

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

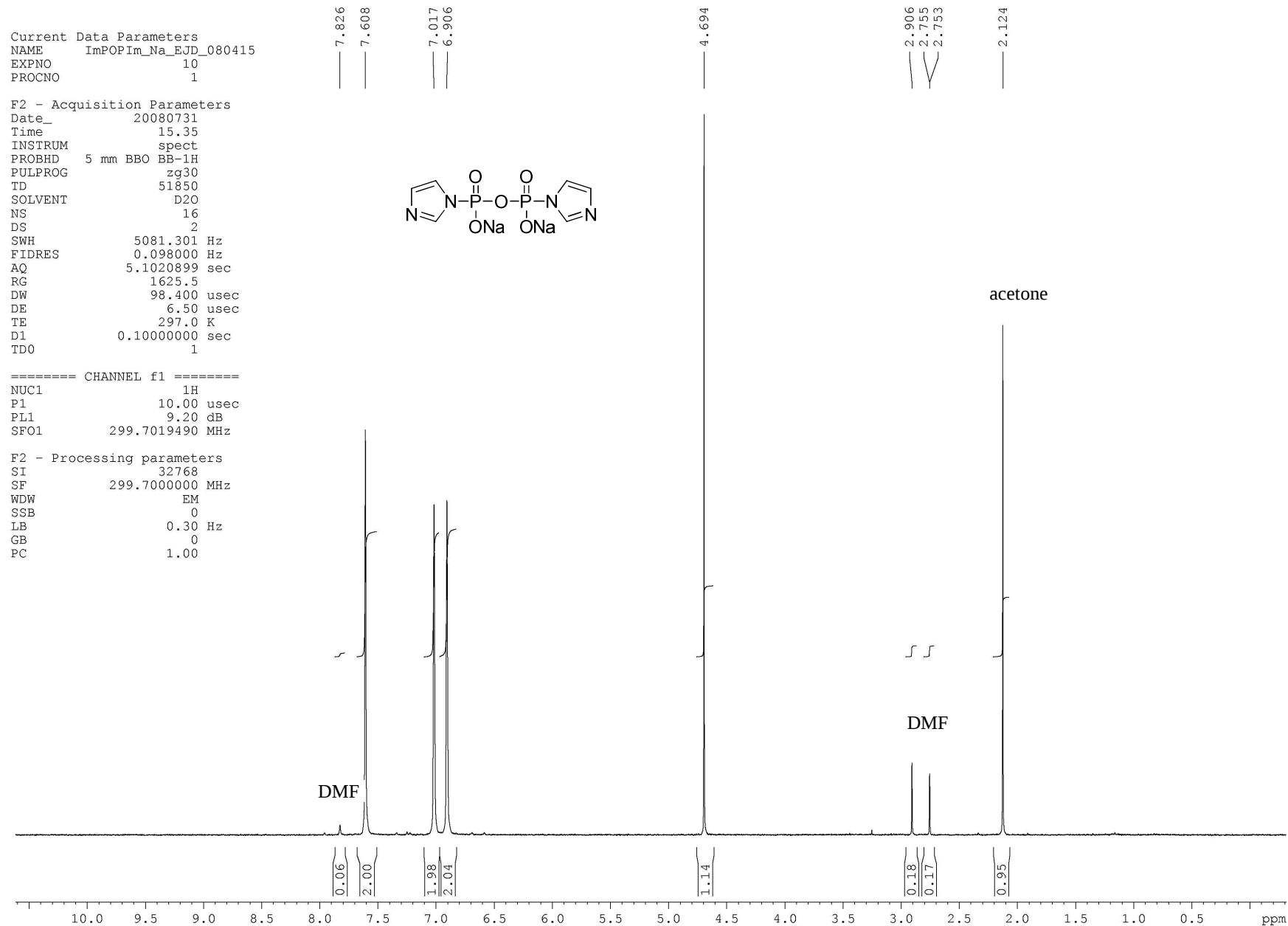
Ivan B. Yanachkov, Edward J. Dix, Milka I. Yanachkova, George E. Wright

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

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

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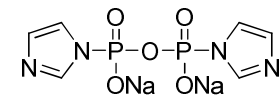
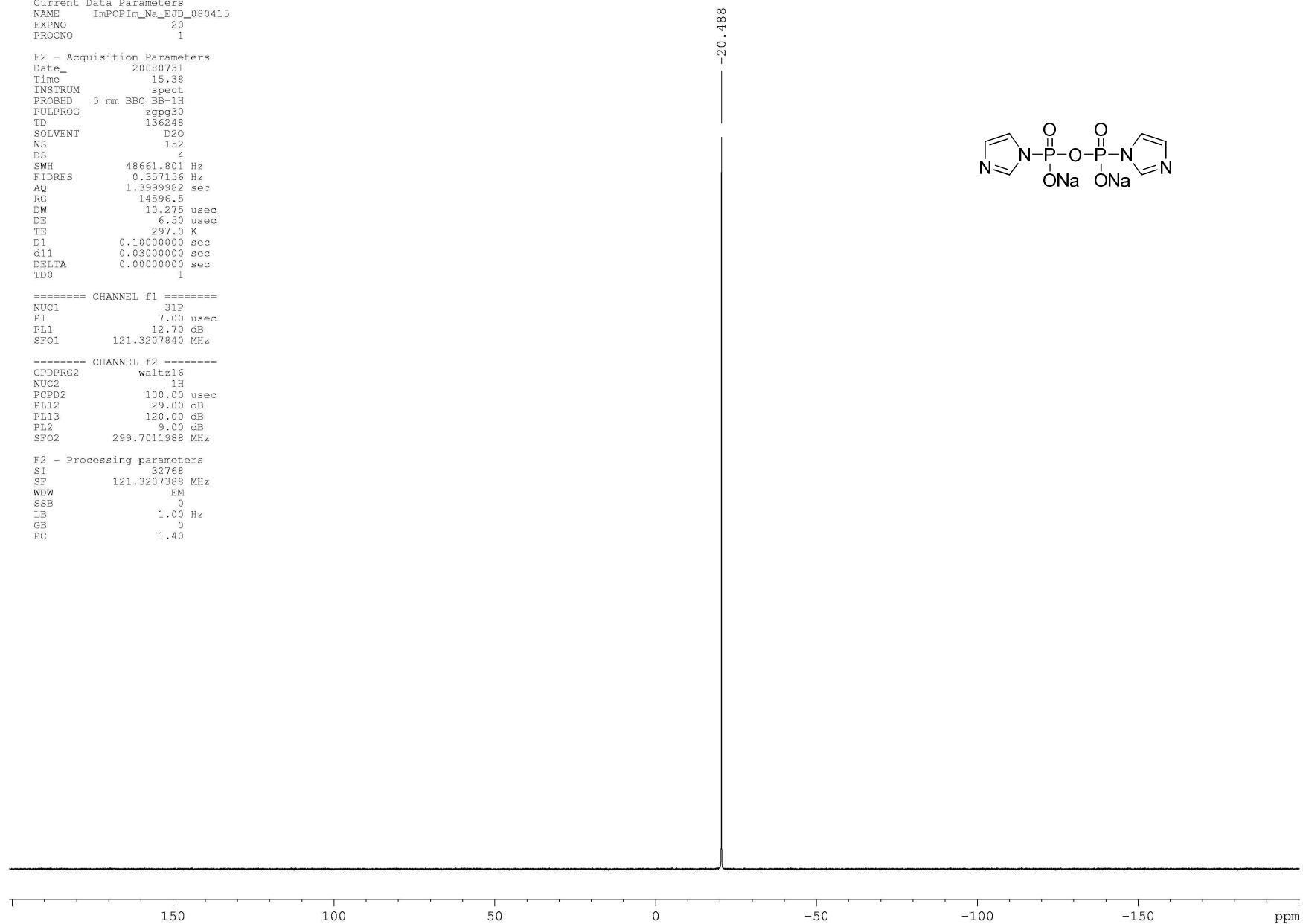
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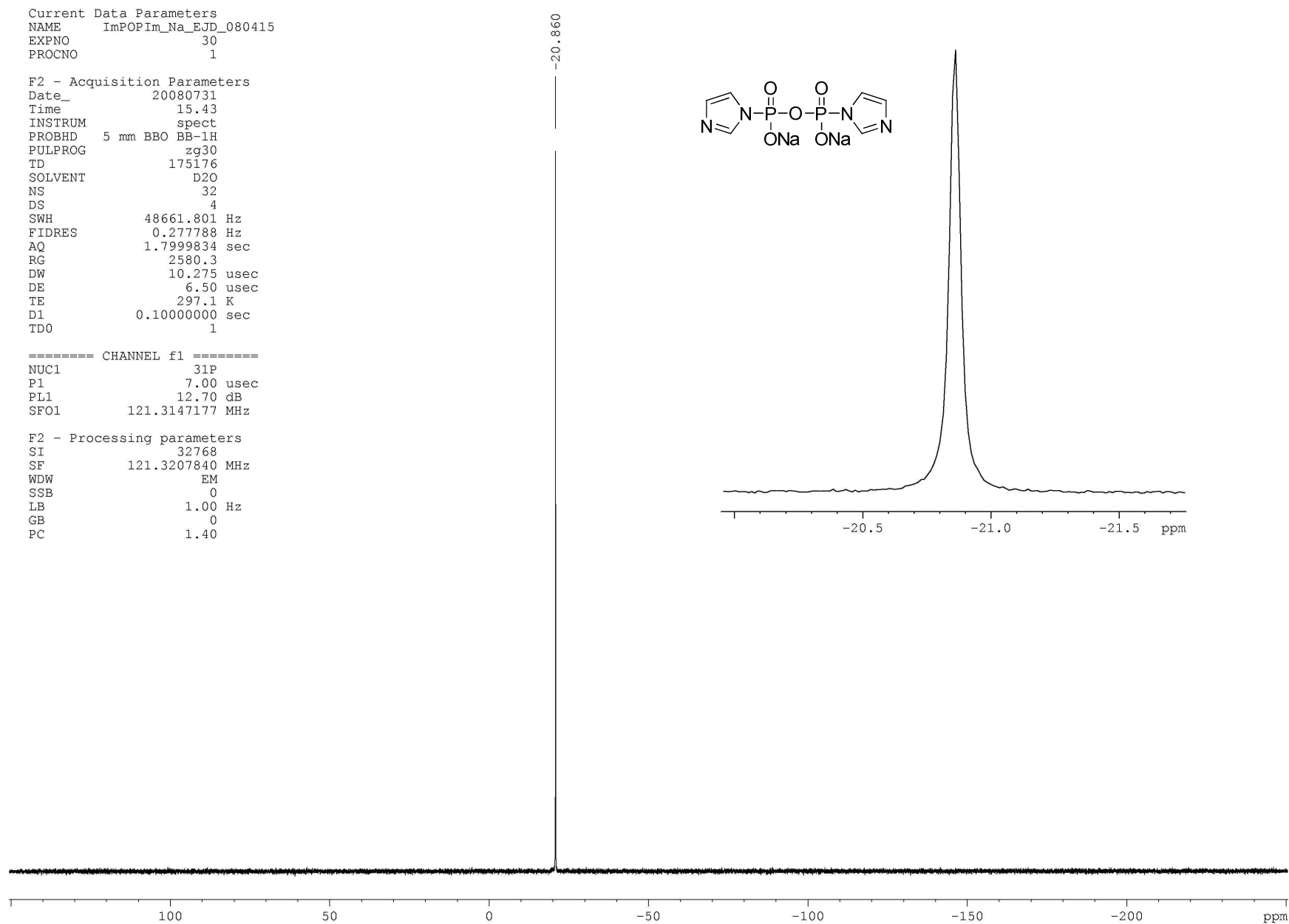
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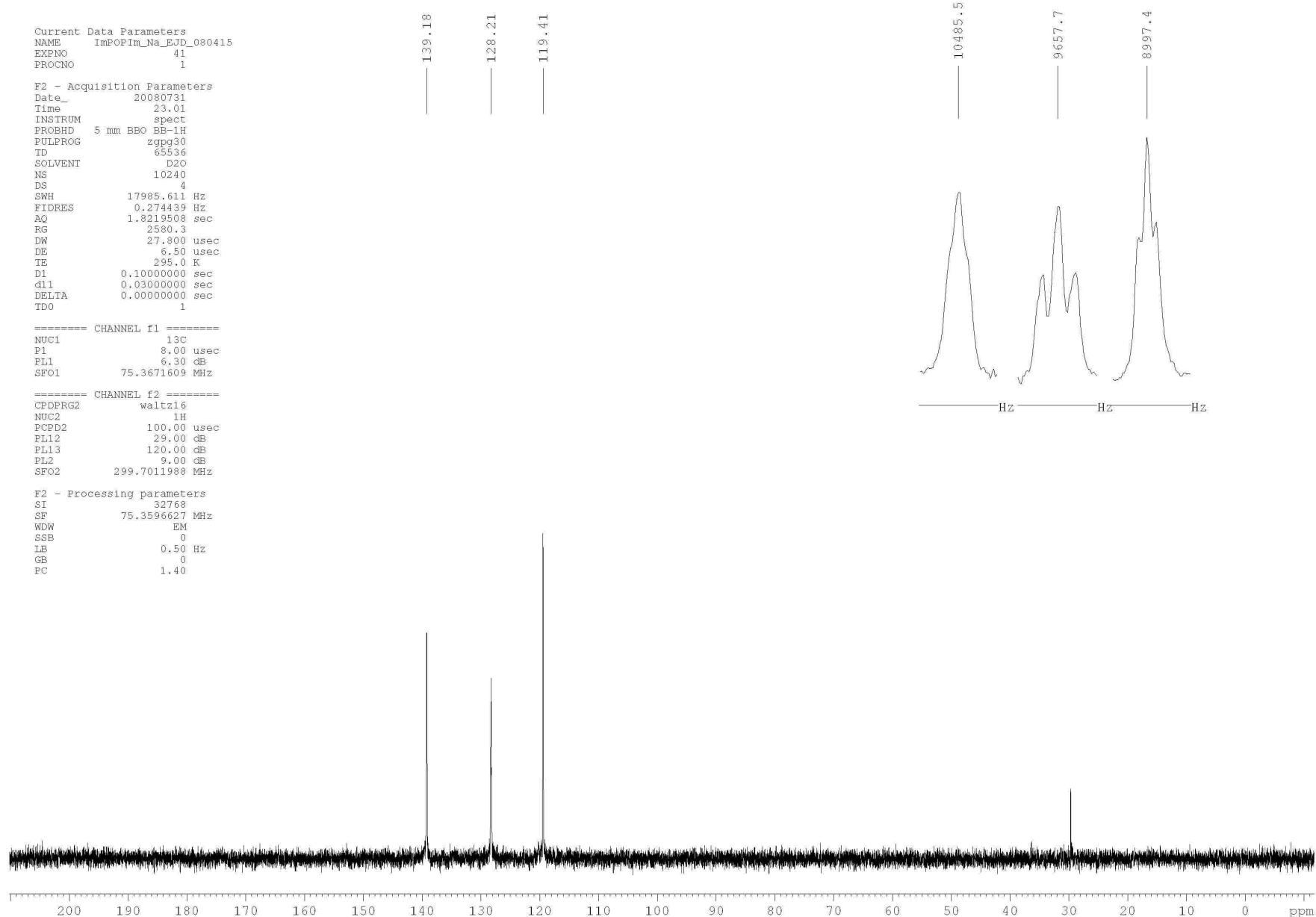
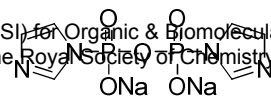
³¹P NMR (proton coupled) of the di-sodium salt of compound **7a** in D₂O

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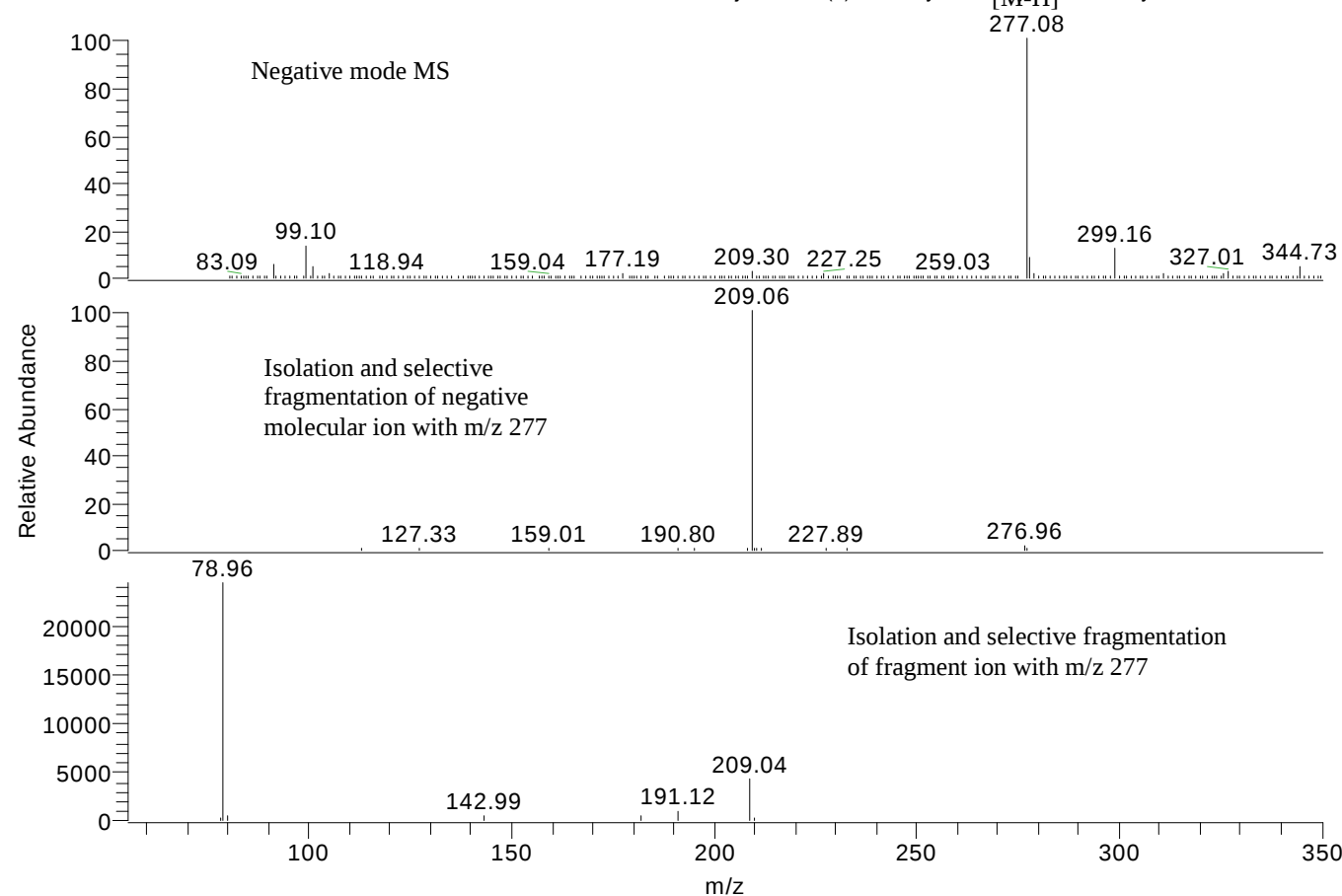
¹³C NMR of the di-sodium salt of compound **7a** in D₂O

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

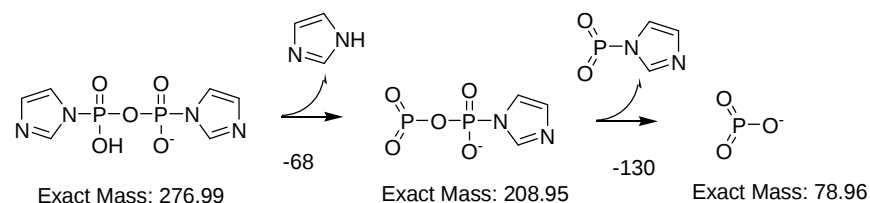
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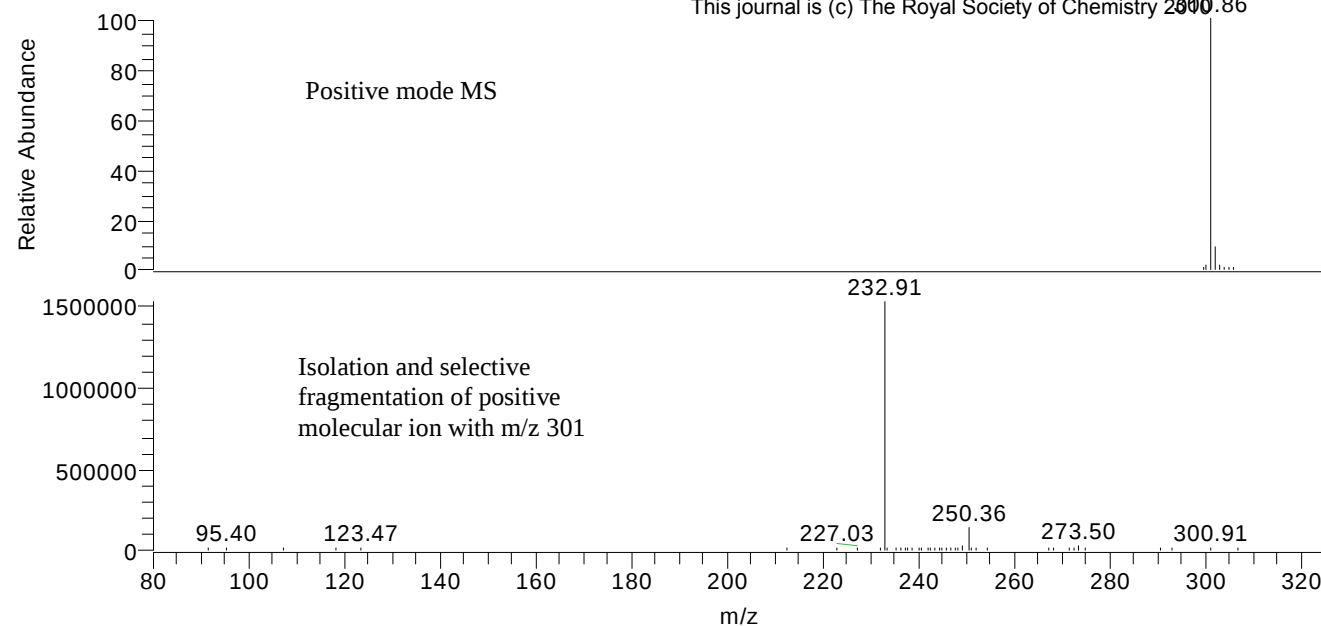
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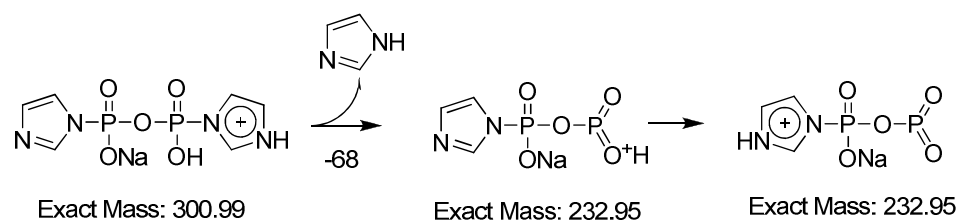
ESI Positive mode MS and selective MS² fragmentation of compound **7a**

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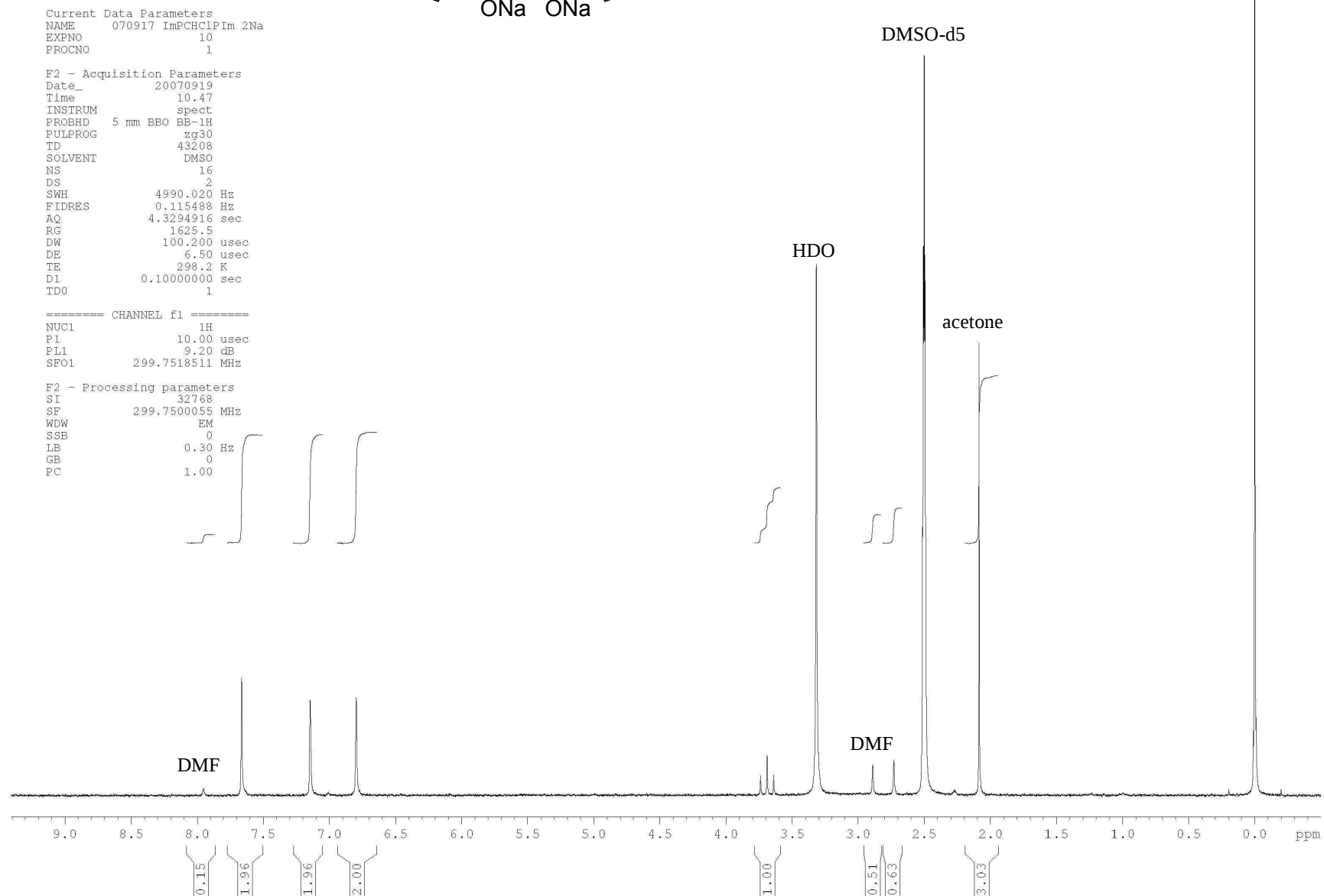
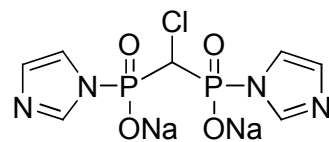
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Positive mode fragmentation scheme

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

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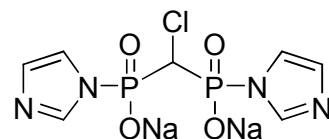


³¹P NMR (proton decoupled) of the di-sodium salt of compound **7b** in DMSO-d₆/D₂O

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³¹P dec of final product



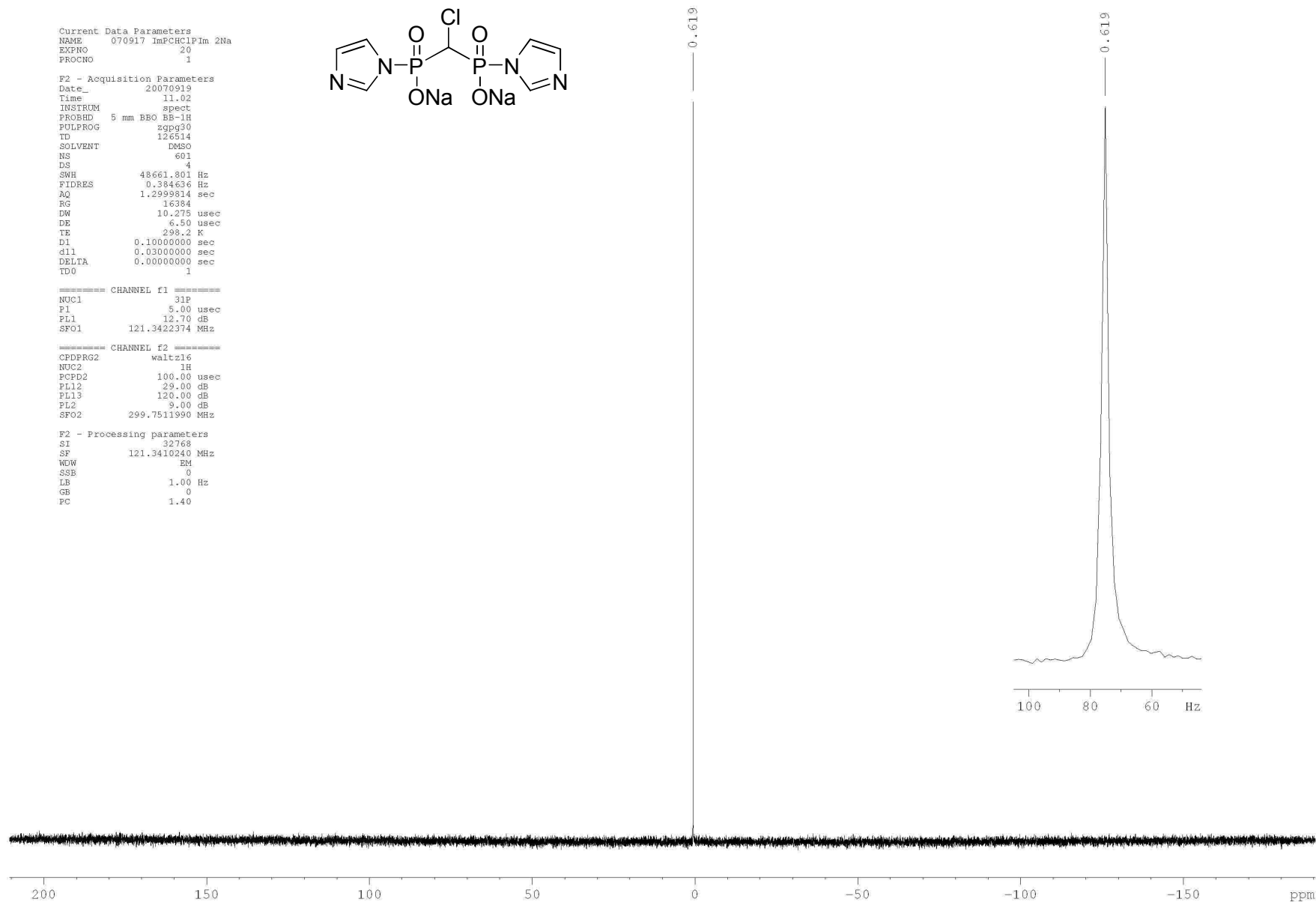
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³¹P NMR (proton coupled) of the di-sodium salt of compound **7b** in DMSO-d₆/D₂O

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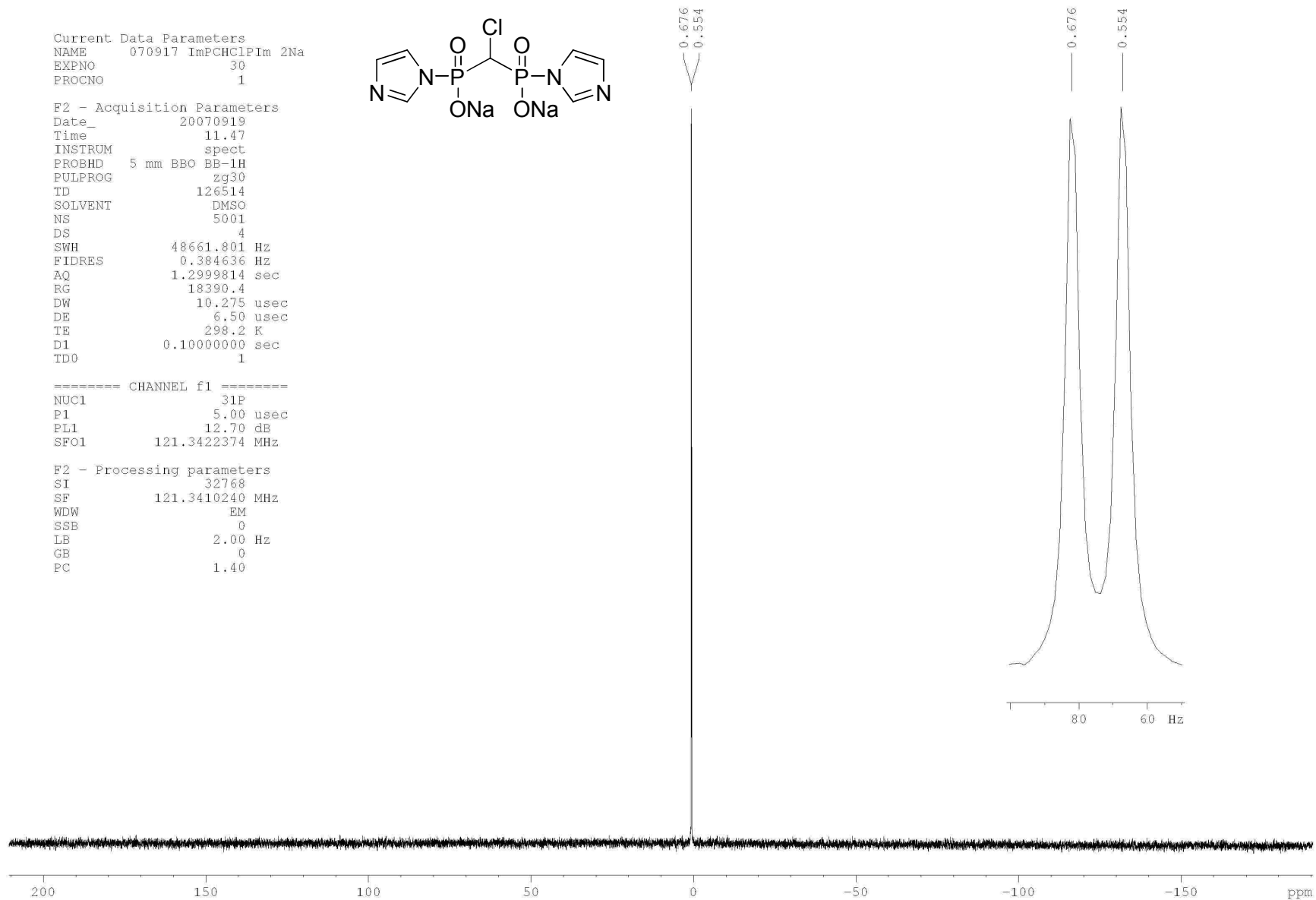
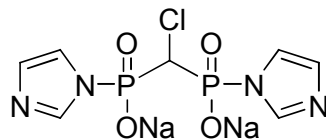
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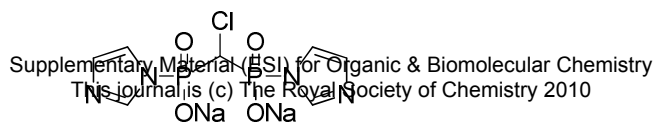
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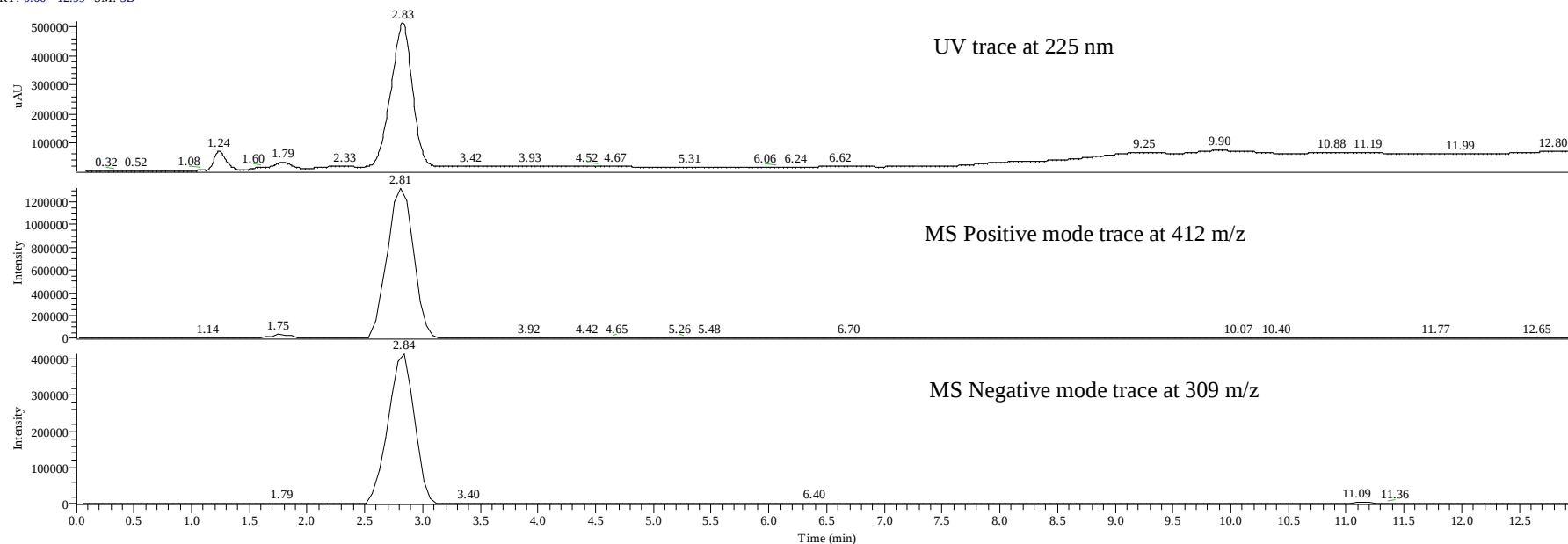
LCMS of the di-sodium salt of compound 7b



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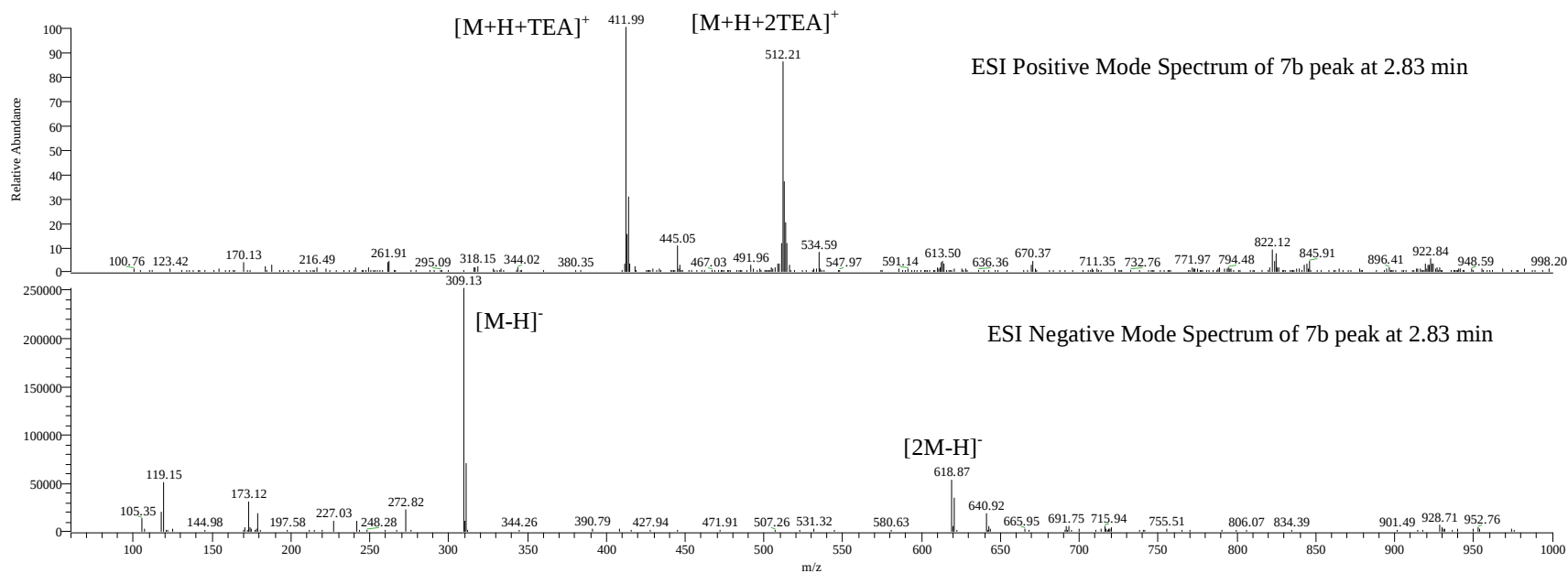
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LCMS of the di-sodium salt of compound 7c

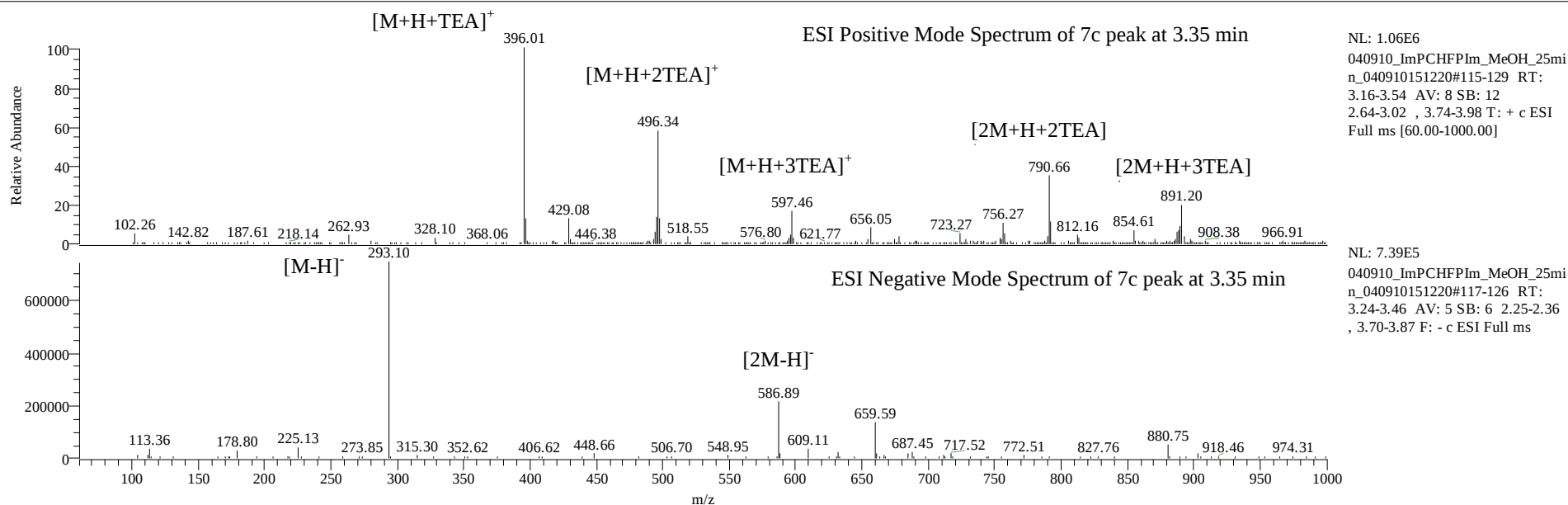
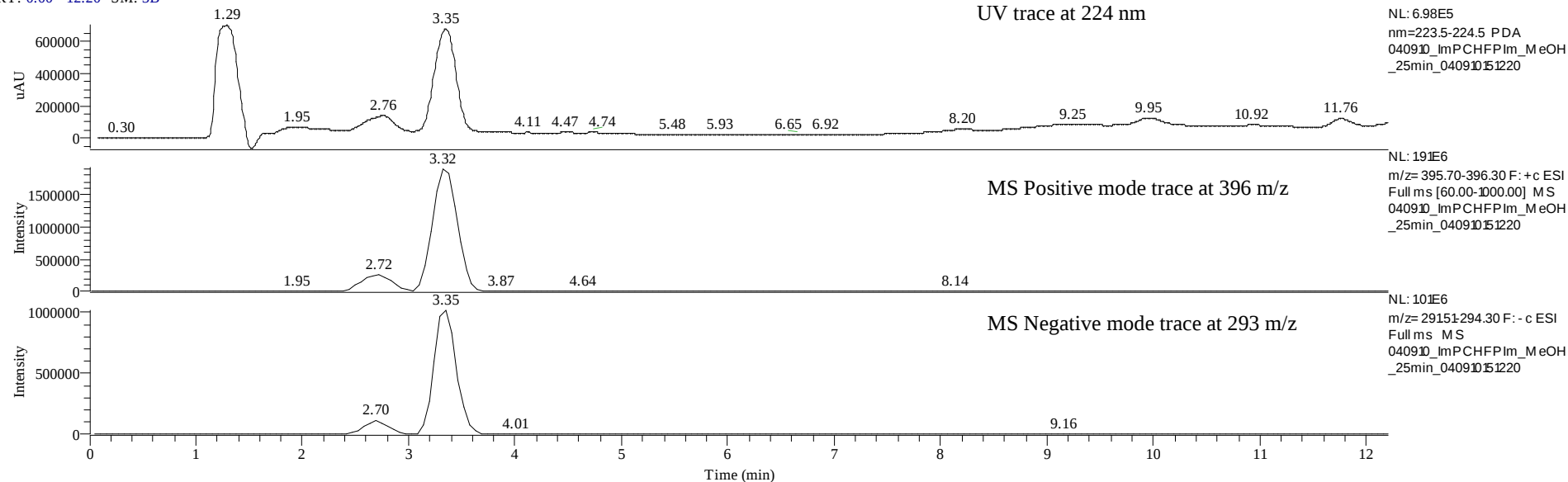


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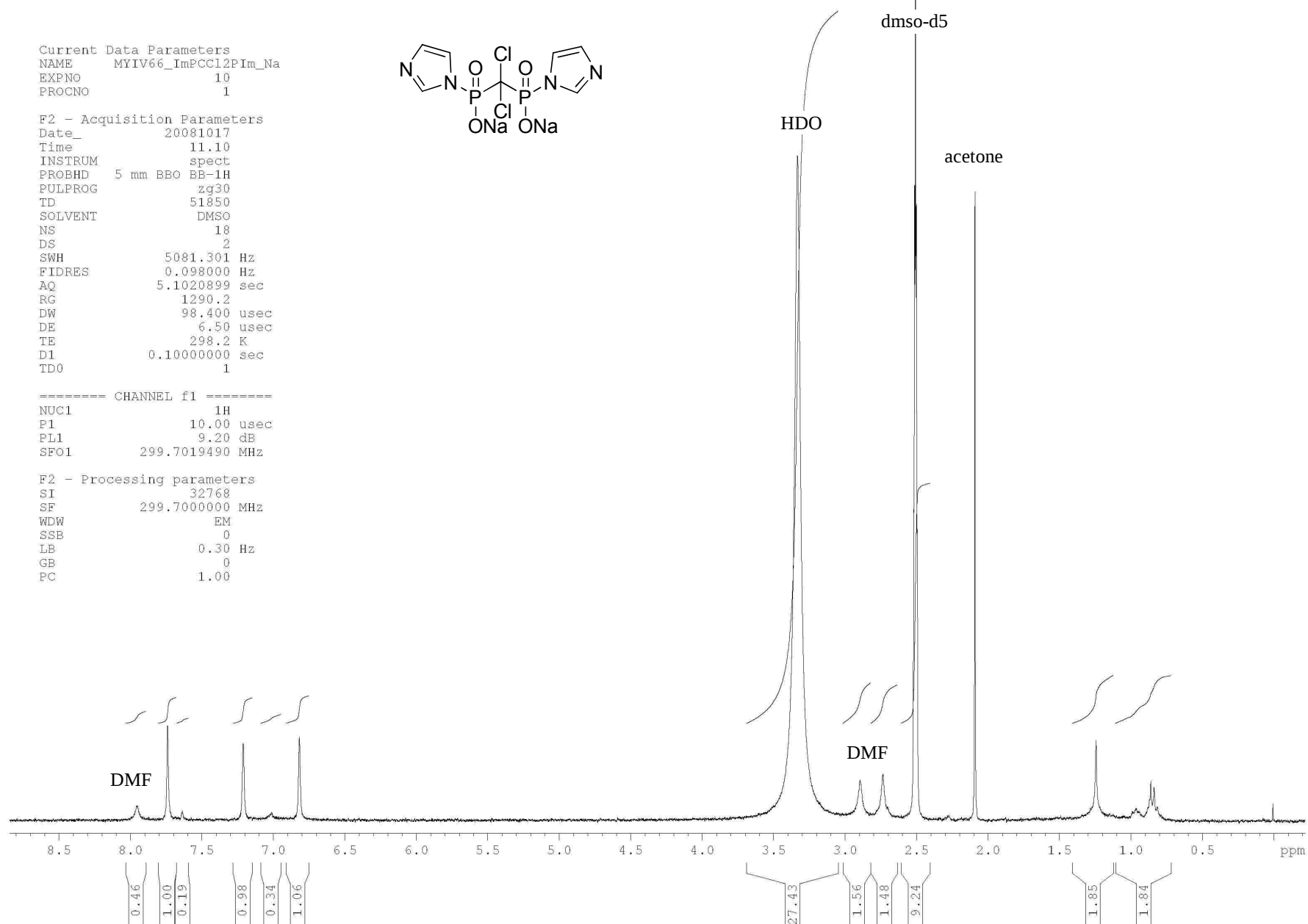
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¹H NMR of the di-sodium salt of compound **7d** in DMSO-d₆

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1H of Na salt in dmsol This journal is (c) The Royal Society of Chemistry 2010



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

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

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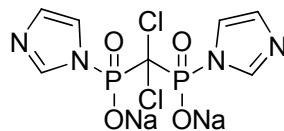
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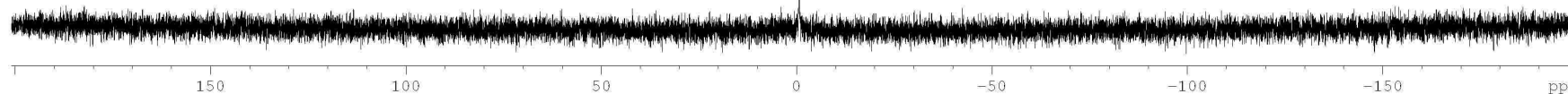
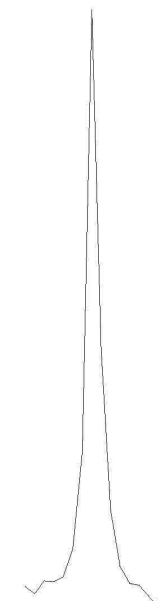
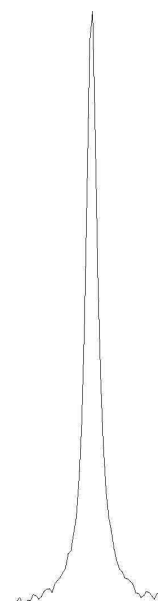
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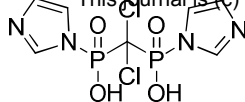
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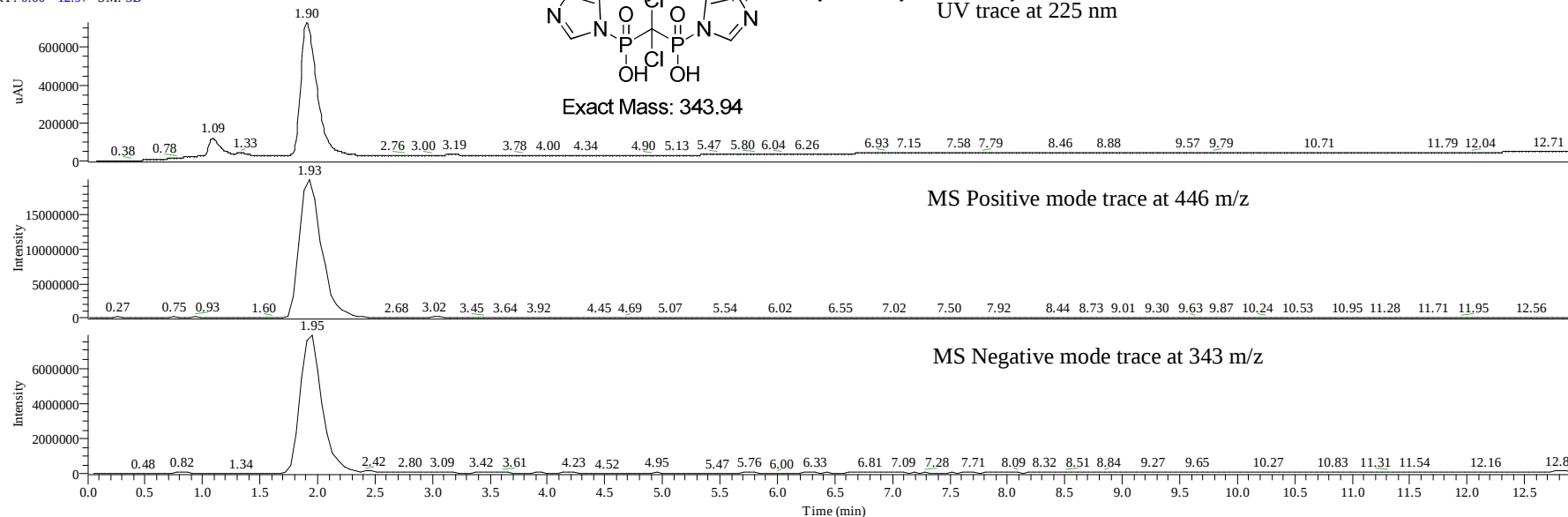
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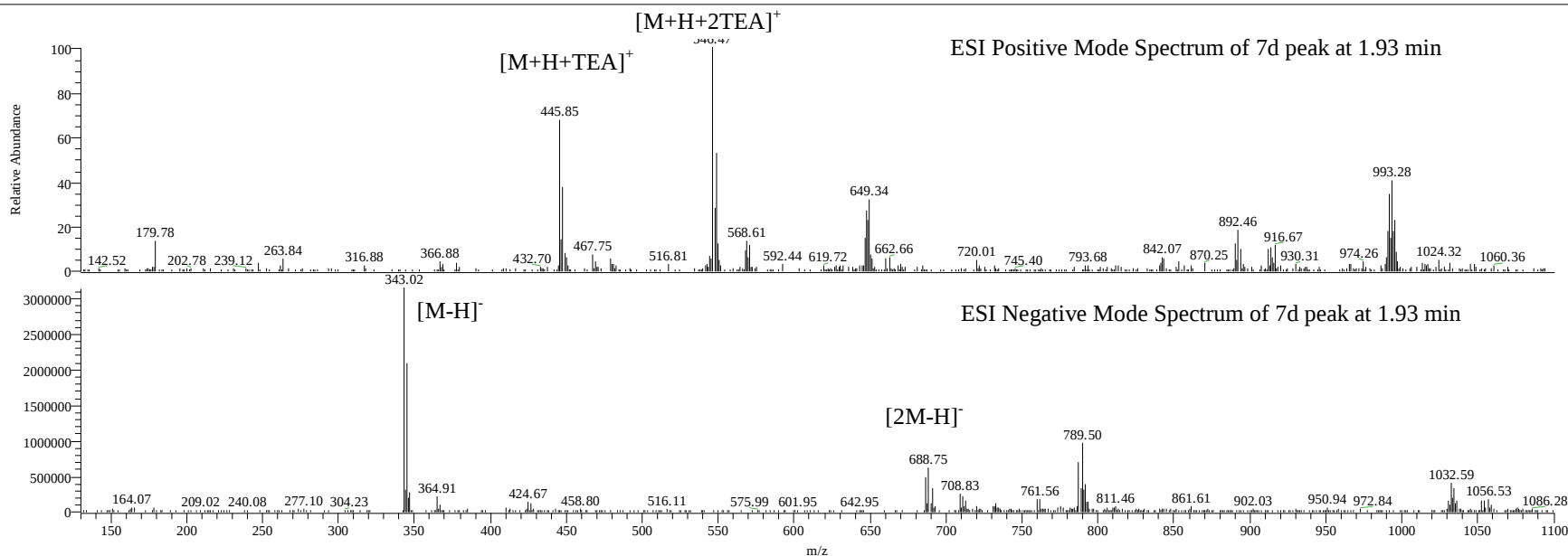
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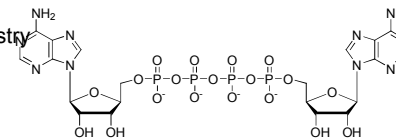


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Full ms

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

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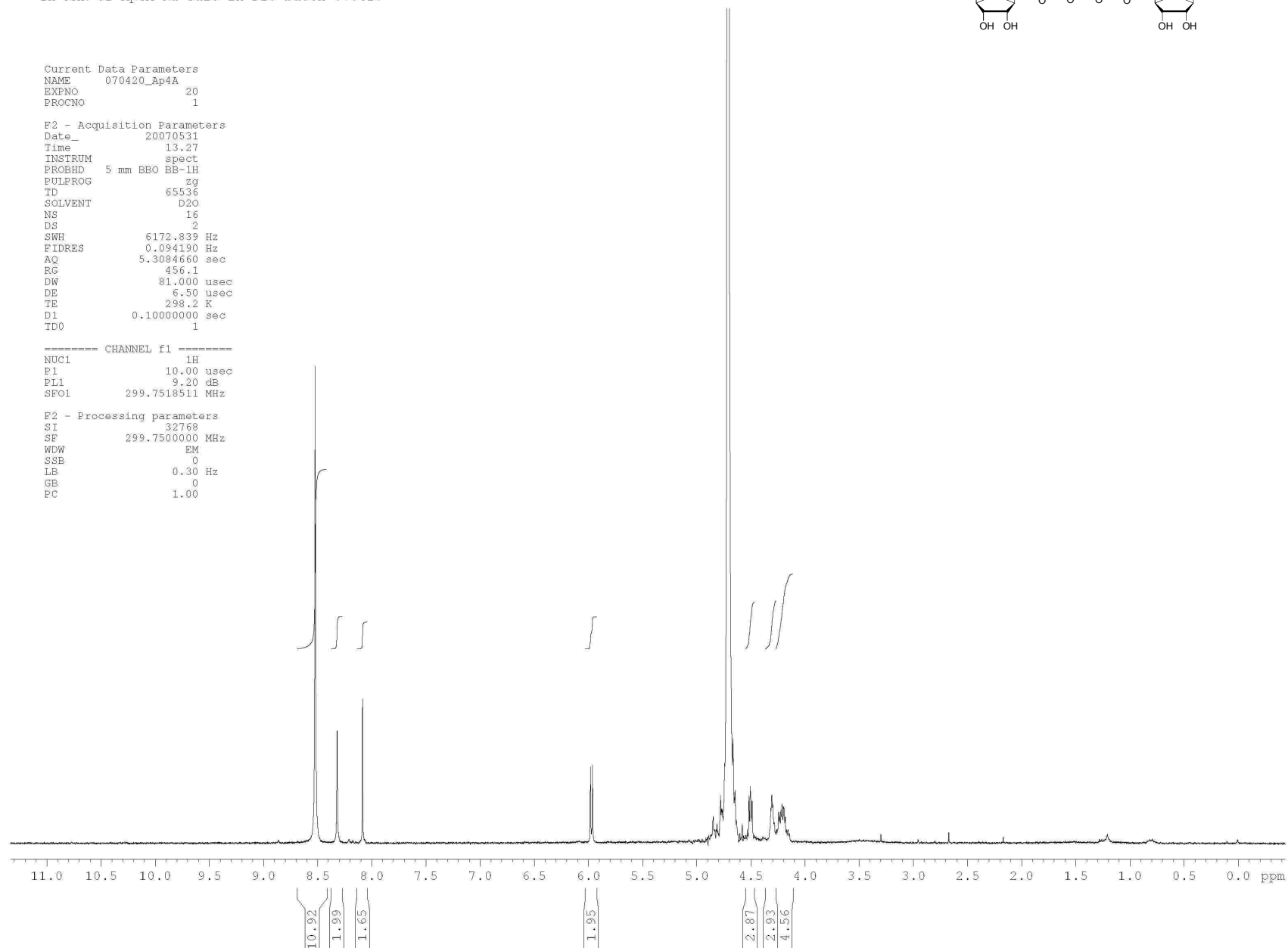
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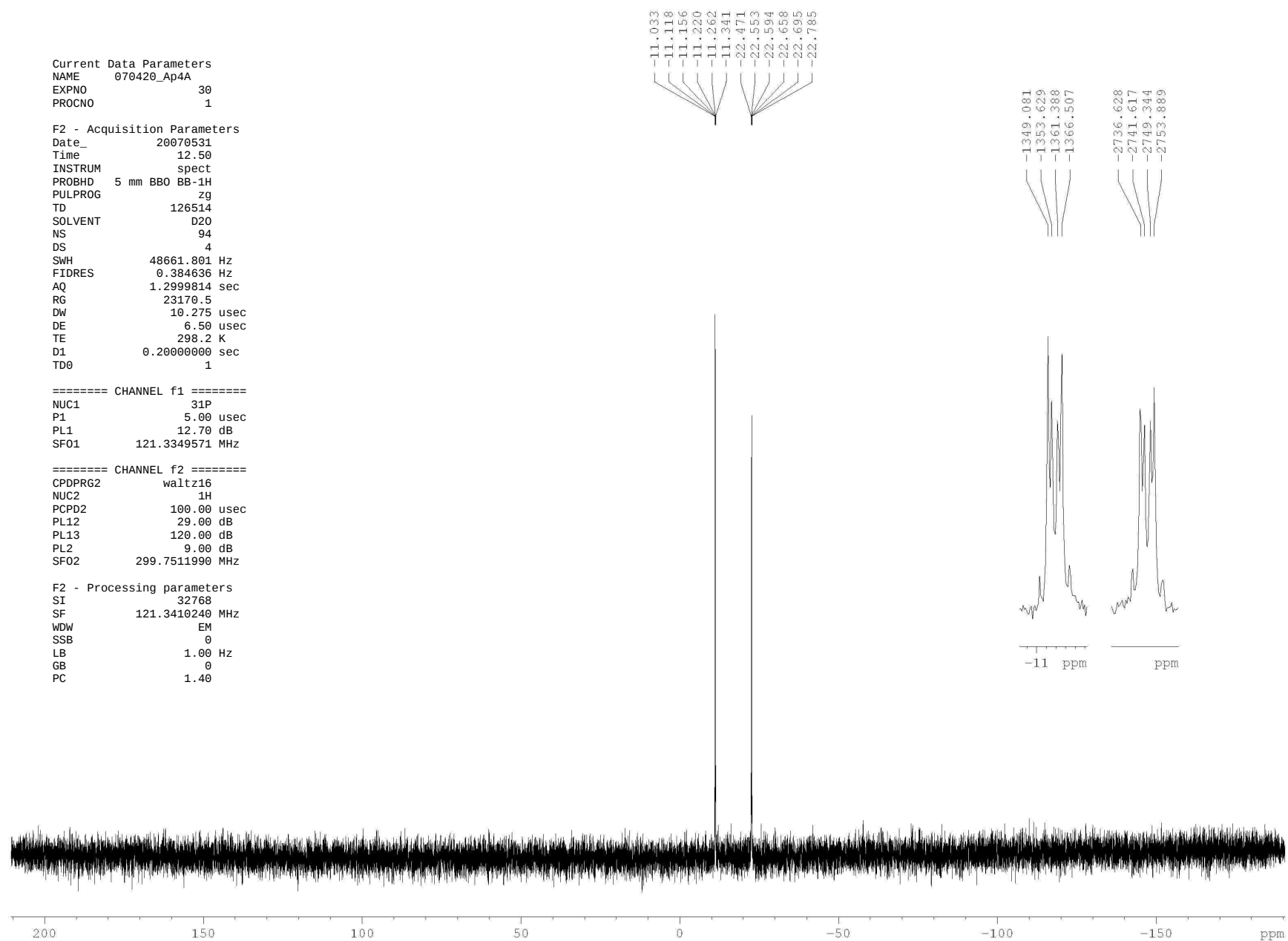
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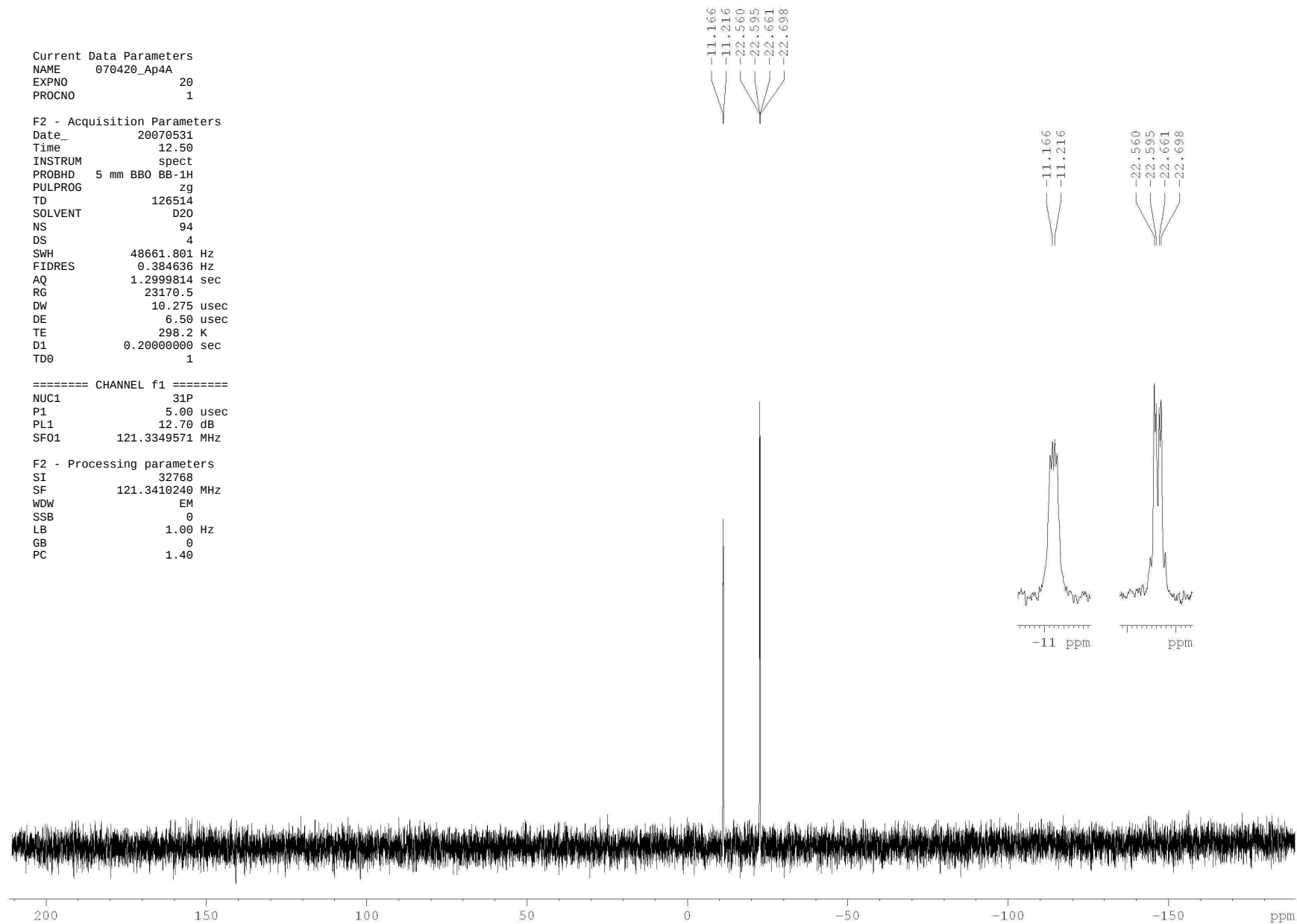
³¹P (proton decoupled) NMR spectrum of Ap₄A sodium salt, **3a** in D₂O

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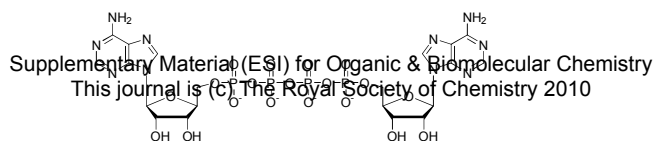


³¹P (proton coupled) NMR spectrum of Ap₄A sodium salt, **3a** in D₂O

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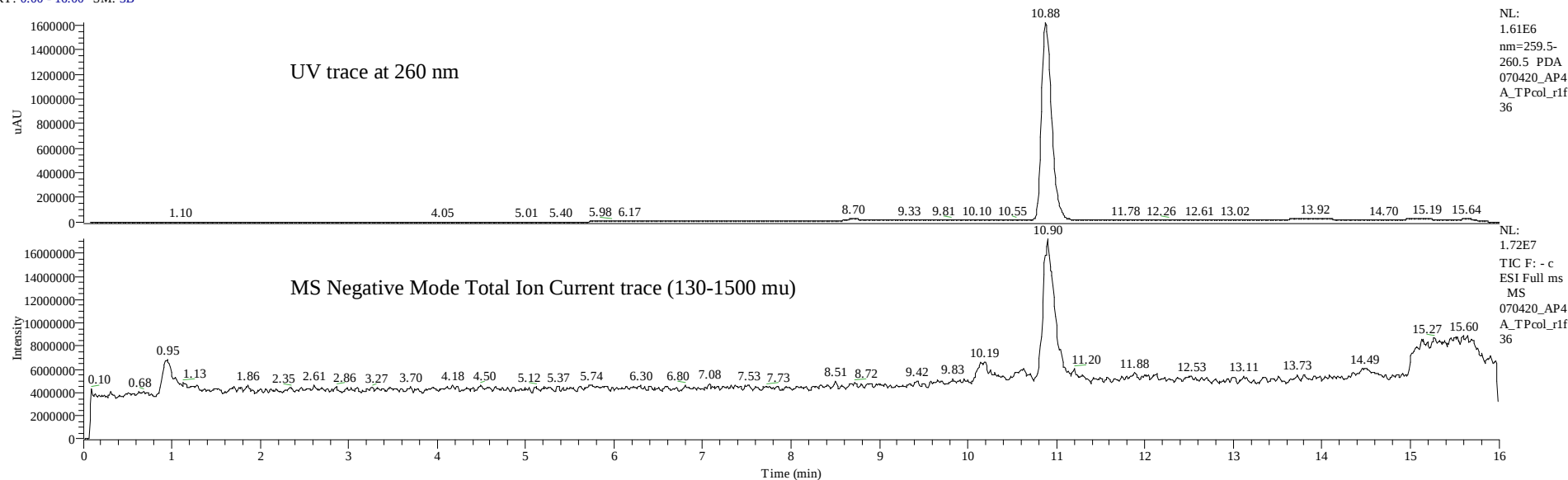
LCMS of Ap₄A, 3a



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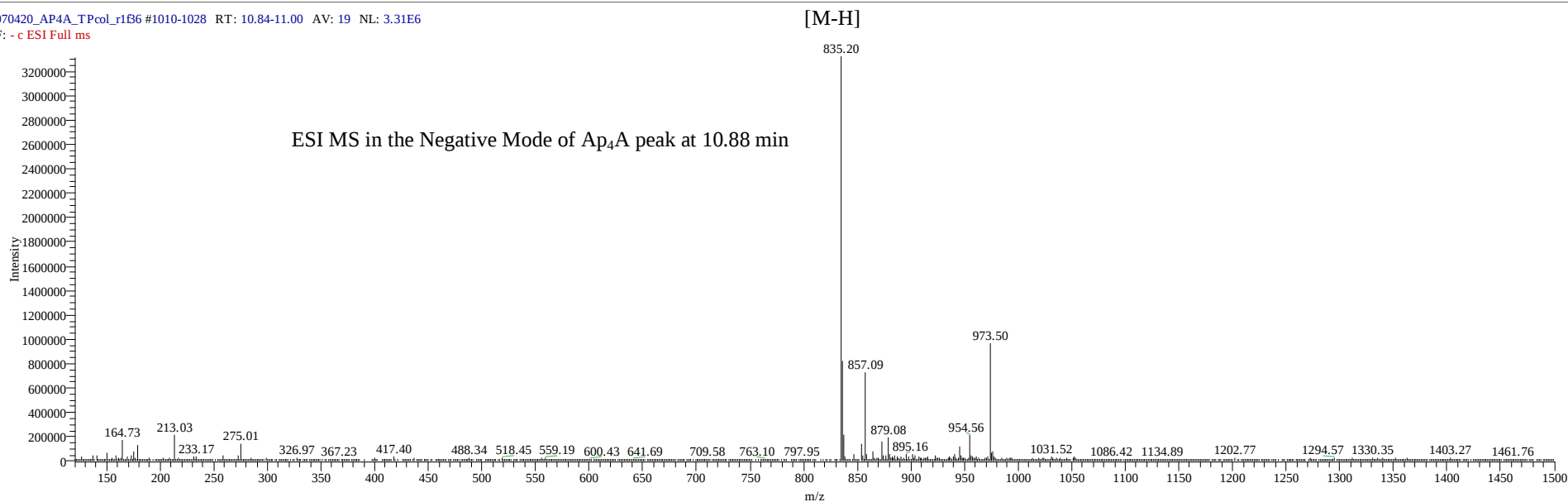
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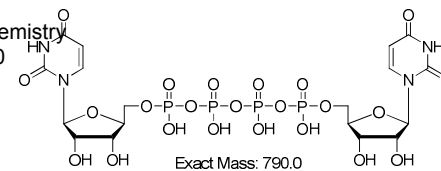
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¹H NMR spectrum of Up₄U sodium salt, **3f** in D₂O

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¹H NMR of UP4U Na salt, 050223 and 050217 in d₂O

```

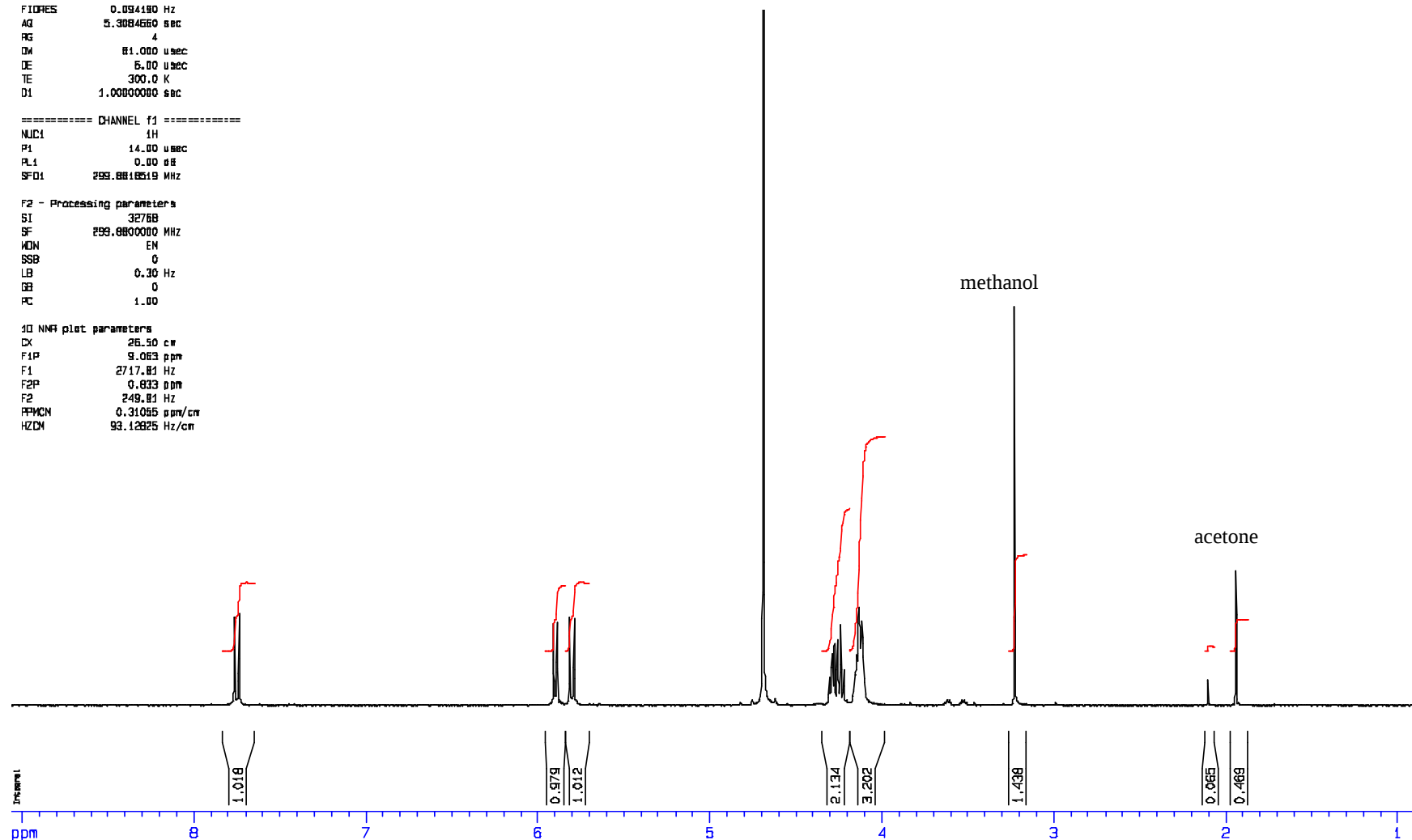
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PROCNO    1

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PULPROG   zg30
TD         65536
SOLVENT   D2O
NS         16
DS         2
SWH        6172.839 Hz
FIDRES     0.094190 Hz
AQ         5.3084660 sec
RG         4
DM         81.000 usec
DE         5.00 usec
TE         300.0 K
D1         1.00000000 sec

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P1         14.00 usec
PL1        0.00 dB
SFO1       299.8818619 MHz

F2 - Processing parameters
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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        0.833 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

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Current Data Parameters
NAME 050227_UP4U_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
SWH 48661.804 Hz
FIDRES 0.333246 Hz
AQ 1.4898946 sec
RG 20642.0
DM 10.275 uspc
DE 5.00 uspc
TE 300.0 K
D1 0.10000000 sec
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d12 0.00020000 sec

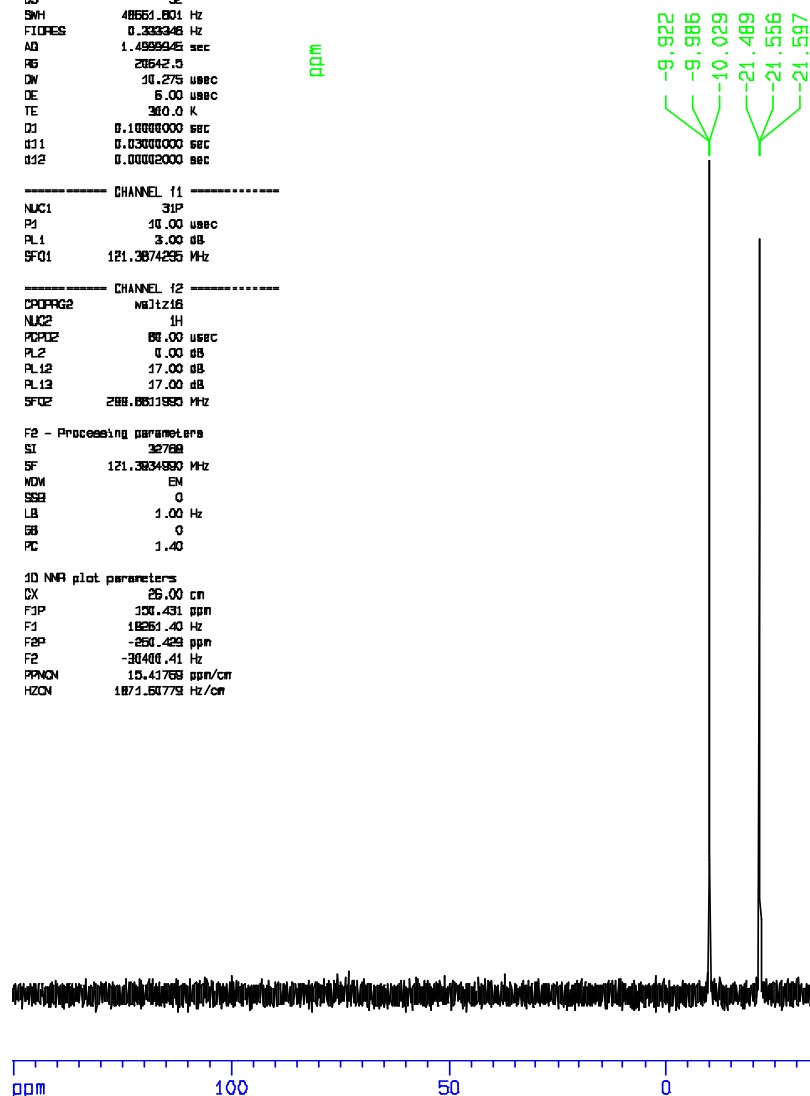
----- CHANNEL f1 -----
NUC1 31P
P1 10.00 uspc
PL1 3.00 dB
SFO1 121.3874255 MHz

----- CHANNEL 12 -----
CHOPRG2 M31218
NUC2 1H
PCPD2 88.00 uspc
PL2 0.00 dB
PL12 17.00 dB
PL13 17.00 dB
SFO2 299.8811995 MHz

F2 - Processing parameters
SI 32768
SF 121.3834990 MHz
WDW 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 15.43769 ppm/cm
HZOM 1871.50775 Hz/cm

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



Current Data Parameters
NAME 050217_UP4U_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
SWH 48661.804 Hz
FIDRES 0.333246 Hz
AQ 1.4898946 sec
RG 20642.0
DM 10.275 uspc
DE 5.00 uspc
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
d12 0.00020000 sec

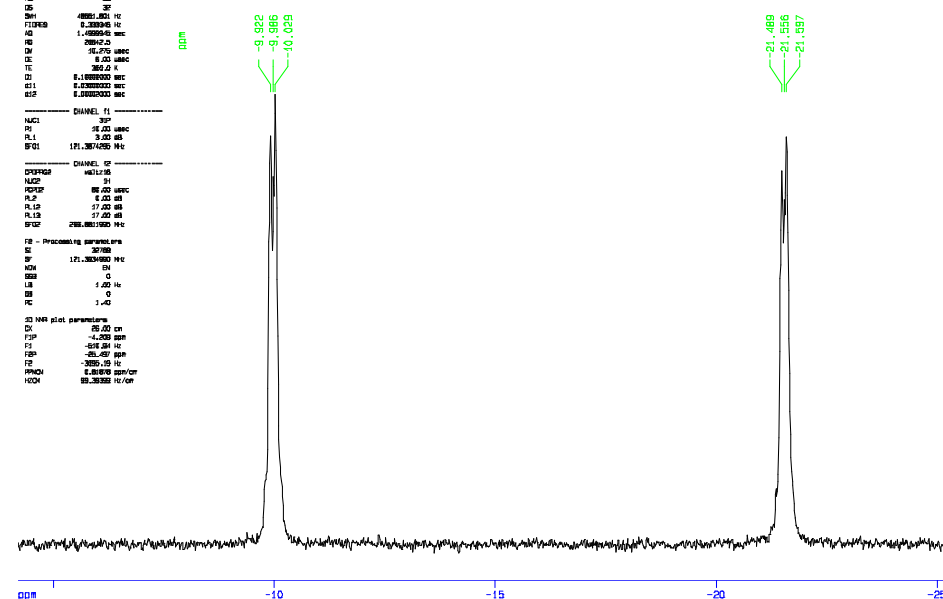
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PL1 3.00 dB
SFO1 121.3874255 MHz

----- CHANNEL 12 -----
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NUC2 1H
PCPD2 88.00 uspc
PL2 0.00 dB
PL12 17.00 dB
PL13 17.00 dB
SFO2 299.8811995 MHz

F2 - Processing parameters
SI 32768
SF 121.3834990 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

2D NMR plot parameters
CX 25.00 cm
F1P 106.431 ppm
F1 18261.40 Hz
F2P -250.429 ppm
F2 -30400.41 Hz
PRNOM 15.43769 ppm/cm
HZOM 1871.50775 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

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

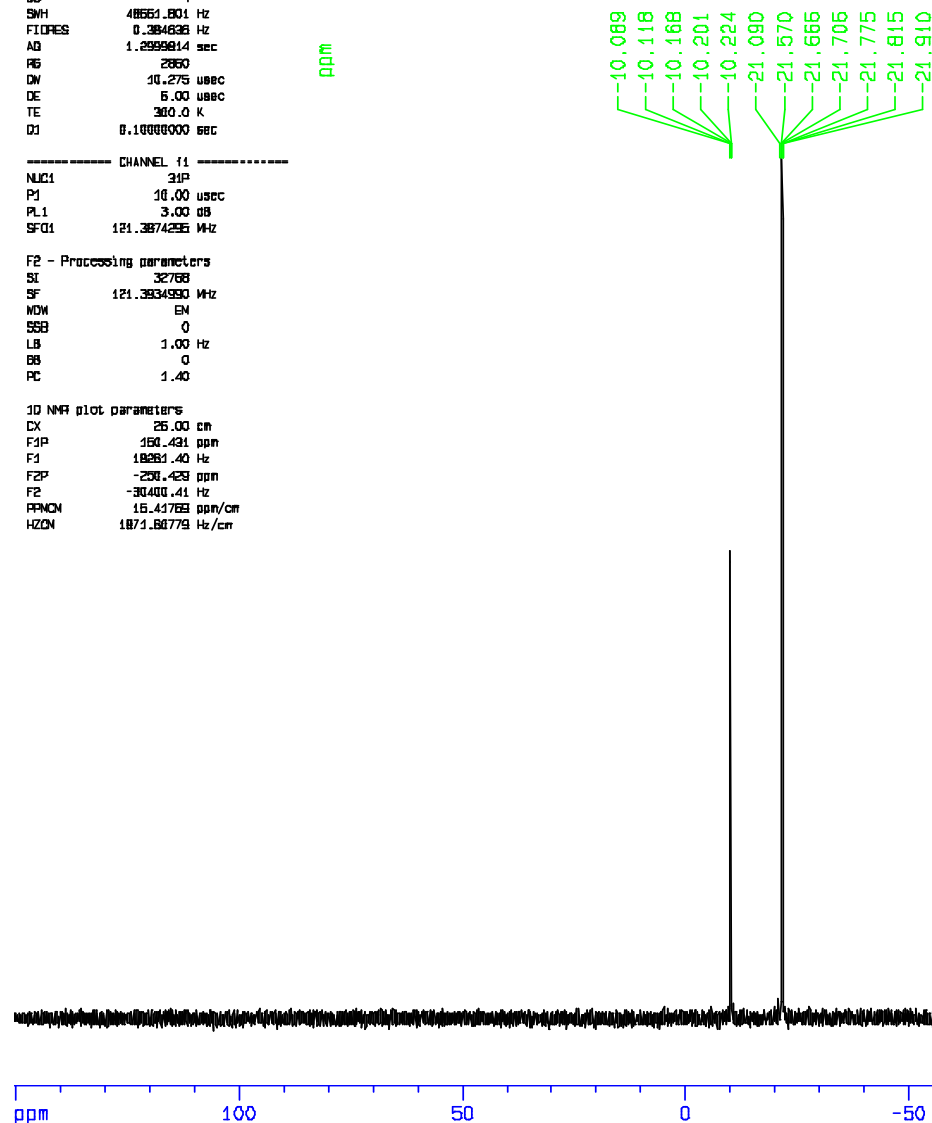
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EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
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Time 10.14
INSTRUM spect
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PULPROG zgpg30
TD 326514
SOLVENT d2o
NS 53
DS 4
SWH 48661.801 Hz
FIDRES 0.384636 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 -----
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P1 16.00 usec
PL1 3.00 dB
SFO1 121.3874256 MHz

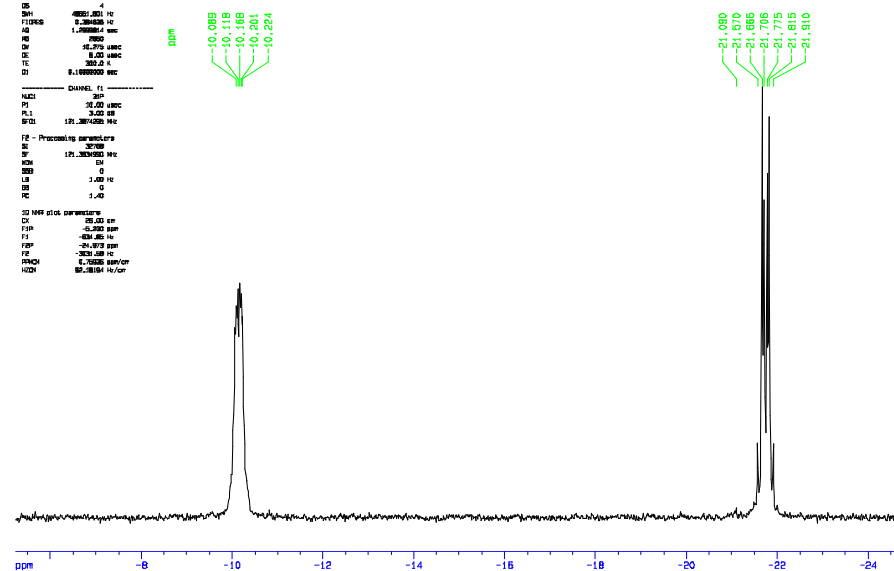
F2 - Processing parameters
SI 32768
SF 121.3834590 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3D NMR plot parameters
CX 25.00 cm
FJP 160.431 ppm
F1 18261.40 Hz
F2P -200.429 ppm
F2 -30400.41 Hz
PRON 16.41769 ppm/cm
HZON 1871.66779 Hz/cm

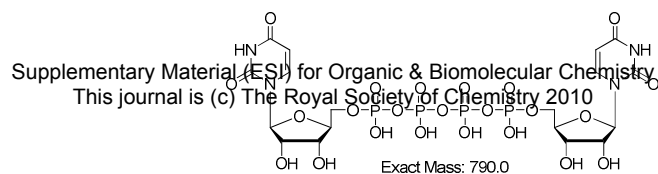


Current Data Parameters
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EXPNO 20
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090311
Time 10.14
INSTRUM spect
PROBHD 5 mm NuSpinuc
PULPROG zgpg30
TD 326514
SOLVENT d2o
NS 53
DS 4
SWH 48661.801 Hz
FIDRES 0.384636 Hz
AQ 1.2999814 sec
RG 2860
DW 10.275 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
----- CHANNEL f1 -----
NUC1 ³¹P
P1 16.00 usec
PL1 3.00 dB
SFO1 121.3874256 MHz
F2 - Processing parameters
SI 32768
SF 121.3834590 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
3D NMR plot parameters
CX 25.00 cm
FJP 160.431 ppm
F1 18261.40 Hz
F2P -200.429 ppm
F2 -30400.41 Hz
PRON 16.41769 ppm/cm
HZON 1871.66779 Hz/cm

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



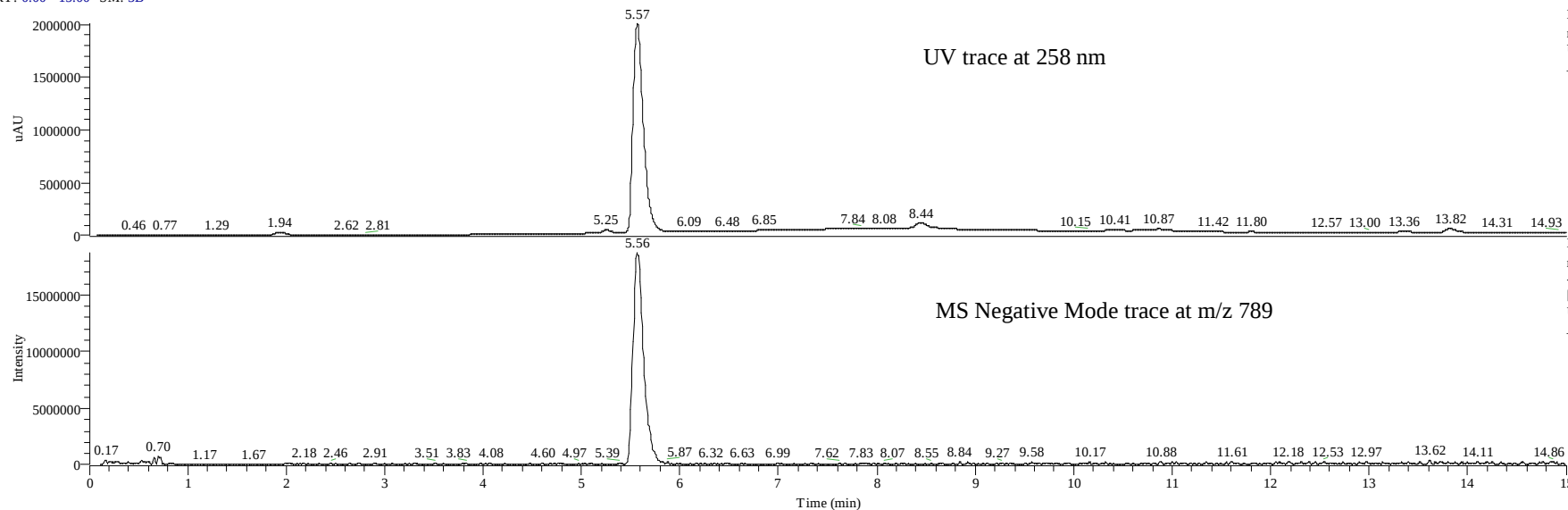
LCMS of Up₄U, 3f



Up4U_NaSalt_29Apr08_080429155436

4/29/2008 3:54:36 PM

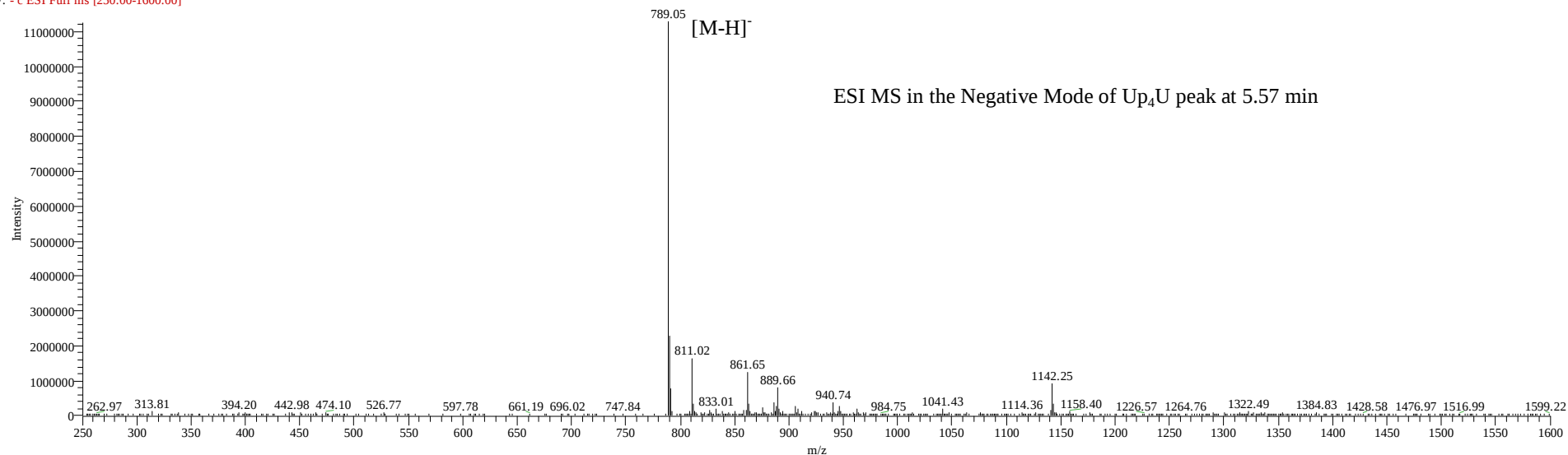
RT: 0.00 - 15.00 SM: 3B



NL: 2.00E6
nm=256.2-258.8 PDA
Up4U_NaSalt_29Apr08_080429155436

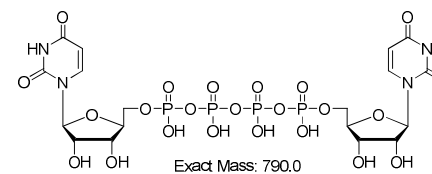
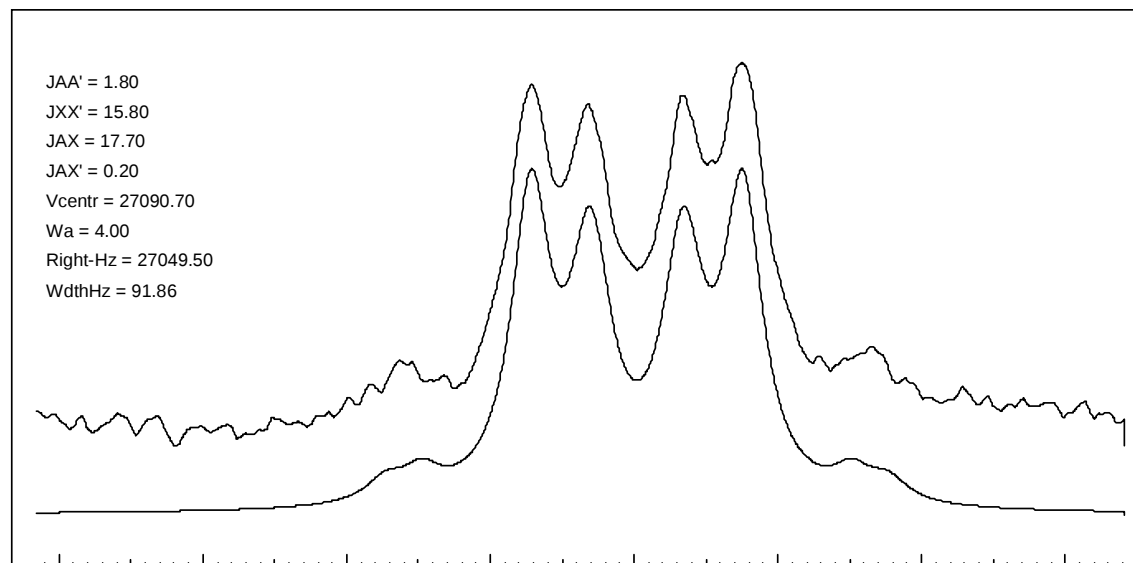
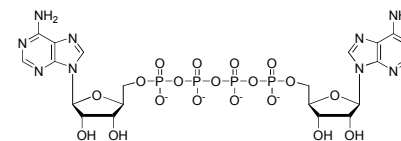
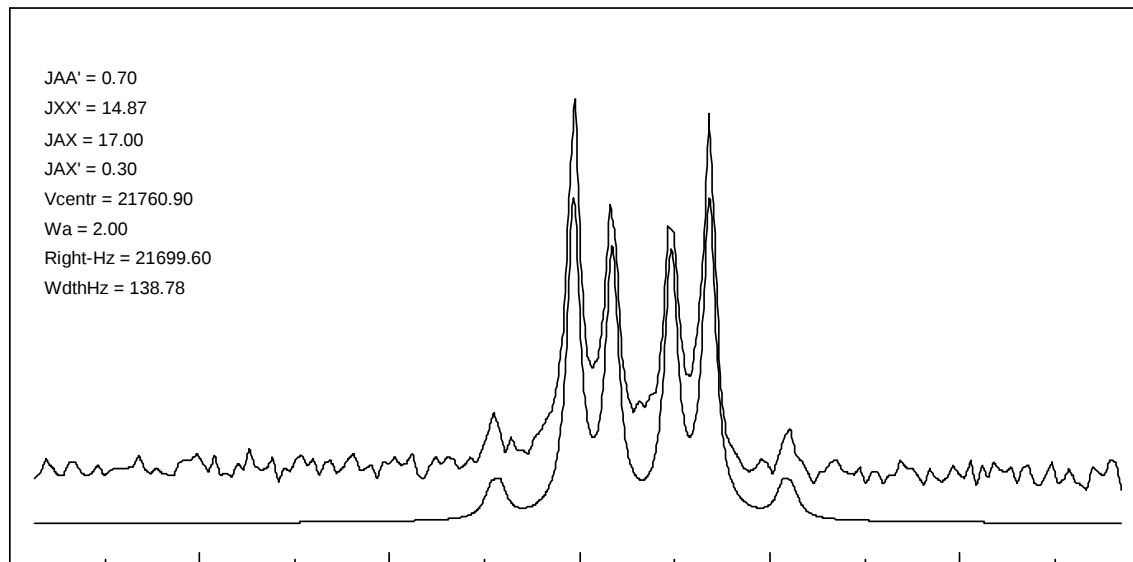
NL: 1.86E7
m/z= 787.62-790.59 F:
- c ESI Full ms
[250.00-1600.00] MS
Up4U_NaSalt_29Apr08_080429155436

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]



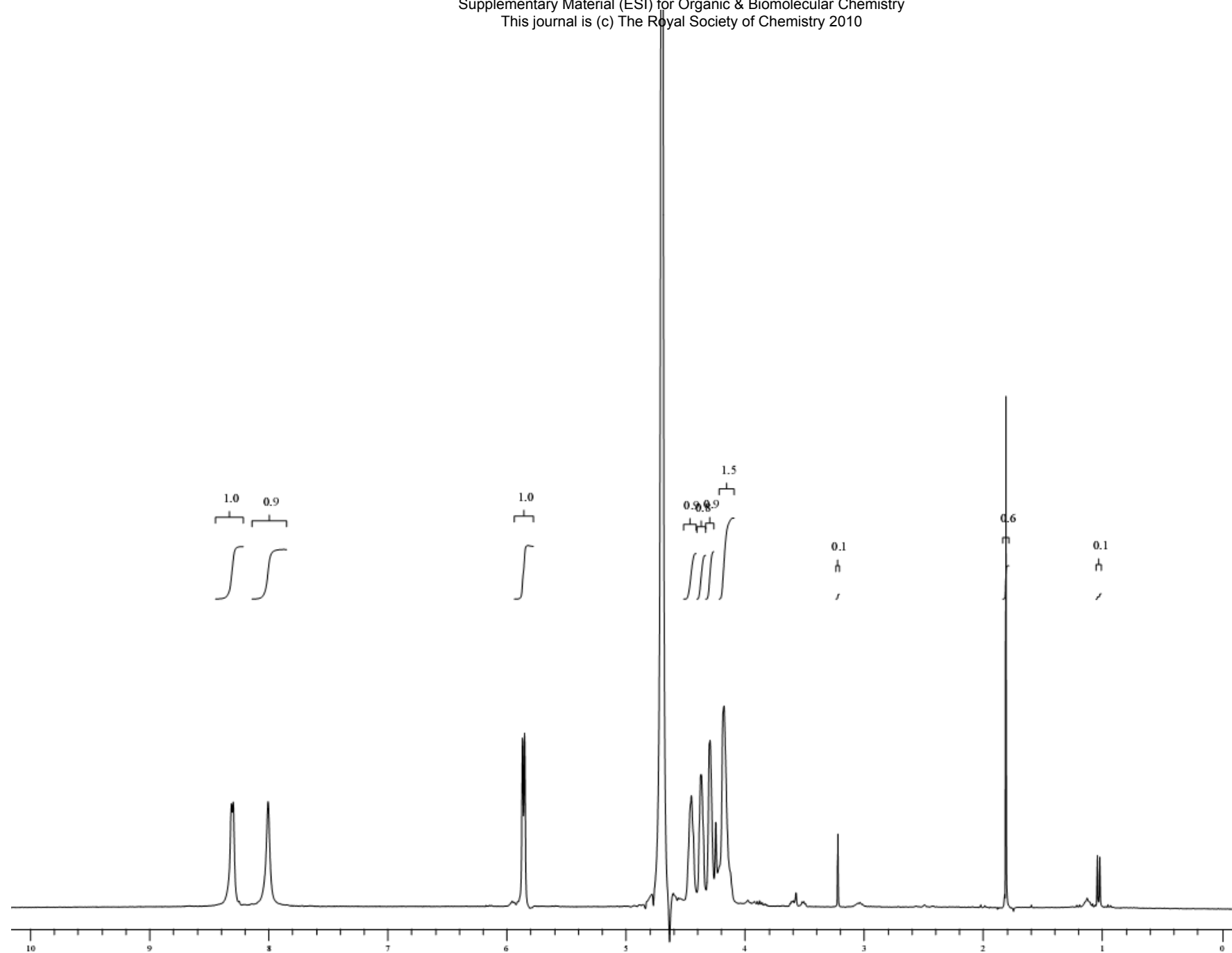
Simulated fitting of an AA'XX' spin system to the experimental ^{31}P NMR spectra of Ap₄A and Up₄U (**3a** and **3f**, resp.):

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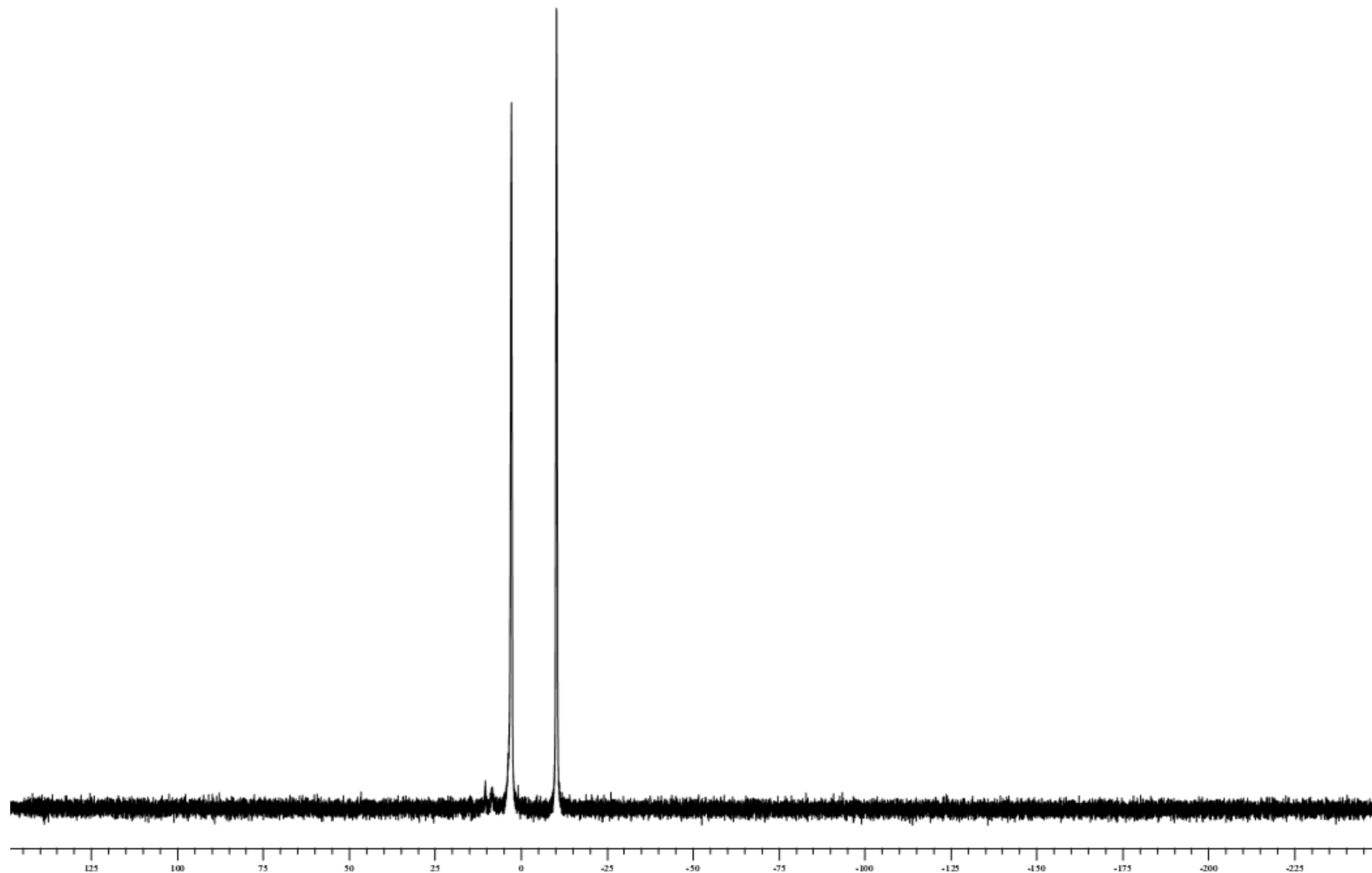
^1H NMR of APPCHClPPA sodium salt, **3c** in D_2O :

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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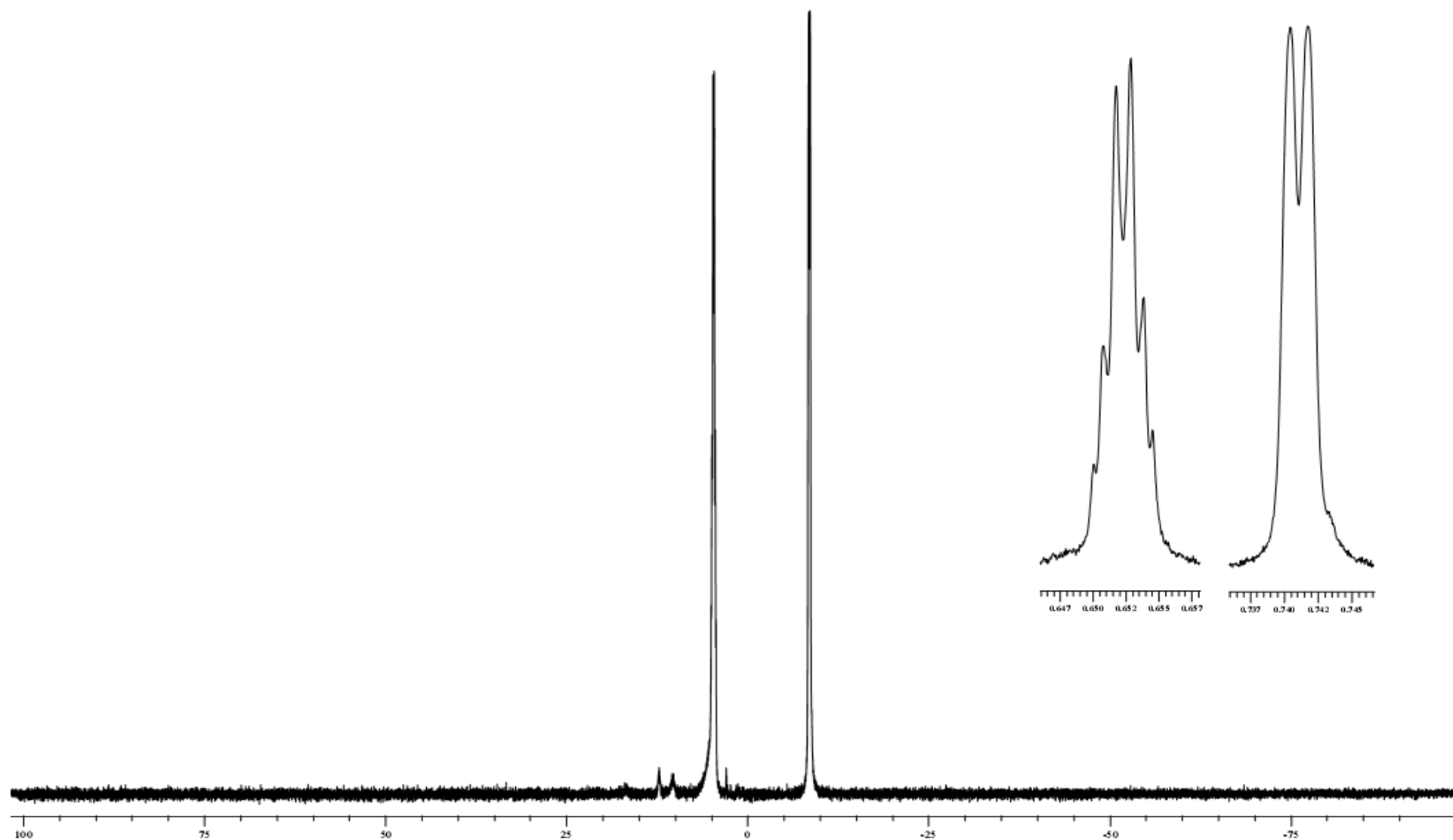
^{31}P NMR (proton decoupled) of APPCHCIPPA sodium salt, **3c** in D_2O :

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is (c) The Royal Society of Chemistry 2010



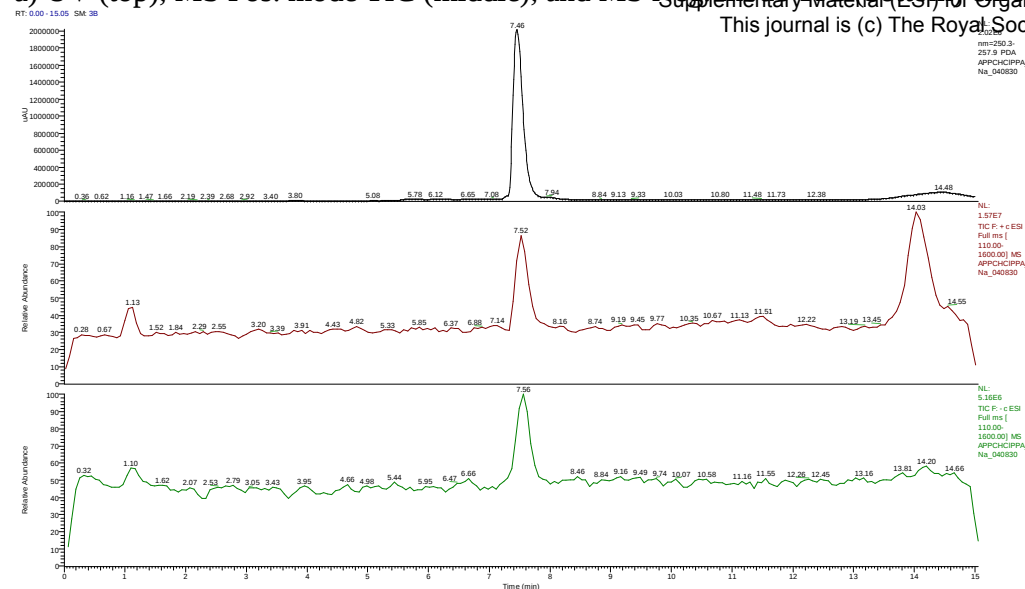
^{31}P NMR (proton coupled) of APPCHClPPA sodium salt, **3c** in D_2O :

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is (c) The Royal Society of Chemistry 2010



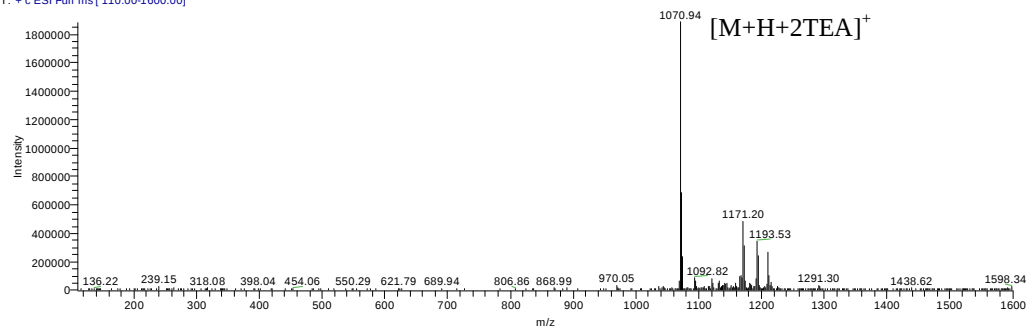
LCMS analysis of APPCHClPPA sodium salt, **3c**:

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



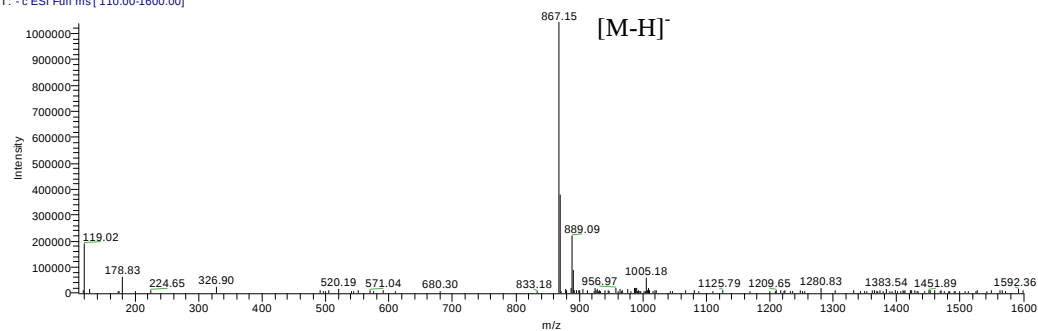
b) Positive mode MS of APPCHClPPA peak at 7.46 min

APPCHClPPA_Na_040830 #231-235 RT: 7.46-7.58 AV: 3 SB: 7.18-7.37, 7.71-7.94 NL: 1.88E6
T: + c-ESI Full ms [110.00-1600.00]



c) Negative mode MS of APPCHClPPA peak at 7.46 min

APPCHClPPA_Na_040830 #231-236 RT: 7.50-7.62 AV: 3 SB: 7.20-7.39, 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:

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Current Data Parameters
NAME 040910TBA1_APPCHFPPA_TBA
EXPNO 20
PROCNO 1

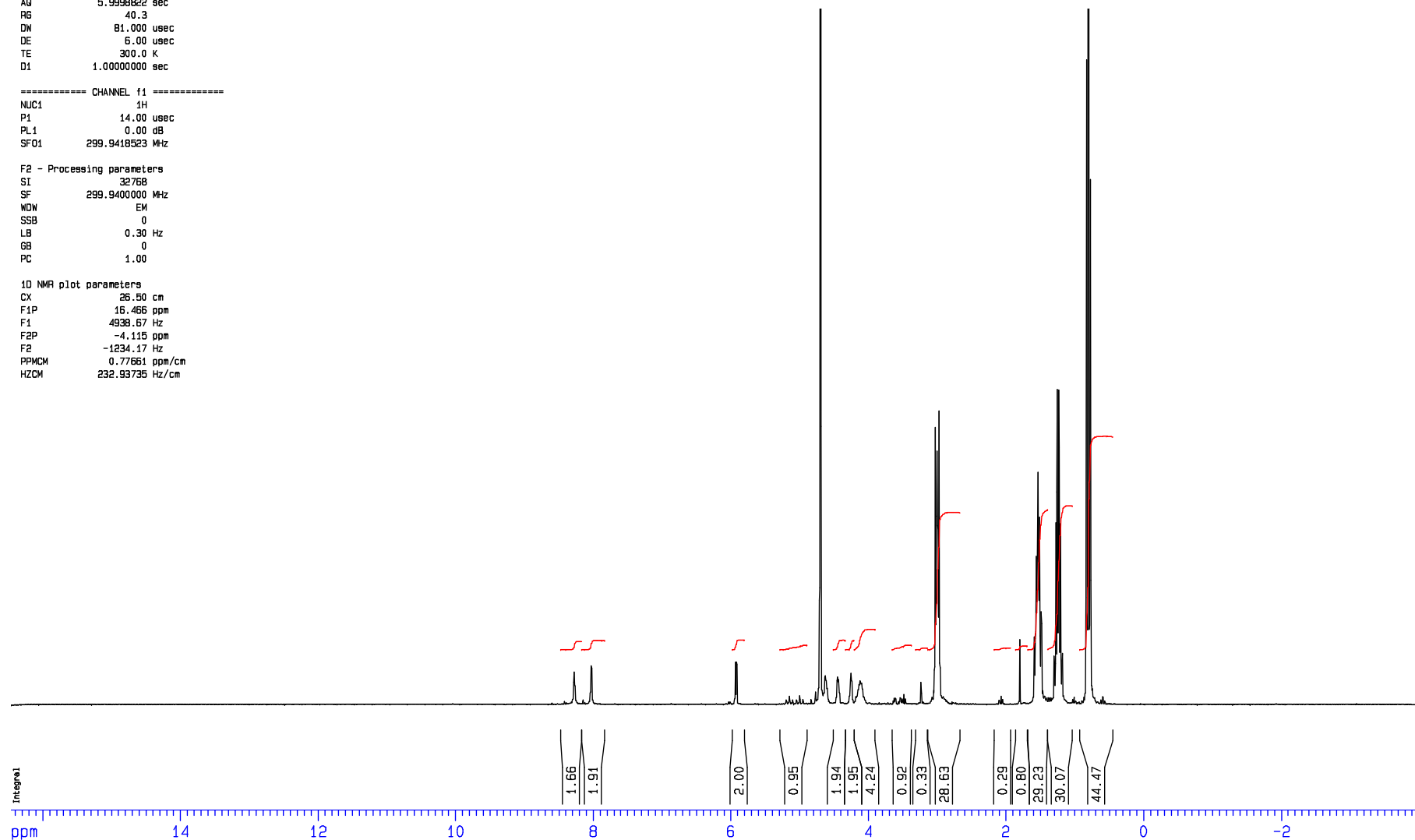
F2 - Acquisition Parameters
Date_ 20041018
Time 14.17
INSTRUM spect
PROBHD 5 mm Multinuc
PULPROG zg30
TD 74072
SOLVENT D2O
NS 8
DS 2
SWH 6172.839 Hz
FIDRES 0.083336 Hz
AQ 5.998822 sec
RG 40.3
DM 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.0000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SF01 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

¹H NMR of APPCHFPPA Bu₃N salt batch IY040910TBA1 in D₂O

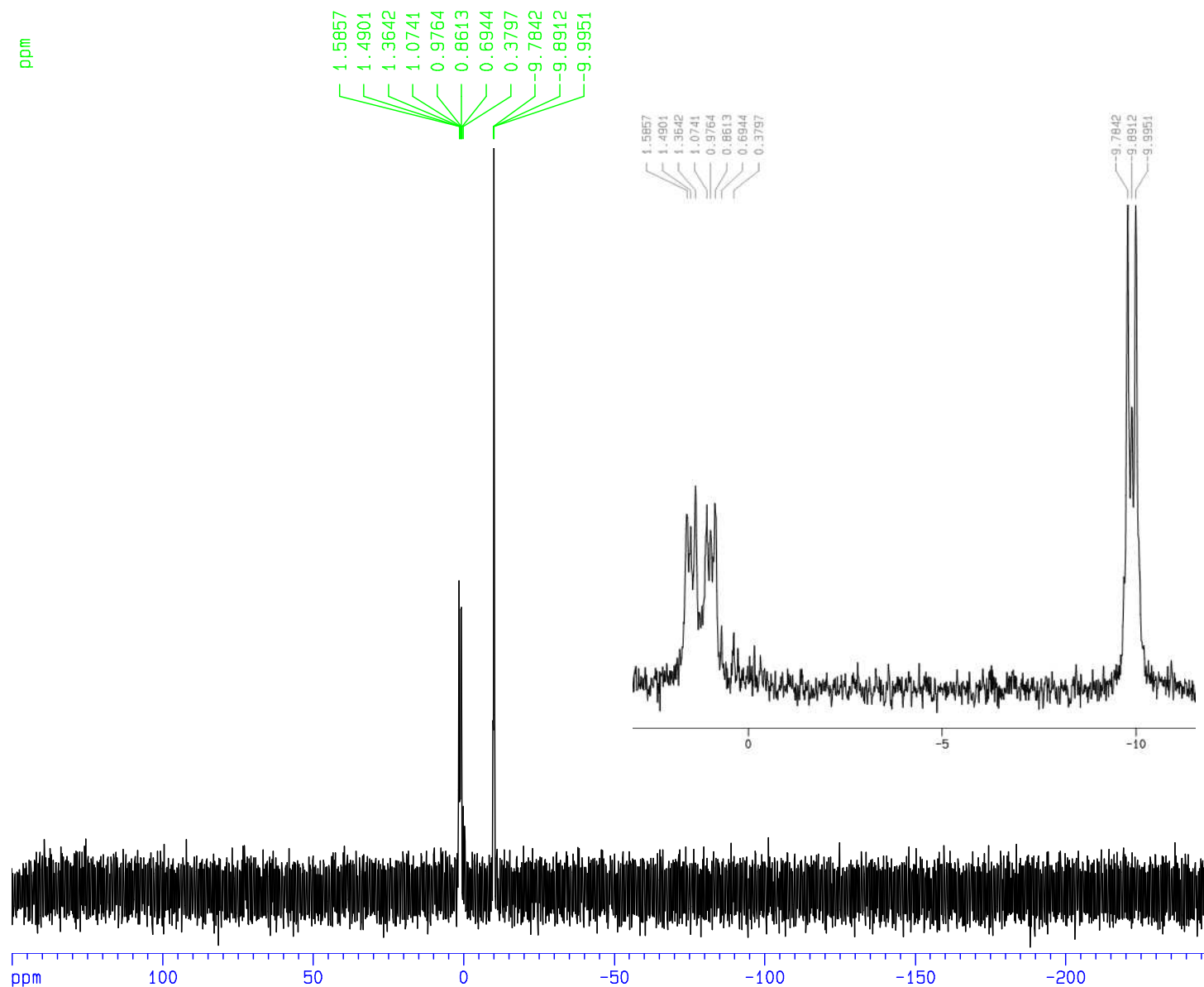


³¹P NMR (proton decoupled) of APPCHFPPA, **3e** as the tetrabutylammonium salt in D₂O:

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



Current Data Parameters
NAME 040910TBA1_APPCHFPPA_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 0.10000000 sec
d11 0.03000000 sec
d12 0.00002000 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
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SF 121.4177880 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

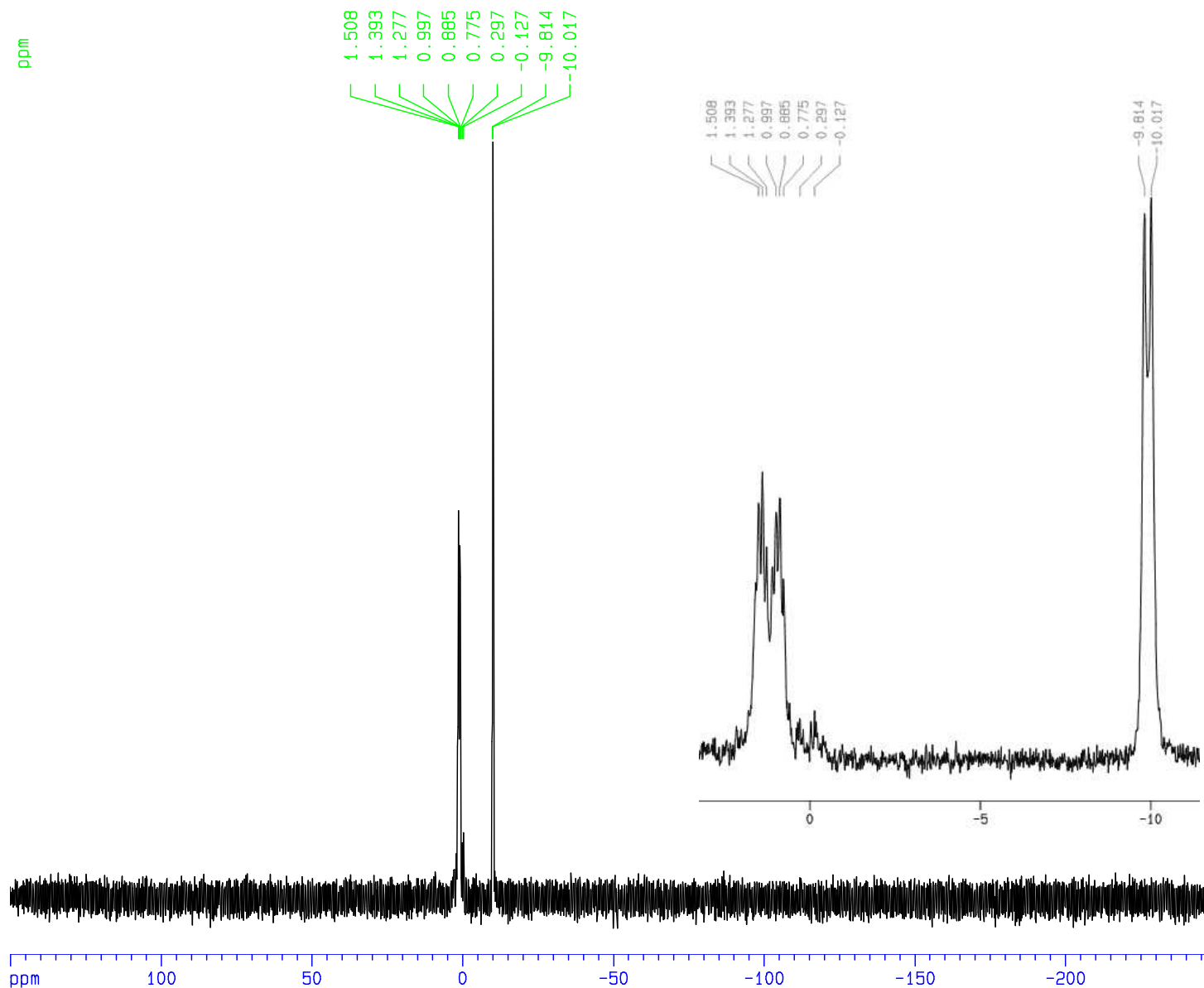
1D NMR plot parameters
CX 20.00 cm
F1P 150.387 ppm
F1 18259.60 Hz
F2P -250.393 ppm
F2 -30402.20 Hz
PPMCM 20.03899 ppm/cm
HZCM 2433.09009 Hz/cm

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

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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 0.10000000 sec

===== CHANNEL f1 =====

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

F2 - Processing parameters

SF 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

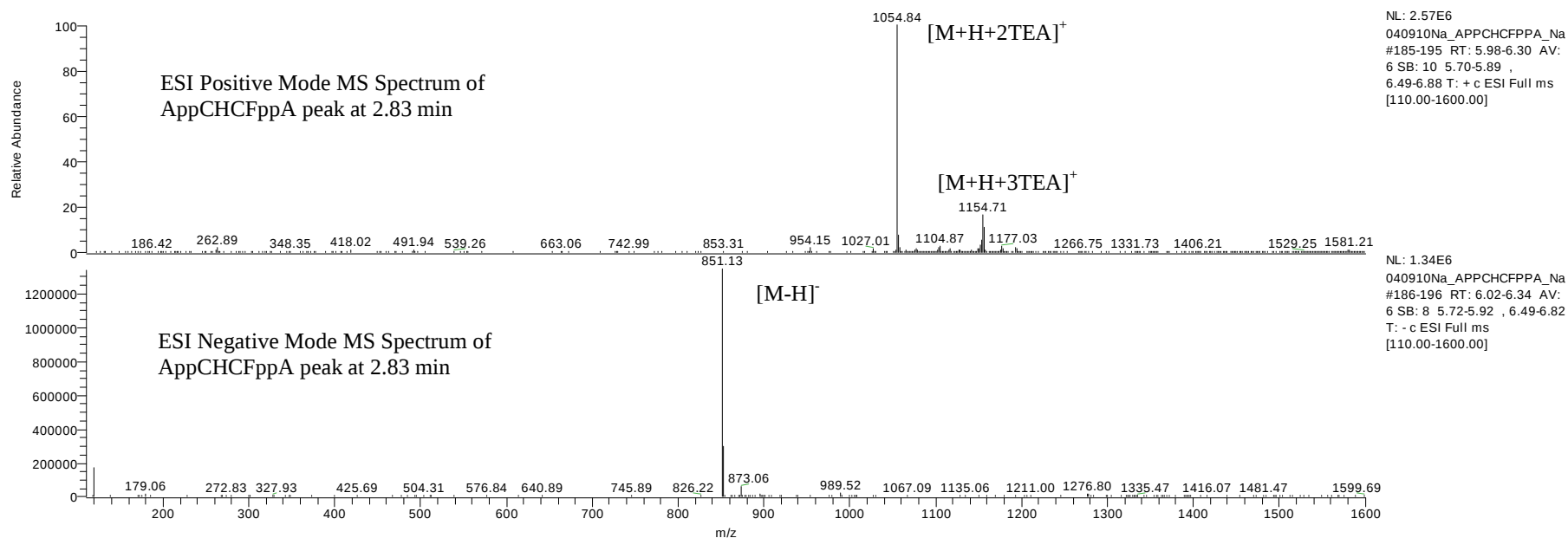
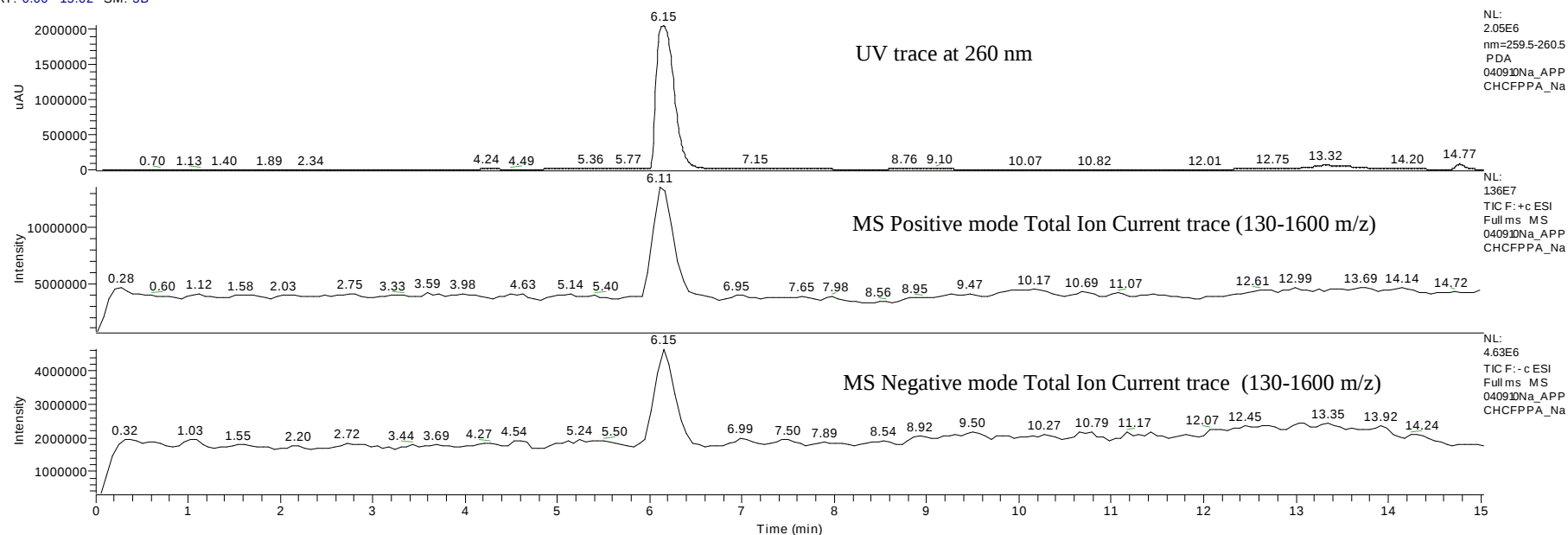
LCMS of APPCHFPPA sodium salt, **3e**:

040910Na_APPCHCFPPA_Na

9/29/2004 5:12:48 PM

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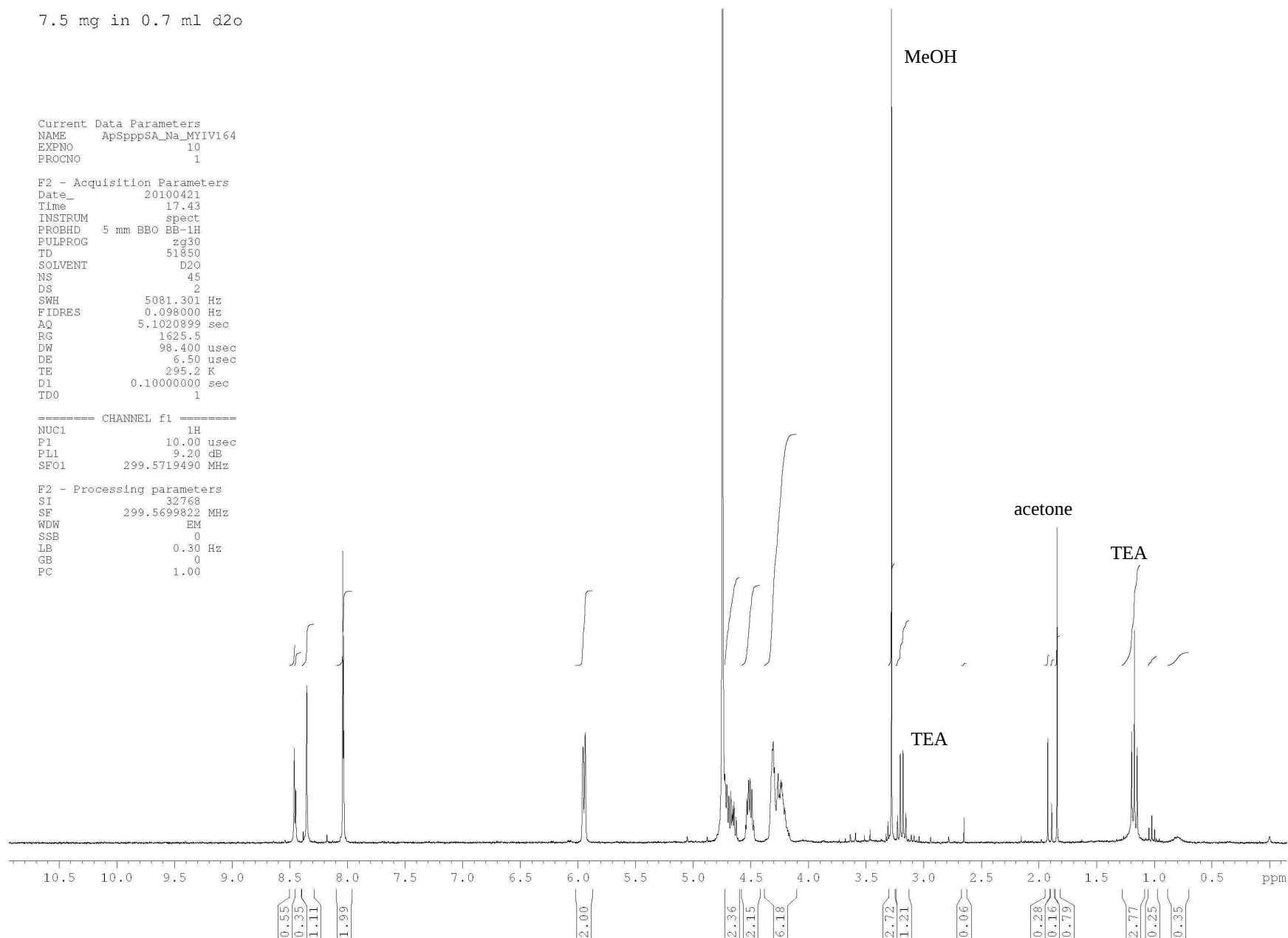
RT: 0.00 - 15.02 SM: 3B



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

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7.5 mg in 0.7 ml d₂o



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

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Current Data Parameters
NAME ApSpppSA_Na_MYIV164
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 =====

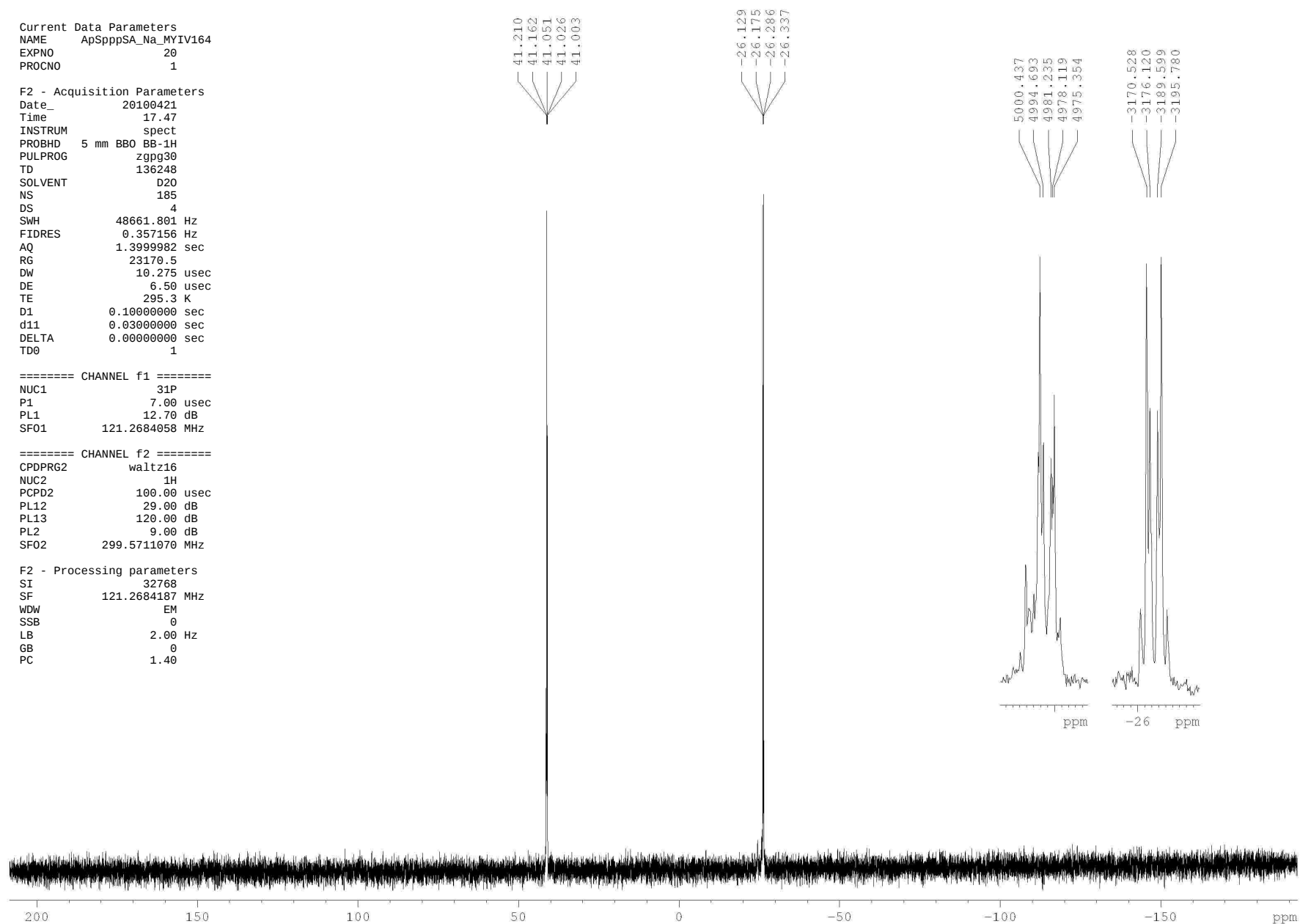
NUC1 31P
P1 7.00 usec
PL1 12.70 dB
SF01 121.2684058 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL12 29.00 dB
PL13 120.00 dB
PL2 9.00 dB
SF02 299.5711070 MHz

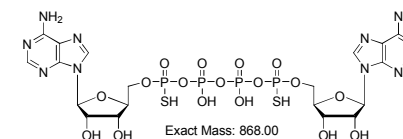
F2 - Processing parameters

SI 32768
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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:

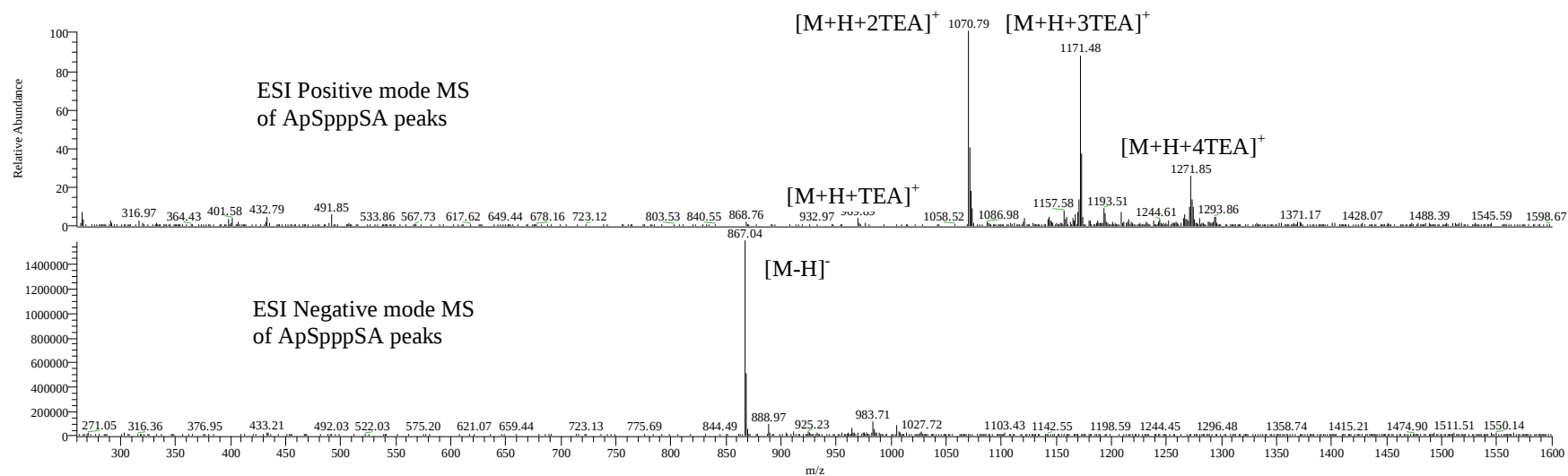
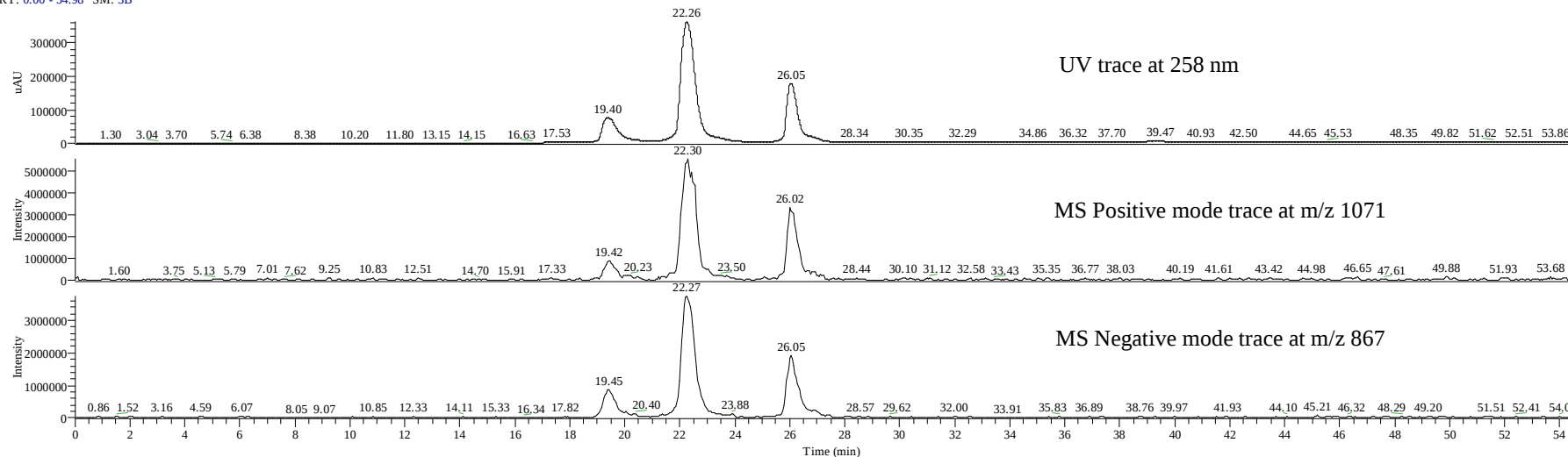
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\\90.0.0.63\c\$\...ApSpppSA_MYIV164_Na

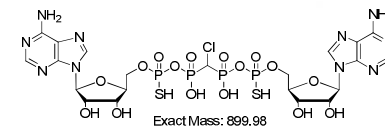
4/22/2010 6:37:19 PM

RT: 0.00 - 54.98 SM: 3B



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

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

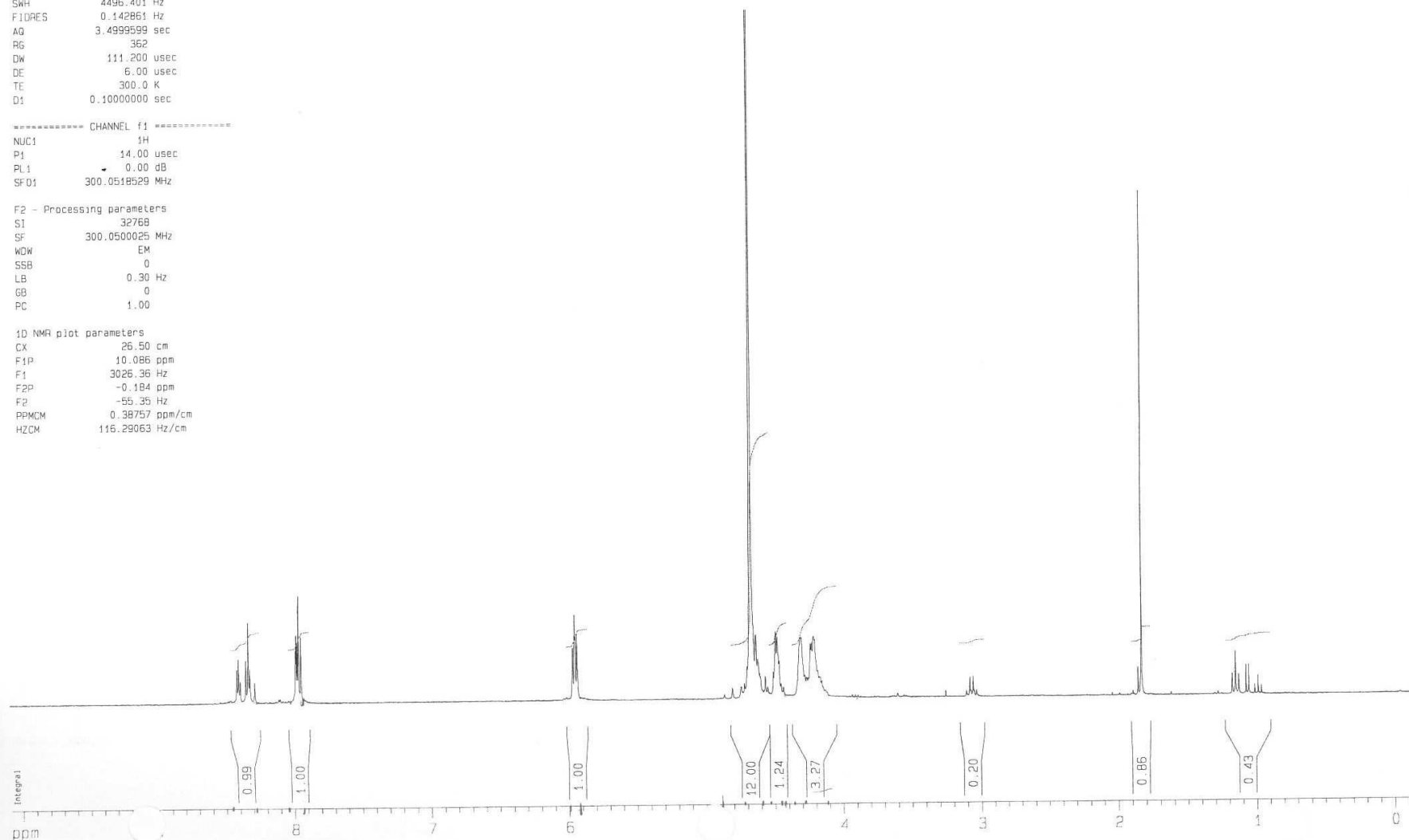
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EXPNO 10
PROCNO 1

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

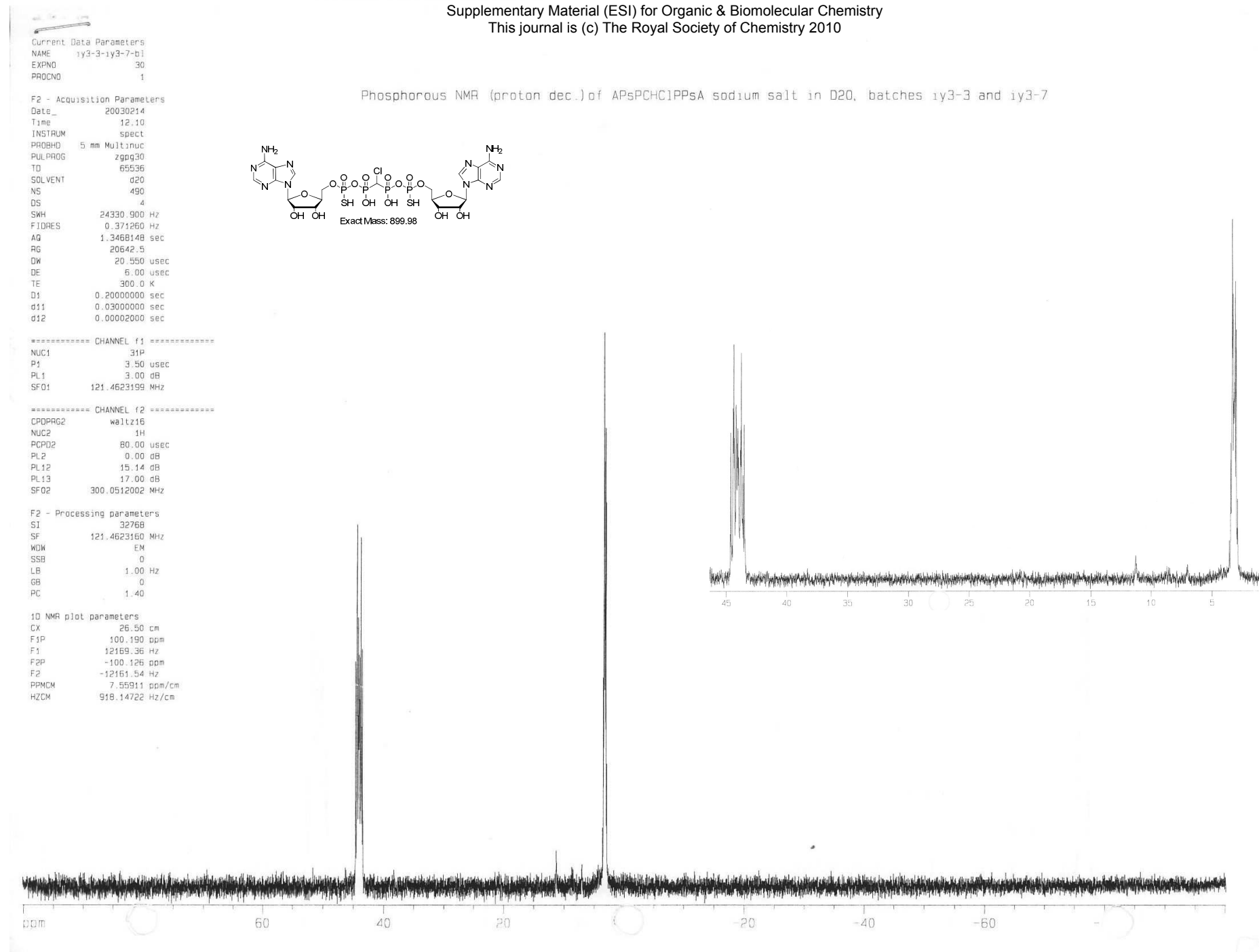
F2 - Processing parameters
S1 32768
SF 300.0500025 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D 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



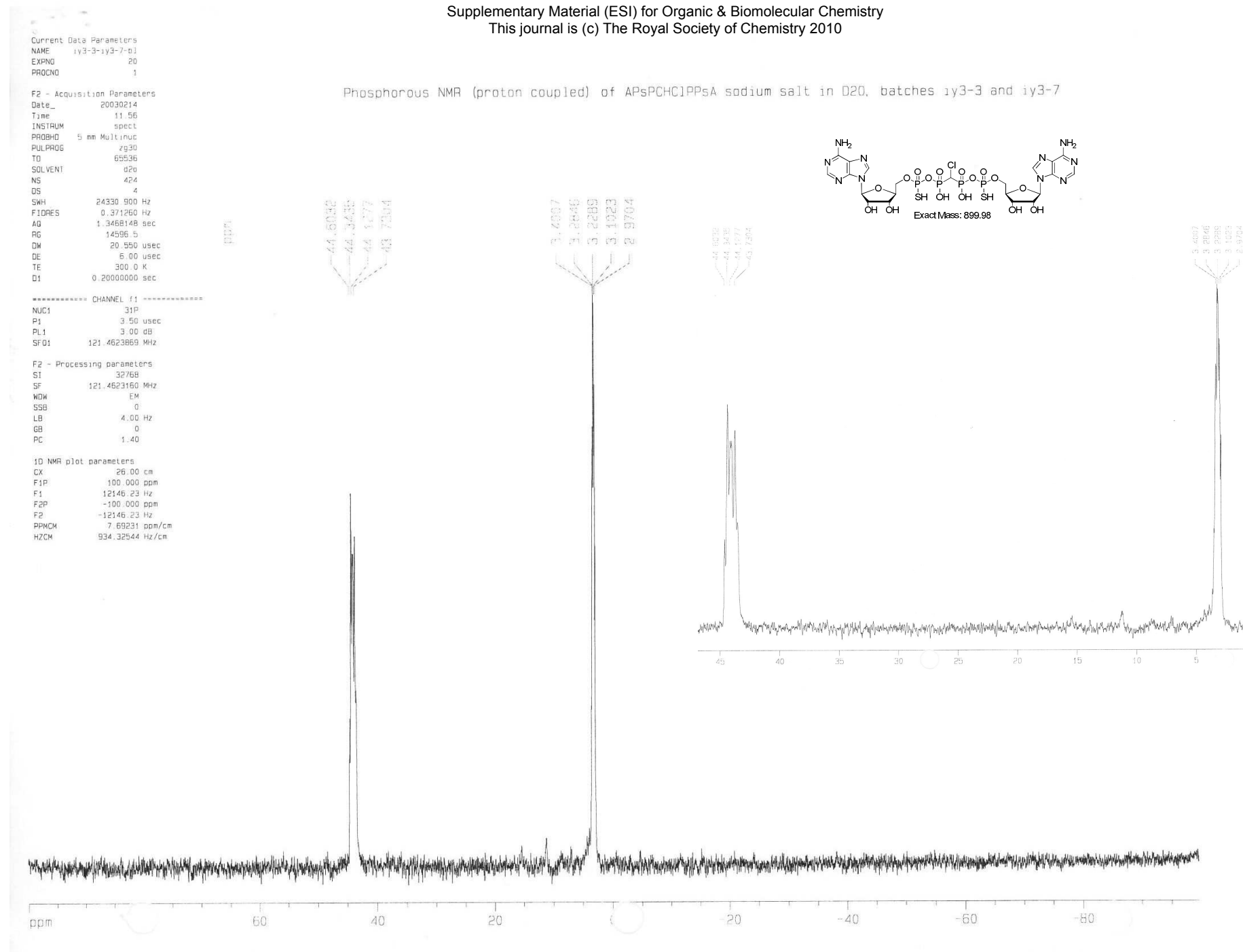
³¹P (proton decoupled) NMR spectrum of AP(S)PCHCIPP(S)A sodium salt, **3d** in D₂O:

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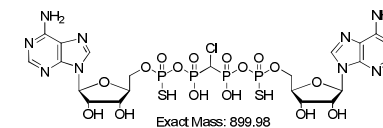
³¹P (proton coupled) NMR spectrum of AP(S)PCHClPP(S)A sodium salt, **3d** in D₂O:

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

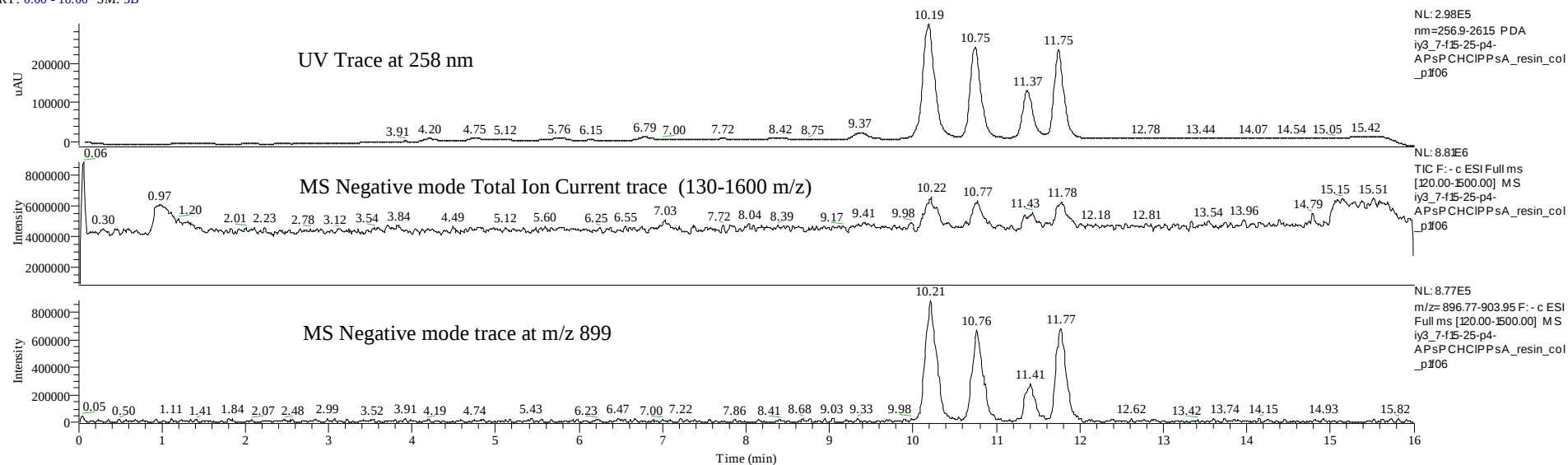
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iy3_7-f15-25-p4-APsPCHClPPsA_resin_co...
1 ul of 1mM sol in 20mM TEAA

3/6/2007 11:50:49 AM

RT: 0.00 - 16.00 SM: 3B



iy3_7-f15-25-p4-APsPCHClPPsA_resin_col_p106 #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]

