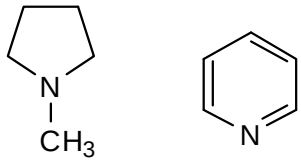
Chemistry 4361/8361 Monday, September 17

Workshop 1

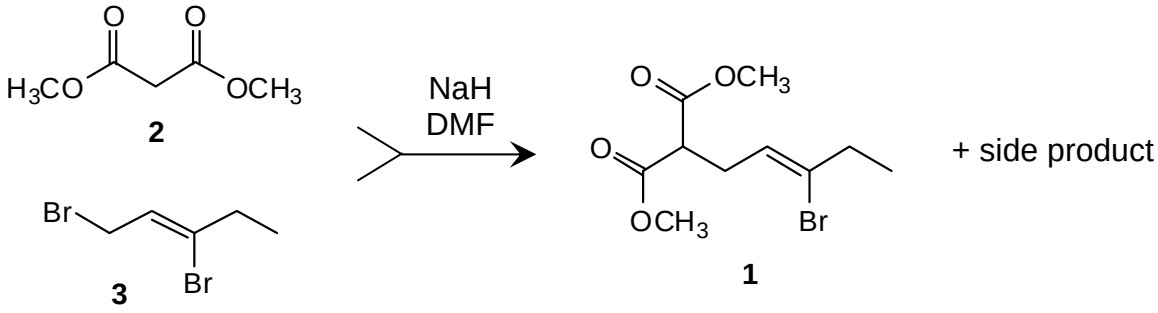
Analyzing 1D NMR Spectra

1. The 400 MHz ^{1}H NMR spectrum of nicotine ($C_{10}H_{14}N_2$) and close-ups are attached to this Workshop. The structure of nicotine consists of an N-methylpyrrolidine ring connected to a pyridine ring. How are the two rings connected? Assign the resonances in the ^{1}H NMR spectrum to your proposed structure for nicotine as best you can. (*Hint:* Think about chemical shifts before you start trying to decipher multiplets.)



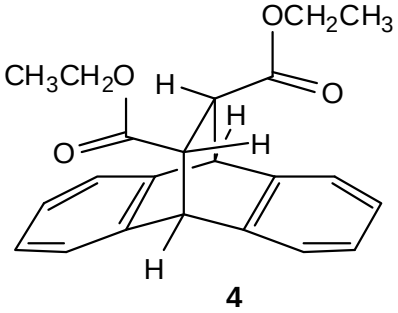
N-methyl pyrrolidine pyridine

2. Trost et al. synthesized the product **1** by reacting dimethylmalonate (**2**) with NaH base and bromoallylbromide **3**. In the synthesis, however, a significant side product was observed.



The ^{1}H NMR of this side product is attached to the Workshop. What is the side product?

3. The Diels-Alder condensation of fumarate with anthracene generates compound **4**. The ^{1}H NMR spectrum of this molecule, including a closeup of the δ = 4.0 ppm region of the spectrum, is attached. How do you explain:



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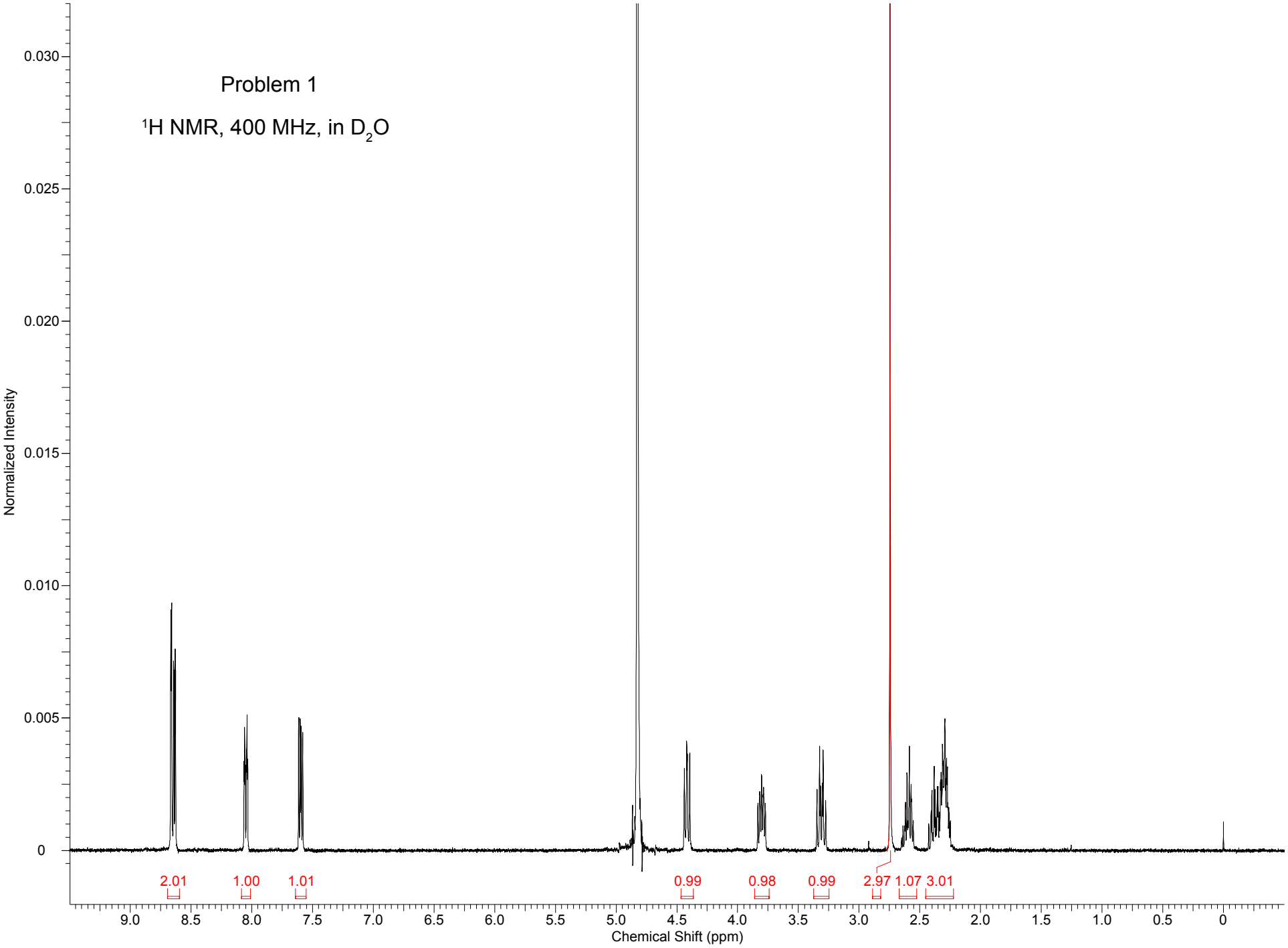
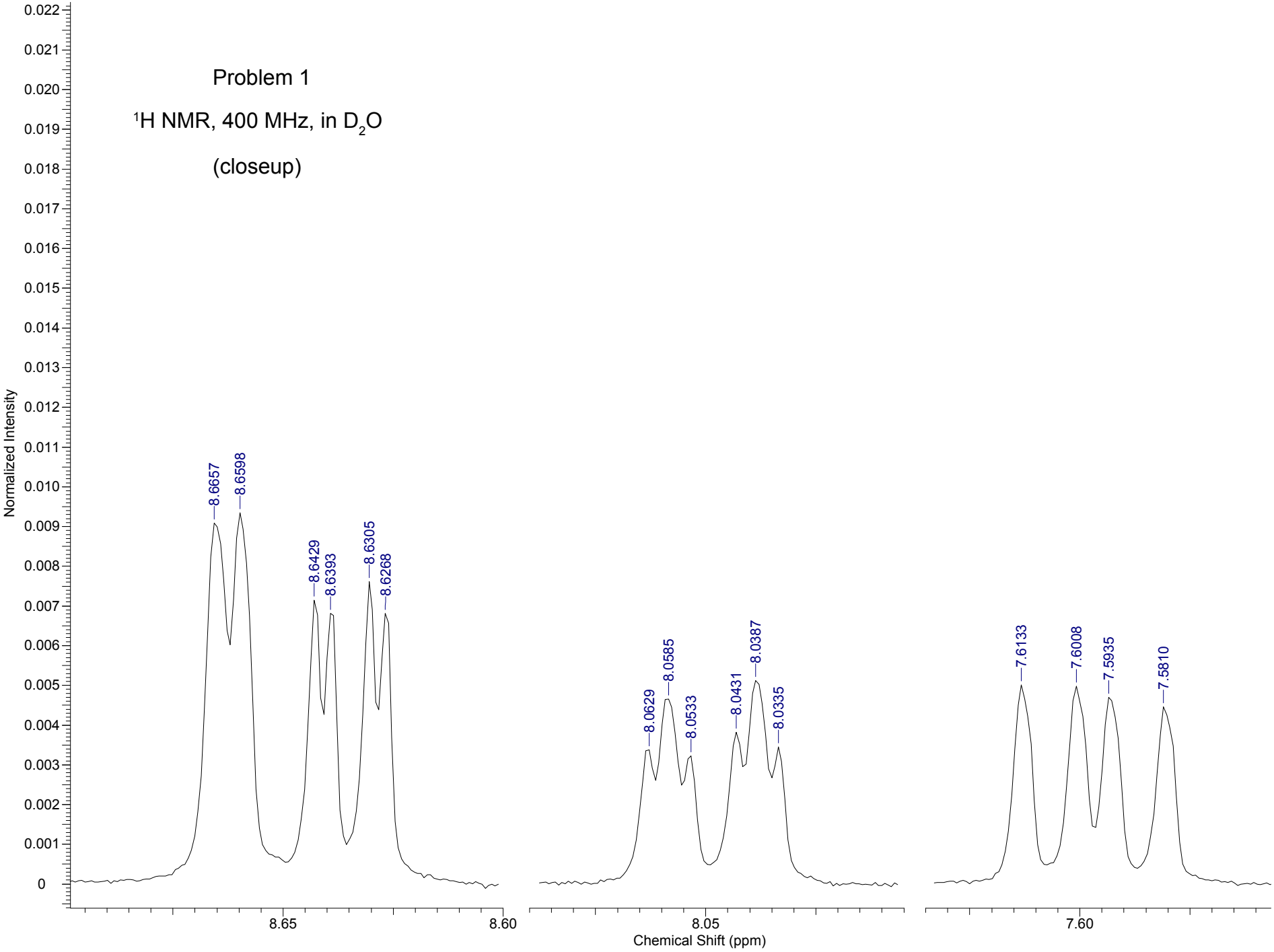
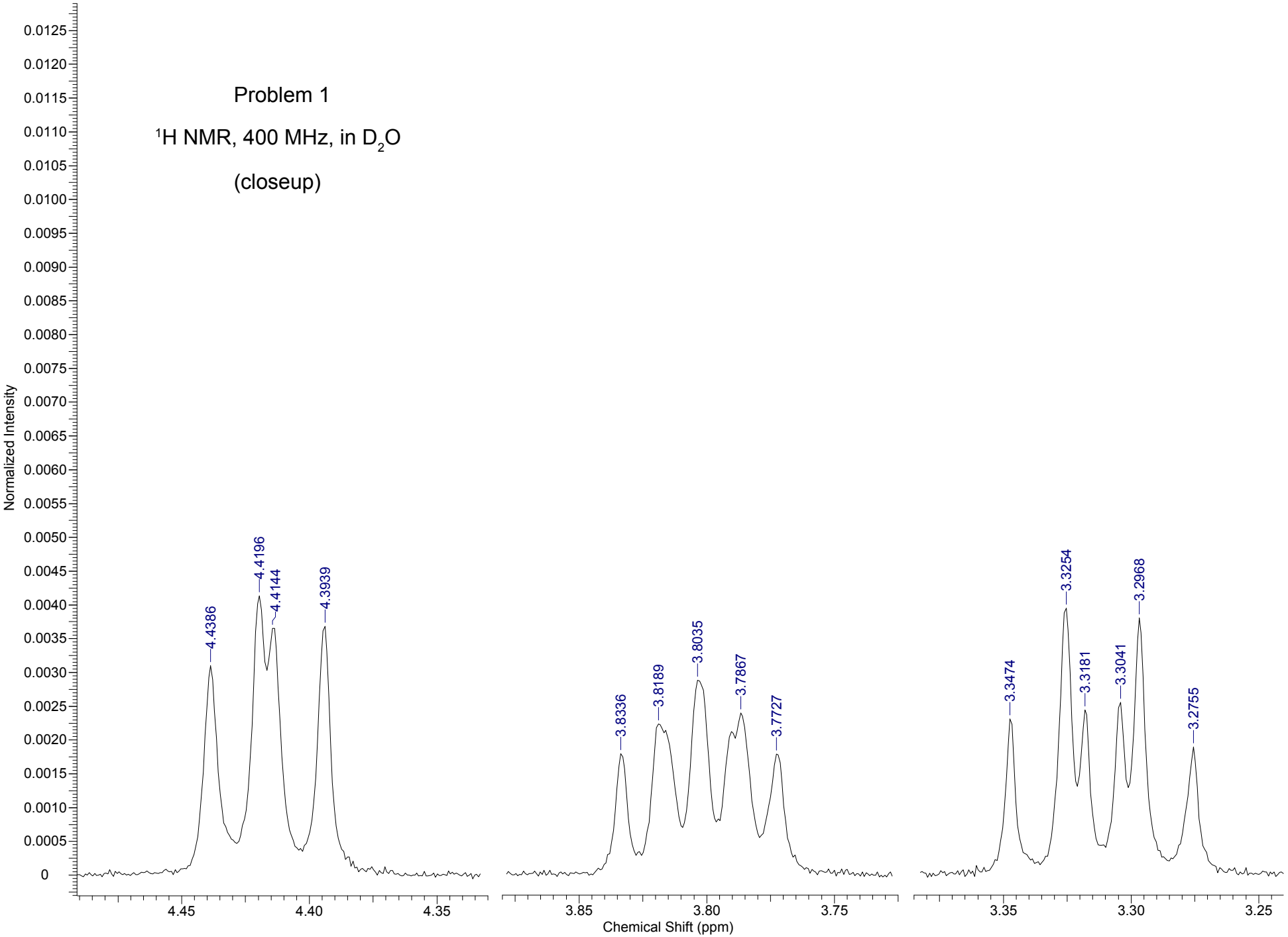
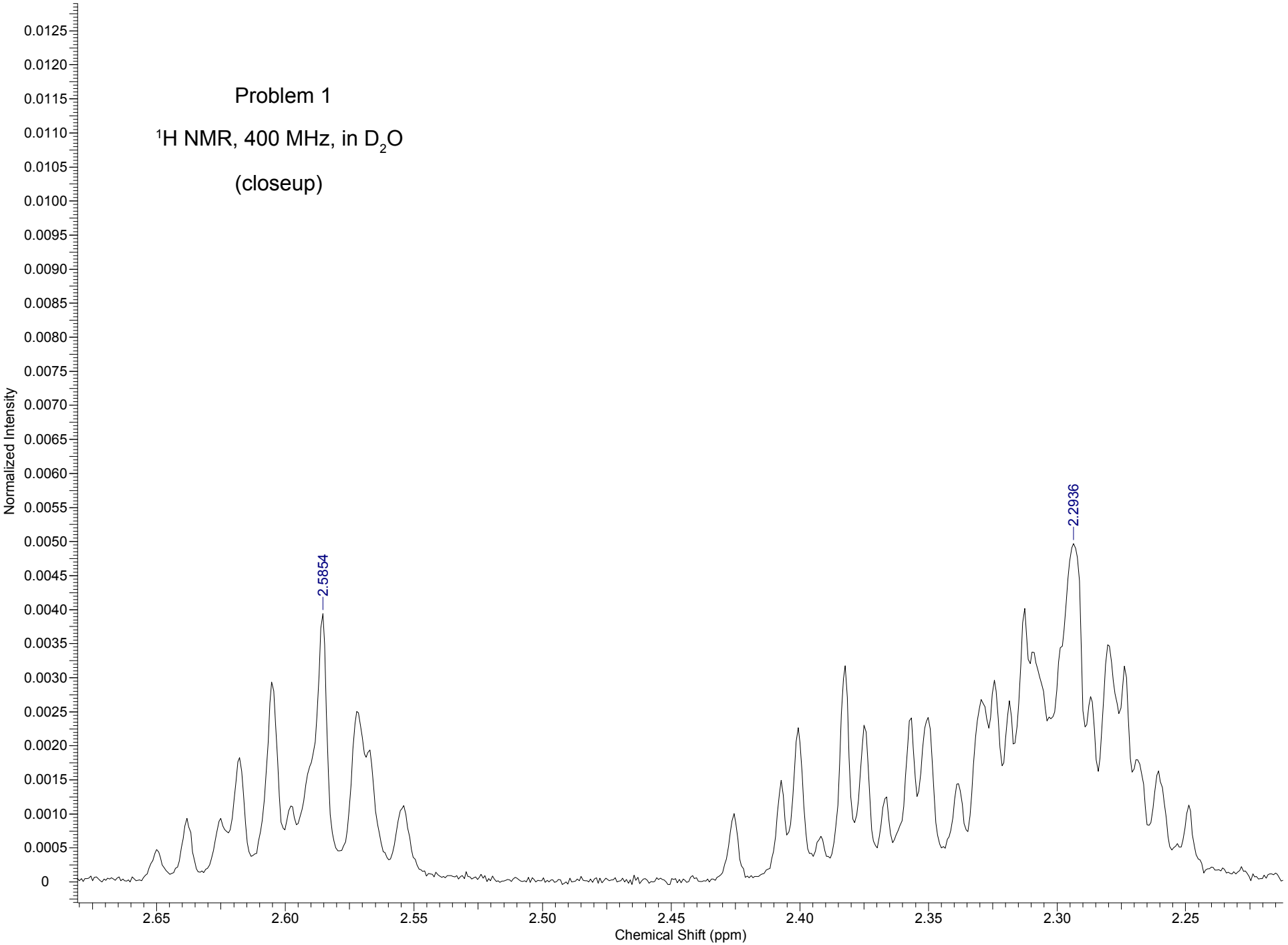
   a. the lack of splitting in the peaks at δ = 3.4 and 4.7 ppm?

   b. the pattern you see at δ = 4.0 ppm?


Problem 1
^{1}H NMR, 400 MHz, in D_2O
Normalized Intensity
0.030
0.025
0.020
0.015
0.010
0.005
0
2.01
1.00
1.01
0.99
0.98
0.99
2.97
1.07
3.01
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
Chemical Shift (ppm)

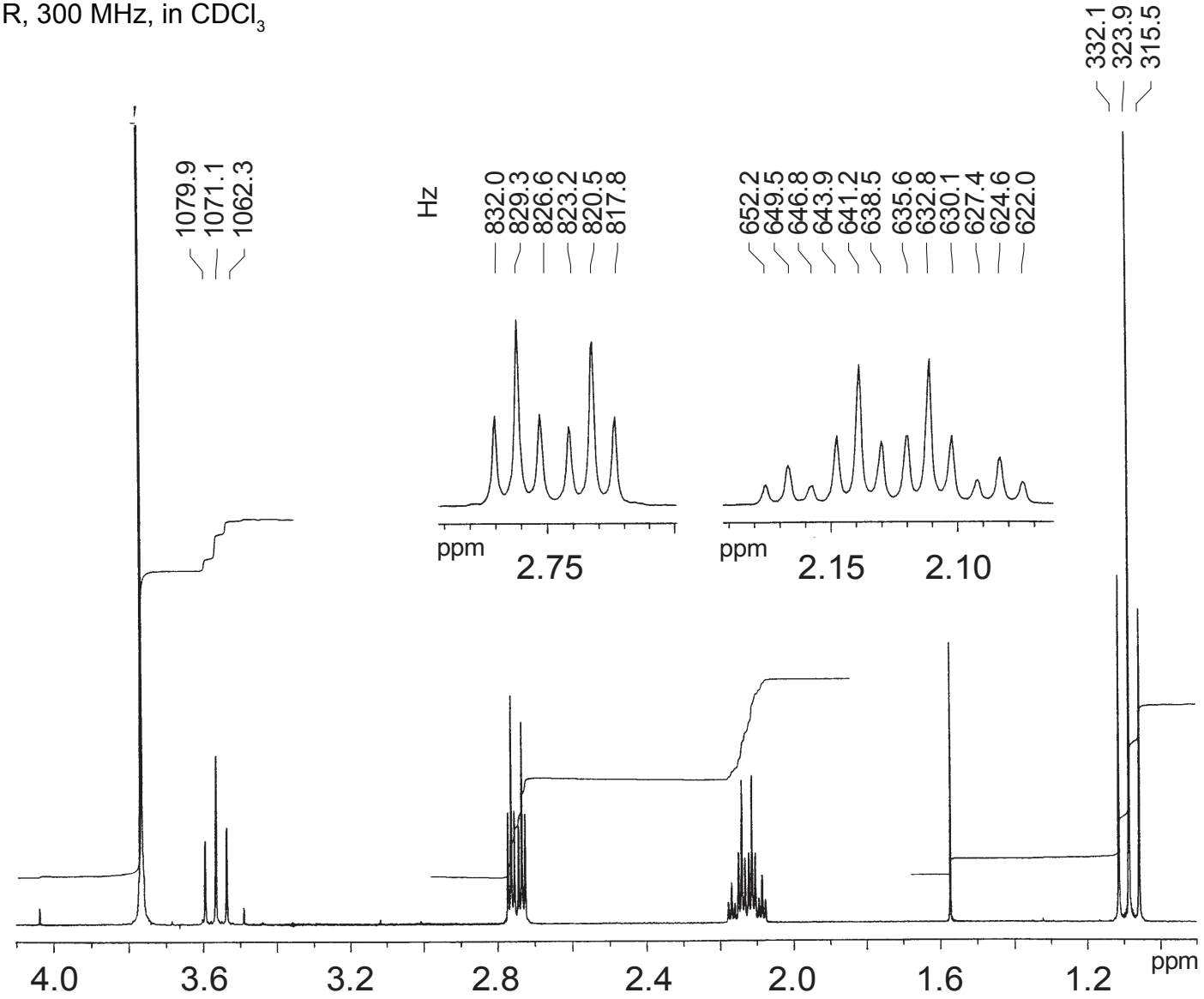

Problem 1
^{1}H NMR, 400 MHz, in D_2O
(closeup)
Normalized Intensity
0.022
0.021
0.020
0.019
0.018
0.017
0.016
0.015
0.014
0.013
0.012
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
8.6657
8.6598
8.6429
8.6393
8.6305
8.6268
8.0629
8.0585
8.0533
8.0431
8.0387
8.0335
7.6133
7.6008
7.5935
7.5810
8.65
8.60
8.05
7.60
Chemical Shift (ppm)


Problem 1
^{1}H NMR, 400 MHz, in D_2O
(closeup)
Normalized Intensity
0.0125
0.0120
0.0115
0.0110
0.0105
0.0100
0.0095
0.0090
0.0085
0.0080
0.0075
0.0070
0.0065
0.0060
0.0055
0.0050
0.0045
0.0040
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0
4.4386
4.4196
4.4144
4.3939
3.8336
3.8189
3.8035
3.7867
3.7727
3.3474
3.3254
3.3181
3.3041
3.2968
3.2755
4.45
4.40
4.35
3.85
3.80
3.75
3.35
3.30
3.25
Chemical Shift (ppm)


Problem 1
^{1}H NMR, 400 MHz, in D_2O
(closeup)
Normalized Intensity
0.0125
0.0120
0.0115
0.0110
0.0105
0.0100
0.0095
0.0090
0.0085
0.0080
0.0075
0.0070
0.0065
0.0060
0.0055
0.0050
0.0045
0.0040
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0
2.5854
2.2936
2.65
2.60
2.55
2.50
2.45
2.40
2.35
2.30
2.25
Chemical Shift (ppm)

Problem 2

^{1}H NMR, 300 MHz, in $CDCl_3$



Problem 3

^{1}H NMR, 300 MHz, in $CDCl_3$