NAME _____

ID # _____

INTERPRETATION OF ORGANIC SPECTRA (4361/8361)

9:05 – 9:55 am, November 17, 2010

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. 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 12 pages, including this one. Please check to make sure that your packet contains 12 pages before beginning your exam.

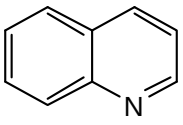
NAME _____

Scoring: 1. _____ / 12 4. _____ / 6

2. _____ / 10 5. _____ / 66

3. _____ / 6

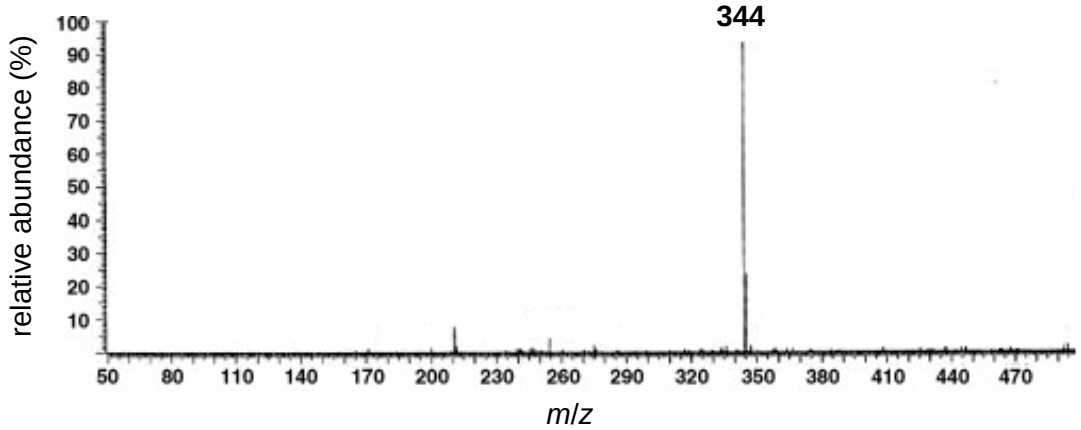
Total Score: _____ / 100



quinoline

Quinoline-based anesthetics are used widely in veterinary medicine, which means that both the anesthetics and their degradation products are sometimes found in agricultural runoff. ^{1}H, ^{1}H-^{1}H 2D-TOCSY and 2D-NOESY spectra of a substituted quinoline anesthetic are attached to the back of this exam. ("Substituted" in this case could mean one substituent, or it could mean multiple substituents.) In addition, other spectra will be introduced in the exam body. A primary goal of the exam will be to identify the unknown quinoline derivative from these spectra.

1. Positive-ion-mode electrospray ionization mass spectrometry (ESI-MS) of the unknown quinoline derivative gave the mass spectrum below. High-resolution analysis of the major (*m*/*z* = 344) peak yielded an experimental exact mass of **344.2339** for this ion.



When this exact mass was entered into an online composition calculator (http://library.med.utah.edu/masspec/elcomp.htm), it gave the following output:

```
Elemental Composition Calculator v1.0

Calculations for :   344.2339 +/-  0.002 amu
monoisotopic mass

  C    12.0000    0   25
  H     1.0078    0   50
  N    14.0030    0   10
  O    15.9949    0   10

  C  H  N  O      mass      diff       ppm

 18 28  6  1   344.2324    0.0014       4.1
 20 30  3  2   344.2338    0.0001       0.2
 22 32  0  3   344.2351   -0.0012      -3.6
  6 32  8  8   344.2343   -0.0004      -1.1
  8 34  5  9   344.2356   -0.0017      -5.0

Number of hits       :     5
Execution time       :     1.326 seconds
```

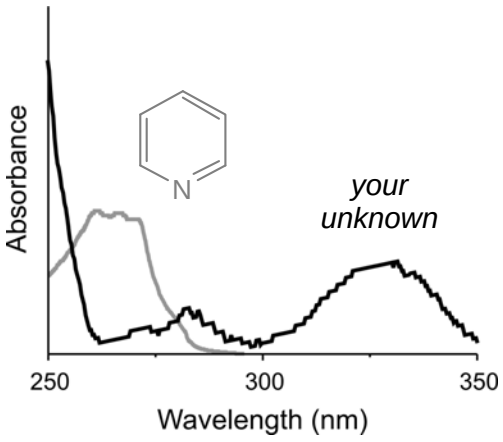
(I instructed the calculator to assume that the ion contained only C, H, O and N atoms.)

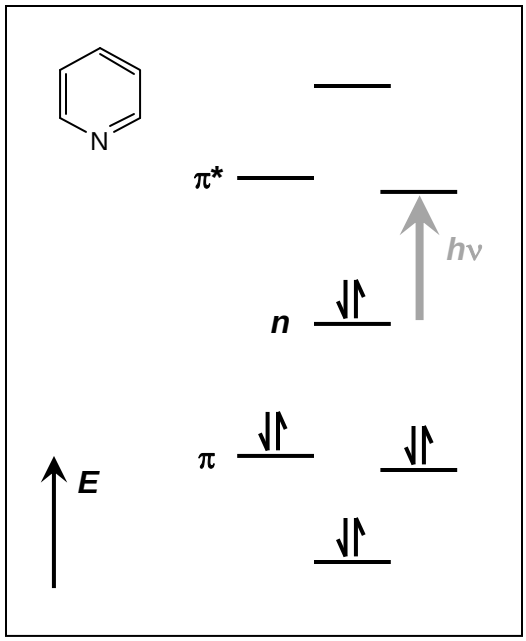
What is the molecular formula of the *m*/*z* = 344 ion?

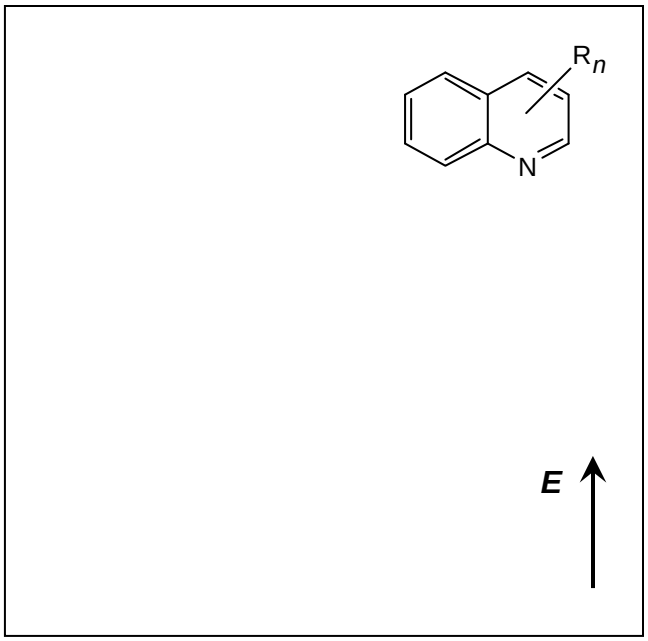
Given this, what is the molecular formula of the substituted quinoline?

2. The UV-vis spectrum of the unknown quinoline derivative (black line) and of pyridine (grey line) are shown at right. The peak in each spectrum corresponds to an *n* - π* transition, where the nitrogen lone pair (*n*) is the HOMO and π* is the LUMO.

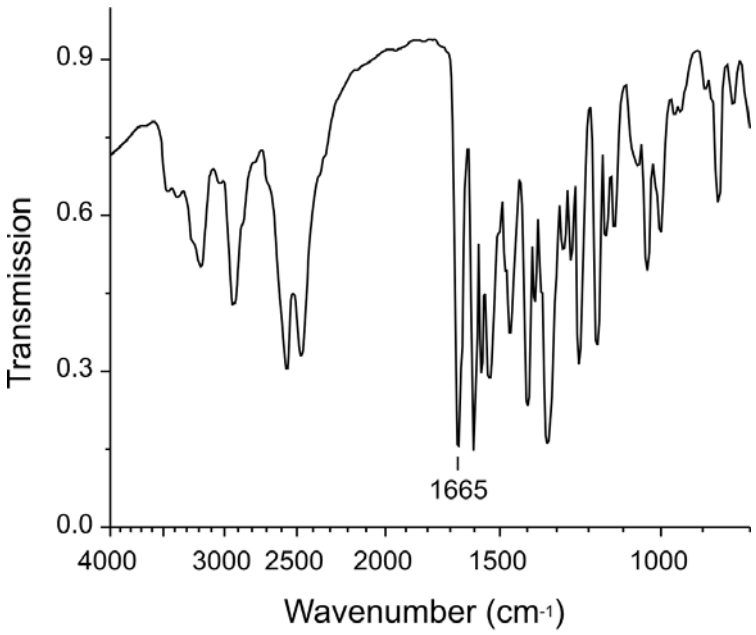
   Molecular orbitals for pyridine are shown on the next page that illustrate the *n* - π* transition. In the answer box, draw orbitals that illustrate the same transition in your unknown, and that explain the difference in λ_{max} between the two molecules.







3. The IR spectrum of the unknown quinoline derivative is shown at right. What functional group might the peak at ν = 1665 cm^{-1} correspond to? (Draw or name in the box below.)



4. There are multiple (somewhat) sharp peaks in the IR spectrum just above ν = 3000 cm^{-1} (at ~3150 cm^{-1}). What type of bonds, between what atoms, do these peaks correspond to? (Draw or name in the box at right.)

5. Each resonance in the 1D ^{1}H NMR spectrum is labeled with a letter ***a***-***m***. A chart of these letters and their chemical shifts, is also given below. In the boxes provided,

   - Draw the structure of the unknown quinoline derivative.

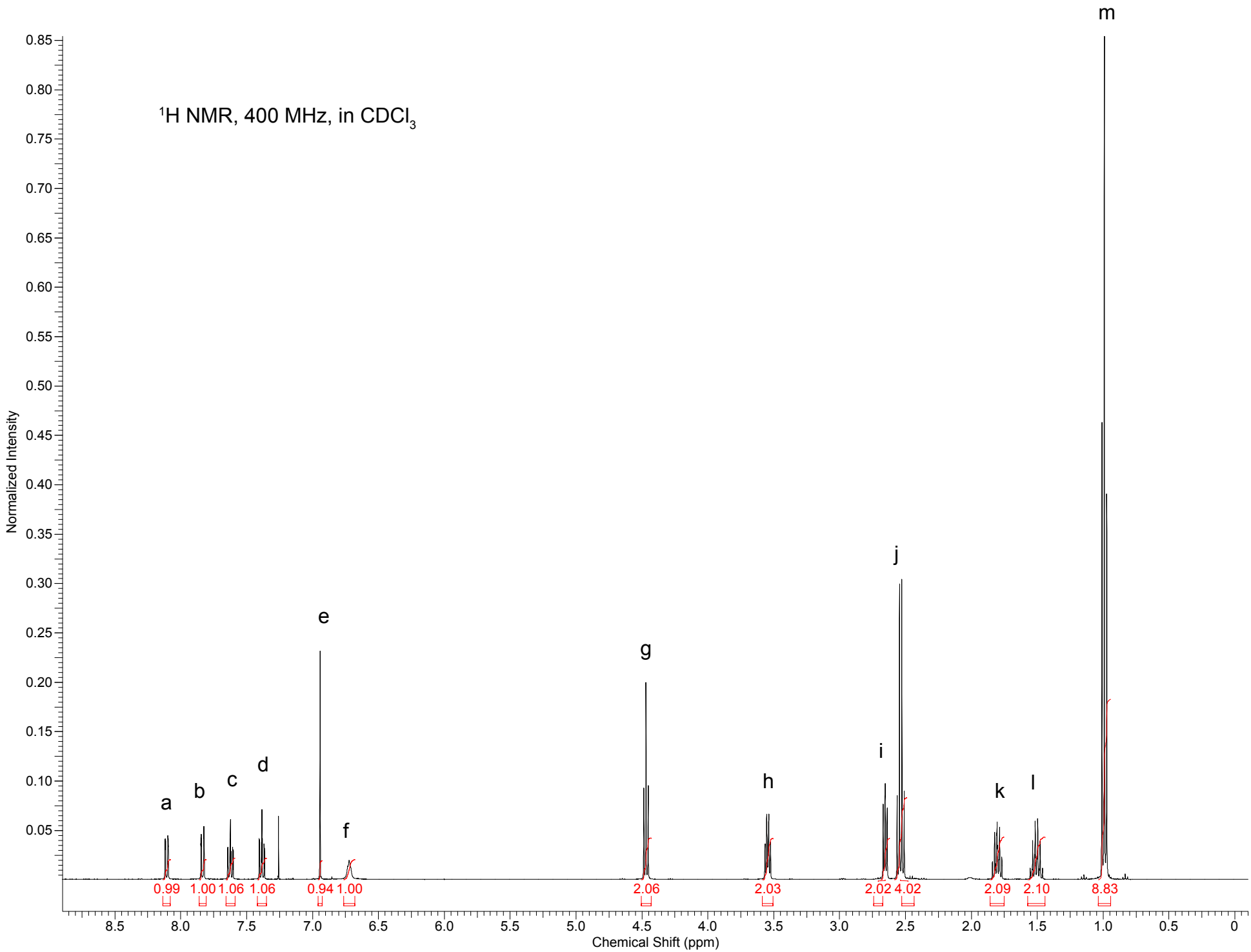
   - Then, draw the structure again, but label each proton in your structure with one of the letters **a**-**m**.

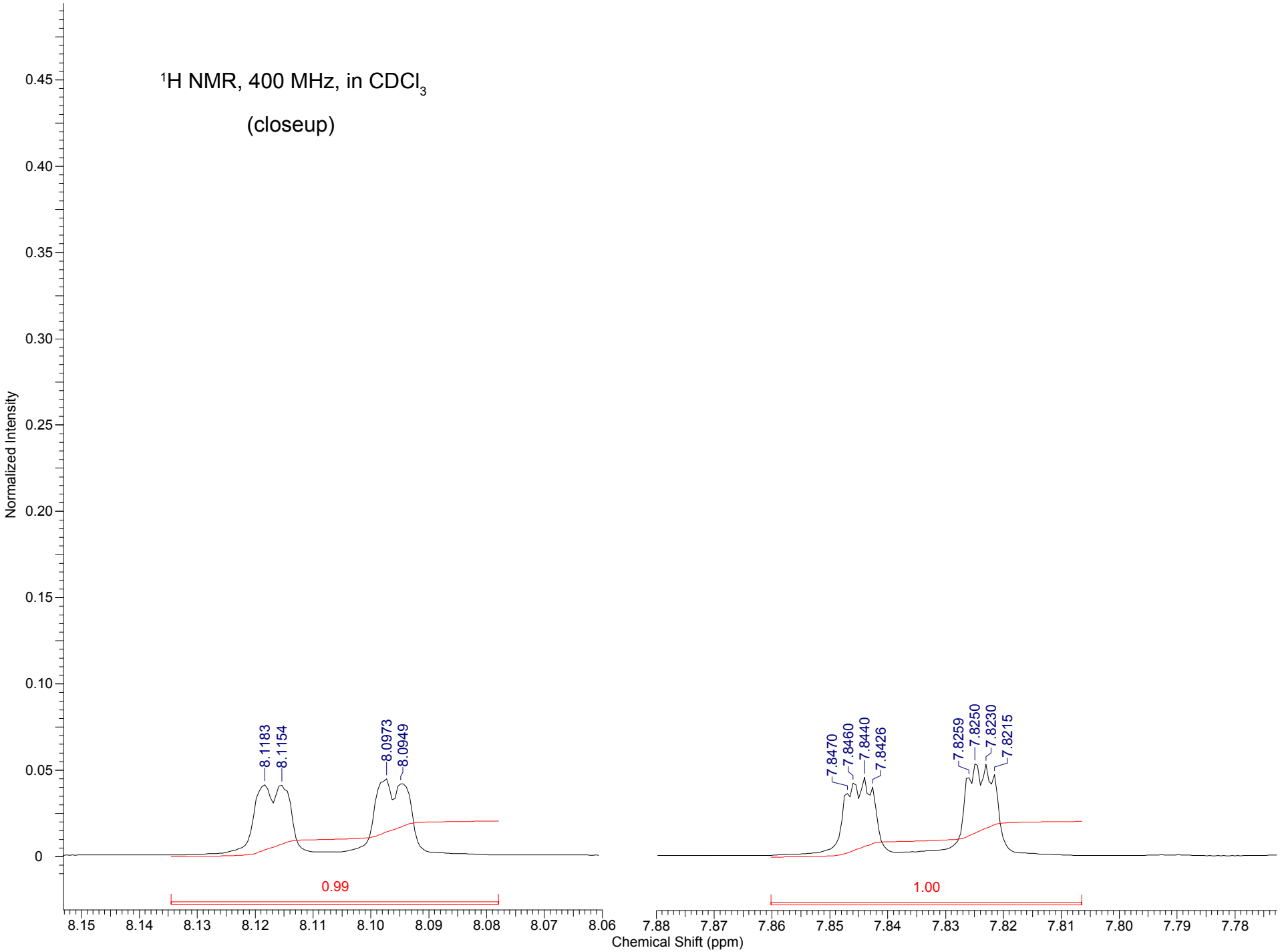
label	δ (ppm)
a	8.11
b	7.83
c	7.62
d	7.38
e	6.94
f	6.72
g	4.47
h	3.54
i	2.65
j	2.54
k	1.81
l	1.50
m	0.99

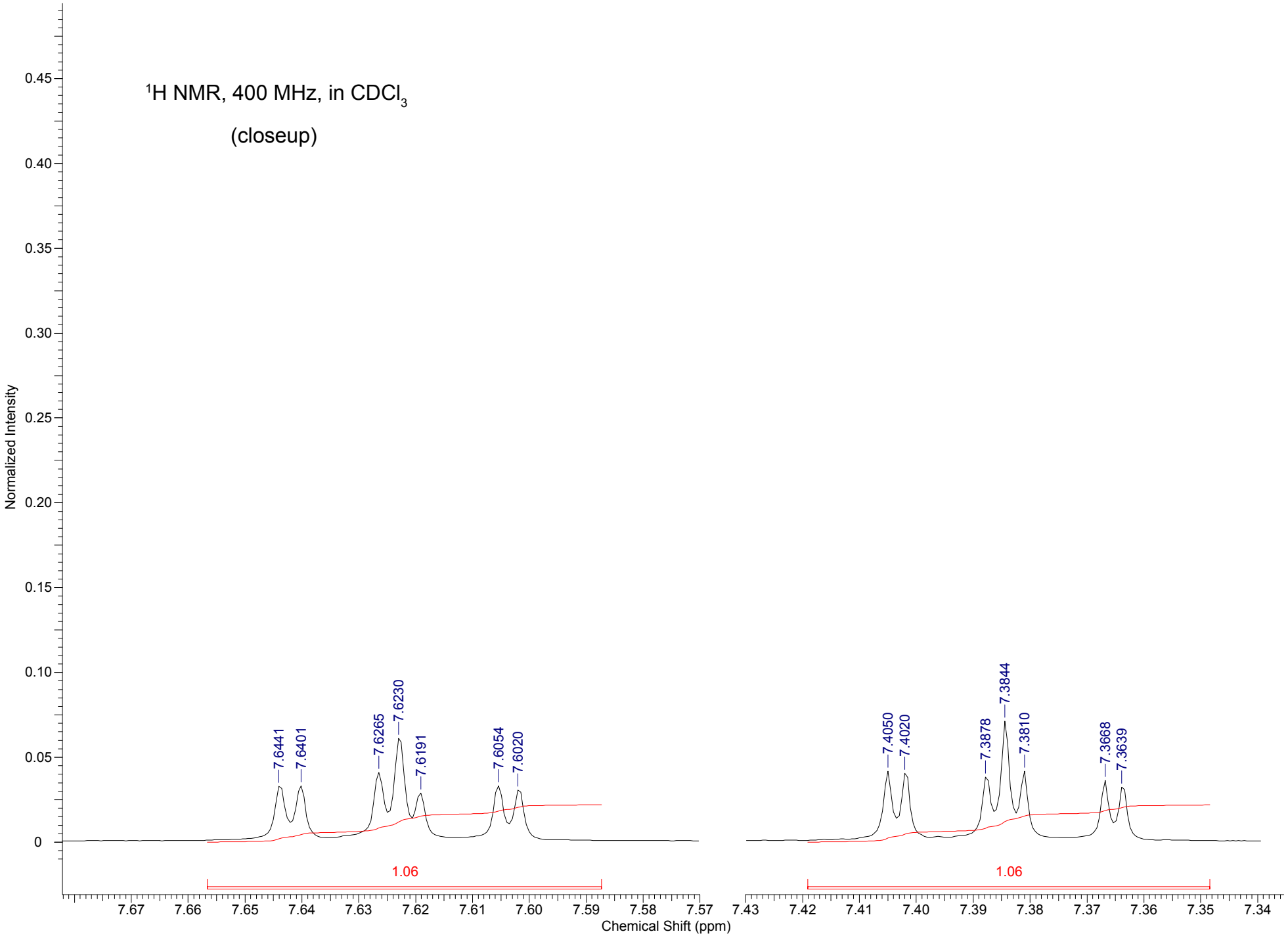
Hints:

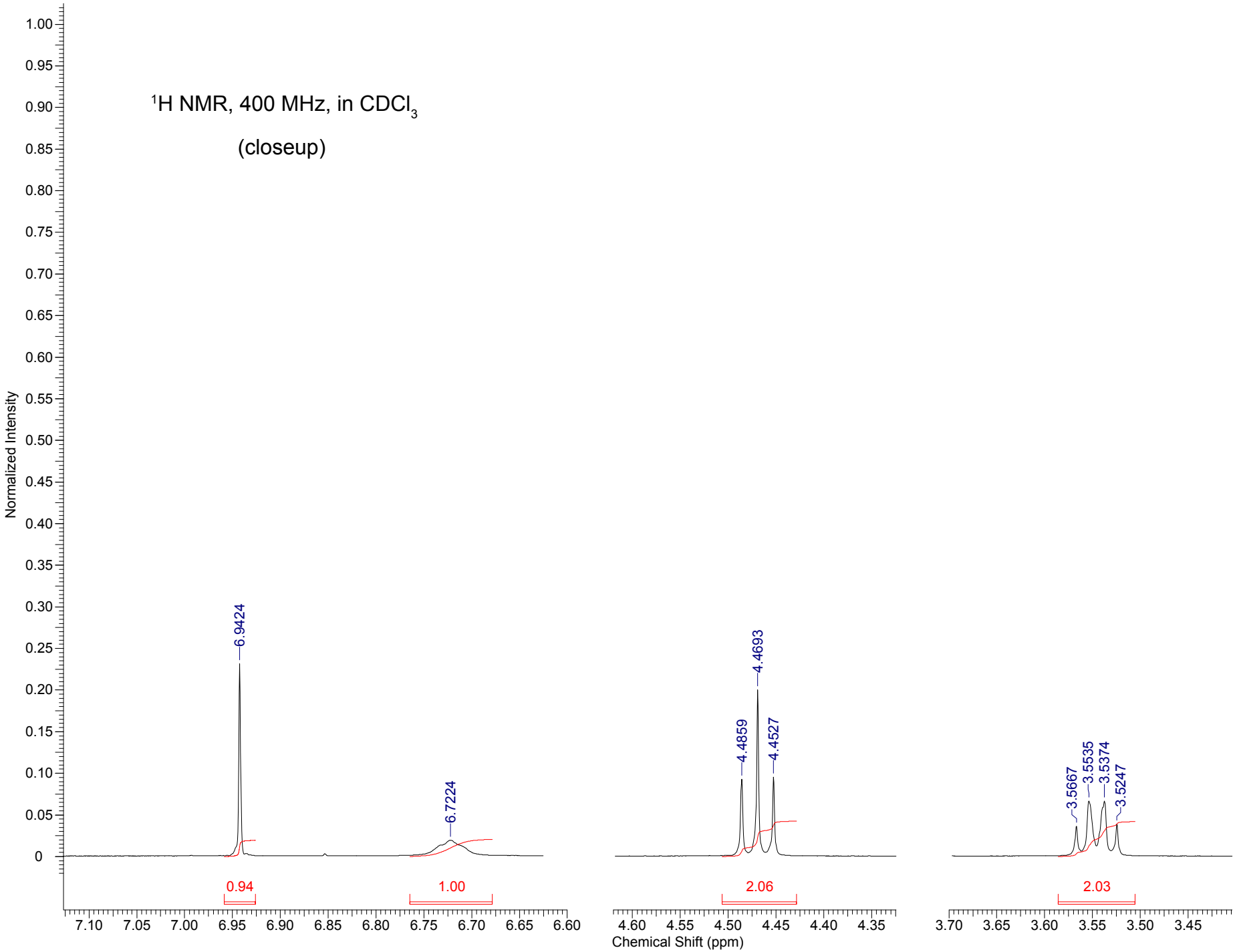
- The 9H-intensity triplet at δ = 0.99 ppm (peak **m**) looks like it might come from one set of 9 equivalent protons. It does not; it comes from two sets of inequivalent protons that happen to have identical splitting and chemical shift.

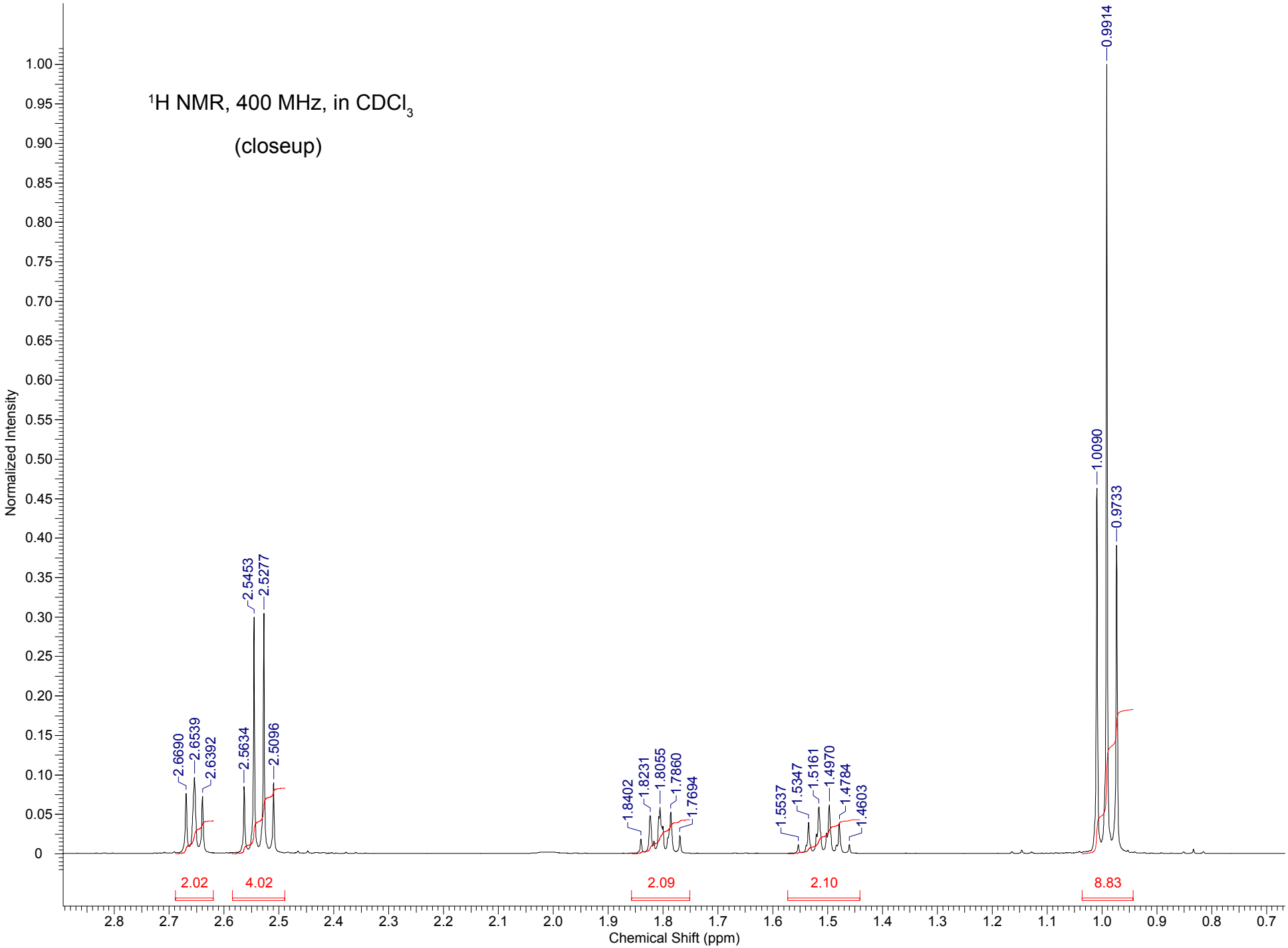
- The sample is extremely dry and clean, so exchangeable protons that might normally be too broadened to see are visible here.


^{1}H NMR, 400 MHz, in $CDCl_3$
Normalized Intensity
Chemical Shift (ppm)
a
b
c
d
e
f
g
h
i
j
k
l
m
0.99
1.00
1.06
1.06
0.94
1.00
2.06
2.03
2.02
4.02
2.09
2.10
8.83

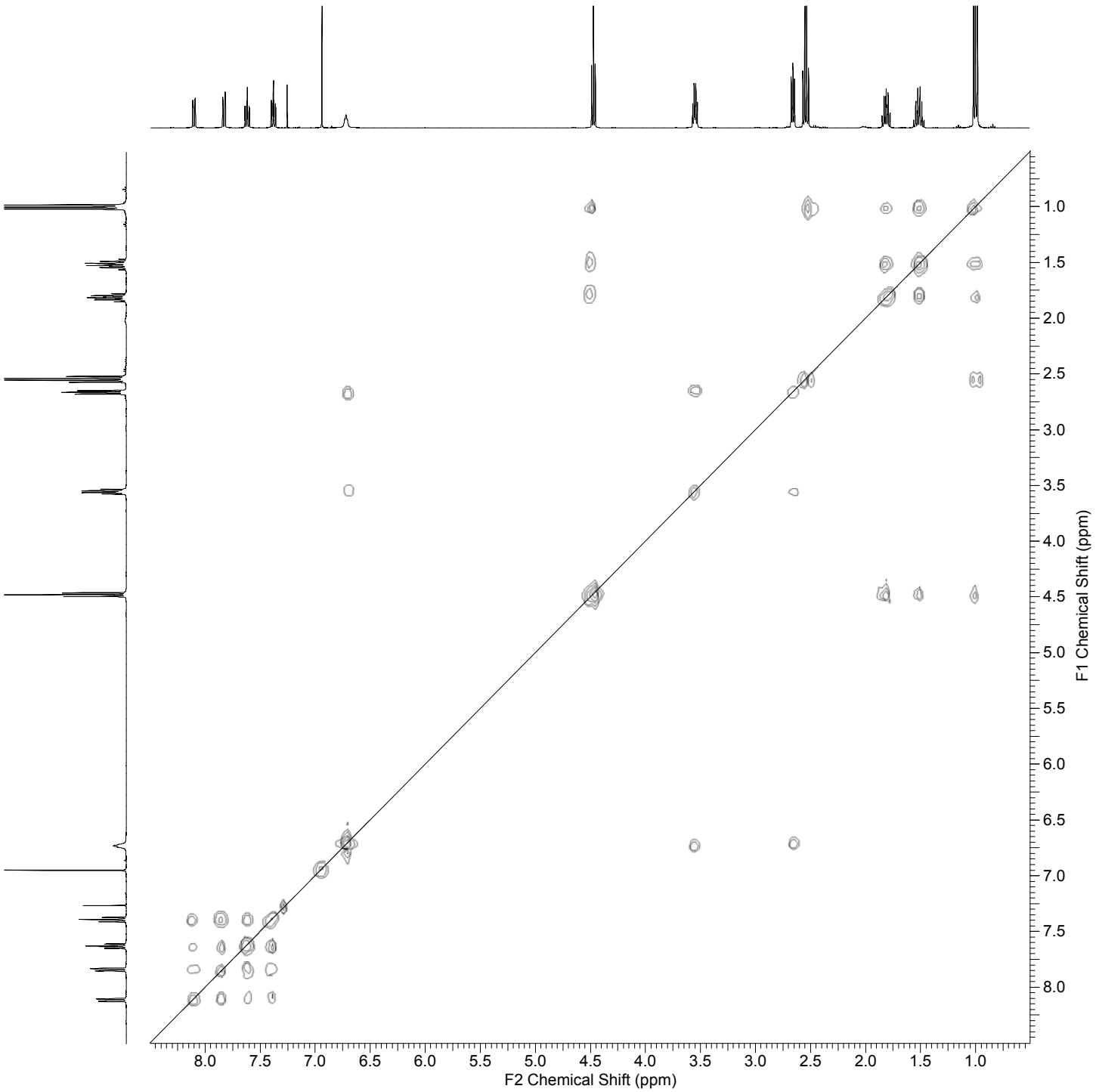

^{1}H NMR, 400 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
8.1183
8.1154
8.0973
8.0949
0.99
7.8470
7.8460
7.8440
7.8426
7.8259
7.8250
7.8230
7.8215
1.00
8.15 8.14 8.13 8.12 8.11 8.10 8.09 8.08 8.07 8.06
7.88 7.87 7.86 7.85 7.84 7.83 7.82 7.81 7.80 7.79 7.78
Chemical Shift (ppm)


^{1}H NMR, 400 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
7.6441
7.6401
7.6265
7.6230
7.6191
7.6054
7.6020
1.06
7.4050
7.4020
7.3878
7.3844
7.3810
7.3668
7.3639
1.06
7.67 7.66 7.65 7.64 7.63 7.62 7.61 7.60 7.59 7.58 7.57
7.43 7.42 7.41 7.40 7.39 7.38 7.37 7.36 7.35 7.34
Chemical Shift (ppm)


^{1}H NMR, 400 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
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
6.9424
6.7224
4.4859
4.4693
4.4527
3.5667
3.5535
3.5374
3.5247
0.94
1.00
2.06
2.03
7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65 6.60
4.60 4.55 4.50 4.45 4.40 4.35
3.70 3.65 3.60 3.55 3.50 3.45
Chemical Shift (ppm)


^{1}H NMR, 400 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
Chemical Shift (ppm)
2.6690
2.6539
2.6392
2.5634
2.5453
2.5277
2.5096
1.8402
1.8231
1.8055
1.7860
1.7694
1.5537
1.5347
1.5161
1.4970
1.4784
1.4603
1.0090
0.9914
0.9733
2.02
4.02
2.09
2.10
8.83

^{1}H-^{1}H TOCSY, 400 MHz, in $CDCl_3$



^{1}H-^{1}H NOESY, 400 MHz, in $CDCl_3$