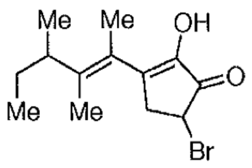
Chem 333, Exam 2
Professor Fox
FALL 2013

Your Name______________________________________

Q1) 15 points
Q2) 24 points
Q3) 16 points
Q4) 45 points

tables at back of exam

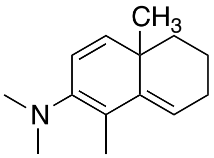
1. Calculate the UV maximum for the following compounds. Show your work as illustrated by the example below (15 points)



EXAMPLE of answer format

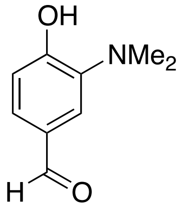
base value	202
increments for:	
double bond extending conjugation	30
alkyl substitutent or ring residues	66
polar groups	35
exocyclic double bond	none
homodiene component	none
total	333

a



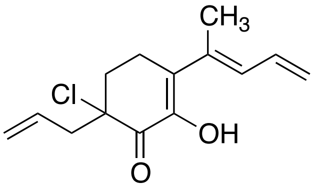
base value	
increments for:	
double bond extenstions	
alkyl substitutent or ring residues	
exocyclic double bond	
polar groups	
total	

b



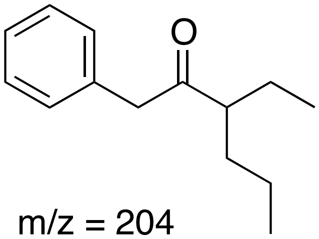
base value	
increments for:	
alkyl or ring residue...	
–OH, –OCH_3, –OAlk..	
–O^- (oxyanion)...........	
–Cl	
–Br	
–NH_2	
–$NHCOCH_3$..............	
–$NHCH_3$...................	
–$N(CH_3)_3$..................	
total	

c



base value	
increments for:	
double bond extending conjugation	
alkyl substitutent or ring residues	
polar groups	
exocyclic double bond	
homodiene component	
total	

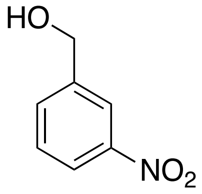
2. Explain how the indicated fragments are formed. Your answer should provide both a chemical structure and a mechanism for the formation of each fragment peak. (24 points)



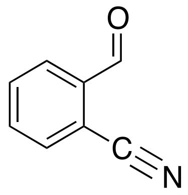
m/z = 204

m/z = 85
m/z = 91
m/z = 113
m/z = 119
m/z = 162
m/z = 176

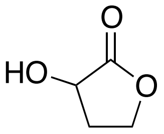
3. Match the following to their IR spectra. Note, only 4 spectra have a match. (16 points)



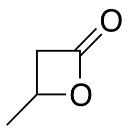
A



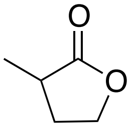
B



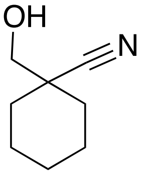
C



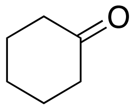
D



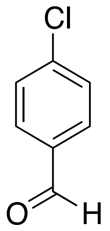
E



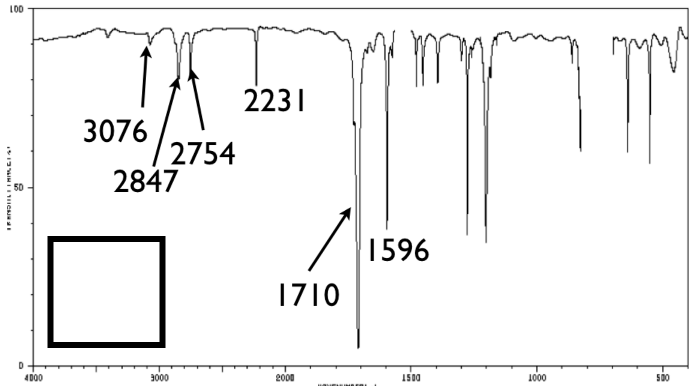
F

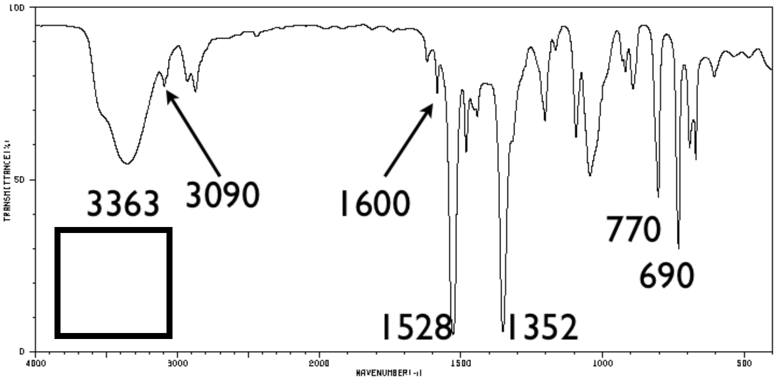


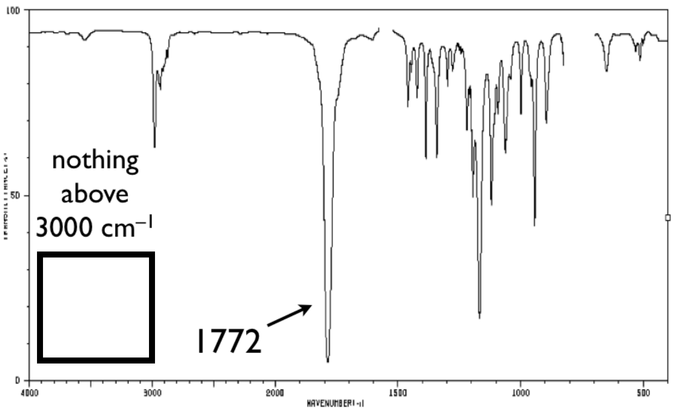
G

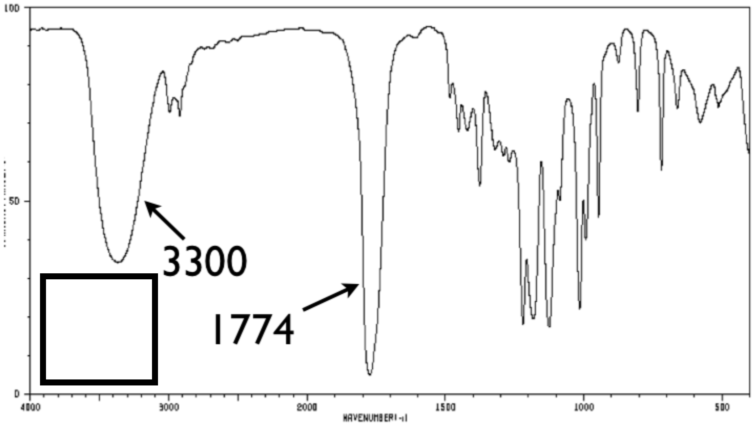


H









4. Elucidate the following structure based on the following spectral data

$C_{12}H_{20}O$

^{1}H NMR
5.77 (ddt, *J* = 17.0, 10.0, 7.0 Hz, 1H)
5.01 (ddt, *J* = 17.0, 2.1, 1.0 Hz, 1H)
4.97 (ddt, *J* = 10.0, 2.1, 1.2 Hz, 1H)
2.56 (ddd, *J* = 12.5, 11.5, 4.0 Hz, 1H)
2.32-2.17 (m, 2H)
1.96-1.90 (m, 2H)
1.87-1.83 (m, 1H)
1.56-1.38 (m, 8H)
1.02 (d, *J* = 7.0 Hz, 3H)

^{13}C NMR
215, s
138, d
115, t
55, d
42, t
36, d
35, t
32, t
30, t
28, t
26, t
21, q

IR (cm^{-1}, neat) : 3079, 2936, 1706, 1640, 1450, 1325, 1248, 998, 915

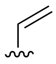
MS 180 (M+, parent peak), 126, 41

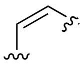
a) Calculate the IHD: __________ (1 point)

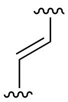
b) How many hydrogens are on carbons? __________ (1 point)

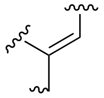
c) Show the substructure that is associated with the following IR peaks (4 points)

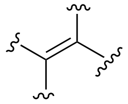
3079 cm^{-1}, 1640 cm^{-1}

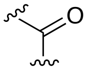

mono-
substituted
alkene


cis-
disubstituted
alkene

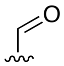

trans-
disubstituted
alkene


trisubstituted
alkene

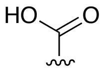

tetrasubstituted
alkene



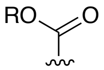
ketone



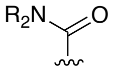
aldehyde



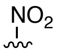
acid



ester

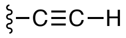


amide

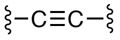


nitro

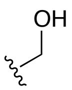
nitrile



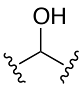
terminal
alkyne



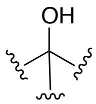
internal
alkyne



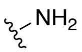
primary
alcohol



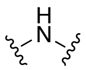
secondary
alcohol



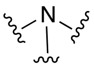
tertiary
alcohol



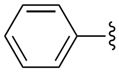
primary
amine

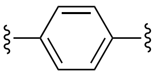


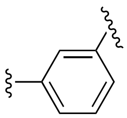
secondary
amine

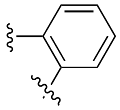


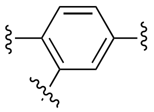
tertiary
amine


monosubstituted
benzene


1,4-disubstituted
benzene


1,3-disubstituted
benzene

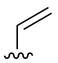

1,2-disubstituted
benzene

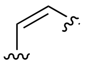

trisubstituted
benzene

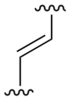
none of the above

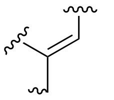
d) Show the substructure that is associated with the following IR peak (4 points).

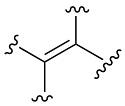
1706 cm $^{-1}$

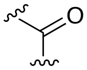

mono-
substituted
alkene


cis-
disubstituted
alkene

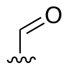

trans-
disubstituted
alkene


trisubstituted
alkene

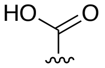

tetrasubstituted
alkene



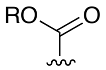
ketone



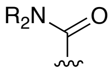
aldehyde



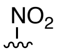
acid



ester

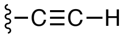


amide

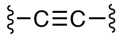


nitro

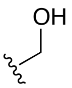
nitrile



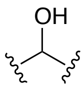
terminal
alkyne



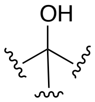
internal
alkyne



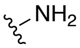
primary
alcohol



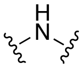
secondary
alcohol



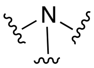
tertiary
alcohol



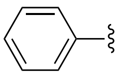
primary
amine

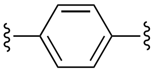


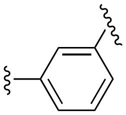
secondary
amine

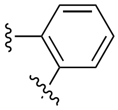


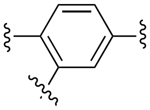
tertiary
amine


monosubstituted
benzene


1,4-disubstituted
benzene


1,3-disubstituted
benzene


1,2-disubstituted
benzene


trisubstituted
benzene

none of the above

e) Assign the following mass spectral fragments (10 points). Draw the structures of the fragments.

126, 41

f) Show the substructure that is associated with the following ^{1}H NMR resonances. Assign the coupling constants. Also, indicate the multiplicity (s,d,t or q) of the carbon to which this substructure is attached. (8 points)

5.77 (ddt, J = 17.0, 10.0, 7.0 Hz, 1H)
5.01 (ddt, J = 17.0, 2.1, 1.0 Hz, 1H)
4.97 (ddt, J = 10.0, 2.1, 1.2 Hz, 1H)

g) Does your compound have a ring? If so, what size? Hint: pay careful attention to the IR peak at 1706 cm–1 (5 points)

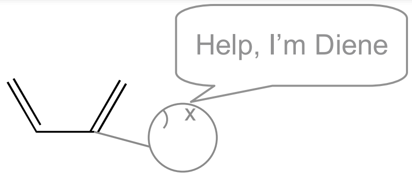
circle the correct ring size

3 4 5 6 7

8 9 10 no ring

h) Draw the structure (12 points)

UV-VIS Calculation Tables

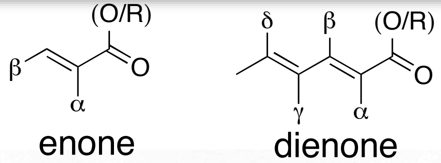


Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5
Polar groupings: OAc	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
$N(Alk)_2$	+60
Solvent correction[b]	+0
	λ_{calc} = Total

---

[a] See L. M. Fieser and M. Fieser, *Steroids*. New York: Reinhold, 1959, pp. 15–24; R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); **64**, 72, 76 (1942); A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*. New York: Pergamon (Macmillan), 1964.

[b] Solvents have negligible effects upon the λ_{max} of these $\pi \rightarrow \pi^*$ transitions.

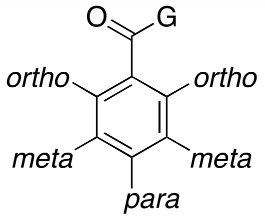


Base values		(nm)
Acyclic α,β-unsaturated ketones		215
Six-membered cyclic α,β-unsaturated ketones		215
Five-membered cyclic α,β-unsaturated ketones		202
α,β-Unsaturated aldehydes		210
α,β-Unsaturated carboxylic acids and esters		195
Increments for		
Double bond extending conjugation		+30
Alkyl group, ring residue	α	+10
	β	+12
	γ and higher	+18
Polar groupings: —OH	α	+35
	β	+30
	δ	+50
—OAc	α,β,δ	+ 6
—OMe	α	+35
	β	+30
	γ	+17
	δ	+31
—SAlk	β	+85
—Cl	α	+15
	β	+12
—Br	α	+25
	β	+30
$—NR_2$	β	+95
Exocyclic double bond		+5
Homodiene component[a]		+39
Solvent correction (see table below)		Variable
		λ_{calc} = Total[b]

---

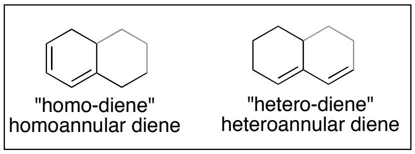
[a] Two conjugated double bonds, both in the same ring.

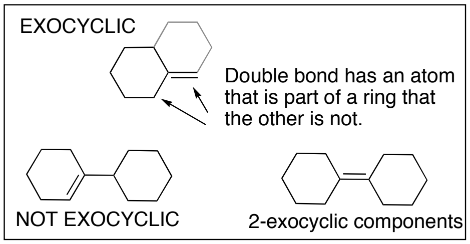
[b] The calculated values usually fall within ±3 nm of the observed values. The molar absorptivities of *cisoid* enones are usually less than 10,000, whereas the molar absorptivities of *transoid* enones are greater than 10,000.



$ArCOR/ArCHO/ArCO_2H/ArCO_2R$		λ_{max}^{EtOH} (nm)
Parent chromophore: Ar = C_6H_5		
G = Alkyl or ring residue, (e.g., ArCOR)		246
G = H, (ArCHO)		250
G = OH, OAlk, ($ArCO_2H$ and $ArCO_2R$)		230
Increment for each substituent on Ar:		
—Alkyl or ring residue	o-, m-	+3
	p-	+10
—OH, $—OCH_3$, —OAlk	o-, m-	+7
	p-	+25
$—O^-$ (oxyanion)	o-	+11
	m-	+20
	p-	+78[b]
—Cl	o-, m-	+0
	p-	+10
—Br	o-, m-	+2
	p-	+15
$—NH_2$	o-, m-	+13
	p-	+58
$—NHCOCH_3$	o-, m-	+20
	p-	+45
$—NHCH_3$	p-	+73
$—N(CH_3)_2$	o-, m-	+20
	p-	+85

Terminology





Carbon NMR essentials

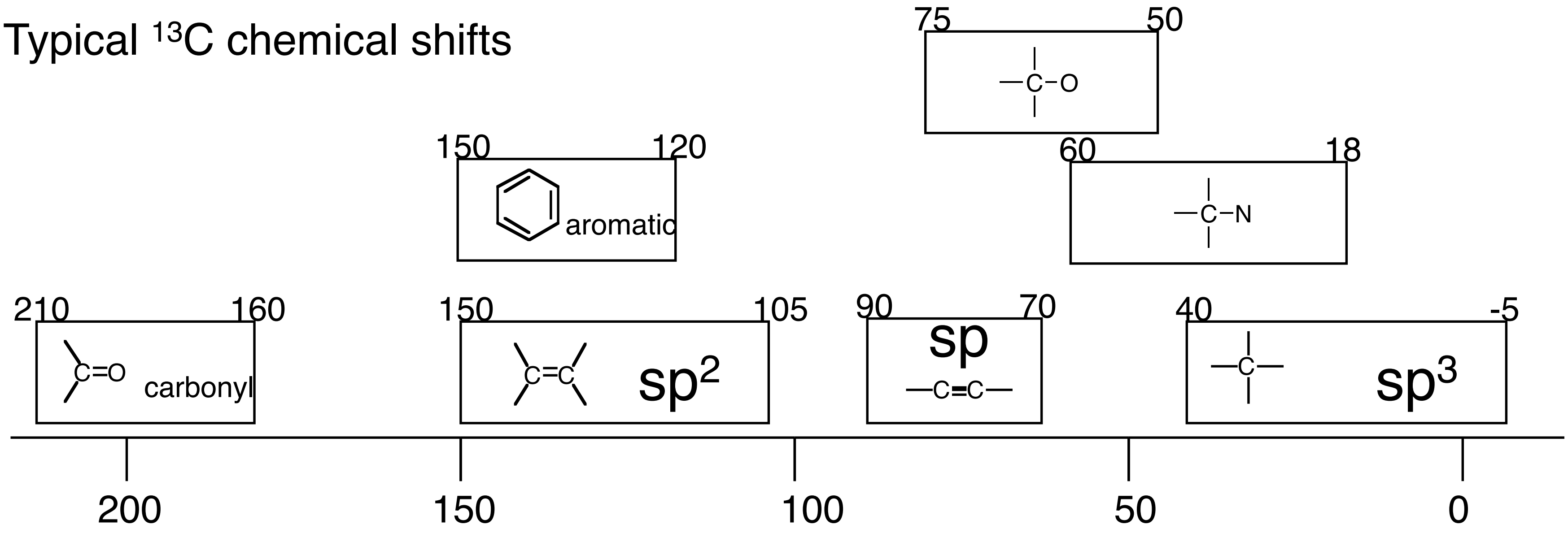
You Should Know:

1. For $C_NH_\#O_\#N_\#$ $\quad \text{IHD} = \dfrac{2N+2 - (\#\text{hydrogens}+\#\text{halogens}) + (\#\text{Ns})}{2}$

2. How to identify symmetry and use it.

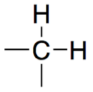
3. Proton Inventory. Identify if any protons are attached to non-carbon atoms by Summing the number of C-attached protons and comparing to molecular formula

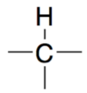
4. Typical ^{13}C chemical shifts

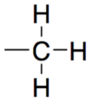


5. multiplicities

(s) singlet 

(t) triplet 

(d) doublet 

(q) quartet 

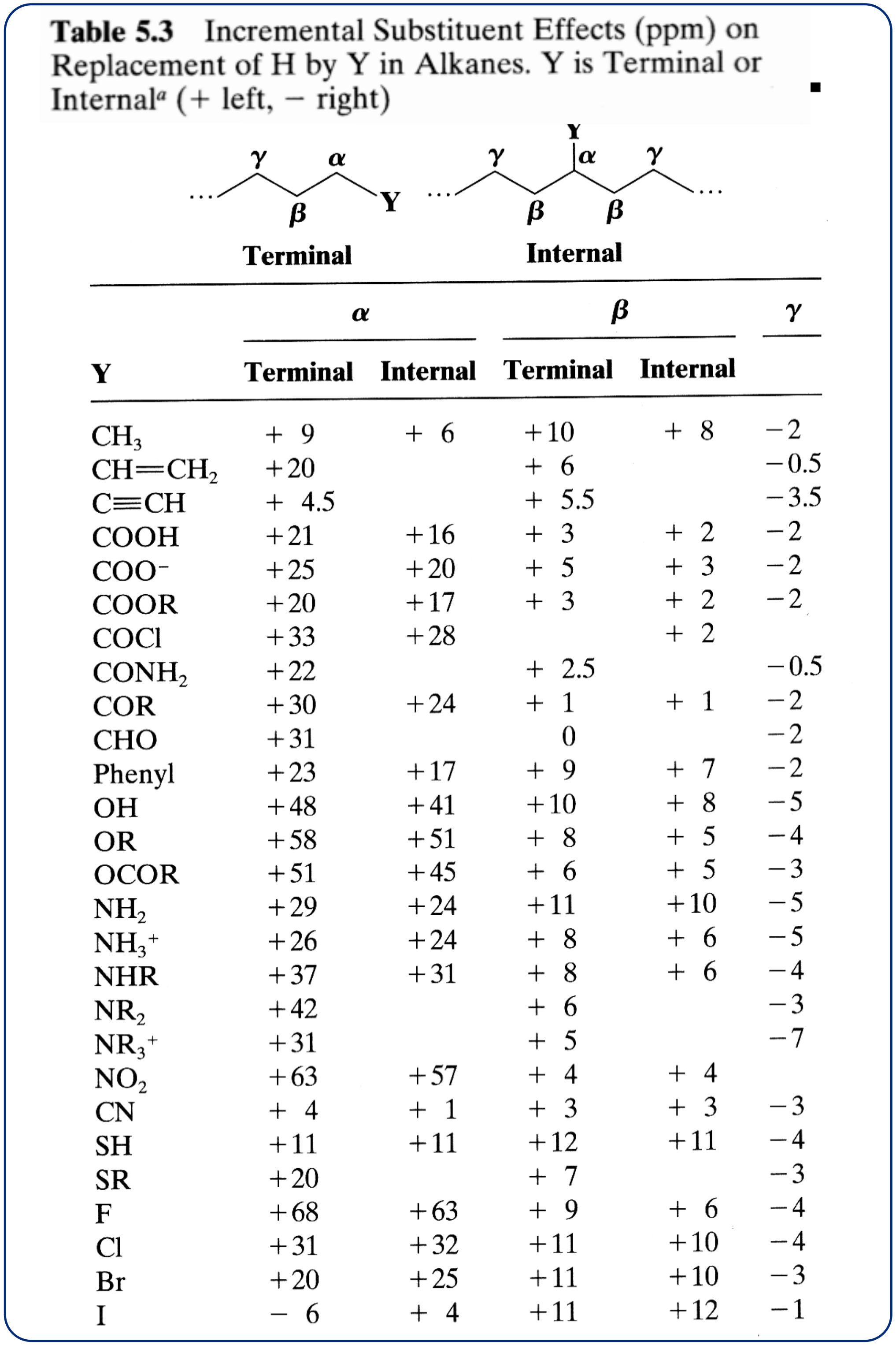


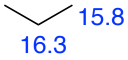
Table 5.3 Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internal[a] (+ left, − right)

	α		β		γ
Y	**Terminal**	**Internal**	**Terminal**	**Internal**	
CH_3	+9	+6	+10	+8	−2
$CH{=}CH_2$	+20		+6		−0.5
$C{\equiv}CH$	+4.5		+5.5		−3.5
COOH	+21	+16	+3	+2	−2
COO^-	+25	+20	+5	+3	−2
COOR	+20	+17	+3	+2	−2
COCl	+33	+28		+2	
$CONH_2$	+22		+2.5		−0.5
COR	+30	+24	+1	+1	−2
CHO	+31		0		−2
Phenyl	+23	+17	+9	+7	−2
OH	+48	+41	+10	+8	−5
OR	+58	+51	+8	+5	−4
OCOR	+51	+45	+6	+5	−3
NH_2	+29	+24	+11	+10	−5
NH_3^+	+26	+24	+8	+6	−5
NHR	+37	+31	+8	+6	−4
NR_2	+42		+6		−3
NR_3^+	+31		+5		−7
NO_2	+63	+57	+4	+4	
CN	+4	+1	+3	+3	−3
SH	+11	+11	+12	+11	−4
SR	+20		+7		−3
F	+68	+63	+9	+6	−4
Cl	+31	+32	+11	+10	−4
Br	+20	+25	+11	+10	−3
I	−6	+4	+11	+12	−1

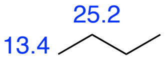
base values

CH_4 -2.3 methane

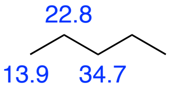
ethane $H_3C{-}CH_3$ 5.7



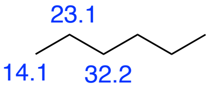
propane



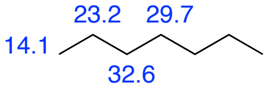
butane



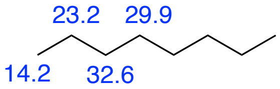
pentane



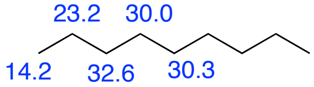
hexane



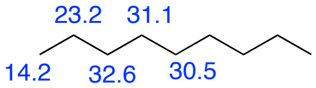
heptane



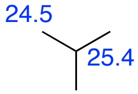
octane



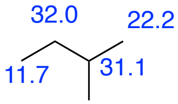
nonane



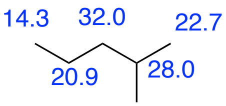
decane



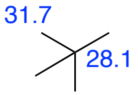
isobutane



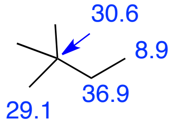
isopentane



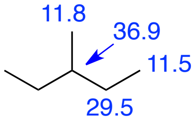
isohexane



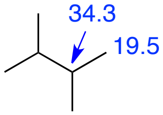
neopentane



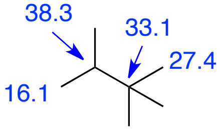
2,2-dimethylbutane



3-methylpentane



2,3-dimethylbutane



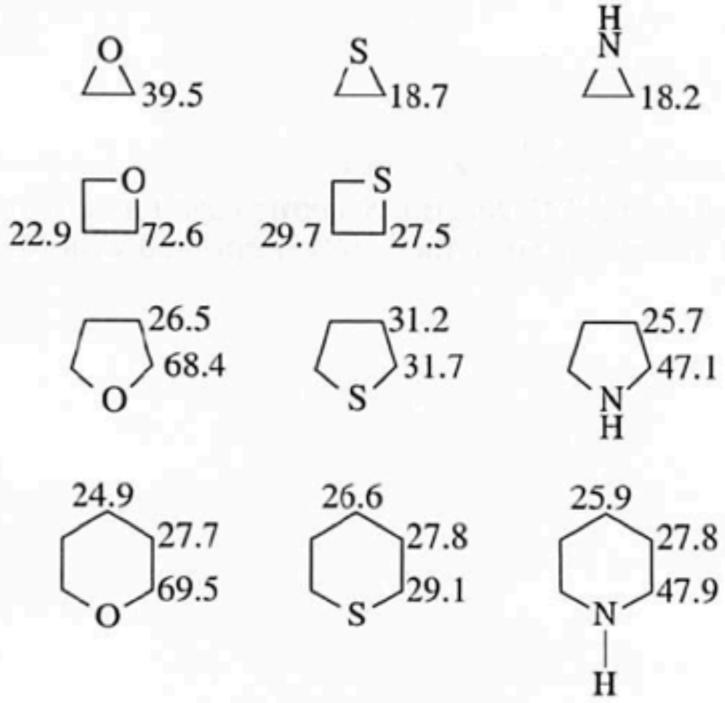
2,2,3-trimethylbutane

Cycloalkanes

C_3H_6	−2.9	C_7H_{14}	28.4
C_4H_8	22.4	C_8H_{16}	26.9
C_5H_{10}	25.6	C_9H_{18}	26.1
C_6H_{12}	26.9	$C_{10}H_{20}$	25.3

Table 12.2 Saturated Heterocyclics

Unsubstituted



Substituted

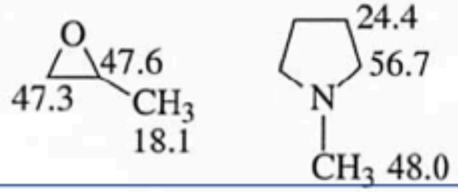
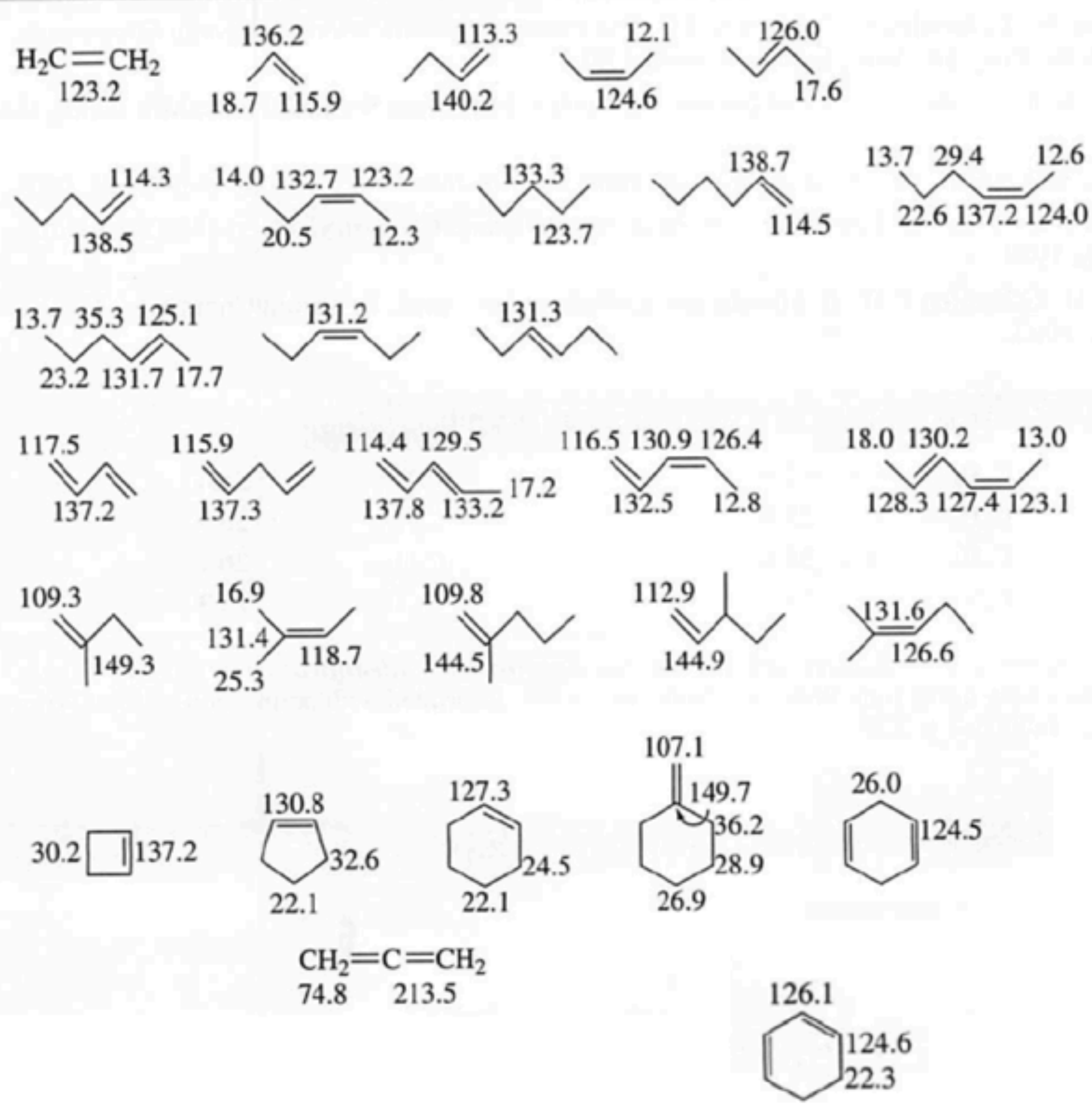


Table 12.3 Alkene and Cycloalkene Chemical Shifts (ppm from TMS)



Alcohols

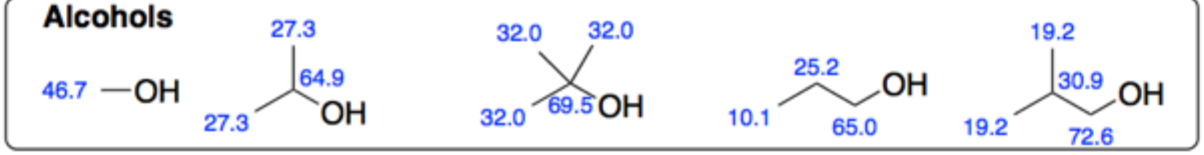
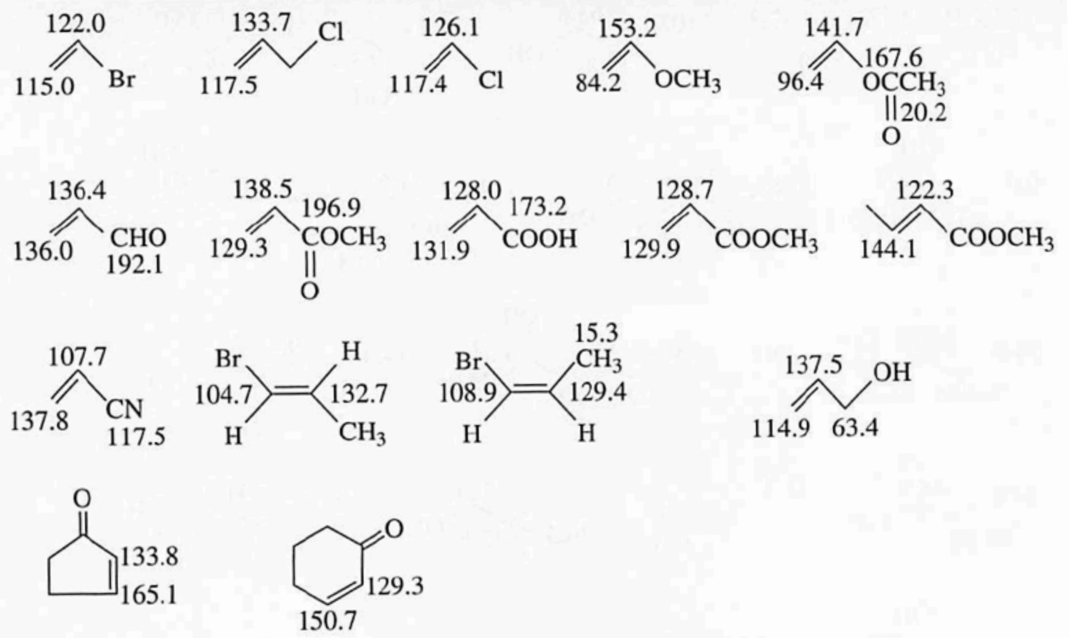
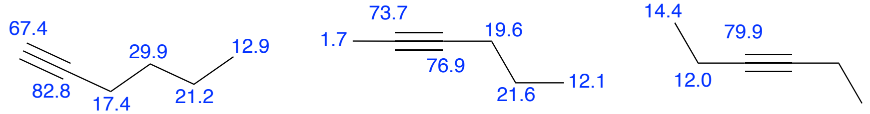


Table 12.4 Chemical Shifts of Substituted Alkenes (ppm from TMS)



Alkyne Chemical Shifts



Amine Chemical Shifts

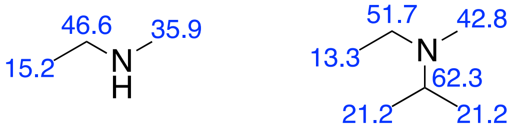


Table 12.7 Chemical Shifts of Ethers, Acetals, and Epoxides

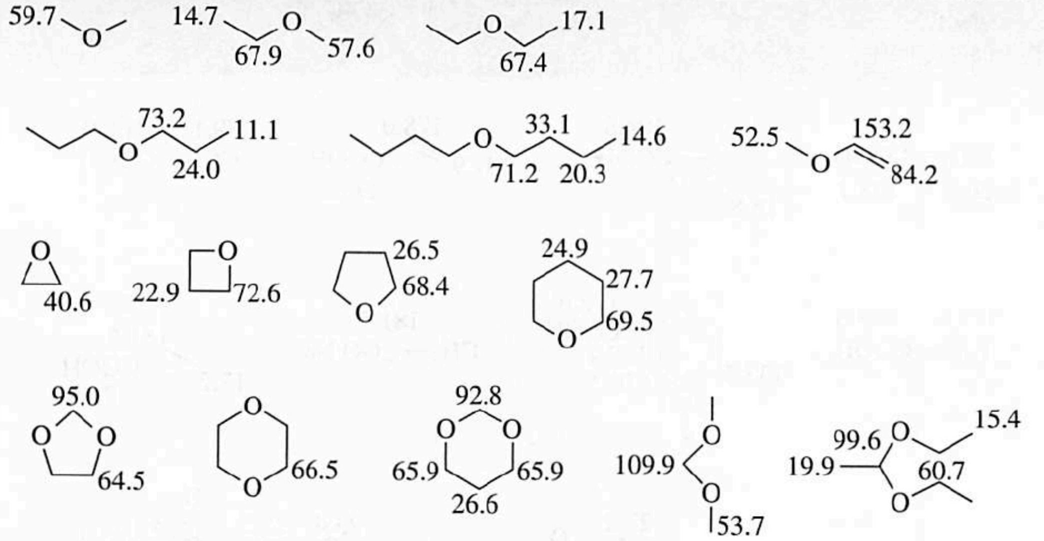


Table 12.8 Ketones and Aldehydes

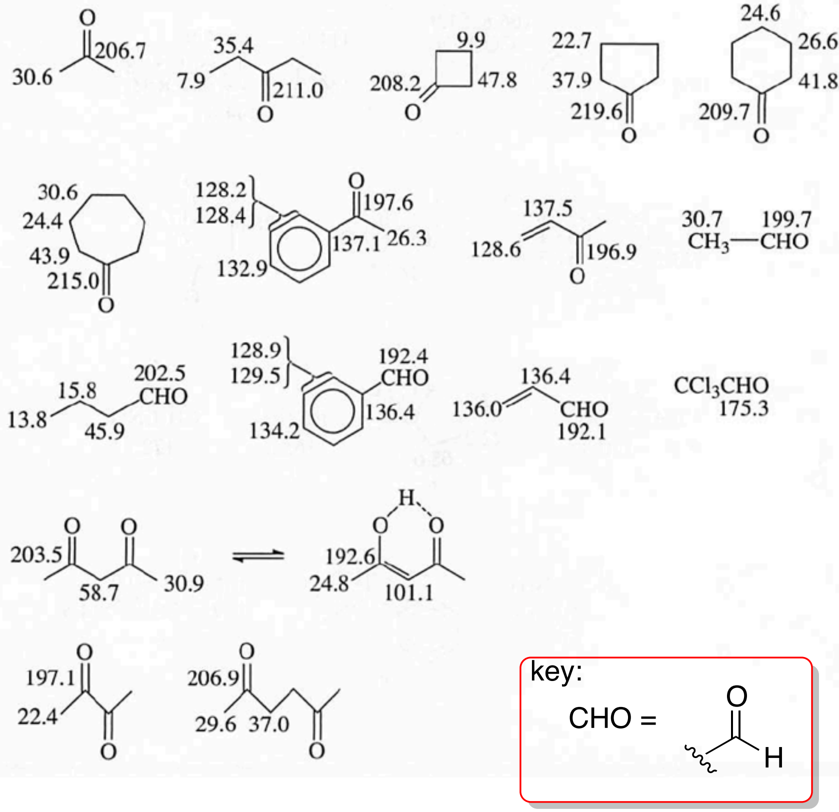
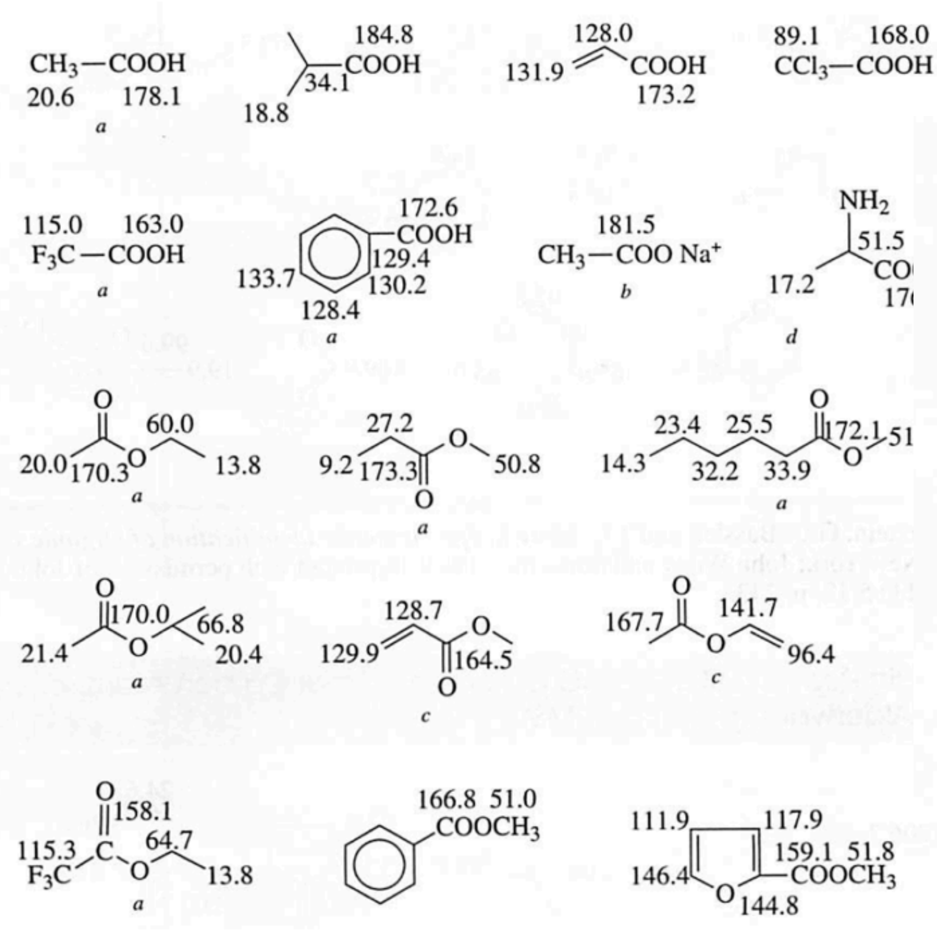
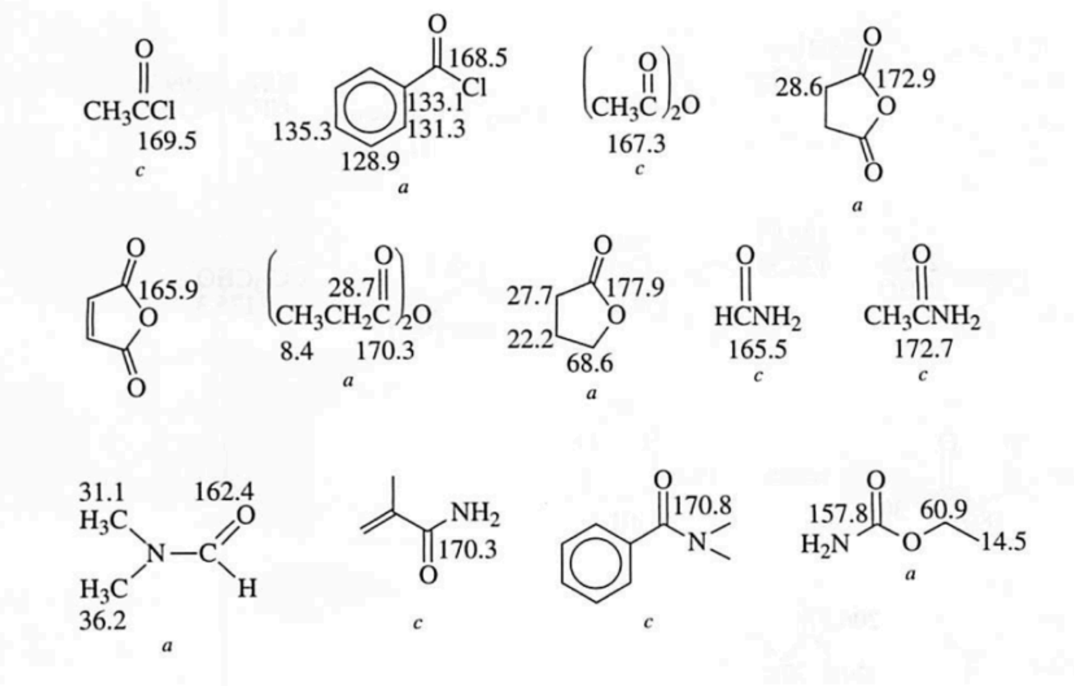
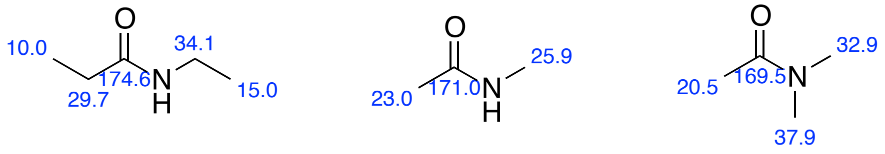
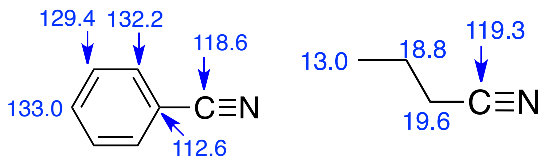


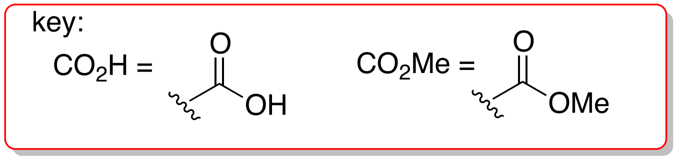
Table 12.9 Shift Positions for the C═O Group and Other Carbon Atoms of Carboxylic Acids, Esters, Lactones, Chlorides, Anhydrides, Amides, Carbamates, and Nitriles (ppm from TMS)



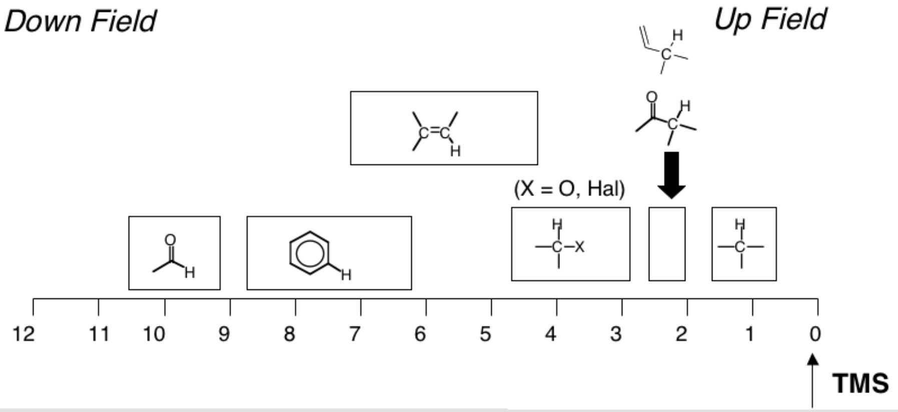


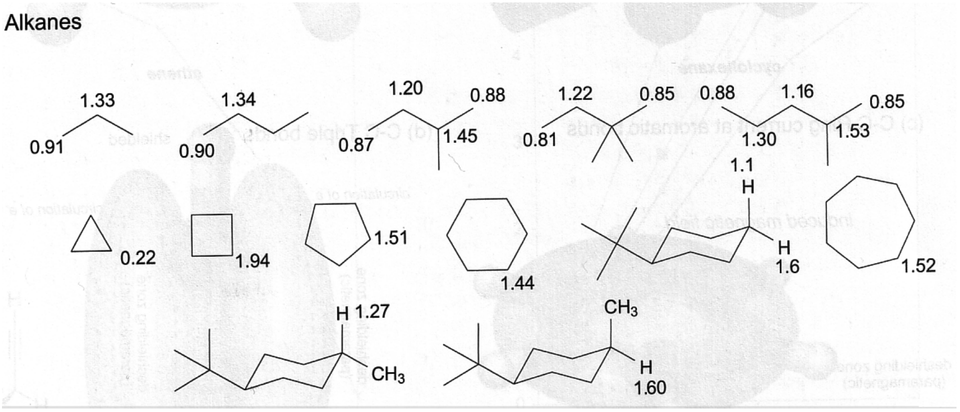




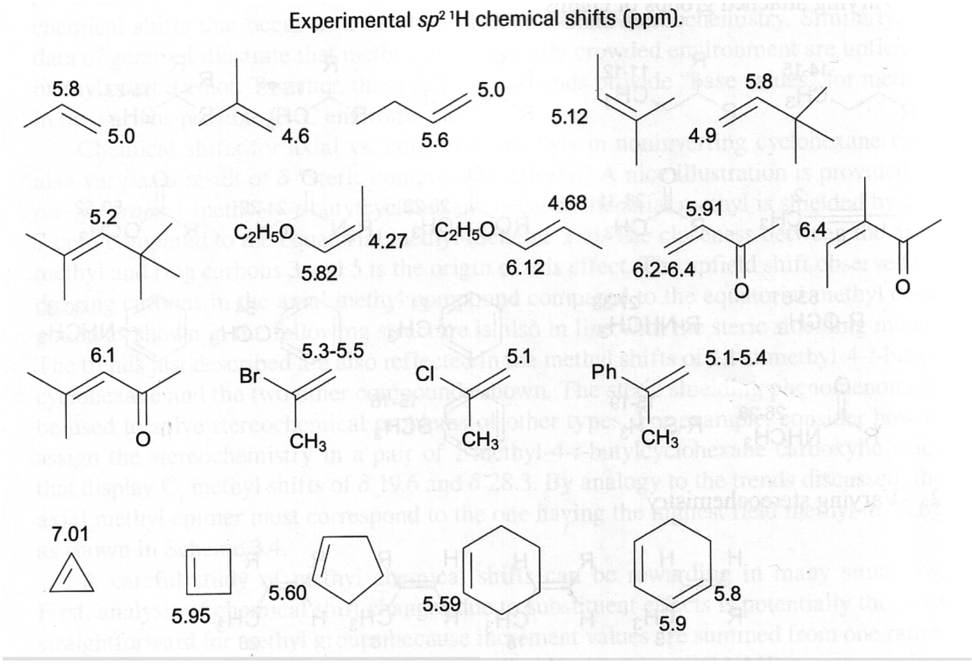


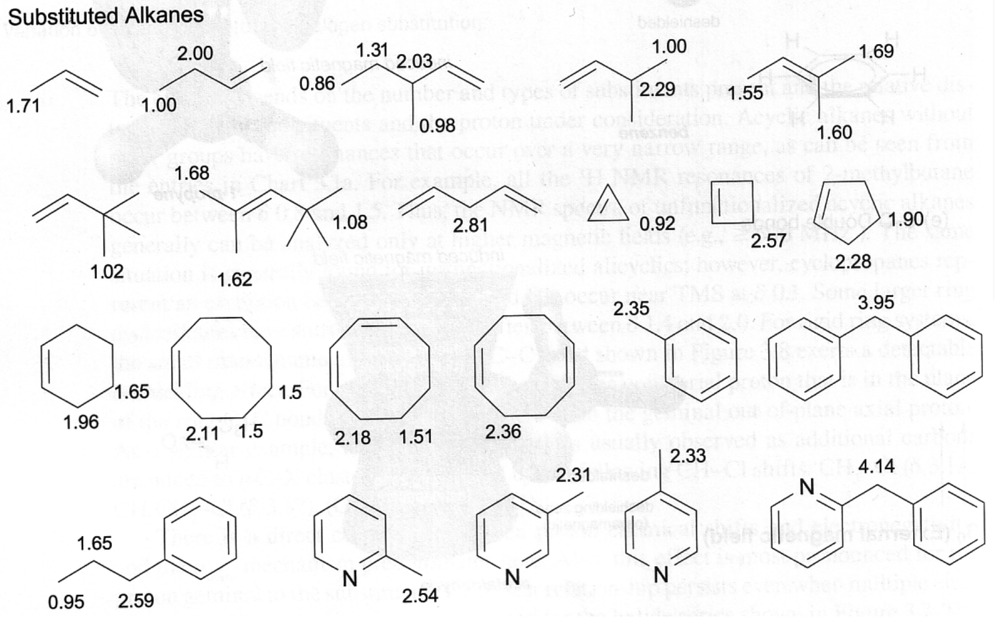
Overview of *typical* ^{1}H NMR shifts



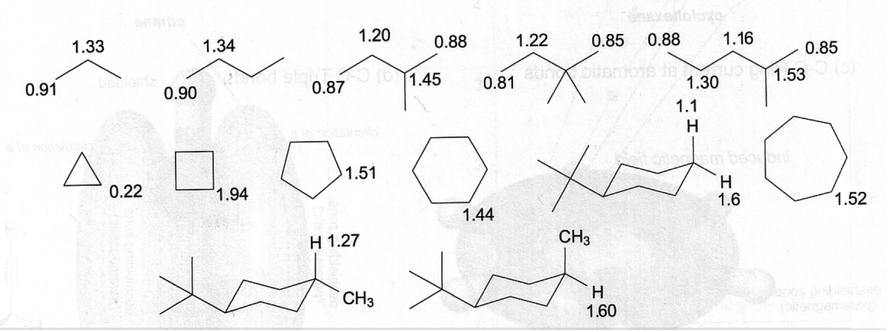


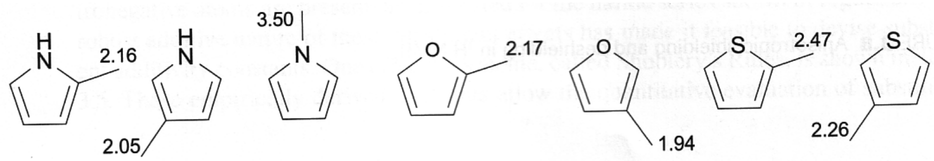
^{1}H NMR Tables





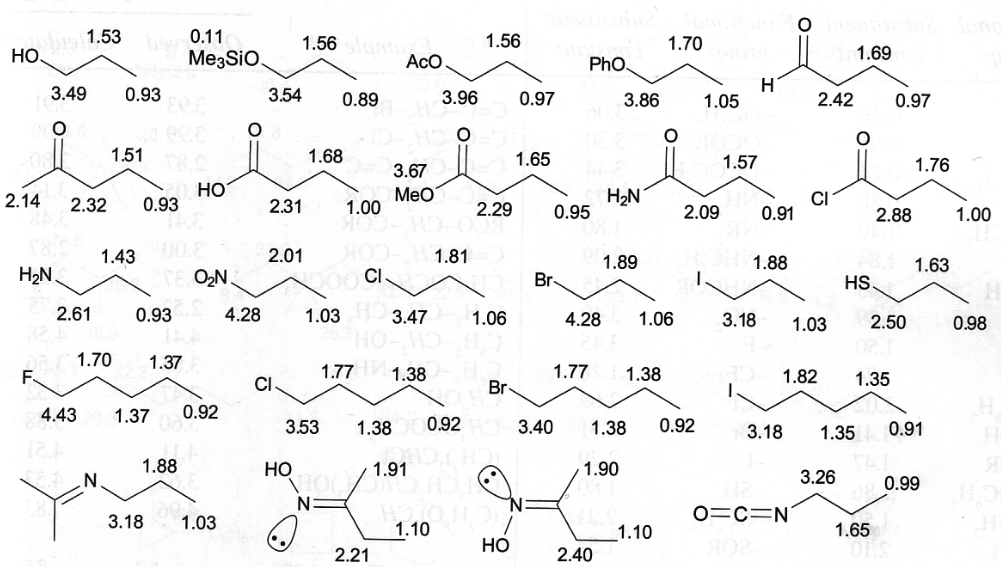
Alkanes

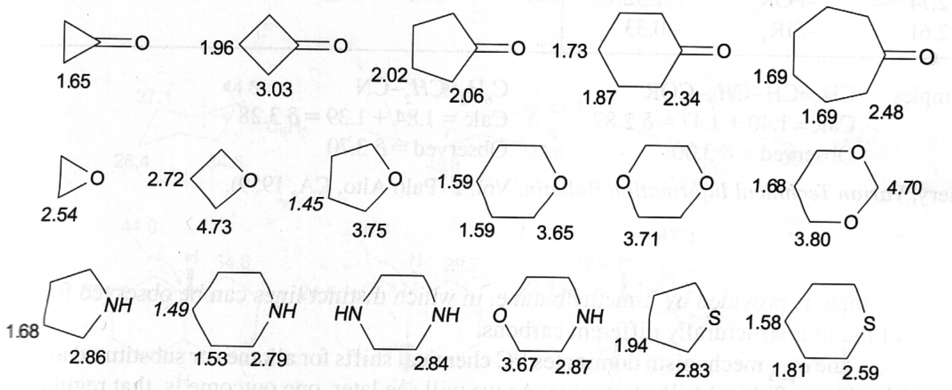




Experimental sp^3 ^1H chemical shifts (ppm) (*cont.*).

Functionalized Alkanes





Substituted Alkynes and C≡N

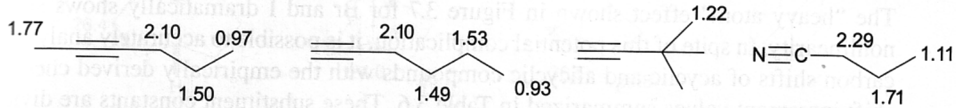


Table 13.1 Chemical Shifts of Protons on a Carbon Atom Adjacent (α Position) to a Functional Group in Aliphatic Compounds (M—Y)

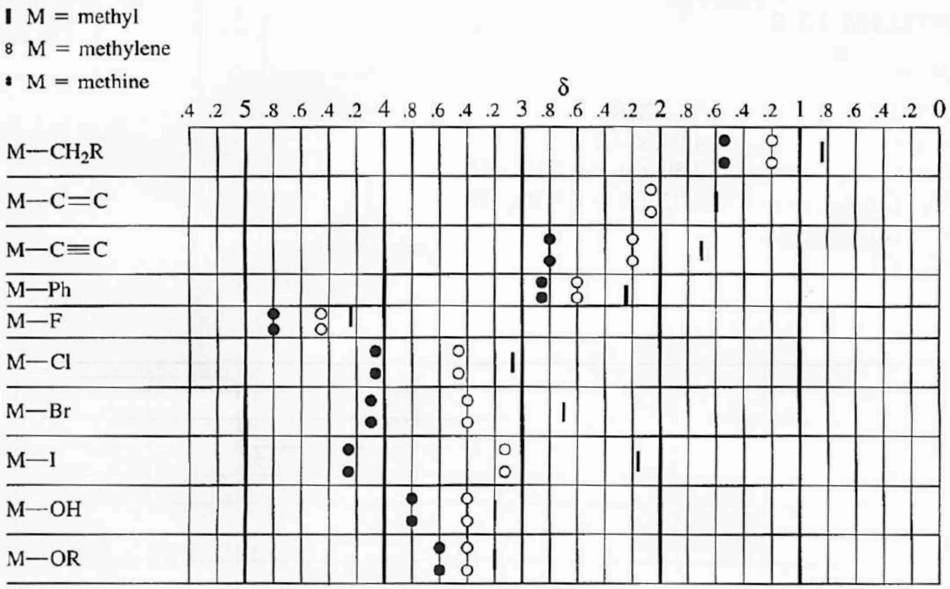
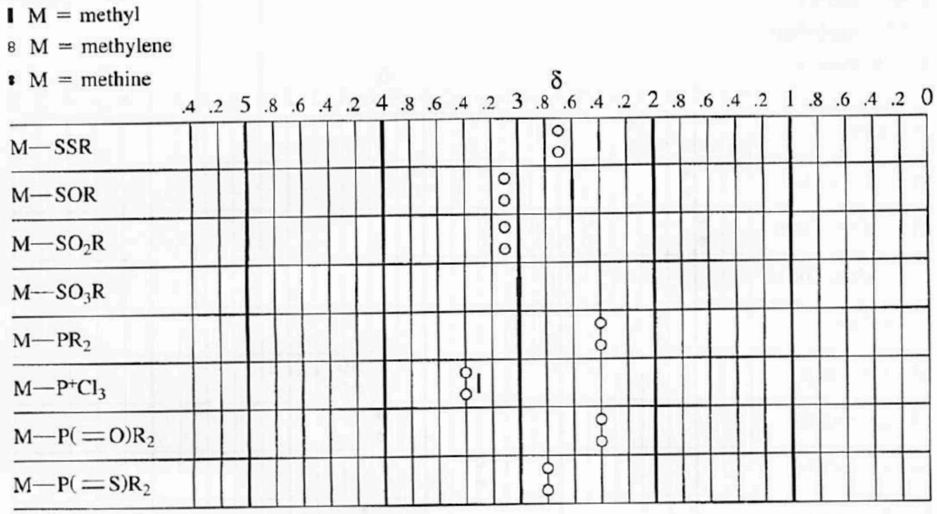


Table 13.1 (Continued)



*OTs is

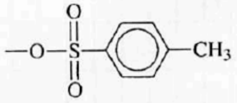


Table 13.1 (Continued)

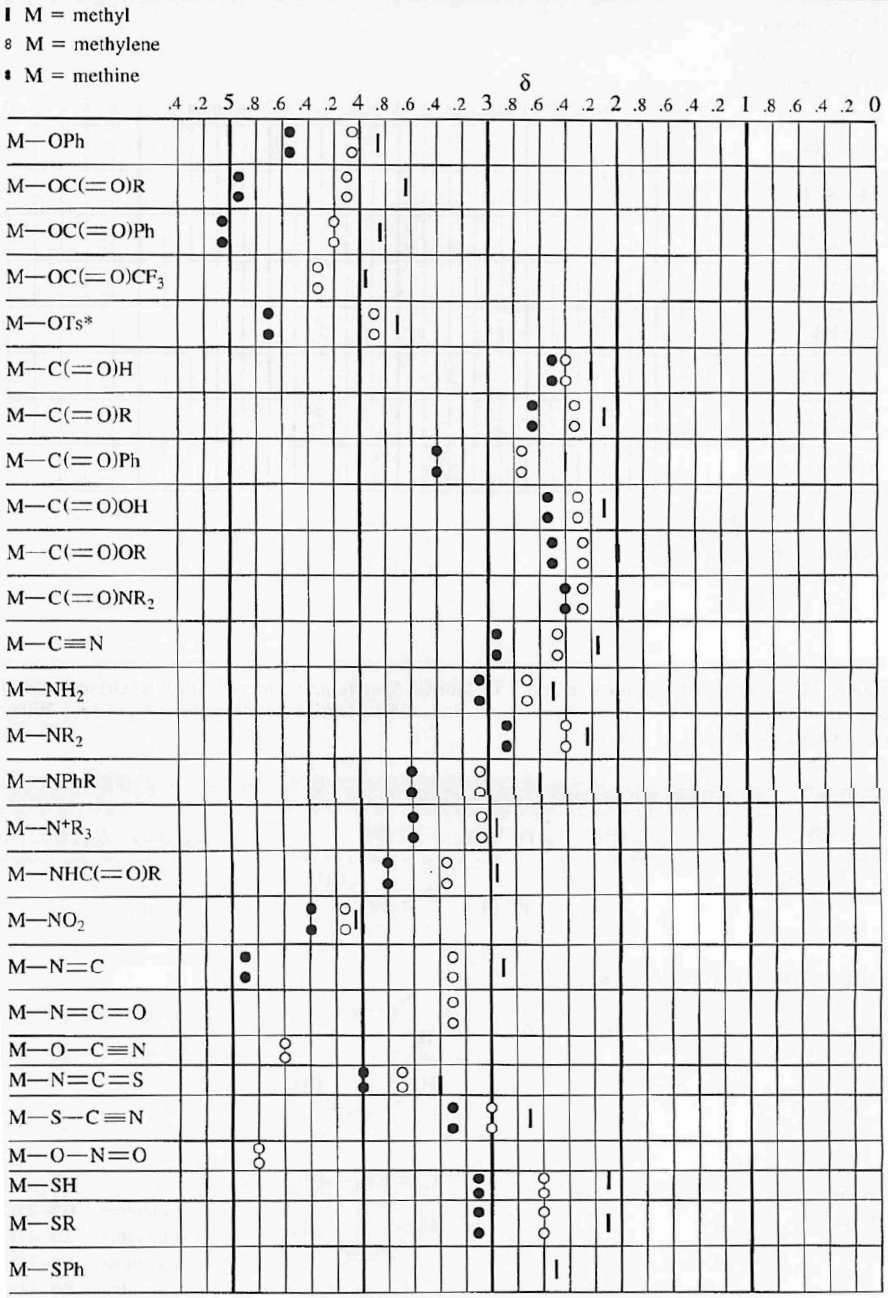


Table 13.2 Proton Spin-Coupling Constants

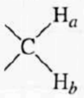
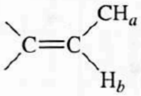
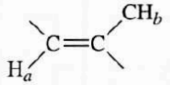
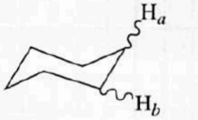
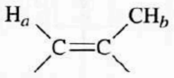
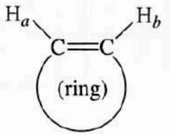
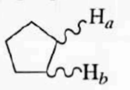
TYPE	J_{ab} (Hz)	J_{ab} TYPICAL	TYPE	J_{ab} (Hz)	J_{ab} TYPICAL
	0–30	12–15		4–10	7
$CH_a—CH_b$ (free rotaion)	6–8	7		0–3	1.5
$CH_a—\overset{\vert}{\underset{\vert}{C}}—CH_b$	0–1	0			
				0–3	2
ax–ax	6–14	8–10	$C{=}CH_a—CH_b{=}C$	9–13	10
ax–eq	0–5	2–3		3 member	0.5–2.0
eq–eq	0–5	2–3		4 member	2.5–4.0
	*cis* 5–10			5 member	5.1–7.0
	trans 5–10			6 member	8.8–11.0
(cis or trans)				7 member	9–13
				8 member	10–13

Table 13.2 (Continued)

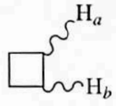
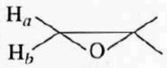
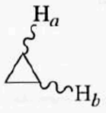
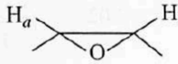
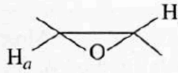
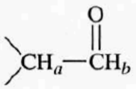
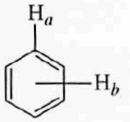
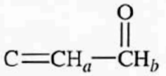
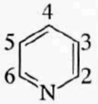
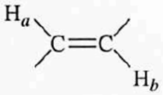
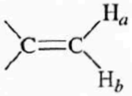
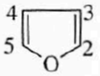
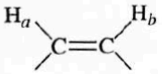
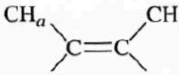
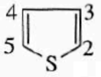
TYPE	J_{ab} (Hz)	J_{ab} TYPICAL	TYPE	J_{ab} (Hz)	J_{ab} TYPICA
			$CH_a—C{\equiv}CH_b$	2–3	
 (cis or trans)	*cis* 4–12 *trans* 2–10		$—CH_a—C{\equiv}C—CH_b—$	2–3	
					6
 (cis or trans)	*cis* 7–13 *trans* 4–9				4
					2.5
$CH_a—OH_b$ (no exchange)	4–10	5			
	1–3	2–3			
			J (ortho)	6–10	9
			J (meta)	1–3	3
			J (para)	0–1	~0
	5–8	6			
			J (2–3)	(5–6)	5
			J (3–4)	(7–9)	8
	12–18	17	J (2–4)	(1–2)	1.5
			J (3–5)	(1–2)	1.5
			J (2–5)	(0–1)	1
			J (2–6)	(0–1)	~0
	0–3	0–2			
			J (2–3)	1.3–2.0	1..8
			J (3–4)	3.1–3.8	3.6
			J (2–4)	0–0	~0
	6–12	10	J (2–5)	1–2	1.5
	0–3	1–2			
			J (2–3)	4.9–6.2	5.4
			J (3–4)	3.4–5.0	4.0
			J (2–4)	1.2–1.7	1.5
			J (2–5)	3.2–3.7	3.4

Table 13.3 Chemical Shifts in Alicyclic Rings

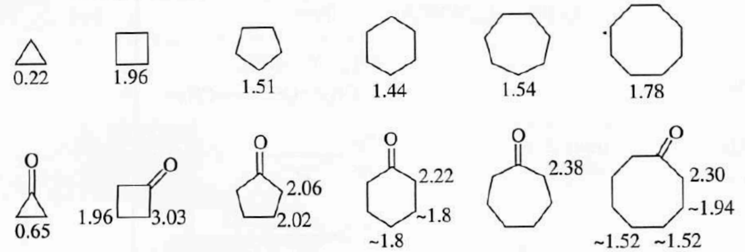
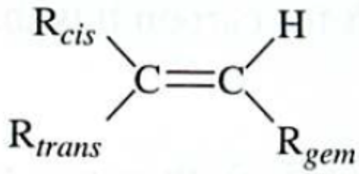


Table 14.3 Chemical Shifts of Alkyne Protons

$HC{\equiv}CR$	1.73–1.88
$HC{\equiv}C—COH$	2.23
$HC{\equiv}C—C{\equiv}CR$	1.95
$HC{\equiv}CH$	1.80
$HC{\equiv}CAR$	2.71–3.37
$HC{\equiv}C—C{\equiv}CR$	2.60–3.10

CALCULATING THE ^{1}H NMR CHEMICAL SHIFTS OF ALKENES



$$\delta_H = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$$

FROM TABLE 14.4 (LABBOOK)
OR TABLE H.6 (SPEC BOOK)

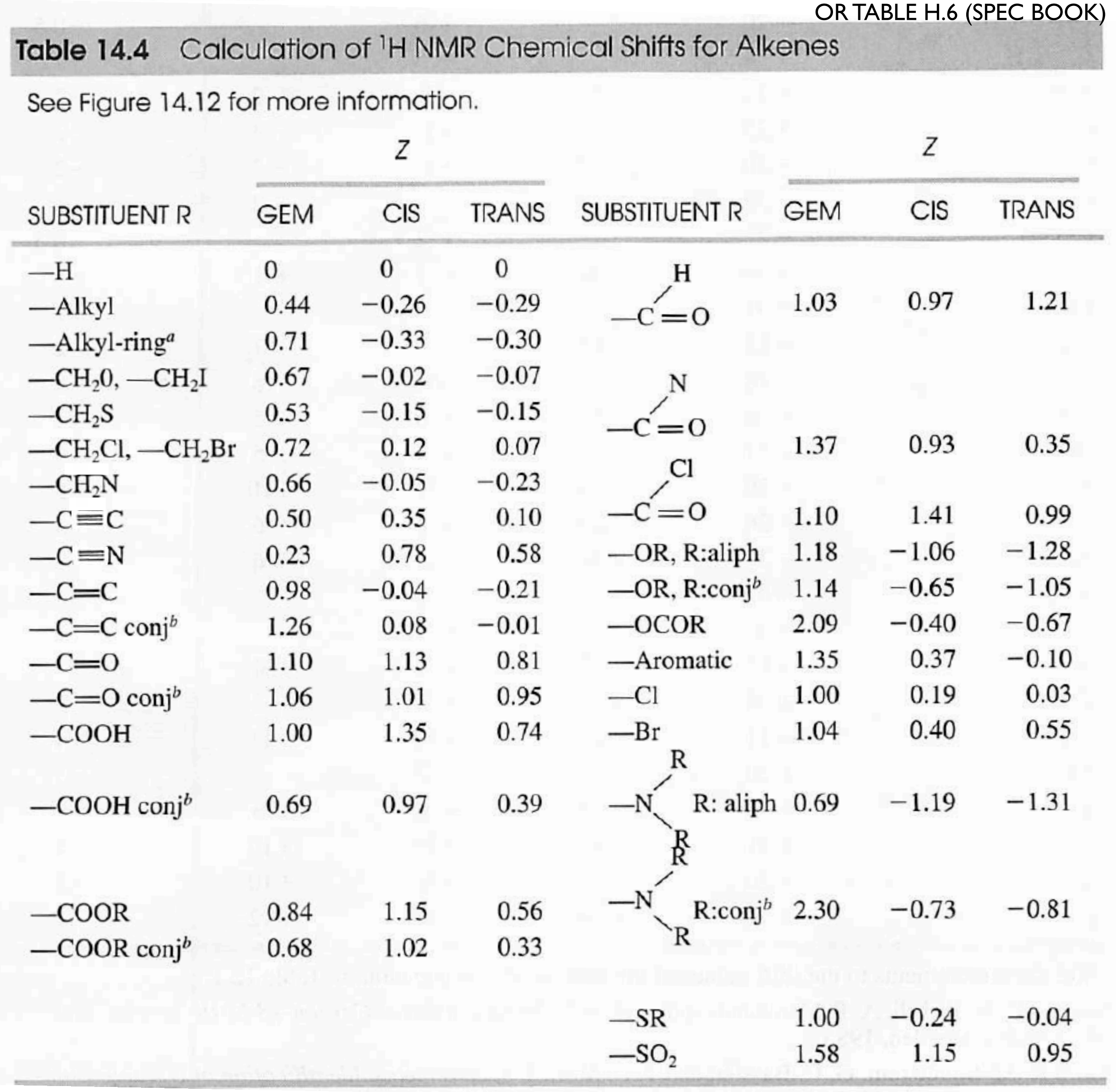


Table 14.4 Calculation of ^{1}H NMR Chemical Shifts for Alkenes

See Figure 14.12 for more information.

	Z				Z		
SUBSTITUENT R	GEM	CIS	TRANS	SUBSTITUENT R	GEM	CIS	TRANS
—H	0	0	0				
—Alkyl	0.44	−0.26	−0.29	$—\overset{\text{H}}{\text{C}}{=}\text{O}$	1.03	0.97	1.21
—Alkyl-ring[a]	0.71	−0.33	−0.30				
—CH_2O, —CH_2I	0.67	−0.02	−0.07				
—CH_2S	0.53	−0.15	−0.15				
—CH_2Cl, —CH_2Br	0.72	0.12	0.07	$—\overset{\text{N}}{\text{C}}{=}\text{O}$	1.37	0.93	0.35
—CH_2N	0.66	−0.05	−0.23				
—C≡C	0.50	0.35	0.10	$—\overset{\text{Cl}}{\text{C}}{=}\text{O}$	1.10	1.41	0.99
—C≡N	0.23	0.78	0.58	—OR, R:aliph	1.18	−1.06	−1.28
—C=C	0.98	−0.04	−0.21	—OR, R:conj[b]	1.14	−0.65	−1.05
—C=C conj[b]	1.26	0.08	−0.01	—OCOR	2.09	−0.40	−0.67
—C=O	1.10	1.13	0.81	—Aromatic	1.35	0.37	−0.10
—C=O conj[b]	1.06	1.01	0.95	—Cl	1.00	0.19	0.03
—COOH	1.00	1.35	0.74	—Br	1.04	0.40	0.55
—COOH conj[b]	0.69	0.97	0.39	$—\text{N}\genfrac{}{}{0pt}{}{\text{R}}{\text{R}}$ R: aliph	0.69	−1.19	−1.31
—COOR	0.84	1.15	0.56	$—\text{N}\genfrac{}{}{0pt}{}{\text{R}}{\text{R}}$ R:conj[b]	2.30	−0.73	−0.81
—COOR conj[b]	0.68	1.02	0.33				
				—SR	1.00	−0.24	−0.04
				—SO_2	1.58	1.15	0.95

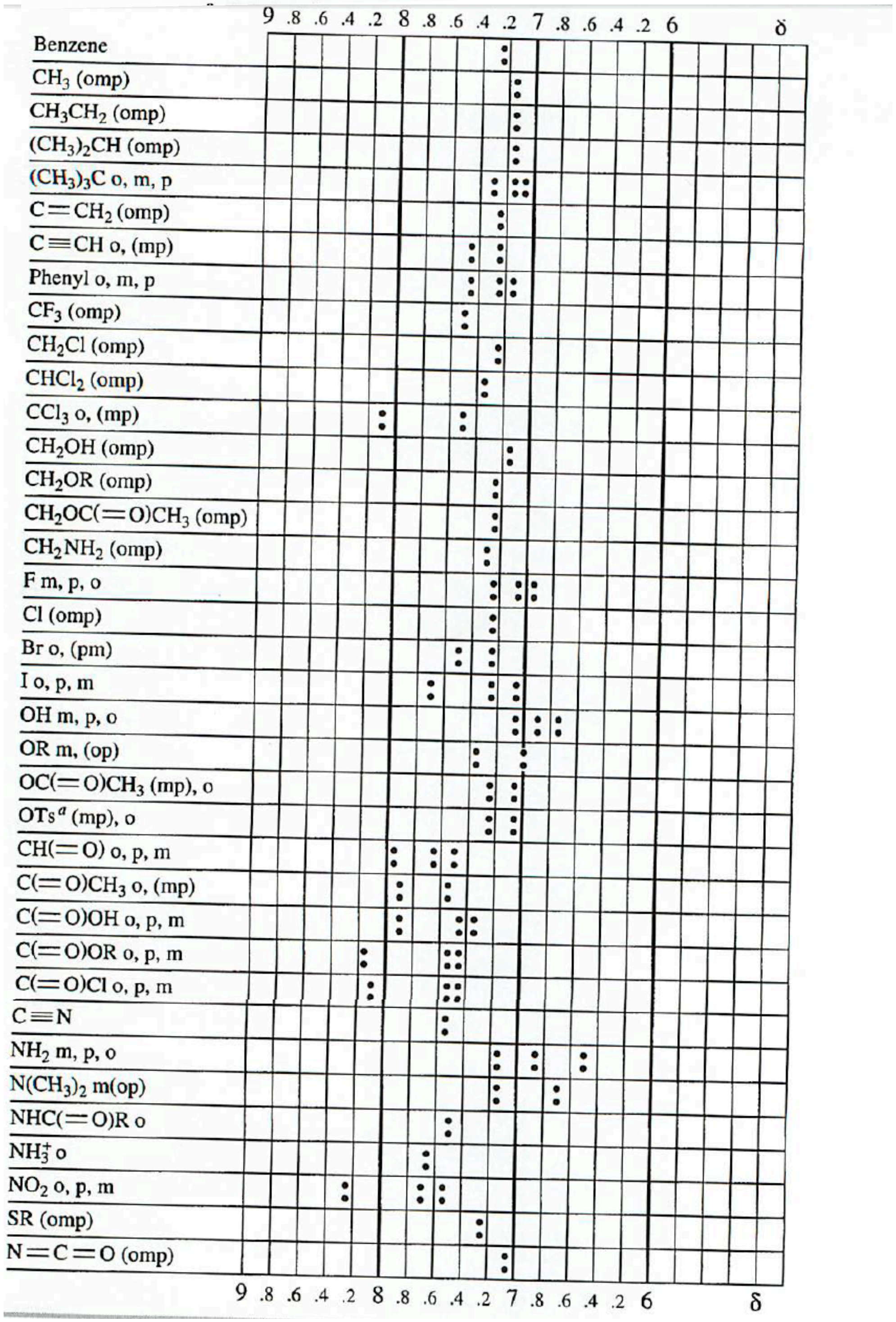
Table 14.5 Incremental Shifts of the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from Benzene at 128.5 ppm, + downfield, − upfield). Carbon Atom of Substituents in parts per million from TMS[a]

SUBSTITUENT	C-1 (ATTACHMENT)	C-2	C-3	C-4	C OF SUBSTITUENT (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH_3	9.3	+0.7	−0.1	−2.9	21.3
CH_2CH_3	+15.6	−0.5	0.0	−2.6	29.2 (CH_2), 15.8 (CH_3)
$CH(CH_3)_2$	+20.1	−2.0	0.0	−2.5	34.4 (CH), 24.1 (CH_3)
$C(CH_3)_3$	+22.2	−3.4	−0.4	−3.1	34.5 (C), 31.4 (CH_3)
$CH{=}CH_2$	+9.1	−2.4	+0.2	−0.5	137.1 (CH), 113.3 (CH_2)
$C{\equiv}CH$	−5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C_6H_5	+12.1	−1.8	−0.1	−1.6	
CH_2OH	+13.3	−0.8	−0.6	−0.4	64.5
$CH_2O\underset{\underset{O}{\|}}{C}CH_3$	+7.7	~0.0	~0.0	~0.0	20.7 (CH_3), 66.1 (CH_2), 170.5 (C=O)
OH	+26.6	−12.7	+1.6	−7.3	
OCH_3	+31.4	−14.4	+1.0	−7.7	54.1
OC_6H_5	+29.0	−9.4	+1.6	−5.3	
$O\overset{\overset{O}{\|}}{C}CH_3$	+22.4	−7.1	−0.4	−3.2	23.9 (CH_3), 169.7 (C=O)
$\overset{\overset{O}{\|}}{C}H$	+8.2	+1.2	+0.6	+5.8	192.0
$\overset{\overset{O}{\|}}{C}CH_3$	+7.8	−0.4	−0.4	+2.8	24.6 (CH_3), 195.7 (C=O)
$\overset{\overset{O}{\|}}{C}C_6H_5$	+9.1	+1.5	−0.2	+3.8	196.4 (C=O)
$\overset{\overset{O}{\|}}{C}CF_3$	−5.6	+1.8	+0.7	+6.7	
$\overset{\overset{O}{\|}}{C}OH$	+2.9	+1.3	+0.4	+4.3	168.0
$\overset{\overset{O}{\|}}{C}OCH_3$	+2.0	+1.2	−0.1	+4.8	51.0 (CH_3), 166.8 (C=O)
$\overset{\overset{O}{\|}}{C}Cl$	+4.6	+2.9	+0.6	+7.0	168.5
$C{\equiv}N$	−16.0	+3.6	+0.6	+4.3	119.5
NH_2	+19.2	−12.4	+1.3	−9.5	
$N(CH_3)_2$	+22.4	−15.7	+0.8	−11.8	40.3
$NH\overset{\overset{O}{\|}}{C}CH_3$	+11.1	−9.9	+0.2	−5.6	

Table 14.5 (Continued)

SUBSTITUENT	C-1 (ATTACHMENT)	C-2	C-3	C-4	C OF SUBSTITUENT (ppm from TMS)
NO_2	+19.6	−5.3	+0.9	+6.0	
$N{=}C{=}O$	+5.7	−3.6	+1.2	−2.8	129.5
F	+35.1	−14.3	+0.9	−4.5	
Cl	+6.4	+0.2	+1.0	−2.0	
Br	−5.4	+3.4	+2.2	−1.0	
I	−32.2	+9.9	+2.6	−7.3	
CF_3	+2.6	−3.1	+0.4	+3.4	
SH	+2.3	+0.6	+0.2	−3.3	
SCH_3	+10.2	−1.8	+0.4	−3.6	15.9
SO_2NH_2	+15.3	−2.9	+0.4	+3.3	
$Si(CH_3)_3$	+13.4	+4.4	−1.1	−1.1	

Table 14.6 Chemical Shifts of Protons on Monosubstituted Benzene Rings



FROM TABLE 14.6 (LABBOOK)
OR TABLE H.4 (SPEC BOOK)

Infrared spectra: It is important to remember that the absence of an absorption band can often provide more information about the structure of a compound than the presence of a band. Be careful to avoid focusing on selected absorption bands and overlooking others. Use the examples linked to the table to see the profile and intensity of bands.

Look for absorption bands in decreasing order of importance:

1.the C-H absorption(s) between 3100 and 2850 cm-1. An absorption above 3000 cm-1 indicates C=C, either alkene or aromatic. Confirm the aromatic ring by finding peaks at 1600 and 1500 cm-1 and C-H out-of-plane bending to give substitution patterns below 900 cm-1. Confirm alkenes with an absorption generally at 1640-1680 cm-1. C-H absorption between 3000 and 2850 cm-1 is due to aliphatic hydrogens.

2. the carbonyl (C=O) absorption between 1690-1760cm-1; this strong band indicates either an aldehyde, ketone, carboxylic acid, ester, amide, anhydride or acyl halide. The an aldehyde may be confirmed with C-H absorption from 2840 to 2720 cm-1.

3. the O-H or N-H absorption between 3200 and 3600 cm-1. This indicates either an alcohol, N-H containing amine or amide, or carboxylic acid. For -NH2 a doublet will be observed.

4.the C-O absorption between 1080 and 1300 cm-1. These peaks are normally rounded like the O-H and N-H peak in 3. and are prominent. Carboxylic acids, esters, ethers, alcohols and anhydrides all containing this peak.

5.the CC and CN triple bond absorptions at 2100-2260 cm-1 are small but exposed.

6.structure of aromatic compounds may also be confirmed from the pattern of the weak overtone and combination tone bands found from 2000 to 1600 cm-1.

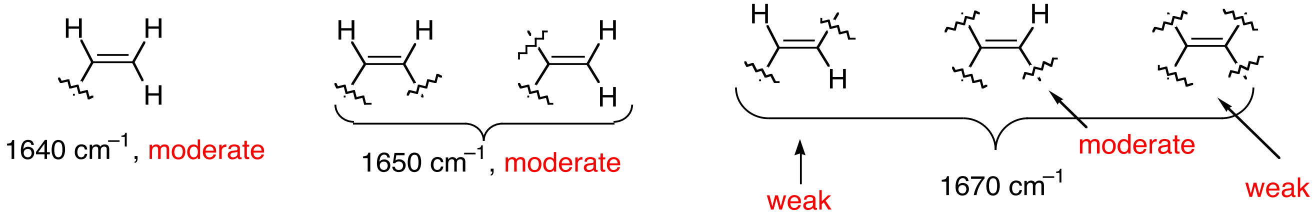
Table 11.2 Structural Units and Absorption Frequencies

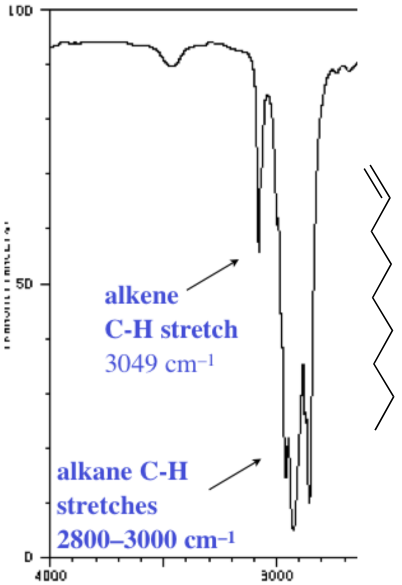
BOND		TYPE OF COMPOUND	FREQUENCY (CM^{-1})
—C—H	(stretch)	Alkane	2800–3000
=C—H	(stretch)	Alkenes, aromatics	3000–3100
≡C—H	(stretch)	Alkynes	3300
—O—H	(stretch)	Alcohols, phenols	3600–3650 (free) 3200–3500 (H-bonded) (broad)
—OH	(stretch)	Carboxylic acids	2500–3300
—N—H	(stretch)	Amines	3300–3500 (doublet for NH_2)
O ‖ —C—H	(stretch)	Aldehyde	2720 and 2820
—C=C—	(stretch)	Alkenes	1600–1680
—C=C—	(stretch)	Aromatic	1500 and 1600
—C≡C—	(stretch)	Alkynes	2100–2270
O ‖ —C—	(stretch)	Aldehydes, ketones	1680–1740
—C≡N	(stretch)	Nitriles	2220–2260
C—N	(stretch)	Amines	1180–1360
—C—H	(bending)	Alkane	1375 (methyl)
—C—H	(bending)	Alkane	1460 (methyl and methylene)
—C—H	(bending)	Alkane	1370 and 1385 (isopropyl split)
—C—H	(bending)	R—CH=CH_2	1000–960 and 940–900
—C—H	(bending)	R_2C=CH_2	915–870
—C—H	(bending)	*cis* RCH=CHR	790–650
—C—H	(bending)	*trans* RCH=CHR	990–940
—C—H	(out-of-plane bending)	*mono* subst. benzene	770–730 and 710–690
—C—H	(out-of-plane bending)	*o*-subst. benzene	770–735
—C—H	(out-of-plane bending)	*m*-subst. benzene	810–750 and 710–690
—C—H	(out-of-plane bending)	*p*-subst. benzene	860–800
—C—O	(stretch)	Primary alcohol	1050–1085
—C—O	(stretch)	Secondary alcohol	1085–1125
—C—O	(stretch)	Tertiary alcohol	1125–1200
—C—O	(stretch)	Phenol	1180–1260

Unconjugated Alkenes

- C=**C–H**:
  - stretch: ≥ 3000 cm^{-1}

- linear alkenes:
  - C=C stretch: moderate to weak absorption at 1667-1640 cm^{-1}

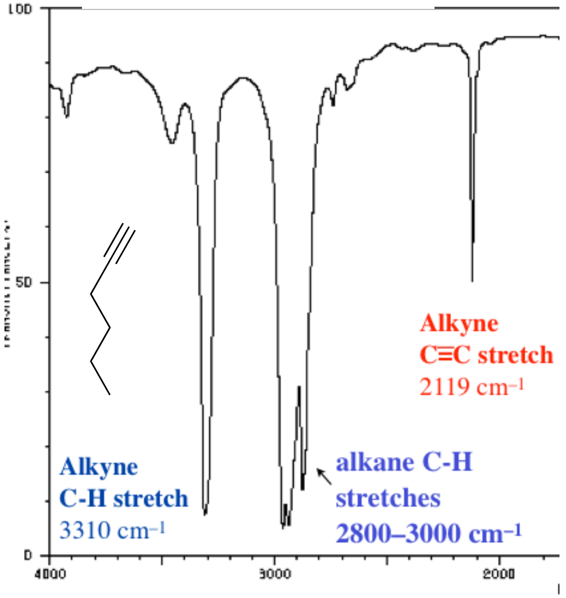




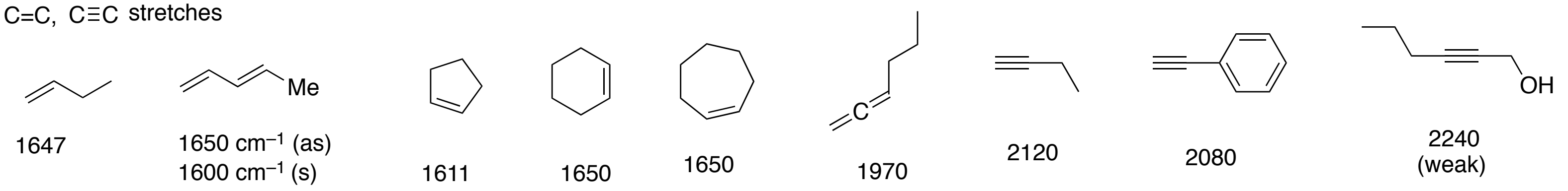
Alkynes

- —C≡C— stretch: weak absorption at 2260-2100 cm^{-1}
  - not observed for symmetrical alkynes (v. weak for 'pseudo' symmetric alkynes
  - terminal alkynes (R-C≡C-H) absorptions are stronger than internal (R-C≡C-R) absorptions

- C≡**C–H** stretch:
  - 3333–3267 cm^{-1}
  - strong, narrow (as compared to OH or NH)



examples of
C=C, C≡C stretches



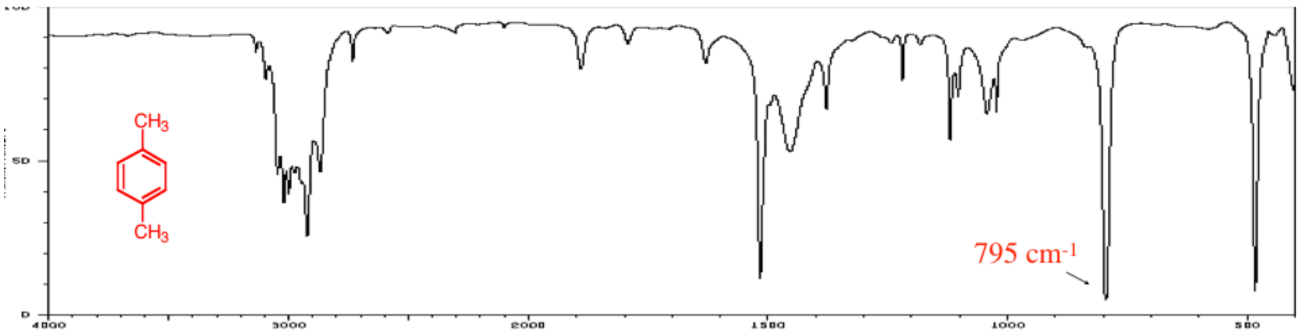
Mononuclear Aromatic Hydrocarbons (benzene)

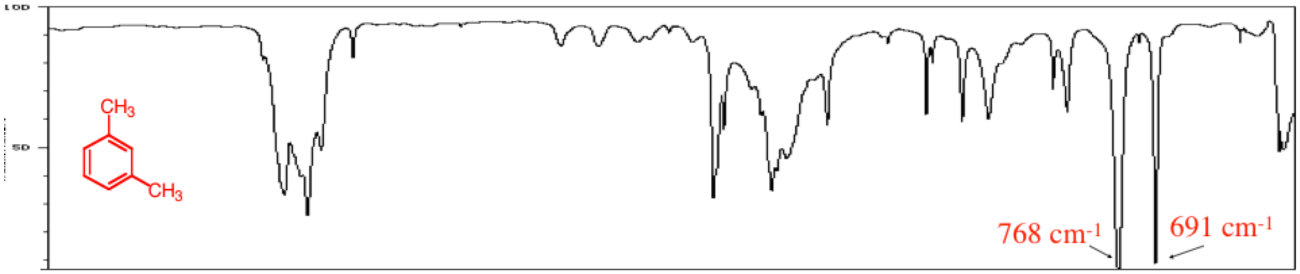
- Out of plane bending of aromatic C-H bonds: most informative
  - 900–675 cm^{-1}
  - intense bands, strongly coupled to adjacent hydrogens on the ring
  - position and number of bands gives information about the substitution pattern (particularly useful for alkyl substituted aromatics. Substitution of polar groups can give rise to exceptions)

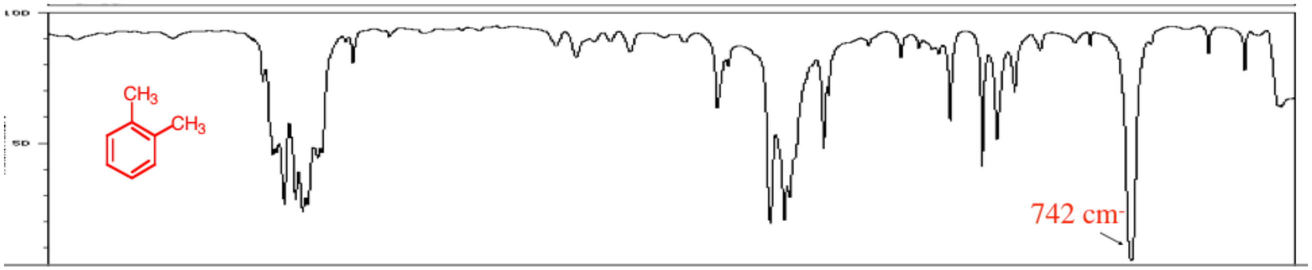
- C=C–H stretch: 3100–3000 cm^{-1}
- C=C stretch: 1600-1585; 1500-1400 cm^{-1}
- C=C out of plane ring bending: 600-420 cm^{-1}

disubstituted benzenes

Out of plane bending of aromatic C-H bonds used to distinguish para, meta, ortho isomers







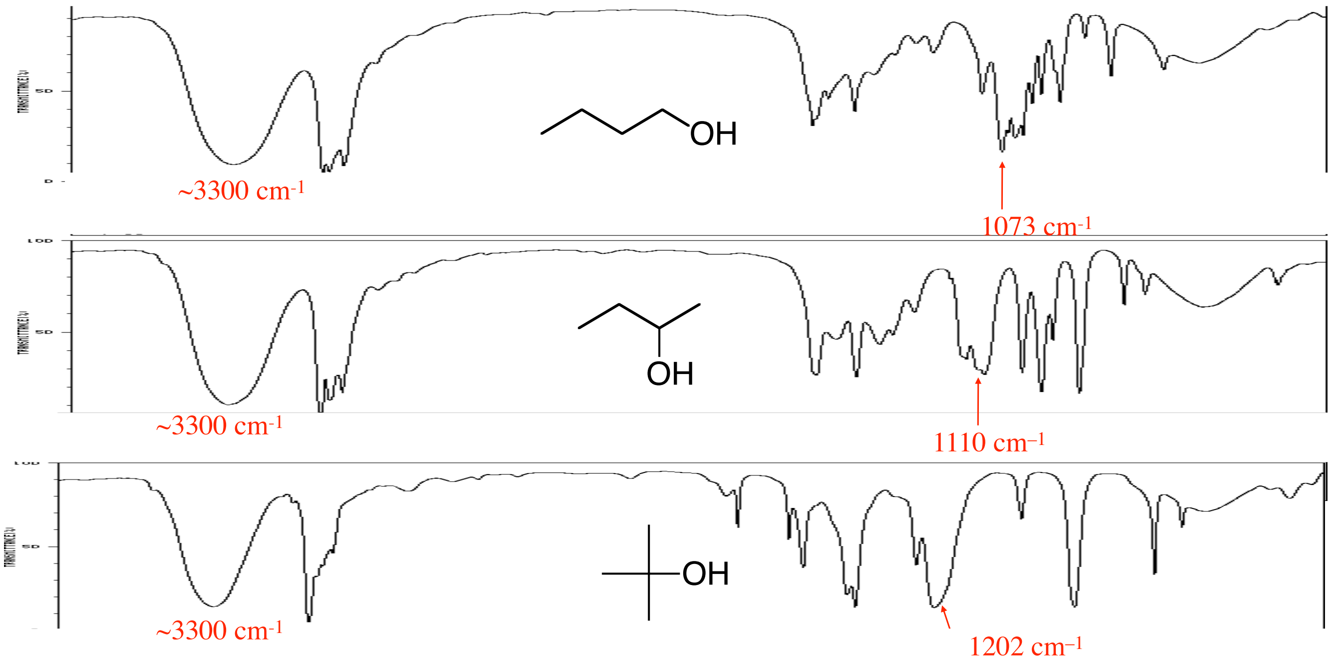
Alcohols

CH stretch typically occurs as a broad peak centered @ 3300 cm $^{-1}$ (spanning 3550-3200 cm^{-1}).
This peak is broad due to H-bonding
In rare cases where H-bonding is not present, the peak is sharp and at higher frequency

C–O stretching Vibrations

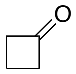
- Alcohols (1260-1000 cm$^{-1)}$
- Phenols (1800-1260 cm^{-1})

primary alcohol: 1050-1085 cm^{-1}
secondary alcohol: 1085-1125^{-1}
tertiary alcohol: 1125-1200 cm^{-1}

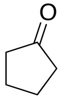


Ketones C=O stretch (see tables)

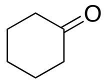
- aliphatic: ‘normal’ position of a neat aliphatic ketone is 1715 cm^{-1}
- conjugation: shifts position to lower frequency
  alkene or phenyl group causes absorption in the 1685-1666 cm^{-1} region. For α,β-unsaturated carbonyls, 2 absorptions may be observed
- cyclic ketones The bond angle influences the absorption frequency of the C=O



1788



1750

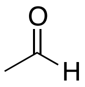


1715

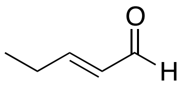
Aldehydes

C=O stretch (see tables)

- Aliphatic aldehydes: C=O stretch at 1740-1720 cm^{-1}
- Electron withdrawing groups shift to higher frequency
- Conjugative groups shift to lower frequency (1710-1685 cm^{-1})



1730



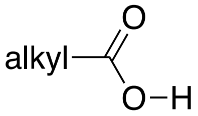
1685

C–H stretch

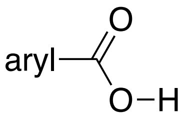
2830–2695 cm^{-1} Often, two bands are observed

Carboxylic Acids

OH stretch in the 3300–2500 cm^{-1} region centered near 3000 cm^{-1}



1720–1706 cm^{-1}



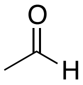
1710-1680 cm^{-1}

C=O stretch

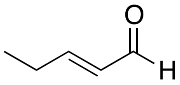
- 1720-1705 for aliphatic acids
- 1710–1680 for conjugated acids

C=O stretch tables

aldehydes, C=O



1730



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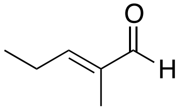
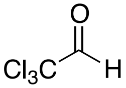
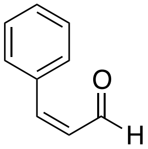


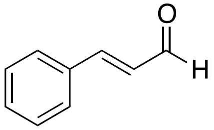
1690



1768 cm^{-1}



1684



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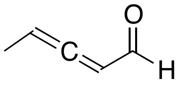
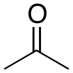
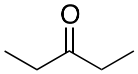


1688 (C=O)
1932 (C=C)

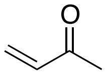
ketones, C=O



1715



1720



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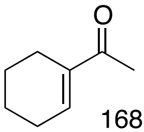

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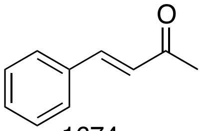

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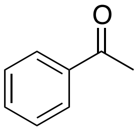

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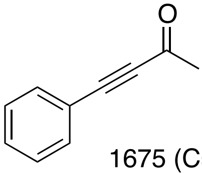
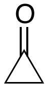
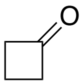


1675 (C=C)
2203 (C=O)



1813



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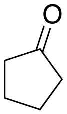
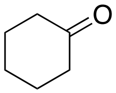


1750



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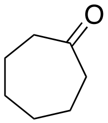
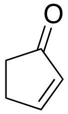


1706



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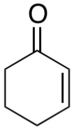
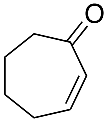
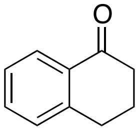


1680



1665



1687

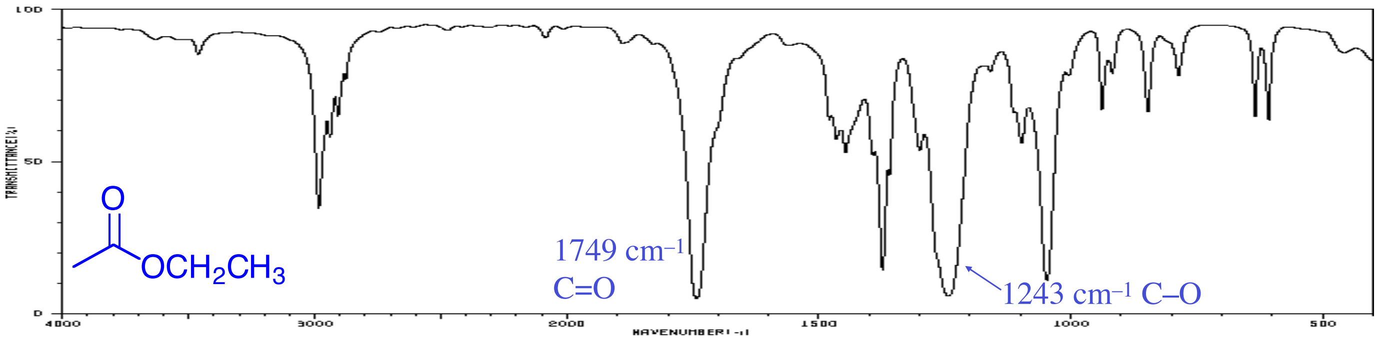
Esters

C=O stretch

- saturated aliphatic esters: C=O: 1750–1735 cm^{-1}
- formates, α,β-unsaturated, and benzoate esters: 1730-1715 cm^{-1}
- phenyl or vinyl esters: 1770-1780 cm^{-1}

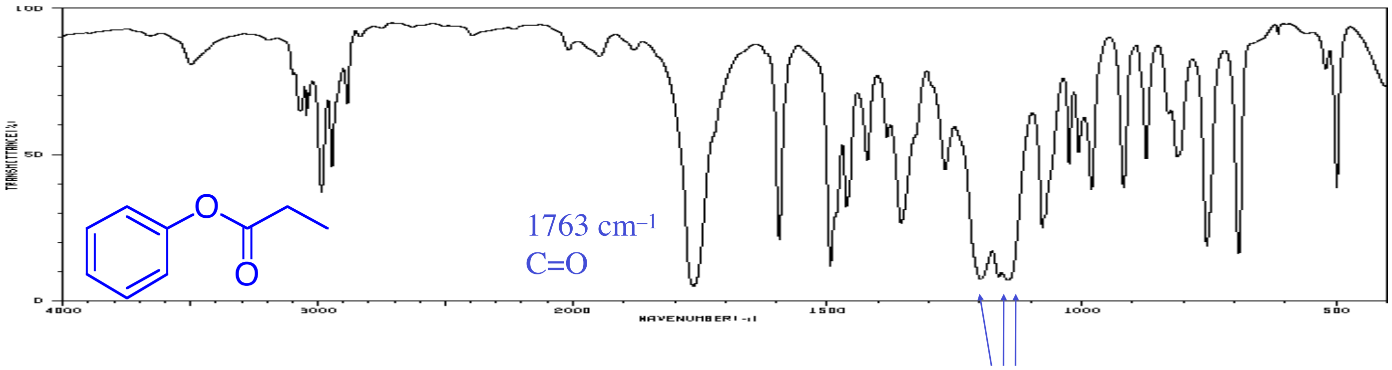
C–O stretches (strong absorptions; asymmetrical coupled vibrations)

- saturated aliphatic esters (except acetates): C–O: 1210–1163 cm^{-1}
- acetates: 1240 cm^{-1}
- α,β-unsaturated esters: 1300–1160 cm^{-1}
- benzoate esters: 1310–1250 cm^{-1}



1749 cm^{-1}
C=O

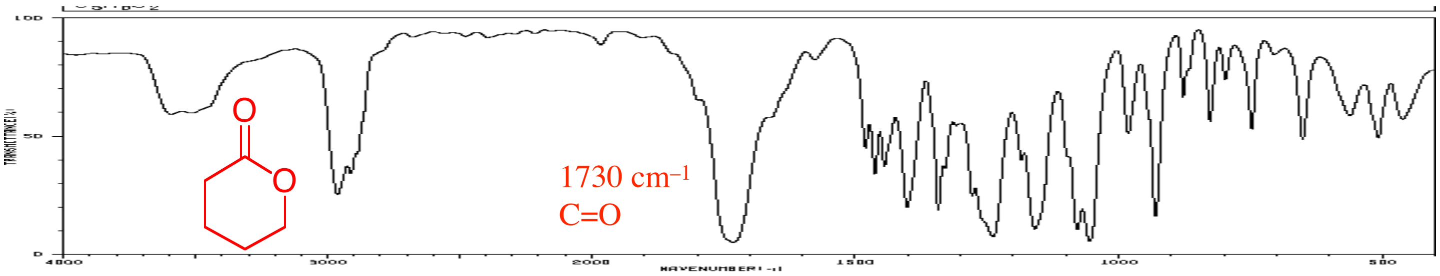
1243 cm^{-1} C–O



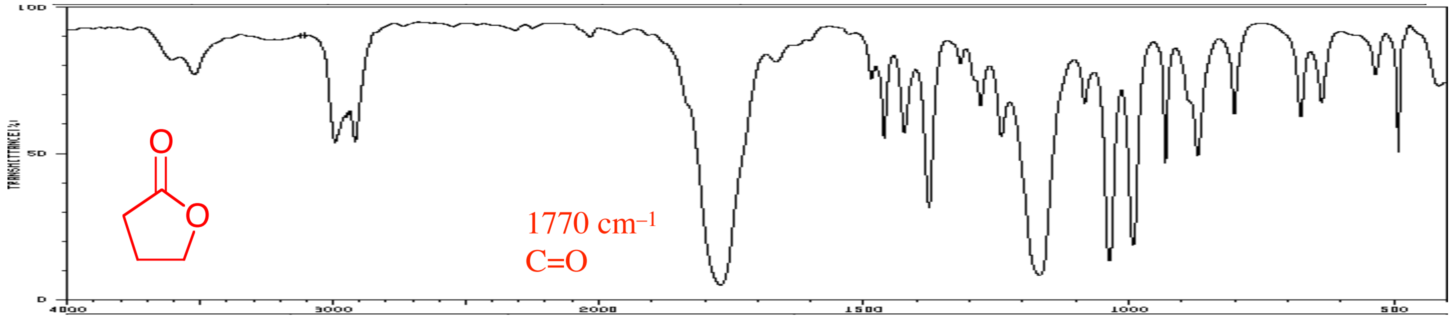
1763 cm^{-1}
C=O

1199, 1164, 1145 cm^{-1} C–O

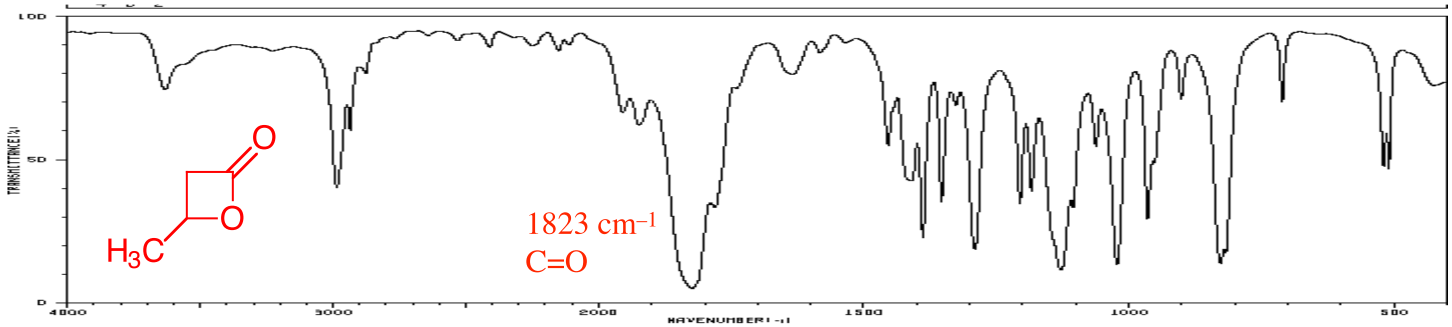
Lactones: effect of Ring sizes



1730 cm^{-1}
C=O

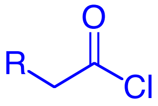


1770 cm^{-1}
C=O

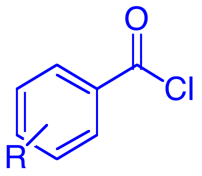


1823 cm^{-1}
C=O

Acid Halides



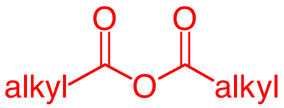
1815–1785 cm^{-1}



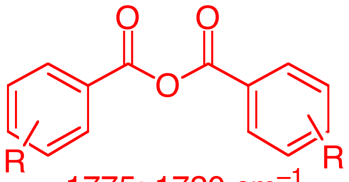
1800–1770 cm^{-1}

Anhydrides

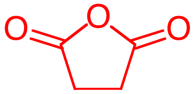
- Two carbonyl stretches (symmetrical and asymmetrical)



1818; 1750 cm^{-1}



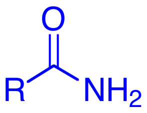
1775; 1720 cm^{-1}



1865; 1782 cm^{-1}

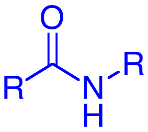
amides

NH stretch(es): Primary amides produce two N-H stretch absorptions, secondary amides only one, and tetriary none.



Two bands

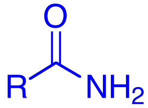
3520 (as), 3400 (s) cm–1



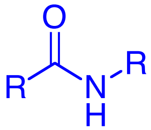
one bands

3500–3400 cm–1

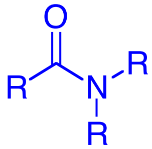
C=O stretching (Amide I band):



1690 cm–1 (dilute)

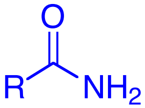


1680-1700 cm–1 (dilute)

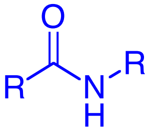


1680-1630 cm–1

NH Bending (Amide II band):

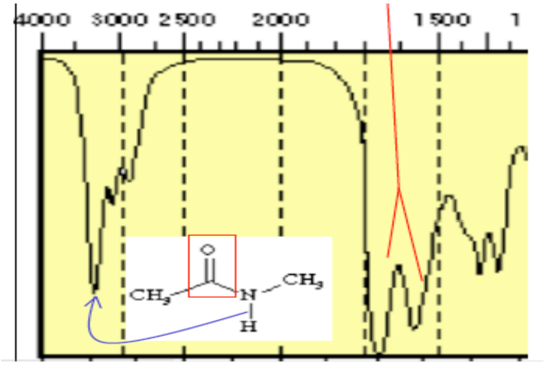


1620-1590 cm–1

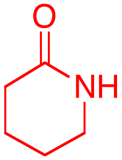


1550-1510 cm–1

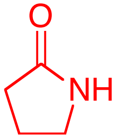
amide bands I and II



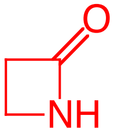
Lactams



1650 cm–1



1750-1700 cm–1



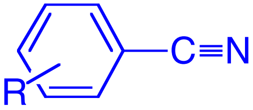
1760-1730 cm–1

- NH stretching
  - primary amines (RNH_2) display <u>two</u> bands, near 3500 and 3400 cm^{-1}. These represent 'free' asymmetrical and symmetrical stretches.
  - secondary amines (R_2NH) display <u>one</u> band near 3350-3310 cm^{-1}.
  - weaker and sharper than OH

Nitriles

alkyl—C≡N

2260-2240 cm^{-1}



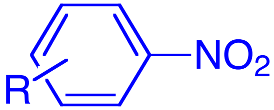
2240-2222 cm^{-1}

Nitro compounds

- 2 bands from the asymmetrical and symmetrical stretching of the $N=O$ bond

$alkylNO_2$

1550 cm^{-1} and 1372 cm^{-1}



1550-1500 cm^{-1} and 1360-1290 cm^{-1}