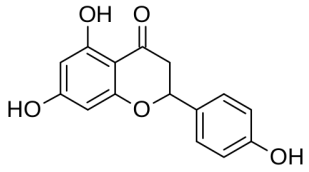
C8953
NMR structural analysis - seminar
Vector model of NMR experiments + 2D spectra, COSY

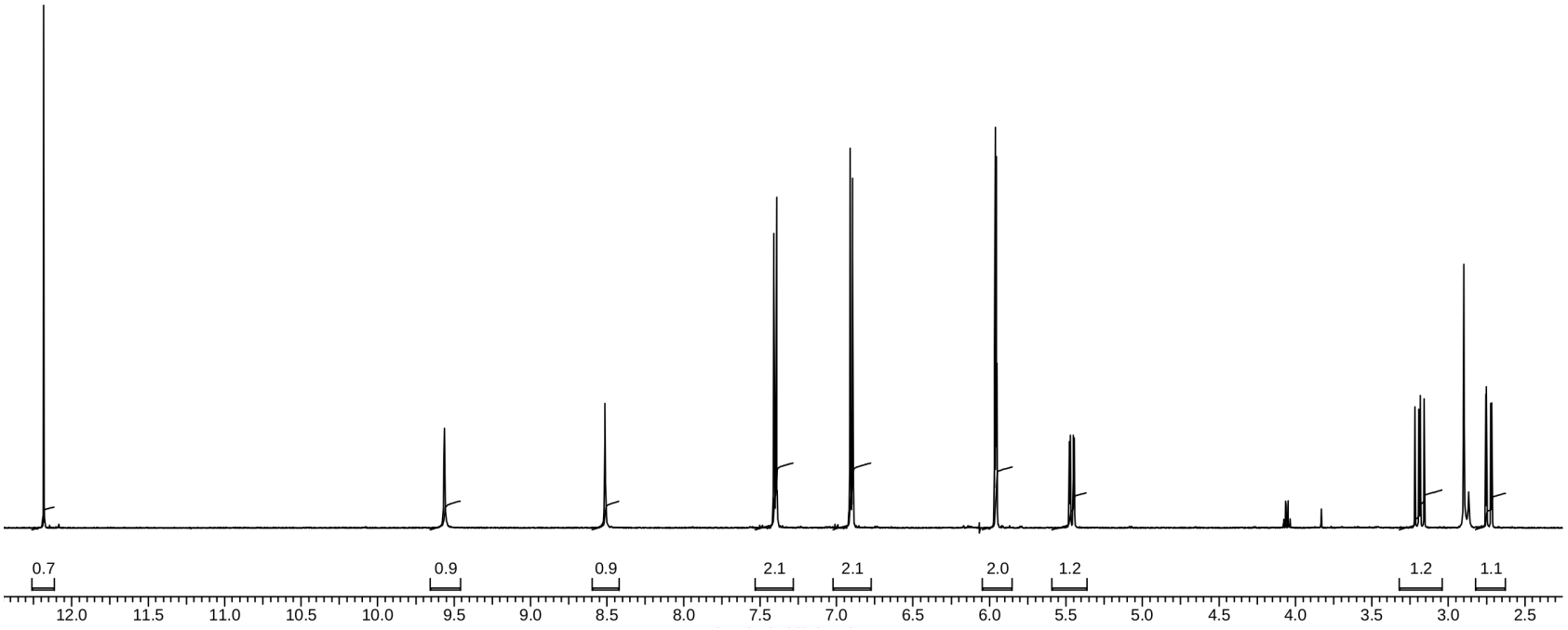
Jan Novotný
novotnyjan@mail.muni.cz

March 21, 2018

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



naringenin



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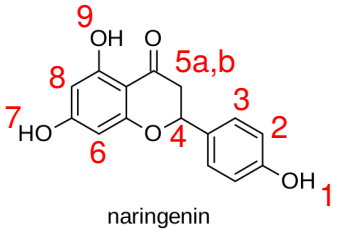
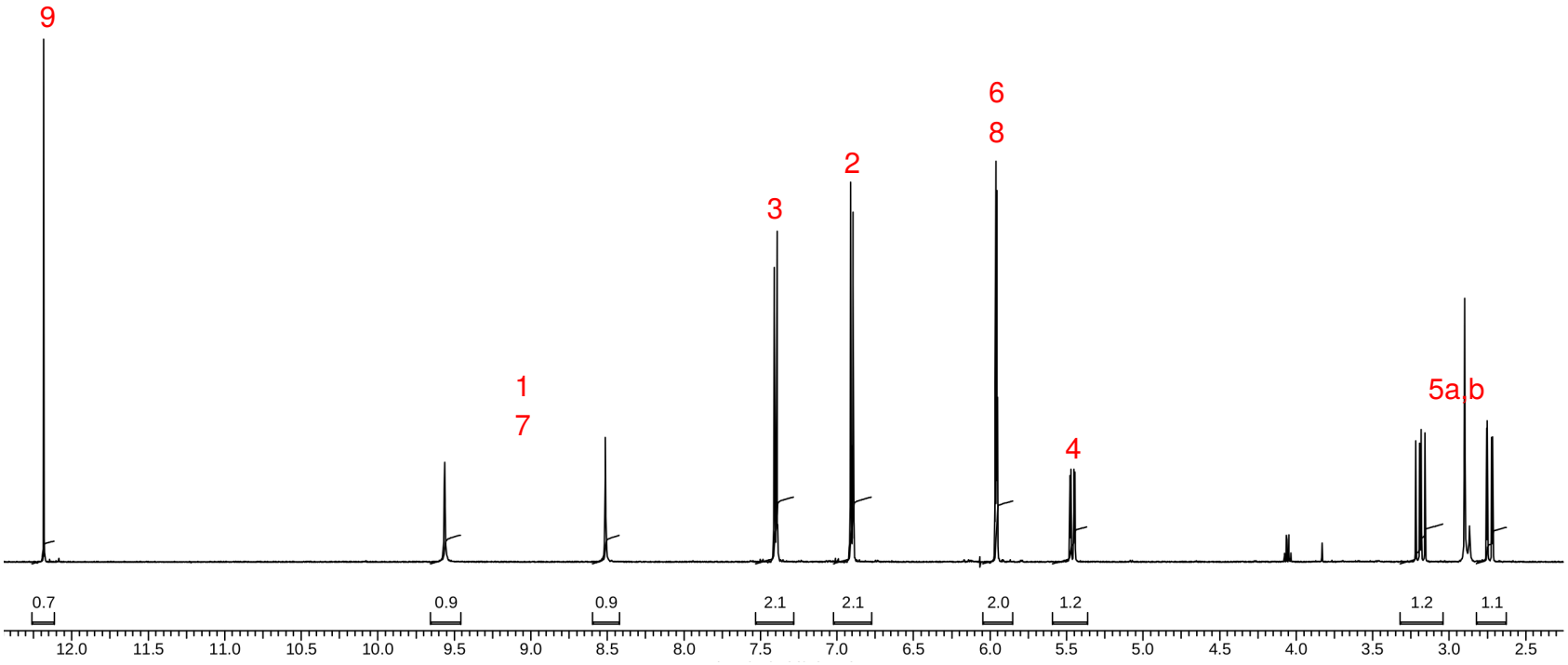
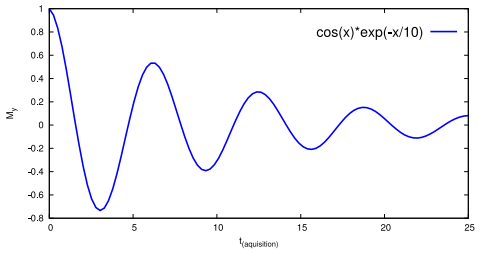
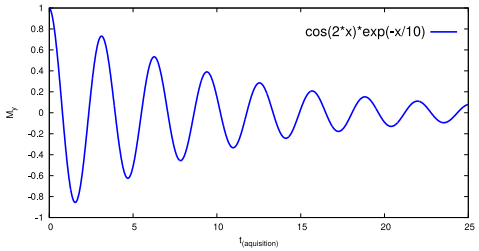


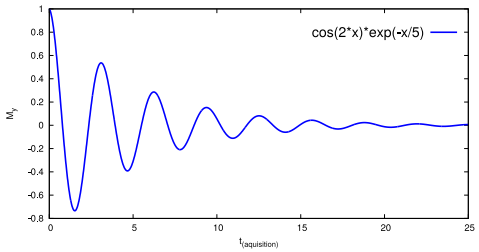
naringenin

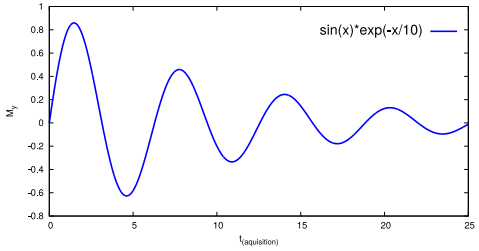


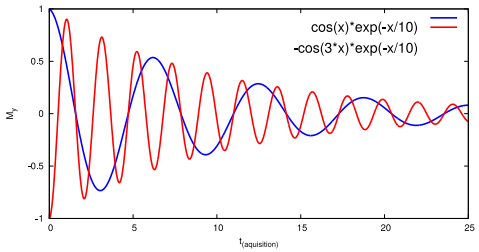
Basics of 1D FT spectroscopy





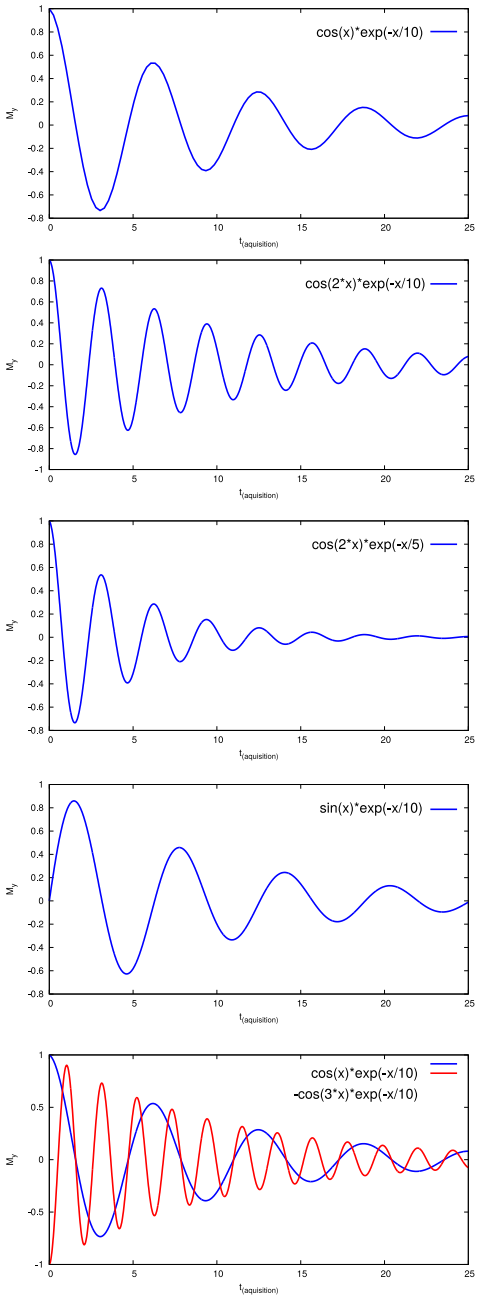






Draw FT representation of attached FID records (reciever is located in the $+y$ direction):

Basics of 1D FT spectroscopy



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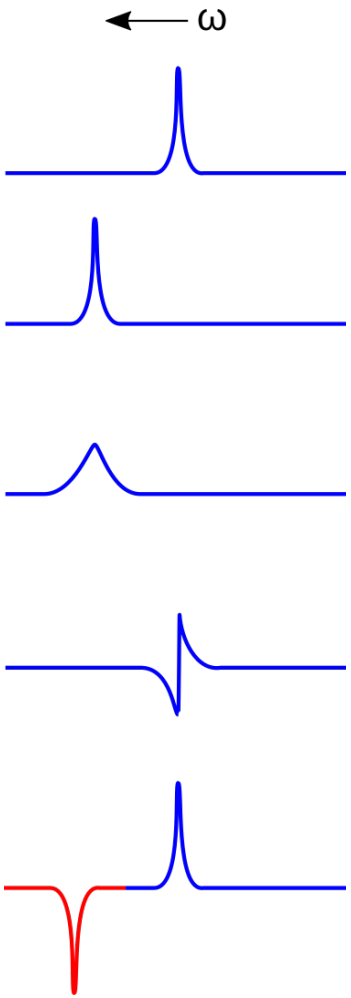
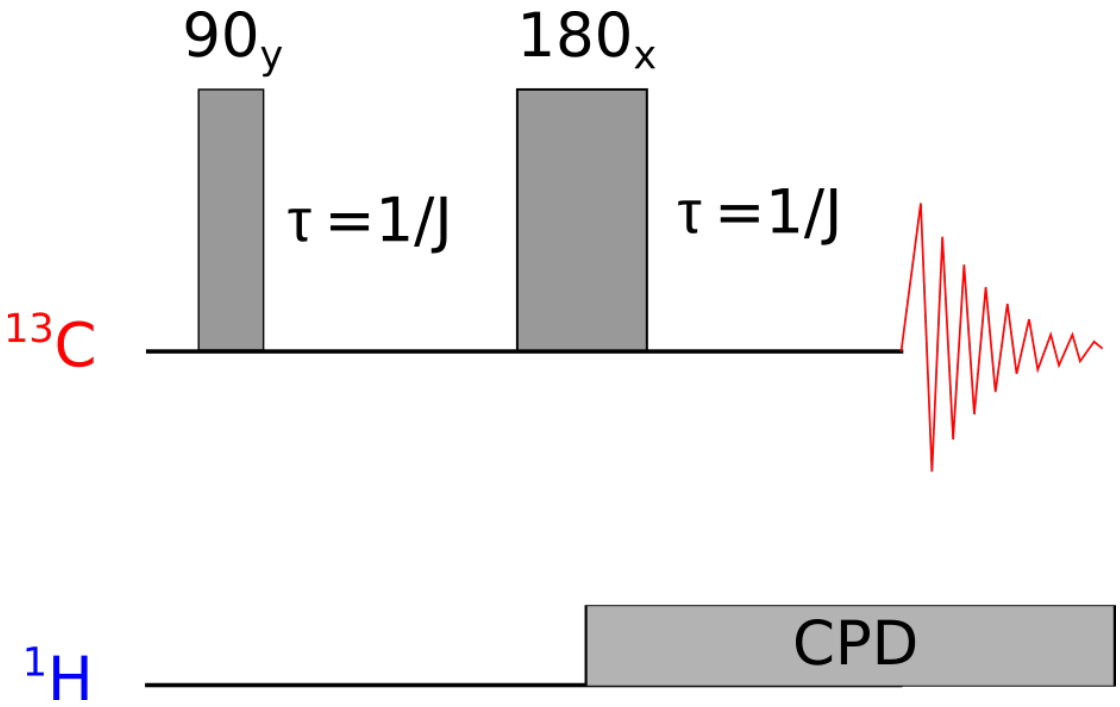


Heteronuclear spin echo of ^{13}C-^{1}H$_3$ group

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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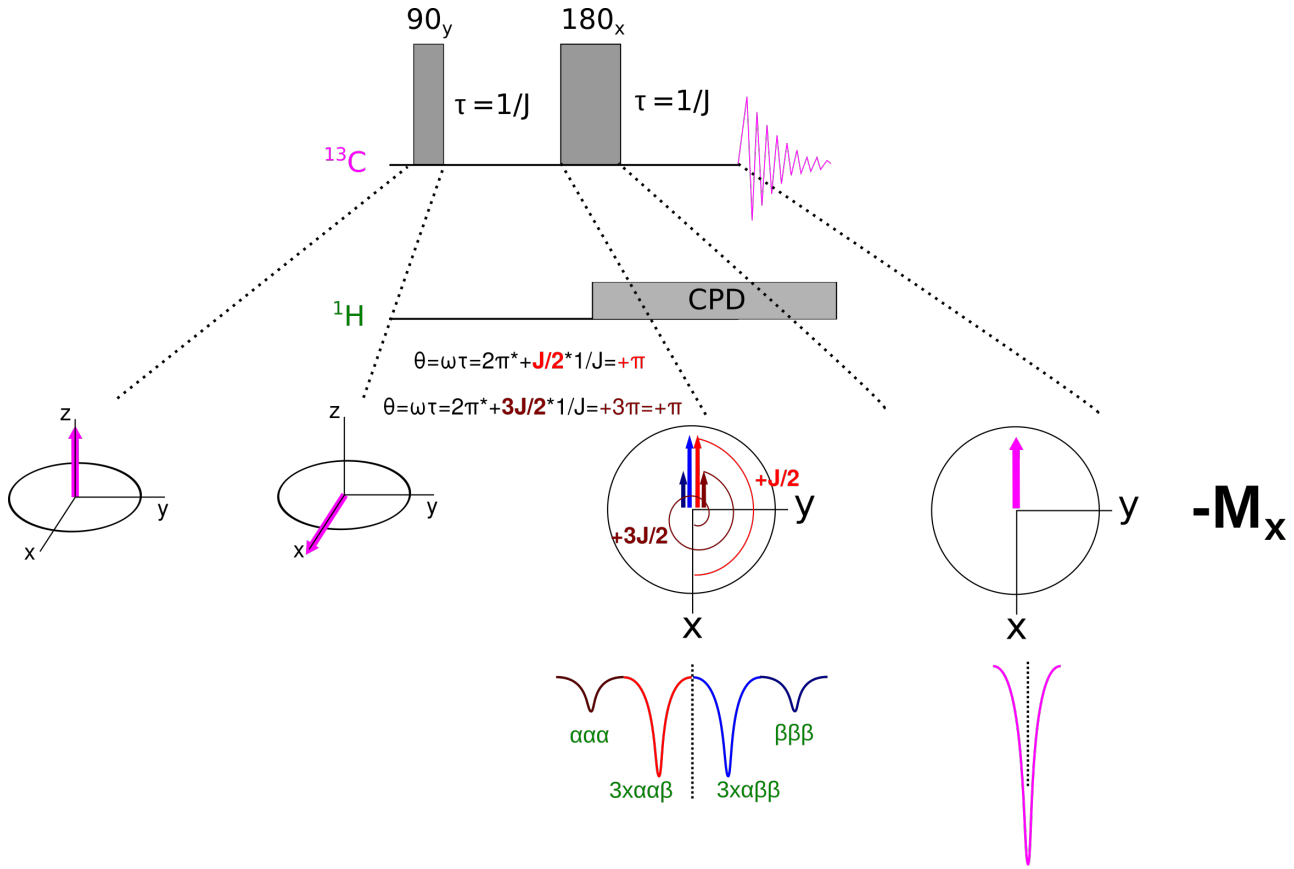
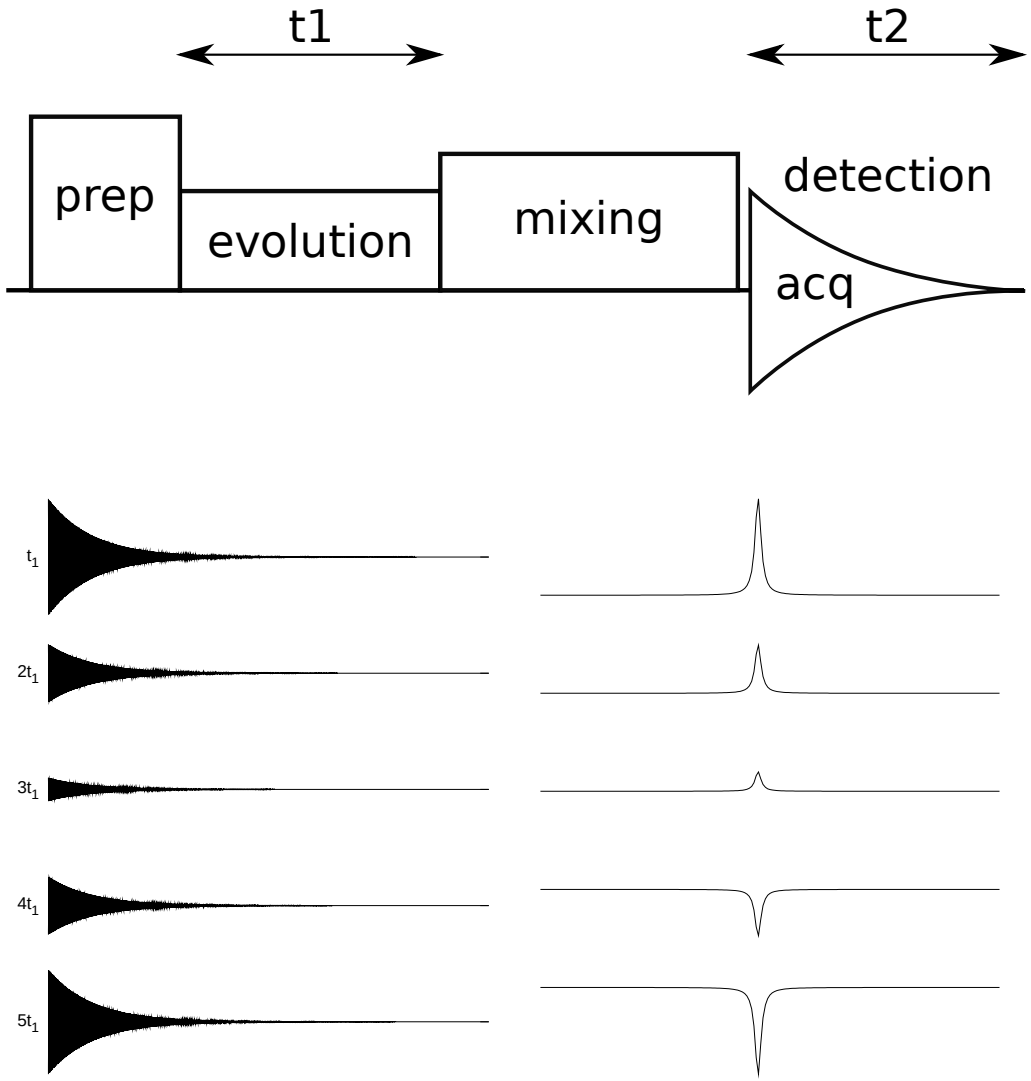


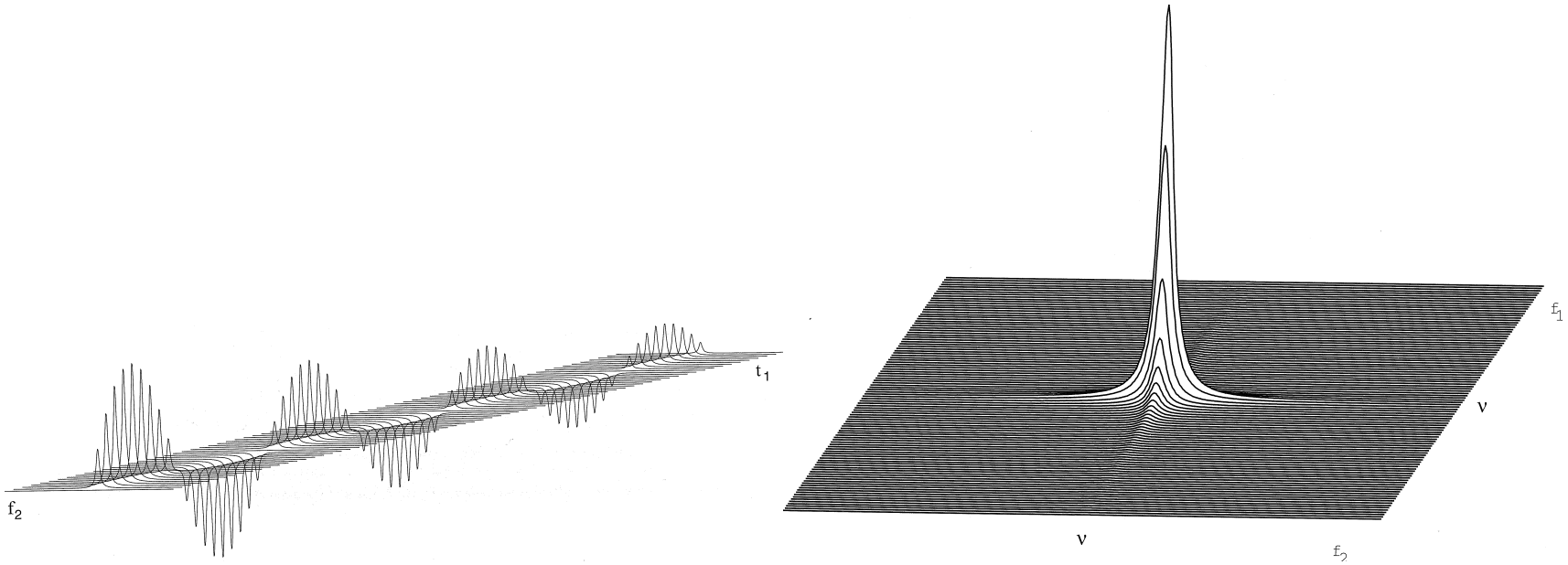
2D NMR

Second dimension f_1

- preparation period
  $\Longrightarrow$ 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

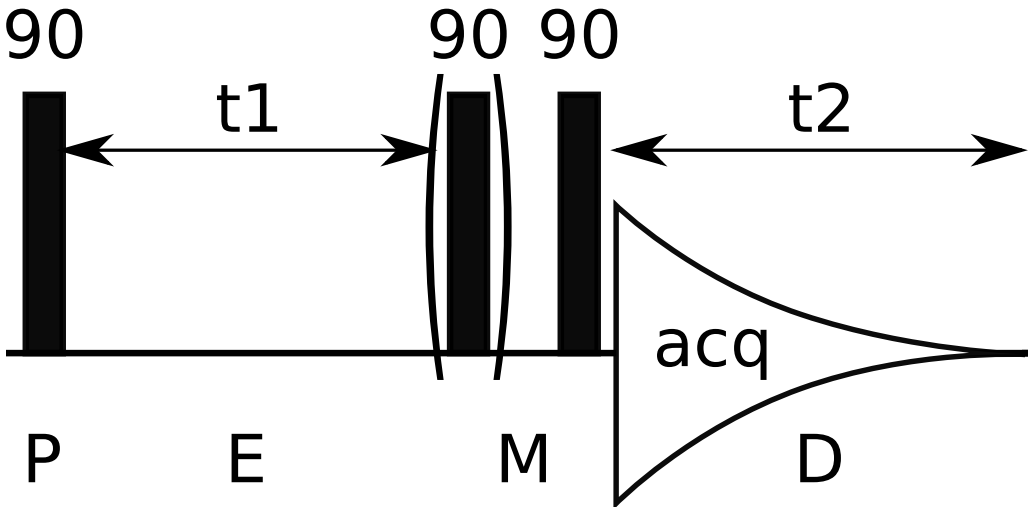


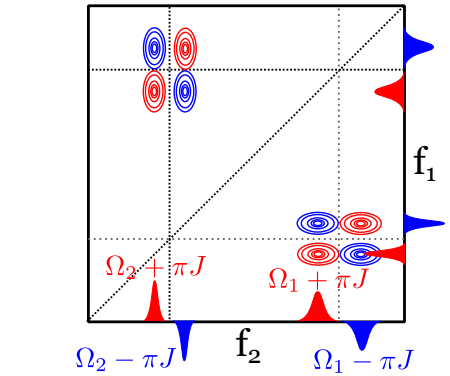
2D spektrum

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

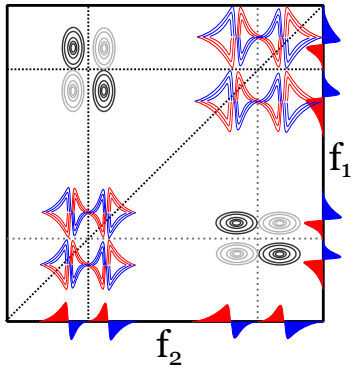
COSY

- 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





$1/2[\cos(\Omega t_1 + \pi J t_1) - \cos(\Omega t_1 - \pi J t_1)]$

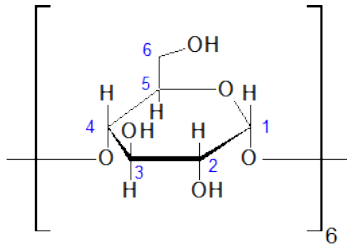


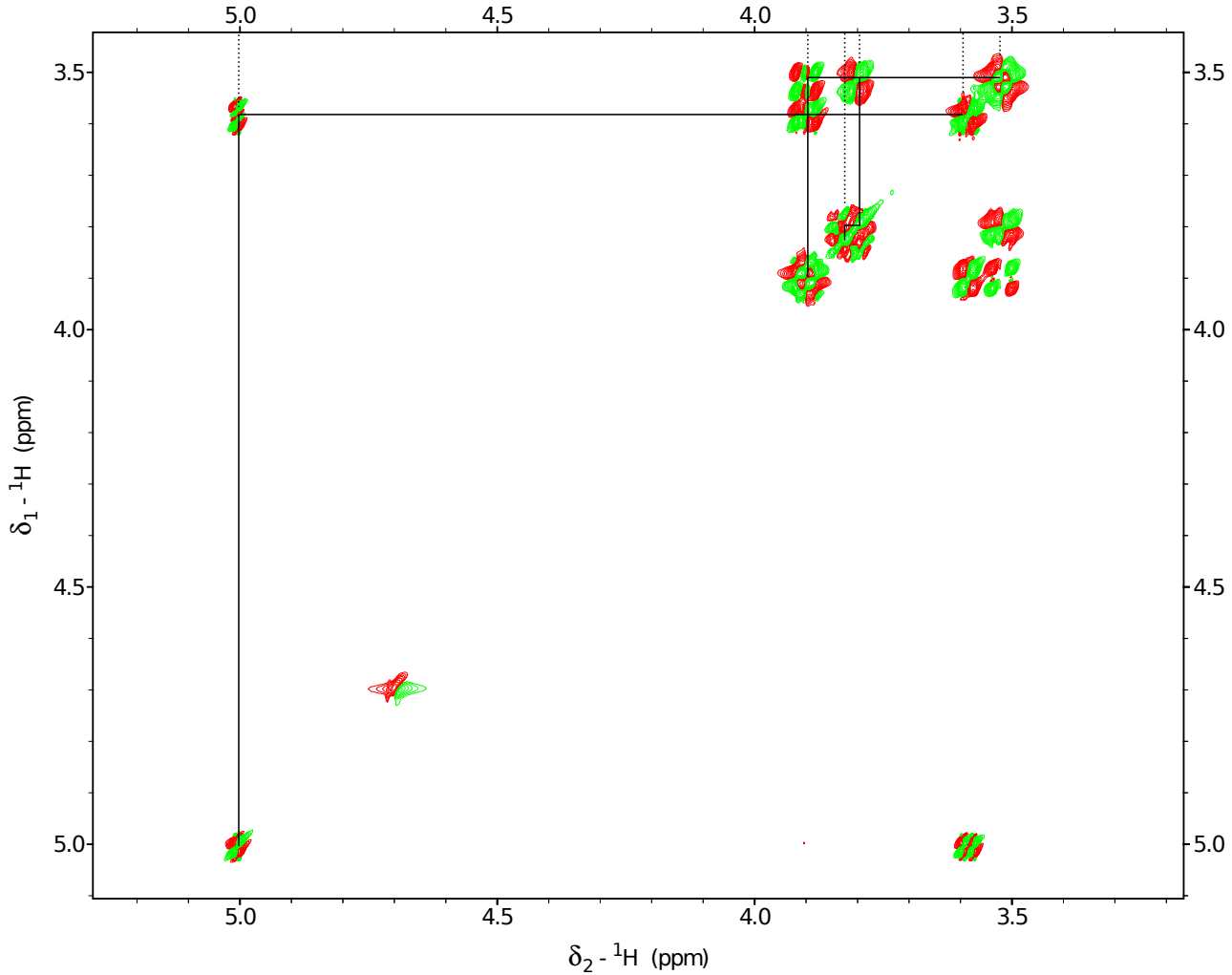
$1/2[\sin(\Omega t_1 + \pi J t_1) + \sin(\Omega t_1 - \pi J t_1)]$

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 : β-cyclodextrine





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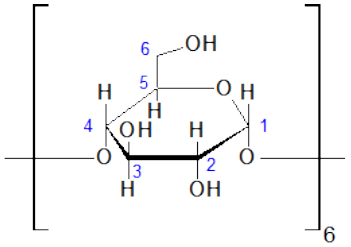
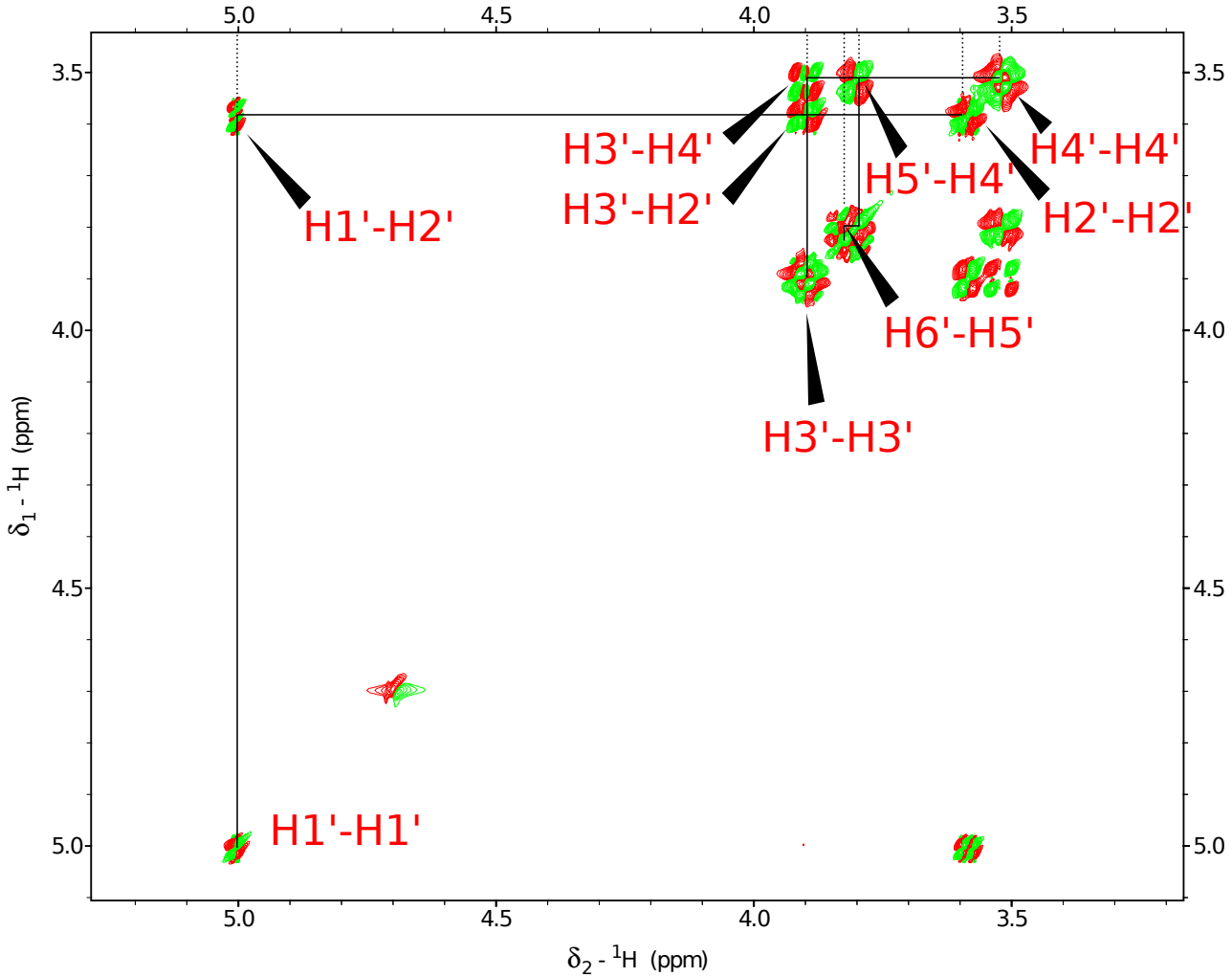
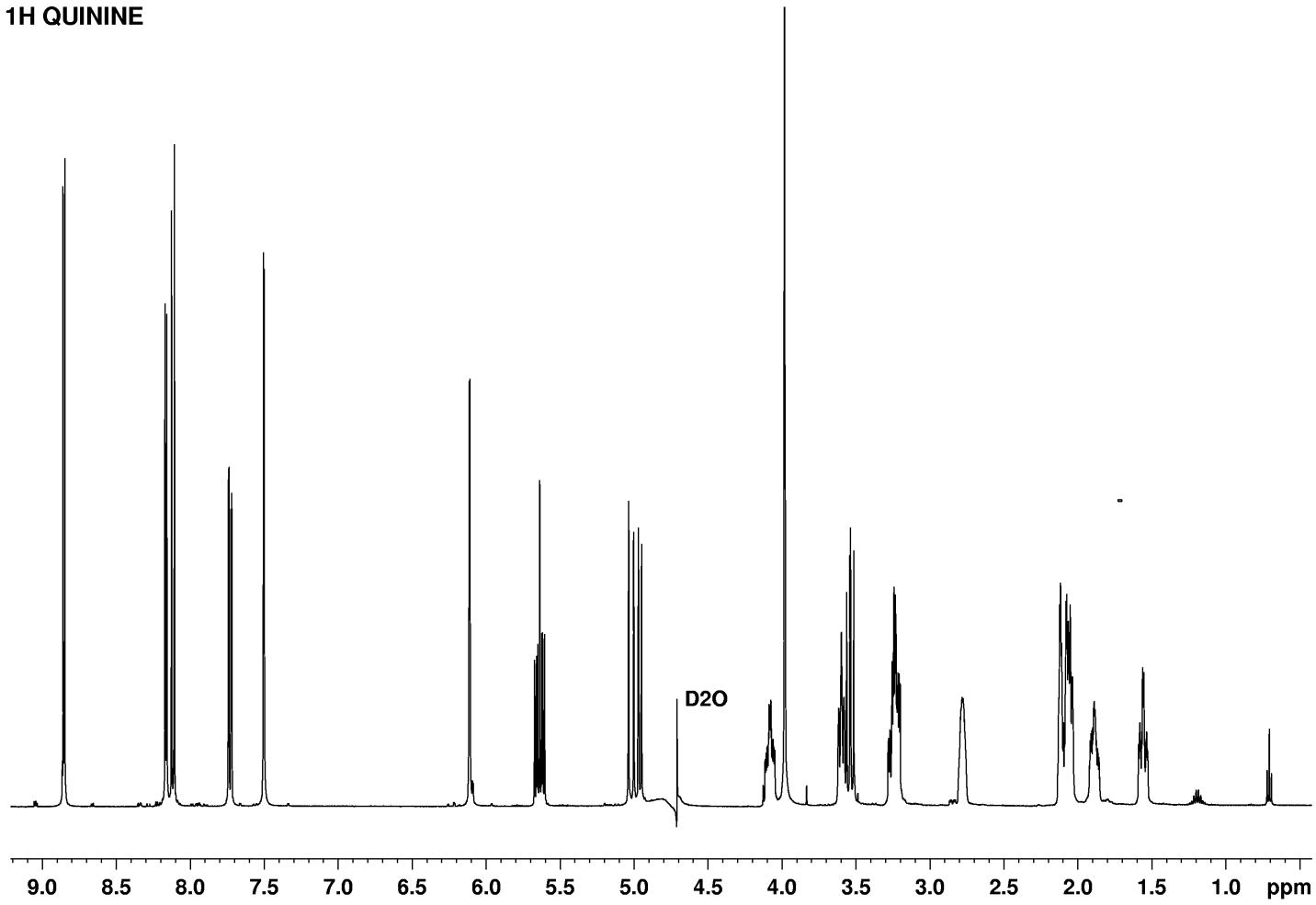
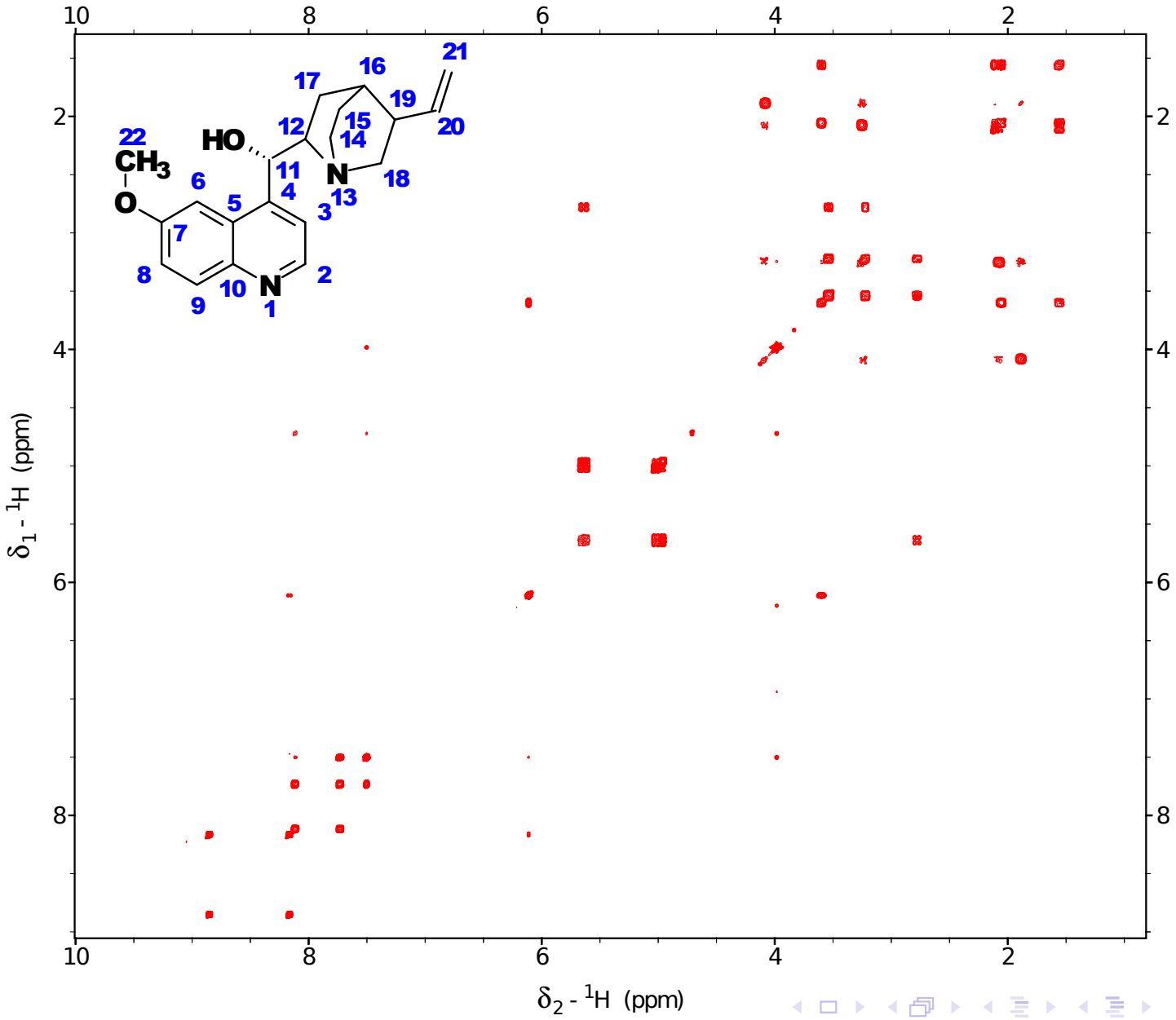




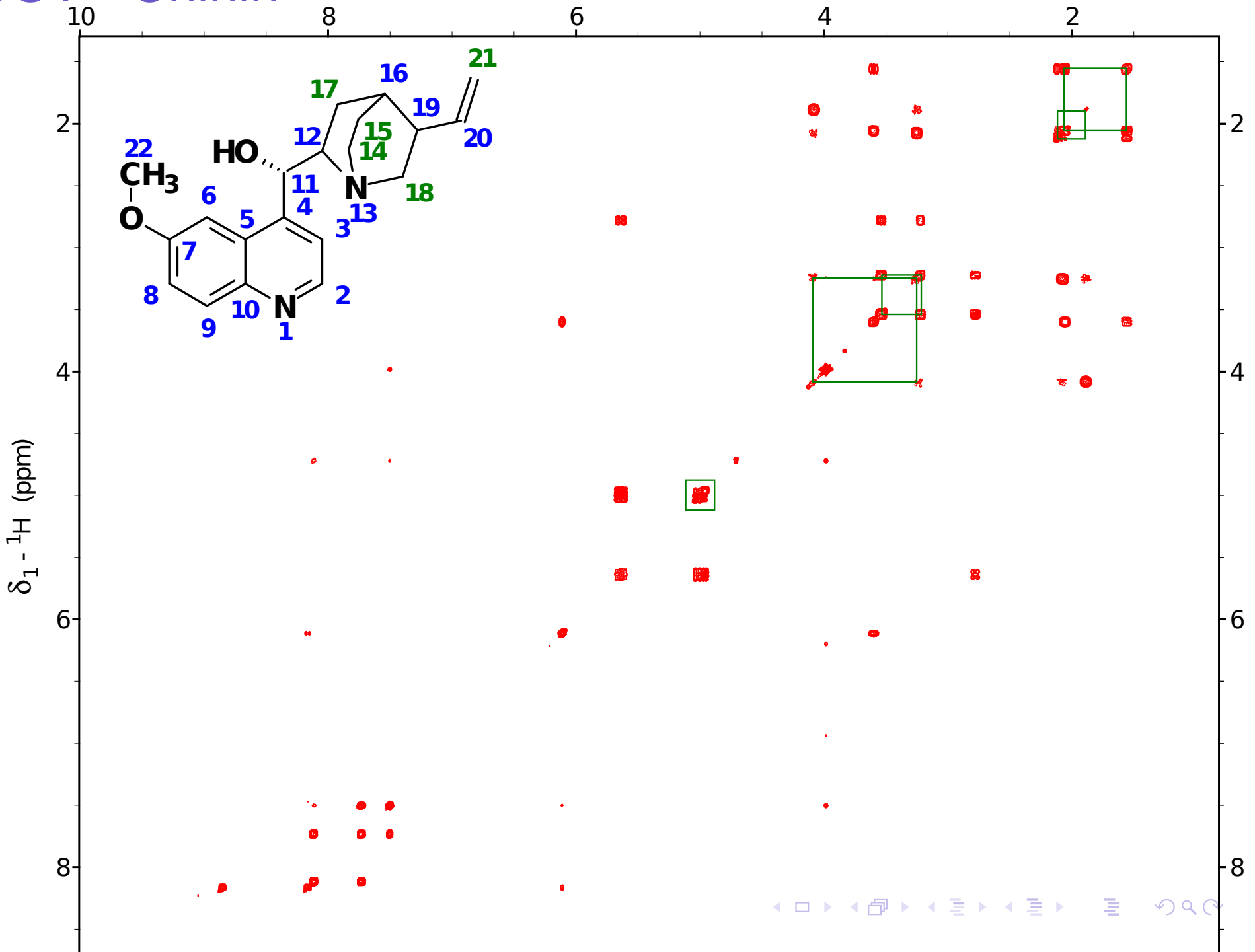
Chinin - 1D ^{1}H



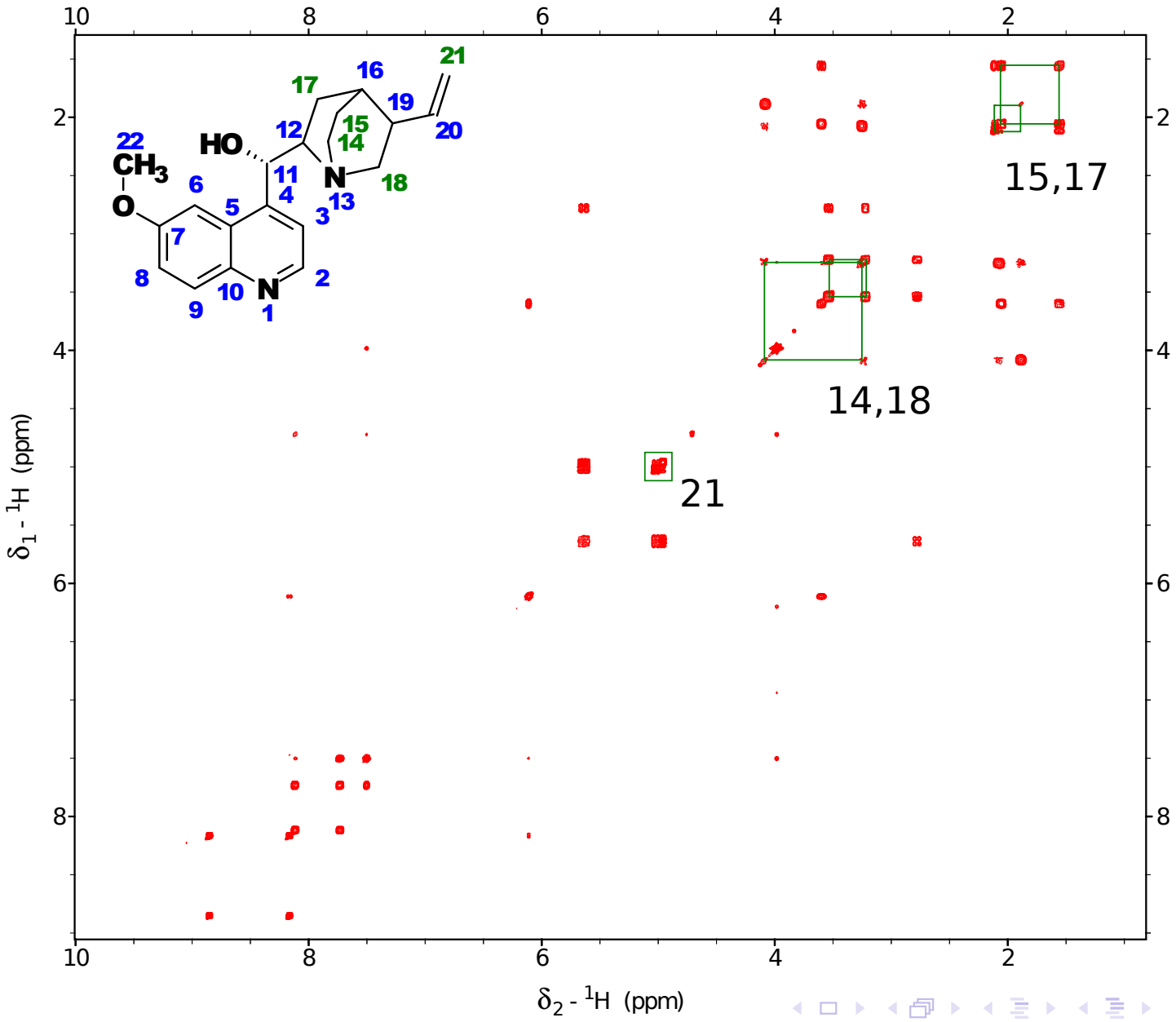
COSY - Chinin


10
8
6
4
2
HO
CH3
O
N
N
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
δ1 - 1H (ppm)
δ2 - 1H (ppm)

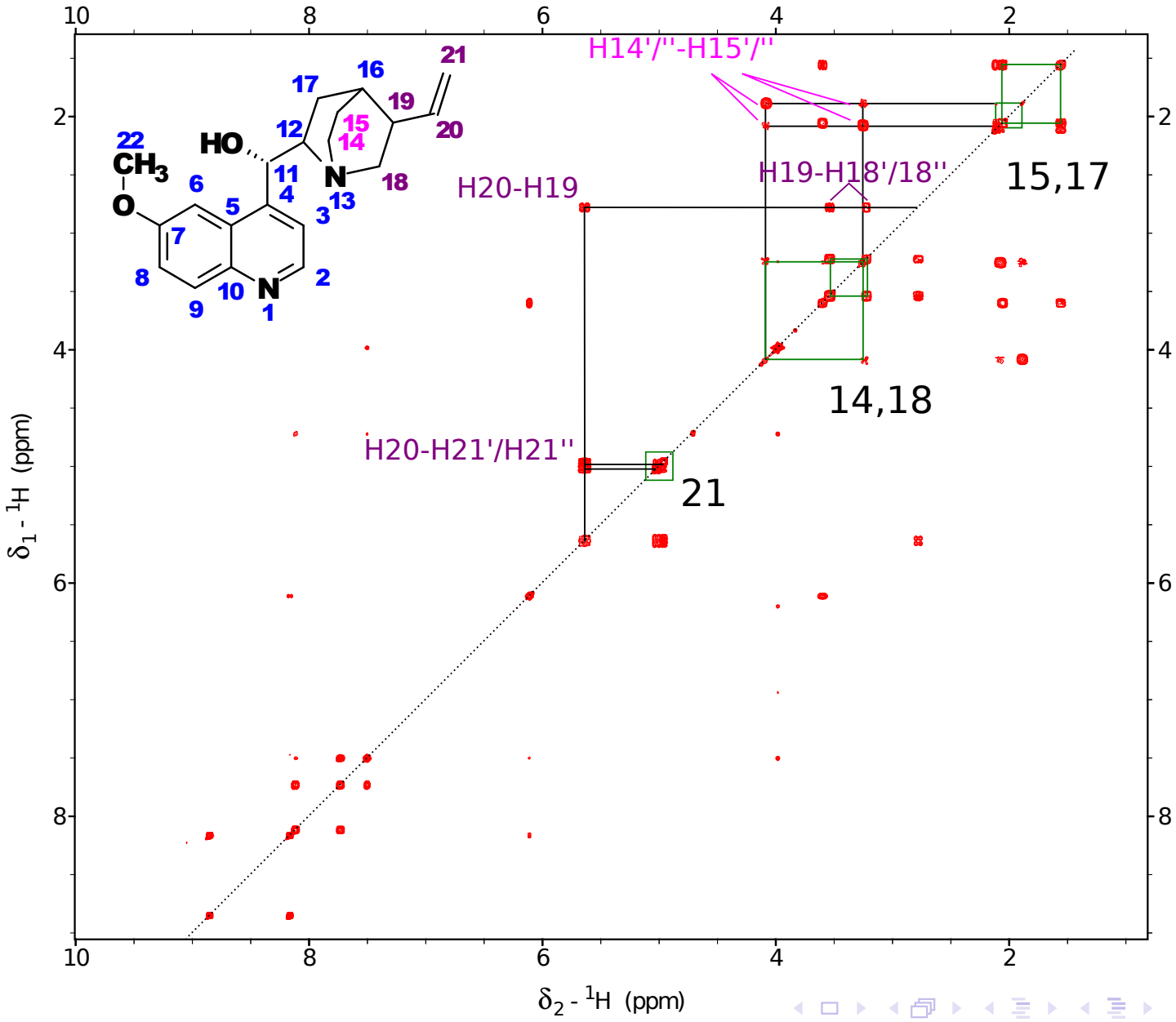
COSY - Chinin


10
8
6
4
2
δ_1 - ^{1}H (ppm)
HO
CH_3
O
N
N
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22

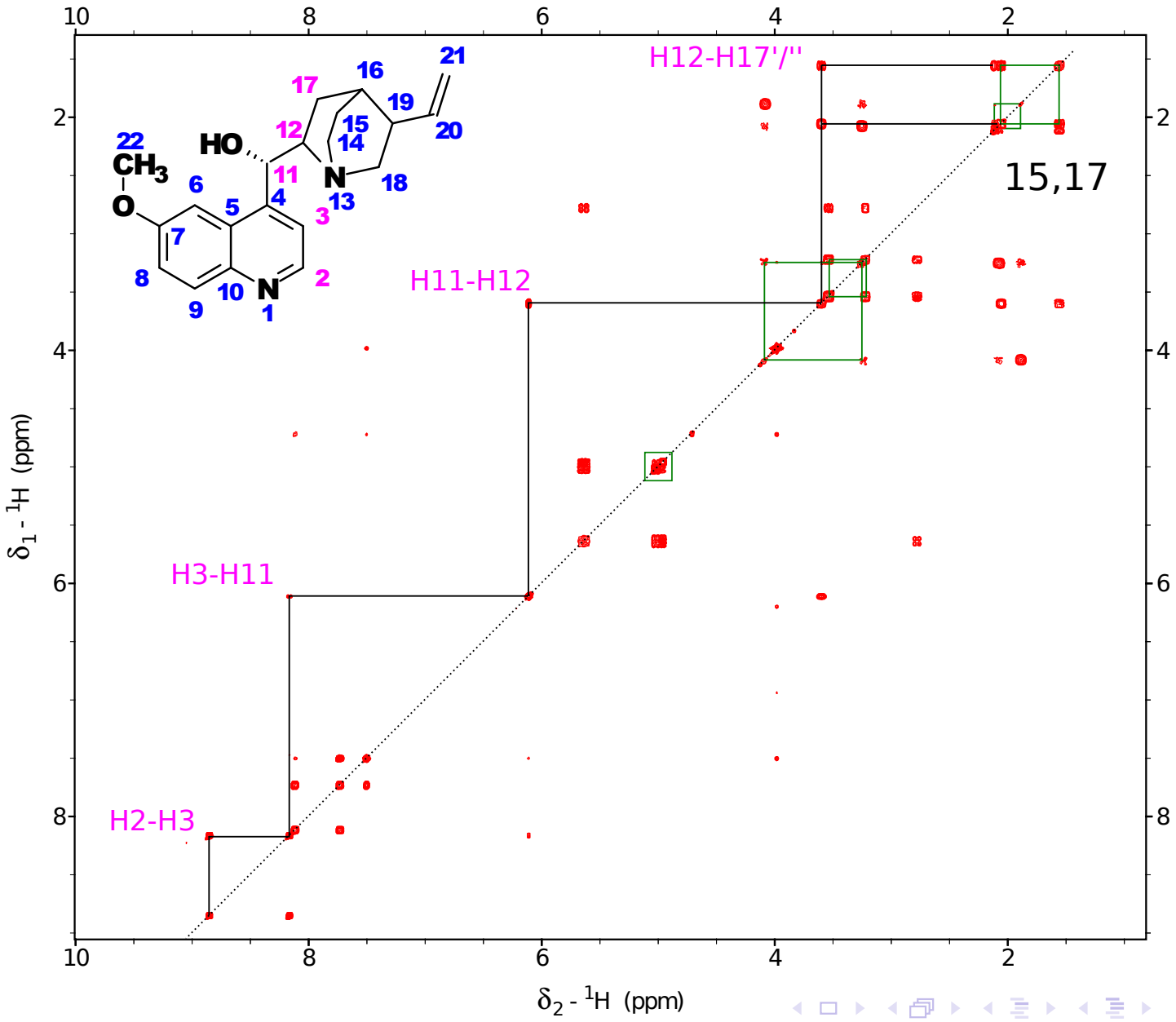
COSY - Chinin



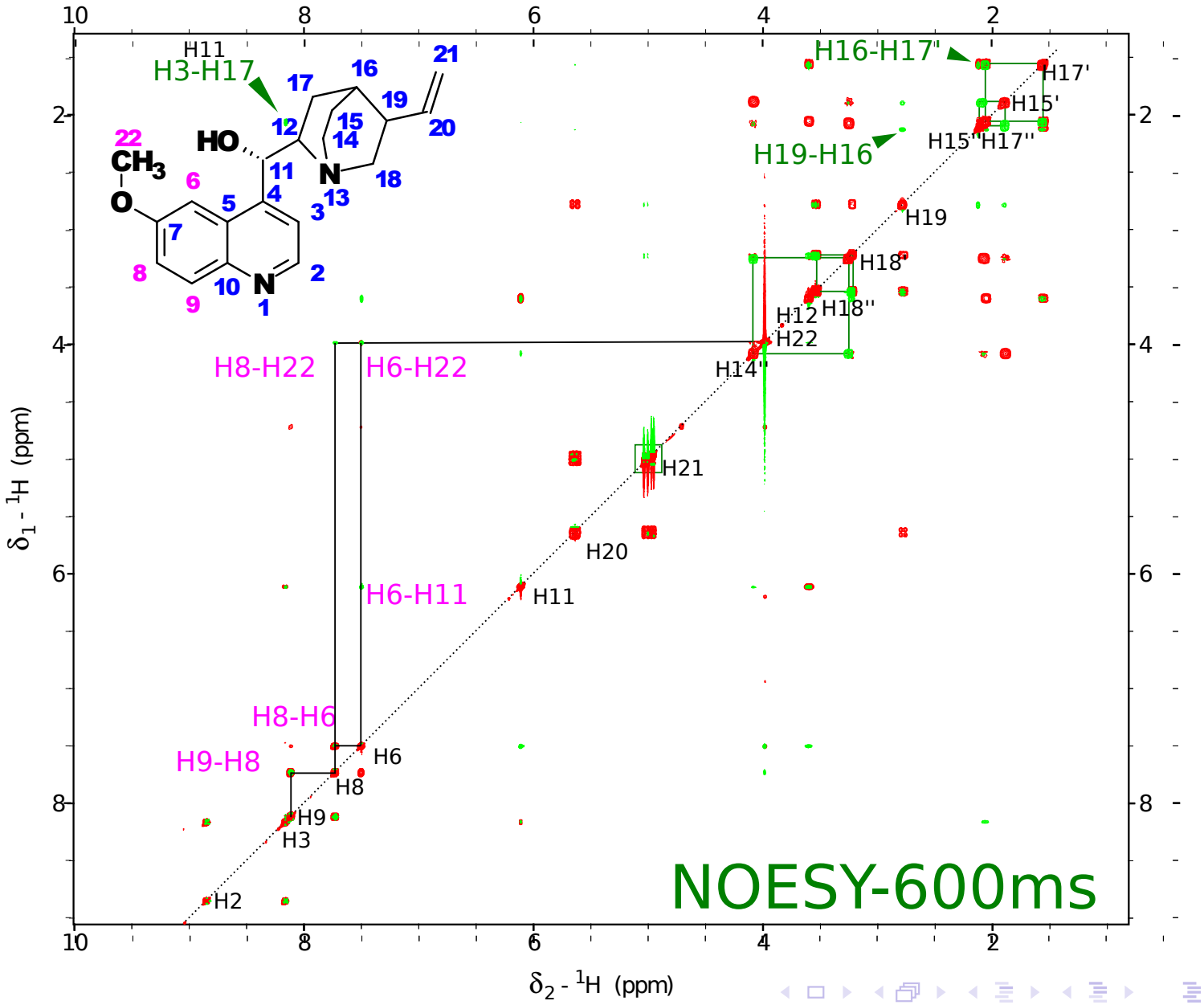
COSY - Chinin


H14'/''-H15'/''
H19-H18'/18''
H20-H19
15,17
14,18
H20-H21'/H21''
21
HO
N
O
CH3
δ1 - 1H (ppm)
δ2 - 1H (ppm)

COSY - Chinin


H12-H17'/''
15,17
H11-H12
H3-H11
H2-H3
HO
N
O
CH3
δ1 - 1H (ppm)
δ2 - 1H (ppm)
10
8
6
4
2

COSY - Chinin


H11
H3-H17
H16-H17''
H19-H16
H8-H22
H6-H22
H6-H11
H8-H6
H9-H8
H17'
H15'
H15''
H17''
H19
H18'
H18''
H12
H22
H14''
H21
H20
H11
H6
H8
H9
H3
H2
NOESY-600ms
δ_1 - ^{1}H (ppm)
δ_2 - ^{1}H (ppm)

Next topic

^{1}H-^{1}H correlations (NOESY, ROESY, TOCSY)