

Electronic Supplementary Information
for
**Molybdenum Complex Bearing Tetrphosphine Ligand as a Precursor for
Heterobimetallic Complexes**

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Additional comments on crystallography

For $[\text{CpMo}(\kappa^4\text{-P4})][\text{OTf}] \cdot 2.7\text{CH}_2\text{Cl}_2$ (**4** $[\text{OTf}] \cdot 2.7\text{CH}_2\text{Cl}_2$), 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 $[\text{CpMo}(\kappa^4\text{-P4})][\text{Cl}] \cdot 0.78\text{DMF} \cdot 0.22\text{Et}_2\text{O}$ (**4** $[\text{Cl}] \cdot 0.78\text{DMF} \cdot 0.22\text{Et}_2\text{O}$), 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 $[\text{CpMoH}(\mu\text{-P4-1}\kappa^3:2\kappa)\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)] \cdot 3\text{CH}_2\text{Cl}_2$ (**6** $\cdot 3\text{CH}_2\text{Cl}_2$) 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 $[\text{CpMoCl}(\mu\text{-P4-1}\kappa^3:2\kappa)\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)] \cdot 2.5\text{CH}_2\text{Cl}_2$ (**11** $\cdot 2.5\text{CH}_2\text{Cl}_2$). 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 CH₂Cl₂ molecule in [CpMo(μ-H){μ-(**P4**^{-Ph})-1κ³:2κ²)PdCl]·0.75CH₂Cl₂ (**12**·0.75CH₂Cl₂) 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 CH₂Cl₂, 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.

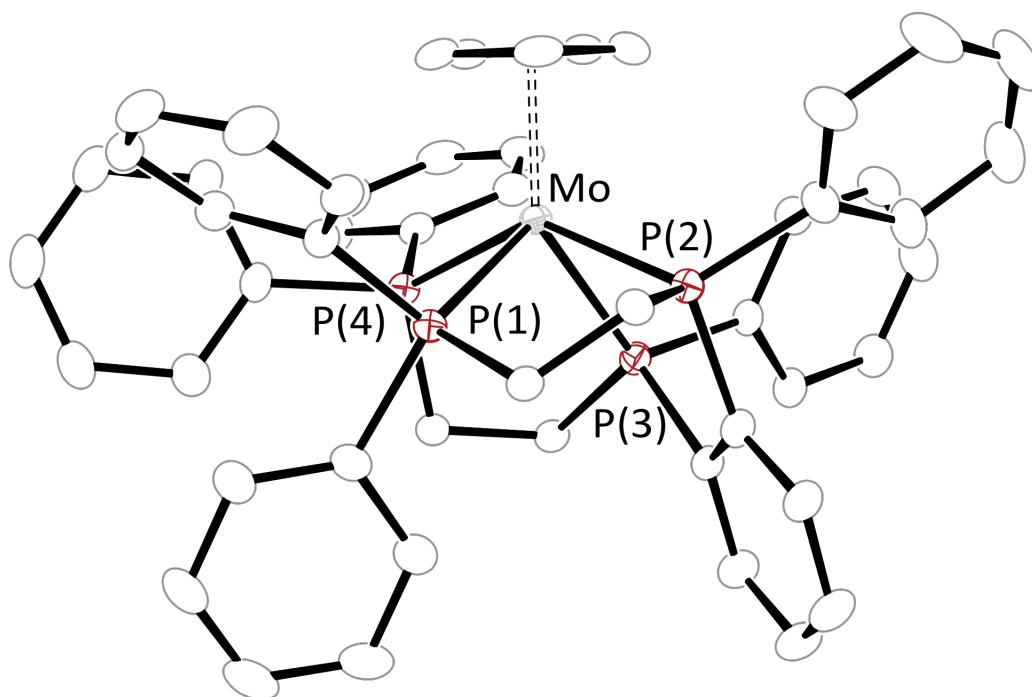


Fig. S-1 The molecular structure of the cationic part of $[\text{CpMo}(\kappa^4\text{-P4})][\text{Cl}]\cdot 0.78\text{DMF}\cdot 0.22\text{Et}_2\text{O}$ ($4\text{Cl}\cdot 0.78\text{DMF}\cdot 0.22\text{Et}_2\text{O}$) depicting the view from the axis parallel to the Cp ring. Hydrogen atoms are omitted for clarity. The Mo–Cent distance is 2.001(2) Å.

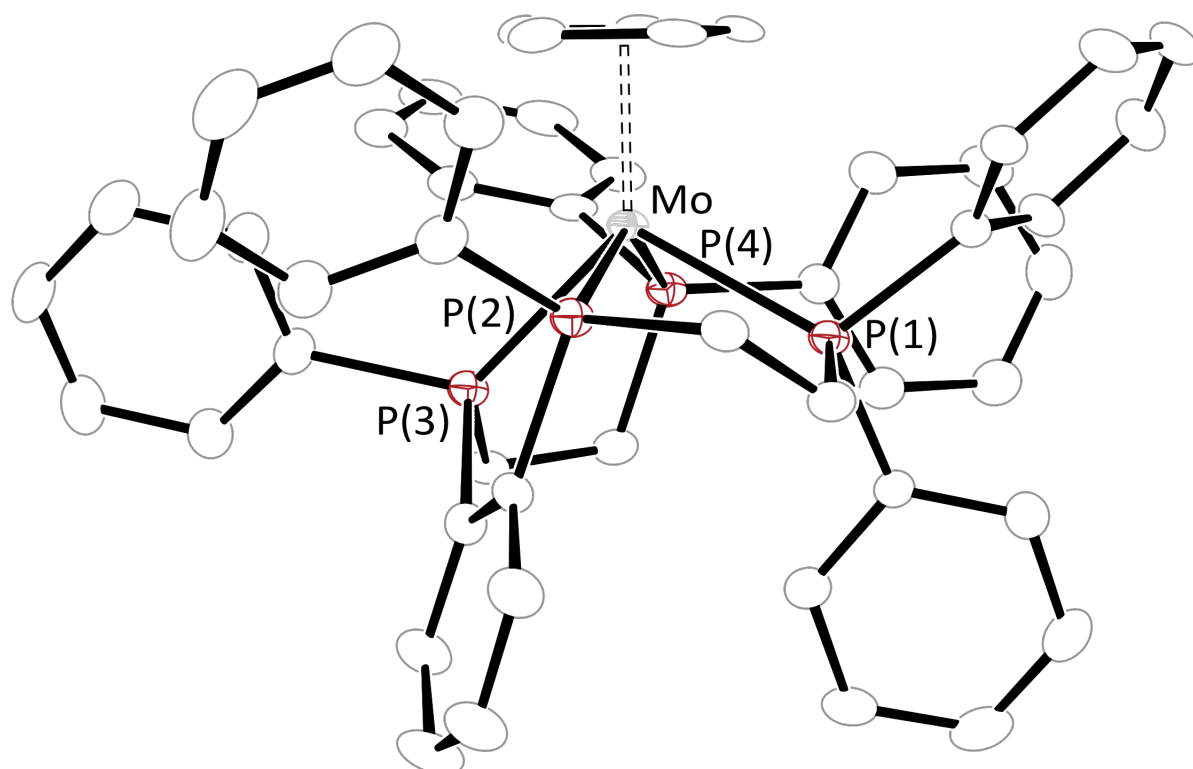


Fig. S-2 The molecular structure of the cationic part of $[\text{CpMo}(\kappa^4\text{-P4})][\text{OTf}] \cdot 2.7\text{CH}_2\text{Cl}_2$ ($4[\text{OTf}] \cdot 2.7\text{CH}_2\text{Cl}_2$) showing thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) 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: $\text{C}_{54.7}\text{H}_{52.4}\text{Cl}_{5.4}\text{F}_3\text{MoO}_3\text{P}_4\text{S}$, $M = 1258.15$, space group $P2_1/c$ (no. 14), $a = 13.665(5)$, $b = 19.171(6)$, $c = 21.184(7)$ Å, $\beta = 96.763(2)^\circ$, $V = 5511(4)$ Å³, $Z = 4$, $\mu = 0.707 \text{ mm}^{-1}$, transmn factor = 0.540–0.868, 43149 reflections collected, 12571 independent, $R_{\text{int}} = 0.0735$, the final R_1 ($I > 2\sigma(I)$) = 0.0577 and wR_2 (all data) = 0.1717 on 716 parameters.

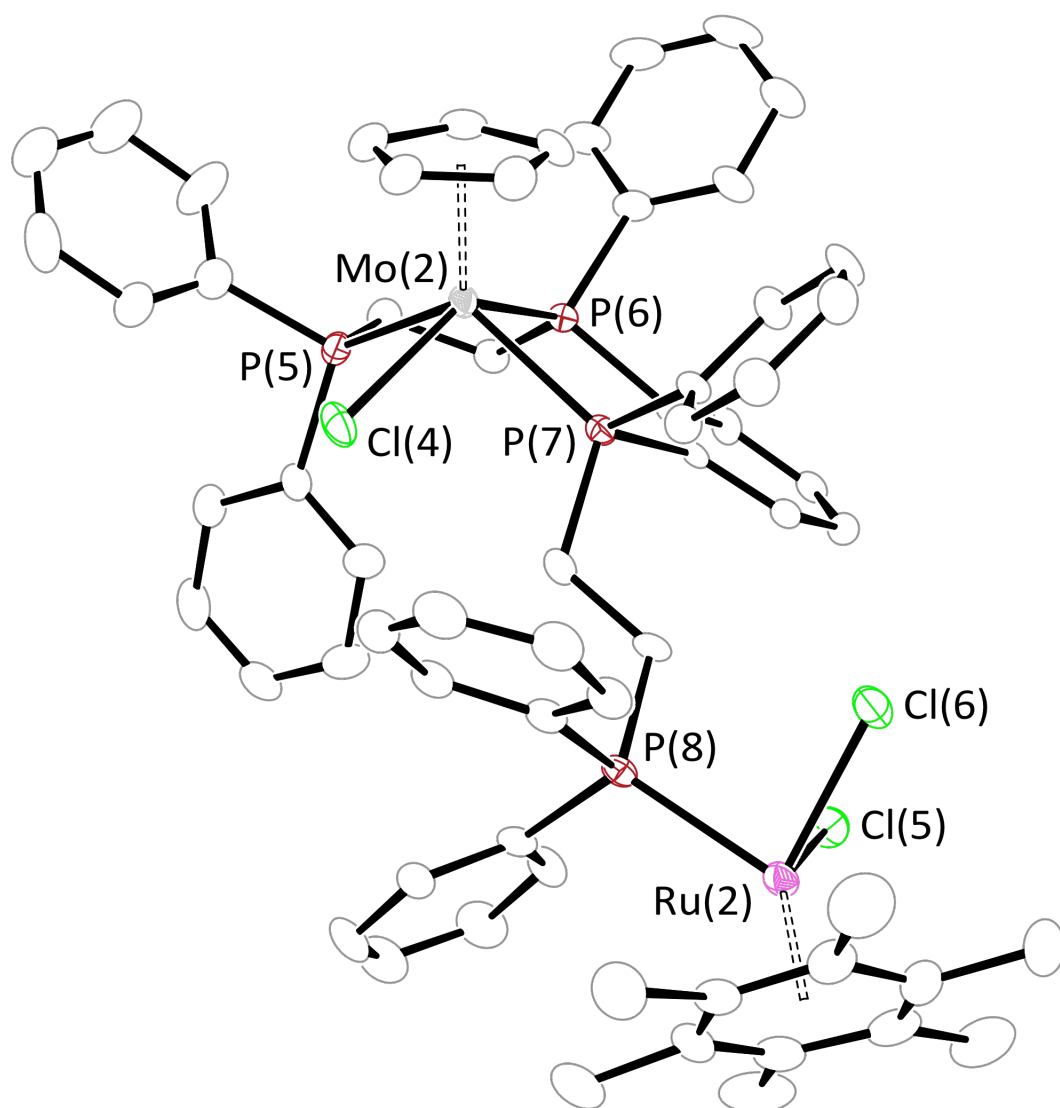


Fig. S-3 The crystal structure of the second independent molecule in the asymmetric unit of $[\text{CpMoCl}(\mu\text{-P4-1}\kappa^3\text{:2}\kappa)\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)]\cdot 2.5\text{CH}_2\text{Cl}_2$ (**11** $\cdot 2.5\text{CH}_2\text{Cl}_2$).

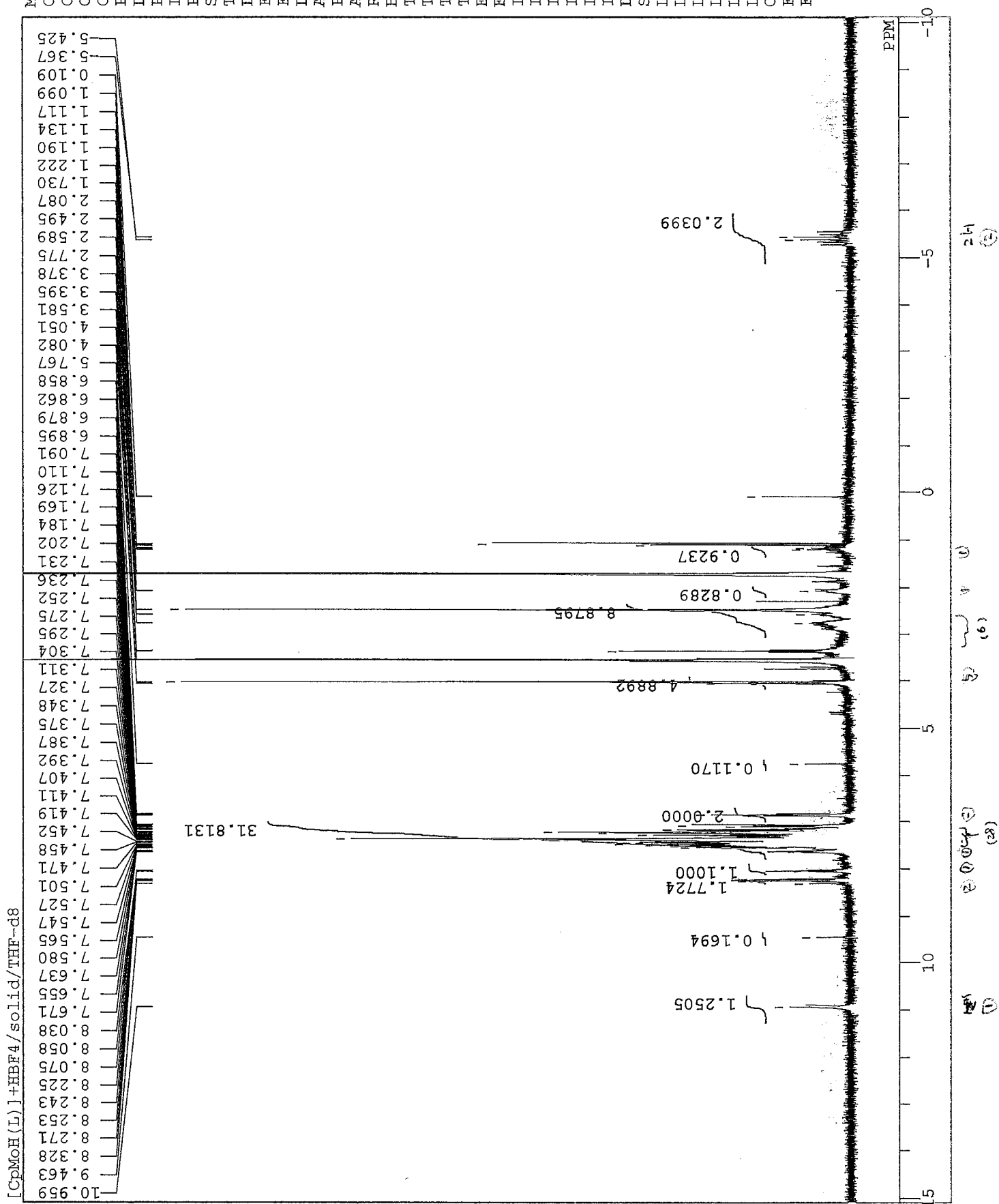


Fig. S-4 ¹H NMR spectrum of [CpMoH₂(κ³-P₄)] [BF₄] (3[BF₄]) at +20 °C (sample before recrystallization)

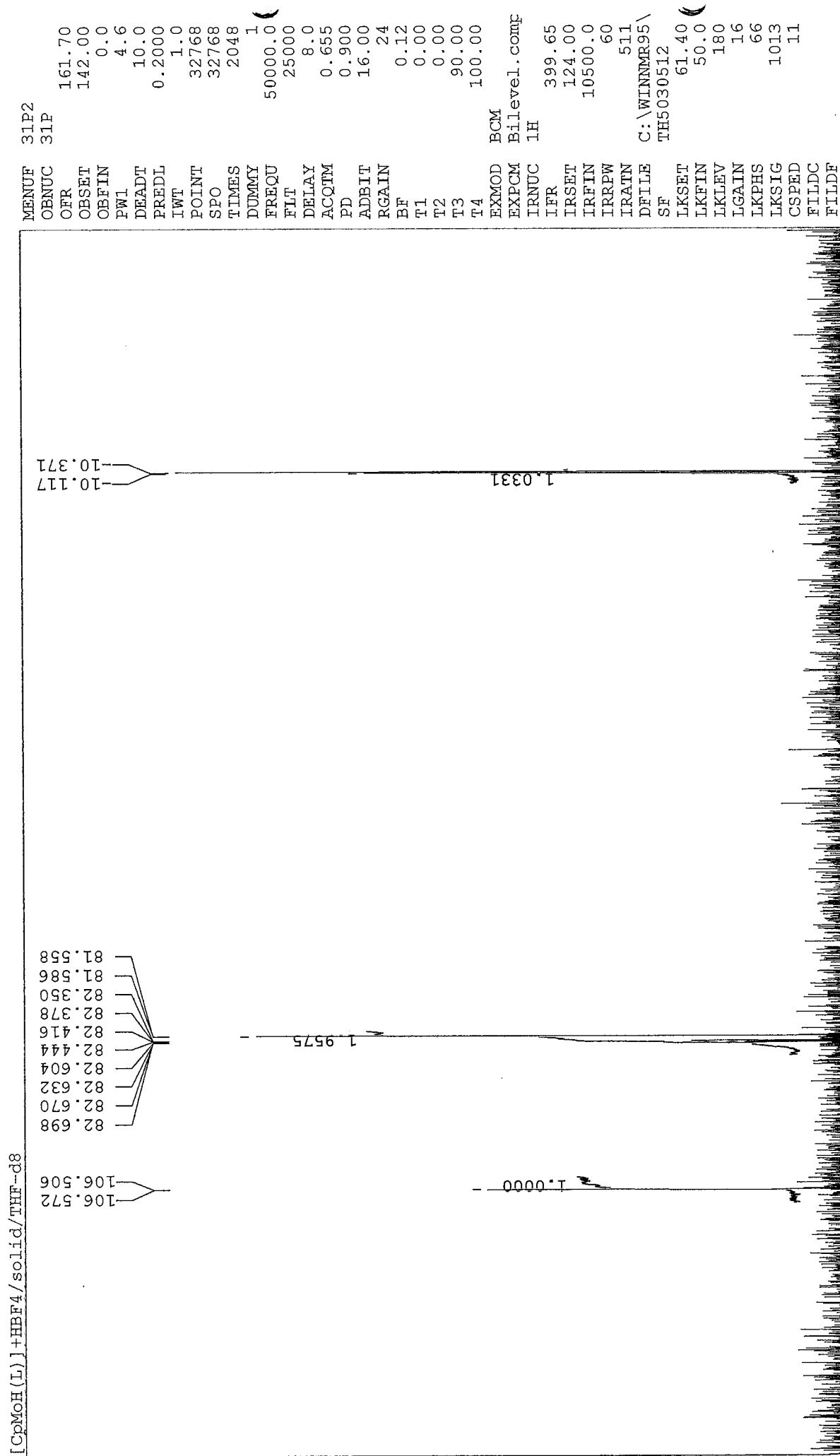
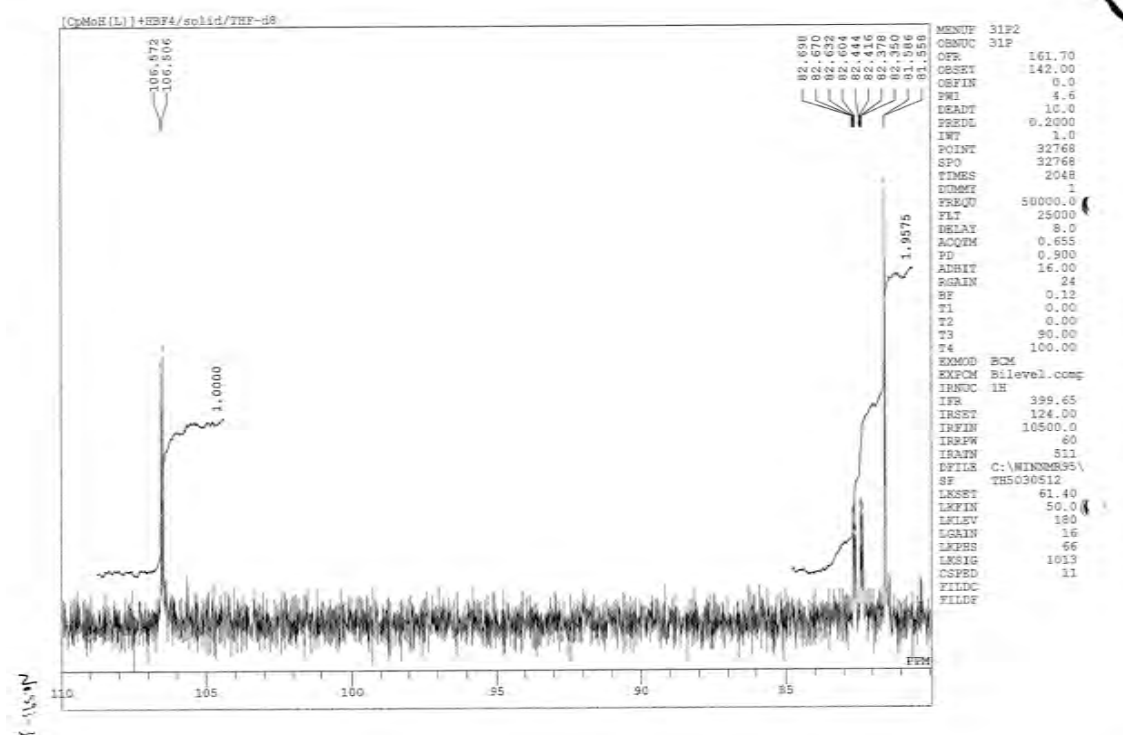
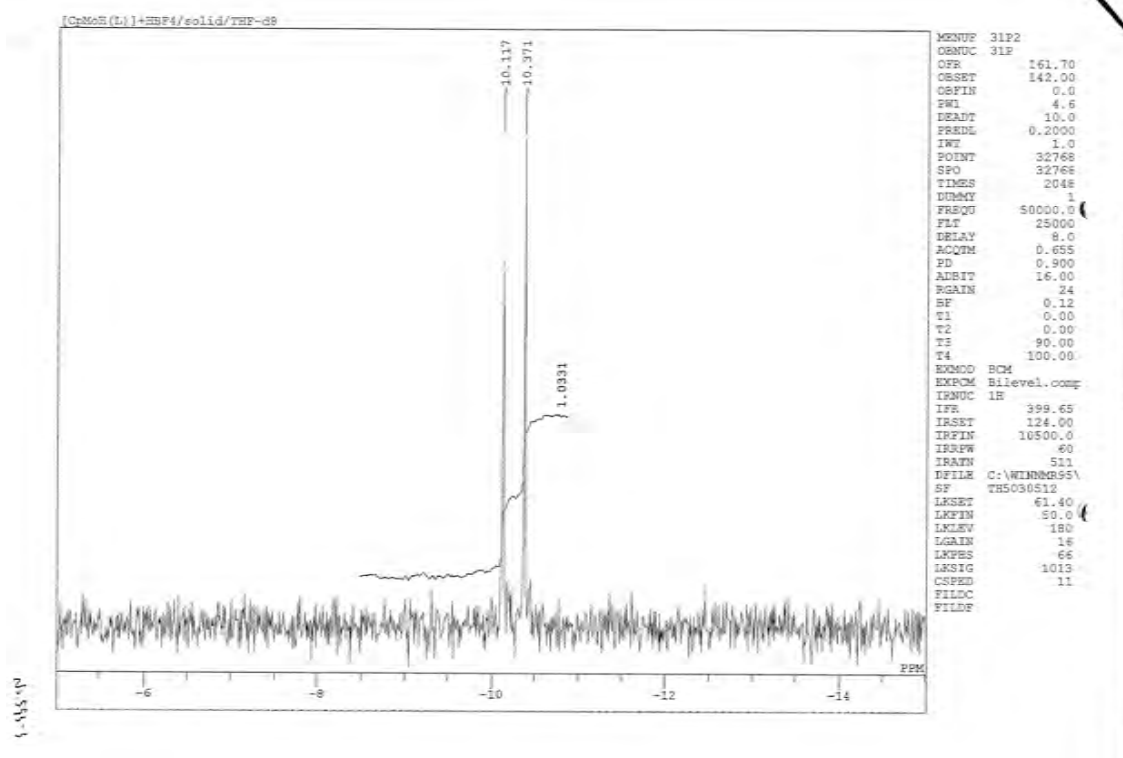


Fig. S-5 31P{1H} NMR spectrum of [CpMoH₂(κ₃-P₄)](BF₄) (3[BF₄]) at +20 °C (sample before recrystallization)



$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CpMoH}_2(\kappa^3\text{-P4})][\text{BF}_4]$ ($3[\text{BF}_4]$)
THF- d_8 , 20 °C

Fig. S-5(2) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CpMoH}_2(\kappa^3\text{-P4})][\text{BF}_4]$ ($3[\text{BF}_4]$) at +20 °C (sample before recrystallization)

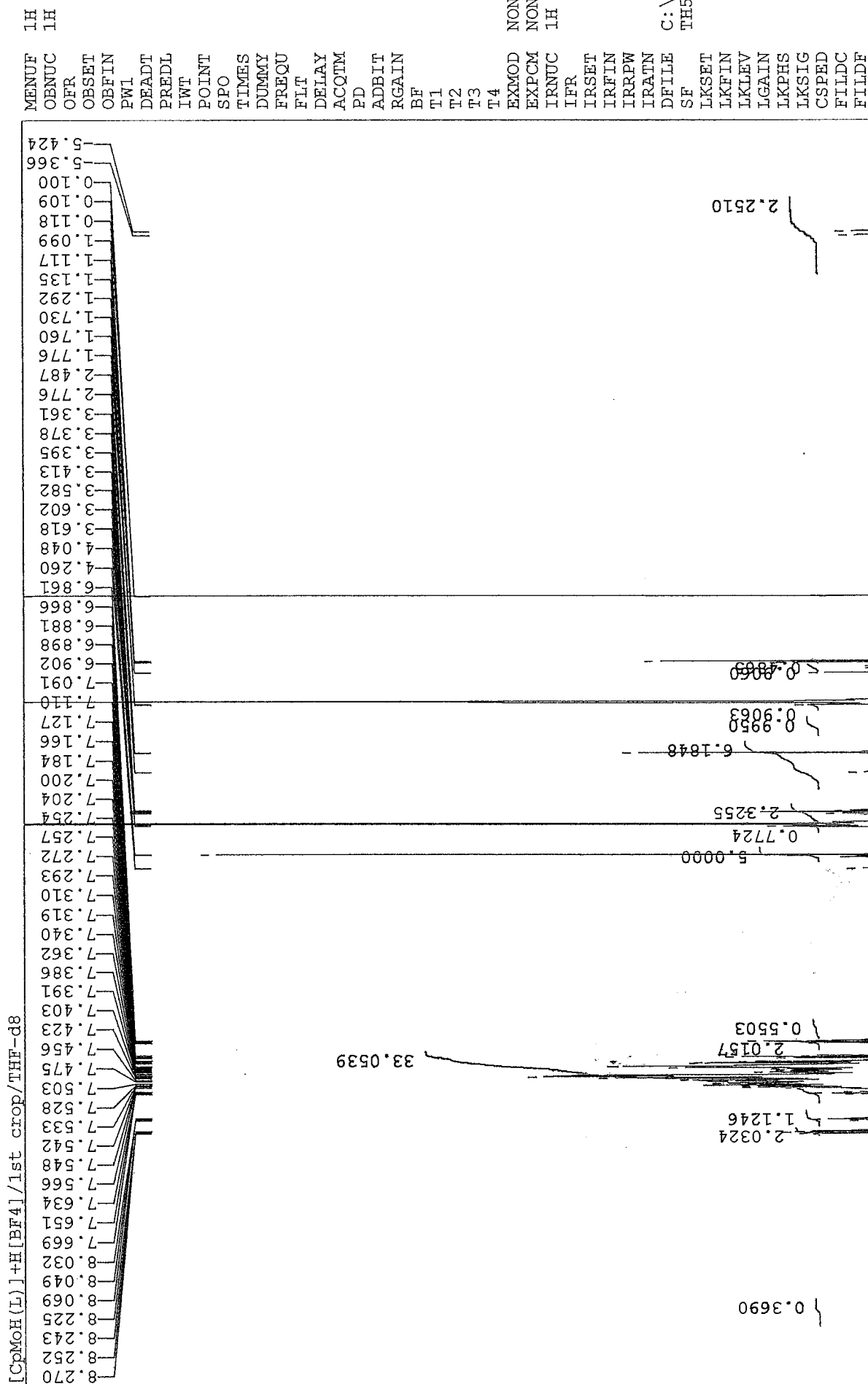


Fig. S-6 1H NMR spectrum of [CpMoH2(κ3-P4)][BF4] (3[BF4]) at +20 °C (recrystallized sample)

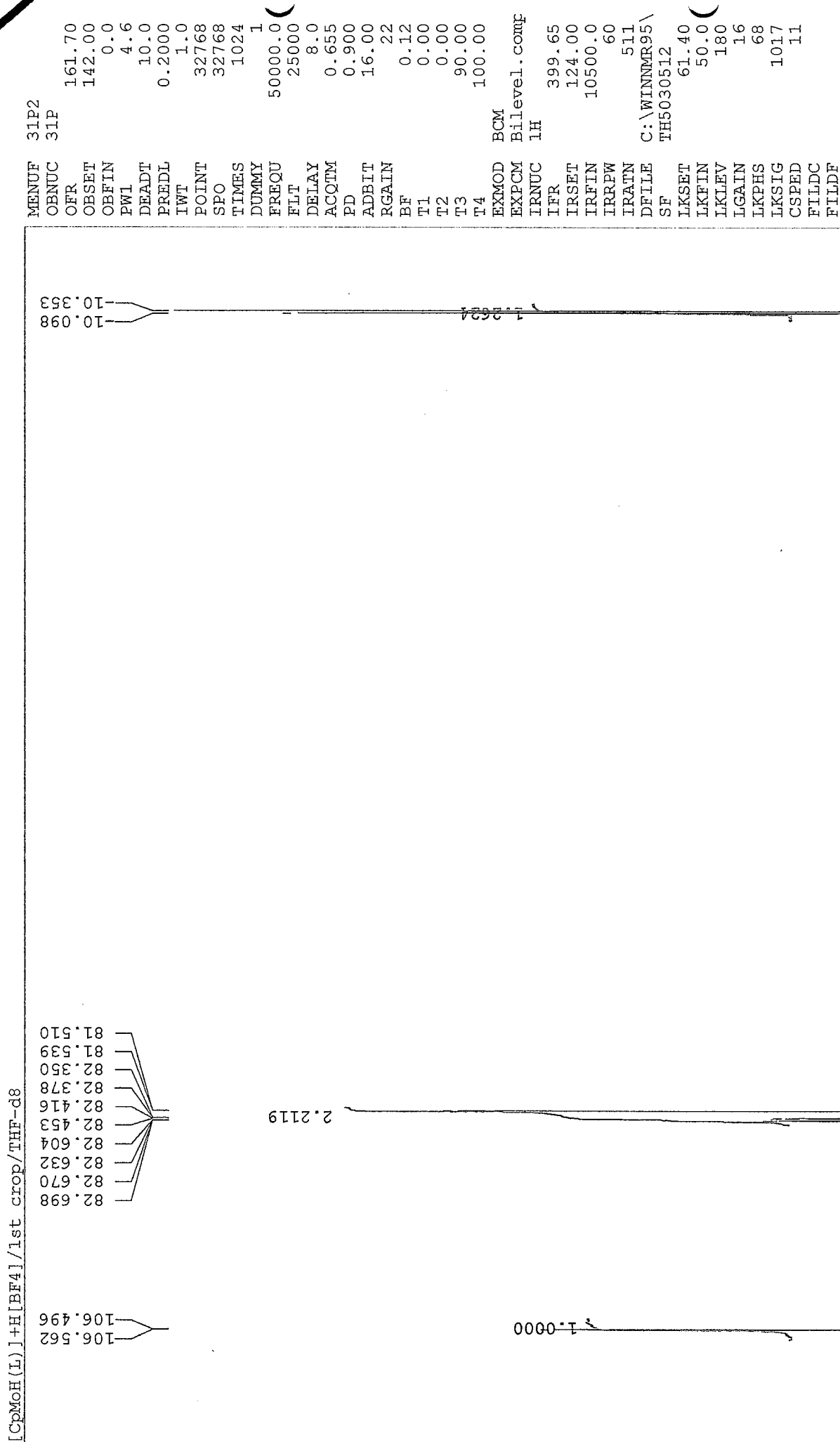


Fig. S-7 31P{1H} NMR spectrum of [CpMoH₂(κ₃-P₄)](BF₄) (3[BF₄]) at +20 °C (recrystallized sample)

MENUF 1H
OENUC 1H

399.65

124.00

8500.0

6.3

34.3

0.2000

1.0

65536

65536

64

1

16000.0

8000

25.0

4.096

2.904

16.00

23

0.12

0.00

0.00

90.00

100.00

NON

EXMOD

EXPCM

NON:Single.c

1H

IRNUC

IFR

399.65

124.00

10500.0

60

511

D:\CPMOH2L\

TH5030512

61.40

50.0

180

16

68

717

12

)

[CpMoH2(L)][BF4]/THF-d8/-70deg

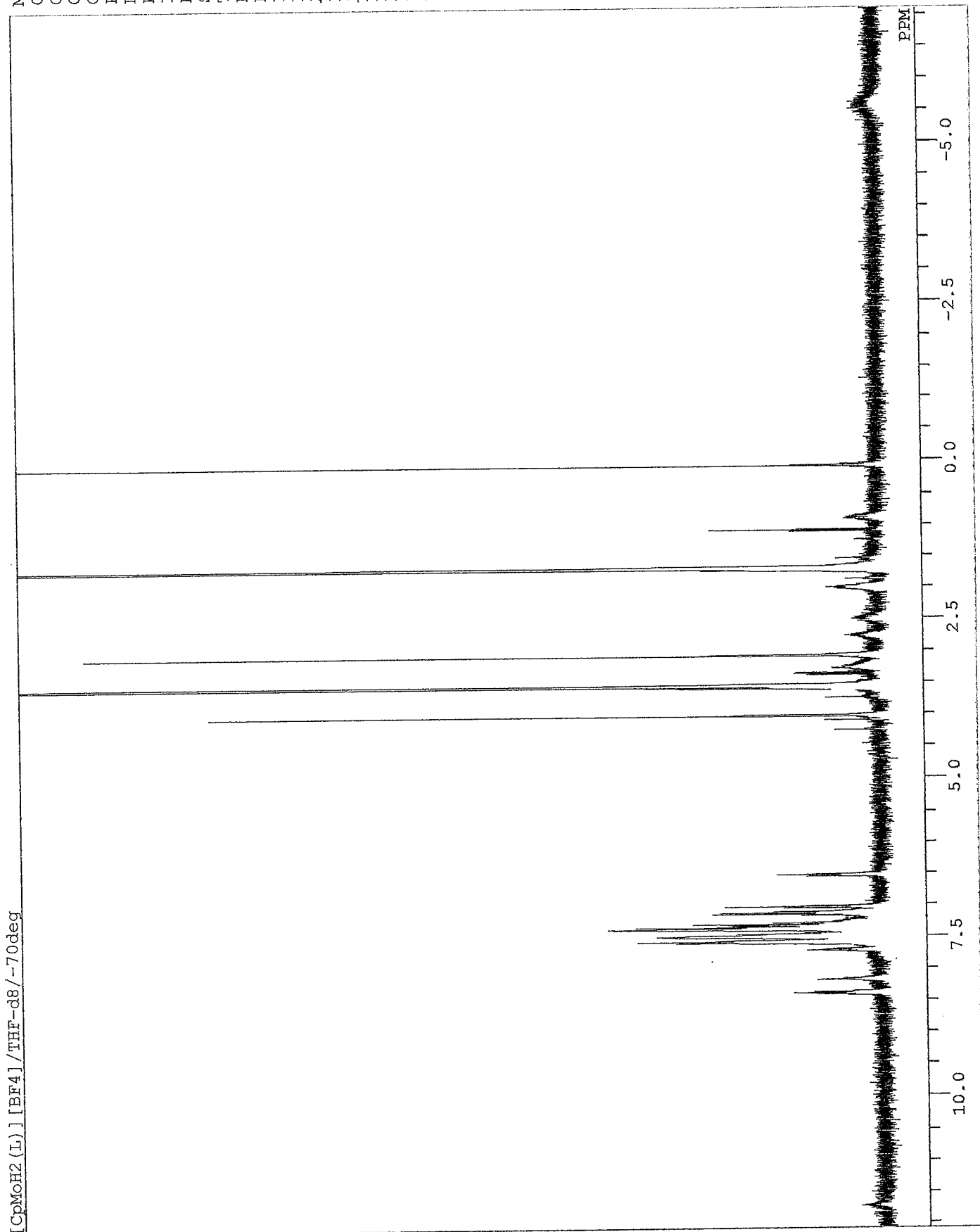


Fig. S-9 1H NMR spectrum of [CpMoH2(κ3-P4)][BF4] (3[BF4]) at -70 °C (recrystallized sample)

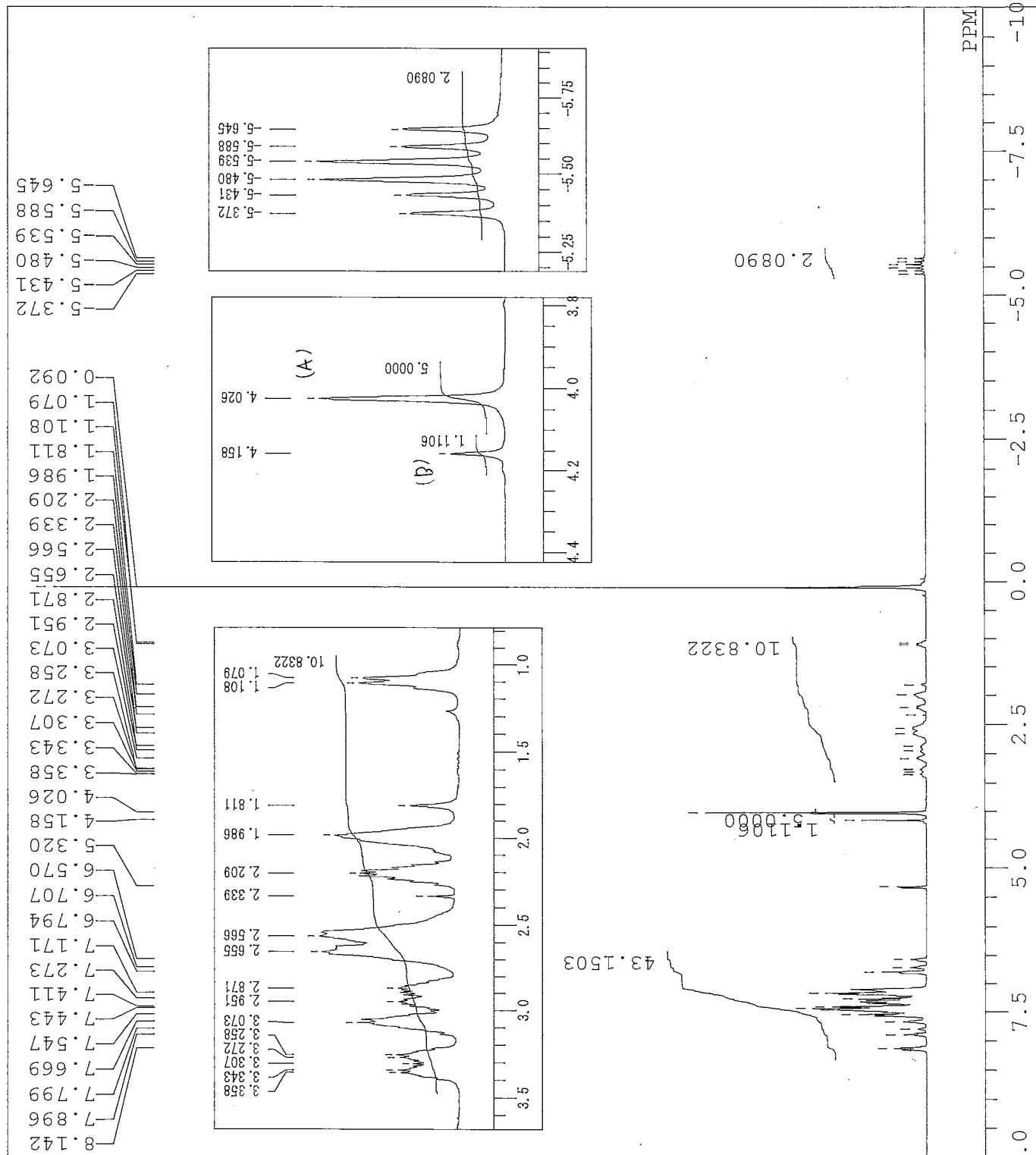
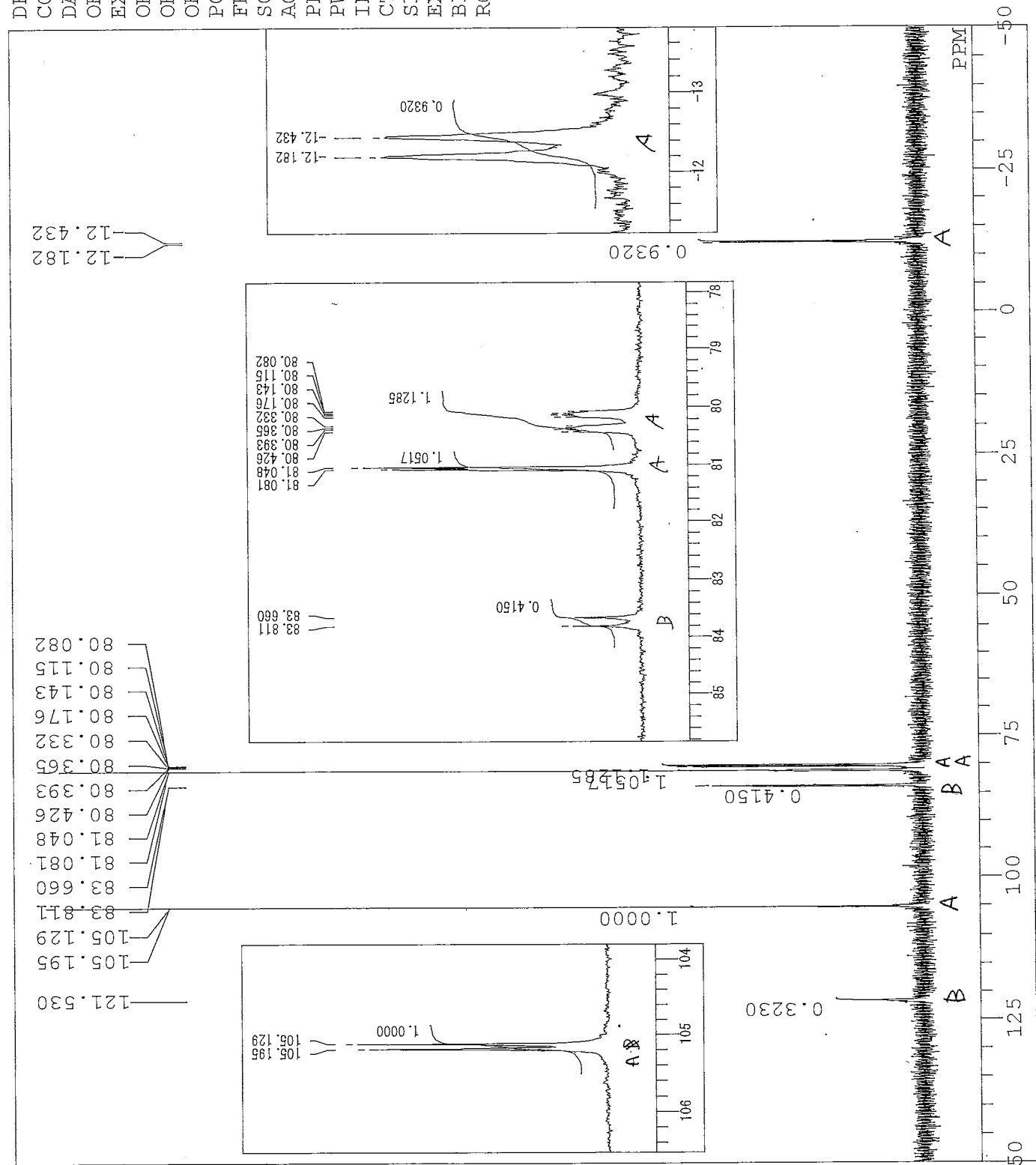


Fig. S-10 1H NMR spectrum of a mixture of [CpMoH2(κ3-P4)][OTf] (3[OTf]) and [CpMo(κ4-P4)][OTf] (4[OTf]) (crude reaction mixture)

DDFILE	C:\Users\IWA\NMR\ofbfNfj
COMNT	
DATIM	Mon May 08 16:46:31 2006
OBNUC	31P
EXMOD	BCM
OBFRQ	161.70 MHz
OBSET	142.00 KHz
OBFIN	0.0 Hz
POINT	65536
FREQU	50000.0 Hz
SCANS	542
ACQTM	0.655 sec
PD	0.900 sec
PW1	4.6 us
IRNUC	1H
CTEMP	20.9 C
SLVNT	CD2CL
EXREF	0.00 ppm
BF	1.20 Hz
RGAIN	24



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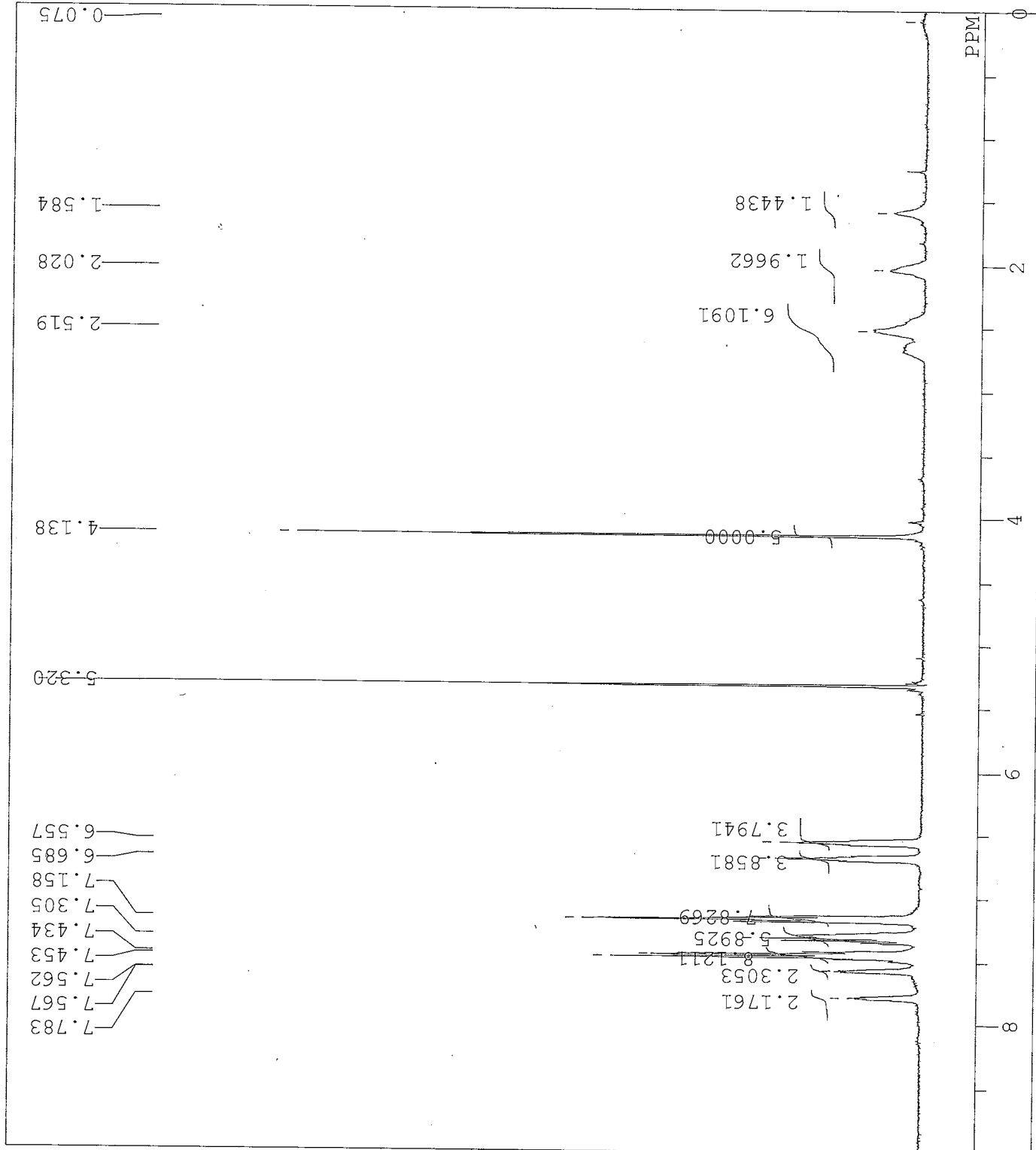
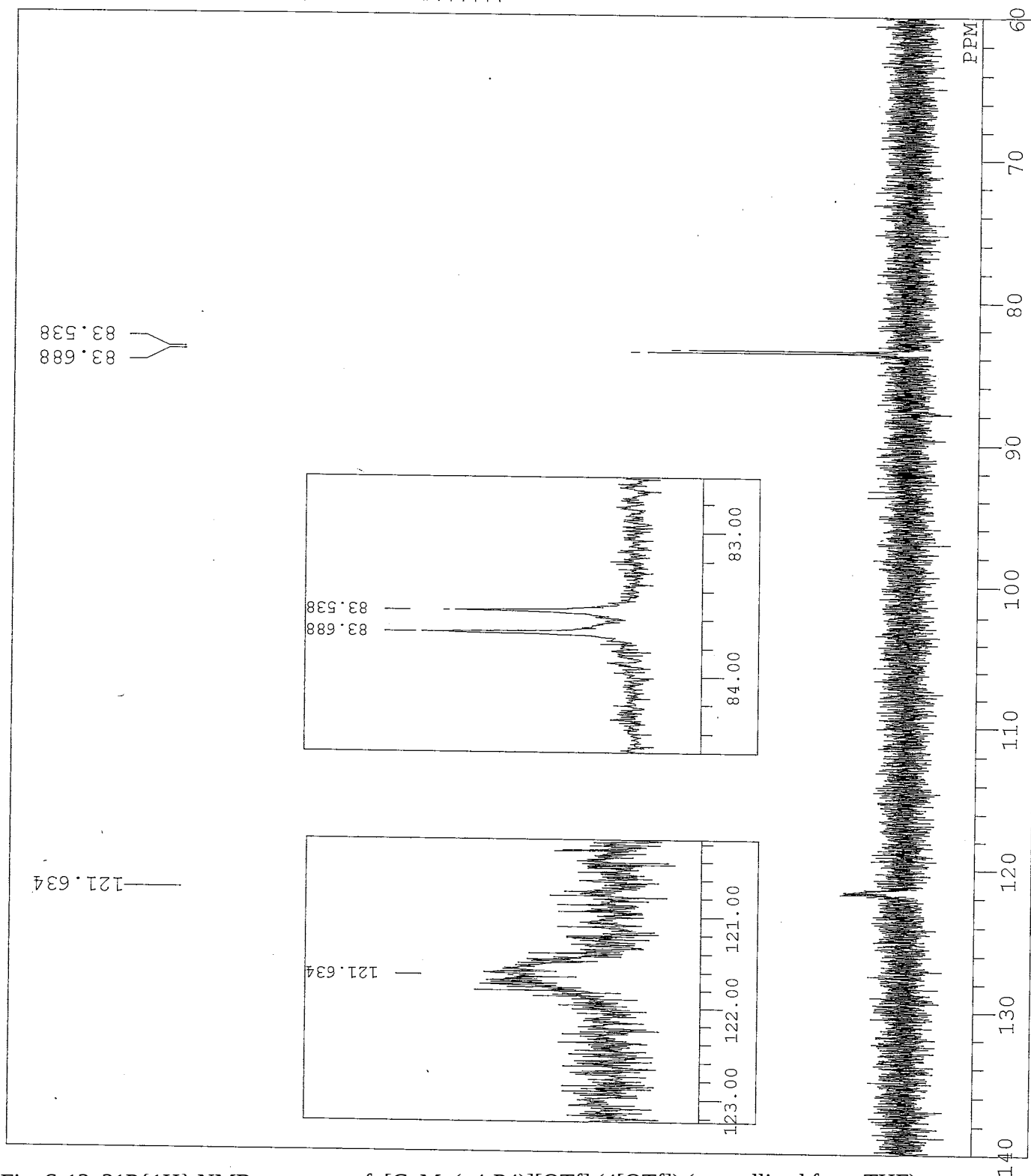
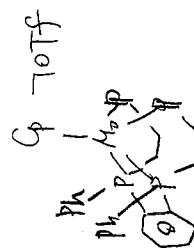


Fig. S-12 ¹H NMR spectrum of $[\text{CpMo}(\kappa^4\text{-P4})][\text{OTf}]$ (4[OTf]) (crystallized from THF)



DFILE C:\Users\IWA\NMR\ofbfNfAfbfv
 COMNT
 DATIM Tue May 16 18:27:02 2006
 OBNUC 31P
 EXMOD BCM
 OBFRQ 161.70 MHz
 OBSET 142.00 KHz
 OBFIN 0.0 Hz
 POINT 65536
 FREQU 50000.0 Hz
 SCANS 258
 ACQTM 0.655 sec
 PD 0.900 sec
 PW1 4.6 us
 IRNUC 1H
 CTEMP 20.5 C
 SLVNT CD2CL
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 24



$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of
 [CpMo(κ^4 -P4)][OTf]
 (4[OTf])
 CD₂Cl₂, 20.5 °C

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

DFILE 140318 1-1.jdf
 COMNT [CpMo(P4)]Cl/CD2Cl2
 DATIM 2014-03-18 15:22:60
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 16384
 FREQU 7503.00 Hz
 SCANS 16
 ACQTM 2.1837 sec
 PD 5.0000 sec
 PW1 5.10 usec
 IRNUC 1H
 CTEMP 20.1 C
 SLVNT CD2Cl2
 EXREF 5.32 ppm
 BF 0.12 Hz
 RGAIN 50

¹H NMR spectrum of
 [CpMo(κ⁴-P4)][Cl]·CH₂Cl₂
 (4[Cl]·CH₂Cl₂)
 CD₂Cl₂, 20.1 °C

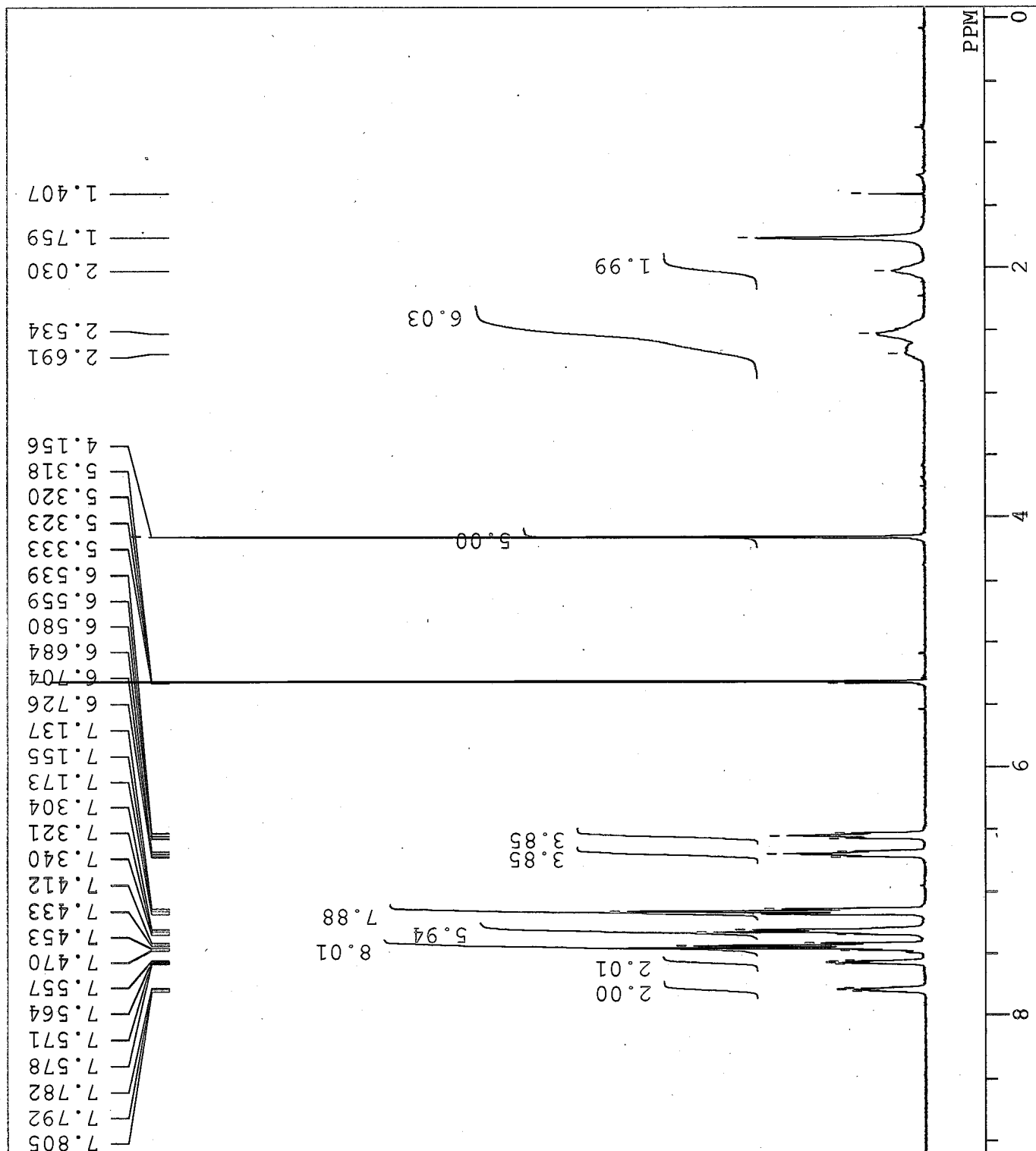
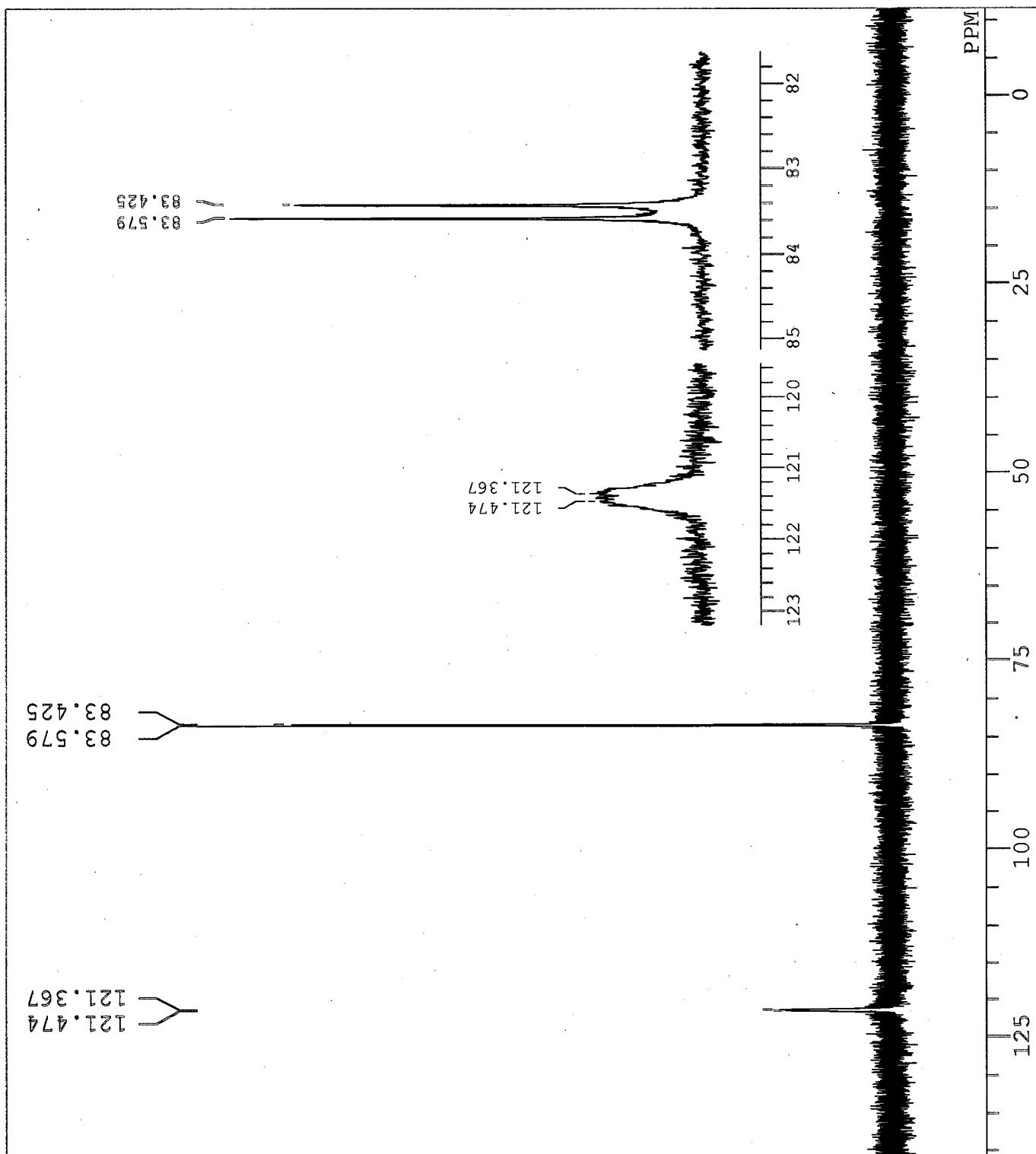


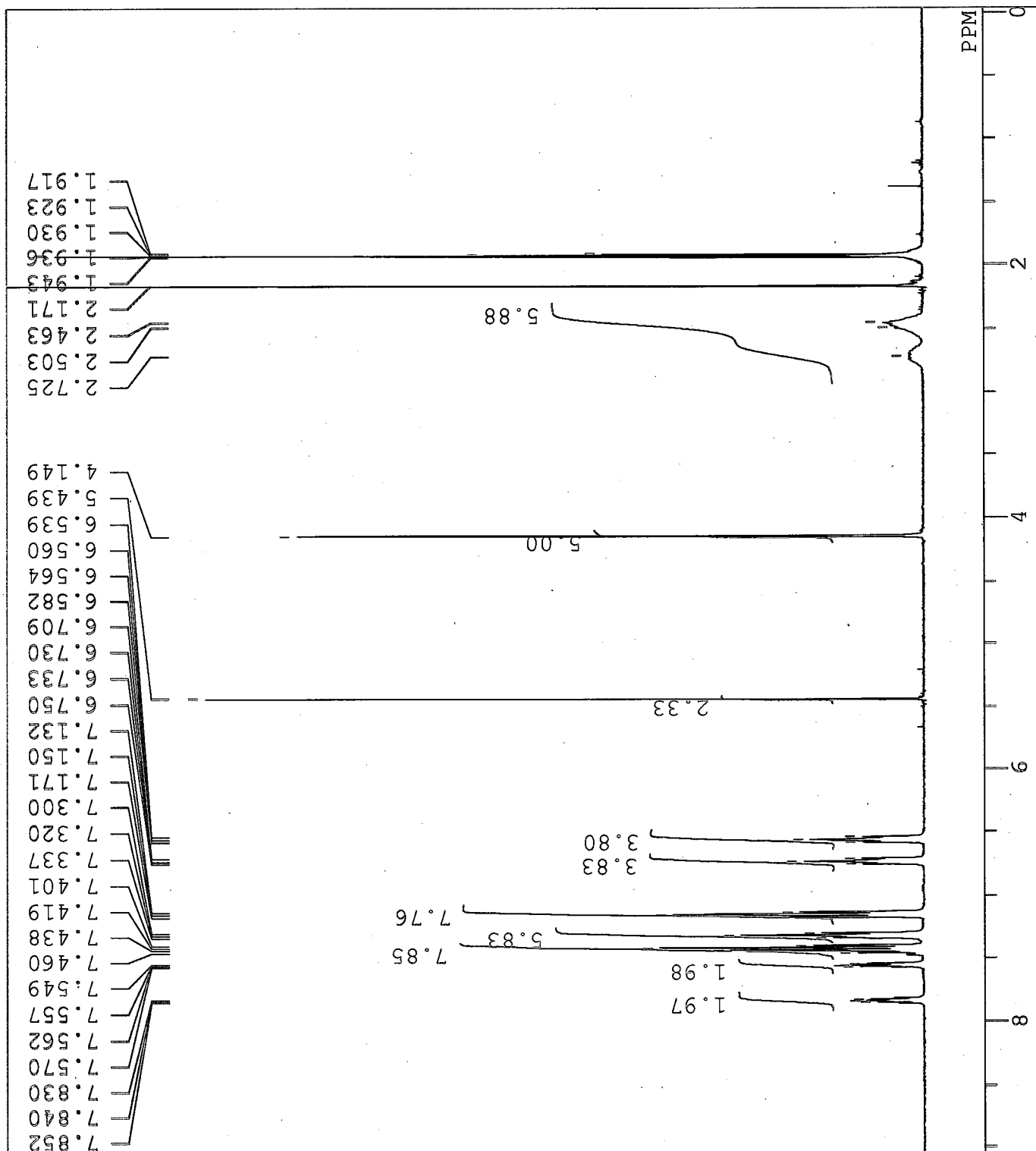
Fig. S-14 ¹H NMR spectrum of [CpMo(κ⁴-P4)][Cl]·CH₂Cl₂ (4[Cl]·CH₂Cl₂) in CD₂Cl₂

DFILE 140318 2-1.jdf
 COMNT [CpMo(P4)]Cl/CD2Cl2
 DATIM 2014-03-18 15:30:23
 OBNUC 31P
 EXMOD single_pulse_dec
 OBFRQ 161.84 MHz
 OBSET 6.83 KHz
 OBFIN 0.69 Hz
 POINT 65536
 FREQU 71022.72 Hz
 SCANS 258
 ACQTM 0.4614 sec
 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



$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of
 [CpMo(κ^4 -P4)][Cl]·CH₂Cl₂
 (4[Cl]·CH₂Cl₂)
 CD₂Cl₂, 20.4 °C

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



DFILE 130313 1-1.jdf
 COMNT [CpMo(P4)]Cl/plate f
 DATIM 2013-03-13 19:17:36
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 16384
 FREQU 7503.00 Hz
 SCANS 16
 ACQTM 2.1837 sec
 PD 4.5000 sec
 PW1 5.10 usec
 IRNUC 1H
 CTEMP 19.5 C
 SLVNT CD3CN
 EXREF 1.93 ppm
 BF 0.12 Hz
 RGAIN 48

1H NMR spectrum of
 [CpMo(κ^4 -P4)][Cl]·CH₂Cl₂
 (4[Cl]·CH₂Cl₂)
 CD₃CN, 19.5 °C
 for determination of CH₂Cl₂

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

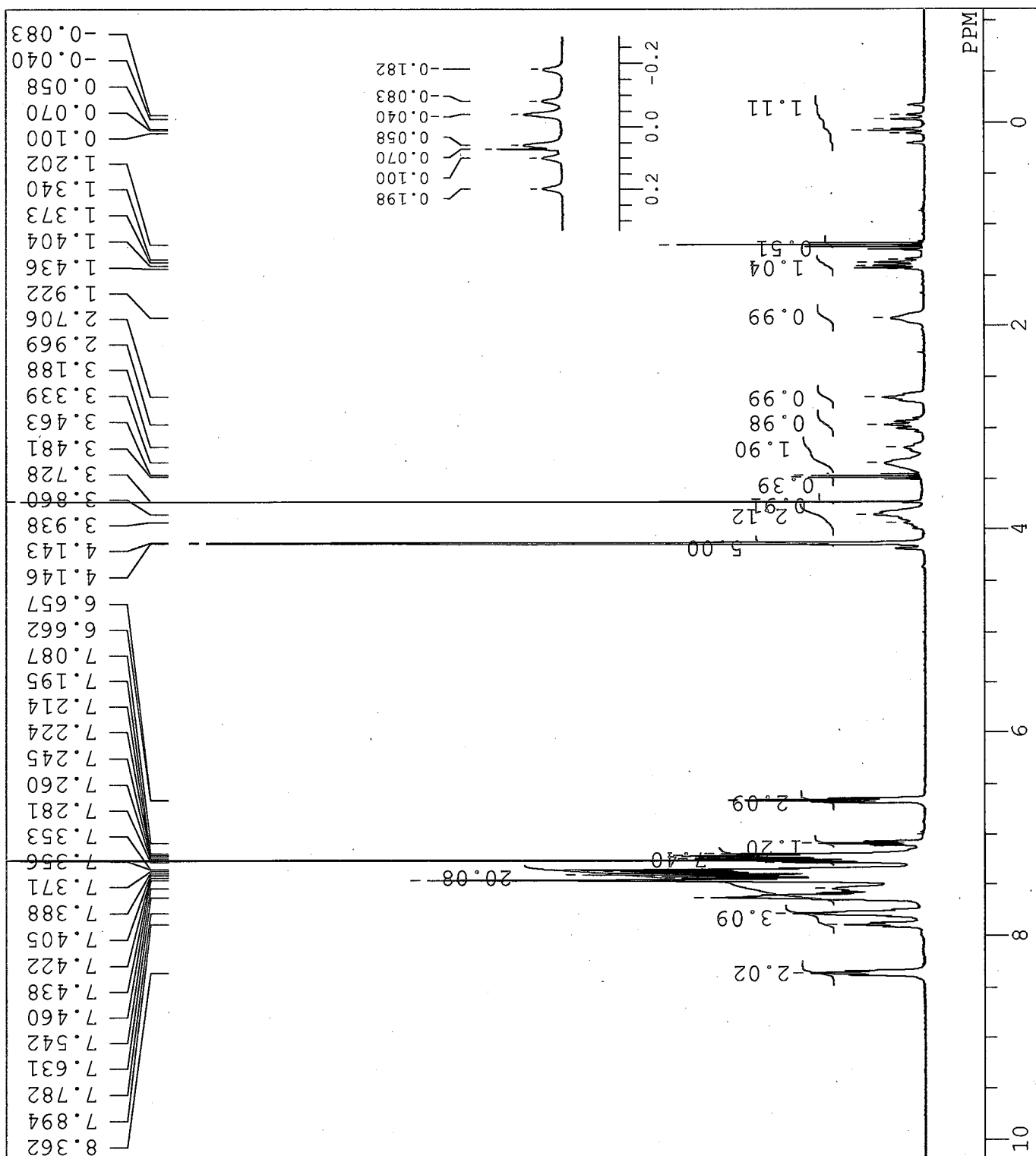


Fig. S-17 ¹H NMR spectrum of [CpMoHI(κ³-P4)][I] (5[I])

DFILE 140405 9-1.jdf
 COMNT [CpMoHI(P4)][I]/CDCl
 DATIM 2014-04-06 02:38:55
 OBNUC 31P
 EXMOD single_pulse_dec
 OBFRQ 161.84 MHz
 OBSET 6.83 KHz
 OBFIN 0.69 Hz
 POINT 65536
 FREQU 71022.72 Hz
 SCANS 261
 ACQTM 0.4614 sec
 PD 1.0000 sec
 PW1 4.68 usec
 IRNUC 1H
 CTEMP 21.3 C
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 58

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of
 [CpMoHI($\kappa^3\text{-P4}$)]I] (5[I])
 CDCl₃, 21.3 °C

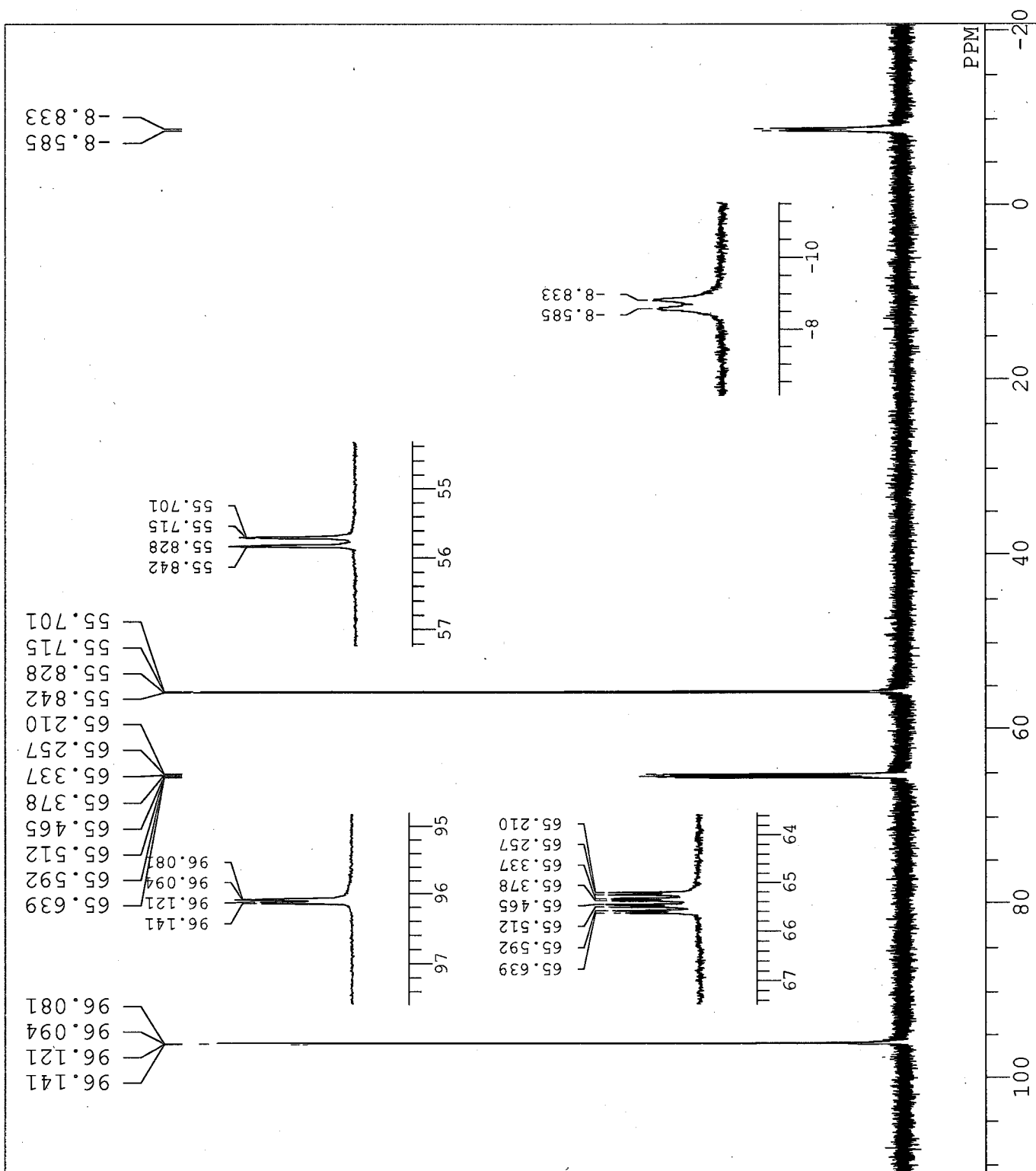
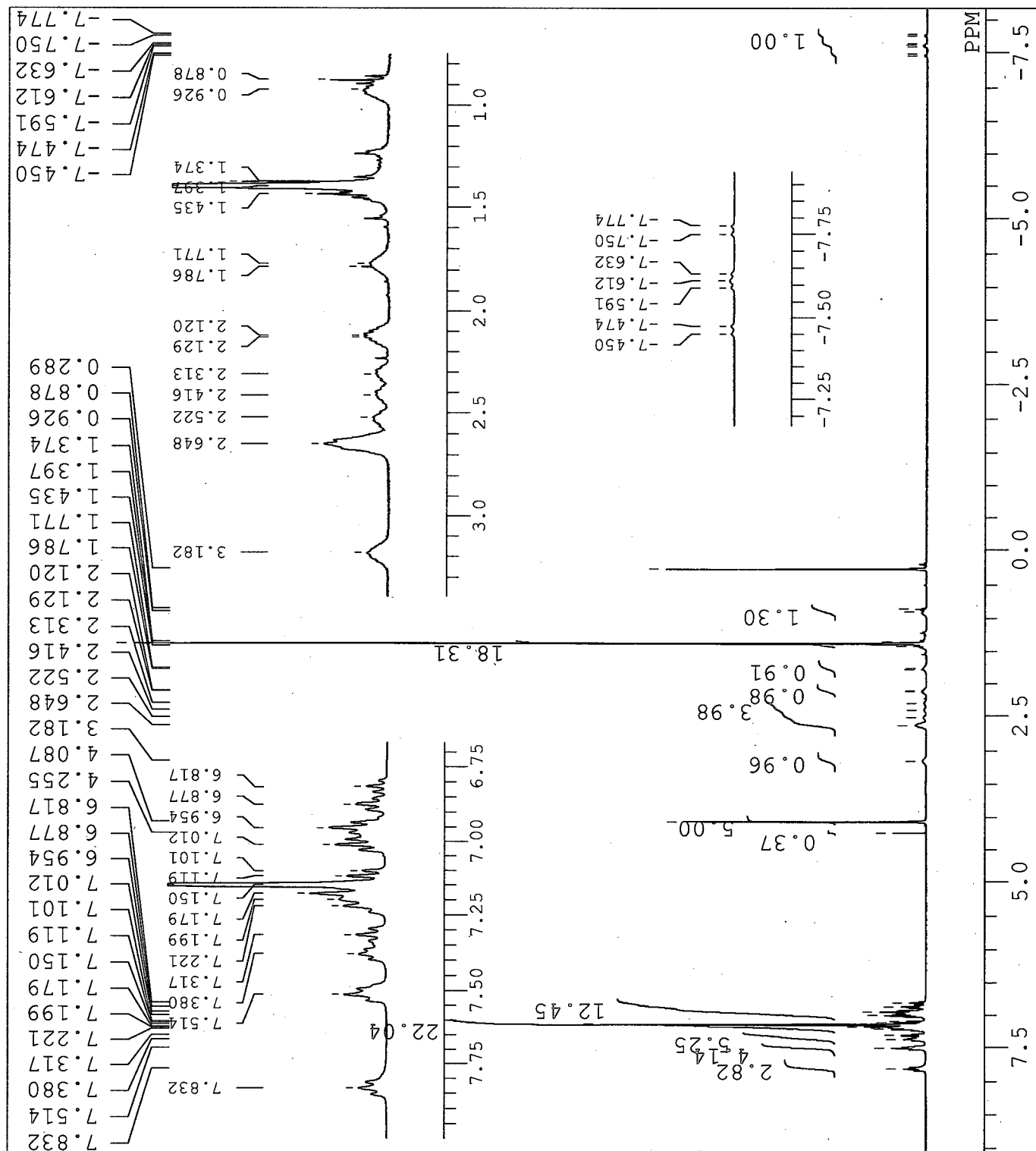


Fig. S-18 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of [CpMoHI($\kappa^3\text{-P4}$)]I] (5[I])

DFILE 140406 5-1.jdf
 COMNT [CpMoH(P4)RuCl2Hmb]/
 DATIM 2014-04-07 01:50:34
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 2.19 KHz
 OBFIN 8.38 Hz
 POINT 65536
 FREQU 15024.04 Hz
 SCANS 16
 ACQTM 2.1810 sec
 PD 10.0000 sec
 PW1 5.10 usec
 IRNUC 1H
 CTEMP 21.1 C
 SLVNT C6D6
 EXREF 7.15 ppm
 BF 0.12 Hz
 RGAIN 42

¹H NMR spectrum of
 [CpMoH(μ-P4-1κ³:2κ)Ru-
 Cl₂(η⁶-C₆Me₆)]·0.25CH₂Cl₂
 (6·0.25CH₂Cl₂)
 C₆D₆, 21.1 °C



DFILE 140406 6-1.jdf
 COMNT [CpMoH(P4)RuCl2Hmb]/
 DATIM 2014-04-07 02:15:17
 OBNUC 31P
 EXMOD single_pulse_dec
 OBFRQ 161.84 MHz
 OBSET 6.83 KHz
 OBFIN 0.69 Hz
 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

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of
 [CpMoH(μ -P4-1 κ^3 :2 κ)Ru-
 Cl $_2$ (η^6 -C $_6$ Me $_6$)]·0.25CH $_2$ Cl $_2$
 (6·0.25CH $_2$ Cl $_2$)
 C $_6$ D $_6$, 21.6 °C

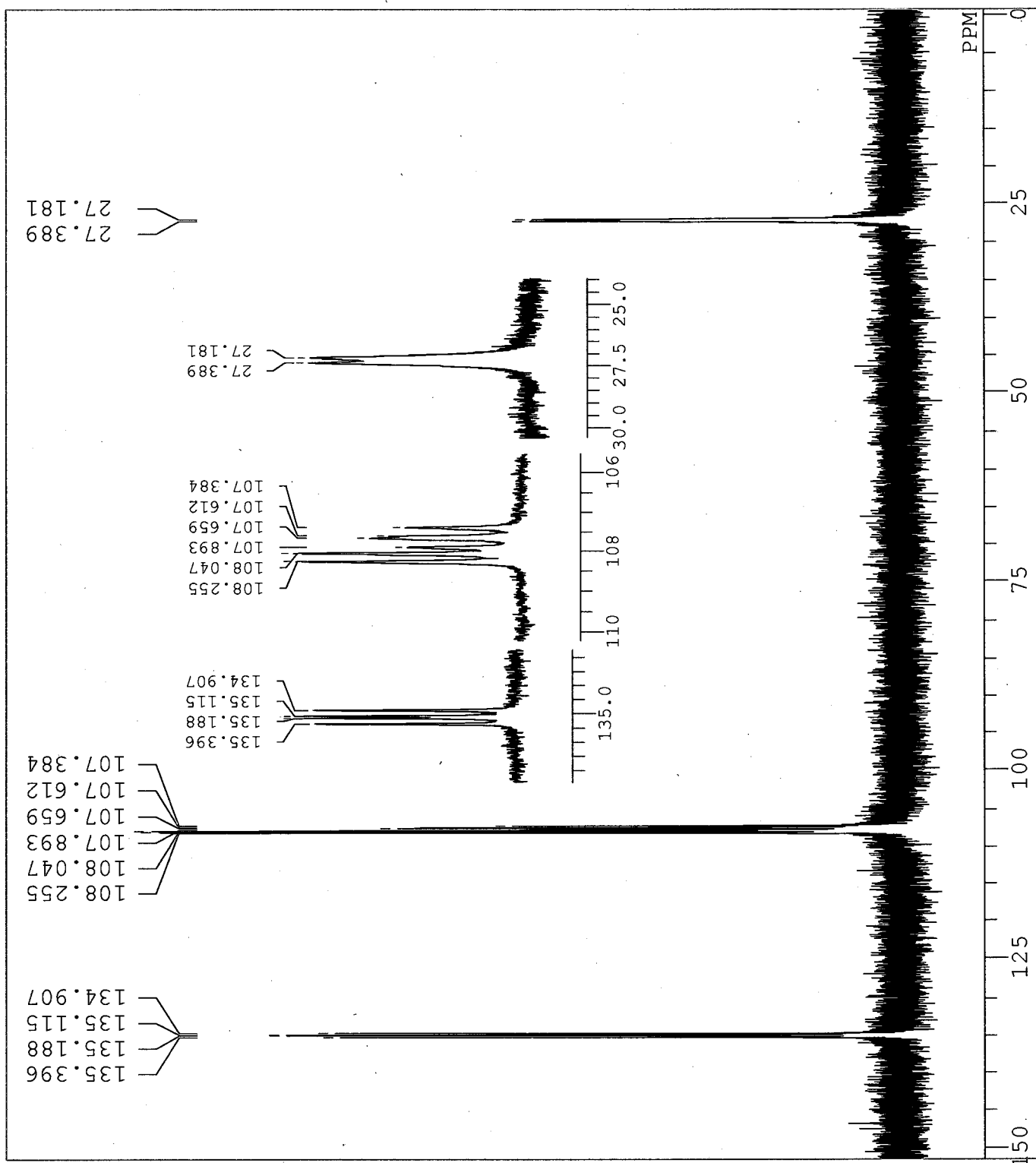
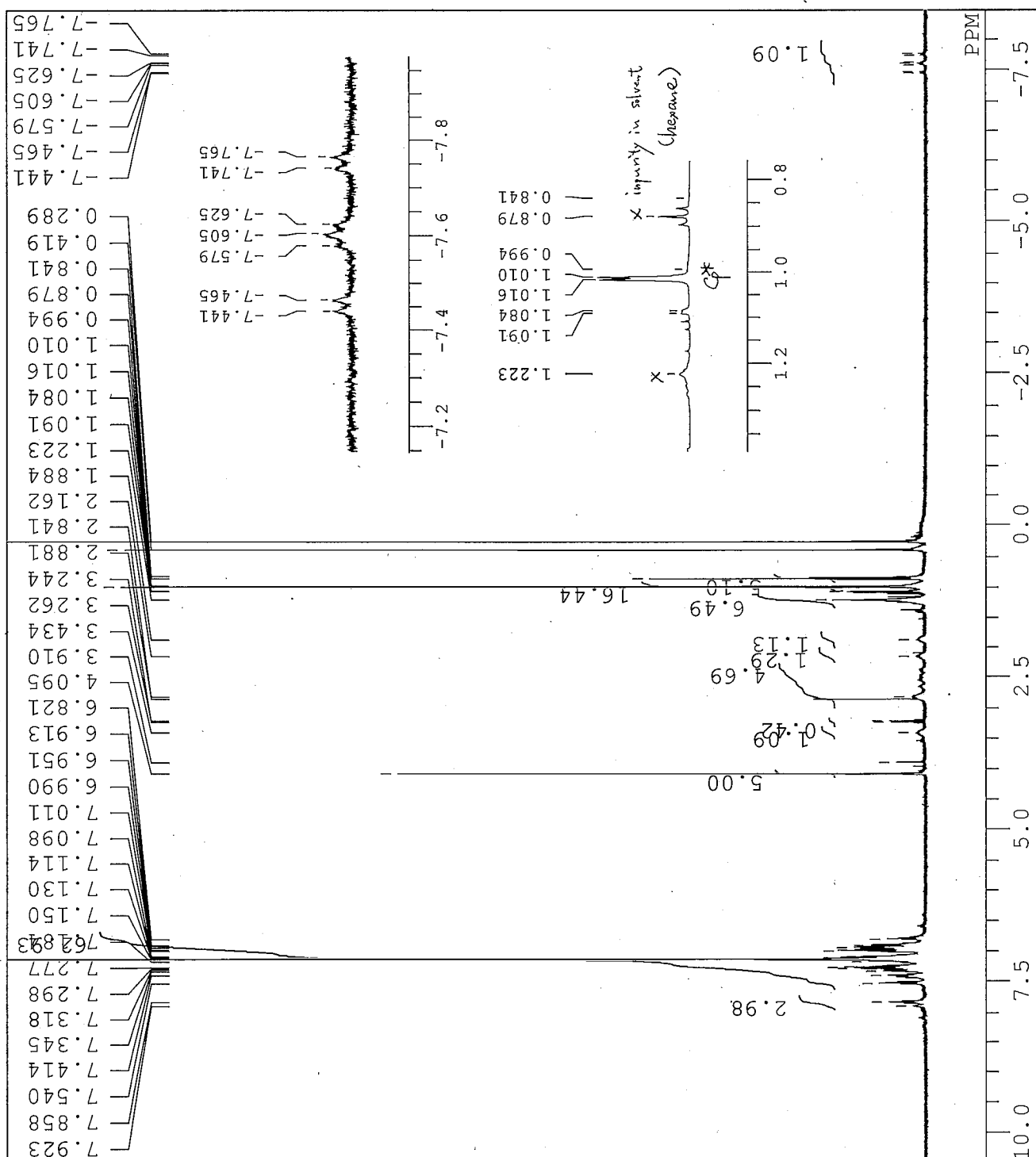


Fig. S-20 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of [CpMoH(μ -P4)RuCl $_2$ (C $_6$ Me $_6$)]·0.25CH $_2$ Cl $_2$ (6·0.25CH $_2$ Cl $_2$)

DFILE exp10-crystal-1H.ALS
 COMNT
 DATIM Wed Jul 15 15:47:10 2005
 OBNUC 1H
 EXMOD NON
 OBFRQ 399.65 MHz
 OBSET 124.00 KHz
 OBFIN 5500.00 Hz
 POINT 131072
 FREQU 16000.00 Hz
 SCANS 37
 ACQTM 4.0960 sec
 PD 2.9040 sec
 PW1 6.50 usec
 IRNUC 1H
 CTEMP 20.9 C
 SLVNT C6D6
 EXREF 7.15 ppm
 BF 0.12 Hz
 RGAIN 21



DFILE exp10-crystal-31P.ALS
 COMNT
 DATIM Wed Jul 15 15:40:55 2009
 OBNUC 31P
 EXMOD BCM
 OBFRQ 161.70 MHz
 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

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of
 $[\text{CpMoH}(\mu\text{-P4-1}\kappa^3\text{2}\kappa)\text{-IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)]$ (7)
 C_6D_6 , 22.7 °C

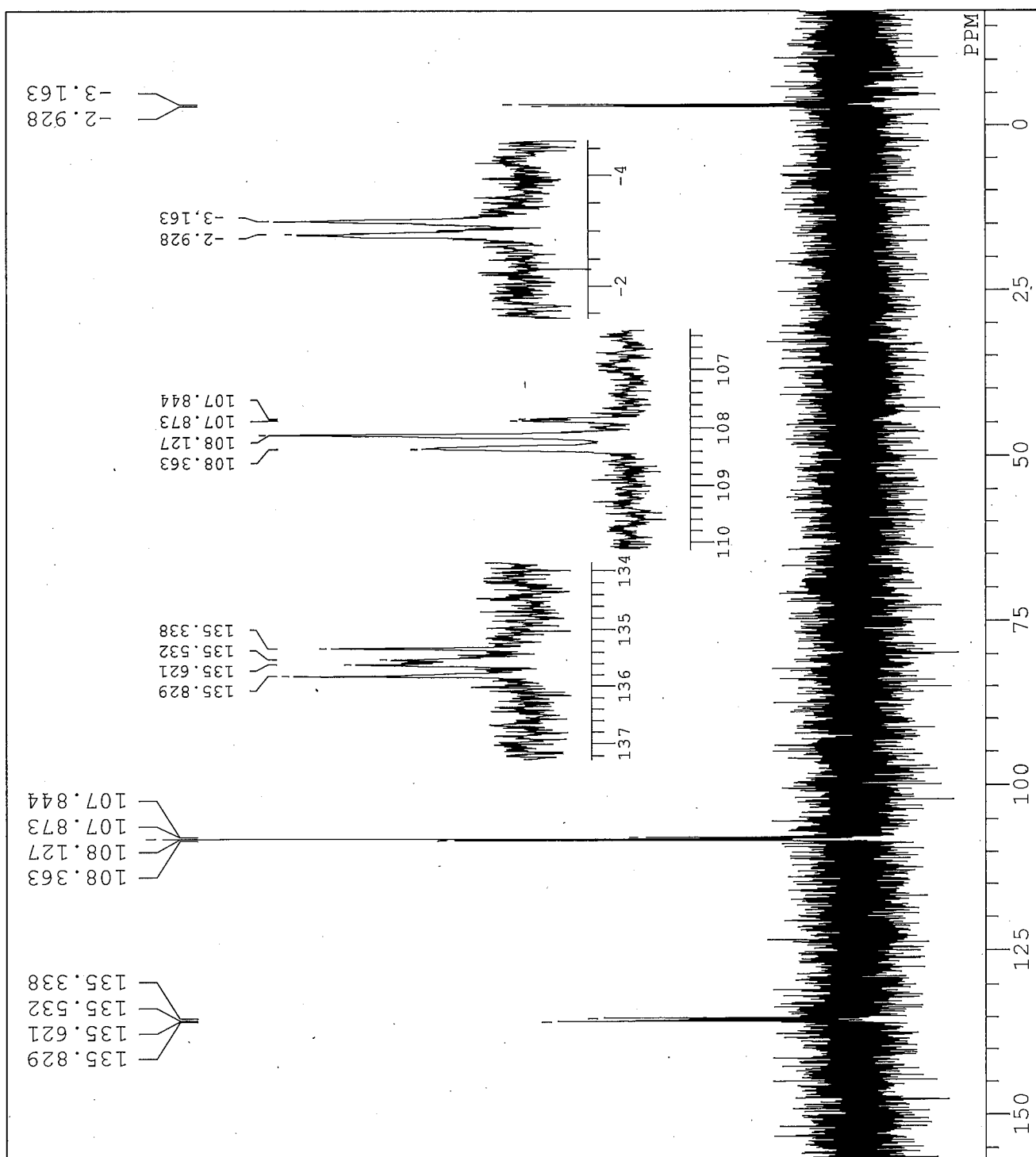


Fig. S-22 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CpMoH}(\mu\text{-P4})\text{IrCl}_2(\text{C}_5\text{Me}_5)]$ (7)

C:\Users\IWA\NMRfobfNfAfbfv\exp.401-450\exp.413-1' [CpMoH(P4)RhCl(cod)] .ALS

C:\Users\IWA\NMRfobfNfAfbfv

Tue Apr 25 15:32:36 2001

1H

NON

399.65 MHz

124.00 KHz

5500.0 Hz

131072

16000.0 Hz

35

4.096 sec

2.904 sec

6.5 us

20.0 c

7.15 ppm

0.12 Hz

18

DFILE

COMNT

DATIM

OBNUC

EXMOD

OBFRQ

OBSET

OBFIN

POINT

FREQU

SCANS

ACQTM

PD

FW1

IRNUC

CTEMP

SLVNT

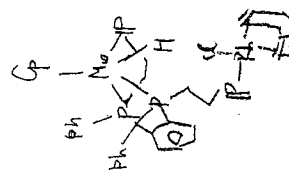
EXREF

BF

RGAIN

1H

C6D6



¹H NMR spectrum of

[CpMoH(μ-P4-1κ³.2κ)-

RhCl(η⁴-C₈H₁₂)] (8)

C₆D₆, 20.0 °C

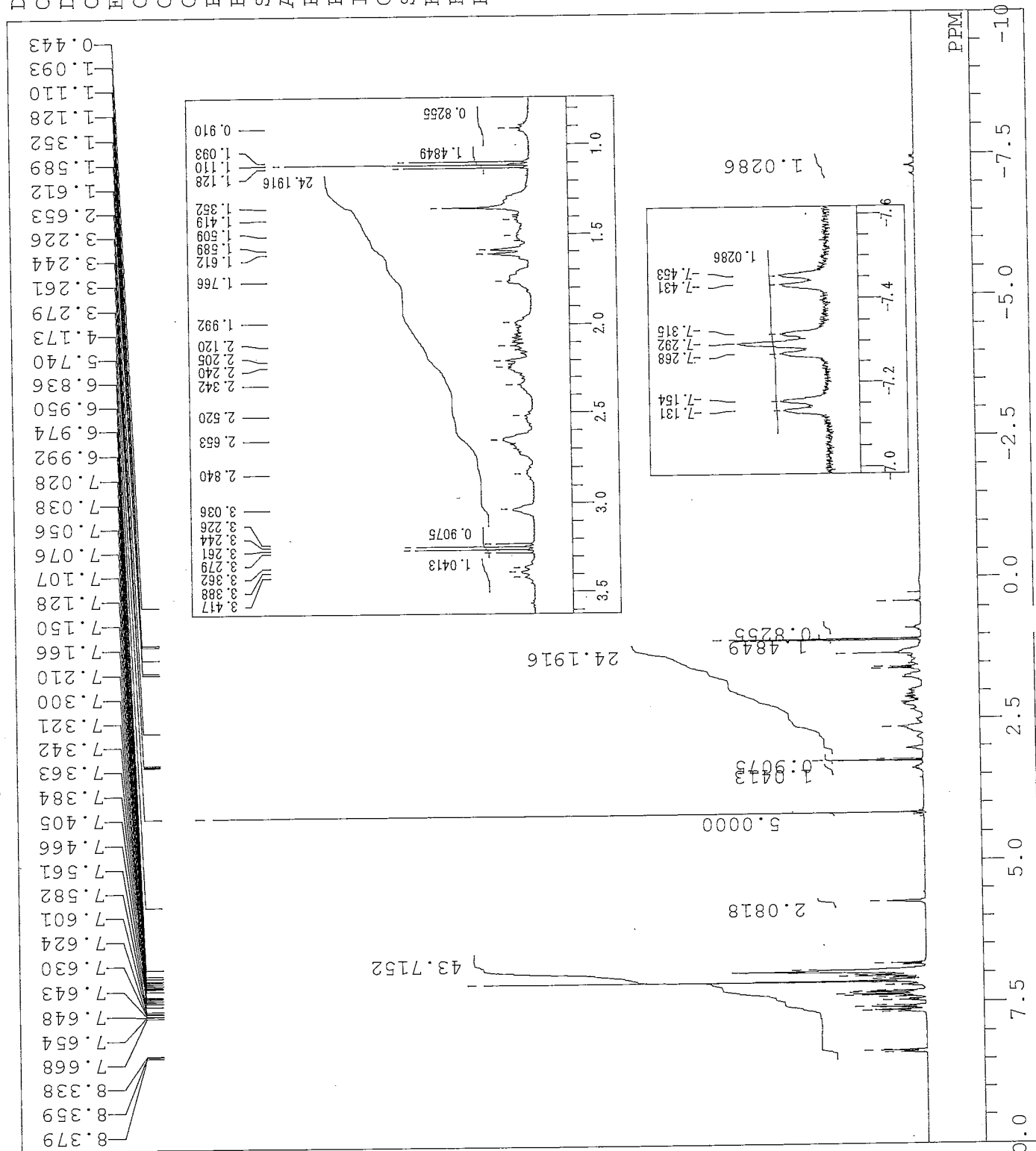
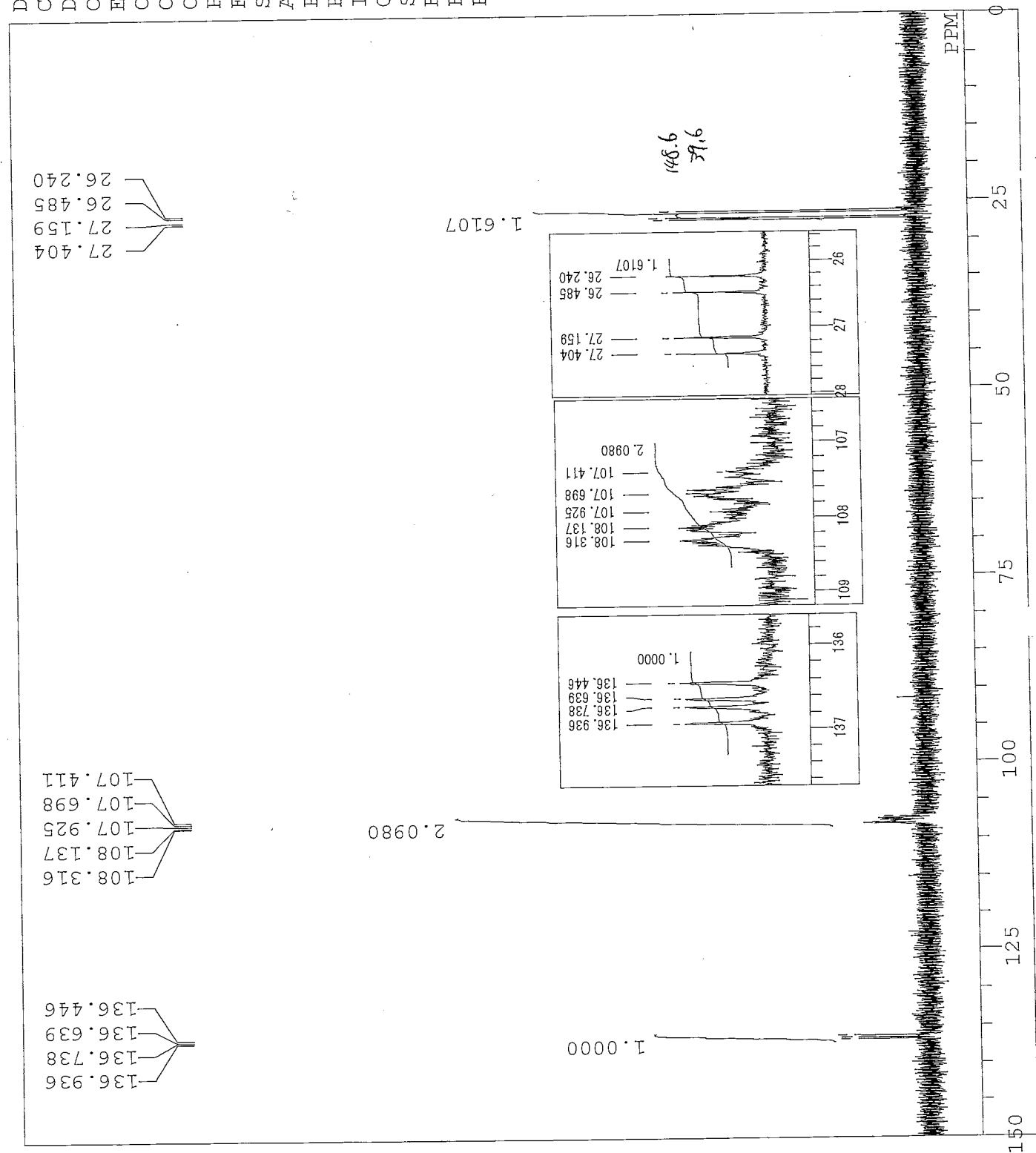


Fig. S-23 ¹H NMR spectrum of [CpMoH(μ-P4)RhCl(C8H12)] (8)

C:\Users\IWA\NMRfobfNfAfbfv\exp.401-450\exp.413-1P' [CpMoH(P4)RhCl(cod)].als



DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRO
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\Users\IWA\NMRfobfNfAfbfv
Tue Apr 25 15:47:07 2001
31P
BCM
161.70 MHz
142.00 KHz
0.0 Hz
65536
50000.0 Hz
518
0.655 sec
0.900 sec
4.6 us
1H
20.4 C
0.00 ppm
0.12 Hz
24

31P{1H} NMR spectrum of
[CpMoH(μ-P4-1κ³:2κ)-
RhCl(η⁴-C₈H₁₂)] (8)
C₆D₆, 20.4 °C

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

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

```
C:\Users\IWA\NMRfobfNfz
DFTILE
COMNT
DATIM Tue Apr 25 15:56:15 2006
OBNUC 1H
EXMOD NON
```

OBFRQ	399.65 MHz
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

¹H NMR spectrum of
[CpMoH(μ-P4-1κ³:2κ)-
IrCl(η⁴-C₈H₁₂)] (9)
C₆D₆, 20.0 °C

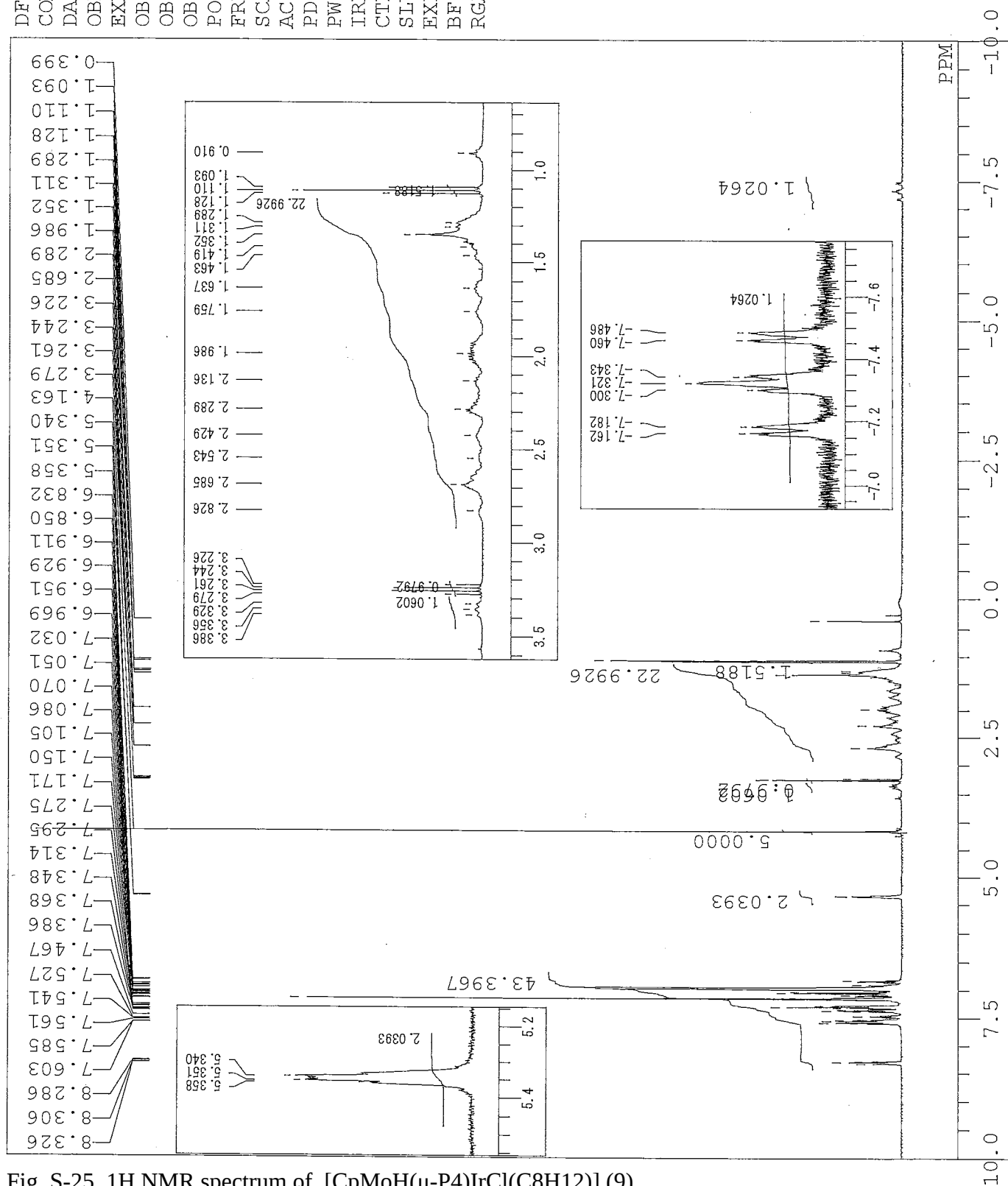
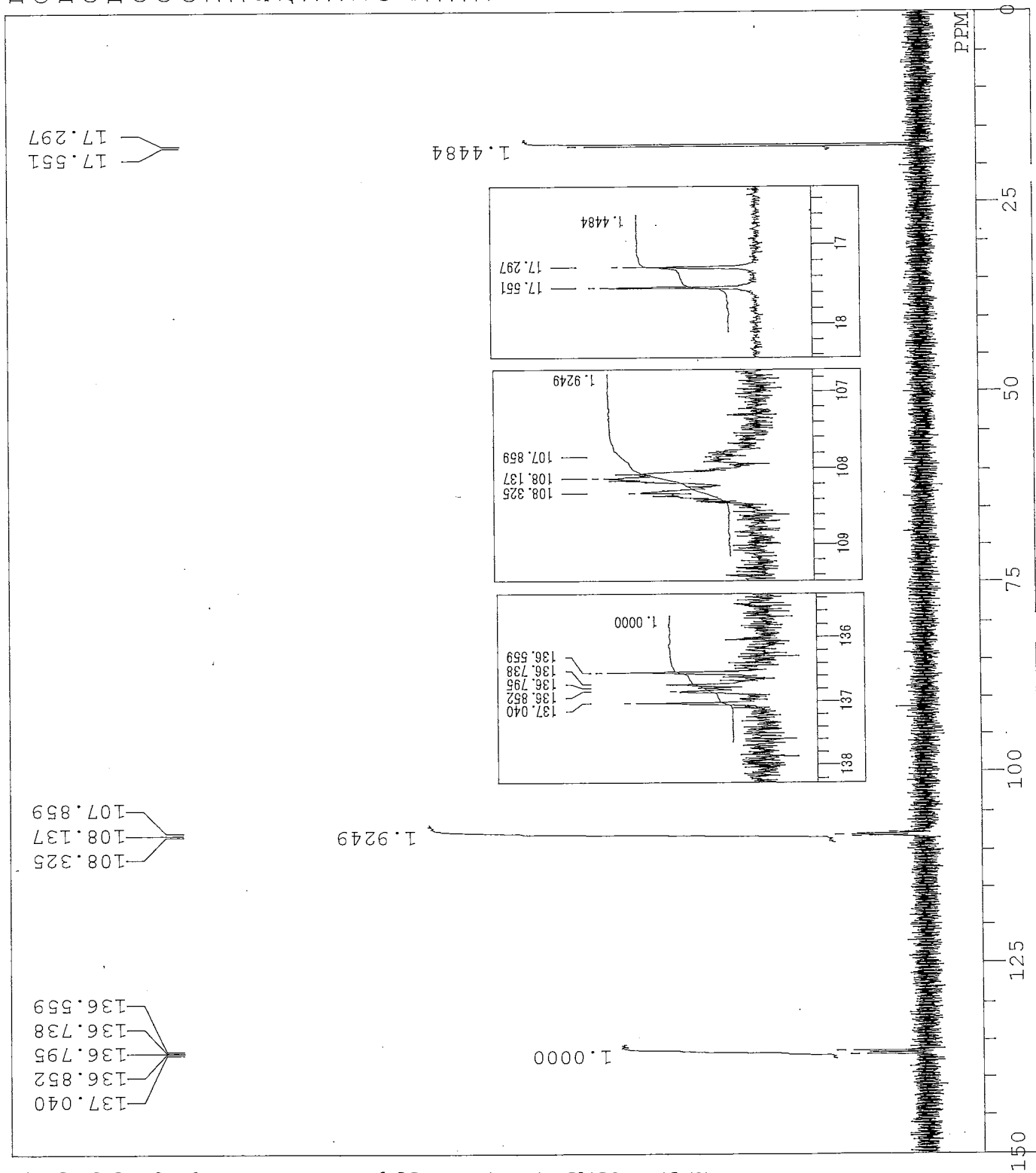


Fig. S-25 ^1H NMR spectrum of $[\text{CpMoH}(\mu\text{-P4})\text{IrCl}(\text{C}_8\text{H}_{12})]$ (9)



DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\Users\IWA\NMR\ofbNfAfbfv
Tue Apr 25 16:11:38 2001
31P
BCM
161.70 MHz
142.00 KHz
0.0 Hz
65536
50000.0 Hz
566
0.655 sec
0.900 sec
4.6 us
1H
20.3 c
C6D6
0.00 ppm
0.12 Hz
24

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of
[CpMoH(μ -P4-1 κ^3 :2 κ)-
IrCl(η^4 -C₈H₁₂)] (9)
C₆D₆, 20.3 °C

Fig. S-26 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of [CpMoH(μ -P4)IrCl(C₈H₁₂)] (6)

DFILE	exp31-10h-1H.ALS
COMMT	
DATIM	Thu Sep 24 16:12
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	5500.00 Hz
POINT	131072
FREQU	16000.00 Hz
SCANS	16
ACQTM	4.0960 sec
PPD	2.9040 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	20.2 c
SIVNT	C6D6
EXREF	7.16 ppm
BBF	0.12 Hz
RGAIN	18

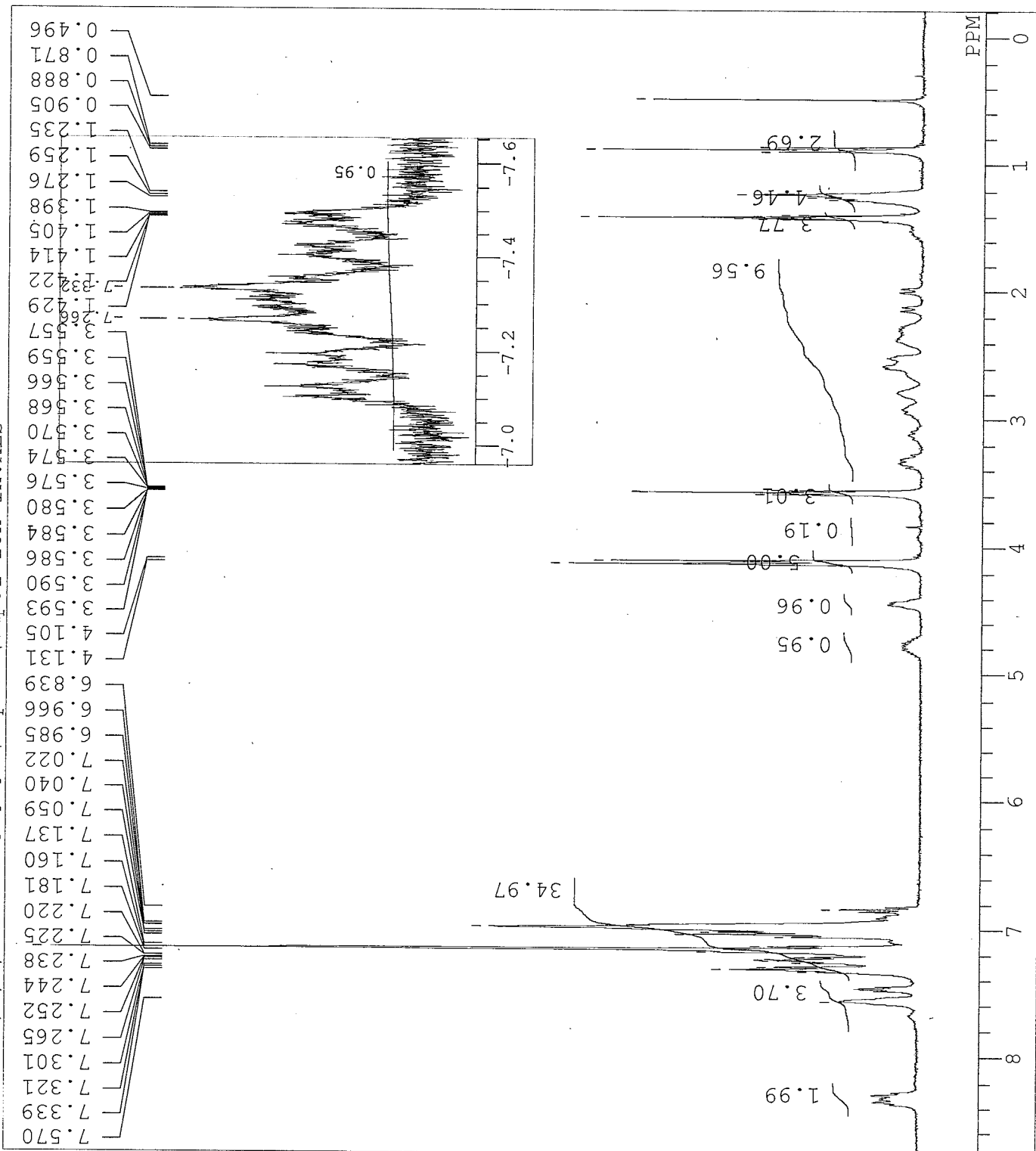


Fig. S-27 ^1H NMR spectrum of $[\text{CpMoH}(\mu\text{-P4})\text{PdCl}(\text{C}_3\text{H}_5)] \cdot 0.75\text{THF} \cdot 0.5\text{hexane}$ ($10\text{-}0.75\text{THF} \cdot 0.5\text{hexane}$)

C:\Users\á,·\fofbfNfAfbfv\exp29~\exp31-10h-31P.ALS

DFILE exp31-10h-31P.ALS
 COMNT
 DATIM Thu Sep 24 16:09:03 2
 OBNUC 31P
 EXMOD BCM
 OBFRQ 161.70 MHz
 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

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of
 [CpMoH(μ -P4-1 κ^3 :2 κ)PdCl-
 (η^3 -C₃H₅)]·0.75THF·0.5hexane
 (10·0.75THF·0.5hexane)
 C₆D₆, 21.5 °C

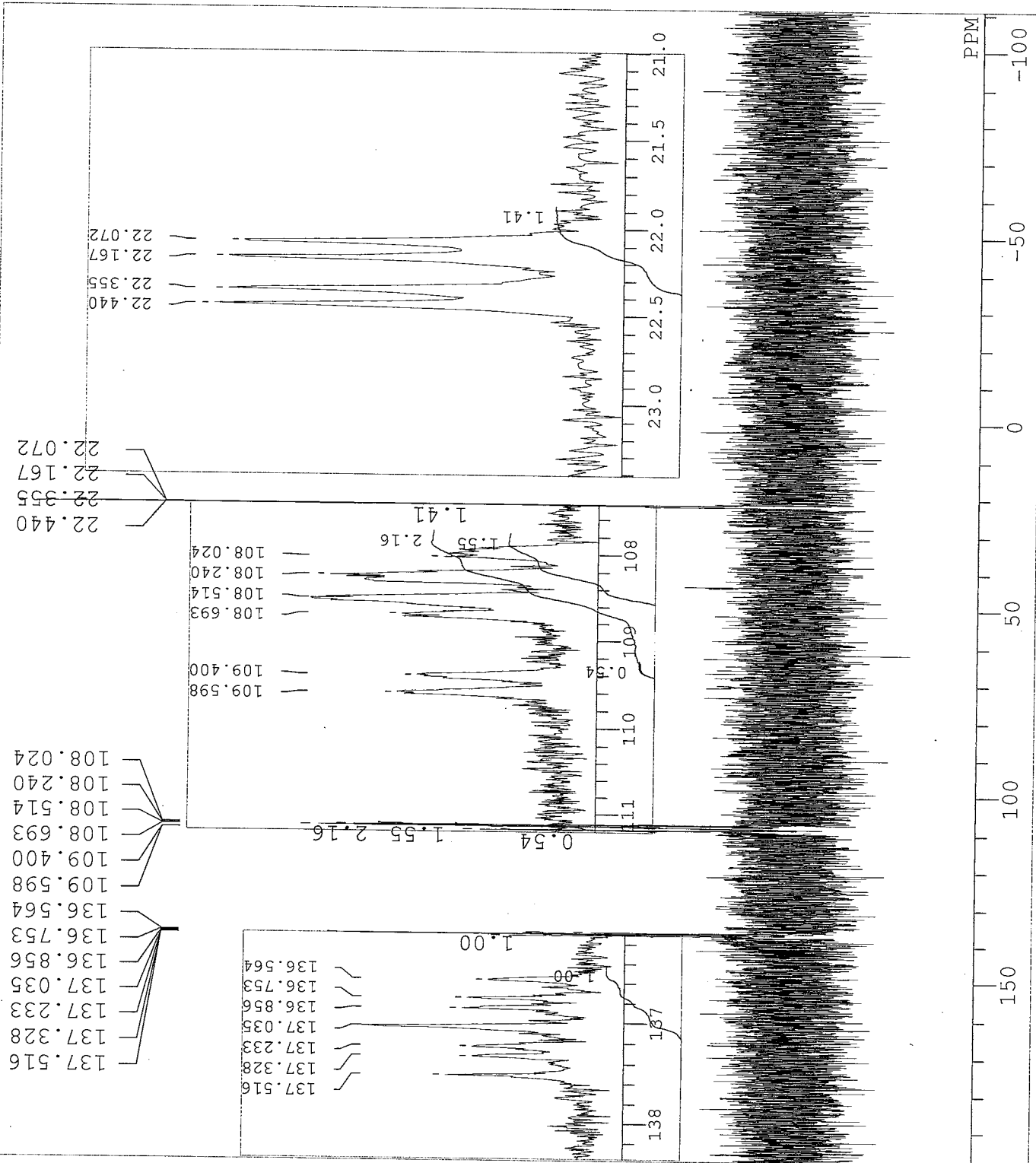


Fig. S-28 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of [CpMoH(μ -P4)PdCl(C₃H₅)]·0.75THF·0.5hexane (10·0.75THF·0.5hexane)

¹H NMR spectrum (CDCl₃) of 1,4-bis(4-oxocyclohex-1-en-1-yl)benzene. The spectrum shows peaks from 0 to 10 ppm. Key features include a singlet at 7.76 ppm (1H), a multiplet between 7.15-7.89 ppm (10H), a multiplet at 6.82-6.99 ppm (4H), a multiplet at 5.68 ppm (2H), a multiplet at 3.42 ppm (2H), a multiplet at 2.13 ppm (2H), a multiplet at 1.54 ppm (4H), and a multiplet at 1.43 ppm (2H). Integration values are provided for several regions: 0.78, 1.96, 2.00, 2.00, 1.00, 2.61, 14.36, 19.24, 1.70, 0.93, 5.68, 2.13, 3.42, 0.99, and 20.23. A TMS reference peak is at 0.288 ppm.

exp35-cryst-31P.ALS
 DFILE COMNT
 DATIM Fri Nov 20 19:54:50 2009
 OBNUC 31P
 EXMOD BCM
 OBFRQ 161.70 MHz
 OBSET 142.00 KHz
 OBFIN 0.00 Hz
 POINT 32768
 FREQU 50000.00 Hz
 SCANS 523
 ACQTM 0.6554 sec
 PD 0.9000 sec
 PW1 6.50 usec
 IRNUC 1H
 CTEMP 23.1 c
 SLVNT C6D6
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 25

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of
 $[\text{CpMoCl}(\mu\text{-P4-1}\kappa^3\text{:2}\kappa)\text{Ru-}$
 $\text{Cl}_2(\eta^6\text{-C}_6\text{Me}_6)]\cdot 0.5\text{CH}_2\text{Cl}_2$
 $(11\cdot 0.5\text{CH}_2\text{Cl}_2)$
 C_6D_6 , 23.1 °C, recrystallized

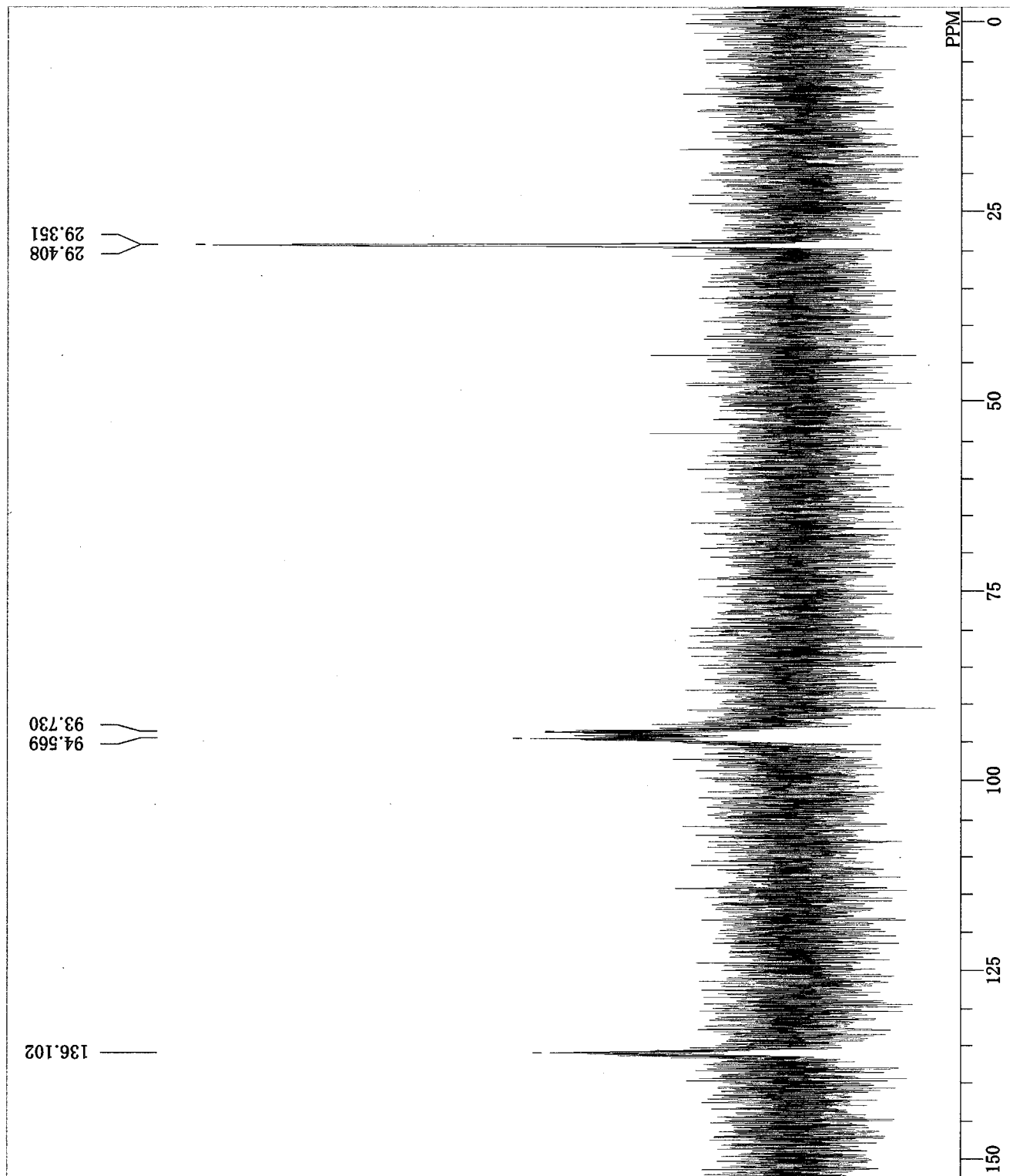


Fig. S-30 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CpMoCl}(\mu\text{-P4})\text{RuCl}_2(\text{C}_6\text{Me}_6)]\cdot 0.5\text{CH}_2\text{Cl}_2 (11\cdot 0.5\text{CH}_2\text{Cl}_2)$

13C NMR spectrum of poly(2-vinylpyridine) showing chemical shifts (PPM) on the x-axis and integration curves on the y-axis. The spectrum displays several distinct peaks corresponding to different carbon environments in the polymer chain.

Chemical shifts (PPM) and integration values are listed below the spectrum:

- 26.964
- 28.973
- 29.107
- 31.746
- 32.027
- 28.973 (0.134)
- 29.107
- 93.179
- 93.313 (0.161)
- 93.340 (0.214)
- 93.393
- 93.460 (0.160)
- 93.514 (0.160)
- 93.674
- 94.116
- 94.224 (0.108)
- 94.357 (0.241)
- 94.465 (0.108)
- 93.179
- 93.313
- 93.340
- 93.393
- 93.460
- 93.514
- 93.674
- 94.116
- 94.224
- 94.357
- 94.465
- 107.697
- 134.576
- 134.791
- 134.871
- 135.059
- 135.608 (0.214)
- 135.822 (0.228)
- 136.050
- 134.576
- 134.791
- 134.871
- 135.059
- 135.608
- 135.822
- 136.050

DFILE	exp217_heat_24h_31P-1.jdf
COMMT	single pulse decoupled gated NOE
DATIM	2010-12-14 11:13:30
OBNUC	31P
EXMOD	single pulse dec
OBFRQ	161.84 MHz
OBSET	6.83 KHz
OBFIN	0.69 Hz
POINT	32768
FREQU	71022.72 Hz
SCANS	260
ACQTM	0.4614 sec
PD	1.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	21.4 c
SLVNT	C6D6
EXREF	29.00 ppm
BF	1.00 Hz
RGAIN	58

$^{31}\text{P}\{\text{H}\}$ NMR spectrum of
[CpMoCl($\mu\text{-P4-1}\kappa^3\text{:2}\kappa$)Ru-
Cl $_2$ ($\eta^6\text{-C}_6\text{Me}_6$)] $\cdot 0.5\text{CH}_2\text{Cl}_2$
(11 $\cdot 0.5\text{CH}_2\text{Cl}_2$)
C $_6\text{D}_6$, 21.4 $^\circ\text{C}$
Resolved spectrum of crude reaction
mixture at high concentration for
assignment of P-P couplings

Fig. S-31 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a mixture containing $[\text{CpMoCl}(\mu\text{-P4})\text{RuCl}_2(\text{C6Me}_6)]$ (11) in high concentration (used for coupling assignments)

DFILE exp33-1H.ALS
 COMNT
 DATIM Fri Oct 09 11:35:30 2009
 OBNUC 1H
 EXMOD NON
 OBFRQ 399.65 MHz
 OBSET 124.00 KHz
 OBFIN 5500.00 Hz
 POINT 6536
 FREQU 16000.00 Hz
 SCANS 16
 ACQTM 4.0960 sec
 PD 2.9040 sec
 PW1 6.50 usec
 IRNUC 1H
 CTEMP 18.9 c
 SLVNT C6D6
 EXREF 7.15 ppm
 BF 0.12 Hz
 RGAIN 22

¹H NMR spectrum of
 [CpMo(μ-H){μ-(P4^{Ph})-1κ³:2κ²}-
 PdCl]·0.75CH₂Cl₂ (12·0.75CH₂Cl₂)
 C₆D₆, 18.9 °C

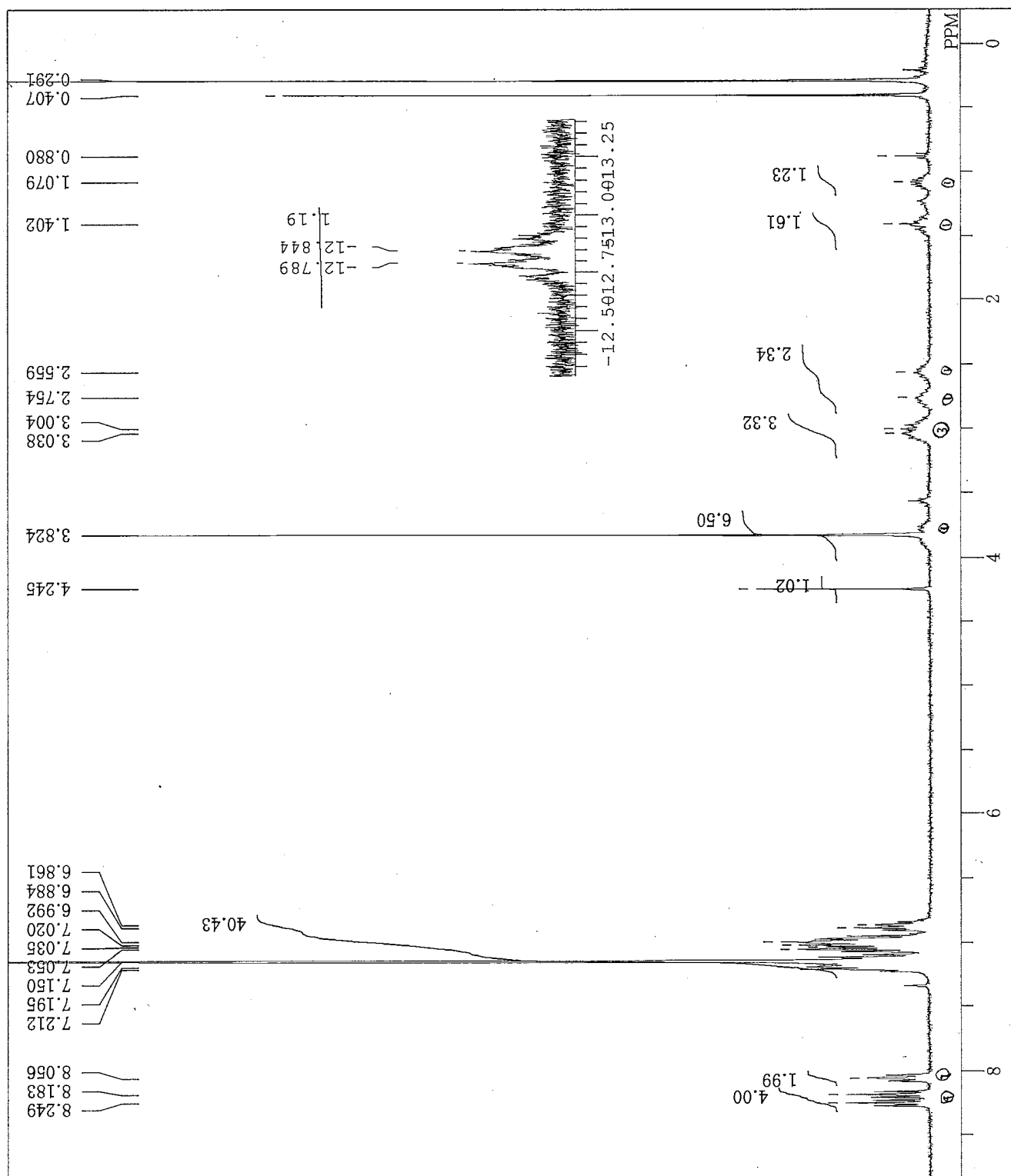


Fig. S-32 ¹H NMR spectrum of [CpMo(μ-H)(μ-P4-Ph)PdCl]·0.75CH₂Cl₂ (12·0.75CH₂Cl₂)

13C NMR spectrum of poly(2-vinylpyridine) showing chemical shift (PPM) on the x-axis. The spectrum displays several distinct peaks with corresponding chemical shift values and integration values.

Chemical shift values (PPM) and integration values are provided for the labeled peaks:

- 1.339 (Integration: 1.622)
- 1.622 (Integration: 0.283)
- 94.258 (Integration: 0.66)
- 94.328 (Integration: 0.24)
- 94.361 (Integration: 0.29)
- 94.479 (Integration: 0.91)
- 94.508 (Integration: 0.29)
- 94.550 (Integration: 0.24)
- 94.574 (Integration: 0.24)
- 138.629 (Integration: 0.23)
- 138.652 (Integration: 0.23)
- 138.761 (Integration: 0.23)
- 138.784 (Integration: 0.23)
- 138.850 (Integration: 0.23)
- 138.879 (Integration: 0.23)
- 138.978 (Integration: 0.23)
- 139.011 (Integration: 0.23)
- 252.484 (Integration: 0.66)
- 252.550 (Integration: 0.66)
- 252.409 (Integration: 0.52)
- 252.357 (Integration: 0.52)
- 250.924 (Integration: 0.52)
- 250.867 (Integration: 0.52)
- 250.801 (Integration: 0.52)
- 250.749 (Integration: 0.52)

- 39 -