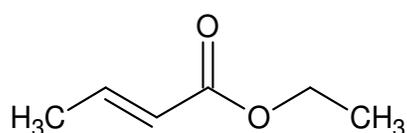


## Ethyl crotonate

### Example of benchtop NMR on small organic molecules

Ethyl crotonate (C<sub>6</sub>H<sub>10</sub>O<sub>2</sub>) is a colourless liquid at room temperature. It is soluble in water, and is used as a solvent for cellulose esters as well as a plasticizer for acrylic resins. It is known for its pungent odour.



The <sup>1</sup>H NMR spectrum of 25% ethyl crotonate in CDCl<sub>3</sub> is shown in Figure 1. The spectrum was recorded in a single scan, taking 7 seconds to acquire. All peaks and <sup>1</sup>H-<sup>1</sup>H couplings are well resolved, and can be assigned to the molecular structure.

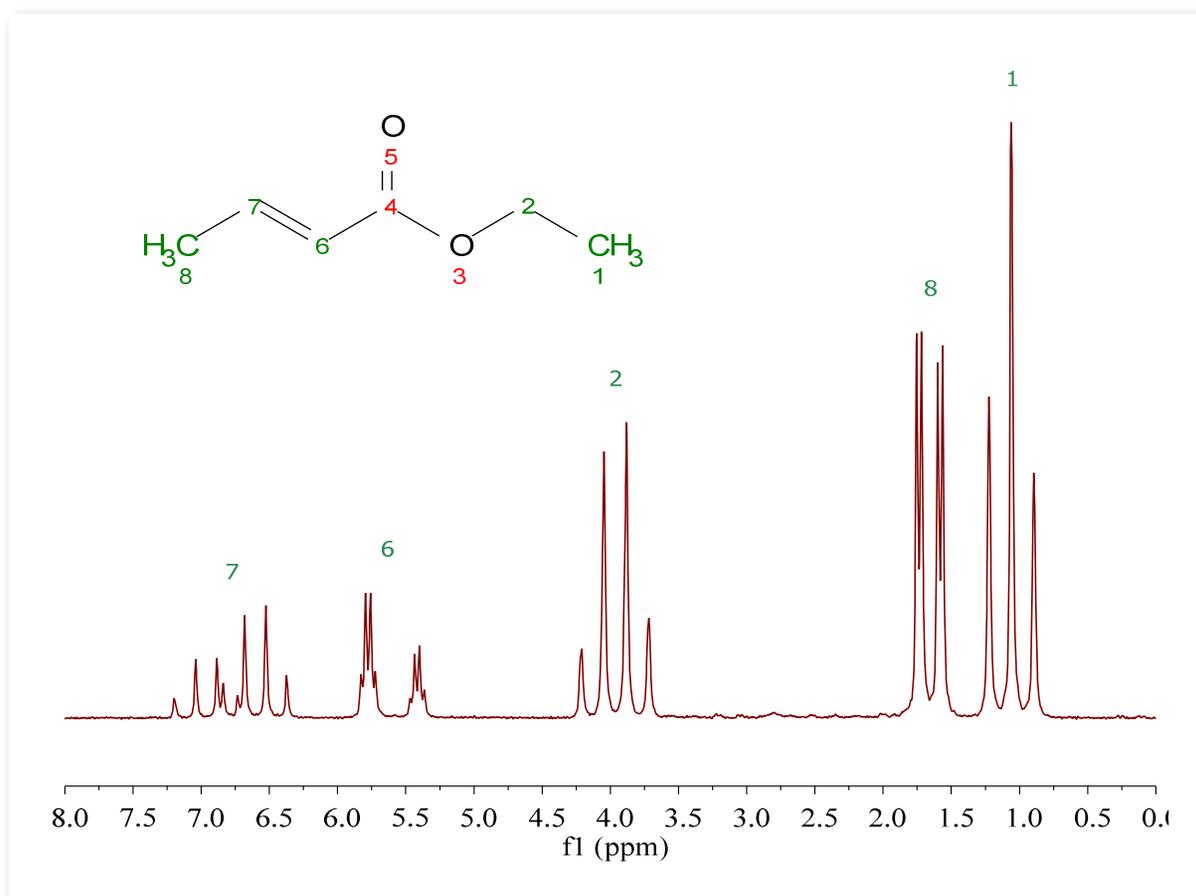
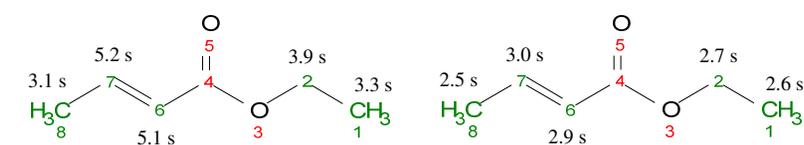


Figure 1: Proton NMR spectrum of 25% ethyl crotonate in CDCl<sub>3</sub>.

# <sup>1</sup>H NMR RELAXATION

The relaxation time measurements are shown in Figures 2 - 4. Note that the relaxation times are longest for the CH protons and shortest for the CH<sub>3</sub> protons. The amplitude of the first data point scales with the number of protons for the corresponding peak.



Proton T<sub>1</sub> (left) and T<sub>2</sub> (right) relaxation time for each proton position of the molecule.

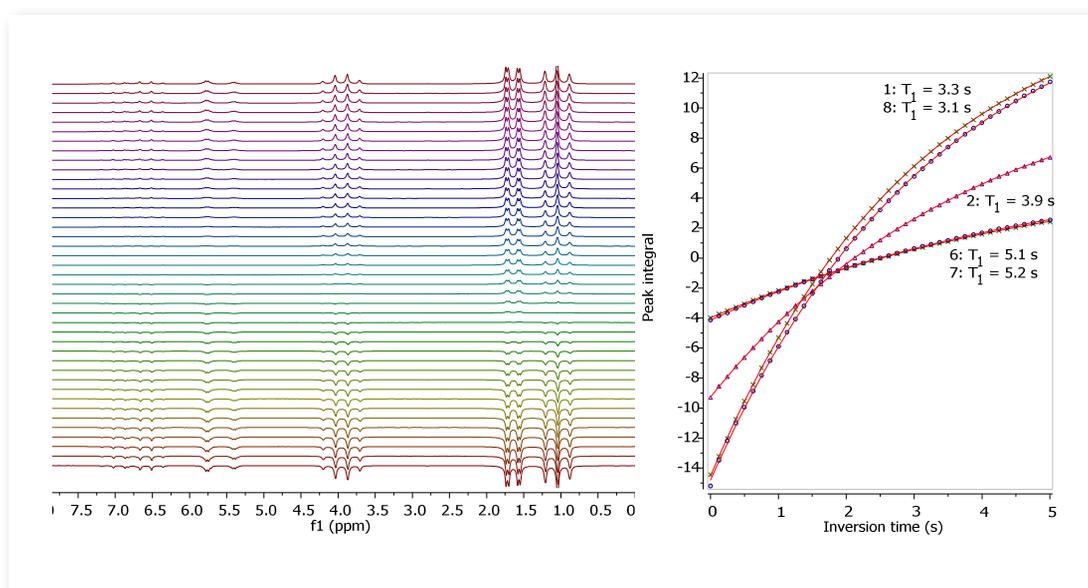


Figure 2: Proton T<sub>1</sub> relaxation time measurement of 25% ethyl crotonate in CDCl<sub>3</sub>.

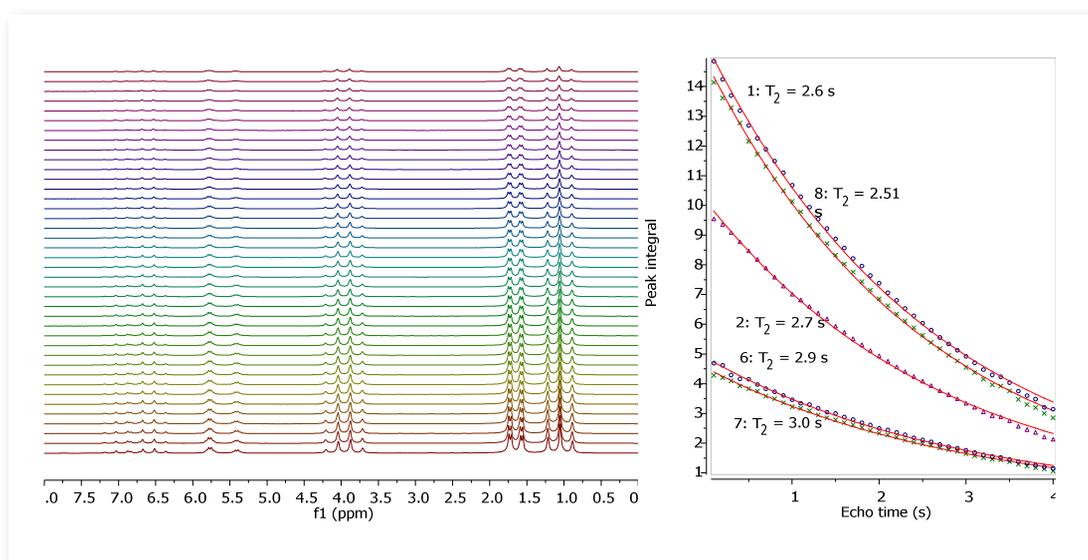


Figure 3: Proton T<sub>2</sub> relaxation time measurement of 25% ethyl crotonate in CDCl<sub>3</sub>.

## 2D COSY

The 2D COSY spectrum is shown in Figure 4. It clearly shows two spin systems (1,2) and (6,7,8). For example, the methyl group at position 1 only couples to the ethylene group at position 2, whilst the methyl group at position 8 couples to the two CH groups at positions 6 and 7. There is no coupling of positions (6,7,8) to either 1 or 2.

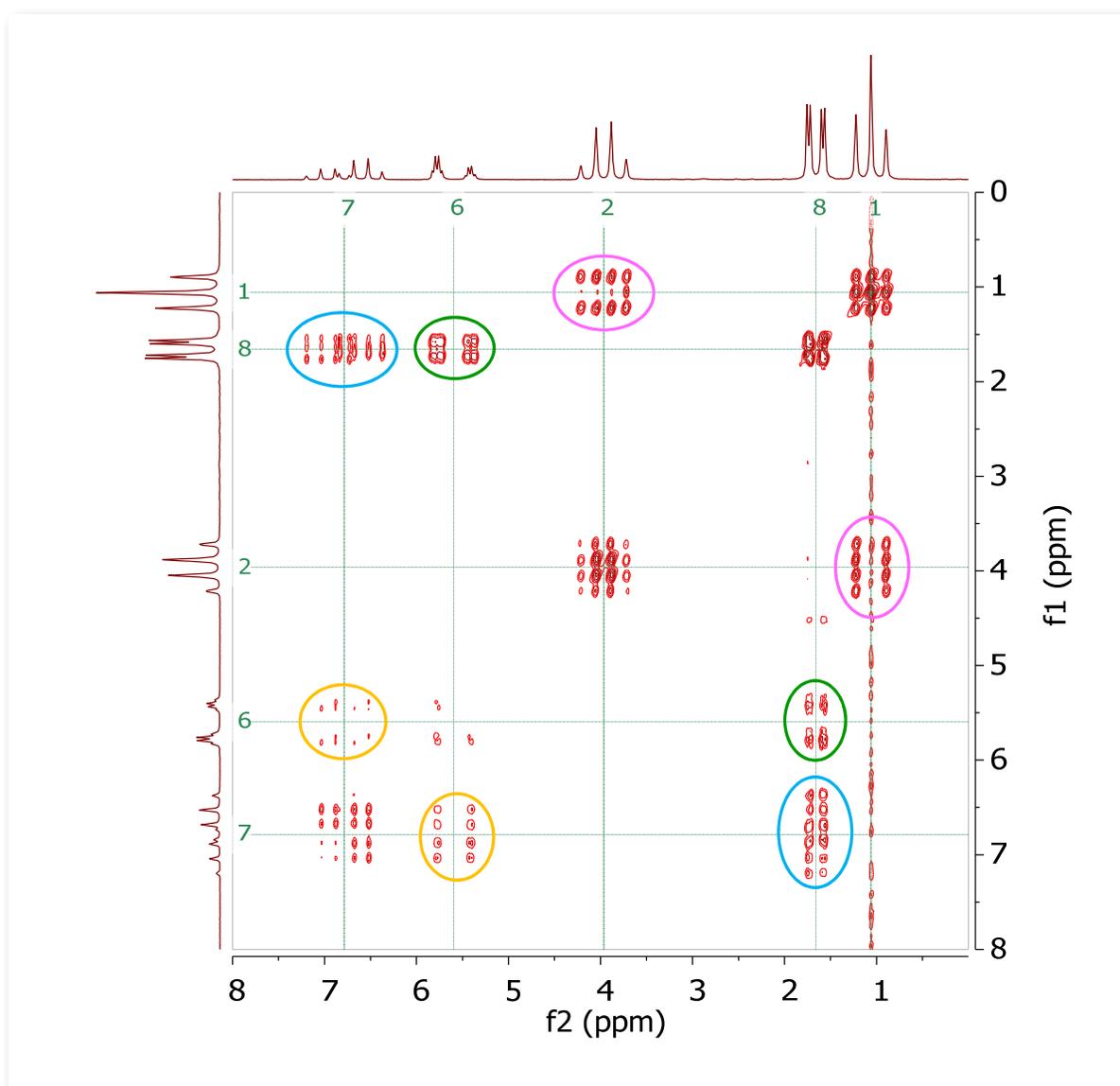
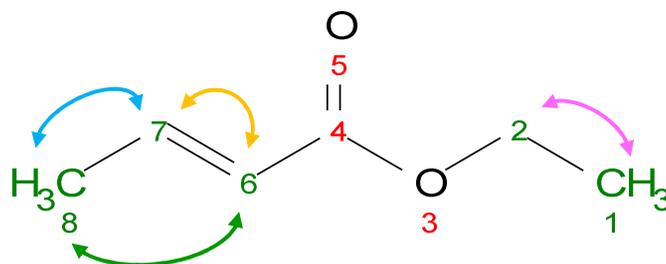


Figure 4: COSY spectrum of 25% ethyl crotonate in  $\text{CDCl}_3$ . The cross-peaks and corresponding exchanging protons are marked by colour-coded ellipses and arrows.

## 2D HOMONUCLEAR J-RESOLVED SPECTROSCOPY

In the 2D homonuclear *j*-resolved spectrum the chemical shift is along the direct (*f2*) direction and the effects of proton-proton coupling along the indirect (*f1*) dimension. This allows the full assignment of chemical shifts of overlapping multiplets, and can allow otherwise unresolved couplings to be measured. The projection along the *f1* dimension yields a “decoupled” 1D proton spectrum. Figure 5 shows the 2D homonuclear *j*-resolved spectrum of ethyl crotonate, along with the 1D proton spectrum as blue line. The vertical projection shows how the multiplets collapse into a single peak, which greatly simplifies the 1D spectrum. Vertical traces through the peaks in the 2D spectrum yield the peak multiplicities, as shown by the green lines in Figure 5, and enables the easurement of proton-proton coupling frequencies. By comparing the coupling frequencies between

different peaks, it is possible to extract information about which peaks are coupled to each other. For example, both the triplet at 1.06 ppm and the quartet at 3.96 ppm have a splitting of 7.10 Hz, suggesting that these groups are coupled to each other. The size of the coupling frequency provides information about the coupling strength. For example, the splitting of 1.53 Hz is due to the long range coupling between positions 6 and 8. All these couplings confirm the findings of the COSY experiment in Figure 4.

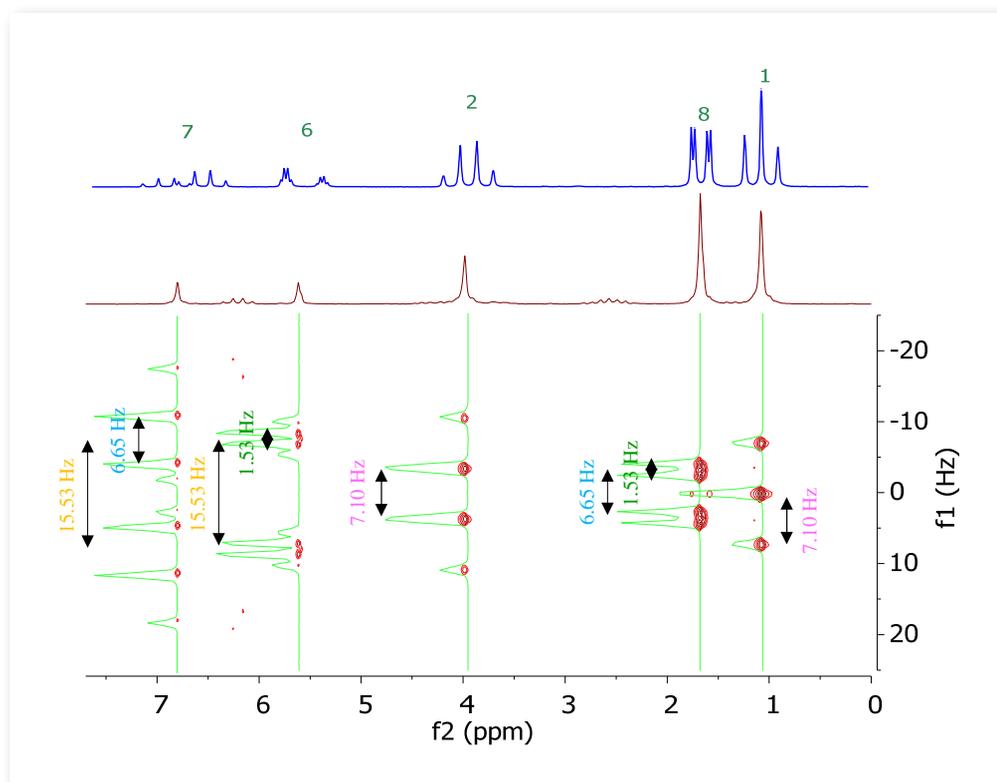
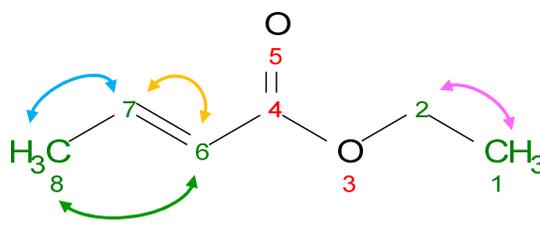


Figure 5: Homonuclear *j*-resolved spectrum of 25% ethyl crotonate in CDCl<sub>3</sub>. The multiplet splitting frequencies for different couplings are colour-coded as in Figure 4.

## 2D HOMONUCLEAR J-RESOLVED SPECTROSCOPY

One unusual and often neglected feature of this experiment is that second order coupling effects show up in the indirect (f1) direction as extra peaks equidistant from the coupling partners well removed from the zero frequency in the indirect dimension. These peaks are often neglected as artefacts, but provide direct evidence of second order coupling partners.

These extra peaks and coupling partners are marked by colour-coded ellipses and arrows in Figure 6. Note that this spectrum is based on the same data as Figure 5, only the scaling has changed.

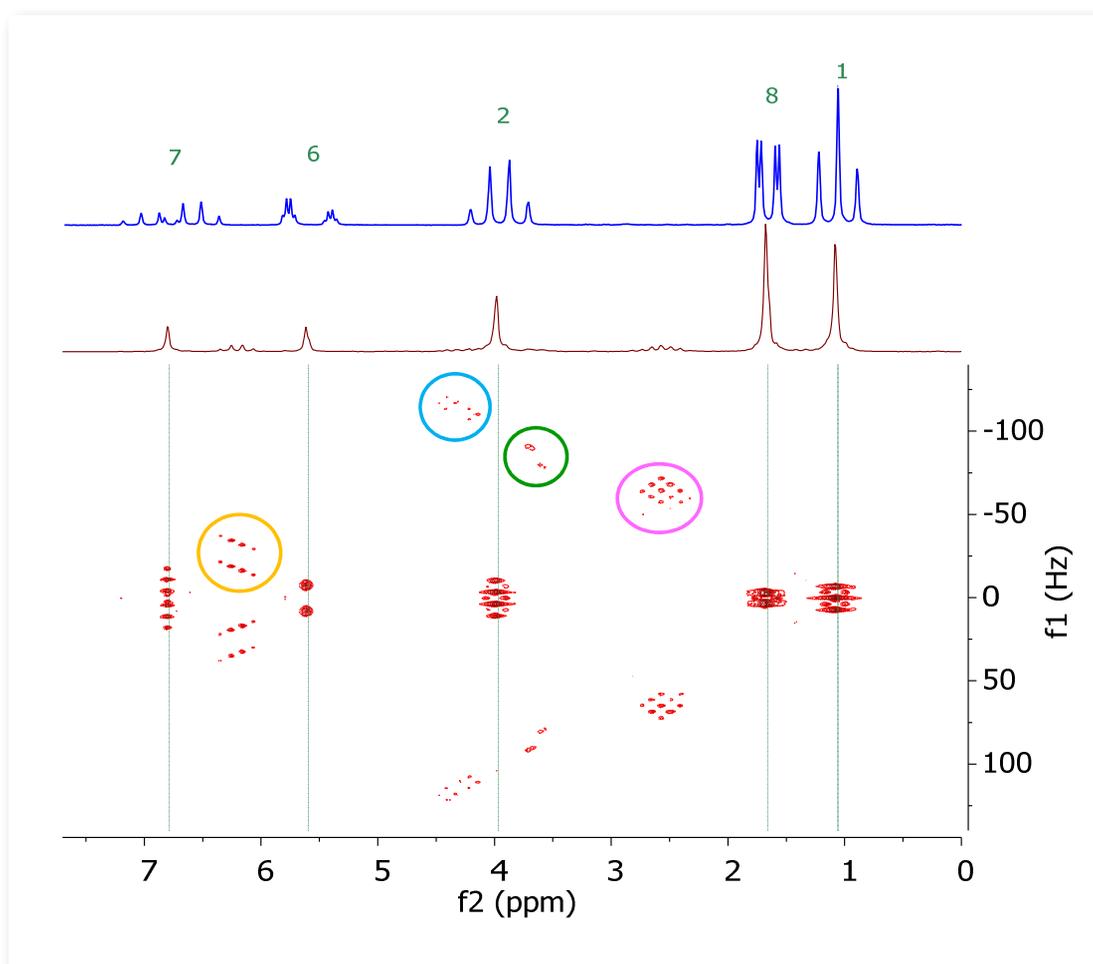
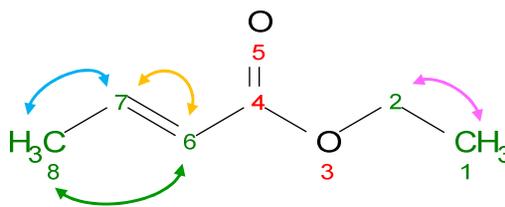


Figure 6: Homonuclear  $J$ -resolved spectrum of 25% ethyl crotonate in  $\text{CDCl}_3$  showing the extra peaks due to strong couplings.

## 1D $^{13}\text{C}$ SPECTRA

The  $^{13}\text{C}$  NMR spectra of 25% ethyl crotonate in  $\text{CDCl}_3$  are shown in Figure 7. The 1DCarbon experiment is sensitive to all  $^{13}\text{C}$  nuclei in the sample. It clearly resolves 6 resonances, as well as a weak solvent triplet between 70 and 80 ppm. The  $^{13}\text{C}$  DEPT experiment uses polarisation transfer between proton and carbon nuclei and can be used for spectral editing. Only carbons directly attached to protons are visible in these experiments. Since the peak at 167 ppm does not show in the DEPT spectra it must belong to the quaternary carbon at position 4. The DEPT-90 experiment gives only signal of CH groups, whilst the DEPT-45 and DEPT-135 give

signals of CH,  $\text{CH}_2$  and  $\text{CH}_3$  groups, but the  $\text{CH}_2$  groups appear as negative peaks in the DEPT-135. This is the case for the peak at 60 ppm, which must therefore belong to the carbon at position 2. By combining the three DEPT spectra, it is possible to confirm the peak assignment shown in Figure 7. The peaks at 144 and 123 ppm belong to the methyne groups at positions 7 and 6, and the peaks at 18 and 14 ppm belong to the methyl groups at positions 8 and 1.

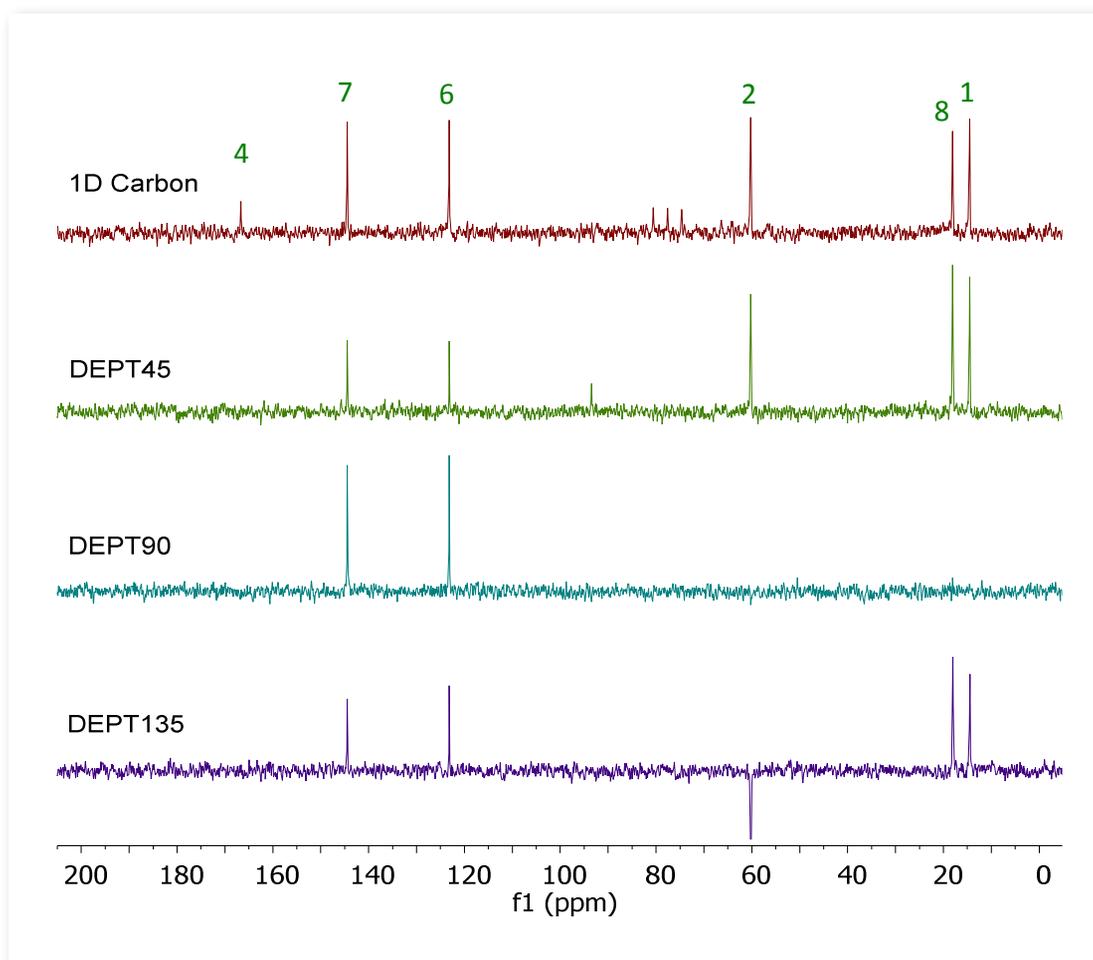
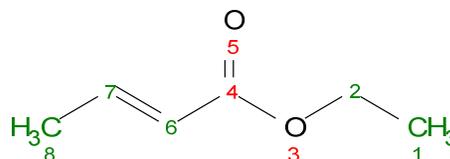


Figure 7: Carbon spectra of 25% ethyl crotonate in  $\text{CDCl}_3$ .

## HETCOR

Similar to the 2D COSY experiment, which detects proton-proton coupling partners, a series of heteronuclear 2D NMR experiments have been devised to detect coupling partners of different nuclei. The Heteronuclear Correlation (HETCOR) experiment is used to correlate proton resonances to the carbons directly bonded to those protons. The HETCOR experiment detects the carbon

signal along the direct dimension and the proton signal along the indirect dimension. The HETCOR spectrum of 25% ethyl crotonate in  $\text{CDCl}_3$  is shown in Figure 8, with the 1D proton and carbon spectra from Figures 1 and 7 as vertical and horizontal traces. The peaks in the 2D spectrum show which proton is bonded to which carbon.

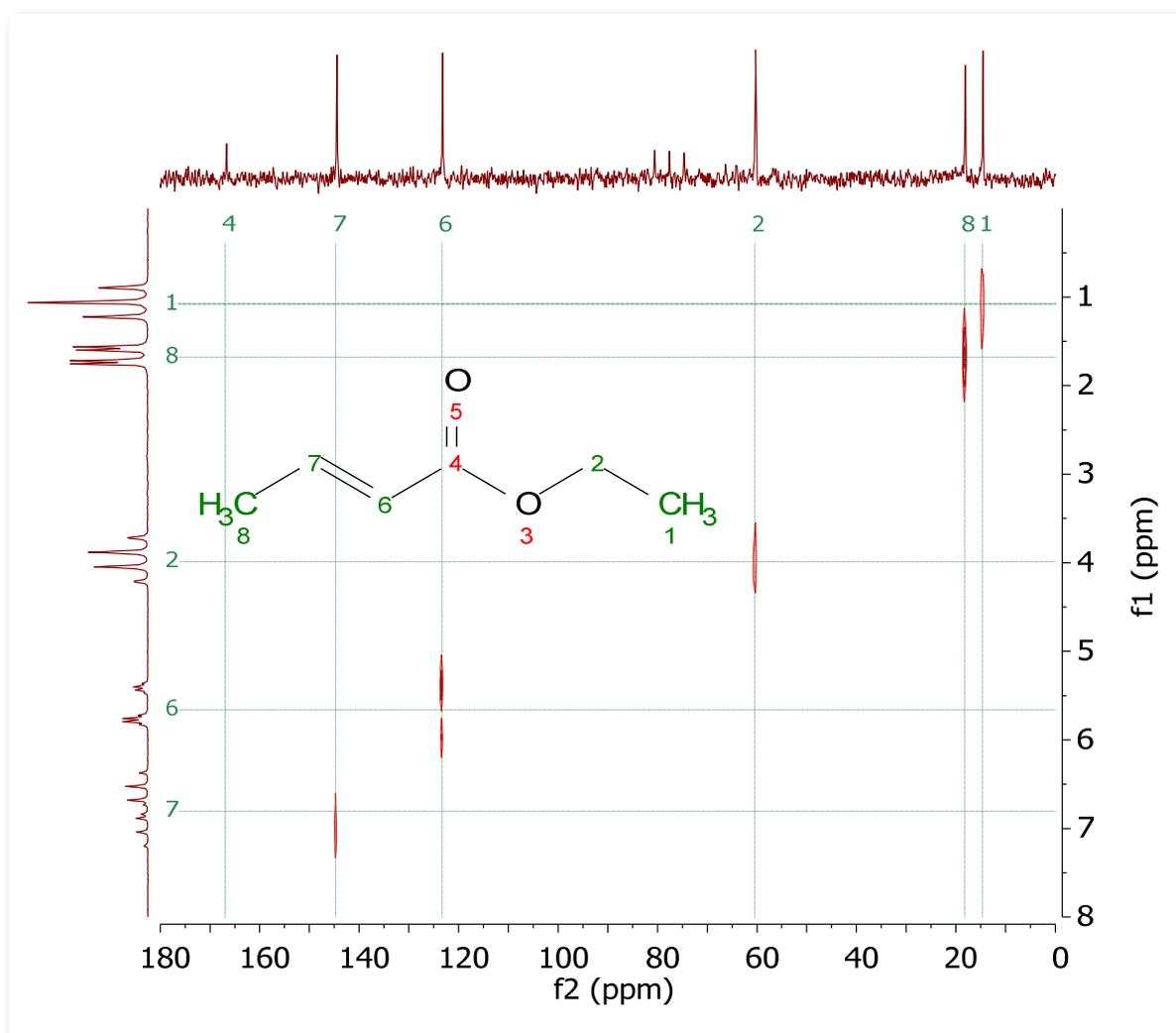


Figure 8: HETCOR spectrum of 25% ethyl crotonate in  $\text{CDCl}_3$ .

## HMQC

Another heteronuclear 2D correlation experiment is the Heteronuclear Multiple Quantum Coherence (HMQC) experiment. Similar to HETCOR, it is used to correlate proton resonances to the carbons directly bonded to those protons. However, in the HMQC experiment the carbon signal appears along the indirect dimension, and the proton signal along the direct dimension.

The HMQC spectrum of 25% ethyl crotonate in  $\text{CDCl}_3$  is shown in Figure 9, with the 1D proton and carbon spectra from Figures 1 and 7 as horizontal and vertical traces. The peaks in the 2D spectrum show which proton is bonded to which carbon.

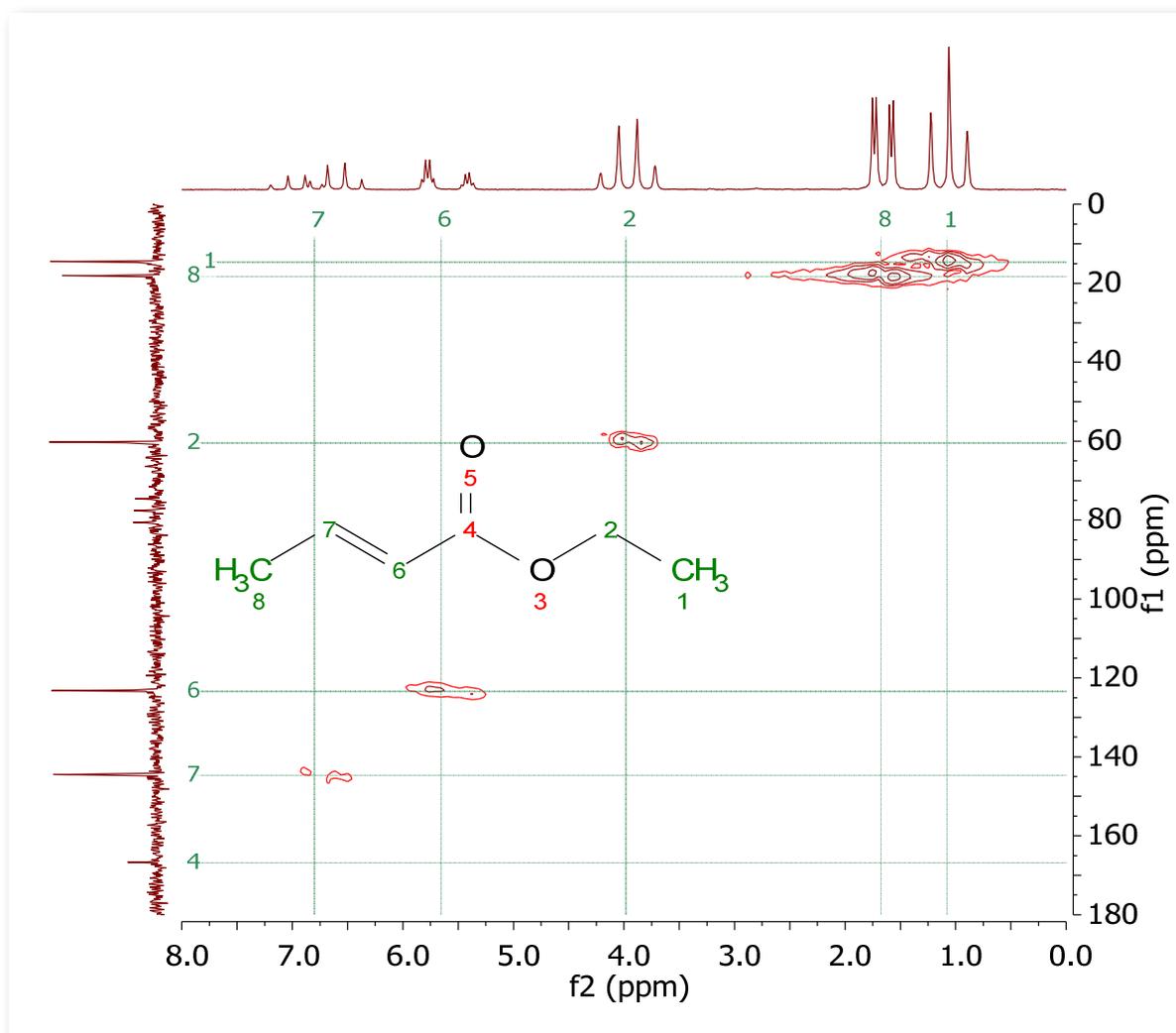


Figure 9: HMQC spectrum of 25% ethyl crotonate in  $\text{CDCl}_3$ .

## HMBC

The HMQC experiment shown on the previous page was designed to correlate protons and carbons which are connected through a one bond coupling. To obtain long-range proton-carbon correlations through two or three bond couplings, the Heteronuclear Multiple Bond Correlation (HMBC) experiment can be used. Like in the HMQC experiment the carbon signal appears along the indirect dimension, and the proton signal along the direct dimension. The HMBC spectrum of 25% ethyl crotonate in CDCl<sub>3</sub> is shown in Figure 10, with the 1D proton and carbon spectra from Figures 1 and 7 as horizontal and vertical traces. The peaks in the 2D spectrum show which protons

are connected to which carbons via a long-range coupling. The couplings between molecular positions look similar to the ones found from the COSY spectrum, but the HMBC additionally shows couplings to quaternary carbons, which are not visible in the COSY or HMQC. For example, there are clear multibond couplings from the carbon at position 4 to the protons at positions 7 and 2, marked as dark blue in Figure 10.

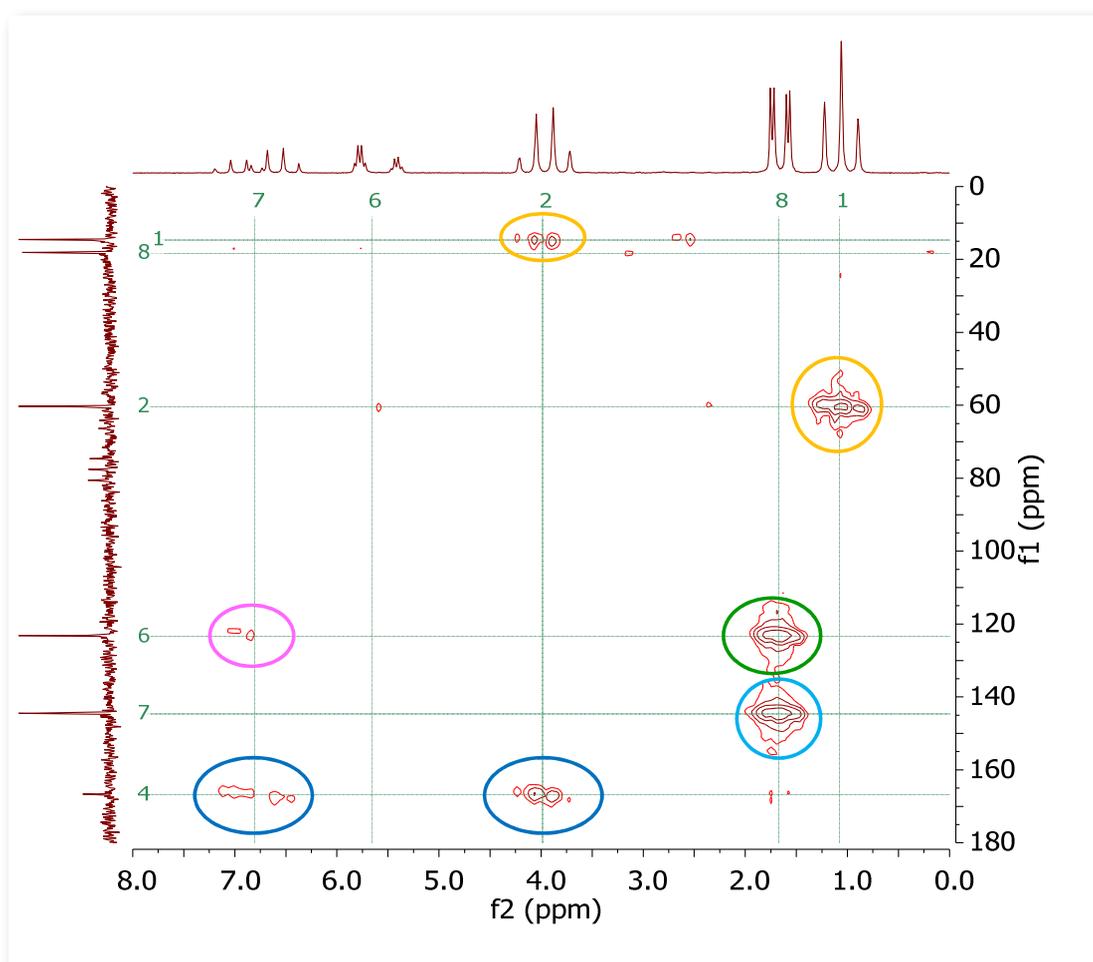
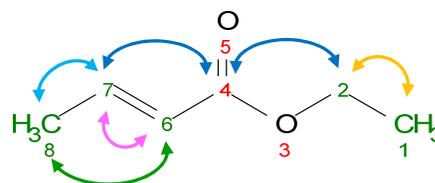


Figure 10: HMBC spectrum of 25% ethyl crotonate in CDCl<sub>3</sub>.



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