

C8953
NMR strukturní analýza
seminář

Procvičování ^1H - ^1H korelací

Jan Novotný

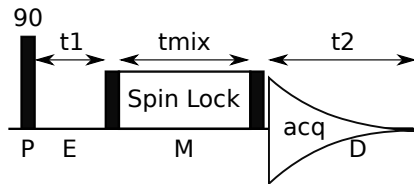
176003@mail.muni.cz

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TOCSY & ROESY

spin lock - isotropic mixing

- ▶ série krátkých 180° pulzů
- ▶ různá pulzní schémata (MLEV-17, DIPSI, ...)
- ▶ precesní pohyb kolem $B_{Spinlock} < B_0 \rightarrow$ "uzamknutí" spinů v transverzální rovině
- ▶ u TOCSY vyšší výkon, offset na střed
- ▶ u ROESY nižší výkon, offset na kraj
- ▶ crosstalk (ROE u TOCSY, J u ROESY)



TOCSY (TOtal Correlation Spectroscopy)

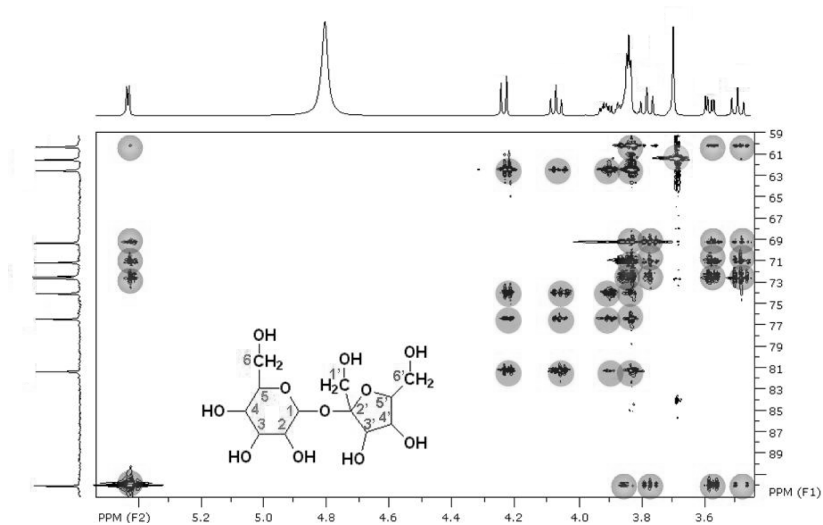
HOHAHA (HOmonuclear HArtmann-HAhn)

korelace na základě J

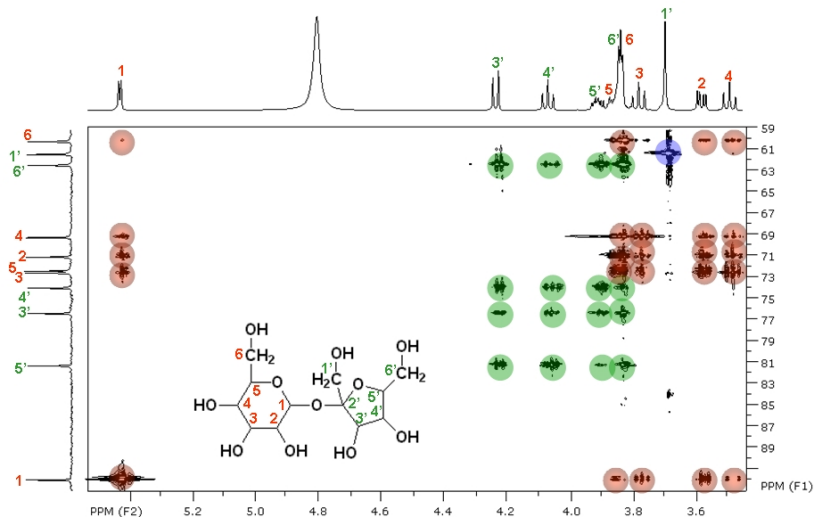
- ▶ koreluje *všechny* protony v rámci jednoho spinového systému navzájem
- ▶ $\tau_{\text{mix}} \approx 20 - 120$ ms
- ▶ intenzita crosspeaků závislá na τ_{mix} a hodnotě J



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

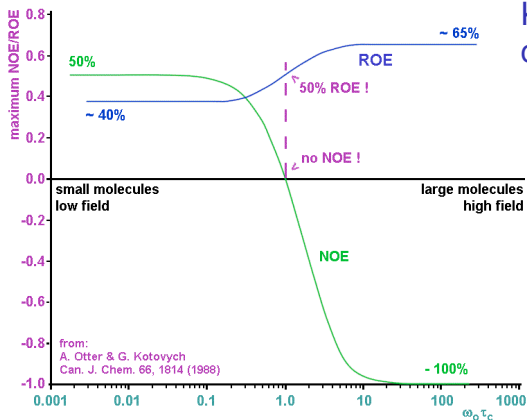


^1H - ^{13}C HSQC - TOCSY



ROESY-Rotating frame Overhauser Enhancement Spectroscopy

CAMELPSIN – Cross-relaxation Appropriate for Minimolecules Emulated by Locked SPINs

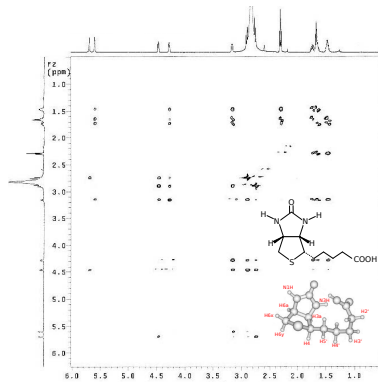
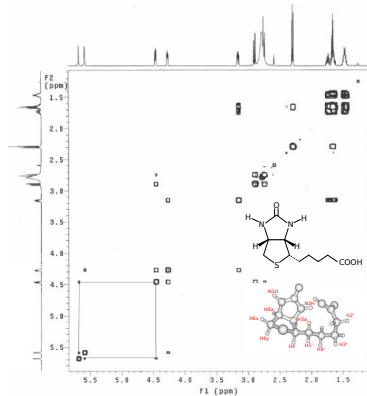


Korelace na základě cross-relaxace

- ▶ ROE vždy pozorovatelné
- ▶ intenzita závisí na r_{HH} a τ_{mix}
- ▶ opačná fáze ROE crosspeaků
- ▶ výměnné a TOCSY crosspeaky(J) se stejnou fází

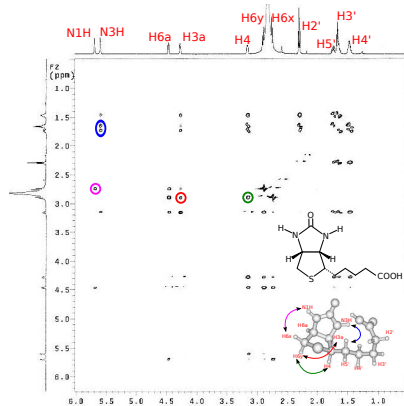
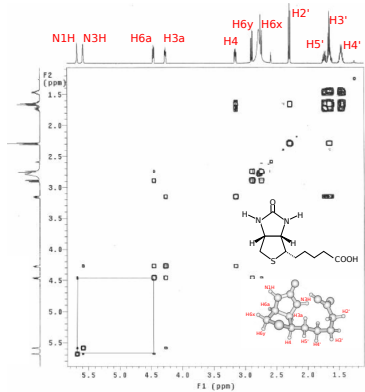
Biotin - COSY vs. ROESY

(G. T. Crisp and Yu-Lin Jiang, 2001)



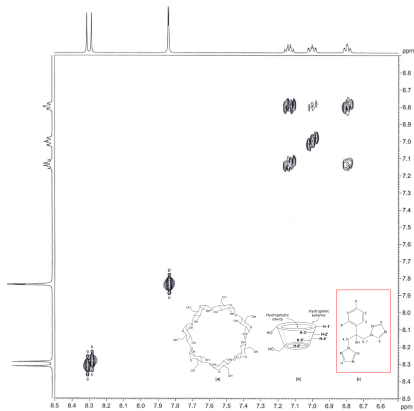
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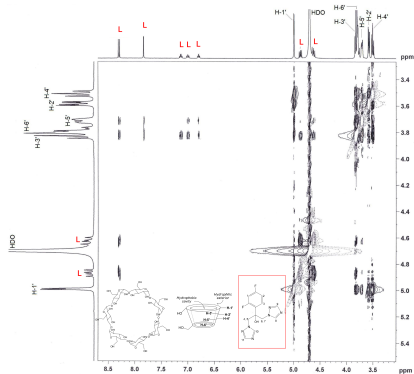


Cyklodextrinový komplex

COSY - aromatická část

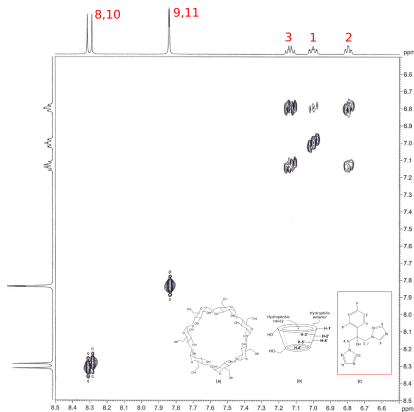


ROESY

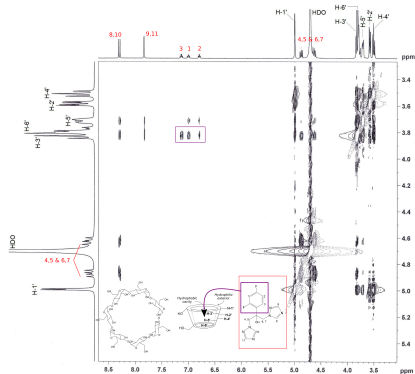


Cyklodextrinový komplex

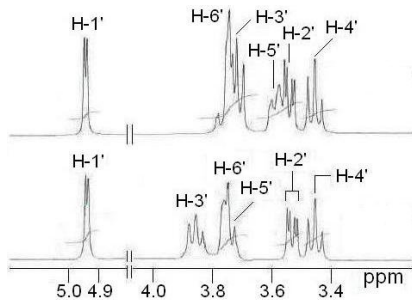
COSY - aromatická část



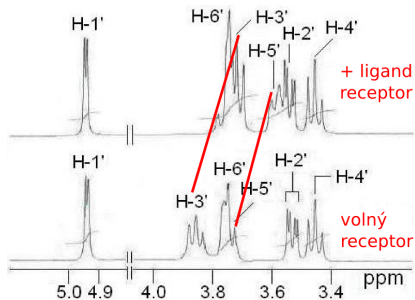
ROESY



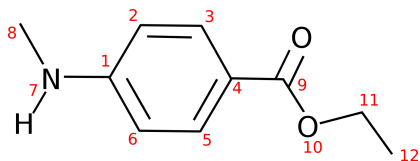
Sekundární chemický posun



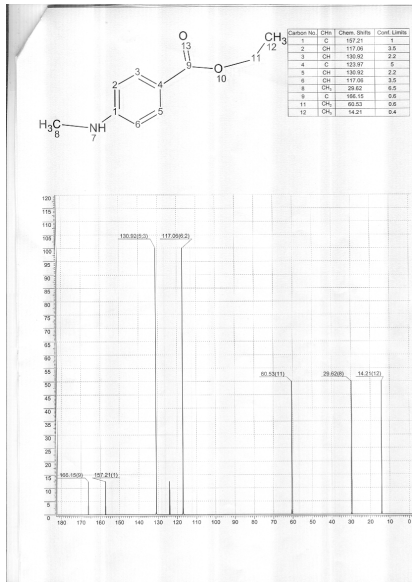
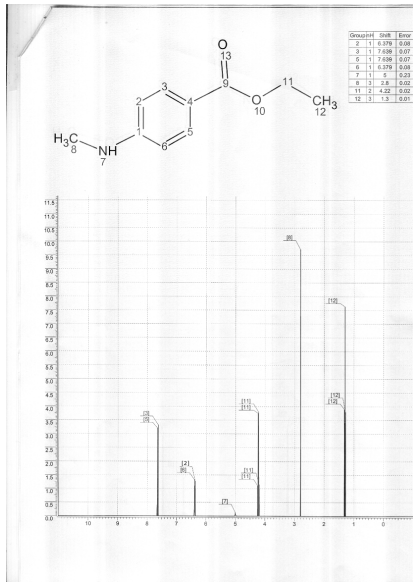
Sekundární chemický posun



Simulace 1D NMR spekter



$^1\text{H}/^{13}\text{C}$ simulace



Příště

^1H - $^{15}\text{N}/^{13}\text{C}$ HMBC