C8953
NMR strukturní analýza
seminář

TOCSY, ROESY, Introduction to heteronuclear correlations

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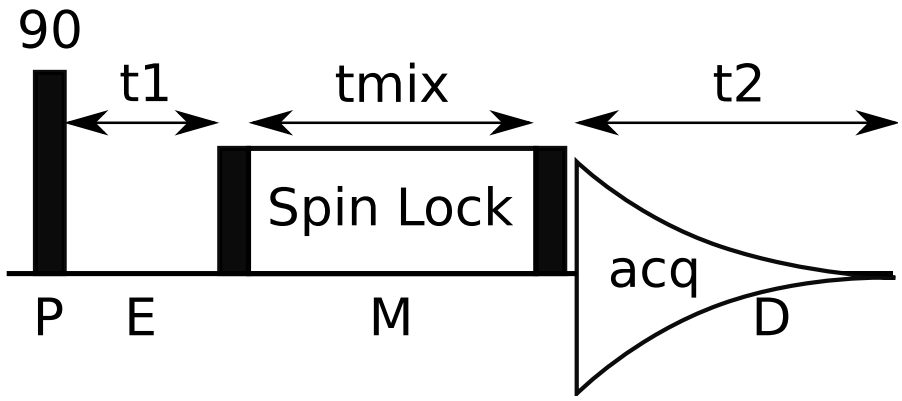
April 12, 2017

TOCSY & ROESY

spin lock - isotropic mixing

- series of 180 ° pulses
- various pulse schemes (MLEV-17, DIPSI,. . .)
- precession around $B_{Spinlock} < B_0 \rightarrow$ “locking" spins in transversal plane (xy)
- TOCSY: lower power, offset in the center of spectrum
- ROESY: higher power, offset on edge
- crosstalk (ROE in TOCSY, J in ROESY)



TOCSY (TOtal Correlation SpectroscopY)

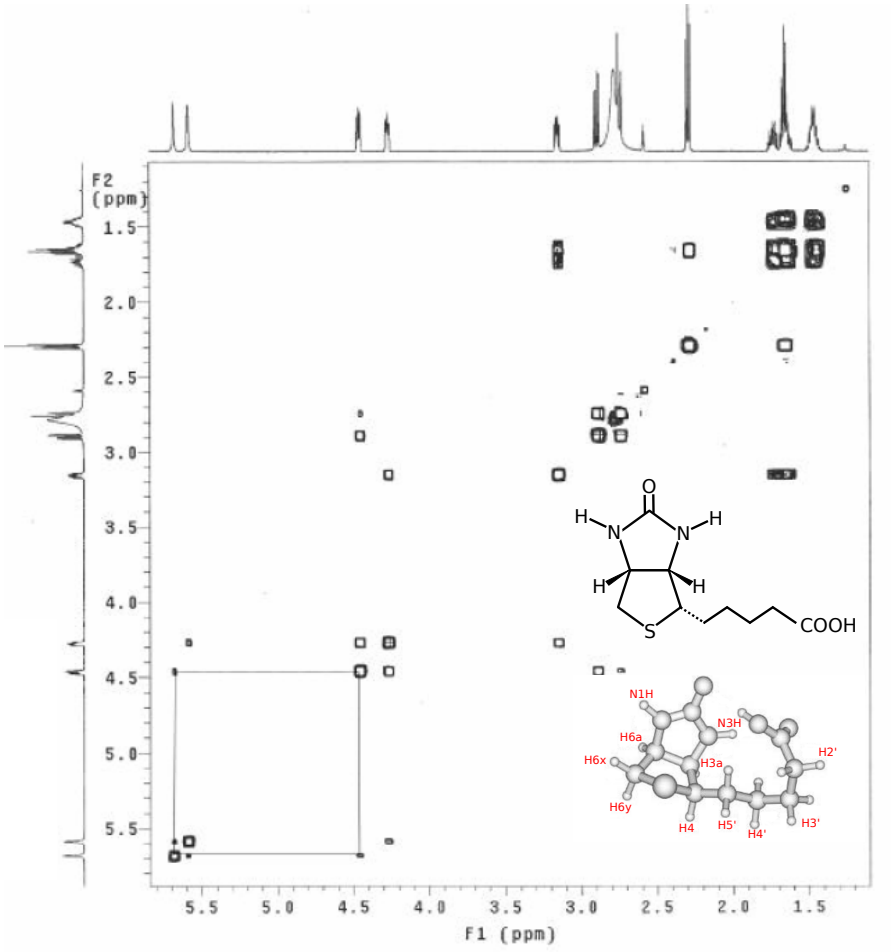
HOHAHA (HOmonuclear HArtmann-HAhn)

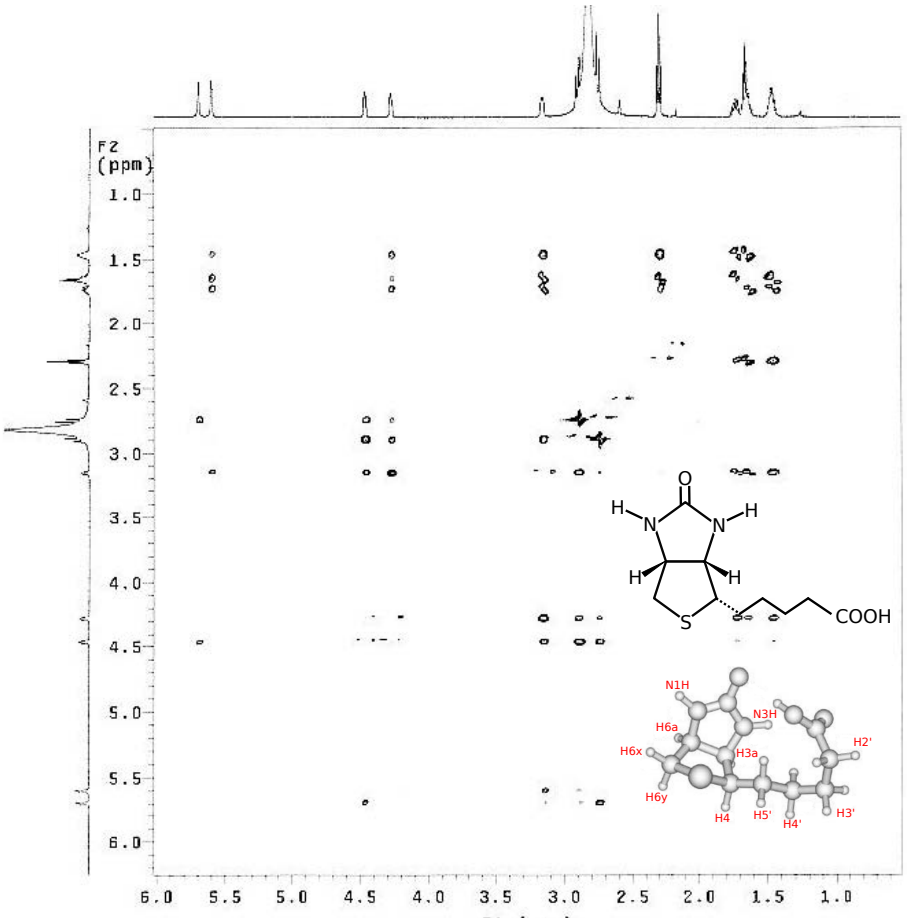
correlation based on J, like COSY

- correlate mutually *all* protons within a spin system
- $\tau_{mix} \approx 20 - 120\,ms$
- intensity depends on τ_{mix} and J value

$$H_A \overset{J_{AB}}{\Longleftrightarrow} H_B \overset{J_{BC}}{\Longleftrightarrow} H_C \overset{J_{CD}}{\Longleftrightarrow} H_D$$

Biotin - COSY vs. ROESY
(*G. T. Crisp and Yu-Lin Jiang*, **2001**)





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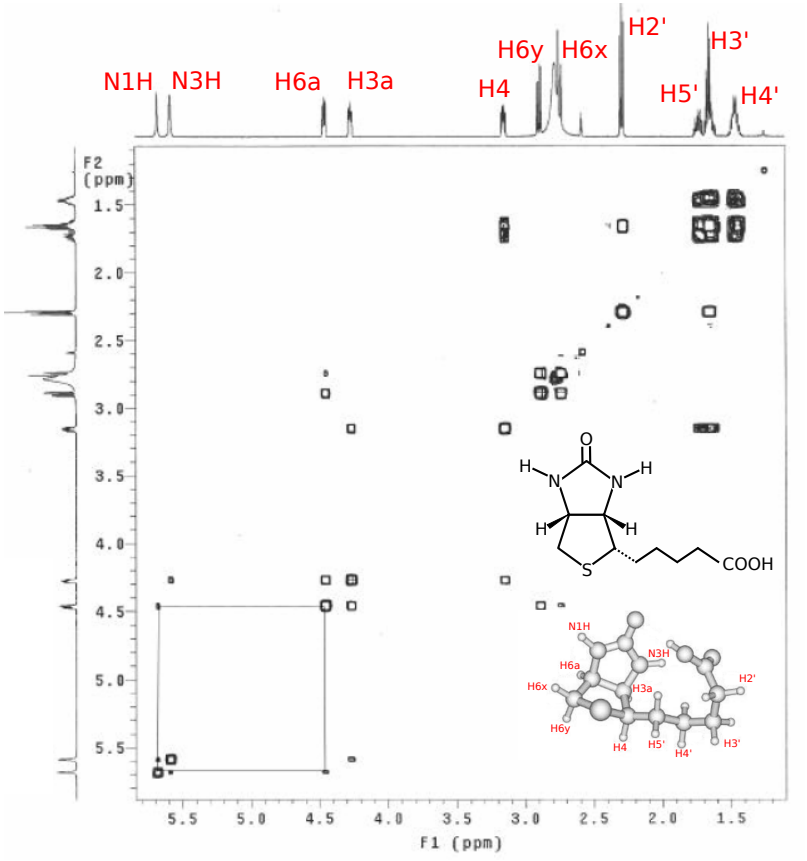
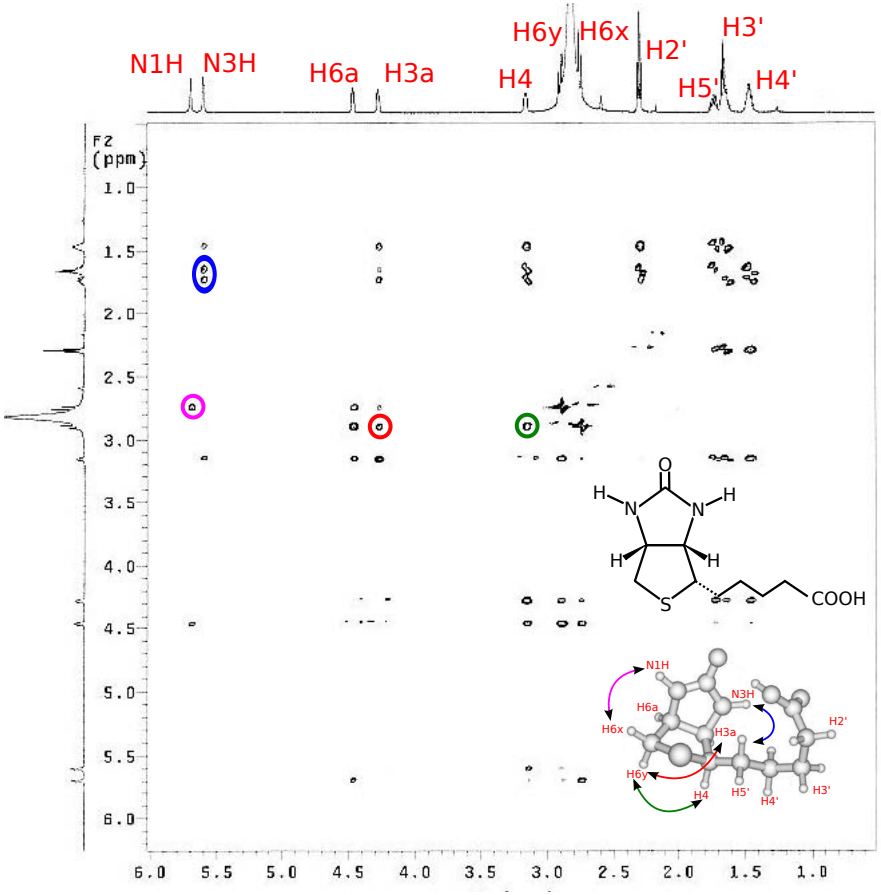




HMQC (Heteronuclear Multiple Quantum Correlation)
HSQC (Heteronuclear Single Quantum Correlation)

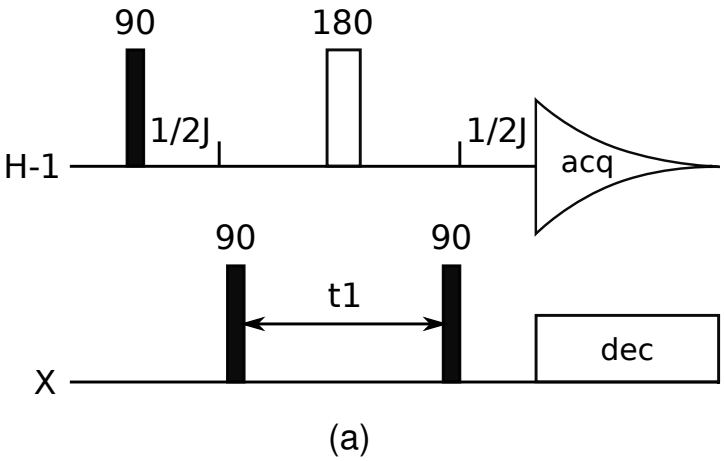
correlate ^{1}H-X (X=^{13}C, ^{15}N,...) based on $^{1}J_{HX}$

HMQC (a)

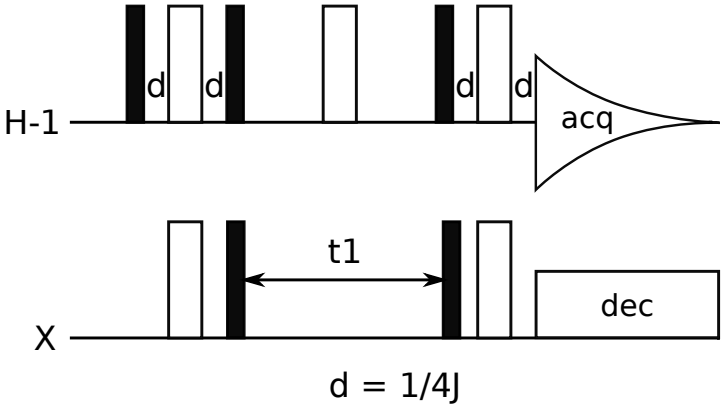
- \+ more robust experiment
- \+ change of parameters - HMBC
- \- lower sensitivity and worse resolution

HSQC (b)

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



(a)



d = 1/4J

(b)

Practical notes ^{1}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)

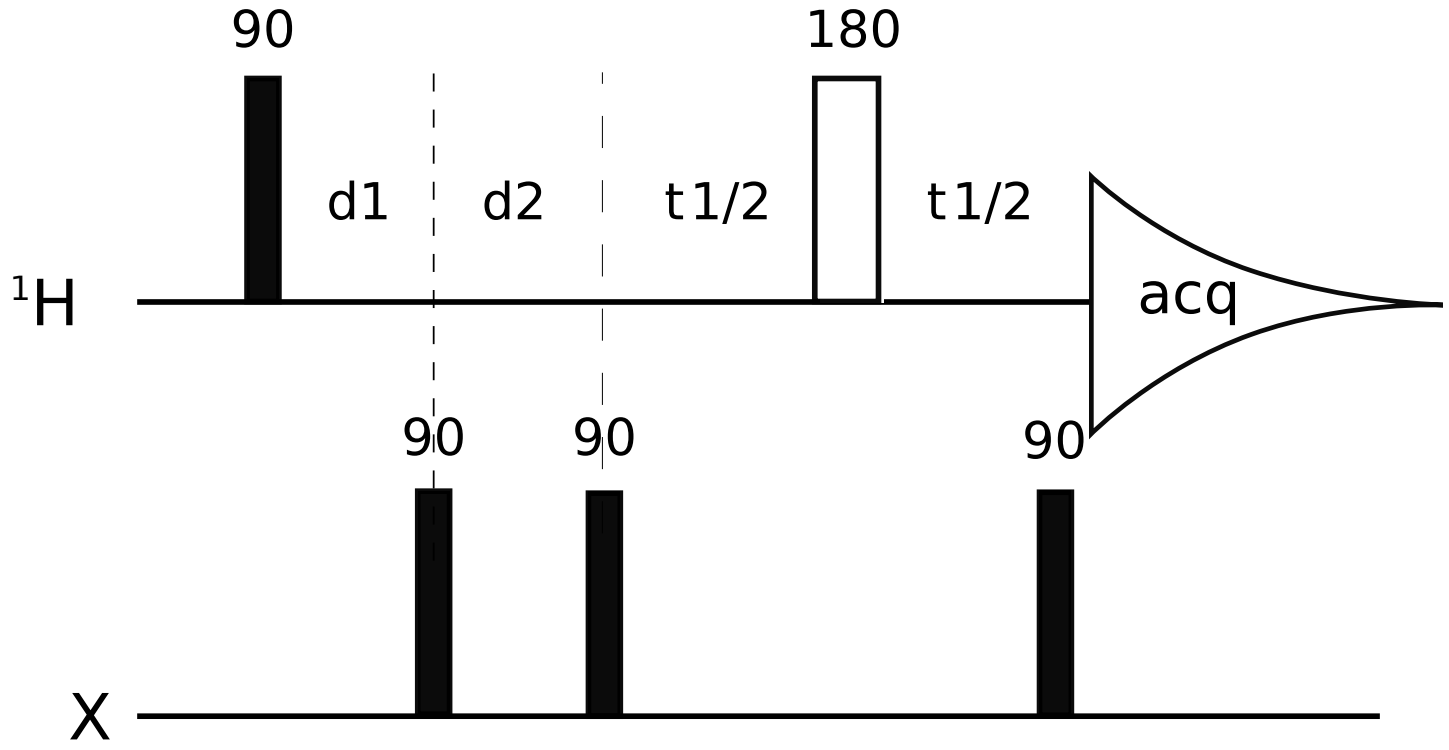
heteronuclear correlation based on long-range H-X spin-spin interaction(${}^{n}J_{HX}$, n>1)

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

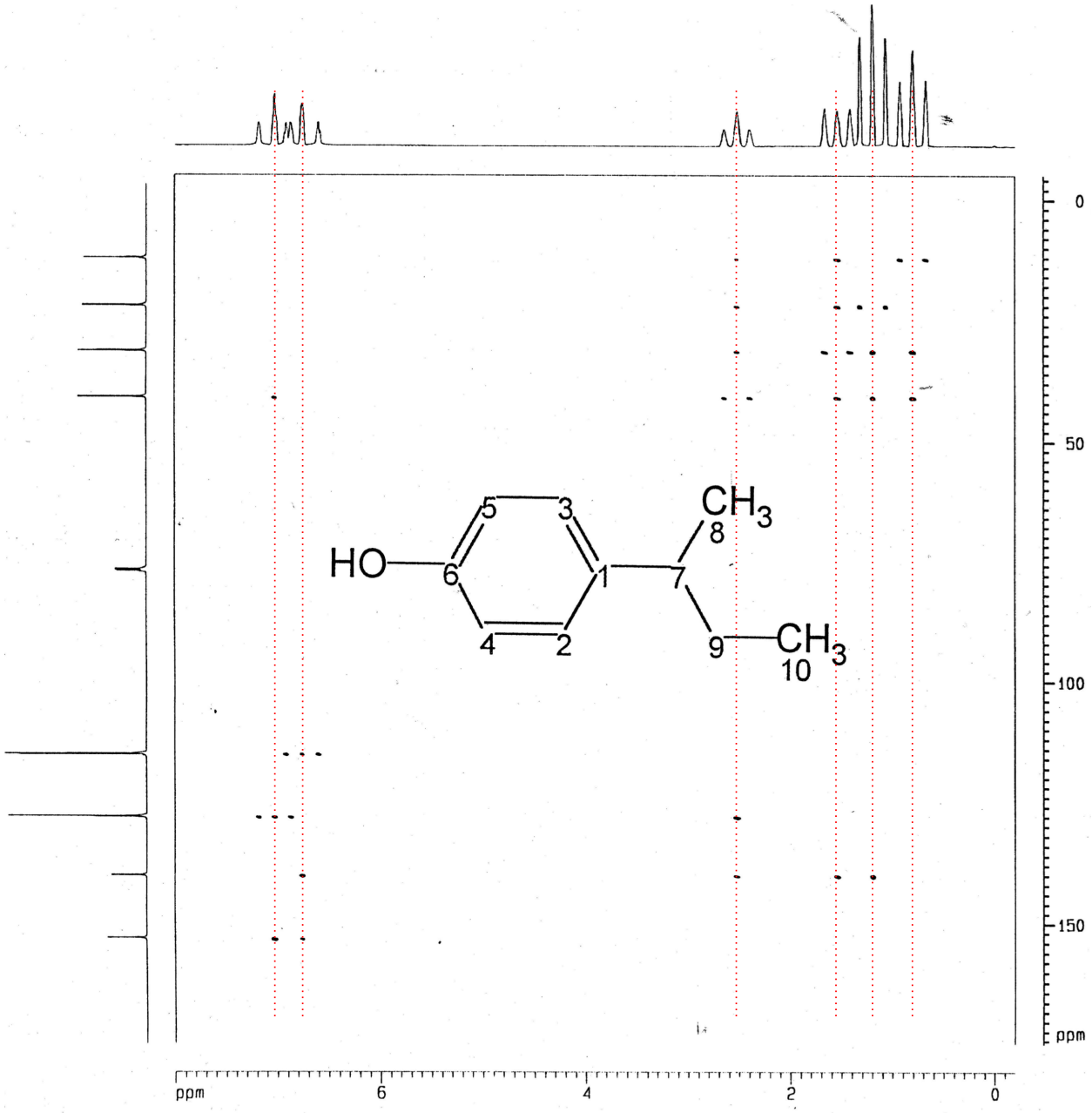
HMBC

correct settings of d1, d2 fo evolution of *J*-coupling necessary

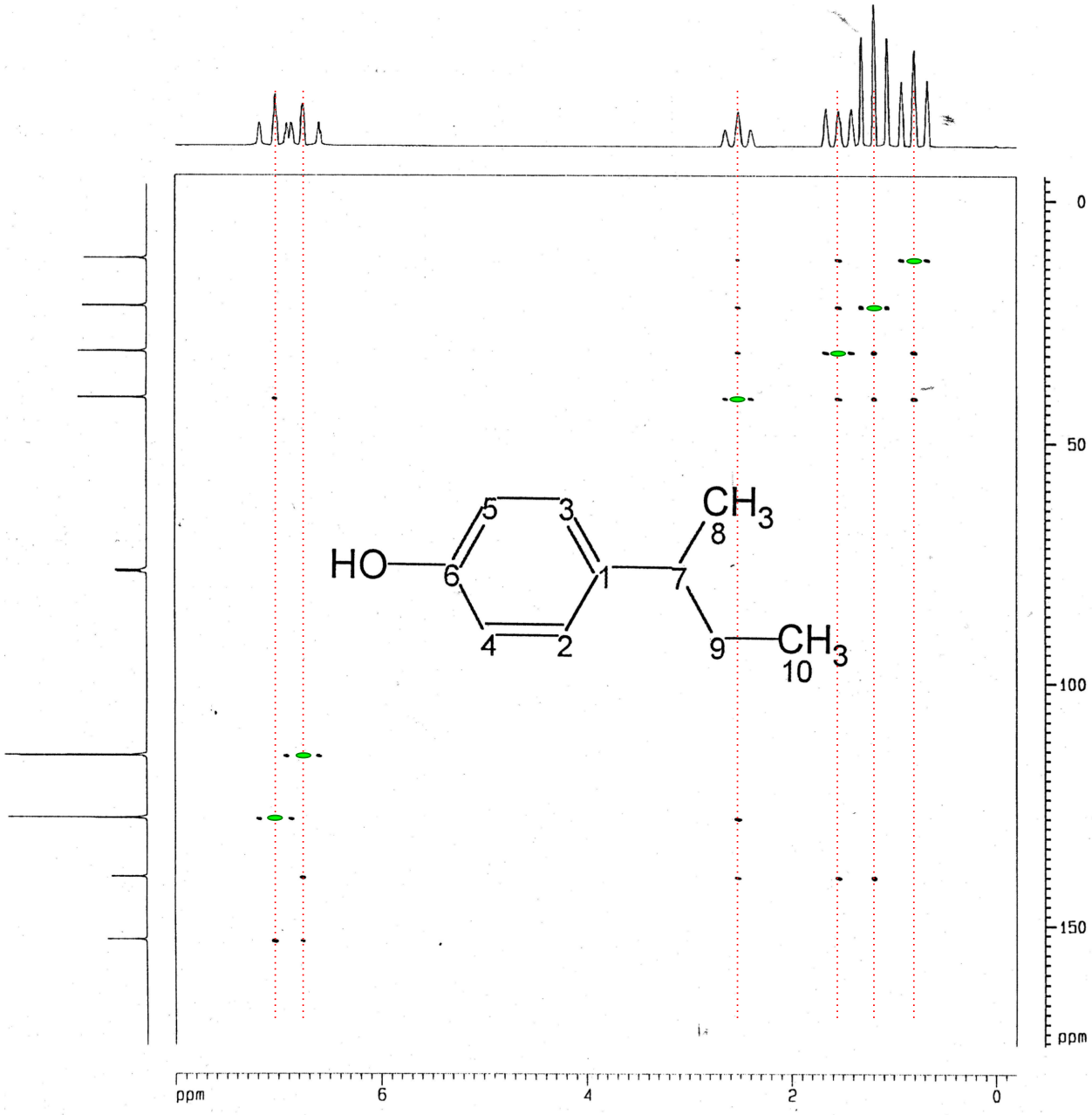
- d1=$1/2 * {}^{1}J_{C-H}$ - (120-180 Hz)
- d2=$1/2 * {}^{2-5}J_{C-H}$ - (3-12 Hz)



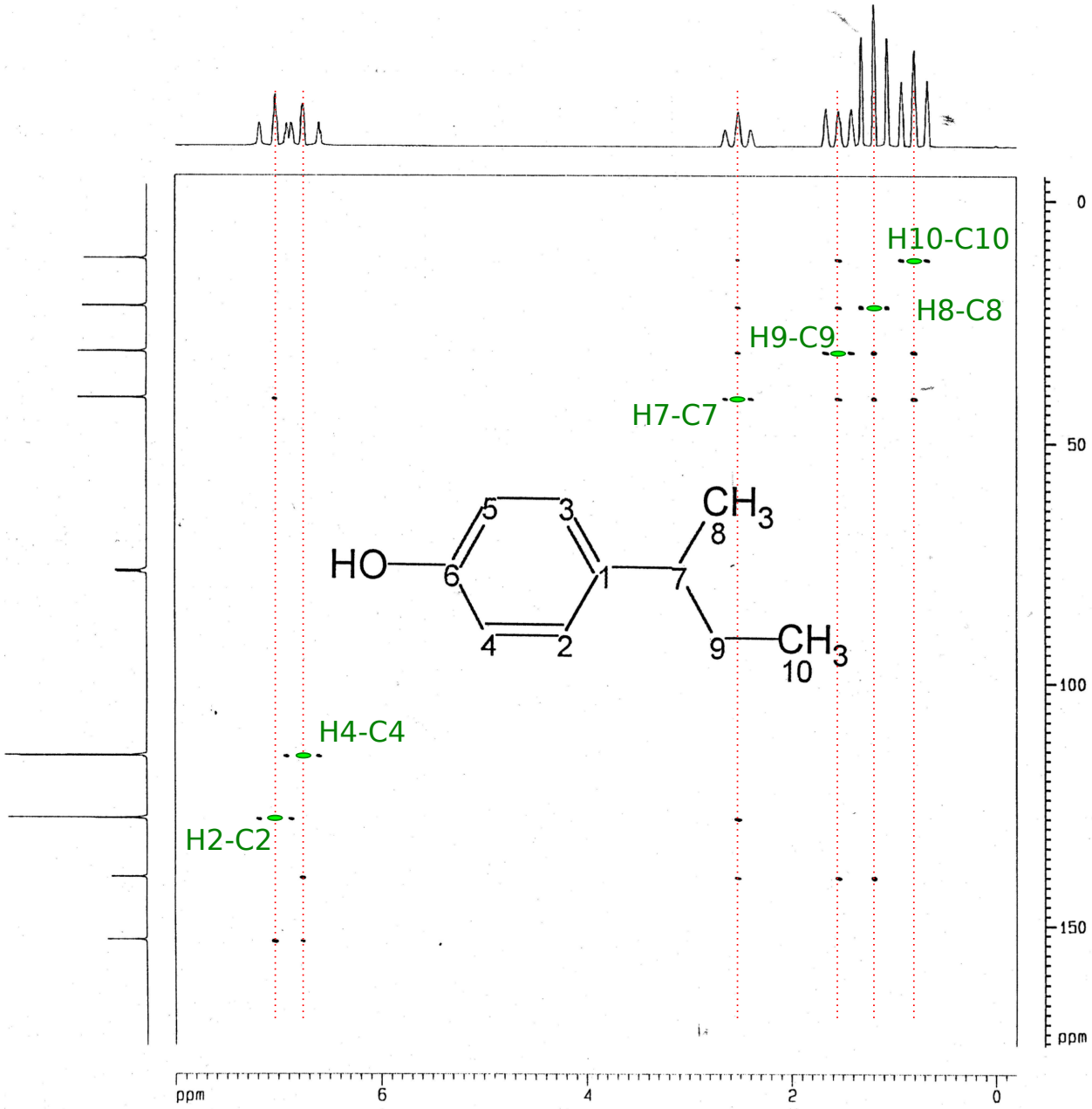
^{1}H-^{13}C HMBC



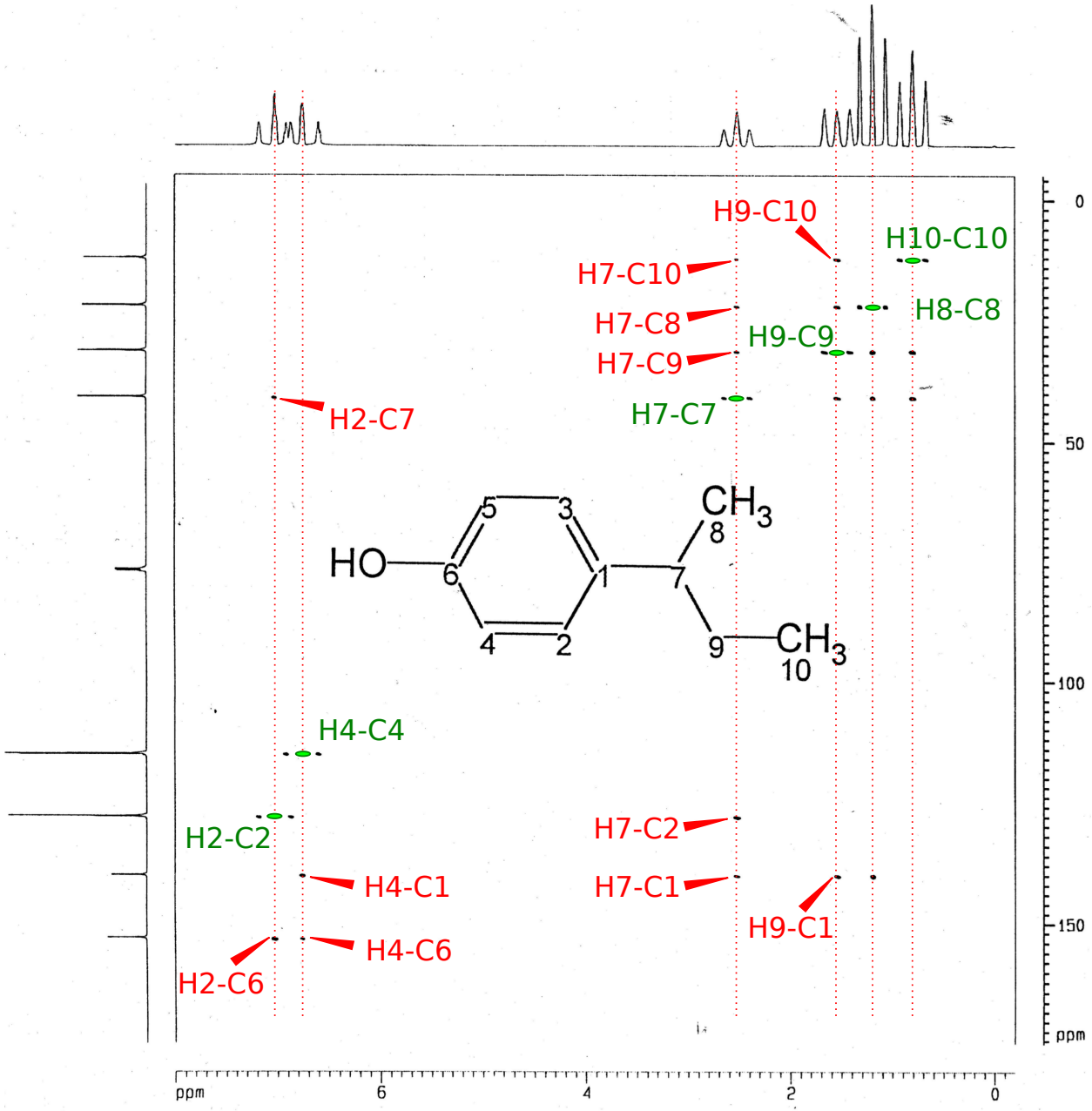
^{1}H-^{13}C HMBC



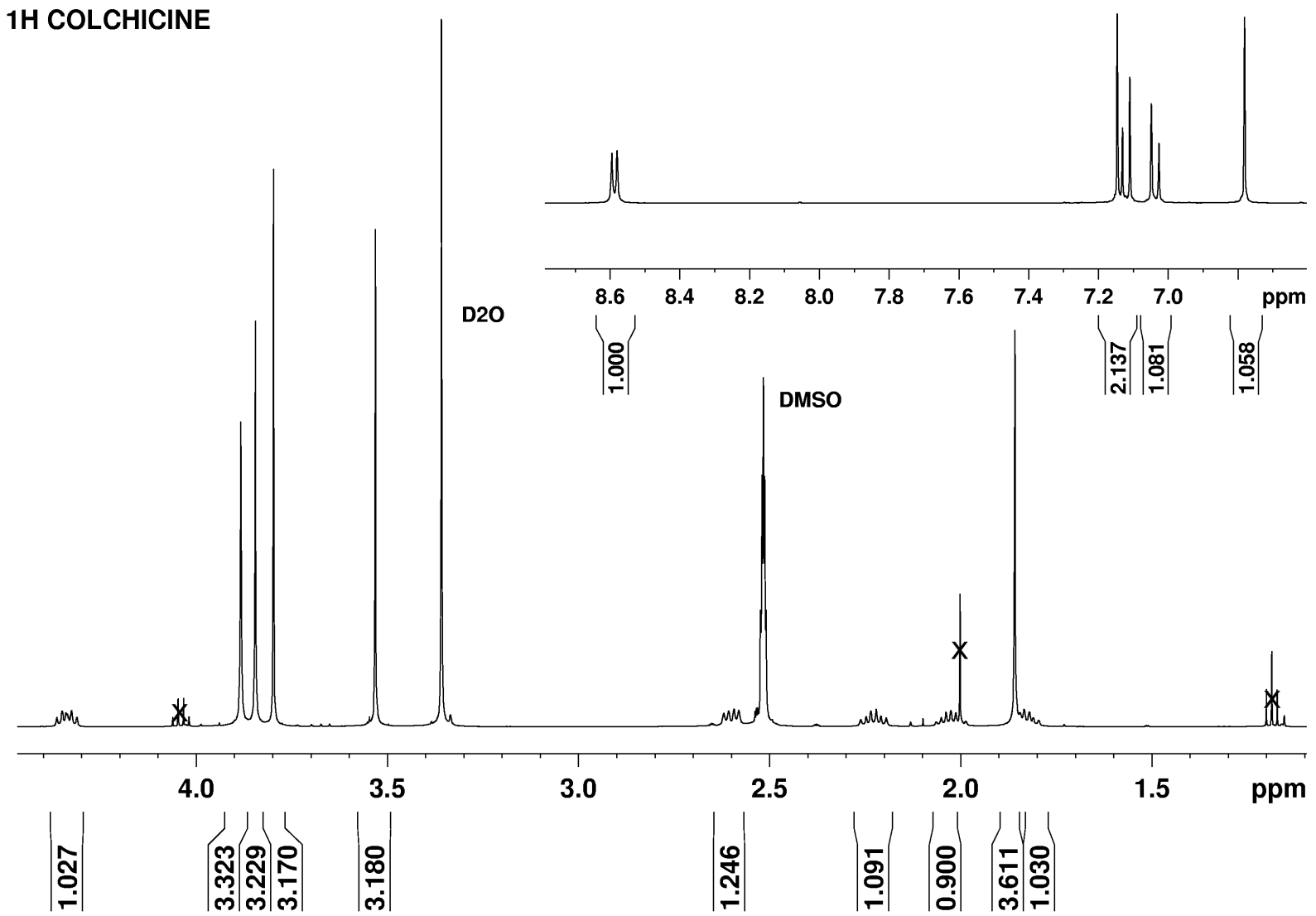
^{1}H-^{13}C HMBC


H10-C10
H8-C8
H9-C9
H7-C7
H4-C4
H2-C2
HO
CH3
8
CH3
10
1
2
3
4
5
6
7
9
0
50
100
150
ppm
ppm
6
4
2
0

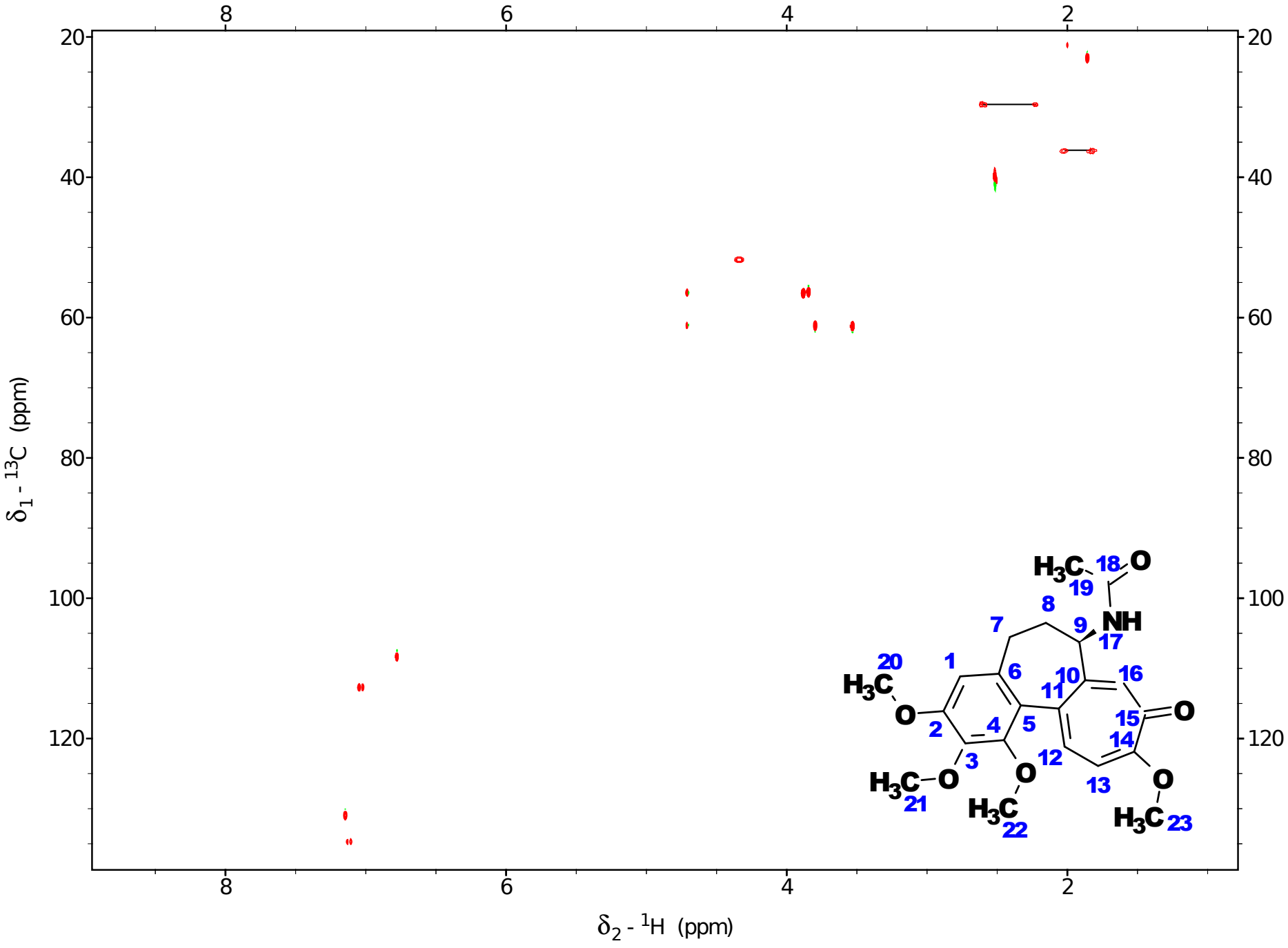
^{1}H-^{13}C HMBC


H9-C10
H10-C10
H7-C10
H8-C8
H7-C8
H9-C9
H7-C9
H2-C7
H7-C7
HO
CH3
8
5
3
6
1
7
4
2
9
CH3
10
H4-C4
H2-C2
H7-C2
H4-C1
H7-C1
H9-C1
H4-C6
H2-C6
0
50
100
150
ppm
ppm
6
4
2
0

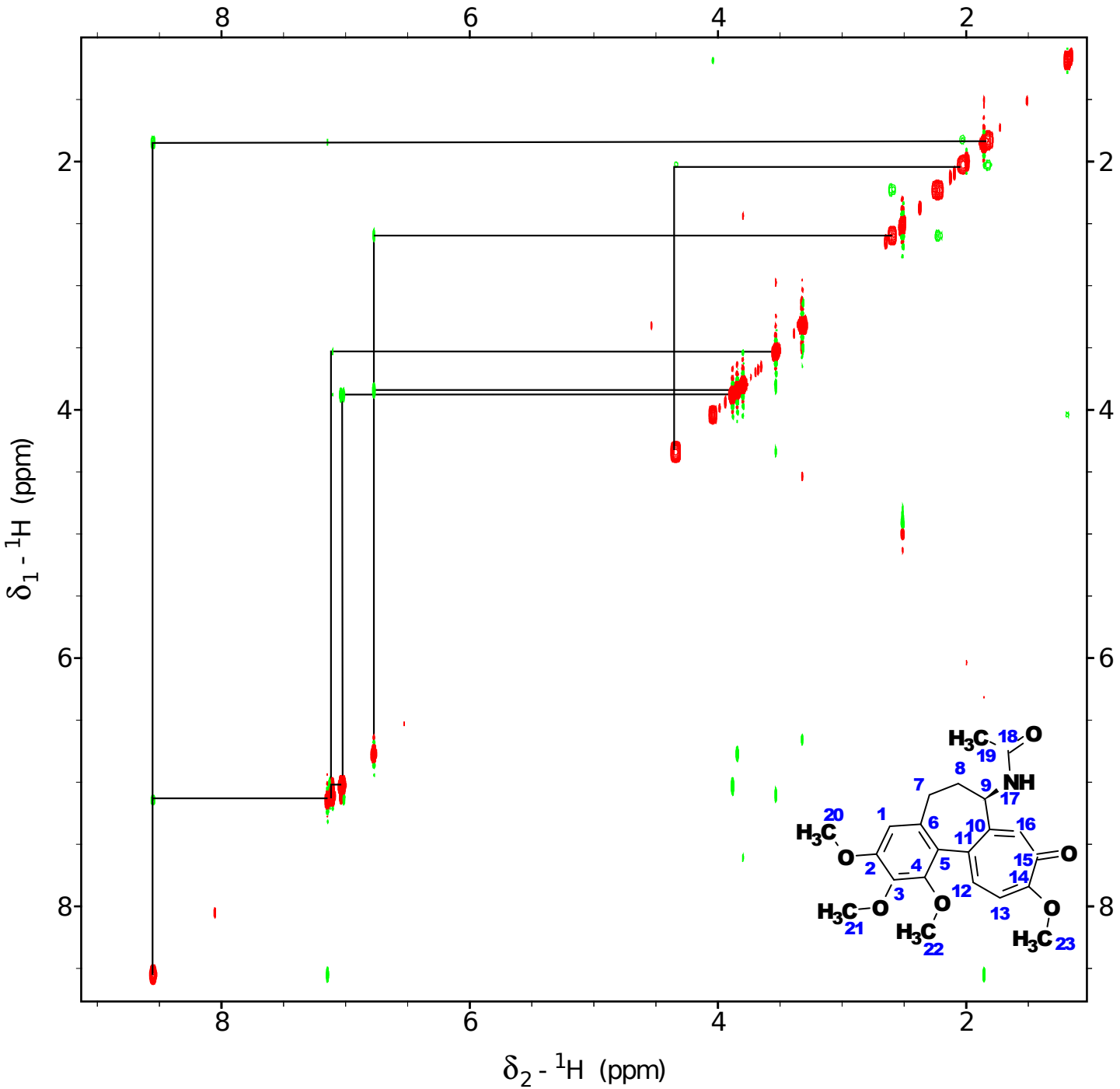
Colchicine 1D-^{1}H



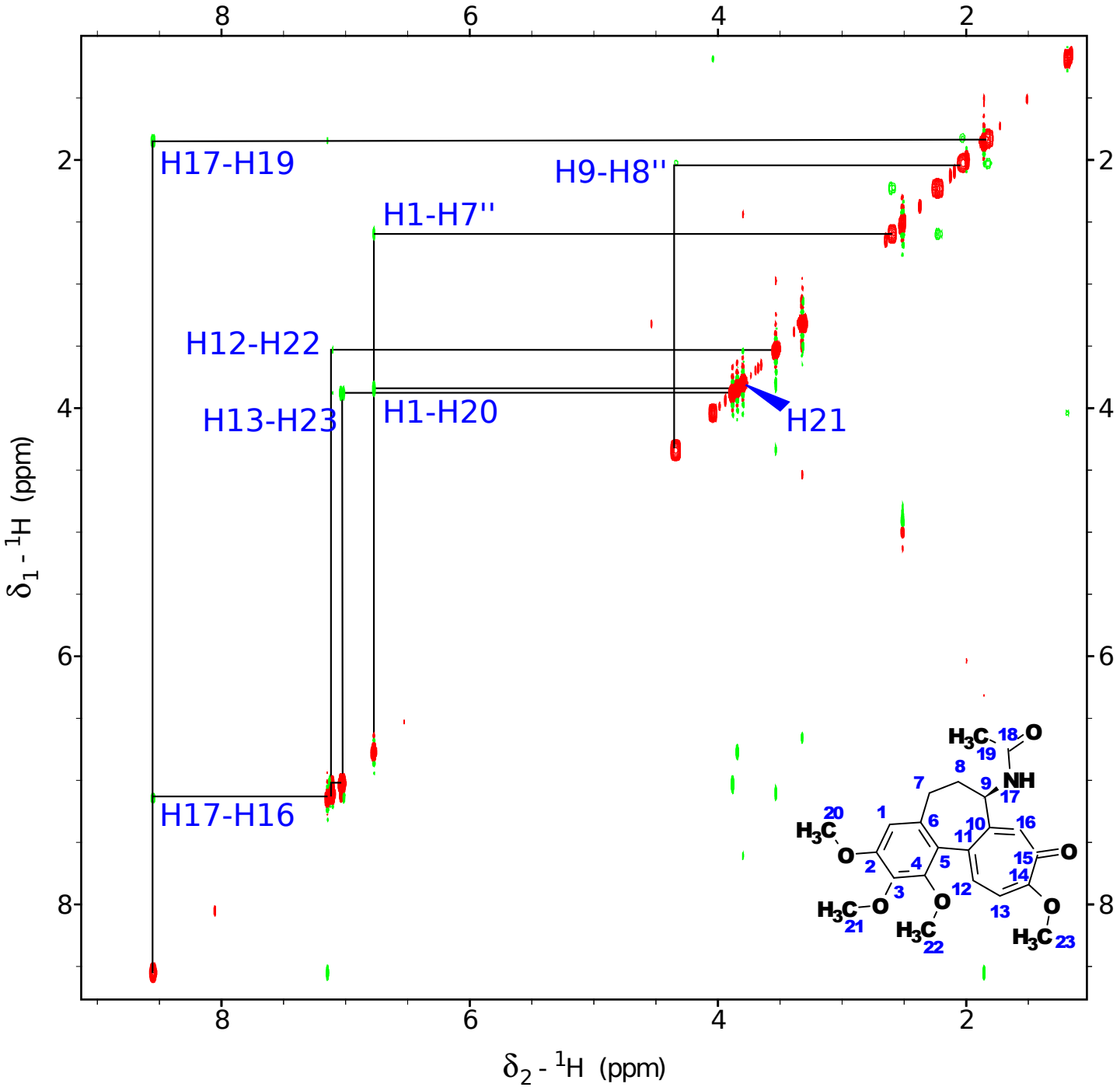
Colchicine - ^{1}H-^{13}C HSQC



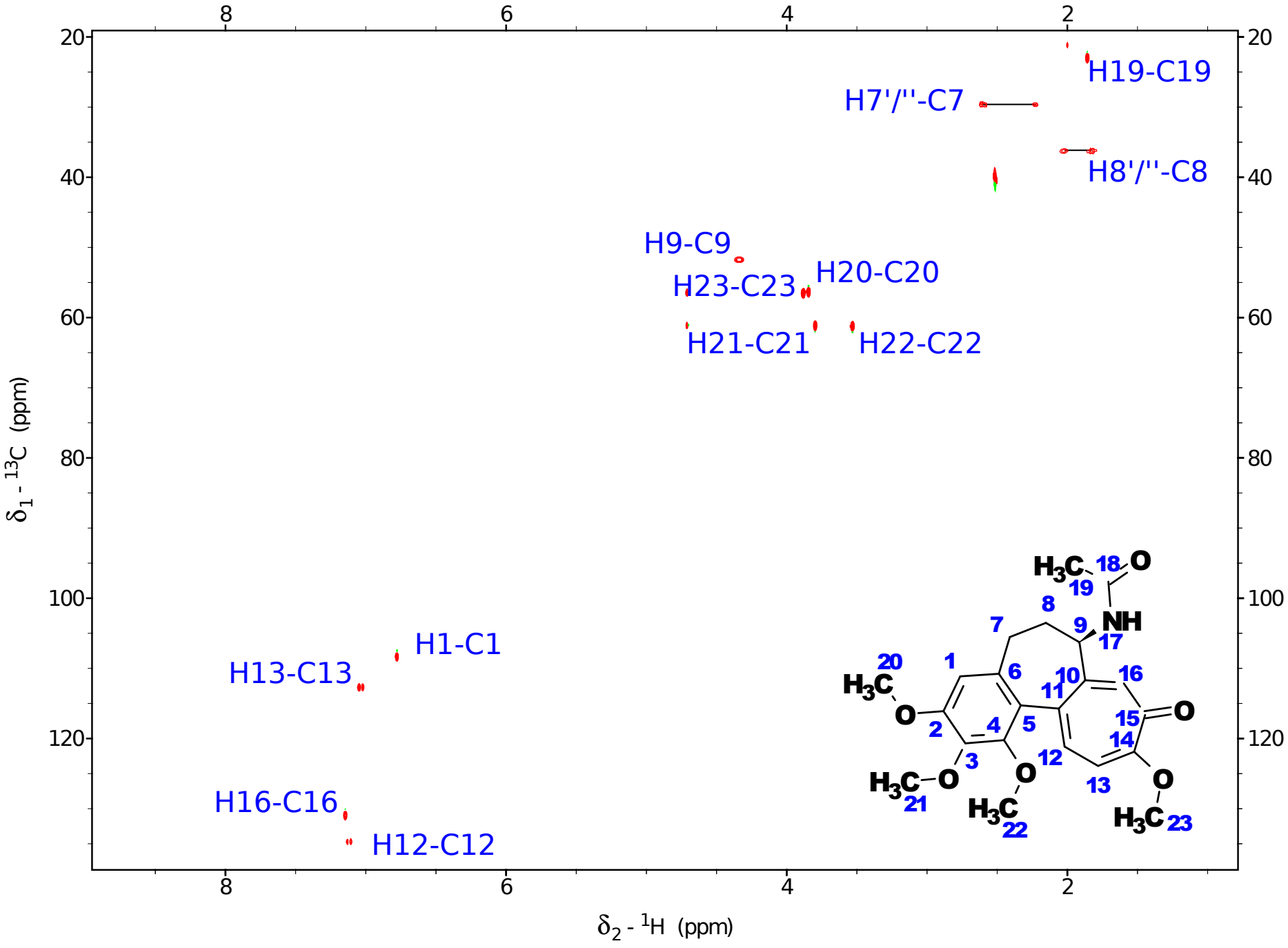
Colchicine - NOESY



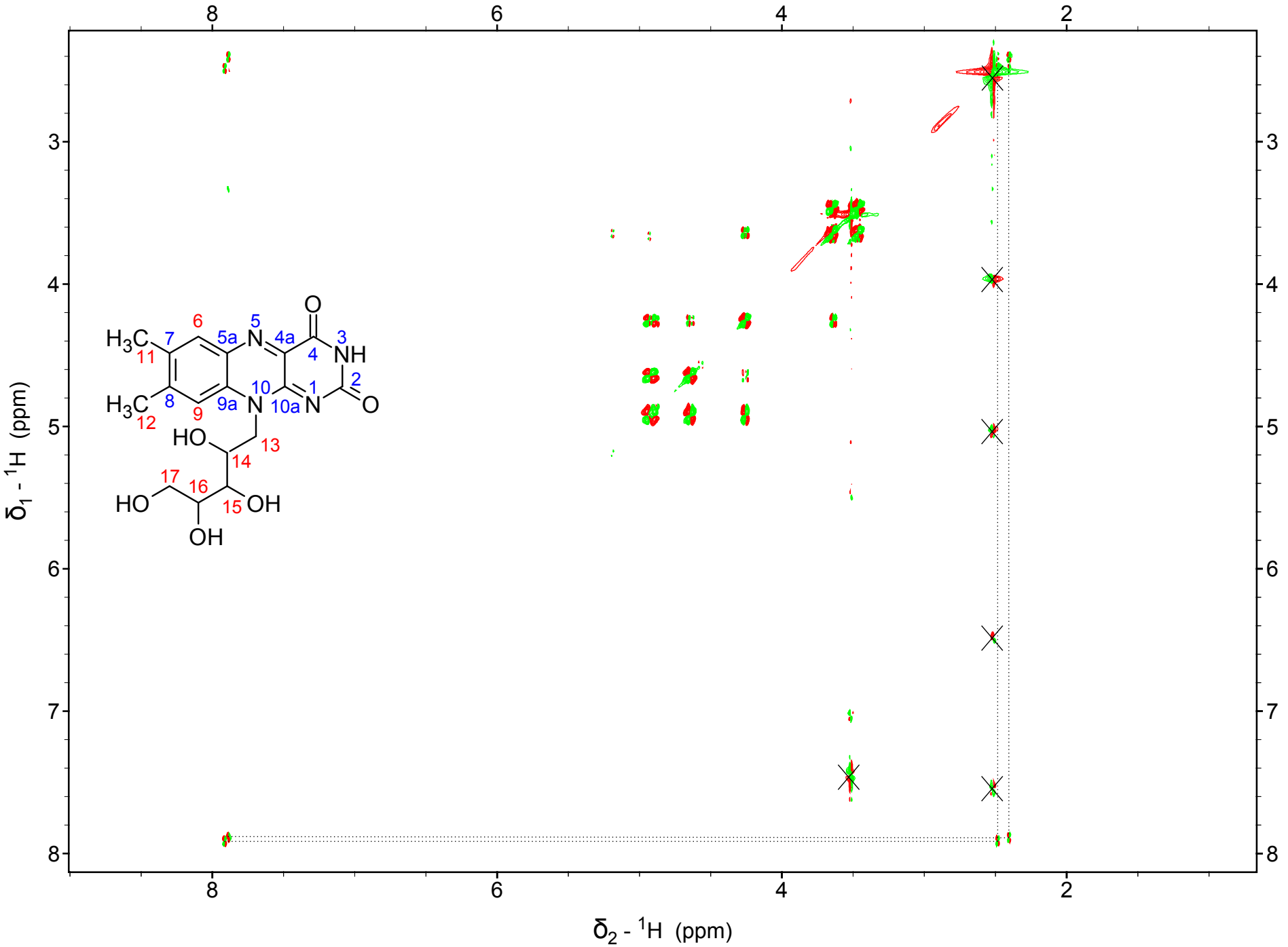
Colchicine - NOESY



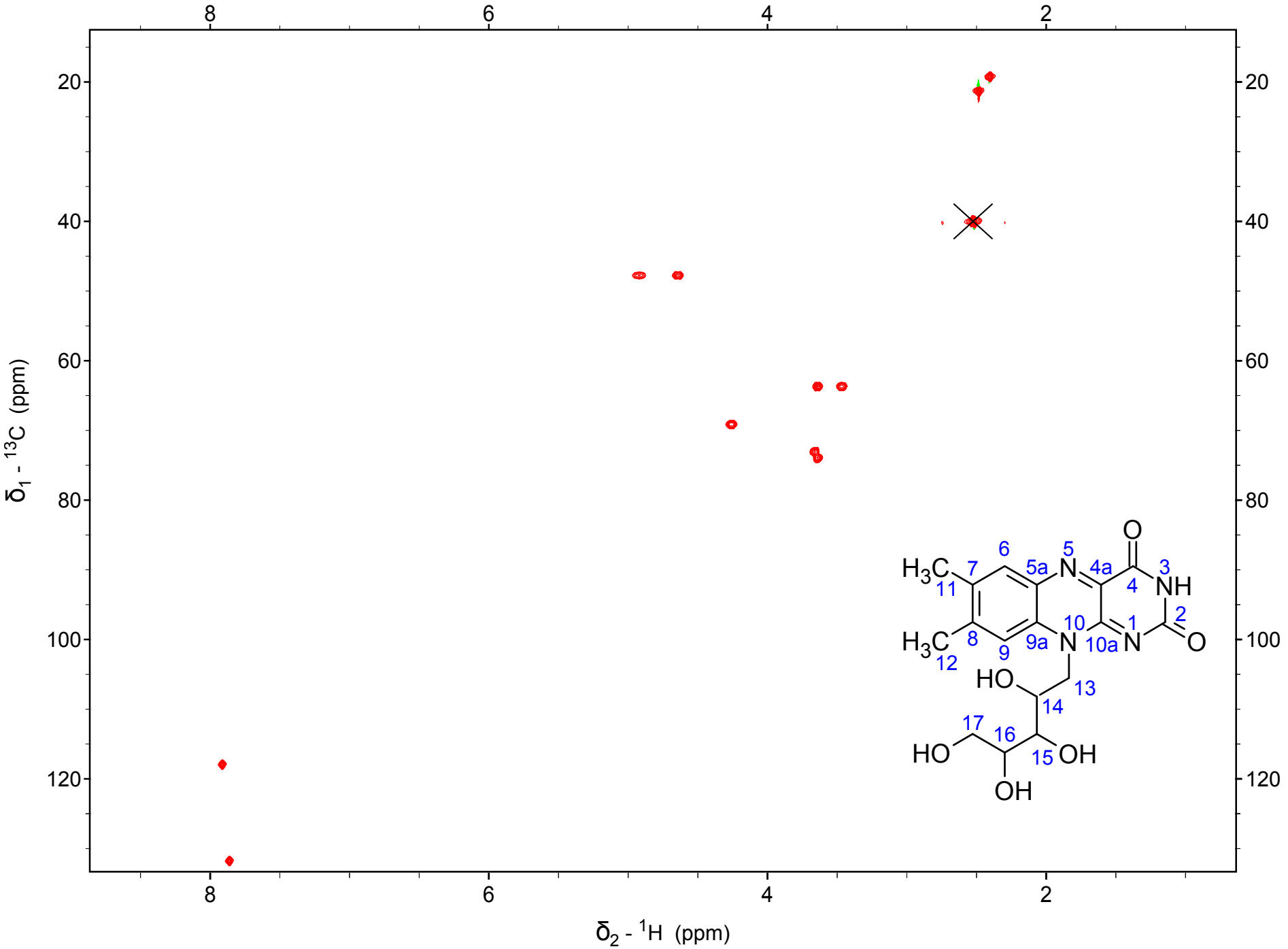
Colchicine - ^{1}H-^{13}C HSQC



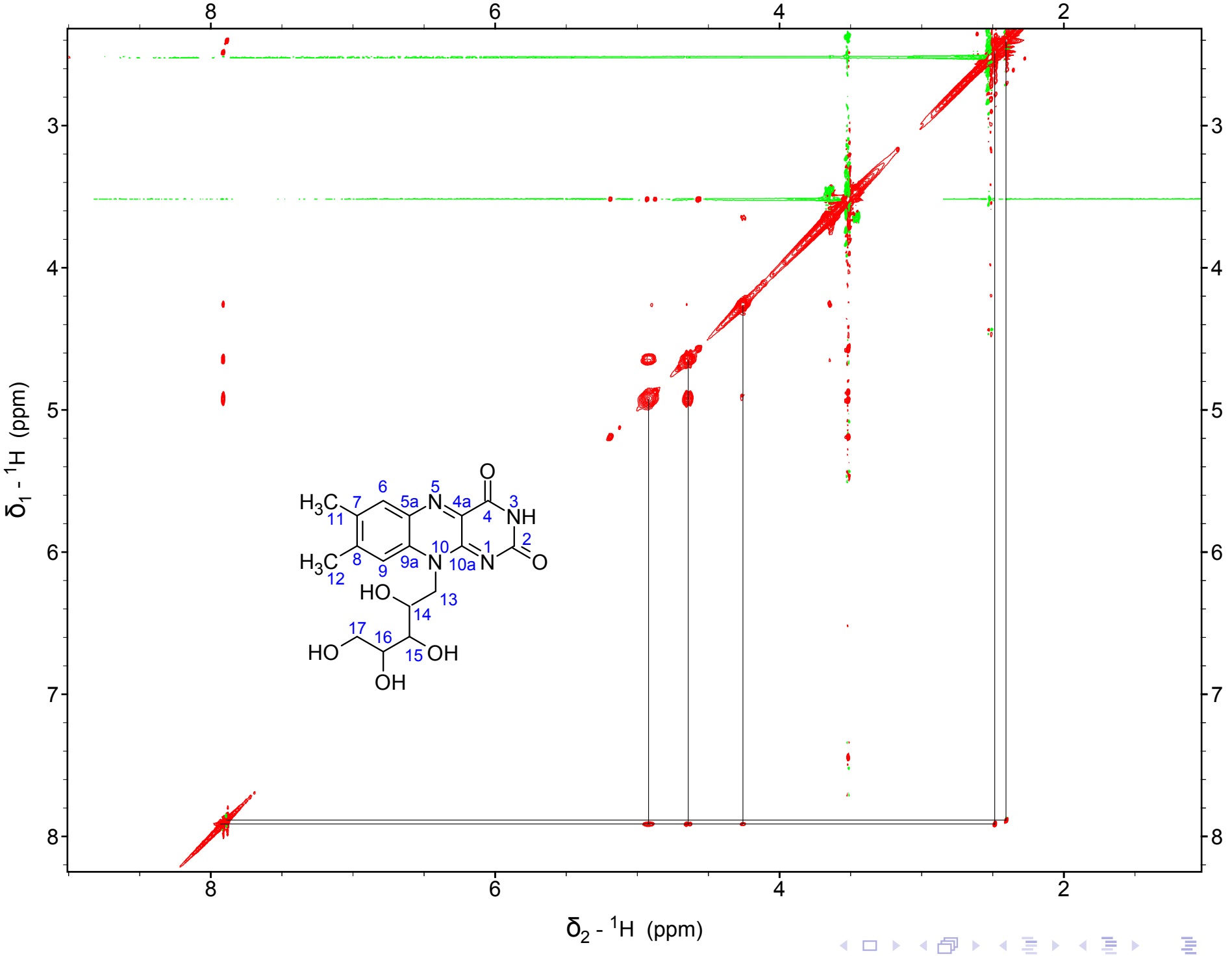
Riboflavine: DQF-COSY



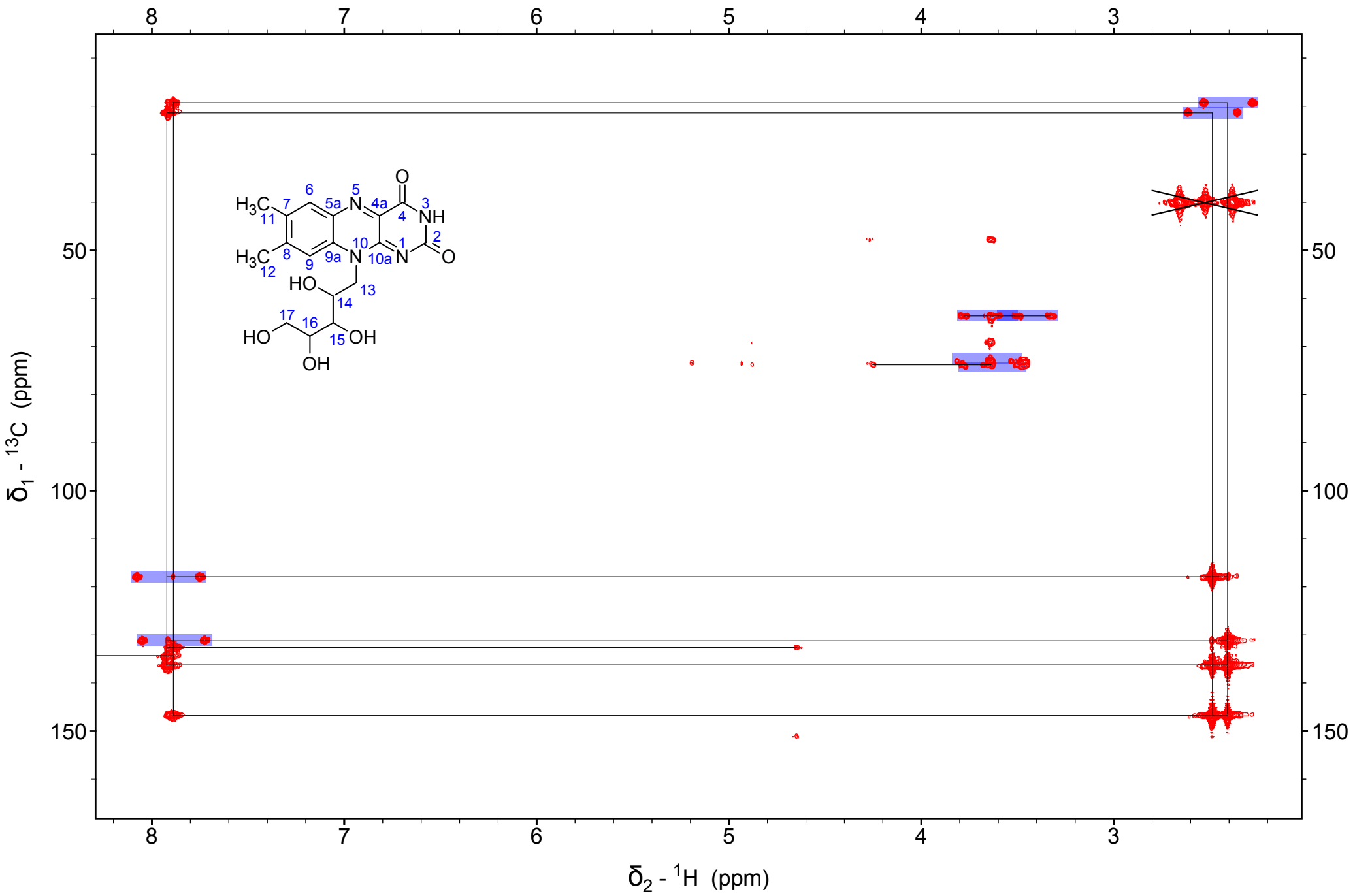
Riboflavine: ^{1}H-^{13}C HSQC



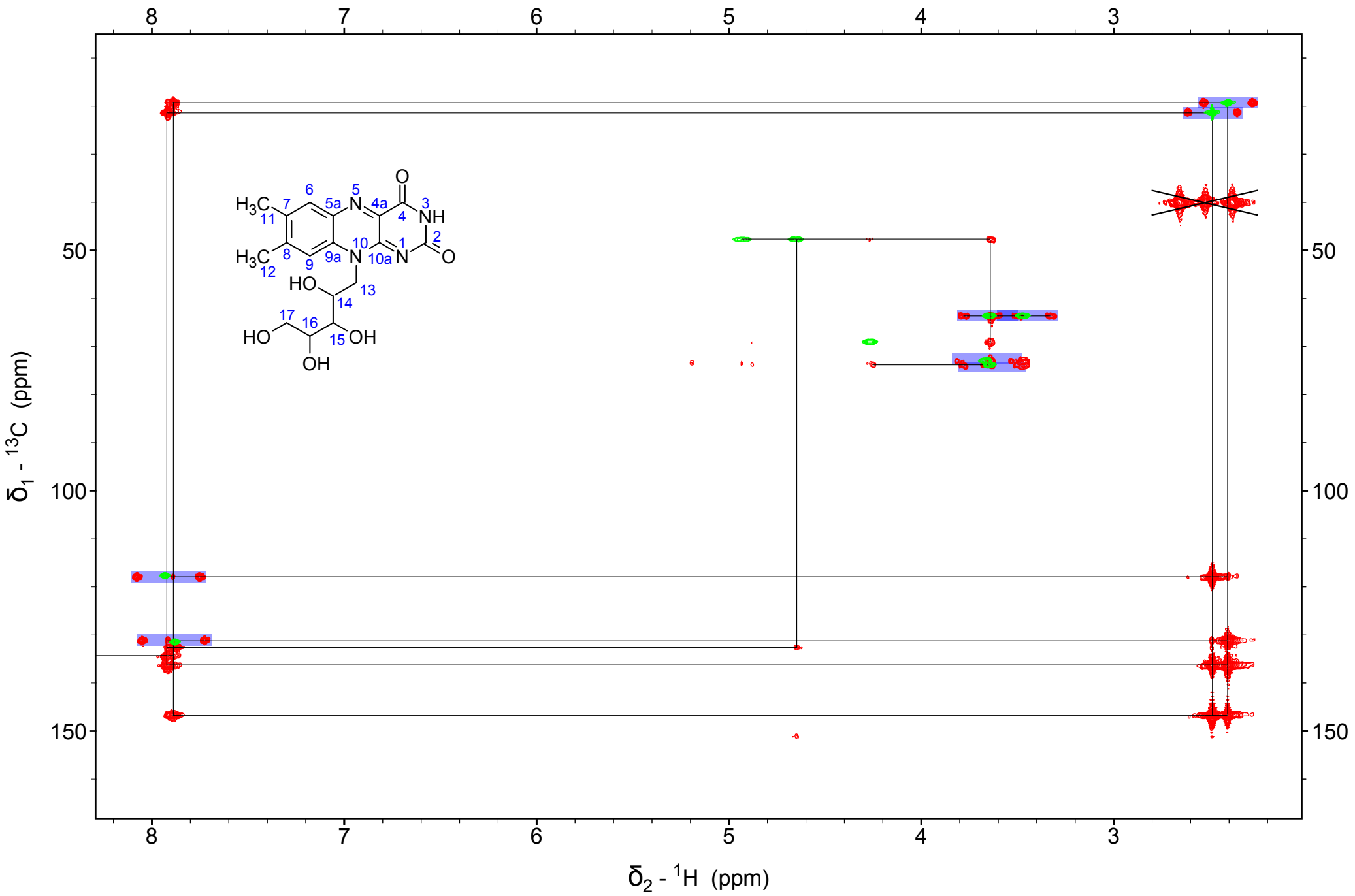
Riboflavine: NOESY



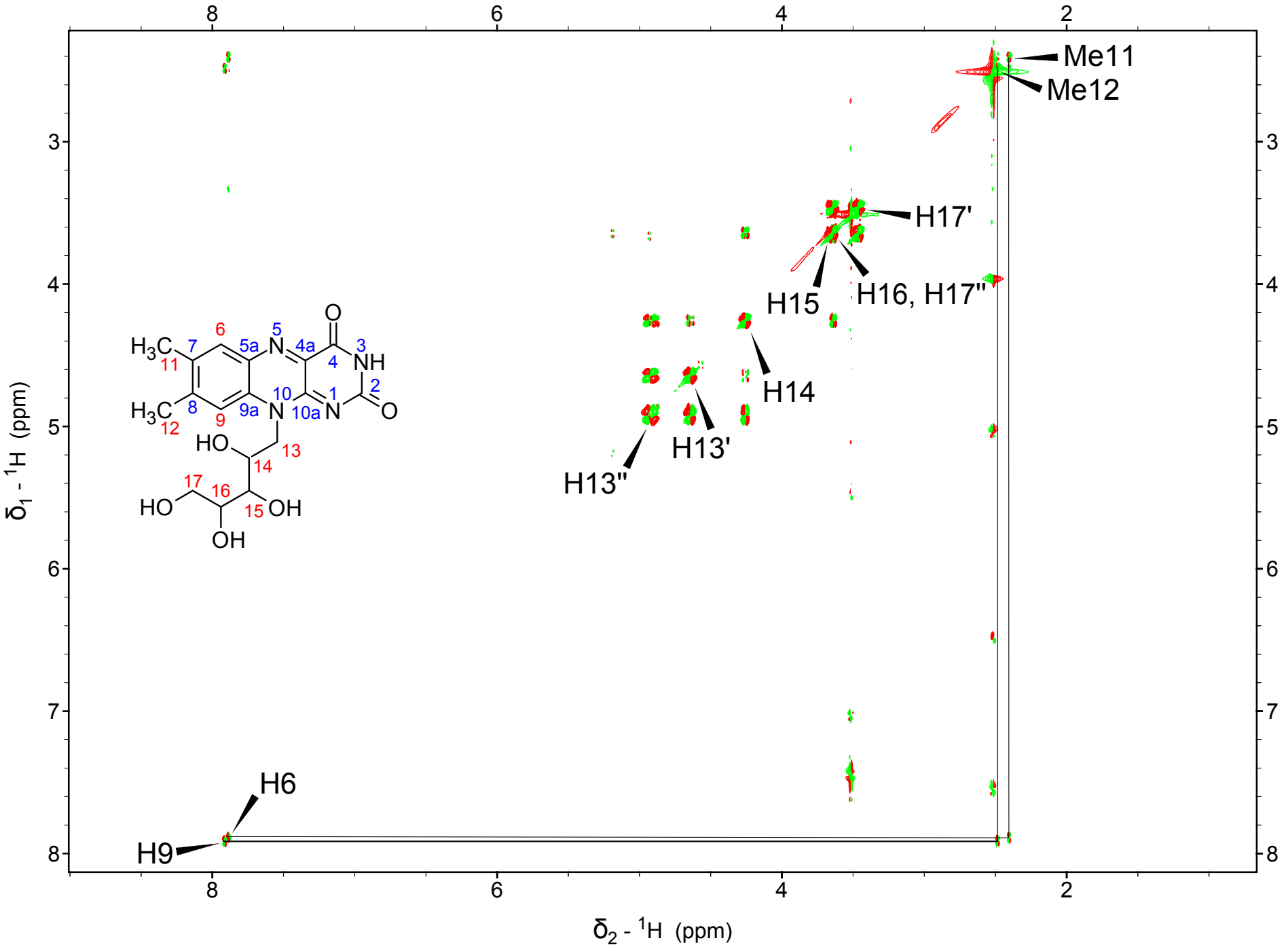
Riboflavine: ^{1}H-^{13}C HMBC



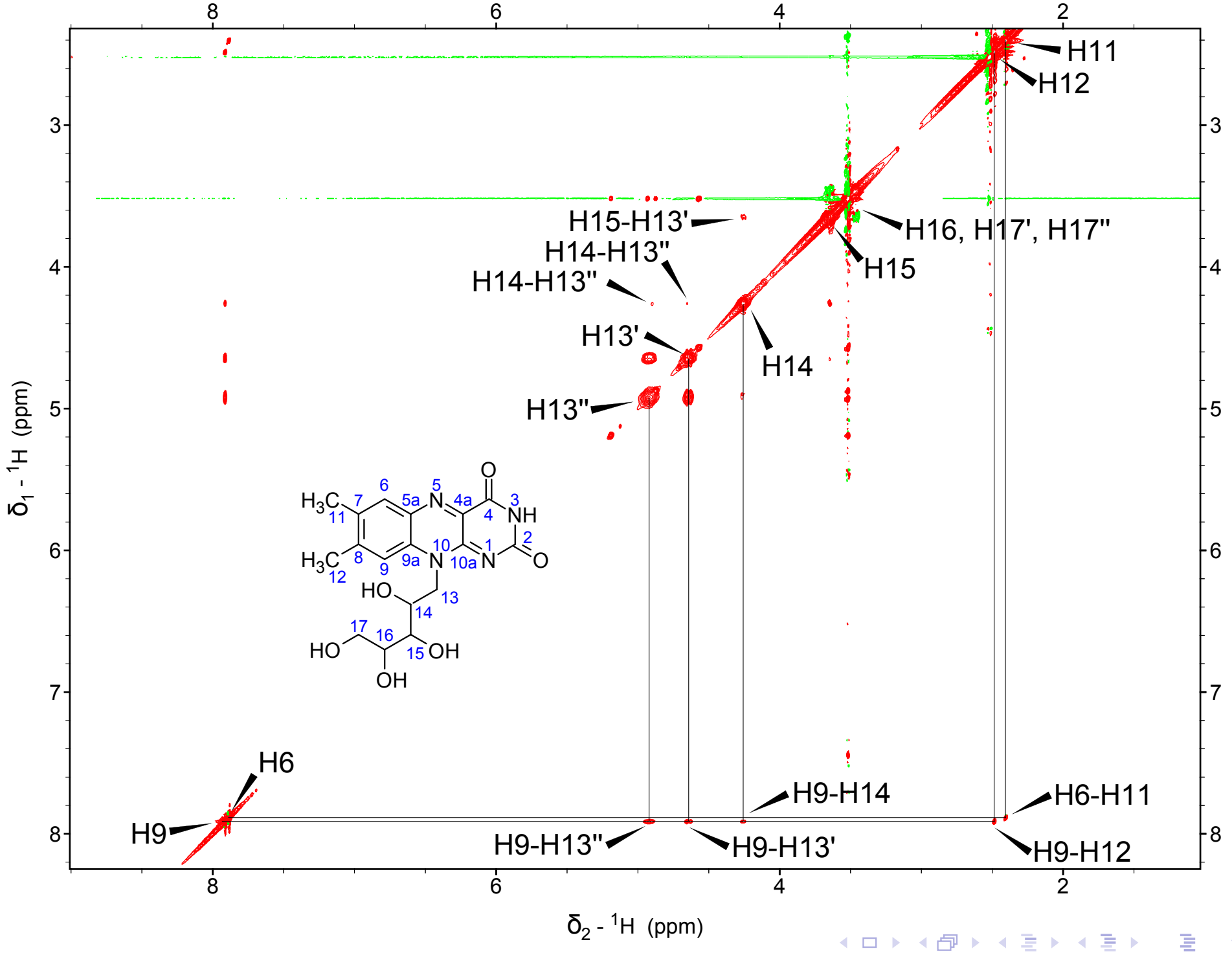
Riboflavine: ^{1}H-^{13}C HMBC + HSQC



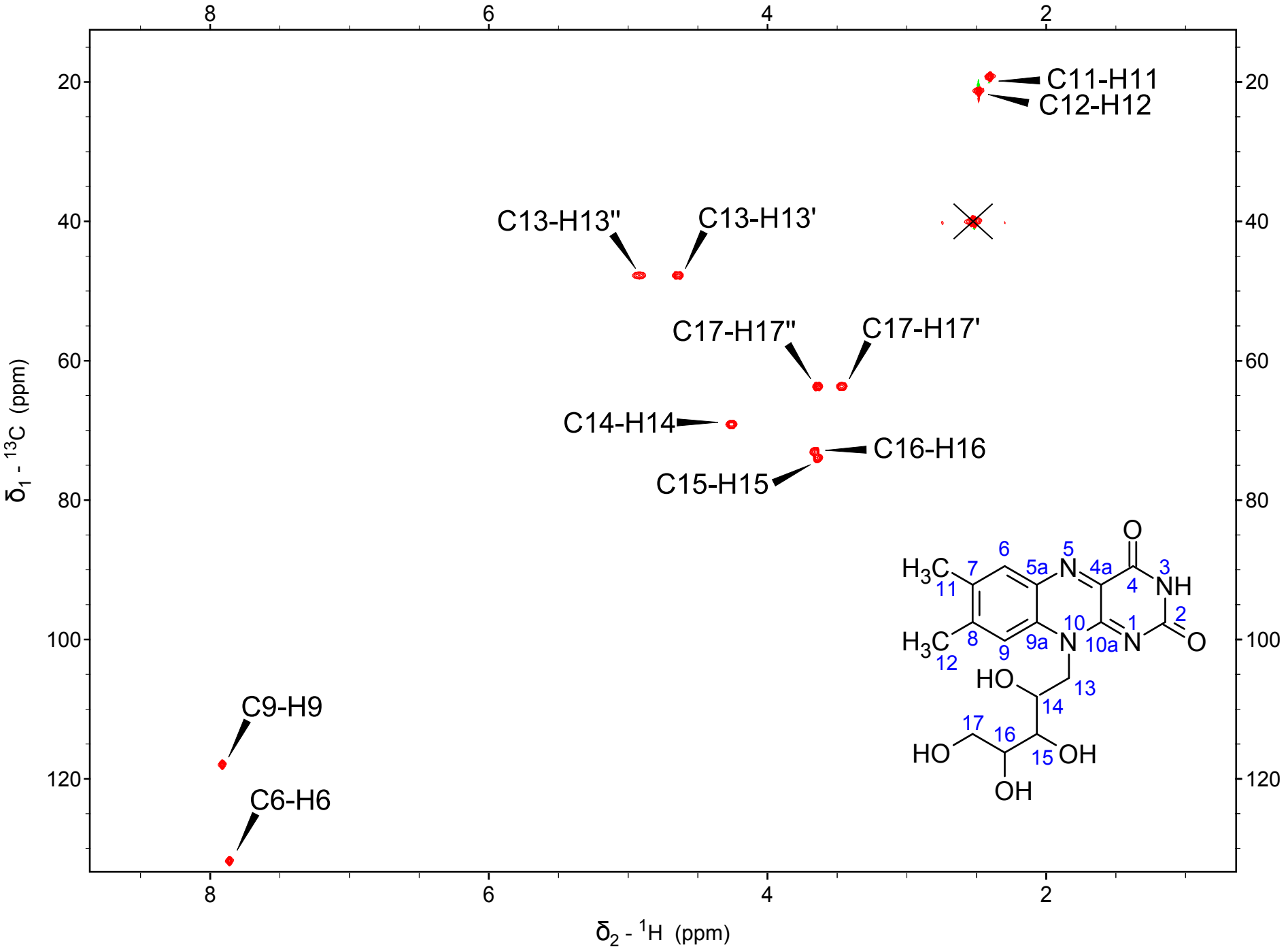
Riboflavine: DQF-COSY



Riboflavine: NOESY



Riboflavine: ^{1}H-^{13}C HSQC



Next session:

Midterm test + Complex exercises