

NAME _____

ID # _____

INTERPRETATION OF ORGANIC SPECTRA (4361/8361)

8:00 – 10:00 am, December 20, 2010

Final Exam

This exam is open book and open note. You are permitted to use any written materials you have brought as aids on this exam. You may also use a simple calculator. Other than this, please do not use any other electronic devices (cell phones, computers, recording devices, etc.) during the exam.

You may use pen or pencil. However, re-grades will be considered only for exams completed in pen.

Please write your answers in the boxes/spaces provided. If your answer is not in the appropriate space (say, for example, it's on the back of the page), draw us an arrow and/or note telling us where to look.

Feel free to remove the corner staple if this helps you analyze the spectra; you will have the opportunity to re-staple your exam at the end. The exam in this packet is designed to take 1 hour to complete. You will be given 2 hours total to finish the test. This exam contains one problem, which is split into parts. Many of these parts can be answered independently. *Do not get stuck* on one part and then assume that you will be unable to answer the rest of the question—move on. In addition, partial credit will be given for incorrect but still plausible answers, so *guess* on problems you cannot answer perfectly.

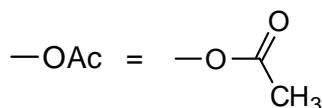
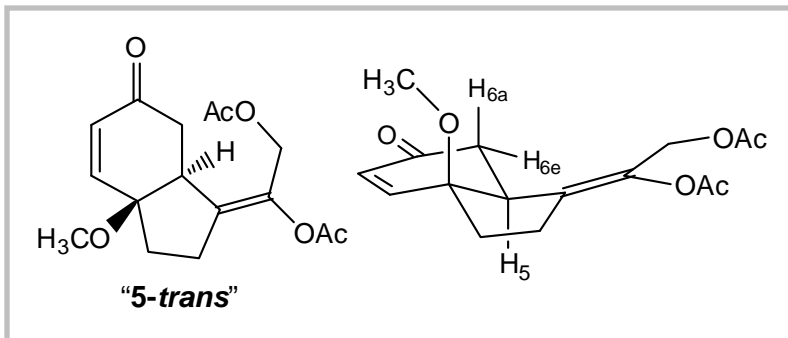
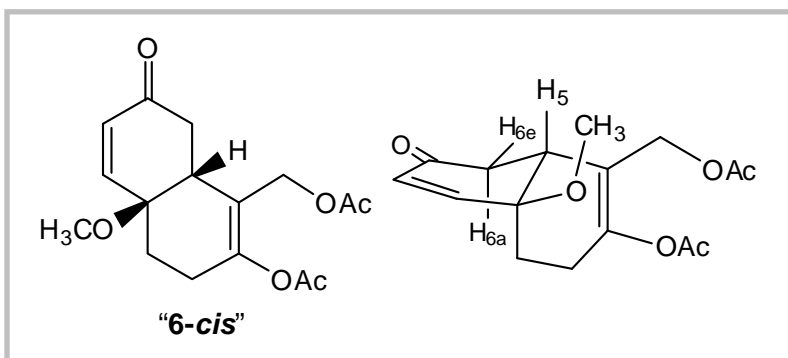
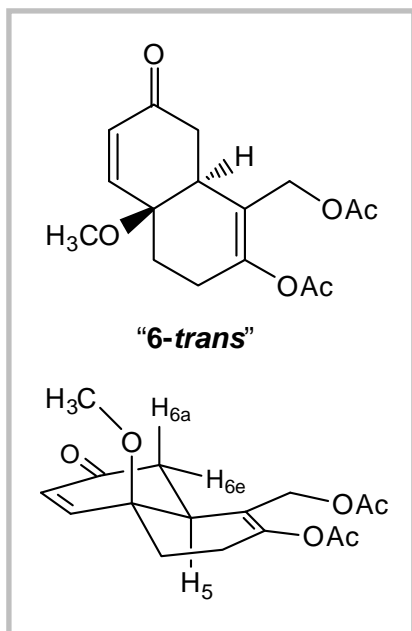
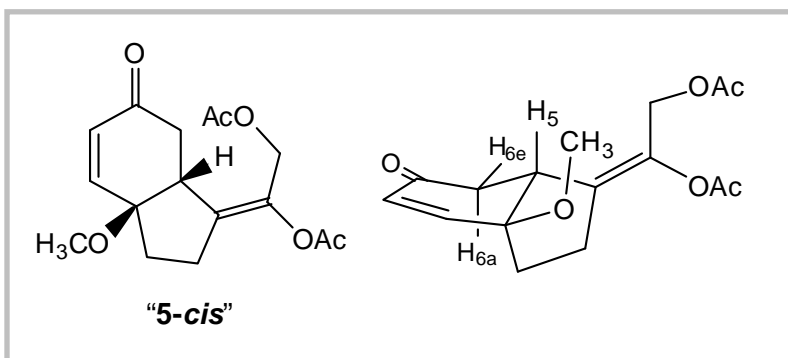
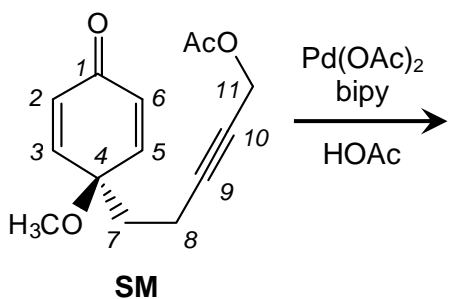
At the end of the 2 hour exam period you will be asked to return your exam to the proctor. Please do not take any part of the exam packet with you when you are done; everything will be returned to you after the exams are graded. This packet should contain 22 pages, including this one. Please check to make sure that your packet contains 22 pages before beginning your exam.

NAME _____

Scoring: 1. _____ / 7 5. _____ / 5 9. _____ / 8
 2. _____ / 56 6. _____ / 20 10. _____ / 20
 3. _____ / 15 7. _____ / 16 11. _____ / 5
 4. _____ / 35 8. _____ / 13

Total Score: _____ / 100

Rodolfo Tello (Harned Group) has investigated the palladium-mediated, intramolecular C-C bond formation reactions of alkynes. For example, the starting material (**SM**) shown below could, in principle, cyclize to form any of four products:



I've named the four potential products according to the ring size formed in the reaction (**5-** or **6-**membered) and whether the bicyclic product is *cis*- or *trans*-fused. The C/H numbering scheme in all of the products is based on the starting material, with the two H₆ protons further distinguished by whether they are pseudo-axial [H(6a)] or pseudoequatorial [H(6e)].

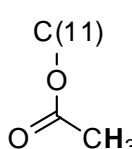
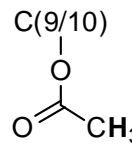
In the end, the Rodolfo only isolated one of these four products from the reaction. One primary goal of this exam is to identify which of the four products Rodolfo selectively synthesized. However, it is important to note that the overall structures and C-H connectivities of the four molecules are identical, and it will be possible for you to receive almost full credit for this exam even if you choose the wrong product structure.

1-D ¹H, ¹³C, DEPT and NOE (NMR) spectra, as well as 2-D COSY, HMQC, and HMBC spectra, are attached to the back of this exam.

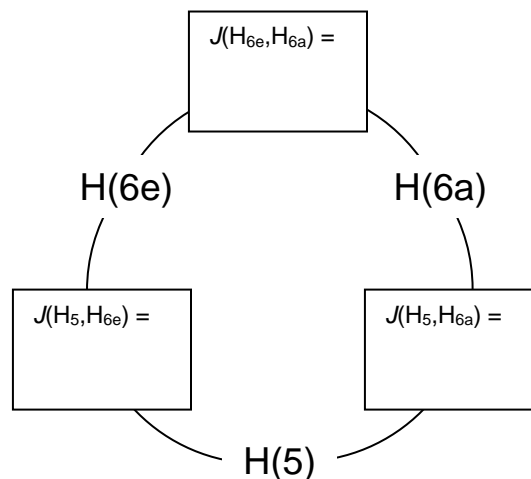
- (7 pts) On the previous page, circle the structure of the product that Rodolfo isolated from his reaction. (You will probably want to wait until the end of the exam to answer this question, but because it affects the way we grade your exam, I'm asking it first.)
- (56 pts) In the chart below, assign chemical shift (δ) values to each of the protons listed. Answer to within 0.01 ppm.

proton	δ (ppm)
H(2)	
H(3)	
-OCH ₃	
H(5)	

proton	δ (ppm)
H(6a)	
H(6e)	
H(7)	
[x2]	
H(8)	
[x2]	

proton	δ (ppm)
H(11)	
[x2]	
	
	

3. (15 pts) H(5), H(6a) and H(6e) are coupled to one another. In each box at right, enter the coupling constant J between each pair of protons. Answer to within 1.0 Hz.



4. (35 pts) All four of the potential product structures share the same methylene (-CH₂-) and methane (-CH-) carbons. In the chart on the right, assign chemical shift (δ) values to each of the -CH₂- and -CH- carbons listed. Answer to within 1 ppm.

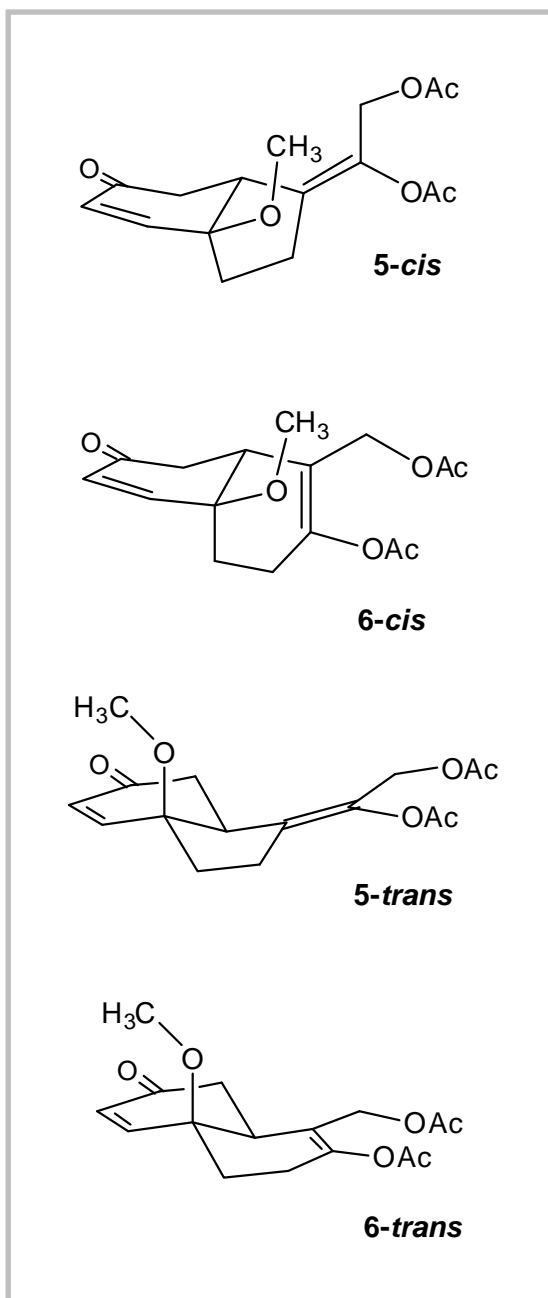
-CH ₂ - carbon	δ (ppm)
C(6)	
C(7)	
C(8)	
C(11)	

-CH- carbon	δ (ppm)
C(2)	
C(3)	
C(5)	

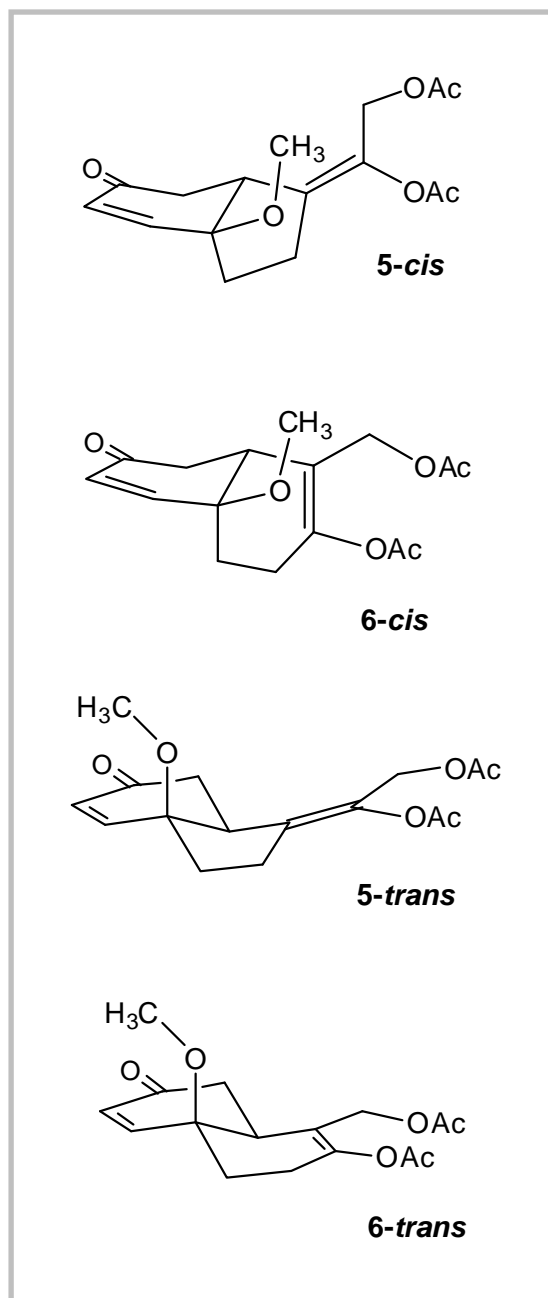
5. (5 pts) Some peaks that appear in the ¹³C NMR do not appear in the DEPT-135 spectrum or the DEPT-90 spectrum. How many protons are attached to each carbon that doesn't contribute to either DEPT spectrum? (Answer in the box at right.)

6. (20 pts) There are two 1-D NOE spectra attached to the exam. For each NOE experiment (1 and 2), illustrate the transfer of spin polarization (NOE enhancement) on the product structure you think is the correct one. (Keep in mind, you will not be penalized for choosing the wrong structure. Pick one structure only.) Draw each transfer as double headed arrow originating at the excited resonance. I have left out most protons on these drawings, so you will have to draw in any protons you need to describe the experiments.

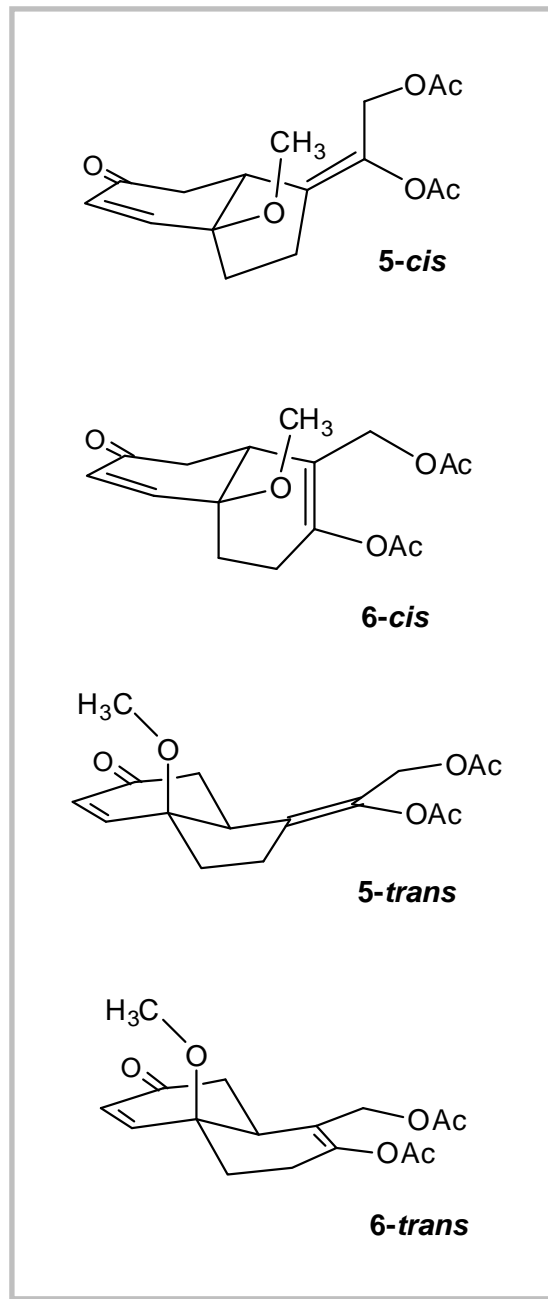
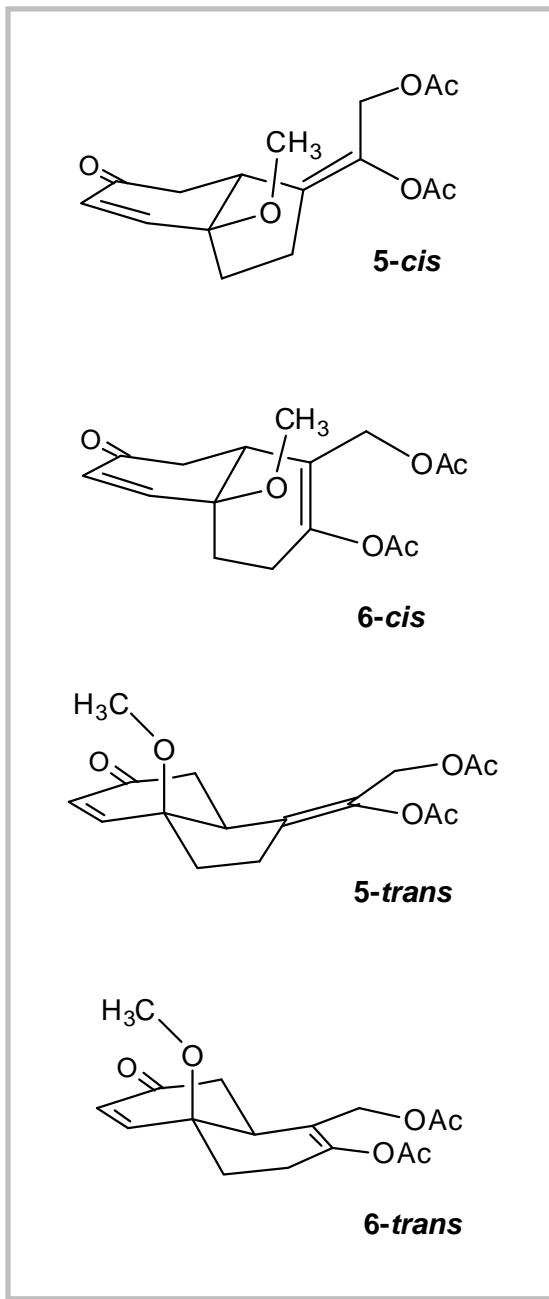
Experiment 1



Experiment 2



7. (16 pts) The HMBC (close-up) spectra have four cross-correlations highlighted with different shapes. Below, on the product structure you have chosen, illustrate each of these correlations with a double-headed arrow. Again, because I have omitted protons from these drawings, you may have to draw some in. Indicate which arrow corresponds to which shape.



8. (13 pts) Rodolfo didn't monitor the progress of his reaction *in situ* by infrared (IR) spectroscopy, but he could have. What frequency ν (to within 50 cm^{-1}) could he have monitored, using an immersion probe, to unambiguously confirm the disappearance of starting material?

$\nu =$

What functional group absorbs IR light at this frequency?

Would you expect transmittance (%T) at this frequency to

increase *or* **decrease**

as the reaction progressed? (Circle one answer.)

9. (8 pts) All four of the potential product structures have the same molecular formula ($\text{C}_{16}\text{H}_{20}\text{O}_6$). Electrospray-ionization mass spectrometry (ESI-MS) on the unknown product gave a parent mass peak of $m/z = 309$, potentially corresponding to $[\text{M}+\text{H}]^+$ ($\text{C}_{16}\text{H}_{21}\text{O}_6^+$).

To within 0.01 Da, what would you expect the exact mass of this parent ion peak to be?

Would you say that this ion exhibited a

negative mass defect *or a* **positive mass defect** ?

(Circle one answer.)

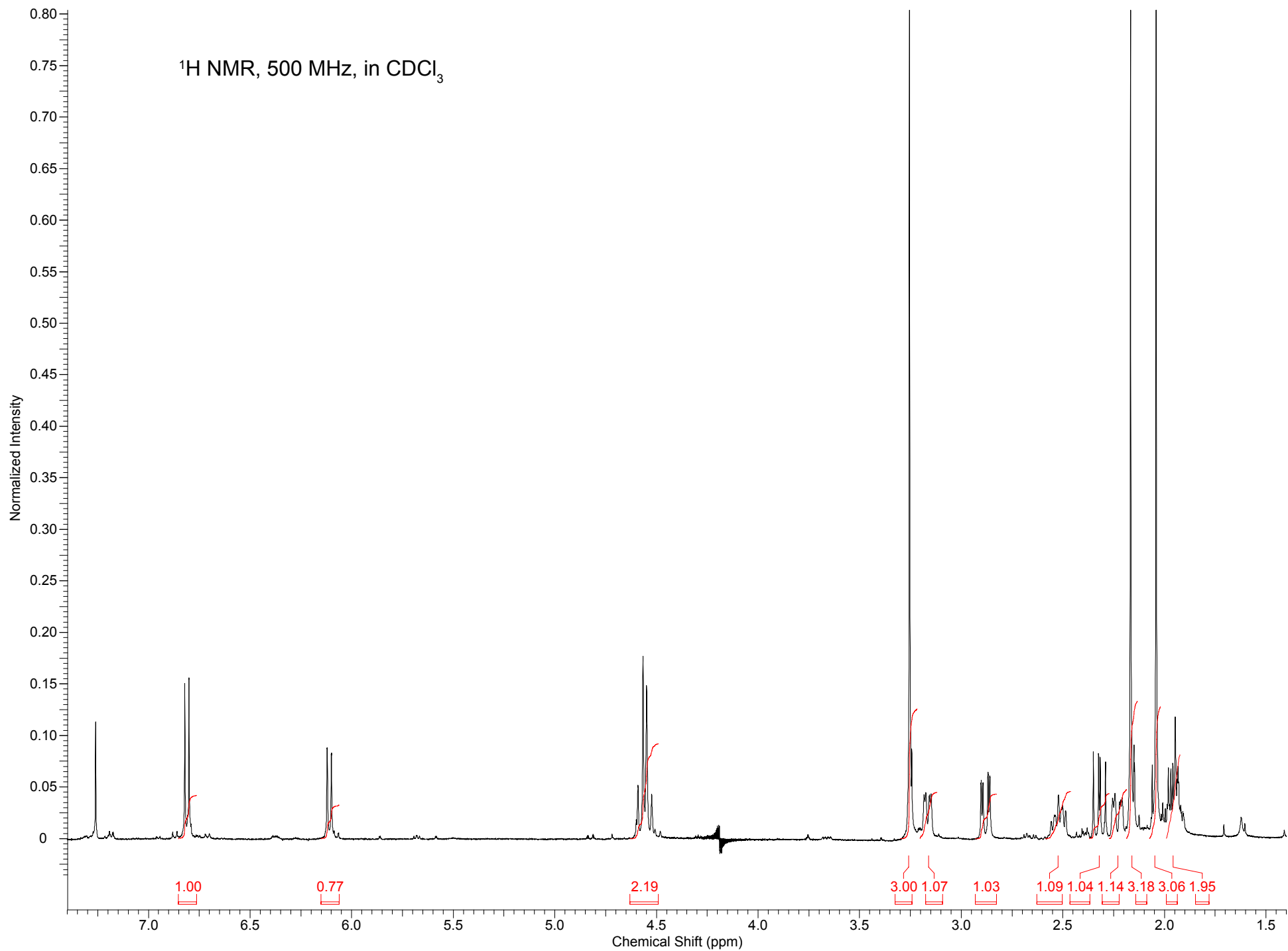
10. (20 pts) The ESI-MS spectrum of the unknown product, in addition to showing the parent ion, also showed a significant peaks at $m/z = 249$ and 217 . Draw a mechanism that explains the fragmentation of the parent to these daughter ion masses.



11. (5 pts) Name one ionization technique other than ESI-MS that you would expect to generate the same parent and fragment ion masses as described in problems 9-10.

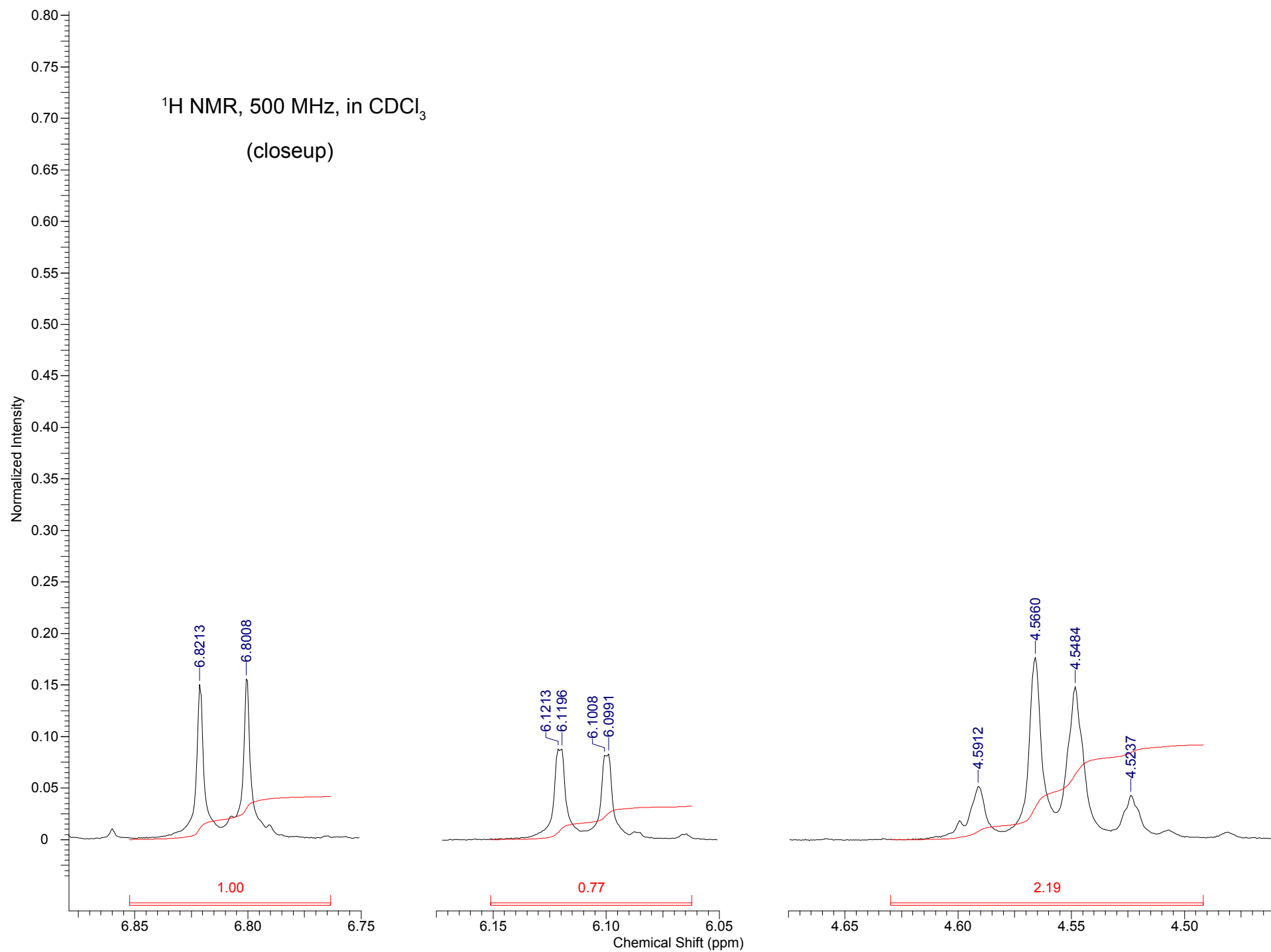


^1H NMR, 500 MHz, in CDCl_3



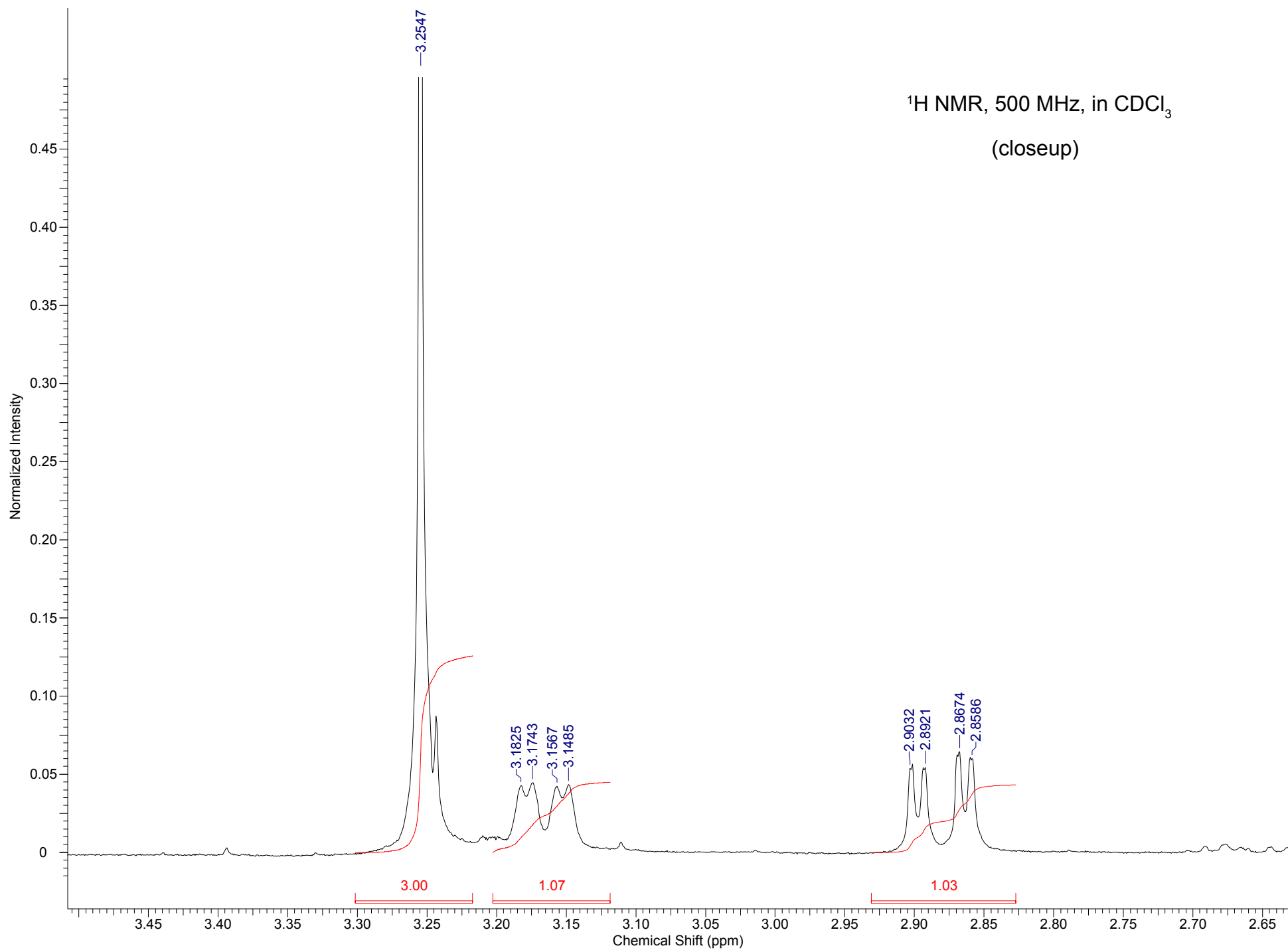
^1H NMR, 500 MHz, in CDCl_3

(closeup)

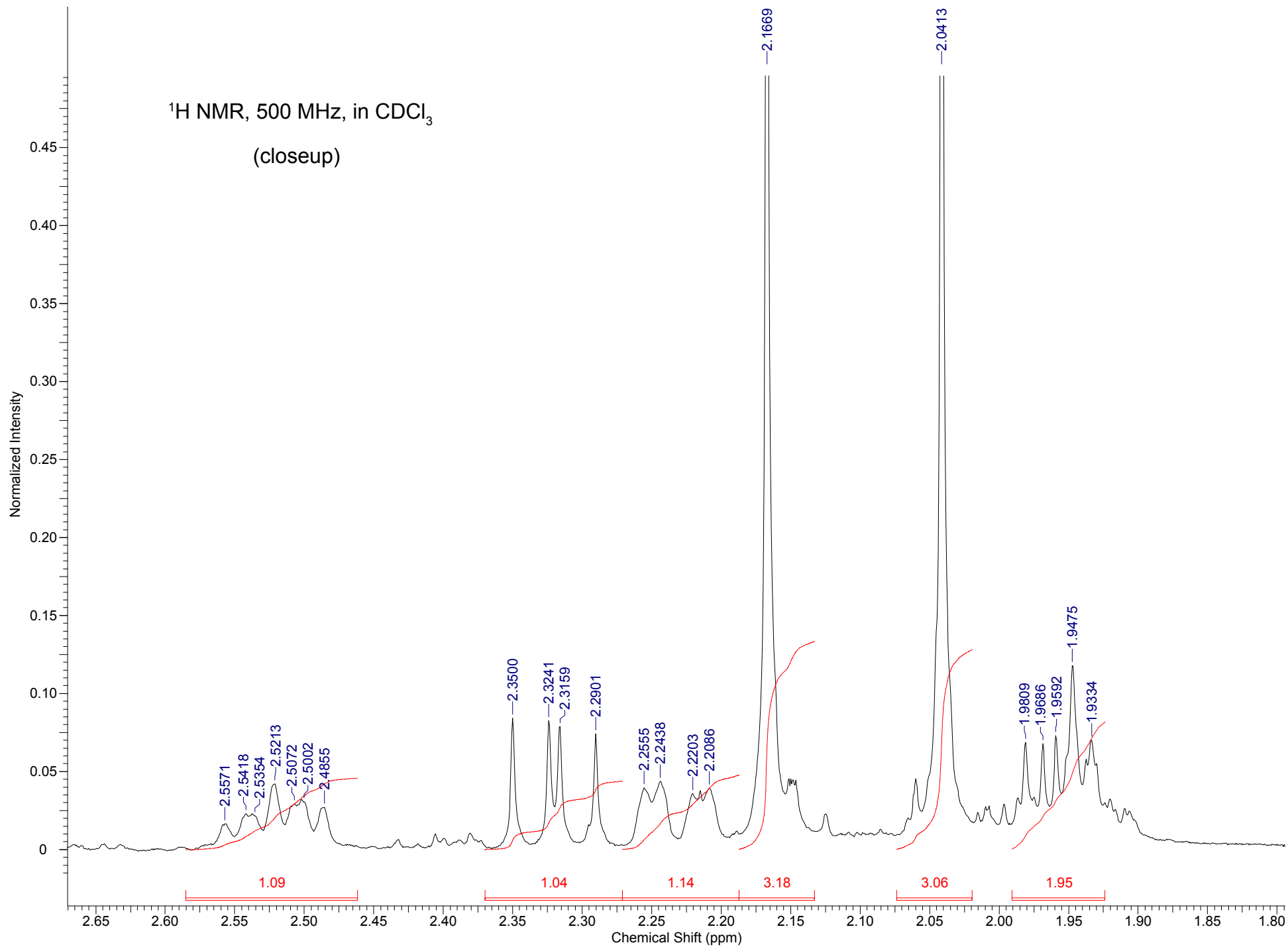


^1H NMR, 500 MHz, in CDCl_3

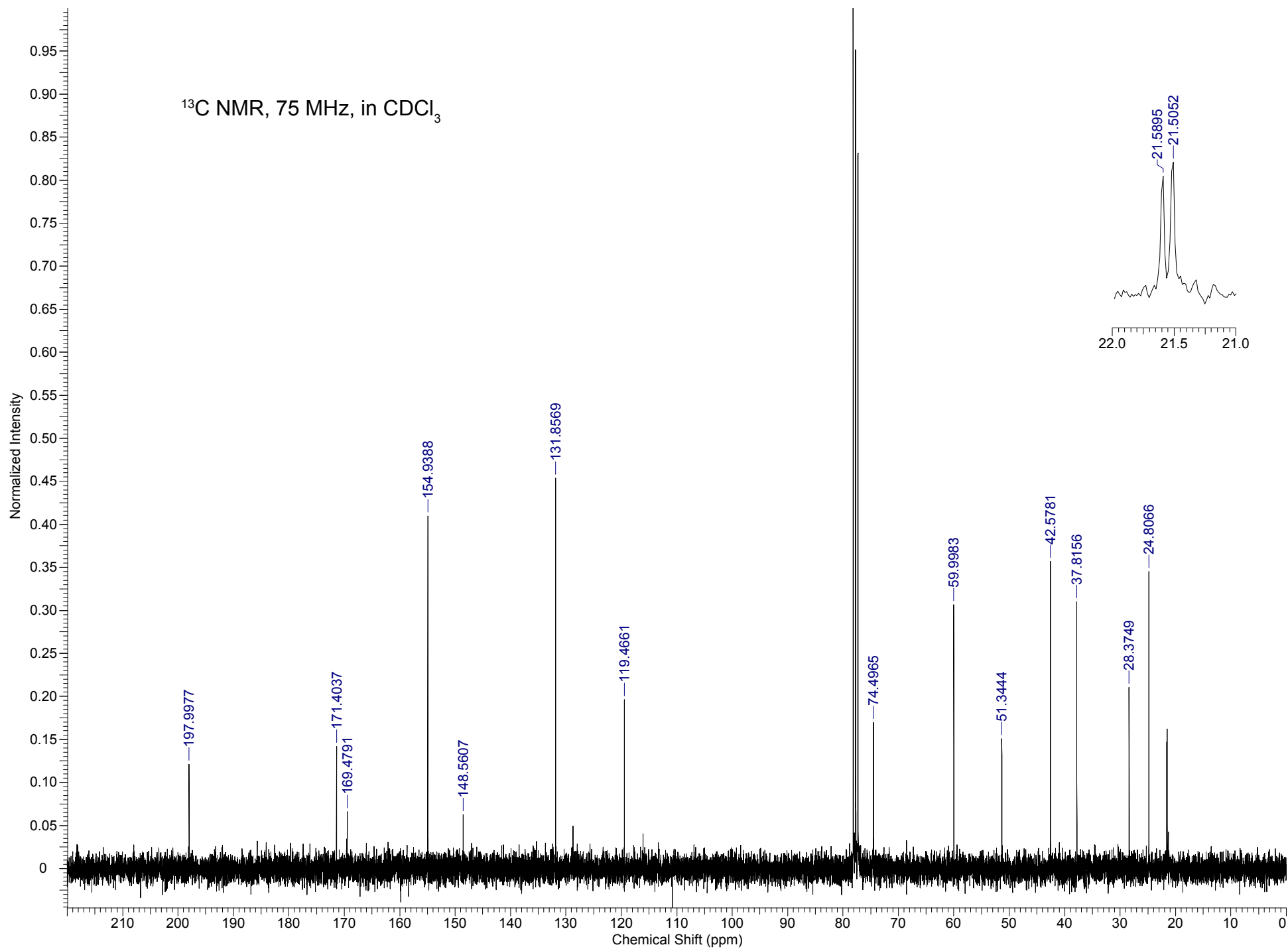
(closeup)

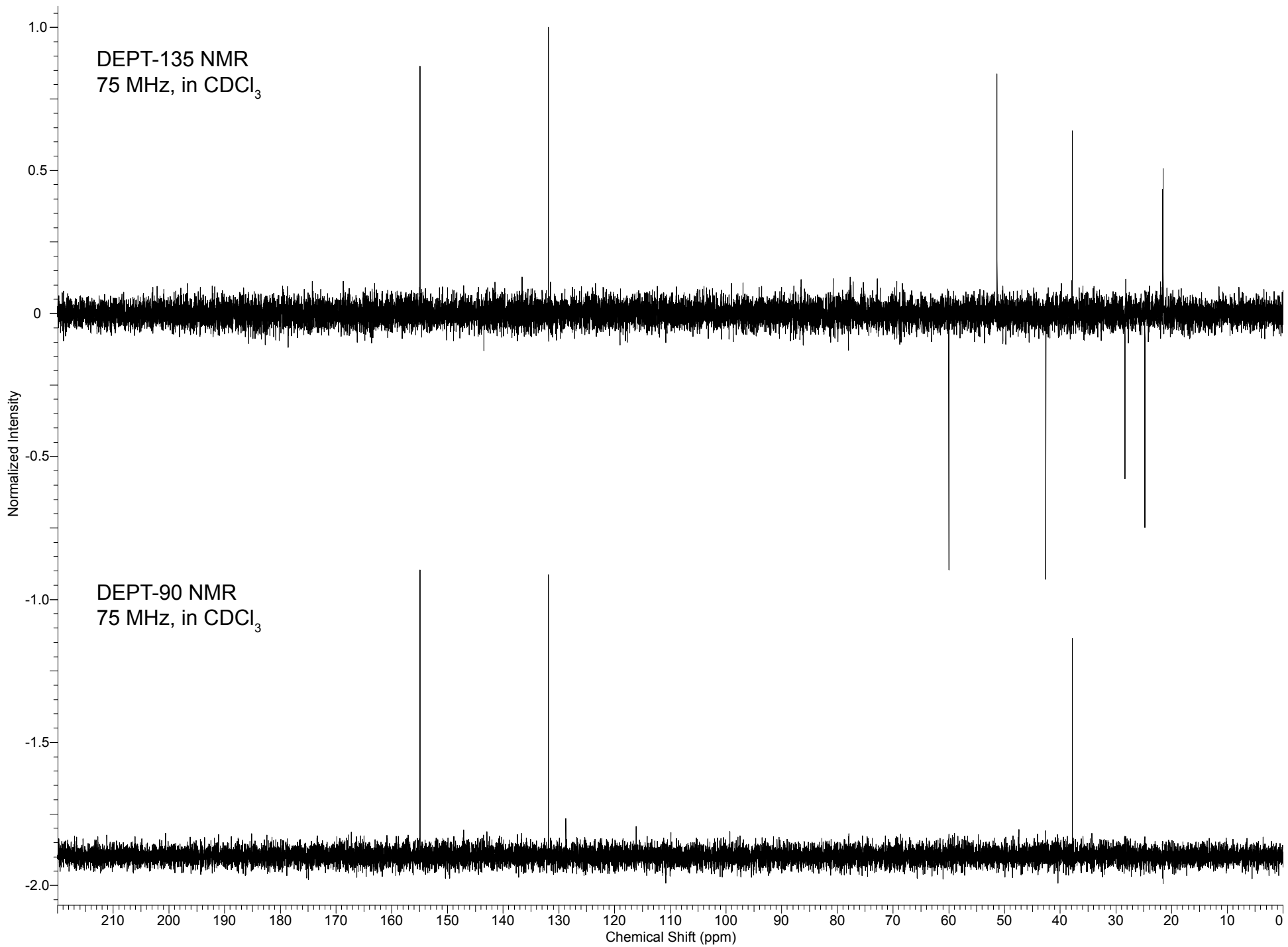


^1H NMR, 500 MHz, in CDCl_3
(closeup)



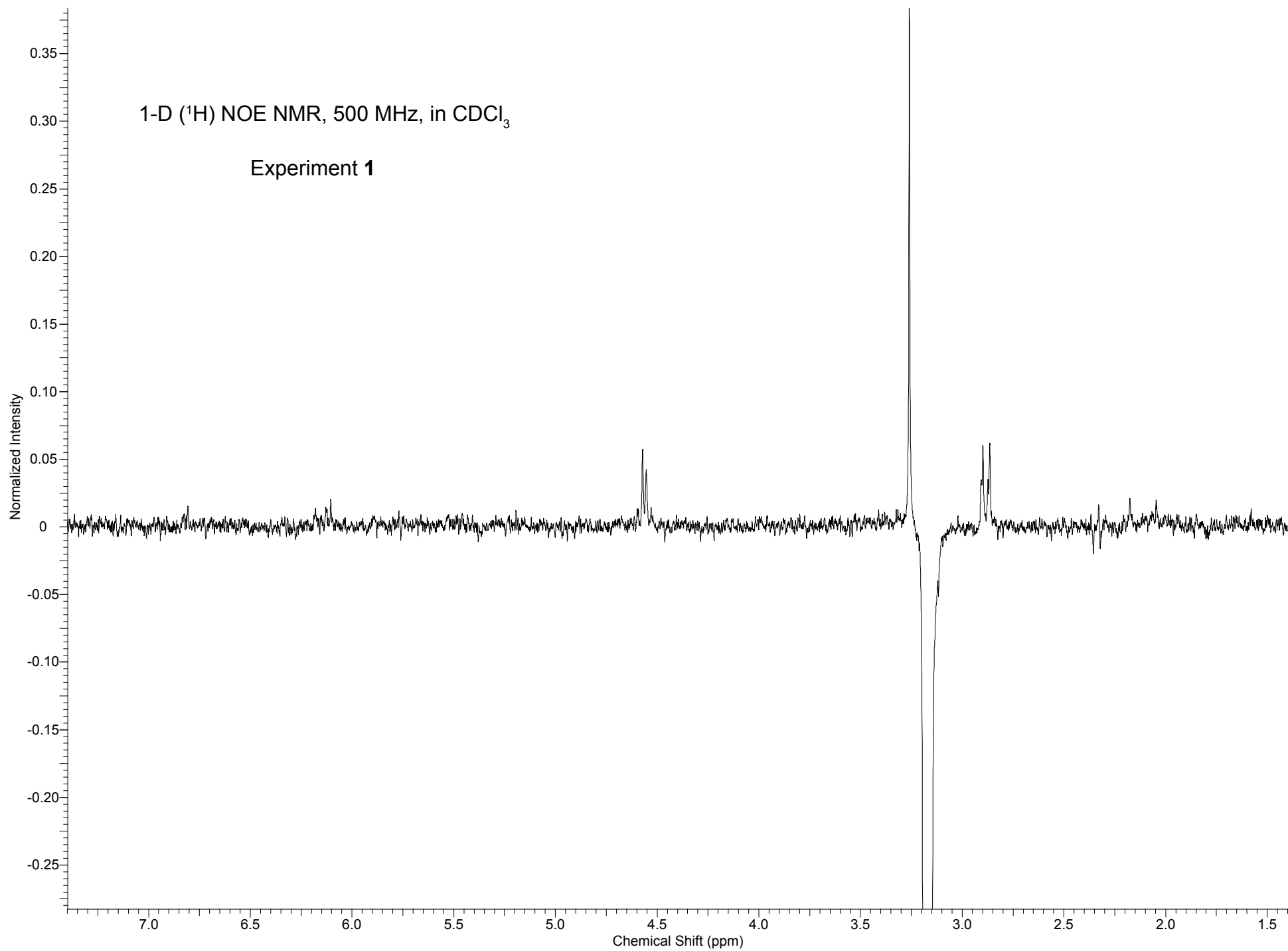
^{13}C NMR, 75 MHz, in CDCl_3





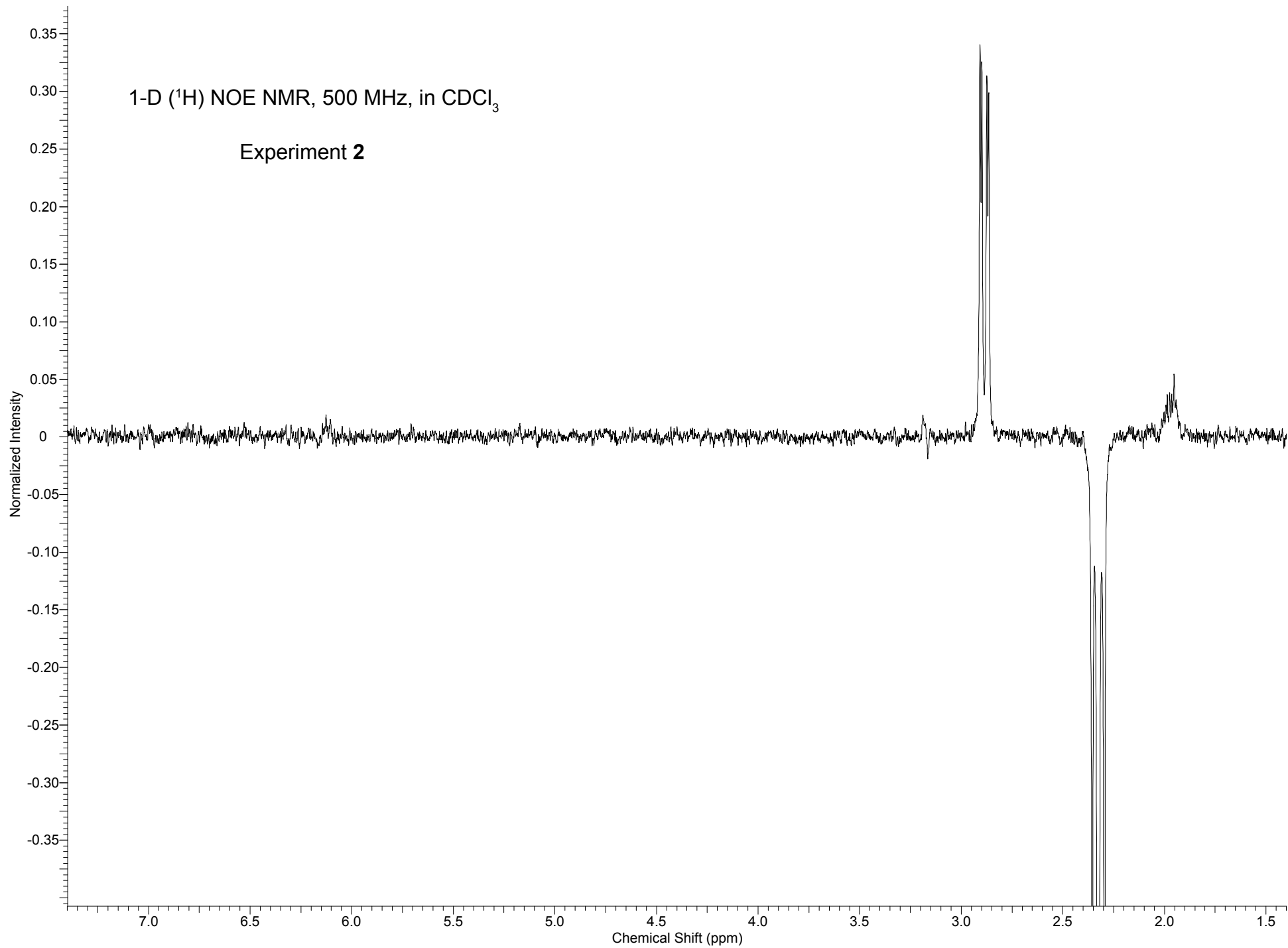
1-D (¹H) NOE NMR, 500 MHz, in CDCl₃

Experiment 1

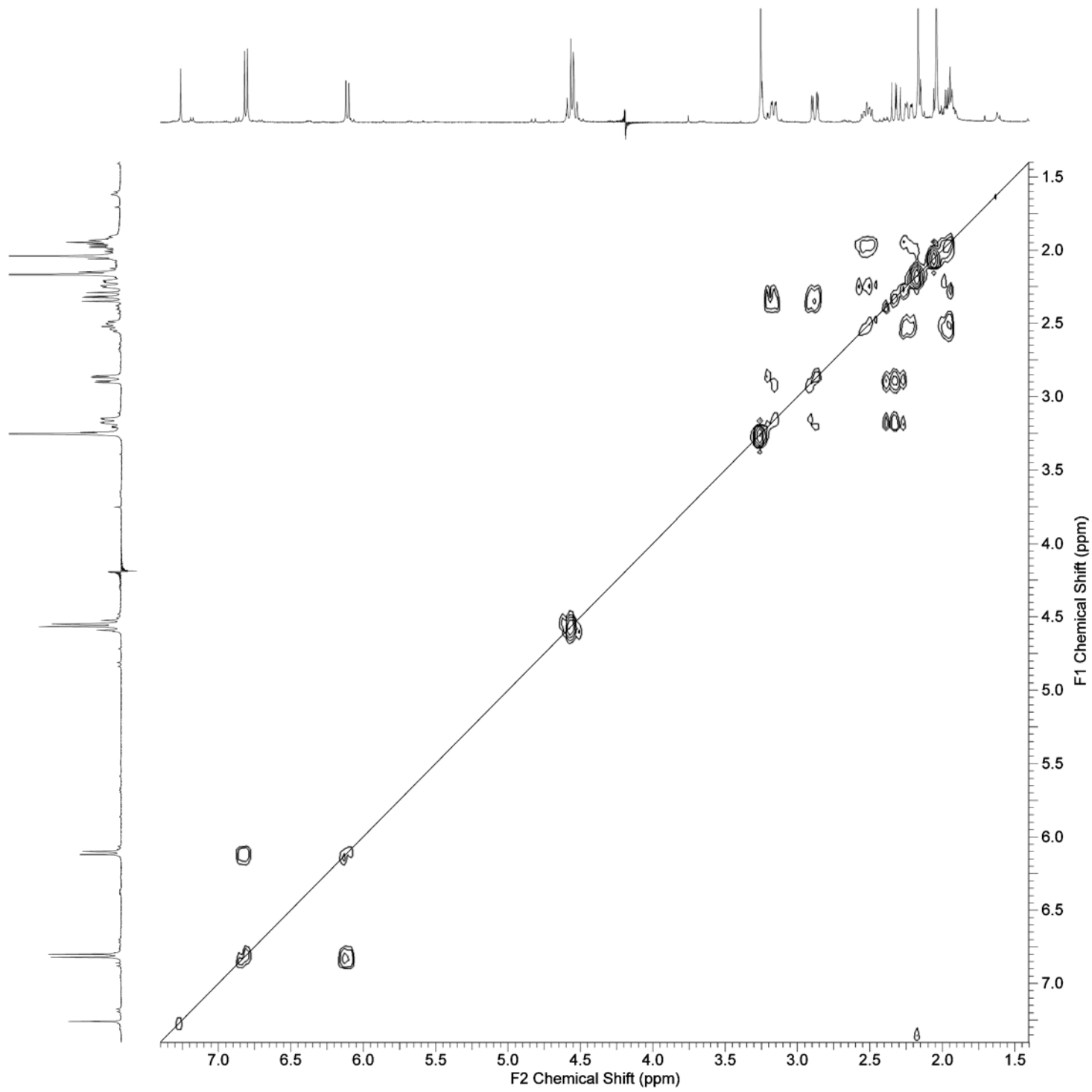


1-D (¹H) NOE NMR, 500 MHz, in CDCl₃

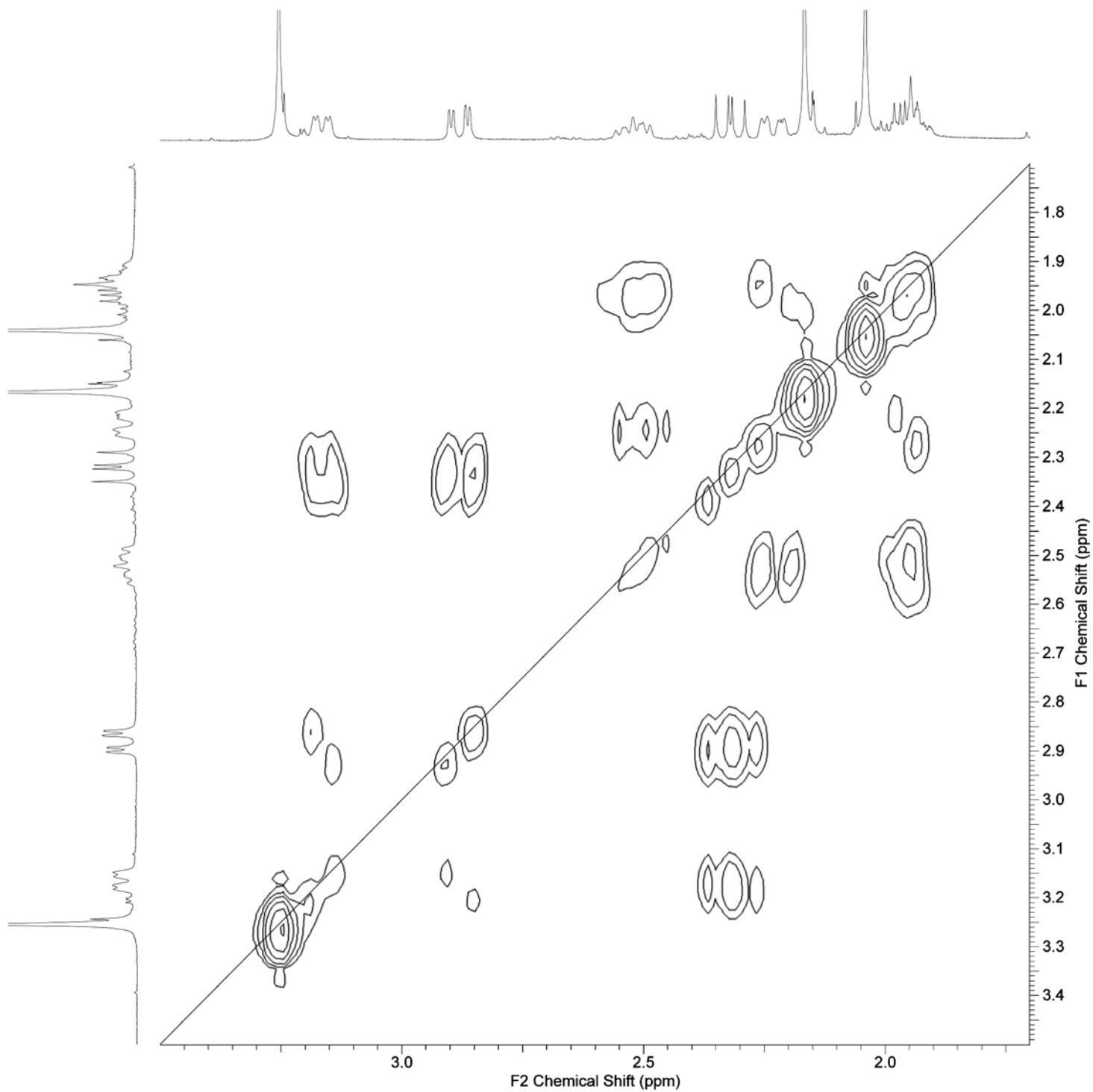
Experiment 2



^1H - ^1H COSY, 300 MHz, in CDCl_3

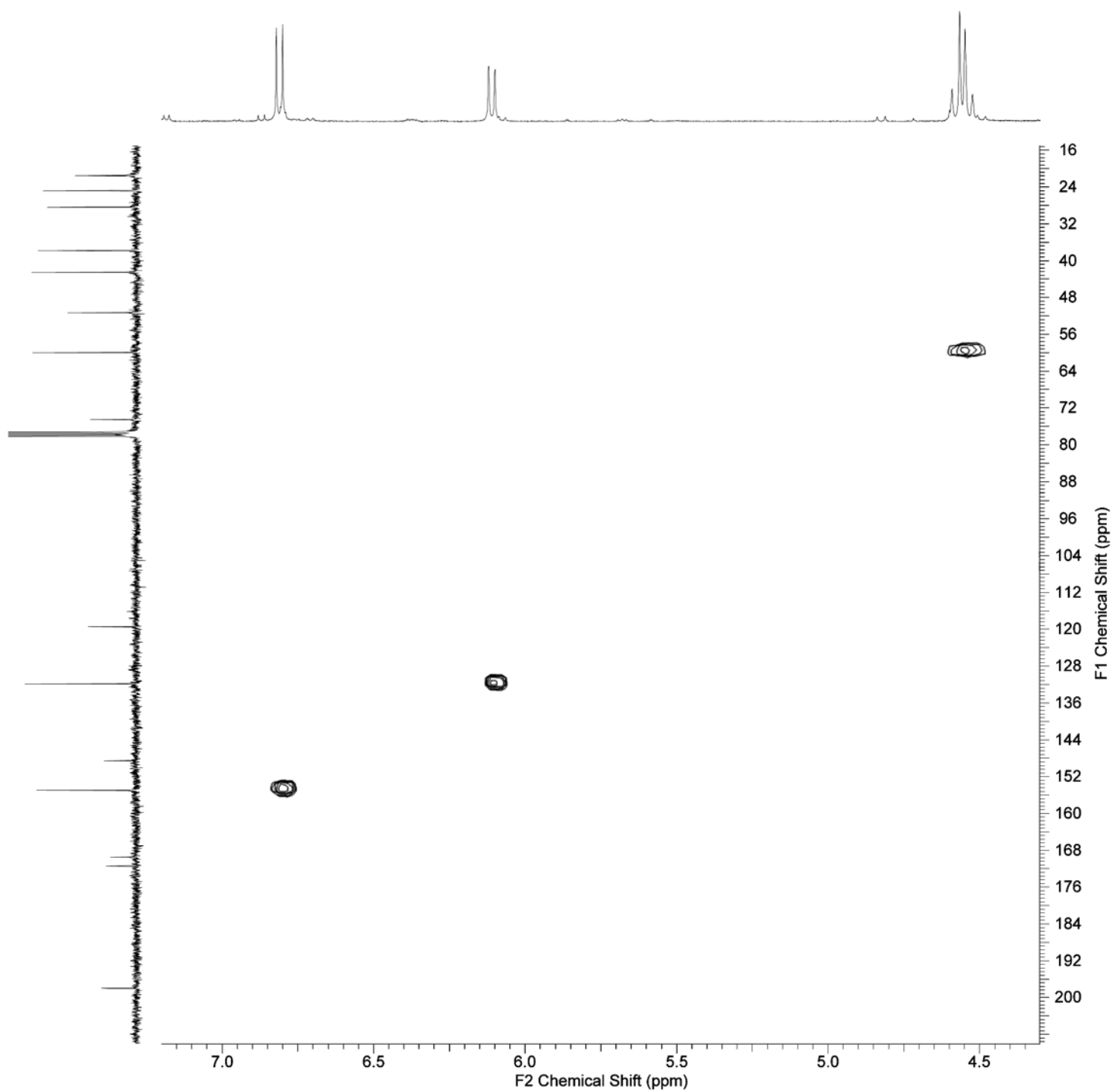


^1H - ^1H COSY, 300 MHz, in CDCl_3
(closeup)



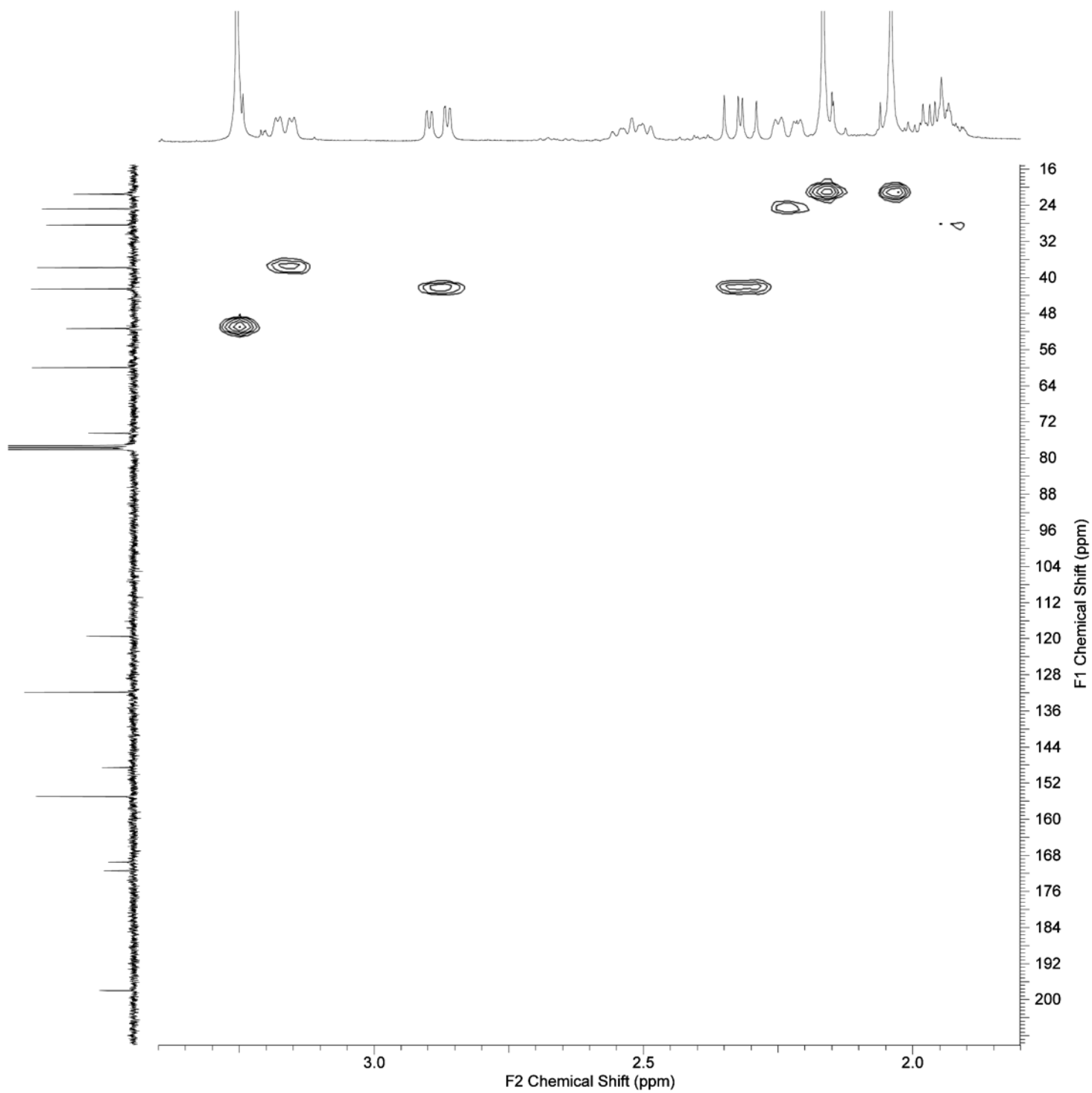
^1H - ^{13}C HMQC, in CDCl_3

(closeup)



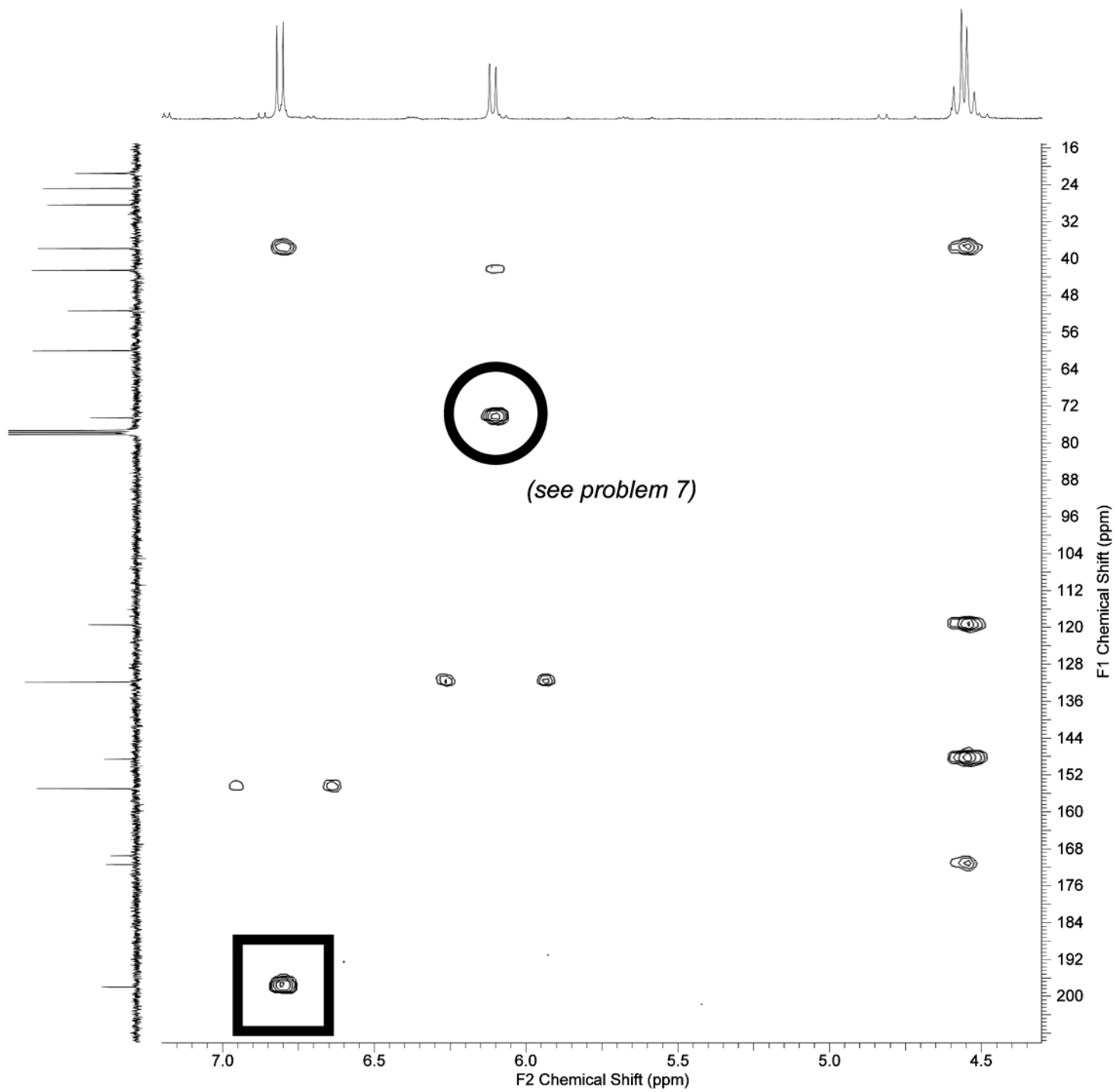
^1H - ^{13}C HMQC, in CDCl_3

(closeup)



^1H - ^{13}C HMBC, in CDCl_3

(closeup)



^1H - ^{13}C HMBC, in CDCl_3

(closeup)

