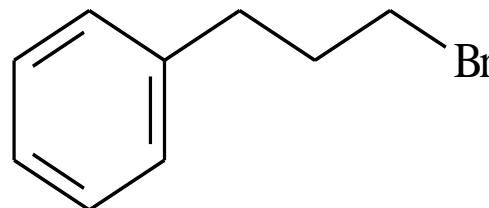


# Applications of PMR

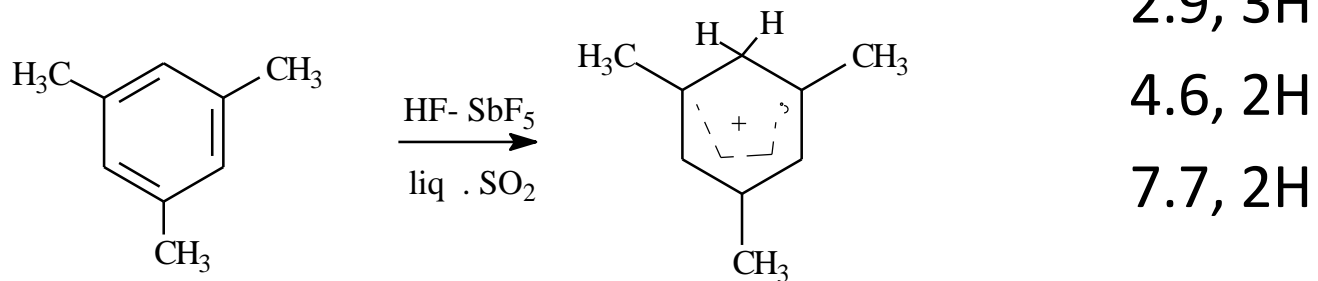
# Applications of $^1\text{H-NMR}$

## In structure elucidation

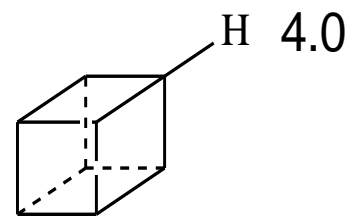
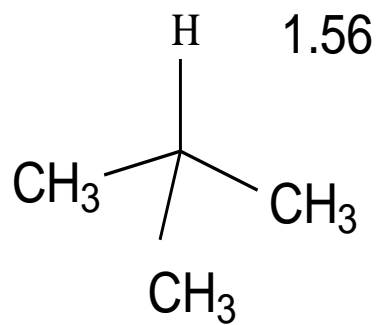
$\delta$  2.15, 2H, pentet  
2.75, 2H, triplet  
3.38, 2H, triplet  
7.22, 5H, singlet



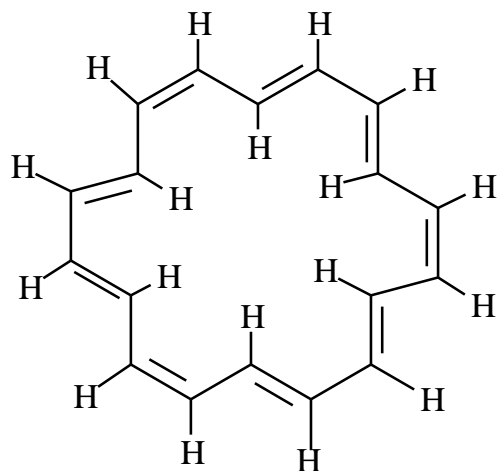
## In reaction mechanisms



# Electronegativity information



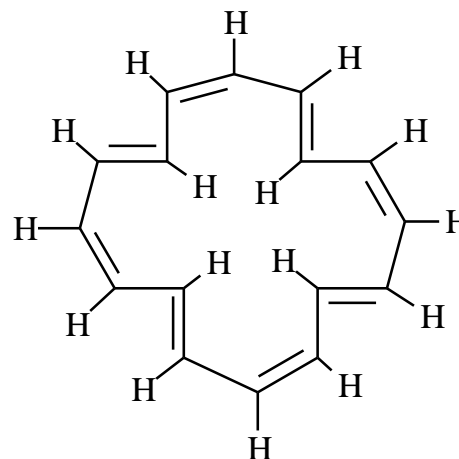
## In aromaticity and anti-aromaticity



[18] - Annulene ( Diatropic )

8.9, 12H

- 1.8, 6 H

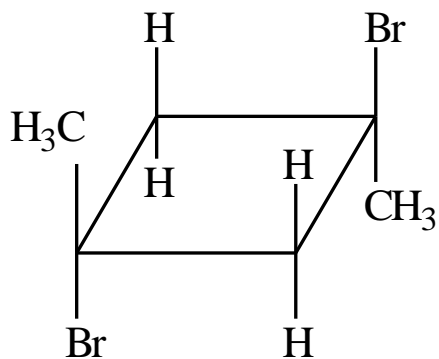


[16] -Annulene ( Paratropic )

10.56, 4 H

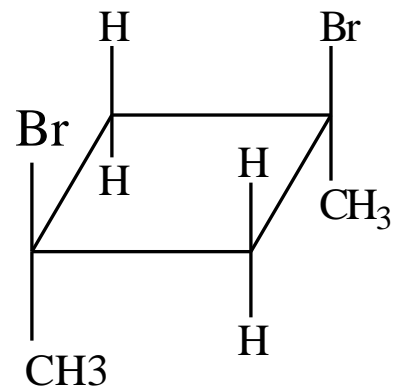
5.33, 12 H

## In stereochemistry



2.13, 6 H, s

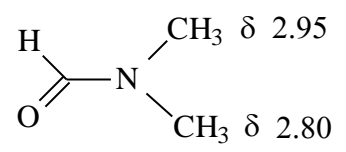
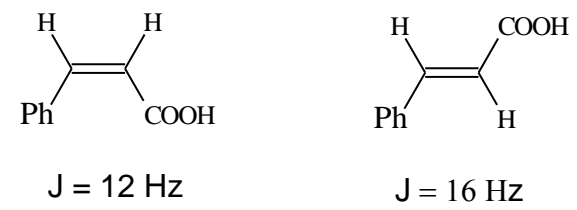
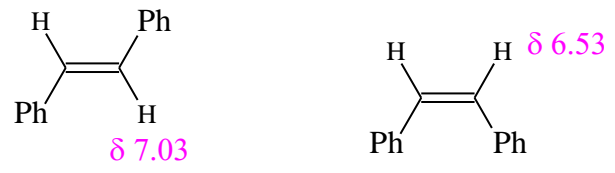
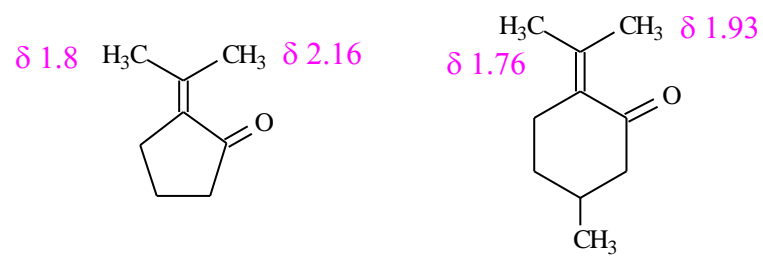
3.21, 4 H, s

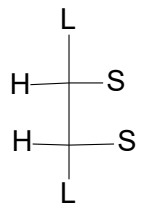


1.88, 6 H, s

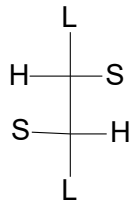
2.84, 2 H, d

3.54, 2 H, d

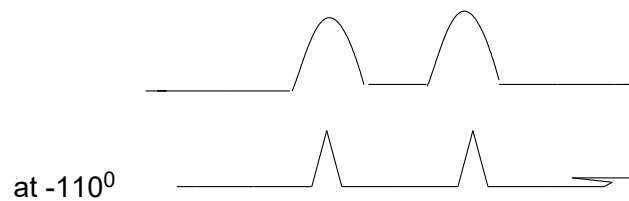
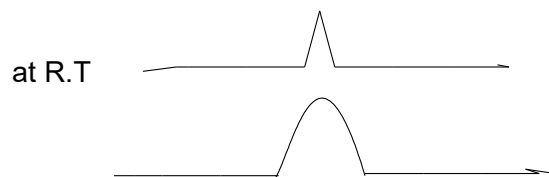
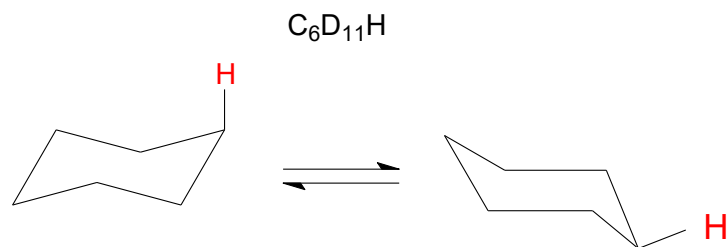




$J_{\text{H,H}} = 10 \text{ Hz}$   
( $180^\circ$ )



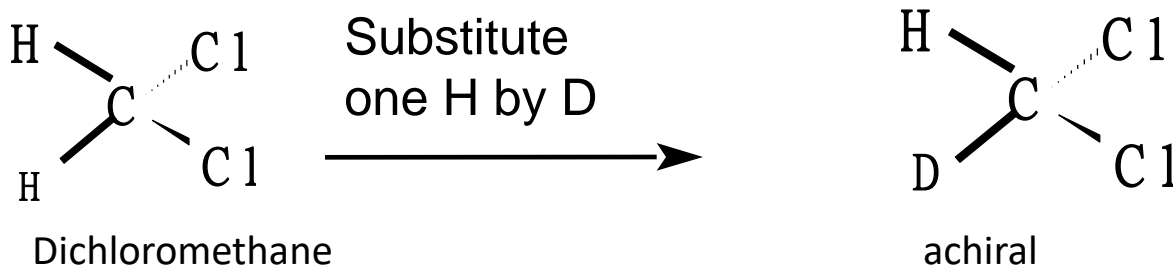
$J_{\text{H,H}} = 4.5 \text{ Hz}$   
( $60^\circ$ )





# Homotopic atoms or groups

- Homotopic atoms or groups

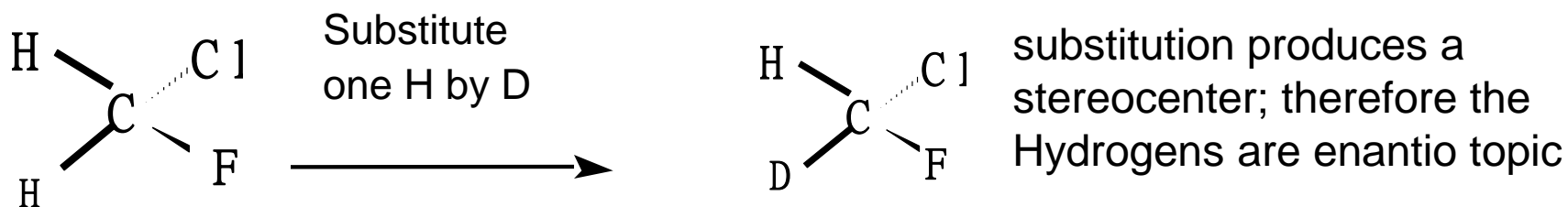


- Dichloromethane  
achiral

- Substitution does not produce a stereo centre,  
therefore hydrogens are achiral

– homotopic atoms or groups have identical chemical shifts under all conditions

# Enantiotopic groups



- Chloro fluoromethane (Achiral)

Chiral

- enantiotopic atoms or groups have identical chemical shifts in achiral environments
- they have different chemical shifts in chiral environments

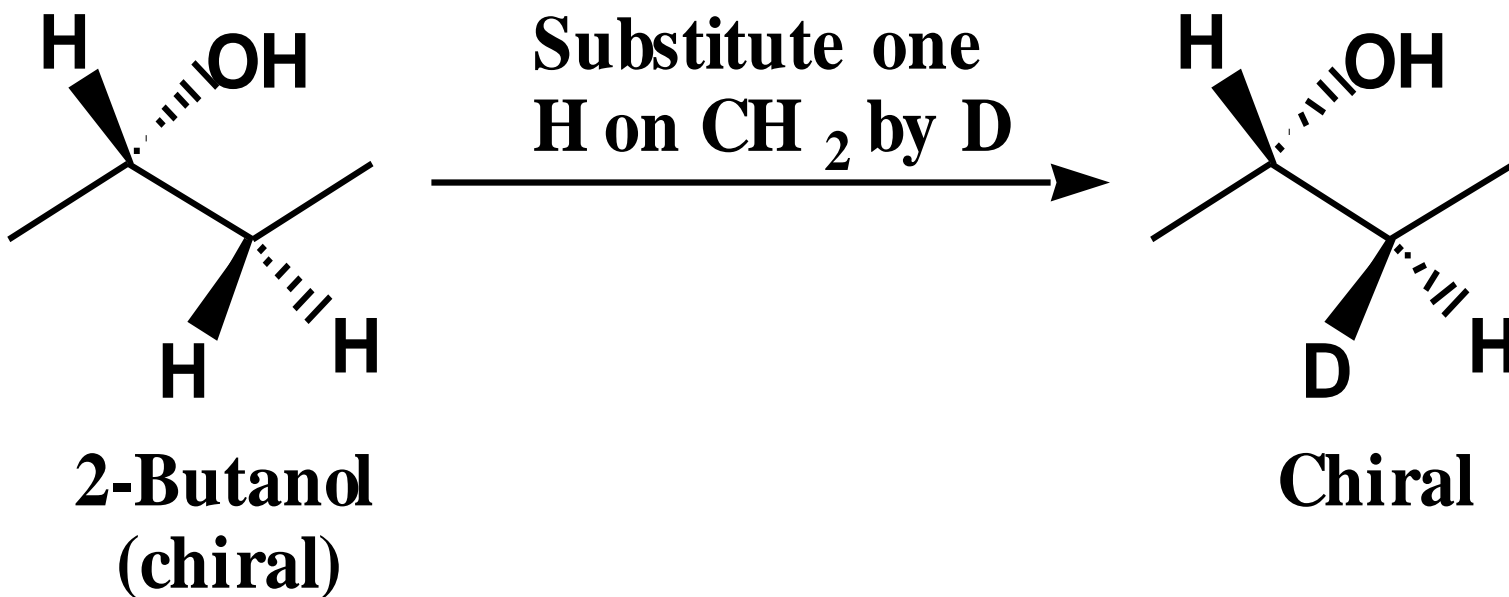
Diastereotopic groups:

H atoms on C-3 of 2-butanol are diastereotopic.

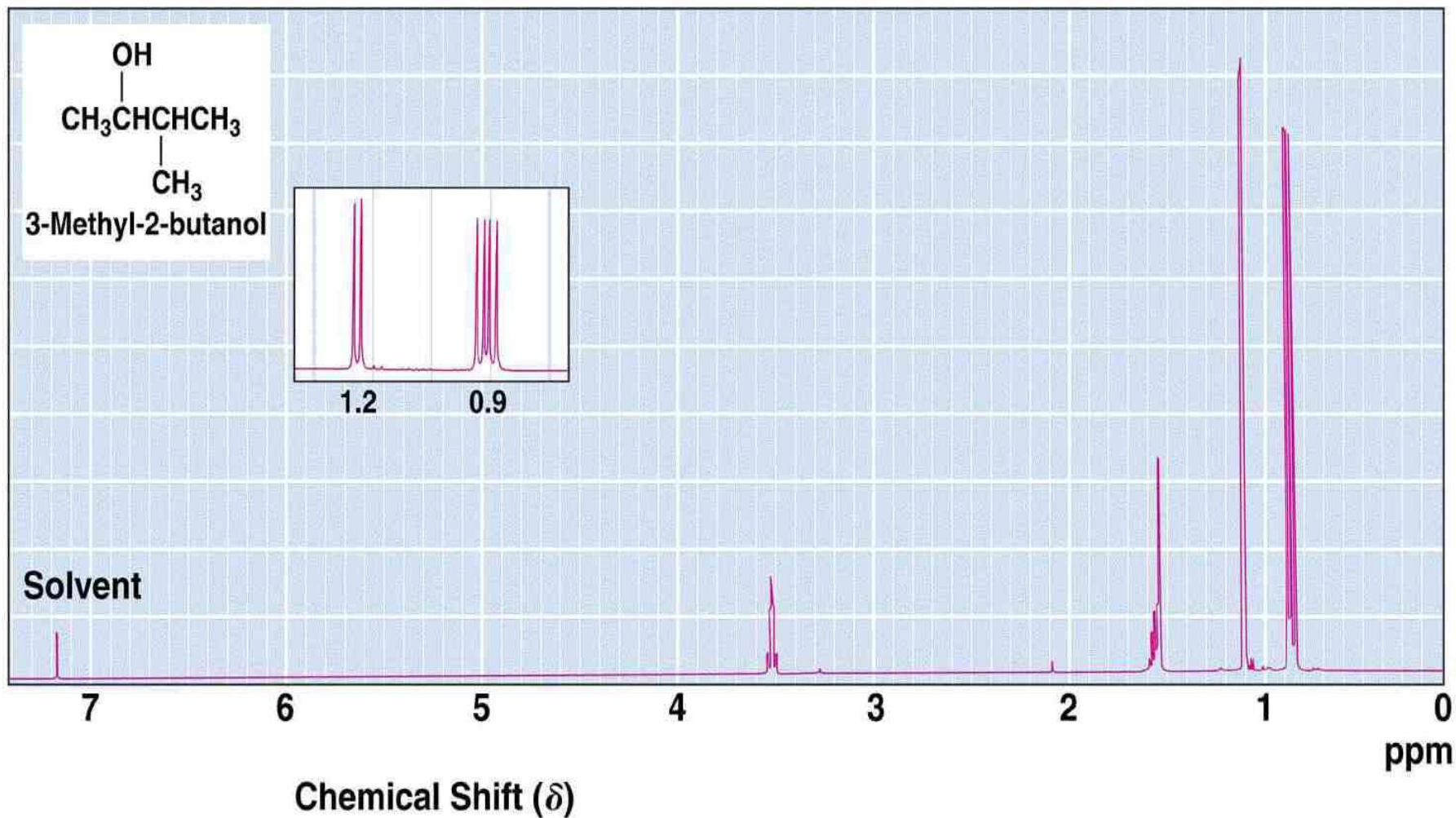
substitution by deuterium creates a chiral center.

because there is already a chiral center in the molecule,  
diastereomers are now possible

**diastereotopic hydrogens have different chemical shifts under all conditions**

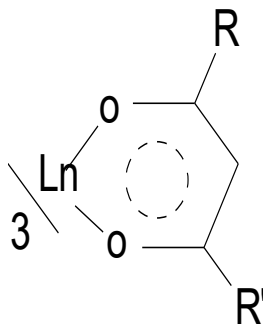


$^1\text{H}$ -NMR spectrum of 3-methyl-2-butanol  
the methyl groups on carbon 3 are diastereotopic and  
appear as two doublets



# <sup>1</sup>H-NMR in optical purity

- Shift reagents would distinguish enantiomeric protons.
- Shift reagents generally used are europium and praseodymium complexes of Hfod (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione) and/or HDPM (dipivalomethane)

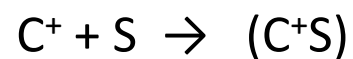
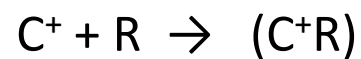


R, R<sup>1</sup> = t - butyl

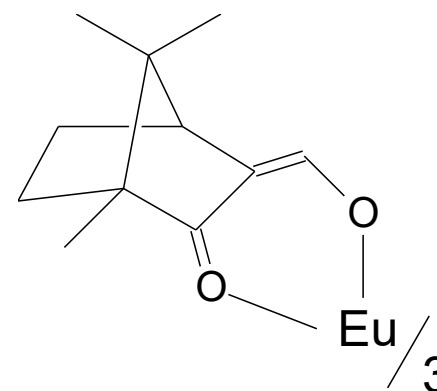
R = t - butyl, R<sup>1</sup> = perfluoroprop

- Chiral shift reagent

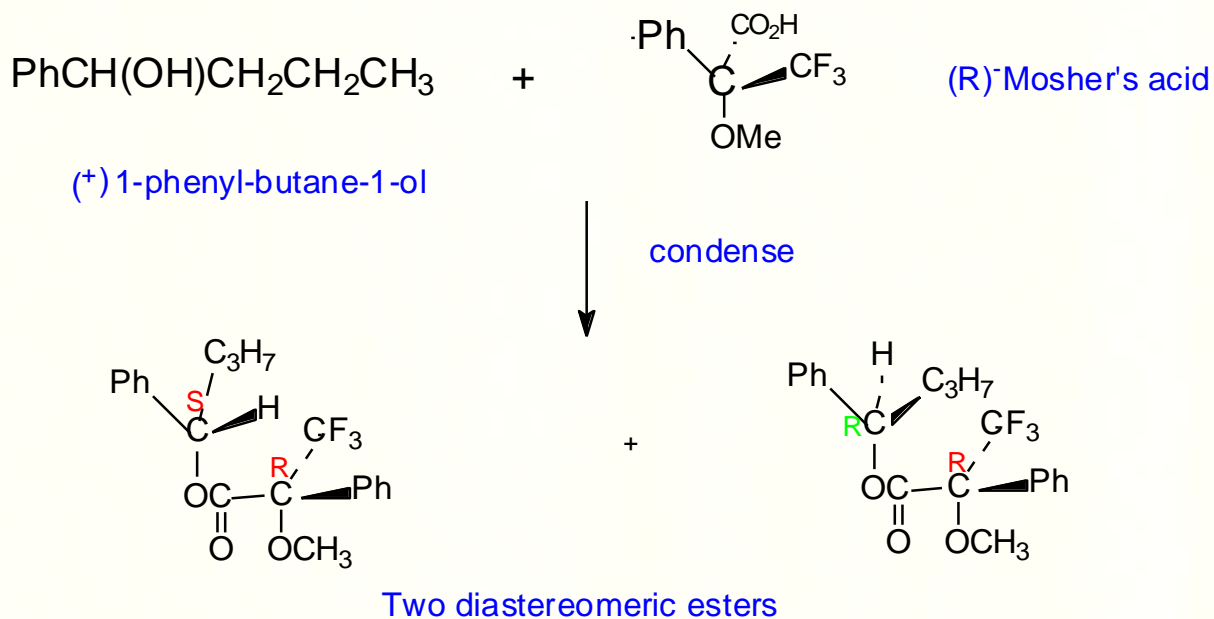
tris[3-(tert-butylhydroxymethylene)-d-camphorato]europium III



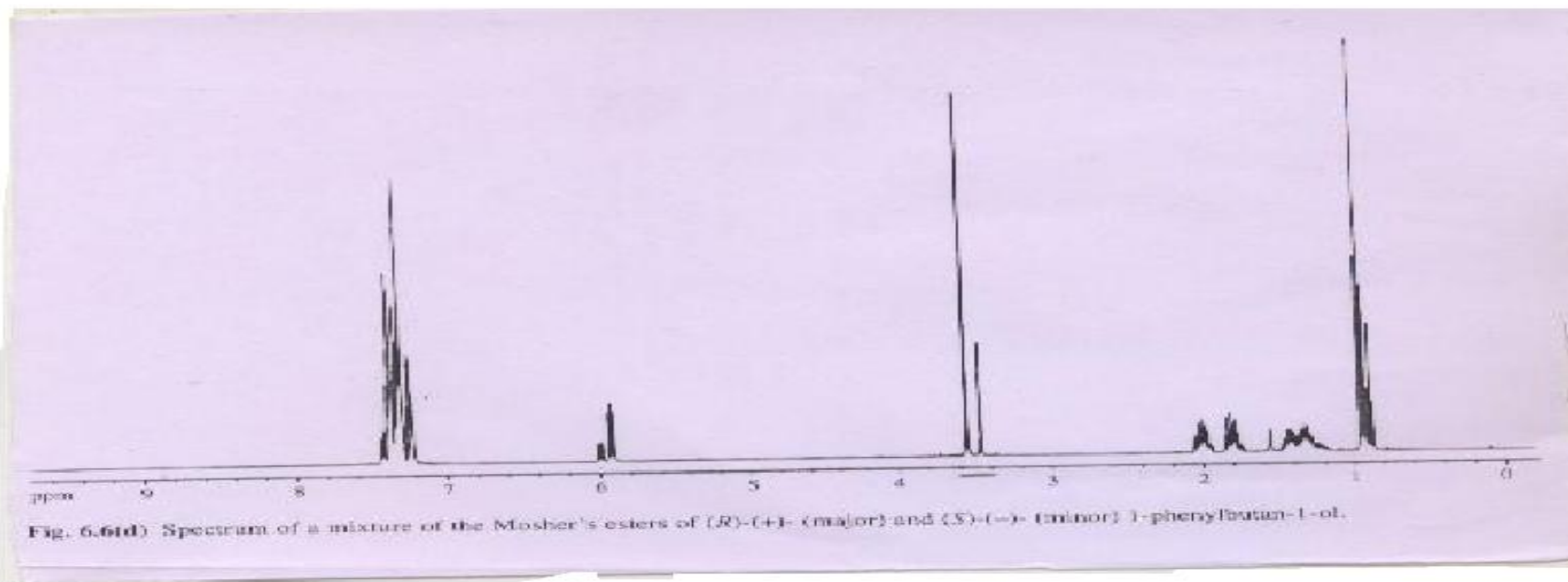
$$E P = \frac{nR - nS}{nR + nS}$$



# Chiral derivatization of ( $\pm$ ) 1-phenyl-butane-1-ol with (R)Mosher's acid



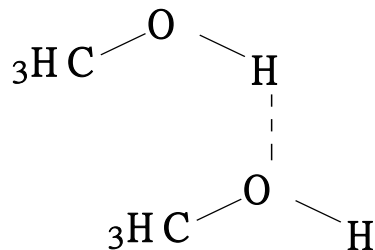
The comparison of OCH<sub>3</sub> signals in <sup>1</sup>HNMR of (RR) and SR diastereomers shows different chemical shifts and also different signal heights indicating the ratio of diastereomers and indirectly the ratio of enantiomers in the mixture.



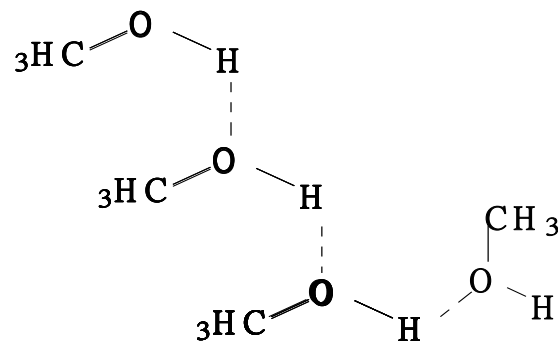


# Hydrogen Bonding (Intermolecular)

- The shift position of OH proton varies depending on hydrogen bonding
- In polymeric associated alcohols the signal is deshielded



dimeric association

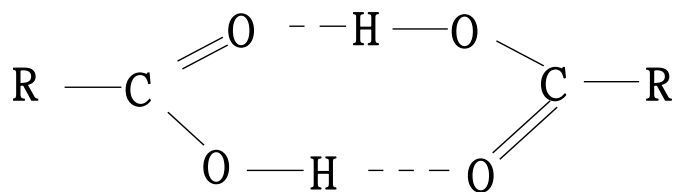


polymeric association

- if alcohol is dissolved in a non H-bonding solvent at high dilution ( $\text{CCl}_4$ , DMSO) the OH signal moves up field (0.5 -4.0  $\delta$ )
- Increase of temperature decreases H-bonding and moves the signal up field.

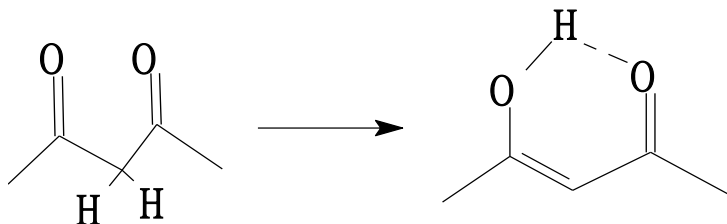
# H-bonding in carboxylic acids

- Carboxylic acids exist in solution as hydrogen bonded dimers
- The down field signal for COOH proton (10-13 $\delta$ ) is a measure of hydrogen bonding



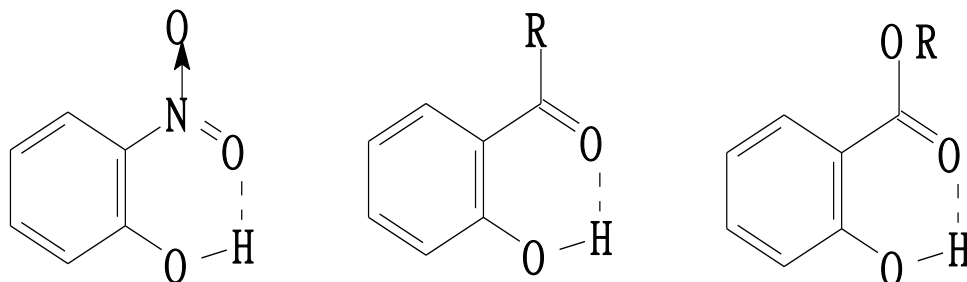
dimeric association

- Dilution and increase of temperature has no effect on this dimeric association and the NMR signal is little affected.
- **Intramolecular Hydrogen bonding:**
- Highly deshields the hydroxy proton signal ( 11-16  $\delta$  )

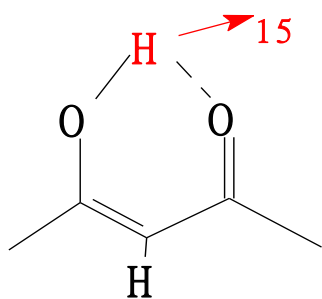


## Intramolecular Hydrogen bonding:

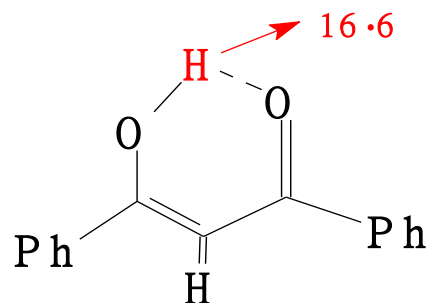
- Chelation of OH proton moves the signal downfield ( $\sim 11 \delta$ )



- Dilution has no effect on intramolecular H-bonding
- Keto-enol tautomerism: enolic proton is more deshielded than alcoholic protons



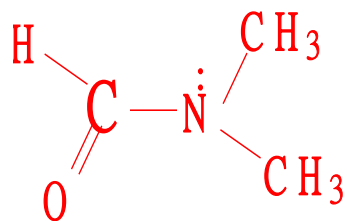
enol of acetylacetone



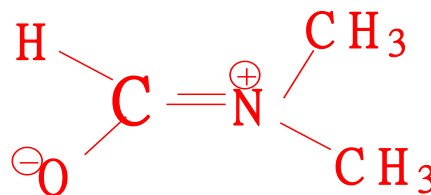
enol of dibenzoylmethane

# Hindered rotation

- Dimethyl formamide shows two different chemical shifts for the two methyls at room temperature
- At  $>120^{\circ}\text{C}$  the two signals coalesce and gives a singlet



Singlet for two methyl's  $2.8\delta$



Two signals for two methyl's at  $2.8$  and  $2.95\delta$

**Thank you for your attention**