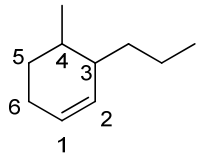
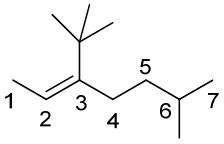
CHEMISTRY 31 **Name:** _____
Exam #1, 100 pts
June 25, 2010

1. (4 pts) Provide the complete IUPAC name for each of the following compounds.

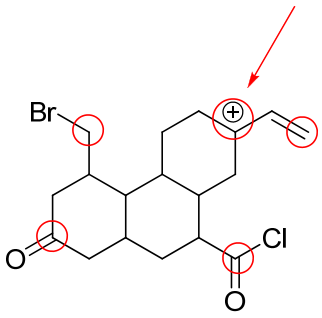


4-methyl-3-propylcyclohexene

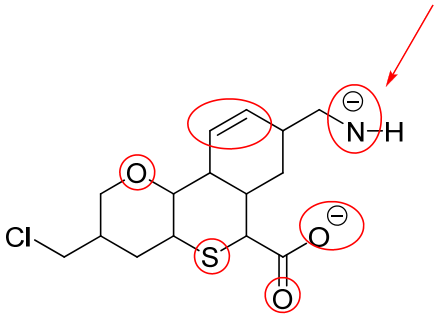


(Z)-3-tert-butyl-6-methyl-2-heptene

2. (6 pts) (a) Identify (by circling) all electrophilic positions in compound A and all nucleophilic positions in compound B given below:



Compound A



Compound B

(b) Using an arrow, point to the **most reactive** electrophile in compound A and the **most reactive** nucleophile in compound B.

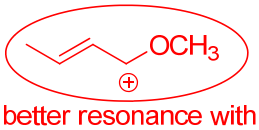
(c) Provide a brief (1-2 sentence) explanation for **one** of your answers in part b.

For compound A, electrophiles will have full plus or partial plus charges and/or atoms with an incomplete octet. Be careful, you must consider resonance structures to recognize why I circled one of the alkene carbons. The most reactive would be the carbocation with a full plus one charge and an incomplete octet.

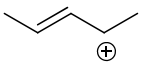
For compound B, nucleophiles will have full minus charge, partial minus charge, or a pi bond. For alkene, either carbon of the pi bond could be a nucleophile. For a carbonyl, the oxygen would act like the nucleophile. The most reactive would be the nitrogen atom with the full minus charge (it is less electronegative and does not have resonance stabilization like the oxygen with the minus charge).

3. (18 pts) Evaluate each of the following sets of compounds according to the given criterion. Circle your choice and give a brief (<10 word) explanation for your reasoning.

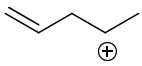
(a) Which compound is the more stable cation?



better resonance with full octets

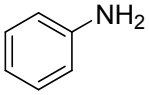


resonance with incomplete octets

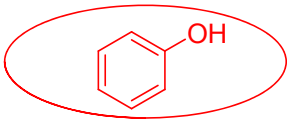


no resonance

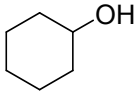
(b) Which compound is the strongest acid?



minus charge on less EN atom with resonance

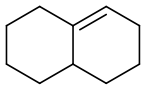


minus charge on more EN atom with resonance

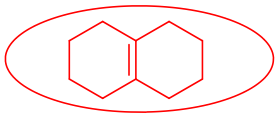


no resonance

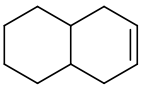
(c) Which compound is the most stable?



trisubstituted

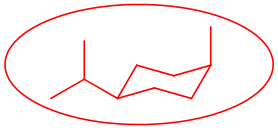


tetrasubstituted more sub more stable

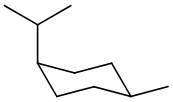


disubstituted

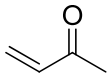
(d) Which compound is the most stable?



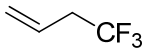
better to put bigest group in the equatorial position



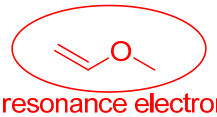
(e) Which alkene is the most reactive nucleophile?



resonance electron withdrawing group



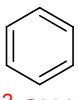
inductive electron withdrawing group



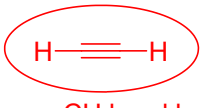
resonance electron donating group

(f) Which compound has the strongest carbon-hydrogen bonds?

sp^3 CH bond

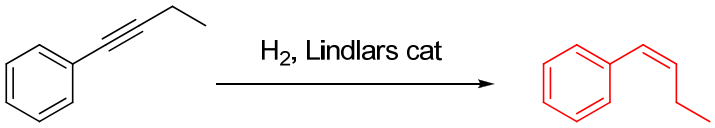


sp^2 CH bond

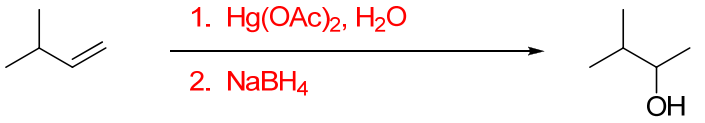


sp CH bond has better orbital overlap with similar size orbitals

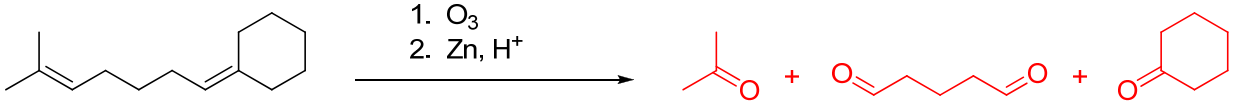
4. (26 pts) Provide the major organic product(s) or supply missing reagents for each of the following reactions.



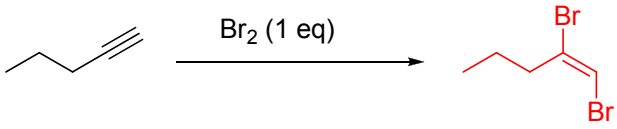
must be cis alkene



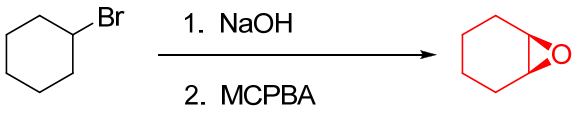
must be oxymercuration-demercuration
H_2SO_4, H_2O would give rearrangement



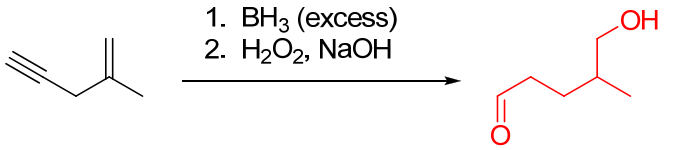
will react at both alkenes to give 3 products



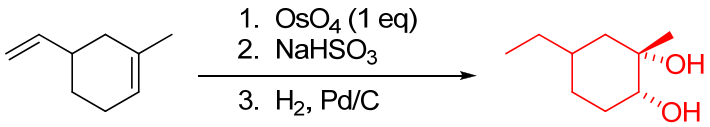
must show anti addition



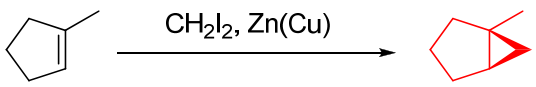
make alkene, then make epoxide
with syn addition



anti-Markovnikov hydration of
alkene and alkyne

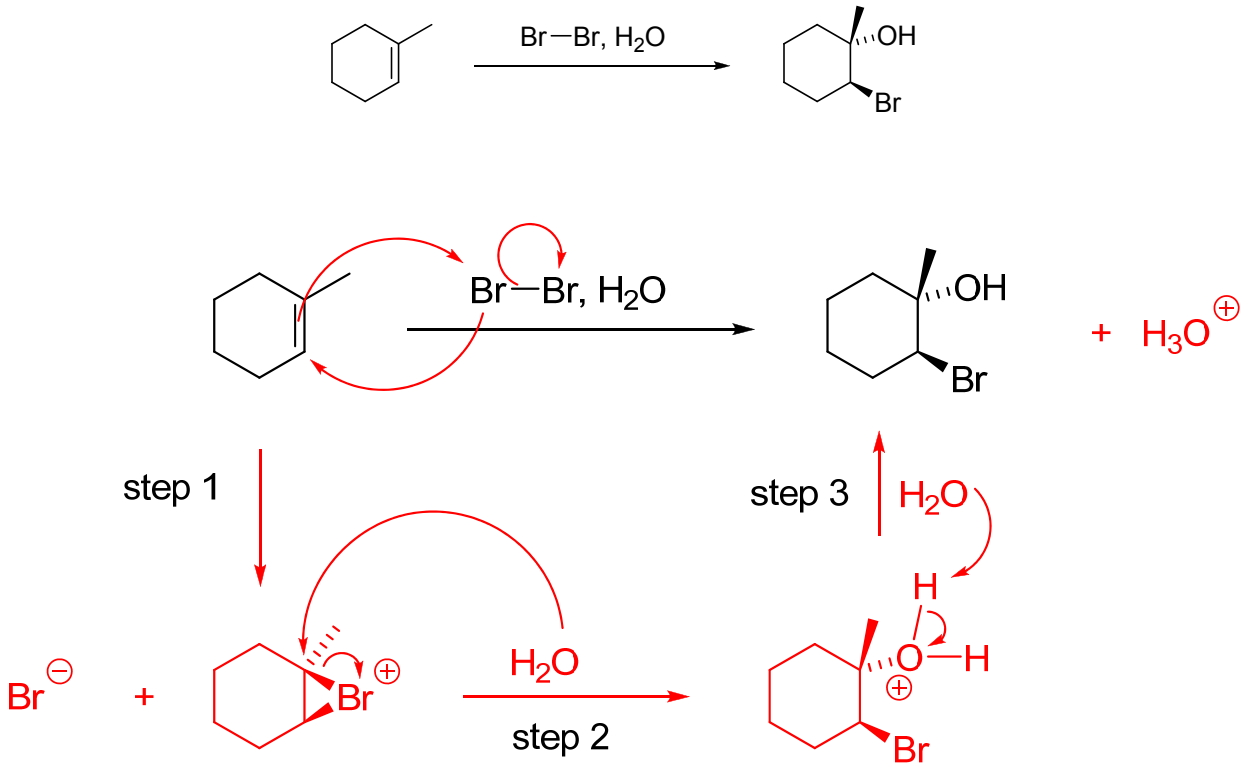


syn dihydroxylation at most reactive
alkene, then hydrogenation

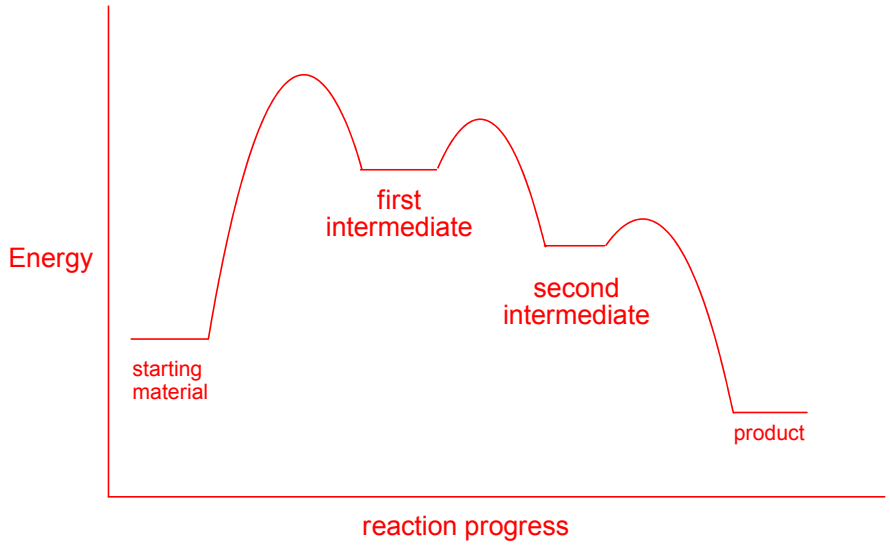


syn cyclopropane formation

5. (10 pts) (a) Provide a detailed stepwise mechanism using curved arrows for the following reaction. Be sure to show each individual step and include the structure of each intermediate formed.

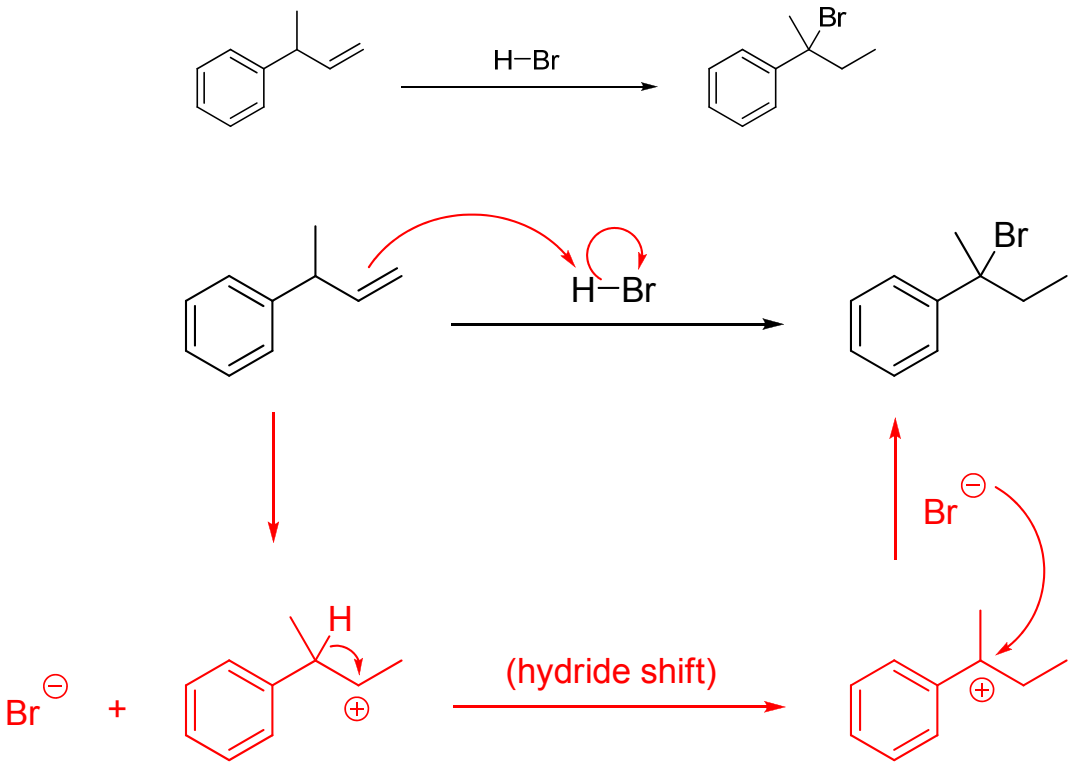


(b) Draw an energy diagram for your mechanism above and label the position of starting material, intermediates, and the product.



Three step reaction with two intermediates. Final product lower in energy than starting material with intermediates higher in energy than starting material.

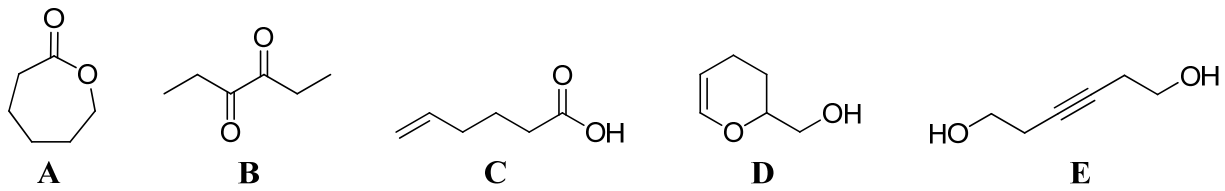
6. (10 pts) (a) Provide a detailed stepwise mechanism using curved arrows for the following reaction. Be sure to show each individual step and include the structure of each intermediate formed.



(b) Is this reaction expected to be thermodynamically favorable? Briefly explain why or why not (1-2 sentences).

YES, this reaction will be thermodynamically favored. We break a relatively weak H-Br bond with poor overlap and a weak C-C pi bond, and form a strong C-H sigma bond and moderate C-Br bond. Overall we form stronger bonds so the reaction is thermodynamically favorable.

7. (10 pts) Shown below are five isomers, **A-E**, all with the molecular formula $C_6H_{10}O_2$.



(a) What is the degree of unsaturation for these compounds? (show your work)

Hsat = 2(6) +2 = 14

DoU = (14-10)/2 = 2

(b) Which compounds would react with exactly 2 molar equivalents of Br_2?

Provide all letter answers that apply: E only

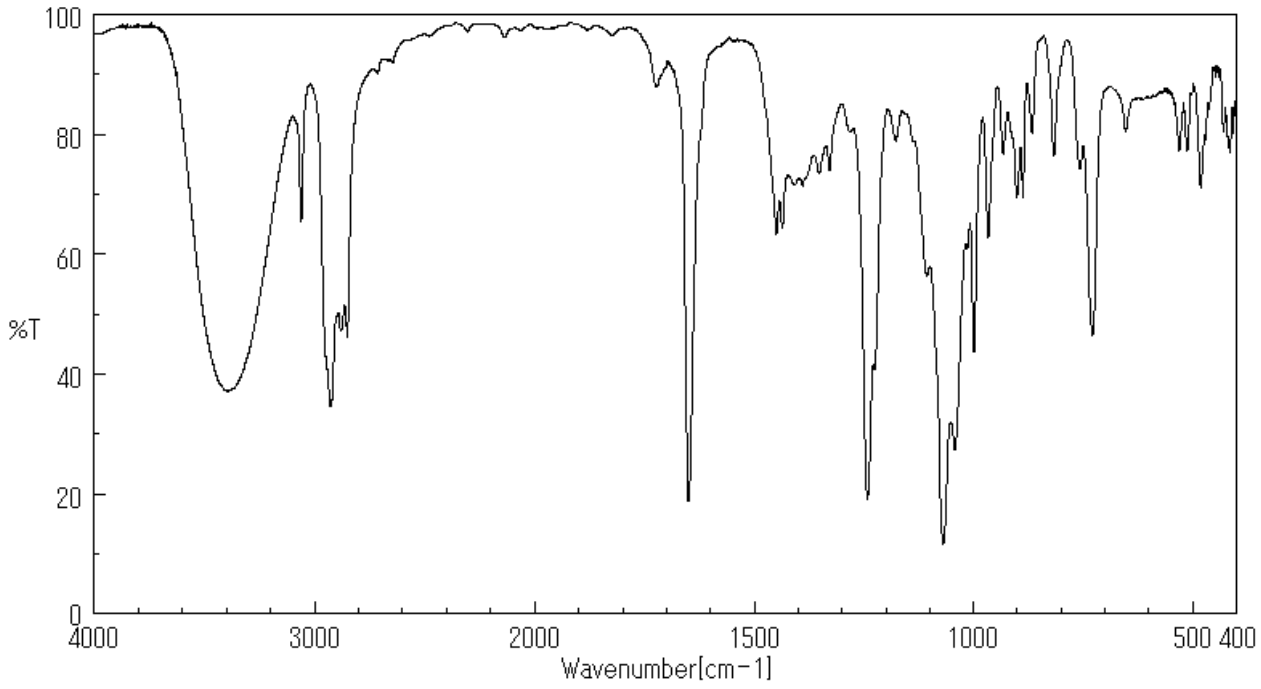
(c) Which compounds would only display three signals in ^{13}C NMR spectroscopy?

Provide all letter answers that apply: B and E

(d) Which compounds will produce CO_2 as a product upon reaction with O_3 then NaOH, H_2O_2?

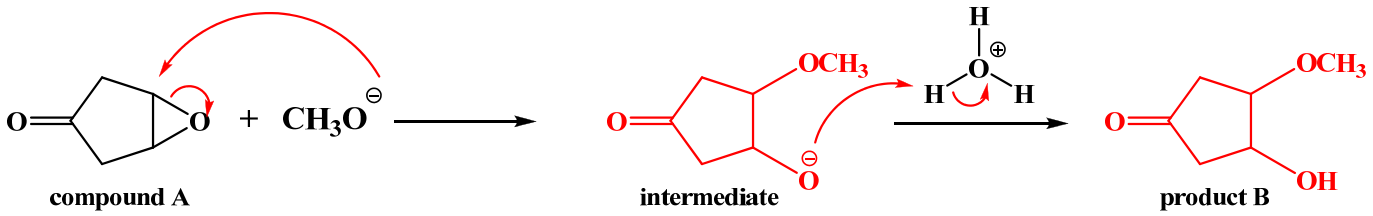
Provide all letter answers that apply: C only

(e) Which compound matches the IR spectrum given below? D



OH =CH CH (sp3) C=C

8. (10 pts) Consider the two step reaction sequence shown below reacting compound A with CH_3O^- to give an intermediate, followed by reaction with H_3O^+ giving product B.



(a) When conducted in the lab, product B provides the spectroscopic data given below. Using this data, what is the structure of the isolated product B? Draw the structure of the intermediate, product B, and provide the curved arrows for both steps in the above reaction scheme.

^{13}CNMR: 6 peaks

IR major peaks:

3300 cm^{-1}, strong and broad

2900, 2800 cm^{-1}, strong to medium

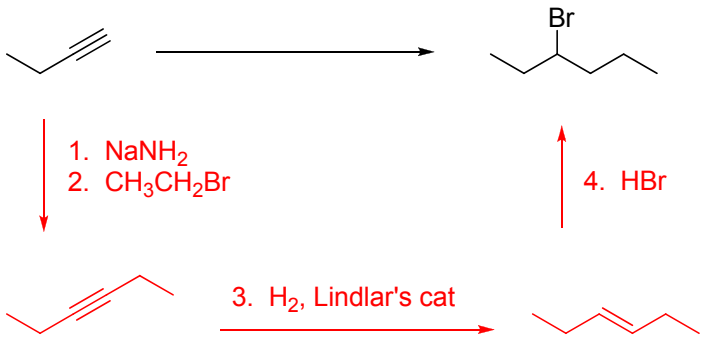
1720 cm^{-1}, strong

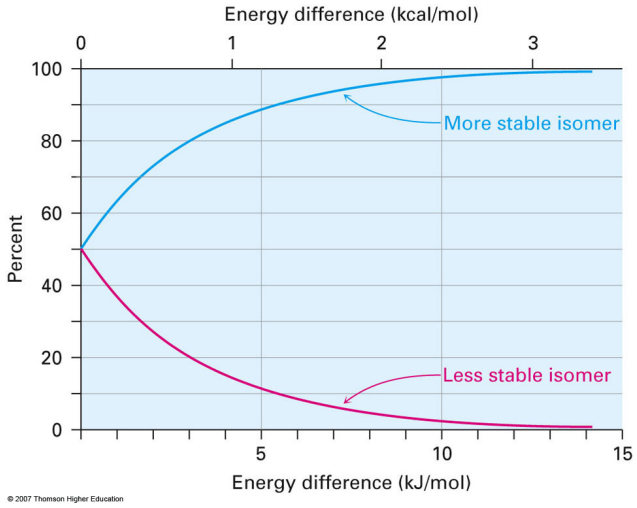
(b) Do you think this reaction is thermodynamically favorable? Circle YES or NO

(c) Briefly (10-20 words) explain your answer in part b.

This reaction would relieve the ring strain in the three membered ring.

9. (6 pts) Propose a sequence of steps to synthesize the following product from the given starting material.





Destabilizing Strain Energies

1,3-Diaxial Interactions	Gauche Interactions	Eclipsing Interactions
$CH_3 - H$ = 3.8 kJ/mol	$CH_3 - CH_3$ = 3.8 kJ/mol	H – H = 4.0 kJ/mol
$CH(CH_3)_2 - H$ = 4.6 kJ/mol	$CH(CH_3)_2 - CH_3$ = 4.6 kJ/mol	$CH_3 - H$ = 6.0 kJ/mol
$CH(CH_3)_2 - CH_3$ = 8.4 kJ/mol		$CH_3 - CH_3$ = 11.0 kJ/mol

Table 12.1 Characteristic IR Absorptions of Some Functional Groups

Functional Group	Absorption (cm^{-1})	Intensity
Alkane		
C–H	2850–2960	Medium
Alkene		
=C–H	3020–3100	Medium
C=C	1640–1680	Medium
Alkyne		
≡C–H	3300	Strong
C≡C	2100–2260	Medium
Alkyl halide		
C–Cl	600–800	Strong
C–Br	500–600	Strong
Alcohol		
O–H	3400–3650	Strong, broad
C–O	1050–1150	Strong
Arene		
C–H	3030	Weak
Aromatic ring	1660–2000	Weak
	1450–1600	Medium

Functional Group	Absorption (cm^{-1})	Intensity
Amine		
N–H	3300–3500	Medium
C–N	1030–1230	Medium
Carbonyl compound		
C=O	1670–1780	Strong
Carboxylic acid		
O–H	2500–3100	Strong, broad
Nitrile		
C≡N	2210–2260	Medium
Nitro		
NO_2	1540	Strong
Aldehyde		
C-H	2800 - 2700	Medium