Hour Exam #1
Chemistry 345
Professor Gellman
18 February 2015
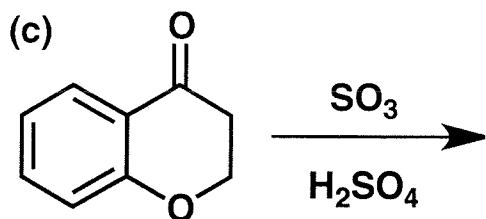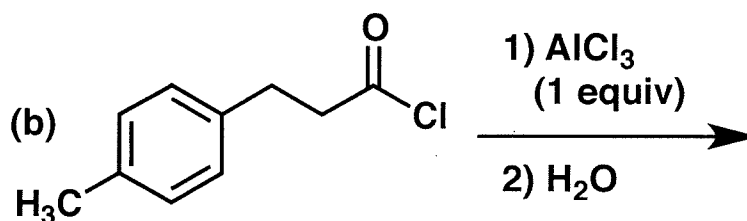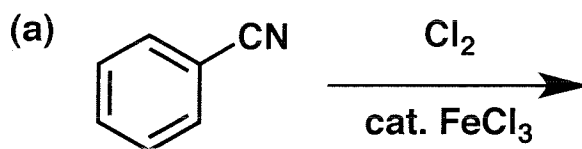
Last Name _____

First Name _____

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

(a)

$$\xrightarrow[\text{cat. FeCl}_3]{\text{Cl}_2}$$

(b)

$$\xrightarrow[\text{2) H}_2\text{O}]{\substack{\text{1) AlCl}_3 \\ \text{(1 equiv)}}}$$

(c)

$$\xrightarrow[\text{H}_2\text{SO}_4]{\text{SO}_3}$$

2. (17 points)

Name _____

For each molecular drawing below, put a circle around sets of H atoms that you expect to be NMR-equivalent to one another (achiral solvent). In many cases you will have to draw in the H atoms yourself. Designate sets of <u>non-equivalent</u> H atoms as "#1", "#2", etc., as illustrated in the example below (propane). (Note: The numerical order (1, 2, etc.) does not matter.)
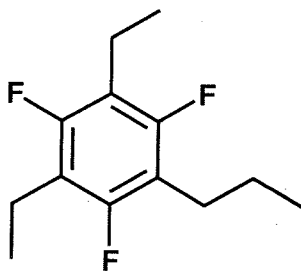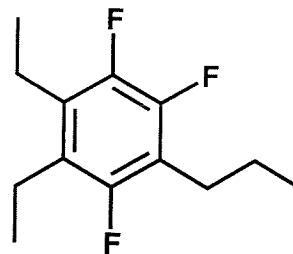
Example:

Answer

#1

#2

(a)

(b)

CH₃

H

CH₃

H

H

H
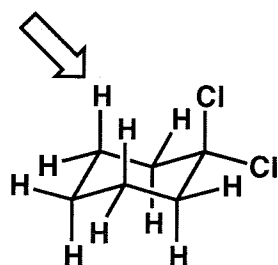
(c)

F

F

F

(d)

F

F

F
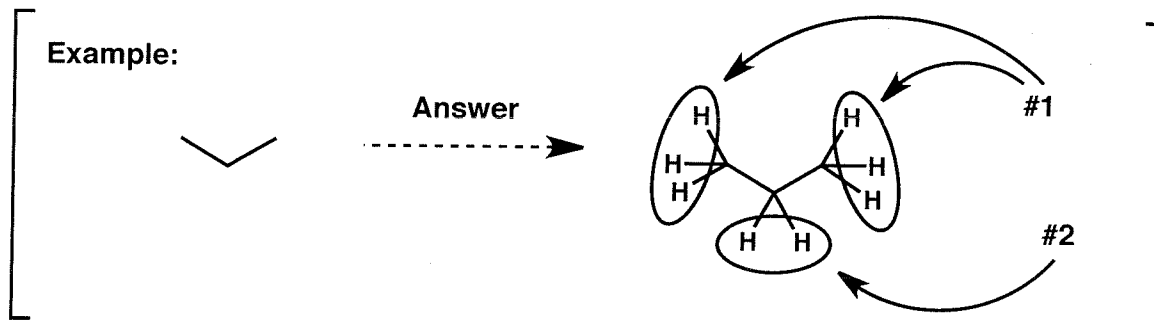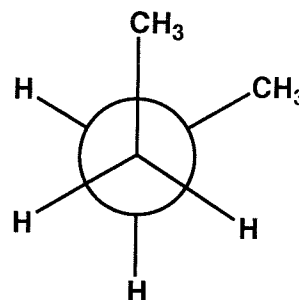
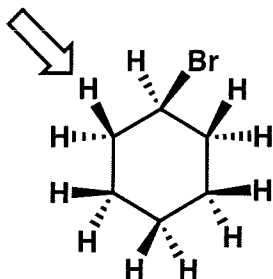## 3. (14 points)

Name _____

For each molecule drawn below, with reference to the H indicated by the arrow, 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.

(Be sure to label only those H's that are appropriate.)
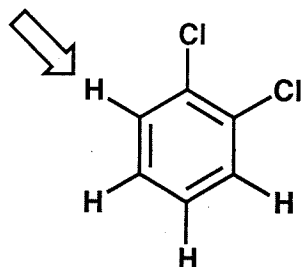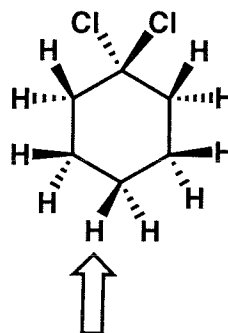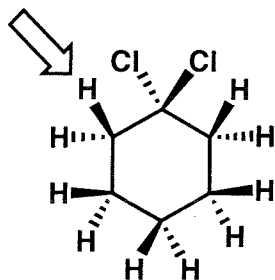
4. (12 points) In class we discussed nitration of aromatic rings with a mixture of HNO_3 and H_2SO_4. Provide a mechanism (curved arrows) for the reaction shown below, which begins <u>after</u> the key electrophile has been generated. Draw all important resonance structures for intermediates.
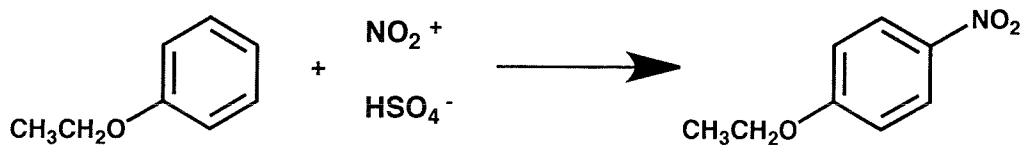
Name _____

5. (12 points) Propose a structure for products A and B formed in the reaction shown below. Your proposal should be consistent with the available data.
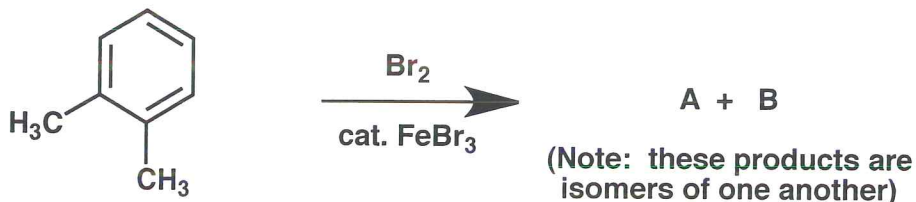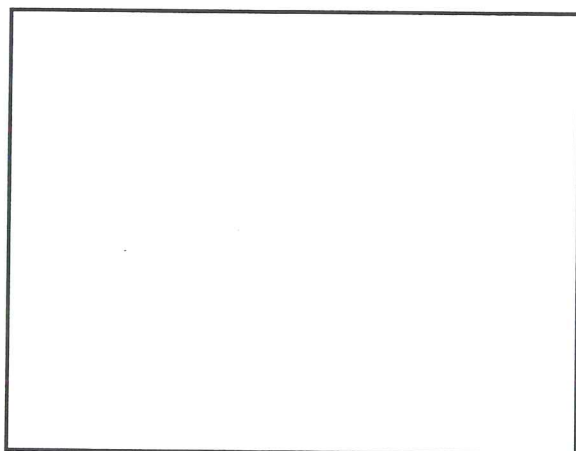
H_3C — [benzene ring with CH₃ substituent] — CH_3

$\xrightarrow[\text{cat. FeBr}_3]{\text{Br}_2}$ A + B

(Note: these products are isomers of one another)

The ^1H NMR spectrum of this molecule has the following features:

A singlet δ2.3

Two doublets in the range δ7-8, coupling constant ~8 Hz.

Singlet integration 3x larger than each doublet integration.

A =

^1H NMR spectrum includes the following:

Two singlets near δ2.3, 1:1 integration

Three resonances in the range δ7-8, each a doublet-of-doublets. For one, both coupling constants are large (~8 Hz); for the other two, one coupling constant is large (~8 Hz) and the other is small (~1 Hz).

B =

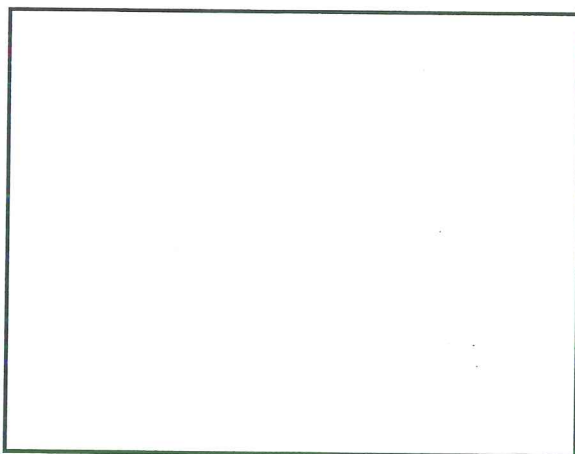^1H NMR spectrum includes the following:

Two singlets near δ2.3, 1:1 integration

Three resonances in the range δ7-8. Two are doublets, one with a large coupling constant (~8 Hz) and the other with a small coupling constant (~1 Hz). The third is a doublet-of-doublets, with one large coupling constant (~8 Hz) and one small (~1 Hz).

Name _____

6. (15 points) For each of the molecules drawn below, place as many of the indicated numerals as appropriate on the line below the structure

1 = IR spectrum contains a strong signal at 1710 cm^{-1}

2 = ^{13}C NMR spectrum contains exactly 2 resonances

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

4 = ^{13}C NMR spectrum contains exactly 7 resonances

5 = ^{13}C NMR spectrum contains exactly 9 resonances

6 = ^{13}C NMR spectrum contains one and only one resonance at $\delta > 200$

7 = All ^{1}H resonances at at $\delta < 3.0$

8 = The only kind of resonance in the ^{1}H NMR spectrum is a singlet

9 = ^{1}H NMR spectrum contains only one triplet and one quartet

_____

_____

_____

_____

_____

_____
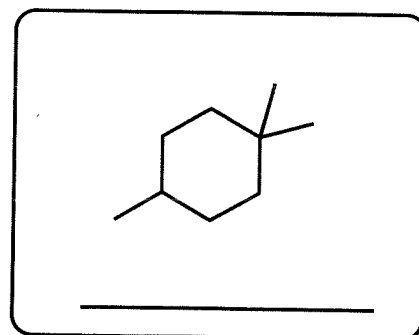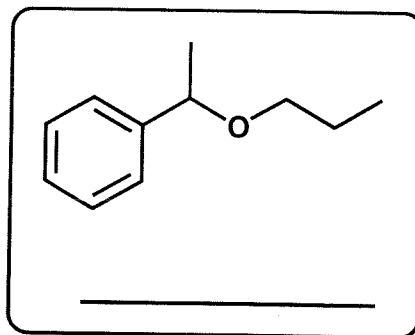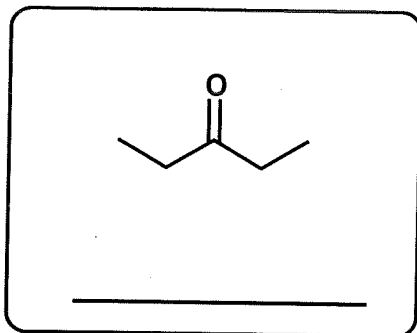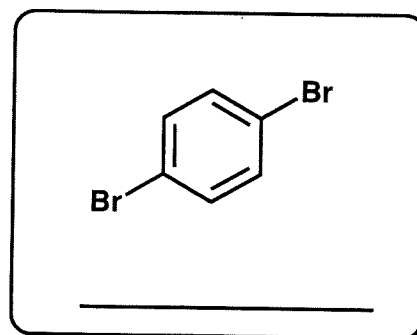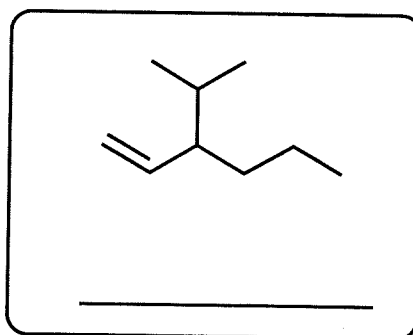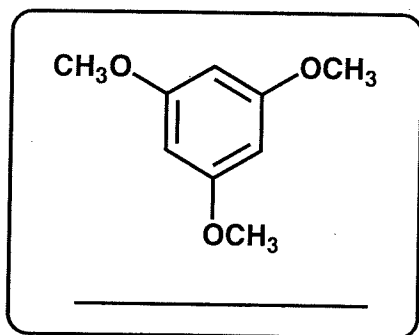
Name _____

7. (12 points) For each set of four molecules shown below, rank them in order of INCREASING reactivity for an electrophilic aromatic substitution reaction (e.g., chlorination).

(a)

A   B   C   D
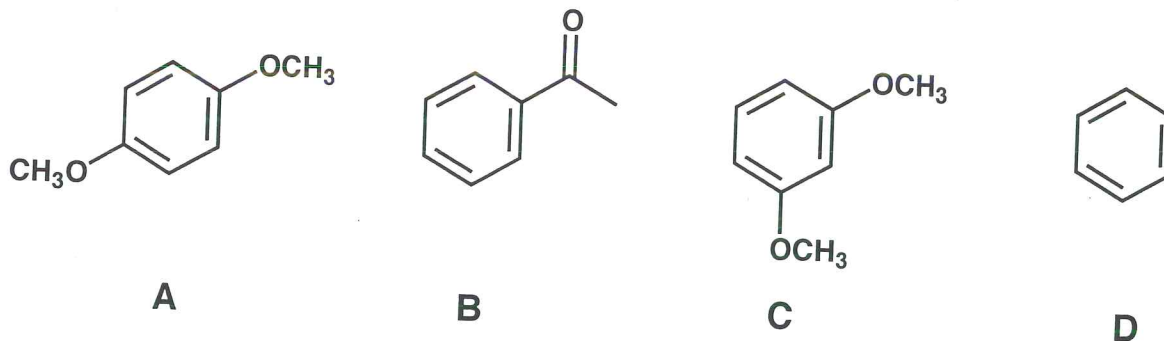
EAS reactivity increases in the order: _____ < _____ < _____ < _____

(b)

A'   B'   C'   D'
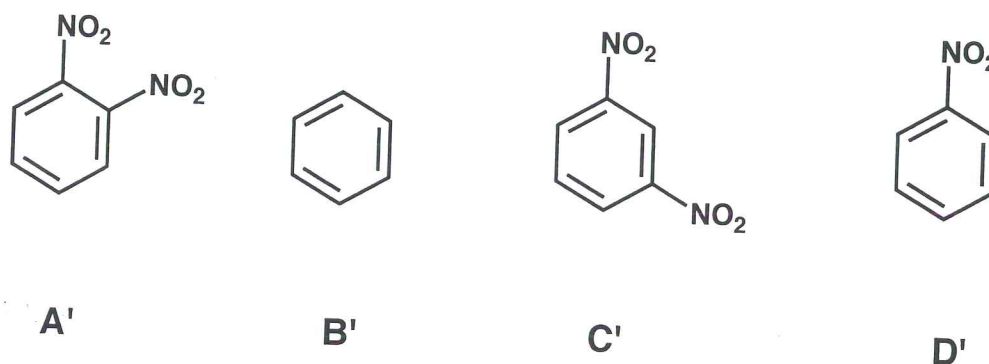
EAS reactivity increases in the order: _____ < _____ < _____ < _____

Periodic Table of the Elements

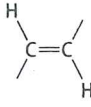| 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.011	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	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*** (265)	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.

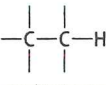| Type of absorption	Frequency, cm^{-1} (Intensity)*	Comment
Alkanes		
C—H stretch	2850–3000 (m)	occurs in all compounds with aliphatic C—H bonds
Alkenes		
C=C stretch —CH=CH$_2$	1640 (m)	
$\diagdown$C=CH$_2$ $\diagup$	1655 (m)	
others	1660–1675 (w)	not observed if alkene is symmetrical
=C—H stretch	3000–3100 (m)	
=C—H bend		
—CH=CH$_2$	910–990 (s)	
$\diagdown$C=CH$_2$ $\diagup$	890 (s)	
H$\diagdown$C=C$\diagup$ $\diagup$ $\diagdown$H	960–980 (s)	
H$\diagdown$ H$\diagup$ C=C $\diagup$ $\diagdown$	675–730 (s)	position is highly variable
H$\diagdown$C=C$\diagup$ $\diagup$ $\diagdown$	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)	

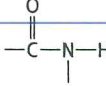*(s) = strong; (m) = medium; (w) = weak.
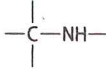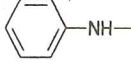
Type of absorption	Frequency, cm^{-1} (Intensity)*	Comment
Aldehydes		
C=O stretch		
ordinary	1720–1725 (s)	
α,β-unsaturated	1680–1690 (s)	
benzaldehydes	1700 (s)	
C—H stretch	2720 (m)	
Ketones		
C=O stretch		
ordinary	1710–1715 (s)	increases with decreasing ring size (Table 21.3, p. 996)
α,β-unsaturated	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≡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
—C—C—H	0.7–1.5	O ‖ —C—H	9–11
C=C (H)	4.6–5.7	O ‖ —C—N—H	7.5–9.5
—O—H	varies with solvent and with acidity of O—H	—C—NH—	0.5–1.5
—C≡C—H	1.7–2.5		
(phenyl)—H	6.5–8.5	(phenyl)—NH—	2.5–3.5

B. Protons Adjacent to Functional Groups

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

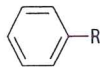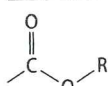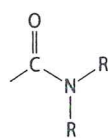$$H-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-G$$
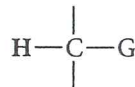
in which G is a group listed in column 1, and the two other bonds are to carbon or hydrogen. The remaining columns give the approximate chemical shifts for methyl protons (H_3C—G),

methylene protons (—CH_2—G), and methine protons (—CH—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 H₃C—G, ppm	Chemical shift of —CH₂—G, ppm	Chemical shift of —CH—G, ppm
—H	0.2		
—CR₃	0.9	1.2	1.4
—F	4.3	4.5	4.8
—Cl	3.0	3.4	4.0
—Br	2.7	3.4	4.1
—I	2.2	3.2	4.2
—CR=CR₂ (R = H, alkyl)	1.8	2.0	2.3
—C≡CR (R = alkyl, H)	1.8	2.2	2.8
(phenyl)	2.3	2.6	2.8
RO— (R = alkyl, H)	3.3 (R = alkyl) 3.5 (R = H)	3.4	3.6
RO— (R = aryl)	3.7	4.0	4.6
RS— (R = alkyl, H)	2.4	2.6	3.0
O‖ R—C—	2.1 (R = alkyl) 2.6 (R = aryl)	2.4 (R = alkyl) 2.7 (R = aryl)	2.6 (R = alkyl) 3.4 (R = aryl)
O‖ RO—C— (R = alkyl, H)	2.1	2.2	2.5
O‖ R—C—O— (R = alkyl, H)	3.6 (R = alkyl) 3.8 (R = aryl)	4.1 (R = alkyl, aryl)	5.0 (R = alkyl, aryl)
O‖ R₂N—C— (R = alkyl, H)	2.0	2.2	2.4
O‖ R—C—N—R (R = alkyl, H)	2.8	3.4	3.8
—NR₂ (R = alkyl, H)	2.2	2.4	2.8
—N(R)phenyl (R = alkyl, H)	2.6	3.1	3.6
N≡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
—CH$_3$	8–23
—CH$_2$—	20–30
—CH—	21–33
—C—	17–29
C=C	105–150*
—C≡C—	66–93*
⬡—R	125–150*
O‖C	200–220
O‖C—O—R R = H, alkyl	170–180
O‖C—N—R R = H, alkyl	165–175
—C≡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$_2$C=CR—		14–40
HC≡C—		18–28
(phenyl)—		29–45
F—		83–91
Cl—		44–68
Br—		32–65
I—		5–42
HO—		62–70
RO—	R = alkyl, H	70–79
R—C(=O)—	R = alkyl, H	43–50
RO—C(=O)—	R = alkyl, H	33–44
R$_2$N—	R = alkyl, H	41–51 (R = H) 53–60 (R = alkyl)
N≡C—		16–28