Electronic Supplementary Information

for

Molybdenum Complex Bearing Tetraphosphine Ligand as a Precursor for Heterobimetallic Complexes

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Additional comments on crystallography

For [CpMo(κ^4-**P4**)][OTf]·2.7CH_2Cl_2 (**4**[OTf]·2.7CH_2Cl_2), one of three CH_2Cl_2 solvate in the asymmetric unit was packed with disordered orientations, the major part of which is composed of Cl5–C55–Cl6. Because the distance between Cl5 and its symmetrically equivalent Cl5* is shorter than the sum of the van der Waals radii, occupancy of this part is set at the maximum value of 0.50. The minor orientation is defined by Cl7–C56–Cl8, and its occupancy has been determined to be 0.20 so as to have the U_{eq} values comparable to the major disorder part. These disordered C atoms as well as the Cl atoms of the minor part are refined isotropically, and hydrogen atoms are not placed for both parts.

In the asymmetric unit of [CpMo(κ^4-**P4**)][Cl]·0.78DMF·0.22Et_2O (**4**[Cl]·0.78DMF·0.22Et_2O), the solvating molecules were found at one site and were refined as DMF (O1, N1, C52–54) and Et_2O (O2, C55–58) occupying with 0.78 and 0.22 probabilities. Hydrogen atoms of these molecules are not included in the refinement.

The crystal of [CpMoH(μ-**P4**-1κ^3:2κ)$RuCl_2$(η^6-C_6Me_6)]·3CH_2Cl_2 (**6**·3CH_2Cl_2) contains three CH_2Cl_2 molecules in the asymmetric unit. One of them has been refined free from disorders (Cl3–C64–Cl4), while the second one orients in two different directions (Cl5–C65–Cl6 and Cl7–C65–Cl8 in 80% and 20% probabilities). The third molecule has been modeled with three orientations: Cl9–C66–Cl10 (50%), Cl9–C66–Cl11 (40%), and Cl12–C67–Cl13 (10%, refined isotropically with restraints of C–Cl bond distances). Hydrogen atoms of the disordered CH_2Cl_2 are not included in the refinement except for the major component of the second molecule (H69 and H70 with 80% occupancies for Cl5–C65–Cl6).

There are two independent complex molecules in the asymmetric unit of [CpMoCl(μ-**P4**-1κ^3:2κ)$RuCl_2$(η^6-C_6Me_6)]·2.5CH_2Cl_2 (**11**·2.5CH_2Cl_2). Solvating CH_2Cl_2 molecules are found at crystallographically independent five positions, and details of their treatments are as follows. Cl7–C64–Cl8 (100% occupancy) for site 1; Cl9–C65–Cl11 (57.5%), Cl9–C65–Cl12 (25%), and Cl10–C65–Cl12 (17.5%) for site 2; Cl13–C66–Cl15 (70%) and Cl14–C66–Cl16 (30%) for site 3; Cl17–C67–Cl18 (57.5%) and Cl19–C68–Cl20 (42.5%) for site 4; Cl21–C69–Cl22 (85%) and Cl23–C70–Cl24 (15%, distances and angle restrained) for site 5. Carbon atoms with occupancies less than 1.0 and Cl atoms with 0.15 occupancies have been refined isotropically, and H atoms are not added for the disordered molecules.

The CH_2Cl_2 molecule in [CpMo(μ-H){μ-(**P4**$^{-Ph}$)-1κ^3:2κ^2)PdCl]·0.75CH_2Cl_2 (**12**·0.75CH_2Cl_2) has shown no signs of orientational disorders, although refinement of this molecule with 100% occupancy has resulted in quite large U_{eq} values. Therefore, this site is regarded to be partially occupied by CH_2Cl_2, and reasonable U_{eq} values have been obtained with the occupancy at 75% level.

Table S-1 Comparison of bond distances (Å) and angles (deg) in the dinuclear complexes.[a]

	2 (X = H)[b]	**6** (X = H, M = Ru)	**7** (X = H, M = Ir)	**11** (X = Cl, M = Ru)	
				molecule 1	molecule 2
Mo–P(1)	2.376(1)	2.3846(11)	2.3825(9)	2.450(2)	2.447(2)
Mo–P(2)	2.362(1)	2.3538(9)	2.3643(9)	2.384(2)	2.390(2)
Mo–P(3)	2.360(1)	2.3875(9)	2.3767(9)	2.443(2)	2.447(2)
Mo–Cnt	2.003(6)	1.998(2)	1.999(2)	1.990(3)	1.999(3)
Mo–X	1.71(4)	1.56	1.62	2.544(2)	2.552(2)
P(1)–Mo–P(2)	78.29(3)	77.56(4)	77.27(3)	76.96(6)	76.70(6)
P(1)–Mo–P(3)	110.33(3)	109.26(3)	109.17(3)	120.05(6)	119.89(6)
P(2)–Mo–P(3)	78.69(3)	78.70(3)	78.78(4)	77.61(6)	77.55(6)
P(1)–Mo–X	73(2)	71	69	79.06(5)	78.83(6)
P(2)–Mo–X	128(2)	127	125	135.00(6)	135.78(5)
P(3)–Mo–X	73(2)	73	73	82.39(5)	83.67(5)
Cnt–Mo–P(1)	125.2(1)	125.02(6)	125.84(7)	118.85(10)	119.3(1)
Cnt–Mo–P(2)	122.6(1)	121.63(5)	123.40(7)	115.02(8)	114.53(9)
Cnt–Mo–P(3)	122.7(1)	124.29(6)	123.10(7)	121.09(9)	120.79(10)
Cnt–Mo–X	110(1)	111	112	109.86(8)	109.51(8)
M–Cl(1)		2.4196(10)	2.3881(10)	2.421(2)	2.415(2)
M–Cl(2)		2.3985(8)	2.4105(9)	2.430(2)	2.422(2)
M–P(4)		2.3427(9)	2.3095(8)	2.376(2)	2.372(2)
Cl(1)–M–Cl(2)		86.61(3)	88.21(3)	87.53(6)	86.53(7)
Cl(1)–M–P(4)		87.41(3)	86.74(3)	86.44(5)	85.62(5)
Cl(2)–M–P(4)		86.52(3)	90.45(3)	86.21(5)	87.12(6)
M–Cnt		1.728(2)	1.829(2)	1.724(3)	1.716(3)
Cnt–M–P(4)		134.17(6)	132.26(6)	134.28(9)	134.11(9)
Cnt–M–Cl(1)		124.12(6)	123.87(6)	122.79(9)	123.91(9)
Cnt–M–Cl(2)		123.63(6)	122.54(6)	125.3(1)	124.85(11)

[a] Cnt is the center of gravity of η^5-Cp or η^6-arene ring. [b] From reference 14. Average of two independent molecules.

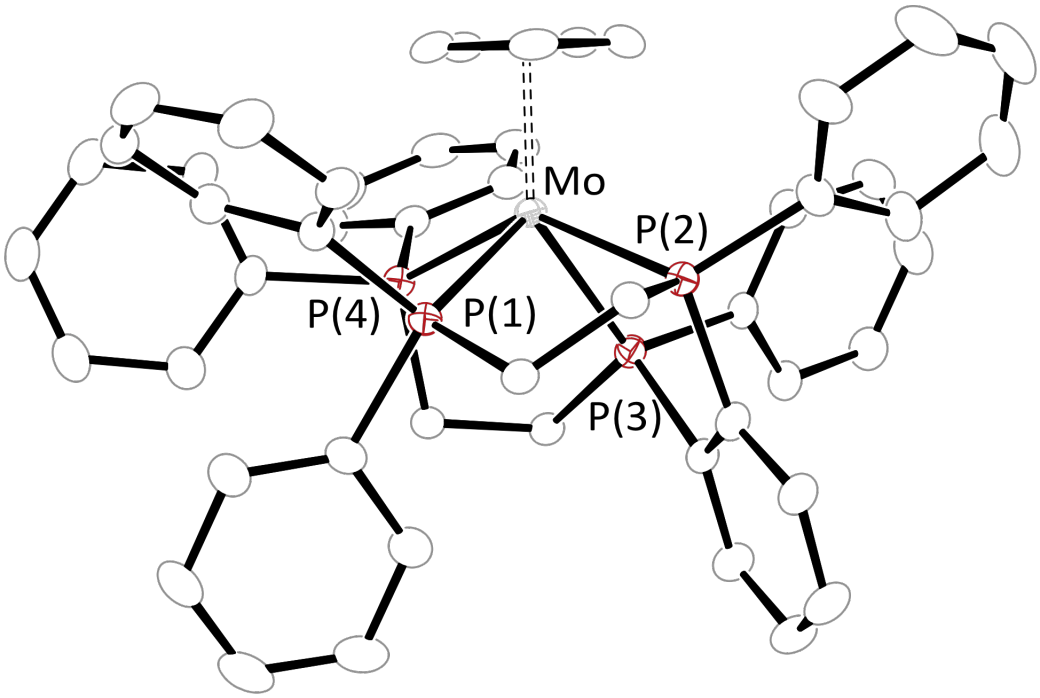


Fig. S-1 The molecular structure of the cationic part of [CpMo(κ^4-**P4**)][Cl]·0.78DMF·0.22Et_2O (**4**Cl·0.78DMF·0.22Et_2O) depicting the view from the axis parallel to the Cp ring. Hydrogen atoms are omitted for clarity. The Mo–Cnt distance is 2.001(2) Å.

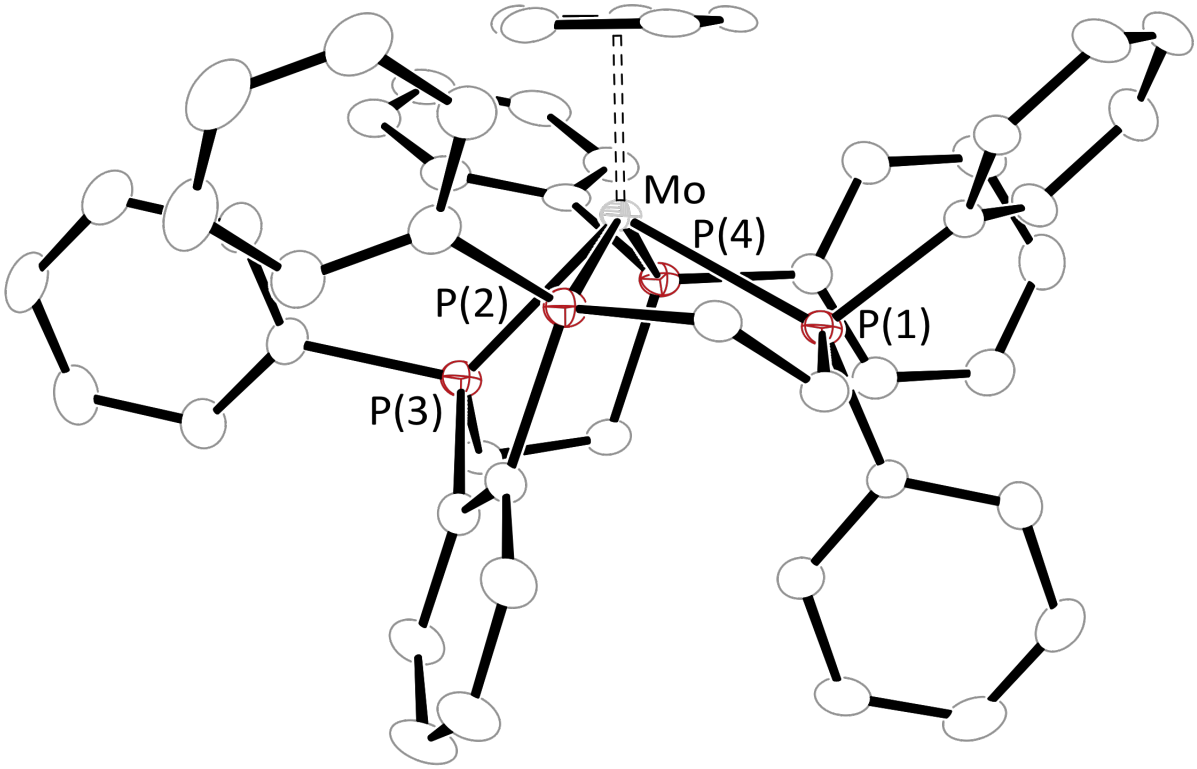


Fig. S-2 The molecular structure of the cationic part of [CpMo(κ^4-**P4**)][OTf]·2.7CH_2Cl_2 (**4**[OTf]·2.7CH_2Cl_2) showing thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Mo–P(1), 2.452(1); Mo–P(2), 2.450(1); Mo–P(3), 2.429(1); Mo–P(4), 2.487(1); Mo–Cnt, 2.001(2); P(1)–Mo–P(2), 75.82(4); P(1)–Mo–P(3), 107.13(4); P(1)–Mo–P(4), 89.74(4); P(2)–Mo–P(3), 75.16(4); P(2)–Mo–P(4), 141.60(4); P(3)–Mo–P(4), 75.57(4); Cnt–Mo–P(1), 118.63(6); Cnt–Mo–P(2), 110.18(7); Cnt–Mo–P(3), 133.96(6); Cnt–Mo–P(4), 107.98(6), where Cnt is the centroid of the Cp ligand. Crystallographic data: $C_{54.7}H_{52.4}Cl_{5.4}F_3MoO_3P_4S$, M = 1258.15, space group $P2_1/c$ (no. 14), a = 13.665(5), b = 19.171(6), c = 21.184(7) Å, β = 96.763(2)°, V = 5511(4) Å^3, Z = 4, μ = 0.707 mm^{-1}, transmn factor = 0.540—0.868, 43149 reflections collected, 12571 independent, R_{int} = 0.0735, the final R_1 ($I > 2\sigma(I)$) = 0.0577 and $_wR_2$ (all data) = 0.1717 on 716 parameters.

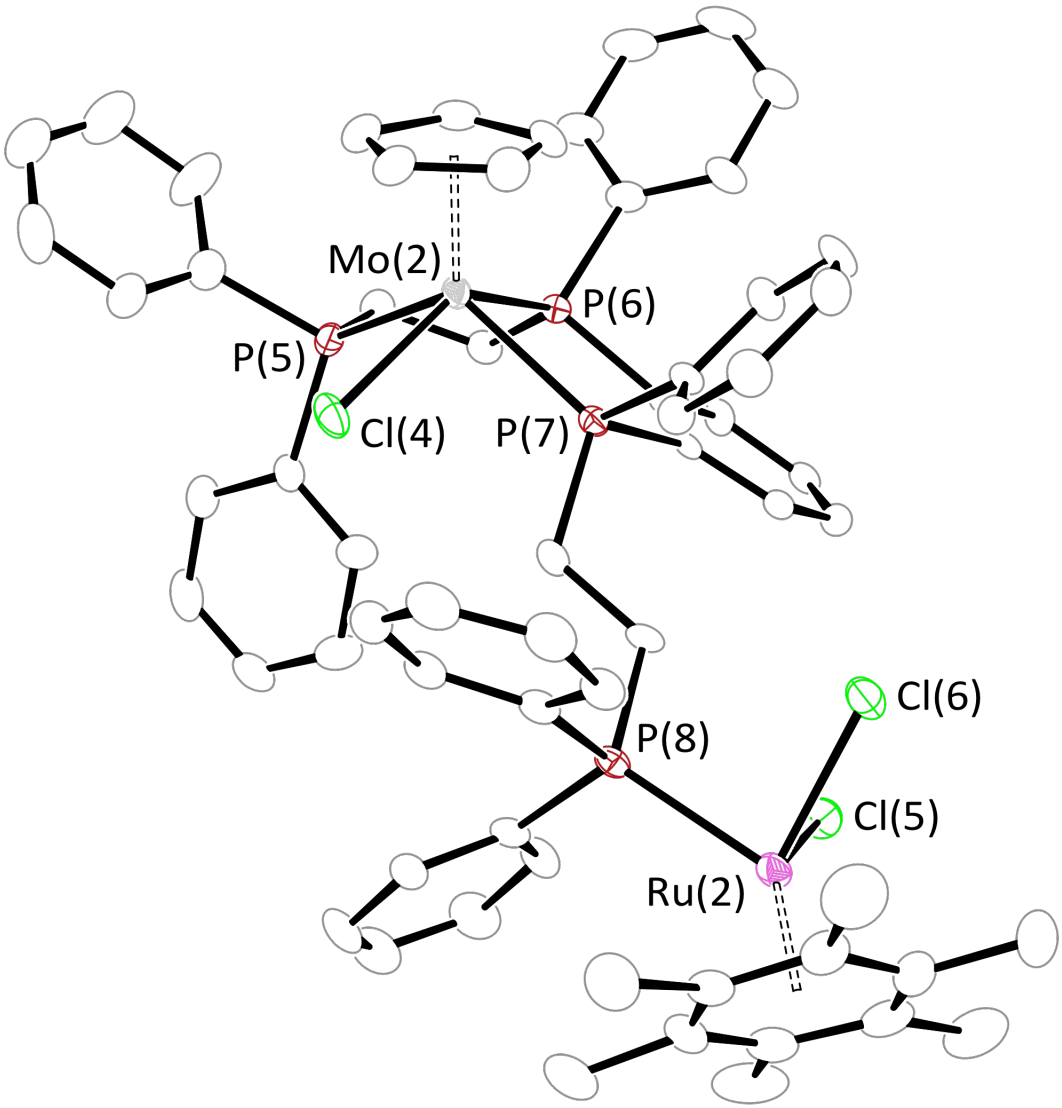


Fig. S-3 The crystal structure of the second independent molecule in the asymmetric unit of [CpMoCl(μ-**P4**-1κ^3:2κ)RuCl$_2$(η^6-C$_6$Me$_6$)]·2.5CH$_2$Cl$_2$ (**11**·2.5CH$_2$Cl$_2$).

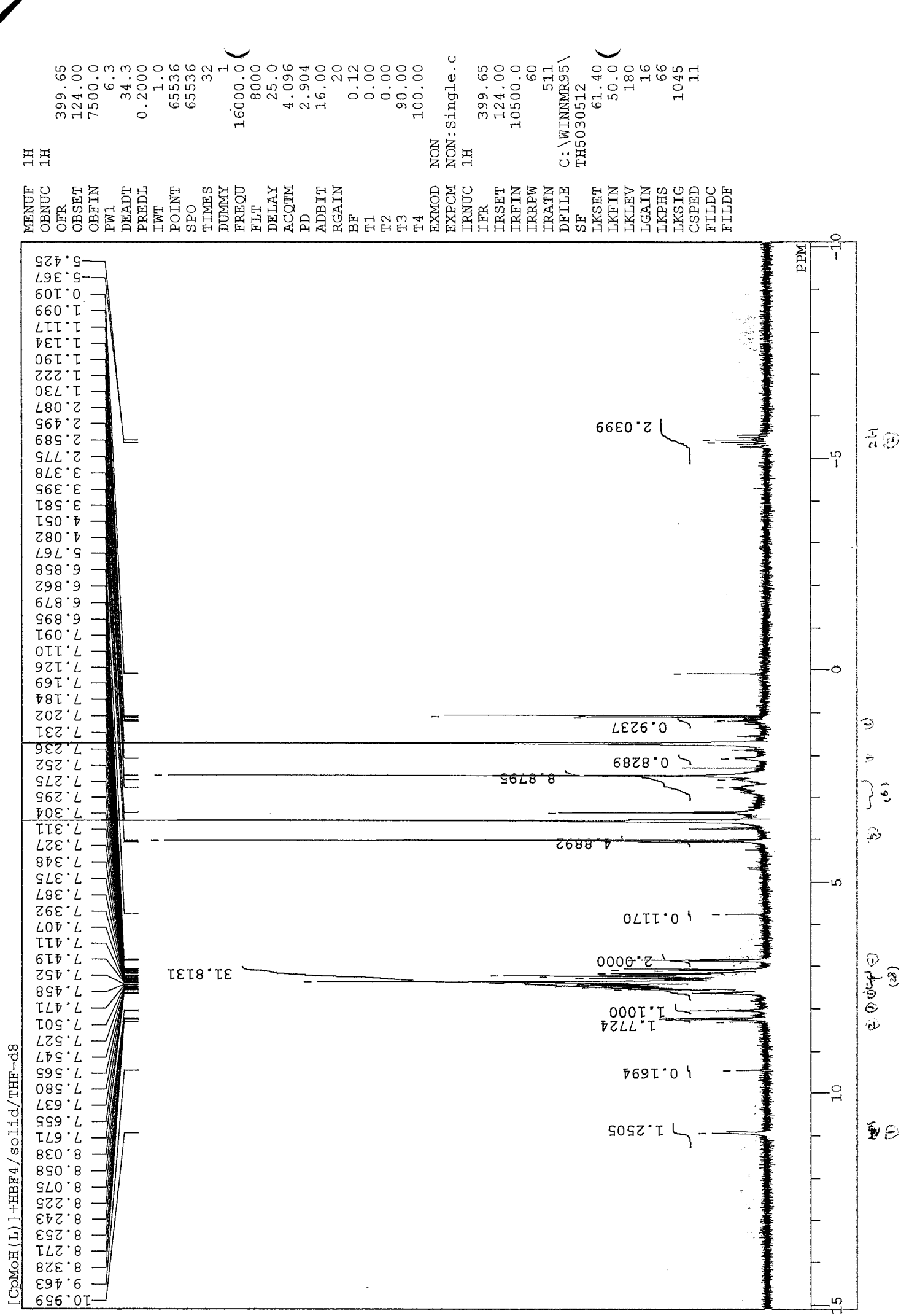


Fig. S-4 1H NMR spectrum of [CpMoH2(κ3-P4)][BF4] (3[BF4]) at +20 °C (sample before recrystallization)

J0.593-3

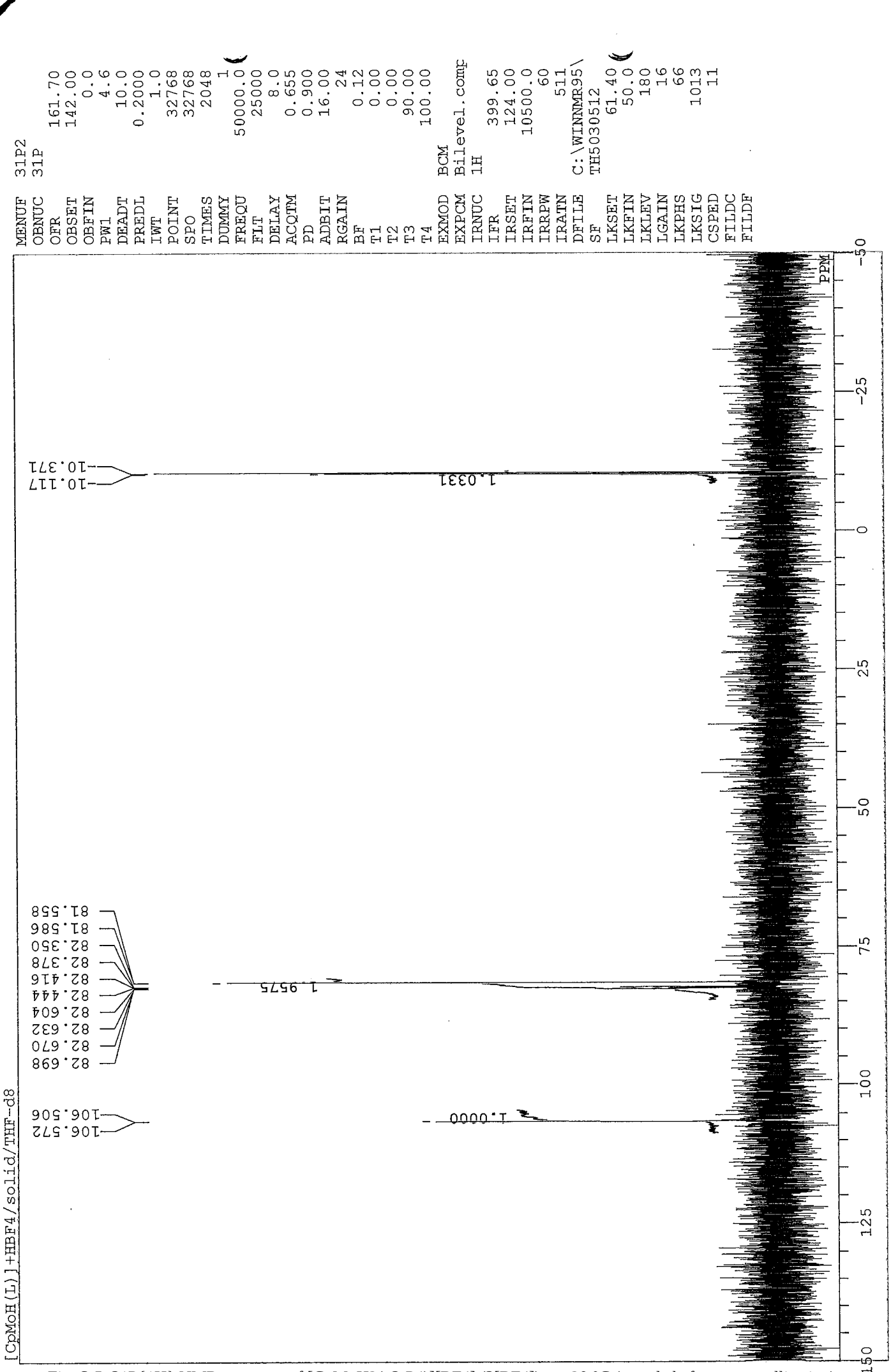
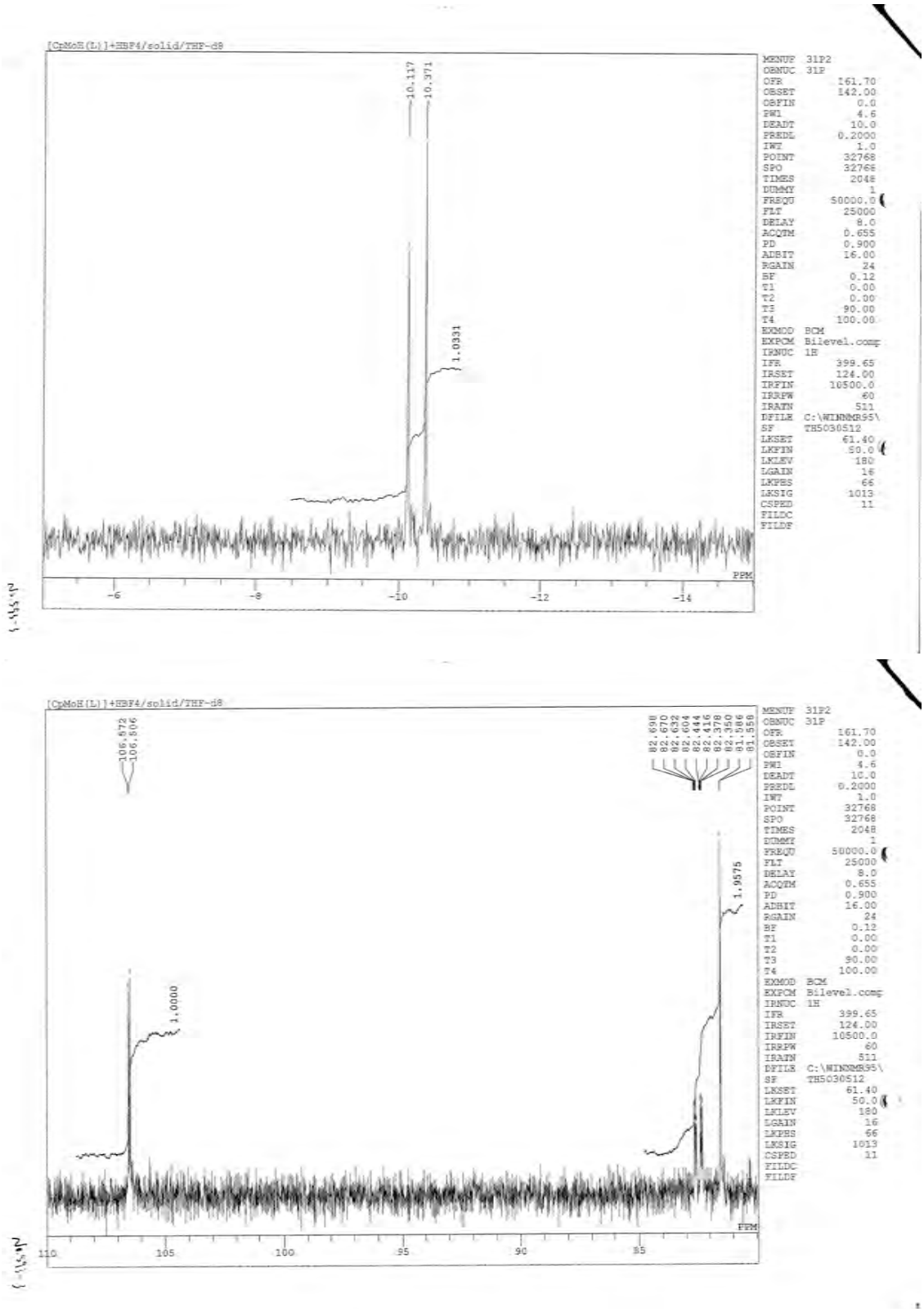


Fig. S-5 31P{1H} NMR spectrum of [CpMoH2(κ3-P4)][BF4] (3[BF4]) at +20 °C (sample before recrystallization)

No.593-3



$^{31}P\{^{1}H\}$ NMR spectrum of $[CpMoH_2(\kappa^3\text{-}\mathbf{P4})][BF_4]$ (**3**$[BF_4]$) THF-d_8, 20 °C

Fig. S-5(2) 31P{1H} NMR spectrum of [CpMoH2(κ3-P4)][BF4] (3[BF4]) at +20 °C (sample before recrystallization)

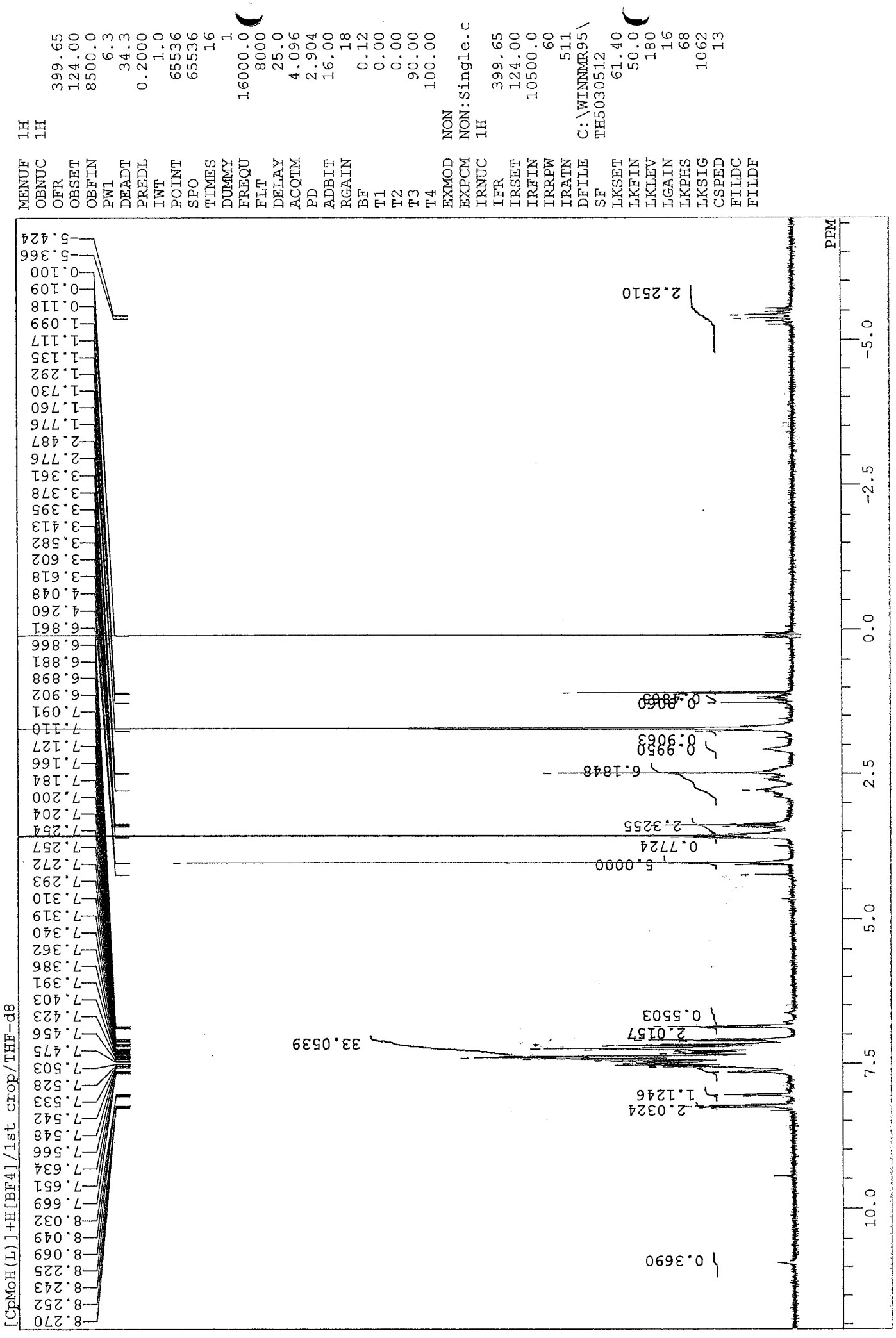


Fig. S-6 1H NMR spectrum of [CpMoH2(κ3-P4)][BF4] (3[BF4]) at +20 °C (recrystallized sample)

No.593-4

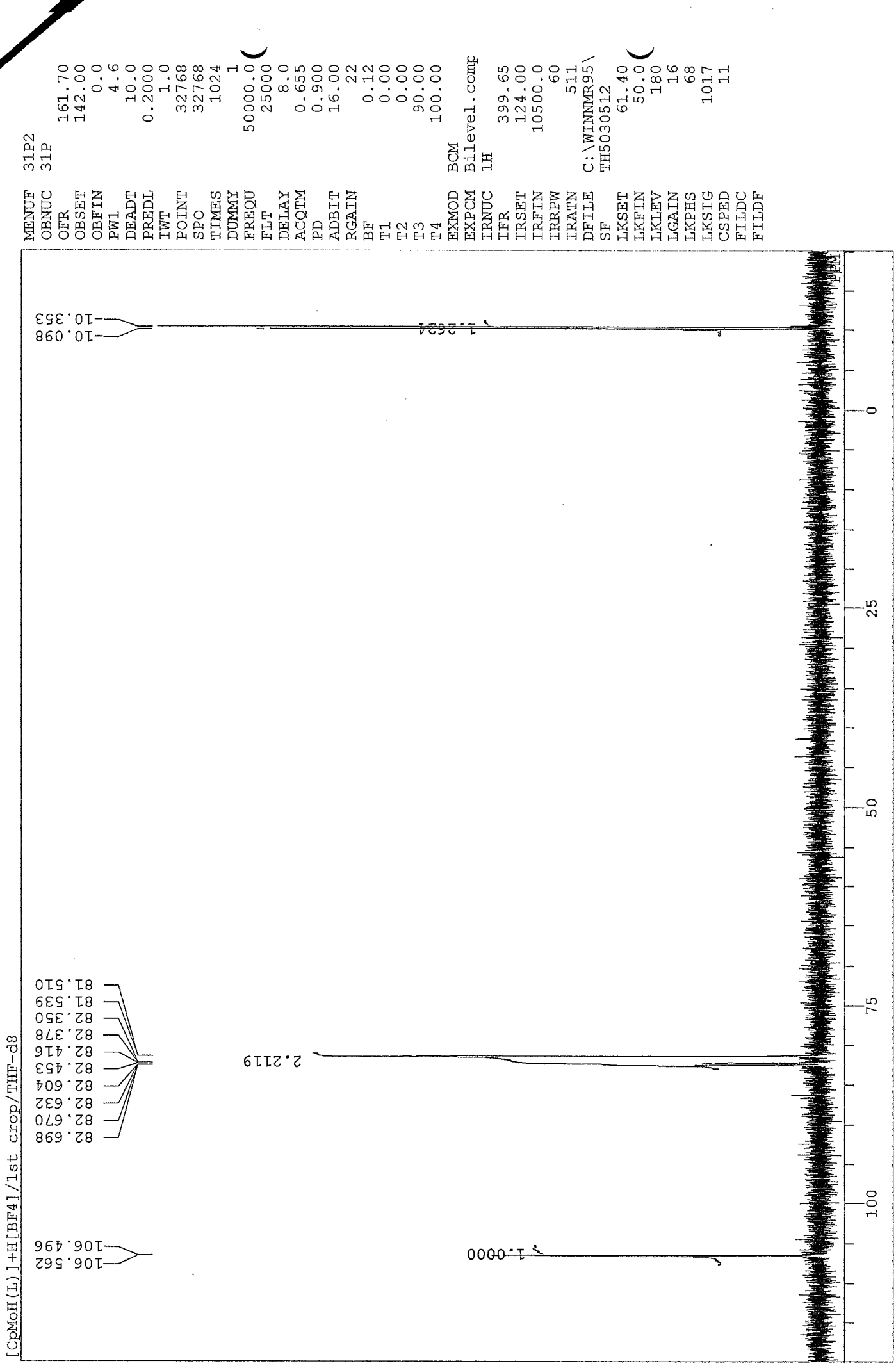


Fig. S-7 31P{1H} NMR spectrum of [CpMoH2(κ3-P4)][BF4] (3[BF4]) at +20 °C (recrystallized sample)

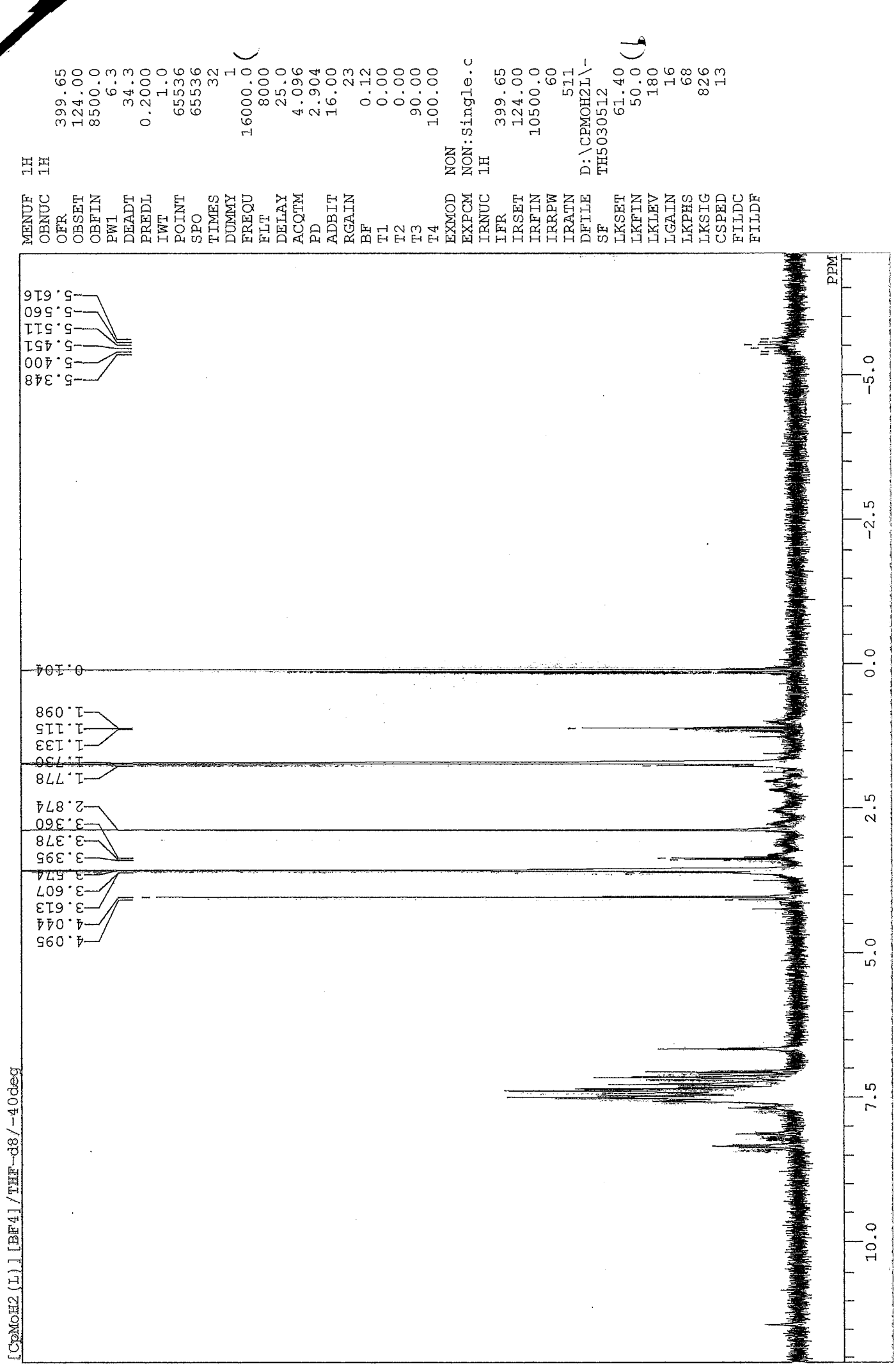


Fig. S-8 1H NMR spectrum of [CpMoH2(κ3-P4)][BF4] (3[BF4]) at -40 °C (recrystallized sample)

Zo.593-4

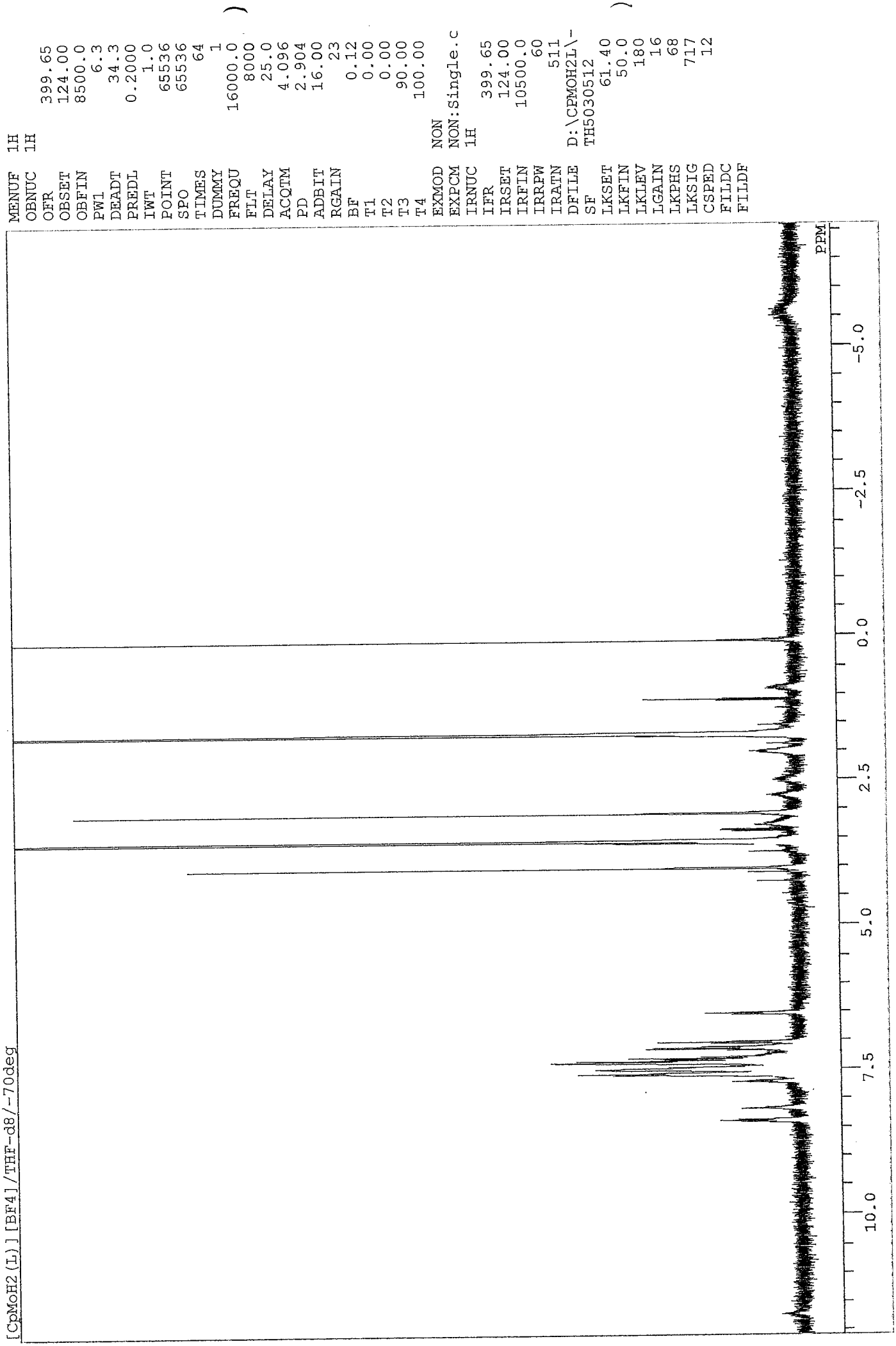


Fig. S-9 1H NMR spectrum of [CpMoH2(κ3-P4)][BF4] (3[BF4]) at -70 °C (recrystallized sample)

No.593-4

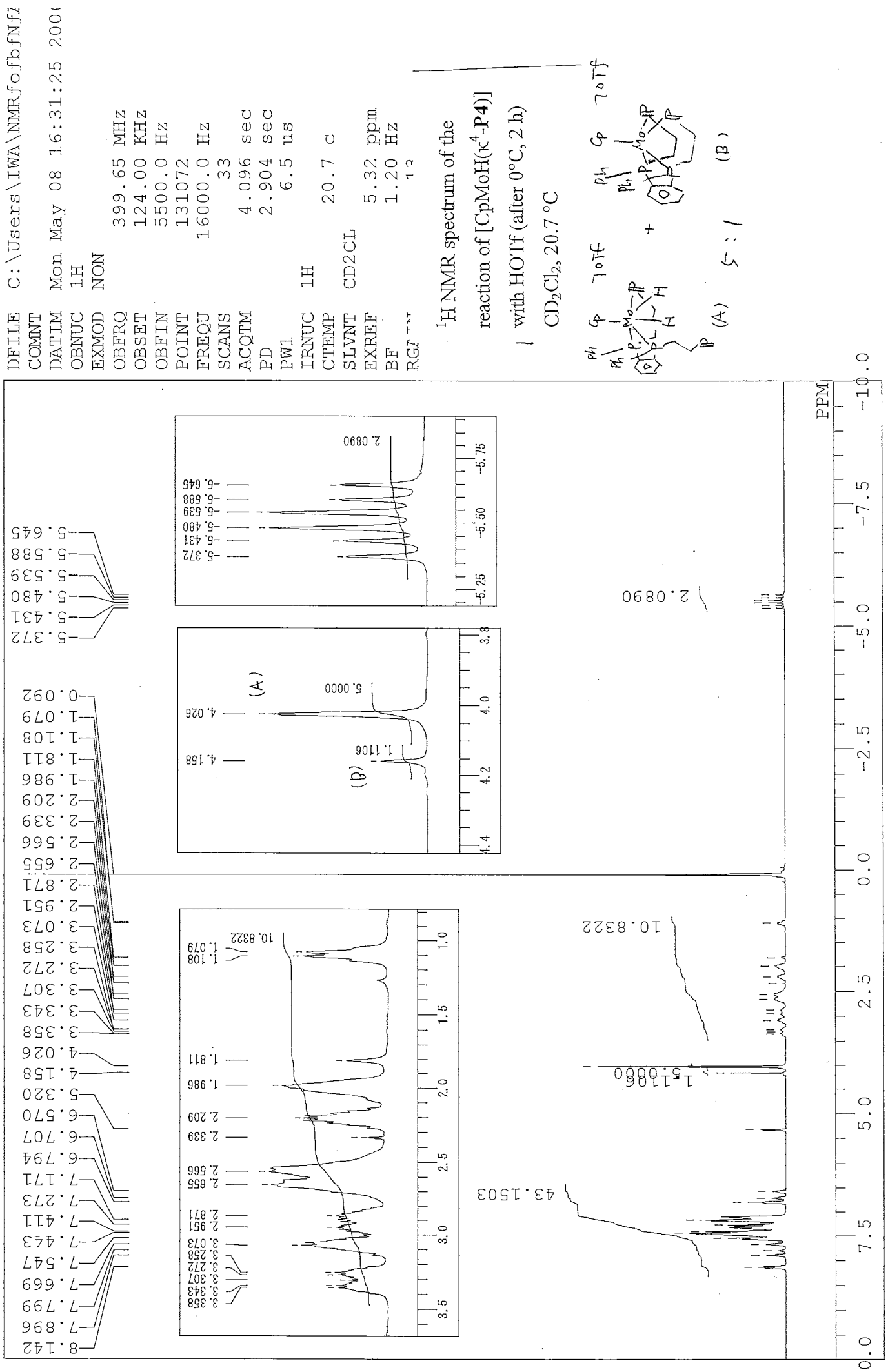
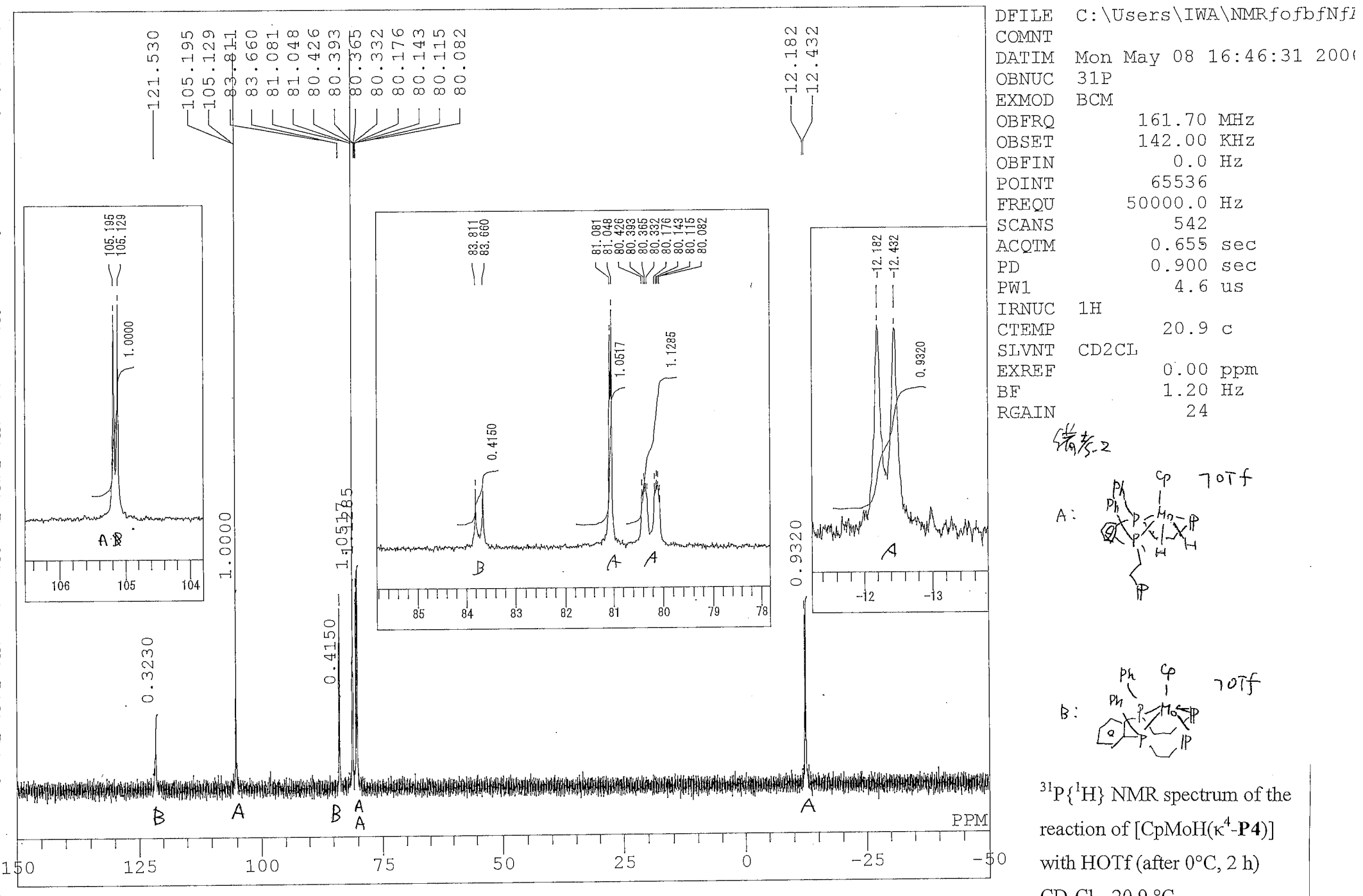
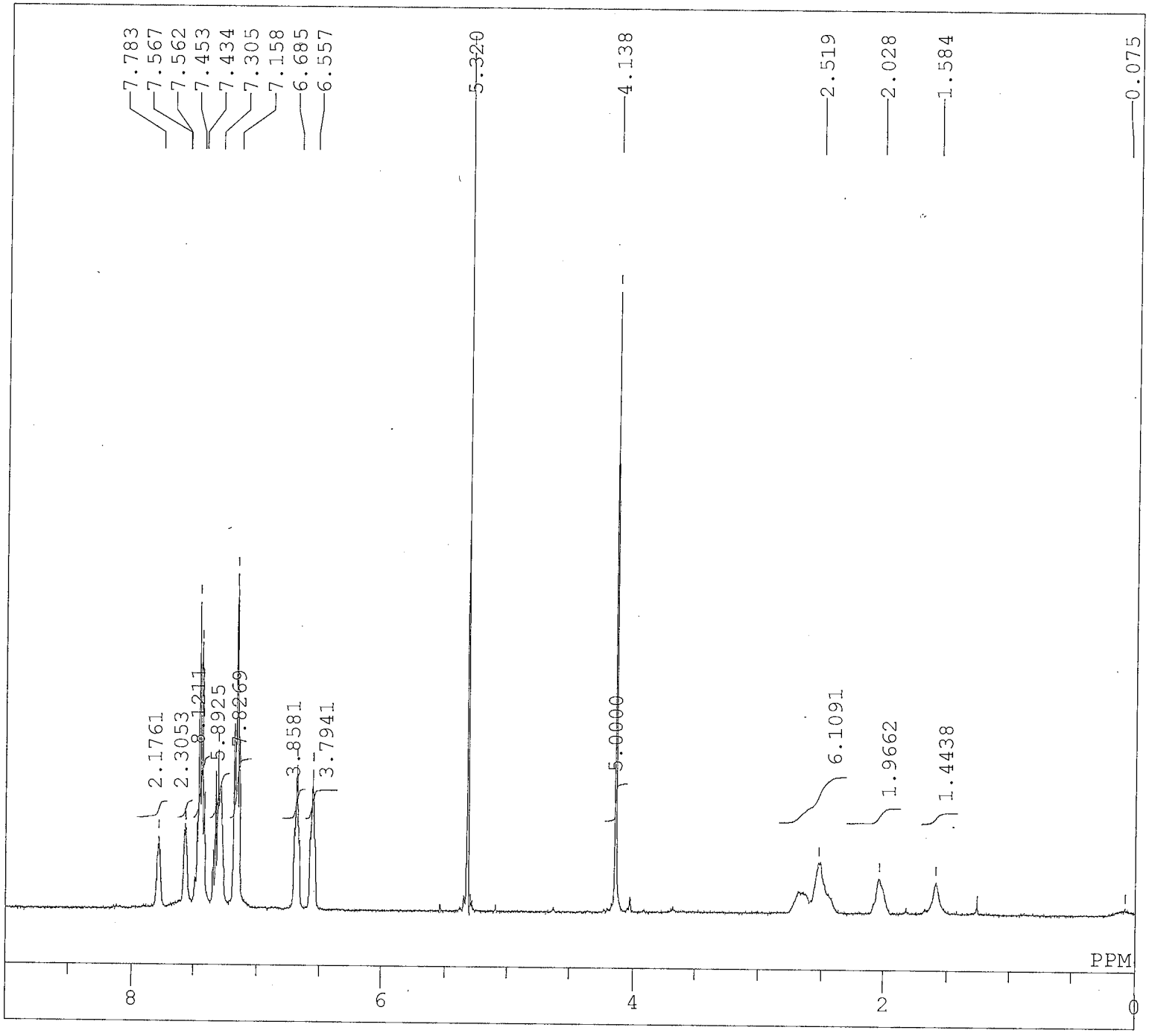


Fig. S-10 1H NMR spectrum of a mixture of [CpMoH2(κ3-P4)][OTf] (3[OTf]) and [CpMo(κ4-P4)][OTf] (4[OTf]) (crude reaction mixture)



$^{31}P\{^{1}H\}$ NMR spectrum of the reaction of [CpMoH(κ^4-**P4**)] with HOTf (after 0°C, 2 h) CD_2Cl_2, 20.9 °C

Fig. S-11 31P{1H} NMR spectrum of a mixture of [CpMoH2(κ3-P4)][OTf] (3[OTf]) and [CpMo(κ4-P4)][OTf] (4[OTf]) (crude reaction mixture)



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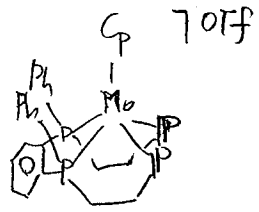
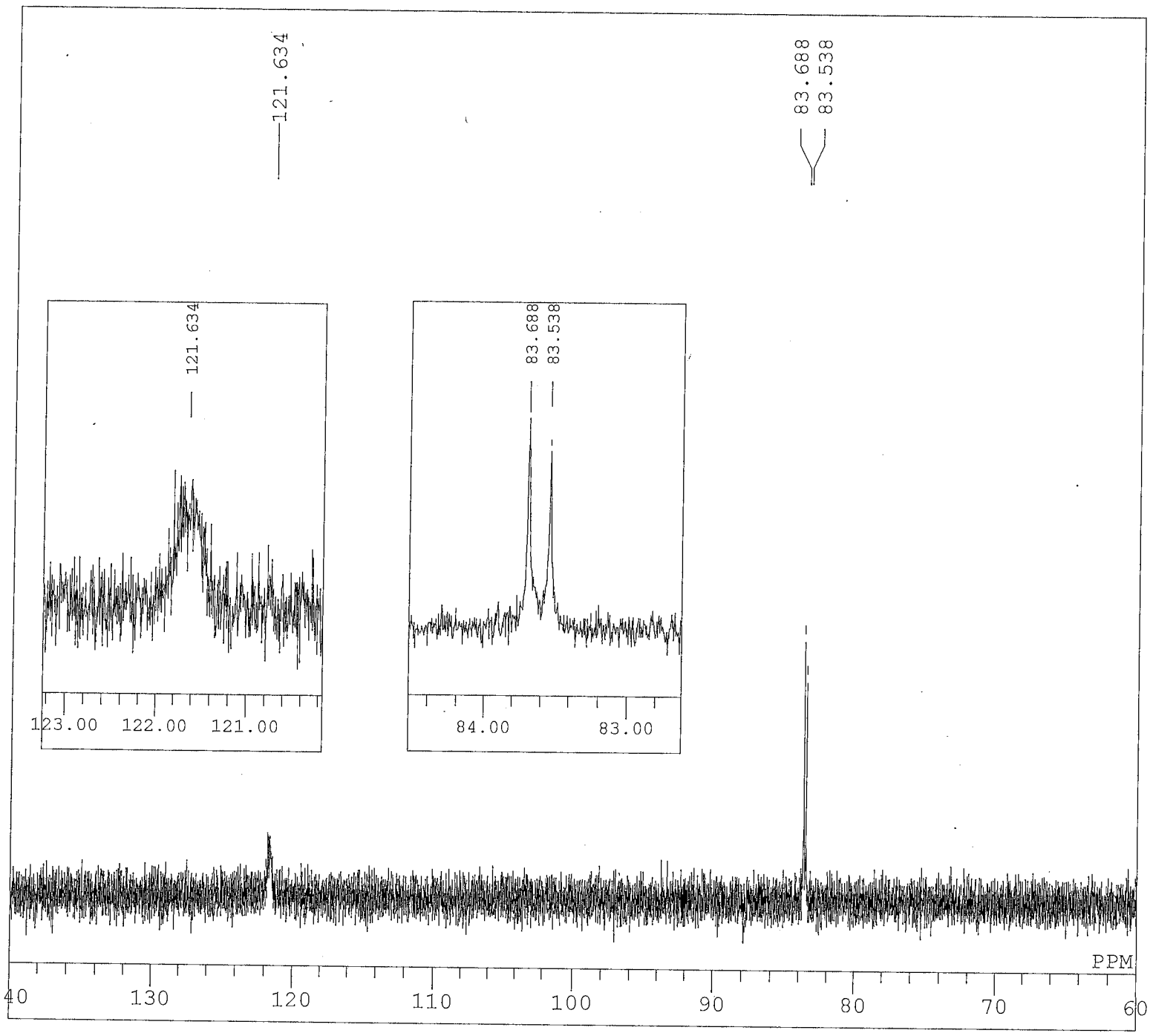
POINT	65536
FREQU	16000.0 Hz
SCANS	21
ACQTM	4.096 sec
PD	2.904 sec
PW1	6.5 us
IRNUC	1H
CTEMP	19.7 c
SLVNT	CD2CL
EXREF	5.32 ppm
BF	0.12 Hz
RGAIN	19



^{1}H NMR spectrum of
[CpMo(κ^4-**P4**)][OTf]
(**4**[OTf])
CD_2Cl_2, 19.7 °C

Fig. S-12 1H NMR spectrum of [CpMo(κ4-P4)][OTf] (4[OTf]) (crystallized from THF)



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POINT 65536
FREQU 50000.0 Hz
SCANS 258
ACQTM 0.655 sec
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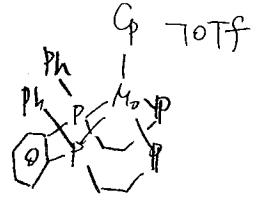
IRNUC 1H
CTEMP 20.5 c
SLVNT CD2CL
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24



$^{31}P\{^{1}H\}$ NMR spectrum of
[CpMo(κ^4-**P4**)][OTf]
(**4**[OTf])
CD_2Cl_2, 20.5 °C

Fig. S-13 31P{1H} NMR spectrum of [CpMo(κ4-P4)][OTf] (4[OTf]) (crystallized from THF)

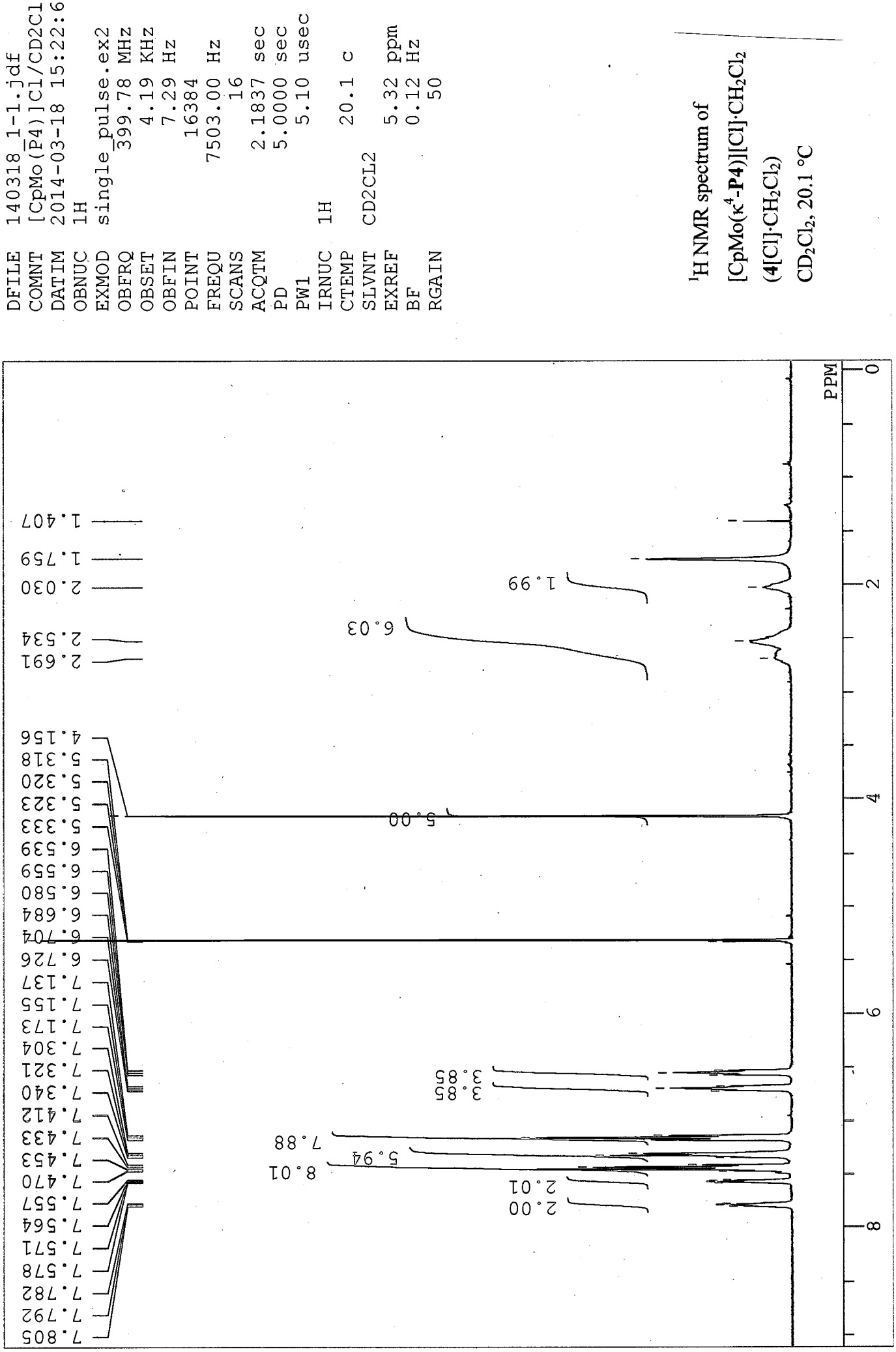


Fig. S-14 1H NMR spectrum of [CpMo(κ4-P4)][Cl]·CH2Cl2 (4[Cl]·CH2Cl2) in CD2Cl2

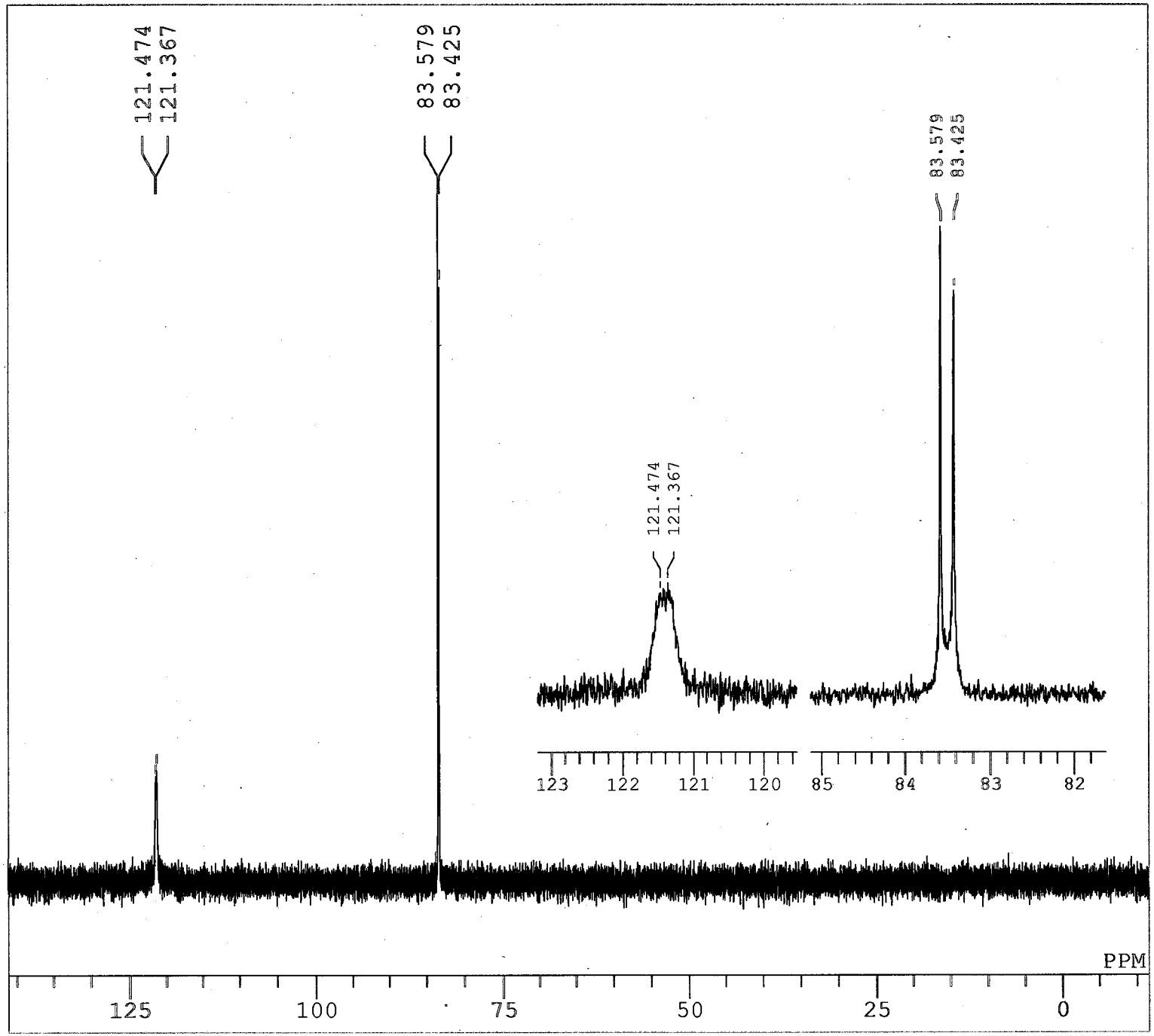


Fig. S-15 31P{1H} NMR spectrum of [CpMo(κ4-P4)][Cl]·CH2Cl2 (4[Cl]·CH2Cl2) in CD2Cl2

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POINT          65536
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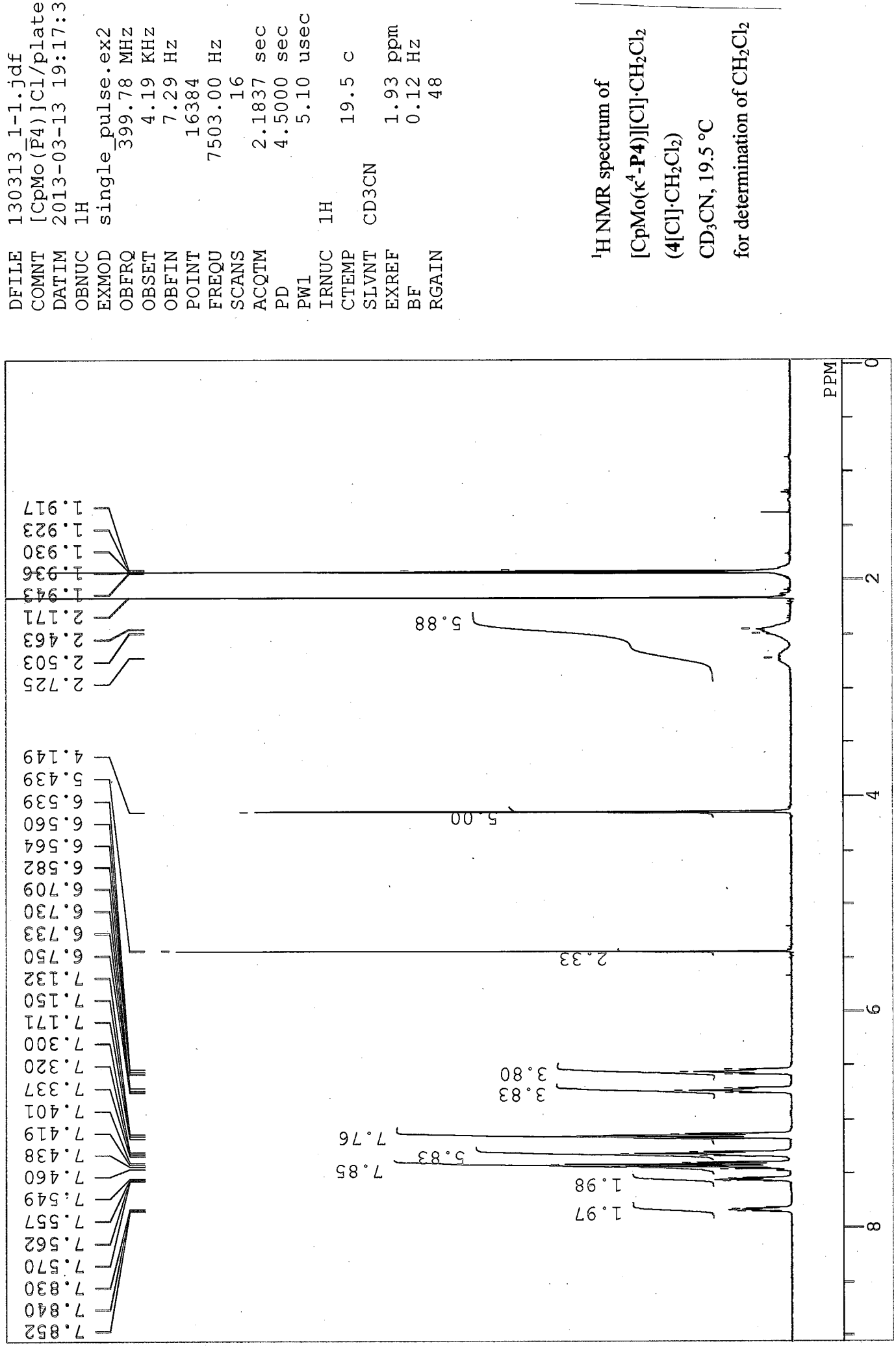
PD            1.0000 sec
PW1             4.68 usec
IRNUC   1H
CTEMP           20.4 c
SLVNT   CD2CL2
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             56
```

$^{31}P\{^{1}H\}$ NMR spectrum of
[CpMo(κ^4-**P4**)][Cl]·CH_2Cl_2
(**4**[Cl]·CH_2Cl_2)
CD_2Cl_2, 20.4 °C



^{1}H NMR spectrum of
[CpMo(κ^4-**P4**)][Cl]·CH_2Cl_2
(**4**[Cl]·CH_2Cl_2)
CD_3CN, 19.5 °C
for determination of CH_2Cl_2

Fig. S-16 1H NMR spectrum of [CpMo(κ4-P4)][Cl]·CH2Cl2 (4[Cl]·CH2Cl2) in CD3CN

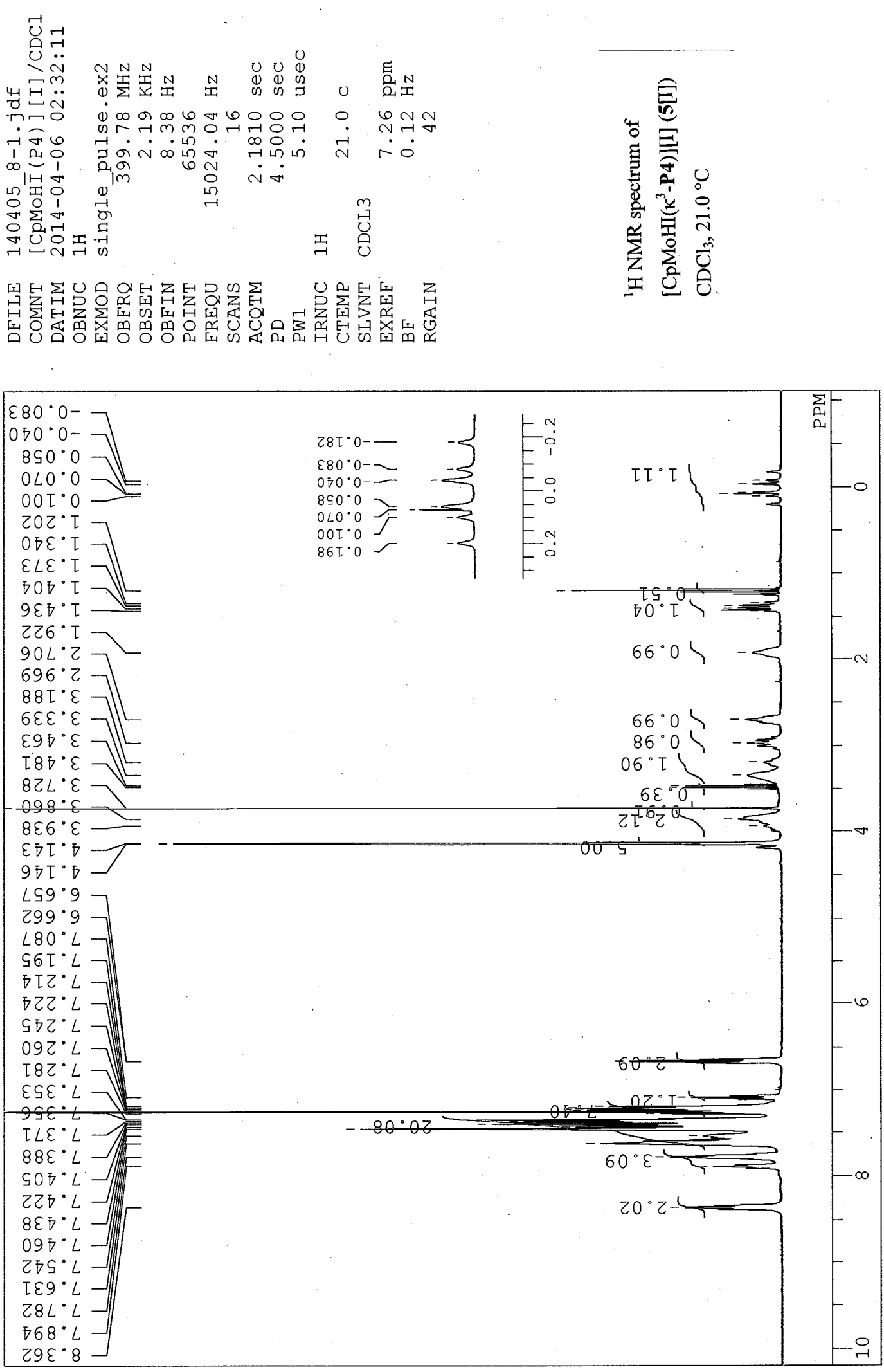


Fig. S-17 1H NMR spectrum of [CpMoHI(κ3-P4)][I] (5[I])

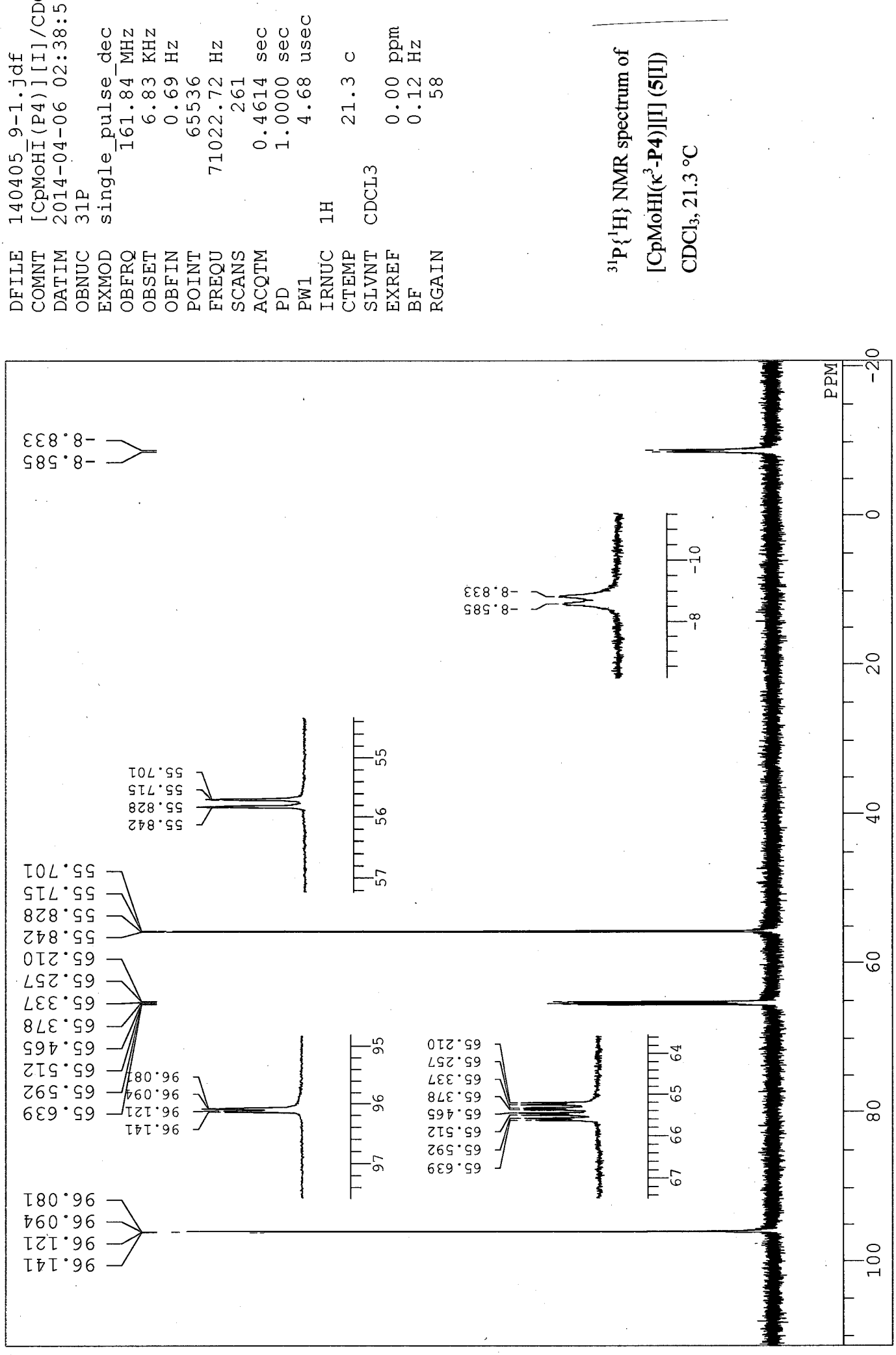


Fig. S-18 31P{1H} NMR spectrum of [CpMoHI(κ3-P4)][I] (5[I])

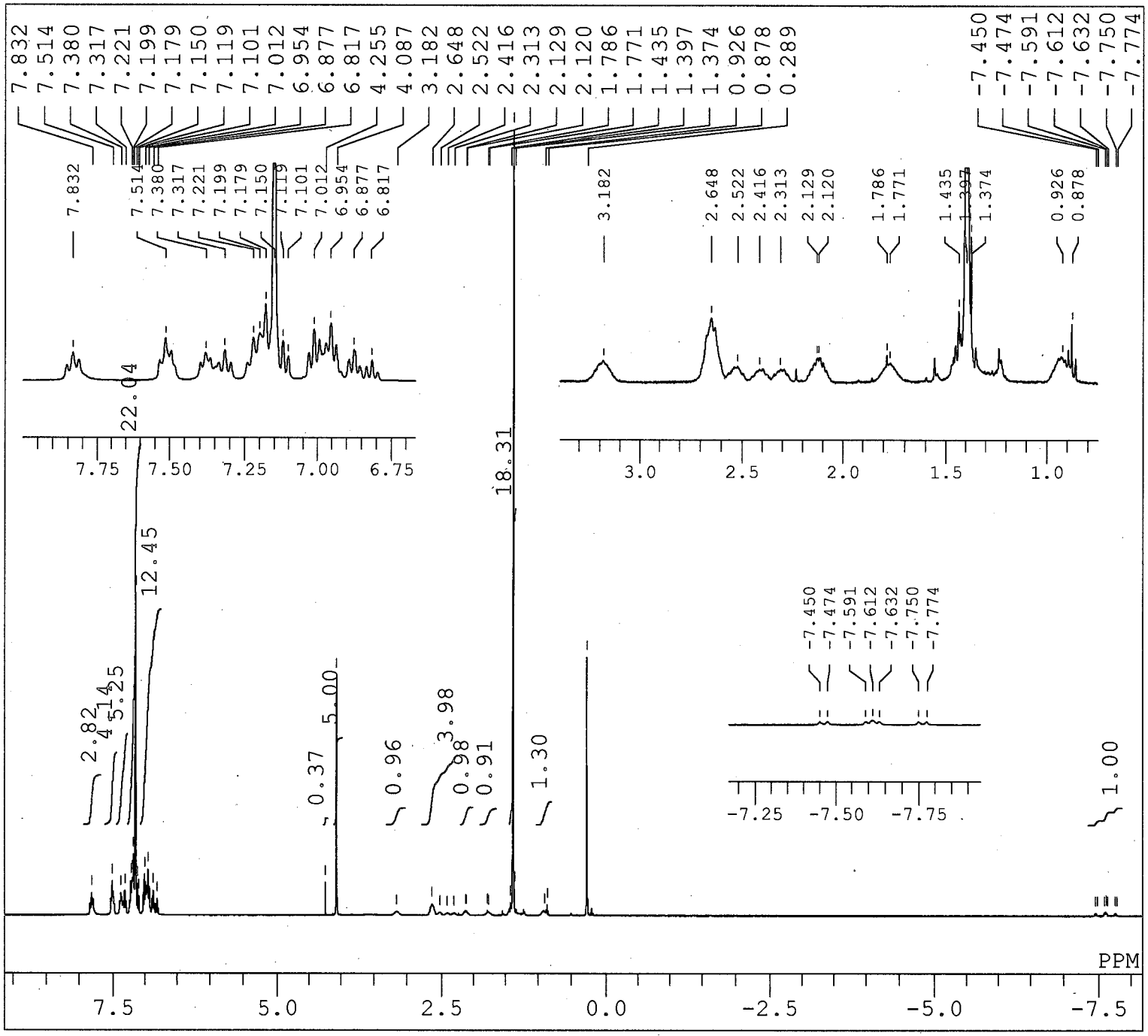


Fig. S-19 1H NMR spectrum of [CpMoH(μ-P4)RuCl2(C6Me6)]·0.25CH2Cl2 (6·0.25CH2Cl2)

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PW1              5.10 usec
IRNUC   1H
CTEMP             21.1 c
SLVNT   C6D6
EXREF             7.15 ppm
BF                0.12 Hz
RGAIN               42
```

^{1}H NMR spectrum of [CpMoH(μ-**P4**-1κ^3:2κ)Ru-Cl$_2$(η^6-C$_6$Me$_6$)]·0.25CH$_2$Cl$_2$ (**6**·0.25CH$_2$Cl$_2$) C$_6$D$_6$, 21.1 °C

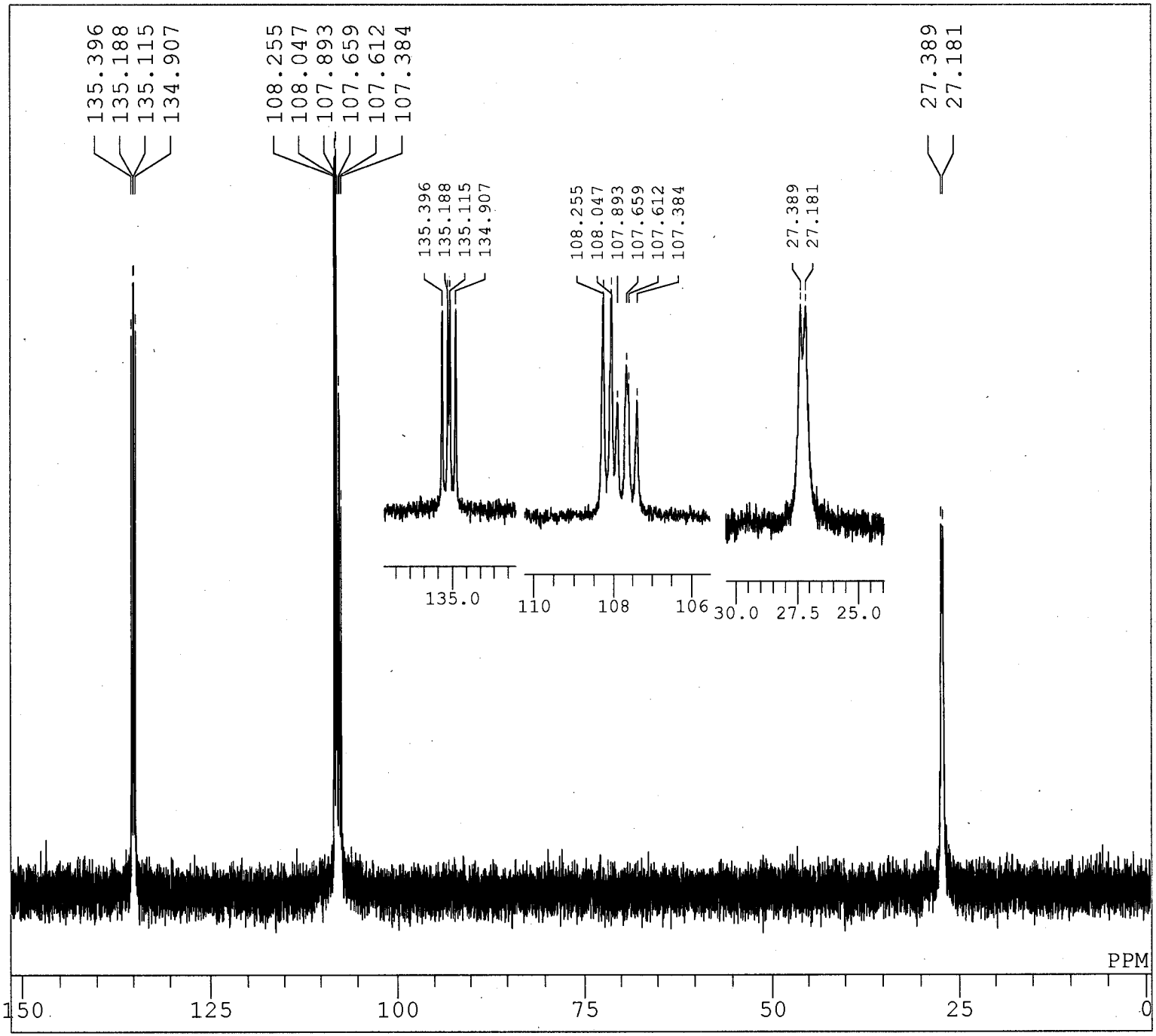

Fig. S-20 31P{1H} NMR spectrum of [CpMoH(μ-P4)RuCl2(C6Me6)]·0.25CH2Cl2 (6·0.25CH2Cl2)

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POINT         65536
FREQU      71022.72 Hz
SCANS          1000
ACQTM        0.4614 sec
PD           1.0000 sec
PW1             4.68 usec
IRNUC  1H
CTEMP          21.6 c
SLVNT  C6D6
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            58
```

$^{31}P\{^{1}H\}$ NMR spectrum of [CpMoH(μ-**P4**-1κ^3:2κ)Ru-Cl_2(η^6-C_6Me_6)]·0.25CH_2Cl_2 (**6**·0.25CH_2Cl_2) C_6D_6, 21.6 °C

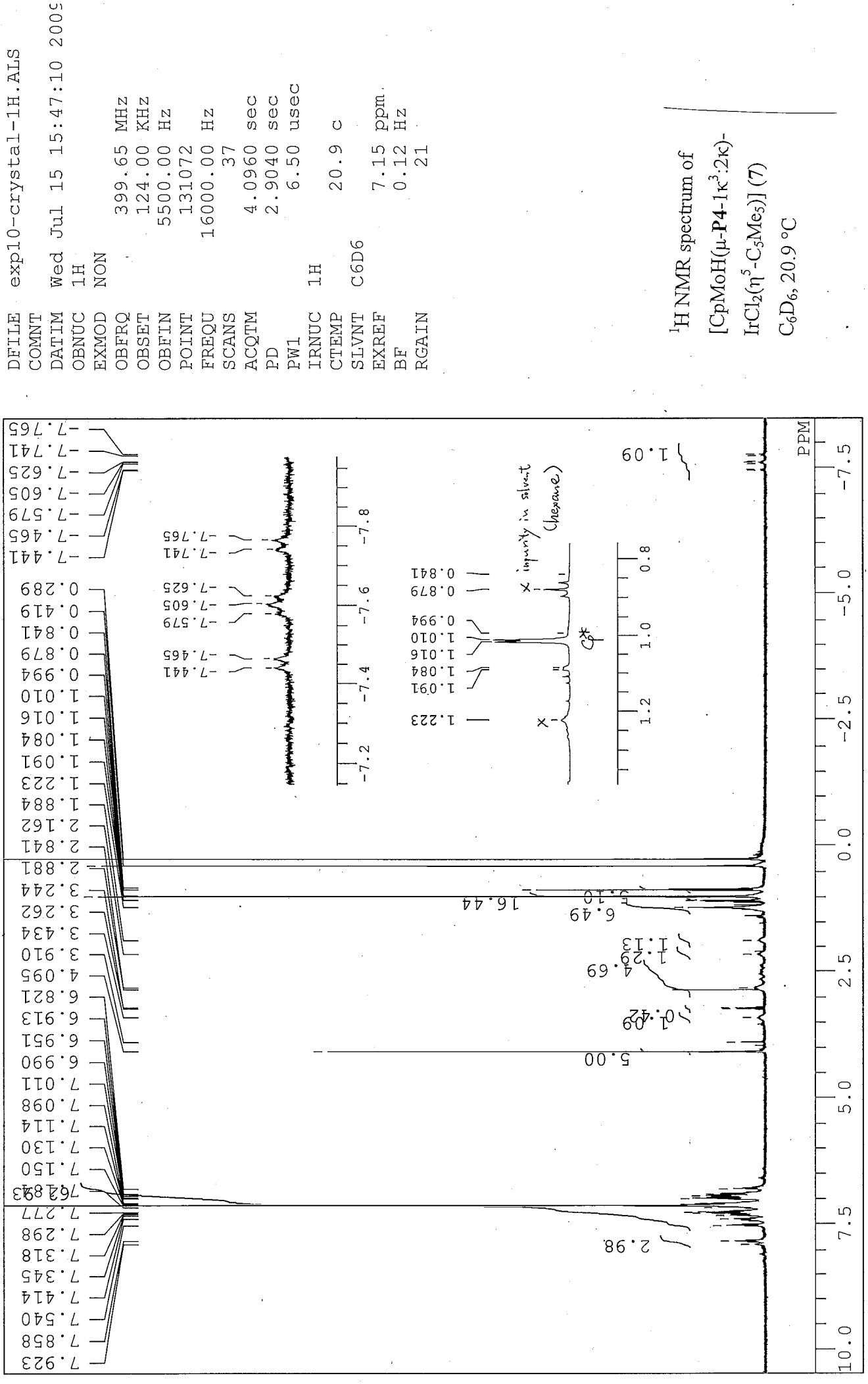

Fig. S-21 1H NMR spectrum of [CpMoH(μ-P4)IrCl2(C5Me5)] (7)

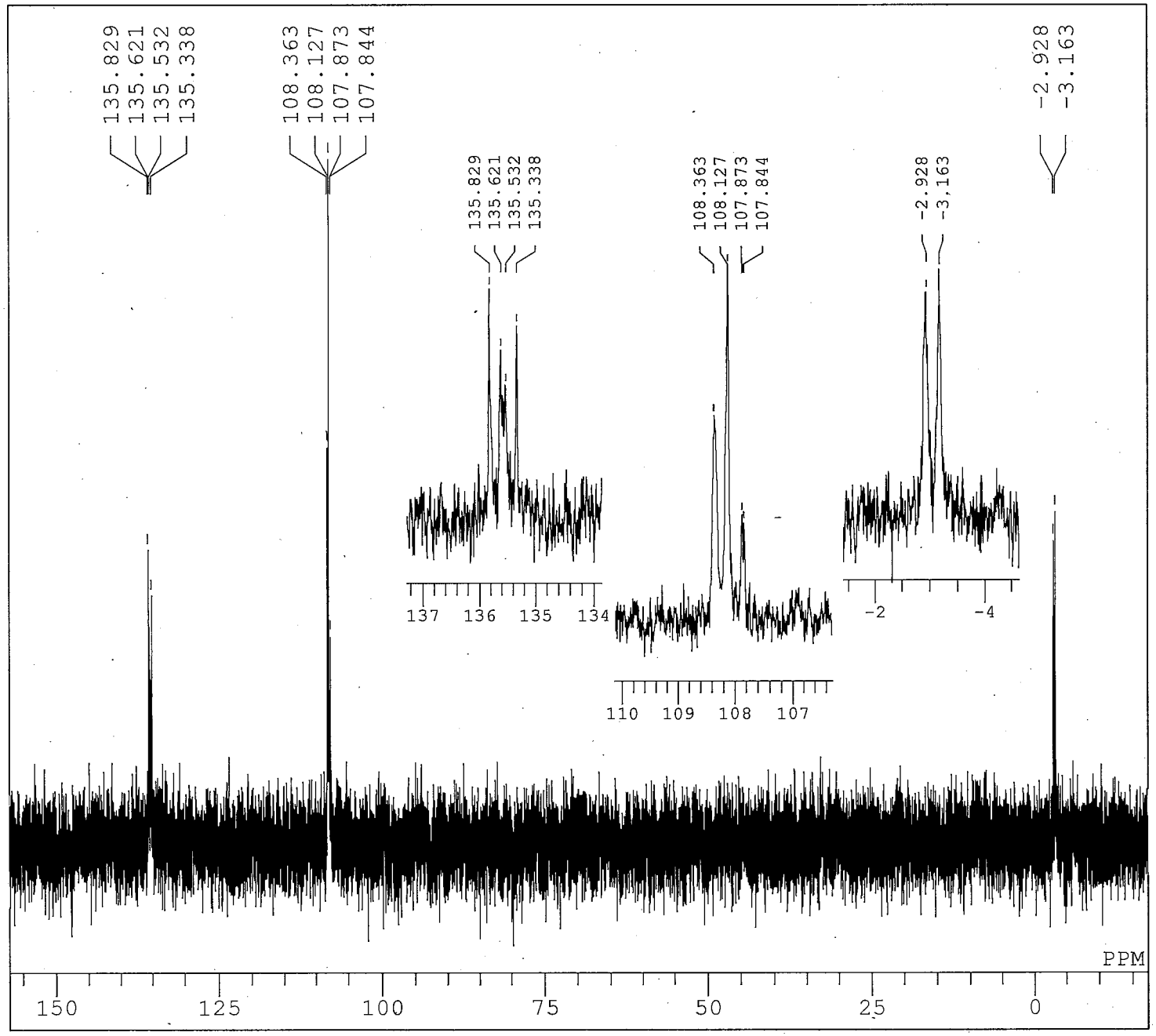

Fig. S-22 31P{1H} NMR spectrum of [CpMoH(μ-P4)IrCl2(C5Me5)] (7)


```
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COMNT
DATIM  Wed Jul 15 15:40:55 2009
OBNUC  31P
EXMOD  BCM
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OBSET          142.00 KHz
OBFIN            0.00 Hz
POINT           65536
FREQU        50000.00 Hz
SCANS            1024
ACQTM          0.6554 sec
PD             0.9000 sec
PW1              6.50 usec
IRNUC  1H
CTEMP            22.7 c
SLVNT  C6D6
EXREF            0.00 ppm
BF               1.20 Hz
RGAIN              25
```

$^{31}P\{^{1}H\}$ NMR spectrum of [CpMoH(μ-**P4**-1κ^{3}:2κ)-$IrCl_2(\eta^5\text{-}C_5Me_5)$] (**7**) C_6D_6, 22.7 °C

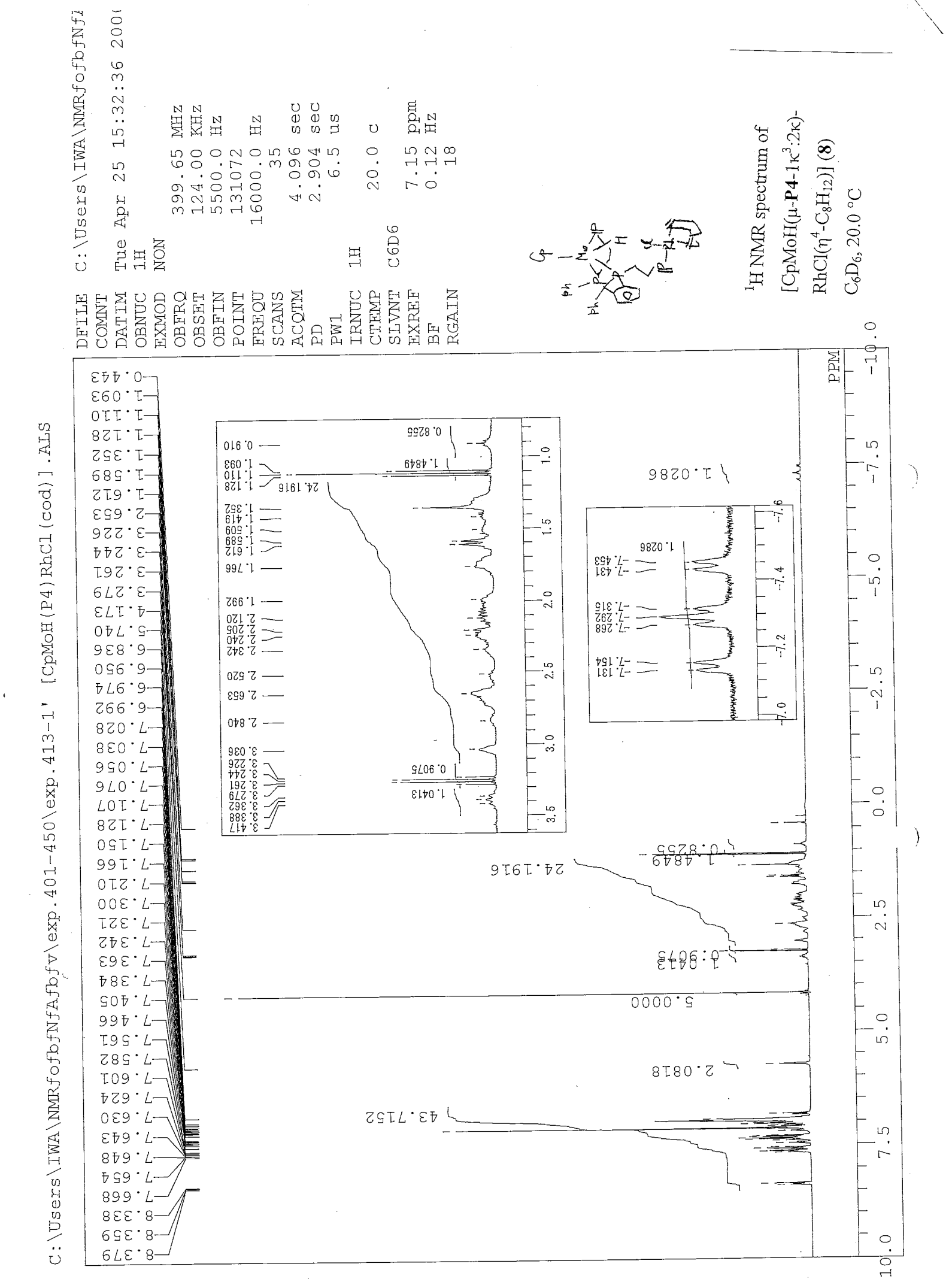

Fig. S-23 1H NMR spectrum of [CpMoH(μ-P4)RhCl(C8H12)] (8)

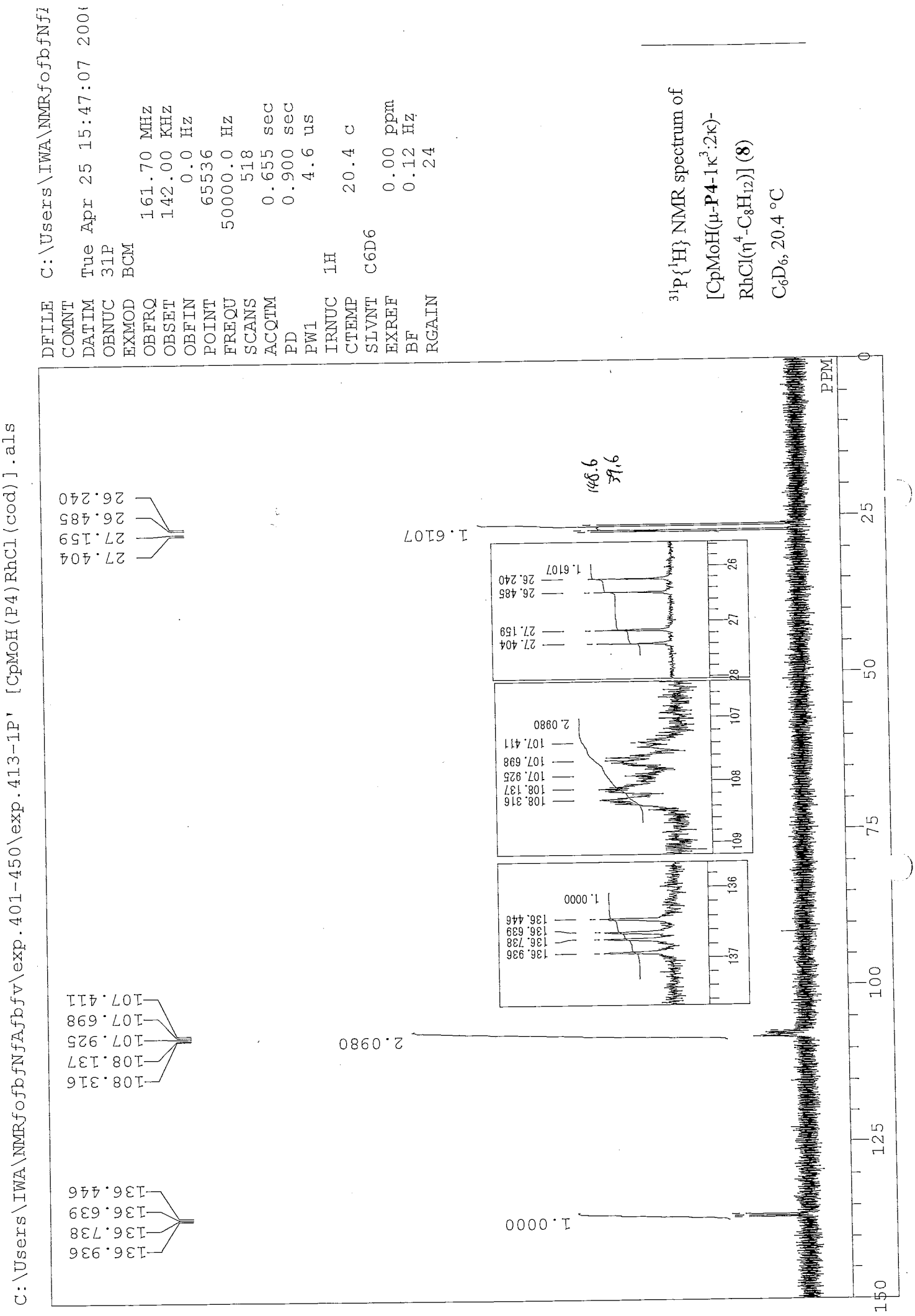

Fig. S-24 31P{1H} NMR spectrum of [CpMoH(μ-P4)RhCl(C8H12)] (8)

C:\Users\IWA\NMRfofbfNfAfbfv\exp.401-450\exp.414-1' [CpMoH(P4)IrCl(cod)].als

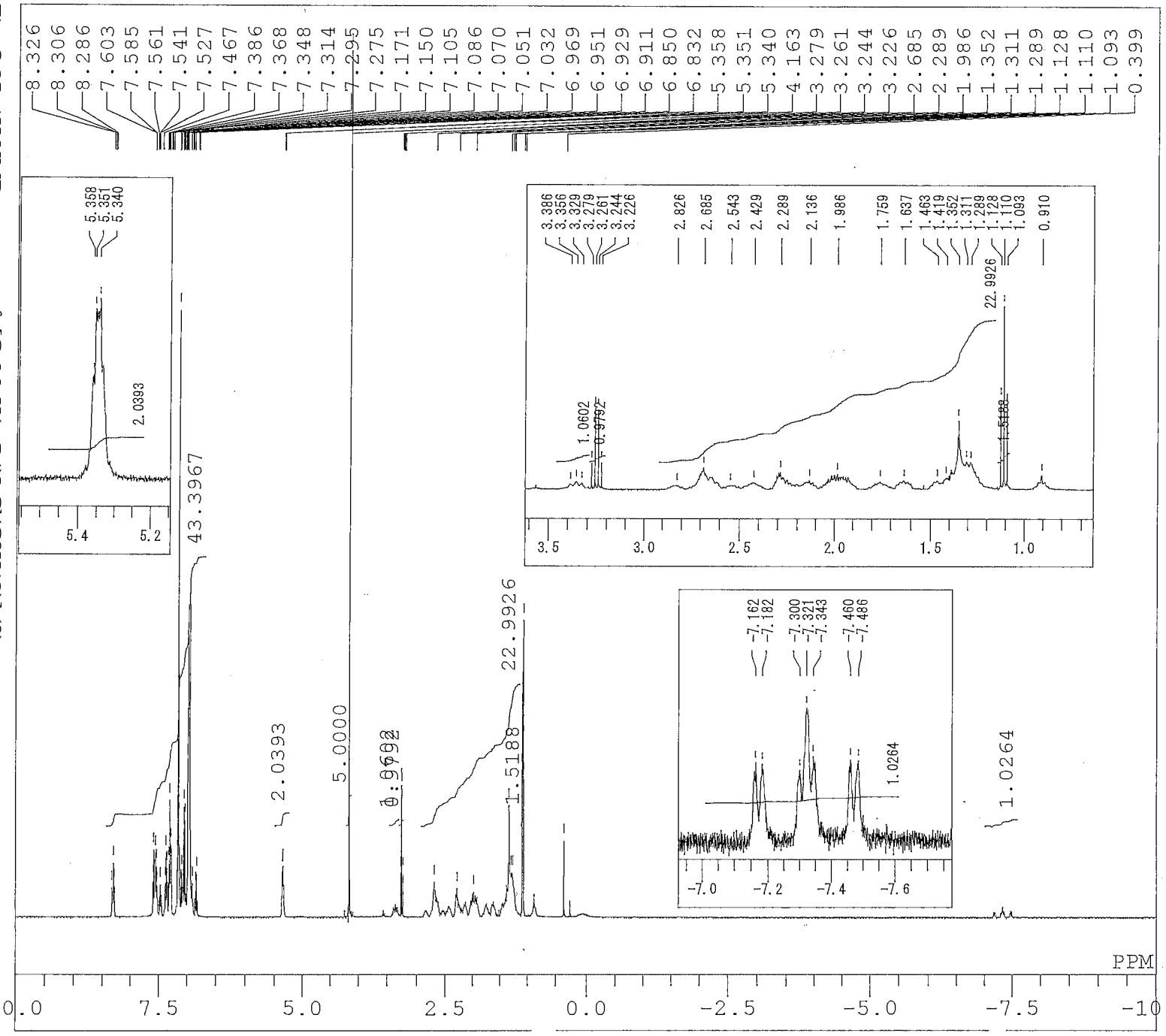

Fig. S-25 1H NMR spectrum of [CpMoH(μ-P4)IrCl(C8H12)] (9)

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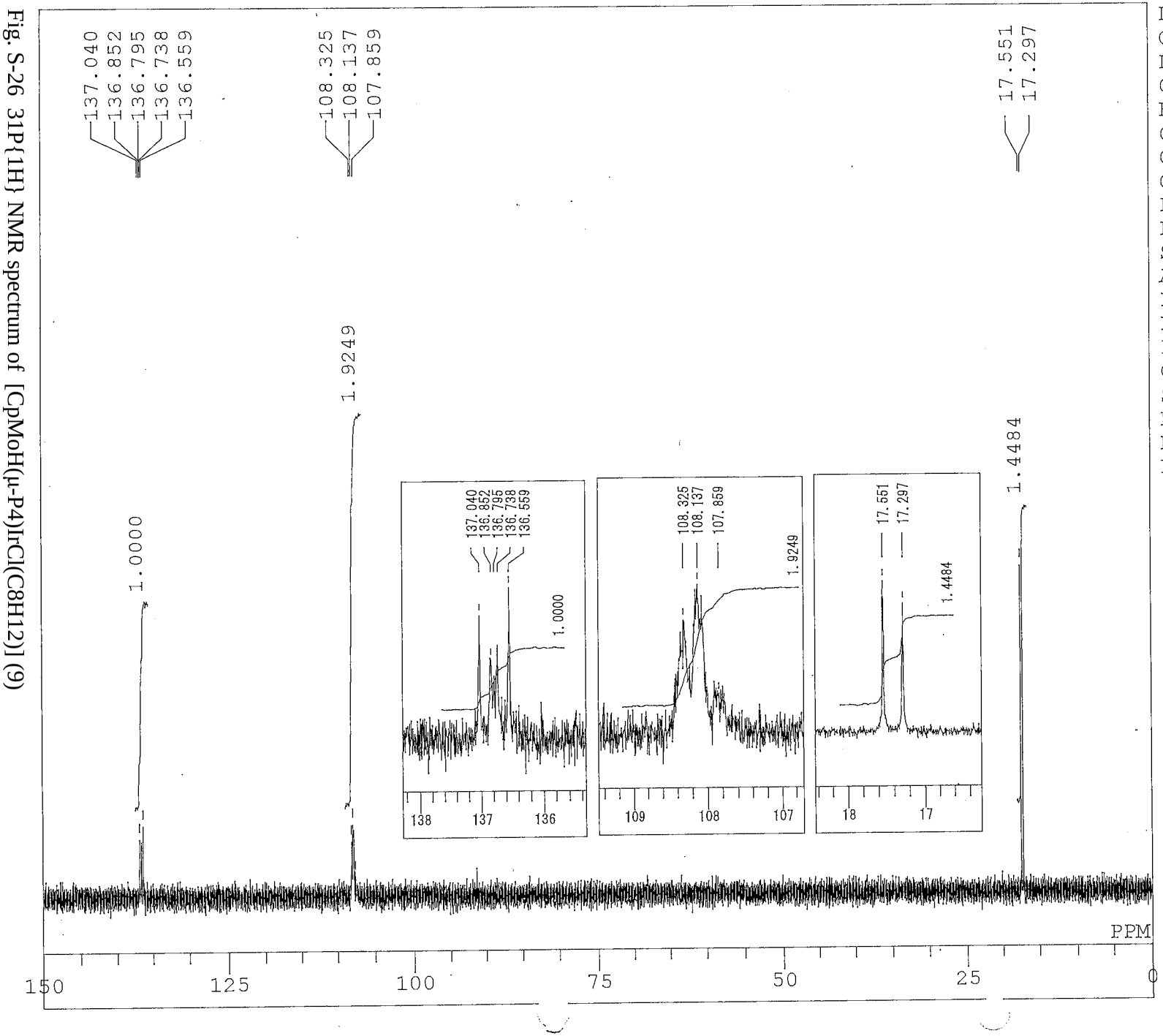
OBSET         124.00 KHz
OBFIN          5500.0 Hz
POINT          131072
FREQU         16000.0 Hz
SCANS               33
ACQTM            4.096 sec
PD               2.904 sec
PW1                6.5 us
IRNUC   1H
CTEMP             20.0 c
SLVNT   C6D6
EXREF             7.15 ppm
BF                0.12 Hz
RGAIN               19
```

^{1}H NMR spectrum of
[CpMoH(μ-**P4**-1κ^3:2κ)-
IrCl(η^4-C_8H_{12})] (**9**)
C_6D_6, 20.0 °C



DFILE C:\Users\IWA\NMRfofbfNf
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EXMOD BCM
OBFRQ 161.70 MHz
OBSET 142.00 KHz
OBFIN 0.0 Hz
POINT 65536
FREQU 50000.0 Hz
SCANS 566
ACQTM 0.655 sec
PD 0.900 sec
PW1 4.6 us
IRNUC 1H
CTEMP 20.3 c
SLVNT C6D6
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24

Fig. S-26 31P{1H} NMR spectrum of [CpMoH(μ-P4)IrCl(C8H12)] (9)

$^{31}P\{^{1}H\}$ NMR spectrum of [CpMoH(μ-**P4**-1κ^{3}:2κ)-IrCl(η^{4}-C_8H_{12})] (**9**) C_6D_6, 20.3 °C

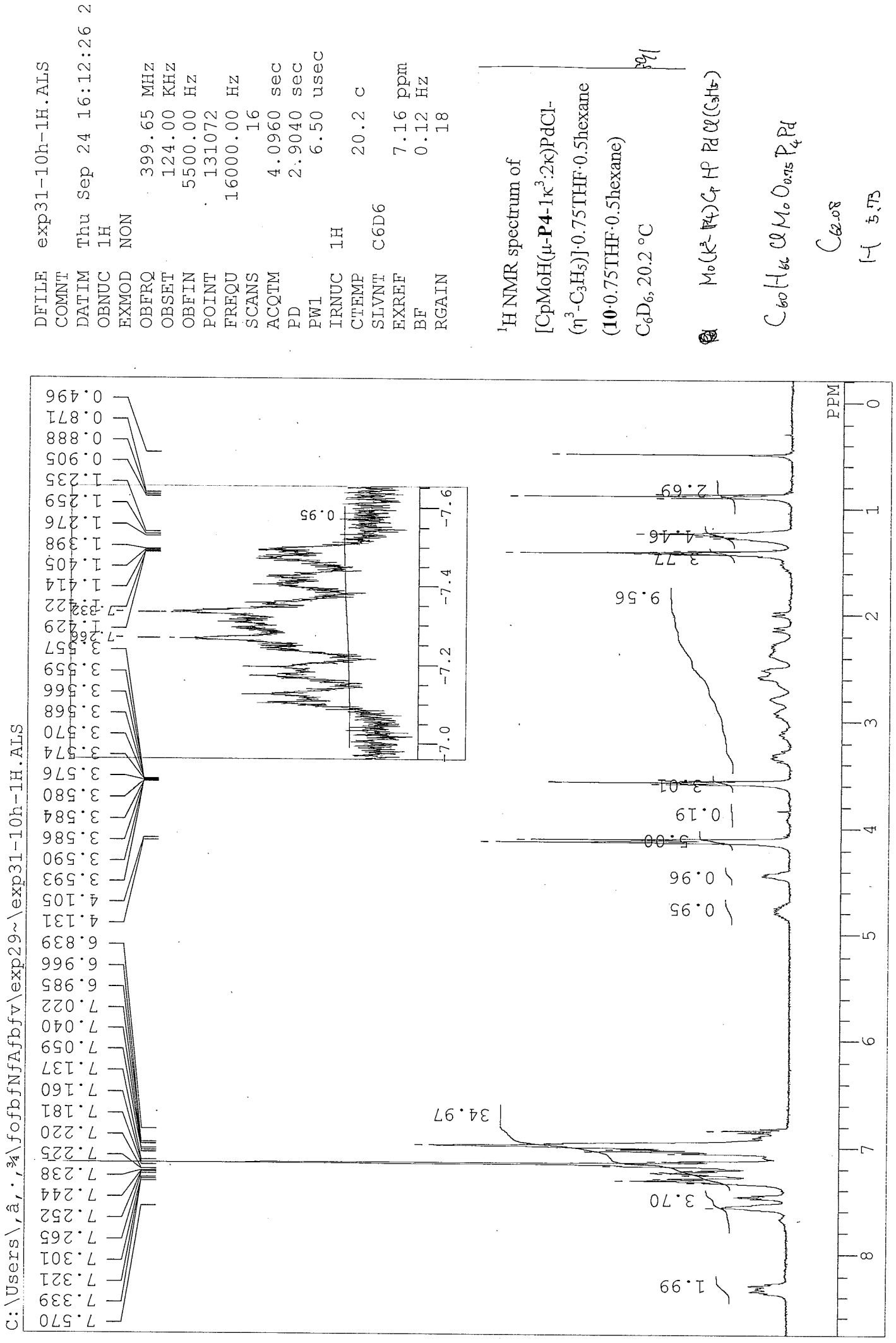
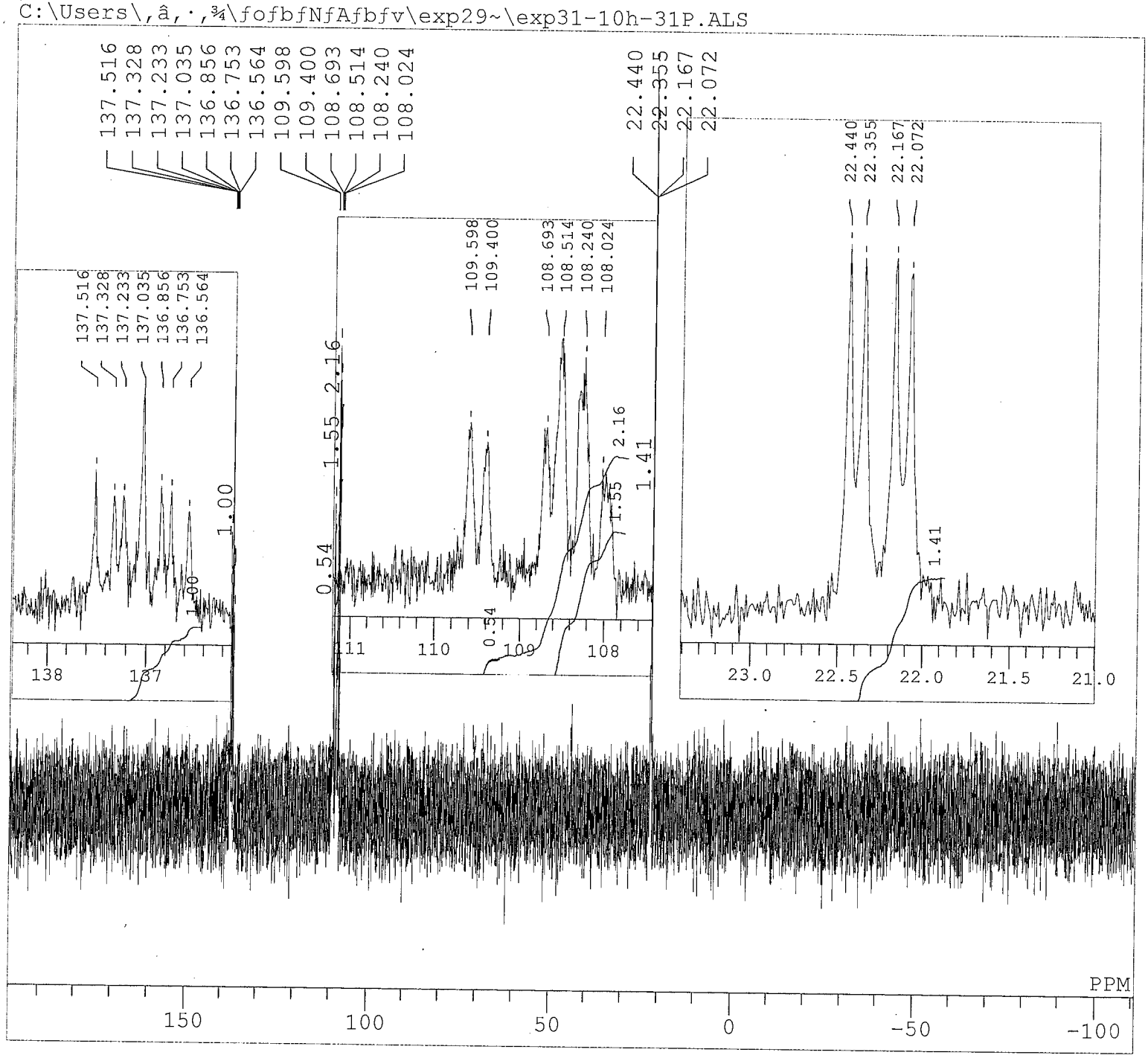


Fig. S-27 1H NMR spectrum of [CpMoH(μ-P4)PdCl(C3H5)]·0.75THF·0.5hexane (10·0.75THF·0.5hexane)

Fig. S-28 31P{1H} NMR spectrum of [CpMoH(μ-P4)PdCl(C3H5)]·0.75THF·0.5hexane (10·0.75THF·0.5hexane)

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EXMOD   BCM
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OBSET          142.00 KHz
OBFIN            0.00 Hz
POINT           32768
FREQU        50000.00 Hz
SCANS              266
ACQTM           0.6554 sec
PD              0.9000 sec
PW1               6.50 usec
IRNUC   1H
CTEMP             21.5 c
SLVNT   C6D6
EXREF             0.00 ppm
BF                0.12 Hz
RGAIN               24
```

$^{31}P\{^{1}H\}$ NMR spectrum of [CpMoH(μ-**P4**-1κ^3:2κ)PdCl-(η^3-C_3H_5)]·0.75THF·0.5hexane (**10**·0.75THF·0.5hexane) C_6D_6, 21.5 °C

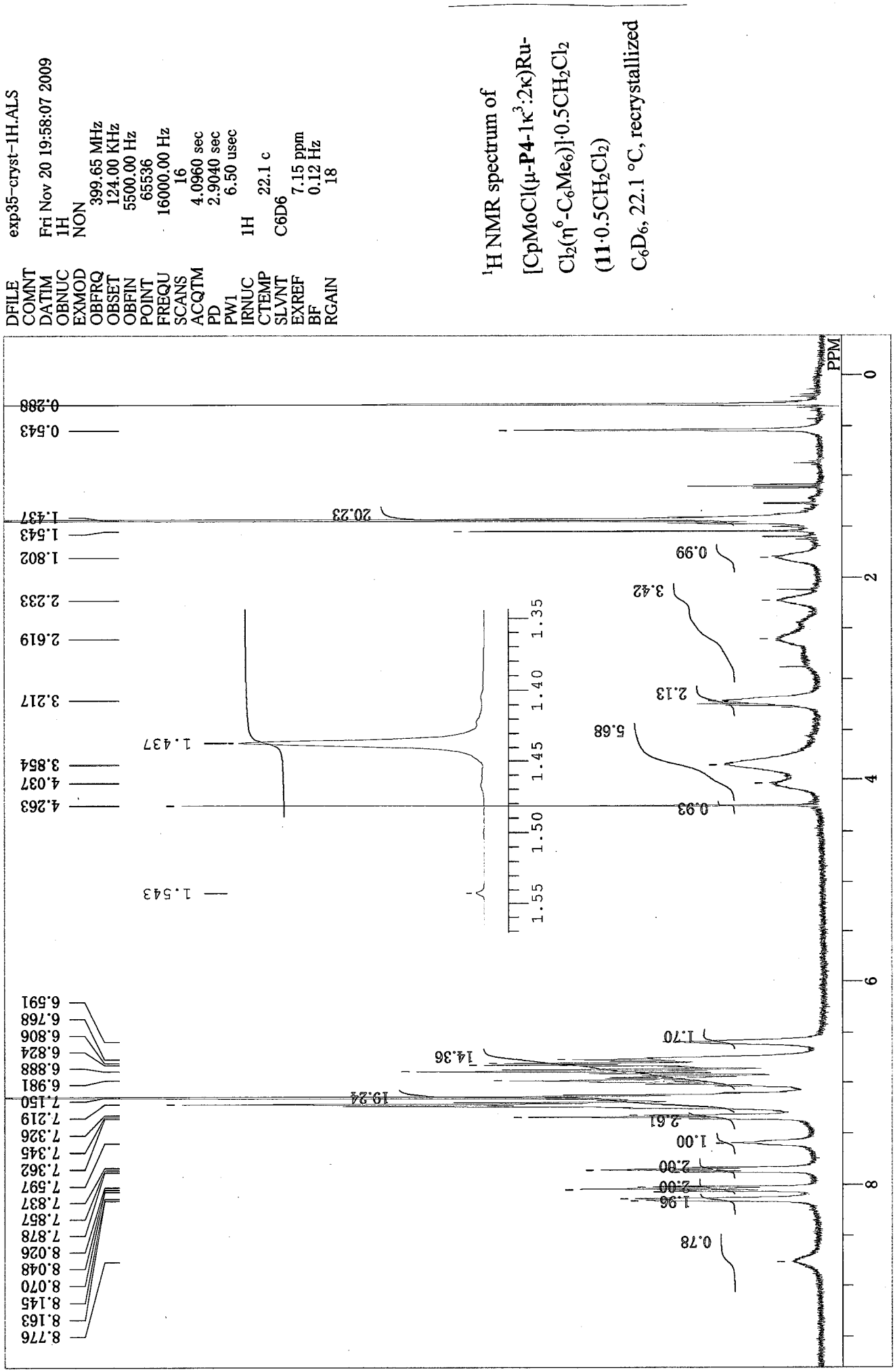


Fig. S-29 1H NMR spectrum of [CpMoCl(μ-P4)RuCl2(C6Me6)]·0.5CH2Cl2 (11·0.5CH2Cl2)

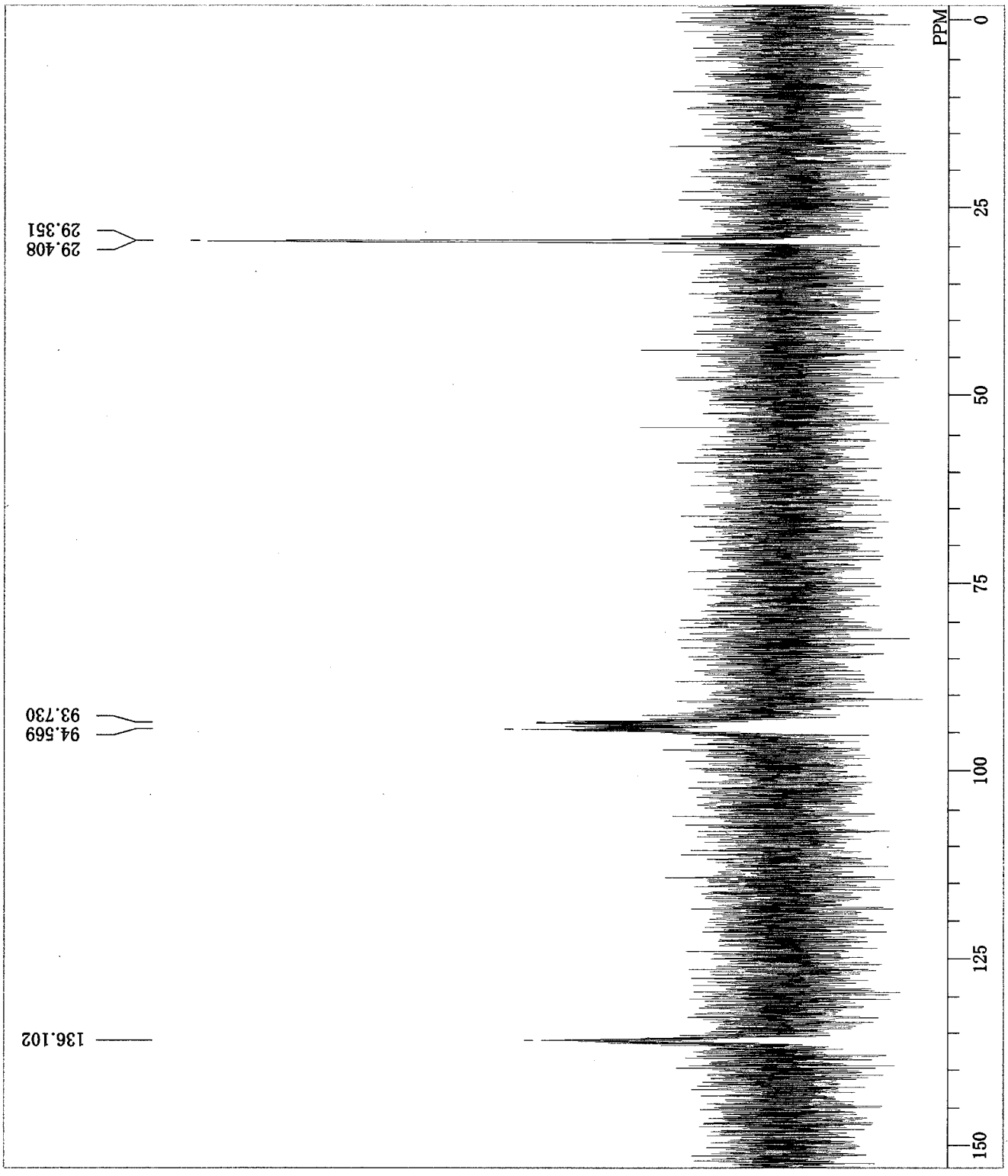
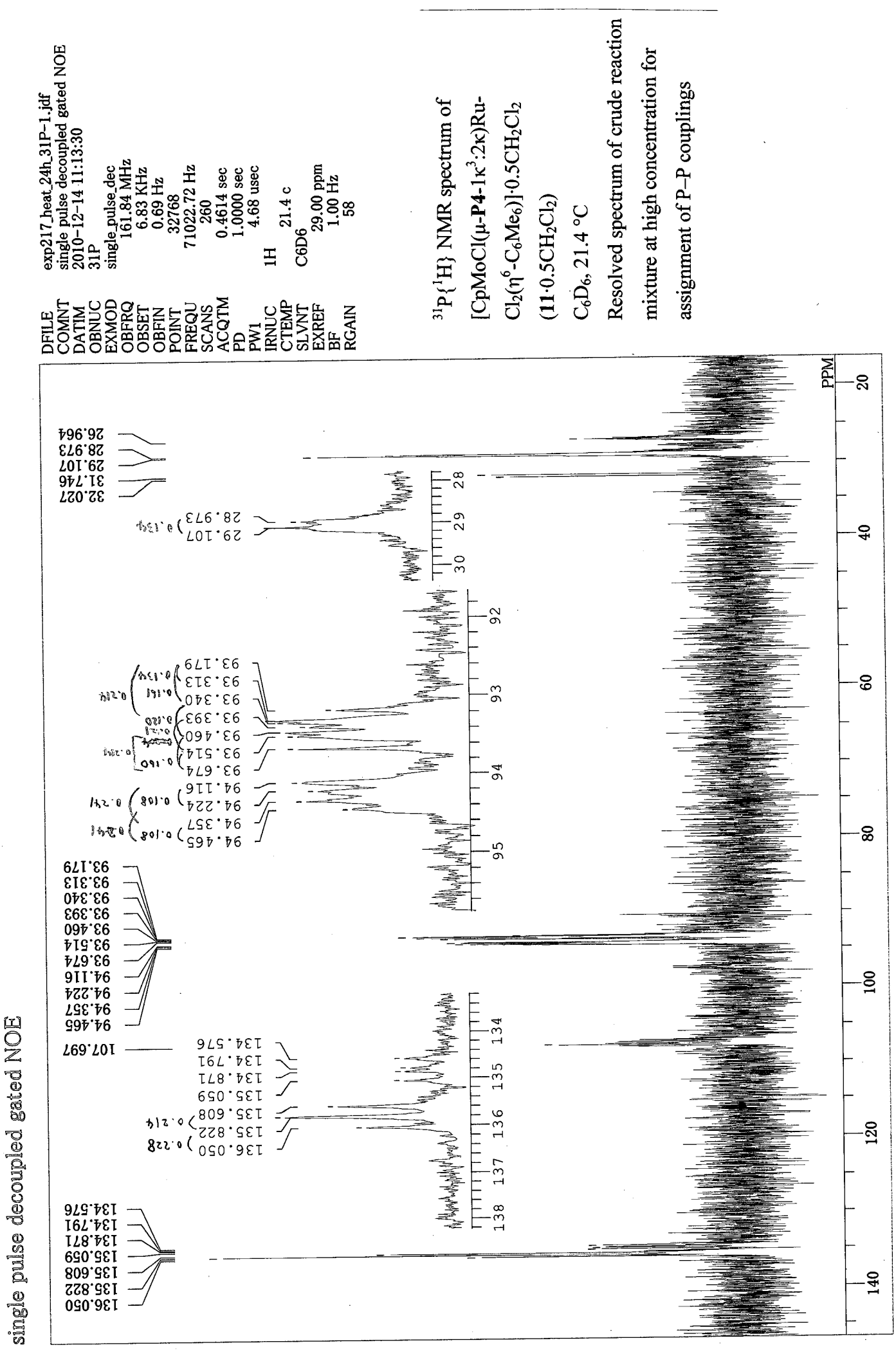


Fig. S-30 31P{1H} NMR spectrum of [CpMoCl(μ-P4)RuCl2(C6Me6)]·0.5CH2Cl2 (11·0.5CH2Cl2)



$^{31}P\{^{1}H\}$ NMR spectrum of [CpMoCl(μ-**P4**-1κ^3:2κ)Ru-Cl$_2$(η^6-C$_6$Me$_6$)]·0.5CH$_2$Cl$_2$ (**11**·0.5CH$_2$Cl$_2$) C$_6$D$_6$, 21.4 °C

Resolved spectrum of crude reaction mixture at high concentration for assignment of P–P couplings

Fig. S-31 31P{1H} NMR spectrum of a mixture containing [CpMoCl(μ-P4)RuCl2(C6Me6)] (11) in high concentration (used for coupling assignments)

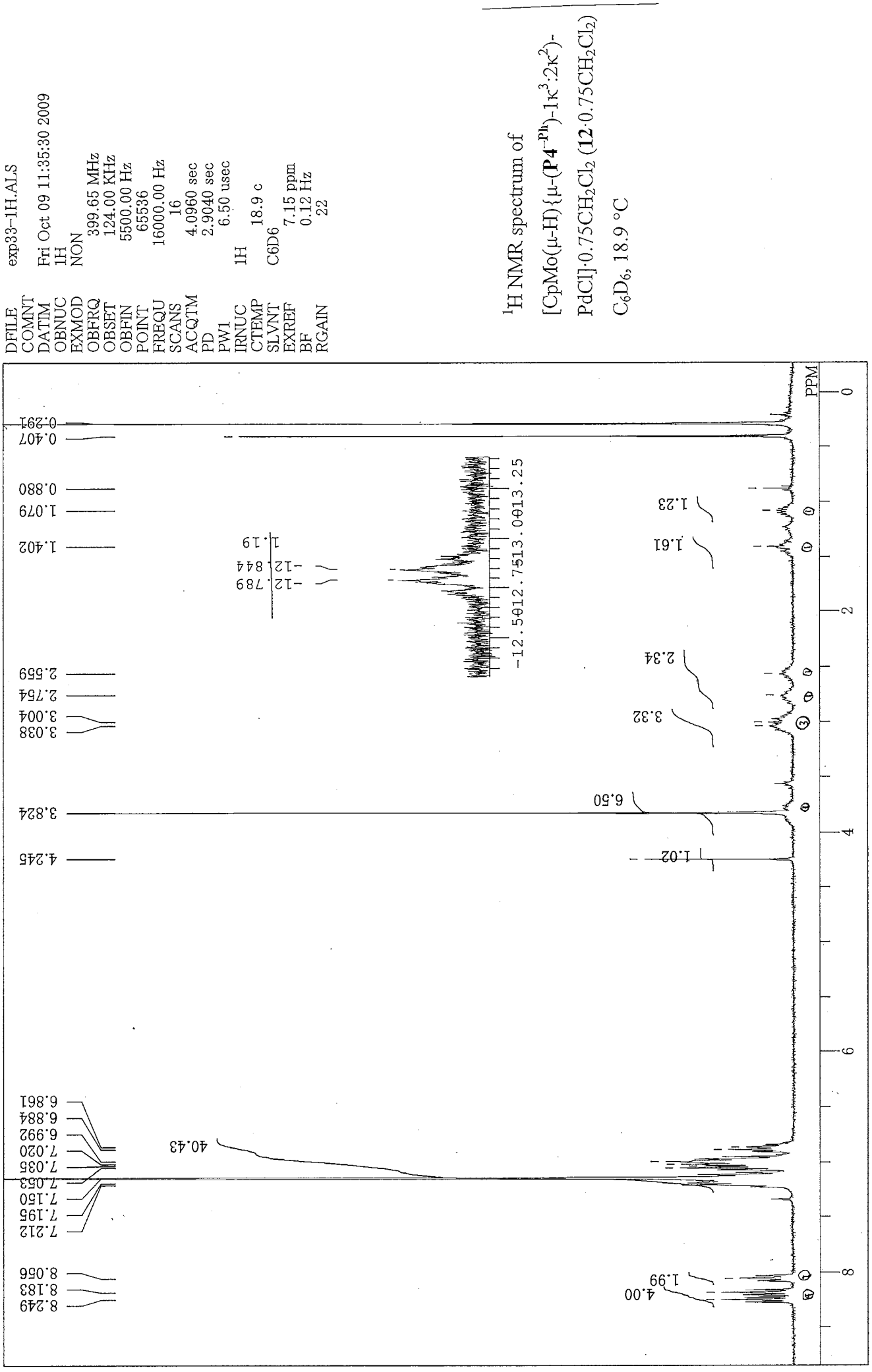


Fig. S-32 1H NMR spectrum of [CpMo(μ-H)(μ-P4-Ph)PdCl]·0.75CH2Cl2 (12·0.75CH2Cl2)

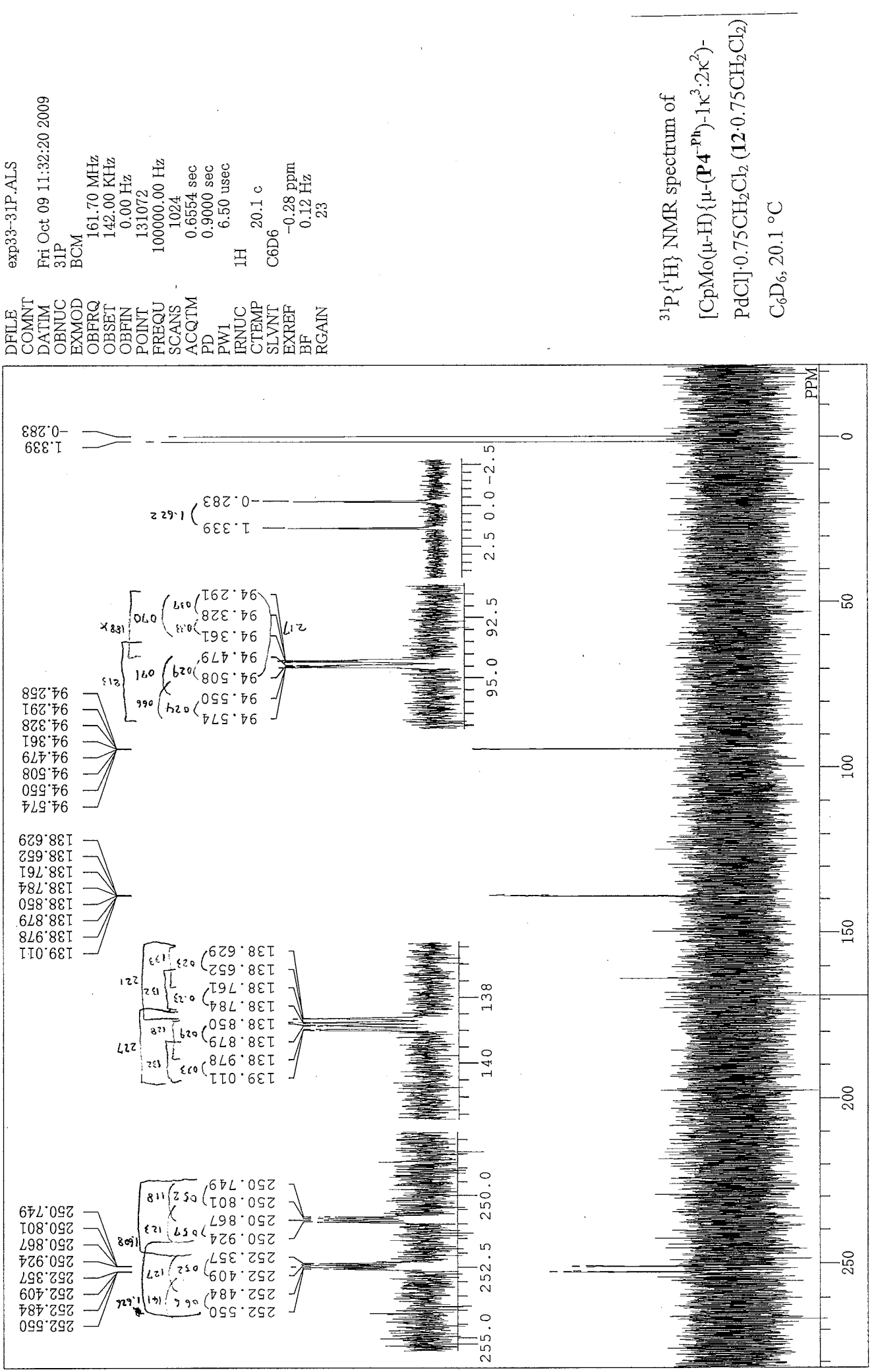


Fig. S-33 31P{1H} NMR spectrum of [CpMo(μ-H)(μ-P4-Ph)PdCl]·0.75CH2Cl2 (12·0.75CH2Cl2)