

NMR Assignments For 4-Allylanisole

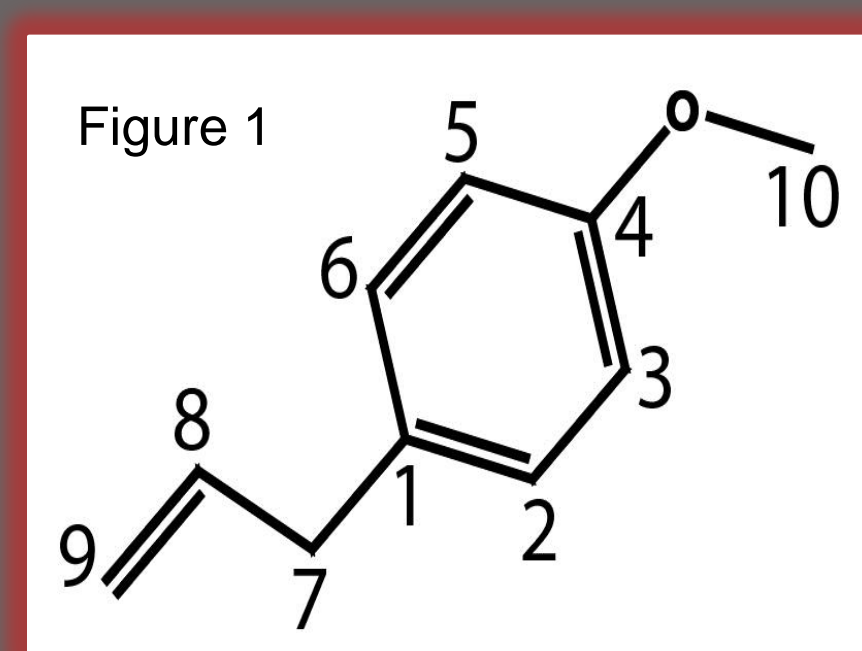
Chad Austin Service and Peter F. Flynn

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Introduction-

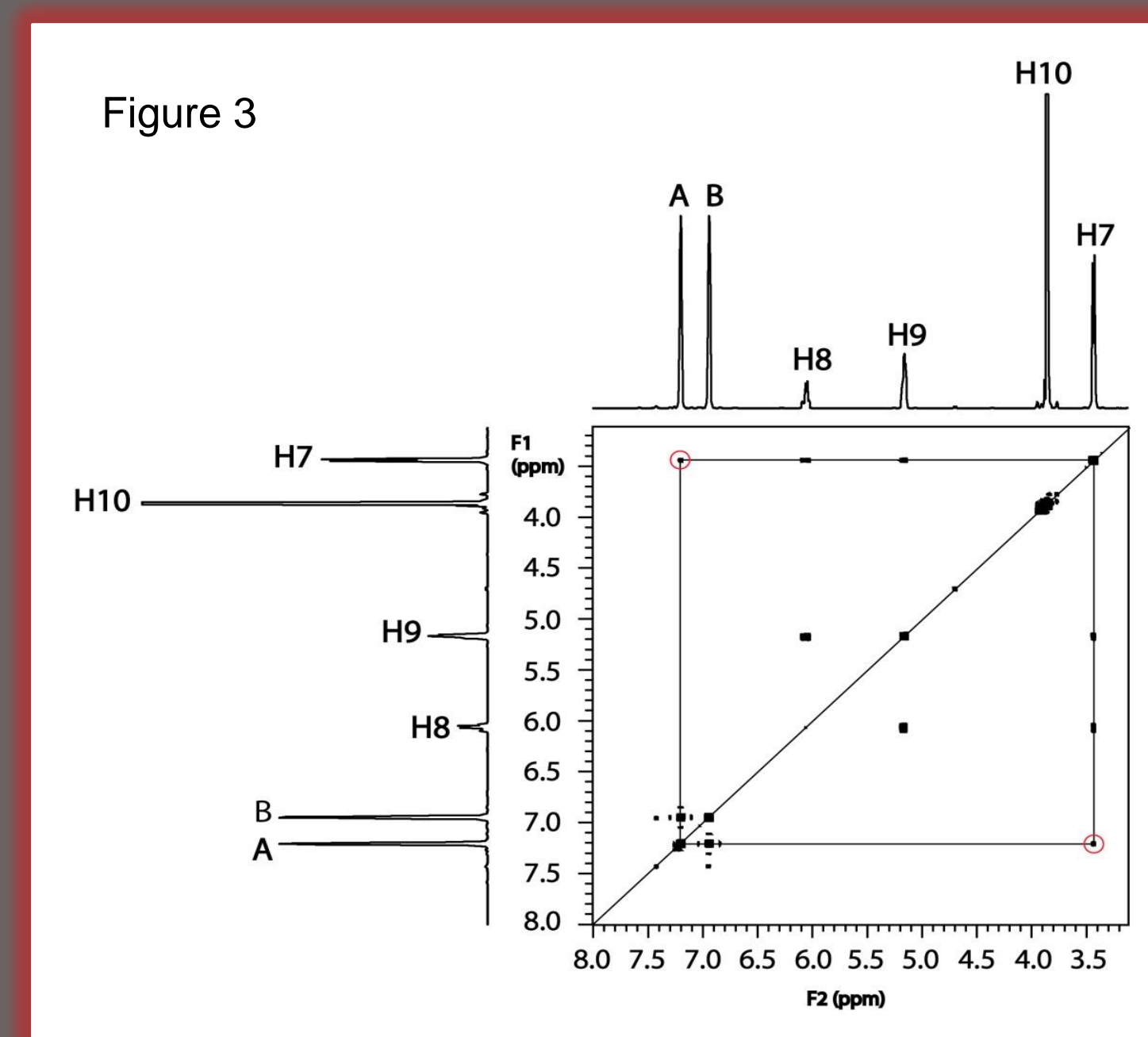
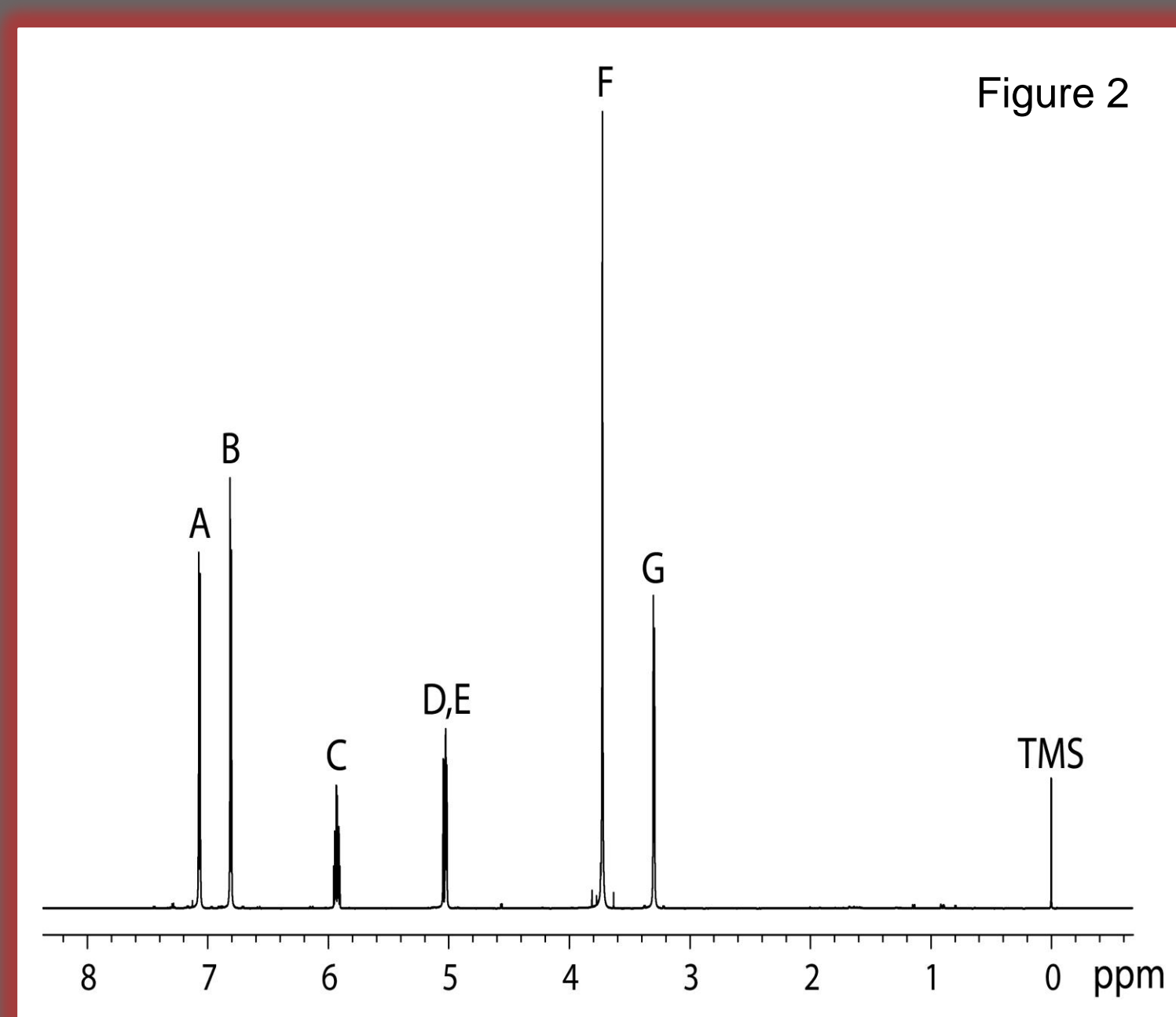
4-allylanisole, or estragole, is a naturally occurring organic compound that is found in various herbs. It is commercially used as a food additive for flavor and in the preparation of perfume fragrances. It is a phenylpropene compound that is

composed of a para-disubstituted benzene ring with methoxy and propenyl functional groups, as seen in figure 1. The molecular formula for 4-allylanisole is $C_{10}H_{12}O$. It has a molecular weight of $148.2 \text{ g}\cdot\text{mol}^{-1}$ and boiling point of 216°C . The IUPAC designation for this molecule is 1-allyl-4-methoxybenzene. The sample was prepared in deuterated chloroform with 1% TMS.



^1H NMR 1D Spectrum-

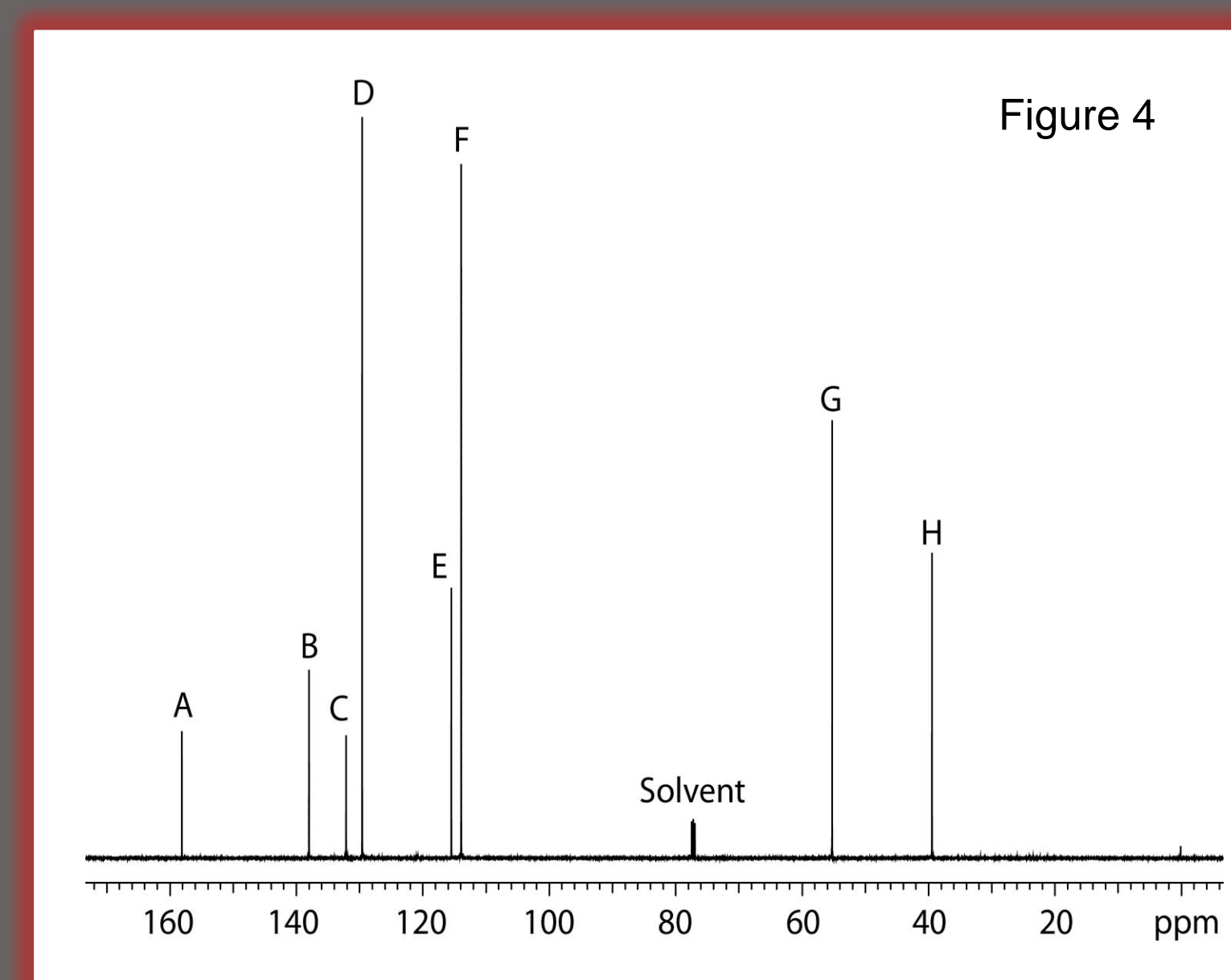
The 1D ^1H NMR of 4-allylanisole is shown in figure 2. The spectrum was recorded at 800 MHz (^1H) with a spectral width of 9842.52 Hz and 16384 complex points. Peaks A and B are downfield resonances centered around 7.07 and 6.81 ppm, respectively. These peaks correspond to the four aromatic protons. Due to the internal symmetry of the molecule H5 and H3 are chemically equivalent and will have identical chemical shifts. Similarly, H6 and H2 will be equivalent. Resolution of the H6/H2 and H5/H3 assignments will be made using the gCOSY spectrum. Peak F is a singlet positioned at 3.72 ppm. This peak will correspond to the methyl protons of carbon 10. This resonance is shifted downfield by the inductive effects of the oxygen atom and will not experience any splitting because of its isolation from other protons. There are two methylene carbons in this molecule, C7 and C9. The two protons of C7 are expected to be further upfield than the protons of C9 due to the pi bond between C9 and C8 (sp² hybridization). Peak G is an upfield doublet located at 3.30 ppm. This peak must correspond to the two methylene protons of C7 because of its upfield location and the doublet fine structure, caused by the single proton on C8. Therefore, Peaks D and E must be the remaining methylene protons on C9. Two peaks are present around 5.03 and 5.02 ppm because the protons of C9 are chemically inequivalent. The remaining resonance, peak C, must correspond to the methine proton on C8. The fine structure shows a complex multiplet, as expected for H8 due to the four nearby inequivalent protons. Therefore, peak C, at 5.93 ppm, is H8.



coupled to H7 as expected. There is also one resonance in the aromatic region that is coupled to H7. Due to the limited range of the gCOSY experiment, the only potential coupling partners are the protons attached to carbons 2 and 6. Therefore peak A is the resonance for H6 and H2, and peak B corresponds to H5 and H3.

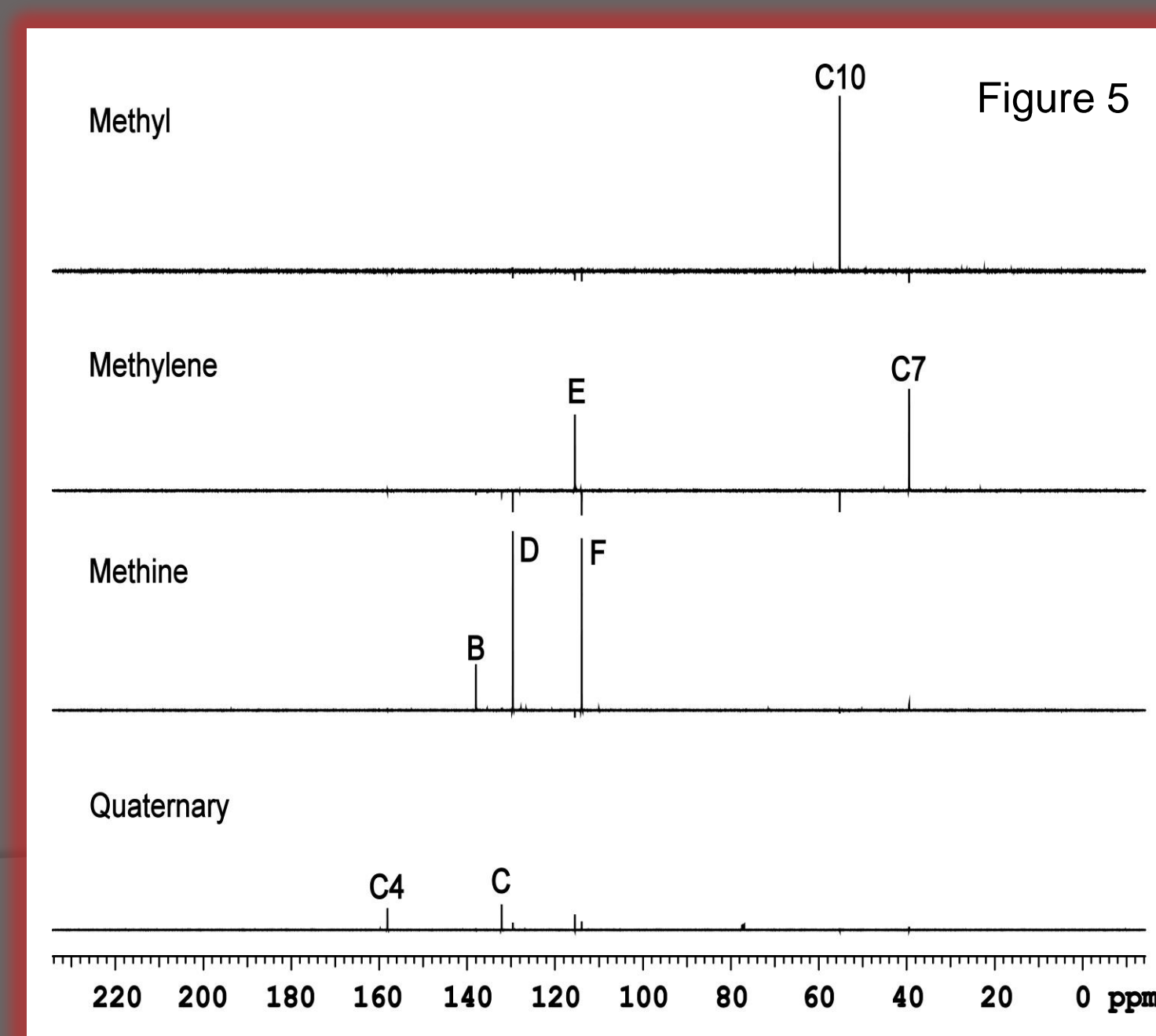
^{13}C 1D NMR Spectrum-

Figure 4 shows the results of the 1D ^{13}C NMR experiment. The spectrum was recorded at 500 MHz (^1H) with a spectral width of 31250 Hz and 32768 complex points. Peak A, which is the furthest downfield, corresponds to the quaternary carbon at position 4. This assignment is intuitive based on the aromatic nature of C4 and the proximity to the methoxy group, e.g., compare to the other quaternary carbon at position 1. Peaks G and H are the furthest upfield. Similar to the proton assignments, these peaks correspond to the methyl carbon at position 10 and the methylene at position 7. Peak G is C10, which is shifted downfield due to the inductive effect of oxygen. Therefore peak H is C7. The remaining peaks, B through F, will be assigned using the ^{13}C DEPT and gHMQC data.



^{13}C DEPT Spectra-

Figure 5 shows the sub-spectrum series of a ^{13}C DEPT experiment. These spectra were recorded at 500 MHz (^1H) with a spectral width of 31250 Hz and 32768 complex points. The DEPT experiment shows the hybridization states of the ^{13}C nuclei in 4-allylanisole. The previous assignments for C10 and C7 are confirmed by this spectrum. Peak E, which is the remaining methylene, must be C9. Peak C, the upfield quaternary carbon, corresponds to C1. There are three remaining peaks, corresponding to the methine resonances. Peak B is the furthest downfield and is expected to be the aliphatic methine carbon at position 8. This means that peaks D and F correspond to C6/C2 and C5/C3, respectively. The ambiguities in the methine carbons will be resolved using the HMQC data.

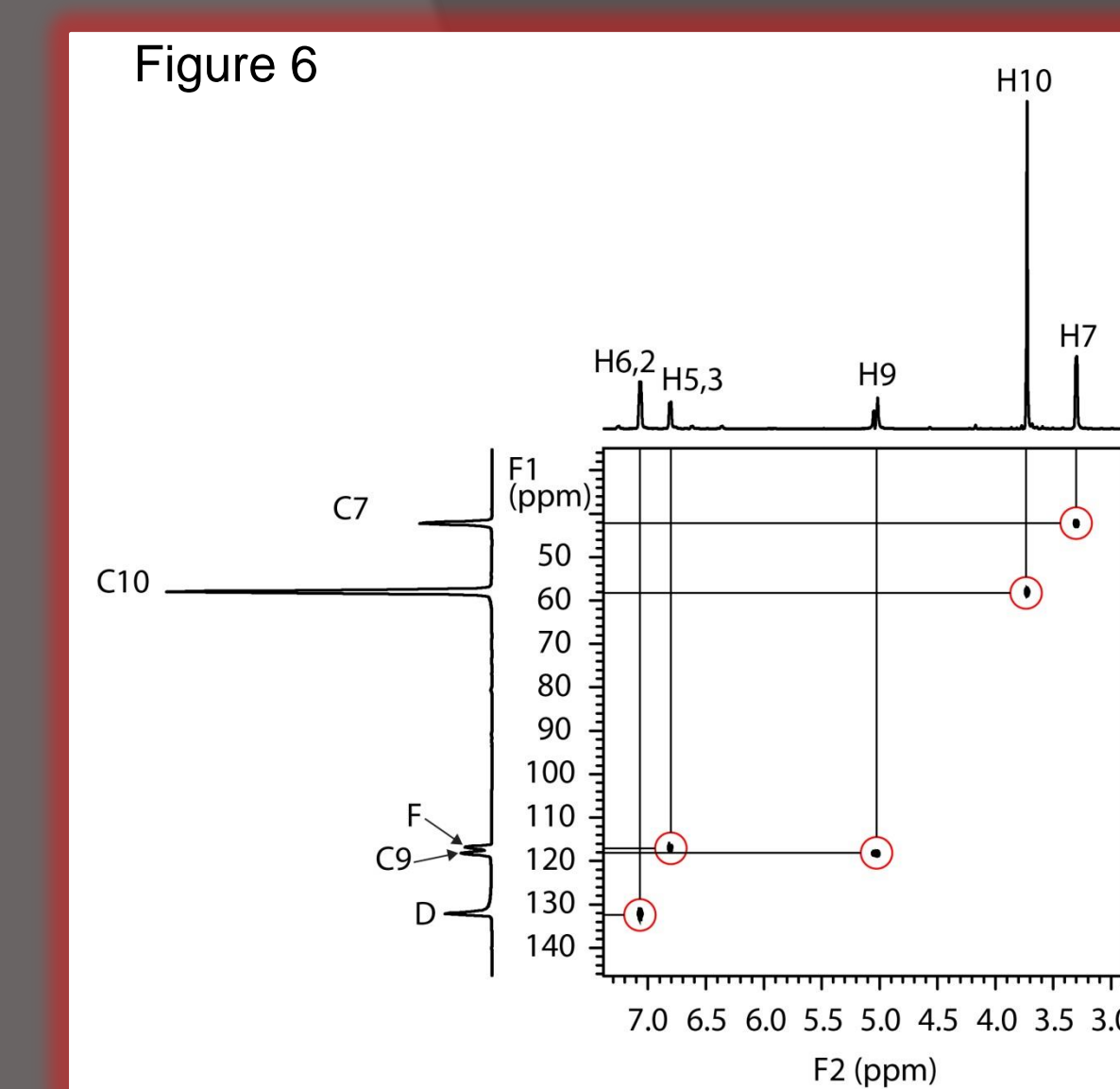


gCOSY Spectrum-

The gCOSY spectrum for this compound is shown in figure 3. This spectrum was recorded at 800 MHz (^1H) with a spectral width of 9842.52 Hz and 4096 complex points. By analyzing the off-diagonal peaks in the gCOSY spectrum, the ambiguities between peaks A and B in the ^1H NMR data can be resolved. The methylene protons on C7 should be coupled to the protons within two or three chemical bonds. H8 and H9 are

gHMQC Spectrum-

The two-dimensional spectrum for 4-allylanisole is shown in figure 6. This spectrum was recorded at 800 MHz (^1H) with a spectral width of 7530.12 Hz in the direct ($^1\text{H}/\text{F2}$) dimension and 34188 Hz in the indirect ($^{13}\text{C}/\text{F1}$) dimension. The ^1H assignments that have already been made are mapped to the F2 projection of the gHMQC. The correlations present in the gHMQC spectrum resolve the ambiguities in the methine carbons, particularly peaks F and D. Peak F correlates to peak H5/H3 in the proton dimension; therefore, peak F corresponds to the chemically equivalent carbons C5 and C3. Similarly, peak D is correlated to H6/H2. Peak D therefore corresponds to the carbons at positions 6 and 2. This completes the carbon assignments for 4-allylanisole.



Results and Conclusion-

Using the experiments described above, complete proton and carbon assignments have been made for 4-allylanisole. ^1H resonances were assigned using the 1D ^1H NMR and gCOSY experiments. ^{13}C resonances were assigned by inspection of the ^{13}C 1D NMR, ^{13}C DEPT, and gHMQC experiments. The following is a complete list of all ^1H and ^{13}C chemical shift values (ppm) for this molecule.

^1H NMR Assignments (ppm)

H6/H2	H5/H3	H8	H9	H10	H7
7.07	6.81	5.93	5.03/ 5.02	3.72	3.30

^{13}C NMR Assignments (ppm)

C4	C8	C1	C6/C2	C9	C5/C3	C10	C7
158.12	138.01	132.15	129.60	115.49	113.94	55.25	39.45

References and Acknowledgments-

Claridge, Timothy D. *High-Resolution NMR Techniques in Organic Chemistry*. Second ed. Oxford: Elsevier, 2009. Print.

"AIST:RIO-DB Spectral Database for Organic Compounds,SDBS." *AIST:RIO-DB Spectral Database for Organic Compounds,SDBS*. N.p., n.d. Web. 22 May 2013. <http://sdb.sdb.sdb.aist.go.jp/sdb/cgi-bin/direct_frame_top.cgi>.

"AIST:RIO-DB Spectral Database for Organic Compounds,SDBS." *AIST:RIO-DB Spectral Database for Organic Compounds,SDBS*. N.p., n.d. Web. 22 May 2013. <http://sdb.sdb.sdb.aist.go.jp/sdb/cgi-bin/direct_frame_top.cgi>.