

# ORGANIC CHEMISTRY 30B

(Prof. Yves Rubin)

UCLA, FALL 2006

## MIDTERM EXAM I

On my honor, I have neither given nor received any aid on this exam  
(There are no regrades, so you may use pencil or ink):

\_\_\_\_\_  
Signature

\_\_\_\_\_  
I. D. Number

\_\_\_\_\_  
Full Name (**Please Print !**)

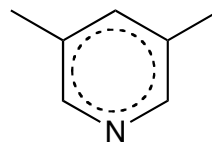
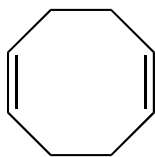
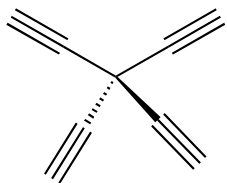
Question	Points
1 (30)	
2 (15)	
3 (15)	
4 (40)	

Total (100)

=====

### I. SPECTROSCOPY

1. a) (12 points) Give the number of expected signals (*ignore splittings*) in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the following compounds:



$^1\text{H}$  NMR:

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

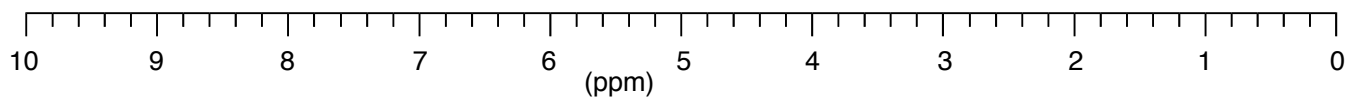
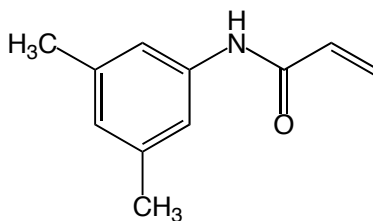
$^{13}\text{C}$  NMR:

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

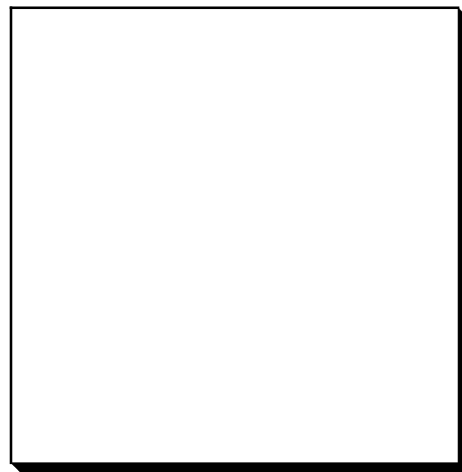
b) (18 points) Sketch the  $^1\text{H}$  NMR spectrum for the compound below. Be sure to consider *chemical shifts*, *coupling patterns*, and *relative intensities* between each spin system when drawing your spectrum. **Label all non-symmetrically related H's on the structure (e.g. a,b,c, etc) and show what peak they correspond to on the spectrum:**



\_\_\_\_\_  
Name

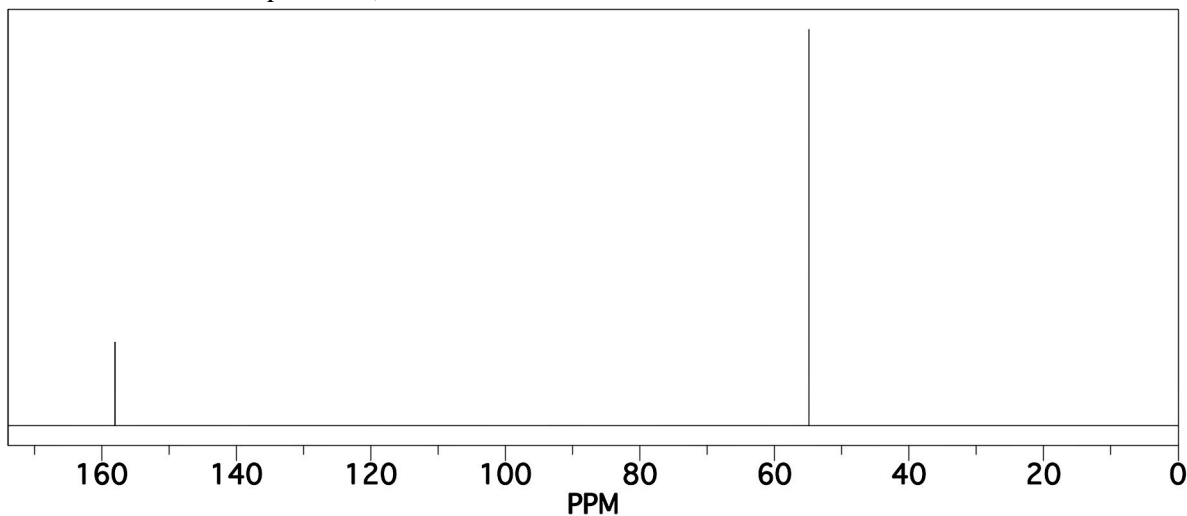
2. (15 points) A compound with molecular formula  $C_3H_6O_3$  has the following  $^{13}C$  NMR spectrum.  
**Assign** the signals on the spectrum and provide its structure in the box below:

Degree of Unsaturation: \_\_\_\_\_



**Compound  $C_3H_6O_3$**

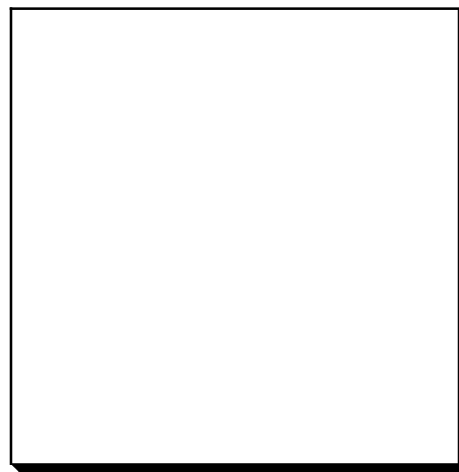
*(Assign peaks on or below the spectrum)*



\_\_\_\_\_  
Name

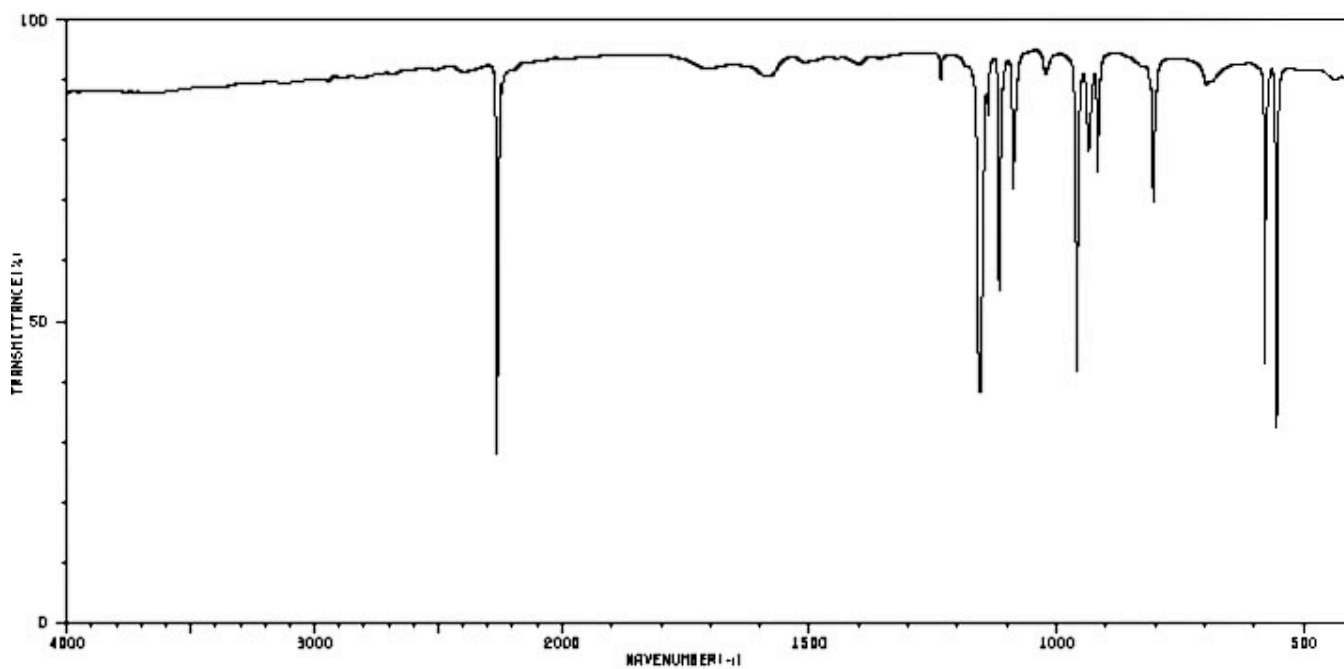
3. (15 points) A compound with molecular formula  $C_6N_4$  has the following IR spectrum. Its  $^{13}C$  NMR spectrum has only two lines. From this information only, deduce its structure and assign any recognizable peak. Keep in mind that the compound is highly symmetric. **You MUST provide all the relevant information (peak assignment)** to get maximum credit:

Degree of Unsaturation: \_\_\_\_\_



Compound  $C_6N_4$

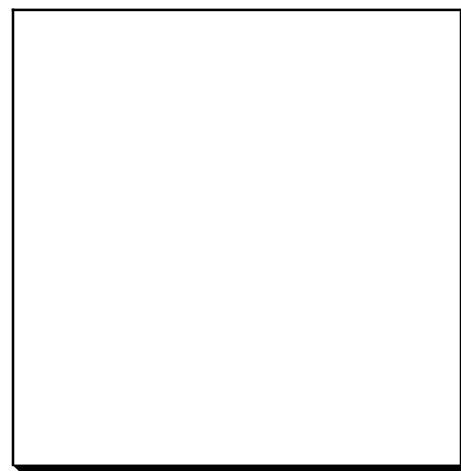
**IR spectrum:**



\_\_\_\_\_  
Name

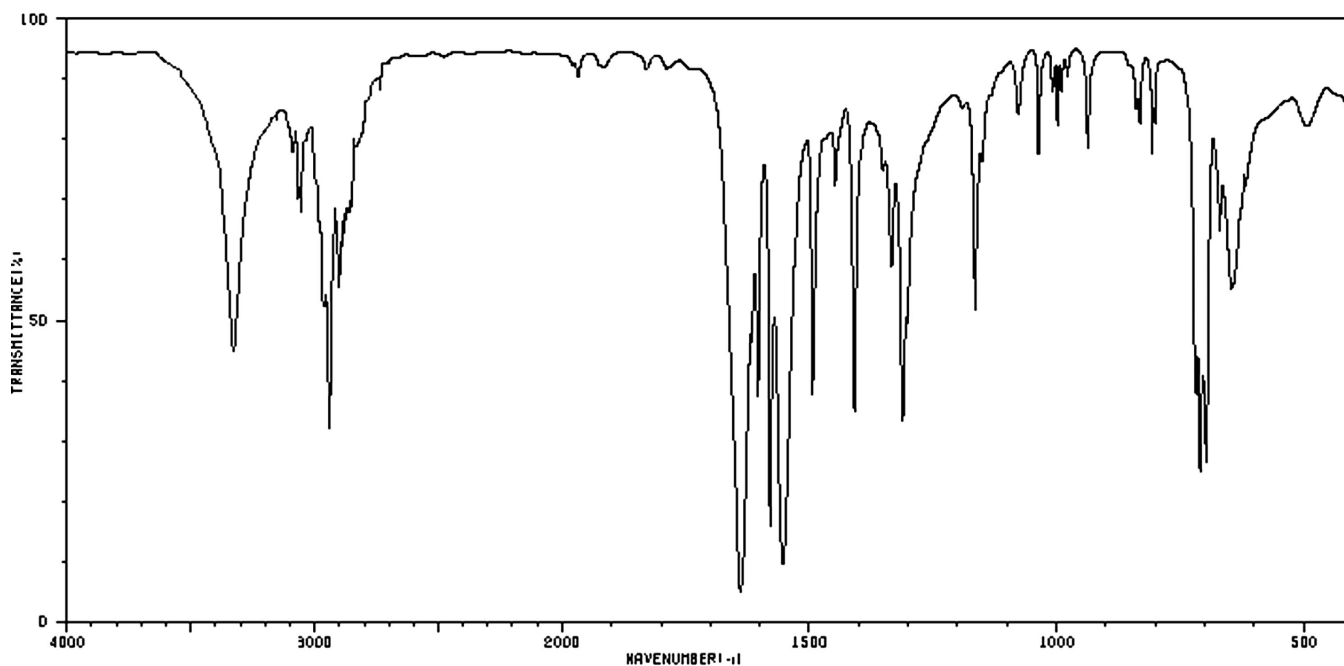
4. (40 points) A compound has the molecular formula  $C_{11}H_{14}ClNO$ . Deduce its structure from the IR,  $^1H$  NMR, and  $^{13}C$  NMR spectra given below. **You MUST provide all the relevant information (peak assignments) to get maximum credit.** Draw the structure in the box provided:

Degree of Unsaturation: \_\_\_\_\_



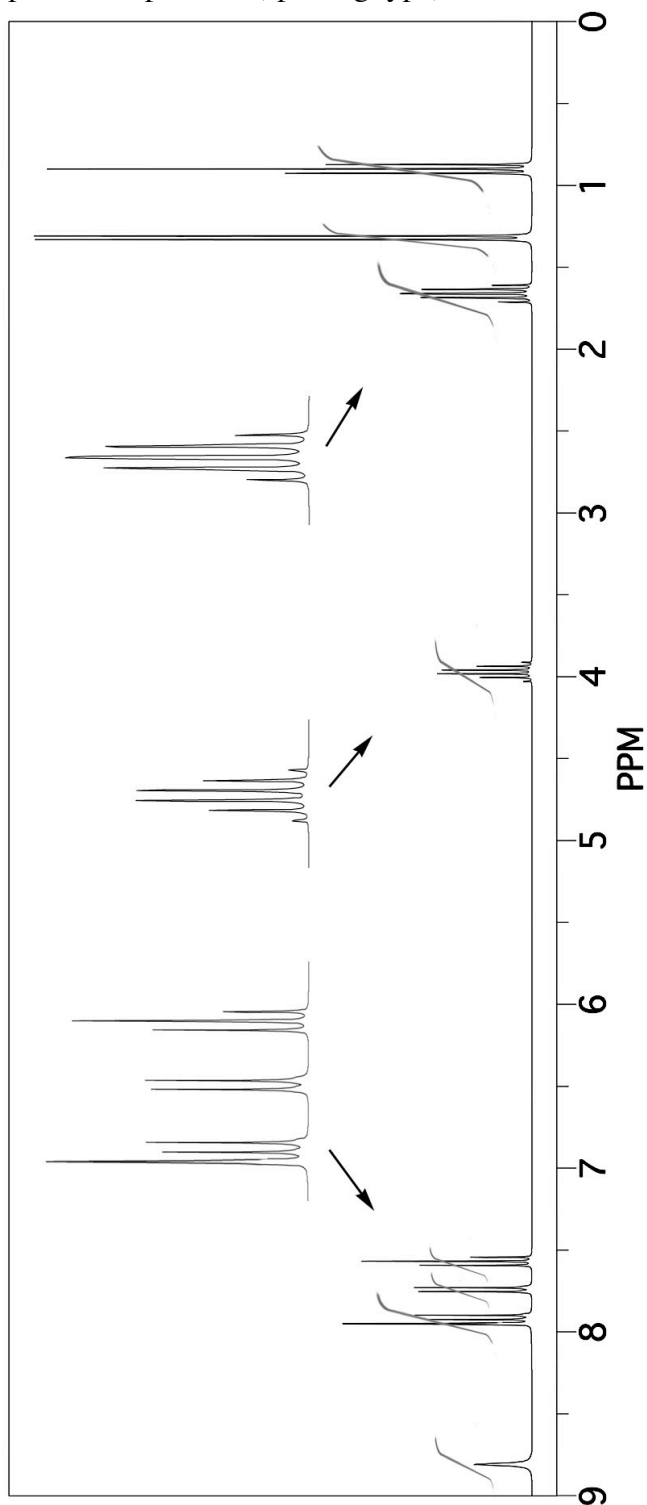
Compound  $C_{11}H_{14}ClNO$

IR (KBr; assign all recognizable IR stretch frequencies):



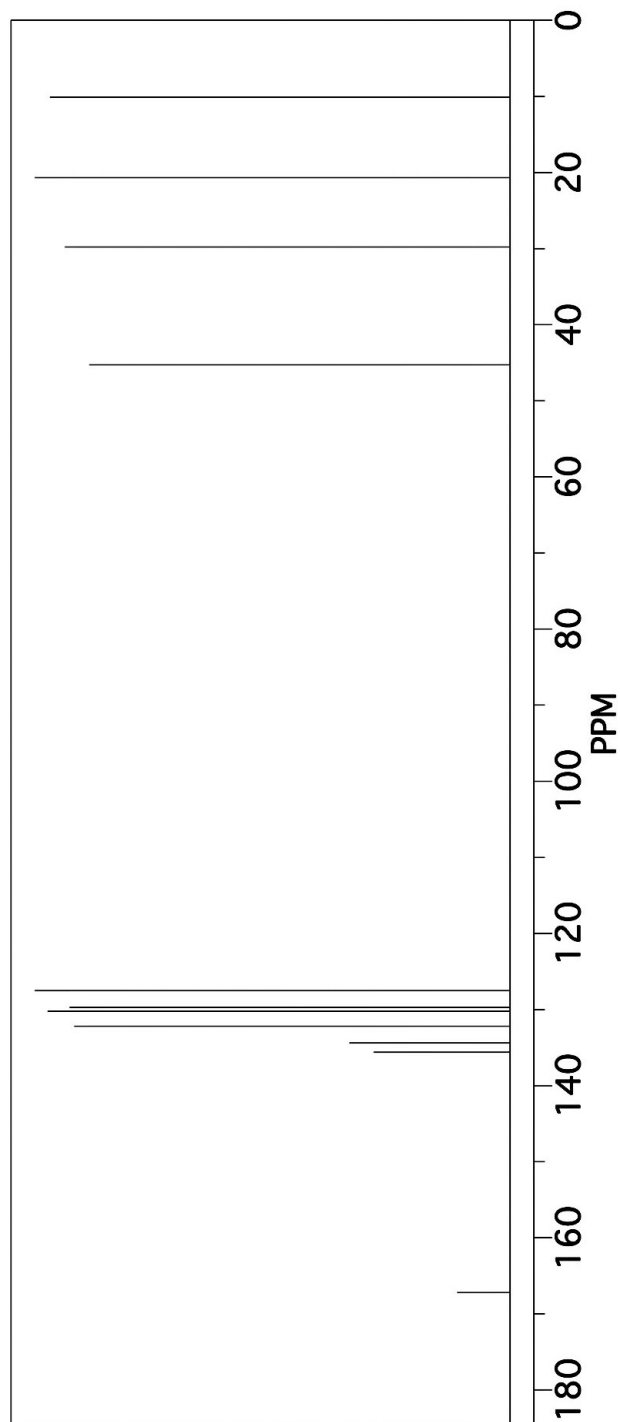
\_\_\_\_\_  
Name

**<sup>1</sup>H NMR:** Draw structure here as well and label all non-symmetrically related H's on the structure (e.g. with **a,b,c**, etc). Show which peak the labels correspond to on the spectrum by drawing arrows to them. Provide labels for integration values (1H, 2H, 3H) and peak multiplicities (splitting type):



\_\_\_\_\_  
Name

**$^{13}\text{C}$  NMR** spectrum for question 4. Draw the structure here again and assign the  $^{13}\text{C}$  signals to specific carbons on the structure. However, aliphatic carbons do not need to be assigned, but you should label the alkene or aromatic peaks as such, but not assign them to specific positions since you cannot calculate precise chemical shifts:



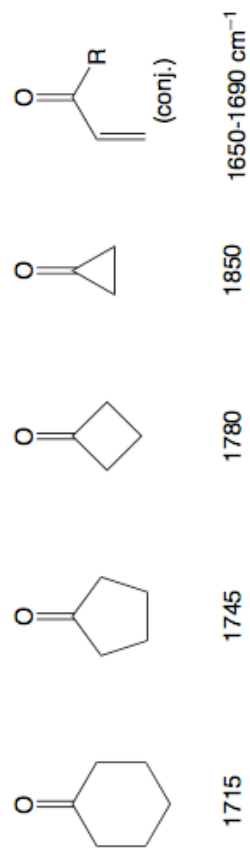
**Infrared Spectroscopy Table**  
(by John Mouser)

Functional Group	Frequency (cm <sup>-1</sup> )	intensity
water OH stretch	3700-3100	strong
alcohol OH stretch	3600-3200	strong, broad
carboxylic acid OH stretch	3600-2500	strong, broad
N-H stretch	3500-3350 (1 for NH, 2 for NH <sub>2</sub> )	strong
=C-H stretch	~3300	strong
=C-H stretch	3100-3000	variable
-C-H stretch	2950-2840	variable
-C-H aldehydic	2850-2750	variable
C=N stretch	~2250	strong
C≡C stretch	2260-2100	variable
C=O aldehyde	1740-1720	strong
C=O anhydride	1840-1800, 1780-1740	weak, strong
C=O ester	1750-1720	strong
C=O ketone	1745-1715	strong
C=O amide	1700-1500	strong
C=C alkene	1680-1600	variable
C=C aromatic	1600-1400	variable
CH <sub>2</sub> bend	1480-1440	medium
CH <sub>3</sub> bend	1465-1440, 1390-1365	medium
C-O-C stretch	1250-1050 several	strong
C-OH stretch	1200-1020	strong
C-F	1400-1000	strong
C-Cl	800-600	strong
C-Br	750-500	strong
C-I	~500	strong

**Characteristic Infrared Absorption Frequencies**







Bonding	Frequency (cm <sup>-1</sup> )	Intensity*	Type of Vibration (stretching unless noted)
C—H	2850–3000 1375 and 1450 1450	w–m w–m m	out-of-plane bending out-of-plane bending
—CH <sub>3</sub> —CH <sub>2</sub> —	3000–3100 650–1000	w–m s	out-of-plane bending
alkene	3300 3000–3100 690–900	s s s	out-of-plane bending
alkyne	2700–2800 2800–2900	w w	out-of-plane bending
aromatic	(not interpretatively useful)		
aldehyde	1600–1680 1450 and 1600	w–m w–m	
C—C	2100–2250 1050–1250	w–m s	
C=C	1630–1680 1700–1750	s s	
C≡C	1705–1780 1705–1740	s s	
C—O	1735–1800 1760 and 1810 1800	s s s	
alkane	3600–3650	m	
alkene	3200–3500	m	
aromatic	2400–3400	m	
alkyne	3100–3500	m–s	
alcohol, ether, ester, carboxylic acid, anhydride	2200–2250	m	
amide	1630–1680	s	
carboxylic acid	1700–1750	s	
ketone	1705–1780	s	
aldehyde	1705–1740	s	
ester	1735–1800	s	
anhydride	1760 and 1810	s	
acid chloride	1800	s	
O—H	3600–3650 3200–3500	m m	
alcohol, phenol	2400–3400	m	
free	3100–3500	m–s	
hydrogen bonded	2200–2250	m	
carboxylic acid			
amine and amide			
nitrile			

\* s = strong, m = medium, w = weak



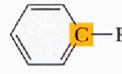






## Characteristic <sup>1</sup>H-NMR Chemical Shifts

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
(CH <sub>3</sub> ) <sub>4</sub> Si	0 (by definition)		3.7–3.9
RCH <sub>3</sub>	0.8–1.0		4.1–4.7
RCH <sub>2</sub> R	1.2–1.4	RCH <sub>2</sub> I	3.1–3.3
R <sub>3</sub> CH	1.4–1.7	RCH <sub>2</sub> Br	3.4–3.6
R <sub>2</sub> C=CRCH <sub>2</sub> R <sub>2</sub>	1.6–2.6	RCH <sub>2</sub> Cl	3.6–3.8
RC≡CH	2.0–3.0	RCH <sub>2</sub> F	4.4–4.5
ArCH <sub>3</sub>	2.2–2.5	ArOH	4.5–4.7
ArCH <sub>2</sub> R	2.3–2.8	R <sub>2</sub> C=CH <sub>2</sub>	4.6–5.0
ROH	0.5–6.0	R <sub>2</sub> C=CHR	5.0–5.7
RCH <sub>2</sub> OH	3.4–4.0	ArH	6.5–8.5
RCH <sub>2</sub> OR	3.3–4.0		9.5–10.1
R <sub>2</sub> NH	0.5–5.0		10–13
	2.1–2.3		
	2.2–2.6		

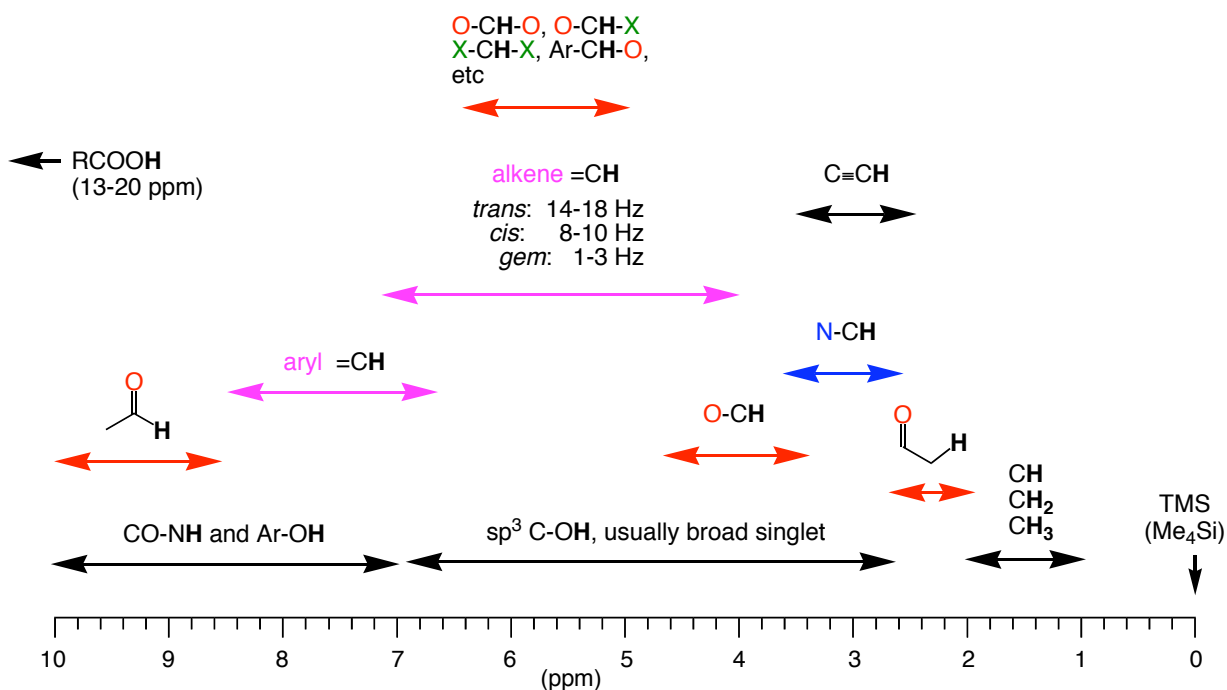
\* Values are approximate. Other atoms within the molecule may cause the signal to appear outside these ranges.

## Characteristic <sup>13</sup>C-NMR Chemical Shifts

Type of Carbon	Chemical Shift (δ)	Type of Carbon	Chemical Shift (δ)
RCH <sub>3</sub>	0–40		110–160
RCH <sub>2</sub> R	15–55		160–180
R <sub>3</sub> CH	20–60		165–180
RCH <sub>2</sub> I	0–40		175–185
RCH <sub>2</sub> Br	25–65		180–210
RCH <sub>2</sub> Cl	35–80		
R <sub>3</sub> COH	40–80		
R <sub>3</sub> COR	40–80		
RC≡CR	65–85		
R <sub>2</sub> C=CR <sub>2</sub>	100–150		

## CHEM 30C, COMMON <sup>1</sup>H NMR CHEMICAL SHIFT RANGES

Common NMR solvents:  
CDCl<sub>3</sub>, D<sub>3</sub>C-SO-CD<sub>3</sub>, D<sub>2</sub>O  
CD<sub>3</sub>OD



## CHEM 30B, COMMON <sup>13</sup>C NMR CHEMICAL SHIFT RANGES

