Chemistry 3351
Organic Chemistry/Final Exam/CHEM 142
Monday: Dec. 13th from **7:30 pm → 10:00pm**

Name:_____ (please print)

Page	Possible Points	Score
2	9	_____
3	10	_____
4	12	_____
5	14	_____
6	14	_____
7	10	_____
8	6	_____
9	10	_____
10	18	_____
11	10	_____
12	9	_____
13	8	_____
14	10	_____
15	10	_____
TOTAL	150	_____

1. (9 pts) Clickers in Action:

   i) Your assignment is to convert (1*R*, 2*S*)-2-methylcyclopentanol to (1*R*, 2*S*)-1-cyano-2-methylcyclopentane. The reagents provided are:

   (1) NaCN, acetone
   (2) TsCl, pyridine
   (3) NaI, acetone

   Select the best sequence of reactions, starting with substrate, to obtain the highest yield of product.

   A) 1
   B) 2, 1
   C) 2, 3
   D) 2, 3, 1

   ii) Propose a synthetic route for isopropyl propyl ether using any of the reagents shown below. Select the sequence in which you will use the reagents.

   1) 1-Propanol
   2) 2-Propanol
   3) 1-Bromopropane
   4) 2-Bromopropane
   5) NaH, THF

   A) 1, 5, 4
   B) 2, 5, 3
   C) 3, 5, 2
   D) 4, 5, 1

   iii) Consider the reaction of propene with $Hg(OAc)_2$ in THF-H_2O, followed by reaction with $NaBH_4$ in aqueous NaOH. Classify this reaction using oxidation-reduction concepts.

   A) Oxidation
   B) Reduction
   C) Neither

2. (10 pts) Arrange the compounds within each of the following sets in order of increasing boiling point, and give your reasoning (concisely).

(a) 1-pentanol, 2-methyl-1-butanol

(b) 1-hexanol, 2-pentanol, *tert*-butyl alcohol

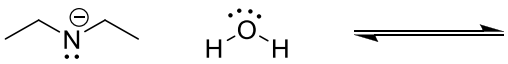
(c) 1-hexanol, 1-hexene, 1-chloropentane

(d) diethyl ether, propane, 1,2-propanediol

(e) cyclooctane, chlorocyclobutane, cyclobutane

3. (12 pts) Acid-Base Chemistry

a. Complete the following equation. Use curved arrow notation and show all formal charges and lone pairs. Also, clearly label the Bronsted acid-base pairs.



b. Using the choices from the table provided, identify the acidic and basic components of the following solutions:

10% H_2SO_4 in H_2O

Acidic:

Basic:

15% NH_3 in H_2O

Acidic:

Basic:

Choices

H_2O

$H_3O^{\oplus}$

$^{\ominus}OH$

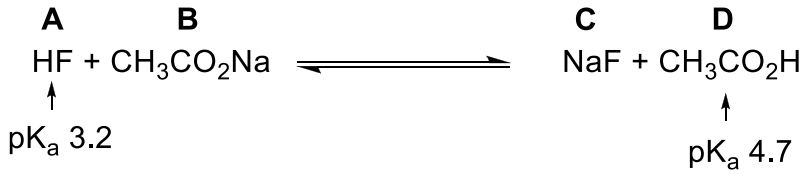
H_2SO_4

$HSO_4^{\ominus}$

NH_3

$^{\oplus}NH_4$

c. Answer the questions concerning the following reaction:

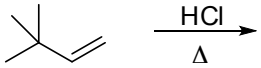


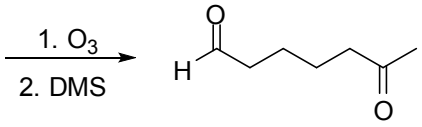
i. Which species act as acids?

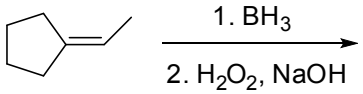
ii. What is the strongest base?

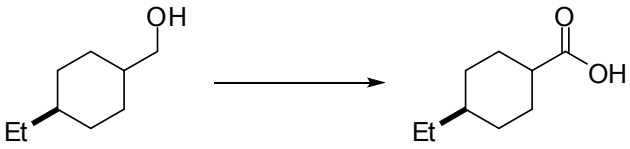
iii. To which side does the equilibrium lie?

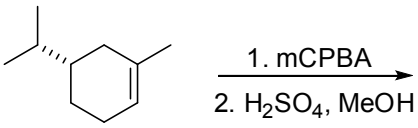
4. (14 pts) Provide the missing products or reactants for the following reactions. For reactions that produce stereoisomers, draw ALL possible stereoisomers and INDICATE if they would be formed in equal or unequal amounts.

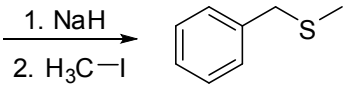
a) 

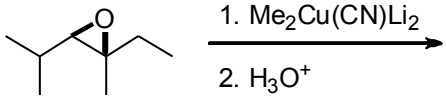
b) 

c) 

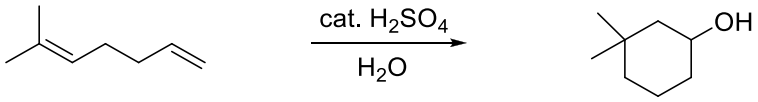
d) 

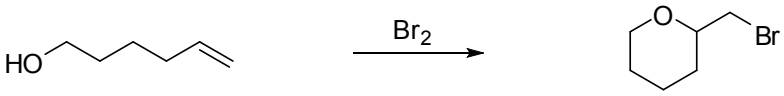
e) 

f) 

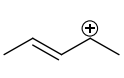
g) 

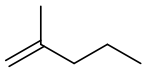
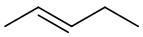
5. (14 pts) Provide full and complete mechanisms for the reactions below. Be sure to include every intermediate and all arrows required for each step of the reaction.

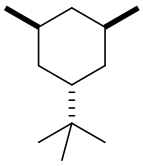
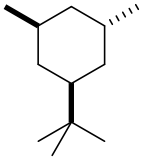
a) 

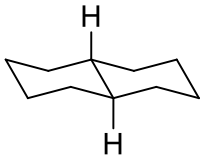
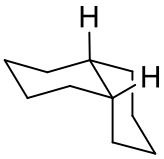
b) 

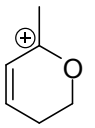
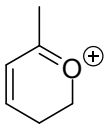
6. (10 pts) Circle the most stable structure in each pair of structures below.

a)  or 

b)  or 

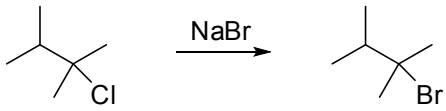
c)  or 

d)  or 

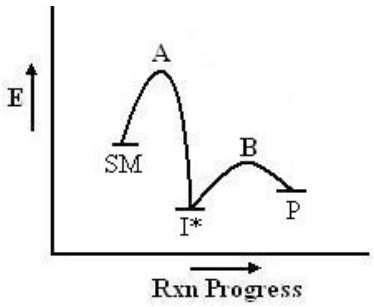
e)  or 

7. (6 pts)

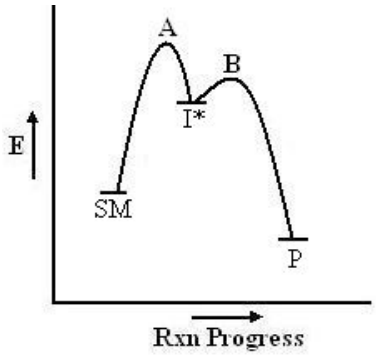
a) Which energy diagram best represents the reaction shown below? Please circle your answer. (SM: Starting material, I*: Intermediate, P: Product)



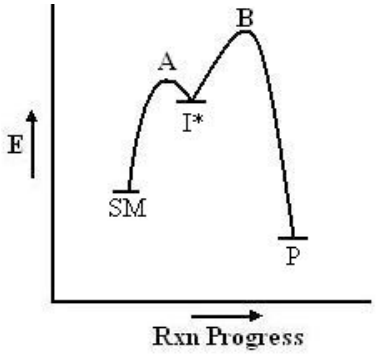
A.



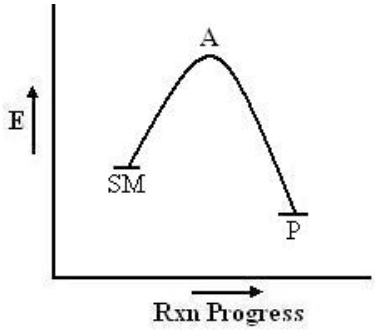
B.



C.



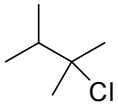
D.



b) In regards to your answer for part a), which step is rate limiting? Please circle your answer.

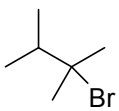
i. Step A
ii. Step B
iii. Neither Step A nor Step B

c) In regards to the reaction above, which of the following compounds is the nucleophile? Please circle your answer.

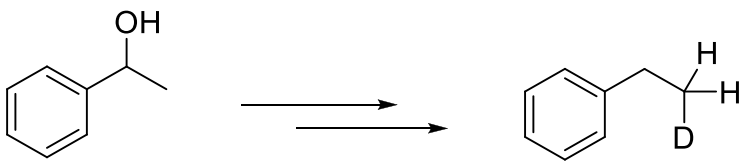
a. 

b. NaBr

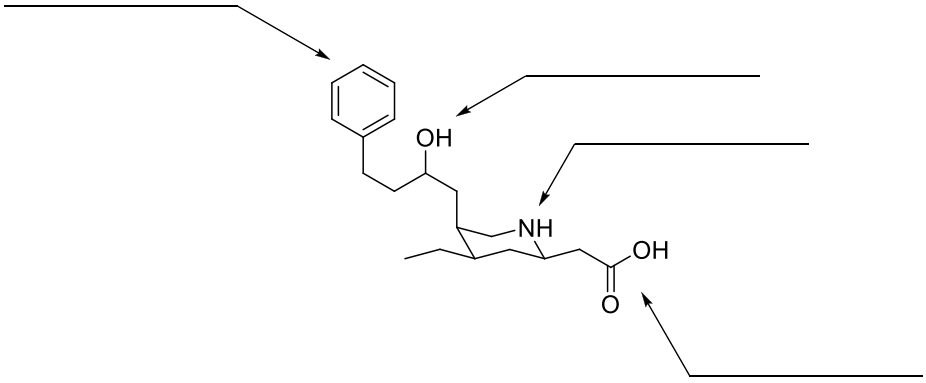
c. NaCl

d. 

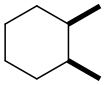
8. (10 pts) Design a synthetic route for the transformation below. The synthesis requires more than one step; therefore, please show all intermediates for full credit.



9. (10 pts) a) Label all functional groups in the following compound.



b) Identify the following compounds as either chiral, achiral, or achiral/meso.



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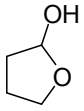

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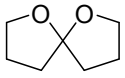

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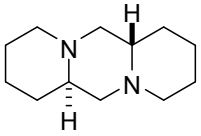

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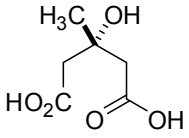

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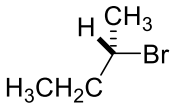
10. (10 pts) Identify the relationship between the following pairs. Are they identical, constitutional isomers, enantiomers, or diastereomers?



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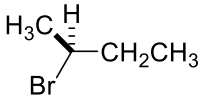

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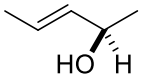

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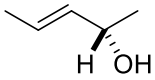

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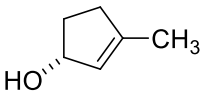

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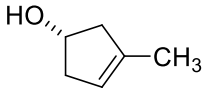

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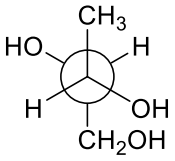
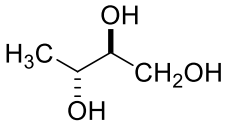


and



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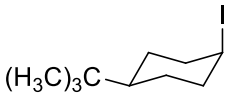

and

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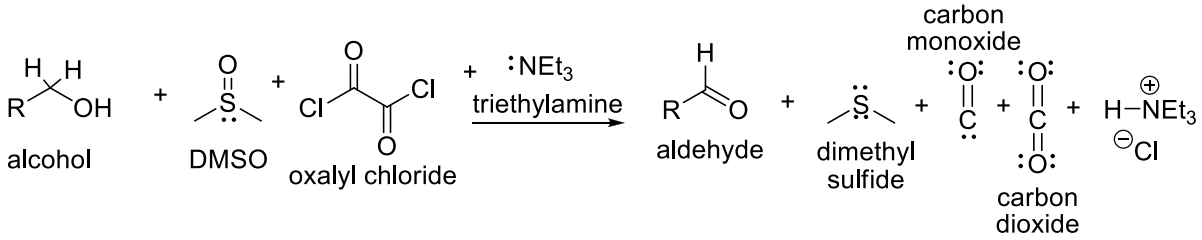
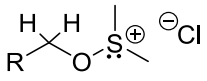
11. (9 pts) The *Swern oxidation*, shown below is a very mild procedure for oxidizing primary and secondary alcohols.



(a) How many electrons are involved in this oxidation from the alcohol to the aldehyde? Explain.

(b) What is the oxidizing agent?

(c) The following compound is a key intermediate in this oxidation. Give a curved-arrow mechanism for the reaction of this intermediate with triethylamine as the base to give the product aldehyde (RCHO).

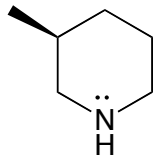


12. (8 pts) Explain how you could differentiate between the compounds in each of the following pairs by using simple physical or chemical tests that give readily observable results, such as obvious solubility differences, color changes, evolution of gases, or formation of precipitates.

(a) 3-ethoxypropene and 1-ethoxypropane

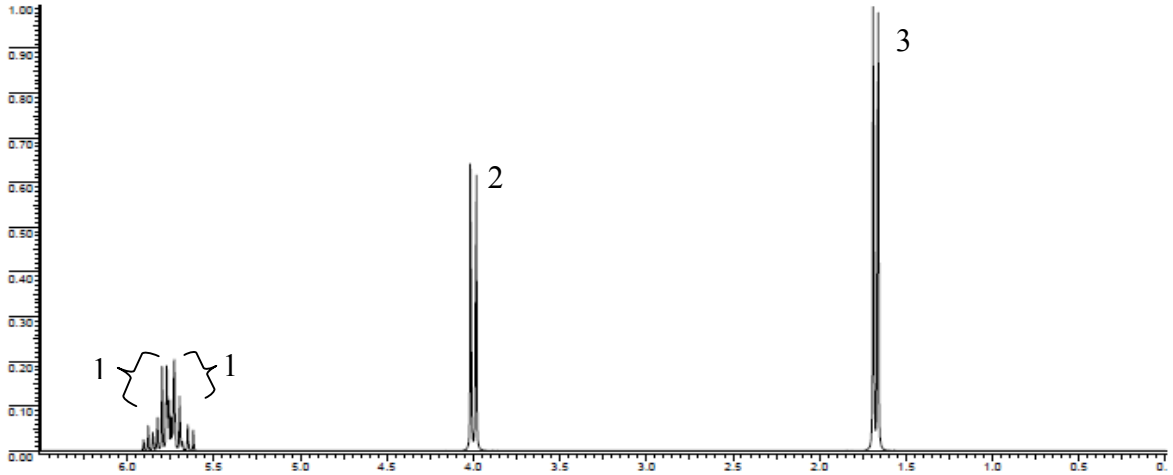
(b) 1-pentanol and 1-methoxybutane

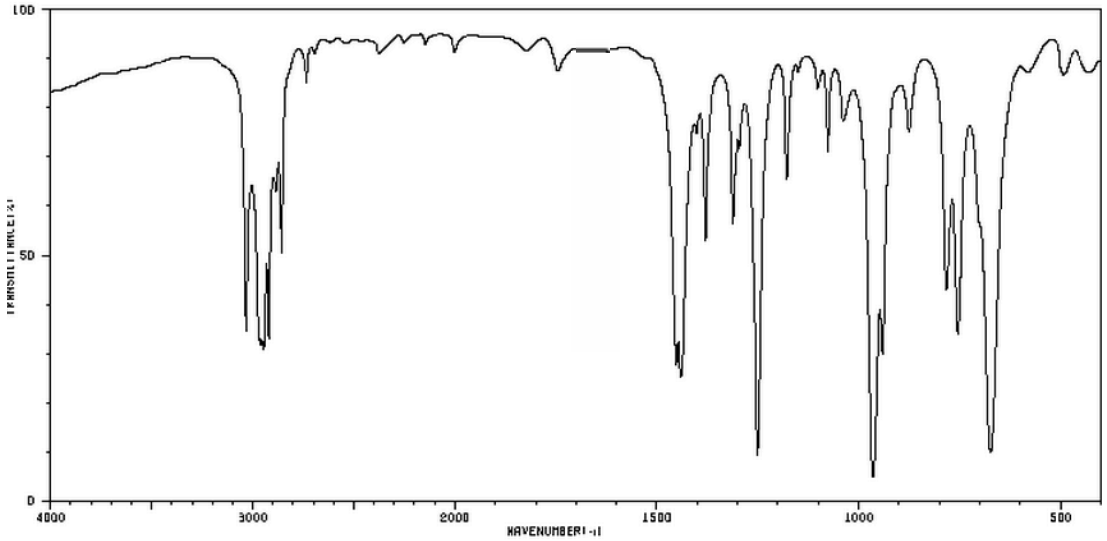
13. (10 pts) Draw a chair conformation for (*S*)-methylpiperidine showing the sp^3 orbital that contains the nitrogen unshared electron pair. How many chair conformations of this compound are in rapid equilibrium?

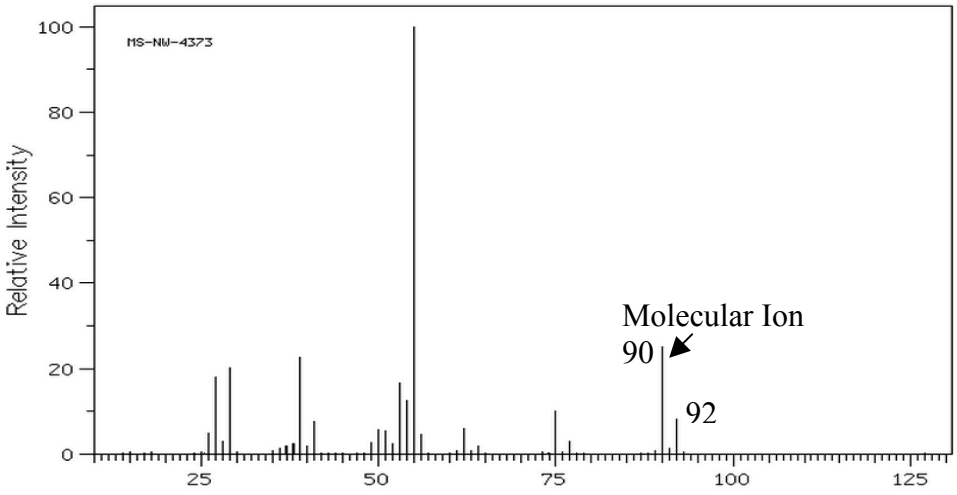


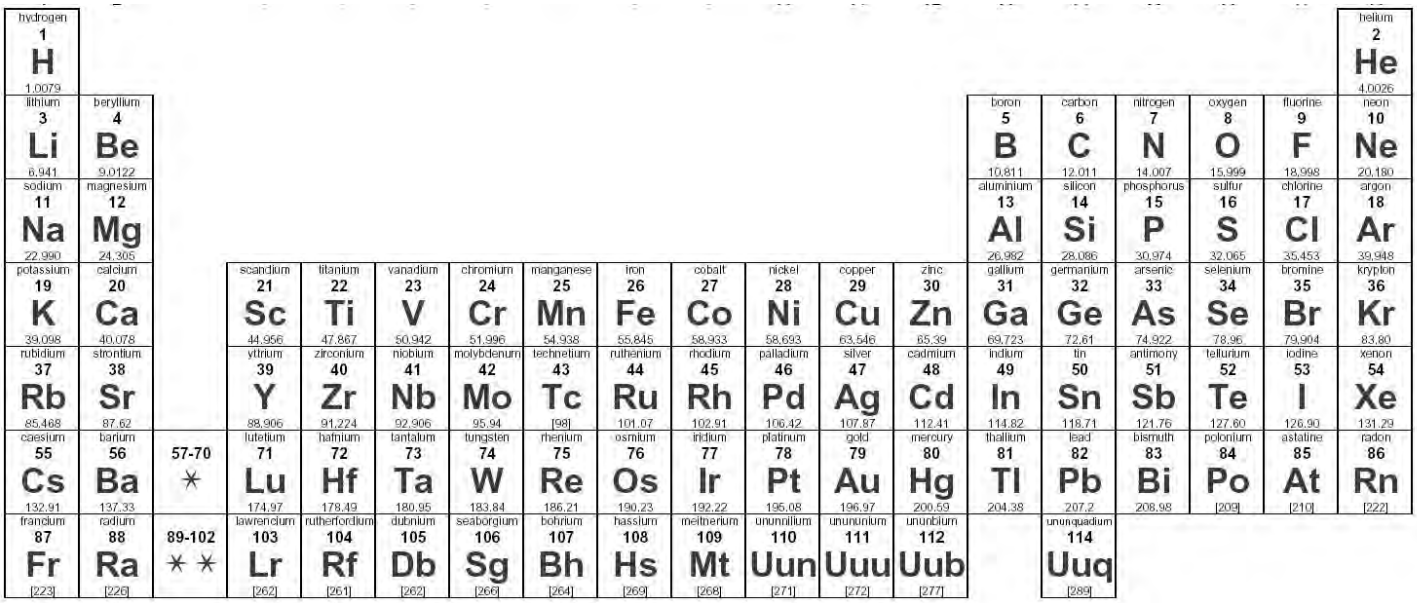
(*S*)-3-methylpiperidine

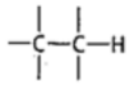
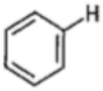
14. (10 pts) Propose a structure for the compound (C_nH_mX, X= halogen) given the spectra shown below. Be sure to show your reasoning by labeling definitive signals on each spectrum. Also, please label the hydrogens in your proposed structure and match them to their corresponding signals on the NMR spectrum.









Group	Chemical shift, ppm
	0.7–1.5
	4.6–5.7
—O—H	varies with solvent and with acidity of O—H
—C≡C—H	1.7–2.5
	6.5–8.5

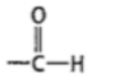
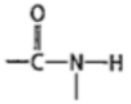
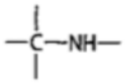
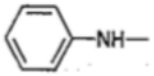
Group	Chemical shift, ppm
	9–11
	7.5–9.5
	0.5–1.5
	2.5–3.5

TABLE 12.1 Regions of the Infrared Spectrum

Wavenumber range, cm^{-1}	Type of absorptions	Name of region
3400–2800	O—H, N—H, C—H stretching	Functional group
2250–2100	C≡N, C≡C stretching	
1850–1600	C=O, C=N, C=C stretching	
1600–1000	C—C, C—O, C—N stretching; various bending absorptions	Fingerprint
1000–600	C—H bending	C—H bending

Table of Characteristic IR Absorptions

frequency, cm^{-1}	*bond*	*functional group*
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1˚, 2˚ amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1˚ amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag ($–CH_2X$)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1˚, 2˚ amines
900–675 (s)	C–H “oop”	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp