Supporting Information

Syntheses of (–)-Funebrine and (–)-Funebral Using Sequential Transesterification and Intramolecular Cycloaddition of a Chiral Nitrone

Osamu Tamura,* Nobutaka Iyama, and Hiroyuki Ishibashi*

Table of Contents

S2: Comparison between oxime **6** and its cyclohexylidene congener in sequential transesterification and intramolecular cycloaddition.

S4: Calculation for TS X (PM3) in Scheme 3

S6: Calculation for TS X (6-31G**) in Scheme 3

S7: Calculation for TS XI (PM3) in Scheme 3

S10: Calculation for TS XI (6-31G**) in Scheme 3

S12, 13: ^{1}H and ^{13}C NMR spectra of compound **7**

S14, 15: ^{1}H and ^{13}C NMR spectra of compound **8**

S16, 17: ^{1}H and ^{13}C NMR spectra of compound **9**

S18, 19: ^{1}H and ^{13}C NMR spectra of compound **10**

S20, 21: ^{1}H and ^{13}C NMR spectra of compound (–)-**3**•HCl

S22, 23: ^{1}H and ^{13}C NMR spectra of compound **12a**

S24, 25: ^{1}H and ^{13}C NMR spectra of compound **12b**

S26, 27: ^{1}H and ^{13}C NMR spectra of compound **14**

S28, 29: ^{1}H and ^{13}C NMR spectra of compound **15**

S30, 31: ^{1}H and ^{13}C NMR spectra of compound (–)-**2**

S32, 33: ^{1}H and ^{13}C NMR spectra of compound (–)-**1**

Comparison between oxime 6 and its cyclohexylidene congener in sequential transesterification and intramolecular cycloaddition.

We reported that heating cyclohexylidene congener **A** of **6** with aldehyde **5** followed by treatment with cinnamyl alcohol and a catalytic amount of $TiCl_4$ in the presence of MS 4A gave cycloadduct **B** as a sole product in 77% yield (Scheme S1 and Table S1).[7] To compare influence of protective group of the chiral auxiliary, a similar reaction using oxime **6** was conducted, and the reaction gave a 98:2 mixture of cycloadducts **B** and **C** in 94 % yield. Use of oxime **6** gave higher chemical yield and comparable stereoselectivity.

SCHEME S1

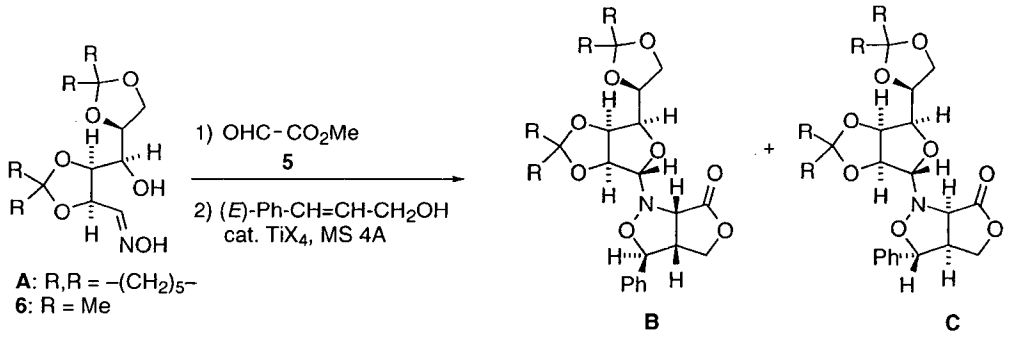

Table S1

Oxime	Conditions	Ratio (B:C)	Yield (%)
A	cat. $TiCl_4$, MS 4A toluene-$(CH_2Cl)_2$, 100 °C	**B**, single isomer	77
6	cat. $Ti(O^iPr)_4$, MS 4A benzene, reflux	98:2	94

(3*S*,3a*R*,6a*S*)-1-(2',3':5',6'-*O*-Diisopropylidene-α-L-gulofuranosyl)-3-phenyltetrahydrofuru[3,4-c]isoxazol-6-one (B, R = Me). A mixture of oxime **6** (71.3 mg, 0.662 mmol) and methyl glyoxylate (**5**) (100.5 mg, 0.365 mmol) in dry benzene (2 mL) was heated under reflux with azeotropic removal of water using Dean-Stark trap under an argon atmosphere. After 8 h, oxime **6** was consumed, and the Dean-Stark equipment was removed. To the mixture were added $Ti(O^iPr)_4$ (25 μL,

84.7 μmol), (*E*)-cinnamyl alcohol (132 mg, 0.987 mmol), and MS 4A (1 g), and the mixture was heated under reflux for 3 h. The mixture was diluted with $CHCl_3$, and filtered through a pad of Celite®. To the filtrate was added a 10% aqueous solution of potassium sodium tartrate (15 drops), and the mixture was stirred. After 1 h, $MgSO_4$ and Celite® were added to the mixture, and the mixture was further stirred for 30 min. The mixture was filtered through a pad of Celite®, and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (*n*-hexane-Et_2O, 1:2) to give compound **B** (149.5 mg, 92%). mp 203-206 °C (*n*-hexane-AcOEt); $[\alpha]^{25}_{D}$ −1.62 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 1790 cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 1.29 (3H, s), 1.38 (3H, s), 1.46 (3H, s), 1.48 (3H, s), 3.34 (1H, m), 3.76 (1H, m), 4.19 (1H, m), 4.35 (4H, m), 4.59 (1H, d, *J* = 8.6 Hz), 4.66 (1H, s), 4.76 (1H, dd, *J* = 3.3, 5.9 Hz), 4.84 (1H, d, *J* = 8.3 Hz), 5.01 (1H, d, *J* = 5.9 Hz), 7.38 (5H, br); ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ 24.7, 25.6, 26.0, 26.6, 49.5, 64.4, 66.0, 67.5, 75.8, 80.3, 84.1, 84.4, 85.4, 98.5, 110.0, 112.9, 126.5, 129.0, 129.1, 136.5, 174.0. Anal.: Calcd for $C_{23}H_{29}NO_8$: C, 61.73, H, 6.53, N, 3.13. Found: C, 61.43, H, 6.59, N, 3.12.

Calculation for TS X (PM3) in Scheme 3

```
MacSPARTAN PRO Semi-Empirical Program:  (PowerPC)            Release 1.0.2
 Job run on machine : (G3/500)
 Run type: Transition state optimization
        (Analytical Gradient)
        (Analytical Frequency in TSOPT)
        (Analytical Gradient in FREQ)
        (Numerical Frequency)
 Model: RHF/PM3
 Number of shells:  63
  42 S shells
  21 P shells
 Number of basis functions: 105
 Number of electrons: 118
 Use of molecular symmetry disabled
 Molecular charge:   0
 Spin multiplicity:  1

 Point Group = C1  Order =  1 Nsymop =  1
 This system has 120 degrees of freedom

 Heat of Formation:     -150.277 kcal/mol
  Calculating Hessian
 Memory Used:        17.106 Mb
 Reason for exit: Successful completion
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 Semi-Empirical Program Wall Time: 000:12:54.1

MacSPARTAN PRO Properties Program:  (PowerPC)            Release 1.0.2
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 Molecular charge:   0
 Spin multiplicity:  1
 Electrons:       118
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Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C8	-0.7310999	-0.5768457	1.0359757
2	C	C7	0.2193607	-0.1859741	-0.1294717
3	N	N1	1.4562235	0.5835170	0.3277714
4	C	C2	2.4274574	0.8506498	-0.6012908
5	H	H2	2.3368659	0.4058861	-1.6054222
6	C	C1	3.8329967	1.1445595	-0.1864593
7	O	O3	4.6569069	0.3749861	0.2591953
8	O	O2	4.3276127	2.3998266	-0.3334906
9	C	C3	3.4098680	3.3649412	-0.8404175
10	H	H1	3.6558627	4.2735872	-0.2630479
11	C	C4	1.9736321	2.9568383	-0.7084460
12	C	C5	1.2907214	3.1904203	0.4813360
13	C	C6	-0.1815223	3.4170979	0.4662012
14	H	H4	-0.6950464	2.8299065	-0.3081624
15	H	H9	-0.3908592	4.4776687	0.2674702
16	H	H10	-0.6421746	3.1679358	1.4313139
17	H	H8	1.8336654	3.6216746	1.3393067
18	H	H7	1.4034441	2.8967301	-1.6464095
19	H	H6	3.6889895	3.5395383	-1.8948310
20	O	O1	1.3625840	1.3646549	1.3303463
21	O	O4	0.6816820	-1.3715005	-0.7498004
22	C	C10	0.4623442	-2.5116450	0.1036613
23	C	C9	-0.6191738	-2.1123335	1.1397088
24	H	H12	-0.3861396	-2.5081199	2.1492322
25	O	O6	-1.9249479	-2.5959262	0.8659271
26	C	C11	-2.7571012	-1.5389632	0.3639670
27	O	O5	-2.0877739	-0.3167838	0.7186191
28	C	C12	-2.9397728	-1.6469432	-1.1553487
29	H	H5	-1.9981642	-1.4872182	-1.6987845

30	H	H13	-3.6603935	-0.9009249	-1.5134040
31	H	H14	-3.3171049	-2.6405027	-1.4301041
32	C	C14	-4.1066584	-1.5904352	1.0865203
33	H	H15	-3.9937461	-1.5412033	2.1771531
34	H	H20	-4.6364487	-2.5212253	0.8469665
35	H	H21	-4.7434972	-0.7510377	0.7790363
36	C	C13	0.1196248	-3.6998397	-0.7746777
37	H	H16	0.9301011	-3.9175567	-1.4825071
38	H	H18	-0.7955146	-3.5343627	-1.3614360
39	H	H19	-0.0370485	-4.5935759	-0.1577280
40	H	H17	1.4270222	-2.6950607	0.6335870
41	H	H11	-0.3018758	0.3874152	-0.9363182
42	H	H3	-0.5509019	-0.0098560	1.9742617

Point Group = C1 Order = 1 Nsymop = 1

Reason for exit: Sucessful completion

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Calculation for TS X (6-31) in Scheme 3**

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Job run on machine : (G3/500)

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Run type: Single point energy

Model: RHF/6-31G**

Number of shells: 147

63 S shells

21 P shells

42 SP shells

21 6D shells

Number of basis functions: 420

Number of electrons: 160

Number of heavy atoms: 21

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Number of hydrogens:        21
Use of molecular symmetry disabled
Molecular charge:   0
Spin multiplicity:  1
Memory model: direct   48.5 Mb

Point Group = C1  Order =  1 Nsymop =  1
This system has 120 degrees of freedom

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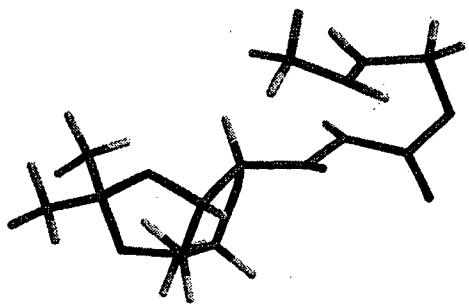

Geometry of TS **X**

Calculation for TS XI (PM3) in Scheme 3

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  Run type: Transition state optimization
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          (Analytical Frequency in TSOPT)
          (Analytical Gradient in FREQ)
          (Numerical Frequency)
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Model: RHF/PM3

Number of shells: 63

42 S shells

21 P shells

Number of basis functions: 105

Number of electrons: 118

Use of molecular symmetry disabled

Molecular charge: 0

Spin multiplicity: 1

Point Group = C1 Order = 1 Nsymop = 1

This system has 120 degrees of freedom

Heat of Formation: -149.880 kcal/mol

Calculating Hessian

Memory Used: 17.106 Mb

Reason for exit: Successful completion

Semi-Empirical Program CPU Time : 000:09:19.2

Semi-Empirical Program Wall Time: 000:11:29.9

MacSPARTAN PRO Properties Program: (PowerPC) Release 1.0.2

Use of molecular symmetry disabled

Molecular charge: 0

Spin multiplicity: 1

Electrons: 118

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z
1 O O4	0.7381640	-0.6556360	-0.2542104
2 C C7	0.1649850	0.4093631	0.4784431
3 N N1	-1.1110208	-0.0592168	1.1629315
4 C C2	-1.0267350	-0.5300558	2.4468034

5	H	H2	-0.0352502	-0.5825810	2.9242389
6	C	C1	-2.1563197	-0.3614859	3.4121486
7	O	O3	-2.5426429	0.6632079	3.9324786
8	O	O2	-2.8507403	-1.4490016	3.8314174
9	C	C3	-2.4501654	-2.6832933	3.2431655
10	H	H1	-1.8480930	-3.2153720	4.0012038
11	C	C4	-1.6983355	-2.5154654	1.9566233
12	C	C5	-2.3959034	-2.3238920	0.7663540
13	C	C6	-1.8613285	-2.8618070	-0.5140771
14	H	H4	-2.2169848	-2.2862016	-1.3795215
15	H	H9	-2.2056821	-3.8973657	-0.6478190
16	H	H10	-0.7627438	-2.8750475	-0.5478924
17	H	H8	-3.4906812	-2.1898777	0.8042051
18	H	H7	-0.7035531	-2.9817279	1.9192478
19	H	H6	-3.4047206	-3.2241379	3.1184115
20	O	O1	-2.1508050	-0.3436082	0.4850061
21	H	H3	0.9269342	0.6593606	1.2581578
22	C	C8	-0.1026667	1.5981861	-0.4893737
23	H	H11	-1.1203522	2.0310614	-0.3941522
24	C	C9	0.2688410	1.0620435	-1.8866632
25	H	H12	-0.5036955	1.1988254	-2.6708261
26	C	C10	0.6048604	-0.4347435	-1.6721892
27	C	C14	1.8720494	-0.9235440	-2.3480127
28	H	H16	1.7971294	-0.7913407	-3.4346354
29	H	H20	2.0410801	-1.9900352	-2.1494685
30	H	H21	2.7638327	-0.3787579	-2.0060719
31	H	H17	-0.2672215	-1.0549051	-1.9953146
32	O	O5	1.3534471	1.8714505	-2.3157452
33	C	C11	1.8274945	2.6905454	-1.2360602
34	O	O6	0.7792250	2.6807745	-0.2511689
35	C	C13	2.0108484	4.1227515	-1.7467643
36	H	H14	1.0903178	4.5248382	-2.1890388
37	H	H18	2.7946072	4.1606978	-2.5140364

38	H	H19	2.3072066	4.7913502	-0.9282858
39	C	C12	3.1355757	2.1399370	-0.6536898
40	H	H5	3.5376238	2.8197654	0.1080767
41	H	H13	3.8925175	2.0285347	-1.4408016
42	H	H15	2.9989016	1.1564064	-0.1830948

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Calculation for TS XI (6-31G) in Scheme 3**

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Run type: Single point energy

Model: RHF/6-31G**

Number of shells: 147

63 S shells

21 P shells

42 SP shells

21 6D shells

Number of basis functions: 420

Number of electrons: 160

Number of heavy atoms: 21

Number of hydrogens: 21

Use of molecular symmetry disabled

Molecular charge: 0

Spin multiplicity: 1

Memory model: direct 48.5 Mb

Point Group = C1 Order = 1 Nsymop = 1

This system has 120 degrees of freedom

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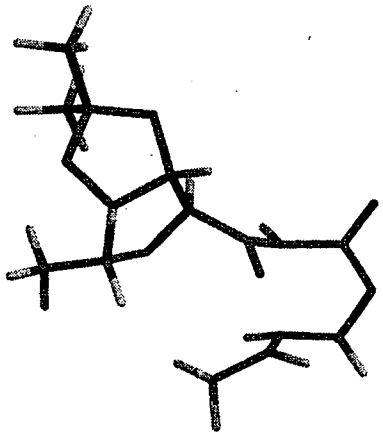
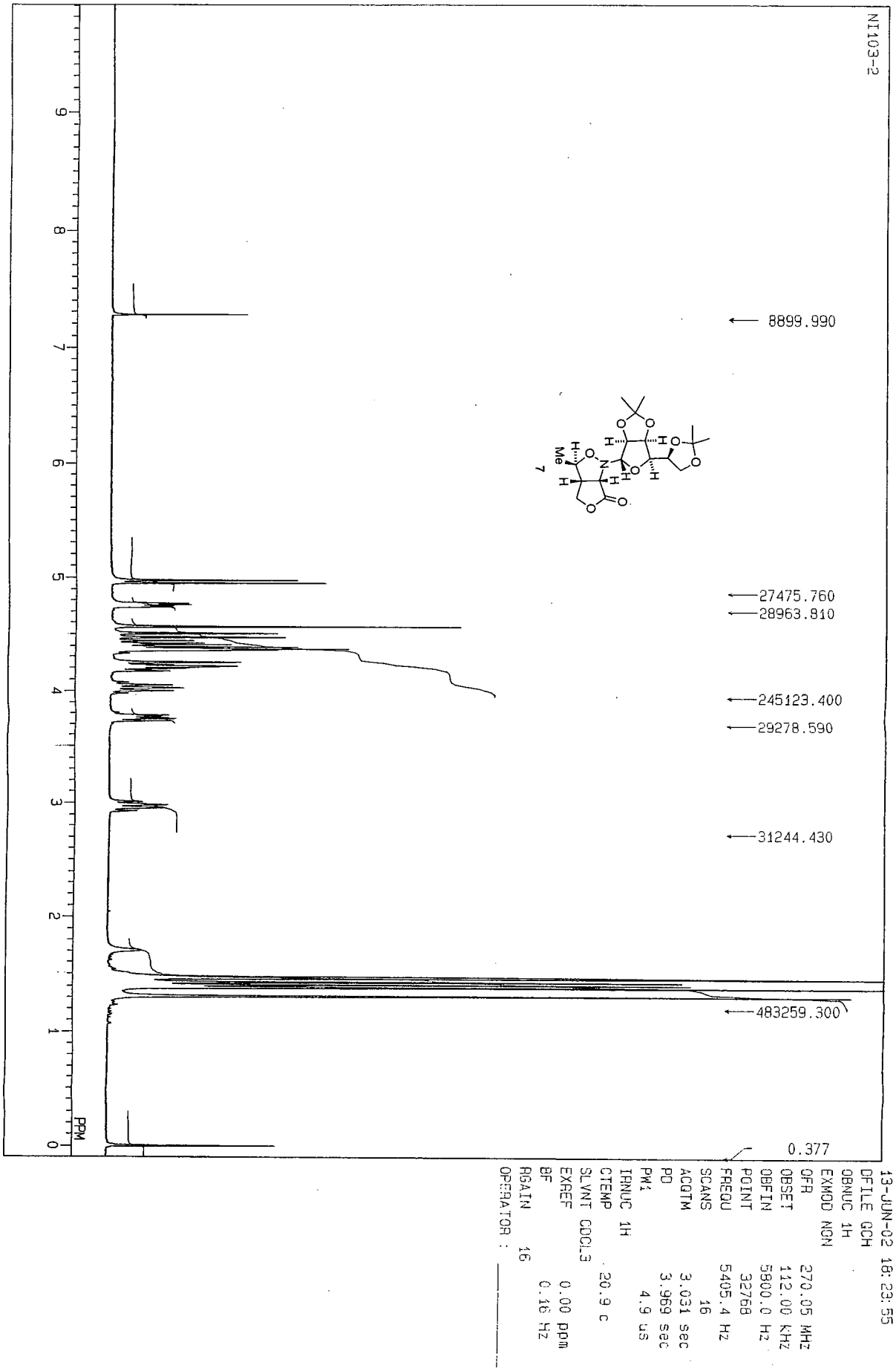


Geometry of TS **XI**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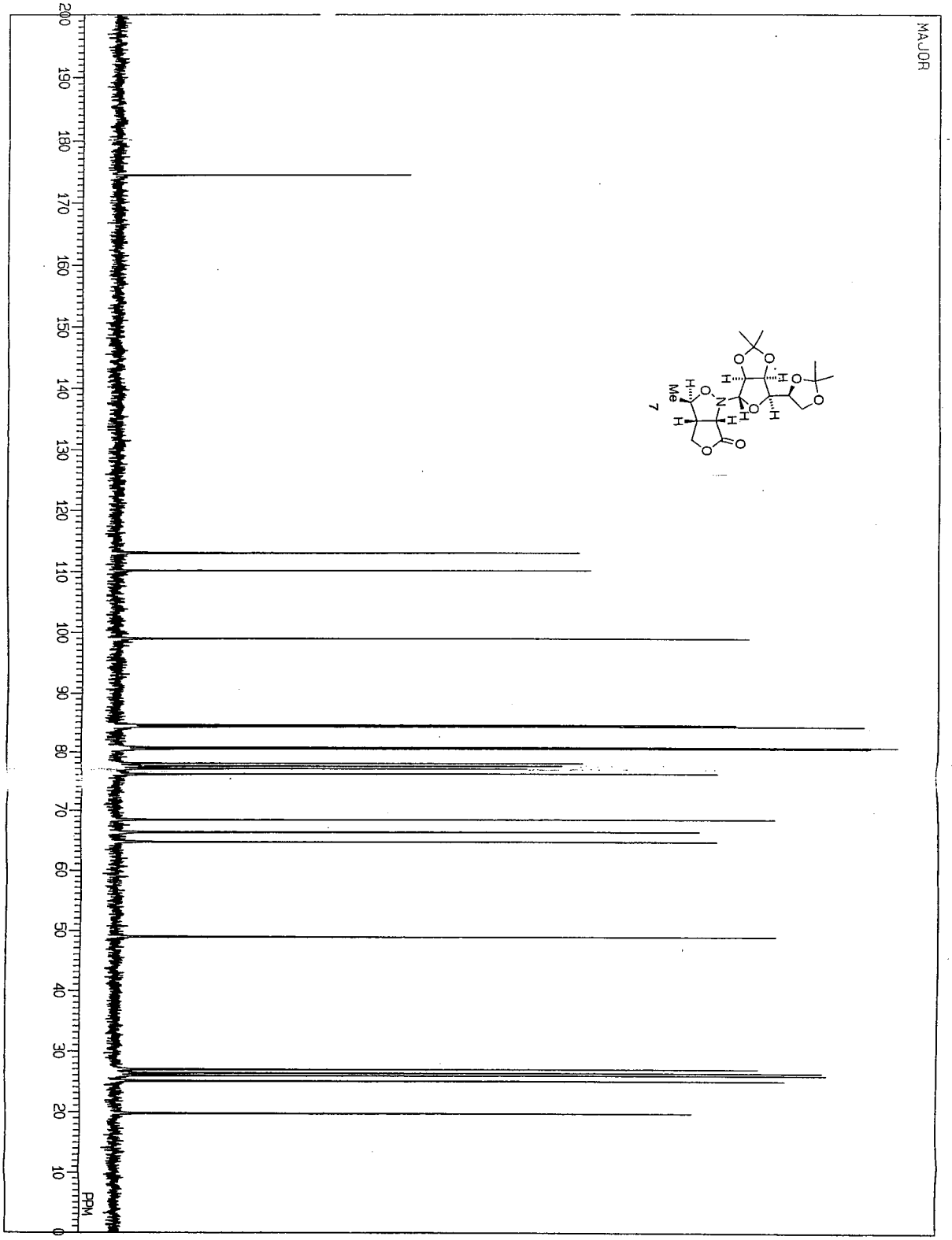

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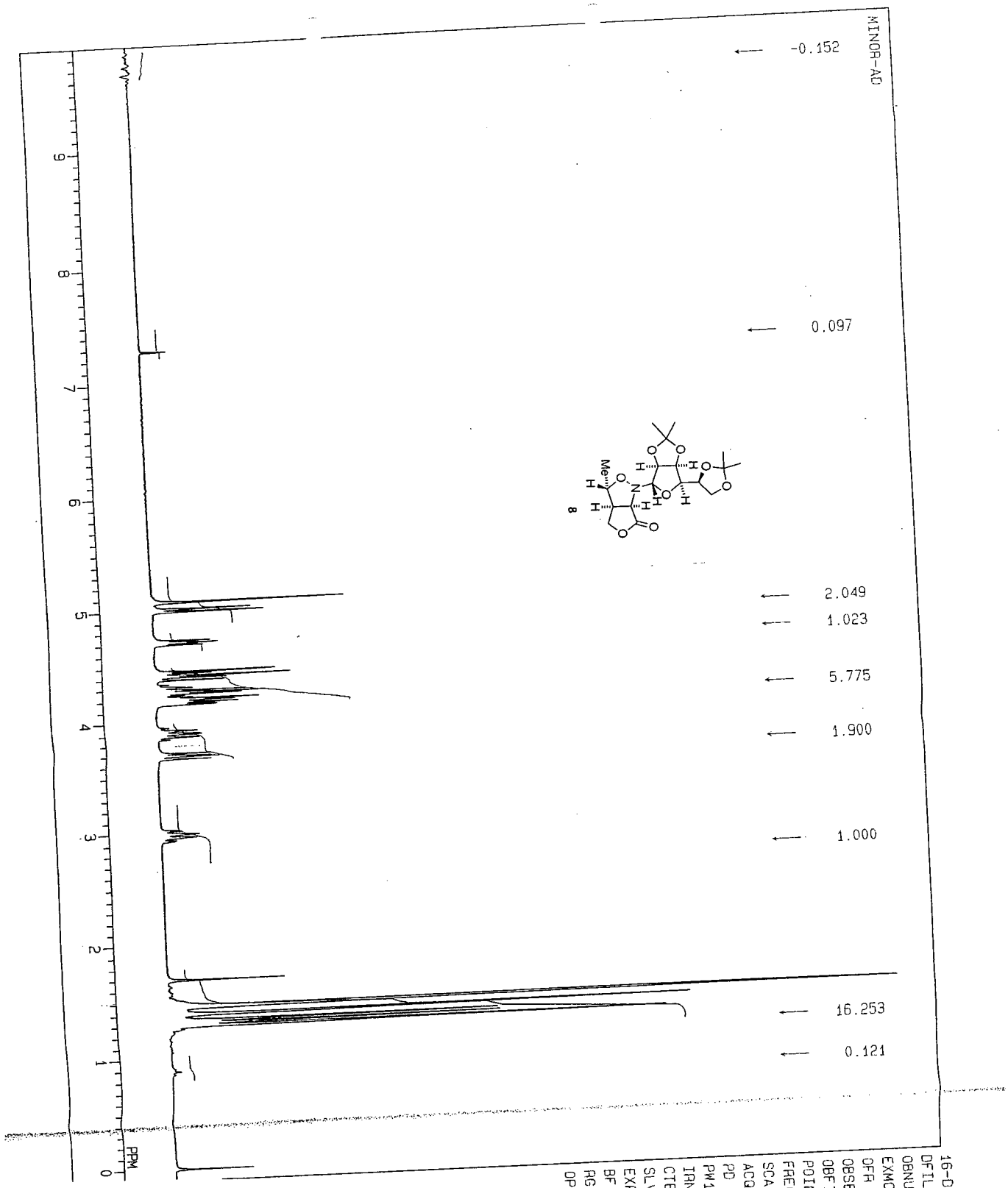
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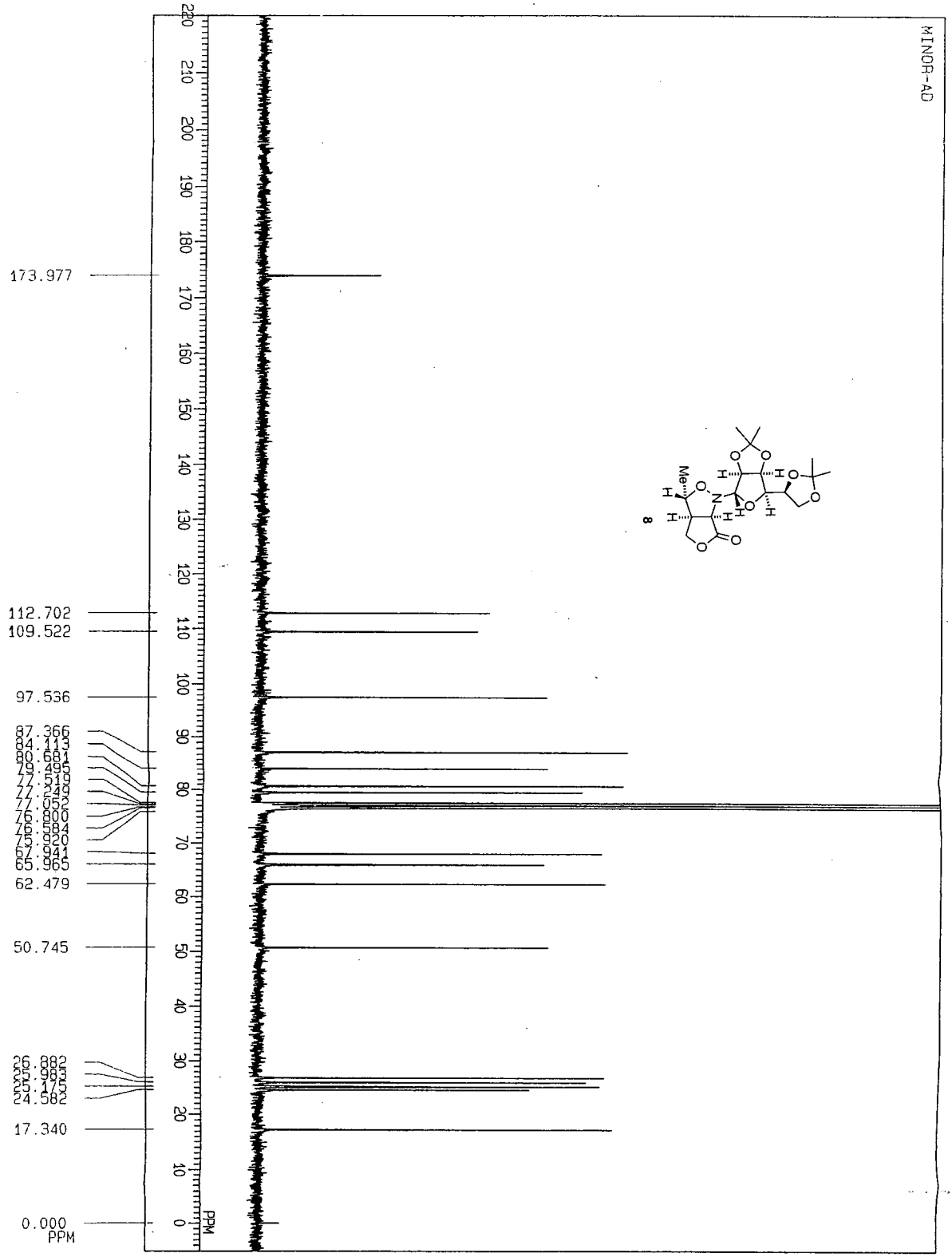

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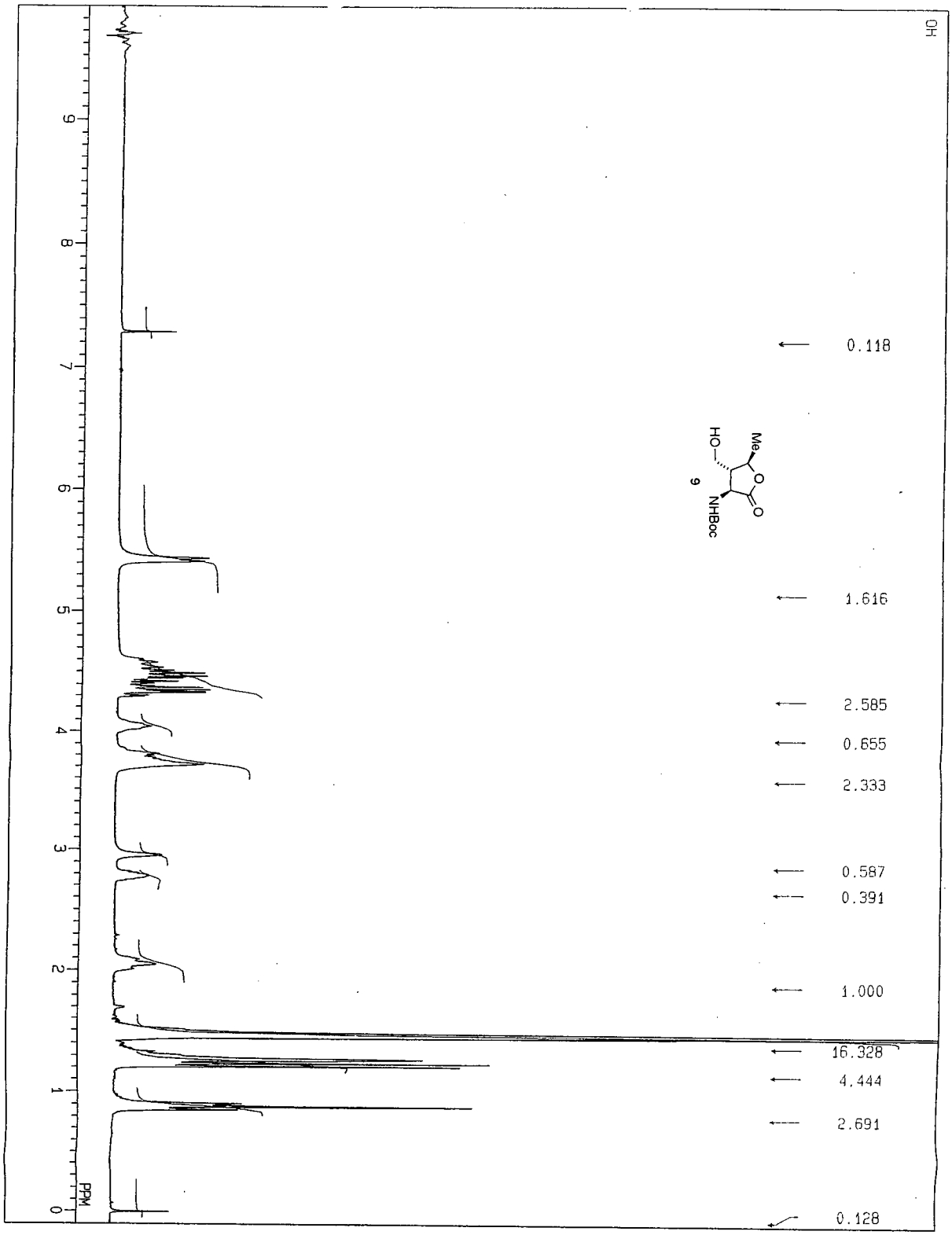

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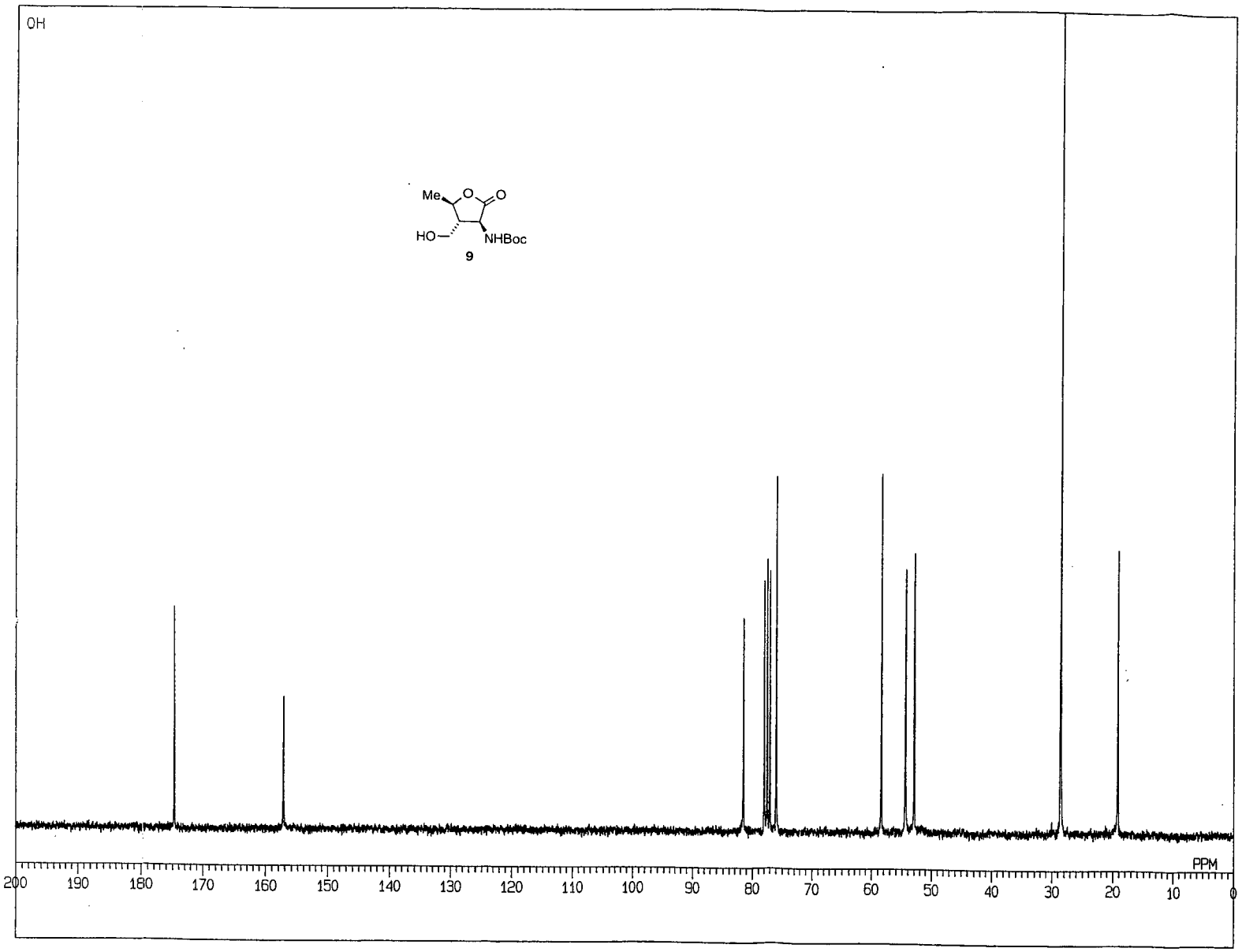

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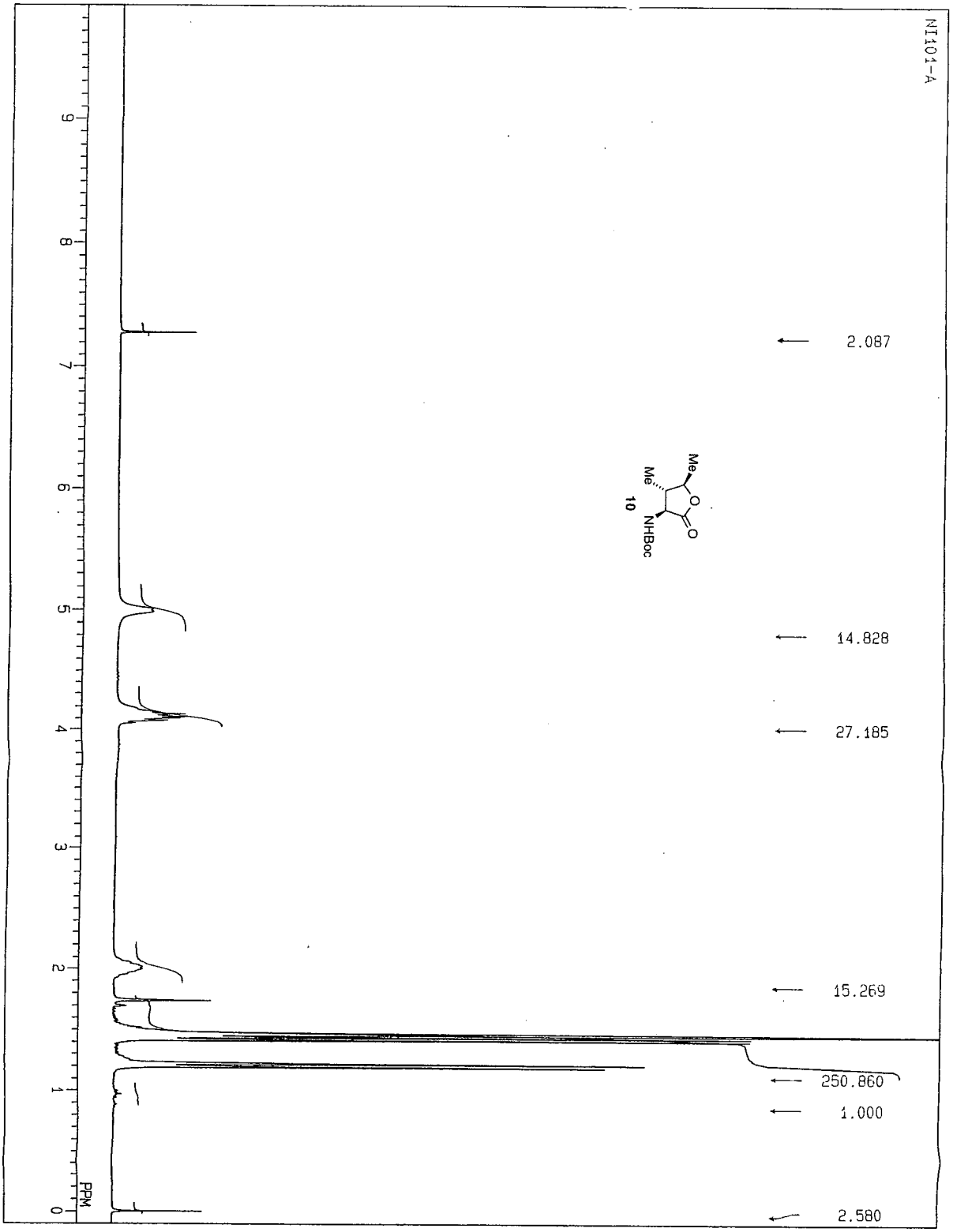

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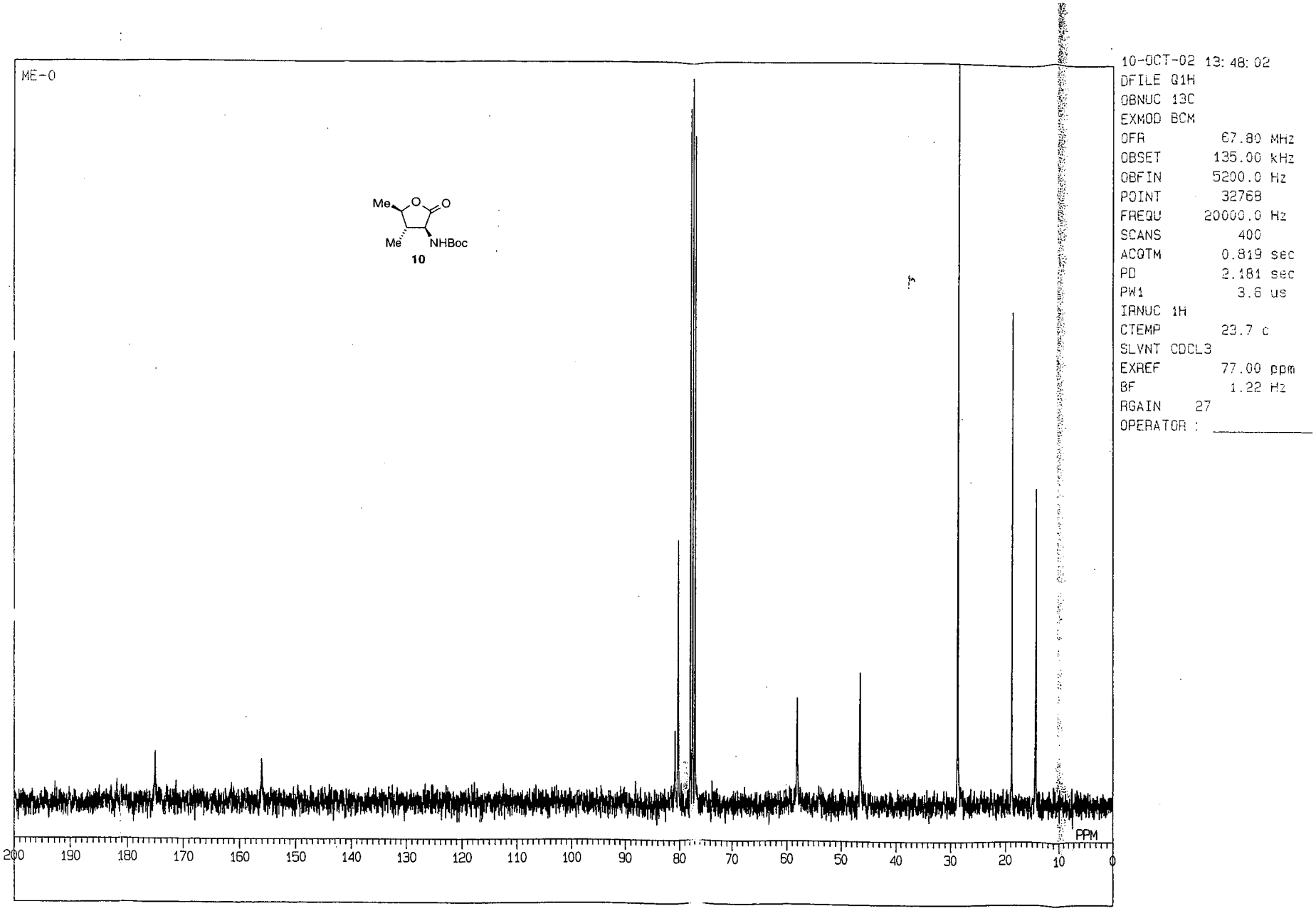

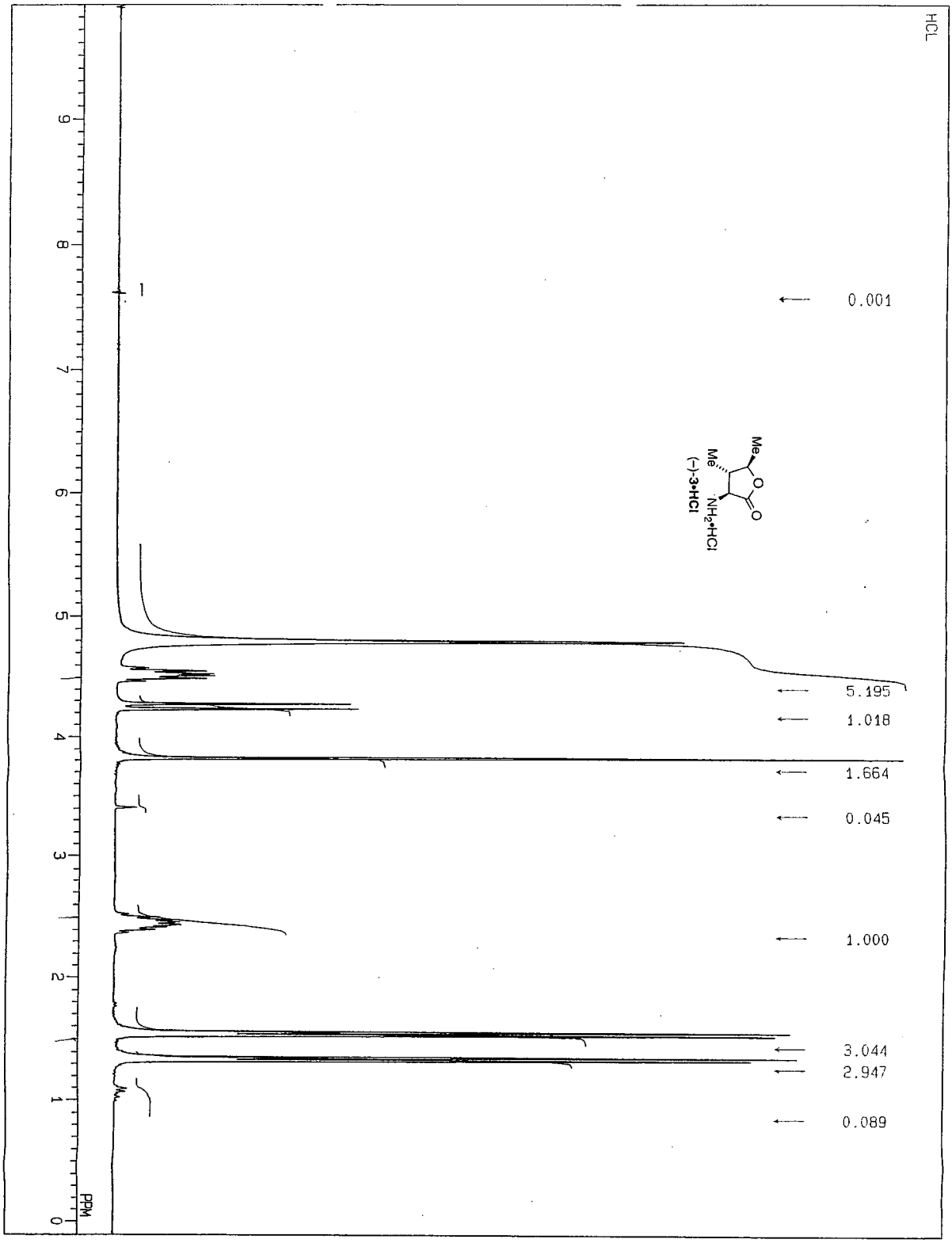

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SCANS 16
ACQTM 3.031 sec
PD 3.969 sec
PW1 4.9 us
IRNUC 1H
CTEMP 26.9 c
SLVNT D2O
EXREF 4.79 ppm
BF 0.16 Hz
RGAIN 15
OPERATOR : _____

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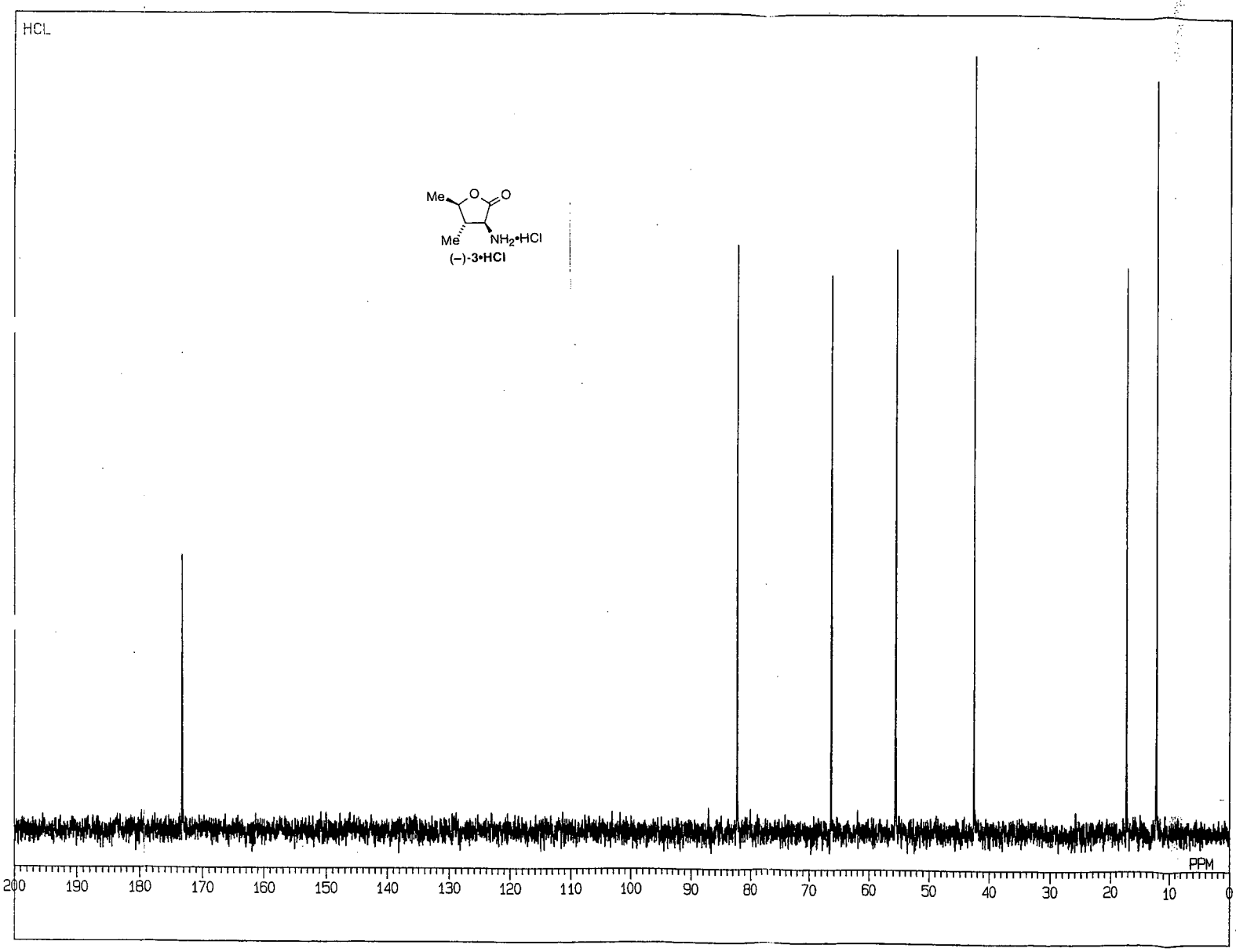
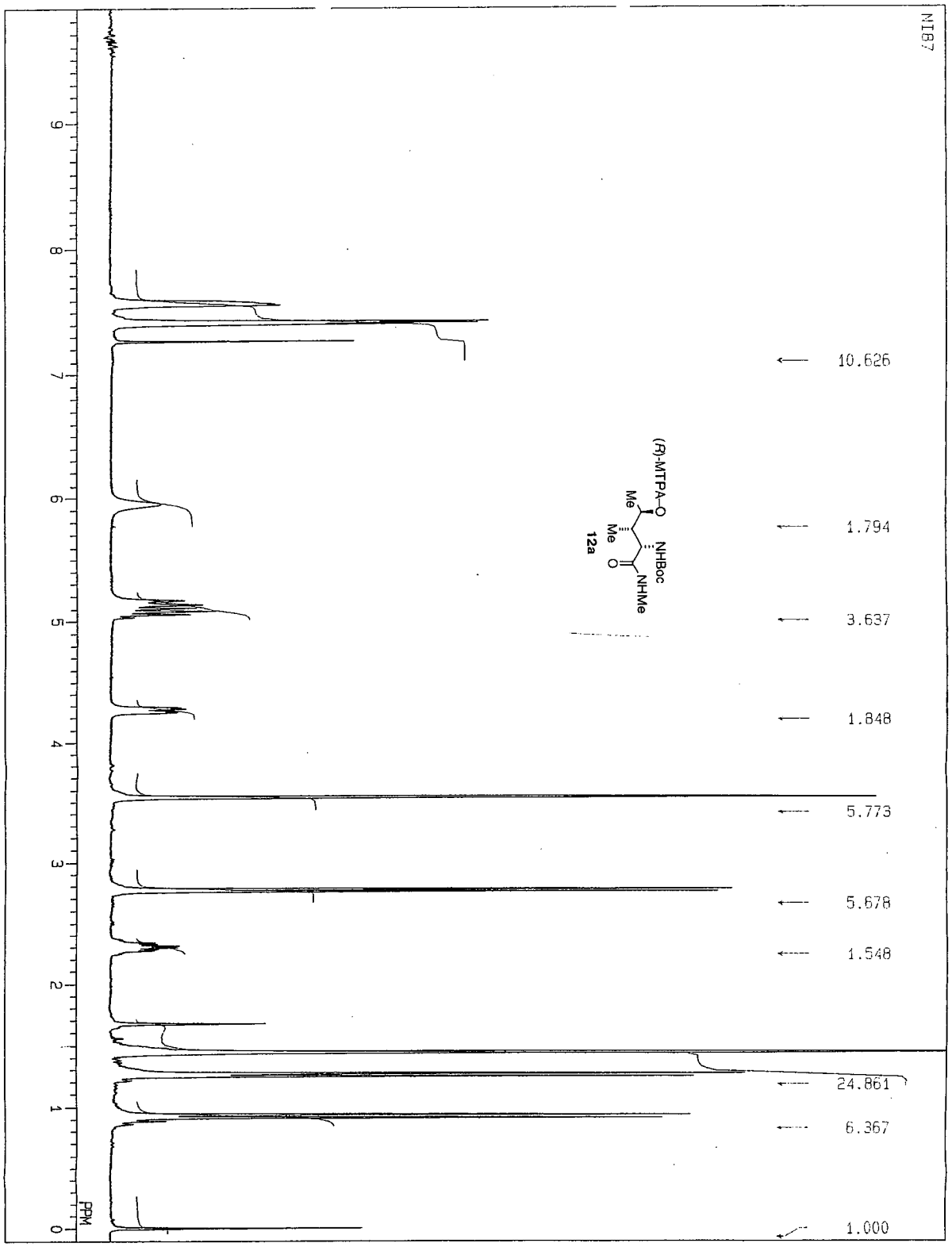
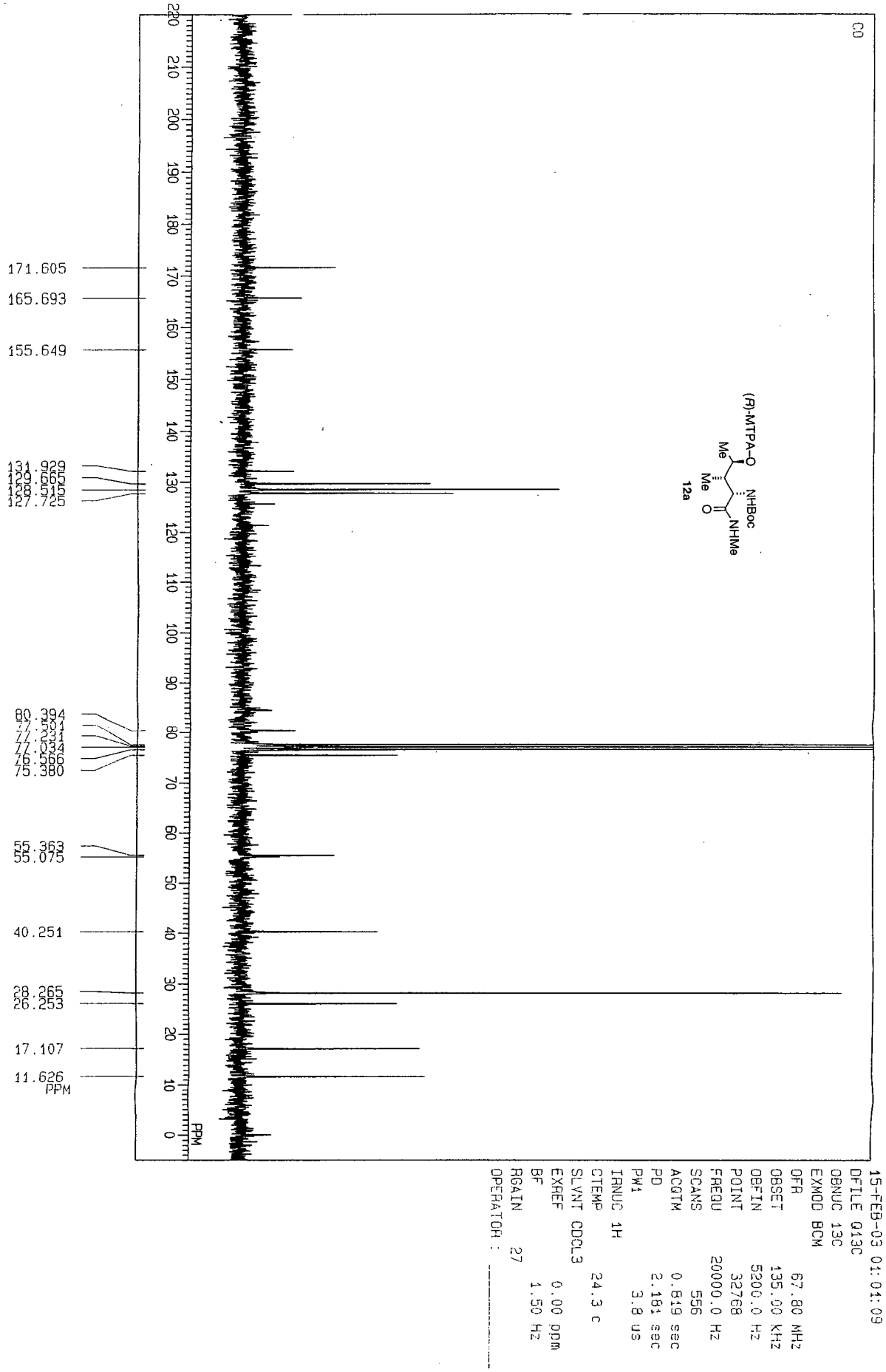
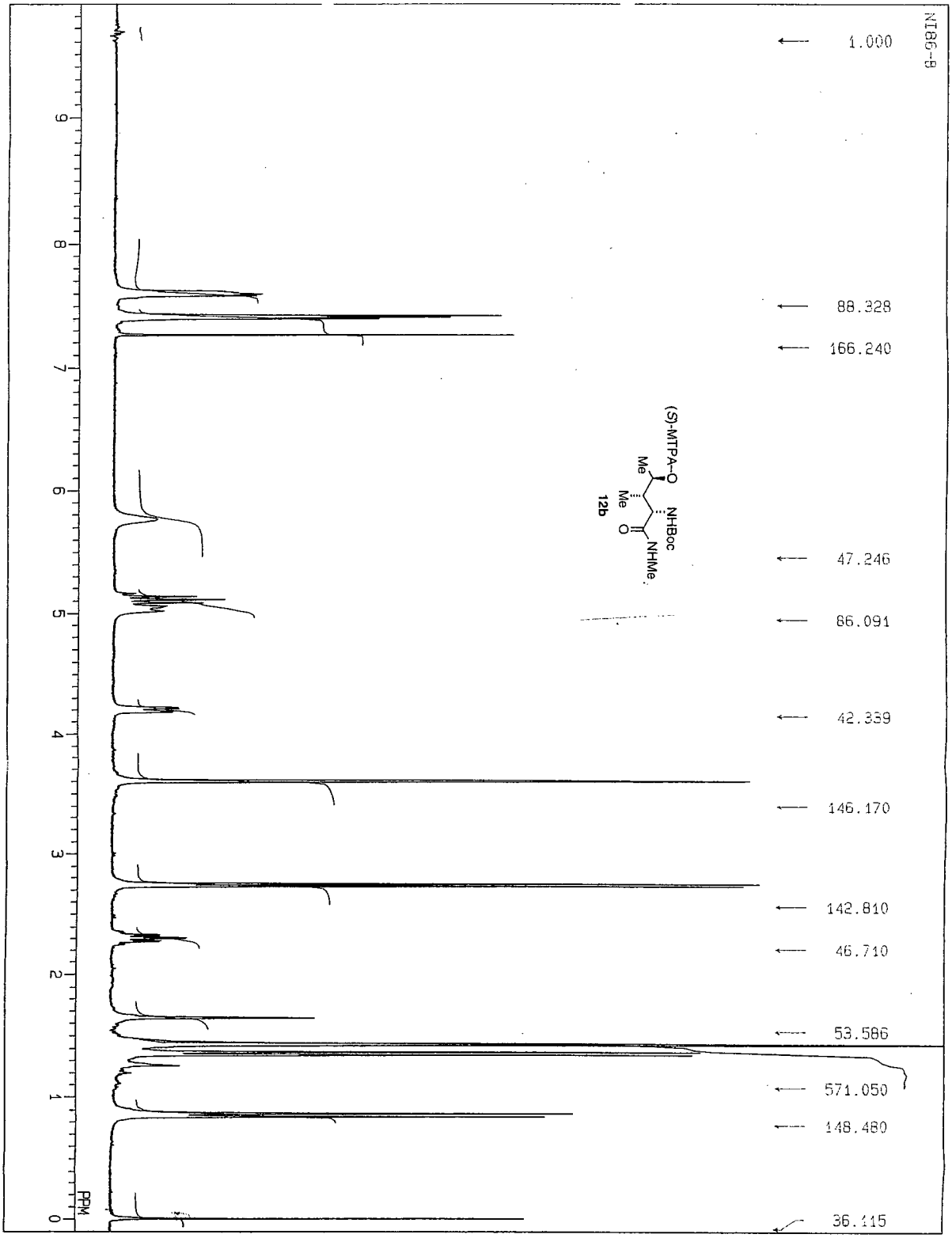


13-NOV-02 14:25:53
DFILE Q1H
OBNUC 13C
EXMOD BCM
OFR 67.80 MHz
OBSET 135.00 kHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 20000.0 Hz
SCANS 400
ACQTM 0.819 sec
PD 2.181 sec
PW1 3.6 us
IRNUC 1H
CTEMP 27.6 c
SLVNT D2O
EXREF 66.50 ppm
BF 1.22 Hz
RGAIN 28
OPERATOR : _____

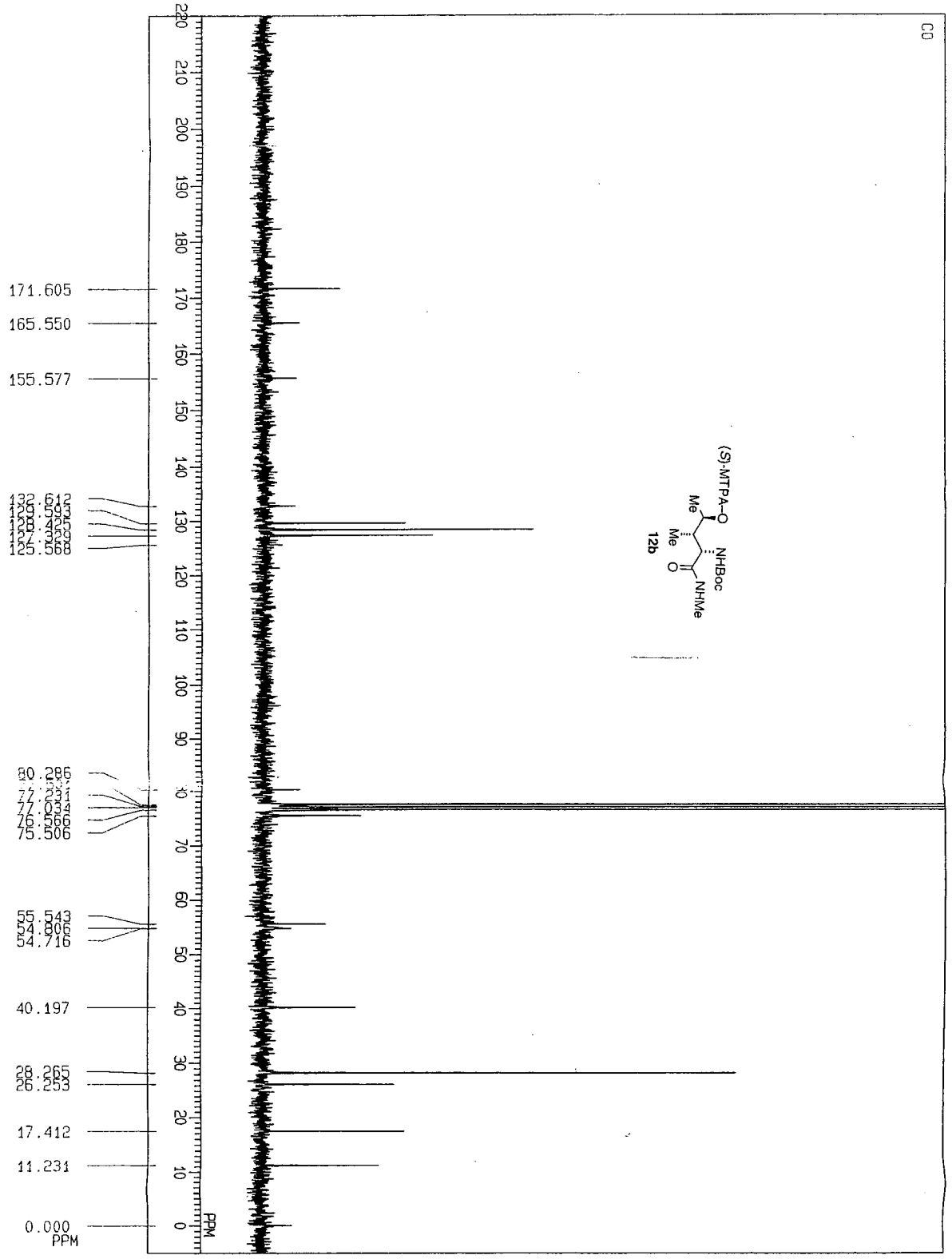


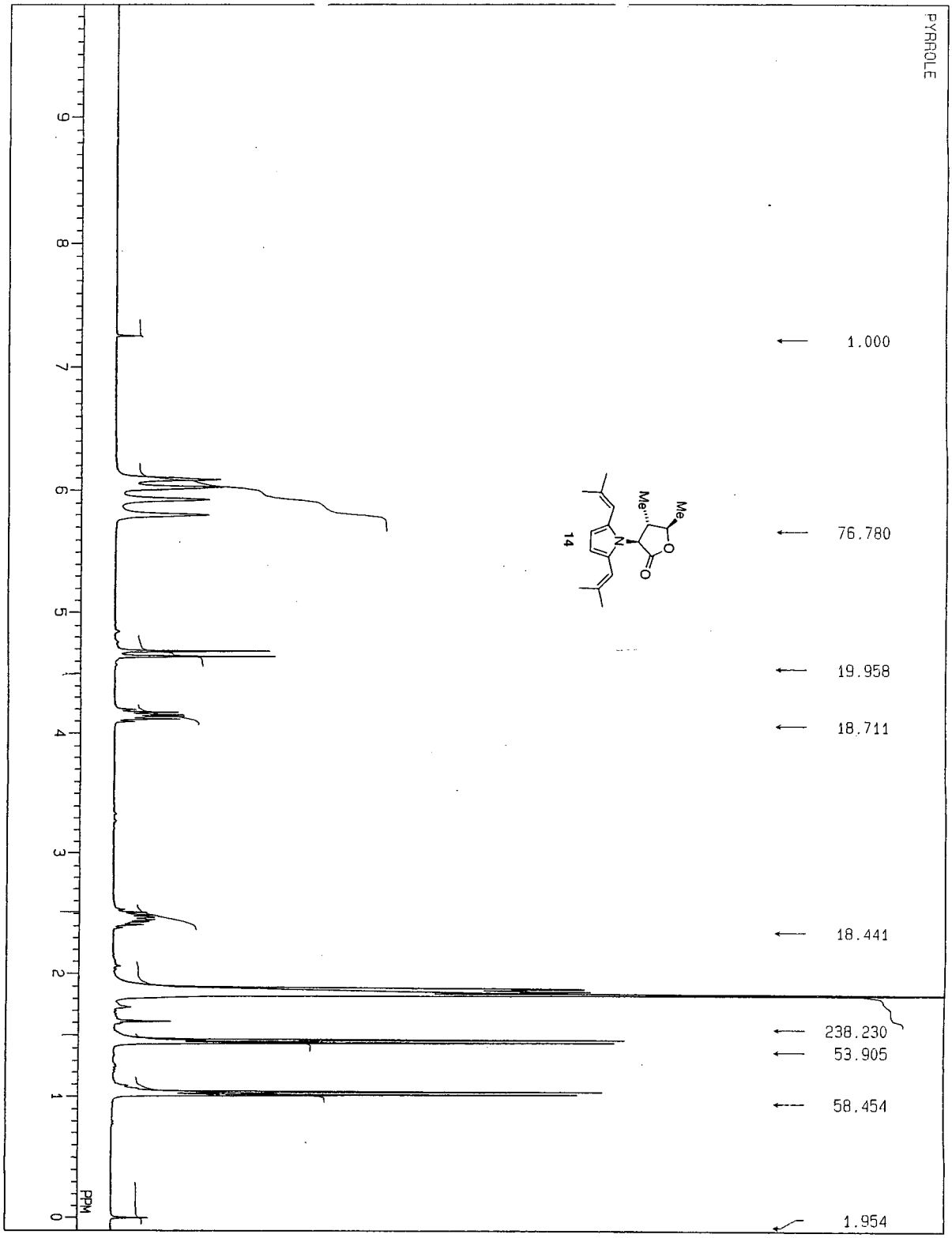
09-MAR-02 12:22:30
DFILE GIH
OBNUC 1H
EXMOD NOM
OFR 270.05 MHz
OBSET 112.00 kHz
OBFIN 5800.0 Hz
POINT 32768
FREQU 5405.4 Hz
SCANS 16
ACQTM 3.031 sec
PD 3.969 sec
PW1 4.9 us
TRNUC 1H
CTEMP 26.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.16 Hz
RGAIN 18
OPERATOR :


CO
(R)-MTPA-O
NHBoc
NHMe
Me
Me
O
12a
171.605
165.693
155.649
131.929
129.665
128.515
127.725
80.394
77.501
77.231
77.034
76.566
75.380
55.363
55.075
40.251
28.265
26.253
17.107
11.626
PPM
15-FEB-03 01:01:09
DFILE G13C
OBNUC 13C
EXMOD BCM
OFR 67.80 MHz
OBSET 135.00 kHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 20000.0 Hz
SCANS 556
ACQTM 0.819 sec
PD 2.181 sec
PW1 3.8 us
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.50 Hz
RGAIN 27
OPERATOR :



06-MAR-02 13:05:21
DFILE G4H
DEUNUC 1H
EXMOD NON
OFR 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.0 Hz
POINT 32768
FREQU 5405.4 Hz
SCANS 16
ACQTM 3.031 sec
PD 3.969 sec
PW1 4.9 us
IRNUC 1H
CTEMP 25.3 C
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.16 Hz
RGAIN 19
OPERATOR :


CO
(S)-MTPA-O
NHBoc
NHMe
Me
Me
O
12b
171.605
165.550
155.577
132.612
129.593
128.425
127.320
125.568
80.286
77.031
77.024
76.566
75.506
55.543
54.806
54.716
40.197
28.265
26.253
17.412
11.231
0.000
PPM
25-JAN-03 02:04:46
DFILE Q13C
OBNUC 13C
EXMOD BCM
OFR 67.80 MHz
OBSET 135.00 kHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 20000.0 Hz
SCANS 1200
ACQTM 0.819 sec
PD 2.181 sec
PW1 3.8 us
IRNUC 1H
CTEMP 24.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.50 Hz
RGAIN 28
OPERATOR :



31-OCT-02 17:12:14
DFILE Q1H
OBNUC 1H
EXMOD NON
OFR 270.05 MHz
OBSET 112.00 kHz
OBFIN 5600.0 Hz
POINT 32768
FREQU 5405.4 Hz
SCANS 16
ACQTM 3.031 sec
PD 3.969 sec
PW1 4.9 us
IRNUC 1H
CTEMP 23.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.16 Hz
RGAIN 13
OPERATOR :

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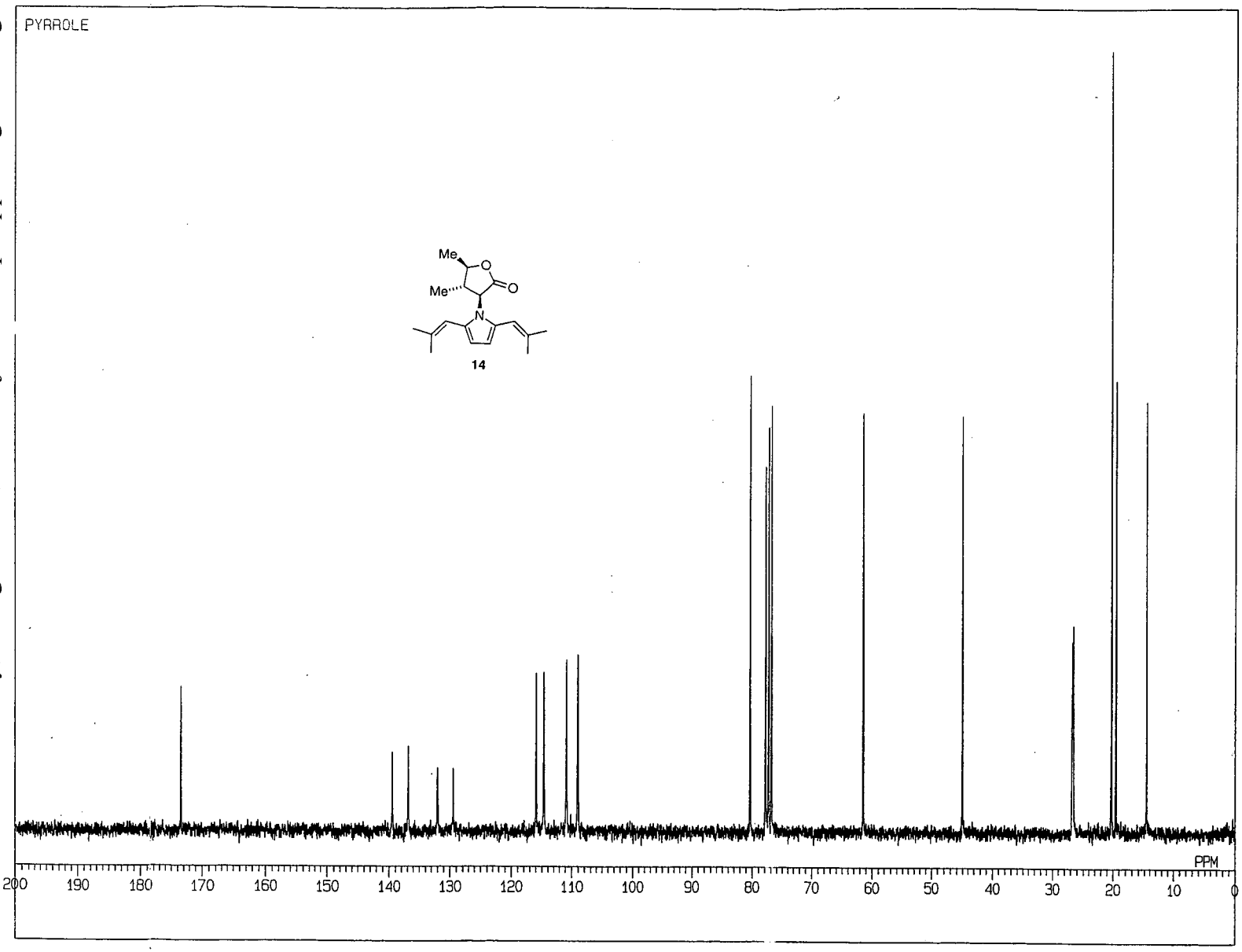
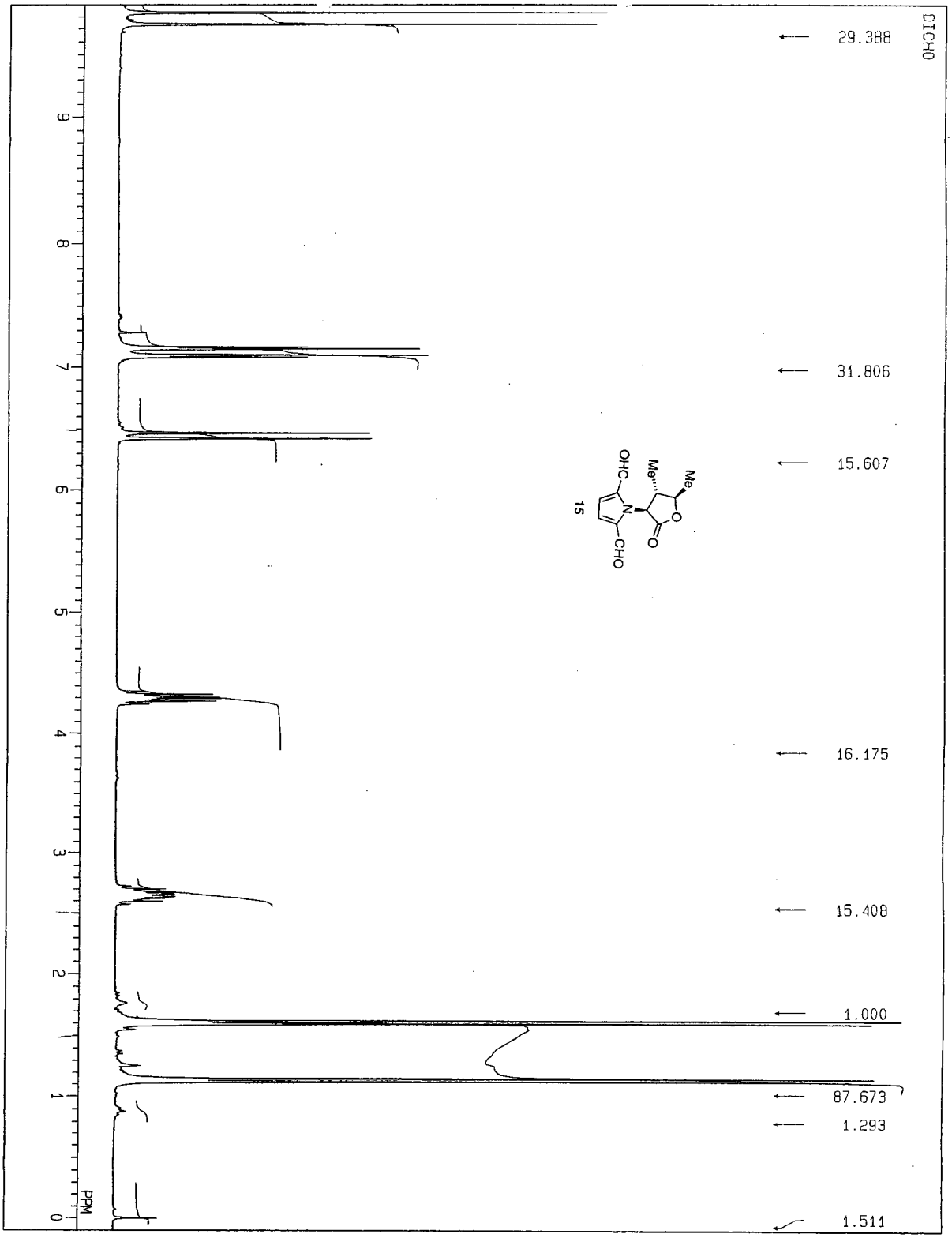


31-OCT-02 17:03:31
DFILE Q1H
OBNUC 13C
EXMOD BCM
OFR 67.80 MHz
OBSET 135.00 kHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 20000.0 Hz
SCANS 400
ACQTM 0.819 sec
PD 2.181 sec
PW1 3.6 us
IRNUC 1H
CTEMP 23.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.22 Hz
RGAIN 27
OPERATOR : _____



31-OCT-02 14:31:21
DFILE Q1H
OBNUC 1H
EXMOD NON
OFR 270.05 MHz
OBSET 112.00 kHz
OBFIN 5800.0 Hz
POINT 32768
FREQU 5405.4 Hz
SCANS 16
ACQTM 3.031 sec
PD 3.969 sec
PW1 4.9 us
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.16 Hz
RGAIN 15
OPERATOR :

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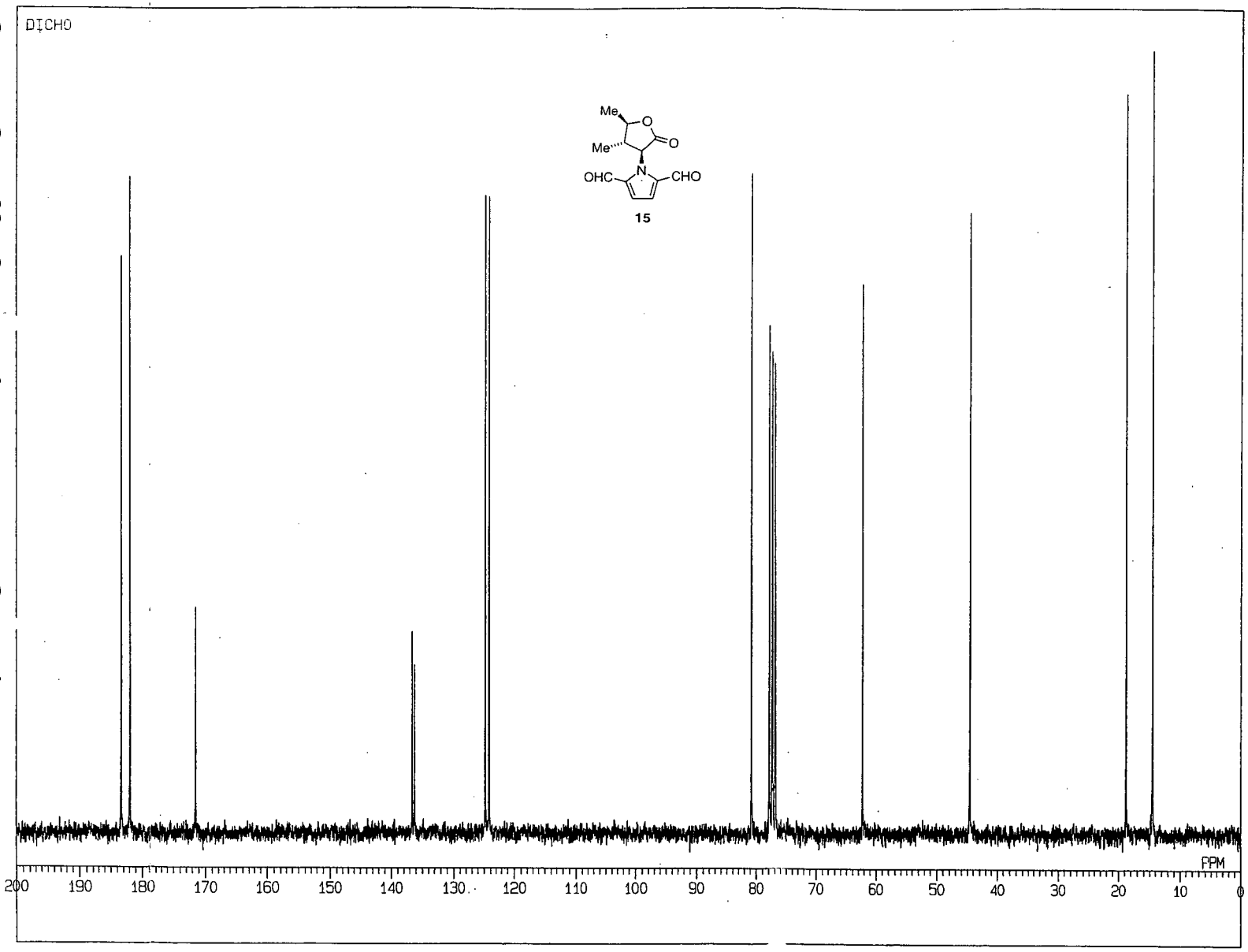
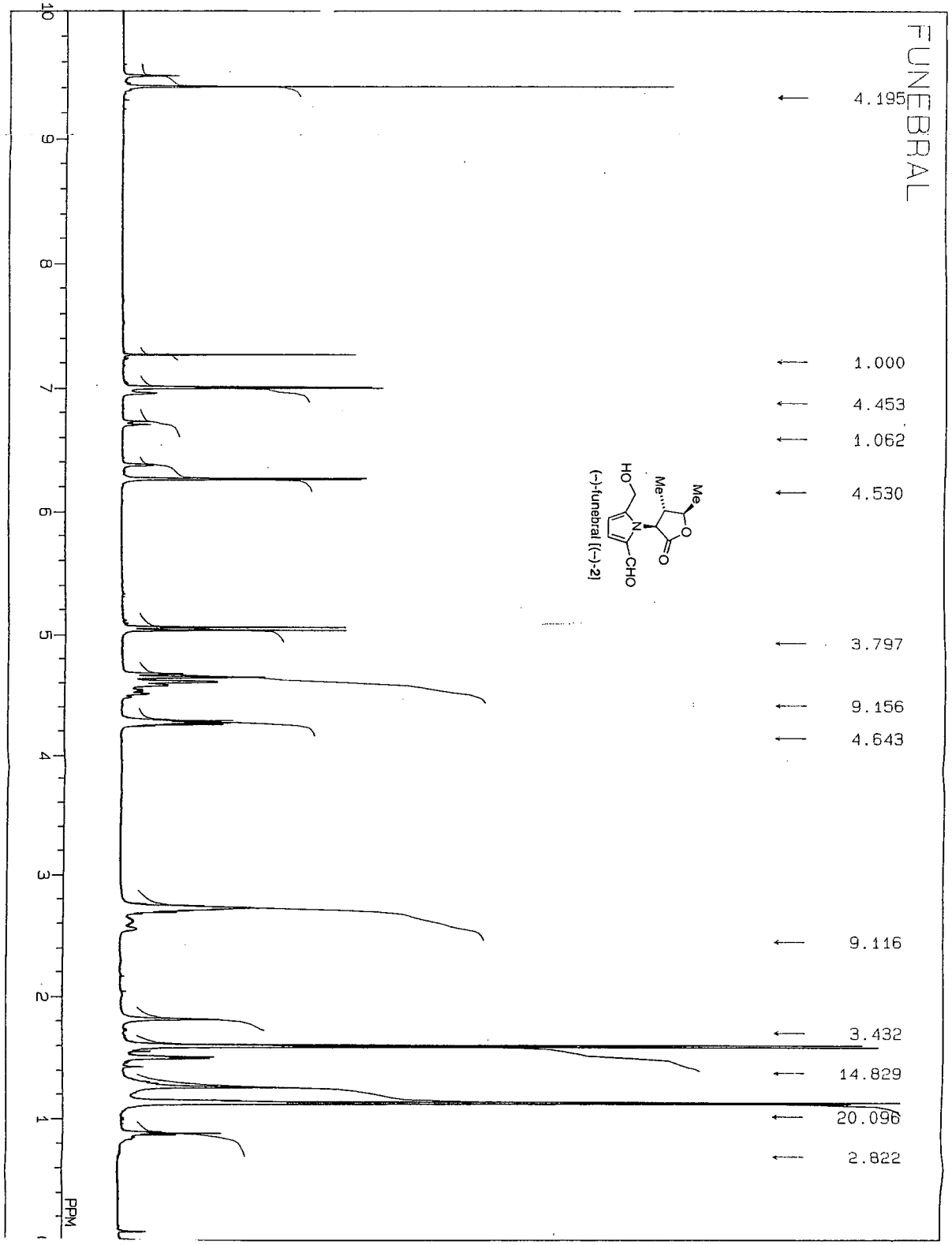


31-OCT-02 14:22:05
DFILE G1H
OBNUC 13C
EXMOD BCM
OFR 67.80 MHz
OBSET 135.00 kHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 20000.0 Hz
SCANS 400
ACQTM 0.819 sec
PD 2.181 sec
PW1 3.6 us
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.22 Hz
RGAIN 27
OPERATOR : _____

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30-OCT-02 11:06:34
DFILE DU1:
COMNT FUNEBRAL
EXMOD SGNON
OBNUC 1H
OBFIN        10300.0 Hz
POINT           32768
FREQU         8000.0 Hz
SCANS             16
ACQTM          2.048 se
PD             1.000 se
PW1              4.0 us
IRFIN        10157.0 Hz
IRATN             500
IRAPW              50 us
TEMP.        22.0 c
SLVNT CDCL3
EXREF            0.00 pp
BF               0.20 Hz
RGAIN              18
XE           5001.6000 Hz
XS          -116.5225 Hz
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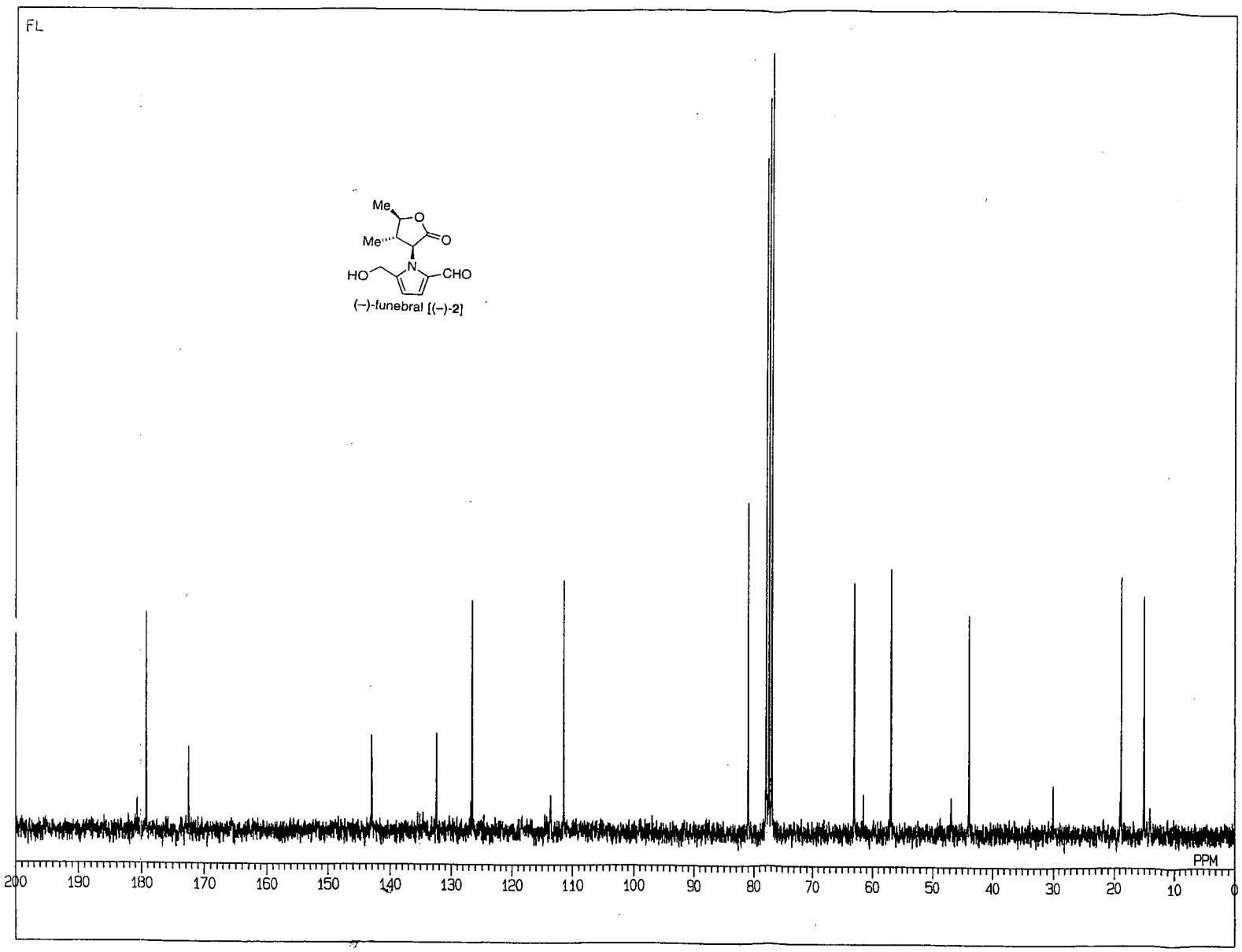
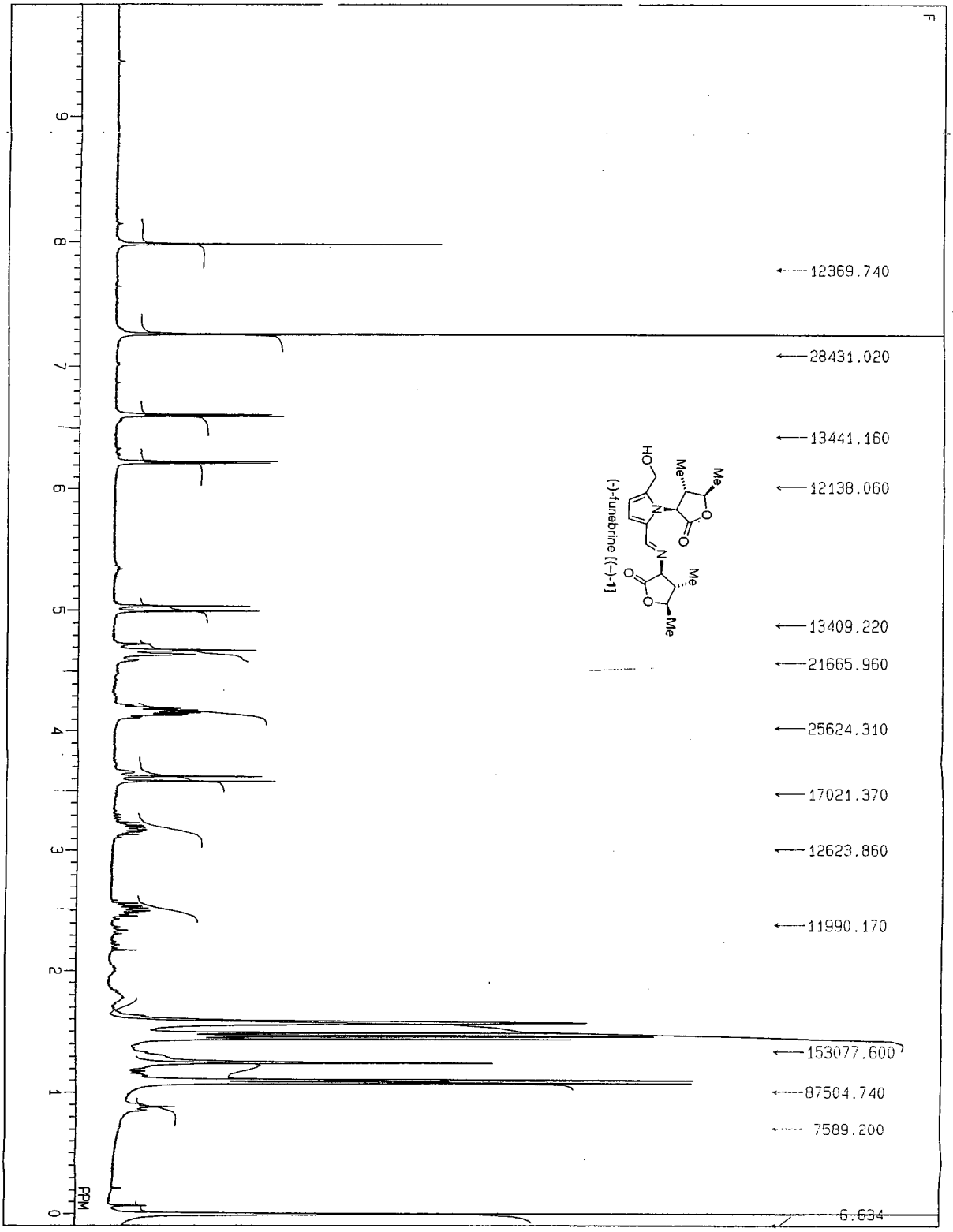


01-NOV-02 12:38:24
DFILE Q1H
OBNUC 13C
EXMOD BCM
OFR 67.80 MHz
OBSET 135.00 kHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 20000.0 Hz
SCANS 640
ACQTM 0.819 sec
PD 2.181 sec
PW1 3.6 us
IRNUC 1H
CTEMP 24.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.22 Hz
RGAIN 27
OPERATOR : _____

C21



15-OCT-02 12:29:44
DFILE Q1H
OBNUC 1H
EXMOD NON
DFR 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.0 Hz
POINT 32768
FREQU 5405.4 Hz
SCANS 256
ACQTM 3.031 sec
PD 3.969 sec
PW1 4.9 us
IRNUC 1H
CTEMP 21.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.16 Hz
RGAIN 27
OPERATOR :

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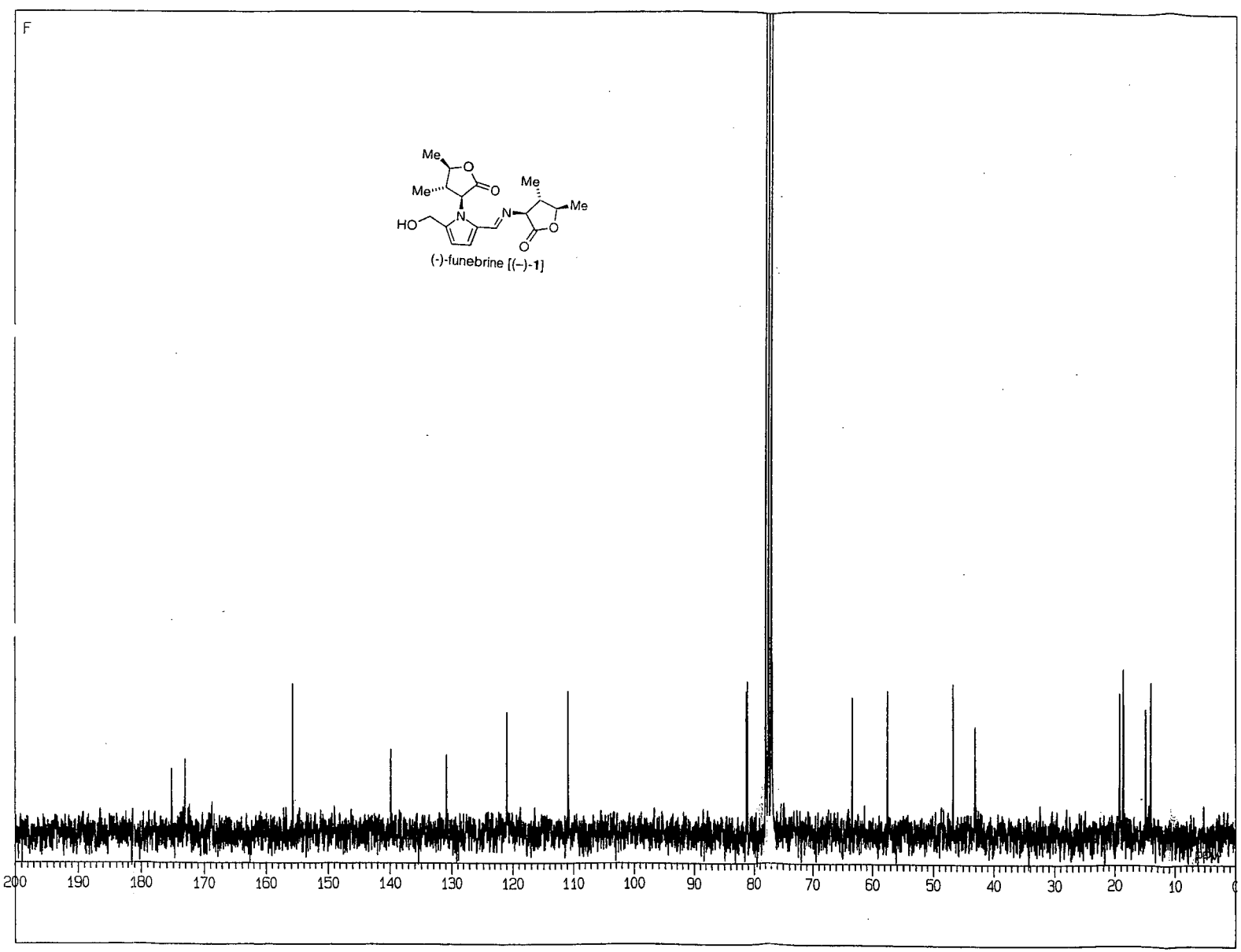

26-NOV-02 21:26:38
DFILE G1H
OBNUC 13C
EXMOD BCM
OFR 67.80 MHz
OBSET 135.00 kHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 20000.0 Hz
SCANS 512
ACQTM 0.819 sec
PD 2.181 sec
PW1 3.6 us
IRNUC 1H
CTEMP 27.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.22 Hz
RGAIN 28
OPERATOR :