

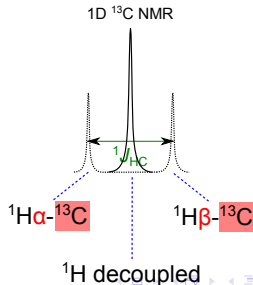
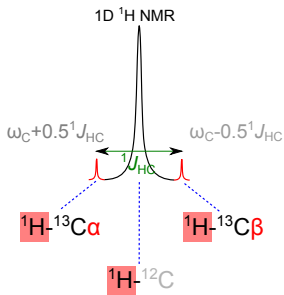
C8953  
NMR structural analysis - seminar  
1D  $^{13}\text{C}$ -NMR + APT

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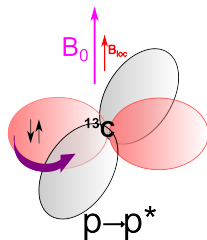
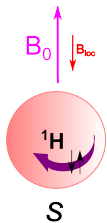
# $^1\text{H}$ vs $^{13}\text{C}$ NMR

	$^1\text{H}$	$^{13}\text{C}$
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	$\sigma_{\text{dia}}$	$\sigma_{\text{dia}} + \sigma_{\text{para}}$
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

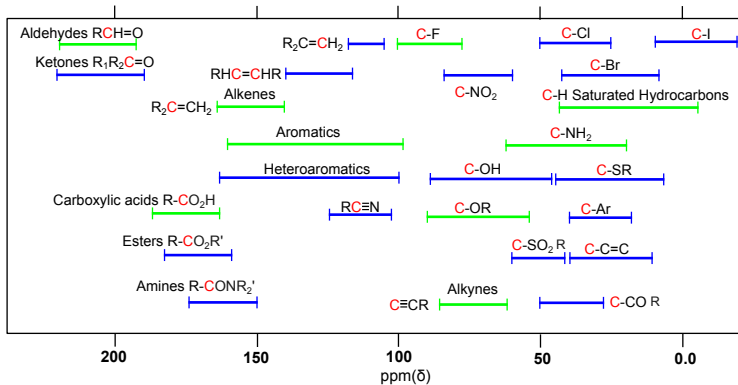


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# Important regions of $^{13}\text{C}$ chemical shifts



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

- ▶  $\text{-C-H } ^1J_{\text{CH}} \approx 125 \text{ Hz}$
- ▶  $\text{=C-H } ^1J_{\text{CH}} \approx 160 \text{ Hz}$
- ▶  $\text{\equiv C-H } ^1J_{\text{CH}} \approx 250 \text{ Hz}$
- ▶ 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 Hz)

- ▶ often not observable

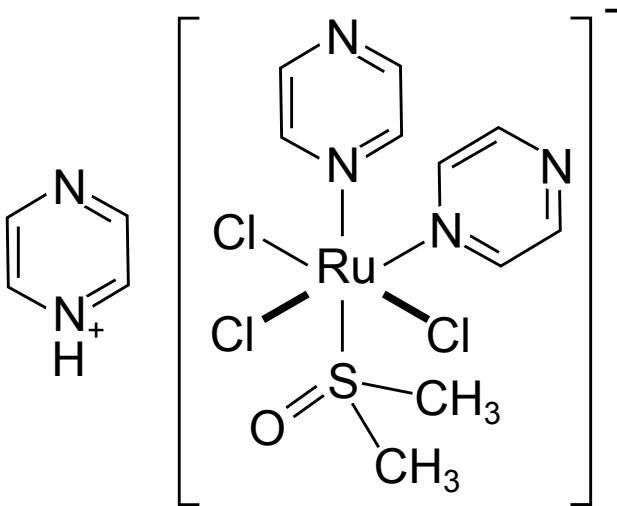
## Values of chemical shift of important solvents

<b>Abbr.</b>	<b>Formula</b>	<b><math>^1\text{H}</math></b>	<b><math>^{13}\text{C}</math></b>
<b>ACN</b>	$\text{CH}_3\text{CN}$	1.9	118
<b>Benzene</b>	$\text{C}_6\text{H}_6$	7.2	128
	$\text{CHCl}_3$	7.2	77
<b>DCM</b>	$\text{CH}_2\text{Cl}_2$	5.3	54
<b>DMF</b>	$(\text{CH}_3)_2\text{NCHO}$	2.9, 8.0	32, 163
<b>DMSO</b>	$(\text{CH}_3)_2\text{SO}$	2.5	40
<b>MeOH</b>	$\text{CH}_3\text{OH}$	3.3, 4.8	49
<b>Water</b>	$\text{H}_2\text{O}$	4.8	-

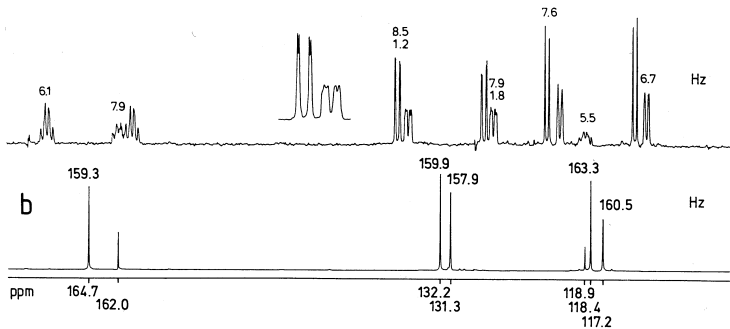
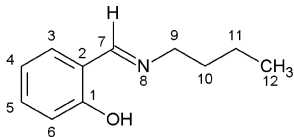
Effect of solvent on the position of residual  $^1\text{H}$  water signal:

$\text{CHCl}_3$  - 1.6, ACN - 2.1, DMSO - 3.3, MeOH - 4.9

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

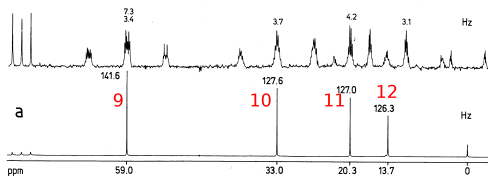
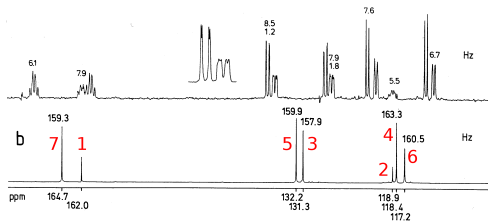
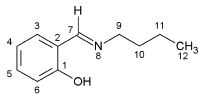


# 1D $^{13}\text{C}$ -NMR 1





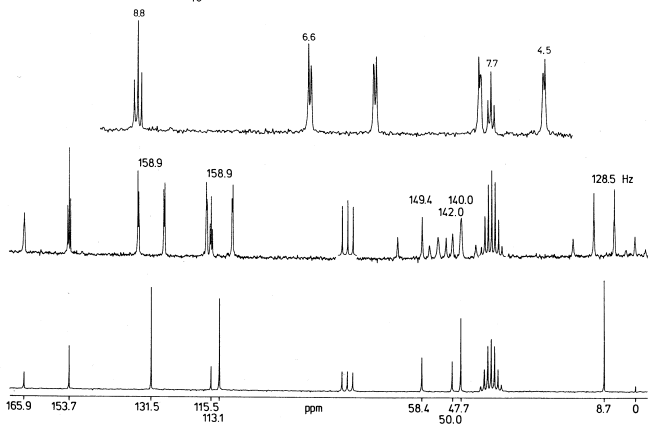
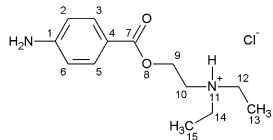
# 1D $^{13}\text{C}$ -NMR 1



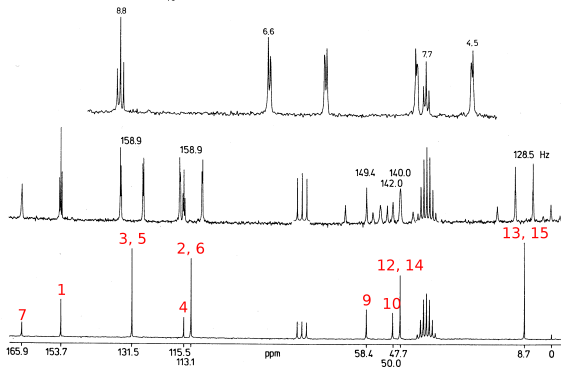
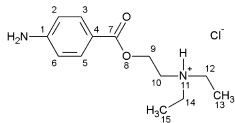
Notes:

- ▶ **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 $^{13}\text{C}$ -NMR 2



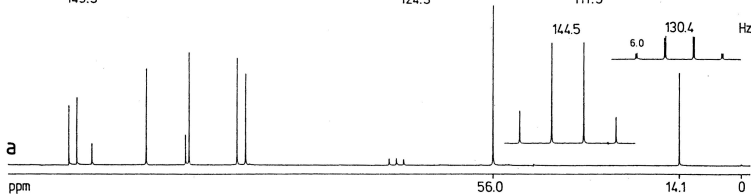
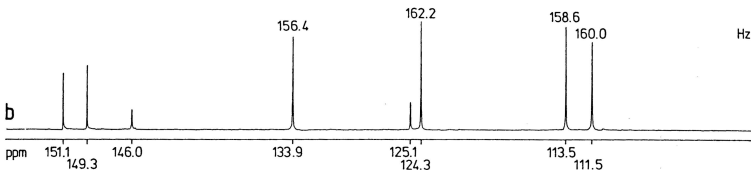
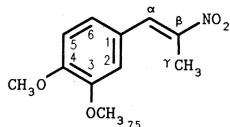
# 1D $^{13}\text{C}$ -NMR 2



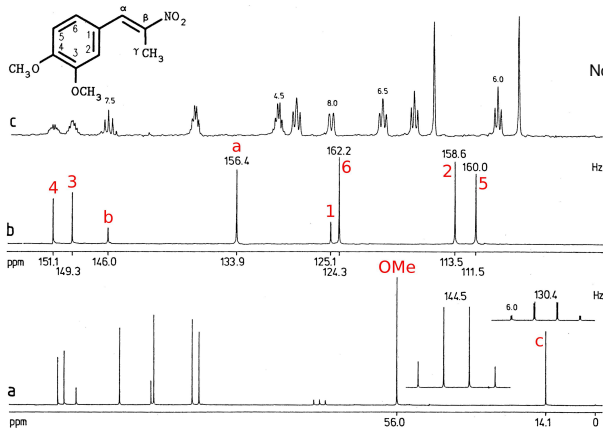
## Notes:

- ▶ **C7** carbonyl, **C1** attached to N
- ▶ **C3/5** deshielded by M-CO, **C2/6** shielded by M+ of  $\text{NH}_2$
- ▶ **C4** last quaternary aromatic signal
- ▶ **C9** effect of ester group, ? **C10** affected by NH exchange
- ▶ **C12/C14 + C13/C15** decaying effect of N+

# 1D <sup>13</sup>C-NMR 3



# 1D <sup>13</sup>C-NMR 3



Notes:

- ▶ **C3/C4** quaternary aromatic deshielded by O, **C $\beta$**  quaternary coupled by CH<sub>3</sub> and C $\alpha$ H
- ▶ **C $\alpha$**  deshielded by NO<sub>2</sub>
- ▶ **C1** last quaternary aromatic signal
- ▶ **C2/C6** coupled mutually and with C $\alpha$ , **C5** isolated (constrained)
- ▶ quartets **OMe**, **C $\gamma$**

# APT - Attached Proton Test

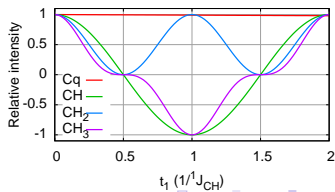
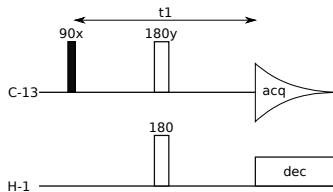
based on heteronuclear spin echo

▶  $t_1 = 1/{}^1J_{CH}$

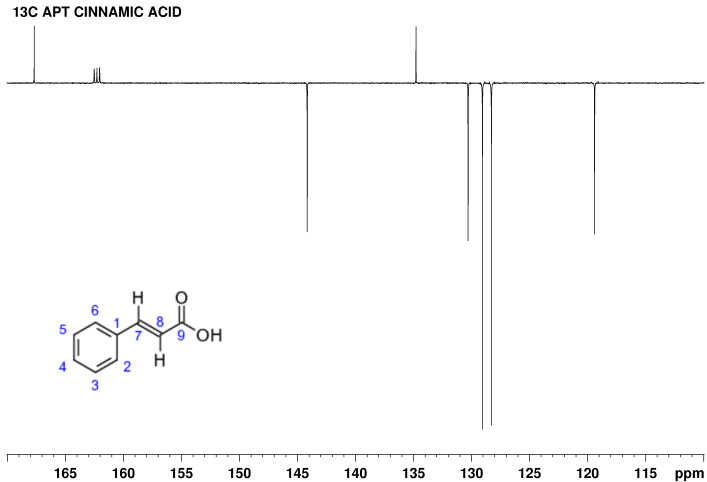
${}^{13}C$  signals are differentiated according to the number of directly bound  ${}^1H$

- ▶ Cq, CH<sub>2</sub> positive
- ▶ CH, CH<sub>3</sub> negative

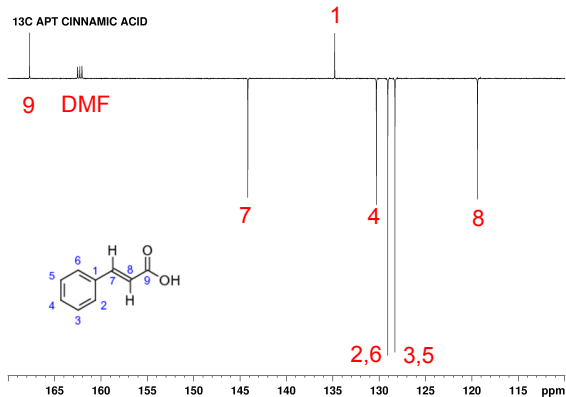
Evolution of signal governed by the value of  ${}^1J_{CH} \implies$  reflected by the intensity of APT signal



# $^{13}\text{C}$ APT Cinnamic acid



# $^{13}\text{C}$ APT Cinnamic acid

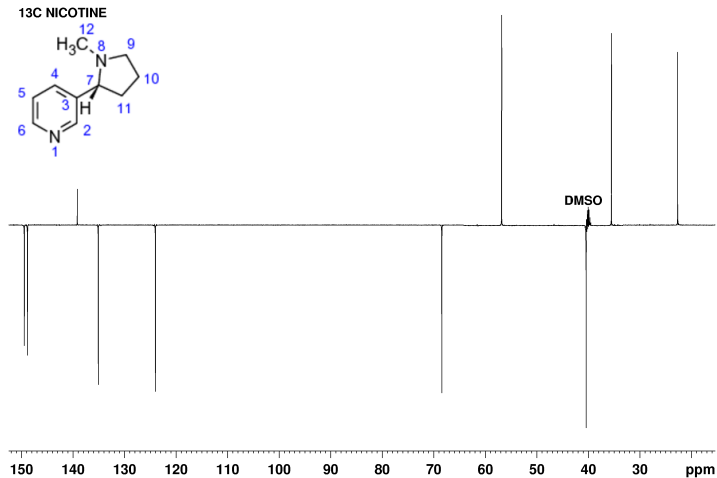


Notes:

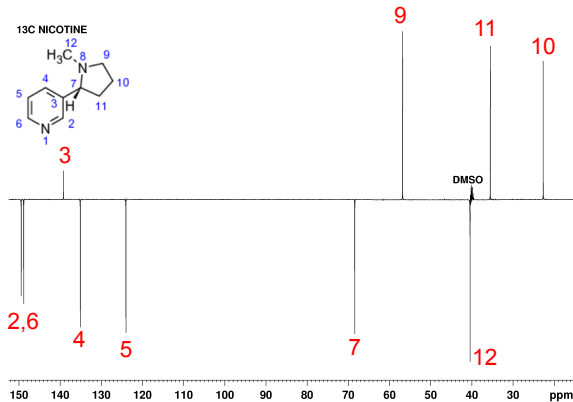
- ▶ **C9, C4** positive quaternary
- ▶ **C7** deshielded by -M effect of carboxyl group + in neighbourhood of aromatic system
- ▶ equivalent **C2/6**, **C3/5** in aromatic region, para **C4** less sensitive



# $^{13}\text{C}$ APT of Nicotine



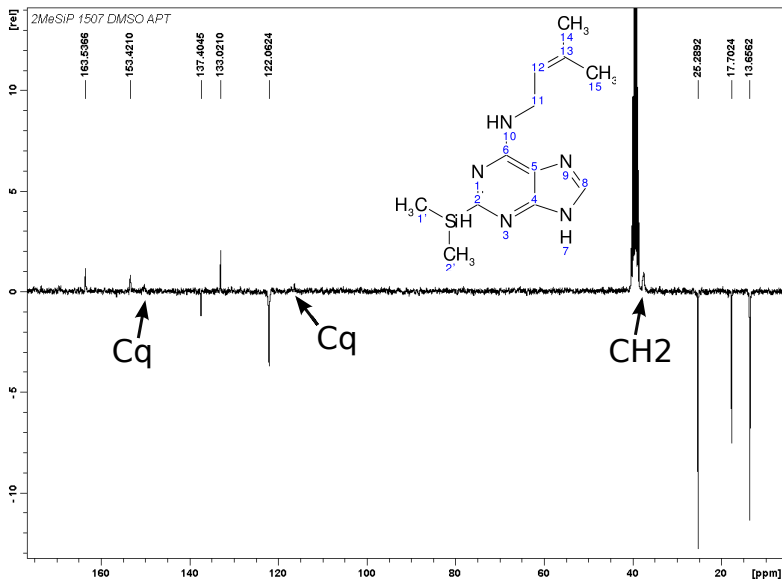
# $^{13}\text{C}$ APT of Nicotine



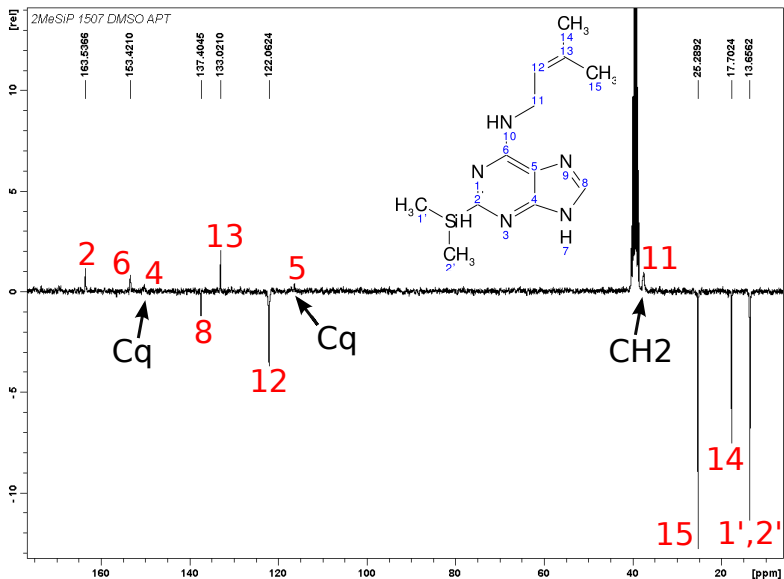
Notes:

- ▶ **C2, C6** CH negative connected to N
- ▶ **C3** quaternary, **C4** more deshielded
- ▶ **C7** tertiary carbon, in neighbourhood of aromatic system and N
- ▶ **C9** secondary, close to N; **C12** primary attached to N
- ▶ **C11** connected to tertiary carbon

# $^{13}\text{C}$ APT 4



# <sup>13</sup>C APT 4



Next topic

Vector Model