

C8953  
NMR strukturní analýza  
seminář

Introduction to heteronuclear correlations

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# Polarization transfer

- ▶ bigger population difference of  $^1\text{H}$  nucleus is transferred via J-coupling to less sensitive nucleus X ( $^{13}\text{C}$ ,  $^{15}\text{N}$ )
- ▶ 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.**

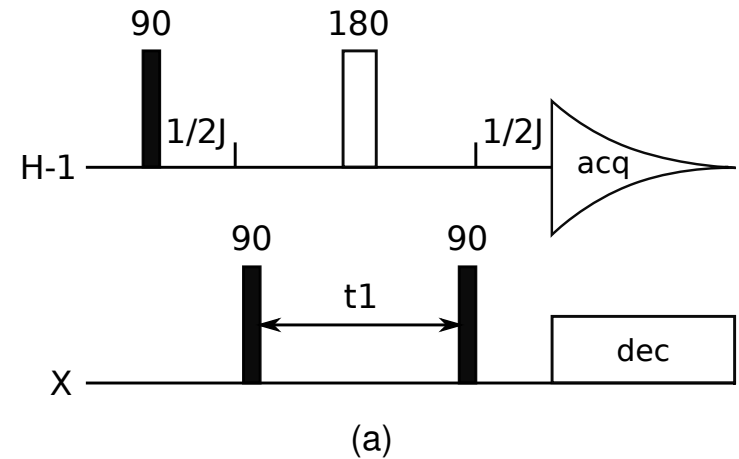
# HMQC (Heteronuclear Multiple Quantum Correlation)

## HSQC (Heteronuclear Single Quantum Correlation)

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

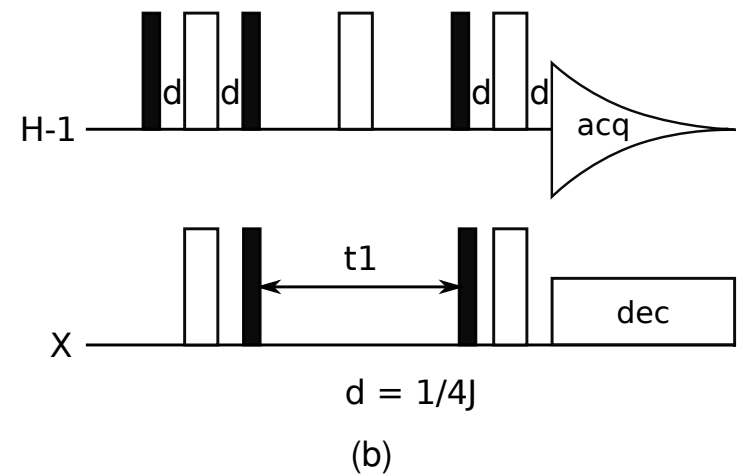
### HMQC (a)

- + 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)

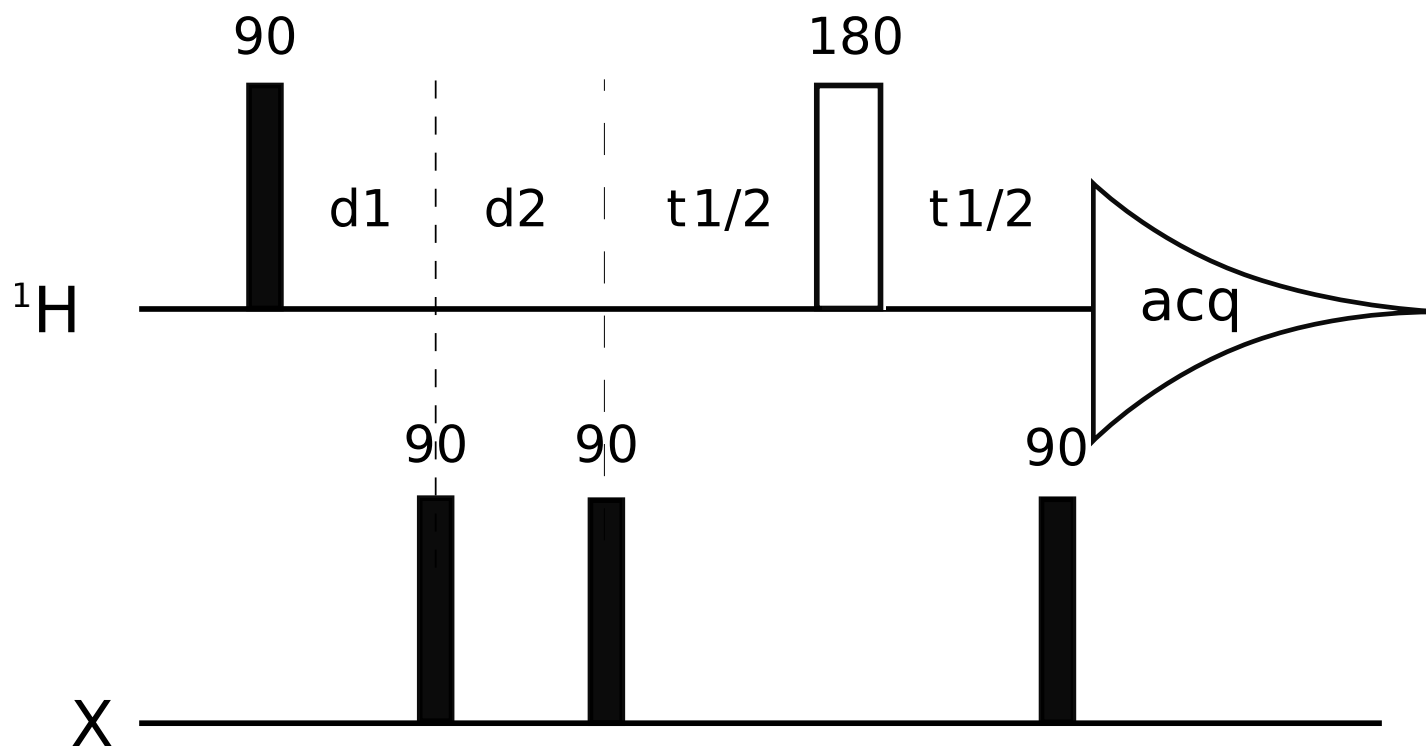
heteronuclear correlation based on long-range H-X spin-spin interaction(  ${}^n J_{HX}$ ,  $n > 1$  )

- ▶ 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

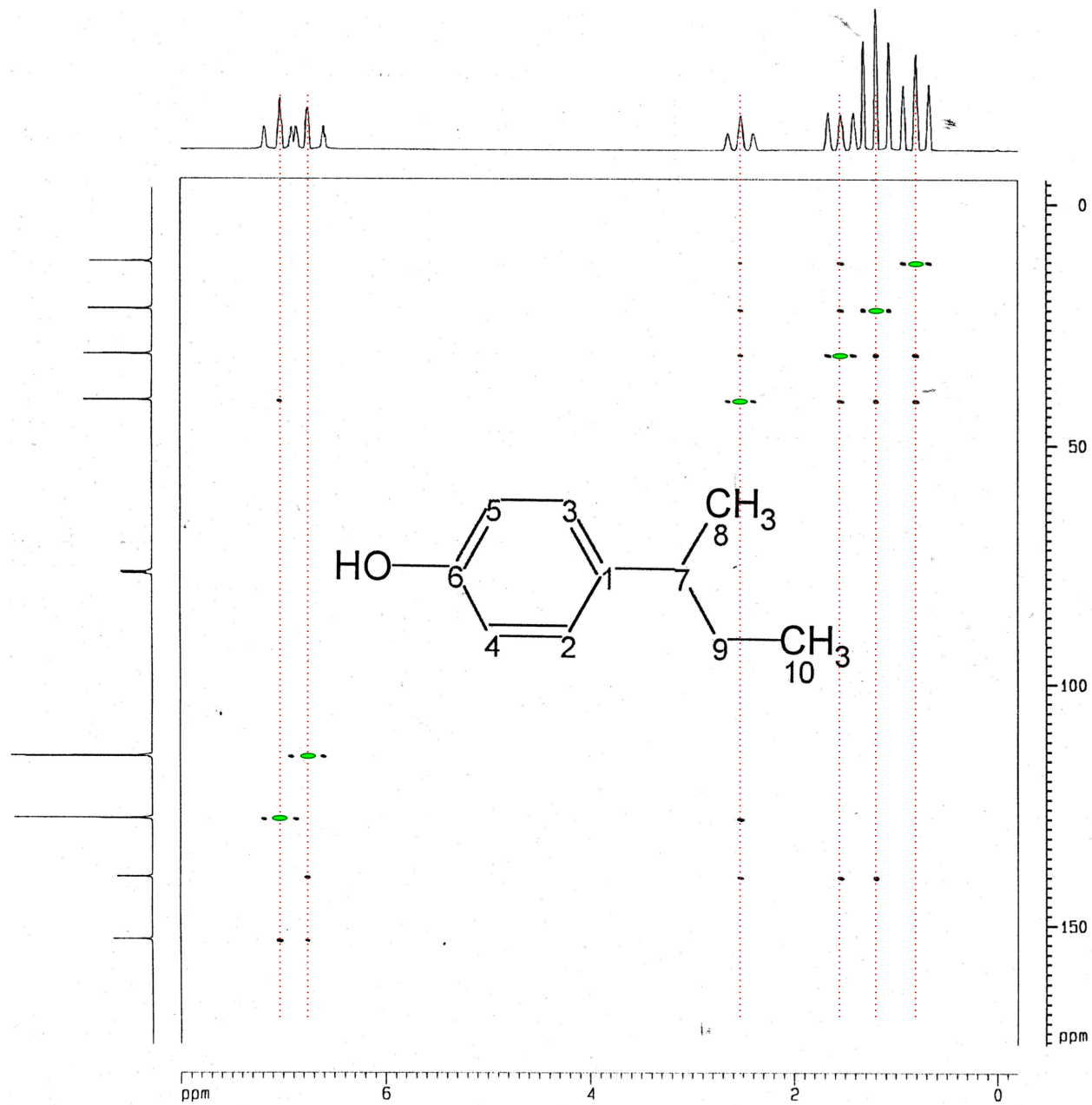
# HMBC

correct settings of  $d_1$ ,  $d_2$  fo 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)

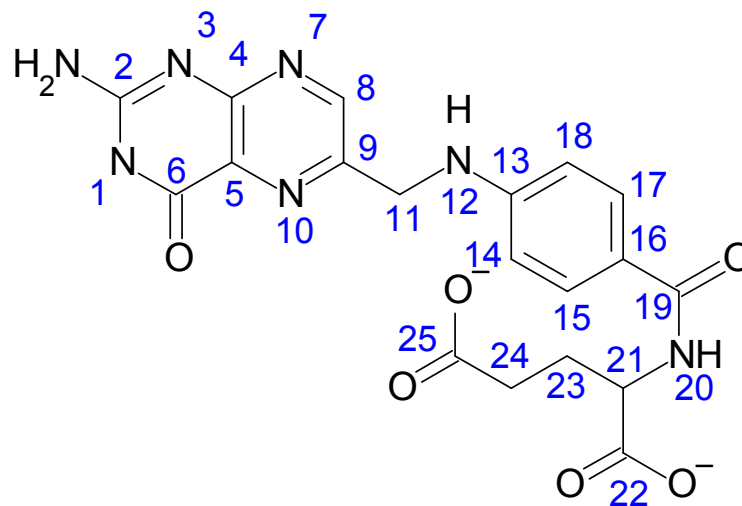


# $^1\text{H}$ - $^{13}\text{C}$ HMBC + $^1\text{H}$ - $^{13}\text{C}$ HSQC

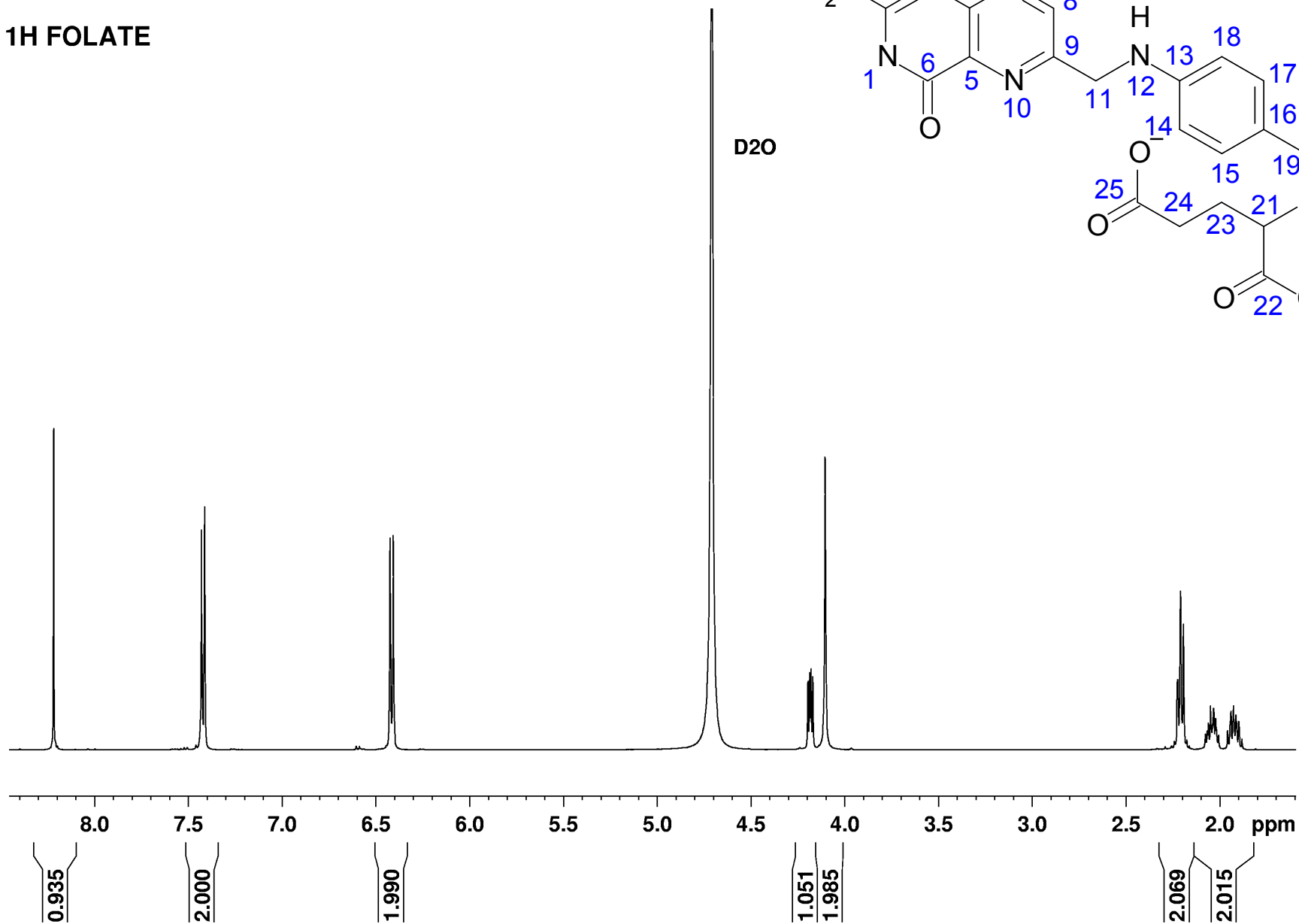


# Folic Acid: $^1\text{H}$ 1D

1H FOLATE



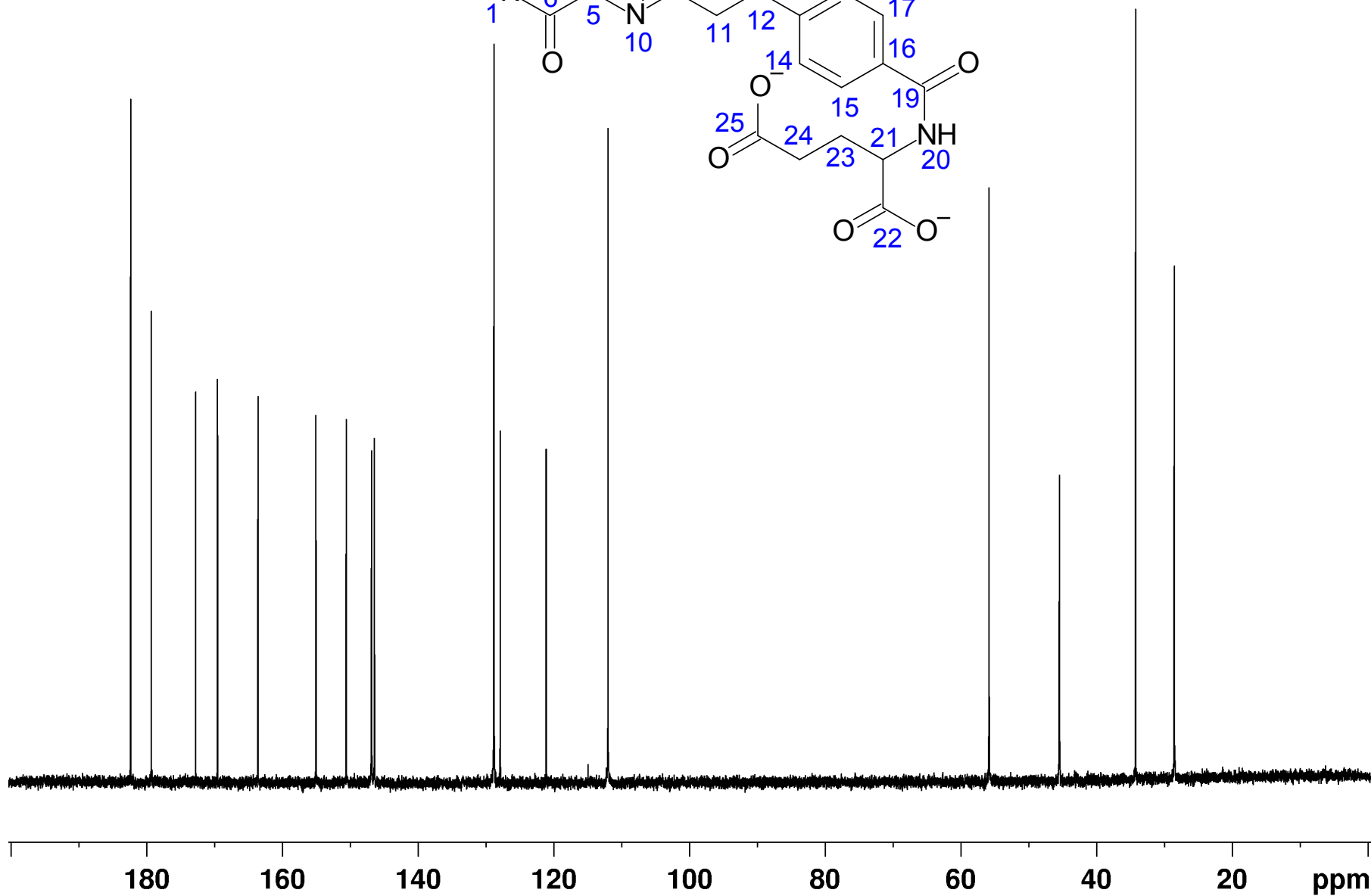
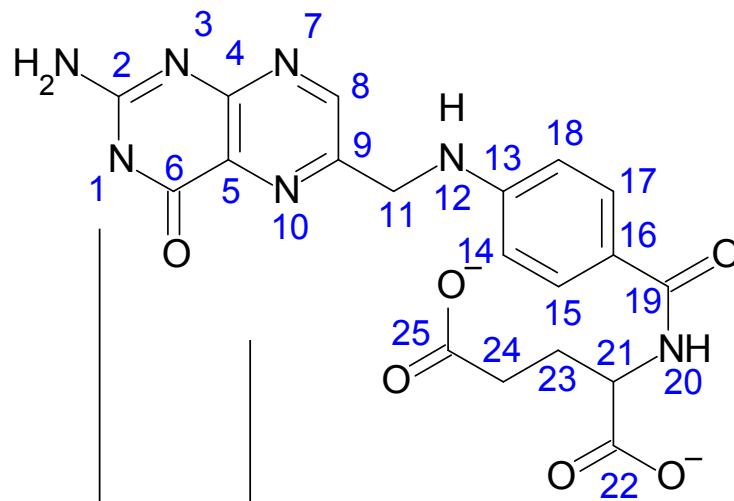
D2O



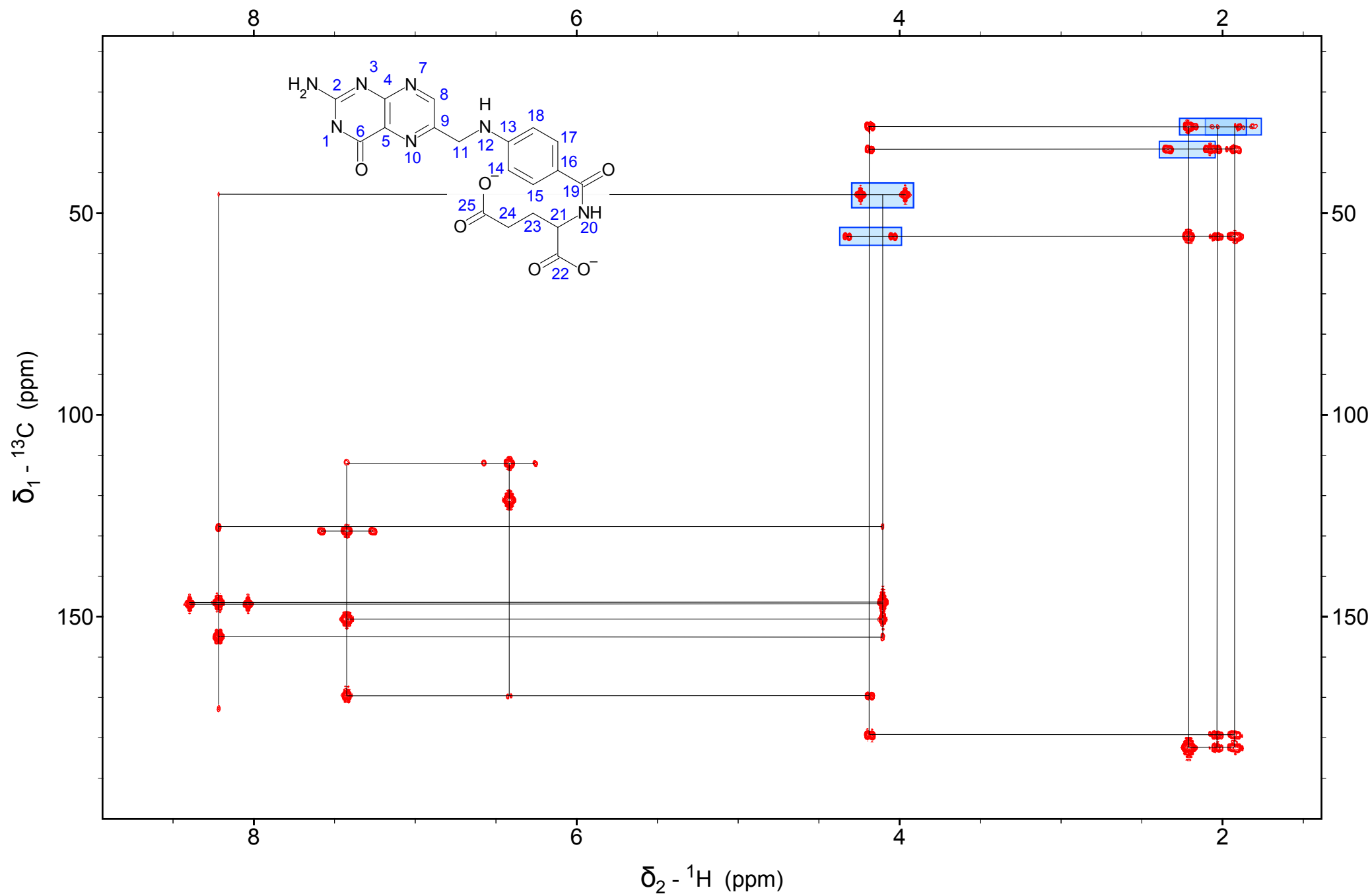


# Folic Acid: $^{13}\text{C}$ 1D

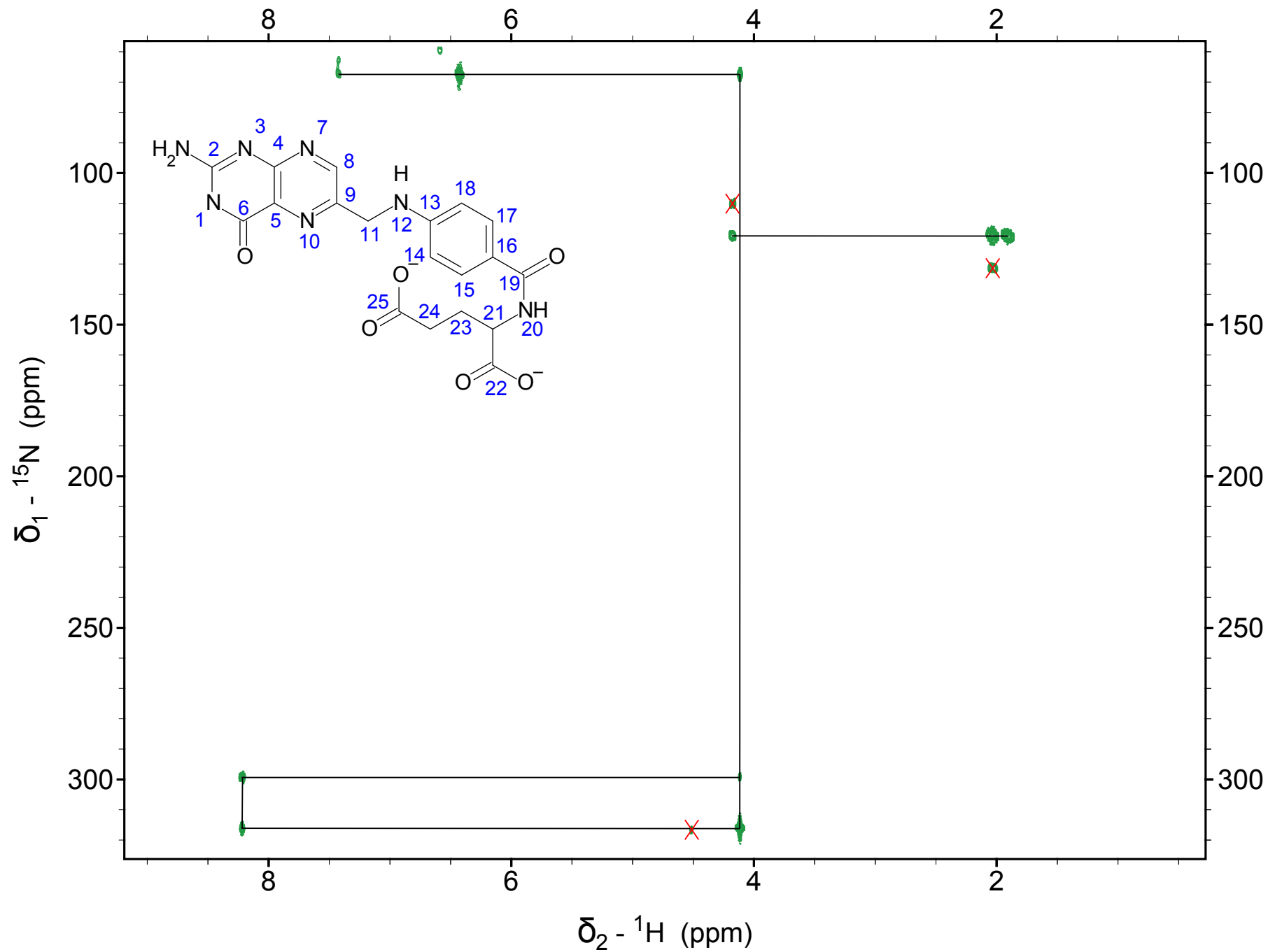
$^{13}\text{C}$  FOLATE



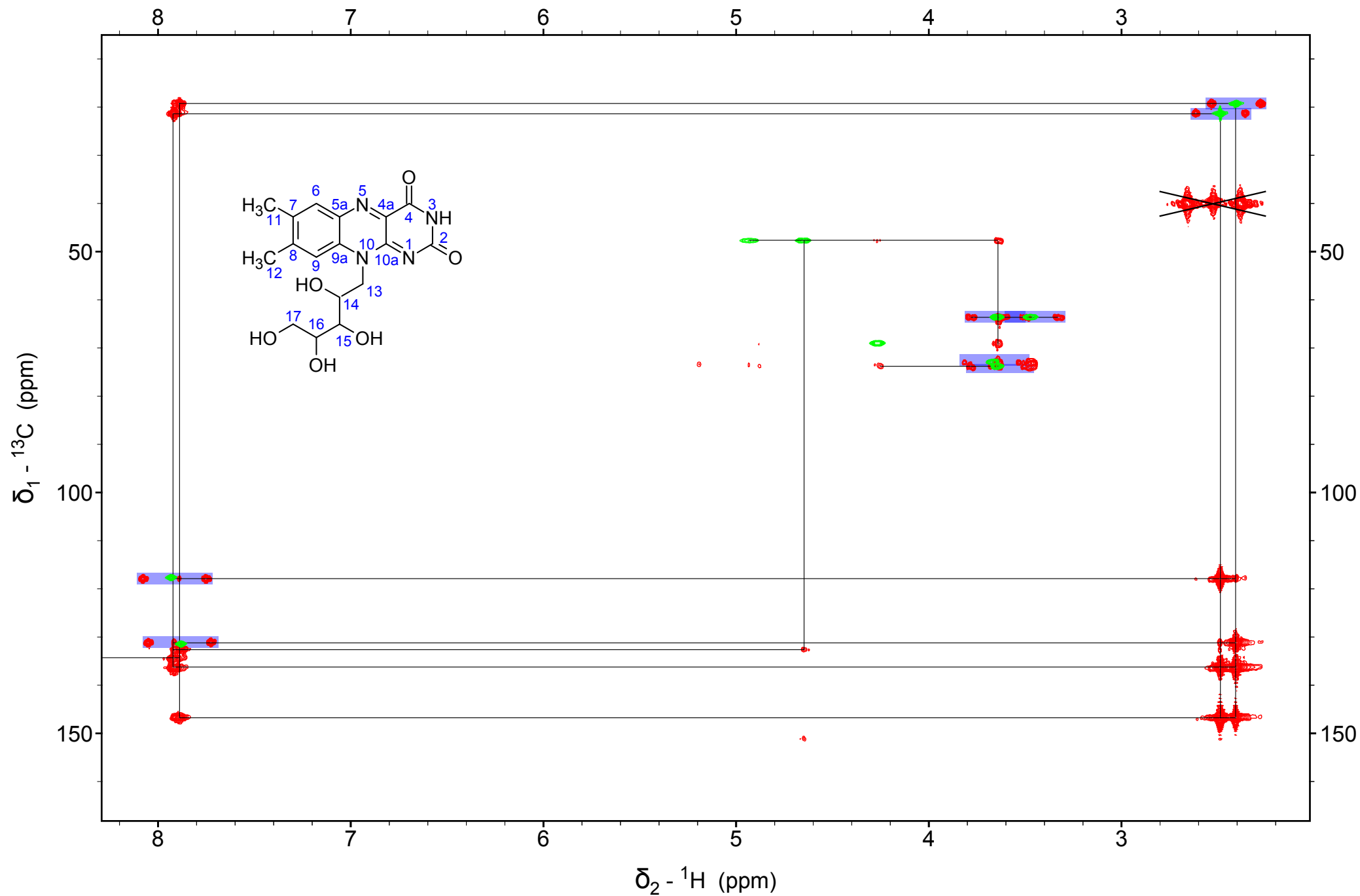
# Folic Acid: $^1\text{H}$ - $^{13}\text{C}$ HMBC



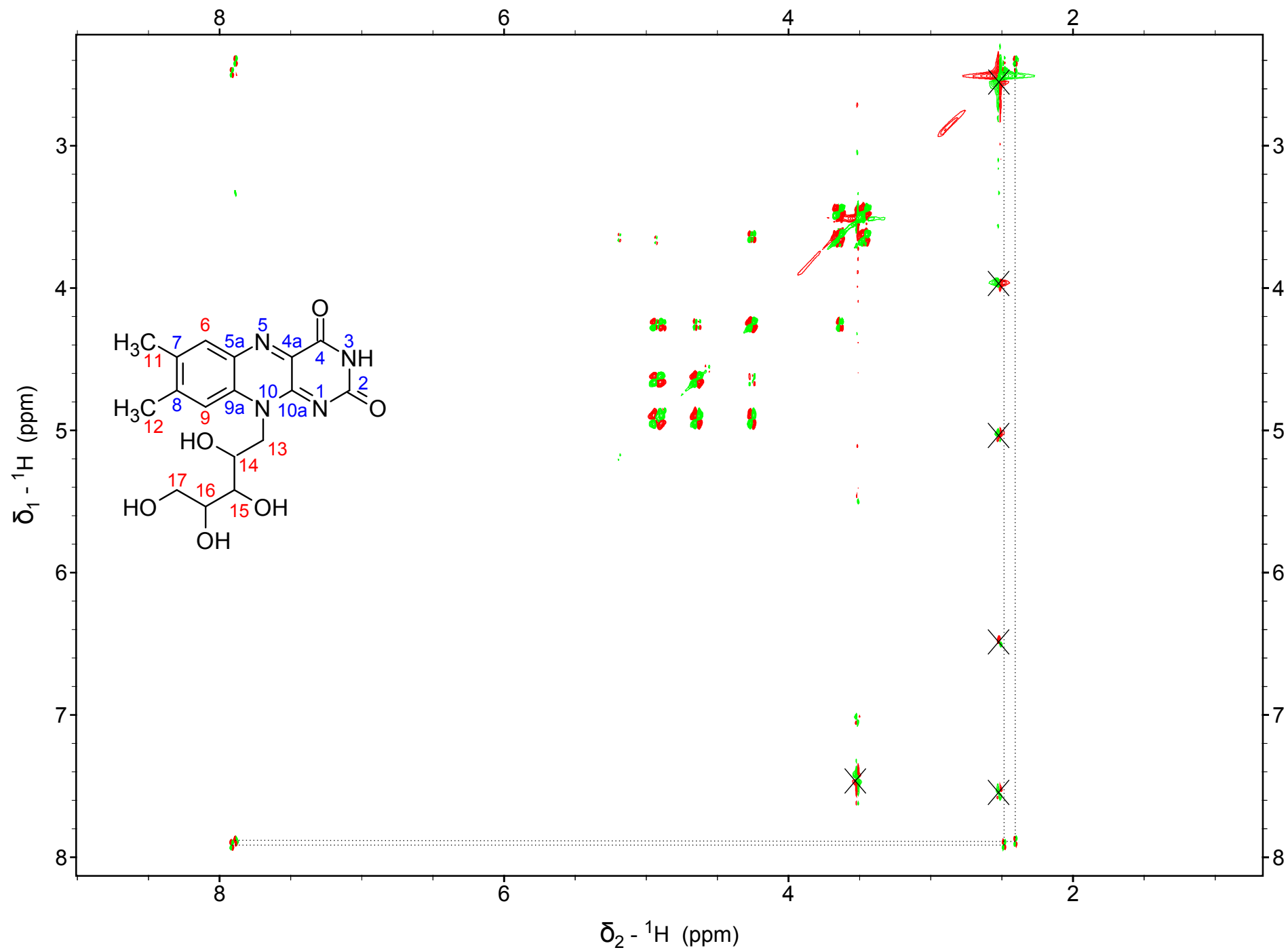
# Folic Acid: $^1\text{H}$ - $^{15}\text{N}$ HMBC



# Riboflavine: $^1\text{H}$ - $^{13}\text{C}$ HMBC + HSQC



# Riboflavine: DQF-COSY



Next session:

Complex exercises