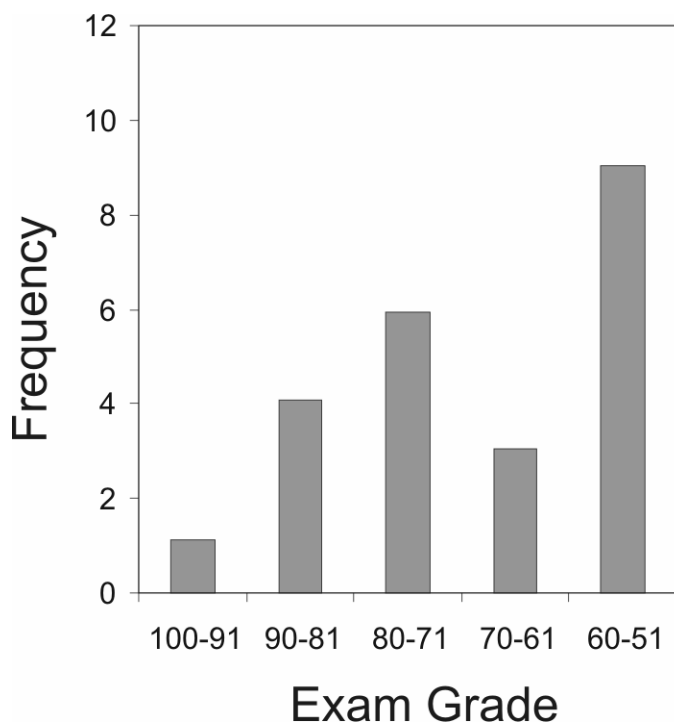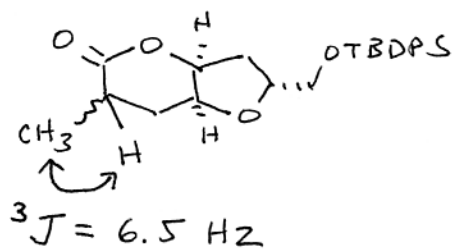**Midterm Exam 1**
Answer Key

Exam 1 Mean: 68
Exam 1 Median: 68
Exam 1 St. Dev.: 14

1. a) REGARDLESS OF WHETHER THE STRUCTURE

IS 3 OR 4, THE METHYL GROUP IS ONLY

COUPLED TO ONE PROTON, H14. THIS

RESULTS IN A

DOUBLET AT

$\delta = 1.3$ ppm.

THE $\Delta\delta$ FOR

THIS DOUBLET

$^3J = 6.5$ Hz

IS 0.013 ppm, AND SO

$$J = (0.013 \text{ ppm})(500 \text{ MHz})$$

$$= 6.5 \text{ Hz} \quad (\text{ignoring the whole MHz} \rightarrow \text{Hz conversion bit})$$
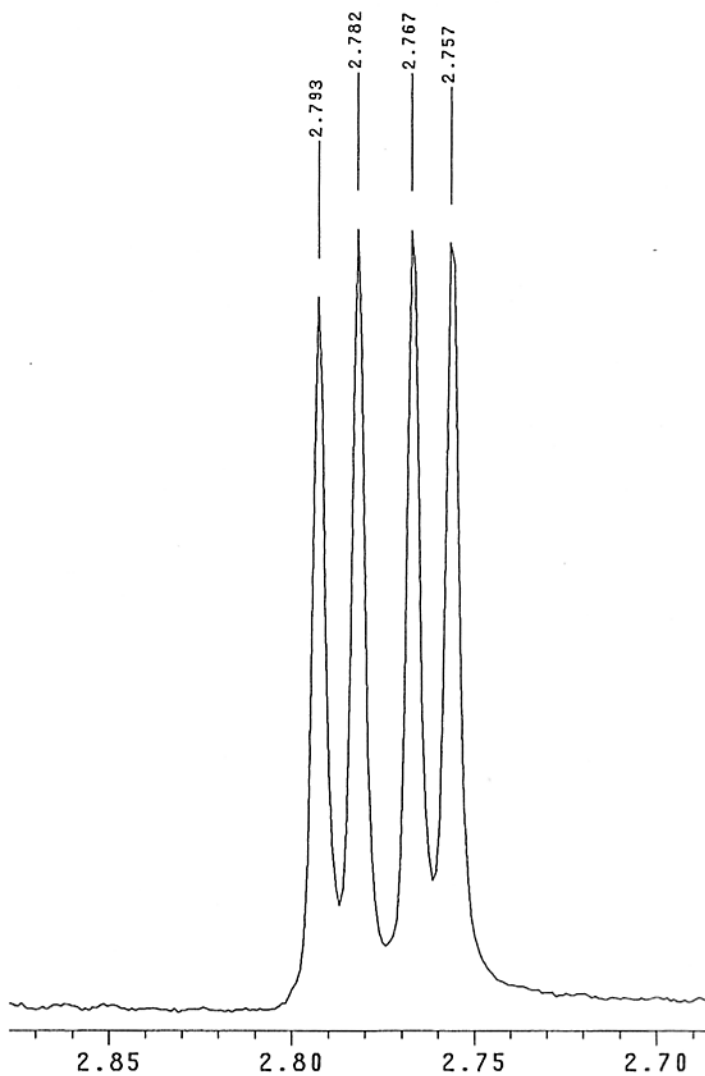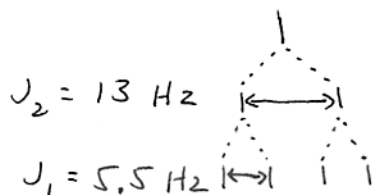
H14 as partner : 5 pts.

J = 6.5 Hz : 5 pts.

b) THE ONLY REAL DIFFERENCE BETWEEN THE TWO SPECTRA IS THE CHANGE OBSERVED IN THE MULTIPLET AT $\delta = 2.77$ ppm. THIS IS PRETTY OBVIOUS FROM THE CLOSE-UPS ON PAGES 6 AND 9. (THE SPECTRUM ALSO LOOKS DIFFERENT AT $\delta = 1.3$ ppm, BUT REMEMBER, IRRADIATION EFFECTIVELY OBLITERATES INFORMATION AT THE IRRADIATED FREQUENCY.) ~~FALSE~~

DECOUPLING ELIMINATES THE COUPLING BETWEEN THE METHYL AND H14, AND LEAVES ONLY COUPLING BETWEEN H14 AND H15$_{ax}$ AND H15$_{eq}$. AS A RESULT, THE "SEPTET" IS REDUCED TO A DOUBLET OF DOUBLETS.

> MENTIONING THAT COUPLING AT
> $\delta = 2.77$ ppm IS CHANGED: 5 pts.
> SPECIFICALLY POINTING OUT THAT
> MULTIPLICITY IS REDUCED
> TO A DOUBLET OF DOUBLETS: 5 pts.

c) THE dd CAN BE ANALYZED BY THE USUAL INVERSE SPLITTING TREE:

$$J_1 = 5.5 \text{ Hz} : \quad 3 \text{ pts}$$
$$J_2 = 13 \text{ Hz} : \quad 3 \text{ pts}$$

$J_2 = 13 \text{ Hz}$

$J_1 = 5.5 \text{ Hz}$

2.793   2.782   2.767   2.757

2.85   2.80   2.75   2.70

HOWEVER, THIS INFORMATION DOES NOT

HELP DISTINGUISH BETWEEN 3 AND 4.

THE REASON IS BECAUSE EACH STRUCTURE

HAS H14 INVOLVED IN ONE TRANS

COUPLING $(\phi = 180°)$ AND ONE GAUCHE COUPLING

$(\phi = 60°)$.

3

4
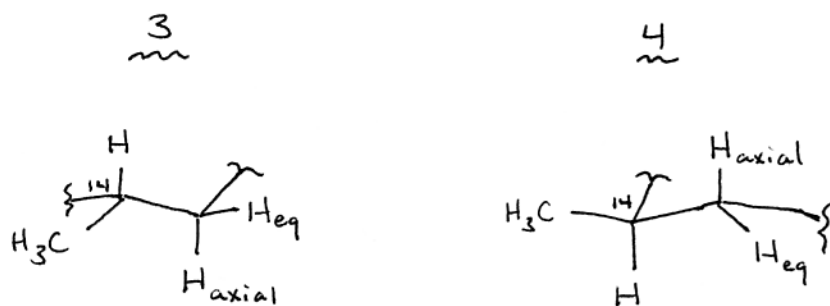

IN EITHER CASE, $\phi_{H_{14}-H_{15ax}} = 180°$,

$$J = 13 \text{ Hz};$$

$$\phi_{H_{14}-H_{15eq}} = 60°,$$

$$J = 5.5 \text{ Hz}.$$

SO, INFORMATION DOES NOT HELP (THOUGH,

IF MOLECULE WERE DIFFERENT, IT CERTAINLY MIGHT

HAVE).

"NO" AS ANSWER: 3 pts.

EXPLANATION OF ~~how~~ WHY NOT
      BASED ON GEOMETRY OF 3
      AND 4 : 1 pt.

d) NOE EXPERIMENTS ARE DESIGNED TO ILLUSTRATE THROUGH-SPACE RATHER THAN THROUGH-BOND INTERACTIONS, AND THUS THEY WERE IDEALLY SUITED TO ANSWER AMY'S QUESTIONS ABOUT THE SPATIAL RELATIONSHIP BETWEEN H14 AND H19. IRRADIATING H14 PRODUCED EXCITATION TRANSFER TO H19 (AS SHOWN BY THE POSITIVE PEAK AT $\delta = 4.3$ ppm ON PAGE 11), BUT IRRADIATING THE METHYL PROTONS DID NOT. AS A RESULT, H14 MUST BE SPATIALLY CLOSE TO H19, AND THE METHYL GROUP MUST NOT BE. THIS IS ONLY CONSISTENT WITH STRUCTURE 3:
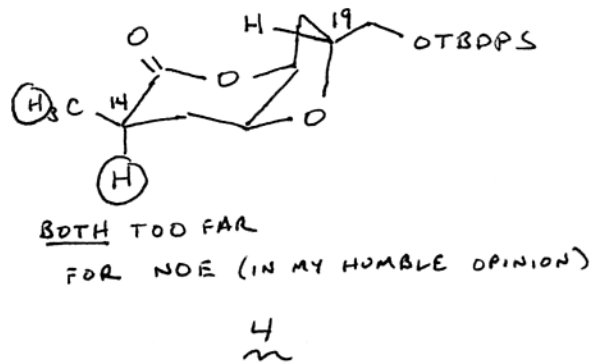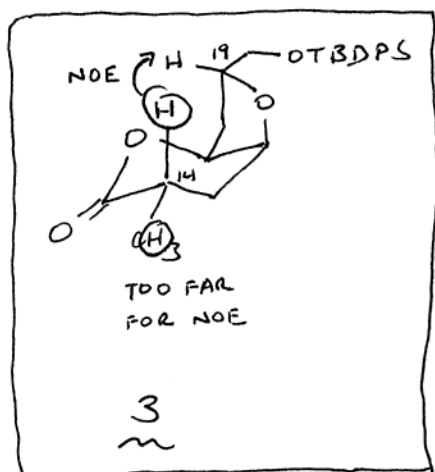
3

4

2. a)

Proton	Chemical shift (δ)	Multiplicity	Coupling partners	Coupling constants (J)
1a	~ 3.49	dd	1b 2	9.6 Hz 5.5 Hz
1b	~ 3.45	dd	1a 2	9.6 Hz 5.5 Hz
2	3.95	quintet	1a, 1b, 3a, 3b	5.5 Hz
3a	2.49	ddd	3b 2 5	16.5 Hz 5.5 Hz 2.7 Hz
3b	2.36	ddd	3a 2 5	16.5 Hz 5.5 Hz 2.7 Hz
5	1.95	t	3a, 3b	2.7 Hz

SCORING MATRIX

Proton	Chemical shift (δ)	Multiplicity	Coupling partners	Coupling constants (J)
1a	|	|	|	1 ea. (2 total)
1b	|	|	|	1 ea. (2 total)
2	|	|	|	|
3a	|	|	|	1 ea. (3 total)
3b	|	|	|	1 ea. (3 total)
5	|	|	|	|

↑

FOR <u>ALL</u>

PARTNERS.
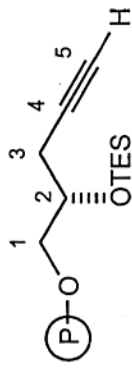
ROUTE TO SOLVING 2(a):

I STARTED, OFF THE BAT, BY ASSIGNING THE WAY-UPFIELD PEAKS TO $-Si(CH_2CH_3)_3$. $\delta \sim 0$ WORKS WELL FOR SILANE (JUST LIKE TMS). INTEGRATED INTENSITIES OF THESE WERE 9 & 6, RESPECTIVELY. THIS ALLOWED ME TO DETERMINE ALL OTHER INTENSITIES (SEE NEXT PAGE).

WE NEED TO ASSIGN 6 PROTONS, AND IT'S LIKELY THAT ALL ARE COUPLED TO ONE ANOTHER. SO WE'RE LOOKING FOR MULTIPLETS, IT JUST SO HAPPENS THAT THERE IS 6H WORTH OF MULTIPLETS:
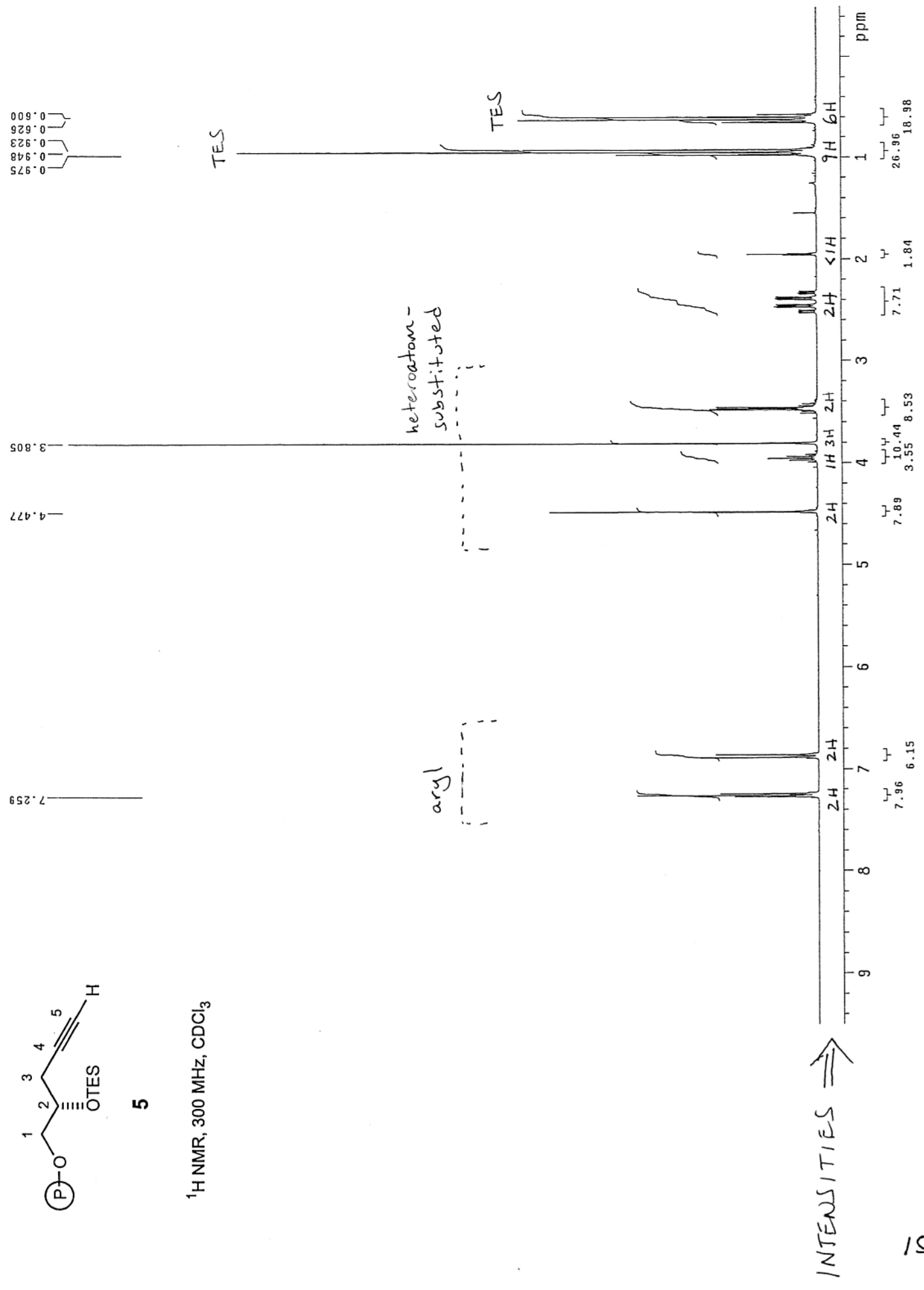
$\delta = 3.95$ (1H) quint!

~ 3.47 (2H)

$2.3 - 2.5$ (2H)

1.95 (ALMOST 1H)

H_{1a}, H_{1b} AND H_2 ARE HETEROATOM SUBSTITUTED, BUT ONLY H_2 COULD GIVE A SIMPLE QUINTET (w/ 4 COUPLING PARTNERS). H_{1a} AND H_{1b} MUST BE $\delta \sim 3.47$. IF H_{1a} & H_{1b} WERE EQUIVALENT, THEY WOULD ⌐↓
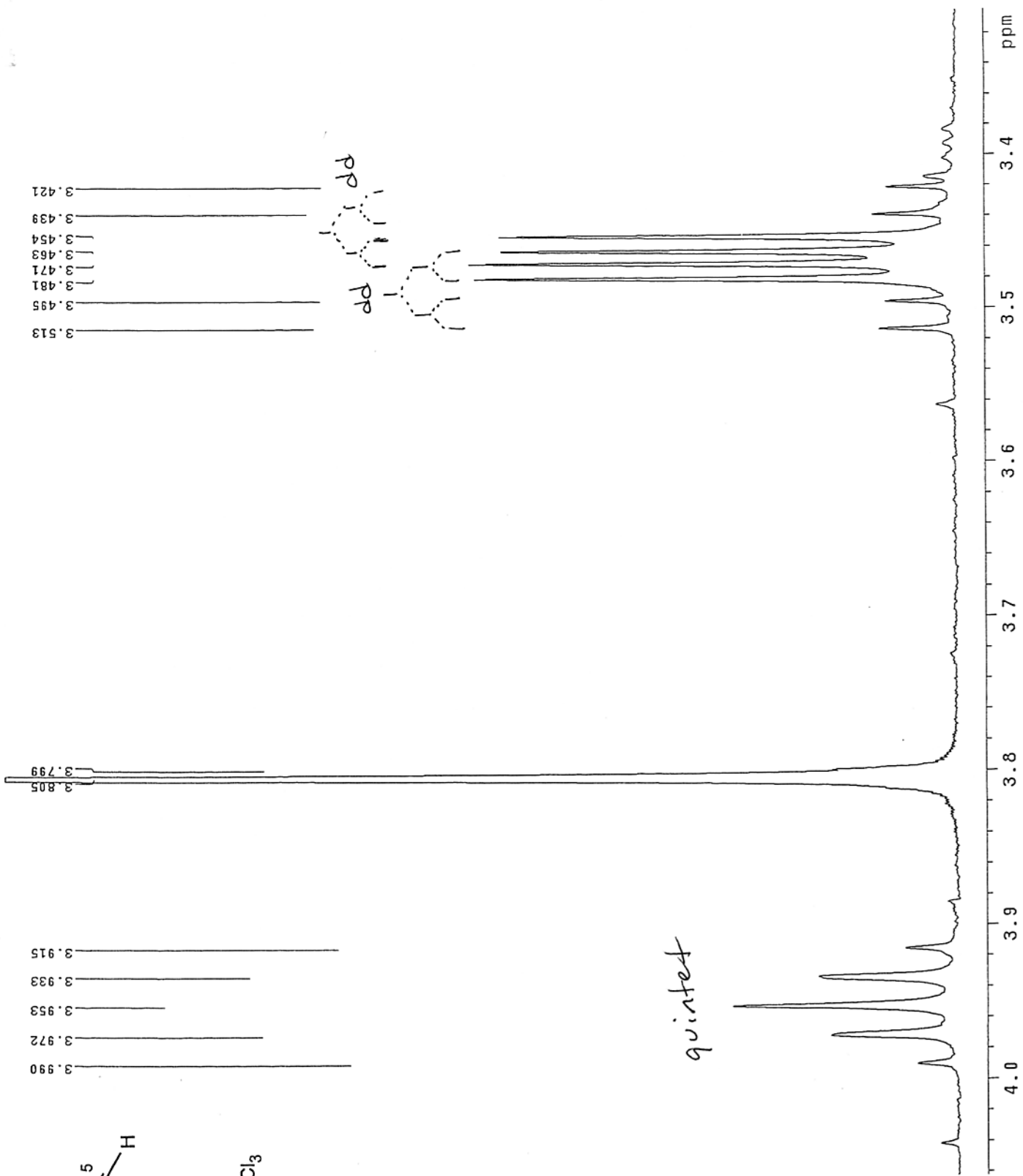
5

^{1}H NMR, 300 MHz, CDCl$_3$

1H NMR, 300 MHz, CDCl₃
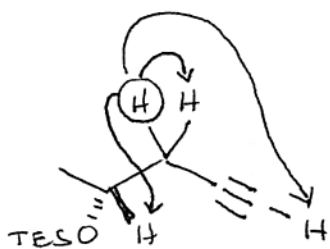
5

3.421
3.439
3.454
3.463
3.471
3.481
3.495
3.513

3.799
3.805

3.915
3.933
3.953
3.972
3.990

dd
dd

quintet

ppm 3.4 3.5 3.6 3.7 3.8 3.9 4.0

GIVE ONLY A DOUBLET. SO, THEY MUST BE INEQUIVALENT, ∴ EACH MUST BE A dd.

THIS IS IN FACT OBSERVED. (SEE NEXT PAGE.)

3a & 3b PROBABLY INEQUIVALENT IN THE SAME WAY; TO WORK RIGHT, EACH H MUST

HAVE THREE PARTNERS. THIS GIVES ddd (x2), SHOWN ON NEXT PAGE. MULTIPLET IS <u>NOT</u> A ddq; DISTANCES BETWEEN PEAKS ISN'T RIGHT FOR THIS.

exaggerated.

5 IS THEN TRIPLET AT $\delta = 1.95$, COUPLED TO 3a & 3b.

^{1}H NMR, 300 MHz, CDCl$_3$

5

easy triplet.

ddd

1.943
1.952
1.961

2.316
2.325
2.335
2.345

2.372
2.381
2.391
2.400

2.446
2.454
2.466
2.475

2.501
2.510
2.522
2.530

ppm
2.0
2.1
2.2
2.3
2.4
2.5
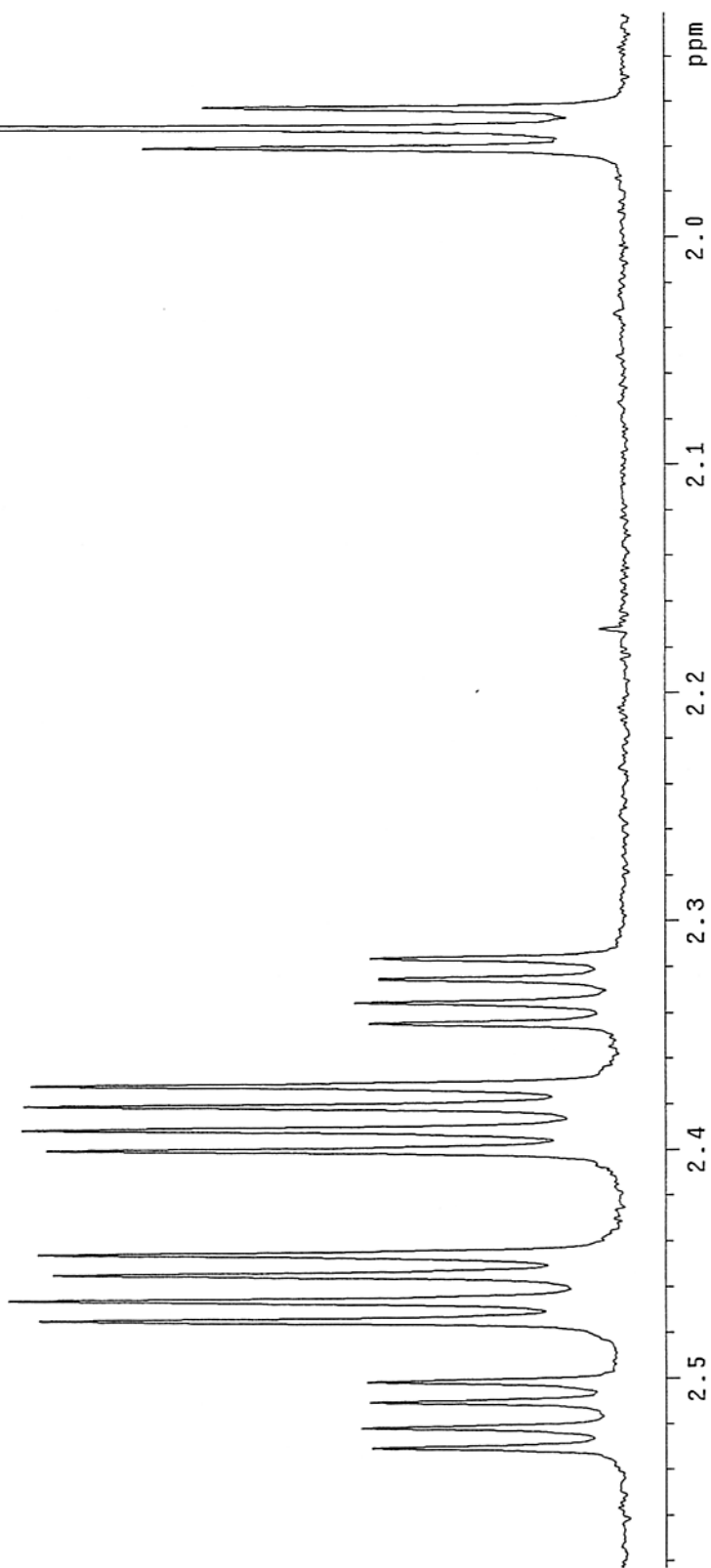
b) AFTER ASSIGNING ABOVE RESONANCES, ONLY PROTECTING GROUPS REMAIN.

$-O-Si$ ... $\delta = 0.95$ ppm

$\delta = 0.6$ ppm
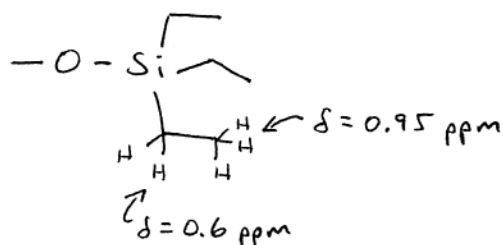
THIS EXPLAINS UPFIELD PEAKS.

REMAINING:

$\delta =$			
7.26	d (obscured by $CHCl_3$)	2 H	ARYL; LOOKS para-subst. BY SYMMETRY
6.9	d	2 H	
4.48	S	2 H	$-CH_2-$ NOT COUPLED TO ANYTHING?
3.8	S	3 H	METHYL GROUP?

SOME OF THIS IS CLEARLY ARYL, AND MIGHT BE para-SUBSTITUTED ARYL. AT ANY RATE, MUST BE 4H-ARYL, mass = 76 ($-C_6H_4-$). THIS LEAVES MASS 45 UNEXPLAINED. IF OTHER H'S ARE DUE TO $-CH_3$ AND $-CH_2-$, (mass = 15 AND 14), THAT LEAVES MASS 16 UNEXPLAINED: ONE OXYGEN ATOM.

$-\boxed{P} = -CH_2-\langle O \rangle -O-CH_3$ MASS = 121.

$\downarrow$ NEXT TO OXYGEN, AND ARYL, SO PRETTY DOWNFIELD.
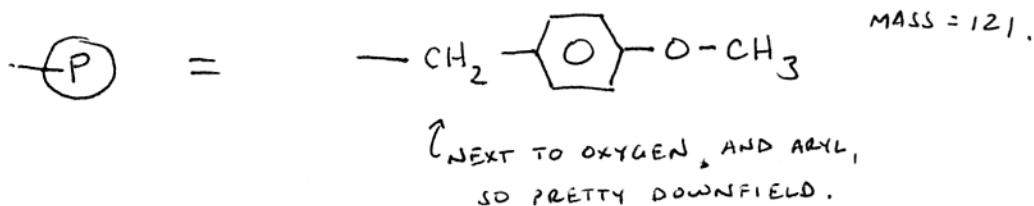
CONTAINS ARYL RING : 4 pts

METHYL GROUP : 2 pts

$-CH_2-$ ANYWHERE : 2 pts

CONNECTED RIGHT : 2 pts

c) CENTER FOUR PEAKS ARE REALLY BIG,
AND OUTER FOUR ARE TINY:
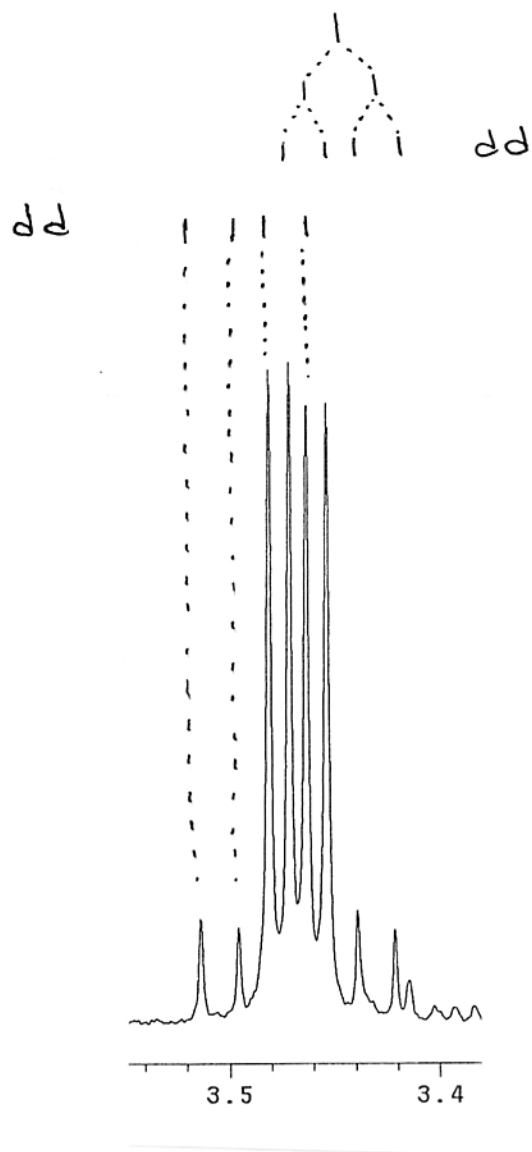
THIS IS BECAUSE H_{1a} AND H_{1b} ARE VERY
SIMILAR, CHEMICAL SHIFTS ARE VERY CLOSE,

SO,

~~BECAUSE~~ $\Delta\nu(= \nu_{1a} - \nu_{1b})$

IS SMALL COMPARED TO $J_{H_{1a}, H_{1b}}$.

WHEN THIS HAPPENS, PEAKS DISTORT.

(EXPLAINED IN ENCYCLOPEDIC DETAIL $N

CREWS, PP. 111-125.)

```
  ┌ ─  ─  ─  ─  ·  ─  ─  ─ ─ ─  ─  ┐
  │  ANYTHING MENTIONING 1a-1b      │
  │       INEQUIVALENCE:      5 pts │
  │  ANYTHING MENTIONING FACT       │
  │      THAT  1a & 1b ARE          │
  │      SIMILAR/CLOSE IN           │
  │      CHEMICAL SHIFT:      2 pts  │
  │   Δν/J RELATIONSHIP:     3 pts   │
  └ ─  ─  ─  ─  ─  ─  ─ ─ ─  ─  ─ ─ ┘
```

d) THE RELATIONSHIP BETWEEN INTEGRAL INTENSITY AND # OF PROTONS ONLY WORKS IF PROTONS HAVE THE OPPORTUNITY TO RELAX FULLY DURING FID COLLECTION (I.E., IF COLLECTION TIME $\gtrsim 5T_1$). MAIN MECHANISM OF RELAXATION IS TRANSFER OF ENERGY TO NEARBY, LIGHTWEIGHT NUCLEI. BUT H_5 IS ONLY BOUND TO ONE NUCLEUS — ~~THE~~ C_5 — AND THERE ARE FEW OTHER NUCLEI NEARBY. SO H_5 RELAXES SLOWLY, AND ITS INTEGRAL IS TOO SMALL, (JUST LIKE A QUATERNARY CARBON IN ^{13}C NMR.)

MENTION OF
SLOW RELAXATION TIME OR T_1 : 5 pts.
RELATING THIS TO
ACETYLENIC H LOCATION, NO
NEARBY NEIGHBORS : : 5 pts.