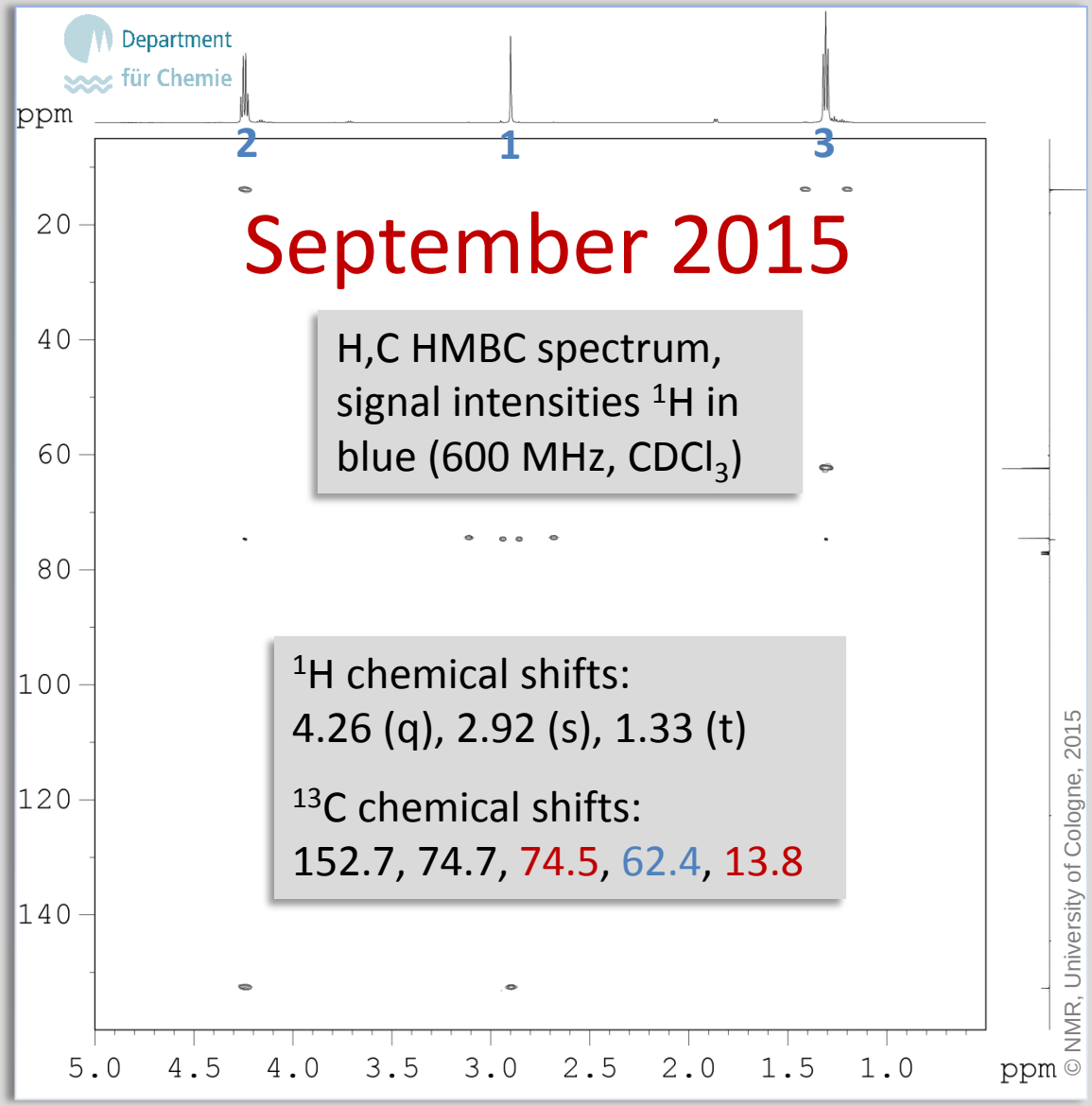
Problem of the Month:



September 2015

H,C HMBC spectrum, signal intensities ^{1}H in blue (600 MHz, $CDCl_3$)

^{1}H chemical shifts:
4.26 (q), 2.92 (s), 1.33 (t)

^{13}C chemical shifts:
152.7, 74.7, 74.5, 62.4, 13.8

Problem of the Month:
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Strategy

(1) The only NMR experiment required to solve this month's problem is the H,C long range correlation (‚HMBC') shown on the previous page. It shows connectivities between proton and carbon ranging from one (in some cases) up to five bonds .

(2) Besides the correlation information, the inspection of the 1D ^{1}H NMR spectrum (projection on top, intensities given in blue numbers) presents a simple spin system.

(3) The molecular formula is $C_5H_6O_2$, which allows to determine the number of DBE (i.e. degree of saturation) for the structure.

(4) To facilitate assignment, ^{13}C chemical shifts are labelled in red (CH or CH_3), blue (CH_2) and black (quaternary C).

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Hints

(1) Do a subspectrum search for the three chemical shifts that appear at the highest frequencies (152.7, 74.7, 74.5) and check which are the most common fragments. Include the multiplicity (S, D, …) in your search.

(2) The H,C long range correlation experiment needs to be assigned with special care - the expansion shown on the next page allows a clearer insight in the most overcrowded shift range in ^{13}C. Note: The size of the ^{1}J couplings is explicitely printed on the spectrum. It helps to use the empirical rule valid for the degree of hybridization of C-H orbitals and the size of $^{1}J_{CH}$.

Problem of the Month:

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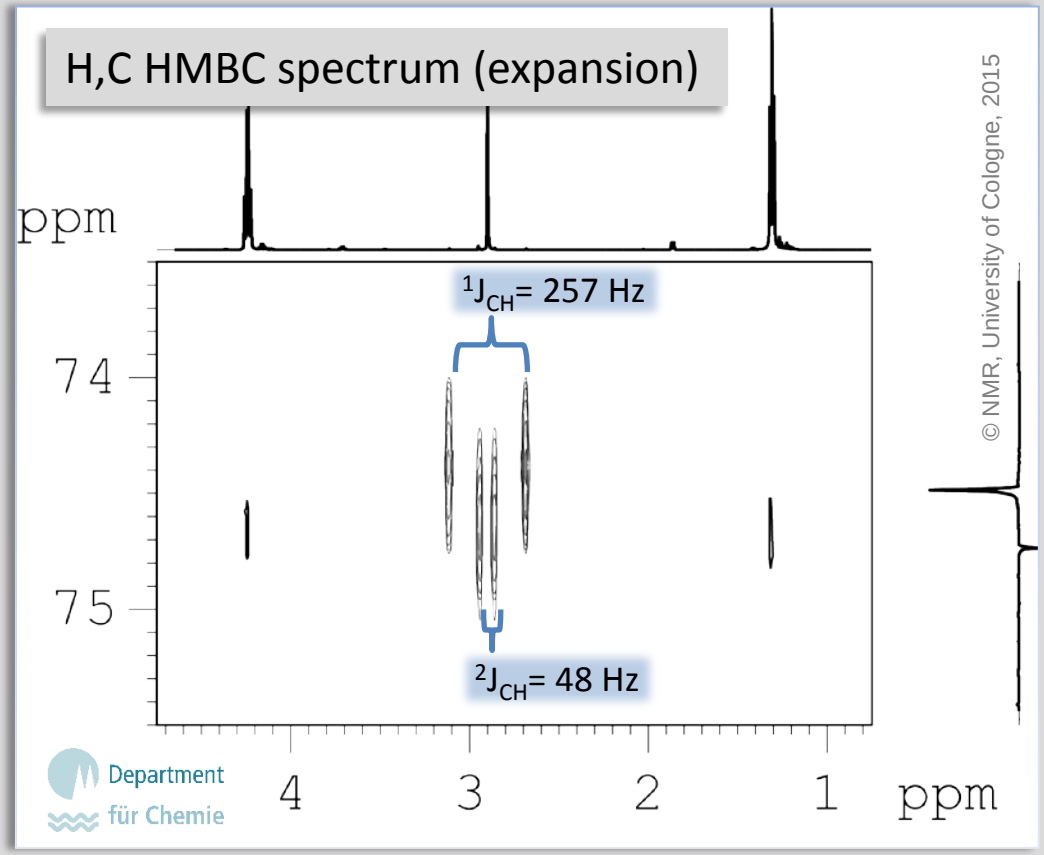

Problem of the Month:
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Solution

(1) The target molecule contains, according to DBE (3) and carbon chemical shifts, a carbonyl double bond as well as an alkyne triple bond (result of subspectrum search).

(2) ^{1}H NMR allows the observation of an A_2X_3 spin system (ethyl group) which is bound to an oxygen atom (δ_H 4.26, 1.33). The remaining signal (δ_H 2.92) stems from the alkyne; extraordinarily large J_{CH} can be detected from the HMBC (^{2}J ~ 50 Hz, ^{1}J ~ 250 Hz are typical for sp hybridized carbons).

(2) Try to compare the predicted ^{13}C chemical shifts, when entering your structure in the editor using the prediction menu of nmrshiftdb2. This month‘s molecule is **not** yet in our database, however, agreement of experimental and predicted shifts is very good. No solution? Enter the chemical shifts of the ^{13}C signals in nmrshiftdb2 as a „spectrum search“ (option „complete“) after October 15th.