**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.

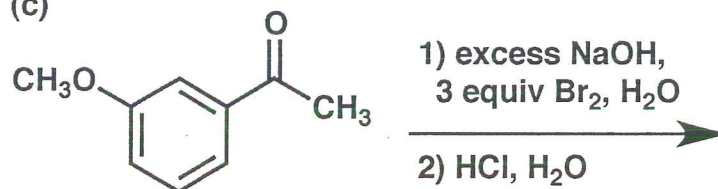1. (40 points) Show the major product or products expected from each reaction.

(a)

1) LiAlH$_4$, Et$_2$O

2) H$_2$O

(b)

1) NaOH, H$_2$O

2) H$_2$O, H$_2$SO$_4$
   Δ
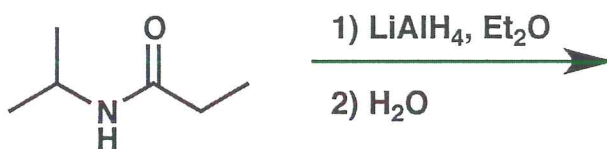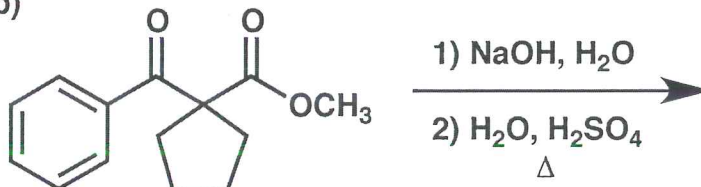
[Hint: The starting material has strong IR signals at ~1690 cm^{-1}
and ~1740 cm^{-1}, but the product has only a ~1690 cm^{-1} signal
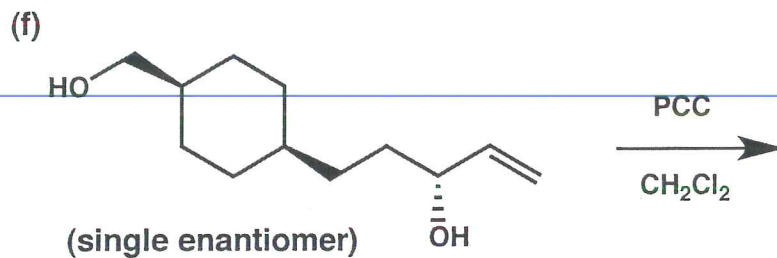(no other strong signals between 1650 and 1800 cm^{-1}).]

(c)

1) excess NaOH,
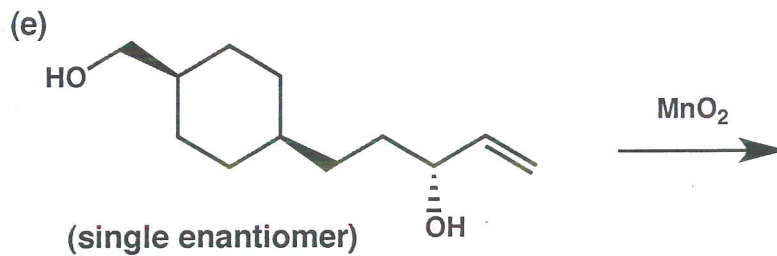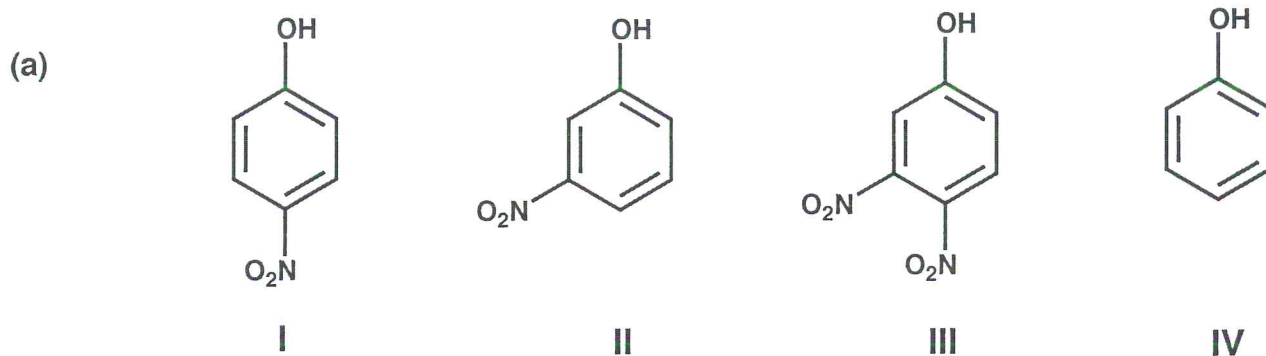   3 equiv Br$_2$, H$_2$O

2) HCl, H$_2$O

(d)

NaCNBH$_3$, AcOH

(cont. on next page)

Name _____

1. (cont.)

(e)

HO

MnO$_2$

(single enantiomer) OH
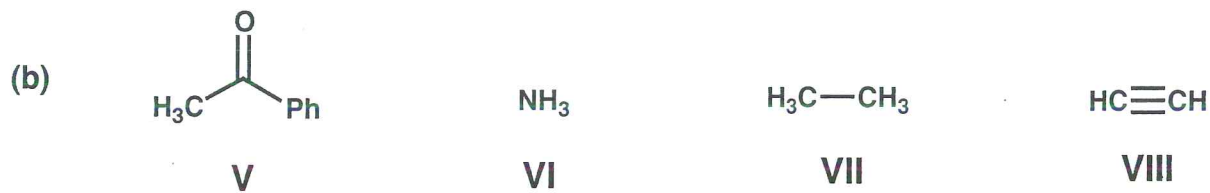
(f)

HO

PCC

CH$_2$Cl$_2$

(single enantiomer) OH

2. (14 points) For each set of four species below, indicate the expected order of pKa values, from LOWEST (left) to HIGHEST (right).
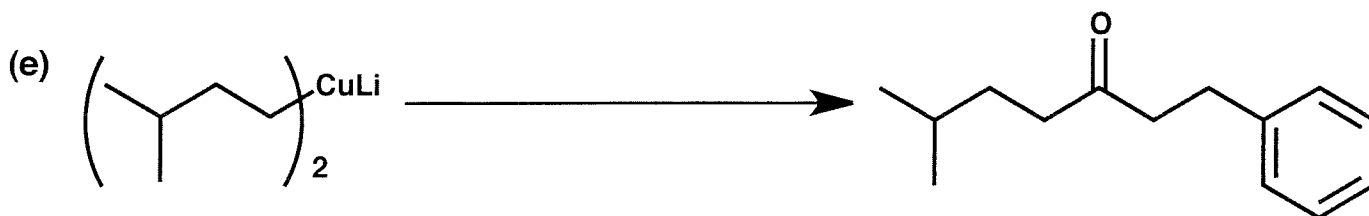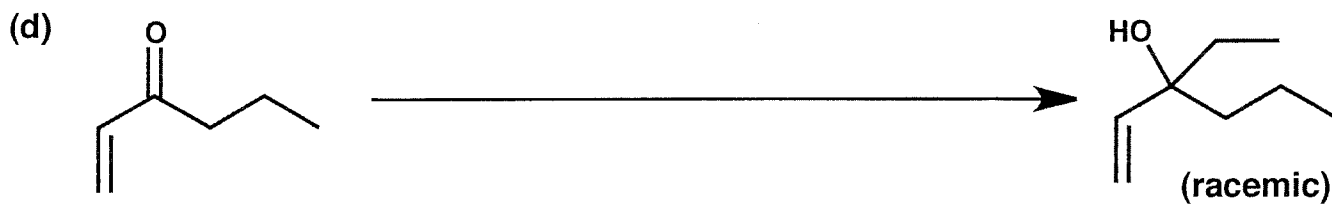
(a)

I   II   III   IV

INCREASING pKa: _____ < _____ < _____ < _____

(b)

V   VI   VII   VIII
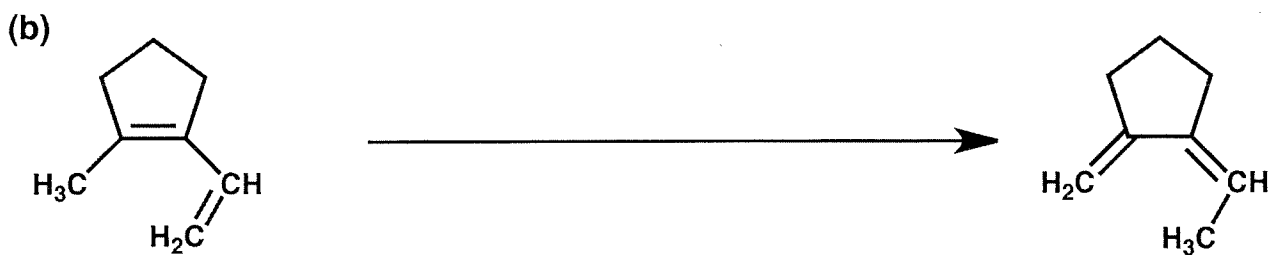
INCREASING pKa: _____ < _____ < _____ < _____

06018

3. (26 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)

(racemic)

(b)

(c)

(racemic)

(d)

(racemic)

(e)
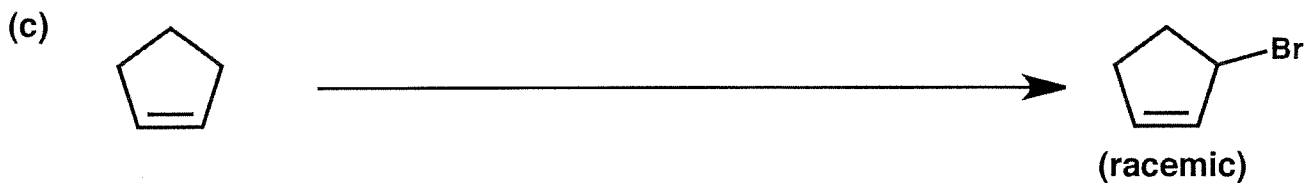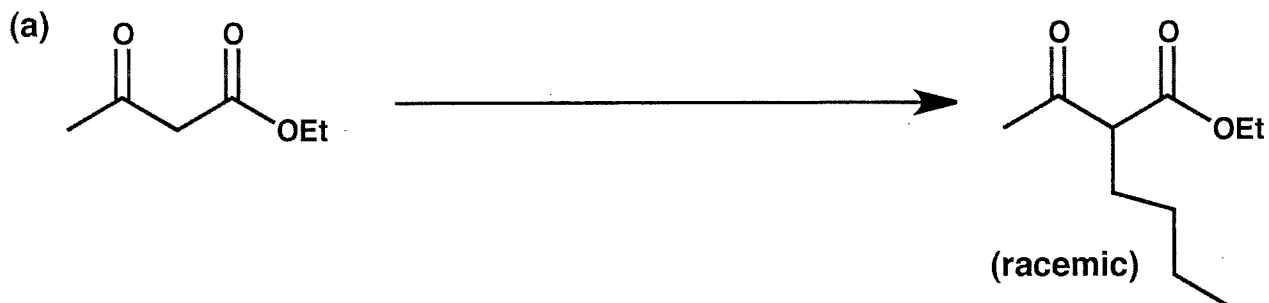
4. (33 points) Provide a mechanism (curved arrows) for each reaction shown below. Draw all important resonance structures for intermediates.

$$CH_3O^- \ Na^+$$

$$\xrightarrow{\hspace{2cm}}$$

$$CH_3OH$$
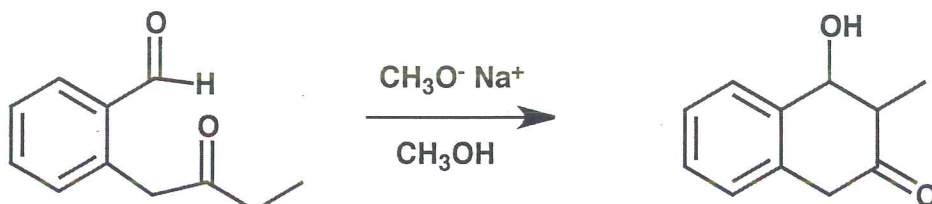
(Do not be concerned about product stereochemistry.)

4. (cont.)

(b)

(Do not be concerned
about stereochemistry.)

(cont. on next page)

4. (cont.)

(c)

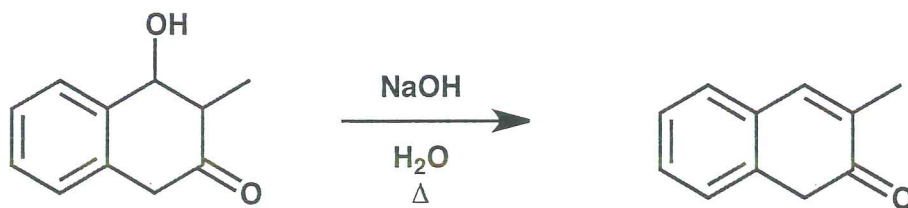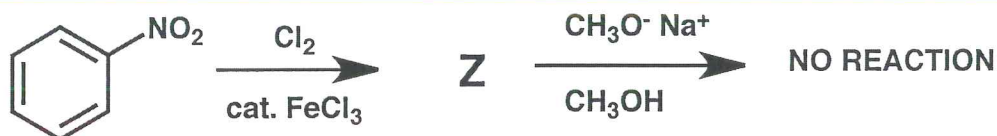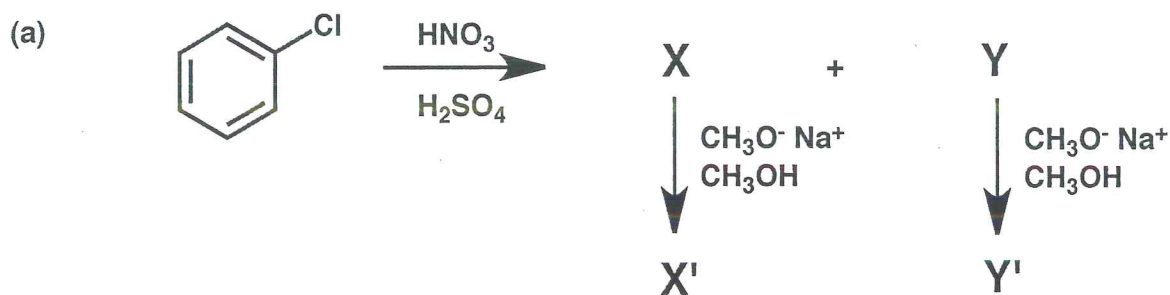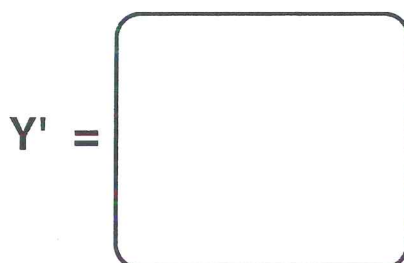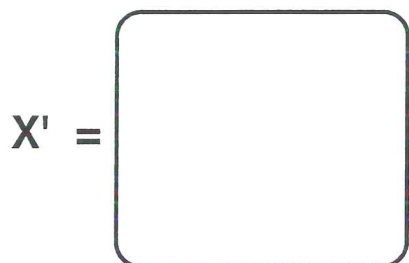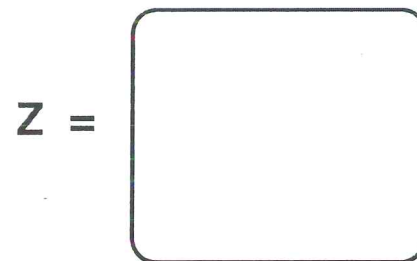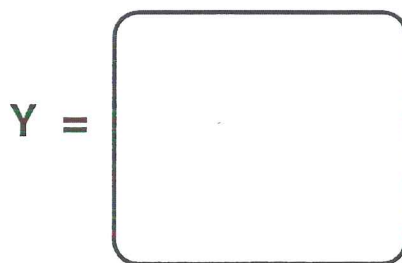**5. (36 points)** For each reaction or set of related reactions shown below, draw the structures of the indicated products in the boxes. Your structures must be consistent with the spectroscopic data given for these compounds.

(a)

$$\text{C}_6\text{H}_5\text{Cl} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3} \quad X \quad + \quad Y$$

X $\xrightarrow[\text{CH}_3\text{OH}]{\text{CH}_3\text{O}^- \text{Na}^+}$ X'

Y $\xrightarrow[\text{CH}_3\text{OH}]{\text{CH}_3\text{O}^- \text{Na}^+}$ Y'

$$\text{C}_6\text{H}_5\text{NO}_2 \xrightarrow[\text{cat. FeCl}_3]{\text{Cl}_2} \quad Z \xrightarrow[\text{CH}_3\text{OH}]{\text{CH}_3\text{O}^- \text{Na}^+} \quad \text{NO REACTION}$$

In the boxes below, provide structures for molecules X, Y, Z, X' and Y' that are consistent with the following spectroscopic data.

-- The ^{13}C NMR spectrum of X has FOUR resonances, all with $\delta > 100$.

-- The ^{13}C NMR spectrum of X' has FIVE resonances, four with $\delta > 100$ and one with $\delta < 80$.

-- The ^{13}C NMR spectrum of Y has SIX resonances, all with $\delta > 100$.

-- The ^{13}C NMR spectrum of Y' has SEVEN resonances, six with $\delta > 100$ and one with $\delta < 80$.

-- The ^{13}C NMR spectrum of Z has SIX resonances, all with $\delta > 100$.

X = [ ]

Y = [ ]

Z = [ ]

X' = [ ]

Y' = [ ]

-- cont. on next page --

5. (cont.)

(b)

OH
[phenol]   NaOH
            /=_Br (allyl bromide)   → A —Δ→ B

OH
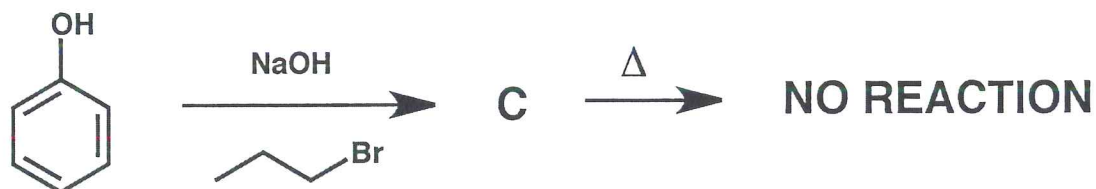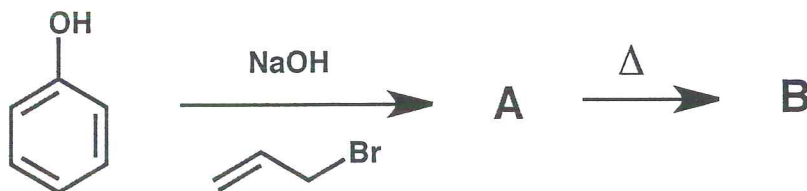[phenol]   NaOH
            /_Br (propyl bromide)   → C —Δ→ NO REACTION

A =

[box]
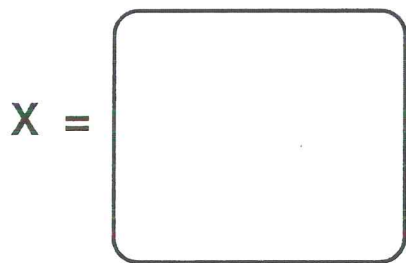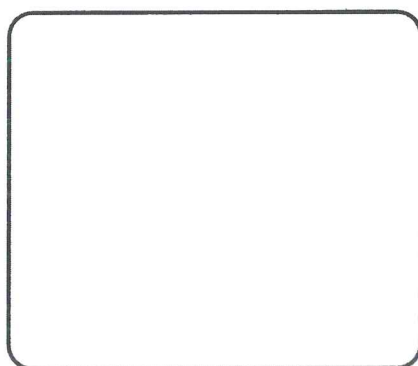
^1H NMR spectrum includes:

3 signals 6.8-7.2 ppm (2H, 2H, 1H)*

3 signals 5.0-6.0 ppm (1H each)

1 signal ~4 ppm (2H)

B =

[box]
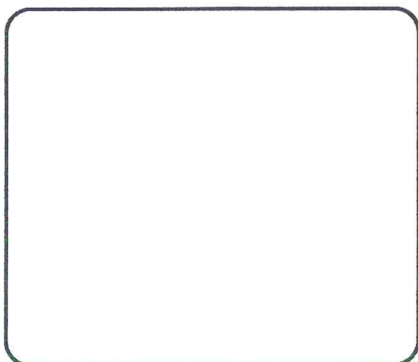
^1H NMR spectrum includes:

4 signals 6.8-7.2 ppm (1H each)*

3 signals 5.0-6.0 ppm (1H each)

1 signal ~3.5 ppm (2H)

C =

[box]
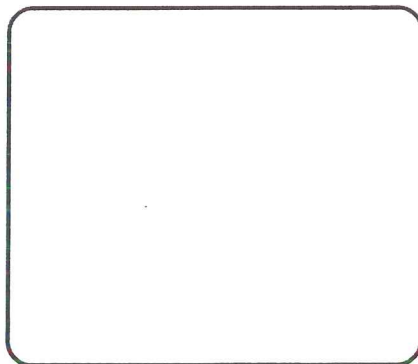
^1H NMR spectrum includes:

3 signals 6.8-7.2 ppm (2H, 2H, 1H)*

1 signal ~3.5 ppm (2H)

1 signal ~1.6 ppm (2H)

1 signal ~1.0 ppm (3H)

*Note: "1H" means that the integration corresponds to 1 proton, etc.

6. (10 points) Shown below is an example of a [3,3]-sigmatropic rearrangement.
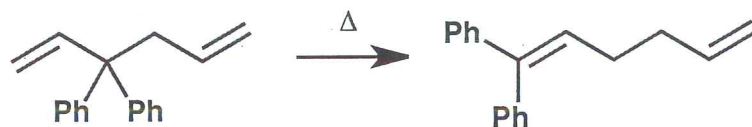
Draw the transition state for this reaction below, using dotted lines to indicate bonds that are forming or breaking.

Name _____

7. (9 points)

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

    Put a CIRCLE around any homotopic H's.

    Put a TRIANGLE around any enantiotopic H's.

    Put a SQUARE around any diastereotopic H's.
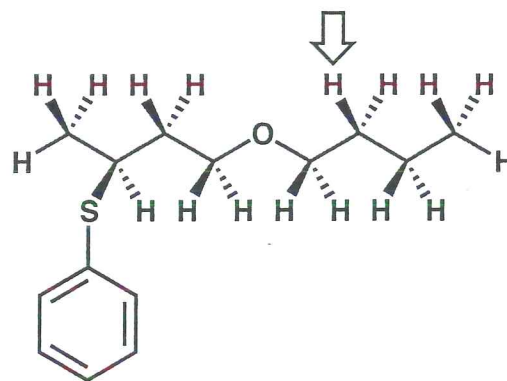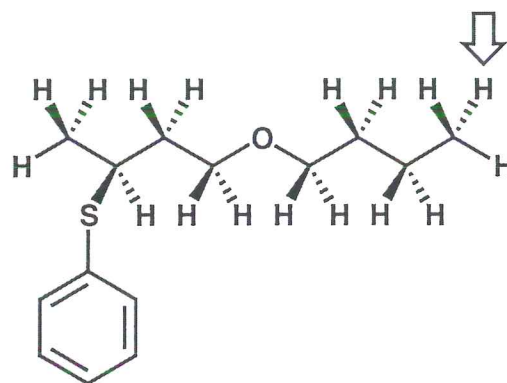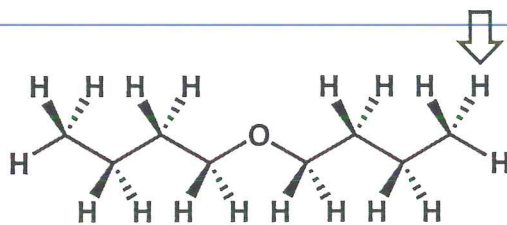
8. (32 points)

(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.
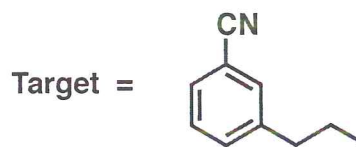
Starting material =

Target =

8. (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)

Problem #	Score
1	/ 40
2	/ 14
3	/ 26
4	/ 33
5	/ 36
6	/ 10
7	/ 9
8	/ 32

_____
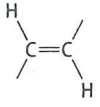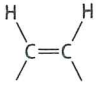
Total: / 200

Periodic Table of the Elements

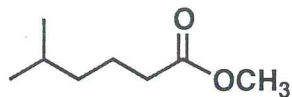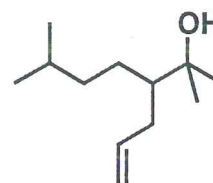| 1																		18
1 **H** 1.008																		2 **He** 4.003
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.011	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17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

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

*Symbol (and name) provisional.

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)	
C=CH$_2$	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)	
C=CH$_2$	890 (s)	
C=C (H...H)	960–980 (s)	
C=C (H H)	675–730 (s)	position is highly variable
C=C (H)	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.
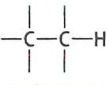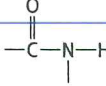
(Table continues)
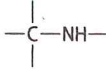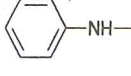
Type of absorption	Frequency, cm^{-1} (Intensity)*	Comment
Aldehydes		
C=O stretch		
ordinary	1720–1725 (s)	
α,β-unsaturated	1680–1690 (s)	
benzaldehydes	1700 (s)	
C—H stretch	2720 (m)	
Ketones		
C=O stretch		
ordinary	1710–1715 (s)	increases with decreasing ring size (Table 21.3, p. 996)
α,β-unsaturated	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
—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		
⬡—H	6.5–8.5	⬡—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
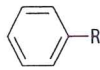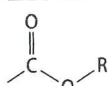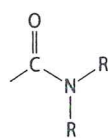
$$H-\underset{|}{\overset{|}{C}}-G$$
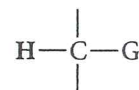
in which G is a group listed in column 1, and the two other bonds are to carbon or hydrogen. The remaining columns give the approximate chemical shifts for methyl protons (H_3C—G), methylene protons (—CH_2—G), and methine protons (—CH—G), respectively. The shifts in the following table are typical; some 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
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)
R₂N—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
—NR₂ (R = alkyl, H)	2.2	2.4	2.8
—N(R)—⬡ (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 (ketone)	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.

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—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)
$N{\equiv}C{-}$	16–28