Hour Exam #1
Chemistry 345
Professor Gellman
17 February 2016

Last Name _____

First Name _____

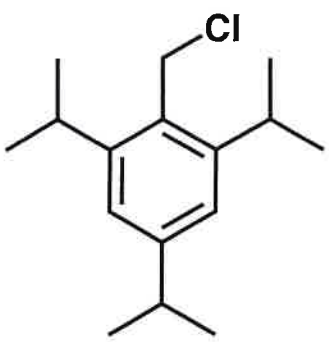
General Instructions:

(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) The resonances observed in the ^{1}H NMR spectrum of the molecule shown below are listed. Draw in all the H atoms on the molecular structure, and indicate which H's give rise to each of the ^{1}H NMR signals in the list (that is, indicate which H's are H_a, which are H_b, etc.).



H_a = Doublet, 6H, δ1.25

H_b = Doublet, 12H, δ1.29

H_c = Septet, 1H, δ2.88

H_d = Septet, 2H, δ3.31

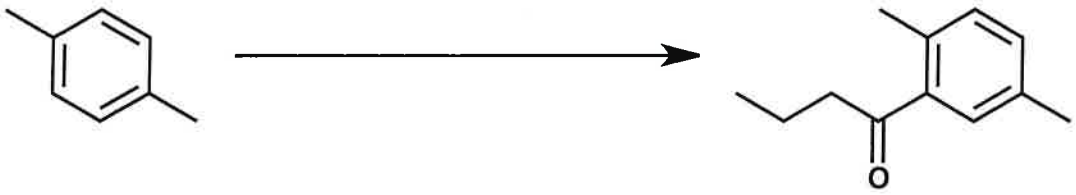
H_e = Singlet, 2H, δ4.75

H_f = Singlet, 2H, 7.02

Name _____

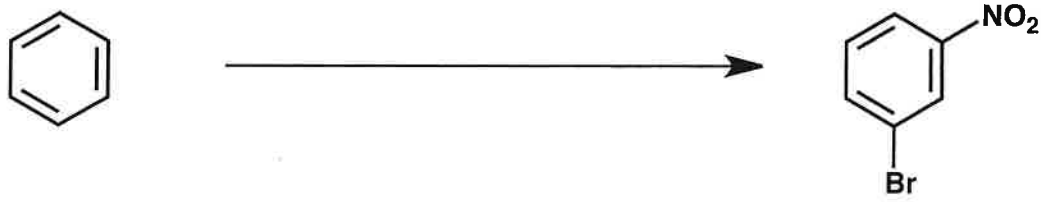
2. (17 points) Show the reagents and other organic molecules required to convert the starting material to the indicated product. Be sure to differentiate clearly between distinct steps, by using "1)", "2)", etc. over or under the arrow.

(a)



(b)

(c)



3. (17 points)

Name _____

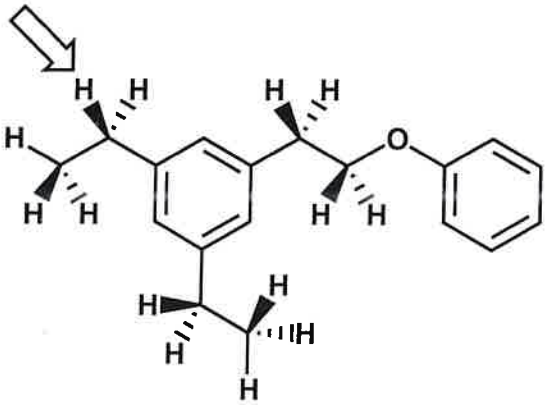
For each molecule drawn below, with reference to the H indicated by the arrow, label other H's as indicated...

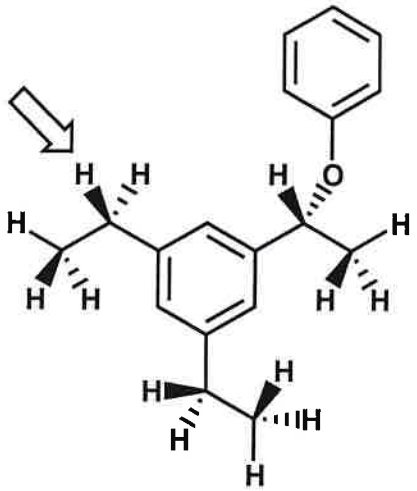
...Put a CIRCLE around any homotopic H's.

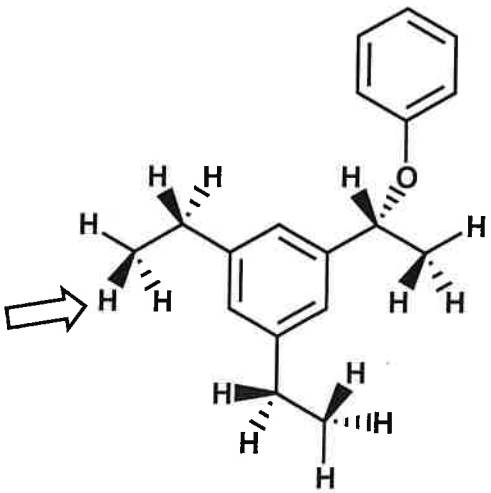
...Put a TRIANGLE around any enantiotopic H's.

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

(Be sure to label only those H's that are appropriate.)

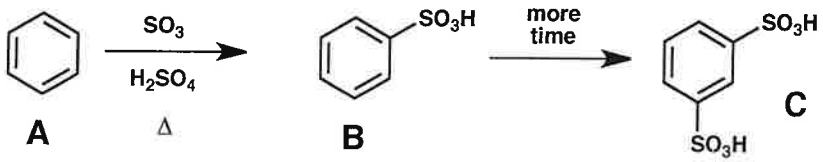


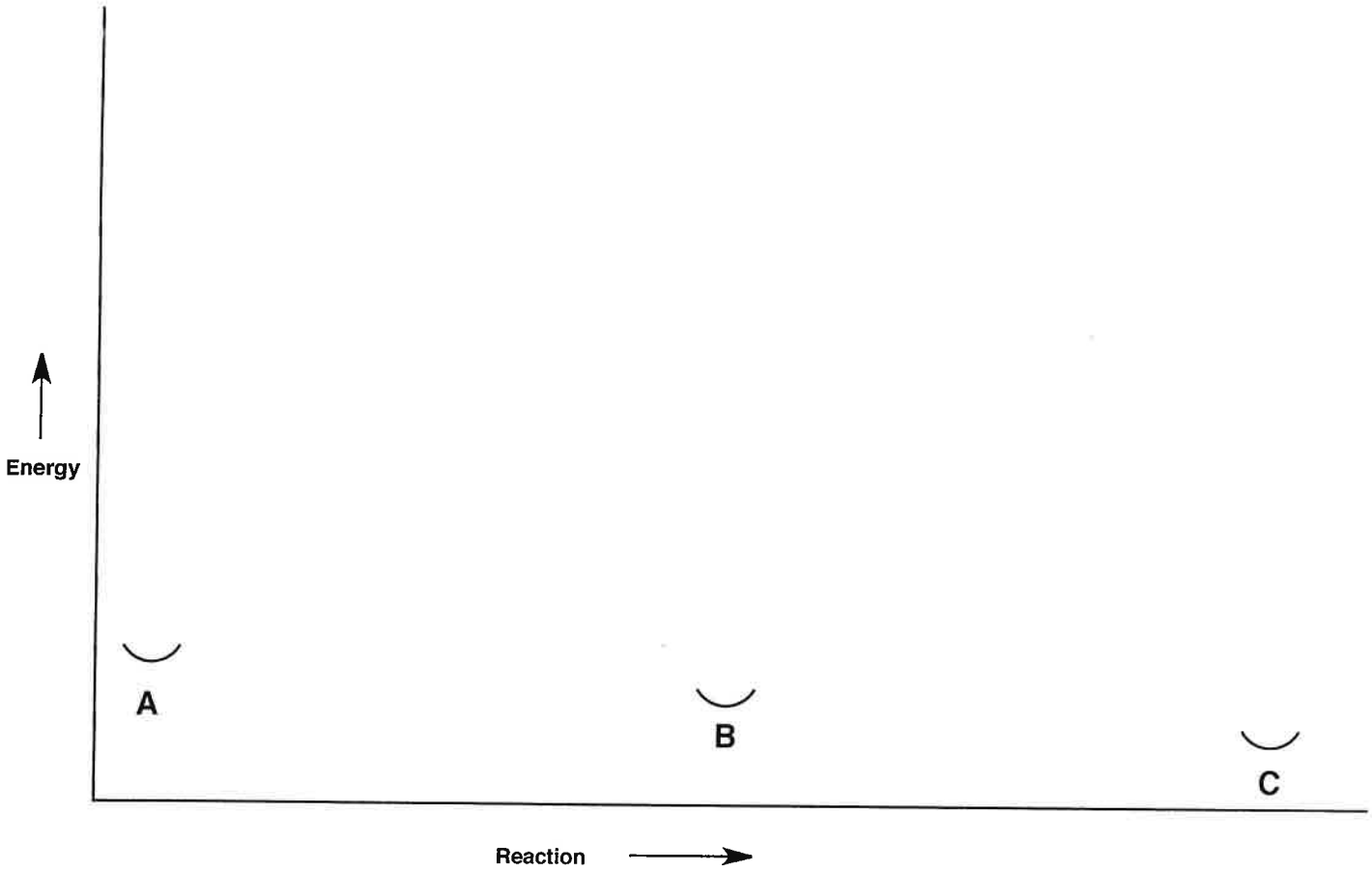




Name _____

4. (11 points) As shown below, reaction of benzene (A) with the indicated reagents and heating initially generates B, but after more time product C is formed. Fill in the reaction energy diagram, given the positions of A, B and C as indicated.





Name _____

5. (22 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 3300 cm^{-1}

2 = IR spectrum contains a strong signal at 1720 cm^{-1}

3 = ^{13}C NMR spectrum contains a total of 3 resonances

4 = ^{13}C NMR spectrum contains a total of 4 resonances

5 = ^{13}C NMR spectrum contains a total of 5 resonances

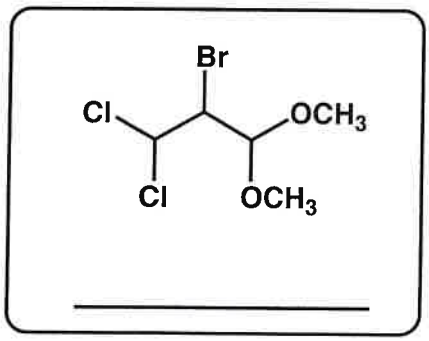
6 = ^{13}C NMR spectrum contains a total of 6 resonances

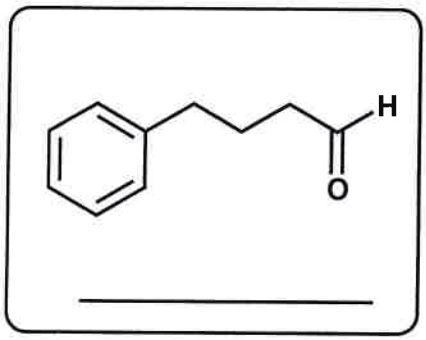
7 = ^{13}C NMR spectrum contains a total of 7 resonances

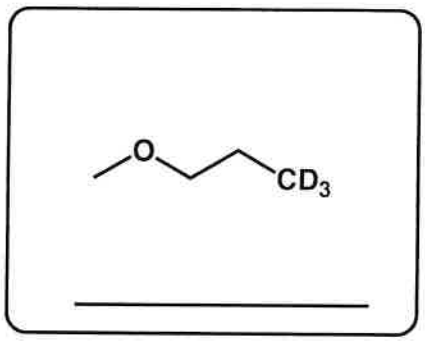
8 = ^{1}H NMR spectrum consists of 2 triplets and 1 singlet

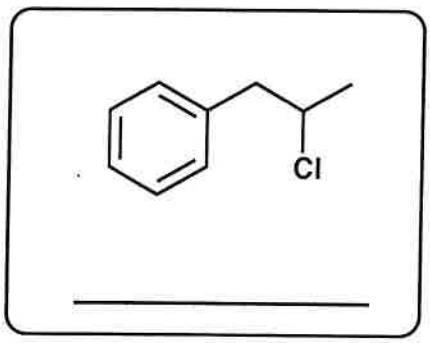
9 = All ^{1}H resonances appear at $\delta > 3.0$

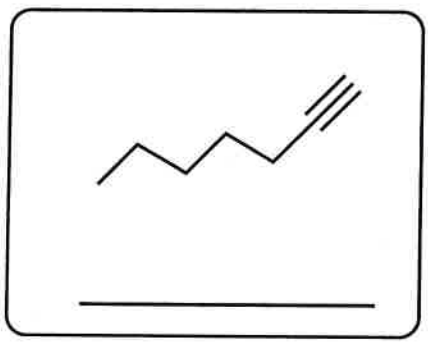
10 = All ^{1}H resonances appear at $\delta < 3.0$

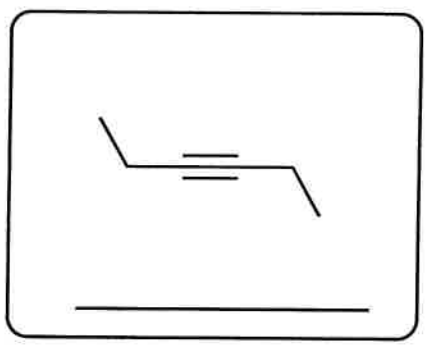












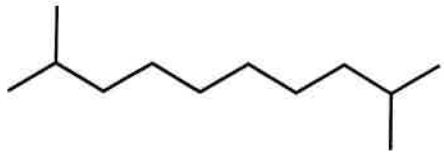
6. (15 points) Name _____

(a) When molecule X is allowed to react with H_2 in the presence of Pd/C, 1 mole of H_2 is consumed per mole of X, and the product is alkane AA, shown below.

The ^{13}C NMR spectrum of molecule X contains a total of 5 resonances; only 1 of these resonances is found above 100 ppm, and the remainder occur below 50 ppm.

The ^{1}H NMR spectrum of molecule X contains a total of 5 resonances (don't worry about the splitting of these resonances), with only 1 resonance above 4 ppm; the remainder are below 2.5 ppm.

Propose two possible structures for molecule X (in the boxes).

AA = 

(b) When molecule Z is allowed to react with H_2 in the presence of Pd/C, 1 mole of H_2 is consumed per mole of Z, and the product is alkane AA, shown above.

The ^{13}C NMR spectrum of molecule Z contains a total of 10 resonances; only 2 of these resonances are found above 100 ppm, and the remainder occur below 50 ppm.

The ^{1}H NMR spectrum of molecule Z contains a total of 10 resonances (don't worry about the splitting of these resonances), with only 1 resonance above 4 ppm; the remainder are below 2.5 ppm.

Propose a structure for molecule Z (in the box).

Name _____

Problem #	Score
1	/ 18
2	/ 17
3	/ 17
4	/ 11
5	/ 22
6	/ 15

_____

Total: / 100

Periodic Table of the Elements

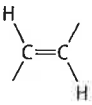
																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.011	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	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.

00147

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)

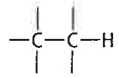
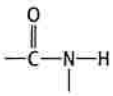
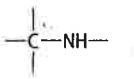
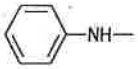
Type of absorption	Frequency, cm^{-1} (Intensity)*	Comment
	Aldehydes	
C=O stretch		
ordinary	1720–1725 (s)	
α,β-unsaturated	1680–1690 (s)	
benzaldehydes	1700 (s)	
C—H stretch	2720 (m)	
	Ketones	
C=O stretch		
ordinary	1710–1715 (s)	increases with decreasing ring size (Table 21.3, p. 996)
α,β-unsaturated	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≡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

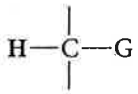
This appendix is subdivided into a table of chemical shifts for protons that are *part of* functional groups and a table of chemical shifts for protons that are *adjacent to* functional groups.

A. Protons within Functional Groups

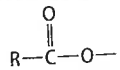
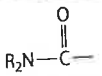
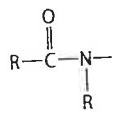
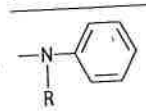
Group	Chemical shift, ppm	Group	Chemical shift, ppm
	0.7–1.5		9–11
	4.6–5.7		7.5–9.5
	varies with solvent and with acidity of O—H		0.5–1.5
	1.7–2.5		
	6.5–8.5		2.5–3.5

B. Protons Adjacent to Functional Groups

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



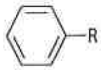
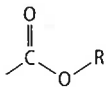
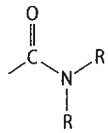
in which G is a group listed in column 1, and the two other bonds are to carbon or hydrogen. The remaining columns give the approximate chemical shifts for methyl protons (H_3C—G), methylene protons (—CH_2—G), and methine protons ( —G), respectively. The shifts in the following table are typical; some 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 H_3C—G, ppm	Chemical shift of —CH_2—G, ppm	Chemical shift of —CH(—)—G, ppm
—H	0.2		
—CR_3	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=CR_2 (R = H, alkyl)	1.8	2.0	2.3
—C≡CR (R = alkyl, H)	1.8	2.2	2.8
	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
	2.1 (R = alkyl) 2.6 (R = aryl)	2.4 (R = alkyl) 2.7 (R = aryl)	2.6 (R = alkyl) 3.4 (R = aryl)
	2.1	2.2	2.5
	3.6 (R = alkyl) 3.8 (R = aryl)	4.1 (R = alkyl, aryl)	5.0 (R = alkyl, aryl)
	2.0	2.2	2.4
	2.8	3.4	3.8
—NR_2 (R = alkyl, H)	2.2	2.4	2.8
	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
		21–33
		17–29
		105–150*
$-C\equiv C-$		66–93*
		125–150*
		200–220
	R = H, alkyl	170–180
	R = H, alkyl	165–175
$-C\equiv N$		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.

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 = alkyl, H	43–50
 R = alkyl, H	33–44
$R_2N{-}$ R = alkyl, H	41–51 (R = H) 53–60 (R = alkyl)
$N{\equiv}C{-}$	16–28