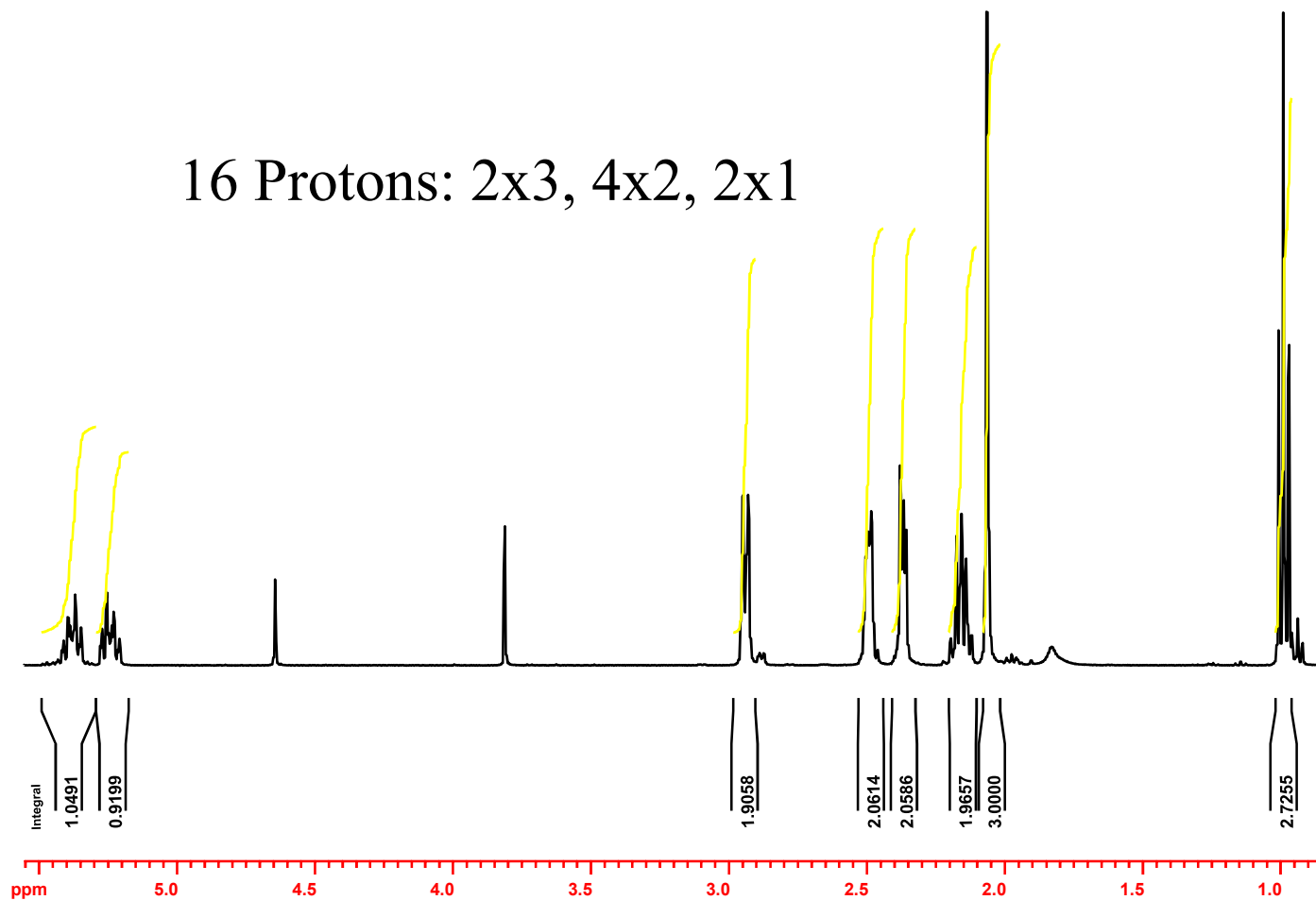


# NMR assignment of an unknown

By Roy Hoffman

# Number of protons from integrals

16 Protons: 2x3, 4x2, 2x1

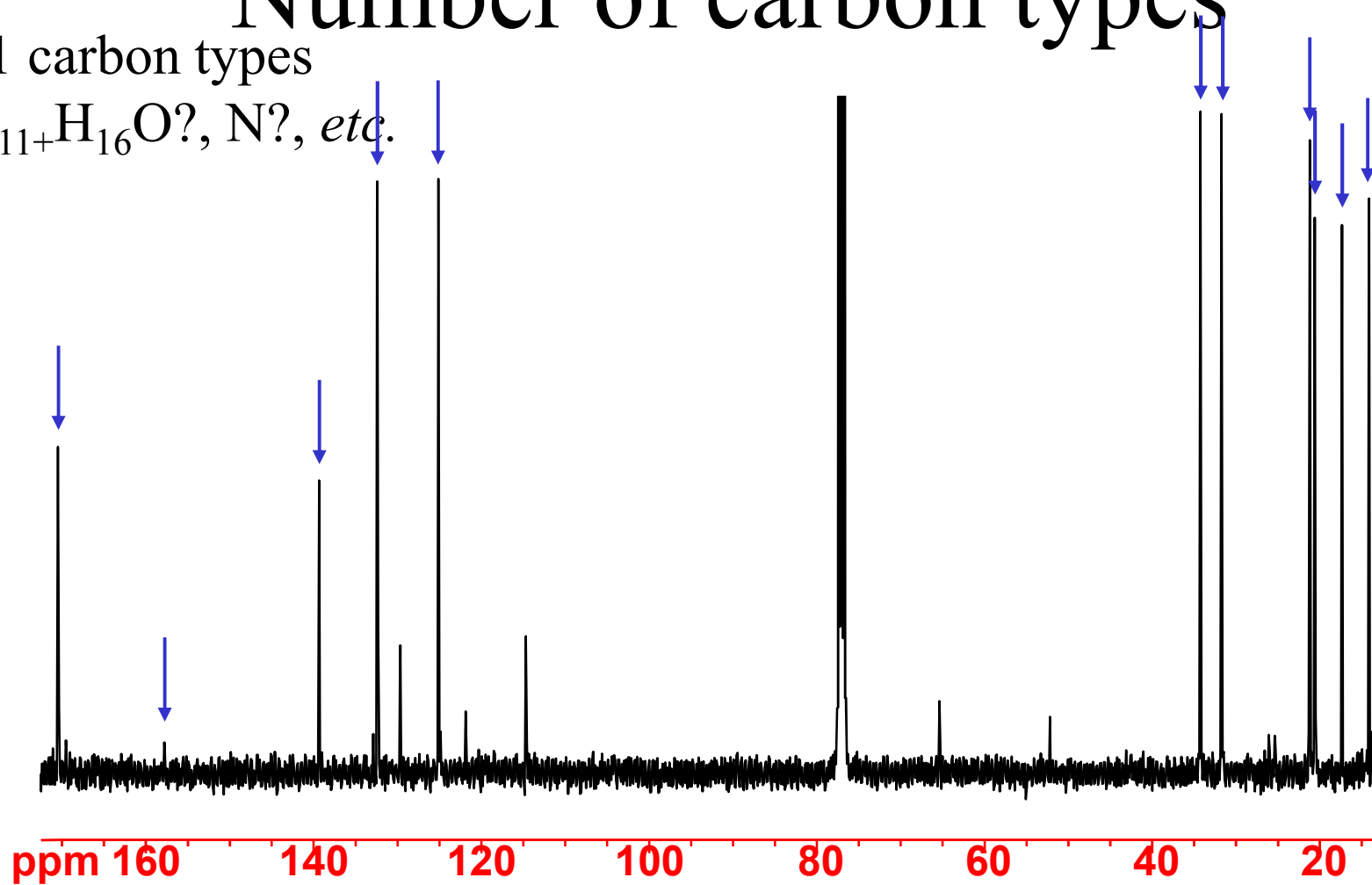


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# Number of carbon types

11 carbon types

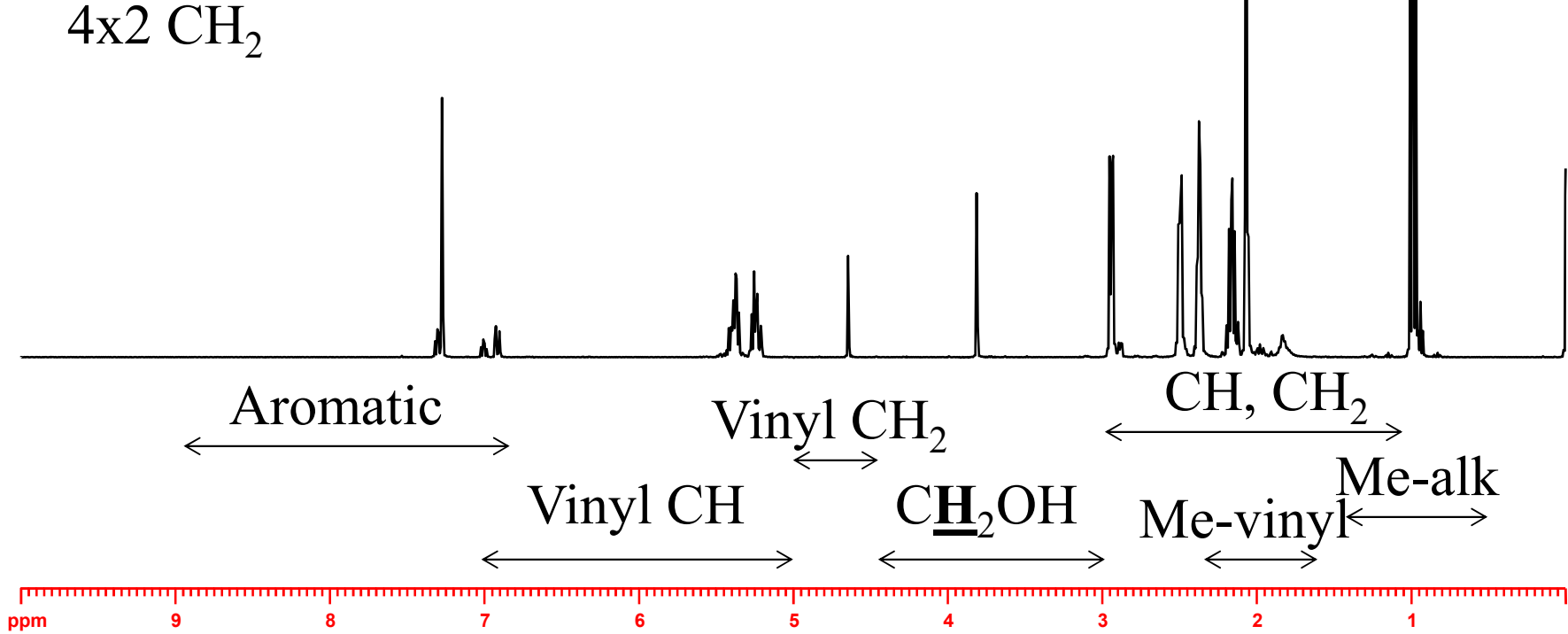
$C_{11}H_{16}O?$ ,  $N?$ , *etc.*



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# Functionality from $^1\text{H}$ chemical shifts

2x1 vinyl CH  
1x3 methyl alkyl  
4x2  $\text{CH}_2$

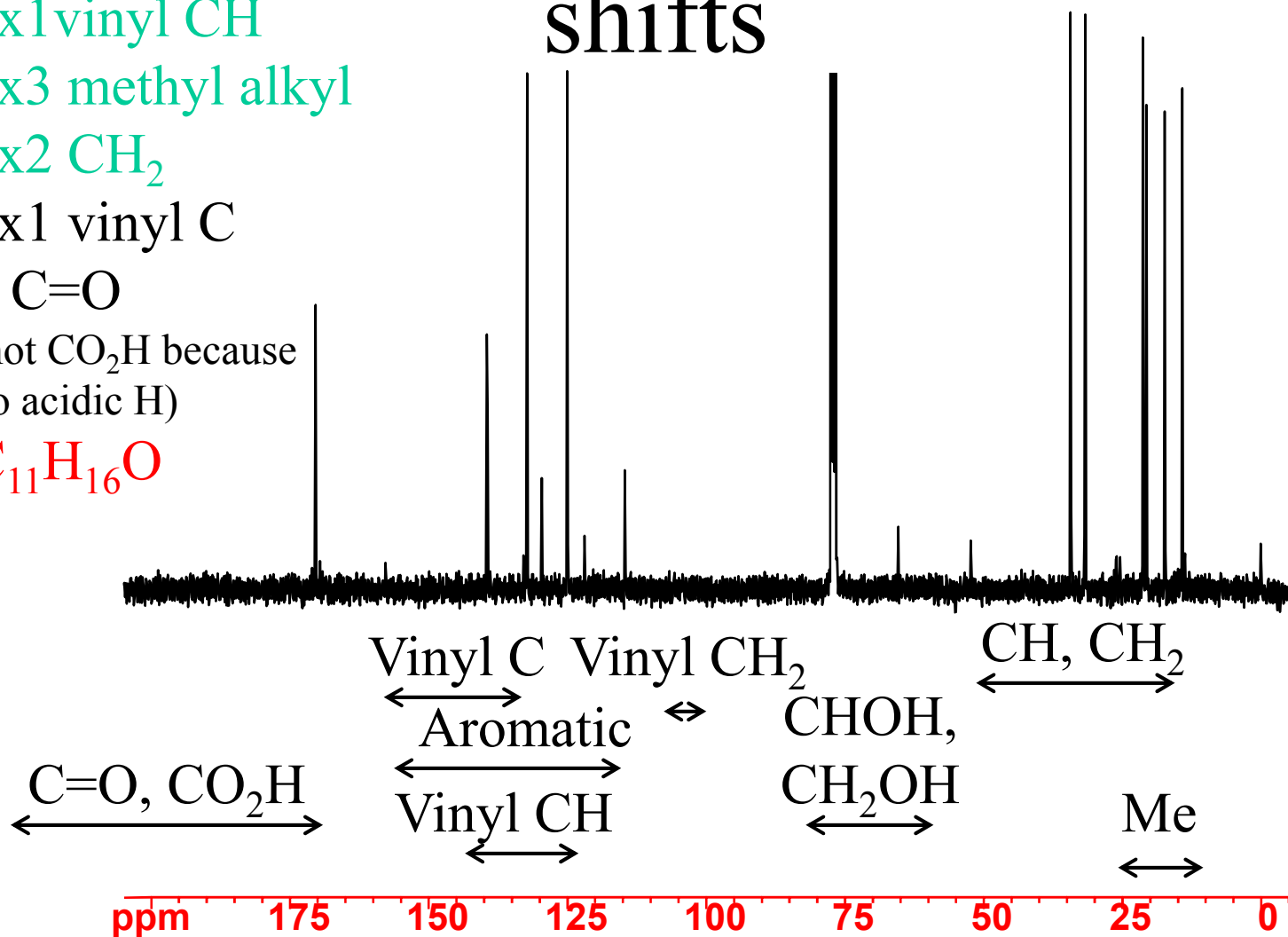


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# Functionality from $^{13}\text{C}$ chemical shifts

2x1 vinyl CH  
 1x3 methyl alkyl  
 4x2  $\text{CH}_2$   
 2x1 vinyl C  
 1  $\text{C}=\text{O}$   
 (not  $\text{CO}_2\text{H}$  because  
 no acidic H)  
 $\text{C}_{11}\text{H}_{16}\text{O}$

shifts

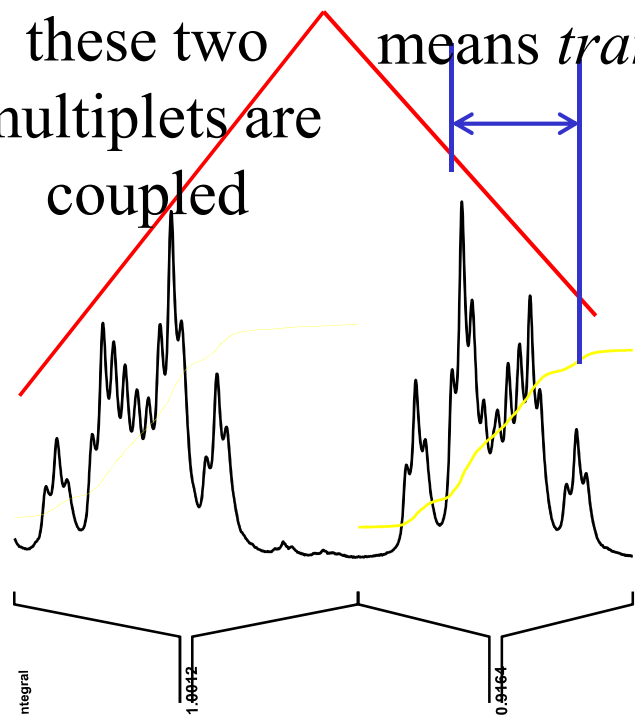


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# Connectivity from 2nd order coupling – the roofing effect

Roofing effect

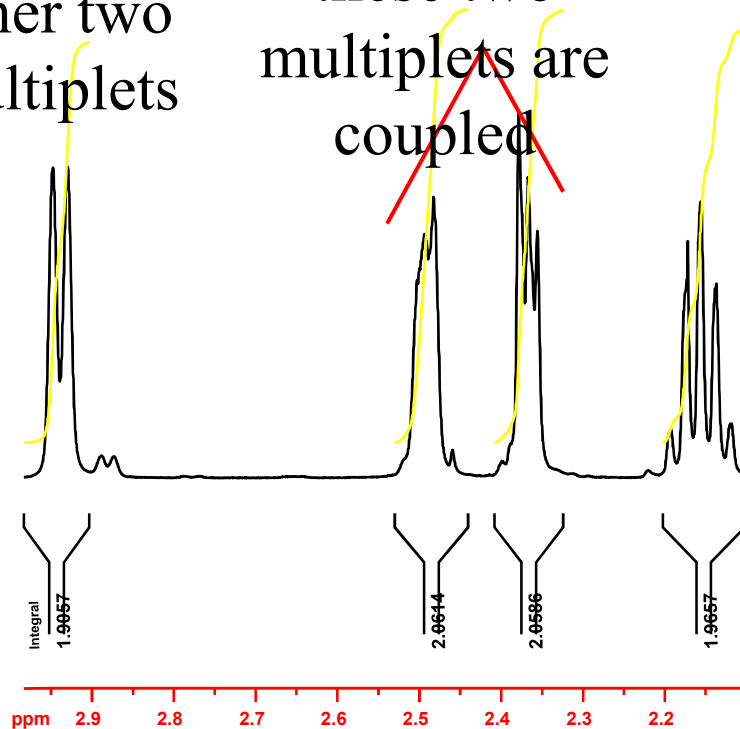
means that these two multiplets are coupled



No roofing effect on the other two multiplets

Roofing effect

means that these two multiplets are coupled

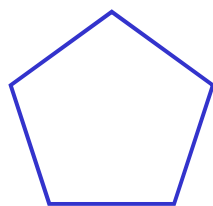


# The situation so far

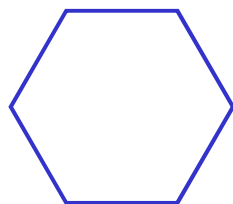
- $C_{11}H_{16}O$  with  $C=O$  and 2 double bonds.
- This requires one ring (Without it would be  $C_{11}H_{18}O$ ).
- There are 2 terminal methyls.
- One of the vinyls has two *trans* H's
- Look for the following ring structures

# Ring structures in the exercise

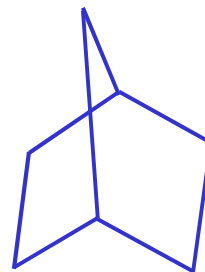
- Look for the following ring structures
- They may be unsaturated
- They may be fused
- There may not be any rings



cyclopentane



cyclohexane

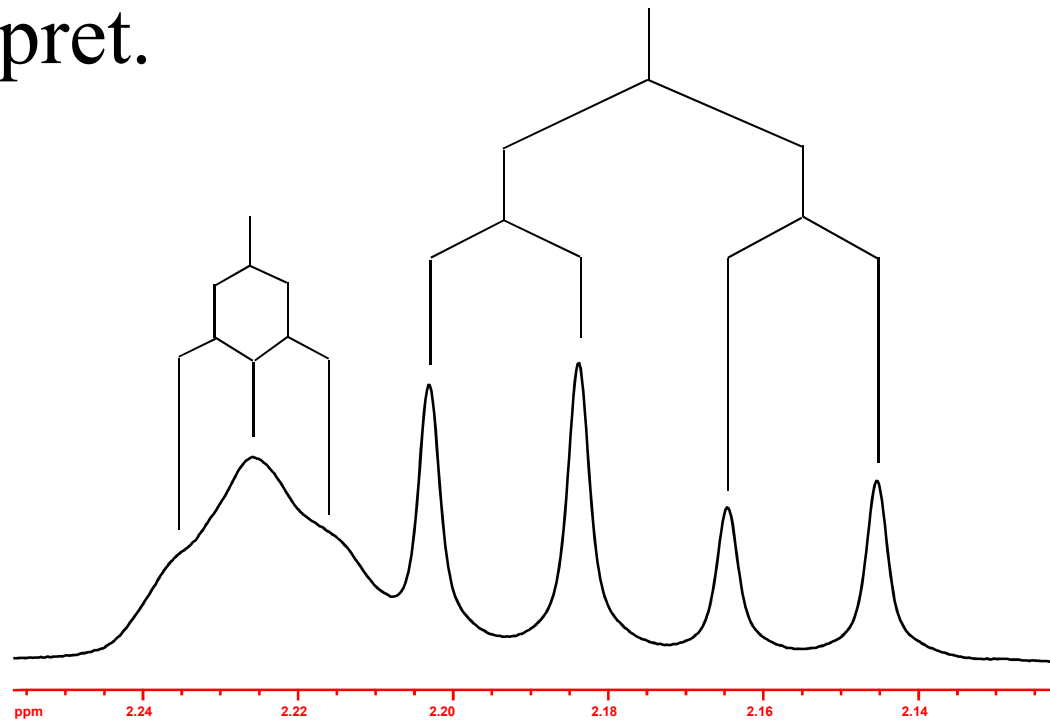


norbornane



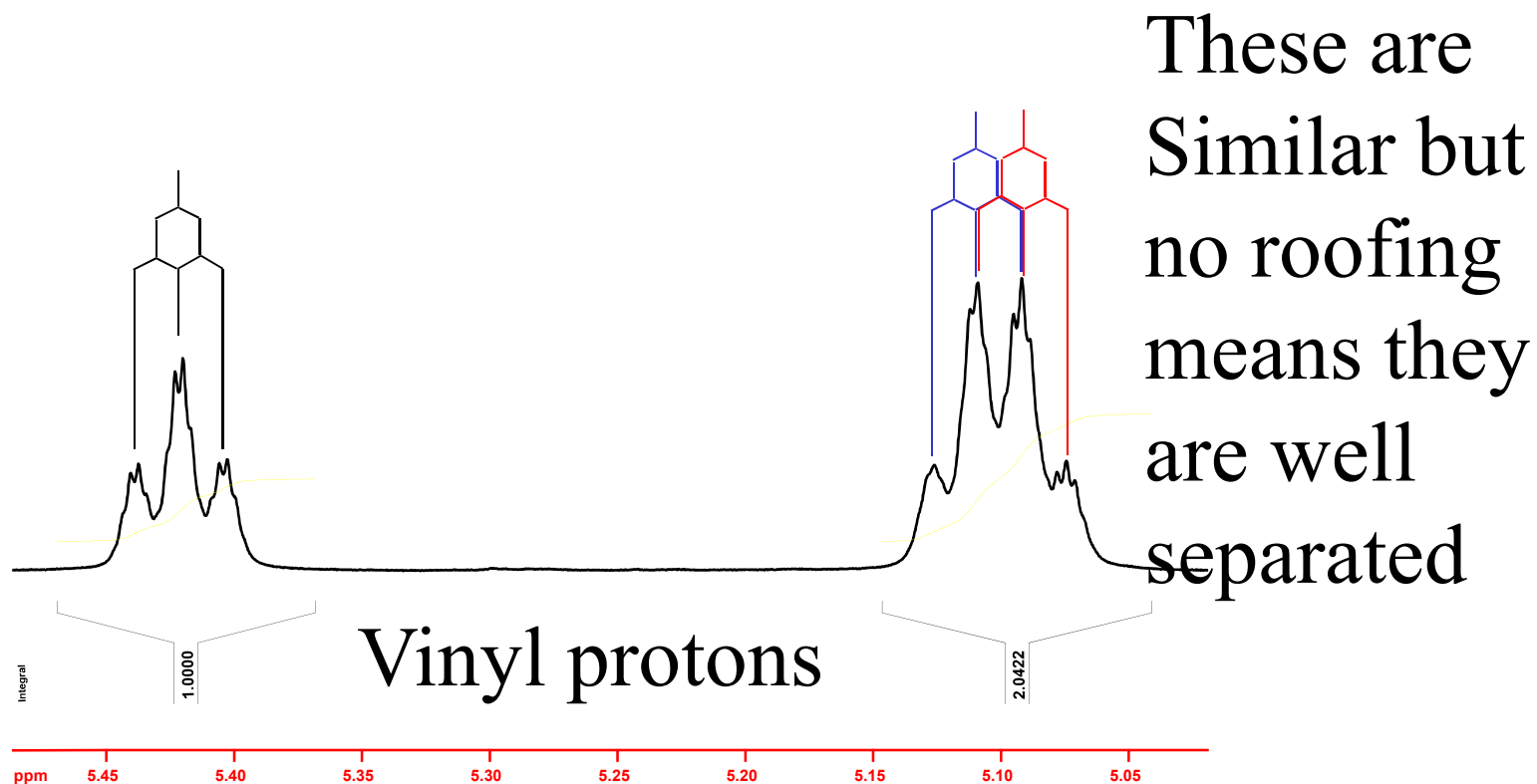
# Overlapping multiplets

- If the overlap is slight then it is still easy to interpret.



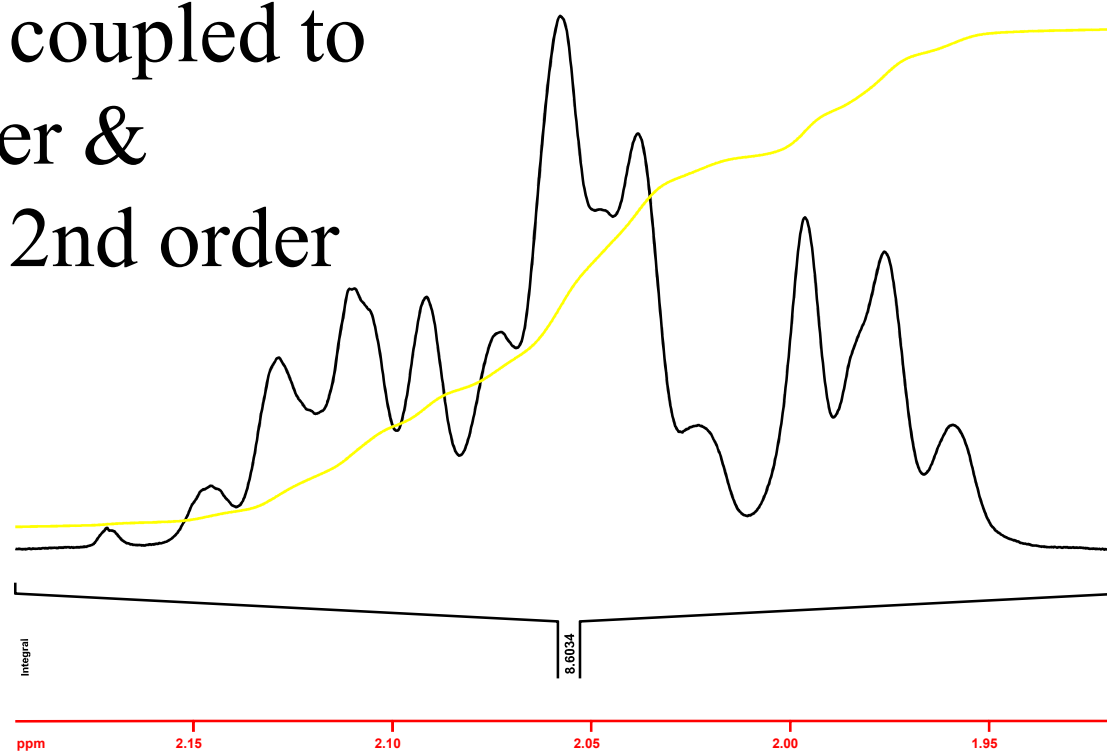
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# Overlapping of similar structures suggests almost identical chemical environments.



# More complex structures require 2D interpretation.

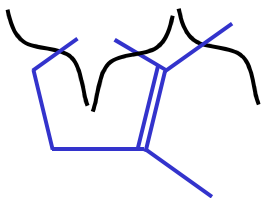
- 4 pairs of protons strongly coupled to each other & displays 2nd order splitting



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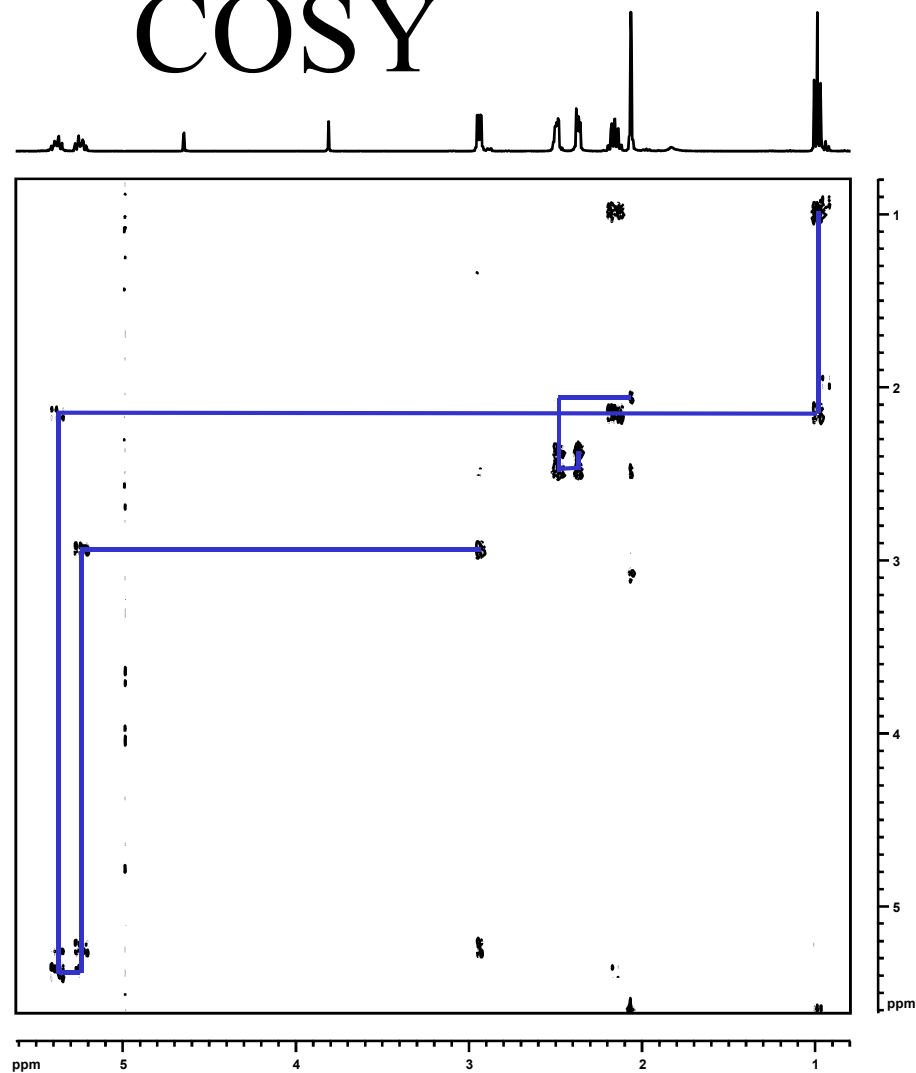
# COSY

Two networks:  
 $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2$



and  $\text{C}=\text{O}$

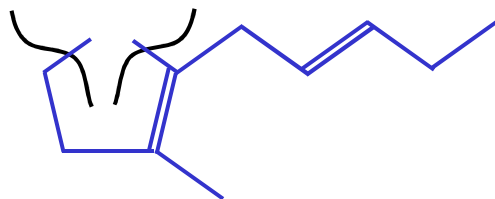
Strong signals are 2  
& 3 bond, weak  
signals are 4 bond



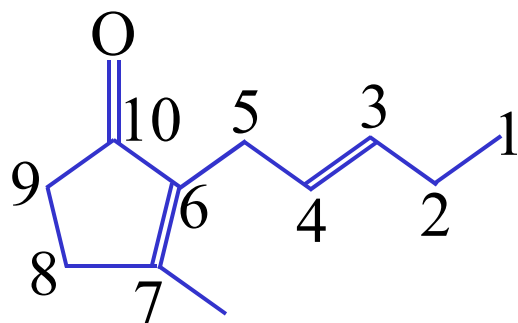
NMR assignment of an unknown by  
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# NOESY

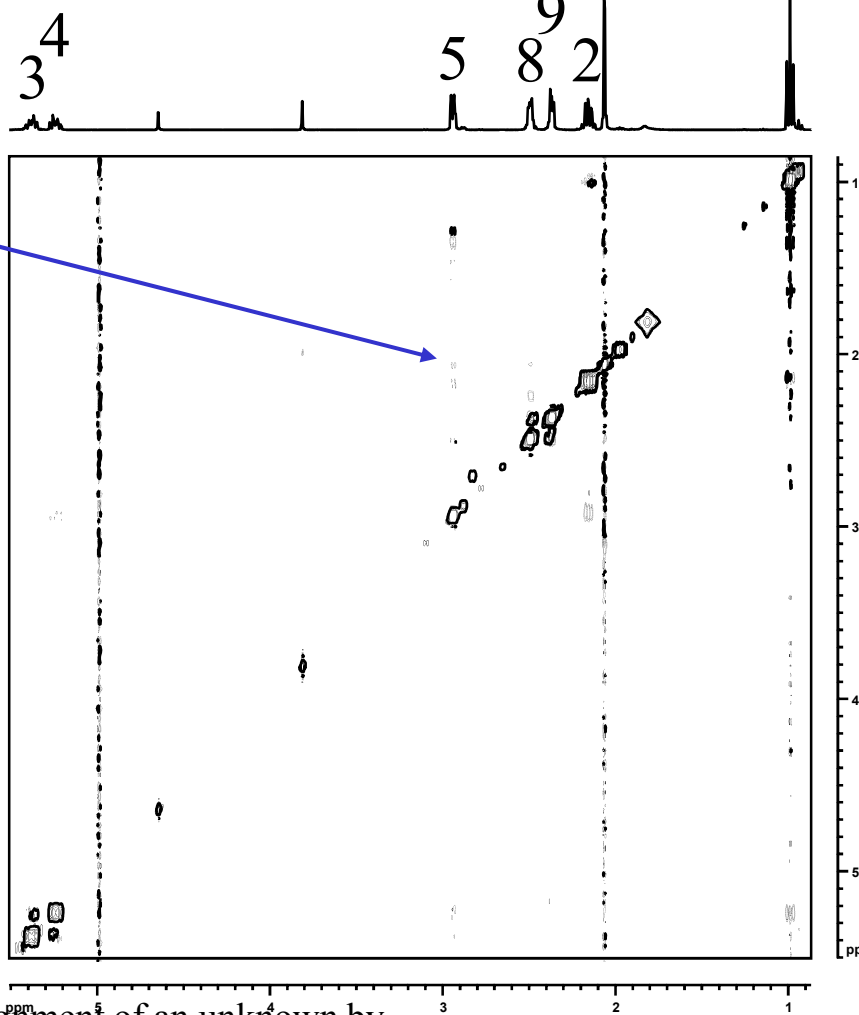
Correlation between the two networks



A ring is required so close with C=O

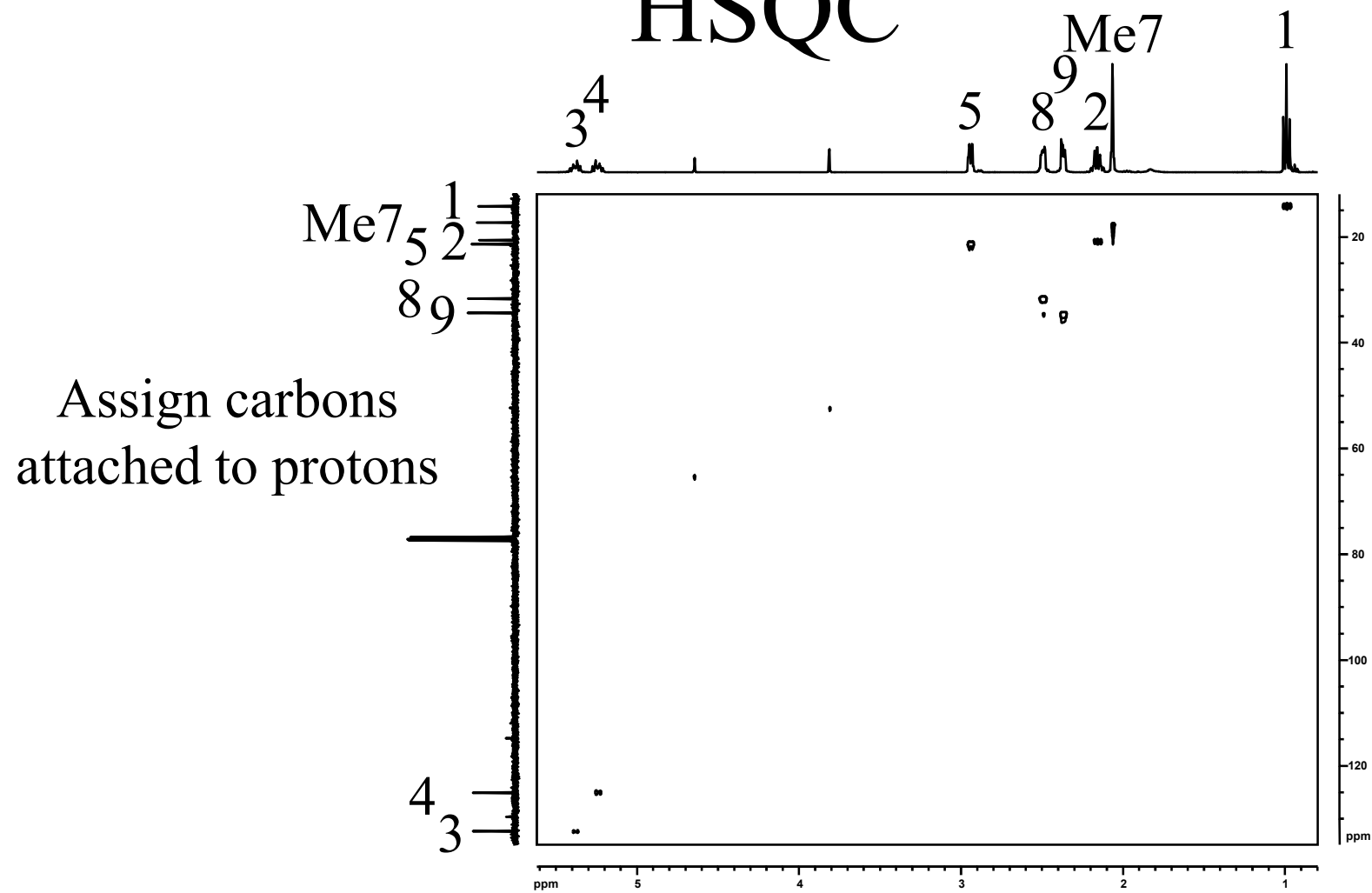


$^1\text{H}$  NMR is assigned Me7 1



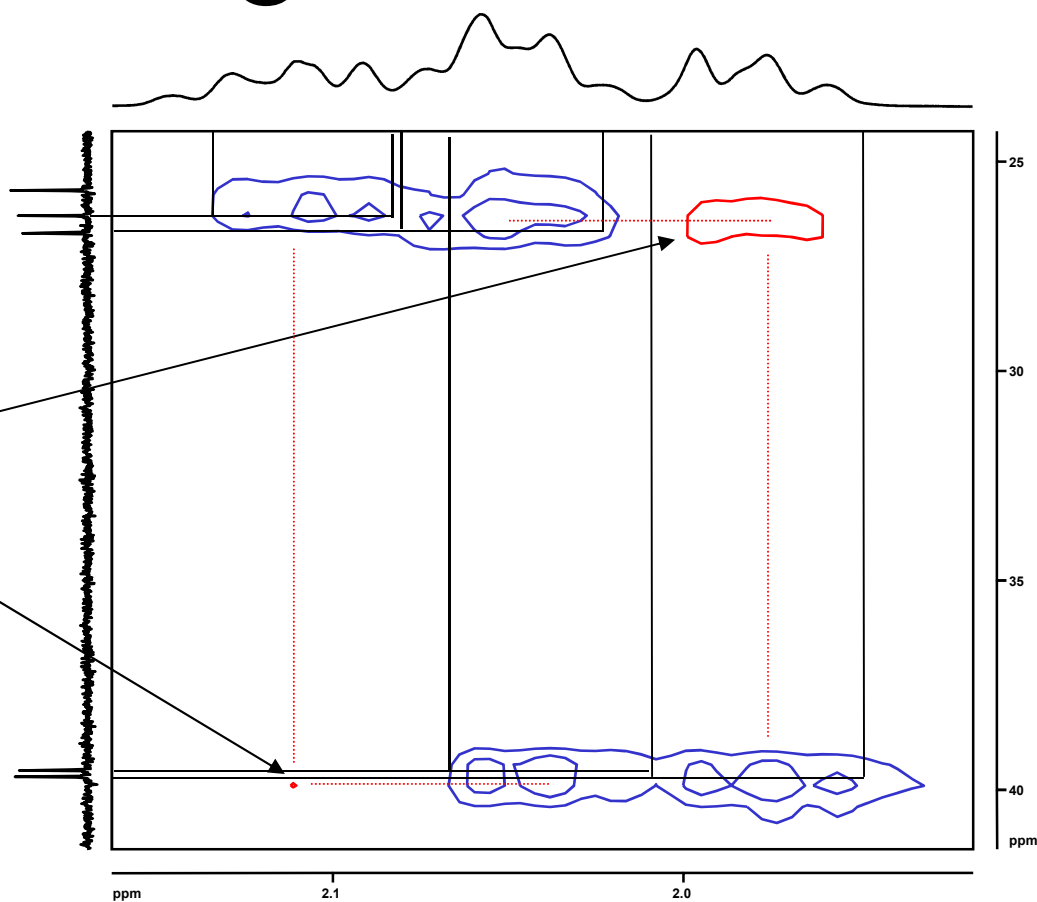
NMR assignment of an unknown by Roy Hoffman

# HSQC



# HSQC to separate & correlate $^1\text{H}$ signals

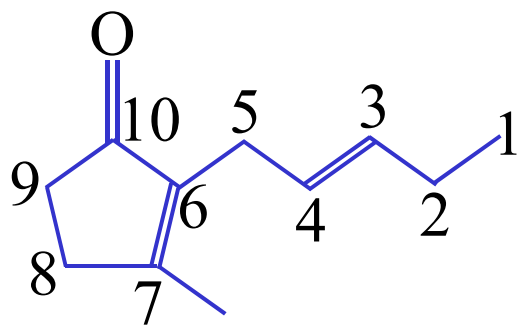
Use NOESY artifacts to determine proton connectivity







# Use correlation table



	H1	H2	H3	H4	H5	Me7	H8	H9
C1		2						
C2	2			3				
C3	3	2			3			
C4		3			2			
C5			3					
C6					2	3	3	
C7					3			3
Me7								
C8						3		2
C9							2	
C10					3	4	3	