NAME _____

ID # _____

INTERPRETATION OF ORGANIC SPECTRA (4361/8361)

1:30 – 3:30 pm, December 22, 2011

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. You will be given 2 hours total to finish the test. This exam contains <u>two</u> main problems, which are 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.

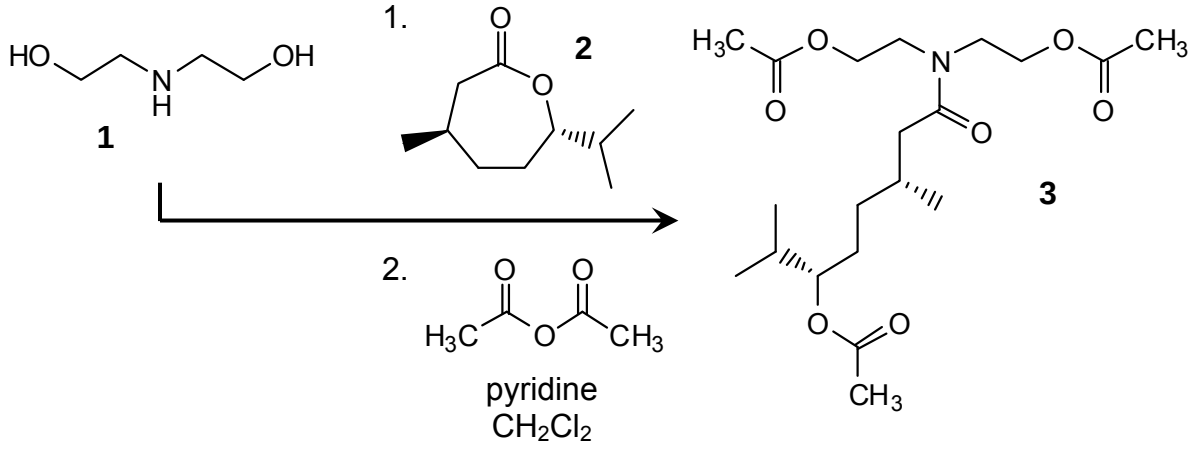
At the end of the 2 hour exam period you will be asked to return your exam to the proctor. Please do not take any part of the exam packet with you when you are done; everything will be returned to you after the exams are graded. This packet should contain 22 pages, including this one. Please check to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

NAME _____

Scoring:			
	1. _____ / 48	5. _____ / 9	9. _____ / 60
	2. _____ / 32	6. _____ / 3	10. _____ / 8
	3. _____ / 9	7. _____ / 3	11. _____ / 8
	4. _____ / 4	8. _____ / 6	12. _____ / 10

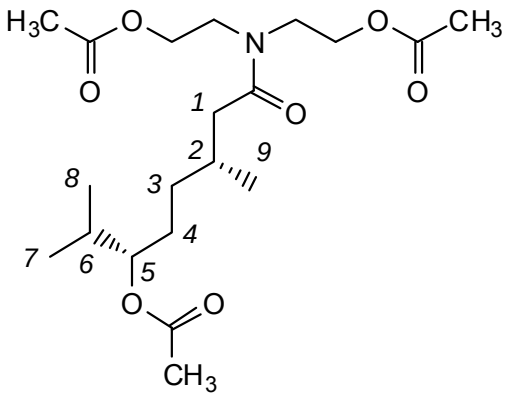
Total Score: _____ / 200

Susie Emond (Hoye group) sequentially reacted diethanolamine (**1**) with the chiral lactone **2**, and then with excess acetic anhydride, in an effort to synthesize product **3**. Susie did isolate one major product from her reaction, which she characterized using ^{1}H and ^{1}H-^{1}H COSY NMR spectroscopy, FT-IR spectroscopy, and electron ionization mass spectrometry (EI-MS). Problems 1-4 of this exam deal with Susie's effort to confirm that **3** was her product.



1. NMR spectra of Susie's reaction product are attached to the back of this exam. Assuming that her product was molecule **3**, on the chart on the next page, assign chemical shifts to labeled protons in the structure drawing of **3**. Answer to within 0.01 ppm.

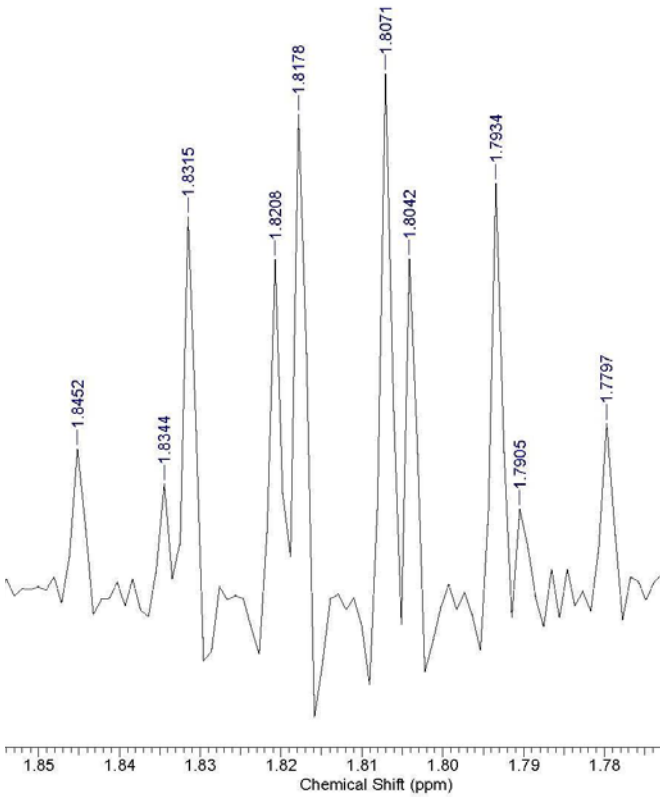
proton	δ (ppm)
H(1)	
[x2]	
H(2)	
H(3)	
[x2]	
H(4)	
[x2]	
H(5)	



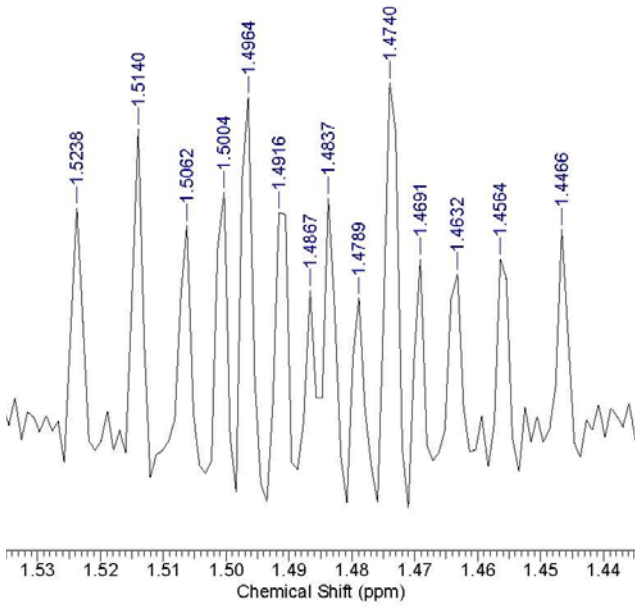
H(6)	
H(7)	
H(8)	
H(9)	

2. Resolution-enhanced close-ups of two resonances are shown below. What coupling constants can you measure from these multiplets? If you observe the same coupling constant multiple times, list it multiple times.

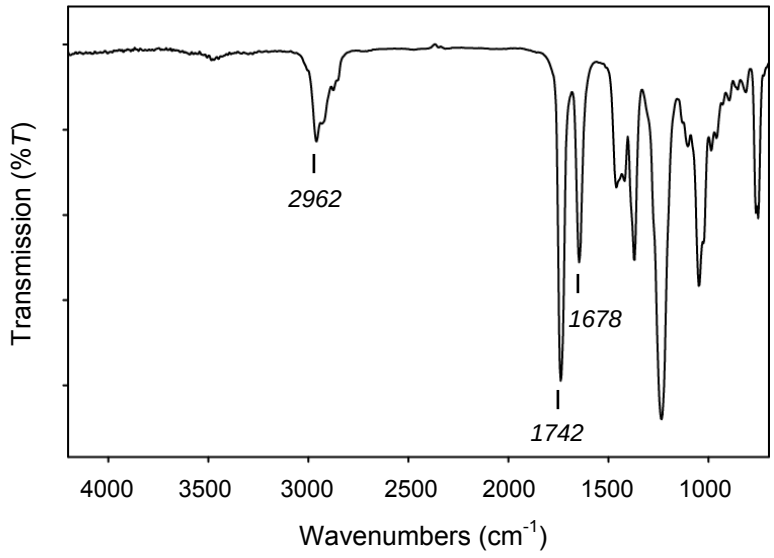
coupling constants (Hz)



coupling constants (Hz)



3. Susie took an IR spectrum of her product, shown below. What functional groups are responsible for each of the peaks labeled on the spectrum?

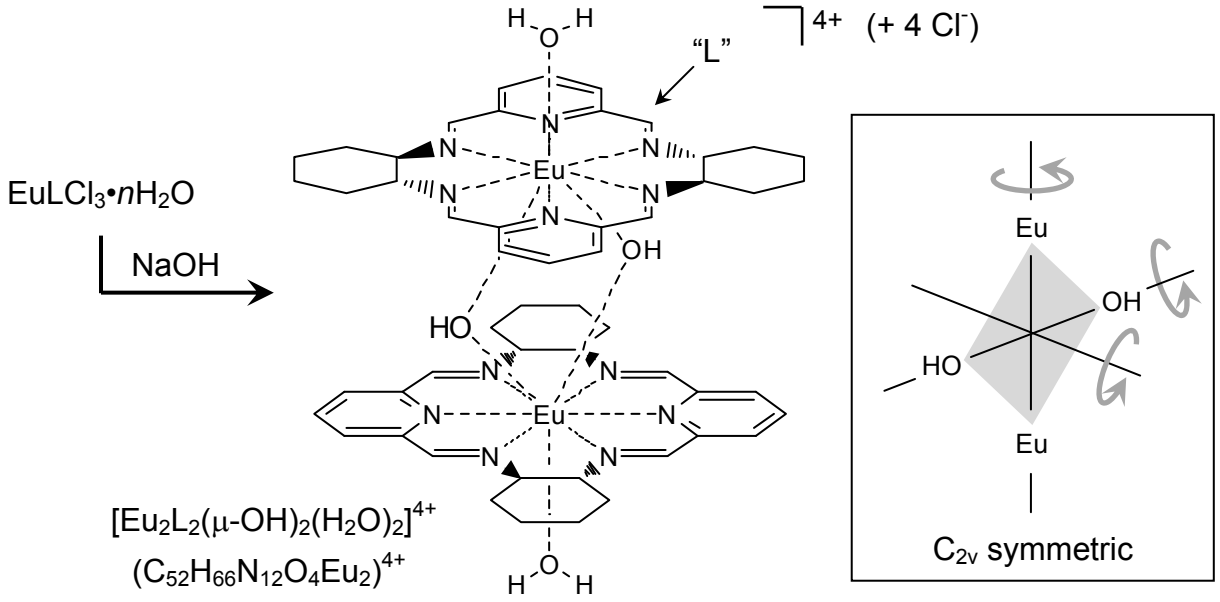


<u>functional group</u>

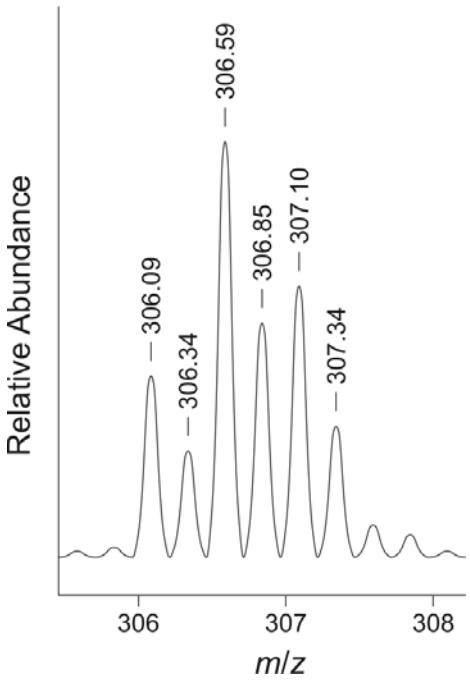
ν = 2962 cm^{-1}
ν = 1742 cm^{-1}
ν = 1678 cm^{-1}

4. Susie attempted to do EI-MS using the Hoye lab GC/MS instrument, but she observed only fragments, and not the expected parent mass. Reducing the electron beam voltage did not solve this problem. What other MS technique might she use, on the same instrument, to better observe the parent mass? (Just name the technique, no need to describe it.)

Prof. Jerzy Lisowski, at the University of Wrocław, Poland, recently studied the reaction of chiral macrocyclic europium (Eu) complexes with hydroxide ion in H_2O, using 1D and 2D NMR, fluorescence spectroscopy, and electrospray ionization mass spectrometry (ESI-MS).[1] X-ray crystallography had previously showed that the reaction products crystallized into a C_{2v}- symmetric, μ-hydroxide dimer; the goal of these experiments was to confirm that the same dimer was also present in solution. Problems 5-12 deal with these experiments.



5. Positive-mode ESI-MS yielded mainly one set of peaks near *m*/*z* = 307, shown in close-up at right. What is the most likely chemical formula for the ions represented by each of the peak masses listed below? In each formula, give not only the atomic symbol for each element, but also the isotope number for any element that is not >90% abundant in nature. Make sure to indicate the charge state of the ion.



Example of answer format:

m/*z* = 42.042: $C_2(^{13}C)_1H_5^+$

(please answer on the next page)

[1] Lisowski, J. *Inorg. Chem.* **2011**, *50*, 5567-5576.

m/*z* = 306.34:

m/*z* = 306.59:

m/*z* = 306.85:

6. If Prof. Lisowski had performed an ion mobility spectrometry experiment on his reaction mixture using a drift cell, would you expect the dimer to emerge from the collision cell

   earlier, **later**, *or* **at the same time** (*circle one*)

   compared to the monomer starting material?

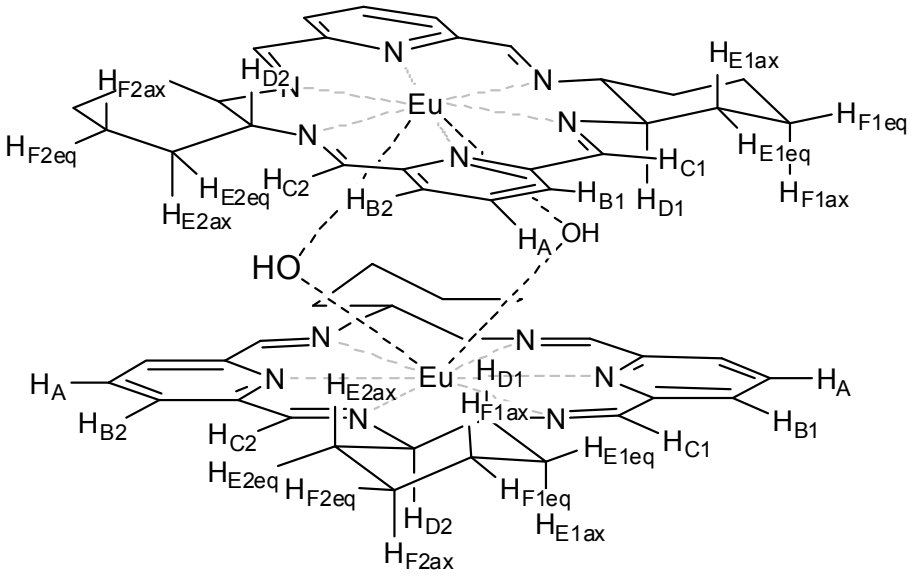
7. The product Eu complex was fluorescent. Would you expect the wavelength of maximum fluorescence intensity ($\lambda_{max,fl}$) to be

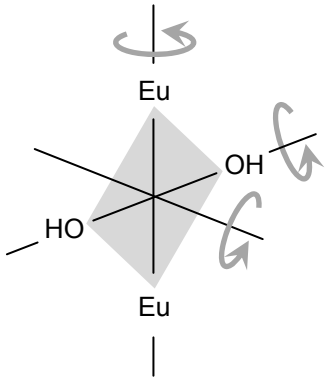
   greater than, **less than**, *or* **equal to** (*circle one*)

   the wavelength of maximum absorbance ($\lambda_{max,abs}$)?

8. ^{1}H NMR, ^{1}H-^{1}H COSY, ^{1}H-^{1}H NOESY, and ^{1}H-^{13}C HMQC spectra of Dr. Lisowski's reaction product, dissolved in D_2O, are attached to the back of this exam. Many of the ^{1}H chemical shifts in the complex are far downfield of where you would expect them, based on functionality and chemical shift tables alone. Why?

9. Assuming the solid-state (crystal) structure was the same as in solution, Dr. Lisowski expected 15 inequivalent protons in his dimer, as illustrated below:





Based on his work and others', Dr. Lisowski knew that protons closest to the μ-hydroxide groups should be upfield of other protons in the molecule. He also knew that coupling constants were typically difficult to measure in lanthanide complexes, and that the 2D spectra would be critical to understanding coupling relationships in these molecules.

In the chart below, assign chemical shift (δ) values to each of the 15 inequivalent protons in the complex. Answer to within 0.05 ppm.

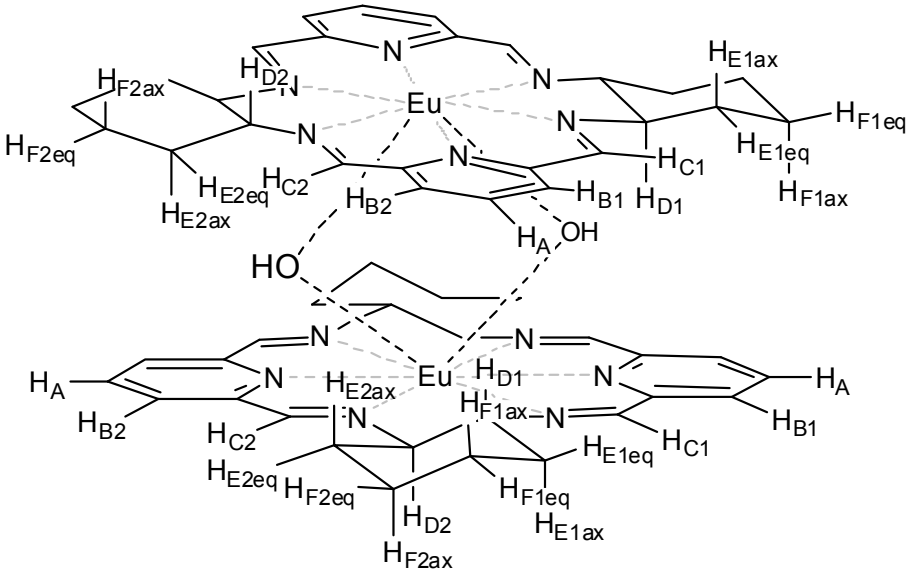
proton	δ (ppm)
H_A	
H_{B1}	
H_{B2}	
H_{C1}	
H_{C2}	

proton	δ (ppm)
H_{D1}	
H_{D2}	
H_{E1eq}	
H_{E1ax}	
H_{E2eq}	

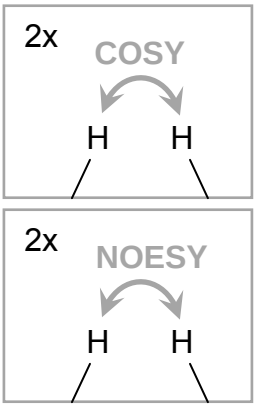
proton	δ (ppm)
H_{E2ax}	
H_{F1eq}	
H_{F1ax}	
H_{F2eq}	
H_{F2ax}	

10. The crosspeaks in the ^{1}H-^{1}H COSY spectrum showed mostly ^{2}J (geminal) and ^{3}J (vicinal) couplings, but there were a few corresponding to longer-range ^{1}H-^{1}H couplings. On the chemical structure below, illustrate <u>two</u> long-range couplings observable as COSY crosspeaks with double-headed arrows. Label your two double-headed arrows "COSY".

11. Dr. Lisowski was convinced that the μ-hydroxide dimer was formed in solution, based on ^{1}H-^{1}H NOESY crosspeaks that could only be explained by interactions between the sandwiched ligands. On the chemical structure below, illustrate <u>two</u> NOE interactions observable as NOESY crosspeaks with double-headed arrows. Illustrate NOE interactions that could *only* be explained by a dimer structure, and that wouldn't be observed in a EuL monomer. Label your two double-headed arrows "NOESY".



On the left, draw:

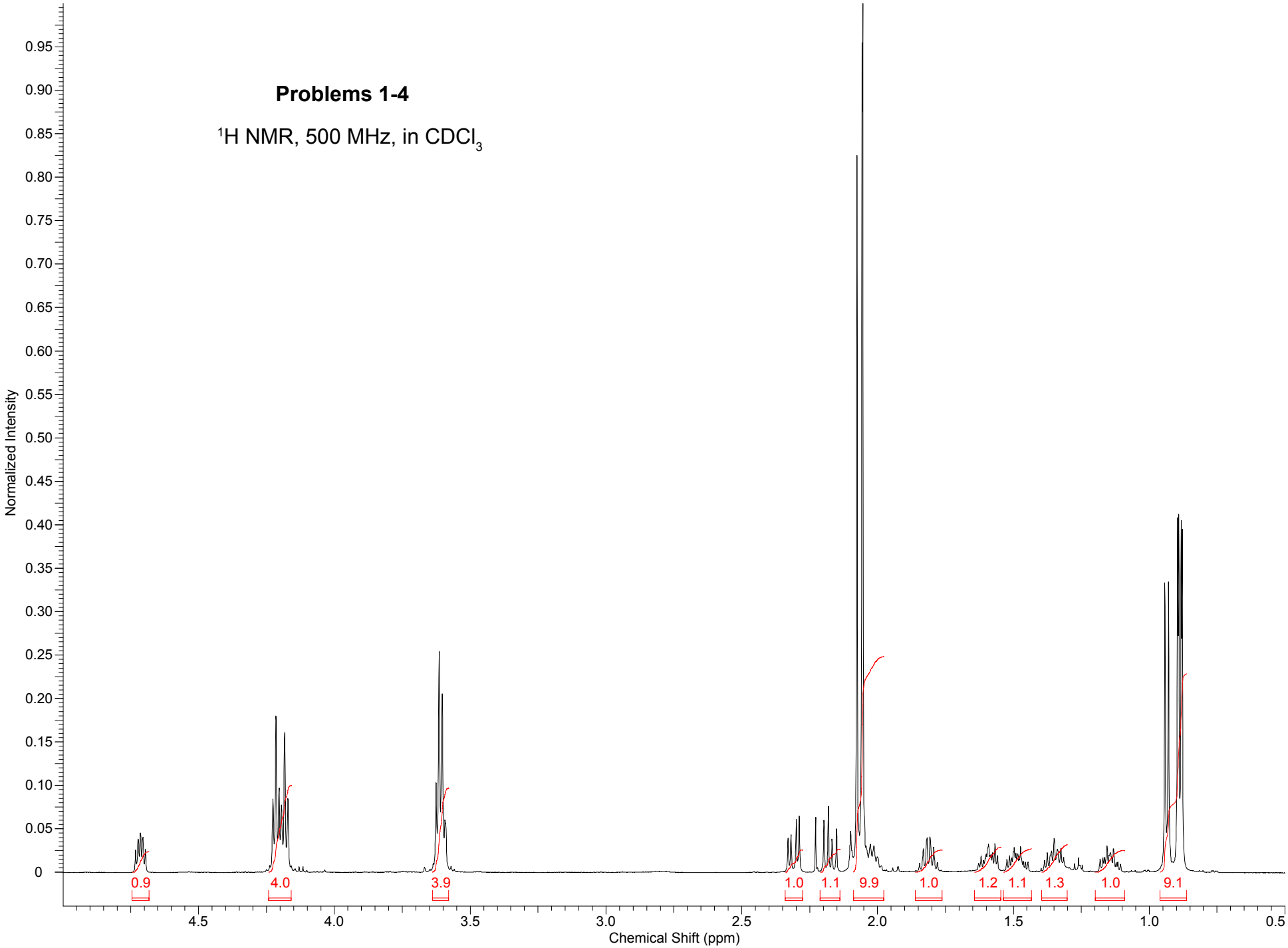


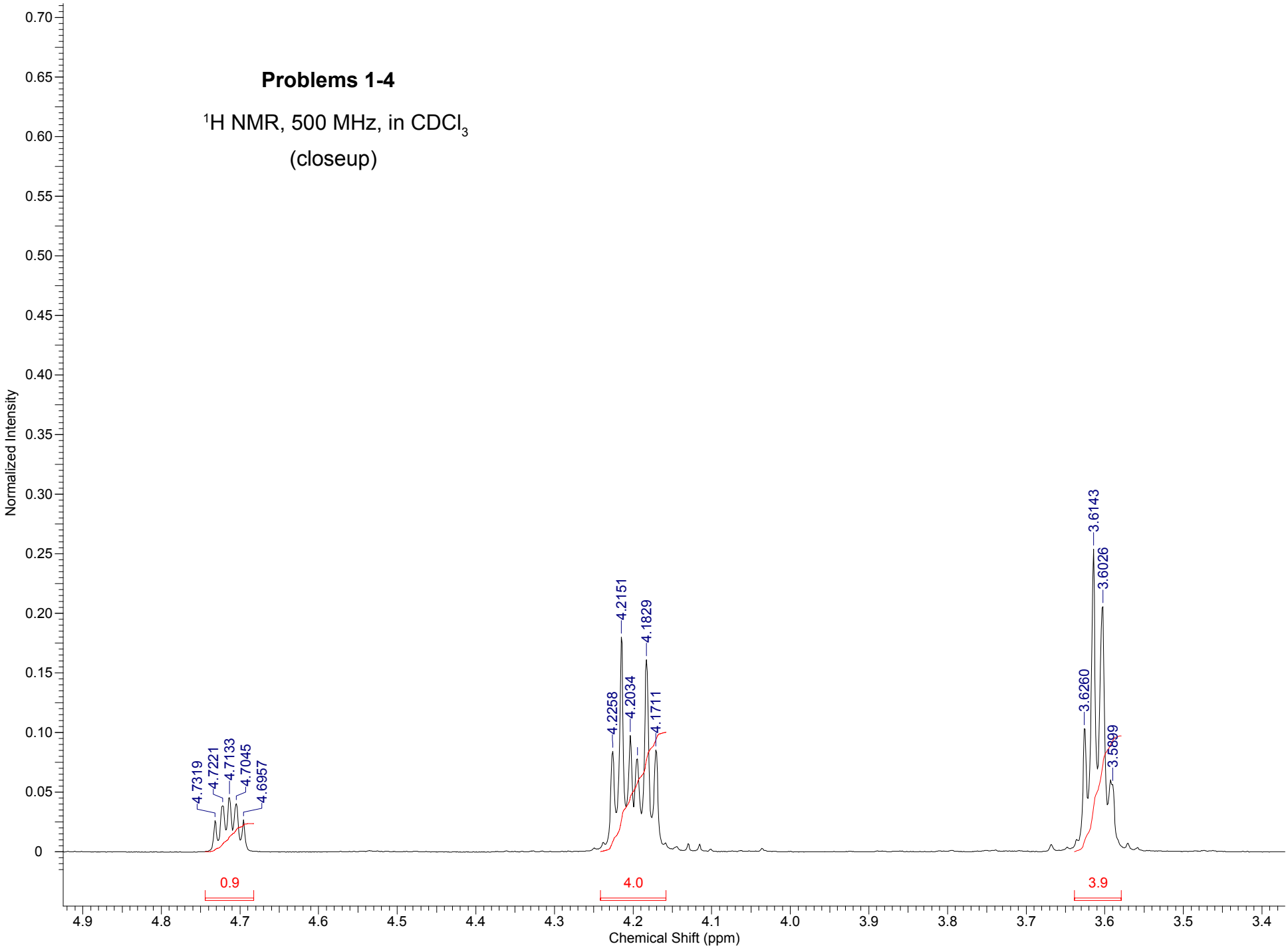
12. Dr. Lisowski hypothesized that this dimer might be in equilibrium with two monomers (as shown at right). Describe an NMR experiment that he might have performed, and the results he would need to see, to confirm his hypothesis.

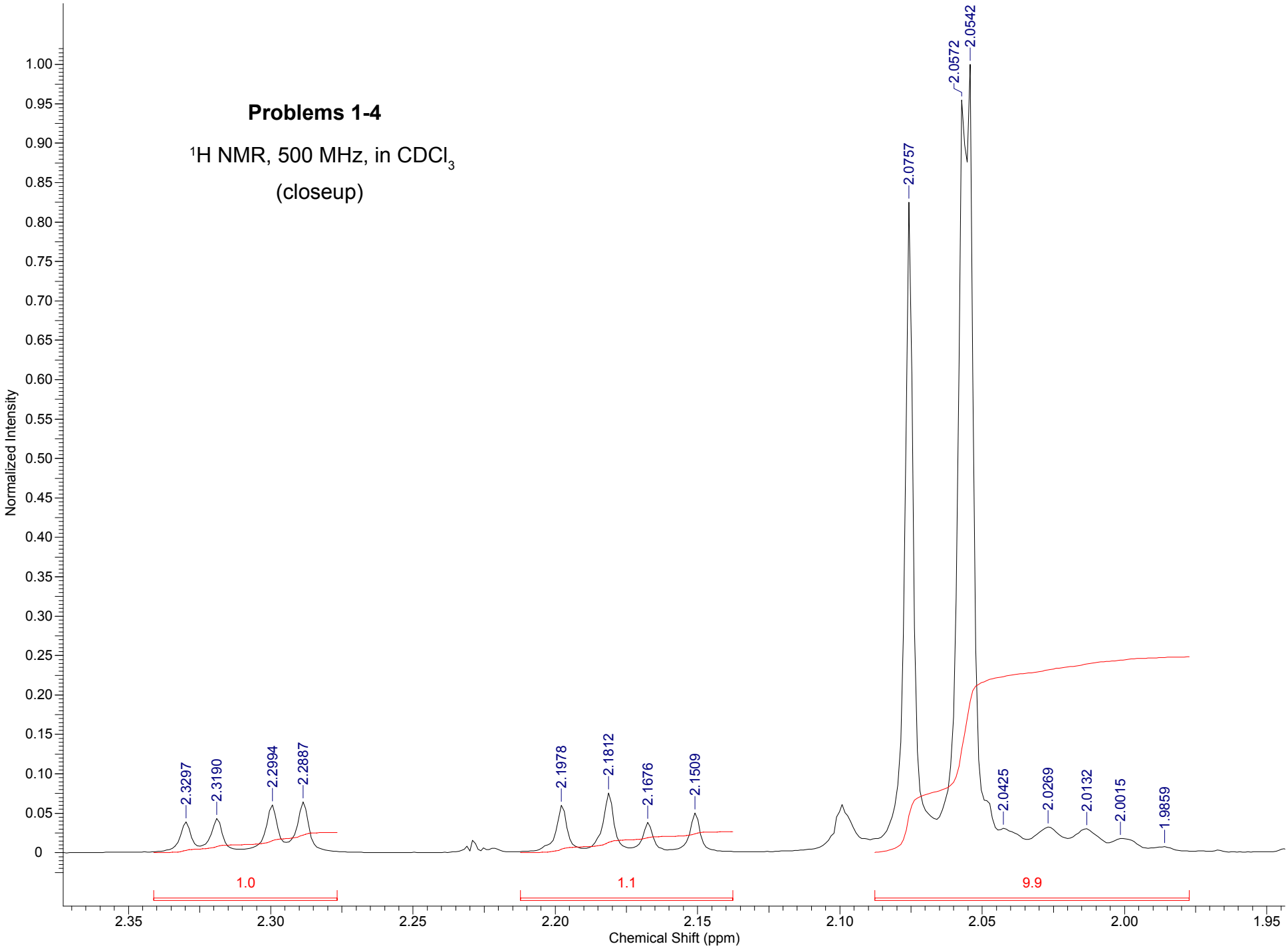
$[Eu_2L_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$

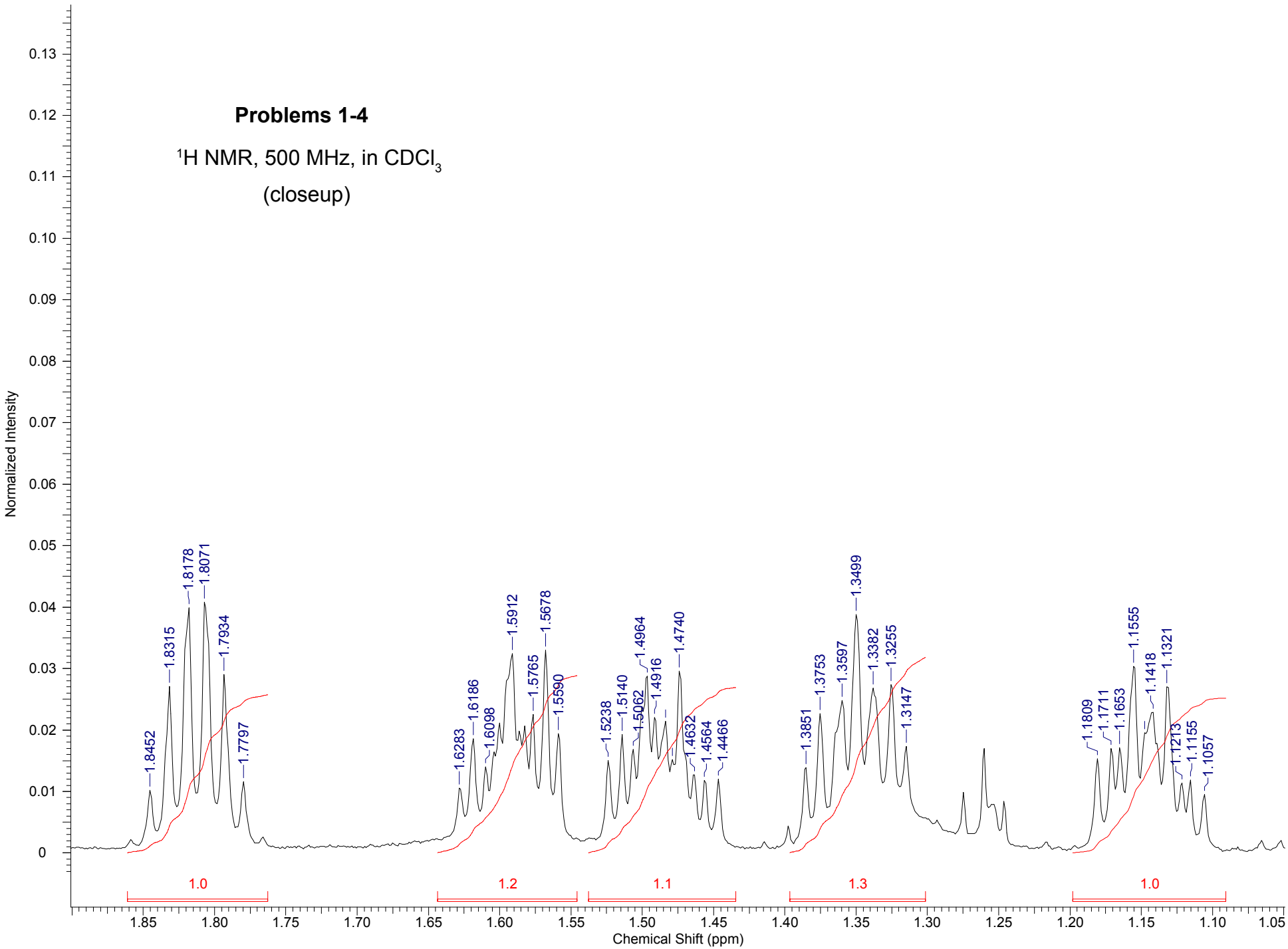
?

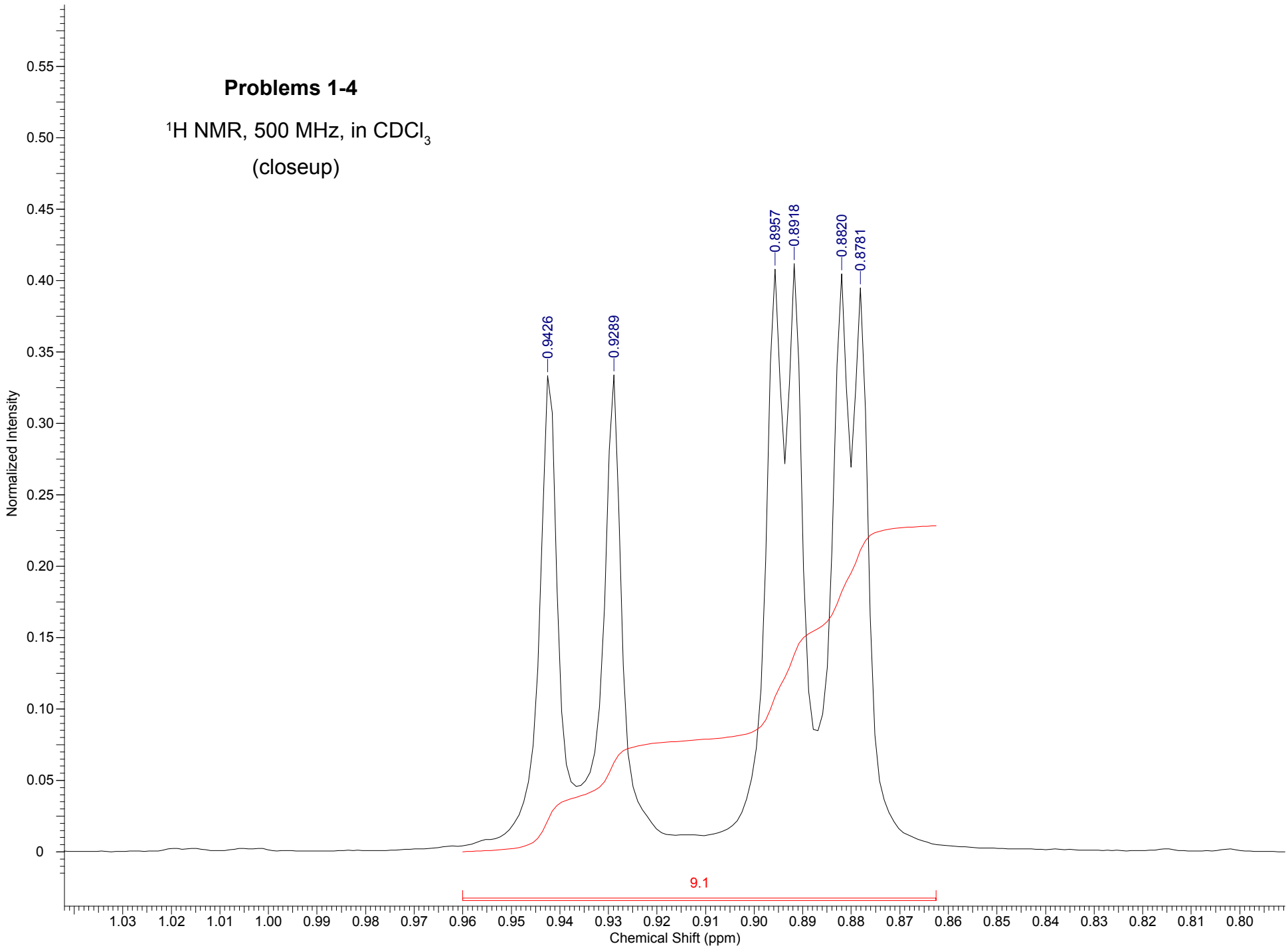
$2\ [EuL(OH)(H_2O)]^{2+}$


Problems 1-4
^{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
0
0.9
4.0
3.9
1.0
1.1
9.9
1.0
1.2
1.1
1.3
1.0
9.1
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


Problems 1-4
1H NMR, 500 MHz, in CDCl3
(closeup)
Normalized Intensity
Chemical Shift (ppm)
4.7319
4.7221
4.7133
4.7045
4.6957
4.2258
4.2151
4.2034
4.1829
4.1711
3.6260
3.6143
3.6026
3.5899
0.9
4.0
3.9

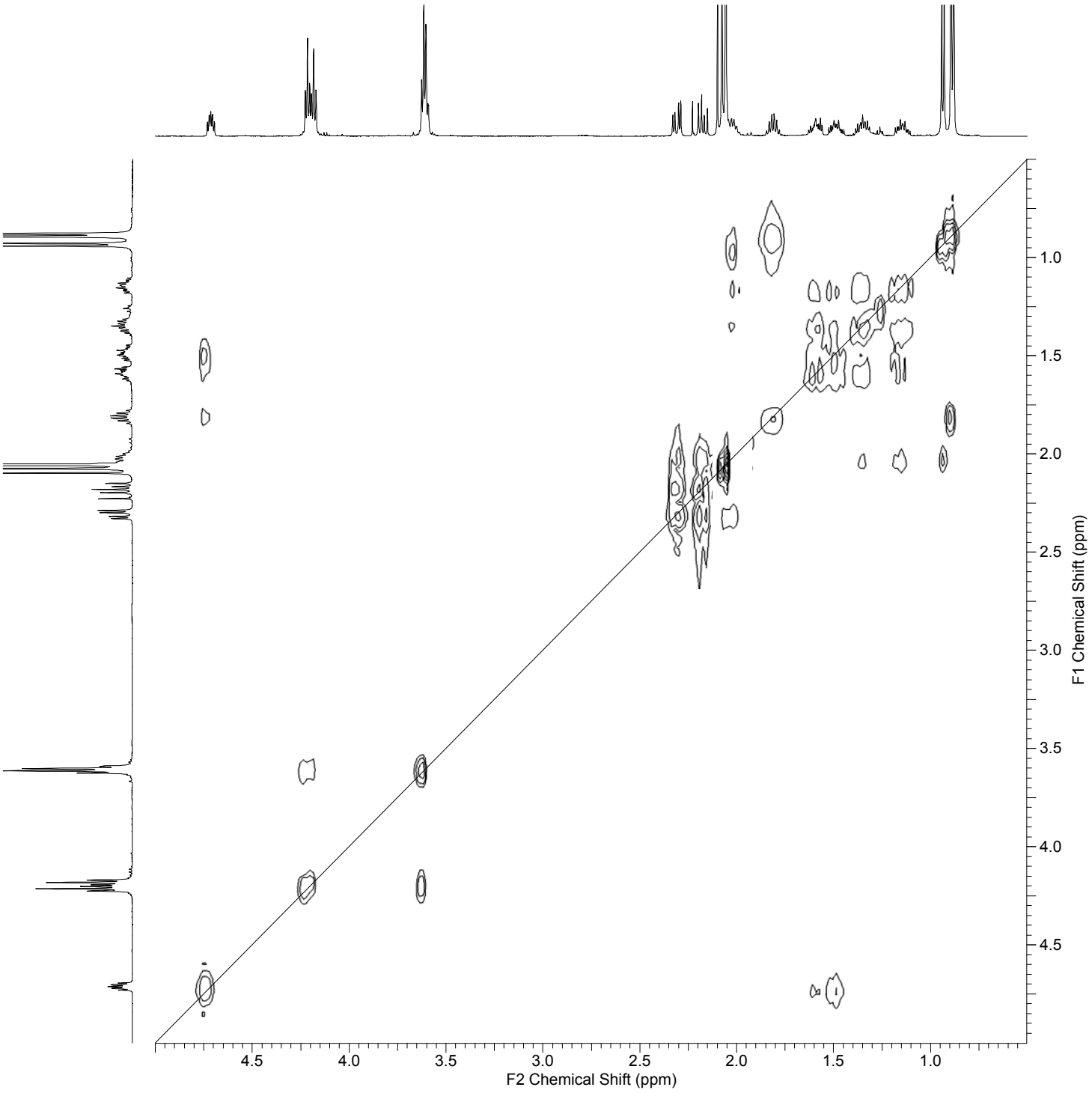

Problems 1-4
^{1}H NMR, 500 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
Chemical Shift (ppm)
2.3297
2.3190
2.2994
2.2887
2.1978
2.1812
2.1676
2.1509
2.0757
2.0572
2.0542
2.0425
2.0269
2.0132
2.0015
1.9859
1.0
1.1
9.9

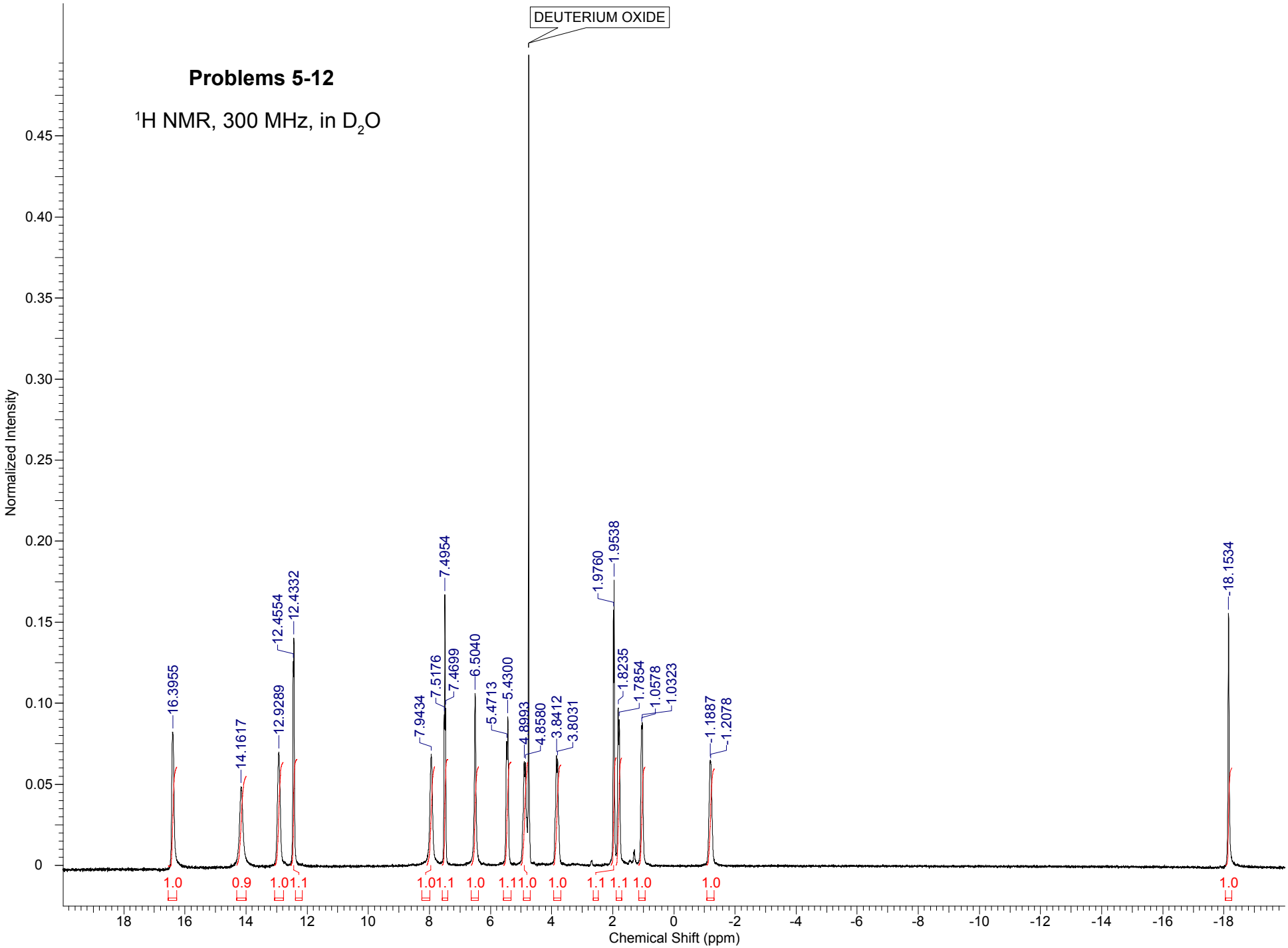

Problems 1-4
1H NMR, 500 MHz, in CDCl3
(closeup)
Normalized Intensity
Chemical Shift (ppm)
1.8452
1.8315
1.8178
1.8071
1.7934
1.7797
1.6283
1.6186
1.6098
1.5912
1.5765
1.5678
1.5590
1.5238
1.5140
1.5062
1.4964
1.4916
1.4740
1.4632
1.4564
1.4466
1.3851
1.3753
1.3597
1.3499
1.3382
1.3255
1.3147
1.1809
1.1711
1.1653
1.1555
1.1418
1.1321
1.1213
1.1155
1.1057
1.0
1.2
1.1
1.3
1.0

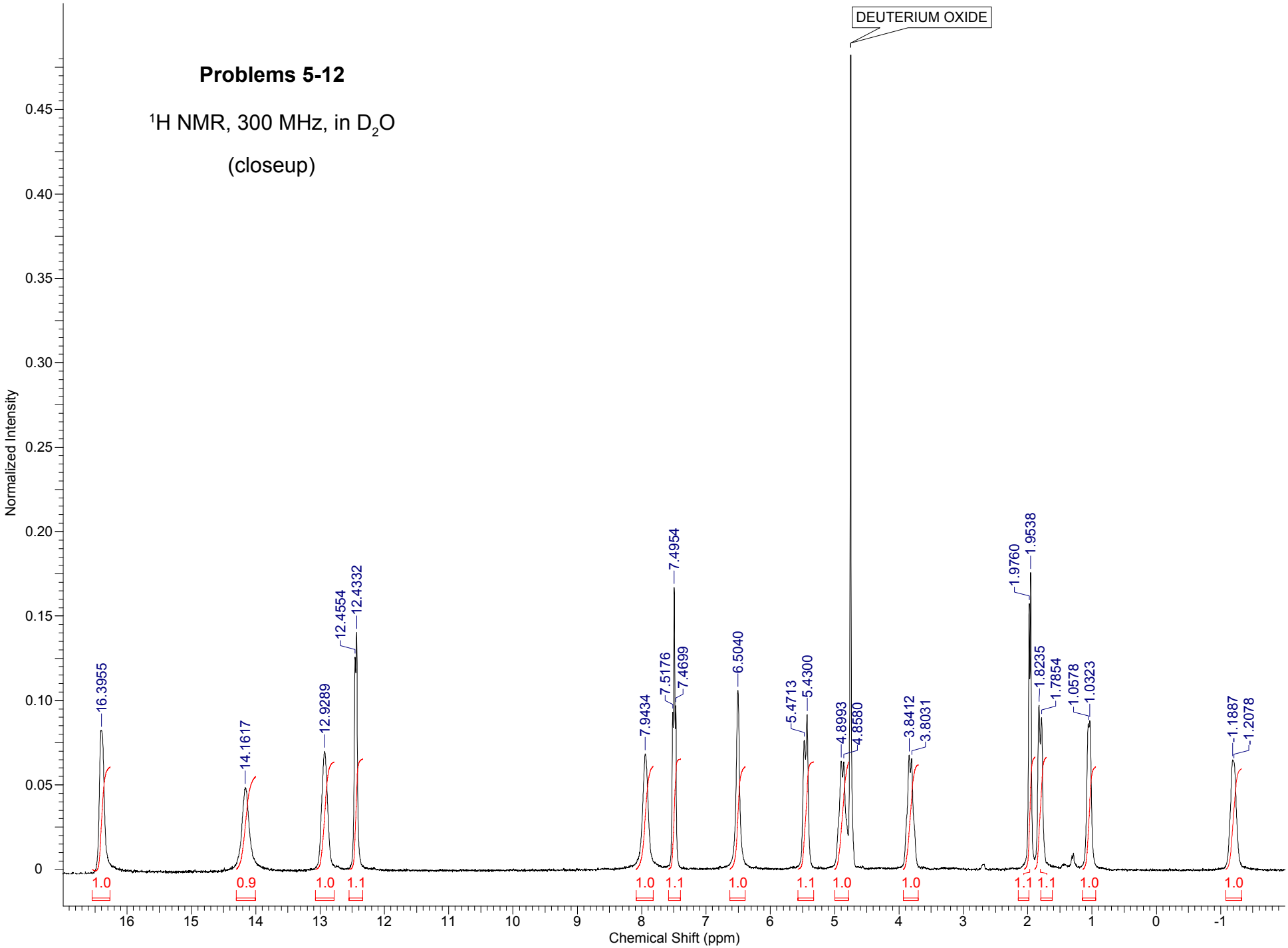

Problems 1-4
^{1}H NMR, 500 MHz, in $CDCl_3$
(closeup)
0.9426
0.9289
0.8957
0.8918
0.8820
0.8781
9.1
Normalized Intensity
Chemical Shift (ppm)

Problems 1-4

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

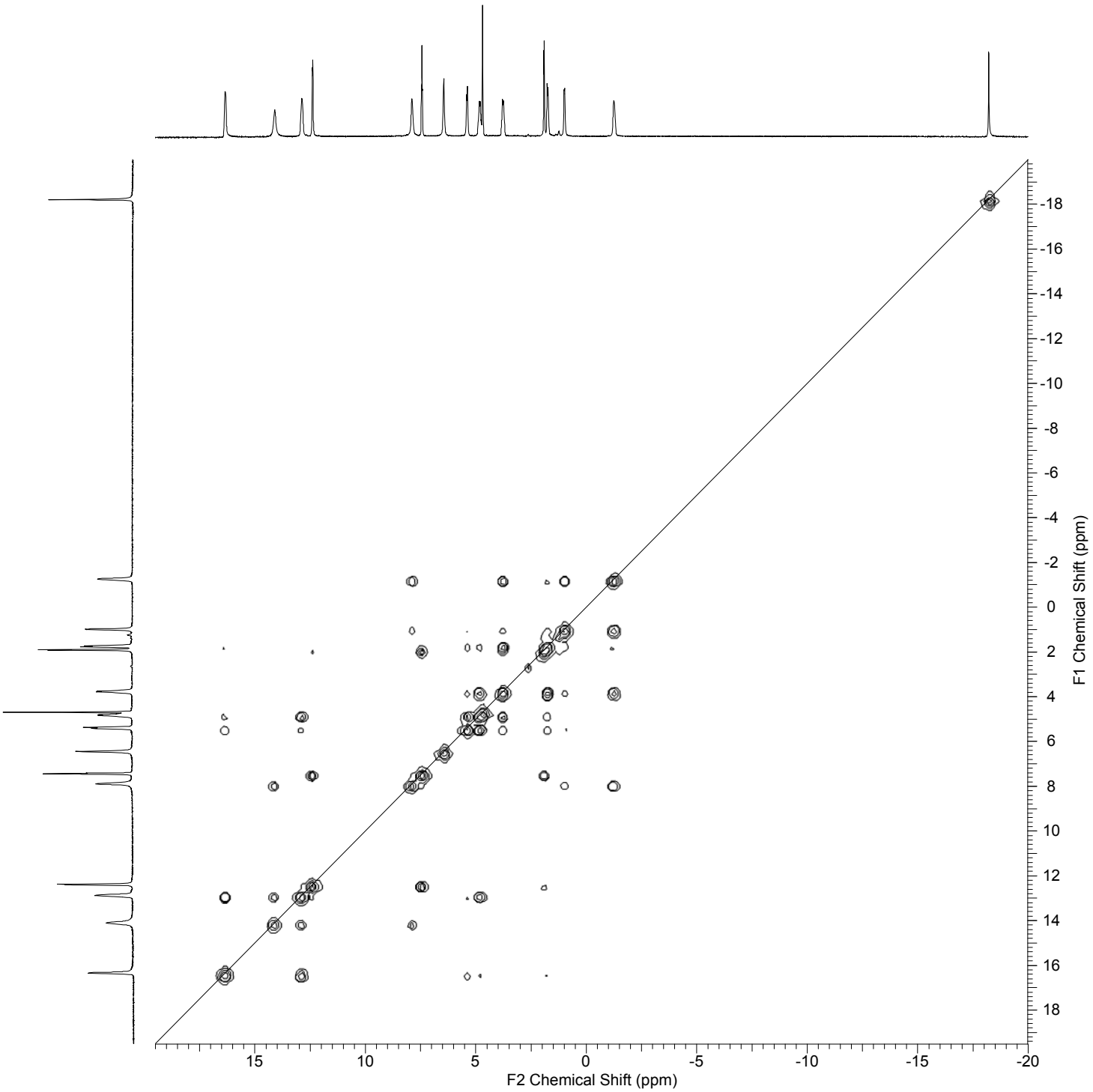



Problems 5-12
^{1}H NMR, 300 MHz, in D_2O
DEUTERIUM OXIDE
Normalized Intensity
Chemical Shift (ppm)
16.3955
14.1617
12.9289
12.4554
12.4332
7.9434
7.5176
7.4954
7.4699
6.5040
5.4713
5.4300
4.8993
4.8580
3.8412
3.8031
1.9760
1.9538
1.8235
1.7854
1.0578
1.0323
1.1887
1.2078
18.1534
1.0 0.9 1.0 1.1 1.0 1.1 1.0 1.1 1.0 1.0 1.1 1.1 1.0 1.0 1.0


Problems 5-12
1H NMR, 300 MHz, in D2O
(closeup)
DEUTERIUM OXIDE
Normalized Intensity
Chemical Shift (ppm)
16.3955
14.1617
12.9289
12.4554
12.4332
7.9434
7.5176
7.4954
7.4699
6.5040
5.4713
5.4300
4.8993
4.8580
3.8412
3.8031
1.9760
1.9538
1.8235
1.7854
1.0578
1.0323
1.1887
1.2078
1.0
0.9
1.0
1.1
1.0
1.1
1.0
1.1
1.0
1.0
1.1
1.1
1.0
1.0

Problems 5-12

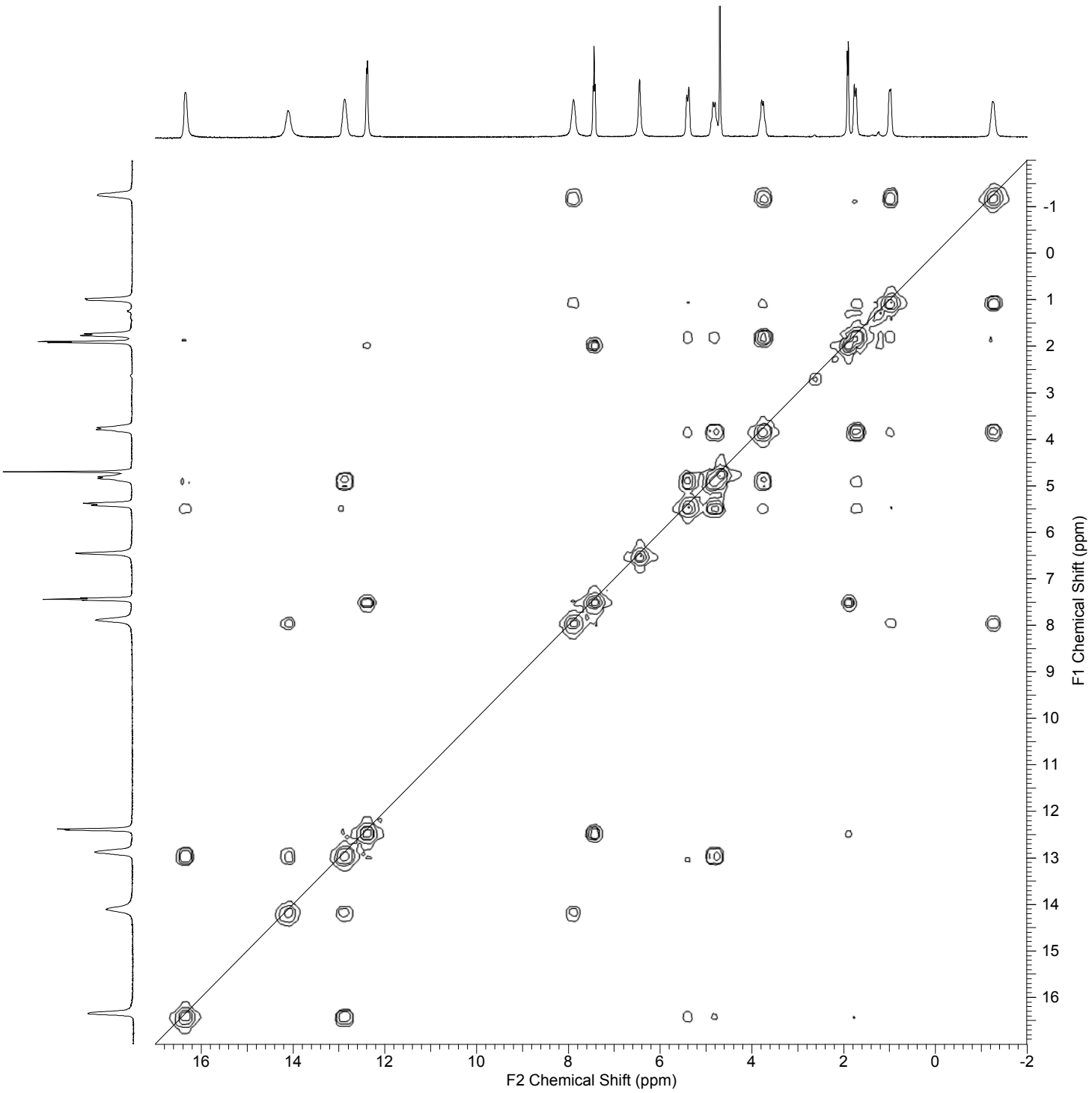
^{1}H-^{1}H COSY, 300 MHz, in D_2O



Problems 5-12

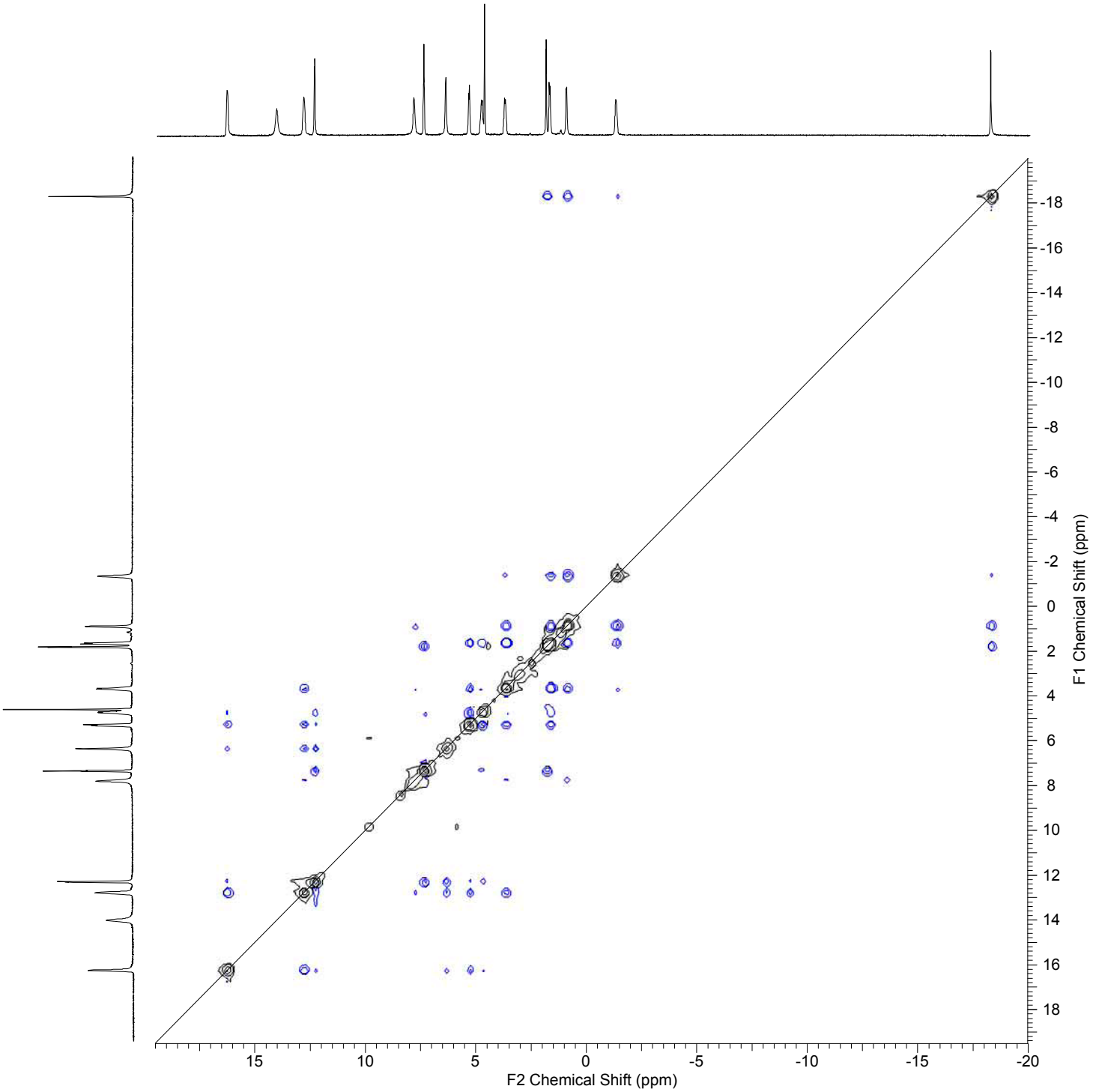
^{1}H-^{1}H COSY, 300 MHz, in D_2O

(closeup)



Problems 5-12

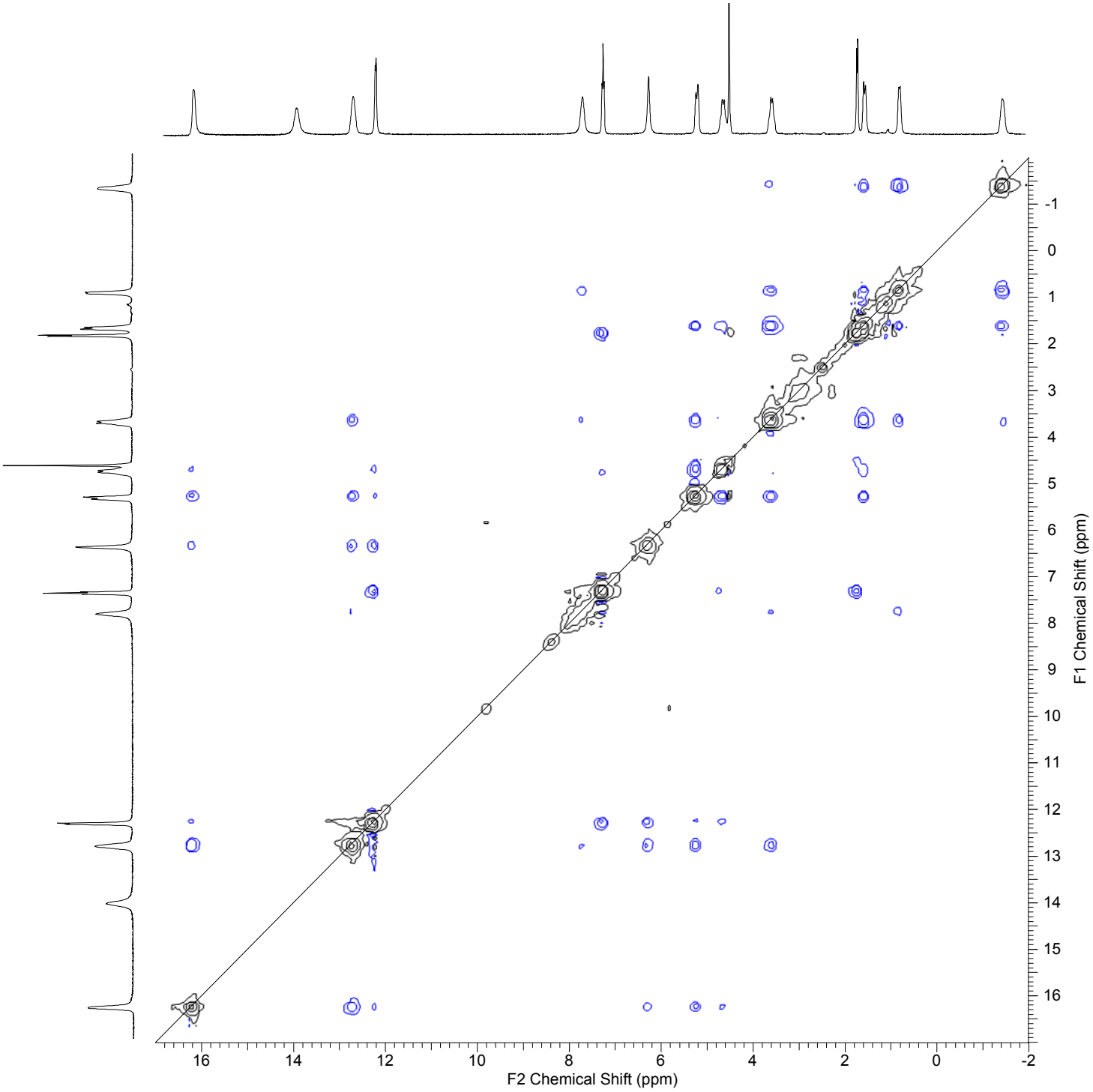
^{1}H-^{1}H NOESY, 300 MHz, in D_2O



Problems 5-12

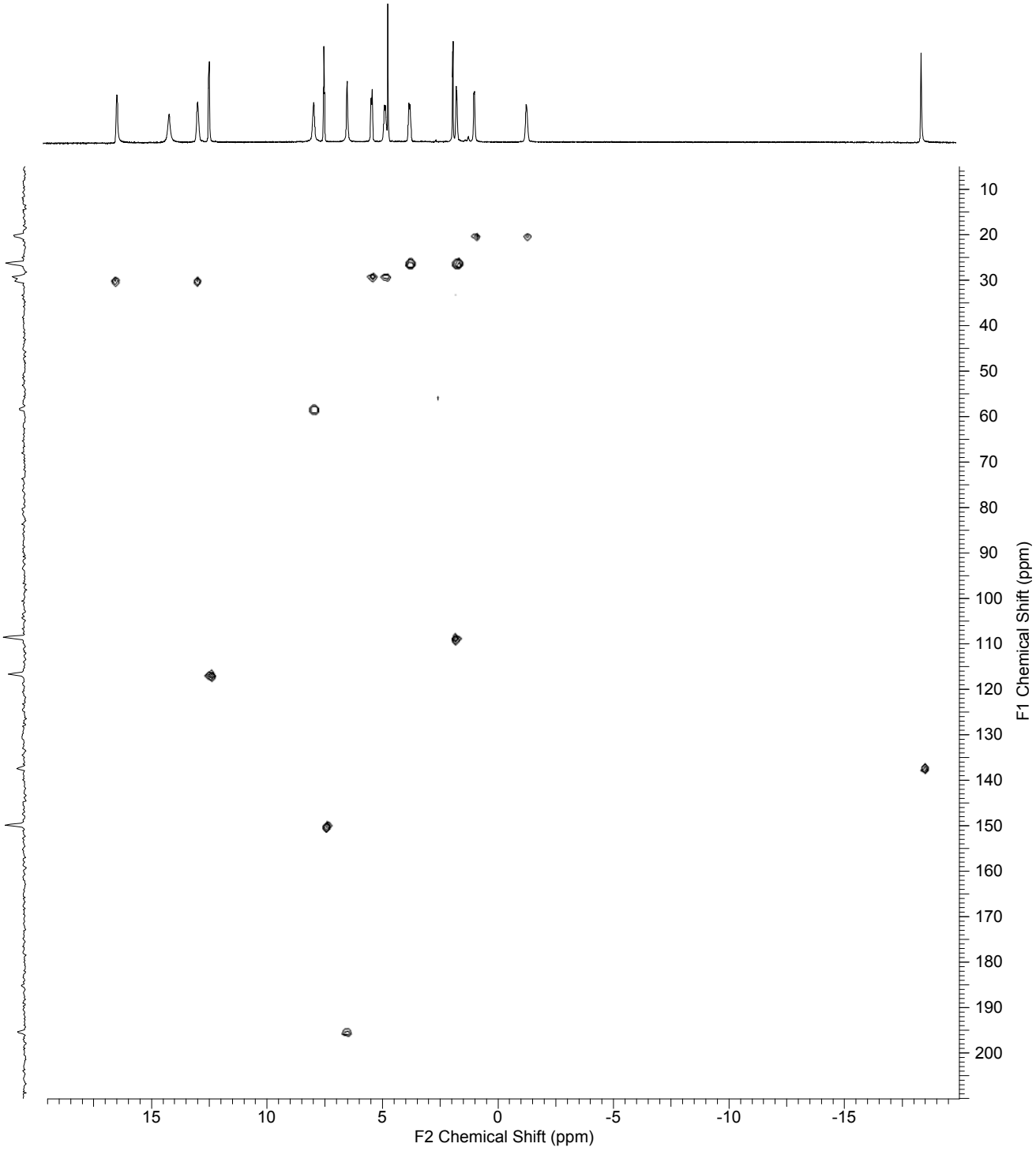
^{1}H-^{1}H NOESY, 300 MHz, in D_2O

(closeup)



Problems 5-12

^{1}H-^{13}C HMQC, 300/75 MHz, in D_2O



Problems 5-12

^{1}H-^{13}C HMQC, 300/75 MHz, in D_2O

(closeup)