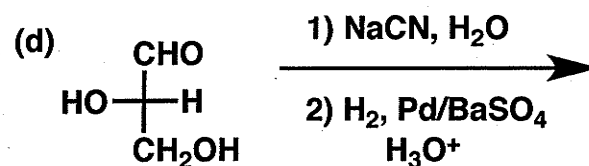
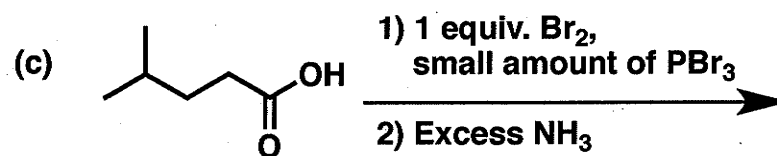
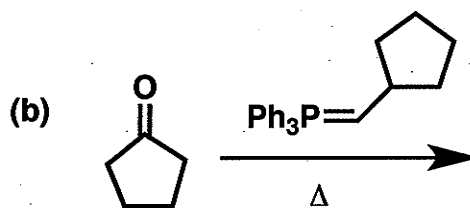
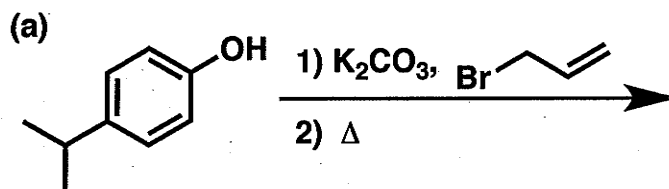


General Instructions:

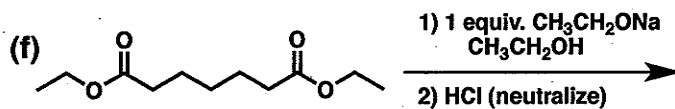
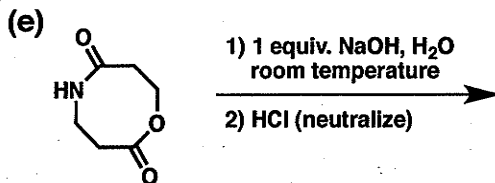
- (i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit.
- (ii) Print your name on each page.

1. (39 points) Show the major product or products expected from each reaction:



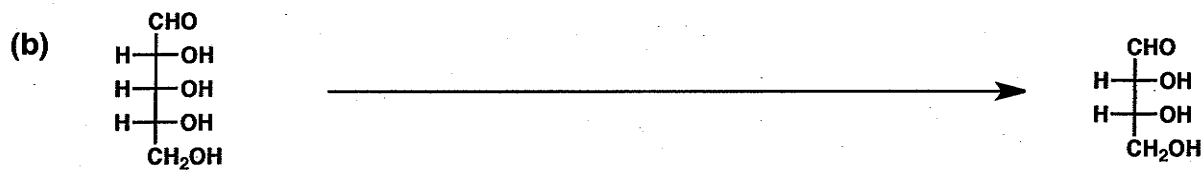
Name _____

1. (cont.)



[Note: In the IR region 1700 - 1800 cm⁻¹, the starting material has a single strong signal at 1745 cm⁻¹, but the product has two signals, at 1745 cm⁻¹ and 1725 cm⁻¹.]

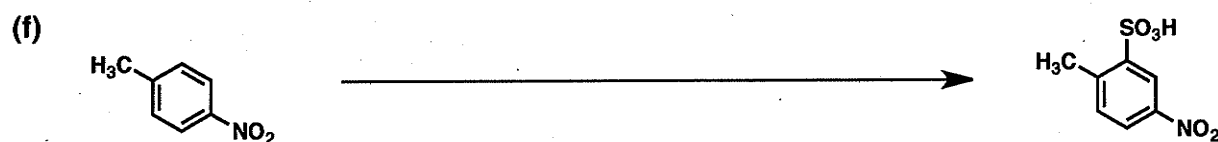
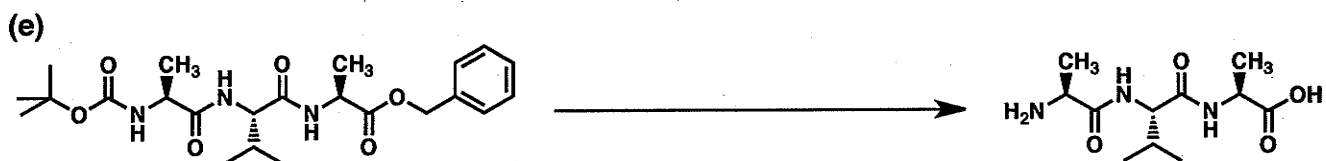
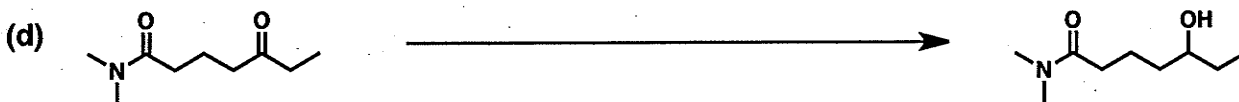
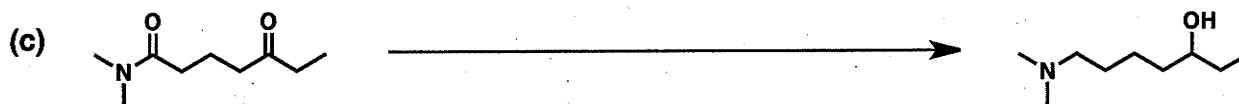
2. (45 points) Show the reagents and other organic molecules required to convert the starting material to the indicated product. Be sure to differentiate clearly between distinct steps, by using "1)", "2)", etc.



(cont. on next page)

Name _____

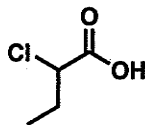
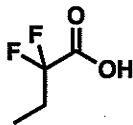
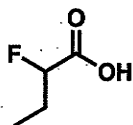
2. (cont.)



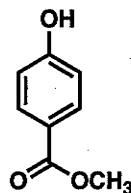
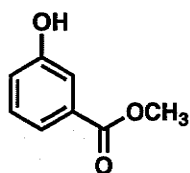
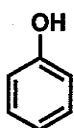
Name _____

3. (8 points) For each set of compounds below, rank the molecules, left to right, from lowest pK_a to highest pK_a (i.e., your answer should have the form $X < Y < Z$).

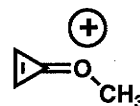
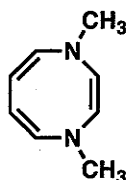
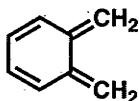
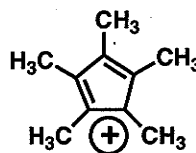
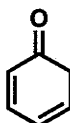
(a)



(b)

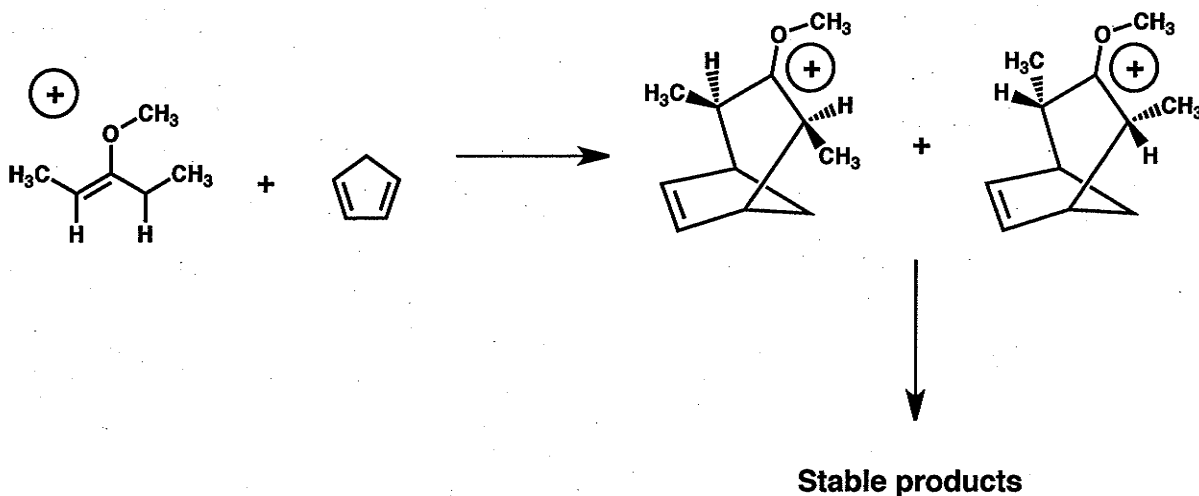


4. (12 points) Among the species shown below, **CIRCLE** those that you would expect to benefit from aromatic stabilization.



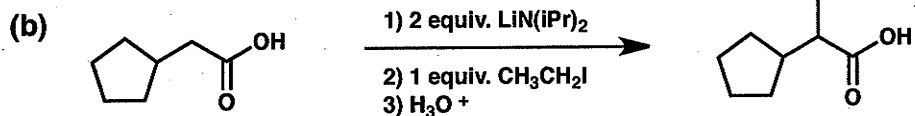
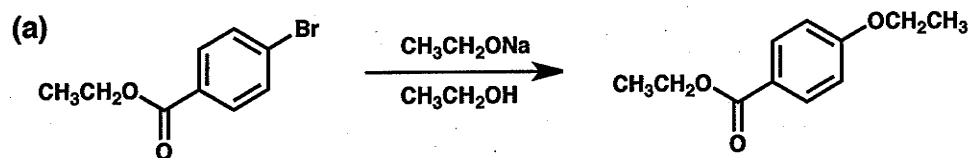
Name _____

5. (10 points) The cation shown on the left below would be expected to react with cyclopentadiene to form the two isomeric bicyclic cations shown on the right (these intermediate would then go on to form more stable species). Provide a molecular orbital rationale for the expectation that these specific bicyclic cations would form (and not isomers with *trans* methyl groups).



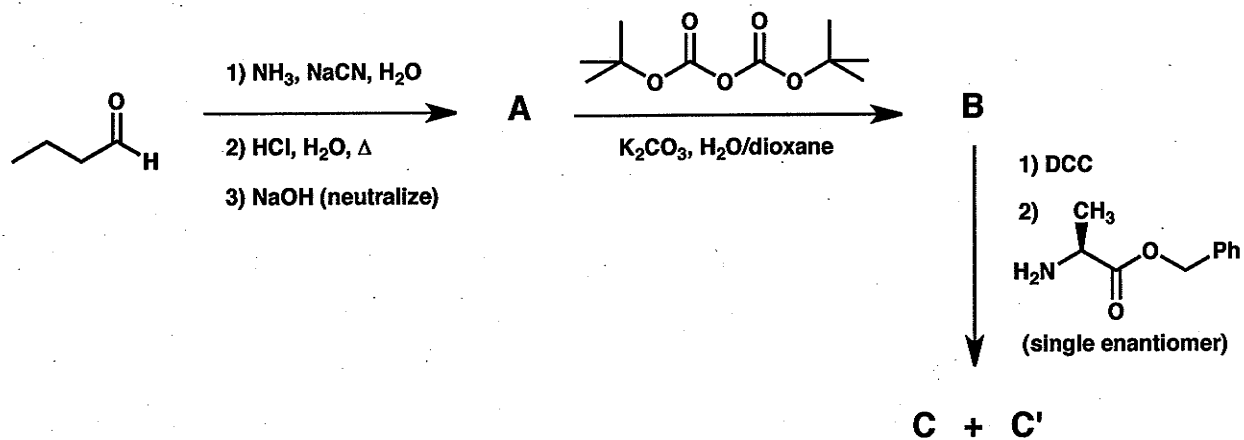
Name _____

6. (18 points) Draw a mechanism (curved arrows) for the reaction shown below.



Name _____

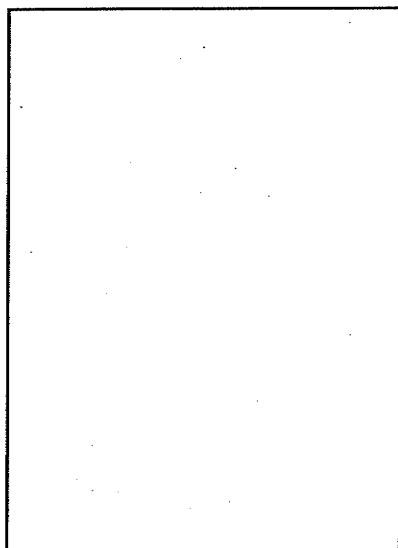
7. (20 points) When the aldehyde shown below is subjected to the sequential reaction conditions indicated, A is formed. Further reactions, as shown, generate B and then a final product that turns out to have two chromatographically separable and isomeric components, C and C'. Give the structures of A, B, C and C'.



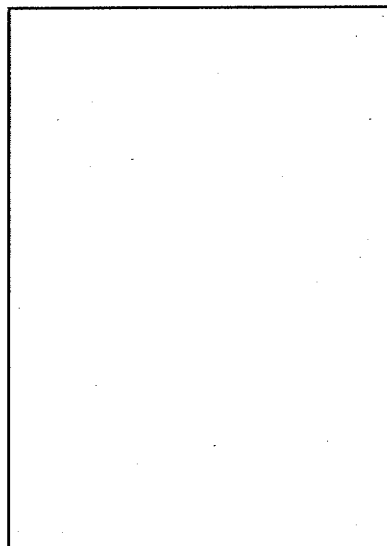
Name _____

8. (20 points)

(a) Draw the Fischer projection of D-glucose (open chain form; not cyclic).

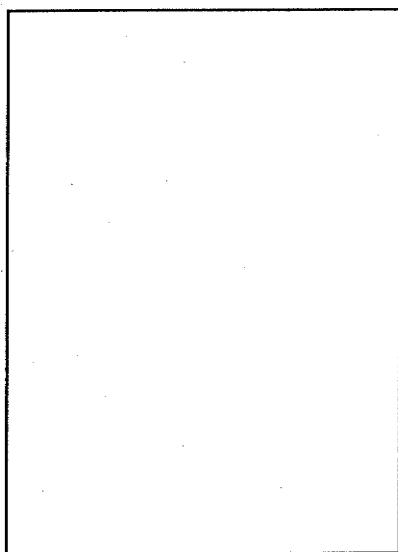


(b) Mannose is the 2-epimer of glucose. Draw the Fischer projection of L-mannose (open chain form; not cyclic).

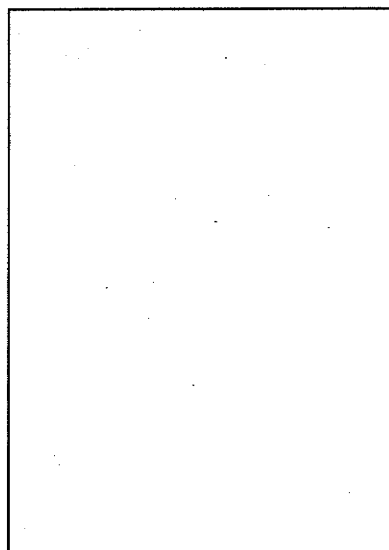


(c) Compound X is an aldohexose. When X is treated with 3 equivalents of PhNHNH_2 in acetic acid, the osazone formed is different from the osazone obtained from D-glucose or D-mannose (these two give the same osazone). However, when X is subjected to two cycles of the Wohl degradation process, the resulting aldotetrose, D-erythrose, is the same as the aldotetrose generated from two cycles of Wohl degradation of D-glucose or D-mannose.

Draw the Fischer projection of D-erythrose.



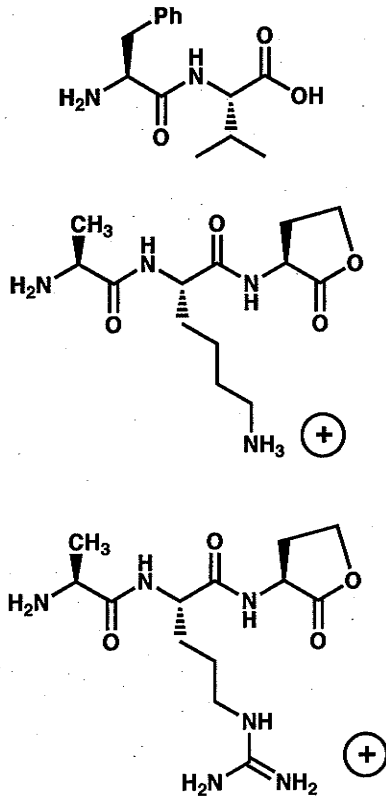
Draw the Fischer projection of X.



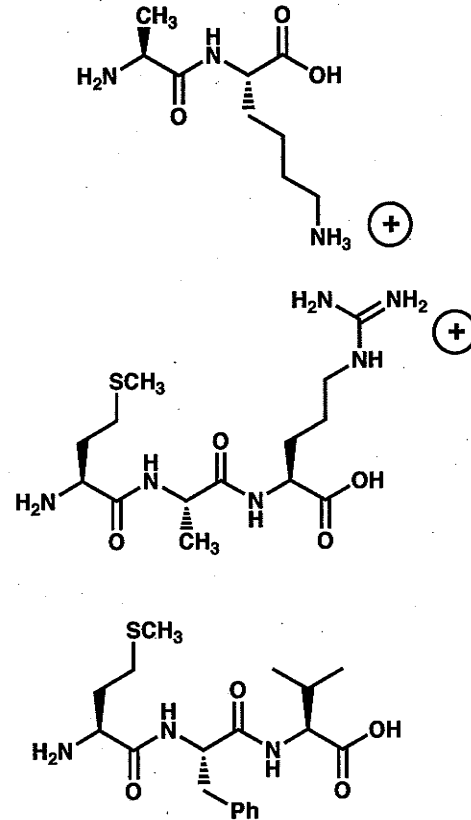
Name _____

9. (12 points) When peptide Z is treated with CNBr, three short fragments are generated, as shown below. When peptide Z is instead treated with the enzyme trypsin, a different set of three short fragments is generated, as shown. Based on this information, what is peptide Z?

Fragments from degradation with CNBr:



Fragments from degradation with trypsin:

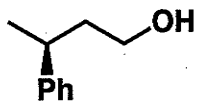


Peptide Z =

Name _____

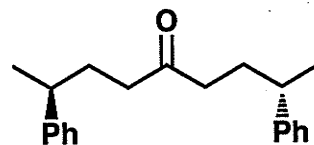
10. (16 points) Propose a synthesis of the target molecule shown below from the indicated starting material. You may use other reagents that contain no more than one carbon atom.

Starting Material =



(single enantiomer)

Target =



Name _____

<u>Problem</u>	<u>Score</u>
1	/ 39
2	/ 45
3	/ 8
4	/ 12
5	/ 10
6	/ 18
7	/ 20
8	/ 20
9	/ 12
10	/ 16

Total:**/ 200**

PERIODIC TABLE OF THE ELEMENTS

1 IA

18 VIIA

1 H Hydrogen 1.00794	2 He Helium 4.002602
3 Li Lithium 6.941	4 Be Beryllium 9.00947
5 B Boron 10.811	6 C Carbon 12.011

Atomic number →
Symbol →
Name (IUPAC) →
Atomic mass →

6 C Carbon 12.011

IUPAC recommendations →
Chemical Abstracts Service group notation →

19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.9559	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.9961	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.409	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.922	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798	37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.32	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29	55 Cs Cesium 132.91	56 Ba Barium 137.33	57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.97	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
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*Lanthanide Series

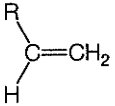
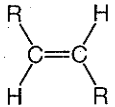
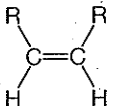
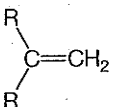
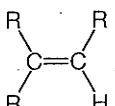
Actinide Series

90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)
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Although this complexity may seem confusing at first, it is usually possible to gain a lot of information about the groups present in a molecule, even if we cannot assign all the bands, or draw a complete structure of the sample molecule. It is a great help in structure assignment to know what types of bonds are present in a molecule. There is also an important side benefit to these complicated IR spectra. The very complexity of the spectrum means that IR spectra of quite similar molecules are different. Each spectrum serves as a fingerprint of the molecule. If two IR spectra are identical (not similar—my old boss insisted on there being no difference greater than the width of the pen line drawn by the recorder) the compounds must be the same.


Table 15.3 gives the general positions of absorptions of a variety of functional groups, and once again we come to the question of memorization. Should one learn this chart by heart? Personally, I think not. It is important to know that this kind of general correlation exists, and you should have a rough idea of where some important functional groups absorb. If you come to use IR often, you will automatically learn the relevant details of the chart, as you work out what the signals in your IR spectra tell you.

TABLE 15.3 Typical Infrared Absorptions of Functional Groups^a

Functional Group	Position (cm ⁻¹)	Intensity ^b
Alkanes		
C—H	2980–2850	m-s (stretch)
C—C	1480–1420	m (bend)
Alkenes		
=C—H	3150–3000	m (stretch)
C=C	1680–1620	m-w (stretch)
(conj) C=C	1630–1600	m-w (stretch)
	995–985 915–905	s (out-of-plane bend)
	980–960	s (out-of-plane bend)
	730–665	s (out-of-plane bend) (br, variable)
	895–885	s (out-of-plane bend)
	840–790	m (out-of-plane bend)

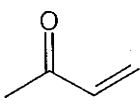
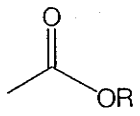
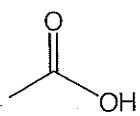
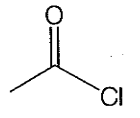
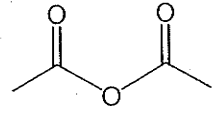
(continued)

TABLE 15.3 Typical Infrared Absorptions of Functional Groups^a (Continued)

Functional Group	Position (cm ⁻¹)	Intensity ^b
Alkynes		
≡C-H	3350-3300	s (stretch)
C≡C	2260-2100	m-w (stretch)
Alcohols		
O-H		
free	3650-3580	m (stretch)
hydrogen bonded	3550-3300	br, s (stretch)
C-O	1260-1000	s (stretch)
	1150-1050	
Amines		
N-H	3500-3100 (two bands for primary amines, one band for secondary amines)	br, m (stretch)
C-N	~1200	m (stretch)
Aromatic compounds		
=C-H	3080-3020	m-w (stretch)
C=C	1600-1580	m-w (stretch)
C-H		
mono	770-730	s (out of plane bend)
	710-690	
ortho	770-735	s (out-of-plane bend)
meta	900-860	m (out of plane bend)
	810-750	s (out-of-plane bend)
	725-680	m (out-of-plane bend)
para	860-800	s (out-of-plane bend)
Carbonyl compounds aldehydes, ketones		
	C=O	
	1730-1700 (higher in strained cyclic molecules)	s (stretch)

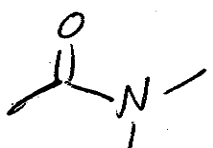
(continued)

TABLE 15.3 Typical Infrared Absorptions of Functional Groups^a (Continued)

Functional Group	Position (cm ⁻¹)	Intensity ^b
Carbonyl compounds aldehydes, ketones		
	1680-1660	s (stretch)
C-H (aldehydes)	2900-2700 (two bands)	w (stretch)
Esters		
	1750-1735 1300-1000	s (C=O) (stretch) s (C-O) (stretch)
Acids		
	1730-1700 3200-2800	s (C=O) (stretch) s, br (O-H) (stretch)
Acid chlorides		
	1820-1770	s (C=O) (stretch)
Anhydrides		
	1820-1750 (two bands) 1150-1000	s (C=O) (stretch) s (C-O) (stretch)
Imines		
C=N	1680-1640	m (stretch)
Cyanides (nitriles)		
C≡N	~2250	s (stretch)

^aCAUTION! There certainly is some subjectivity in this table, and the values represent average positions for "normal" compounds. Conjugation generally lowers double-bond stretching vibrations by about 20 cm⁻¹.

^bMedium = m, strong = s, weak = w, broad = br.

Amides  1620-1680 cm⁻¹ s (stretch)

