CH 336
Midterm Exam 2
Monday, May 16, 2016 Name_____

You may use a molecular model kit, but no other notes or material with chemical information. Electronic gadgets (including but not limited to: calculators, phones, MP3 players, smart watches) are prohibited; we may ask you to leave electronic watches at the front of the room or in your backpack for the exam period.

Please ask questions if a question is not clear.

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]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
**Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Score Table:

Section I _____/24

Section II _____/30

Section III _____/22

Section IV _____/24

Total: _____/100

Table 10-2 Typical Hydrogen Chemical Shifts in Organic Molecules

Type of hydrogen[a]	Chemical shift δ in ppm	
Primary alkyl, RCH_3	0.8–1.0	Alkane and alkane-like hydrogens
Secondary alkyl, RCH_2R'	1.2–1.4	
Tertiary alkyl, R_3CH	1.4–1.7	
Allylic (next to a double bond), $R_2C{=}C(CH_3)R'$	1.6–1.9	Hydrogens adjacent to unsaturated functional groups
Benzylic (next to a benzene ring), $ArCH_2R$	2.2–2.5	
Ketone, $RCCH_3$ (O)	2.1–2.6	
Alkyne, $RC{\equiv}CH$	1.7–3.1	
Chloroalkane, RCH_2Cl	3.6–3.8	Hydrogens adjacent to electronegative atoms
Bromoalkane, RCH_2Br	3.4–3.6	
Iodoalkane, RCH_2I	3.1–3.3	
Ether, RCH_2OR'	3.3–3.9	
Alcohol, RCH_2OH	3.3–4.0	
Terminal alkene, $R_2C{=}CH_2$	4.6–5.0	Alkene hydrogens
Internal alkene, $R_2C{=}CH(R')$	5.2–5.7	
Aromatic, ArH	6.0–9.5	
Aldehyde, RCH (O)	9.5–9.9	
Alcoholic hydroxy, ROH	0.5–5.0	(variable)
Thiol, RSH	0.5–5.0	(variable)
Amine, RNH_2	0.5–5.0	(variable)

[a] R, R′, alkyl groups; Ar, aromatic group (not argon).

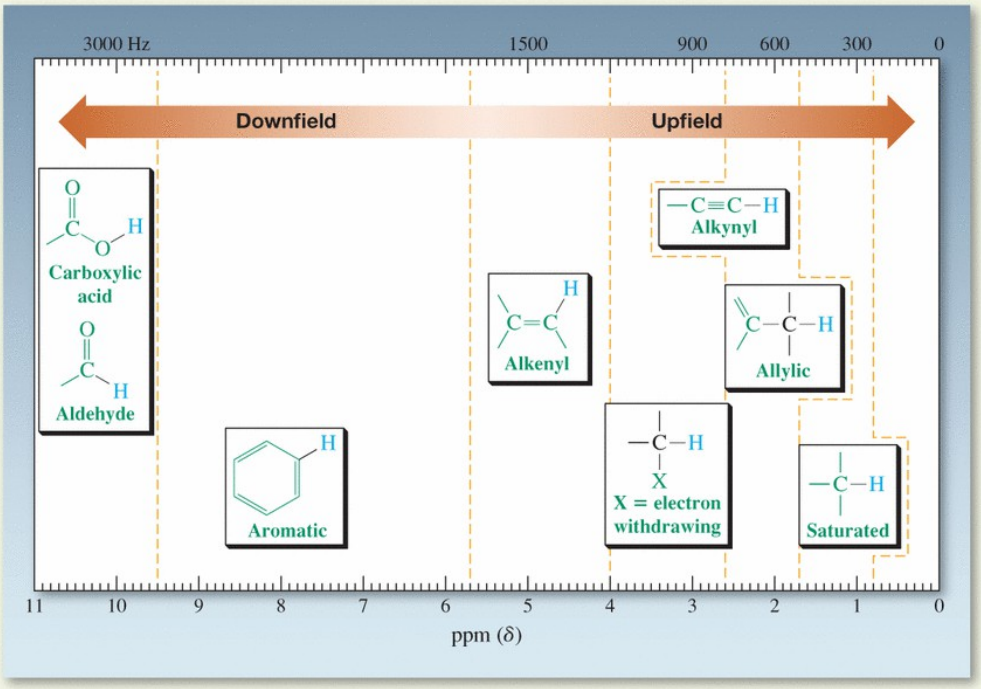
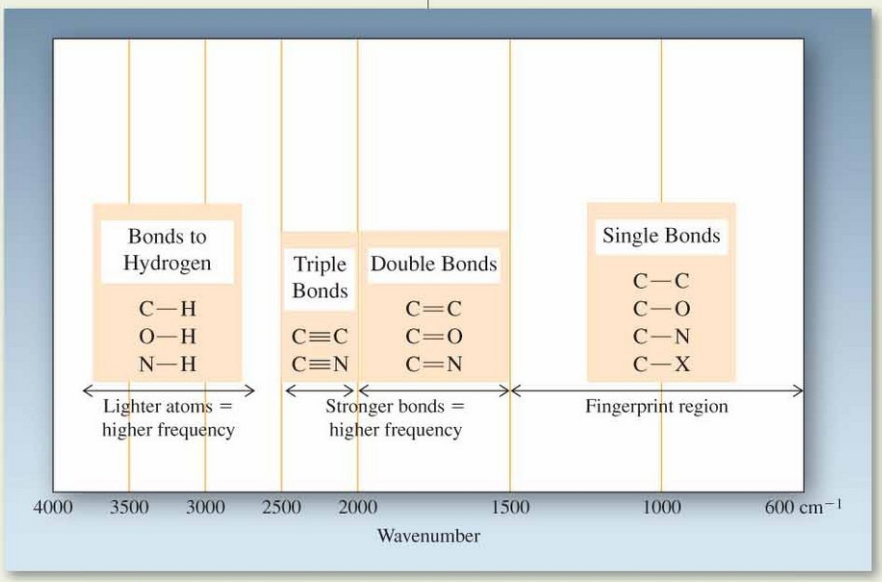


Table 11-4 Characteristic Infrared Stretching Wavenumber Ranges of Organic Molecules

Bond or Functional Group	$\tilde{\nu}$ (cm^{-1})	Bond or Functional Group	$\tilde{\nu}$ (cm^{-1})
RO—H (alcohols)	3200–3650	RC≡N (nitriles)	2220–2260
RCO—H (carboxylic acids)	2500–3300	RCH, RCR′ (aldehydes, ketones)	1690–1750
R_2N—H (amines)	3250–3500	RCOR′ (esters)	1735–1750
RC≡C—H (alkynes)	3260–3330	RCOH (carboxylic acids)	1710–1760
C=C (alkenes)	3050–3150	C=C (alkenes)	1620–1680
—C—H (alkanes)	2840–3000	RC—OR′ (alcohols, ethers)	1000–1260
RC≡CH (alkynes)	2100–2260		



Increasing wavenumber (energy)

Section I (4 points each) Select the best answer among the possibilities given and circle it.

1. Select the strongest Brønsted base.

a. H_2O

b. $CH_3CO_2^-$

c. NH_3

d. *cyclo*-$C_6H_{11}NH_2$

2. Select the strongest Brønsted acid.

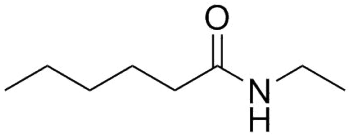
a. H_2O

b. CF_3COOH

c. CH_3COOH

d. *cyclo*-$C_6H_{11}NH_3^+$

3. Select the best name for the following compound:



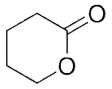
a. Pentyl ethylaminoketone

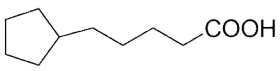
b. *N*-ethylhexanamide

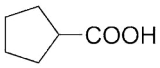
c. Ethyl hexanoyl amine

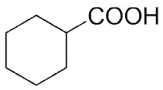
d. Ethyl hexanoyl lactam

4. Select the structure whose name is cyclopentanecarboxylic acid.

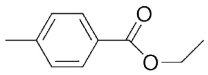
a. 

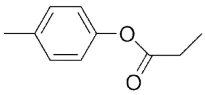
b. 

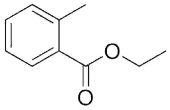
c. 

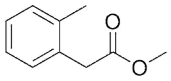
d. 

5. Select the structure best fitting the following spectroscopic data:
Molecular formula $C_{10}H_{12}O_2$
IR: 1741, 1280, 1111, 747 cm^{-1}.
^1H NMR: 7.77 2H d, J = 8 Hz
7.13 2H d, J = 8 Hz
4.20 2H q, J = 7 Hz
2.40 3H s
1.10 3H t, J = 7 Hz

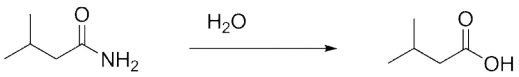
a. 

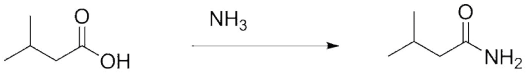
b. 

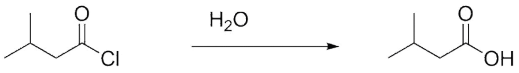
c. 

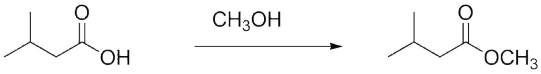
d. 

6. Select the reaction below that would proceed to completion most readily (without application of heat or additional reagents).

a. 

b. 

c. 

d. 

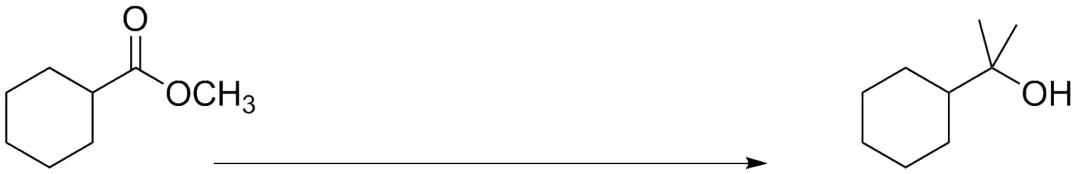
Section II. (5 points each) Draw (above the arrow) the reagents/conditions required for each of the following reactions. If you need sequential application of different reagents, indicate the numerical order (1. ...2. ...3. etc.) Include aqueous acid as a last step when necessary.

7. 

8. 

9. 

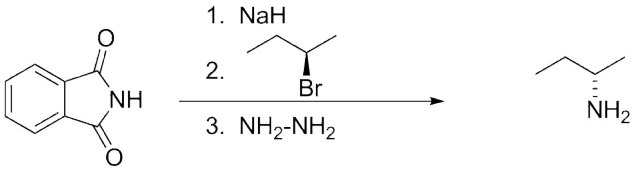
10. 

11. 

12. 

Section III. (22 points)

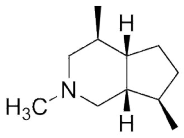
13. Write a mechanism for each step in the following transformation. Use electron-pushing arrows correctly, designate lone pairs where necessary, and make sure charges are correctly shown. If resonance is a stabilizing influence for any structure, show appropriate resonance forms. (Hint: write out the reaction occurring in each step first.) Continue on the back of the page if you need more space.



Section IV. (24 points: 3 points per structure; 3 points per rationale)

14. Historically, degradation of an unknown to a compound with a known structure has been a method of identifying new compounds. The following sequence of reactions was applied to the alkaloid skytanthine, isolated from a Chilean plant that makes a range of bioactive compounds. Partial NMR data is given for each compound in the sequence; IR spectra with frequencies (in cm^{-1}) of strong peaks noted are on the following page.

Identify each structure represented by an empty box (A-D). For each, provide a rationale for structure based on either chemistry or IR/NMR data for the new compound created. (If you cannot provide a complete structure, show as much as you can figure out for partial credit.)



Skytanthine
$C_{11}H_{21}N$

^{1}H NMR: 1.20 3H d, J = 7 Hz
1.33 3H, d, J = 7 Hz
2.32 3H, s
1.3-2.7, 12H, m

^{13}C NMR: 57.8, 53.5, 47.6
47.4, 46.0, 42.3, 35.6
32.7, 24.5, 18.6, 16.2

1. CH_3I
2. Ag_2O

A

$C_{12}H_{23}N$

^{13}C NMR now has peaks at 108.5 and 141.9 ppm.

Rationale:

O_3, Me_2S workup

1 eq. HCHO plus

B

$C_{11}H_{21}NO$

^{1}H NMR methyl signals are now 1.02 3H d, J = 7 Hz; 1.95 3H s;and 2.31 6H s.

Rationale:

mCPBA, NaOH

C

$C_{11}H_{21}NO_2$

There is a ^{1}H NMR peak at 5.02 ppm that is a ddd (J = 6, 5, 3 Hz) and ^{13}C NMR peaks at 170 and 87.8 ppm.

Rationale:

1. KOH, H_2O, Δ
2. Jones' reagent

D

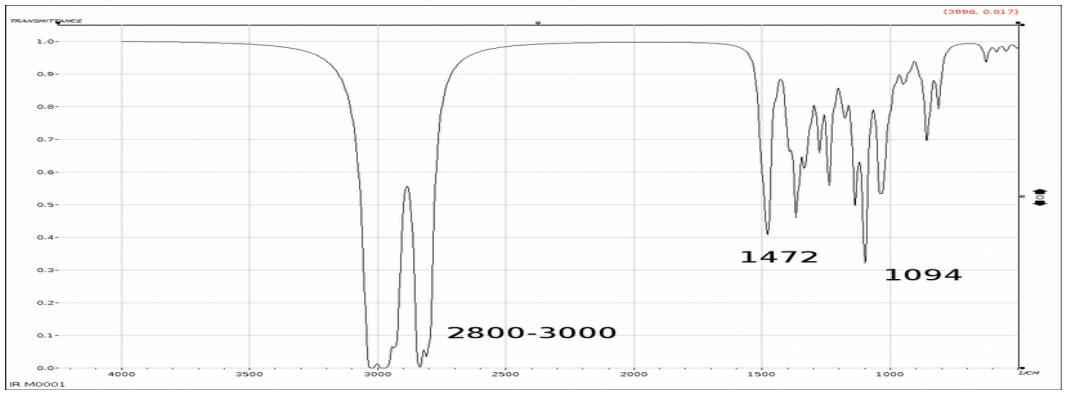
$C_9H_{17}NO$

^{13}C NMR: 219, 59.7, 49.5, 42.6, 41.3, 38.6, 32.4, 20.0

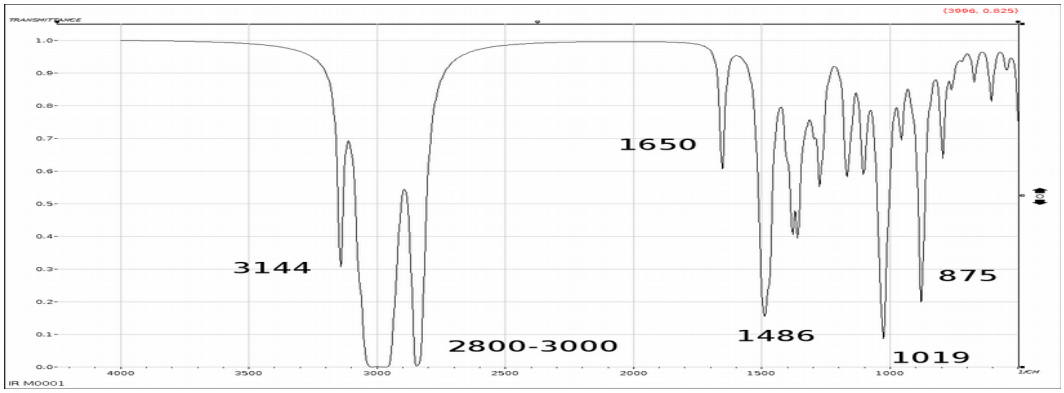
^{1}H NMR methyl signals:
1.10 3H d, J = 7 Hz
2.22 6H, s

Rationale:

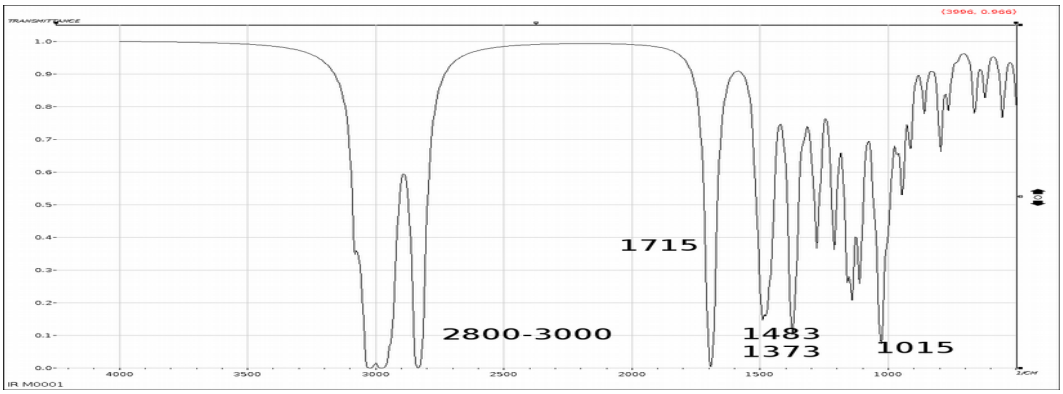
IR of skytanthine:



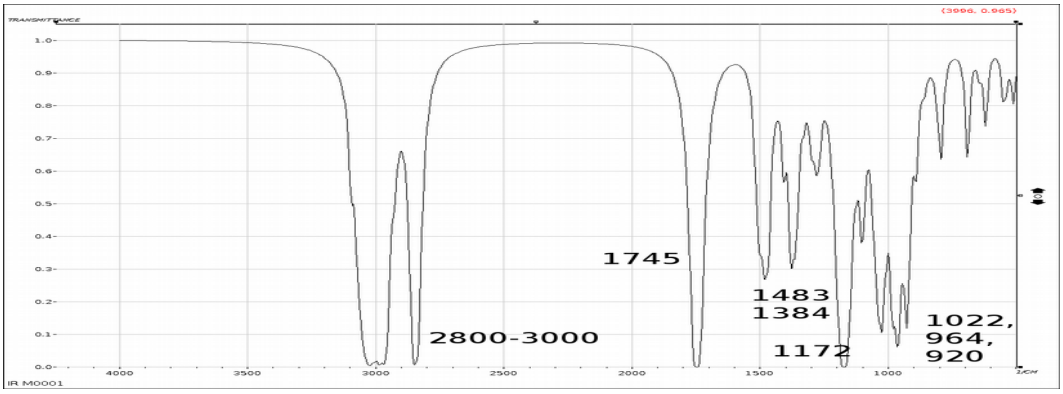
IR of A:



IR of B:



IR of C:



IR of D: