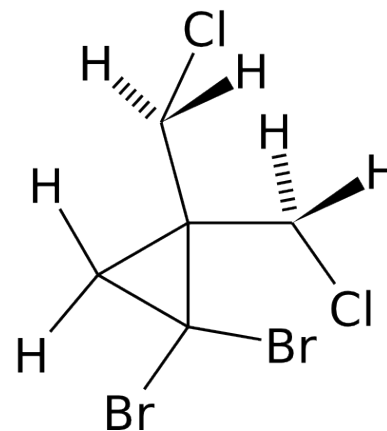
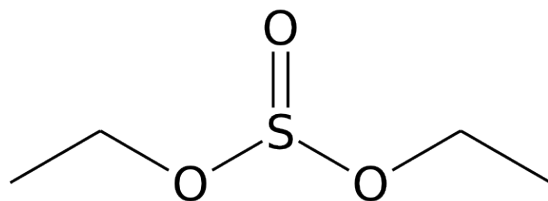
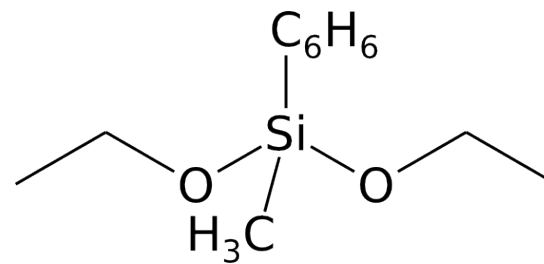
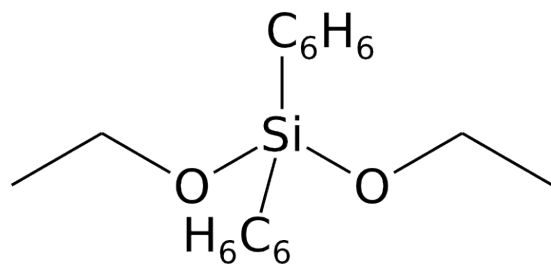


C8953  
NMR structural analysis - seminar  
1D  $^{13}\text{C}$ -NMR

Matúš Durec  
211166@mail.muni.cz

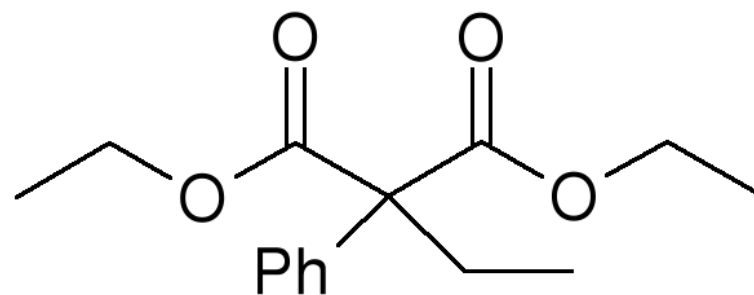
March 6, 2017

# Diastereotopicity<sup>1</sup>



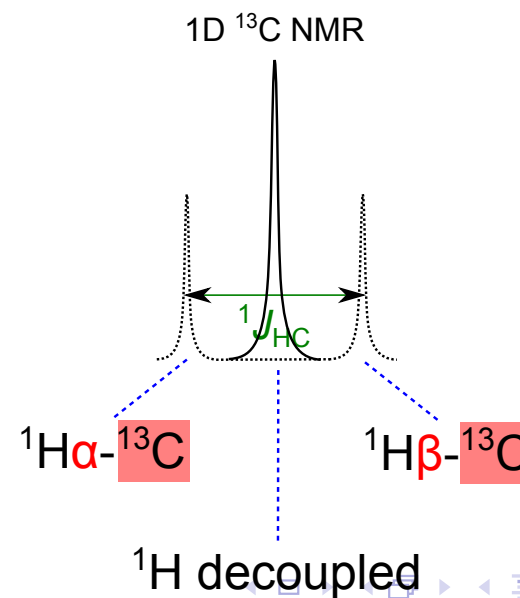
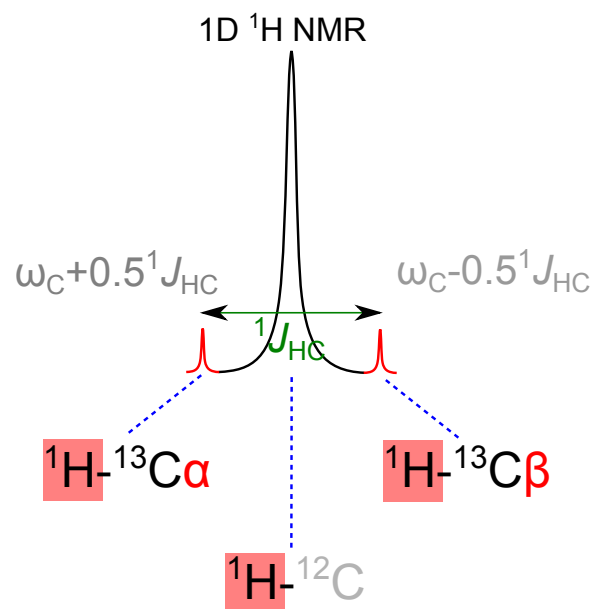
<sup>1</sup><http://www.chem.wisc.edu/areas/reich/chem605/>

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



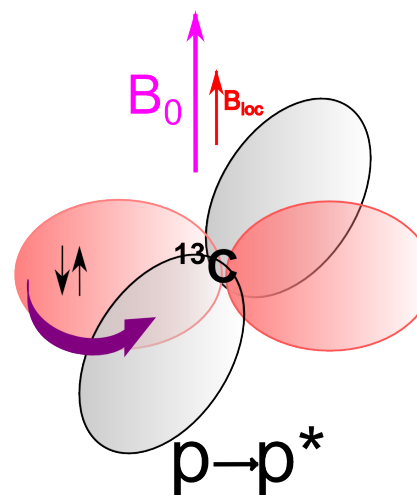
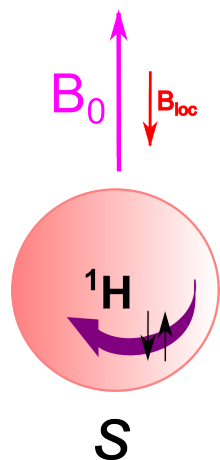
# $^1\text{H}$ vs $^{13}\text{C}$ NMR

	$^1\text{H}$	$^{13}\text{C}$
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 ✗ decoupling

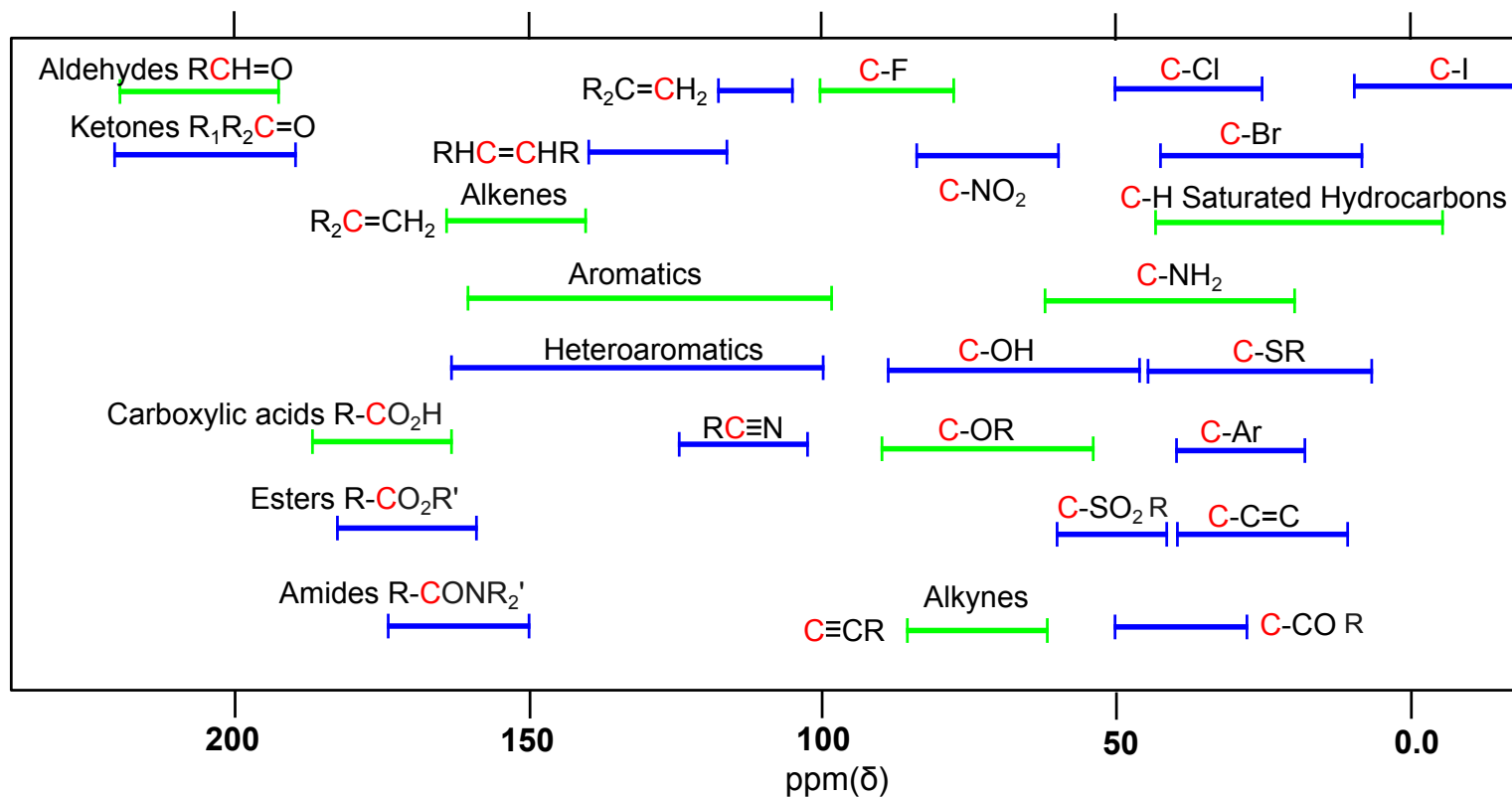


# $^1\text{H}$ vs $^{13}\text{C}$ NMR

	$^1\text{H}$	$^{13}\text{C}$
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 ✗ decoupling



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

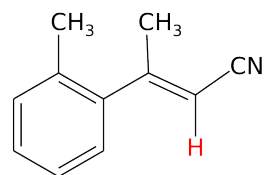
<b>Abbr.</b>	<b>Formula</b>	<b><math>^1\text{H}</math></b>	<b><math>^{13}\text{C}</math></b>
<b>ACN</b>	$\text{CH}_3\text{CN}$	1.9	118
<b>Benzene</b>	$\text{C}_6\text{H}_6$	7.2	128
	$\text{CHCl}_3$	7.2	77
<b>DCM</b>	$\text{CH}_2\text{Cl}_2$	5.3	54
<b>DMF</b>	$(\text{CH}_3)_2\text{NCHO}$	2.9, 8.0	32, 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:

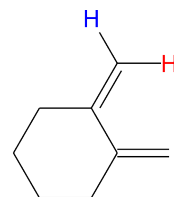
$\text{CHCl}_3$  - **1.6**, ACN - **2.1**, DMSO - **3.3**, MeOH - **4.9**



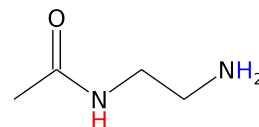
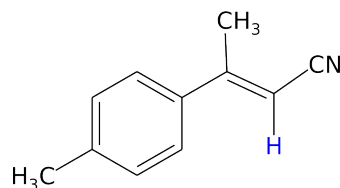
# Assign correct value of chemical shift to labelled NMR active atoms<sup>1</sup>:



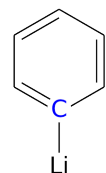
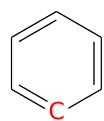
5.22 5.46



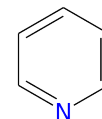
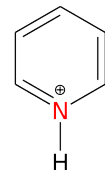
4.64 4.92



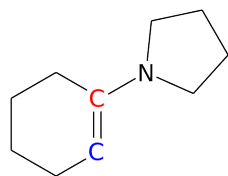
1.5 7.0



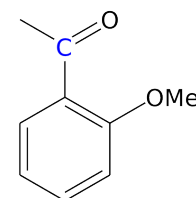
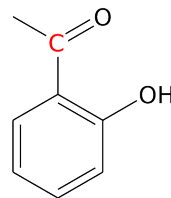
129 200



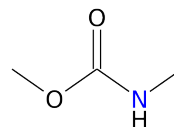
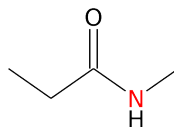
-166 -68



93 142

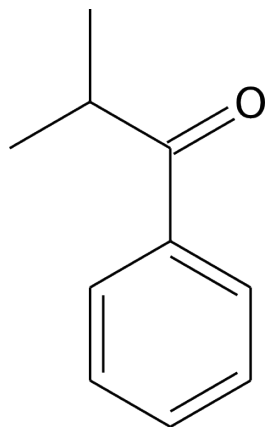


188 197

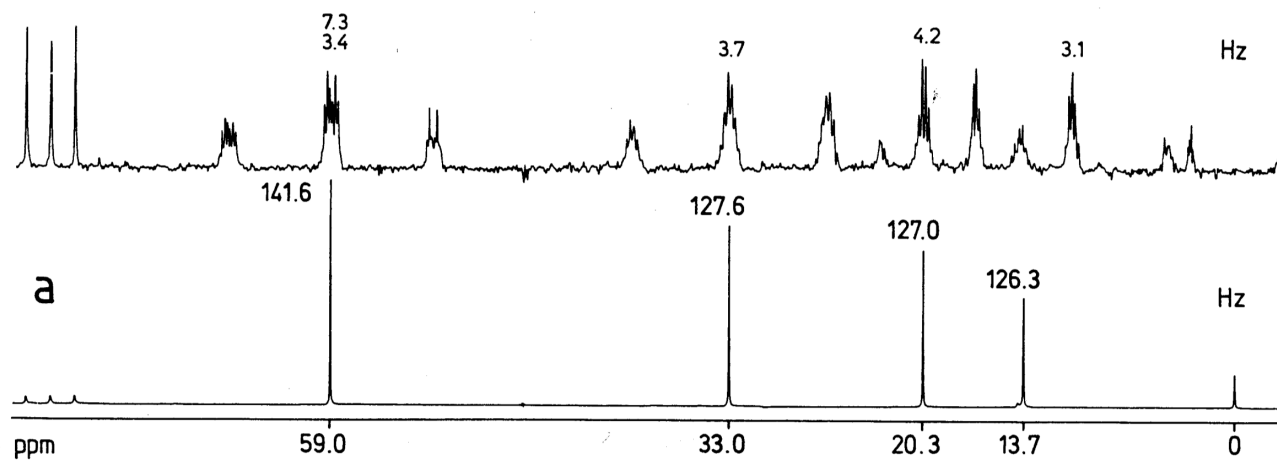
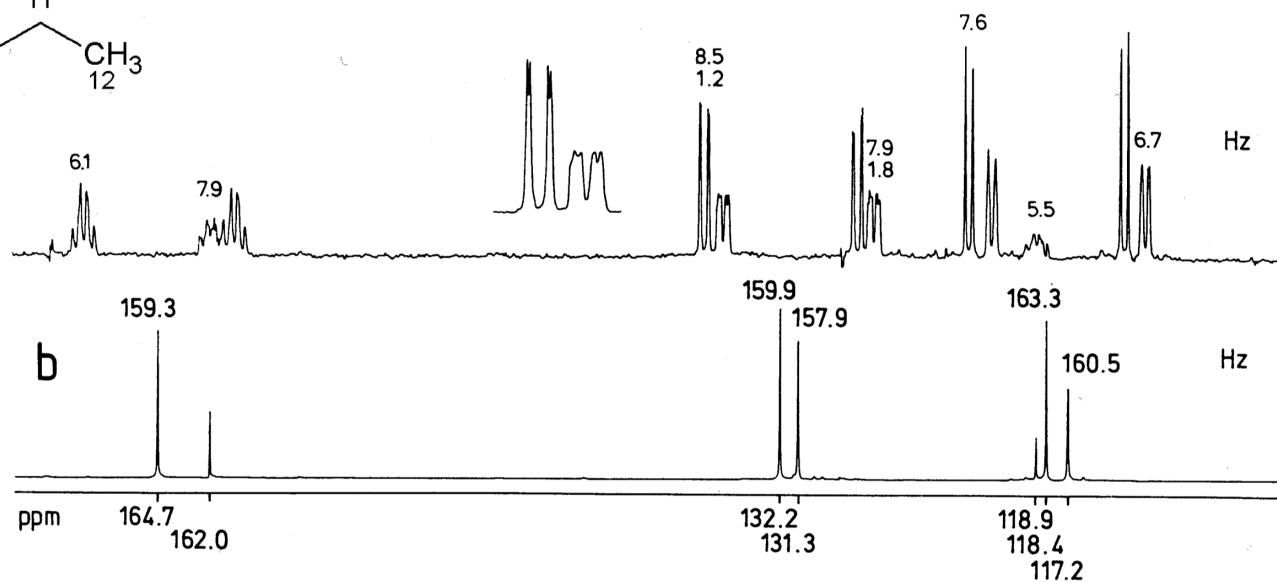
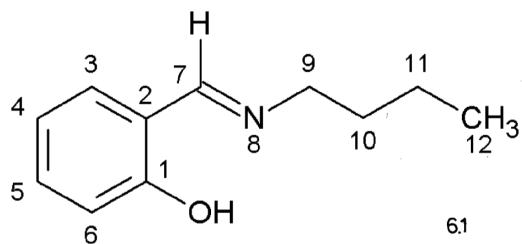


<sup>1</sup><http://www.chem.wisc.edu/areas/reich/chem605/>

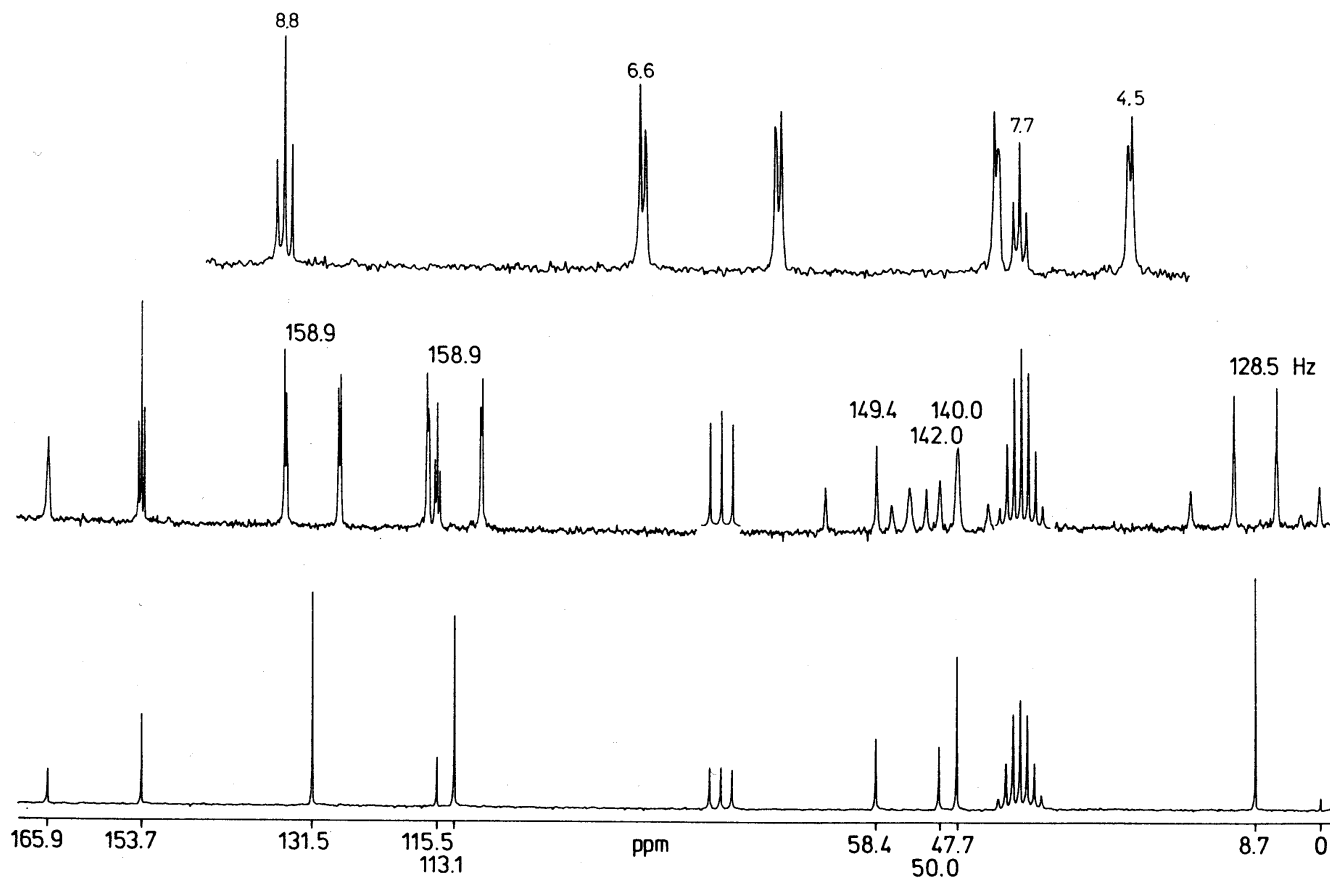
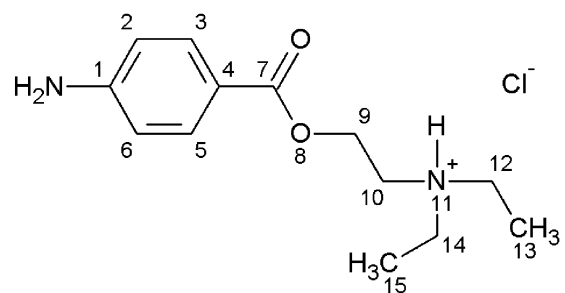
Draw the estimate of  $^{13}\text{C}$  NMR spectrum (with and without  $^1\text{H}$  decoupling):



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



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





# Next topic

## Vector model and APT experiment