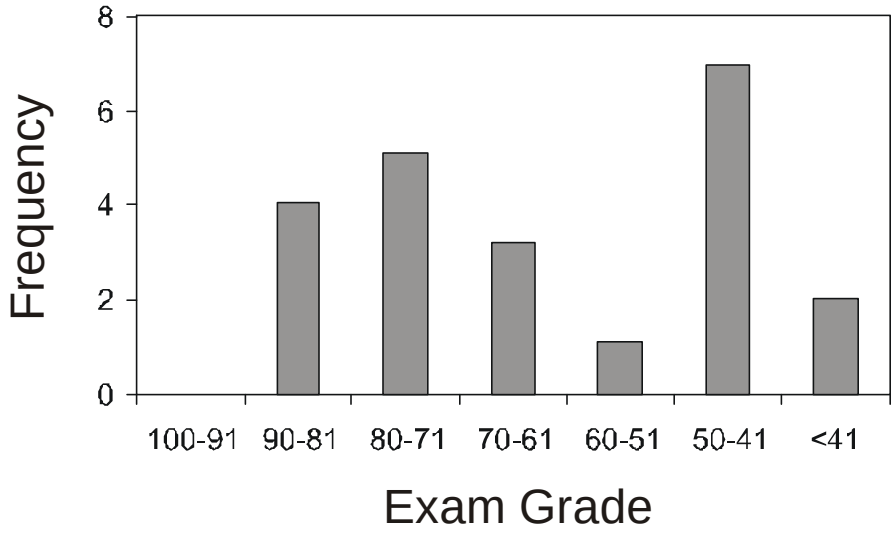
Final Exam
Answer Key

Exam 2 Mean: 61
Exam 2 Median: 67
Exam 2 St. Dev.: 19



FINAL EXAM KEY

a) THE IR SPECTRUM LACKS MANY OF THE SPECTRAL FEATURES YOU MIGHT EXPECT FOR 2:

- OLEFINIC C-H STRETCH. 2 HAS TWO OLEFINIC PROTONS THAT SHOULD GIVE $\nu > 3000\ cm^{-1}$. BUT THERE ARE NO PEAKS $> 3000\ cm^{-1}$. [5 POINTS]

- OLEFINIC C=C STRETCH. α,β-UNSATURATED KETONES GIVE A PEAK AT $\nu \sim 1600\text{-}1650\ cm^{-1}$ FOR THE OLEFIN STRETCH, BUT THERE'S NOTHING THERE EITHER. [5 POINTS]

- COO-H STRETCH. ALL O-H's GIVE BLOBBY PEAKS IN THE $\nu = 3000\text{-}3400\ cm^{-1}$ RANGE. BUT THIS ONE DOESN'T. [5 POINTS]

(LESS IMPORTANT:)

- C=O STRETCH, α,β-UNSAT. KETONE, SHOULD BE $\nu < 1700\ cm^{-1}$, BUT ALL C=O STRETCHES ARE $1760 > \nu > 1720$, BUT TOUGH TO TELL. [2 POINTS IF NEEDED.]

** SO, WE LEARN: OLEFIN IS GONE.
THERE IS NO CARBOXYLIC ACID.

b) THE MASS SPECTRUM HAS SOME VERY DISTINCTIVE PEAK PATTERNS. FIRST, EACH PEAK APPEARS TO BE ACCOMPANIED BY AN M+2 PARTNER, WITH ABOUT 65% OF INTENSITY OF M. CAN'T BE BROMINE (WOULD BE 1:1 INTENSITY), CAN'T BE JUST 1 CHLORINE, BUT COULD BE 2 CHLORINES. THEN, M WOULD BE $^{35}Cl^{35}Cl$, AND M+2 WOULD BE $^{35}Cl^{37}Cl$ (AND M+4 WOULD BE $^{37}Cl^{37}Cl$). THESE WOULD HAVE ~ 1 : 0.64 : 0.10 RATIO.

SECOND, MS SHOWS TWO SETS OF PEAKS SEPARATED BY m/z = 17. THIS IS CHARACTERISTIC OF CI-MS USING NH_3 AS A REAGENT GAS; ALL IONS ARE $[M+H]^+$ AND $[M+NH_4]^+$ VARIANTS. SO,

m/z = 437 : $\left[M(^{35}Cl^{35}Cl) + H\right]^+$

439 : $\left[M(^{35}Cl^{37}Cl) + H\right]^+$

454 : $\left[M(^{35}Cl^{35}Cl) + NH_4\right]^+$

456 : $\left[M(^{35}Cl^{37}Cl) + NH_4\right]^+$

(BASE MASS OF M WOULD BE 436 FOR $^{35}Cl^{35}Cl$.)

SCORING:

5 POINTS FOR ANY HALOGENIC ISOTOPE PATTERN.

5 POINTS FOR RECOGNIZING NH_3 APPEARS IN HIGHER MASSES.

3 POINTS FOR RECOGNIZING TWO CHLORINES IN ANSWERS.

2 POINTS FOR CORRECT SERIES.

c) OKAY, STRUCTURE HAS GAINED TWO CHLORINE ATOMS. SO, IF WE STARTED W MASS OF 2 (MW = 368) AND JUST ADDED TWO CHLORINE ATOMS, WE'D BE AT MW = 438. AWFULLY CLOSE TO WHERE WE WANT TO BE (436). FROM MOLECULAR FORMULA OF 2, COULD ALSO LOSE 2 H'S, OR MAYBE TRADE AN O FOR A C & AND GAIN 2 H'S:

2: $C_{18}H_{28}SiO_6$ (MW = 368) $\longrightarrow$ $C_{18}H_{26}SiO_6Cl_2$ (MW = 436)

OR

$C_{19}H_{30}SiO_5Cl_2$ (MW = 436)

FOR $[M(^{35}Cl^{35}Cl)+H]^+$ PEAK, exact mass = 437.0983.

$[C_{18}H_{26}SiO_6Cl_2 + H]$:

18 (12.0000)	^{12}C
27 (1.00783)	^{1}H
1 (27.9769)	^{32}Si
6 (15.9949)	^{16}O
2 (34.9689)	^{35}Cl
= 437.0955	

close!

$[C_{19}H_{28}SiO_5Cl_2 + H]$:

$19(12.0000)$	^{12}C
$31(1.00783)$	^{1}H
$1(27.9769)$	^{32}Si
$5(15.9949)$	^{16}O
$2(34.9689)$	^{35}Cl
$= 437.1319$	(whoa, way off)

MY GUESS IS, MOLECULAR FORMULA IS

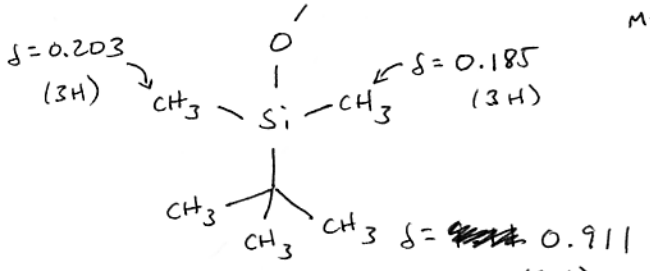
$C_{18}H_{26}SiO_6Cl_2$.

SCORING: 5 POINTS FOR ANY CALCULATION USING CORRECT ISOTOPE MASSES.

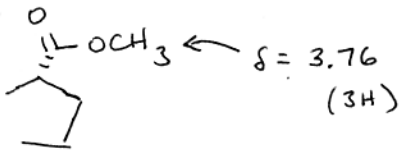
5 POINTS FOR CORRECT MOLECULAR FORMULA.
3 POINTS FOR CORRECT ION FORMULA INSTEAD,
5 POINTS FOR ANY MW = 436 MOLECULE.

d) AND e)

CLEARLY THE CORE OF THE EXAM. FIRST, IT WAS IMPORTANT TO DO SOME OBVIOUS ASSIGNMENTS:

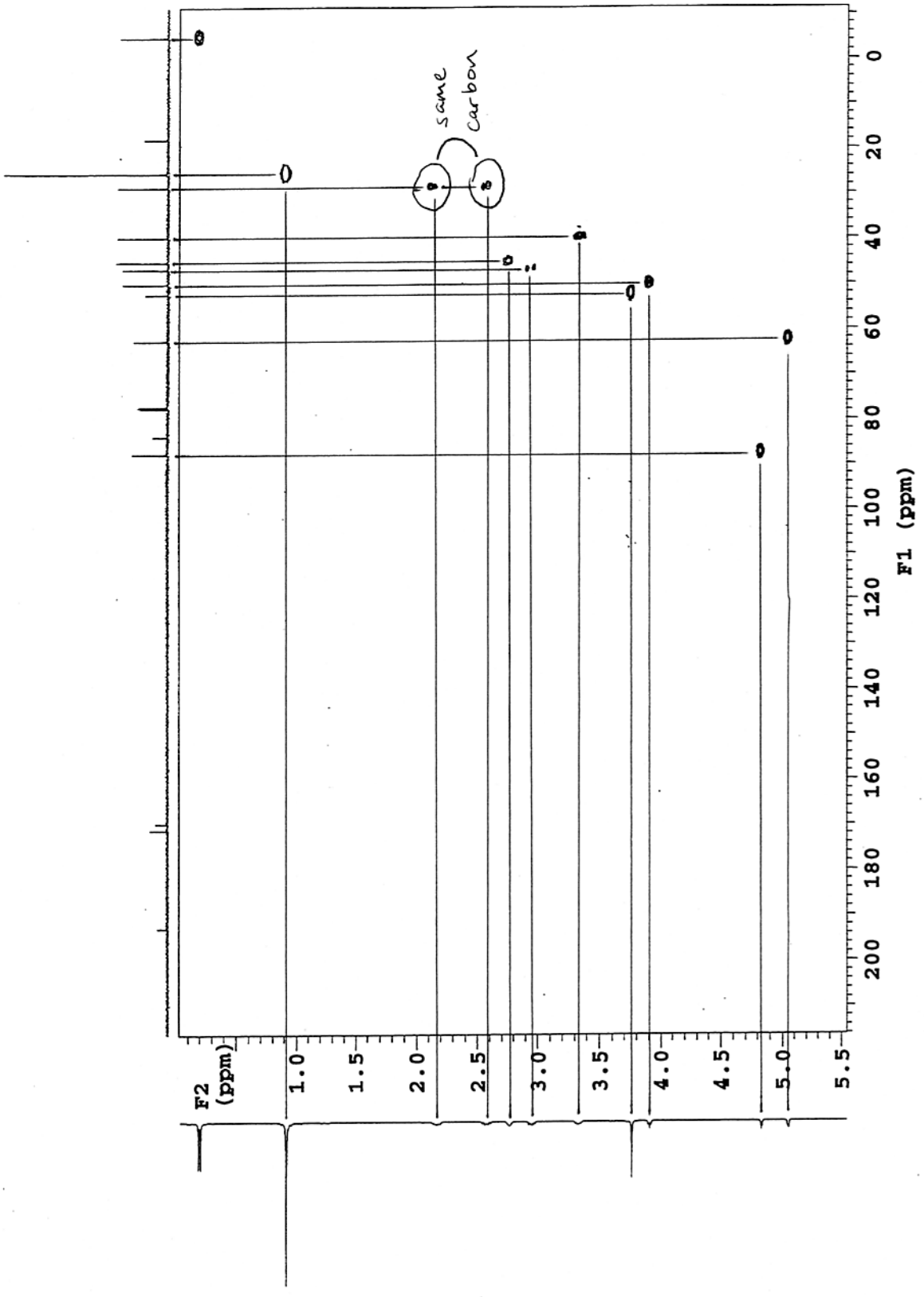


METHYLS ARE ACTUALLY DIASTEREOTOPIC, SO INEQUIVALENT. INTEGRATION ON THESE IS NOT QUITE RIGHT - BUT CLOSE.



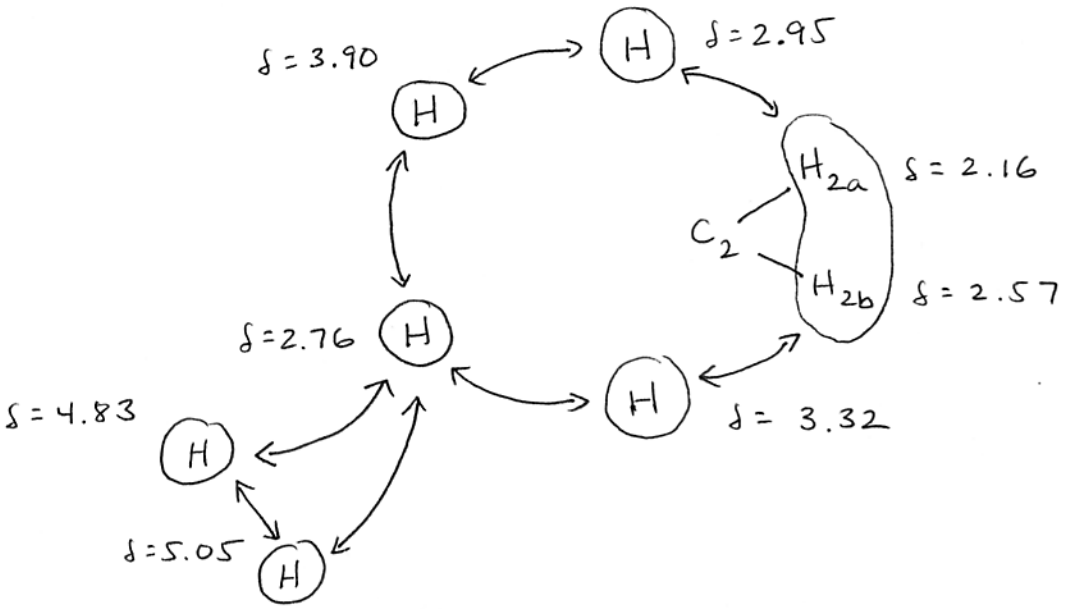
ALL OF THESE WERE BIG SINGLETS.

THEN, THERE ARE 8 MORE PROTONS IN THE ^1H NMR THAT WE HAVE TO ASSIGN. I FELT, [redacted] THAT HMQC WAS [redacted] AN IMPORTANT TOOL TO FIGURE THIS OUT. HMQC SHOWS THAT [redacted] SIX OF THESE EIGHT PROTONS ARE ON DIFFERENT CARBONS, AND THAT 2 OF THEM ARE ON THE SAME CARBON, (SEE NEXT PAGE): δ = 2.16 & AND δ = 2.57. CARBON #2 IS AN EXCELLENT CANDIDATE FOR THIS CARBON - IT ALREADY HAS 2 ATTACHED PROTONS TO START WITH. WE'LL CALL THESE PROTONS H_{2a} AND H_{2b}.

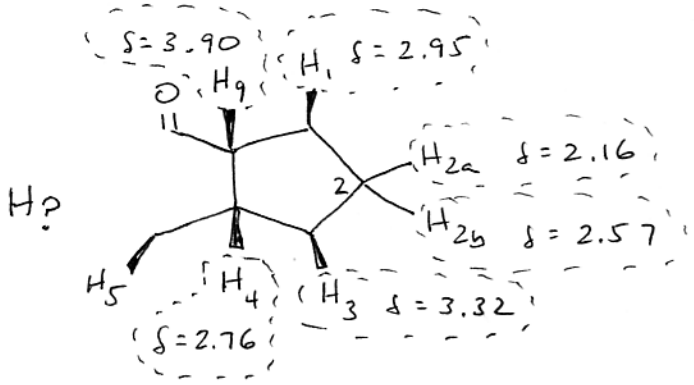


^{1}H-^{13}C HMQC NMR, 500 MHz, $CDCl_3$

H_{2a} & H_{2b} COULD BE COUPLED TO H_1 & H_3 IN OUR STRUCTURE FOR $\underset{m}{3}$ - AND, SURE ENOUGH, THE COSY SHOWS TWO PROTONS COUPLED TO H_{2a} & H_{2b}. BUT WE DON'T KNOW WHICH IS H_1 & WHICH IS H_3. THESE, IN TURN, MIGHT BE COUPLED TO H_9 AND H_4, RESPECTIVELY. BUT AGAIN, WE DON'T KNOW WHICH IS WHICH. LET'S MAP THIS OUT:

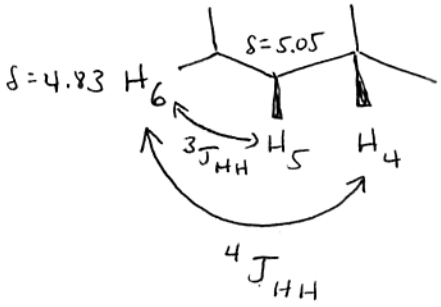


THIS LOOKS <u>VERY</u> MUCH LIKE OUR STARTING MATERIAL:



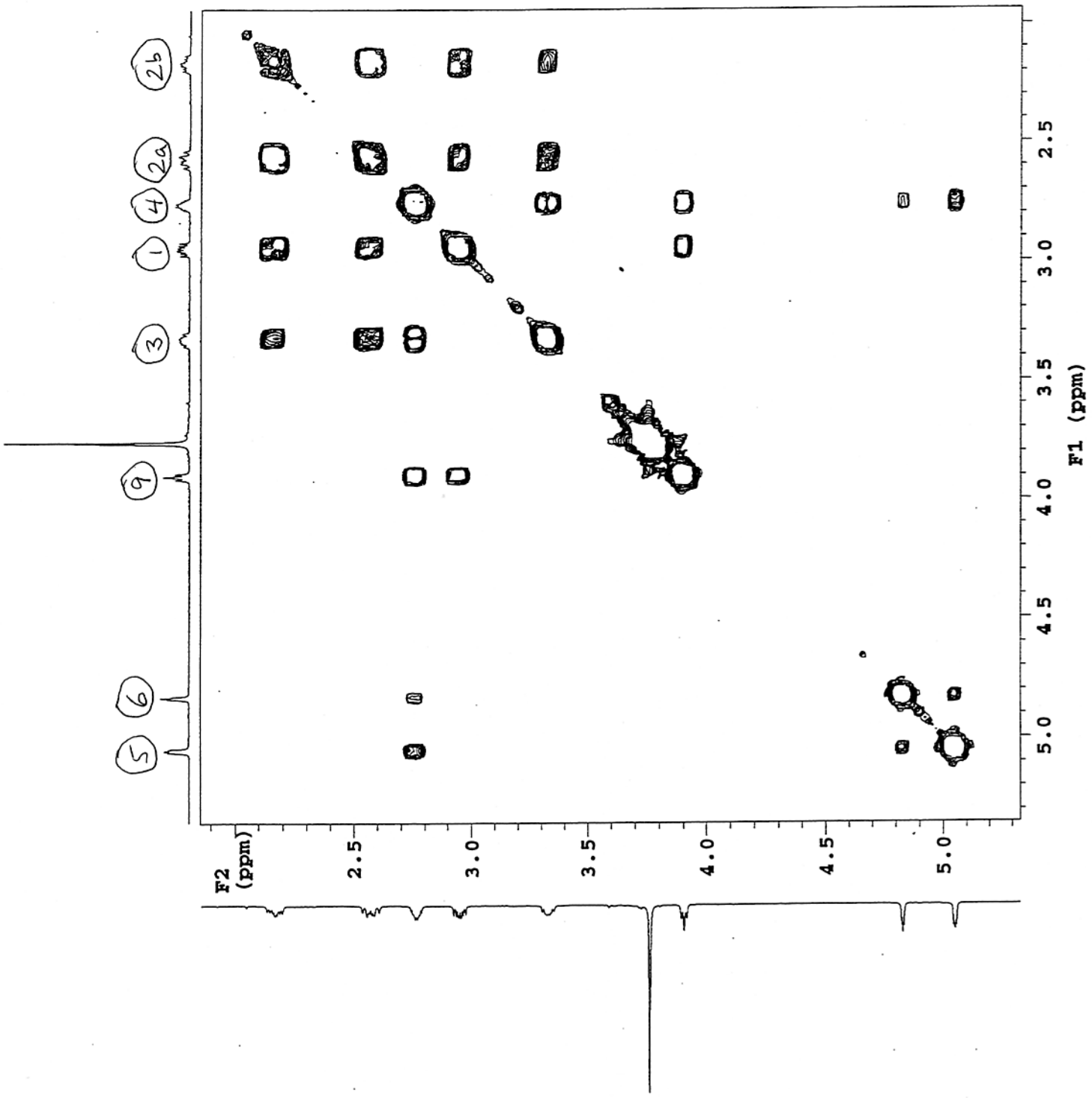
AT THIS POINT, WE DON'T EVEN KNOW WHAT THE MOLECULE IS AND WE'VE ALREADY ASSIGNED MOST OF THE SPECTRUM!

NOW COMES THE HARD PART: ASSIGNING THE * PROTONS COUPLED TO H_4. KEY HERE WAS THE HINT ~~[illegible]~~ ON PAGE 3, WHICH SAYS THAT ONE COUPLING OF THE TWO UNKNOWN PROTONS IS A * $^4J_{HH}$ AND THE OTHER IS A $^3J_{HH}$. THIS IS SATISFIED FOR



AND THAT'S IT. THERE'S NO MORE PROTONS TO ASSIGN.

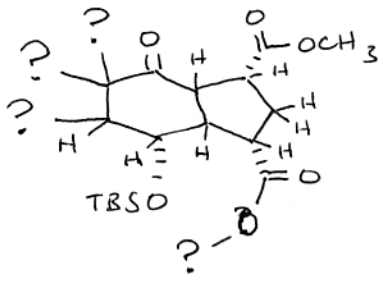
carbon #	^{1}H δ (ppm)
1	2.95
2	2.16, 2.57
3	3.32
4	2.76
5	5.05
6	4.83
7	—
8	—
9	3.90



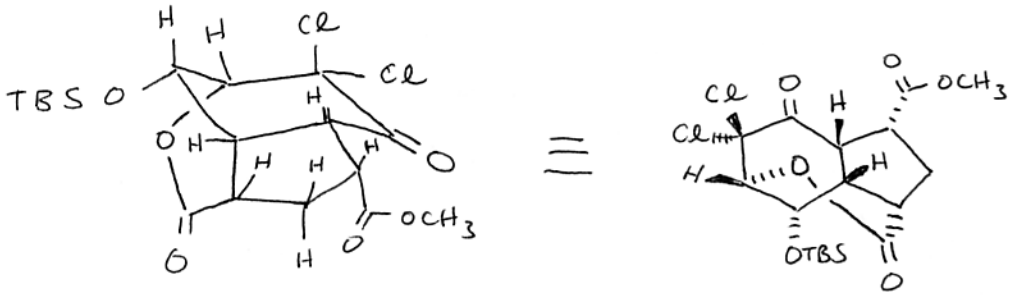
^{1}H-^{1}H COSY NMR, 500 MHz, $CDCl_3$

OKAY, NOW FOR THE <u>REALLY</u> HARD PART - ASSIGNING THE STRUCTURE. WE KNOW

- NO OLEFIN.
- NO ACID.
- 2 CHLORINES HAVE BEEN ADDED.
- MOLECULE HAS SKELETON:

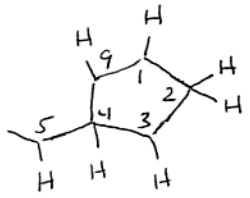


TWO OF "?" ARE PROBABLY CHLORINES. IF SO, MOLECULAR FORMULA WOULD BE $C_{18}H_{26}SiO_6Cl_2$ - WHICH IS WHAT WE WANT! OTHER TWO "?"'S MUST BE <u>CONNECTED</u>.



SCORING ON (d):

5 POINTS FOR ANY STRUCTURE THAT SHOWS



2 POINTS FOR EIGHTH "H" SOMEWHERE THAT CAN COUPLE WITH OTHER THINGS.

3 POINTS FOR RIGHT ANSWER (OR PLAUSIBLY CLOSE, DETERMINED BY PROF. TATON).

SCORING ON (e):

3 POINTS EACH FOR H_1, H_{2a}, H_{2b}, H_3, H_9 & H_4. THESE MUST BE CORRECTLY ASSIGNED. (18 POINTS TOTAL)

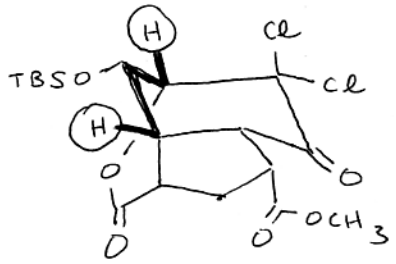
3 POINTS (EACH) FOR H_5 & H_6 RESONANCES, ACCORDING TO ANSWER IN (d).

2 POINTS FOR COUPLING MAKING SENSE,
1 POINT FOR CHEMICAL SHIFT MAKING SENSE.

1 AUTOMATIC BONUS POINT!

(25 TOTAL POINTS)

f)



TWO WORDS: W-COUPLING.

(OKAY, ONE WORD AND A LETTER.)

ANSWER IS NOT KARPLUS EQUATION - THIS APPLIES ONLY TO $^3J_{HH}$.

5 POINTS FOR SHOWING ANY W-COUPLING ON STRUCTURE.
5 POINTS FOR "W-COUPLING".

g)

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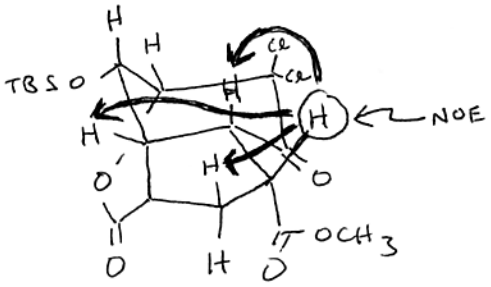

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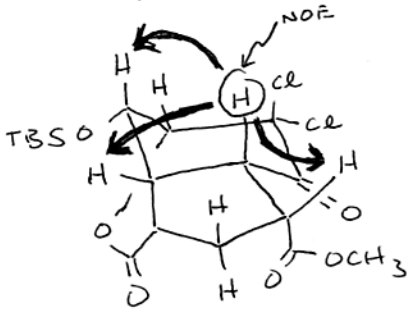

$H_1 \longrightarrow H_{2a}, H_4, H_9$

2 POINTS FOR 1st & 2nd CORRECT ARROW EACH,
1 POINT FOR 3rd.
ASSIGNMENTS AND NOE DISTANCES MUST MAKE SENSE.

← DITTO