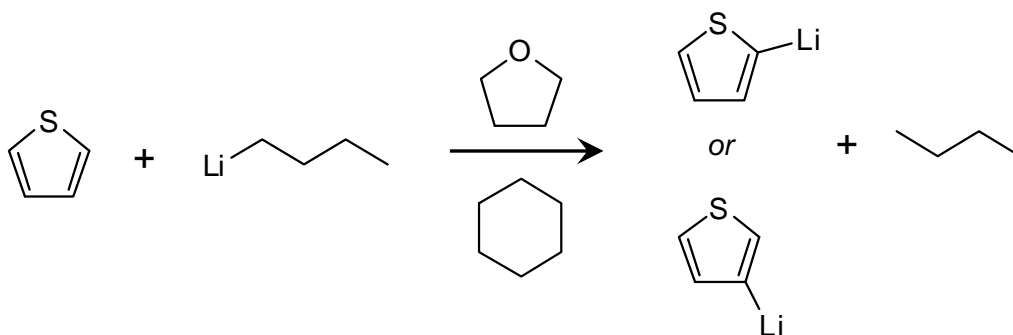


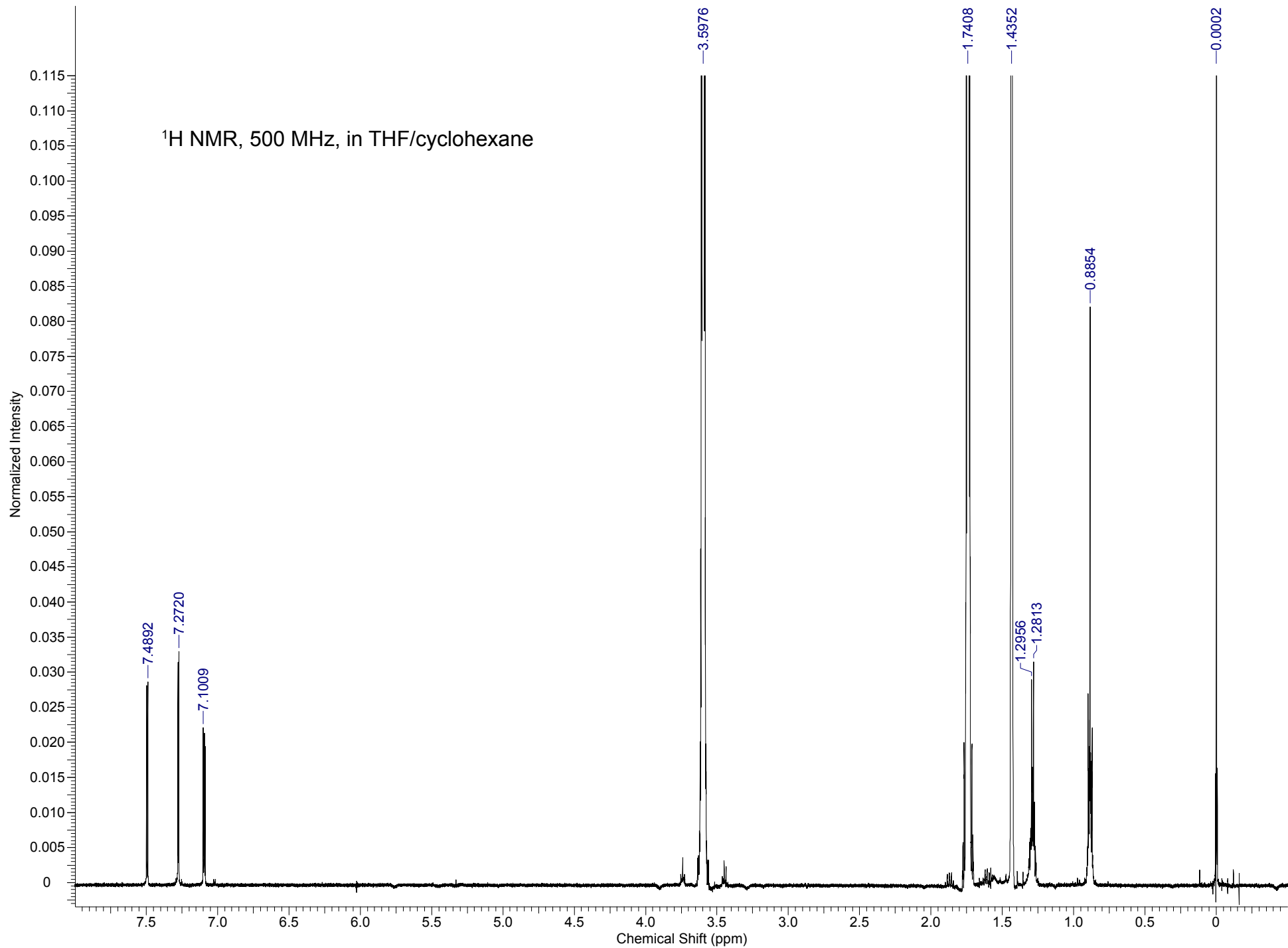
**Problem Set 5**  
Heteronuclear Correlation Spectroscopy  
**Due:** Wednesday, October 31

1. When thiophene is treated with *n*-butyllithium, it can be deprotonated to form either 2-thiophenyllithium or 3-thiophenyllithium. Jen Green (Hoye group) monitored this process directly by NMR in ordinary (not deuterated) tetrahydrofuran (THF) as the NMR solvent, and using TMS as an internal reference.  $^1\text{H}$ ,  $^{13}\text{C}$ , HMQC and HMBC spectra of the thiophenyllithium product are shown on the following pages. These spectra also contain cyclohexane from the *n*-butyllithium solution, and butane formed by proton transfer to the *n*-butyllithium.

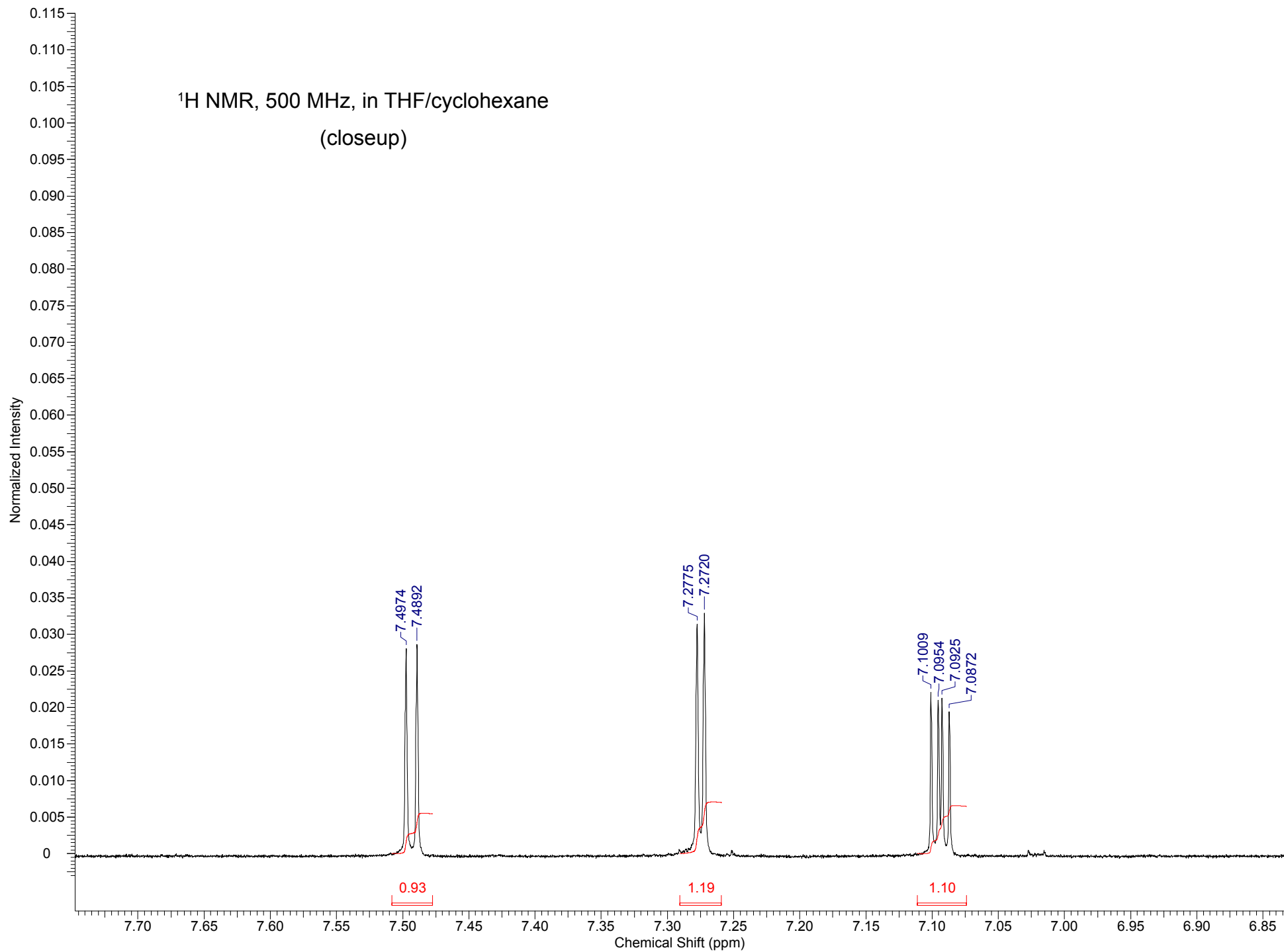


- Identify *all* peaks in the  $^1\text{H}$  and  $^{13}\text{C}$  NMRs. You don't need to assign coupling constants, but what molecule does each peak come from?
- Which thiophenyllithium was formed?
- Assign chemical shifts to each of the proton and carbon atoms in your proposed thiophenyllithium.
- The HMBC spectrum has some peaks that don't seem to line up with  $^1\text{H}$  NMR peaks on the horizontal axis. Why not?

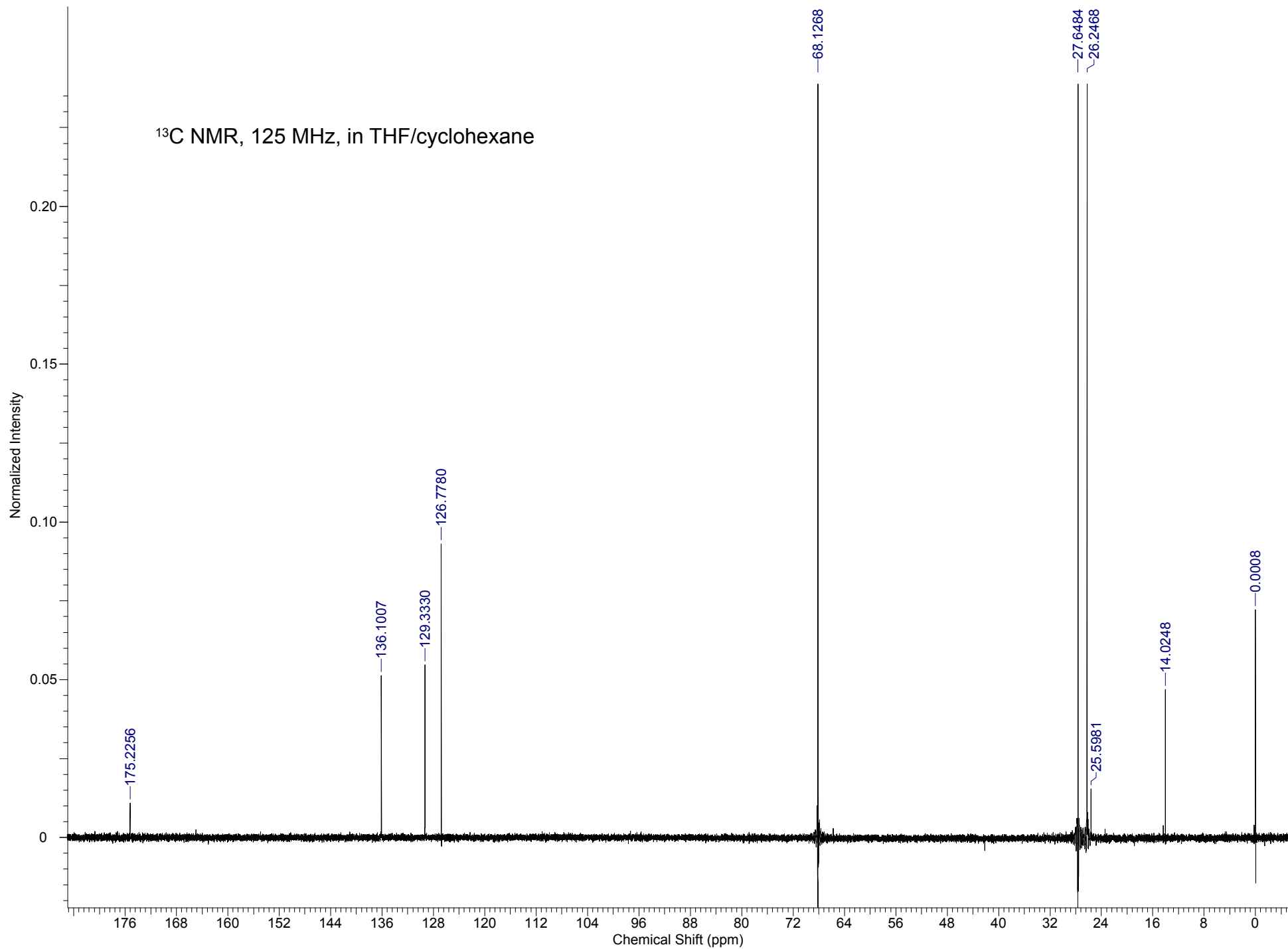
<sup>1</sup>H NMR, 500 MHz, in THF/cyclohexane



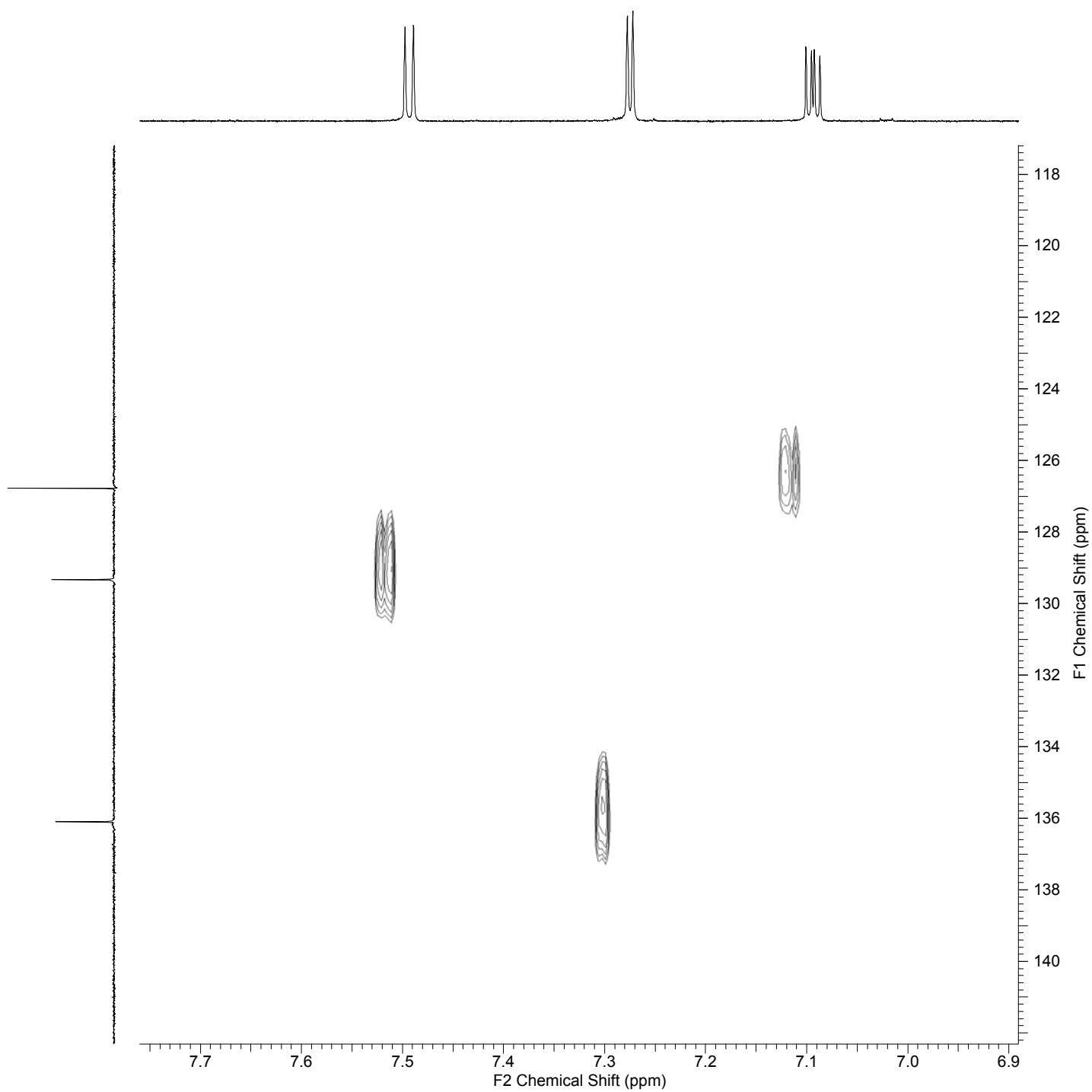
<sup>1</sup>H NMR, 500 MHz, in THF/cyclohexane  
(closeup)



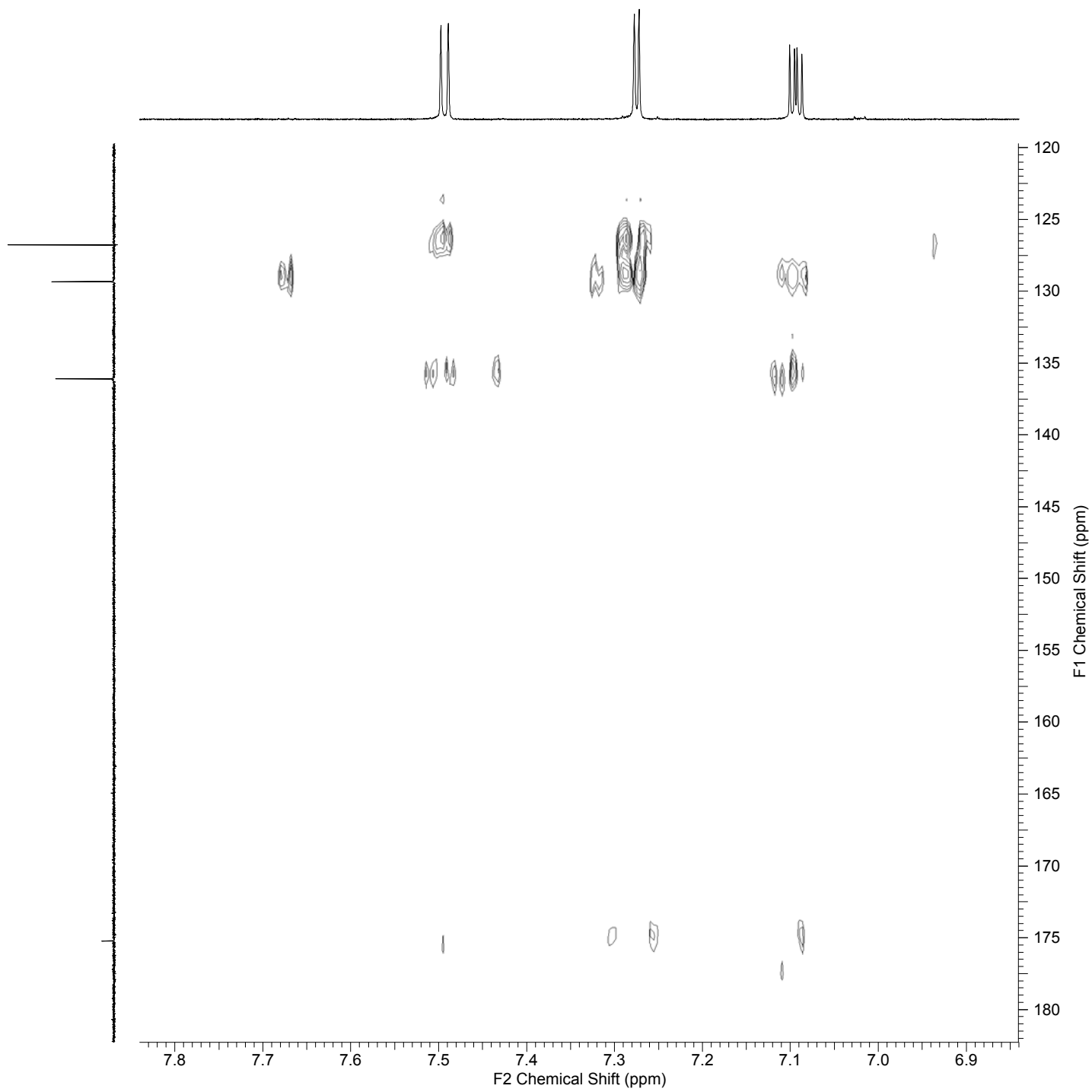
<sup>13</sup>C NMR, 125 MHz, in THF/cyclohexane



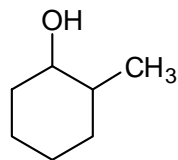
$^1\text{H}$ - $^{13}\text{C}$  HMQC, in THF/cyclohexane  
(closeup)



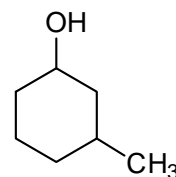
$^1\text{H}$ - $^{13}\text{C}$  HMBC, in THF/cyclohexane  
(closeup)



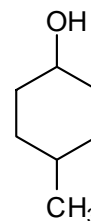
2. In the In-Class Exercise titled "Heteronuclear Correlations in HMQC", you used  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$ - $^1\text{H}$  COSY, and  $^1\text{H}$ -decoupled HMQC spectra to characterize an unknown methylcyclohexanol. In this problem, you will do it again.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$ - $^1\text{H}$  COSY, and  $^1\text{H}$ -decoupled HMQC spectra for *another*



2-methyl-cyclohexanol



3-methyl-cyclohexanol



4-methyl-cyclohexanol

methylcyclohexanol follow this page. To restate the instructions from the In-Class Exercise:

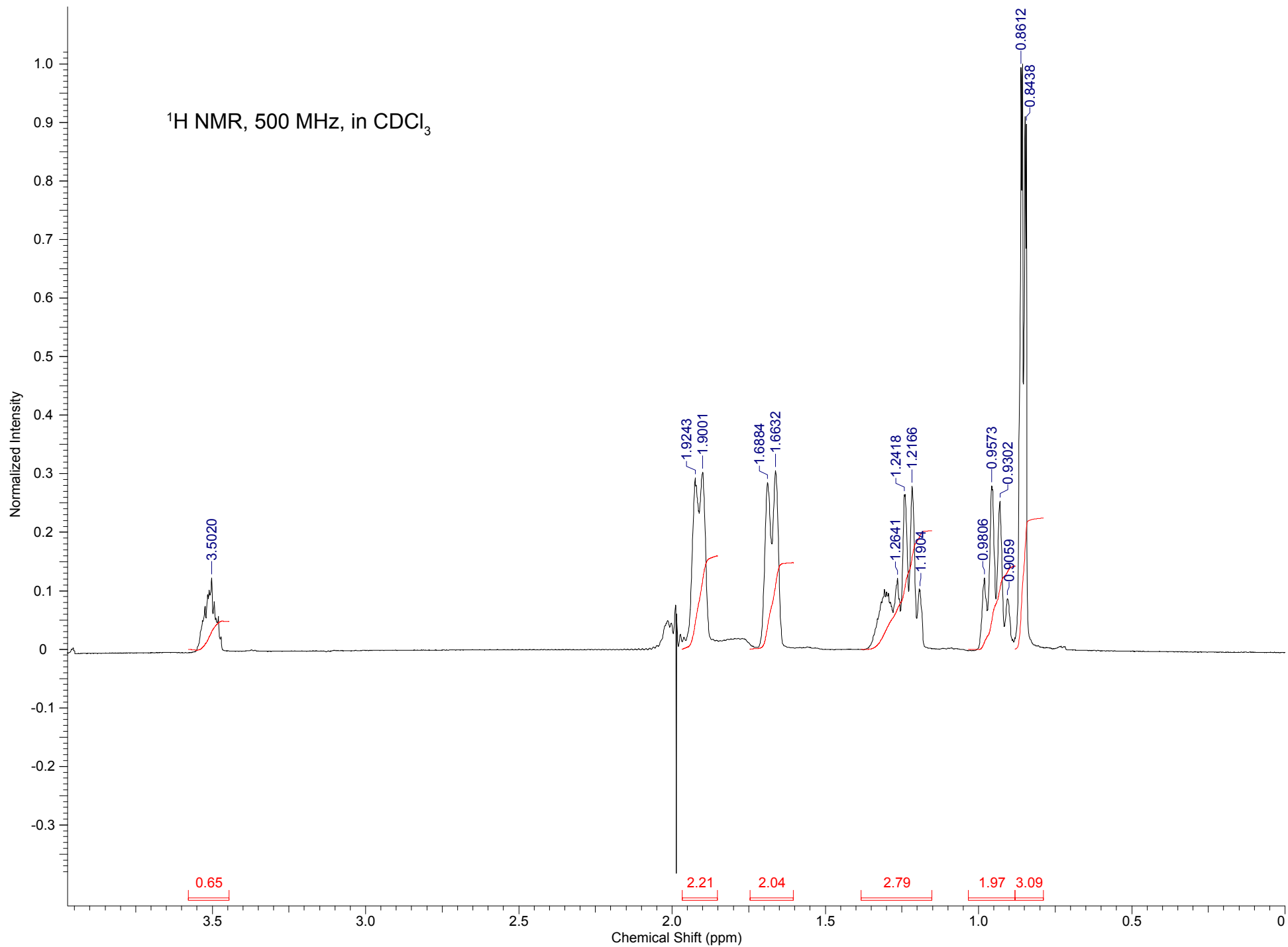
- a. Assign chemical shifts to each of the protons and carbons in one of the three structures shown above. Do not worry about assigning *cis*- or *trans*- to the two substituents just yet; simply locate the substituents on the ring. Also, in cases where two protons are attached to the same carbon, don't worry about which one is which (axial vs. equatorial, up vs. down) in this part of the problem.

*Note:* It looks as though one  $^1\text{H}$ - $^{13}\text{C}$  correlation is missing from the HMQC; I think you can deduce which one is missing, and what H and C it belongs to.

The large cross-shaped peak in the HMQC spectrum is an experimental artifact. Please ignore it.

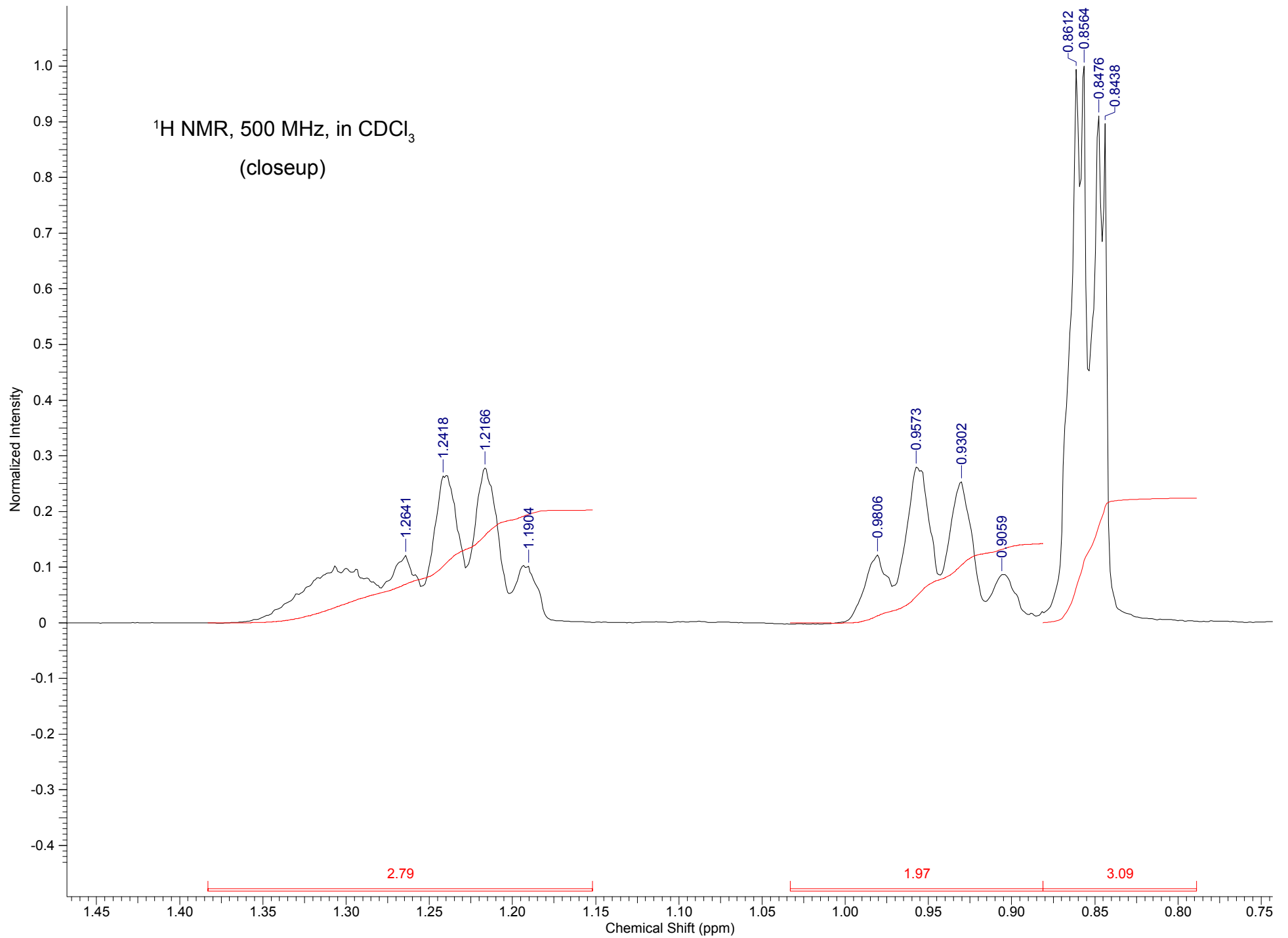
- b. Is the molecule *cis*- or *trans*-disubstituted? Can you tell?

$^1\text{H}$  NMR, 500 MHz, in  $\text{CDCl}_3$

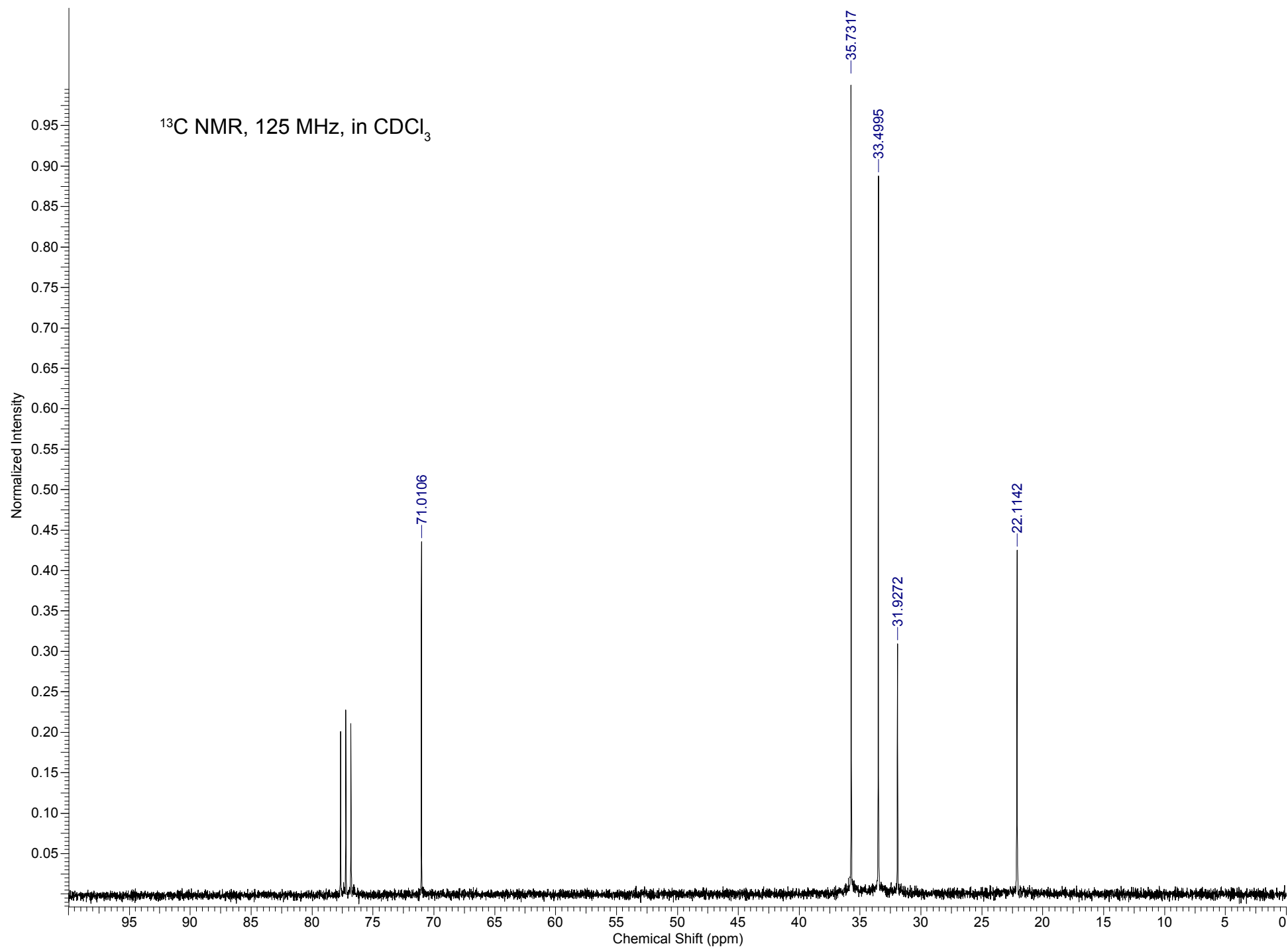




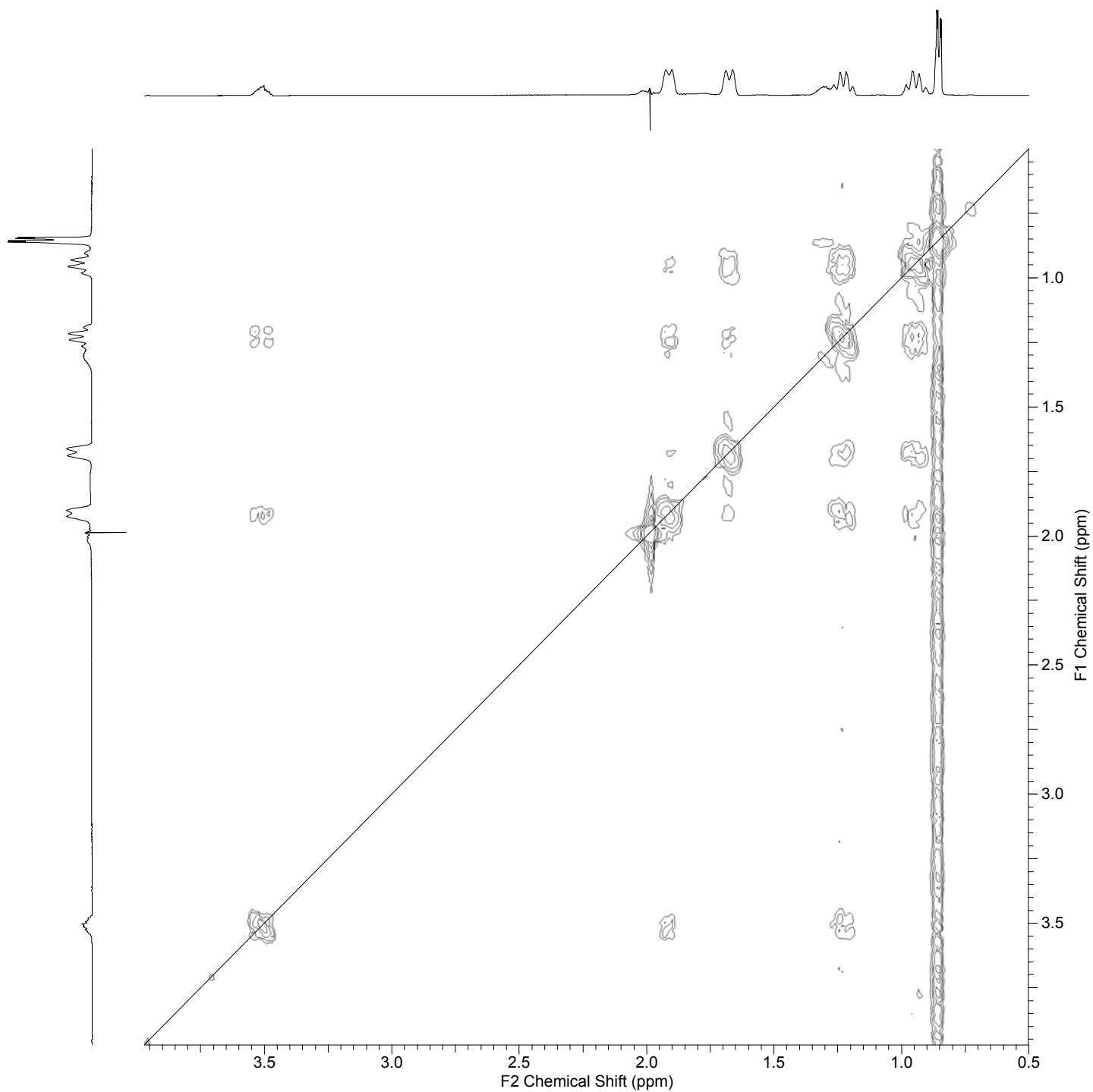
$^1\text{H}$  NMR, 500 MHz, in  $\text{CDCl}_3$   
(closeup)



$^{13}\text{C}$  NMR, 125 MHz, in  $\text{CDCl}_3$



$^1\text{H}$ - $^1\text{H}$  COSY, 500 MHz, in  $\text{CDCl}_3$



$^1\text{H}$ - $^{13}\text{C}$  HMQC, 500/125 MHz, in  $\text{CDCl}_3$

