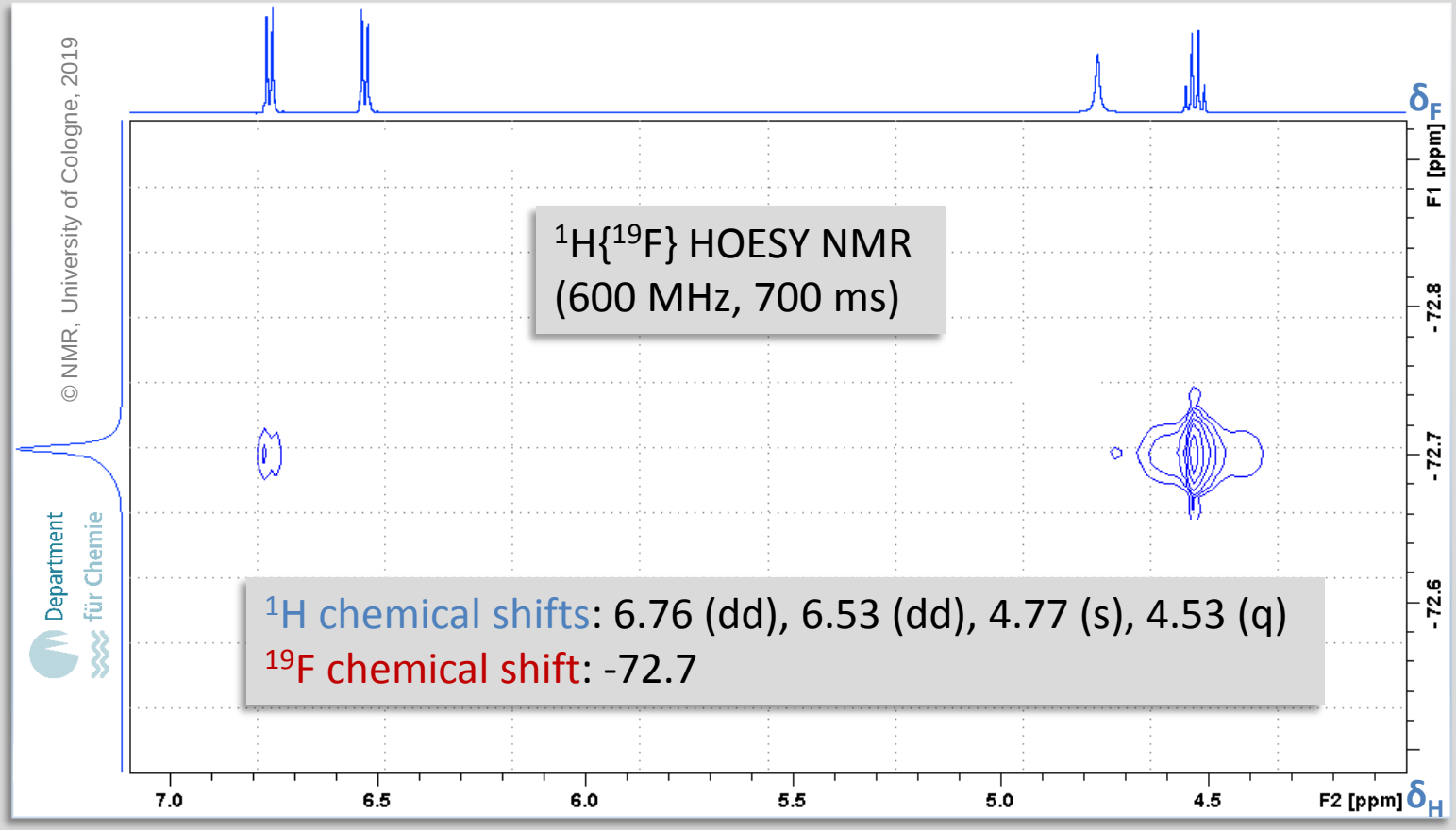
Problem of the Month:

December 2019



Problem of the Month:
December 2019

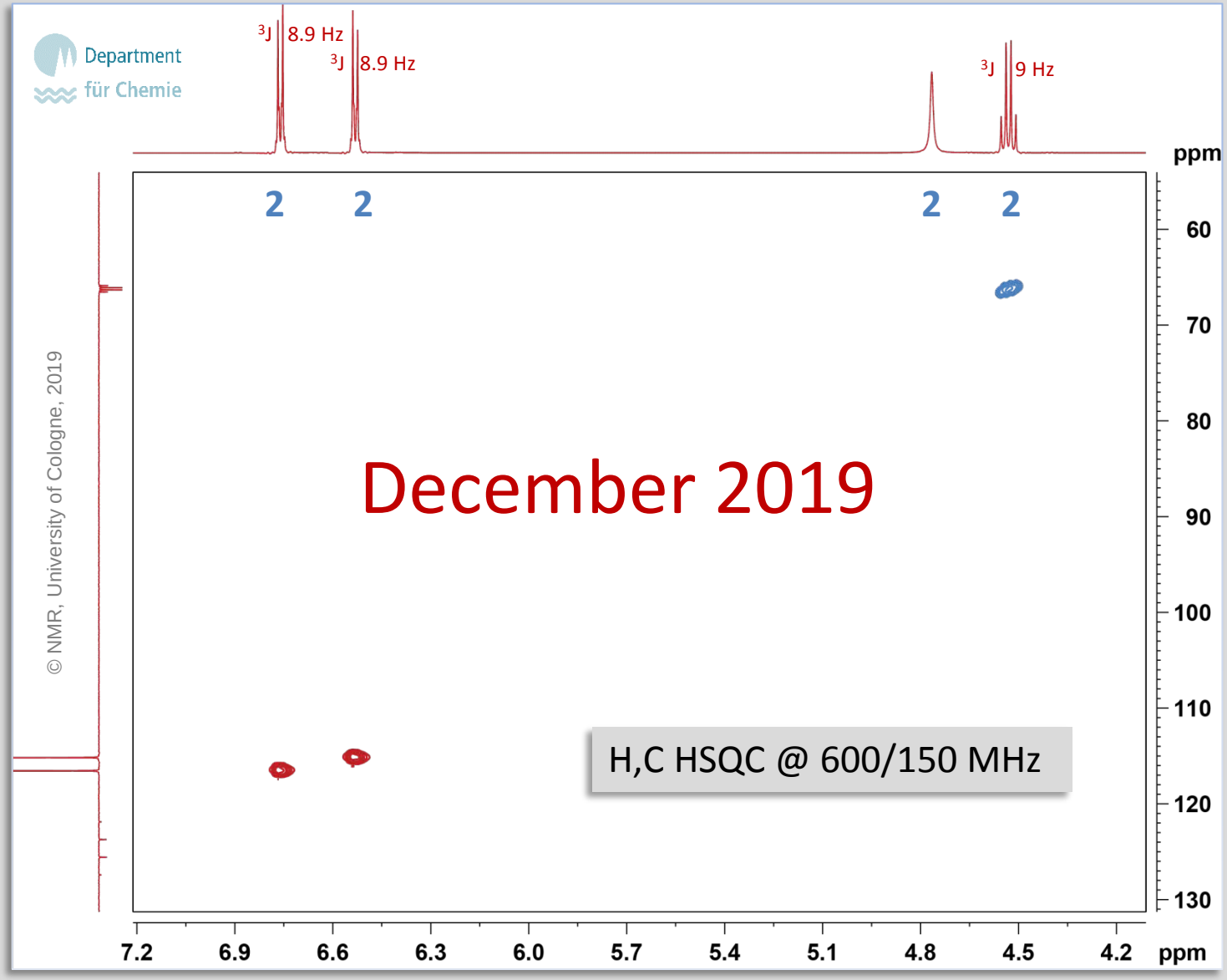
Strategy

(1) HOESY (**H**eteronuclear **O**verhauser **E**ffect **S**pectroscop**Y**) experiments allow detection of spatial proximity between NMR-active nuclei of different isotopes. The title spectrum shows interactions between ^{1}H and ^{19}F atoms that are no further apart than ca. 5 Å.

(2) On the next page, an ‚edited' HSQC is given. I.e. CH and CH_3 groups show positive cross peaks, CH_2 groups produce negative cross peaks. Quaternary carbons, as well as exchangeable protons, generate no cross peaks. ^{1}H integrals are indicated by blue numbers underneath the projection.

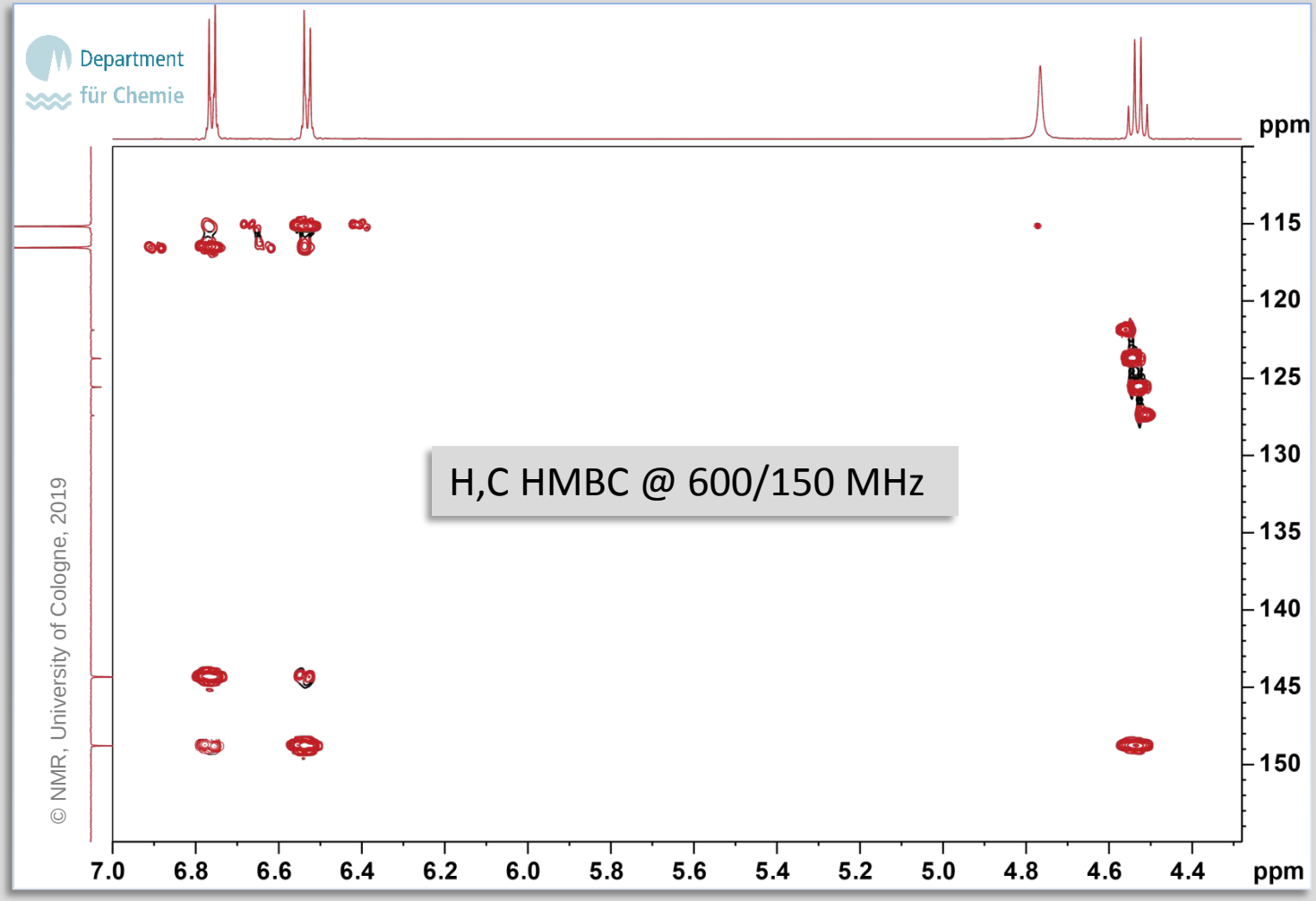
(3) Also, you might calculate the degree of unsaturation (DBE) from the molecular formula: $C_8H_8F_3NO$.

Problem of the Month:



Problem of the Month:

December 2019



Problem of the Month:
December 2019

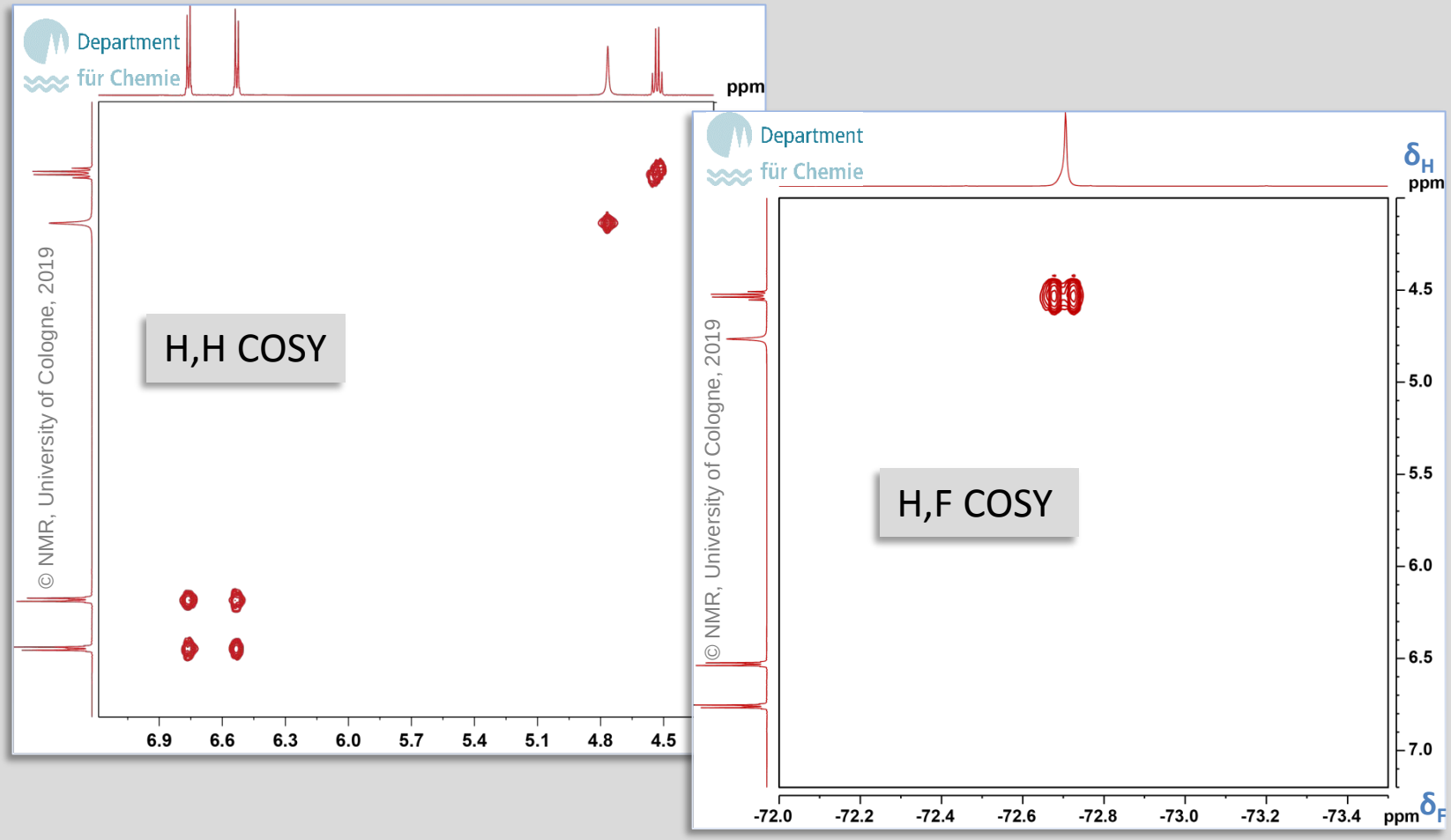
Hints

(1) Connectivity between fragments is derived from the H,C HMBC experiment (rule of thumb: for sp^2 carbons, $^3J_{CH}$ cross peaks are more intense than $^2J_{CH}$ cross peaks).

(2) There are two types of spin systems in this molecule, each coupling over three bonds - they can be identified from carefully analysing the 1D ^1H spectrum on depicted on top of the HSQC experiment, and from H,H COSY and H,F COSY spectra (see next page).

Problem of the Month:

December 2019



Problem of the Month:
December 2019

Solution

(1) The molecule of December contains a homonuclear, aromatic AA‘XX‘ spin system and a heteronuclear, aliphatic A_2X_3. The exchangeable amine proton has a long range coupling on the corresponding, quaternary carbon. Assignment of the aromatic part is possible through HMBC correlations, note the F,C splitting of the CF_3 group.

(2) On nmr.cheminfo.org, there is a tool to simulate ^{1}H NMR spin systems: In the forth row, compare with ‚simulate spin system‘an AB (A_2X_2 case) vs. an ABCD system (AA‘XX‘ case) for the aromatic part [so far, heteronuclei and exchangeable hydrogens cannot be considered].

(3) If you are still in doubt - the correct structure will be uploaded in nmrshiftdb as a new entry in January 2020.