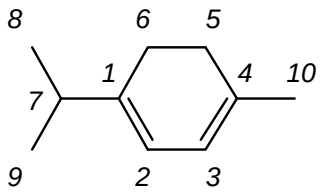
Chemistry 4361/8361 Wednesday, October 17

In-Class Exercise:
Multiple-Bond Correlations in HMBC

The ^{1}H, ^{13}C, ^{1}H-^{13}C HMQC and ^{1}H-^{13}C HMBC spectra shown on the following pages are of α-terpinene. α-Terpinene is achiral, and the central ring is nearly planar. As a result, all six H_8 & H_9 protons are equivalent, as are C_8 and C_9; the two H_5 protons are nearly equivalent; and the two H_6 protons are nearly equivalent. Assign all of the resonances in the ^{1}H and ^{13}C spectrum to a nucleus in α-terpinene, by filling in the chart below:



α-terpinene

^{1}H resonances:

δ (ppm)	Name(s) of hydrogen(s)
5.65	
5.61	
2.31	
2.14	
2.11	
1.79	
1.05	

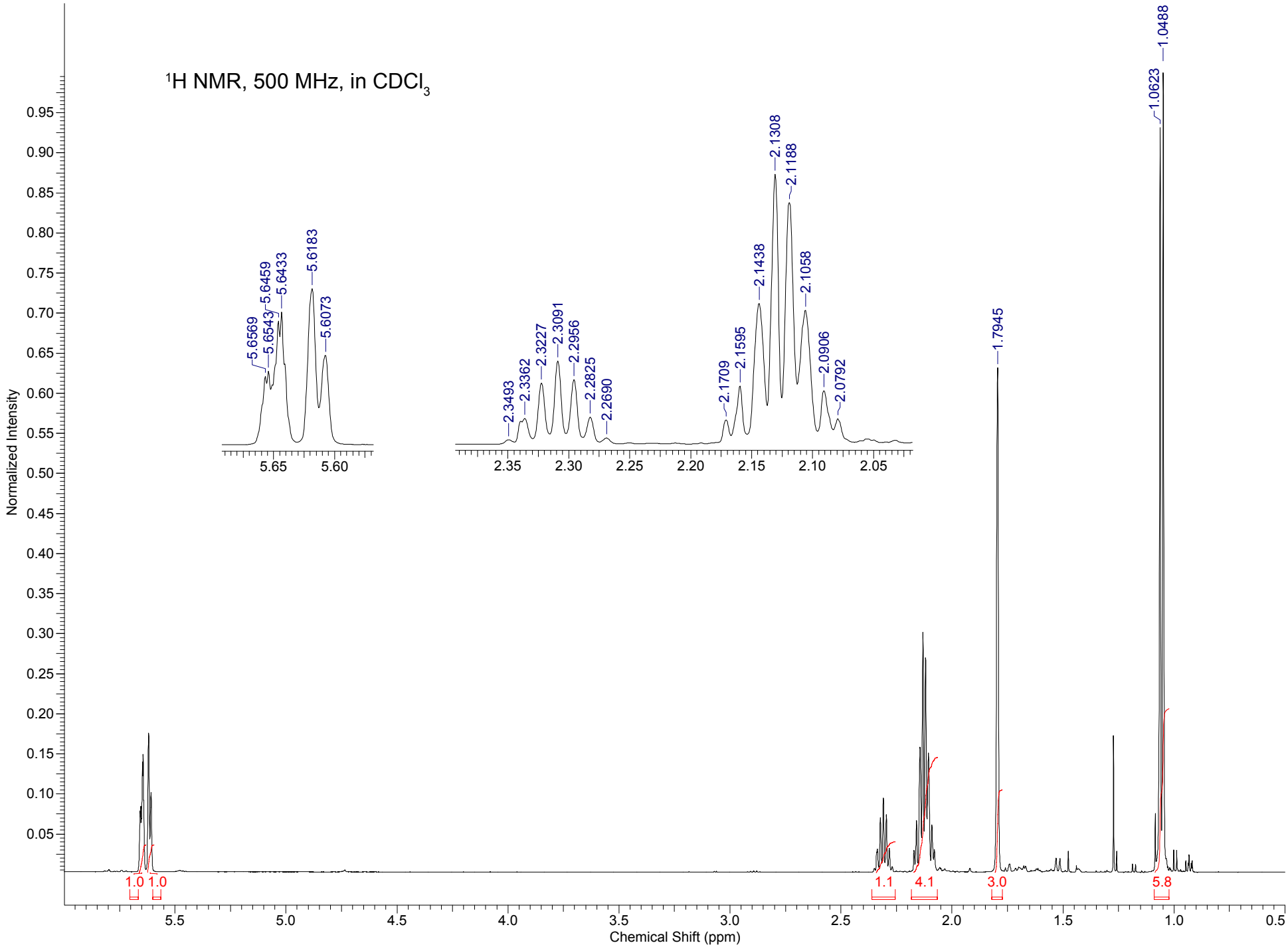
^{13}C resonances:

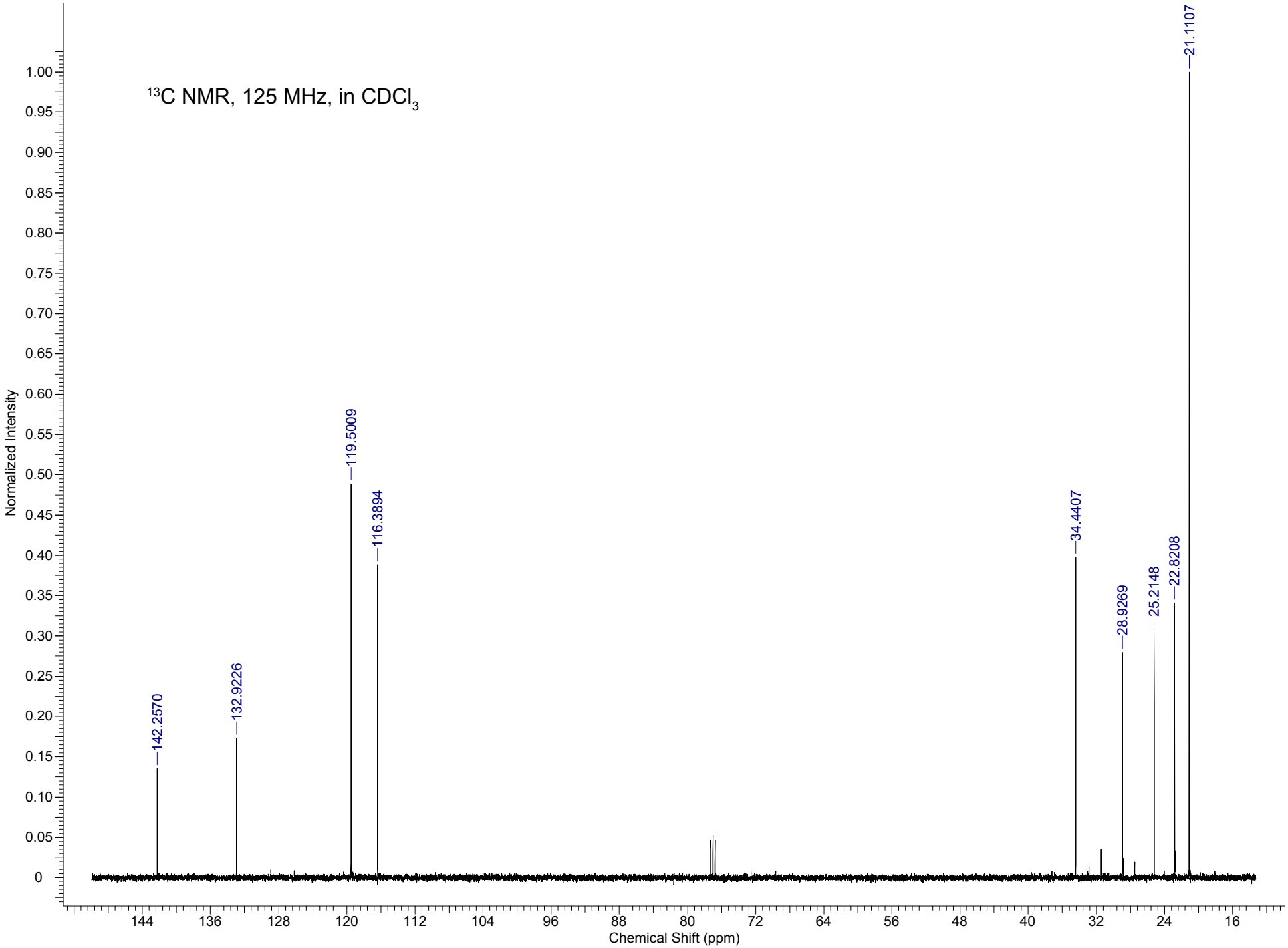
δ (ppm)	Name(s) of carbon(s)
142.3	
132.9	
119.5	
116.4	
34.4	
28.9	
25.2	
22.8	
21.1	

Some notes on the attached spectra:

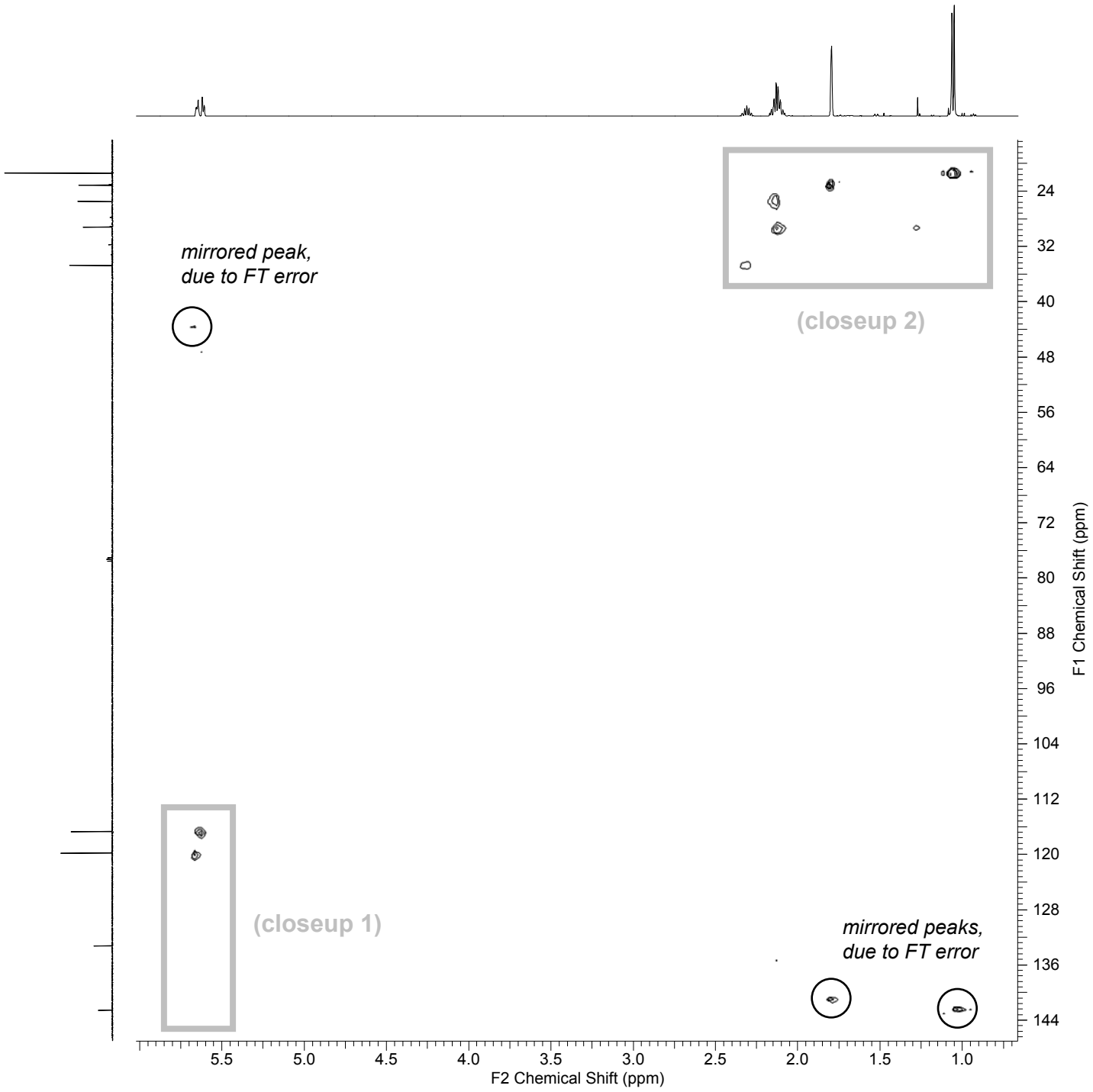
- In the HMQC spectrum, the ^{13}C pulse frequency was set to be centered about ~80 ppm. Using a complex Fourier transform (including imaginary terms, rather than only real ones) makes it possible to obtain data on ^{13}C nuclei both above and below this frequency. However, the complex FT sometimes generates mirrored peaks on both sides of the frequency center. Usually—as in this case—it is fairly easy to determine which peaks are real cross-peaks, and which are “ghost” peaks.

- 2D NMR methods sometimes have baseline trouble with resonances of vastly different intensities, and this is illustrated in the full HMBC spectrum. The tall methyl group resonances generate false, baseline peaks at many ^{13}C frequencies; these can be eliminated by setting the cutoff “floor” high above these peaks. Unfortunately, when you do that, crosspeaks from weak resonances (like those on the left-hand side of the spectrum) disappear. To address this issue, the close-up spectra have floors set appropriate to their region of the spectrum. As a result, I think you will find the HMBC close-ups more useful than the full HMBC spectrum.


^{1}H NMR, 500 MHz, in $CDCl_3$
Normalized Intensity
Chemical Shift (ppm)
5.6569
5.6543
5.6459
5.6433
5.6183
5.6073
2.3493
2.3362
2.3227
2.3091
2.2956
2.2825
2.2690
2.1709
2.1595
2.1438
2.1308
2.1188
2.1058
2.0906
2.0792
1.7945
1.0623
1.0488
1.0
1.0
1.1
4.1
3.0
5.8

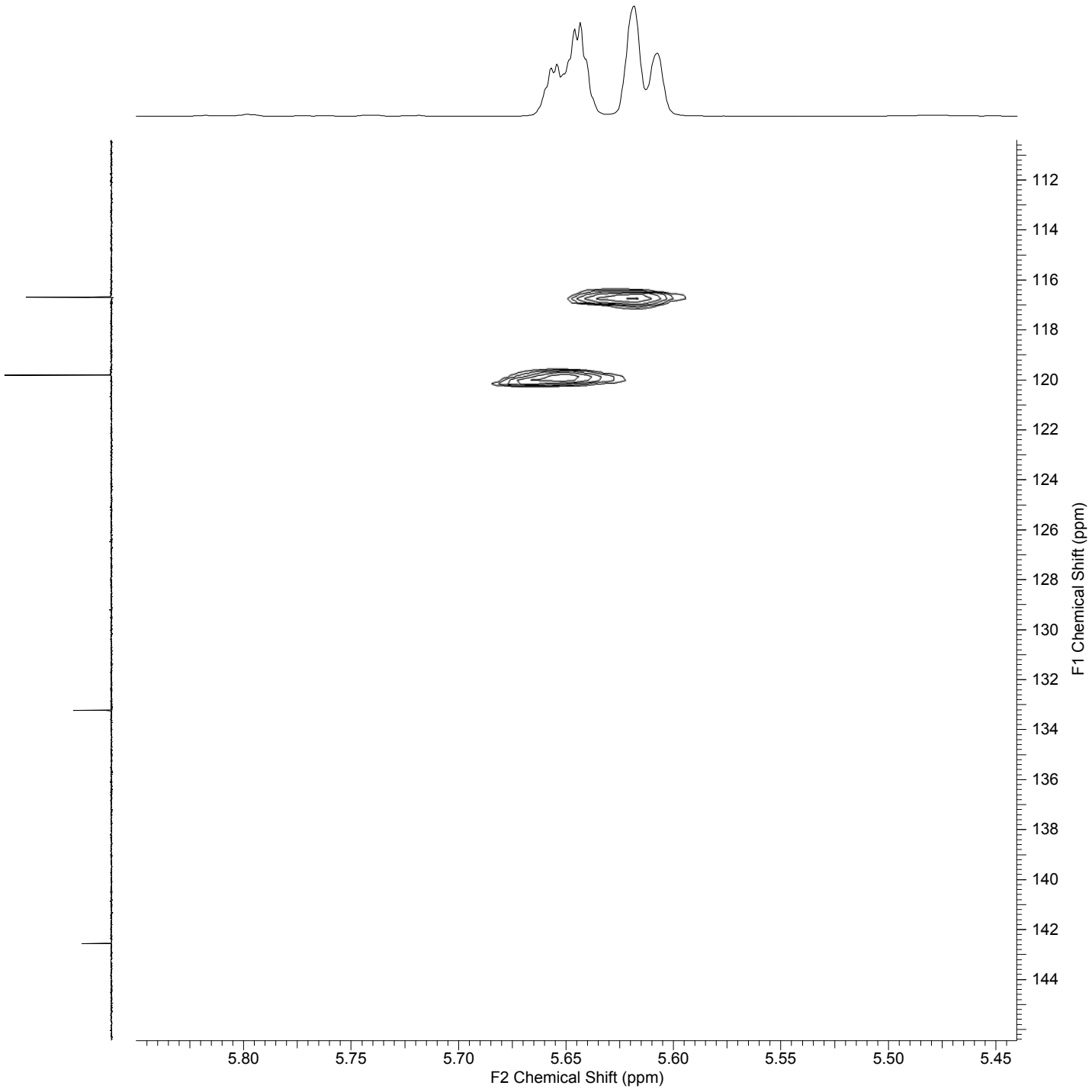

^{13}C NMR, 125 MHz, in $CDCl_3$
Normalized Intensity
Chemical Shift (ppm)
142.2570
132.9226
119.5009
116.3894
34.4407
28.9269
25.2148
22.8208
21.1107

^{1}H-^{13}C HMQC, 500/125 MHz, in $CDCl_3$



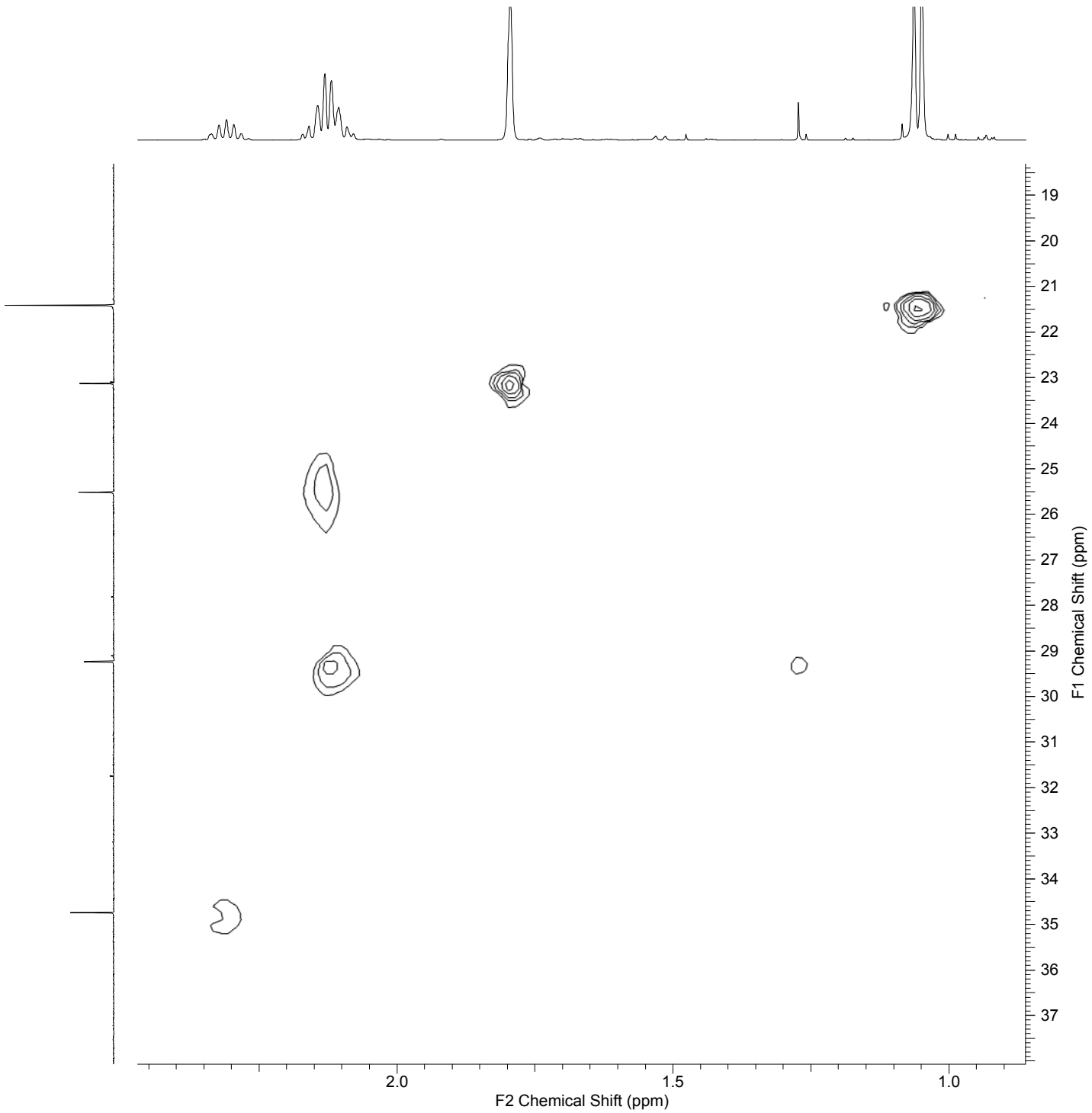
^{1}H-^{13}C HMQC, 500/125 MHz, in $CDCl_3$

(closeup 1)

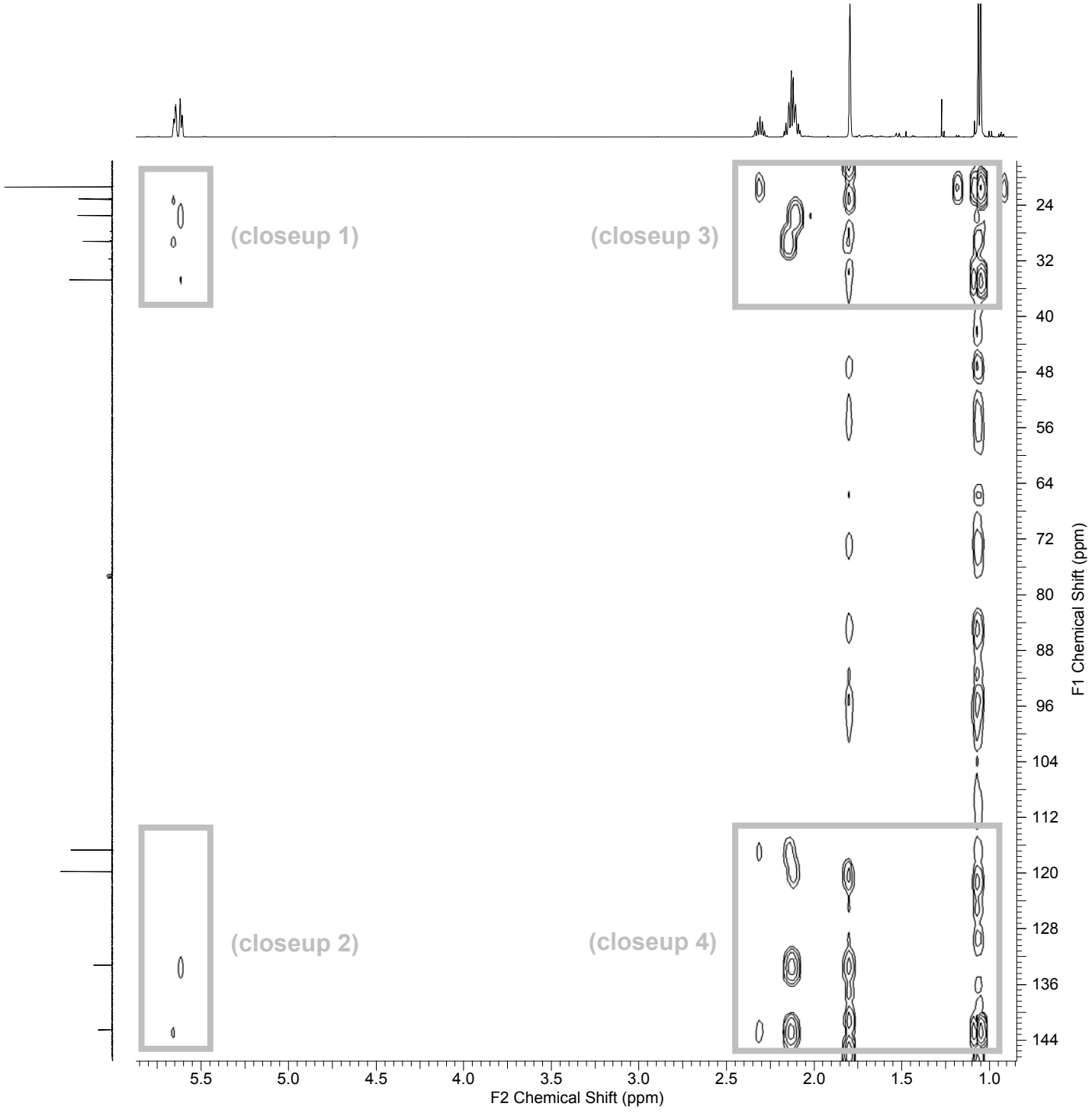


^{1}H-^{13}C HMQC, 500/125 MHz, in $CDCl_3$

(closeup 2)

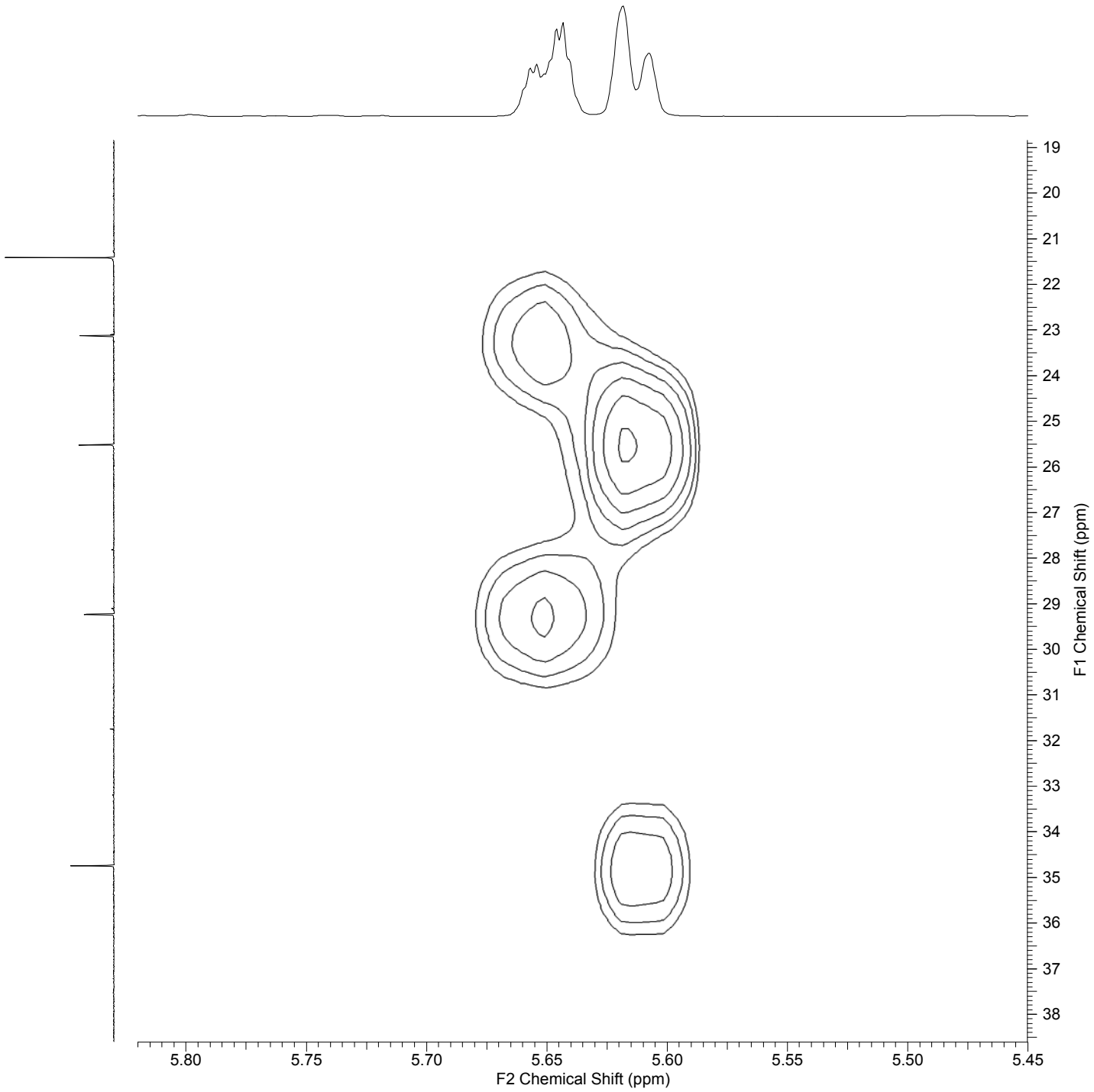


^{1}H-^{13}C HMBC, 500/125 MHz, in $CDCl_3$



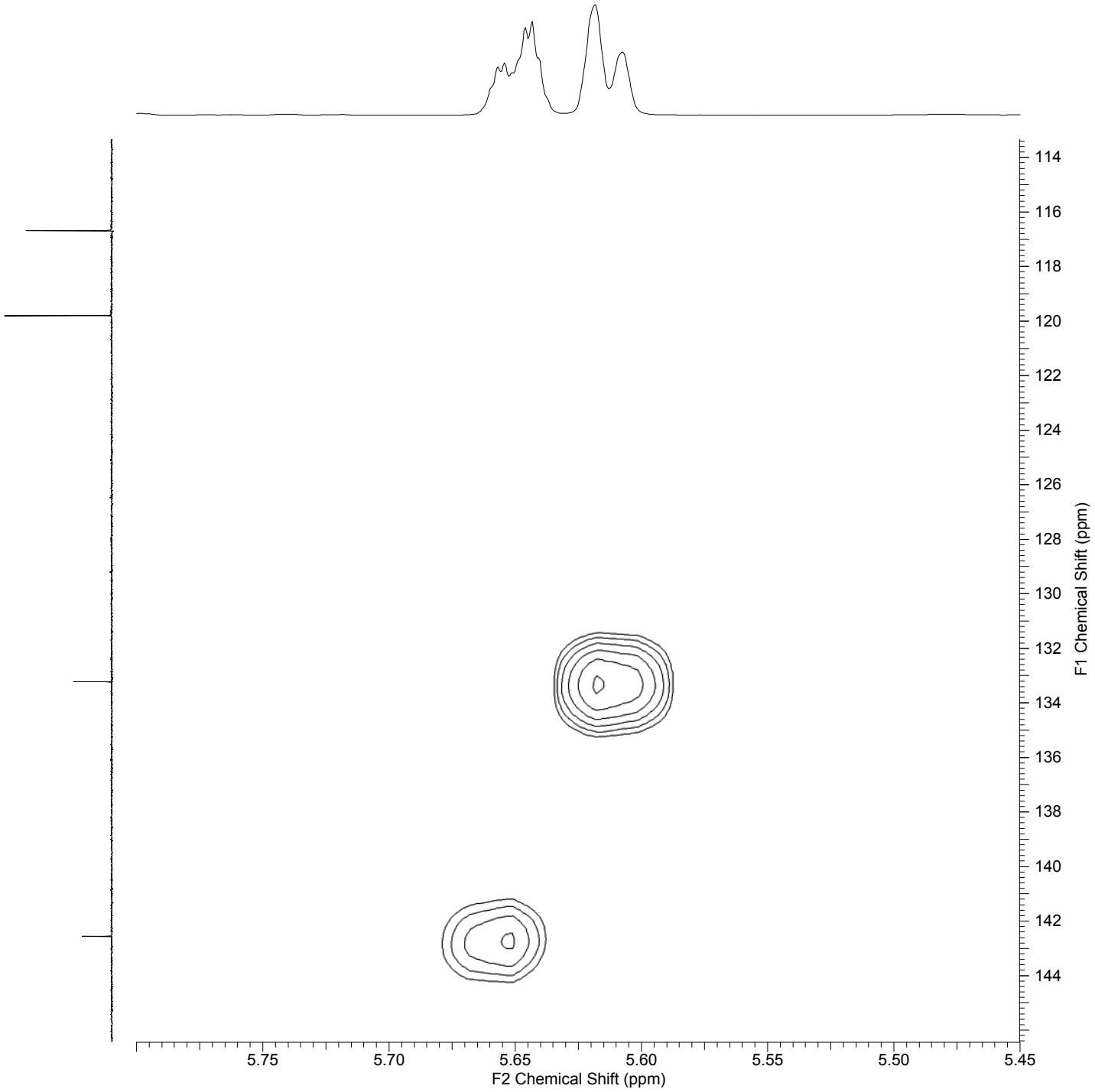
^{1}H-^{13}C HMBC, 500/125 MHz, in $CDCl_3$

(closeup 1)



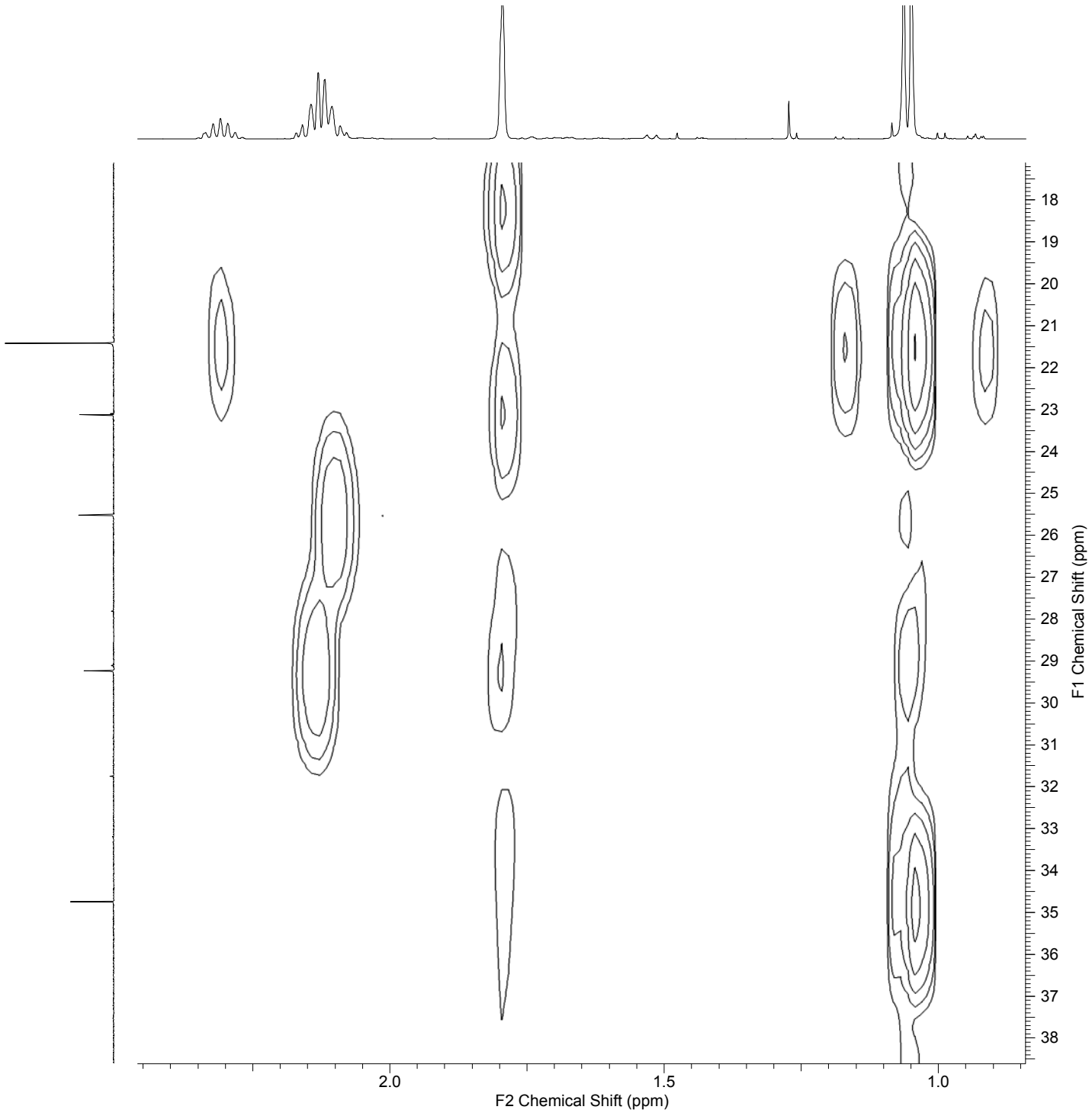
^{1}H-^{13}C HMBC, 500/125 MHz, in $CDCl_3$

(closeup 2)



^{1}H-^{13}C HMBC, 500/125 MHz, in $CDCl_3$

(closeup 3)



^{1}H-^{13}C HMBC, 500/125 MHz, in $CDCl_3$

(closeup 4)