NAME _____

ID # _____

INTERPRETATION OF ORGANIC SPECTRA (4361/8361)

9:05 – 9:55 am, October 26, 2011

Exam 2

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. You will be given 50 minutes 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 50 minute 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 12 pages, including this one. Please check to make sure that your packet contains 12 pages before beginning your exam.

NAME _____

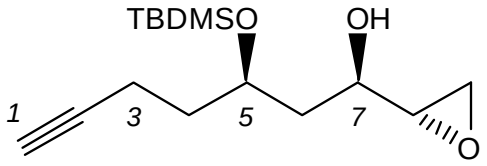
Scoring: 1. _____ / 69 4. _____ / 6

2. _____ / 6 5. _____ / 9

3. _____ / 10

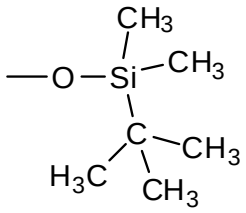
Total Score: _____ / 100

In her studies on the synthesis of oocydin A, Mandy Schmit (Hoye group) ran an epoxidation reaction that produced a racemic mixture of the epoxide shown at right. In this exam, you will answer questions about this molecule, using the ^{1}H, ^{1}H-^{1}H COSY, and ^{1}H-^{13}C HMQC spectra of Mandy's product attached to the back of this exam.



(+ enantiomer)

-OTBDMS =



1. In the chart below and on the next page, list chemical shifts for the listed proton atoms (to within 0.05 ppm) and carbon atoms (to within 5 ppm) according to the numbering scheme on the molecule.

carbon	δ (ppm)
C(3)	
C(4)	
C(5)	
C(6)	

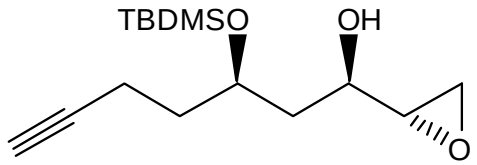
carbon	δ (ppm)
C(7)	
C(8)	
C(9)	

proton	δ (ppm)
H(1)	
H(3a)	
H(3b)	
H(4a)	
H(4b)	

proton	δ (ppm)
H(5)	
H(6a)	
H(6b)	
H(7)	
H(8)	

proton	δ (ppm)
H(9a)	
H(9b)	
-OH	
-Si(C**H**$_3$)$_2$	
[x2]	
-SiC(C**H**$_3$)$_3$	

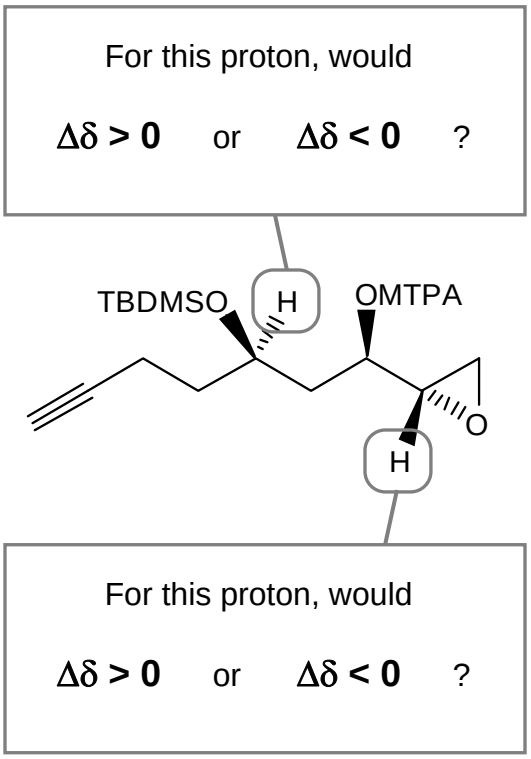
2. Two crosspeaks are circled in grey on the ^{1}H-^{1}H COSY spectrum. What correlations do these crosspeaks represent? Draw each one on the structure at right as a double-headed arrow.



3. Mandy was concerned that the conditions of her epoxidation might lead to silyl transfer--might move the TBDMS protecting group from the oxygen on the left to the alcohol group on the right. Describe one NMR experiment that Mandy could have performed to confirm that the TBDMS group was still on the left-hand oxygen.

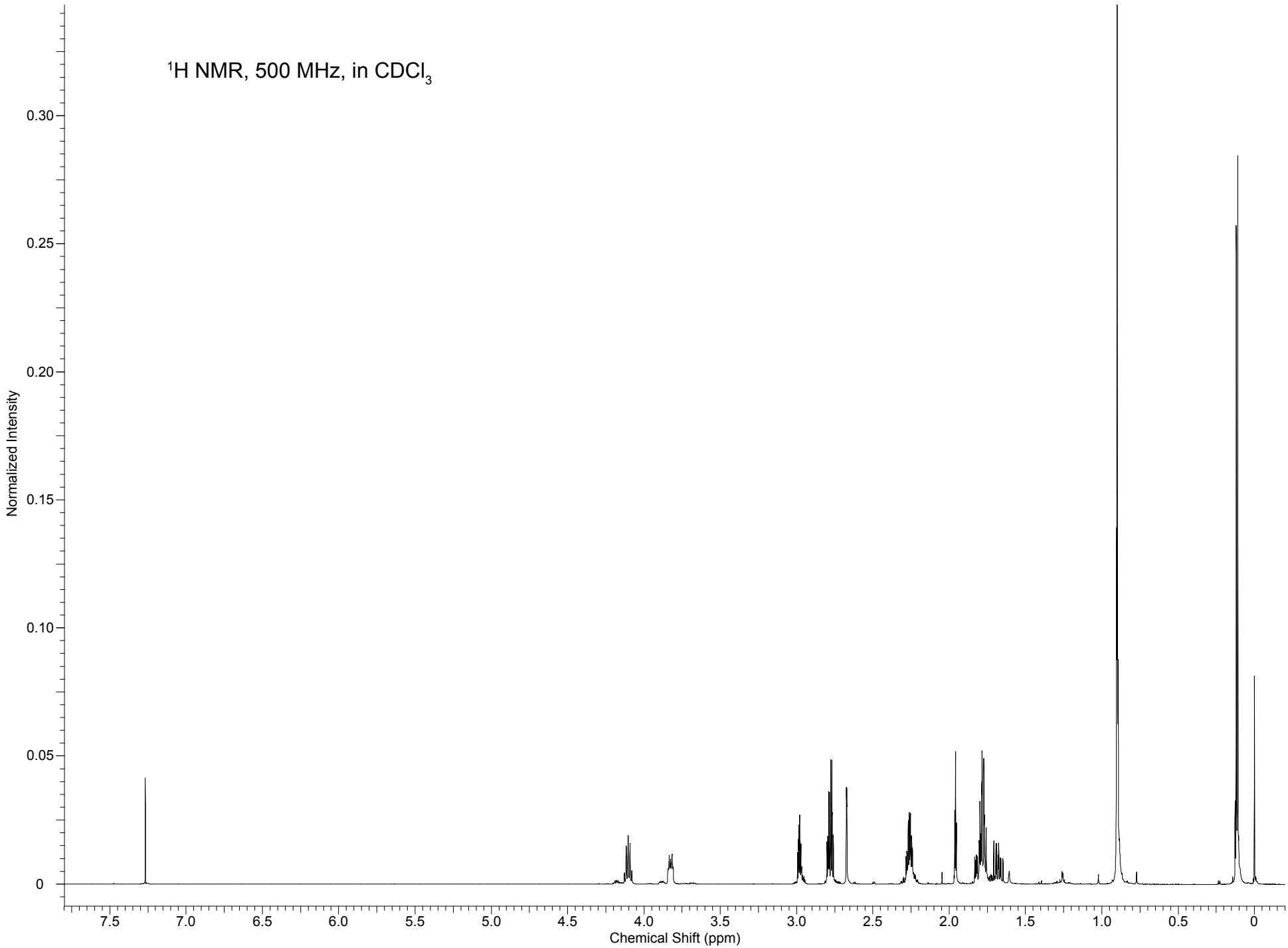
4. One goal of Mandy's research was to synthesize enantiopure oocydin A, and to do that, Mandy needed just one enantiomer of the racemic mixture she analyzed by NMR. Mandy was able to separate the two enantiomers from each other by chiral HPLC. She then took one of the pure enantiomeric alcohols, converted it into (*S*)- and (*R*)-MTPA esters, and collected an ^{1}H NMR spectrum of each ester.

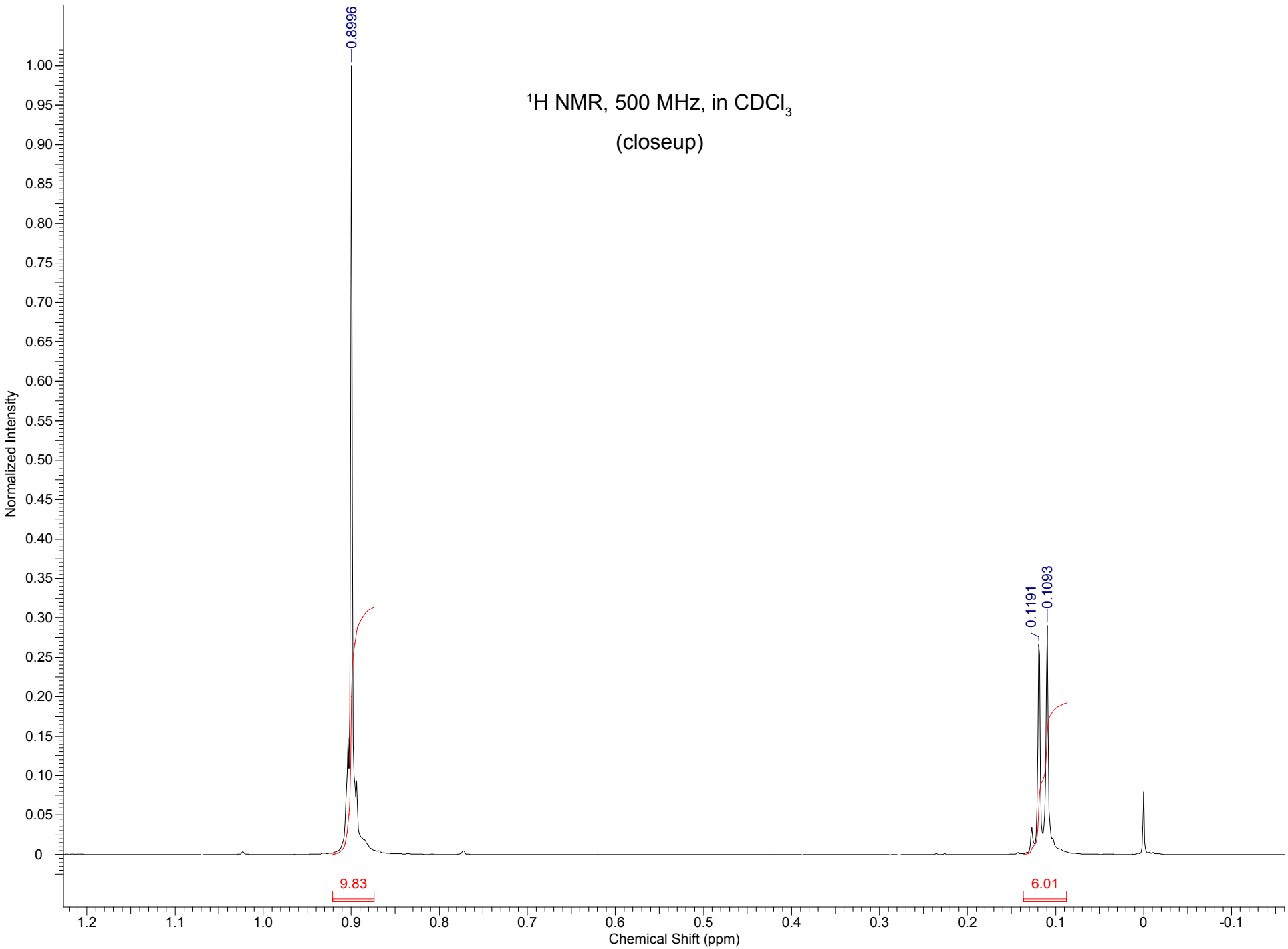
   Let's assume that the enantiomer she isolated is the one we've been using to represent the racemic mixture, and that she made the MTPA esters shown at right. What would have to be true about $\Delta\delta = \delta_S - \delta_R$ for each of the labeled protons? Circle one answer for each proton.

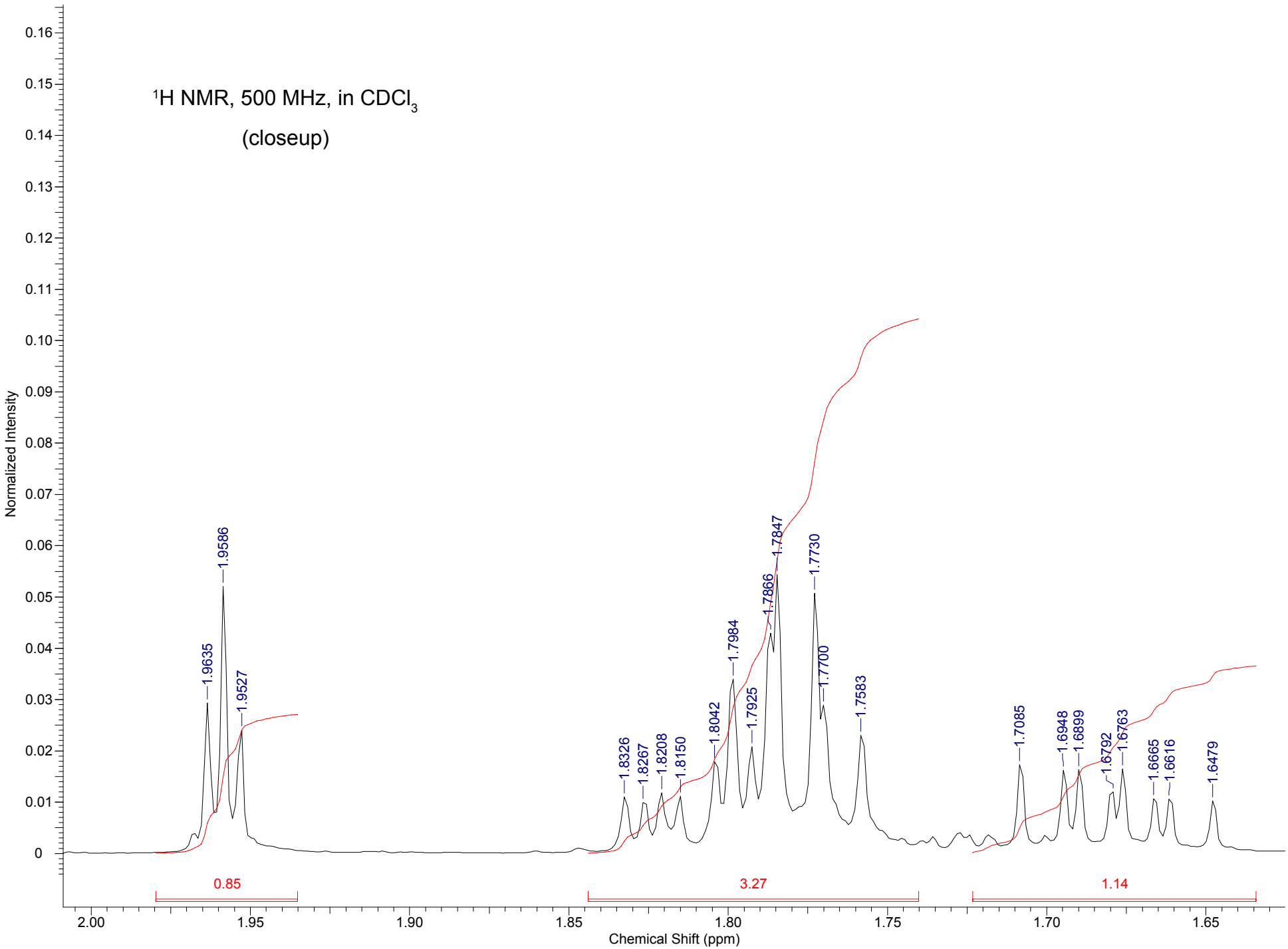


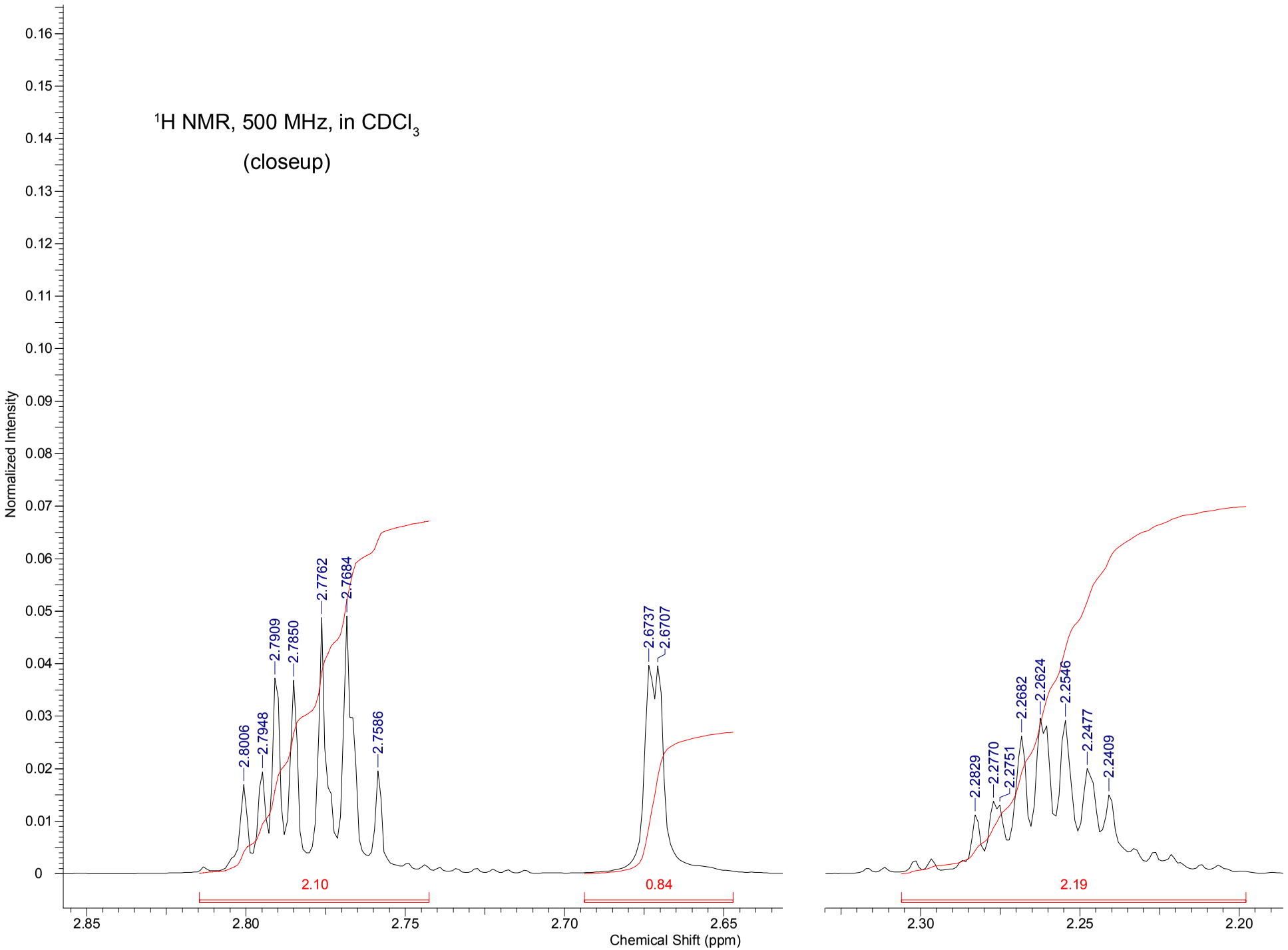
5. Mandy didn't perform DEPT experiments on her molecule. If she had, would she have observed a positive-intensity peak (**+**), a negative-intensity peak (**–**), or no peak (**0**) for each of the following carbon atoms? (Circle one answer in each box.)

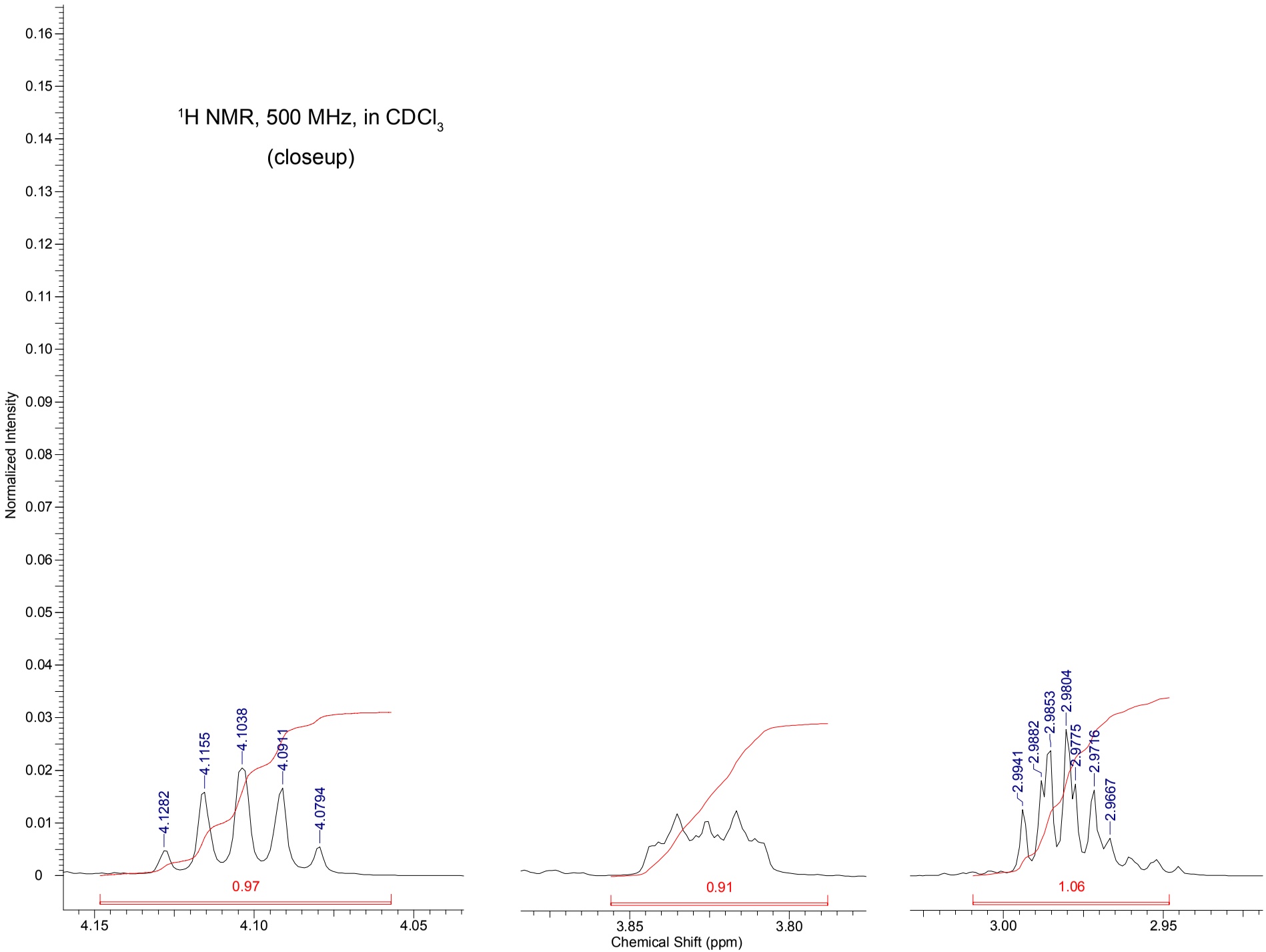
carbon	DEPT-135	DEPT-90
C(1)	**+** **–** *or* **0** ?	**+** **–** *or* **0** ?
C(2)	**+** **–** *or* **0** ?	**+** **–** *or* **0** ?
C(3)	**+** **–** *or* **0** ?	**+** **–** *or* **0** ?


^{1}H NMR, 500 MHz, in $CDCl_3$
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

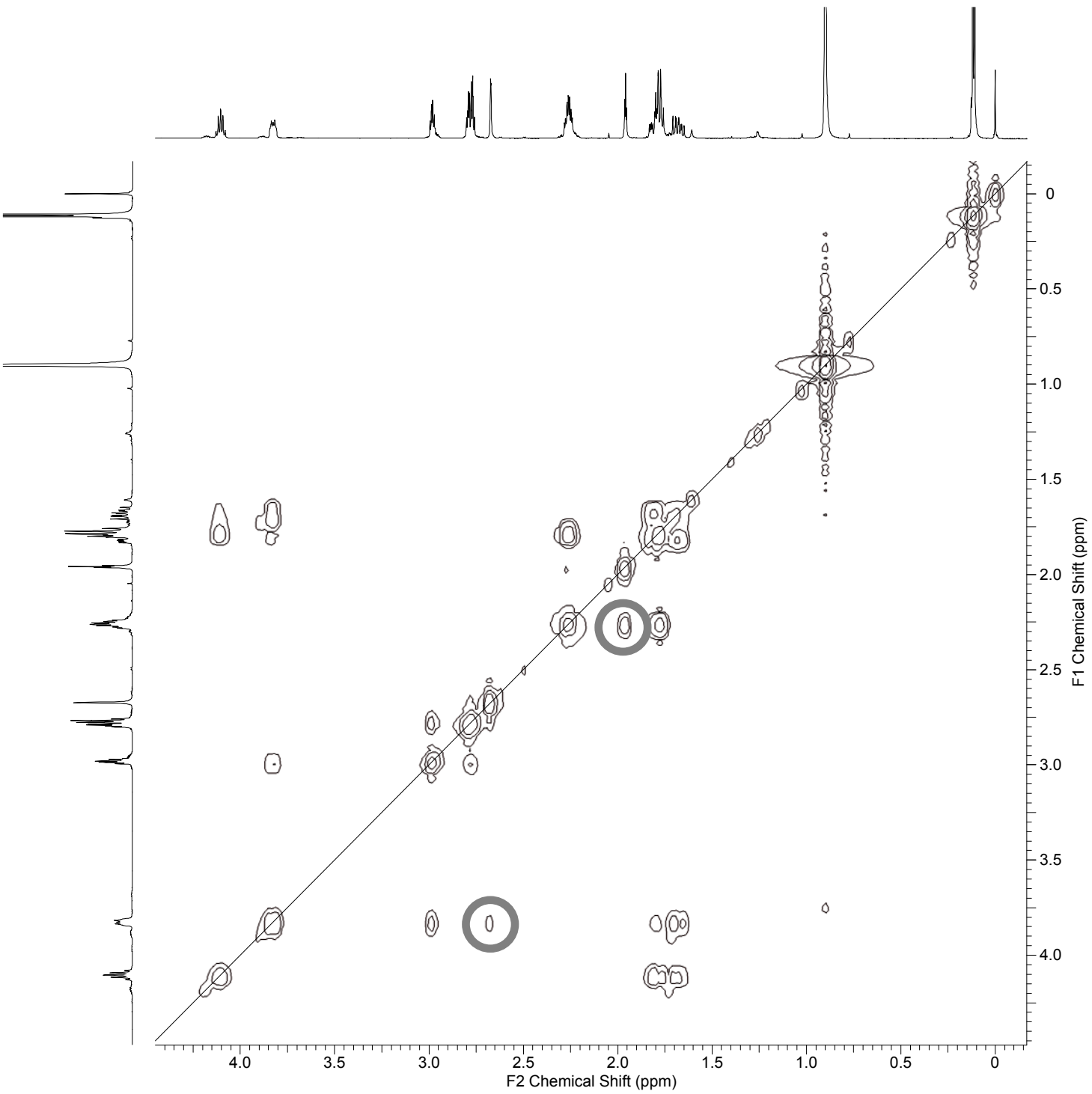

^{1}H NMR, 500 MHz, in $CDCl_3$
(closeup)
0.8996
0.1191
0.1093
9.83
6.01
Normalized Intensity
Chemical Shift (ppm)
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1


^{1}H NMR, 500 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
Chemical Shift (ppm)
1.9635
1.9586
1.9527
1.8326
1.8267
1.8208
1.8150
1.8042
1.7984
1.7925
1.7866
1.7847
1.7730
1.7700
1.7583
1.7085
1.6948
1.6899
1.6792
1.6763
1.6665
1.6616
1.6479
0.85
3.27
1.14


^{1}H NMR, 500 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
Chemical Shift (ppm)
2.8006
2.7948
2.7909
2.7850
2.7762
2.7684
2.7586
2.6737
2.6707
2.10
0.84
2.2829
2.2770
2.2751
2.2682
2.2624
2.2546
2.2477
2.2409
2.19

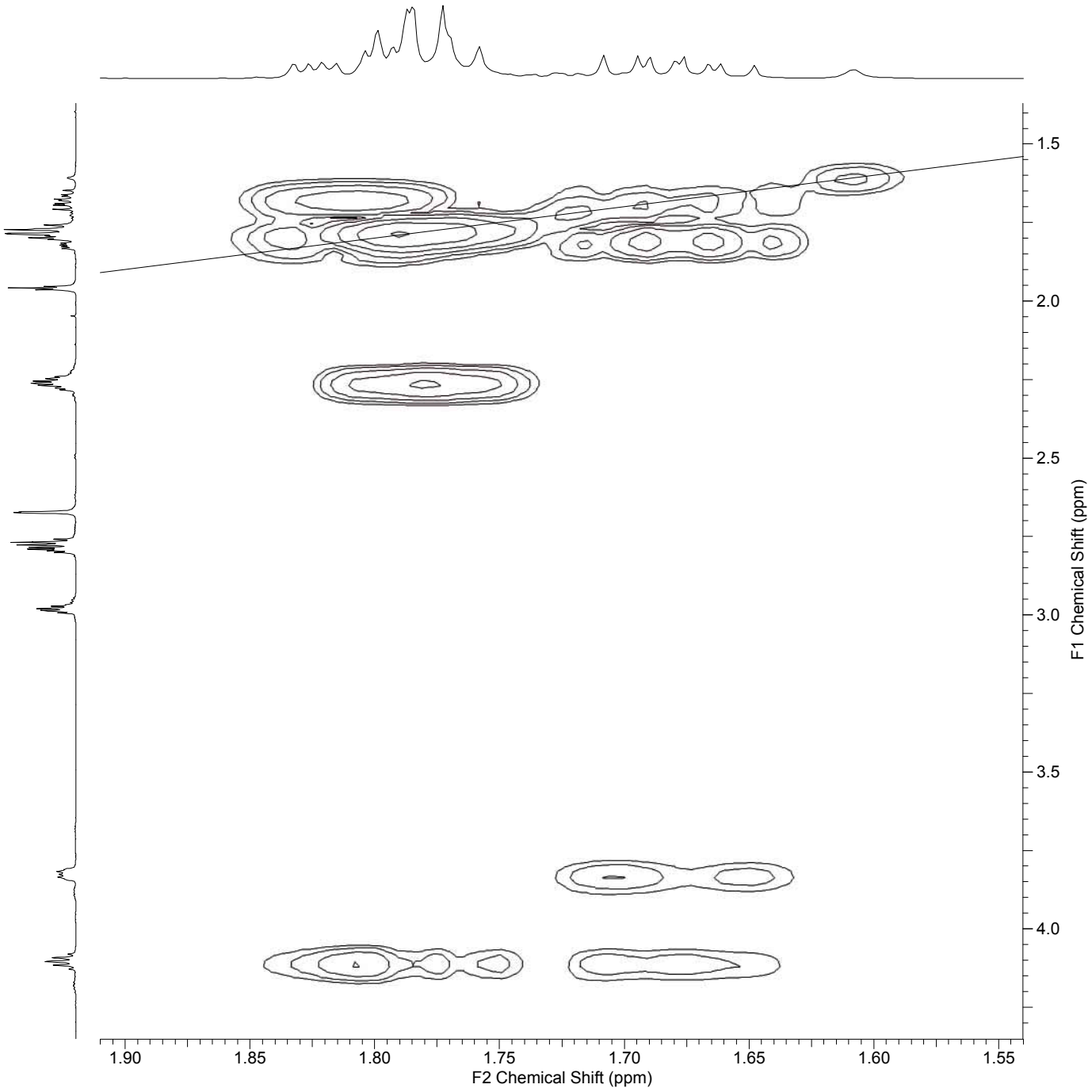

^{1}H NMR, 500 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
4.1282
4.1155
4.1038
4.0911
4.0794
0.97
4.15
4.10
4.05
0.91
3.85
3.80
2.9941
2.9882
2.9853
2.9804
2.9775
2.9716
2.9667
1.06
3.00
2.95
Chemical Shift (ppm)

^{1}H-^{1}H COSY, 500 MHz, in $CDCl_3$



^{1}H-^{1}H COSY, 500 MHz, in $CDCl_3$

(closeup)



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