

C8953

# NMR structural analysis - seminar

$^1\text{H}$ - $^{13}\text{C}$  APT + 2D NMR spectra, COSY

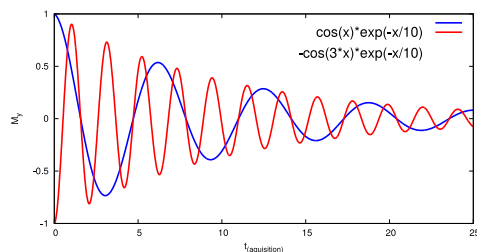
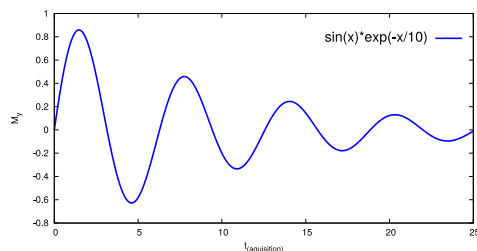
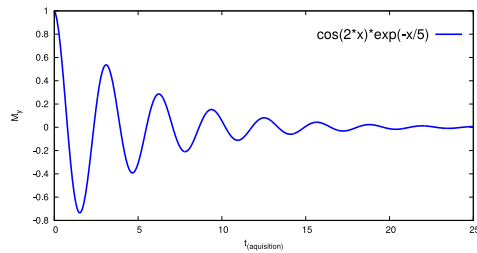
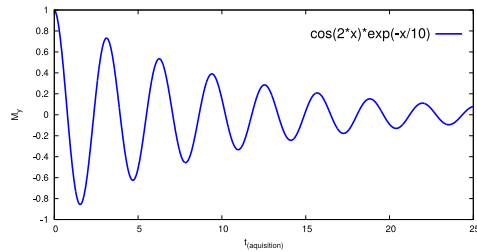
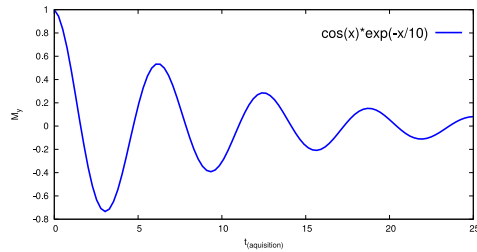
Jan Novotný

novotnyjan@mail.muni.cz

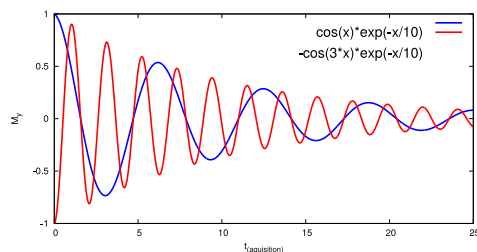
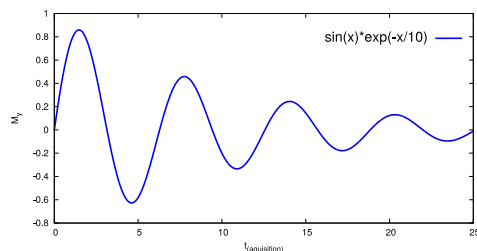
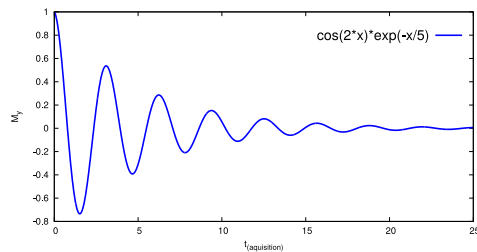
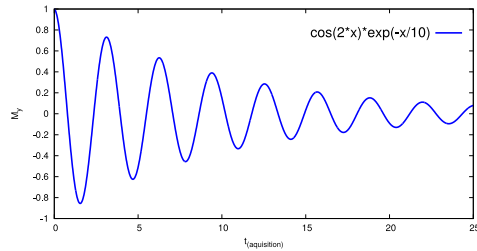
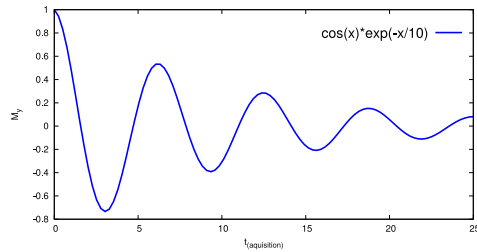
March 20, 2019

# Basics of 1D FT spectroscopy

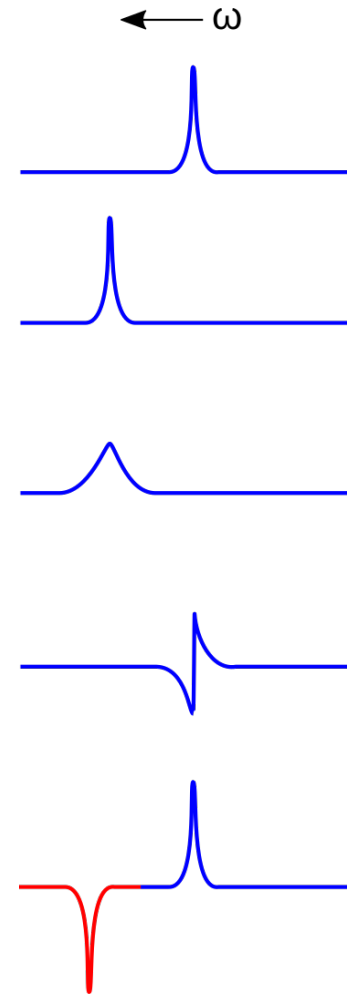
Draw FT representation of attached FID records (reciever is located in the  $+y$  direction):



# Basics of 1D FT spectroscopy



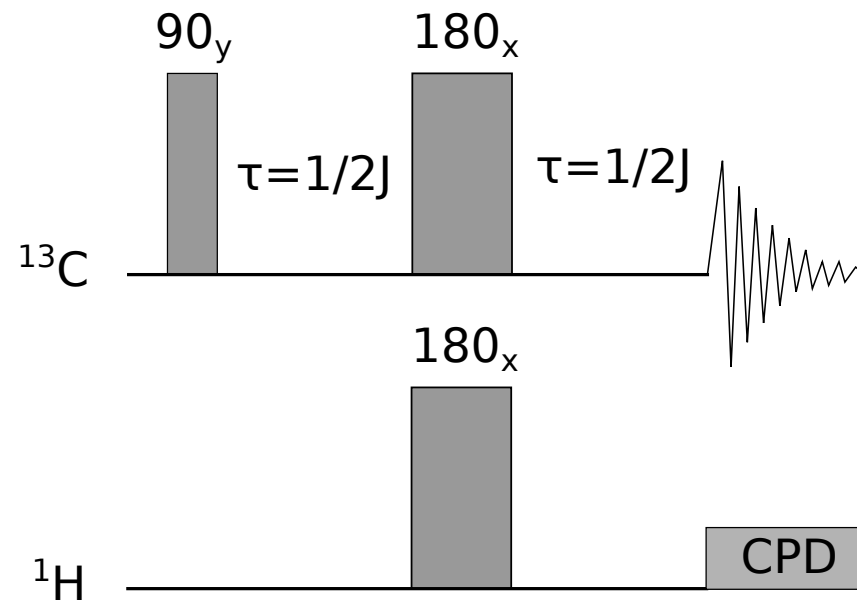
Draw FT representation of attached FID records (receiver is located in the  $+y$  direction):



# Heteronuclear spin echo

By using vector diagrams determine the result of attached pulse sequence.

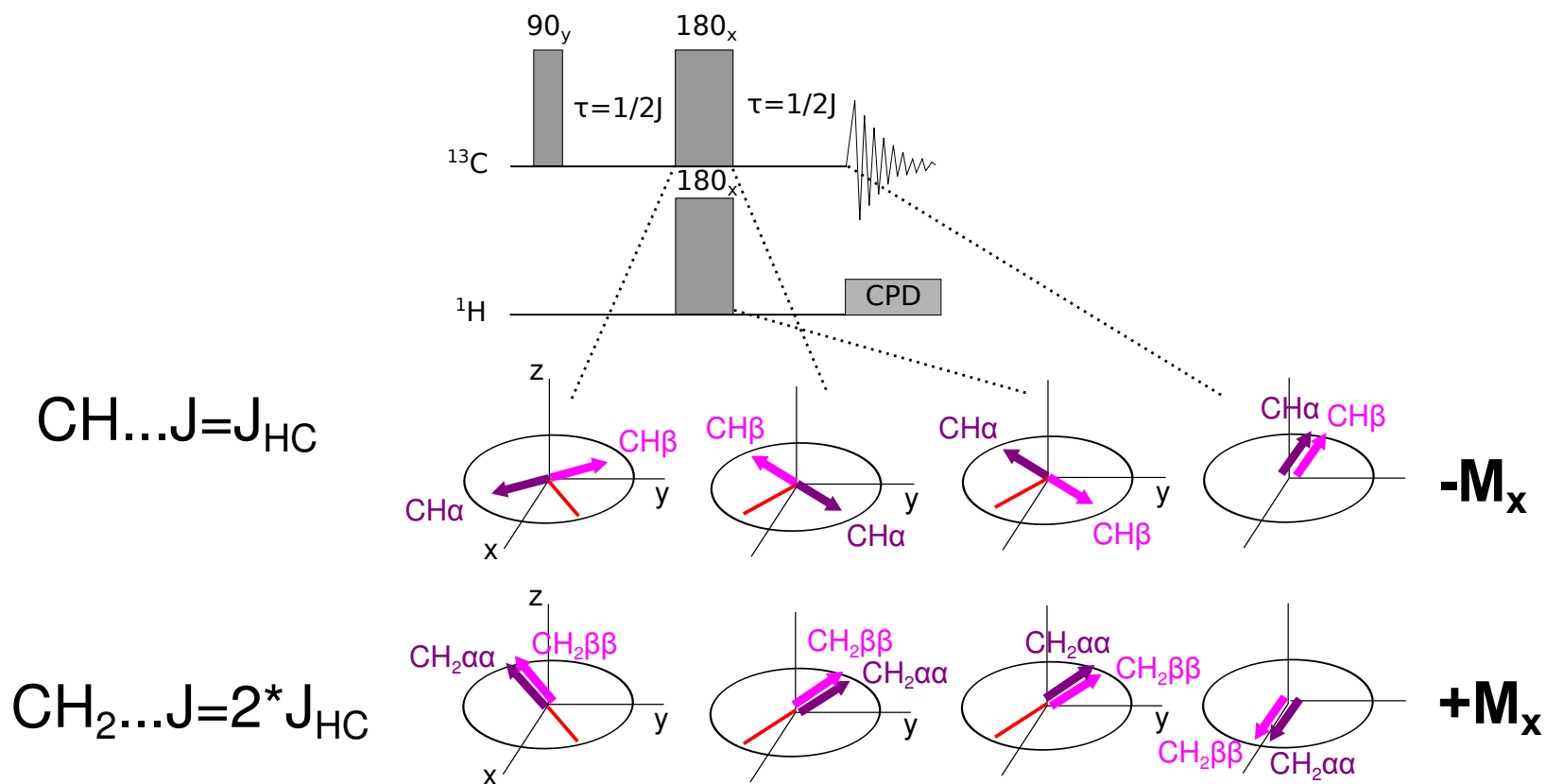
Lets consider isolated spin systems **a)**  $^{13}\text{C}-^1\text{H}$  and **b)**  $^{13}\text{C}-^1\text{H}_2$ .



# Heteronuclear spin echo

By using vector diagrams determine the result of attached pulse sequence.

Lets consider isolated spin systems **a)**  $^{13}\text{C}-^1\text{H}$  and **b)**  $^{13}\text{C}-^1\text{H}_2$ .



# APT - Attached Proton Test

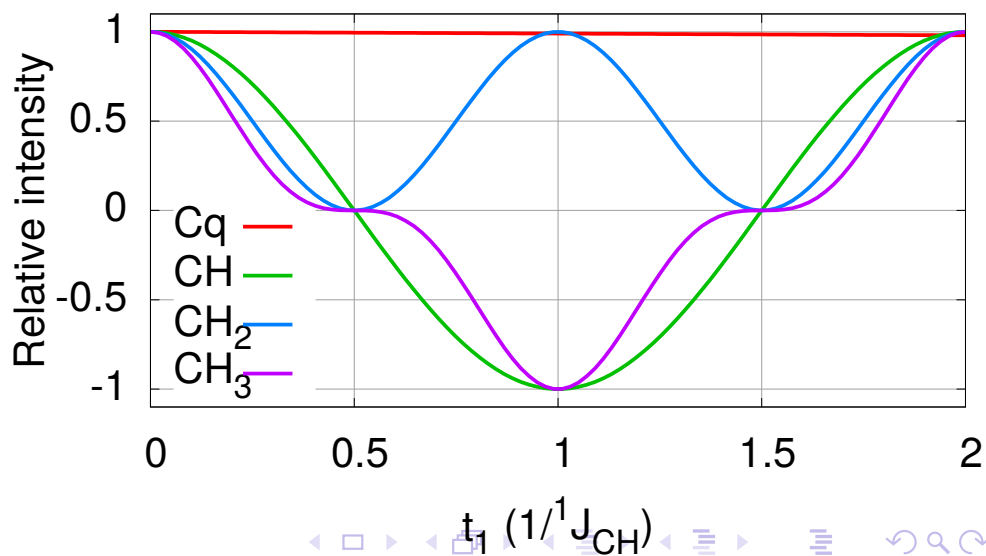
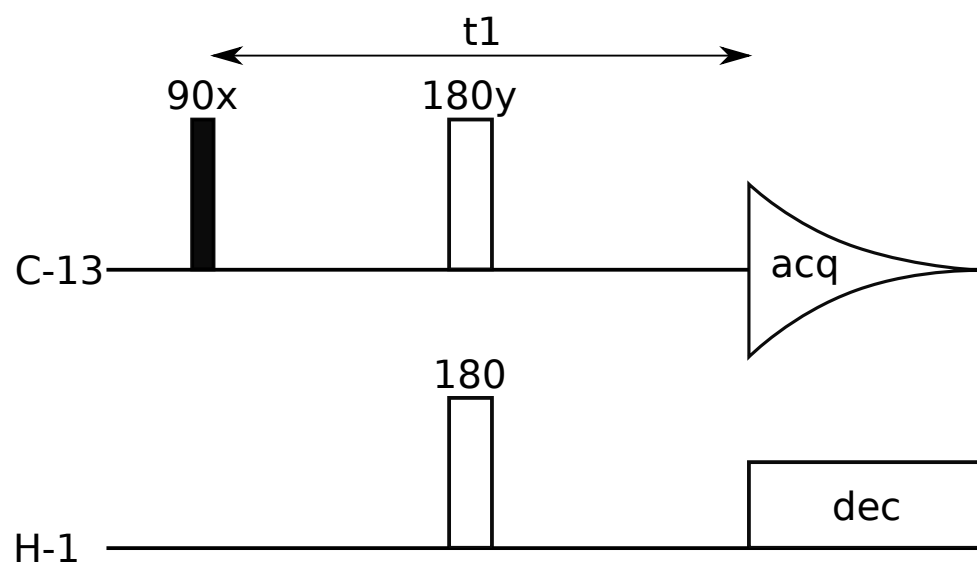
vychází z heteronukleárního spinového echa

▶  $t_1 = 1/{}^1J_{CH}$

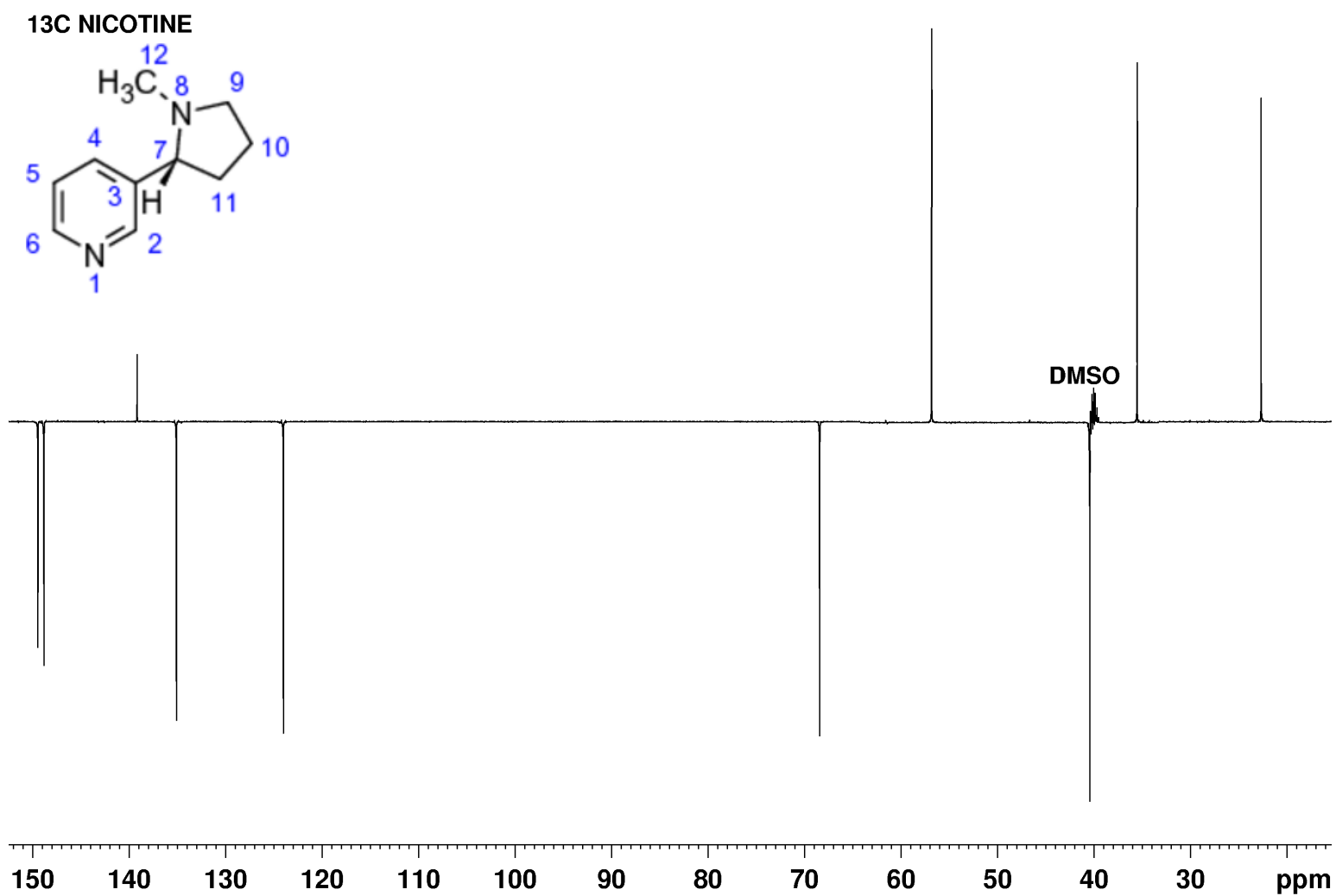
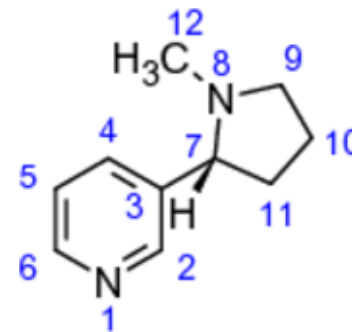
rozlišení signálů C podle počtu navázaných H

- ▶ Cq, CH<sub>2</sub> kladné
- ▶ CH, CH<sub>3</sub> záporné

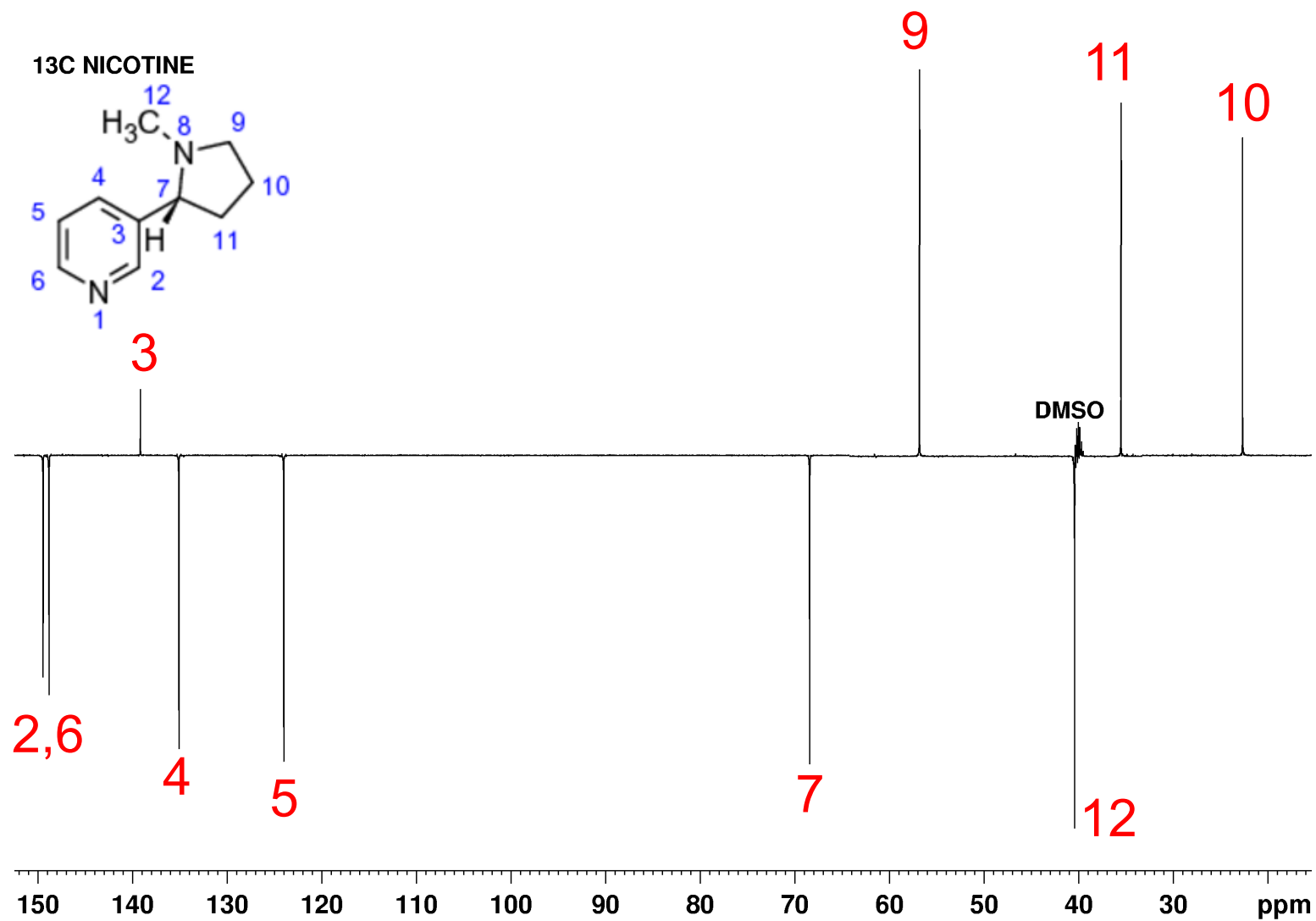
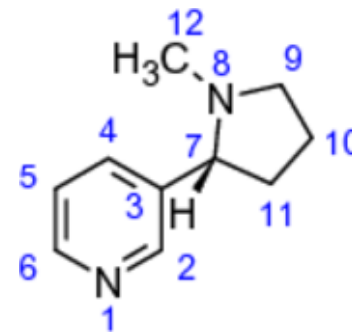
Rozdílná  ${}^1J_{CH} \implies$  různé intenzity



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

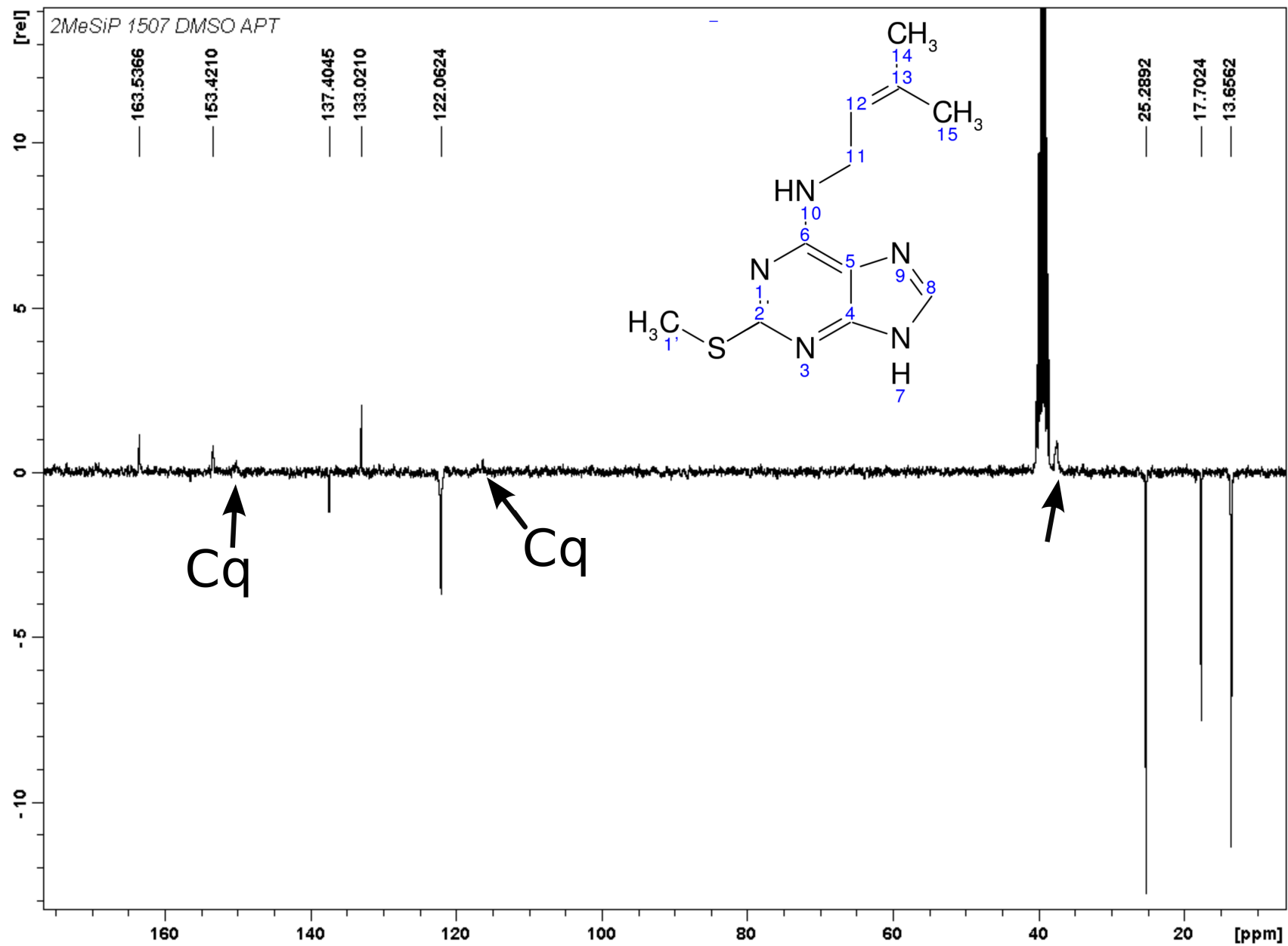


# $^{13}\text{C}$ APT Nicotine

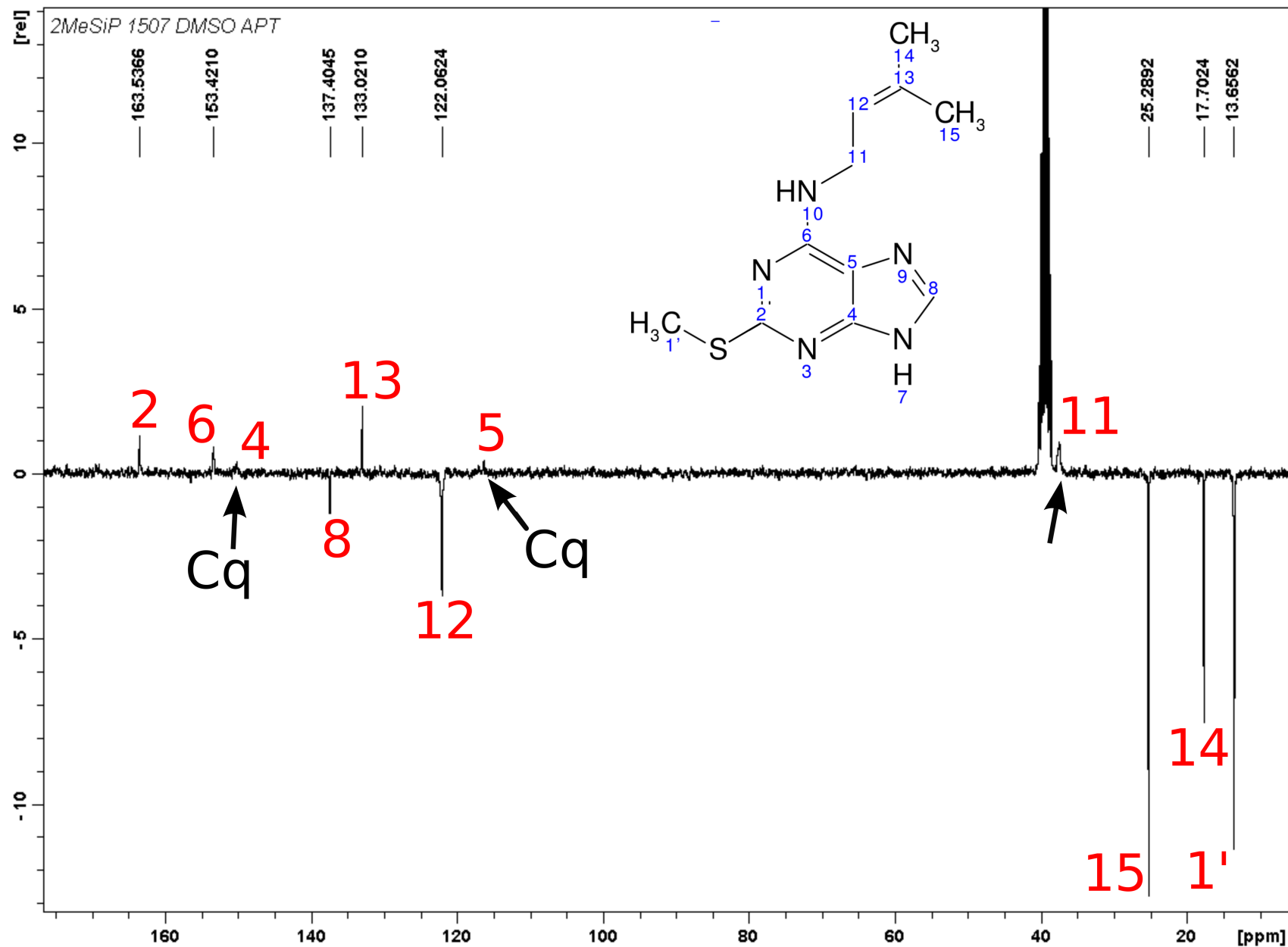




# $^{13}\text{C}$ APT 4



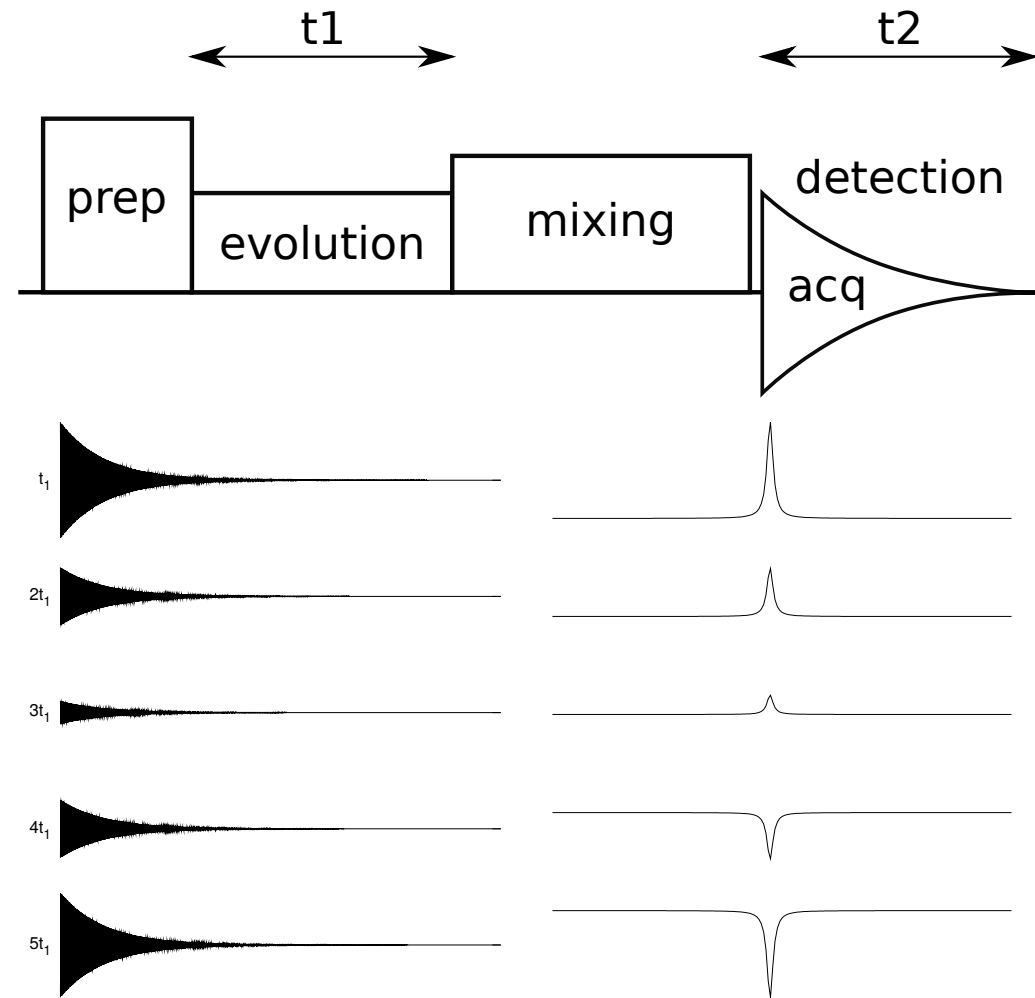
# $^{13}\text{C}$ APT 4



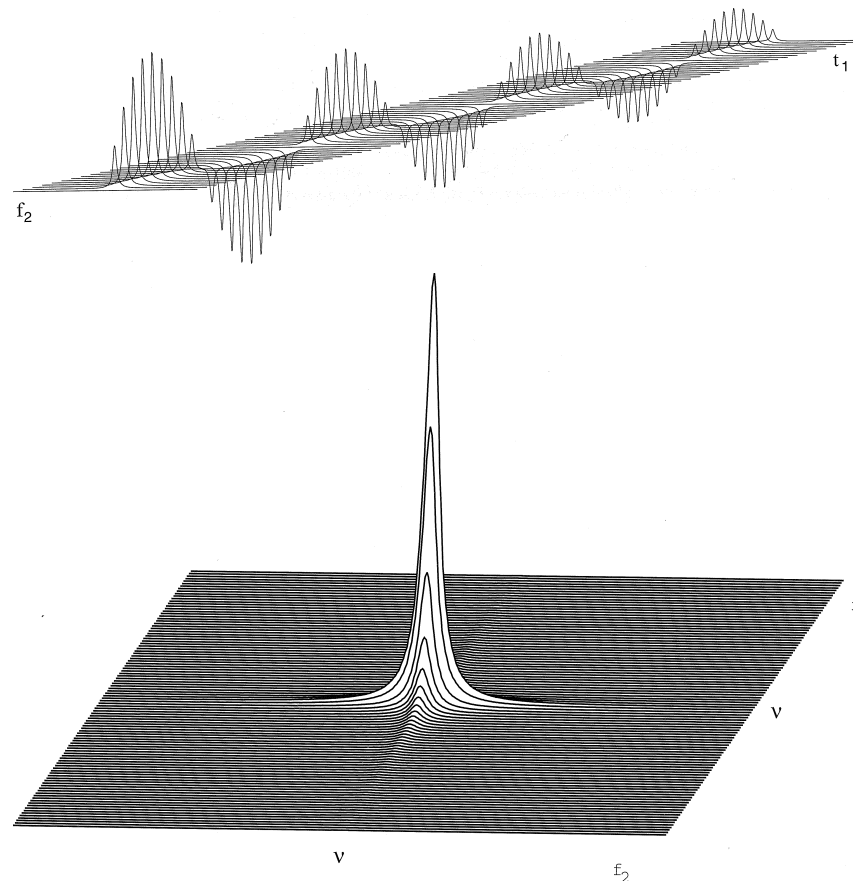
# 2D NMR

## Second dimension $f_1$

- ▶ preparation period  
⇒ coherence
- ▶ evolution period  
 $t_1 \xrightarrow{\text{FT}} f_1$ 
  - ▶ increments
  - ▶ evolution of coherence
- ▶ mixing period
  - ▶ transfer of encoded magnetisation
  - ▶ measurable signal
- ▶ detection of signal  
 $t_2 \xrightarrow{\text{FT}} f_2$



# 2D NMR

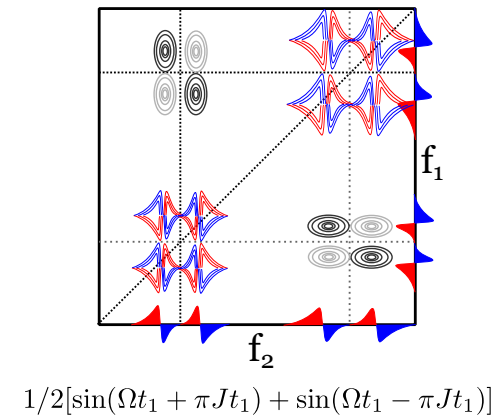
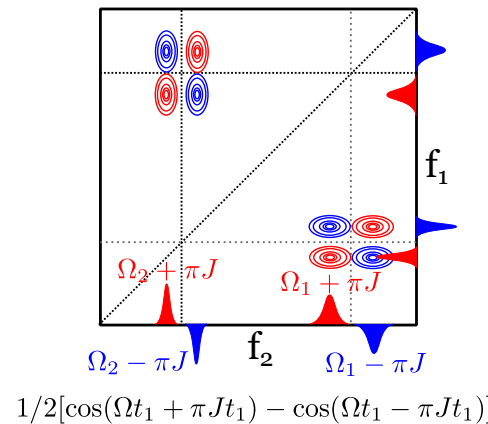
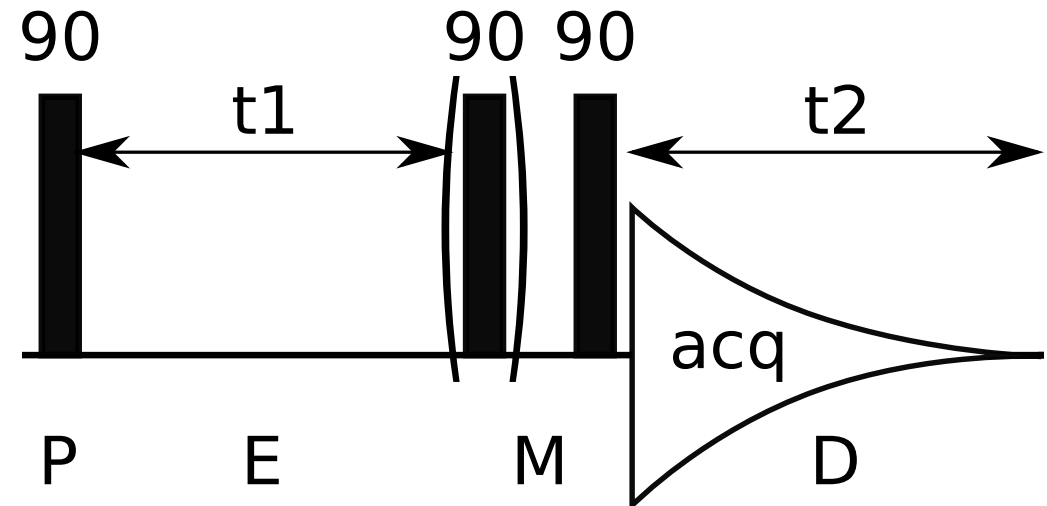


## 2D spektrum

- ▶ FT in  $t_1$  - modulated 1D spectra
- ▶ FT in  $t_2$  - 2D spectrum

# COSY

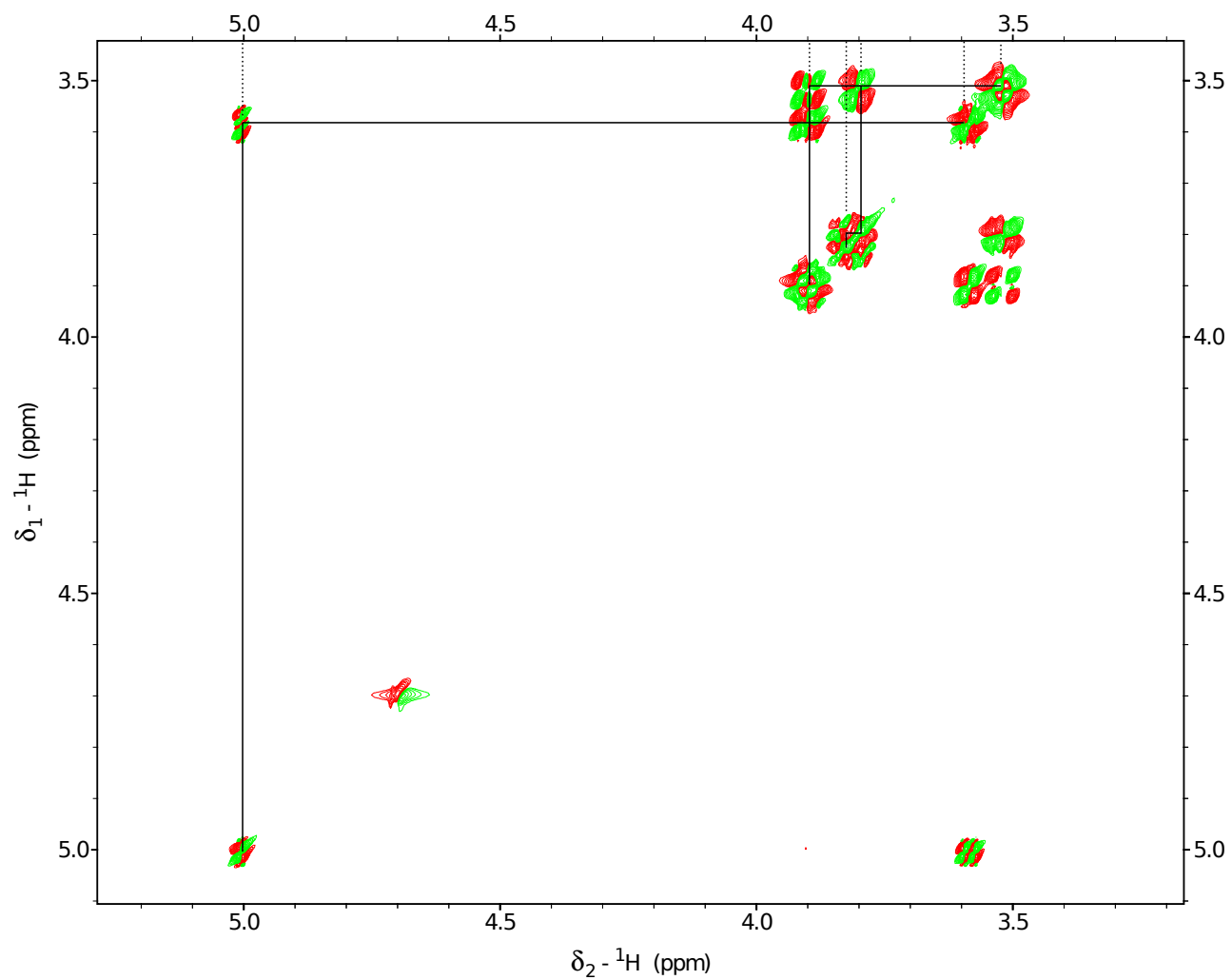
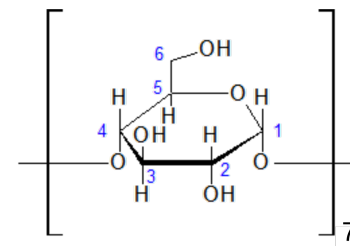
- ▶ easiest 2D experiment
- ▶ **correlates H nuclei based on  $^{2/3}J$  coupling**
- ▶ through 2, 3, (4) bonds
- ▶ antiphase off-diagonal crosspeak between coupled atoms
- ▶ DQF-COSY - modification of basic sequence, diagonal crosspeaks in absorption phase



# Hints for beginners

- ▶ Determination of **individual spin systems** - sharing **off-diagonal crosspeaks**
- ▶ Isolated protons - only diagonal crosspeak
- ▶ Already known rules: symmetry, diastereotopicity, most shielded/deshielded atoms etc.

# COSY : $\beta$ -cyclodextrine



# COSY : $\beta$ -cyclodextrine

