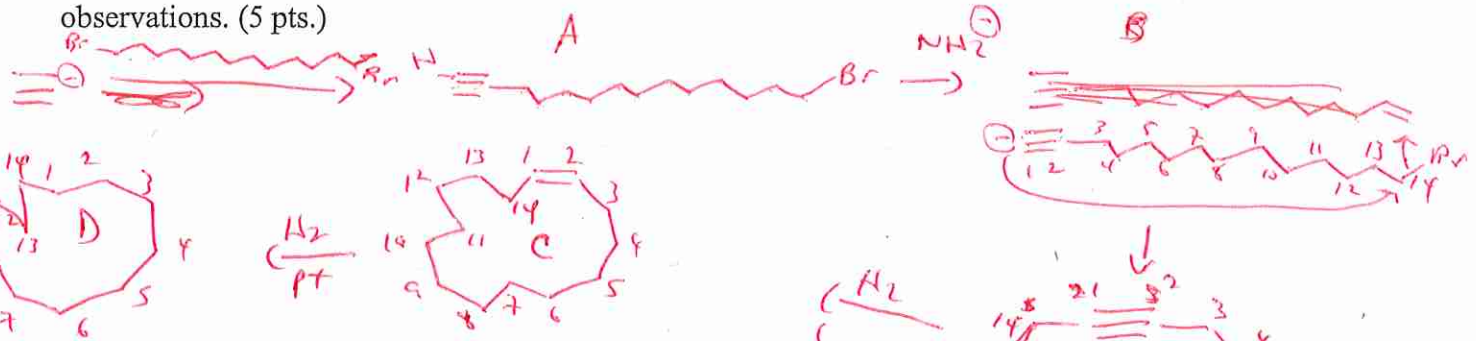
Organic 211 Test # 4 A2_B2 November 12, 2020

Name:_____

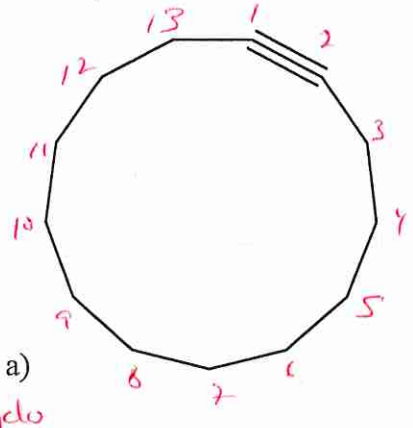
Directions: The exam is worth 106 points but scored out of 100.

1) Compound A has the molecular formula $C_{14}H_{25}Br$ and was obtained by reaction of sodium acetylide with 1,12-dibromododecane. On treatment with compound A with sodium amide, it was converted to compound B ($C_{14}H_{24}$). Ozonolysis of compound B gave the diacid $H_2OC(CH_2)_{12}CO_2H$. Catalytic hydrogen of compound B over Lindlar palladium gave compound C ($C_{14}H_{26}$), and hydrogenation over platinum gave compound D ($C_{14}H_{28}$). C yielded $O{=}C(CH_2)_{12}C{=}O$ on ozonolysis. Assign structures for A, B, C, and D that is consistent with these observations. (5 pts.)



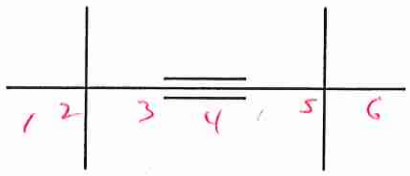
2) Give the name for the following molecules. (3 pts. each)

a)



cyclo
1-tridecyne

b)



2,2,5,5-tetramethylhex-3-yne

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

a) pent-4-yn-1-ylcyclopropane

b) heptadeca-1,16-dien-5,7,9-triyne

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

Primary: 1

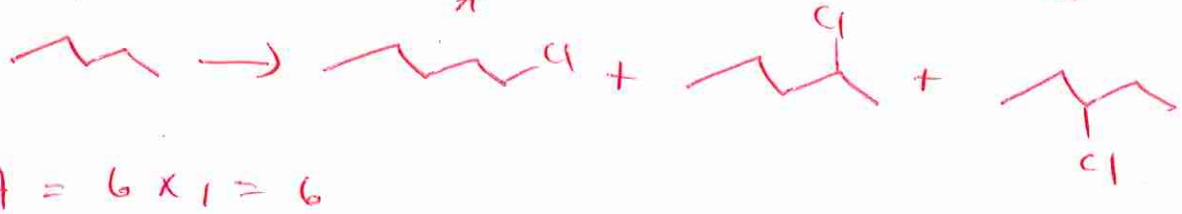
Secondary: 3.9

Tertiary: 9.5

20.4 — 6/29.4 — A

53.1 — 15.6/29.4 — B

26.5 — 7.8/29.4 — C



A = 6 x 1 = 6

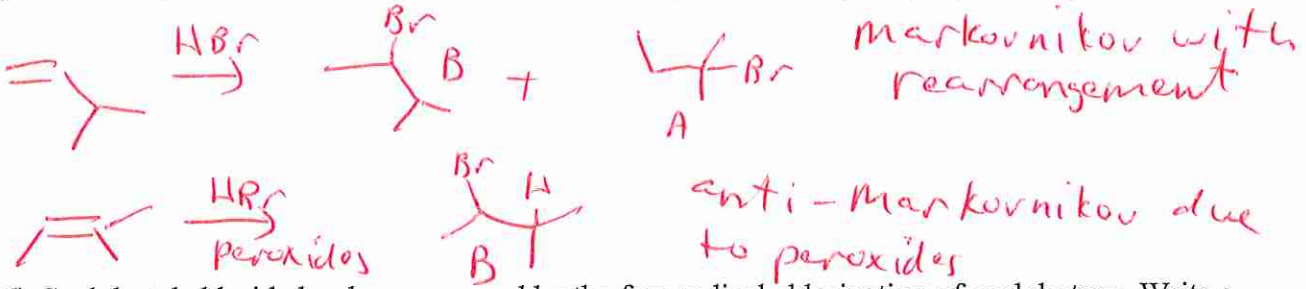
B = 4 x 3.9 = 15.6

C = 2 x 3.9 = 7.8

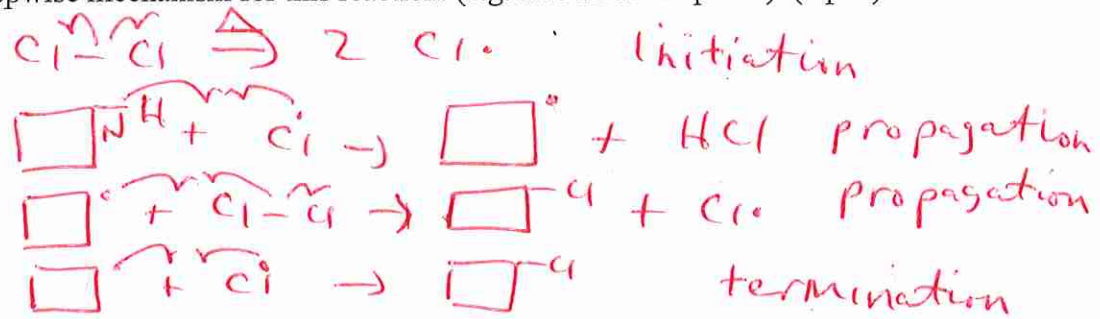
3 / 3.9 / 4 / 15.6

1 / 7.8 / 15.6 / 23.4 / 6 / 29.4

5) Electrophilic addition of HBr to $CH_2{=}CHCH(CH_3)_2$ gives a mixture of two constitutional isomers A and B. Only B is formed, however, when $CH_3CH{=}C(CH_3)_2$ reacts with HBr in the presence of peroxides. Identify A and B and explain your reasoning. (4 pts.)



6) Cyclobutyl chloride has been prepared by the free-radical chlorination of cyclobutane. Write a stepwise mechanism for this reaction. (e.g. arrows are required). (6 pts.)



7) Which would you expect to be more shielded, the carbonyl carbon of an aldehyde or a ketone? Explain your answer. (4 pts.)

ketone

vs

aldehyde

So ketone more shielded

CH_3 is electron donating so 2 CH_3 groups

H is not electron donating

8) Ethylene lacks a peak in its IR spectrum for C=C stretching. Why? (4 pts.)

a dipole moment is needed for an IR stretch. ethylene is symmetrical so no IR stretch (peak).

9) Give a possible molecular formula for molecule A that contains 4 nitrogens and weighs 336 grams per mole. Show your work. (4 pts.)

N 14 × 4 = 56

336 − 56 = 280

280 ÷ 13 = 21 · x

280 − 260 = 20

21 = 12 + 9 = 12 + 1 + 8

12 × 21 = 252

1 × 21 = 21

8 × 21 = 168

21 + 168 = 189

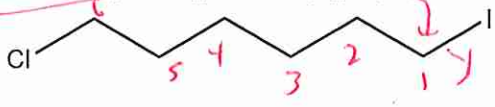
252 + 189 = 441

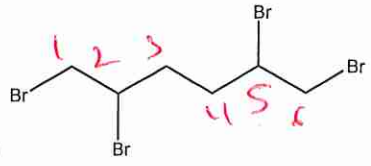
280 − 252 = 28

$\therefore C_{21}H_{28}N_4$

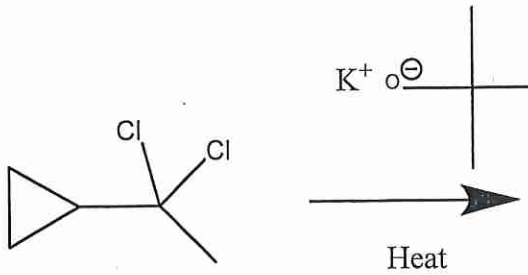
10) You think your molecule has bromine in it. How could you determine whether it does or not? (4 pts.) look at M+ and M+2 peak in mass spectrum. Bromine has two equal peaks. this is because Br^{79} and Br^{81} are roughly equal isotopes.

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. (3 pts.)

a) 1 eq.  +  → ????

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

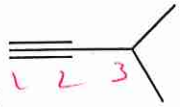
c)



DMSO

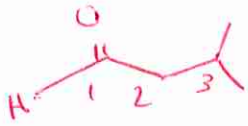
????

d)

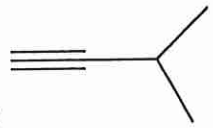


1) $(sia)_2BH$
2) H_2O_2/OH^-

?????

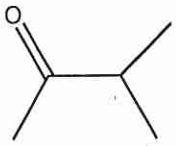


e)

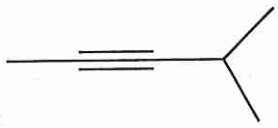


???? H_2SO_4

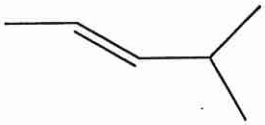
$HgSO_4$



f)



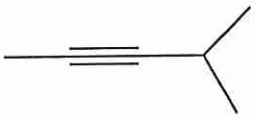
????



Na / NH_3 or Li / NH_3

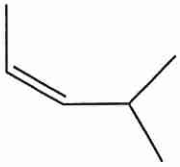
g)

h)



???? H_2

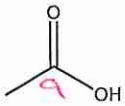
Lindlar's catalyst



i)

????

O_3/H_2O



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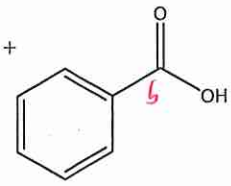
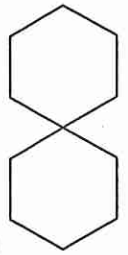
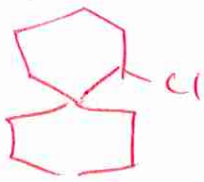


j)



Cl_2/Heat

?????



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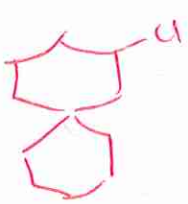


+

+ e

+ e

12) Outline a synthesis of 1-pentyne from 2-propanol using any required organic or inorganic reagents. (5 pts.)

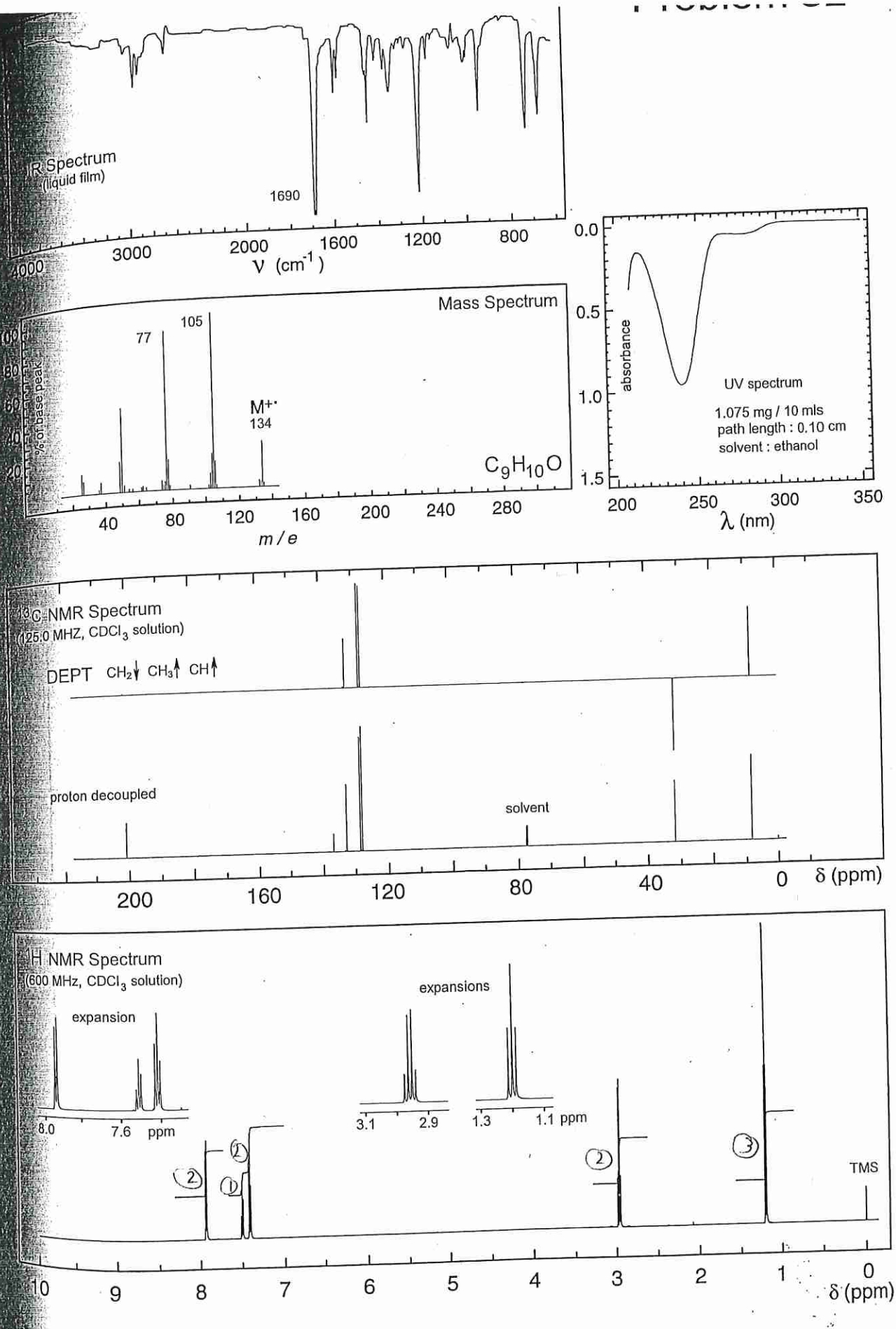
13) Give a structure that gives the following spectra on the three following sheets. 1st sheet is a, 2nd sheet is b, 3rd sheet is c. (5 pts. Each)

a)

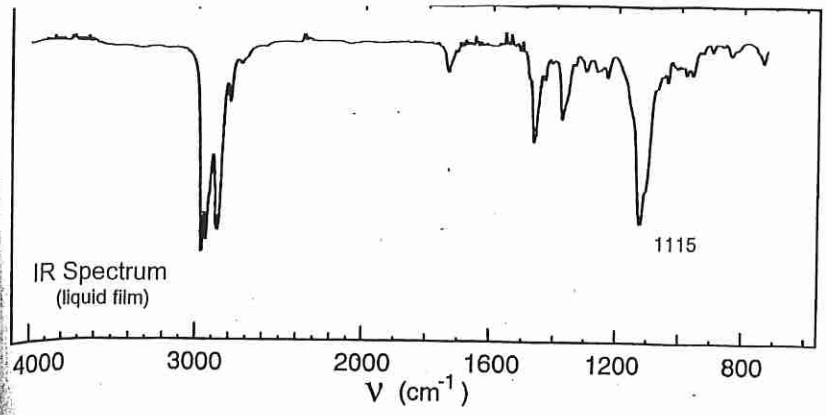
b)

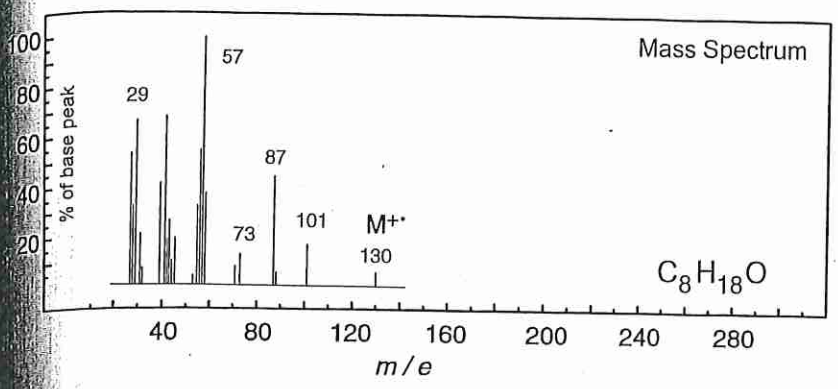
c)

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

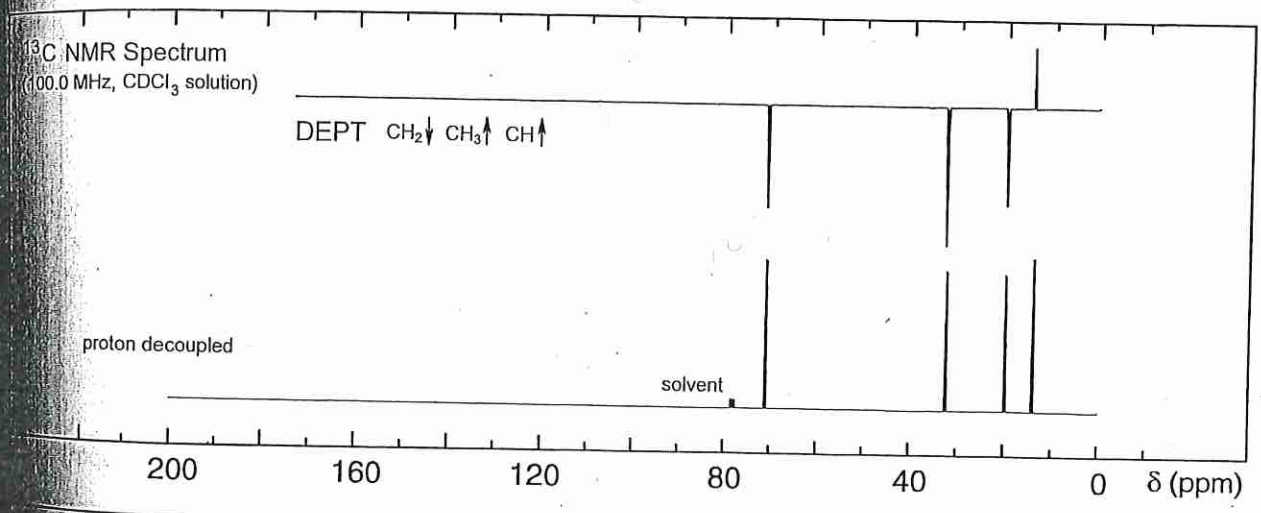

IR Spectrum
(liquid film)
1690
4000
3000
2000
1600
1200
800
ν (cm-1)
Mass Spectrum
77
105
M+·
134
C9H10O
% of base peak
40
80
120
160
200
240
280
m/e
absorbance
0.0
0.5
1.0
1.5
UV spectrum
1.075 mg / 10 mls
path length : 0.10 cm
solvent : ethanol
200
250
300
350
λ (nm)
13C NMR Spectrum
(125.0 MHZ, CDCl3 solution)
DEPT CH2 CH3 CH
proton decoupled
solvent
200
160
120
80
40
0
δ (ppm)
1H NMR Spectrum
(600 MHz, CDCl3 solution)
expansion
8.0
7.6
ppm
expansions
3.1
2.9
1.3
1.1 ppm
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

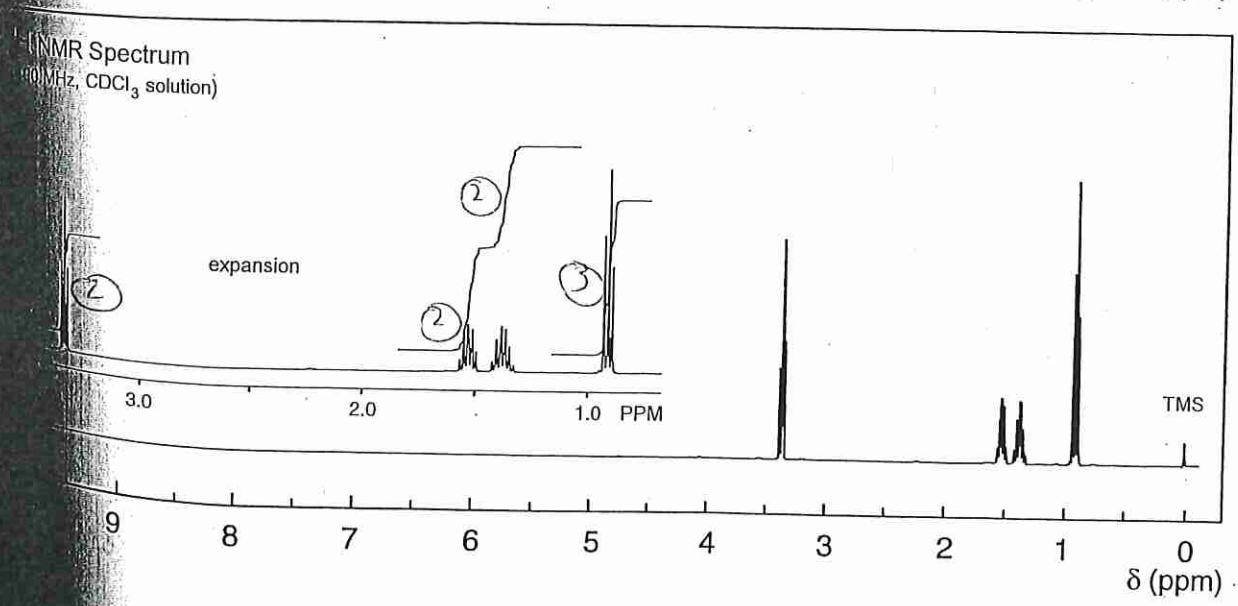
Problem 98

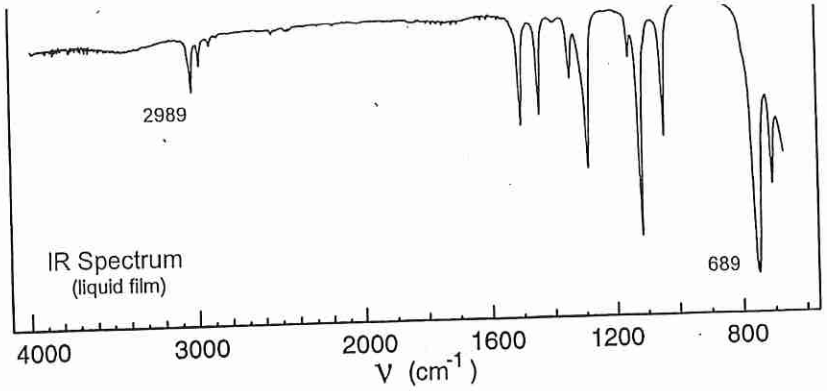


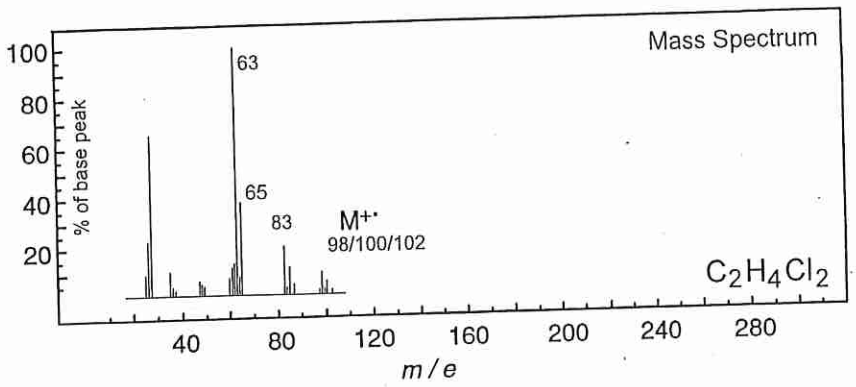


No significant UV absorption above 220 nm

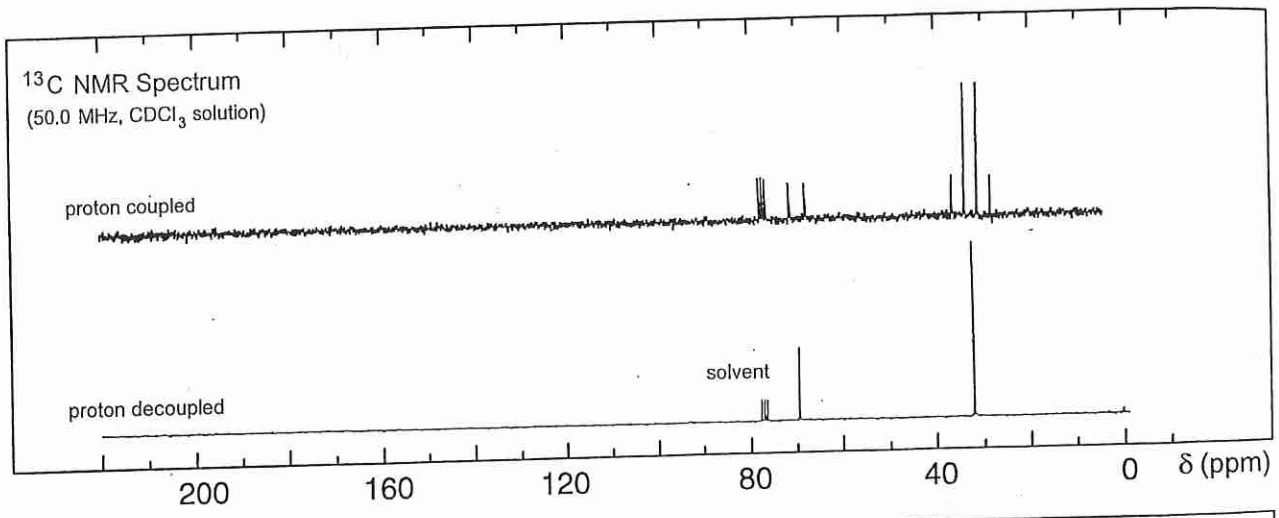








No significant UV absorption above 220 nm



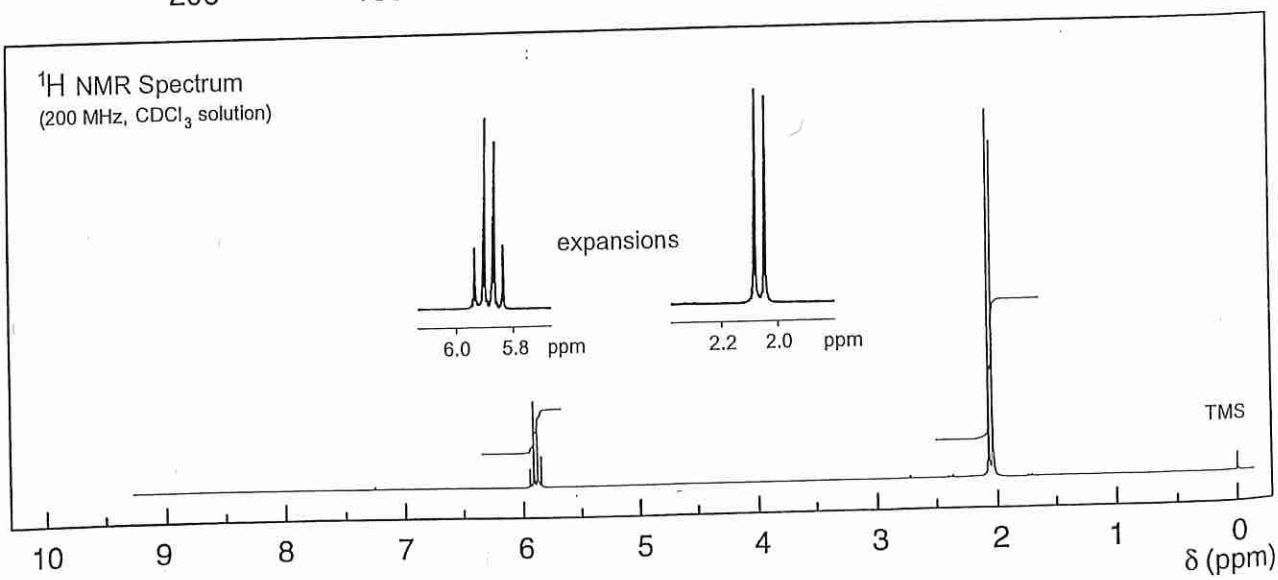
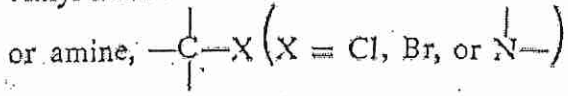
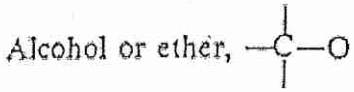
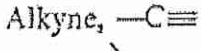
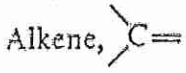
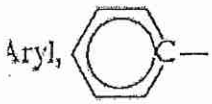
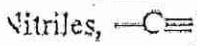
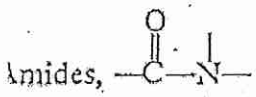
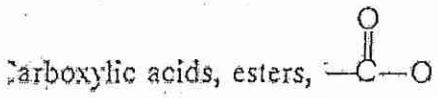
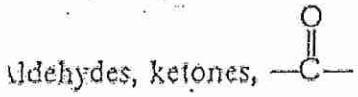


TABLE 13.1 Approximate Proton Chemical Shifts

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, $RC(=O)CH_3$	2.1–2.6
Aldehyde, $RC(=O)H$	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, $RC(=O)OH$	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