5.46: Organic Structure Determination
Hour Exam 1

Prof. Tim Jamison
April 16, 2004

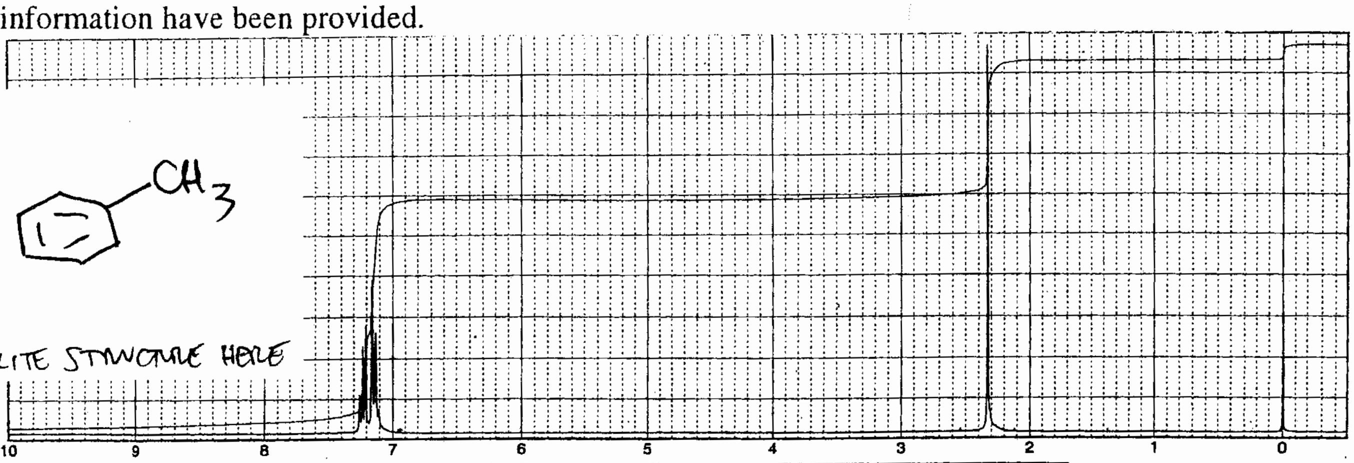
Your Name: KEY

Instructions: You have **50 minutes** to complete this **closed book, closed notes** exam. You may use a calculator, but no notes, books or other information are allowed. Please read through the entire exam before beginning. Where applicable, show your work to receive partial credit.

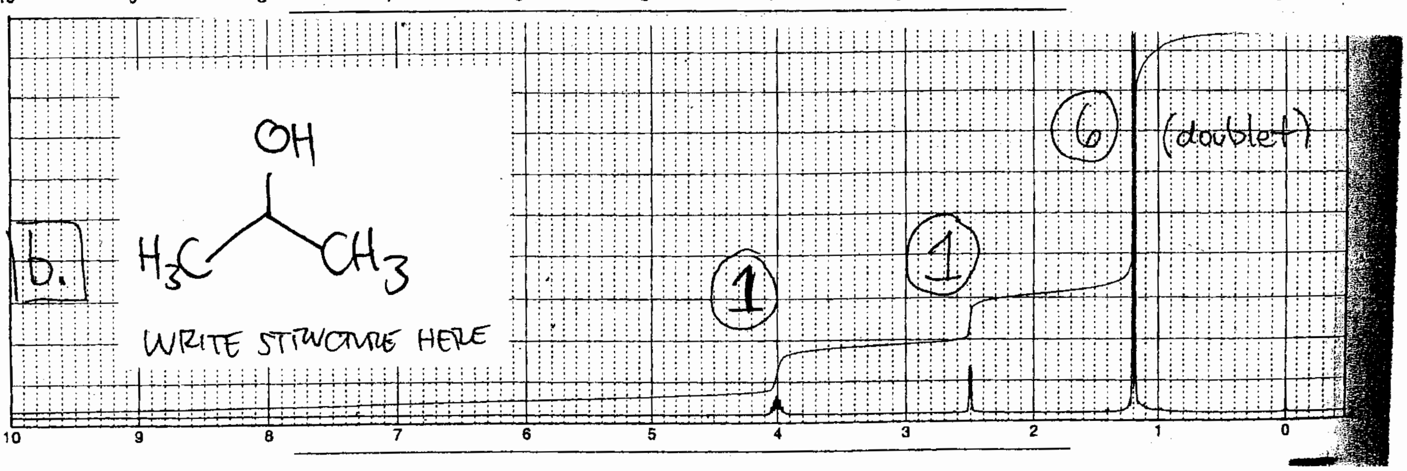
Question	Points Received/Possible
1.	____ / 15
2.	____ / 5
3.	____ / 20
4.	____ / 20
5.	____ / 20
6.	____ / 20
Total:	____ / 100

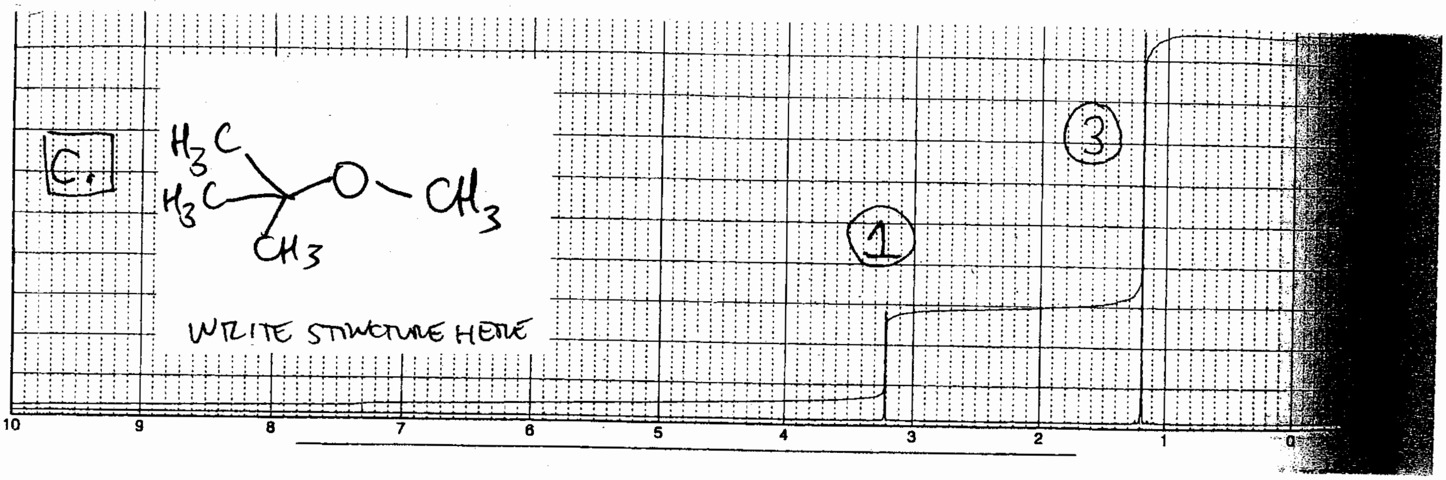
1. **(20 points total, 2 points each)** ^{1}H NMR spectra of 10 **common organic solvents** are provided below and on the following 2 pages. For each, neatly **draw the structure** (i.e. not formula, acronym) in the white space provided on each spectrum. In some cases, the relative integration values (circled numbers) and/or other information have been provided.

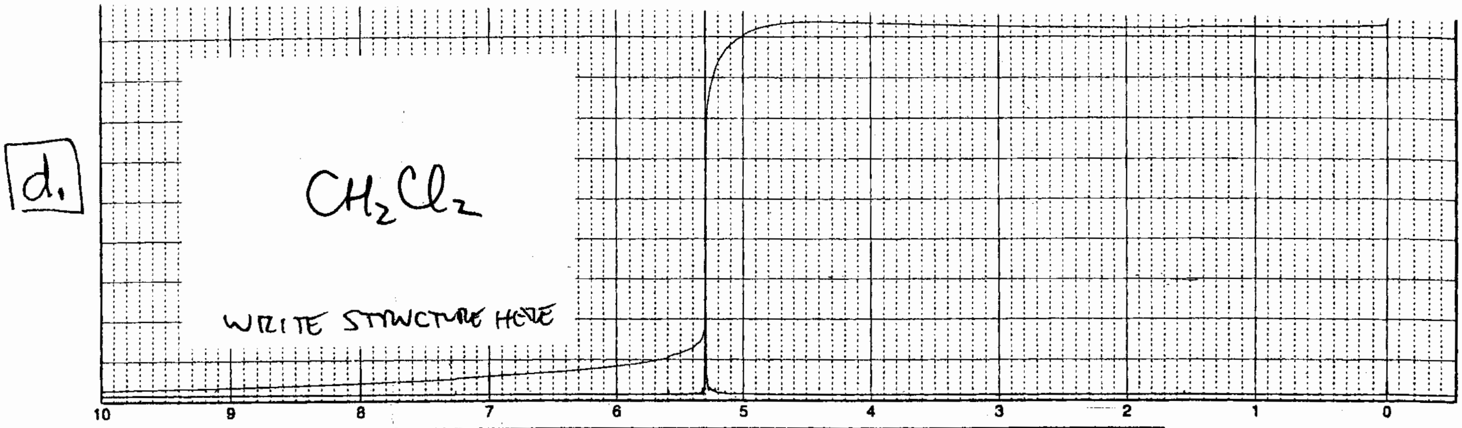
a.

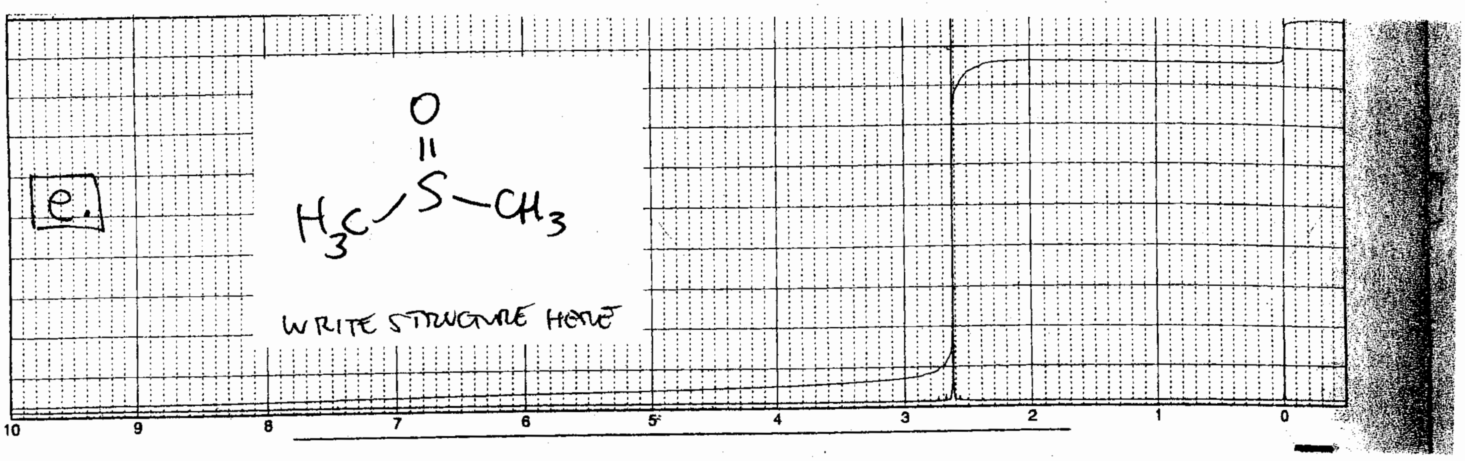


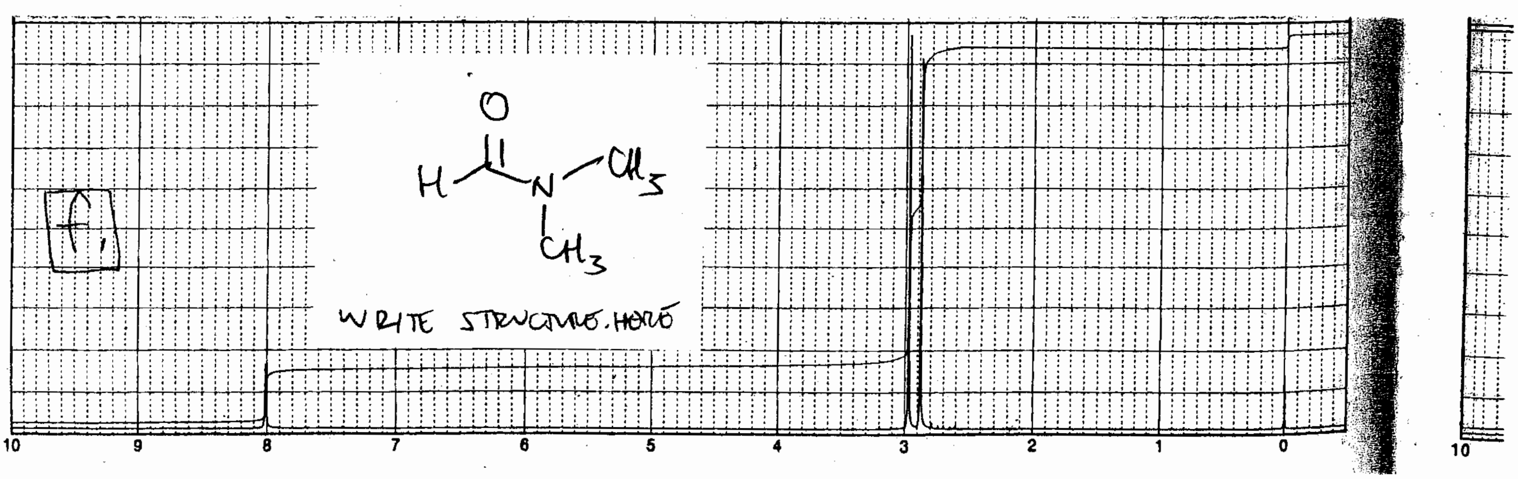
b.



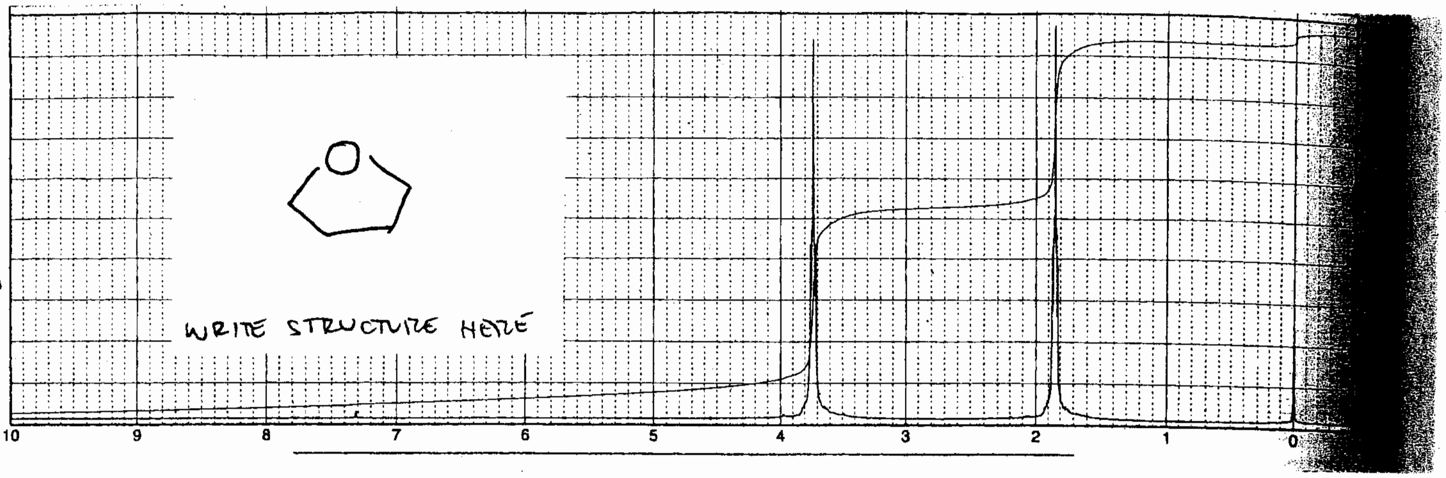

c.
CH_3
3
1
WRITE STRUCTURE HERE
10 9 8 7 6 5 4 3 2 1 0

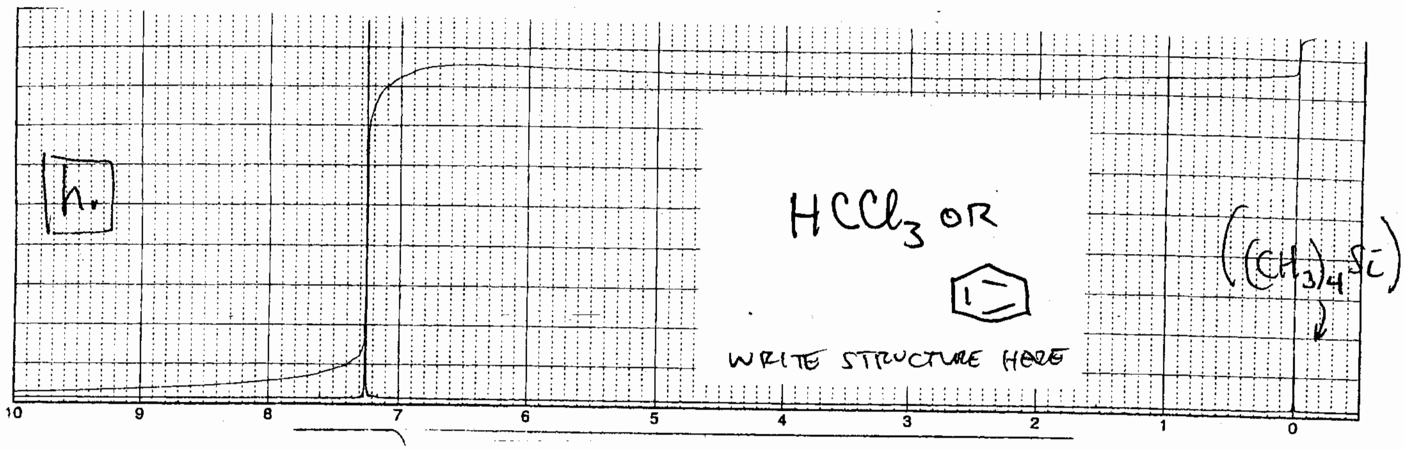

d.
CH_2Cl_2
WRITE STRUCTURE HERE
10 9 8 7 6 5 4 3 2 1 0

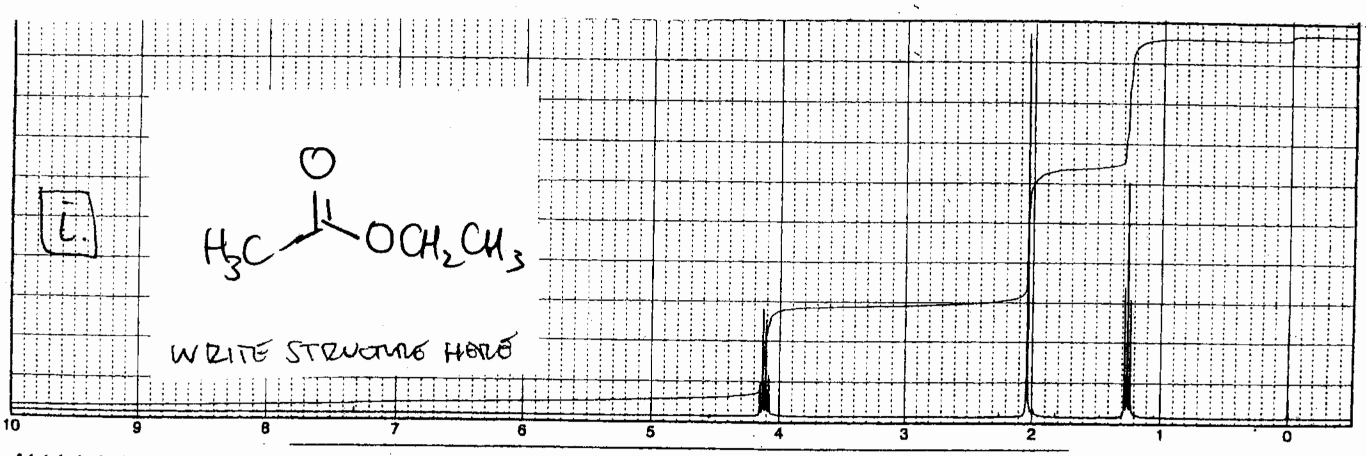

e.
WRITE STRUCTURE HERE
10 9 8 7 6 5 4 3 2 1 0

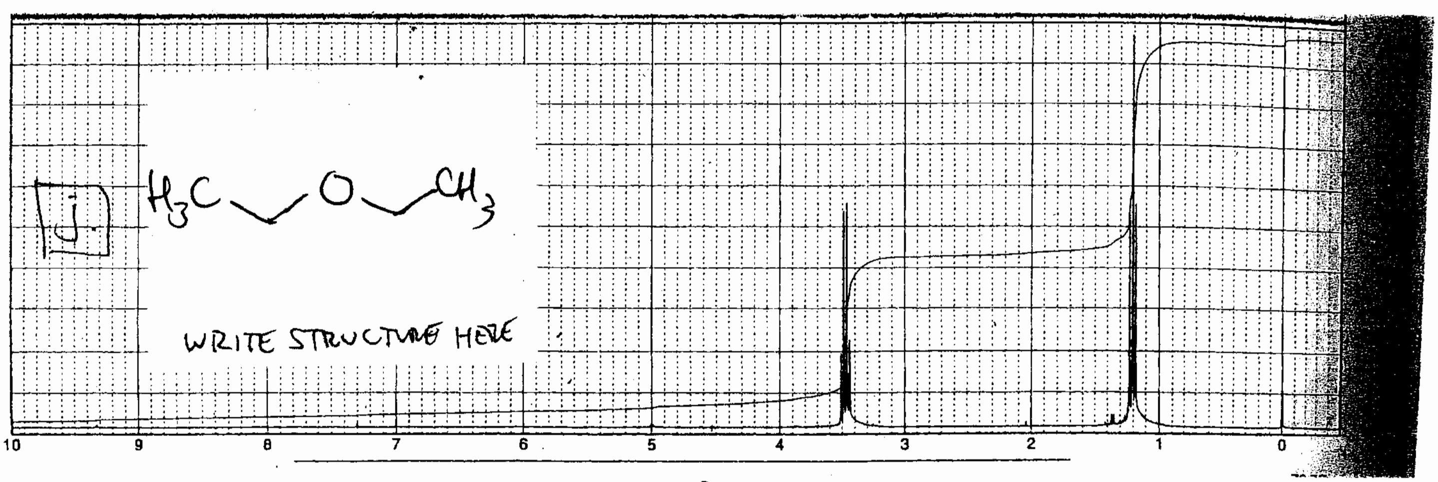

f.
WRITE STRUCTURE HERE
10 9 8 7 6 5 4 3 2 1 0

g.


O
WRITE STRUCTURE HERE
10 9 8 7 6 5 4 3 2 1 0


h.
$HCCl_3$ OR
WRITE STRUCTURE HERE
$((CH_3)_4Si)$
10 9 8 7 6 5 4 3 2 1 0

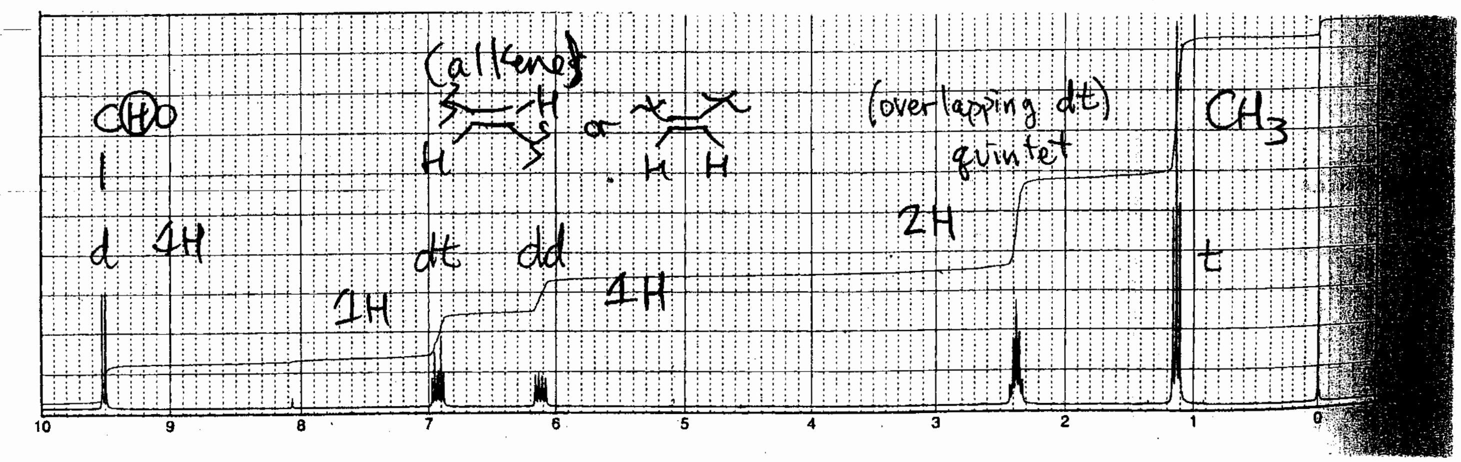

i.
O
H_3C OCH_2CH_3
WRITE STRUCTURE HERE
10 9 8 7 6 5 4 3 2 1 0


j.
H_3C O CH_3
WRITE STRUCTURE HERE
10 9 8 7 6 5 4 3 2 1 0

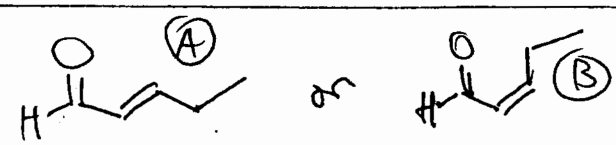
2. (5 points) Despite the fact that carbon atoms generally have at least one hydrogen (^{1}H nucleus, $I = 1/2$) atom attached to them, the signals for CH_n groups (n = 1, 2, or 3) in ^{13}C spectra usually appear as singlets (e.g. cyclohexane, C_6H_{12}, has one signal (singlet) at 27.1 ppm). Explain (briefly and succinctly).

^{13}C NMR SPECTRA ARE TYPICALLY ACQUIRED WITH "PROTON DECOUPLING"

3. (20 points) There are **5 signals** in the ^{13}C NMR spectrum of the compound with the following ^{1}H NMR spectrum, and this unknown has molecular weight (MW) = 84 g/mol. **Draw the structure** of this compound in the box provided, and explicitly show stereochemistry, double bond geometry, etc., if applicable.



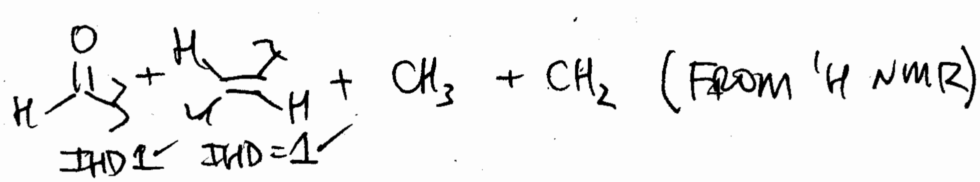
^{13}C : 5 SIGNALS
^{1}H : 5 DIFF H
⇒ PROB C_5
• "RULE OF 13": $\frac{84}{13} = 6 + \frac{6}{13}$
⇒ C_6H_{12}
• AT LEAST 1 O ATOM (CHO GROUP IN ^{1}H NMR)
$O \Rightarrow CH_4$
⇒ C_5H_8O
IHD = 2

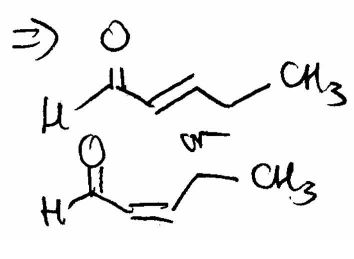


NEED J FOR ALKENE H'S TO DIFFERENTIATE.
(IT'S A.)

(**draw the structure** of the compound in this box.)

• CH_3 + CH_2 COUPLED
⇒ CH_3-CH_2-
• alkene CONJUGATED TO CHO
(↑doublet + δ OF ALKENE H)





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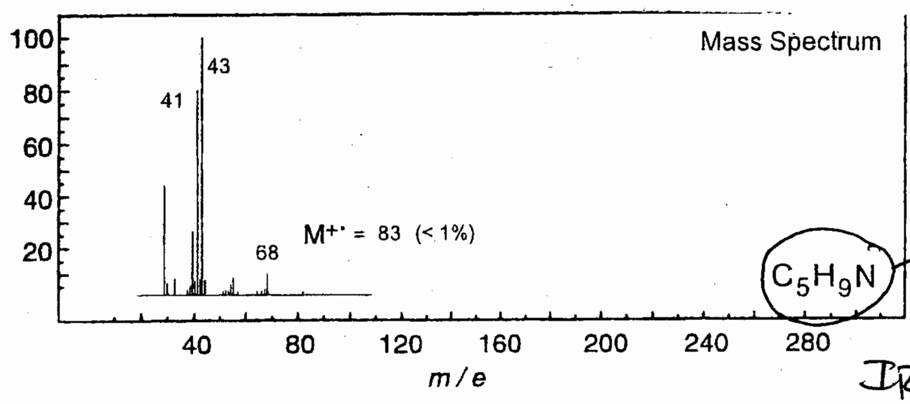
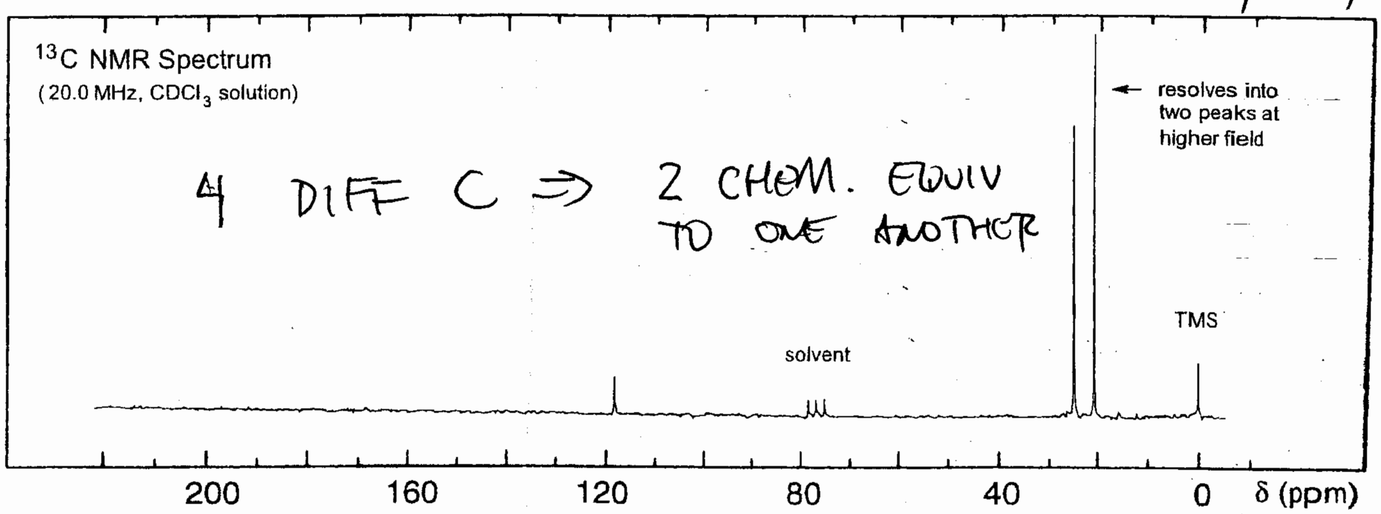
4. **(20 points)** In the box provided on the following page, **draw the structure** of the compound that satisfies the data provided (IR spectrum on following page). Explicitly show stereochemistry, double bond geometry, etc., if applicable.

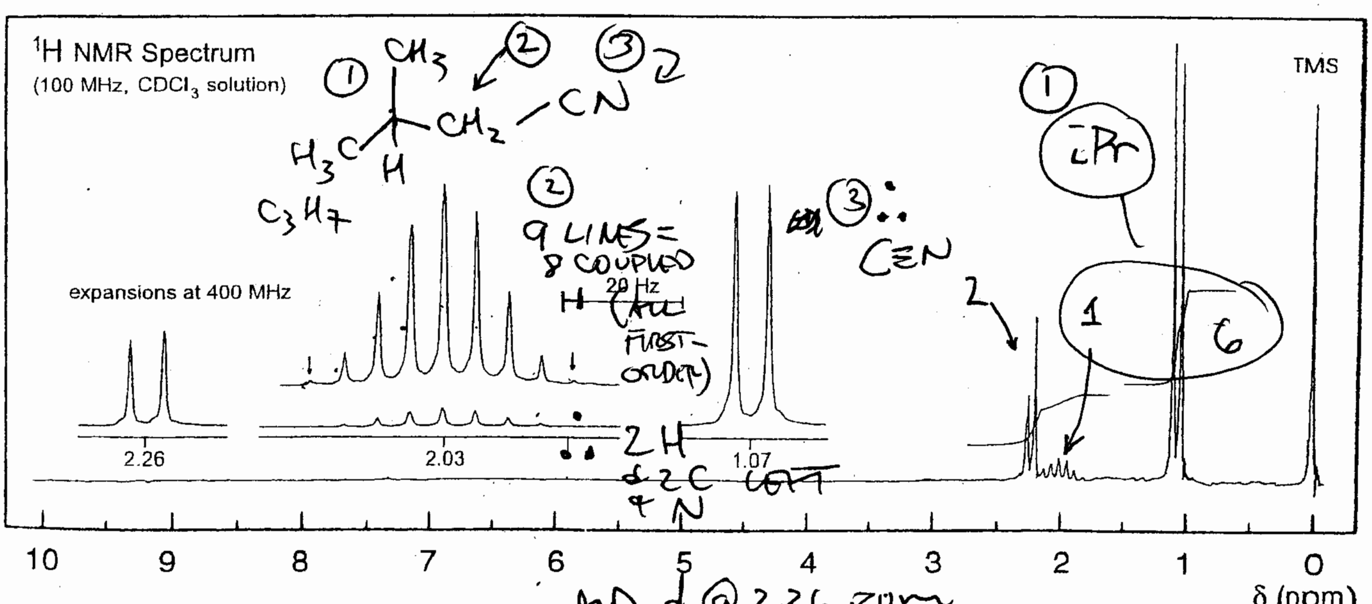


$C_5H_9N \rightarrow$ IHD = $5 - \frac{9}{2} + \frac{1}{2} + 1 = 2$

IR: C≡C, C≡N, or C=C=C



4 DIFF C ⇒ 2 CHEM. EQUIV TO ONE ANOTHER



① ② ③ 2

C_3H_7

② 9 LINES = 8 COUPLED H (ALL FIRST-ORDER)

③ C≡N

2 H & 2 C ~~LEFT~~ + N

① iPr

1

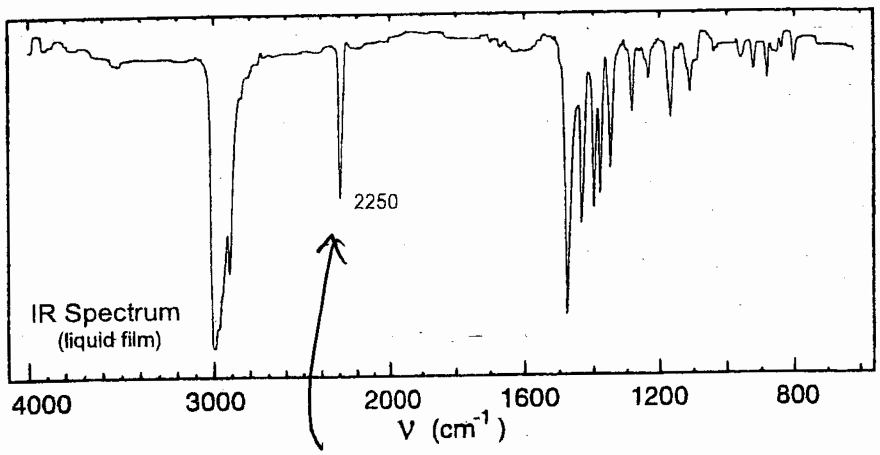
6

2

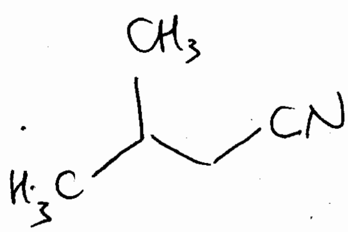
AND d @ 2.26 ppm MUST BE COUPLED TO nonet AT 2.03 ppm

C & N LEFT + 2 IHD LEFT

4. (continued)



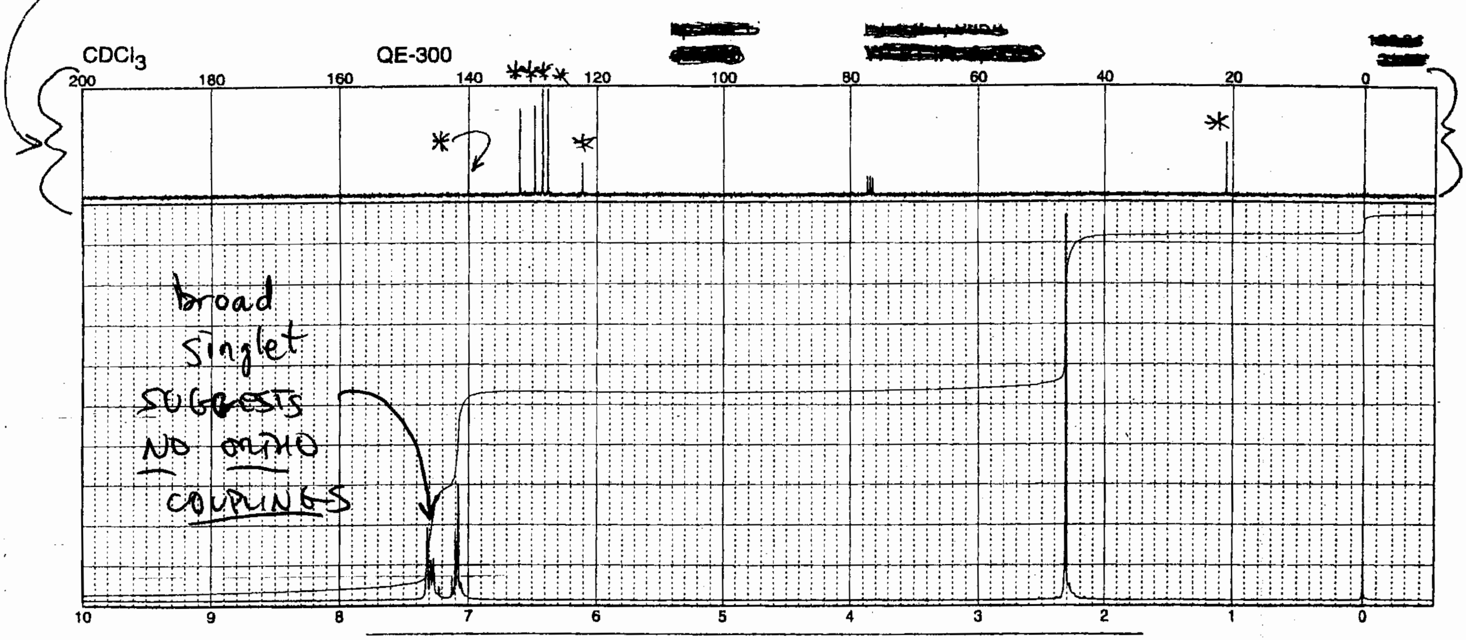
CN or C≡C or C=C=C



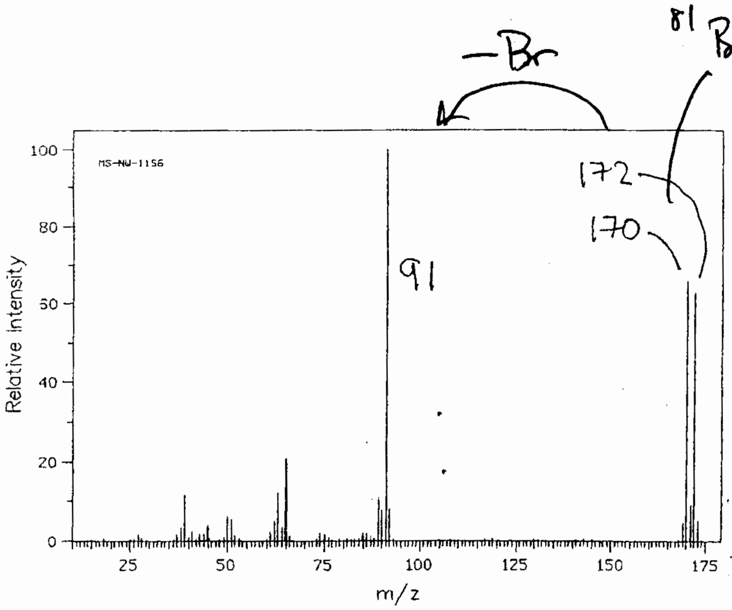
(**draw the structure** of the compound in this box.)

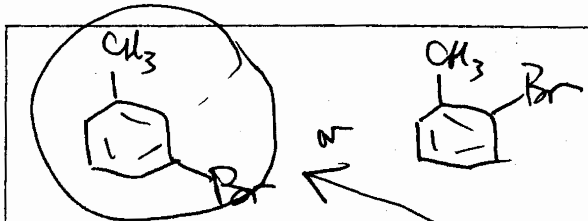
5. **(20 points)** In the box provided, **draw the structure** of the compound that satisfies the data provided. The relevant signals in the ^{13}C NMR spectrum are indicated with an asterisk (*). Explicitly show stereochemistry, double bond geometry, etc., if applicable.

^{13}C SPECTRUM



81 Br + 79 Br ISOTOPES ~ 1:1 NAT ABUNDANCE





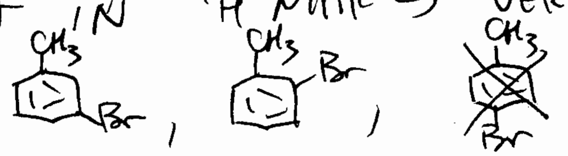
NEED J VALUES TO DIFFERENTIATE.

⇒ br. s @ 7.32 ppm SUGGESTS

(draw the structure of the compound in this box.)

1. ^{13}C: 6 AROMATIC C, 1 NOT ⇒ PROB C_7
2. Br FROM MS FRAG ⇒ 91 COULD BE C_7H_7
3. 4 Ar H, 3 NOT IN ^{1}H NMR ⇒ VERY LIKELY C_7H_7

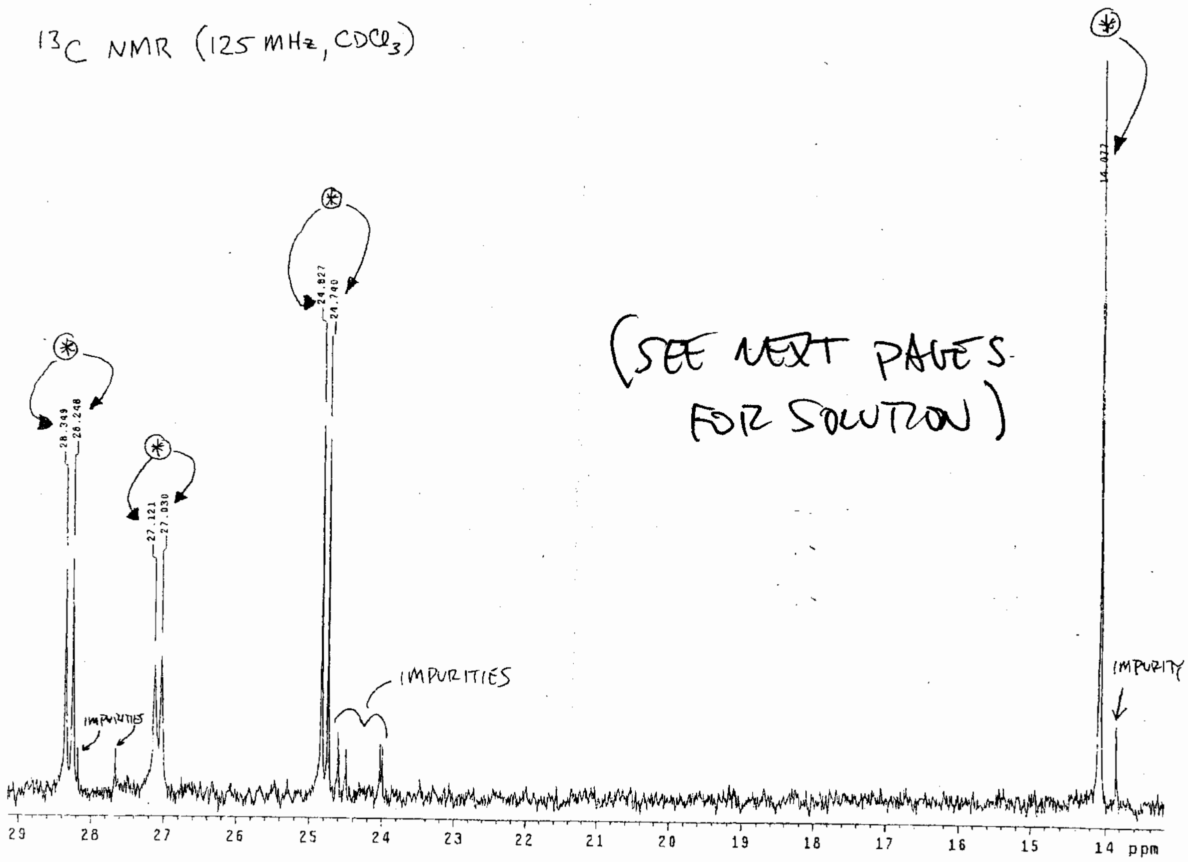
POSS STRUCTURES:

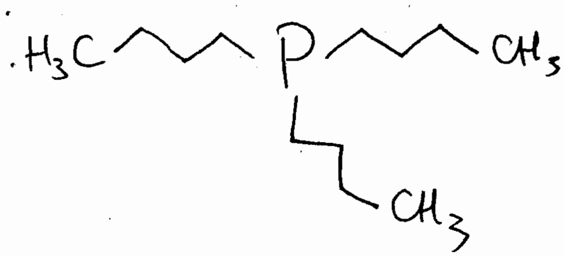


(SPLITTING IN ^{1}H NMR)

6. (20 points) The compound with the following ^{1}H NMR data and ^{13}C NMR spectrum has MW = 202. **In the box provided, draw the structure** of the compound that satisfies the data provided. The relevant peaks are indicated by circled asterisks (*) and arrows. Explicitly show stereochemistry, double bond geometry, etc., if applicable.

^{1}H NMR (ppm relative to $SiMe_4$): 1.3-1.4 (broad m, relative ratio = **2**); 0.89 (t, J = 7; relative ratio = **1**)





(**draw the structure** of the compound in this box.)

6. THE KEY IS RECOGNIZING THAT SEVERAL OF THE ^{13}C SIGNALS ARE <u>SPLIT</u>, EVEN THOUGH ACQUIRED WITH PROTON DECOUPLING (cf. PROB. #2). IF YOU DIDN'T NOTICE THIS AT FIRST, PROBLEM CAN STILL BE SOLVED WITH INFO PROVIDED:

a. MW = 202, $\begin{array}{r} 15 \\ 13\overline{)202} \\ \underline{13} \\ 72 \\ \underline{65} \\ 7 \end{array}$ ⇒ $\underline{C_{15}H_{22}}$ – DOESN'T ACCOUNT FOR SPLITTING IN ^{13}C NMR, AND NO WAY TO ACCOUNT FOR ^{1}H NMR RATIOS: $2:1 \Rightarrow 2x + x = 22$

$x = 7\frac{1}{3}$ NOT POSSIBLE.

b. SO, TRY REPLACEMENTS:

- PROB. NOT OXYGEN (δ IN ^{13}C NMR (& ^{1}H NMR))
- COULD BE N. SINCE MW IS EVEN, MUST BE 2, 4, ... N $2N \Rightarrow (CH_2)_2 = 28$

⇒ $C_{13}H_{18}N_2$ NOT OUT OF THE QUESTION, BUT DIFFICULT TO EXPLAIN SYMMETRY (WILL REVISIT)

c. <u>^{1}H NMR</u>: 3H t @ 0.89 ppm = CH_3 (REL RATIO = 1)

KEY POINT ⊛ → ∴ MUST BE 6 H FOR EACH CH_3 GROUP.

A POSSIBILITY: $(CH_2)_3$ + CH_3 ⇒ nBu, ~~iBu~~, ~~sBu~~, ~~tBu~~

⊛ → COULD BE $(CH_3CH_2CH_2CH_2)_nX$ (SEE NEXT PAGE)

$C_4H_9 = 57$ MW

$202 - 57 = 145$ (1 Bu)

$145 - 57 = 88$ (2 Bu)

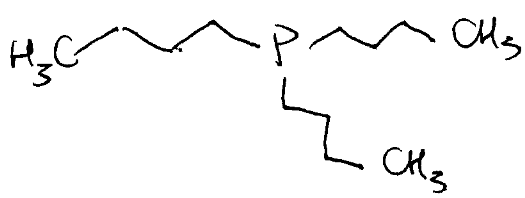
$88 - 57 = 31$ (3 Bu)

⇒ $(C_4H_9)_3X$

• $(C_4H_9)_3X$ MUST ACCT FOR

1. X MW = 31
2. SPLITTING IN ^{13}C

$\Rightarrow$ ^{31}P $(I = 1/2)$ (NOT "DECOUPLED" IN TYPICAL ^{13}C ACQUISITION)

$\therefore$ 

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n-Bu vs ~~i-Bu~~ vs s-Bu vs ~~t-Bu~~

4C ~~3C~~ 4C ~~2C~~

WOULD EXPECT CH_3 DOUBLET