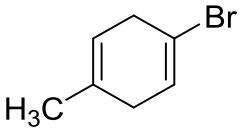
CHEMISTRY 3331 Name_____
FINAL EXAM (print, **legibly**) Last First
Dr. O. Daugulis
May 4, 2016 Last 4 digits of peoplesoft # _____

Seat Number_____

Please **read all directions carefully.** Write all answers legibly in the appropriate spaces and ***THINK*** about what you are doing. (200 pts total).

1. (16 pts.) Give a complete and acceptable name for each of the following structures. Indicate stereochemistry if required.

(a)



1-bromo-4-methylcyclohexa-1,4-diene 1,4 can be before cyclohexa

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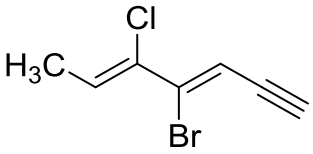
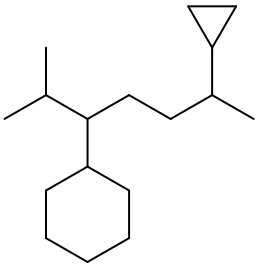
(b)



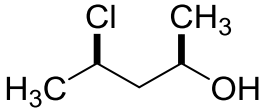
Z,Z-4-bromo-5-chlorohept-3,5-dien-1-yne; Z,Z anywhere OK; 3,5-heptadien-1-yne also OK; cis OK

(c)



3-cyclohexyl-6-cyclopropyl-2-methylheptane

(d)



4R-chloropentan-2R-ol OK if use hydroxy; R, R anywhere OK

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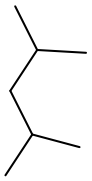
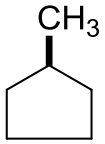
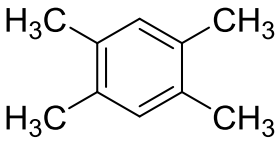
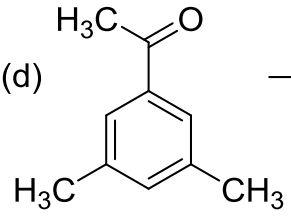
4 pts ea

2. (12 pts) For each of the molecules shown below, indicate the number of non-equivalent protons (the number of different signals you would expect in the proton NMR)

(a)  3

(b)  6

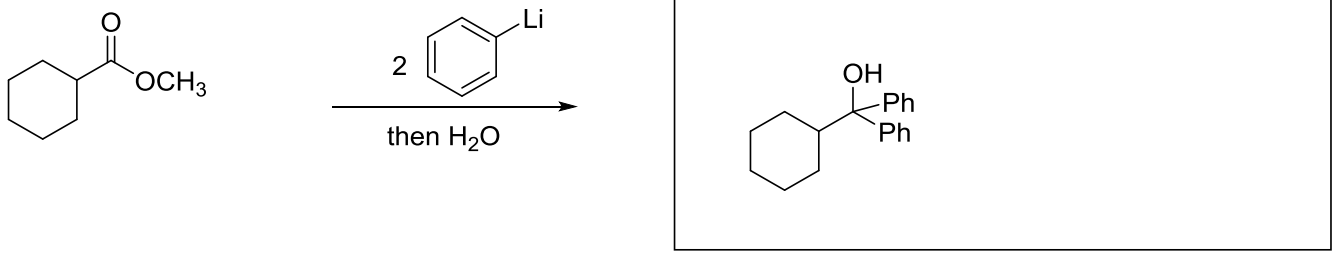
(c)  2

(d)  4

3 pts ea

3. (44 pts) For each of the following reactions or series of reactions, draw the structure of the required reagent(s) (over the arrow) or the reactant or major organic product (in the box). Be sure to indicate stereochemistry where this is pertinent. **4 pts ea, partial credit for intermediates**

(a)

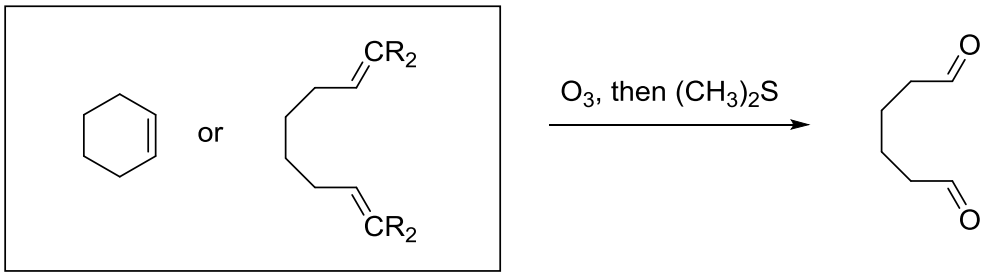


answer is NOT CH_3OH

(b)

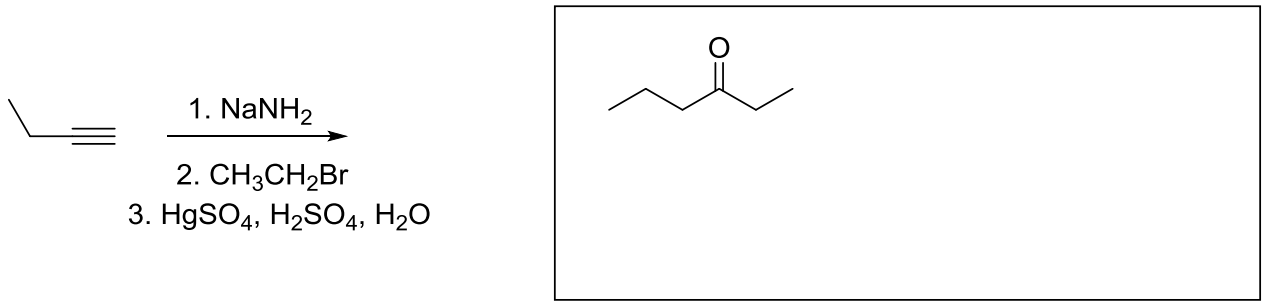
quiz 7, exam 3

(c)

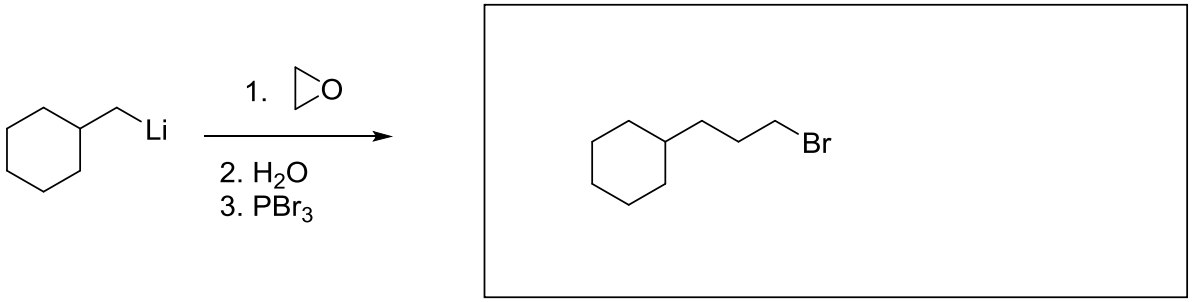


12-memb ring w/2 db also OK

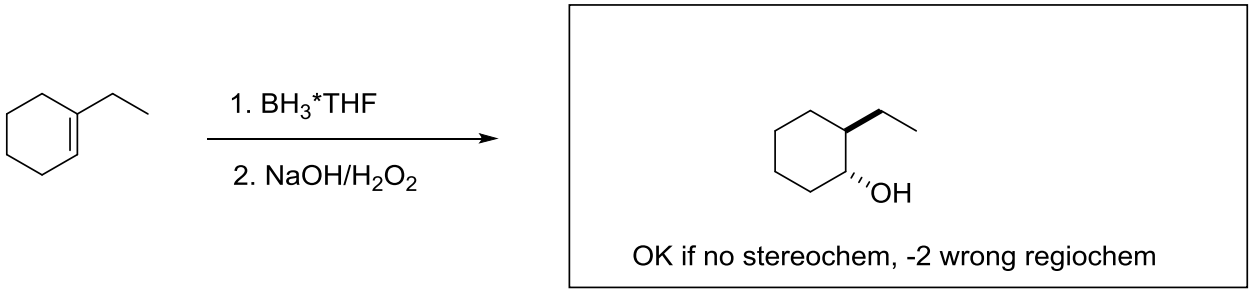
(d)



(e)

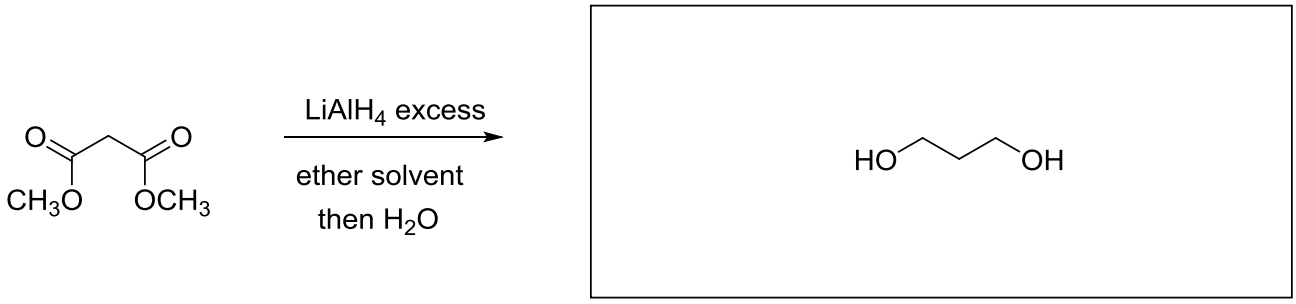


(f)



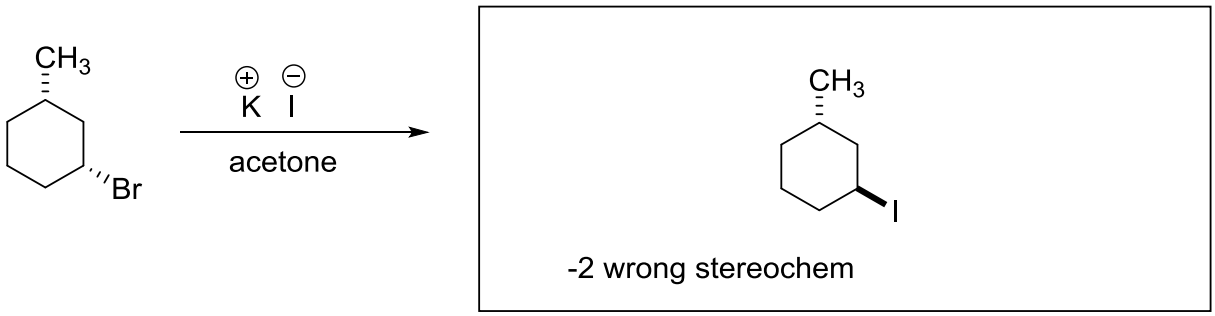
OK if no stereochem, -2 wrong regiochem

(g)



answer is NOT CH_3OH

(h)



-2 wrong stereochem

(i)

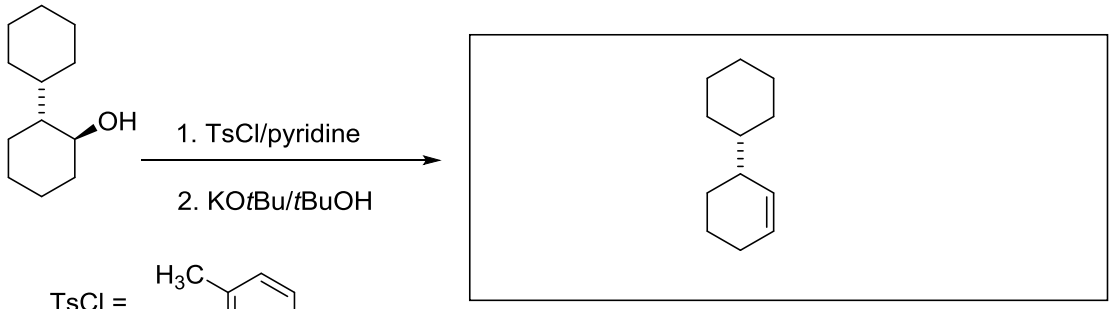
monobrominated product

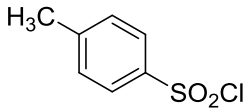
2 enantiomers of this also OK

monobrominated product

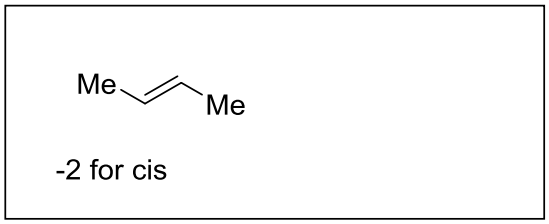
exam 2, exam 3

(j)



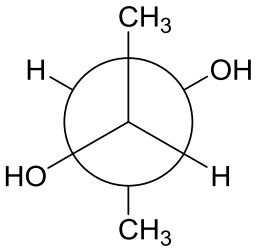
TsCl = 

(k)



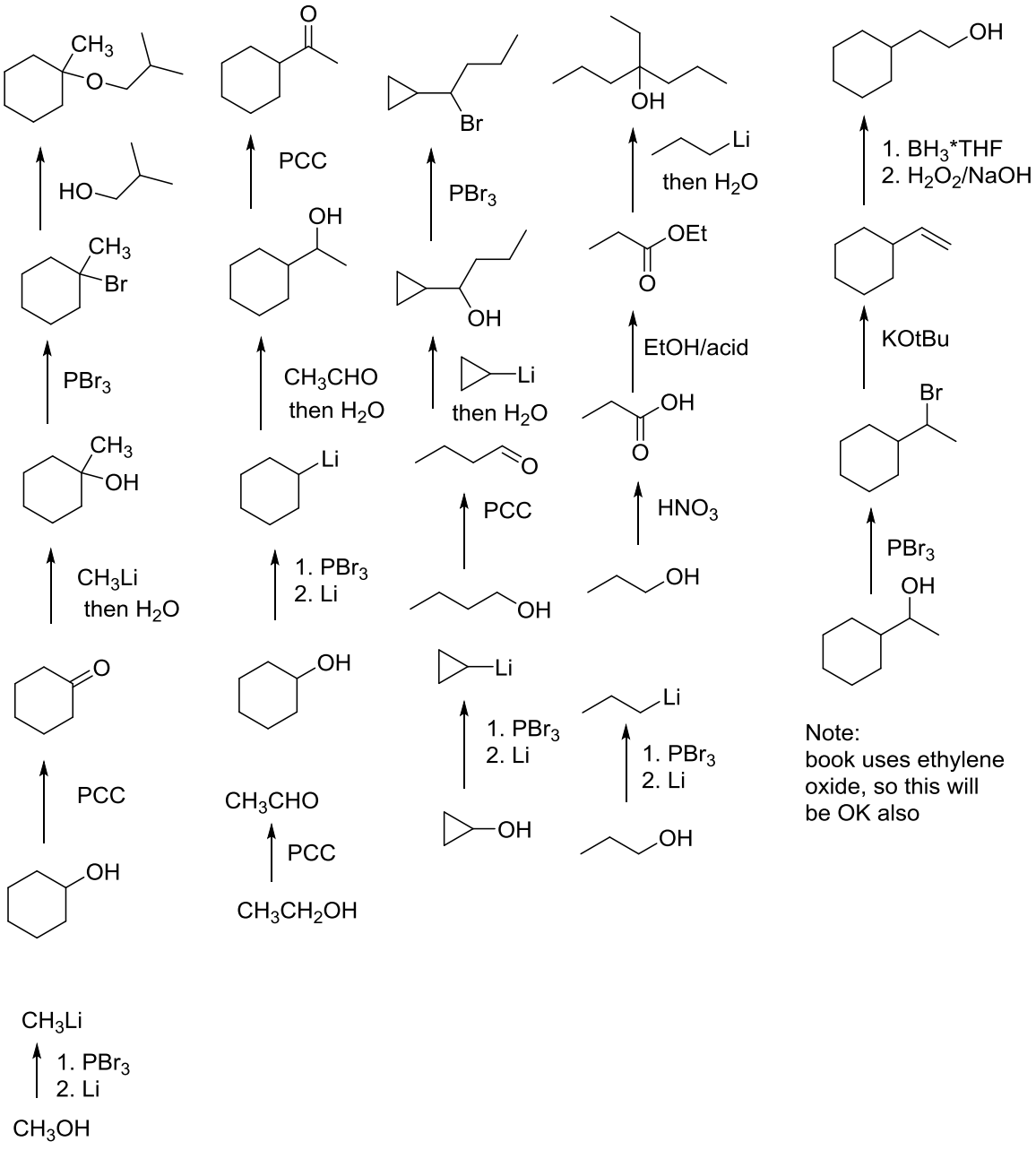
-2 for cis

1. mCPBA
2. $H_2O/H^{\oplus}$



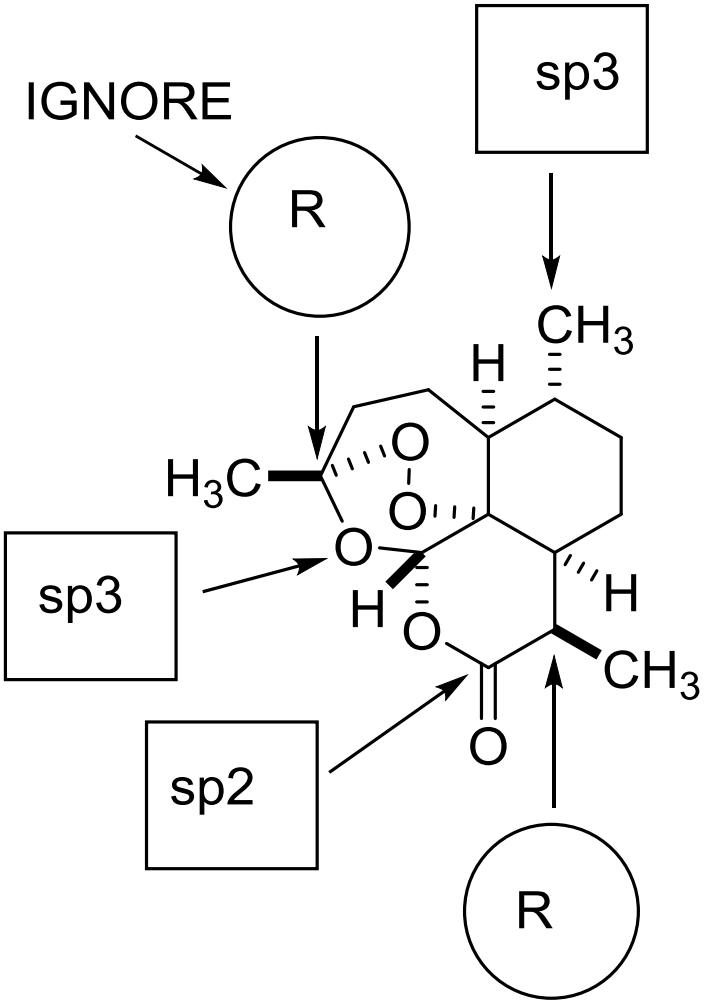
mCPBA =
meta-chloroperoxybenzoic acid

4. (30 pts) Give a complete *and efficient* syntheses which will produce **three** out of five compounds shown below. Show each step and each intermediate. DO NOT draw mechanisms. As starting materials, you can use cyclohexanol, any alcohols containing four or less carbon atoms, and any inorganic reagents. **PROBLEM 11-56. 10 pts ea**



Many other possibilities in each case

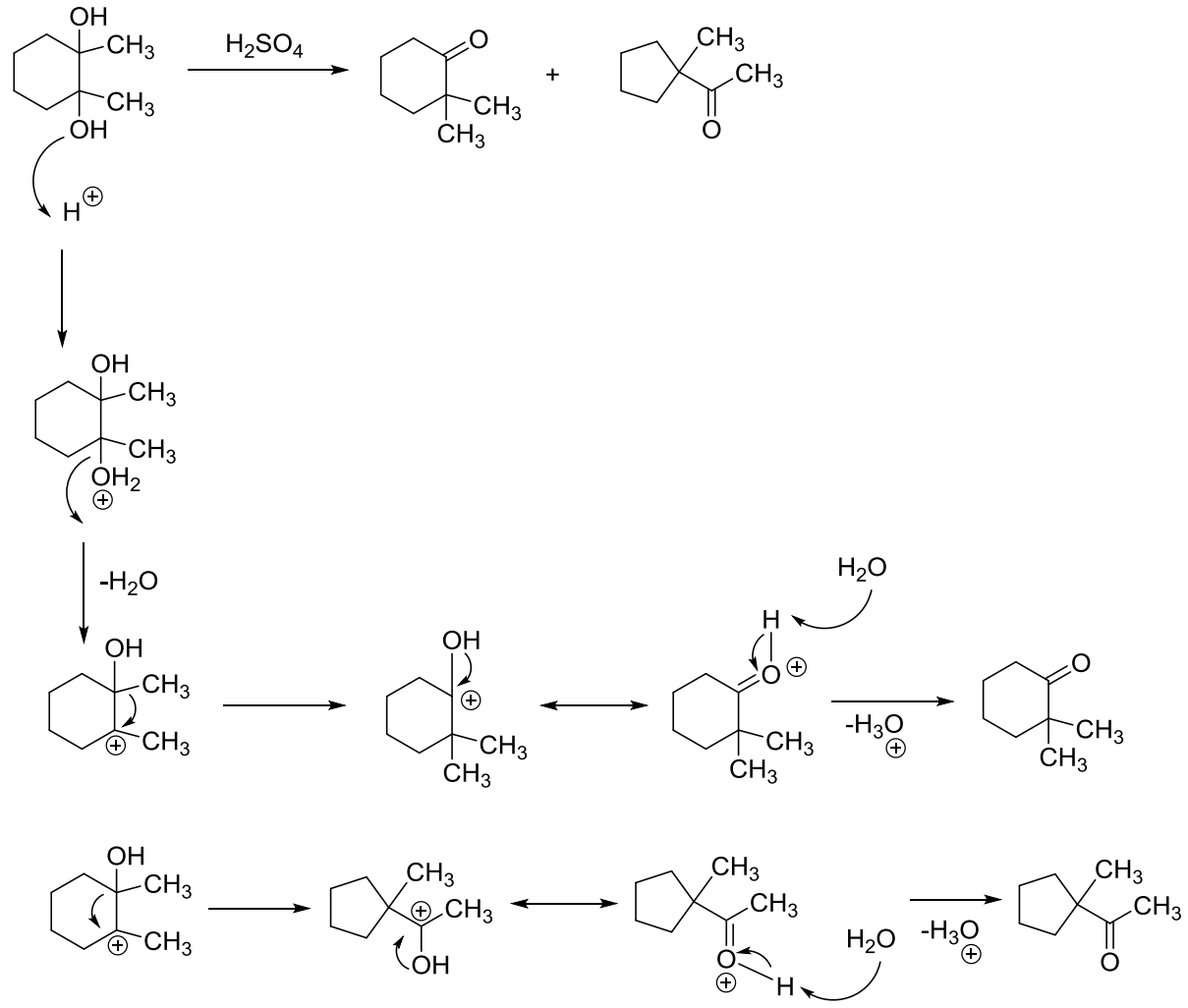
5. (18 pts) The molecule shown below is **Artemisinin**, which is a drug that possesses the most rapid action of all current drugs against malaria. It was discovered by Tu Youyou, a Chinese scientist, who was awarded half of the 2015 Nobel Prize in Medicine for her discovery. Artemisinin is isolated from sweet wormwood, a herb employed in Chinese traditional medicine. (a) Determine the hybridization of the indicated atoms and place the answers in the square boxes provided. (b) Assign the R, S stereochemistry of the indicated atoms and place the answers in the circles provided. (c) Write the number of chiral carbon atoms (chirality centers) in Artemisin in the box provided to the right of the structure. **3 pts ea**



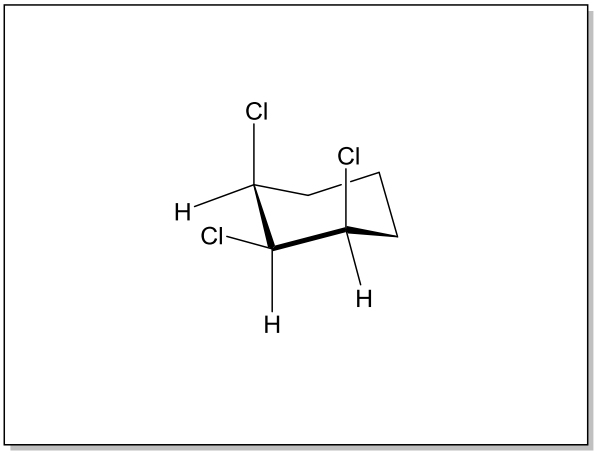
7

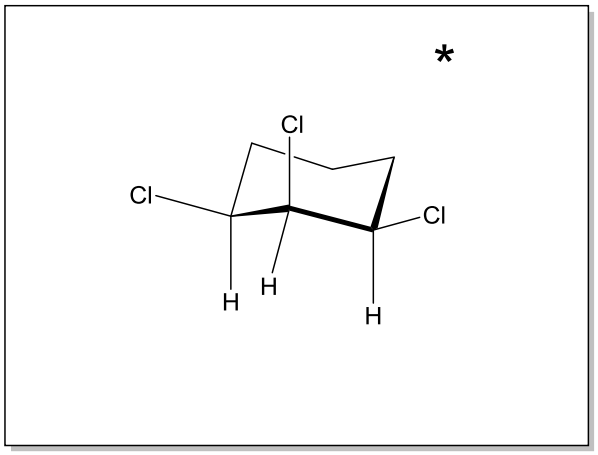
number of chiral carbon atoms in Artemisin

6. (20 pts) Propose reaction mechanisms, showing all intermediates (no transition states), all charges and/or unpaired electrons, and indicate the flow of electrons with arrows, for the formation of two products shown in transformation below. ***Covered in lecture***

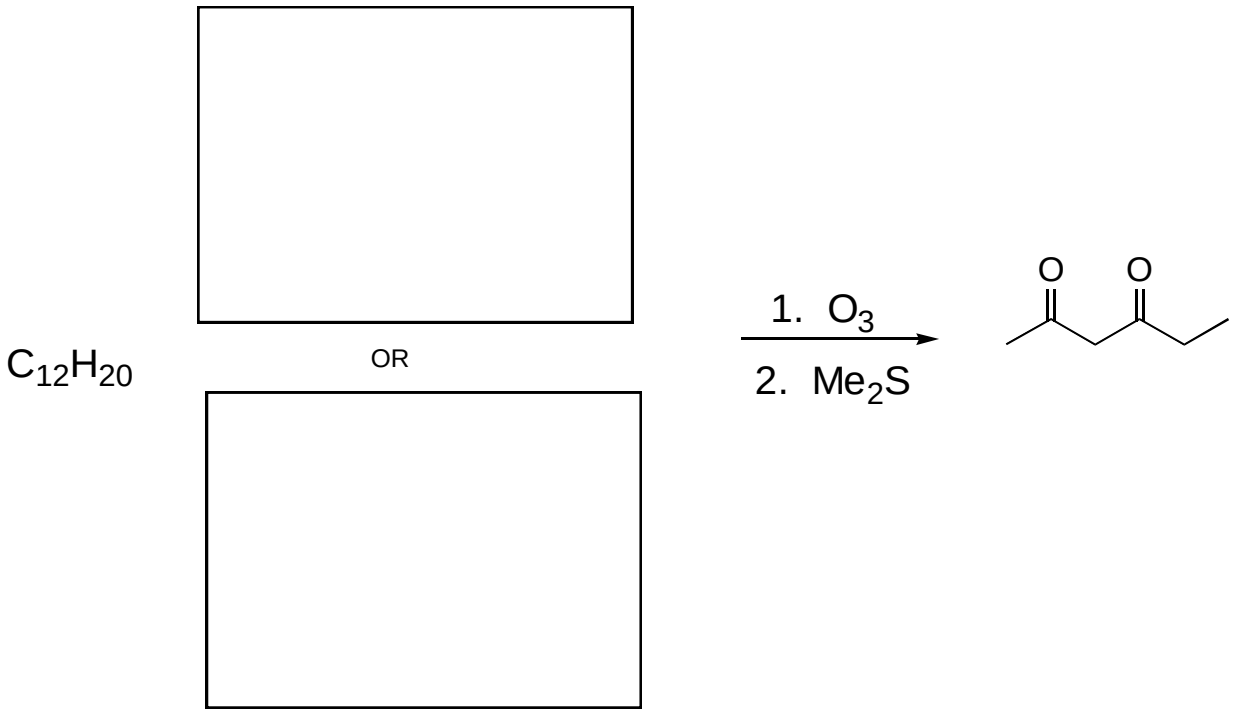


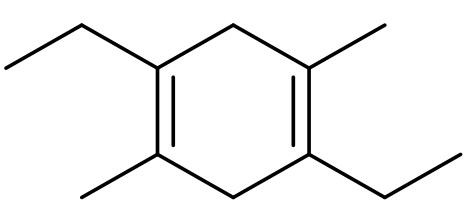
7. (6 pts) In the two boxes below, carefully draw the two chair conformations of *cis*, *cis*-1,2,3-trichlorocyclohexane. Put a star in the box of the most stable conformation. **2 pts each structure, 2 pts star**

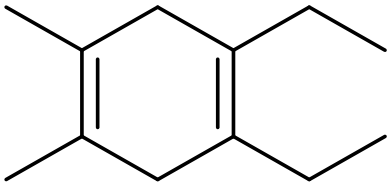




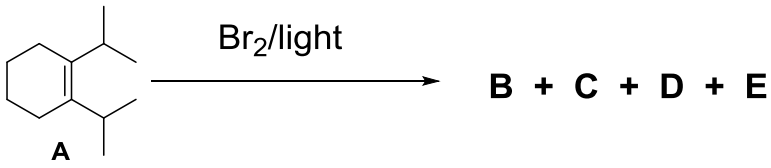
8. (12 pts) Ozonolysis followed by reductive workup (Me_2S) of a compound with the formula $C_{12}H_{20}$ gives only the diketone shown below. Draw two possible structures for this compound. **6 pts each structure**





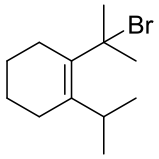


9. (12 pts) Alkene shown below can be mono-brominated to give four different products. Draw structures of these products in the boxes provided. Draw all geometric isomers, but if product is formed as a pair of enantiomers, draw only one enantiomer. **2 pts each structure, 2 pts A or B below; if 4 or more below then 0 pts**

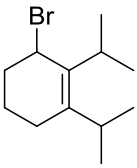


A

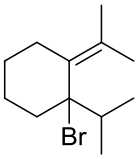
B



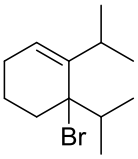
C



D

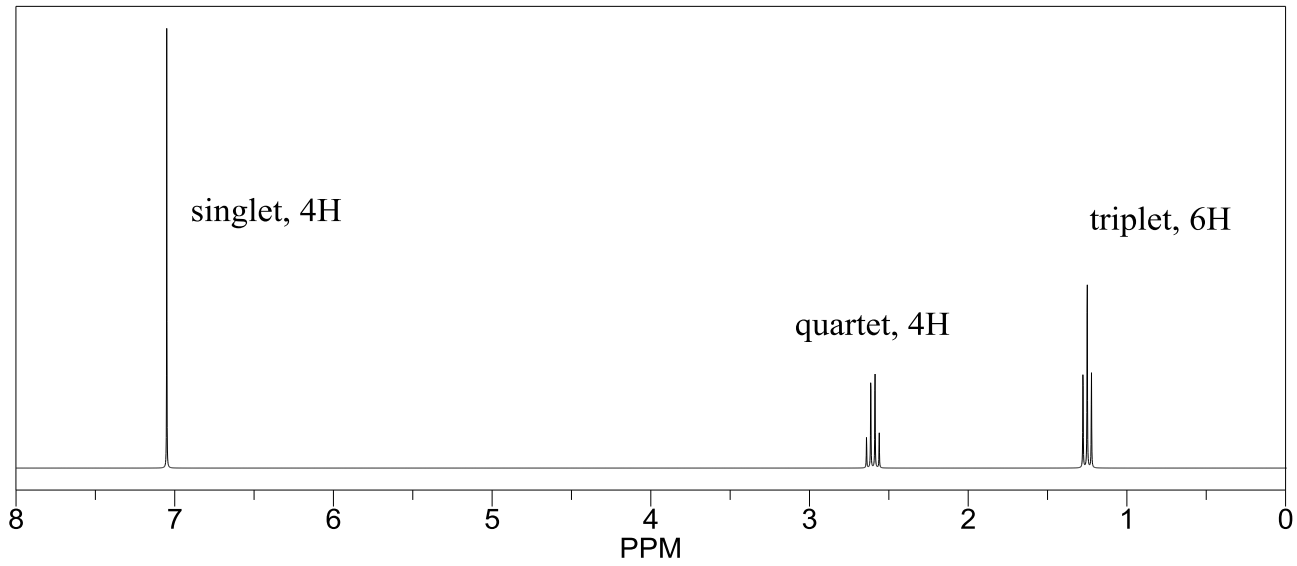


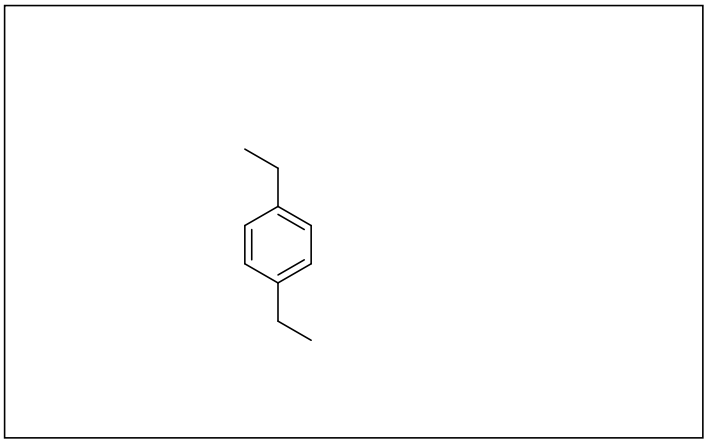
E



Are any of the compounds A to E achiral? If yes, write which ones: __A, B_____

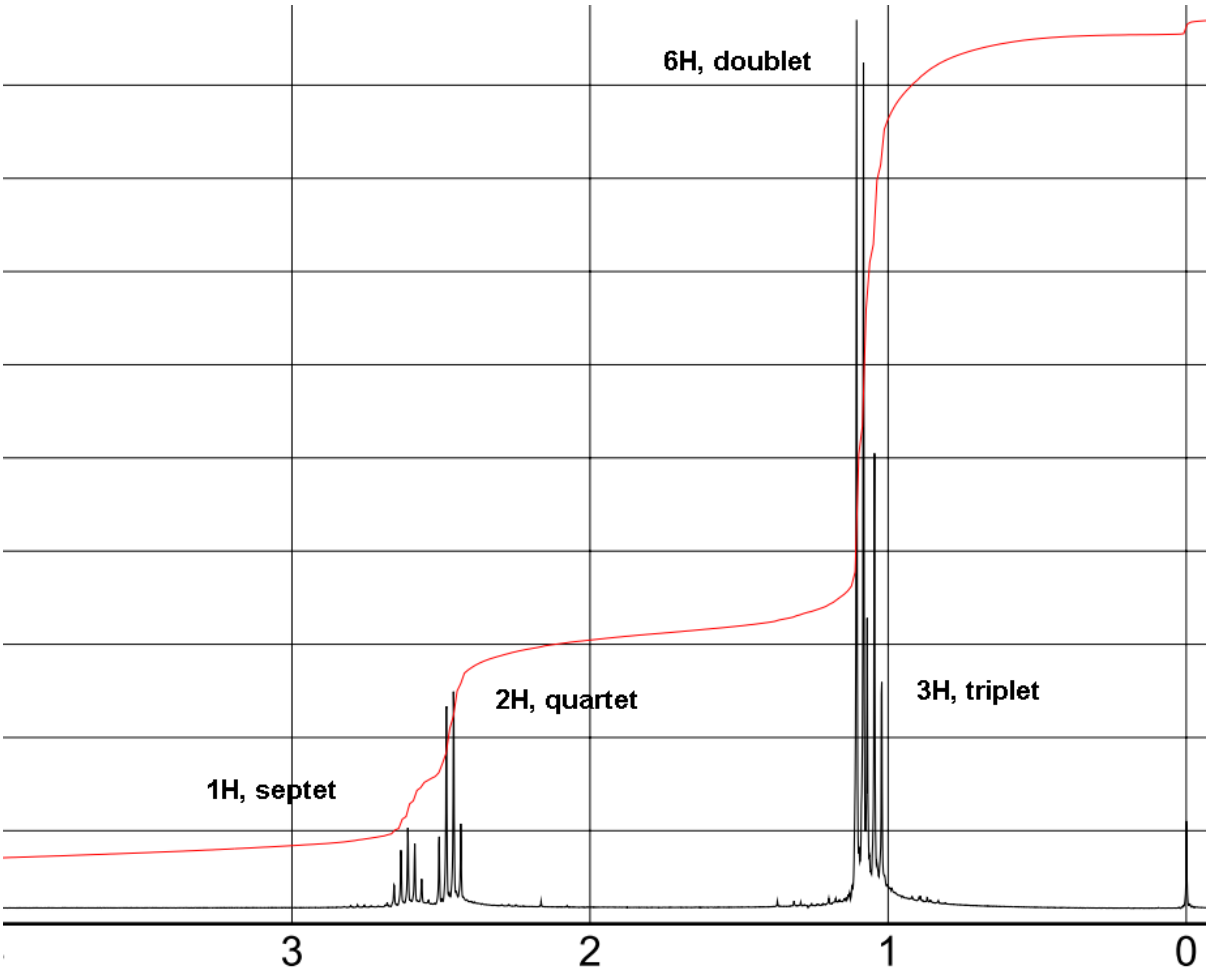
10. (8 pts) A molecule with formula $C_{10}H_{14}$ has the proton NMR spectrum shown below. Draw structure in the box provided and include any reasoning for partial credit.

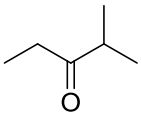




Partial credit: ethyl gp 2 pts, benzene ring 2 pts, 1,4-disubstituted benzene 3 pts

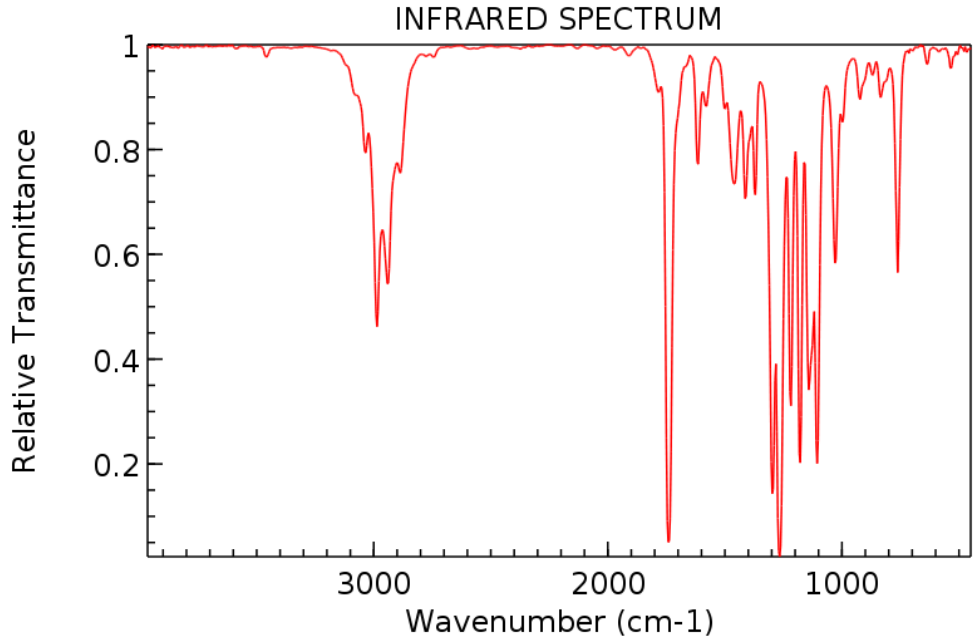
11. (10 pts) A molecule with formula $C_6H_{12}O$ shows the NMR spectrum reproduced below. In IR spectrum, an intensive peak at 1715 cm^{-1} is observed. Draw its structure in the box on next page and be sure to include any reasoning for partial credit.



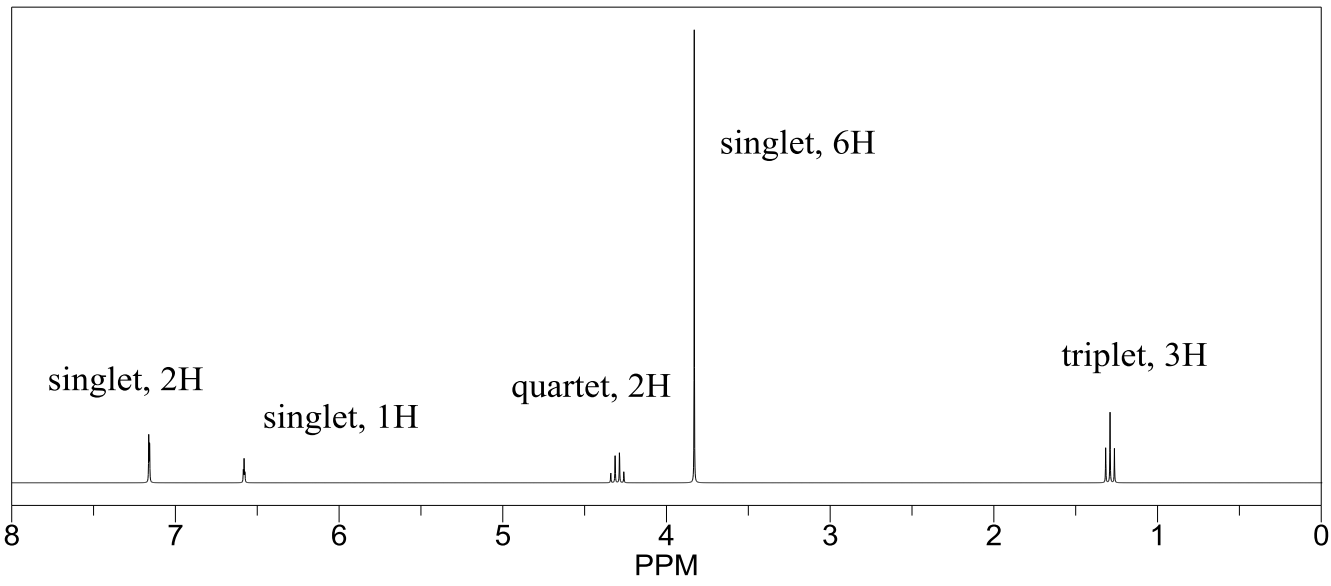


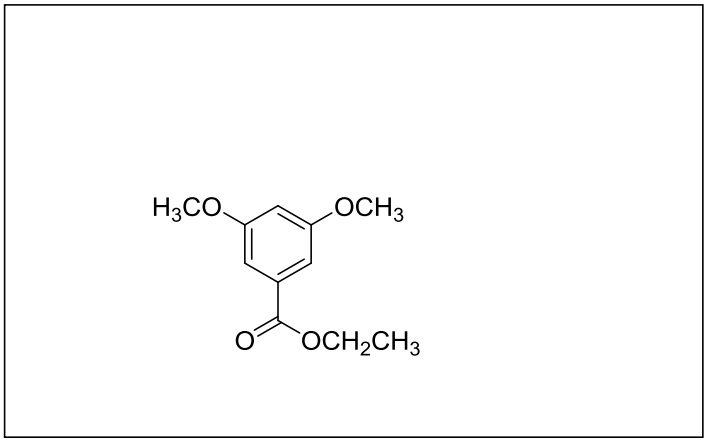
Partial credit – ethyl 2 pts, iPr 2 pts, ketone 2 pts

12. (12 pts) A molecule with formula $C_{11}H_{14}O_4$ shows IR and NMR spectra that are reproduced below. Draw its structure in the box and be sure to include any reasoning for partial credit.



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)





Partial credit – OMe 2 pts, ethyl 2 pts, C=O 2 pts, benzene ring 2 pts, 1,3,5-trisubstituted benzene 4 pts
Structure with aldehyde and 2H on ring also acceptable

Extra Credit Above 200 Pts (18 pts)

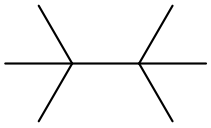
In the boxes provided below, draw molecules that have the molecular formulas given and that show only one line in their ^{1}H (proton) NMR spectra:

CH_3OCH_3

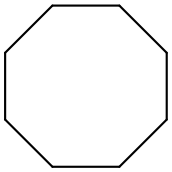
C_2H_6O

CH_3OOCH_3

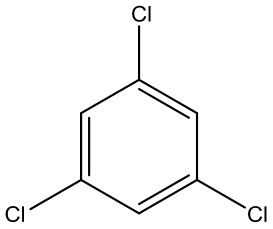
$C_2H_6O_2$



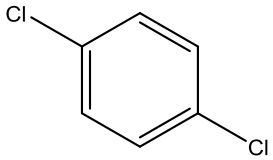
C_8H_{18}



C_8H_{16}



$C_6H_3Cl_3$



$C_6H_4Cl_2$

3 pts ea

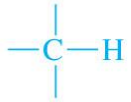
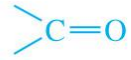
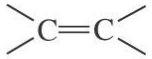
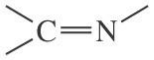
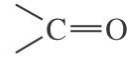
THIS IS THE END OF THE EXAM – HAVE A FANTASTIC SUMMER!

The Periodic Table of the Elements

1 **H** Hydrogen 1.00794																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
11 **Na** Sodium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973761	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.955910	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938049	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933200	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96655	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

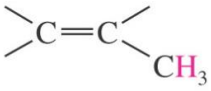
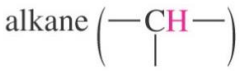
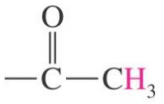
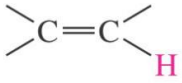
58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	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 (262)

TABLE 12-2 Summary of IR Stretching Frequencies

Frequency (cm^{-1})	Functional Group		Comments
3300	alcohol	O—H	always broad
	amine, amide	N—H	may be broad, sharp, or broad with spikes
	alkyne	≡C—H	always sharp, usually strong
3000	alkane		just below 3000 cm^{-1}
	alkene		just above 3000 cm^{-1}
	acid	O—H	very broad
2200	alkyne	—C≡C—	just below 2200 cm^{-1}
	nitrile	—C≡N	just above 2200 cm^{-1}
1710 (very strong)	carbonyl		ketones, aldehydes, acids esters higher, about 1735 cm^{-1} conjugation lowers frequency amides lower, about 1650 cm^{-1}
1660	alkene		conjugation lowers frequency aromatic C=C about 1600 cm^{-1}
	imine		stronger than C=C
	amide		stronger than C=C (see above)

Ethers, esters, and alcohols also show C—O stretching between 1000 and 1200 cm^{-1}.

TABLE 13-3 Typical Values of Chemical Shifts

Type of Proton	Approximate δ	Type of Proton	Approximate δ
alkane ($-CH_3$)	0.9		1.7
alkane ($-CH_2-$)	1.3		
alkane 	1.4	Ph—H	7.2
		Ph—CH_3	2.3
	2.1	R—CHO	9–10
—C≡C—H	2.5	R—COOH	10–12
R—CH_2—X	3–4	R—OH	variable, about 2–5
(X = halogen, O)		Ar—OH	variable, about 4–7
		R—NH_2	variable, about 1.5–4
	5–6		

Note: These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present. A more complete table of chemical shifts appears in Appendix 1.