

7-29-99

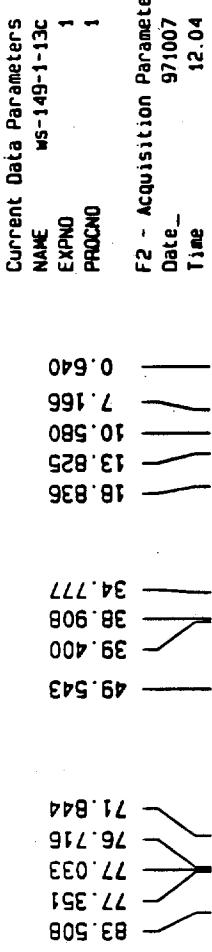
Supporting Information for:**Synthesis of Four Diastereomeric 3,5-Dialkoxy-2,4-dimethylalkanals by a Simple Extension of the Non-aldol Aldol Process to Bis(propionates)****Michael E. Jung,* Woo Song Lee, and Daqing Sun****General Procedure For Epoxide Rearrangement****Rearrangement of Epoxides From *E*-allylic Alcohols**

The epoxide silyl ether **9** or **11** (0.17 mmol, 1 eq) was dissolved in 3 ml of dichloro-methane and treated with diisopropylethylamine (DIPEA, 6 eq). The solution was cooled to -78°C and treated with trimethylsilyl triflate (TMSOTf, 6 eq). After the solution stirred for 3.5 h, the reaction mixture was quenched with water and extracted with ether. The organic layers were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and the resulting oil was chromatographed (50% ether/ 50% hexane) to give the aldehyde **10** or **12** in 82% or 70% yield respectively.

Rearrangement of Epoxides From *Z*-allylic Alcohols

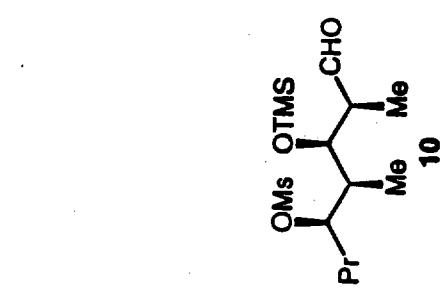
A solution of the epoxy alcohol **13** (0.1 mmol, 1 eq) in 5 ml of dichloromethane was treated successively with DIPEA (2 eq) and triethylsilyl chloride (TESCl, 1.5 eq) at 25 °C. After the solution stirred for 3 h, the mixture was poured onto 50 ml of ether and shaken with 25 ml of 0.2 M pH 7 phosphate buffer. The layers were separated, extracted with ether, washed with 0.2 M pH 7 phosphate buffer, brine, dried over MgSO₄, and concentrated to give the silyl epoxide. The silyl epoxide was then dissolved in 4 ml of dichloromethane and treated with DIPEA (6 eq). The solution was cooled to -42 °C and treated with TMSOTf (6 eq). After the solution stirred for 3 h, the solution was poured onto 50 ml of ether and shaken with 25 ml of 0.2 M pH 7 phosphate buffer. The layers were separated, extracted with ether, washed with 0.2 M pH 7 phosphate buffer, brine, dried (MgSO₄), and concentrated to give a mixture of the aldehyde **14** and the allylic silyl ether **15** in a 4:1 ratio.

Default parameters for C-13 with proton decoupling



204.685

ppm

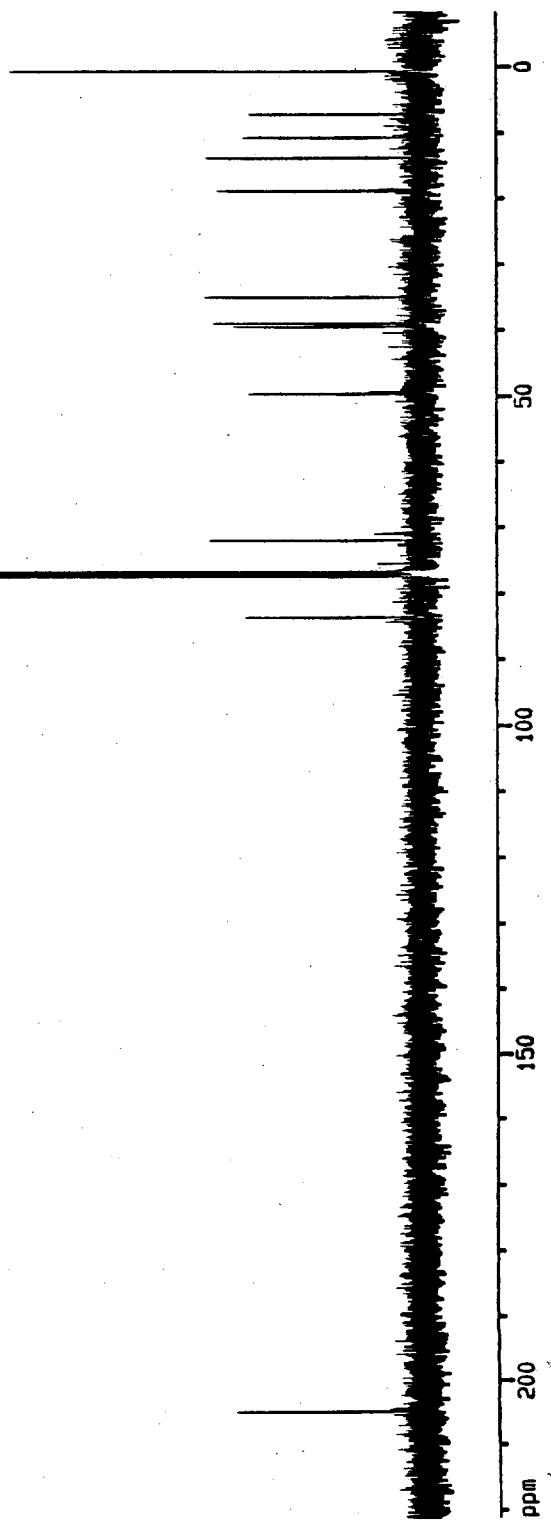


F2 - Processing parameters

SI	65536
SF	100.6127710 MHz
NDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	221.171 ppm
F1	22252.59 Hz
F2P	-8.252 ppm
F2	-834.24 Hz
PPMCM	11.47311 ppm/cm
HZCM	1154.34143 Hz/cm

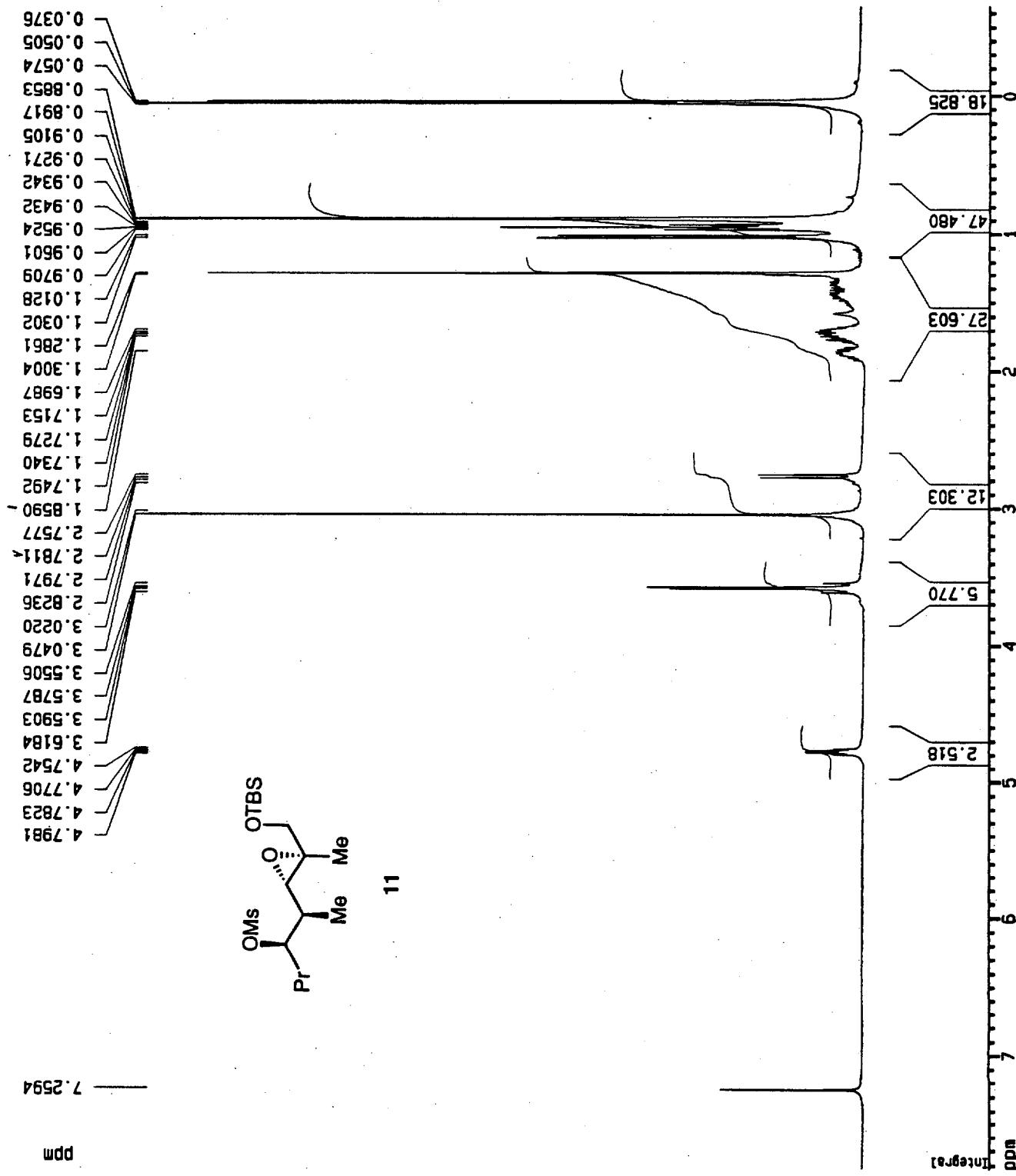


proton default parameters

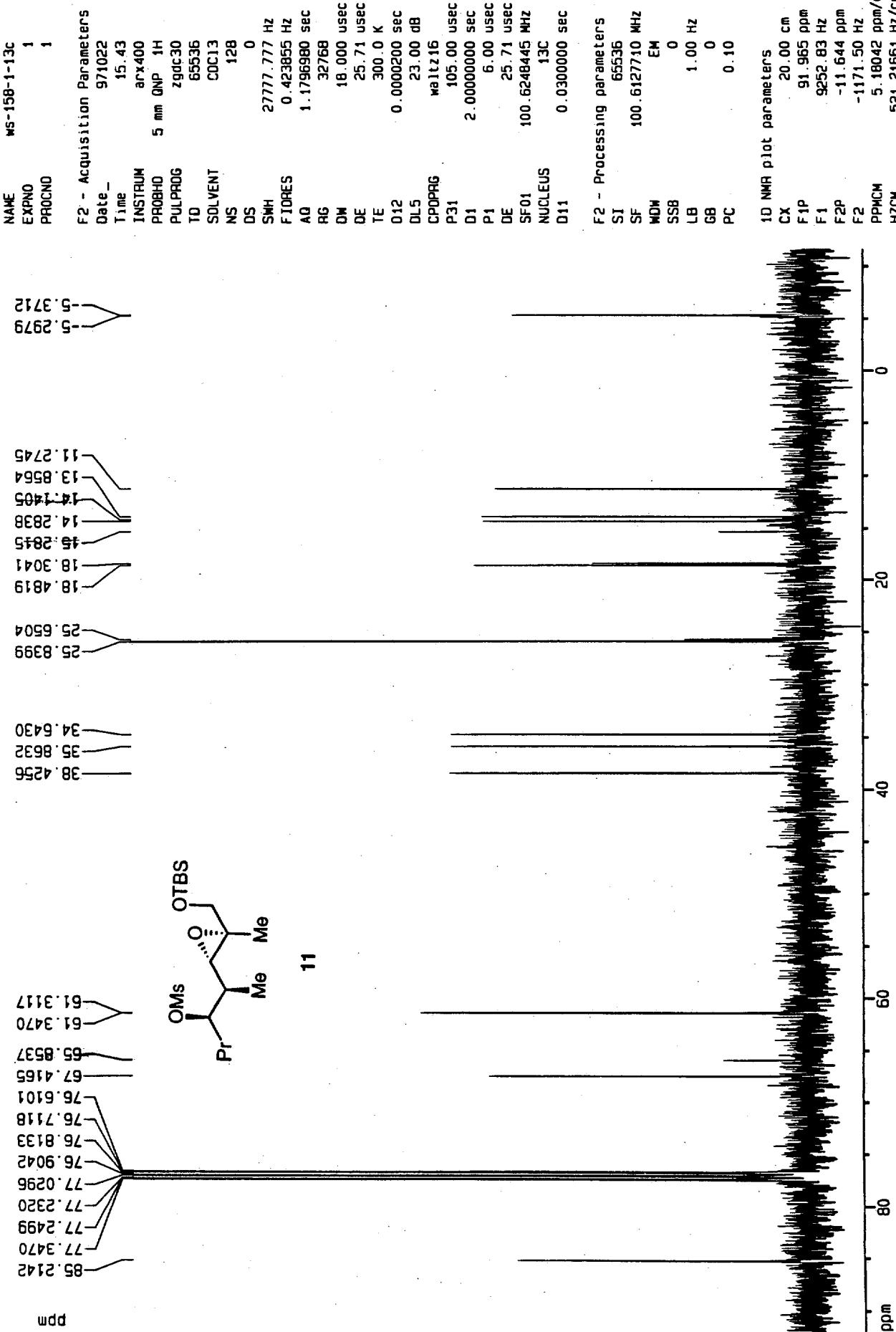
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 PROCNO 1

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 SOLVENT CDCl₃
 NS 16
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 SWH 8064.516 Hz
 FIDRES 0.123055 Hz
 AQ 4.0632820 sec
 RG 715
 DM 62.000 usec
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 TE 300.0 K
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 NUCLEUS 1H

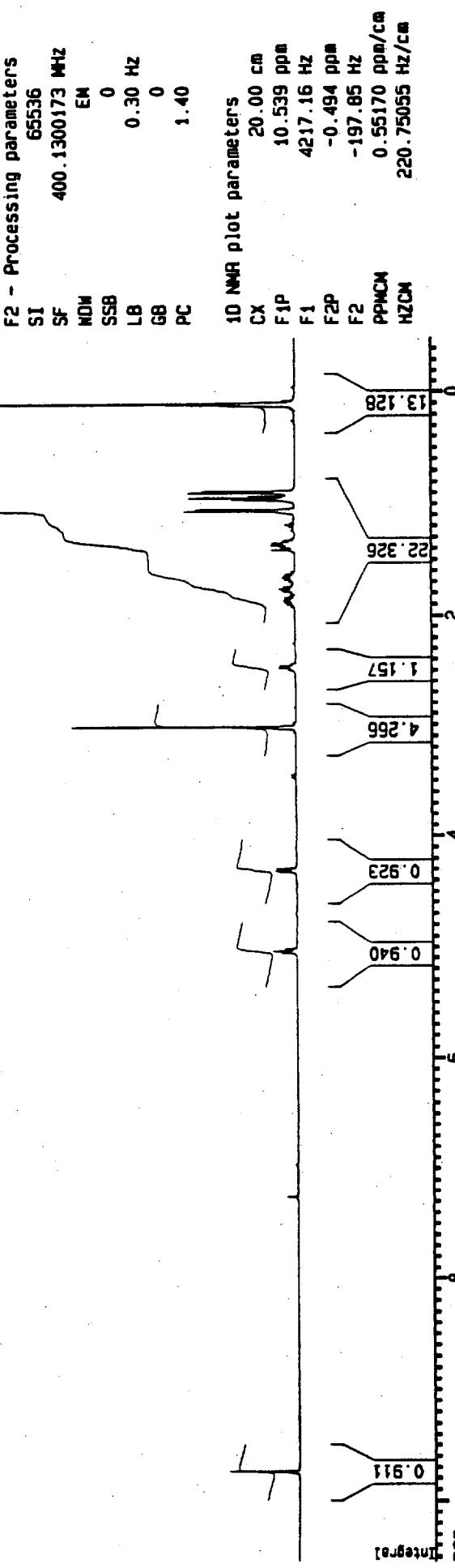
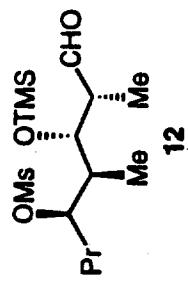
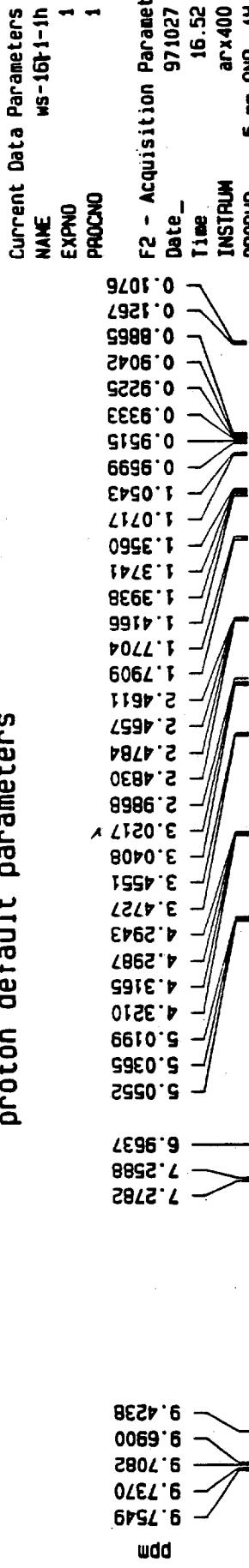
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 HZCM 169.56845 Hz/cm



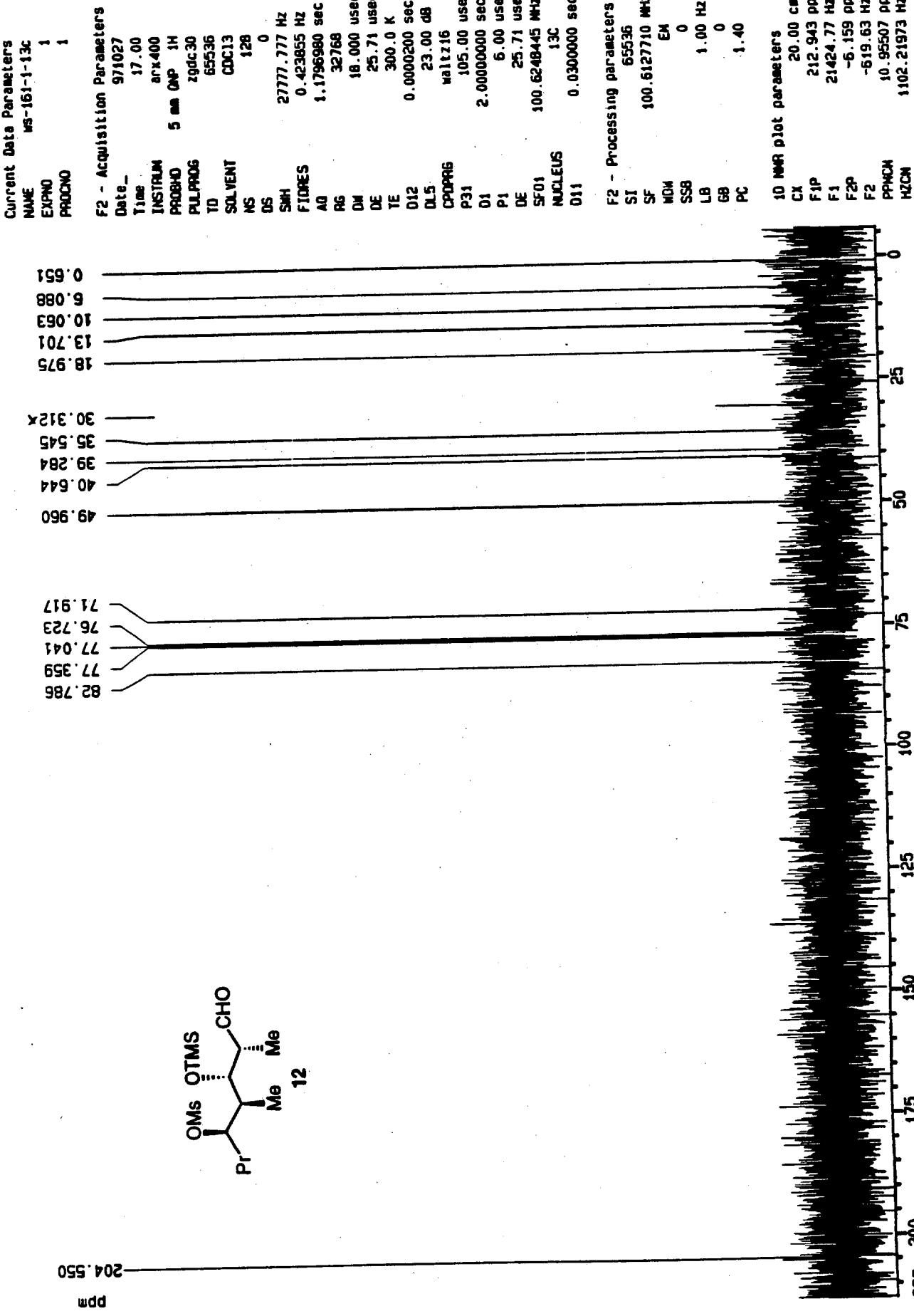
Default parameters for C-13 with proton decoupling



proton default parameters



Default parameters for C-13 with proton decoupling



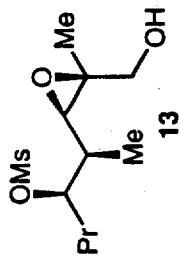
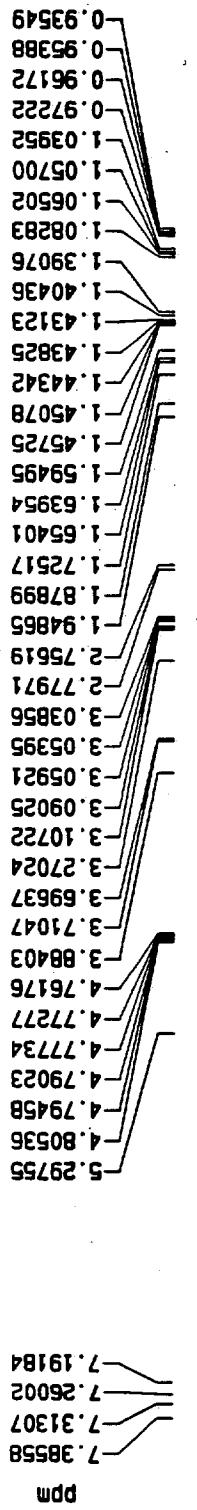
proton default parameters

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SOLVENT	DCCl ₃
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DS	0
SWH	8064.516 Hz
FINRES	0.123055 Hz
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R6	1024
DM	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.0000000 sec
P1	8.25 usec
SFO1	400.1324008 MHz
NUCLEUS	1H



ppm

F2 - Processing parameters

SI	65536
SF	400.1300173 MHz
NDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	7.880 ppm
F1	3153.09 Hz
F2P	-0.293 ppm
F2	-117.37 Hz
PPCM	0.40868 ppm/cm
HZCM	163.52330 Hz/cm

Integral

Default parameters for C-13 with proton decoupling



Current Data Parameters
NAME dq-0127c1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

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PULPROG	290c30
TD	65536
SOLVENT	CDC13
NS	600
DS	0
SWH	27777.777 Hz
ETRIMES	0.423855 Hz
AD	1.1795980 sec
RG	32768
DW	16.000 usec
DE	25.71 usec
TE	300.0 K
D12	0.0000200 sec
DQ5	-23.50 dB
CPDPG6	Wait216
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SFO1	100.624845 MHz
NUCLEUS	¹³ C
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F2 - Processing parameters

CX	65536
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NDM	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40
PPNORM	5.87928 ppm/cm
HZCM	591.53064 Hz/cm

1D NMR plot parameters

CX	20.00 cm
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F1	11550.33 Hz
F2P	-2.766 ppm
F2	-280.28 Hz

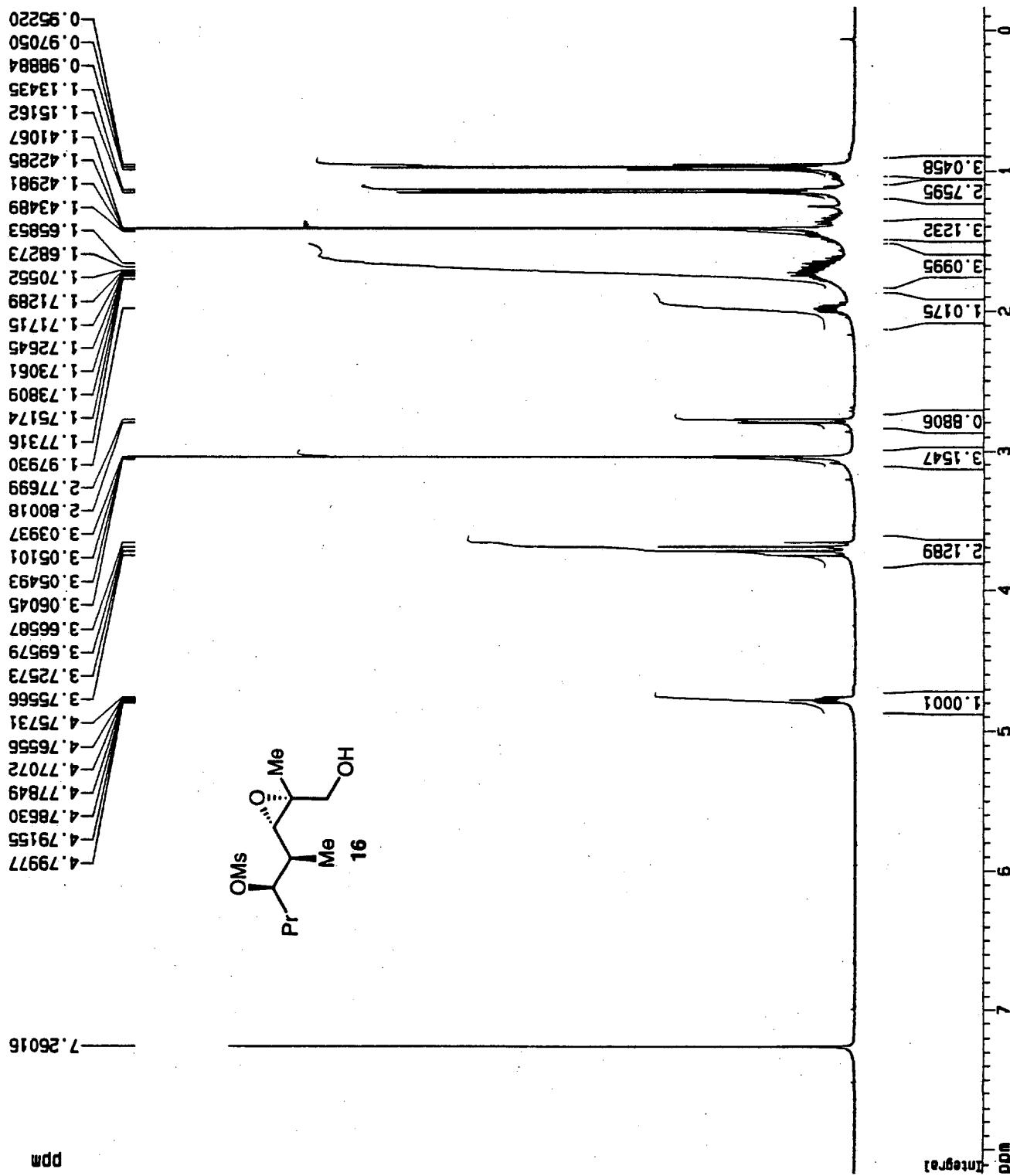
proton default parameters

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PROCNO 1

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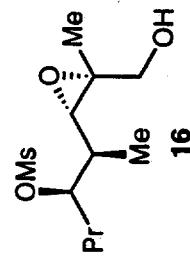
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FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 2048
DM 62.000 usec
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NUCLEUS 1H



Default parameters for C-13 with proton decoupling



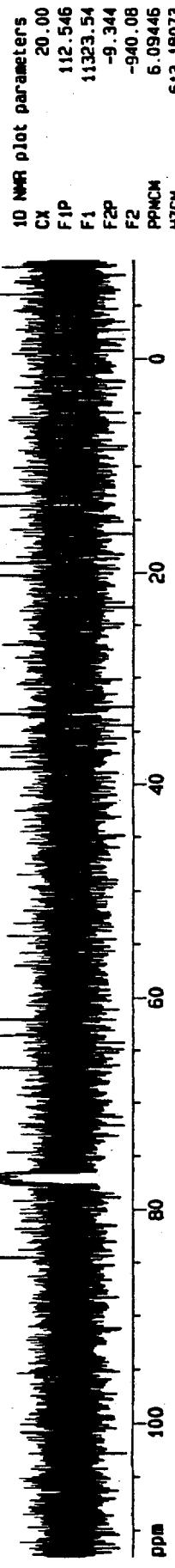
ppm



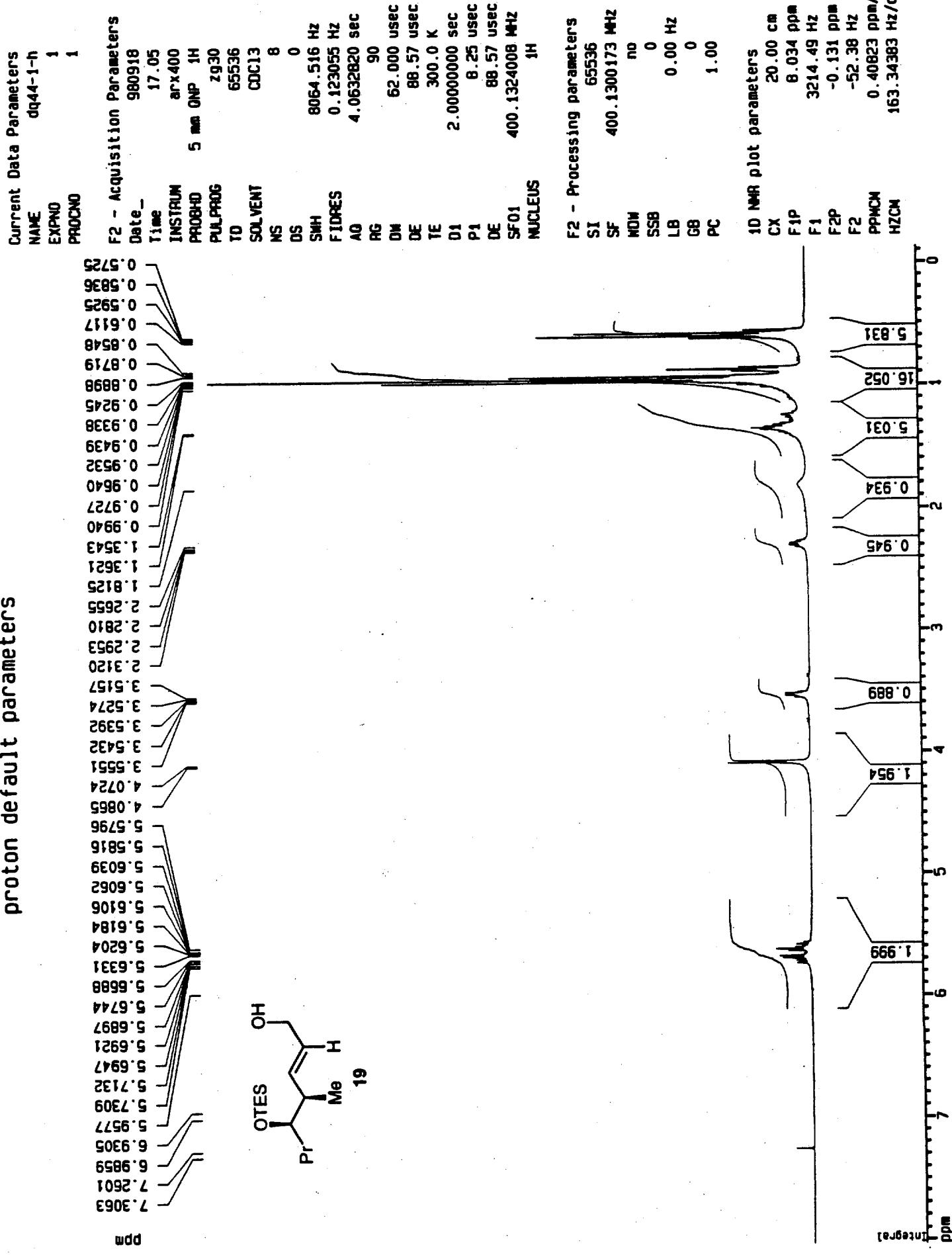
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SOLVENT CDC13
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FIDRES 0.4236855 Hz
AQ 1.1796980 sec
RG 32768
DM 18.000 usec
DE 25.71 usec
TE 300.0 K
D12 0.0000200 sec
Q1 23.50 dB
CPDPFG
P31 100.00 usec
D1 2.0000000 sec
P1 6.25 usec
SF01 100.6208445 MHz
NUCLEUS ¹³C
D11 0.0300000 sec

F2 - Processing parameters
SI 65536
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SSB 0
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GB 0
PC 1.40



proton default parameters



D044-2-13C

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129.621

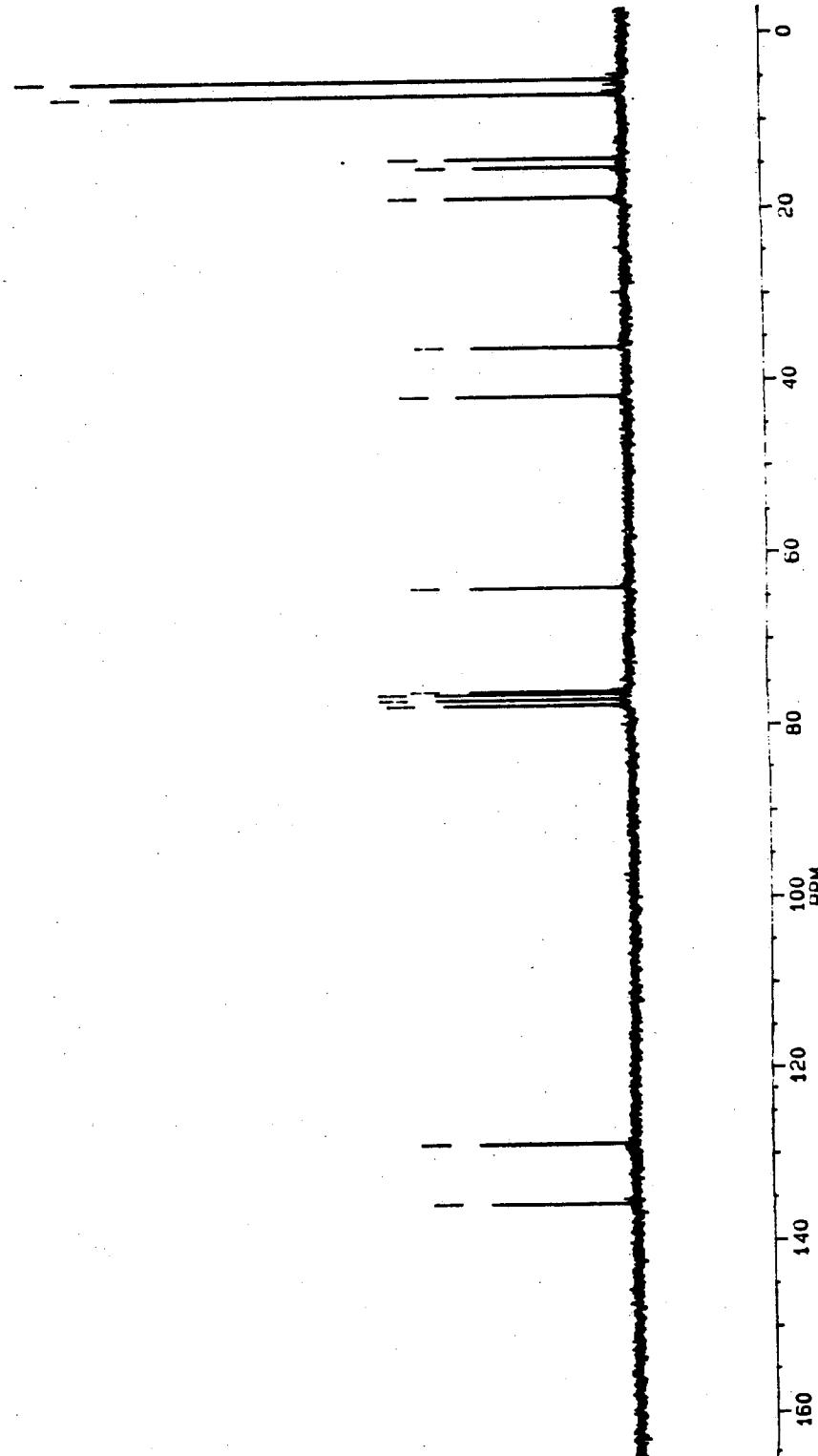
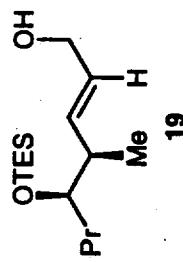
63.869

44.738

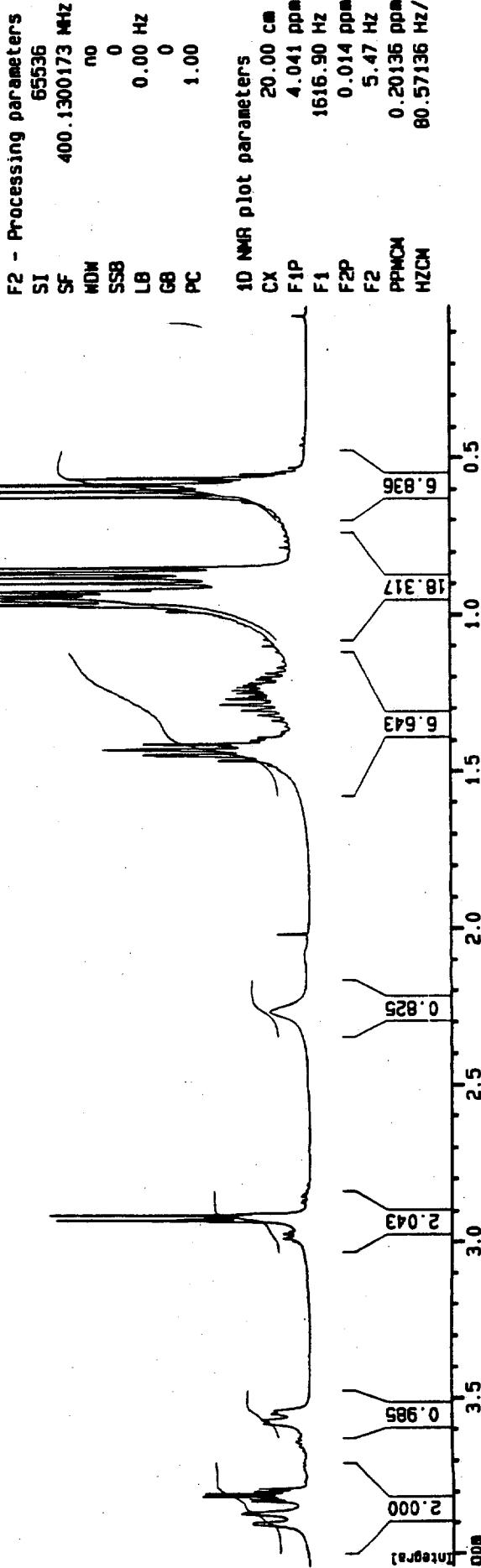
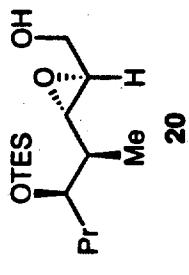
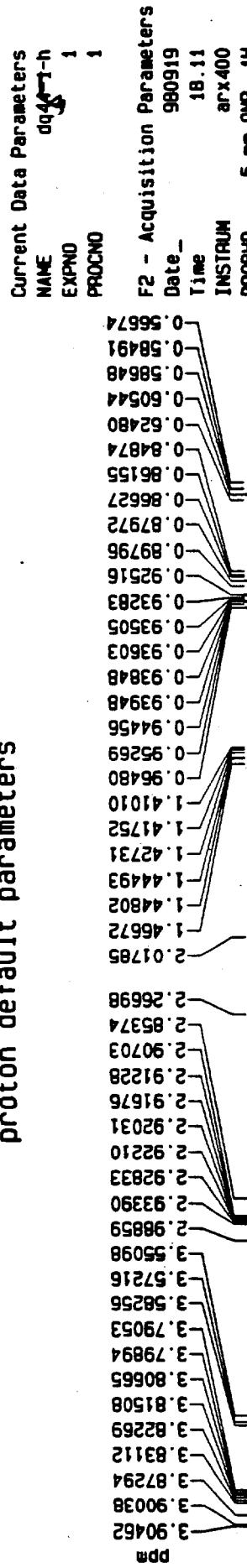
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15.368
14.252
6.930
5.384~~BEST~~

S1820F.143

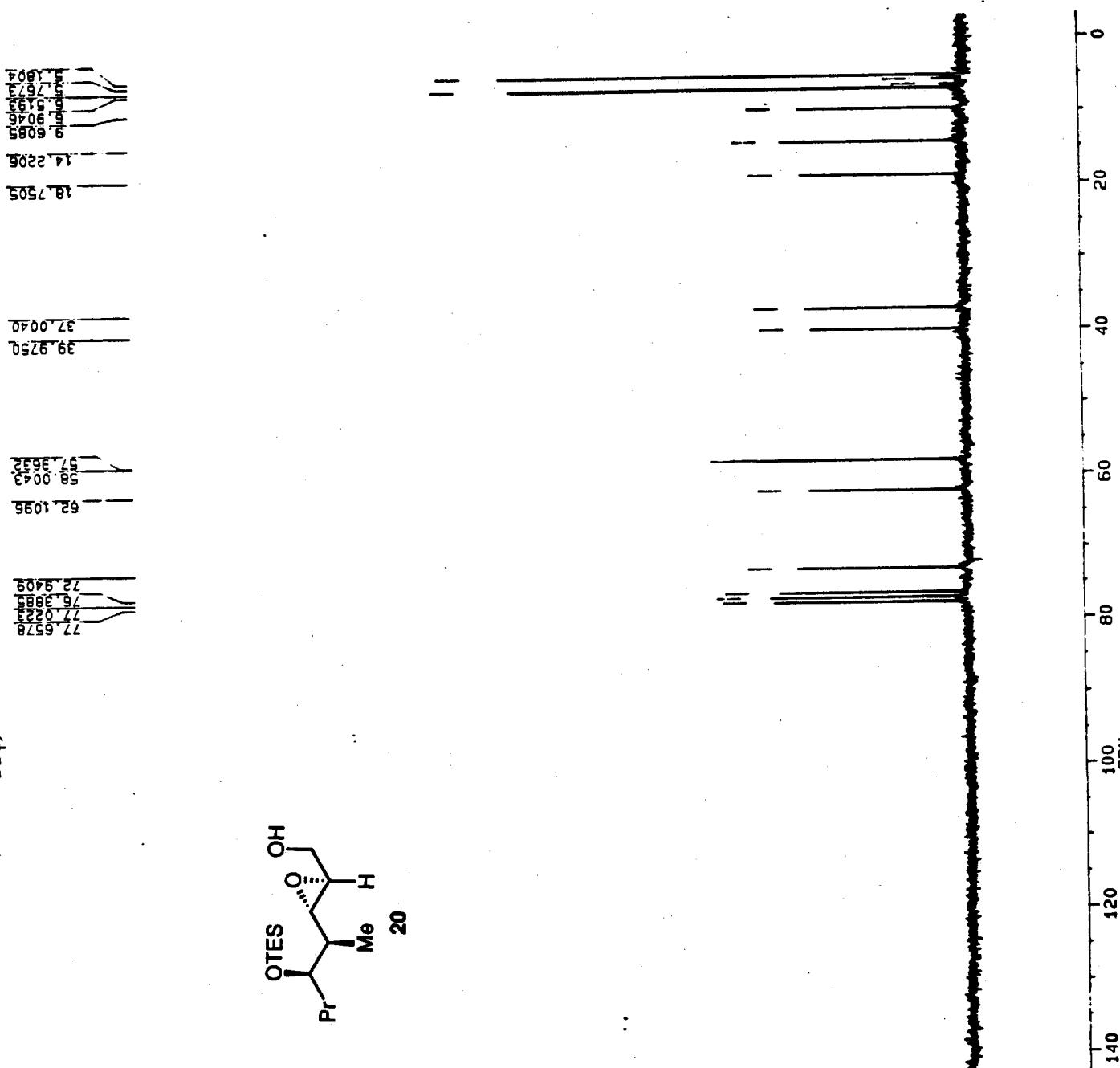
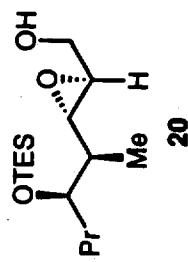
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DM 40
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DP 17H BBLB 1.000
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CY 10.00
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PPM/CH 6.375IS 1
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proton default parameters



DQ45-2-C13



S1820F.148
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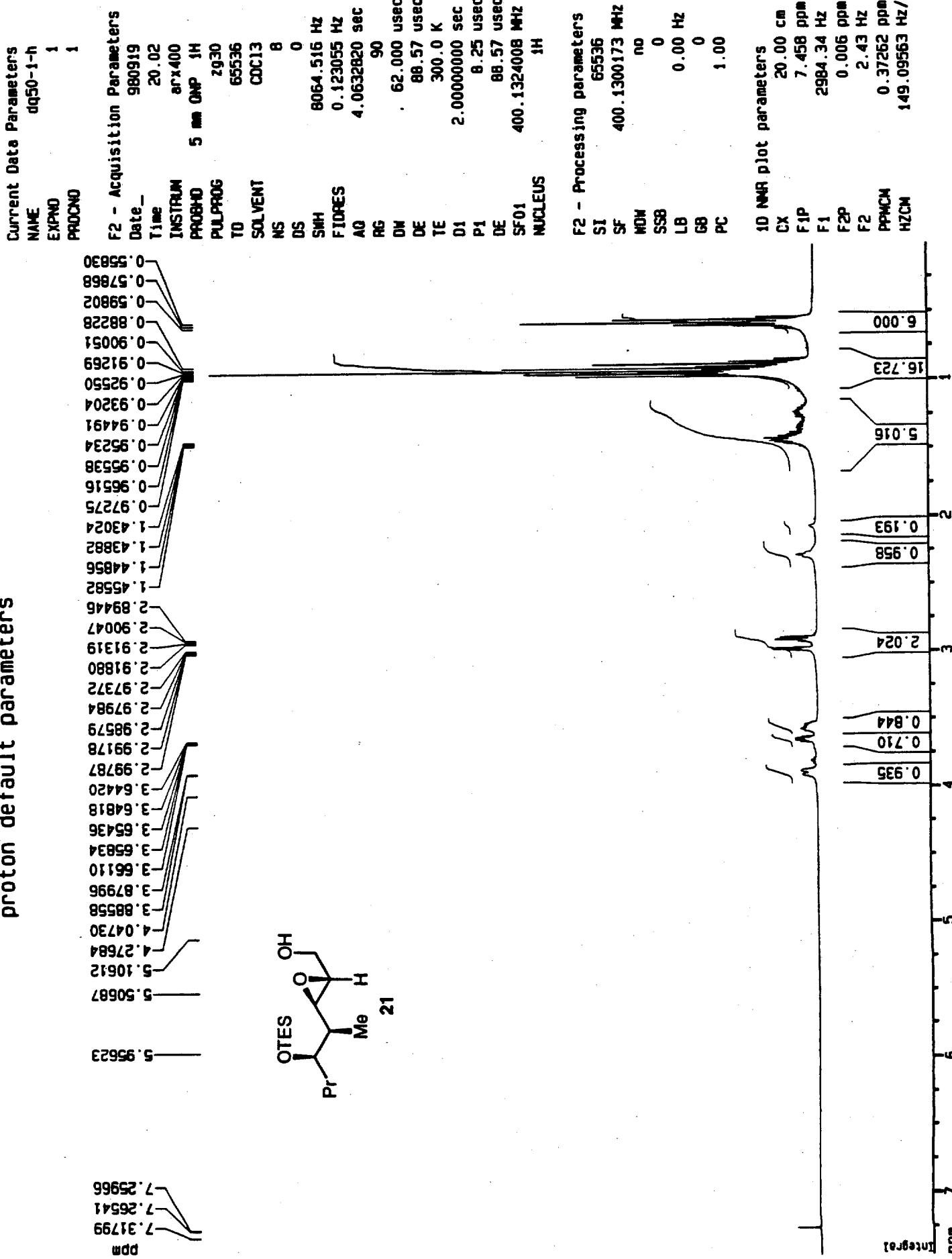
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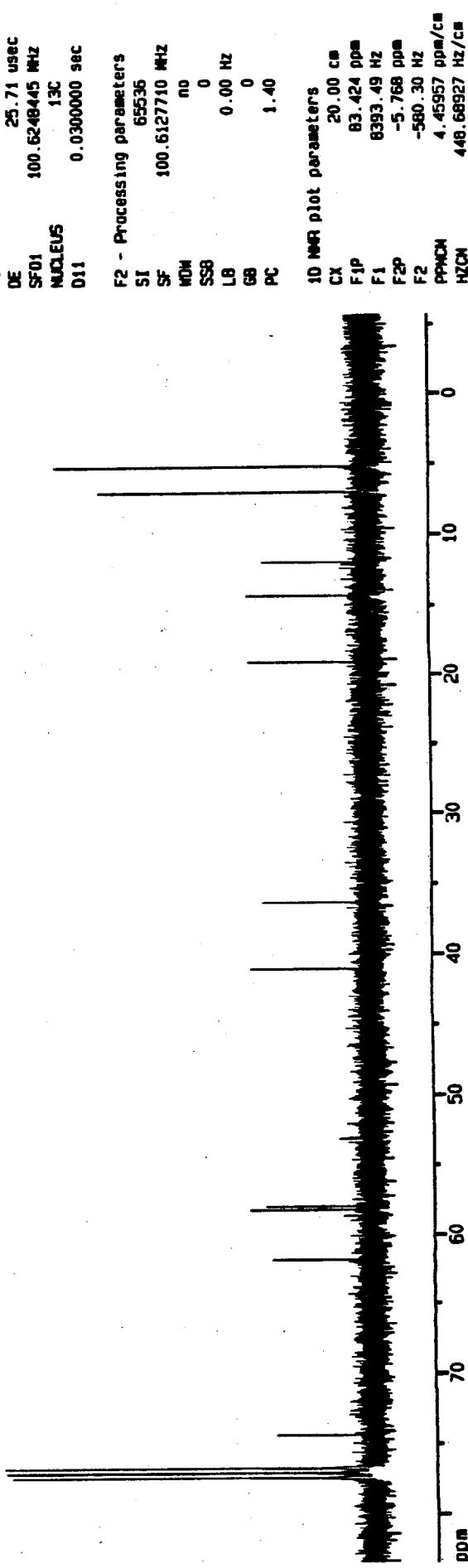
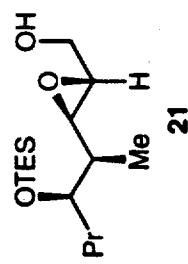
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14.2205
9.6055
5.1673
3.5193
1.804

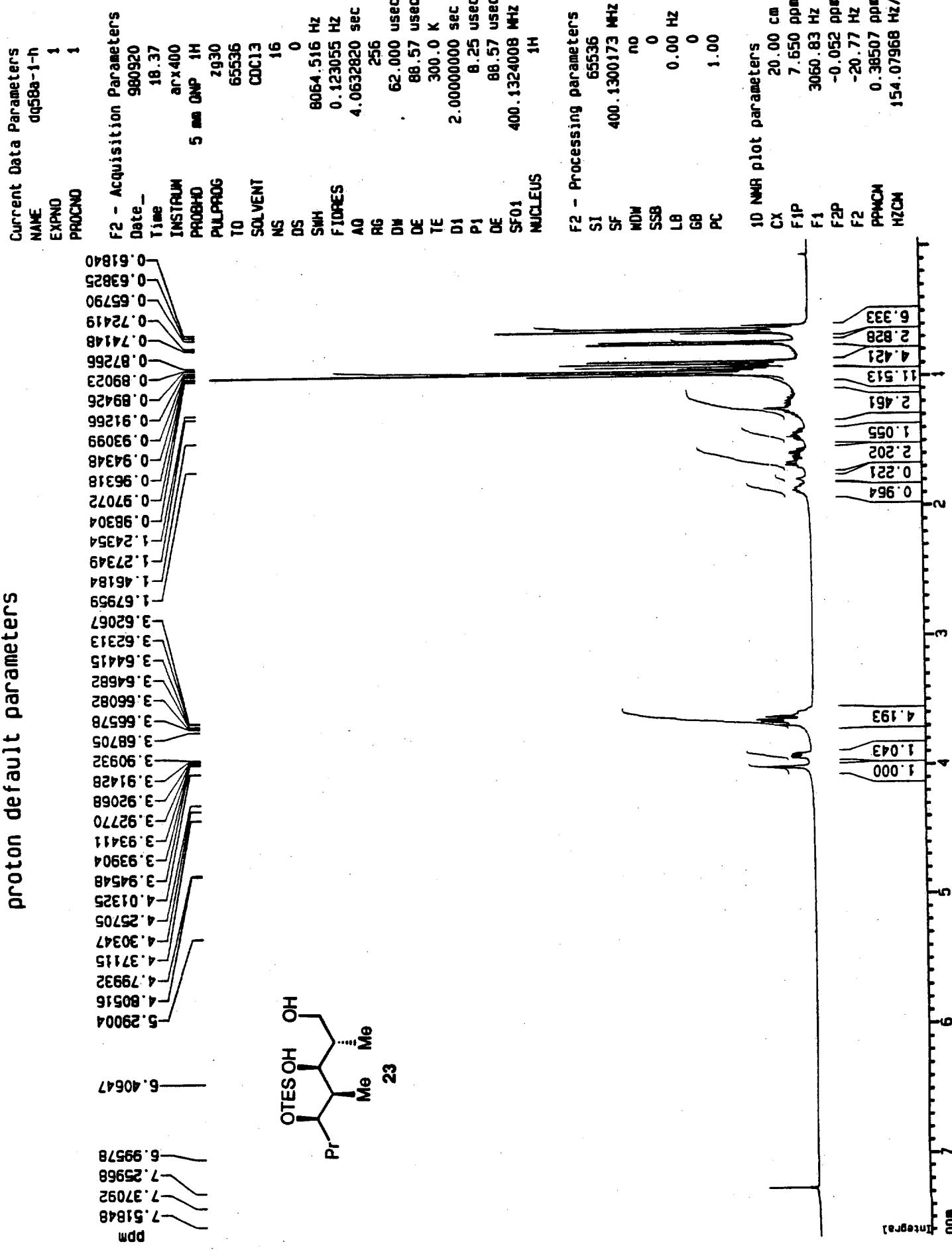
proton default parameters



Default parameters for C-13 with proton decoupling



proton default parameters



~~BEST
FR~~

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TD 32768
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R6 200
NS 500
DE 50.0
DR 12
DW 40
FW 15700
Q2 3545.000
DP 17H BB

LB 1.000
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CX 32.00
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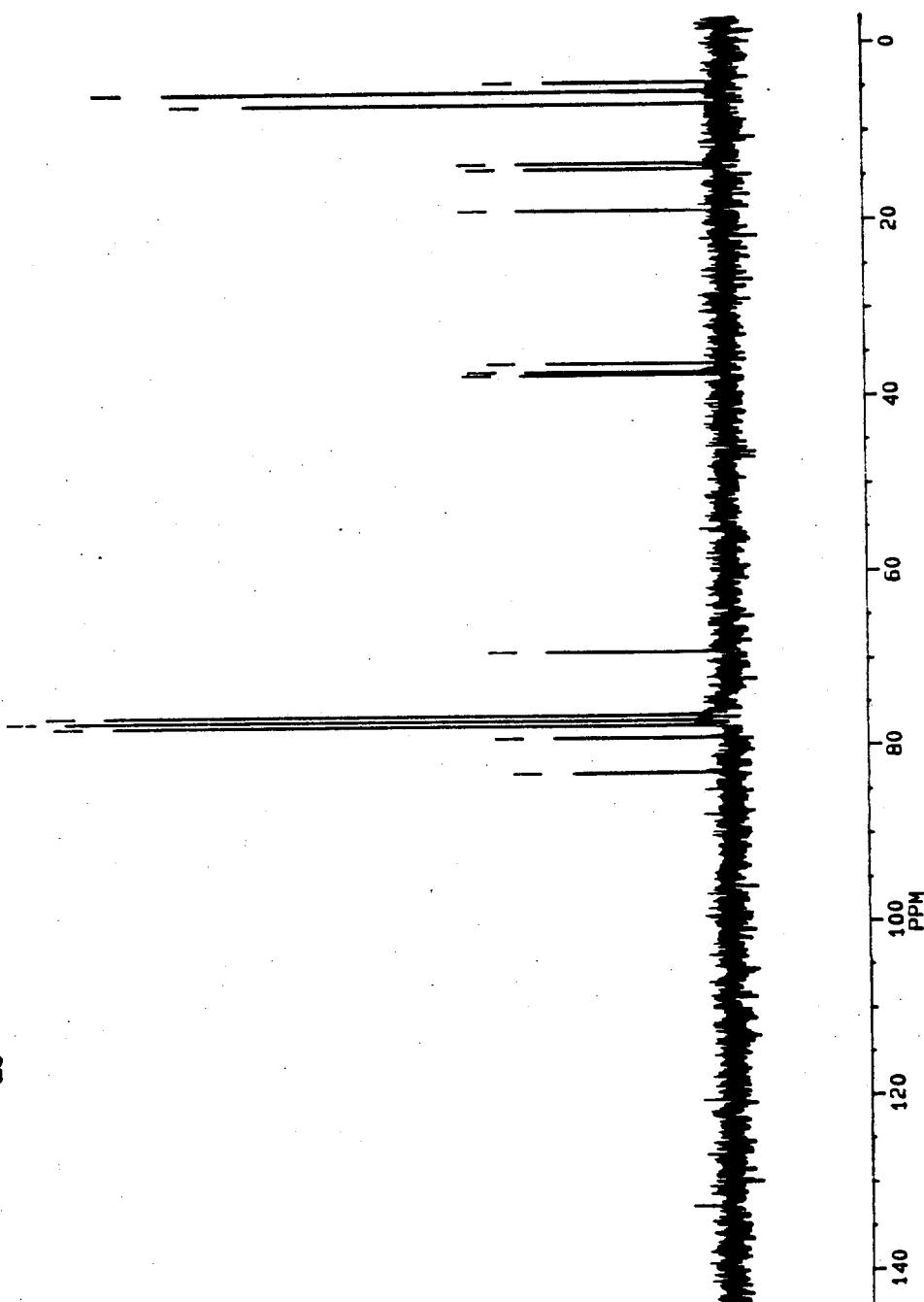
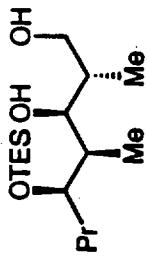
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14.1162
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35.1652
37.5388

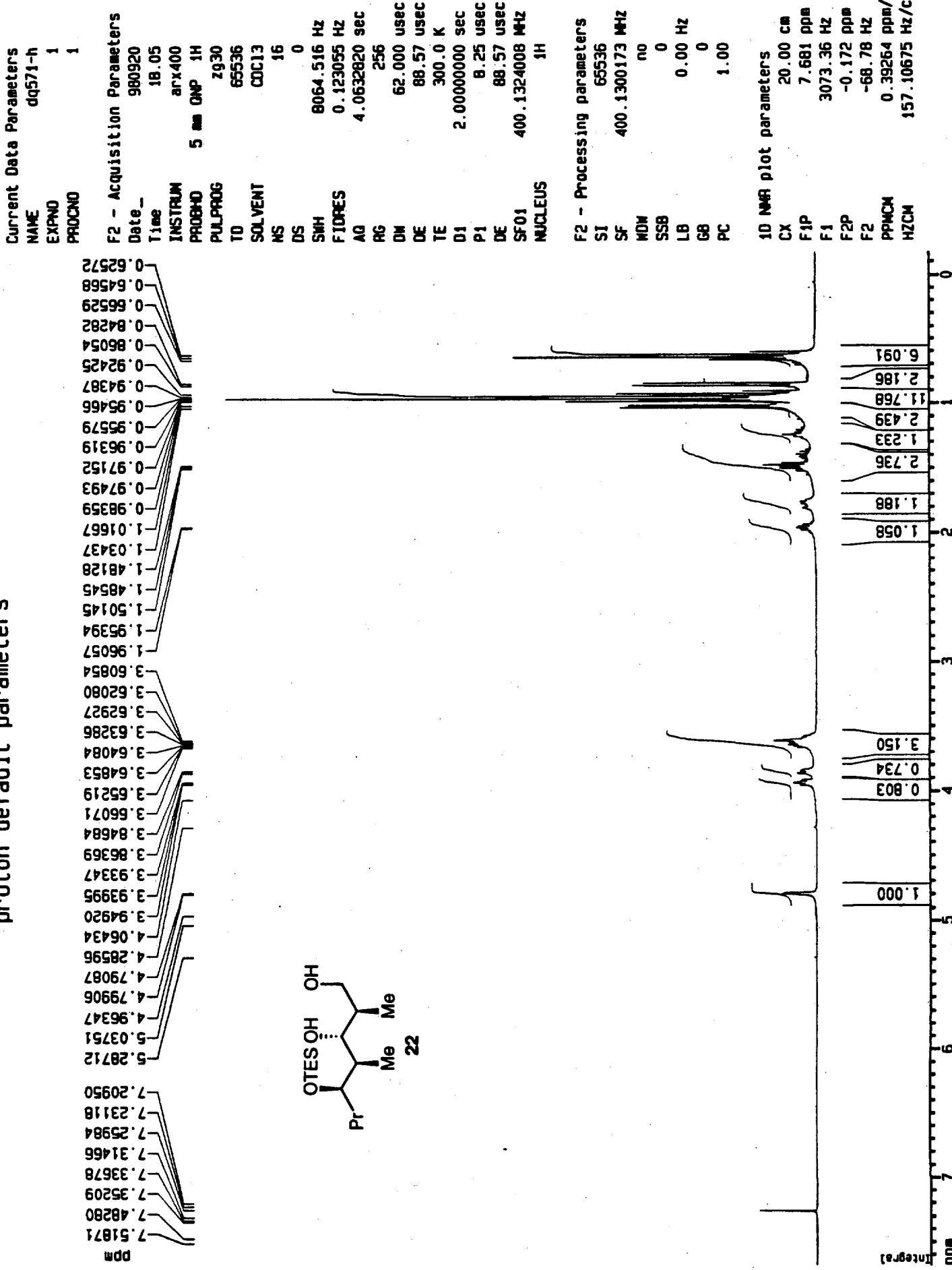
68.9980

76.3652
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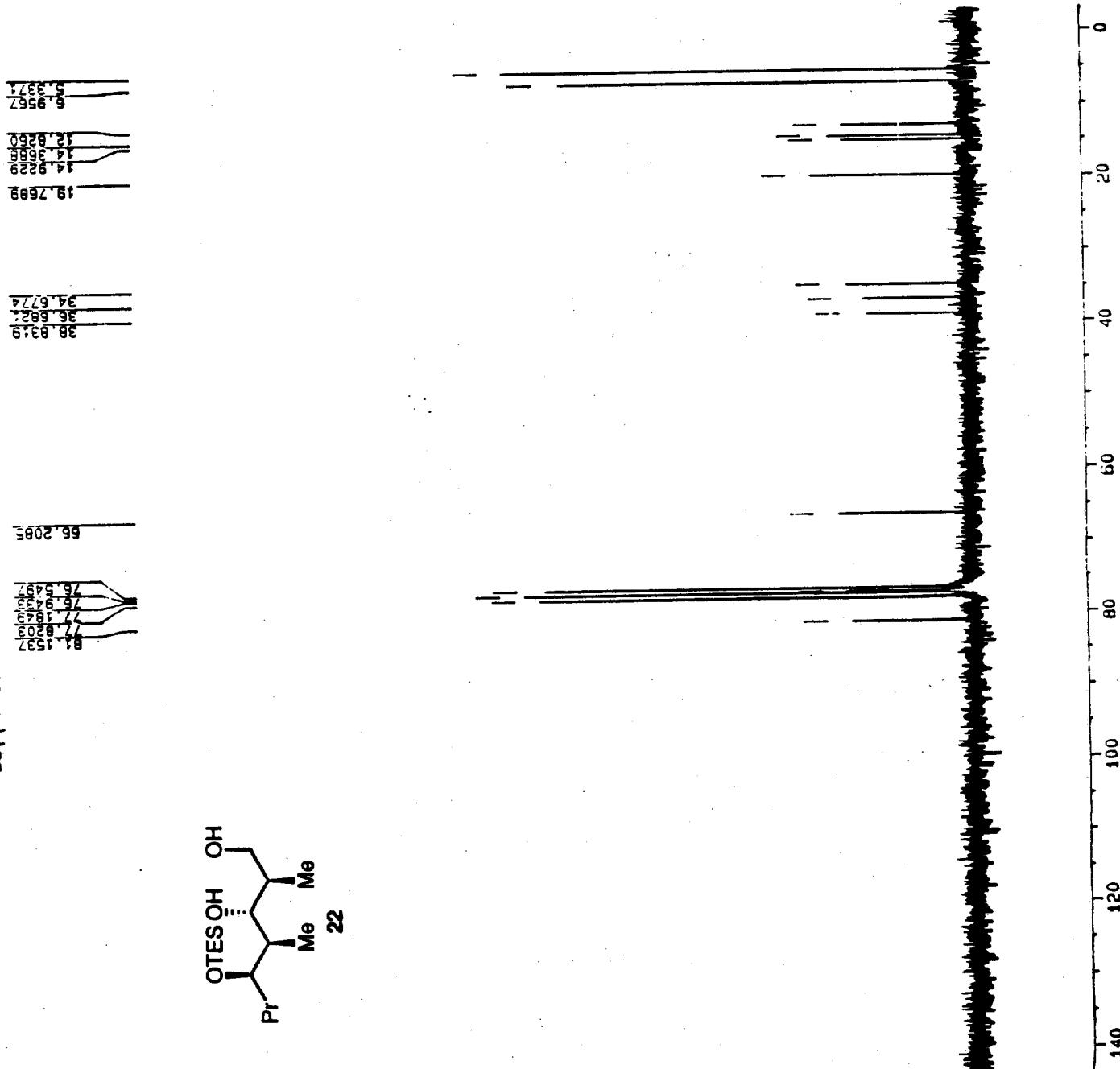
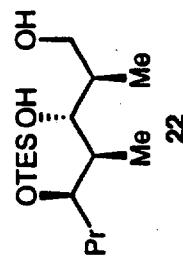
D050-2-13C



proton default parameters



D044-2-13C



proton default parameters

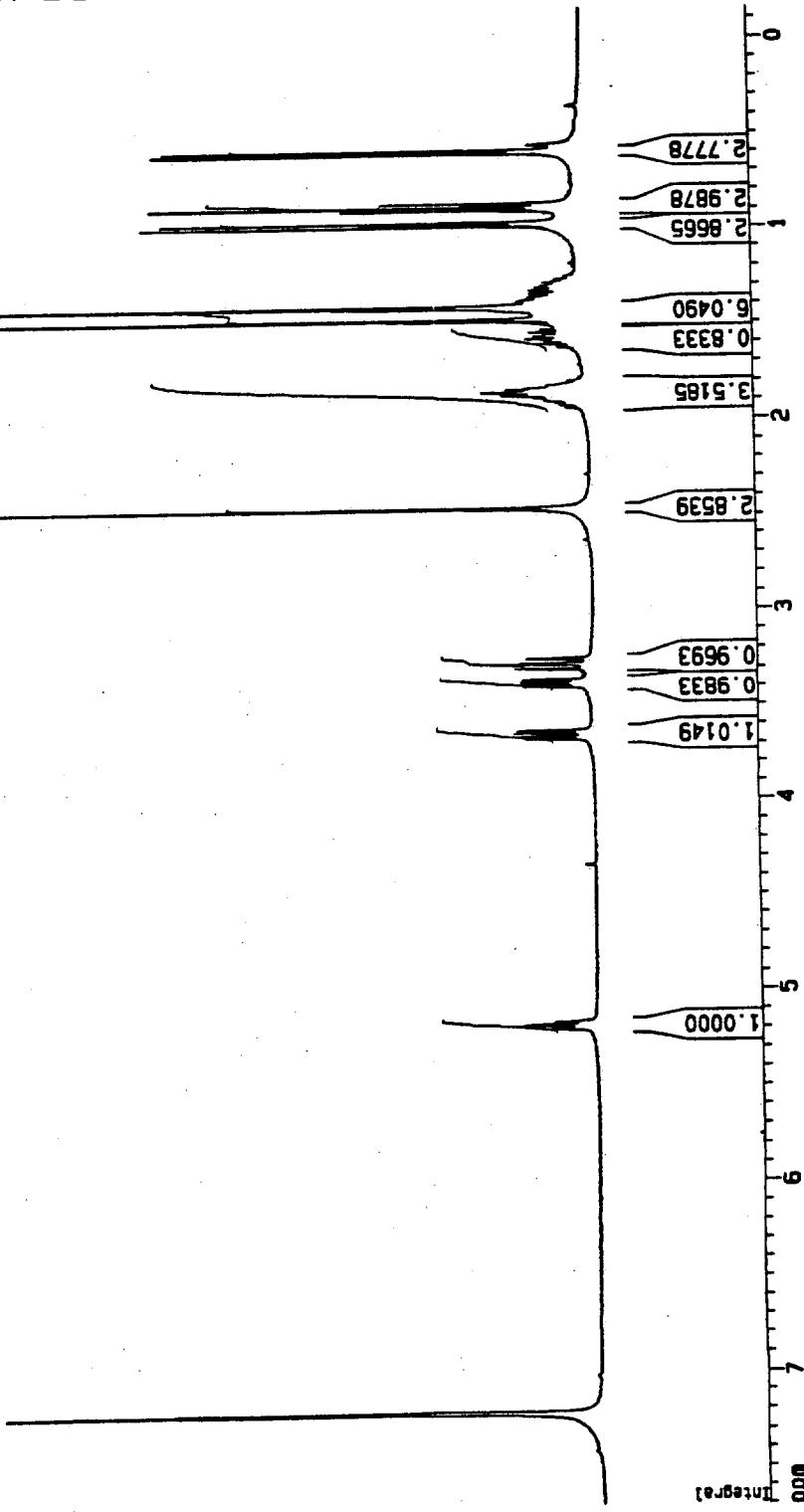
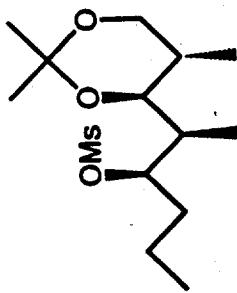
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RG	715
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NUCLEUS	1H

F2 - Acquisition Parameters

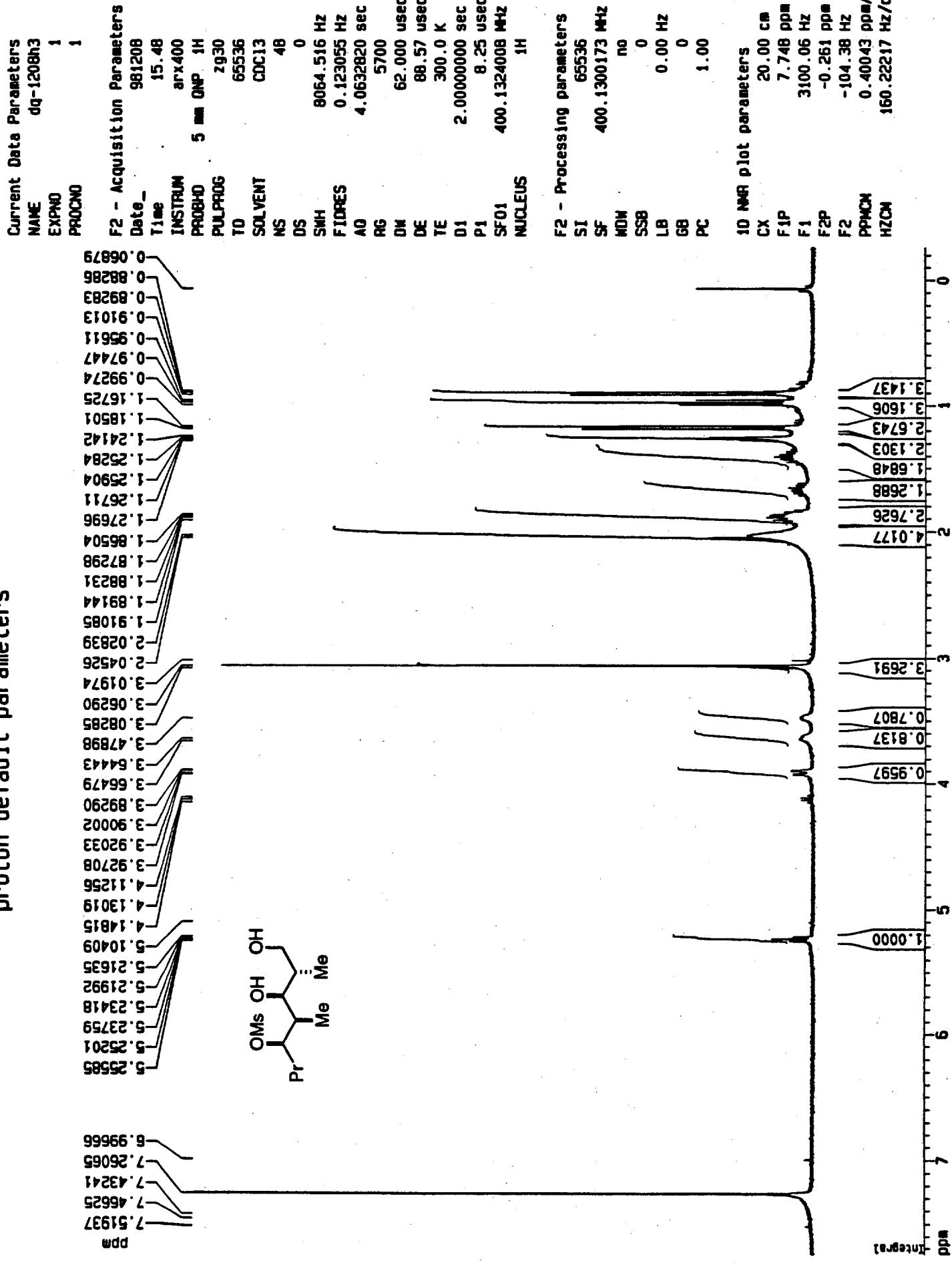
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DS	1.38377
SWH	1.38956
FINRES	1.41458
AQ	1.48435
RG	1.58460
DW	1.84094
DE	1.84791
TE	1.86369
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NUCLEUS	2.72495

F2 - Processing parameters

SI	65536
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proton default parameters



Default parameters for C-13 with proton decoupling



Current Data Parameters

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PROCNO	1

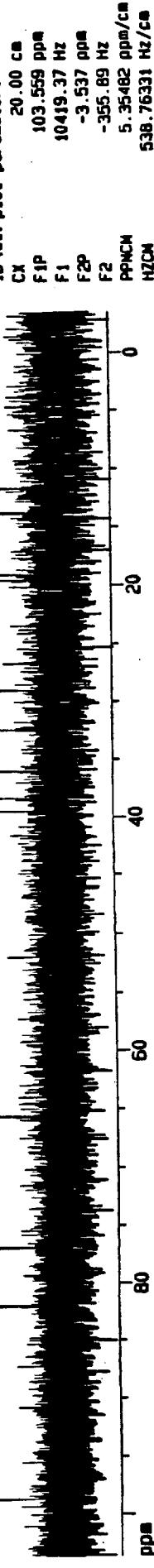
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TD	65536
SOLVENT	C6D6
NS	400
DS	0
SWH	27777.777 Hz
ETRATES	0.423855 Hz
AD	1.179690 sec
RG	16384
DW	18.000 usec
DE	25.71 usec
TE	300.0 K
D1	0.0000200 sec
D1.5	23.50 dB
CPDPRG	Waitz16
P31	100.00 usec
D1	2.0000000 sec
P1	6.25 usBC
SF01	100.6248445 MHz
NUCLEUS	¹³ C
D11	0.0300000 sec

F2 - Processing parameters

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PC	1.40

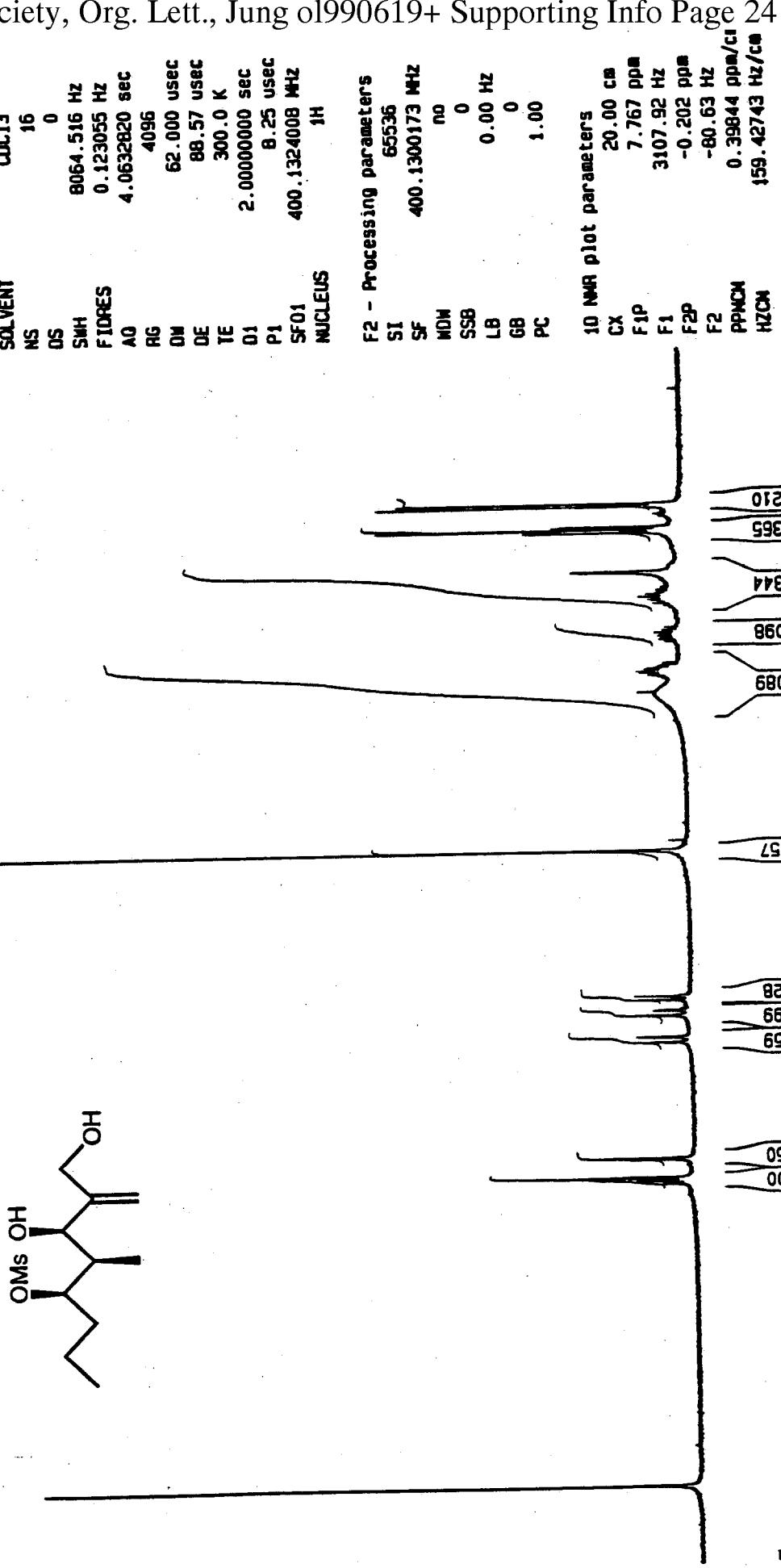
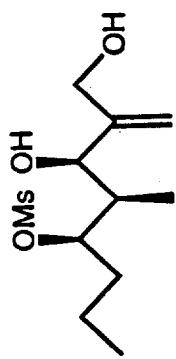
1D NMR plot parameters



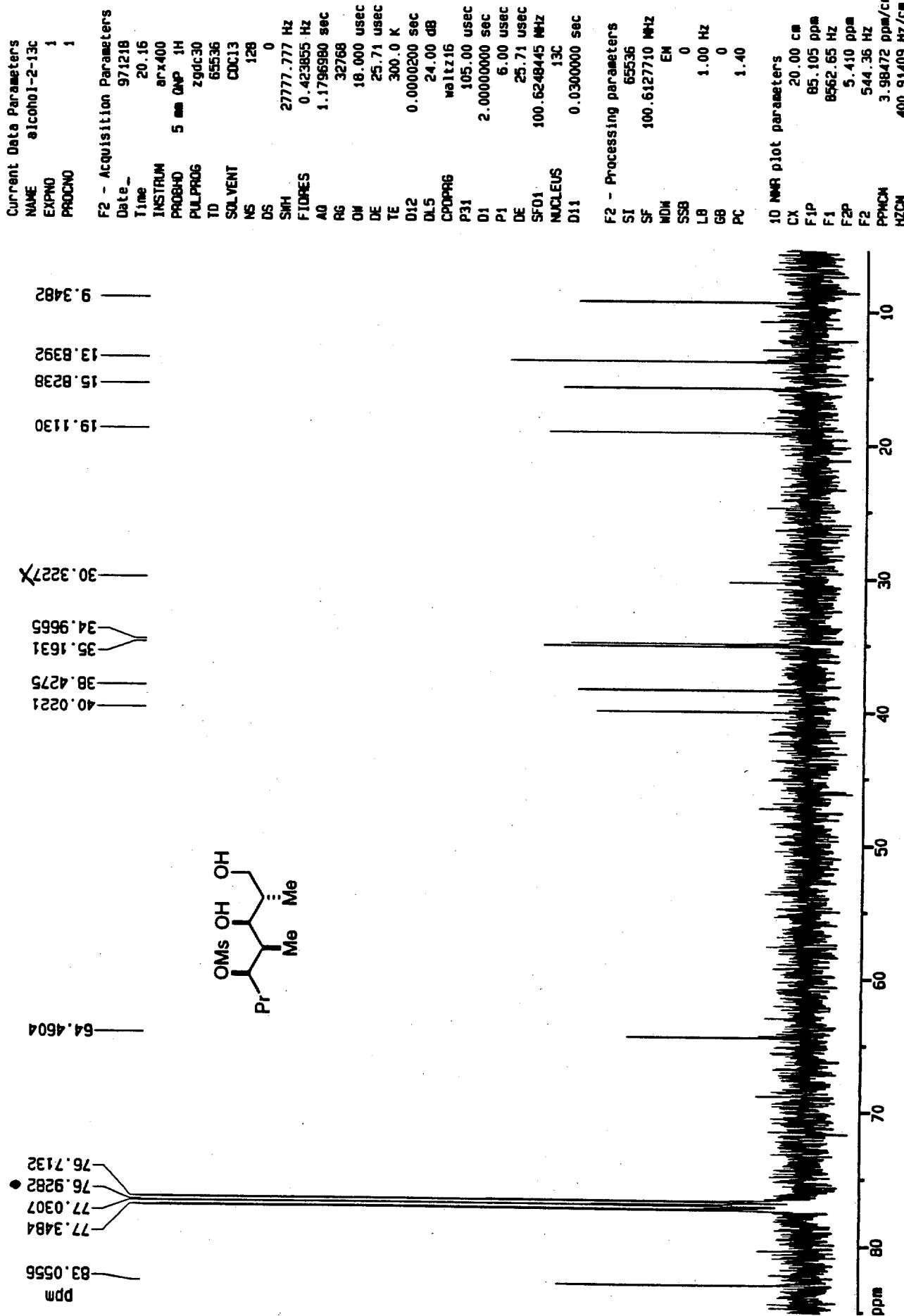
proton default parameters

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PROCNO	1

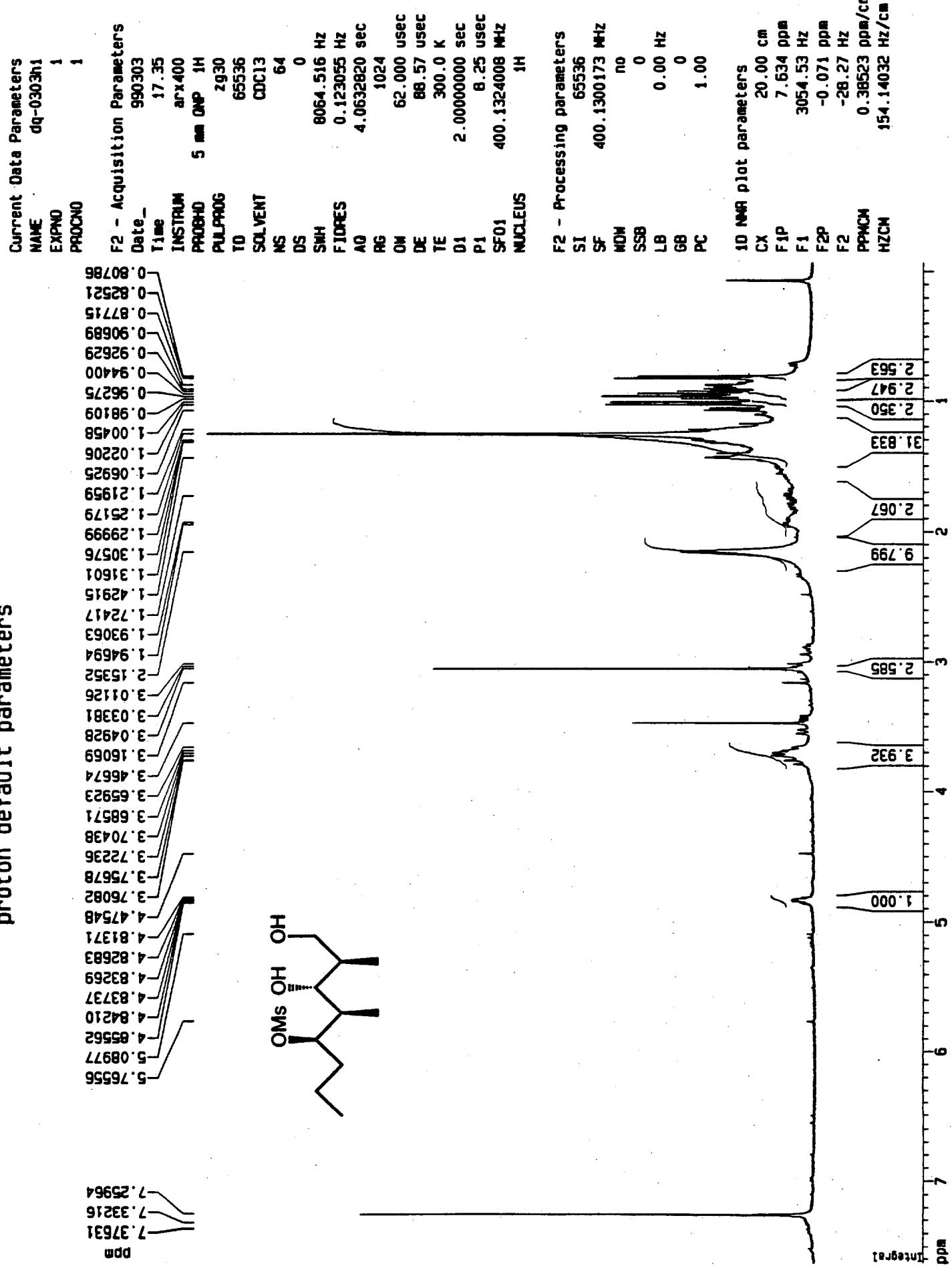
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FINRES	0.123055 Hz
AQ	4.0632820 sec
RG	4096
DW	62.000 usec
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TE	300.0 K
D1	2.0000000 sec
P1	8.25 usec
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NUCLEUS	1H



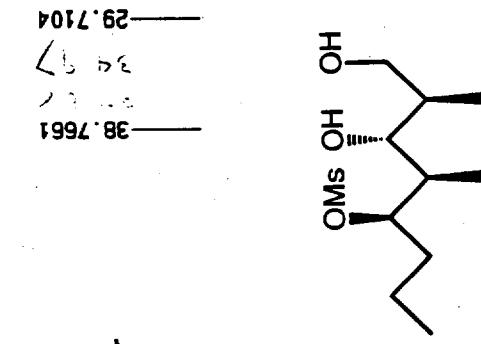
Default parameters for C-13 with proton decoupling



proton default parameters



Default parameters for C-13 with proton decoupling



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77.0244
76.7065

38.7661
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29.7104

18.6407
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24.24
24
17.52
14
2

87.12

ppm

Current Data Parameters
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PROC0 1

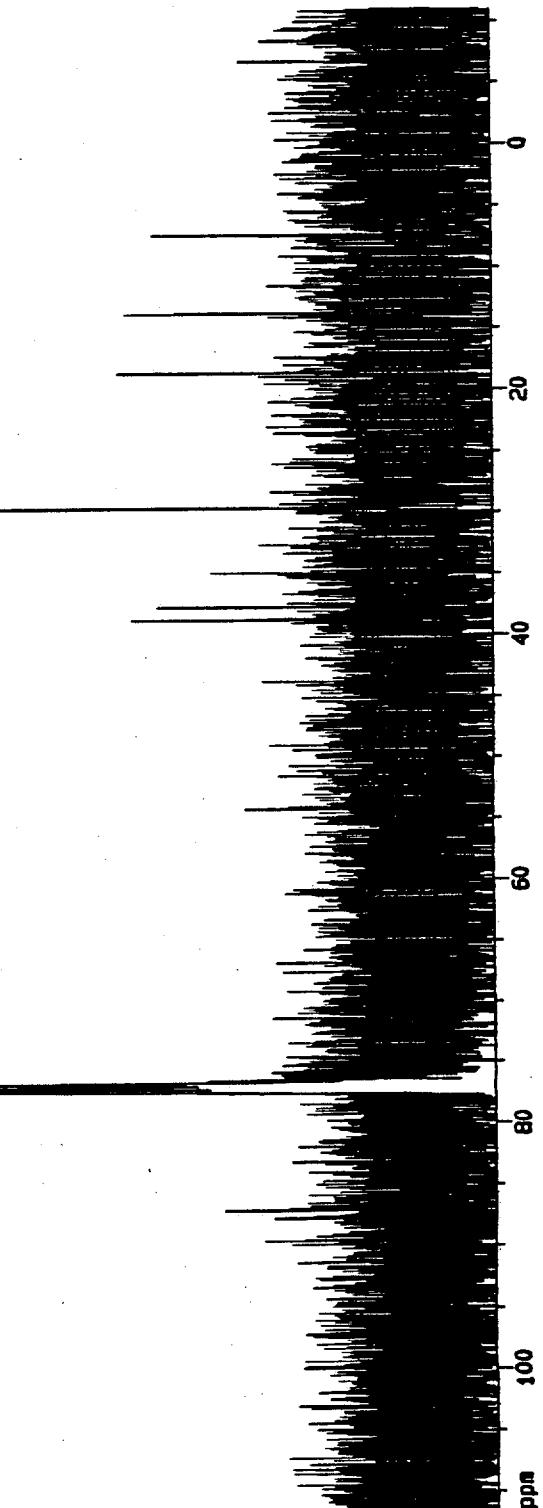
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DS 0
SWH 27777.777 Hz
FIDRES 0.463855 Hz
AD 1.1796980 sec
RG 32768
DW 18.000 usec
DE 25.71 usec
TE 300.0 K
D1 0.0000200 sec
Q1 23.50 dB
CPDPRG Wait216
P31 100.00 usec
D1 2.0000000 sec
P1 6.25 usec
SF01 100.624645 MHz
NUCLEUS 13C
D11 0.0300000 sec

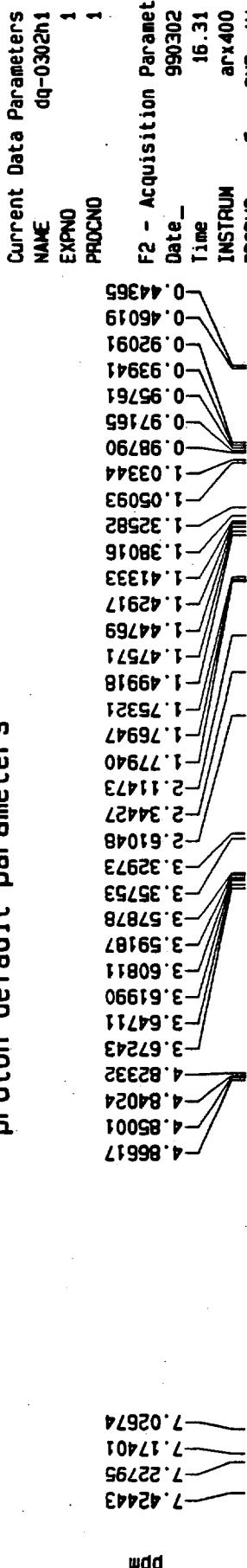
F2 - Processing parameters

SI 65536
SF 100.6127710 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

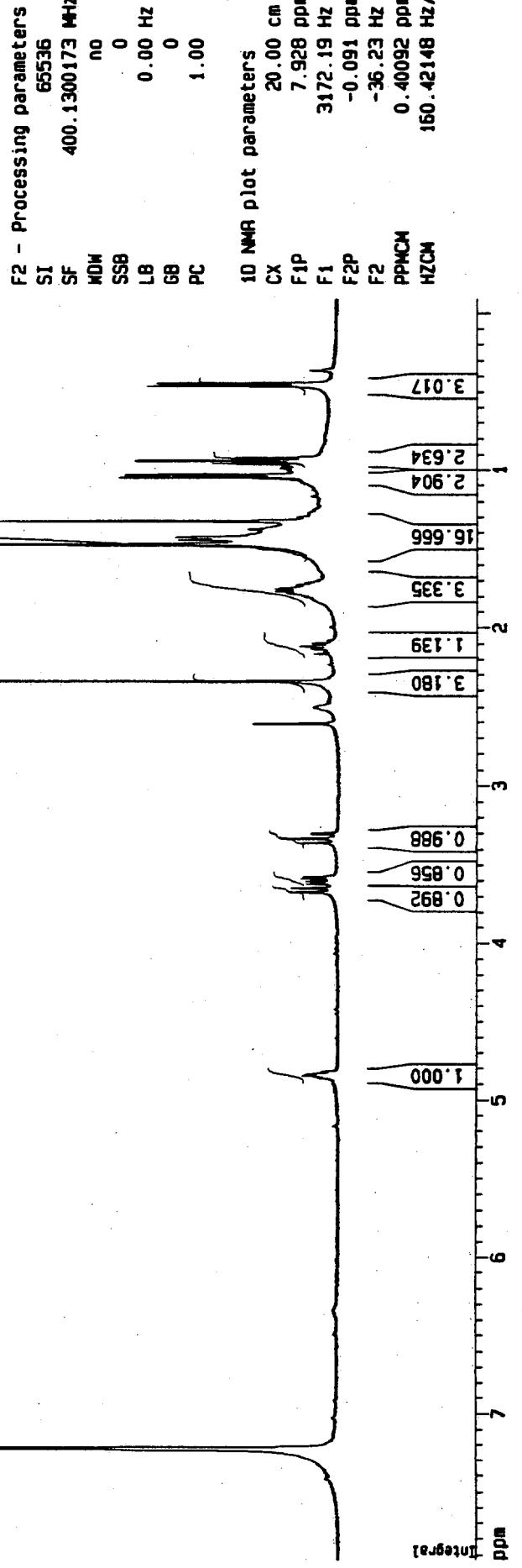
10 NMR plot parameters
CX 20.00 ppm
F1P 111.517 ppm
F1 11220.00 Hz
F2P -11.058 ppm
F2 -1112.53 Hz
PPM/C 6.12871 ppm/cm
Hz/cm



proton default parameters



ppm



Integral

Default parameters for C-13 with proton decoupling

Current Data Parameters
 NAME dq-0302c1
 EXPNO 1
 PROTONO 1

F2 - Acquisition Parameters
 Date_ 990302
 TIME 16.54
 INSTRNMN arx400
 PROBHD 5 mm QNP 1H
 PULPROG zgdc30
 TD 65536
 SOLVENT C6D6
 NS 400
 DS 0
 SWH 27777.777 Hz
 FIDRES 0.423855 Hz
 AD 1.1796980 sec
 RG 16384
 DM 18.000 usec
 DE 25.71 usec
 TE 300.0 K
 D12 0.0000200 sec
 QL5 23.50 dB
 CPDR16
 P31 100.00 usec
 D1 2.0000000 sec
 P1 6.25 usec
 SF01 100.624645 MHz
 NUCLEUS ¹³C
 D11 0.0300000 sec

F2 - Processing parameters
 SI 65536
 SF 100.612710 MHz
 MDW no
 SSBB 0
 LB 0.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 F1P 100.888 ppm
 F1 10150.67 Hz
 F2P 7.005 ppm
 F2 704.83 Hz
 PPRCM 4.69416 ppm/cm
 HZCM 472.29199 Hz/cm

ppm

97.0875
 85.11
 83.54
 05.59
 37.7870
 29.6791
 14.32
 11.33
 7.14
 4.46
 1.75
 1.31
 1.21
 18.6968

