

# Putting the pieces together

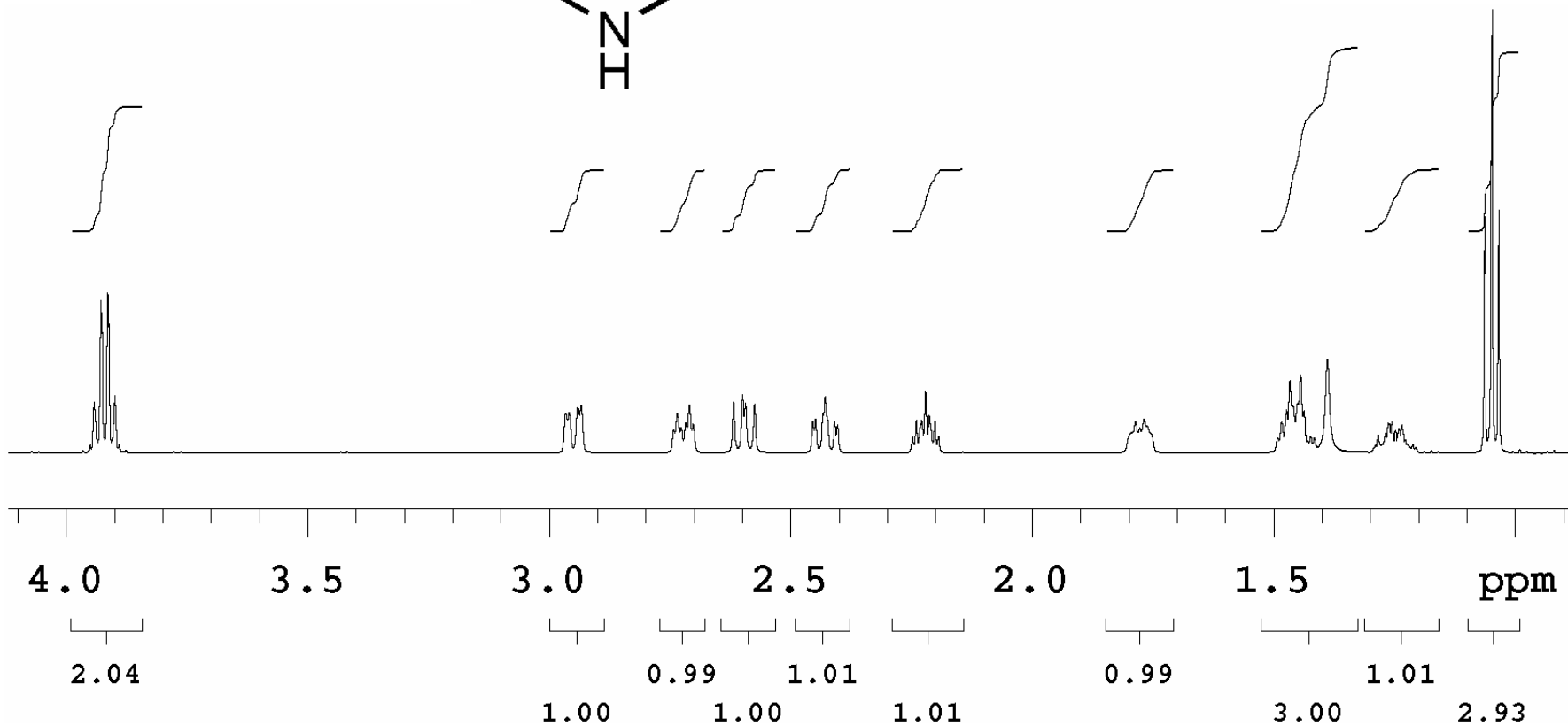
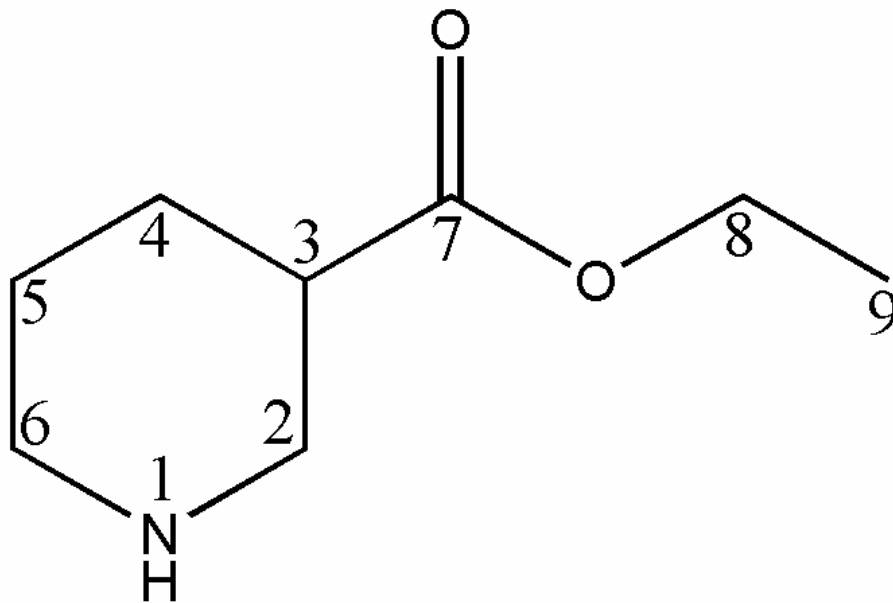


Image courtesy of Weston Boyd and Minh Nguyễn

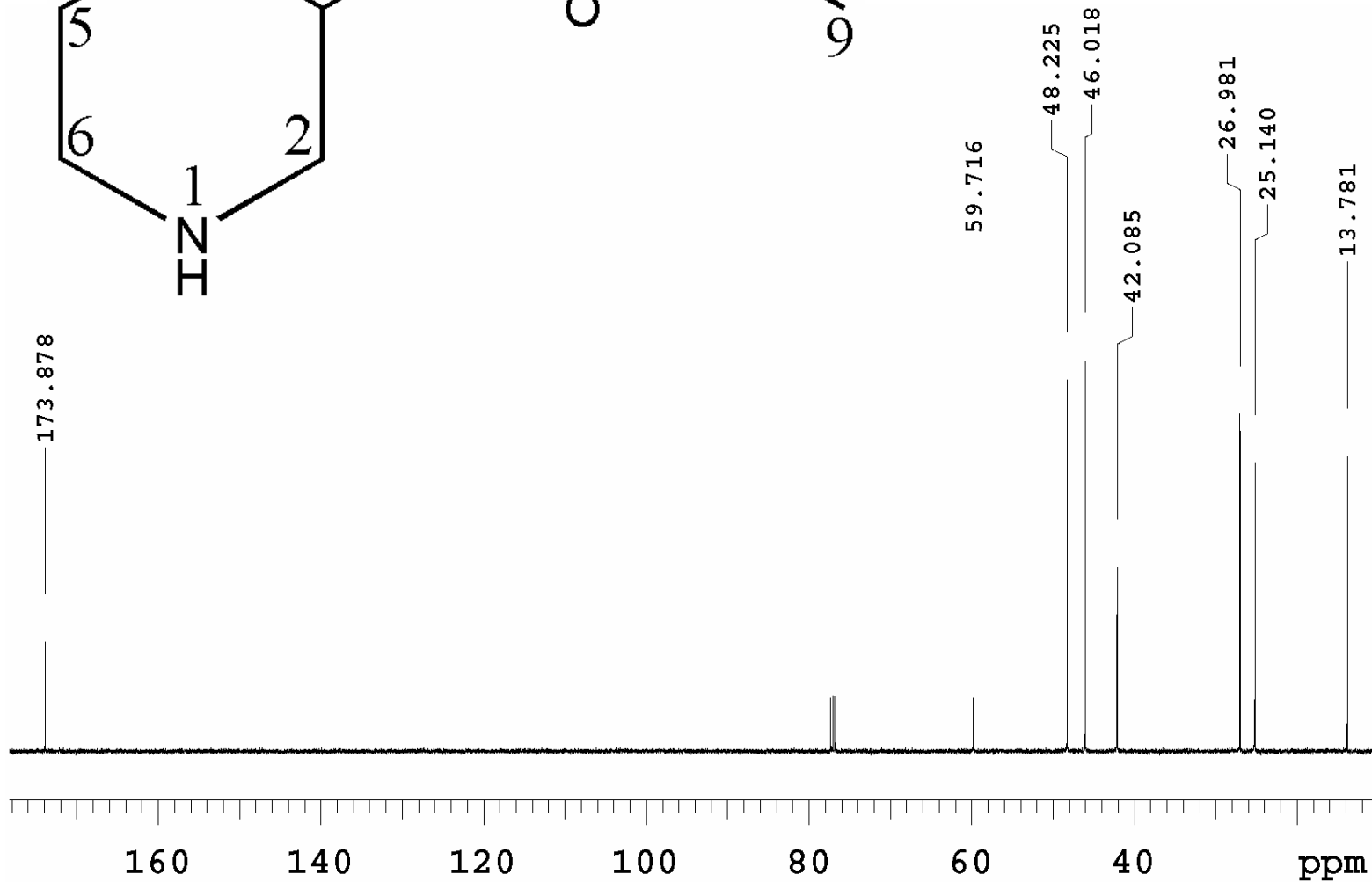
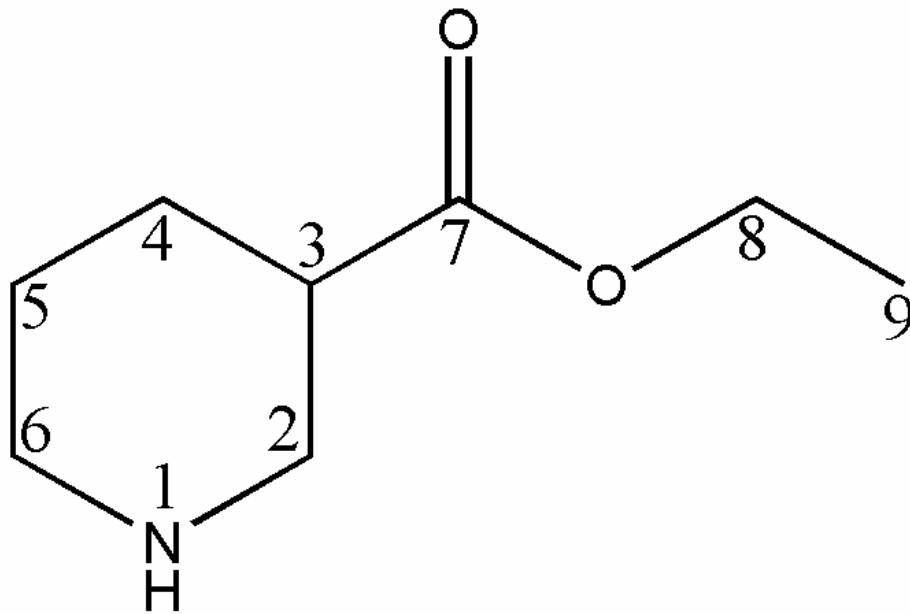
# Chemical Shifts

- Depend on electronegativity of neighbors

$^1\text{H}$  1-D



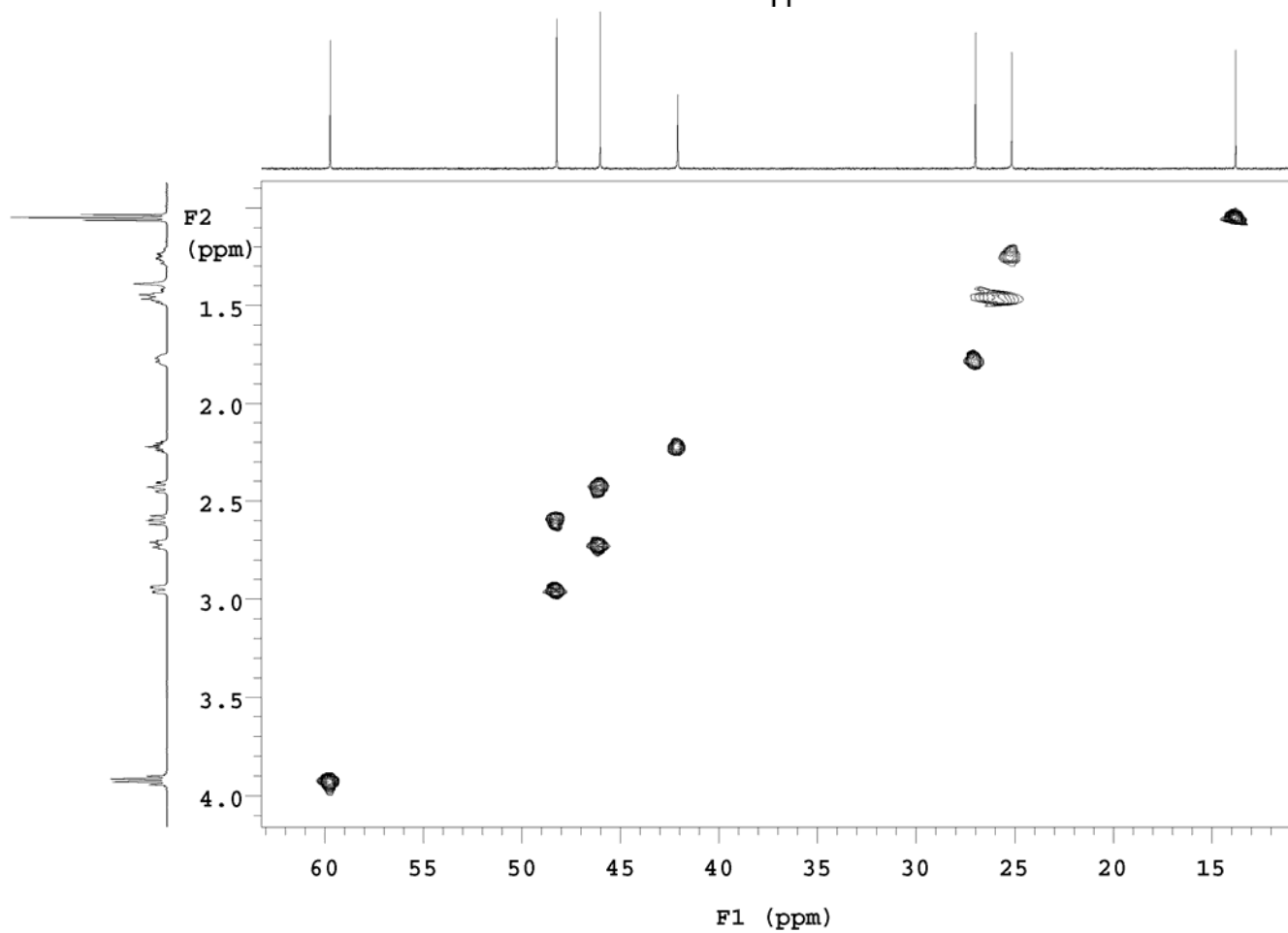
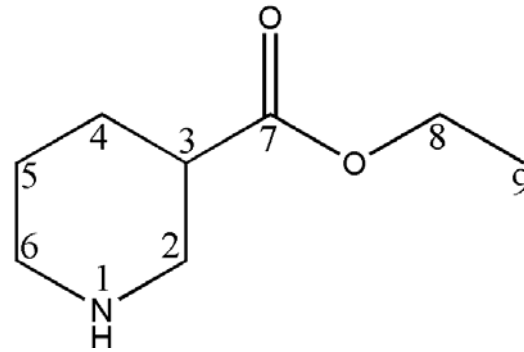
# $^{13}\text{C}$ 1-D



# Chemical Shifts

- Depend on electronegativity of neighbors
- Depend on axial versus equatorial position

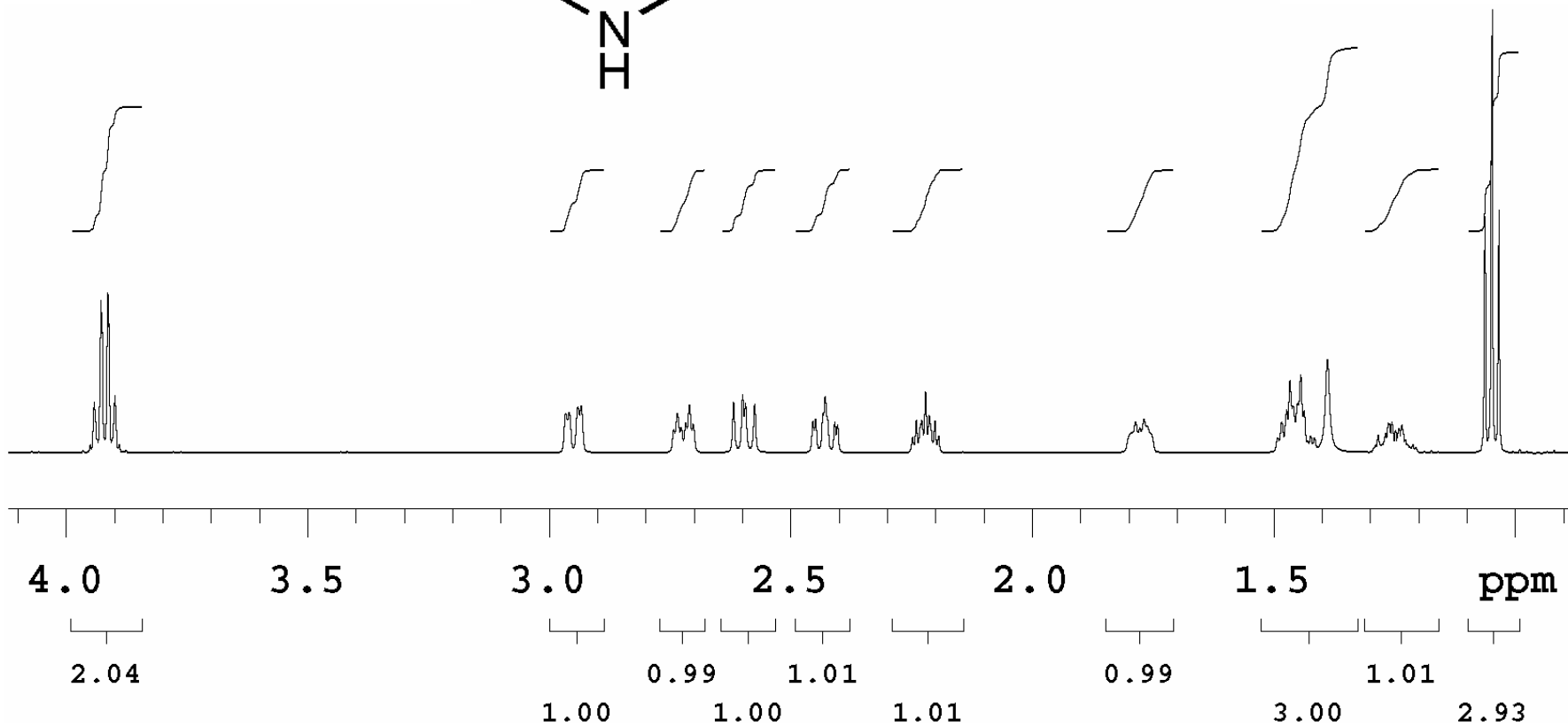
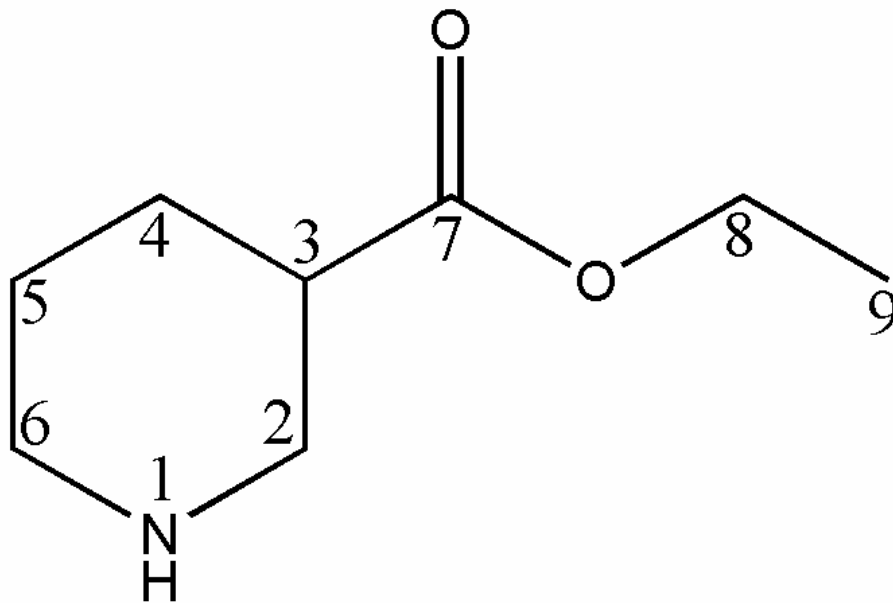
# $^1\text{H}$ - $^{13}\text{C}$ HMQC



# Chemical Shifts

- Depend on electronegativity of neighbors
- Depend on axial versus equatorial position
- Despite overlap, they can be read more accurately if we understand the couplings

$^1\text{H}$  1-D

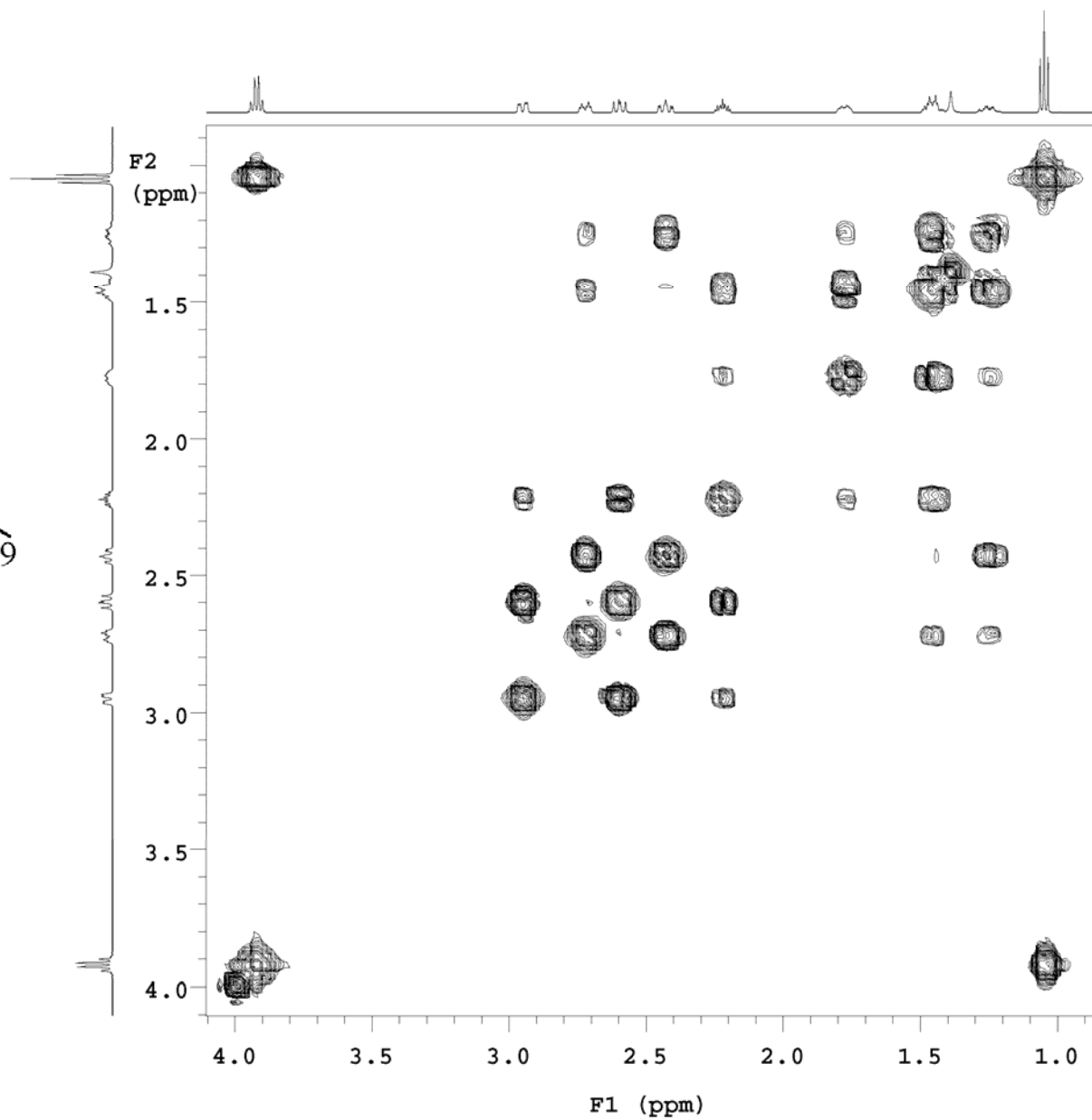
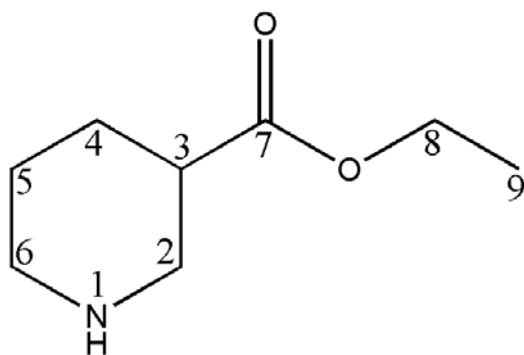




# Chemical Shifts

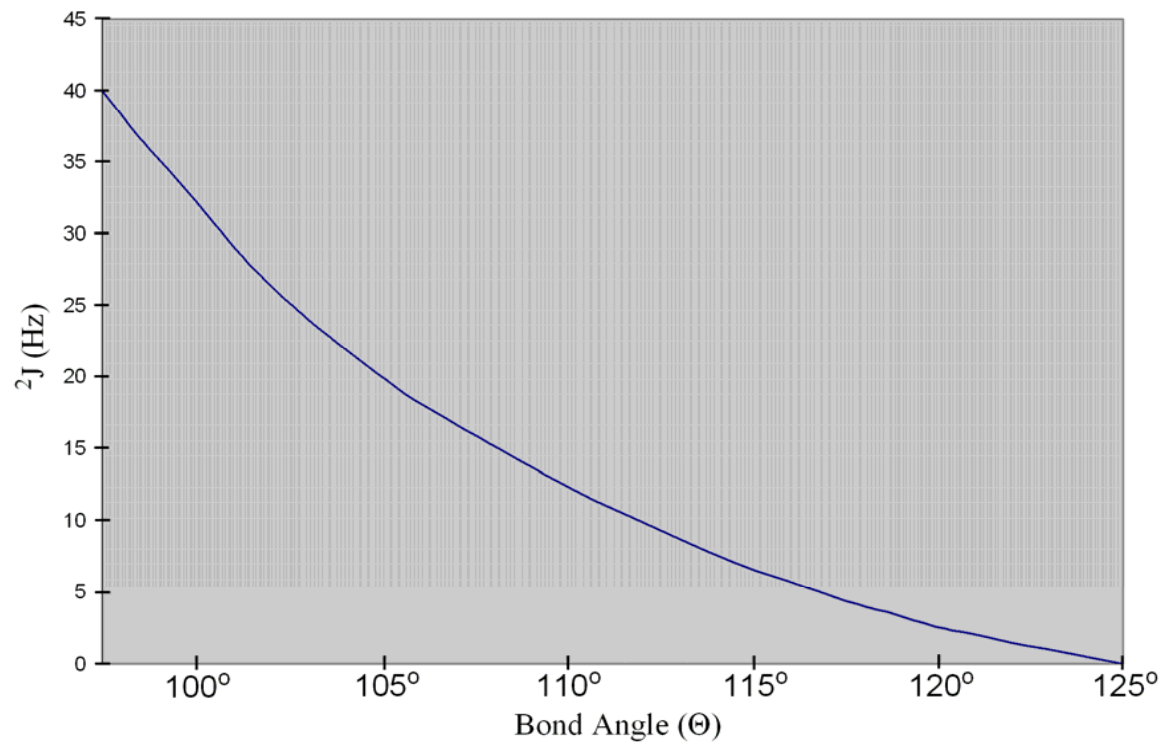
- Depend on electronegativity of neighbors
- Depend on axial versus equatorial position
- Despite overlap, they can be read more accurately if we understand the couplings
- Can be read accurately using gCOSY

# $^1\text{H}$ - $^1\text{H}$ gCOSY

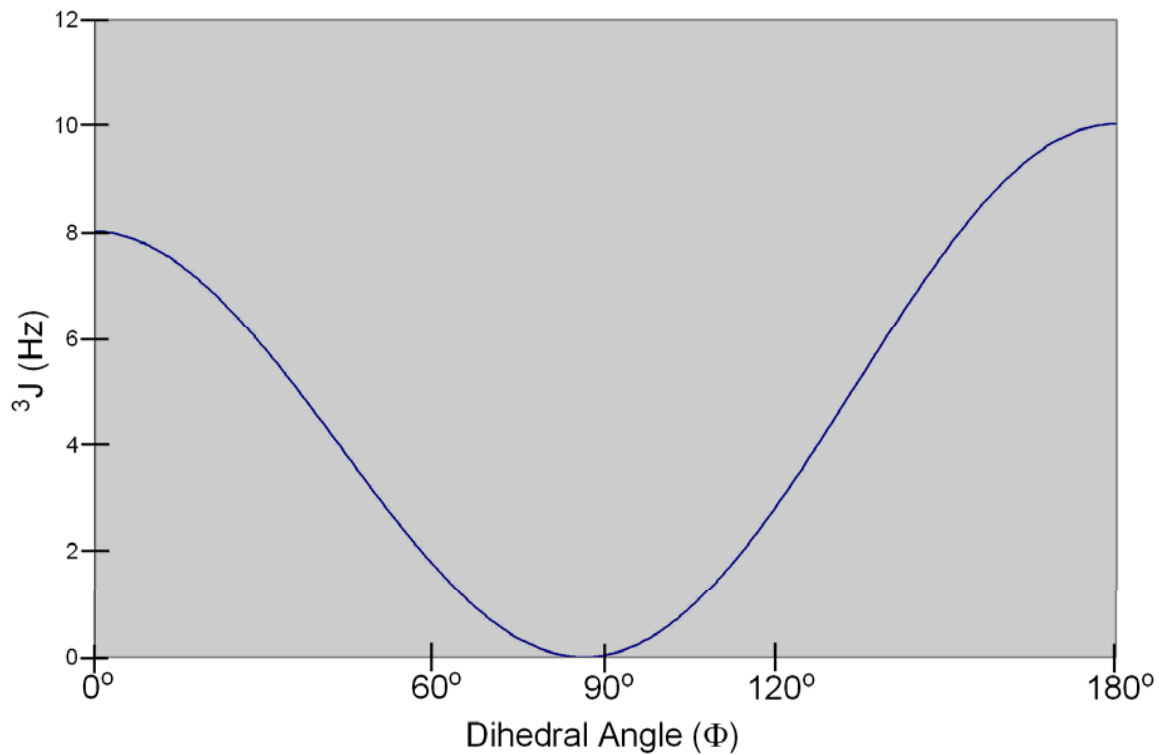


gCOSY cross peaks vary as a  
function of the J-coupling

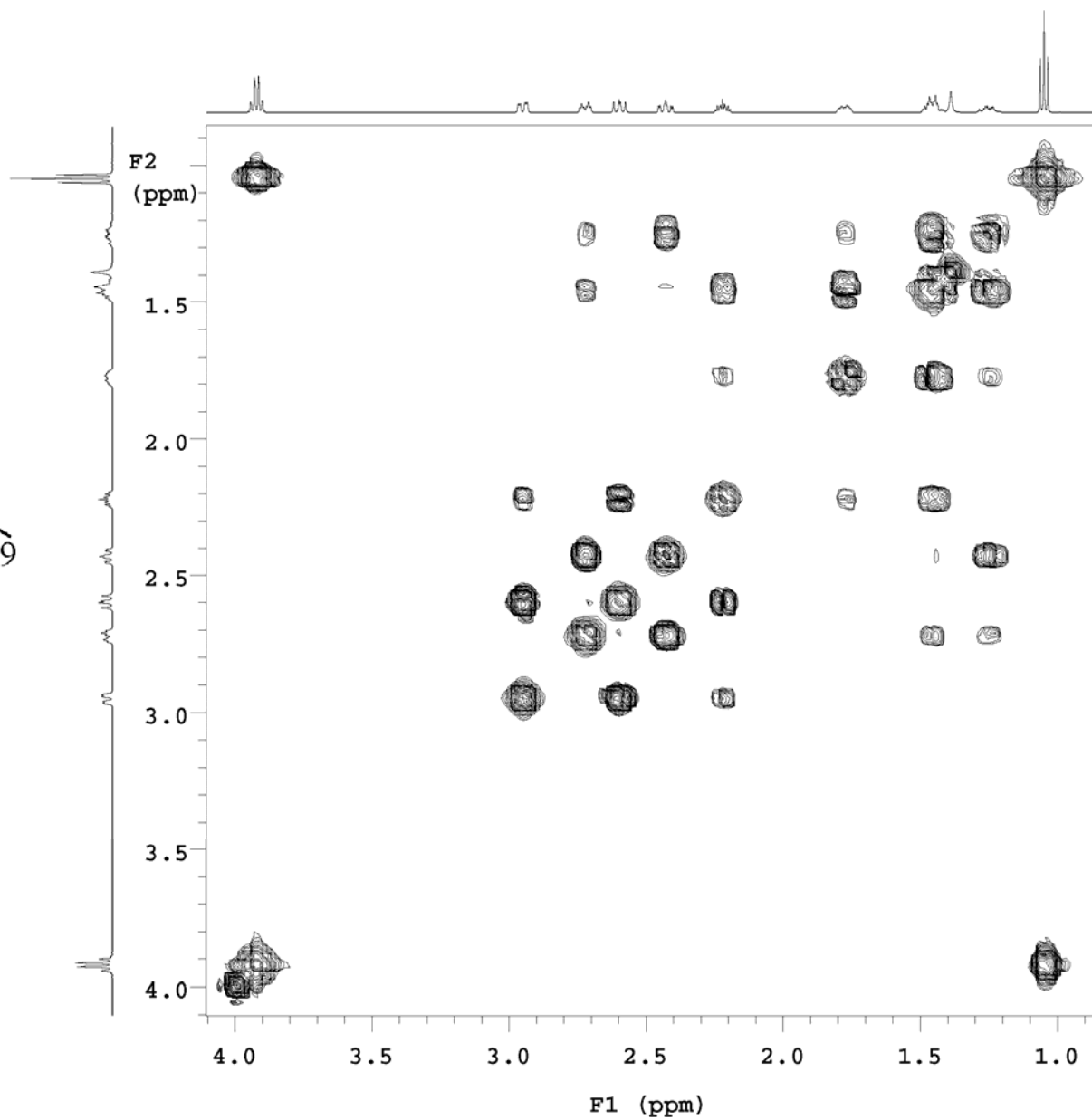
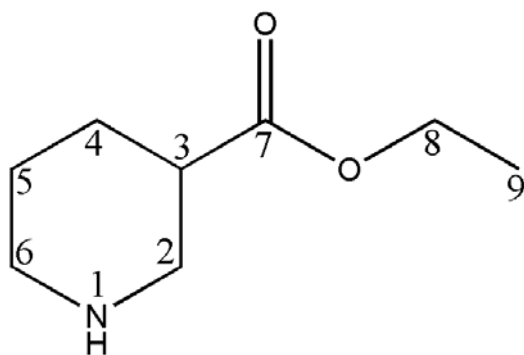
# $^2J$ Karplus relationship



# $^3J$ Karplus relationship



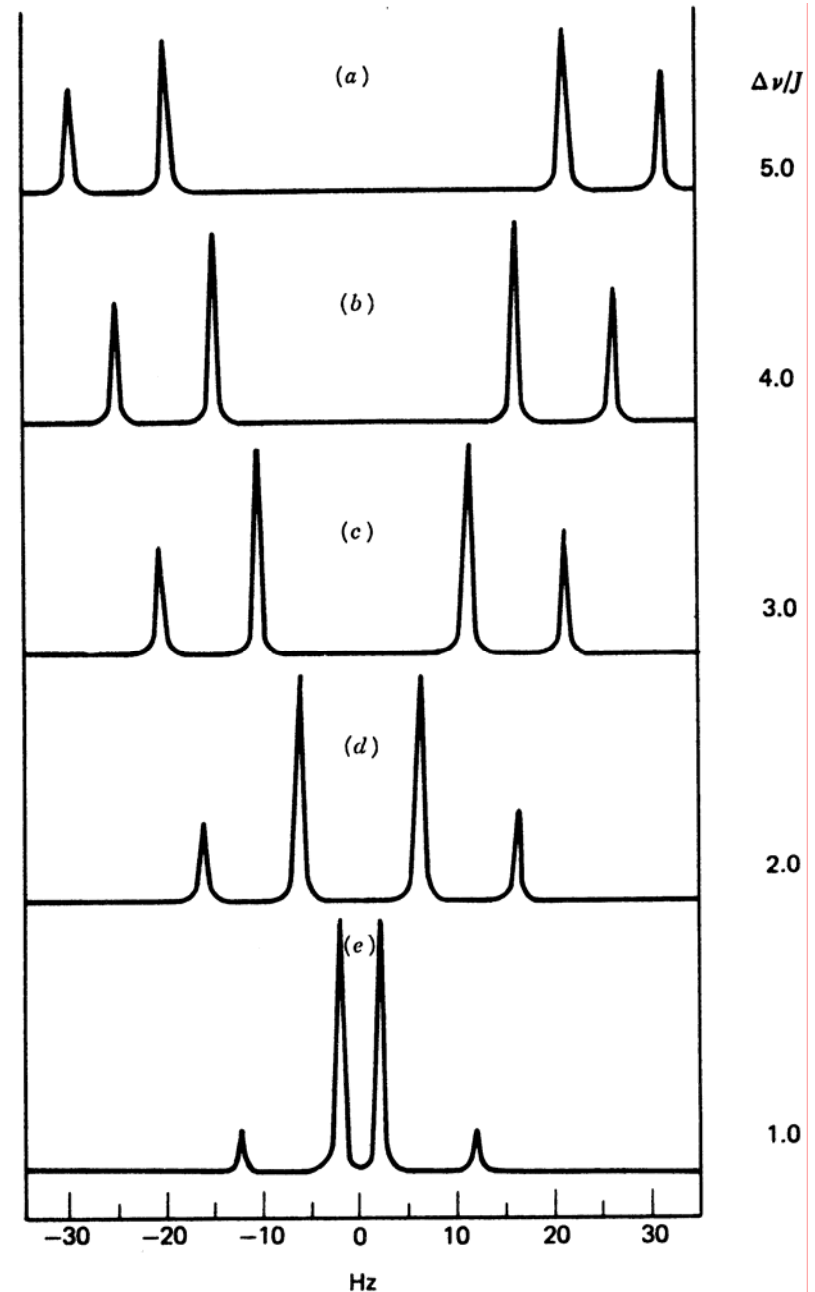
# $^1\text{H}$ - $^1\text{H}$ gCOSY



# Multiplicities tell us about

- Chemical exchange
- The number of nearby spins (2 & 3 bonds distant)
- $\Delta\delta$  versus J

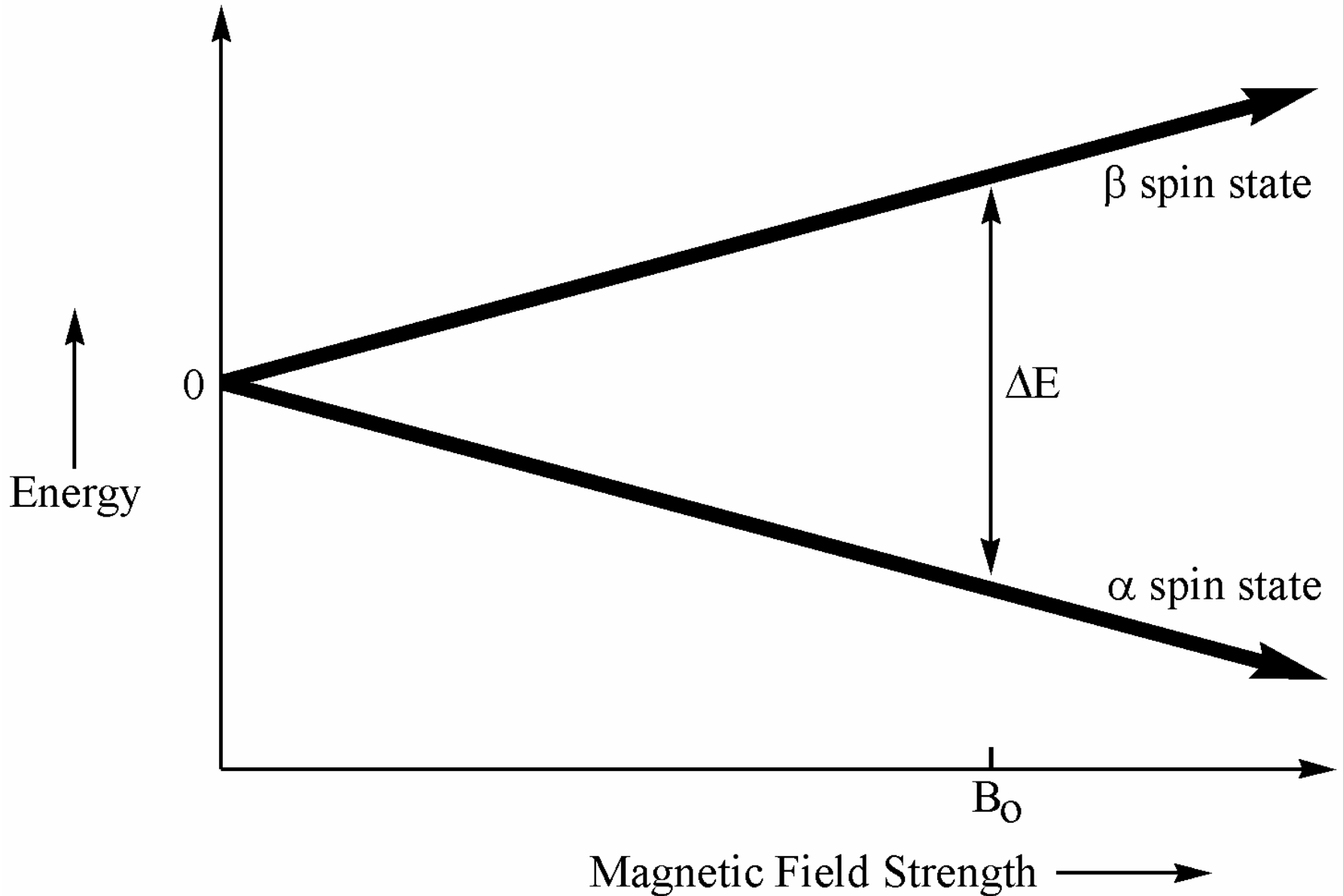
Dach Effect:  
As two  
coupled spins  
approach each  
other, their  
outer legs  
decrease

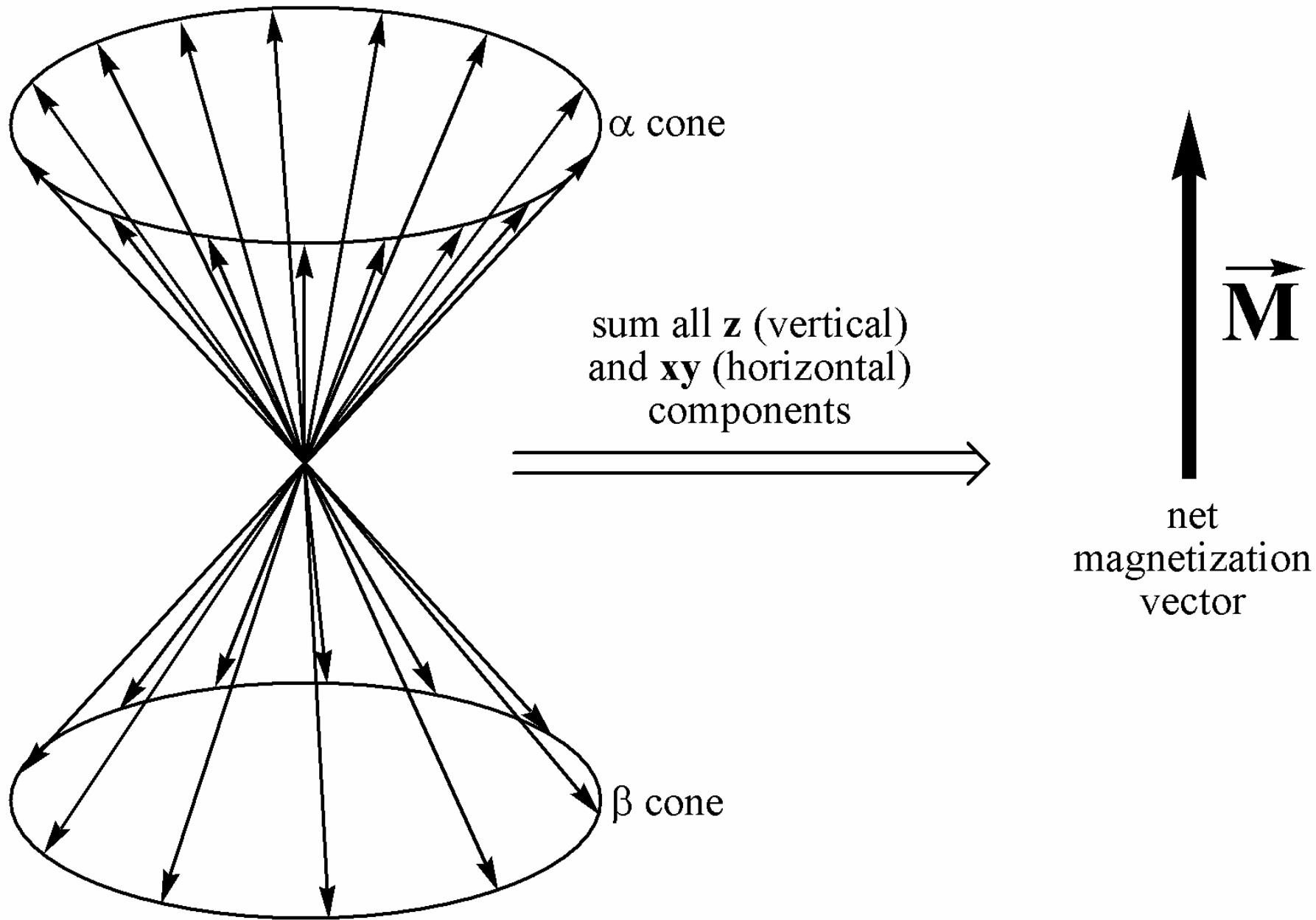


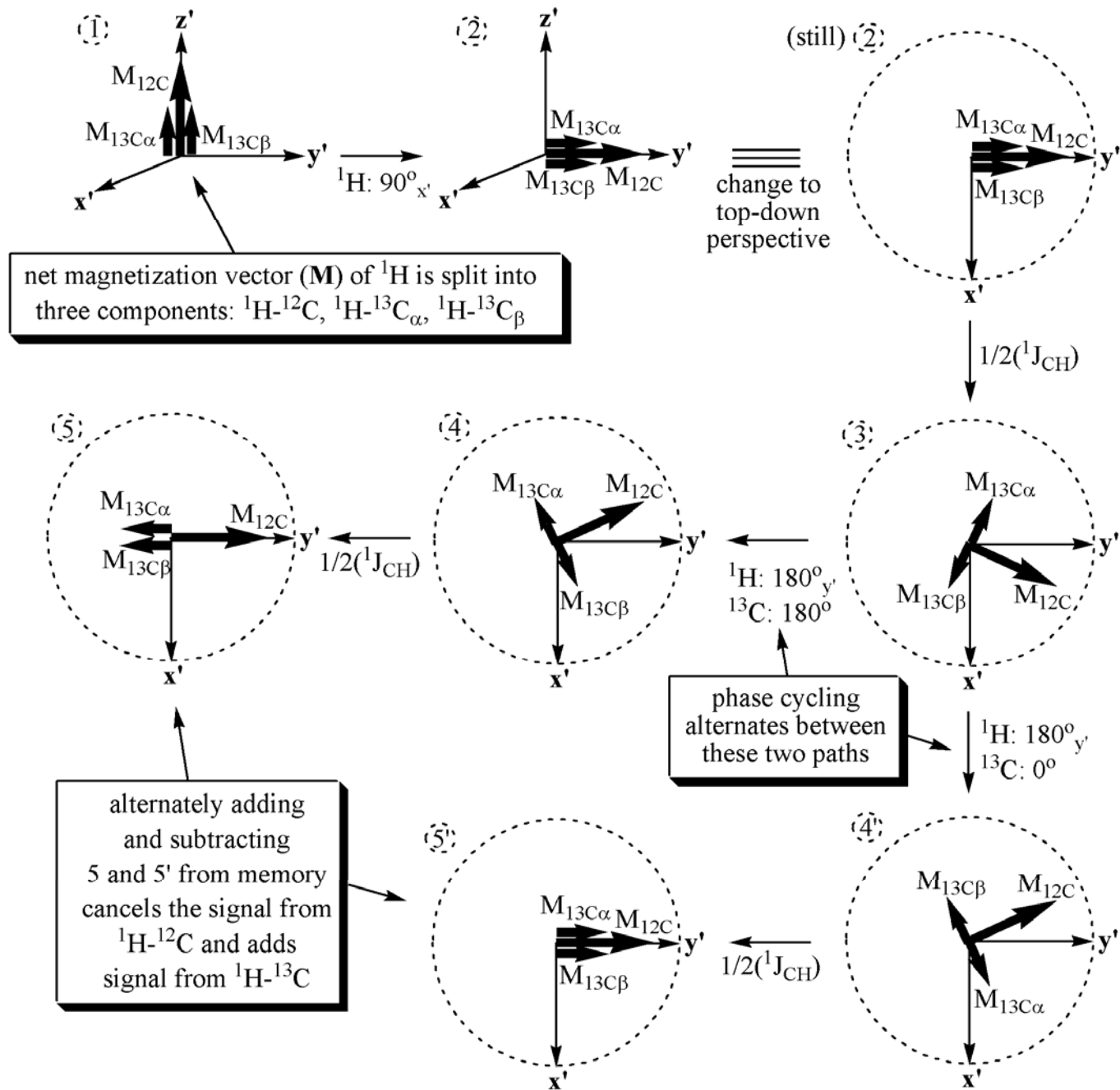


HMQC and HSQC cross peaks  
also vary as a function of J

# Zeeman Energy Diagram



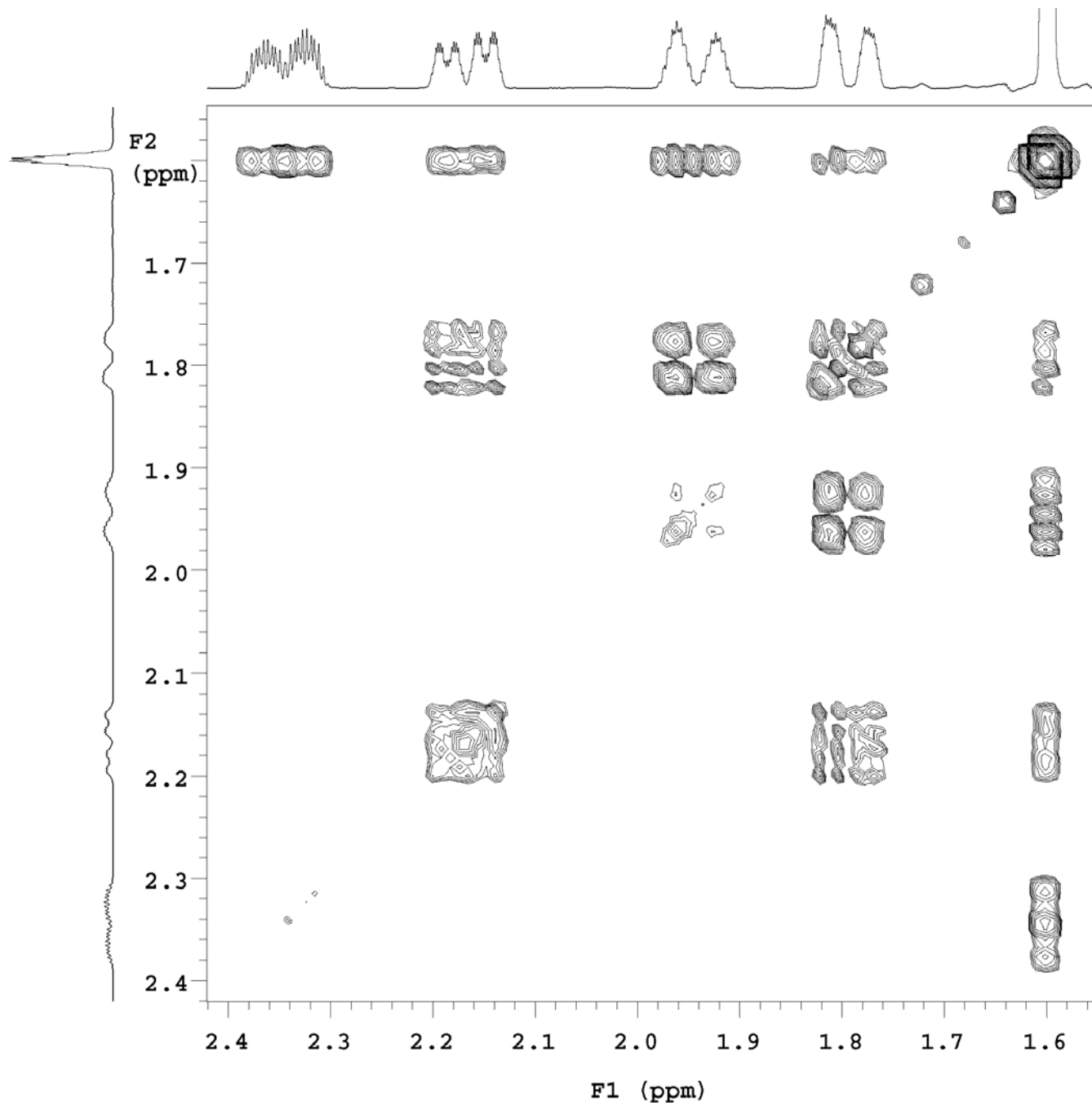


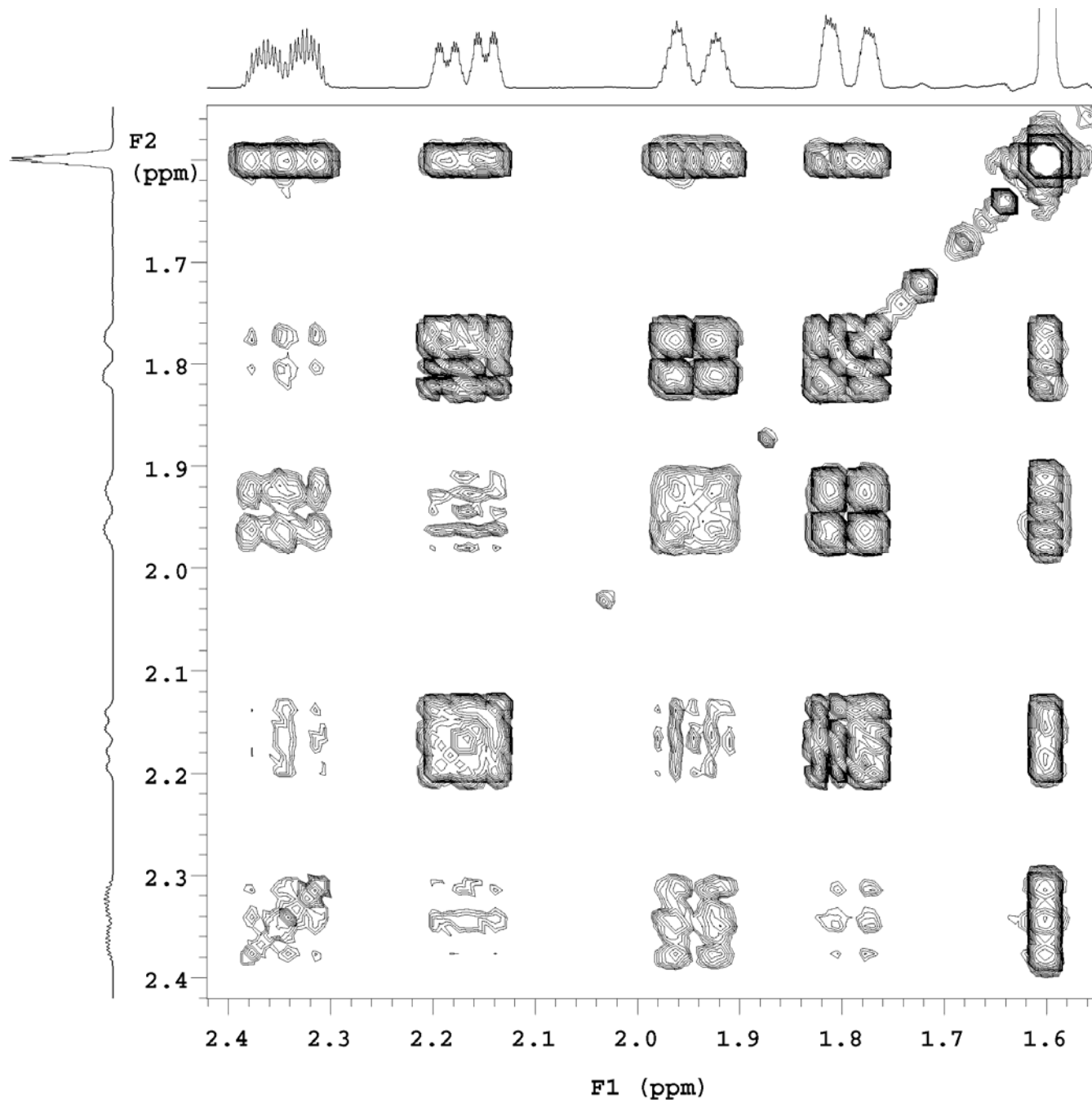


HSQC cross peak intensities	$^1J_{CH}$ upon which 1/2J HSQC delay is based				
observed $^1J_{CH}$ (Hz)	120	140	160	170	205
128/129	1.00	0.31	0.21	0.03	0.25
145	0.51	0.86	0.62	0.06	0.23
160-163	0.59	0.87	0.89	-	-
167-170	0.43	0.84	0.99	0.90	0.80
178	-	0.40	-	0.89	1.00
204	-	0.03	-	0.31	0.86

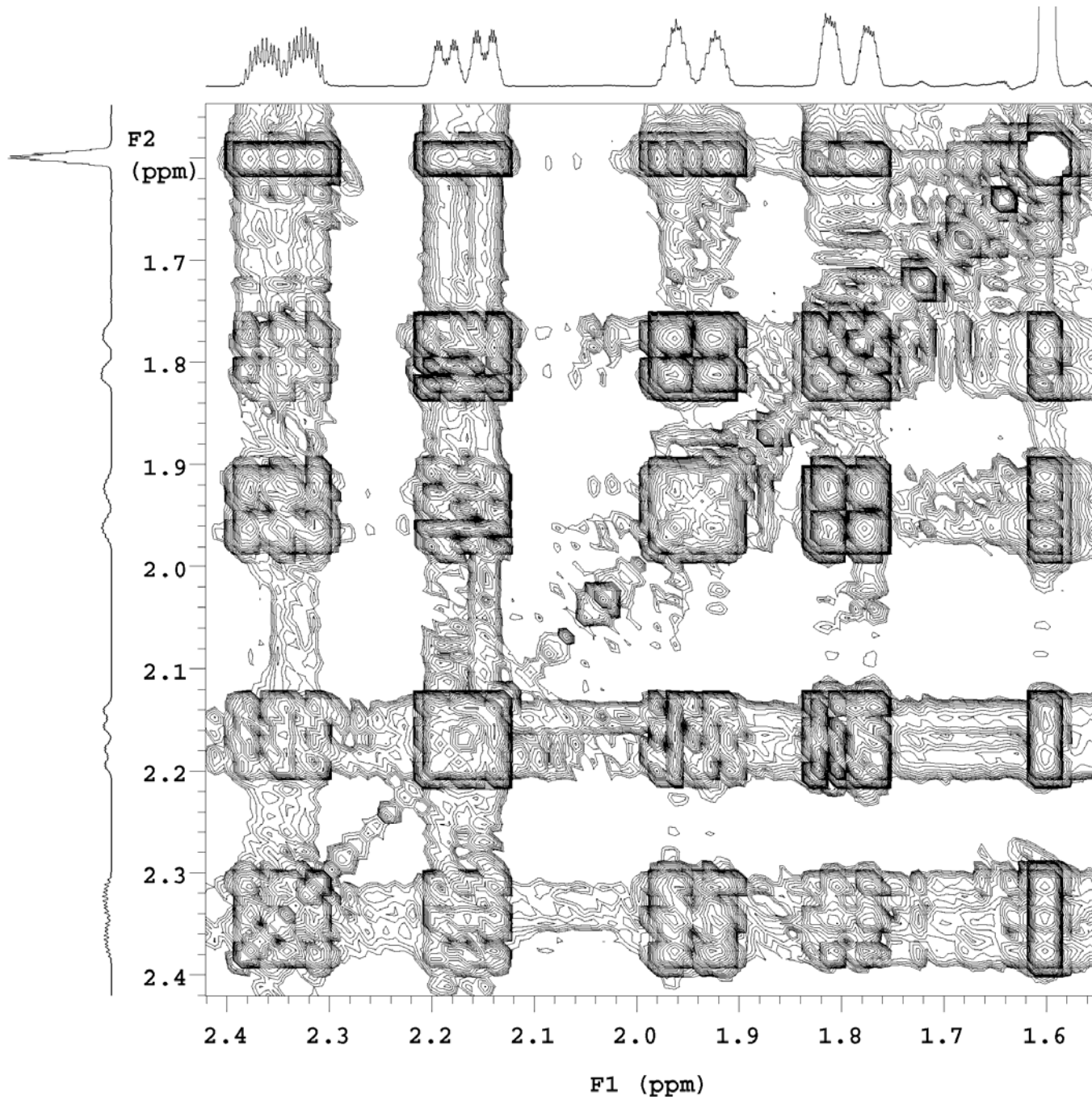
# Other problems with 2-D cross peaks intensities

- Should use volume integral
- Spread out resonances may generate visually weaker cross peaks









We need to figure out how to  
place non-protonated carbon  
atoms

# Bornyl acetate

