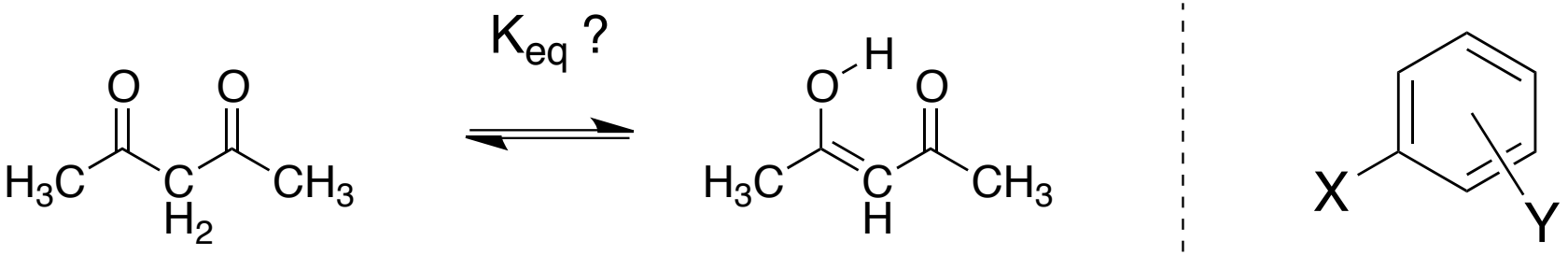
REPORT 2 DUE FRIDAY (MARCH 9) AT 12 NOON

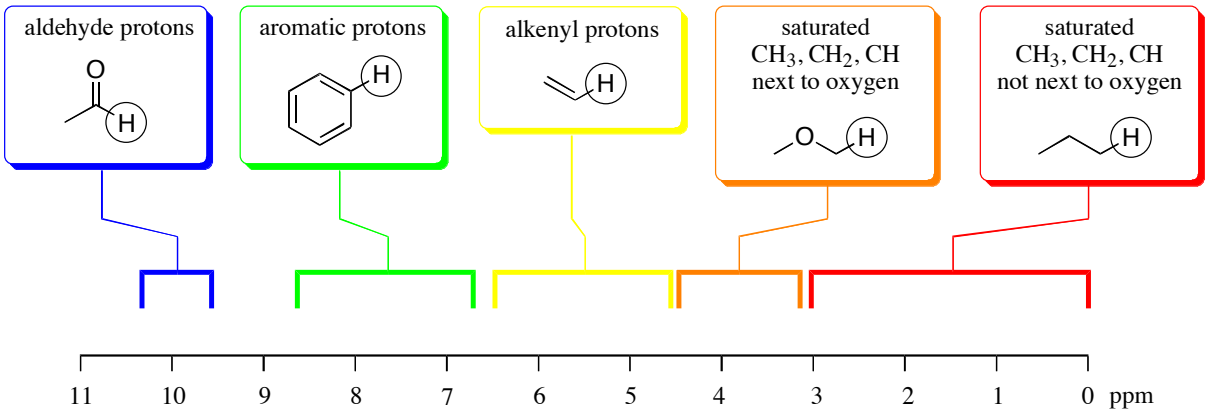
CH362/362H
Week 9 Lecture
Structure Elucidation Strategy
(2-Dimensional NMR)

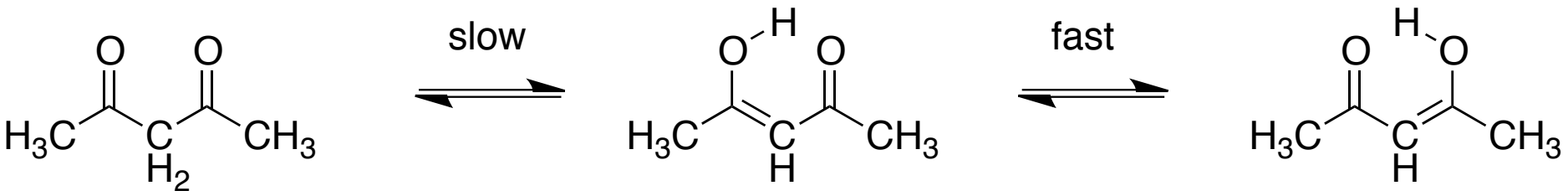


keto tautomer

enol tautomer

?

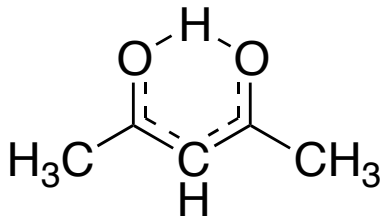




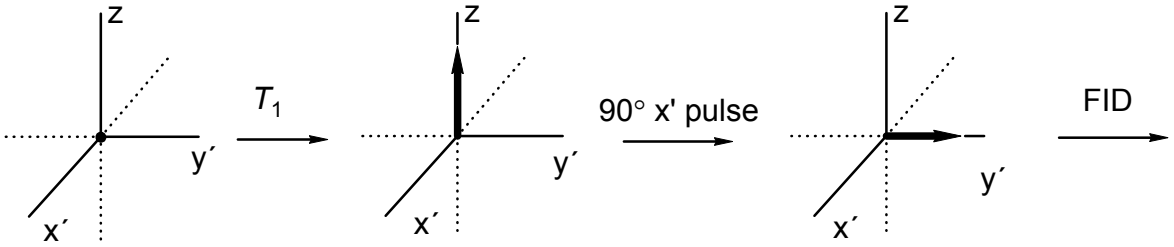
keto tautomer

enol tautomer 1

enol tautomer 1



on NMR time scale

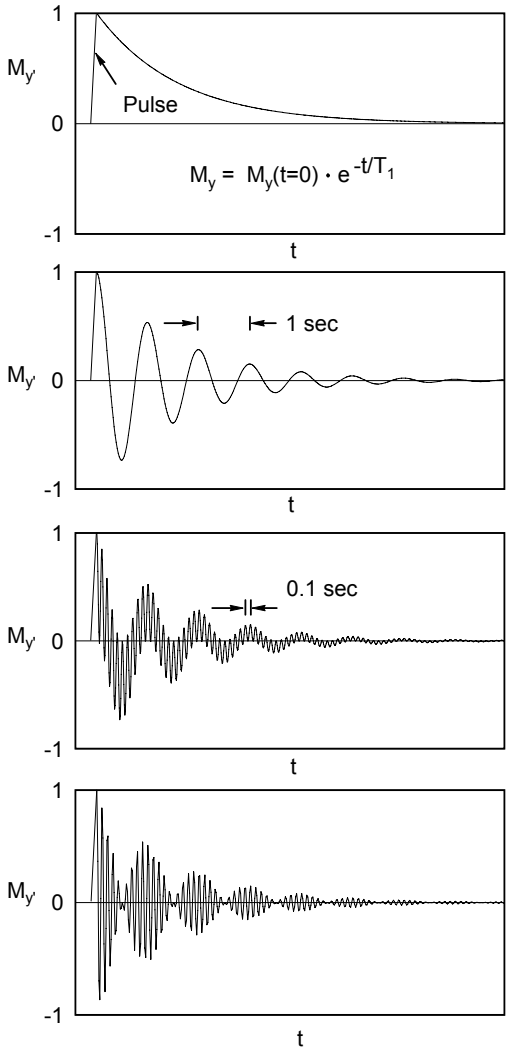


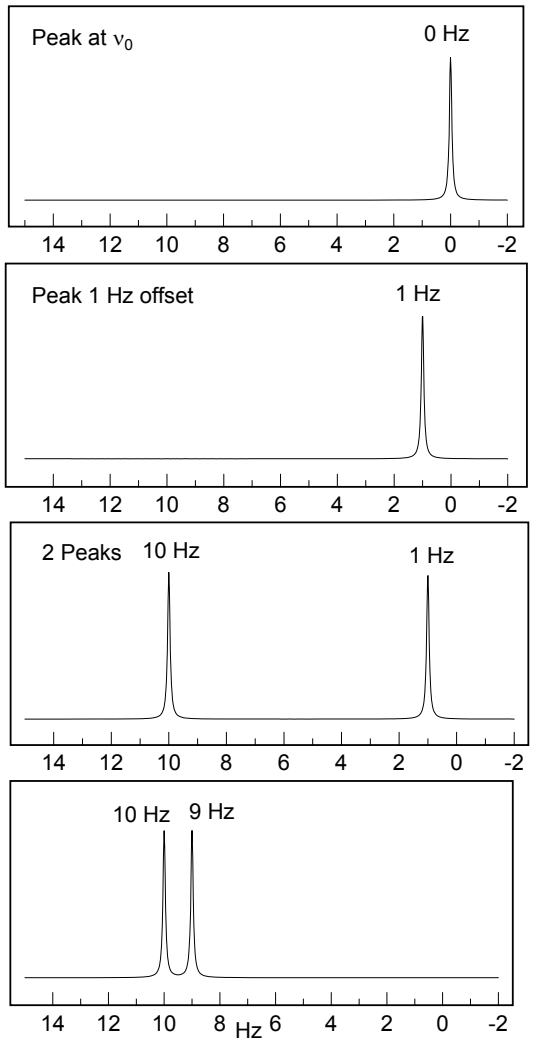
No magnet.

Magnet

Free Induction Decay

Spectrum





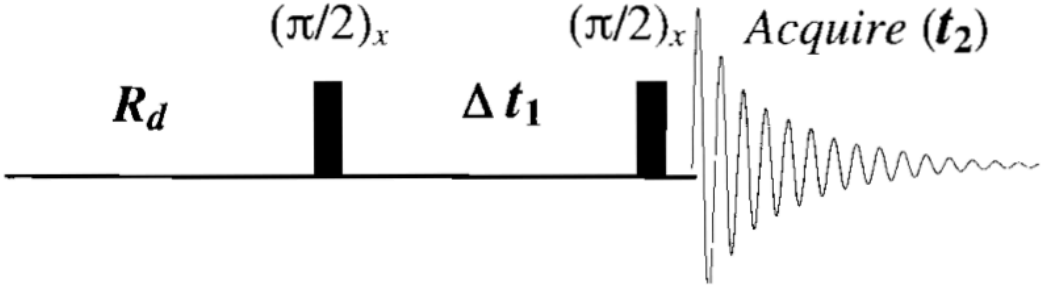
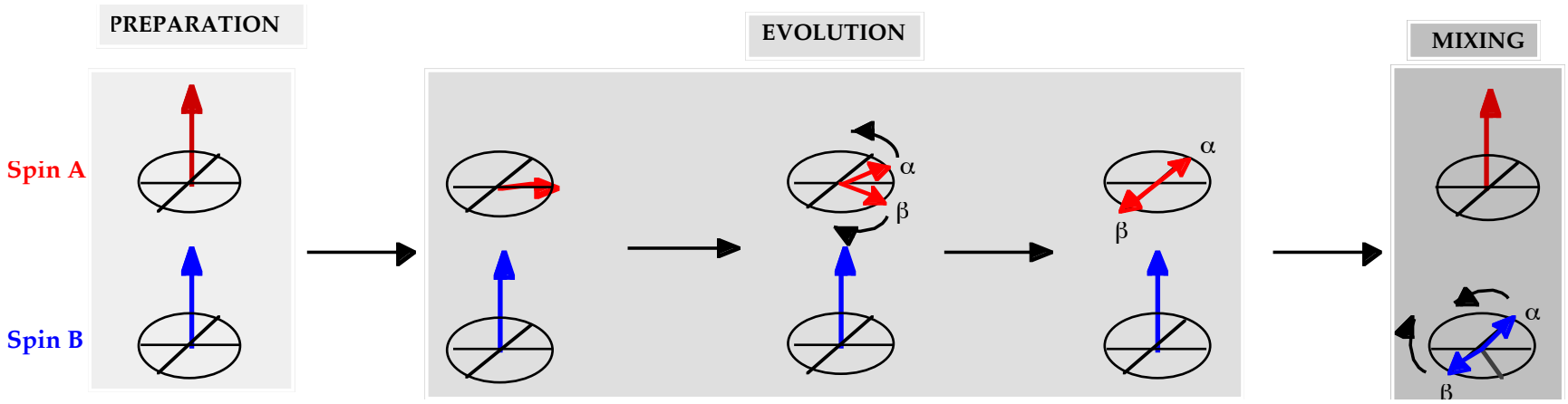


FIGURE 5.3 Prototype pulse sequence for a 2-D NMR. The incremental delay, Δt_1, and the acquisition time, t_2, are Fourier transformed into frequencies, ν_2 and ν_1, respectively. $(\pi/2)_x$ represents a 90° pulse along the x axis. The interval t_1 is of the order of microseconds; t_2 is of the order of seconds.

1. Preparation: Excite nucleus A, creating magnetization in the x-y plane
2. Evolution: Measure the chemical shift of nucleus A.
3. Mixing: Transfer magnetization from nucleus A to nucleus B (*via J or NOE*).
4. Detection: Measure the chemical shift of nucleus B.



stacked plot of acetone

Interferogram (eg 1024, for each column)
Time-domain spectrum, as function of t1
(data constructed point by point)

=> F1 axis of 2D NMR
VERSUS
FID, function of t2
(data obtained in real time)

Second FT on each of the
Interferograms

=> F2 axis of 2D NMR

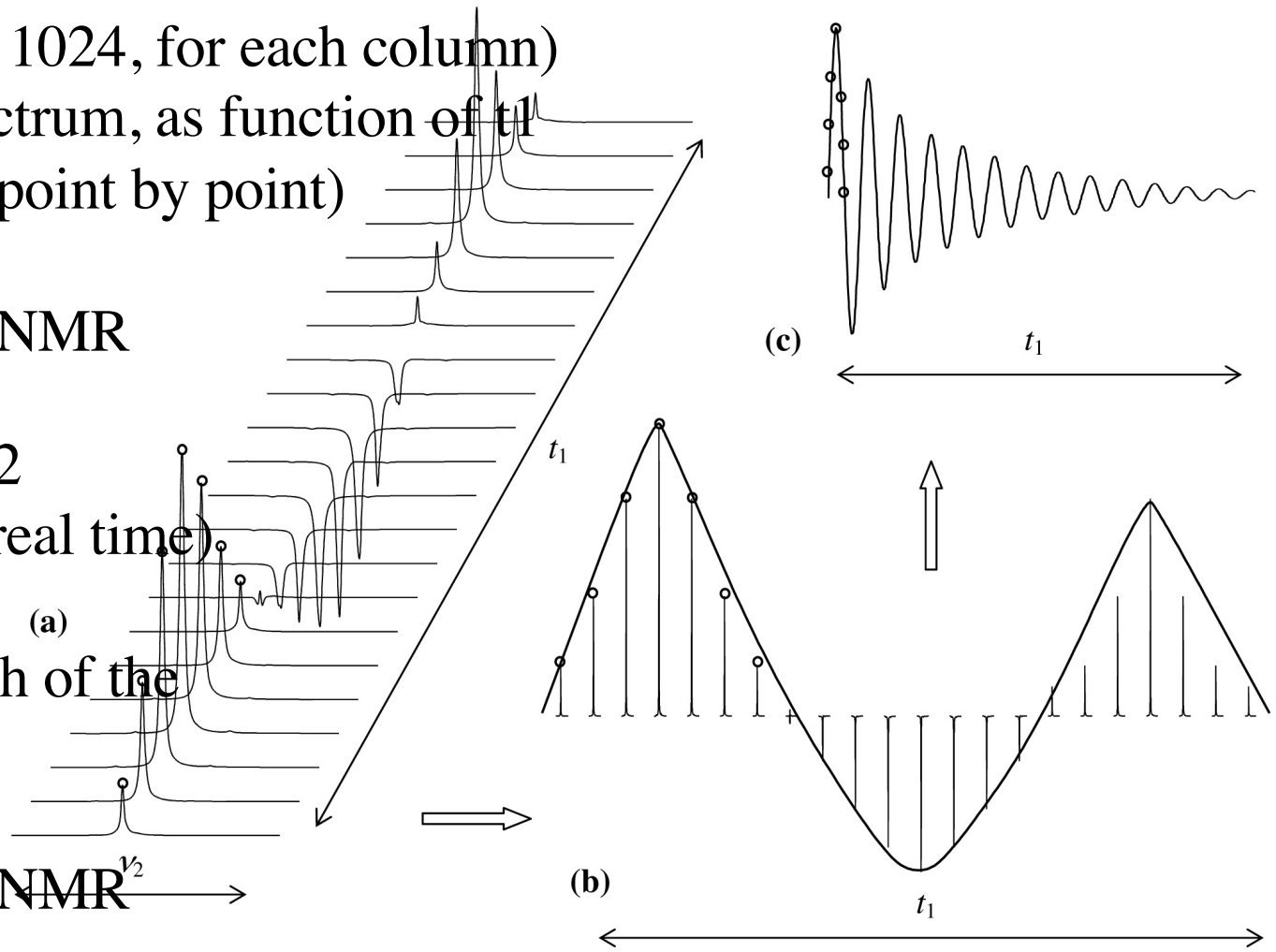


FIGURE 5.5 (a) Stacked plot of 22 "spectra" from acetone in which t_1 is varied incrementally. (b) "Projection" of (a) showing the sinusoidal behavior of the maxima and minima along t_1 for a single column. (c) Resulting interferogram representing a slice parallel with t_1 through the tops of peaks in (a) for one column.

Fourier transformation of series of interferograms:

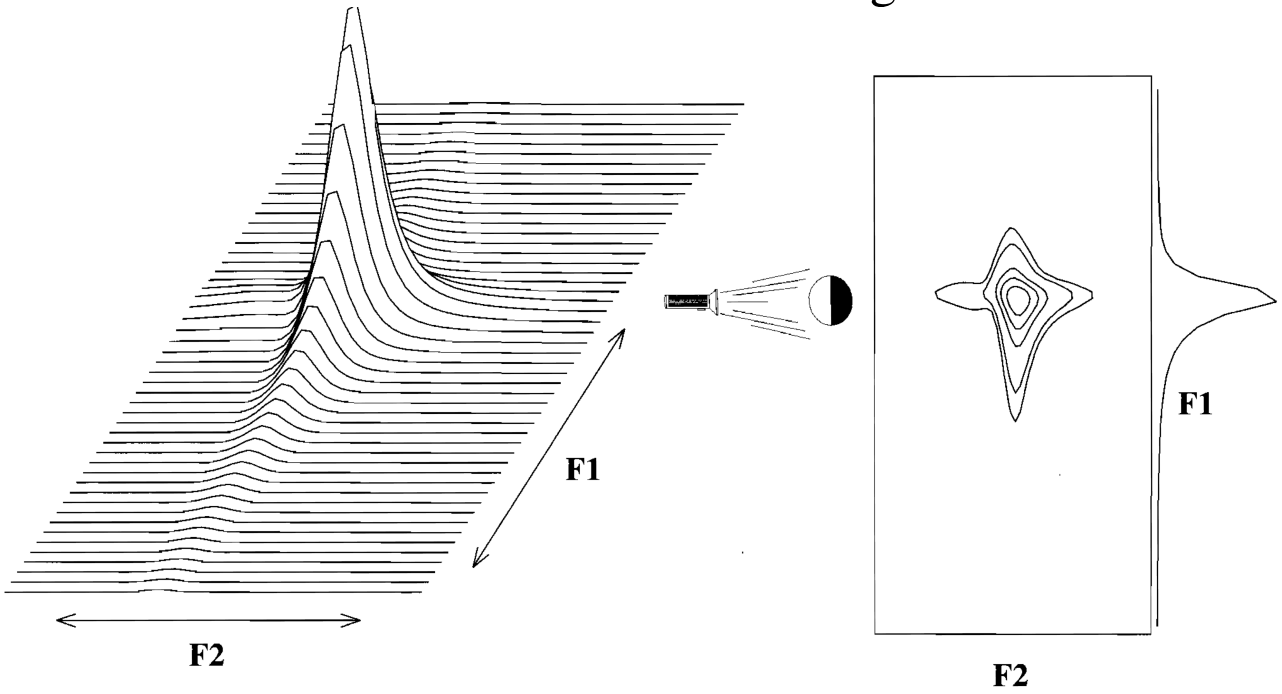
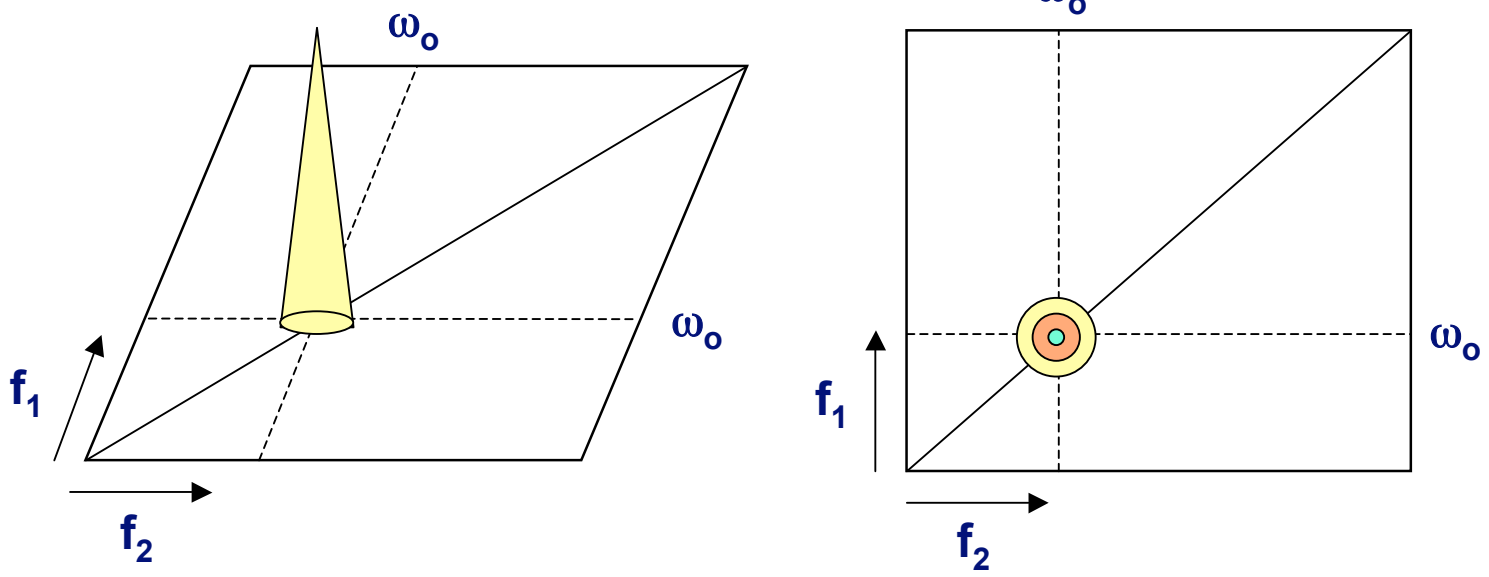
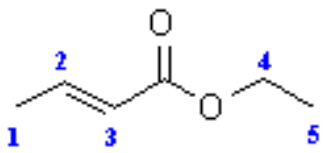


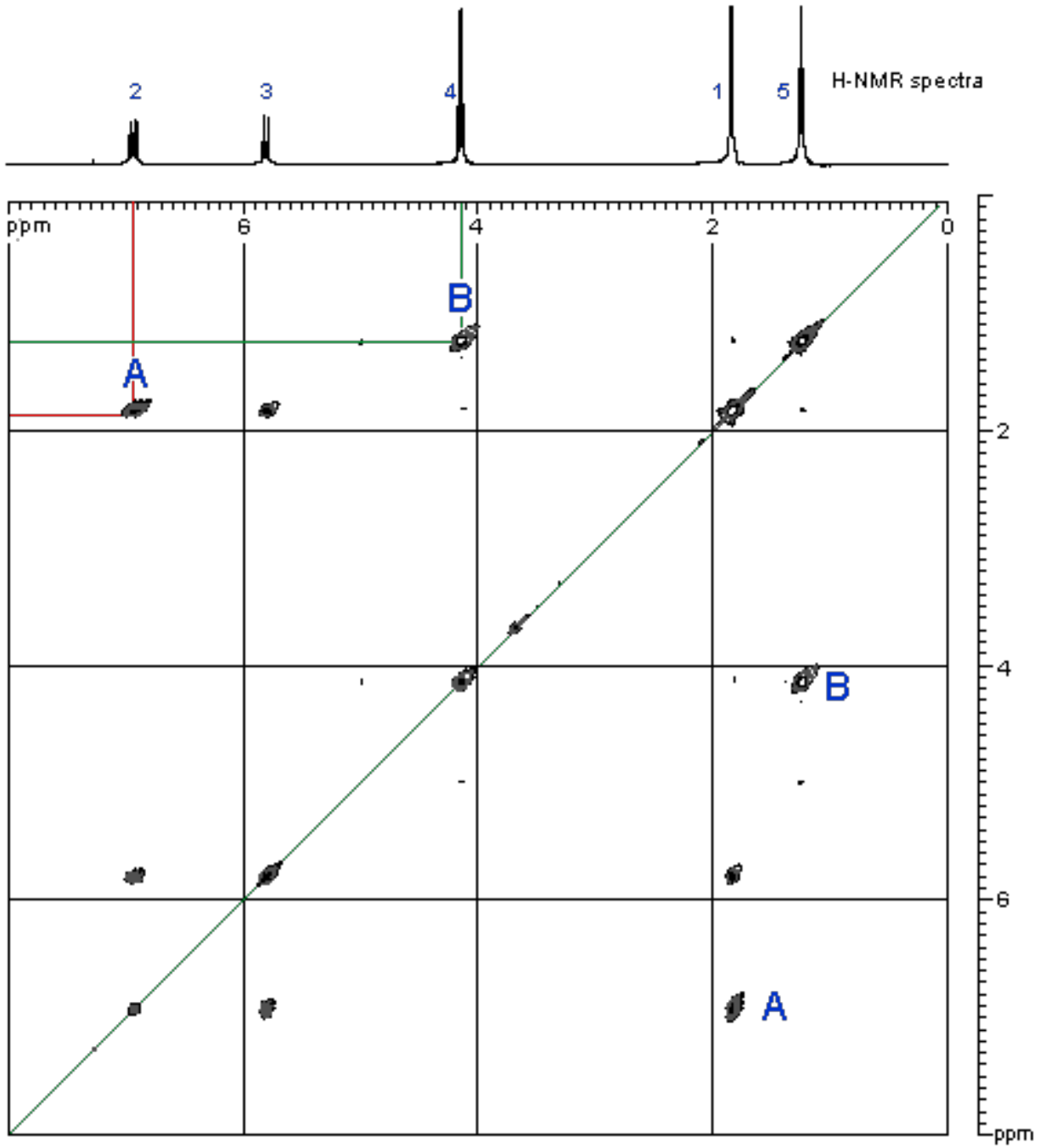
FIGURE 5.6 Fourier transformation of a series of FIDs like the ones in Figure 5.5 (C) to give the frequency-domain spectrum as both a peak and as contours. The contour plot also shows a projection parallel to **F2**.

contour plot

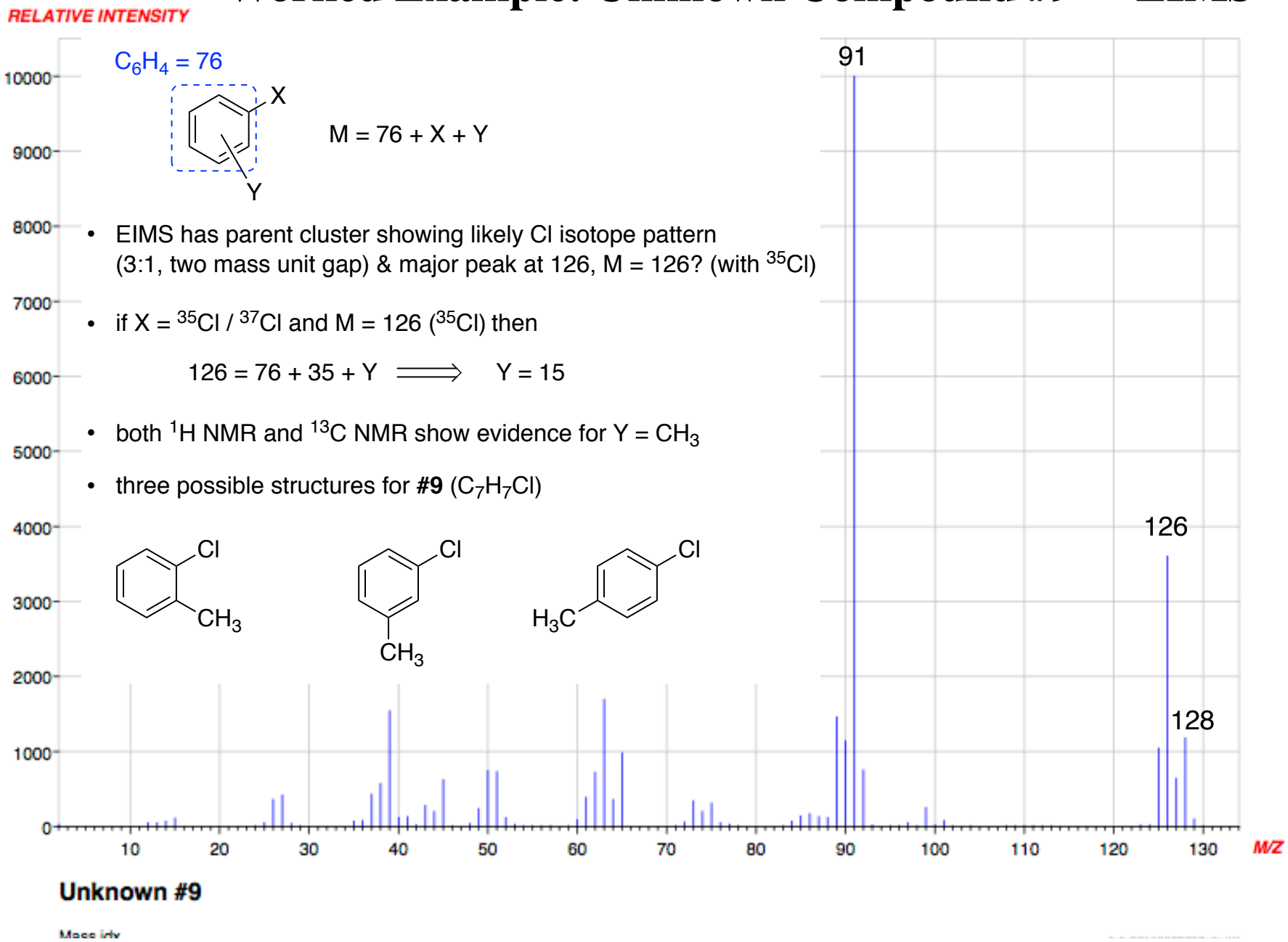


COSY





Worked Example: Unknown Compound #9 EIMS



C_6H_4 = 76

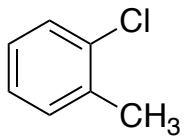
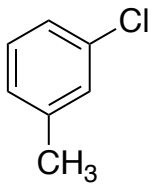
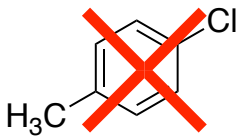
M = 76 + X + Y

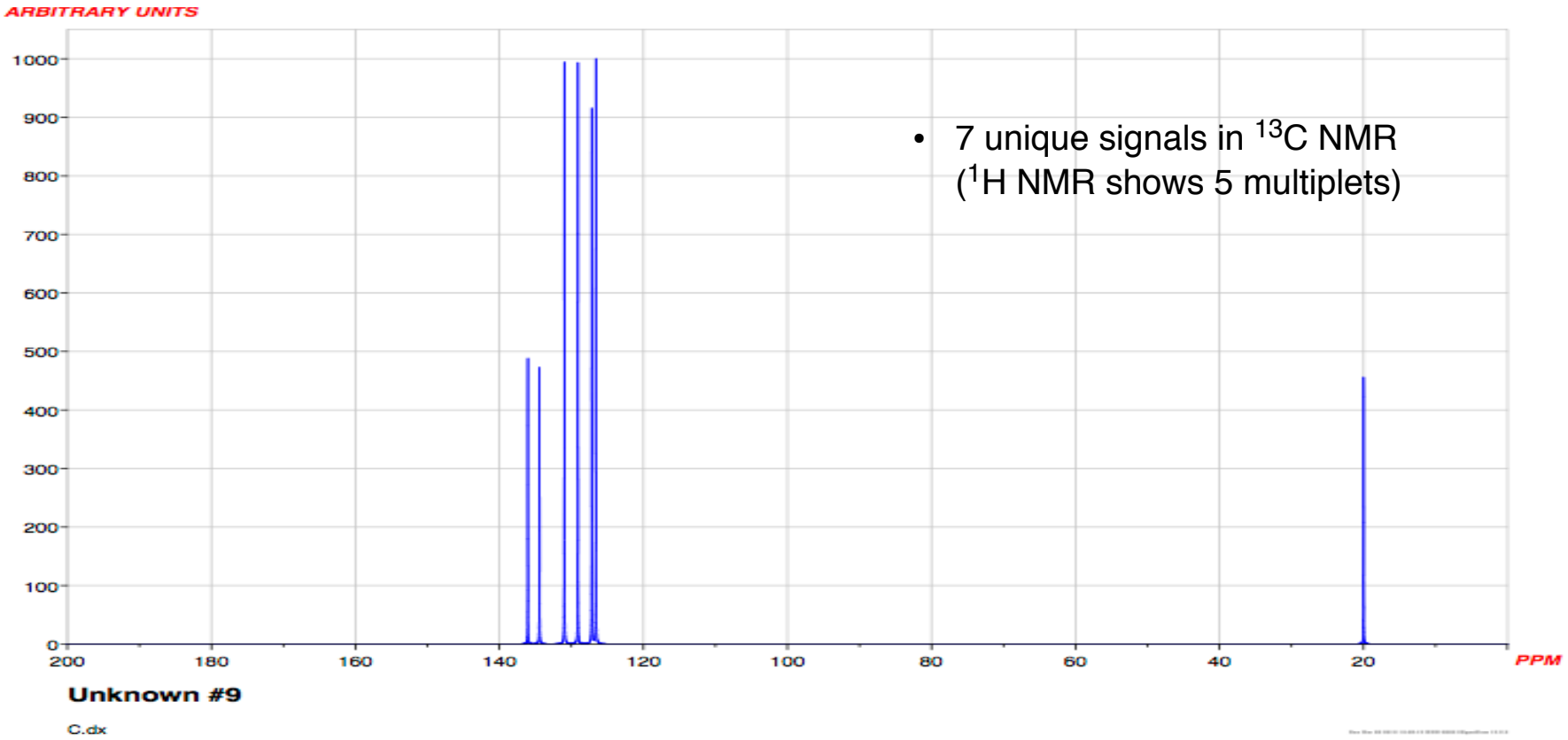
- EIMS has parent cluster showing likely Cl isotope pattern (3:1, two mass unit gap) & major peak at 126, M = 126? (with ^{35}Cl)
- if X = ^{35}Cl / ^{37}Cl and M = 126 (^{35}Cl) then

  126 = 76 + 35 + Y $\Longrightarrow$ Y = 15

- both ^{1}H NMR and ^{13}C NMR show evidence for Y = CH_3
- three possible structures for **#9** (C_7H_7Cl)

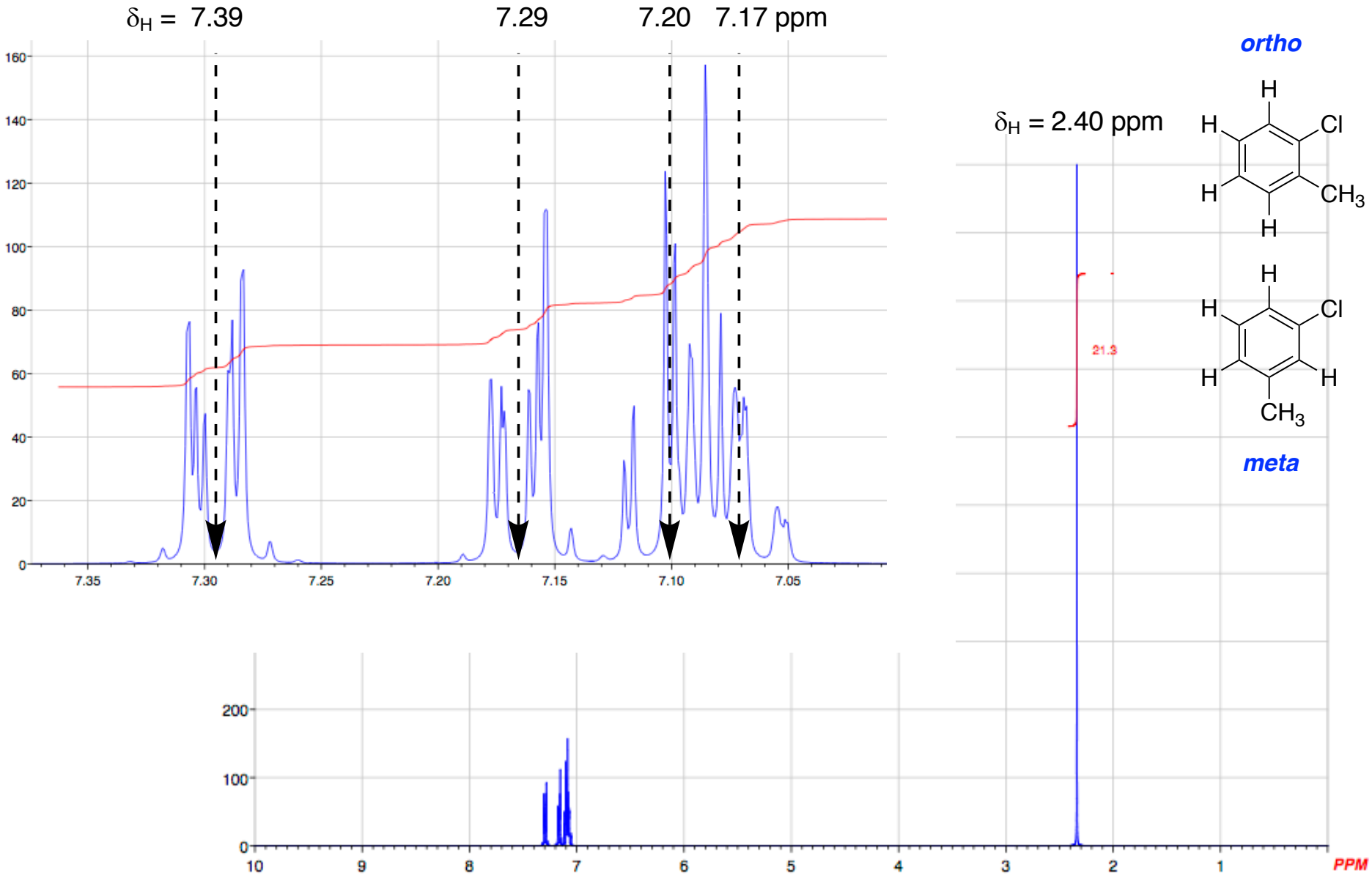
Symmetry Considerations & NMR Data Limit Choices Immediately

# unique chemical environments			
H-atoms	5	5	3
C-atoms	7	7	5

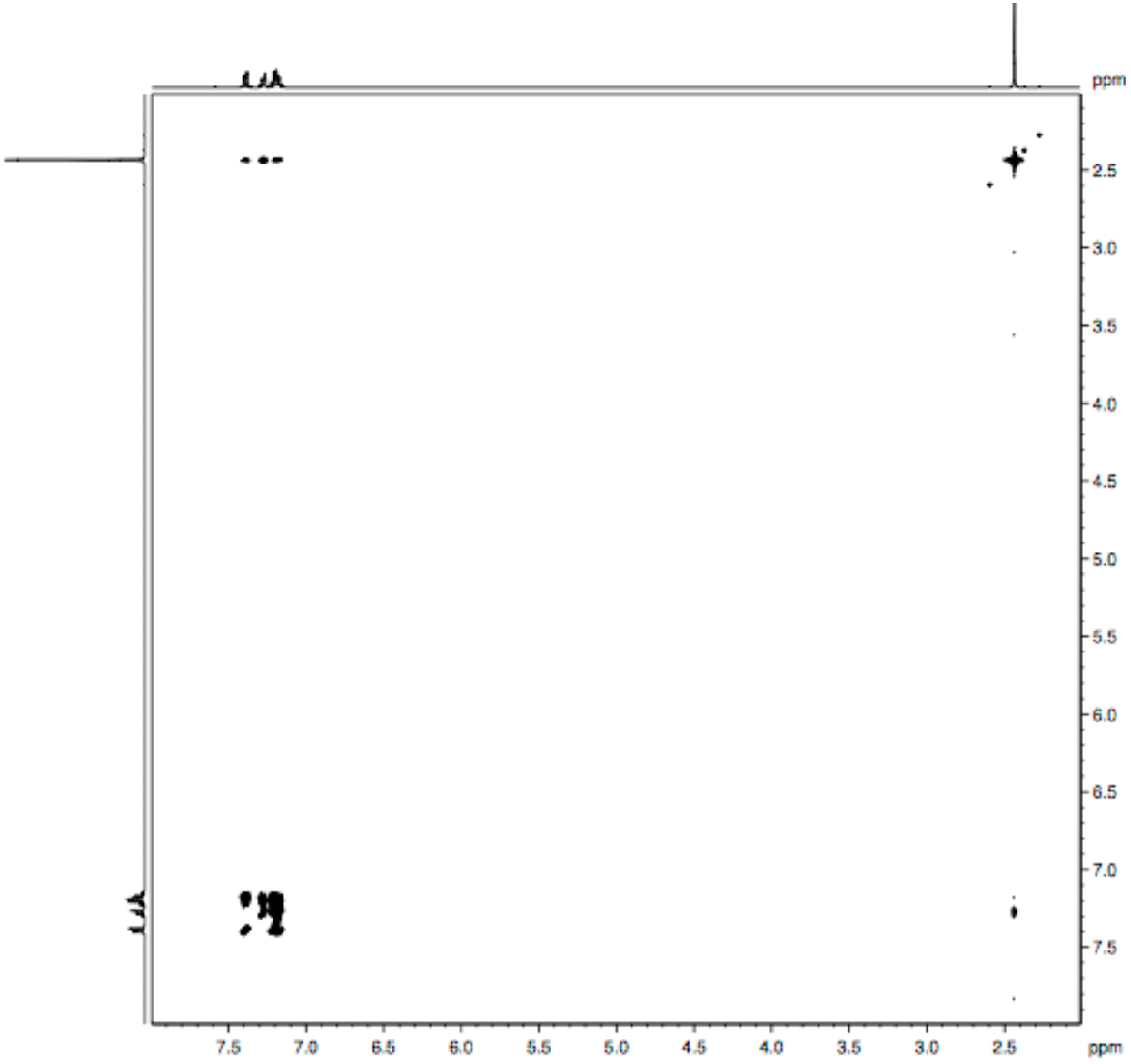


- 7 unique signals in ^{13}C NMR (^{1}H NMR shows 5 multiplets)

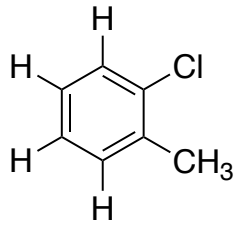
Worked Example: Unknown Compound #9 ^{1}H NMR

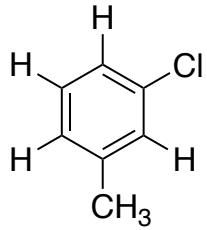


COSY Reveals H-H Correlations (J Coupled)



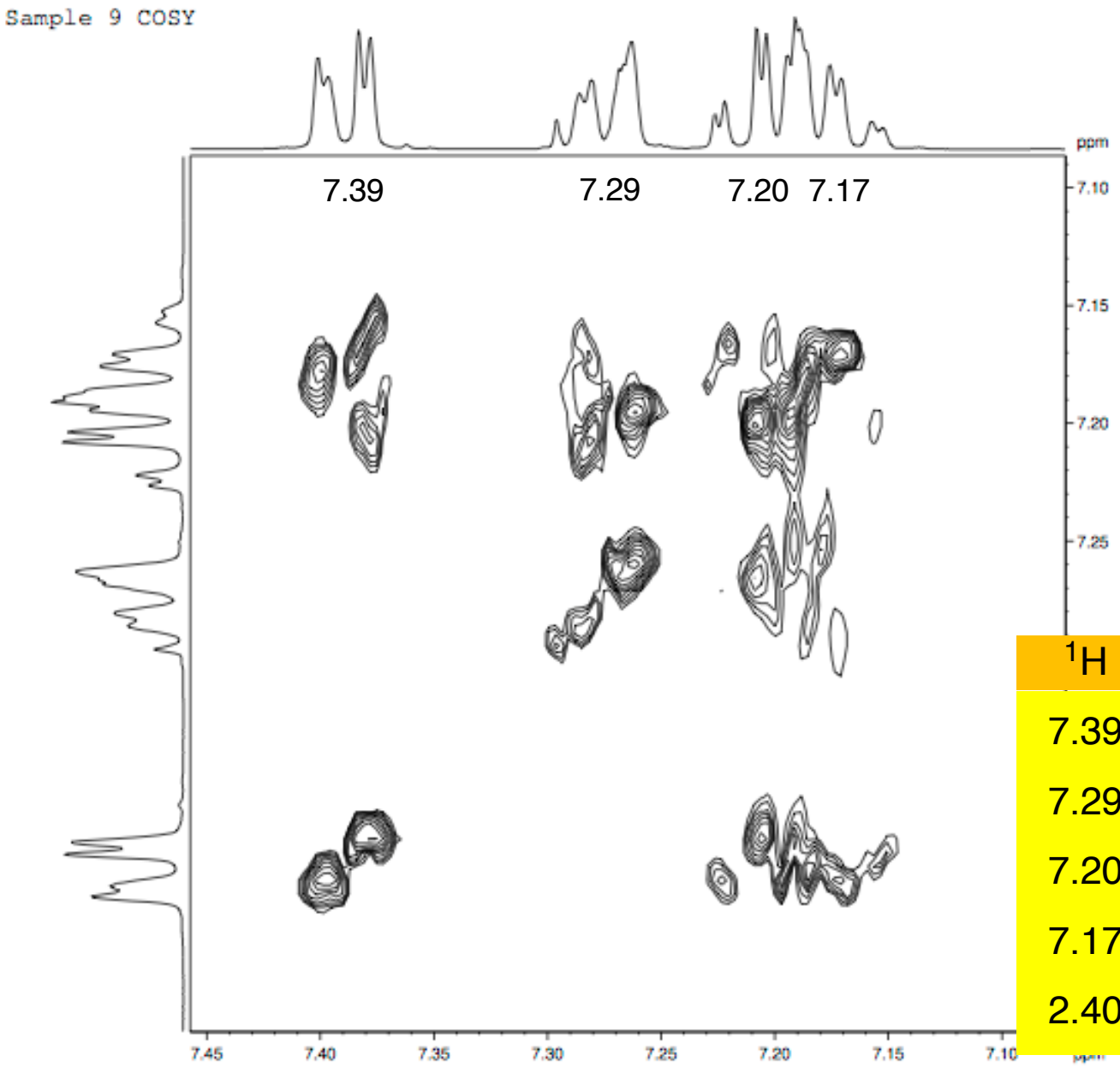
ortho





meta

COSY Reveals H-H Correlations (J Coupled)



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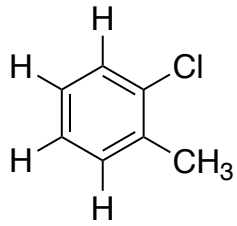
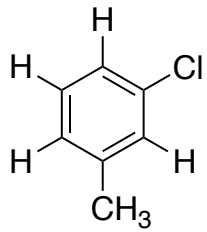
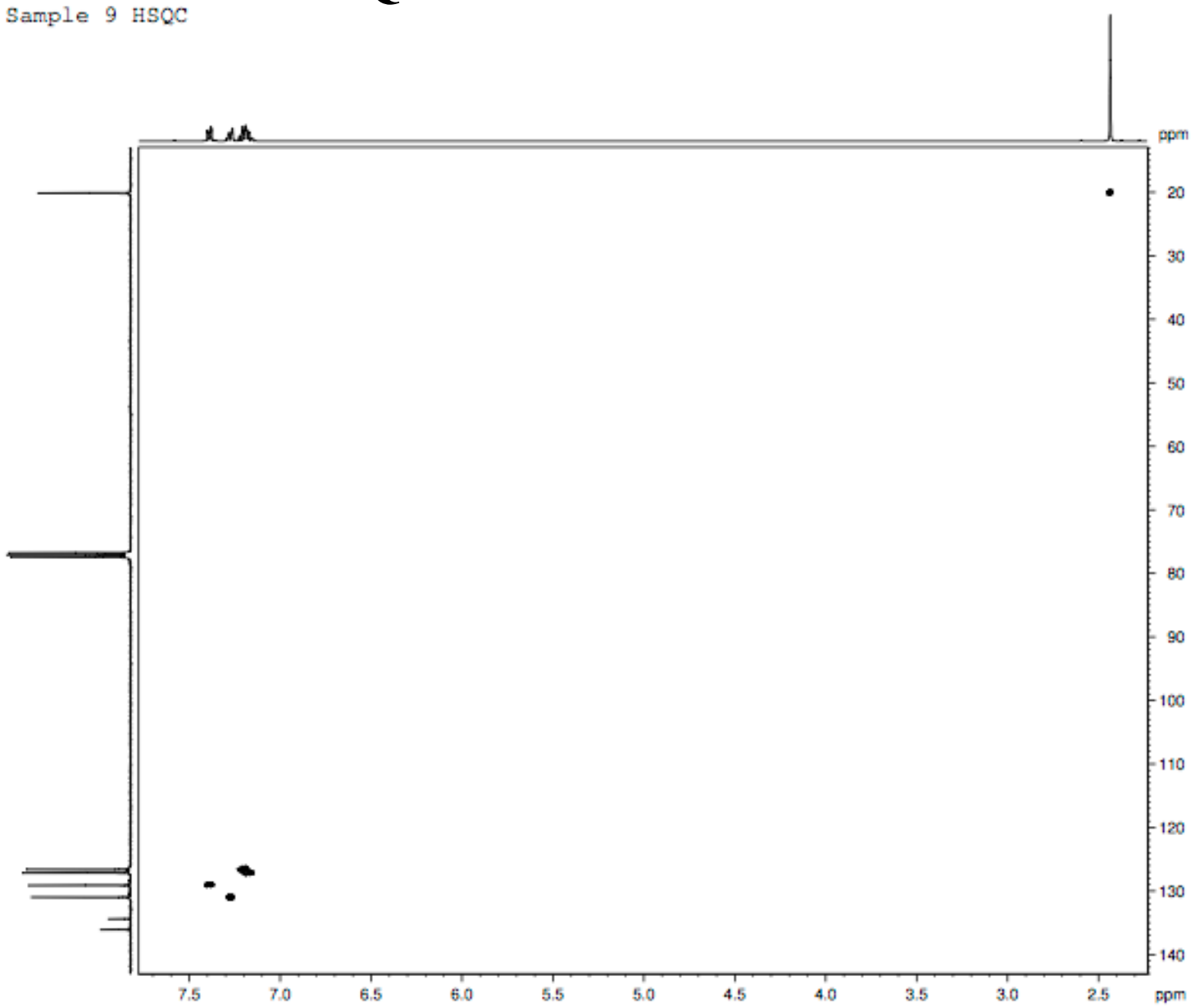




meta

^{1}H	COSY correlations		
7.39		7.20	7.17
7.29		7.20	7.17
7.20	7.39	7.29	7.17
7.17	7.39	7.29	7.20
2.40	none		

HSQC Reveals 1-Bond C-H Correlations



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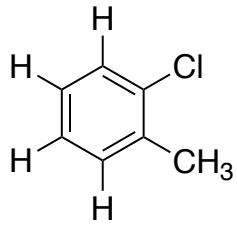
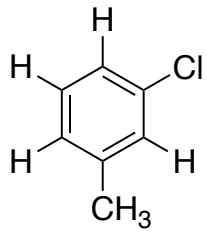
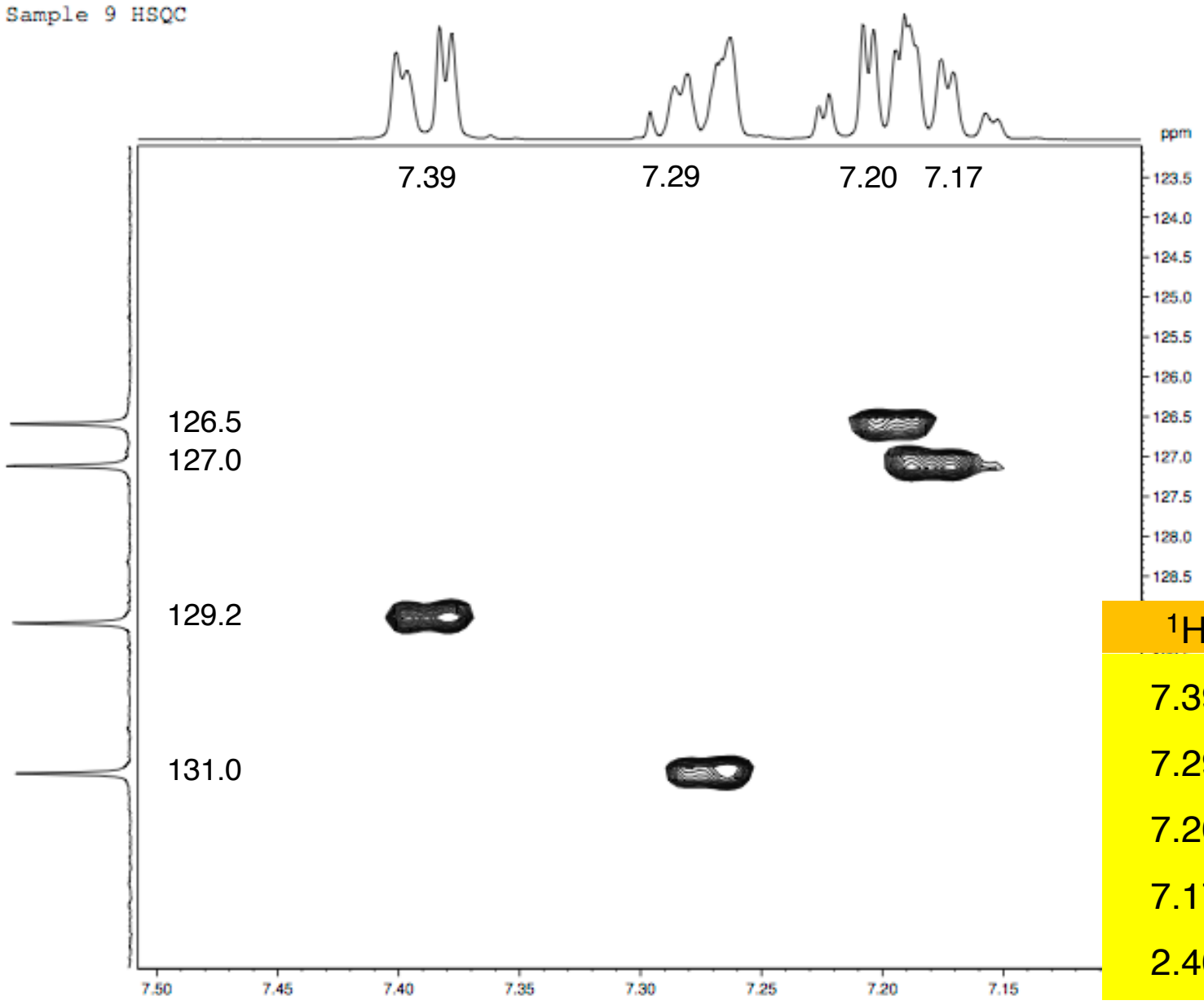




meta

HSQC Reveals 1-Bond C-H Correlations



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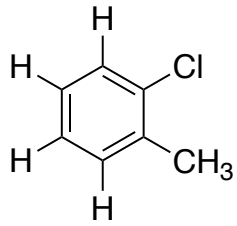
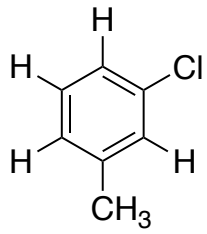
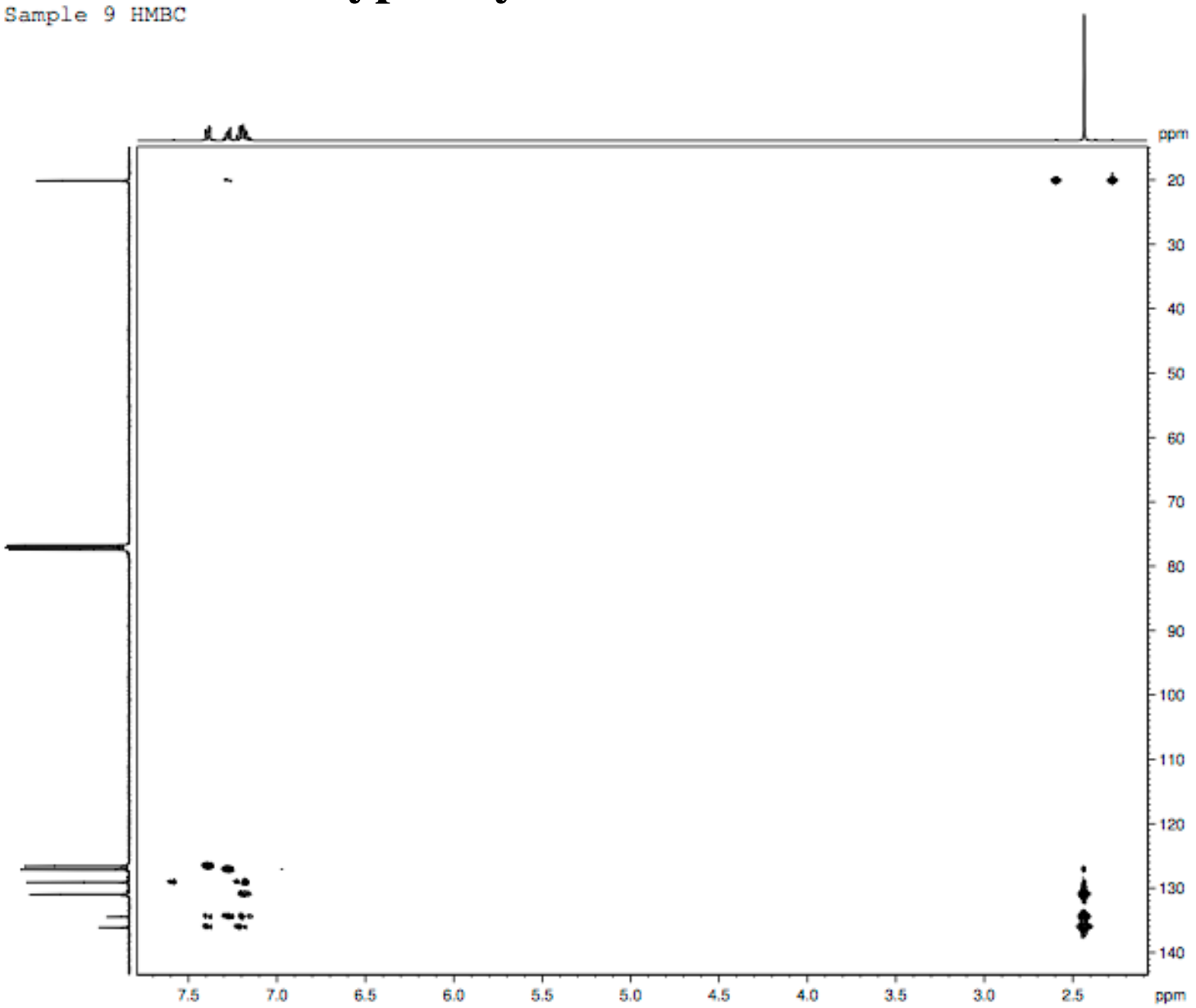




meta

^{1}H	HSQC
7.39	129.2
7.29	131.0
7.20	126.5
7.17	127.0
2.40	20.0

HMBC Typically Reveals 2 or 3-Bond C-H Correlations



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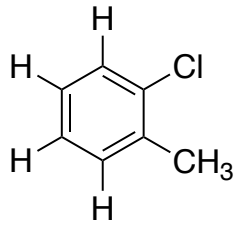

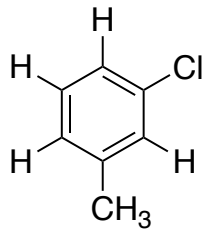

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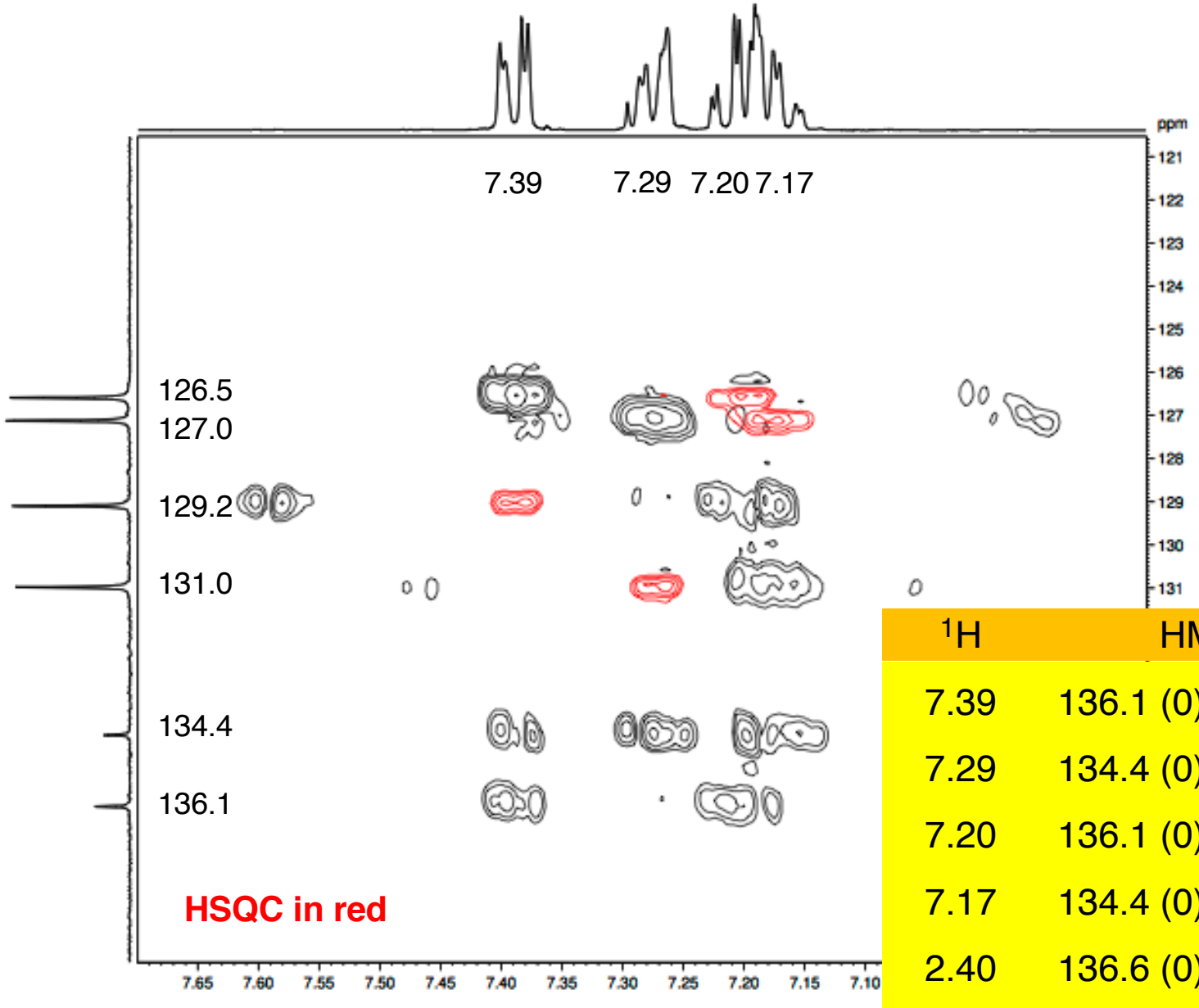
HMBC Typically Reveals 2 or 3-Bond C-H Correlations



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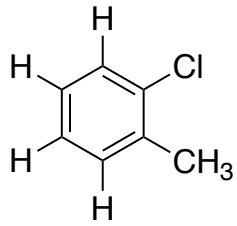
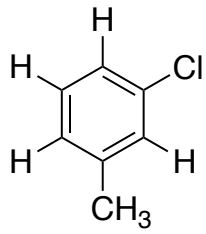


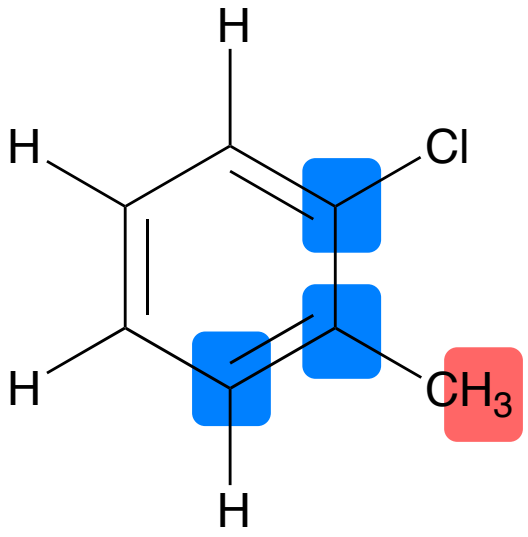


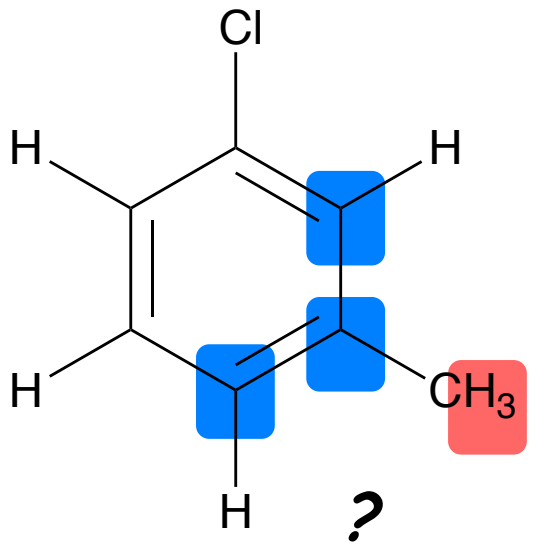
meta

^{1}H	HMBC correlations		
7.39	136.1 (0)	134.4 (0)	126.5 (1)
7.29	134.4 (0)	127.0 (1)	20.0 (3)
7.20	136.1 (0)	129.2 (1)	
7.17	134.4 (0)	129.2 (1)	
2.40	136.6 (0)	134.4 (0)	131.0 (1)

Complete Spectral Data Correlation Table

^{1}H	COSY correlations			HSQC	HMBC correlations		
7.39		7.20	7.17	129.2	136.1 (0)	134.4 (0)	126.5 (1)
7.29		7.20	7.17	131.0	134.4 (0)	127.0 (1)	20.0 (3)
7.20	7.39	7.29	7.17	126.5	136.1 (0)	129.2 (1)	
7.17	7.39	7.29	7.20	127.0	134.4 (0)	129.2 (1)	
2.40	none			20.0	136.6 (0)	134.4 (0)	131.0 (1)





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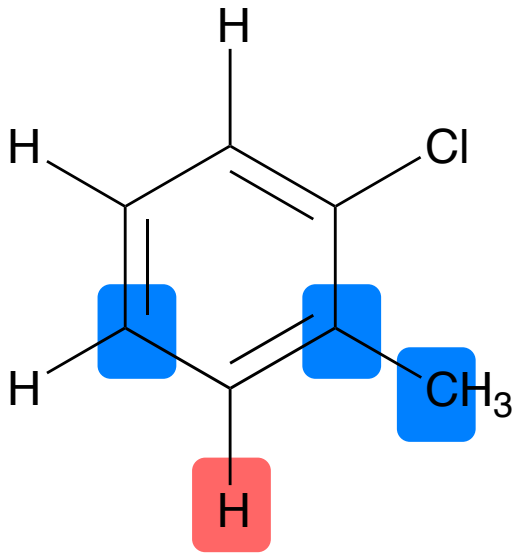
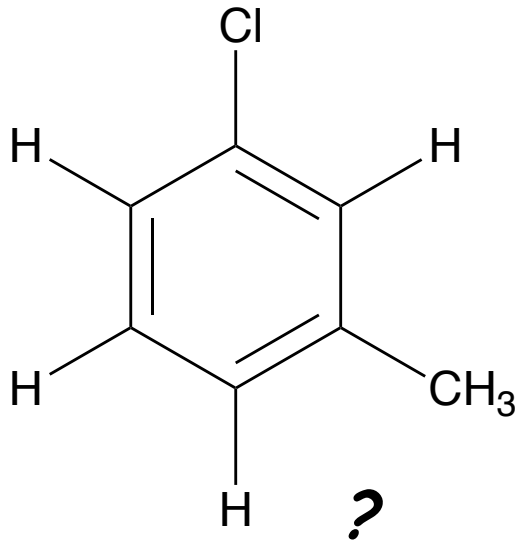
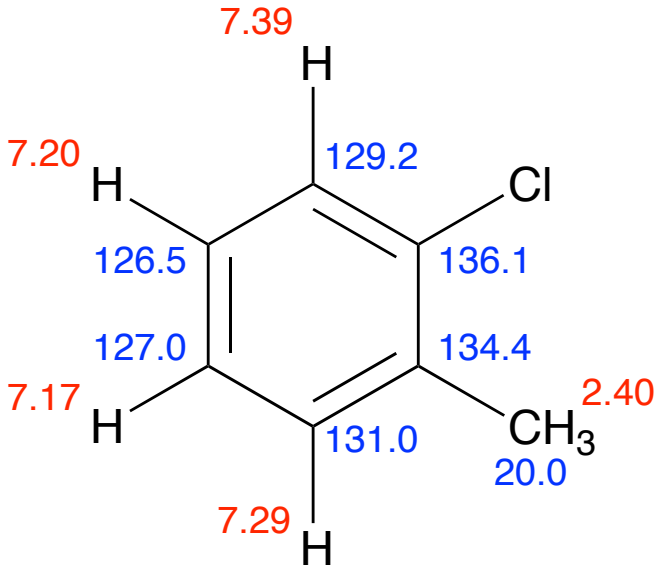
7.29		7.20	7.17	131.0	134.4 (0)	127.0 (1)	20.0 (3)
7.20	7.39	7.29	7.17	126.5	136.1 (0)	129.2 (1)	
7.17	7.39	7.29	7.20	127.0	134.4 (0)	129.2 (1)	
2.40	none			20.0	136.6 (0)	134.4 (0)	131.0 (1)

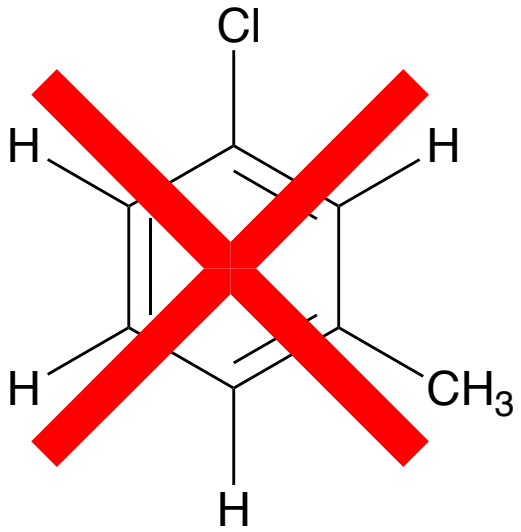




Complete Spectral Data Correlation Table

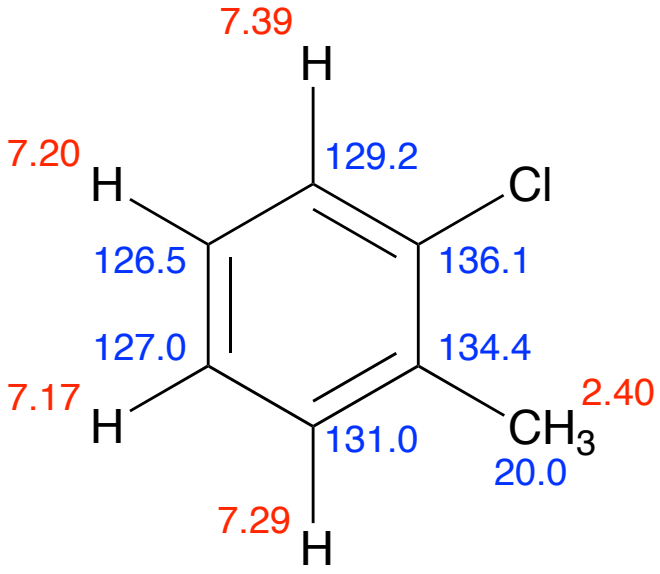
^{1}H	COSY correlations			HSQC	HMBC correlations		
7.39		7.20	7.17	129.2	136.1 (0)	134.4 (0)	126.5 (1)
7.29		7.20	7.17	131.0	134.4 (0)	127.0 (1)	20.0 (3)
7.20	7.39	7.29	7.17	126.5	136.1 (0)	129.2 (1)	
7.17	7.39	7.29	7.20	127.0	134.4 (0)	129.2 (1)	
2.40	none			20.0	136.6 (0)	134.4 (0)	131.0 (1)

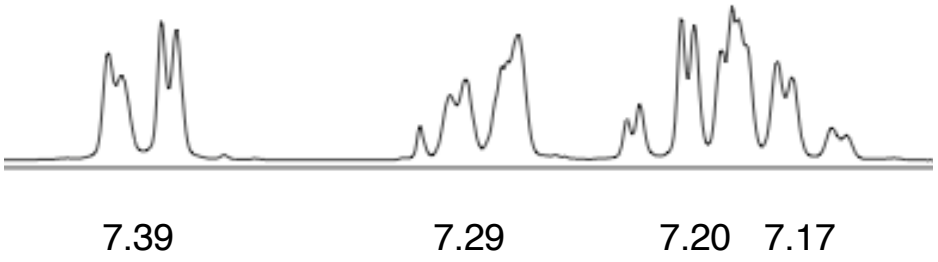




Complete Spectral Data Correlation Table

	^{1}H	COSY correlations			HSQC	HMBC correlations		
(dd)	7.39		7.20	7.17	129.2	136.1 (0)	134.4 (0)	126.5 (1)
(dd)	7.29		7.20	7.17	131.0	134.4 (0)	127.0 (1)	20.0 (3)
(td)	7.20	7.39	7.29	7.17	126.5	136.1 (0)	129.2 (1)	
(td)	7.17	7.39	7.29	7.20	127.0	134.4 (0)	129.2 (1)	
(s)	2.40	none			20.0	136.6 (0)	134.4 (0)	131.0 (1)





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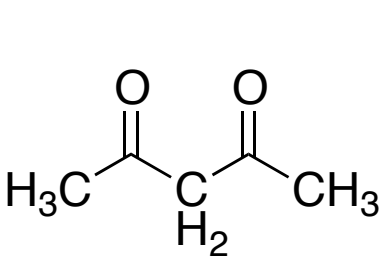
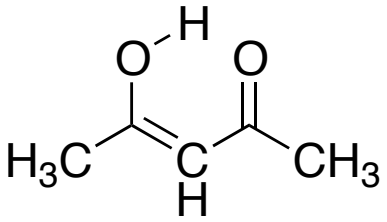
Good Luck !

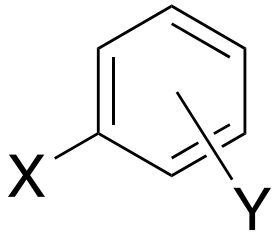


keto tautomer

K_{eq} ?



enol tautomer



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