

## WORKSHEET II\_Keys

1. On a 90 MHz spectrometer, calculate the frequency at which a proton absorbs if it appears at 4.20 ppm.

$$\delta(\text{ppm}) = \nu_{\text{sample}} / \nu_{\text{machine}}, \text{ meaning that } \nu_{\text{sample}} = \delta(\text{ppm}) \times \nu_{\text{machine}}$$

$$= 4.20 \times 10^{-6} \times 90 \times 10^6 \text{ Hz} = 378 \text{ Hz.}$$

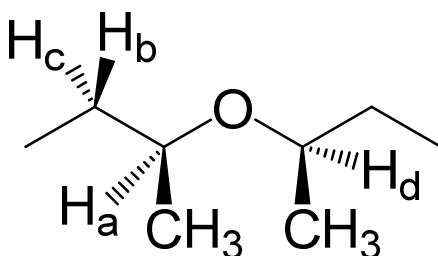
2. Using a 60 MHz spectrometer, the protons in dichloromethane appear at 5.30 ppm. When the same sample is placed in a 100 MHz instrument, where does the signal appear?

- A) 8.33      B) 5.30      C) 3.18      D) cannot be determined from information given

**The  $\delta$  scale is the same for any instrument**

3. State the relationship between the protons indicated in the structure below (as: equivalent, enantiotopic, diastereotopic, or unrelated)

**A**



**H<sub>a</sub> and H<sub>b</sub> = Unrelated**

**H<sub>a</sub> and H<sub>c</sub> = Unrelated**

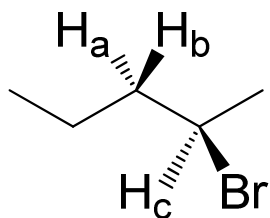
**H<sub>a</sub> and H<sub>d</sub> = Enantiotopic**

**H<sub>b</sub> and H<sub>c</sub> = Diastereotopic**

**H<sub>b</sub> and H<sub>d</sub> = Unrelated**

**H<sub>c</sub> and H<sub>d</sub> = Unrelated**

**B**

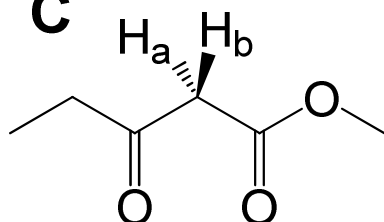


**H<sub>a</sub> and H<sub>b</sub> = Diastereotopic**

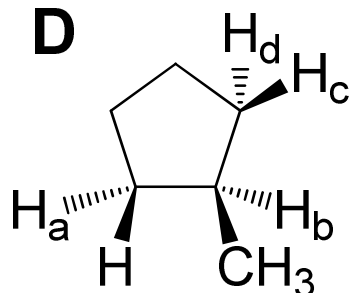
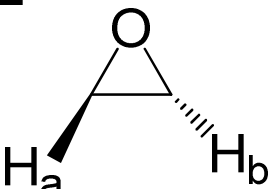
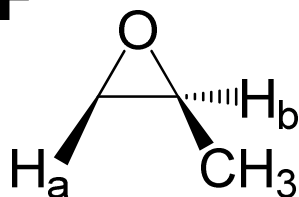
**H<sub>a</sub> and H<sub>c</sub> = Unrelated**

**H<sub>b</sub> and H<sub>c</sub> = Unrelated**

**C**



**H<sub>a</sub> and H<sub>b</sub> = Enantiotopic**

**D** $H_a$  and  $H_b$  = Unrelated $H_a$  and  $H_c$  = Diastereotopic $H_a$  and  $H_d$  = Enantiotopic $H_b$  and  $H_c$  = Unrelated $H_b$  and  $H_d$  = Unrelated $H_c$  and  $H_d$  = Diastereotopic**E** $H_a$  and  $H_b$  = Equivalent or Homotopic**F** $H_a$  and  $H_b$  = Unrelated

4. The chair form of cyclohexane has protons in two distinct environments, axial and equatorial. When the proton NMR of cyclohexane is run on a 100-MHz instrument at 23°C, only one signal for the compound is observed. Explain this apparent contradiction.

**The two chair conformers of cyclohexane interconvert into each other as fast as the temperature increases. At very low temperature, the interconversion is so slow that axial hydrogens are distinguishable from the equatorial ones, but as it comes rises toward room temperature, the interconversion is too fast to observe the equatorial protons from the axial ones. As a result, only one signal is observed for all of them.**

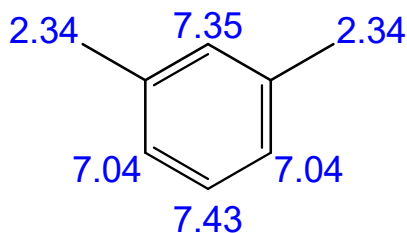
5. How might the proton spectrum of ultrapure dimethylamine,  $(CH_3)_2NH$ , differ from the spectrum of the same compound to which  $D_2O$  has been added?

**In the absence of  $D_2O$ , the NH proton is observed as a broad singlet. However, in the presence of  $D_2O$ , NH proton is interconverted with deuterium, which is NMR inactive, and as such, the NH signal disappears.**

6. Predict the number of signals expected (disregarding splitting) in the  $^1\text{H}$  spectrum of the following compounds:

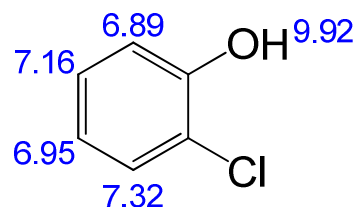
**A** *m*-xylene (1,3-dimethylbenzene)

**4 signals are observed**



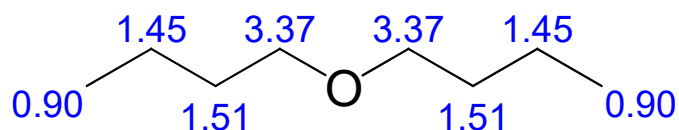
**B** *o*-chlorophenol (2-chlorophenol)

**Technically 5 signals are expected, but only 2 or 3 signals will be observed due to signal overlap.**



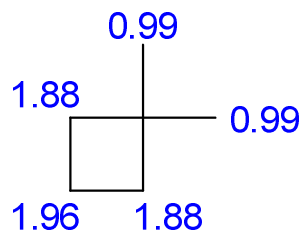
**C** dibutyl ether

**4 signals are observed**



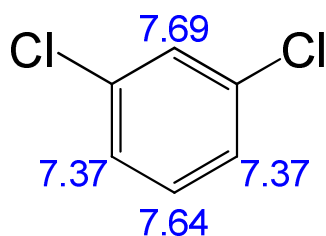
**D** 1,1-dimethylcyclobutane

**3 signals are observed**



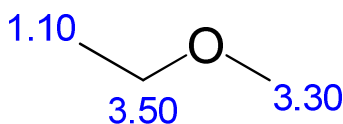
**E** *m*-dichlorobenzene (1,3-dichlorobenzene)

**3 signals are observed**



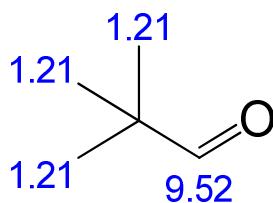
7. Predict the number of signals expected, their splitting, and their relative area in the  $^1\text{H}$ -NMR spectrum of the following compounds

**A**



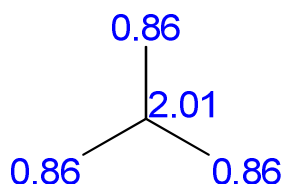
**$\delta$ (ppm): 1.10 (3H, triplet), 3.30 (3H, singlet), 3.50 (2H, quartet)**

B



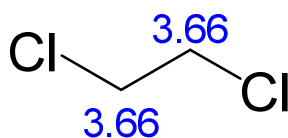
$\delta(\text{ppm})$ : 1.21 (9H, singlet), 9.52 (1H, singlet)

C



$\delta(\text{ppm})$ : 0.86 (9H, doublet), 2.01 (1H, multiplet)

D

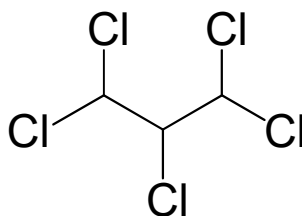


$\delta(\text{ppm})$ : 3.66 (4H, singlet)

8. Deduce the identity of the following compound from the <sup>1</sup>H-NMR data given.

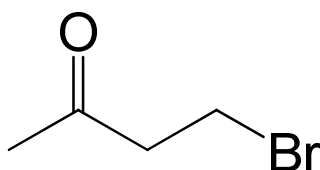
(a) C<sub>3</sub>H<sub>3</sub>Cl<sub>5</sub>:  $\delta$  4.5 (1H, triplet), 6.1 (2H, doublet) (ppm)

$$\text{NI} = 3 + 1 - \frac{1}{2} 8 = 0$$



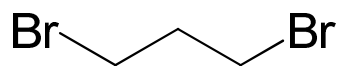
(b) C<sub>4</sub>H<sub>7</sub>BrO:  $\delta$  2.2 (3H, singlet), 3.5 (2H, triplet), 4.5 (2H, triplet) (ppm)

$$\text{NI} = 4 + 1 - \frac{1}{2} 8 = 1$$



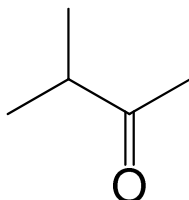
(c)  $\text{C}_3\text{H}_6\text{Br}_2$ :  $\delta$  2.4 (2H, quintet), 3.5 (4H, triplet) (ppm)

$$\text{NI} = 3 + 1 - \frac{1}{2} 8 = 0$$



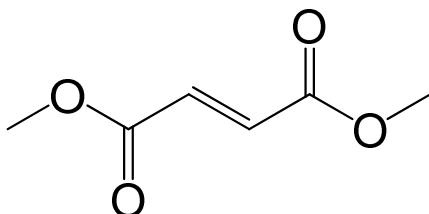
(d)  $\text{C}_5\text{H}_{10}\text{O}$ :  $\delta$  1.1 (6H, doublet), 2.2 (3H, singlet), 2.5 (1H, septet) (ppm)

$$\text{NI} = 5 + 1 - \frac{1}{2} 10 = 1$$



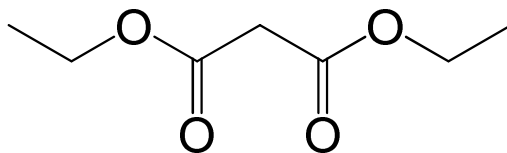
(e)  $\text{C}_6\text{H}_8\text{O}_4$ :  $\delta$  3.9 (6H, singlet), 6.1 (2H, singlet) (ppm)

$$\text{NI} = 6 + 1 - \frac{1}{2} 8 = 3$$



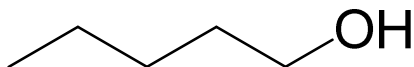
(f)  $\text{C}_7\text{H}_{12}\text{O}_4$ :  $\delta$  1.3 (6H, triplet), 3.4 (2H, singlet), 4.2 (4H, quartet) (ppm)

$$\text{NI} = 7 + 1 - \frac{1}{2} 12 = 2$$



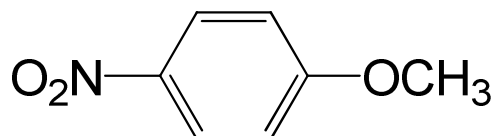
(g)  $\text{C}_5\text{H}_{12}\text{O}$ :  $\delta$  1.0 (3H, triplet), 1.2-1.8 (6H, multiplet), 3.0 (1H, broad singlet), 3.8 (2H, triplet) (ppm)

$$\text{NI} = 5 + 1 - \frac{1}{2} 12 = 0$$



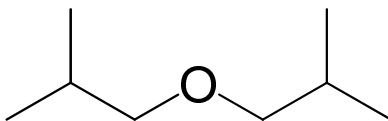
(h)  $\text{C}_7\text{H}_7\text{NO}_3$ :  $\delta$  3.9 (3H, singlet), 6.9 (2H, doublet), 8.1 (2H, doublet) (ppm)

$$\text{NI} = 7 + 1 - \frac{1}{2} 7 + \frac{1}{2} = 5$$



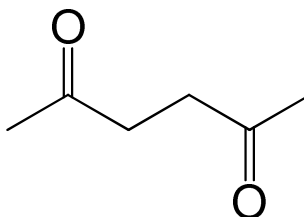
(i)  $C_8H_{18}O$ :  $\delta$  0.89 (6H, doublet), 1.87 (1H, multiplet), 3.17 (2H, doublet)(ppm)

$$NI = 8 + 1 - \frac{1}{2} 18 = 0$$



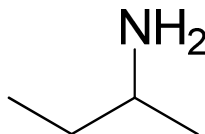
(j)  $C_6H_{10}O_2$ :  $\delta$  2.19 (3H, singlet), 2.70 (2H, singlet) (ppm)

$$NI = 6 + 1 - \frac{1}{2} 10 = 2$$



(k)  $C_4H_{11}N$ :  $\delta$  0.90 (3H, triplet), 1.07 (3H, doublet), 1.14 (2H, broad singlet), 1.34 (2H, multiplet), 2.79 (1H, multiplet) (ppm)

$$NI = 4 + 1 - \frac{1}{2} 11 + \frac{1}{2} = 0$$

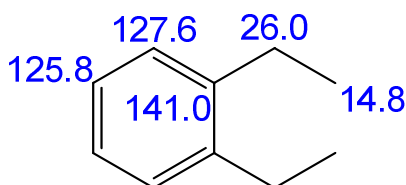


9. What is the approximate chemical shift of an alkynyl carbon in  $^{13}C$ -NMR spectroscopy?

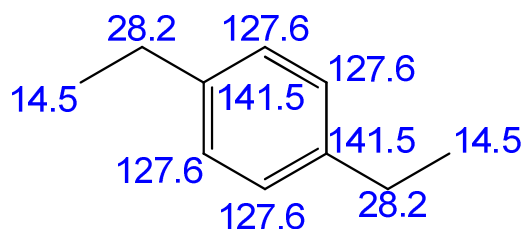
- A) 10 ppm      B) 30 ppm      **C) 70 ppm**      D) 120 ppm      E) 200 ppm

10. Predict the number of signals expected in the proton spin decoupled  $^{13}C$ -NMR spectrum of the following compounds:

(a) *o*-diethylbenzene (1,2-diethylbenzene).      **5 signals**

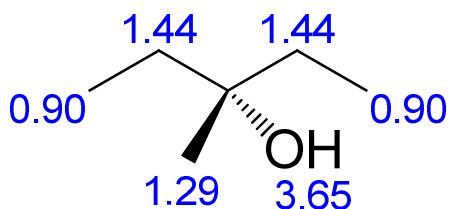


(b) *p*-diethylbenzene (1,4-diethylbenzene). **4 signals**

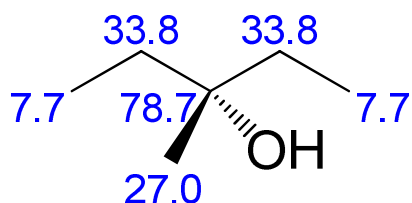


11. Predict the number of signals expected (disregarding splitting) in the  $^1\text{H}$ -NMR and in the proton spin decoupled  $^{13}\text{C}$  NMR spectra of the compound shown below.

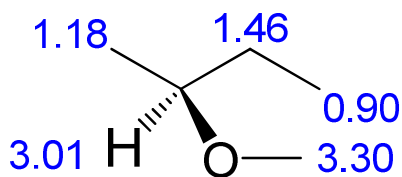
**A** Proton 4 signals



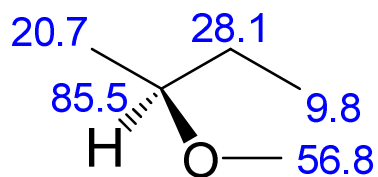
Carbon 4 signals



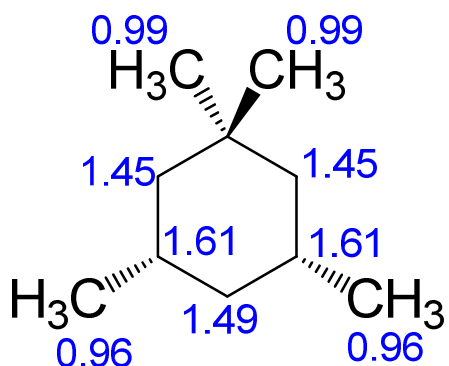
**B** Proton 5 signals



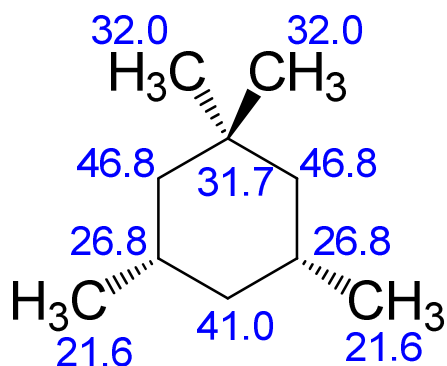
Carbon 5 signals



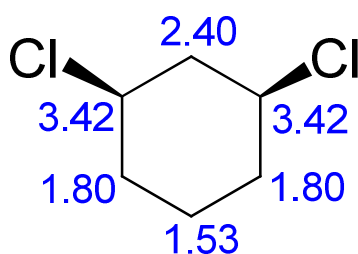
**C** Proton 5 signals



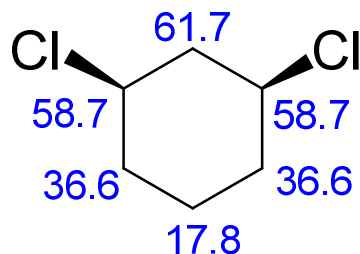
Carbon 6 signals



**D** Proton 4 signals

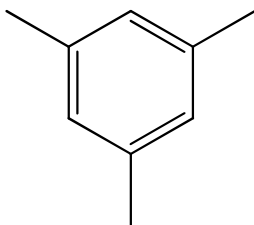


Carbon 4 signals



12. Deduce the identity of the following compound from the  $^{13}\text{C}$  NMR data given.  
 $\text{C}_9\text{H}_{12}$ :  $\delta$  21.3 (quartet), 127.2 (doublet), 138.0 (singlet) (ppm)

$$\text{NI} = 9 + 1 - \frac{1}{2} 12 = 4$$

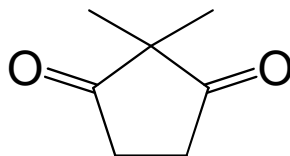


13. Deduce the identity of the following compound from the given spectral data.

(a)  $\text{C}_7\text{H}_{10}\text{O}_2$ :  $^1\text{H}$ -NMR,  $\delta$  1.16 (3H, singlet), 2.21 (2H, singlet)

$^{13}\text{C}$ -NMR:  $\delta$  216.25 (singlet), 52.57 (singlet), 34.51 (triplet), 20.22 (quartet) (ppm)

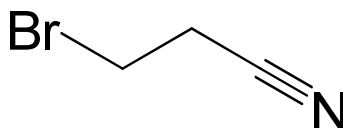
$$\text{NI} = 7 + 1 - \frac{1}{2} 10 = 3$$



(b)  $\text{C}_3\text{H}_4\text{BrN}$ :  $^1\text{H}$ -NMR,  $\delta$  2.98 (2H, triplet), 3.53 (2H, triplet)

$^{13}\text{C}$ -NMR:  $\delta$  21.05 (triplet), 23.87 (triplet), 118.08 (singlet) (ppm); IR, 2963, 2254  $\text{cm}^{-1}$

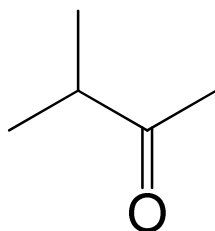
$$\text{NI} = 3 + 1 - \frac{1}{2} 5 + \frac{1}{2} = 2$$



(c)  $\text{C}_5\text{H}_{10}\text{O}$ :  $^1\text{H}$ -NMR,  $\delta$  1.2 (6H, doublet), 2.1 (3H, singlet), 2.8 (1H, septet) (ppm)

IR: 2980, 1710  $\text{cm}^{-1}$ ; MS,  $m/z$  71, 43

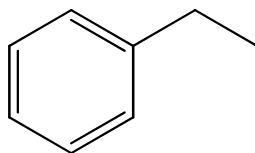
$$\text{NI} = 5 + 1 - \frac{1}{2} 10 = 1$$



(d)  $\text{C}_8\text{H}_{10}$ :  $^1\text{H}$ -NMR,  $\delta$  1.20 (3H, triplet), 2.60 (2H, quartet), 7.12 (5H, multiplet) (ppm)

IR: 3050, 2970, 1600  $\text{cm}^{-1}$ ; MS,  $m/z$  91

$$\text{NI} = 8 + 1 - \frac{1}{2} 10 = 4$$

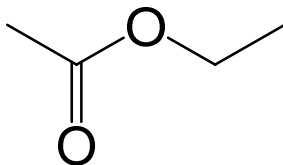




(e)  $C_4H_8O_2$ :  $^1H$ -NMR ( $\delta$ ) 1.23 (3H, triplet), 2.00 (3H, singlet), 4.02 (2H, quartet) (ppm)

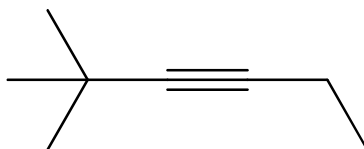
IR: 2980, 1740  $cm^{-1}$

$$NI = 4 + 1 - \frac{1}{2} 8 = 1$$



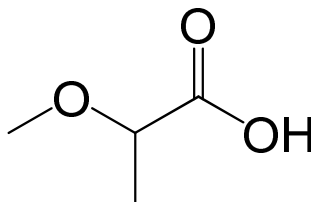
(f)  $C_8H_{14}$ : IR ( $cm^{-1}$ ): 2950, 2180;  $^1H$ -NMR ( $\delta$ ): 0.9 (3H, t), 1.0 (9H, s), 2.3 (2H, q) (ppm).

$$NI = 8 + 1 - \frac{1}{2} 14 = 2$$



(g)  $C_4H_8O_3$ : IR ( $cm^{-1}$ ): 2800-3300 (broad), 2950, 1750;  $^{13}C$ -NMR ( $\delta$ ): 17.7 (q), 65.4 (q), 72.3 (d), 210.8 (s) (ppm)

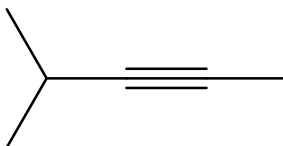
$$NI = 4 + 1 - \frac{1}{2} 8 = 1$$



(h)  $C_6H_{10}$ : IR ( $cm^{-1}$ ): 2950, 2230;  $^1H$ -NMR ( $\delta$ ): 2.0 (1H, septet), 1.8 (3H, s), 0.9 (6H, d) ppm

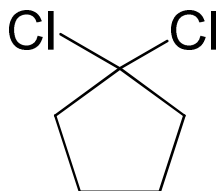
$^{13}C$ -NMR ( $\delta$ ): 78, 72, 45, 18, 15 ppm

$$NI = 6 + 1 - \frac{1}{2} 10 = 2$$



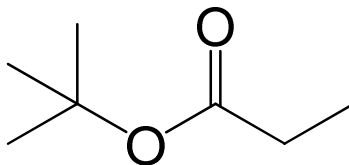
(i)  $C_5H_8Cl_2$ : IR ( $cm^{-1}$ ): 2950;  $^1H$ -NMR ( $\delta$ ): 1.4 (4H, t), 1.2 (4H, t) ppm;  $^{13}C$ -NMR ( $\delta$ ): 62, 26, 23 ppm

$$NI = 5 + 1 - \frac{1}{2} 10 = 1$$



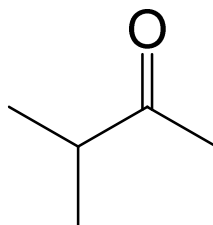
(j)  $C_7H_{14}O_2$ : IR ( $cm^{-1}$ ): 2950, 1740;  $^1H$ -NMR ( $\delta$ ): 0.9 (9H, s), 1.0 (3H, t), 2.3 (2H, q) ppm  
 $^{13}C$ -NMR ( $\delta$ ): 185, 78, 29, 14, 12 ppm

$$NI = 7 + 1 - \frac{1}{2} 14 = 1$$



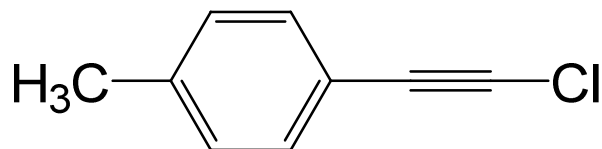
(k)  $C_5H_{10}O$ : IR ( $cm^{-1}$ ): 2950, 1720;  $^1H$ -NMR ( $\delta$ ): 2.6 (1H, septet), 2.1 (3H, s), 1.0 (6H, d) ppm  
 $^{13}C$ -NMR ( $\delta$ ): 195, 42, 18, 11 ppm

$$NI = 5 + 1 - \frac{1}{2} 10 = 1$$



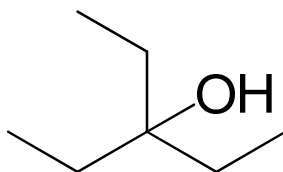
(l)  $C_9H_7Cl$ : IR ( $cm^{-1}$ ): 3050, 2950, 2220, 1620;  $^1H$ -NMR ( $\delta$ ): 7.8 (2H, d), 7.2 (2H, d), 2.1 (3H, s) ppm  
 $^{13}C$ -NMR: 140, 132, 125, 122, 88, 83, 18 ppm

$$NI = 9 + 1 - \frac{1}{2} 8 = 6$$



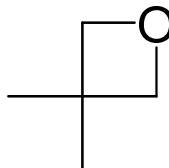
(m)  $C_7H_{16}O$ : IR ( $cm^{-1}$ ): 3200-3600 (broad), 2950;  $^1H$ -NMR ( $\delta$ ): 2.9 (1H, broad s), 1.2 (6H, q), 0.9 (9H, t) ppm;  $^{13}C$ -NMR ( $\delta$ ): 70, 25, 12 ppm

$$NI = 7 + 1 - \frac{1}{2} 16 = 0$$



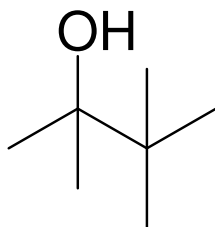
(n)  $C_5H_{10}O$ : IR ( $cm^{-1}$ ): 2950;  $^1H$ -NMR ( $\delta$ ): 3.5 (4H, s), 0.9 (6H, s) ppm;  $^{13}C$ -NMR ( $\delta$ ): 64, 41, 12 ppm

$$NI = 5 + 1 - \frac{1}{2} 10 = 1$$



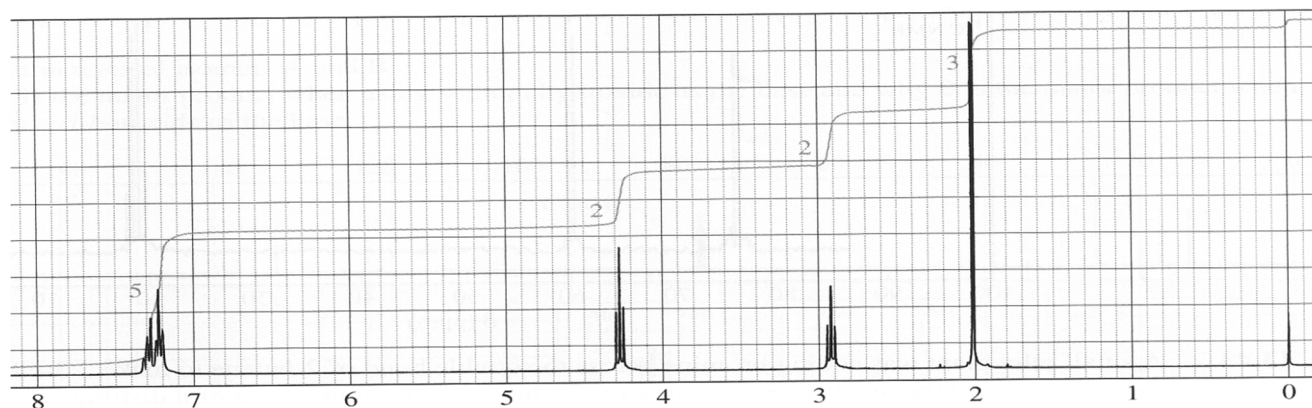
(o)  $C_7H_{16}O$ : IR ( $cm^{-1}$ ): 3200-3600 (broad), 2950;  $^1H$ -NMR ( $\delta$ ): 2.8 (1H, broad s), 1.0 (6H, s), 0.9 (9H, s) ppm;  $^{13}C$ -NMR ( $\delta$ ): 68, 39, 16, 13 ppm

$$NI = 7 + 1 - \frac{1}{2} 16 = 0$$

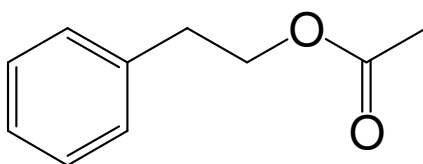


14. Deduce the identity of the following compound from the  $^1H$ - NMR spectrum and the data given.

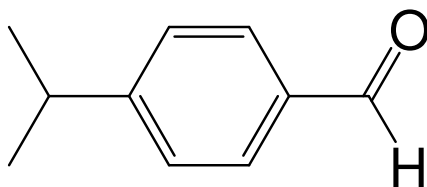
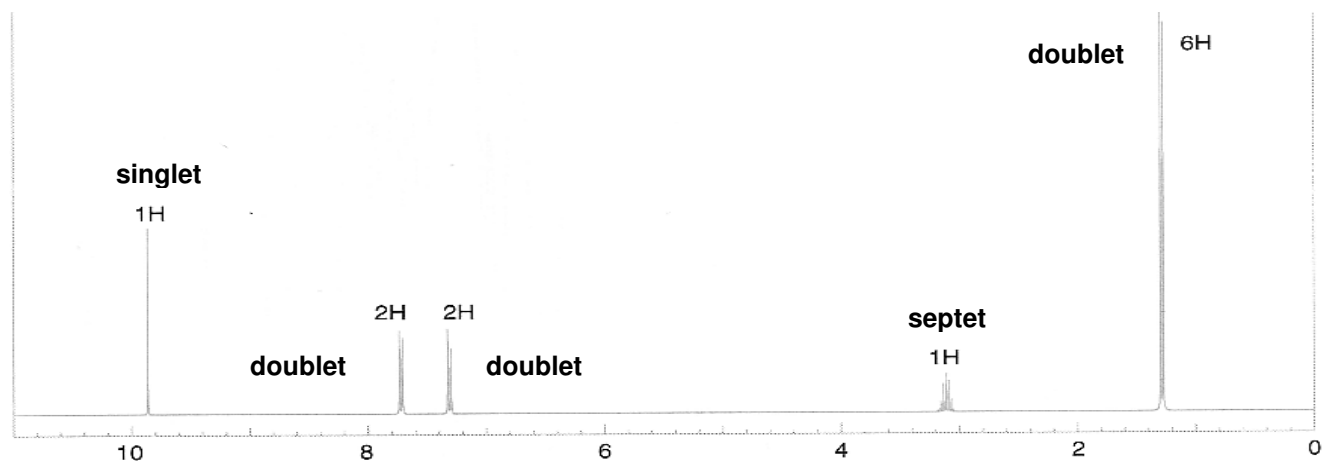
**A**  $C_{10}H_{12}O_2$



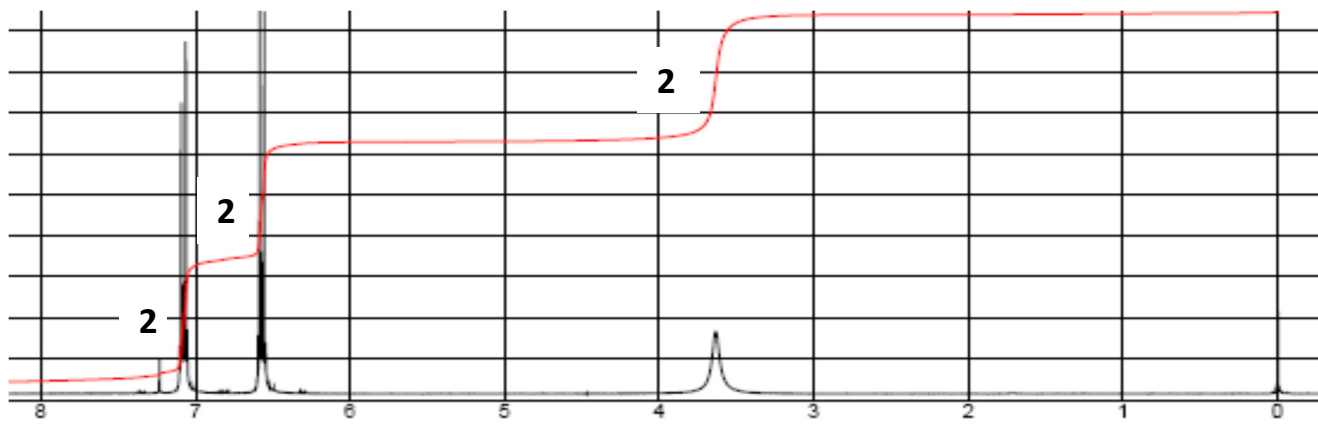
$$NI = 10 + 1 - \frac{1}{2} 12 = 5$$



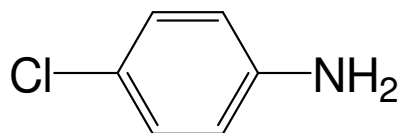
**B**       $\text{C}_{10}\text{H}_{12}\text{O}$   
 $\text{NI} = 10 + 1 - \frac{1}{2} 12 = 5$



**C**       $\text{C}_6\text{H}_6\text{NCl}$



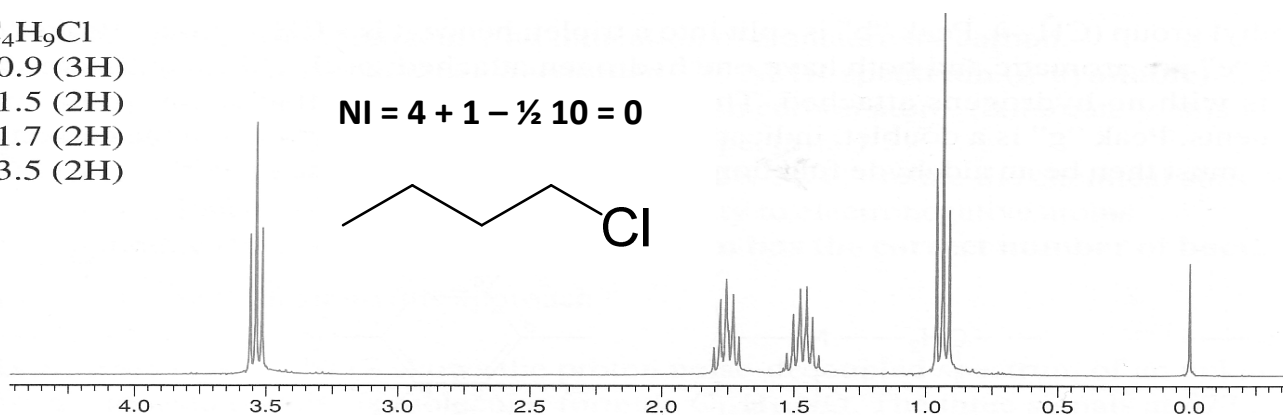
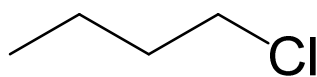
$\text{NI} = 6 + 1 - \frac{1}{2} 7 + \frac{1}{2} = 4$



**D**

$C_4H_9Cl$   
 $\delta 0.9$  (3H)  
 $\delta 1.5$  (2H)  
 $\delta 1.7$  (2H)  
 $\delta 3.5$  (2H)

$$NI = 4 + 1 - \frac{1}{2} 10 = 0$$

**E**

$C_6H_{14}O$   
 $\delta 0.9$  (6H)  
 $\delta 1.6$  (4H)  
 $\delta 3.4$  (4H)

$$NI = 6 + 1 - \frac{1}{2} 14 = 0$$

