Exam Booklet No.

Student Name (Printed)	
Student Signature	

Examination Instructions

DO NOT TURN THE PAGE ON THIS BOOKLET UNTIL DIRECTED TO BEGIN

Please Make Sure to Do the Following Before Starting Your Exam

1. Both print your name and sign the front of the answer sheet and this exam booklet in the appropriate boxes above.

2. Also print your name at the top of the back of the answer sheet.

3. Write the serial number of this exam booklet on your answer sheet in the appropriate box.

4. Check the "Hold for Pick-Up" box on the back of the answer sheet if you want your graded sheet withheld from the distribution pile on Monday and handed back to you privately. Checking this box will slightly delay your receipt of your graded exam.

Please Make Sure to Do the Following After Completing Your Exam

1. Ensure that all of your multiple choice letters are legible.

2. Submit all materials back to the front table: your answer sheet, exam booklet, data tables, and scratch paper. You may not remove these items from the exam room.

DO NOT TURN THE PAGE ON THIS BOOKLET UNTIL DIRECTED TO BEGIN

CHEM 2430 – Organic Chemistry 1 for Majors – Fall 2019

Instructor: Paul Bracher

Hour Examination #4

Monday, December 9th, 2019

6:05–8:05 p.m. in Lee Lecture Hall at Saint Louis University

Student Name (Printed)	
Student Signature	

Instructions & Scoring

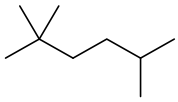
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- You may use a handwritten note sheet and a molecular model kit. No electronic resources are permitted, and you may not communicate with others.
- Your exam answer sheet may be copied or scanned.
- The examination room may be monitored by photography and/or video recording.

Problem	Points Earned	Points Available
I		24
II		16
III		18
IV		18
V		24
TOTAL		100

Questions, Required Information, Supplementary Explanation, Grading Notes, Where You've Seen It

Problem I. Multiple Choice (24 points total). Correct answers score +3 points, intentionally blank answers score +1 point, and incorrect answers score 0 points. For each question, select the best and most complete answer of the choices given. Write your answer clearly in the spaces provided on the answer sheet.

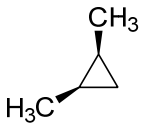
(1) B How many signals (arising from sets of inequivalent carbon atoms) appear in the ^{13}C NMR spectrum of compound **A**?



A

(A) 5 signals
(B) 6 signals
(C) 7 signals
(D) 8 or more signals

(2) B How many signals (arising from sets of inequivalent hydrogens) appear in the ^{1}H NMR spectrum of compound **B**?



B

(A) 3 signals
(B) 4 signals
(C) 5 signals
(D) 6 signals

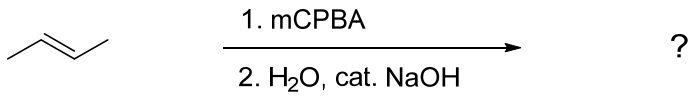
Note that the two 3° protons are enantiotopic, so they contribute to the same signal.

(3) A Which of the following is most likely to correspond to the base peak in the electron-impact mass spectrum (EI-MS) of 3-pentanol?

(A) m/z 59
(B) m/z 71
(C) m/z 72
(D) m/z 73

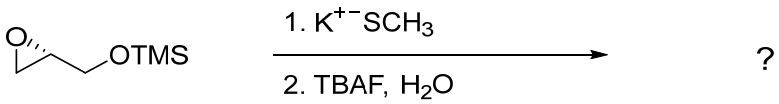
Following α-cleavage.

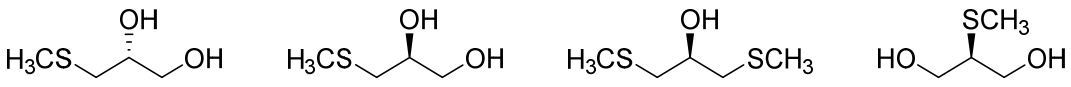
(4) A What best describes the expected product(s) of the following reaction?



(A) an achiral diol
(B) a chiral diol
(C) a racemic mixture of two enantiomeric diols
(D) a racemic mixture of two diastereomeric diols

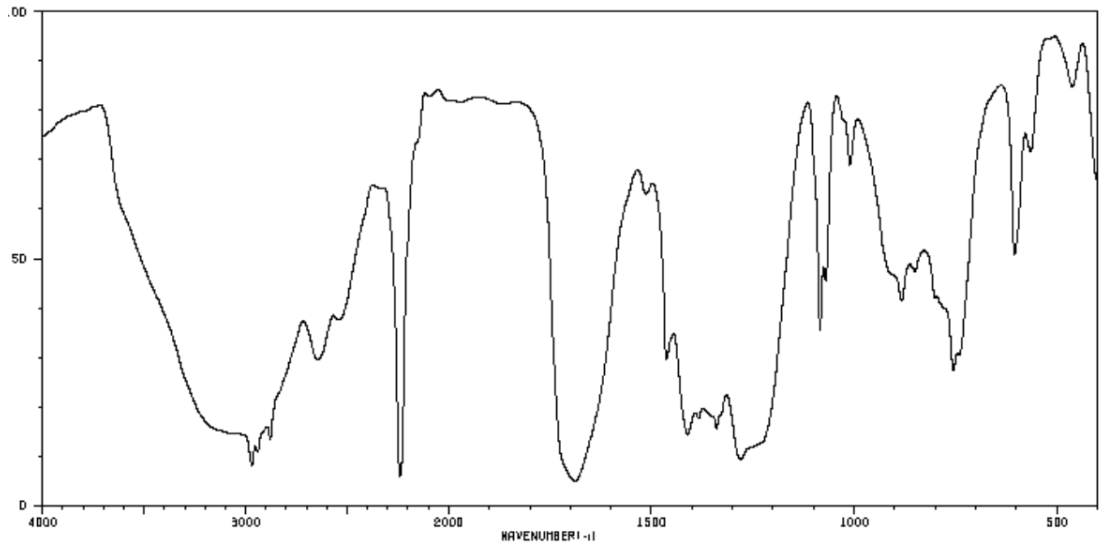
(5) A What is the major product of the following reaction?



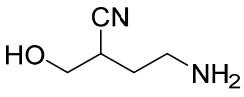


(A) (B) (C) (D)

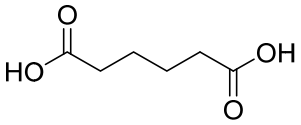
(6) D The IR spectrum below corresponds to which of the following compounds?



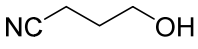
Source: Spectral Database for Organic Compounds, 2-hexynoic acid, #19962
http://sdbs.db.aist.go.jp/



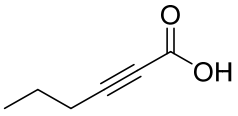
(A)



(B)

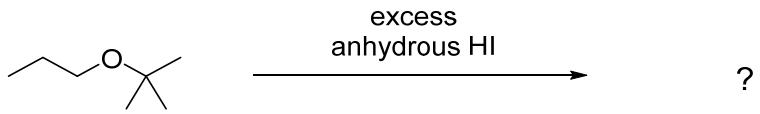


(C)



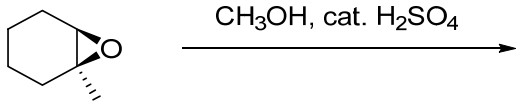
(D)

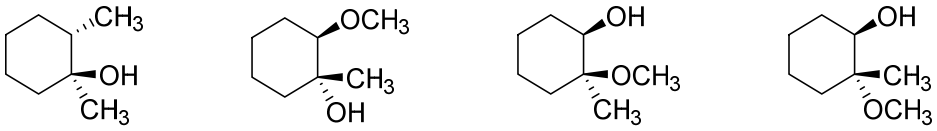
(7) D Which of the following products will form when the ether below is reacted with excess anhydrous HI?



(A) 1-iodopropane, and not 2-methyl-2-iodopropane
(B) 2-iodopropane, and not 2-methyl-2-iodopropane
(C) 2-methyl-2-iodopropane, and not 1-iodopropane
(D) both 1-iodopropane and 2-methyl-2-iodopropane

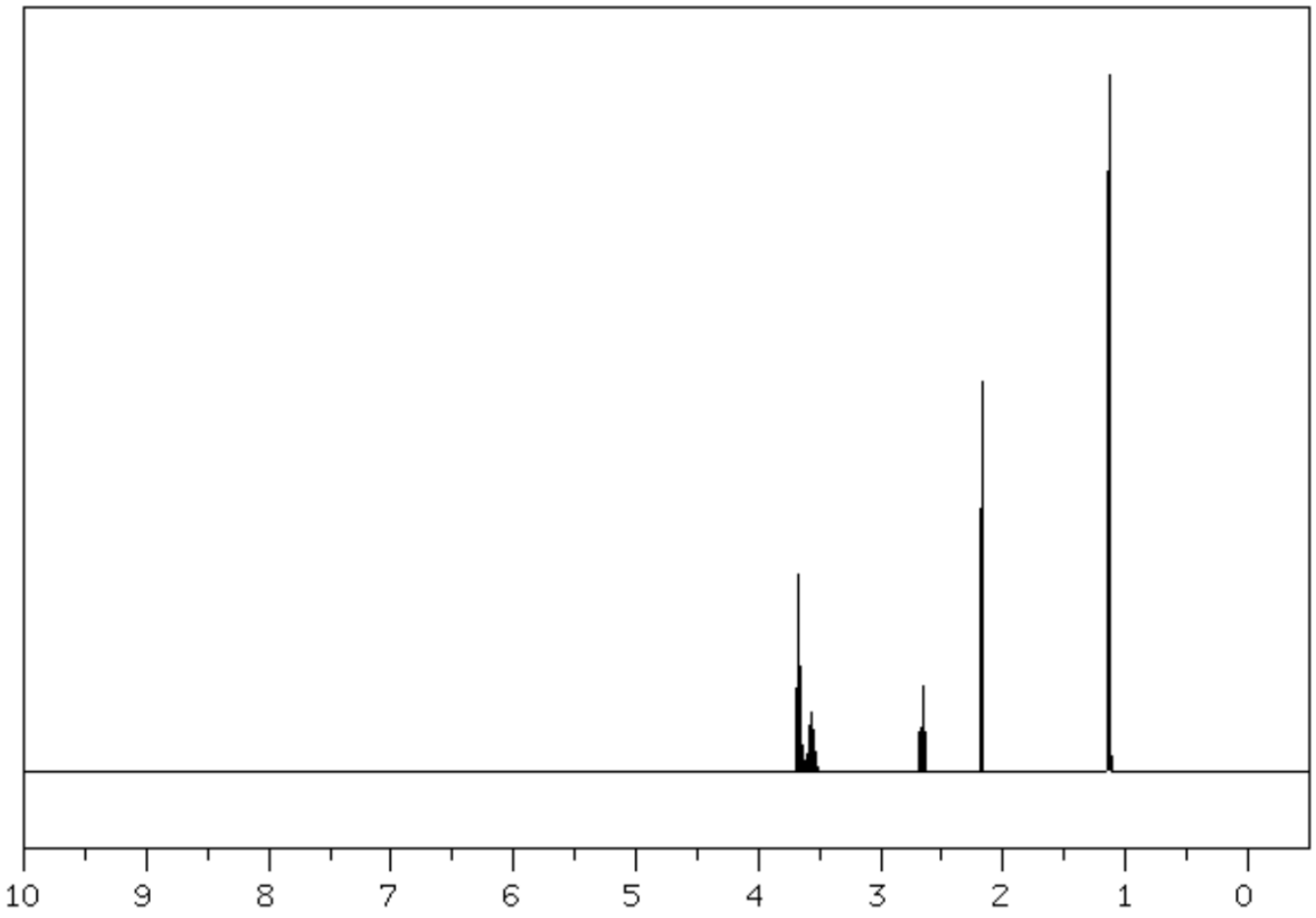
(8) D Which of the following compounds will be produced in the highest yield from the reaction drawn below?





(A) (B) (C) (D)

Problem II. Assignment of an NMR Spectrum (16 points). High-resolution mass spectral analysis of a pure sample of compound **AA** reveals it to have a molecular formula of $C_7H_{14}O_2$. The ^1H NMR spectrum of **AA** is:



Source: Spectral Database for Organic Compounds, 4-isopropoxy-2-butanone, #17109
http://sdbs.db.aist.go.jp/

Label	Chemical Shift (ppm)	Multiplicity	Integration
A	3.67	triplet	11
B	3.58	septet	5
C	2.66	triplet	10
D	2.18	singlet	14
E	1.14	doublet	29

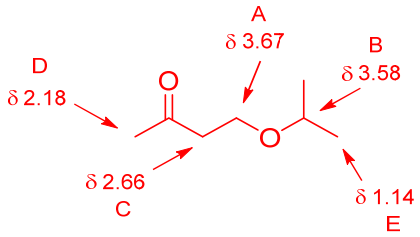
In the space provided on your official answer sheet:

(i) Draw a Lewis structure for compound **AA** consistent with the data provided above. (Molecular formula: $C_7H_{14}O_2$)

(ii) For each chemical shift, draw an arrow from that signal to a hydrogen that gives rise to it. (Or you can use letters/labels instead—essentially, make sure to assign the spectrum.)

AA

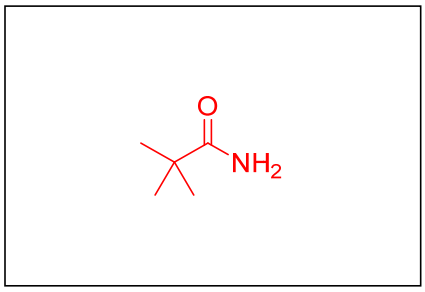
4-isopropoxy-2-butanone



Problem III. Structure Determination (18 points). Given the four spectra shown below for compound **BB**, provide its structure.

Grading and partial credit: Your structure will be scored +6 points if correct and zero points if incorrect. The remaining 12 points are based on three multiple choice questions about **BB** that can be answered independently without knowing the full structure of **BB**. These questions are scored +4 points for a correct answer and zero points for an incorrect answer or blank answer.

Compound **BB** (6 points)



pivalamide
SDBS No. 4737

(1) C Which of the following elements is present in compound **BB**?

(A) bromine
(B) chlorine
(C) nitrogen
(D) none of the above elements is in compound **BB**

(2) B Which of the following functional groups is present in compound **BB**?

(A) hydroxyl (O–H) group
(B) carbonyl (C=O) group
(C) cyano (C≡N) group
(D) none of the above functional groups is in compound **BB**

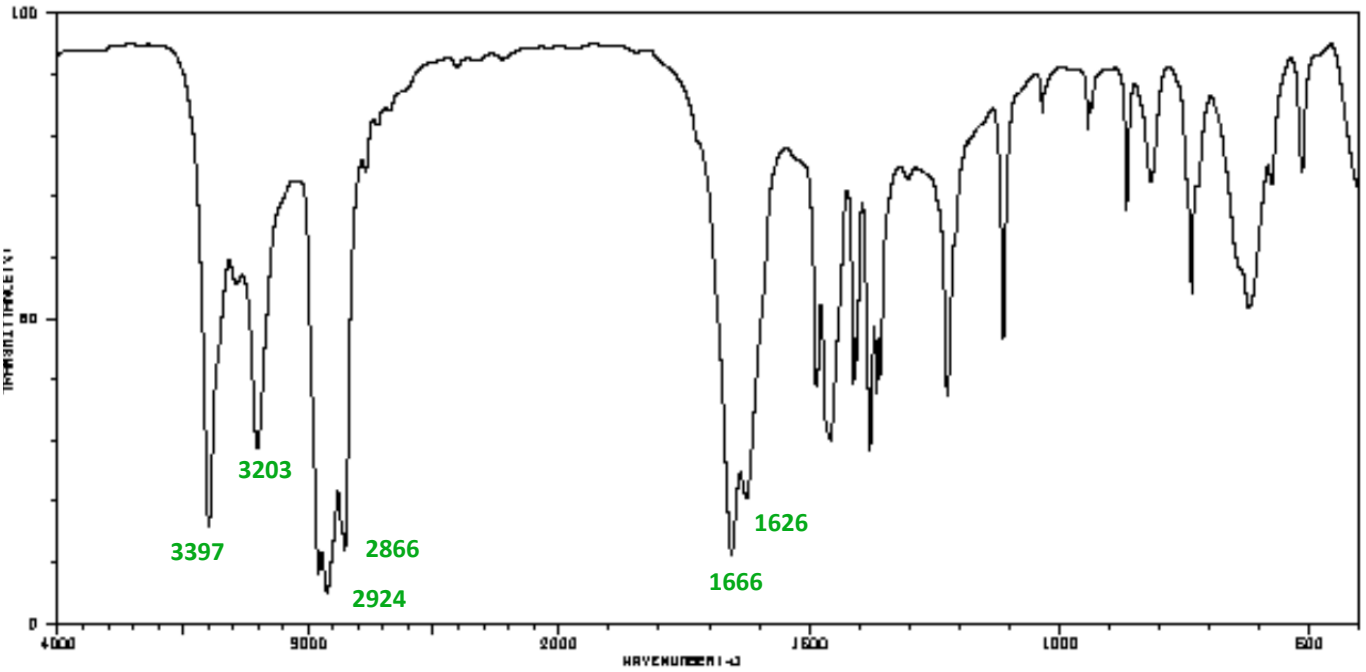
(3) D Which of the following is present in compound **BB**?

(A) a methyl group (that is not part of any of the groups below)
(B) an ethyl group (that is not part of any of the groups below)
(C) an isopropyl group (that is not part of any of the groups below)
(D) a *tert*-butyl group

Approach:

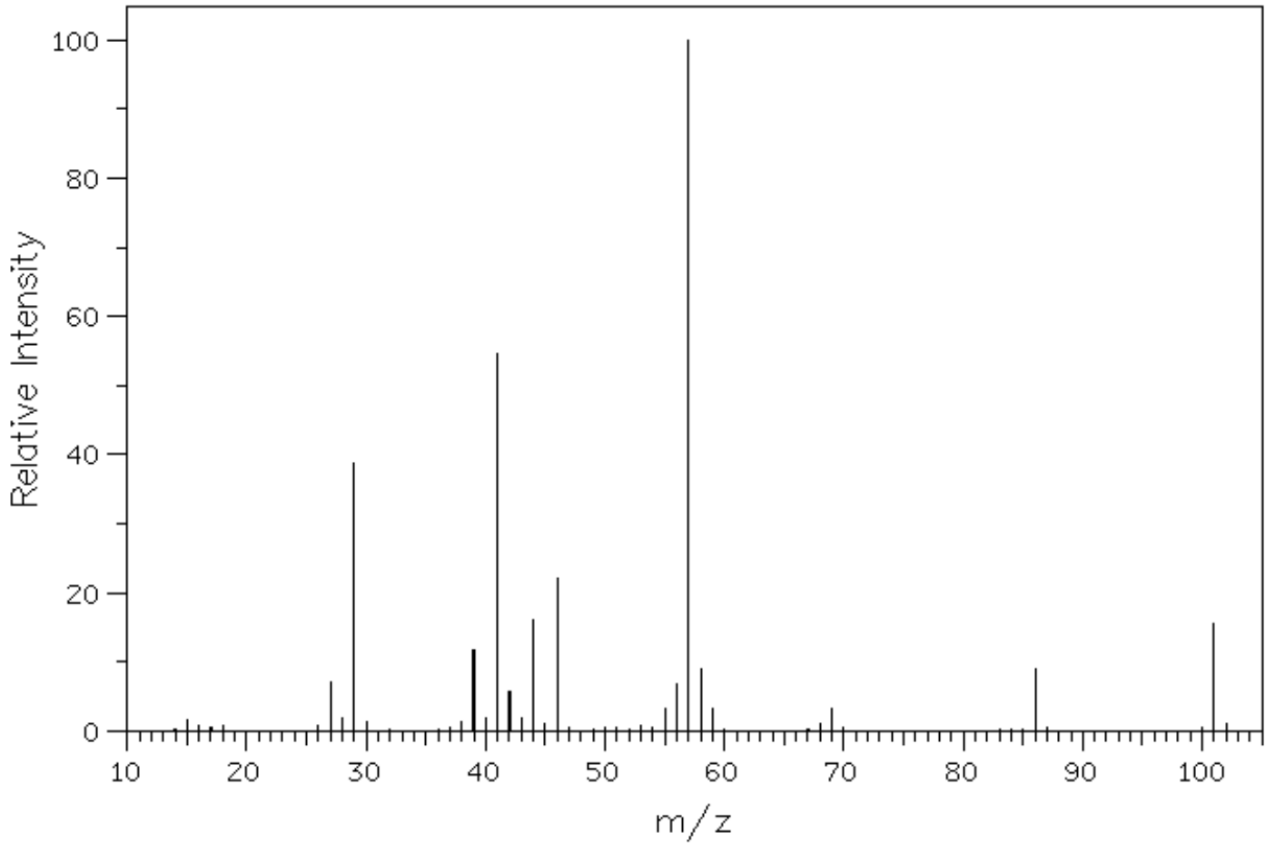
- IR stretching region has two N–H stretches suggestive of –NH2 group. Possible low-energy C=O stretch indicative of conjugated carbonyl or amide.
- Minimum of three carbon atoms in ^{13}C NMR spectrum and one appears to be a carbonyl group
- Identify odd M^+ peak in MS as corroboration of a nitrogen atom
- M^+ = 101 amu. At least 3 × 12 amu = 36 amu is from carbon, plus 14 amu for the nitrogen, plus 16 amu for the oxygen in the possible carbonyl group. That leaves 101 – 36 – 14 – 16 = 35 amu left to assign. Too much for 3 additional carbon atoms, so maybe 2 C (24) and 11 H (11)?
- Candidate molecular formula now = $C_5H_{11}NO$ (101 amu)
- ^1H NMR seems remarkably simple. Low chemical shift singlet possible a tert-butyl group. The broad singlet mid-spectrum might be the NH_2 group?
- Put all the pieces together...

IR Spectrum:



Source: Spectral Database for Organic Compounds, pivalamide, #4737
http://sdbs.db.aist.go.jp/

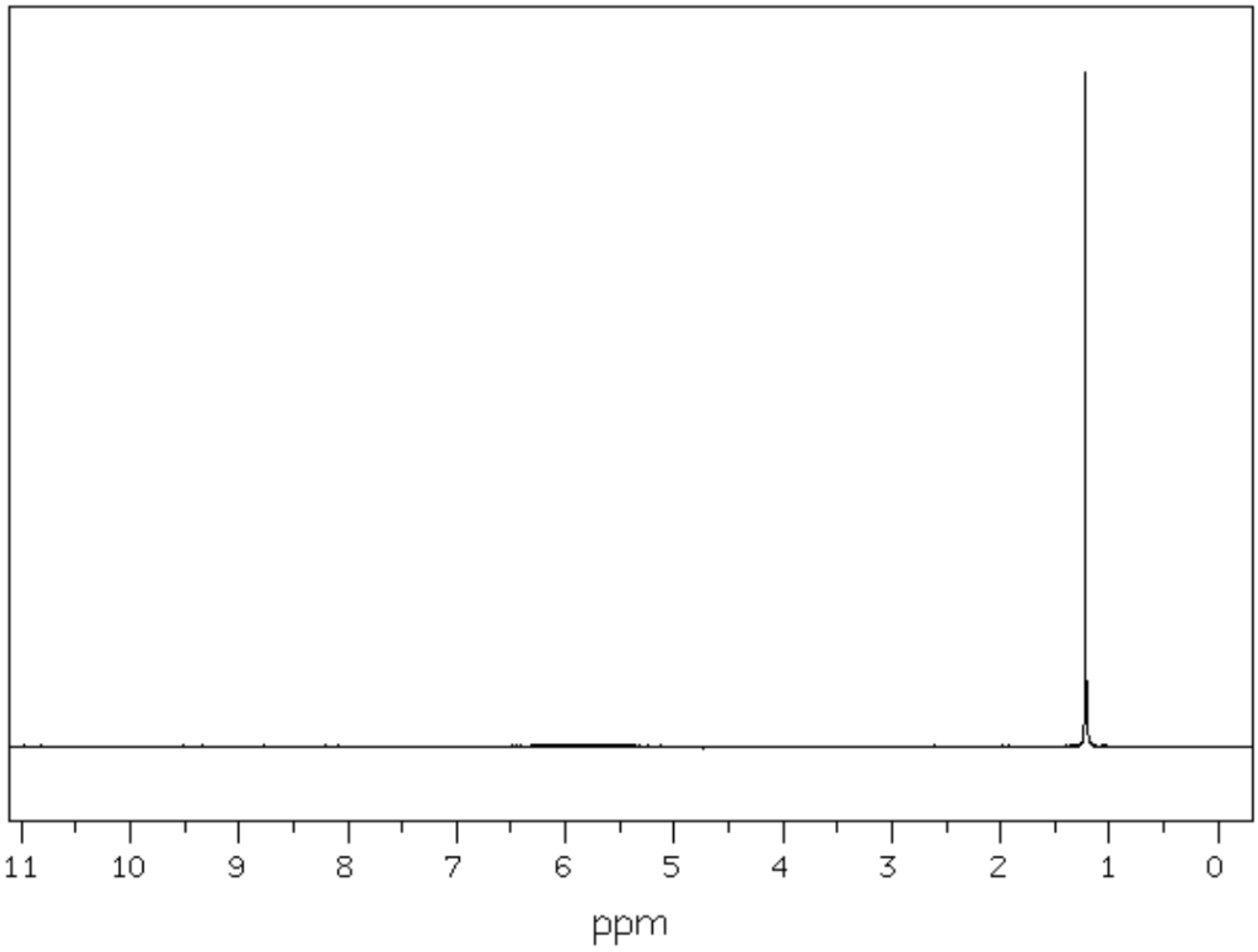
Mass Spectrum:



Source: Spectral Database for Organic Compounds, pivalamide, #4737
http://sdbs.db.aist.go.jp/

m/z	intensity
15.0	1.7
27.0	7.2
28.0	1.8
29.0	38.8
30.0	1.3
38.0	1.2
39.0	11.8
40.0	1.9
41.0	54.5
42.0	5.6
43.0	1.9
44.0	16.2
45.0	1.1
46.0	22.0
55.0	3.3
56.0	6.7
57.0	100.0
58.0	9.0
59.0	3.3
68.0	1.0
69.0	3.2
86.0	8.9
101.0	15.6
102.0	1.1

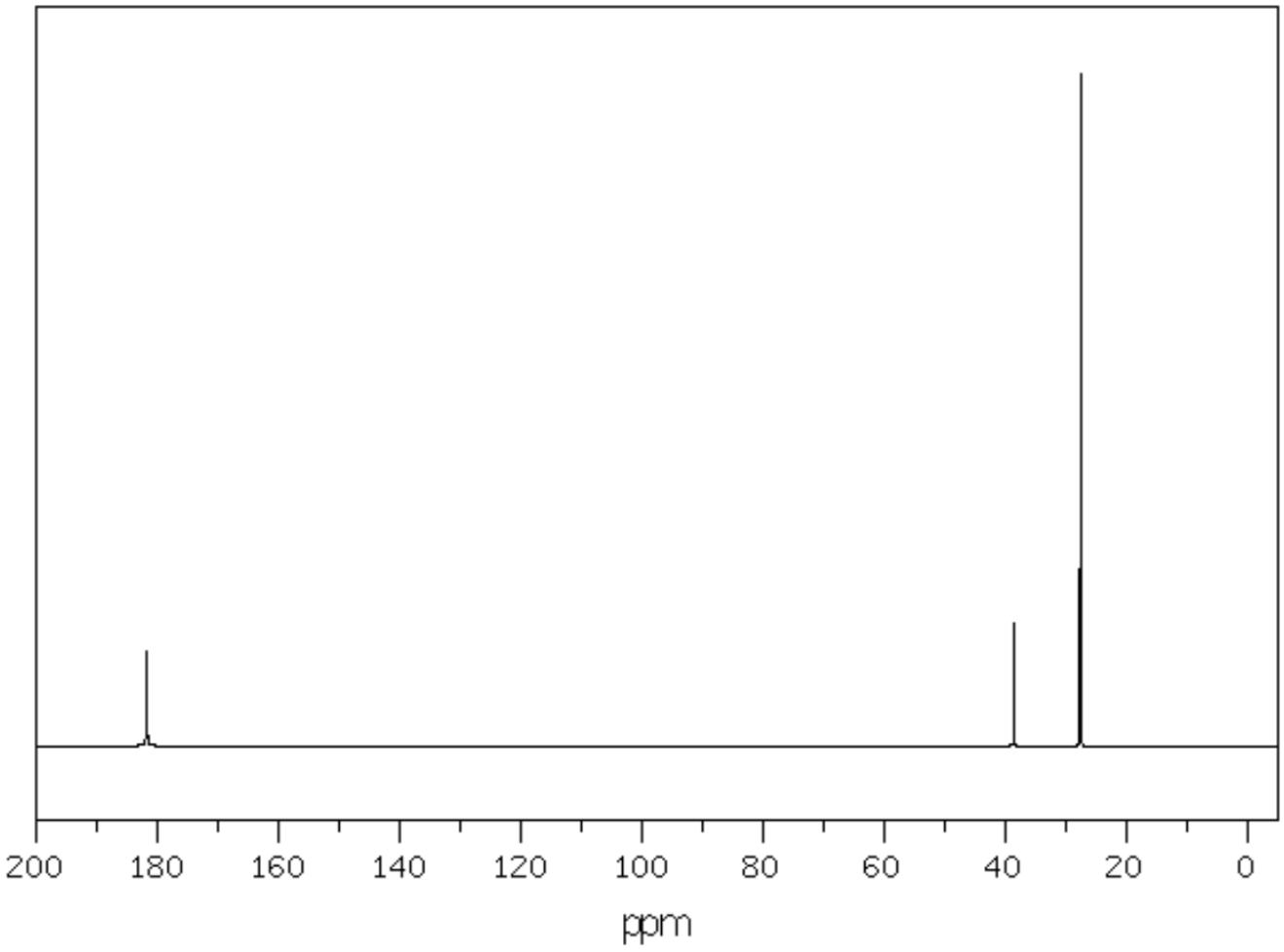
^{1}H NMR Spectrum:



Source: Spectral Database for Organic Compounds, pivalamide, #4737
http://sdbs.db.aist.go.jp/

Chemical Shift (ppm)	Multiplicity	Integration
~6	very broad singlet	13
1.22	singlet	59

^{13}C NMR Spectrum:



Source: Spectral Database for Organic Compounds, pivalamide, #4737
http://sdbs.db.aist.go.jp/

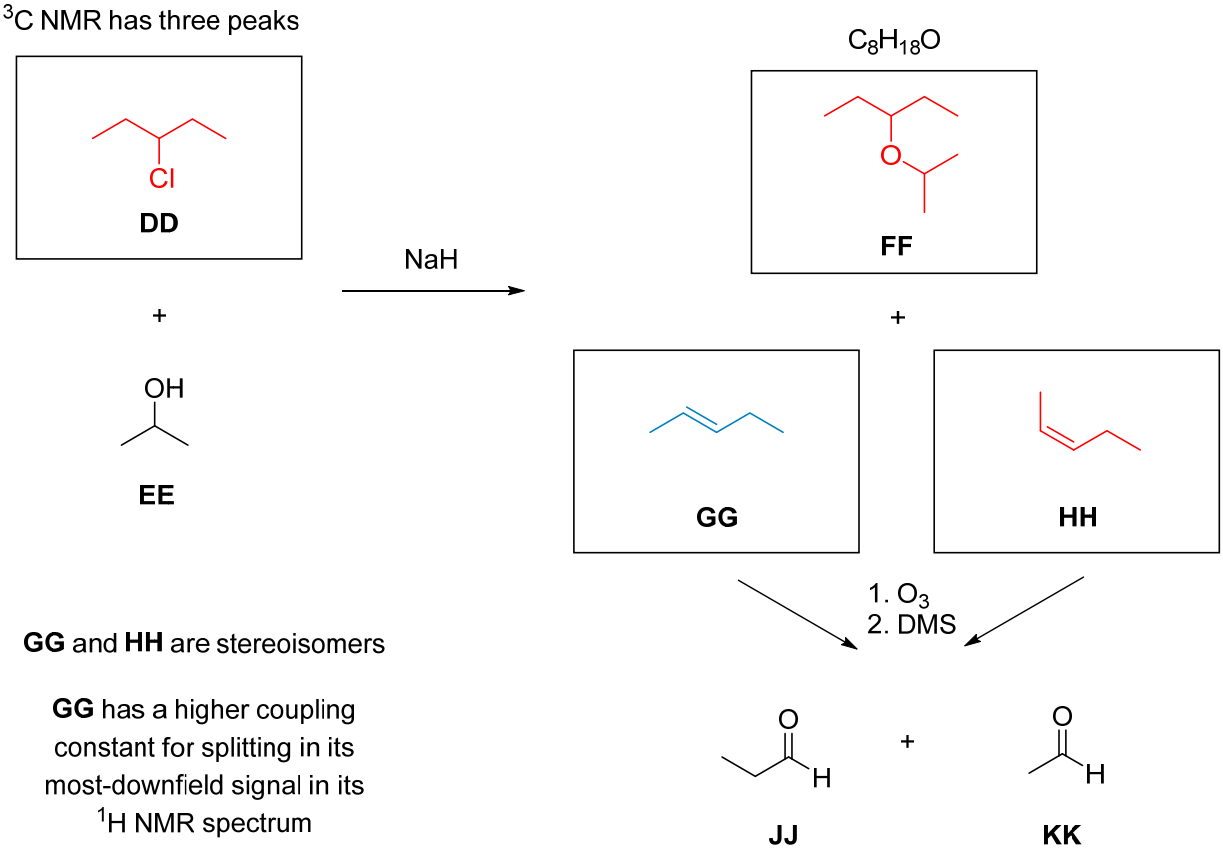
Chemical Shift (ppm)	Intensity
181.79	141
38.60	181
27.63	1000

Problem IV. Reaction Roadmap (18 points). Unknown compound **DD**, with molecular ion of 106 a.m.u. and M+2 of 108 a.m.u. (3:1 ratio of intensities), has a ^{13}C NMR spectrum with three signals. Compound **DD** reacts with isopropanol (**EE**) and sodium hydride to give three new products (**FF**, **GG**, and **HH**). **FF** has the molecular formula $C_8H_{18}O$. Compounds **GG** and **HH** are stereoisomers that both produce compounds **JJ** and **KK** upon ozonolysis. The most-downfield signal in the ^1H NMR spectrum of **GG** has a larger spacing between its daughter peaks than the most-downfield signal of **HH**. Compound **HH** has a larger dipole moment and higher boiling point than **GG**.

On your answer sheet, provide structures for compounds **DD**, **FF**, and **HH**. Your proposals should be consistent with all of the data provided above.

M^+ ion = m/z 106,108 (3:1 ratio)

^{13}C NMR has three peaks



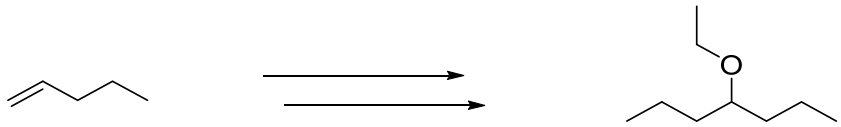
GG and **HH** are stereoisomers

GG has a higher coupling constant for splitting in its most-downfield signal in its ^1H NMR spectrum

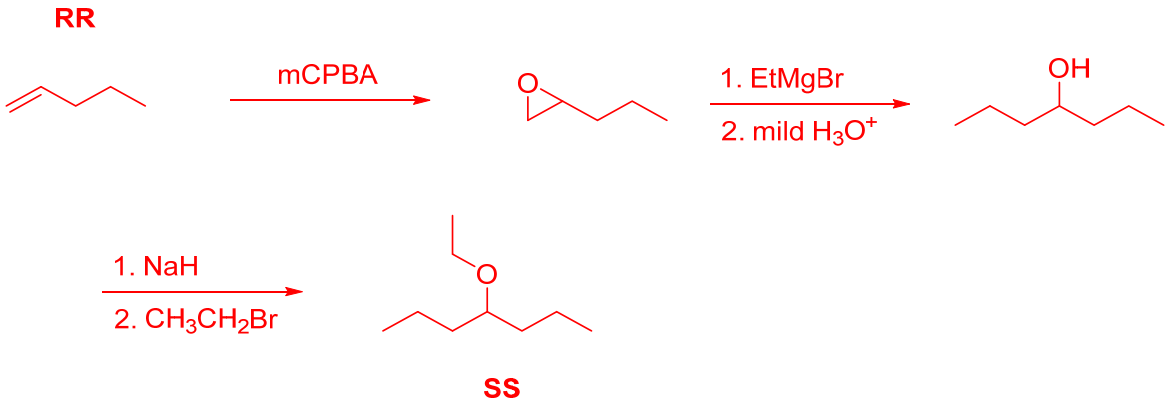
HH has a larger dipole moment and higher b.p. than **GG**

Problem V. Synthesis (24 points). These transformations will require multiple steps. Provide the reagents for each step and draw out your proposed synthetic intermediates. Please do not draw curved arrows; this problem is not asking for mechanisms. You do not need to provide solvents for the reactions.

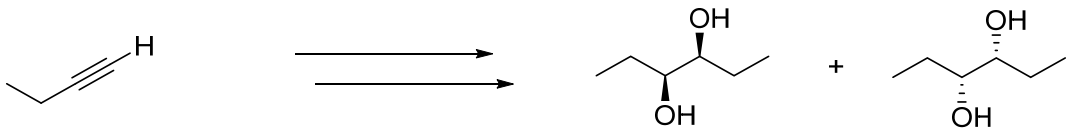
(1) (12 points) Provide a synthetic route—i.e., a sequence of reactions—to produce compound **SS** from compound **RR** using any other starting materials and reagents you wish.



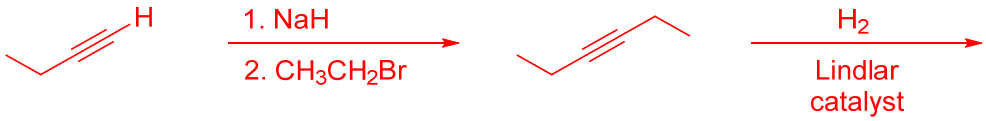
RR **SS**



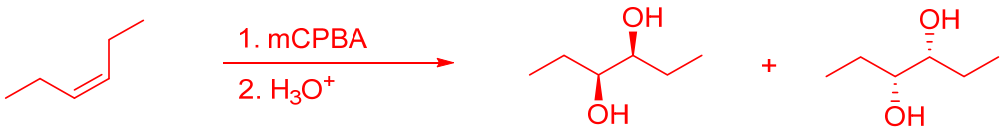
(2) (12 points) Provide a synthetic route—i.e., a sequence of reactions—to produce a racemic mixture of compounds **VV** and **XX** using compound **TT** and any other reagents and starting materials you wish.



TT **VV** **XX**



TT



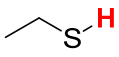
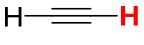
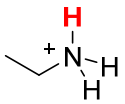
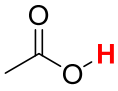
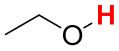
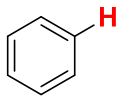
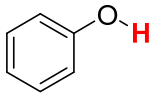
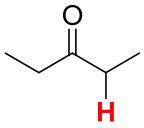
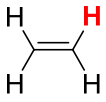
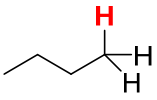
VV **XX**

Another valid approach is to perform syn-dihydroxylation of (3*E*)-hex-3-ene.

1 **H** hydrogen 1.008																	2 **He** helium 4.003
3 **Li** lithium 6.94	4 **Be** beryllium 9.01											5 **B** boron 10.81	6 **C** carbon 12.011	7 **N** nitrogen 14.007	8 **O** oxygen 15.999	9 **F** fluorine 18.998	10 **Ne** neon 20.180
11 **Na** sodium 22.990	12 **Mg** magnesium 24.305											13 **Al** aluminum 26.982	14 **Si** silicon 28.085	15 **P** phosphorus 30.974	16 **S** sulfur 32.06	17 **Cl** chlorine 35.45	18 **Ar** argon 39.948
19 **K** potassium 39.098	20 **Ca** calcium 40.078	21 **Sc** scandium 44.956	22 **Ti** titanium 47.867	23 **V** vanadium 50.942	24 **Cr** chromium 51.996	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 65.38	31 **Ga** gallium 69.723	32 **Ge** germanium 72.631	33 **As** arsenic 74.922	34 **Se** selenium 78.972	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 95.95	43 **Tc** technetium (98)	44 **Ru** ruthenium 101.07	45 **Rh** rhodium 102.91	46 **Pd** palladium 106.42	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	* lanthanides	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)
87 **Fr** francium (223)	88 **Ra** radium (226)	** actinides	104 **Rf** rutherfordium (267)	105 **Db** dubnium (268)	106 **Sg** seaborgium (269)	107 **Bh** bohrium (270)	108 **Hs** hassium (277)	109 **Mt** meitnerium (278)	110 **Ds** darmstadtium (281)	111 **Rg** roentgenium (282)	112 **Cn** copernicium (285)	113 **Nh** nihonium (286)	114 **Fl** flerovium (289)	115 **Mc** moscovium (290)	116 **Lv** livermorium (293)	117 **Ts** tennessine (294)	118 **Og** oganesson (294)

* lanthanides	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 173.05	71 **Lu** lutetium 174.97
** actinides	89 **Ac** actinium (227)	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 (266)

pK_a Table

	-8.0		10-11		25
	-1.7		10.6		36
	3.2		15.7		38
	4.8		15.9		43
	10.0		19–20		44
					~50

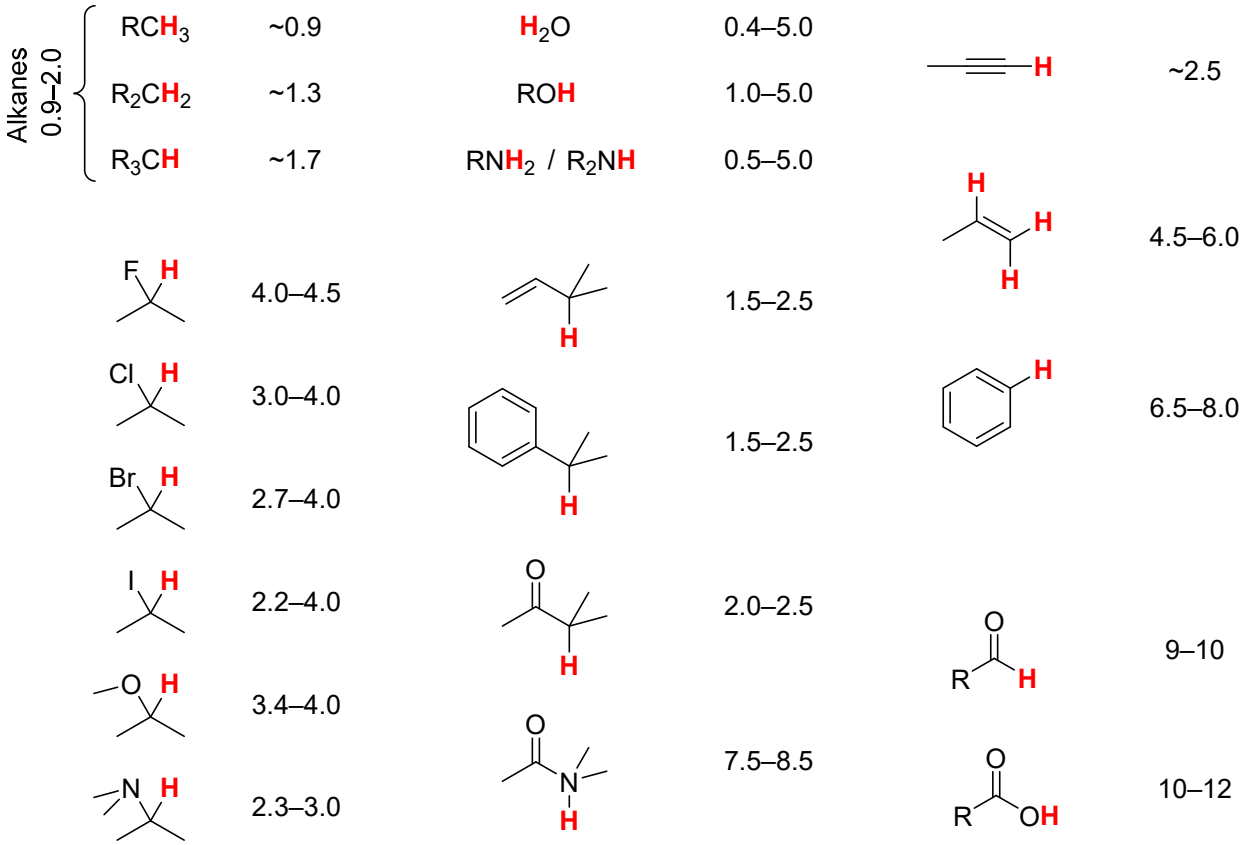
Bond Dissociation Energies (BDEs)

Average Bond Dissociation Energies, *D* (kJ/mol)[a]									
H—H	436[a]	C—H	410	N—H	390	O—H	460	F—F	159[a]
H—C	410	C—C	350	N—C	300	O—C	350	Cl—Cl	243[a]
H—F	570[a]	C—F	450	N—F	270	O—F	180	Br—Br	193[a]
H—Cl	432[a]	C—Cl	330	N—Cl	200	O—Cl	200	I—I	151[a]
H—Br	366[a]	C—Br	270	N—Br	240	O—Br	210	S—F	310
H—I	298[a]	C—I	240	N—I	—	O—I	220	S—Cl	250
H—N	390	C—N	300	N—N	240	O—N	200	S—Br	210
H—O	460	C—O	350	N—O	200	O—O	180	S—S	225
H—S	340	C—S	260	N—S	—	O—S	—		
Multiple covalent bonds									
C=C	611	C≡C	835	C=O	732	O=O	498[a]	N≡N	945[a]

[a] Exact value

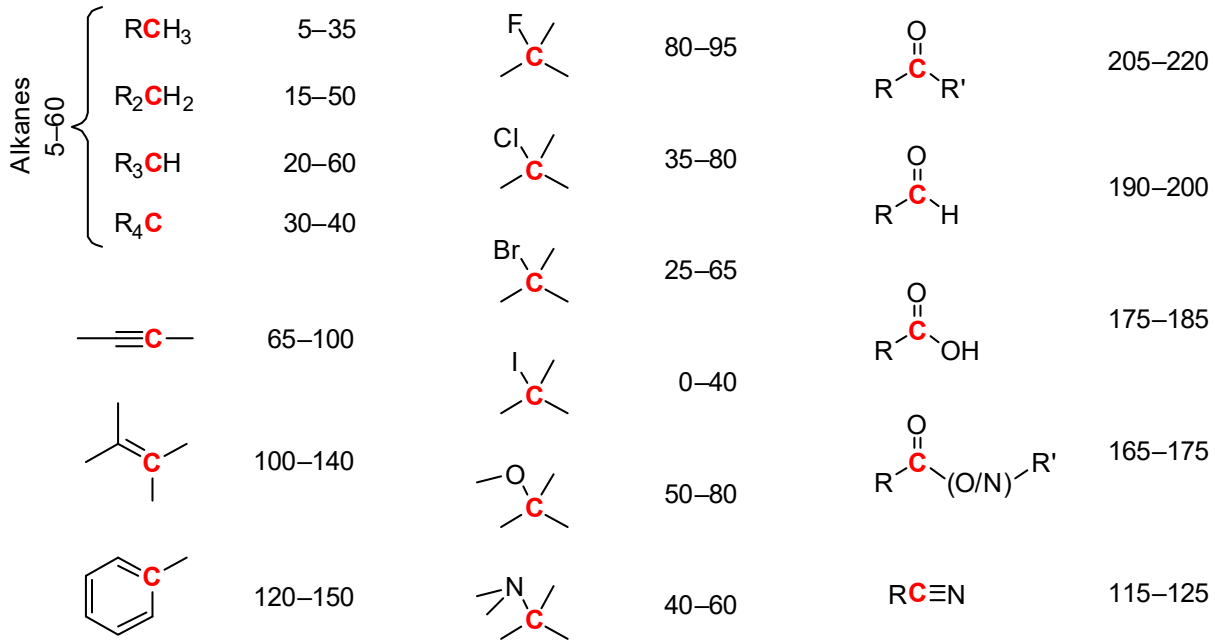
Typical ^{1}H NMR Chemical Shifts (δ / ppm)

(signals may stray from these ranges)



Typical ^{13}C NMR Chemical Shifts (δ / ppm)

(signals may stray from these ranges)



Typical IR Stretching Absorptions

(absorptions may stray from these ranges)

Bond	Functional Group		Wavenumber (cm^{-1})	Comments
O–H	ROH	alcohol	3200–3600	strong, broad
	RCOOH	carboxylic acid	2500–3500	strong, very broad
N–H	RNH_2	primary amine	3300–3500	two peaks
	R_2NH	secondary amine	3300–3500	one peak
	RCONH(H/R')	amide	3200–3400	two or one peak (1° vs. 2°)
C–H	C_{sp}–H	terminal alkyne	3300	medium/strong, sharp
	C_{sp2}–H	alkene or aromatic	3000–3150	medium
	C_{sp3}–H	alkane	2850–3000	strong
	R(CO)–H	aldehyde	2700–2830	
C≡C	RC≡C(H/R')	alkyne	2250	medium
C≡N	RC≡N	nitrile	2250	medium
C=O	R(C=O)Cl	acid chloride	1800	strong
	R(C=O)O(C=O)R'	acid anhydride	1760–1800	strong, two peaks
	R(C=O)OR'	ester	1735–1745	strong
	R(C=O)H	aldehyde	1730	strong
	R(C=O)R'	ketone	1715	strong
	$(H/R)_2C=C–(C=O)R'$	conjugated ketone	1680	strong
	R(C=O)OH	carboxylic acid	1710	strong
	$R(C=O)N(H/R')_2$	amide	1630–1680	strong
C=C		alkene	1650	medium
		aromatic ring	1500–1600	medium
C=N		imine	1650	medium

Natural Abundances of Common Isotopes in Organic Compounds

	M		M+1		M+2	
hydrogen	^{1}H	99.99%	^{2}H	0.01%		
carbon	^{12}C	98.93%	^{13}C	1.07%		
nitrogen	^{14}N	99.63%	^{15}N	0.37%		
oxygen	^{16}O	99.76%	^{17}O	0.04%	^{18}O	0.20%
fluorine	^{19}F	100.00%				
phosphorus	^{31}P	100.00%				
sulfur	^{32}S	94.93%	^{33}S	0.76%	^{34}S	4.29%
chlorine	^{35}Cl	75.78%			^{37}Cl	24.22%
bromine	^{79}Br	50.69%			^{81}Br	49.31%
iodine	^{127}I	100.00%				

Scratch Paper

You may rip this sheet out of the exam booklet, but you are responsible for turning it in at the end of the exam.

Exam Booklet No.