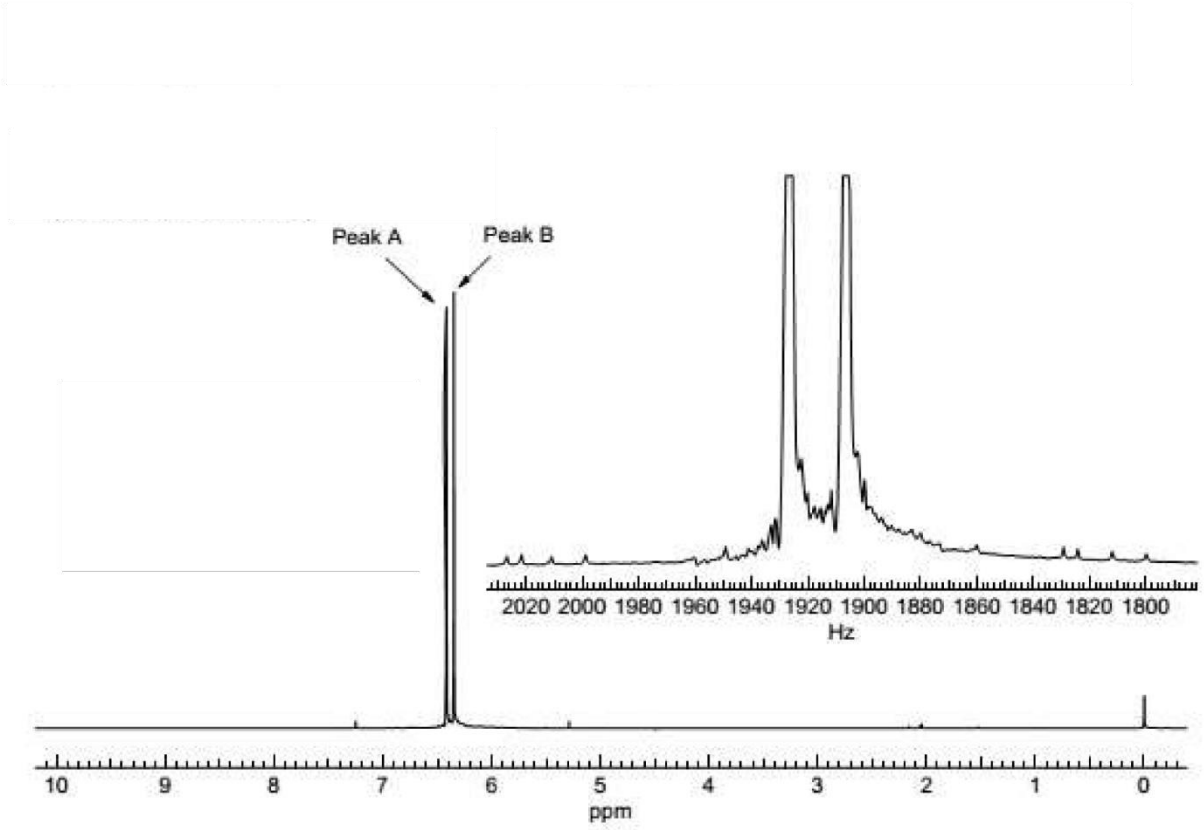
NMR - structural analysis: TEST 2

1. Figure bellow shows ^{1}H NMR spectrum of *Z* and *E* isomer of $C_2H_2Cl_2$. *Hint:* Consider non-equivalent character of H atoms attached to ^{12}C and ^{13}C.

a) By analyzing the splitting of ^{13}C satellites, identify chemical shift of both isomers.

b) Estimate the values of $^{1}J_{HC}$ and $^{3}J_{HH}$.

c) Calculate the optimal delay needed for evolution of anti-phase magnetization in case of heteronuclear coupling. Draw a vector scheme of INEPT sequence.



2. Attached figure shows standard ^{1}H NMR spectrum of presented bicyclic compound and two inserts which are difference spectra (subtraction irradiated - standard) resulting from selective irradiation of signals at either 0.95 or 1.38 ppm.

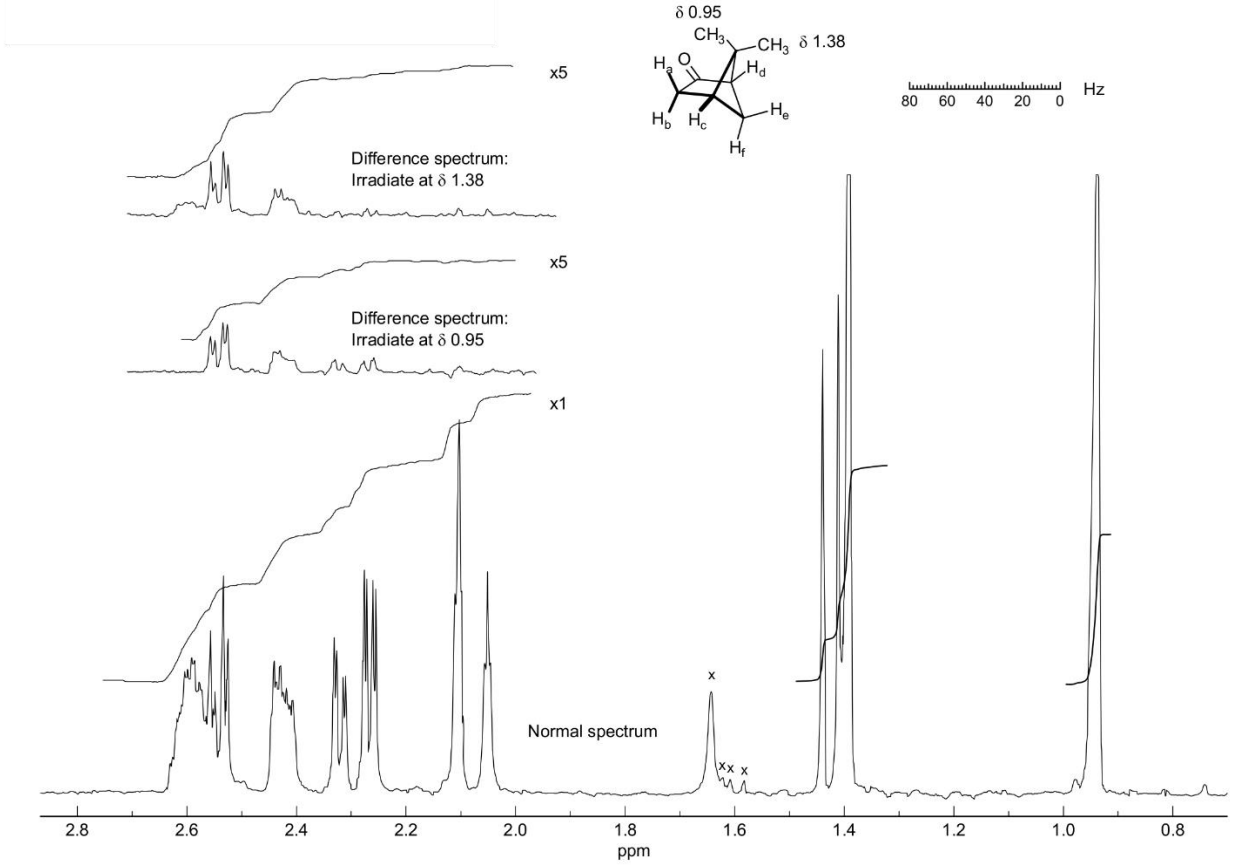
a) What type of phenomena is used in these experiments?

b) Was decoupler active during acquisition of irradiated spectra?

c) Based on comparison of the individual spectra assign resonances of Ha-Hf. Explain your decision.

1.43 2.08 2.28 2.43 2.55 2.60

d) Comment on chemical shift difference between methyl groups as well as He and Hf.

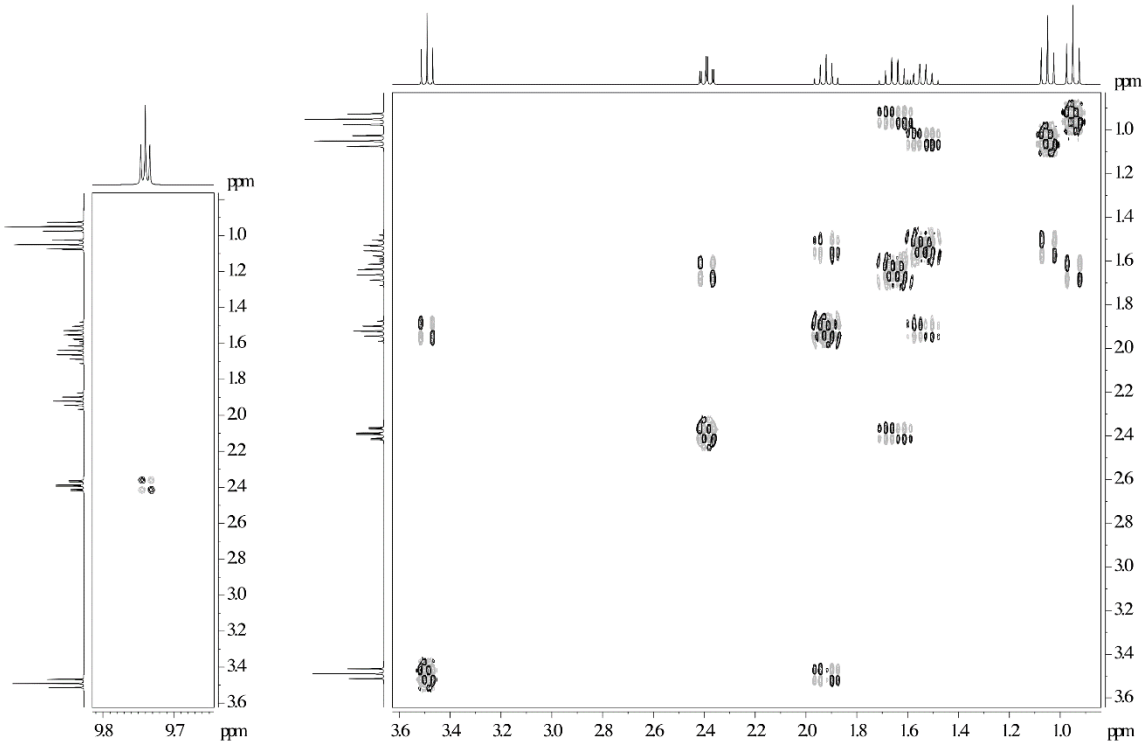


3. ^{1}H-^{1}H COSY spectrum shown below contains mixture of butylbromid and butanal.

a) Assign the signals of both molecules. Comment on the spitting of signal at 2.4 ppm (look at 1D projection at the border).

b) Why do crosspeaks differ in splitting between mirror images?

c) Based on crosspeak 1.6, 2.4 try to describe the meaning of “active” and “passive coupling” terms.



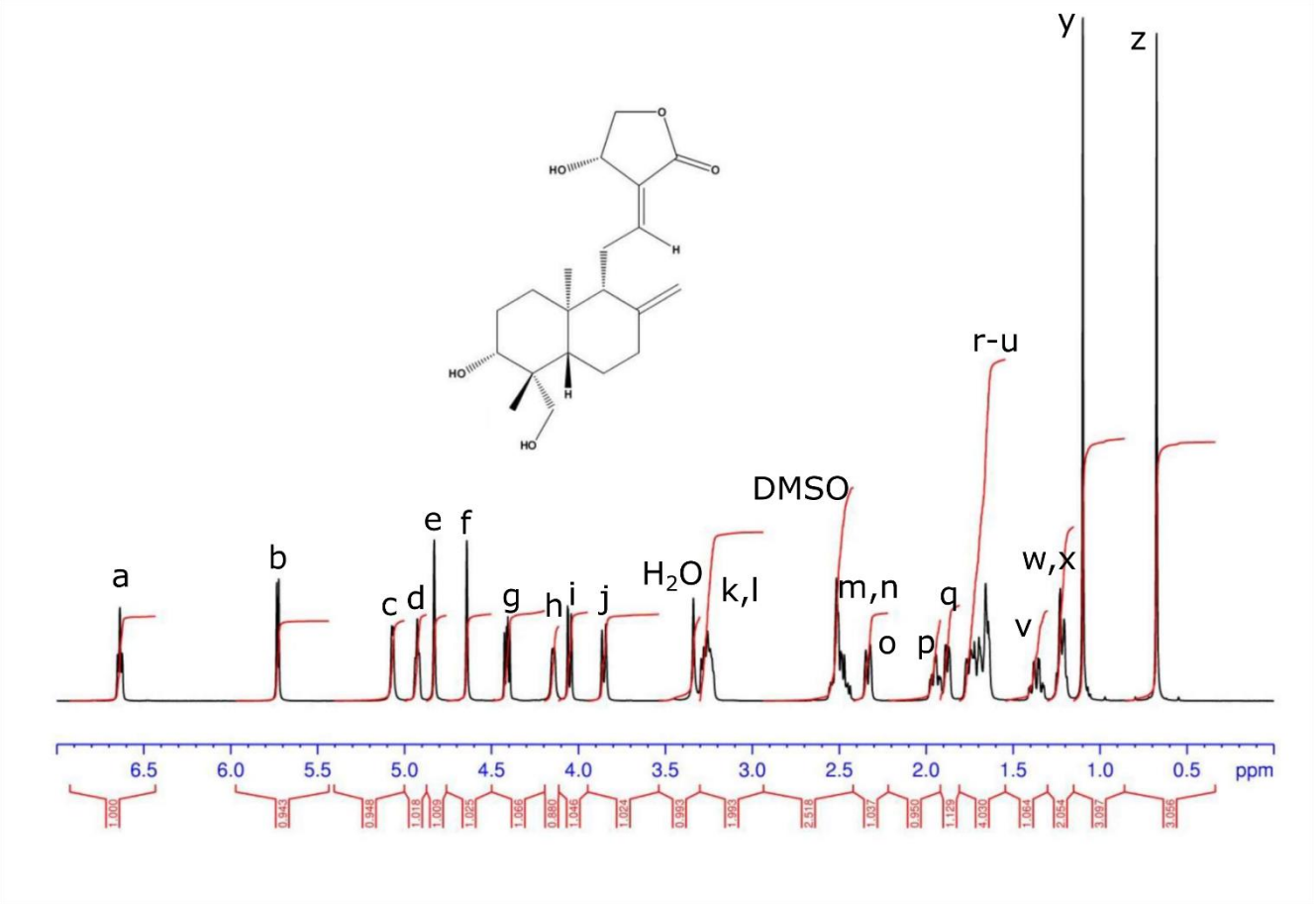
4. Try to identify resolved ^{1}H signals of a diterpenoid-lactone based on 1D NMR spectrum and NOESY correlations.

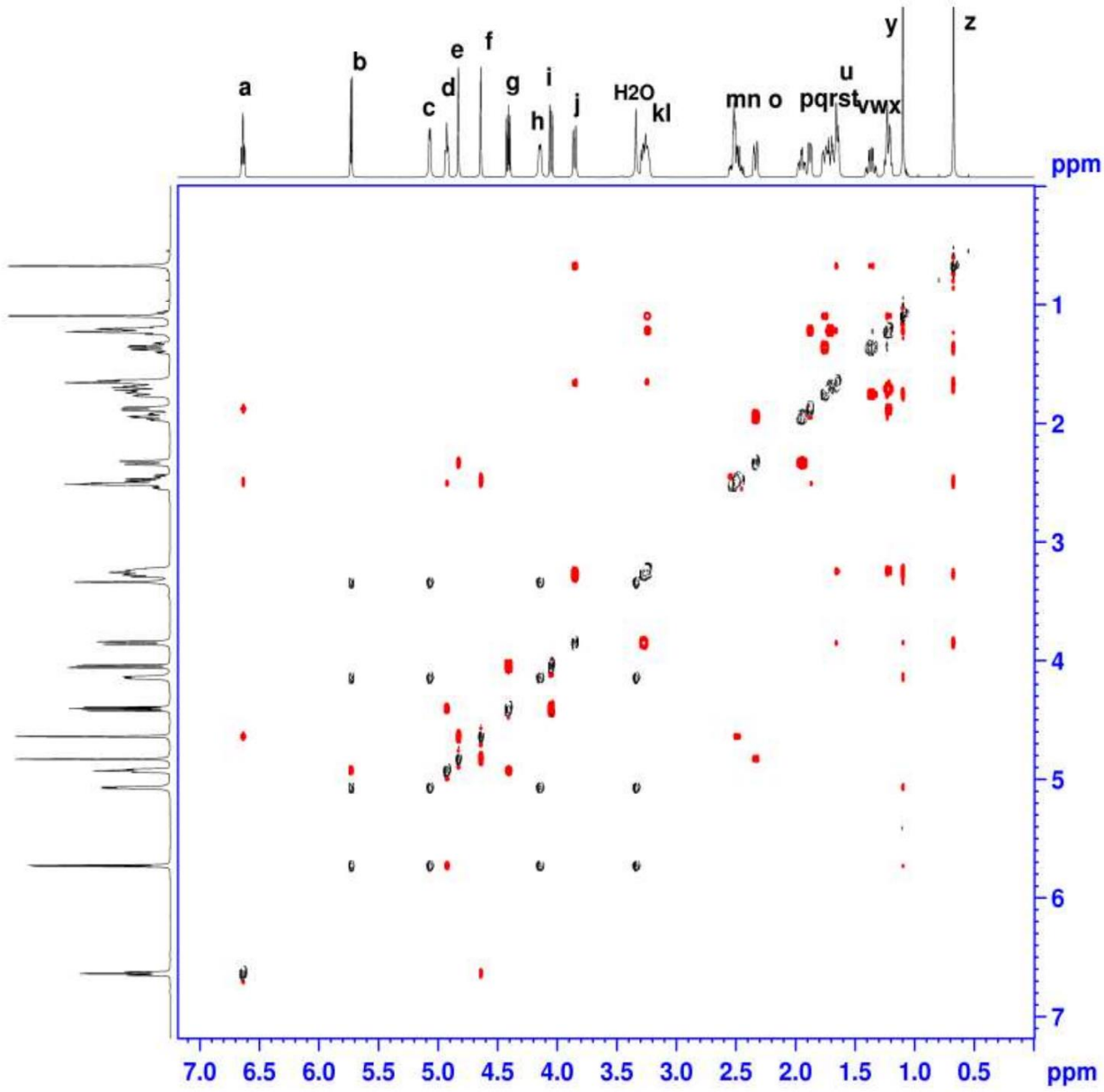
a) Redraw structure into perspective formula and check number of non-equivalent protons. Denote examples of diasteretopic atoms.

b) Based on molecular weight and sign of off-diagonal NOE crosspeak suggest approx. mixing time of recorded NOE experiment. Which cross-relaxation is usually dominant for such type molecules?

c) Explain opposite sign of off-diagonal crosspeak of exchangeable protons and assign them. *Hint* Deshielding effect of attached carbon atom increases from primary to tertiary carbon.

f) Use edited ^{1}H-^{13}C HSQC to find some geminal protons. Try to interpret resolved NOE crosspeaks.

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Multiplicity edited HSQC