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

Jan Novotný
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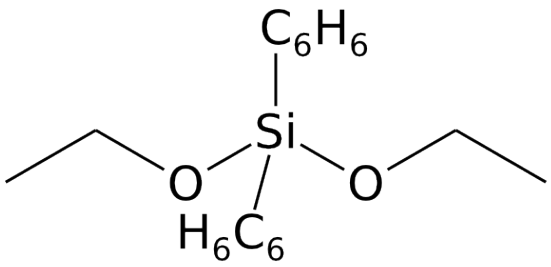
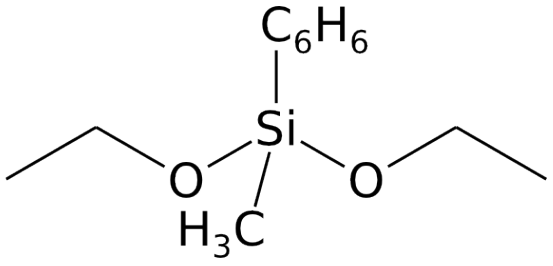
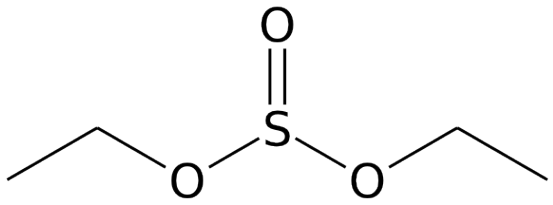
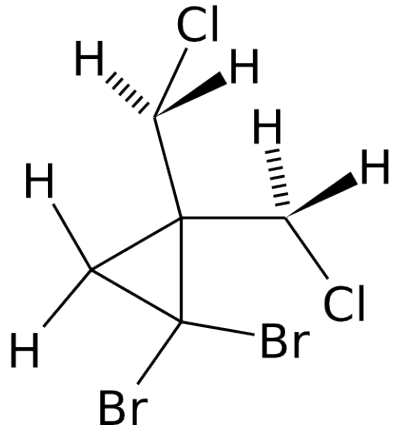
# Diastereotopicity[1]




[1] http://www.chem.wisc.edu/areas/reich/chem605/

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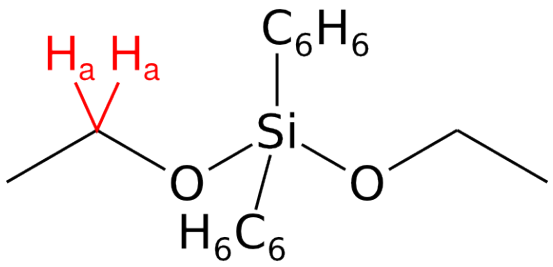


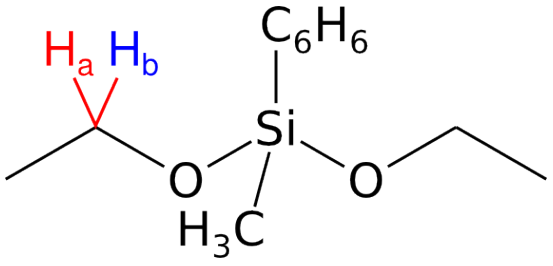


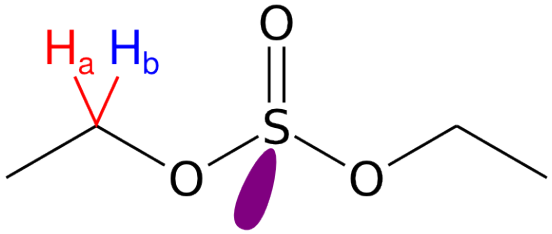


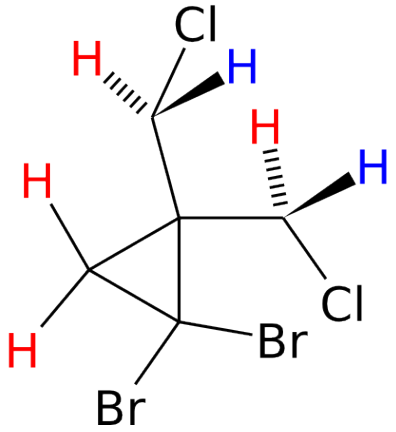


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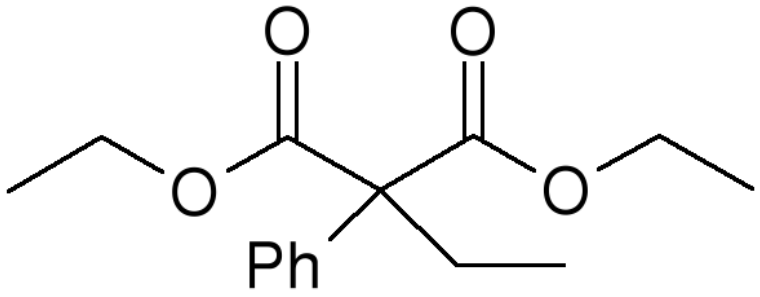
# Determine the number of nonequivalent $^{1}H$ signals :



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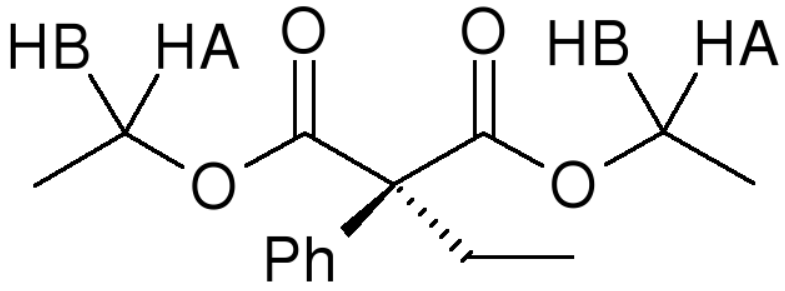
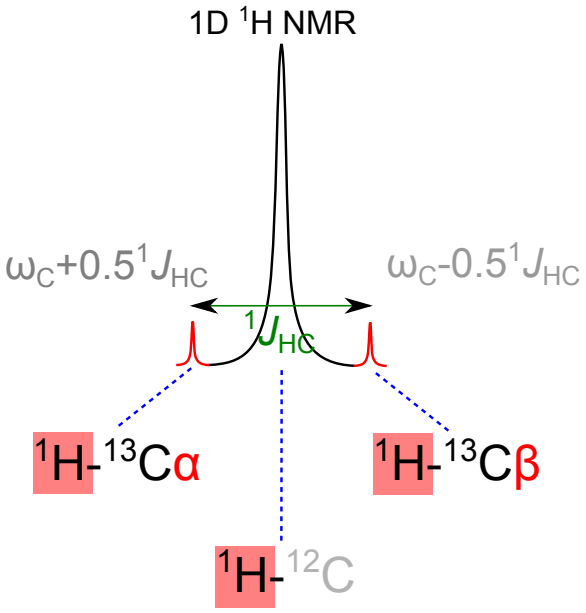
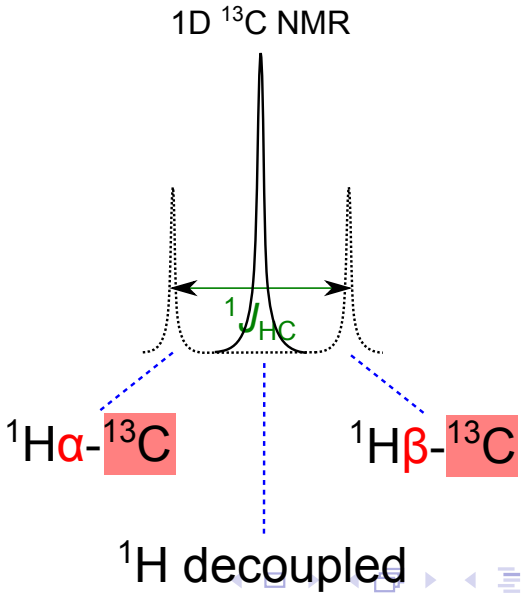


# $^{1}$H vs $^{13}$C NMR

| | $^{1}$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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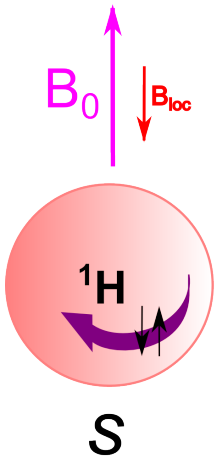
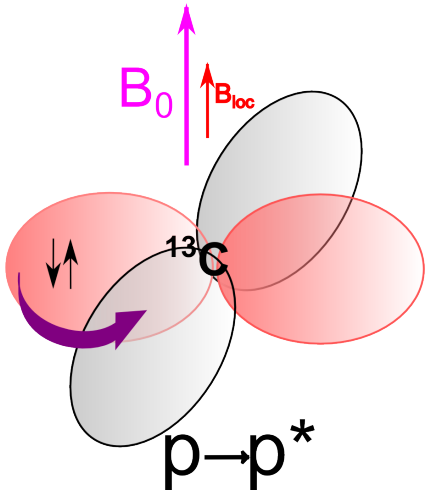
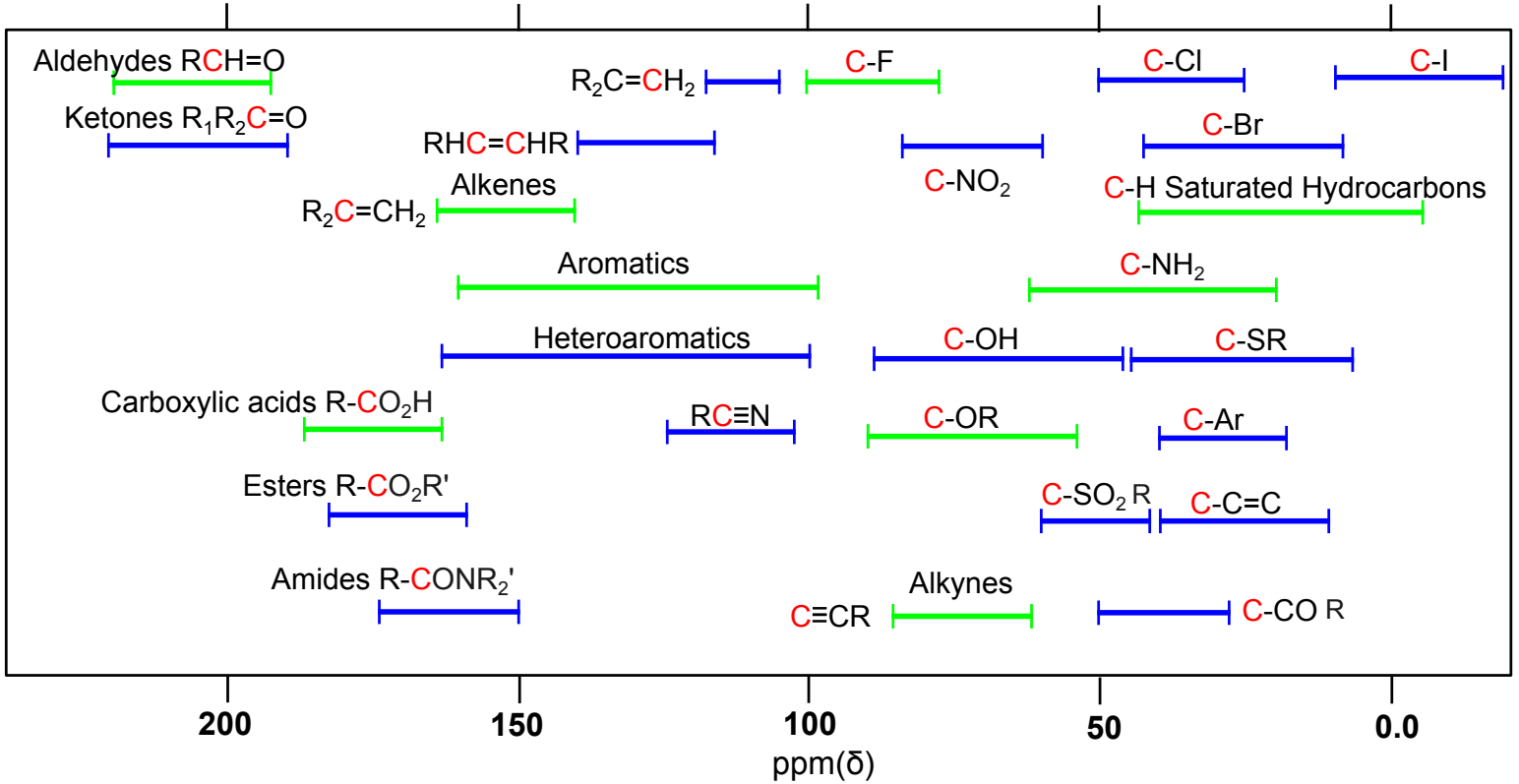


# Important regions of $^{13}C$ chemical shifts



## $^1J_{CH}$ 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

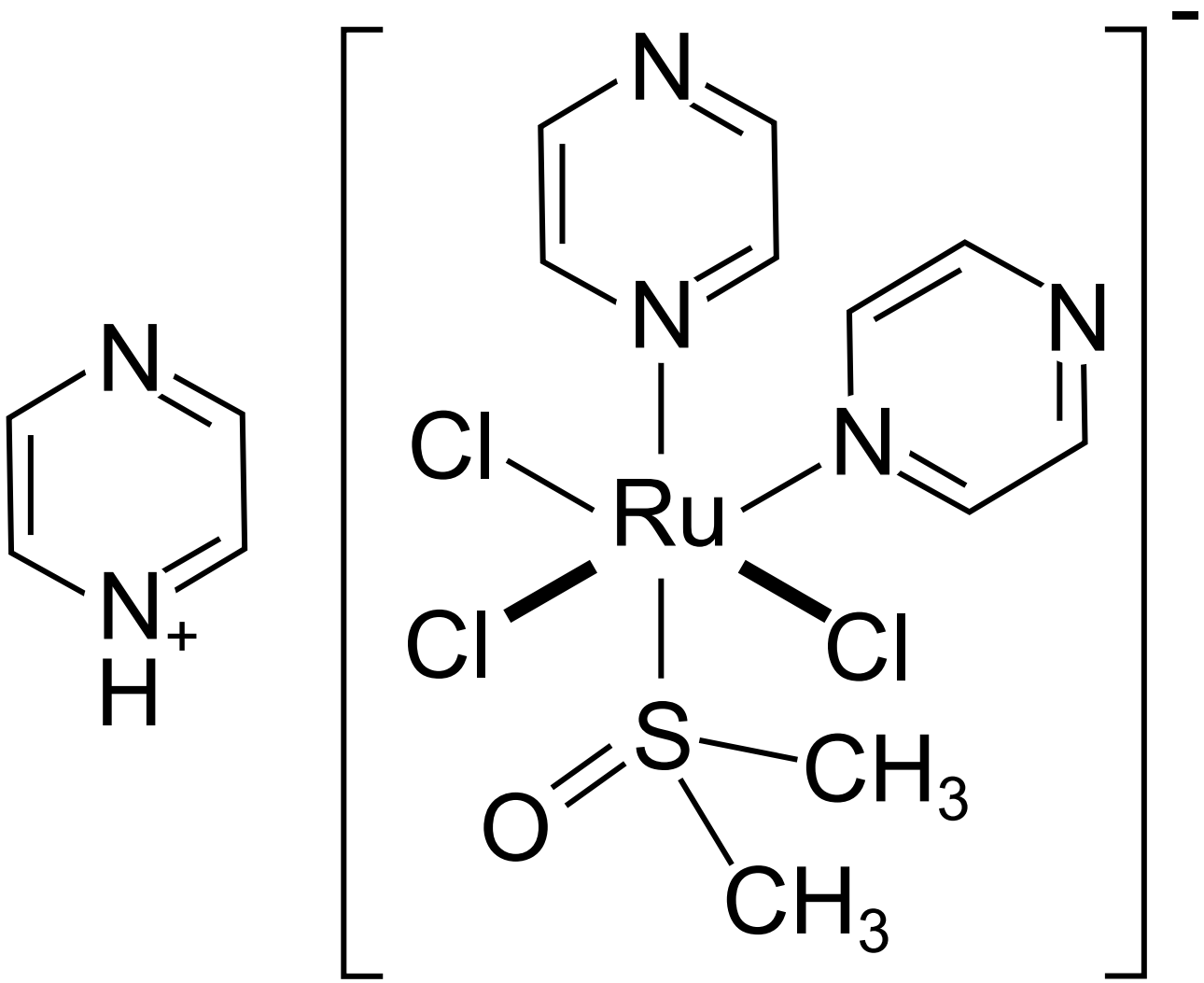
# Values of chemical shift of important solvents

| **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 | - |

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?



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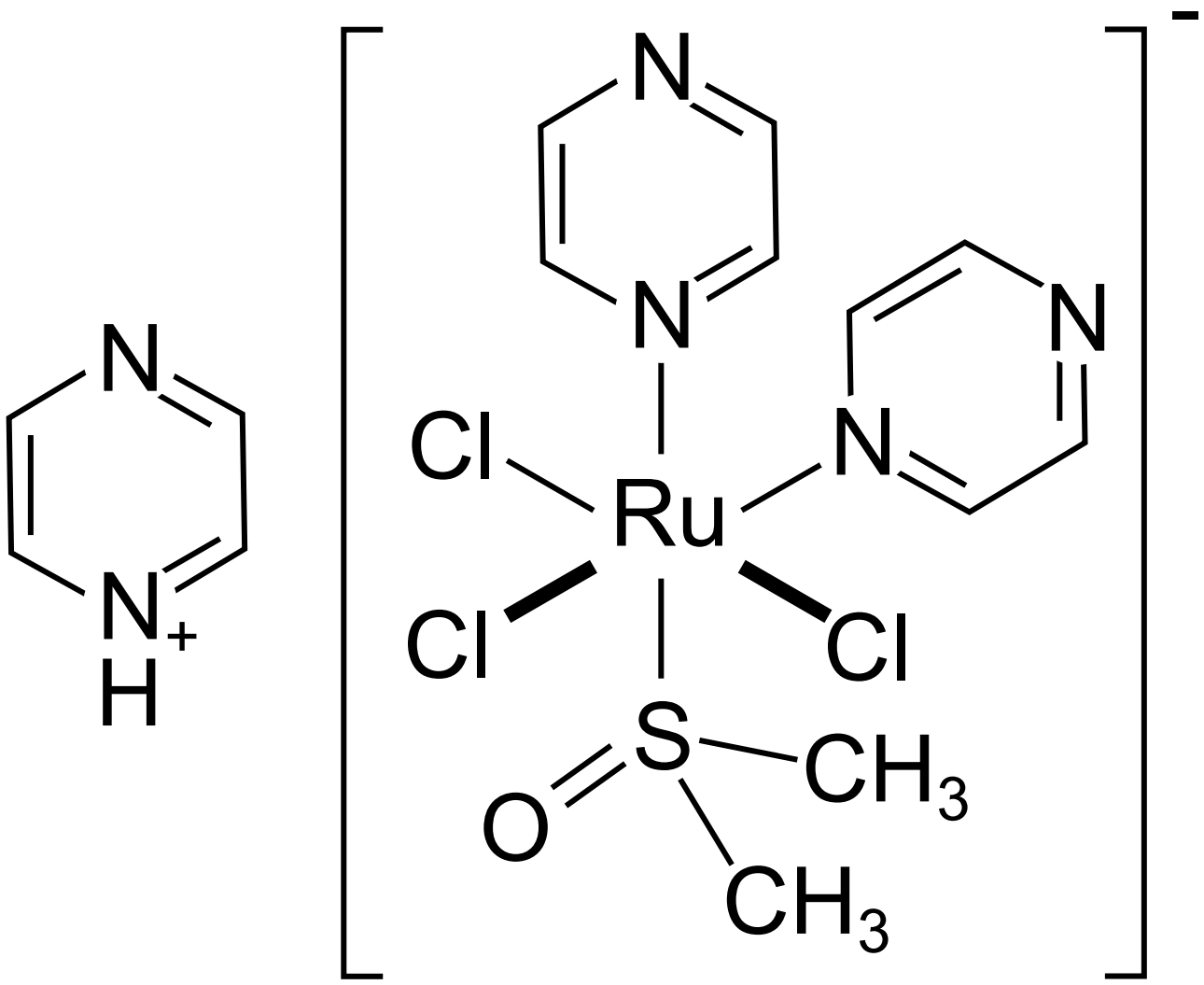
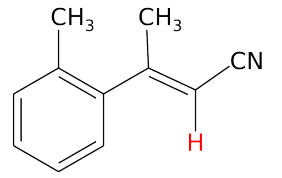
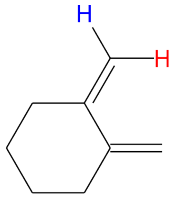


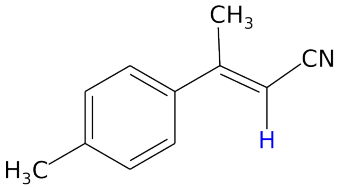
# Assign correct value of chemical shift to labelled NMR active atoms[1]:

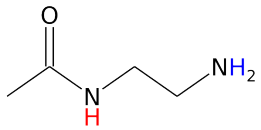



5.22 5.46

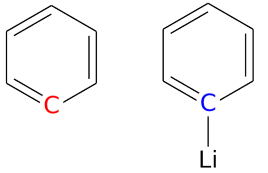



4.64 4.92

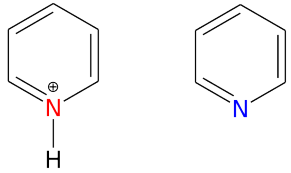


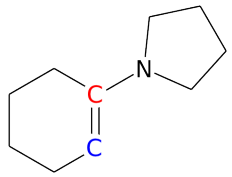

1.5 7.0



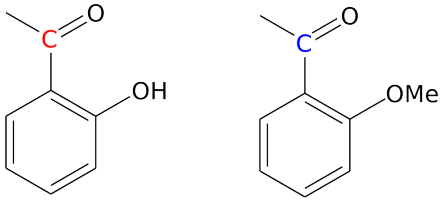

129 200



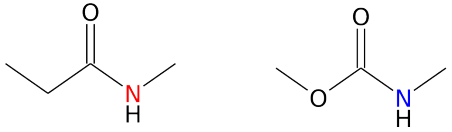

-166 -68




93 142




188 197

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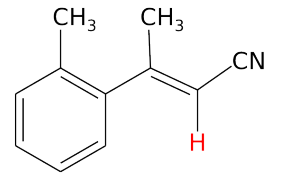


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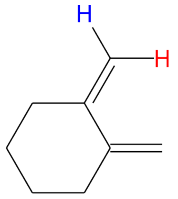


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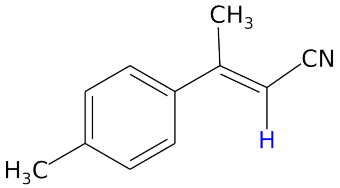


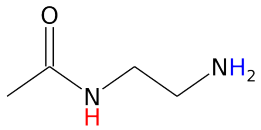


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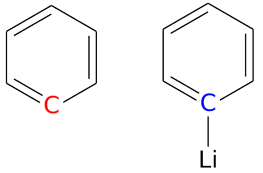
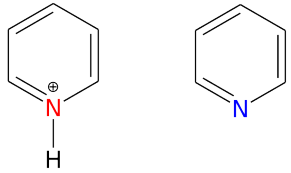
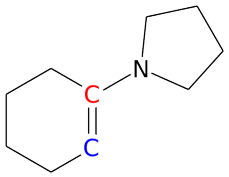


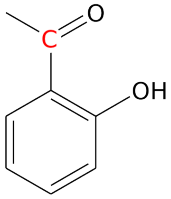

129 200

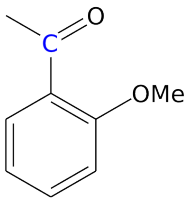



-166 -68

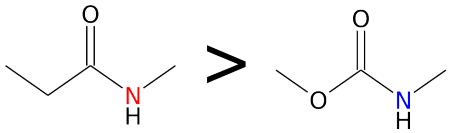



93 142




188 197

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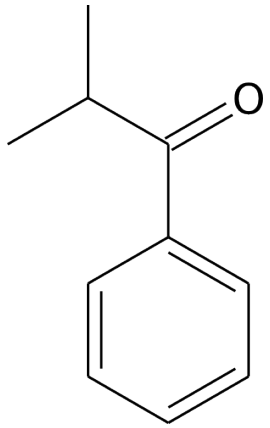
# Draw the estimate of $^{13}C$ NMR spectrum (with and without $^{1}H$ decoupling):



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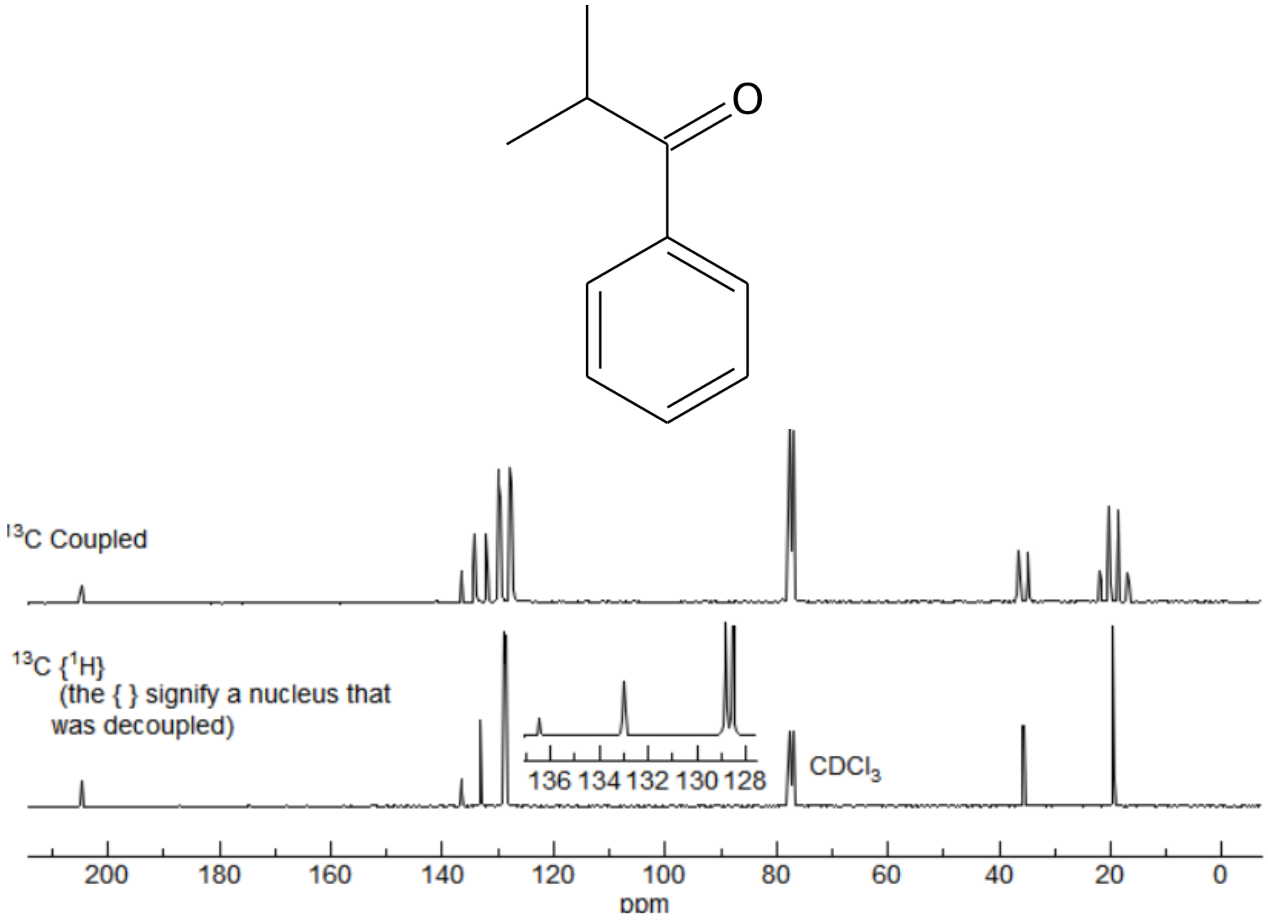

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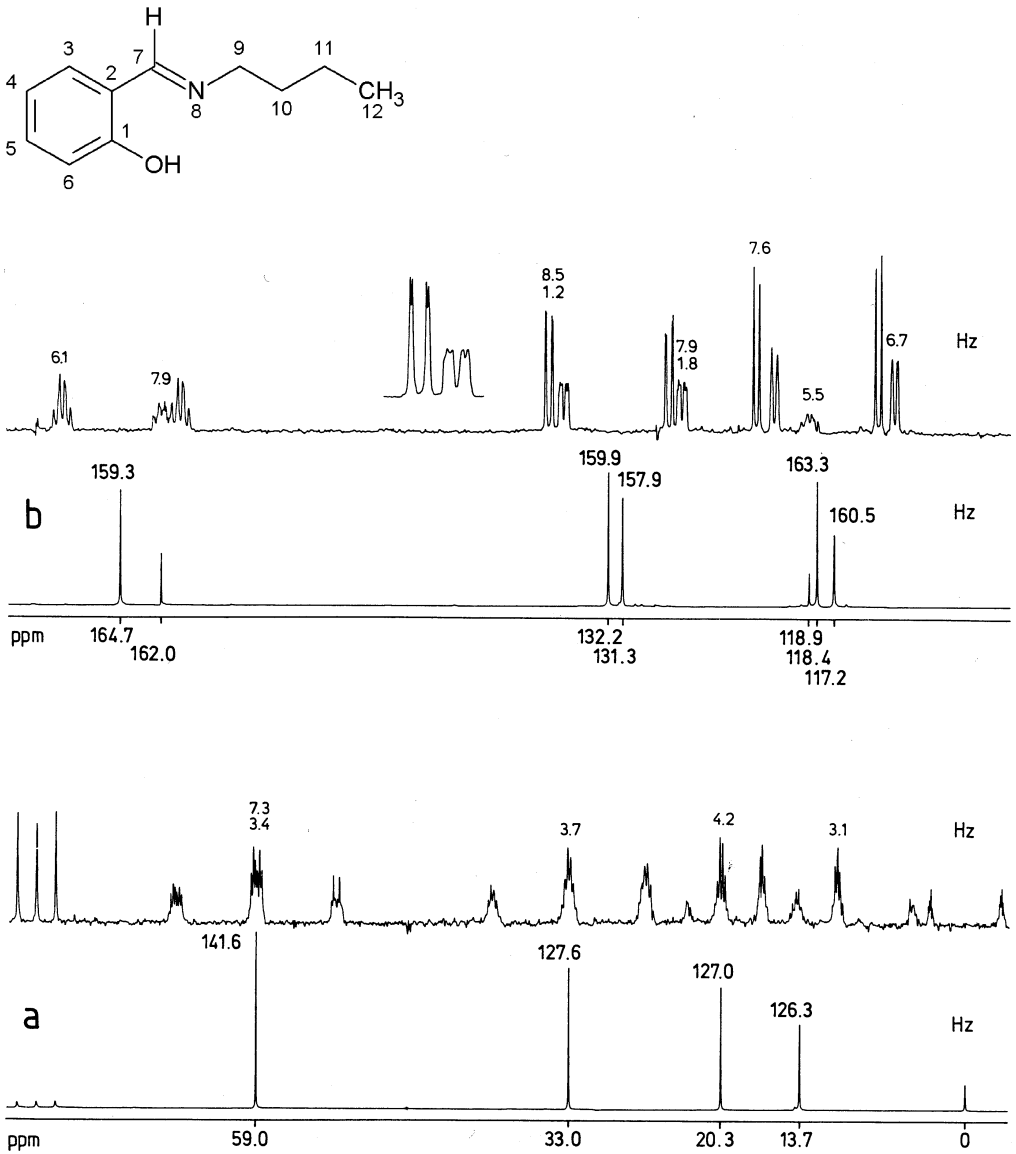
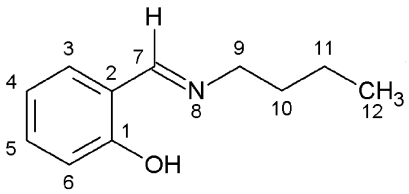
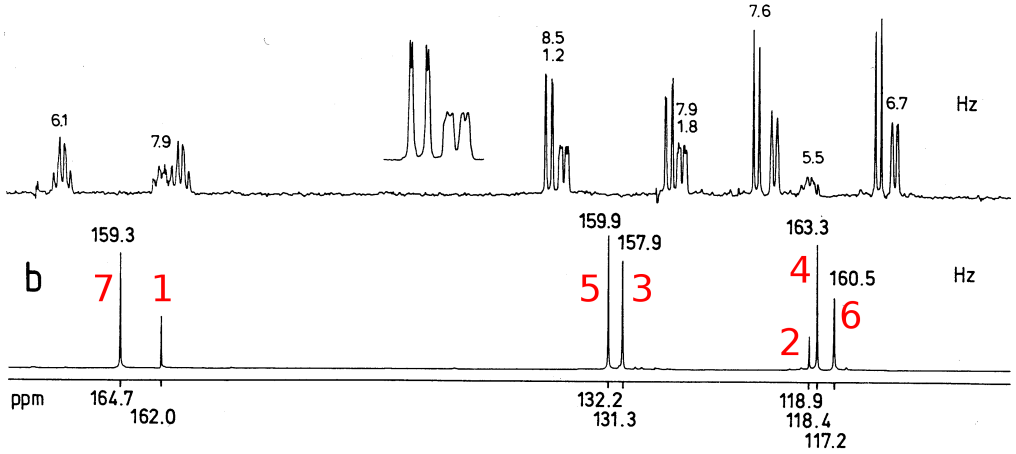
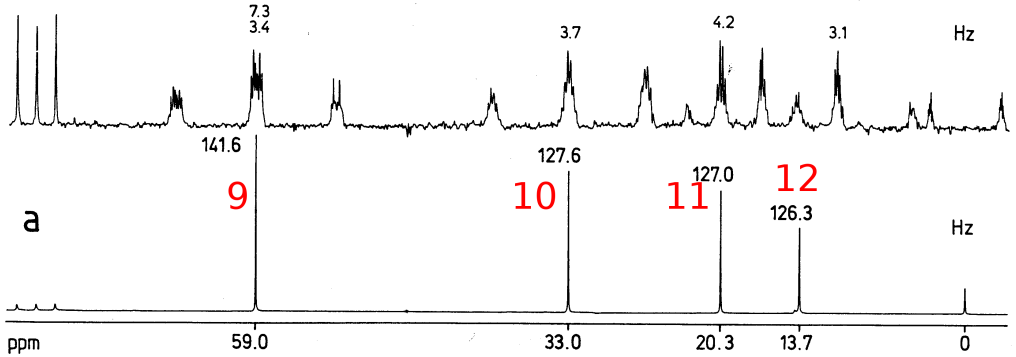

H
3
7
9
11
4
2
N
CH3
8
10
12
1
5
OH
6
7.6
8.5
1.2
6.1
7.9
7.9
1.8
6.7
Hz
5.5
159.3
159.9
157.9
163.3
b
160.5
Hz
ppm
164.7
162.0
132.2
131.3
118.9
118.4
117.2
7.3
3.4
3.7
4.2
3.1
Hz
141.6
127.6
127.0
126.3
a
Hz
ppm
59.0
33.0
20.3
13.7
0

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



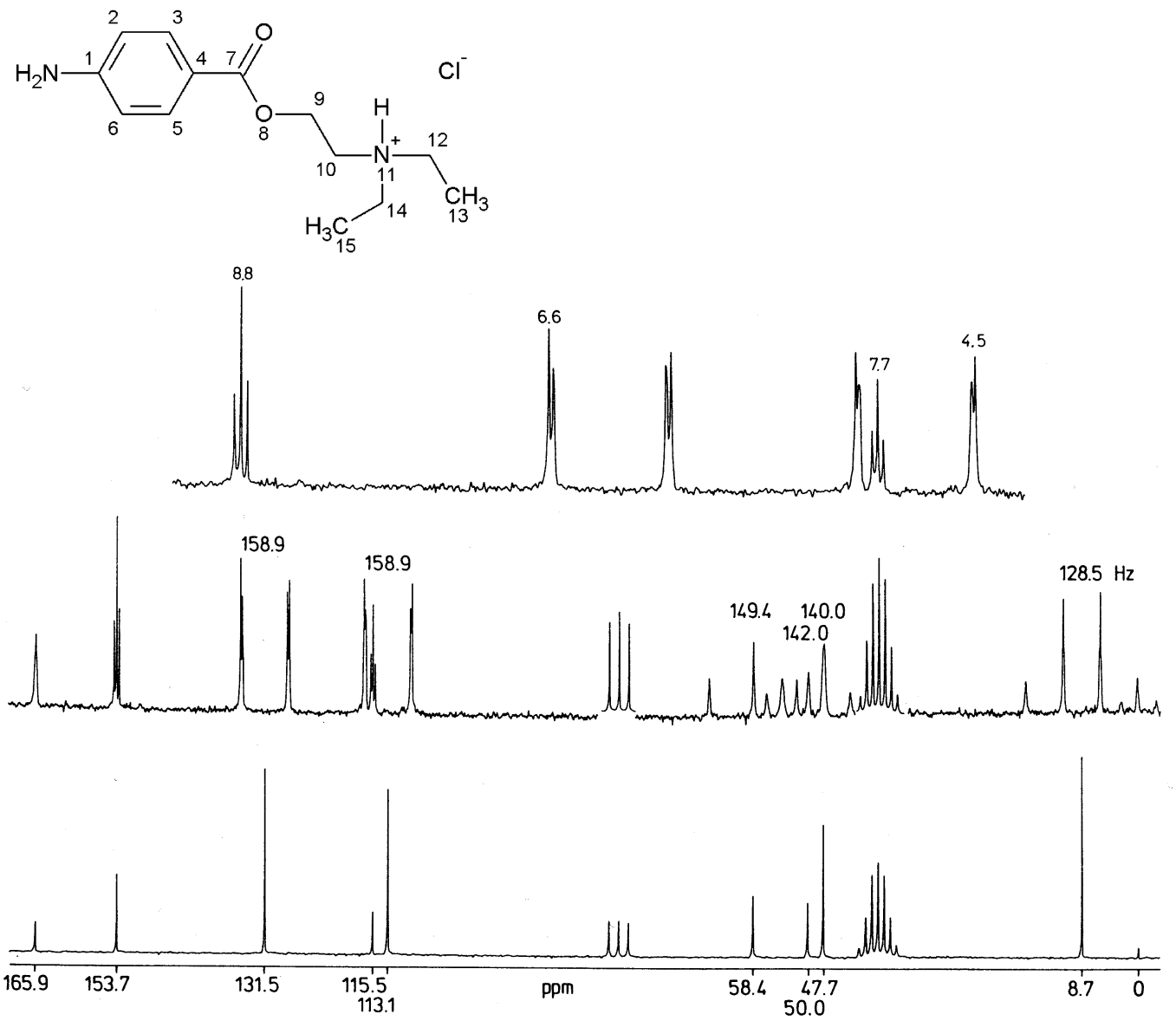



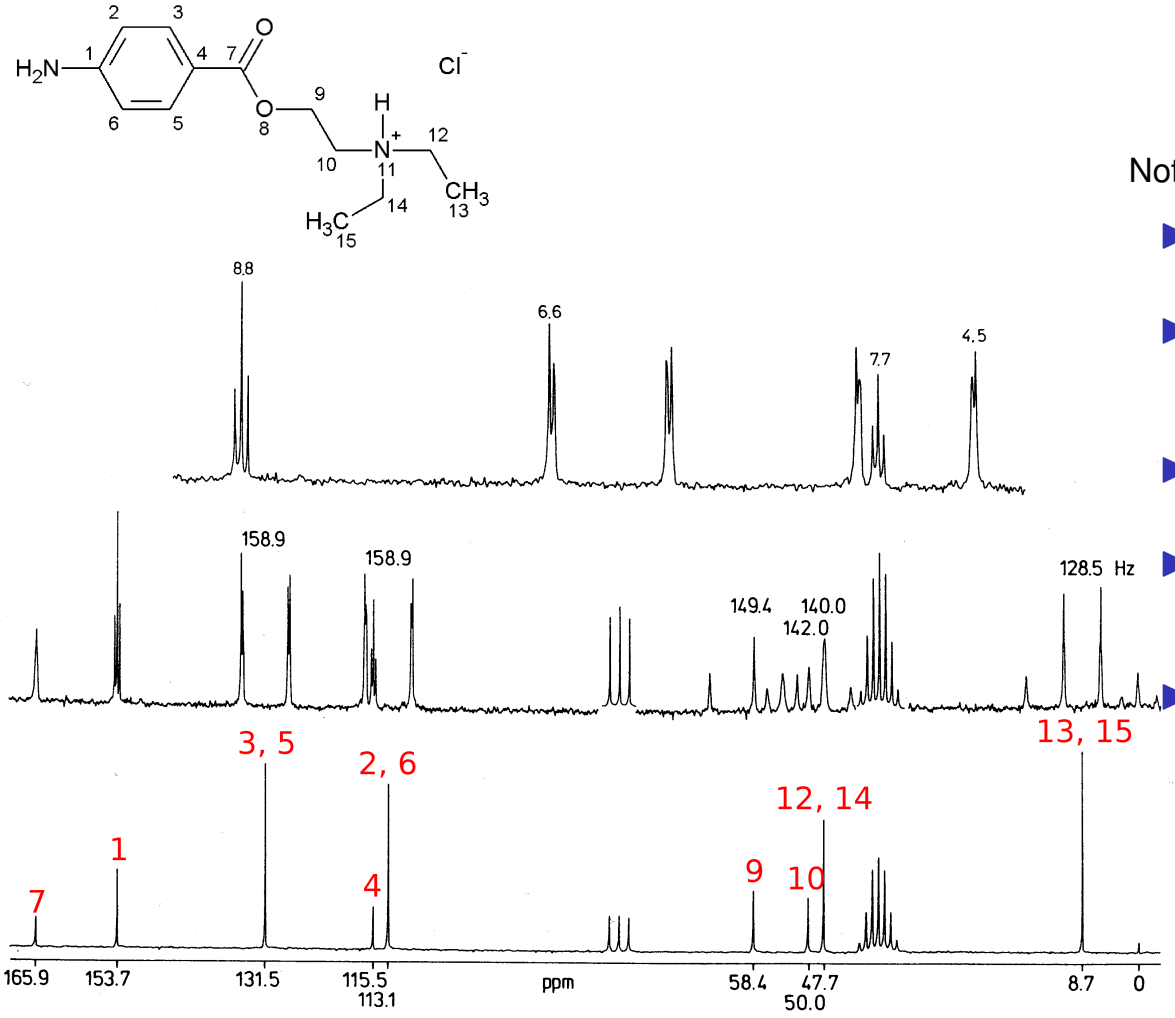

Notes:

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

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


2
3
1
4
7
O
$H_2N$
$Cl^-$
9
H
6
5
O
8
12
N
+
10
11
$CH_3$
13
14
$H_3C$
15
8.8
6.6
7.7
4.5
158.9
158.9
149.4
140.0
142.0
128.5 Hz
165.9
153.7
131.5
115.5
113.1
ppm
58.4
47.7
50.0
8.7
0

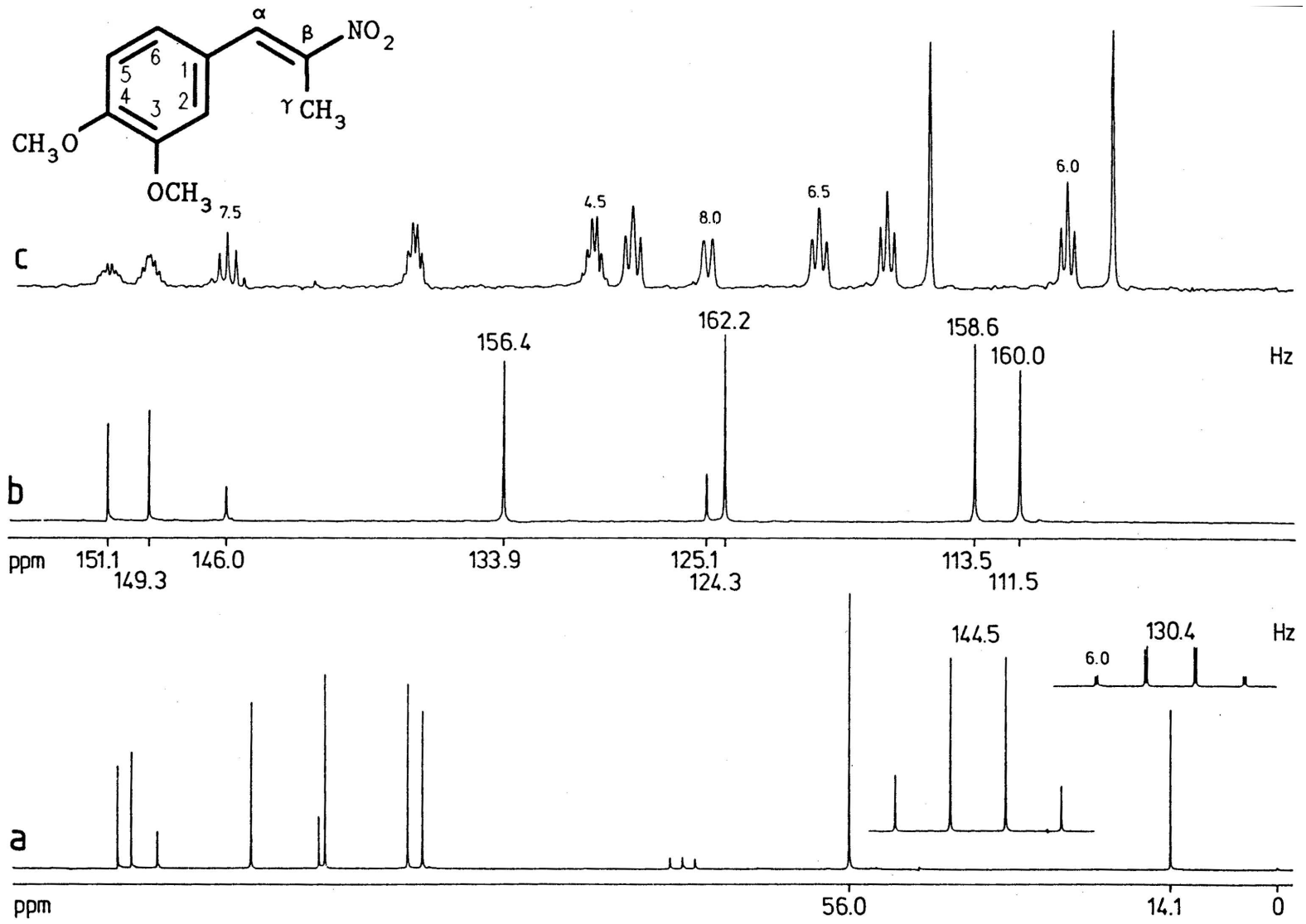
# 1D $^{13}$C-NMR 2



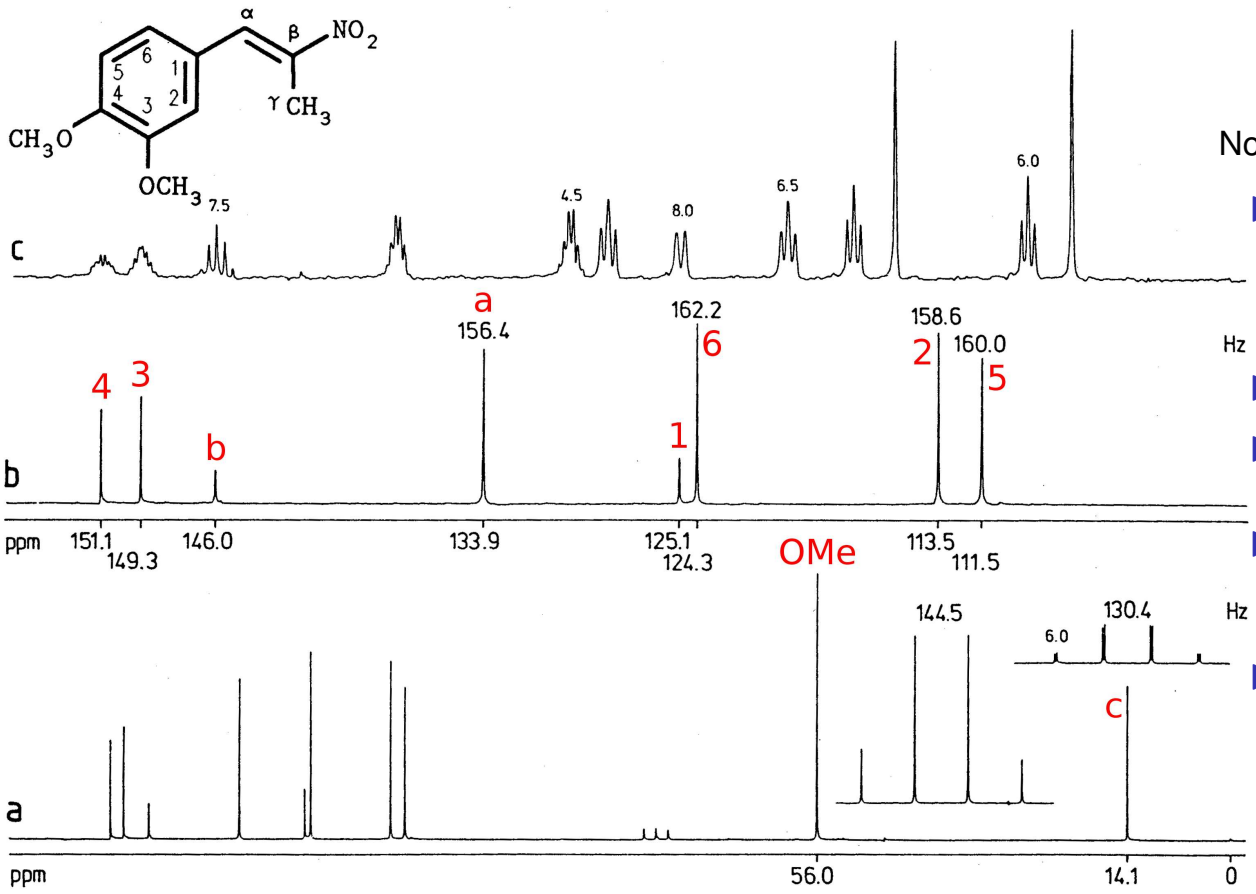

Notes:

- **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


α
β
NO2
γ CH3
CH3O
OCH3
7.5
4.5
8.0
6.5
6.0
c
156.4
162.2
158.6
160.0
Hz
b
ppm
151.1
149.3
146.0
133.9
125.1
124.3
113.5
111.5
144.5
130.4
6.0
Hz
a
ppm
56.0
14.1
0

# 1D $^{13}$C-NMR 3




Notes:

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

# Next topic

Vector model and APT experiment