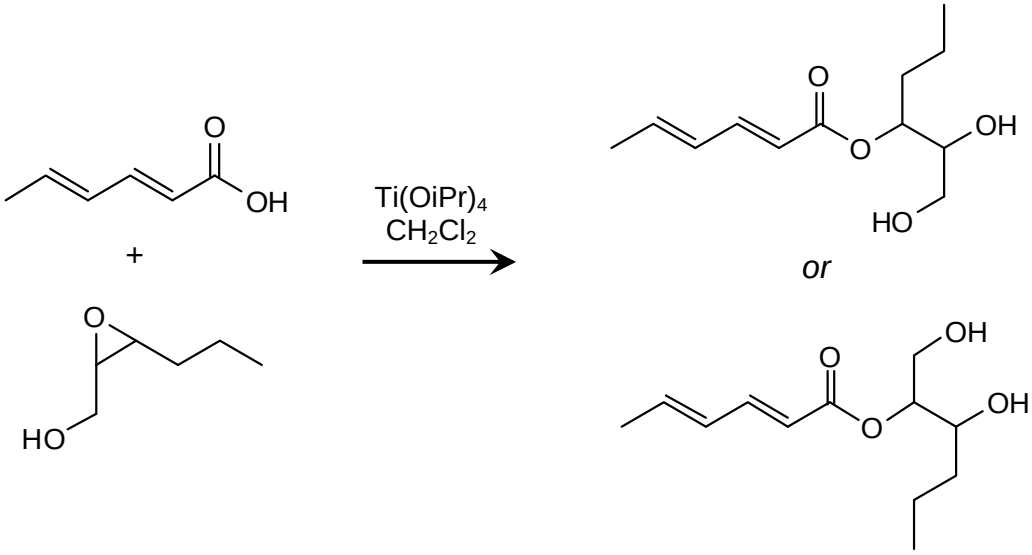
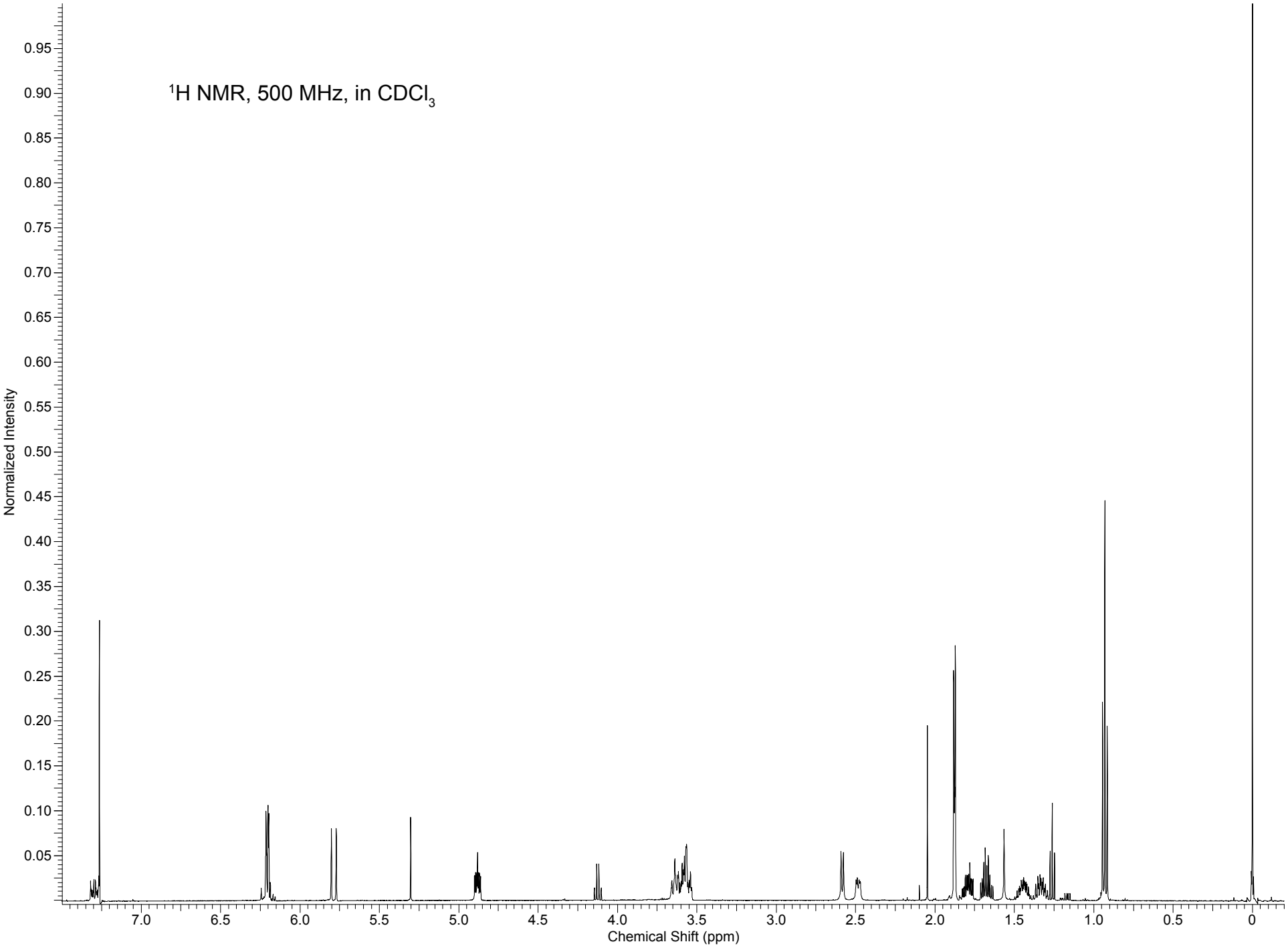
Chemistry 4361/8361 Fall 2012

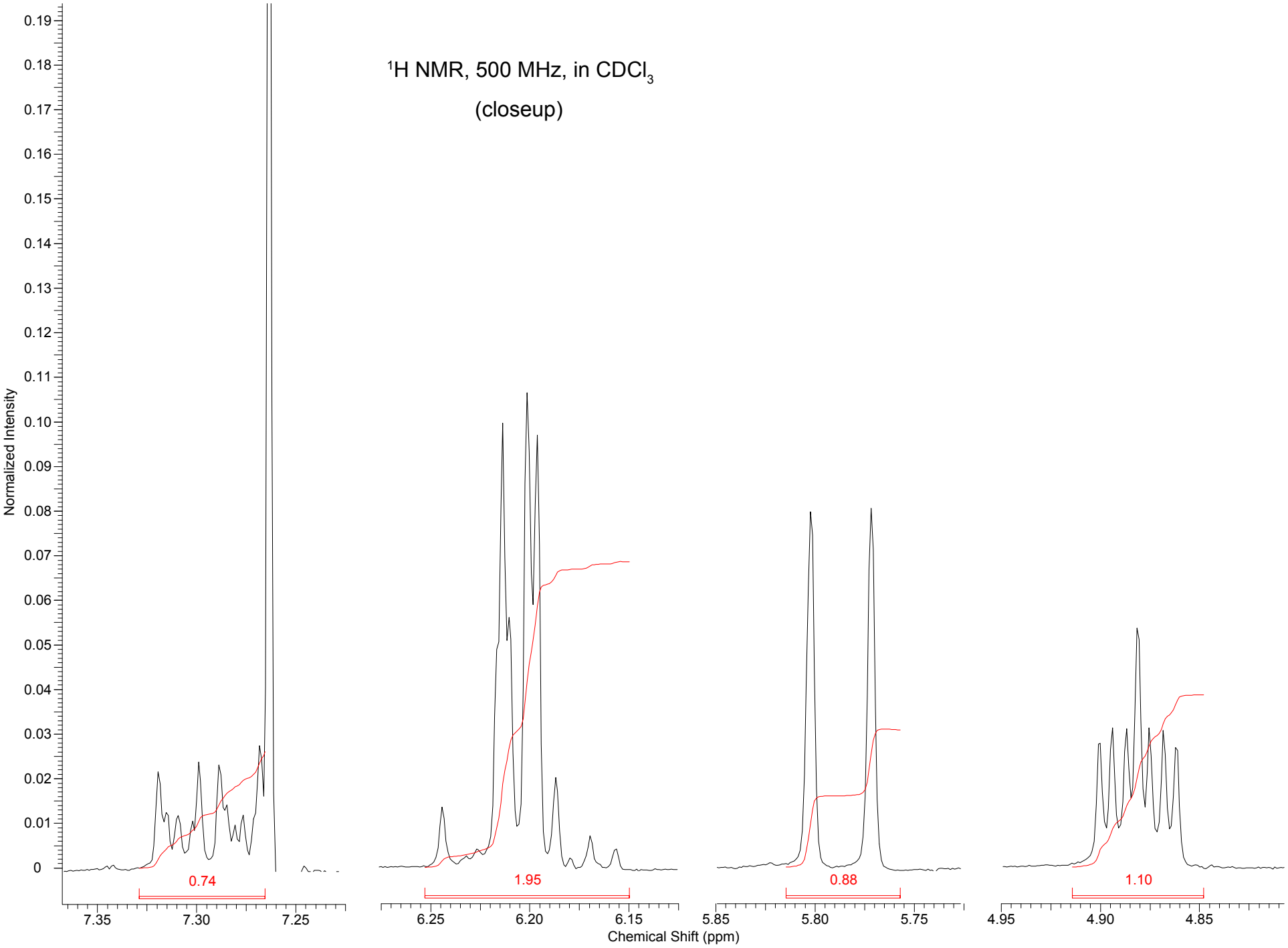
Problem Set 4
2D Correlated NMR Spectroscopy
Due: Wednesday, October 17

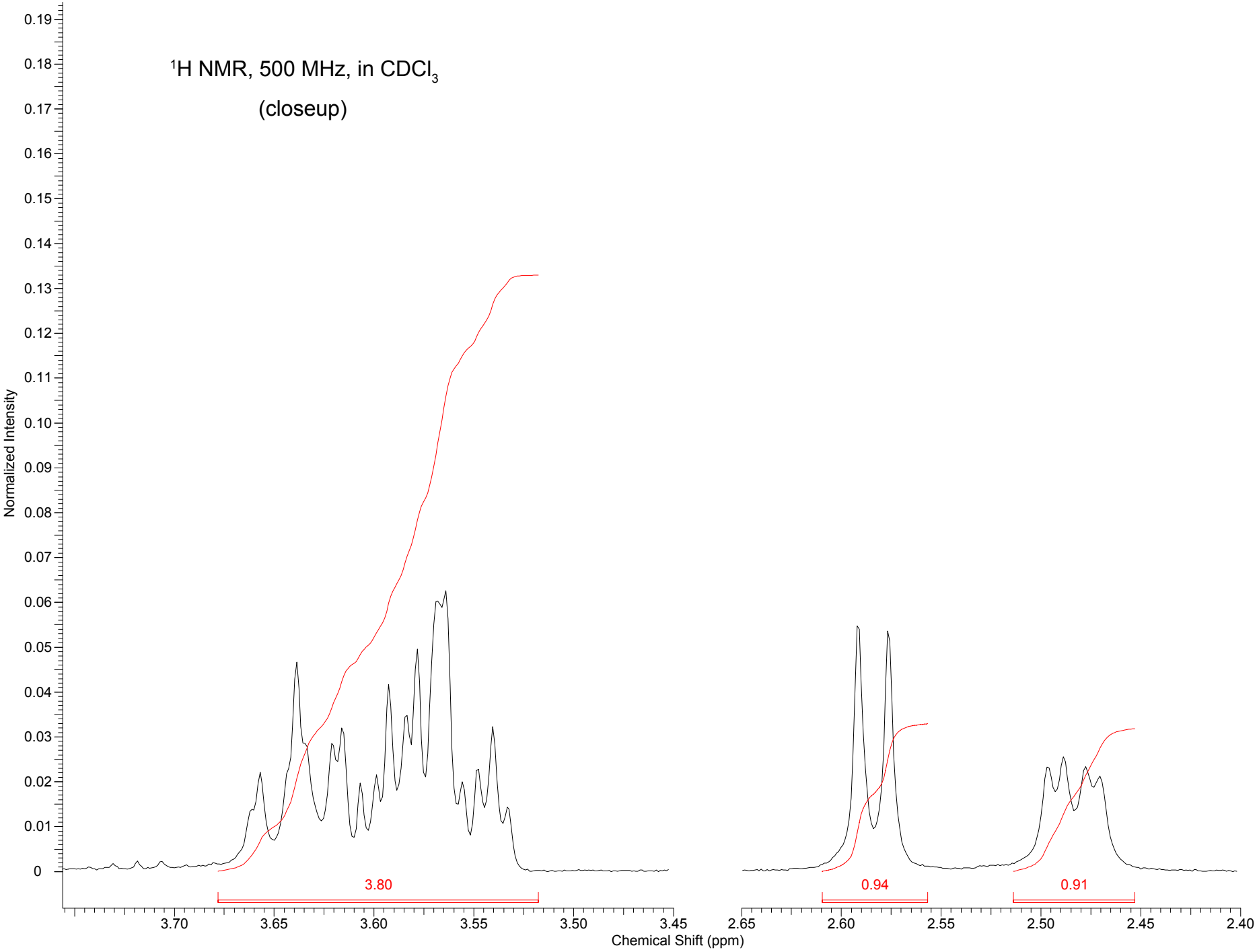
1. In principle, the Lewis-acid-catalyzed addition shown below could occur at either epoxide carbon. However, only one product was isolated in excellent yield.

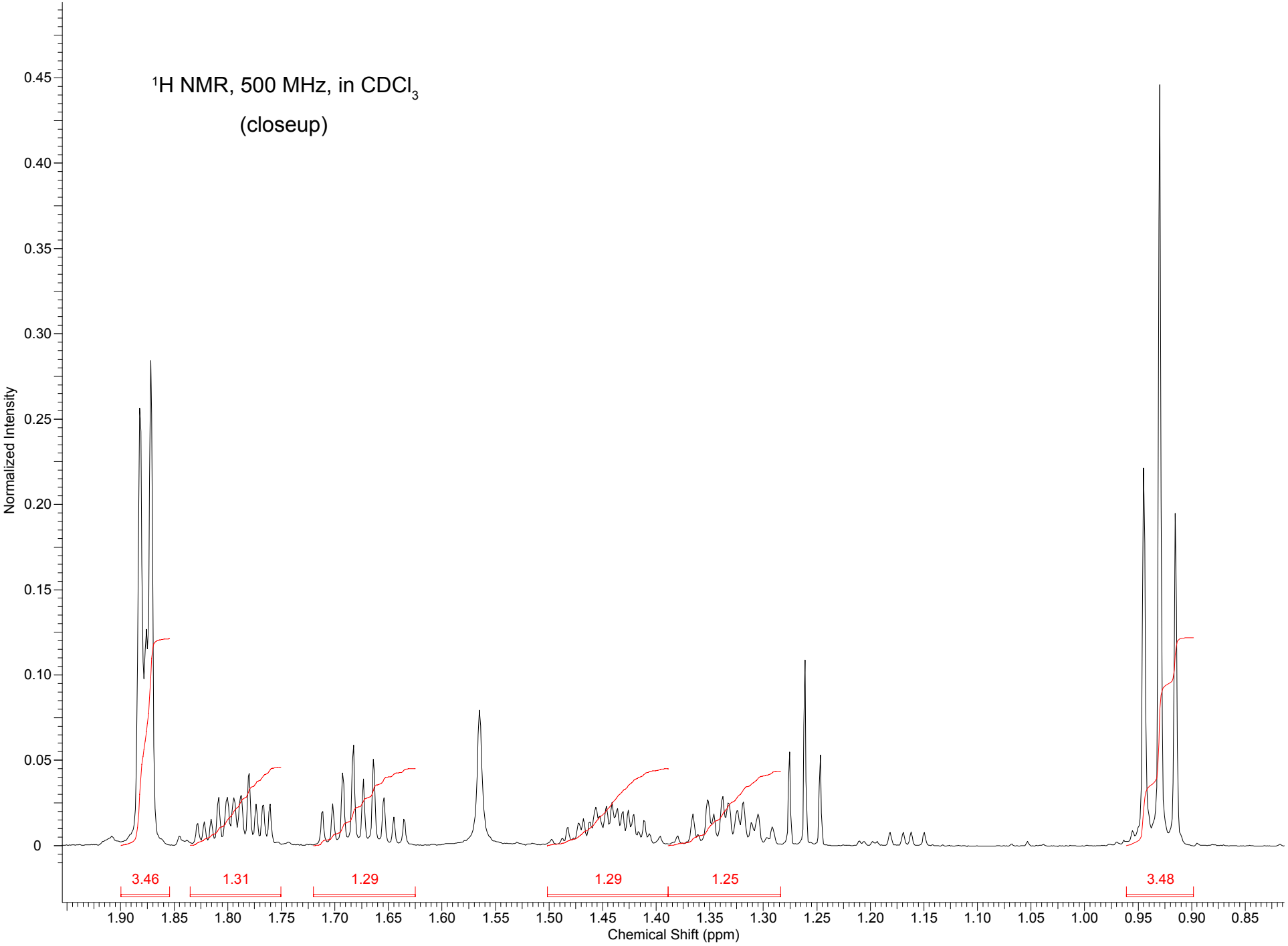


^{1}H and ^{1}H-^{1}H COSY spectra (both 500 MHz, in $CDCl_3$) of that product—contaminated with some leftover CH_2Cl_2 and ethyl acetate from the column—are given on the following pages. Which product was formed?

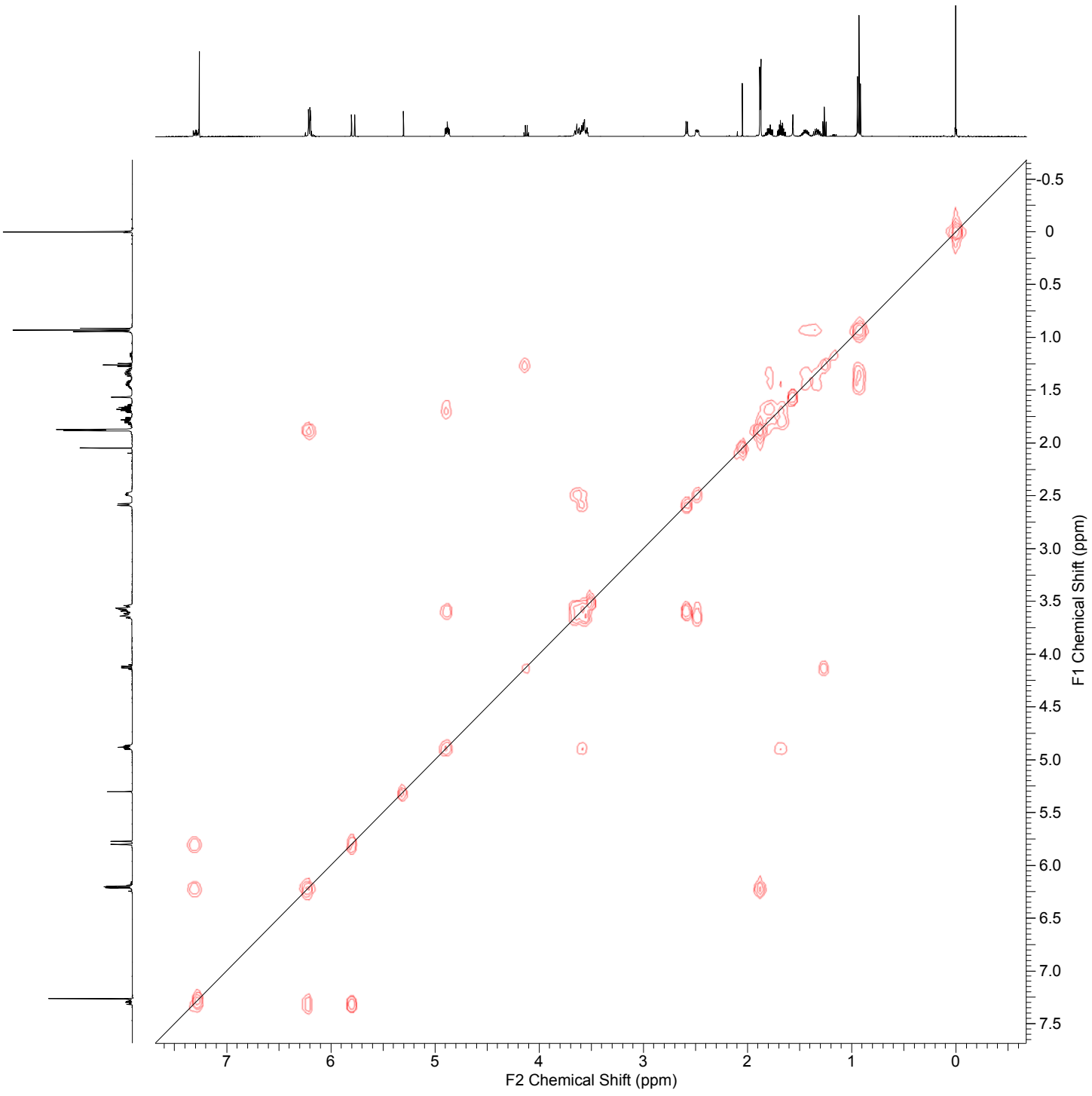

^{1}H NMR, 500 MHz, in $CDCl_3$
Normalized Intensity
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


^{1}H NMR, 500 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0.74
1.95
0.88
1.10
7.35
7.30
7.25
6.25
6.20
6.15
5.85
5.80
5.75
4.95
4.90
4.85
Chemical Shift (ppm)

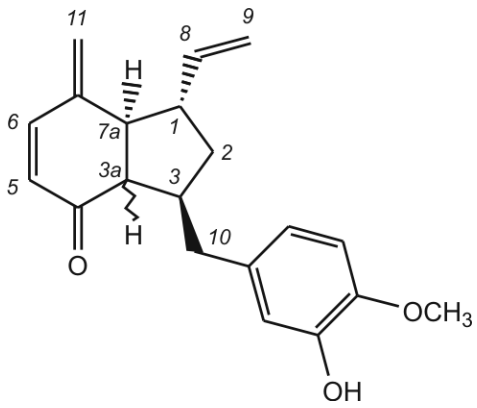

^{1}H NMR, 500 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
3.80
0.94
0.91
3.70
3.65
3.60
3.55
3.50
3.45
2.65
2.60
2.55
2.50
2.45
2.40
Chemical Shift (ppm)


^{1}H NMR, 500 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
3.46
1.31
1.29
1.29
1.25
3.48
1.90
1.85
1.80
1.75
1.70
1.65
1.60
1.55
1.50
1.45
1.40
1.35
1.30
1.25
1.20
1.15
1.10
1.05
1.00
0.95
0.90
0.85
Chemical Shift (ppm)

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



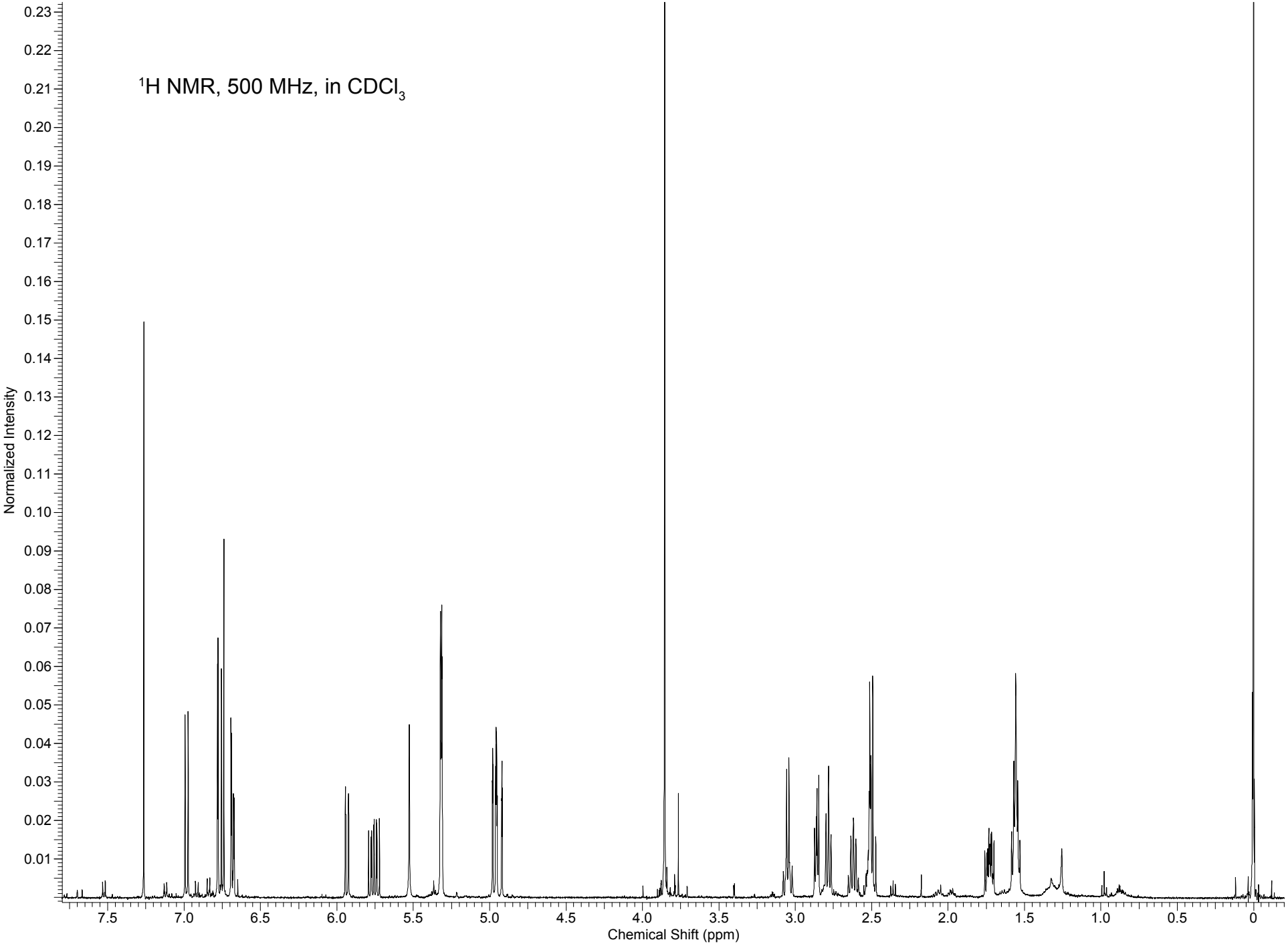
2. As part of her Ph.D. thesis work, Hollie Lewis (Hoye group) attempted to determine stereochemistry at carbon 3a in the structure of ottelione A. ^{1}H and ^{1}H-^{1}H COSY spectra (both 500 MHz, in $CDCl_3$) are shown on the following pages. In this problem, you will re-trace her efforts to use these spectra to assign carbon 3a.

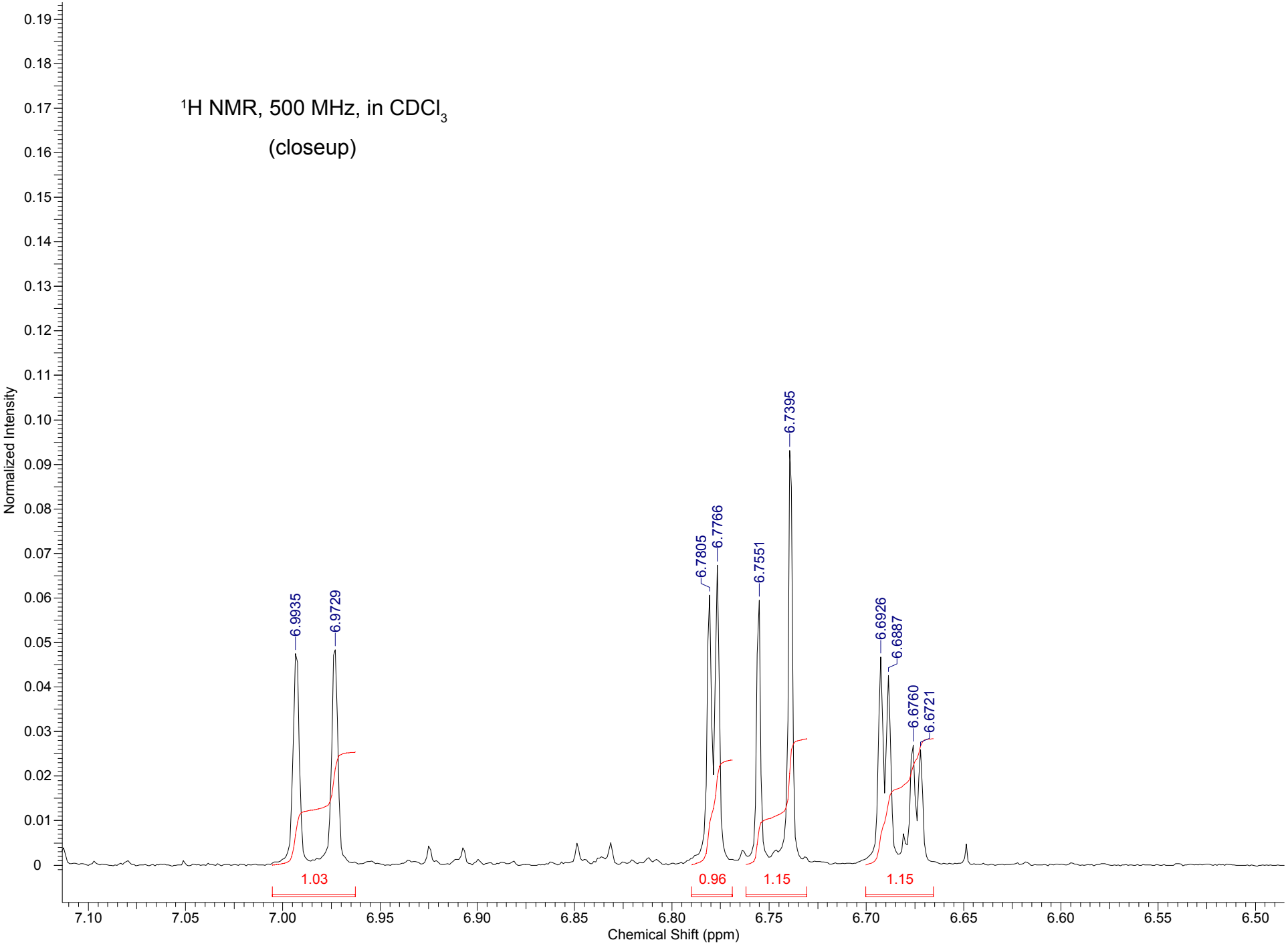


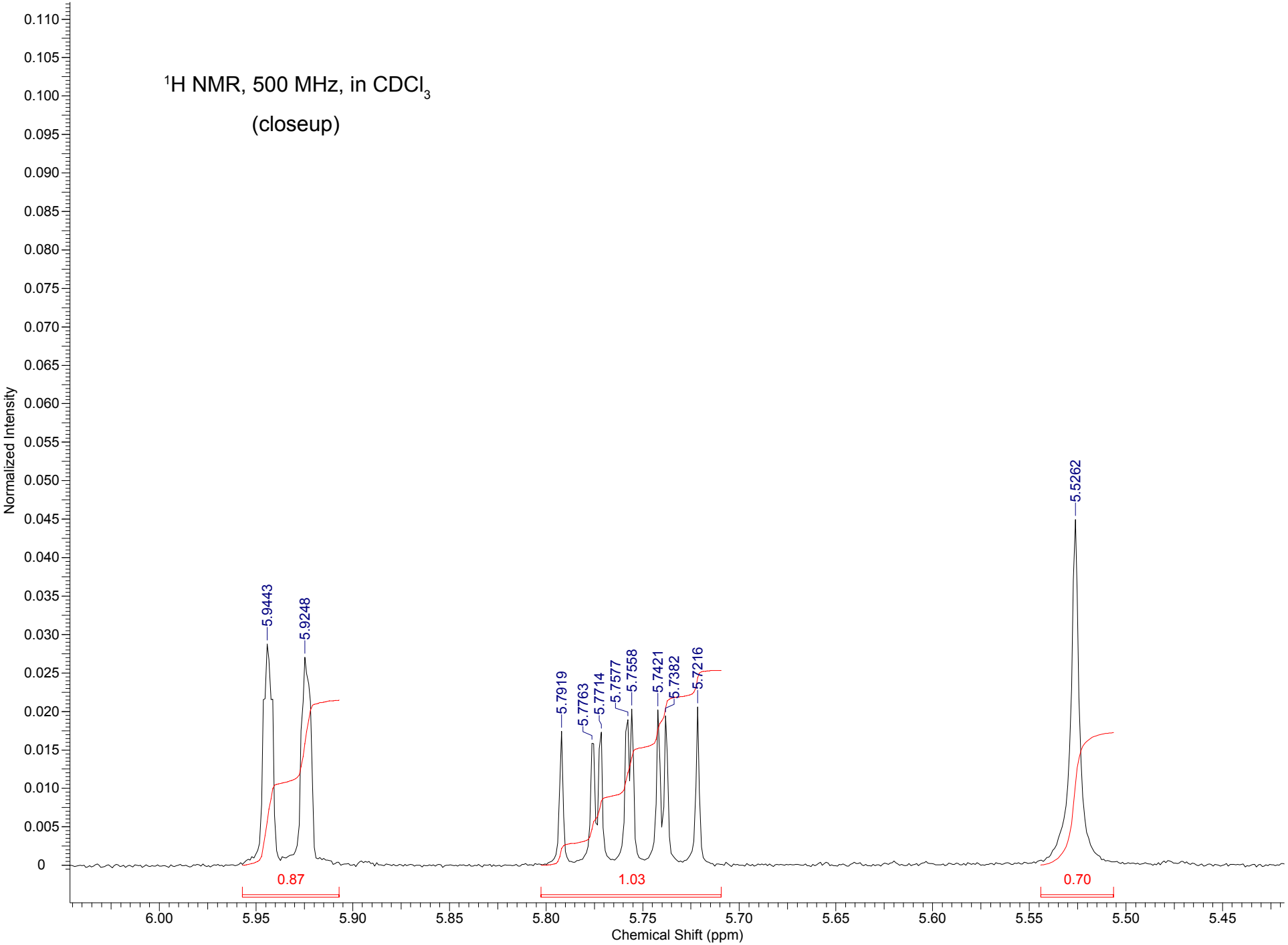
   a. Assign the resonances in the ^{1}H NMR spectrum of ottelione to numbered protons as best you can.

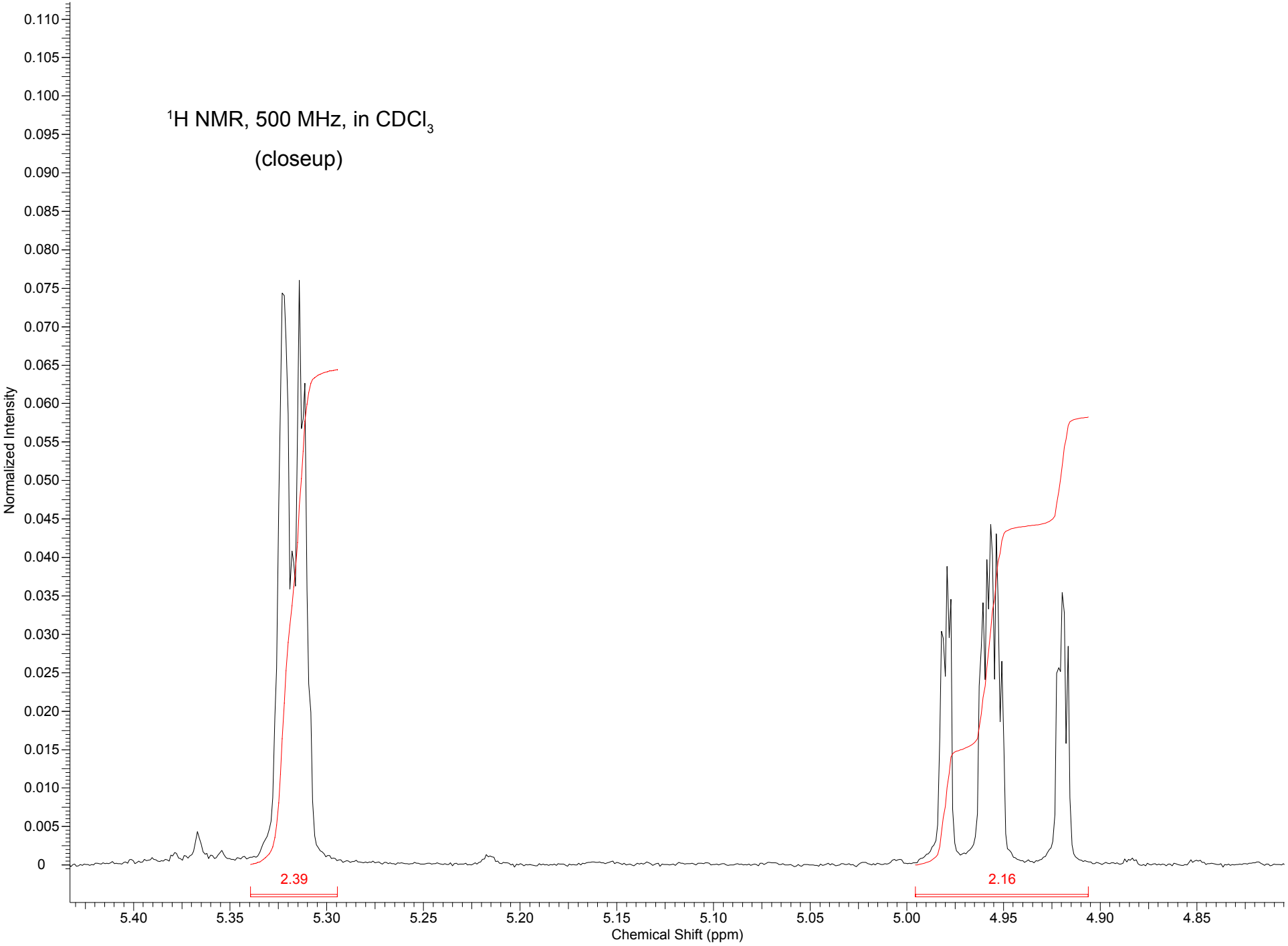
   b. Hollie hoped that determining the coupling constant between H_{3a} and H_{7a} would help her assign the unknown stereochemistry. What is the coupling constant between H_{3a} and H_{7a}?

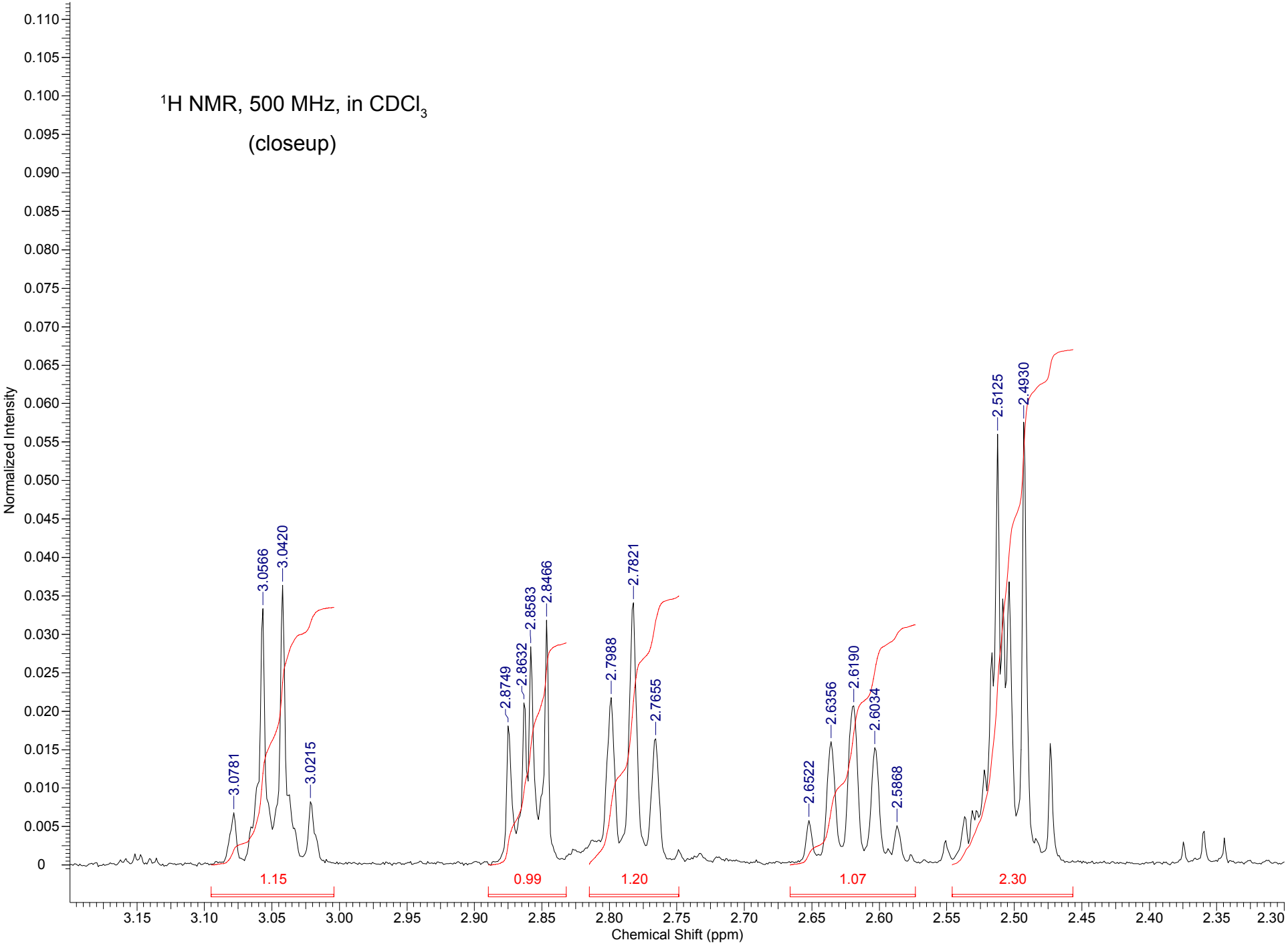
   c. Build structural models of ottelione A (either using a physical model or in a 3D modeling program like CambridgeSoft Chem3D) with H_{3a} above and below the plane of the molecule. What is the dihedral angle between H_{3a} and H_{7a} in each model? Would you consider either of those angles consistent or inconsistent with the coupling constant $J(H_{3a},H_{7a})$ you measured?

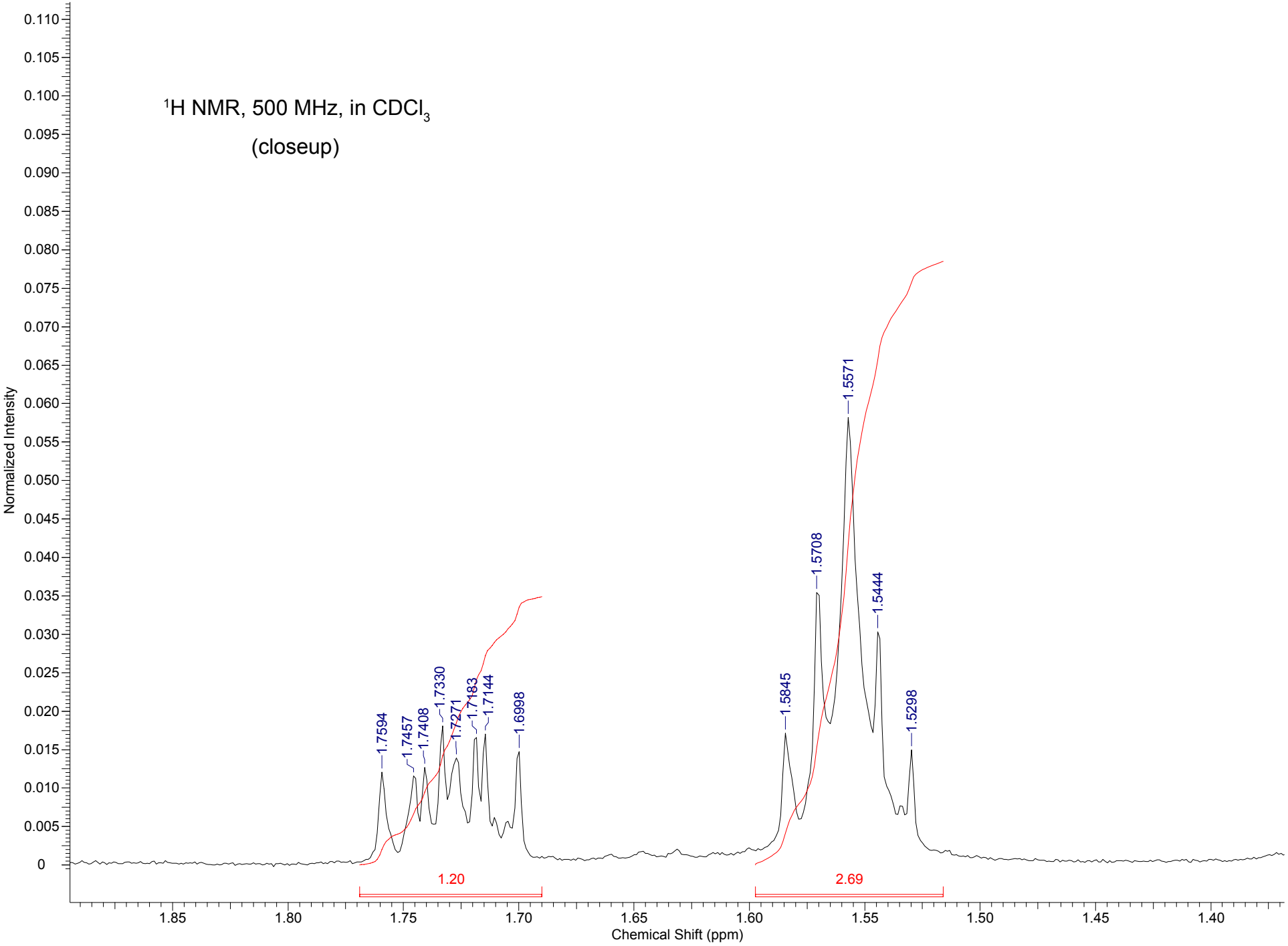

^{1}H NMR, 500 MHz, in $CDCl_3$
Normalized Intensity
0.23
0.22
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


^{1}H NMR, 500 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
Chemical Shift (ppm)
6.9935
6.9729
6.7805
6.7766
6.7551
6.7395
6.6926
6.6887
6.6760
6.6721
1.03
0.96
1.15
1.15

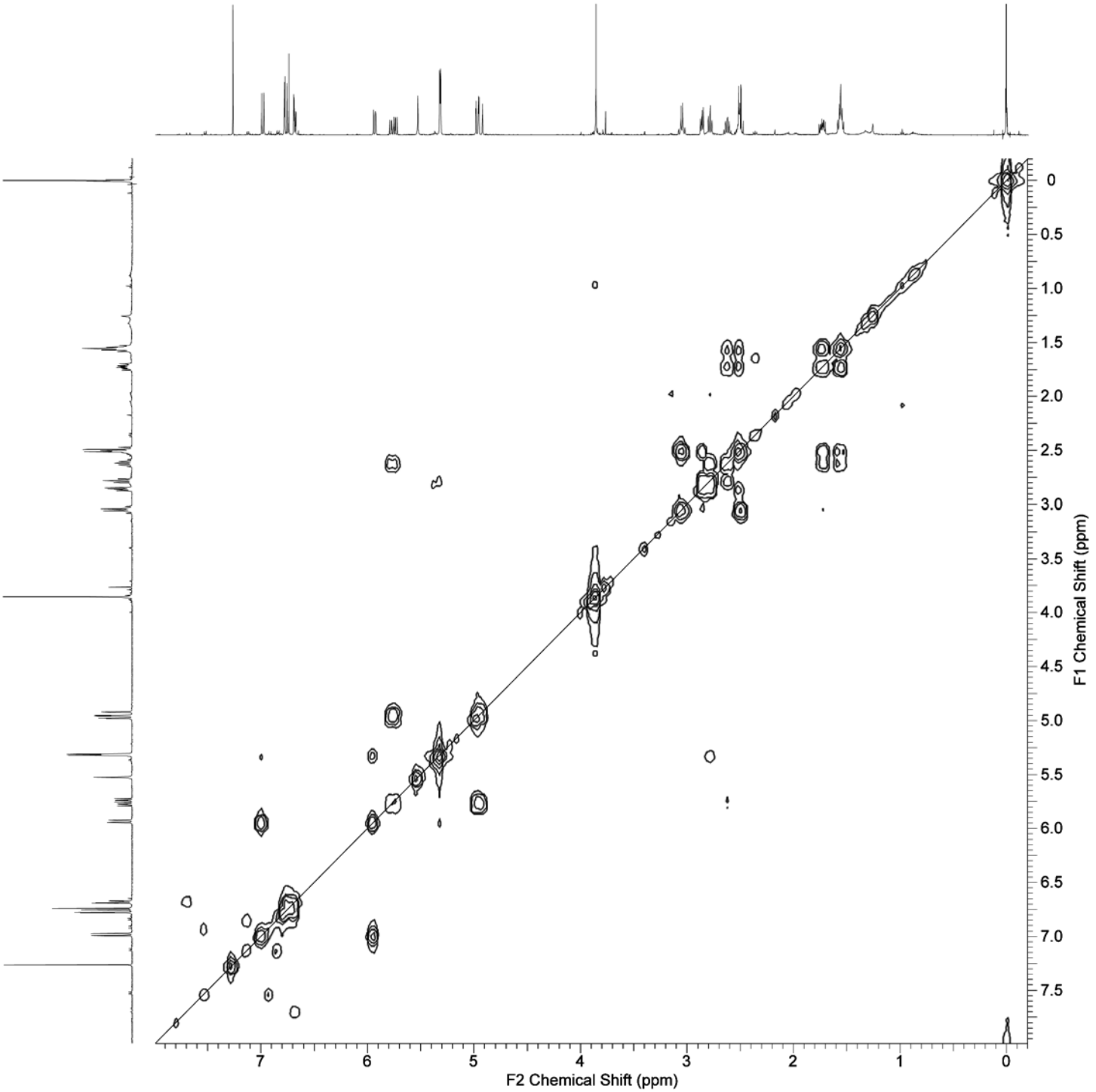

^{1}H NMR, 500 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
Chemical Shift (ppm)
5.9443
5.9248
5.7919
5.7763
5.7714
5.7577
5.7558
5.7421
5.7382
5.7216
5.5262
0.87
1.03
0.70


^{1}H NMR, 500 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
0.110
0.105
0.100
0.095
0.090
0.085
0.080
0.075
0.070
0.065
0.060
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0
2.39
2.16
5.40
5.35
5.30
5.25
5.20
5.15
5.10
5.05
5.00
4.95
4.90
4.85
Chemical Shift (ppm)


^{1}H NMR, 500 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
Chemical Shift (ppm)
3.0781
3.0566
3.0420
3.0215
2.8749
2.8632
2.8583
2.8466
2.7988
2.7821
2.7655
2.6522
2.6356
2.6190
2.6034
2.5868
2.5125
2.4930
1.15
0.99
1.20
1.07
2.30

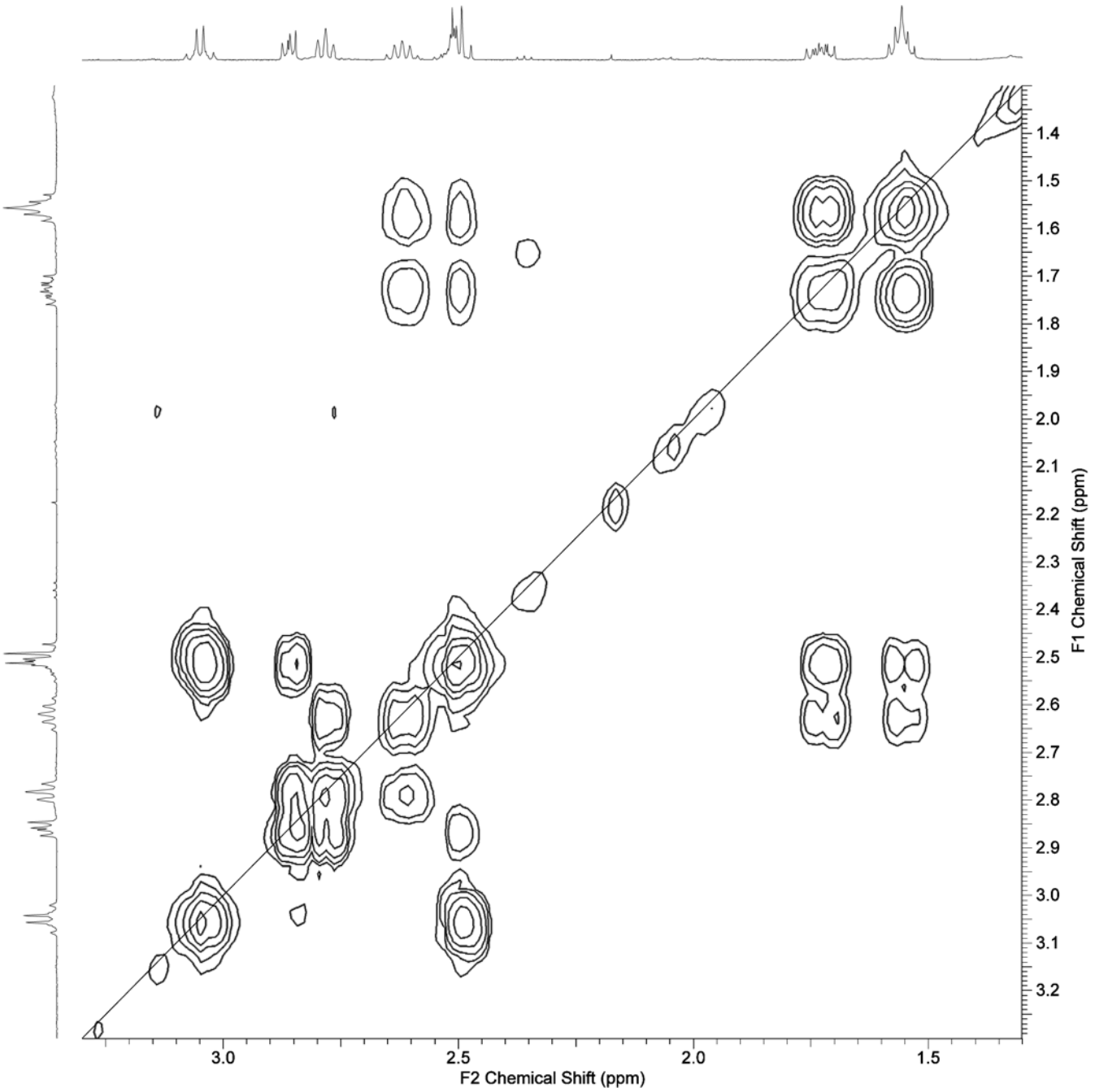

^{1}H NMR, 500 MHz, in $CDCl_3$
(closeup)
Normalized Intensity
Chemical Shift (ppm)
1.7594
1.7457
1.7408
1.7330
1.7271
1.7183
1.7144
1.6998
1.5845
1.5708
1.5571
1.5444
1.5298
1.20
2.69

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



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

(closeup)



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

(closeup)