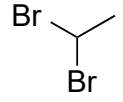
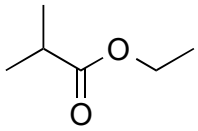
NMR Problem Set

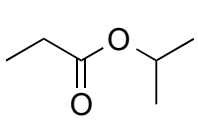
Pages 1-4	Pages 5-8	Page 9
#1 Predict spectra from given structure	**#2-4** Structure elucidation from given spectra	**#5** Summary / Overview

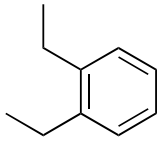
1. Predict the ^{1}H NMR spectrum for compounds **(b)** – **(f)** below.

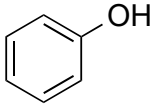
- **Add in the missing hydrogens**
- Determine the **number of ^{1}H NMR signals** in each compound below.
- Label each **type of proton** (A, B, etc.) and fill in the tables provided on the following page with a row for each type of proton (signal).
- Predict the **integration** (#H's), the **chemical shift range** (ppm), and **calculated chemical shift** (ppm), that you would expect for each signal.
    - Determine the **splitting pattern** for each signal using the *n+1 rule*, where *n* is the number of H's on adjacent carbon atoms.
        - Splitting patterns: singlet, doublet, triplet, quartet, pentet, sextet, heptet, or multiplet.
        - There is no splitting through heteroatoms (O, N, S, etc.) – all OH's are singlets!
- **Sketch the predicted ^{1}H NMR spectrum of each compound** and use nmrdb.org to check your work
    - *Approximate* the central chemical shift of the signal on the x-axis and *draw* each splitting pattern.
    - Don't worry about incorporating integration (peak size).

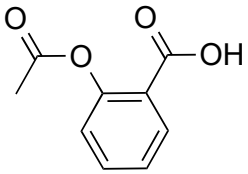
(a) 

(b) 

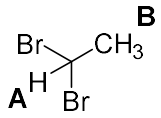
(c) 

(d) 

(e) 

(f) 

(1a) Worked example: Watch the "**How to do the NMR Problem Set**" video on Canvas



Signal	Integration	Splitting n+1 rule	Chemical Shift Range (ppm)	Calculated Chemical Shift (ppm)*
A	*1H*	*quartet*	*2.1 – 4.5*	*5.7*
B	*3H*	*doublet*	*0.8 – 1.9*	*2.3*

Calculate expected chemical shifts using *Table 22.3 of NMR tables – alkyl H's

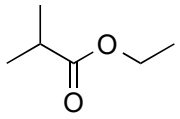
Calculation of Signal **A**

Methine (CH) + 2 x Br (alpha substituent)
1.5 ppm + *(2 x 2.1)* = *5.7 ppm*

Calculation of Signal **B**

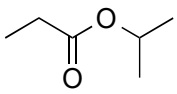
Methyl (CH_3) + 2 x Br (beta substituent)
0.9 ppm + *(2 x 0.7)* = *2.3 ppm*

Tables for #1 – create as many rows as the number of signals in each compound, read page 1 for more!

(1b) 	Signal	Integration	Splitting	Chemical Shift Range (ppm)	Calculated Chemical Shift (ppm)*

Sketch of ^{1}H NMR spectrum:

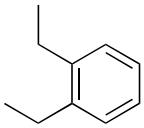
12 **Chemical Shift (ppm)** **0**

(1c) 	Signal	Integration	Splitting	Chemical Shift Range (ppm)	Calculated Chemical Shift (ppm)*

Sketch of ^{1}H NMR spectrum:

12 **Chemical Shift (ppm)** **0**

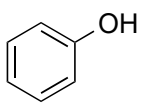
Tables for #1 – create as many rows as the number of signals in each compound, read page 1 for more!

(1d) 	Signal	Integration	Splitting	Chemical Shift Range (ppm)	Calculated Chemical Shift (ppm)*

Note: Use correlation Table 22.4 for aromatic H's and Table 22.3 for alkyl H's

Sketch of ^{1}H NMR spectrum:

12 **Chemical Shift (ppm)** **0**

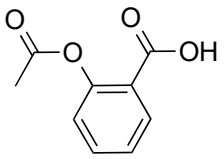
(1e) 	Signal	Integration	Splitting	Chemical Shift Range (ppm)	Calculated Chemical Shift (ppm)*

Note: Use correlation Table 22.4 for aromatic H's; no calculation for OH

Sketch of ^{1}H NMR spectrum:

12 **Chemical Shift (ppm)** **0**

Tables for #1 – create as many rows as the number of signals in each compound, read page 1 for more!

	Signal	Integration	Splitting	Chemical Shift Range (ppm)	Calculated Chemical Shift (ppm)*
(1f) 					

Sketch of ^{1}H NMR spectrum:

12 **Chemical Shift (ppm)** **0**

2. Structural Elucidation: **Draw structures** for compounds that meet the following descriptions.

1. Calculate **degrees of unsaturation** from the **molecular formula** to determine the number of pi bonds or rings
2. Use **IR** to identify potential **bonds & functional group(s)**
3. Draw structure **fragments** for each ^{1}H NMR signal using the **integration & splitting**
    a. Ex. **2H doublet** = C**H$_2$**CH, where the bold H's are determined by integration (2H) and the neighboring CH group is determined by splitting (doublet)
    b. Incorporate functional groups into fragments where possible using **chemical shifts**
        i. Ex. δ 4.0 (2H doublet) = OC**H$_2$**CH
        ii. the 2H's are deshielded by the electronegative oxygen, resulting in a higher chemical shift
4. Put the **fragments** together in the final structure.

Worked examples: Watch the "**How to do the NMR Problem Set**" video on Canvas

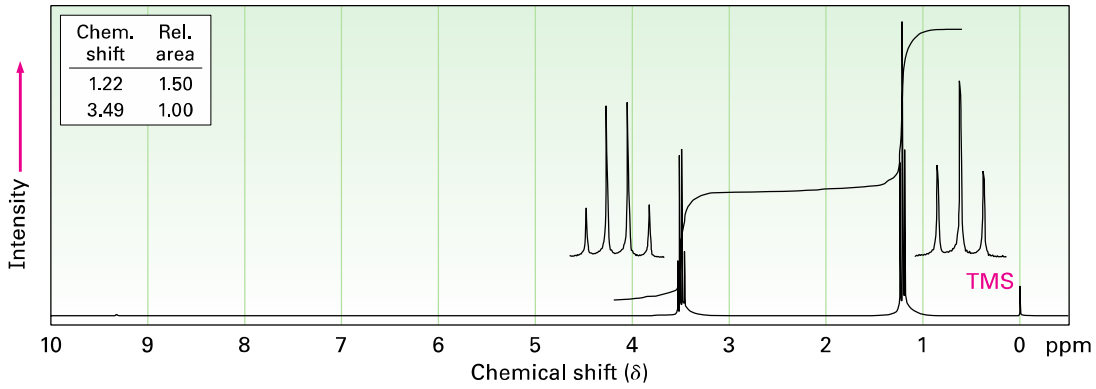
Formula	Degrees Unsat.	Suspected bonds / FG(s) from IR	Fragment(s) from ^{1}H NMR	Final Structure
C_3H_6O	**1**	1720 cm^{-1} **C=O** 2900 cm^{-1} **Alkane sp^3 C-H**	δ 2.0 ppm (6H singlet) 6H's are next to 0 H's C**H$_3$**C$_{(no\ H's)}$ Symmetry - 2 x CH_3 groups	
C_3H_7Cl	**0**	2900 cm^{-1} **Alkane** 800 cm^{-1} **C-Cl bond**	δ 3.7 (6H doublet) ^ next to Cl Doublet = 6H's next to one H (C**H$_3$**)$_2$CHCl δ 1.4 (1H septet) ^ farther from Cl Septet = 1H next to 6 H's (CH$_3$)$_2$C**H**Cl	$(CH_3)_2CHCl$

Formula	Degrees Unsat.	Suspected bonds / FG(s) from IR	Fragment(s) from ^{1}H NMR	Final Structure
(2a) $C_5H_{10}O_2$		1760 cm^{-1} 2900 cm^{-1}	δ 4.1 (2H quartet) δ 2.3 (2H quartet) δ 1.3 (3H triplet) δ 1.1 (3H triplet)	
(2b) $C_4H_8O_2$		1760 cm^{-1} 2900 cm^{-1}	δ 4.0 (2H quartet) δ 2.0 (3H singlet) δ 1.4 (3H triplet)	
(2c) C_3H_8O		3300 cm^{-1} 2900 cm^{-1}	δ 3.8 (1H septet) δ 2.0 (1H broad singlet) δ 1.2 (6H doublet)	

Formula	Degrees Unsat.	Suspected bonds / FG(s) from IR	Fragment(s) from ^{1}H NMR	Final Structure
(2d) Bonus Problem: $C_{10}H_{12}O$		3050 cm^{-1} 1675 cm^{-1} 1620 cm^{-1} 850 cm^{-1}	δ 7.85 (2H doublet) δ 7.28 (2H doublet) δ 2.9 (2H quartet) δ 2.0 (3H singlet) *benzylic δ 1.5 (3H triplet)	

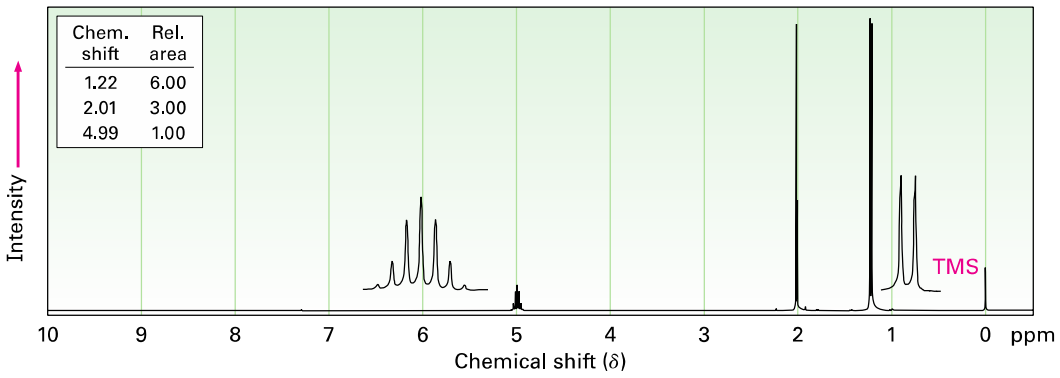
3. Determine the **structure** of a compound with molecular formula $C_4H_{10}O$ and the integrated ^{1}H NMR spectrum below (**rel. area** gives the *ratio* of H's per signal). Identify the splitting pattern from the expanded shapes in the spectrum (**m = n + 1**, where **m** = multiplicity, triplet or quartet and **n** = number of neighboring H's).

- Show your work: **draw fragments** of the molecule in addition to the **full structure**.
  ↓ This box gives the relative area (integration or ratio of H's) of both peaks, identified by chemical shift.



4. Propose a structure for a compound with formula $C_5H_{10}O_2$ and a sharp IR absorbance at 1735 cm^{-1}. Identify the splitting pattern from the expanded shapes in the spectrum (**m = n + 1**, where **m** = multiplicity, triplet or quartet and **n** = number of neighboring H's). The signal at 2.0 is a singlet.

- Show your work: **draw fragments** of the molecule in addition to the **full structure**.
  ↓ This box gives the relative area (integration) of all peaks, identified by chemical shift.



5. *<u>Summarize your process</u>* for (a) predicting spectra and (b) elucidating / solving a structure from spectral data.

(a) Predicting Spectra

(b) Structural Elucidation