CH 335

Final Exam

Thursday, March 20, 2014

Name\_\_\_\_\_

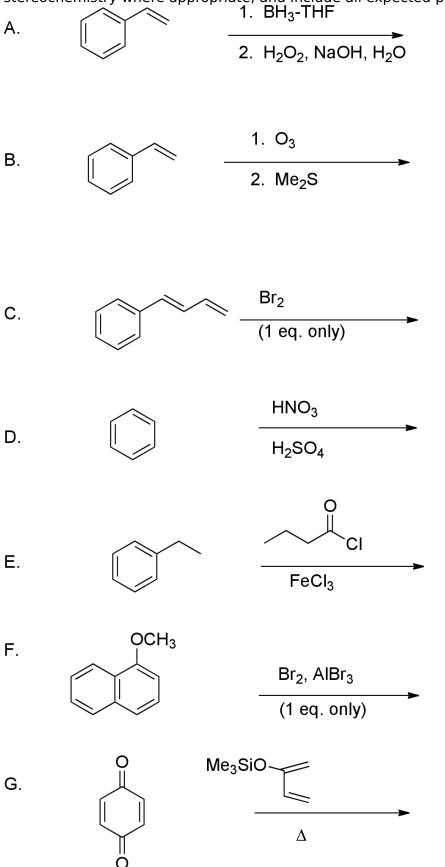
You may use model kits but no other material with chemical information without instructor approval.

Please do not use ipods or other music players.

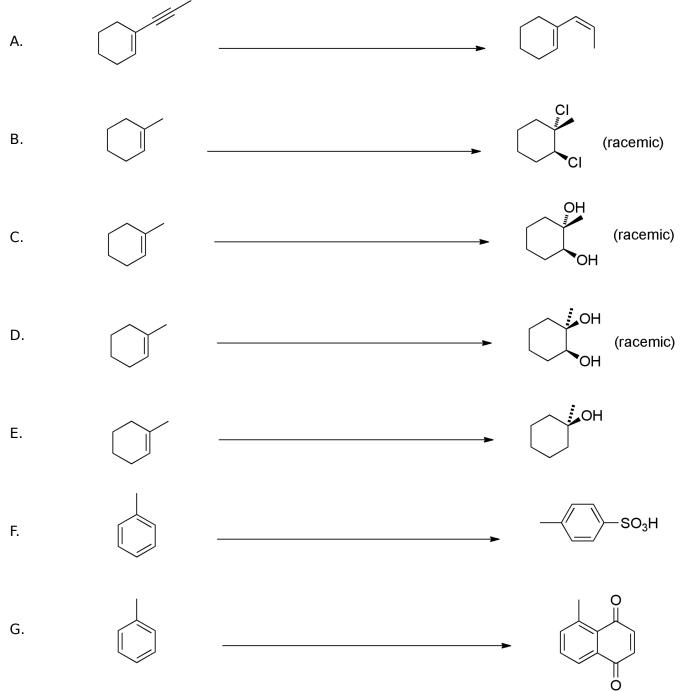
hydrogen 1																	895 B	helium 2
Ĥ																		He
1.0079 lithium 3	beryllium 4											Ī	boron 5	carbon 6	nitrogen 7	oxygen 8	fluorine 9	4.0026 neon 10
Li	Be												В	С	Ν	0	F	Ne
6.941 sodium	9.0122 magnesium												10.811 aluminium	12.011 silicon	14.007 phosphorus	15.999 sulfur	18.998 chlorine	20.180 argon
Na	<sup>12</sup> Mg													<sup>14</sup> Si	15 <b>P</b>	16 S		<sup>18</sup> Ar
22,990	24.305												26.982	28.086	30.974	32.065	35.453	39.948
potassium 19	calcium 20		scandium 21	titanium 22	vanadium 23	chromium 24	manganese 25	iron 26	cobalt 27	nickel 28	copper 29	zinc 30	gallium 31	germanium 32	arsenic 33	selenium 34	bromine 35	krypton 36
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.098	40.078		44.956	47.867	50.942	51.996	54.938	55.845	58,933	58.693	63,546	65.39	69.723	72.61	74.922	78.96	79.904	83.80
rubidium 37	strontium 38		yttrium 39	zirconium 40	niobium 41	molybdenum 42	technetium 43	ruthenium 44	rhodium 45	palladium 46	silver 47	cadmium 48	indium 49	tin 50	antimony 51	tellurium 52	iodine 53	xenon 54
Rb	Sr		Y	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I	Xe
85.468 caesium	87.62 barium		88.906 lutetium	91.224 hafnium	92.906 tantalum	95.94 tungsten	[98] rhenium	101.07 osmium	102.91 iridium	106.42 platinum	107.87 gold	112.41 mercury	114.82 thallium	118.71 lead	121.76 bismuth	127.60 polonium	126.90 astatine	131.29 radon
55	56	57-70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	*	Lu	Hf	Та	W	Re	Os	lr	Pt	Au	Hg	TL	Pb	Bi	Po	At	Rn
132.91 francium	137.33 radium		174.97 lawrencium	178.49 rutherfordium	180.95 dubnium	183.84 seaborgium	186.21 bohrium	190.23 hassium	192.22 meitnerium	195.08 ununnilium	196.97 unununium	200.59 ununbium	204.38	207.2 ununquadium	208.98	[209]	[210]	[222]
87	88	89-102	103	104	105	106	107	108	109	110	111	112		114				
Fr	Ra	* *	Lr	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq				
[223]	[226]		[262]	[261]	[262]	[266]	[264]	[269]	[268]	[271]	[272]	[277]		[289]				

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

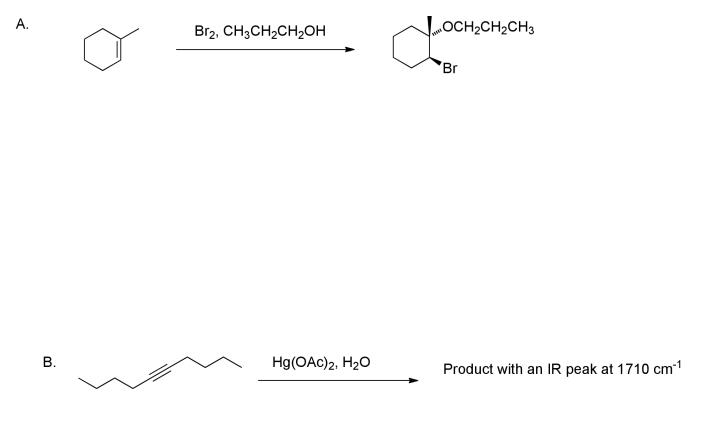
1. (35 points) Write the expected product(s) for each of the following reactions. Specify stereochemistry where appropriate, and include all expected products. 1.  $BH_3$ -THF

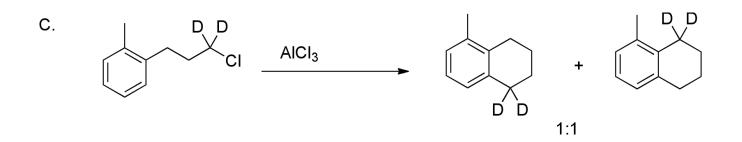


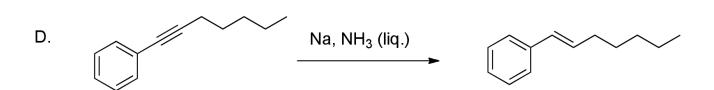
2. (35 points) Write (over the arrow) the reagents and/or conditions needed to accomplish the following transformations.



3. (28 points) 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.

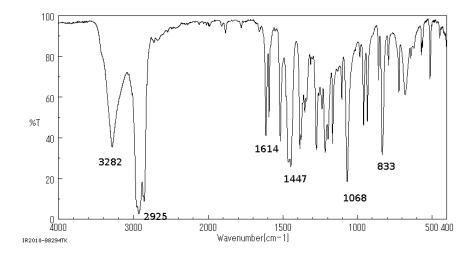




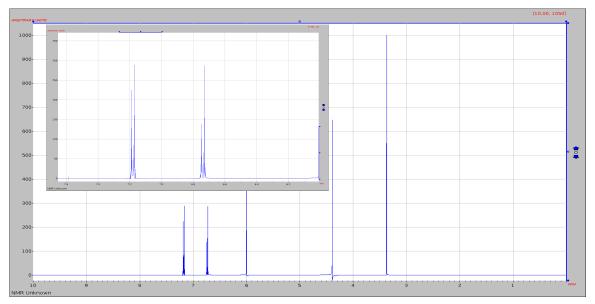


- 4. (25 points) A molecule has the molecular formula  $C_8H_{10}O_2$ .
- A. How many degrees of unsaturation does it have?

B. The infrared spectrum is shown below. Circle any peaks that tell you what functional groups are present, and list those functional groups. Several peaks are identified to help you estimate the scale.



C. The <sup>1</sup>H NMR with expansion (6-7.5 ppm) is shown below; integrations are listed below the spectrum. Propose a structure that is consistent with all this data. (Failing a complete structure, suggest what fragments are present for partial credit.)



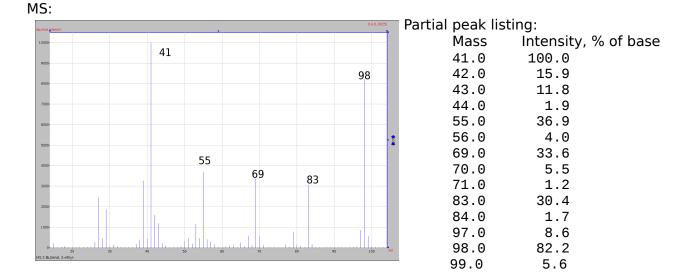
Integrals:

7.18 ppm: 2H 6.74 ppm: 2H

6.00 ppm: 1H

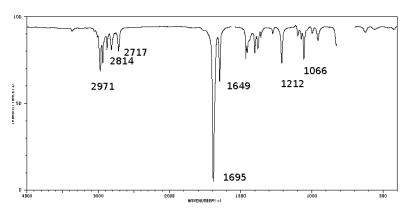
4.39 ppm: 2H

3.37 ppm: 3H

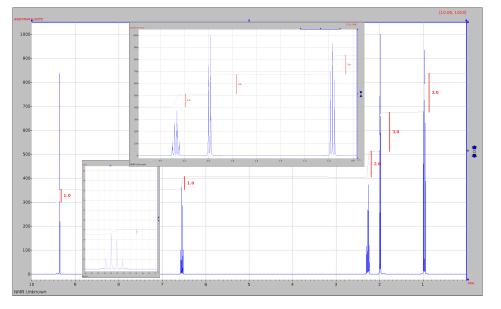


5. (25 points) The mass, IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra for a compound are shown below.

IR:



<sup>1</sup>H NMR (insets are 0.5-2.5 ppm above; 6.2-6.8 ppm below):



Integrals:

9.36 ppm 1H 6.55 ppm 1H 2.27 ppm 2H 1.99 ppm 3H

0.97 ppm 3H

<sup>13</sup>C NMR:

194.84 149.42 146.38 16.96 14.51 12.99

(continued next page)

A. From the mass spectrum (and clues in other spectra), deduce the molecular formula.

B. Propose a structure that fits the data. (If you cannot come up with a complete structure, provide as much analysis of the data as you can.) Be sure to:

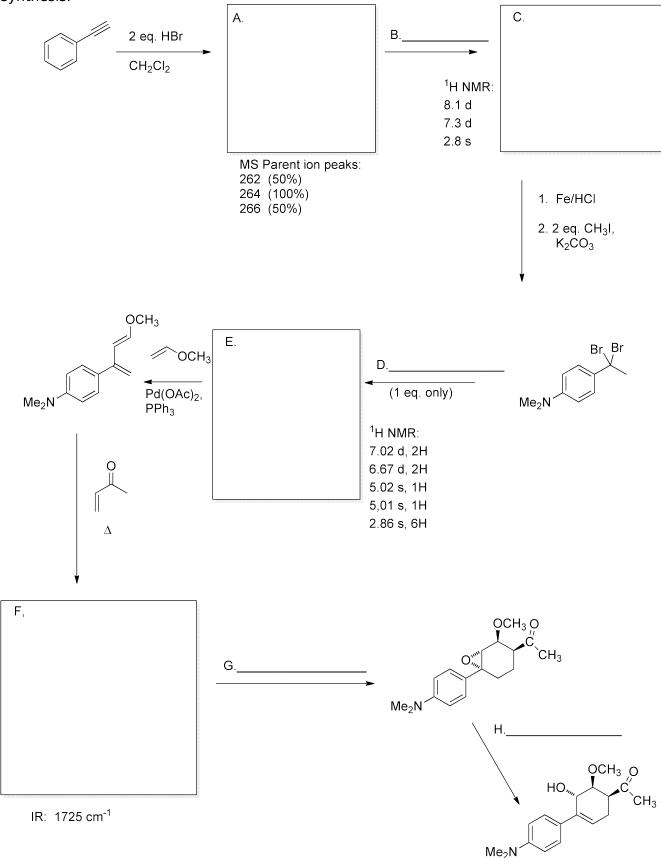
-Calculate the degrees of unsaturation

-Specify functional groups, the evidence you use to identify them, and the impact on the DoU count

-Identify coupling relationships that allow you to identify structural pieces

-Any corroborating evidence you can see that confirms the structure.

6. (32 points) Fill in the missing intermediates or reagents in the following multistep synthesis.

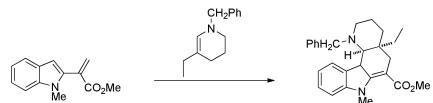


7. (20 points) Normally, the Diels-Alder reaction involves a diene with an electron-donating group reacting with a dienophile that has an electron-withdrawing substituent.

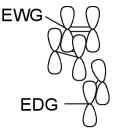
A. Based on the MO diagram below depicting the orbitals in the unsubstituted case (and their energies, in eV), describe why this particular pair of substituents enhances the Diels-Alder reaction. Use the molecular orbital description of the bonding in the reactants and the transition state.

+1.998 +0.368		8	// 
-9.57 -11.64	_		g <sup>8</sup> — -10.6

B. There are examples of what are called "inverse demand" Diels-Alder reactions, where the electron donor is on the dienophile, and the electron-withdrawing group is on the diene. An example is shown:



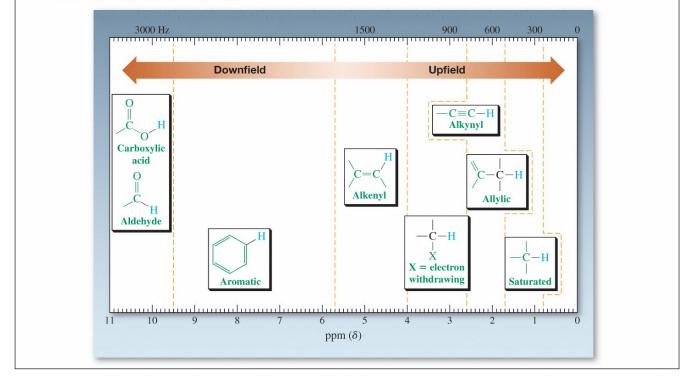
In the diagram below, shade in the phases of the orbitals to represent the major HOMO-LUMO interaction in the transition state for this inverse-demand Diels-Alder reaction. (Hint: think about how you would adapt your answer to Part A to explain what happens here.)



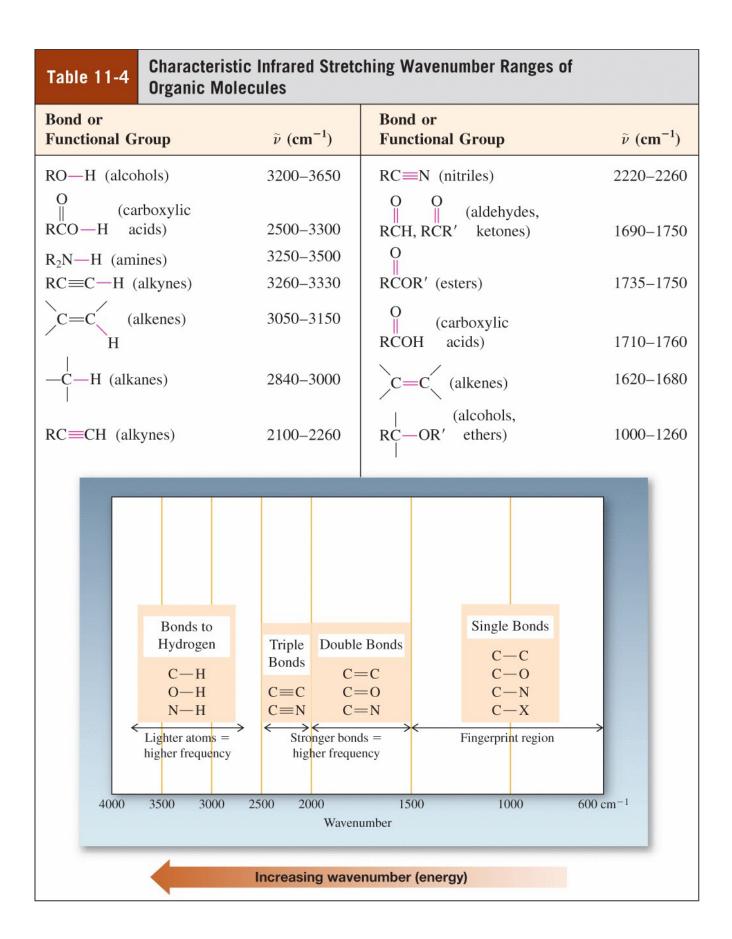
EWG = Electron-Withdrawing Group EDG = Electron-Donating Group

Table 10-2         Typical Hydrogen Chemical Shifts in (	Organic Molecules	
Type of hydrogen <sup>a</sup>		Chemical shift $\delta$ in ppm
Primary alkyl, RCH <sub>3</sub>	0.8-1.0	
Secondary alkyl, RCH <sub>2</sub> R'	1.2–1.4	Alkane and alkane-like hydrogens
Tertiary alkyl, R <sub>3</sub> CH	1.4–1.7 J	
CH <sub>3</sub>		
Allylic (next to a double bond), $R_2C = C$	1.6-1.9	
R'		
Benzylic (next to a benzene ring), ArCH <sub>2</sub> R	2.2-2.5	Hydrogens adjacent to unsaturated functional groups
Ketone, RCCH <sub>3</sub>	2.1-2.6	
0		
Alkyne, RC≡CH	1.7–3.1	
Chloroalkane, RCH <sub>2</sub> Cl	3.6-3.8	
Bromoalkane, RCH <sub>2</sub> Br	3.4–3.6	
Iodoalkane, RCH <sub>2</sub> I	3.1–3.3	Hydrogens adjacent to electronegative atoms
Ether, $RCH_2OR'$	3.3-3.9	
Alcohol, $RCH_2OH$	3.3–4.0 J	
Terminal alkene, $R_2C = CH_2$	4.6–5.0	Alkene hydrogens
Internal alkene, $R_2C = CH$	5.2-5.7	Tinkene Hydrogens
R'		
Aromatic, ArH	6.0-9.5	
Aldehyde, RCH	9.5-9.9	
U O		
Alcoholic hydroxy, ROH	0.5-5.0	(variable)
Thiol, RSH	0.5-5.0	(variable)
Amine, RNH <sub>2</sub>	0.5-5.0	(variable)
<sup><i>a</i></sup> R, R', alkyl groups; Ar, aromatic group (not argon).		

<sup>a</sup>R, R', alkyl groups; Ar, aromatic group (not argon).



Type of carbon	Chemical shift $\delta$ (ppm)
Primary alkyl, RCH <sub>3</sub>	5–20
Secondary alkyl, RCH <sub>2</sub> R'	20-30
Tertiary alkyl, R <sub>3</sub> CH	30-50
Quaternary alkyl, R <sub>4</sub> C	30-45
Allylic, $R_2C = CCH_2R'$	20-40
 R″	
Chloroalkane, RCH <sub>2</sub> Cl	25-50
Bromoalkane, RCH <sub>2</sub> Br	20-40
Ether or alcohol, $RCH_2OR'$ or $RCH_2OH$	50-90
Carboxylic acids, RCOOH	170-180
O O 	
Aldehyde or ketone, $\mathbf{RCH}$ or $\mathbf{RCR}'$	190–210
Alkene, aromatic, $R_2C = CR_2$	100–160
Alkyne, $RC \equiv CR$	65–95
$\begin{array}{c c} R \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	$\begin{array}{c} RCH_2Br \\ RCH_2Cl \\ RCH_2OR' \text{ or } \\ RCH_2OH \\ R'' \\ R_4C \\ R_3CH \end{array}$
220 210 200 190 180 170 160 150 140 130 120 F	$RC \equiv CR$ $RCH_2R'$ $RCH_3$



Bond strengths (kcal/mol):

$\begin{array}{cccccc} {\rm Cl-Cl} & 58 \\ {\rm Br-Br} & 46 \\ {\rm I-I} & 36 \\ {\rm H-F} & 136 \\ {\rm H-Cl} & 103 \\ {\rm H-Br} & 87 \\ {\rm H-I} & 71 \\ {\rm CH}_3-{\rm H} & 105 \\ {\rm CH}_3{\rm CH}_2-{\rm H} & 101 \\ ({\rm CH}_3)_2{\rm CH-{\rm H}} & 98.5 \\ ({\rm CH}_3)_3{\rm C-{\rm H}} & 96.5 \\ {\rm CH}_3-{\rm F} & 110 \\ {\rm CH}_3-{\rm Cl} & 85 \\ {\rm CH}_3-{\rm Rr} & 70 \\ {\rm CH}_3-{\rm I} & 57 \\ {\rm CH}_3{\rm CH}_2-{\rm F} & 111 \\ {\rm CH}_3{\rm CH}_2-{\rm F} & 111 \\ {\rm CH}_3{\rm CH}_2-{\rm Rr} & 70 \\ {\rm CH}_3{\rm CH}_2-{\rm I} & 56 \\ ({\rm CH}_3)_2{\rm CH-{\rm F}} & 111 \\ ({\rm CH}_3)_2{\rm CH-{\rm F}} & 111 \\ ({\rm CH}_3)_2{\rm CH-{\rm F}} & 111 \\ ({\rm CH}_3)_2{\rm CH-{\rm Cl}} & 84 \\ \end{array}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$\begin{array}{ccccccc} H-F & 136 \\ H-Cl & 103 \\ H-Br & 87 \\ H-I & 71 \\ CH_3-H & 105 \\ CH_3CH_2-H & 101 \\ (CH_3)_2CH-H & 98.5 \\ (CH_3)_3C-H & 96.5 \\ CH_3-F & 110 \\ CH_3-Cl & 85 \\ CH_3-Br & 70 \\ CH_3-I & 57 \\ CH_3CH_2-F & 111 \\ CH_3CH_2-F & 111 \\ CH_3CH_2-Cl & 84 \\ CH_3CH_2-Br & 70 \\ CH_3CH_2-I & 56 \\ (CH_3)_2CH-F & 111 \\ \end{array}$
$\begin{array}{ccccc} H-Cl & 103 \\ H-Br & 87 \\ H-I & 71 \\ CH_3-H & 105 \\ CH_3CH_2-H & 101 \\ (CH_3)_2CH-H & 98.5 \\ (CH_3)_3C-H & 96.5 \\ CH_3-F & 110 \\ CH_3-Cl & 85 \\ CH_3-Br & 70 \\ CH_3-I & 57 \\ CH_3CH_2-F & 111 \\ CH_3CH_2-Cl & 84 \\ CH_3CH_2-Br & 70 \\ CH_3CH_2-I & 56 \\ (CH_3)_2CH-F & 111 \\ \end{array}$
$\begin{array}{ccccc} H-Br & 87 \\ H-I & 71 \\ CH_3-H & 105 \\ CH_3CH_2-H & 101 \\ (CH_3)_2CH-H & 98.5 \\ (CH_3)_3C-H & 96.5 \\ CH_3-F & 110 \\ CH_3-Cl & 85 \\ CH_3-Br & 70 \\ CH_3-I & 57 \\ CH_3CH_2-F & 111 \\ CH_3CH_2-Cl & 84 \\ CH_3CH_2-Br & 70 \\ CH_3CH_2-I & 56 \\ (CH_3)_2CH-F & 111 \\ \end{array}$
$\begin{array}{ccccc} H - I & 71 \\ CH_3 - H & 105 \\ CH_3 CH_2 - H & 101 \\ (CH_3)_2 CH - H & 98.5 \\ (CH_3)_3 C - H & 96.5 \\ CH_3 - F & 110 \\ CH_3 - Cl & 85 \\ CH_3 - Br & 70 \\ CH_3 - I & 57 \\ CH_3 CH_2 - F & 111 \\ CH_3 CH_2 - F & 111 \\ CH_3 CH_2 - Cl & 84 \\ CH_3 CH_2 - I & 56 \\ (CH_3)_2 CH - F & 111 \\ \end{array}$
$\begin{array}{cccccc} CH_3-H & 105\\ CH_3CH_2-H & 101\\ (CH_3)_2CH-H & 98.5\\ (CH_3)_3C-H & 96.5\\ CH_3-F & 110\\ CH_3-Cl & 85\\ CH_3-Br & 70\\ CH_3-I & 57\\ CH_3CH_2-F & 111\\ CH_3CH_2-F & 111\\ CH_3CH_2-Cl & 84\\ CH_3CH_2-Br & 70\\ CH_3CH_2-I & 56\\ (CH_3)_2CH-F & 111\\ \end{array}$
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$\begin{array}{ccccc} (CH_3)_2CH-H & 98.5 \\ (CH_3)_3C-H & 96.5 \\ CH_3-F & 110 \\ CH_3-Cl & 85 \\ CH_3-Br & 70 \\ CH_3-I & 57 \\ CH_3CH_2-F & 111 \\ CH_3CH_2-Cl & 84 \\ CH_3CH_2-Br & 70 \\ CH_3CH_2-I & 56 \\ (CH_3)_2CH-F & 111 \\ \end{array}$
$\begin{array}{ccccc} (CH_3)_3C-H & 96.5 \\ CH_3-F & 110 \\ CH_3-Cl & 85 \\ CH_3-Br & 70 \\ CH_3-I & 57 \\ CH_3CH_2-F & 111 \\ CH_3CH_2-Cl & 84 \\ CH_3CH_2-Br & 70 \\ CH_3CH_2-I & 56 \\ (CH_3)_2CH-F & 111 \\ \end{array}$
$\begin{array}{cccc} CH_3 - F & 110 \\ CH_3 - Cl & 85 \\ CH_3 - Br & 70 \\ CH_3 - I & 57 \\ CH_3 CH_2 - F & 111 \\ CH_3 CH_2 - Cl & 84 \\ CH_3 CH_2 - Br & 70 \\ CH_3 CH_2 - I & 56 \\ (CH_3)_2 CH - F & 111 \\ \end{array}$
$\begin{array}{cccc} CH_3-Cl & 85 \\ CH_3-Br & 70 \\ CH_3-I & 57 \\ CH_3CH_2-F & 111 \\ CH_3CH_2-Cl & 84 \\ CH_3CH_2-Br & 70 \\ CH_3CH_2-I & 56 \\ (CH_3)_2CH-F & 111 \\ \end{array}$
$\begin{array}{cccc} CH_3 - Br & 70 \\ CH_3 - I & 57 \\ CH_3 CH_2 - F & 111 \\ CH_3 CH_2 - Cl & 84 \\ CH_3 CH_2 - Br & 70 \\ CH_3 CH_2 - I & 56 \\ (CH_3)_2 CH - F & 111 \\ \end{array}$
$\begin{array}{cccc} CH_{3}\text{-}I & 57 \\ CH_{3}CH_{2}\text{-}F & 111 \\ CH_{3}CH_{2}\text{-}Cl & 84 \\ CH_{3}CH_{2}\text{-}Br & 70 \\ CH_{3}CH_{2}\text{-}I & 56 \\ (CH_{3})_{2}CH\text{-}F & 111 \\ \end{array}$
$\begin{array}{ccc} CH_{3}CH_{2}-F & 111 \\ CH_{3}CH_{2}-Cl & 84 \\ CH_{3}CH_{2}-Br & 70 \\ CH_{3}CH_{2}-I & 56 \\ (CH_{3})_{2}CH-F & 111 \\ \end{array}$
CH <sub>3</sub> CH <sub>2</sub> -Cl         84           CH <sub>3</sub> CH <sub>2</sub> -Br         70           CH <sub>3</sub> CH <sub>2</sub> -I         56           (CH <sub>3</sub> ) <sub>2</sub> CH-F         111
$\begin{array}{ccc} CH_{3}CH_{2}-Br & 70 \\ CH_{3}CH_{2}-I & 56 \\ (CH_{3})_{2}CH-F & 111 \end{array}$
CH <sub>3</sub> CH <sub>2</sub> -I 56 (CH <sub>3</sub> ) <sub>2</sub> CH-F 111
(CH <sub>3</sub> ) <sub>2</sub> CH-F 111
(CH <sub>3</sub> ) <sub>2</sub> CH-Cl 84
(0.1.5)/2011 01
(CH <sub>3</sub> ) <sub>2</sub> CH-Br 71
(CH <sub>3</sub> ) <sub>2</sub> CH-I 56
(CH <sub>3</sub> ) <sub>3</sub> C-F 110
(CH <sub>3</sub> ) <sub>3</sub> C-Cl 85
(CH <sub>3</sub> ) <sub>3</sub> C-Br 71
(CH <sub>3</sub> ) <sub>3</sub> C-I 55

