C8953
NMR structural analysis - seminar
Vector model of NMR experiments + 1D spectra

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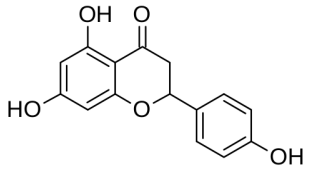
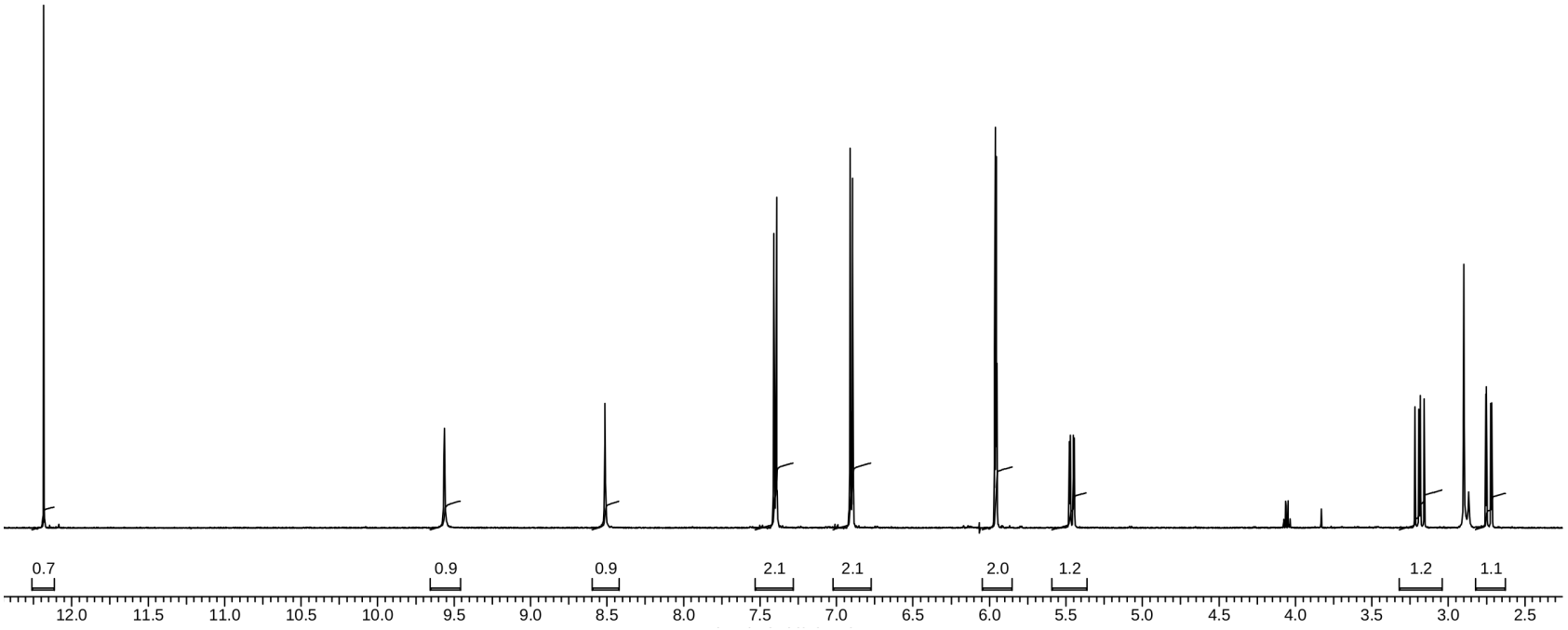
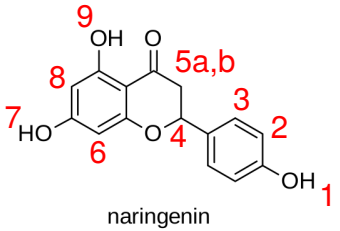
^{1}H NMR spectrum of naringenine in d_6-acetone



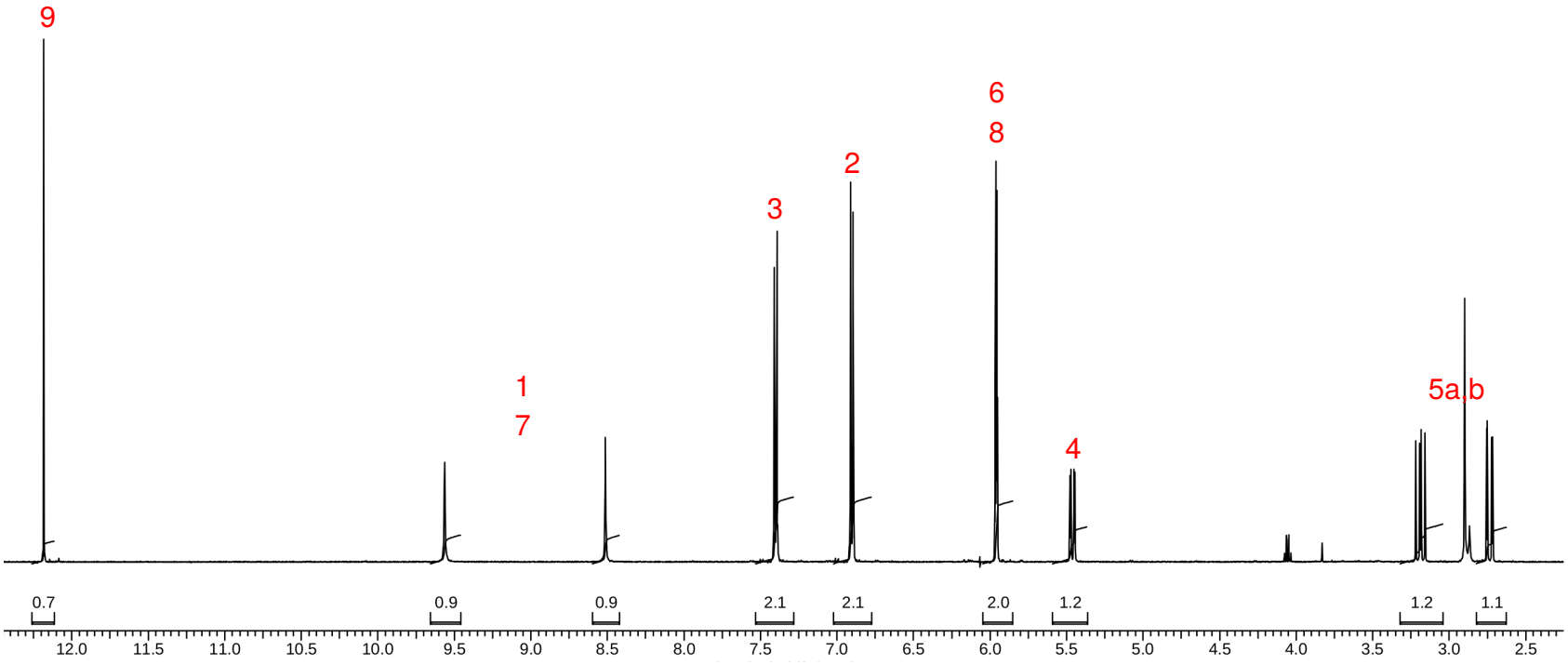
naringenin



^{1}H NMR spectrum of naringenine in d_6-acetone



naringenin



Basics of 1D FT spectroscopy

Draw the expected vector model of following simple pulse sequences (right-handed system, B_0 in $+z$ direction:)

- 90_{-x} :
- 90_{+y} – $\Omega\tau = \pi/2$:
- 90_{+x} – $\Omega\tau = \pi/3$ – 180_{+x} – $\Omega\tau = \pi/3$:
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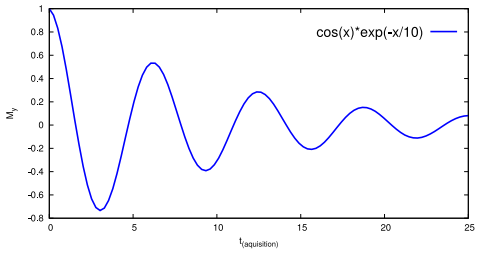
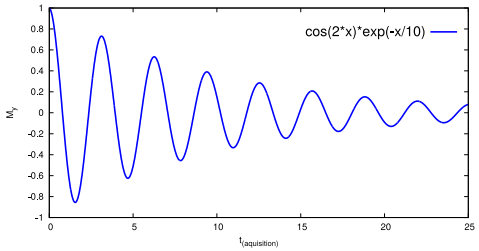
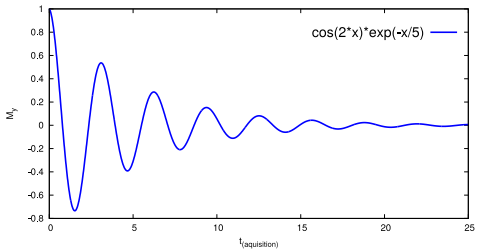
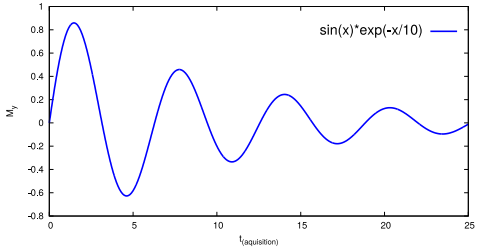
- 90_{-x} : $+y$
- 90_{+y} – $\Omega\tau = \pi/2$: $+x \rightarrow +y$
- 90_{+x} – $\Omega\tau = \pi/3$ – 180_{+x} – $\Omega\tau = \pi/3$:
  $-y \rightarrow -y * cos(60) + x * sin(60) \rightarrow +y * cos(60) + x * sin(60) \rightarrow +y$
- 90_{+x} – $\Omega\tau = \pi/3$ – 180_{+y} – $\Omega\tau = \pi/3$:
  $-y \rightarrow -y * cos(60) + x * sin(60) \rightarrow -y * cos(60) - x * sin(60) \rightarrow -y$

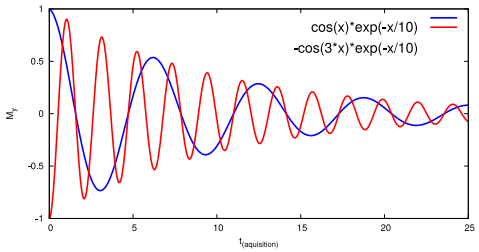
Basics of 1D FT spectroscopy





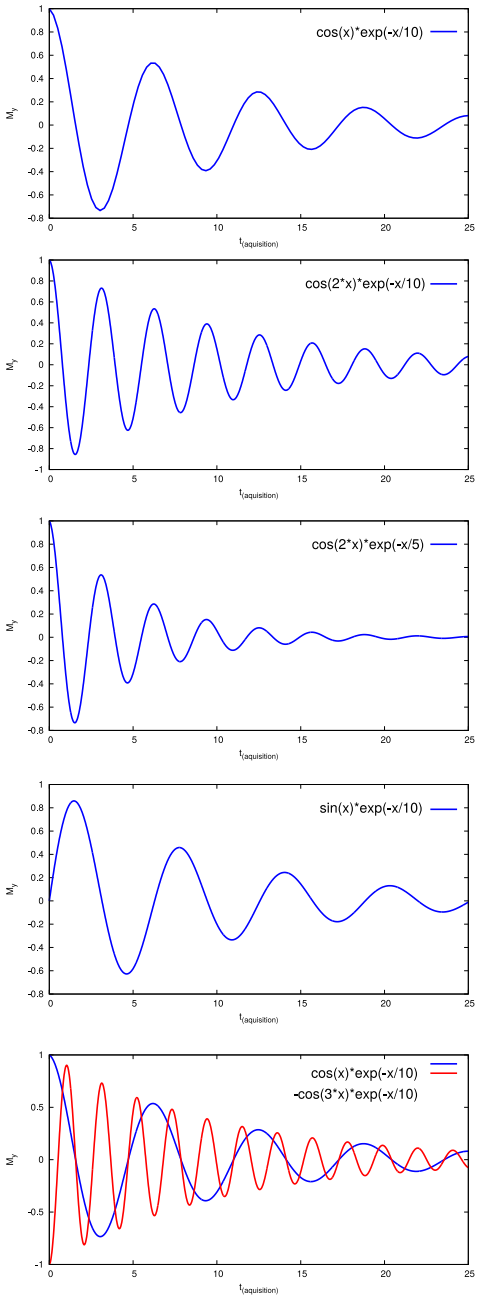






Draw FT representation of attached FID records (reciever is located in the $+y$ direction):

Basics of 1D FT spectroscopy



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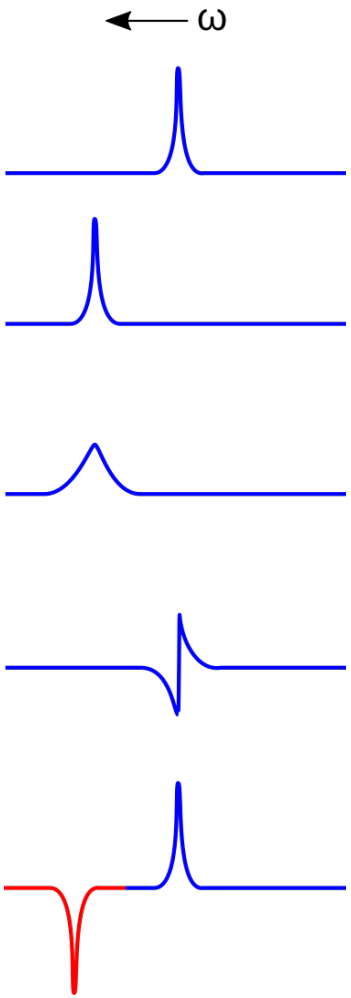

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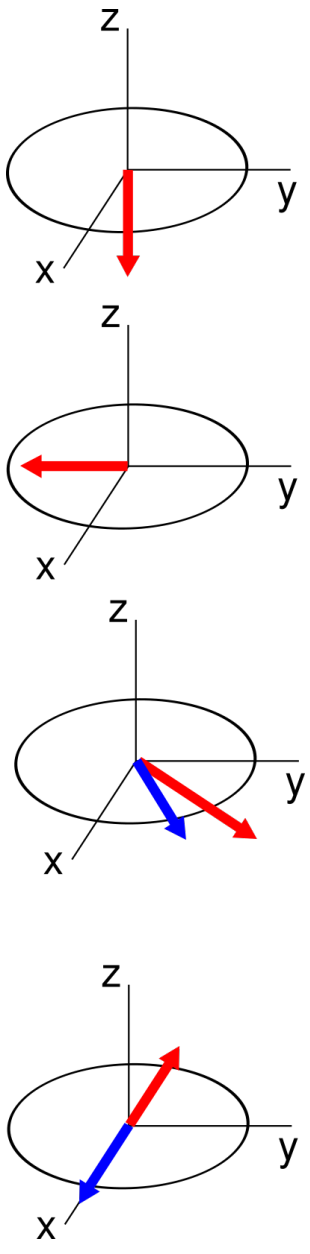
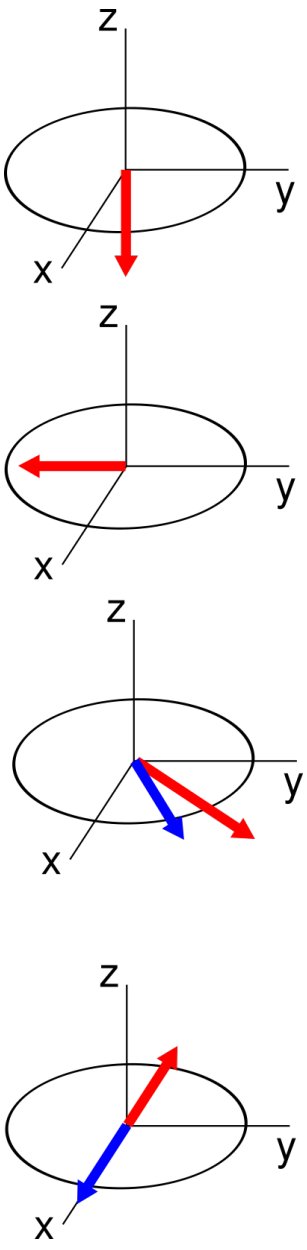


Draw FT representation of vector models (in rotating frame, receiver is located in the $+y$ direction):

Basics of 1D FT spectroscopy



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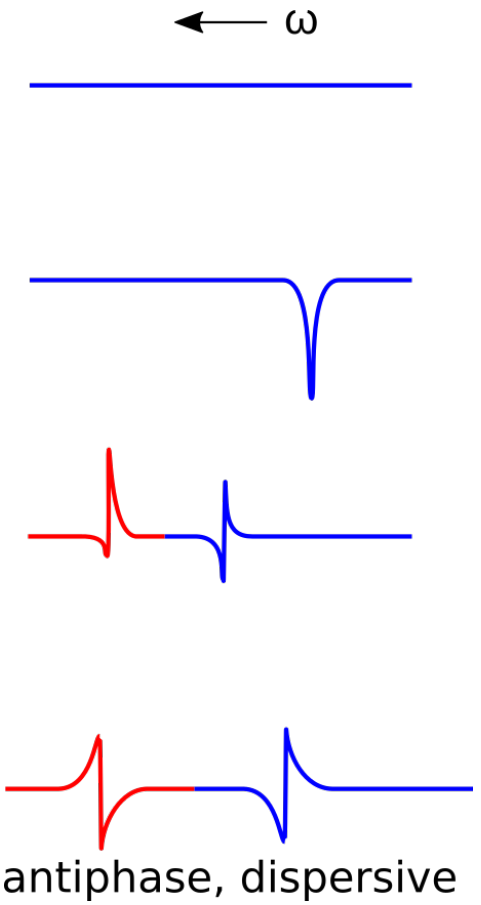
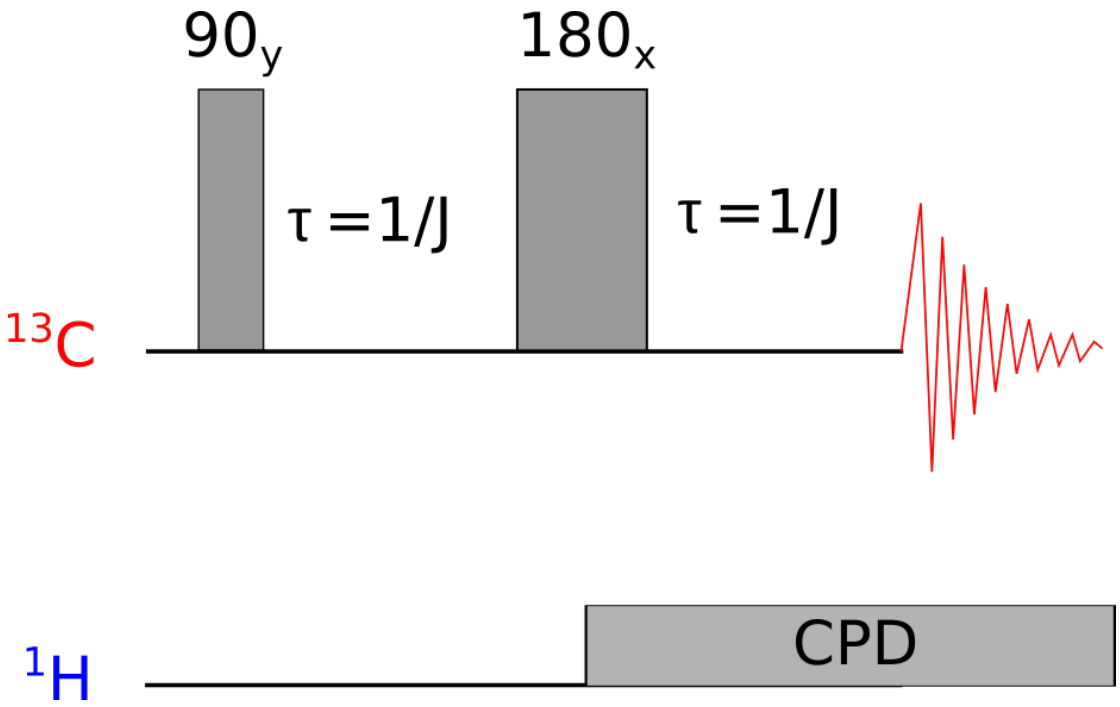


Heteronuclear spin echo of ^{13}C-^{1}H$_3$ group

By using vector diagrams determine the result of attached pulse sequence. First realize what is the evolution of ^{13}C signal resulting from offset? CPD=composite pulse decoupling



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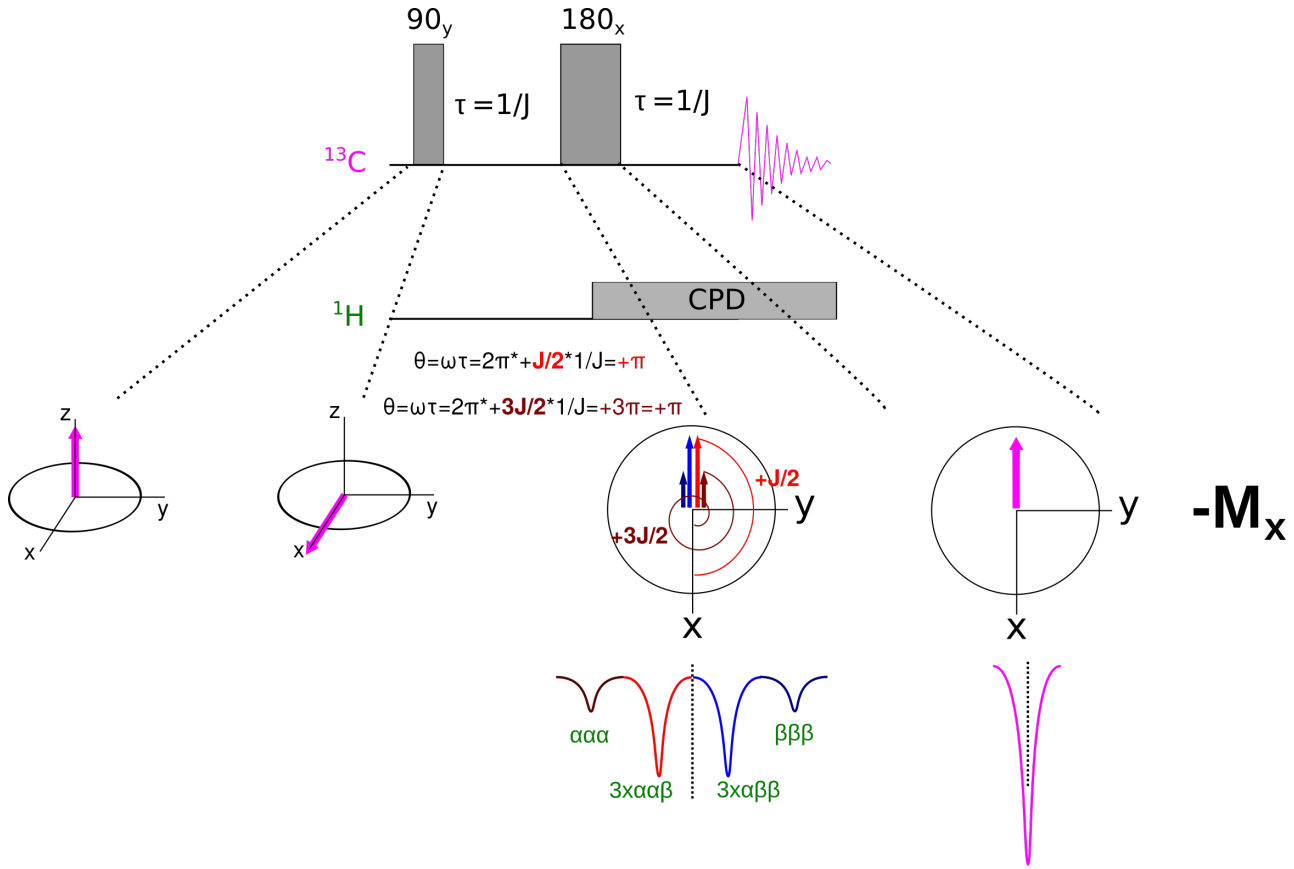


APT - Attached Proton Test

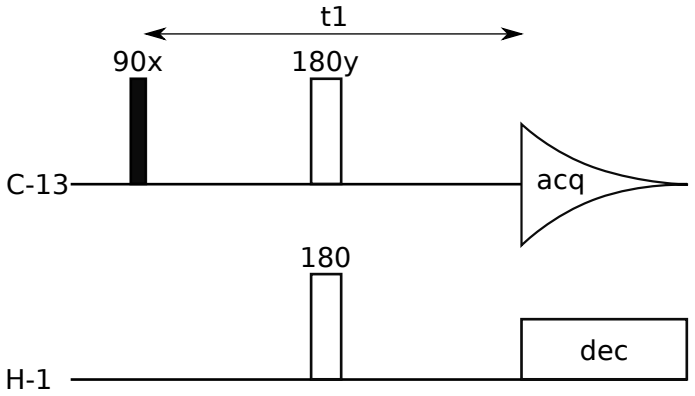
based on heteronuclear spin echo

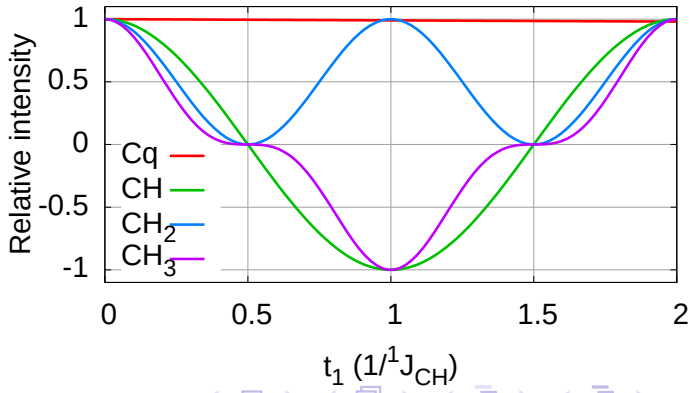
- $t_1 = 1/{}^1J_{CH}$

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

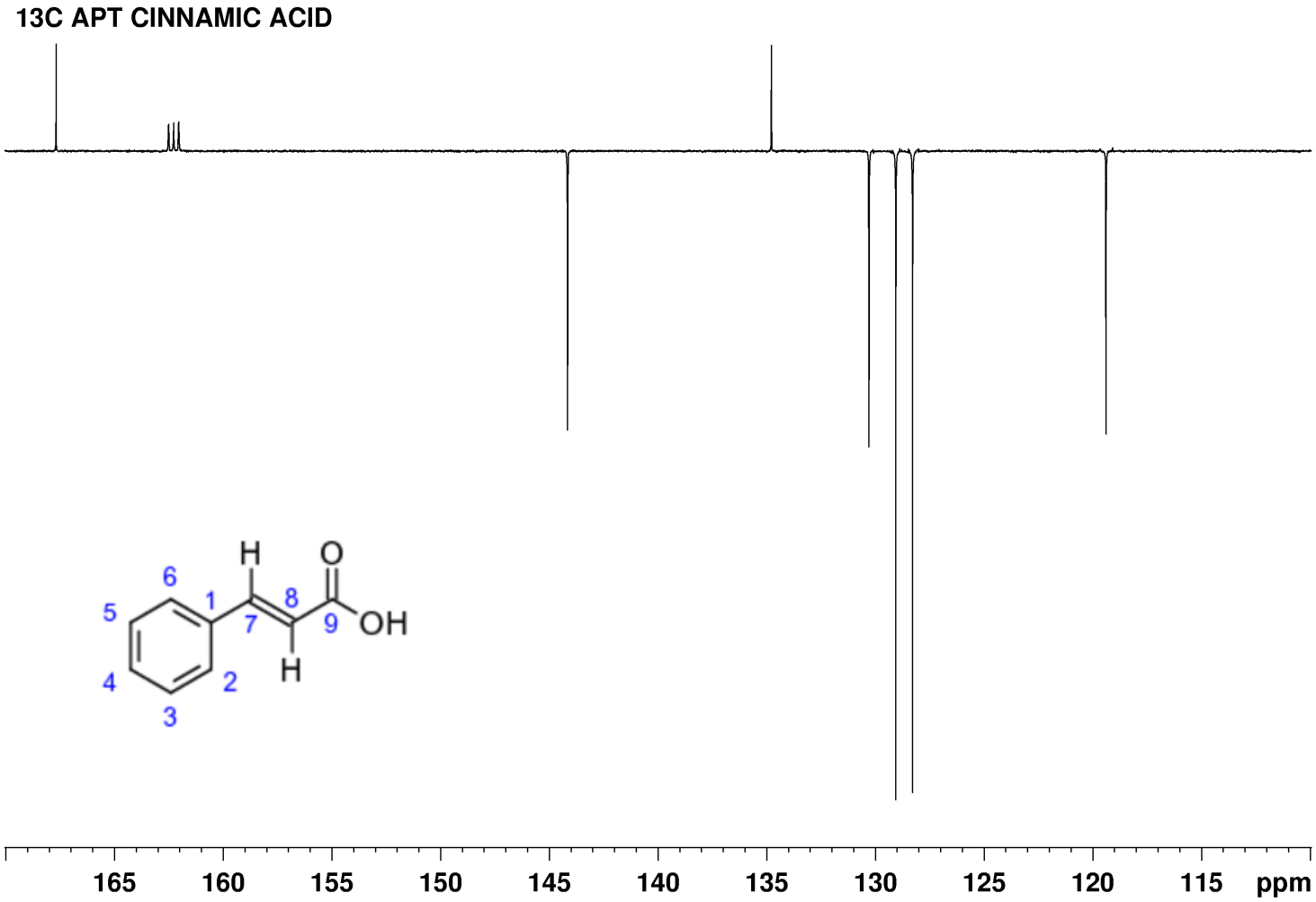
- Cq, CH_2 positive
- CH, CH_3 negative

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





^{13}C APT Cinnamic acid



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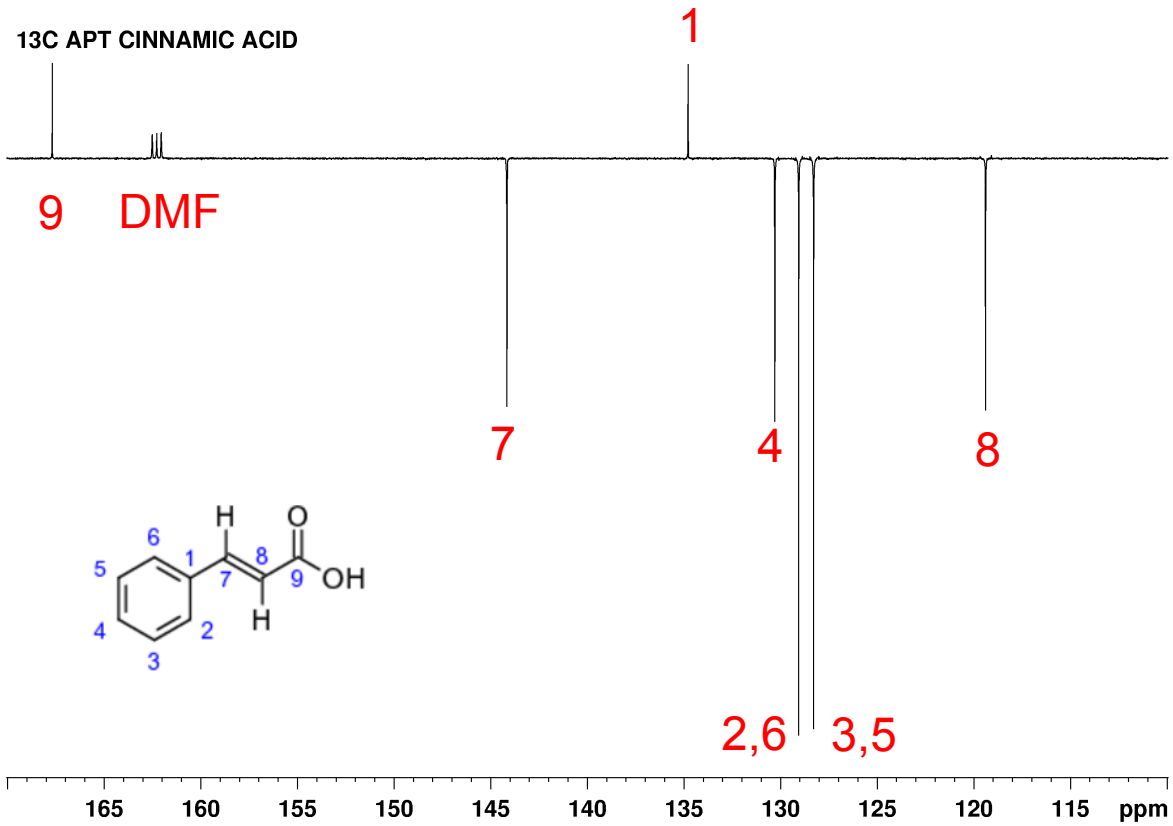
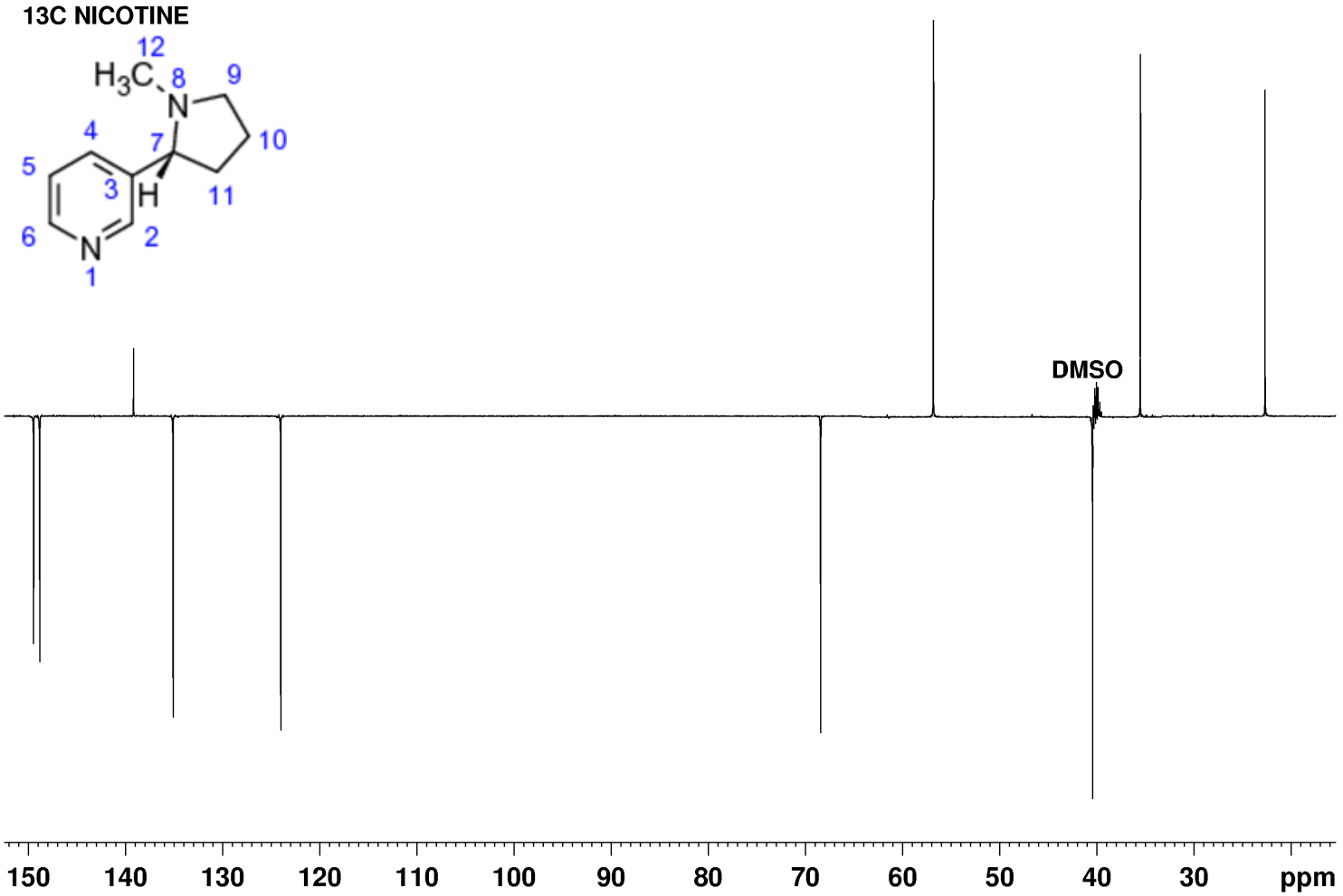


Notes:

- **C9, C1** 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}C APT of Nicotine



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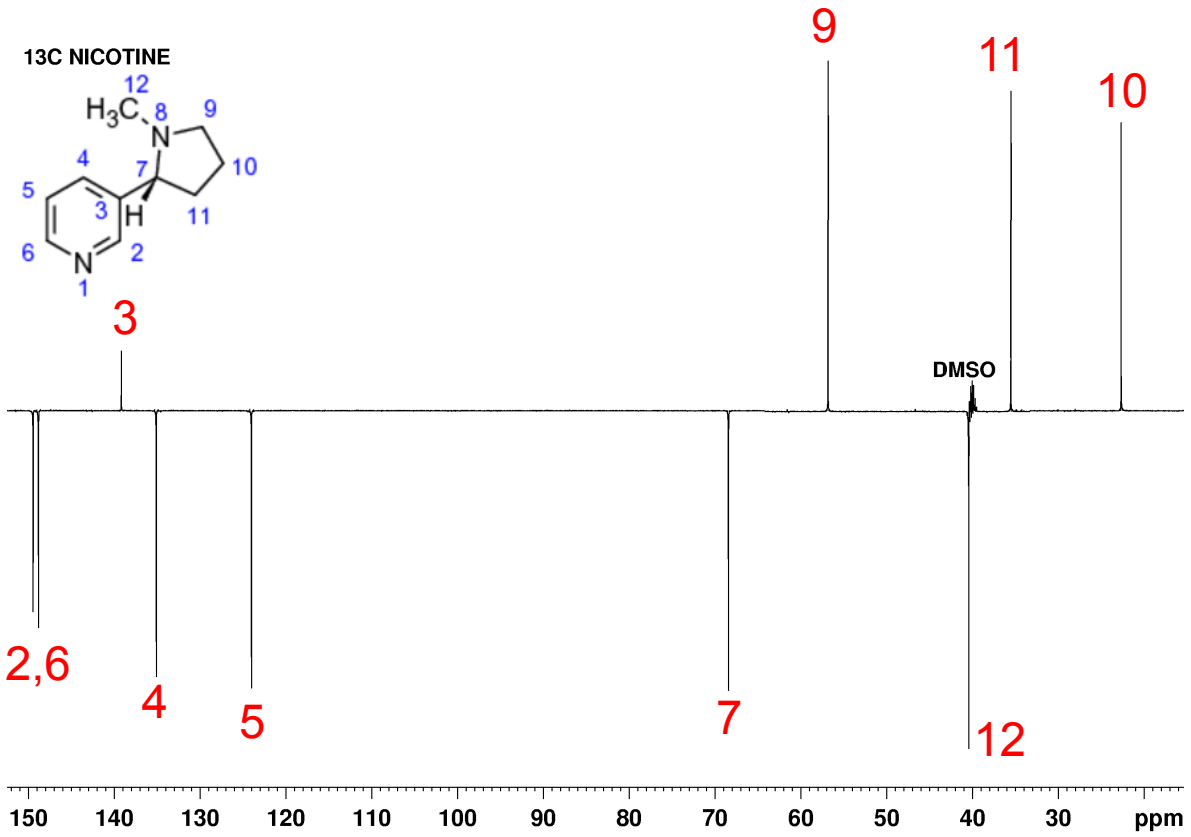
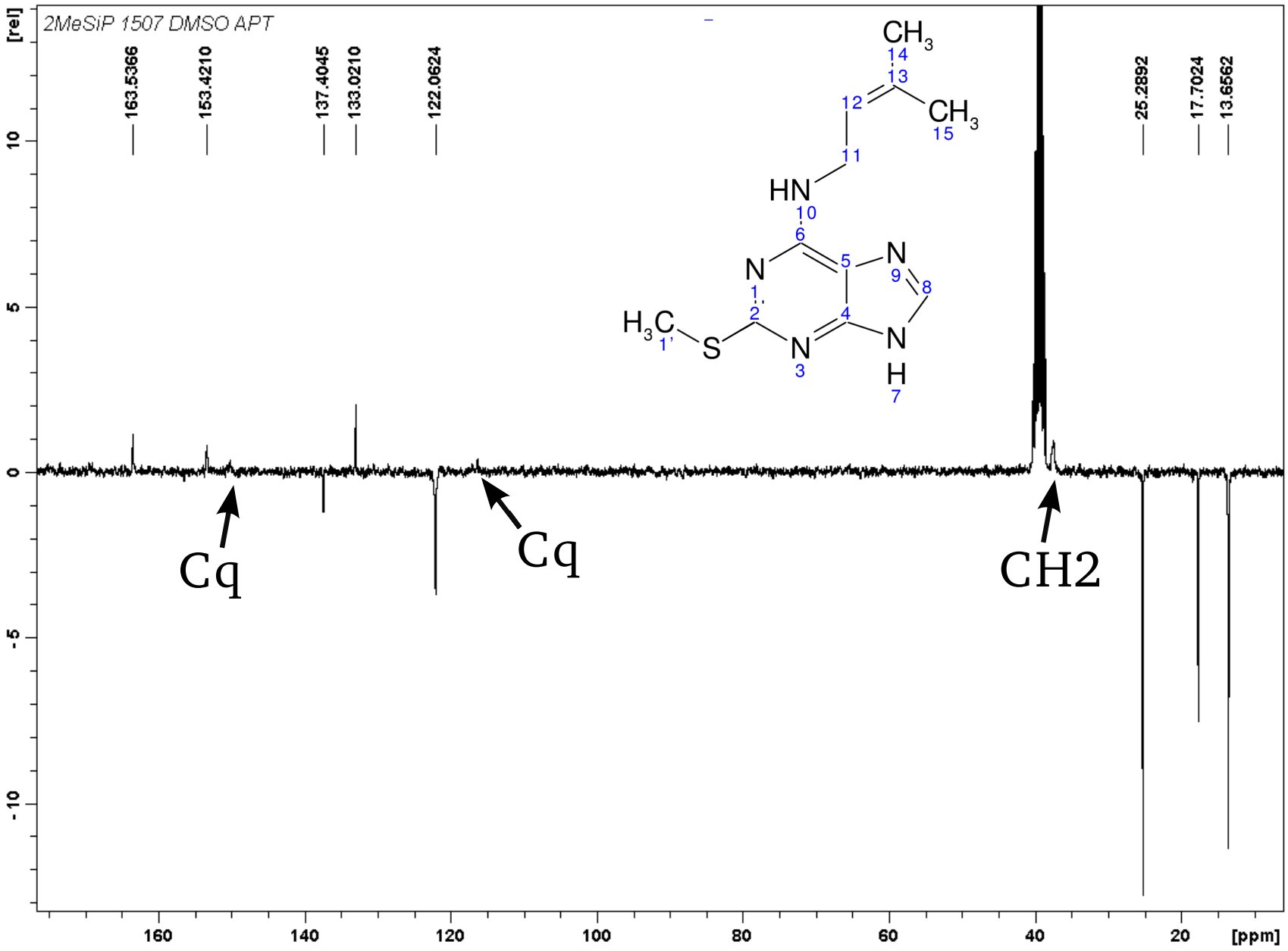


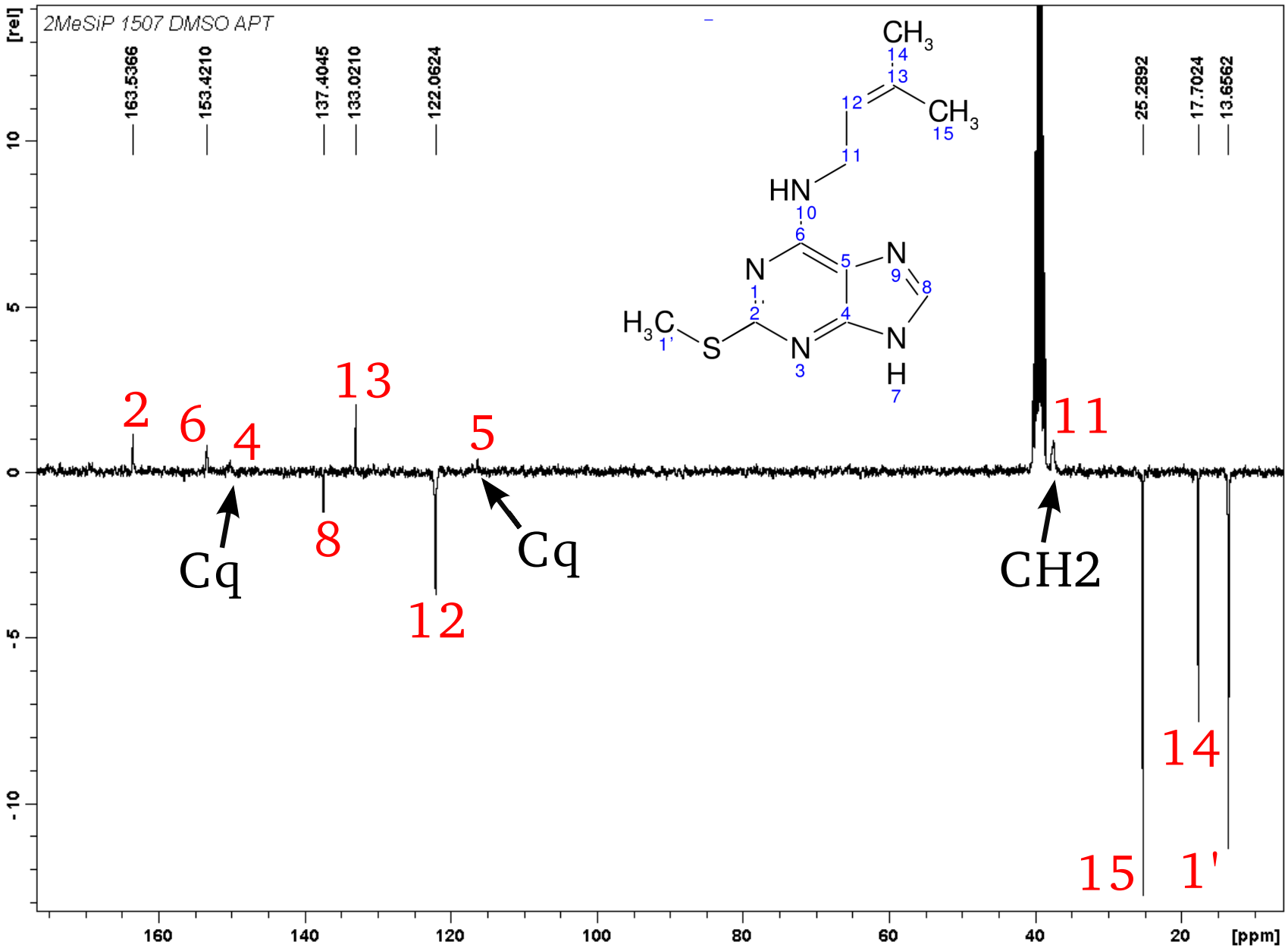
Notes:

- **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}C APT 4


2MeSiP 1507 DMSO APT
[rel]
163.5366
153.4210
137.4045
133.0210
122.0624
25.2892
17.7024
13.6562
Cq
Cq
CH2
[ppm]

^{13}C APT 4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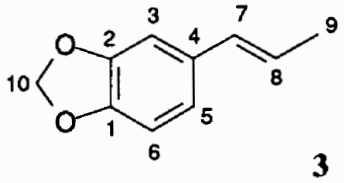
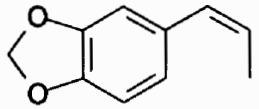
13.6562
2
6
4
13
5
11
8
12
Cq
Cq
CH2
14
15
1'
[ppm]

^{1}H-^{13}C DEPT spectrum



3



4

Which is the major product? Assign the signals as far as possible. Why does the signal at $\delta = 100.8$ exist in the spectrum 3.3.c, although its intensity should be zero?

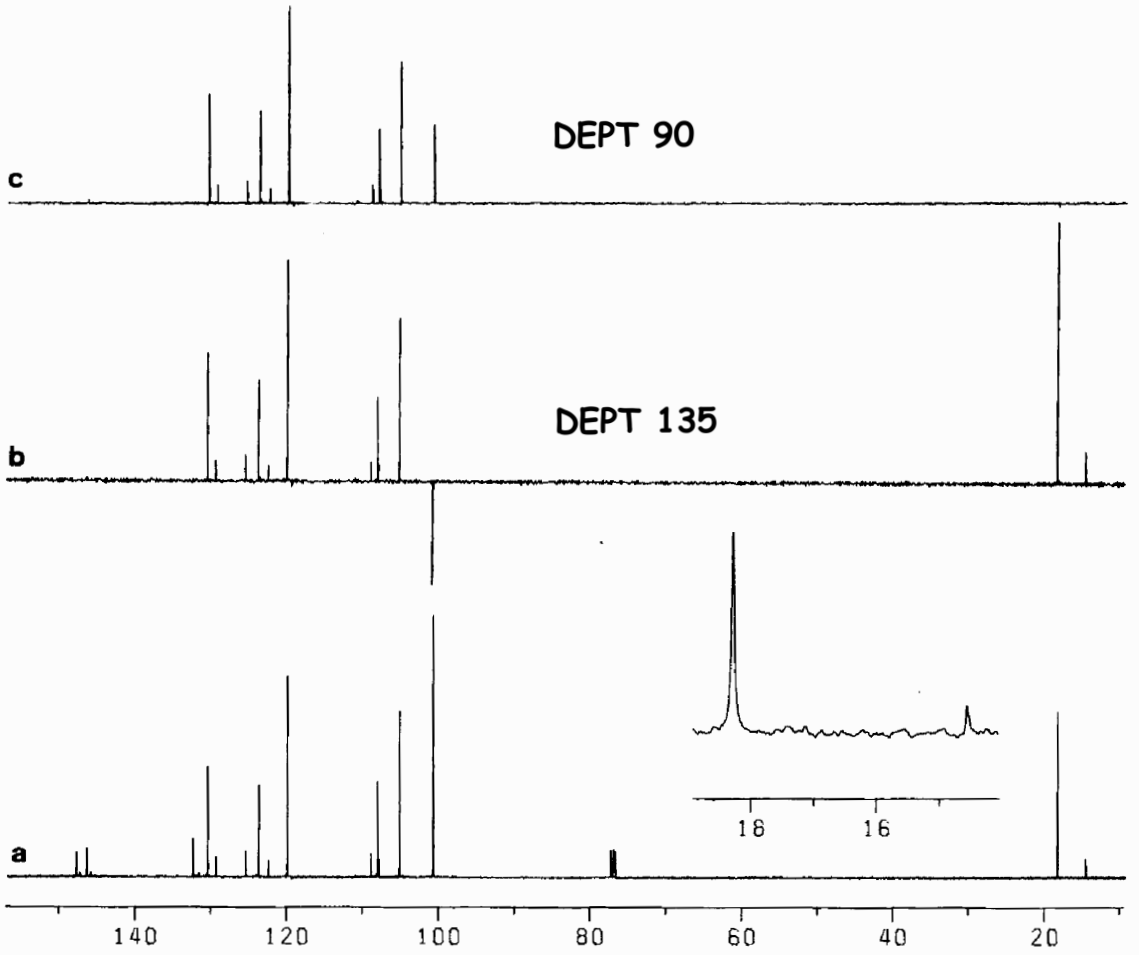
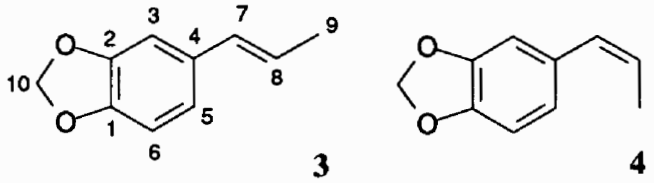


Fig. 3.3. (a) ^{1}H broad-band decoupled ^{13}C NMR spectrum of a mixture of **3** and **4** in $CDCl_3$. Traces (b) and (c) are DEPT spectra.

^{1}H-^{13}C DEPT spectrum



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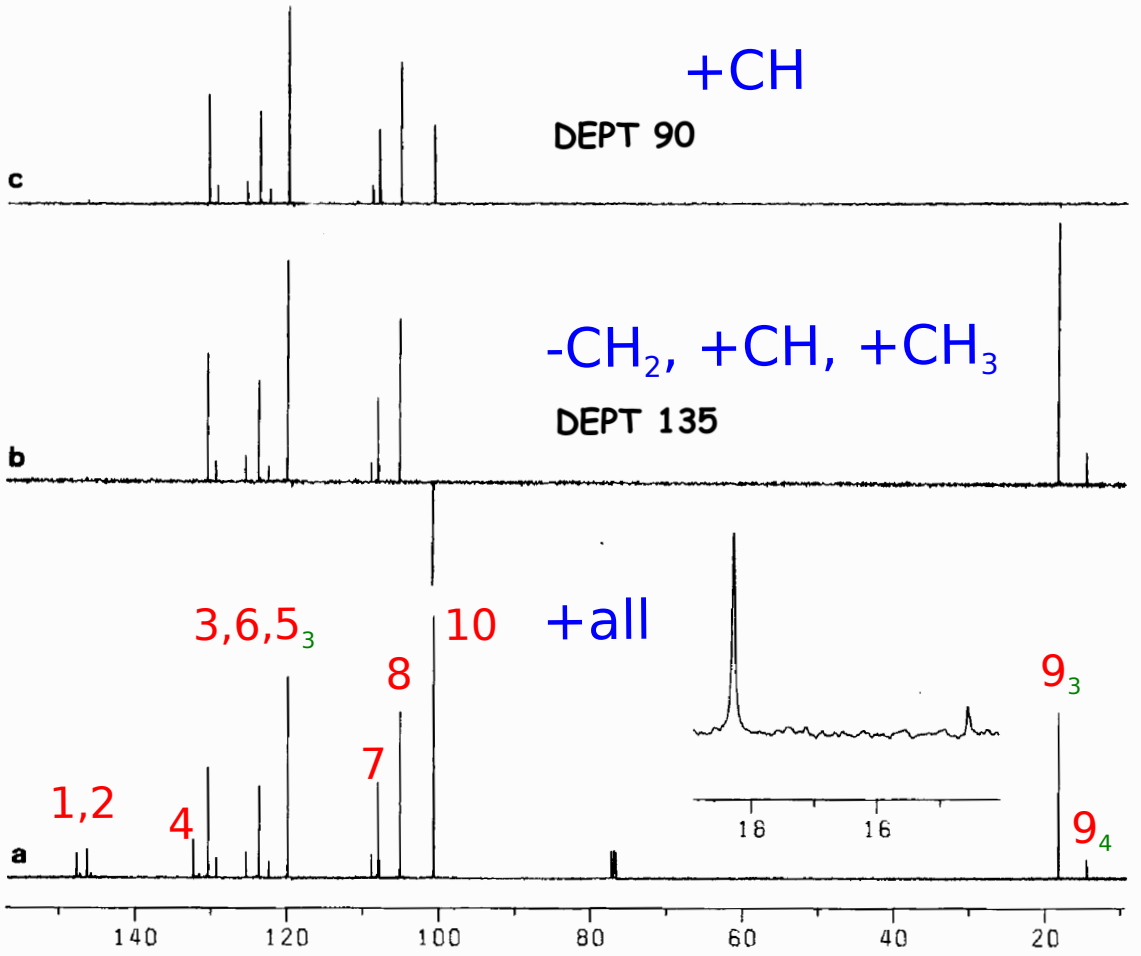

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Next topic

2D spectroscopy