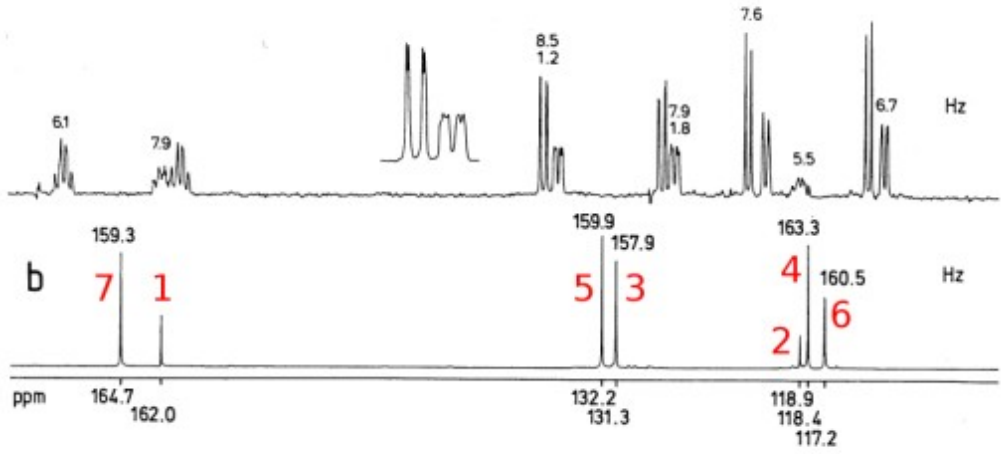
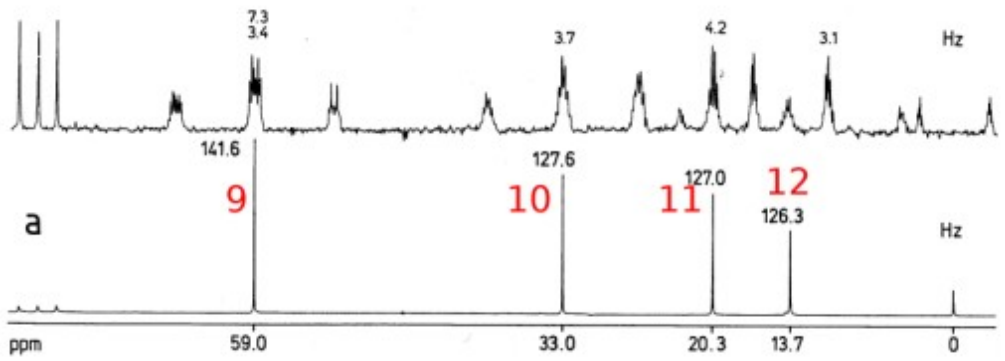


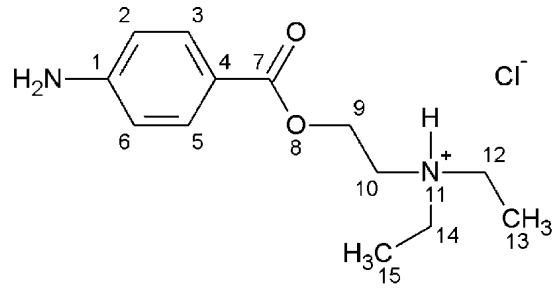



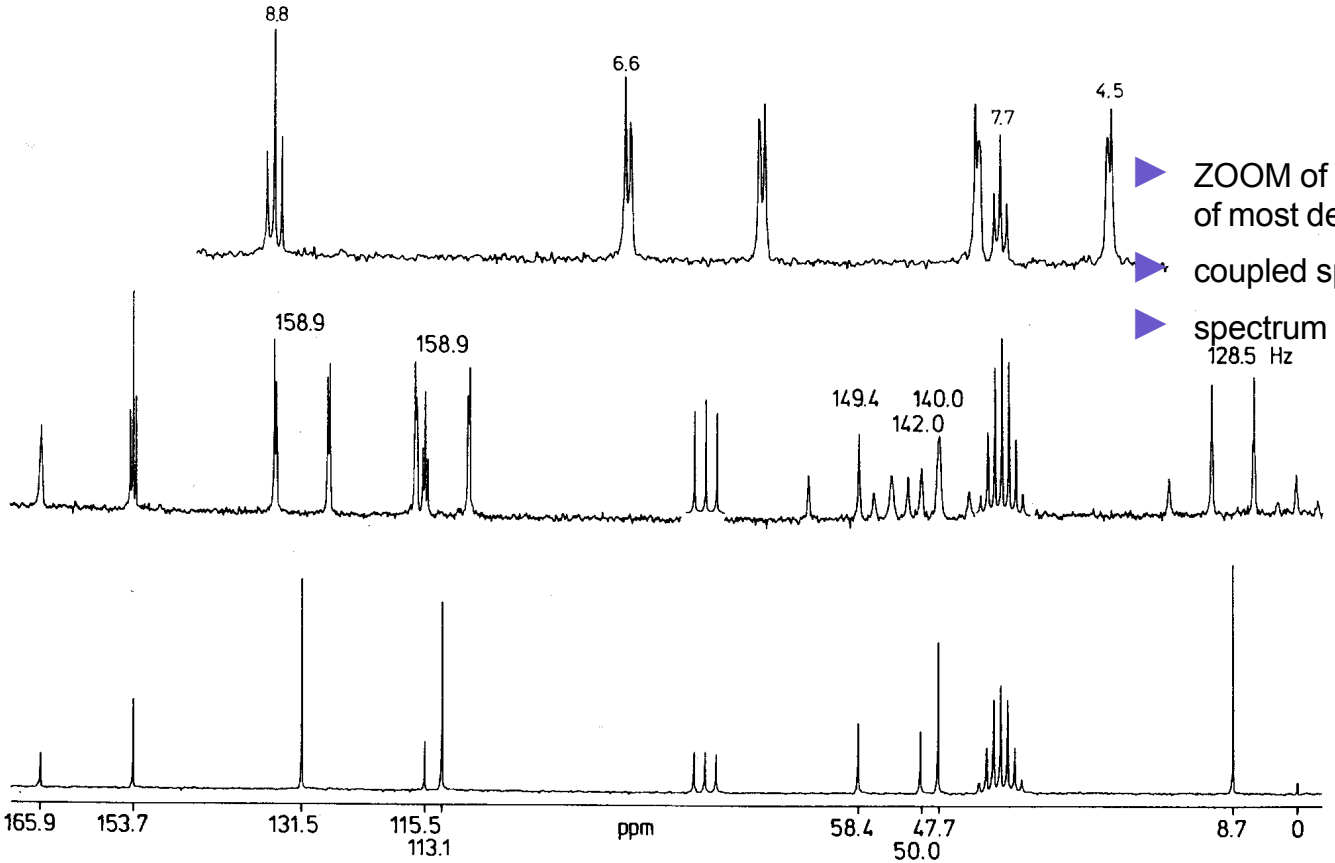




Notes:

- 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→C12**: decaying effect of N8

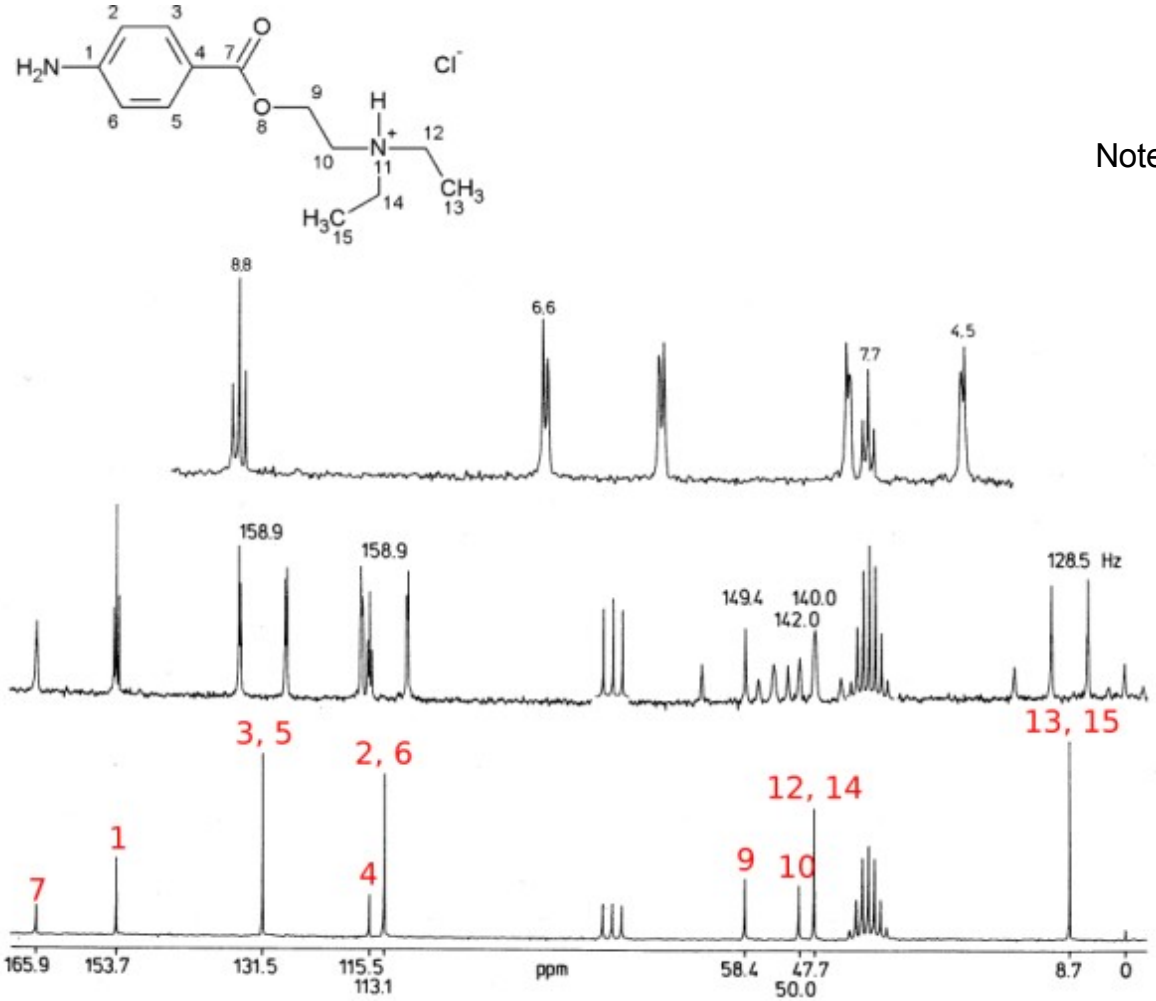
# 1D $^{13}$C-NMR 2




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

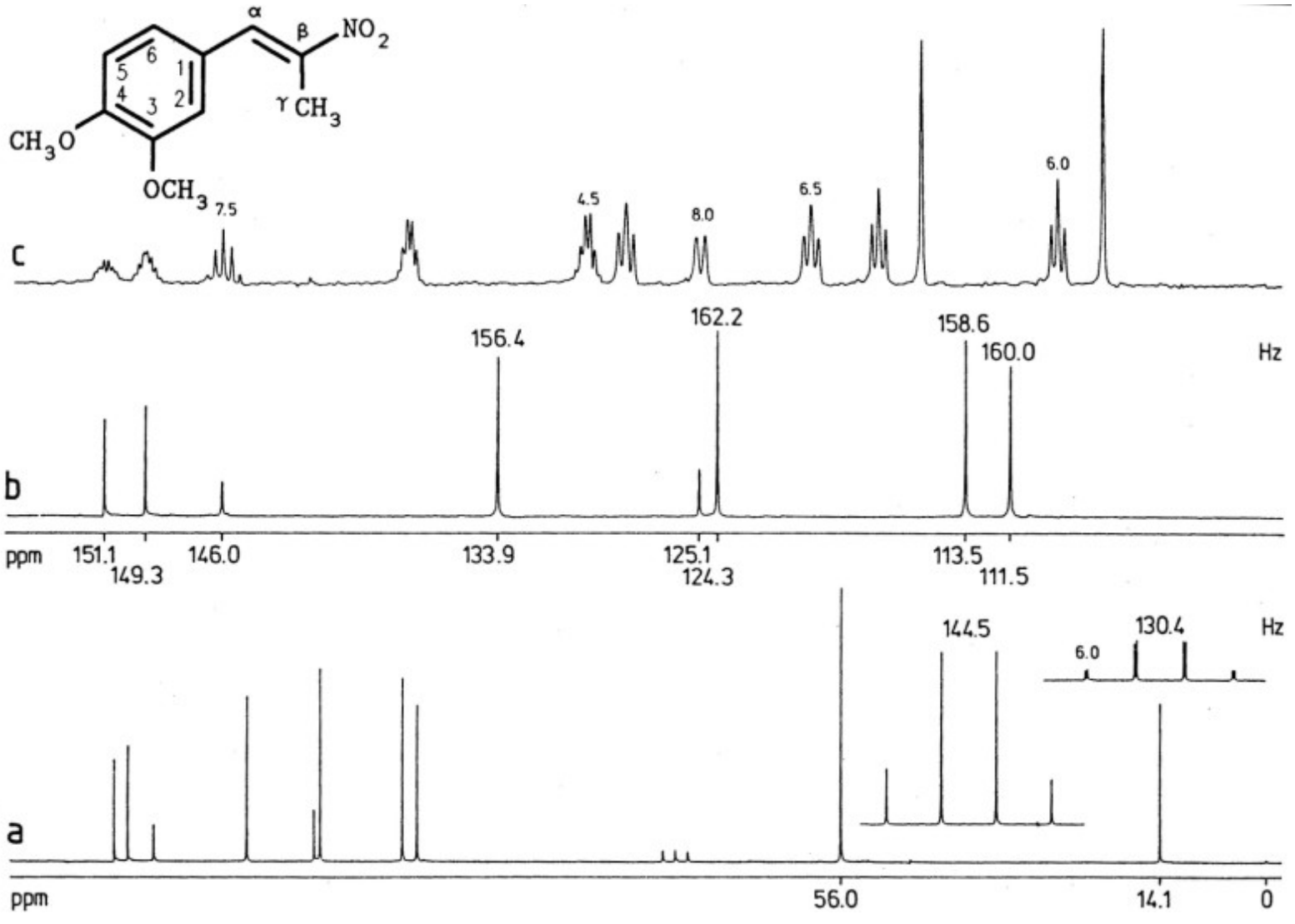
# 1D $^{13}$C-NMR 2




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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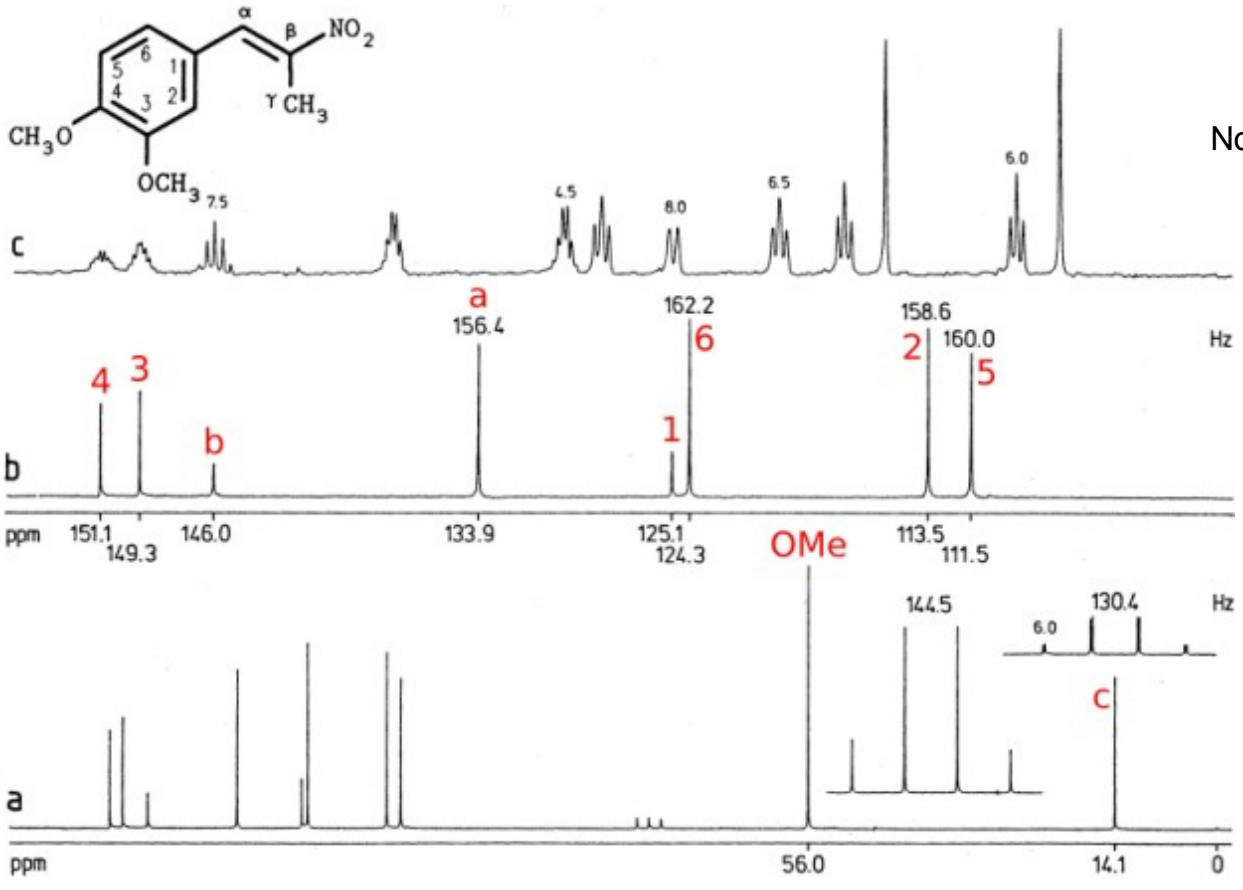
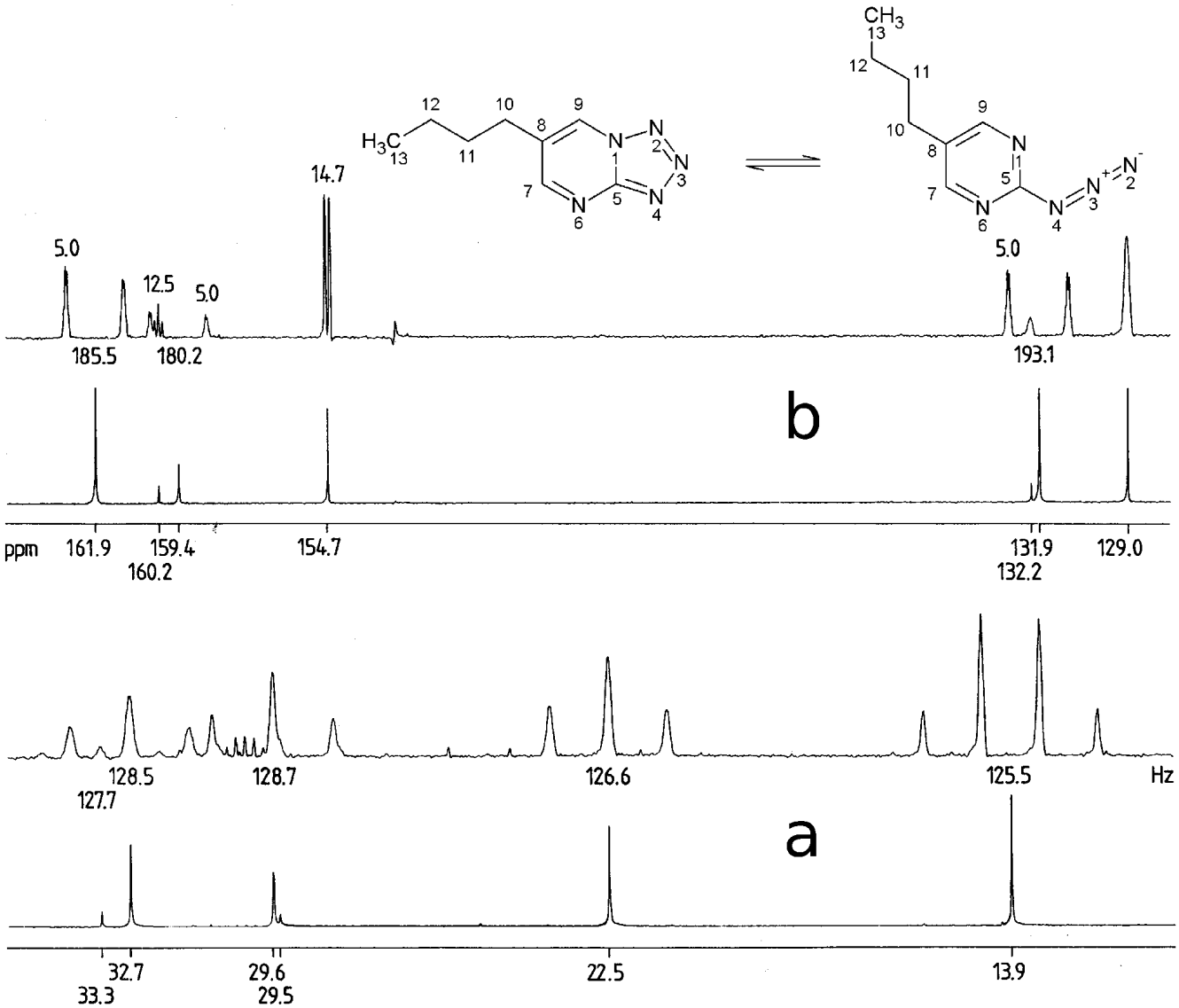



Notes:

- **C3/C4** quaternary aromatic deshielded by O, **C**$\beta$ quaternary coupled by $CH_3$ and C$a$H
- **C**$a$ deshielded by $NO_2$
- **C1** last quaternary aromatic signal
- **C2/C6** coupled mutually and with C$a$, **C5** isolated (contraintuitive)
- quartets **OMe**, **C**$\gamma$

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




Which form dominates and why?

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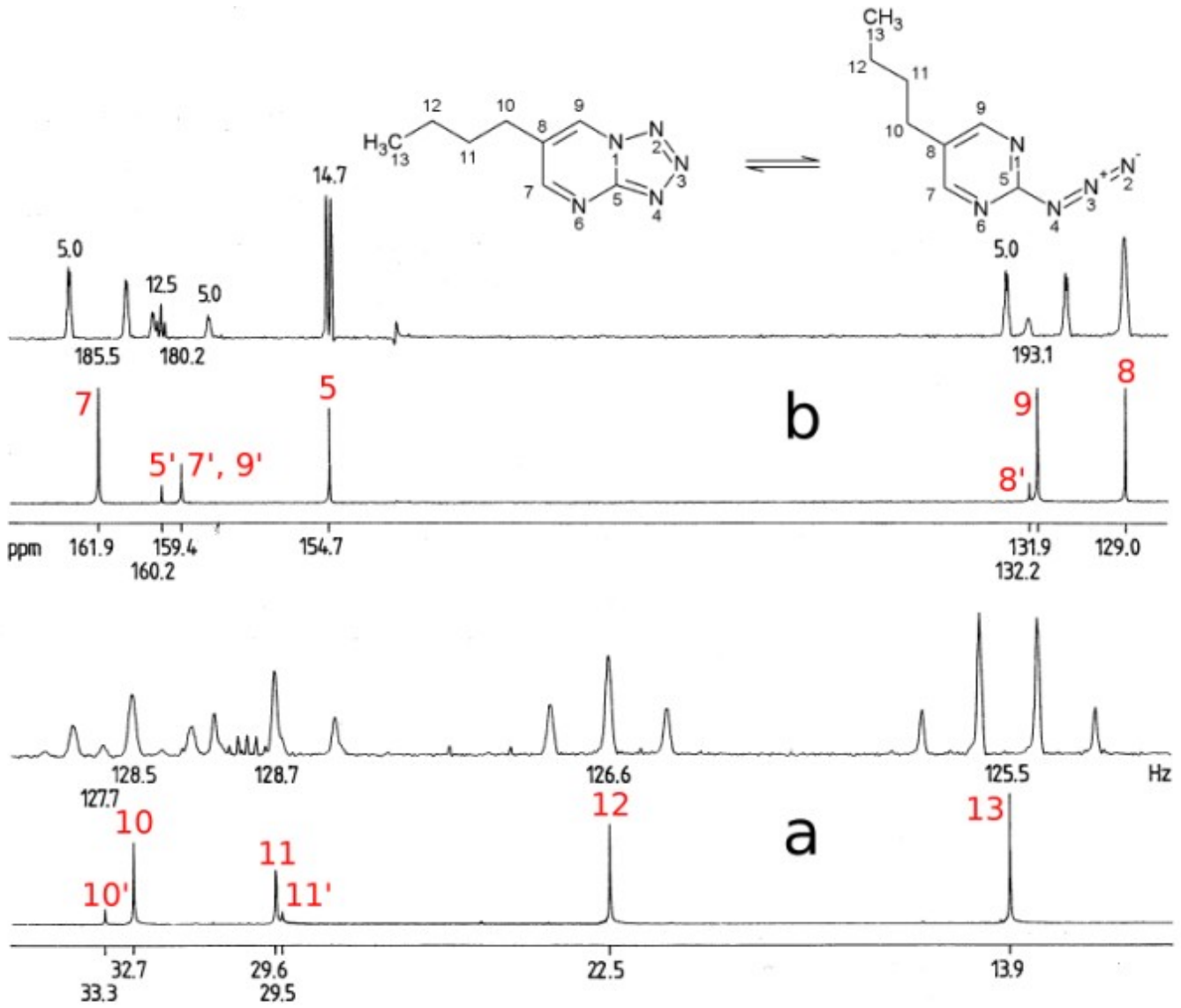
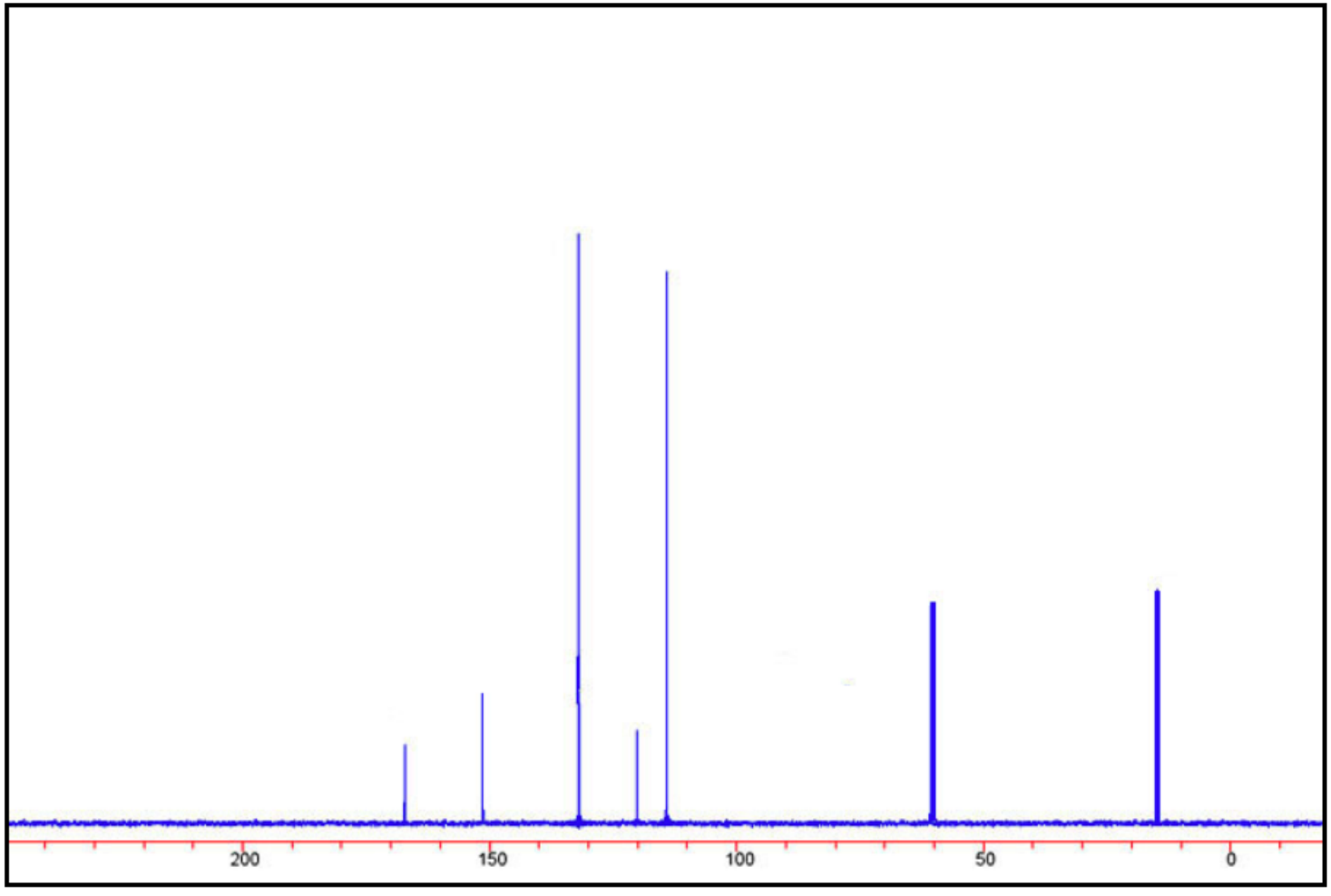



Which form dominates and why?

# Draw structural formula of compound with summary formula $C_9H_{11}NO_2$ (use 1D $^{13}C$ NMR spectrum to find the right structure)



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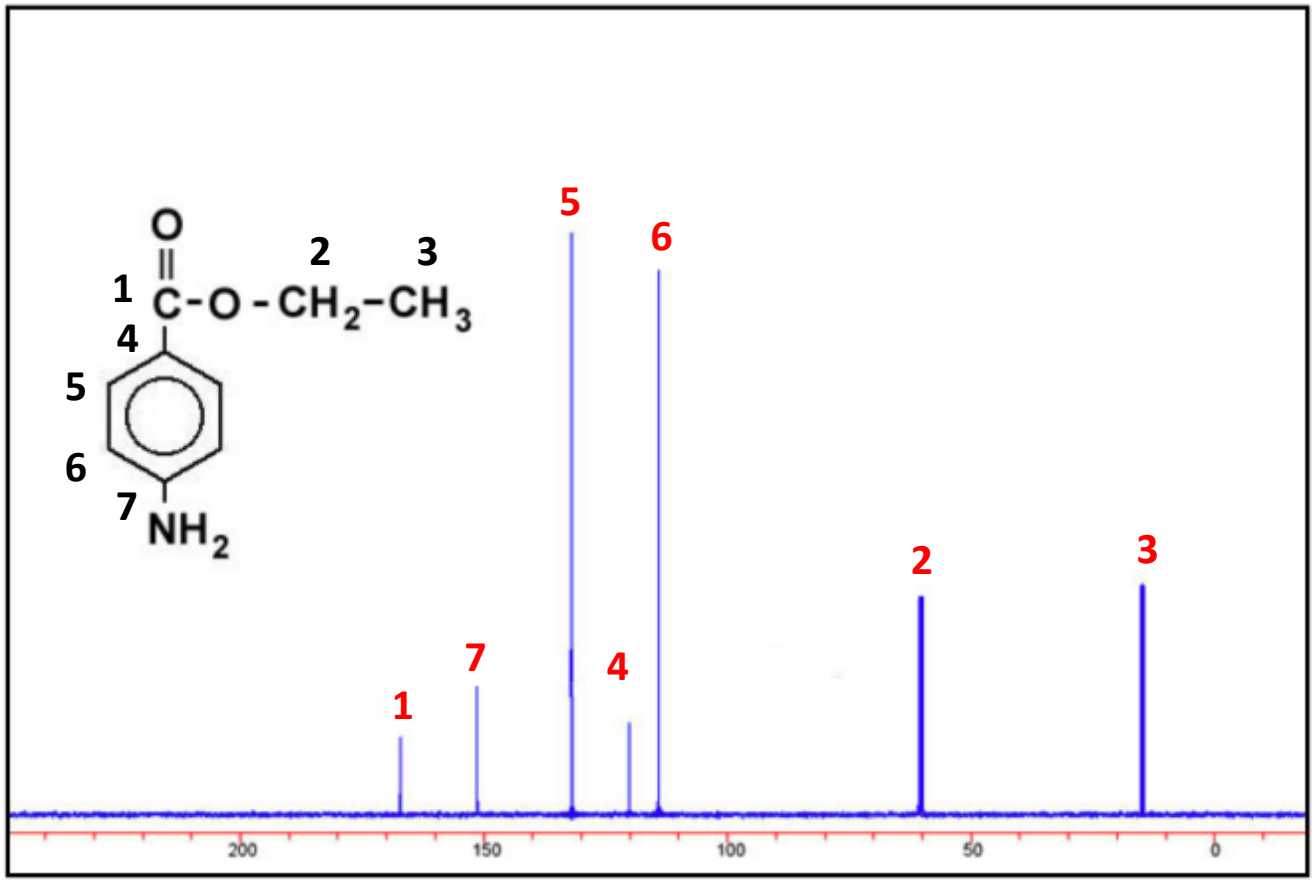


Notes:

- **C1** quaternary carbonyl, **C7** attached to N
- **C5** aromatic,deshielded by $NH_2$, shielded by carbonyl group, **C6** opposite effects
- **C2/C3** decreasing effect of O
- **C4** last quarternaty carbon

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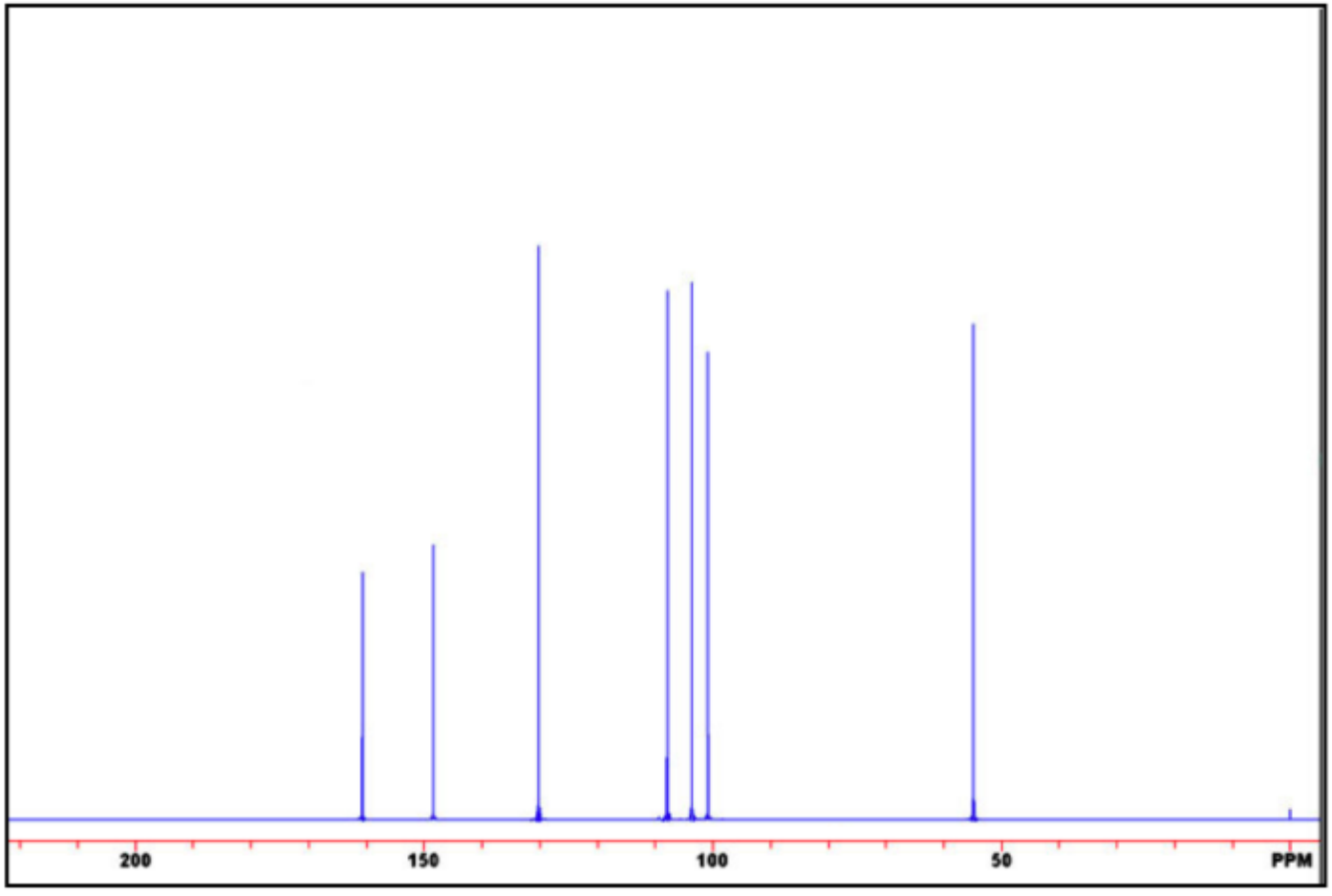

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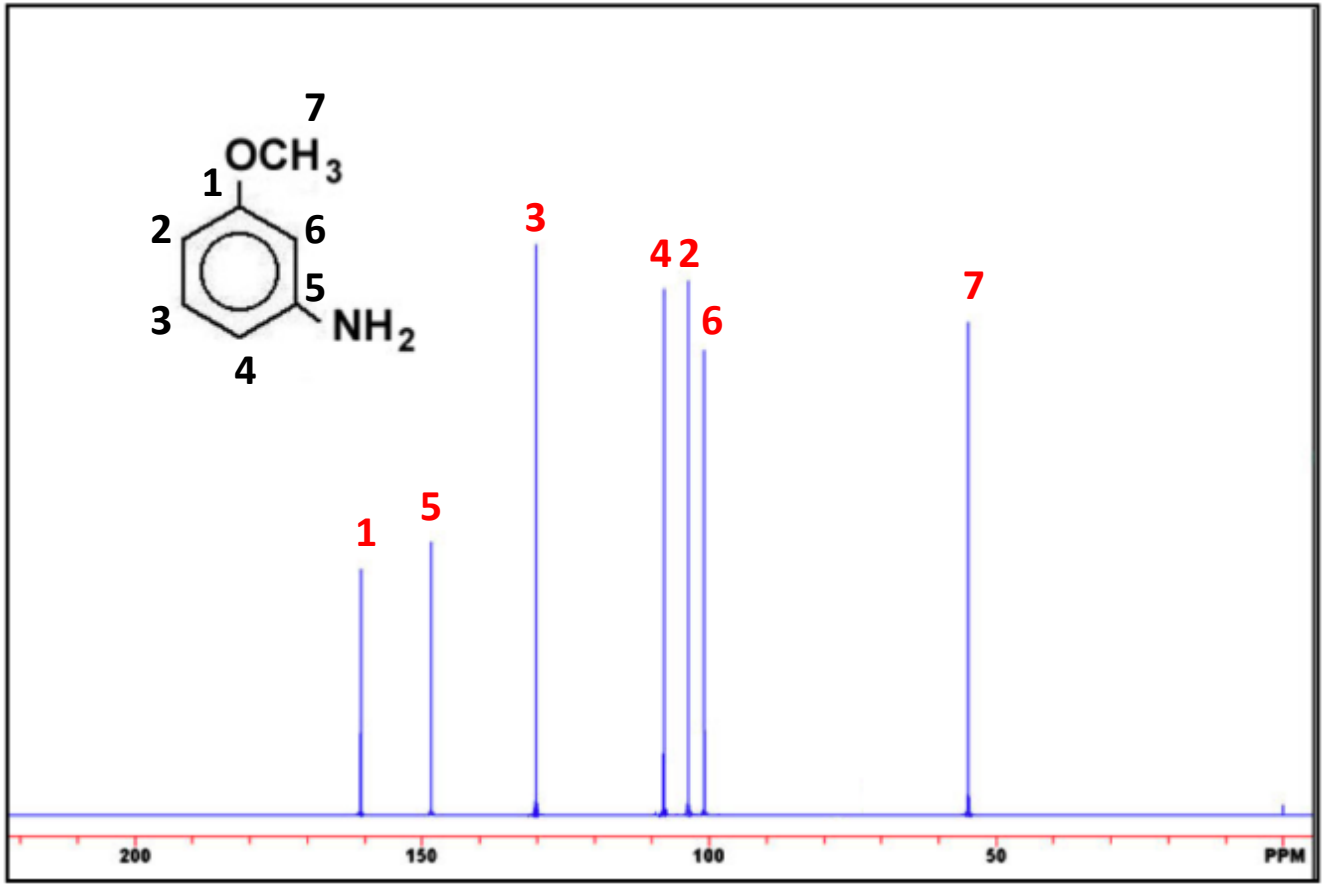


Notes:

- **C1** quaternary deshilded by O, **5** quarternary deshilded by N
- **C3** aromatic,deshielded by $OCH_3$ and $NH_2$
- **C2/C4** shielded by $OCH_3$ and $NH_2$ ,$OCH_3$ shielding effect stronger
- **C6** shielded by both $OCH_3$ and $NH_2$
- **C7** isolated $CH_3$ carbon

# Next topic

Vector Model + $^{13}C$ APT experiment