Supplementary Material

Effect of Substituents in directing the formation of Benzochlorins and isobacteriochlorins in Porphyrin and chlorin systems:

Sashikumar Mettah, Guolin Li, Thamarapu Srikrishnan, Ricky Mehta, Zachary D. Grossman Thomas Dougherty and Ravindra K Pandey*

CRYSTAL DATA AND STRUCTURE REFINEMENT

Compound name	2^1-trifluoromethyl-octaethy benzochlorin
Color/shape	deep red/ rectangular prism
Empirical Formula	$C_{40}H_{47}N_4F_4$
Formula weight	640
Temperature	22±3°C
Crystal system	Triclinic
Space group	P 1
Unit cell dimensions	a (Å) 8.689 (3) α= 73.51 (2)° b (Å) 14. 490 (4) β=81.50(3)° c (Å) 14.953 (5) γ= 77.80(2)°
Volume	1752.4 (9) ($Å^3$)
Z	2 (two per unit cell)
Density calculated	1.213 mg/m^3
Absorption coefficient	0.81 mm^{-1}
Difftractometer	CAD-4
Radiation/wavelength	CuKα / 1.5418Å
F(000)	684
Crystal size	0.25x0.35x0.15 mm
θ range for data collection	0 to 150°
Index ranges	$-10 \leq h \leq 10$; $0 \leq k \leq 17$; $18 \leq l \leq 18$
Reflections collected	7109
Independent/observed reflections	2569 ($I \leq 3\sigma$)
Absorption correction	semi-empirical from psi scans
Range of relat. trasm. factors	0.99 and 0.90
Refinement method	Full-matrix least squares on F^2
Computing	SHELXS-96
Data / restraints/ parameters	2569 /0/1248
Goodness of fit on F^2	1.017
Function minimized	$\Sigma [\| F_o^2 \| - (1/k) \| F_c^2 \|]$
Final R indices [$I > 3\sigma$ (I)]	0.0825
Final extinction coefficient	4.41×10^{-7}
Large diff. peaks and hole	± 0.15 e/$Å^3$

X-ray Crystallography. Crystals of 2^1-trifluoromethyloctaethylbenzochlorin ($C_{40}H_{47}N_4F_6$) were obtained by a slow evaporation of the compound dissolved in methylene chloride and acetone mixture. The crystal are dark red in color and have a rectangular prismatic habit. A crystal of dimensions $0.25 \times 0.35 \times 0.15$ mm was used for the present crystal structural investigation. The crystals belong to the triclinic system, space group $P1$ (two independent molecules) with the following cell dimensions: $a = 8.689(3)$, $b = 14.490(4)$, $c = 14.953(5)$ Å, $\alpha = 73.51(2)$, $\beta = 81.50(3)$, $\gamma = 77.80(2)°$, $V = 1752.4$ Å^3, $\rho_{calc} = 1.213$ g/cm^2, μ (Cu Kα) = 0.81 mm^{-1} and $Z = 2$. Complete three-dimensional data was collected on a CAD-4 computer-controlled diffractometer. A total of 7109 reflections ($2\theta_{max} = 150°$) were collected by the $\omega/2\theta$ method, out of which 2596 were considered significant ($I \geq 3\sigma$). The crystal structure was solved by a routine and straightforward application of SHJELX-96 program on a silicon graphics R10,000 computer. The structure was refined using SHELX-96 package of programs. All the hydrogen atoms were located on a difference Fourier map. Refinements were carried out with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameter for the hydrogen atoms. The final reliability index (R factor) was 0.0825 for the observed 2569 reflections, the goodness of fit parameter $S = 1.267$.

Supporting Material

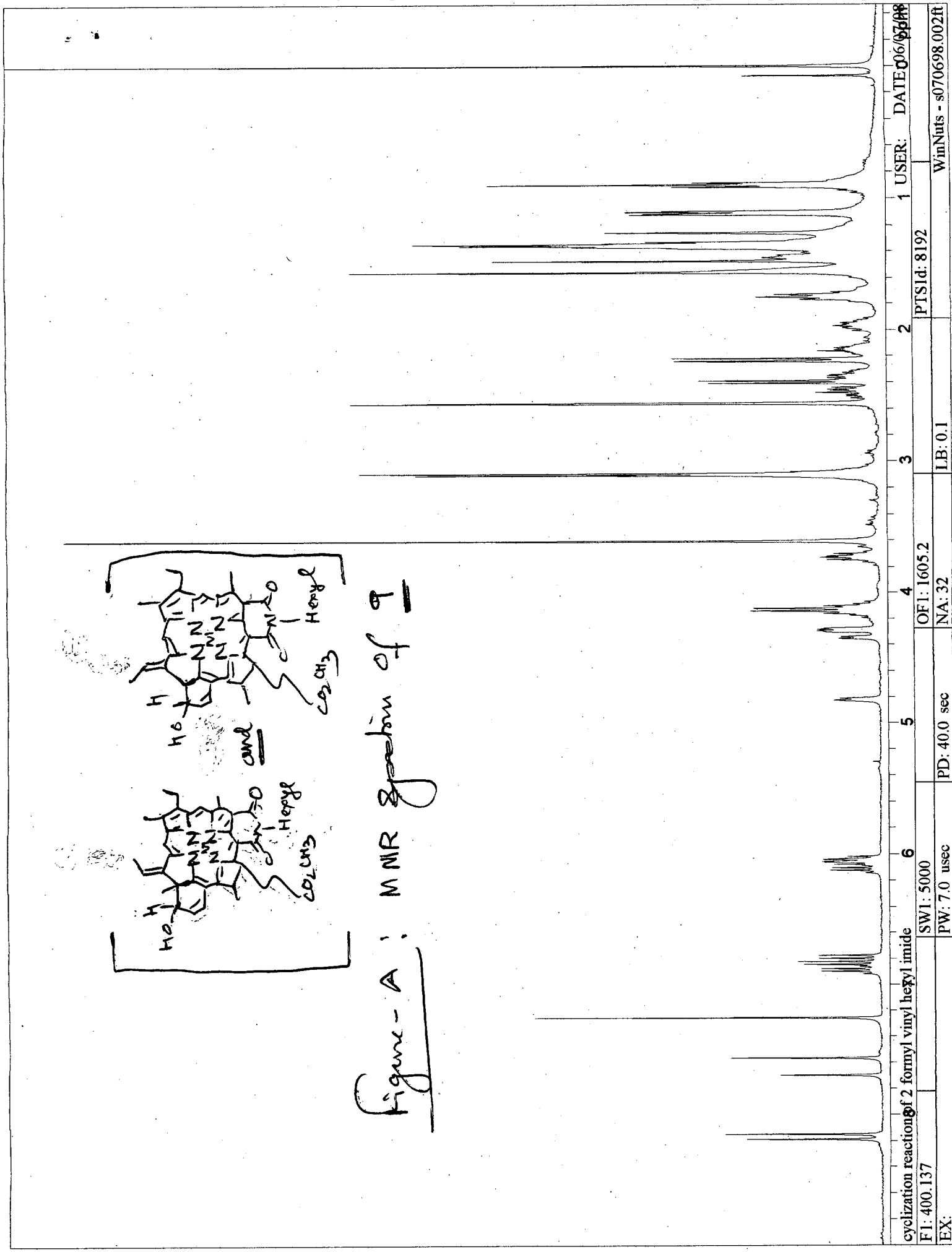


Figure-A : NMR Spectrum of 9 and

SPEC: P201 24-SEP-98 DERIVED SPECTRUM 9
Samp: P-201 (PANDEY) Start : 11:18:44 10
Comm: POS. FAB*m-NITROBENZYL ALCOHOL
Mode: EI +VE +HMR BSCAN (EXP) UP LR
Oper: DUTTA Inlet :
Base: 774.2 Inten : 97452480 Masses: 100 > 1200
Norm: 774.2 RIC : 852226752 # peaks: 1018
Peak: 1000.00 mmu
Data: SY:P201.DT + 'P201' /1>10 - 'BLN92498

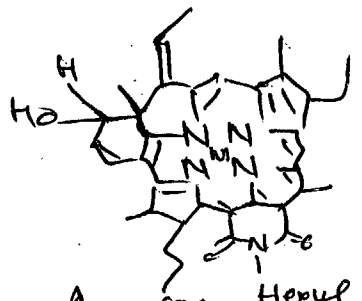


Figure Aa: CO_2CH_3

Mass Spectrum of 9

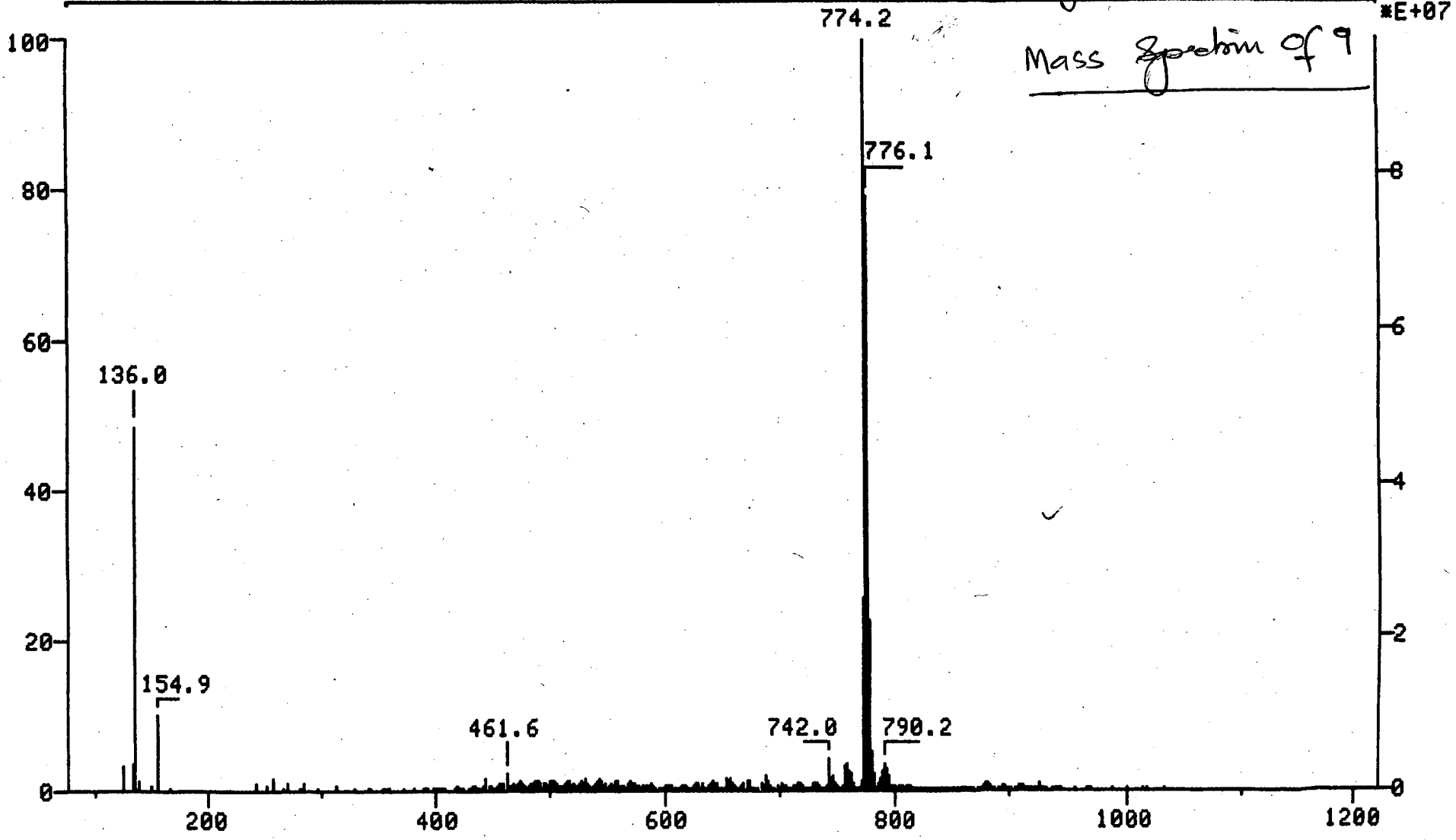
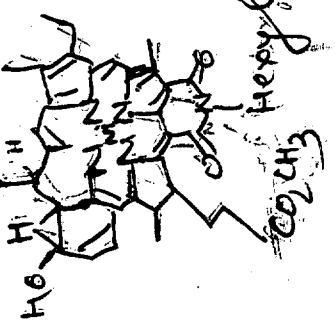
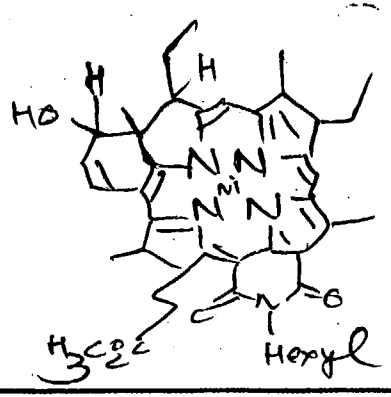


Figure B: ^{1}H NMR Spectrum of 10



Isobacteriochlorin 10

SPEC: P202 6-OCT-98 DERIVED SPECTRUM 9
Samp: P-202 (PANDEY) Start : 14:04:58 10
Comm: POS. FAB*m-NITROBENZYL ALCOHOL
Mode: EI +VE +HMR BSCAN (EXP) UP LR
Oper: DUTTA Inlet :
Base: 776.1 Inten : 66777636 Masses: 100 > 1500
Norm: 776.1 RIC : 570630208 # peaks: 1259
Peak: 1000.00 mmu
Data: SY:P202.DT + 'P202' /1>10 - 'BLN10698



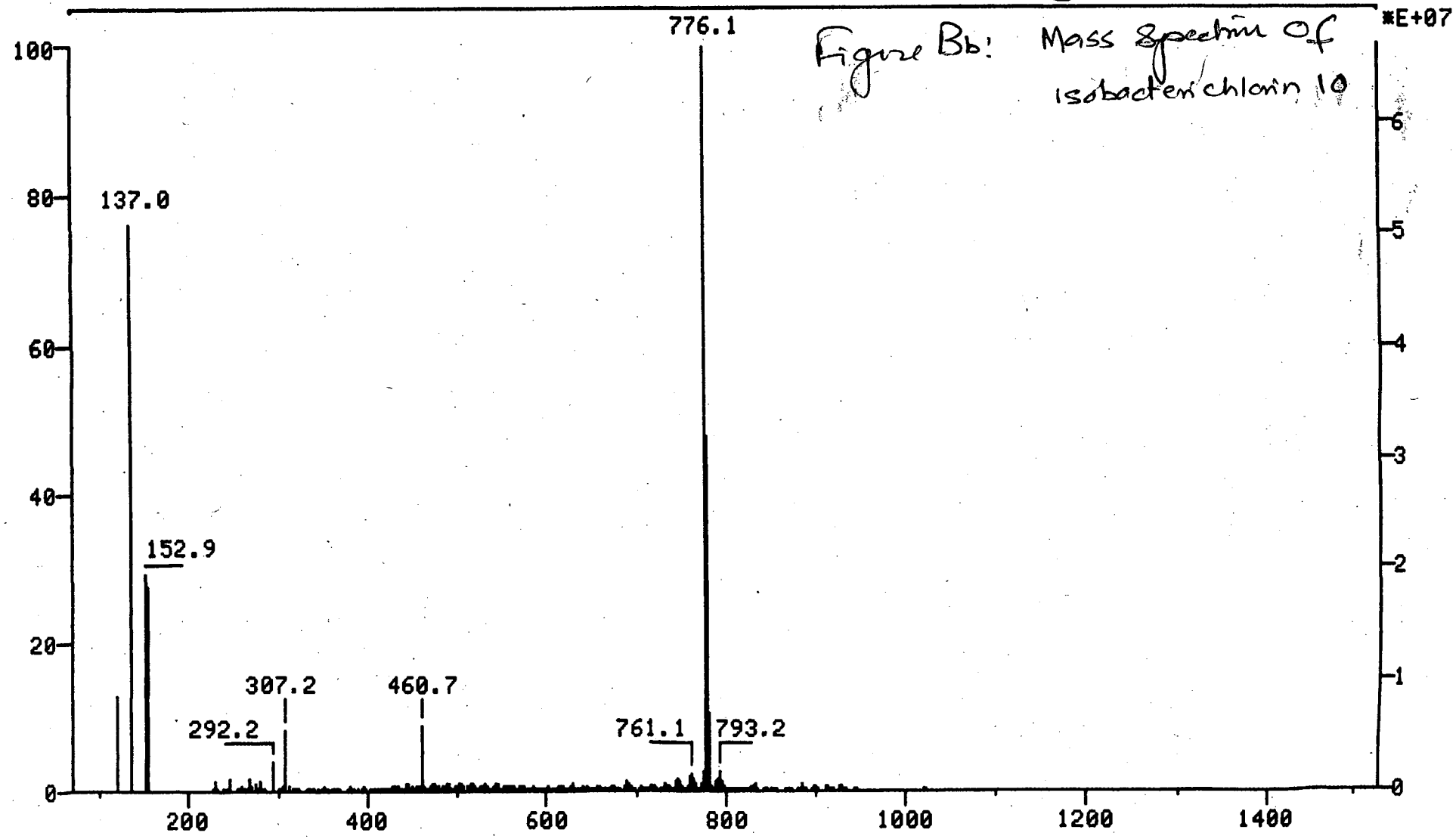


Figure 8b: Mass spectrum of isobacteriochlorin 10

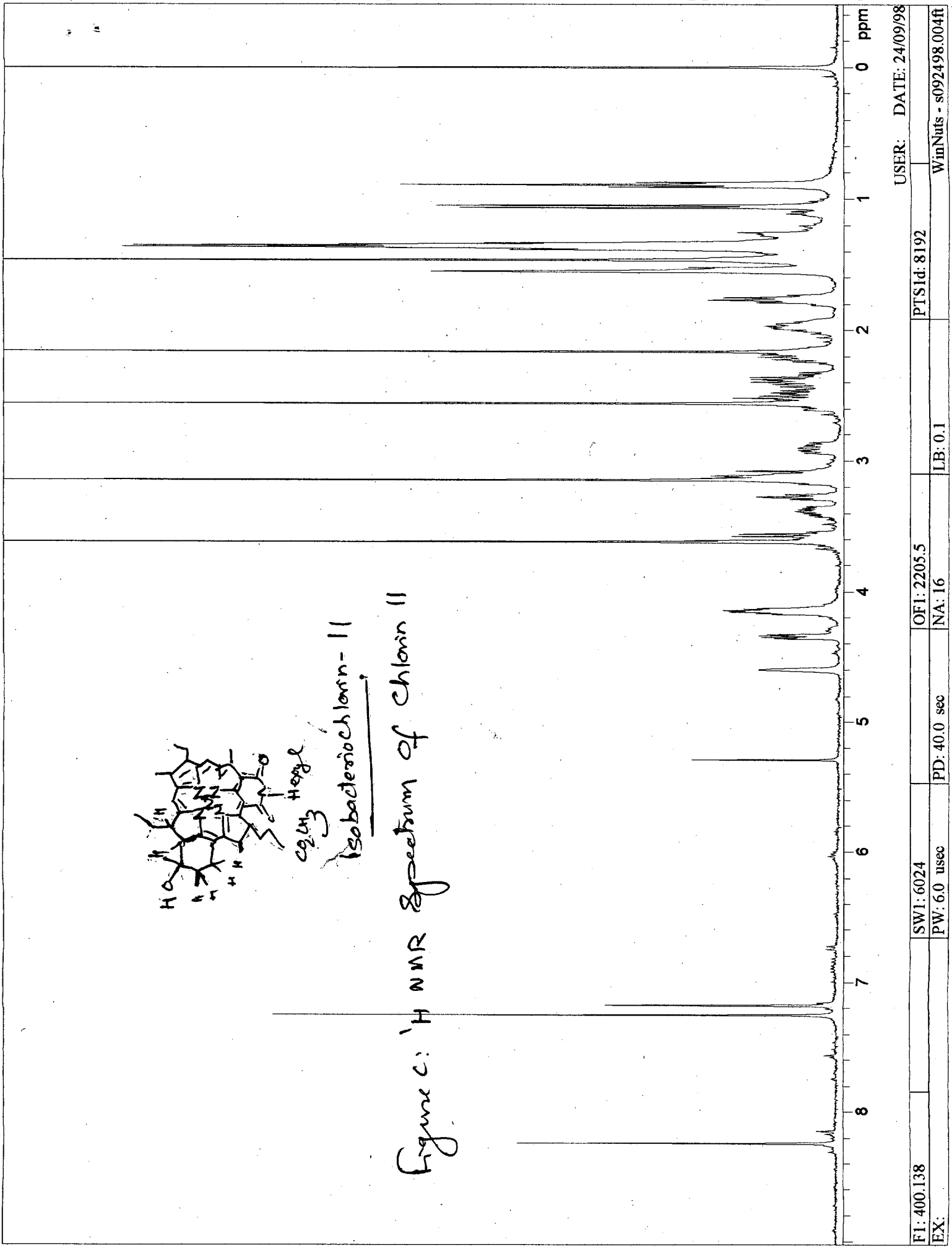
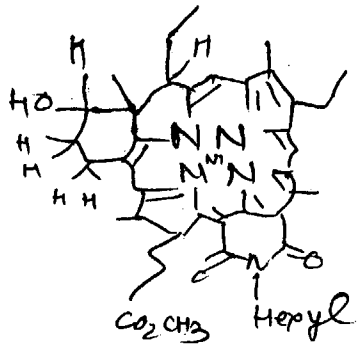


Figure c: ^1H NMR Spectrum of Chlorin II

Isobacteriochlorin - II

C_2H_5 Hexyl CO_2CH_3

SPEC: P202 P-203 24-SEP-98 DERIVED SPECTRUM 9
Samp: P-202 (PANDEY) Start : 11:39:11 10
Comm: POS. FAB*m-NITROBENZYL ALCOHOL
Mode: EI +VE +HMR BSCAN (EXP) UP LR
Oper: DUTTA Inlet :
Base: 778.2 Inten : 123745296 Masses: 100 > 1200
Norm: 778.2 RIC : 944659968 # peaks: 995
Peak: 1000.00 mmu
Data: SY:P202.DT + 'P202' /1>10 - 'BLN92498



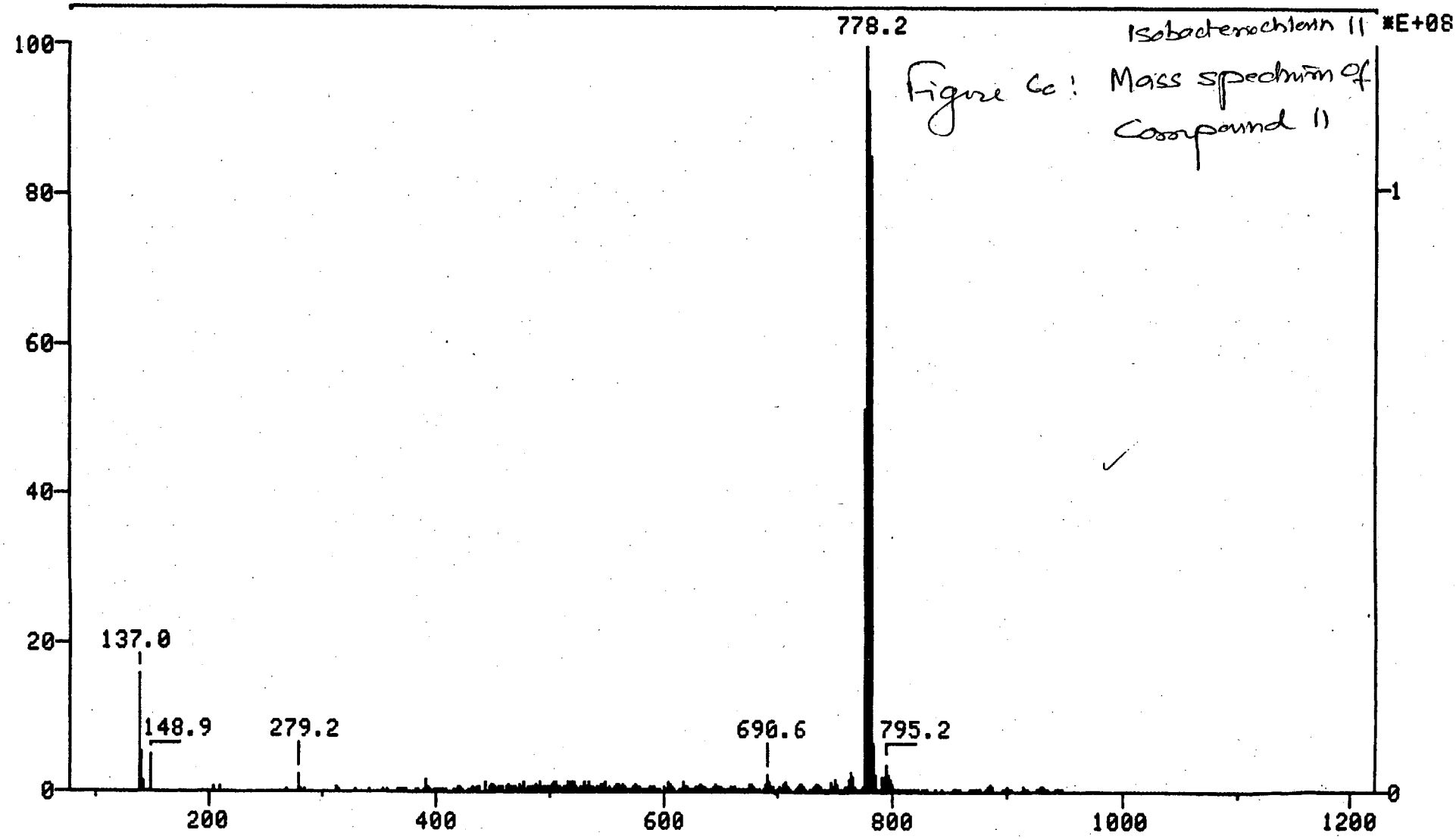
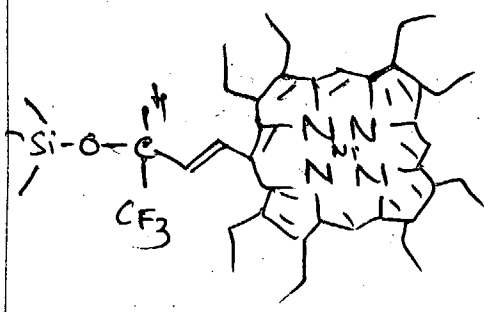


Figure 6c: Mass spectrum of Compound 11



Porphyrin-12

Figure-D

Figure-D: NMR Spectrum of 12

CDCl3, FP-12						USER:	DATE: 27/02/9
F1: 400.138		SW1: 6024		OF1: 2206.2		PTS1d: 8192	
EX:		PW: 7.0 usec	PD: 40.0 sec	NA: 32	LB: 0.1	WinNuts - $Fp12.001	

E

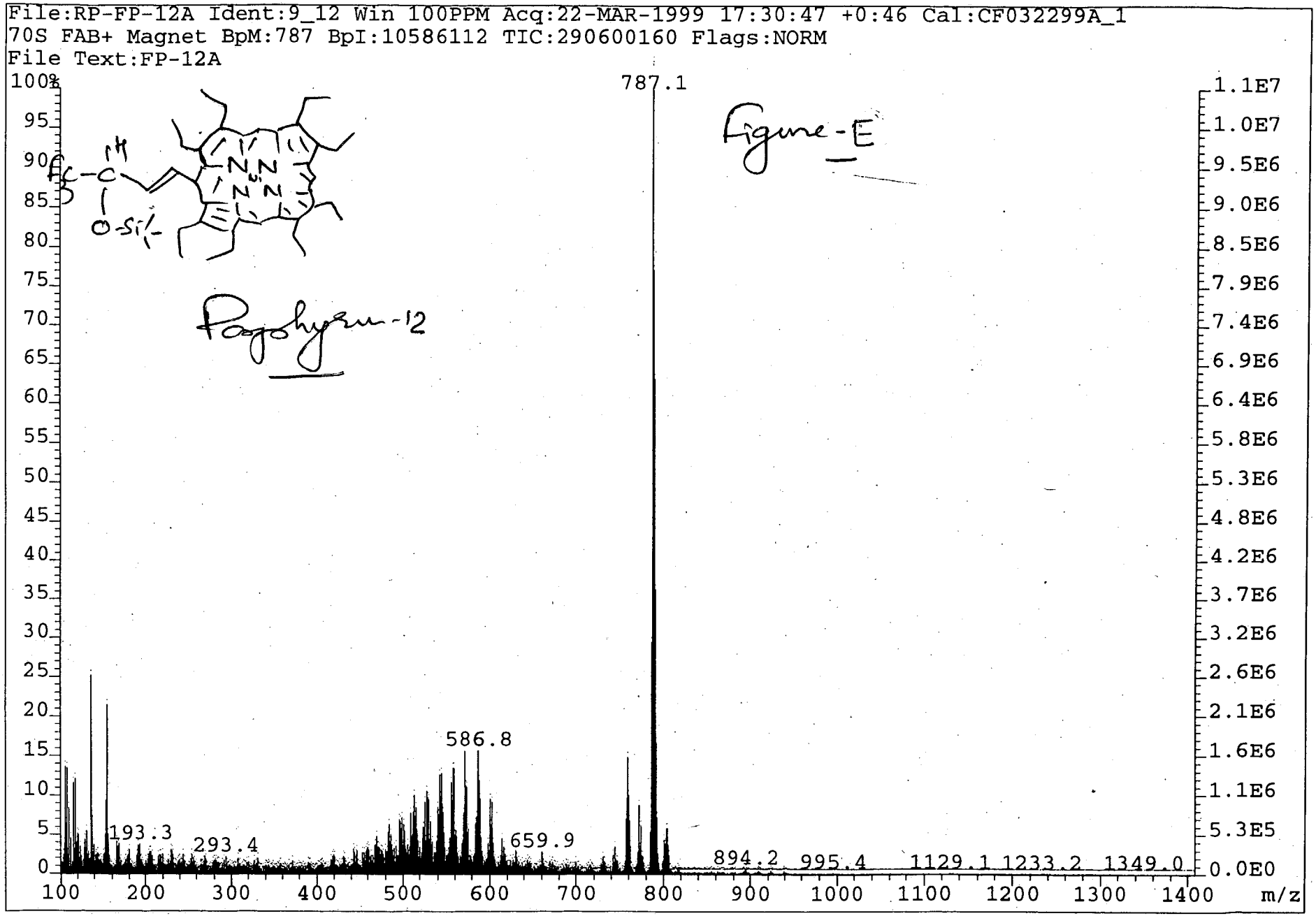
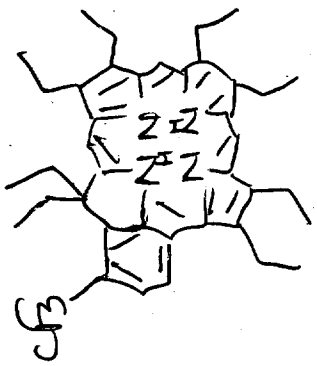


Figure-E

Porphyrin-12

Figure-E. Mass Spectra of porphyrin 12



Benzochlorin 13

Figure-F

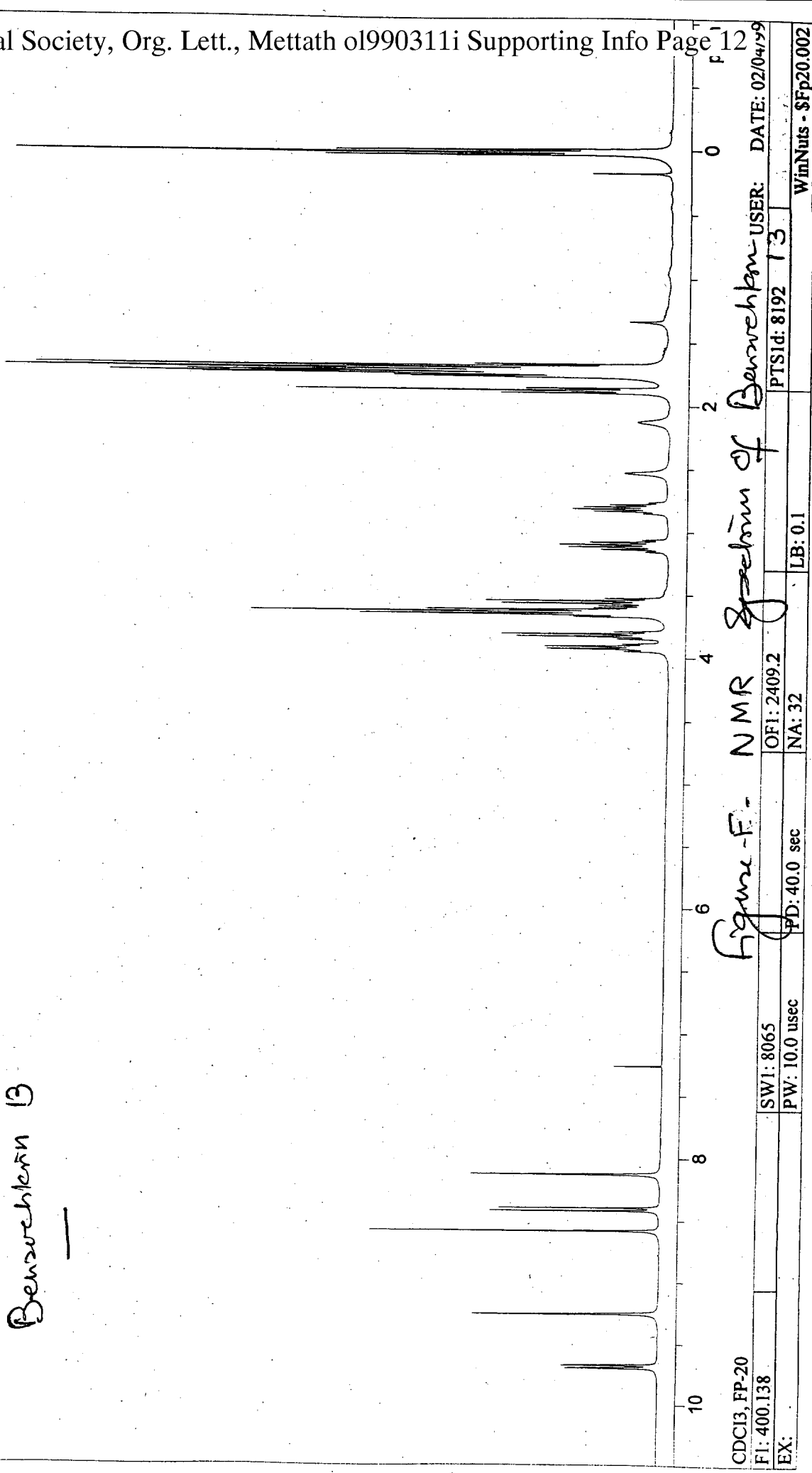
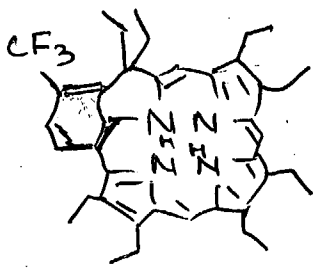


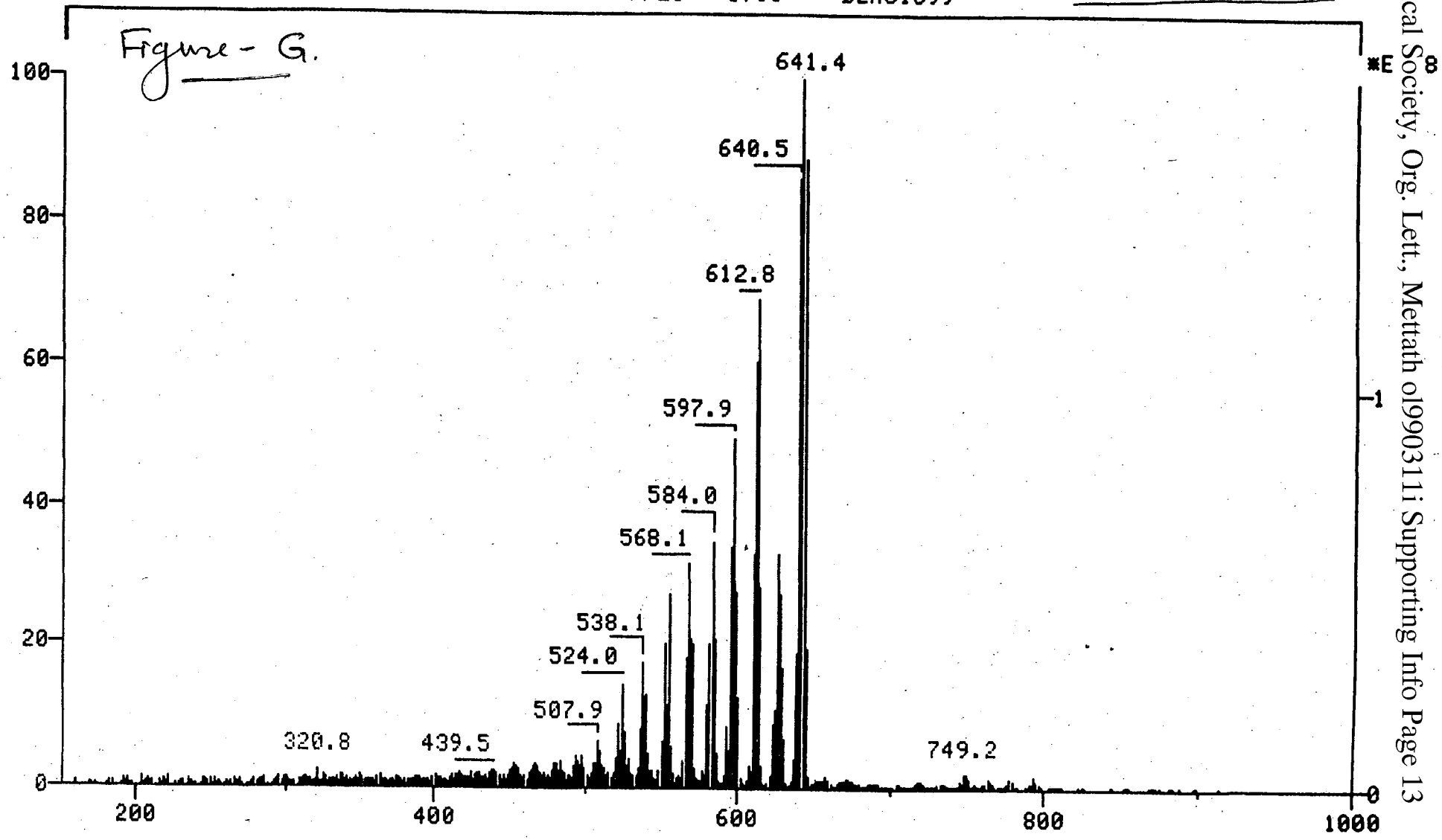
Figure-F. NMR Spectrum of Benzochlorin 13

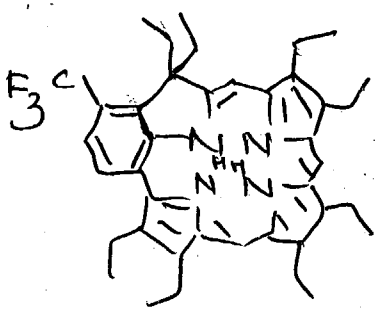
SPEC: FP20 10-MAR-99 DERIVED SPECTRUM 9
Samp: FP-20 (PANDEY) Start : 10:34:22 10
Comm: POS. FAB*m-NITROBENZYL ALCOHOL(1% TFA)
Mode: EI +VE +HMR BSCAN (EXP) UP LR
Oper: DUTTA Inlet :
Base: 641.4 Inten : 177974688 S Masses: 150 > 2000
Norm: 641.4 RIC : 3974349824 # peaks: 1981
Peak: 1000.00 mmu
Data: SY:FP20.DT + 'FP20' /1>10 - 'BLN31099



Benzochlorin - 13

Figure - G.

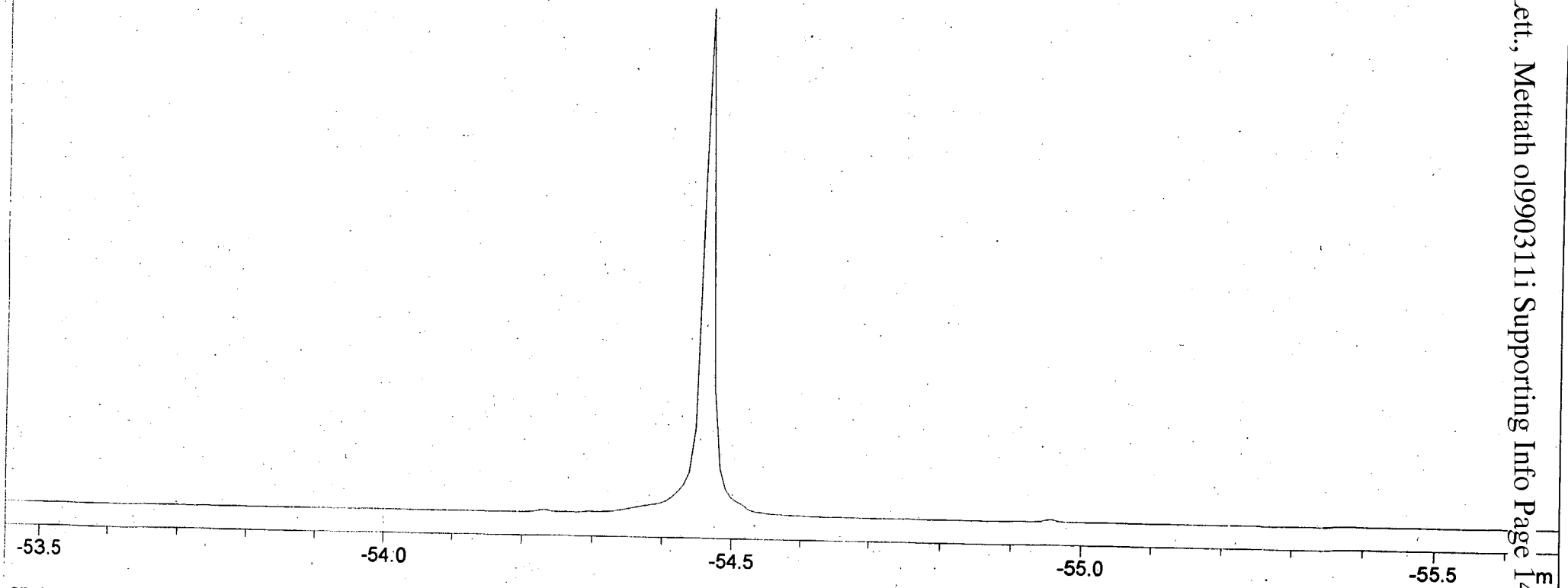




13

Figure-4

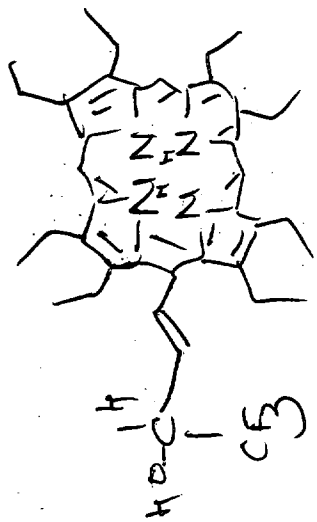
^{19}F NMR Spectrum of Benzochlorin-13



CDCl3, FP-20. F-19 NMR

F1: 376.471		SW1: 26315		OF1: -24724.4			USER: DATE: 03/03/99
EX:		PW: 8.0 usec	PD: 20.0 sec	NA: 24	LB: 2.0	PTS1d: 8192	

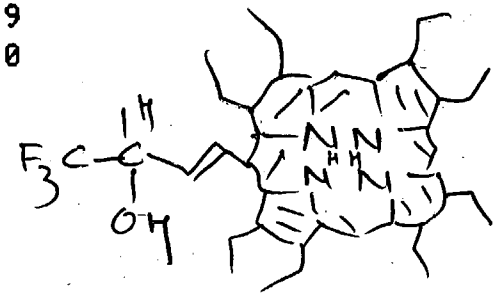
Figure - I : ^{1}H NMR Spectrum of Porphyrin 14.



14

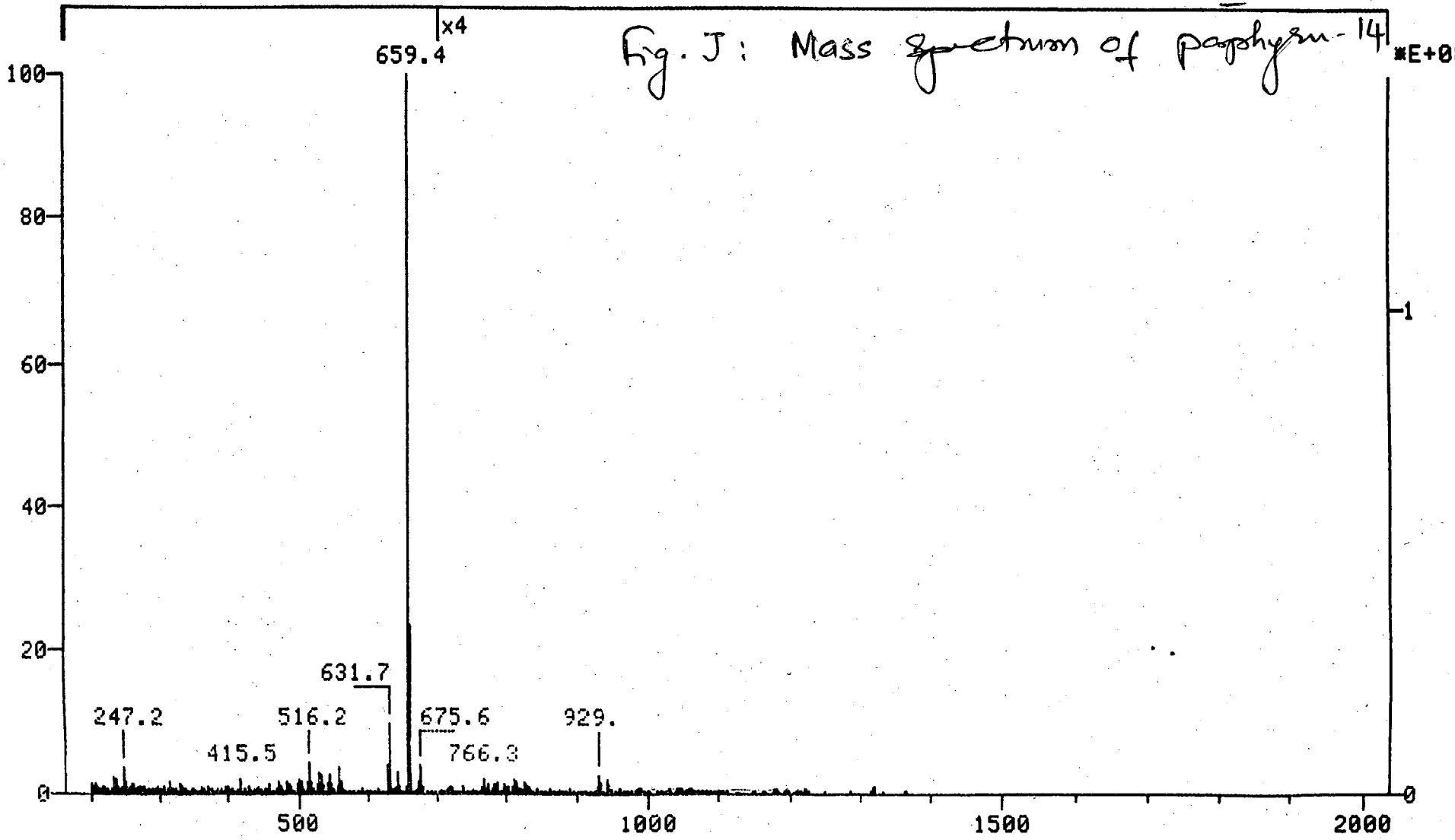
14

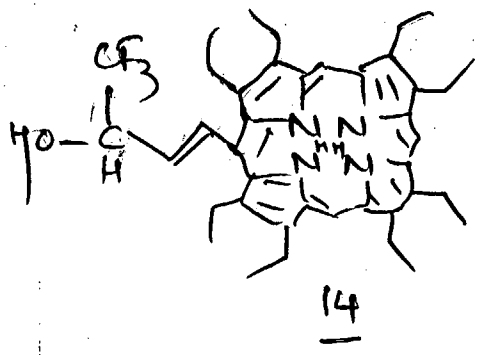
SPEC: FP35 10-JUN-99 DERIVED SPECTRUM 9
Samp: FP-35 (PANDEY) Start : 08:39:19 10
Comm: POS. FAB*m-NITROBENZYL ALCOHOL (1% TFA)
Mode: EI +VE +HMR BSCAN (EXP) UP LR
Oper: DUTTA Inlet :
Base: 659.4 Inten : 147833888 Masses: 200 > 2000
Norm: 659.4 RIC : 1109045248 # peaks: 1850
Peak: 1000.00 mmu
Data: SY:FP35.DT + 'FP35' /1>10 - 'BLN61099



14

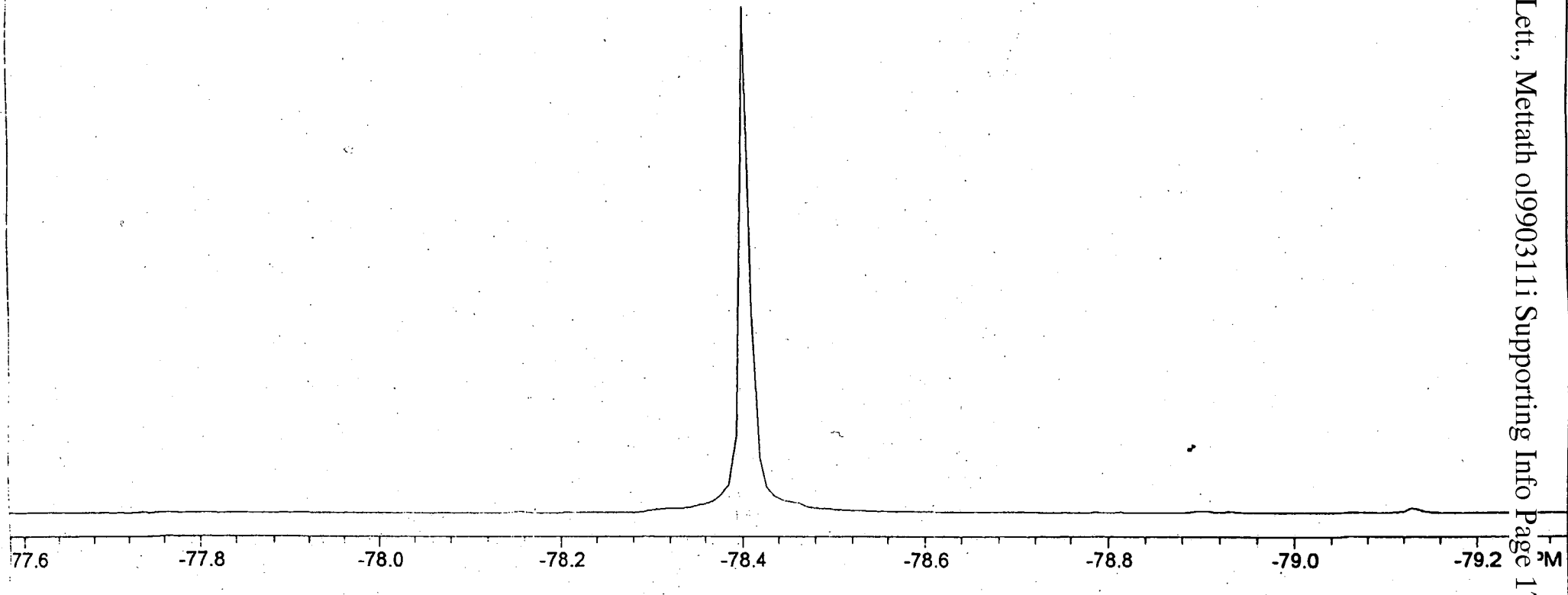
Fig. J: Mass spectrum of porphyrin-14





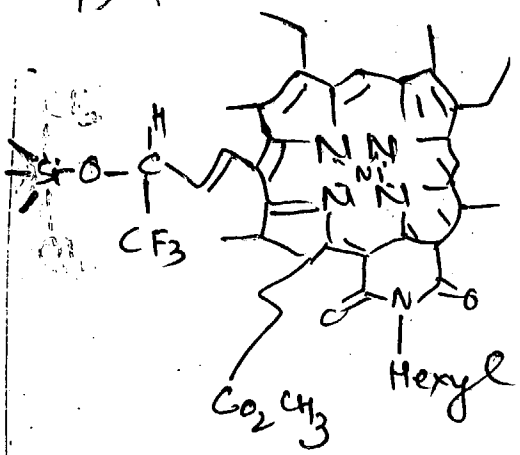
14

Figure k: ^{19}F NMR Spectrum of porphyrin 14



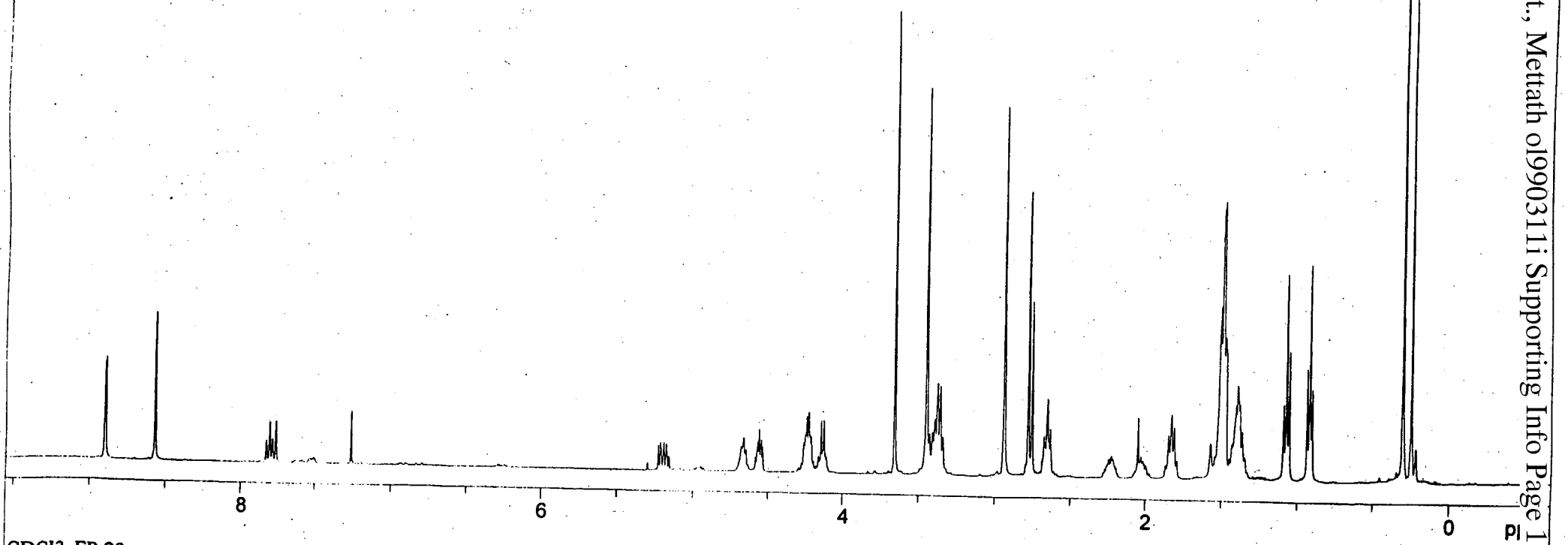
CDCl3, FP-35, F-19 NMR						USER: -- DATE: 31/ 09
F1: 376.471	SW1: 26315		OF1: -24724.4		PTS1d: 8192	
EX:	PW: 8.0 usec	PD: 2.0 sec	NA: 48	LB: 2.0		WinNuts - $Fip35.001

15a



15a

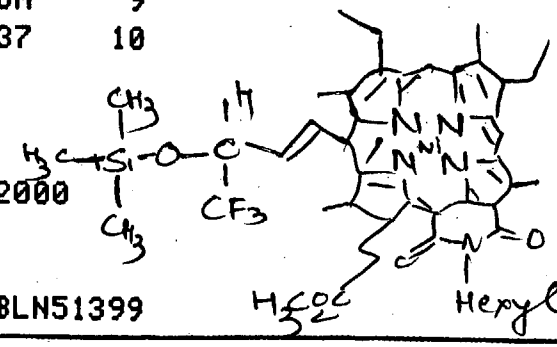
Figure L: ^{1}H NMR Spectrum of Chlorin 15a



CDCl3, FP-23							
F1: 400.138		SW1: 6024		OF1: 2207.3			USER: DATE: 06/03/99
EX:		PW: 7.0 usec	PD: 40.0 sec	NA: 40	LB: 0.1	PTS1d: 8192	WinNuts - $Fp23.001

15a

SPEC: FP23 13-MAY-99 DERIVED SPECTRUM 9
Samp: FP-23 (PANDEY) Start : 13:13:37 10
Comm: POS. FAB*m-NITROBENZYL ALCOHOL
Mode: EI +VE +HMR BSCAN (EXP) UP LR
Oper: DUTTA Inlet :
Base: 916.4 Inten : 115699968 Masses: 200 > 2000
Norm: 916.4 RIC : 2393896192 # peaks: 1931
Peak: 1000.00 mmu
Data: SY:FP23.DT + 'FP23' /1>10 - 'BLN51399



15a

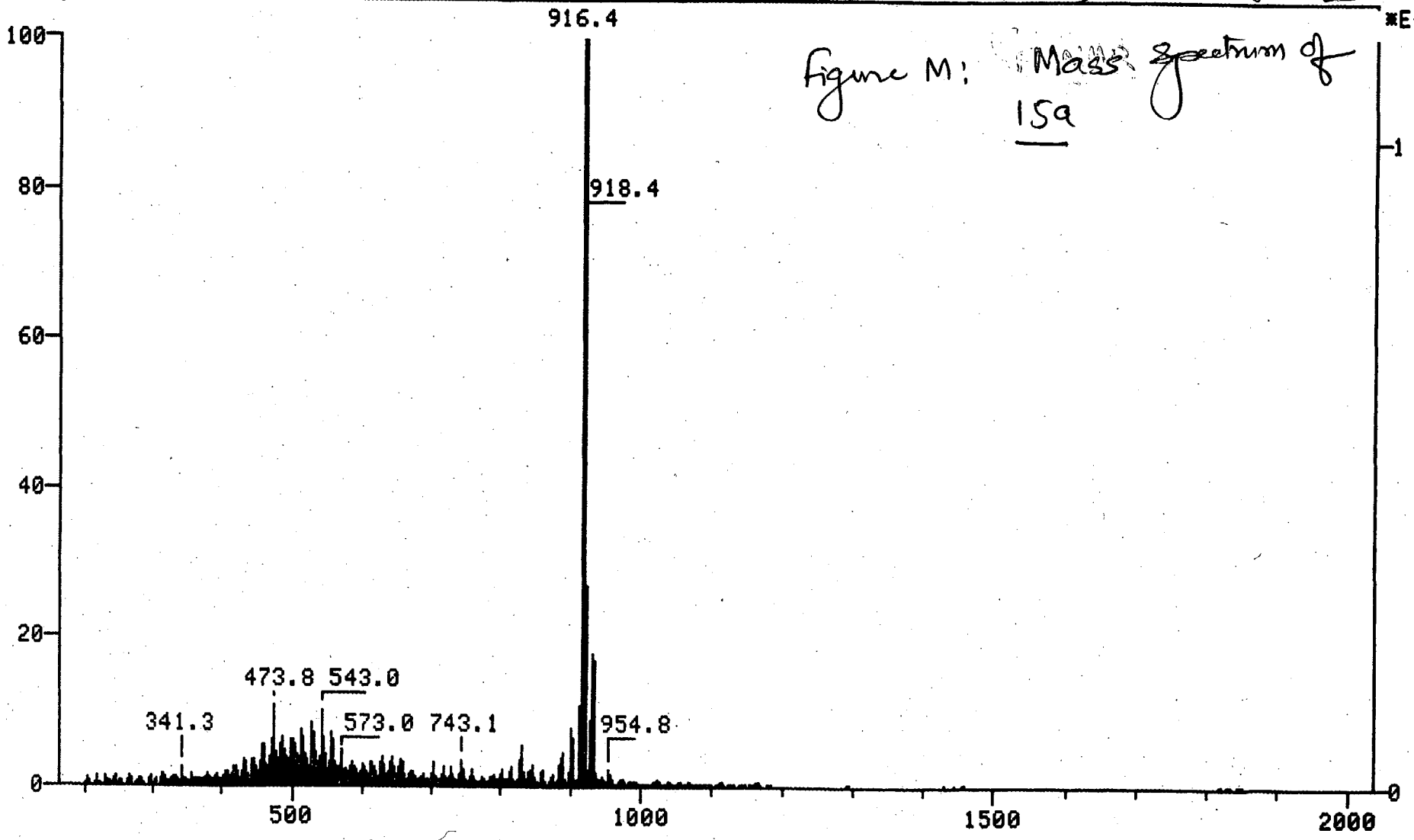
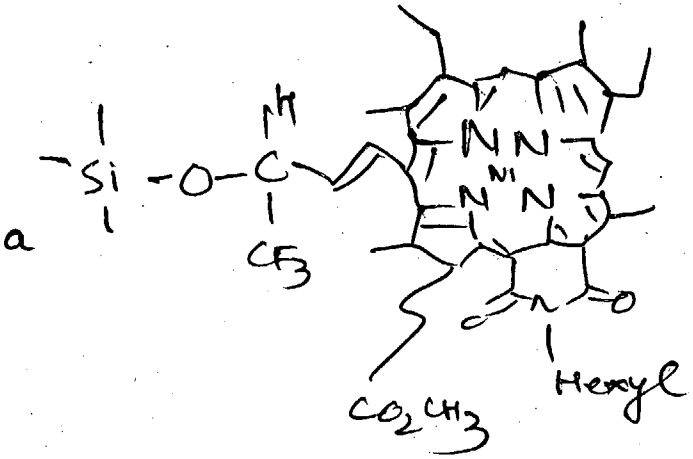
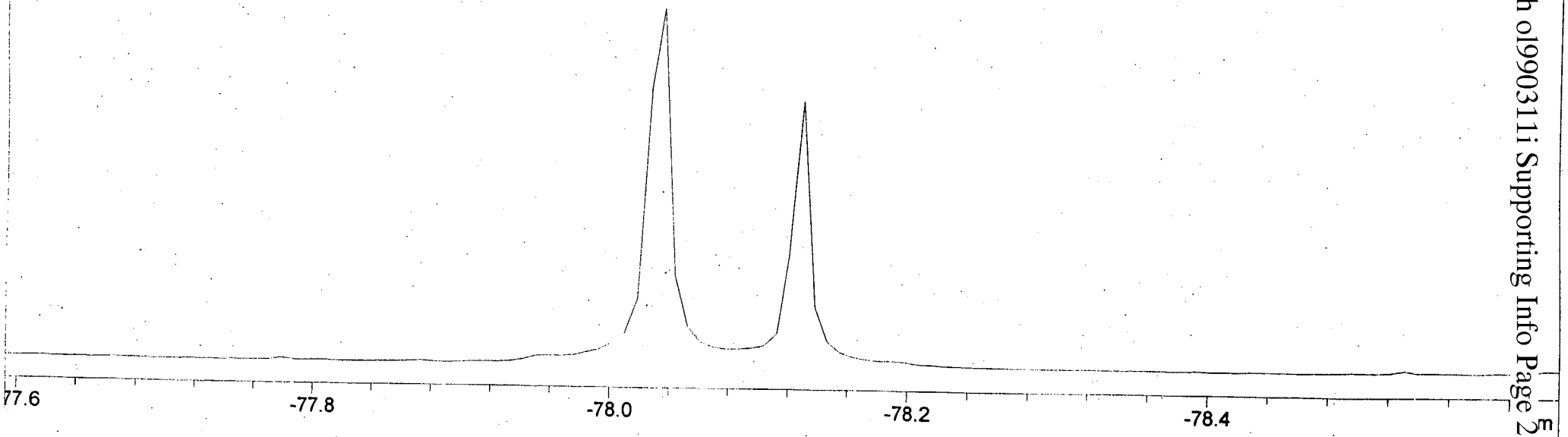


Figure M: Mass spectrum of 15a

Figure N: ^{19}F NMR Spectrum of 15a



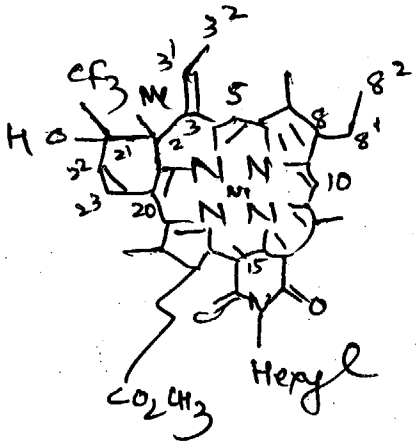


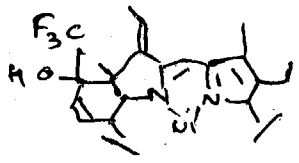
CDCI3, FP-23, F-19 NMR

F1: 376.471		SW1: 26315		OF1: -24724.4		PTS1d: 8192	
EX:		PW: 8.0 usec	PD: 20.0 sec	NA: 40	LB: 2.0		

USER: DATE: 06/03/99

WinNuts - $Ef23.001



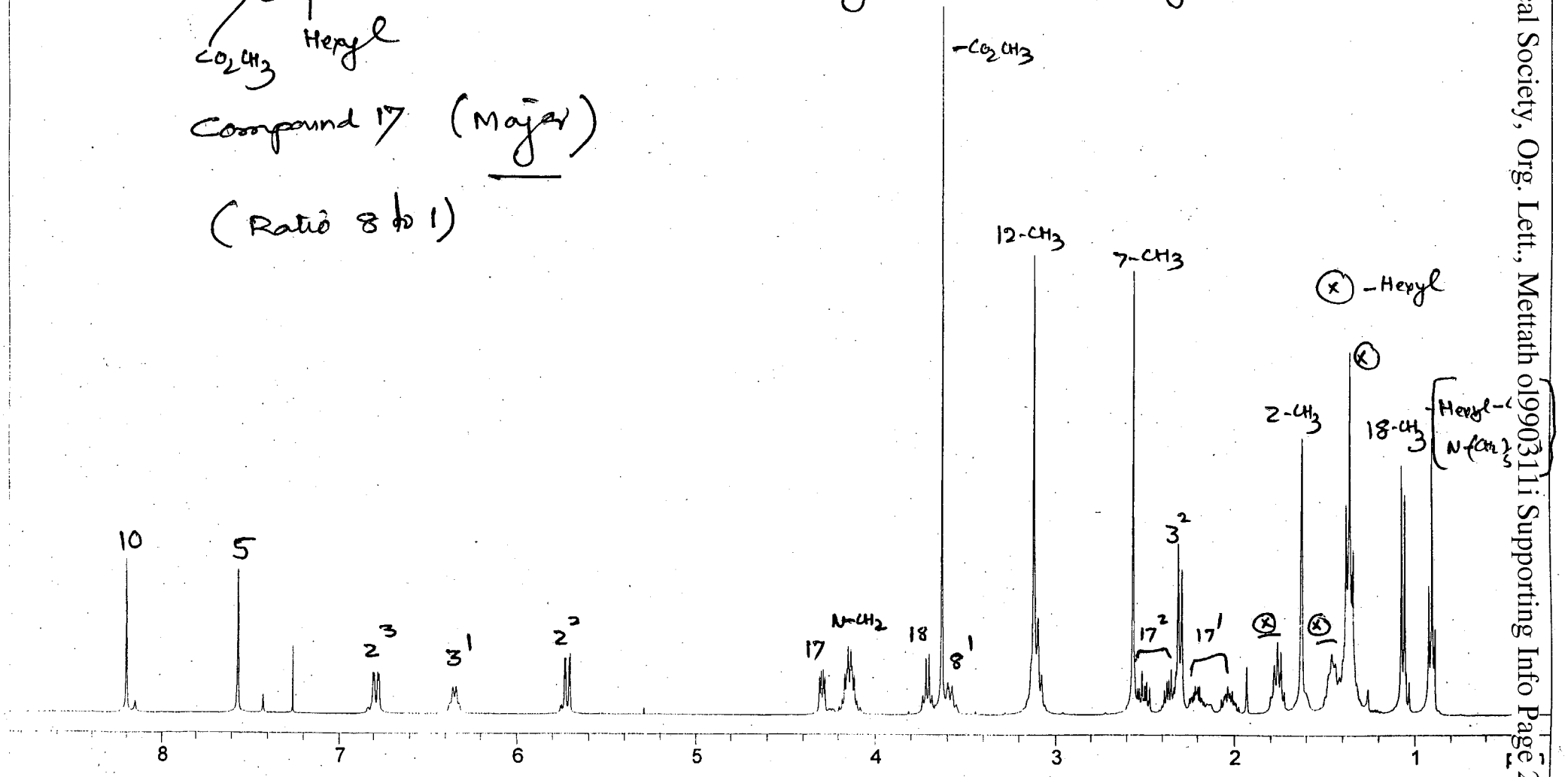


Minor

Compound 17 (Major)

(Ratio 8 to 1)

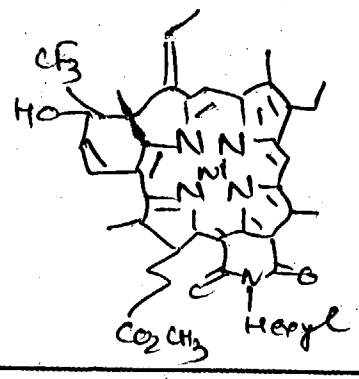
Figure 0: ^{1}H NMR Spectrum of 17



CDCl3, FP-32						USER:	DATE: 16/0..9
F1: 400.138		SW1: 6024		OF1: 2206.0		PTS1d: 8192	
EX:		PW: 7.0 usec	PD: 40.0 sec	NA: 48	LB: 0.1	WinNuts - $Fp32.005	

17

SPEC: FP32 13-MAY-99 DERIVED SPECTRUM 9
Samp: FP-32 (PANDEY) Start : 10:17:30 10
Comm: POS. FAB*m-NITROBENZYL ALCOHOL
Mode: EI +VE +HMR BSCAN (EXP) UP LR
Oper: DUTTA Inlet :
Base: 826.2 Inten : 124787232 Masses: 200 > 2000
Norm: 826.2 RIC : 1653403136 # peaks: 1980
Peak: 1000.00 mmu
Data: SY:FP32.DT + 'FP32' /1>10 - 'BLN51399



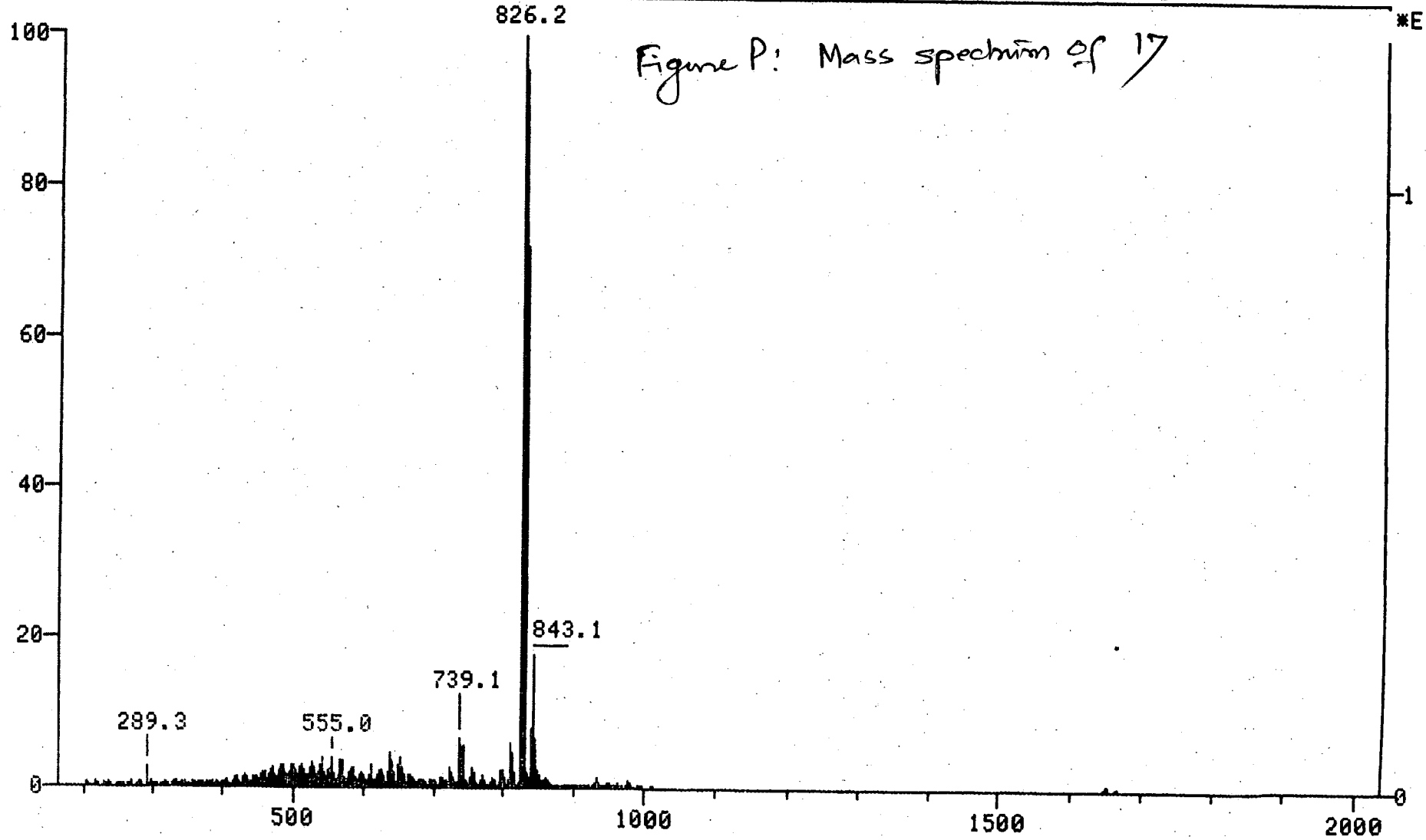
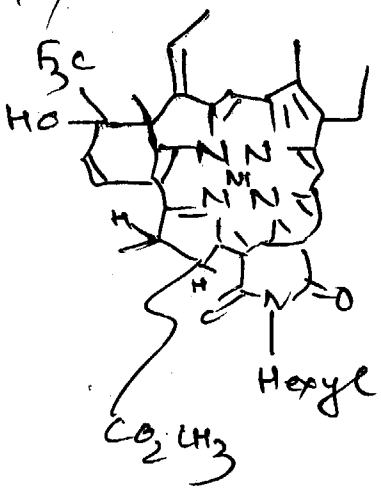
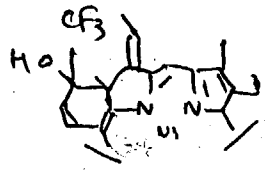


Figure P: Mass spectrum of 17

17



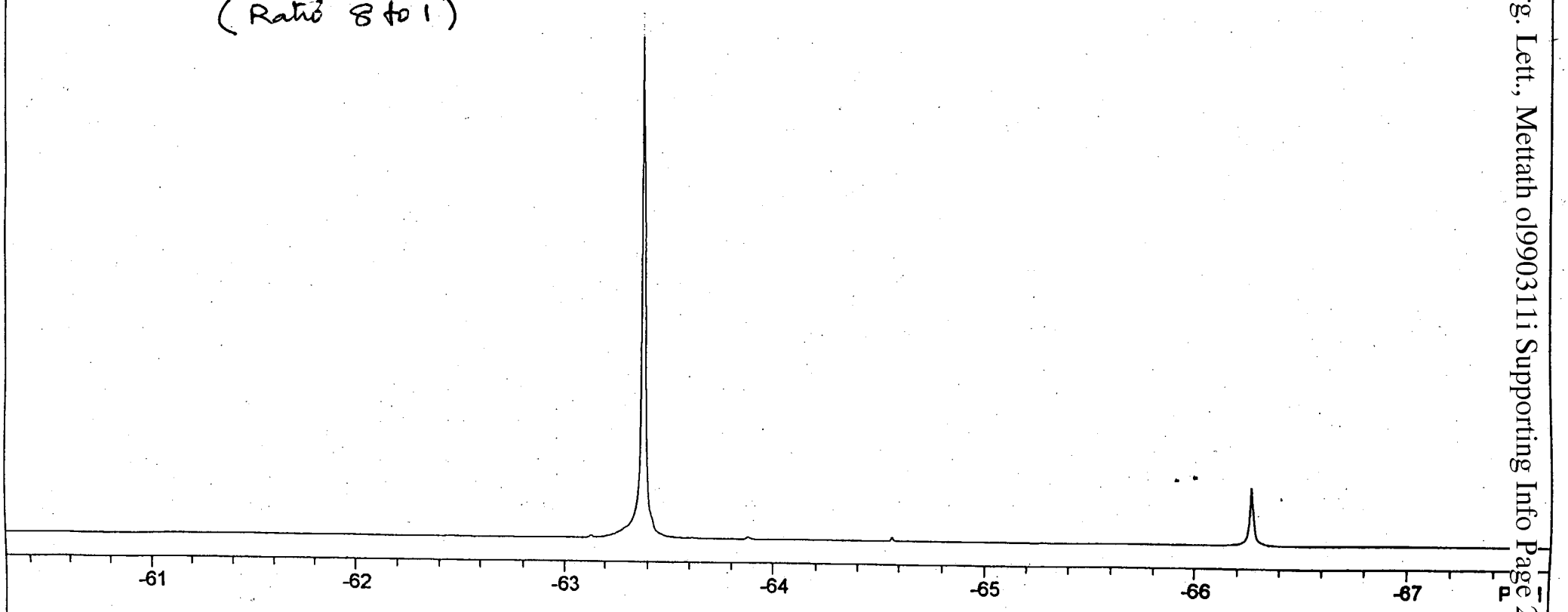
Major



Minor

(Ratio 8 to 1)

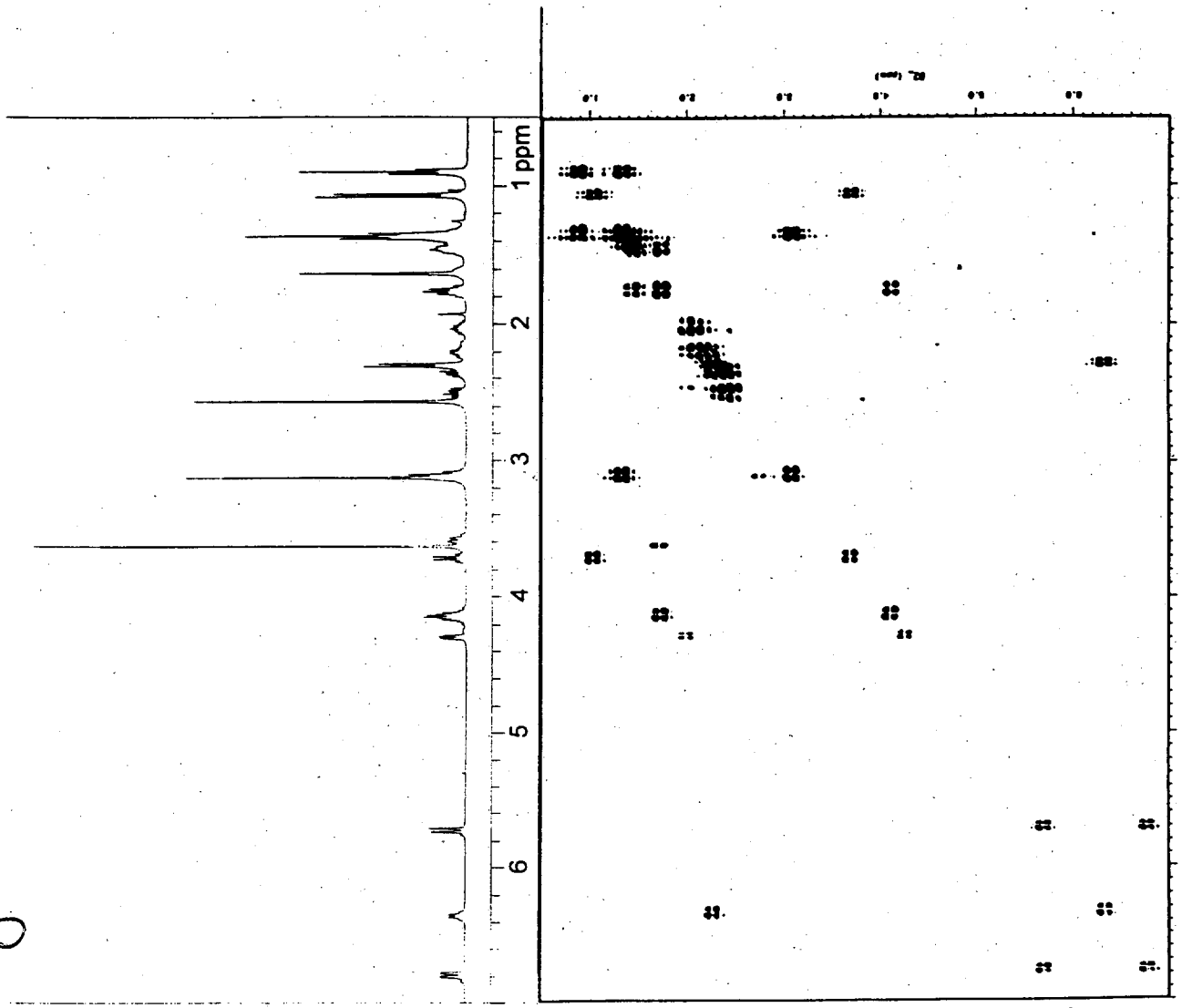
Figure 2: ^{19}F NMR Spectrum of 17 (2 E. isomers).



CDCl3, FFP-32, F-19 NMR

F1: 376.471		SW1: 26315		OF1: -24724.4		PTS1d: 8192	USER: -- DATE: 02/05/
		PW: 8.0 usec	PD: 2.0 sec	NA: 32	LB: 2.0		WinNuts - $Ffp32.001

Fig. R: COSY DATA



ISOBACTERIOCHLORIN 17

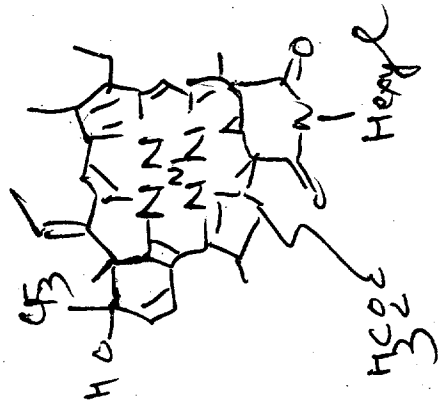
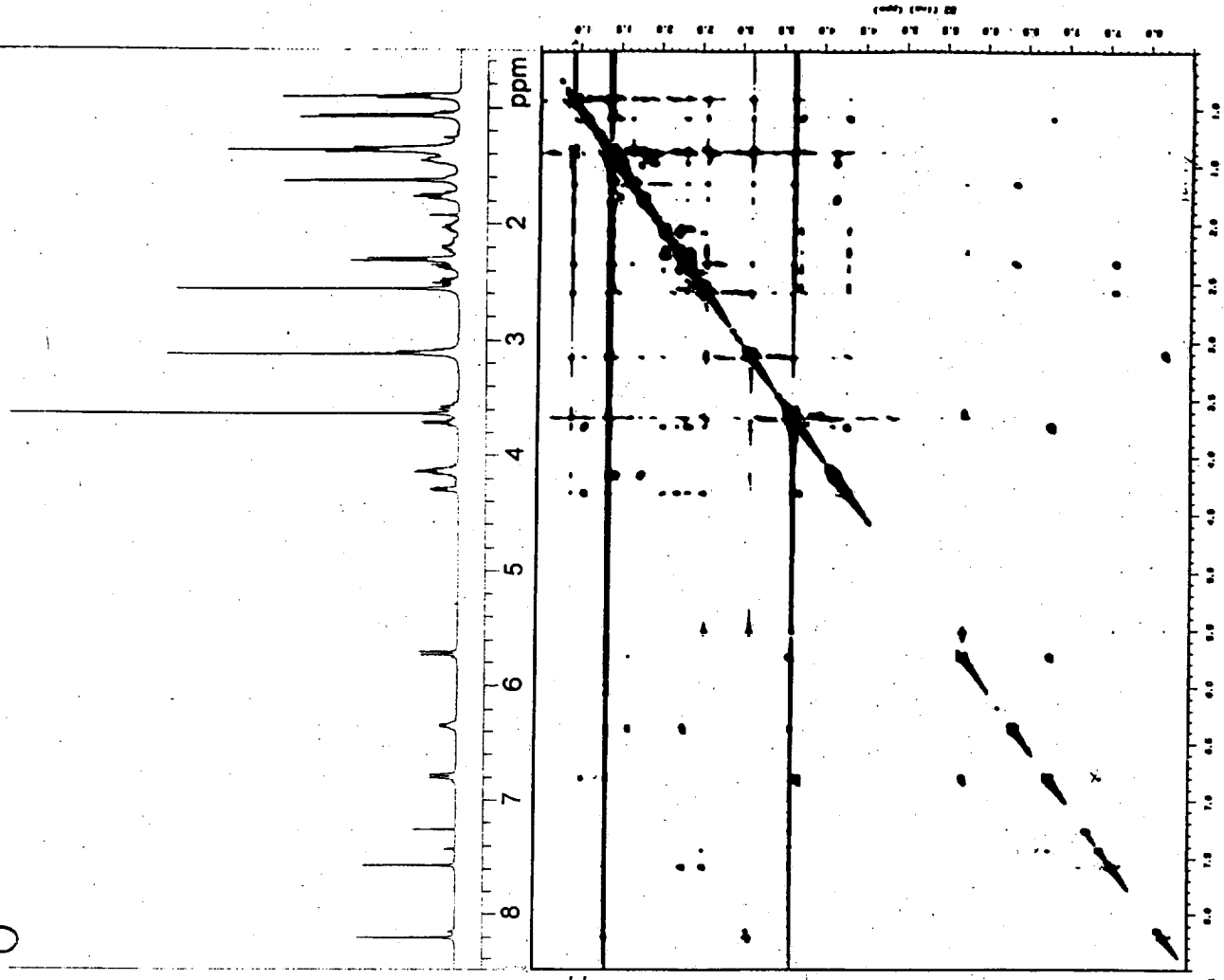
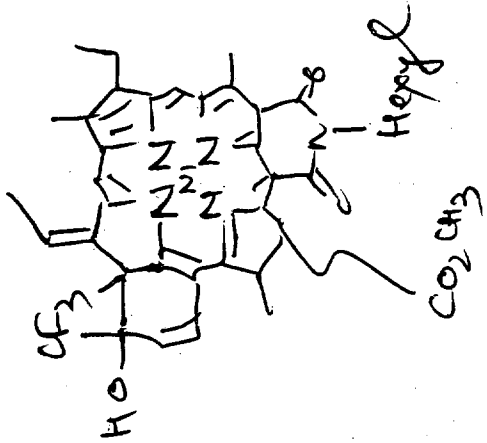


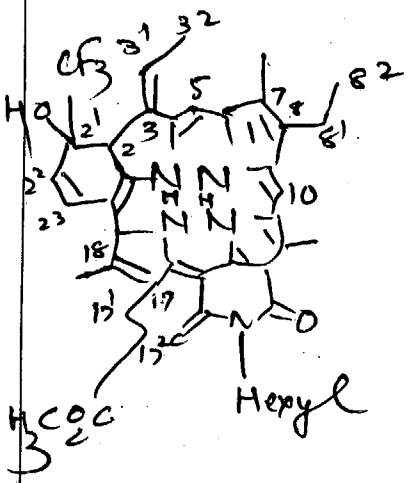
Figure S1 ROESY DATA



ISOBACTERIOCHLORIN 17



18. 600MHz



Chlorin-18

Figure T: ^{1}H NMR Spectrum of Chlorin-18

F1: 600.139		SW1: 8065		OF1: 2267.3		PTS1d: 32768	
EX: iu[		PW: 0.0 usec	PD: 0.0 sec	NA:	LB: 0.1		WinNuts - fp231_600.001

USER: DATE: 00y

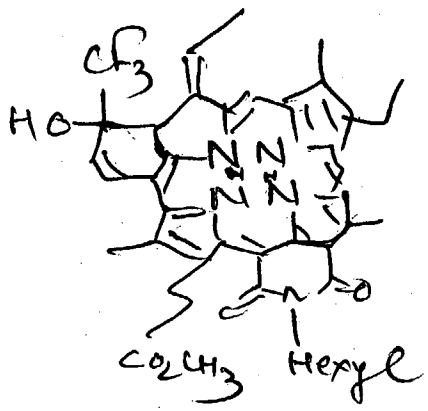
18

SPEC: FP231
Samp: FP-231 (PANDEY)
Comm: POS. FAB*m-NITROBENZYL ALCOHOL
Mode: EI +VE +HMR BSCAN (EXP) UP LR
Oper: DUTTA
Base: 154.9 Inten : 36946288
Norm: 154.9 RIC : 441892160
Peak: 1000.00 mmu
Data: SY:FP231.DT

20-AUG-98 DERIVED SPECTRUM 9
Start : 11:02:48 10

Inlet :
Masses: 100 > 2000
peaks: 1394

+ 'FP231' /1>10 - 'BLN8209



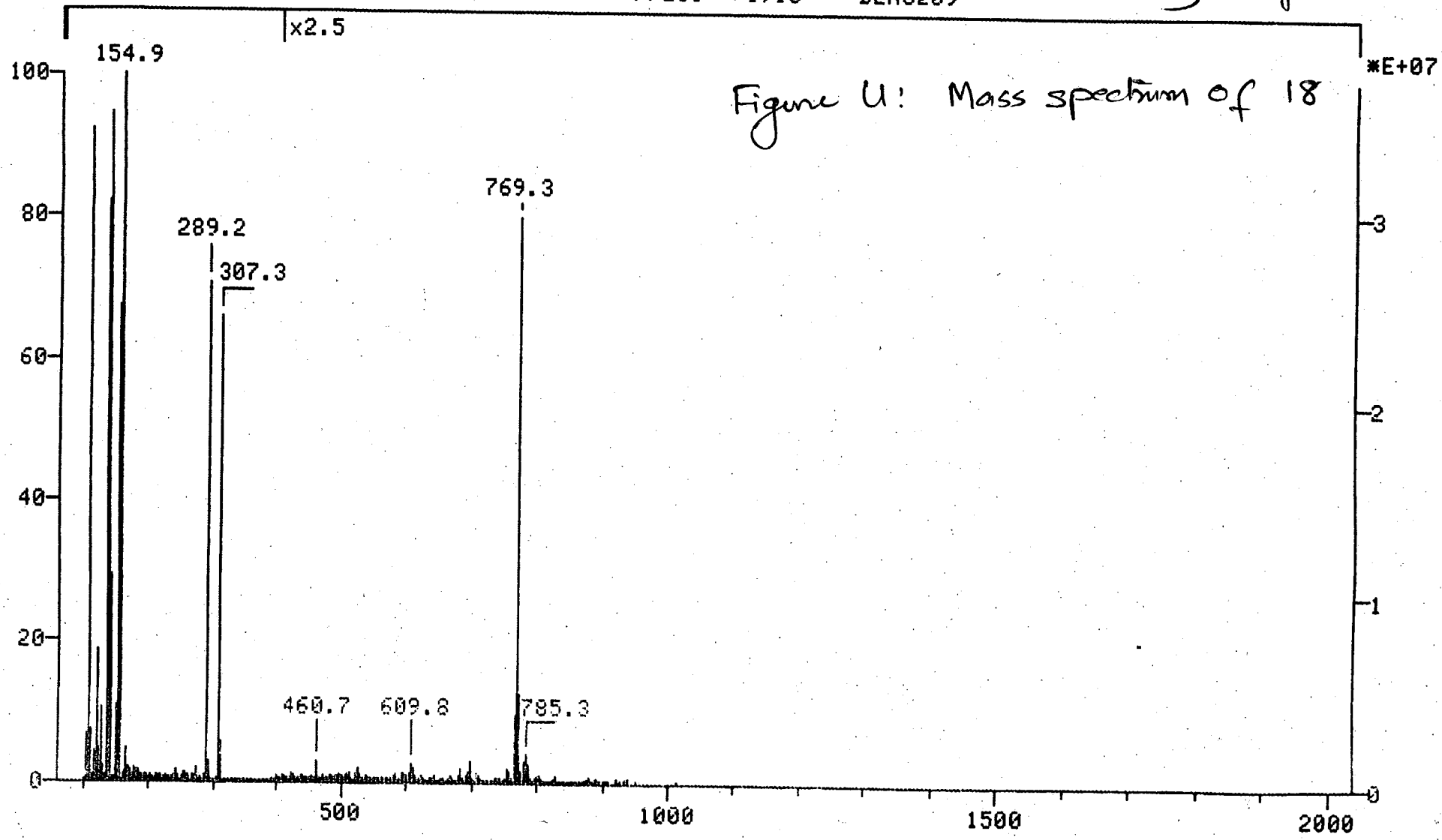
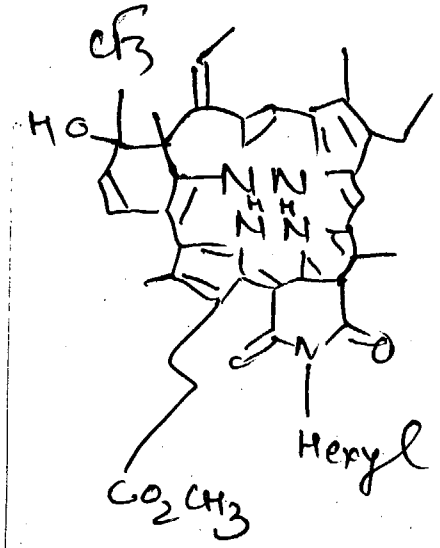
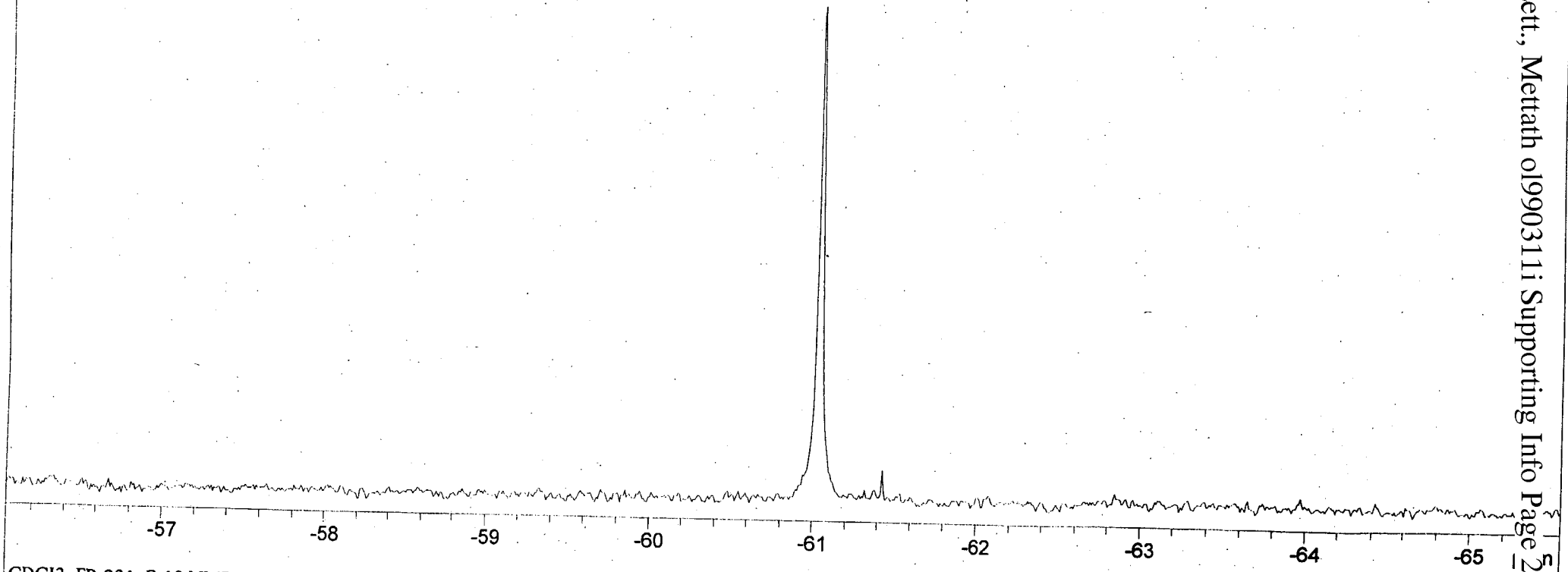


Figure 4: Mass spectrum of 18



Chlorin 18

Figure V: ^{19}F NMR Spectrum of Chlorin 18



CDCl3, FP-231, F-19 NMR

F1: 376.471		SW1: 26315		OF1: -24724.4			USER: DATE: 10/03/99
EX:		PW: 8.0 usec	PD: 20.0 sec	NA: 40	LB: 2.0	PTS1d: 8192	
							WinNuts - $Ffp231.001

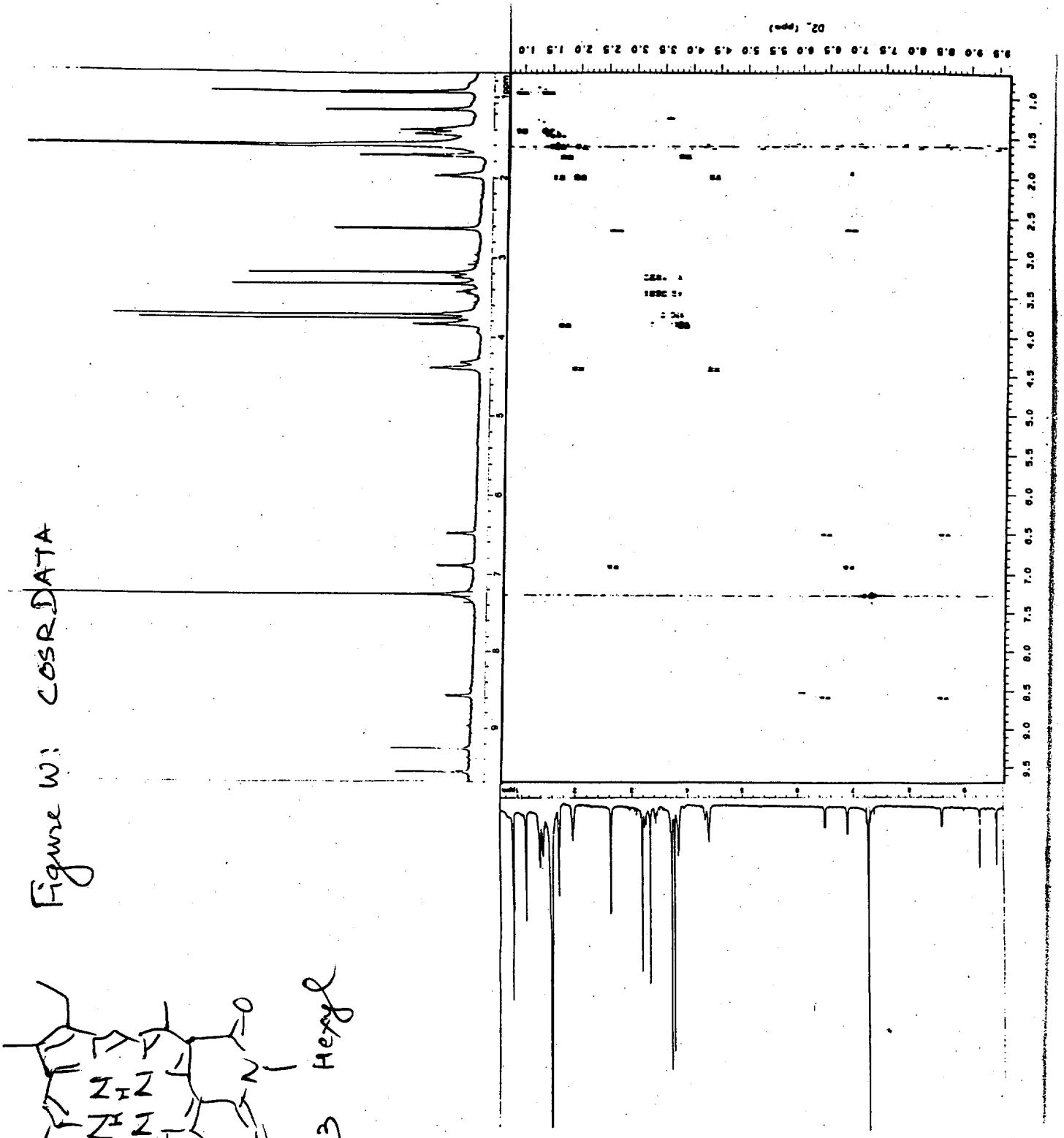


Figure W: COSY DATA

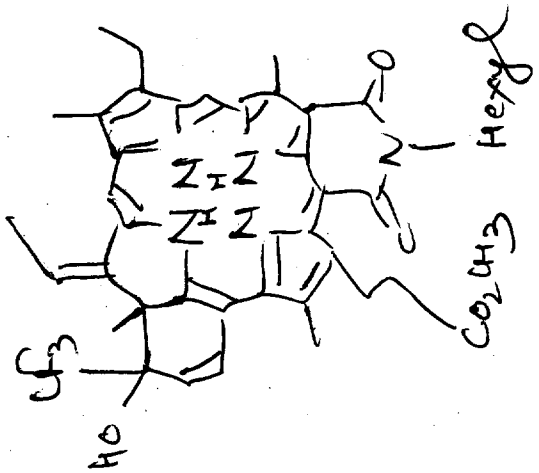
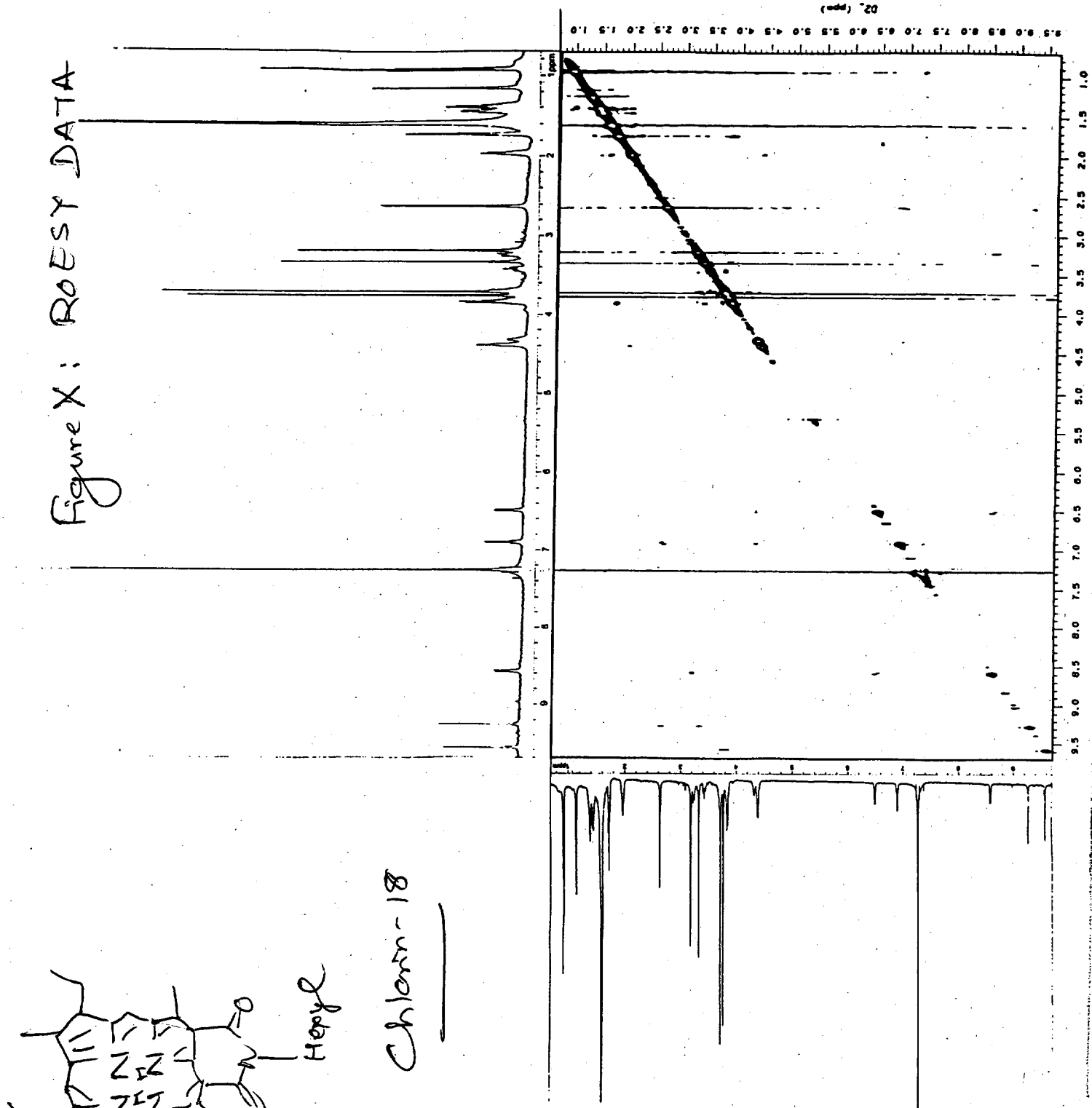
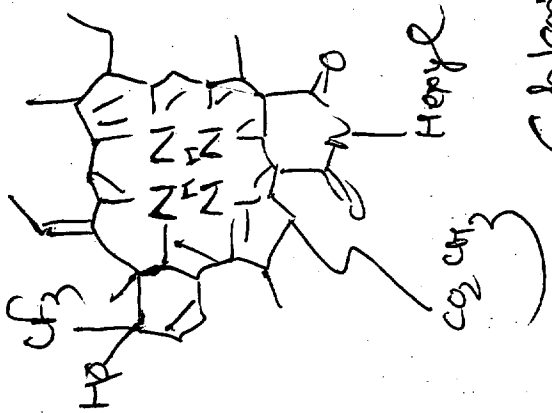


Figure X: ROESY DATA





Chlorin-18