NAME _____

ID # _____

INTERPRETATION OF ORGANIC SPECTRA (4361/8361)

9:05 – 9:55 am, October 6, 2010

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.

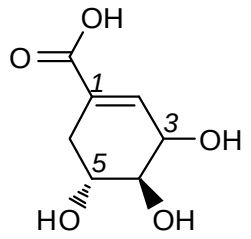
At the end of the 50 minute exam period you will be asked to return your exam to the proctor. Please do not take any part of the exam packet with you when you are done; everything will be returned to you after the exams are graded. This packet should contain 10 pages, including this one. Please check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

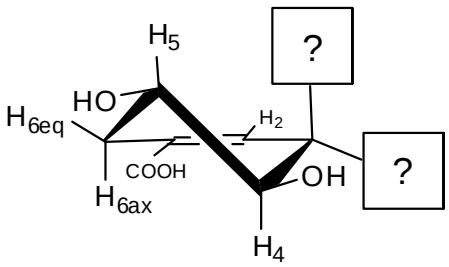
NAME _____

Scoring:	1. _____ / 50	4. _____ / 4
	2. _____ / 9	5. _____ / 21
	3. _____ / 6	6. _____ / 10

Total Score: _____ / 100

Shikimic acid (or shikimate) is an important biosynthetic intermediate in plants, and is also a commercial precursor to oseltamivir (Tamiflu). The most stable conformation for the ring is a pseudo-chair, which I've drawn at right. In both structures on the right, I have omitted stereochemistry at carbon 3. A main goal of this problem will be to assign stereochemistry at this position with the aid of NMR spectra. ^{1}H (400 MHz, in D_2O) and ^{1}H-decoupled ^{13}C NMR (100 MHz, in D_2O) spectra are attached to the end of this problem.



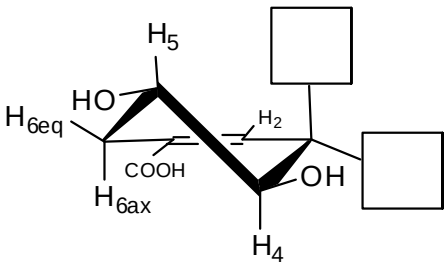


1. In the chart on the next page, assign each resonance in the ^{1}H spectrum to a proton in shikimic acid. If there are chemical shifts you feel you cannot assign definitively to one proton, but you can narrow it down to a few, name all possible protons in the corresponding box. List coupling constants to the nearest 0.3 Hz. Then, for each coupling constant you list, propose a pair of protons that are responsible for that coupling constant. Draw a line to connect each assignment to its *J* value.

   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). Try not to leave any of the boxes blank; put in whatever information you feel you have.

δ (ppm)	Name of proton (H_n)	Coupling constants *J* (Hz)	Assign coupling constants $J(H_m,H_n)$
6.38			
4.34			
3.93			
3.65			
2.71			
2.14			

2. Given this data, what stereochemistry would you assign to C_3? Fill in the two empty boxes on the right. Then, using a double-headed arrow, illustrate one coupling relationship that helped you make this assignment. Label that arrow with the corresponding *J* value.



3. There are a number of protons in shikimic acid—the carboxylic acid proton, as well as the alcohol protons—that are not visible in the ^{1}H NMR spectrum. Why not? Briefly explain in the box below.

4. If the ^{1}H NMR were taken in 1 M $NaOD/D_2O$ instead of in pure D_2O, would the proton at δ = 6.38 ppm

shift upfield *or* **shift downfield** *or* **stay at the same chemical shift**

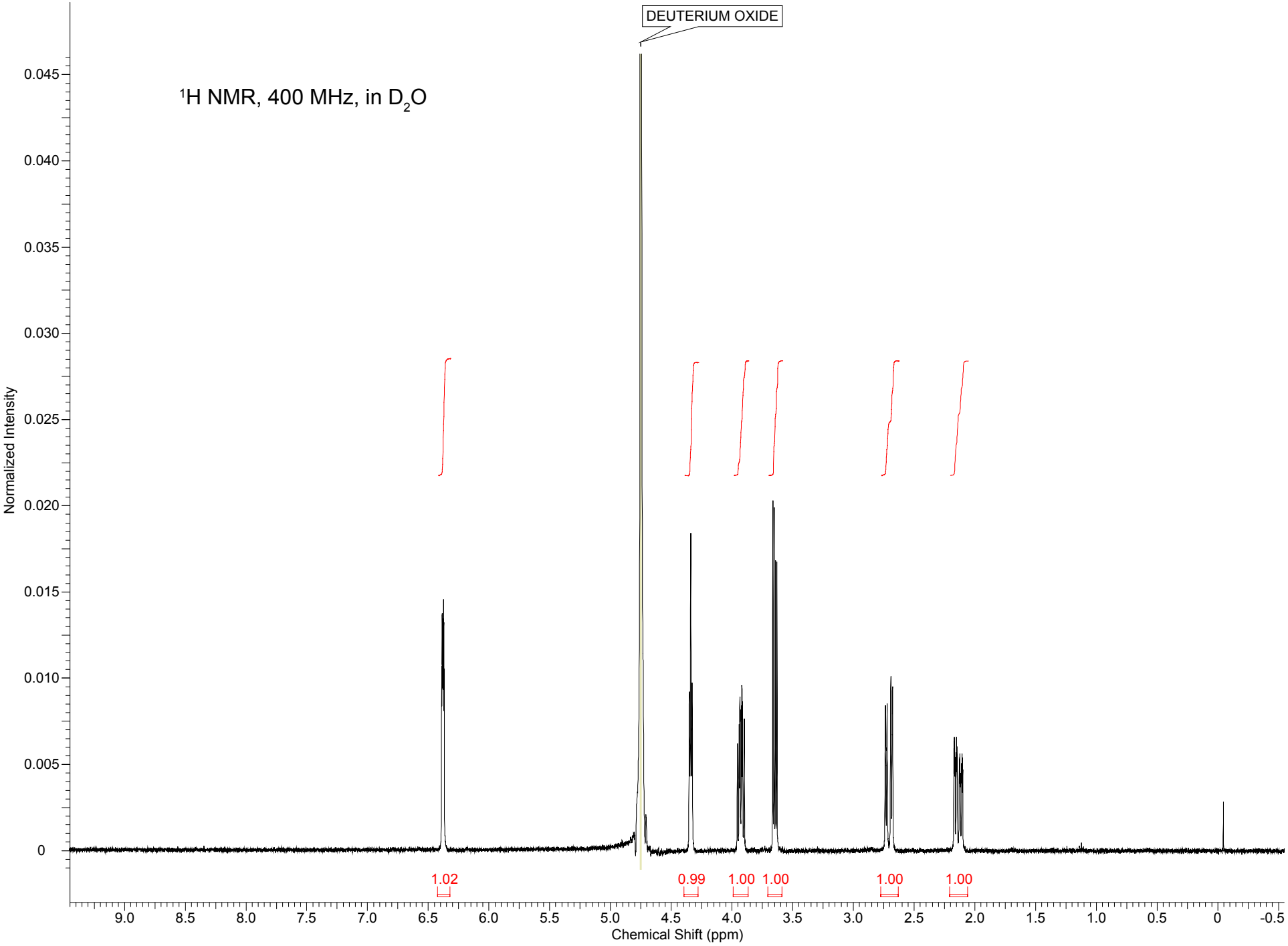
relative to its original δ value? (Circle one answer.)

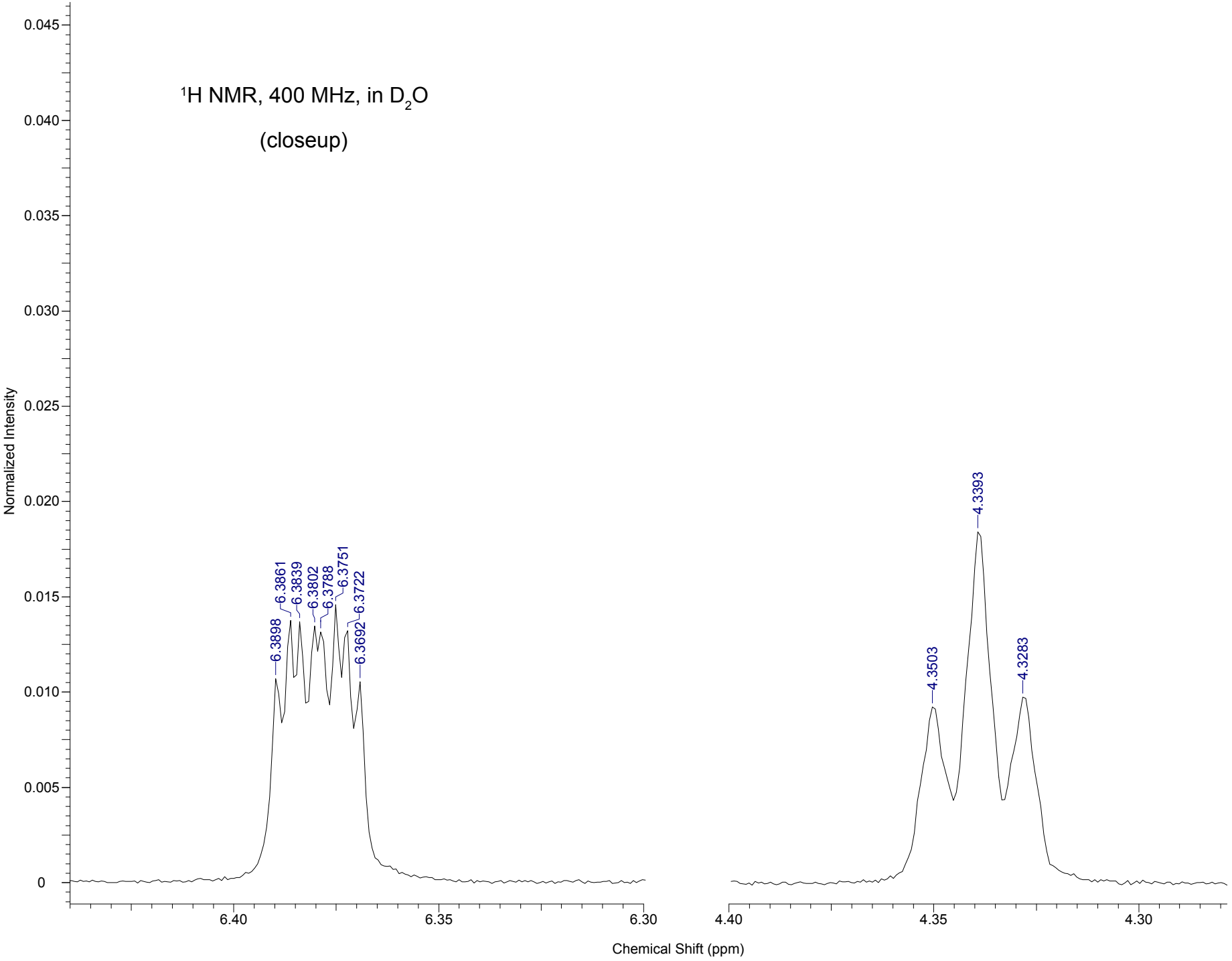
5. In the chart below, assign each resonance in the ^{13}C spectrum to a carbon in shikimic acid. If there are chemical shifts you feel you cannot assign definitively to one carbon, but you can narrow it down to a few, name all possible carbons in the corresponding box.

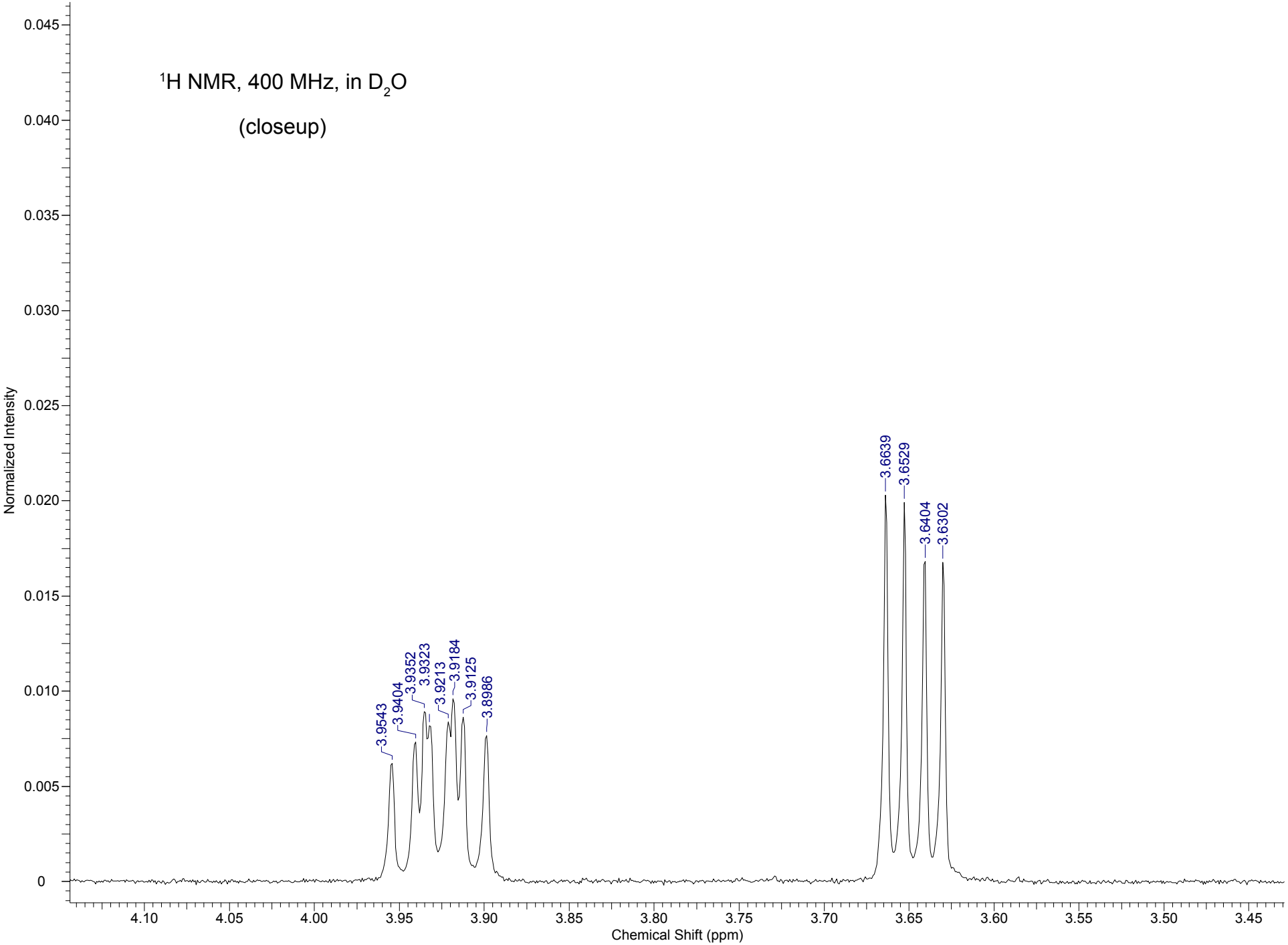
δ (ppm)	Name of carbon
178.1	
138.7	
133.2	
74.8	

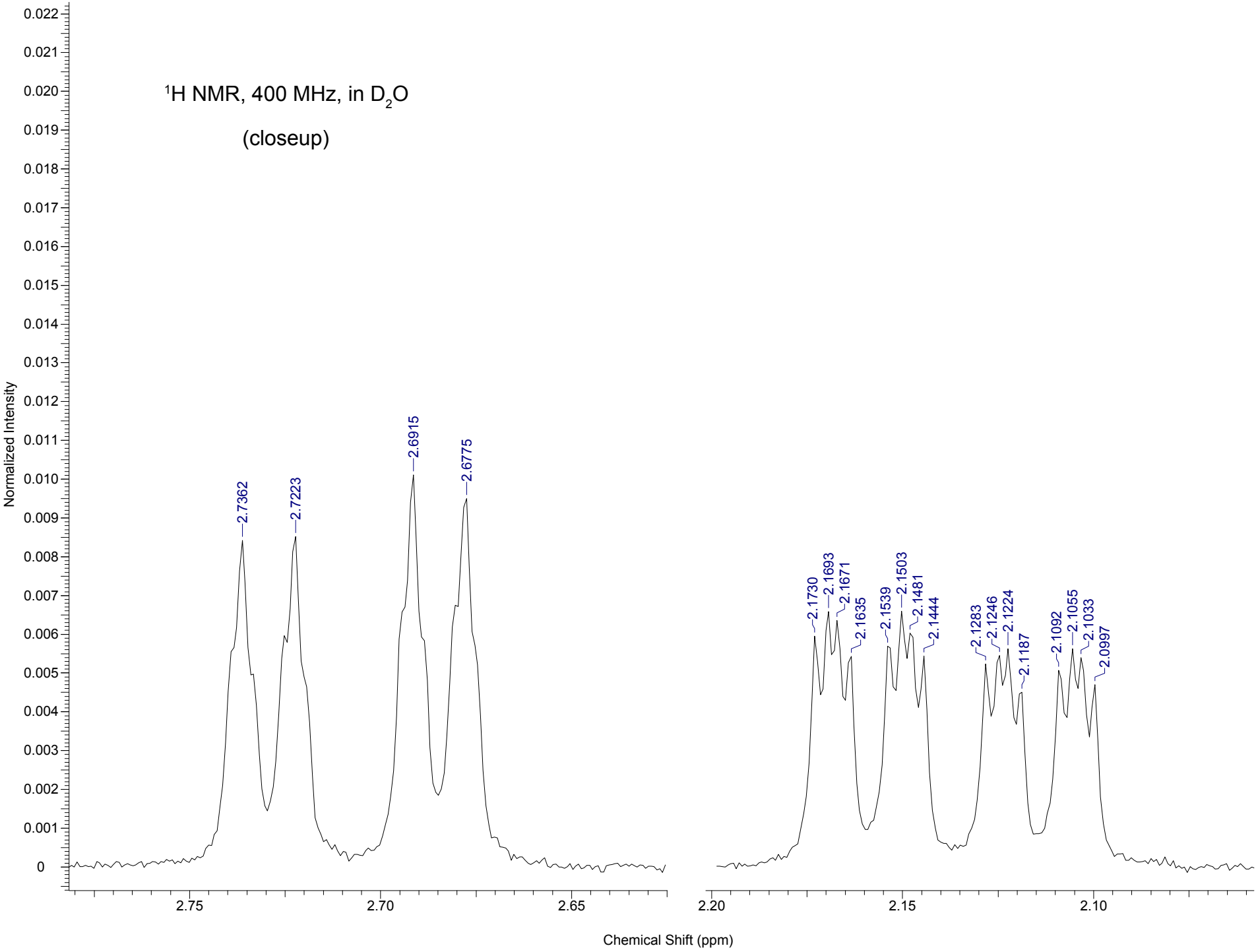
δ (ppm)	Name of carbon
69.5	
69.0	
35.4	

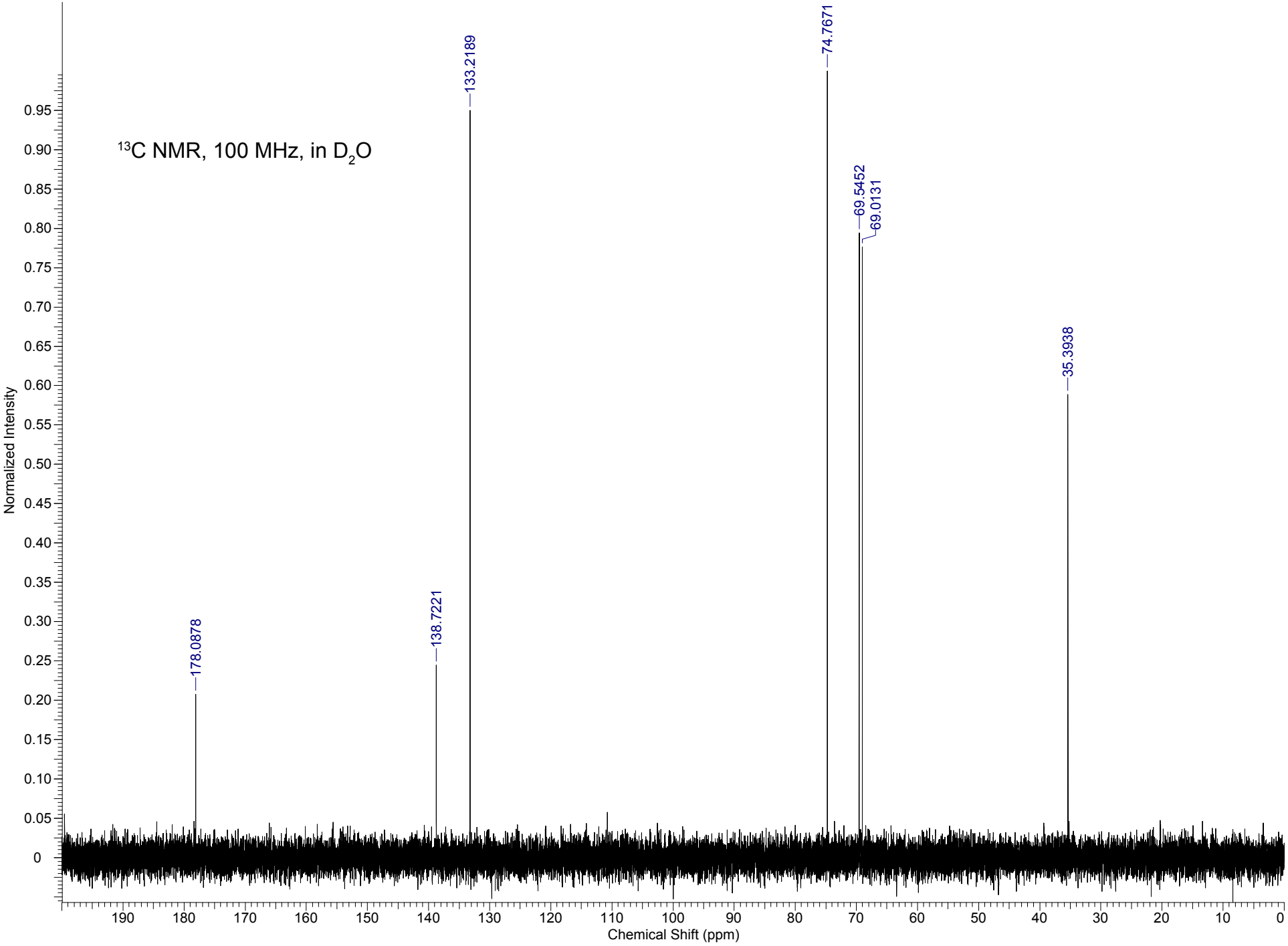
6. The ^{13}C peaks at δ = 178.1 and 138.7 ppm are considerably smaller than the others. Why? In the box below, give <u>two</u> answers that relate to the mechanism of NMR spectroscopy.


DEUTERIUM OXIDE
^{1}H NMR, 400 MHz, in D_2O
Normalized Intensity
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0
1.02
0.99
1.00
1.00
1.00
1.00
9.0
8.5
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
-0.5
Chemical Shift (ppm)


^{1}H NMR, 400 MHz, in D_2O
(closeup)
Normalized Intensity
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0
6.3898
6.3861
6.3839
6.3802
6.3788
6.3751
6.3722
6.3692
4.3503
4.3393
4.3283
6.40
6.35
6.30
4.40
4.35
4.30
Chemical Shift (ppm)


^{1}H NMR, 400 MHz, in D_2O
(closeup)
Normalized Intensity
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0
3.9543
3.9404
3.9352
3.9323
3.9213
3.9184
3.9125
3.8986
3.6639
3.6529
3.6404
3.6302
4.10
4.05
4.00
3.95
3.90
3.85
3.80
3.75
3.70
3.65
3.60
3.55
3.50
3.45
Chemical Shift (ppm)


^{1}H NMR, 400 MHz, in D_2O
(closeup)
Normalized Intensity
Chemical Shift (ppm)
2.7362
2.7223
2.6915
2.6775
2.1730
2.1693
2.1671
2.1635
2.1539
2.1503
2.1481
2.1444
2.1283
2.1246
2.1224
2.1187
2.1092
2.1055
2.1033
2.0997


^{13}C NMR, 100 MHz, in D_2O
178.0878
138.7221
133.2189
74.7671
69.5452
69.0131
35.3938
Normalized Intensity
Chemical Shift (ppm)