

C8953
NMR strukturní analýza
seminář

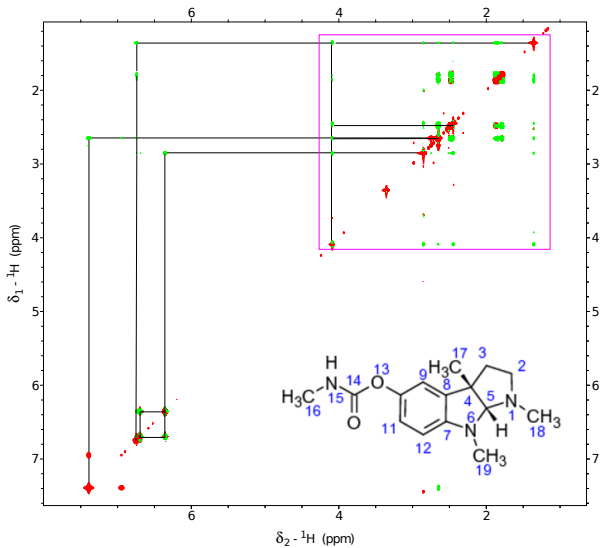
Heteronuclear correlations

Jan Novotný

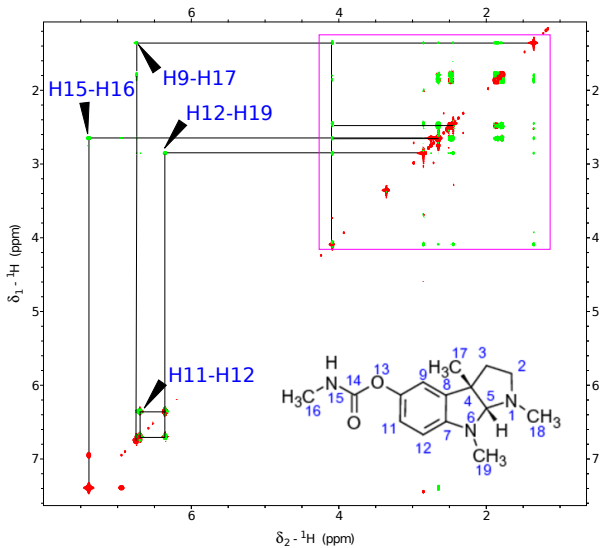
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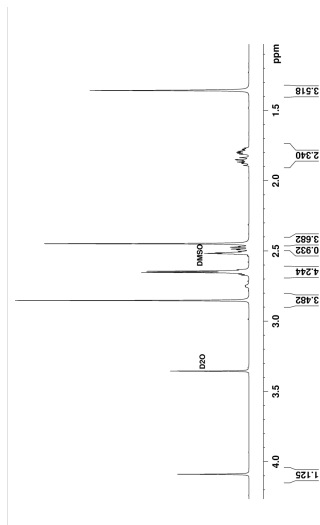
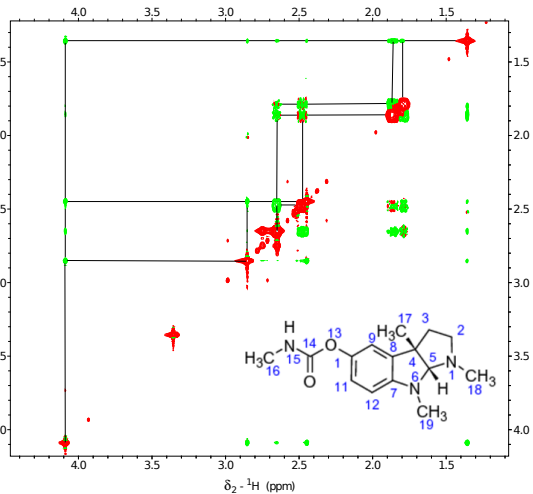
NOESY - Eserine in DMSO



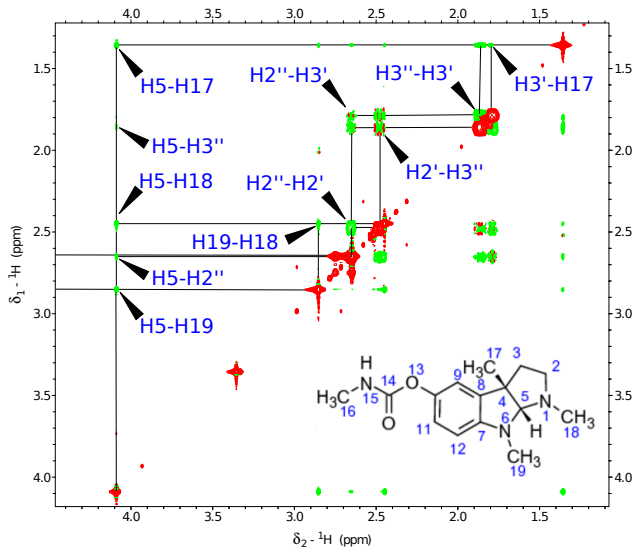
NOESY - Eserine in DMSO



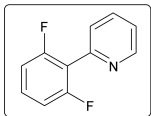
NOESY - Eserine



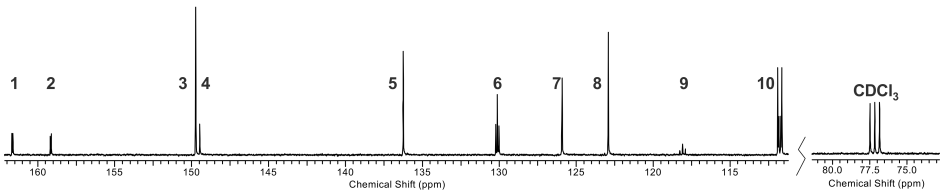
NOESY - Eserine



1D ^{13}C NMR



100 MHz, CDCl_3



Polarization transfer

- ▶ bigger population difference of ^1H nucleus is transferred via J-coupling to less sensitive nucleus X (^{13}C , ^{15}N)
- ▶ fundamental building block of heteronuclear correlation experiments: in 2D-HX experiment each crosspeak manifests interaction of H and X nucleus coupled through bonds
- ▶ **Task: Draw the evolution of magnetization during basic INEPT pulse sequence. Consider C-H interacting pair.**

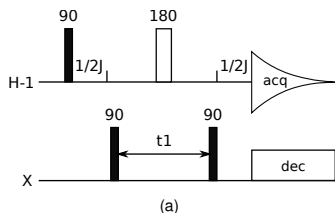
HMQC (Heteronuclear Multiple Quantum Correlation)

HSQC (Heteronuclear Single Quantum Correlation)

correlate $^1\text{H-X}$ ($\text{X} = ^{13}\text{C}, ^{15}\text{N}, \dots$) based on $^1J_{\text{HX}}$

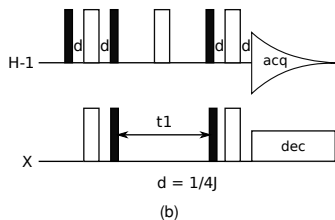
HMQC (a)

- + more robust experiment
- + change of parameters - HMBC
- lower sensitivity and worse resolution



HSQC (b)

- + better resolution, sensitivity
- + part of more complex multidimensional experiments
- less robust



Practical notes $^1\text{H-X}$ HSQC

- ▶ resolution of overlaps
- ▶ routine experiments to control biomolecular sample
- ▶ easy identification of geminal protons
- ▶ indirect determination of protons bonded to NMR inactive heteroatom
- ▶ heteronuclear correlation \Rightarrow no diagonal crosspeak, no symmetry
- ▶ X decoupled during acquisition \Rightarrow singlet crosspeak

HMBC(Heteronuclear Multiple-Bond Correlation)

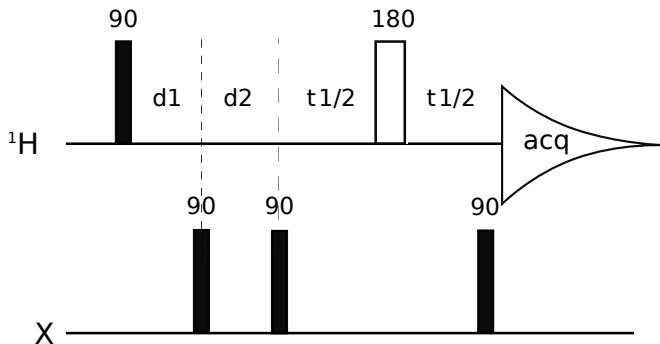
heteronuclear correlation based on long-range H-X spin-spin interaction(${}^nJ_{HX}$, $n>1$)

- ▶ utilizes polarization transfer from H through 2-5 bonds on heteroatom (${}^{13}\text{C}$, ${}^{15}\text{N}$)
- ▶ allows to detect quaternary heteroatoms (Cq) or connect signals among isolated spin systems

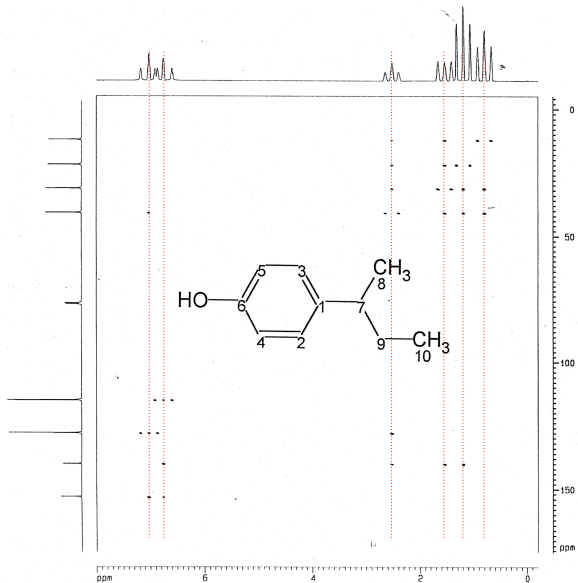
HMBC

correct settings of d_1 , d_2 for evolution of J -coupling necessary

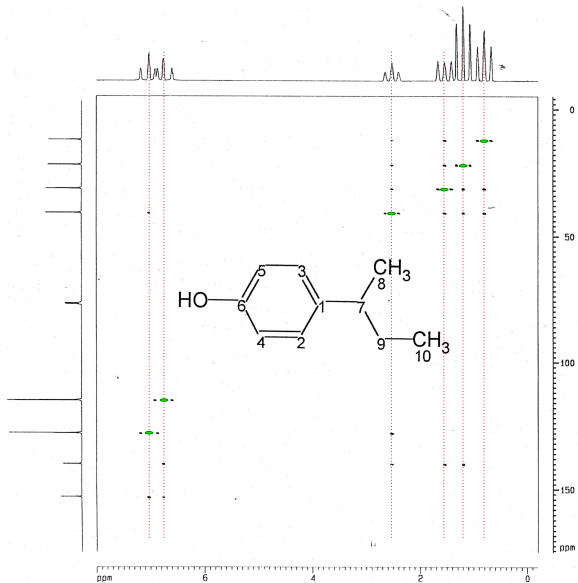
- ▶ $d_1 = 1/2 * {}^1J_{C-H}$ - (120-180 Hz)
- ▶ $d_2 = 1/2 * {}^{2-5}J_{C-H}$ - (3-12 Hz)



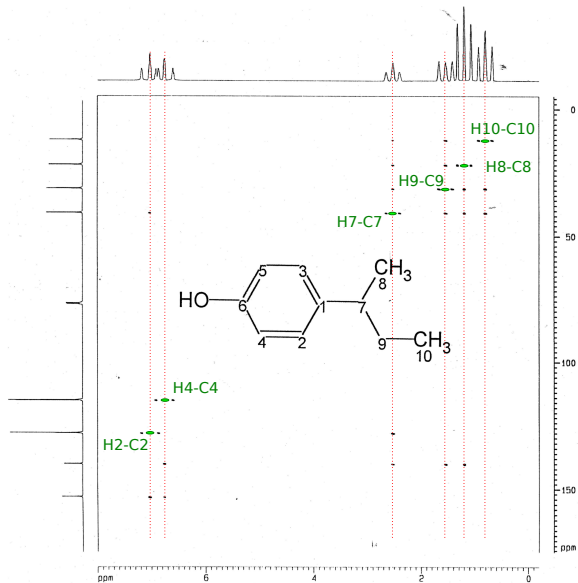
^1H - ^{13}C HMBC + ^1H - ^{13}C HSQC



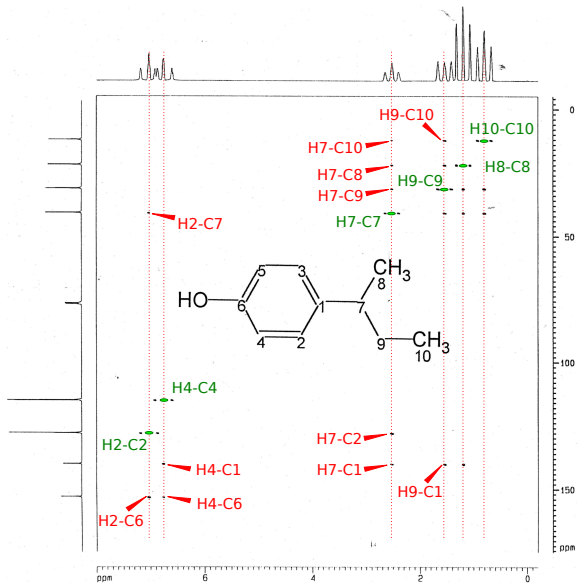
^1H - ^{13}C HMBC + ^1H - ^{13}C HSQC



^1H - ^{13}C HMBC + ^1H - ^{13}C HSQC

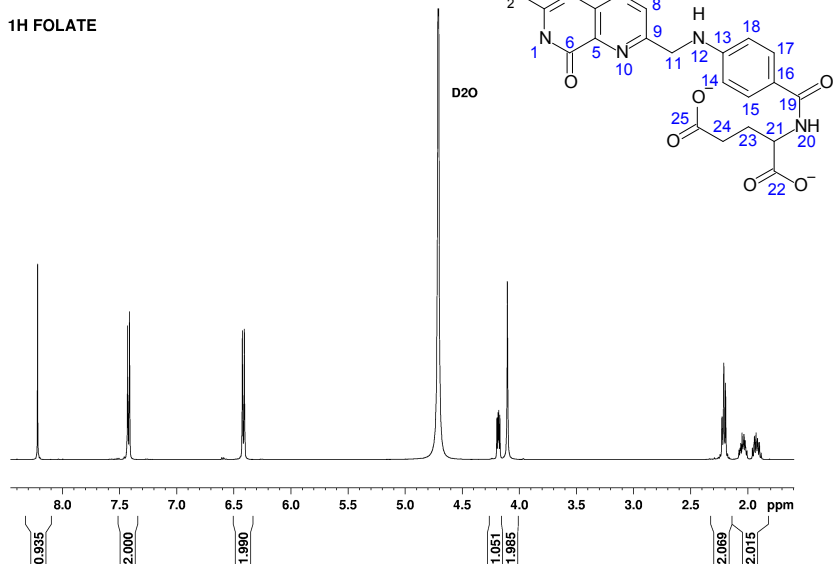


^1H - ^{13}C HMBC + ^1H - ^{13}C HSQC



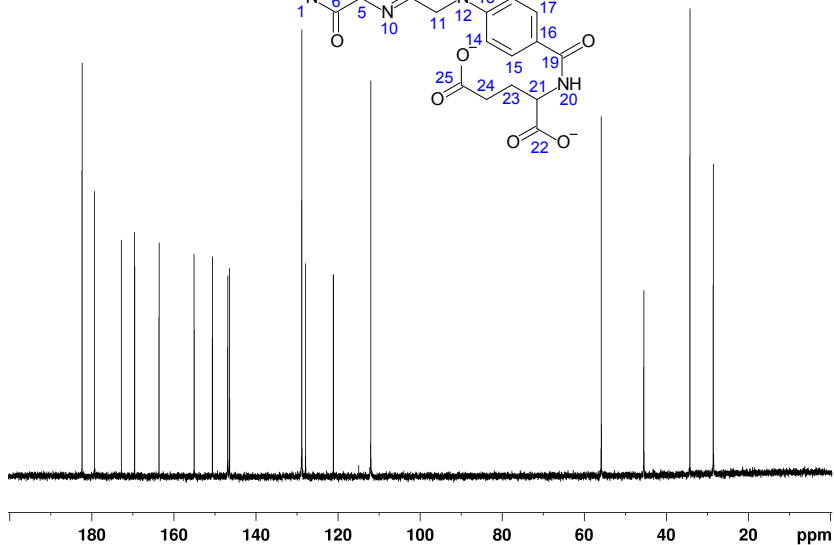
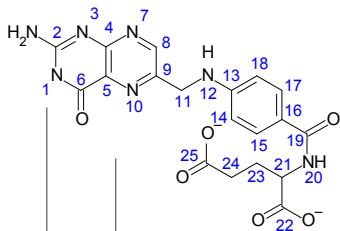
Folic Acid: ^1H 1D

^1H FOLATE

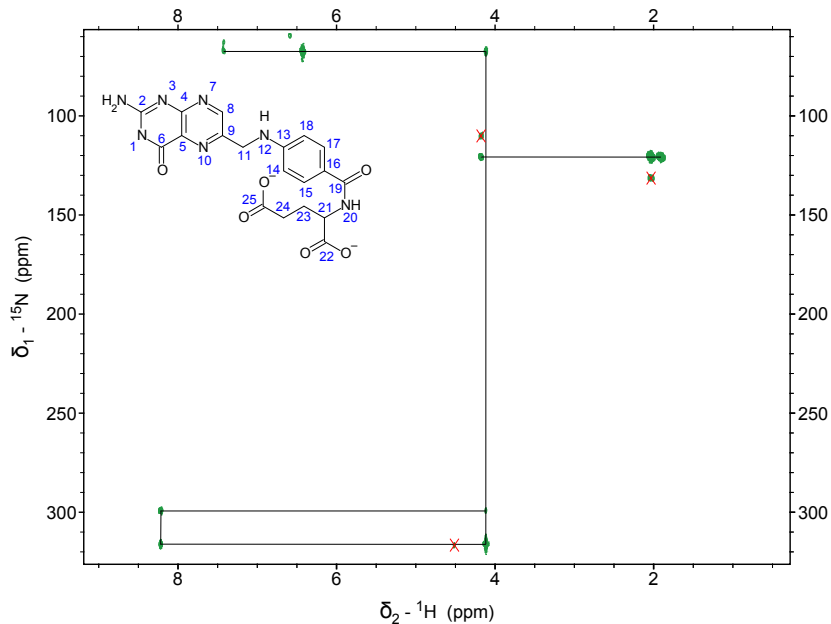


Folic Acid: ^{13}C 1D

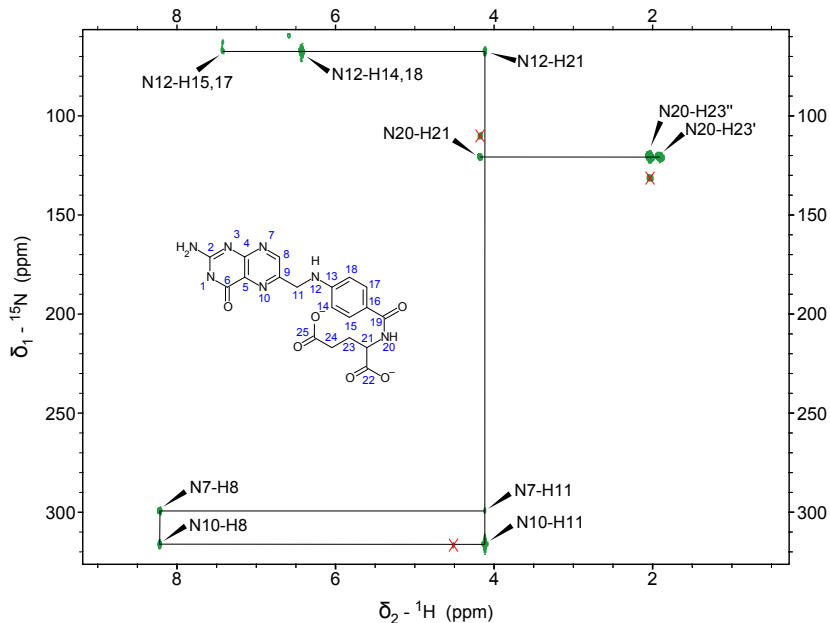
^{13}C FOLATE



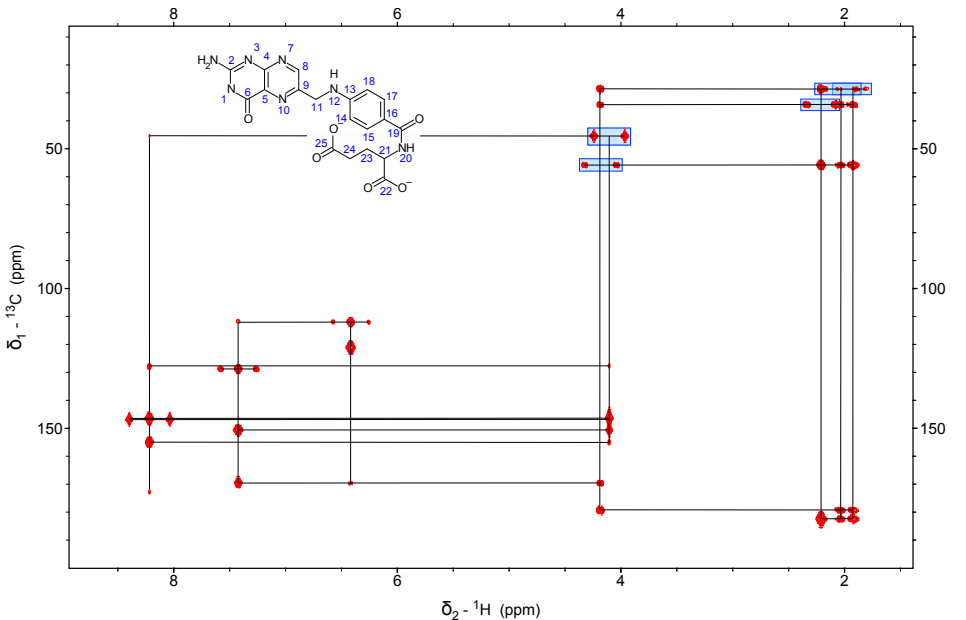
Folic Acid: ^1H - ^{15}N HMBC



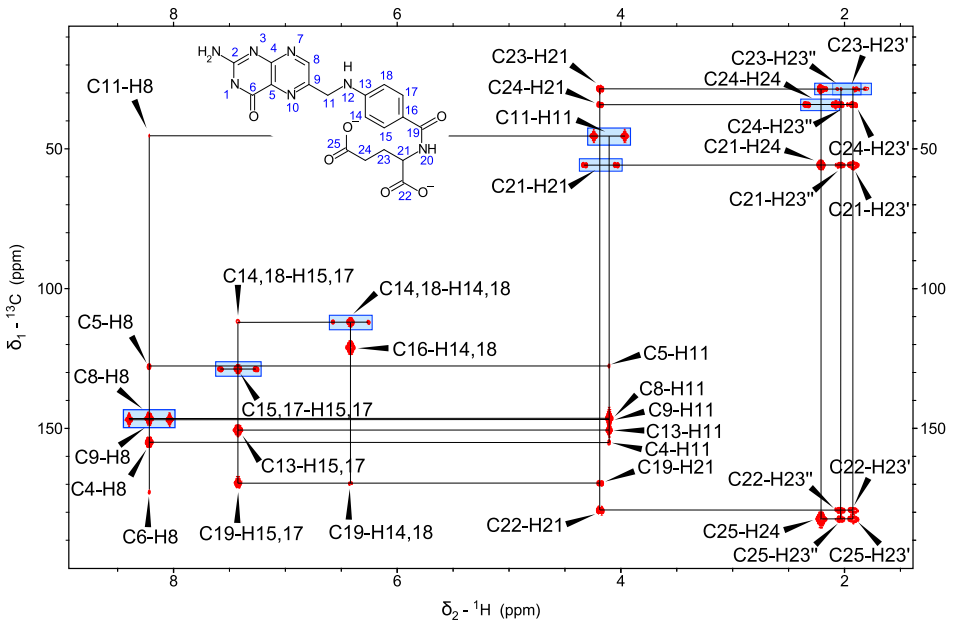
Folic Acid: ^1H - ^{15}N HMBC



Folic Acid: ^1H - ^{13}C HMBC



Folic Acid: ^1H - ^{13}C HMBC



Next session:

Complex tasks