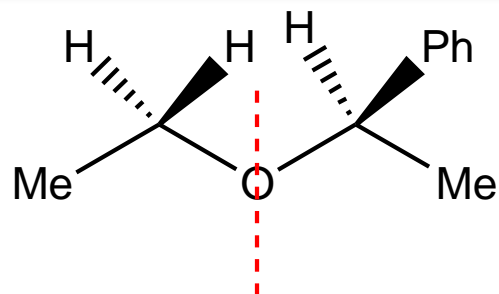


Organic Spectroscopy- Revision

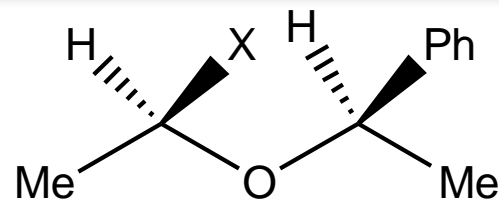
Professor Diwan S Rawat

Department of Chemistry, University of Delhi
Associate Editor-Nature Scientific Reports & RSC Advances

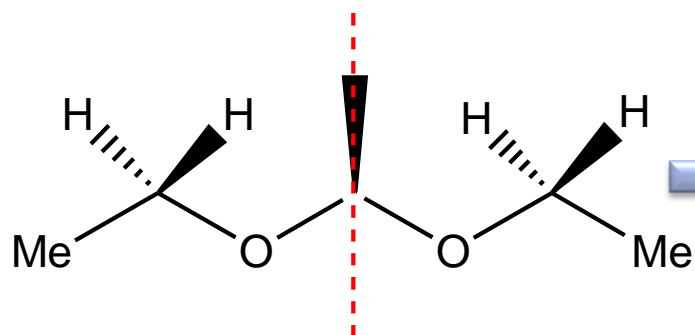
Distereotopicity and Symmetry



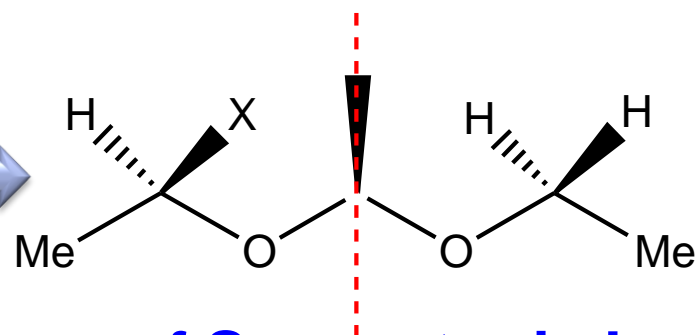
No Plane of Symmetry



6 NMR Signals



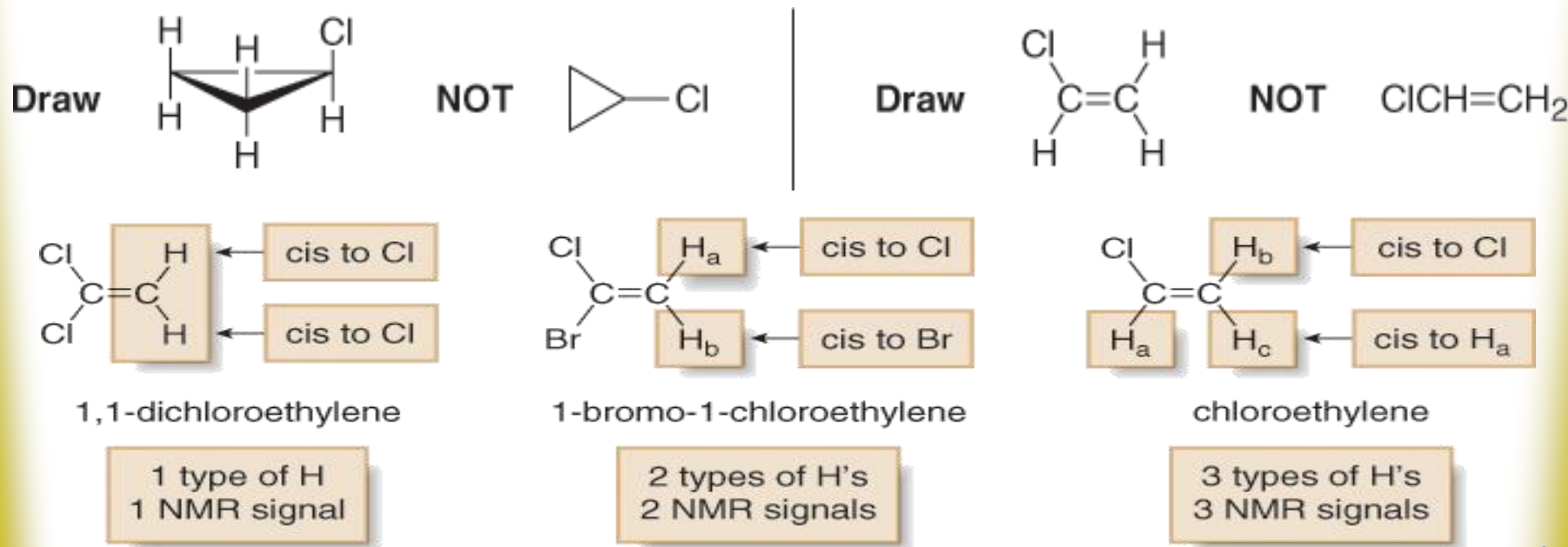
Plane of Symmetry



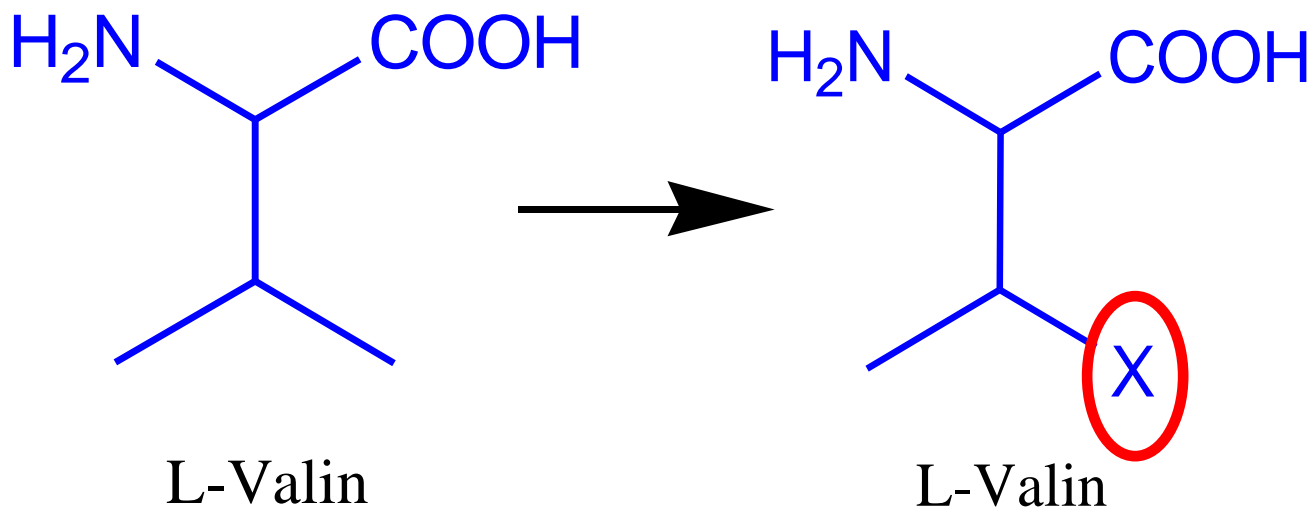
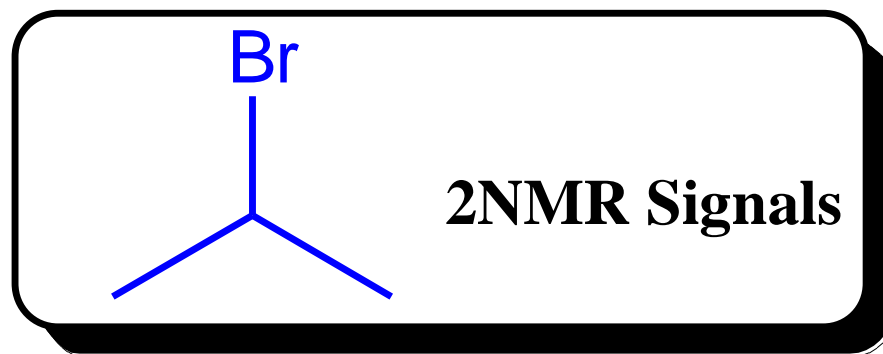
**Plane of Symmetry is Lost
when one of H is replaced
with X, so this CH₂ is
distereotopic**

Equivalent and Non Equivalent Protons

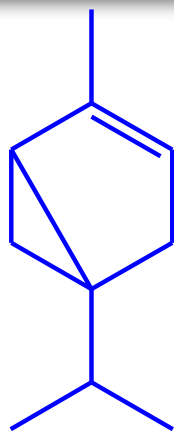
- To determine equivalent protons in cycloalkanes and alkenes, always draw all bonds to hydrogen.



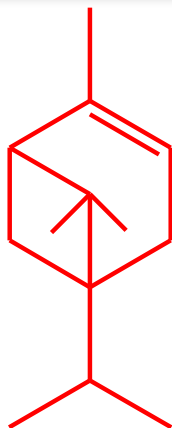
Can Isopropyl Group be Non-Equivalent?



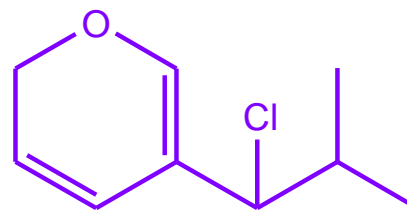
Number of Non-Equivalent Protons



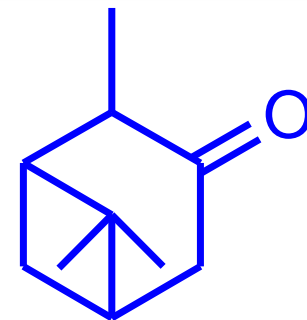
10 Signals



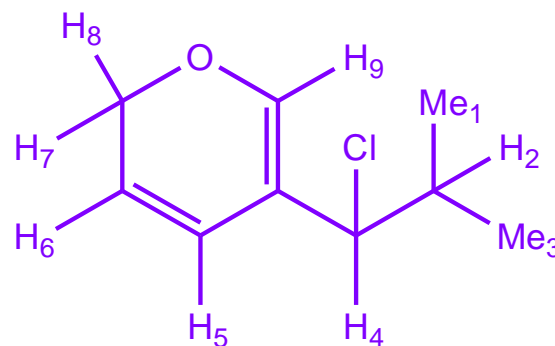
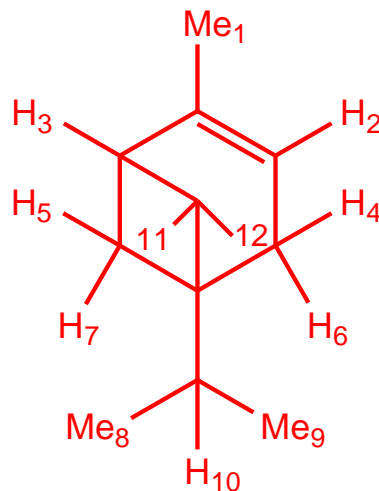
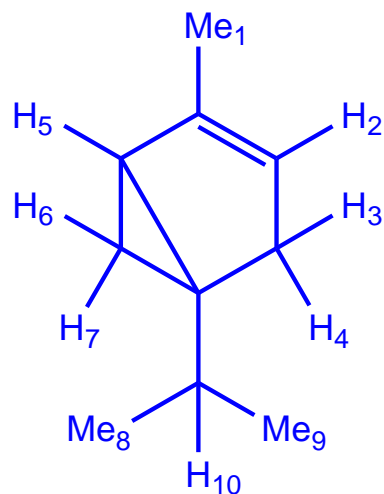
12 Signals



9 Signals



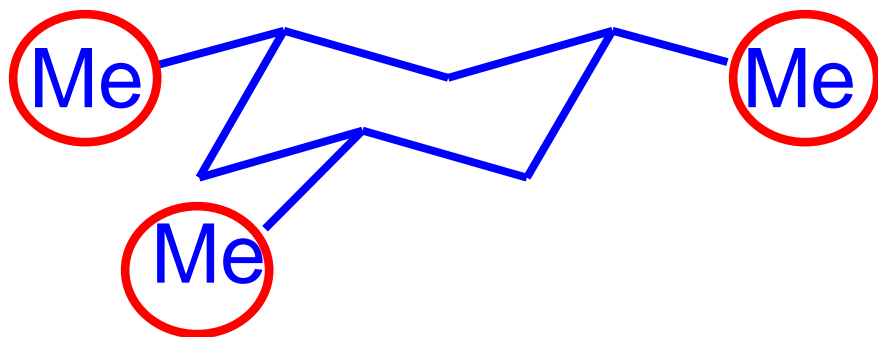
10 Signals



Prof DS Rawat, University of Delhi

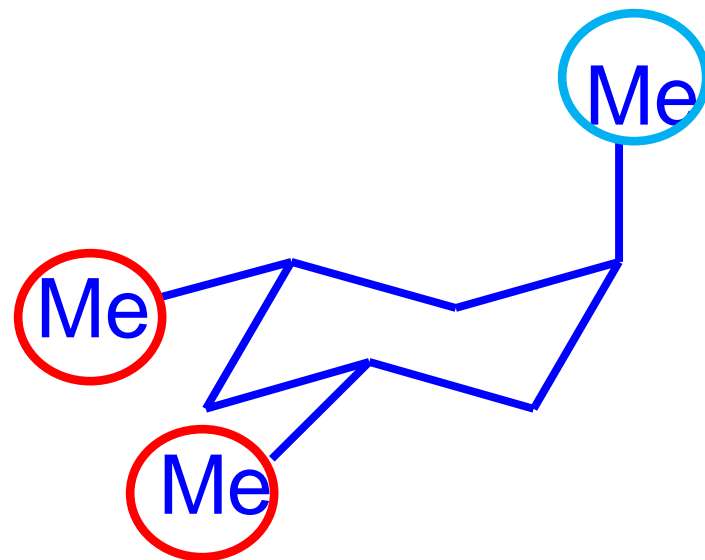
How to differentiate distereoisomers of 1,3,5-Trimethylcyclohexane

Cis-1,3,-Cis-5-Trimethylcyclohexane



3 Signals in ^{13}C NMR

Cis-1,3,-Trans-5-Trimethylcyclohexane

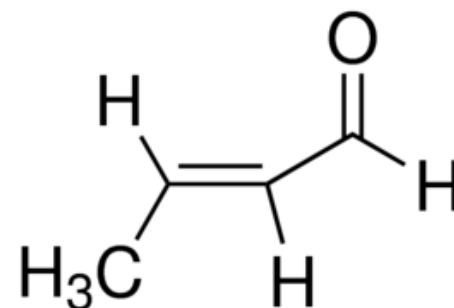


6 Signals in ^{13}C NMR

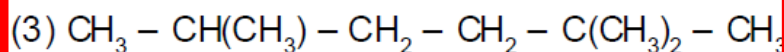
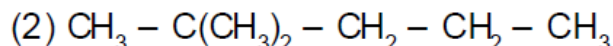
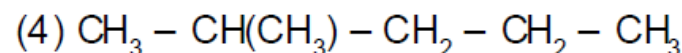
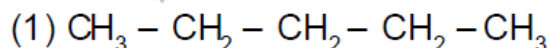
NET Exam

62. The order of chemical shifts (δ value) in the ^1H NMR spectrum of crotonaldehyde is

1. olefinic $>$ CHO $>$ Me
2. CHO $>$ Me $>$ olefinic
3. CHO $>$ olefinic $>$ Me
4. olefinic $>$ Me $>$ CHO



53. The ^{13}C NMR spectrum of a compound shows 6 peaks and the ^1H NMR spectrum shows 5 peaks. Which of the following is this compound?



NET Examination 2015

38. In the mass spectrum of 1,2-dichloroethane, approximate ratio of peaks at m/z values 98, 100, 102 will be

1. 3:1:1

2. 9:6:1

3. 1:1:2

4. 1:2:1

42. The number of chemical shift **non-equivalent** protons expected in ^1H NMR spectrum of α -pinene is



α -pinene

1. 7

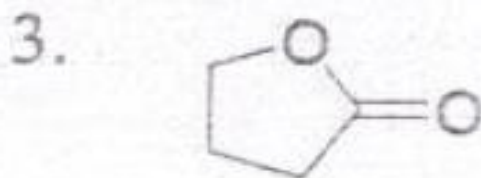
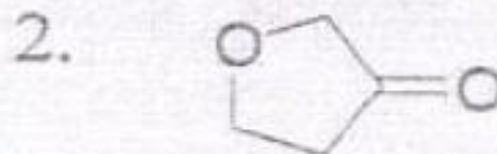
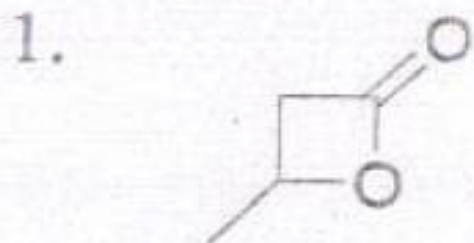
2. 8

3. 9

4. 10

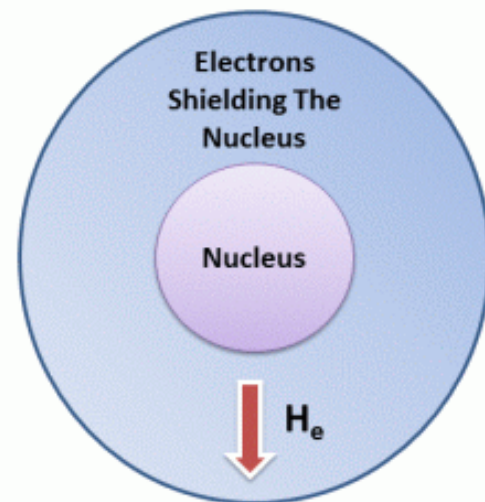
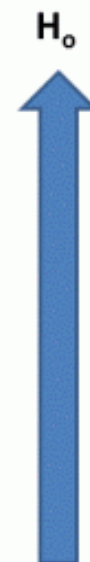
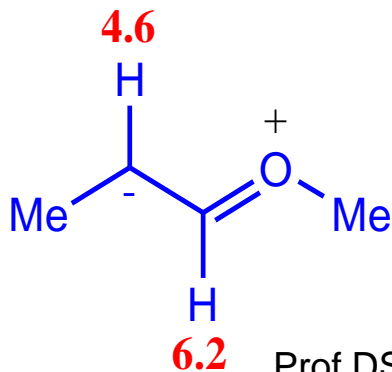
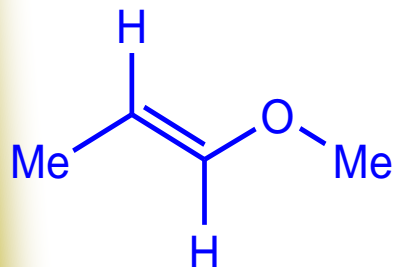
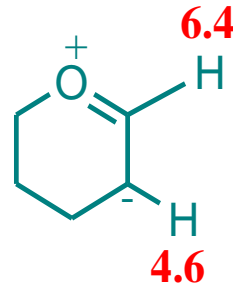
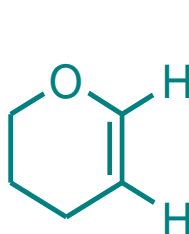
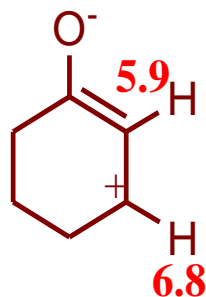
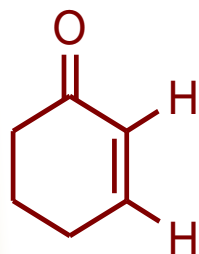
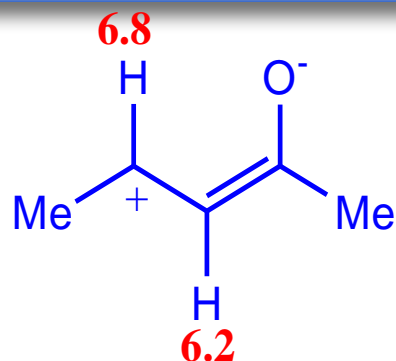
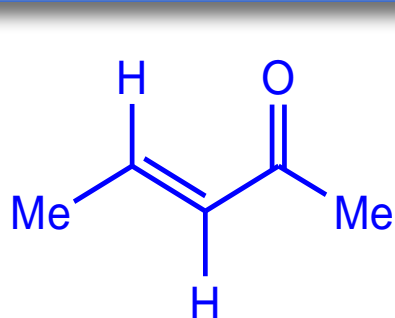
NET Examination 2014

50. A compound with molecular formula $C_4H_6O_2$ shows band at 1770 cm^{-1} in IR spectrum and peaks at 178, 68, 28, and 22 ppm in ^{13}C NMR spectrum. The correct structure of the compound is

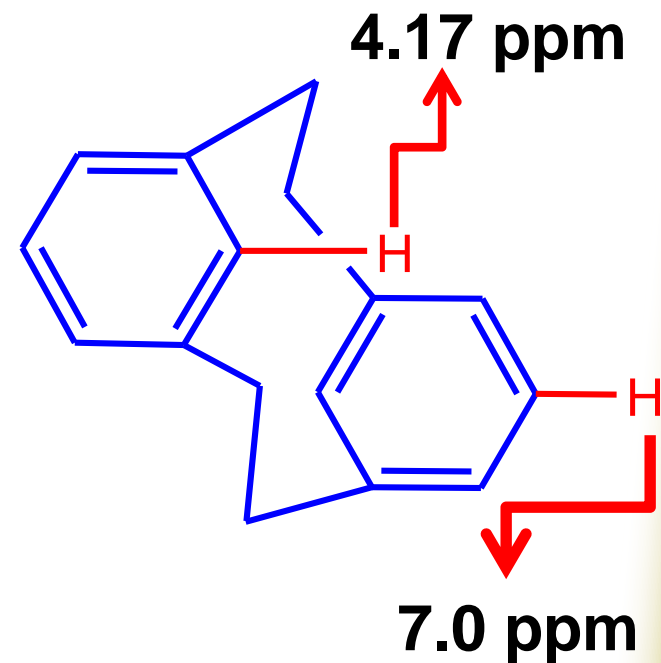
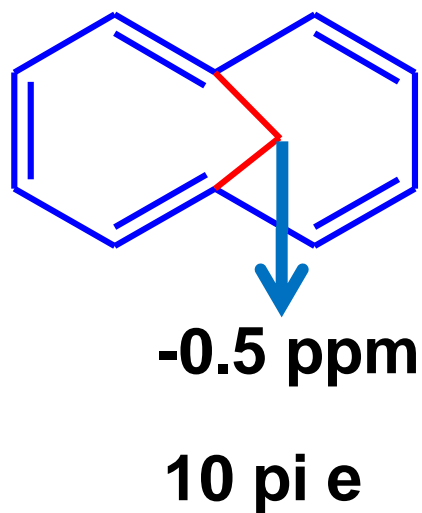
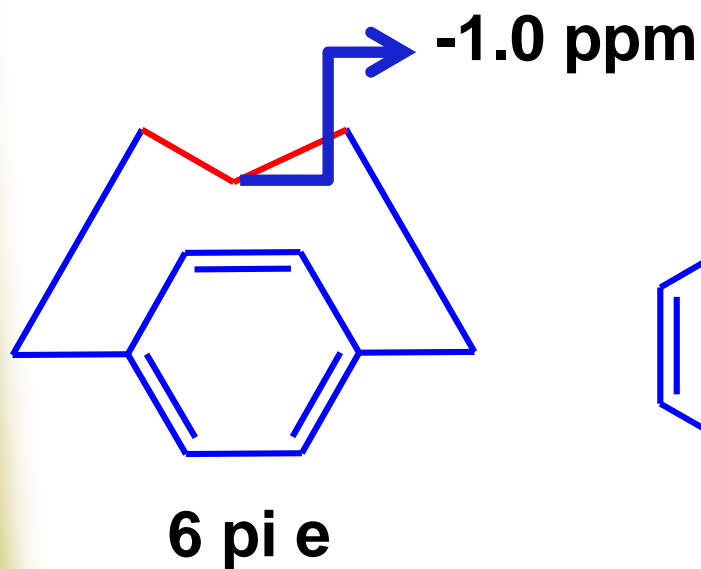


Stretching frequency increases on increasing strain in the ring, six member lactone 1735, five membered 1770, and four membered 1800 cm^{-1}

Shielding and Deshielding



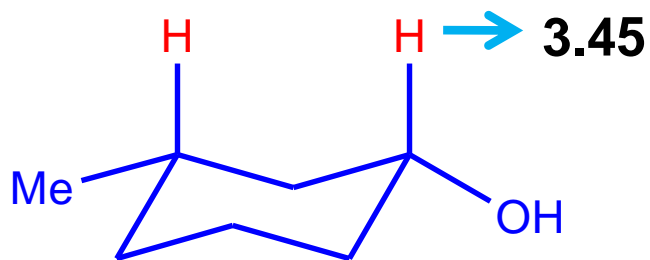
Unusual Chemical Shifts



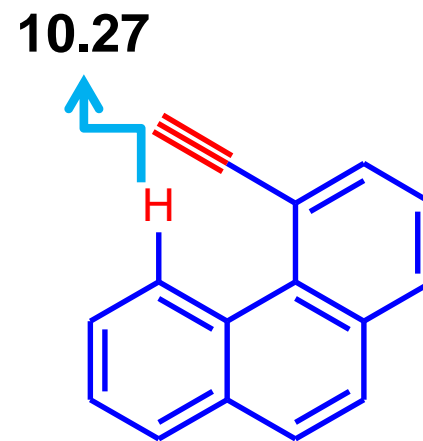
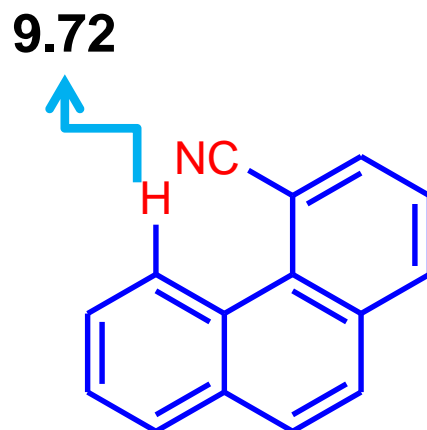
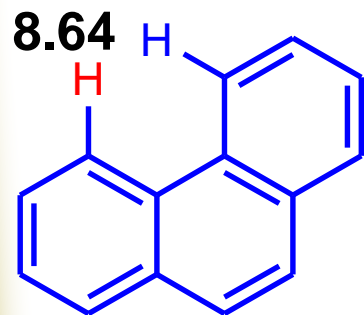
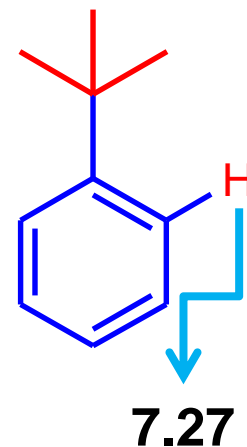
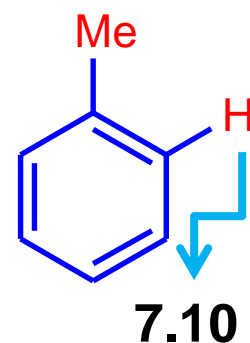
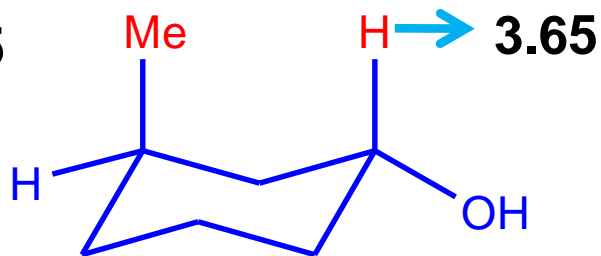
2.2-Metacyclophane

Steric hindrance/Anisotropy and Chemical Shift

No steric hindrance

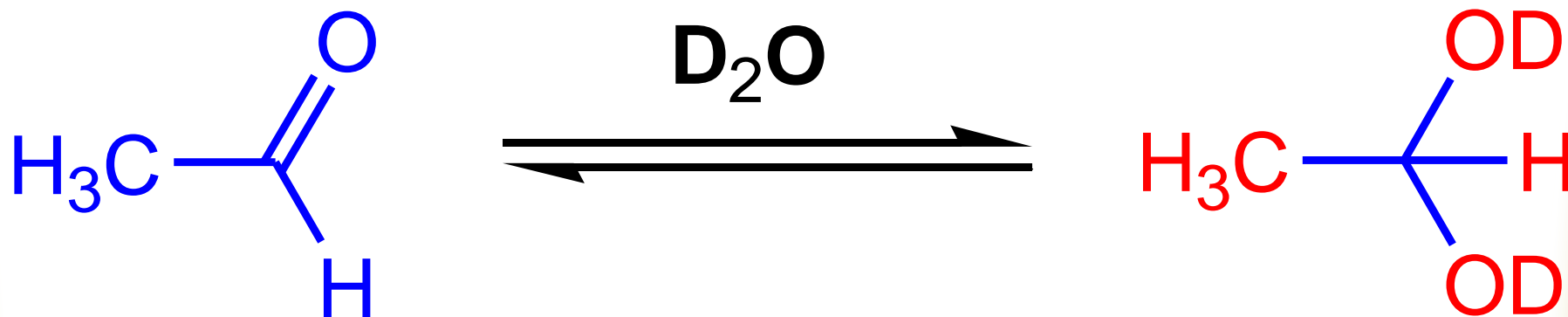


Steric hindrance causes deshielding due to dispersion interaction



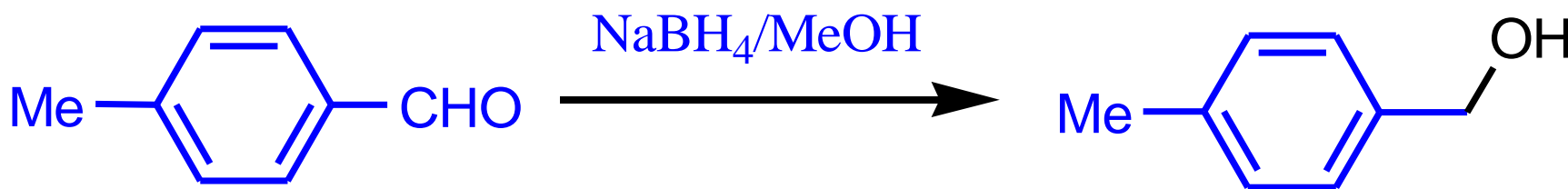
Difficult problem, easy explanation!

- Acetaldehyde shows *two signals at ppm 2.20 and 9.72 ppm in ^1H NMR when spectrum is recorded in CDCl_3 , but shows four signals in D_2O : 1.23, 2.20, 5.13, and 9.72 ppm in D_2O . Why?*



Integration: Use in calculation of yield

- ^1H NMR of reaction mixture consisting p-tolualdehyde and NaBH_4 in MeOH, showed a peak at 4.84 ppm (integration: 300 mm) and 9.80 ppm (integration: 2.5 mm) apart from other peaks. Calculate the % of the product and unreacted p-tolualdehyde.



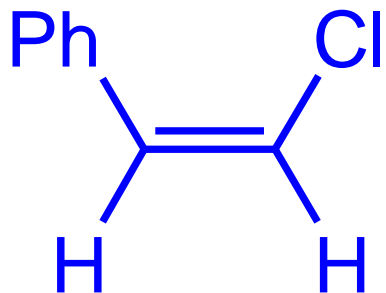
Integration value for CH_2OH at 4.84 ppm = (2H) = 30 mm

Integration value for CHO at 9.80 ppm = (1H) = 2.5 mm = 5.0 mm (for 2H)

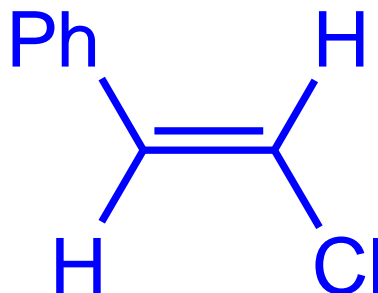
$$\% \text{ of } \text{CH}_2\text{OH} = 30/30+5 = 85.7\%$$

$$\% \text{ of CHO} = 5/30+5 = 14.28\%$$

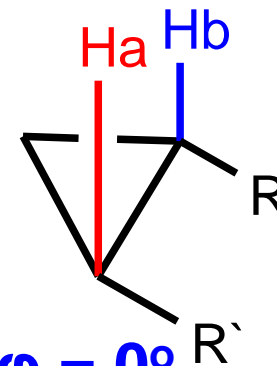
Cis/Trans Isomers



$J_{\text{cis}} = 5-13 \text{ Hz}$

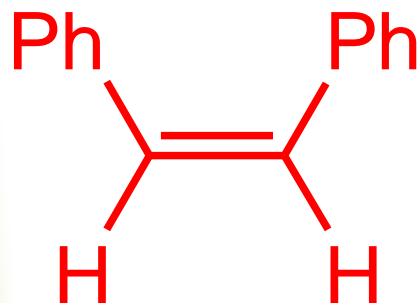


$J_{\text{trans}} = 11-19 \text{ Hz}$

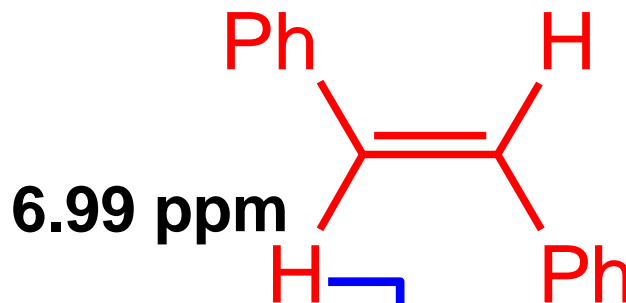


$\phi = 0^\circ$

$J_{\text{ab}} = 6-12 \text{ Hz (cis)}$

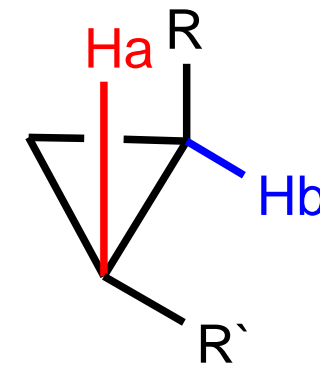


6.49 ppm



6.99 ppm

Sterically hindered
due to two Ph groups

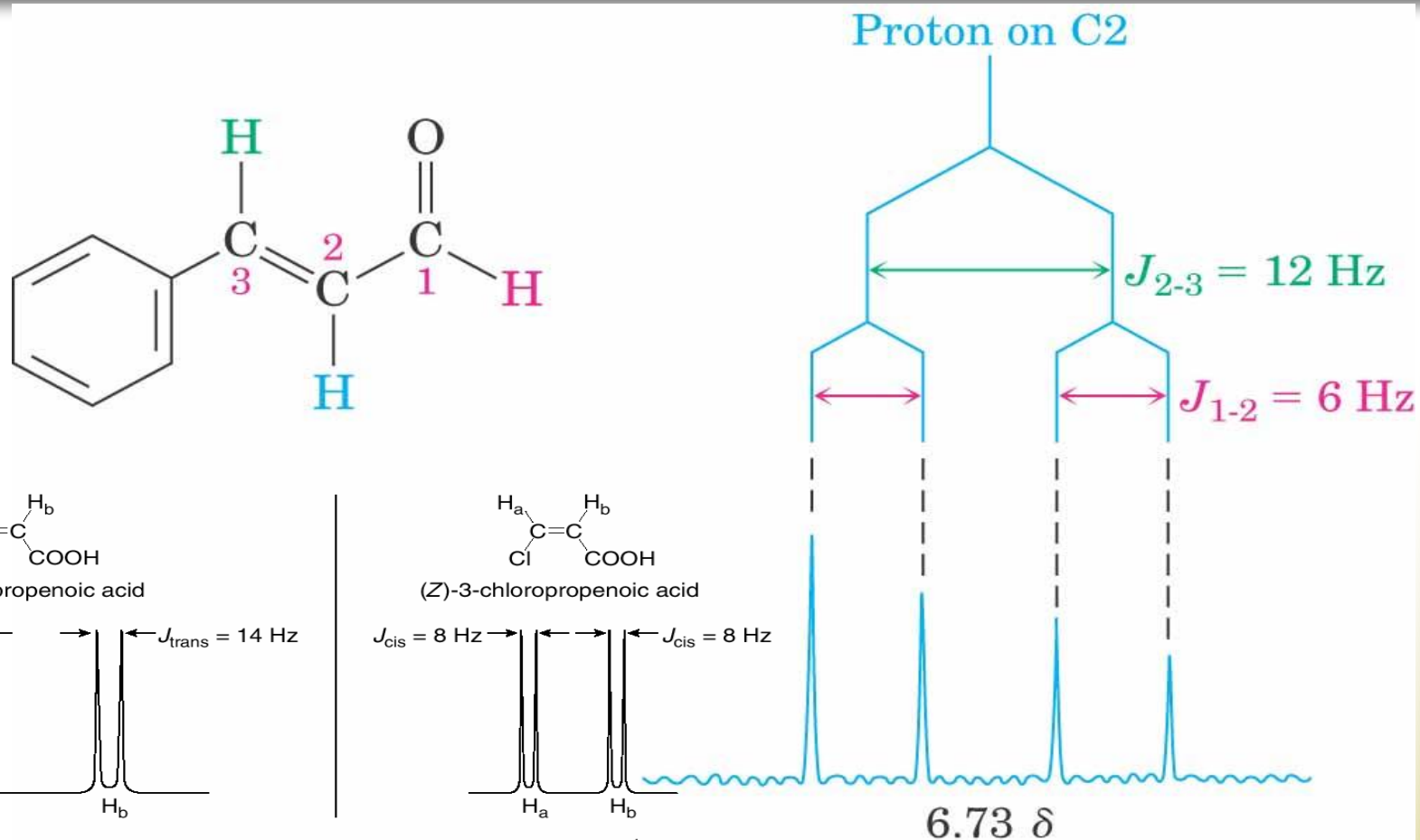


$\phi = 120^\circ$

$J_{\text{ab}} = 2-9 \text{ Hz (trans)}$

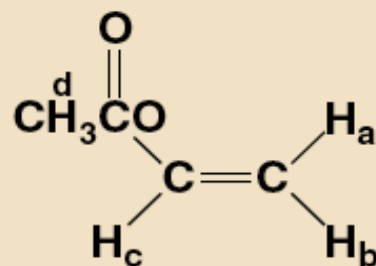
Sterically hindrance cause deshielding due to dispersion effect

Complex Splitting Patterns: Non-equivalent coupling



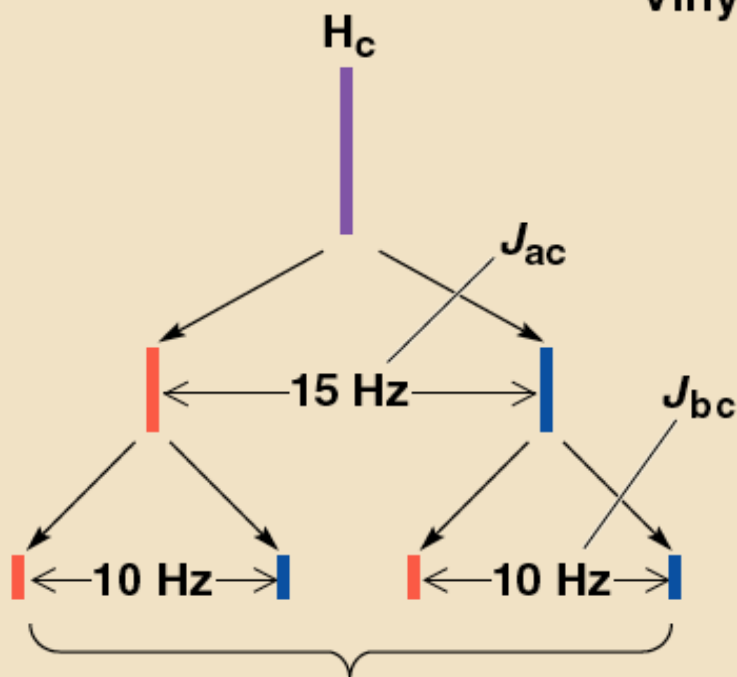
- Although both (E)- and (Z)-3-chloropropenoic acid show two doublets in their ^1H NMR spectra for their alkenyl protons, $J_{\text{trans}} > J_{\text{cis}}$.

Complex Coupling

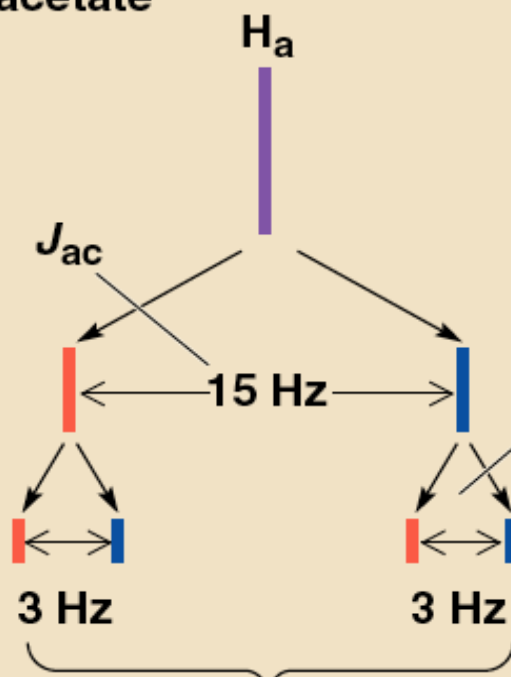


Vinyl acetate

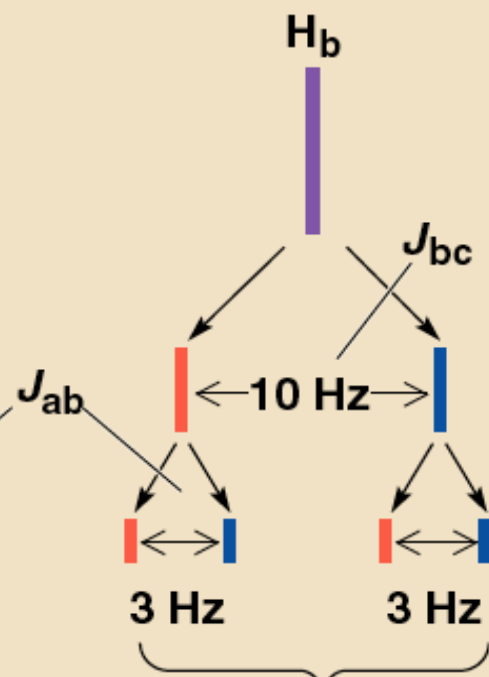
$$\delta = H_c > H_a > H_b$$



A doublet of doublets

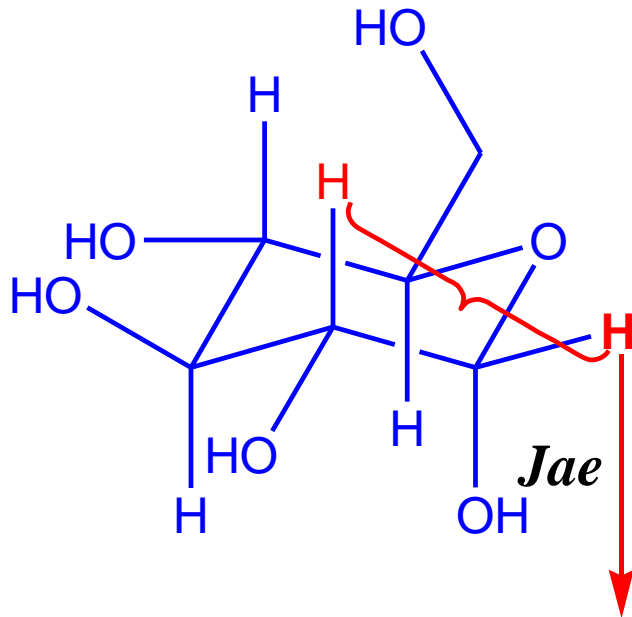


A doublet of doublets

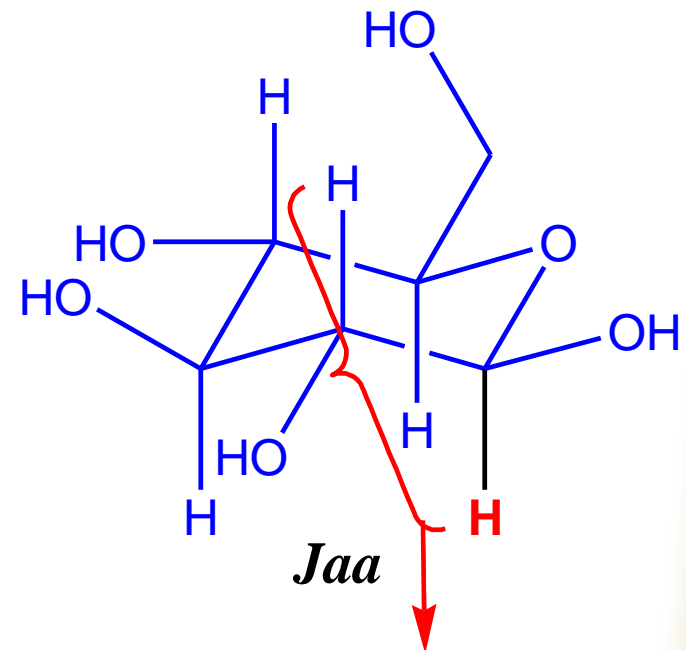


A doublet of doublets

Cyclohexane Systems

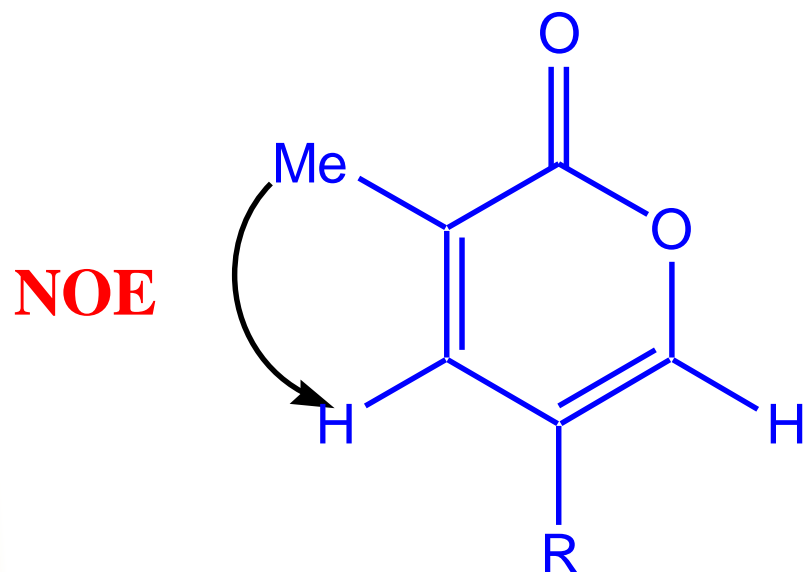


α -D-Glucose
H equatorial, so desheilded
5.2 ppm ($J_{ae} = 3$ Hz)

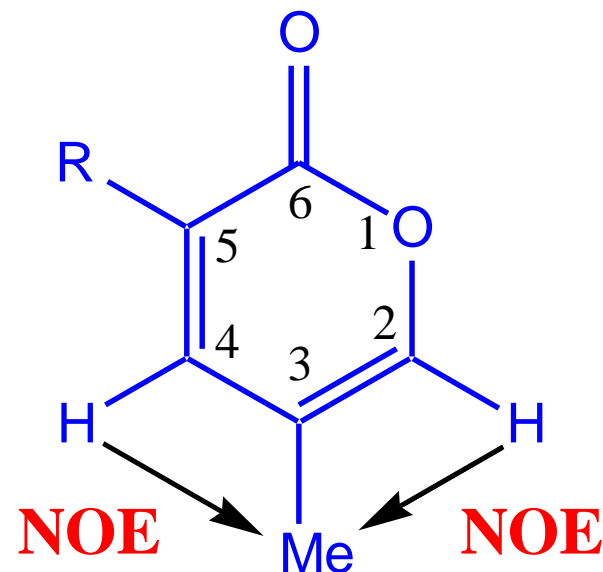


β -D-Glucose
H axial, so sheilded
4.6 ppm ($J_{aa} = 8$ Hz)

Nuclear Overhauser Effect



Double irradiation of Me-5
Increases the intensity of H-4



Double irradiation of Me-3
Increases the intensity of
H-2 and H-4

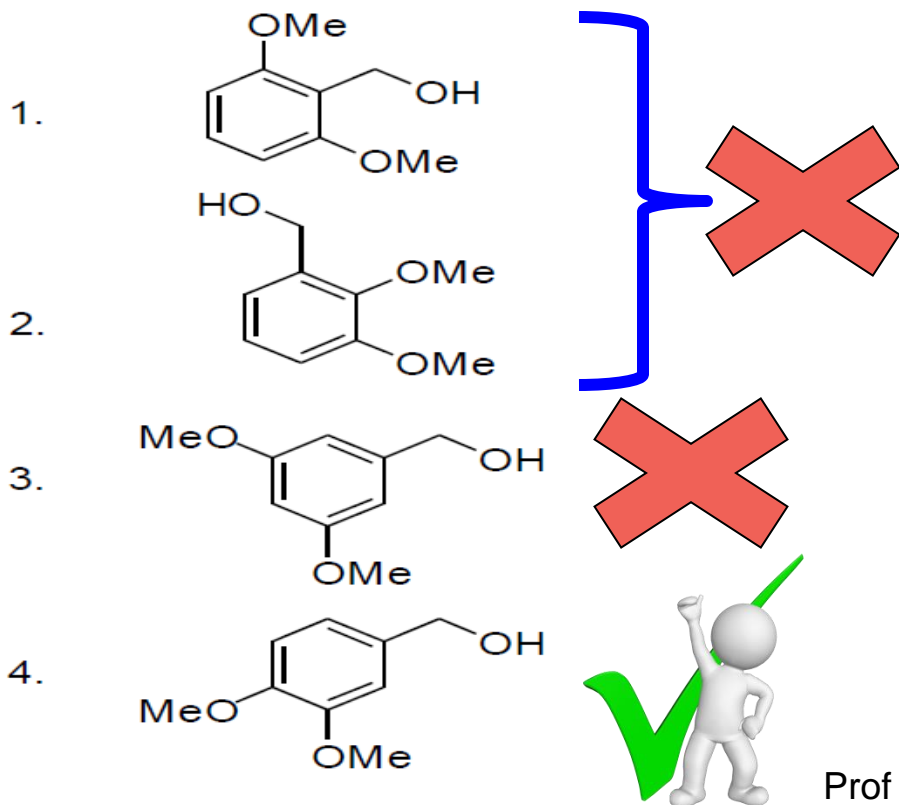
Structure Determination of Organic Compounds

NET Examination 2016

145. In the proton NMR spectrum, an organic compound exhibited the following spectral data

δ 7.2 (1H, dd, $J = 8$ and 1.5 Hz), 6.8 (1H, d, $J = 1.5$ Hz), 6.7 (1H, d, $J = 8$ Hz), 4.9 (2H, s), 3.9 (3H, s), 3.85 (3H, s), 3.5 (1H, br s, exchangeable with D_2O)

The compound among the choices given below is



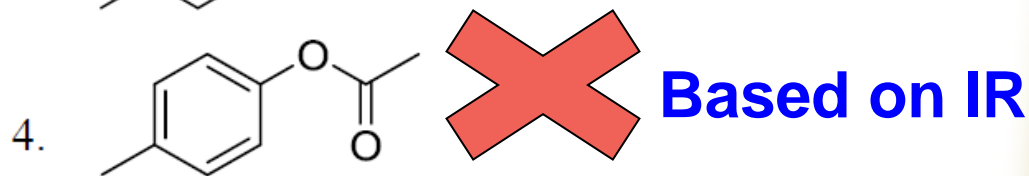
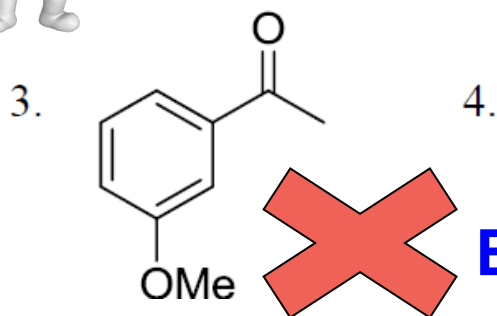
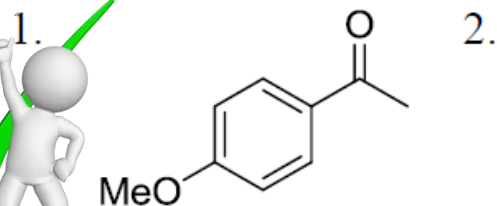
NET Examination 2016

99. A compound displays the following spectral data. The correct structure of the compound is

IR: 1690 cm^{-1}

^1H NMR: δ 2.5 (s, 3H), 3.8 (s, 3H), 6.9 (d, $J = 8\text{ Hz}$, 2H), 7.8 (d, $J = 8\text{ Hz}$, 2H) ppm

^{13}C NMR: δ 197, 165, 130, 129, 114, 56, 26 ppm



Probable Structure for $C_7H_{12}O_2$: NET Examination

1H NMR:

7.10 (1H, dt, $J = 16\text{Hz}$ and 7.2Hz),

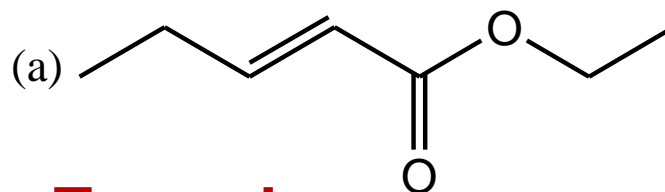
5.90 (1H, d, $J = 16\text{Hz}$),

4.10 (2H, q, $J = 7.2\text{Hz}$),

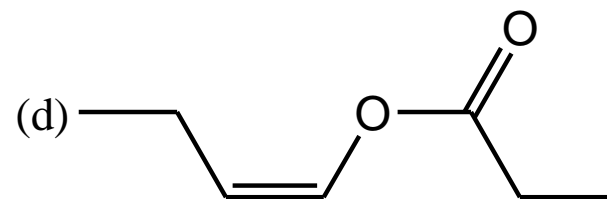
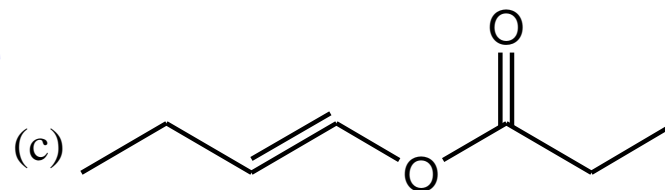
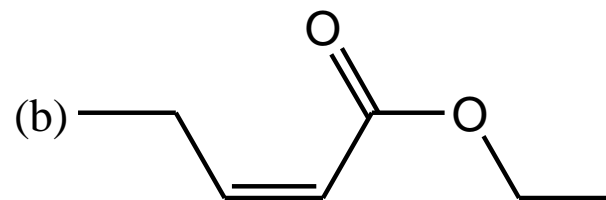
2.10 (2H, m),

1.25 (3H, t, $J = 7.2\text{Hz}$),

0.90 (3H, t, $J = 7.2\text{Hz}$).



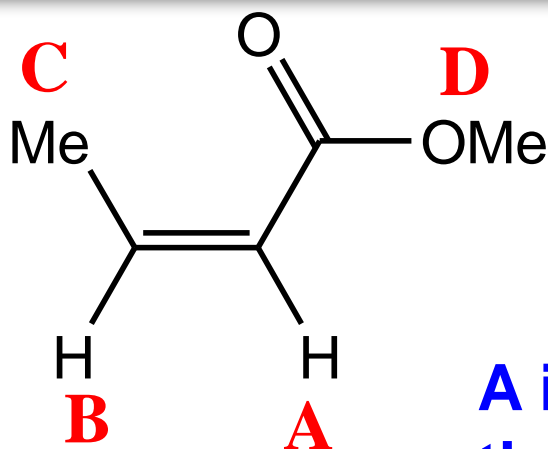
Trans J



No OCH_2 in NMR



Appropriate ^1H NMR chemical shift for protons A – D (NET Examination 2014)



A is more deshielded than B, so b is correct

X (a) A = 6.8; B = 5.7; C = 3.9; D = 2.1 ppm

(b) A = 6.8; B = 5.7; C = 2.1; D = 3.9 ppm

X (c) A = 5.7; B = 6.8; C = 3.9; D = 2.1 ppm

(d) A = 5.7; B = 6.8; C = 2.1; D = 3.9 ppm



Option A and C are wrong, as OMe should be at 4 ppm

NET Examination 2014

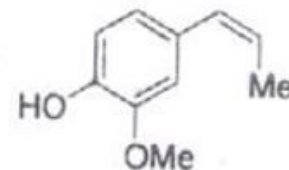
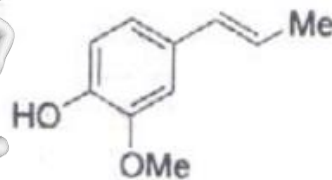
An organic compound having molecular formula $C_{10}H_{12}O_2$ exhibits the following spectral data:

IR: 3400 (br), 1600 cm^{-1} .

1H NMR: δ 1.85 (3H, d, $J = 6$ Hz), 3.8 (3H, s), 5.0 (1H, s, D_2O exchangeable), 6.0 (1H, dq, $J = 18, 6$ Hz), 6.28 (1H, d, $J = 18$ Hz), 6.75 (1H, d, $J = 8$ Hz), 6.8 (1H, s), 6.90 (1H, d, $J = 8$ Hz) ppm;

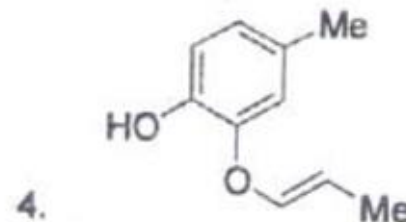
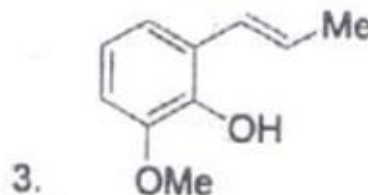
^{13}C NMR: δ 146.5, 144.0, 131.0, 130.5, 123.0, 119.0, 114.0, 108.0, 55.0, 18.0 ppm.

The structure of the compound is



Two H, $J = 18$ Hz

$J = 8$ Hz (2H); s (1H) $J = 18$ Hz, must be trans Structure, so option 2 is ruled out.



X No OMe group ²⁵

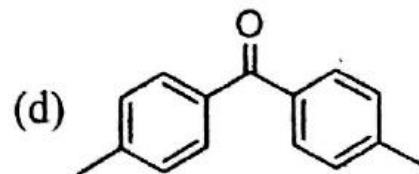
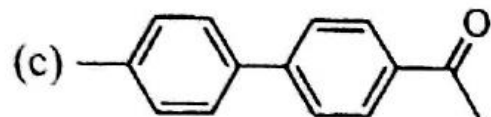
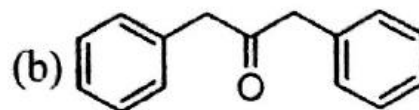
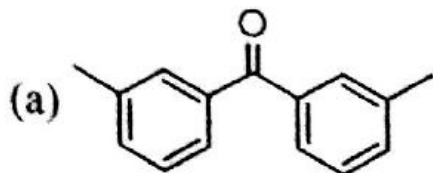
NET Examination 2011

6

An organic compound having molecular formula $C_{15}H_{14}O$ exhibited the following 1H and ^{13}C NMR spectral data.
[NET Dec. 2011]

1H NMR : δ 2.4(s), 7.2(d, $J = 8$ Hz), 7.7(d, $J = 8$ Hz)

^{13}C NMR : δ 21.0, 129.0, 130.0, 136.0, 141.0, 190.0



Appropriate 1H NMR chemical shifts (δ) for the protons A-D for the following compound are

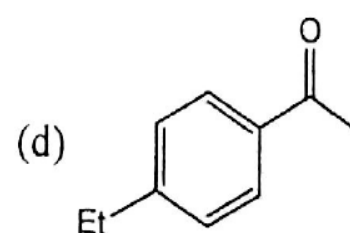
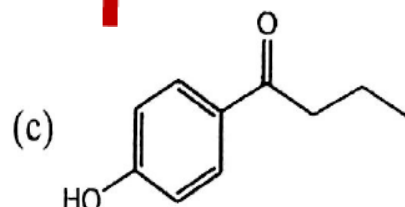
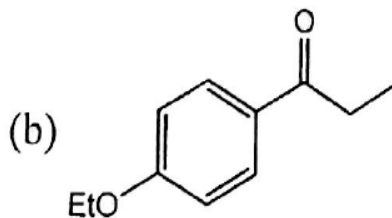
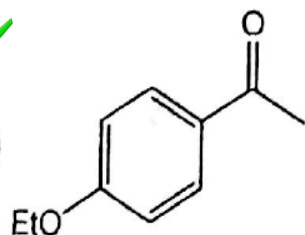


**Compound must be symmetrical
with ortho coupled protons**

27. An organic compound exhibited the following ^1H NMR spectra data: [NET June 2013]

δ 7.80 (2 H, d, $J = 8$ Hz), 6.80 (2 H, d, $J = 8$ Hz), 4.10 (2H, q, $J = 7.2$ Hz),
2.4 (3H, s), 1.25 (3 H, t, $J = 7.2$ Hz)

The compound, among the choices given below is,



14H, Two extra

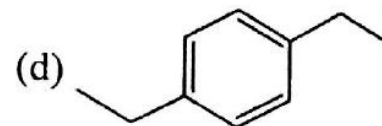
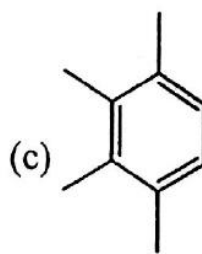
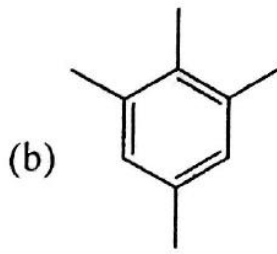
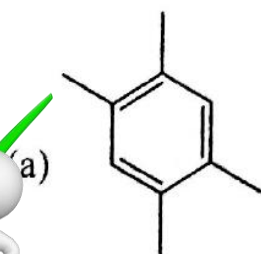
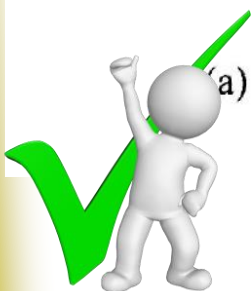


No OCH_2 in NMR

(c) spin-spin coupling constant

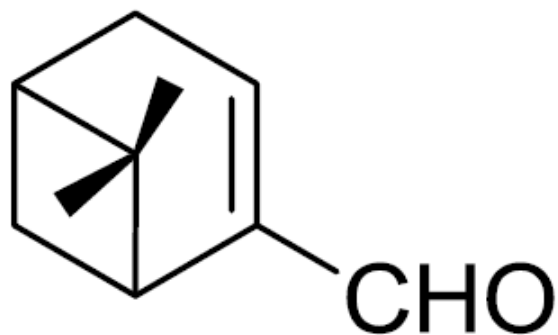
(d) magnetogyric ratio

29. An organic compound having the molecular formula $\text{C}_{10}\text{H}_{14}$ exhibited two singlets in the ^1H NMR spectrum, and three signals in the ^{13}C NMR spectrum. The compound is [NET Dec. 2013]



NET Examination 2016

41. In the ^1H NMR spectrum of myrtenal, the two methyl groups are expected to display signals at (chemical shift values (δ) in ppm)



myrtenal

1. 1.35 (s, 3H) and 5.0 (s, 3H)
2. 0.74 (s, 3H) and 1.33 (s, 3H)
3. 1.22 (s, 6H)
4. 0.70 (s, 6H)