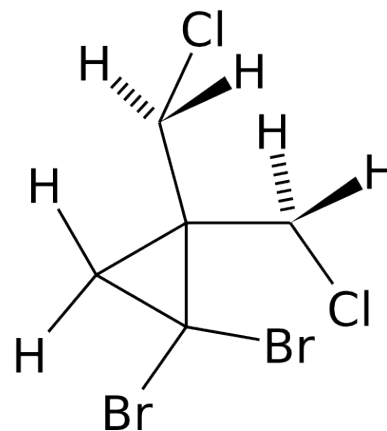
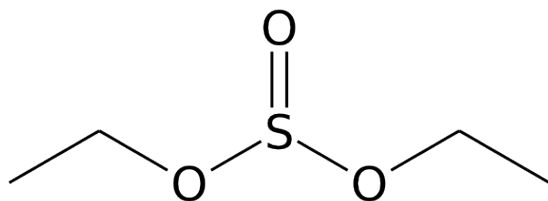
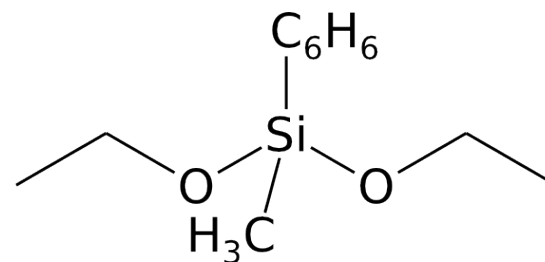
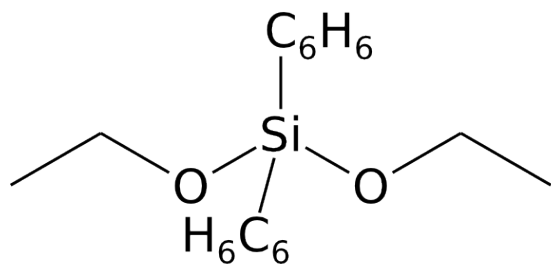


C8953
NMR structural analysis - seminar
1D ^{13}C -NMR

Matúš Durec
211166@mail.muni.cz

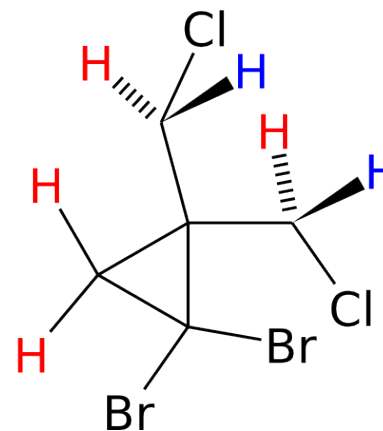
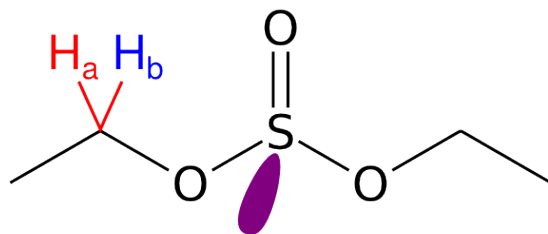
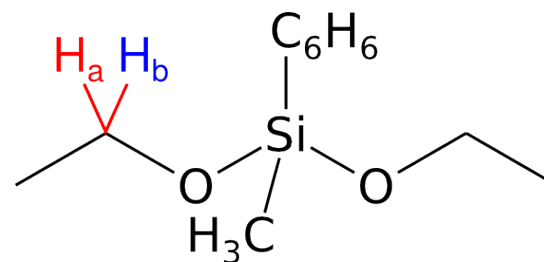
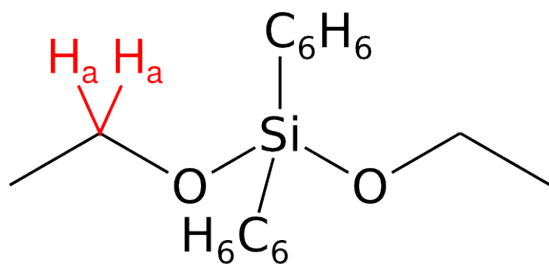
March 6, 2017

Diastereotopicity¹



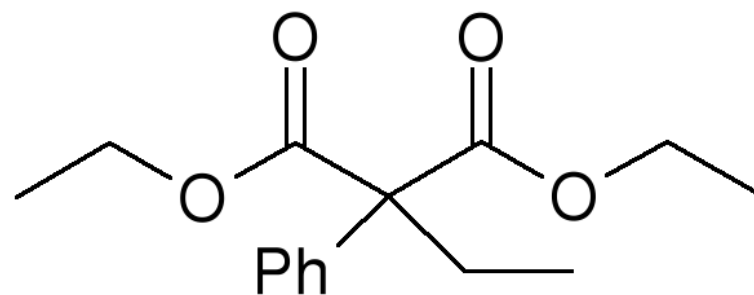
¹<http://www.chem.wisc.edu/areas/reich/chem605/>

Diastereotopicity¹

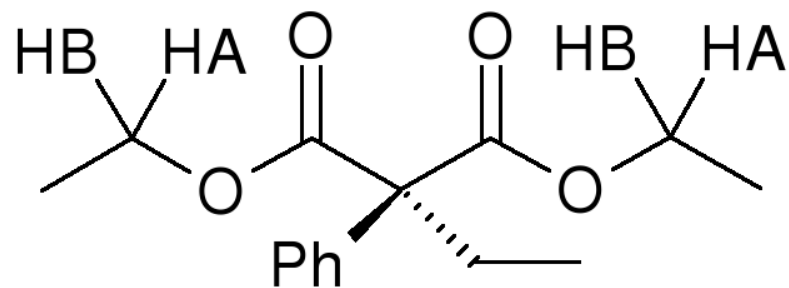


¹<http://www.chem.wisc.edu/areas/reich/chem605/>

Determine the number of nonequivalent ^1H signals :

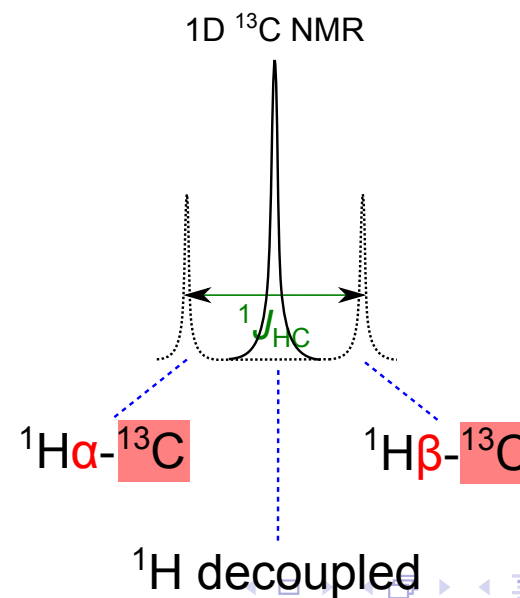
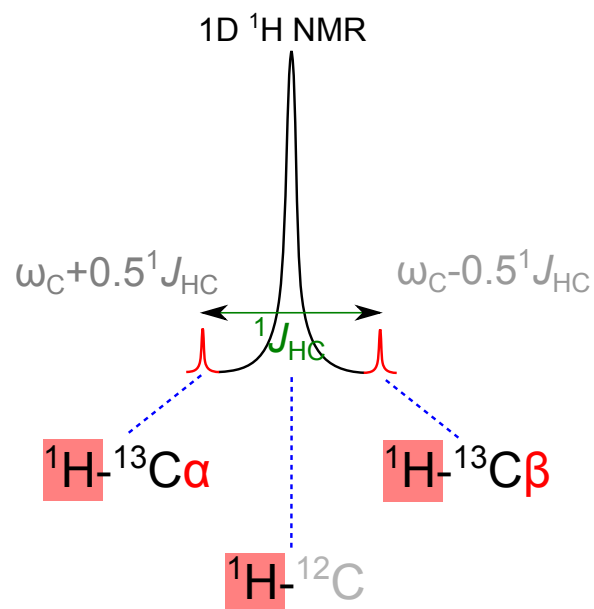


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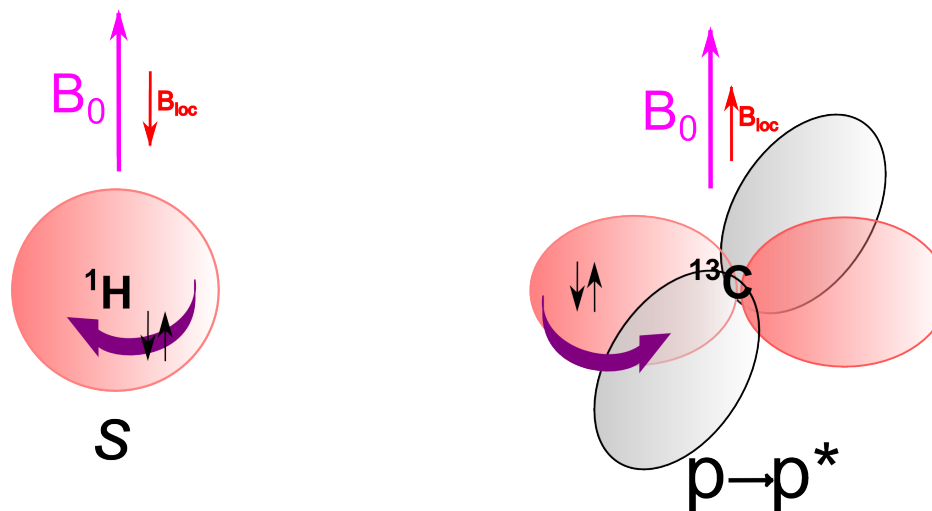
^1H vs ^{13}C NMR

	^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 ✗ decoupling

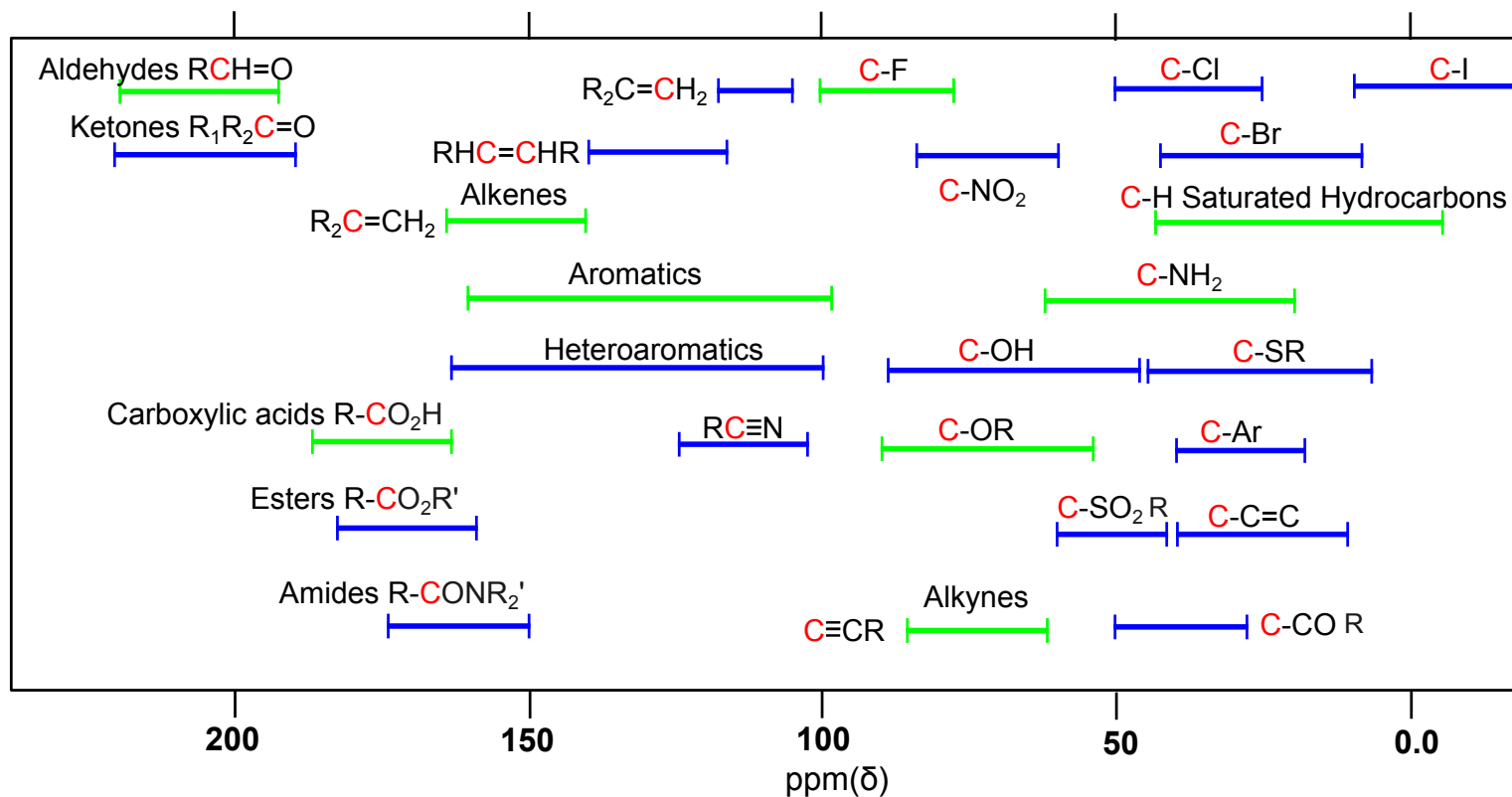


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Important regions of ^{13}C chemical shifts



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

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

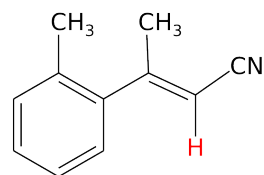
Values of chemical shift of important solvents

Abbr.	Formula	^1H	^{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	$(\text{CH}_3)_2\text{NCHO}$	2.9, 8.0	32, 163
DMSO	$(\text{CH}_3)_2\text{SO}$	2.5	40
MeOH	CH_3OH	3.3, 4.8	49
Water	H_2O	4.8	-

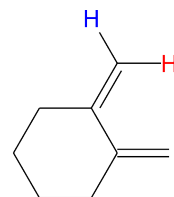
Effect of solvent on the position of residual ^1H water signal:

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

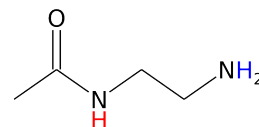
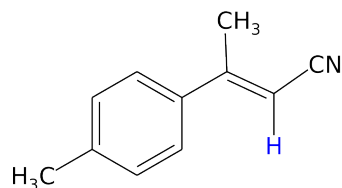
Assign correct value of chemical shift to labelled NMR active atoms¹:



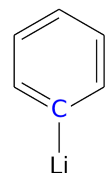
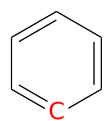
5.22 5.46



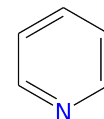
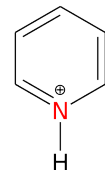
4.64 4.92



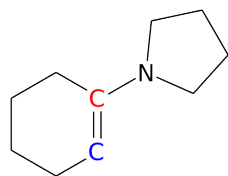
1.5 7.0



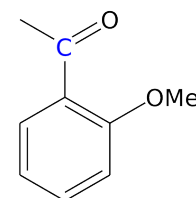
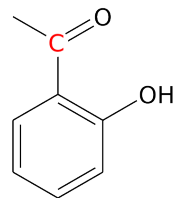
129 200



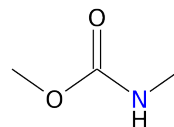
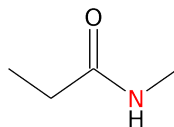
-166 -68



93 142

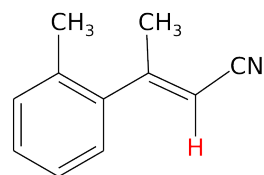


188 197

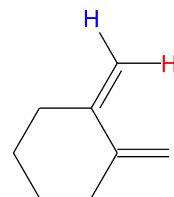


¹<http://www.chem.wisc.edu/areas/reich/chem605/>

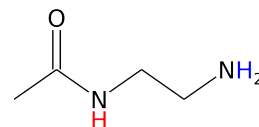
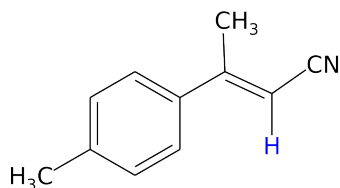
Assign correct value of chemical shift to labelled NMR active atoms¹:



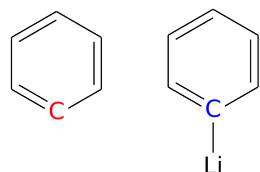
5.22 5.46



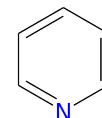
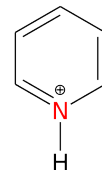
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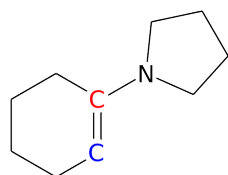
1.5 7.0



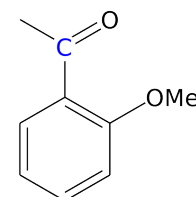
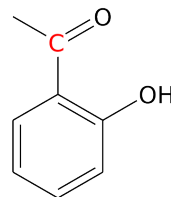
129 200



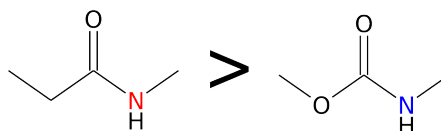
-166 -68



93 142

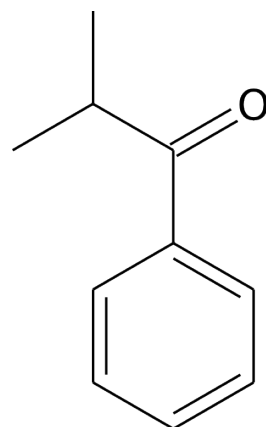


188 197

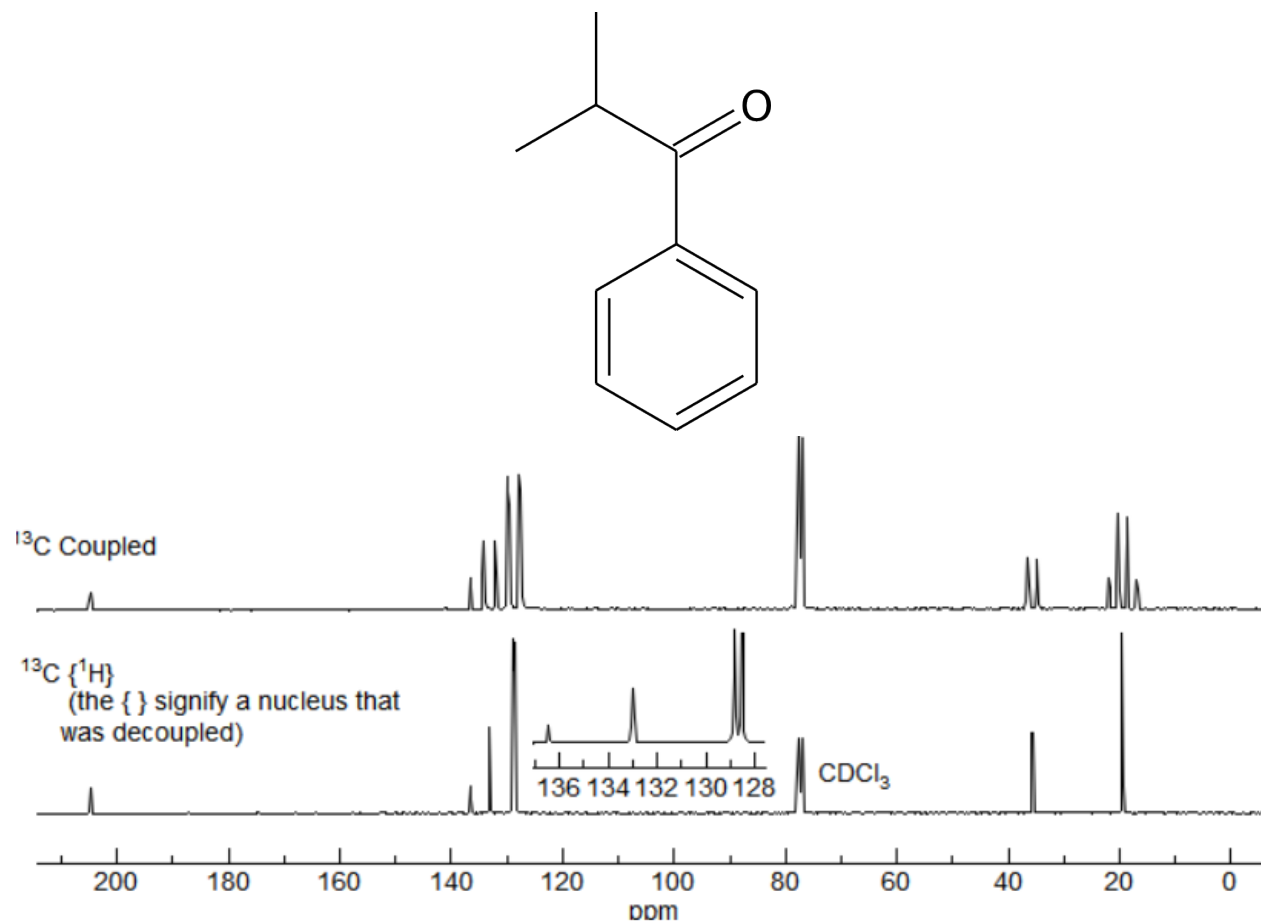


¹<http://www.chem.wisc.edu/areas/reich/chem605/>

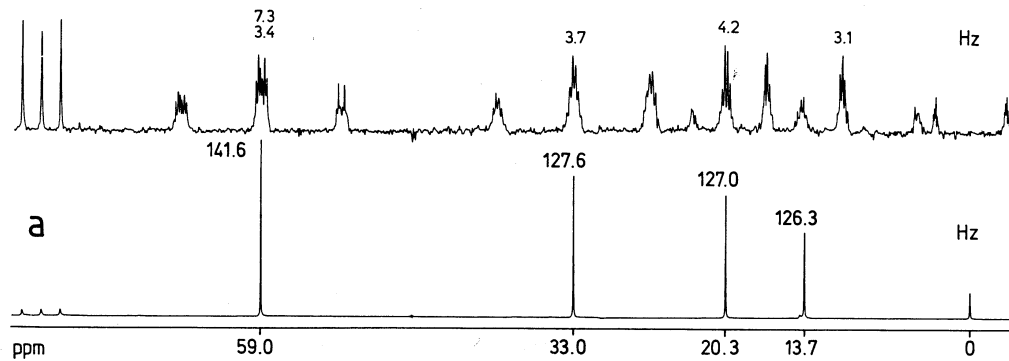
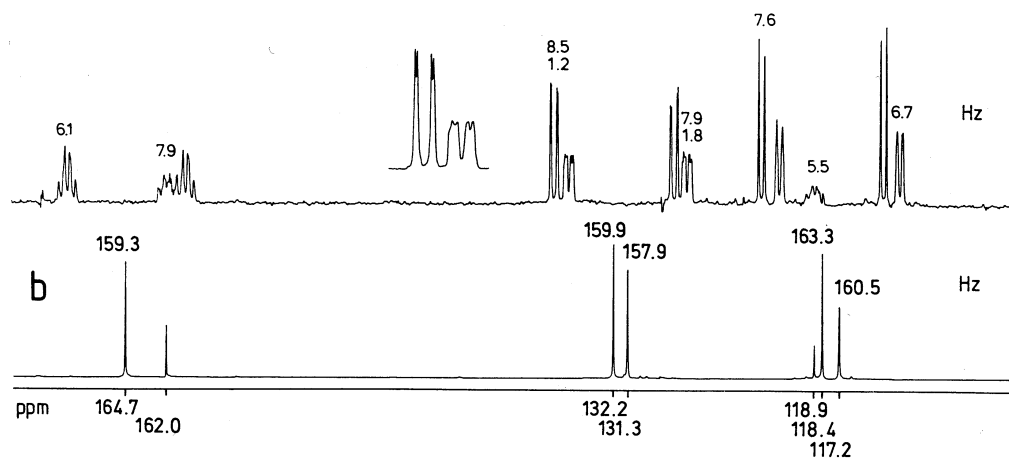
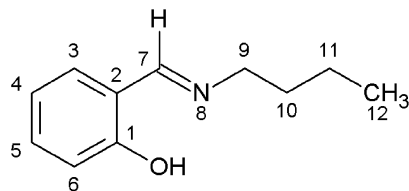
Draw the estimate of ^{13}C NMR spectrum (with and without ^1H decoupling):



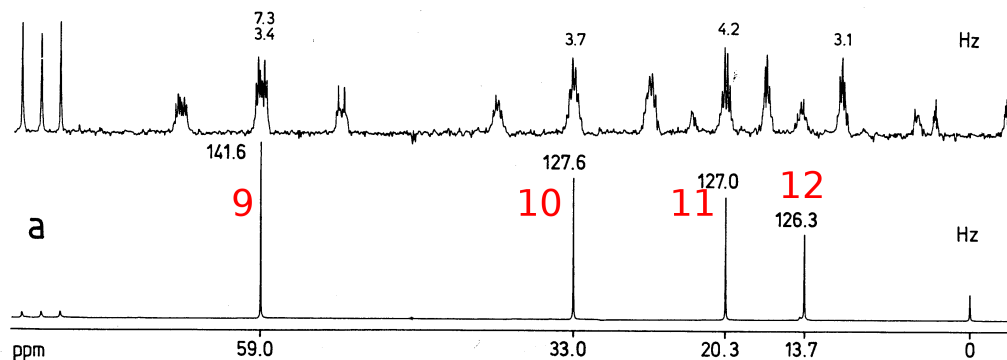
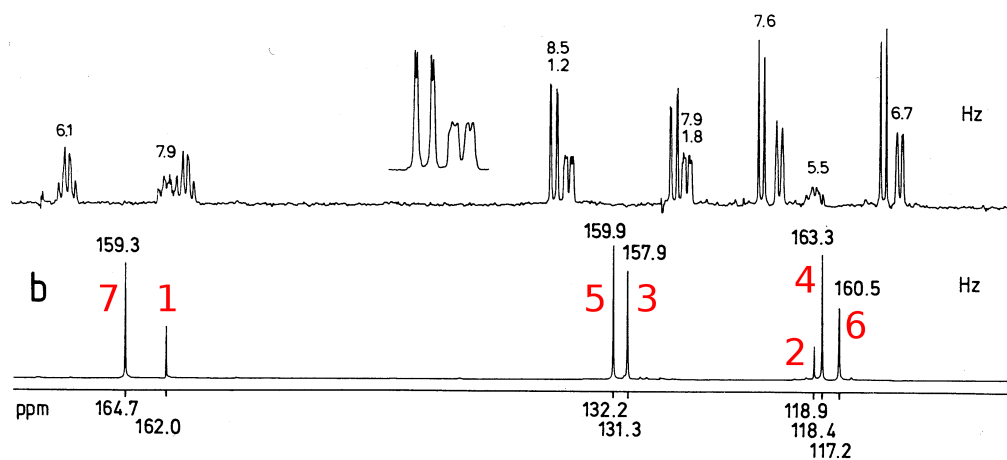
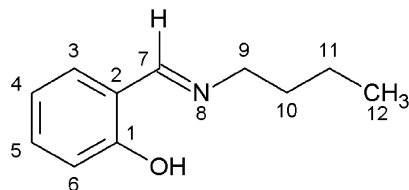
Draw the estimate of ^{13}C NMR spectrum (with and without ^1H decoupling):



1D ^{13}C -NMR 1



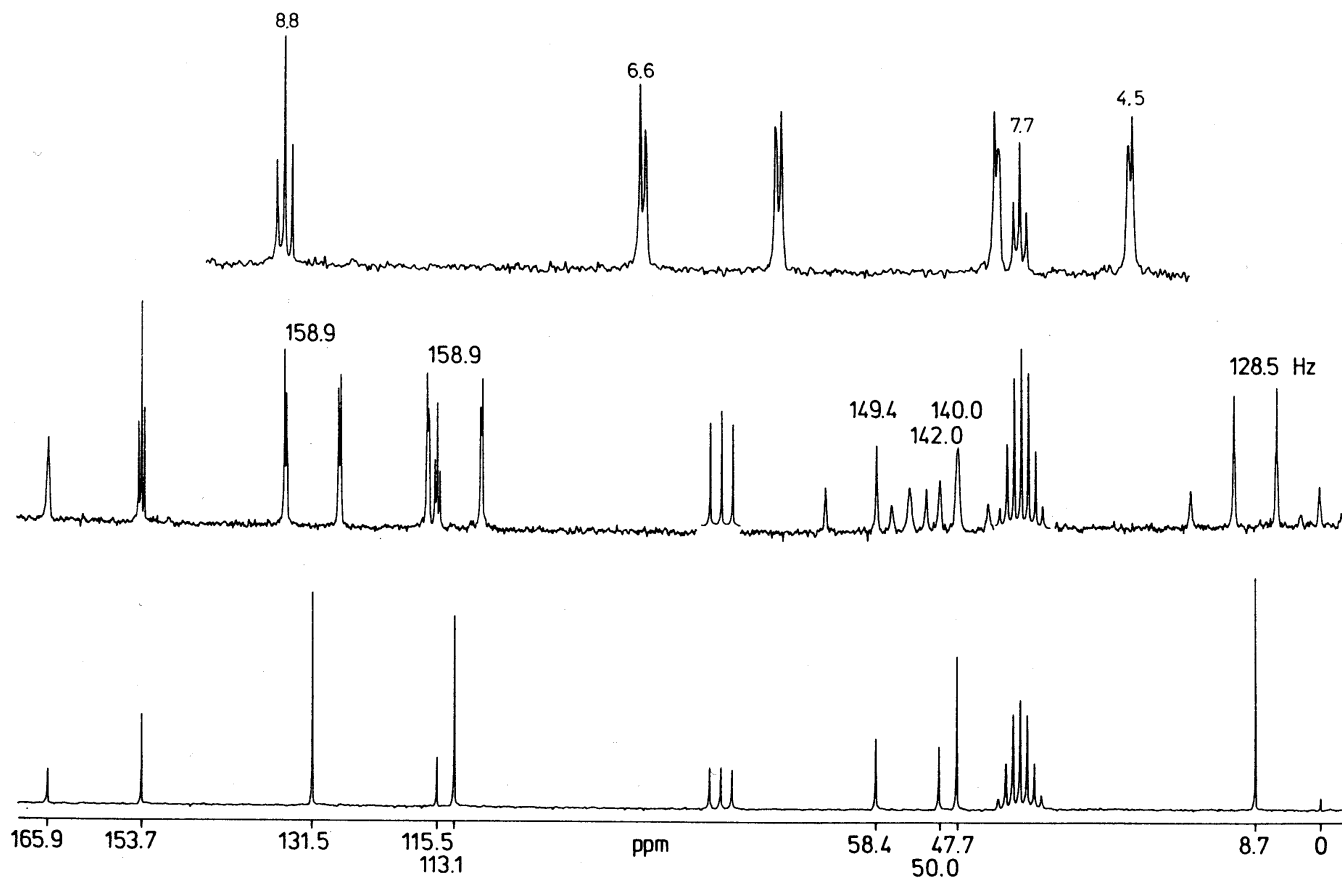
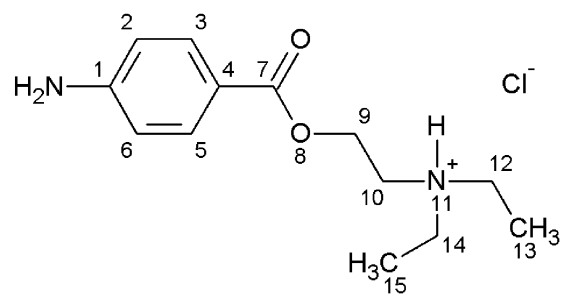
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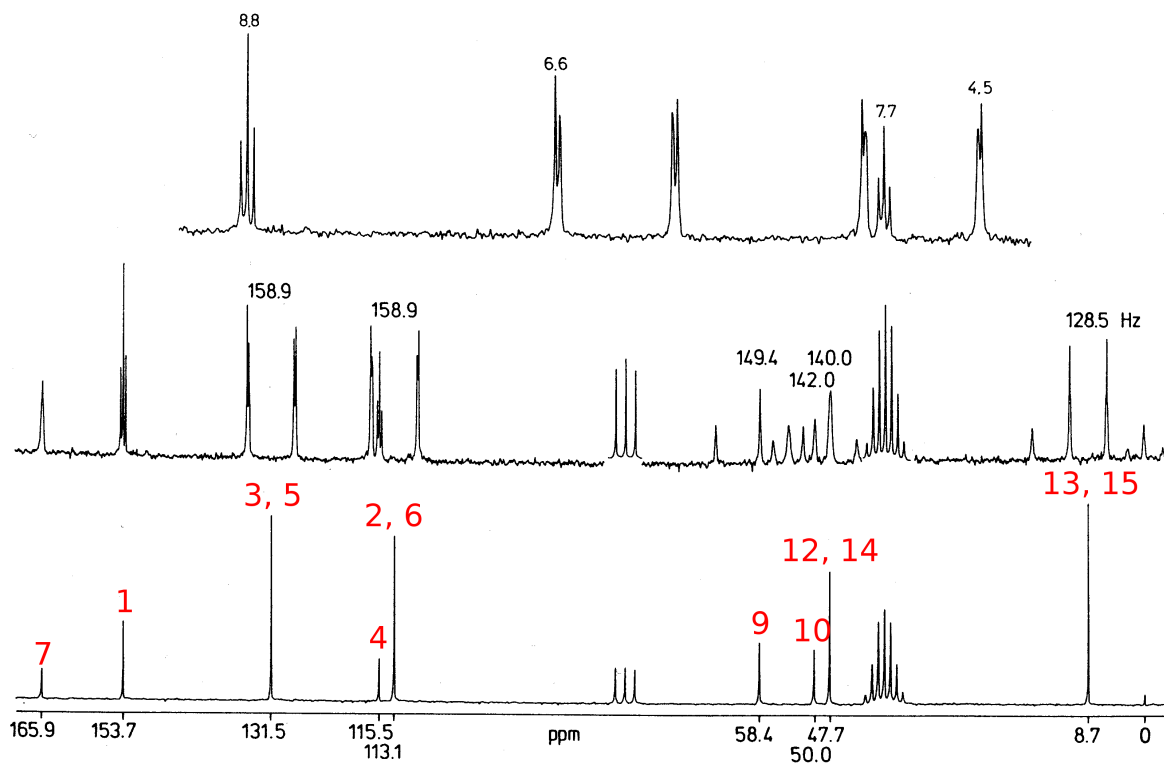
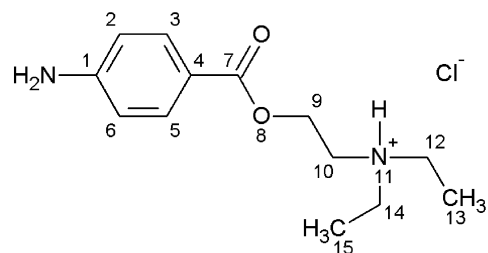
Notes:

- ▶ **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}C -NMR 2



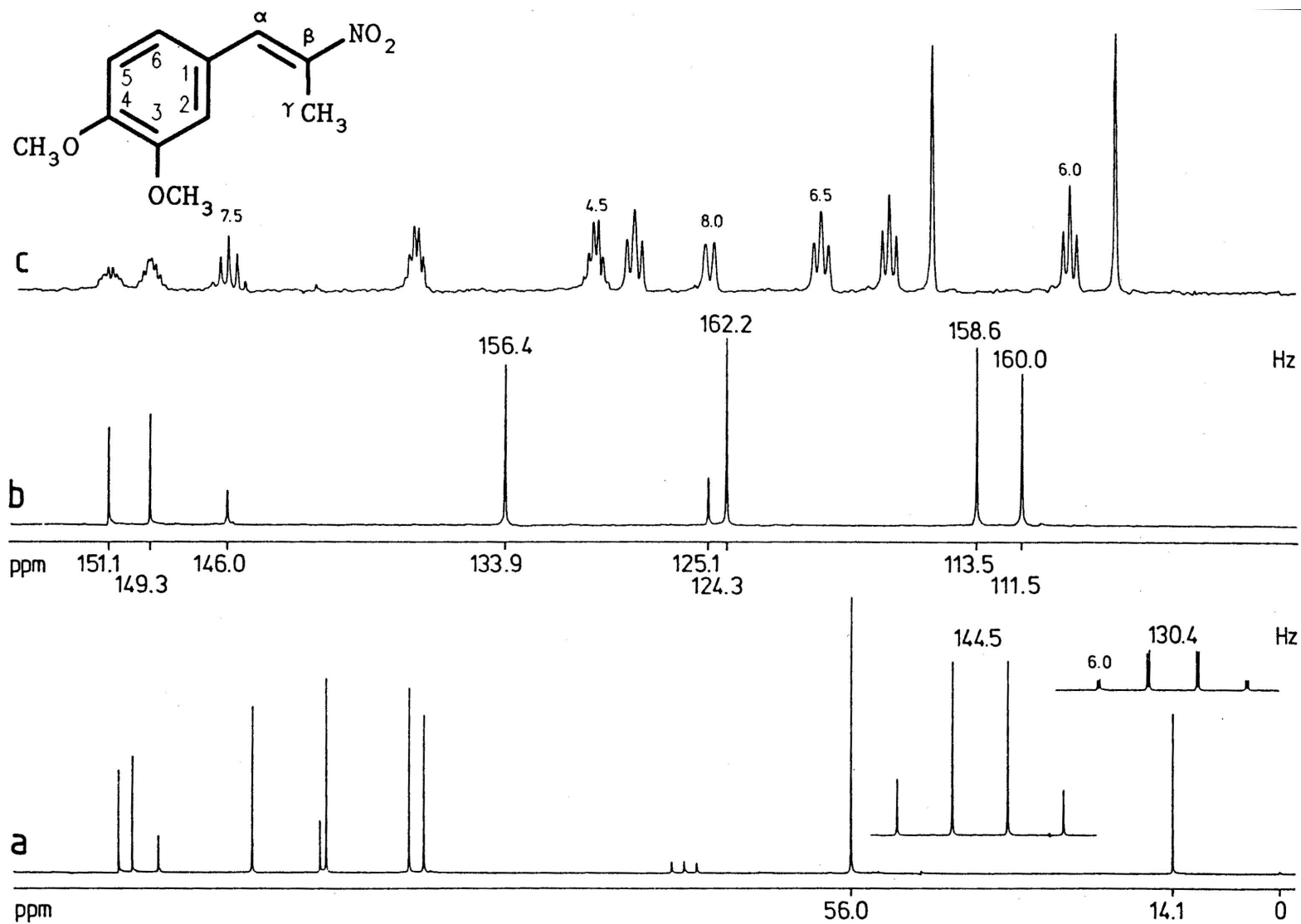
1D ^{13}C -NMR 2



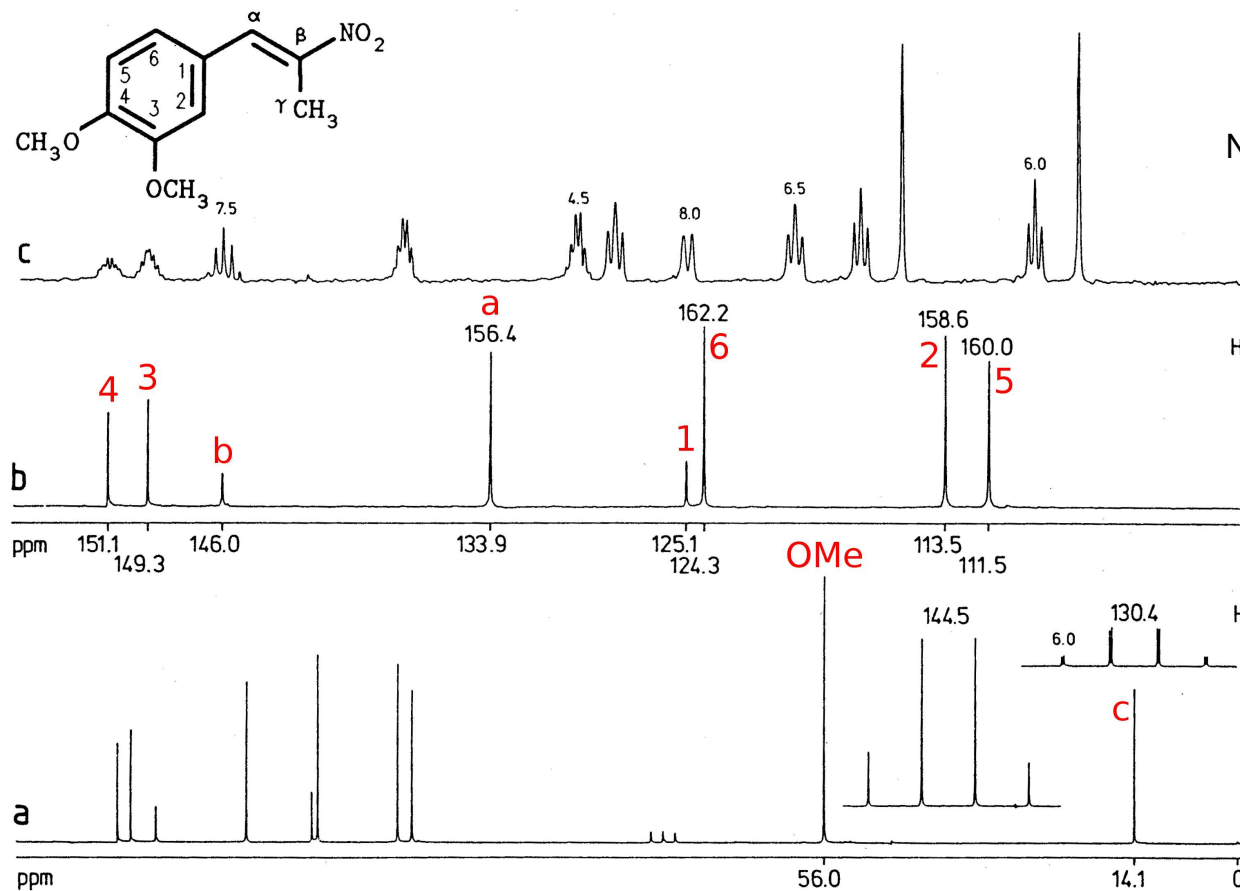
Notes:

- ▶ **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
- ▶ **C9** effect of esteric group, ? **C10** affected by NH exchange
- ▶ **C12/C14 + C13/C15** decaying effect of N^+

1D ^{13}C -NMR 3



1D ¹³C-NMR 3



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 (contraintuitive)
- ▶ quartets **OMe**, **C γ**

Next topic

Vector model and APT experiment