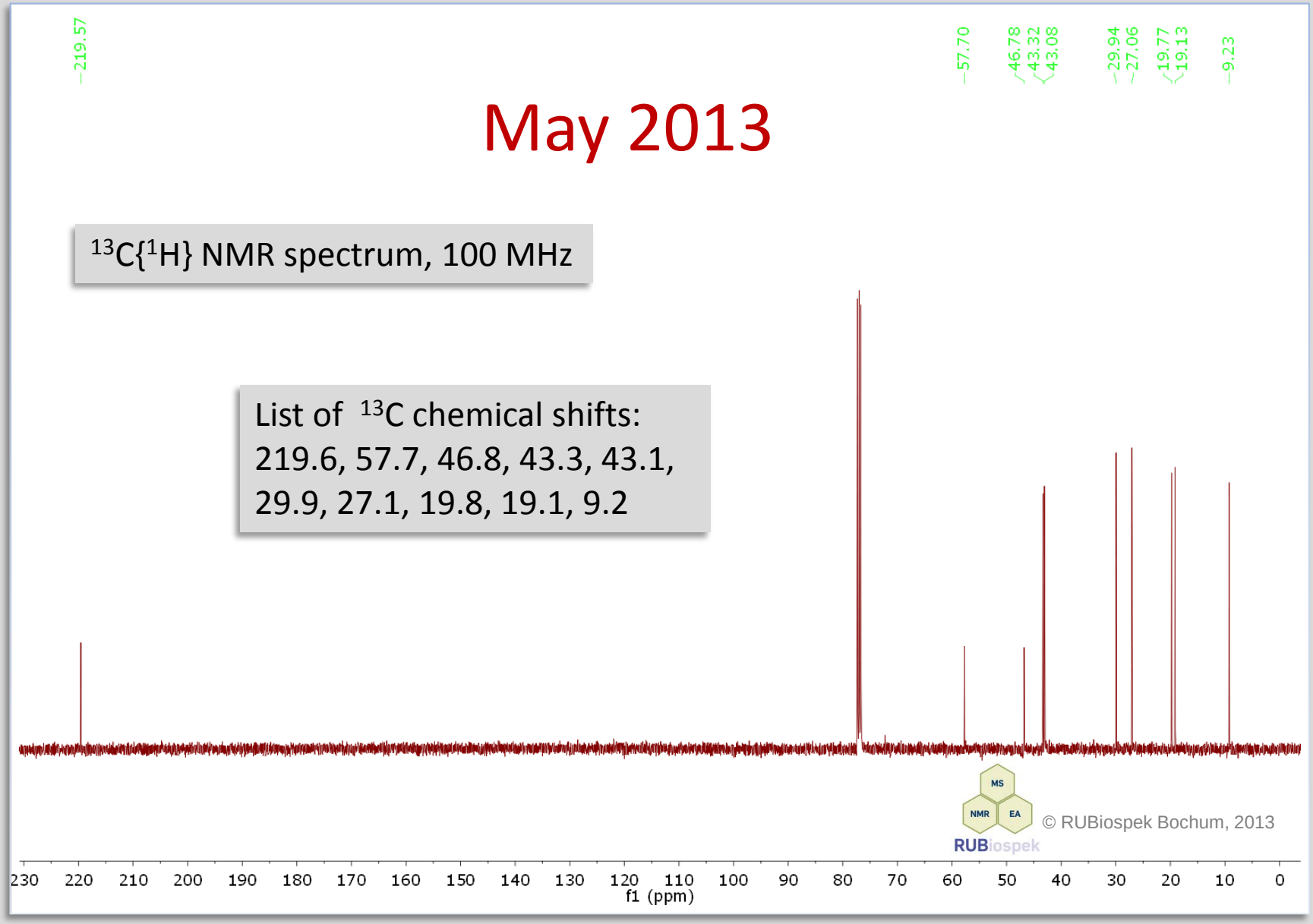
Problem of the Month:

May 2013

$^{13}C\{^{1}H\}$ NMR spectrum, 100 MHz

List of ^{13}C chemical shifts:
219.6, 57.7, 46.8, 43.3, 43.1,
29.9, 27.1, 19.8, 19.1, 9.2



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Strategy

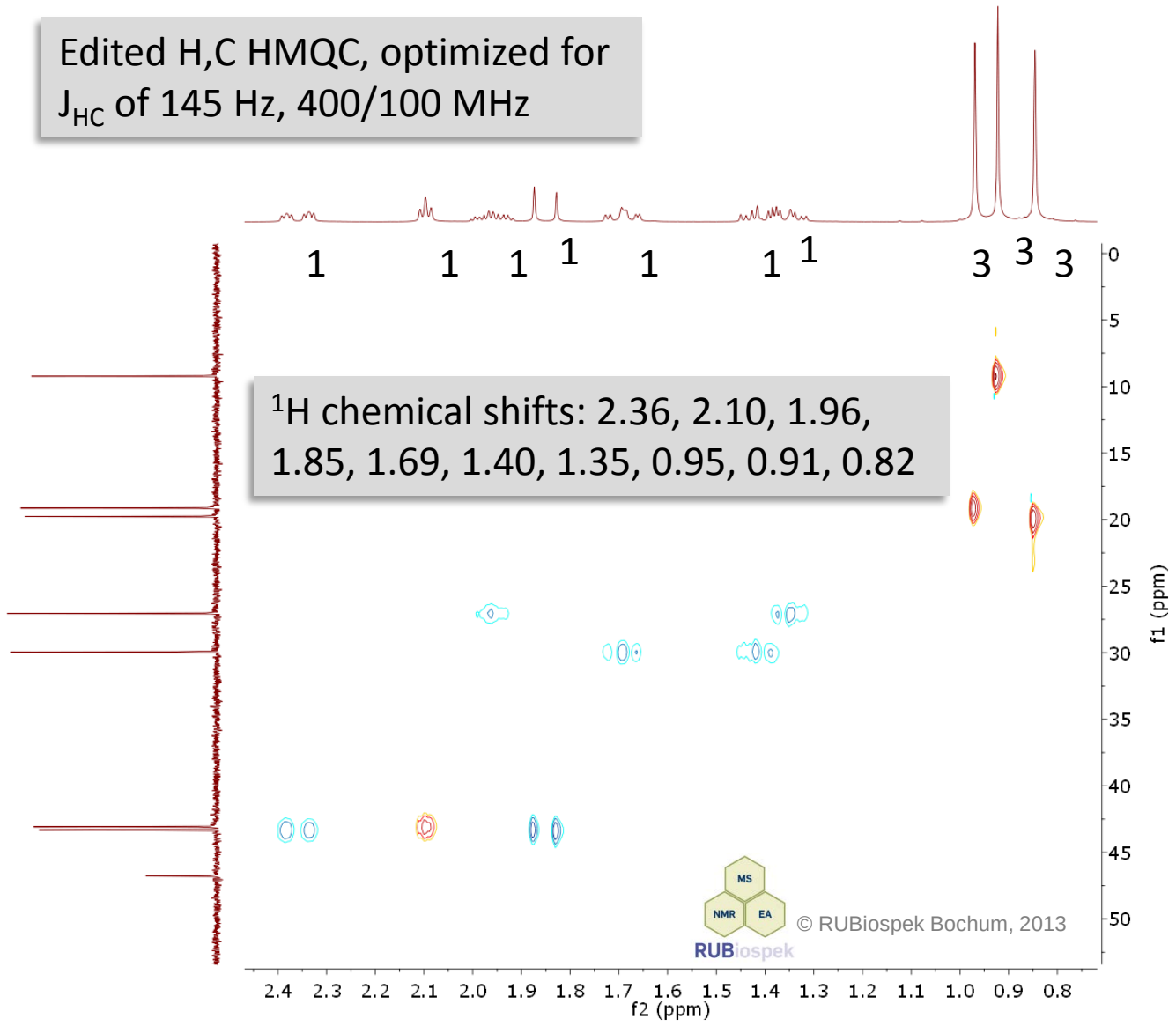
(1) The molecular formula of this month's molecule is $C_{10}H_{16}O$: As a first step, it is always important to determine the number of DBE.

(2) By inspection of the $^{13}C\{^{1}H\}$ NMR spectrum on the first page, the shift at highest frequency clearly indicates one class of compound. If you are not sure, do a „search by spectrum" in nmrshiftdb2 (select option „subspectrum"): Enter the carbon chemical shift (219.6). From the chemical shifts present, an aromatic or olefinic molecule can be excluded. For easier discussion, ^{13}C signals are labelled from left to right (C1-C10).

(3) Assign H,C connectivities from the HMQC (next page). Since this is an edited experiment, cross peaks in red represent CH or CH_3 carbons, while blue peaks signify CH_2 groups. An HMQC also allows to define diastereotopic protons. Integrals of the proton signals are given below the projection.

Problem of the Month:

Edited H,C HMQC, optimized for J_{HC} of 145 Hz, 400/100 MHz



Problem of the Month:
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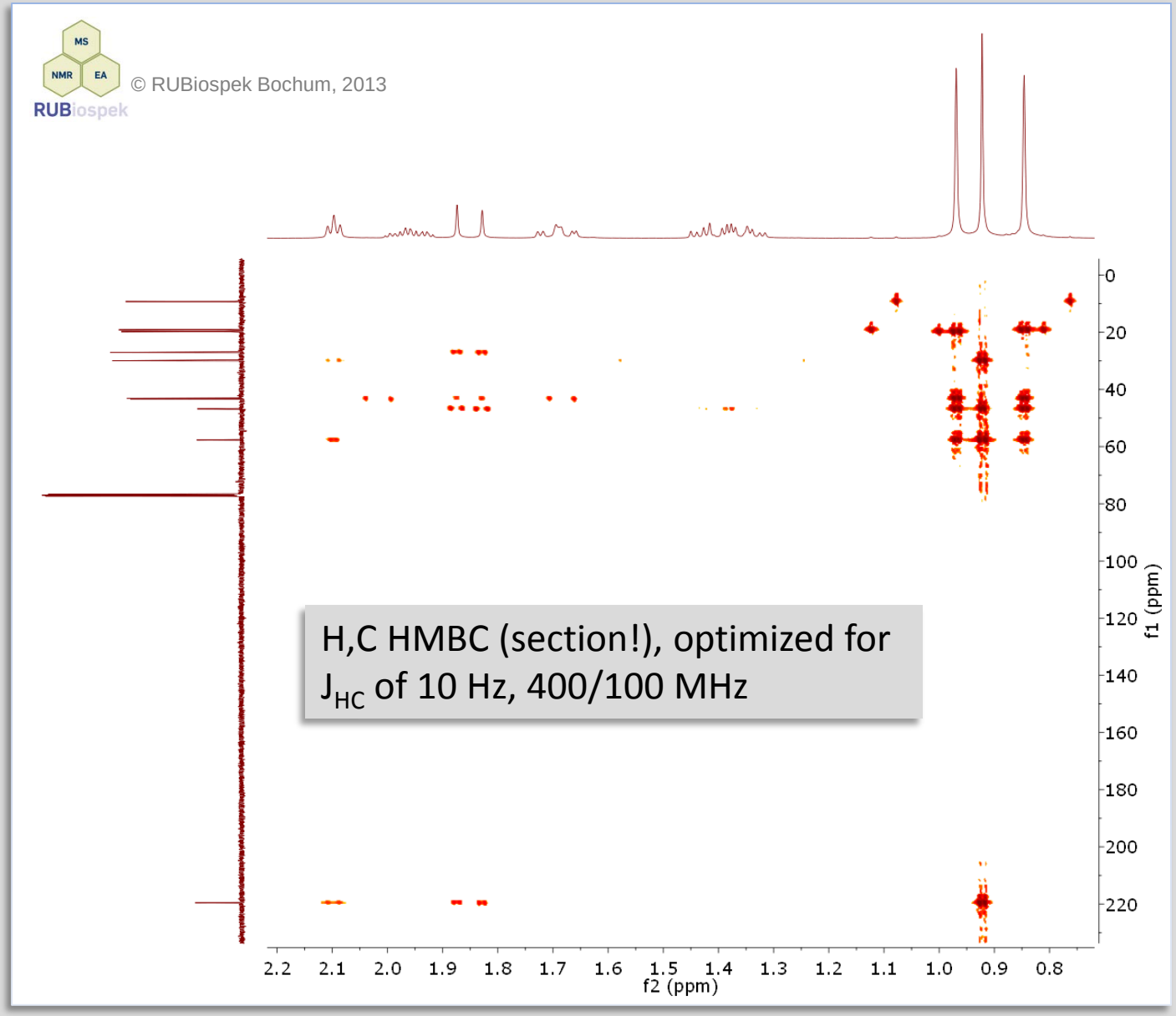
Hints

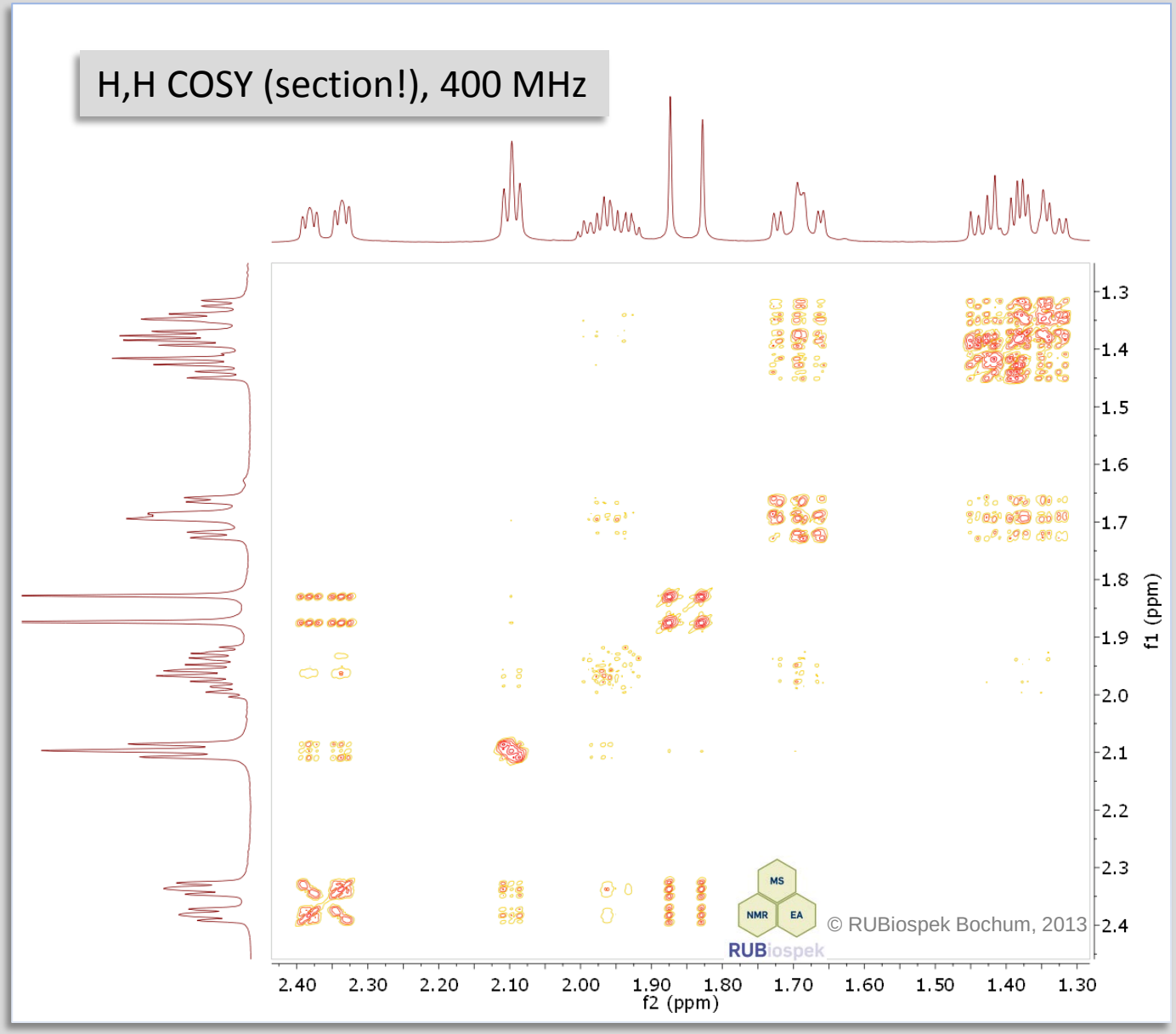
(1) An interesting candidate to look after is the ^{1}H signal at δ_H 2.1. Do a „search by spectrum“ in nmrshiftdb2 (select option „subspectrum“), and enter the carbon shift corresponding to this signal (enter „43.1D“ to indicate a shift at δ_C 43.1 with one proton attached). This brings up some types of molecules which, in combination with the number of DBE, should be helpful.

(2) This month‘s problem can best be solved with the assistance of the HMBC (H,C long range correlation) experiment (next page): E.g., all three methyl groups are connected to quarternary carbons (no splitting in ^{1}H). Also, we are dealing with a bicyclic structure (DBE!). After summing up all H-C correlations, dissect the neighbours (e.g. by relating all correlations to the carbon at δ_C 219.6, etc.). To back up the observations, a COSY spectrum is also provided.

Problem of the Month:



Problem of the Month:



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Solution

(1) The target molecule contains, according to DBE (3) and carbon chemical shifts, a double bond (ketone, result of subspectrum search for δ_C 219.6) and two rings. Also, three methyl groups, attached to the two residual quarternary carbons, are present (δ_H 0.95/0.82 to δ_C 46.8 and δ_H 0.91 to δ_C 57.7).

(2) Subspectrum search for the ^{13}C signal at δ_C 43.1 derives the option of a bridge head carbon. Thus, visible H,C l.r. correlations for this atom are mainly for $^3J_{CH}$ connectivities. In combination with the methyl fragments mentioned above, this allows to distinguish fragments C10-C2, C4 and C5 as the next neighbours of C1. For the assignment of C6/C7, the COSY spectrum elucidates a chain of coupled spins H6-H7-H5-H4.

(3) No solution? Enter the chemical shifts of the ^{13}C signals in nmrsshiftdb2 as a „spectrum search“ (option „complete“) or click here.