

Introduction

Ethyl 3-methyl-3-phenyloxirane-2-carboxylate, also known as strawberry aldehyde, is an organic compound that is used in the artificial flavor industry. Ethyl-3-methyl-3-phenylglycidate is an organic compound composed of a monosubstituted aromatic ring, an epoxide, and an ester. The molecular formula and molecular weight is $\text{C}_{12}\text{H}_{14}\text{O}_3$ and 206.24 g/mol, respectively.

The chiral center located at C2 creates a racemic mixture. Because of its pleasant smell, strawberry aldehyde is also commonly used in the fragrance industry. The structure is shown in Figure 1.

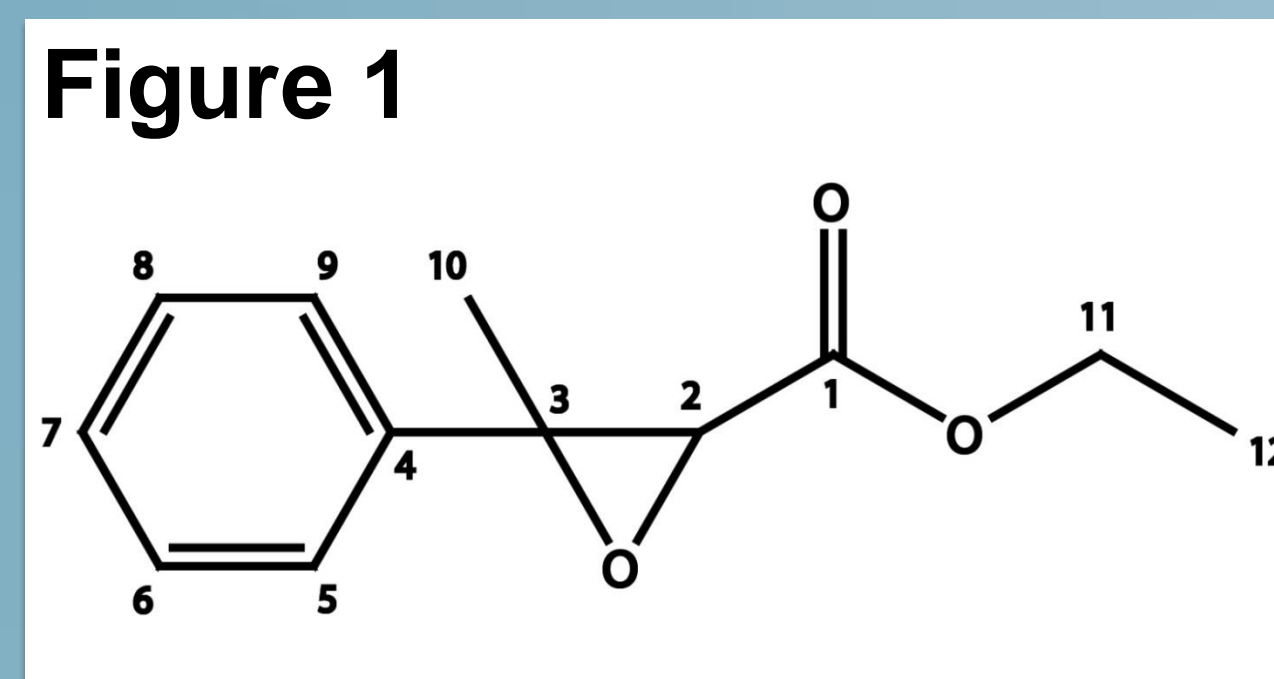


Figure 1

^1H 1D NMR Spectrum

The ^1H 1D spectrum is shown in Figure 2. The spectrum was collected at 800 MHz with a spectral width of 12019.2 Hz and 54824 complex points. The residual resonance from the solvent (CDCl_3) has a

chemical shift 7.27 ppm. Due to the compound being acquired as the racemic mixture, all the resonances appear twice. The fine structure of the resonances for the isomers are identical, however the chemical shifts vary. The concentration of diastereomers is unequal, and this is likewise reflected in the resonance intensities. The integration of the resonances of one diastereomer to the other is directly proportional to the ratio of the isomers in solution. The diastereomeric ratio is 1.4. It is undetermined which isomer is in higher concentration.

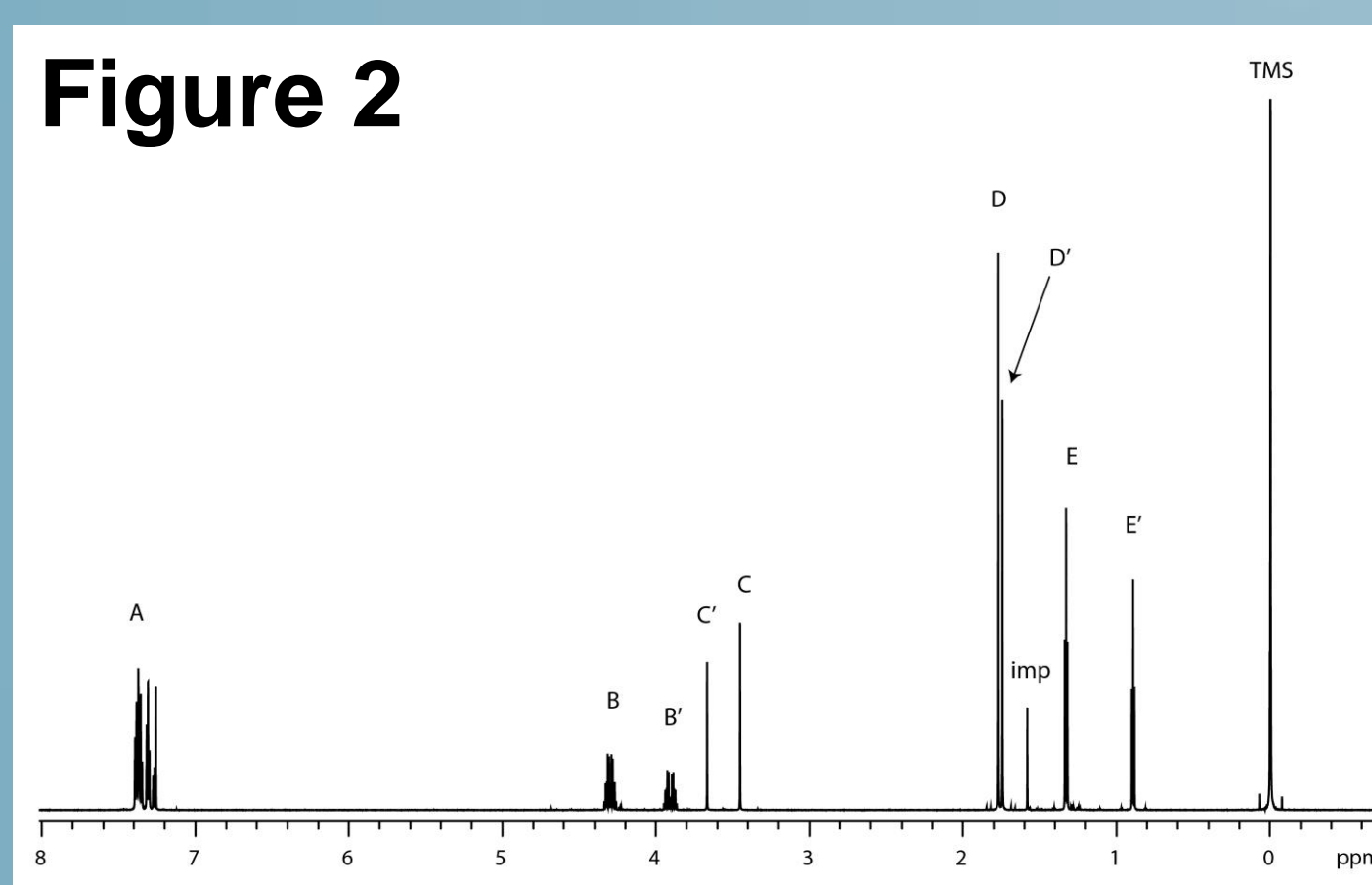


Figure 2

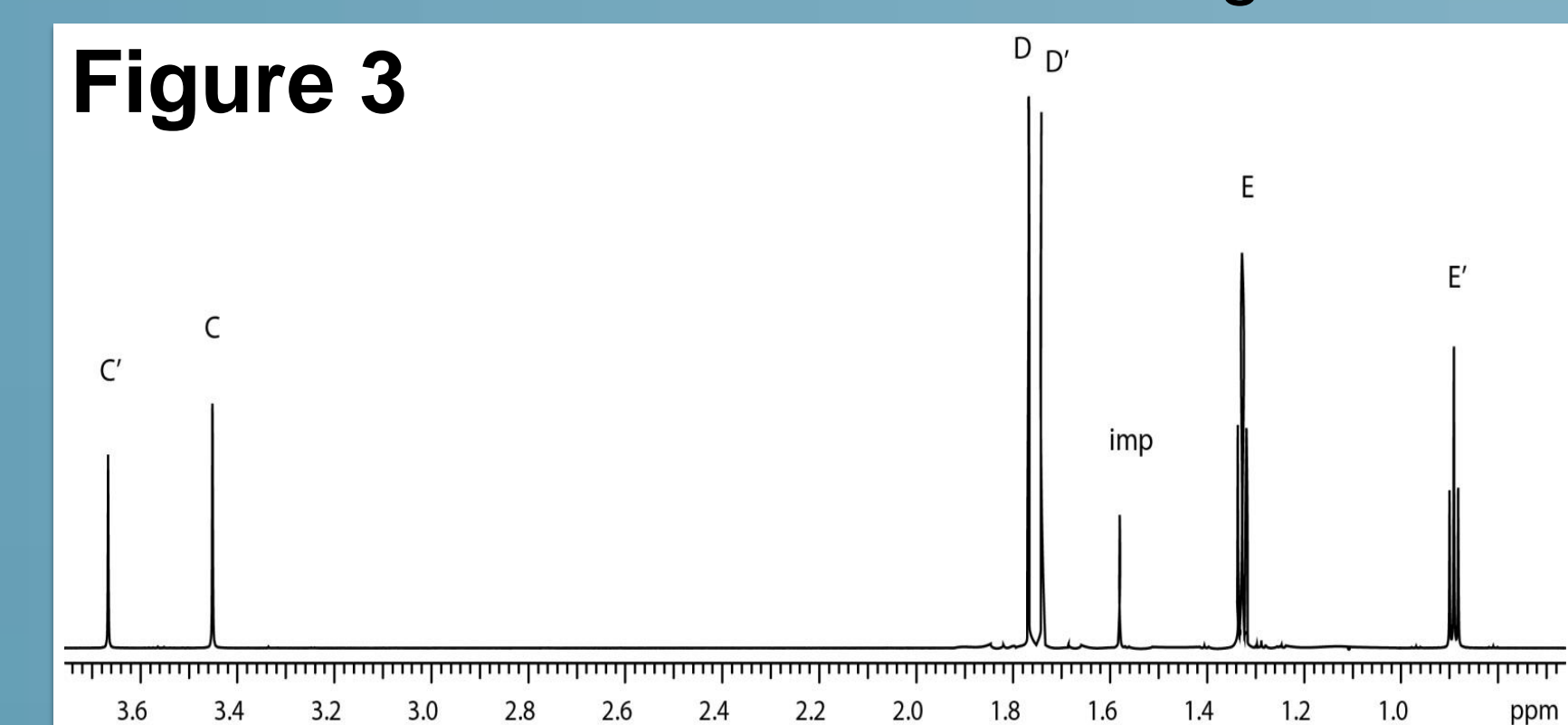


Figure 3: An expanded view of Figure 2 to analyze the fine structure.

group (H11/C11). Resonance C is the most downfield singlet in the spectrum. This splitting pattern suggests there are no neighboring protons. H2 is a methine that is adjacent to two quaternary carbons and an oxygen. The other singlet in the data, resonance D, has a lower chemical shift. H10 is a methyl group adjacent to a quaternary carbon. Furthermore, the intensity of the resonances can be used to differentiate the methine and methyl. H10 is approximately three times the intensity of H2, therefore resonance C belongs to H2 and resonance D belongs to H10. To further rationalize the assignments, resonance C is more deshielded because C2 is directly bonded to an oxygen, thus placing it in a much lower electron rich environment than resonance D, which is the methyl group, H10/C10.

The aromatic region of Ethyl-3-methyl-3-phenylglycidate remains unresolved. The fine structure of resonance group A is further complicated by the presence of the racemic mixture.

An expanded view of the ^1H spectrum is shown in Figure 4. This view supports the analysis of the fine structure of resonance B. The splitting pattern appears to be a doublet of quartets. This pattern can be explained by the proximity of the

resonance to a methylene moiety. The quartet can be rationalized by C11 being adjacent to a methyl group. The two methylene protons, H11A and H11B, are inequivalent and will therefore split each other. This results in the two quartets being further split and leading to a doublet of quartets.

Doublet of Quartets

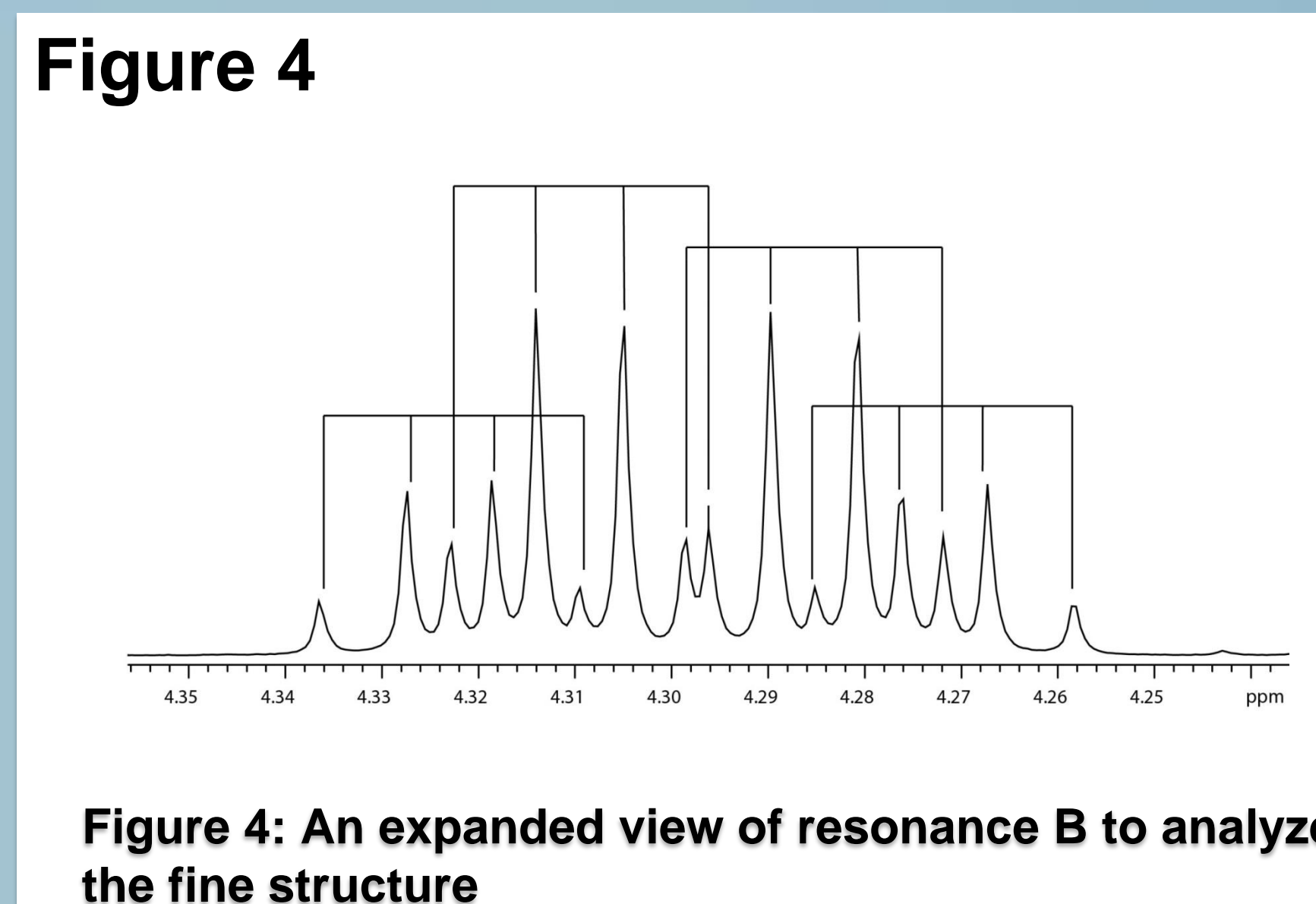
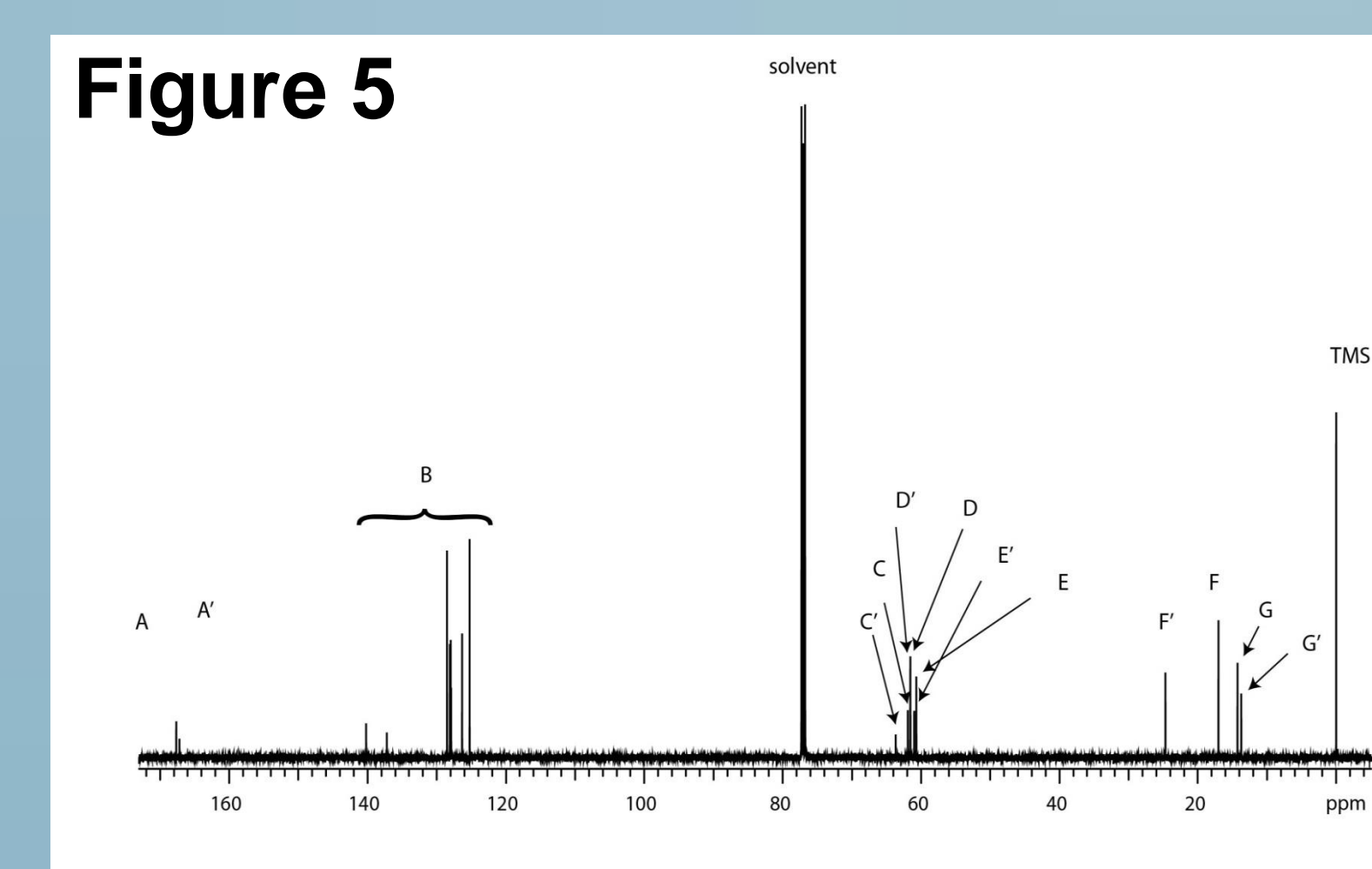


Figure 4: An expanded view of resonance B to analyze the fine structure

^{13}C 1D NMR Spectrum



The ^{13}C spectrum of Ethyl 3-methyl-3-phenyloxirane-2-carboxylate is shown in Figure 5. The spectrum was recorded at 500 MHz with a spectral width of 24038.5 Hz and 65536 complex points. The residual resonance from the solvent (CDCl_3) is a triplet with a chemical shift 77 Hz(ppm). The most downfield signal appears at 167 ppm. This resonance is assigned to C1, the carbonyl carbon of the ester.

gHMQC

The Gradient-Enhanced Heteronuclear Multiple Quantum Correlation spectrum reveals chemical shift correlations between directly bonded hydrogen and carbon nuclei. Since all the protons have been assigned, all carbons with hydrogens can be assigned based on the correlation with directly bound protons. The gHMQC is shown in Figure 6. The data was collected at 500 MHz using spectral widths of 4223.0 Hz in the direct dimension, 23418.1 Hz in the indirect dimension and 1266 complex points. Using the previously made proton assignments, projections in the direct dimension are able to be aligned to projections in the indirect dimension.

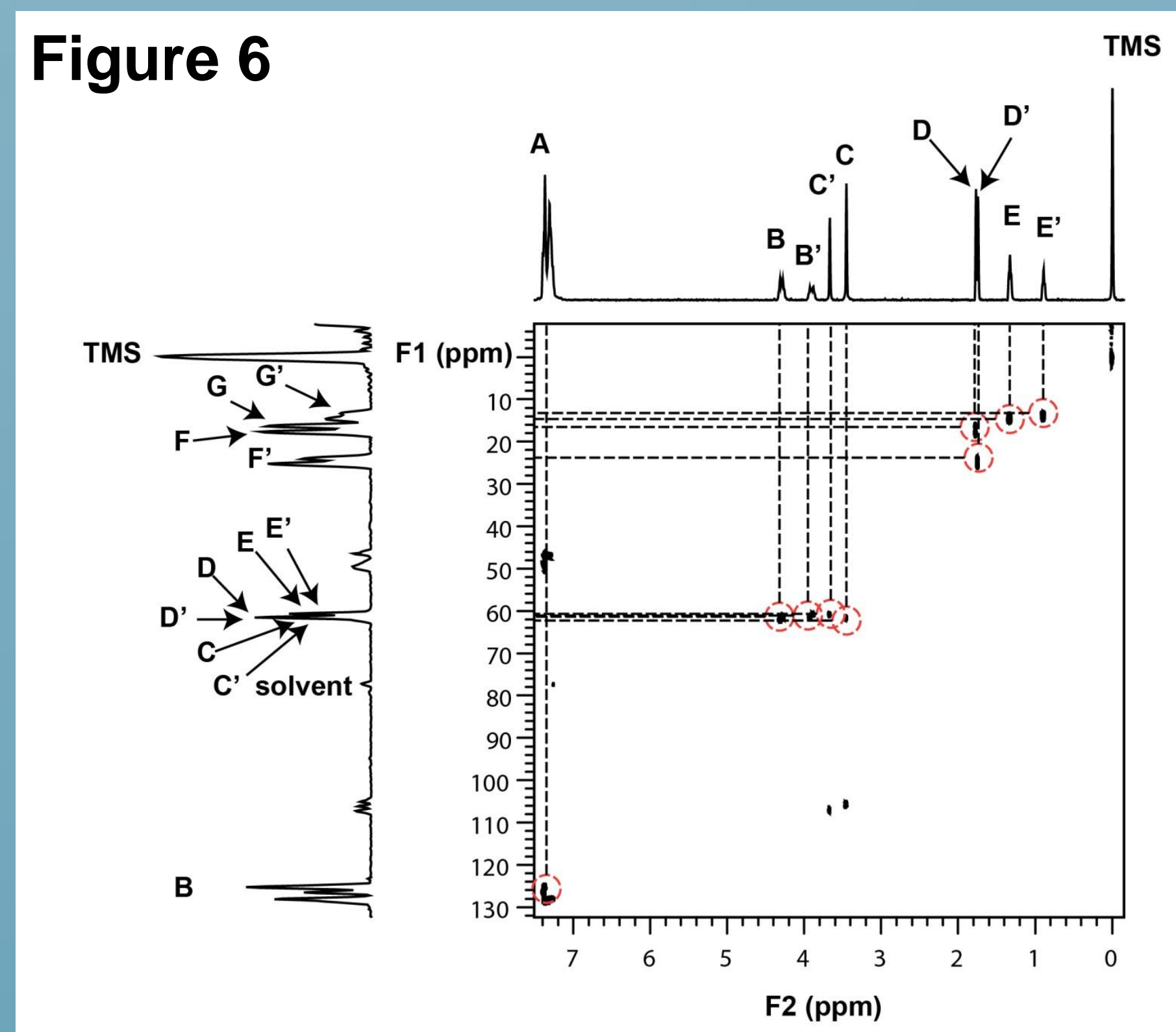


Figure 6

^{13}C DEPT NMR 1D Spectrum

The DEPT spectra series shows the hybridization states of the ^{13}C nuclei. Although the figure is not shown, the spectrum helps assign and identify the three quaternary carbons in strawberry aldehyde. This data was recorded at 500 MHz with spectral width of 23148.1 and 65536 complex points. By comparing this spectrum with Figure 5, resonance A can be assigned to C1 because it is shown in the quaternary state. This carbon is the most deshielded quaternary because it is the carbonyl carbon of the ester. The spectra also identifies the location of two additional quaternary carbons, C3 and C4, with resonances at 62 and 140 ppm, respectively.

gHMBC

The Gradient Heteronuclear Multiple Bond Correlation spectra is shown in Figure 7. This experiment shows correlations between ^1H and ^{13}C nuclei separated from each other by two or three chemical bonds. The data was recorded at 500 MHz using spectral widths of 4223.0 in the direct dimension, 23418.1 in the indirect dimension, and 1266 complex points. By using the previously assigned protons resonances, the projections in the direct dimension will align with the correlated projections in the indirect dimension, therefore distinguishing the ambiguous

quaternary carbons, C3 and C4. Although the individual protons in the aromatic region remain unresolved, C4 has multiple correlations with aromatic protons while C3 only has one correlation with an aromatic proton. Therefore, C3 must be resonance C and C4 is the most downfield part of resonance group B.

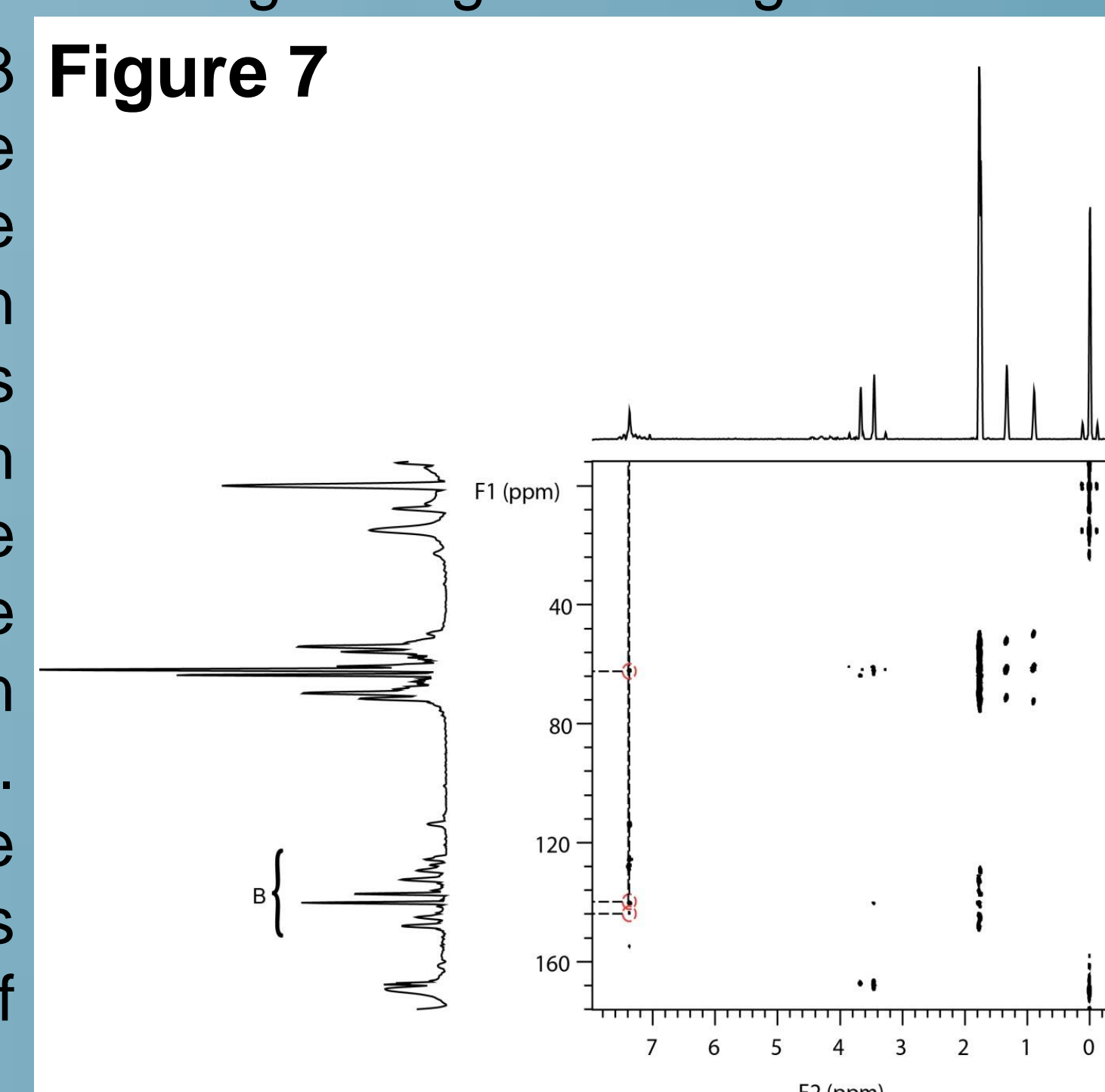


Figure 7

Results and Conclusions

The majority of the ^1H protons resonances could be assigned based on a careful analysis of fine structures and chemical shift values in the ^1H 1D NMR spectrum. The racemic mixture was also identified using the ^1H NMR spectrum while integration values could be used to determine the proportion of each diastereomer. The ^1H assignments were then used to assign the ^{13}C resonances using the 2D gHMQC spectrum. The ambiguous quaternary carbons were then identified with the DEPT and distinguished using the gHMBC.

References

"AIST:Spectral Database for Organic Compounds,SDBS." AIST:Spectral Database for Organic Compounds,SDBS. N.p., n.d. Web. 24 Oct. 2015.