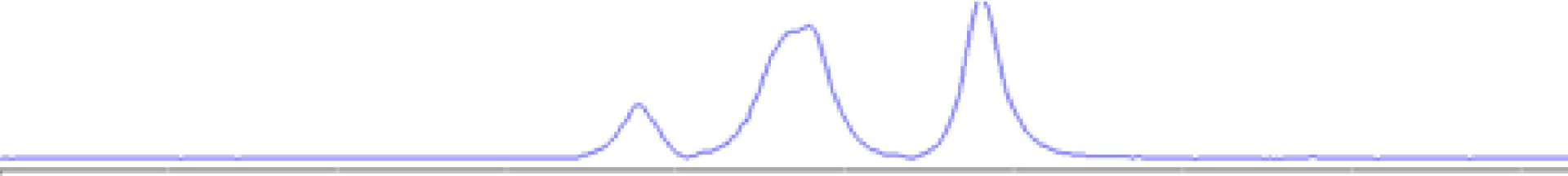
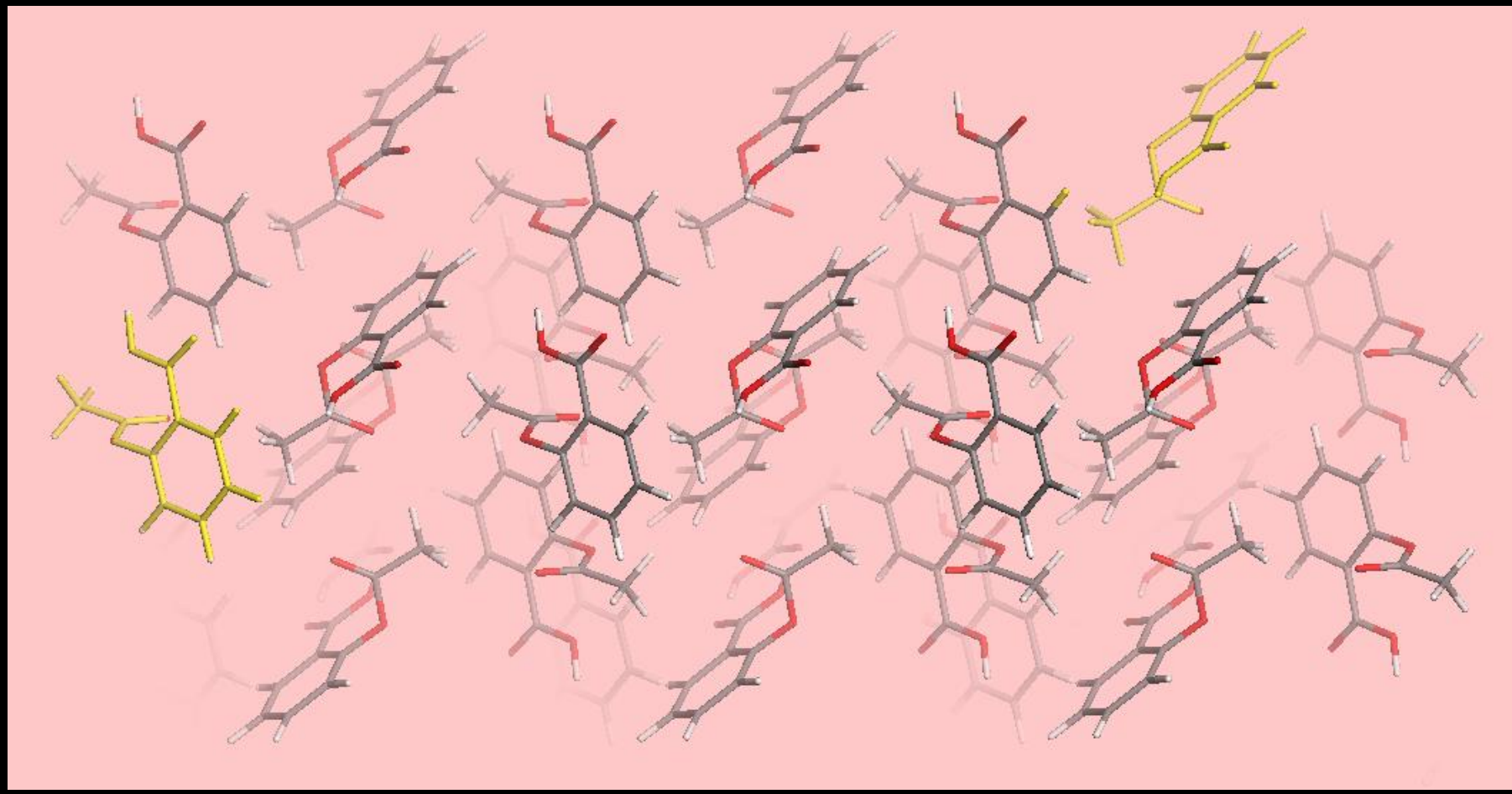


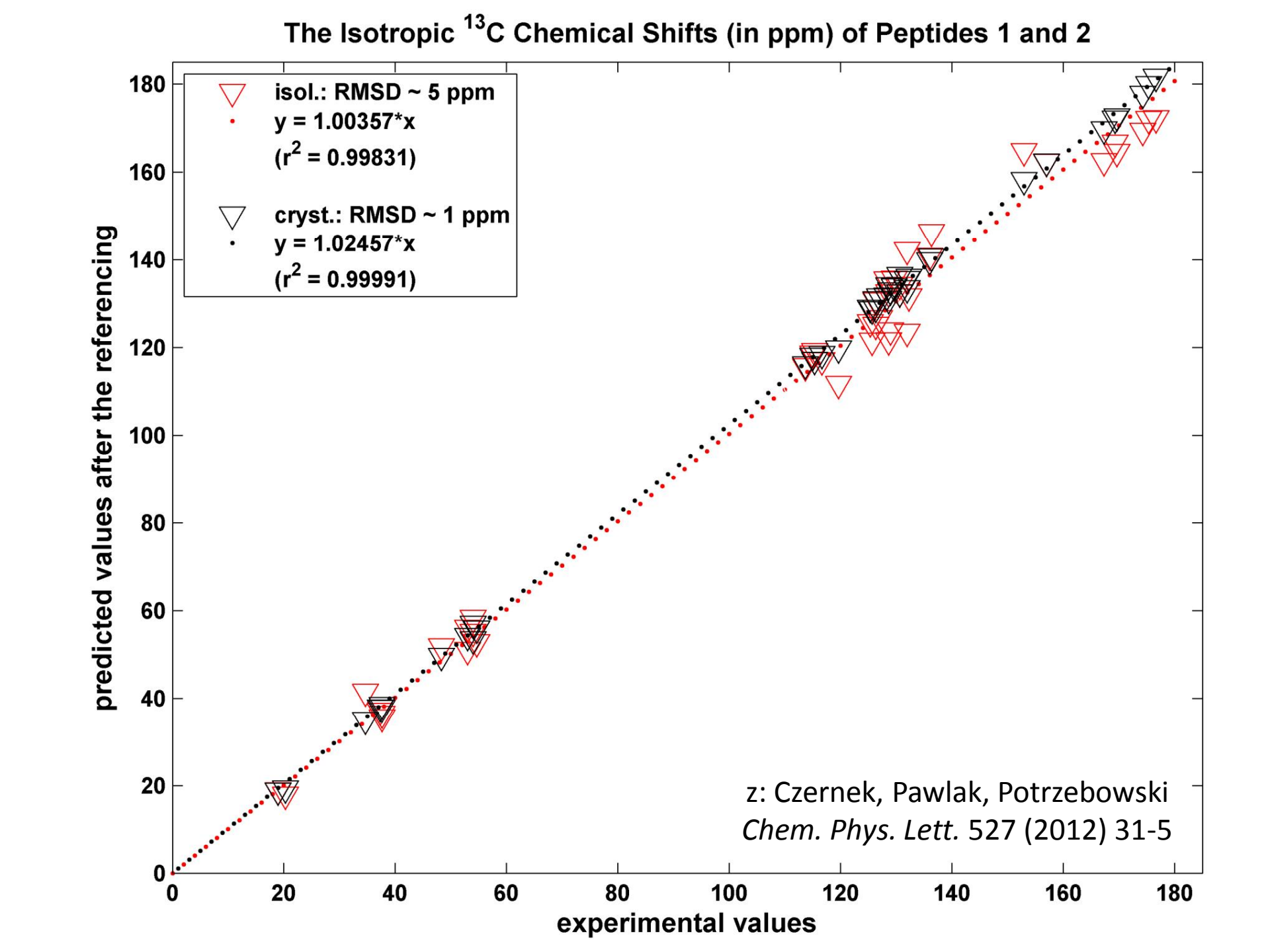
Přiřazování signálů korelačních spekter NMR pevného stavu

Seminář gridového počítání 2014

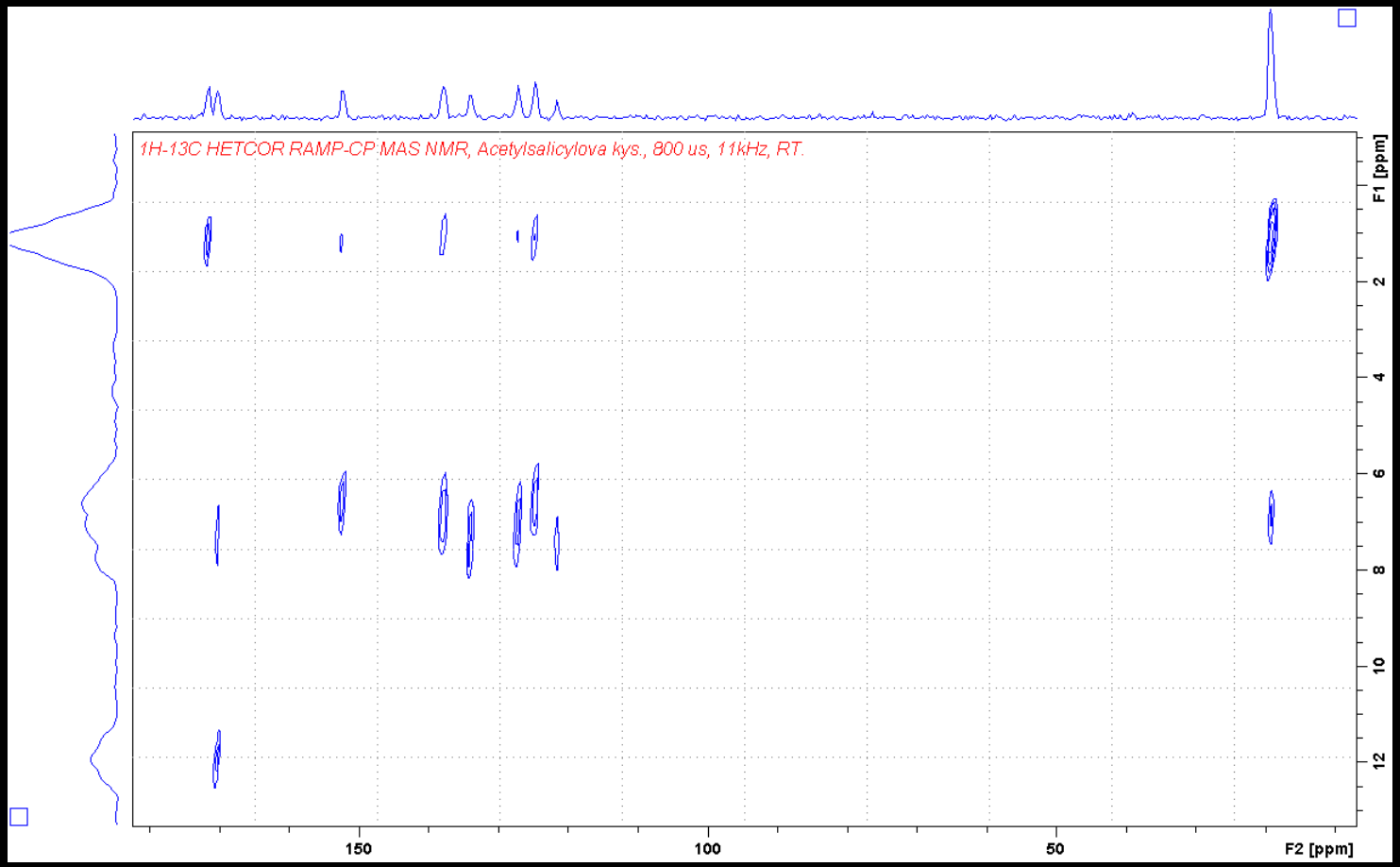
Struktura Aspirinu



kvantově chemické výpočty se zahrnutím periodicity


The Isotropic ^{13}C Chemical Shifts (in ppm) of Peptides 1 and 2
isol.: RMSD ~ 5 ppm
y = 1.00357*x
(r^2 = 0.99831)
cryst.: RMSD ~ 1 ppm
y = 1.02457*x
(r^2 = 0.99991)
predicted values after the referencing
experimental values
0
20
40
60
80
100
120
140
160
180
z: Czernek, Pawlak, Potrzebowski
Chem. Phys. Lett. 527 (2012) 31-5

Korelační spektrum Aspirinu

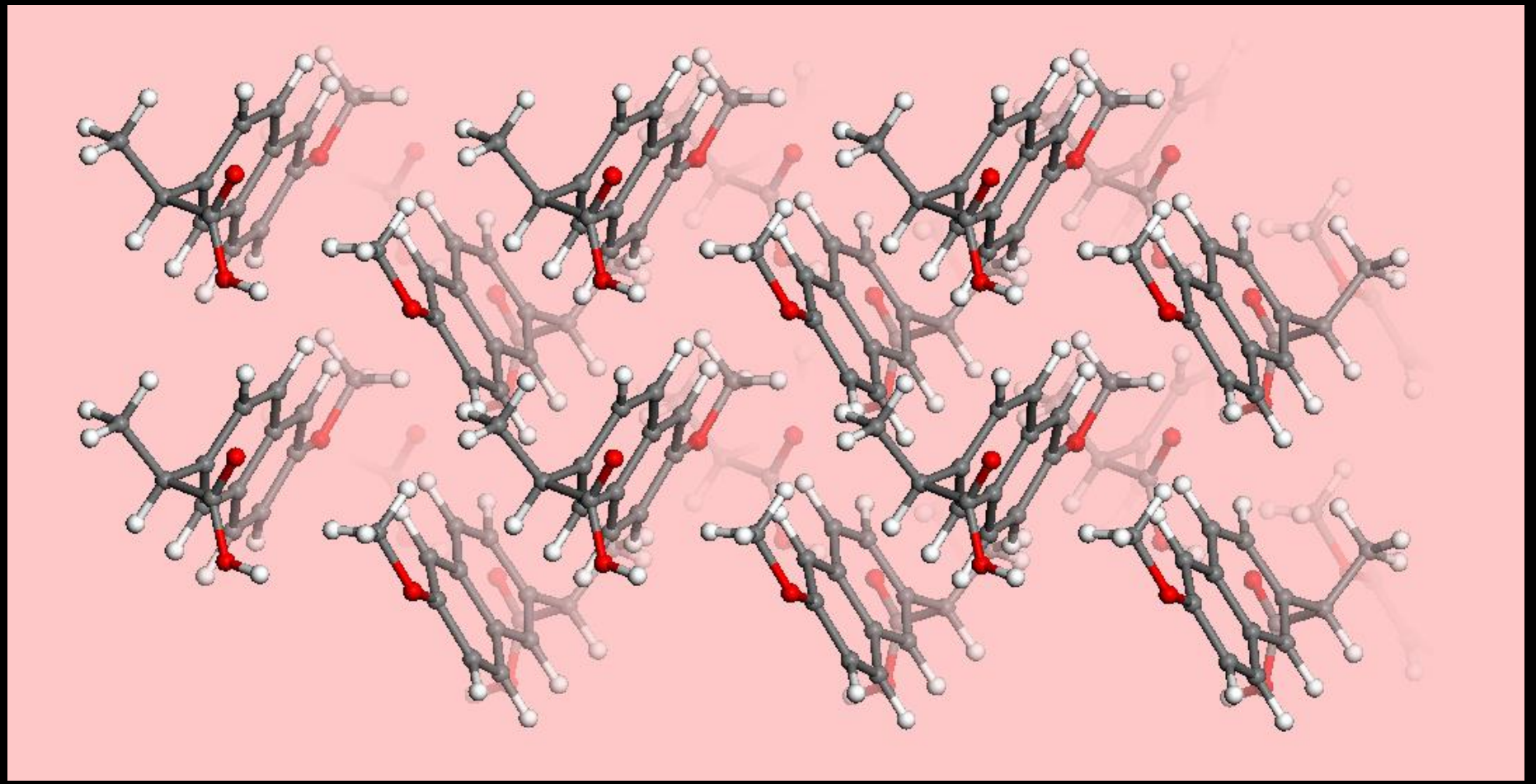


měření: chemický posun (δ); výpočet: chemické stínění (σ)

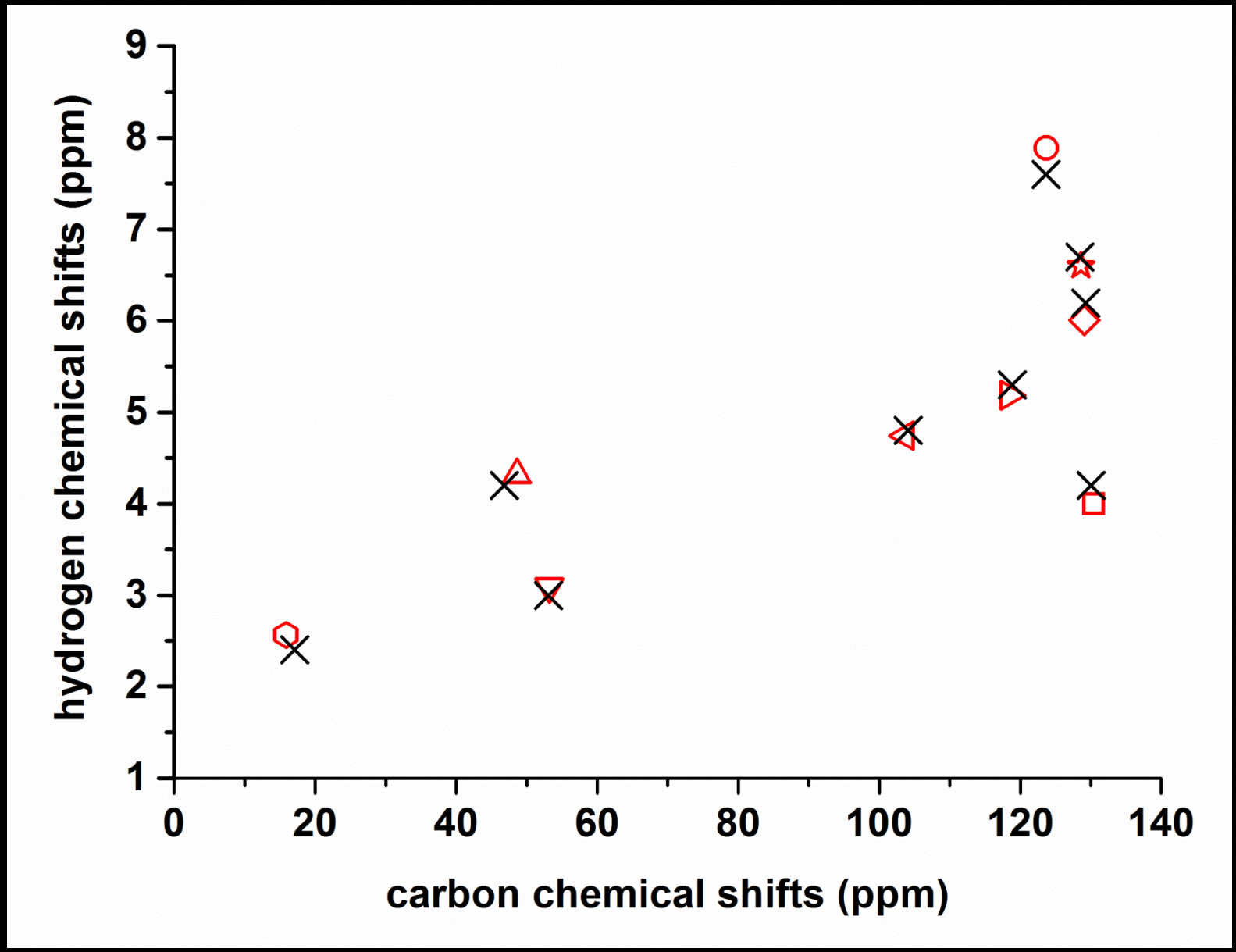
$$\delta = \sigma(\text{standard}) - \sigma$$

hodnoty v ppm

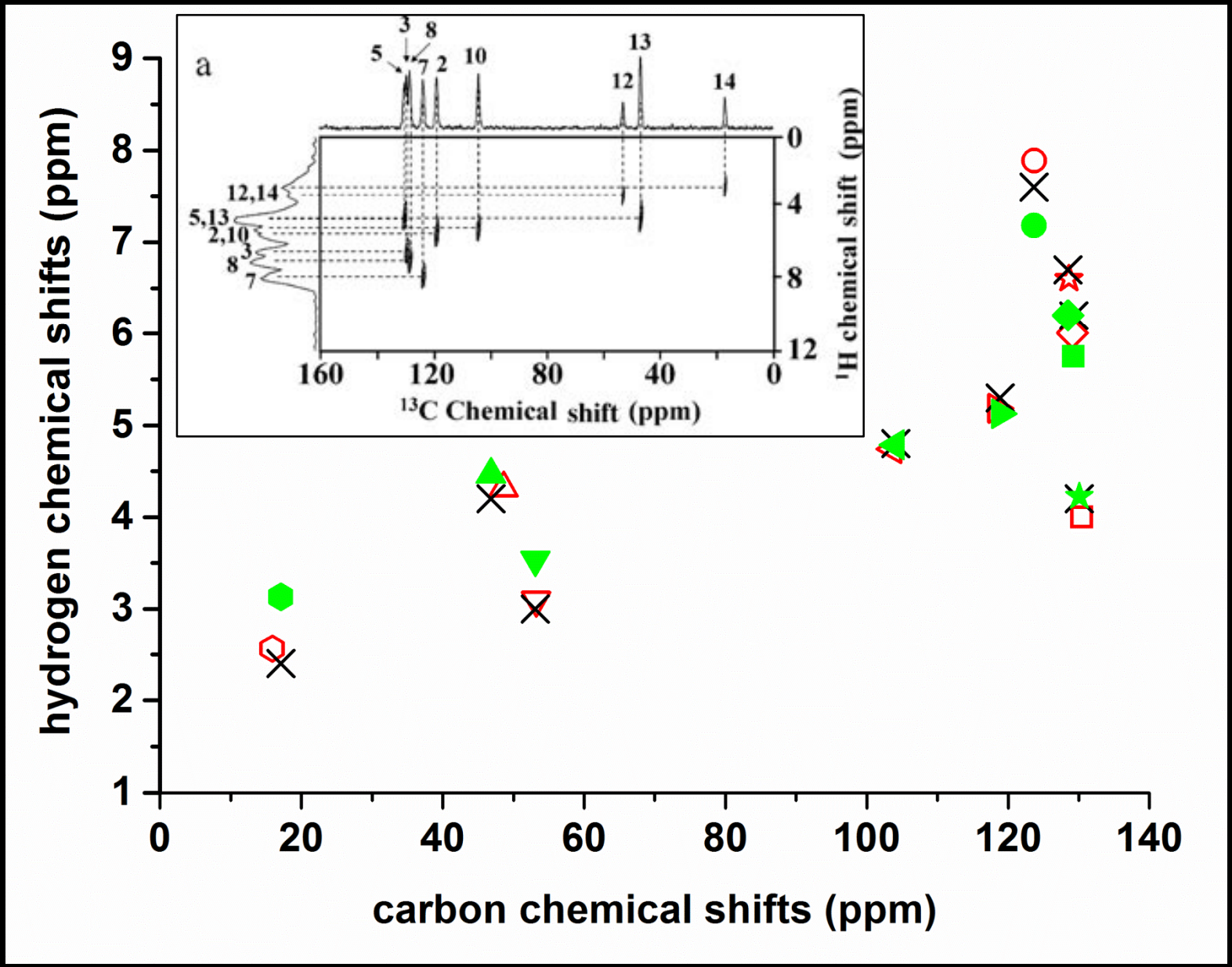
Struktura Naproxenu



Korelační spektrum Naproxenu



Přiřazení spektra Naproxenu



Experimentální (δ) a teoretické (ε) chemické posuny

- $\min\limits_{\delta(\mathrm{C});\, a,b} \sum_{i=1}^{n} (a * \delta(\mathrm{C})_i + b - \sigma(\mathrm{C})_i)^2$
- $\min\limits_{\delta(\mathrm{H});\, c,d} \sum_{j=1}^{m} \left(c * \delta(\mathrm{H})_j + d - \sigma(\mathrm{H})_j\right)^2$

- $\varepsilon(\mathrm{C})_i = a * \sigma(\mathrm{C})_i + b;\ \varepsilon(\mathrm{H})_j = c * \sigma(\mathrm{H})_j + d$

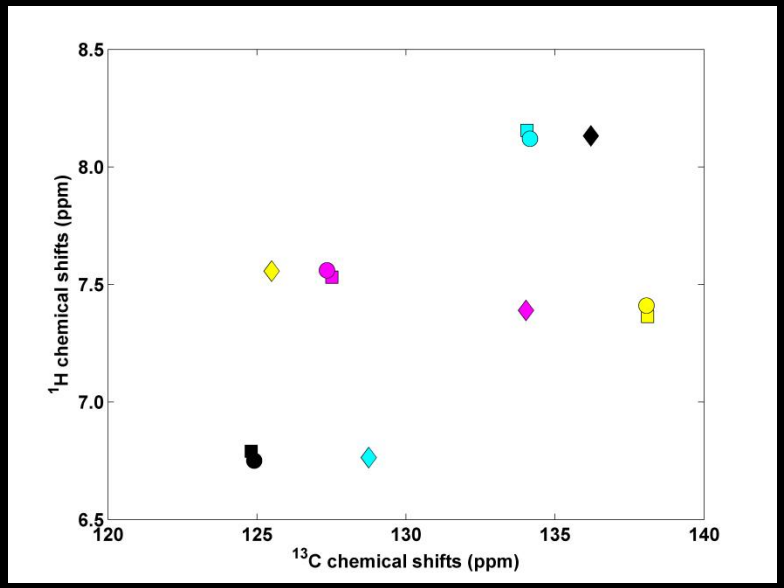
- $n \leq m$: m dvojic $[\delta(\mathrm{C})_k; \delta(\mathrm{H})_k]$ pro $k = 1, 2, \dots, m$

- $\rho(\mathrm{H})_k = \delta(\mathrm{H})_k - \varepsilon(\mathrm{H})_k; \pi(\mathrm{C})_k = \delta(\mathrm{C})_k - \varepsilon(\mathrm{C})_k$
- $n_{(\rho,\pi)} = \|(\rho, \pi)\|_2$ norma … kovariance:
- $s_{\rho\pi} = \frac{1}{m-1} \sum_{k=1}^{m} (\pi(\mathrm{C})_k - \bar{\pi})\,(\rho(\mathrm{H})_k - \bar{\rho})$
- $\bar{\pi} = \frac{1}{m} \sum_{k=1}^{m} \pi(\mathrm{C})_k;\ \bar{\rho} = \frac{1}{m} \sum_{k=1}^{m} \rho(\mathrm{H})_k$

Implementace

testovací: Matlab

- bez nutnosti deklarací
- P = perms(v)
- [B,IX] = sort(A,...)
- vše uloženo (možno např. okamžitě vykreslit řešení):



výpočetní: Fortran 77

- ověřeno pro až 12 párů
- z Internetu (Roseta Code)
- z Internetu (? z psu.edu)
- pro danou permutaci:

  pokud SD (C) < 2 ppm

  pokud SD (H) < 1 ppm

  uložit

  jinak další permutace

  na závěr výpis pro analýzu

- 12 párů: asi 3 minuty CPU

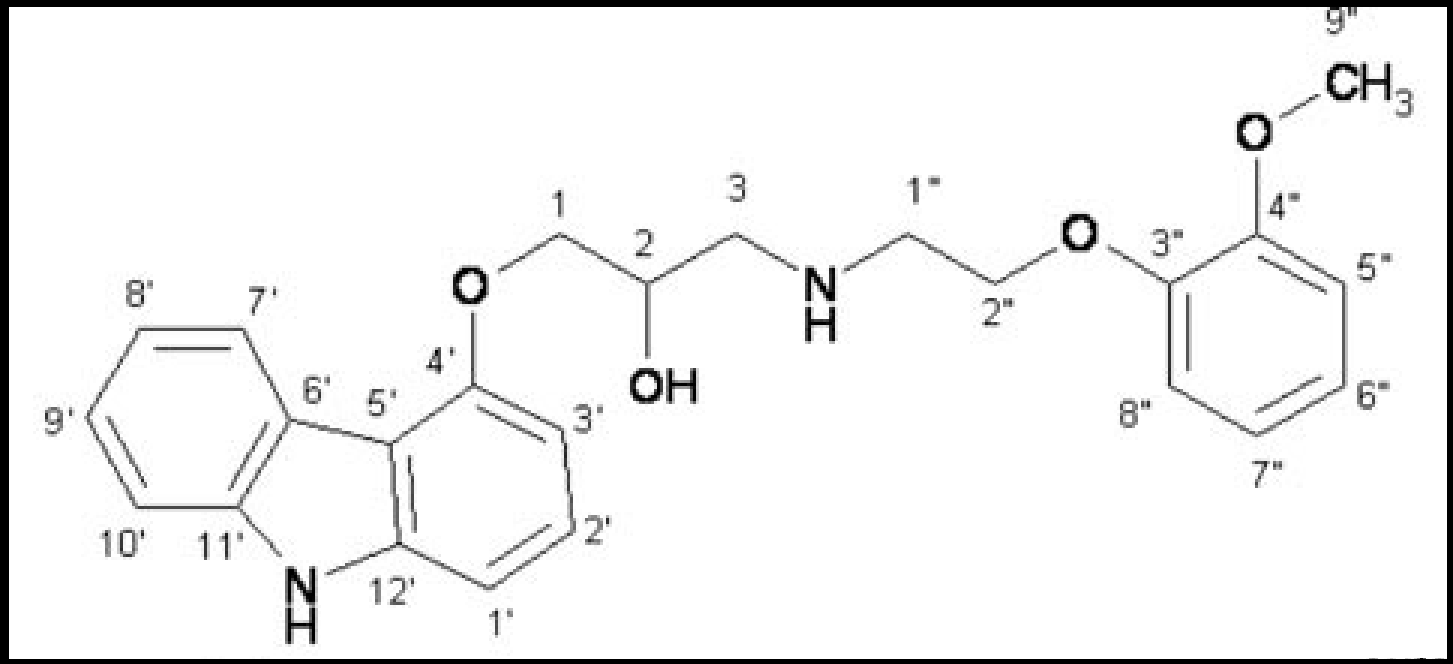
Zdroje + poděkování

- spektra Aspirinu: J. Brus (Czernek & Brus, *Chem. Phys. Lett.* 2014, 608, 334–339)
- spektra Naproxenu: z Ando et al., *J. Pharm. Sci.* 2012, 101, 3214–3221 a jejich simulace z doi:10.106/j.cplett.2014.11.031
- chemické posuny pro 12 ^{13}C – ^{1}H párů: Fred Vogt (Vogt et al., *J. Pharm. Sci.* 2012, 102, 3705–3716)
- GAČR 14-03636S
- hlavně

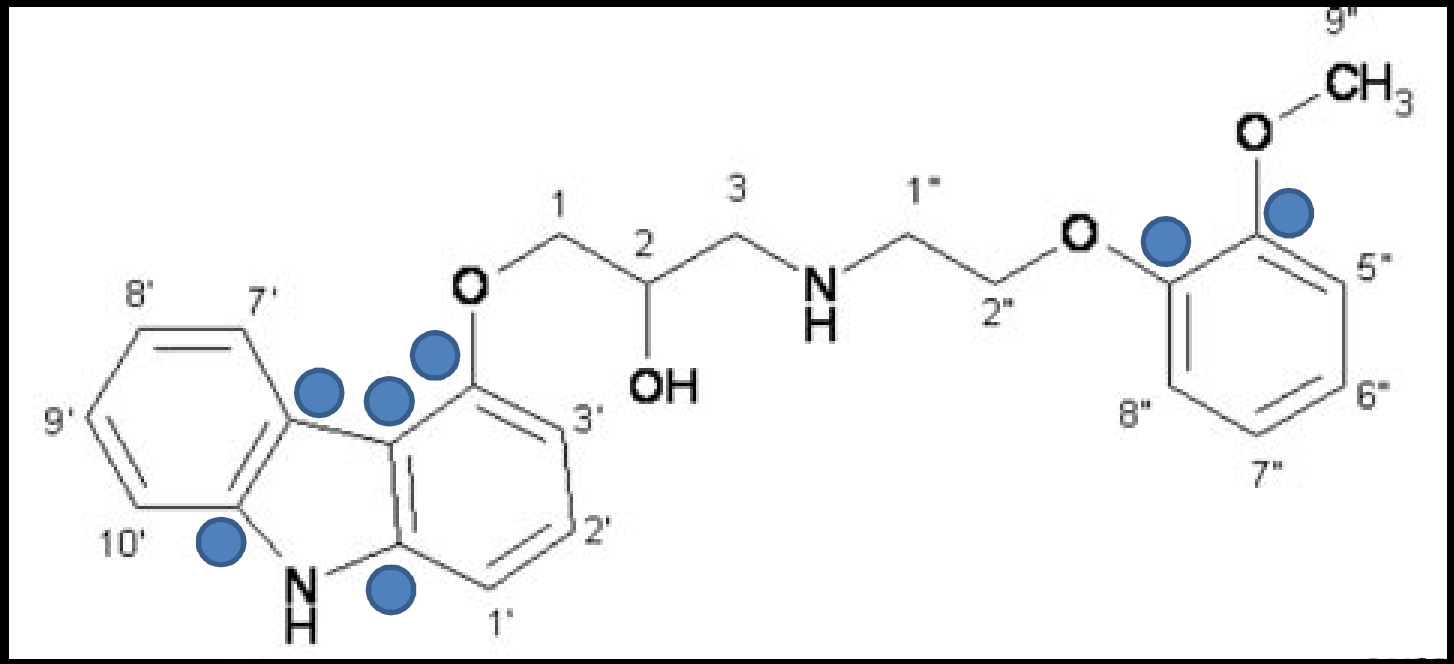
MetaCentrum

cerit scientific cloud

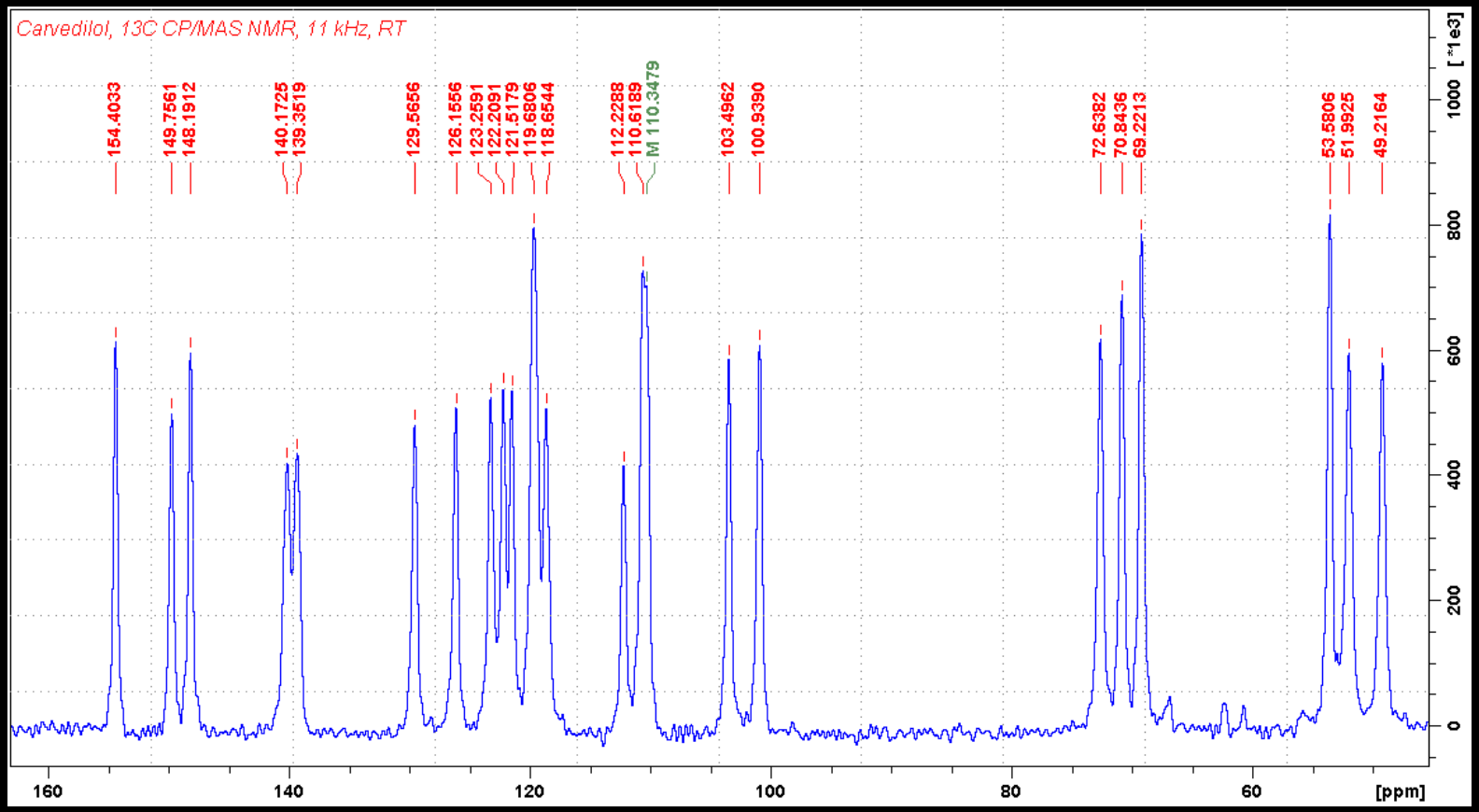
Assigning Carvedilol $C_{24}H_{26}N_2O_4$

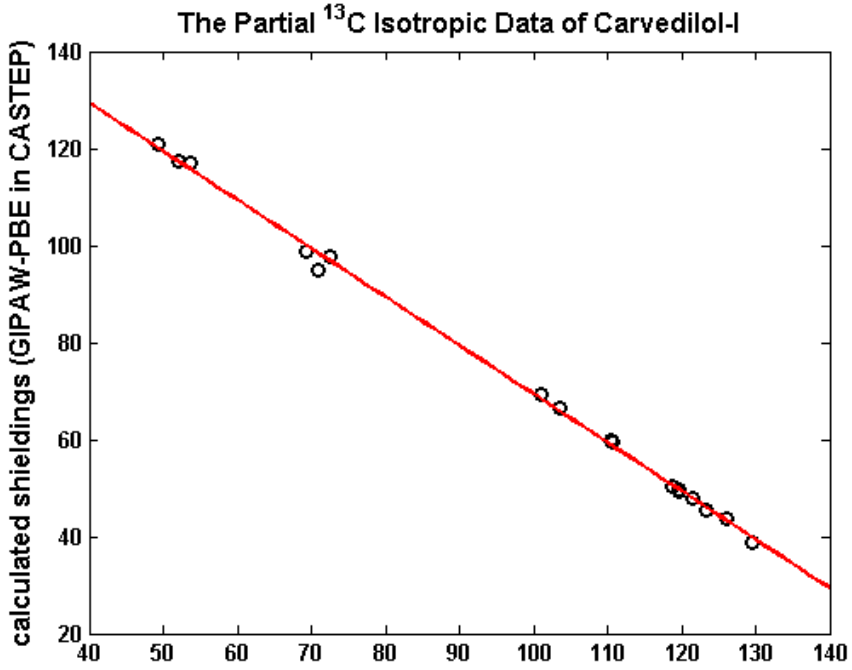


Assigning Carvedilol $C_{24}H_{26}N_2O_4$



Assigning Carvedilol $C_{24}H_{26}N_2O_4$



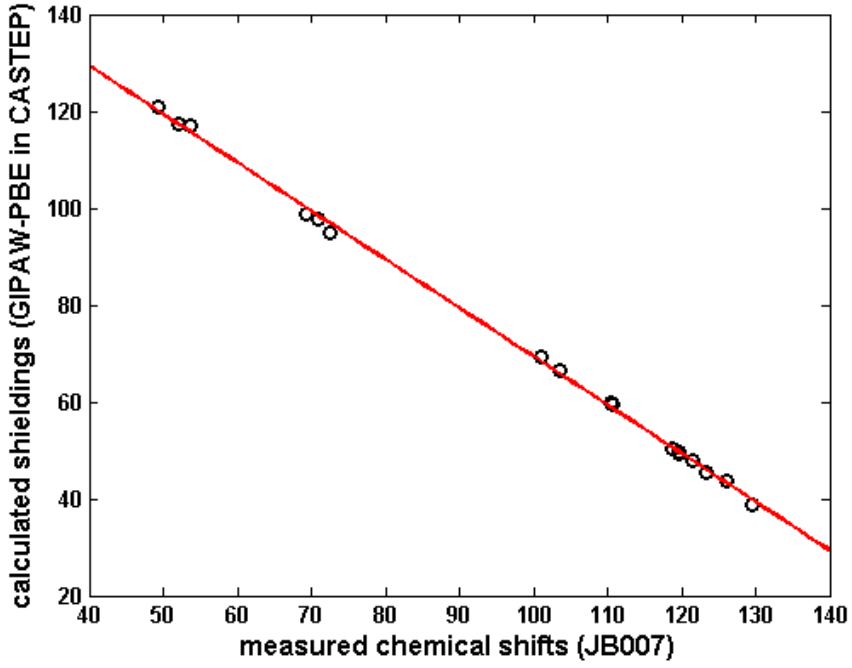


max = 3.65

rmsd =1.18

avg = 0.84

p0 =
–1.0001 169.29



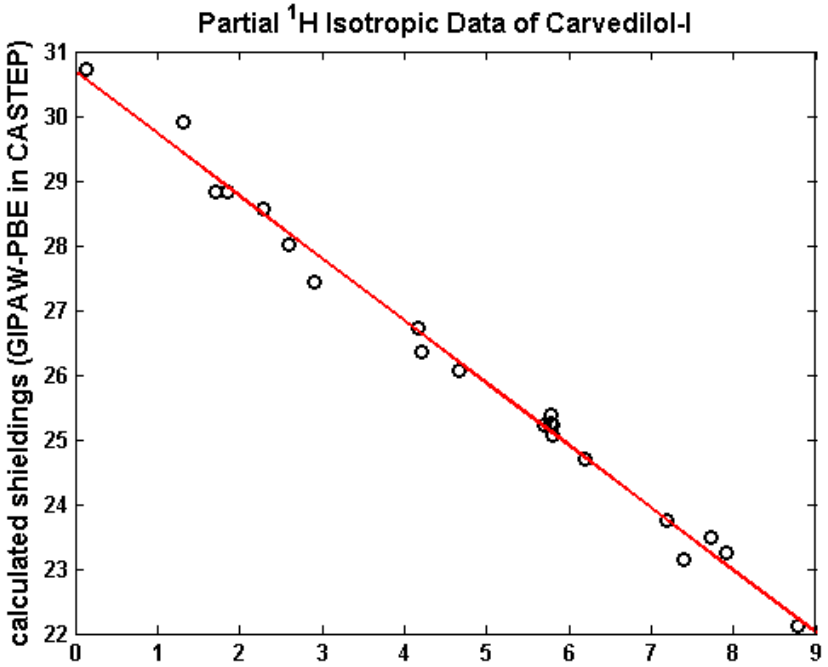
max =1.86

rmsd = 0.87

avg = 0.72

p0 =
–1.0005 169.33

ASIGNING CARVEDILOL

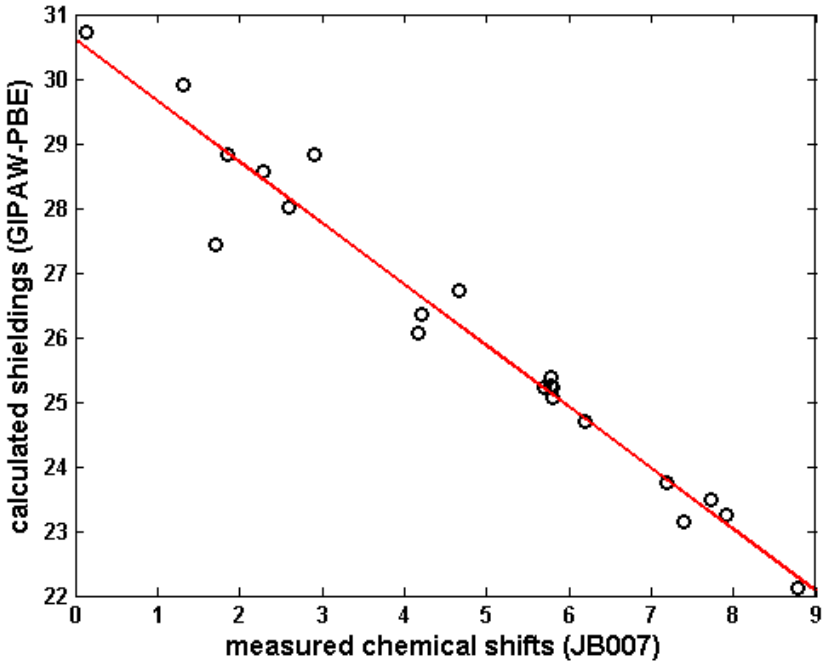


max = 0.48

rmsd = 0.23

avg = 0.17

p0 =
–0.9638 30.69



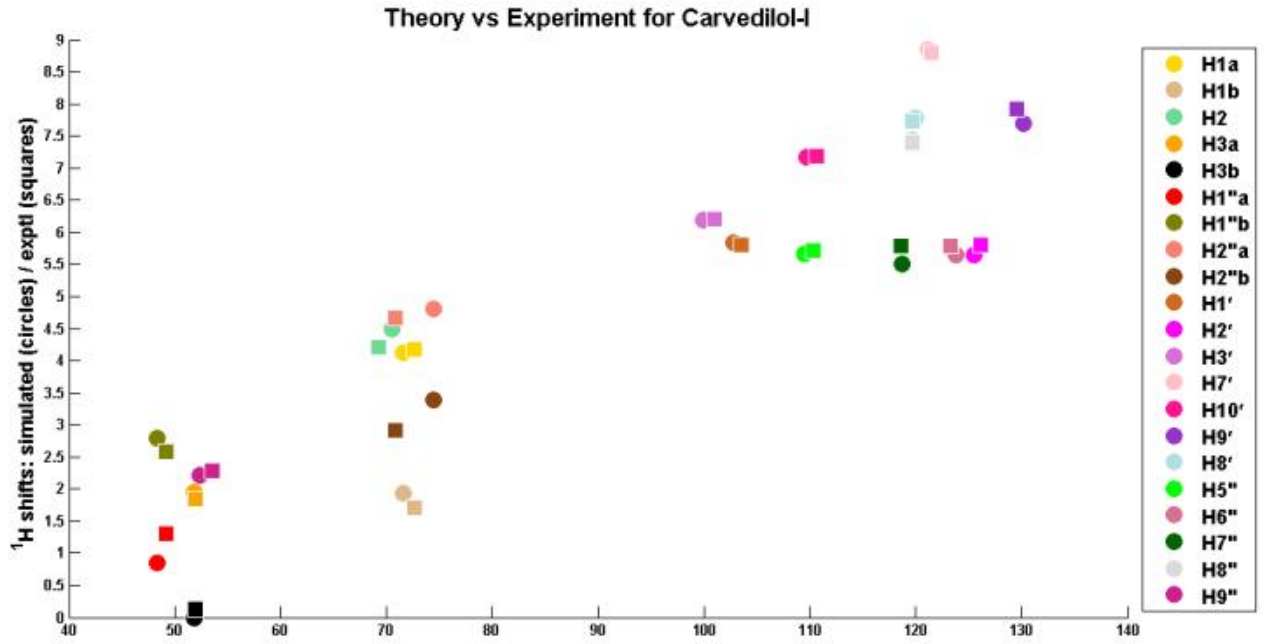
max =1.55

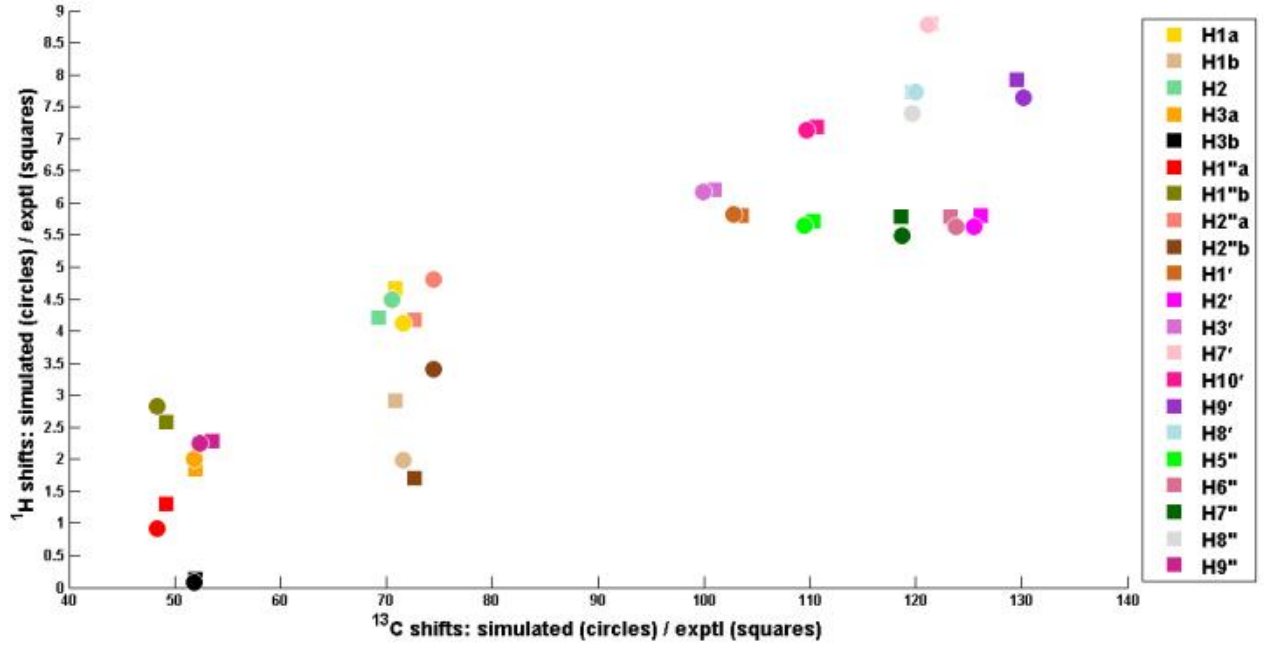
rmsd = 0.49

avg = 0.32

p0 =
–0.9471 30.61

ASIGNING CARVEDILOL





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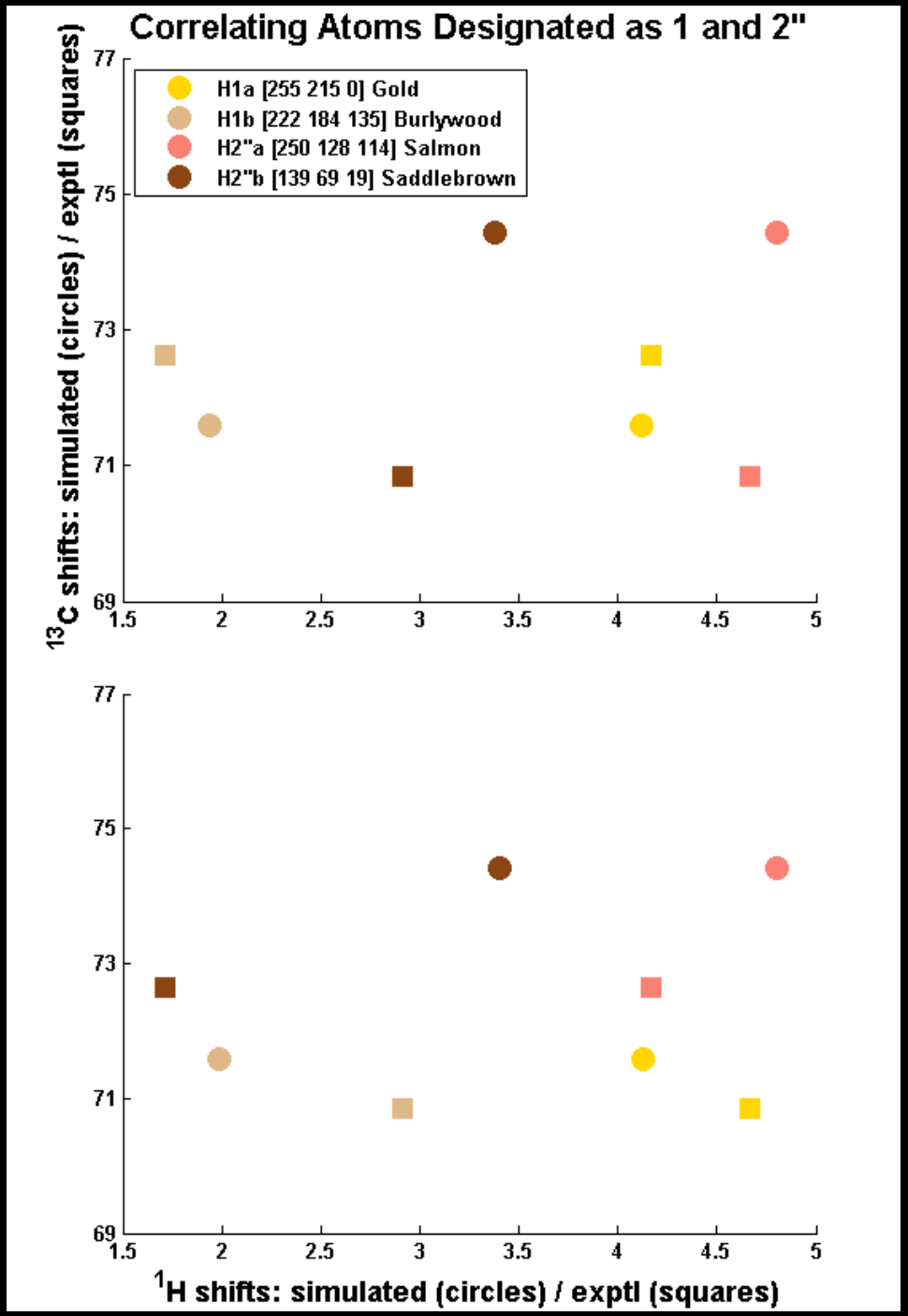
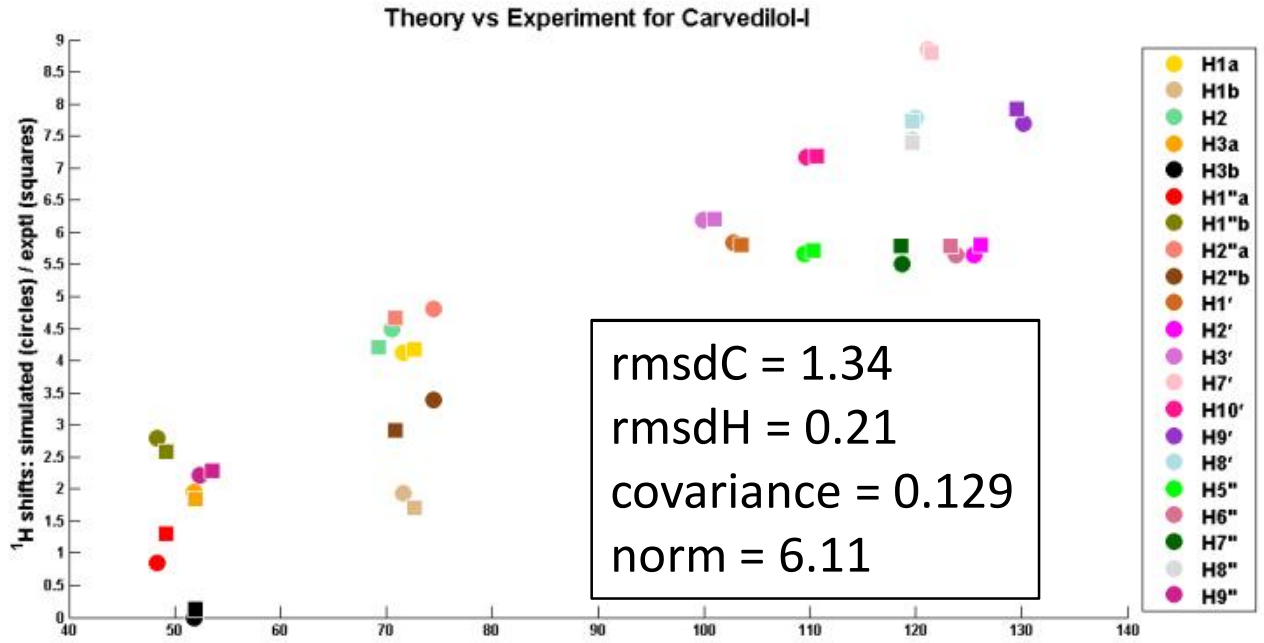
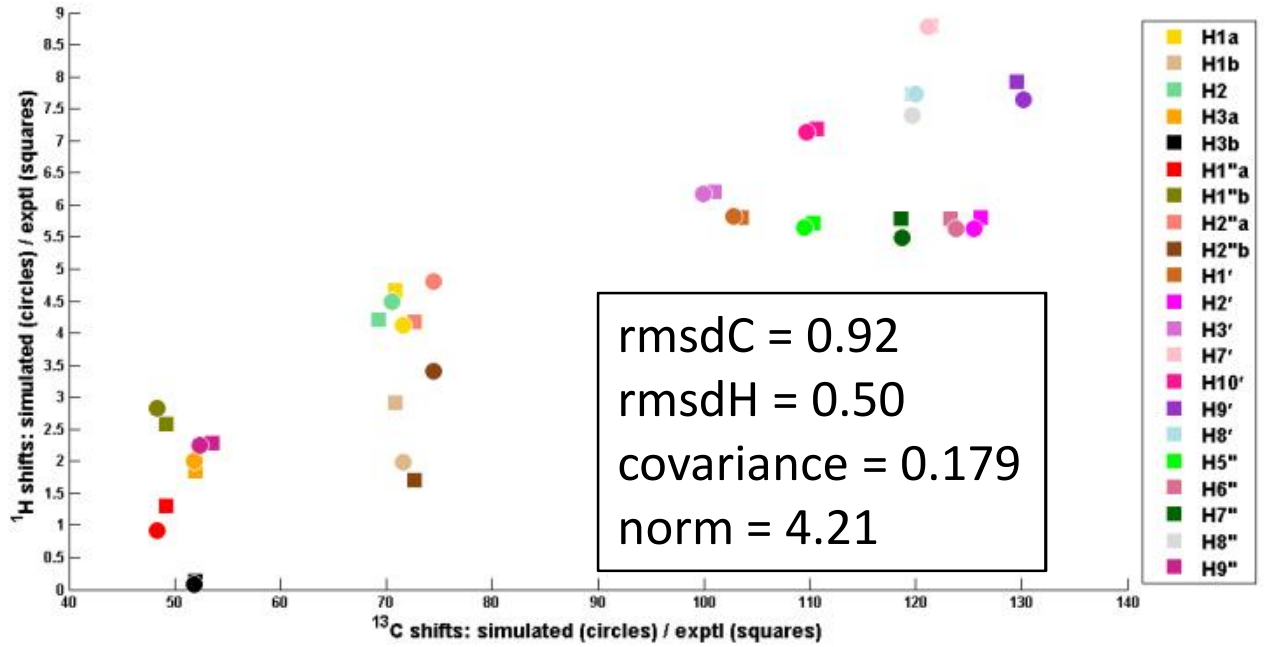


ASIGNING CARVEDILOL





ASIGNING CARVEDILOL