Chemistry 3351
Organic Chemistry/Final Exam
Monday: Dec. 17th from **1:30 pm → 4:00pm**

Name:_____ (please print, 1 pt)

Page	Possible Points	Score
1	1	
2	9	
3	10	
4	12	
5	14	
6	14	
7	10	
8	15	
9	10	
10	10	
11	10	
12	9	
13	16	
14	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) Arrange the acids NH_3, C_2H_5SH, C_2H_5OH, CH_3SO_3H, and HCO_2H in order of increasing strength.

(A) $C_2H_5OH < NH_3 < CH_3SO_3H < C_2H_5SH < HCO_2H$

(B) $C_2H_5OH < NH_3 < C_2H_5SH < HCO_2H < CH_3SO_3H$

(C) $NH_3 < C_2H_5OH < C_2H_5SH < HCO_2H < CH_3SO_3H$

(D) $NH_3 < C_2H_5SH < C_2H_5OH < CH_3SO_3H < HCO_2H$

iii) Which of these reactions involves a free radical mechanism?

(I) Halogenation of alkanes in presence of light
(II) Addition of HBr to alkenes
(III) Addition of HBr to alkenes in the presence of ROOR

(A) I and II
(B) I and III
(C) II and III
(D) I, II and III

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

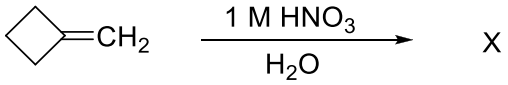
(c) 1-hexanol, 1-hexene, 1-chloropentane

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

(e) cyclooctane, chlorocyclobutane, cyclobutane

3. (12 pts)

a) Give the product X expected when methylenecyclobutane undergoes acid-catalyzed hydration.

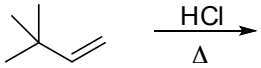


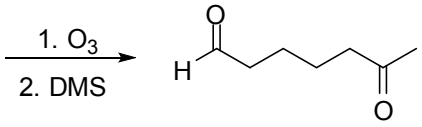
b) The rate-limiting step is protonation of the double bond; use H_3O^+ as the acid catalyst. Draw the structure of the reactive intermediate formed in the rate-limiting step.

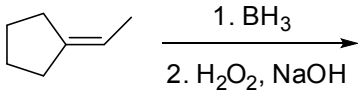
c) Draw the transition state for the rate-limiting step.

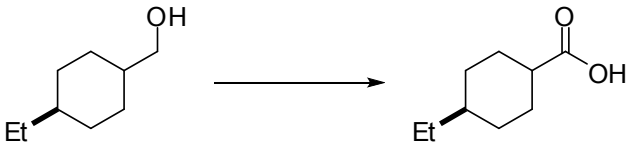
d) What is the rate-limiting step for dehydration of X (the reverse of the reaction shown above)?

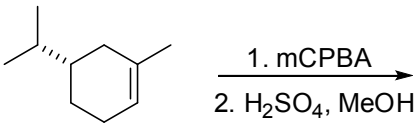
4. (14 pts) Provide the missing products, reactants, or reaction conditions for the following reactions. For reactions that produce stereoisomers, draw ALL possible stereoisomers and INDICATE if they would be formed in equal or unequal amounts.

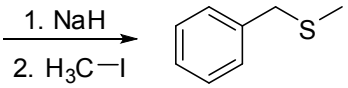
a) 

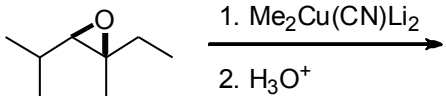
b) 

c) 

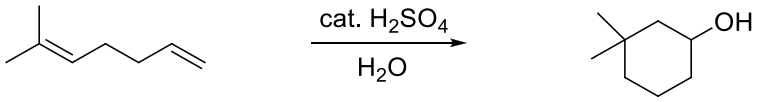
d) 

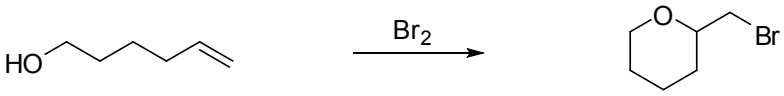
e) 

f) 

g) 

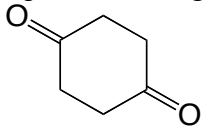
5. (14 pts) Provide full and complete mechanisms for the reactions below. Be sure to include every intermediate and all arrows required for each step of the reaction.

a) 

b) 

6. (10 pts). In the laboratory of the firm "Halides 'R' Us", compound **A** has been found in a vial labeled only "achiral alkyl halide $C_{10}H_{17}Br$". The management feels that the compound might be useful as a pesticide, but they need to know its structure. You have been called in as a consultant at a handsome fee.

Compound **A**, when treated with KOH in warm ethanol, yields two compounds (**B** and **C**), each with the molecular formula $C_{10}H_{16}$. Compound **A** rapidly reacts in aqueous ethanol to give an acidic solution, which, in turn, gives a precipitate of AgBr when tested with $AgNO_3$ solution. Ozonolysis of **A** followed by treatment with $(CH_3)_2S$ affords $(CH_3)_2C{=}O$ (acetone) as one of the products plus an unidentified halogen-containing material. Catalytic hydrogenation of either **B** or **C** gives a mixture of both *trans*- and *cis*-1-isopropyl-4-methylcyclohexane. Compound **A** reacts with one equivalent of Br_2 to give a mixture of two separable compounds, **D** and **E**, both of which are achiral compounds. Finally, ozonolysis of compound B followed by treatment with aqueous H_2O_2 gives acetone and the diketone **F**.

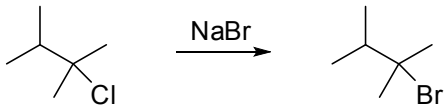


F

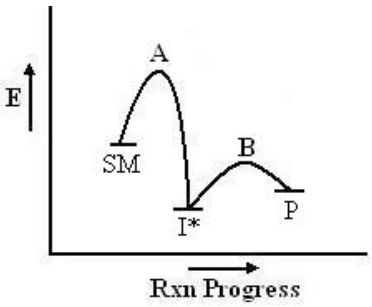
Propose structures for compounds **A** through **E** that best fit the data (and collect your fee).

7. (15 pts)

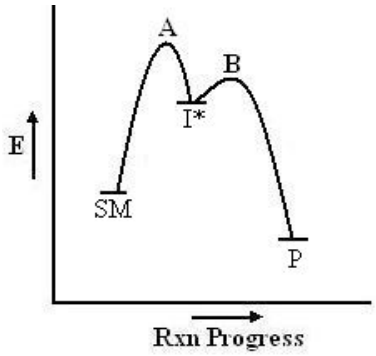
a) Which energy diagram best represents the reaction shown below? Please circle your answer. (SM: Starting material, I*: Intermediate, P: Product)



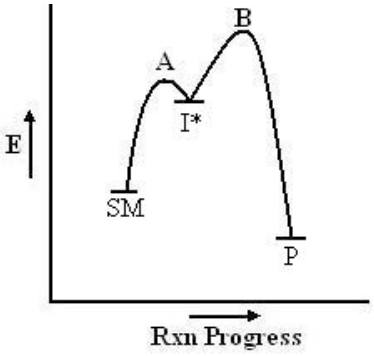
A.



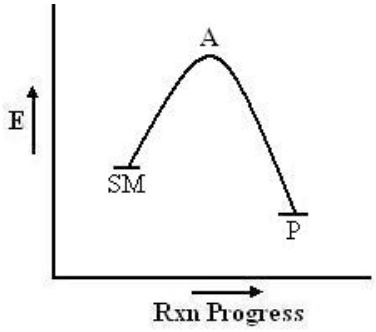
B.



C.



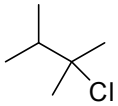
D.



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

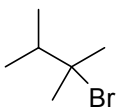
i. Step A
ii. Step B
iii. Neither Step A nor Step B

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

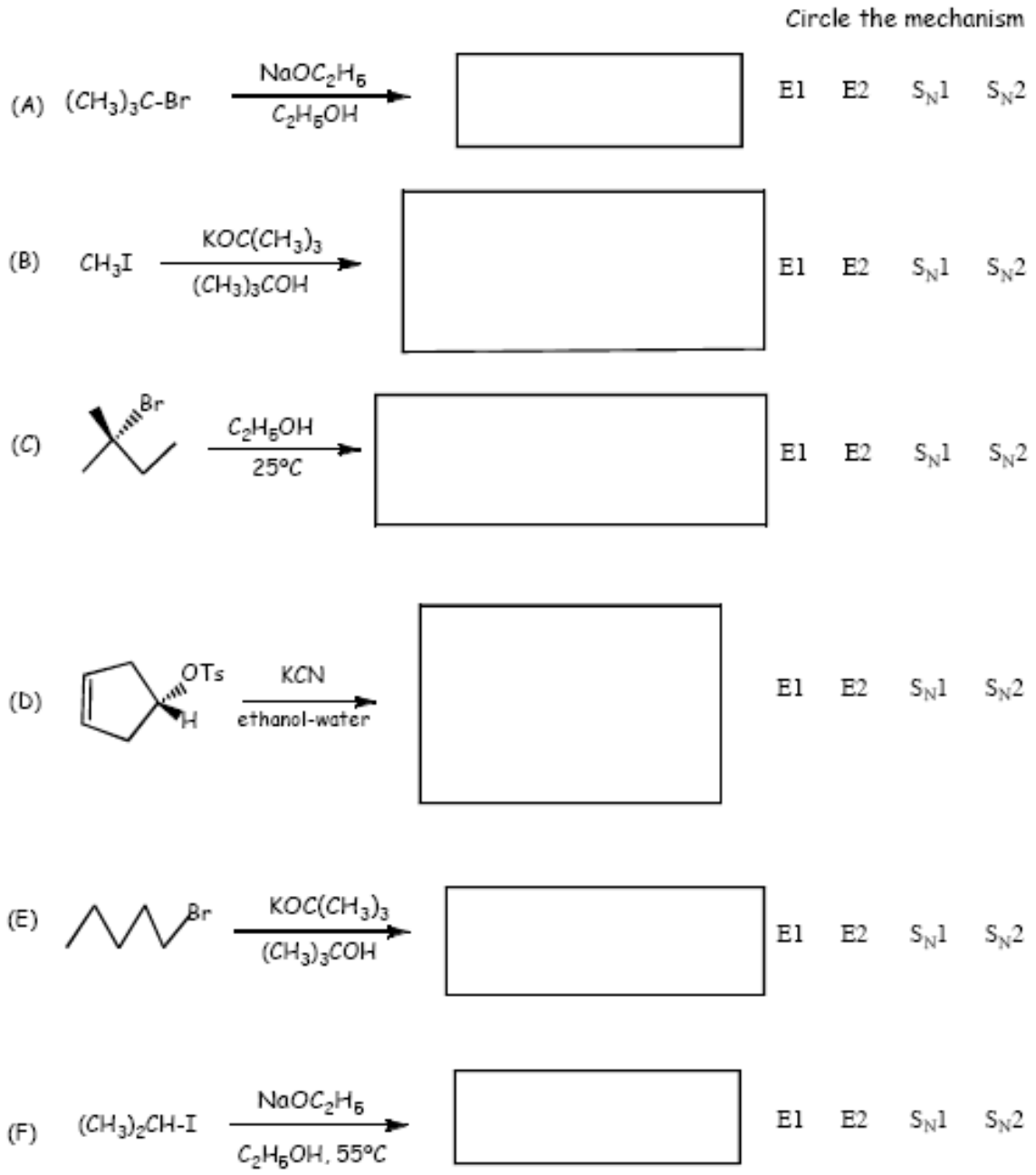
a. 

b. NaBr

c. NaCl

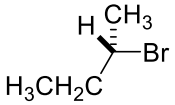
d. 

8. (12 pts) Draw the structure(s) of the major product(s) of each reaction. Be sure to include stereochemistry when appropriate. Circle the mechanism that accounts for the formation of each major product:

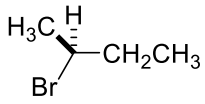


9. (10 pts) Draw every stereoisomer for 1-bromo-2-chloro-1,2-difluorocyclopentane. Use wedge-and-dash bonds for the substitutent groups, and be sure that they are drawn on the outside of the ring, adjacent to each other.

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



and



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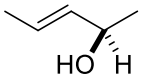
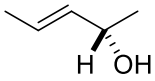


and



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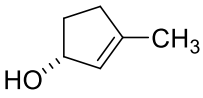
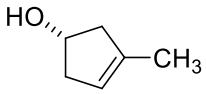


and



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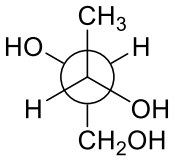
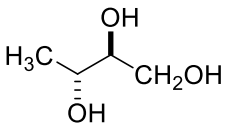


and



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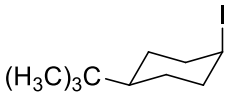
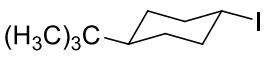


and



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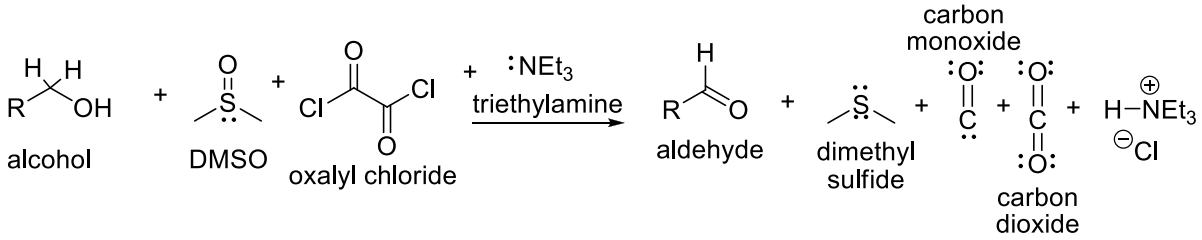
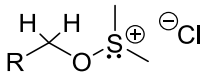
11. (9 pts) The *Swern oxidation*, shown below is a very mild procedure for oxidizing primary and secondary alcohols.



(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).

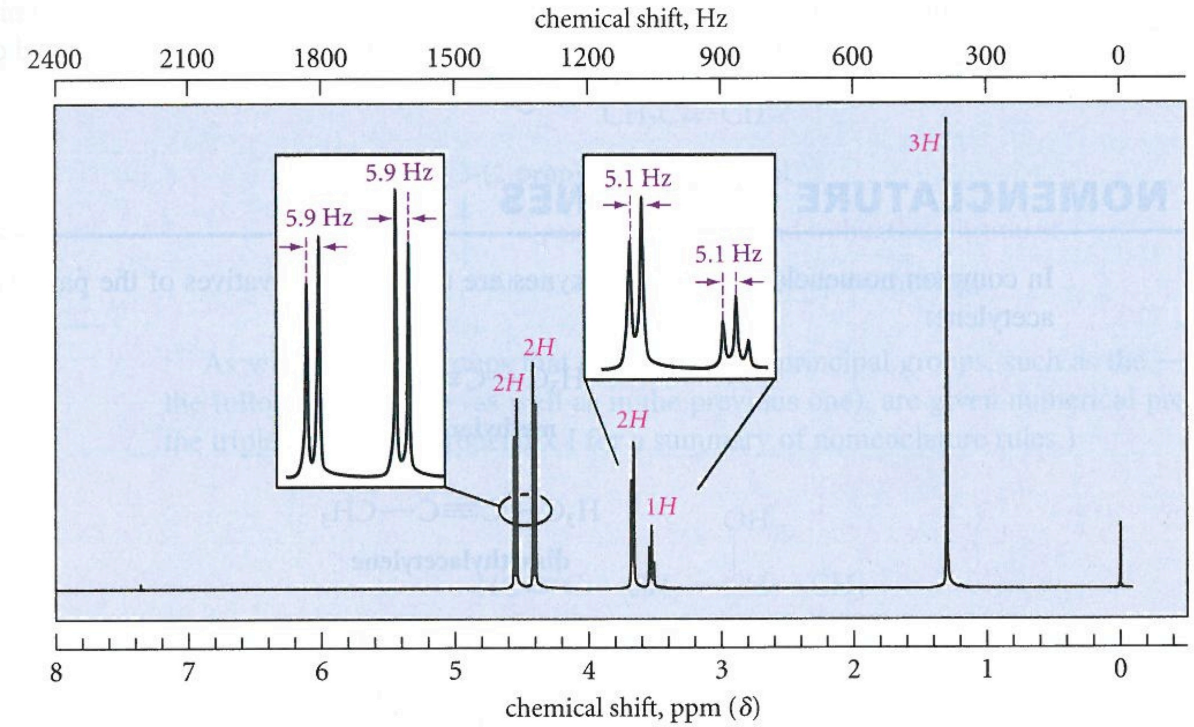


12. (16 pts) Explain how you could differentiate between the compounds in each of the following pairs by using simple physical or chemical tests that give readily observable results, such as obvious solubility differences, color changes, evolution of gases, or formation of precipitates.

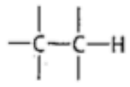
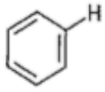
(a) 3-ethoxypropene and 1-ethoxypropane

(b) 1-pentanol and 1-methoxybutane

13. (10 pts) A compound X with the molecular formula $C_5H_{10}O_2$ has an IR spectrum with strong absorption in the 1000-1100 cm^{-1} region; very strong, broad absorption in the 3000-3600 cm^{-1} region; and no absorption in the 1600-1700 cm^{-1} region. The proton NMR spectrum of X is given below. When the sample is shaken with D_2O, the triplet at δ 3.5 disappears the doublet at δ 3.7 becomes a singlet. Propose a structure for this compound, and explain your reasoning.



hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 ✶	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 ✶ ✶	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	ununnium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

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

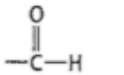
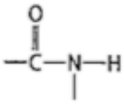
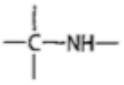
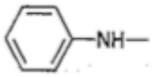
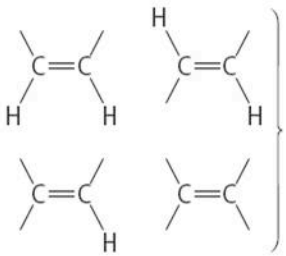
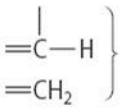
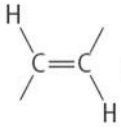
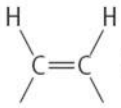
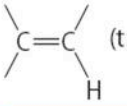
Group	Chemical shift, ppm
	9–11
	7.5–9.5
	0.5–1.5
	2.5–3.5

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 12.2 Important Infrared Absorptions of Alkenes

Functional group	Absorption*
C=C stretching absorptions	
—CH=CH$_2$ (terminal vinyl)	1640 cm^{-1} (m, sh)
C=CH$_2$ (terminal methylene)	1655 cm^{-1} (m, sh)
	1660–1675 cm^{-1} (w) (absent in some compounds)
=C—H stretching absorptions	
	3000–3100 cm^{-1} (m)
=C—H bending absorptions	
—CH=CH$_2$ (terminal vinyl)	910, 990 cm^{-1} (s) two absorptions
C=CH$_2$ (terminal methylene)	890 cm^{-1} (s)
 (*trans*-alkene)	960–980 cm^{-1} (s)
 (*cis*-alkene)	675–730 cm^{-1} (br) (ambiguous and variable for different compounds)
 (trisubstituted)	800–840 cm^{-1} (s)

**Intensity designations:* s = strong; m = moderate; w = weak
Shape designations: sh = sharp (narrow); br = broad (wide)