NAME _____

ID # _____

INTERPRETATION OF ORGANIC SPECTRA (4361/8361)

9:05 – 9:55 am, November 16, 2011

Exam 3

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 9 pages, including this one. Please check to make sure that your packet contains 9 pages before beginning your exam.

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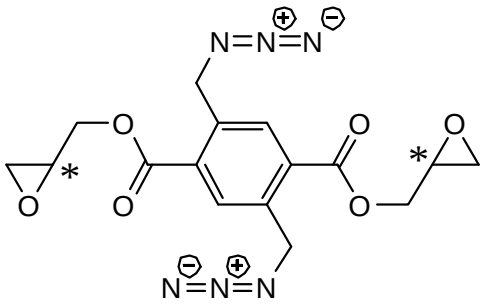
NAME _____

Scoring:	1. _____ / 28	6. _____ / 10
	2. _____ / 6	7. _____ / 12
	3. _____ / 6	8. _____ / 12
	4. _____ / 6	9. _____ / 4
	5. _____ / 10	10. _____ / 6

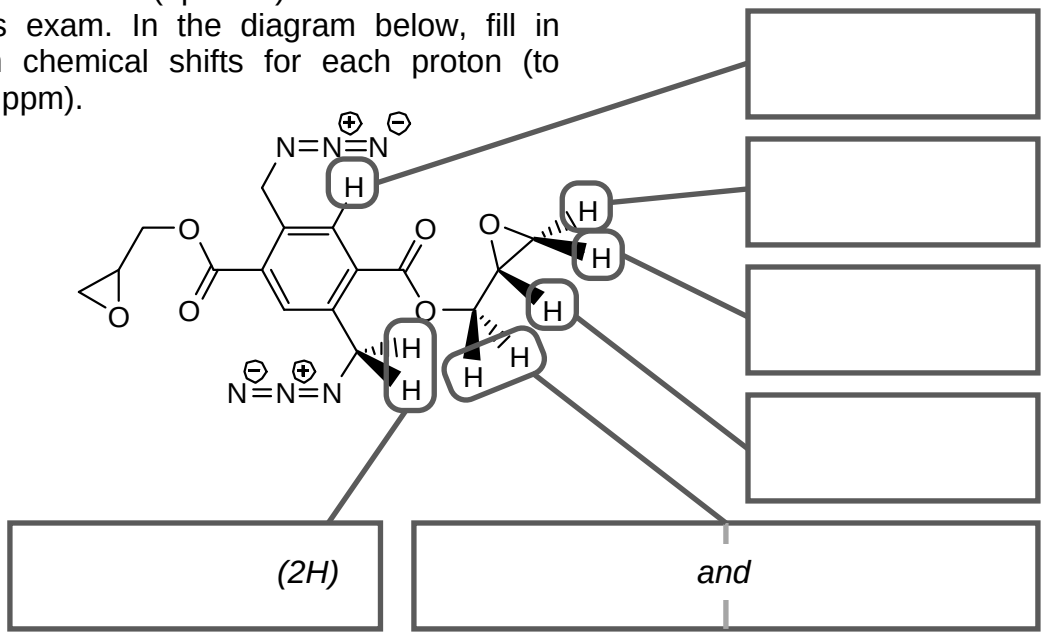
Total Score: _____ / 100

Walt Partlo (Taton group) synthesized the terphthalyl bis(epoxide) shown at right, with the goal of forming epoxy resins and gels in the presence of crosslinking oligo-amines. In this exam, you will answer questions about this bis(epoxide) and molecules related to it. Even though Walt's bis(epoxide) has two stereocenters (indicated by asterisks in the drawing), Walt was not able to separate the molecule's diastereomers from one another, and so all of the questions in this exam refer to a mixture of all possible diastereomers.



$C_{16}H_{16}N_6O_6$ (MW = 388)

1. A ^{1}H NMR of the bis(epoxide) is attached to the end of this exam. In the diagram below, fill in boxes with chemical shifts for each proton (to within 0.05 ppm).



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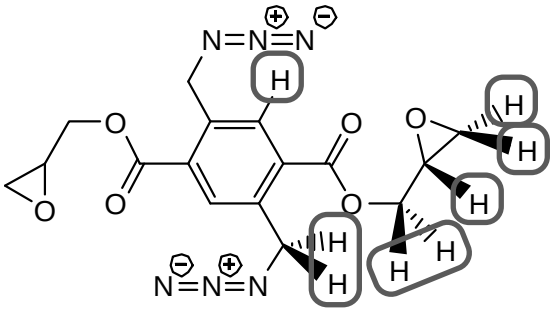
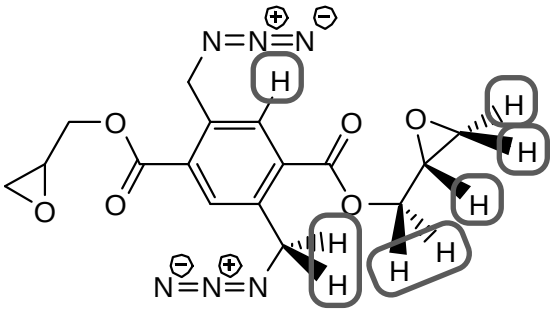
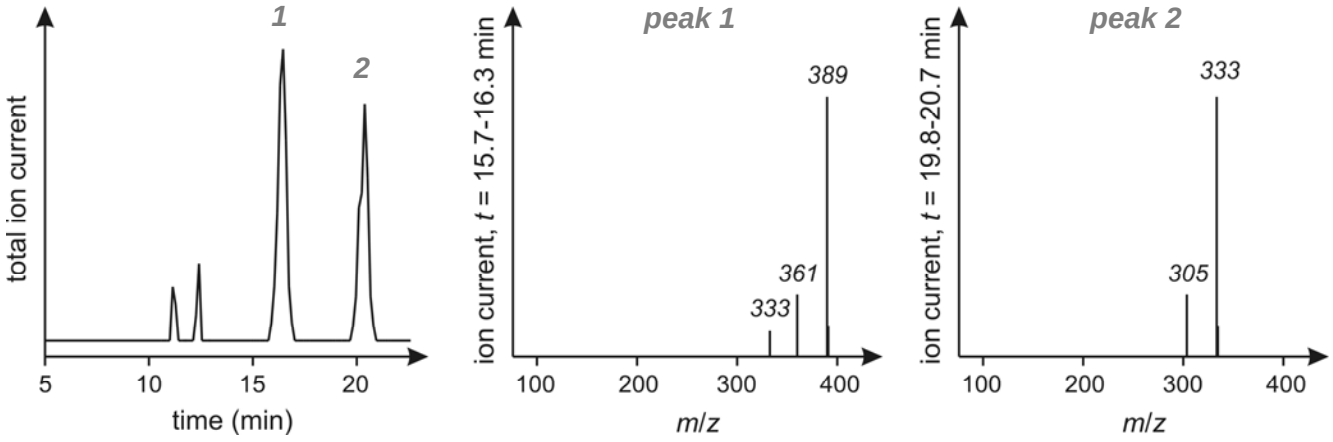
2. Draw two ^{1}H-^{1}H correlations that you would expect to observe in <u>both</u> the ^{1}H-^{1}H NOESY spectrum and the ^{1}H-^{1}H TOCSY spectrum of Walt's bis(epoxide). Draw each correlation as a double-headed arrow on the structure at right.



3. Then, draw two ^{1}H-^{1}H correlations that you would expect to observe in the ^{1}H-^{1}H NOESY spectrum, but <u>not</u> in the ^{1}H-^{1}H TOCSY spectrum of Walt's bis(epoxide). Once again, draw each correlation as a double-headed arrow on the structure at right.



Walt combined his bis(epoxide) with water-soluble tetra-amines, and heated them together in water, to form crosslinked polymer hydrogels. (For reference, Jell-O is also a hydrogel.) When he washed these gels, some material—presumably related to the bis(epoxide) starting material—was recovered from the gel. Walt performed liquid-chromatography/electrospray-ionization mass spectrometry (LC/ESI-MS), in positive-ion mode, on the recovered material. He observed two major peaks in the total-ion-current (TIC) trace, and used ions collected during each peak to construct a mass spectrum of each component. This data is shown below:



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4. Walt assumed that peak 1 corresponded to his bis(epoxide) starting material. What is the structure of the parent ion observed in peak 2?

5. The relative, integrated intensity of peaks 1 and 2 in the TIC trace is about 50/50, but this is not necessarily equal to the ratio of bis(epoxide) to the second molecule. What would Walt need to do to calculate this ratio?

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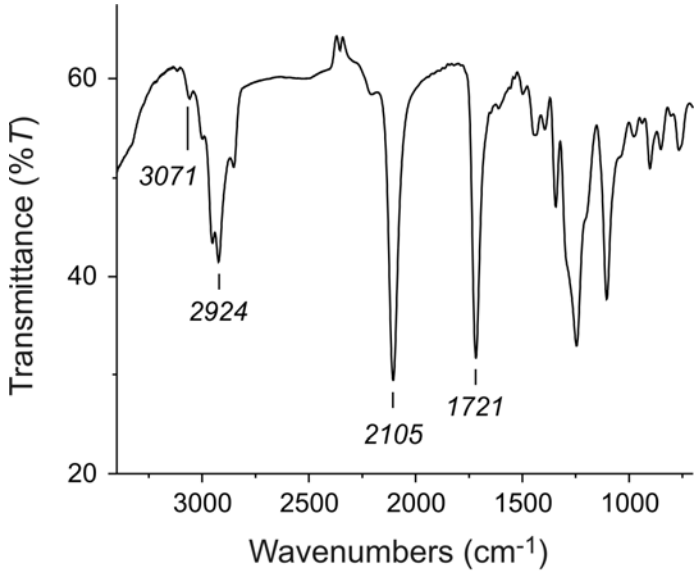
6. Walt observed the same parent masses when he measured the mass spectrum using atmospheric pressure photoionization (APPI) MS, but only when he used toluene as a dopant. Draw a pair of reaction steps—including one photoionization step—that explains how an *m*/*z* = 389 parent would be observed in this experiment.

7. Walt deposited a solution of his bis(epoxide) on an NaCl plate, and collected an IR spectrum of the molecule, shown below. What functional groups are responsible for the four labeled peaks?



ν (cm^{-1})	functional group
3071	
2924	
2105	
1721	

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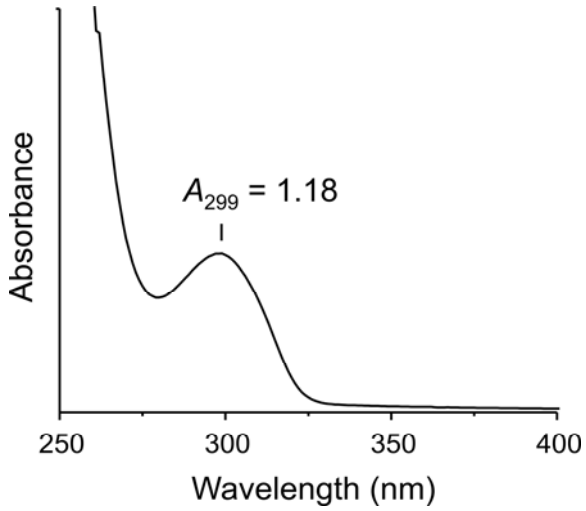
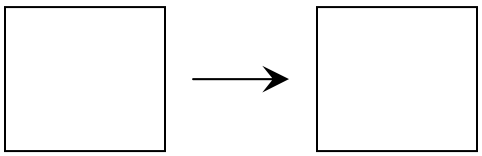
8. Walt wanted to measure a transmission IR spectrum (like the one shown on the previous page) of the functional groups in his crosslinked hydrogel, but found that his materials were too opaque to allow the IR light to pass through. What alternative sampling technique might he use to get around this problem? Your answer should (i) name the technique, and (ii) describe how the configuration of the experiment addresses Walt's issue.

9. Walt collected a UV-vis spectrum of his bis(epoxide), shown at right, as a 0.0086 M solution in chloroform in a cuvette with a 1-cm path length. What is ε_{299} for this molecule?



10. What type of electronic transition is responsible for the absorbance peak at λ = 299 nm? Electrons are excited from what gound-state orbital, to what excited-state orbital?



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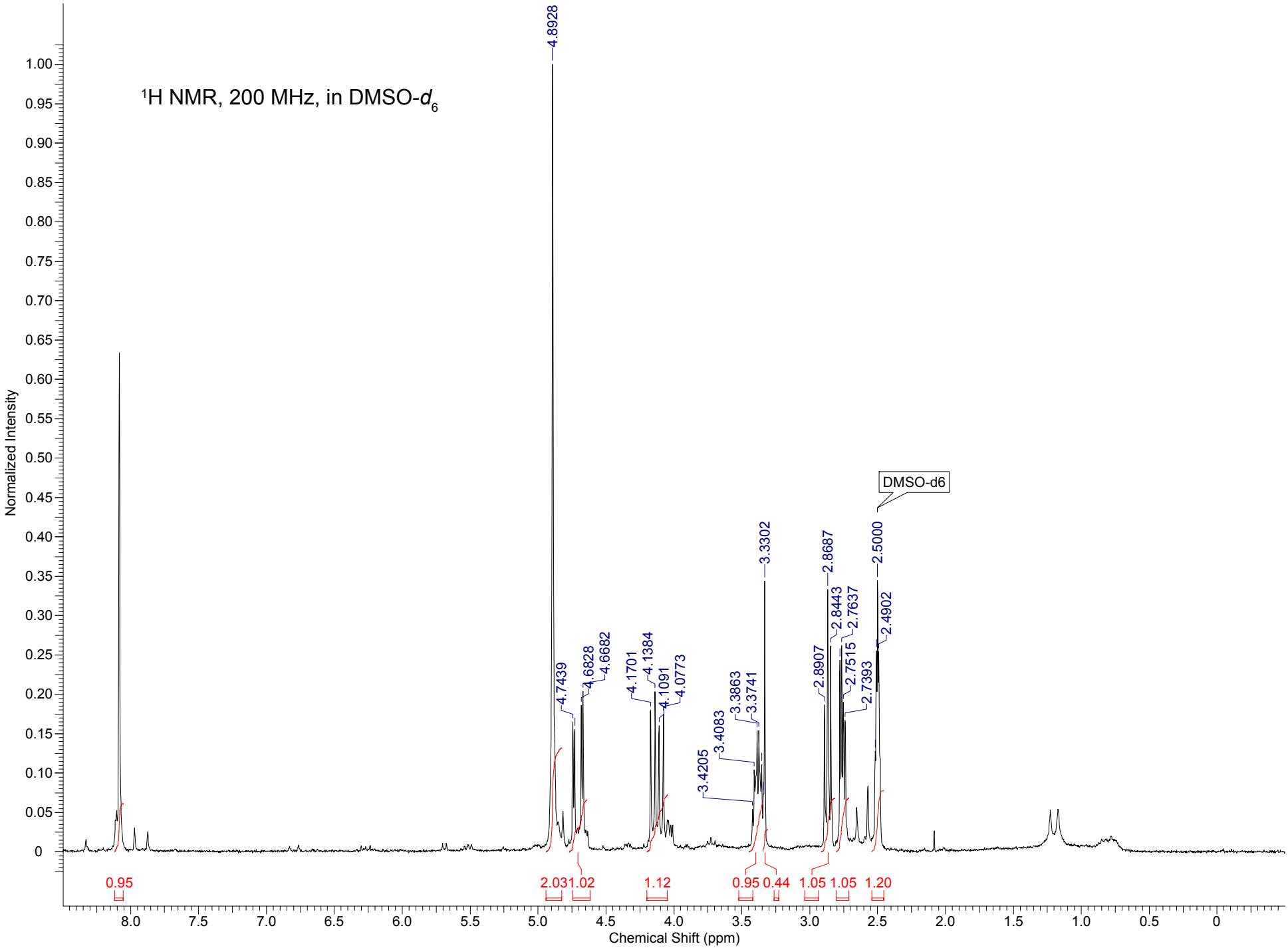
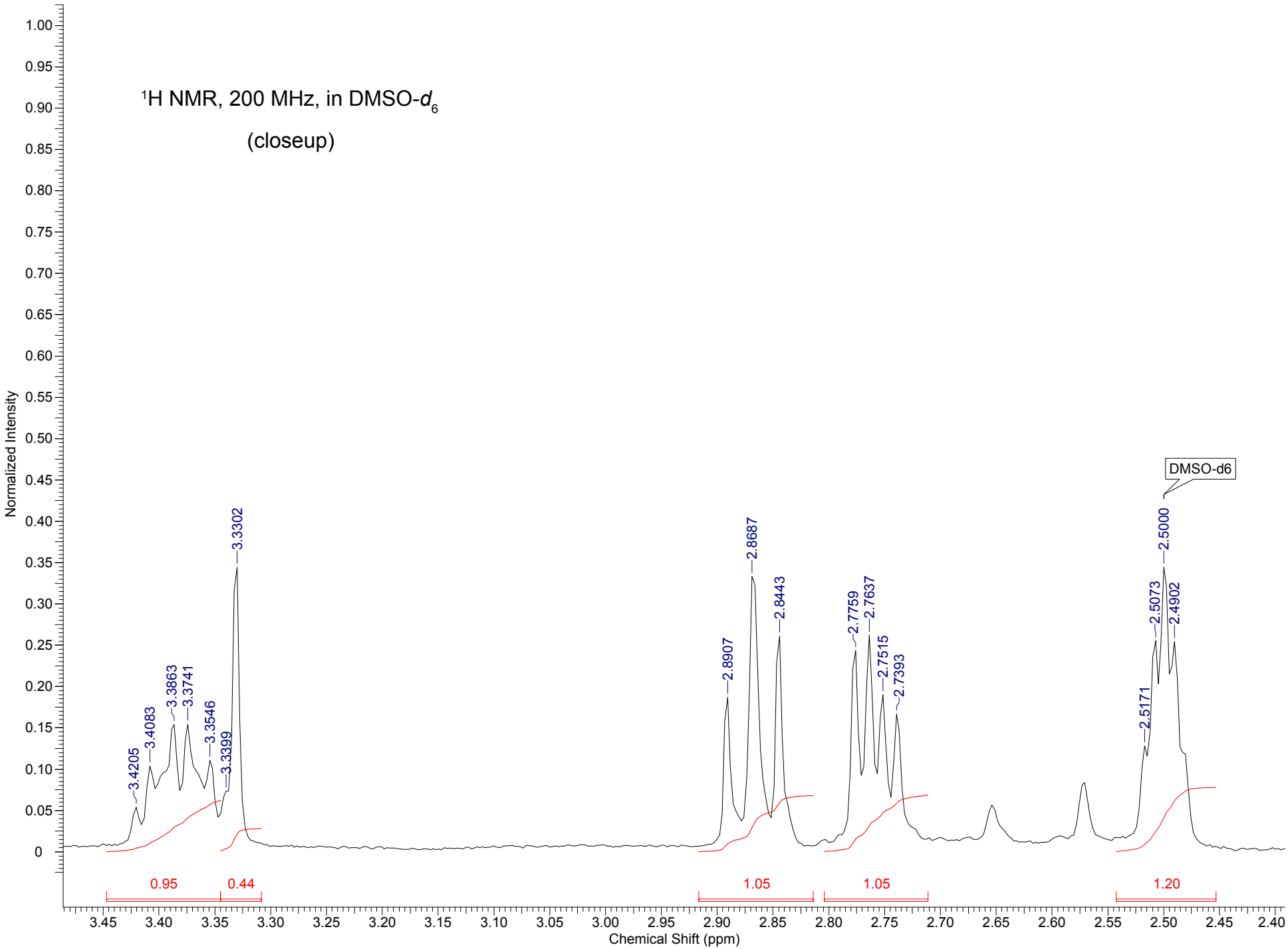
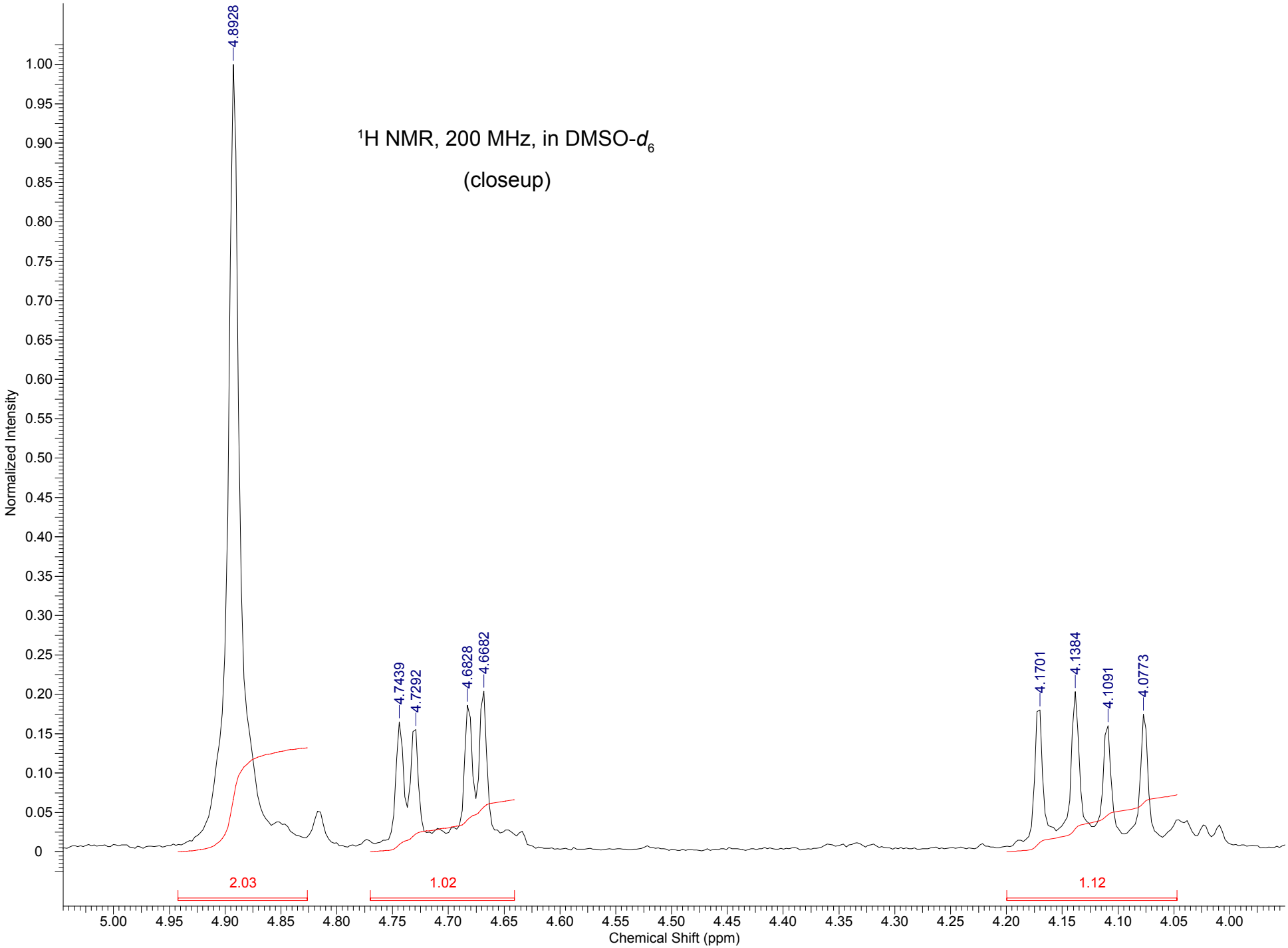

^{1}H NMR, 200 MHz, in DMSO-d_6
Normalized Intensity
Chemical Shift (ppm)
4.8928
4.7439
4.6828
4.6682
4.1701
4.1384
4.1091
4.0773
3.4205
3.4083
3.3863
3.3741
3.3302
2.8907
2.8687
2.8443
2.7637
2.7515
2.7393
2.5000
2.4902
DMSO-d6
0.95
2.03
1.02
1.12
0.95
0.44
1.05
1.05
1.20


^{1}H NMR, 200 MHz, in DMSO-d_6
(closeup)
Normalized Intensity
Chemical Shift (ppm)
DMSO-d6
3.4205
3.4083
3.3863
3.3741
3.3546
3.3399
3.3302
2.8907
2.8687
2.8443
2.7759
2.7637
2.7515
2.7393
2.5171
2.5073
2.5000
2.4902
0.95
0.44
1.05
1.05
1.20



^{1}H NMR, 200 MHz, in DMSO-d_6

(closeup)