Final Exam
Chemistry 345
Professor Gellman
11 May 2014

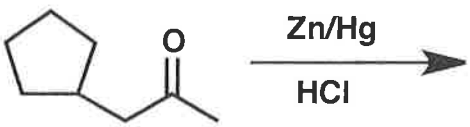
Last Name ____________________

First Name ____________________

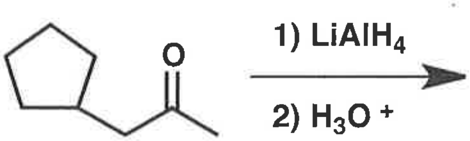
General Instructions:
(i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit. Models are allowed.
(ii) Print your name on each page.
(iii) Please keep your paper covered and your eyes on your own work. Misconduct will lead to failure in the course.

1. (32 points) Show the major product or products expected from each reaction.

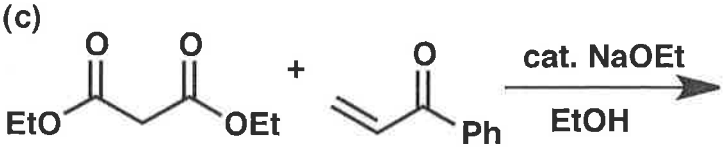
(a)



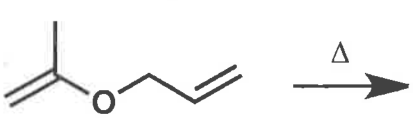
(b)



(c)



(d)



[Hint: The product has a strong IR signal at 1720 cm^{-1}, but the starting material does not.]

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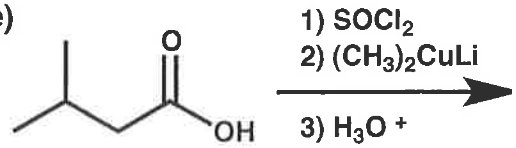
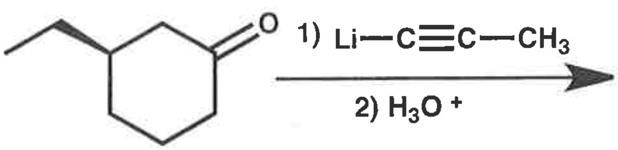
Name ___________________

1. (cont.)

(e)

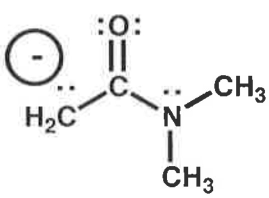


(f)

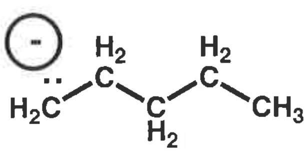


(Single enantiomer)

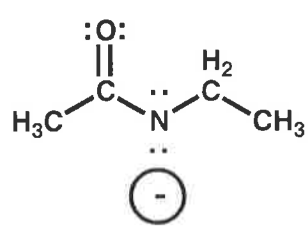
2. (8 points) Rank the four anions below (A, B, C and D) in terms of basicity, with the STRONGEST base on the RIGHT.



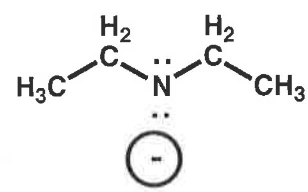
A



B



C



D

INCREASING basicity to the RIGHT:

_________ < _________ < _________ < _________

[Place the letters A, B, C and D in the blanks above, in the proper order.]

Name ______________

3. (30 points) Show the reagents required to convert the starting molecule to the indicated product. If necessary, be sure to differentiate clearly between distinct steps, by using "1)," "2)," etc. over the arrow.

(a)

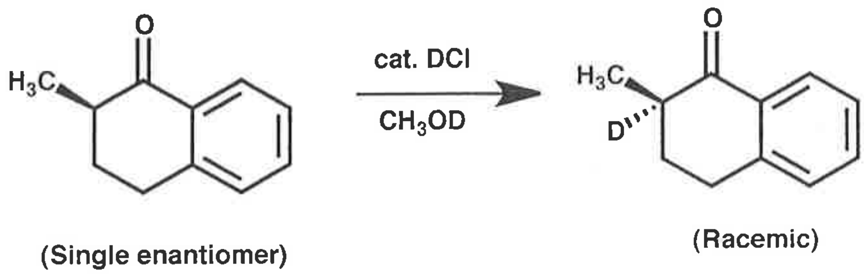
(b)

(c)

(d)

(e)

4. (30 points) Provide a mechanism (curved arrows) for each reaction shown below. Draw all important resonance structures for intermediates.



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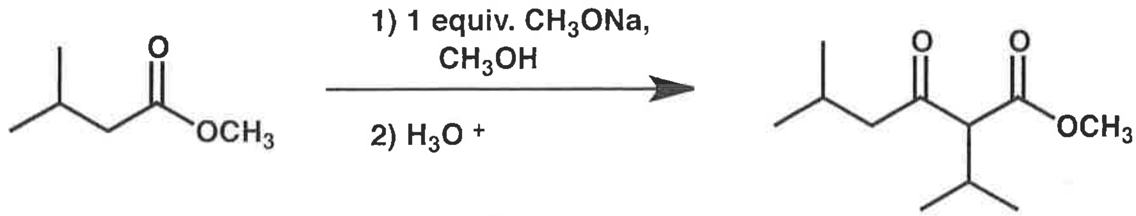
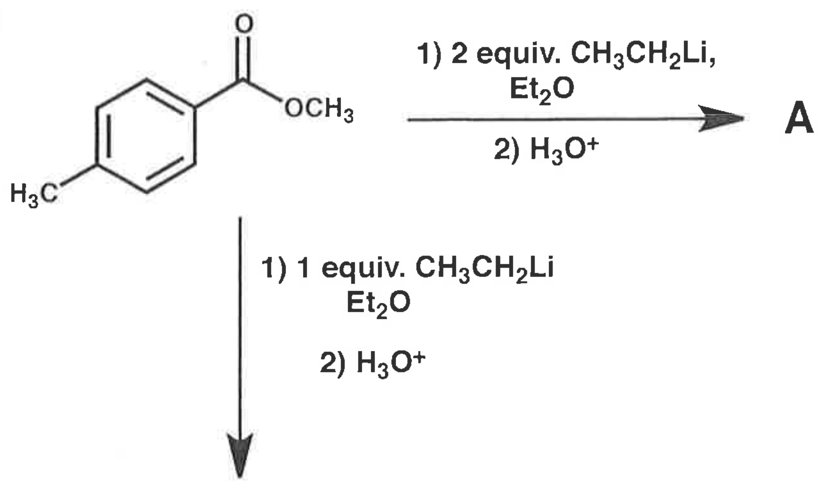
4. (cont.)

(b)



5. (28 points) For each reaction or set of related reactions shown below, draw the structures of the indicated products in the boxes. Your structures must be consistent with the spectroscopic data given for these compounds.

(a)



A + B + recovered starting material

A =

Strong IR signal at 3350 cm^{-1}

No IR signal between 1670 and 1750 cm^{-1}

^{1}H NMR shows one resonance that disappears after shaking with D_2O.

^{1}H NMR resonances that remain after D_2O shake include two doublets that together integrate to 4 H in the range 7-8 ppm, and a triplet and a quartet below 2.5 ppm that together integrate to 10 H.

B =

No IR signal > 3100 cm^{-1}

Strong IR signal at 1685 cm^{-1}

^{1}H NMR resonances include include two doublets that together integrate to 4 H in the range 7-8 ppm, and a triplet and a quartet below 2.5 ppm that together integrate to 5 H. None disappears on shaking with D_2O.

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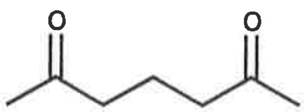
5. (cont.)

(b)



$\xrightarrow{NaOH,\ H_2O}$ C + D

C =

Strong IR signal at 1710 cm^{-1}

Strong IR signal at 3350 cm^{-1}

^1H NMR shows one resonance that disappears after shaking with D_2O.

^1H NMR resonances that remain after D_2O shake are all < 3 ppm.

D =

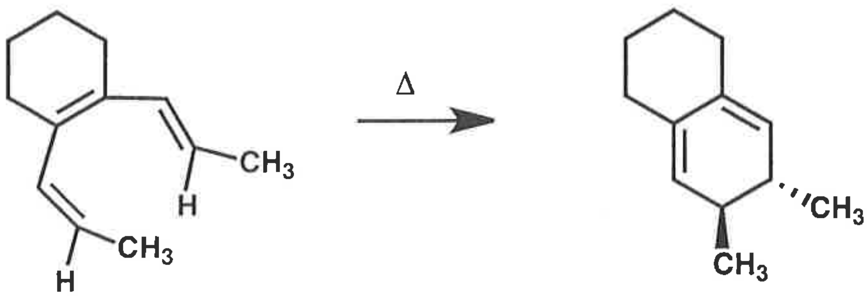
Strong IR signal at 1680 cm^{-1}

No IR signal > 3100 cm^{-1}

^1H NMR resonances include one in the range 4.5-6.0 ppm; the rest are below 3 ppm. None disappears on shaking with D_2O.

6. (15 points) Name ______________ 00232

(a) Provide a mechanism (curved arrows) for the reaction below.



(racemic)

(b) Provide a drawing that shows the symmetry of the π molecular orbital that controls this reactivity. This drawing should focus only on the π system, and not include any substituents.

(c) Provide a drawing that shows the the π molecular orbital from part (b) superimposed on the molecule at the transition state for this reaction. This drawing should provide a rationale for the stereochemistry of the product.

Name ________________

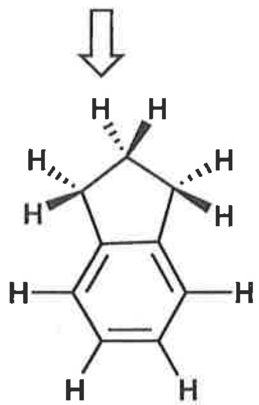
7. (14 points)

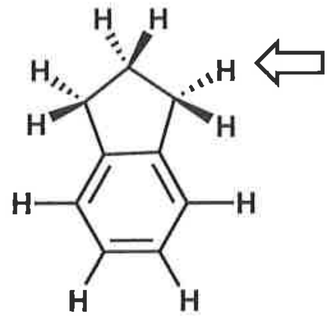
For each molecular drawing below, with reference to the H indicated by the arrow, label other H's as indicated...

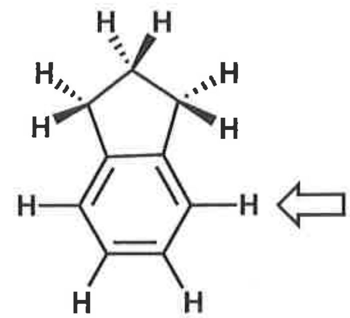
...Put a CIRCLE around any homotopic H's.

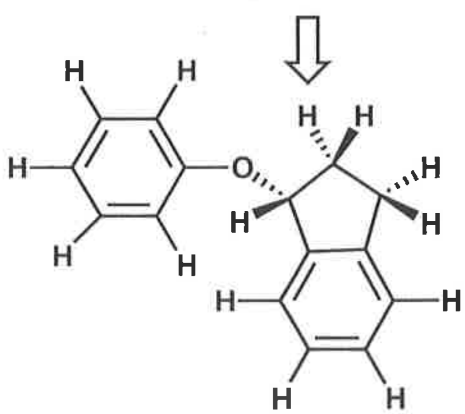
...Put a TRIANGLE around any enantiotopic H's.

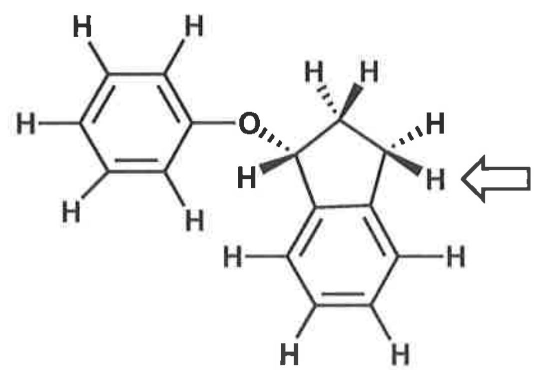
...Put a SQUARE around any diastereotopic H's.





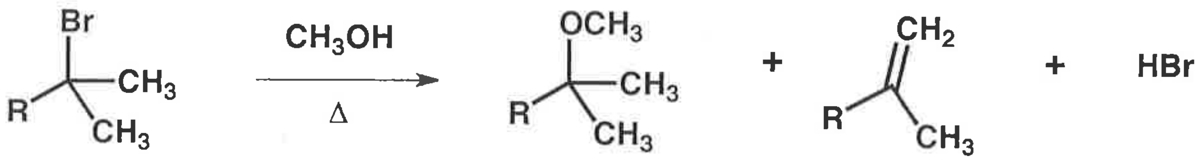


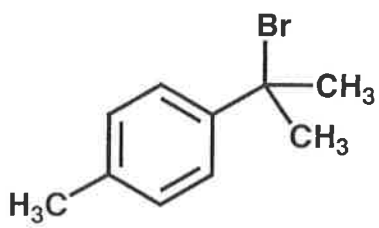




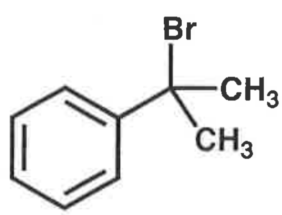
Name ____________ 00232

8. (8 points) Each of the four molecules shown below (A-D) undergoes the reaction shown. Rank these four molecules in terms of increasing reaction rate, with the molecule expected to react MOST rapidly on the RIGHT.

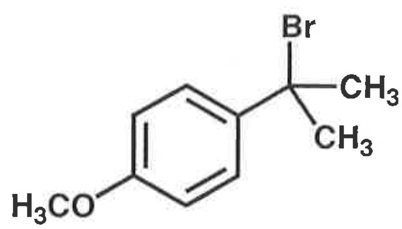




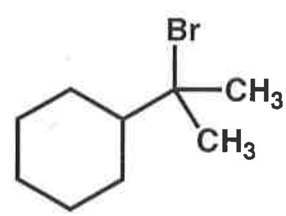
A



B



C



D

INCREASING reaction rate to the RIGHT:

________ < ________ < ________ < ________

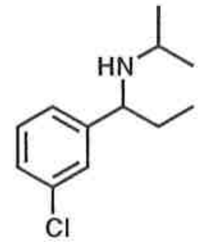
[Place the letters A, B, C and D in the blanks above, in the proper order.]

Name ________________ 00232

9. (35 points)

(a) Propose an efficient synthetic route from the indicated starting material to the target. You may use any other starting materials containing 3 or fewer carbons, and any reagents.

Starting material = 

Target = 

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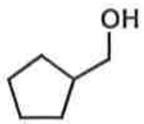
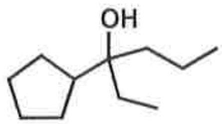
Name ____________________ 00232

9. (cont.)

(b) Propose an efficient synthetic route from the indicated starting material to the target. You may use any other starting materials containing 3 or fewer carbons, and any reagents.

Starting material = 

Target = 

(racemic)

Name ________________ 00232

Problem #	Score
1	/ 32
2	/ 8
3	/ 30
4	/ 30
5	/ 28
6	/ 15
7	/ 14
8	/ 8
9	/ 35

Total: / 200

Periodic Table of the Elements

			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.

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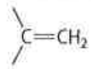
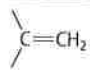
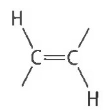
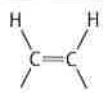
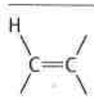
Type of absorption	Frequency, cm^{-1} (Intensity)*	Comment
	Alkanes	
C—H stretch	2850–3000 (m)	occurs in all compounds with aliphatic C—H bonds
	Alkenes	
C=C stretch —CH=CH_2	1640 (m)	
	1655 (m)	
others	1660–1675 (w)	not observed if alkene is symmetrical
=C—H stretch	3000–3100 (m)	
=C—H bend		
—CH=CH_2	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

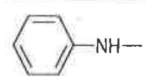
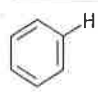
*(s) = strong; (m) = medium; (w) = weak.

00232

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

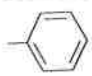
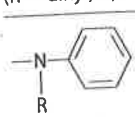
Group	Chemical shift, ppm	Group	Chemical shift, ppm
—C—C—H (alkyl)	0.7–1.5	—C(=O)—H	9–11
>C=C< (with H on carbon)	4.6–5.7	—C(=O)—N—H	7.5–9.5
—O—H	varies with solvent and with acidity of O—H	—C—NH—	0.5–1.5
—C≡C—H	1.7–2.5		2.5–3.5
	6.5–8.5		

B. Protons Adjacent to Functional Groups

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

$$H-\overset{|}{\underset{|}{C}}-G$$

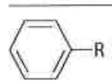
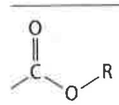
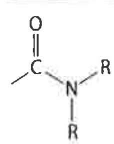
in which G is a group listed in column 1, and the two other bonds are to carbon or hydrogen. The remaining columns give the approximate chemical shifts for methyl protons (H_3C—G), methylene protons (—CH_2—G), and methine protons (—$\overset{|}{C}H$—G), respectively. The shifts in the following table 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 (with a bond drawn up from the C)
—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
R—C(=O)—	2.1 (R = alkyl) 2.6 (R = aryl)	2.4 (R = alkyl) 2.7 (R = aryl)	2.6 (R = alkyl) 3.4 (R = aryl)
RO—C(=O)— (R = alkyl, H)	2.1	2.2	2.5
R—C(=O)—O— (R = alkyl, H)	3.6 (R = alkyl) 3.8 (R = aryl)	4.1 (R = alkyl, aryl)	5.0 (R = alkyl, aryl)
R_2N—C(=O)— (R = alkyl, H)	2.0	2.2	2.4
R—C(=O)—N(R)— (R = alkyl, H)	2.8	3.4	3.8
—NR_2 (R = alkyl, H)	2.2	2.4	2.8
 (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.

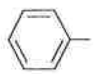
A. Chemical Shifts of Carbons within Functional Groups

Group		Chemical shift range, ppm
$-CH_3$		8–23
$-CH_2-$		20–30
$-\overset{\vert}{C}H-$		21–33
$-\overset{\vert}{\underset{\vert}{C}}-$		17–29
>C=C<		105–150*
—C≡C—		66–93*
		125–150*
		200–220
	R = H, alkyl	170–180
	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.

Group G	Chemical shift of carbon in G—C—
$R_2C{=}CR$—	14–40
HC≡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—C(=O)— R = alkyl, H	43–50
RO—C(=O)— R = alkyl, H	33–44
R_2N— R = alkyl, H	41–51 (R = H) 53–60 (R = alkyl)
N≡C—	16–28