

### Limona Ketone NMR Analysis:

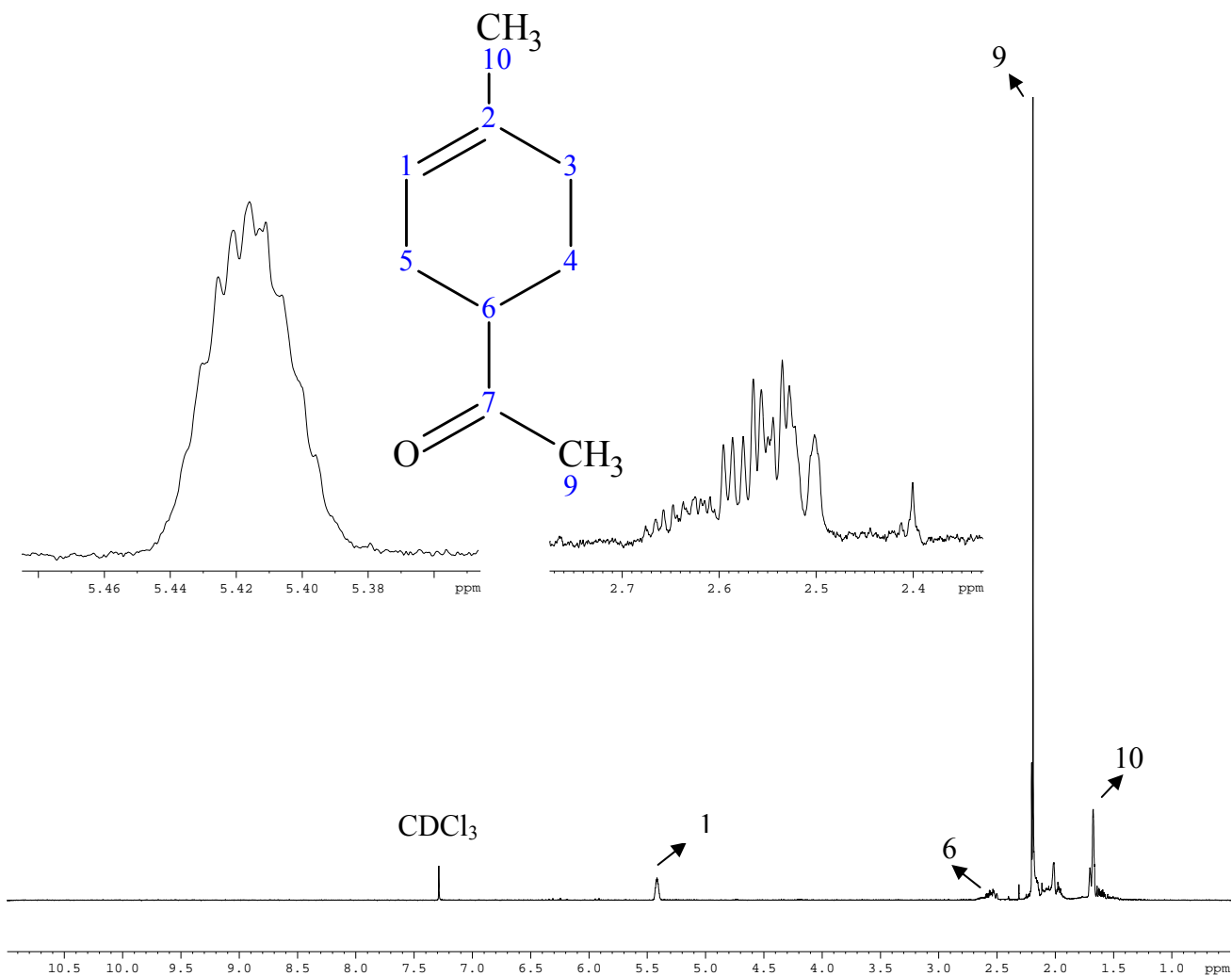
The  $^1\text{H}$ -NMR of Limona Ketone elucidates the structure and successful synthesis of target molecule very well.  $^1\text{H}$ -NMR analysis of the product shows the requisite unsaturated proton at 5.3 ppm and the two methyl groups at 1.65 and 2.15 ppm in both experimental (Fig. S1a) and simulated (Fig. S1b) spectra. Splitting at 1.65 and 2.16 ppm shows the presence of the 5-acetyl-1-methylcyclohexane Diels-Alder *meta* isomer. The peak at 7.3 ppm in the experimental spectrum is attributed to the  $\text{CDCl}_3$  solvent. In the  $^{13}\text{C}$ -NMR spectrum, the major isomer's unsaturated carbons appear at 119 and 134 ppm, with the ketone carbon found at 210 ppm. The ring carbons and methyl groups are found between 23 and 50 ppm, with the experimental data (Fig. S2a) matching the simulation (Fig. S2b) nicely. Finally, the major and minor isomers were structurally elucidated by HMBC proton-carbon long-range coupling experiments in the NMR laboratory. The ratio of Limona Ketone to the 5-acetyl-1-methylcyclohexane isomer was determined to be approximately 3:1 by integration of the methyl proton peaks. HMBC analysis initially shows coupling of the 1-methyl protons (Carbon 10) at 1.64 ppm in the 1D  $^1\text{H}$ -NMR with both isomer's vinylic tertiary  $^{13}\text{C}$ -NMR carbons (Carbon 1) at 119 and 121 ppm (Figure S3a). The major isomer's methyl protons couple with the major vinylic tertiary carbon peak seen in the spectrum at 119 ppm while the minor proton peak couples with the minor vinylic  $^{13}\text{C}$ -NMR peak at 121 ppm. After determining which tertiary vinylic carbon (Carbon 1) was associated with the major compound, long-range coupling (Figure S3b) shows that the 119 ppm major tertiary vinylic carbon couples with the methine proton on the acetyl bound carbon (Carbon 6). The minor vinylic carbon does not show this coupling as it is out of range, three carbons away. It was also noted that the minor isomer's proton, found adjacent to the acetyl substituent, shows a slight coupling with the 134 ppm quaternary vinylic carbon. This proves that the minor isomer has the acetyl substituent 2 carbons away from quaternary unsaturated carbon in the *meta* position while the major product has a *para* substituted acetyl group to C-1. From this analysis, we have drawn the conclusion that the major product is Limona Ketone while the minor product is the *meta* substituted isomer, 4-acetyl-2-methylcyclohexene.

$^1\text{H-NMR}$  (ppm): 1.65 (s, 3H), 2.0 (m, 6H), 2.15 (s, 3H), 2.52 (m, 1H), 5.42 (m, 1H),

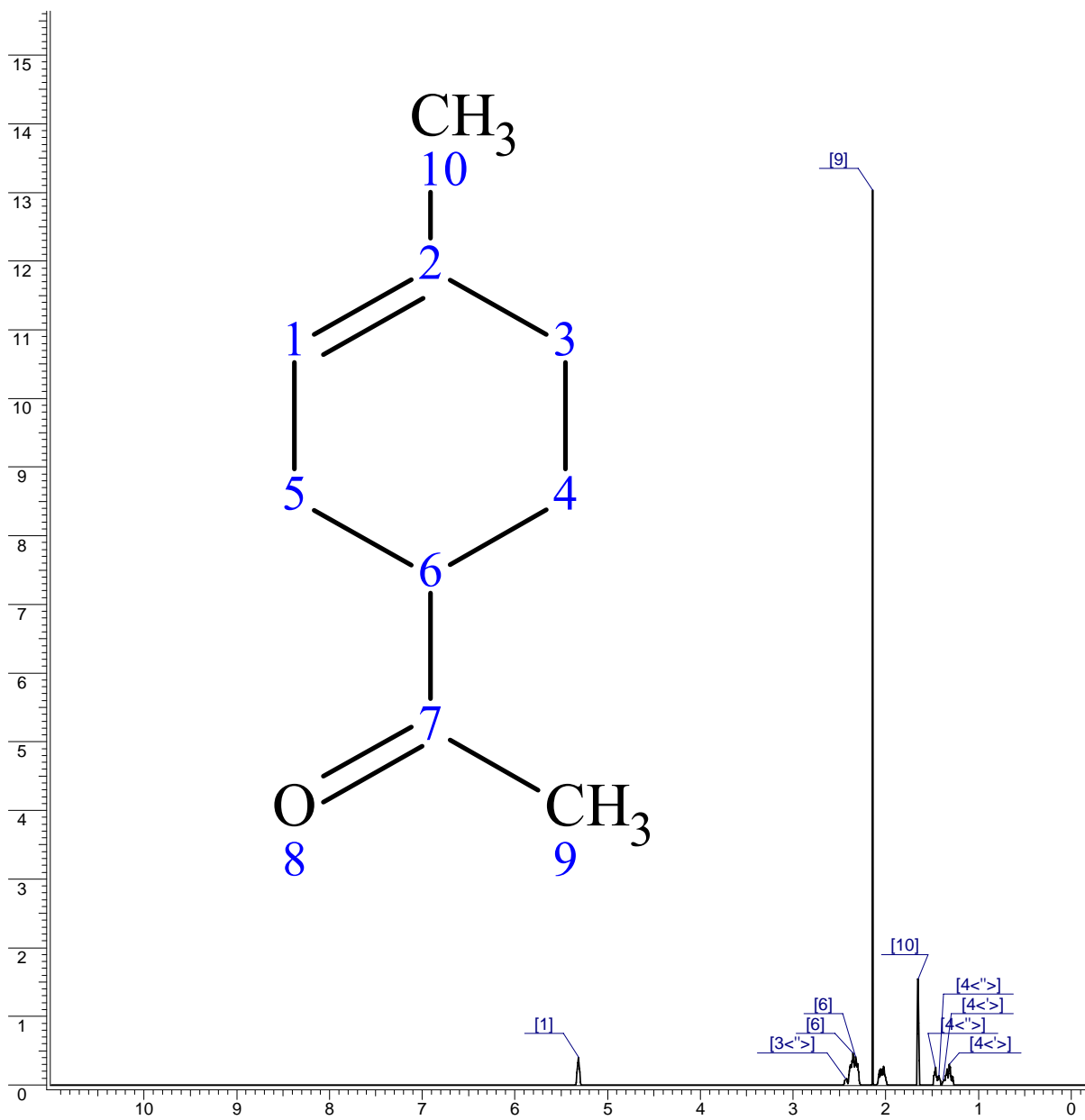
$^1\text{H-NMR}$  Simulation (ppm): 1.39 (m, 2H), 1.65 (s, 3H), 2.06 (m, 2H), 2.14 (s, 3H), 2.35 (m, 1H), 2.43 (m, 2H), 5.31 (s, 1H),

$^{13}\text{C-NMR}$  (ppm): 23.3, 24.8, 26.9, 29.4, 47.2, 47.8, 119.2, 133.8, 211.8.

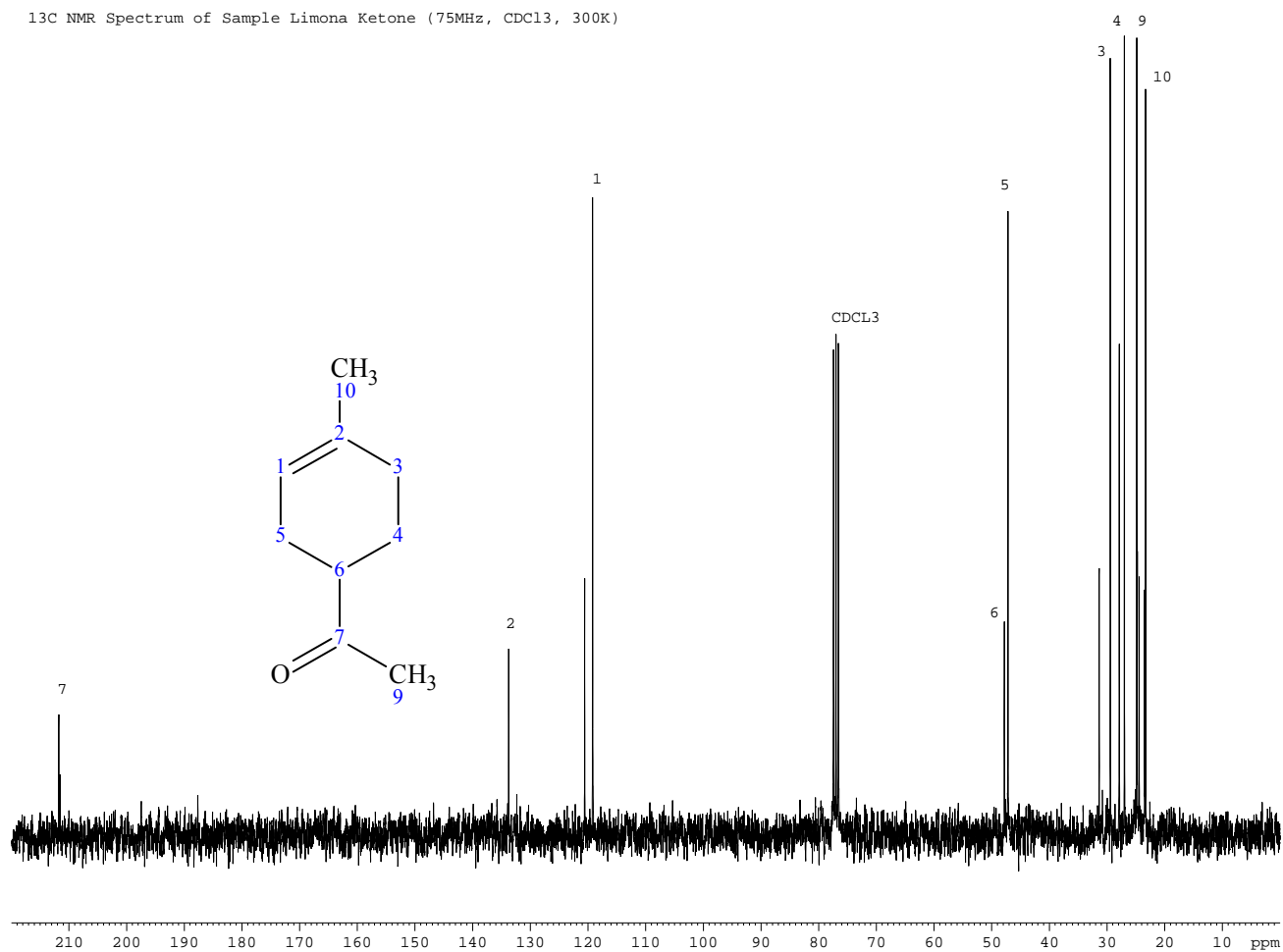
$^{13}\text{C-NMR}$  Simulation (ppm): 23.66, 27.51, 29.14, 29.51, 36.35, 47.38, 118.31, 134.29, 210.44.



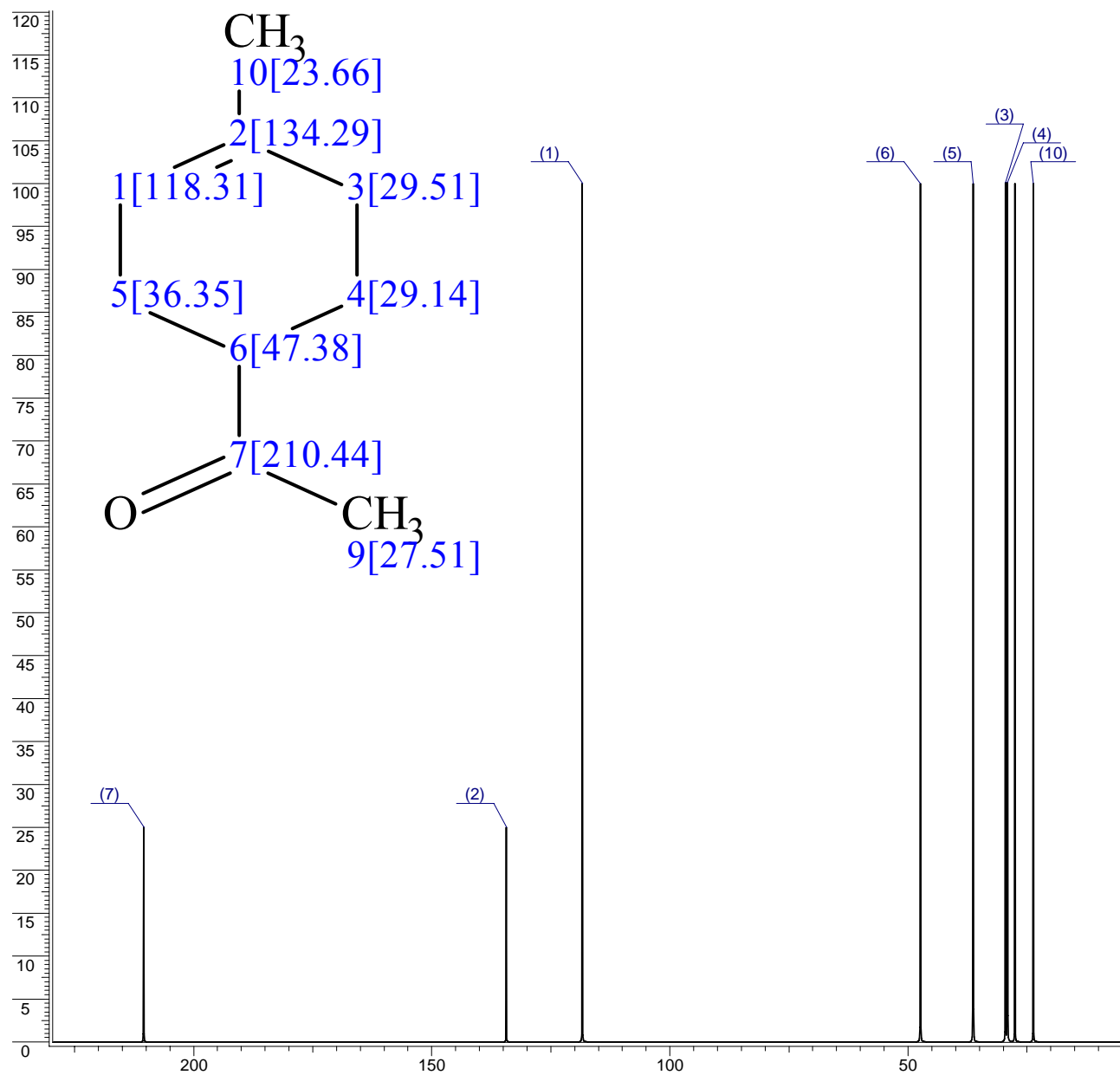
**Figure S1a:** Limona Ketone  $^1\text{H-NMR}$  Spectrum



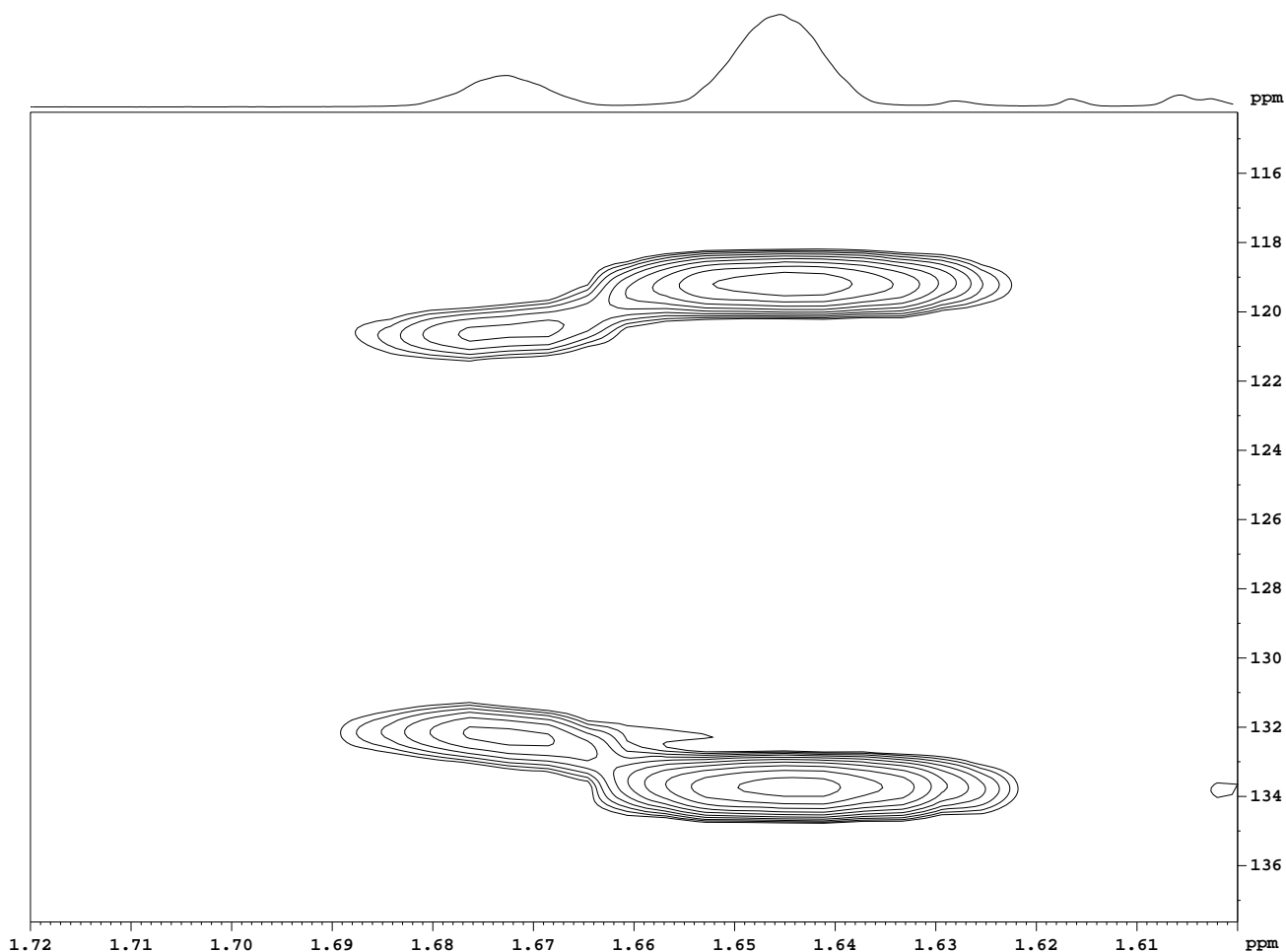
**Figure S1b:** Limona Ketone <sup>1</sup>H-NMR Spectrum Simulation



**Figure S2a:** Limona Ketone <sup>13</sup>C-NMR Spectrum

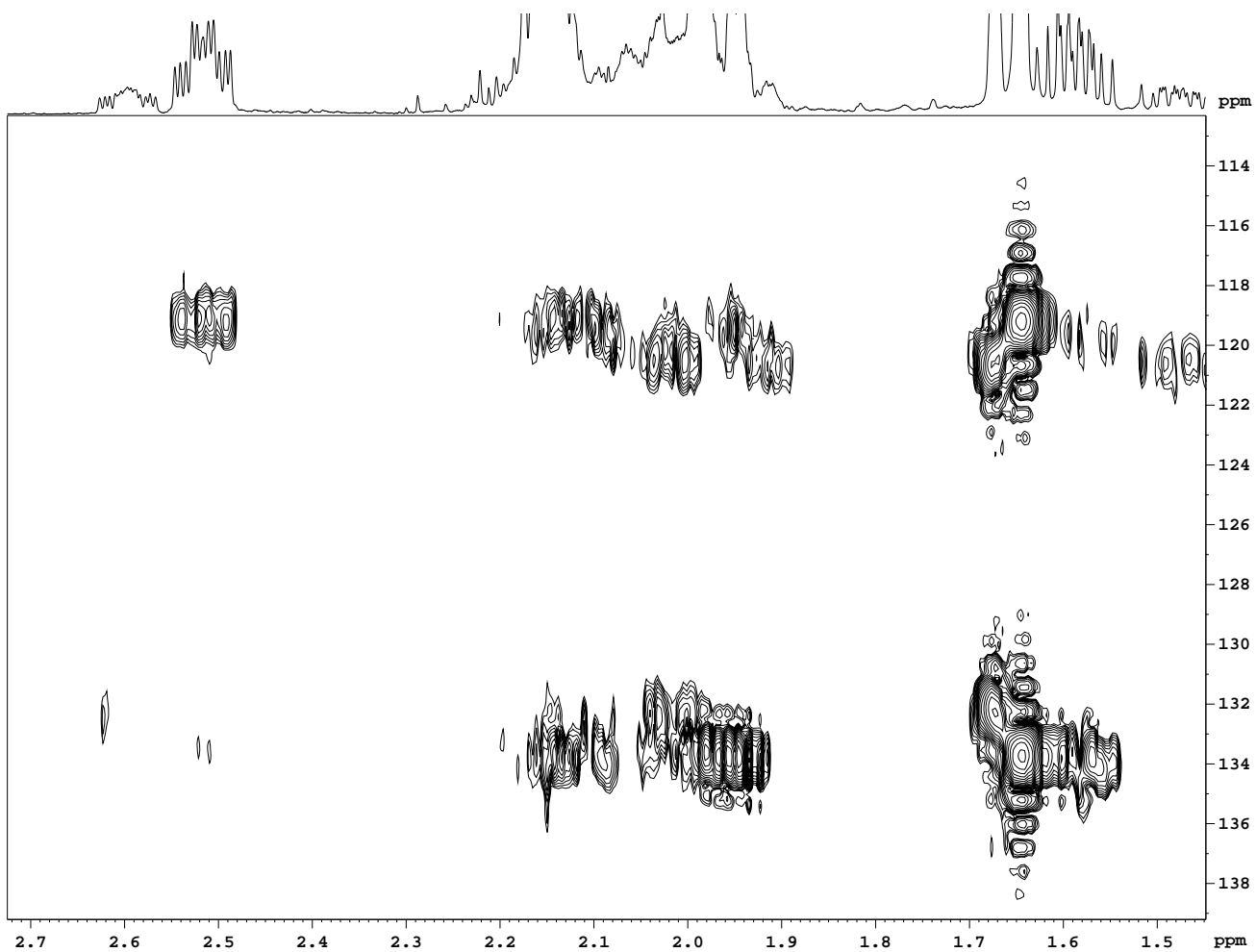


**Figure S2b:** Limona Ketone  $^{13}\text{C}$ -NMR Spectrum Simulation



**Figure S3a:** Heteronuclear Multiple Bond Correlation Spectrum of Limona Ketone

Experiment Plot 1. Coupling between 1-Methyl protons (Carbon 10) (X axis at 1.645 and 1.675 ppm) with vinylic carbons (Carbon 1 and 2) (Y axis). The tertiary vinylic carbon (Carbon 1) is near 120 ppm, with the major product at 119 ppm and the minor product at 221 ppm.



**Figure S3b:** Heteronuclear Multiple Bond Correlation Spectrum of Limona Ketone Experiment Plot 2. The tertiary acetyl carbon (Carbon 6) from the major product at 119 ppm couples strongly to the proton on the methine carbon (Carbon 6) at 2.5 ppm, while the minor product acetyl carbon at 121 ppm shows no coupling because it is out of range (3 carbons distant instead of 2 for the major product).