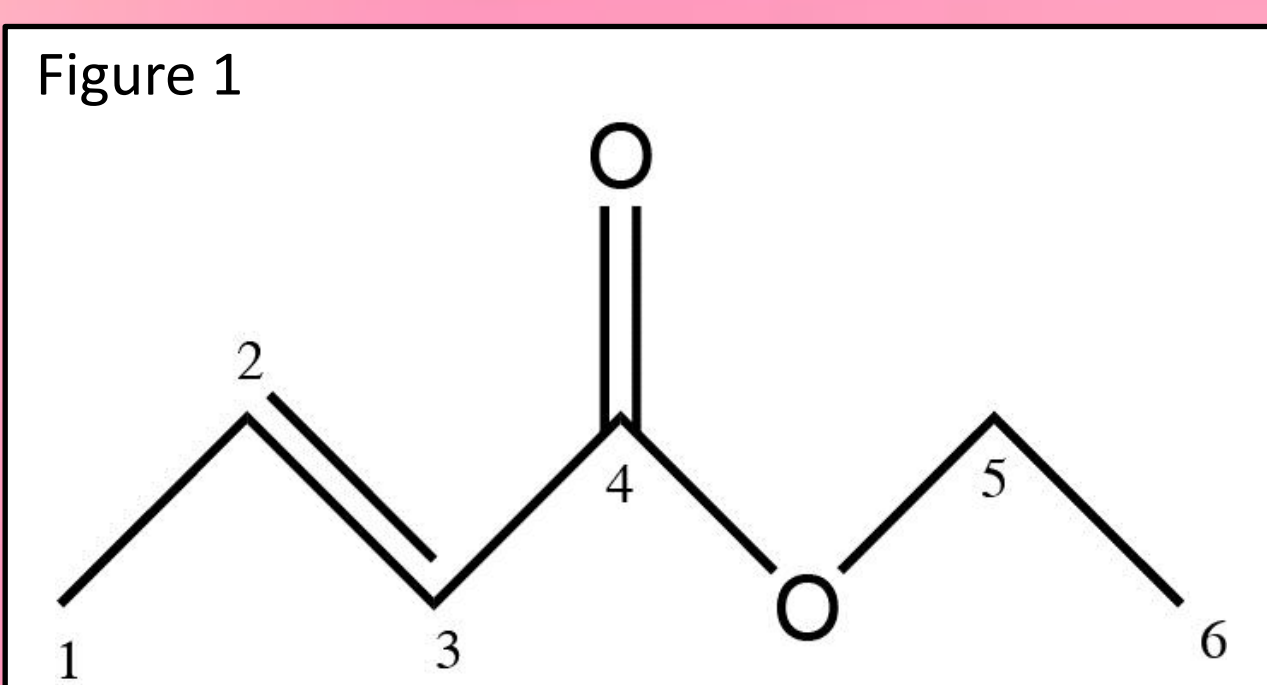


Assignment of $^1\text{H}/^{13}\text{C}$ NMR Resonances of ethyl trans-crotonate

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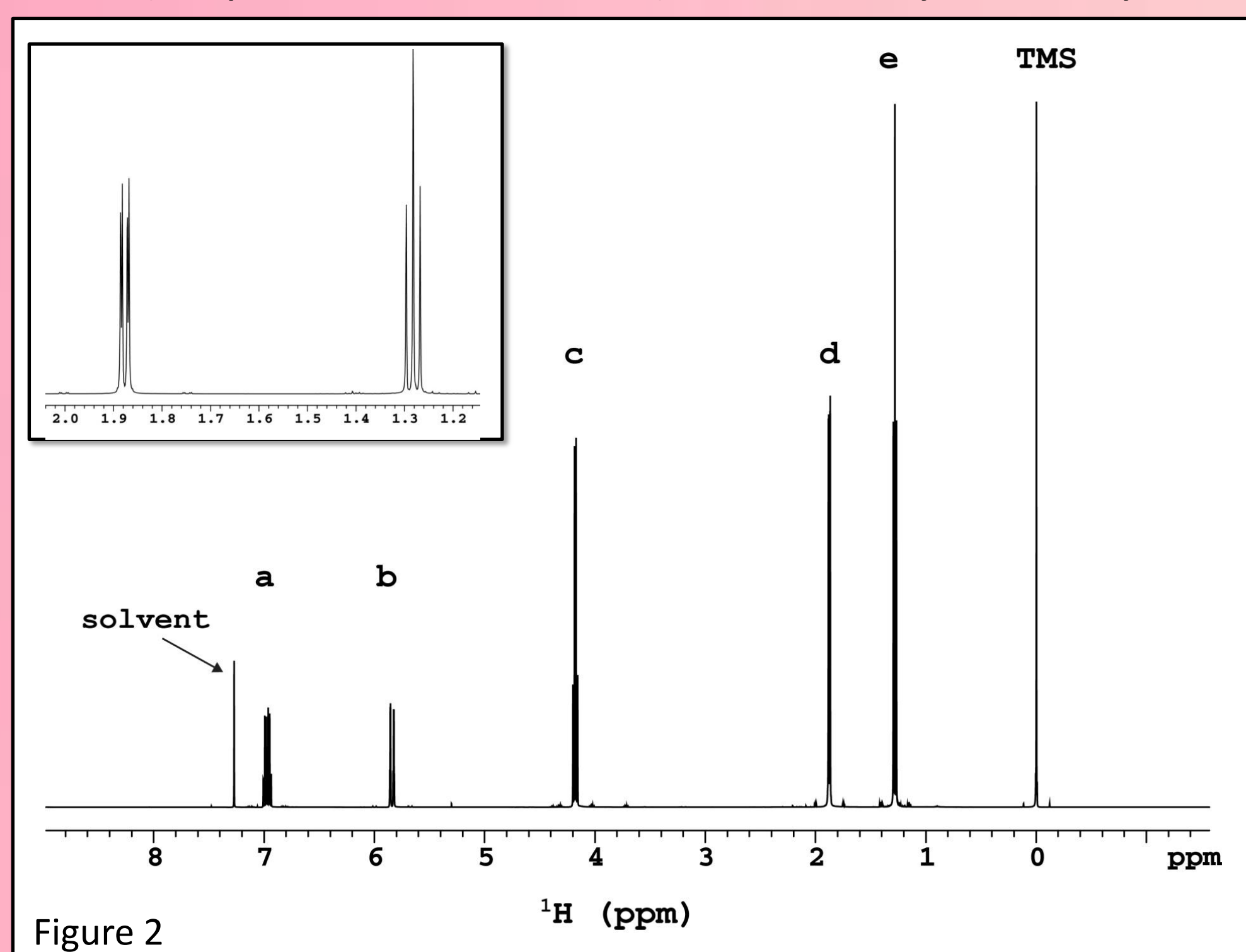
2-butenoic acid ethyl ester, commonly known as ethyl trans-crotonate (ETC), is a six carbon molecule with a trans-double bond between C2 and C3, and an ester linkage between C4 and C5. The molecular formula for ETC is $\text{C}_6\text{H}_{10}\text{O}_2$, and the molecule weight is 114.1424 g/mol. There are 2 degrees of unsaturation in the molecule. The IUPAC numbering for ETC is shown in Figure 1.

^1H NMR Spectrum

The ^1H NMR spectra of ETC is shown in Figure 2. The data were recorded at 500MHz (^1H), using a spectral width of 5274.2 Hz and 16384 complex points (acquisition time of 3s), and a recycle delay of 1 s.

^1H Chemical Shift

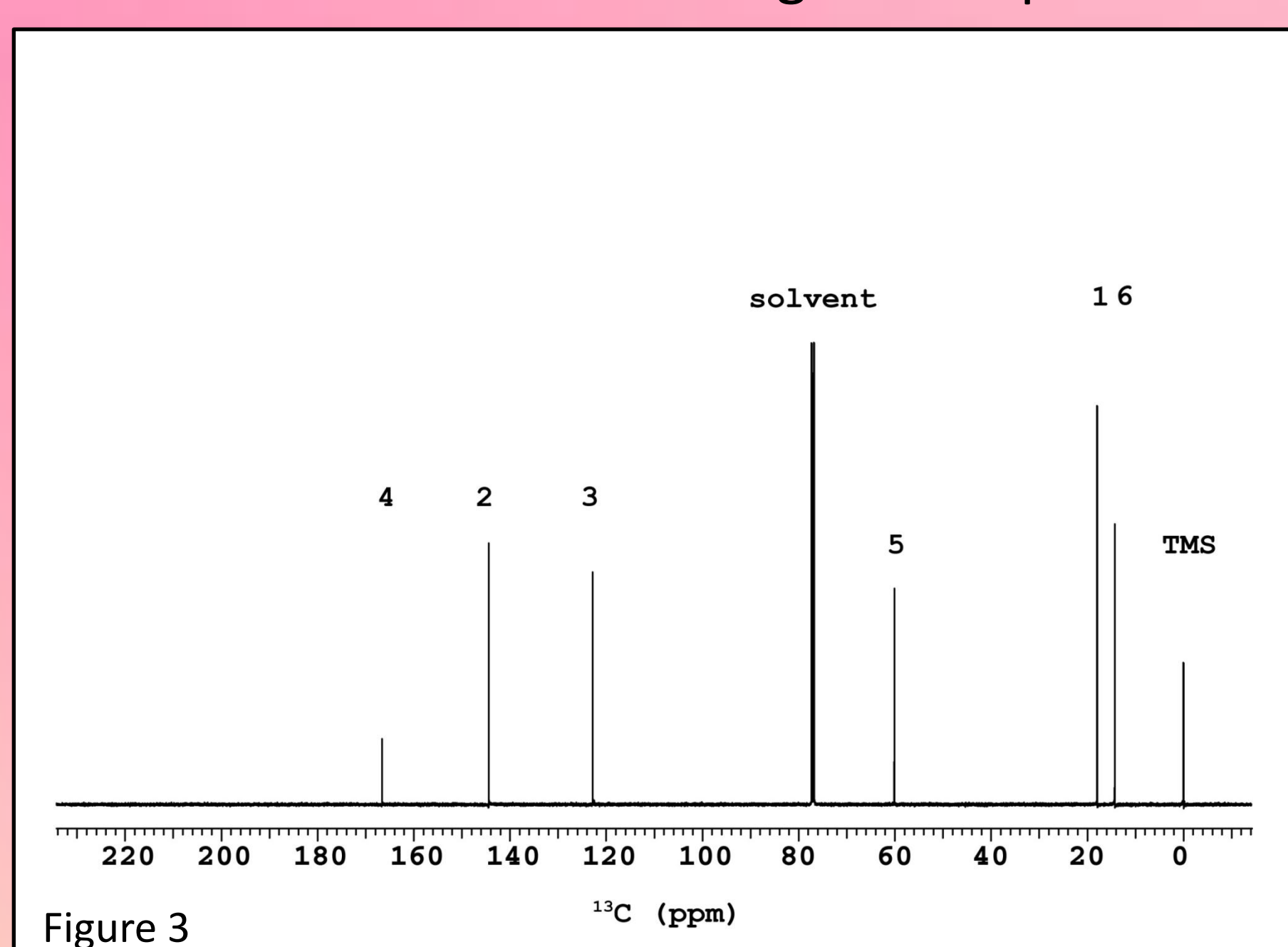
Peak	Chemical shift (ppm)
a	6.978
b	5.841
c	4.1795
d	1.8765
e	1.282



The ^1H resonances are given designations **a** through **e**. Note that the resonance at 7.273 ppm corresponds to residual CHCl_3 in the solvent, and the resonances at 0 ppm correspond to TMS. The resonances present at 1.8765 ppm and 1.282 ppm can confidently be assigned to the two methyl groups based on the anticipated influence of electronic inductive effects. Inspection of the fine structure of these two resonances reveals that the resonance at 1.8765 ppm is a doublet of doublets (one large coupling and one small coupling) while the resonance at 1.282 ppm is a triplet pattern. These patterns allow us to definitively assign **d** to the methyl group at position 1 in the molecule (Figure 1) and **e** to the methyl group at position 6. Close inspection of the remaining resonances reveals that **a** is a complex quartet of doublets, **b** is a doublet (with a hint of quartet character), and **c** is a quartet. These resonances will be assigned in the subsequent analysis.

^{13}C NMR Spectrum

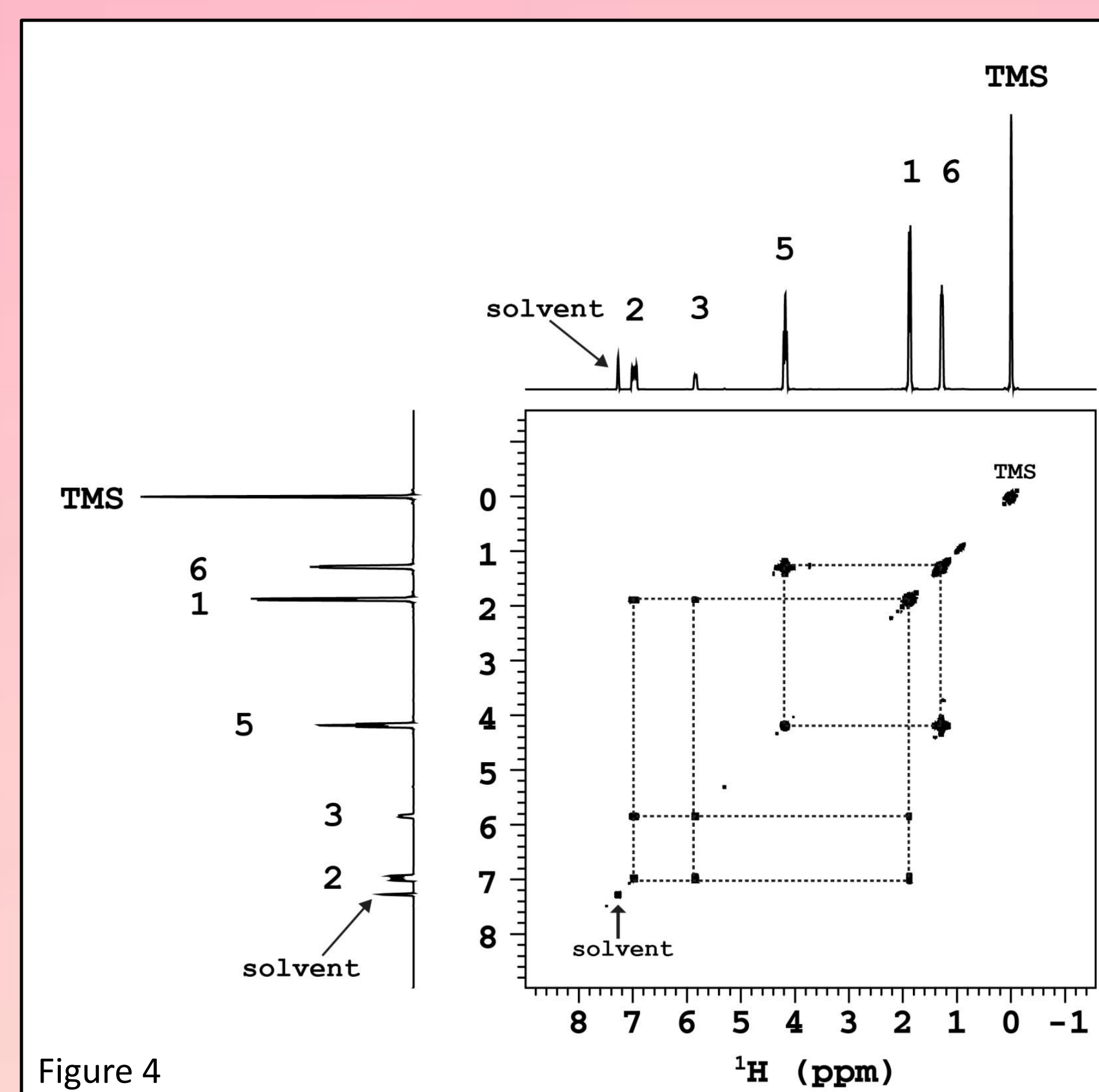
The ^{13}C NMR spectra of ETC is shown in Figure 3. The data were recorded at 500MHz using a spectral width of 31250 Hz and 32768 complex points (acquisition time of 1s). The ^{13}C peak assignments were made based on the ^1H assignments and the direct ^1H - ^{13}C correlations observed in the gHMQC spectra.



^{13}C Chemical Shift

Peak	Chemical shift (ppm)
4	166.577
2	122.794
3	77.017
5	60.075
1	17.923
6	14.26

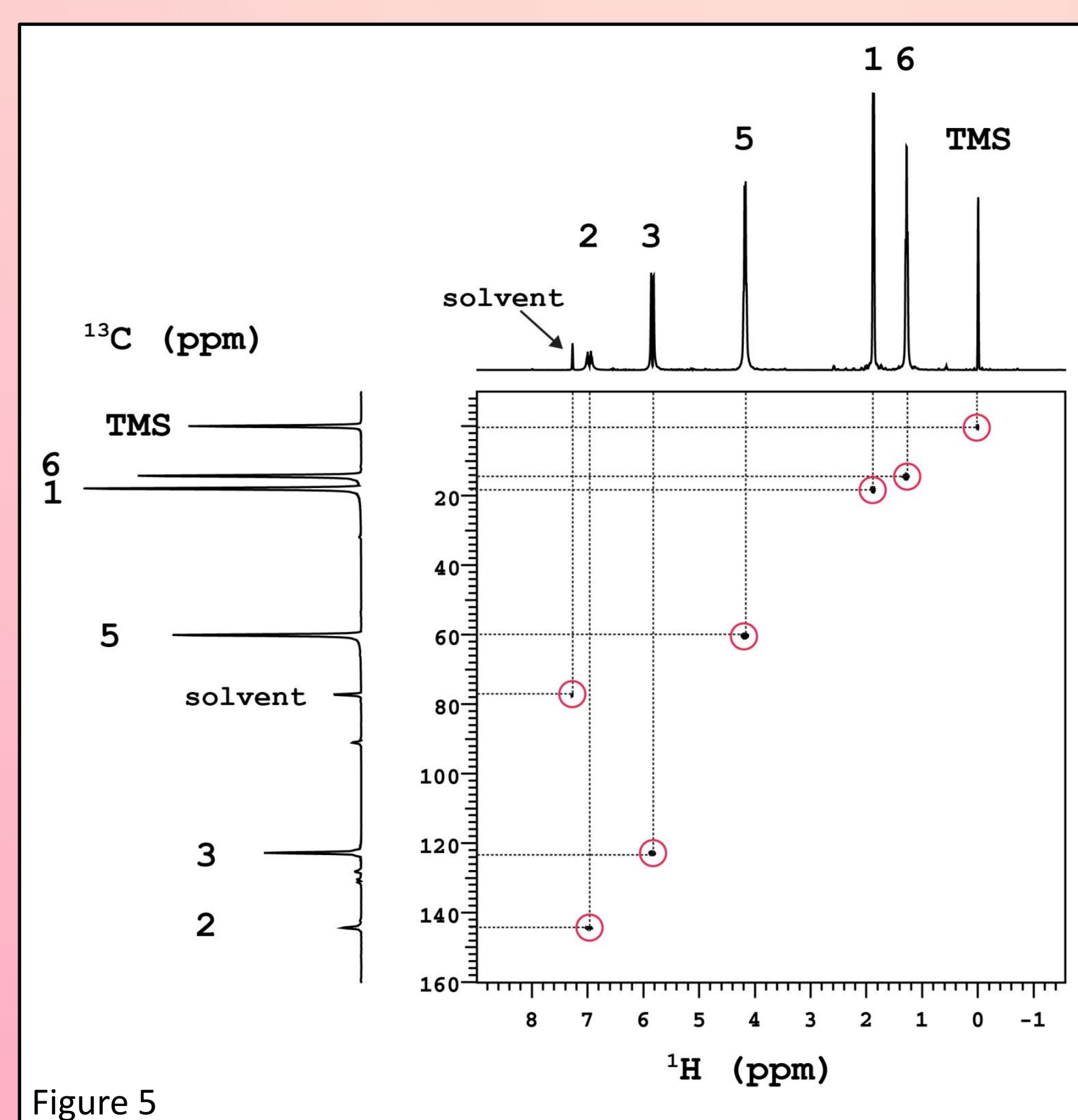
Gradient-Enhanced Correlation Spectroscopy (gCOSY)



The two-dimensional gCOSY for ETC is shown in Figure 4. This data reveals ^1H - ^1H chemical shift correlations between J-coupled nuclei. The data were recorded using spectral widths in the direct (F2, horizontal axis) and indirect (F1, vertical axis) dimensions of 5274.26 Hz, with 1024 complex points in the F2 dimension and 512 complex points in the F1 dimension. The methyl resonance at 1.282 ppm is coupled to the resonance at 4.1795 ppm, consistent with our previous considerations. This confirms that resonance labeled **c** in Figure 1 corresponds to the methylene group at position 5. The methyl resonance at 1.8765 ppm is correlated with the resonances at 6.978 ppm (strong correlation) and at 5.841 ppm (weak correlation). This indicated that resonances labeled **a** and **b** correspond to the vinylic protons at positions 2 and 3. Consideration of the intensity of the COSY resonances, together with the fine structure analysis of the resonances reveals that resonance **a** is the methane moiety at position 2 and that the resonance **b** corresponds to position 3. The ^1H and COSY spectra for ETC reveal the presence of a long-range 4-bond coupling between the methyl ^1H resonances of position 1 and the vinylic proton at position 3.

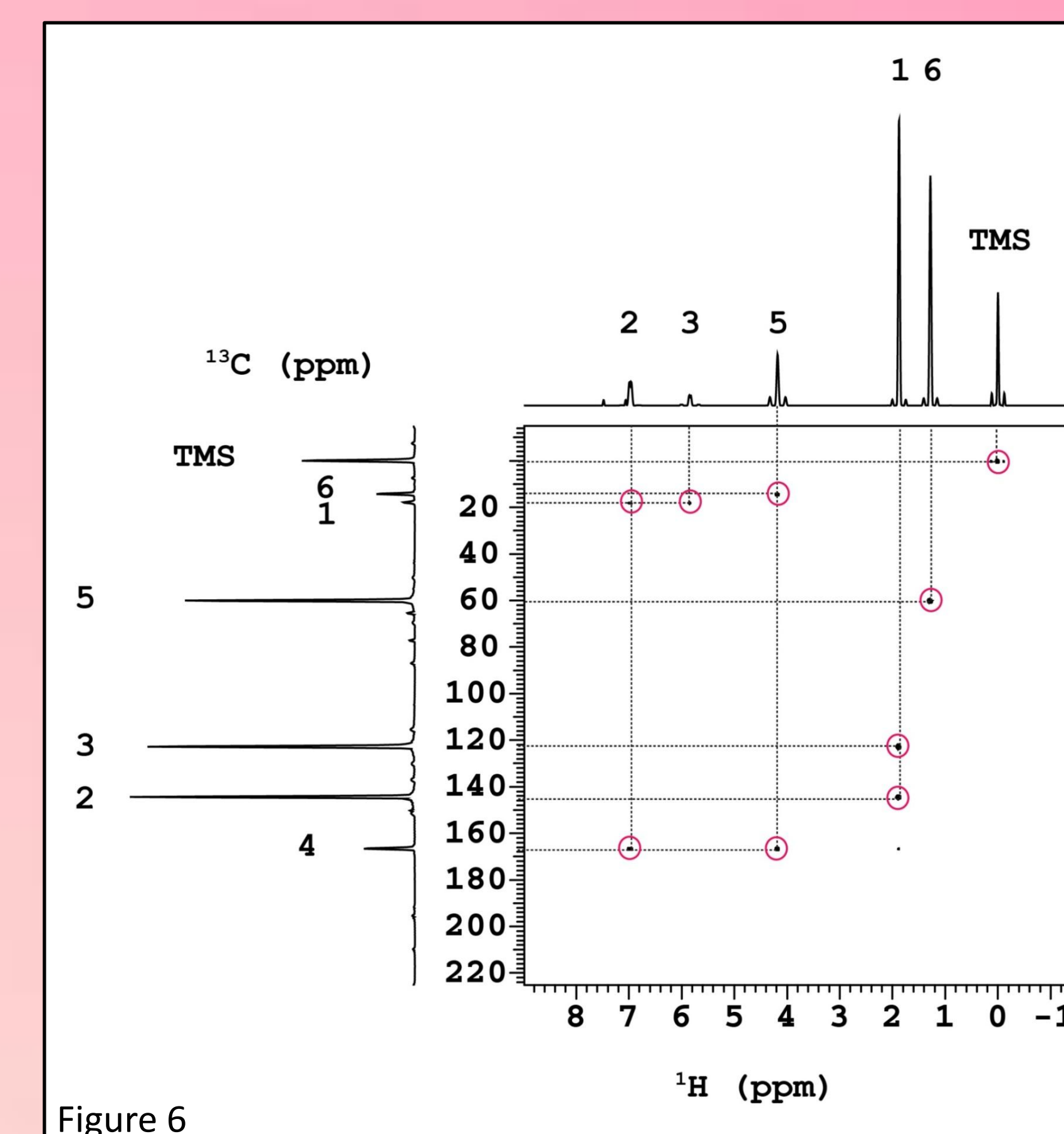
Gradient-Enhanced Heteronuclear Multiple Quantum Coherence Spectroscopy (gHMQC)

The two-dimensional gHMQC spectra for ETC is shown in Figure 4. This data reveals ^{13}C - ^1H chemical shift correlations between directly bonded hydrogen and carbon nuclei. The data were recorded using a spectral width of 5274.26 Hz in the direct (F2, horizontal axis) and 21378.9 Hz in the indirect (F1, vertical axis), with 1024 complex points in the F2 dimension and 512 complex points in the F1 dimension.



Analysis of the gHMQC spectra gives information necessary to assign correlations between carbon and hydrogen in the molecule. Using the assigned ^1H resonances and the resonances present in the gHMQC spectra, we can assign the identities of the ^{13}C spectra. These assignment (based on the IUPAC numbering system in Figure 1. are shown with corresponding resonances on the ^{13}C projection (vertical axis) as well as the one dimensional ^{13}C spectra, Figure 5.

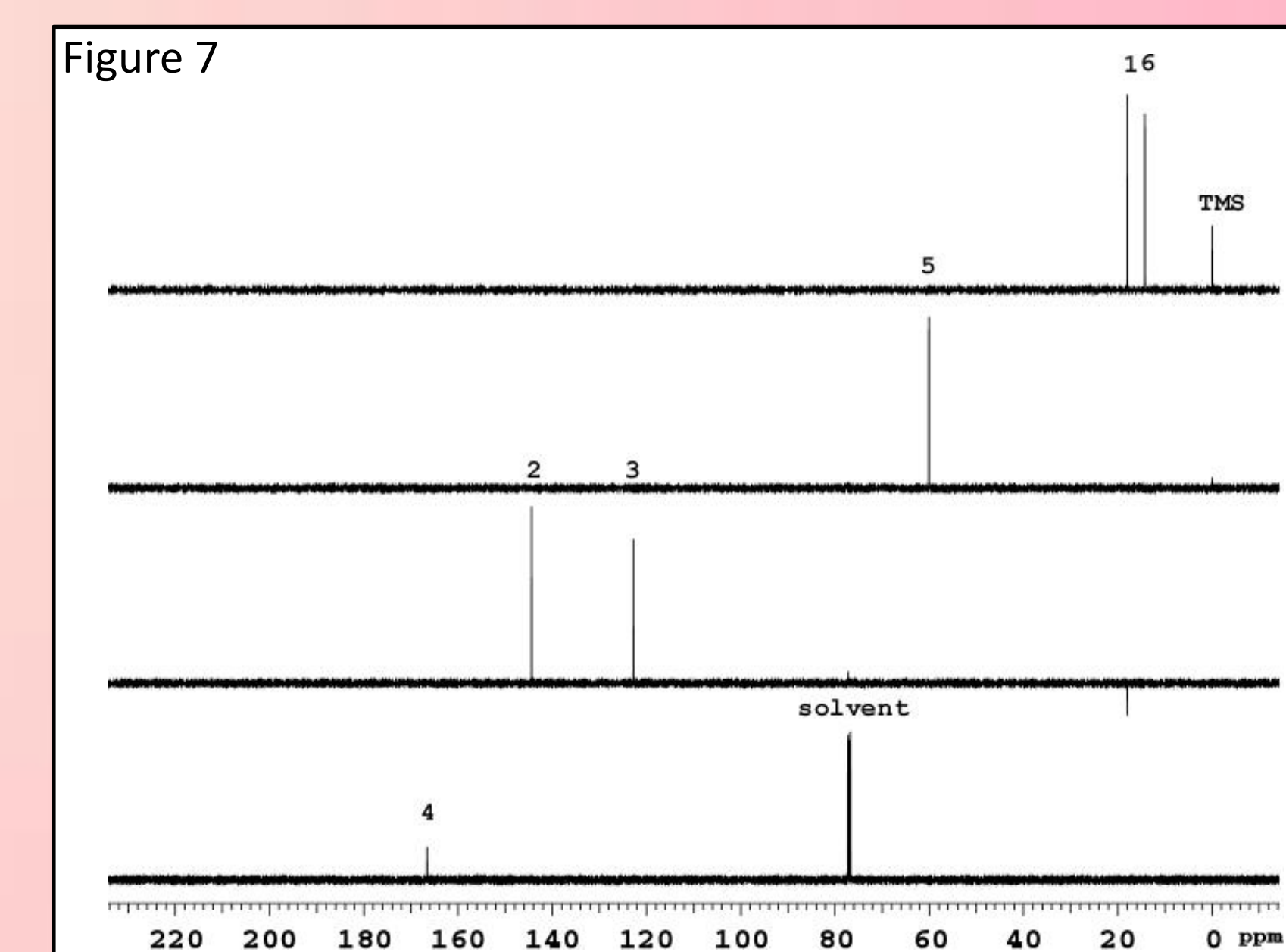
Gradient-Enhanced Heteronuclear Multiple Bond Correlation (gHMBC)



The two-dimensional gHMBC spectra for ETC is shown in Figure 6. This data reveals ^{13}C - ^1H chemical shift correlations between geminal and vicinal couplings. This data was recorded using a spectral width of 5274.26 Hz in the direct (F2, horizontal axis) and 30177.3 Hz in the indirect (F1, vertical axis), with 1024 complex points. The data provided by the gHMBC spectra further confirms the previous assignments made to both the ^1H NMR and ^{13}C NMR spectra by analysis of the cross peak resonances.

Distortionless Enhancement by Polarization Transfer (DEPT)

The one-dimensional DEPT spectra for ETC is shown in Figure 7. The data were collected using a spectral width of 31250 and 32768 complex points (acquisition time of 1s). DEPT is an application of ^{13}C NMR used to identify the presence of primary, secondary, tertiary, and quaternary carbons. There are 3 peaks indicative of primary carbons, 2 for positions 2 and 3 in the molecule and the other from TMS. Likewise, 1 secondary carbon in position 5, 2 tertiary carbons in positions 6 and 1, and 2 quaternary carbons from position 4 and the solvent.



Conclusions

Because of the size and simple structure of ethyl trans-crotonate, proton assignments can be made by examining the fine structure and chemical shift values of the ^1H NMR spectra. These assignment can be further confirmed by the Gradient-Enhanced Correlation Spectroscopy (gCOSY) resonances. The ^{13}C assignments are given by transcribing the confirmed proton assignments to the ^1H projections of the Gradient-Enhanced Heteronuclear Multiple Quantum Coherence Spectroscopy (gHMQC) and identifying the carbon positions in the molecule. These carbon assignments can be examined more closely in the ^{13}C NMR spectra and confirmed even further by the Heteronuclear Multiple Bond Correlation (gHMBC) and the Distortionless Enhancement by Polarization Transfer (DEPT).

References

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