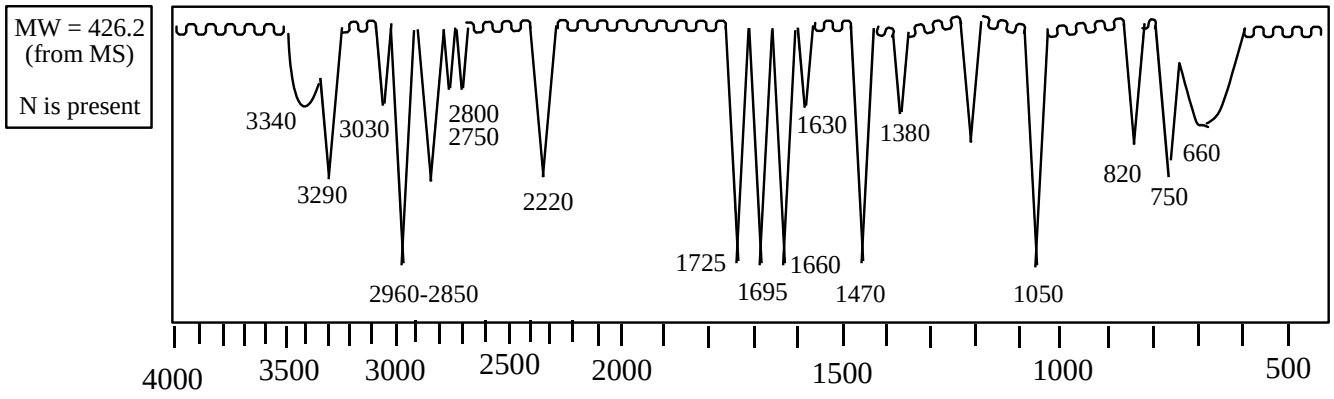
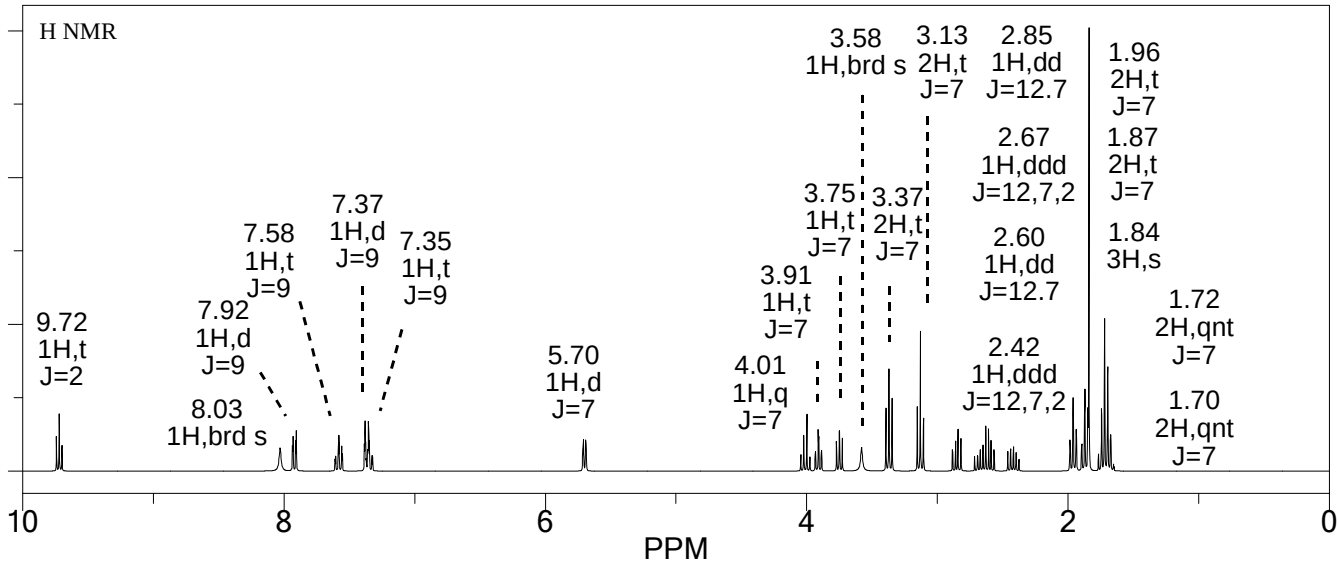
Chem 318/319 Name_____
Beauchamp

Problem 101 - Predict a reasonable structure from the spectral information provided below. As much as possible match the spectral information to the part of the structure that it explains. Show all of your work**.**

IR Spectrum: Interpret as fully as possible from structure. Not every peak is interpretable. (units = cm^{-1})

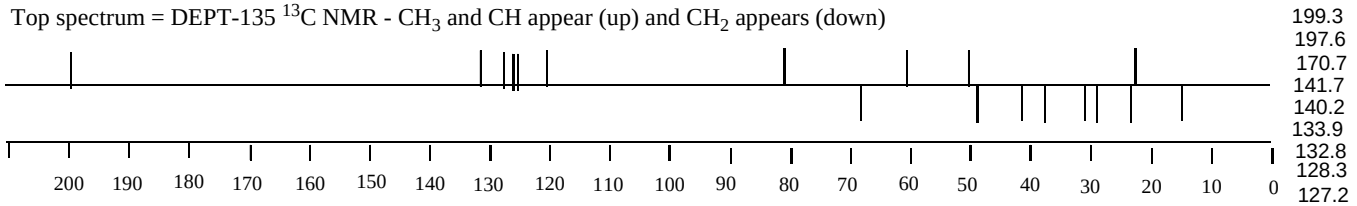


Proton NMR: interpret data (when in doubt calculate chemical shifts to confirm they match actual values, N = # neighbors)

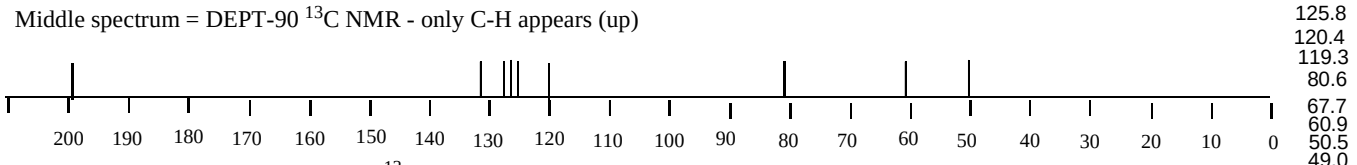


^{13}C and DEPT NMR: As much as possible match the ^{13}C peaks to carbons in your structure.

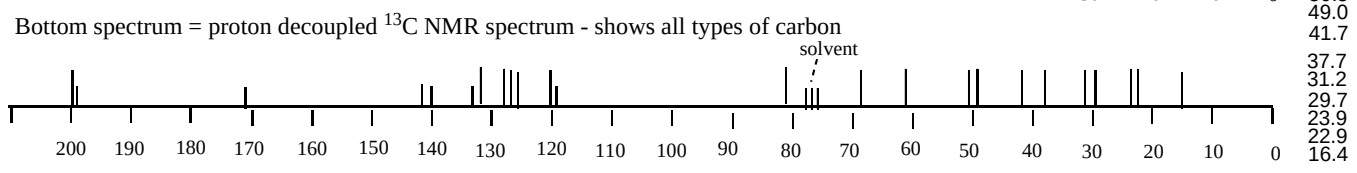
Top spectrum = DEPT-135 ^{13}C NMR - CH_3 and CH appear (up) and CH_2 appears (down)

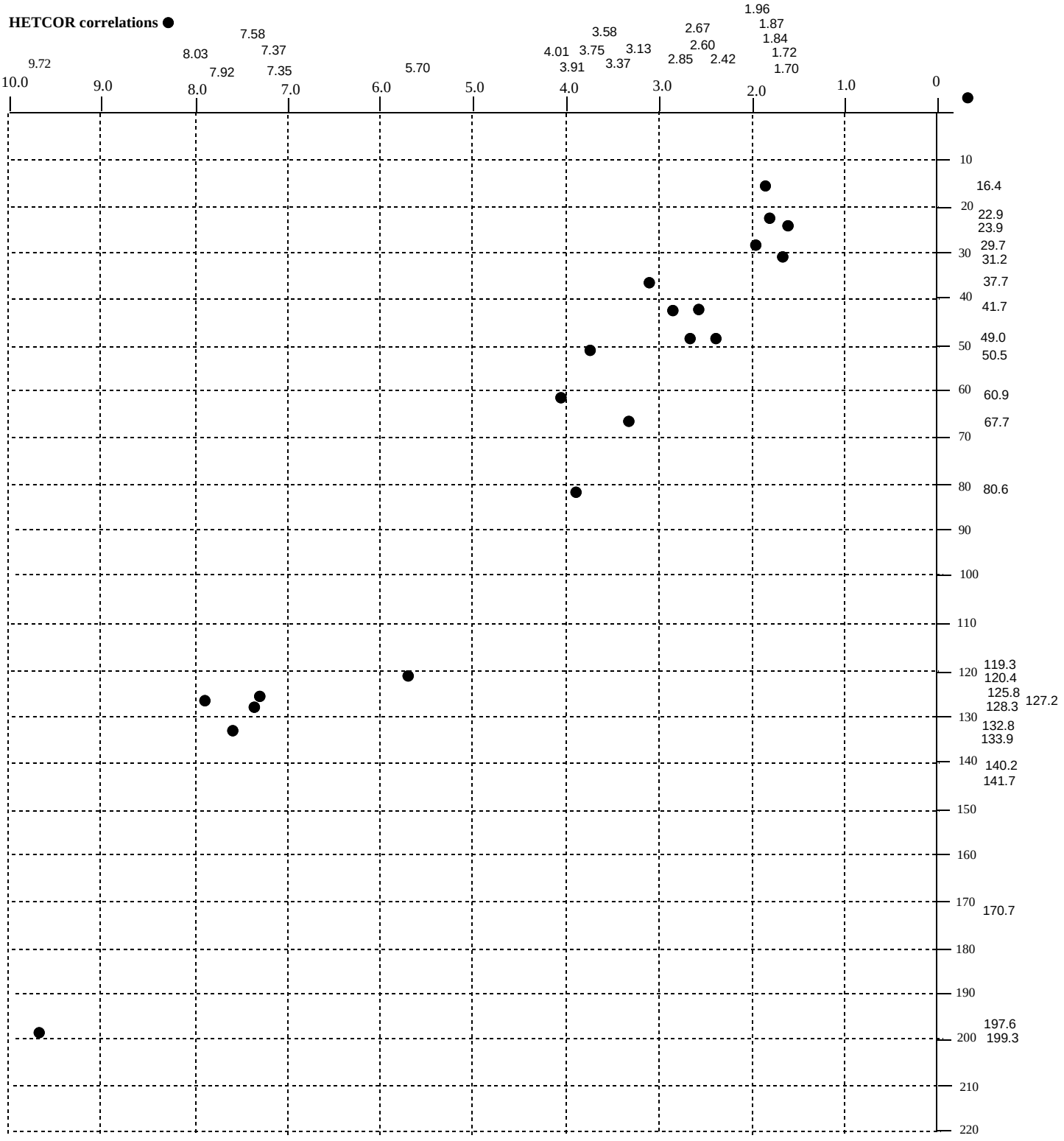


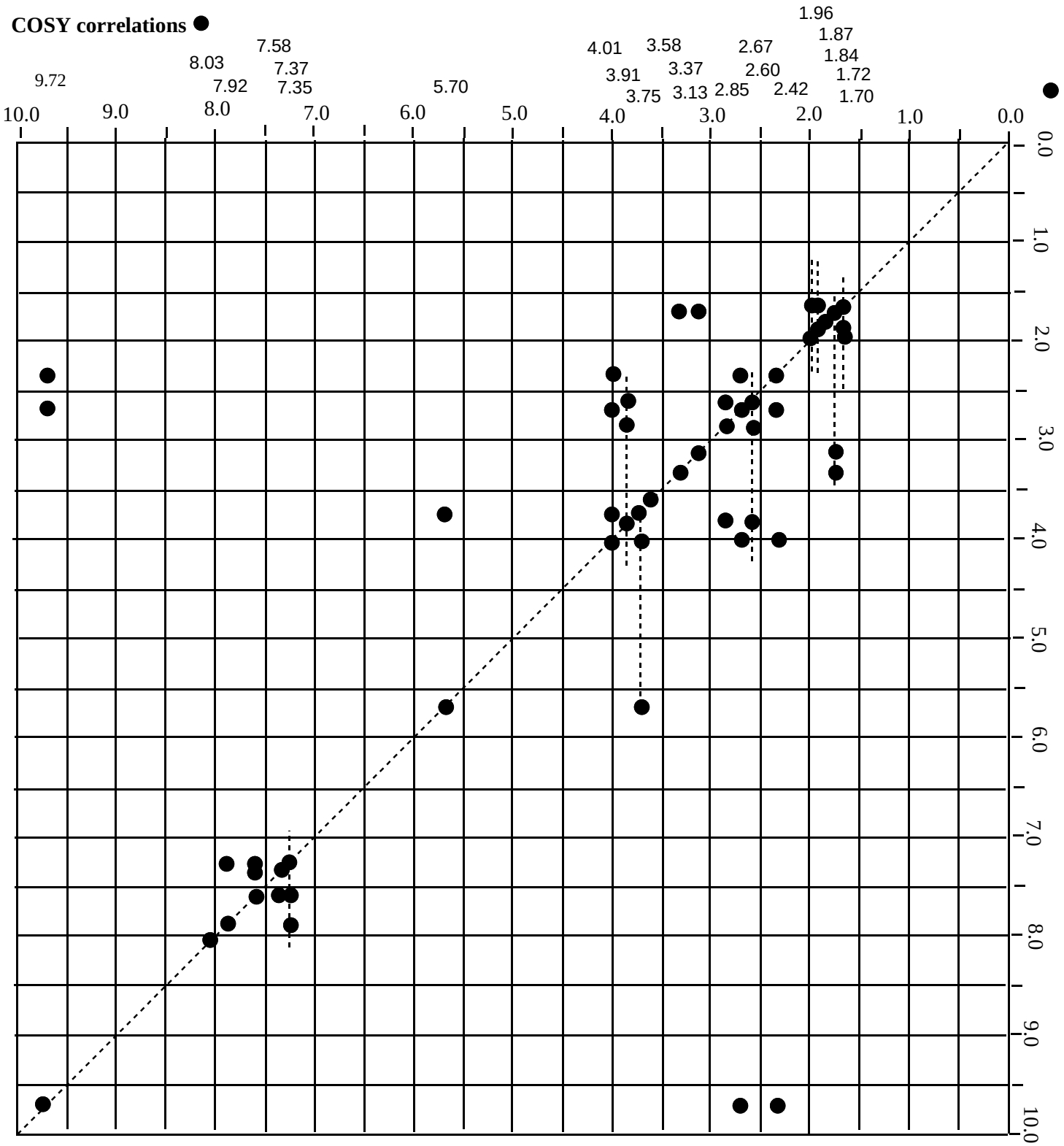
Middle spectrum = DEPT-90 ^{13}C NMR - only C-H appears (up)



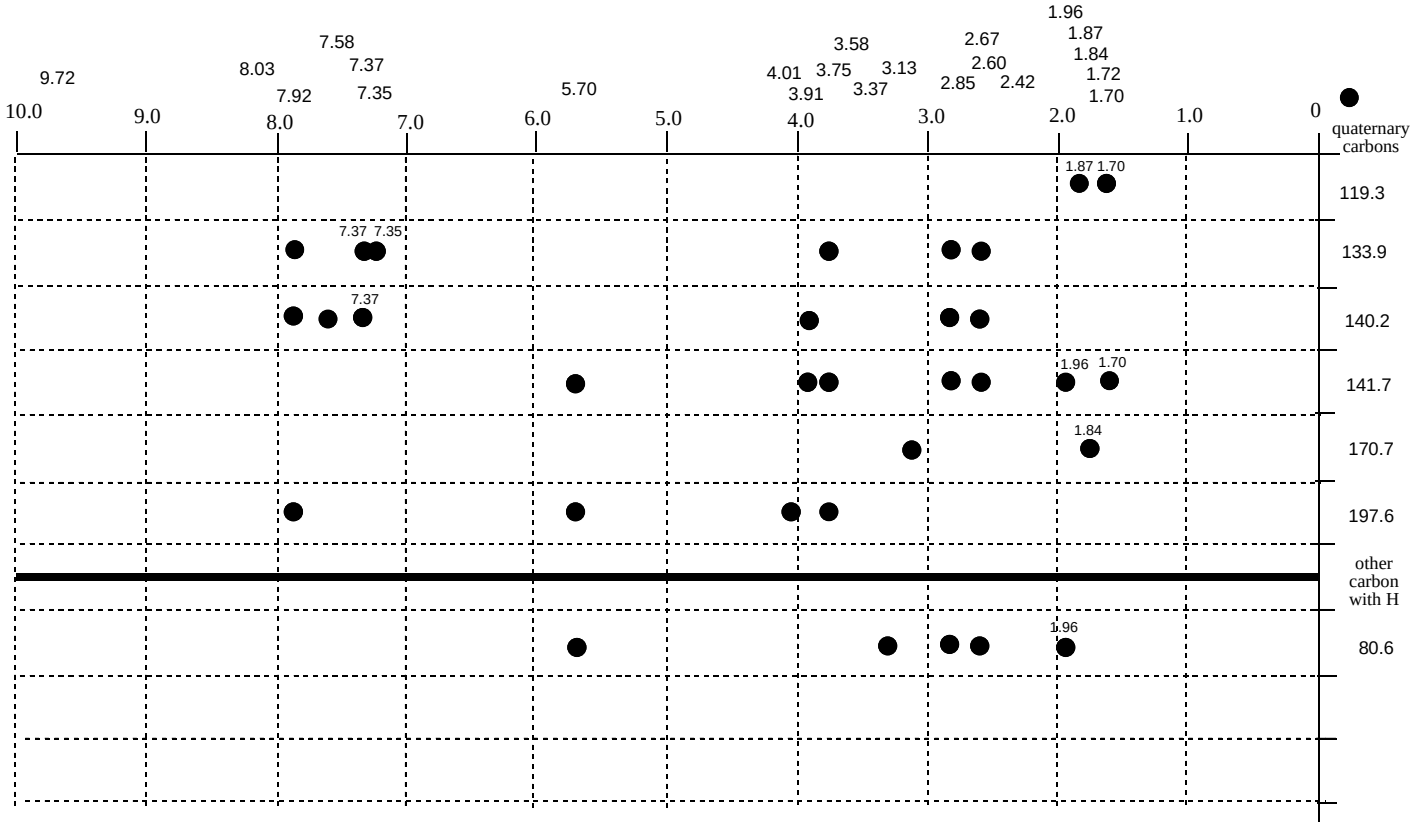
Bottom spectrum = proton decoupled ^{13}C NMR spectrum - shows all types of carbon




HETCOR correlations
9.72
10.0
9.0
8.03
7.92
8.0
7.58
7.37
7.35
7.0
5.70
6.0
5.0
4.01
3.91
3.75
3.58
3.37
3.13
4.0
3.0
2.67
2.60
2.85
2.42
1.96
1.87
1.84
1.72
1.70
2.0
1.0
0
10
16.4
20
22.9
23.9
30
29.7
31.2
37.7
40
41.7
49.0
50
50.5
60
60.9
67.7
70
80
80.6
90
100
110
119.3
120
120.4
125.8
128.3
127.2
130
132.8
133.9
140
140.2
141.7
150
160
170
170.7
180
190
197.6
200
199.3
210
220


COSY correlations
9.72
8.03
7.92
7.58
7.37
7.35
5.70
4.01
3.91
3.75
3.58
3.37
3.13
2.67
2.60
2.85
2.42
1.96
1.87
1.84
1.72
1.70
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

HMBC Correlations for quaternary carbons (mainly, and selected other carbon atoms with protons)

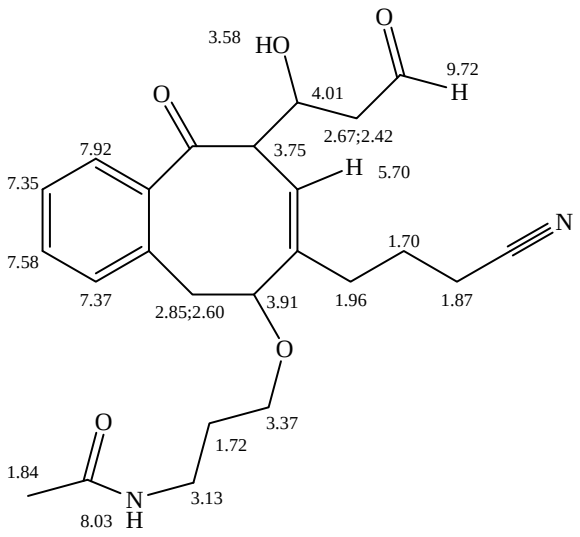


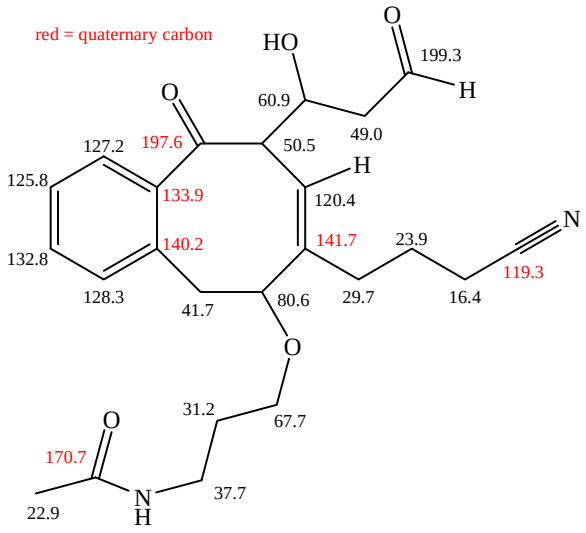
Possible approach for solving a structure problem:

1. Count the number of protons and carbons from the 1D NMR spectra and calculate the C,H mass.
2. Subtract the C,H mass from the molecular weight and estimate the number of N and O (other possibilities include sulfur and halogens). Look for clues for these atoms in the other spectra (IR, H-NMR, C-NMR).
3. Calculate the degrees of unsaturation from the molecular formula (total pi bonds and rings) and subtract the number of pi bonds estimated from the C-NMR (look for supporting evidence in the IR and H-NMR). The difference should be the number of rings in the structure.
4. Tabulate and identify each carbon type using the DEPT. Recheck the number of protons and carbon atoms using the DEPT. Any protons on oxygen or nitrogen will not show up in the DEPT and this may provide clues about O-H and N-H bonds. Look for supporting evidence in the IR and H-NMR spectra.
5. Use the HETCOR to identify which protons are on which carbons. This couples the proton and carbon shifts that are directly attached through one bond ($^1J_{CH}$). Look for diastereotopic CH_2 (two peaks).
6. Use the COSY to generate paths of connectivity (also called "spin systems"). Connects CH pairings from 5.
7. Use the HMBC to connect the COSY spin systems through any quaternary centers (carbons without any protons) and heteroatoms (N, O and S).
8. Double check your structure for chemical shifts and multiplicities in the ^1H and ^{13}C NMRs and functional groups showing in the IR.

Chemical Formula: $C_{24}H_{30}N_2O_5$
Exact Mass: 426.22
Molecular Weight: 426.51
Elemental Analysis: C, 67.59; H, 7.09; N, 6.57; O, 18.76

proton shifts: 9.72, 7.92, 7.58, 7.37, 7.35, 5.70, 4.01, 3.91, 3.75, 3.37, 3.13, 2.85;2.60, 2.67;2.42, 1.96, 1.87, 1.84, 1.72, 1.70





carbon shifts: 199.3, 197.6, 170.7, 141.7, 140.2, 133.9, 132.8, 128.3, 127.2, 125.8, 120.4, 119.3, 80.6, 67.7, 60.9, 50.5, 49.0, 41.7, 37.7, 31.2, 29.7, 23.9, 22.9, 16.4

	^{13}C	DEPT	HETCOR	COSY	HMBC
9.72	199.3	H-C=O	9.72	2.67;2.42	
	197.6	C=O	none		7.92 5.70 4.01 3.75
7.92	170.7	N-C=O	none		3.13 1.84
	141.7	=C	none		5.70 3.91 3.75 2.85;2.60 1.96 1.70
7.37	140.2	=C	none		7.92 7.58 7.37 3.91 2.85;2.60
7.35	133.9	=C	none		7.92 7.37 7.35 3.75 2.85;2.60
5.70	132.8	=C-H	7.58	7.37 7.35	
	128.3	=C-H	7.37	7.58	
4.01	127.2	=C-H	7.92	7.35	
3.91	125.8	=C-H	7.35	7.92 7.58	
3.75	120.4	=C-H	5.70	3.75	
3.37	119.3	-CN	none		1.87 1.70
3.13	80.6	CH-O	3.91	2.85;2.60	5.70 3.37 2.85;2.60 1.96
2.85;2.60	67.7	CH_2-O	3.37	1.72	
2.67;2.42	60.9	CH-O	4.01	3.75 2.67;2.42	
1.96	50.5	CH	3.75	5.70 4.01	
1.87	49.0	CH_2	2.67;2.42	9.72 4.01	
1.84	41.7	CH_2	2.85;2.60	3.91	
1.72	37.7	CH_2-N	3.13	1.72	
1.70	31.2	CH_2	1.72	3.13	
	29.7	CH_2	1.96	1.70	
	23.9	CH_2	1.70	1.96 1.87	
	22.9	CH_3	1.84		
	16.4	CH_2	1.87	1.70	
Total =	24 C	28 H			8.03 3.58 (H not on carbon)

various pieces: none, C=O, H-C=O, O-C=O, =C-O, =C, =C-H, -CN, ≡C—, CH-O, CH_2-O, CH_3-O, CH-Br, CH-N, CH_3-N, CH, CH_2, CH_3

Possible approach (there are many details, look for errors I might have made)

pieces from COSY and HETCOR