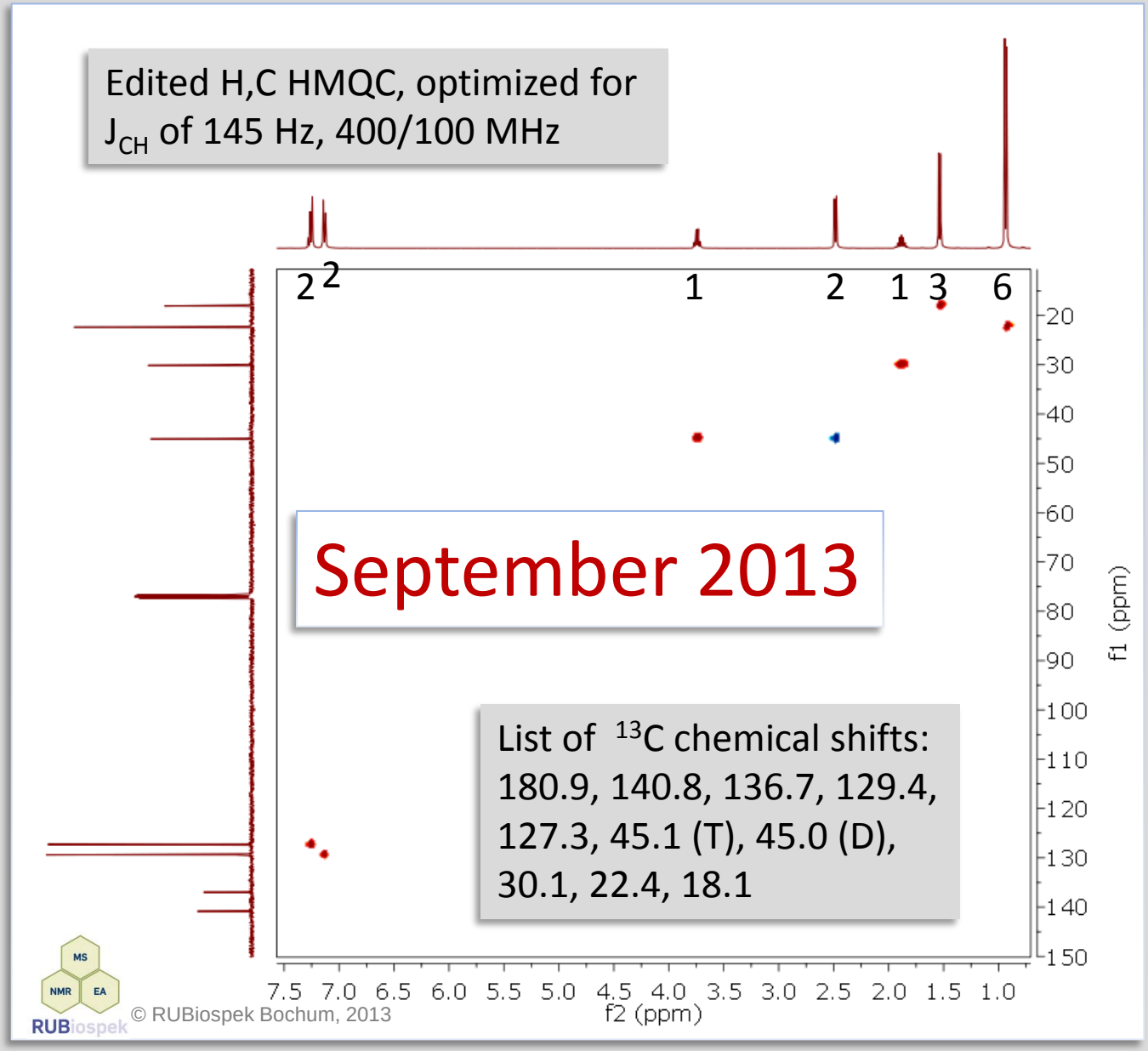
Problem of the Month:



Problem of the Month:
September 2013

Strategy

(1) This month's molecule has the molecular formula **$C_{13}H_{18}O_2$**. H,C connectivities can be assigned from the edited HMQC (cover page). **Note:** In this type of experiment, cross peaks in red represent CH or CH_3 carbons, while blue peaks signify CH_2 groups. Two signals appear at almost identical shifts (multiplicities in brackets). Integrals of the proton signals are given below the 1D projection.

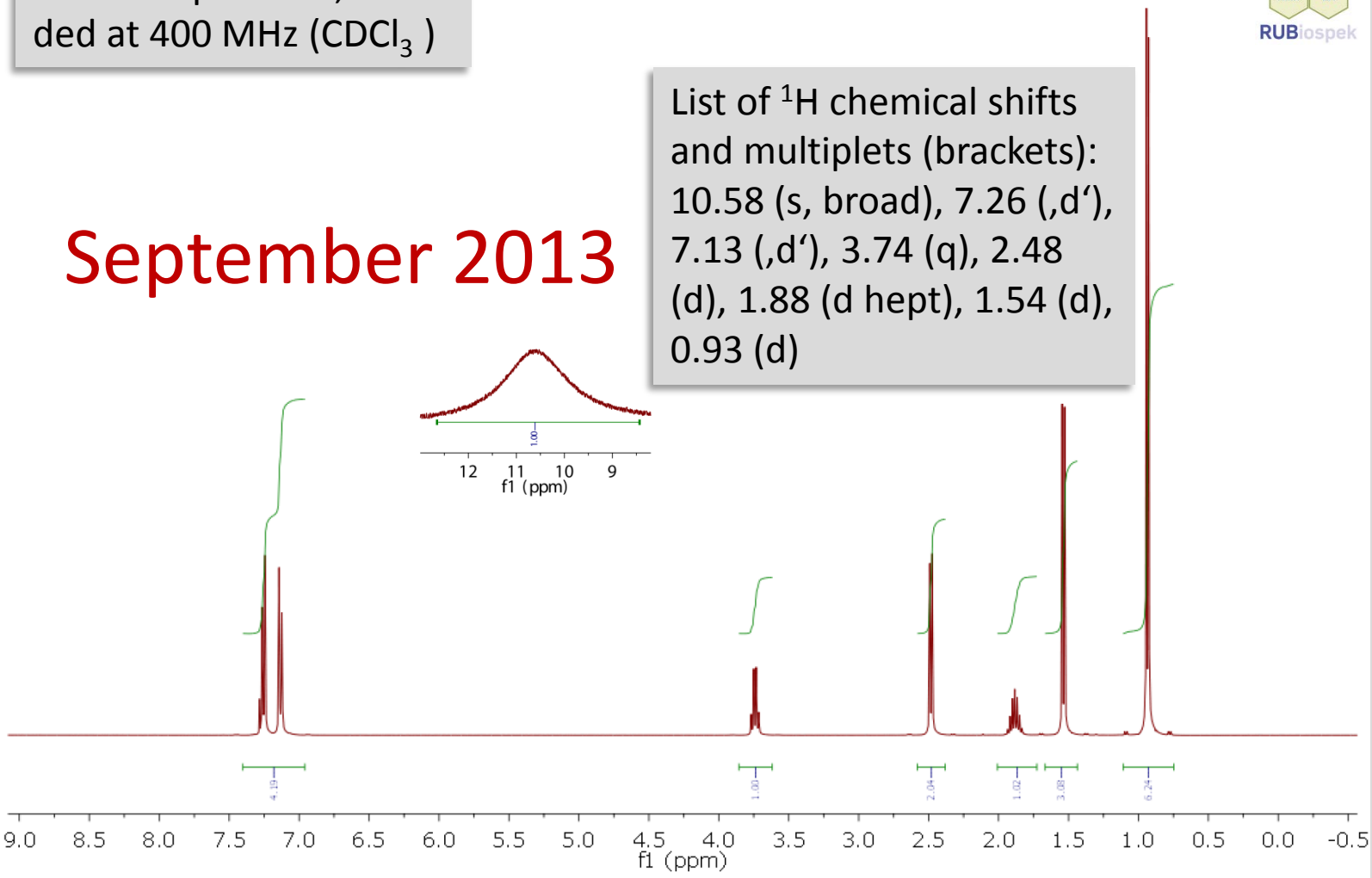
(2) Several ^{13}C signals do not possess cross peaks. By comparison with the ^{1}H NMR spectrum (next page), it can be seen that there is also one proton signal without cross peak. In addition, there must be some symmetry in the target structure (number of signals vs. molecular formula). Although from a standard $^{13}C\{^{1}H\}$ NMR spectrum no quantitative conclusions can be drawn, relative signal intensities (see 1D projection) should give you a clue.

Problem of the Month:

^{1}H NMR spectrum, recorded at 400 MHz ($CDCl_3$)

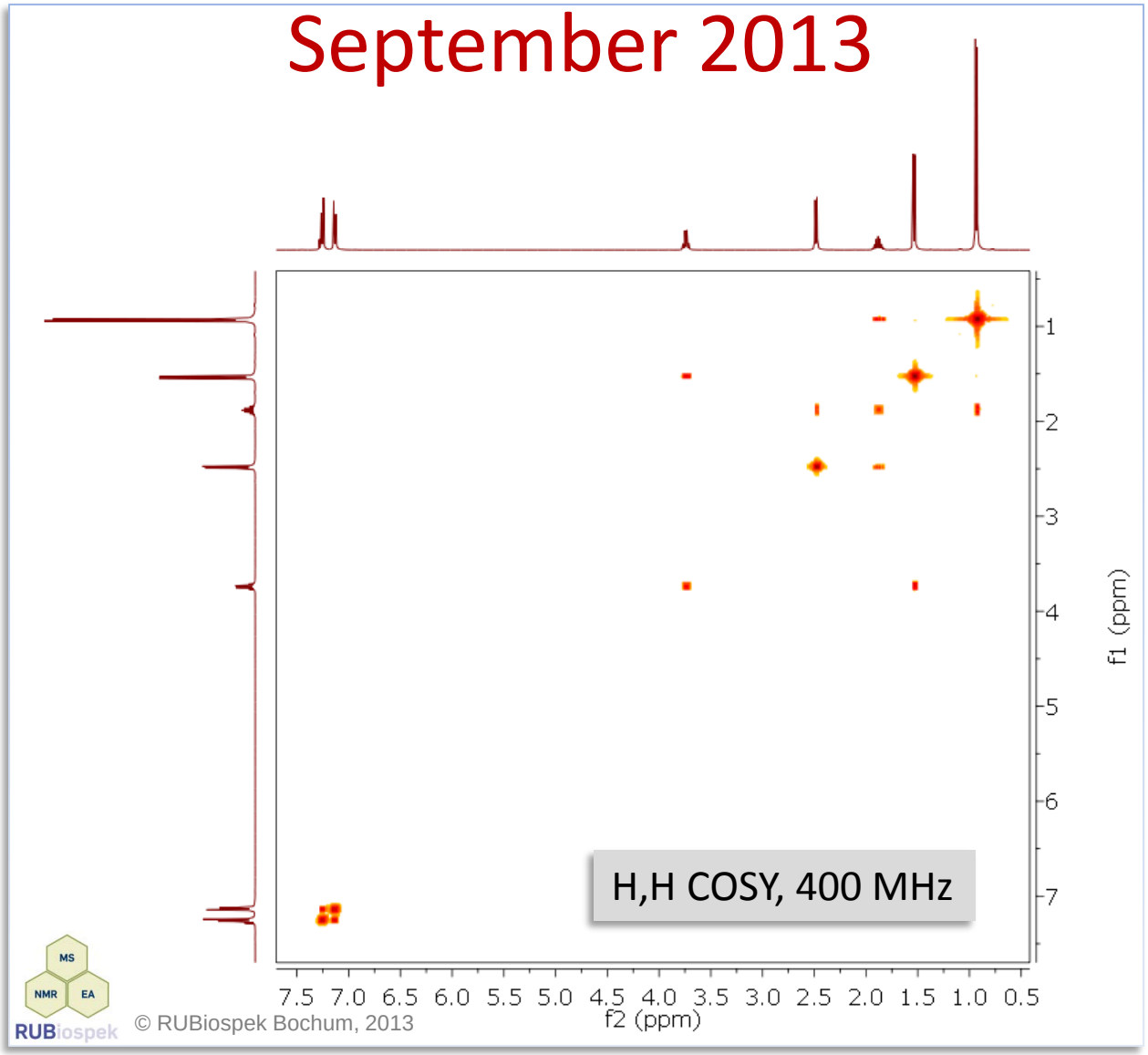
List of ^{1}H chemical shifts and multiplets (brackets): 10.58 (s, broad), 7.26 (‚d'), 7.13 (‚d'), 3.74 (q), 2.48 (d), 1.88 (d hept), 1.54 (d), 0.93 (d)

September 2013



Problem of the Month:

September 2013



Problem of the Month:
September 2013

Hints

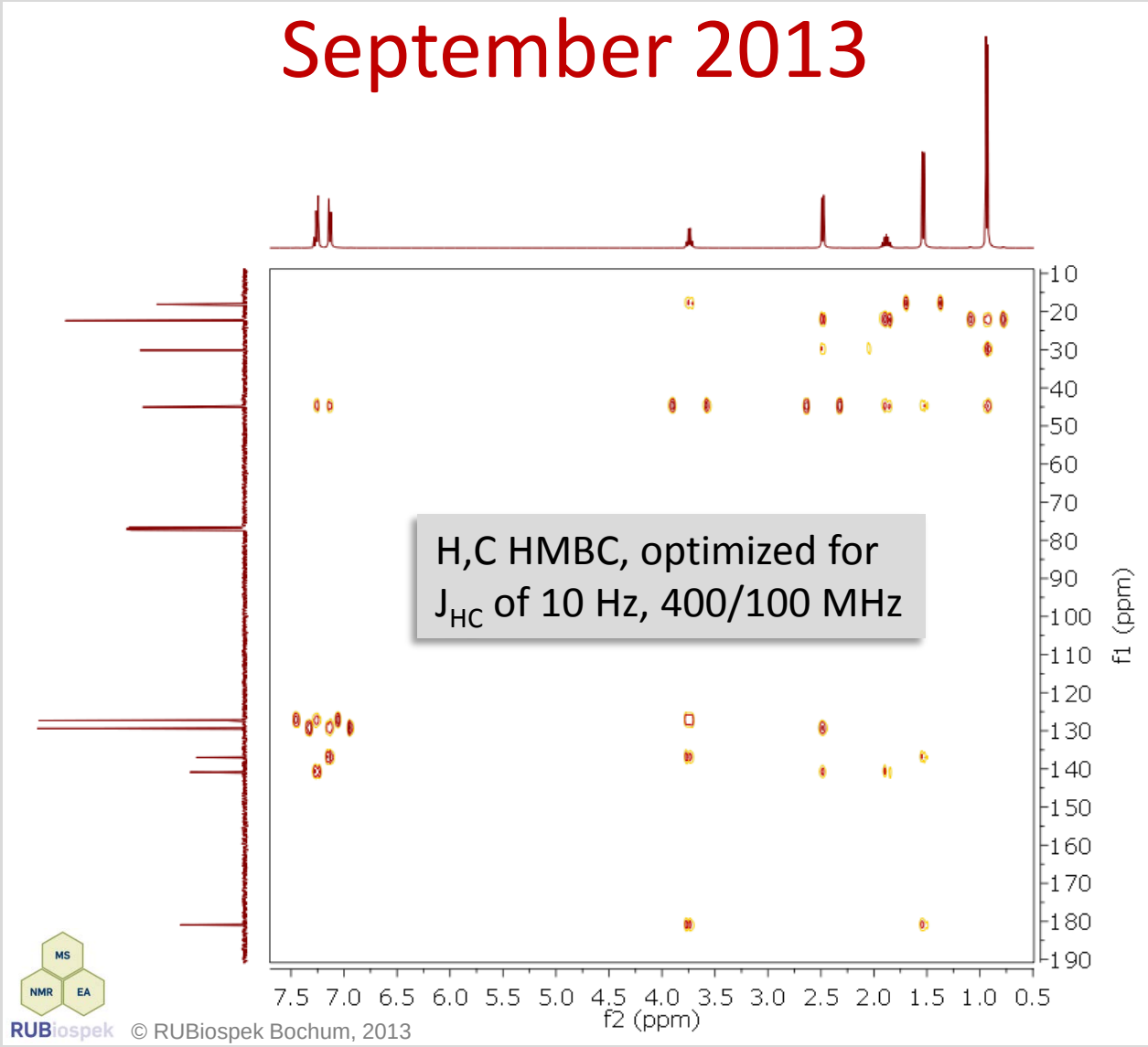
(1) In total, three coupled spin system can be derived from ^{1}H and H,H COSY NMR spectra, amongst them a higher order aromatic pattern. Also, from the number of DBE, an aromatic compound should be considered.

(2) Do a „search by spectrum“ in nmrshiftdb2 for one of the fragments (select option „subspectrum“): First, enter the carbons at δ_C 45.1, 30.1 and 22.4 with their corresponding multiplicity (e.g. „45.1T“ for a carbon with a chemical shift of δ_C 45.1 with two protons attached). Since there are two carbons at δ_C 22.4, you have to enter this value twice! Observe the type of functional group, that results from your search.

(3) If additional information is needed, the fragments that you identified by now can be connected with the HMBC (available on the next page)

Problem of the Month:

September 2013



MS NMR EA

RUBiospek

Problem of the Month:
September 2013

Solution

(1) An AA'XX' system, made up from protons attached to sp^2 hybridized (aromatic) carbons, can be identified. Also, two aliphatic residues (A_2MX_6 and AX_3) are distinguished. The total number of DBE's is 5.

(2) Subspectrum search for the ^{13}C signals indicates an isobutyl group, the signal at δ_C 180.9 in combination with the broad proton signal at δ_H 10.58 a carboxylic acid. Assignment of quaternary aromatic carbons and substitution pattern can be deduced of the HMBC spectrum.

(3) Hint: Enter the chemical shifts of the ^{13}C signals in nmrsshiftdb2 as a „spectrum search" (option „complete", multiply existing carbons that deliver only one signal due to symmetry need to be entered the corresponding number of times). Or click for the solution here.