

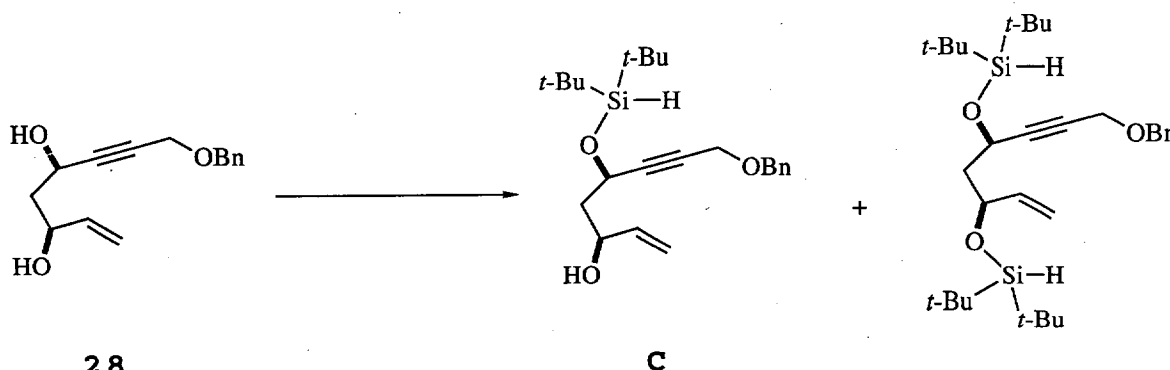
SUPPORTING INFORMATION

Applications of 5-endo-trigonal cyclization: Construction of compounds relevant to the synthesis of prostaglandins and methyl *epi*-jasmonate.

By Mousumi Sannigrahi, Darrin L. Mayhew, and Derrick L. J. Clive*

Chemistry Department, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

(3*R, 5*S**)-(±)-5-[[[Bis(1,1-dimethylethyl)]silyl]oxy]-8-(phenylmethoxy)-1-octen-6-yn-3-ol (C) and (3*R**, 5*S**)-(±)-[Bis(1,1-dimethylethyl)][[5-[[bis(1,1-dimethylethyl)-silyl]oxy]-8-(phenylmethoxy)-1-octen-6-yn-3-yl]oxy]silane.**

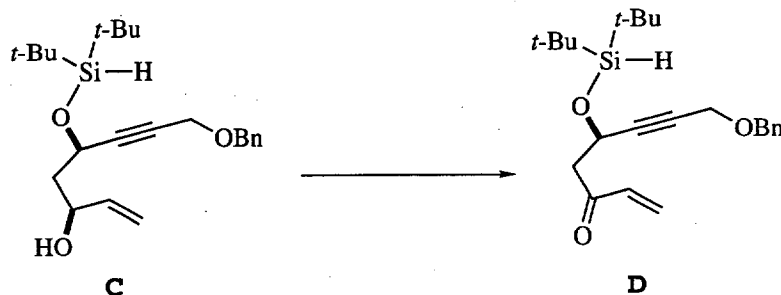


Imidazole (496.3 mg, 7.29 mmol) and *t*-Bu₂SiHCl (0.92 mL, 4.56 mmol) were added consecutively to a stirred solution of **28** (1.043 g, 3.65 mmol) in dry THF (30 mL). After 20 min, water (30 mL) was added and the mixture was extracted with EtOAc until extraction was complete (TLC control, silica, 1:3 EtOAc-hexane). The combined organic extracts were washed with brine, dried (MgSO₄), and evaporated. Flash chromatography of the residue over silica gel (3 x 19 cm), using first 1:19 EtOAc-hexane, and then 1:1

EtOAc-hexane, gave **C** (1.124 g, 79%, 91% based on recovered starting material), the doubly silylated material (91.3 mg, 4%), and starting material (**28**) (263.1 mg) as colorless oils. Compound **C** had: FTIR (CH₂Cl₂ cast) 2096, 3450 cm⁻¹; ¹H NMR (CD₂Cl₂, 300 MHz) δ 1.30 (s, 9 H), 1.50 (s, 9 H), 1.92 (t, J = 6.0 Hz, 2 H), 2.76 (d, J = 3.5 Hz, 1 H), 4.16 (s, 1 H), 4.22 (d, J = 2.0 Hz, 2 H), 4.48-4.65 (m, 3 H), 4.80-4.88 (m, 1 H), 5.11 (dt, J = 10.5, 1.8 Hz, 1 H), 5.29 (dt, J = 17.5, 1.9 Hz, 1 H), 5.82-5.97 (m, 1 H), 7.20-7.42 (m, 5 H); irradiation at δ 4.22 caused the multiplet at δ 4.84 to collapse to a triplet (J = 5.5 Hz); ¹³C NMR (CDCl₃, 50.3 MHz) δ 19.5 (s'), 20.1 (s'), 27.2 (q'), 27.6 (q'), 45.0 (t'), 57.2 (t'), 65.0 (d'), 70.7 (d'), 71.4 (t'), 81.9 (s'), 86.6 (s'), 114.5 (t'), 127.8 (d'), 128.0 (d'), 128.4 (d'), 137.4 (s'), 140.3 (d'); exact mass m/z calcd for C₁₅H₁₉O₃Si (M - C₈H₁₇) 275.1104, found 275.1105.

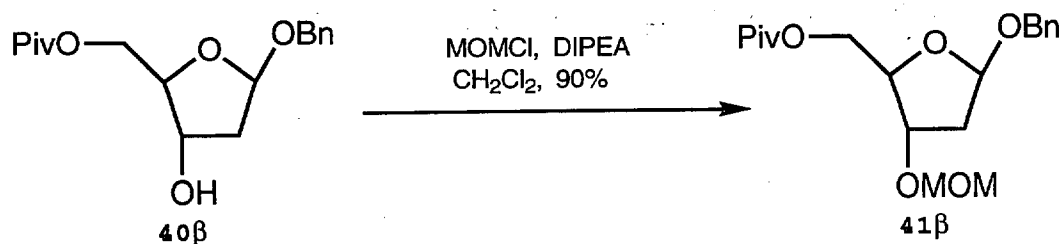
The doubly silylated compound had: FTIR (CH₂Cl₂ cast) 2092 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 0.89-1.10 (m, 36 H), 1.78-1.89 (m, 1 H), 2.04-2.13 (m, 1 H), 4.05 (s, 1 H), 4.15 (s, 1 H), 4.23 (s, 2 H), 4.41-4.49 (m, 1 H), 4.60 (s, 2 H), 4.66-4.72 (m, 1 H), 5.10 (dt, J = 10.2, 1.2 Hz, 1 H), 5.18 (dt, J = 17.4, 2.0 Hz, 1 H), 5.79 (ddd, J = 17.0, 11.1, 10.9 Hz, 1 H), 7.25-7.38 (m, 5 H); ¹³C NMR (CDCl₃, 50.3 MHz) δ 19.7 (s'), 19.9 (s'), 20.0 (s'), 20.2 (s'), 27.3 (q'), 27.4 (q'), 47.1 (t'), 57.3 (t'), 63.6 (d'), 71.3 (t'), 73.9 (d'), 81.4 (s'), 87.4 (s'), 115.4 (t'), 127.8 (d'), 128.1 (d'), 128.4 (d'), 137.6 (s'), 140.2 (d'). Anal. Calcd for C₃₁H₅₄O₃Si₂: C, 70.13; H, 10.25. Found: C, 70.03; H, 10.42.

(±)-5-[Bis[(1,1-dimethylethyl)silyl]oxy]-8-(phenyl-methoxy)-1-octen-6-yn-3-one (D).



Molecular sieves (4Å, 35 mg) and PCC (106 mg, 0.49 mmol) were added consecutively to a stirred solution of **C** (95.4 mg, 0.25 mmol) in dry CH₂Cl₂ (5 mL). After 6 h, the brown mixture was filtered through a pad (2 x 2 cm) of silica gel, the desired compound being eluted with 1:1 EtOAc-hexane (TLC control, silica, 1:4 EtOAc-hexane). Evaporation of the filtrate and flash chromatography of the residue over silica gel (2 x 17 cm), using 1:9 EtOAc-hexane, gave ketone **D** (52.9 mg, 56%) as a colorless oil: FTIR (CH₂Cl₂ cast) 1687, 2102 cm⁻¹; ¹H NMR (CD₂Cl₂, 400 MHz) δ 1.00 (s, 9 H), 1.10 (s, 9 H), 2.95 (dd, *J* = 15.8, 5.8 Hz, 1 H), 3.17 (dd, *J* = 15.8, 7.3 Hz, 1 H), 4.16 (s, 1 H), 4.20 (d, *J* = 1.5 Hz, 2 H), 4.46 (s, 2 H), 5.05-5.10 (m, 1 H), 5.90 (dd, *J* = 10.6, 1.0 Hz, 1 H), 6.25 (dd, *J* = 17.7, 1.0 Hz, 1 H), 6.40 (dd, *J* = 17.7, 10.6 Hz, 1 H), 7.27-7.39 (m, 5 H); ¹³C NMR (CDCl₃, 50.3 MHz) δ 19.6 (s'), 20.0 (s'), 27.2 (q'), 47.8 (t'), 57.2 (t'), 62.3 (d'), 71.3 (t'), 81.2 (s'), 86.6 (s'), 127.8 (d'), 128.1 (d'), 128.4 (d'), 129.0 (t'), 137.0 (d'), 137.4 (s'), 197.1 (s'); exact mass *m/z* calcd for C₁₉H₂₅O₃Si (M - C₄H₉) 329.1573, found 329.1571.

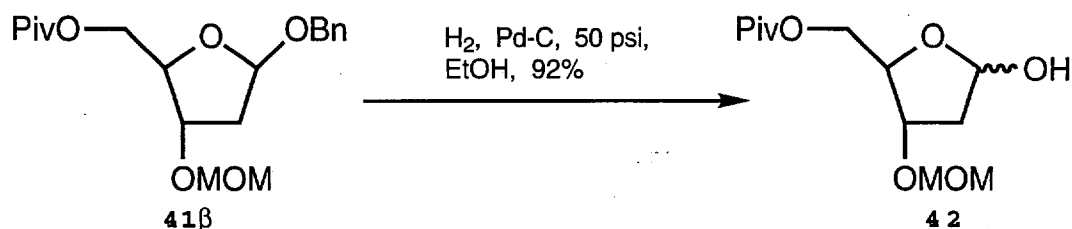
Phenylmethyl 2-Deoxy-5-O-(2,2-dimethylpropanoyl)-3-O-(methoxymethyl)- β -D-erythro-pentofuranoside (41 β).



i-Pr₂NEt (0.12 mL, 0.71 mmol) was added dropwise to a stirred and cooled (0 °C) solution of alcohol **40β** (72.8 mg, 2.63 mmol) in CH₂Cl₂ (5.0 mL). After 15 min, CH₃OCH₂Cl (0.90 mL, 57.09 mmol, 0.71 mmol) was added dropwise over 5 min, and stirring was continued for 1 h. The cold bath was removed, stirring was continued for 12 h, and the mixture was diluted with water (10.0 mL) and extracted with CH₂Cl₂. The combined organic extracts were washed with brine, dried (MgSO₄) and evaporated. Flash chromatography of the residue over silica gel (3 x 20 cm), using 1:4 EtOAc-hexane, gave **41β** (70.4 mg, 90%) as a colorless oil:

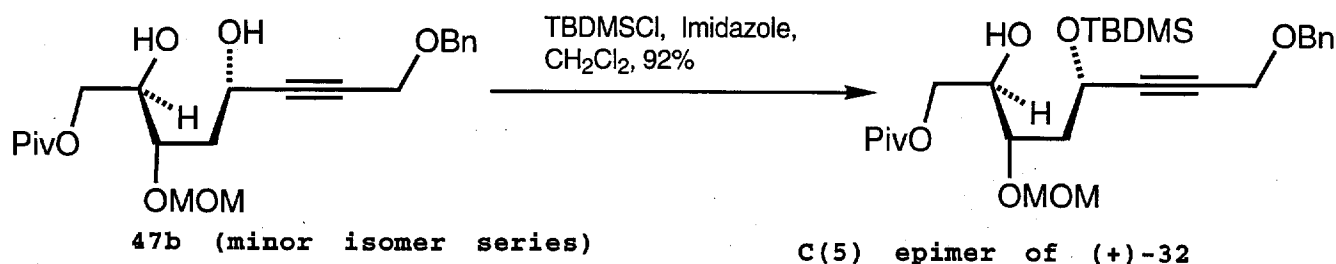
$[\alpha]^{25}_D = -47.8^\circ$ (c 0.93, MeOH); FTIR (CH_2Cl_2 cast) 1731 cm^{-1} ; ^1H NMR (CD_2Cl_2 , 400 MHz) δ 1.21 (s, 9 H), 2.15 (dt, $J = 13.5, 5.7\text{ Hz}$, 1 H), 2.35 (ddd, $J = 13.5, 7.0, 1.9\text{ Hz}$, 1 H), 3.30 (s, 3 H), 4.10–4.20 (m, 3 H), 4.20–4.25 (m, 1 H), 4.44 (d, $J = 11.7\text{ Hz}$, 1 H), 4.60 (s, 2 H), 4.74 (d, $J = 11.7\text{ Hz}$, 1H), 5.27 (dd, $J = 5.4, 1.9\text{ Hz}$, 1 H), 7.20–7.40 (m, 5 H); ^{13}C NMR (CD_2Cl_2 , 50.3 MHz) δ 27.3 (q'), 39.0 (s'), 40.0 (t'), 55.6 (q'), 65.5 (t'), 69.6 (t'), 78.1 (d'), 82.4 (d'), 96.3 (t'), 104.0 (d'), 127.9 (d'), 128.3 (d'), 128.7 (d'), 138.4 (s'), 178.4 (s'); exact mass (HR electrospray) m/z calcd for $\text{C}_{19}\text{H}_{28}\text{NaO}_6$ ($M + \text{Na}$) 375.1784, found 375.1784.

Phenylmethyl 2-Deoxy-5-O-(1,1-dimethylpropanoyl)-3-O-(methoxymethyl)- α/β -D-erythro-pentofuranose (42).



5% Pd-C (10 mg) was added to a solution of **41 β** (535.0 mg, 0.1519 mmol) in EtOH (95%, 10 mL), and the mixture was shaken in a Parr bottle under H_2 (50 psi) until all the starting material was consumed (ca 12 h, TLC control, silica gel, 2:3 EtOAc-hexane, the apparatus being opened periodically for examination by TLC. The mixture was filtered through a pad of silica gel (1 x 2 cm), using EtOAc (50 mL). Evaporation of the filtrate and flash chromatography of the residue over silica gel (2.0 x 10 cm), using 3:2 EtOAc-hexane, gave **42** (366.3 mg, 92%) as a colorless oil containing both anomers and small amounts of the open-chain isomer. These compounds were used directly in the next step.

(2R,3S,5S)-5-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-2-hydroxy-3-(methoxymethoxy)-8-(phenylmethoxy)-6-octynyl 2,2-Dimethylpropanoate [C(5) epimer of (+)-32].



Imidazole (14.34 mg, 0.211 mmol) and *t*-BuMe₂SiCl (17.5 mg, 0.116 mmol) were added consecutively to a stirred solution of **47b** (42.9 mg, 0.105 mmol) in dry CH₂Cl₂ (2.5 mL). Stirring was continued at room temperature for 10 h, at which point all the starting material had been consumed and the bis-silylated product began to form. The mixture was diluted with water (5 mL) and extracted with EtOAc. The combined organic extracts were washed with water and brine, dried (MgSO₄), and evaporated. Flash chromatography of the residue over silica gel (1.5 x 10.0 cm), using 1:4 EtOAc-hexane, gave the C(5) epimer of (+)-**32** (50.4 mg, 92%) as a colorless oil: $[\alpha]_D^{25} = -17.6^\circ$ (*c* 1.00, MeOH); FTIR (CH₂Cl₂ cast) 1730, 3438 cm⁻¹; ¹H NMR (CD₂Cl₂, 400 MHz) δ 0.14 (s, 3 H), 0.18 (s, 3 H), 0.90 (s, 9 H), 1.20 (s, 9 H), 1.88–1.95 (m, 2 H), 3.15 (d, *J* = 5.0 Hz, 1 H), 3.39 (s, 3 H), 3.80–3.86 (m, 2 H), 4.10–4.20 (m, 4 H), 4.59 (s, 2 H), 4.60–4.64 (m, 1 H), 4.71 (AB q, $\Delta\nu_{AB} = 12.0$ Hz, *J* = 6.7 Hz, 2 H), 7.30–7.40 (m, 5 H); ¹³C NMR (CD₂Cl₂, 100.6 MHz) δ -4.8 (q'), -4.7 (q'), 18.3 (s'), 25.9 (q'), 27.3 (q'), 39.0 (s'), 41.1 (t'), 56.2 (q'), 57.7 (t'), 59.8 (d'), 65.4 (t'), 71.8 (t'), 72.1 (d'), 79.3 (d'), 81.0 (s'), 88.2 (s'), 98.2 (t'), 128.0 (d'), 128.3 (d'), 128.7 (d'), 138.2 (s'), 178.7 (s'); exact mass (HR electrospray) *m/z* calcd for C₂₈H₄₆NaO₇Si (*M* + Na) 545.2911, found 545.2910.

S6

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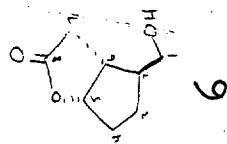
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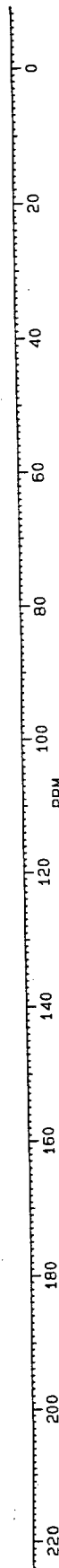
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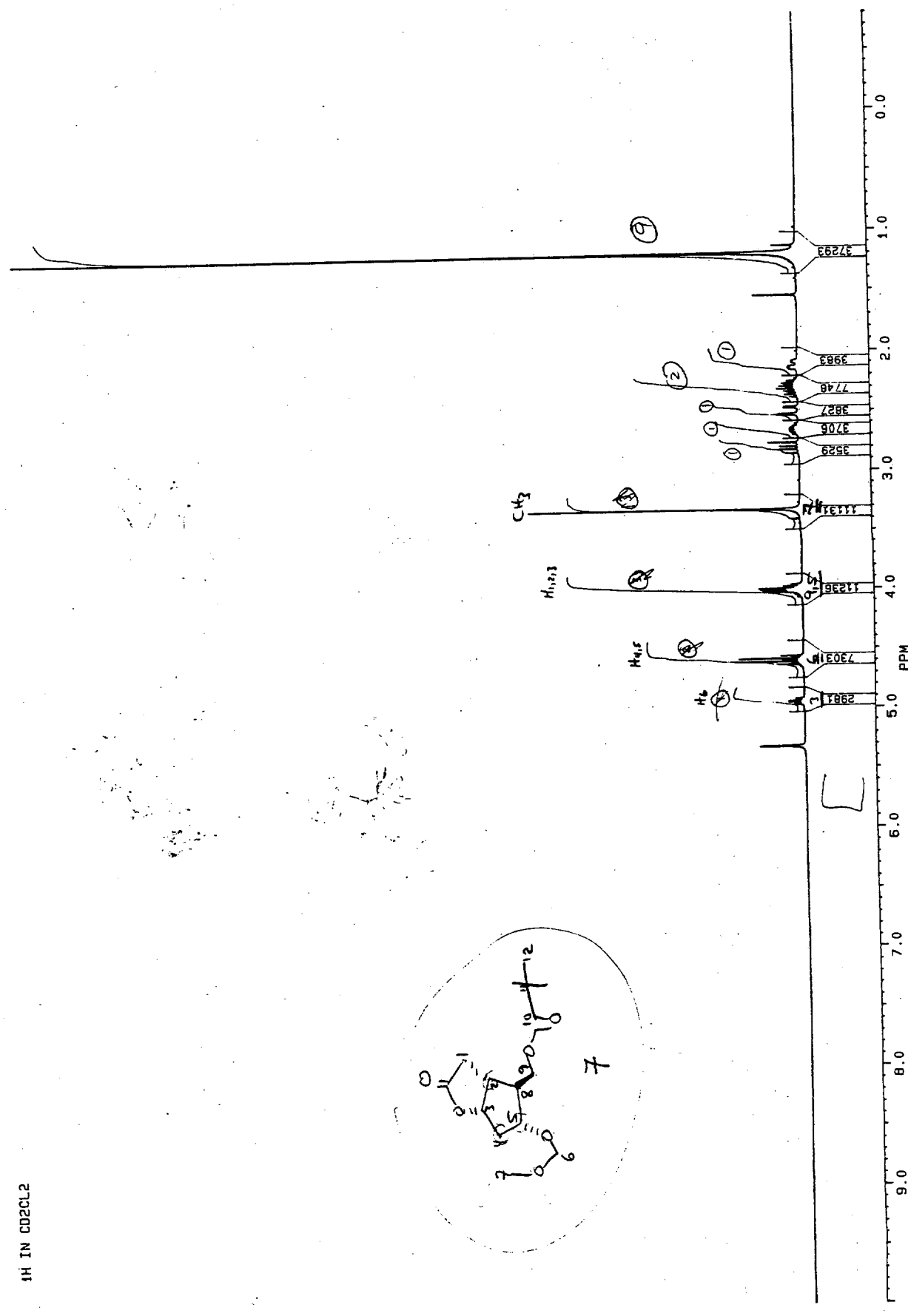
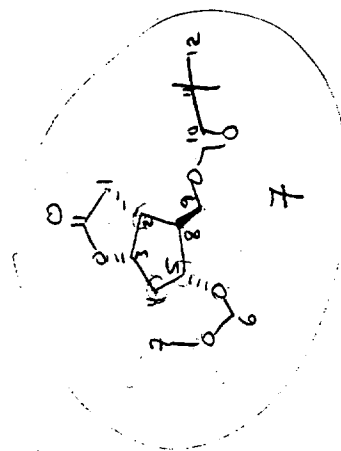


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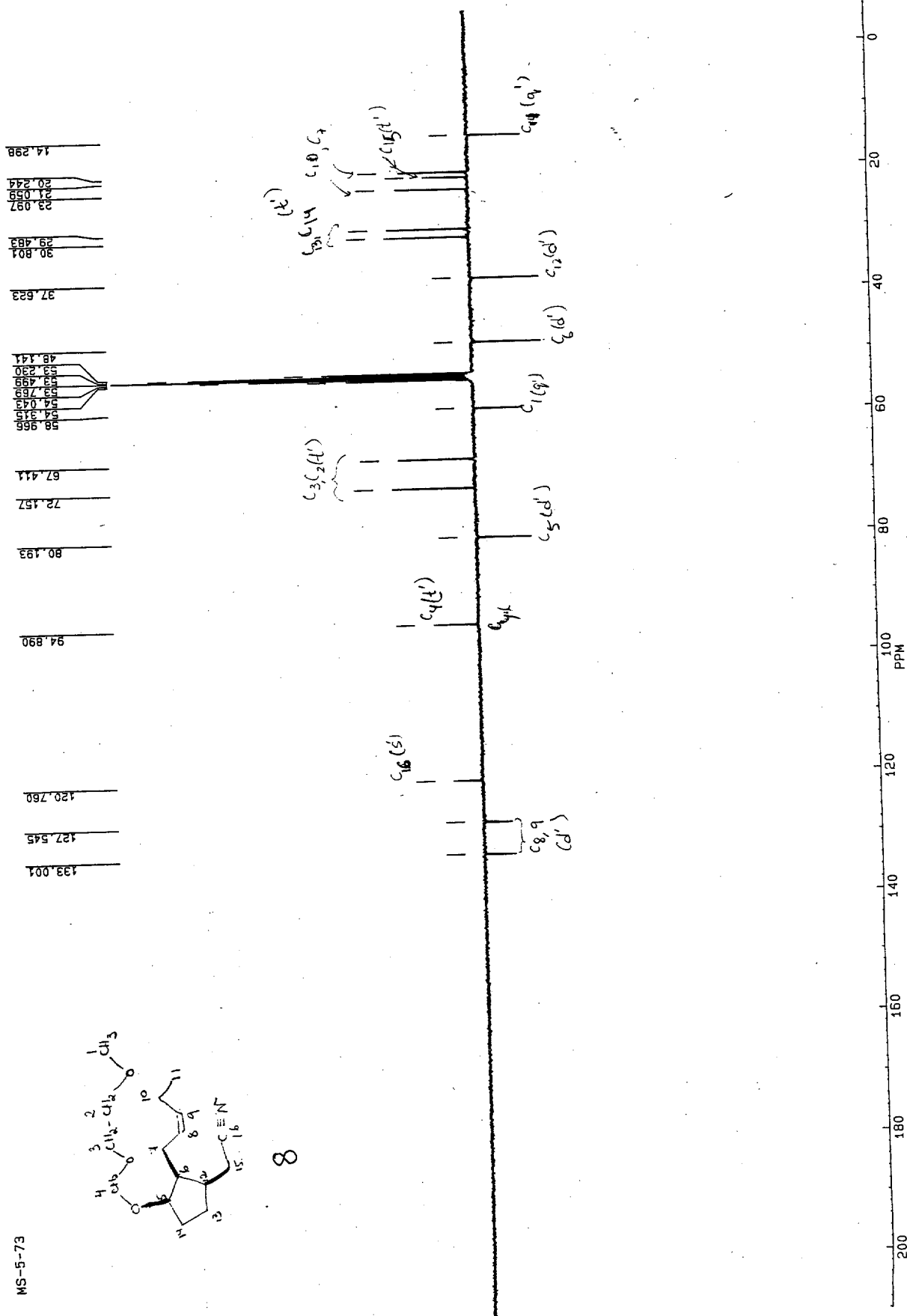
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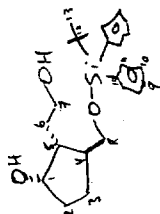




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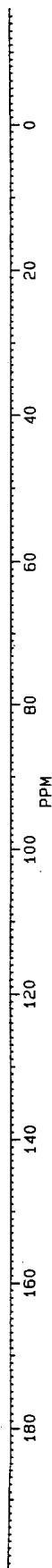
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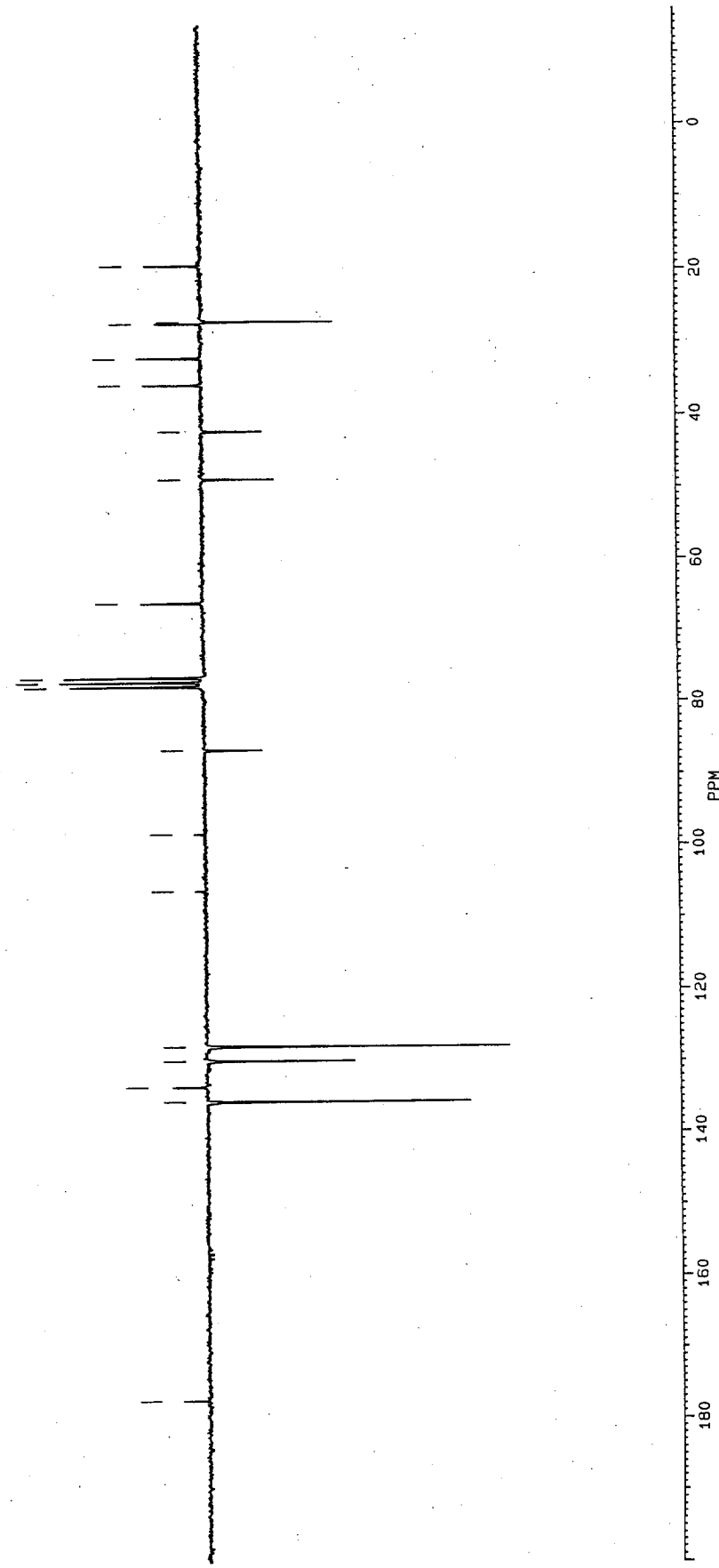
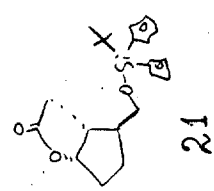
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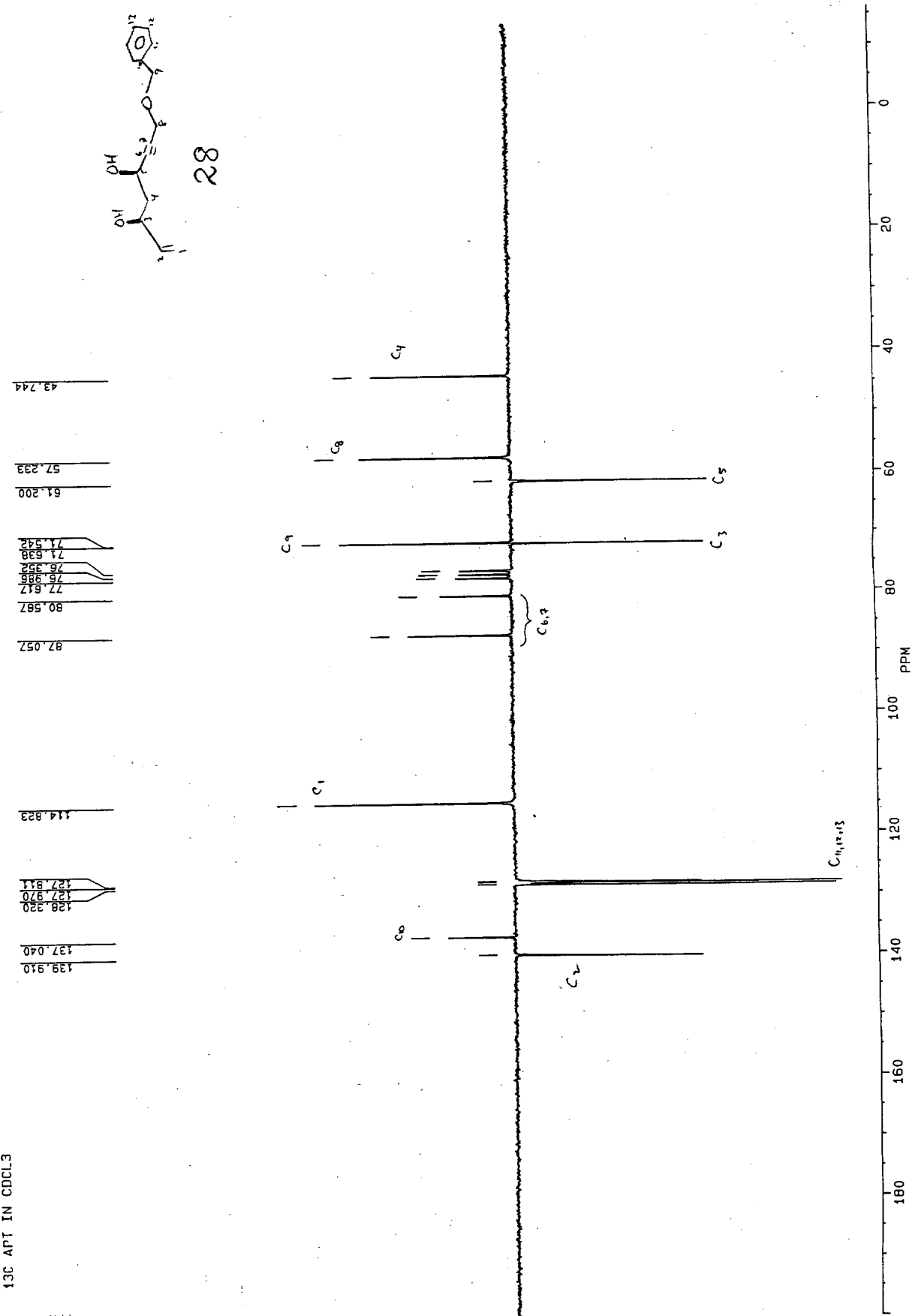
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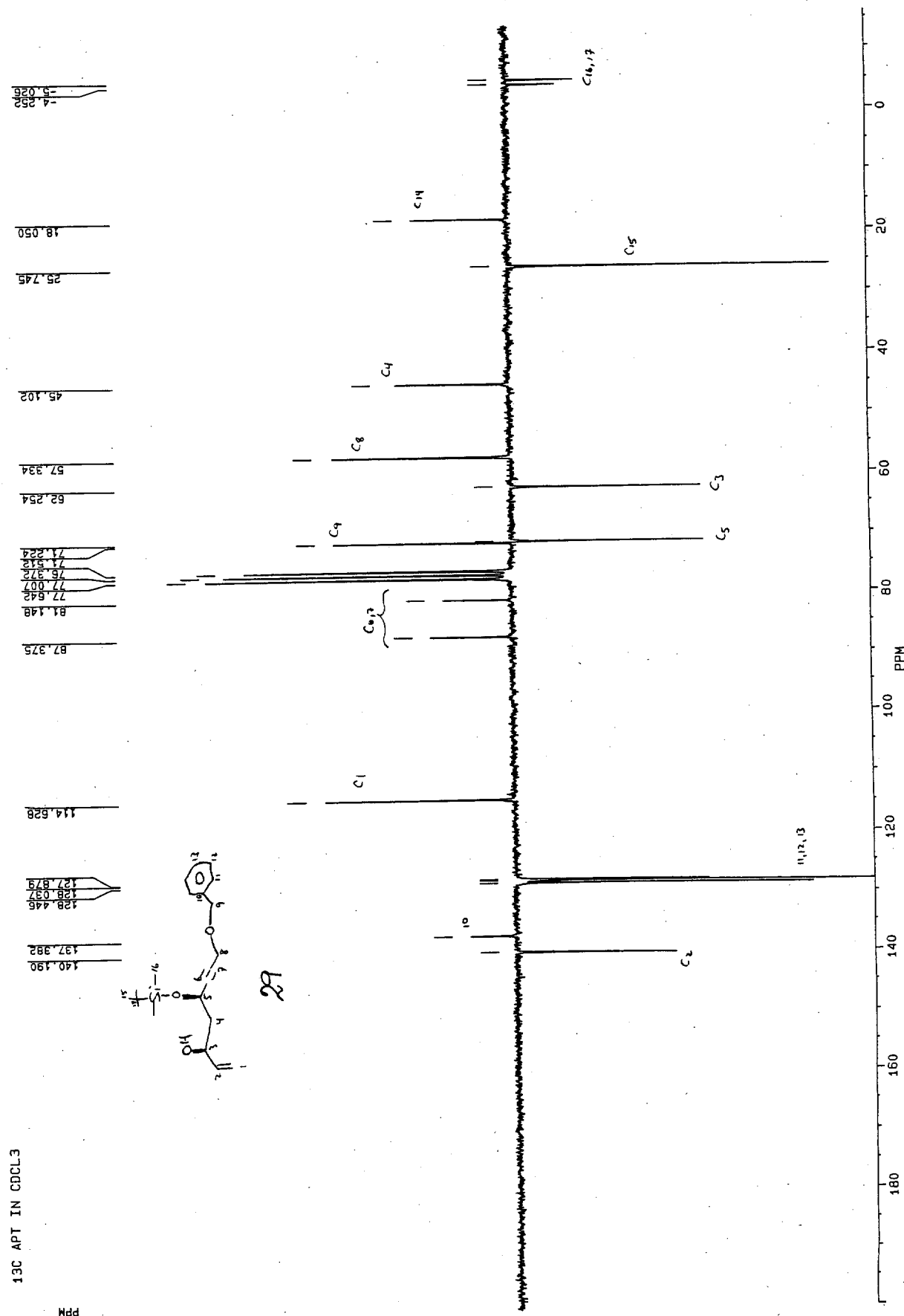
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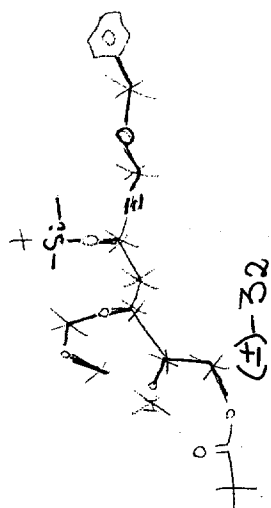
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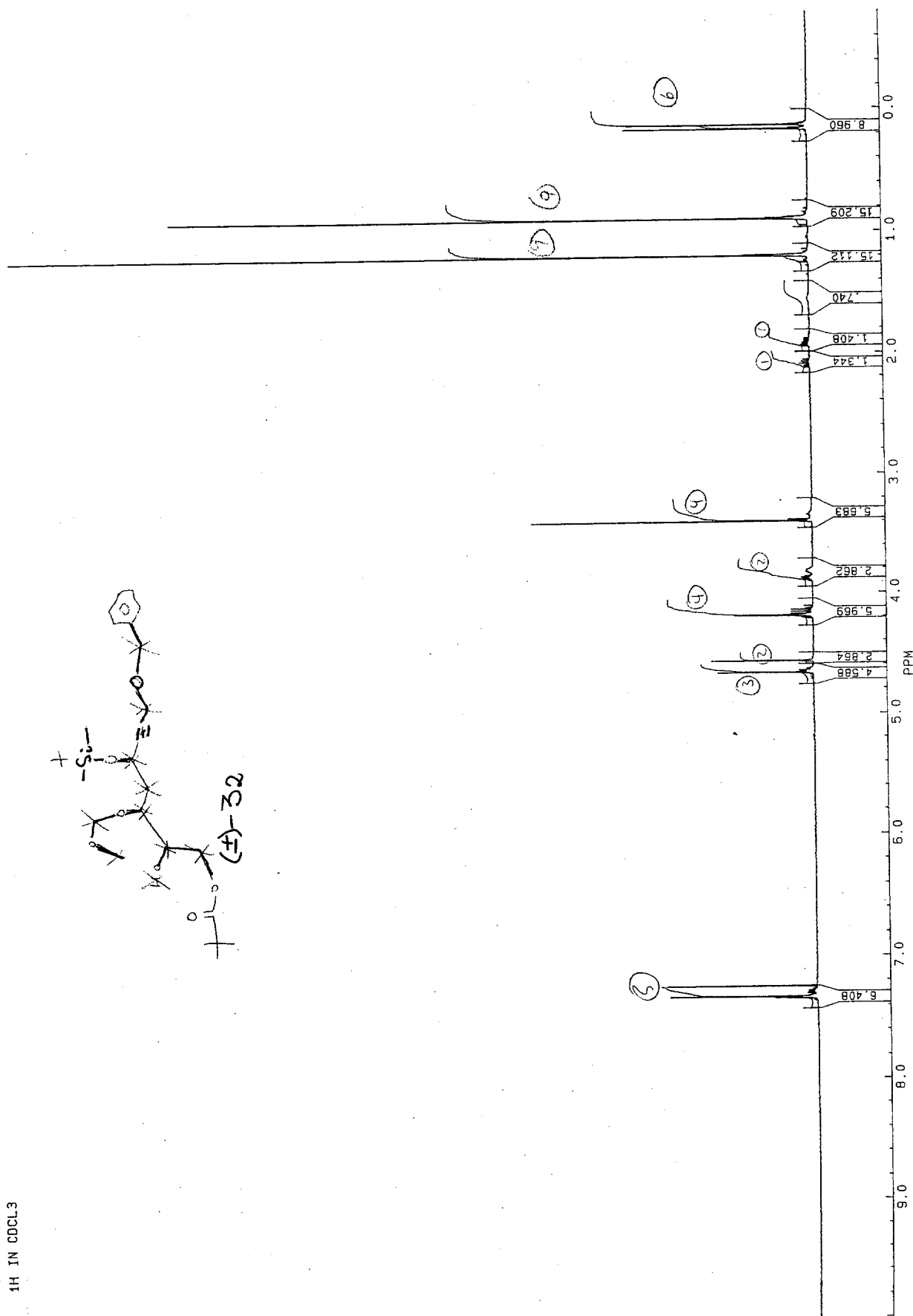


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1H IN CDCL3



~~BOOKER~~

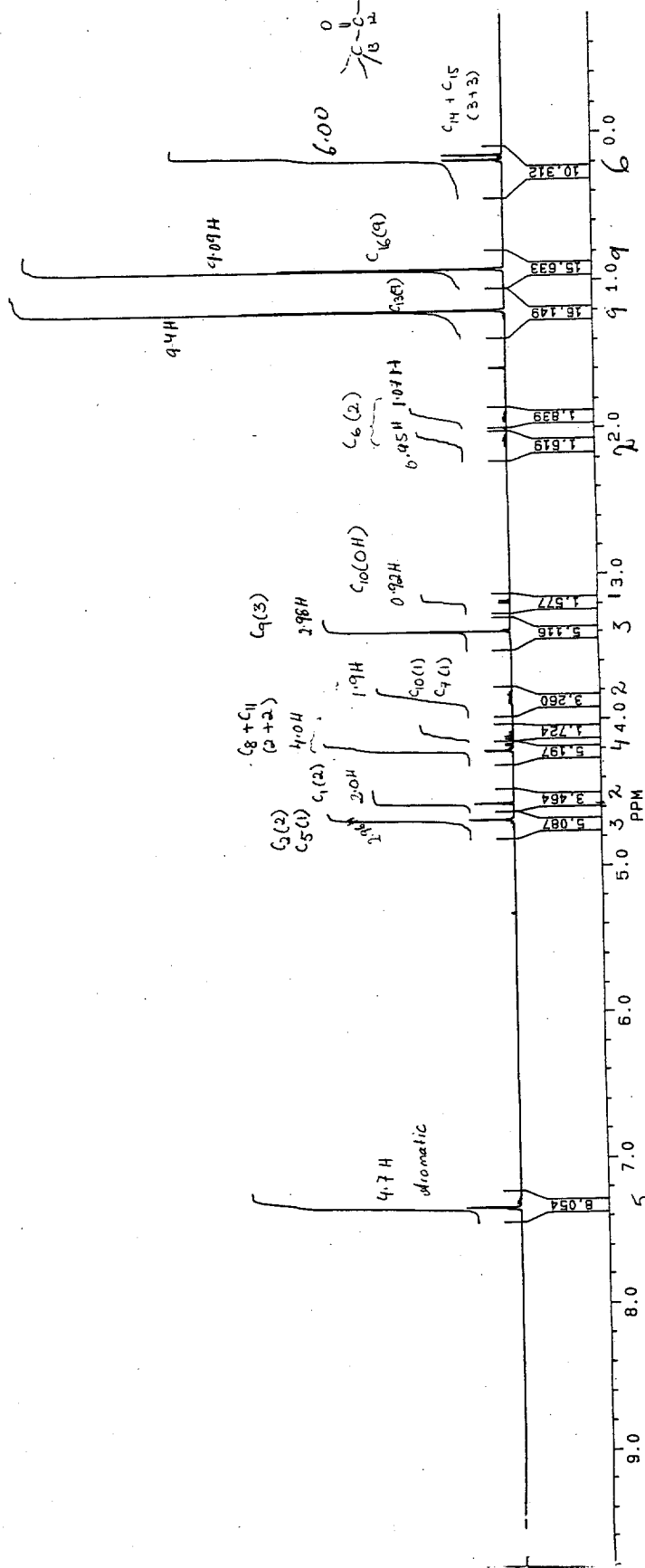
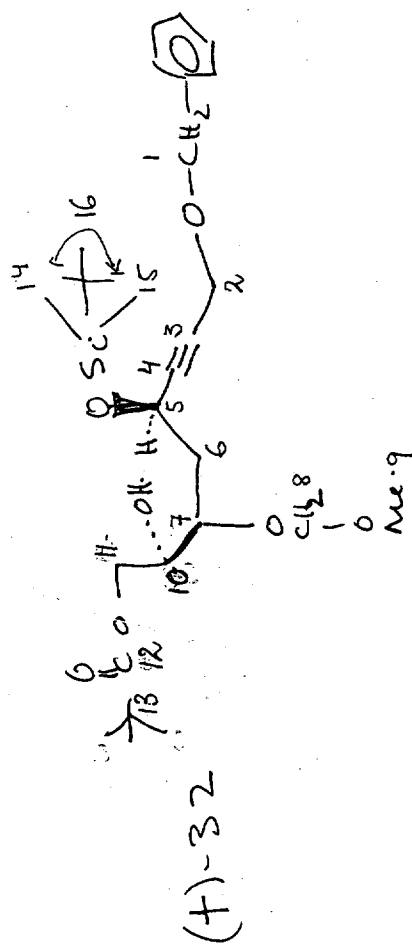
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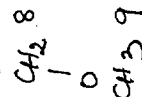
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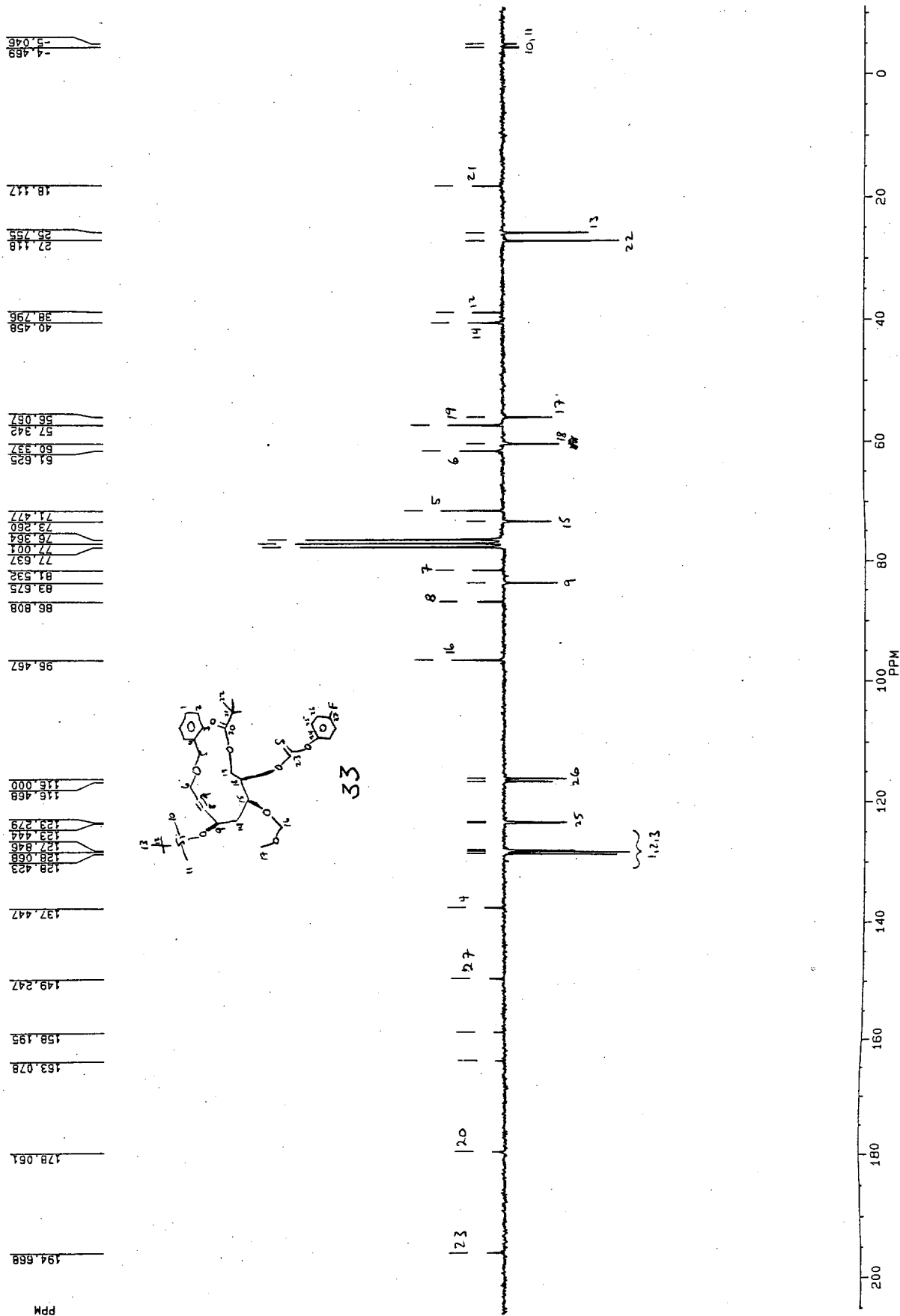


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 AQ .623
 RG 8192
 NS 15349
 TE 297
 FW 16500
 O2 3300.000
 DP 24H CPD
 LB 2.000
 GB 0.0
 CX 36.00
 CY 0.0
 F1 205.021F
 F2 -10.864F
 HZ/CM 301.919
 PPM/CM 6.000
 SR 3317.37
 D1 2.0000000
 S2 24H
 P9 98.00
 D2 .0010000
 P6 1.20
 D3 .0055000
 P6 7.20
 D4 .0001000
 RD 0.0
 PW 0.0
 DE 56.50
 NS 15349
 DS 2

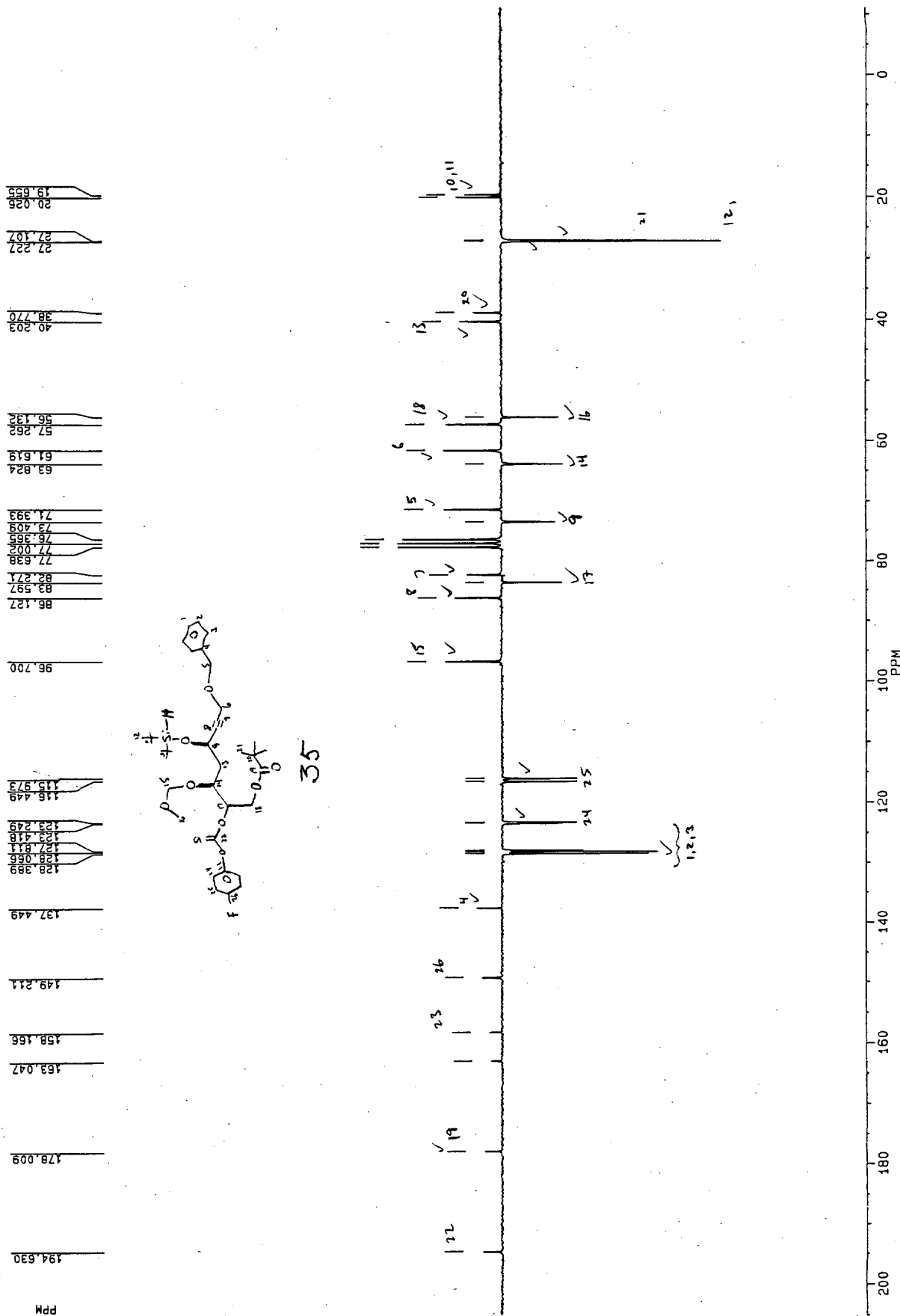
13C APT IN CDCL3

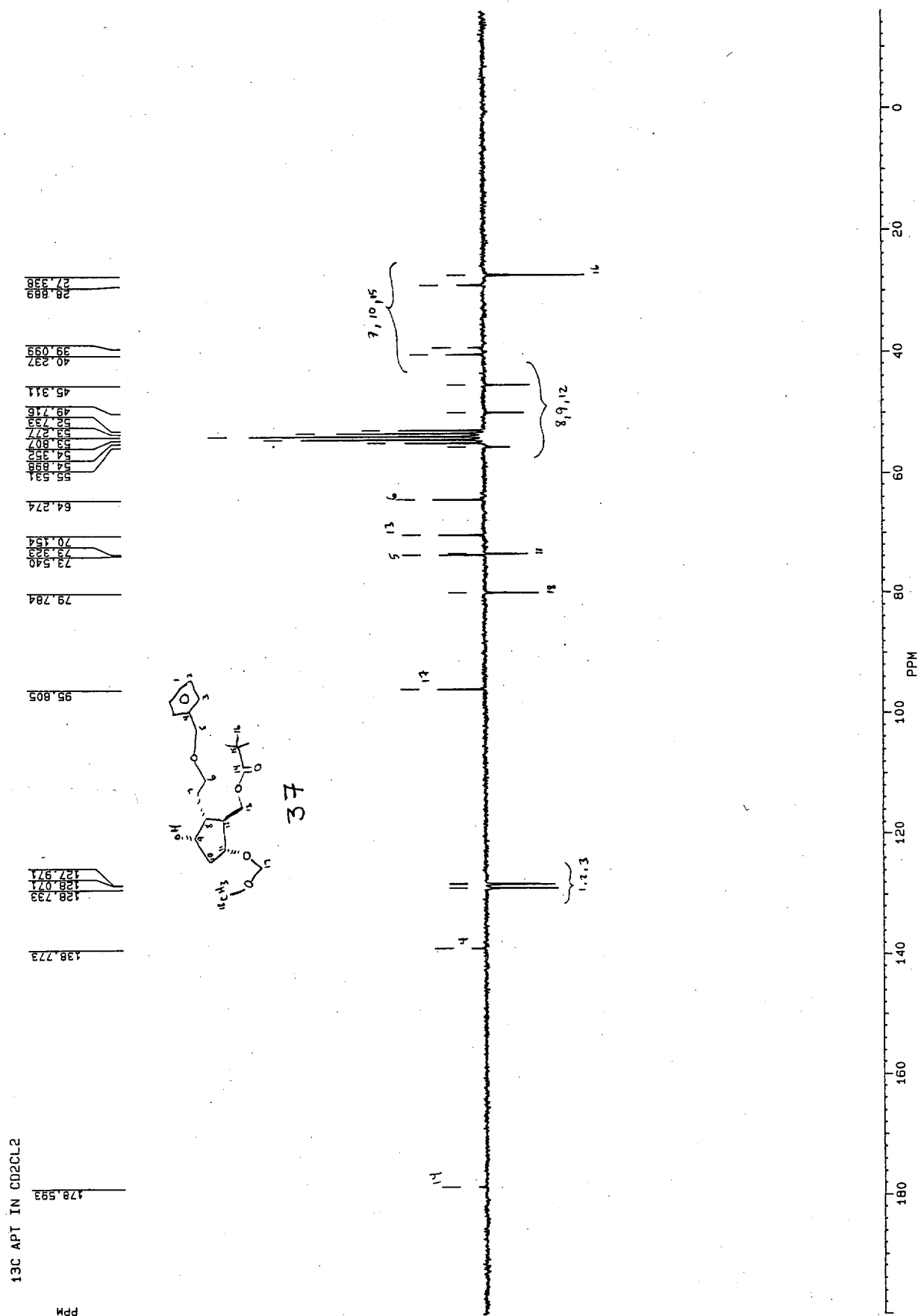




DLM991.001
 AU PROG:
 APTX.H.AU
 DATE 7-1-98
 TIME 10:29
 SF 50.323
 SY 194.0
 O1 9200.000
 SI 16384
 TD 16384
 SW 13157.895
 HZ/PT 1.606
 PW 0.0
 RD 0.0
 AG 8192.623
 RG 15433
 NS 297
 TE 297
 FW 16500
 O2 3300.000
 DP 24H CPD
 LB 2.000
 GB 0.0
 CX 36.00
 CY 0.0
 F1 205.021F
 F2 10.964F
 HZ/CM 301.919
 PPM/CM 6.000
 SR 3318.98
 D1 2.0000000
 S2 24H
 P9 98.00
 D2 .0010000
 P0 1.20
 D3 .0065000
 P6 7.20
 D4 .0001000
 R0 0.0
 PW 0.0
 DE 56.50
 NS 15433
 DS 2

13C APT IN CDCL3



[illegible]

BRUKER

DM9113.001
AU 1806:
APTXH.AU
DATE 21-1-98
TIME 11:51

SF 50.323
SY 194.0
O1 9200.000
SI 16384
TD 16384
SW 15151.515
HZ/PT 1.850

PW 0.0
RD 0.0
AQ 32768
RG 18421
TE 297

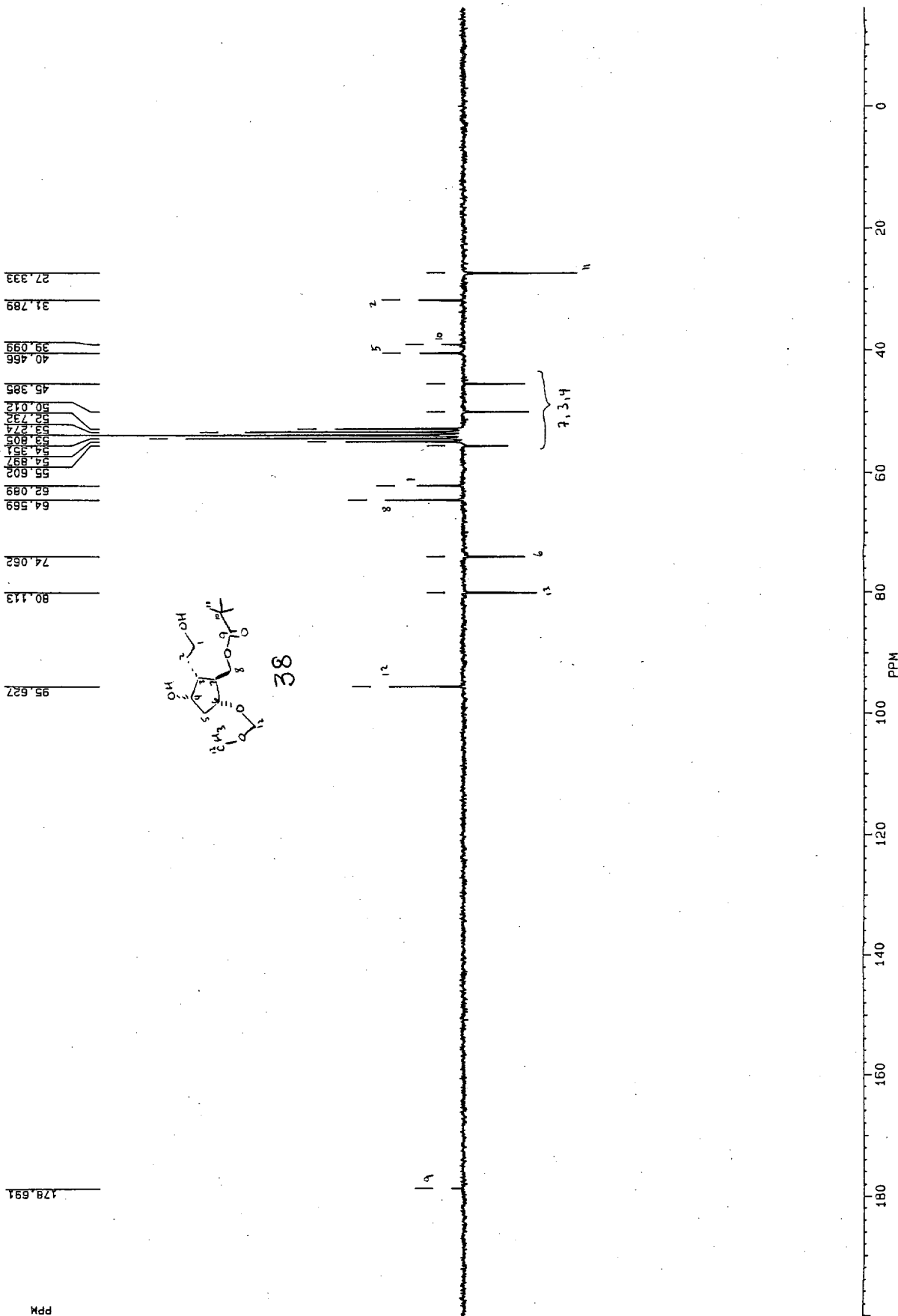
FW 19000
D2 3700.000
DP 24H CPD

LB 2.000
GB 0.0
CX 36.00
CY 0.0
F1 200.005
F2 -15.958
HZ/CM 301.888
PPM/CM 5.999
SR 3392.76

D1 2.0000000
S2 24H
P9 100.00
D2 .0010000
P0 1.20
D3 .0065000
P6 7.20
D4 .0001000
RD 0.0
PW 0.0
DE 49.40
NS 18421
DS 2

13C APT IN CD2CL2

178.691
PPM



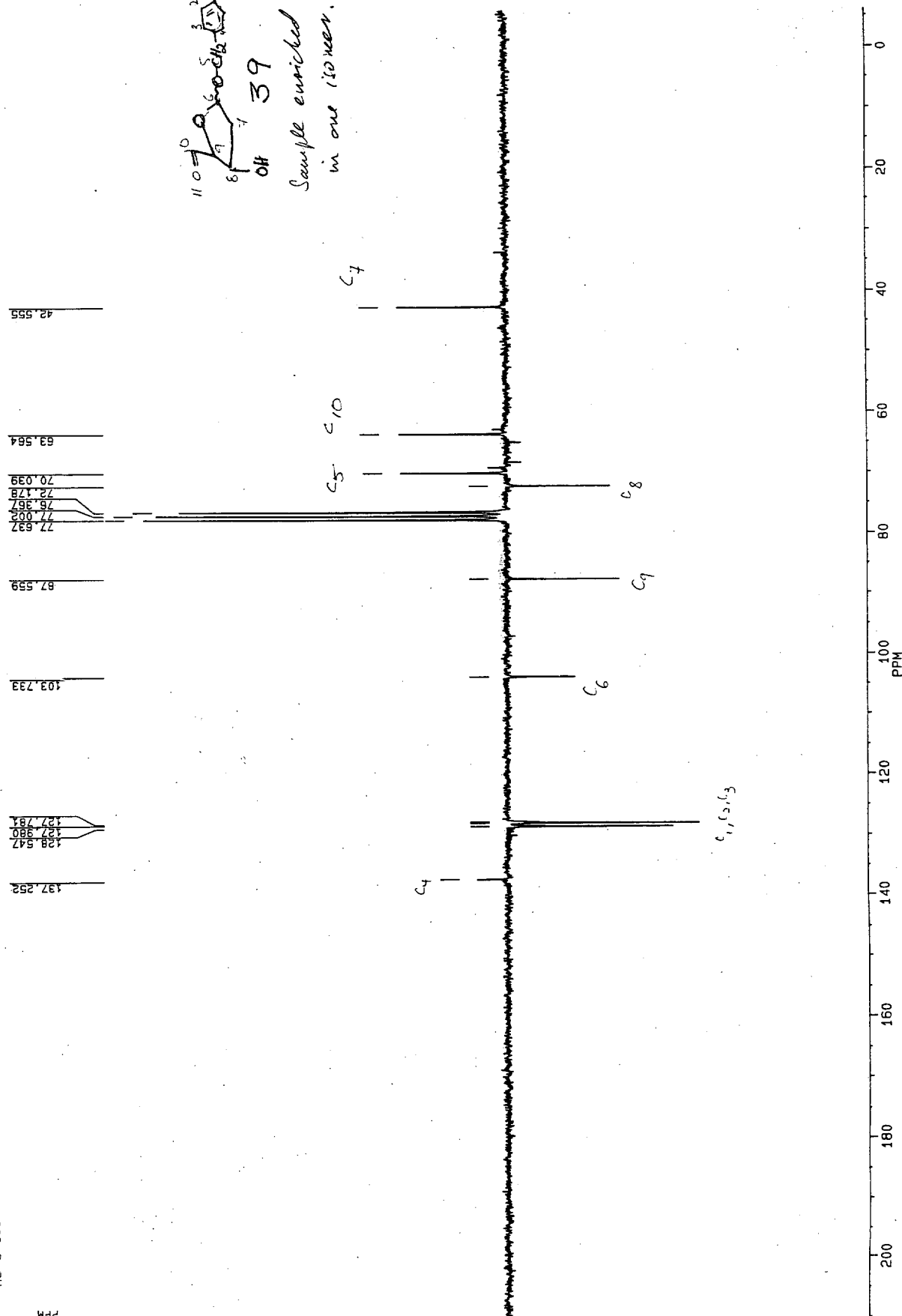
MS-6-165



 MSC6165.005
 AU PROG:
 APTX AU
 DATE 20-10-98
 TIME 8:41
 SF 50.323
 SY 194.0
 O1 9200.000
 SI 16384
 TD 16384
 SW 13157.895
 HZ/PT 1.606
 PW 0.0
 RD 0.0
 AQ 0.623
 RG 8192
 NS 15682
 TE 297
 FW 16500
 O2 3300.000
 DP 24H CPD
 LB 2.000
 GB 0.0
 CY 36.00
 F1 40.00
 F2 210.028P
 HZ/CM 301.919
 PPM/CM 6.000
 SR 3317.56
 D1 2.0000000
 S2 24H
 P9 98.00
 D2 .0010000
 P0 1.20
 D3 .0070000
 P6 7.20
 D4 .0001000
 RD 0.0
 PW 0.0
 DE 56.50
 NS 13682
 DS 2



39
 Sample enriched
 in one isomer.

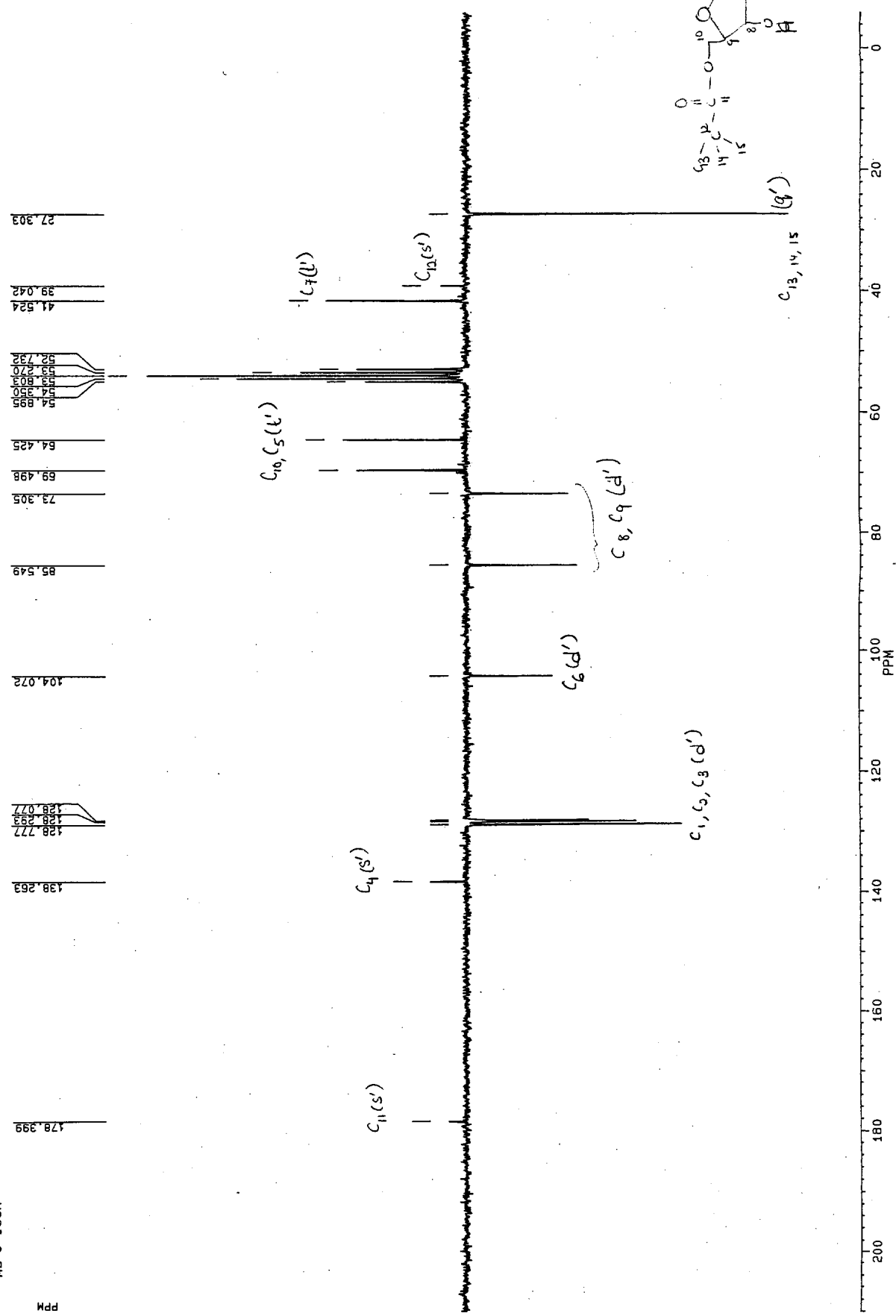


BLUKEP

MS6163A.001
 AUPT006:
 DATE 2-8-98
 TIME 18:04
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 SI 16384
 TD 16384
 SW 15151.515
 HZ/P1 1.850
 PW 0.0
 RD 0.0
 AG 32768
 NS 3902
 TE 297
 FM 19000
 O2 3700.000
 DP 24H CPD
 LB 2.000
 GB 0.0
 CX 36.00
 CY 9.00
 F1 210.038P
 F2 -5.924P
 HZ/CM 301.888
 PPM/CM 5.999
 SR 3392.76
 D1 2.0000000
 S2 24H
 P3 100.00
 D2 .0010000
 P0 1.20
 D3 .0070000
 P6 7.20
 D4 .0001000
 RD 0.0
 PW 0.0
 DE 49.40
 NS 3902
 DS 2

MS-6-163A

PPM



400

BRUKER

MSC6163B.002
AU PROG:
APTXH.AU
DATE 2-8-98
TIME 15:03

SF 50.323
SY 194.0
Q1 9200.000
SI 16384
TD 16384
SM 15151.515
HZ/PT 1.850

PW 0.0
RD 0.0
AQ 32768
RG 4099
NS 297
TE 297

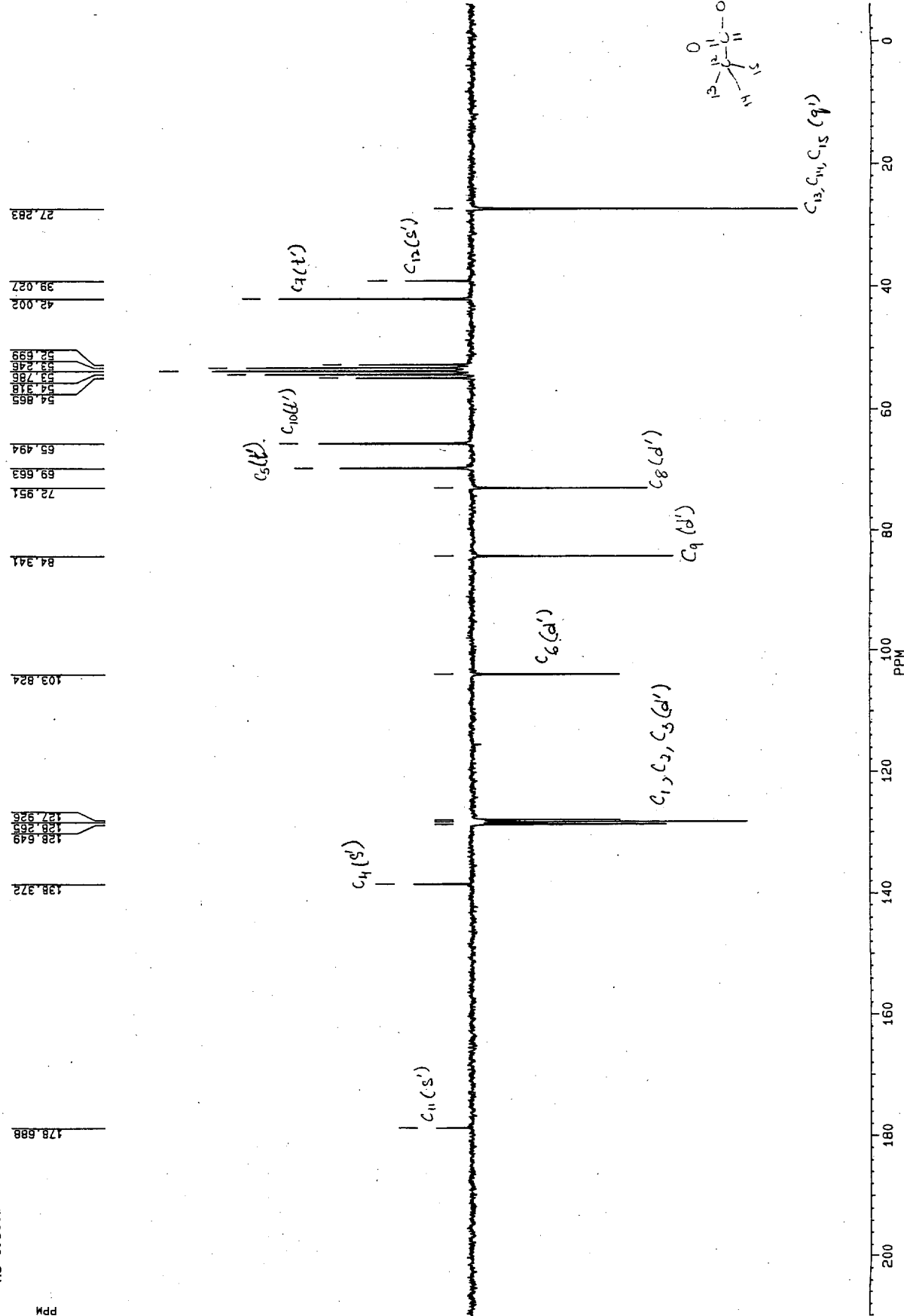
FW 19000
Q2 3700.000
DP 24H P0

LB 2.000
GB 0.0
CX 36.00
CY 9.00
F1 210.038P
F2 -5.924P
HZ/CM 301.888
PPM/CM 5.599
SR 3394.60

D1 2.0000000
S2 24H
P9 100.00
D2 .0010000
P0 1.20
D3 .0070000
P6 7.20
D4 .0001000
RD 0.0
PW 0.0
DE 49.40
NS 4099
DS 2

MS-60163B

PPM



BROKER

MSC6167.003
AU PROG:
APTXH, AU
DATE 7-8-98
TIME 8:31

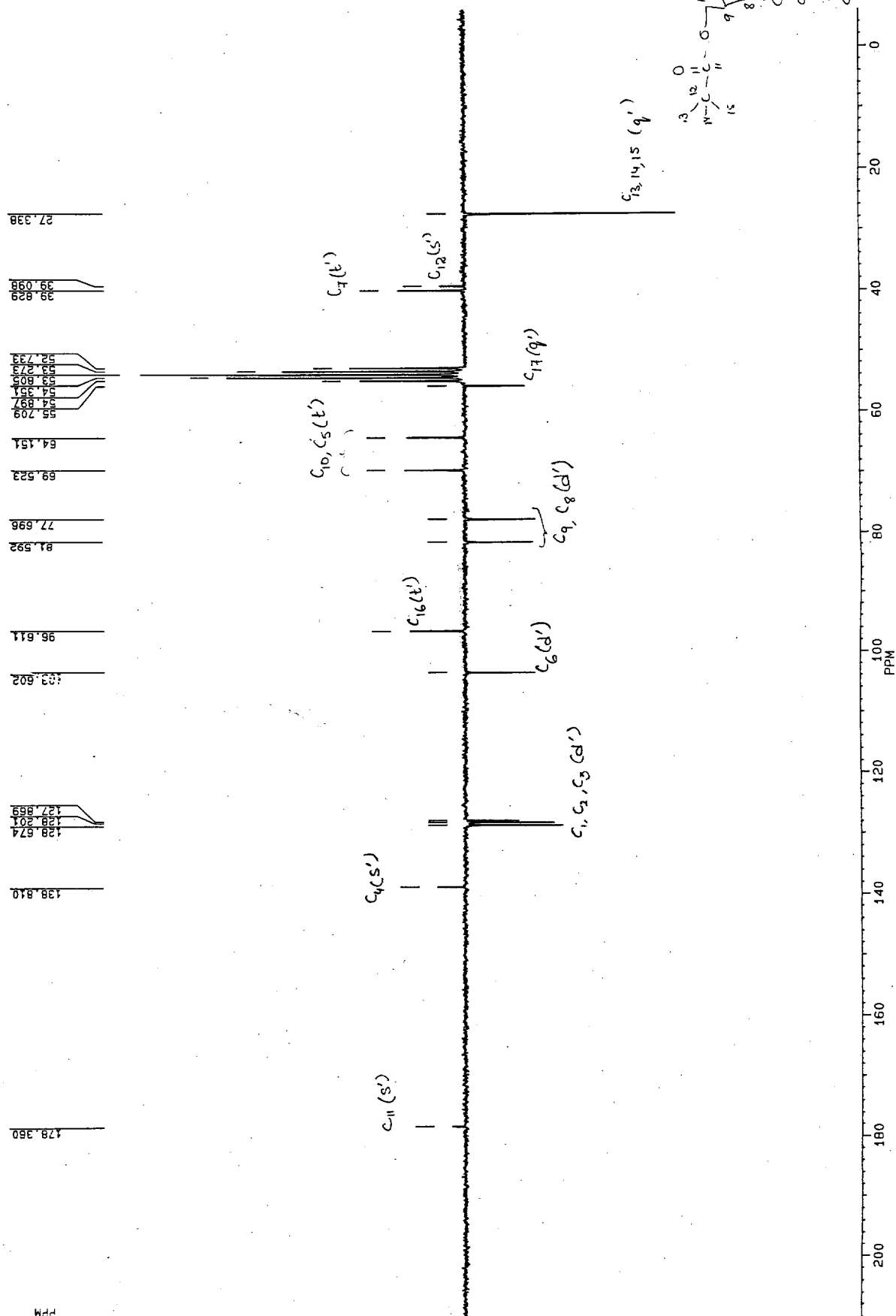
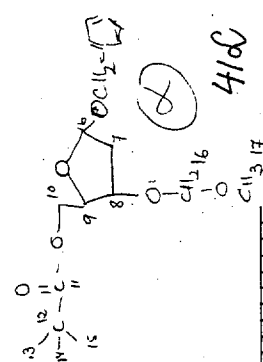
SF 50.323
SY 194.0
O1 9200.000
SI 16384
ID 16384
SW 15151.515
HZ/PT 1.850

PW 0.0
RD 0.0
AQ 32768.541
RG 32768
NS 14030
TE 297

FW 19000
O2 3700.000
DP 24H CPU

LB 2.000
GB 0.0
CX 36.00
CY 9.00
F1 210.038P
F2 -5.924P
HZ/CM 304.888
PPM/CM 5.999
SR 3390.91

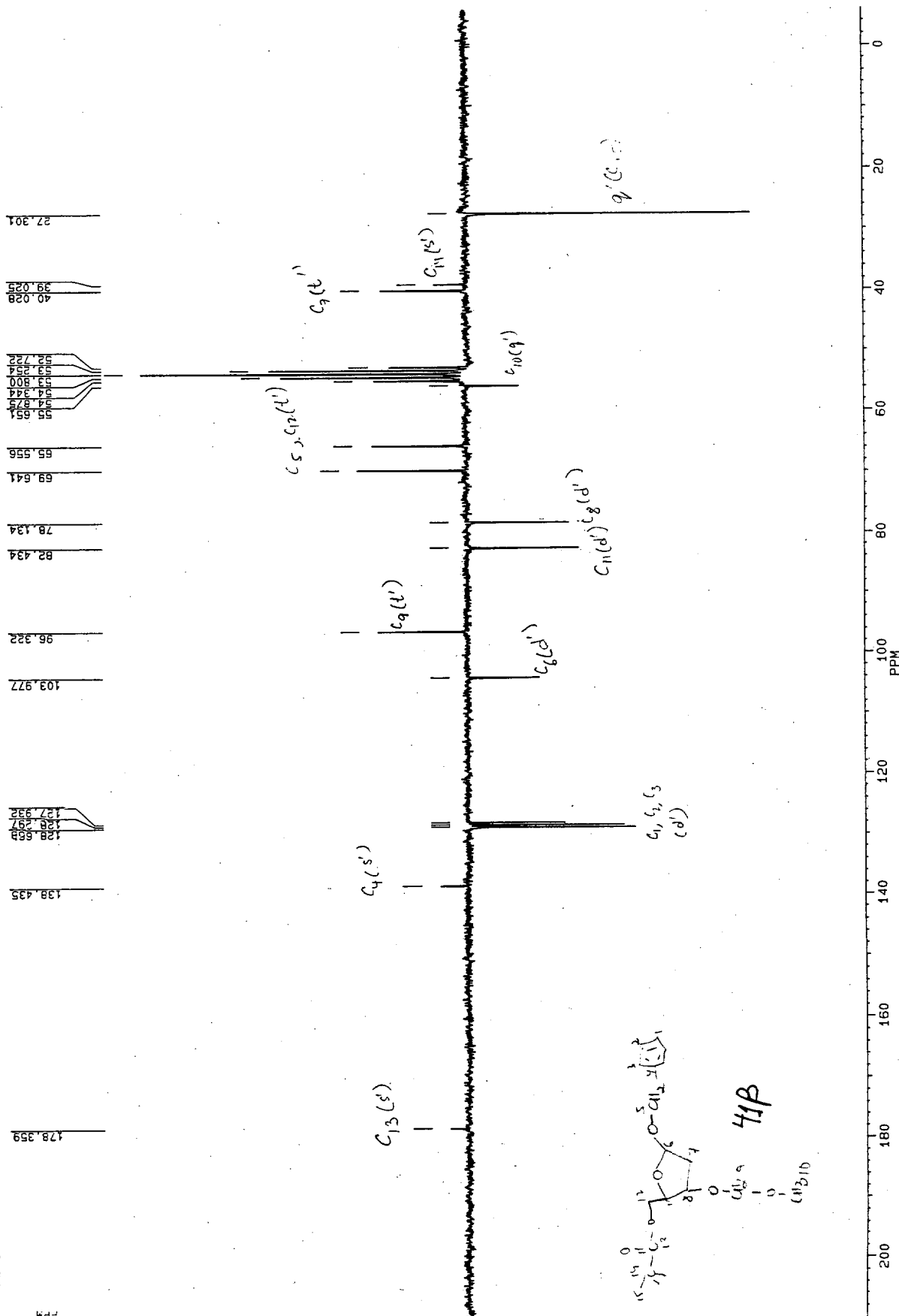
D1 2.0000000
S2 24H
P9 100.00
D2 .0010000
P0 1.20
D3 .0070000
P6 7.20
D4 .0001000
RD 0.0
PW 0.0
DE 49.40
NS 14030
DS 2



S26



MSC6153.001
AU PRQ6:
APTXH.AU
DATE 26-7-98
TIME 18:41
SF 50.323
SY 194.0
Q1 9200.000
SI 16384
TD 16384
SW 15151.515
HZ/PT 1.850
PW 0.0
RD 0.0
AG 0.541
RG 32768
NS 6331
TE 297
FW 19000
Q2 3700.000
DP 24H.CPD
LB 2.000
GB 0.0
CX 36.00
CY 9.00
F1 210.038P
F2 -5.924P
HZ/CM 301.888
PPM/CM 5.999
SR 3392.76
D1 2.0000000
S2 24H
P9 100.00
D2 .0010000
P0 1.20
D3 .0070000
P6 7.20
D4 .0001000
RD 0.0
PW 0.0
DE 49.40
NS 6331
DS 2



S27



MSC61.002
AU PROG:
APTXH-AU
DATE: 3-7-98

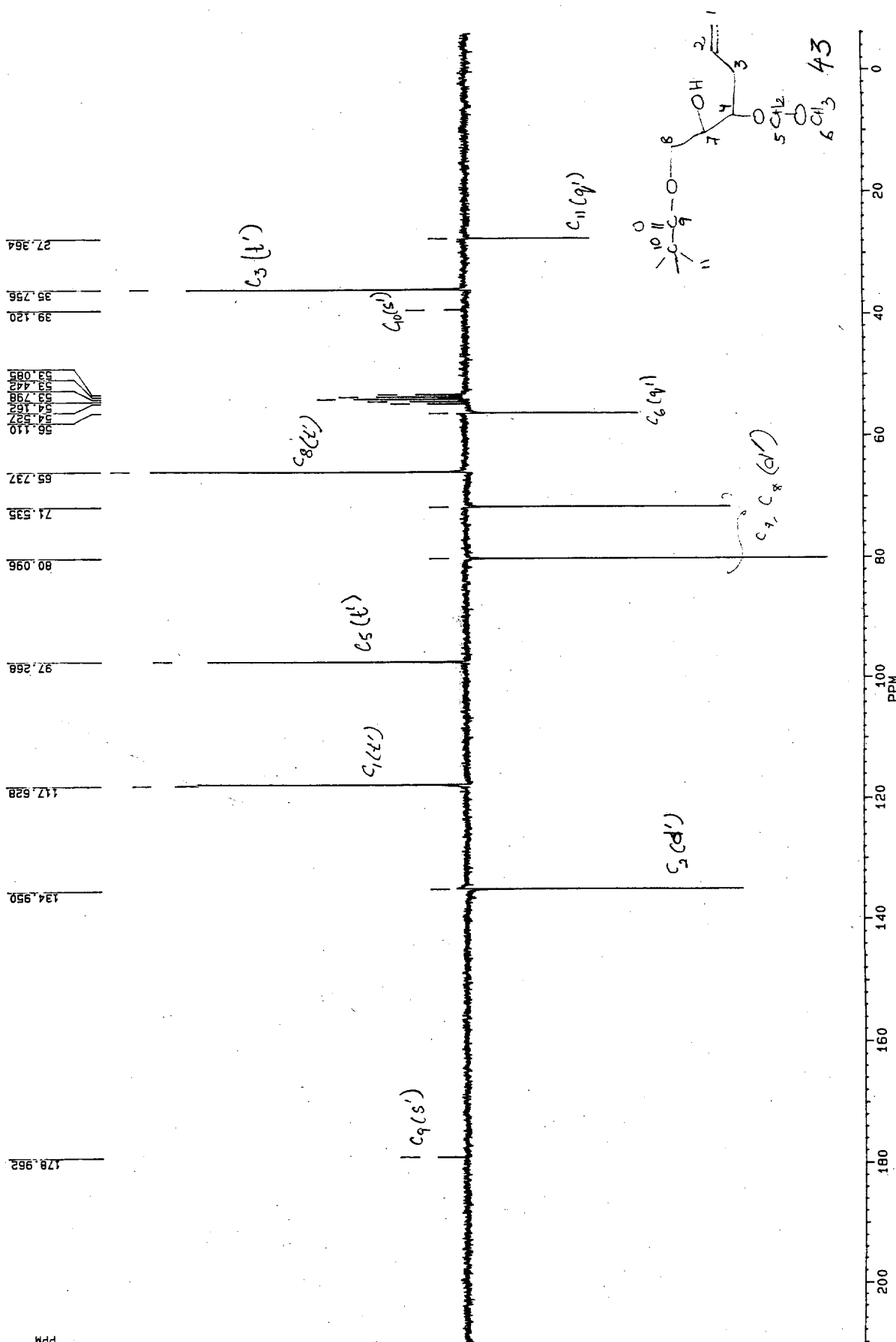
SF 75.46
SY 112.0
O1 7600.00
SI 32768
TD 32768
SW 20000.00
HZ/PT 1.22

PW 0.0
RG 0.0
AQ 0.0
RG 400
NS 6760
TE 297

FW 25000
O2 5300.00
DP 25H CPD

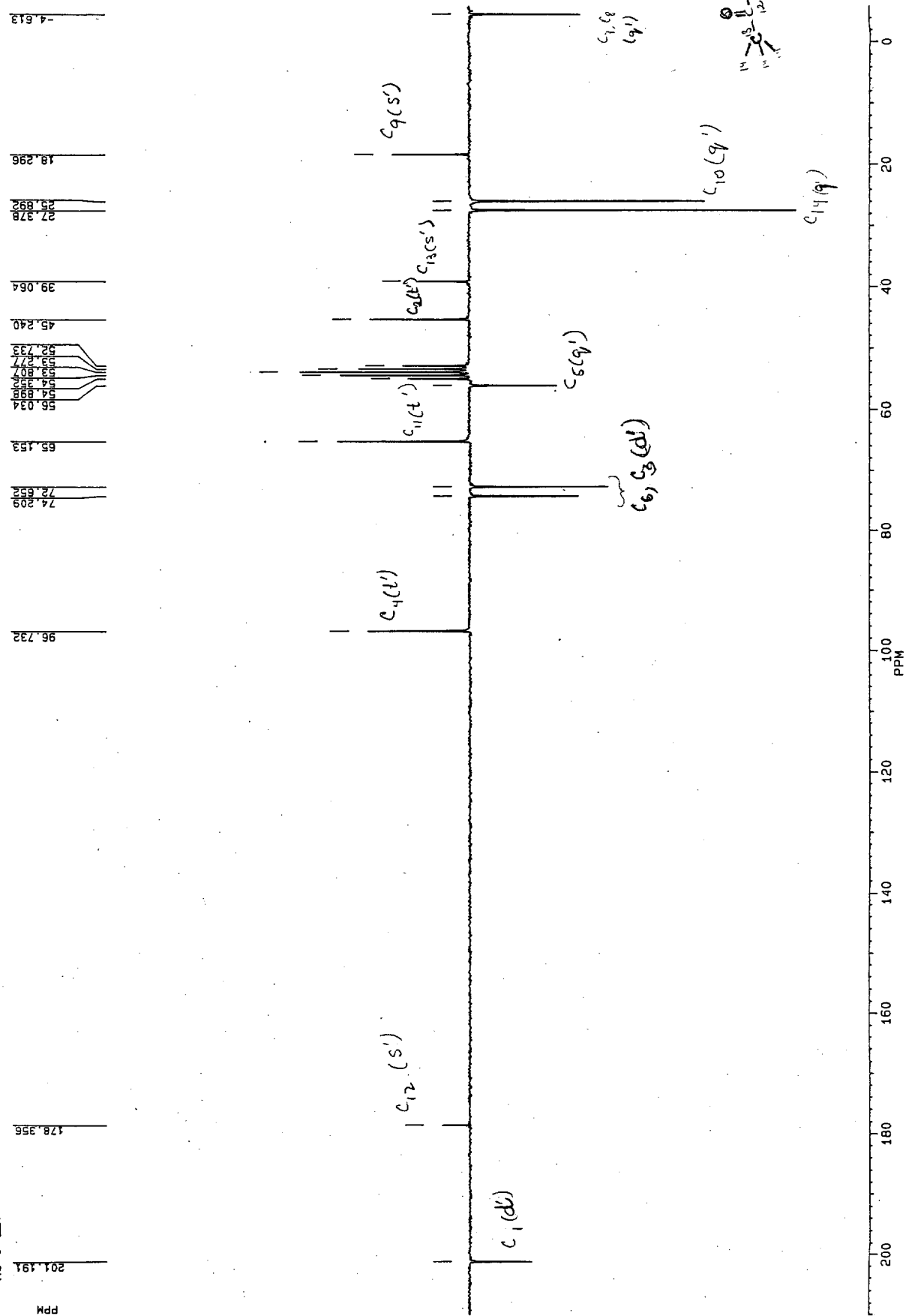
LB 2.00
GB 0.0
CX 36.00
CY 10.00
F1 209.99
F2 55.00
HZ/CM 452.81
PPM/CM 6.00
SR -1295.26

MS-6-121
13C APT IN CD2CL2





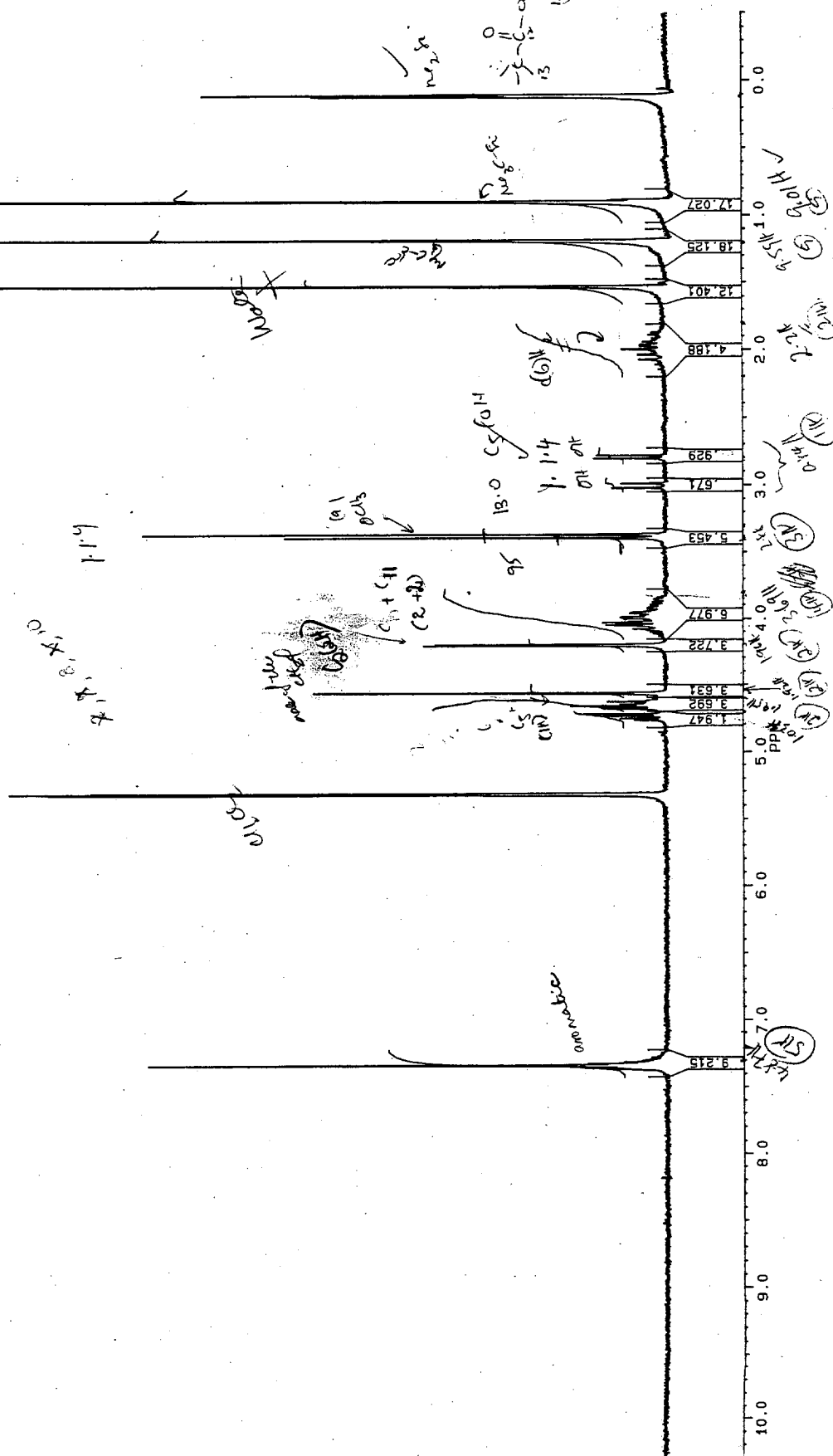
MSC6127.001
AU PROG:
APTXH.AU
DATE 8-7-98
TIME 9:17
SF 50.323
SV 194.0
SI 5200.000
SI 16384
TD 16384
SW 15151.515
HZ/PT 1.850
PW 0.0
RD 0.0
AQ 5.541
RG 32768
NS 14202
TE 297
FW 19000
D2 3700.000
DP 24H CPD
LB 2.000
GB 0.0
CX 36.00
CY 9.00
F1 210.038P
F2 5.928P
F3 301.888P
HZ/CM 5.999
PPM/CM 3390.91
D1 2.0000000
S2 24H
P9 100.00
D2 .0010000
D3 .0070000
D4 .0001000
RD 0.0
PW 0.0
DE 49.40
NS 14202
DS 2



MS-6-129



JN05202C.001
DATE 21-7-98
TIME 21:54
SF 200.133
SY 239.0
Q1 3700.000
S1 32768
T0 32768
SW 2994.012
HZ/PT 163
PW 3.0
RD 4.000
AG 5.472
RG 1024
NS 54
TE 297
FW 3800
O2 2000.000
DP 8L P0
LB 0.200
GB 0.0
CX 36.00
CY 0.0
F1 10.300P
F2 10.501P
WZ/CM 60.045
PPM/CM 300
SR 2728.49

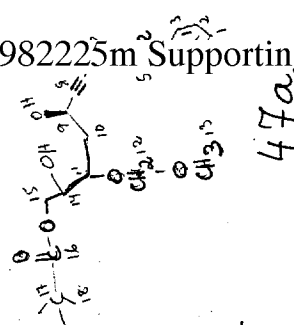
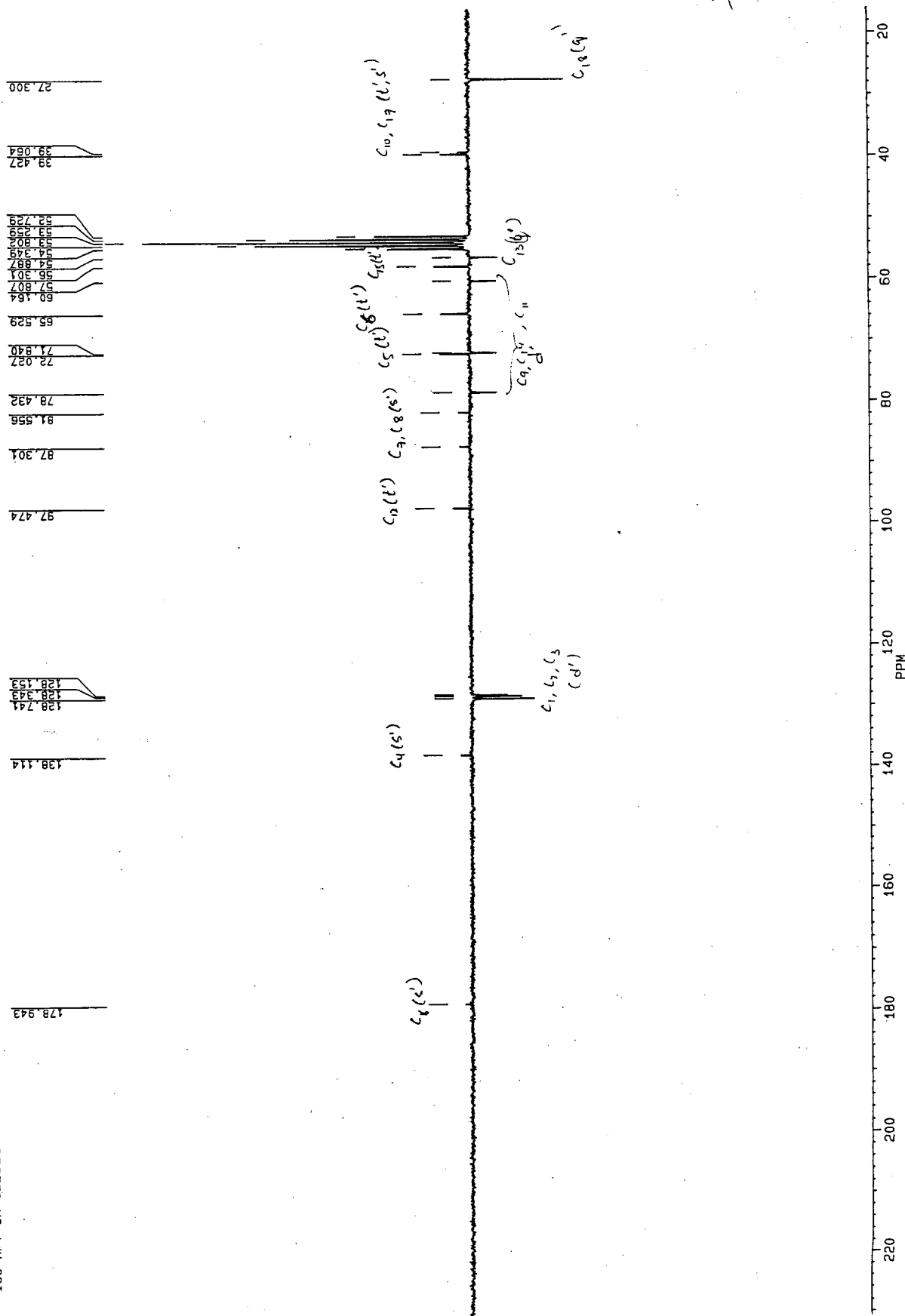


MS-6-1470
13C APT IN CD2CL2

BRUKER

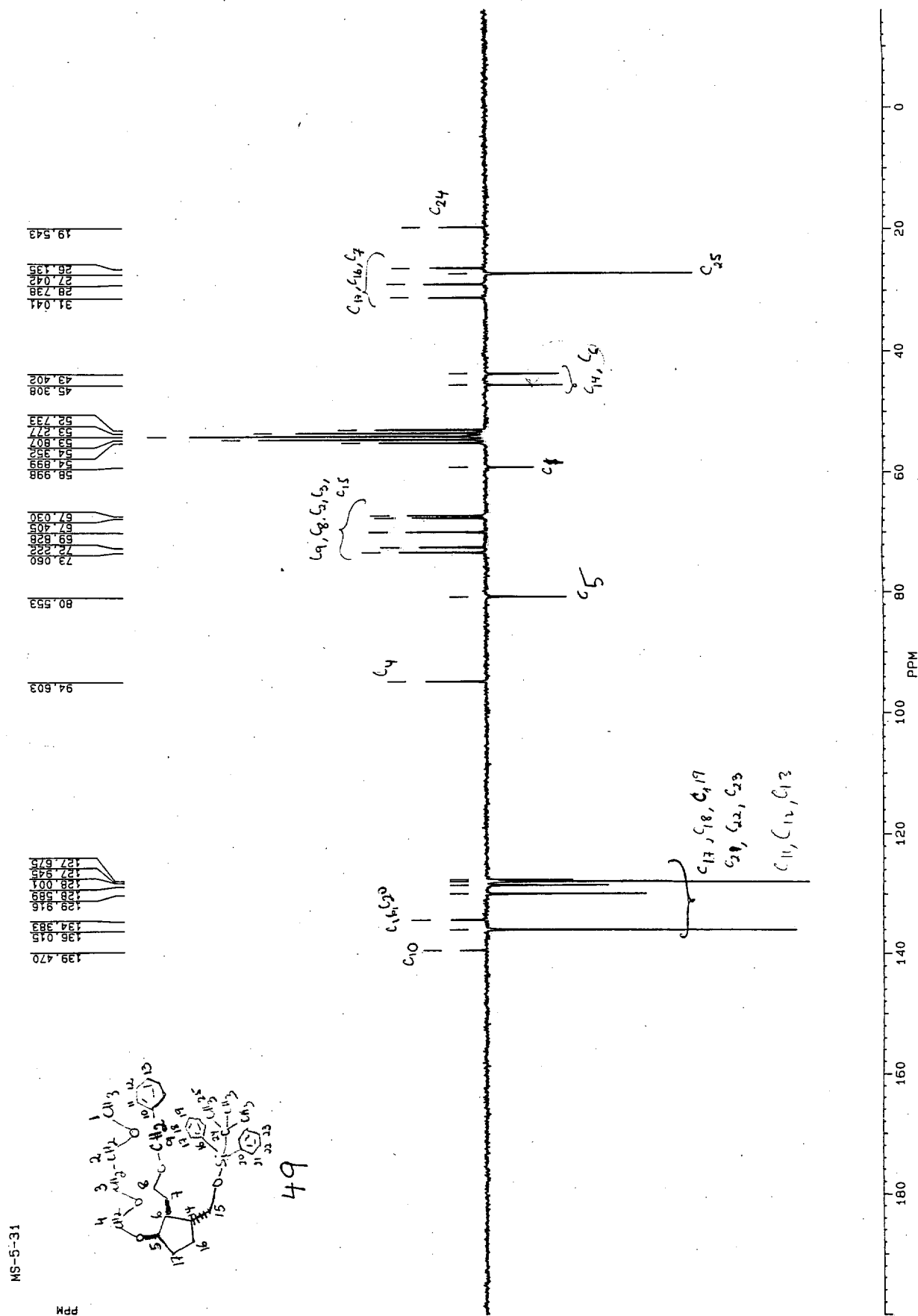
MSC61470.004
AU PROG:
APTXH.AU
DATE 31-7-98
TIME 8:17

SF	50.323
SI	194.0
SI	9200.000
SI	16384
TD	16384
SW	15151.515
HZ/PT	1.850
PW	0.0
RD	0.0
AG	32768
NS	13319
TE	297
FW	19000
O2	3700.000
DP	24H CPD
LB	2.000
GB	0.0
CX	36.00
CY	9.00
F1	232.017P
F2	16.018P
HZ/CM	301.939
PPM/CM	5.000
SR	3392.75
D1	2.00000000
S2	24H
P9	100.00
D2	.00100000
P0	1.20
D3	.00700000
P6	7.20
D4	.00010000
RD	0.0
PW	0.0
DE	49.40
NS	13319
DS	2

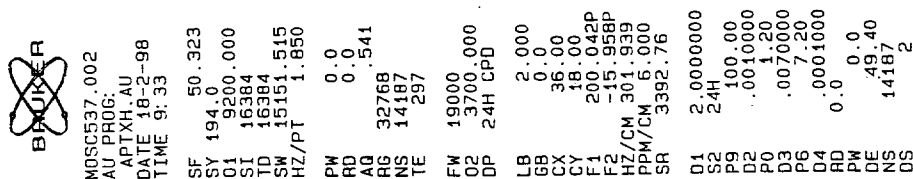
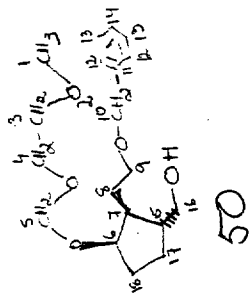




MSC531.002
AU PROB: APTX AU
DATE 15-2-98
TIME 12:28
SF 50.323
SY 194.0
O1 9200.000
SI 16384
TD 16384
SW 15151.515
HZ/PT 1.850
PW 0.0
RD 0.0
RG 32768
NS 18056
TE 297
FW 19000
O2 3700.000
DP 24H P0
LB 2.000
GB 0.0
CX 36.00
CY 9.00
F1 200.00500
F2 -15.994f
HZ/CM 301.939
PPM/CM 6.000
SR 3392.76
D1 2.000000f
S2 24H
P9 100.00
D2 .001000f
P0 1.20
D3 .007000f
P6 7.20
D4 .000100f
RD 0.0
PW 0.0
DE 49.40
NS 18056
DS 2



13C APT IN CD2CL2



BOOKER

MSC549.002
AU PROG:
APTXH:AU
DATE 1-3-98
TIME 12:13

SF 100.614
SY 74.0
D1 12300.000
SI 32768
TD 32768
SW 29411.765
HZ/PT 1.795

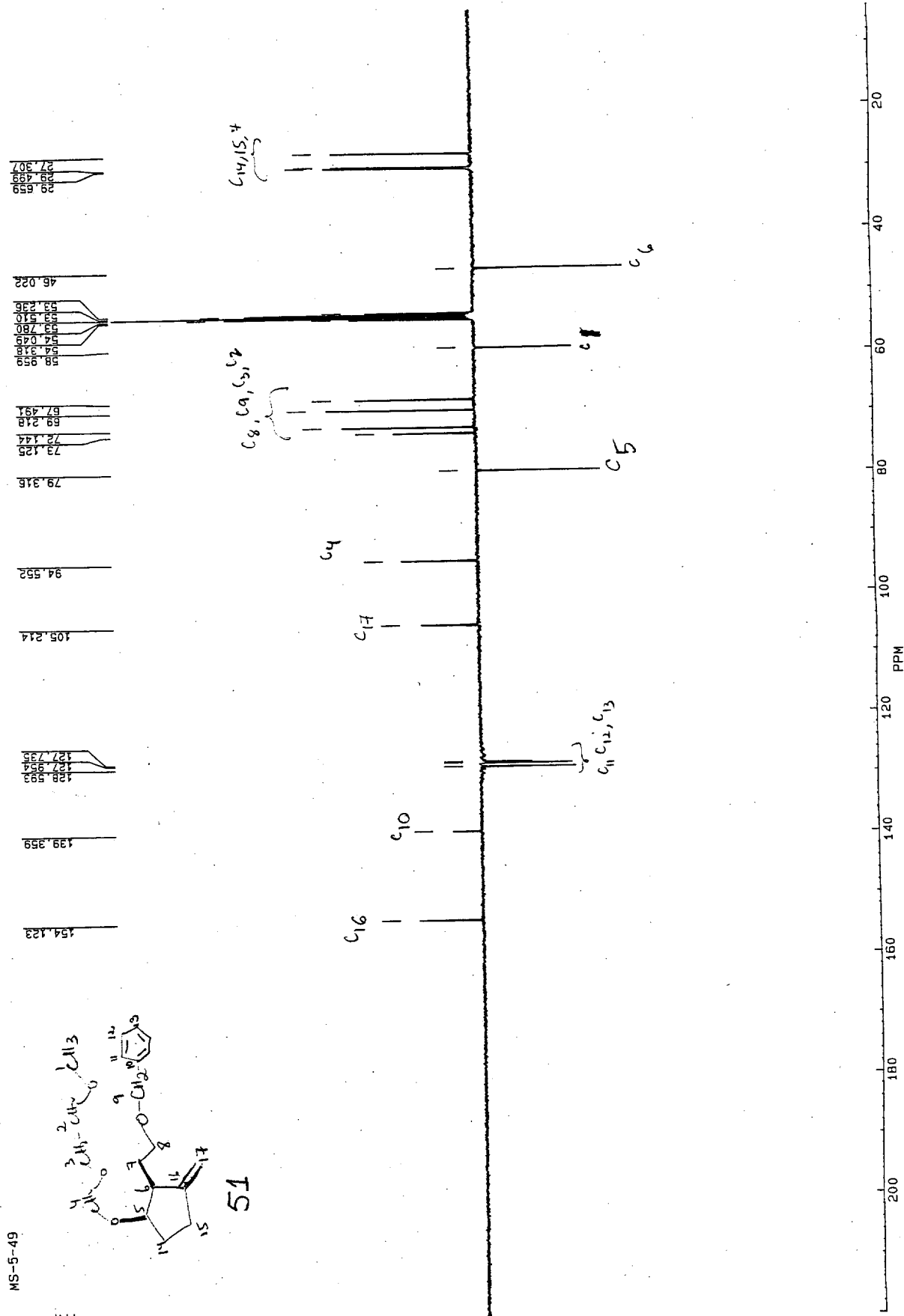
PW 0.0
RO 0.0
AQ .557
RG 400
NS 20493
TE 297

FW 36800
D2 3700.000
DP 15H CPD

LB 2.000
GB 0.0
CX 36.00
CY 10.00
F1 219.998
F2 4.003

HZ/CM 603.670
PPM/CM 6.000
SR 27.69

D1 2.000000
S2 15H
P9 .95.00
D2 .001000
P0 3.00
D3 .007000
P6 14.00
D4 .000100
RD 0.0
PW 0.0
DE 23.80
NS 20493
DS 2

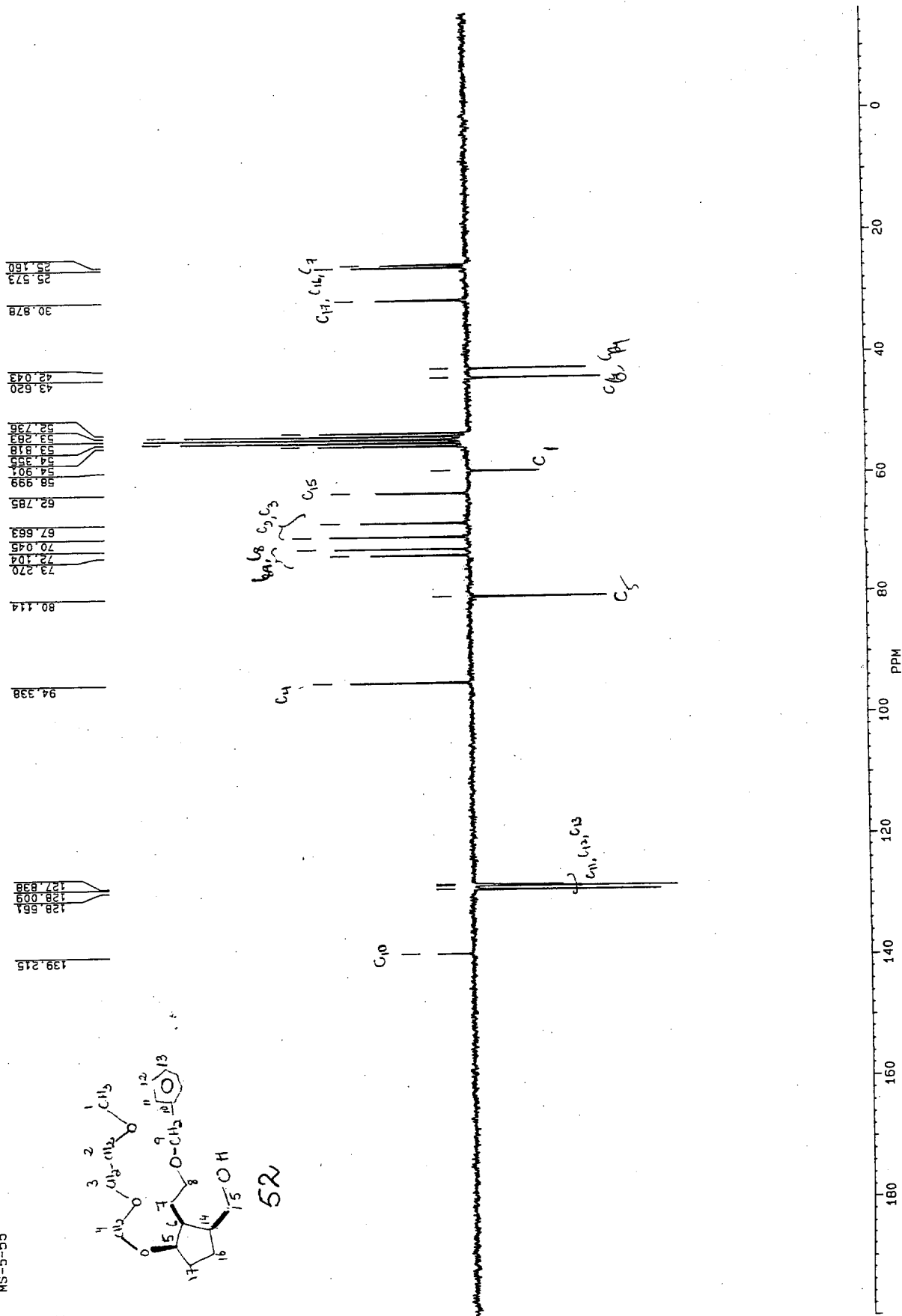


MS-5-49

ppd

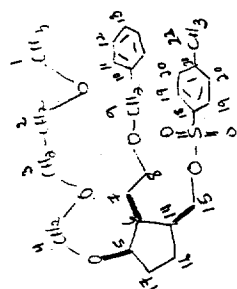


MSC555.002
AU PROG:
APTXH AU
DATE 1-3-98
TIME 13:24
SF 50.323
SY 194.0
O1 9200.000
SI 16384
TD 16384
SW 15151.515
HZ/PT 1.850
PW 0.0
RD 0.0
AD 0.541
RG 32768
NS 21176
TE 297
FM 19000
O2 3700.000
DP 24H CPD
LB 2.000
GB 0.0
CY 36.00
F1 208.005P
F2 15.994P
HZ/CM 301.939
PPM/CM 6.000
SR 3392.76
D1 2.0000000
S2 24H
P9 100.00
D2 .0010000
P0 1.20
D3 .0070000
P6 7.20
D4 .0001000
RD 0.0
PW 0.0
DE 49.40
NS 21176
DS 2



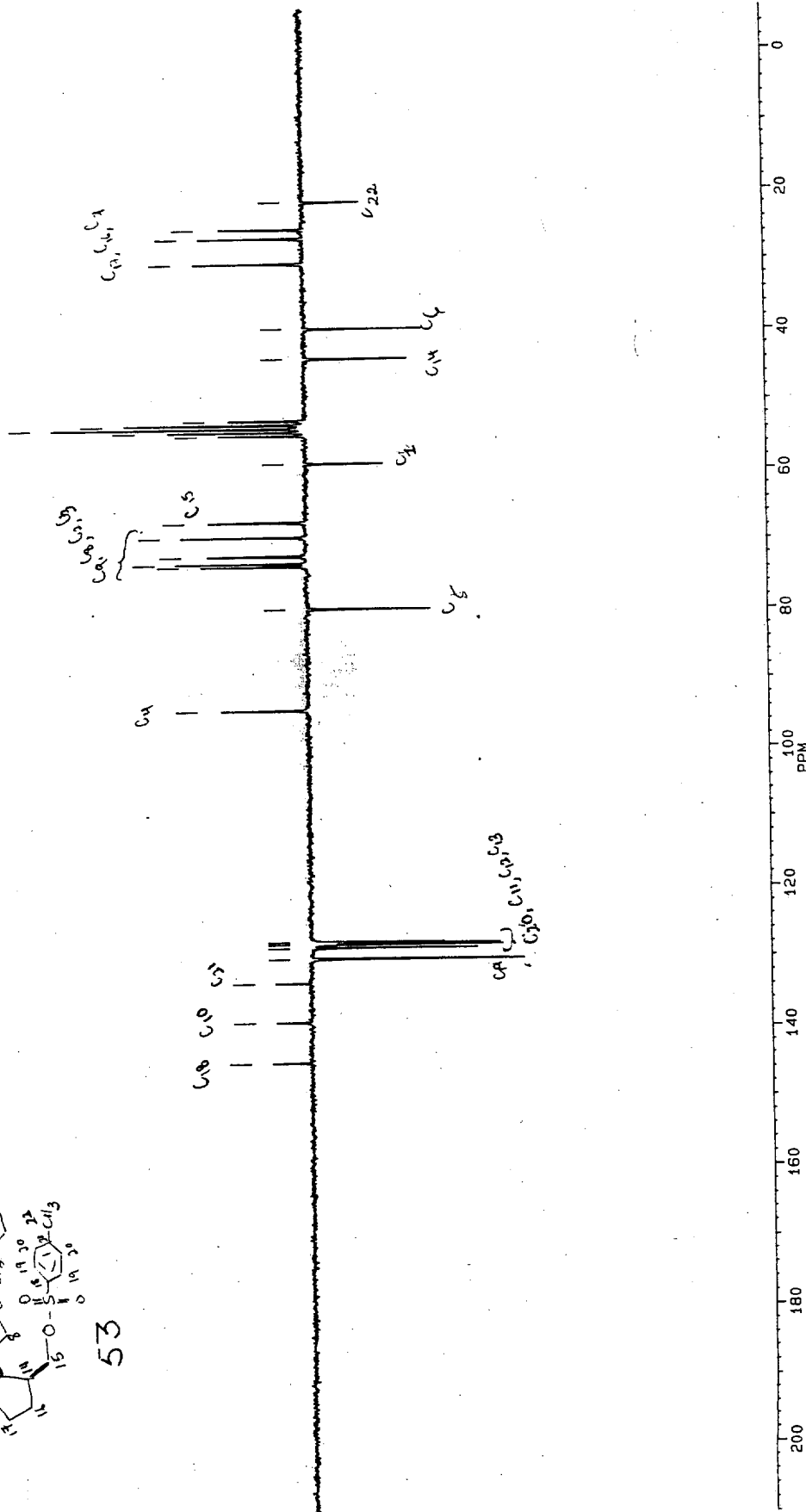
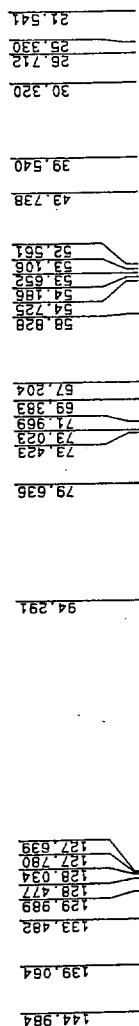
MS-5-55

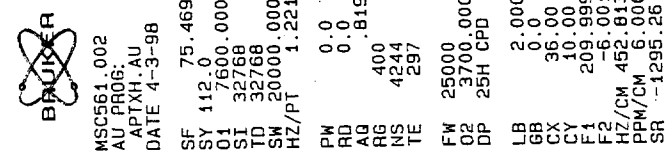
MS-5-54
13C APT IN CD2CL2



BRUKER

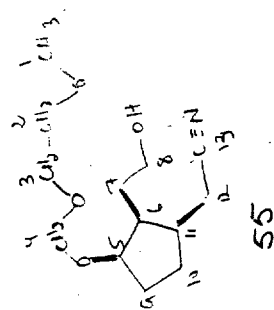
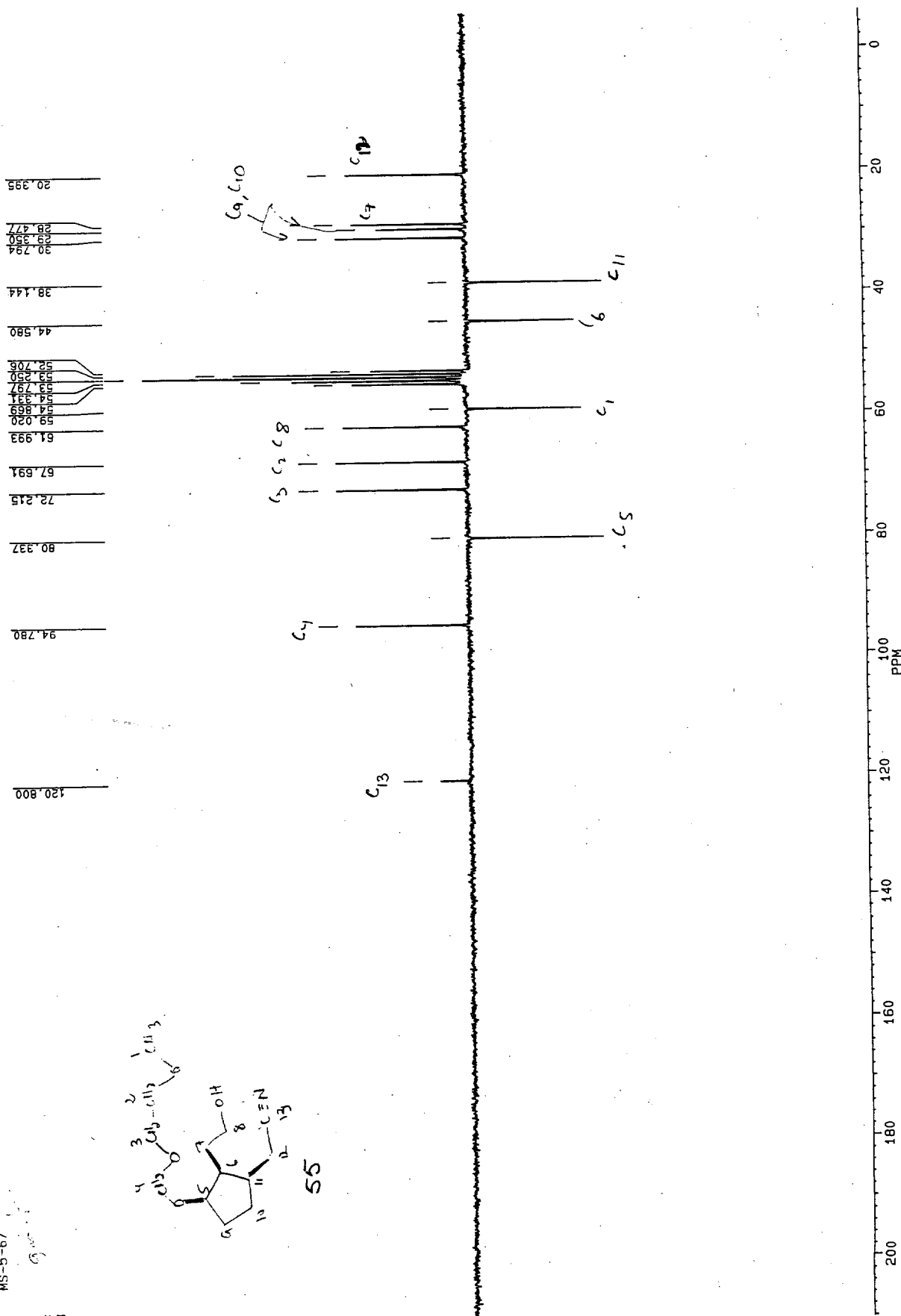
MSC559.002
AU PROC:
APTMR-AU
DATE 3-3-98
TIME 9:48
SF 50.323
SY 194.0
O1 9200.000
SI 16384
TD 16384
SW 15151.515
HZ/PT 1.850
PW 0.0
RD 0.0
RG 32768
NS 14296
TE 297
FW 19000
O2 3700.000
DP 24H CPD
LB 2.000
GB 0.0
CX 36.00
CY 0.0
F1 210.001P
F2 -5.998P
HZ/CM 301.939
PPM/CM 5.000
SR 3402.00
D1 2.0000000
S2 24H
P9 100.00
D2 .0010000
P0 1.20
D3 .0070000
P6 7.20
D4 .0001000
RD 0.0
PW 0.0
DE 49.40
NS 14296
DS 2







MSC567.002
AU 0906
APIXH.AU
DATE 8-1-0
TIME 21:59
SF 50.323
SY 194.0
O1 9200.000
SI 16384
TD 16384
SW 15151.515
HZ/PT 1.850
PW 0.0
RD 0.0
RG 32768
NS 30
TE 297
FW 19000
O2 3700.000
DP 24H CPD
LB 2.000
GB 0.0
CX 36.00
CY 9.00
F1 210.038P
F2 -5.924P
HZ/CM 301.888
PPM/CM 5.999
SR 3394.60
D1 .5000000
S2 24H
P9 100.00
D2 .0010000
P0 1.20
D3 .0070000
P6 7.20
D4 .0001000
RD 0.0
PW 0.0
DE 49.40
NS 30
DS 2

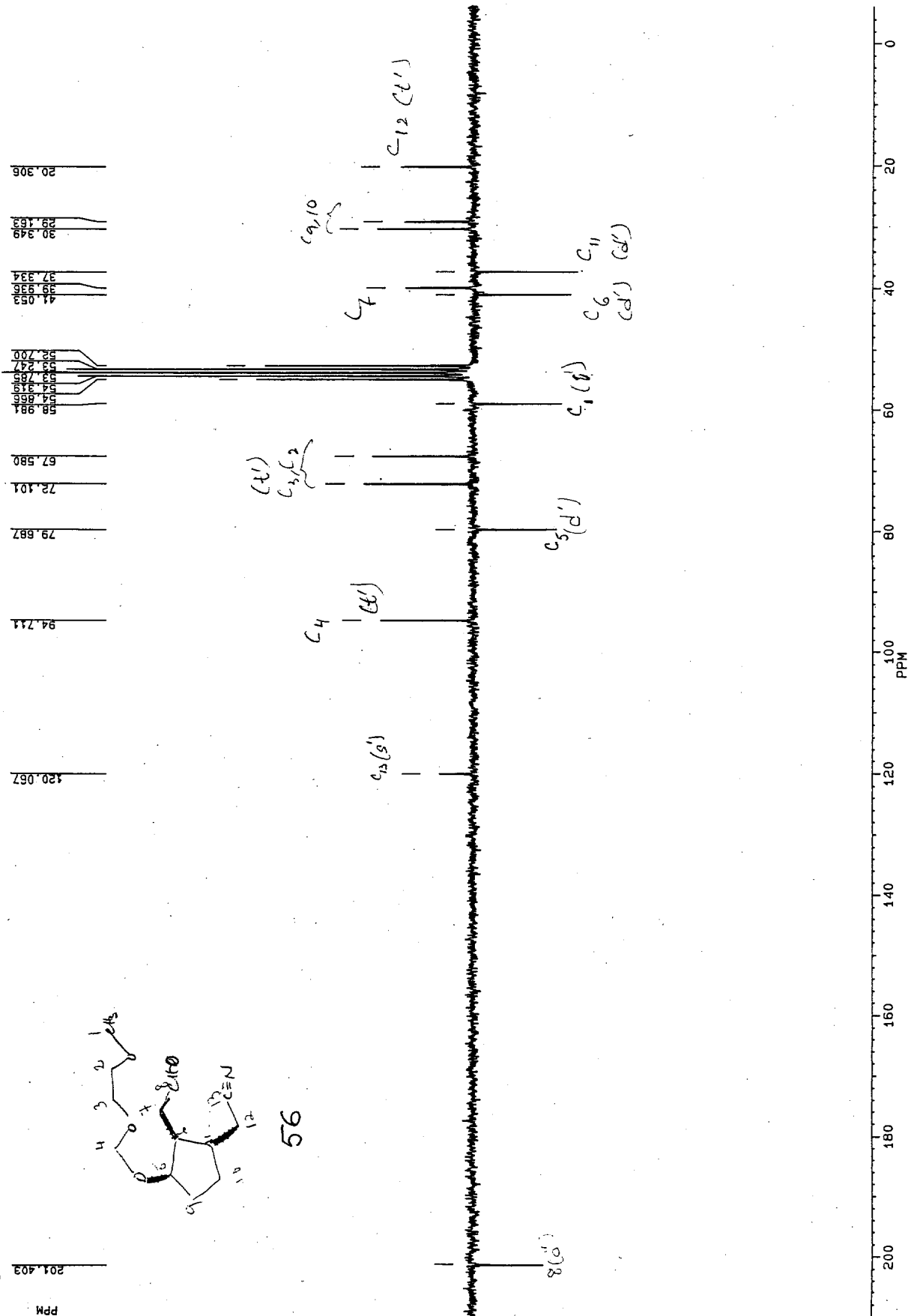
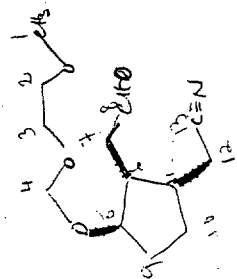


MS-5-67

PPM

13C APT IN CD2CL2 MS-5-69

201.403
PPM



BLUKE

MSC573.002
AU PROG:
APTXH.AU
DATE 13-3-98
TIME 10:13
SF 50.323
SY 194.0
O1 9200.000
SI 16384
TD 16384
SM 15151.515
HZ/PT 1.850
PW 0.0
RD 0.0
RG 32768
NS 15729
TE 297
FW 19000
O2 3700.000
DP 24H CPD
LB 2.000
GB 0.0
CX 36.00
CY 0.0
F1 210.038
F2 -5.924
HZ/CM 301.888
PPM/CM 5.999
SR 3394.50
D1 2.000000
S2 24H
P9 100.00
D2 .001000
P0 1.20
D3 .007000
P6 7.20
D4 .000100
RD 0.0
PW 0.0
DE 49.40
NS 15729
DS 2