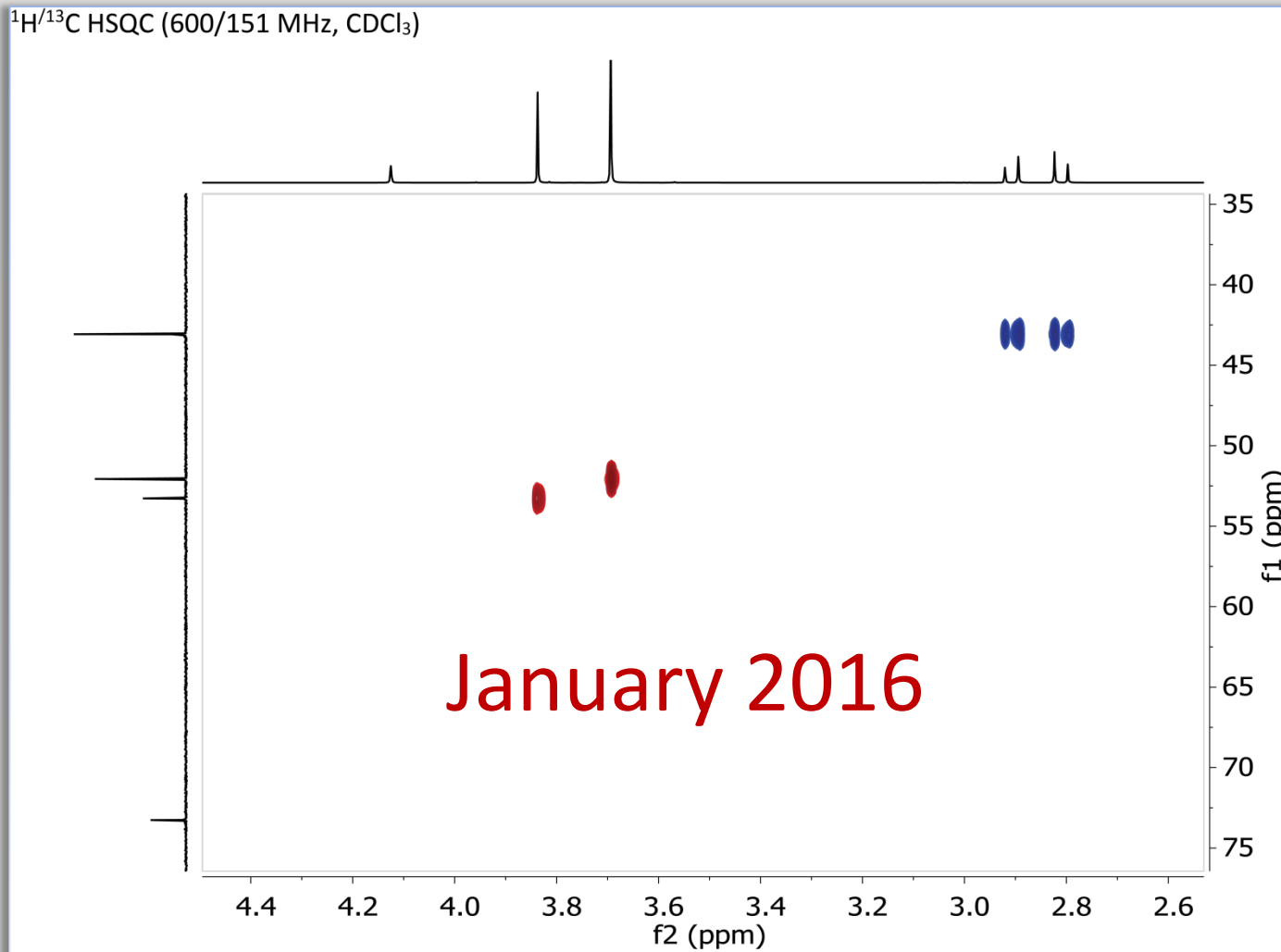


# Problem of the Month:



# Problem of the Month:

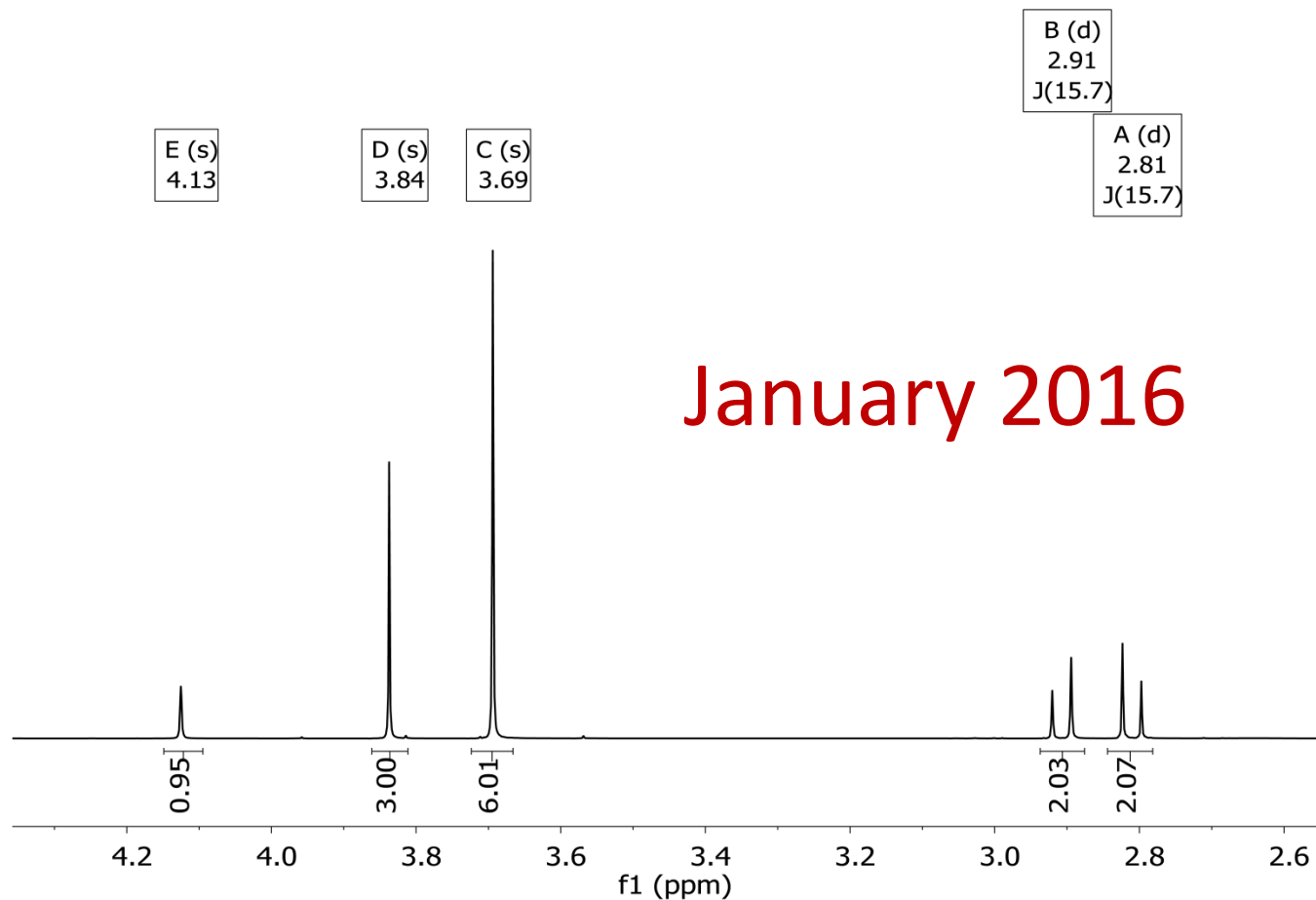
## January 2016

### Strategy

- (1) Given the molecular formula  $C_9H_{14}O_7$ , you can determine the number of double bond equivalents.
- (2) Determine the  $CH_x$  fragments in the molecule from the edited HSQC spectrum. CH and  $CH_3$  groups give positive crosspeaks (red),  $CH_2$  groups give negative crosspeaks (blue). Quaternary carbons, as well as OH protons, will not yield any crosspeaks.
- (3) Besides the correlation information, the inspection of the 1D  $^1H$  NMR spectrum (projection on top, intensities and chemical shifts given in spectrum on the next page) provides only few couplings. Investigate the  $^1H$  chemical shifts at 3.84 & 3.69 through a subspectrum search to get an idea of the type of possible functionalities.

# Problem of the Month:

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



# Problem of the Month:

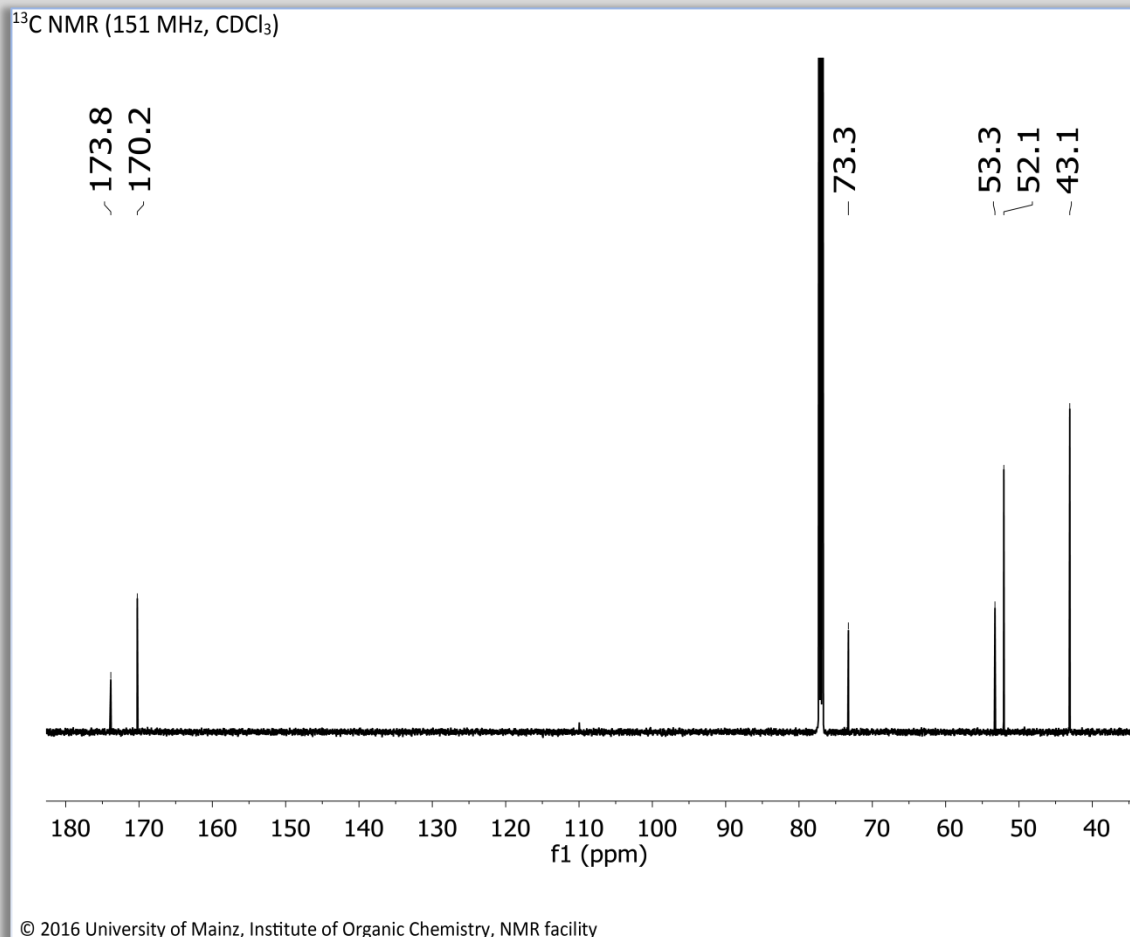
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### Hints

- (1) Do a subspectrum search for the three chemical shifts that appear at the highest frequencies (173.8, 170.2) in the  $^{13}\text{C}$  NMR spectrum displayed on the following page. Check which are the most common fragments. Include the multiplicity (S) in your search. Repeat and then combine the search for the signals at 53.3, 52.1 (Q).
- (2) Determine the connectivity of the fragments using the HMBC experiment (on page after next page). It shows coupling between  $^1\text{H}$  and  $^{13}\text{C}$  over more than one bond.
- (3) You need to analyze the stereochemistry carefully to see why there is coupling between the protons 2.91 and 2.81.

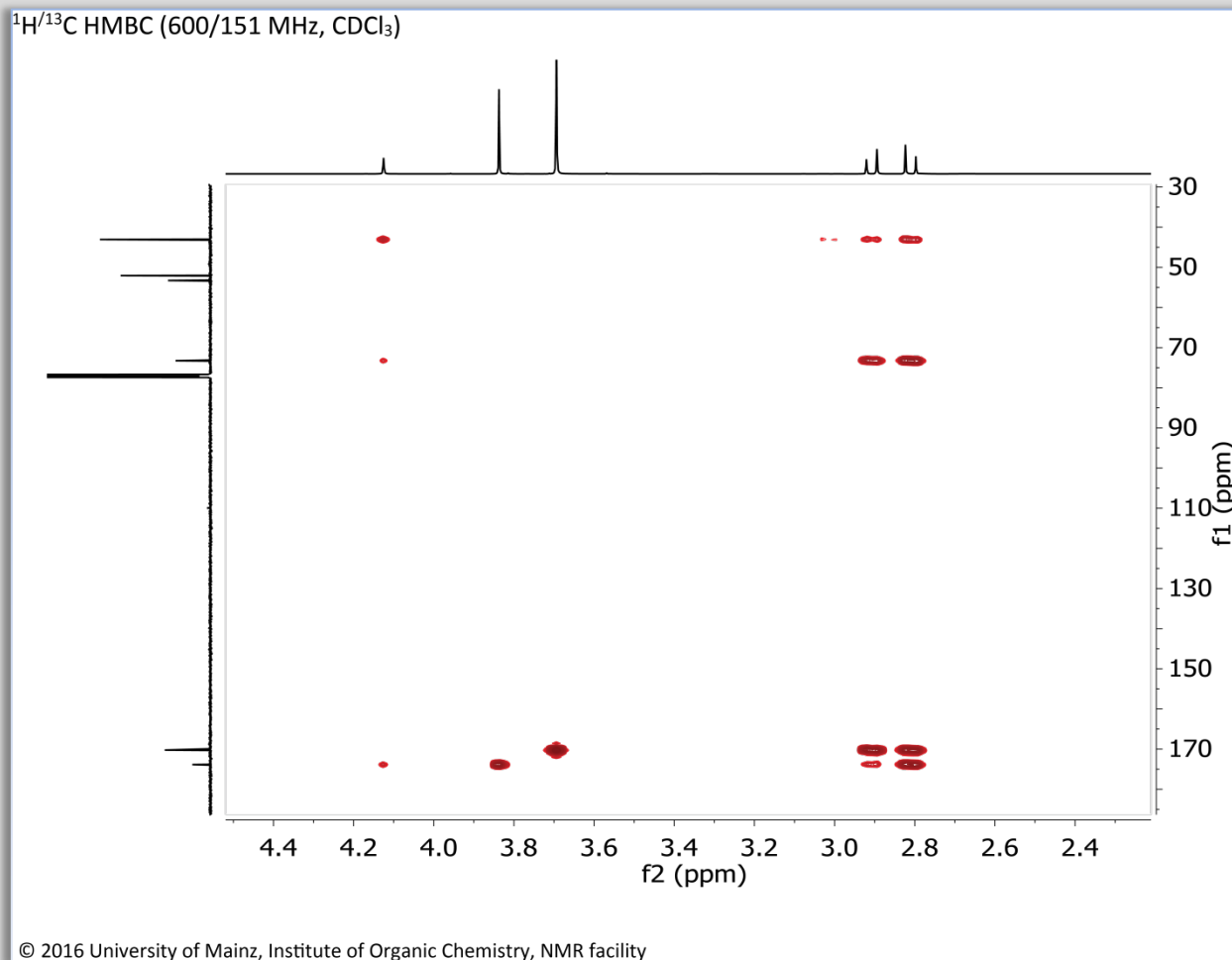
# Problem of the Month:

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# Problem of the Month:

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# Problem of the Month:

## January 2016

### Solution

- (1) The target molecule contains, according to DBE (3) and carbon chemical shifts, three carbonyl double bonds, each of an ester moiety. There must be symmetry in the molecule, as is also reflected in the number of  $^{13}\text{C}$  signals and the relative intensities of e.g. signals C1 vs. C2, and C4 vs. C5, resp.
- (2) In the  $^1\text{H}$  NMR spectrum, symmetry is also detectable: The signals C ( $\delta_{\text{H}}$  3.69) and A/B ( $\delta_{\text{H}}$  2.81/2.91) correspond to double sets of  $\text{CH}_3$  and  $\text{CH}_2$  groups. Only one multiplet (an AB system for signals A/B) with a geminal coupling ( $^2J_{\text{HH}} = 15.7$  Hz) is present, since methylene protons are diastereotopic. Also, there is one OH group, signal E (identified with the aid of HSQC).
- (3) Try to summarize the fragments, before entering your structure in the editor using the prediction menu of nmrshiftdb2. No solution? Enter the chemical shifts of the  $^{13}\text{C}$  signals in nmrshiftdb2 as a „spectrum search“ (option „complete“).