NAME ________________________

ID # ________________________

INTERPRETATION OF ORGANIC SPECTRA (4361/8361)

9:05 – 9:55 am, October 3, 2012

Exam 1

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 30 minutes to complete. 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.

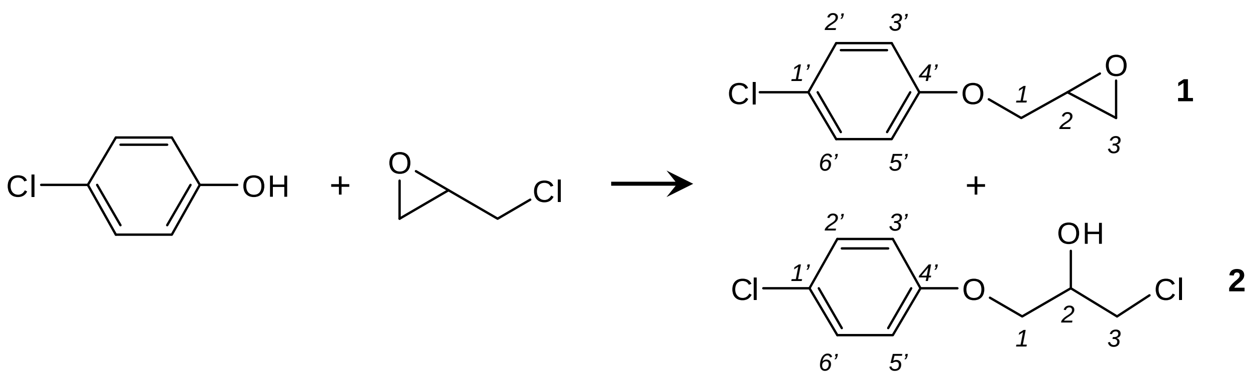
At the end of the 50 minute exam period you will be asked to return your exam to the proctor. Please do not take any part of the exam packet with you when you are done; everything will be returned to you after the exams are graded. This packet should contain 10 pages, including this one. Please check to make sure that your packet contains 10 pages before beginning your exam.

NAME ________________________

Scoring:		
	1. _________ / 51	5. _________ / 6
	2. _________ / 5	6. _________ / 21
	3. _________ / 3	7. _________ / 8
	4. _________ / 6	

Total Score: _________ / 100

p-Chlorophenol reacts with epichlorohydrin to yield a mixture of ether-epoxide **1** and ether-chloroalcohol **2**, as shown below. You run this reaction in the lab, isolate one of the two product, and analyze the purified material by ^{1}H and ^{13}C NMR spectroscopy. In this exam, you will use your ^{1}H and ^{13}C spectra—attached to the back of the exam—to determine which of the two expected products you isolated.



The two products have the same number of protons and pattern of attachment, so I have used the same numbering scheme to label both products. Please note that some carbon atoms have more than one proton attached; to name these protons separately, use "a" and "b" suffixes. (For example, H1a and H1b are both attached to C1.)

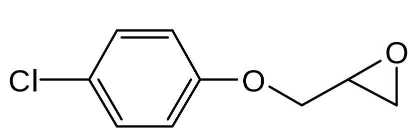
1. In the chart on the next page, assign each resonance in the ^{1}H spectrum to a proton in the unknown product. If the resonance corresponds to more than one (equivalent) proton, name all of the protons in the appropriate box. List coupling constants to the nearest 0.5 Hz. If a coupling constant value appears more than once, then list it more than once. Then, for each coupling constant you list, propose a pair of protons that are responsible for that coupling constant.

*Do the best you can on this chart--we will give partial credit to assignments that are close to the correct answer, or that are indefinite when they could be definite (and vice versa). For some protons, I have given you more boxes than you need—**you do not need to fill all the boxes.** If a box is shaded, we won't be grading it, but feel free to fill it in for your own information.*

δ **(ppm)**	**Name(s) of proton(s)** "Hn"	**Coupling constants *J* (Hz)**	**Assign coupling constants** "*J*(Hm,Hn)"
7.24			
6.85			
4.21			
3.90			

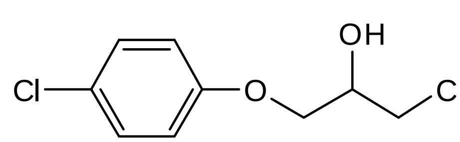
<table>
<tr><th>δ (ppm)</th><th>Name of proton
(H_n)</th><th>Coupling constants J (Hz)</th><th>Assign coupling constants
$J(H_m,H_n)$</th></tr>
<tr><td rowspan="4">3.34</td><td rowspan="4"></td><td></td><td></td></tr>
<tr><td></td><td></td></tr>
<tr><td></td><td></td></tr>
<tr><td></td><td></td></tr>
<tr><td rowspan="4">2.91</td><td rowspan="4"></td><td></td><td></td></tr>
<tr><td></td><td></td></tr>
<tr><td></td><td></td></tr>
<tr><td></td><td></td></tr>
<tr><td rowspan="4">2.75</td><td rowspan="4"></td><td></td><td></td></tr>
<tr><td></td><td></td></tr>
<tr><td></td><td></td></tr>
<tr><td></td><td></td></tr>
</table>

2. Which structure corresponds to your isolated product? (*Circle one structure.*)



1

or



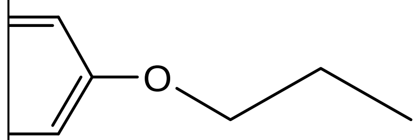
2

?

3. Regardless of which structure you picked, the two protons attached to C3 are not equivalent. Are they

enantiotopic , **diastereotopic** , *or* **neither** ? (*Circle one.*)

4. In the box on the right, show the stereochemical relationship between **H2, H3a, and H3b** by finishing my incomplete drawing with a single enantiomer of your molecule. Make sure that you label each H with its number and letter, and that your drawing is consistent with your answer to problem 1.



5. In each of the multiplets at δ = 7.24 and 6.85 ppm, one of the two tallest peaks is taller than the other. Why?

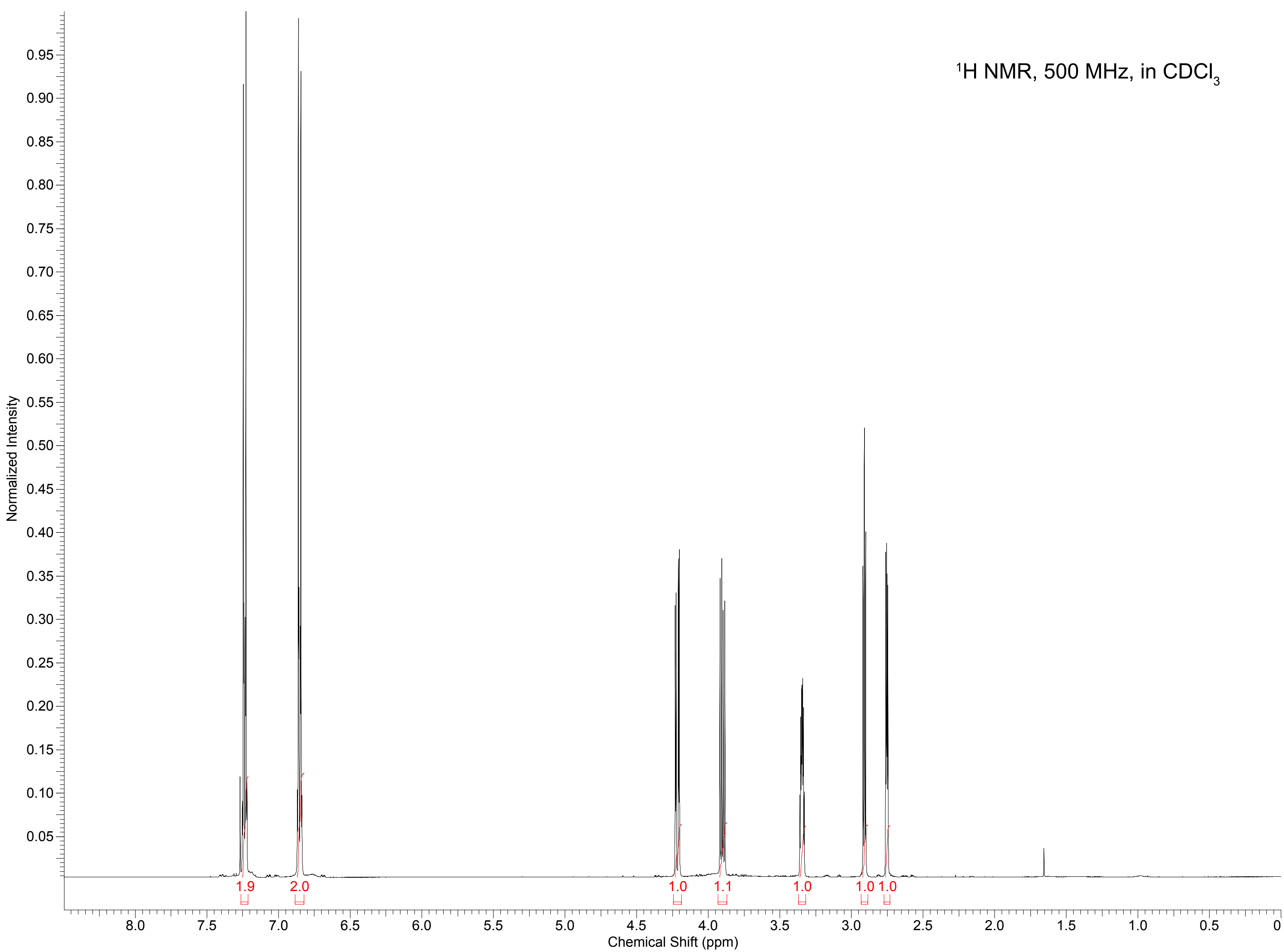
6. In the chart below, assign each resonance in the ^{13}C spectrum to a carbon in your product.

δ (ppm)	**Name of carbon**
157.3	
129.6	
126.3	

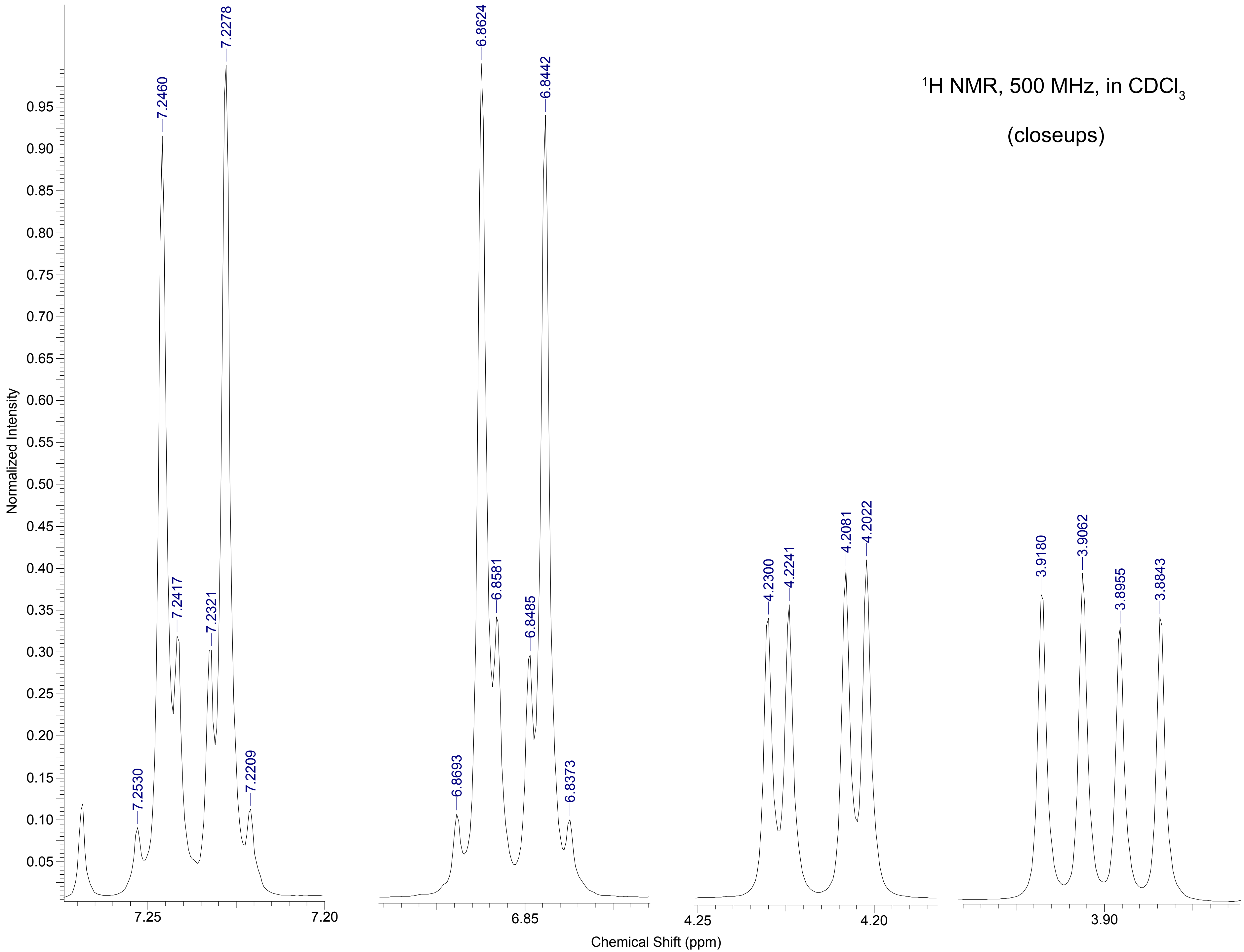
δ (ppm)	**Name of carbon**
116.2	
69.3	

δ (ppm)	**Name of carbon**
50.3	
44.8	

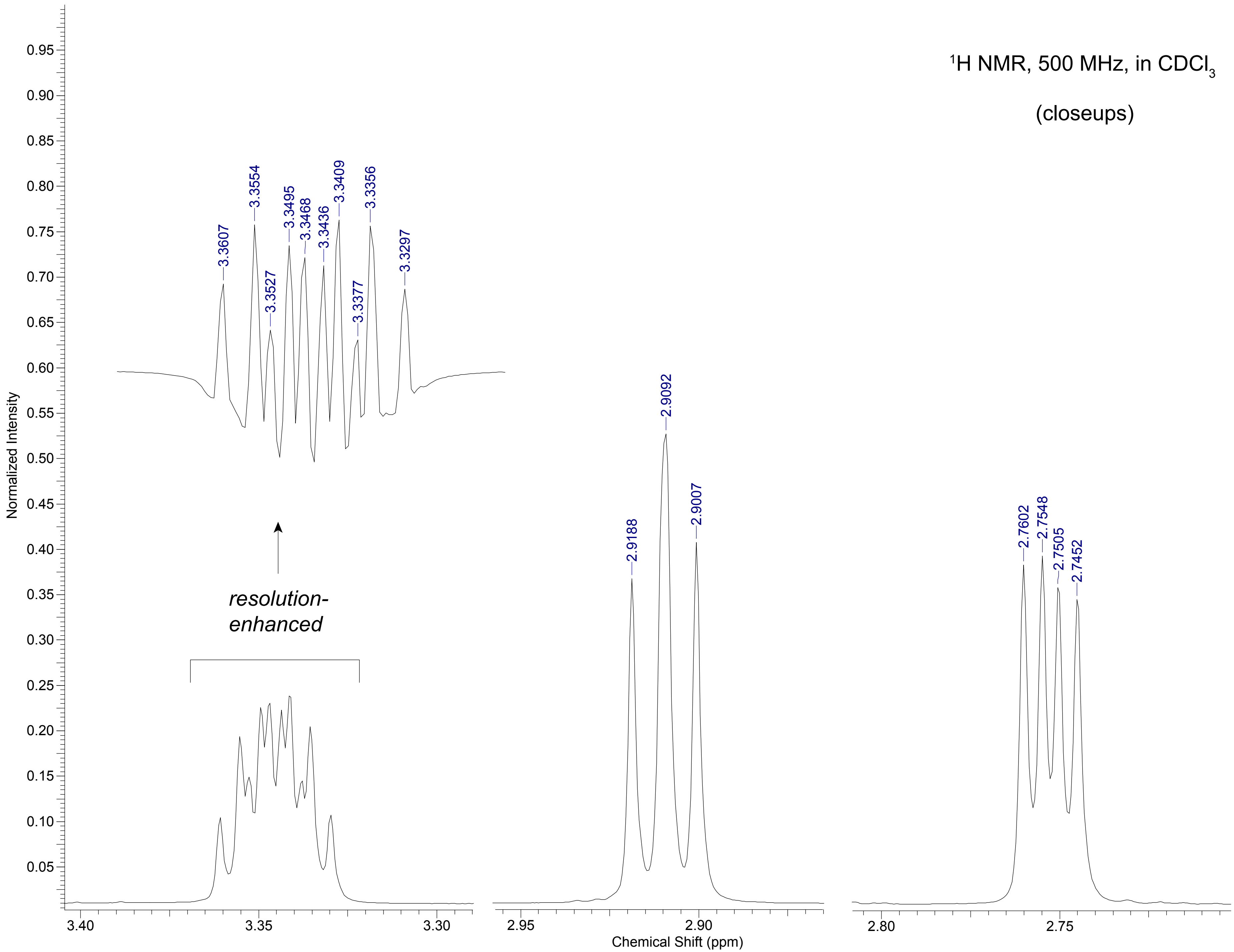
7. In the ^{13}C NMR spectrum, I didn't put peak labels on the 1:1:1 triplet at δ = 77 ppm that corresponds to $CDCl_3$ solvent. This triplet isn't very big, in spite of the fact that over 95% of the ^{13}C in the NMR tube comes from $CDCl_3$. Why is that?



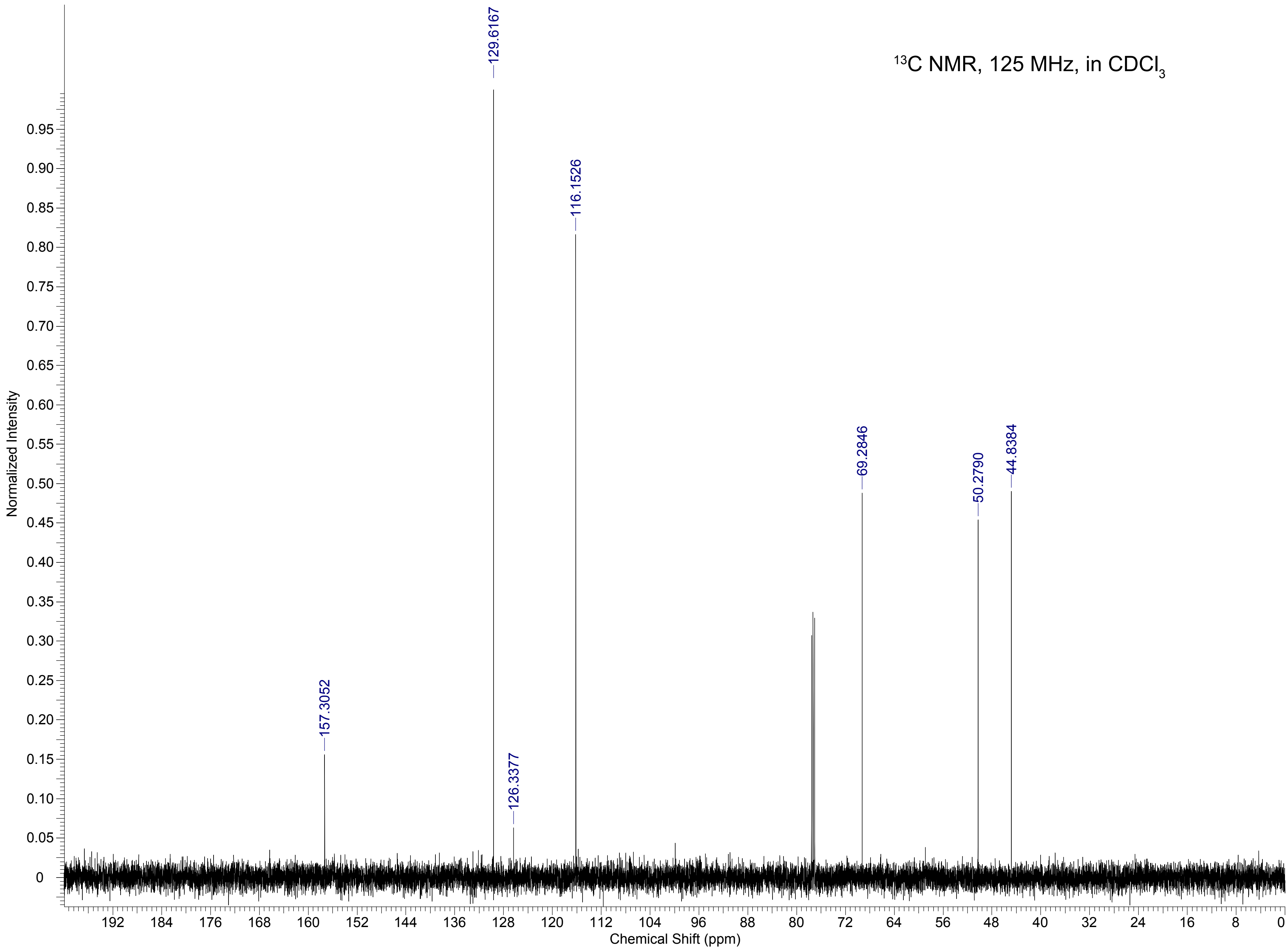
^{1}H NMR, 500 MHz, in $CDCl_3$
Normalized Intensity
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
1.9
2.0
1.0
1.1
1.0
1.0
1.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)



^{1}H NMR, 500 MHz, in $CDCl_3$
(closeups)
Normalized Intensity
Chemical Shift (ppm)
7.2530
7.2460
7.2417
7.2321
7.2278
7.2209
6.8693
6.8624
6.8581
6.8485
6.8442
6.8373
4.2300
4.2241
4.2081
4.2022
3.9180
3.9062
3.8955
3.8843
7.25
7.20
6.85
4.25
4.20
3.90
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



^{1}H NMR, 500 MHz, in $CDCl_3$
(closeups)
resolution-enhanced
3.3607
3.3554
3.3527
3.3495
3.3468
3.3436
3.3409
3.3377
3.3356
3.3297
2.9188
2.9092
2.9007
2.7602
2.7548
2.7505
2.7452
Normalized Intensity
Chemical Shift (ppm)



^{13}C NMR, 125 MHz, in $CDCl_3$
129.6167
116.1526
69.2846
50.2790
44.8384
157.3052
126.3377
Normalized Intensity
Chemical Shift (ppm)
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
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0