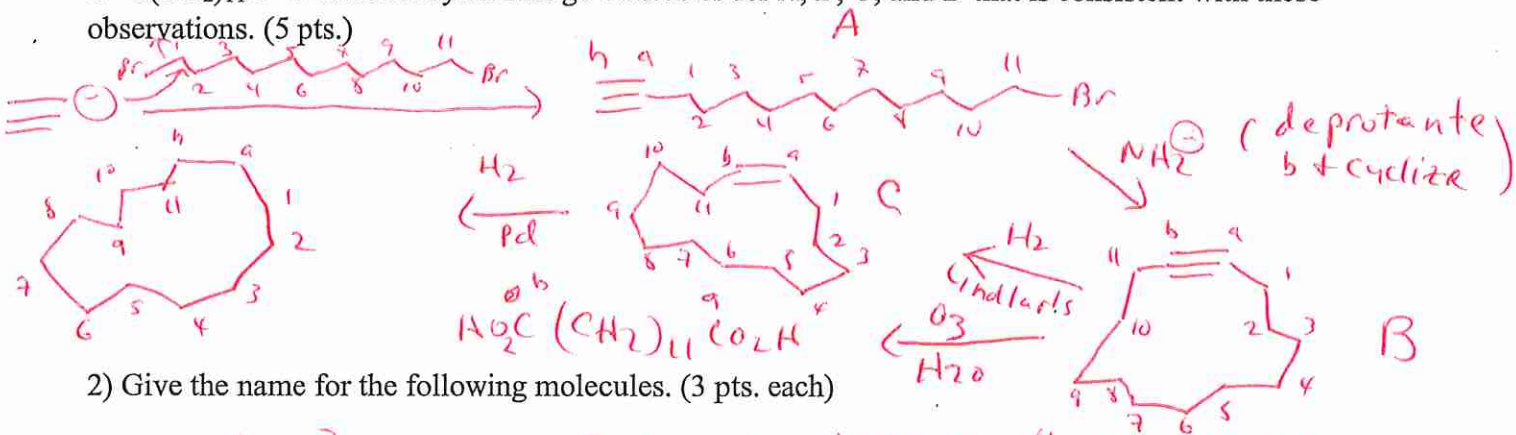
Organic 211 Test # 4 A1_B1 November 12, 2020

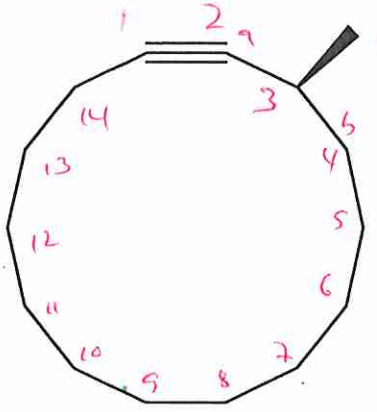
Name:_____

Directions: The exam is worth 106 points but scored out of 100.

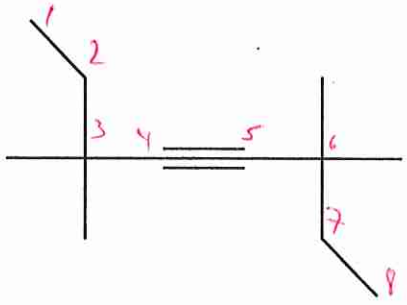
1) Compound A has the molecular formula $C_{13}H_{23}Br$ and was obtained by reaction of sodium acetylide with 1,11-dibromoundecane. On treatment with compound A with sodium amide, it was converted to compound B ($C_{13}H_{22}$). Ozonolysis of compound B gave the diacid $H_2OC(CH_2)_{11}CO_2H$. Catalytic hydrogen of compound B over Lindlar palladium gave compound C ($C_{13}H_{24}$), and hydrogenation over platinum gave compound D ($C_{13}H_{26}$). C yielded $O{=}C(CH_2)_{11}C{=}O$ on ozonolysis. Assign structures for A, B, C, and D that is consistent with these observations. (5 pts.)



2) Give the name for the following molecules. (3 pts. each)

a) 

3,3,6,6-tetramethyl oct-4-yne

b) 

3S-3-methyl cyclotetradec-1-yne

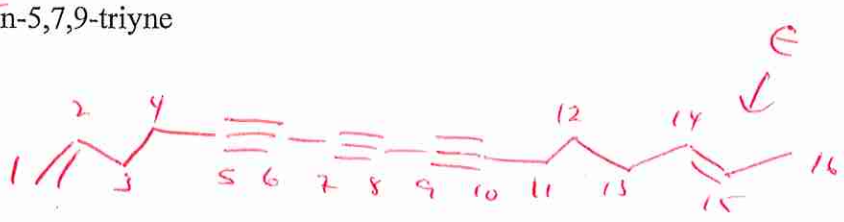
3) Give the structure for the following molecules. (3 pts. each)

a) Pent-4-yn-1-ylcyclobutane

5 carbon chain attached at carbon 1

b) (*E*)-hexadeca-1,14-dien-5,7,9-triyne

16 carbons



4) Given the following reactivities, calculate the relative amounts of 1-chlorohexane, 2-chlorohexane, and 3-chlorohexane obtained in a free-radical chlorination of hexane. SHOW YOUR WORK! (6 pts.)

Primary: 1

Secondary: 4.5

Tertiary: 10.0

A $1 \times 6 = 6$ $\quad 6/42 \quad 14.3\%$

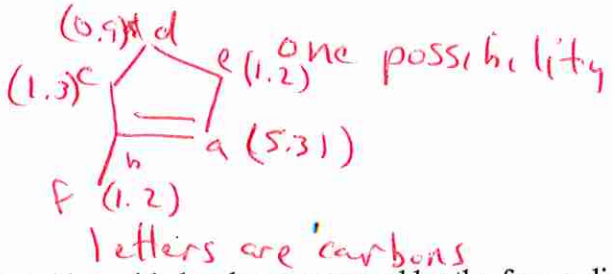
B $4 \times 4.5 = 18$ $\quad 18/42 \quad 42.85\%$

C $4 \times 4.5 = 18$ $\quad 18/42 \quad 42.85$

42

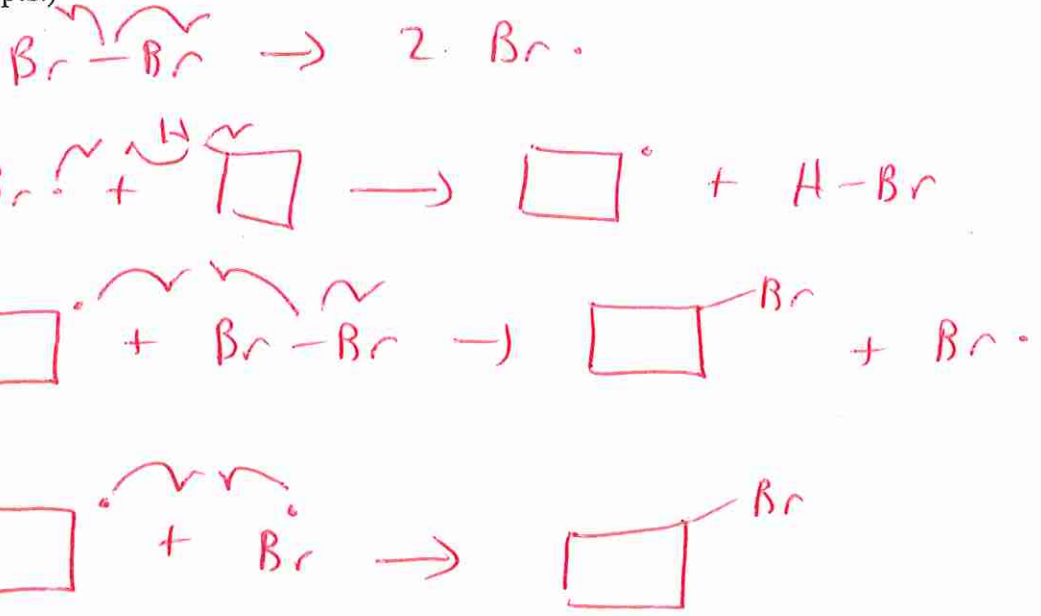
5) Compound A has five types of hydrogen and six types of carbon. The chemical shifts for the protons are 1.2 ppm (3H), 1.3 (2 H), 0.9 (2 H), 1.2 (2 H) and 5.31 (1 H). Give a possible structure for compound A. (4 pts.)

6 carbons

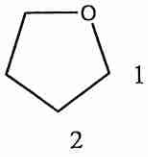


one possibility

6) Cyclobutyl bromide has been prepared by the free-radical bromination of cyclobutane. Write a stepwise mechanism for this reaction. (e.g. arrows are required). Bromine and heat are one of the steps. (6 pts.)



7) Which carbon, 1 or 2, of THF would you expect to be more shielded? Give an explanation. (4 pts.)



Oxygen removes electrons making 1 less shielded than 2.

∴ 2 is more shielded.

8) Your molecule contains either an alcohol or a carboxylic acid. How could you tell which functional group you had using the IR? (4 pts.)

OH 3200 cm⁻¹

9) Give a possible molecular formula for molecule A that contains 5 nitrogens and weighs 351 grams per mole. Show your work. (4 pts.)

$$\begin{array}{r} 14 \\ \times\ 5 \\ \hline 70 \end{array} \qquad \begin{array}{r} 351 \\ -\ 70 \\ \hline 281 \end{array} \qquad \begin{array}{r} 21.XX \\ 13\overline{)281} \\ 26 \\ \hline 21 \end{array} \qquad \begin{array}{r} 21 \\ \times\ 12 \\ \hline 42 \\ 210 \\ \hline 252 \end{array} \qquad \begin{array}{r} 27 \\ 281 \\ -\ 252 \\ \hline 29 \end{array}$$

∴ $C_{21}H_{29}N_5$

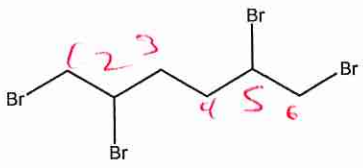
10) You think your molecule has single chlorine in it. How could you determine whether it does or not? (4 pts.)

the M+2 peak will be ⅓ the intensity of the M+ peak in the mass spectrum.

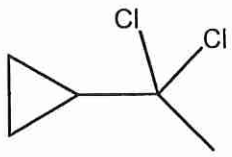
11) Give the missing reactant, reagent, or product for the following reactions. Indicate if no reaction is possible. Show the keto form and not the enol form if possible. Assume monohalogenation. Show stereochemistry if important. Cross out a question you do not want to work. (3 pts.)

a) 1 eq. $\equiv\ominus$ + 

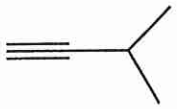
→ ????

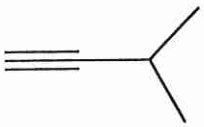
b) 

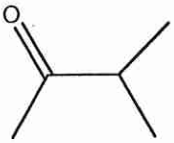
1) excess $NaNH_2/NH_3$
2) H_2O
→ ????

c) 

K^+ $O\ominus$ DMSO
Heat
→ ????

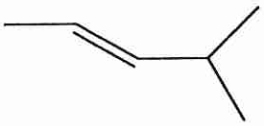
d) 
1) $(sia)_2BH$
2) H_2O_2/OH^-
→ ?????

e) 
→ ????

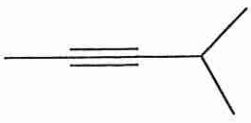


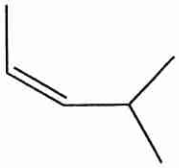
$HgSO_4$
H_2SO_4

f) 
→ ????

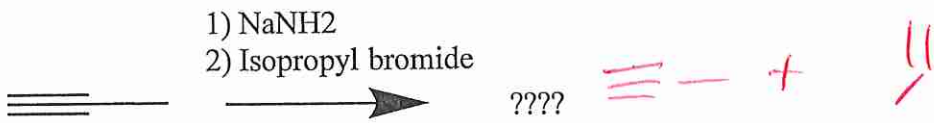


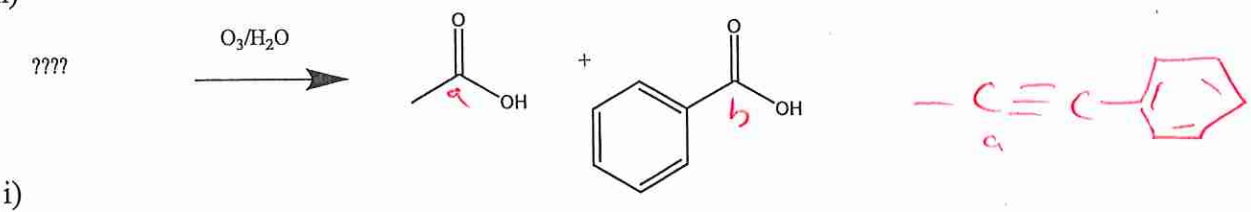
$\xrightarrow[NH_3]{Na}$ or $\xrightarrow[NH_3]{Li}$

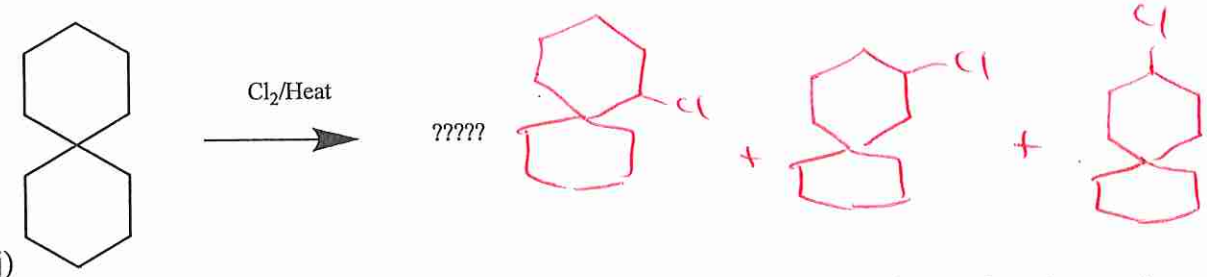
g) 
→ ????



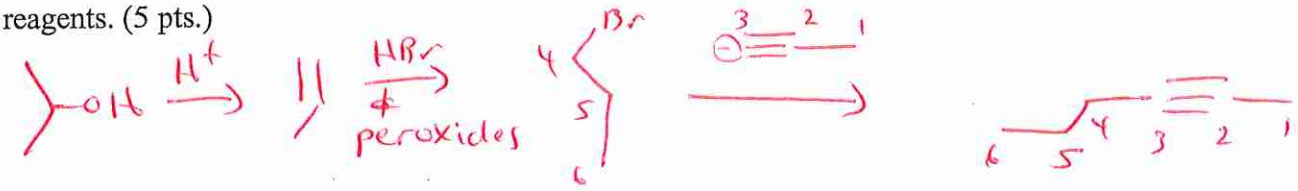
$\xrightarrow{H_2}$
Lindlar's Catalyst

h) 

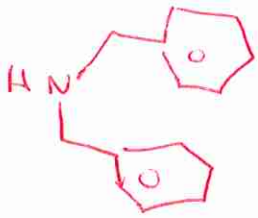
i) 

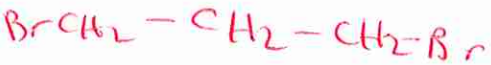
j) 

12) Outline a synthesis of 2-hexyne from 2-propanol using any required organic or inorganic reagents. (5 pts.)



13) Give a structure that gives the following spectra on the three following sheets. 1st sheet is a, 2nd sheet is b, 3rd sheet is c. (5 pts. Each)

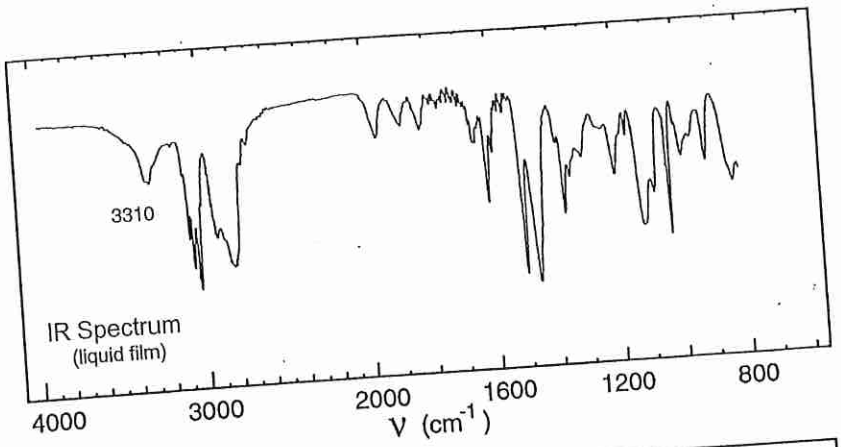
a) 

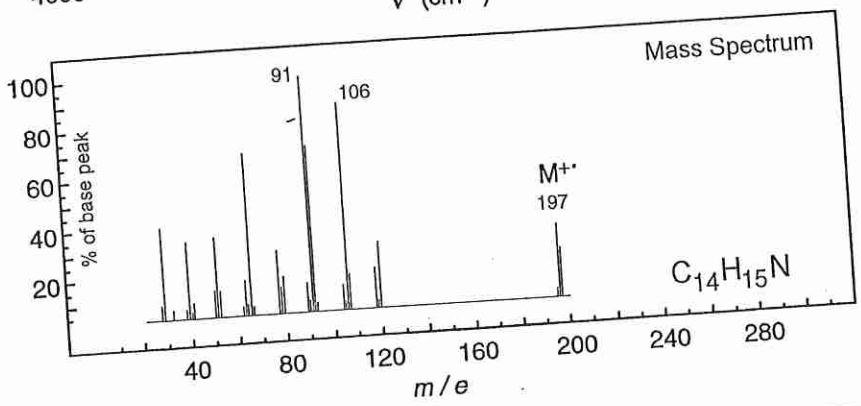
b) 

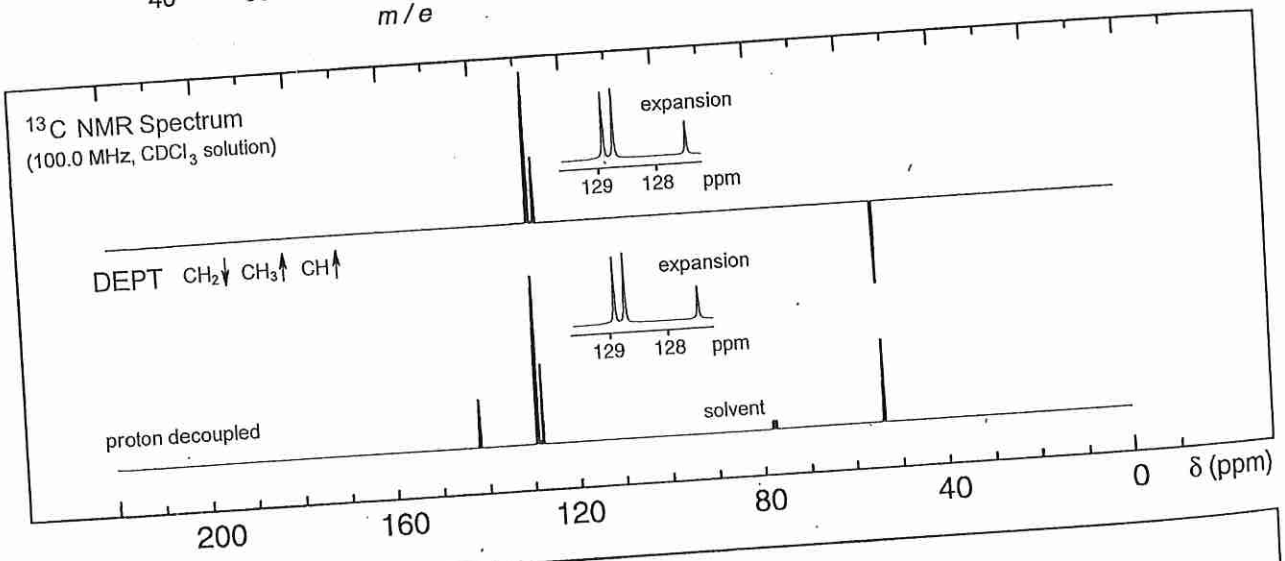
c) 

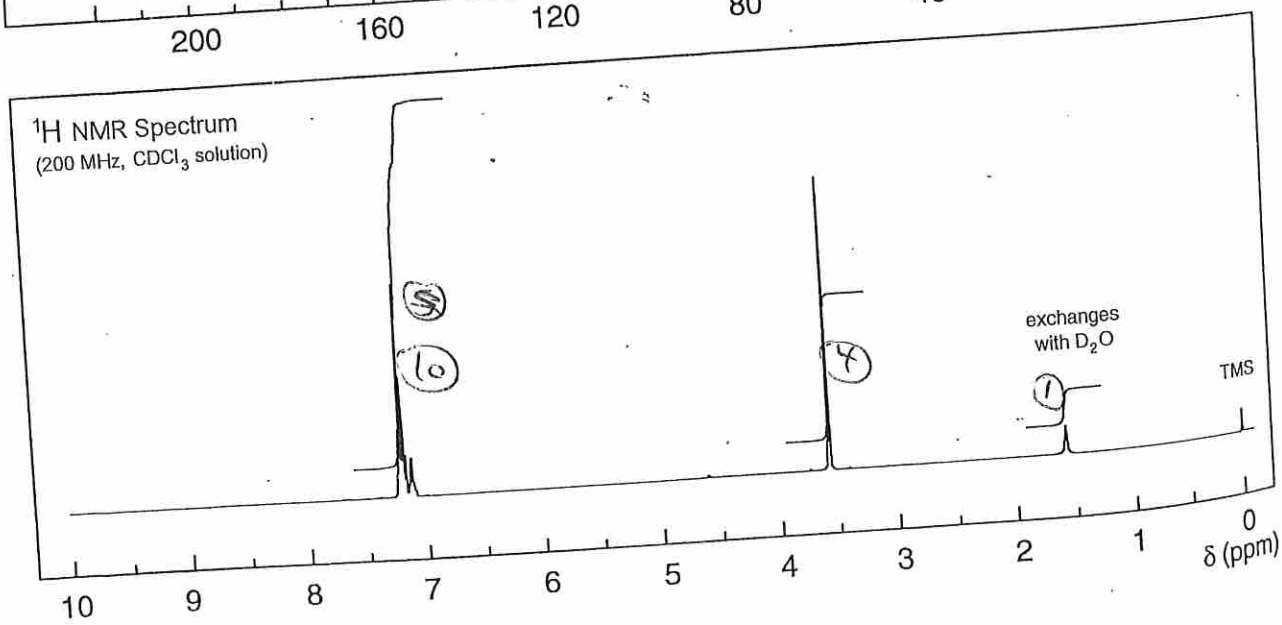
14) Give something that you enjoyed about Organic 1. (7 pts.)

Problem 39

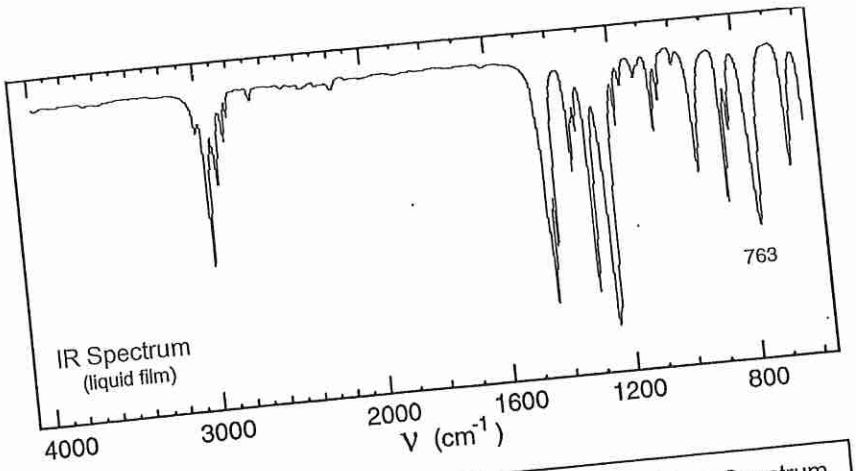

3310
IR Spectrum
(liquid film)
4000
3000
2000
1600
1200
800
ν (cm⁻¹)

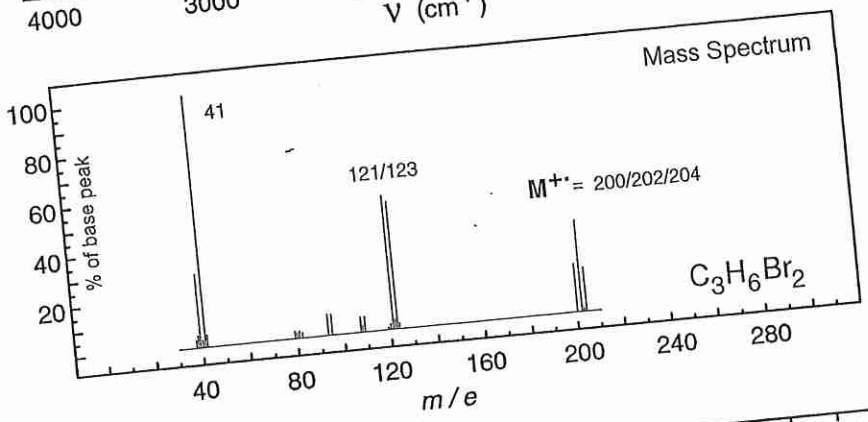

Mass Spectrum
100
80
60
40
20
% of base peak
91
106
M+·
197
C14H15N
40
80
120
160
200
240
280
m/e


13C NMR Spectrum
(100.0 MHz, CDCl3 solution)
expansion
129
128
ppm
DEPT CH2 CH3 CH
expansion
129
128
ppm
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

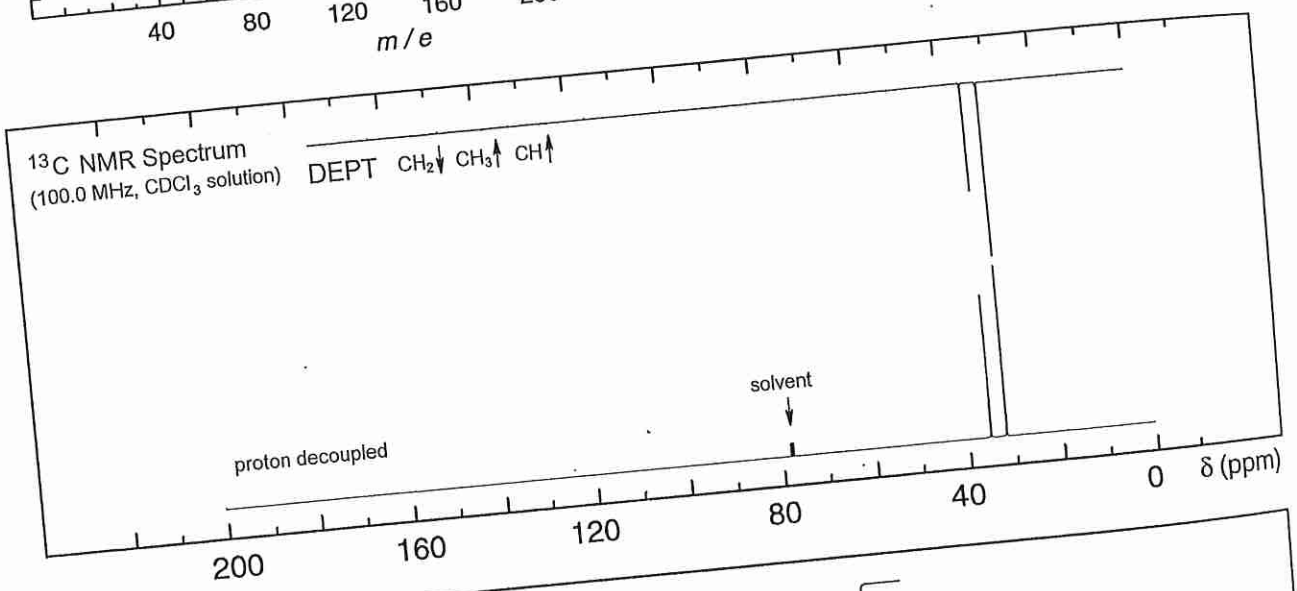

1H NMR Spectrum
(200 MHz, CDCl3 solution)
5
10
4
exchanges
with D2O
1
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

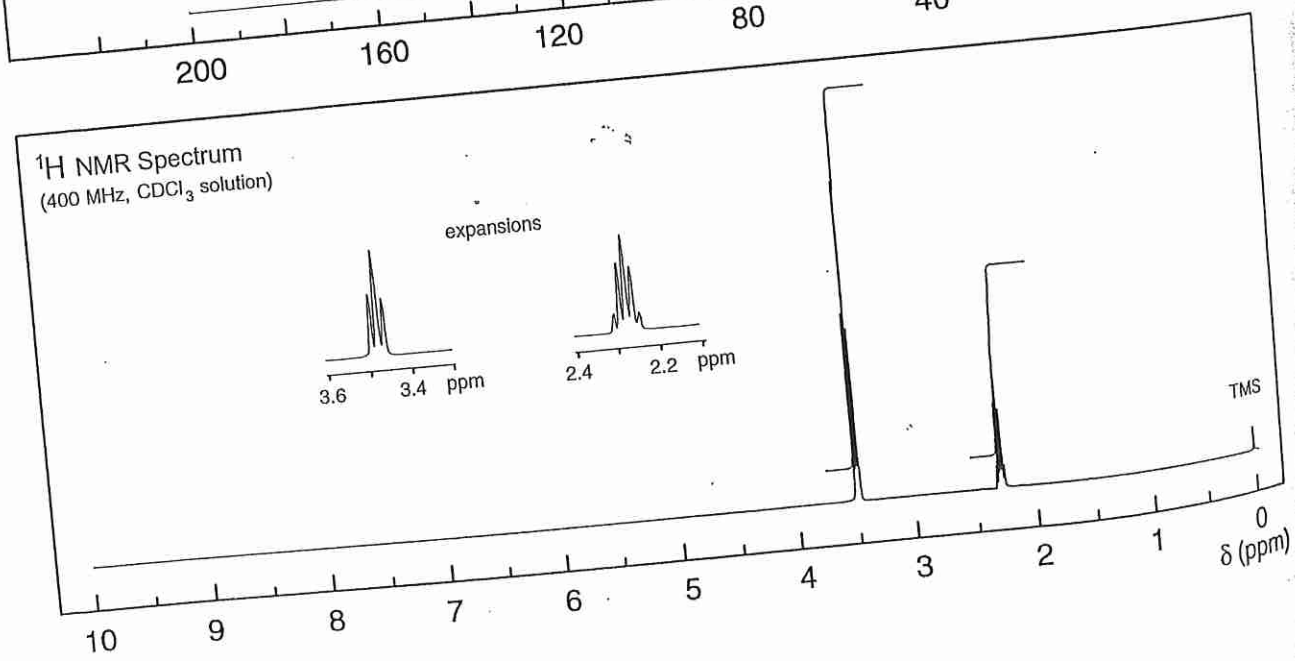
Problem 19



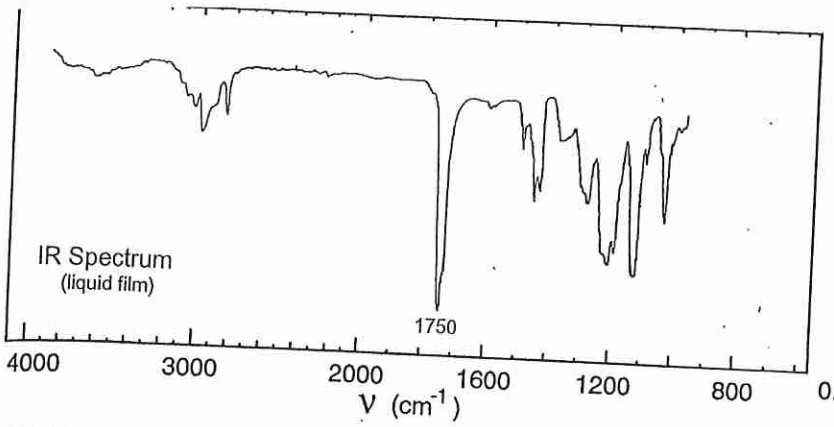


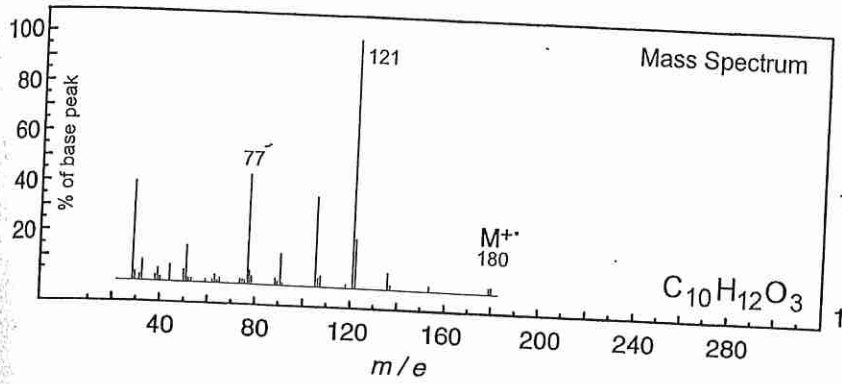
No significant UV absorption above 220 nm

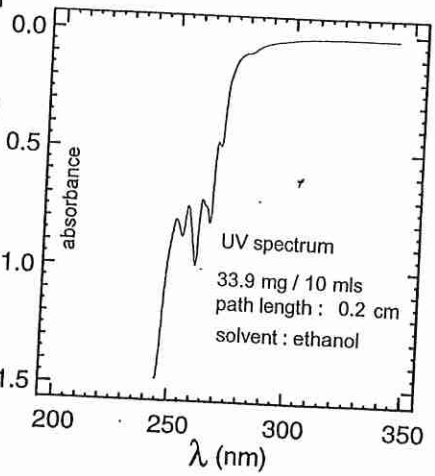


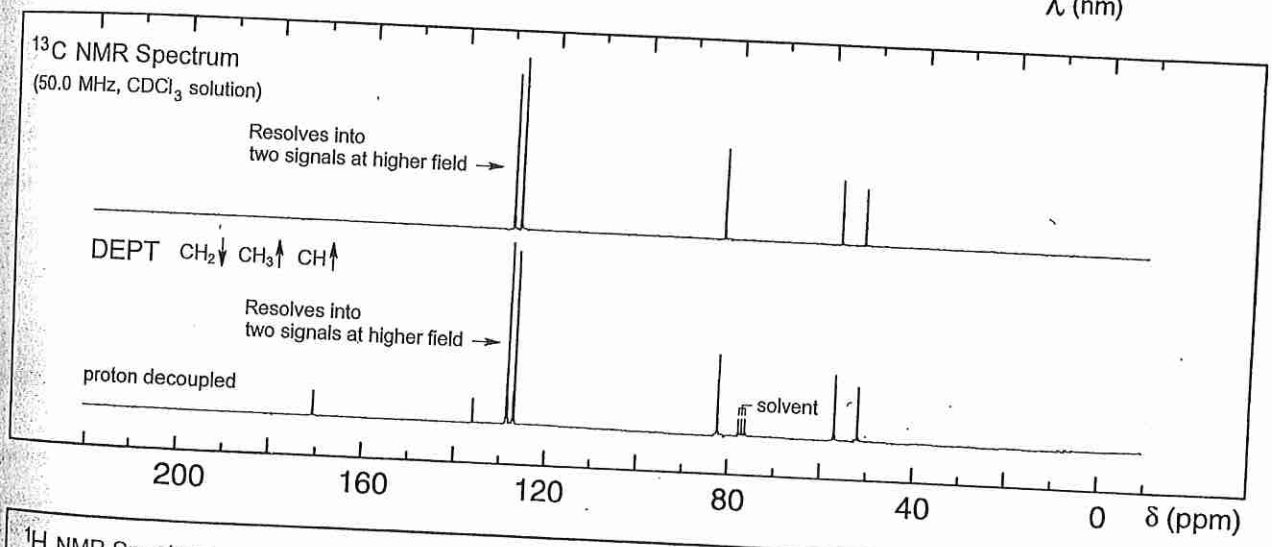


Problem 136


IR Spectrum
(liquid film)
1750
4000
3000
2000
1600
1200
800
ν (cm⁻¹)


Mass Spectrum
% of base peak
100
80
60
40
20
121
77
M+·
180
C10H12O3
40
80
120
160
200
240
280
m/e


absorbance
0.0
0.5
1.0
1.5
UV spectrum
33.9 mg / 10 mls
path length : 0.2 cm
solvent : ethanol
200
250
300
350
λ (nm)


13C NMR Spectrum
(50.0 MHz, CDCl3 solution)
Resolves into
two signals at higher field
DEPT CH2↓ CH3↑ CH↑
Resolves into
two signals at higher field
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)

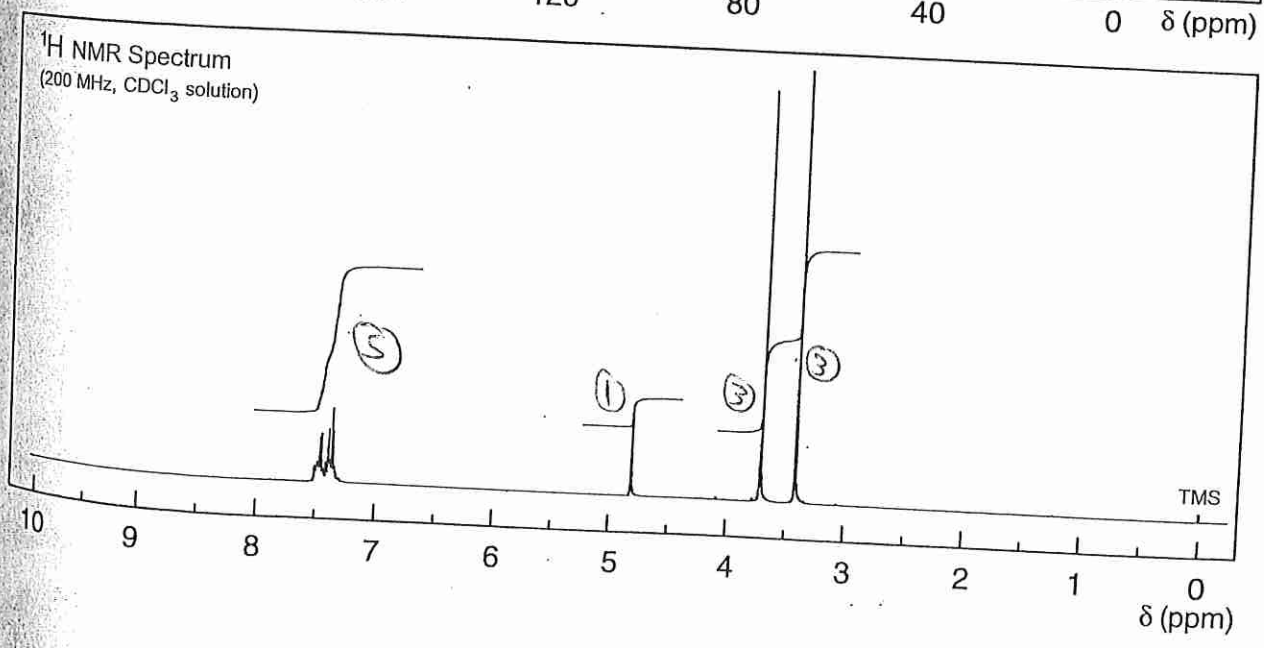

1H NMR Spectrum
(200 MHz, CDCl3 solution)
5
1
3
3
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

TABLE 13.1 Approximate Proton Chemical Shifts

TYPE OF PROTON	CHEMICAL SHIFT, DELTA, PPM
1° Alkyl, RCH_3	0.8–1.0
2° Alkyl, RCH_2R	1.2–1.4
3° Alkyl, R_3CH	1.4–1.7
Allylic, $R_2C{=}C(R){-}CH_3$	1.6–1.9
Benzylic, $ArCH_3$	2.2–2.5
Alkyl chloride, RCH_2Cl	3.6–3.8
Alkyl bromide, RCH_2Br	3.4–3.6
Alkyl iodide, RCH_2I	3.1–3.3
Ether, $ROCH_2R$	3.3–3.9
Alcohol, $HOCH_2R$	3.3–4.0
Ketone, $RCCH_3$ (O)	2.1–2.6
Aldehyde, RCH (O)	9.5–9.6
Vinylic, $R_2C{=}CH_2$	4.6–5.0
Vinylic, $R_2C{=}CH(R)$	5.2–5.7
Aromatic, ArH	6.0–9.5
Acetylenic, $RC{\equiv}CH$	2.5–3.1
Alcohol hydroxyl, ROH	0.5–6.0[a]
Carboxylic, $RCOH$ (O)	10–13[a]
Phenolic, ArOH	4.5–7.7[a]
Amino $R{-}NH_2$	1.0–5.0[a]

[a]The chemical shifts of these groups vary in different solvents and with temperature and concentration.

TABLE 13.2 Approximate Carbon-13 Chemical Shifts

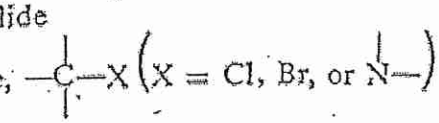
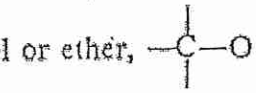
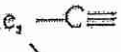
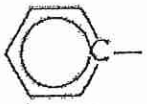
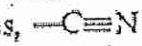
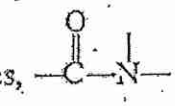
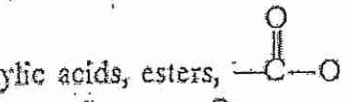
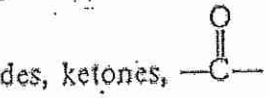
TYPE OF CARBON	CHEMICAL SHIFT, DELTA, PI
1° Alkyl, RCH_3	0–40
2° Alkyl, RCH_2R	10–50
3° Alkyl, $RCHR_2$	15–50
Alkyl halide or amine, 	10–65
Alcohol or ether, 	50–90
Alkyne, 	60–90
Alkene, 	100–170
Aryl, 	100–170
Nitriles, 	120–130
Amides, 	150–180
Carboxylic acids, esters, 	160–185
Aldehydes, ketones, 	185–215

TABLE 13.3 Characteristic Infrared Absorptions of Functional Groups

GROUP		FREQUENCY RANGE cm^{-1}	INTENSITY*
A. Alkyl			
C—H (stretching)		2853–2962	(m–s)
Isopropyl, $—CH(CH_3)_2$		1380–1385	(s)
	and	1365–1370	(s)
tert-Butyl, $—C(CH_3)_3$		1385–1395	(m)
	and	~1365	(s)
B. Alkenyl			
C—H (stretching)		3010–3095	(m)
C=C (stretching)		1620–1680	(v)
$R—CH=CH_2$	(out-of-plane C—H bendings)	985–1000	(s)
	and	905–920	(s)
$R_2C=CH_2$		880–900	(s)
cis-RCH=CHR		675–730	(s)
trans-RCH=CHR		960–975	(s)
C. Alkynyl			
≡C—H (stretching)		~3300	(s)
C≡C (stretching)		2100–2260	(v)
D. Aromatic			
Ar—H (stretching)		~3030	(v)
Aromatic substitution type (C—H out-of-plane bendings)			
Monosubstituted		690–710	(very s)
	and	730–770	(very s)
o-Disubstituted		735–770	(s)
m-Disubstituted		680–725	(s)
	and	750–810	(very s)
p-Disubstituted		800–840	(very s)
E. Alcohols, Phenols, Carboxylic Acids			
OH (alcohols, phenols, dilute solns)		3590–3650	(sharp, v)
OH (alcohols, phenols, hydrogen bonded)		3200–3550	(broad, s)
OH (carboxylic acids, hydrogen bonded)		2500–3000	(broad, v)
F. Aldehydes, Ketones, Esters, and Carboxylic Acids			
C=O stretch		1630–1780	(s)
aldehydes		1690–1740	(s)
ketones		1680–1750	(s)
esters		1735–1750	(s)
carboxylic acids		1710–1780	(s)
amides		1650–1690	(s)
G. Amines			
N—H		3300–3500	(m)
H. Nitriles			
C≡N		2220–2260	(m)

*Abbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.