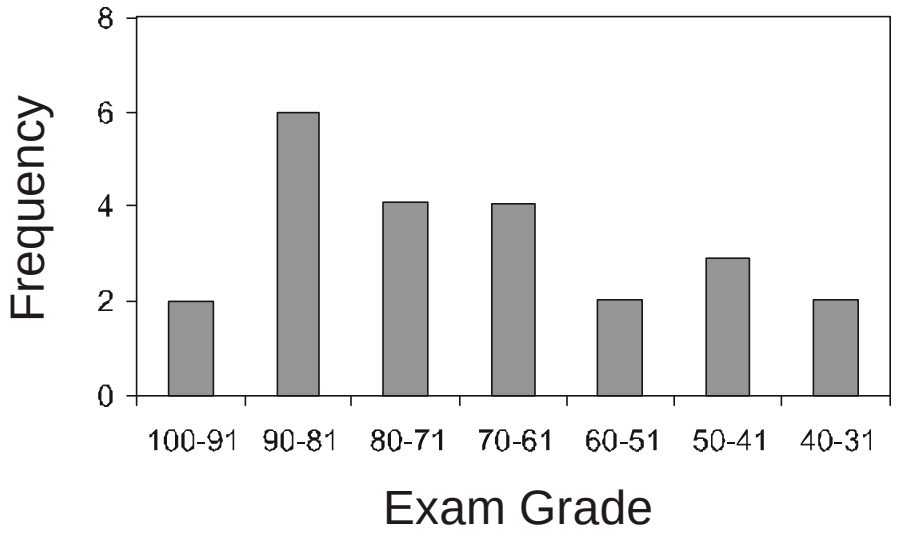
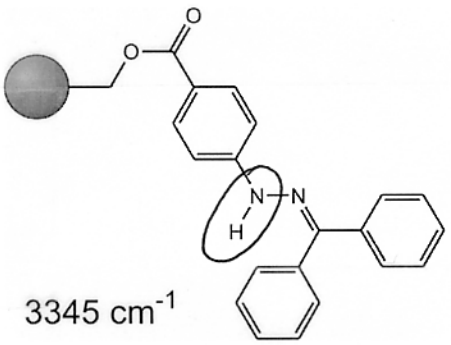
Midterm Exam 2
Answer Key

Exam 2 Mean: 69
Exam 2 Median: 71
Exam 2 St. Dev.: 18

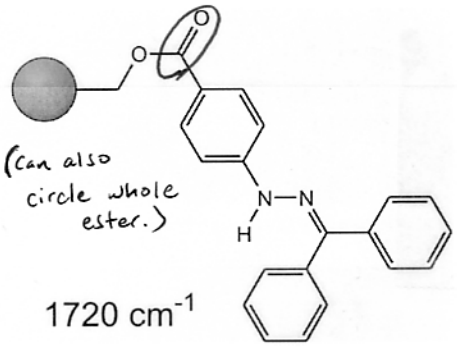


EXAM 2 SOLUTIONS

1. a.



3345 cm^{-1}



1720 cm^{-1}

2 PTS. EACH.

b. – PEAK AT 3345 cm^{-1} DISAPPEARS.

THIS IS BECAUSE N-H IS NO LONGER PRESENT IN 3.

– PEAK APPEARS AT 1760 cm^{-1}.

THIS IS BECAUSE 3 HAS A NEW ALIPHATIC ESTER CARBONYL IN IT.

1 POINT FOR "3345 cm^{-1} DISAPPEARS".
1 POINT FOR "1760 cm^{-1} APPEARS".
2 POINTS FOR EACH EXPLANATION (x2).
(6 POINTS TOTAL.)

C. MOST COMMONLY, IONS IN ELECTROSPRAY MS ARE PRODUCED BY PROTONATION OF M TO $[M+H]^+$.

SO, YOU WOULD EXPECT THE "PARENT" PEAK TO BE ONE MASS UNIT HIGHER. (THIS WOULD NOT BE TRUE IF YAN HAD USED GC-MS w/ EI.)

6 POINTS FOR ANYTHING WITH "M+H" OR "PROTONATED."
2 POINTS FOR ATTRIBUTING TO ELECTROSPRAY.

d. CORRECT STRUCTURE: 5b | 5 POINTS

IR DATA: TRANSFORMING 3 → 4 REALLY DOESN'T PRODUCE ANY NEW, INDICATIVE PEAKS — NO NEW ABSORBANCES IN THE 1690 cm^{-1} AREA THAT MIGHT BE ATTRIBUTABLE TO THE ARYL KETONE IN 5a, AND NOTHING AROUND 1650 cm^{-1} THAT MIGHT GO WITH THE $-CH=CH_2$ OF 5c. BUT THIS IS NEGATIVE NOT POSITIVE EVIDENCE, SO NOT TERRIBLY CONCLUSIVE.

5 POINTS FOR ANY DISCUSSION OF IR DATA.

EXACT MASSES (FOR M+H):

5a:	$21 \times {}^{12}C$	21 (12)
	$15 \times {}^{1}H$	15 (1.00783)
	$3 \times {}^{16}O$	3 (15.9949)
		315.10215

5b:	$20 \times {}^{12}C$	20(12)
	$15 \times {}^{1}H$	15(1.00783)
	$2 \times {}^{14}N$	2(14.0031)
	$2 \times {}^{16}O$	2(15.9949)
		315.11345

5c:	$22 \times {}^{12}C$	$22(12)$
	$18 \times {}^{1}H$	$18(1.00783)$
	$2 \times {}^{16}O$	$2(15.9949)$
		315.13857

HR-MS IS CLEARLY THE MOST CONCLUSIVE EVIDENCE HERE, POINTING TO 5b. OTHER POSSIBILITIES ARE > 0.01 AMU AWAY.

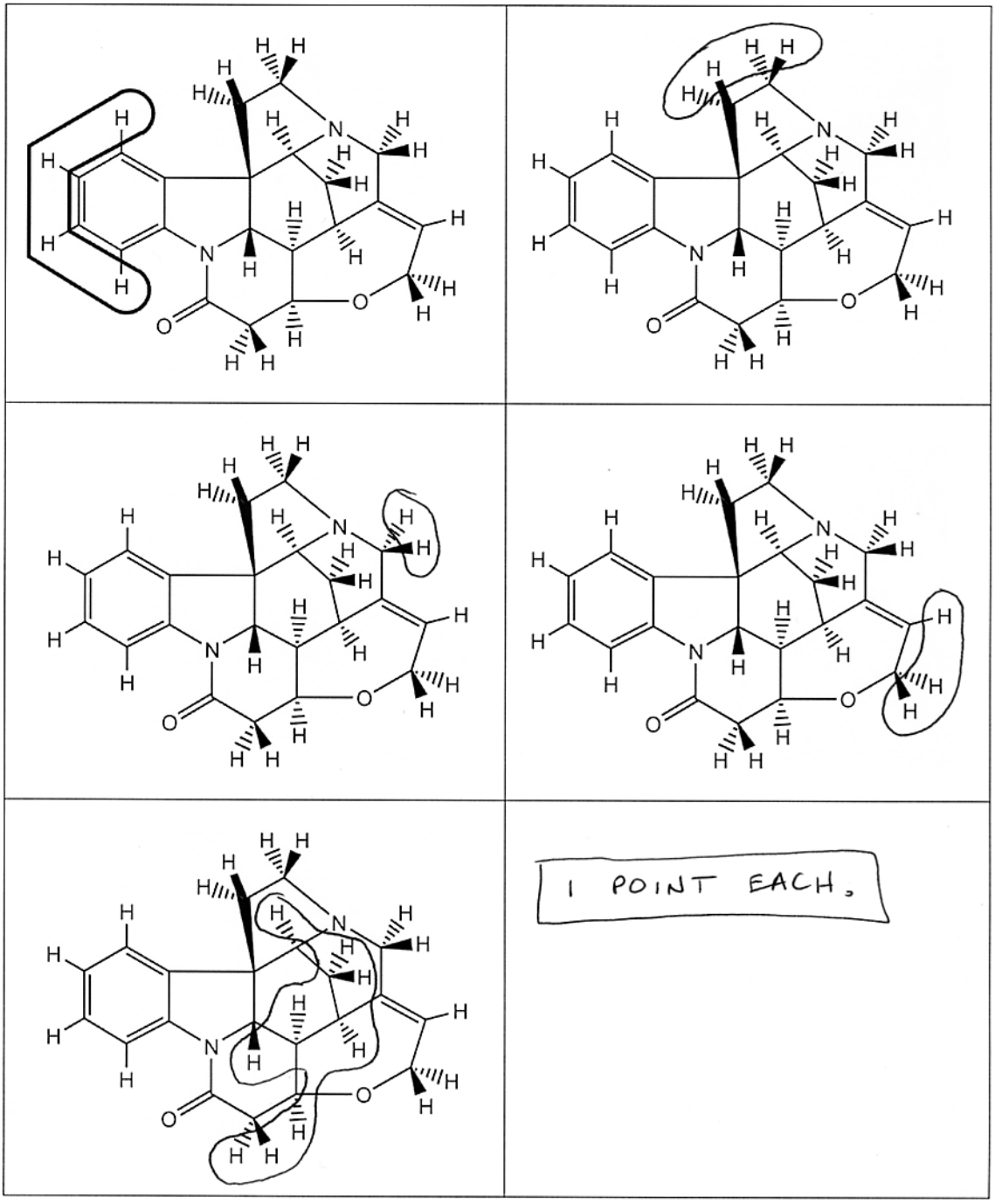
5 POINTS FOR CALCULATIONS, DISCUSSION OF 5b EXACT MASS.

ISOTOPE RATIO:

FOR ALL THREE POSSIBILITIES, CARBON WILL CONTRIBUTE THE MOST TO THE ISOTOPIC PEAKS (SINCE THE ABUNDANCE OF A+1 FOR N, O & H ARE SO LOW). ACCORDING TO THE TABLE AT THE BACK OF THE EXAM, $\%(A+1, 5a) \approx 23\%$, $\%(A+1, 5b) \approx 22\%$, AND $\%(A+1, 5c) \approx 24\%$. ON THE FACE OF IT, ONE MIGHT IMAGINE THIS FITS 5a OR 5b BEST. BUT PEAK INTEGRALS IN MASS SPEC AREN'T SO RELIABLE, AND THE RELATIVE INTENSITIES IN THE CHART ARE $\sim \pm 10\%$. (WE SPOKE ABOUT THIS IN CLASS.) SO, REALLY, THE ISOTOPE RATIOS TELL YOU NOTHING.

3 POINTS FOR ANY DISCUSSION OF ISOTOPE RATIO.
2 POINTS FOR DISCOUNTING (BASED ON INACCURACY)

2. a)

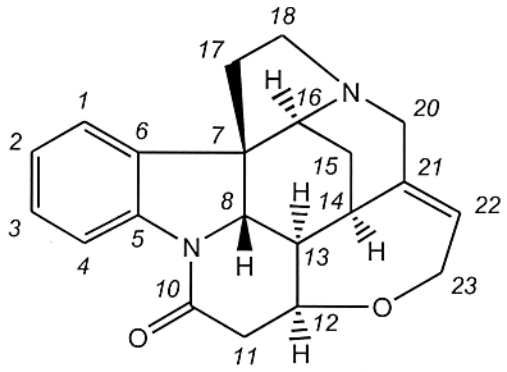


1 POINT EACH.

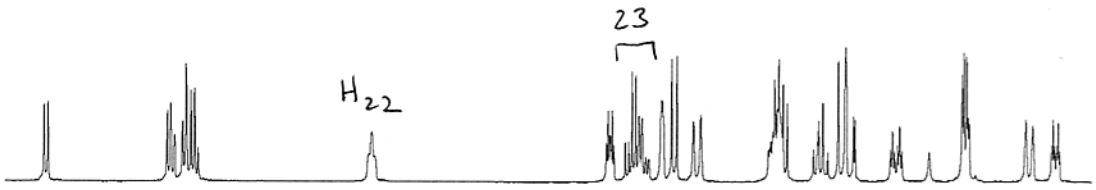
b. THE KEY TO ASSIGNING ALL THE PEAKS IN STRYCHNINE WAS CHOOSING GOOD "STARTING POINTS" IN THE CHAINS OF COUPLED PROTONS. THE EASIEST PLACE TO START WAS PROBABLY H_{22} - THE ONLY ALKENE PROTON, AND WELL SEPARATED FROM ALL OTHERS. IT SHOWS A CROSSPEAK WITH THE PAIR OF DOUBLET OF DOUBLETS AT ~ 4.1 ppm, (SEE NEXT PAGE.) THOUGH WE DON'T KNOW WHICH IS WHICH OF 23a/23b, WE CAN PUT THESE IN THE CHART (SHOWN LATER ON).

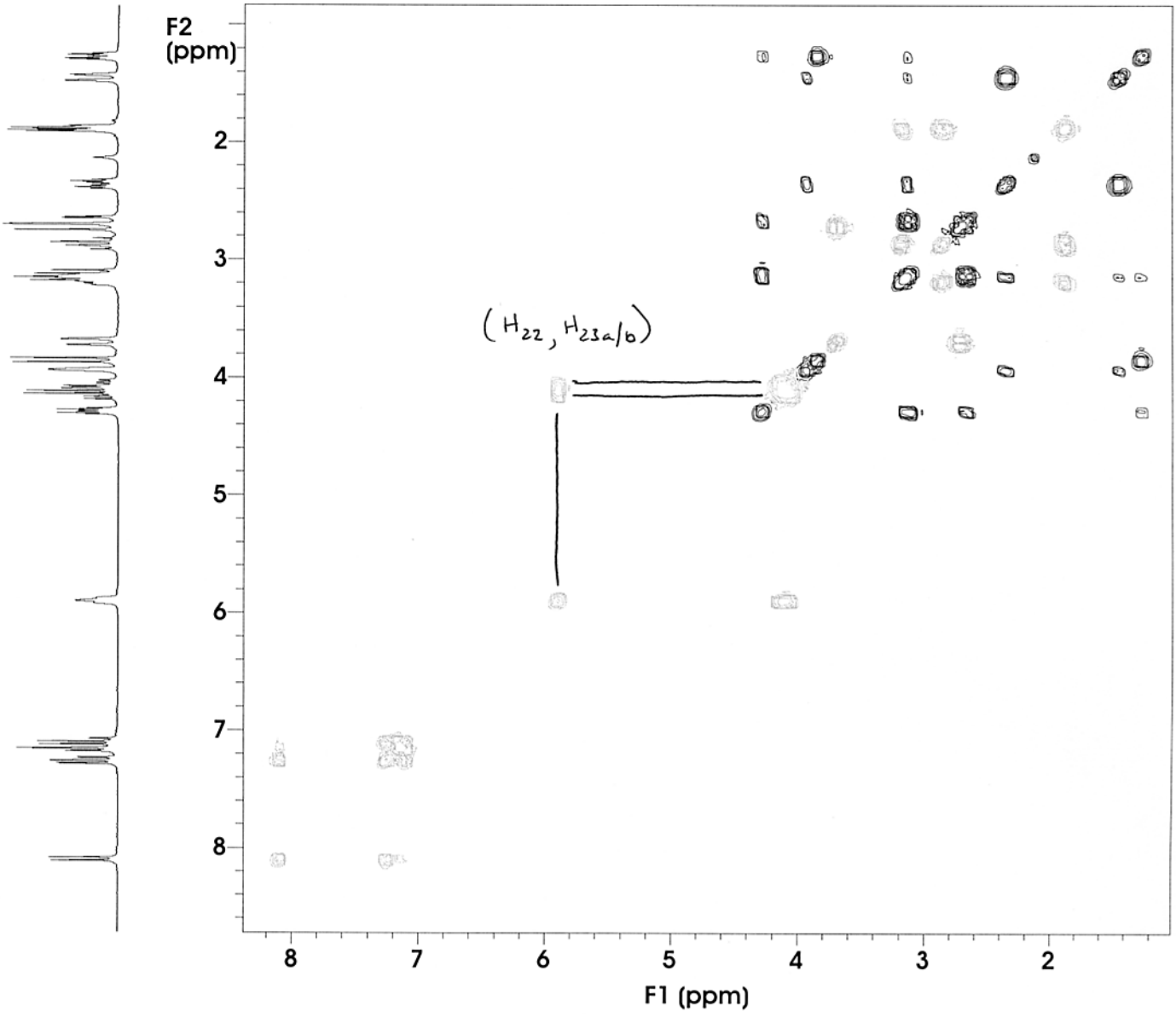
THE CLOSE-UP COSY IS PRETTY MESSY - LOTS OF COUPLED PARTNERS! THE GOAL HERE IS TO START WITH THINGS THAT AREN'T COUPLED TO MUCH. IN THE GREY SET, THERE IS ONE VERY SIMPLE PAIRING - $\delta = 3.70$ AND 2.70. THIS MUST BE H_{20a}-H_{20b} (SINCE THE 17a/17b/18a/18b SET WOULD BE MUCH MORE COMPLICATED.). THE OTHER GRAY CROSSPEAKS AR 17/18 - LET'S IGNORE THEM, THEYRE NOT IN OUR CHART.

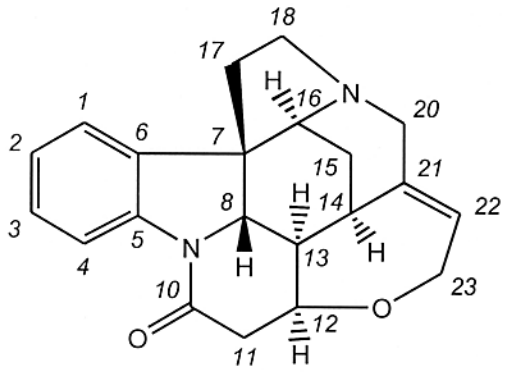
IN THE NASTY COUPLED SET, ONE PROTON IS NOT SO NASTY - H_8 IS ONLY COUPLED TO ONE OTHER PROTON, H_{13}. THERE IS ONLY ONE PEAK IN THE COSY THAT HAS ONLY ONE PARTNER: $\delta = 3.85$ (H_8), COUPLED W/ $\delta = 1.27$ (H_{13}).



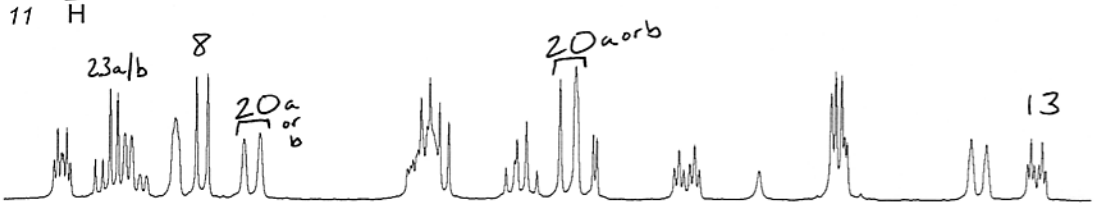
^{1}H-^{1}H COSY, 300 MHz, $CDCl_3$

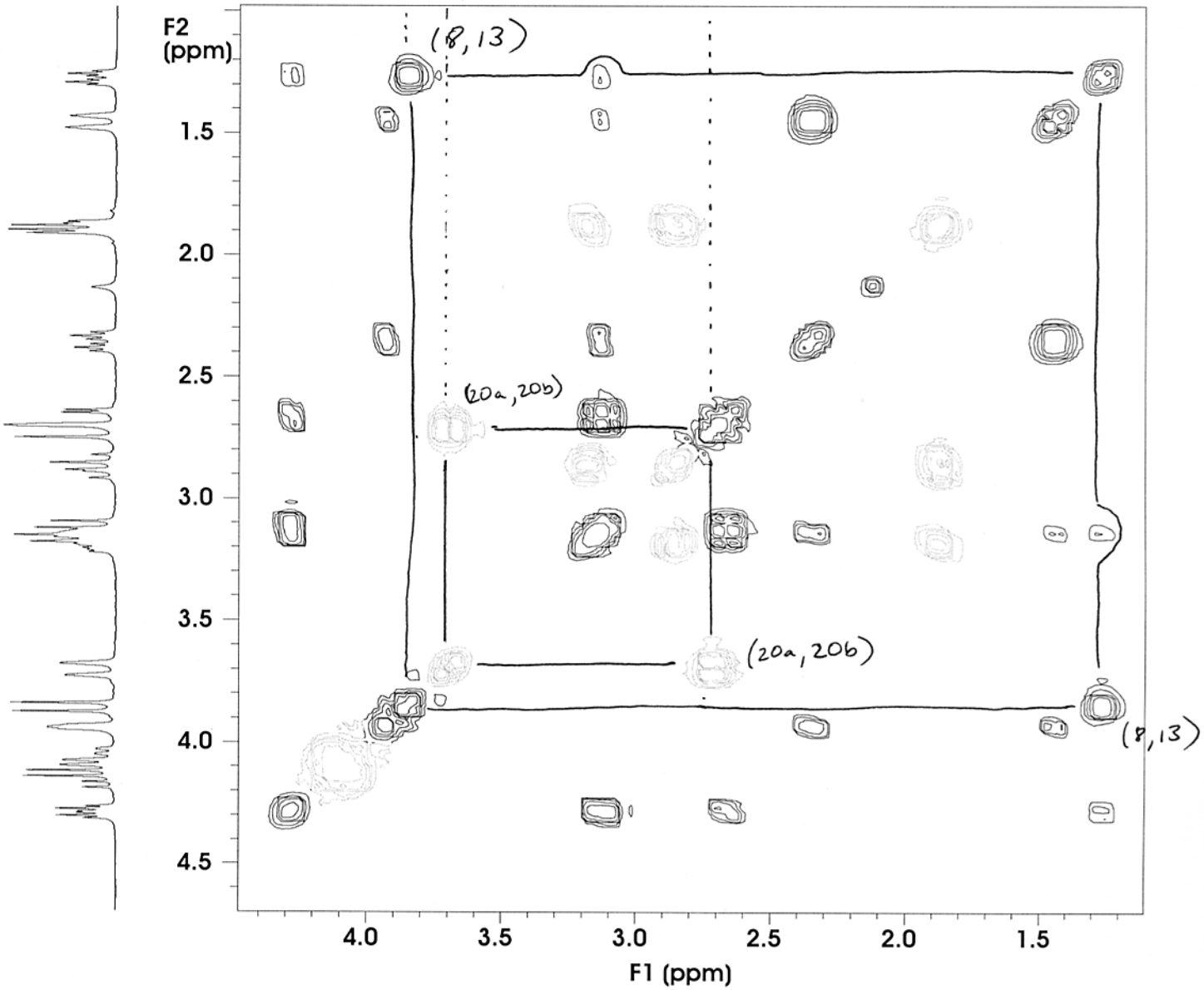






^1H-^1H COSY, 300 MHz, $CDCl_3$

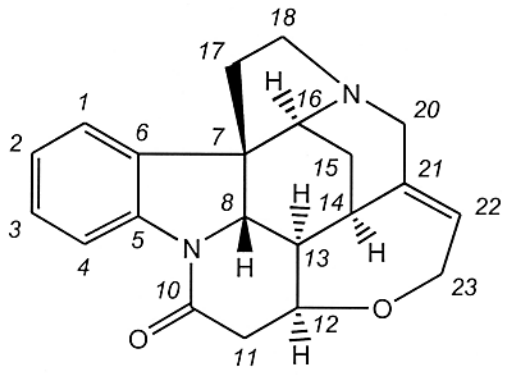




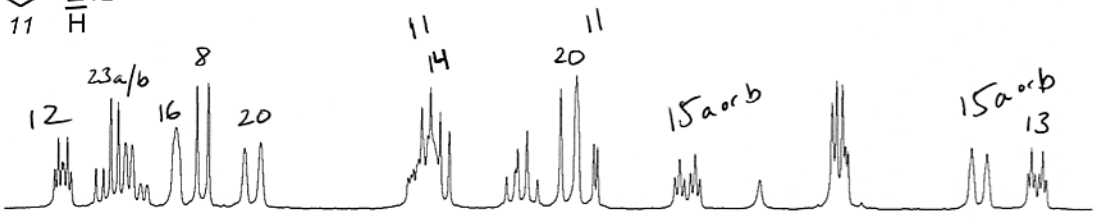
ANOTHER SIMPLE PROTON TO ASSIGN IS H_{16} - THIS ONE IS ONLY COUPLED TO TWO PROTONS, H_{15a} & H_{15b}. THERE IS ONLY ONE COSY PEAK W/ TWO CROSSPEAKS, $\delta = 3.92$ (H_{16}), COUPLED W/ $\delta = 2.35$ & 1.45 ($H_{15a/b}$). 15_a AND 15_b ARE COUPLED TO EACH OTHER, H_{16}, AND ONLY ONE OTHER PROTON, H_{14} ($\delta = 3.11$). H_{14} IS ONE OF A NUMBER OF PROTONS IN A BIG OVERLAPPING MULTIPLET. TO SOME EXTENT, THIS CLOSES THE LOOP W/ H_{13}.

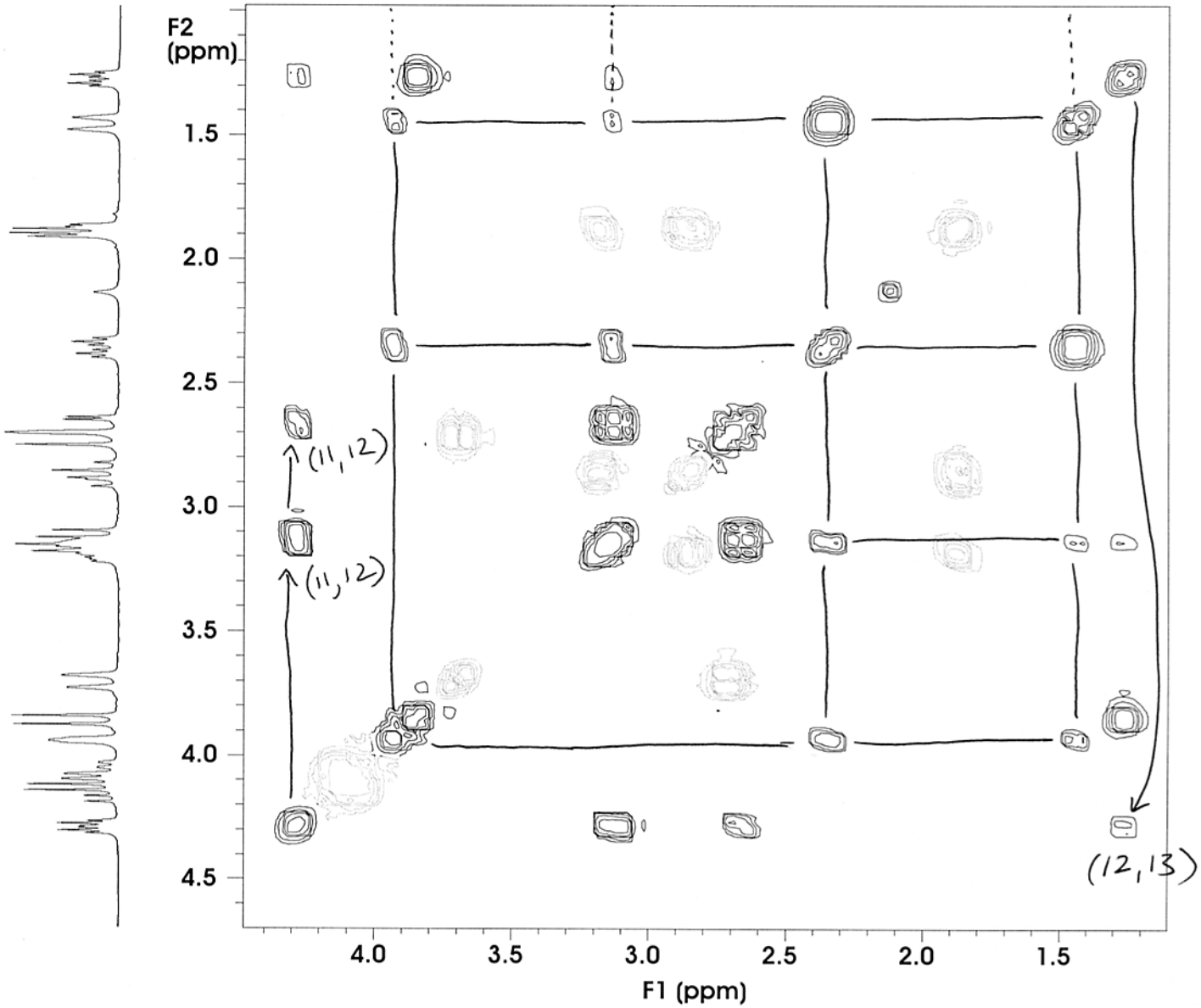
H_{13} IS ALSO COUPLED TO H_{12} ($\delta =$ [redacted] 4.3), [redacted] AND H_{12} LEADS TO THE TWO H_{11} PROTONS ($\delta = 3.15, 2.65$).

proton	δ (ppm)	
H_8	3.88	
H_{11} (x2)	3.15	2.65
H_{12}	4.30	2 POINTS EACH.
H_{13}	1.28	
H_{14}	3.15	
H_{15} (x2)	2.36	1.46
H_{16}	3.94	
H_{20} (x2)	3.71	2.73
H_{23} (x2)	4.15	4.08



^{1}H-^{1}H COSY, 300 MHz, $CDCl_3$





LOOKING AT THE HMQC COULD HAVE HELPED YOU ANSWER PART B — BUT YOU DIDN'T STRICTLY NEED IT.

c) AT THIS POINT, PRETTY EASY. (SEE NEXT PAGE.)

> 2 POINTS FOR EACH PAIR;
> 1 POINT FOR CIRCLES,
> 1 POINT FOR ARROW.

d) NATURALLY, THERE ARE LOTS OF CROSSPEAKS IN THE NOESY SPECTRUM. BUT THE ONLY ONES THAT HELP ASSIGN THE UNASSIGNED PAIRS ARE (1) CROSSPEAKS THAT INVOLVE ONE OF H_{11}, H_{15}, H_{20} OR H_{23}; AND (2) CROSSPEAKS THAT ARE UNIQUE TO ONE OF AN a/b PAIR. (SO, FOR EXAMPLE, 15a ↔ 16 DOESN'T HELP, BECAUSE THERE IS ALSO A 15b ↔ 16 PEAK.) I'VE FOUND FIVE OF THESE (PAGE AFTER NEXT). YOU NEEDED ONLY 3 OF THESE.

> 2 POINTS FOR CIRCLING EACH CROSSPEAK (x3);
> 2 POINTS FOR EACH ARROW (x3).

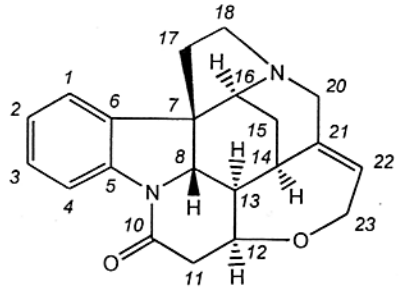
Univ of Minnesota, VI-500

Pulse Sequence: ghmqc

User: 1-14-87
Date: Oct. 26, 2002
Solvent: cdcl3
File: strhmqc
Starting Time: 12:35:02
Completion Time: 12:40:23
Total acq. time 5 minutes

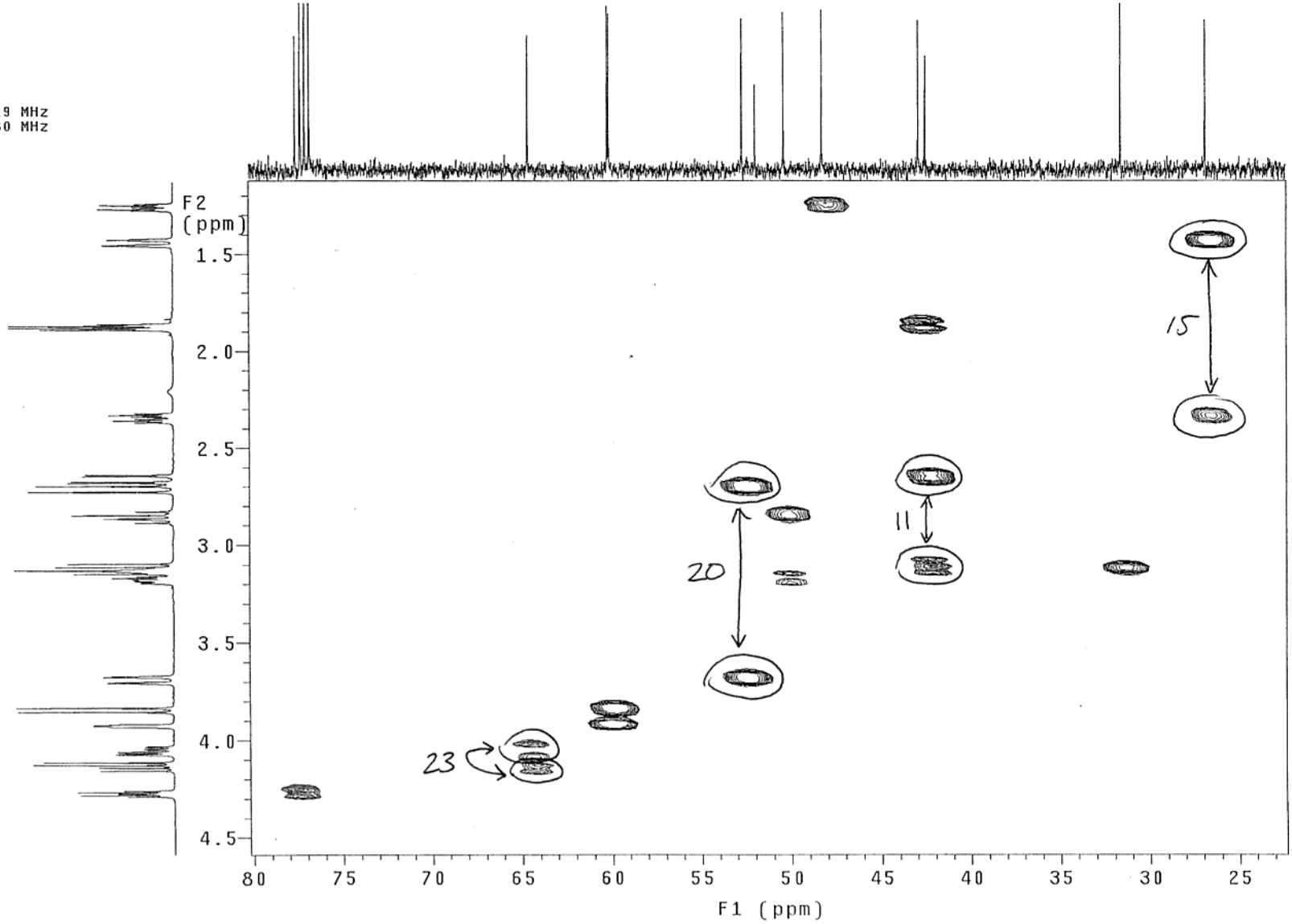
UNITYplus-500 "spectrum"
Temp. 23.0 C / 296.1 K

PULSE SEQUENCE: ghmqc
Relax. delay 1.388 sec
Acq. time 0.112 sec
Width 4559.4 Hz
2D Width 25798.1 Hz
Single scan
192 increments
OBSERVE H1, 499.8671219 MHz
DECOUPLE C13, 125.7039580 MHz
Power 47 dB
on during acquisition
off during delay
wurst modulated
DATA PROCESSING
Sine bell 0.056 sec
F1 DATA PROCESSING
Sine bell 0.004 sec
FT size 1024 x 1024



^{1}H-^{13}C HMQC, 500/125 MHz, $CDCl_3$

Writing on this page **will** *be graded.*



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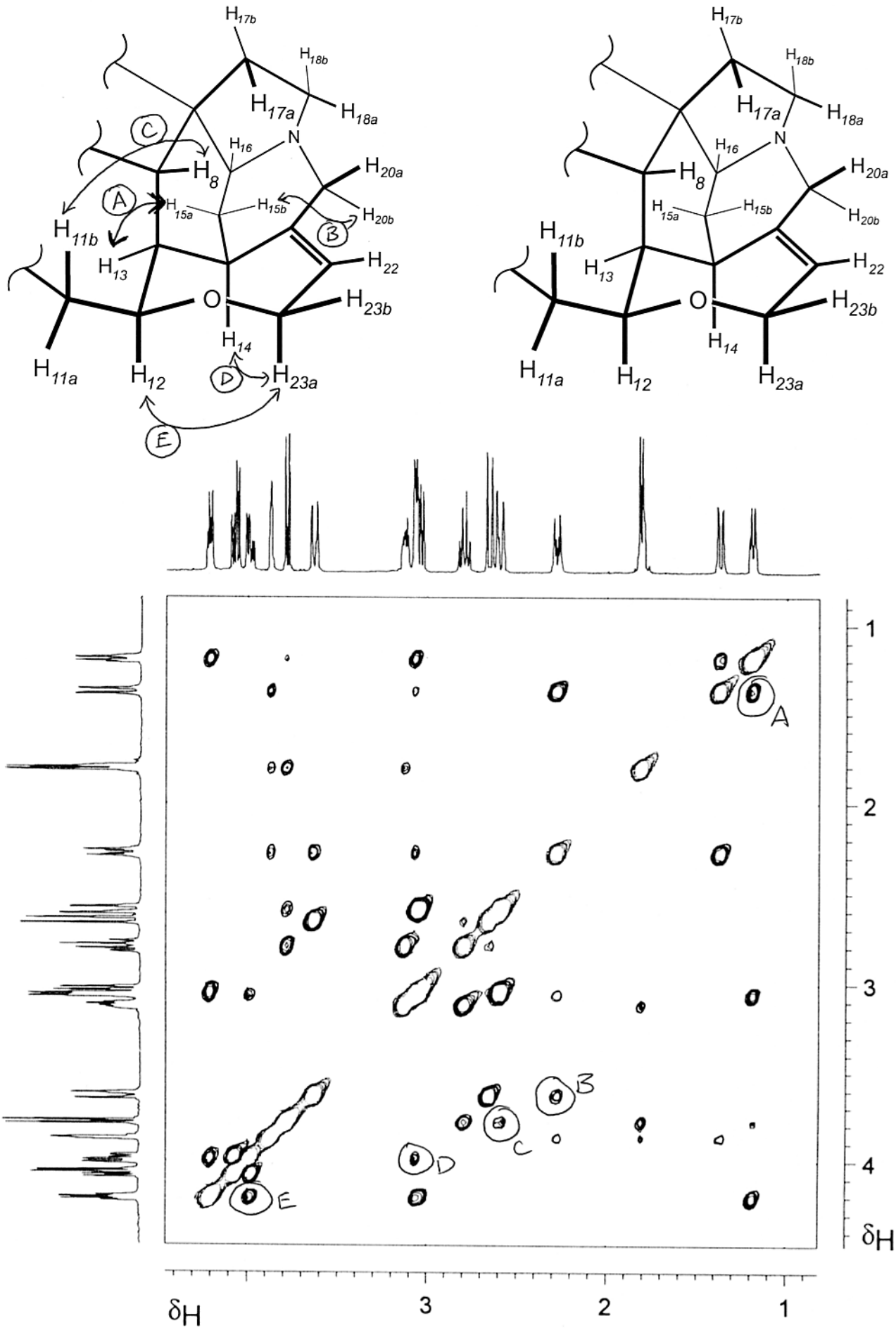
H17b
H18b
H17a
H18a
H16
N
H8
H20a
H15a
H15b
H20b
H11b
H13
H22
O
H23b
H14
H11a
H12
H23a
A
B
C
D
E
δH
1
2
3
4
δH
3
2
1

e.

proton #	δ (ppm) for H_a	δ (ppm) for H_b
H_{11}	3.15	2.65
H_{15}	1.46	2.36
H_{20}	2.73	3.71
H_{23}	4.08	4.15

ONLY NEED 3 OF THESE. IF YOU PUT ALL 4, YOU MUST GET ALL 4 RIGHT (i.e., EVEN IF 3 ARE RIGHT, 1 WRONG = 1 WRONG).

~~3 POINTS~~ 2 POINTS EACH (x 6).