| Last Name | ANSWER | First Name | KEY | MI |

| Student ID Number: | Total Score |

| Circle the name of your TA: | MIKE | ROB |

| Discussion Section – Day: | Time: | / 100 |

Chem 30B Spring 2004

MIDTERM #2
(50 Min)

Weds May 26th

INTERPRETATION OF THE QUESTIONS IS PART OF THE EXAM – DO NOT ASK FOR THE QUESTIONS TO BE EXPLAINED TO YOU

ONLY ANSWERS WRITTEN IN THE BOXES PROVIDED WILL BE GRADED

****DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO****

Q1	/ 20	Q4	/ 15
Q2	/ 20	Q5	/ 30
Q3	/ 15	Bonus	/ 15
		Total	/ 100

"Marge, don't discourage the boy! Weaseling out of things is important to learn. It's what separates us from the animals ... except the weasel." – Homer Simpson
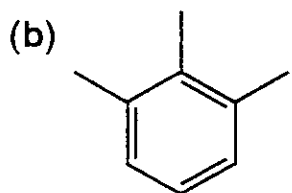
1. Predict the number of signals you would expect to see in the 1H-decoupled 13C-NMR spectrum of each of the molecules shown below. (2 points each)

(a)
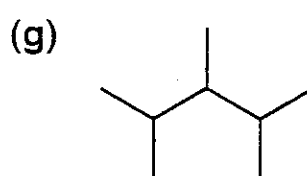
1

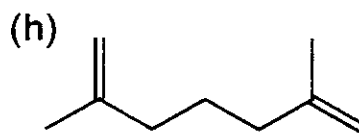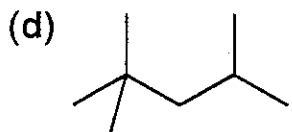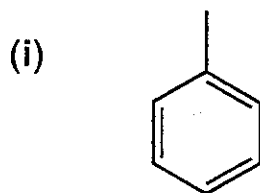(f)
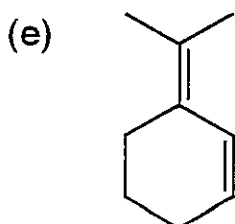
3

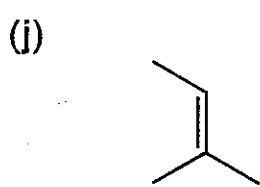(b)

6

(g)

5

(c)

2

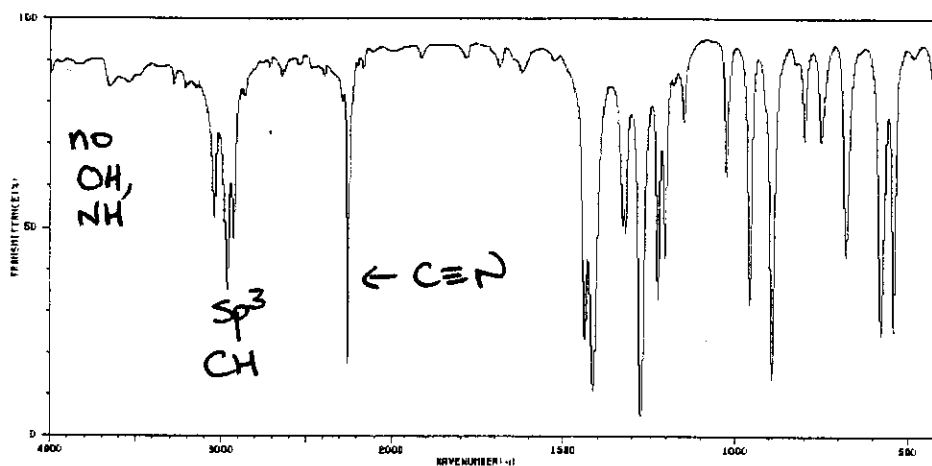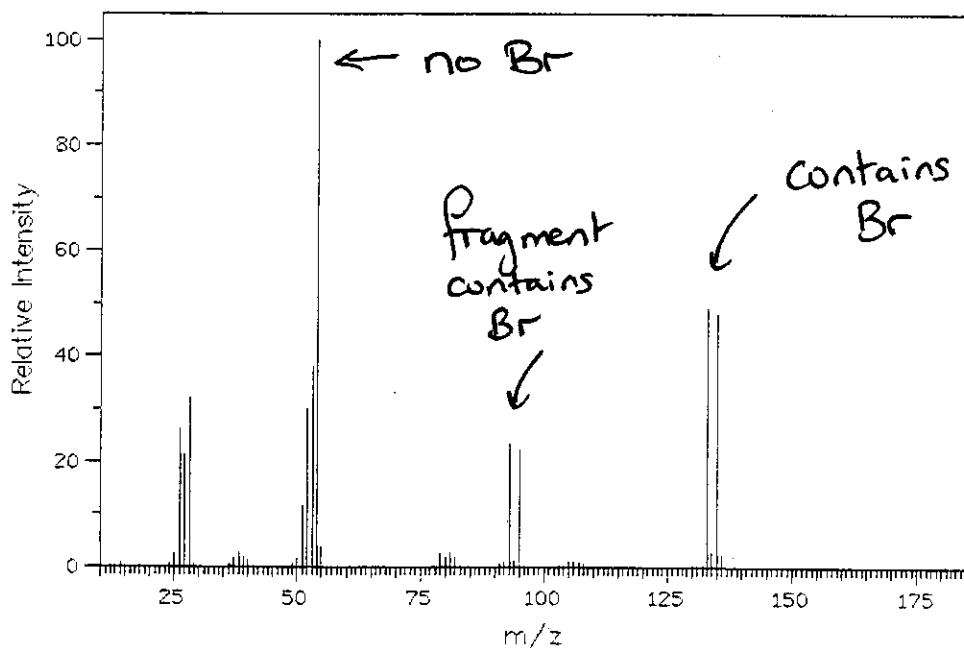(h)

5

(d)

5

(i)

5

(e)

9

(j)
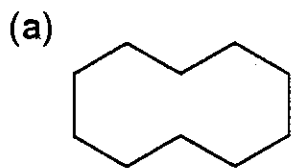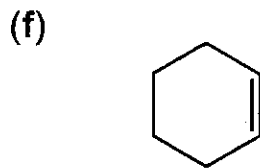
5

2. Some spectroscopic data for an unknown compound (A) are shown below. Use these data to answer the questions on the following page.

IR Spectrum

no OH, NH

sp³ CH

← C≡N

Mass Spectrum

← no Br

fragment contains Br

Contains Br

The base peak (100% intensity) is at $m/z = 54$. The peaks at $m/z = 133, 134, 135,$ and 136, have the following relative intensities (49:2:48:2), respectively.

└ odd M⁺, i.e. contains odd # of nitrogens

1H-NMR Spectrum

$\delta = 3.0$ (triplet, integration = 1), $\delta = 3.5$ (triplet, integration = 1) ppm

└ 2 different sets of Hs
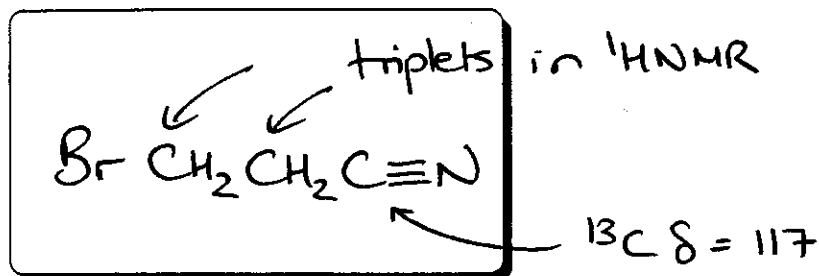
13C-NMR Spectrum

$\delta = 22, 25, 117$ ppm

└ 3 different C atoms

(a) What is the molecular formula of compound A? (3 points)

$$C_3H_4BrN$$
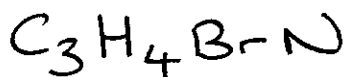
M+1 peak ~ 4% of M+,
hence $4/1.1 = 3.X$,
so contains 3 C atoms

$3C = 3 \times 12 = 36$
$1 Br = 1 \times 79 = 79$
$\overline{115}$
$133 - 115 = 18$
$= 1 N$ and $4H$

(b) What is the structure of compound A? (10 points)

triplets in ^1HNMR

$Br \ CH_2 \ CH_2 \ C\equiv N$

$^{13}C \ \delta = 117$

(c) What is the **precise** structure of the fragment that gives rise to a peak at $m/z = 93$? (2 points)
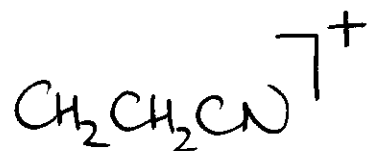
$$^{79}Br - CH_2 \rceil^+$$
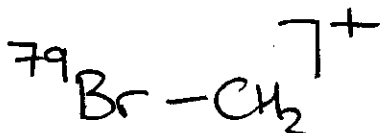
$79 + 14 = 93$
Significant M+2 peak

(d) What is the **precise** structure of the fragment that gives rise to a peak at $m/z = 95$? (Your answer should differ from that given in part (c)) (2 points)
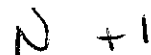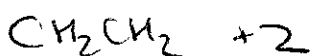
$$^{81}Br - CH_2 \rceil^+$$
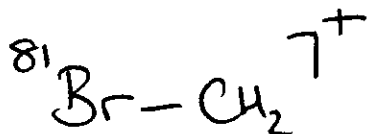
$81 + 14 = 95$
Significant M+2 peak

(e) What is the structure of the fragment that gives rise to the base peak at $m/z = 54$? (3 points)

$$CH_2 CH_2 CN \rceil^+$$
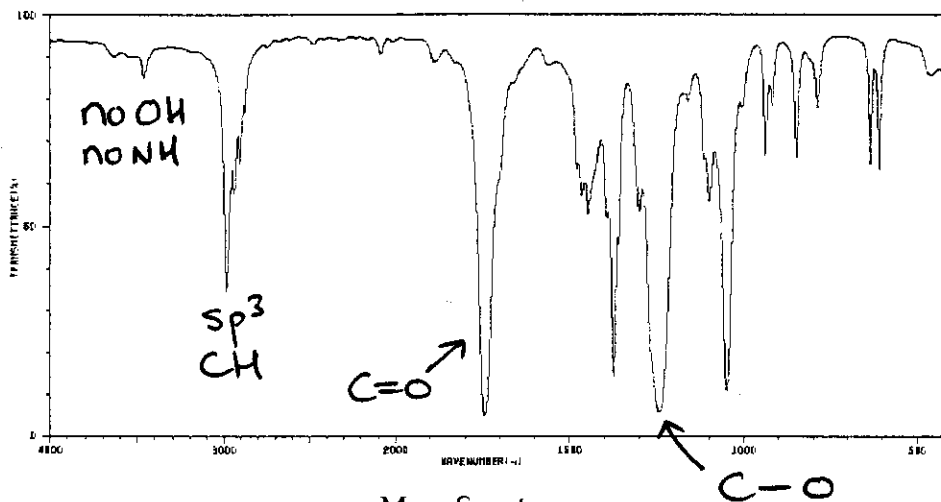
← contains no Br
(no significant M+2 peak)

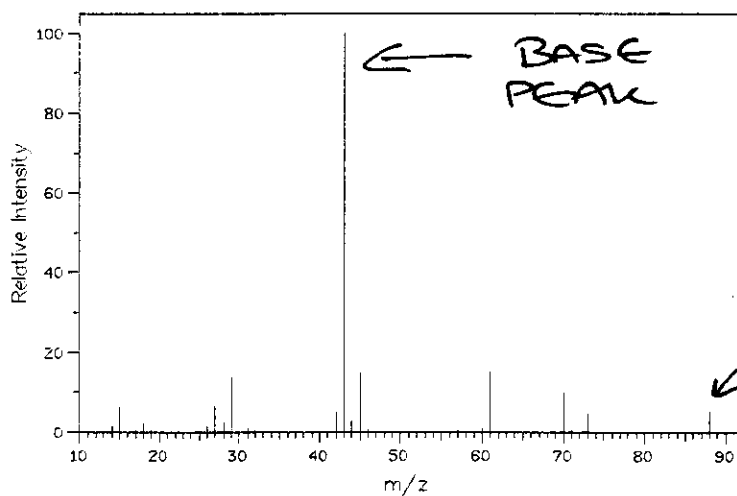$C\equiv N \quad +2 \qquad Br \quad +2 \qquad ^3 \qquad CH_2 CH_2 \quad +2 \qquad N \quad +1$

3. Some spectroscopic data for an unknown compound (B) are shown below. Use these data to answer the questions on the following page.
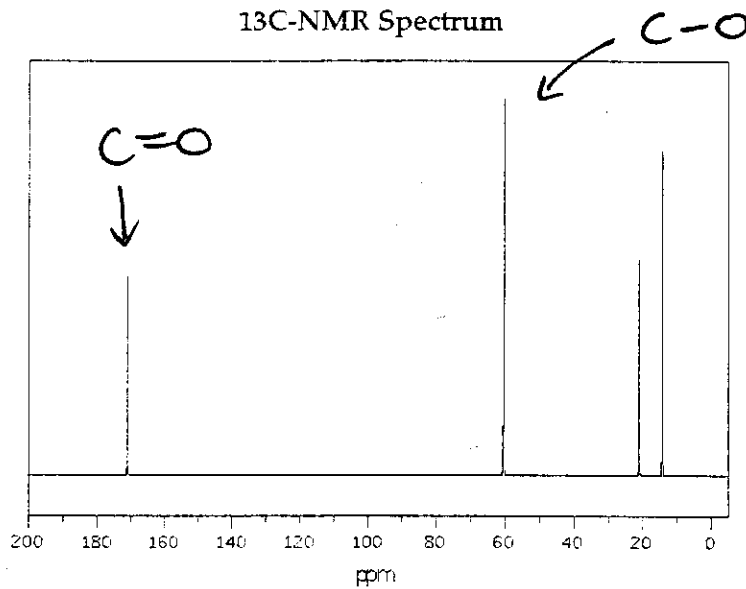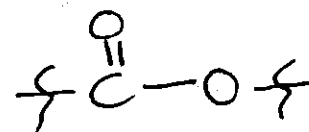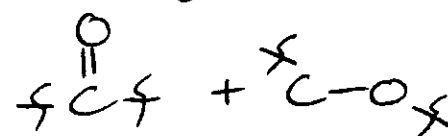
IR Spectrum

no OH
no NH

Sp³ CH

C=O

C—O

Mass Spectrum

BASE PEAK

M⁺ at 88

13C-NMR Spectrum

C—O

C=O

Suggests

Image shows structural fragments drawn in the right margin.

4

CH₃ singlet

Suggestive
of
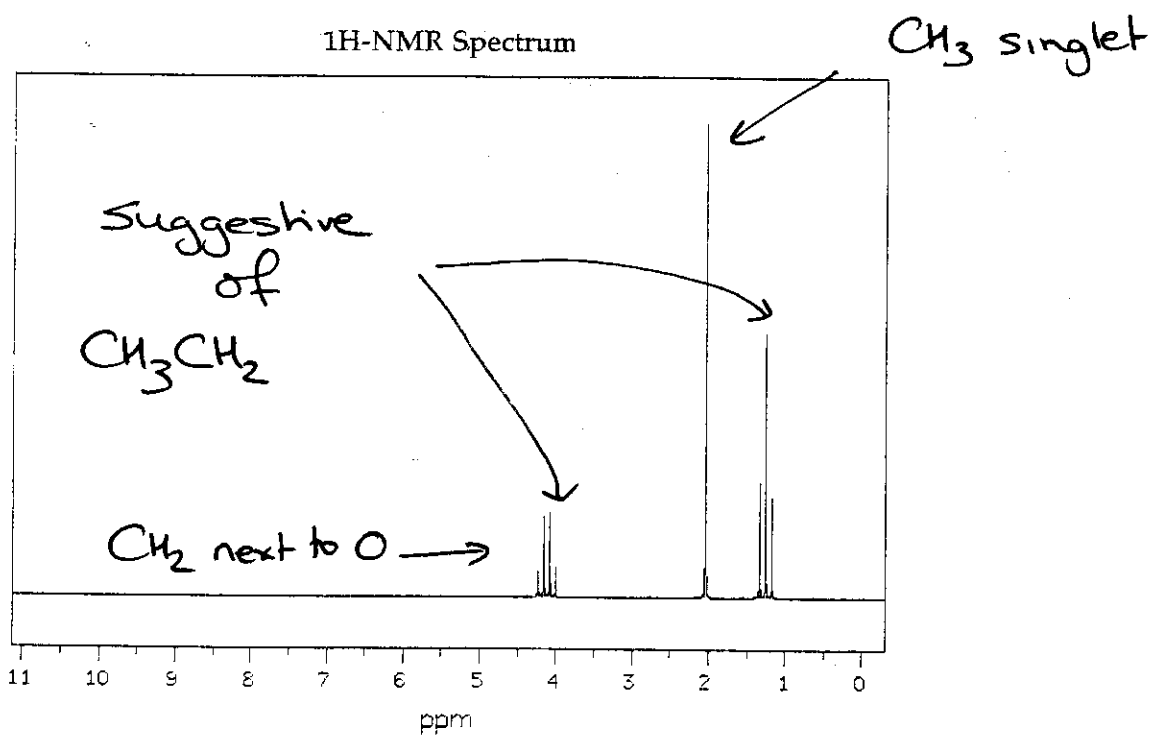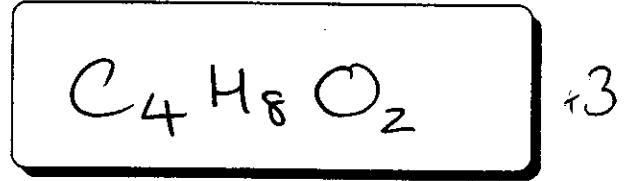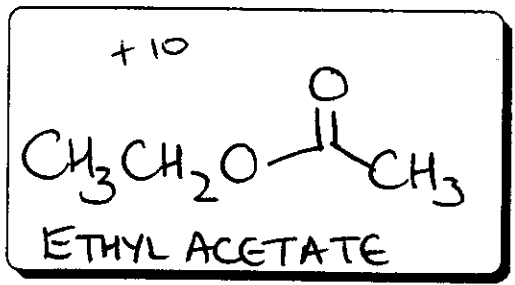CH₃CH₂

CH₂ next to O ⟶

11 10 9 8 7 6 5 4 3 2 1 0

ppm

The relative integration of the peak groupings from left to right are 2:3:3

(a) What is the molecular formula of compound B? (3 points)
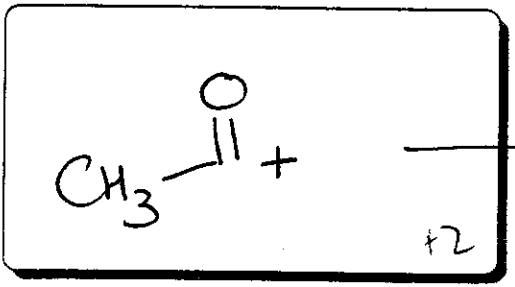
$$C_4 H_8 O_2$$ +3

Contains $2 \times O$ = 32
$88 - 32$ = 56
$56 = C_4 H_8$ or
$56 = C_3 H_{20}$!! $\underline{\underline{NO}}$
·no Ns (even M⁺)
So, $C_4 H_8 O_2$

(b) What is the structure of compound B? (10 points)

+10

$$CH_3 CH_2 O - \overset{O}{\underset{}{\overset{||}{C}}} - CH_3$$

ETHYL ACETATE

$CH_3 CH_2$ (+2)
$-O-$ (+2)
CH_3 isolated (+2)

$\left(CH_3 O - \overset{O}{\underset{}{\overset{||}{C}}} - CH_2 CH_3 \; \frac{+8}{?} \right)$

(c) What is the structure of the fragment that gives rise to the base peak at m/z = 43? (2 points)

$$CH_3 - \overset{O}{\underset{}{\overset{||}{C}}} +$$ +2   ⟶

V. stable, in
resonance
w/ $CH_3 - C \equiv \overset{+}{O}$

5

4. Compounds C, D, and E are isomers with the molecular formula $C_5H_{11}Br$. The 1H-decoupled 13C-NMR spectrum of each compound is shown below, with the assignment from the DEPT spectrum shown above each peak (All peaks are shown, there are no peaks at ppm values > 100). In the boxes provided below, draw the structures of C, D, and E, based upon these spectra. (5 points each)

C

CH₃
CH₂
CH₂
CH

100   75   50   25   0 δ (ppm)

D

CH₃
CH₂
C
CH₃

100   75   50   25   0 δ (ppm)

E

CH₃
3 x CH₂
CH₂

100   75   50   25   0 δ (ppm)

C
CH
CH₂
Br
CH₃
CH₂
Same

D CH₃'s same
CH₂
CH₃
Br
C

E
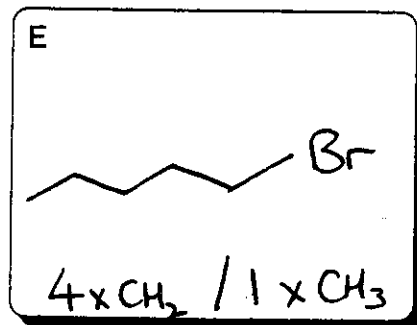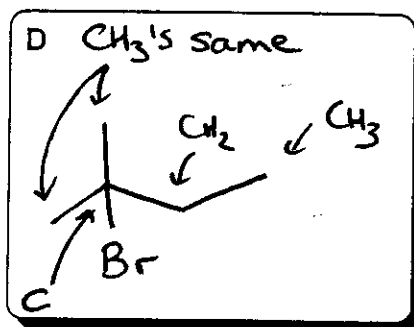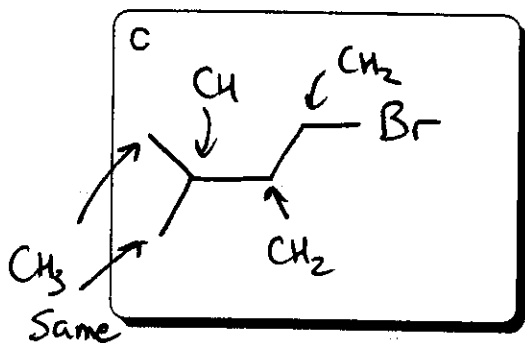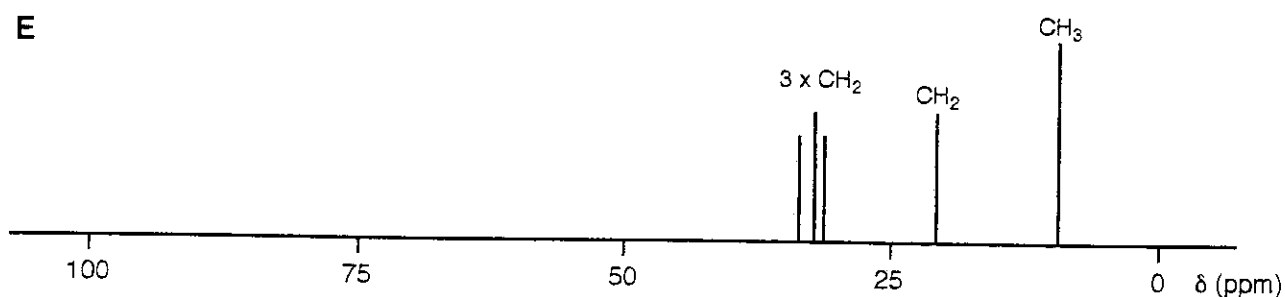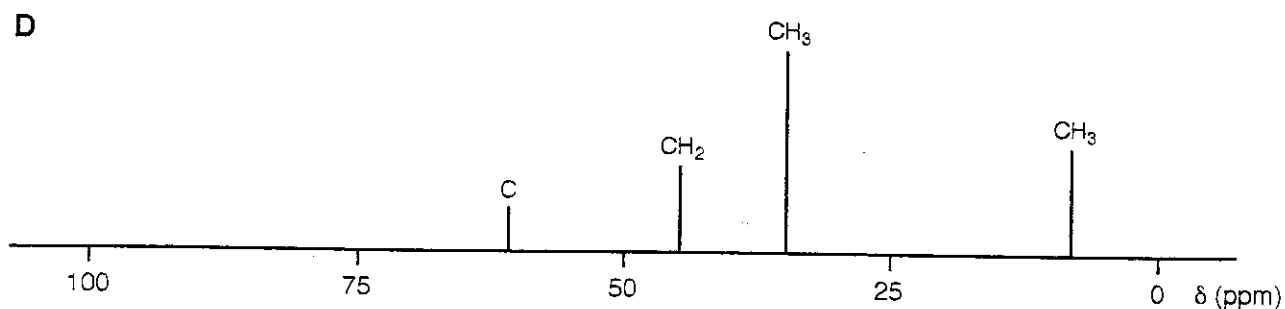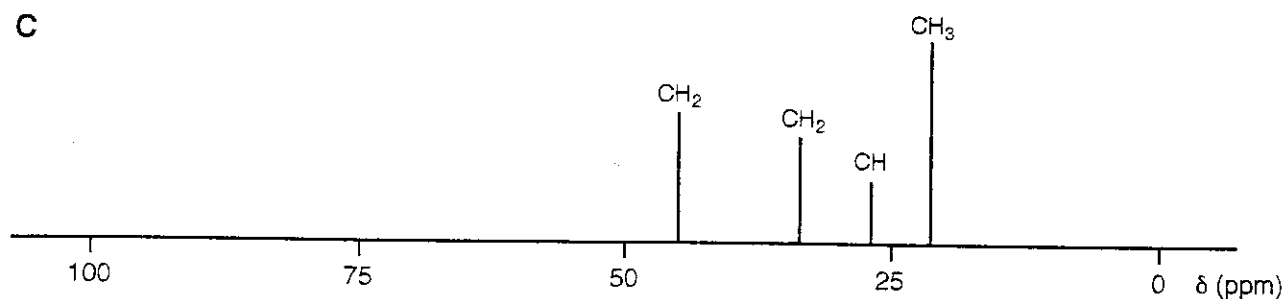
Br
4 x CH₂ / 1 x CH₃
↑
all different

5. The diols shown below react with ketones (acetone in a and b; methyl ethyl ketone in c and d) to form cyclic ketals. In each case, draw the product of the reaction (F, G, and H), note: in d, two different diastereomeric products (J and K) are formed. In parts a and b, predict how many methyl signals will be observed in the 1H NMR spectra of compounds F and G, respectively. In compounds H, J, and K, what are the stereotopical relationships between the phenyl groups in each case. (3 points per box)
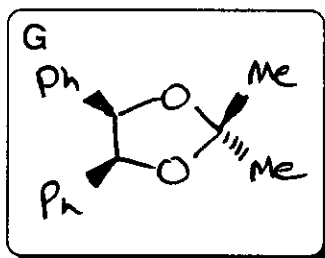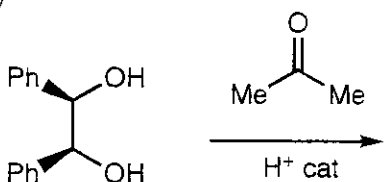
(a)
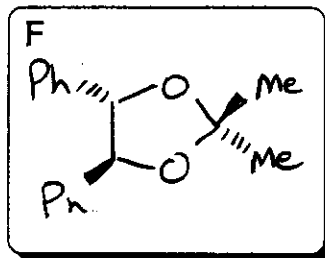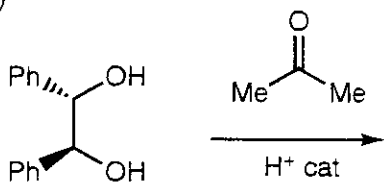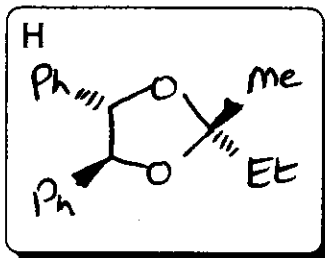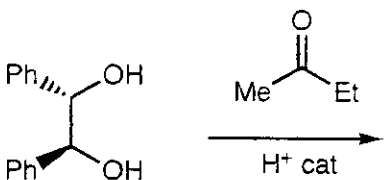

Number of methyl signals in 1H NMR spectrum of F?

ONE

(b)

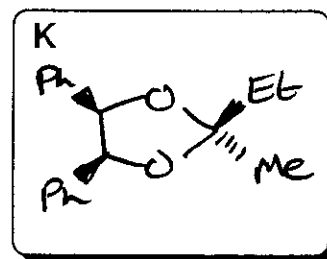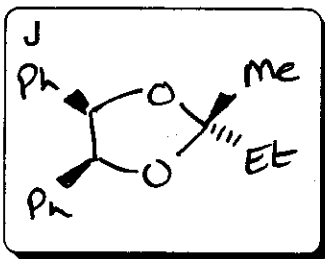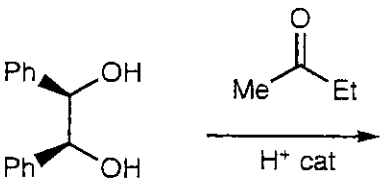Number of methyl signals in 1H NMR spectrum of G?

TWO

(c)

Topicity of Ph groups (Homotopic / Enantiotopic / Diastereotopic) in H?

DIASTEREOTOPIC

(d)

+

Topicity of Ph groups (Homotopic / Enantiotopic / Diastereotopic) in J?

ENANTIOTOPIC

Topicity of Ph groups (Homotopic / Enantiotopic / Diastereotopic) in K?

ENANTIOTOPIC

7

6 (BONUS) At −100 °C, undecadeuteriocyclohexane (L) gives rise to two equal intensity signals in the 1H-NMR spectrum. In contrast, at room temperature, only one signal is observed in the 1H-NMR spectrum.

L
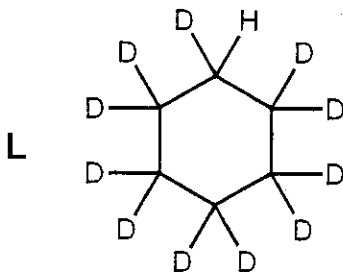
(a) Draw the two different species (L1 and L2) that give rise to the signals at −100 °C (3 points each)

EQUATORIAL

L1

L2   H ← AXIAL

D₁₁

AXIAL | EQUATORIAL ⟹ DIFFERENT ENVIRONMENTS
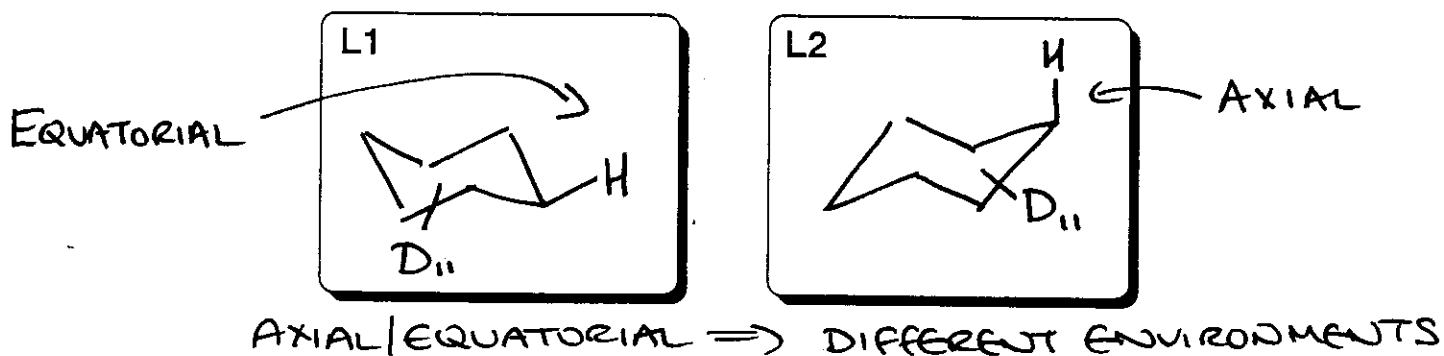
(b) Briefly explain why only one signal is observed in the 1H-NMR spectrum when it is recorded at room temperature (4 points)

D₁₁ ⇌ D₁₁

H RING FLIP IS FAST AT RT, SO AVERAGE SIGNAL IS OBSERVED
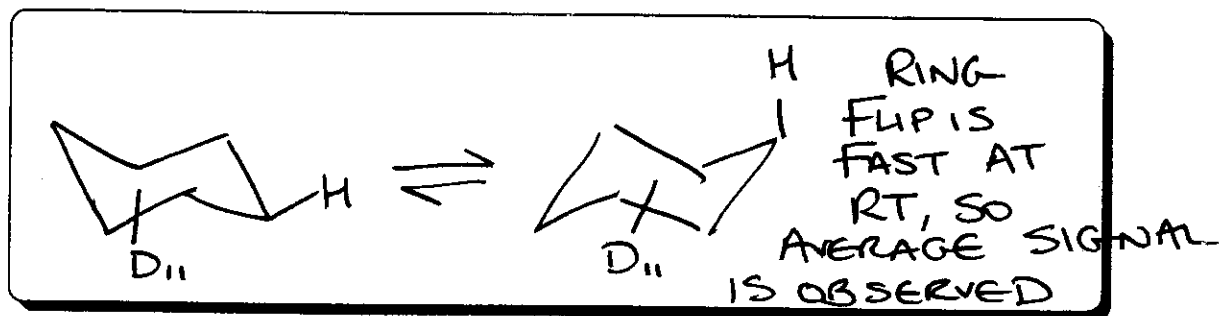
7 (BONUS) Compound M has the molecular formula $C_4H_8O_2$. Only one peak is observed in the 1H-decoupled 13C-NMR spectrum, and only one singlet is observed in the 1H-NMR spectrum. Propose a structure for M. (5 points)

M