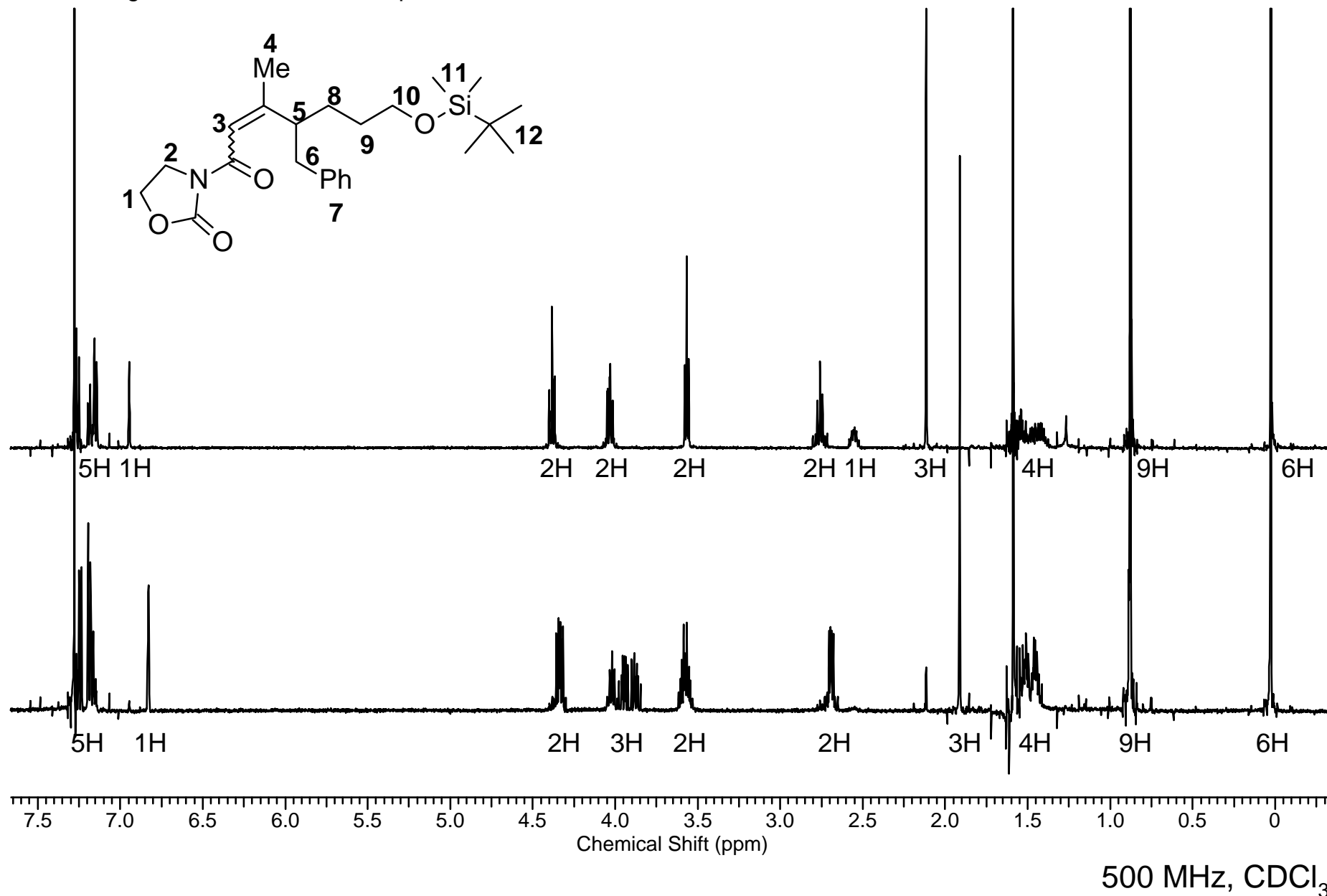


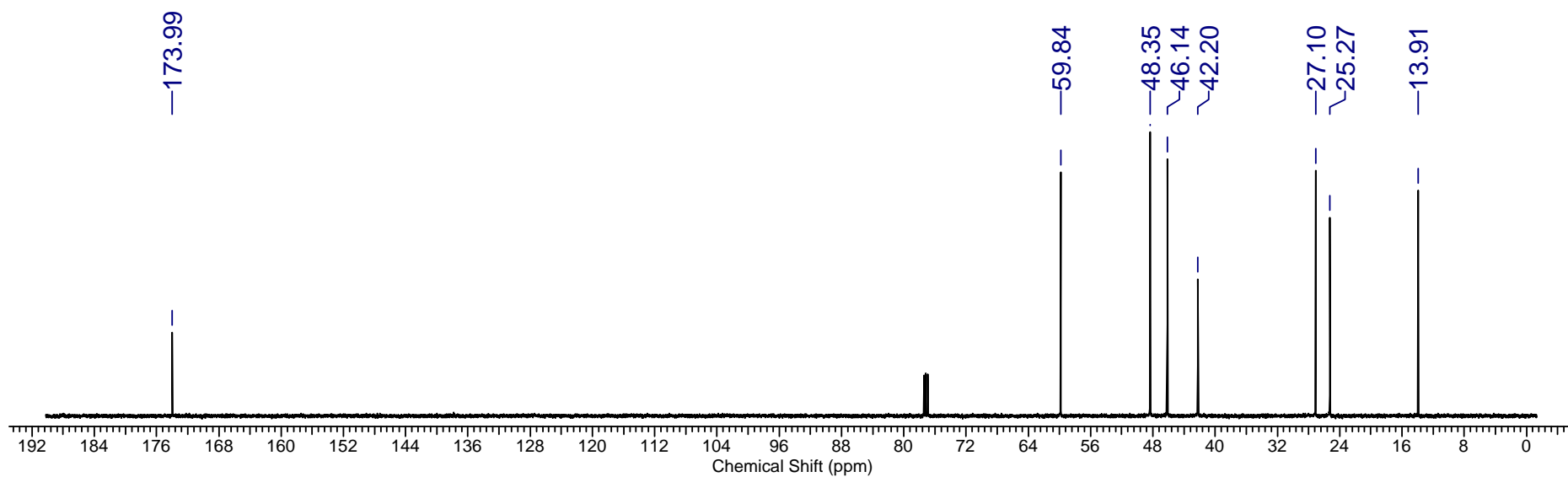
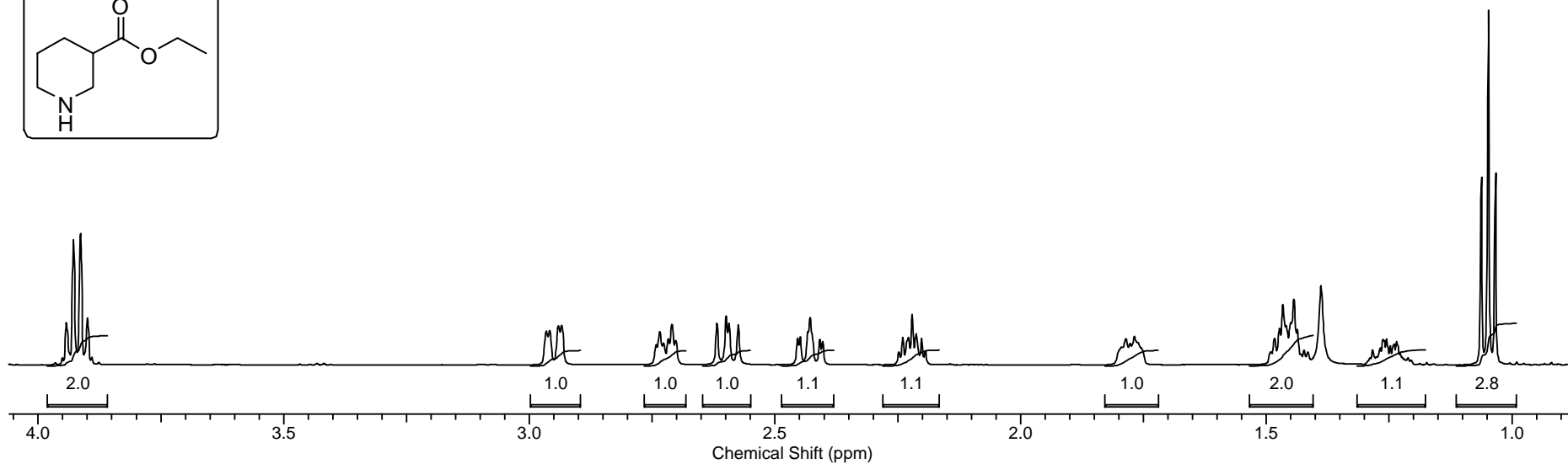
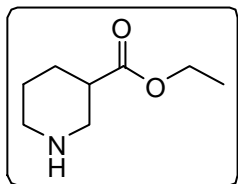
**Problem 1**

The addition of lithium dimethylcuprate to an alkyne produced a mixture of *E* and *Z* isomers which were separated by HPLC. Please assign the resonances in the spectra below and determine which isomer is which.



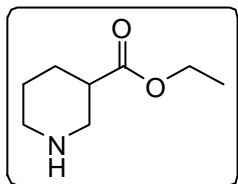
**Problem 2**

Please assign the proton and carbon resonances of ethyl nipecotate. (500 MHz,  $\text{CDCl}_3$ ; spectra are courtesy of Dr. Jeffrey Simpson, MIT. See Simpson, Chapter 9 for his treatment of this problem.)



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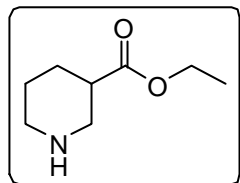


ID	$\delta$ ( $^1\text{H}$ )	$\delta$ ( $^{13}\text{C}$ )	He	Type	J (Hz)	COSY
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						

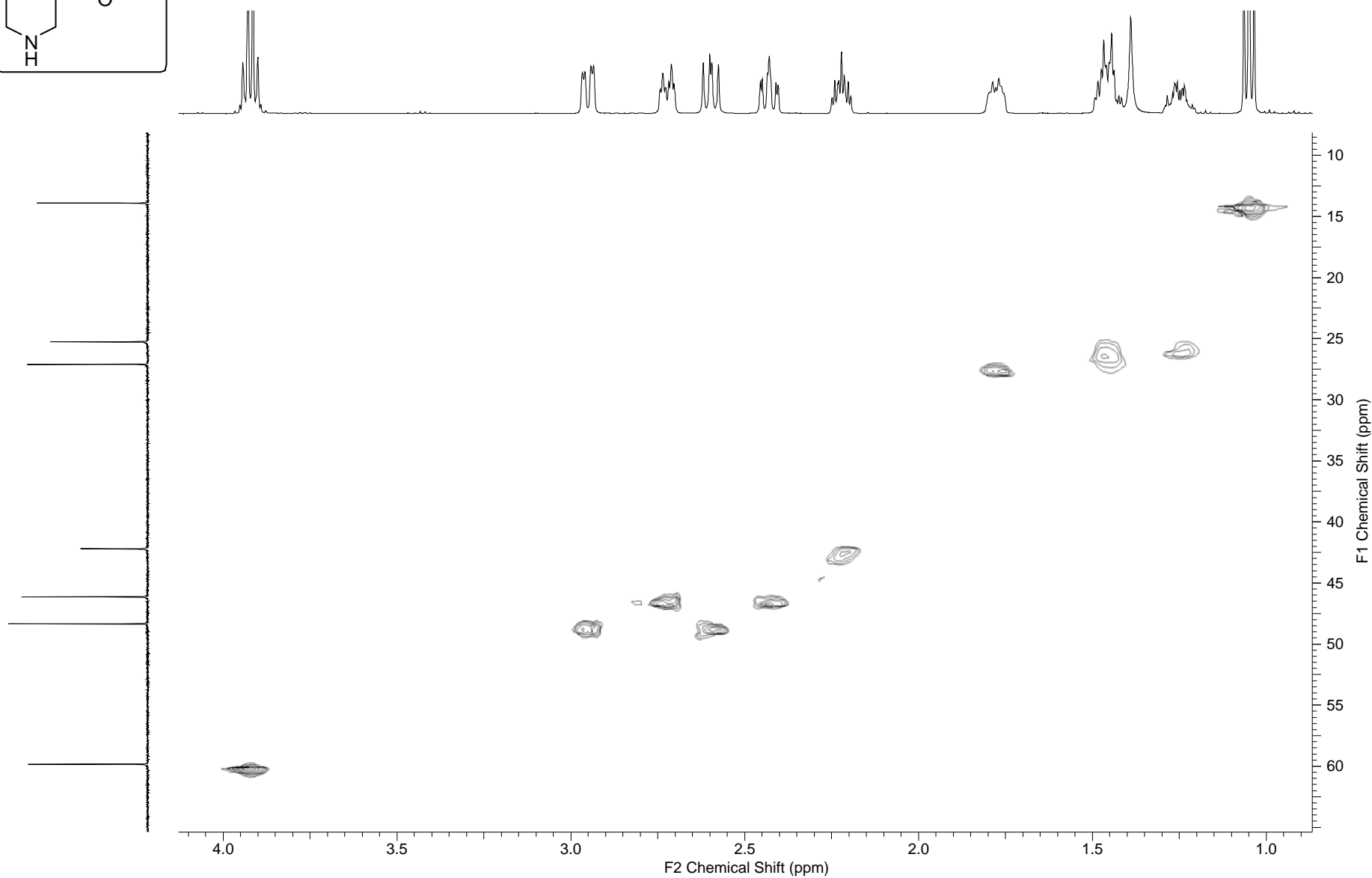
**Quaternary Carbons:**

**Methylene Pairs:**

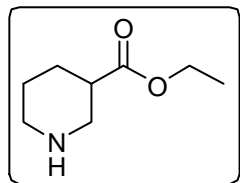
## Problem 2



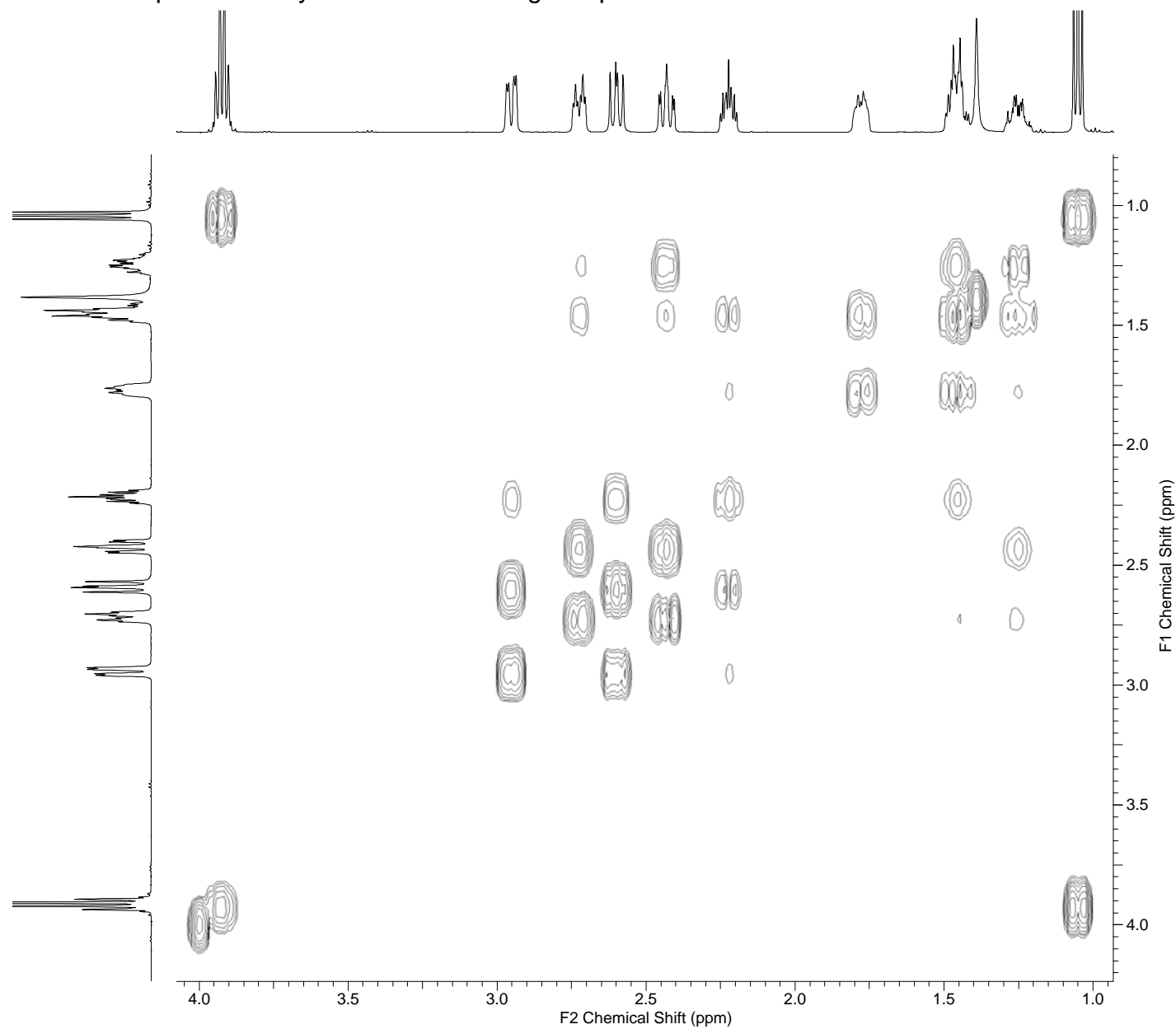
This is the HMQC spectrum. Please number the protons. What are the methylene pairs in this molecule? Are there any quaternary carbons?

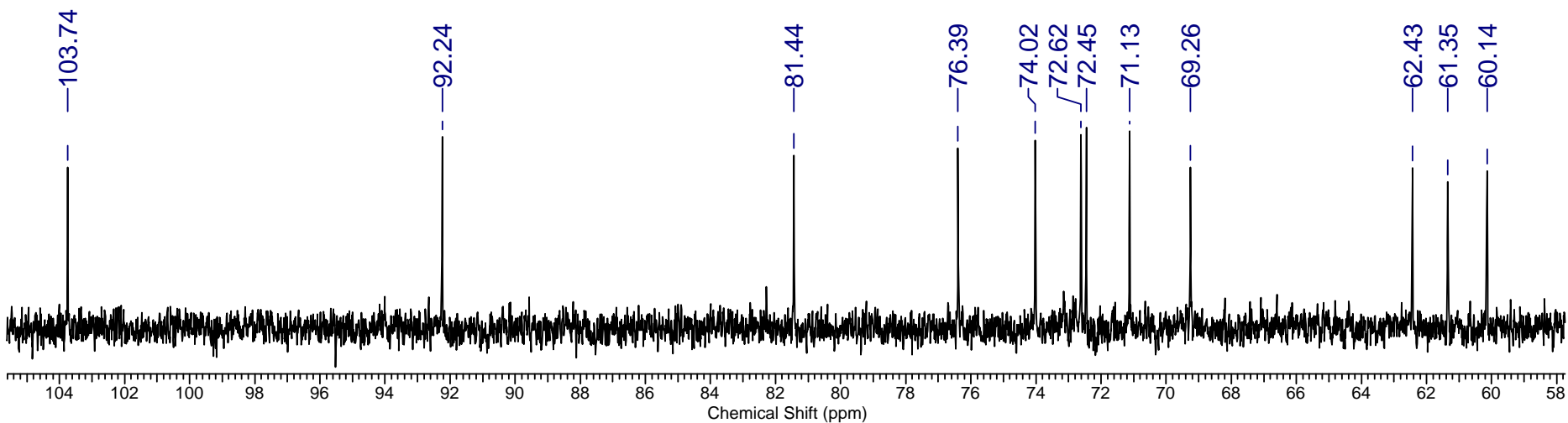
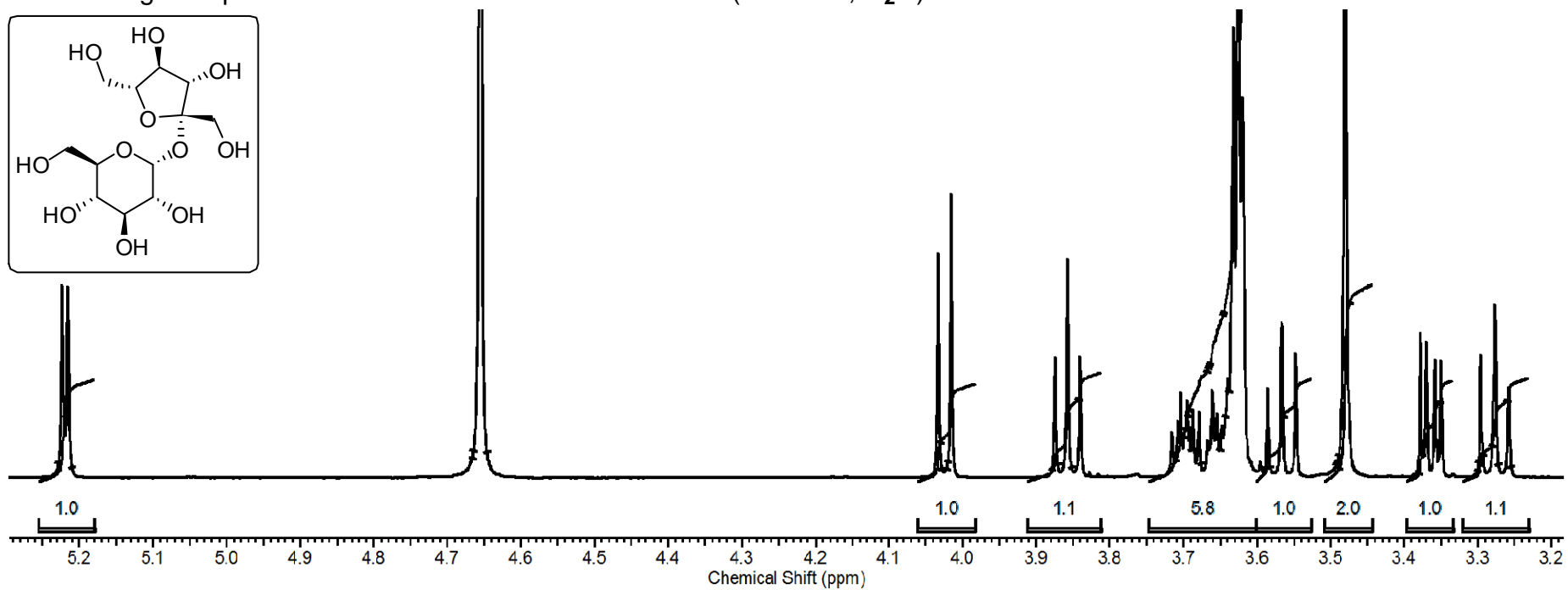
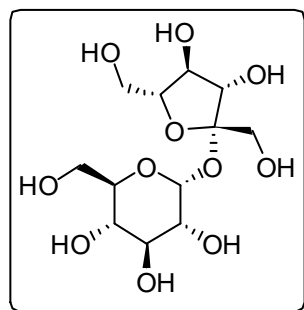


## Problem 2



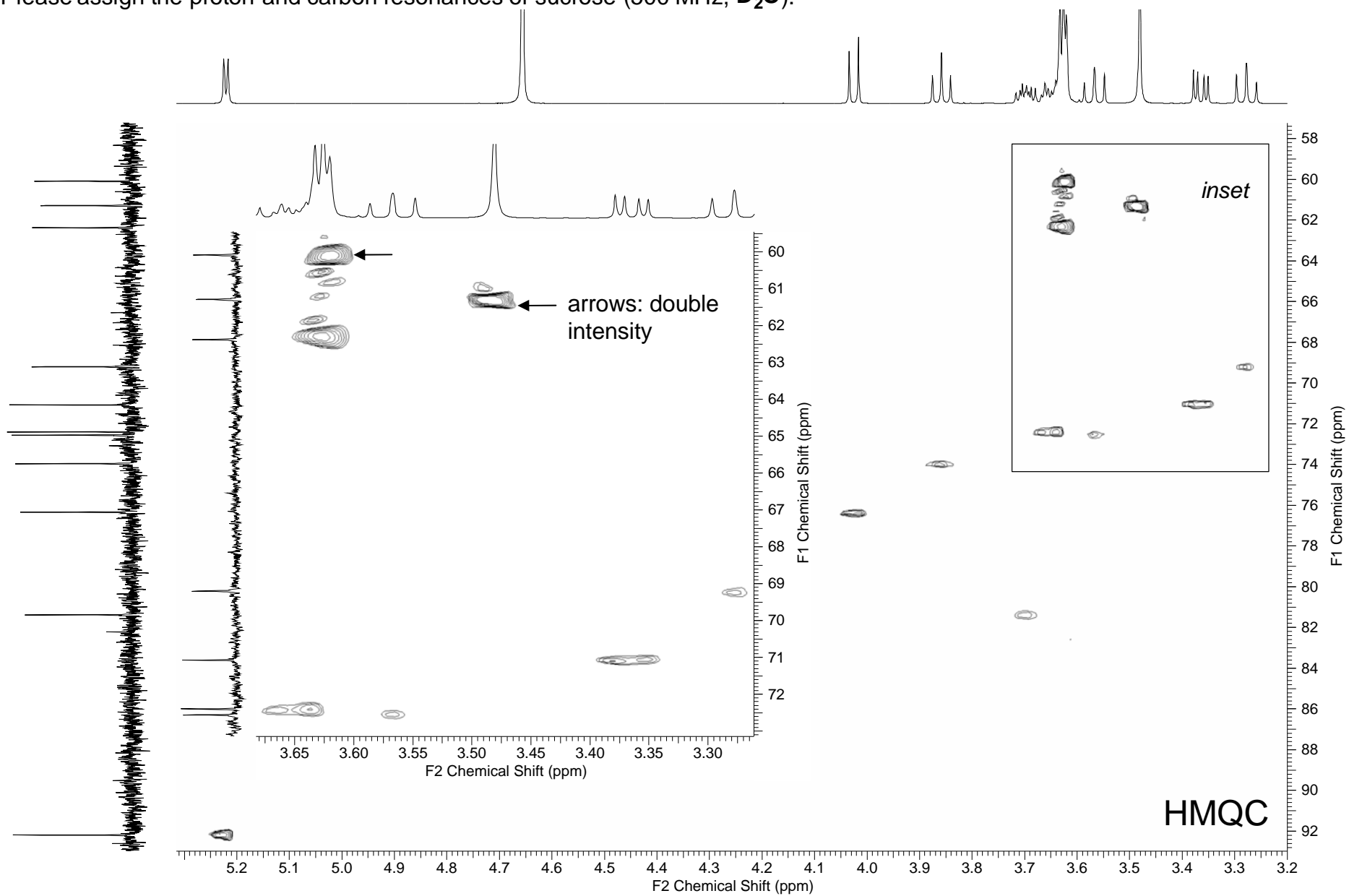
This is the COSY spectrum. Try to label the off-diagonal peaks.



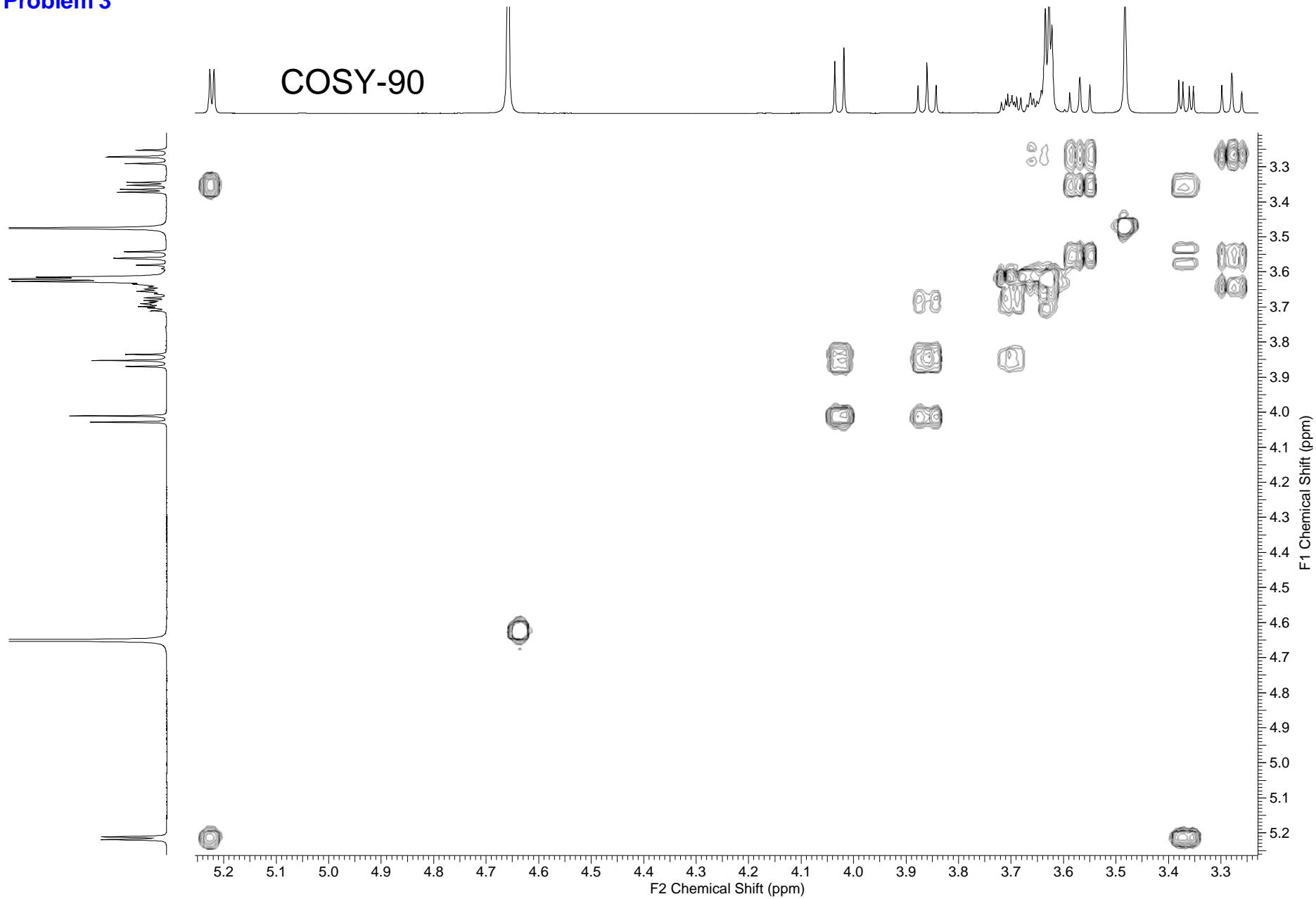
**Problem 3**Please assign the proton and carbon resonances of sucrose (500 MHz,  $D_2O$ ).

## Problem 3

Please assign the proton and carbon resonances of sucrose (500 MHz,  $D_2O$ ).



## Problem 3





**Problem 3**

Here's some space for your data table:

ID	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$	He	Type	J (Hz)	COSY
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						

**Quaternary Carbons:**

**Methylene Pairs:**

**Problem 4**

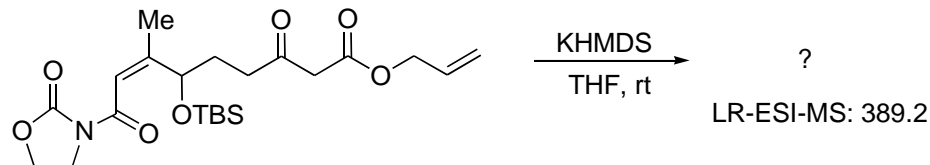
An unknown compound of molecular weight 348 has the spectral data shown below. A singlet near 3.2 ppm disappears on D<sub>2</sub>O addition. Please deduce its molecular formula, skeletal connectivity, assignments, and relative stereochemistry (show key ROESY correlations).

ID	$\delta$ ( <sup>1</sup> H)	$\delta$ ( <sup>13</sup> C)	Hs	Type	J (Hz)	COSY	Key HMBC	Key ROESY
1	5.20	73.1	1	t	9.5x2	3, 2	170.4	4, 7
2	5.08	68.7	1	t	9.5x2	1, 7	169.6	3
3	4.96	71.6	1	dd	9.5, 8.0	4, 1	169.4	2
4	4.59	99.8	1	d	8.0	3		1, 7
5	4.26	62.3	1	dd	12.3, 4.9	6, 7	170.8	7
6	4.11	62.3	1	dd	12.3, 2.5	5, 7	170.8	7
7	3.68	71.8	1	m	--	2, 5, 6		1, 4, 5, 6
8	~3.2	--	1	br s	--	--		
9	2.08	20.95	3	s	--	--	170.8	
10	2.05	20.90	3	s	--	--	169.4	
11	2.02	20.79	3	s	--	--	169.6	
12	2.00	20.83	3	s	--	--	170.4	

Quaternary Carbons: 170.8, 170.4, 169.6, 169.4

Molecular formula: \_\_\_\_\_

## Problem 5



Please deduce the structure and relative stereochemistry of the product.

NMR Data (500 MHz, 45% CDCl<sub>3</sub> in C<sub>6</sub>D<sub>6</sub>)

ID	$\delta$ ( <sup>1</sup> H)	$\delta$ ( <sup>13</sup> C)	Hs	Type	J (Hz)	COSY-45	Key HMBC	NOE
1	5.66	131.5	1	m	--	2, 3, 4		
2	5.13	119.0	1	dd	17.1, 1.5	1, 3, 4		
3	5.02	119.0	1	dd	10.5, 1.2	1, 2		
4	4.39	66.1	2	m	--	1, 2	119.0, 131.5, 168.2	
5	3.80	56.6	1	d	2.4	10	41.3, 43.9, 71.2, 168.2, 200.5	11
6	3.61	71.2	1	dd	9.0, 3.2	9, 11	56.6	10
7	3.10	63.2	1	t	2.9x2	9, 11	71.2, 200.5, 203.4	
8	2.81	43.9	1	d	19.5	10	20.5, 41.3, 56.6, 203.4	
9	1.94	34.2	1	ddd	14.6, 9.3, 2.9	6, 7, 11	63.2, 200.5	
10	1.76	43.9	1	dd	19.5, 2.0	5, 8	20.5, 41.3, 56.6, 71.2, 203.4	6
11	1.52	34.2	1	dt	14.6, 2.9x2	6, 7, 9	71.2, 203.4	5
12	0.94	20.5	3	s	--	--	41.3, 43.9, 56.6, 71.2	
13	0.81	25.9	9	s	--	--	25.7	
14	-0.10	-4.5	6	d	--	--	--	

Quaternary Carbons: 200.5, 203.4, 168.2, 41.3, 25.7; IR: three carbonyls present