CH 335

Final Exam Tuesday, March 15, 2022

Form B

Name___KEY_____

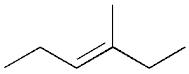
You may use model kits but no other material with chemical information without instructor approval.

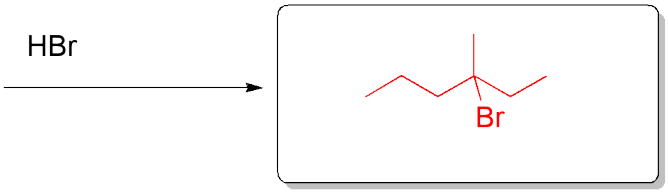
Please do not use any electronic devices except calculators.

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]				

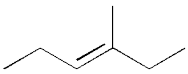
*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 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]

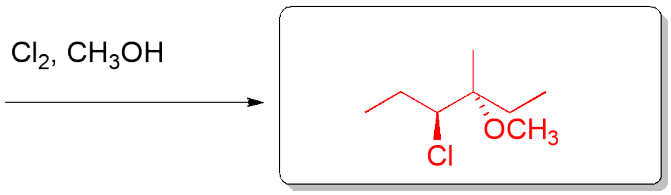
1. (5 points each; 30 total) Write the expected product(s) for each of the following reactions. Specify stereochemistry where appropriate, and include all expected products.

A. 

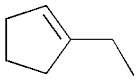


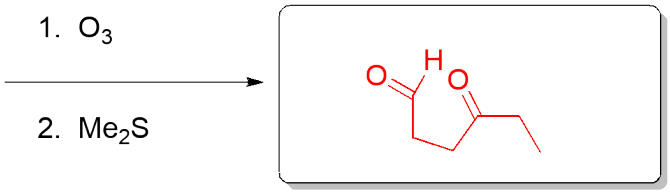
Racemic

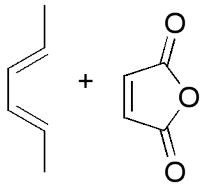
B. 

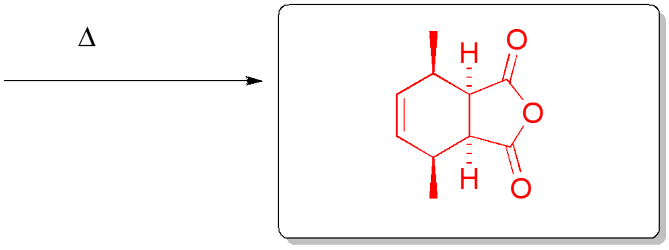


Anti addition; racemic

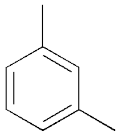
C. 

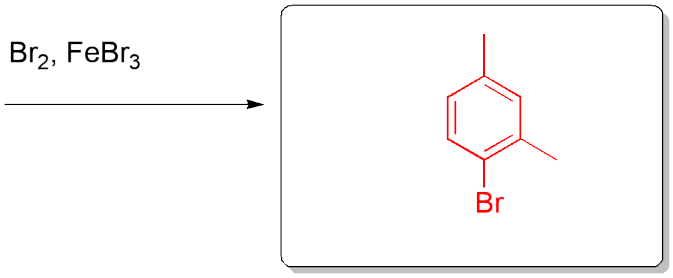


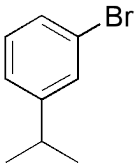
D. 

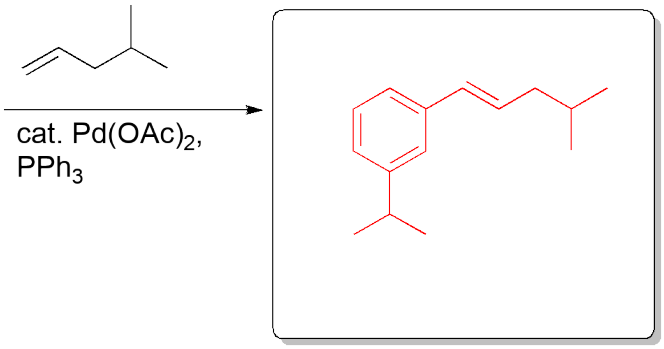


Single diastereomer; racemic

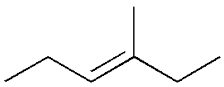
E. 



F. 

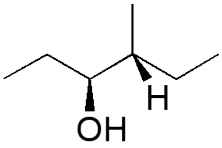


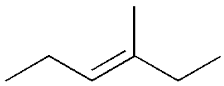
2. (5 points each; 25 total) Write (in the box provided) the reagents and/or conditions needed to accomplish the following transformations.

A. 

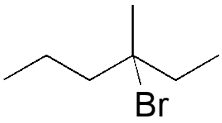
1. BH_3•THF or B_2H_6

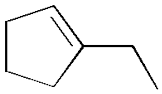
2. H_2O_2, NaOH, H_2O



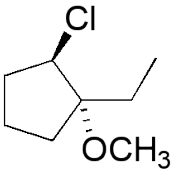
B. 

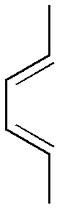
HBr

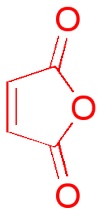


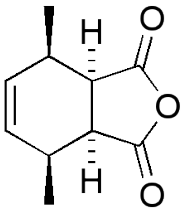
C. 

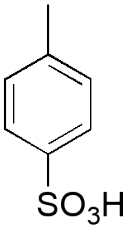
Cl_2, CH_3OH



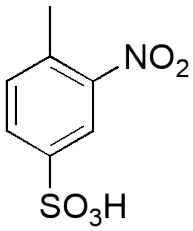
D. 





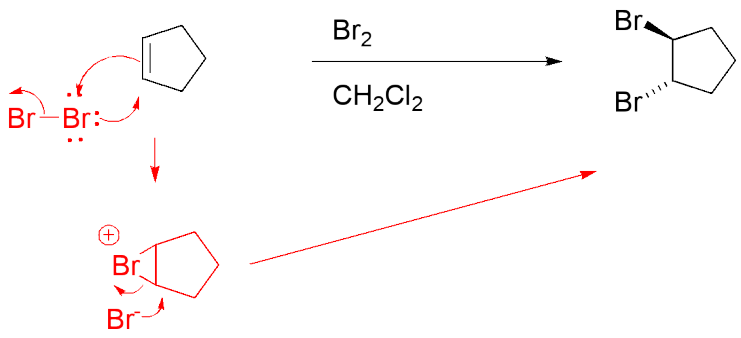
E. 

HNO_3, H_2SO_4

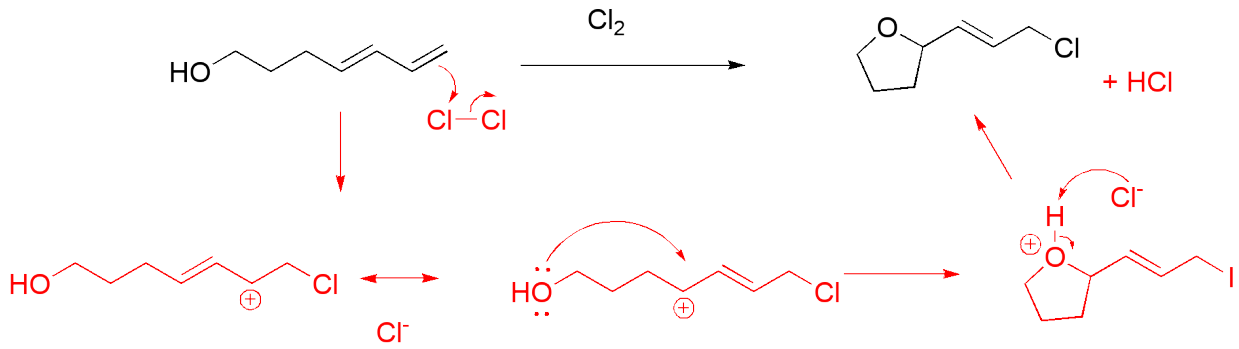


3. (10 points each; 30 total) Write multistep mechanisms (using the correct electron-pushing formalism, and as many steps as needed) for each of the following transformations. Be sure to draw resonance structures for any intermediate so stabilized.

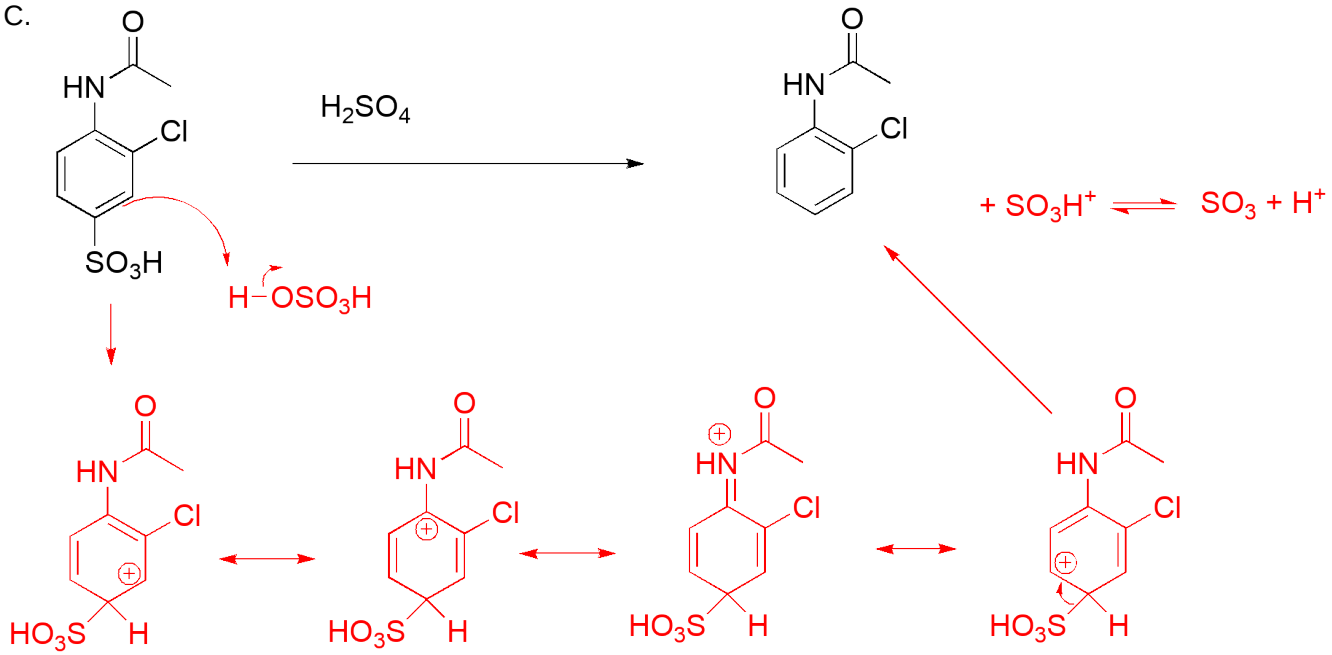
A.



B.

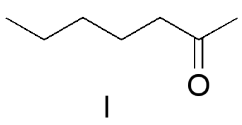


C.

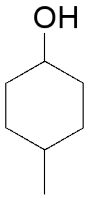


4. (6 points each box; 36 total) Indicate in the box a characteristic spectral peak for one compound whose presence will distinguish each pair of isomers. For each spectrum (IR, 1H NMR, 13C NMR), you need only list ONE peak for ONE of the two compounds that would be absent in the other

A.



I



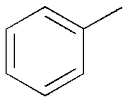
II

IR
I: Ketone 1720 cm^{-1}
II: OH Broad 3300-3600 cm^{-1}

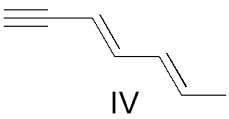
^{1}H NMR
I: 2-2.5 s 3H + t 2H
II: 3.5 quintet 1H

^{13}C NMR
I: Ketone 200 ppm
II: C-O 50-60 ppm

B.



III



IV

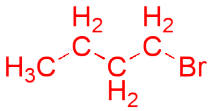
IR
III: 690, 750 cm^{-1}
IV: 3300 cm^{-1} (C-H)
2200 cm^{-1} (C≡C)

^{1}H NMR
III: 3H 1.8 ppm
IV: 1H 2.5-3 ppm
(others possible)

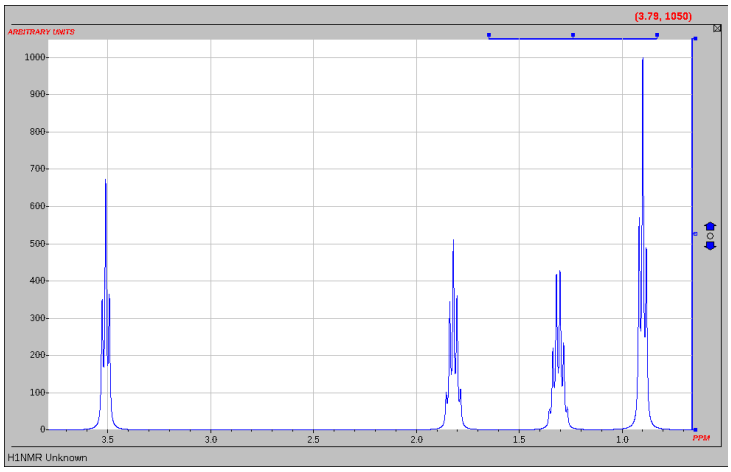
^{13}C NMR
III: 5 carbons
IV: 7 carbons
(2C 90-110)

5 (10 points each; 30 total) Draw each structure with hydrogens, and predict the ^{1}H NMR spectrum (sketch clearly, or list peaks) of each of the following compounds. Include the spin-spin coupling patterns, but you need not specify J values. Estimate chemical shift to within 1 ppm.

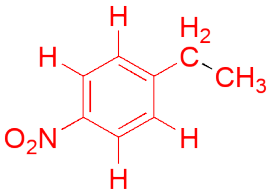
A. 1-Bromobutane



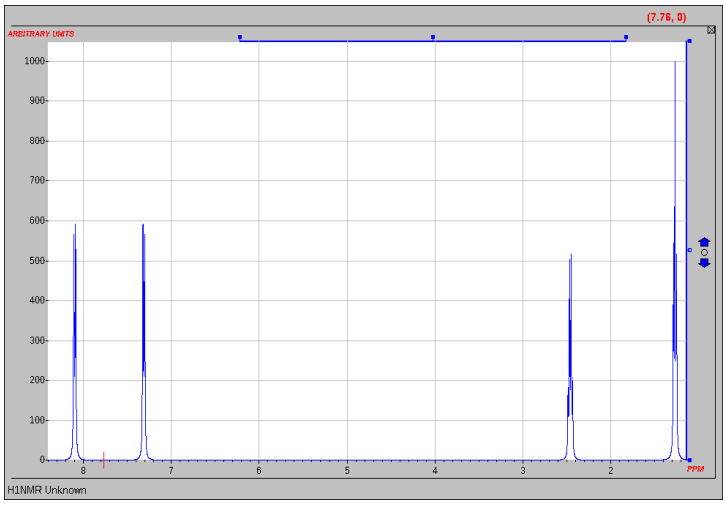
0.90 3H t
1.31 2H sextet
1.82 2H quintet
3.51 t



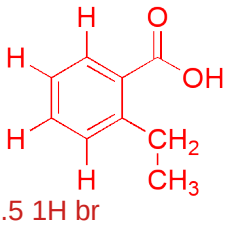
B. (4-nitrophenyl)-ethane



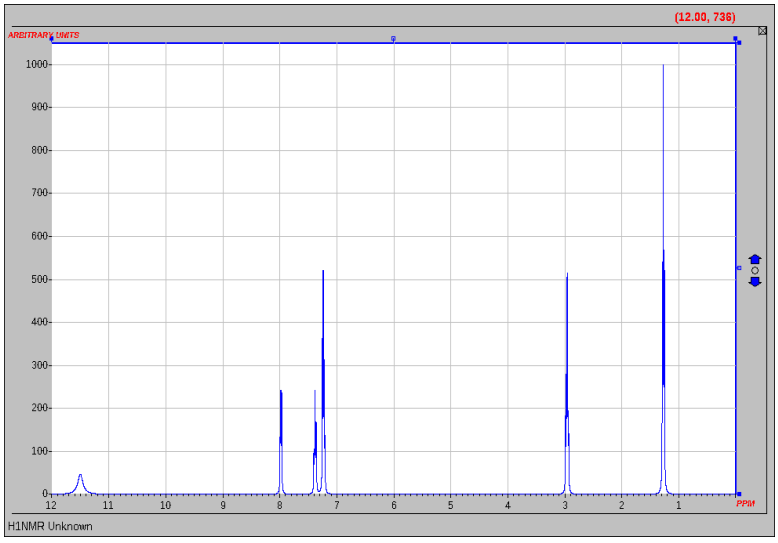
8.10 2H d
7.31 2H d
2.46 2H q
1.27 3H t



C. 2-ethylbenzoic acid



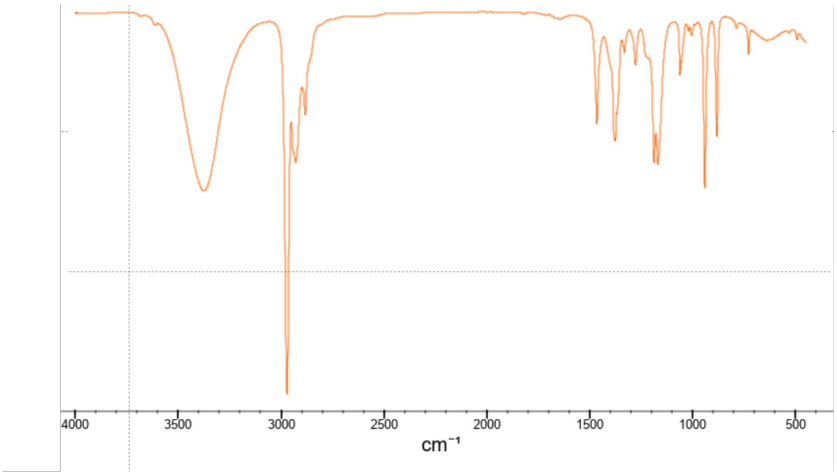
11.5 1H br
7.98 1H dd
7.23 1H td
7.38 1H td
7.24 1H dd
2.96 2H q
1.27 3H t
(note the overlap due to similar chemical shifts)



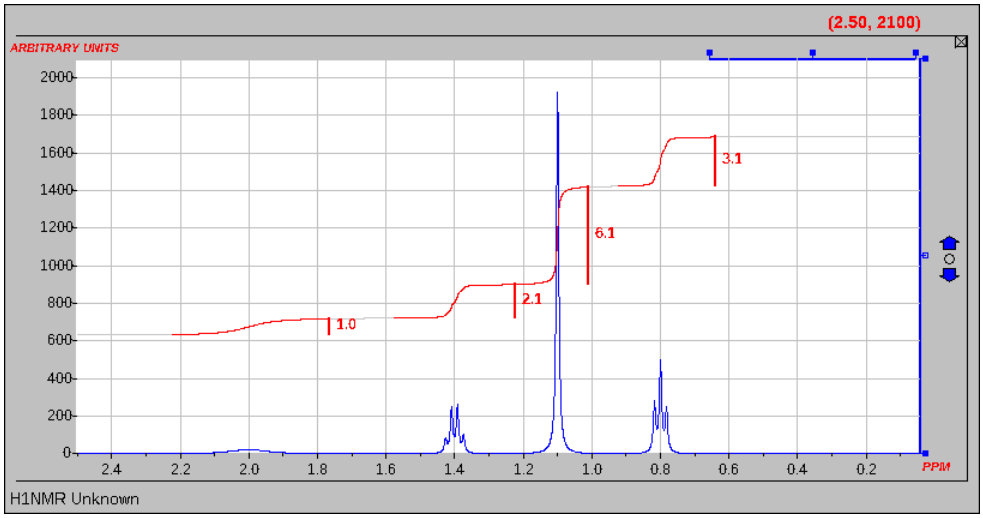
6. (11 points each, 22 points total) Identify each compound based on the spectroscopic information provided. For partial credit, include as much of your analysis (DoU, fragments or functional groups) that you can provide.

A.MS parent ion m/z = 88; M+1 peak is 5.5% of the M peak intensity.

IR: 3300-3600 cm^{-1}.

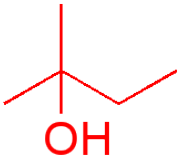


^{1}H NMR: 2.0 s, 1H
1.4 q, 2H
1.1 s, 6H
0.8 t, 3H



(No signals are further downfield.)

MS: 5 carbons in parent ion = 60 mass units. That leaves 28. One O is 16, leaving 12. Molecular formula $C_5H_{12}O$, DoU = 0



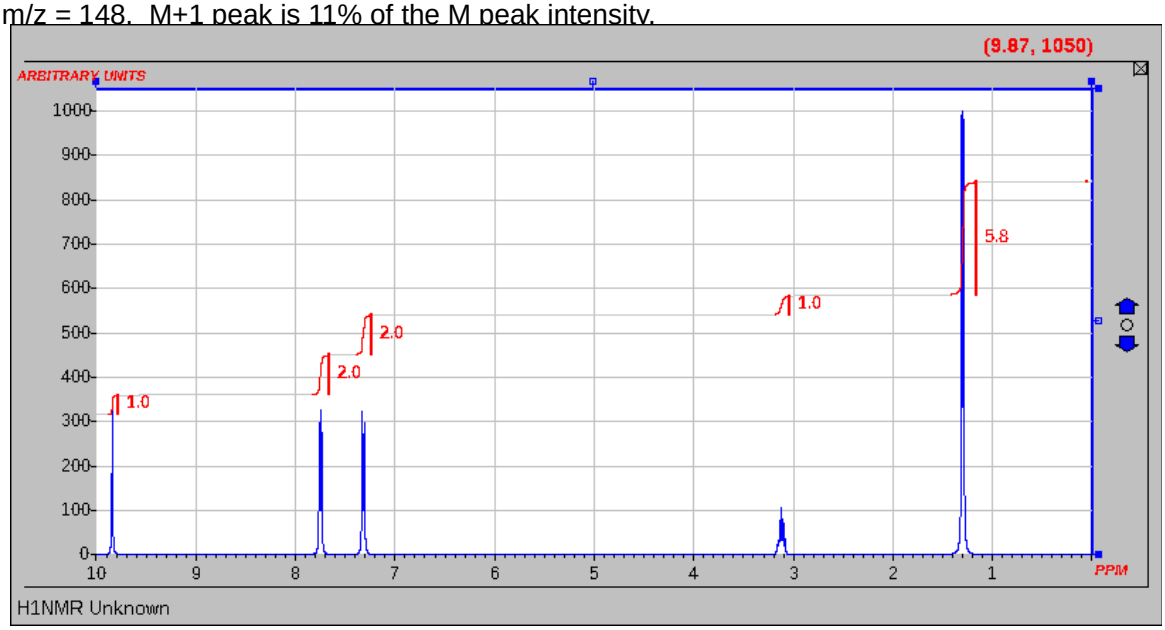
IR: O-H apparent.

^{1}H NMR: 6H singlet = 2 identical methyl groups not coupled to anything;
3H t + 2H q = ethyl group.

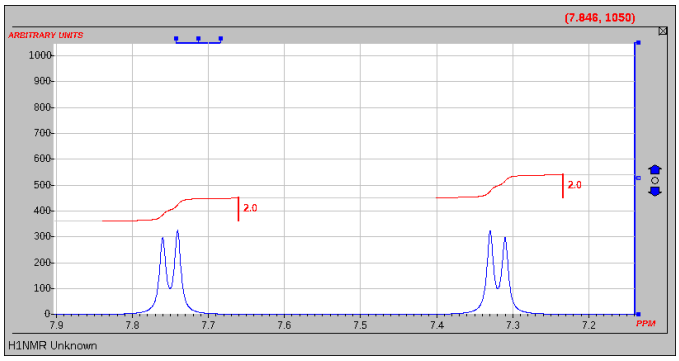
B. MS parent ion: m/z = 148. M+1 peak is 11% of the M peak intensity.

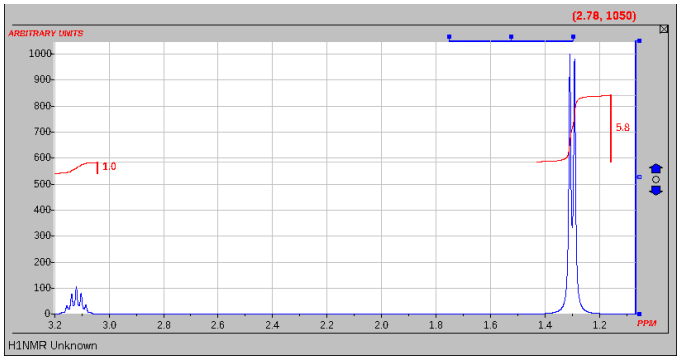
^{1}H NMR:

1.30 d, 6H;
3.12 septet, 1H;
7.32 d, 2H;
7.75 d, 2H;
9.84 s, 1H.



Expansions:

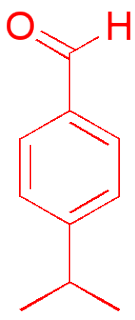




7.1-7.9 ppm

1.1-3.2 ppm

^{13}C NMR: 24.0, 36.2, 127.0, 129.8, 134.0, 155.0, 191.5 ppm.

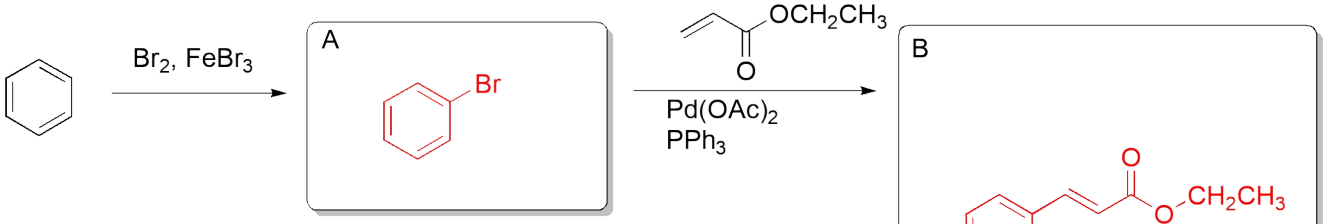


MS: 10 carbons (= 120 mass units) leaves 28; that leaves 1 oxygen (16) and 12 H. $C_{10}H_{12}O$, DoU = 5.

^{1}H NMR: 9.8 indicates an aldehyde; the two doublets in the aromatic region show a para-disubstituted benzene, and the remaining upfield peaks (6H d + 1H septet) an isopropyl group.

^{13}C NMR confirms the aldehyde, 4 aromatic carbons and the 2 isopropyl carbons.

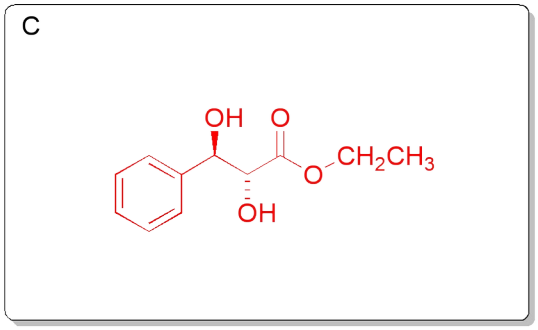
7. (9 points per box, 27 points total) Provide structures for each empty box. Use your understanding of both reaction chemistry and spectroscopic behavior to arrive at the answers. Include stereochemistry.



^{13}C NMR:
131.5
130.0
126.8
122.5

IR: 1712 cm^{-1}. UV: λ_{max} = 297 nm

^{1}H NMR:
7.67 (1 H, d, J= 16.0 Hz)
7.24-7.57 (5H, m)
6.43 (1 H, d, J= 16.0 Hz)
4.24 (2 H, q, J = 7 Hz)
1.32 (3 H, t, J = 7 Hz)



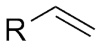
1. mCPBA
2. H^+, H_2O

IR: 3400 (broad), 1736 cm^{-1};
UV: λ_{max} = 260 nm
MS parent ion region:
192 100%
193 11.96%
194 1.36%

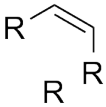
Bond strengths (kcal/mol):

F-F	38
Cl-Cl	58
Br-Br	46
I-I	36
H-F	136
H-Cl	103
H-Br	87
H-I	71
CH_3-H	105
CH_3CH_2-H	101
$(CH_3)_2CH$-H	98.5
$(CH_3)_3C$-H	96.5
CH_3-F	110
CH_3-Cl	85
CH_3-Br	70
CH_3-I	57
CH_3CH_2-F	111
CH_3CH_2-Cl	84
CH_3CH_2-Br	70
CH_3CH_2-I	56
$(CH_3)_2CH$-F	111
$(CH_3)_2CH$-Cl	84
$(CH_3)_2CH$-Br	71
$(CH_3)_2CH$-I	56
$(CH_3)_3C$-F	110
$(CH_3)_3C$-Cl	85
$(CH_3)_3C$-Br	71
$(CH_3)_3C$-I	55

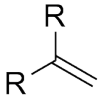
Typical Heats of Hydrogenation



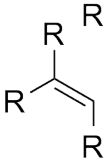
-30 kcal/mol



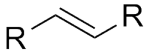
-28.2 kcal/mol



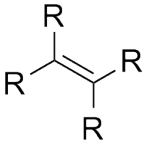
-27.9 kcal/mol



-26.5 kcal/mol



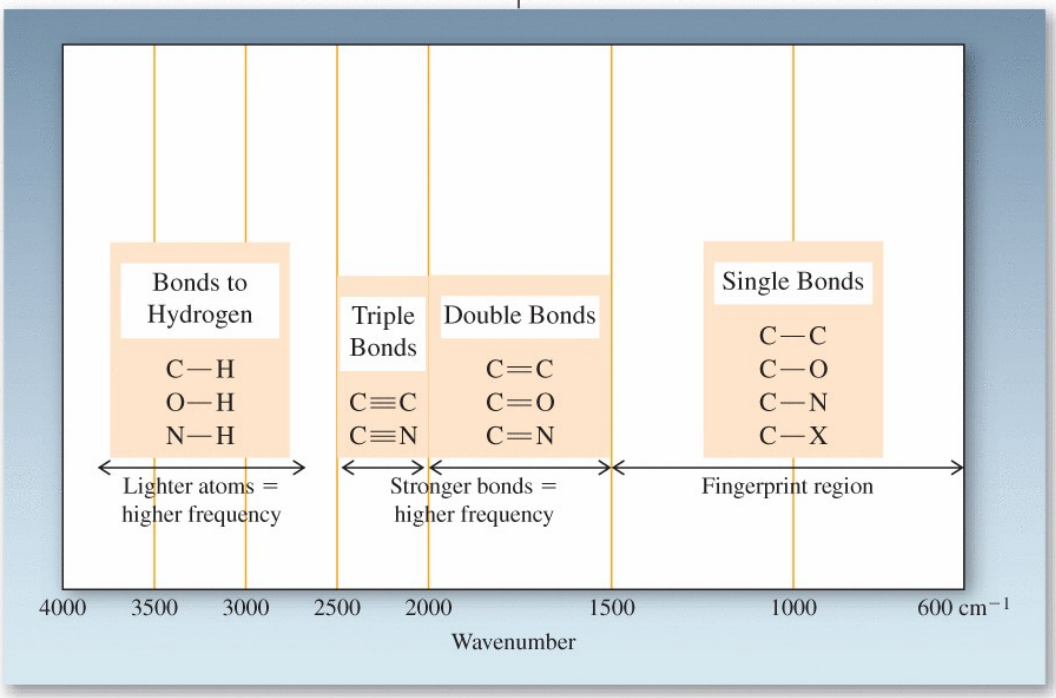
-27.4 kcal/mol



-26.3 kcal/mol

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)

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, $RCCH_3$ (C=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, $R_2C{=}CHR'$	5.2–5.7	
Aromatic, ArH	6.0–9.5	
Aldehyde, RCHO	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).

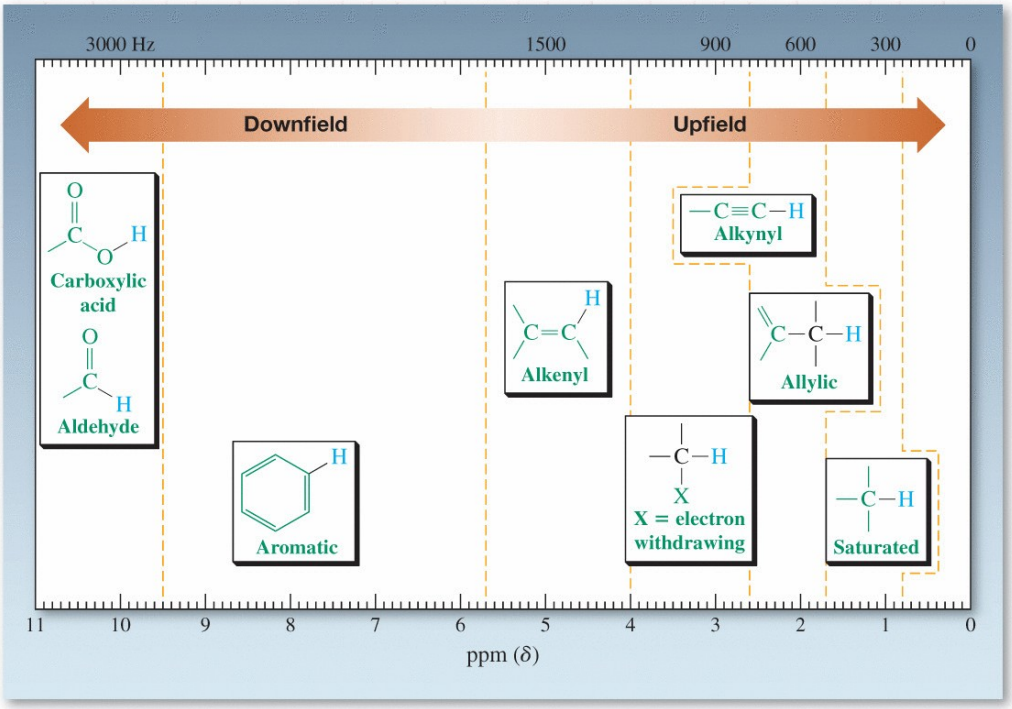


Table 10-6 Typical ^{13}C NMR Chemical Shifts

Type of carbon	Chemical shift δ (ppm)
Primary alkyl, RCH_3	5–20
Secondary alkyl, RCH_2R'	20–30
Tertiary alkyl, R_3CH	30–50
Quaternary alkyl, R_4C	30–45
Allylic, $R_2C{=}C(R'')CH_2R'$	20–40
Chloroalkane, RCH_2Cl	25–50
Bromoalkane, RCH_2Br	20–40
Ether or alcohol, RCH_2OR' or RCH_2OH	50–90
Carboxylic acids, RCOOH	170–180
Aldehyde or ketone, RCH(=O) or RC(=O)R′	190–210
Alkene, aromatic, $R_2C{=}CR_2$	100–160
Alkyne, $RC{\equiv}CR$	65–95