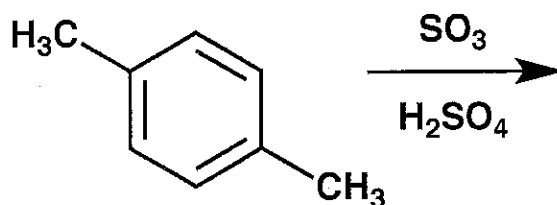


General Instructions:

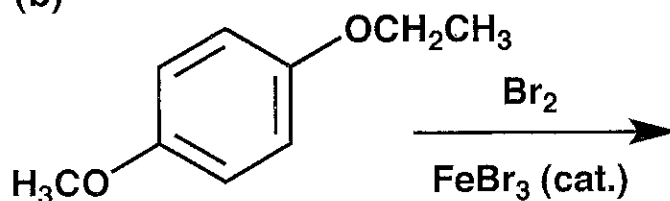
- (i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit. Models are allowed.
- (ii) Print your name on each page.
- (iii) Please keep your paper covered and your eyes on your own work. No electronic devices may be used. Misconduct will lead to failure in the course.

1. (17 points) Show the product(s) expected from the reactions indicated below.

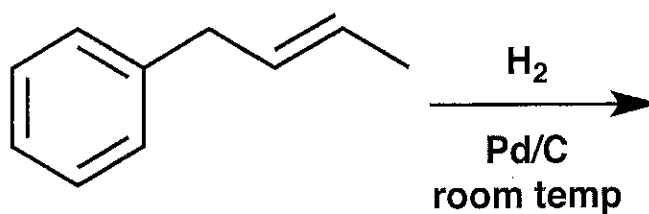
(a)



(b)



(c)



Name _____

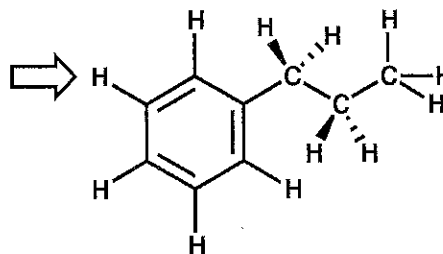
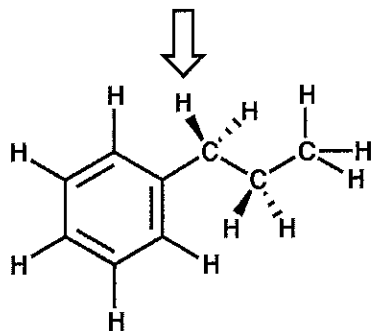
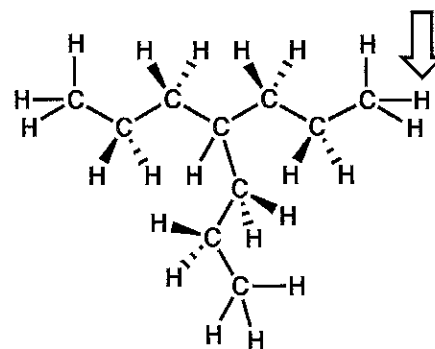
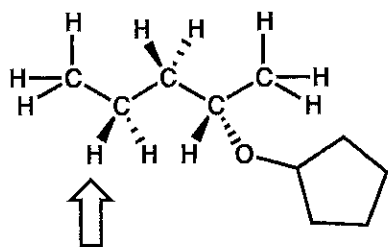
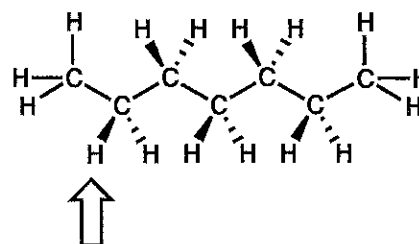
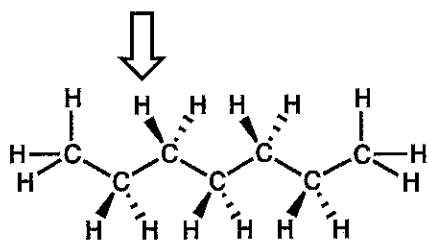
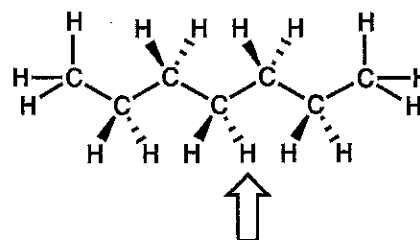
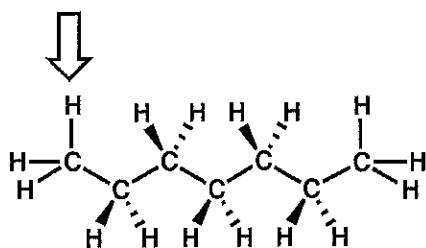
2. (15 points)

For each molecular drawing below, with reference to the H indicated by the arrow, and label other H's as indicated...

...Put a CIRCLE around any homotopic H's.

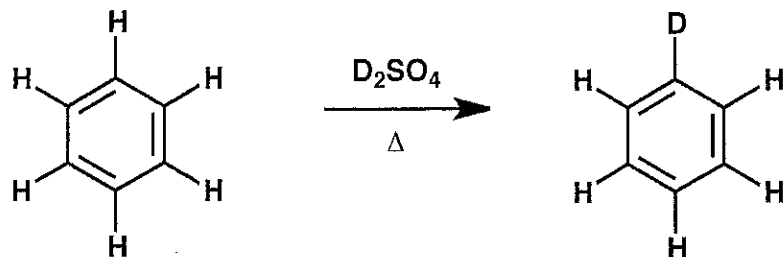
...Put a TRIANGLE around any enantiotopic H's.

...Put a SQUARE around any diastereotopic H's.



Name _____

3. (16 points) If benzene is heated with D_2SO_4 (D is deuterium), H atoms on the ring are slowly replaced with D. Shown below is the result of a single replacement.

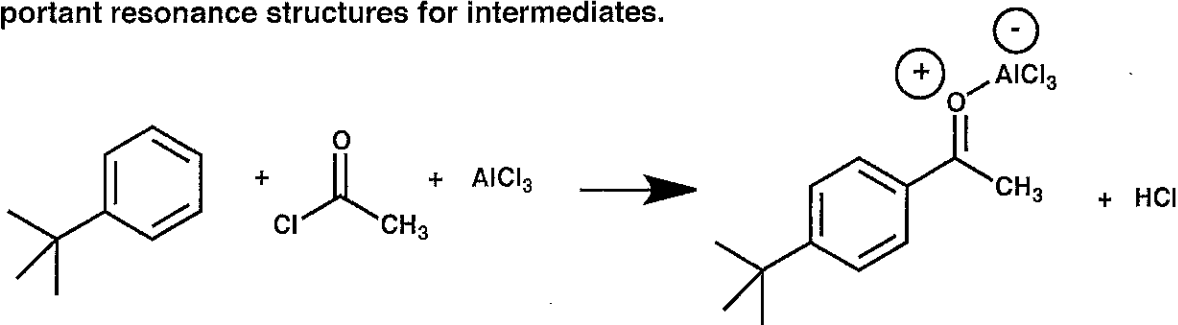


(a) This reaction is an example of electrophilic aromatic substitution. Draw the cationic intermediate for formation of the mono-deuterated product shown above (all resonance structures).

(b) Under special conditions, this intermediate is stable enough that a proton NMR spectrum can be obtained. Below, indicate in the box how many types of H resonances you expect for this intermediate (don't worry about splitting). In the space below the box, provide a drawing of this intermediate in which all H's are shown and for which you indicate each set of magnetically equivalent H's with a distinct symbol (circles, squares, triangles, crosses, etc.).

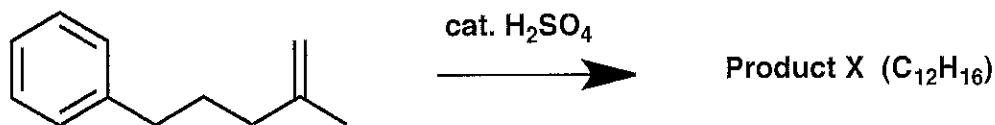
Number of proton resonances =

4. (17 points) We have learned that an acyl group can be added to an aromatic ring via a two-step procedure ("Friedel-Crafts acylation"). Shown below is an example of the first step in such a procedure; the second step involves addition of water to generate the final product. Provide a mechanism (curved arrows) for the reaction shown below. Draw all important resonance structures for intermediates.



Name _____

5. (7 points) Propose a structure for product X formed in the reaction shown below. Your proposal should be consistent with the available data.



The ¹H NMR spectrum of the starting material includes the following features:

Three resonances in the range δ7-8, with a 1:2:2 integration ratio

Two resonances in the range δ5-6, each with integration for 1 H

Several resonances in the range δ0-2, with integration for a total of 9 H.

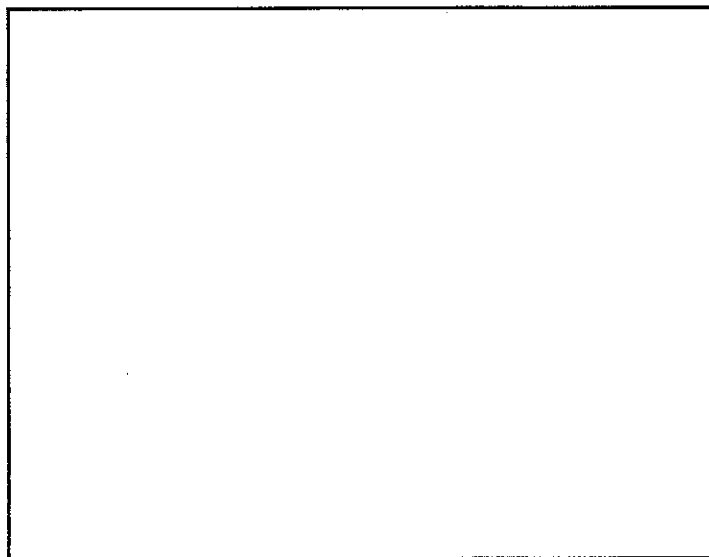
The ¹H NMR spectrum of product X includes the following features:

Four resonances in the range δ7-8, each with integration for 1 H

No resonances in the range δ5-6

Several resonances in the range δ0-2, including a singlet with integration for 6 H and other resonances with integration for a total of 6 H.

X =



Name _____

6. (28 points) For each of the molecules indicated, place as many of the indicated numerals as appropriate on the line below the structure

1 = Consistent with an IR signal at 3400 cm^{-1}

2 = Consistent with an IR signal at 3300 cm^{-1}

3 = Consistent with an IR signal at 3050 cm^{-1}

4 = ^{13}C NMR spectrum contains 3 resonances

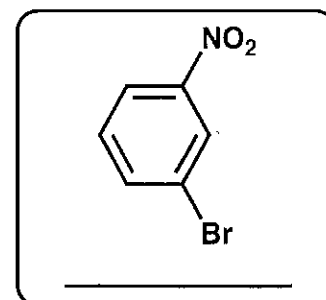
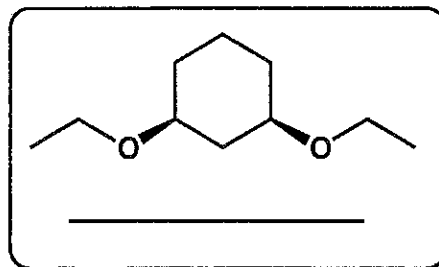
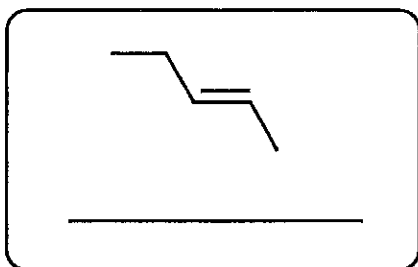
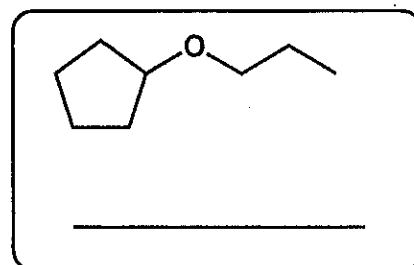
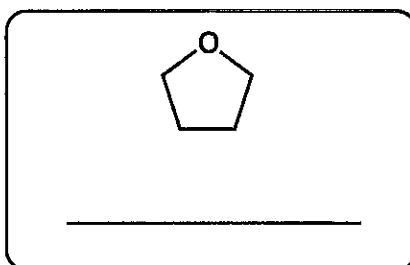
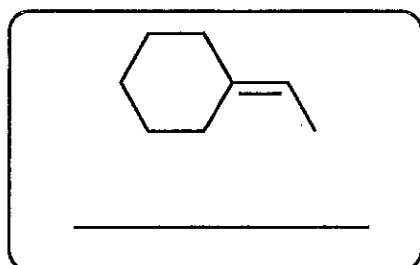
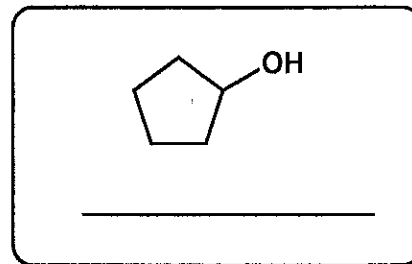
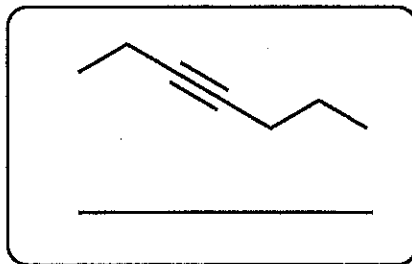
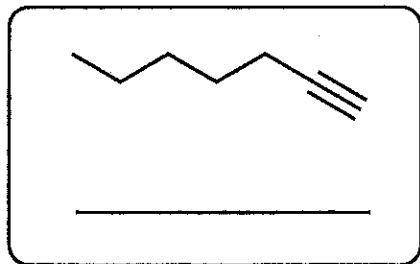
5 = ^{13}C NMR spectrum contains 6 resonances

6 = ^{13}C NMR spectrum contains 7 resonances

7 = One ^1H resonance disappears after the sample is shaken with a few drops of D_2O

8 = One ^1H NMR resonance in the range $\delta 4.5\text{-}6.0$; all other resonances $\delta < 2.5$

9 = ^1H NMR spectrum is two triplets, one at $\delta 3.7$ and the other at $\delta 1.8$



<u>Problem #</u>	<u>Score</u>
1	/ 17
2	/ 15
3	/ 16
4	/ 17
5	/ 7
6	/ 28

Total: / 100



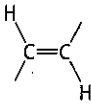


Periodic Table of the Elements

		¹ H 1.008																		² He 4.003	
³ Li 6.94	⁴ Be 9.01															⁹ F 19.00	¹⁰ Ne 20.18				
¹¹ Na 22.99	¹² Mg 24.31															¹⁷ Cl 35.45	¹⁸ Ar 39.95				
¹⁹ K 39.10	²⁰ Ca 40.08	²¹ Sc 44.96	²² Ti 47.90	²³ V 50.94	²⁴ Cr 52.00	²⁵ Mn 54.94	²⁶ Fe 55.85	²⁷ Co 58.93	²⁸ Ni 58.71	²⁹ Cu 63.55	³⁰ Zn 65.37	³¹ Ga 69.72	³² Ge 72.59	³³ As 74.92	³⁴ Se 78.96	³⁵ Br 79.90	³⁶ Kr 83.80				
³⁷ Rb 85.47	³⁸ Sr 87.62	³⁹ Y 88.91	⁴⁰ Zr 91.22	⁴¹ Nb 92.91	⁴² Mo 95.94	⁴³ Tc 98.91	⁴⁴ Ru 101.07	⁴⁵ Rh 102.91	⁴⁶ Pd 106.4	⁴⁷ Ag 107.87	⁴⁸ Cd 112.40	⁴⁹ In 114.82	⁵⁰ Sn 118.69	⁵¹ Sb 121.75	⁵² Te 127.60	⁵³ I 126.90	⁵⁴ Xe 131.30				
⁵⁵ Cs 132.91	⁵⁶ Ba 137.34	⁵⁷ La 138.91	⁷² Hf 178.49	⁷³ Ta 180.95	⁷⁴ W 183.85	⁷⁵ Re 186.2	⁷⁶ Os 190.2	⁷⁷ Ir 192.2	⁷⁸ Pt 195.09	⁷⁹ Au 196.97	⁸⁰ Hg 200.59	⁸¹ Tl 204.37	⁸² Pb 207.19	⁸³ Bi 208.98	⁸⁴ Po (209)	⁸⁵ At (210)	⁸⁶ Rn (222)				
⁸⁷ Fr (223)	⁸⁸ Ra 226.03	⁸⁹ Ac (227)	¹⁰⁴ Unq* (261)	¹⁰⁵ Unp* (262)	¹⁰⁶ Unh* (263)	¹⁰⁷ Uns* (262)	¹⁰⁸ Uno* (263)	¹⁰⁹ Una* (266)													

Lanthanides		⁵⁸ Ce 140.12	⁵⁹ Pr 140.91	⁶⁰ Nd 144.24	⁶¹ Pm (145)	⁶² Sm 150.35	⁶³ Eu 151.96	⁶⁴ Gd 157.25	⁶⁵ Tb 158.93	⁶⁶ Dy 162.50	⁶⁷ Ho 164.93	⁶⁸ Er 167.26	⁶⁹ Tm 168.93	⁷⁰ Yb 173.04	⁷¹ Lu 174.97
Actinides		⁹⁰ Th 232.04	⁹¹ Pa (231)	⁹² U 238.03	⁹³ Np (237)	⁹⁴ Pu (244)	⁹⁵ Am (243)	⁹⁶ Cm (247)	⁹⁷ Bk (249)	⁹⁸ Cf (249)	⁹⁹ Es (254)	¹⁰⁰ Fm (257)	¹⁰¹ Md (258)	¹⁰² No (259)	¹⁰³ Lr (260)

*Symbol (and name) provisional.

Numbers in parentheses: available radioactive isotope of longest half-life.

Type of absorption	Frequency, cm^{-1} (Intensity)*	Comment
Alkanes		
C—H stretch	2850–3000 (m)	occurs in all compounds with aliphatic C—H bonds
Alkenes		
C=C stretch —CH=CH ₂	1640 (m)	
	1655 (m)	
others	1660–1675 (w)	not observed if alkene is symmetrical
=C—H stretch	3000–3100 (m)	
=C—H bend		
—CH=CH ₂	910–990 (s)	
	890 (s)	
	960–980 (s)	
	675–730 (s)	position is highly variable
	800–840 (s)	
Alcohols and Phenols		
O—H stretch	3200–3400 (s)	
C—O stretch	1050–1250 (s)	also present in other compounds with C—O bonds: ethers, esters, etc.
Alkynes		
C≡C stretch	2100–2200 (m)	not present or weak in many internal alkynes
≡C—H stretch	3300 (s)	present in 1-alkynes only
Aromatic Compounds		
C=C stretch	1500, 1600 (s)	two absorptions
C—H bend	650–750 (s)	
overtone	1660–2000 (w)	

* (s) = strong; (m) = medium; (w) = weak.

(Table continues)

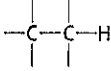


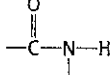

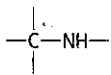

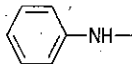

Type of absorption	Frequency, cm^{-1} (Intensity)*	Comment
Aldehydes		
C=O stretch		
ordinary	1720–1725 (s)	
α,β -unsaturated	1680–1690 (s)	
benzaldehydes	1700 (s)	
C—H stretch	2720 (m)	
Ketones		
C=O stretch		
ordinary	1710–1715 (s)	increases with decreasing ring size (Table 21.3, p. 996)
α,β -unsaturated	1670–1680 (s)	
aryl ketones	1680–1690 (s)	
Carboxylic Acids		
C=O stretch		
ordinary	1710 (s)	
benzoic acids	1680–1690 (s)	
O—H stretch	2400–3000 (s)	very broad
Esters and Lactones		
C=O stretch	1735–1745 (s)	increases with decreasing ring size (Table 21.3, p. 996)
Acid Chlorides		
C=O stretch	1800 (s)	a second weaker band sometimes observed at 1700–1750
Anhydrides		
C=O stretch	1760, 1820 (s)	two bands; increases with decreasing ring size in cyclic anhydrides
Amides and Lactams		
C=O stretch	1650–1655 (s)	increases with decreasing ring size (Table 21.3, p. 996)
N—H bend	1640 (s)	
N—H stretch	3200–3400 (m)	doublet absorption observed for some primary amides
Nitriles		
C \equiv N stretch	2200–2250 (m)	
Amines		
N—H stretch	3200–3375 (m)	several absorptions sometimes observed, especially for primary amines

*(s) = strong; (m) = medium; (w) = weak.

APPENDIX III. PROTON NMR CHEMICAL SHIFTS IN ORGANIC COMPOUNDS

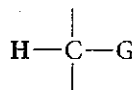
This appendix is subdivided into a table of chemical shifts for protons that are *part of* functional groups and a table of chemical shifts for protons that are *adjacent to* functional groups.

A. Protons within Functional Groups

Group	Chemical shift, ppm	Group	Chemical shift, ppm
	0.7-1.5		9-11
	4.6-5.7		7.5-9.5
	varies with solvent and with acidity of O—H		0.5-1.5
	1.7-2.5		2.5-3.5
	6.5-8.5		




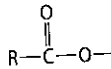
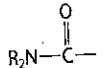
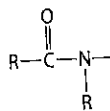
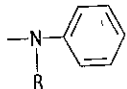
B. Protons Adjacent to Functional Groups

In this table, a range of chemical shifts is given for protons in the general environment



in which G is a group listed in column 1, and the two other bonds are to carbon or hydrogen. The remaining columns give the approximate chemical shifts for methyl protons ($\text{H}_3\text{C}-\text{G}$),



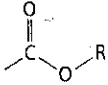
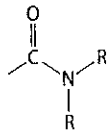
methylene protons ($-\text{CH}_2-\text{G}$), and methine protons ($-\text{CH}-\text{G}$), respectively. The shifts in the following table are typical; some variation with structure of a few tenths of a ppm can be expected. The chemical shifts of methine protons are usually further downfield than those of methylene protons, which are further downfield than methyl protons. Each additional carbon substitution increases the chemical shift by 0.3-1.0 ppm.

Group, G	Chemical shift of $\text{H}_3\text{C}-\text{G}$, ppm	Chemical shift of $-\text{CH}_2-\text{G}$, ppm	Chemical shift of $-\text{CH}-\text{G}$, ppm
$-\text{H}$	0.2		
$-\text{CR}_3$	0.9	1.2	1.4
$-\text{F}$	4.3	4.5	4.8
$-\text{Cl}$	3.0	3.4	4.0
$-\text{Br}$	2.7	3.4	4.1
$-\text{I}$	2.2	3.2	4.2
$-\text{CR}=\text{CR}_2$ (R = H, alkyl)	1.8	2.0	2.3
$-\text{C}\equiv\text{CR}$ (R = alkyl, H)	1.8	2.2	2.8
	2.3	2.6	2.8
$\text{RO}-$ (R = alkyl, H)	3.3 (R = alkyl) 3.5 (R = H)	3.4	3.6
$\text{RO}-$ (R = aryl)	3.7	4.0	4.6
$\text{RS}-$ (R = alkyl, H)	2.4	2.6	3.0
	2.1 (R = alkyl) 2.6 (R = aryl)	2.4 (R = alkyl) 2.7 (R = aryl)	2.6 (R = alkyl) 3.4 (R = aryl)
 (R = alkyl, H)	2.1	2.2	2.5
 (R = alkyl, H)	3.6 (R = alkyl) 3.8 (R = aryl)	4.1 (R = alkyl, aryl)	5.0 (R = alkyl, aryl)
 (R = alkyl, H)	2.0	2.2	2.4
 (R = alkyl, H)	2.8	3.4	3.8
$-\text{NR}_2$ (R = alkyl, H)	2.2	2.4	2.8
 (R = alkyl, H)	2.6	3.1	3.6
$\text{N}\equiv\text{C}-$	2.0	2.4	2.9

APPENDIX IV. ^{13}C NMR CHEMICAL SHIFTS IN ORGANIC COMPOUNDS

This section is divided into a table of chemical shifts for carbons within functional groups and a table of chemical shifts for alkyl carbons adjacent to functional groups. A typical range of shifts is given for each case.

A. Chemical Shifts of Carbons within Functional Groups


Group	Chemical shift range, ppm
$-\text{CH}_3$	8-23
$-\text{CH}_2-$	20-30
$-\text{CH}-$	21-33
$-\text{C}-$	17-29
$\text{C}=\text{C}$	105-150*
$-\text{C}\equiv\text{C}-$	66-93*
	125-150*
	200-220
 R = H, alkyl	170-180
 R = H, alkyl	165-175
$-\text{C}\equiv\text{N}$	110-120

*Alkyl substitution typically increases chemical shift.

B. Chemical Shifts of Carbons Adjacent to Functional Groups

In most cases, alkyl substitution on the carbon increases chemical shift. Methyl carbons will have shifts in the low end of the range; tertiary and quaternary carbons will have shifts in the upper end of the range.

A-8 APPENDICES

Group G	Chemical shift of carbon in G—C—
$R_2C=CR-$	14-40
$HC\equiv C-$	18-28
	29-45
F—	83-91
Cl—	44-68
Br—	32-65
I—	5-42
HO—	62-70
RO— R = alkyl, H	70-79
$R-\overset{\text{O}}{\parallel}{C}-$ R = alkyl, H	43-50
$RO-\overset{\text{O}}{\parallel}{C}-$ R = alkyl, H	33-44
R_2N- R = alkyl, H	41-51 (R = H) 53-60 (R = alkyl)
$N\equiv C-$	16-28

