

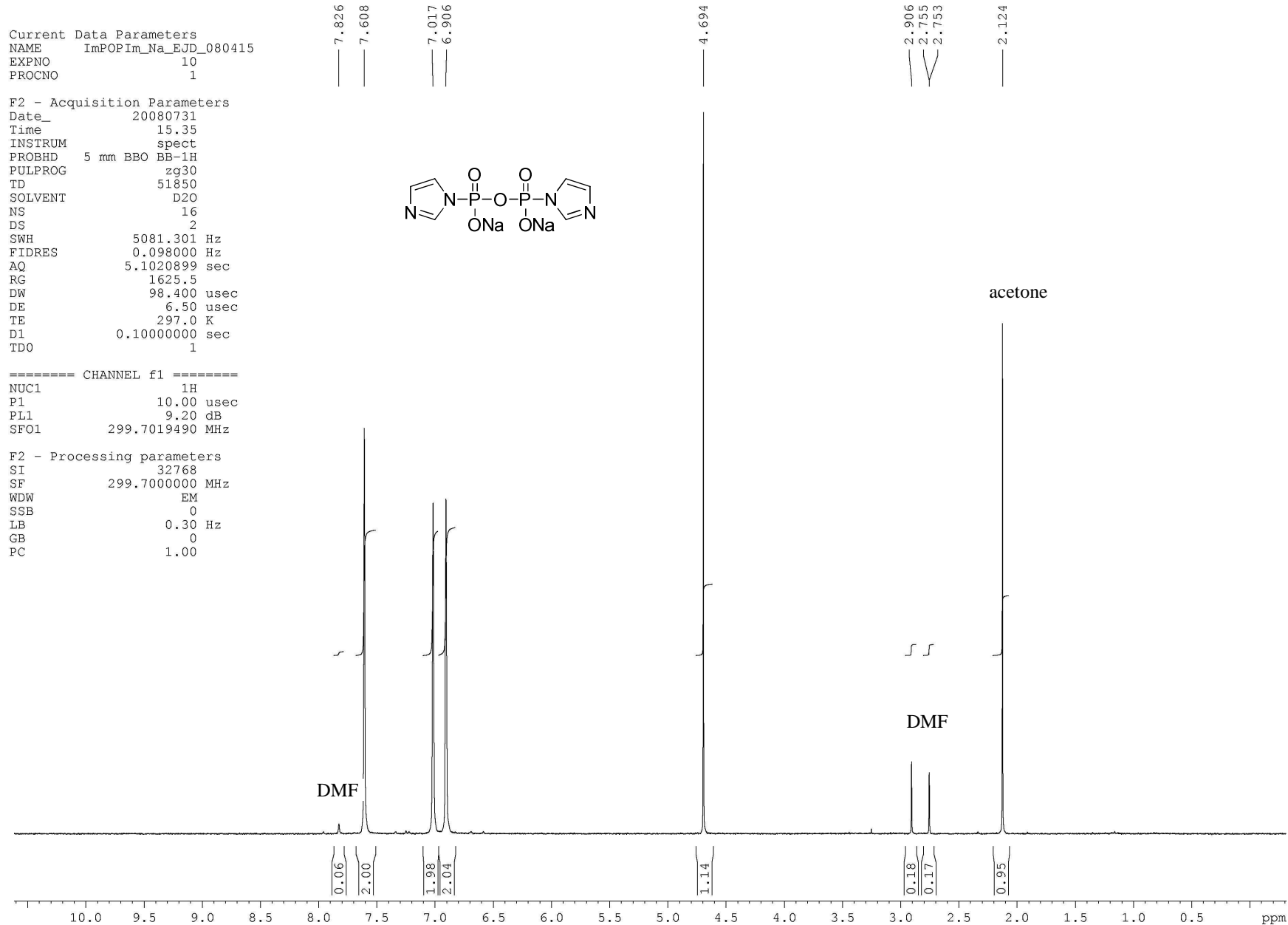
*P*¹,*P*²-Diimidazolyl derivatives of pyrophosphate and *bis*-phosphonates – Synthesis, Properties, and Use in Preparation of Dinucleoside Tetraphosphates and Analogs

Ivan B. Yanachkov, Edward J. Dix, Milka I. Yanachkova, George E. Wright

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¹H NMR of the di-sodium salt of compound 7a in D₂O



³¹P NMR (proton decoupled) of the di-sodium salt of compound **7a** in D₂O

Current Data Parameters
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EXPNO 20
PROCNO 1

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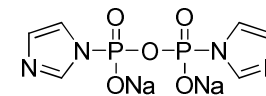
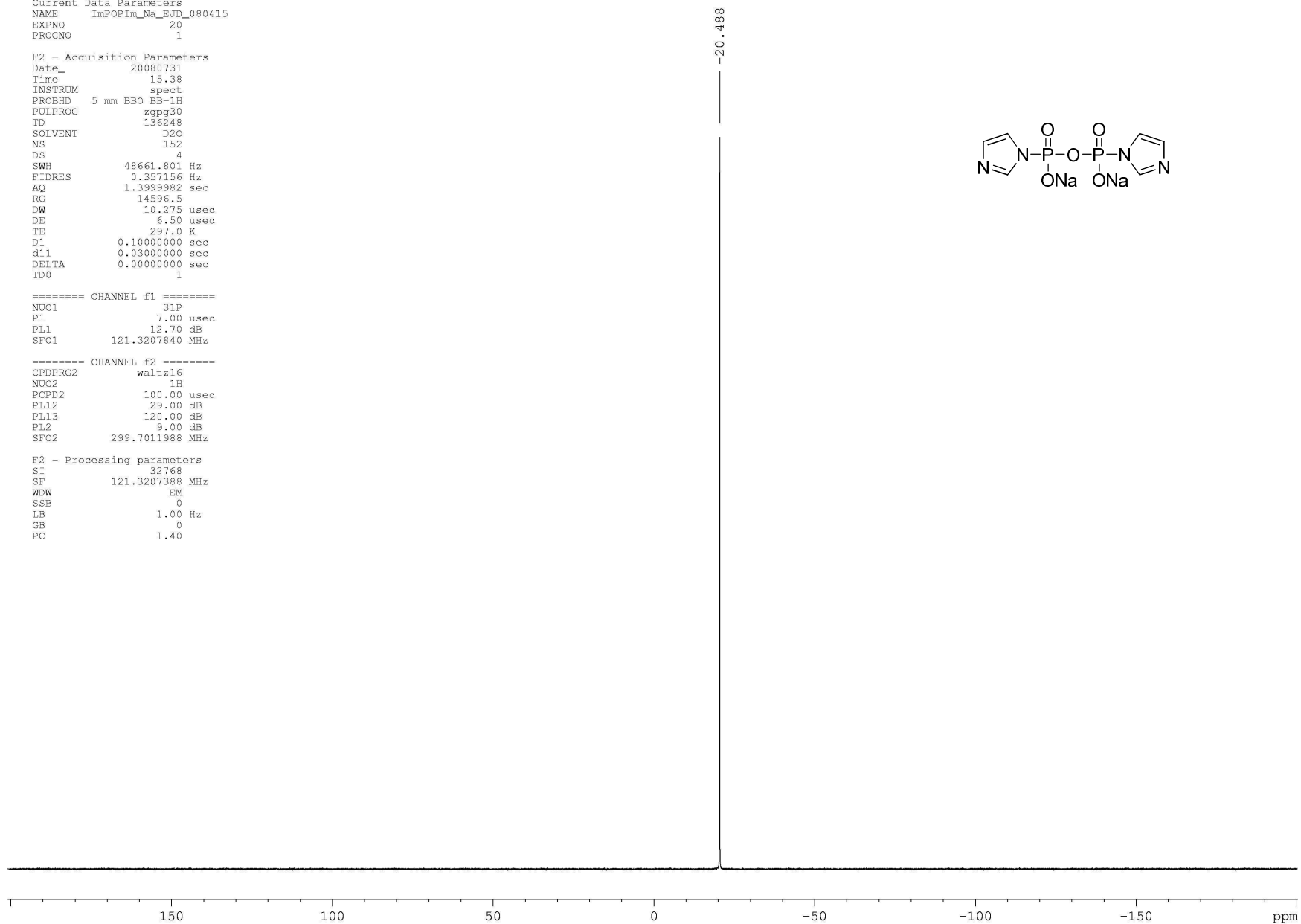
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F2 - Processing parameters

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³¹P NMR (proton coupled) of the di-sodium salt of compound **7a** in D₂O

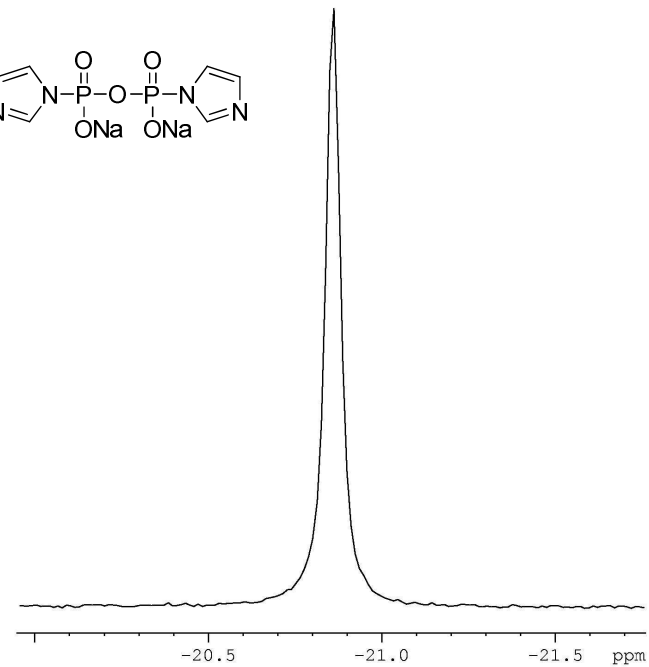
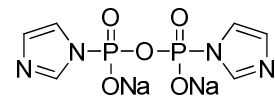
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TE 297.1 K
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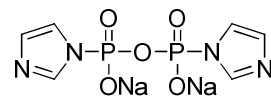
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-20.860



100 50 0 -50 -100 -150 -200 ppm

¹³C NMR of the di-sodium salt of compound **7a** in D₂O



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PROCNO 1

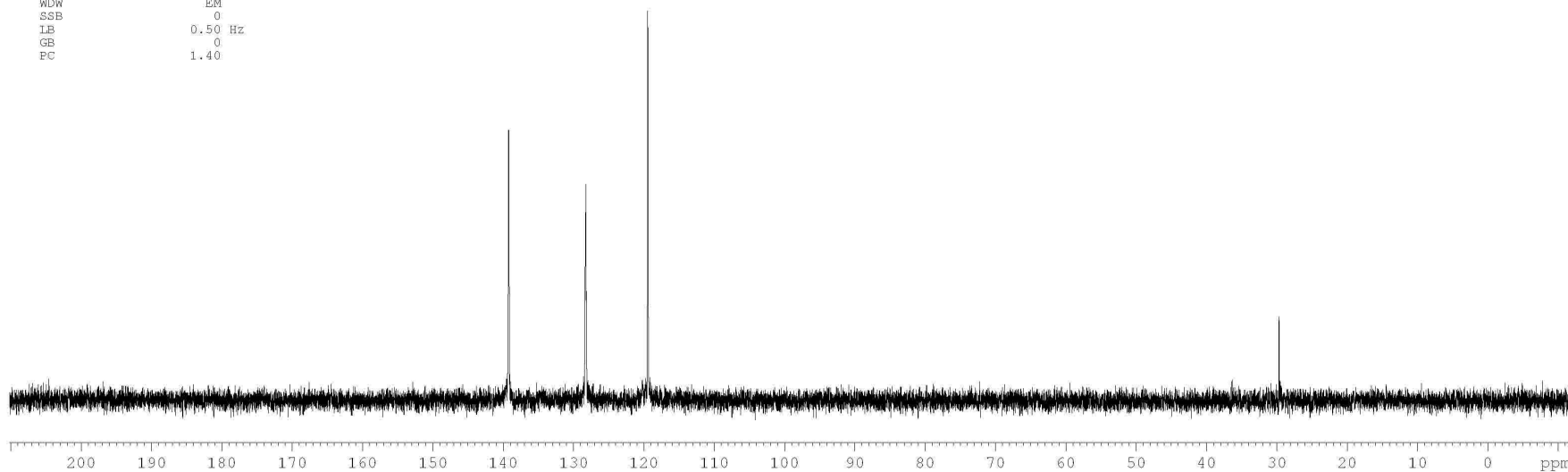
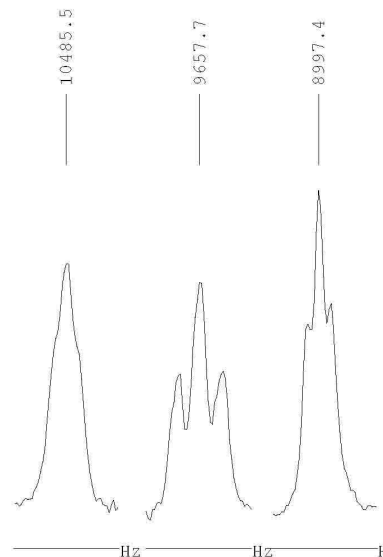
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NS 10240
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FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 2580.3
DW 27.800 usec
DE 6.50 usec
TE 295.0 K
D1 0.10000000 sec
d11 0.03000000 sec
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TDO 1

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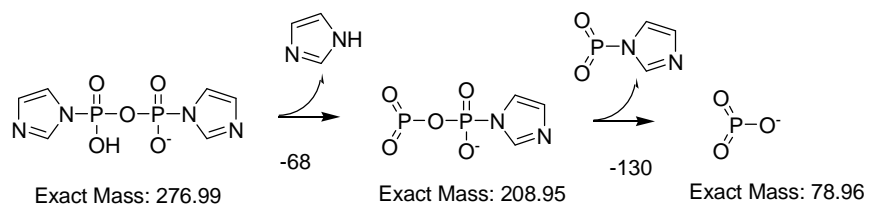
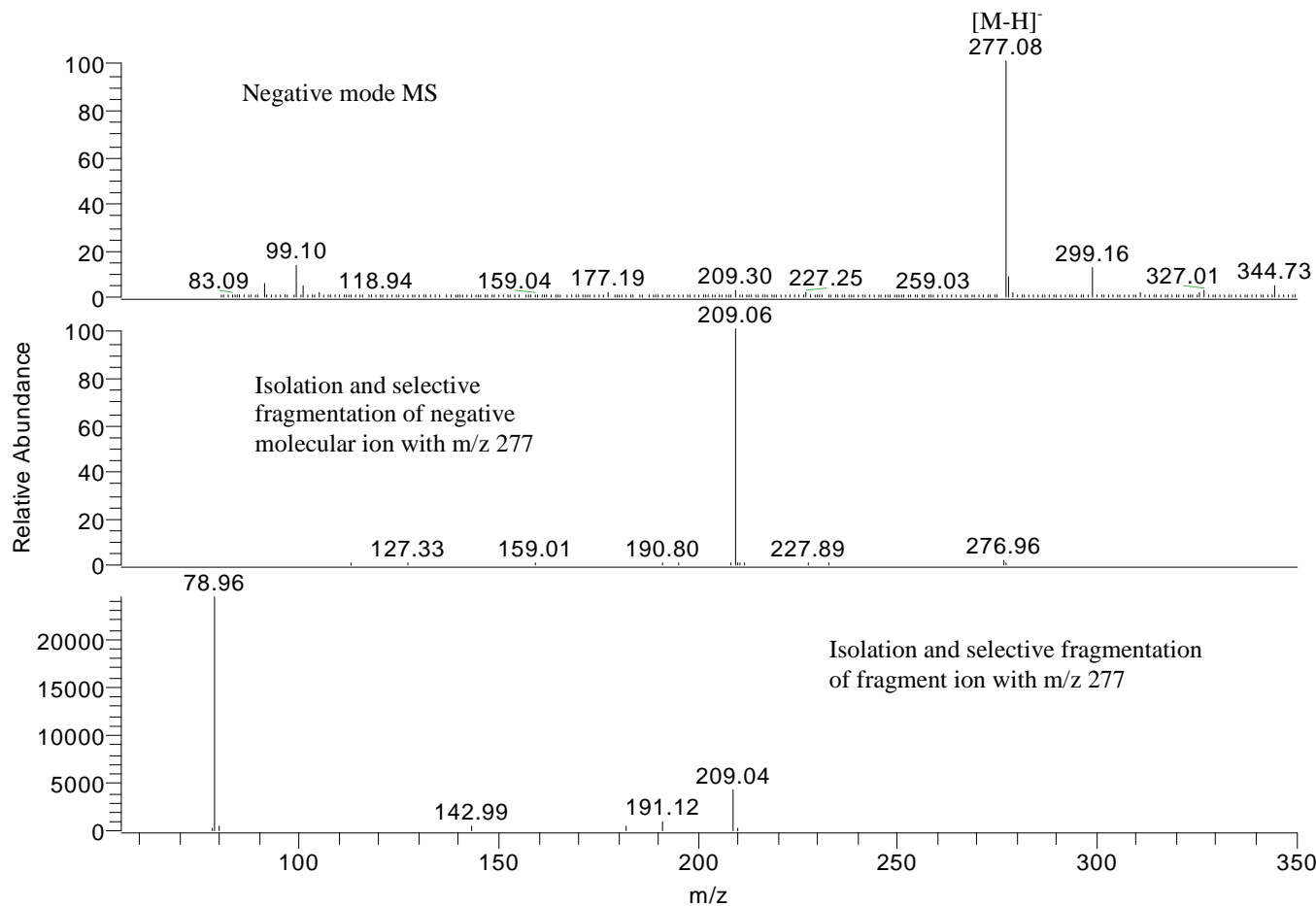
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139.18
128.21
119.41

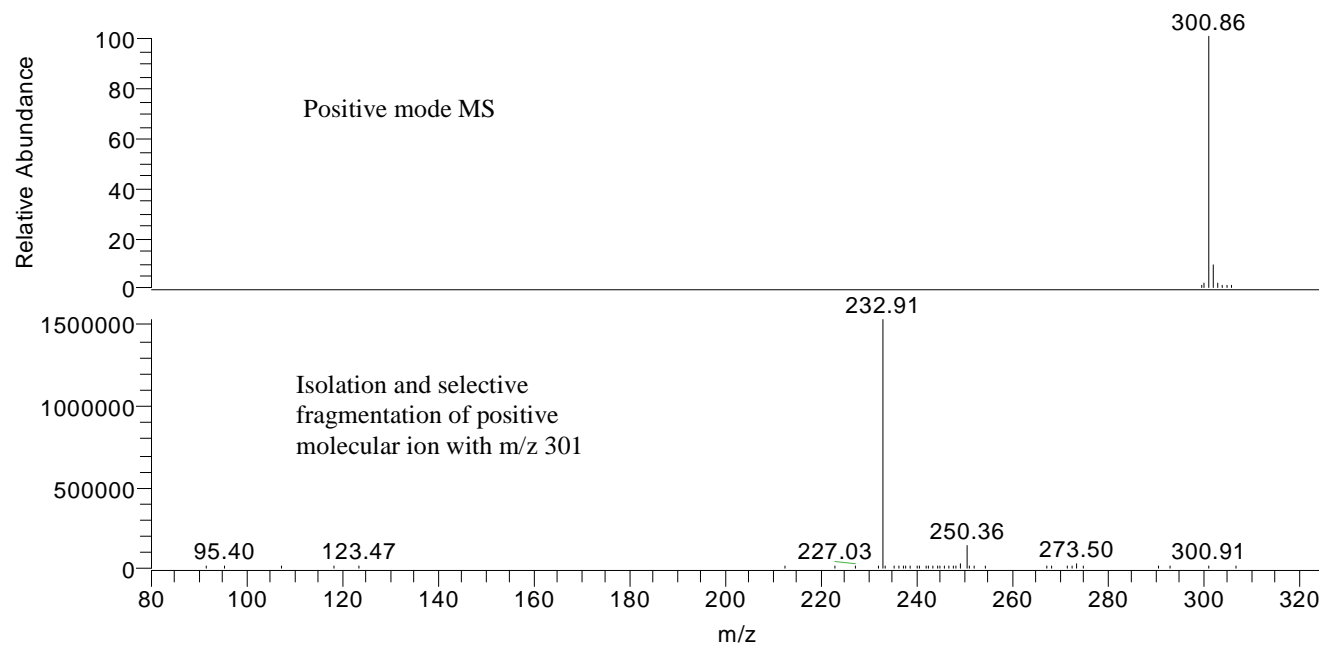


ESI Negative mode MS and selective MS² and MS³ fragmentation of compound **7a**



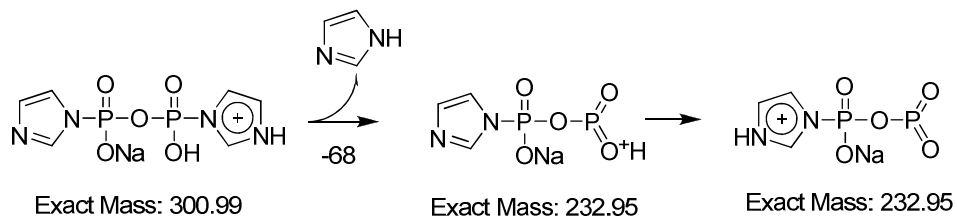
Negative mode fragmentation scheme

ESI Positive mode MS and selective MS² fragmentation of compound **7a**



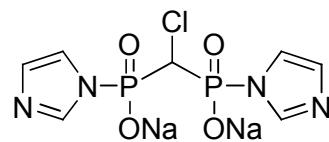
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 107 T: + c ESI Full ms
 [299.00-306.00]

NL: 1.53E6
 ImPOPI_m_Na_{inf}#1455-
 1509 RT: 18.27-19.01 AV:
 55 T: + c ESI Full ms²
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 [80.00-325.00]



Positive mode fragmentation scheme

¹H NMR of the di-sodium salt of compound **7b** in DMSO-d₆/D₂O

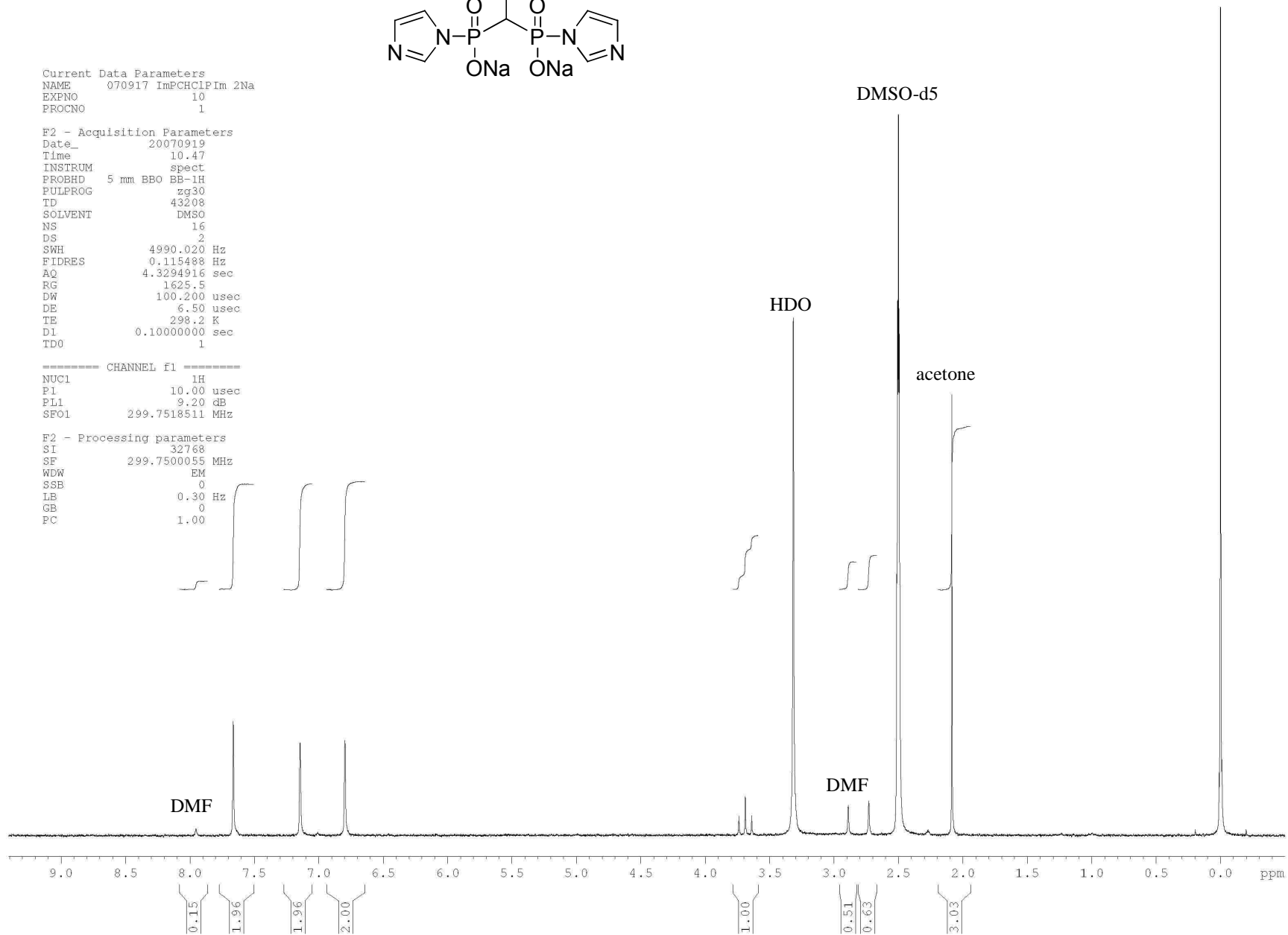


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EXPNO 10
PROCNO 1

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PULPROG zg30
TD 43208
SOLVENT DMSO
NS 16
DS 2
SWH 4990.020 Hz
FIDRES 0.115488 Hz
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RG 1625.5
DW 100.200 usec
DE 6.50 usec
TE 298.2 K
DL 0.10000000 sec
TD0 1

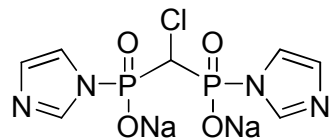
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SSB 0
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³¹P NMR (proton decoupled) of the di-sodium salt of compound **7b** in DMSO-d6/D₂O

31P dec of final product



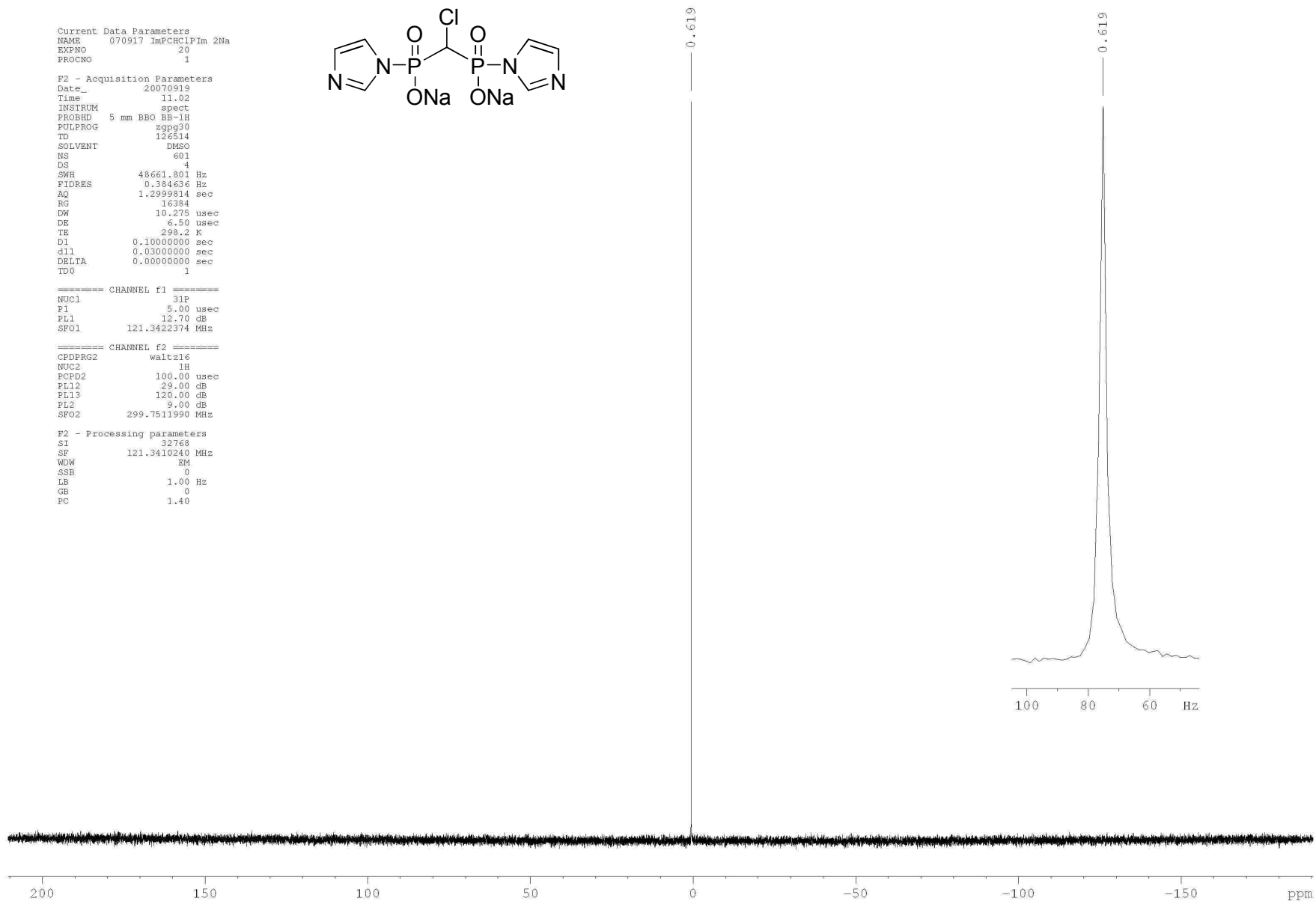
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FIDRES 0.384636 Hz
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DE 6.50 usec
TE 298.2 K
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d11 0.03000000 sec
DELTA 0.00000000 sec
TD0 1

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NUC1 31P
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SFO1 121.3422374 MHz

===== CHANNEL f2 =====
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PL2 9.00 dB
SFO2 299.7511990 MHz

F2 - Processing parameters
SI 32768
SF 121.3410240 MHz
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³¹P NMR (proton coupled) of the di-sodium salt of compound **7b** in DMSO-d₆/D₂O

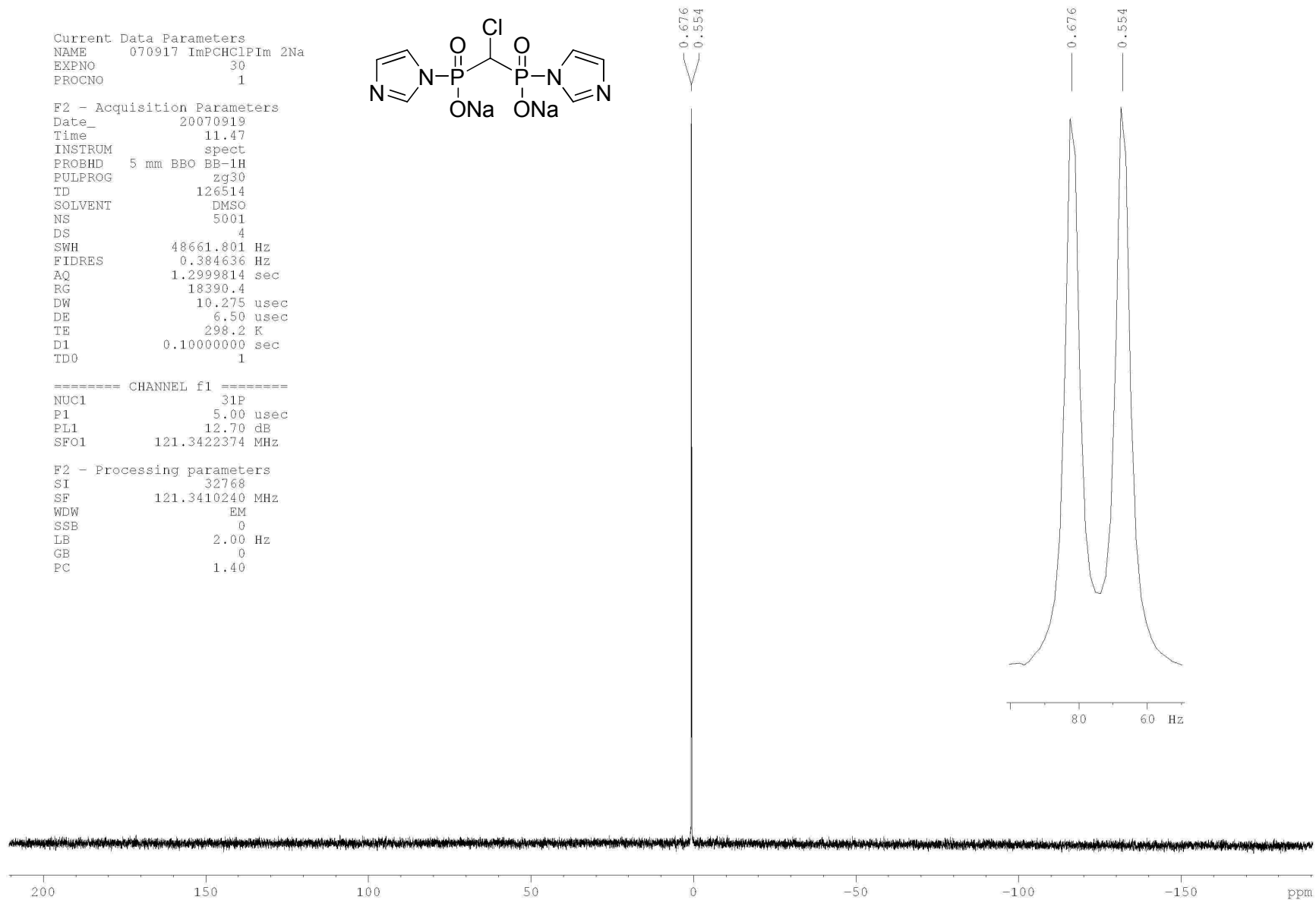
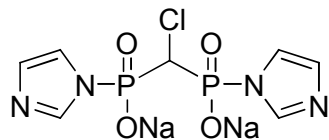
³¹P of final product

Current Data Parameters
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EXPNO 30
PROCNO 1

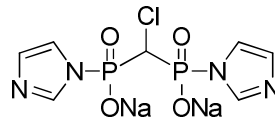
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SOLVENT DMSO
NS 5001
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FIDRES 0.384636 Hz
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RG 18390.4
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TE 298.2 K
D1 0.10000000 sec
TD0 1

==== CHANNEL f1 =====
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PL1 12.70 dB
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F2 - Processing parameters
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LB 2.00 Hz
GB 0
PC 1.40



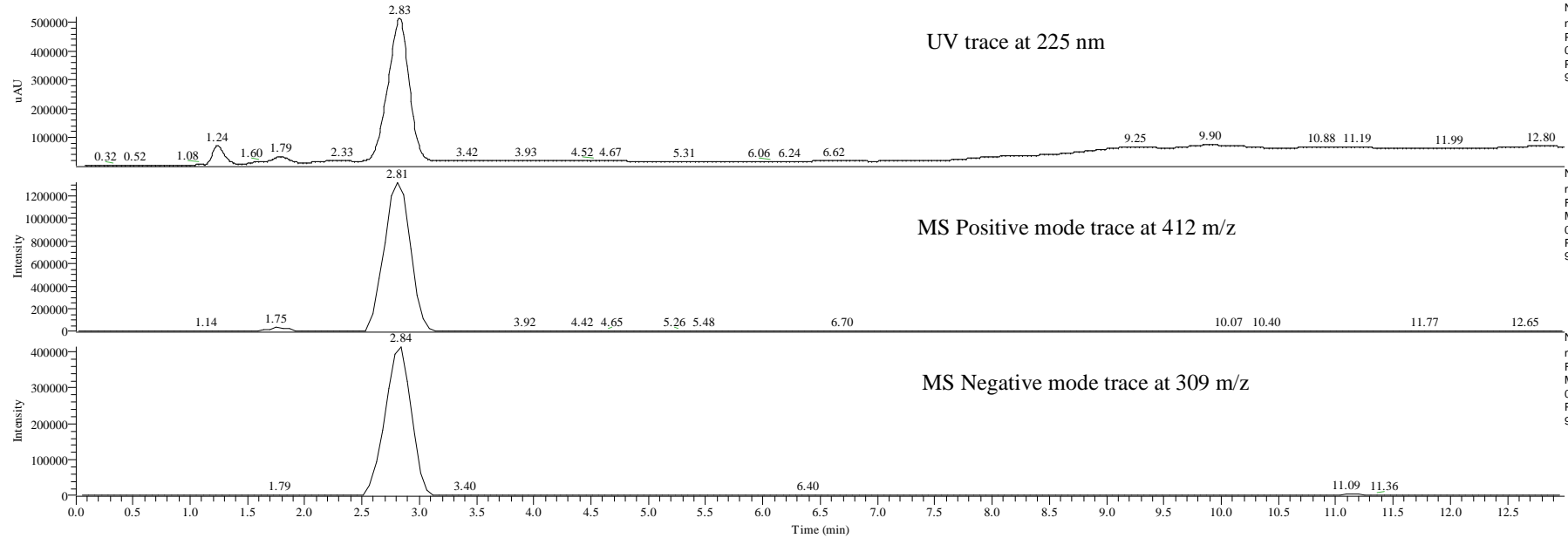
LCMS of the di-sodium salt of compound 7b



040825_lmPPCHCIPlm_Na_040909172926

9/9/2004 5:29:26 PM

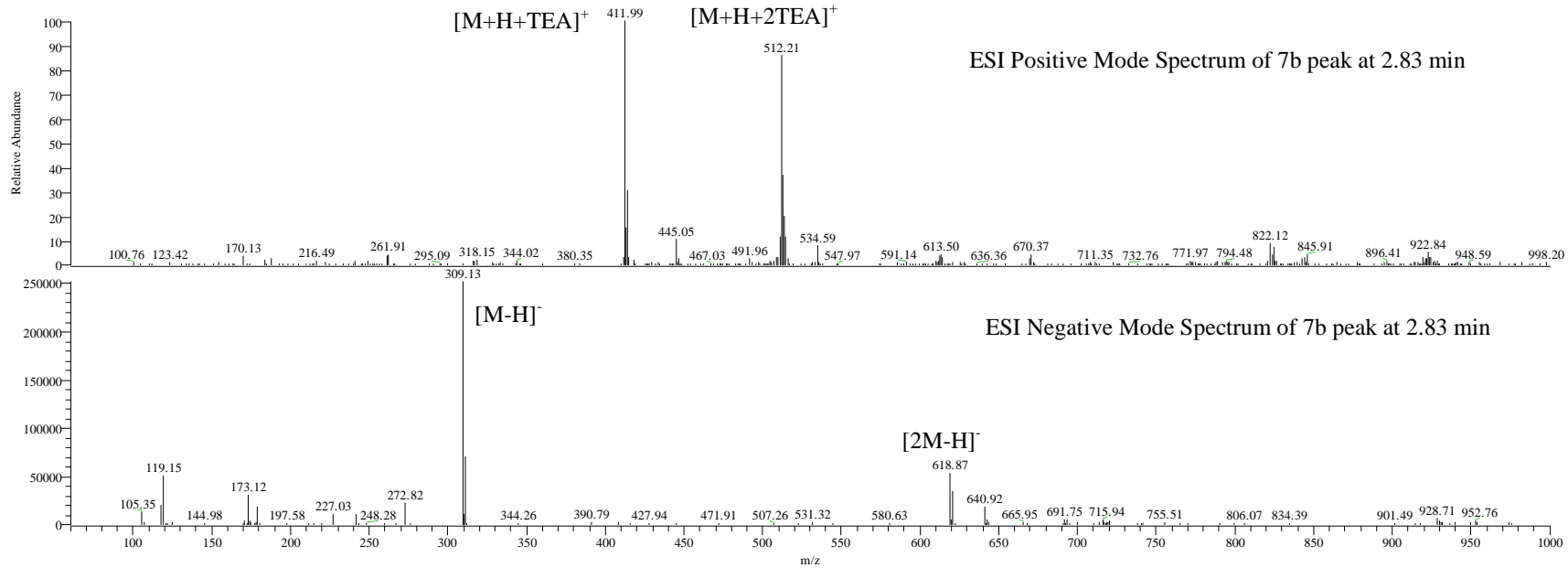
RT: 0.00 - 12.99 SM: 3B



NL: 5.16E5
nm=224.4-225.4
PDA
040825_lmPPCHCI
Plm_Na_040909172
926

NL: 132E6
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F: + c ESI Full ms
MS
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Plm_Na_040909172
926

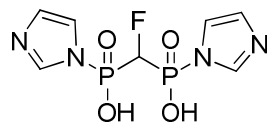
NL: 4.12E5
m/z= 307.63-312.63
F: - c ESI Full ms
MS
040825_lmPPCHCI
Plm_Na_040909172
926



NL: 1.18E6
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909172926#96-103 RT:
2.70-2.87 AV: 4 SB: 7
MS
2.40-2.53 , 3.12-3.31 T: + c
ESI Full ms [60.00-1000.00]

NL: 2.51E5
040825_lmPPCHCIPlm_Na_040
909172926#97-107 RT:
2.73-2.95 AV: 5 SB: 10
MS
2.34-2.53 , 3.07-3.34 F: - c ESI
Full ms

LCMS of the di-sodium salt of compound 7c

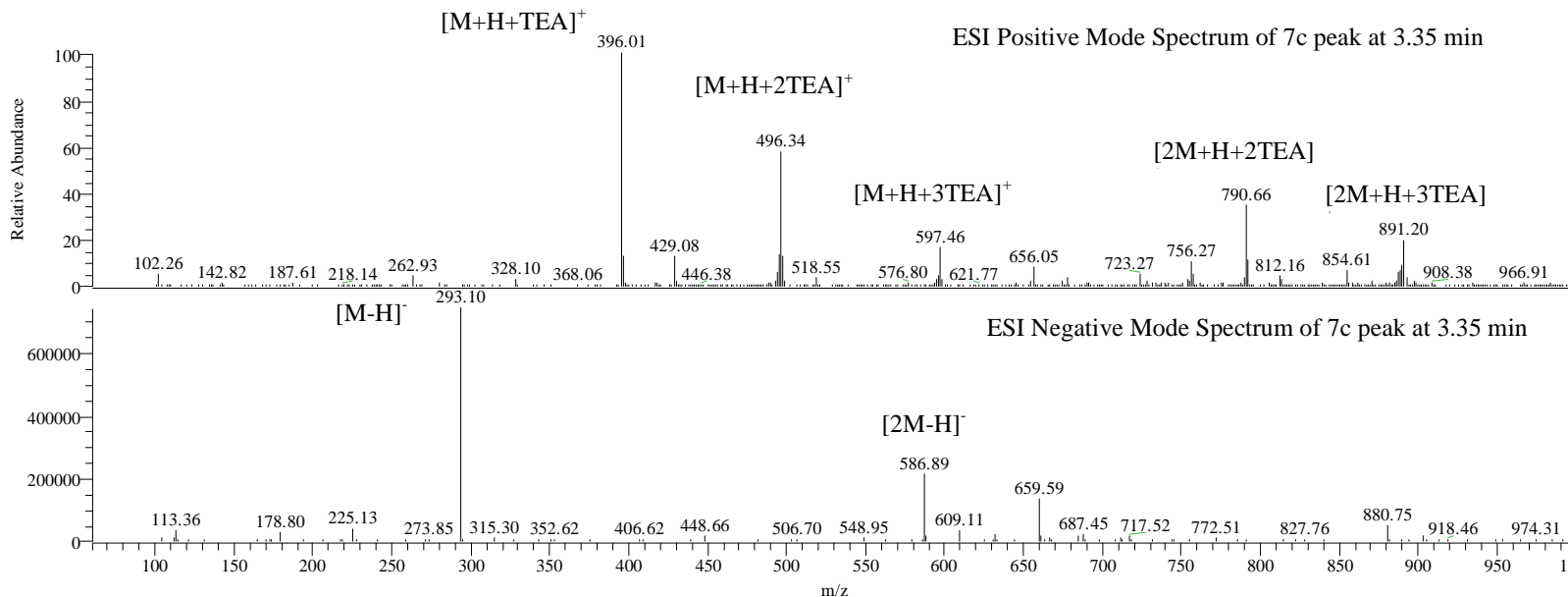
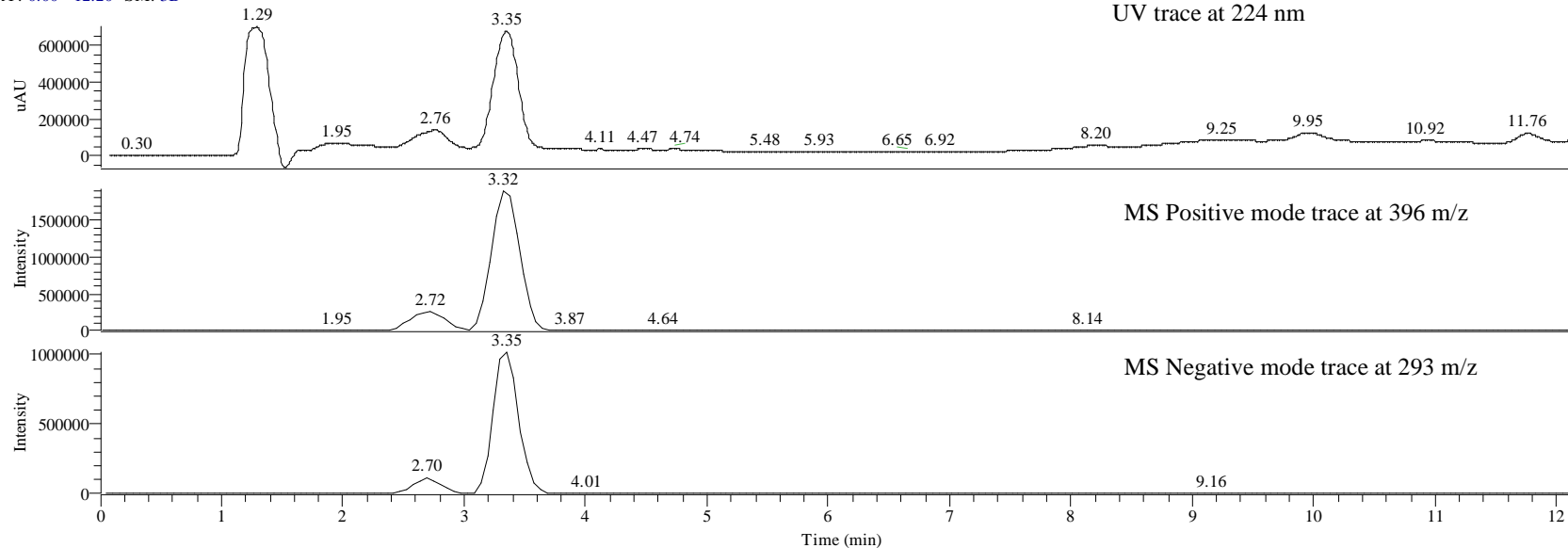


Exact Mass: 294.01

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9/10/2004 3:12:20 PM

RT: 0.00 - 12.20 SM: 3B



¹H NMR of the di-sodium salt of compound **7d** in DMSO-d₆

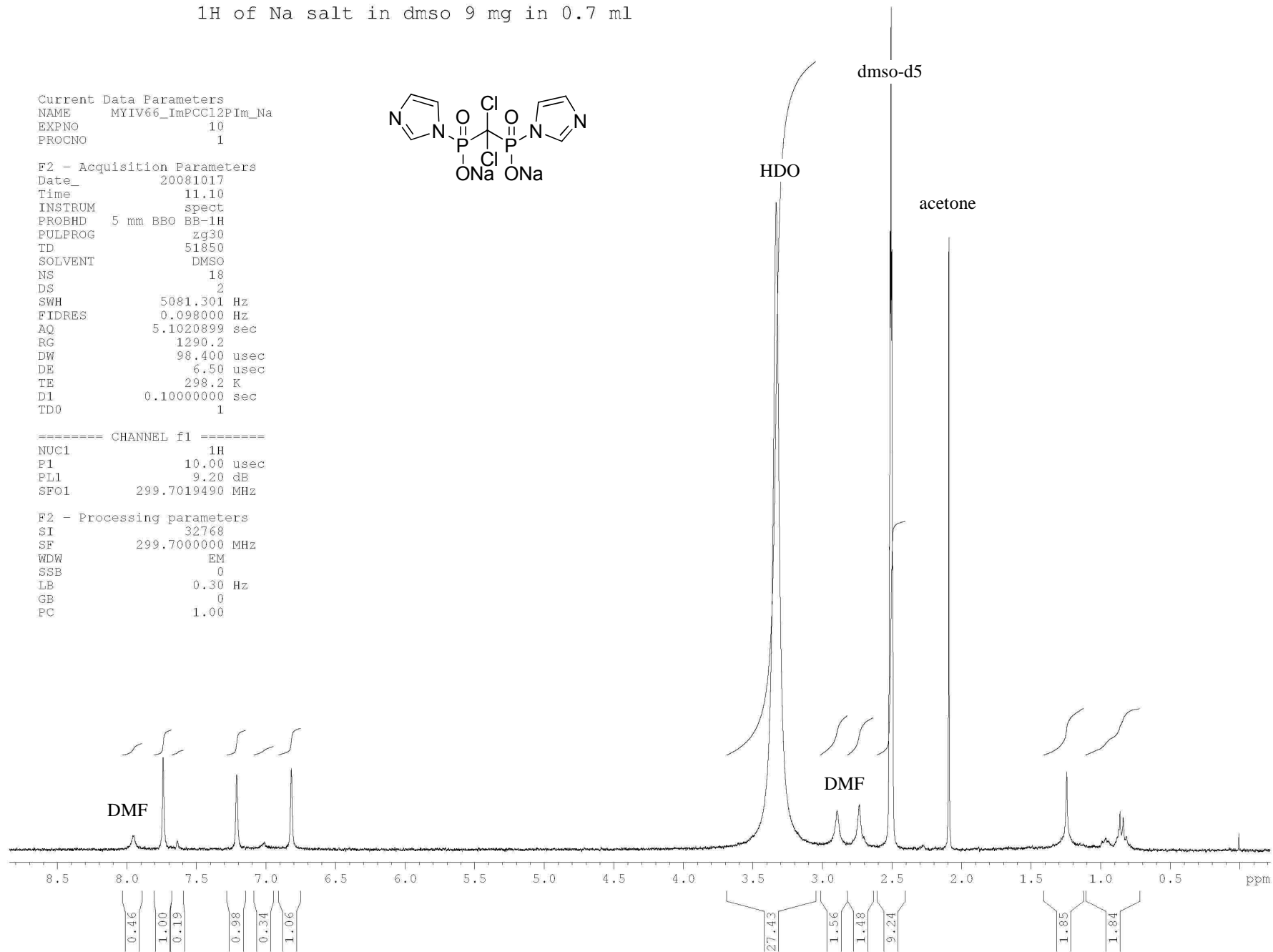
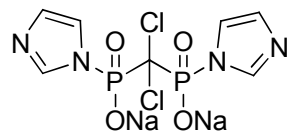
1H of Na salt in dms0 9 mg in 0.7 ml

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PROCNO 1

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PULPROG zg30
TD 51850
SOLVENT DMSO
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DS 2
SWH 5081.301 Hz
FIDRES 0.098000 Hz
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RG 1290.2
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DE 6.50 usec
TE 298.2 K
D1 0.10000000 sec
TD0 1

===== CHANNEL f1 =====
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SFO1 299.7019490 MHz

F2 - Processing parameters
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LB 0.30 Hz
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PC 1.00



³¹P NMR (proton decoupled) of the di-sodium salt of compound **7d** in DMSO-d₆

31P dec of Na salt in dms0 9 mg in 0.7 ml

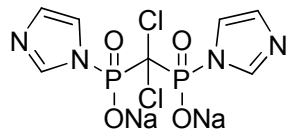
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SOLVENT DMSO
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SWH 48661.801 Hz
FIDRES 0.357156 Hz
AQ 1.3999982 sec
RG 16384
DW 10.275 usec
DE 6.50 usec
TE 298.2 K
D1 0.10000000 sec
d11 0.03000000 sec
DELTA 0.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 31P
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PL1 12.70 dB
SFO1 121.3207840 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL12 29.00 dB
PL13 120.00 dB
PL2 9.00 dB
SFO2 299.7011988 MHz

F2 - Processing parameters
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LB 1.00 Hz
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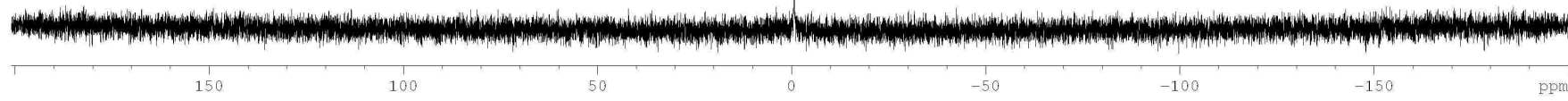
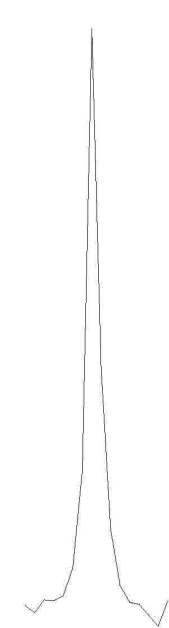
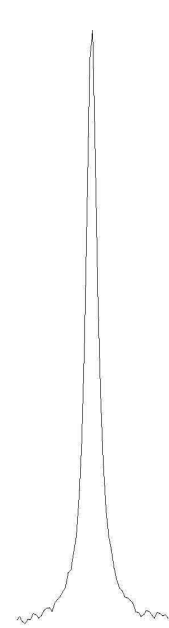
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proton
decoupled

proton
coupled

-0.658

-0.659

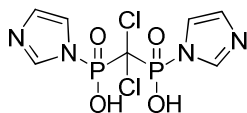


LCMS of the di-sodium salt of compound 7d

\\90.0.0.63\csl\...MYIV66_impCC12plm_ol
5 mg/ml in 20 mM TEAA

5/27/2009 6:00:40 PM

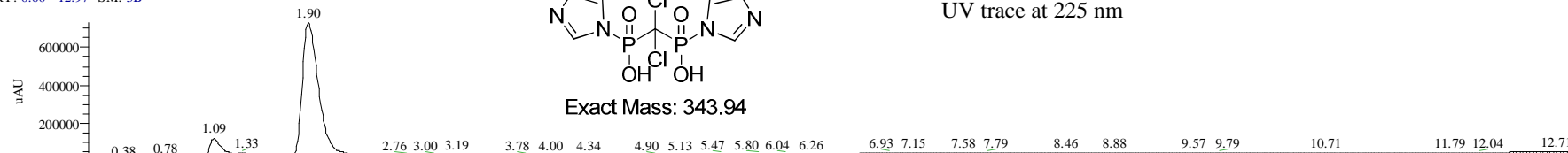
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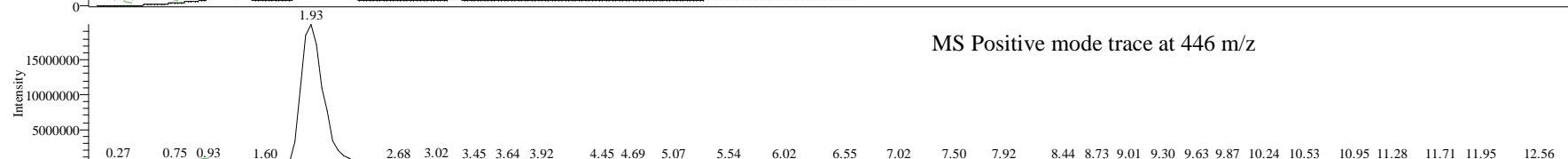
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PDA
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plm_ol



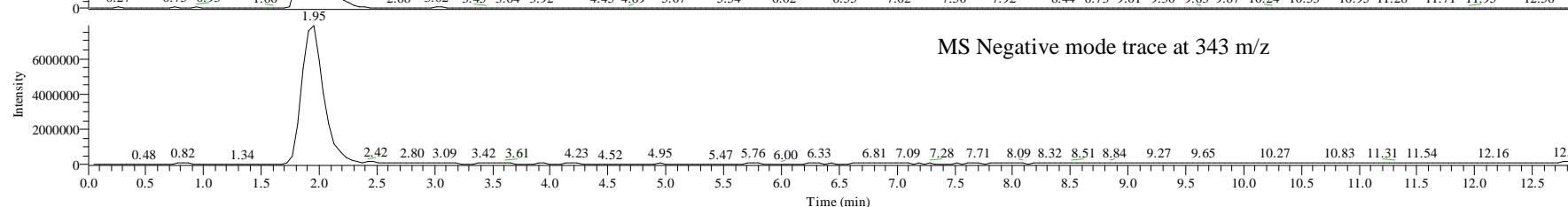
MS Positive mode trace at 446 m/z

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MS
MYIV66_impCC12
plm_ol



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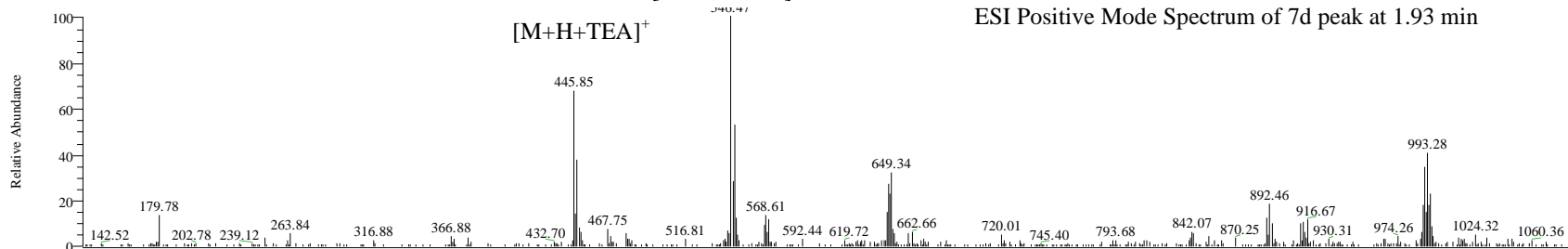
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m/z=
34198-345.93 F: -
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MYIV66_impCC12
plm_ol



$[M+H+2TEA]^+$

ESI Positive Mode Spectrum of 7d peak at 1.93 min

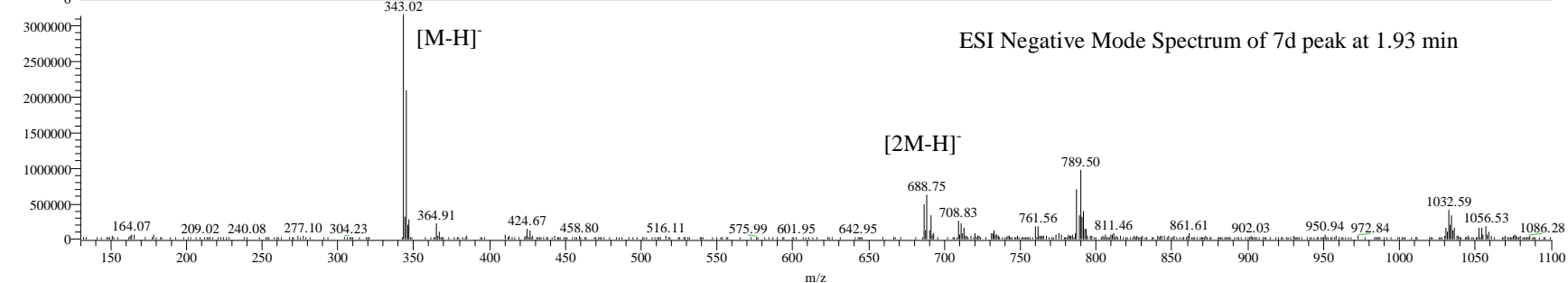
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d#76-87 RT: 1.84-2.06
AV: 6 SB: 14 1.48-1.74
, 2.21-2.54 F: + c ESI
Full ms



$[M-H]^-$

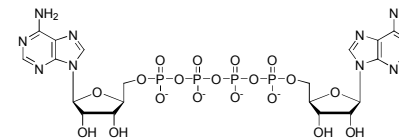
ESI Negative Mode Spectrum of 7d peak at 1.93 min

NL: 3.13E6
MYIV66_impCC12plm_ol
d#75-86 RT: 1.81-2.04
AV: 6 SB: 12 1.46-1.72
, 2.18-2.42 F: - c ESI
Full ms



$[2M-H]^-$

1H NMR spectrum of Ap4A sodium salt, **3a** in D₂O



1H NMR of Ap4A Na salt in D2O batch 070420

Current Data Parameters

NAME 070420_Ap4A
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters

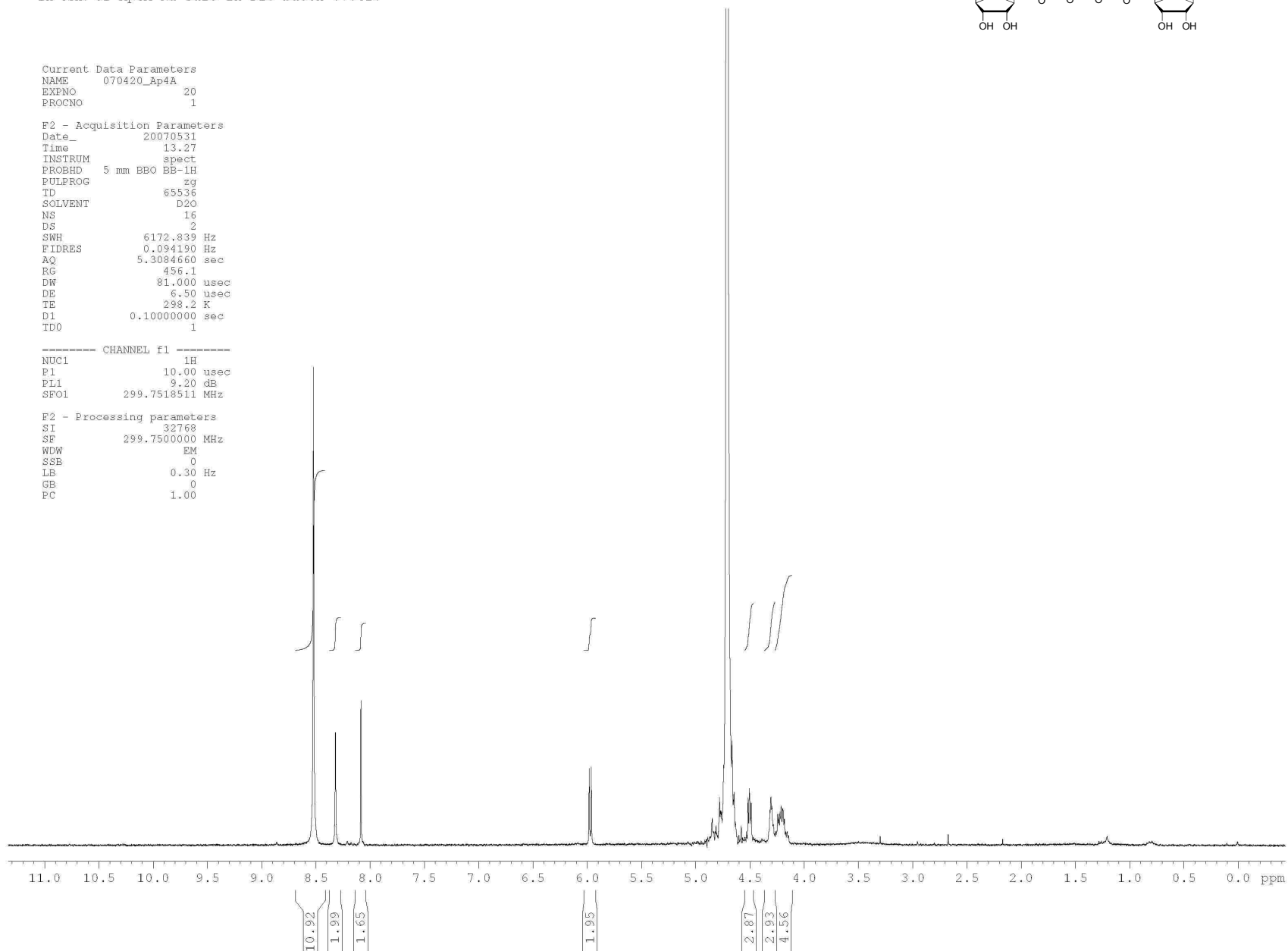
Date_ 20070531
Time 13.27
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 65536
SOLVENT D2O
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 456.1
DW 81.000 usec
DE 6.50 usec
TE 298.2 K
D1 0.1000000 sec
TD0 1

CHANNEL f1

NUC1 1H
P1 10.00 usec
PL1 9.20 dB
SFO1 299.7518511 MHz

F2 - Processing parameters

SI 32768
SF 299.7500000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



³¹P (proton decoupled) NMR spectrum of Ap₄A sodium salt, **3a** in D₂O

Current Data Parameters
 NAME 070420_Ap4A
 EXPNO 30
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070531
 Time 12.50
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg
 TD 126514
 SOLVENT D2O
 NS 94
 DS 4
 SMH 48661.801 Hz
 FIDRES 0.384636 Hz
 AQ 1.2999814 sec
 RG 23170.5
 DW 10.275 usec
 DE 6.50 usec
 TE 298.2 K
 D1 0.20000000 sec
 TD0 1

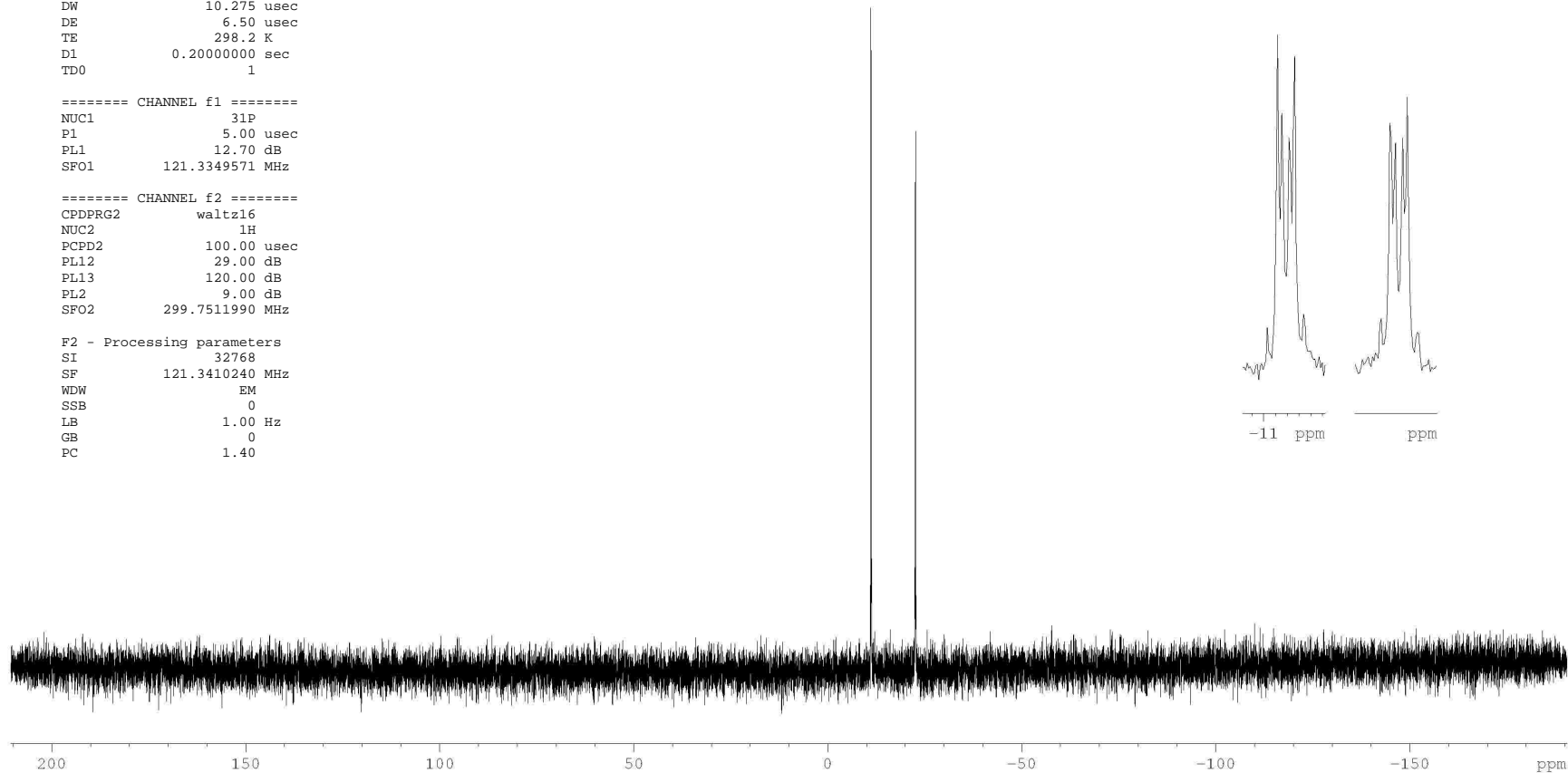
==== CHANNEL f1 =====
 NUC1 31P
 P1 5.00 usec
 PL1 12.70 dB
 SFO1 121.3349571 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL12 29.00 dB
 PL13 120.00 dB
 PL2 9.00 dB
 SFO2 299.7511990 MHz

F2 - Processing parameters
 SI 32768
 SF 121.3410240 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

-11.033
 -11.118
 -11.156
 -11.220
 -11.262
 -11.341
 -22.471
 -22.553
 -22.594
 -22.658
 -22.695
 -22.785

-1349.081
 -1353.629
 -1361.388
 -1366.507
 -2736.628
 -2741.617
 -2749.344
 -2753.889



³¹P (proton coupled) NMR spectrum of Ap₄A sodium salt, **3a** in D₂O

Current Data Parameters

NAME 070420_Ap4A
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters

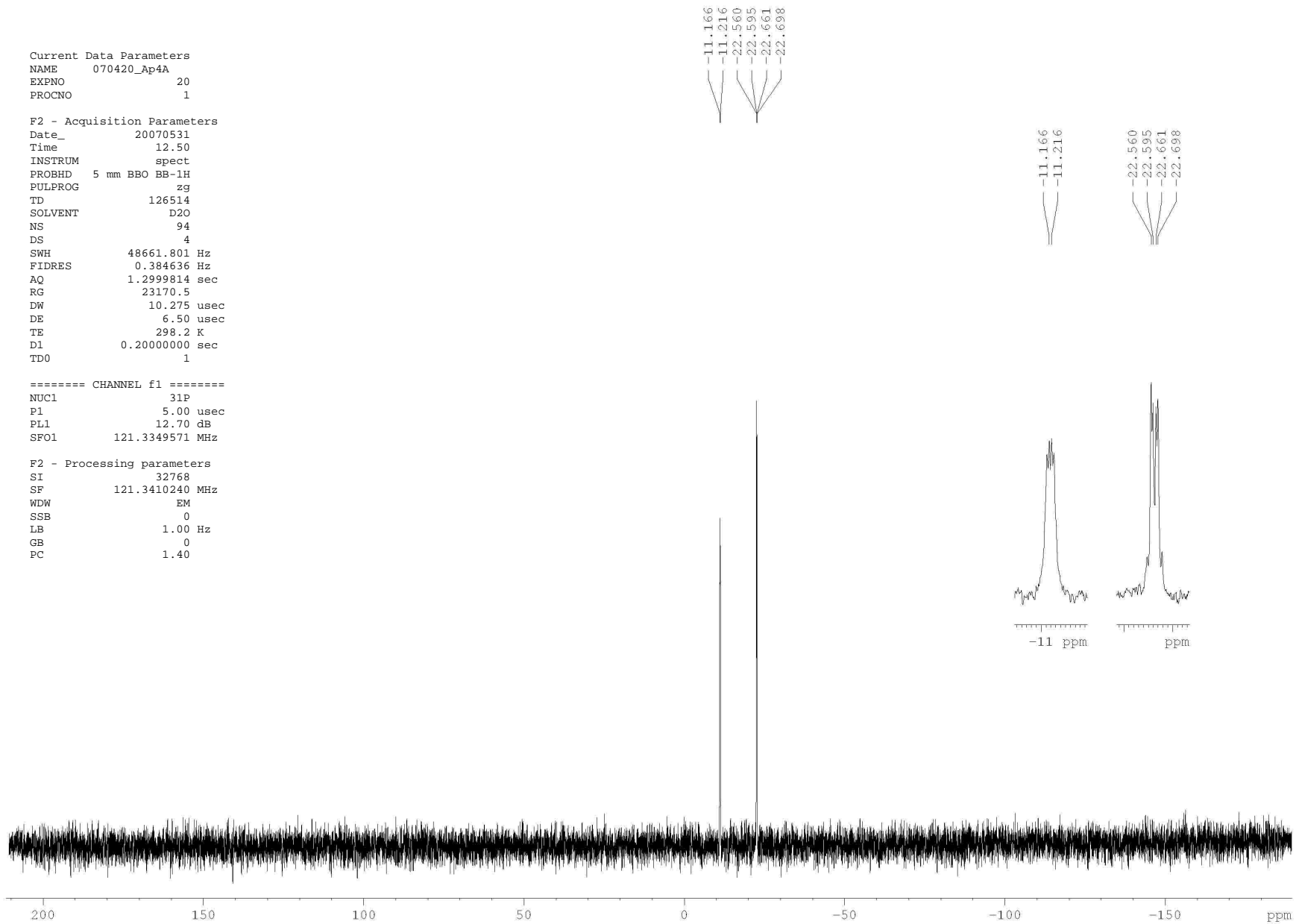
Date_ 20070531
Time 12.50
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 126514
SOLVENT D2O
NS 94
DS 4
SWH 48661.801 Hz
FIDRES 0.384636 Hz
AQ 1.2999814 sec
RG 23170.5
DW 10.275 usec
DE 6.50 usec
TE 298.2 K
D1 0.20000000 sec
TDO 1

==== CHANNEL f1 =====

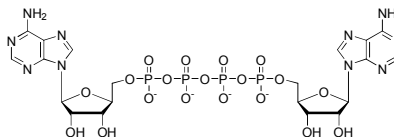
NUC1 31P
P1 5.00 usec
PL1 12.70 dB
SFO1 121.3349571 MHz

F2 - Processing parameters

SI 32768
SF 121.3410240 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



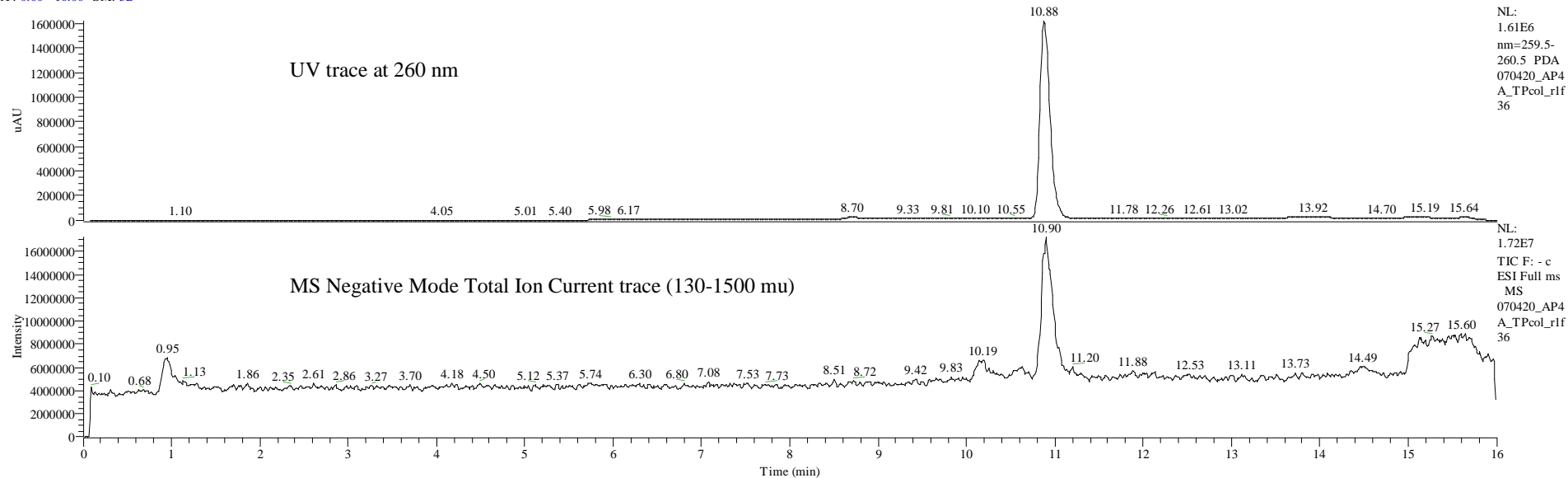
LCMS of Ap₄A, 3a



070420_AP4A_TPcol_r1f6

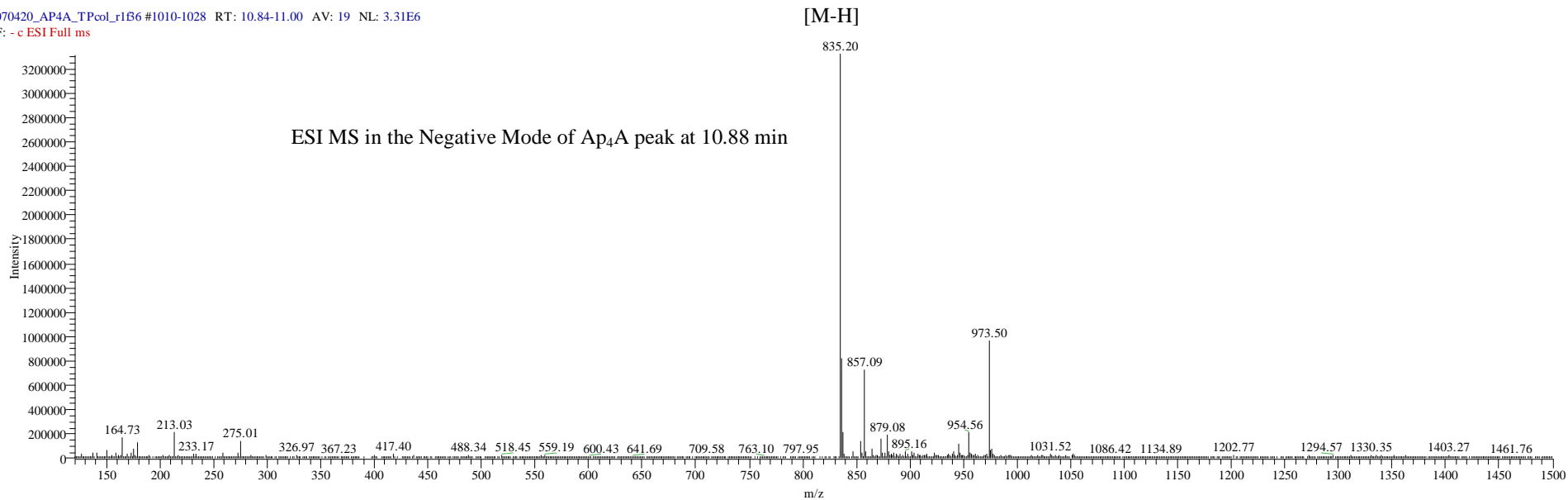
5/4/2007 9:15:19 AM

RT: 0.00 - 16.00 SM: 3B

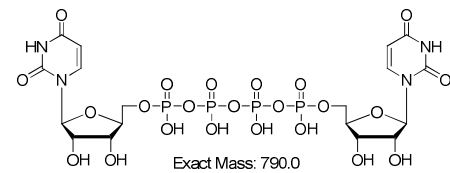


070420_AP4A_TPcol_r1f6 #1010-1028 RT: 10.84-11.00 AV: 19 NL: 3.31E6

F: - c ESI Full ms



1H NMR spectrum of Up₄U sodium salt, **3f** in D₂O



1H NMR of UP4U Na salt, 050223 and 050217 in d2o

```

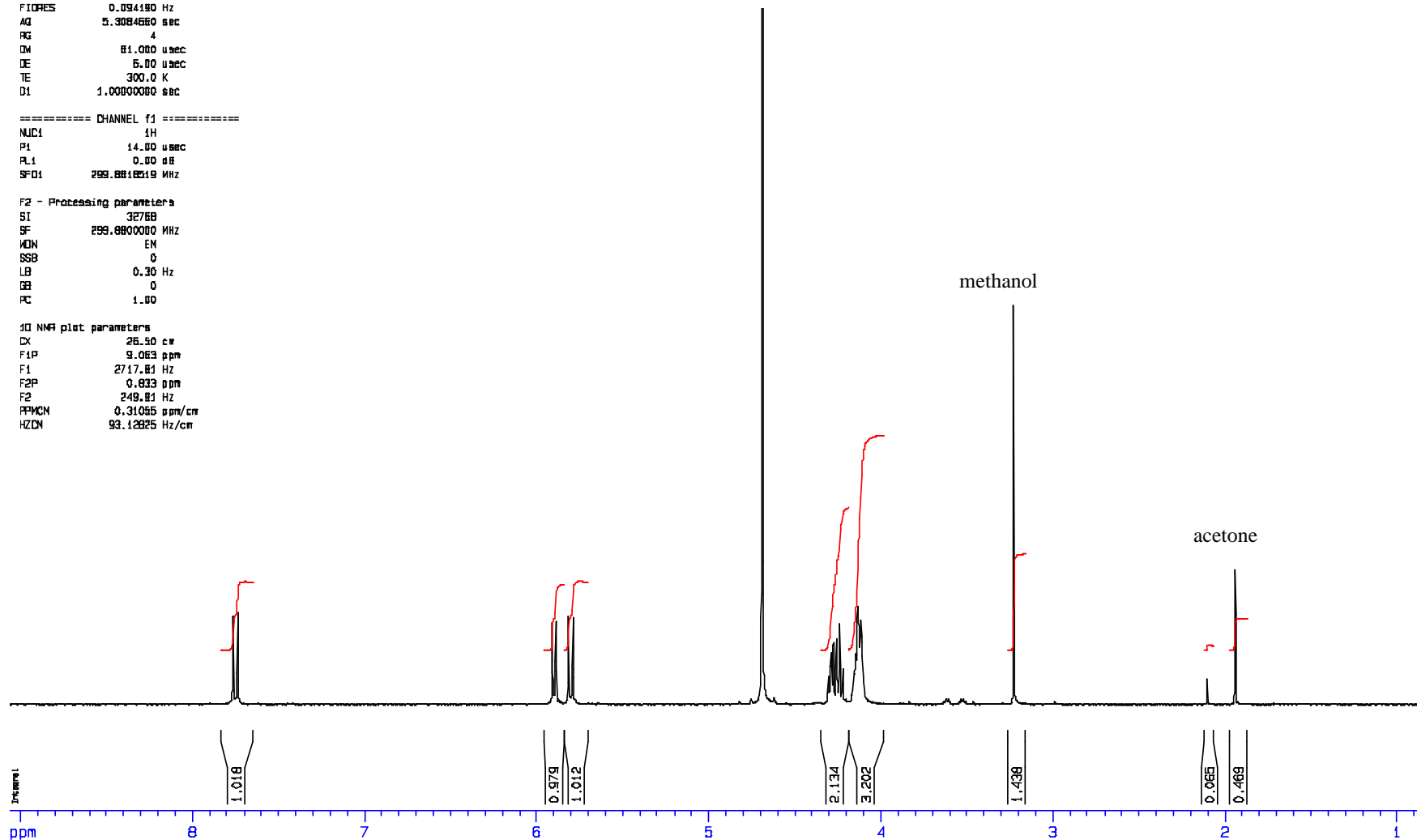
Current Data Parameters
NAME      050227_UP4U_Na
EXPNO    10
PROCNO    1

F2 - Acquisition Parameters
Date_     20050311
Time      10.05
INSTRUM   spect
PROBHD    5 mm Multinuc
PULPROG   zg30
TD        65536
SOLVENT   D2O
NS        16
DS        2
SWH       6172.839 Hz
FIDRES    0.094190 Hz
AQ        0.3084660 sec
RG        4
DM        81.000 usec
DE        5.00 usec
TE        300.0 K
D1        1.0000000 sec

===== CHANNEL f1 =====
NUC1      1H
P1        14.00 usec
PL1       0.00 dB
SFO1      299.8818219 MHz

F2 - Processing parameters
SI        32768
SF        299.8800000 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00

4D NMR plot parameters
CX        26.50 cm
F1P       9.063 ppm
F1        2717.81 Hz
F2P       0.633 ppm
F2        249.81 Hz
PPMCM    0.31055 ppm/cm
HZCM     93.12825 Hz/cm
    
```



³¹P (proton decoupled) NMR spectrum of Up₄U sodium salt, **3f** in D₂O

Current Data Parameters
 NAME 050227_LP4U_No
 EXPNO 40
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050311
 Time 10.31
 INSTRUM spect
 PROBHD 5 mm Multinuc
 PULPROG zgpg30
 TD 145980
 SOLVENT d2o
 NS 88
 DS 32
 SSB 48661.801 Hz
 FIDRES 0.333246 Hz
 AQ 1.4898945 sec
 RG 28643.0
 DW 10.275 usec
 DE 5.00 usec
 TE 300.0 K
 D1 0.10000000 sec
 d11 0.03000000 sec
 d12 0.00000000 sec

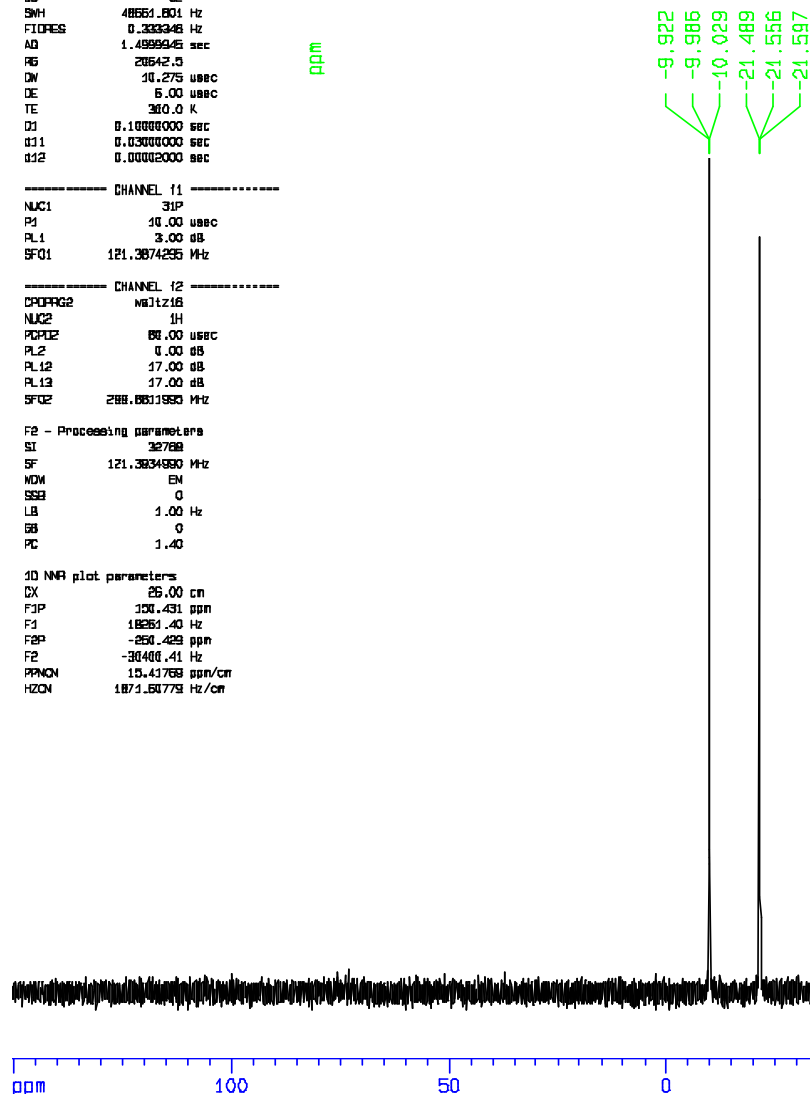
----- CHANNEL f1 -----
 NUC1 ³¹P
 P1 10.00 usec
 PL1 3.00 dB
 SFO1 121.3874255 MHz

----- CHANNEL f2 -----
 CHARGE2 m31z128
 NUC2 ¹H
 PPRG2 88.00 usec
 PL2 0.00 dB
 PL12 17.00 dB
 PL13 17.00 dB
 SFO2 288.8811993 MHz

F2 - Processing parameters
 SI 32768
 SF 121.3834930 MHz
 MDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 25.00 cm
 F1P 106.431 ppm
 F1 18261.40 Hz
 F2P -250.429 ppm
 F2 -30400.41 Hz
 PRNOM 15.41769 ppm/cm
 HZOM 1871.6075 Hz/cm

³¹P {1H dec.} of UP4U Na salt, 050223 and 050217 in d2o



Current Data Parameters
 NAME 050217_LP4U_No
 EXPNO 40
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050311
 Time 10.28
 INSTRUM spect
 PROBHD 5 mm Multinuc
 PULPROG zgpg30
 TD 145980
 SOLVENT d2o
 NS 88
 DS 32
 SSB 48661.801 Hz
 FIDRES 0.333246 Hz
 AQ 1.4898945 sec
 RG 28643.0
 DW 10.275 usec
 DE 5.00 usec
 TE 300.0 K
 D1 0.10000000 sec
 d11 0.03000000 sec
 d12 0.00000000 sec

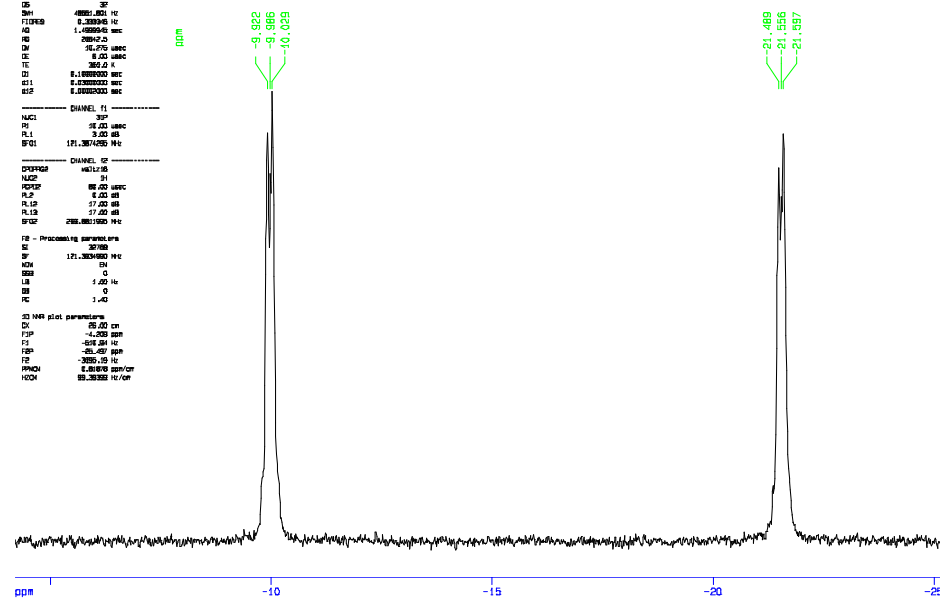
----- CHANNEL f1 -----
 NUC1 ³¹P
 P1 10.00 usec
 PL1 3.00 dB
 SFO1 121.3874255 MHz

----- CHANNEL f2 -----
 CHARGE2 m31z128
 NUC2 ¹H
 PPRG2 88.00 usec
 PL2 0.00 dB
 PL12 17.00 dB
 PL13 17.00 dB
 SFO2 288.8811993 MHz

F2 - Processing parameters
 SI 32768
 SF 121.3834930 MHz
 MDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 25.00 cm
 F1P 106.431 ppm
 F1 18261.40 Hz
 F2P -250.429 ppm
 F2 -30400.41 Hz
 PRNOM 15.41769 ppm/cm
 HZOM 1871.6075 Hz/cm

³¹P {1H dec.} of UP4U Na salt, 050223 and 050217 in d2o



³¹P (proton coupled) NMR spectrum of Up₄U sodium salt, **3f** in D₂O

Current Data Parameters
 NAME 050227_UP4U_Na
 EXPNO 20
 PROCNO 1

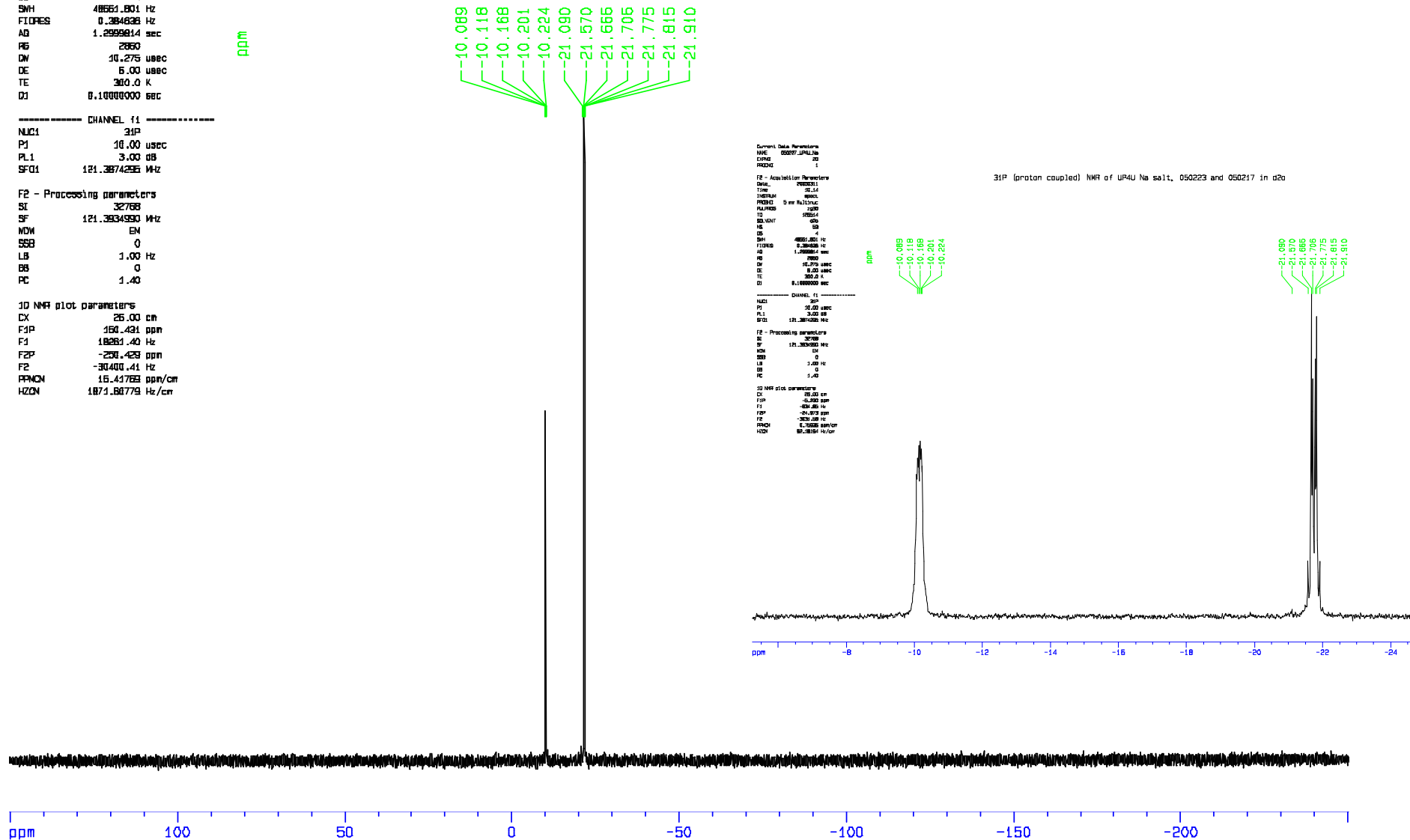
F2 - Acquisition Parameters
 Date_ 20090311
 Time 10.14
 INSTRUM spect
 PROBR0 5 mm Nu1Hinc
 PULPROG zg30
 TD 326514
 SOLVENT d2o
 NS 53
 DS 4
 SWH 40669.801 Hz
 FIDRES 0.384638 Hz
 AQ 1.2999814 sec
 RG 2860
 DW 10.275 usec
 DE 6.00 usec
 TE 300.0 K
 D1 0.10000000 sec

----- CHANNEL f1 -----
 NUC1 31P
 P1 10.00 usec
 PL1 3.00 dB
 SFO1 124.3874256 MHz

F2 - Processing parameters
 SI 32768
 SF 124.3834590 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 BB 0
 PC 1.40

3D NMR plot parameters
 CX 25.00 cm
 FJP 160.431 ppm
 FJ 18269.40 Hz
 FZP -200.429 ppm
 FZ -30400.41 Hz
 PRMCH 16.41769 ppm/cm
 HZCN 1871.68779 Hz/cm

³¹P (proton coupled) NMR of UP4U Na salt, 050223 and 050217 in d2o



Current Data Parameters
 NAME 050227_UP4U_Na
 EXPNO 20
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20090311
 Time 10.14
 INSTRUM spect
 PROBR0 5 mm Nu1Hinc
 PULPROG zg30
 TD 326514
 SOLVENT d2o
 NS 53
 DS 4
 SWH 40669.801 Hz
 FIDRES 0.384638 Hz
 AQ 1.2999814 sec
 RG 2860
 DW 10.275 usec
 DE 6.00 usec
 TE 300.0 K
 D1 0.10000000 sec

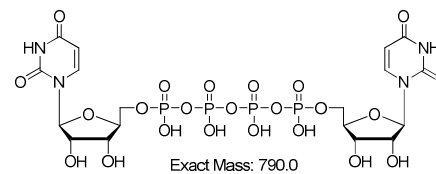
----- CHANNEL f1 -----
 NUC1 31P
 P1 10.00 usec
 PL1 3.00 dB
 SFO1 124.3874256 MHz

F2 - Processing parameters
 SI 32768
 SF 124.3834590 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 BB 0
 PC 1.40

3D NMR plot parameters
 CX 25.00 cm
 FJP 160.431 ppm
 FJ 18269.40 Hz
 FZP -200.429 ppm
 FZ -30400.41 Hz
 PRMCH 16.41769 ppm/cm
 HZCN 1871.68779 Hz/cm

³¹P (proton coupled) NMR of UP4U Na salt, 050223 and 050217 in d2o

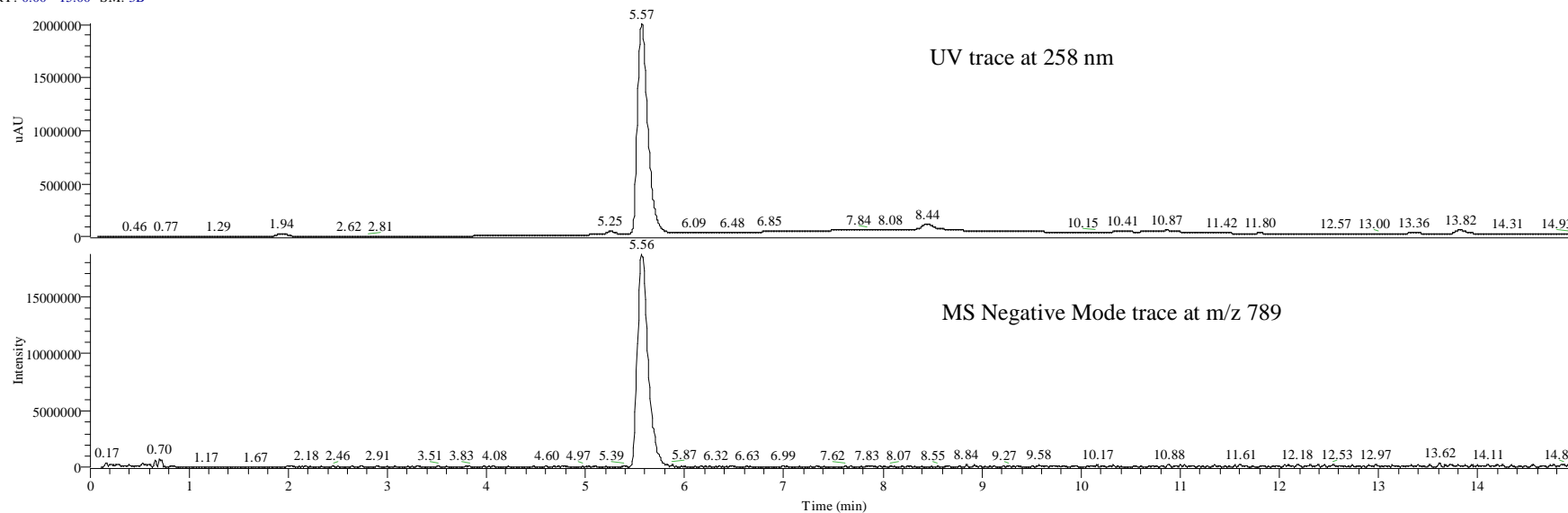
LCMS of Up₄U, 3f



Up4U_NaSalt_29Apr08_080429155436

4/29/2008 3:54:36 PM

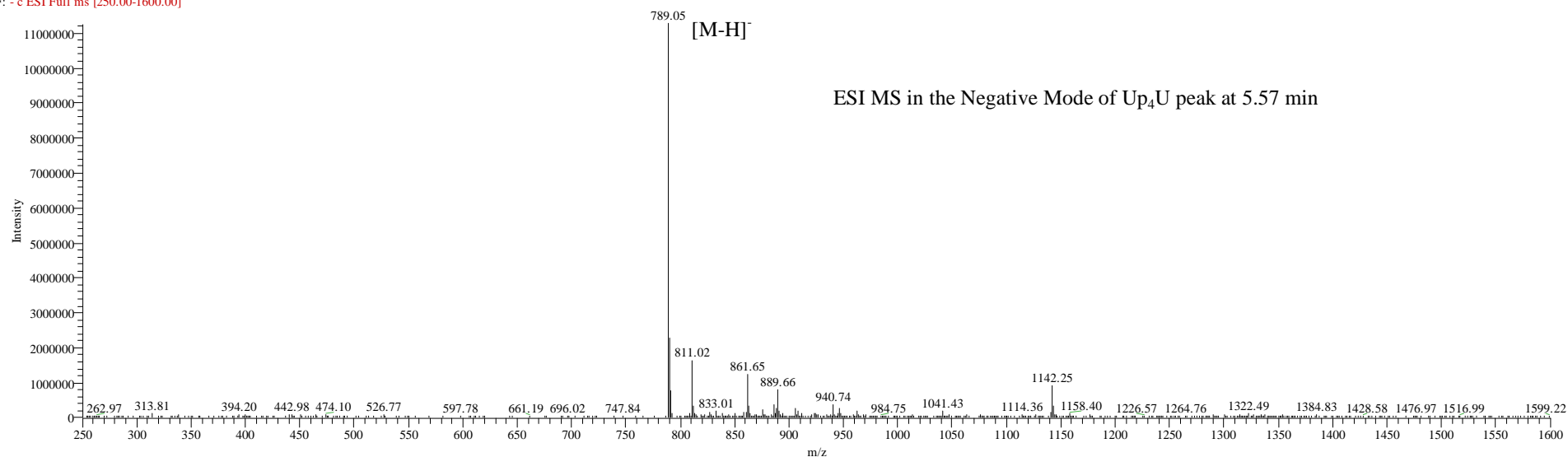
RT: 0.00 - 15.00 SM: 3B



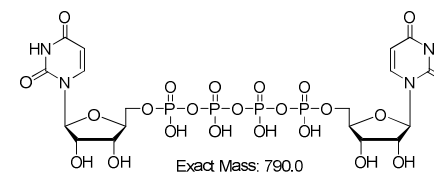
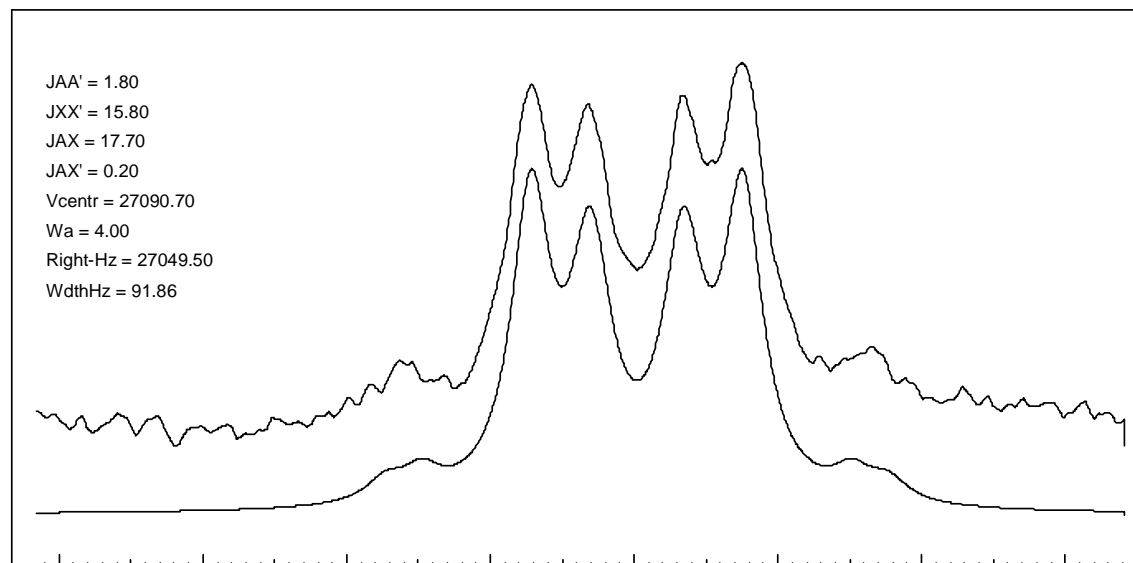
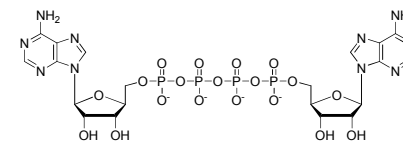
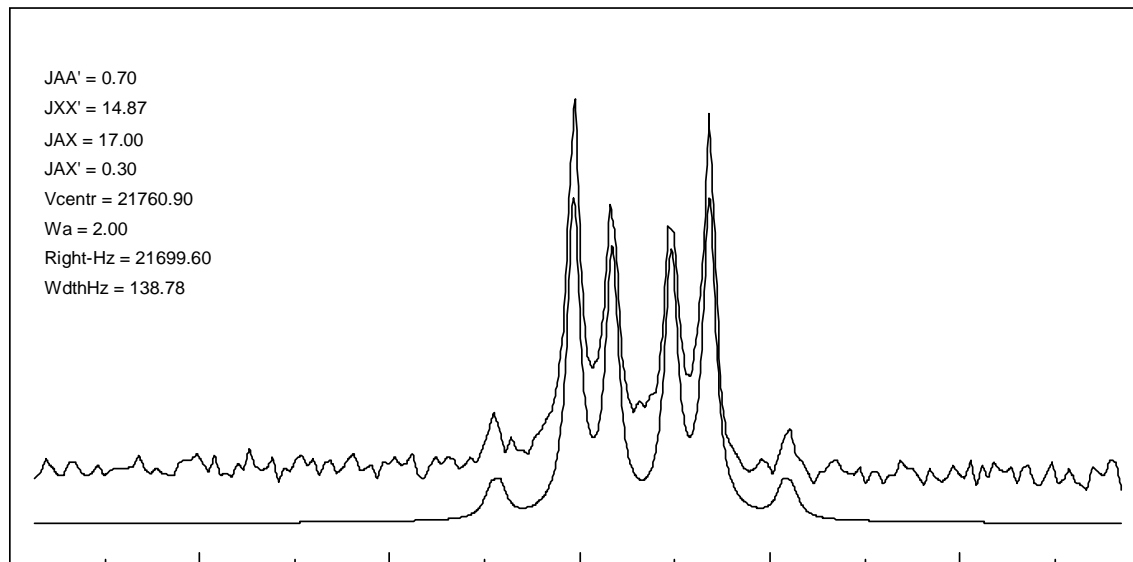
NL: 2.00E6
nm=256.2-258.8 PDA
Up4U_NaSalt_29Apr08_080429155436

NL: 1.86E7
m/z= 787.62-790.59 F:
- c ESI Full ms
[250.00-1600.00] MS
Up4U_NaSalt_29Apr08_080429155436

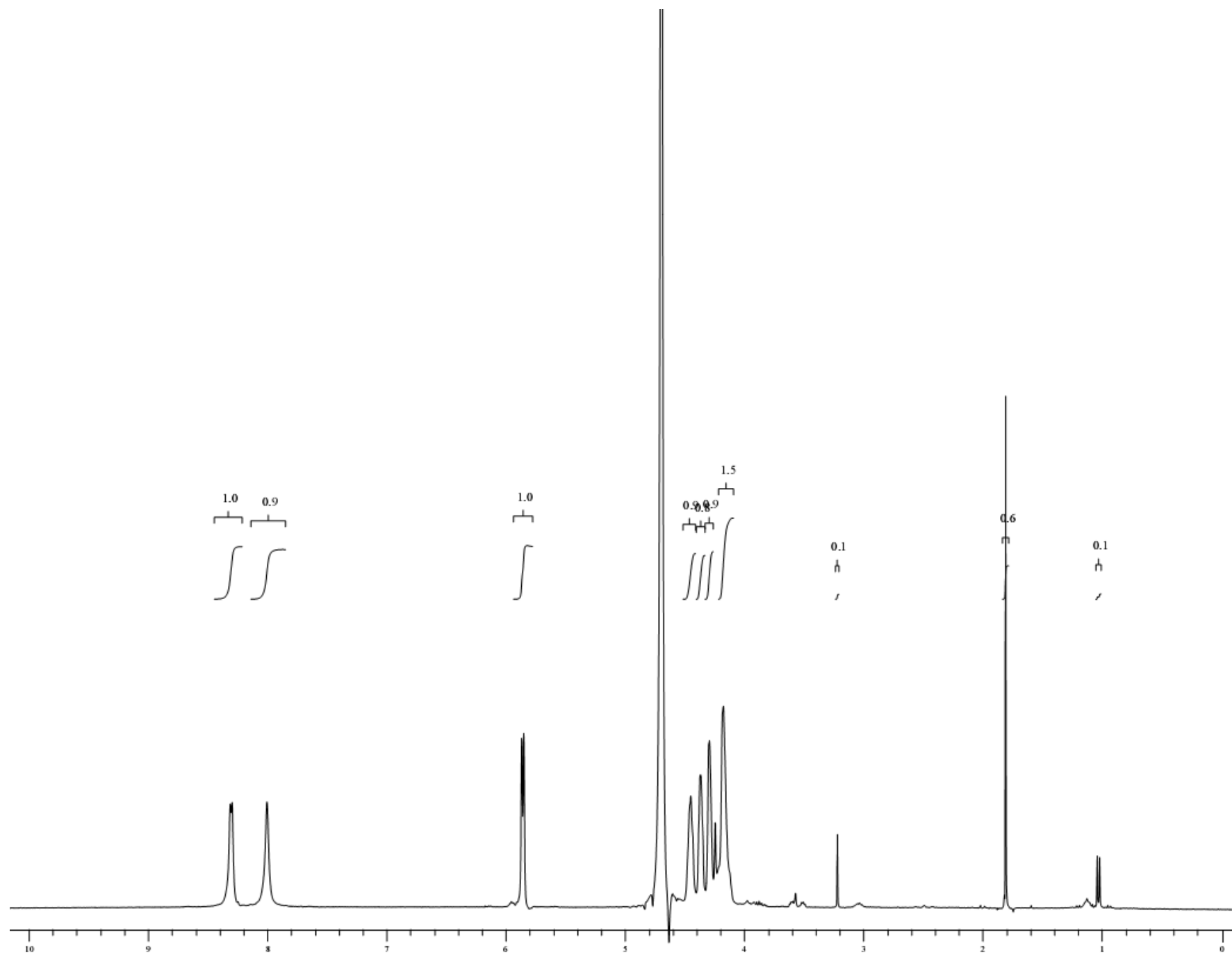
Up4U_NaSalt_29Apr08_080429155436 #674-691 RT: 5.51-5.63 AV: 18 SB: 39 5.36-5.48, 5.67-5.84 NL: 1.12E7
F: - c ESI Full ms [250.00-1600.00]



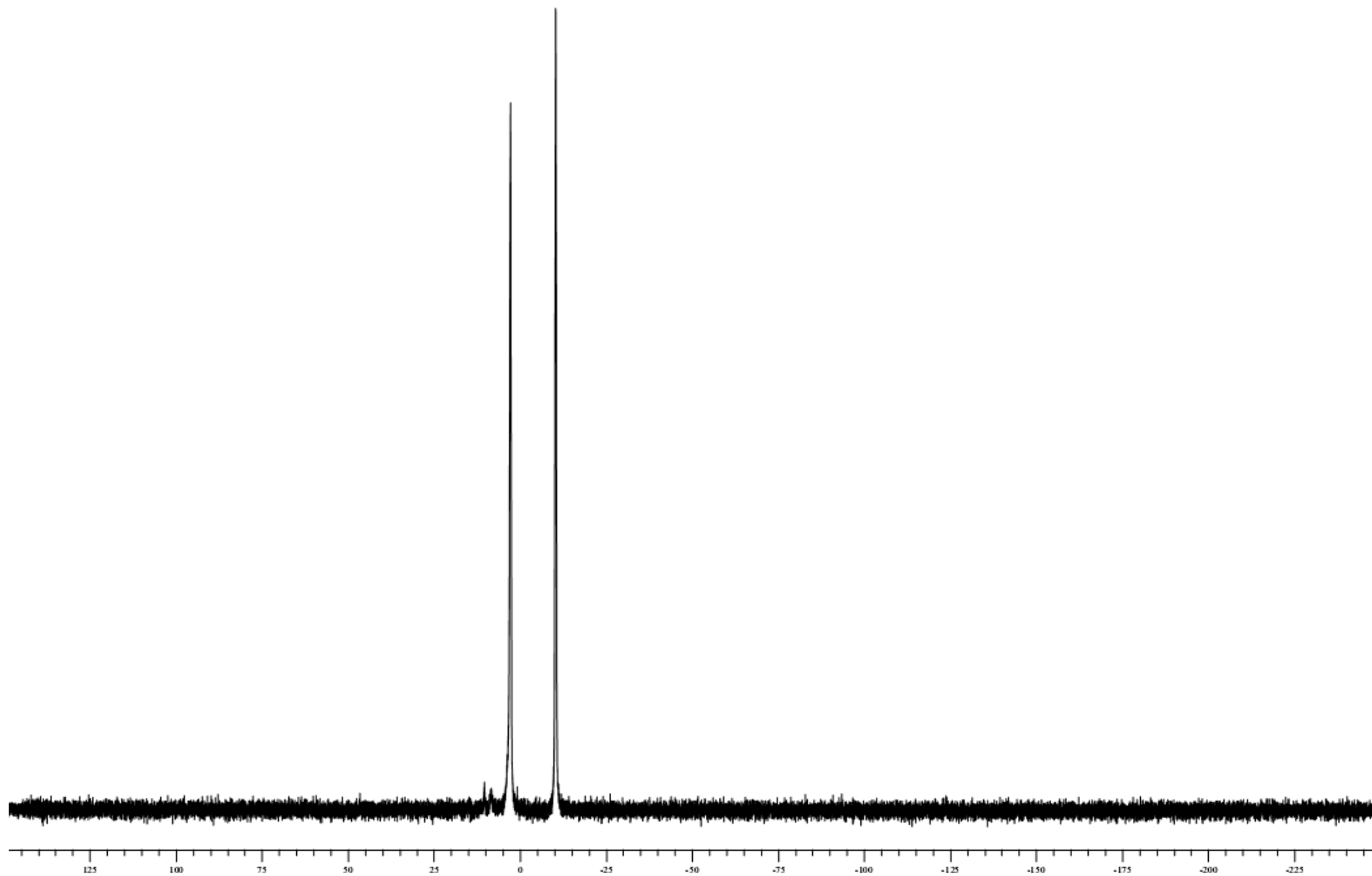
Simulated fitting of an AA'XX' spin system to the experimental ^{31}P NMR spectra of Ap₄A and Up₄U (**3a** and **3f**, resp.):



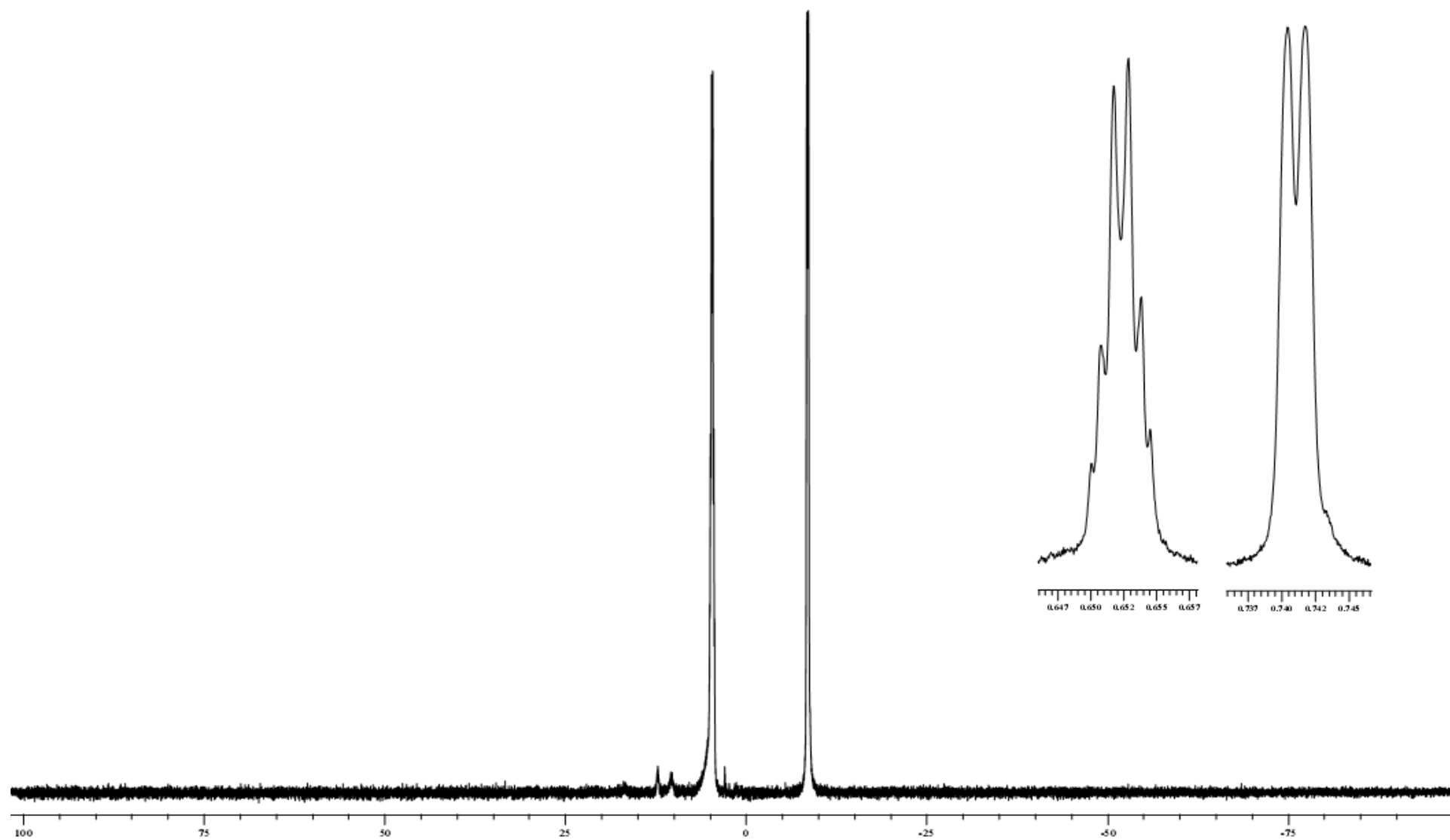
^1H NMR of APPHCIPPA sodium salt, **3c** in D_2O :



^{31}P NMR (proton decoupled) of APPHCIPPA sodium salt, **3c** in D_2O :

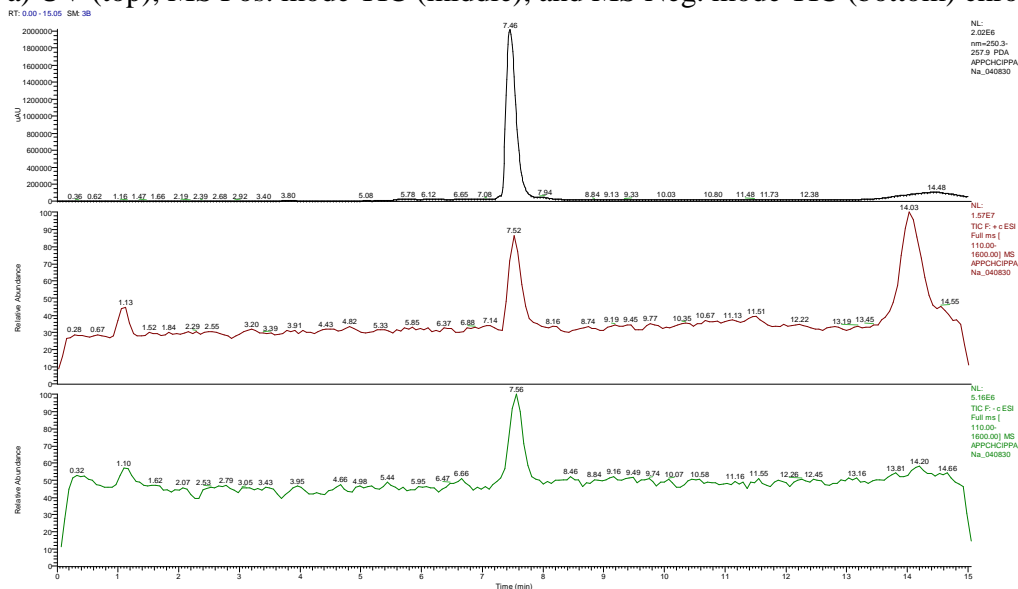


^{31}P NMR (proton coupled) of APPHCIPPA sodium salt, **3c** in D_2O :



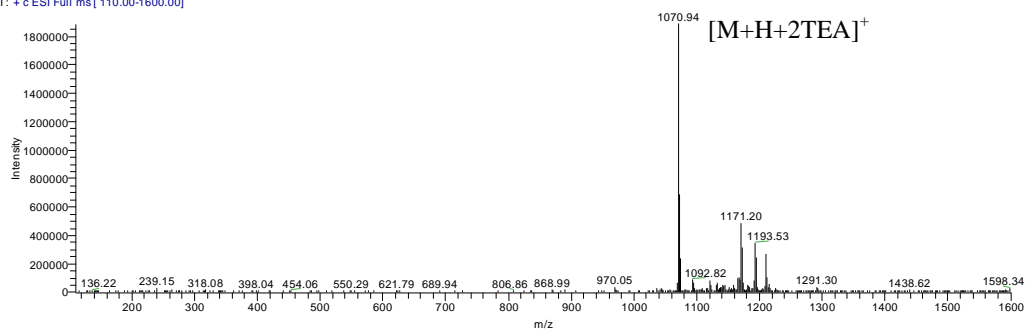
LCMS analysis of APPCHCIPPA sodium salt, **3c**:

a) UV (top), MS Pos. mode TIC (middle), and MS Neg. mode TIC (bottom) chromatograms:



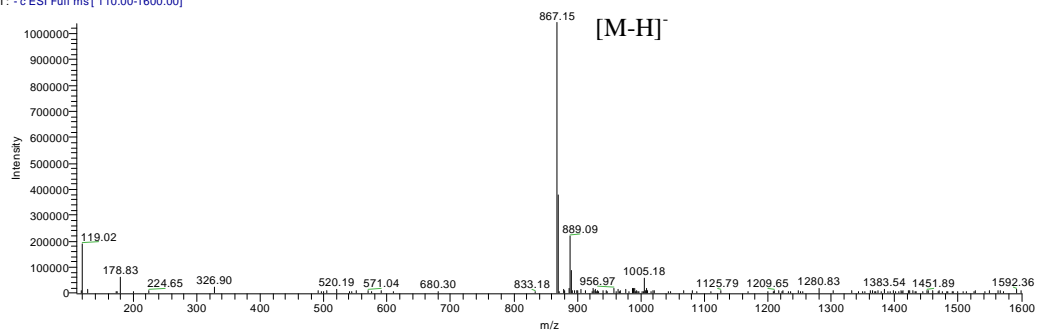
b) Positive mode MS of APPCHCIPPA peak at 7.46 min

APPCHCIPPA_Na_040830 #231-235 RT: 7.46-7.58 AV: 3 SB: 7.718-7.37, 7.71-7.94 NL: 1.88E6
T: + c ESI Full ms [110.00-1600.00]



c) Negative mode MS of APPCHCIPPA peak at 7.46 min

APPCHCIPPA_Na_040830 #231-236 RT: 7.50-7.62 AV: 3 SB: 7.720-7.39, 7.71-7.94 NL: 1.04E6
T: - c ESI Full ms [110.00-1600.00]



¹H NMR of APPCHFPPA, **3e** as the tetrabutylammonium salt in D₂O:

Current Data Parameters
NAME 040910TBA1_APPCHFPPA_TBA
EXPNO 20
PROCNO 1

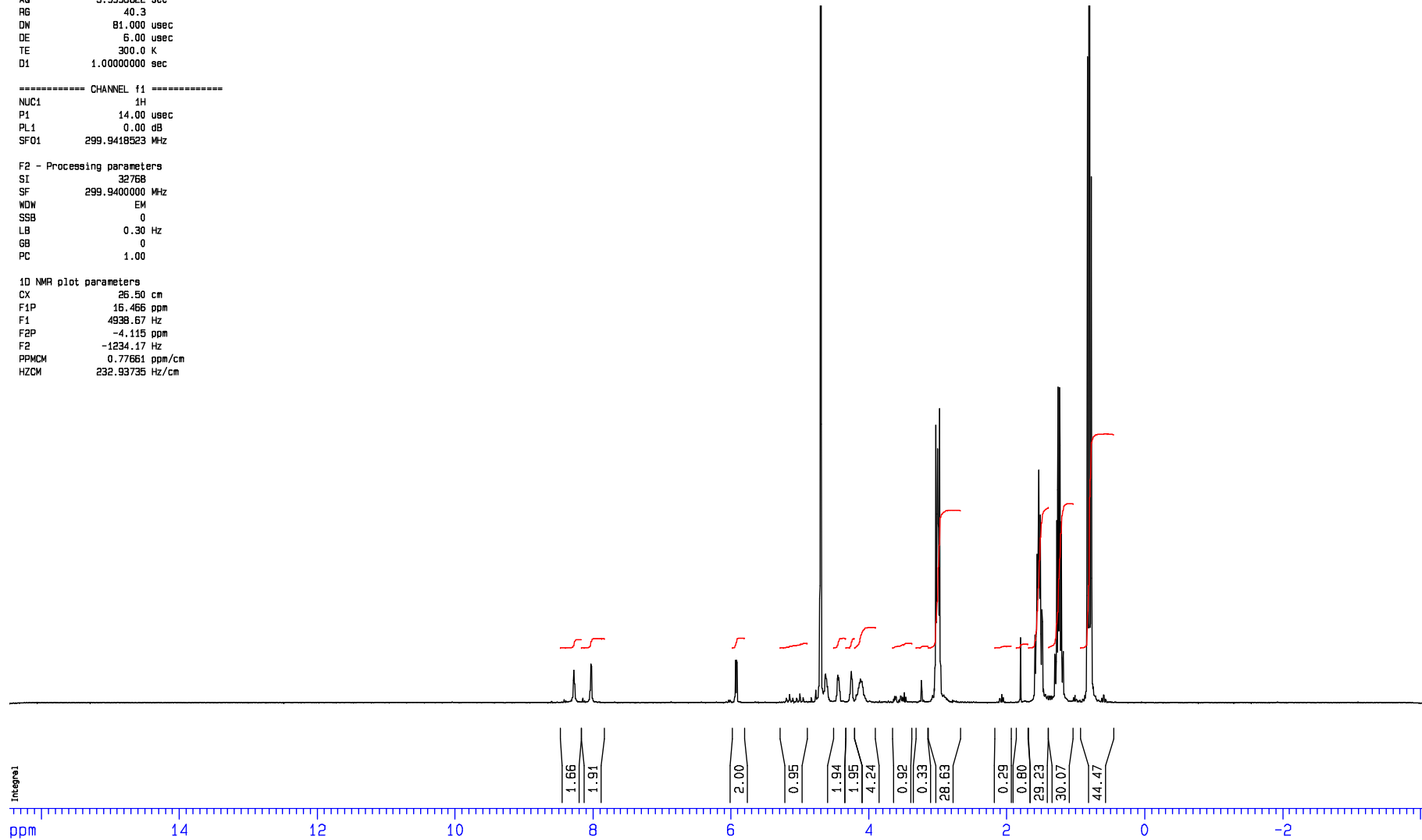
F2 - Acquisition Parameters
Date_ 20041018
Time 14.17
INSTRUM spect
PROBHD 5 mm Multinuc
PULPROG zg30
TD 74072
SOLVENT D2O
NS 8
DS 2
SWH 6172.839 Hz
FIDRES 0.083336 Hz
AQ 5.9998822 sec
RG 40.3
DM 81.000 usec
DE 5.00 usec
TE 300.0 K
D1 1.0000000 sec

¹H NMR of APPCHFPPA Bu₃N salt batch IY040910TBA1 in D₂O

----- CHANNEL f1 -----
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 299.9418523 Mhz

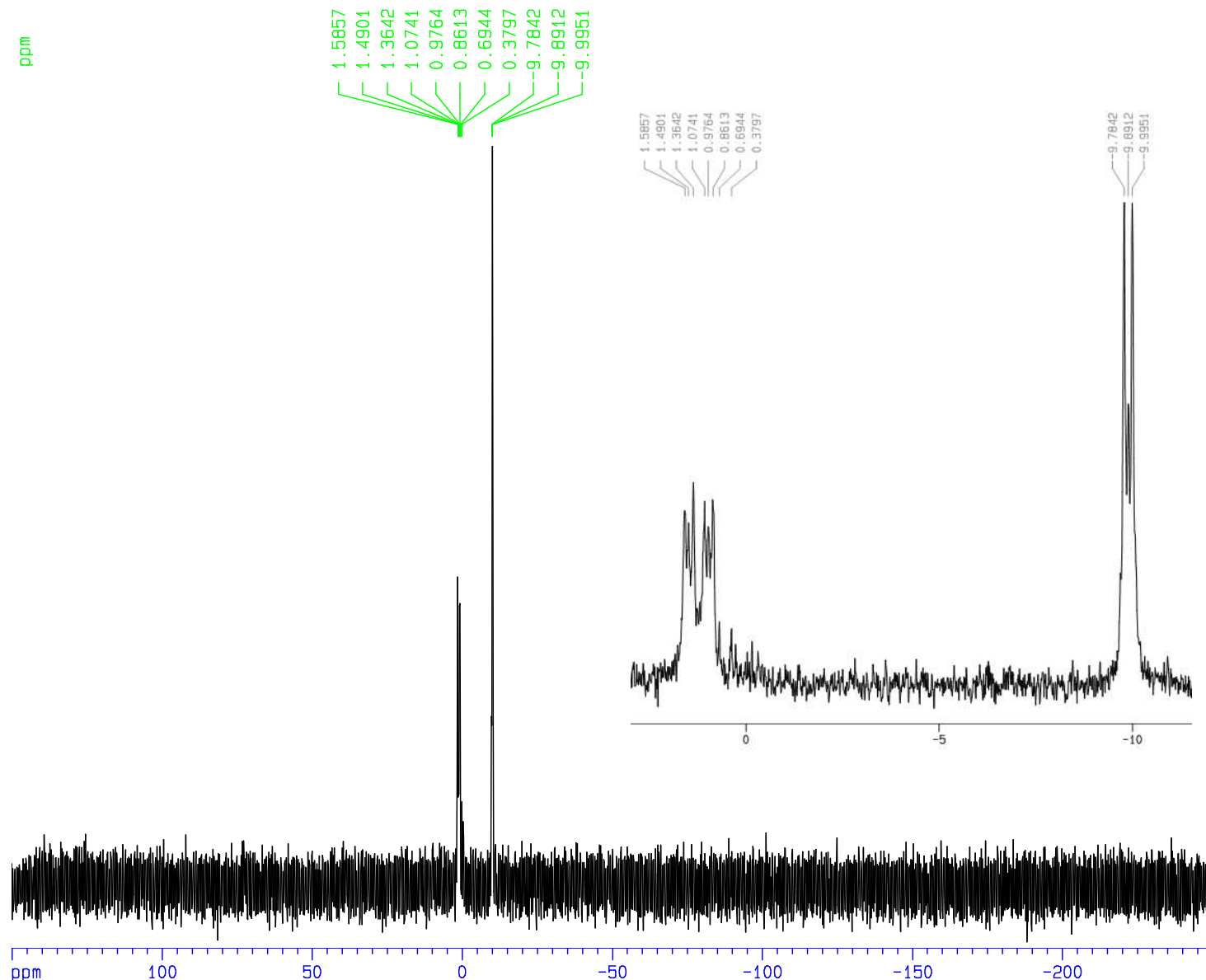
F2 - Processing parameters
SI 32768
SF 299.9400000 Mhz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 25.50 cm
F1P 15.466 ppm
F1 4938.67 Hz
F2P -4.115 ppm
F2 -1234.17 Hz
PPMCM 0.77661 ppm/cm
HZCM 232.93735 Hz/cm



³¹P NMR (proton decoupled) of APPCHFPPA, **3e** as the tetrabutylammonium salt in D₂O:

31P NMR (proton decoupled) of APPCHCFPPA Bu₃N salt batch IY040910TBA1 in D₂O



Current Data Parameters
 NAME 040910TBA1_APPCHCFPPA_TBA
 EXPNO 40
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20041018
 Time 14.58
 INSTRUM spect
 PROBHD 5 mm Multinuc
 PULPROG zgpg30
 TD 126514
 SOLVENT d2o
 NS 24
 DS 4
 SWH 48661.801 Hz
 FIDRES 0.384636 Hz
 AQ 1.2999814 sec
 RG 16384
 DW 10.275 usec
 DE 6.00 usec
 TE 300.0 K
 D1 0.1000000 sec
 d11 0.0300000 sec
 d12 0.0002000 sec

===== CHANNEL f1 =====
 NUC1 31P
 P1 10.00 usec
 PL1 3.00 dB
 SFO1 121.4117167 MHz

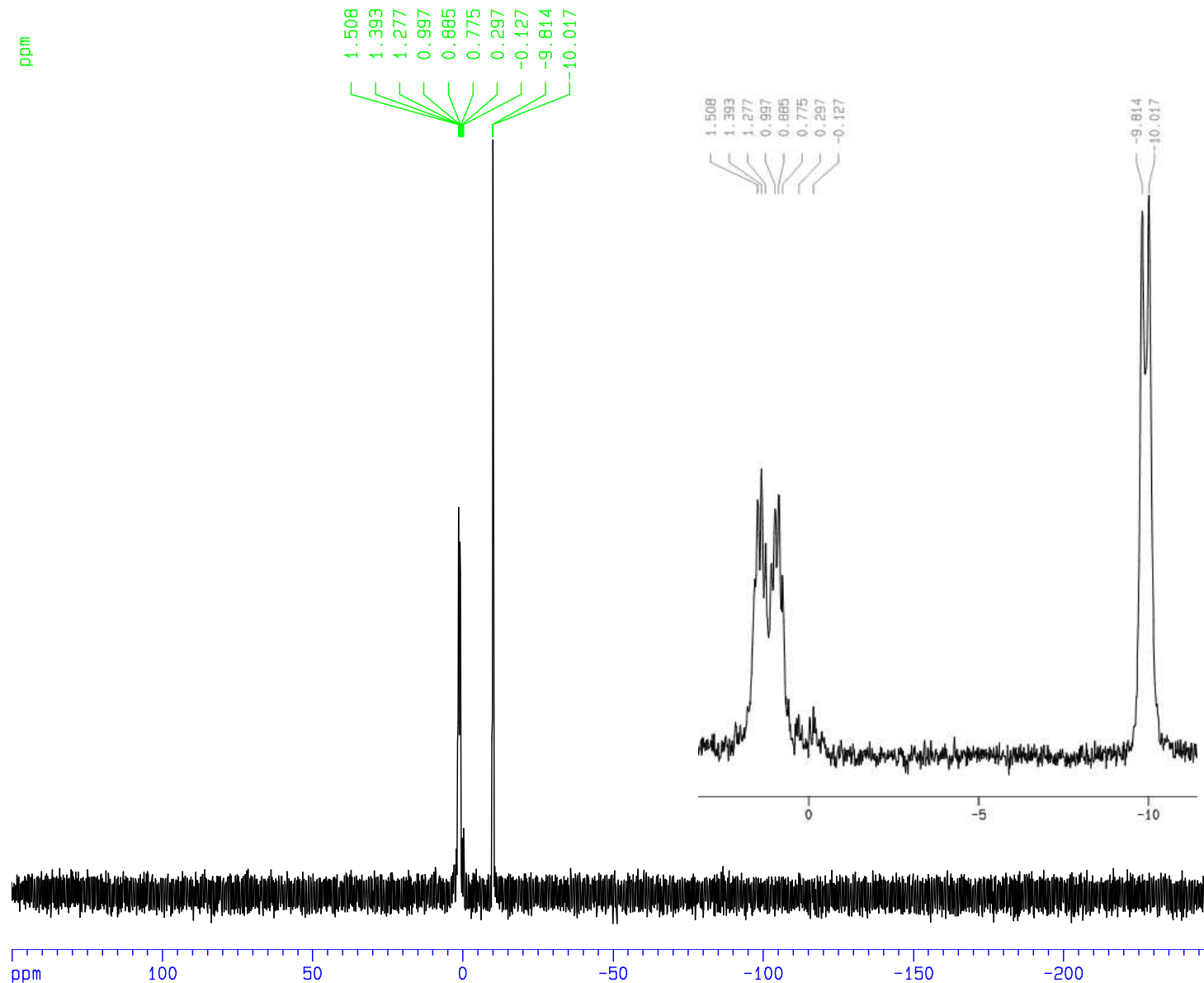
===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 0.00 dB
 PL12 16.00 dB
 PL13 17.00 dB
 SFO2 299.9411998 MHz

F2 - Processing parameters
 SI 32768
 SF 121.4177880 MHz
 HDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 F1P 150.387 ppm
 F1 18259.60 Hz
 F2P -250.393 ppm
 F2 -30402.20 Hz
 PPMCM 20.03899 ppm/cm
 HZCM 2433.09009 Hz/cm

³¹P NMR (proton coupled) of APPCHFPPA, **3e** as the tetrabutylammonium salt in D₂O:

31P NMR (proton coupled) of APPCHCFPPA Bu₃N salt batch IY040910TBA1 in D2O



Current Data Parameters
NAME 040910TBA1_APPCHFPPA_TBA
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20041018
Time 14.44
INSTRUM spect
PROBHD 5 mm Multinuc
PULPROG zg30
TD 126514
SOLVENT d2o
NS 157
DS 4
SWH 48661.801 Hz
FIDRES 0.384636 Hz
AQ 1.2999814 sec
RG 2580.3
DW 10.275 usec
DE 6.00 usec
TE 300.0 K
D1 0.1000000 sec

===== CHANNEL f1 =====
NUC1 31P
P1 10.00 usec
PL1 3.00 dB
SFO1 121.4117167 MHz

F2 - Processing parameters
SI 32768
SF 121.4177880 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

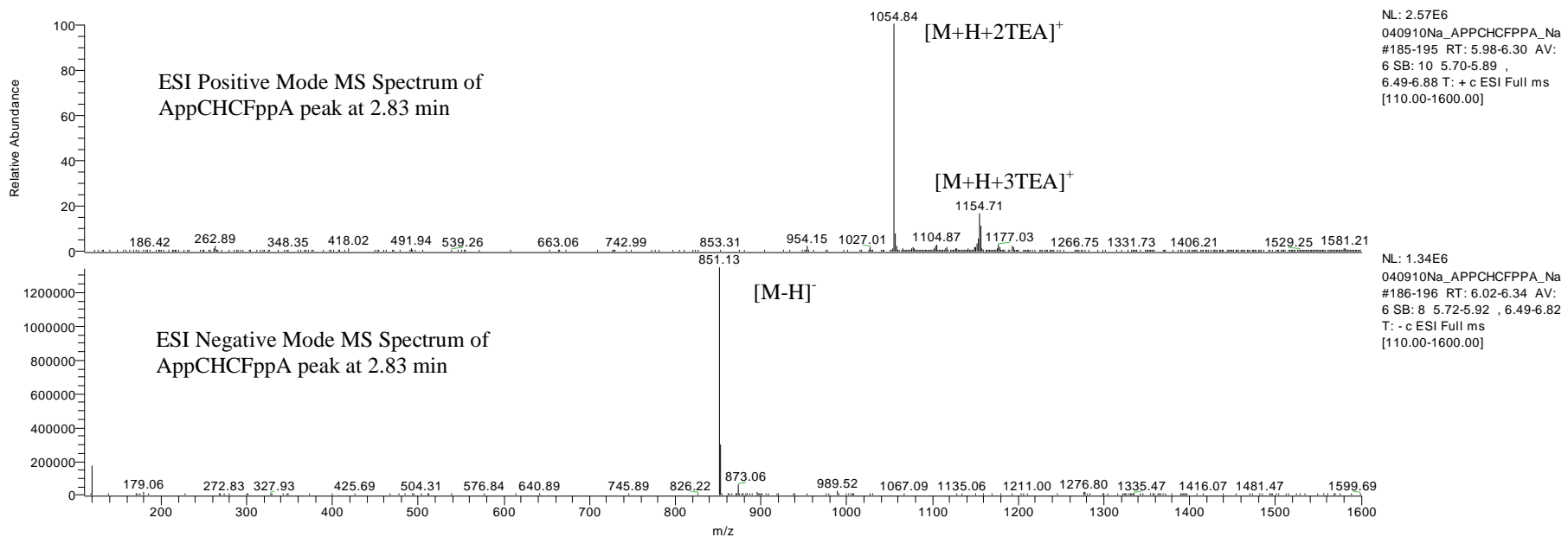
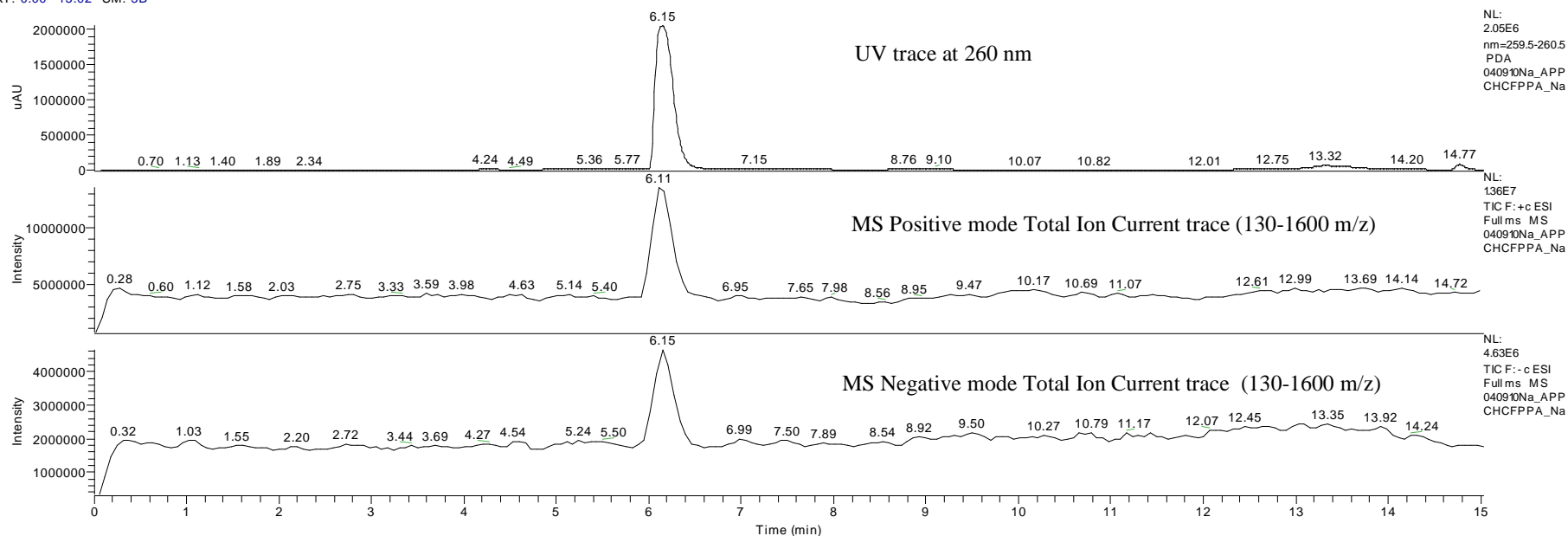
1D NMR plot parameters
CX 20.00 cm
F1P 150.387 ppm
F1 18259.60 Hz
F2P -250.393 ppm
F2 -30402.20 Hz
PPMCM 20.03899 ppm/cm
HZCM 2433.09009 Hz/cm

LCMS of APPCHFPPA sodium salt, **3e**:

040910Na_APPCHCFPPA_Na

9/29/2004 5:12:48 PM

RT: 0.00 - 15.02 SM: 3B



¹H NMR of AP(S)PPP(S)A sodium salt, **3b** in D₂O:

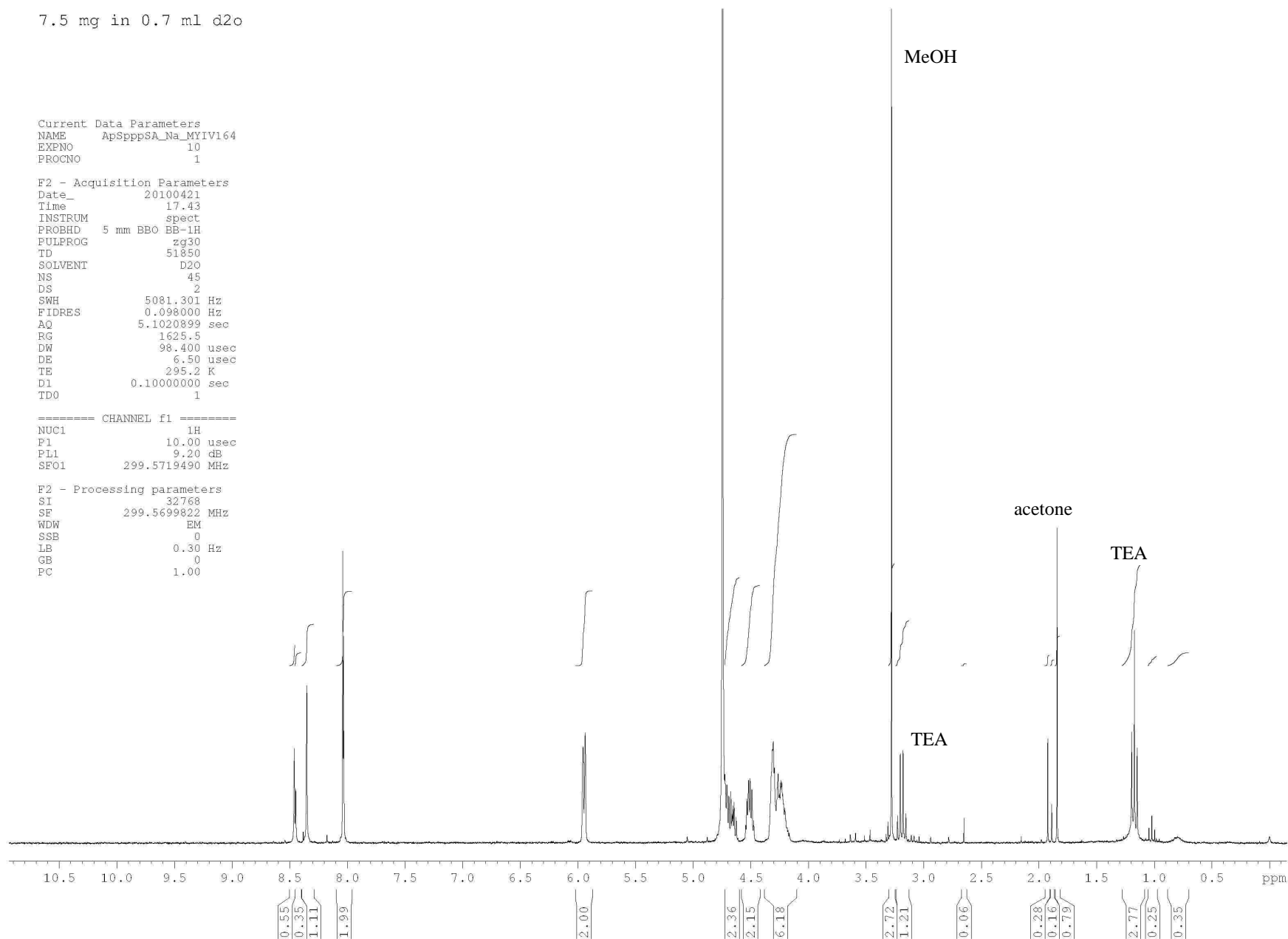
7.5 mg in 0.7 ml d2o

Current Data Parameters
NAME ApSpppSA_Na_MYIV164
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100421
Time 17.43
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 51850
SOLVENT D2O
NS 45
DS 2
SWH 5081.301 Hz
FIDRES 0.098000 Hz
AQ 5.1020899 sec
RG 1625.5
DW 98.400 usec
DE 6.50 usec
TE 295.2 K
D1 0.10000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 9.20 dB
SF01 299.5719490 MHz

F2 - Processing parameters
SI 32768
SF 299.5699822 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



³¹P (proton decoupled) NMR of AP(S)PPP(S)A sodium salt, **3b** in D₂O:

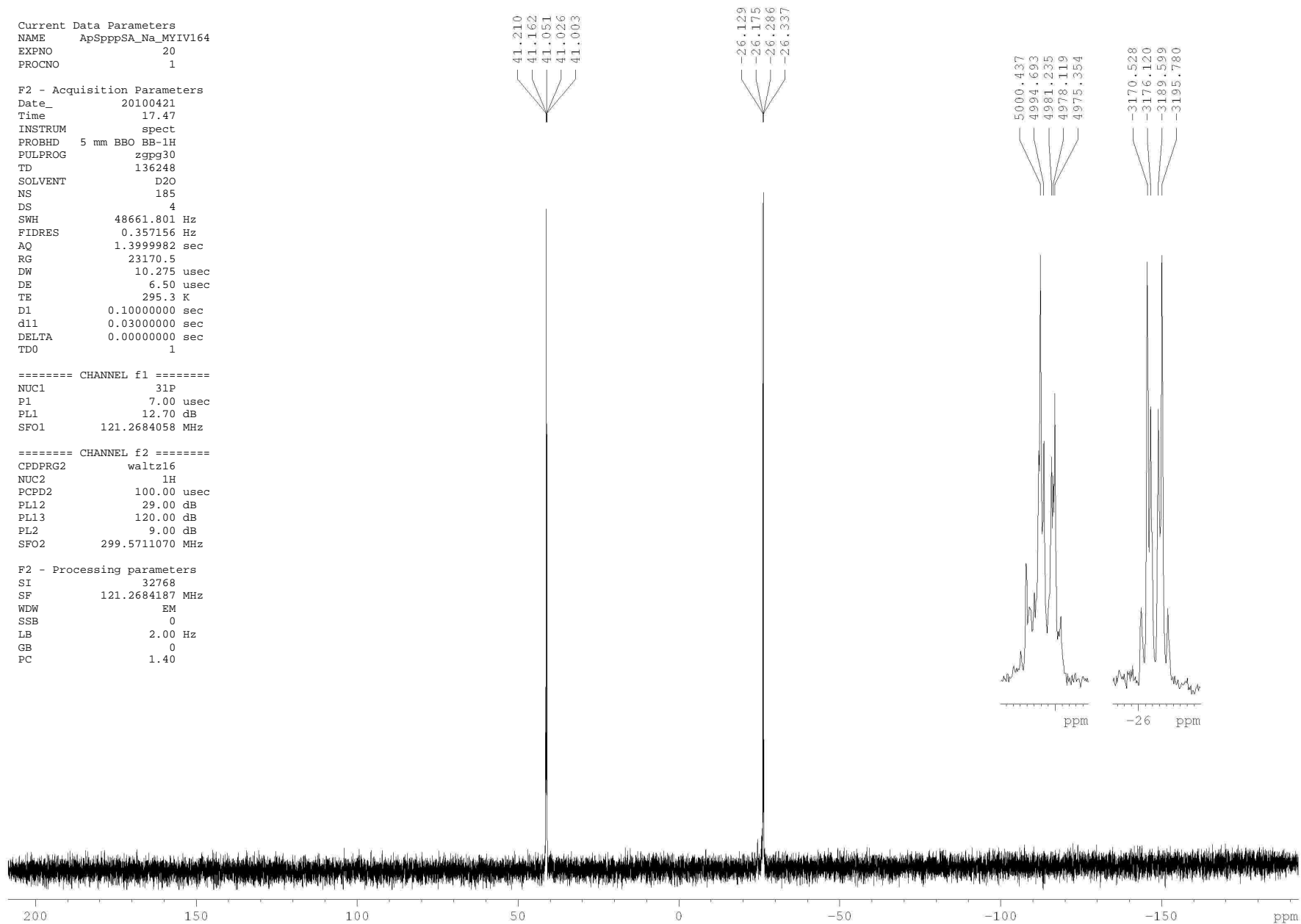
Current Data Parameters
NAME ApSpppSA_Na_MXIV164
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100421
Time 17.47
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 136248
SOLVENT D2O
NS 185
DS 4
SWH 48661.801 Hz
FIDRES 0.357156 Hz
AQ 1.3999982 sec
RG 23170.5
DW 10.275 usec
DE 6.50 usec
TE 295.3 K
D1 0.10000000 sec
d11 0.03000000 sec
DELTA 0.00000000 sec
TD0 1

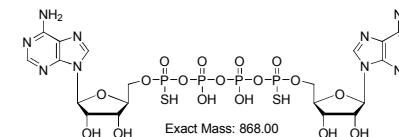
==== CHANNEL f1 =====
NUC1 31P
P1 7.00 usec
PL1 12.70 dB
SFO1 121.2684058 MHz

==== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL12 29.00 dB
PL13 120.00 dB
PL2 9.00 dB
SFO2 299.5711070 MHz

F2 - Processing parameters
SI 32768
SF 121.2684187 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40



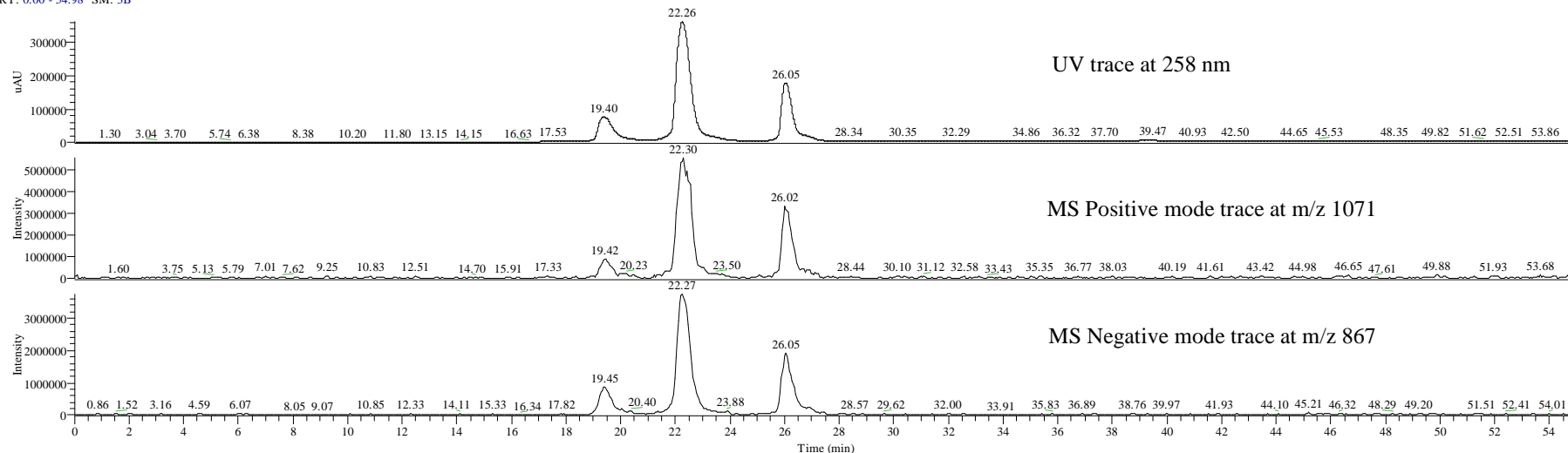
Separation of the three diastereomers of AP(S)PPP(S)A, **3b** by reverse phase ion-pairing chromatography:



\\90.0.0.63(c\$)...ApSpppSA_MYIV164_Na

4/22/2010 6:37:19 PM

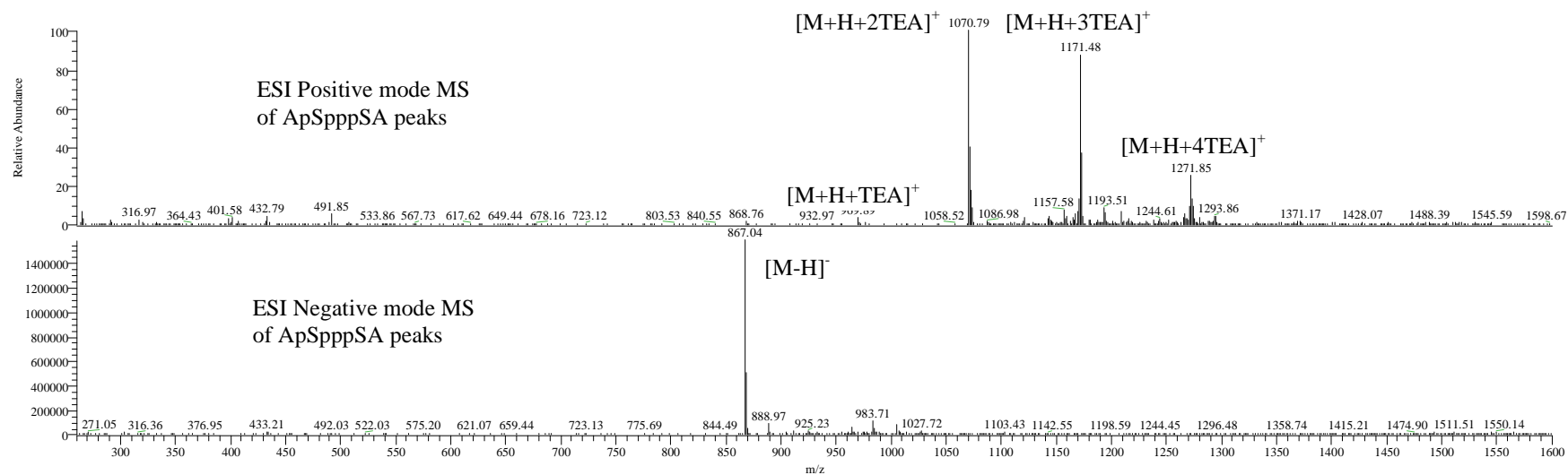
RT: 0.00 - 54.98 SM: 3B



NL: 3.6E5
nm=255.9-2611
PDA
ApSpppSA_MYIV
164_Na

NL: 5.53E6
m/z=
1068.74-1074.09 F:
+c ESI Full ms
MS
ApSpppSA_MYIV
164_Na

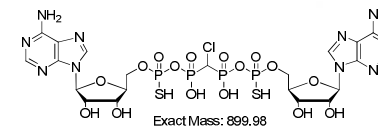
NL: 3.73E6
m/z=
864.88-869.59 F:
-c ESI Full ms
MS
ApSpppSA_MYIV
164_Na



NL: 2.26E6
ApSpppSA_MYIV164_Na#
862-893 RT: 21.95-22.70
AV: 16 SB: 22
21.24-21.67, 23.96-24.56
F: +c ESI Full ms

NL: 1.58E6
ApSpppSA_MYIV164_Na#
862-895 RT: 21.93-22.72
AV: 17 SB: 17
21.12-21.45, 23.40-23.91
F: -c ESI Full ms

¹H NMR spectrum of AP(S)PCHCIPP(S)A sodium salt, **3d** in D₂O:



¹H NMR of APsPCHCIPPsA sodium salt in D₂O, batches iy3-3 and iy3-7

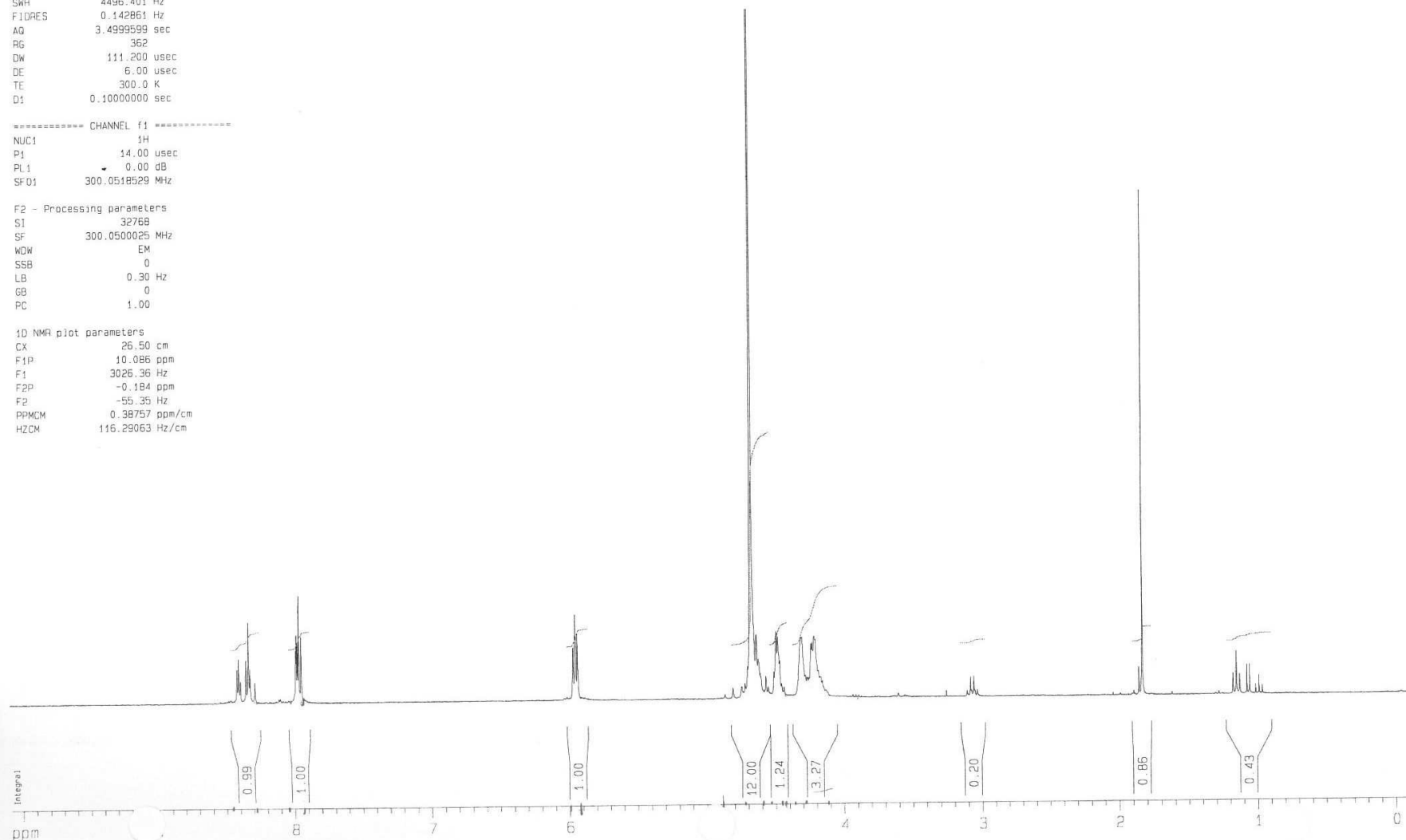
Current Data Parameters
NAME iy3-3-iy3-7-b1
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030214
Time 11.44
INSTRUM spect
PROBHD 5 mm Multinuc
PULPROG zg30
TD 31474
SOLVENT D2O
NS 16
DS 2
SWH 4496.401 Hz
FIDRES 0.142861 Hz
AQ 3.4999599 sec
RG 362
DW 111.200 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec

----- CHANNEL f1 -----
NUC1 ¹H
P1 14.00 usec
PL1 0.00 dB
SF01 300.0518529 MHz

F2 - Processing parameters
S1 32768
SF 300.0500025 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

3D NMR plot parameters
CX 26.50 cm
F1P 10.086 ppm
F1 3026.36 Hz
F2P -0.184 ppm
F2 -55.35 Hz
PPMCM 0.38757 ppm/cm
HZCM 116.29063 Hz/cm

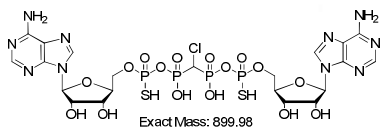


³¹P (proton decoupled) NMR spectrum of AP(S)PCHCIPP(S)A sodium salt, **3d** in D₂O:

Current Data Parameters
NAME iy3-3-iy3-7-b1
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030214
Time 12.10
INSTRUM spect
PROBHD 5 mm Multinuc
PULPROG zgpg30
TD 65536
SOLVENT d2o
NS 490
DS 4
SWH 24330.900 Hz
FIDRES 0.371260 Hz
AQ 1.3468148 sec
RG 20642.5
DW 20.550 usec
DE 5.00 usec
TE 300.0 K
D1 0.20000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

Phosphorous NMR (proton dec.) of APsPCHCIPPsa sodium salt in D2O, batches iy3-3 and iy3-7

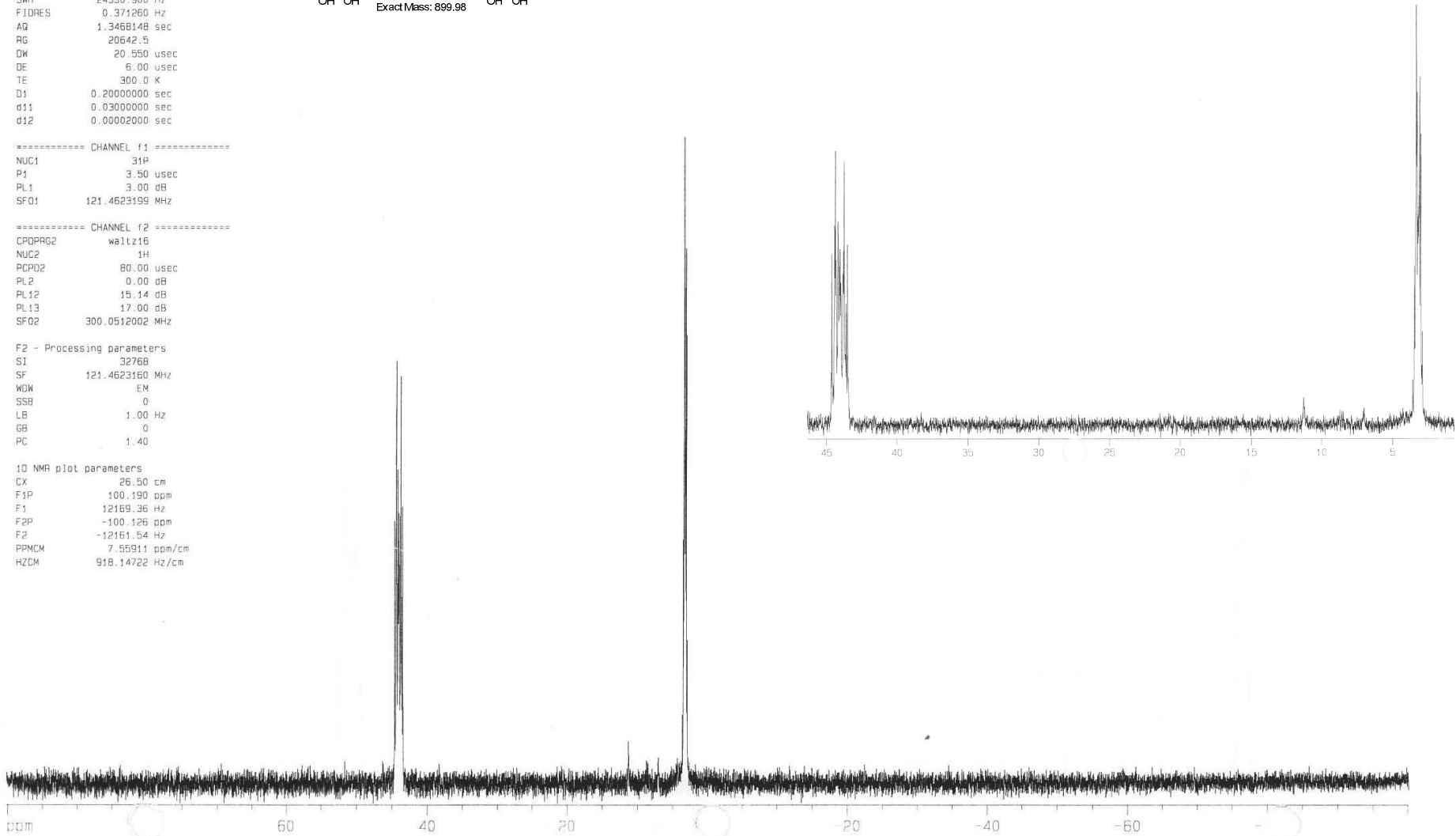


===== CHANNEL f1 =====
NUC1 31P
P1 3.50 usec
PL1 3.00 dB
SFO1 121.4623199 MHz

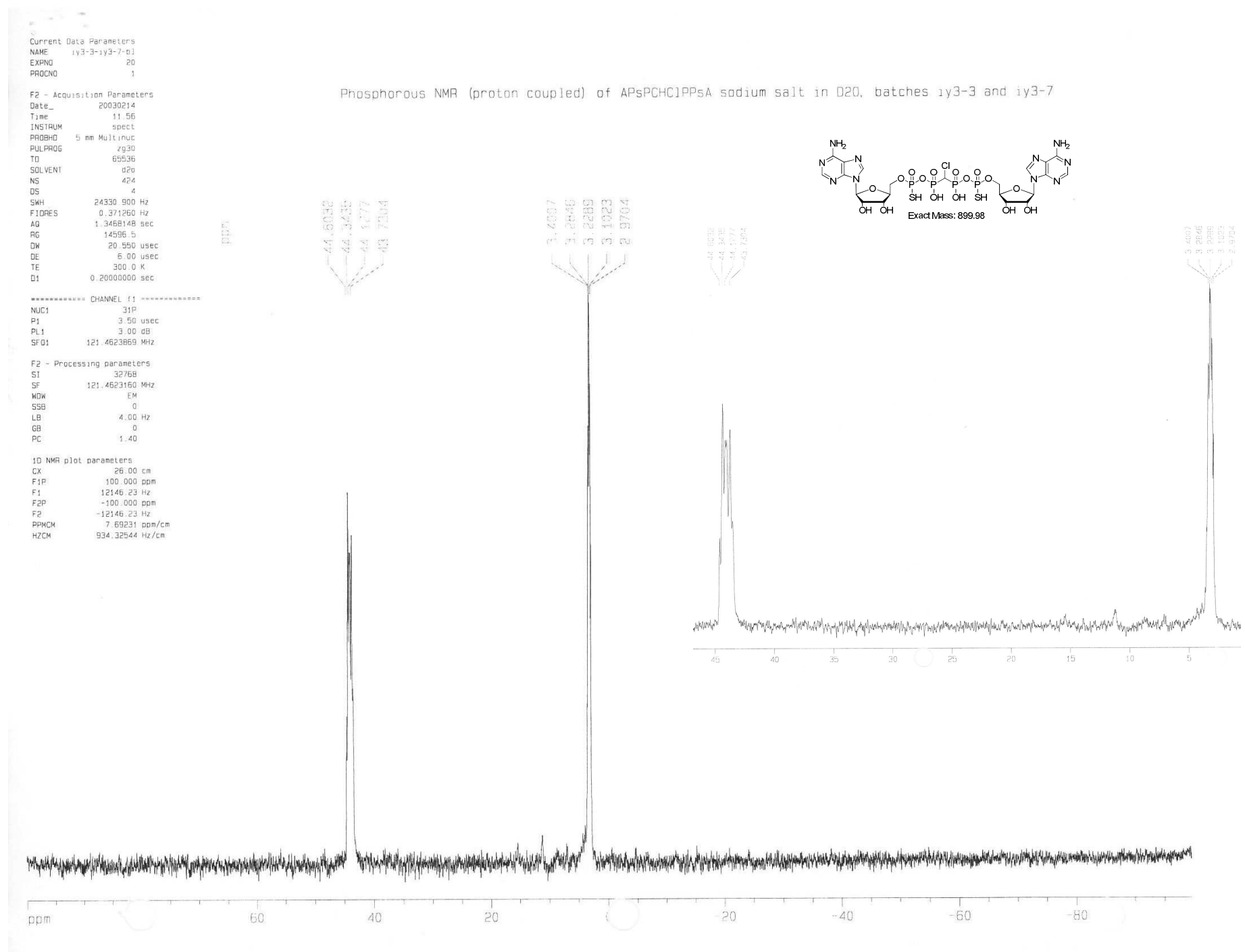
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.14 dB
PL13 17.00 dB
SFO2 300.0512002 MHz

F2 - Processing parameters
SI 32768
SF 121.4623160 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

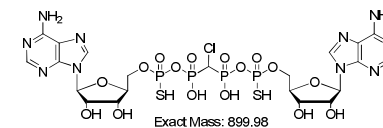
1D NMR plot parameters
CX 26.50 cm
F1P 100.190 ppm
F1 12169.36 Hz
F2P -100.126 ppm
F2 -12161.54 Hz
PPMCM 7.55911 ppm/cm
HZCM 918.14722 Hz/cm



³¹P (proton coupled) NMR spectrum of AP(S)PCHCIPP(S)A sodium salt, **3d** in D₂O:



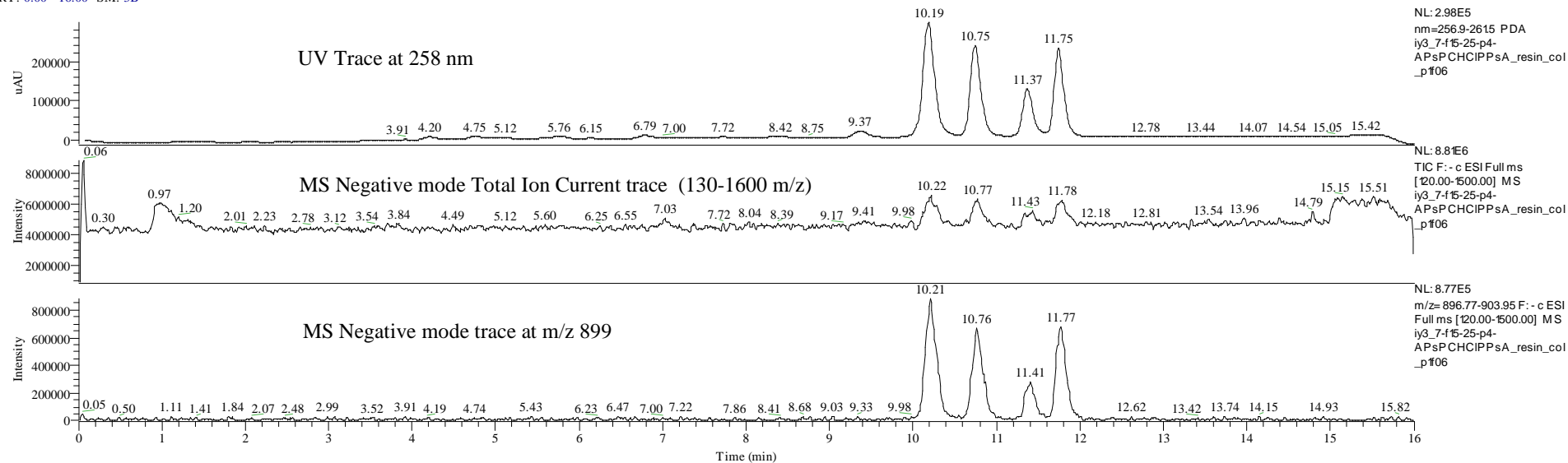
Separation of the four diastereomers of AP(S)PPCHCIP(S)A, **3d** by reverse phase ion-pairing chromatography:



iy3_7-fl5-25-p4-APsPCHCIPsA_resin_co...
1 ul of 1mM sol in 20mM TEAA

3/6/2007 11:50:49 AM

RT: 0.00 - 16.00 SM: 3B



iy3_7-fl5-25-p4-APsPCHCIPsA_resin_col_p1f06 #959-979 RT: 10.11-10.33 AV: 21 SB: 23 9.88-9.97, 10.42-10.55 NL: 2.79E5
F: - c ESI Full ms [120.00-1500.00]

