Chemistry 4361/8361 Monday, September 24

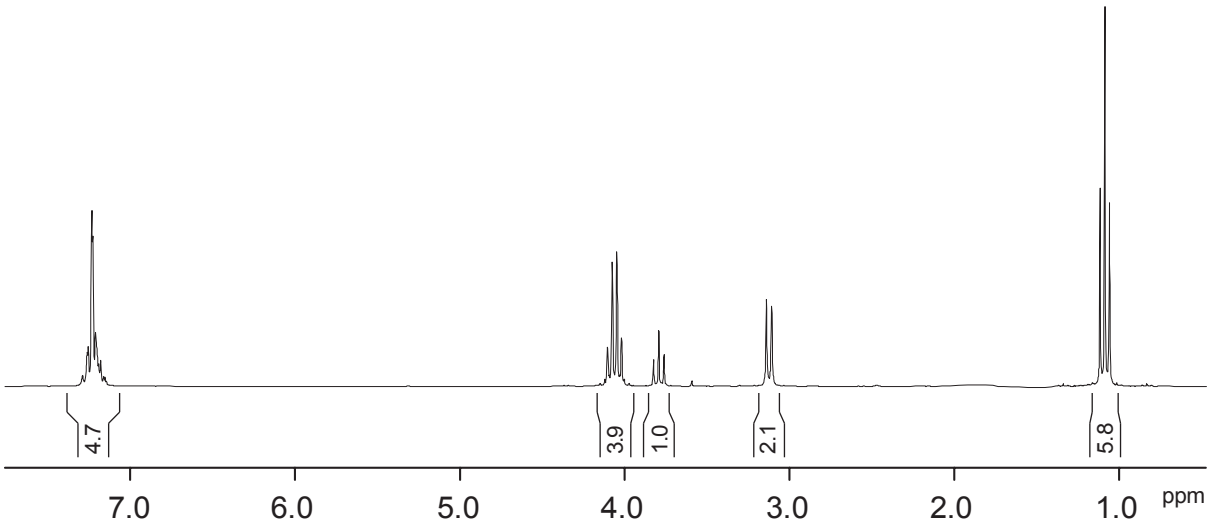
Workshop 2

Structure Determination w/ Complex 1D NMR

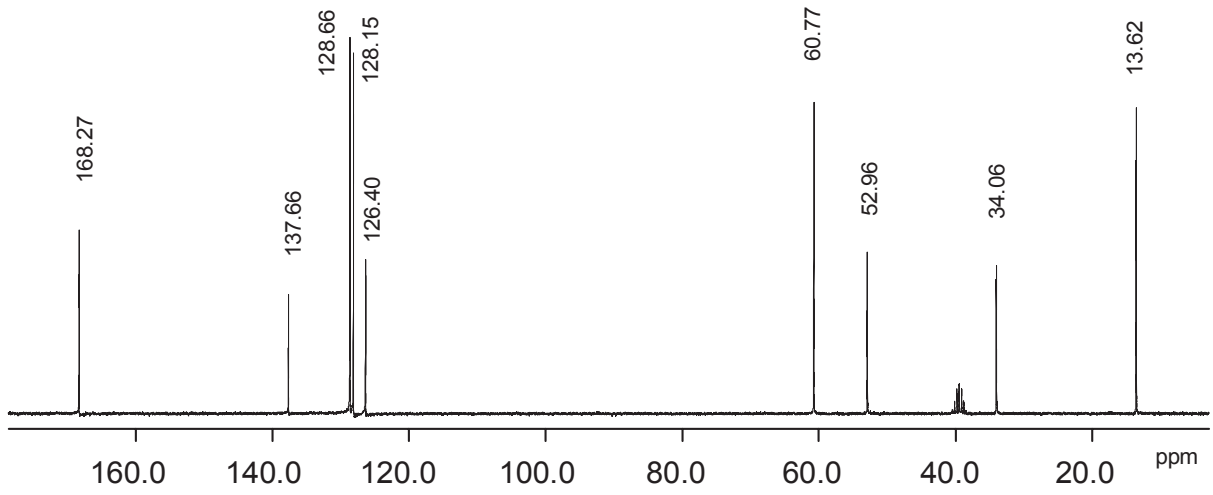
1. a. The ^{1}H and ^{1}H-decoupled ^{13}C NMR shown on the next page are of a compound you just fished out of your reaction. You've got no clue what it is—no chemical formula, doesn't have any functional groups in common with what was in your reaction, came off your silica column with medium polarity. (So it's not an alkane, and it's not a carboxylic acid or an amine, but other than that, no other hints.) Maybe it sloshed into your flask from the rotovap bump trap, maybe it was residue from the last labmate who used your flask, or maybe it's the main product of your reaction!

   What is it?

   b. On the third page, just for fun, I've attached the ^{1}H-coupled (or non-decoupled, you might say) ^{13}C NMR of the same compound. Can you explain the splitting patterns observed in terms of your proposed structure?



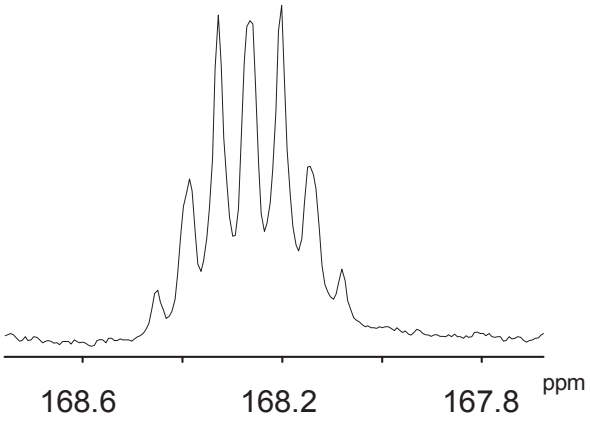
^{1}H NMR (200 MHz, in DMSO-d_6)

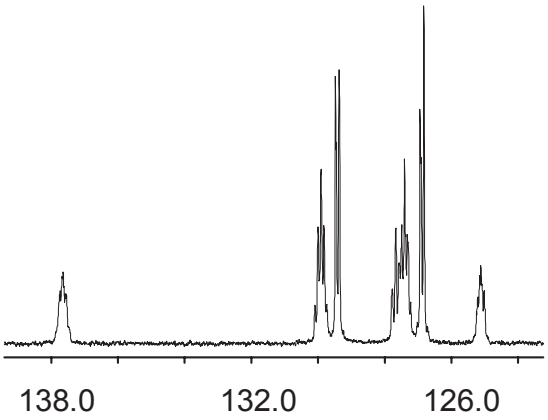


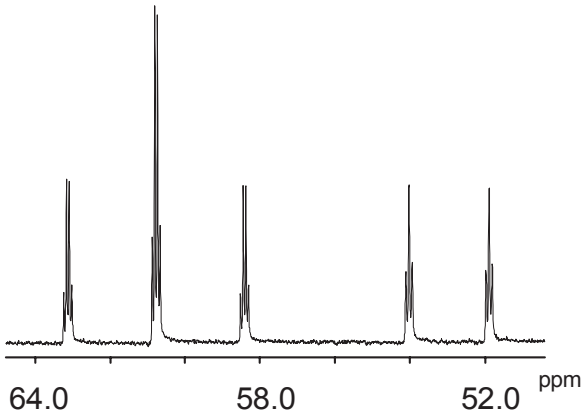
^{13}C NMR (50 MHz, in DMSO-d_6)

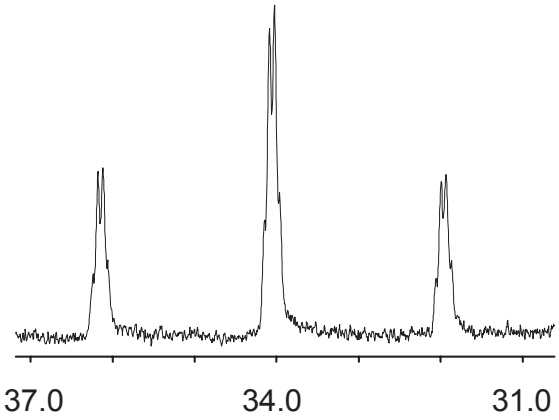
^{13}C NMR (^{1}H-coupled;
50 MHz, in DMSO-d_6)

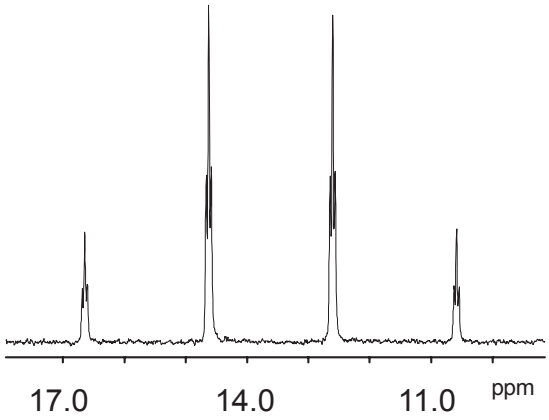
Horizontal scales in these close-ups are not the same; beware comparing them to each other.





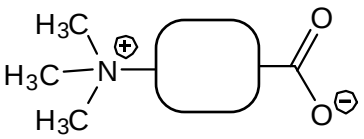






2. A water-soluble neurotransmitter was isolated in large quantities from sea slug neurons and subjected to ^{1}H NMR and (^{1}H-decoupled) ^{13}C NMR analysis in D_2O; the NMR spectra are attached. Low-resolution mass spectrometry indicated that the molecule had a nominal molecular mass of 161.

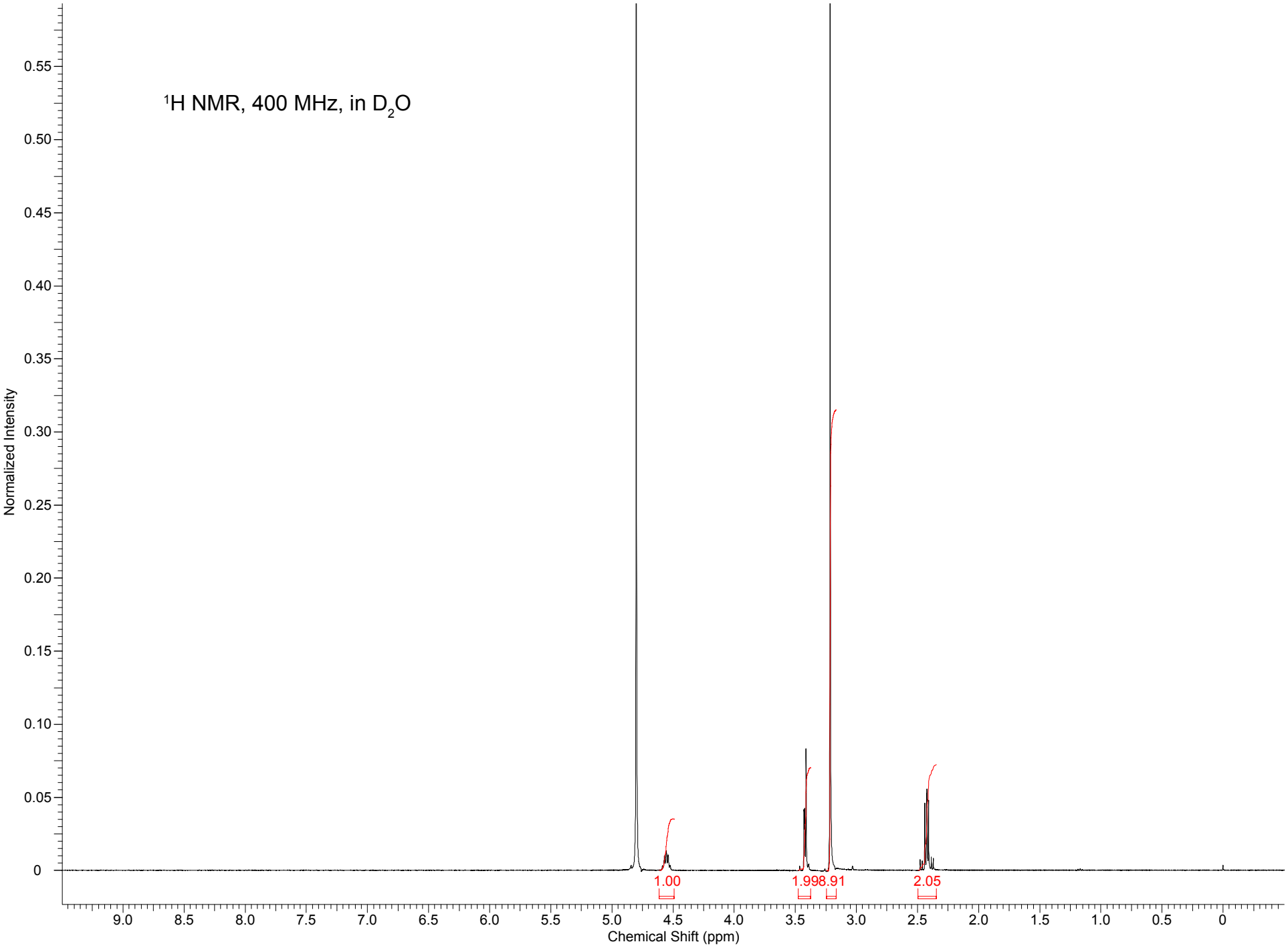
   a. Hydrophilic neurotransmitters are commonly zwitterionic, and often contain cationic trimethylammonium and anionic carboxylate groups. Are the NMR spectra consistent with the presence of those groups?

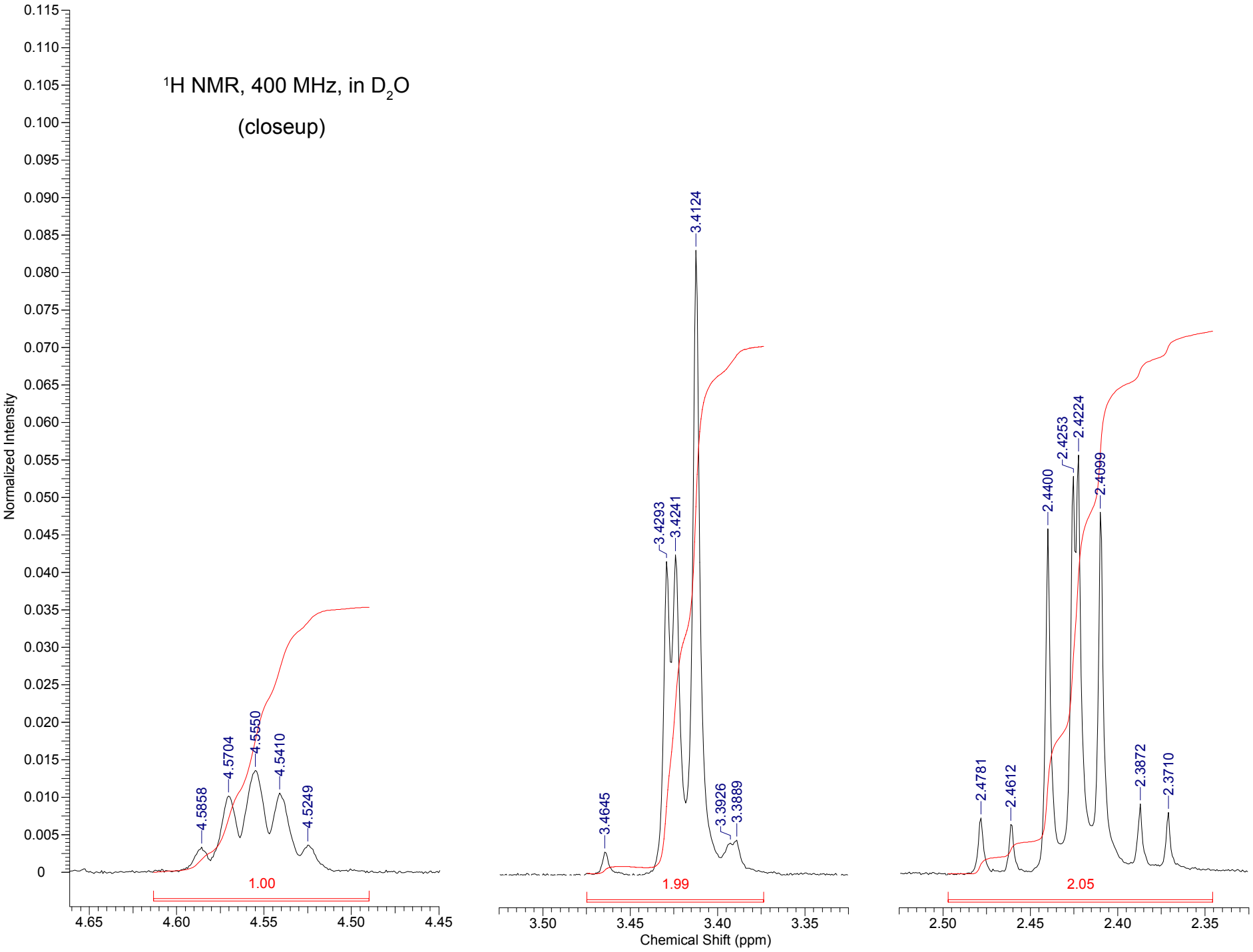


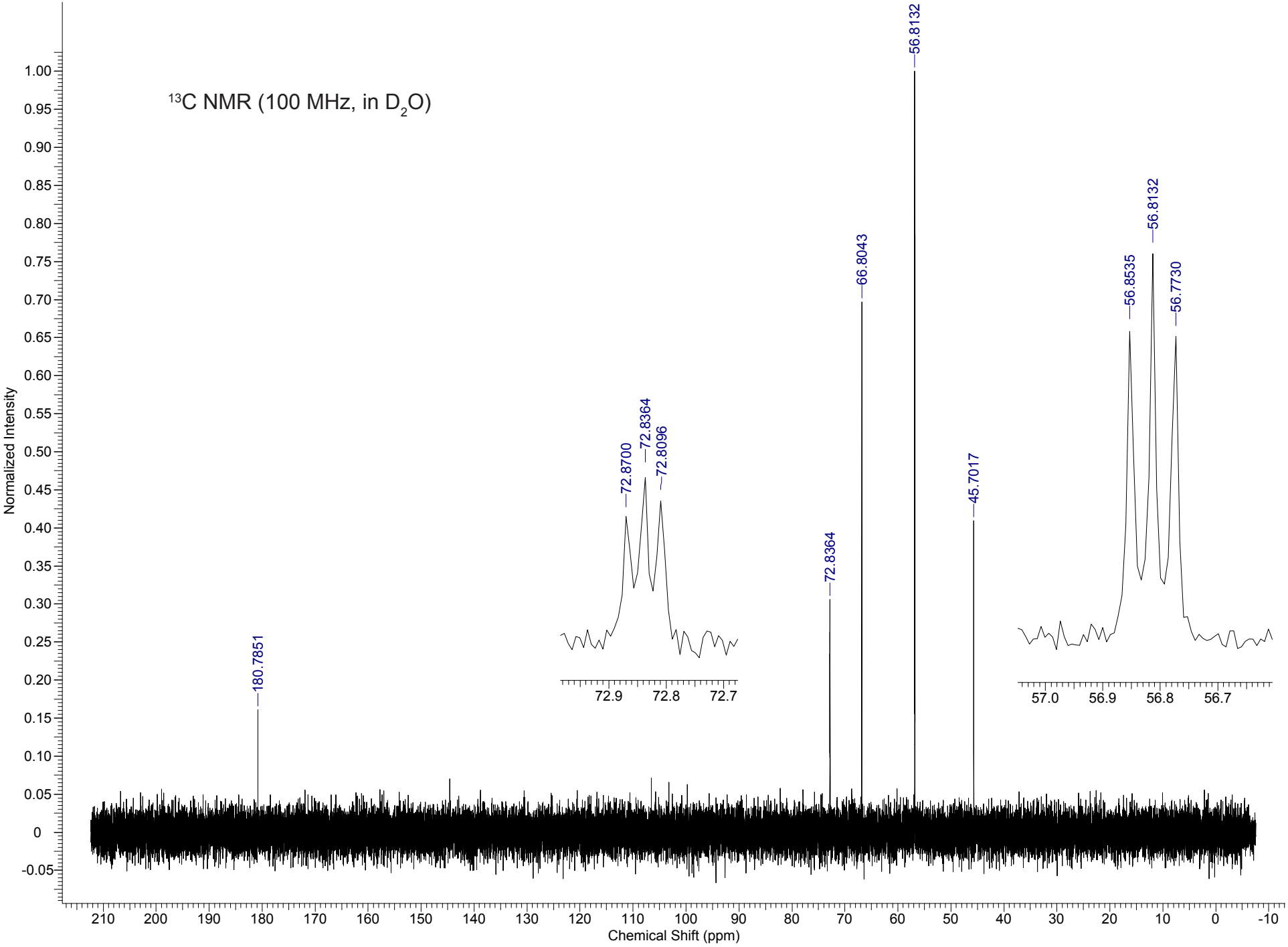
   b. What is the structure of the neurotransmitter?

   c. The ^{1}H NMR spectrum contains some complex splitting patterns, indicating that chemical shift differences and coupling constants are of comparable magnitude (i.e., that $\Delta\nu/J$ is small). How would you describe the spin system in this molecule in letter notation? (For example, we discussed an AA'BB' system in class. What letters would you use for this molecule?)

   d. Two of the five ^{13}C resonances are split into multiplets, and three are not. Why?


^{1}H NMR, 400 MHz, in D_2O
Normalized Intensity
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
1.00
1.99
8.91
2.05
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)


^{1}H NMR, 400 MHz, in D_2O
(closeup)
Normalized Intensity
Chemical Shift (ppm)
4.5858
4.5704
4.5550
4.5410
4.5249
1.00
3.4645
3.4293
3.4241
3.4124
3.3926
3.3889
1.99
2.4781
2.4612
2.4400
2.4253
2.4224
2.4099
2.3872
2.3710
2.05


^{13}C NMR (100 MHz, in D_2O)
Normalized Intensity
Chemical Shift (ppm)
180.7851
72.8700
72.8364
72.8096
72.8364
66.8043
56.8132
45.7017
56.8535
56.8132
56.7730