ORGANOMETALLICS
Organometallics, 1996, 15(15), 3244-3246, DOI:10.1021/om960418z

Synthesis, Spectral and Analytical Data for 3b.

In a helium-filled glove box, a 25 mL scintillation vial was charged with a magnetic stir bar, 0.203 g (0.31 mmol) of molybdenum alkylidene **1b** and approximately 2mL of dry diethyl ether. 100 μL (1.1 mmol) of t-butylphosphaalkyne **2** was added at 25 °C and the vial was sealed to stir overnight (16 h) at room temperature. The solvent was removed under vacuum and the residue dissolved in a minimum amount of dry pentane. Cooling to -35 °C yielded 169 mg (72% yield based on starting **1b**) of dark yellow crystals of molybdenum alkylidyne complex **3b** after 24 h.

Spectroscopic data for **3b**: ^{1}H NMR (400.1 MHz, C_7D_{14}, for major isomer at -30 °C, ext. TMS ref.): δ = 8.48 (d, 1H, $^{2}J_{P-H}$ = 14 Hz, Mo[N(2,6-(i-Pr)$_2$C$_6$H$_3$)-P=C(*H*)(C(CH$_3$)$_2$C$_6$H$_5$]), 7.17 (m, 8H, Mo[N(2,6-(i-Pr)$_2$C$_6$*H*$_3$)-P=C(H)(C(CH$_3$)$_2$C$_6$*H*$_5$]), 3.25 (septet, 2H, $^{3}J_{H-H}$ = 7 Hz, [(2,6-(*i-Pr*)$_2$C$_6$H$_3$)N]Mo), 1.54 (s, 12H, [(*H*$_3$C)$_2$CF$_3$CO]$_2$Mo), 1.46 (s, 6H, Mo[N(2,6-(i-Pr)$_2$C$_6$H$_3$)-P=C(H)(C(C*H*$_3$)$_2$C$_6$H$_5$]), 1.30, 1.13 (each a d, 12H, $^{3}J_{H-H}$ = 7 Hz, [(2,6-(*i-Pr*)$_2$C$_6$H$_3$)N]Mo), 0.76 (s, 9H, Mo≡C-C(C*H*$_3$)$_3$). ^{13}C NMR (100.6 MHz, C_7D_{14}, for major isomer at -30 °C, referenced to solvent): δ = 317.2 (s, Mo≡*C*-C(CH$_3$)$_3$), 180.0 (d, $^{1}J_{P-C}$ = 52 Hz, Mo[N(2,6-(i-Pr)$_2$C$_6$H$_3$)-P=*C*(H)(C(CH$_3$)$_2$C$_6$H$_5$]), 155.3, 147.8, 142.2, 128.4, 126.6, 126.5, 126.4, 123.8 (Mo[N(2,6-(i-Pr)$_2$*C*$_6$H$_3$)-P=C(H)(C(CH$_3$)$_2$*C*$_6$H$_5$]), 126.9 (q, $^{1}J_{C-F}$ = 284 Hz, [(H$_3$C)$_2$*C*F$_3$CO]$_2$Mo), 80.0 (q, $^{2}J_{C-F}$ = 29 Hz, [(H$_3$C)$_2$CF$_3$*C*O]$_2$Mo), 53.9 (Mo≡C-*C*(CH$_3$)$_3$), 30.4 (Mo≡C-C(*C*H$_3$)$_3$), 43.8 (d, $^{2}J_{P-C}$ = 14 Hz, Mo[N(2,6-(i-Pr)$_2$C$_6$H$_3$)-P=C(H)(*C*(CH$_3$)$_2$C$_6$H$_5$]), 28.5, 26.6, 23.1 (Mo[N(2,6-(*i-Pr*)$_2$C$_6$H$_3$)-P=C(H)(C(CH$_3$)$_2$C$_6$H$_5$]), 26.2 (s, Mo[N(2,6-(i-Pr)$_2$C$_6$H$_3$)-P=C(H)(C(*C*H$_3$)$_2$C$_6$H$_5$]), 25.6 (s, [(H$_3$*C*)$_2$CF$_3$CO]$_2$Mo). ^{31}P {^{1}H} NMR (121.4 MHz, C_7H_{14}, for major isomer at 25 °C, ext. H_3PO_4): δ = 260.74 (s). IR (C_6D_6): ν = 2965, 2926, 2867, 1465, 1324, 1164, 1165, 1124, 1006, 901, 828, 700 cm^{-1}. Anal. Calcd for $C_{35}H_{50}NO_2F_6PMo$: C, 55.48; H, 6.65; N, 1.85. Found: C, 55.24; H, 6.78; N, 1.68.

Table 1. Data Collection and Reduction, Structure Solution and Refinement for **3b.**

Data Collection and Reduction.

Diffractometer type	Siemens P4
Radiation source	normal-focus sealed tube
Monochromator type	graphite
Radiation	MoKα
Wavelength	0.71073 Å
Temperature	168 K
Cell measurement reflections	41 ($4.62^{\circ} < \theta < 11.75^{\circ}$)
Intensity measurement method	$2\theta/\omega$ scans
θ range for data collection	2.10 to 22.50°
Limiting indices	$0 \le h \le 19$, $0 \le k \le 12$, $-20 \le l \le 20$
Scan width (in ω)	1.2° plus α_1,α_2 separation
Scan speed (in ω)	3.0°/min
Reflections collected	5123
Independent reflections	4935 (R_{int} = 0.0189)
Observed reflections	4009 (I >2sigma(I))
Number of standards	3
Interval between standards	97
Decay of standards	n/a
Absorption correction	None

Unit cell refinement and data collection were carried out by use of the Siemens XSCAnS system, Version 2.10b. Data were processed with a local version of CARESS (R.W. Broach et al.), which employs a modified version of the Lehman-Larsen algorithm to obtain integrated intensities and standard deviations from the measured 96-step peak profiles.

Structure Solution and Refinement.

Structure solution method	direct methods
Refinement method	Full-matrix least-squares on F^2
Scattering Factor Source	International Tables Vol C Tables 4.2.6.8 and 6.1.1.4
Final refinement: Data	4933
Restraints	0
Parameters	416
Final R indices [$I>2\sigma(I)$]	R1 = 0.0480, wR2 = 0.1145
R indices (all data)	R1 = 0.0647, wR2 = 0.1256
Goodness-of-fit on F^2	1.097
Extinction coefficient	0.0007(2)
Largest diff. peak and hole	0.782 and -0.710 $eÅ^{-3}$
Maximum Δ/σ in final cycle	0.000
Mean Δ/σ in final cycle	0.000

Final weighting scheme:

calc $w=1/[\sigma^2(Fo^2)+(0.0406P)^2+16.0207P]$

where $P=(Fo^2+2Fc^2)/3$

R-factor definitions:

$R1 = \sum||F_o|-|F_c||/\sum|F_o|$

$wR2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$

Structure solution, refinement, and generation of figures and tables were carried out by use of Version 5.03 of the Siemens SHELXTL program package.

Table 2. Crystal data and structure refinement for 3b.

Empirical formula	$C_{35}H_{50}F_6MoNO_2P$
Formula weight	757.67
Temperature	168 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 17.7187(13) Å $\alpha = 90^\circ$ b = 11.3585(8) Å $\beta = 91.677(11)^\circ$ c = 18.753(4) Å $\gamma = 90^\circ$
Volume, Z	3772.6(8) $Å^3$, 4
Density (calculated)	1.334 Mg/m^3
Absorption coefficient	0.449 mm^{-1}
F(000)	1576
Crystal size	0.47 x 0.36 x 0.33 mm
θ range for data collection	2.10 to 22.50°
Limiting indices	$0 \le h \le 19$, $0 \le k \le 12$, $-20 \le l \le 20$
Reflections collected	5123
Independent reflections	4935 (R_{int} = 0.0189)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4933 / 0 / 416
Goodness-of-fit on F^2	1.097
Final R indices [I>2σ(I)]	R1 = 0.0480, wR2 = 0.1145
R indices (all data)	R1 = 0.0647, wR2 = 0.1256
Largest diff. peak and hole	0.782 and -0.710 $eÅ^{-3}$

$$R1 = \sum||F_o|-|F_c||/\sum|F_o|$$

$$wR2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$$

Table 3. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor for 3b.

	x	y	z	U(eq)
Mo(1)	2377(1)	1553(1)	1203(1)	24(1)
P(1)	1964(1)	2862(1)	2527(1)	30(1)
N(1)	2057(2)	1450(4)	2189(2)	24(1)
O(1)	3421(2)	1815(3)	1127(2)	34(1)
O(2)	1791(2)	2615(3)	649(2)	31(1)
C(1)	2189(3)	127(5)	911(3)	34(1)
C(2)	2035(4)	-1136(5)	689(3)	48(2)
C(3)	2423(5)	-1405(6)	-10(4)	70(2)
C(4)	1201(5)	-1355(7)	610(6)	105(4)
C(5)	2357(6)	-1949(6)	1280(4)	87(3)
C(6)	1797(3)	490(4)	2613(2)	25(1)
C(7)	2347(3)	-218(5)	2965(3)	31(1)
C(8)	2097(3)	-1140(5)	3386(3)	35(1)
C(9)	1345(4)	-1358(5)	3463(3)	44(2)
C(10)	812(3)	-657(5)	3123(3)	37(1)
C(11)	1025(3)	279(5)	2691(3)	29(1)
C(12)	3183(3)	18(5)	2890(3)	40(2)
C(13)	3675(4)	-1088(7)	2933(4)	68(2)
C(14)	3469(4)	913(6)	3448(4)	60(2)
C(15)	409(3)	1039(5)	2348(3)	34(1)
C(16)	-17(4)	1720(6)	2909(3)	52(2)
C(17)	-139(4)	328(6)	1884(3)	53(2)
C(18)	2788(3)	3480(5)	2349(3)	32(1)
C(19)	2991(3)	4769(5)	2459(3)	41(2)
C(20)	3338(3)	5235(5)	1771(3)	43(2)
C(21)	3991(4)	5906(6)	1780(5)	68(2)
C(22)	4275(4)	6315(7)	1128(6)	83(3)
C(23)	3907(6)	6082(8)	491(5)	84(3)
C(24)	3269(5)	5418(6)	490(4)	70(2)
C(25)	2986(4)	5007(5)	1114(3)	49(2)
C(26)	3549(5)	4804(7)	3100(4)	77(3)

C(27)	2288(4)	5510(5)	2626(4)	60(2)
C(28)	4062(3)	1333(6)	793(3)	45(2)
C(29)	4708(4)	2113(7)	1040(5)	63(2)
C(30)	3939(5)	1423(10)	-12(4)	106(4)
C(31)	4215(4)	79(6)	1035(5)	72(2)
C(32)	1290(3)	2734(5)	50(3)	39(1)
C(33)	617(5)	3327(9)	327(5)	86(3)
C(34)	1074(6)	1580(8)	-283(5)	118(4)
C(35)	1668(5)	3537(12)	-474(4)	141(6)
F(1)	5365(2)	1727(4)	766(3)	85(2)
F(2)	4812(2)	2081(5)	1736(3)	85(1)
F(3)	4628(3)	3206(4)	839(3)	104(2)
F(4)	119(3)	3603(5)	-205(3)	115(2)
F(5)	815(4)	4376(5)	650(3)	139(3)
F(6)	273(3)	2694(8)	796(3)	144(3)

Table 4. Bond lengths [Å] and angles [°] for 3b.

Mo(1)-C(1)	1.739(6)	Mo(1)-O(1)	1.883(3)
Mo(1)-O(2)	1.883(3)	Mo(1)-N(1)	1.952(4)
P(1)-C(18)	1.663(6)	P(1)-N(1)	1.735(4)
N(1)-C(6)	1.434(6)	O(1)-C(28)	1.424(7)
O(2)-C(32)	1.420(6)	C(1)-C(2)	1.516(8)
C(2)-C(4)	1.501(10)	C(2)-C(3)	1.530(9)
C(2)-C(5)	1.539(10)	C(6)-C(11)	1.400(7)
C(6)-C(7)	1.413(7)	C(7)-C(8)	1.391(8)
C(7)-C(12)	1.517(8)	C(8)-C(9)	1.367(8)
C(9)-C(10)	1.376(8)	C(10)-C(11)	1.396(7)
C(11)-C(15)	1.520(8)	C(12)-C(13)	1.530(9)
C(12)-C(14)	1.534(9)	C(15)-C(17)	1.518(8)
C(15)-C(16)	1.523(8)	C(18)-C(19)	1.521(8)
C(19)-C(26)	1.535(9)	C(19)-C(20)	1.539(8)
C(19)-C(27)	1.543(9)	C(20)-C(21)	1.387(9)
C(20)-C(25)	1.389(9)	C(21)-C(22)	1.413(11)
C(22)-C(23)	1.371(12)	C(23)-C(24)	1.359(12)
C(24)-C(25)	1.368(9)	C(28)-C(29)	1.509(10)
C(28)-C(31)	1.517(9)	C(28)-C(30)	1.523(9)
C(29)-F(3)	1.304(8)	C(29)-F(2)	1.312(9)
C(29)-F(1)	1.359(8)	C(32)-C(33)	1.477(11)
C(32)-C(34)	1.497(10)	C(32)-C(35)	1.512(10)
C(33)-F(6)	1.302(11)	C(33)-F(4)	1.349(8)
C(33)-F(5)	1.377(11)		

C(1)-Mo(1)-O(1)	107.6(2)	C(1)-Mo(1)-O(2)	109.0(2)
O(1)-Mo(1)-O(2)	112.6(2)	C(1)-Mo(1)-N(1)	100.6(2)
O(1)-Mo(1)-N(1)	113.2(2)	O(2)-Mo(1)-N(1)	113.0(2)
C(18)-P(1)-N(1)	102.9(2)	C(6)-N(1)-P(1)	117.6(3)
C(6)-N(1)-Mo(1)	132.7(3)	P(1)-N(1)-Mo(1)	108.9(2)
C(28)-O(1)-Mo(1)	140.5(4)	C(32)-O(2)-Mo(1)	145.0(3)
C(2)-C(1)-Mo(1)	177.4(4)	C(4)-C(2)-C(1)	110.6(6)
C(4)-C(2)-C(3)	110.4(7)	C(1)-C(2)-C(3)	110.0(5)
C(4)-C(2)-C(5)	108.4(7)	C(1)-C(2)-C(5)	108.1(5)
C(3)-C(2)-C(5)	109.3(6)	C(11)-C(6)-C(7)	121.1(5)
C(11)-C(6)-N(1)	121.3(4)	C(7)-C(6)-N(1)	117.6(5)

C(8)-C(7)-C(6)	117.8(5)	C(8)-C(7)-C(12)	121.0(5)
C(6)-C(7)-C(12)	121.2(5)	C(9)-C(8)-C(7)	121.6(5)
C(8)-C(9)-C(10)	120.2(5)	C(9)-C(10)-C(11)	121.1(5)
C(6)-C(11)-C(10)	118.2(5)	C(6)-C(11)-C(15)	123.4(5)
C(10)-C(11)-C(15)	118.4(5)	C(7)-C(12)-C(13)	114.0(5)
C(7)-C(12)-C(14)	110.9(5)	C(13)-C(12)-C(14)	109.4(5)
C(17)-C(15)-C(11)	112.4(5)	C(17)-C(15)-C(16)	110.2(5)
C(11)-C(15)-C(16)	111.1(4)	C(19)-C(18)-P(1)	125.7(5)
C(18)-C(19)-C(26)	106.0(5)	C(18)-C(19)-C(20)	108.4(5)
C(26)-C(19)-C(20)	112.6(5)	C(18)-C(19)-C(27)	111.3(5)
C(26)-C(19)-C(27)	109.4(6)	C(20)-C(19)-C(27)	109.1(5)
C(21)-C(20)-C(25)	117.8(6)	C(21)-C(20)-C(19)	122.2(6)
C(25)-C(20)-C(19)	120.0(5)	C(20)-C(21)-C(22)	119.2(8)
C(23)-C(22)-C(21)	121.2(8)	C(24)-C(23)-C(22)	118.8(8)
C(23)-C(24)-C(25)	121.0(8)	C(24)-C(25)-C(20)	121.9(7)
O(1)-C(28)-C(29)	104.3(5)	O(1)-C(28)-C(31)	111.5(5)
C(29)-C(28)-C(31)	109.4(6)	O(1)-C(28)-C(30)	108.5(5)
C(29)-C(28)-C(30)	110.6(6)	C(31)-C(28)-C(30)	112.3(7)
F(3)-C(29)-F(2)	108.9(8)	F(3)-C(29)-F(1)	106.5(6)
F(2)-C(29)-F(1)	105.7(6)	F(3)-C(29)-C(28)	113.3(6)
F(2)-C(29)-C(28)	111.9(6)	F(1)-C(29)-C(28)	110.2(7)
O(2)-C(32)-C(33)	104.9(5)	O(2)-C(32)-C(34)	113.2(5)
C(33)-C(32)-C(34)	110.3(7)	O(2)-C(32)-C(35)	107.0(5)
C(33)-C(32)-C(35)	109.4(7)	C(34)-C(32)-C(35)	111.8(8)
F(6)-C(33)-F(4)	108.6(8)	F(6)-C(33)-F(5)	107.4(9)
F(4)-C(33)-F(5)	106.0(7)	F(6)-C(33)-C(32)	112.6(8)
F(4)-C(33)-C(32)	111.3(7)	F(5)-C(33)-C(32)	110.6(8)

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 3b.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + \ldots + 2hka^*b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Mo(1)	24(1)	27(1)	21(1)	2(1)	2(1)	3(1)
P(1)	39(1)	25(1)	28(1)	-2(1)	8(1)	-2(1)
N(1)	28(2)	21(2)	24(2)	2(2)	-1(2)	2(2)
O(1)	22(2)	43(2)	38(2)	-4(2)	9(2)	8(2)
O(2)	29(2)	36(2)	29(2)	7(2)	0(2)	2(2)
C(1)	38(3)	39(3)	25(3)	-2(3)	2(2)	3(3)
C(2)	63(5)	33(3)	48(4)	-16(3)	5(3)	0(3)
C(3)	113(7)	50(4)	48(4)	-20(4)	14(4)	-5(4)
C(4)	75(6)	56(5)	186(11)	-38(6)	12(6)	-25(5)
C(5)	169(10)	32(4)	61(5)	-6(4)	-3(5)	11(5)
C(6)	33(3)	23(3)	19(3)	-1(2)	3(2)	-1(2)
C(7)	40(3)	27(3)	26(3)	-1(2)	1(2)	2(3)
C(8)	47(4)	28(3)	30(3)	6(2)	-2(3)	8(3)
C(9)	64(5)	31(3)	37(3)	12(3)	2(3)	-4(3)
C(10)	39(4)	36(3)	35(3)	6(3)	5(3)	-12(3)
C(11)	34(3)	29(3)	23(3)	-2(2)	1(2)	-1(3)
C(12)	35(3)	49(4)	36(3)	11(3)	-3(3)	10(3)
C(13)	58(5)	68(5)	77(5)	12(4)	-1(4)	24(4)
C(14)	49(4)	62(5)	68(5)	0(4)	-10(4)	-3(4)
C(15)	32(3)	40(3)	29(3)	5(3)	2(2)	-8(3)
C(16)	56(4)	50(4)	51(4)	2(3)	0(3)	13(3)
C(17)	45(4)	57(4)	56(4)	-8(3)	-15(3)	-1(3)
C(18)	40(3)	29(3)	26(3)	1(2)	-3(2)	-4(3)
C(19)	49(4)	30(3)	43(3)	-4(3)	0(3)	-13(3)
C(20)	44(4)	26(3)	59(4)	4(3)	11(3)	-1(3)
C(21)	49(5)	54(5)	102(6)	28(4)	-2(4)	-3(4)
C(22)	39(4)	65(6)	145(9)	45(6)	26(5)	-5(4)
C(23)	86(7)	73(6)	96(7)	36(5)	38(6)	10(5)
C(24)	106(7)	46(4)	60(5)	8(4)	30(4)	2(5)
C(25)	76(5)	31(3)	41(4)	0(3)	18(3)	-11(3)
C(26)	101(7)	70(5)	59(5)	-1(4)	-26(4)	-45(5)

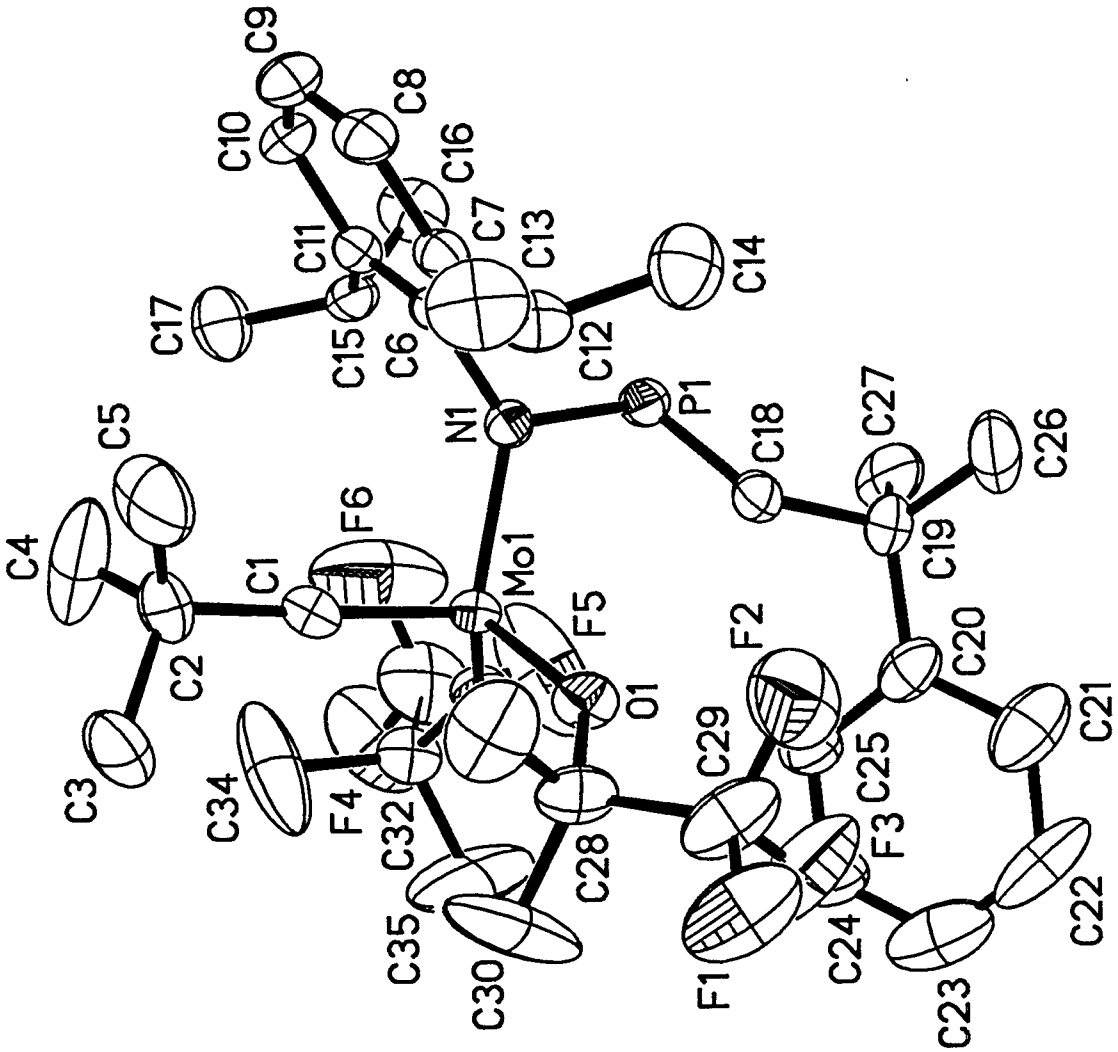
C(27)	86(6)	28(3)	68(5)	-13(3)	33(4)	-8(4)
C(28)	29(3)	59(4)	46(4)	2(3)	16(3)	8(3)
C(29)	38(4)	60(5)	93(6)	29(4)	17(4)	10(4)
C(30)	77(6)	206(12)	35(4)	-11(6)	19(4)	46(7)
C(31)	47(4)	55(5)	116(7)	-13(4)	29(4)	18(4)
C(32)	33(3)	46(4)	36(3)	7(3)	-5(3)	10(3)
C(33)	73(6)	113(8)	68(5)	20(6)	-32(5)	20(6)
C(34)	166(10)	71(6)	112(8)	-36(6)	-101(7)	35(6)
C(35)	83(7)	273(16)	66(6)	105(8)	-32(5)	-62(8)
F(1)	31(2)	96(3)	128(4)	31(3)	24(2)	16(2)
F(2)	50(3)	125(4)	80(3)	-12(3)	-12(2)	-8(3)
F(3)	55(3)	64(3)	196(6)	41(3)	34(3)	-1(2)
F(4)	105(4)	137(5)	99(4)	-13(3)	-49(3)	62(4)
F(5)	164(6)	106(4)	143(5)	-56(4)	-80(5)	85(4)
F(6)	80(4)	266(9)	86(4)	48(5)	13(3)	28(5)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 3b.

	x	y	z	U(eq)
H(3A)	2967(5)	-1258(6)	49(4)	105
H(3B)	2213(5)	-899(6)	-389(4)	105
H(3C)	2340(5)	-2233(6)	-138(4)	105
H(4A)	1113(5)	-2174(7)	466(6)	158
H(4B)	984(5)	-827(7)	245(6)	158
H(4C)	962(5)	-1206(7)	1066(6)	158
H(5A)	2902(6)	-1819(6)	1338(4)	131
H(5B)	2262(6)	-2772(6)	1147(4)	131
H(5C)	2111(6)	-1775(6)	1729(4)	131
H(8A)	2457(3)	-1629(5)	3627(3)	42
H(9A)	1189(4)	-1996(5)	3752(3)	53
H(10A)	292(3)	-814(5)	3184(3)	44
H(12A)	3251(3)	377(5)	2409(3)	48
H(13A)	4206(4)	-870(7)	2880(4)	101
H(13B)	3521(4)	-1632(7)	2550(4)	101
H(13C)	3614(4)	-1471(7)	3396(4)	101
H(14A)	4010(4)	1051(6)	3389(4)	90
H(14B)	3387(4)	604(6)	3928(4)	90
H(14C)	3194(4)	1655(6)	3384(4)	90
H(15A)	658(3)	1625(5)	2035(3)	40
H(16A)	343(4)	2176(6)	3205(3)	78
H(16B)	-288(4)	1167(6)	3210(3)	78
H(16C)	-378(4)	2256(6)	2673(3)	78
H(17A)	-525(4)	853(6)	1675(3)	79
H(17B)	-382(4)	-271(6)	2175(3)	79
H(17C)	135(4)	-55(6)	1501(3)	79
H(18A)	3166(3)	2983(5)	2161(3)	38
H(21A)	4246(4)	6090(6)	2219(5)	82
H(22A)	4729(4)	6759(7)	1132(6)	99
H(23A)	4095(6)	6379(8)	57(5)	101
H(24A)	3015(5)	5238(6)	51(4)	84
H(25A)	2536(4)	4551(5)	1097(3)	59

H(26A)	3699(5)	5621(7)	3196(4)	116
H(26B)	3997(5)	4337(7)	2994(4)	116
H(26C)	3308(5)	4477(7)	3520(4)	116
H(27A)	2436(4)	6334(5)	2695(4)	90
H(27B)	2062(4)	5213(5)	3062(4)	90
H(27C)	1919(4)	5453(5)	2228(4)	90
H(30A)	3518(5)	912(10)	-163(4)	159
H(30B)	4398(5)	1175(10)	-249(4)	159
H(30C)	3821(5)	2240(10)	-142(4)	159
H(31A)	3796(4)	-428(6)	875(5)	108
H(31B)	4263(4)	57(6)	1557(5)	108
H(31C)	4685(4)	-201(6)	830(5)	108
H(34A)	1524(6)	1196(8)	-465(5)	178
H(34B)	709(6)	1714(8)	-678(5)	178
H(34C)	846(6)	1074(8)	75(5)	178
H(35A)	2116(5)	3146(12)	-658(4)	212
H(35B)	1820(5)	4269(12)	-233(4)	212
H(35C)	1315(5)	3717(12)	-871(4)	212

Figure 3. Thermal plot showing complete atomic numbering scheme for **3b**.


C9
C10
C8
C16
C11
C7
C13
C14
C17
C15
C6
C12
N1
P1
C18
C27
C26
C5
C4
F6
C1
Mo1
C19
F5
F2
C20
C2
O1
C21
C29
C3
C34
F4
C32
C25
C28
F3
C35
C22
C24
C30
F1
C23

Synthesis, Spectral and Analytical Data for 4b.

A 5 mm NMR tube was charged with 0.185 g (0.24 mmol) of **3b** and approximately 1 mL of dry C_6D_6 in a helium-filled dry box. After sealing the tube, the solution was placed in an oil bath at 80 °C for 8 h, during which time the conversion to **4b** was monitored by ^1H NMR spectroscopy. Upon consumption of **3b**, the NMR tube was cooled and the contents dried under vacuum. The residue was dissolved in a minimum of dry pentane and cooled to -35 °C overnight. 183 mg (75% yield) of orange crystals of **4b** were isolated.

Spectroscopic data for **4b**: ^1H NMR (300 MHz, C_6D_6 at 25 °C): δ = 7.20 (m, 8H, [(2,6-(i-Pr)$_2$C$_6$*H*$_3$)N]Mo and Mo-C(H)(C(CH$_3$)$_2$C$_6$*H*$_5$)), 4.88 (d, 1H, $^2J_{P-H}$ = 7 Hz, Mo-C(*H*)(C(CH$_3$)$_2$C$_6$H$_5$)), 4.01 (septet, 2H, $^3J_{H-H}$ = 7 Hz, [(2,6-(*i-Pr*)$_2$C$_6$H$_3$)N]Mo), 1.41 (s, 9H, Mo(=C(C(C*H*$_3$)$_3$))), 1.41, 1.24 (each a d, 12H, $^3J_{H-H}$ = 7 Hz, [(2,6-(*i-Pr*)$_2$C$_6$H$_3$)N]Mo), 1.37, 1.32, 1.27, 1.17, 0.83, 0.64 (each a s, 18H, Mo-C(H)(C(C*H*$_3$)$_2$C$_6$H$_5$), P(OC(C*H*$_3$)$_2$CF$_3$), [F$_3$C(C*H*$_3$)$_2$CO]Mo). ^{13}C NMR (75 MHz, C_6D_6 at 25 °C): δ = 247.9 (d, $^1J_{P-C}$ = 80 Hz, Mo(=*C*(C(CH$_3$)$_3$), 154.0, 152.5, 144.7, 128.8, 126.7, 126.4, 125.9, 123.4 ([(2,6-(i-Pr)$_2$*C*$_6$H$_3$)N]Mo and Mo-C(H)(C(CH$_3$)$_2$*C*$_6$H$_5$)), 127.3, 125.7 (each a q, $^1J_{C-F}$ = 284 Hz, P(OC(CH$_3$)$_2$*C*F$_3$), [(F$_3$*C*)$_2$CH$_3$CO]Mo), 119.3 (d, $^2J_{P-C}$ = 65 Hz, Mo-*C*(H)(C(CH$_3$)$_3$), 79.0 (q, $^2J_{C-F}$ = 29 Hz, [F$_3$C(CH$_3$)$_2$*C*O]Mo), 77.1 (doublet of quartets, $^2J_{C-F}$ = 29 Hz, $^2J_{P-C}$ = 7 Hz, P(O*C*(CH$_3$)$_2$CF$_3$)), 45.5 (d, $^2J_{P-C}$ = 25 Hz, Mo(=C(*C*(CH$_3$)$_3$))), 43.2 (d, $^2J_{P-C}$ = 19 Hz, Mo-C(H)(*C*(CH$_3$)$_2$C$_6$H$_5$)), 34.0 (coincident d, $^3J_{P-C}$ = 8 Hz, Mo-C(H)(C(*C*H$_3$)$_2$C$_6$H$_5$)), 33.6 (d, $^3J_{P-C}$ = 7 Hz, Mo(=C(C(*C*H$_3$)$_3$))), 28.1, 24.3, 24.0, 23.9 (all singlets, [(2,6-(*i-Pr*)$_2$C$_6$H$_3$)N]Mo), 21.8, 21.7, 21.4, 21.2 (P(OC(*C*H$_3$)$_2$CF$_3$) and [F$_3$C(*C*H$_3$)$_2$CO]Mo). ^{31}P {^1H} NMR (121.4 MHz, C_6H_6, 25 °C, ext. H_3PO_4): δ = -110.4. IR (C_6D_6): ν = 2964, 2868, 1471, 1327, 1164, 1129, 1009, 967, 889, 773, 700 cm^{-1}. Anal. Calcd for $C_{35}H_{50}NO_2F_6PMo$: C, 55.48; H, 6.65; N, 1.85. Found: C, 55.20; H, 6.71; N, 1.62.

Table 1. Data Collection and Reduction, Structure Solution and Refinement for **4b.**

Data Collection and Reduction.

Diffractometer type	Siemens P4
Radiation source	rotating-anode
Monochromator type	graphite
Radiation	MoKα
Wavelength	0.71073 Å
Temperature	158 K
Cell measurement reflections	33 ($3.45^{\circ} < \theta < 10.82^{\circ}$)
Intensity measurement method	$2\theta/\omega$ scans
θ range for data collection	2.00 to 22.50°
Limiting indices	$-10 \le h \le 10$, $-10 \le k \le 19$, $-22 \le l \le 21$
Scan width (in ω)	1.2° plus α_1,α_2 separation
Scan speed (in ω)	3.0°/min
Reflections collected	5064
Independent reflections	4744 (R_{int} = 0.0488)
Observed reflections	2982 (I >2sigma(I))
Number of standards	3
Interval between standards	97
Decay of standards	n/a
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	0.9408 and 0.9179

Unit cell refinement and data collection were carried out by use of the Siemens XSCAnS system, Version 2.10b. Data were processed with a local version of CARESS (R.W. Broach et al.), which employs a modified version of the Lehman-Larsen algorithm to obtain integrated intensities and standard deviations from the measured 96-step peak profiles.

Structure Solution and Refinement.

Structure solution method	direct methods
Refinement method	Full-matrix least-squares on F^2
Scattering Factor Source	International Tables Vol C Tables 4.2.6.8 and 6.1.1.4
Final refinement: Data	4742
Restraints	0
Parameters	415
Final R indices [$I>2\sigma(I)$]	R1 = 0.0547, wR2 = 0.1061
R indices (all data)	R1 = 0.1158, wR2 = 0.1253
Goodness-of-fit on F^2	1.157
Largest diff. peak and hole	0.466 and -0.453 $eÅ^{-3}$
Maximum Δ/σ in final cycle	0.000
Mean Δ/σ in final cycle	0.000

Final weighting scheme:

calc $w=1/[\sigma^2(Fo^2)+(0.0103P)^2+19.9982P]$

where $P=(Fo^2+2Fc^2)/3$

R-factor definitions:

$R1 = \sum||F_o|-|F_c||/\sum|F_o|$

$wR2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$

Structure solution, refinement, and generation of figures and tables were carried out by use of Version 5.03 of the Siemens SHELXTL program package.

Table 2. Crystal data and structure refinement for 4b.

Empirical formula	$C_{35}H_{50}F_6MoNO_2P$
Formula weight	757.67
Temperature	158 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 9.9707(10) Å α = 90° b = 17.866(2) Å β = 103.30(9)° c = 20.897(2) Å γ = 90°
Volume, Z	3622.7(7) $Å^3$, 4
Density (calculated)	1.389 Mg/m^3
Absorption coefficient	0.468 mm^{-1}
F(000)	1576
Crystal size	0.20 x 0.10 x 0.10 mm
θ range for data collection	2.00 to 22.50°
Limiting indices	$-10 \le h \le 10$, $-10 \le k \le 19$, $-22 \le l \le 21$
Reflections collected	5064
Independent reflections	4744 (R_{int} = 0.0488)
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	0.9408 and 0.9179
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4742 / 0 / 415
Goodness-of-fit on F^2	1.157
Final R indices [I>2σ(I)]	R1 = 0.0547, wR2 = 0.1061
R indices (all data)	R1 = 0.1158, wR2 = 0.1253
Largest diff. peak and hole	0.466 and -0.453 $eÅ^{-3}$

$$R1 = \sum||F_o|-|F_c||/\sum|F_o|$$

$$wR2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$$

Table 3. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor for 4b.

	x	y	z	U(eq)
Mo(1)	539(1)	743(1)	1845(1)	16(1)
P(1)	-1357(2)	1769(1)	1674(1)	17(1)
O(1)	-25(5)	-34(3)	1215(2)	20(1)
O(2)	-2584(5)	1430(3)	1066(2)	20(1)
N(1)	2074(6)	564(3)	2442(3)	17(2)
C(1)	-898(7)	1011(4)	2253(3)	16(2)
C(2)	-1557(8)	949(4)	2842(4)	20(2)
C(3)	-1167(9)	1627(5)	3291(4)	31(2)
C(4)	-3130(8)	899(5)	2600(4)	36(2)
C(5)	-1023(10)	225(5)	3213(4)	40(3)
C(6)	-3551(7)	1917(4)	636(4)	17(2)
C(7)	-4726(9)	1398(5)	368(4)	29(2)
C(8)	-4061(9)	2550(4)	1010(4)	31(2)
C(9)	-2930(8)	2207(5)	84(4)	29(2)
C(10)	250(8)	1793(4)	1371(4)	17(2)
C(11)	1093(8)	2526(4)	1497(4)	18(2)
C(12)	1417(9)	2719(5)	2235(4)	29(2)
C(13)	2462(8)	2363(5)	1311(4)	30(2)
C(14)	282(8)	3155(4)	1090(4)	19(2)
C(15)	-700(8)	3551(4)	1307(4)	20(2)
C(16)	-1531(9)	4093(4)	917(4)	31(2)
C(17)	-1311(9)	4254(5)	314(4)	35(2)
C(18)	-296(10)	3888(5)	78(4)	37(2)
C(19)	503(9)	3333(5)	463(4)	31(2)
C(20)	3177(7)	254(4)	2900(4)	17(2)
C(21)	3762(8)	-421(4)	2746(4)	21(2)
C(22)	4852(7)	-730(5)	3211(4)	21(2)
C(23)	5378(8)	-379(5)	3808(4)	27(2)
C(24)	4815(8)	287(5)	3945(4)	29(2)
C(25)	3708(8)	621(4)	3512(3)	19(2)
C(26)	3228(8)	-792(5)	2080(3)	21(2)

C(27)	3788(10)	-387(5)	1554(4)	41(3)
C(28)	3520(10)	-1626(5)	2079(4)	42(3)
C(29)	3166(8)	1366(4)	3659(4)	22(2)
C(30)	2913(10)	1405(5)	4356(4)	38(2)
C(31)	4147(9)	1982(5)	3546(4)	37(2)
C(32)	-1117(8)	-518(4)	919(4)	21(2)
C(33)	-448(10)	-1298(5)	936(5)	38(2)
C(34)	-1672(9)	-286(5)	209(4)	33(2)
C(35)	-2250(8)	-544(5)	1294(4)	28(2)
F(1)	-5764(5)	1759(3)	-46(2)	38(1)
F(2)	-5293(5)	1100(3)	835(2)	38(1)
F(3)	-4395(5)	817(3)	31(2)	42(1)
F(4)	615(5)	-1301(3)	647(3)	47(2)
F(5)	-1360(5)	-1803(3)	635(3)	54(2)
F(6)	35(5)	-1533(3)	1551(3)	49(2)

Table 4. Bond lengths [Å] and angles [°] for 4b.

Mo(1)-N(1)	1.767(6)	Mo(1)-C(1)	1.889(7)
Mo(1)-O(1)	1.906(5)	Mo(1)-C(10)	2.110(7)
Mo(1)-P(1)	2.599(2)	P(1)-O(2)	1.662(5)
P(1)-C(1)	1.804(7)	P(1)-C(10)	1.854(8)
O(1)-C(32)	1.416(9)	O(2)-C(6)	1.447(8)
N(1)-C(20)	1.396(9)	C(1)-C(2)	1.529(10)
C(2)-C(3)	1.526(11)	C(2)-C(5)	1.537(11)
C(2)-C(4)	1.536(11)	C(6)-C(7)	1.499(11)
C(6)-C(8)	1.525(10)	C(6)-C(9)	1.520(10)
C(7)-F(3)	1.338(9)	C(7)-F(2)	1.346(9)
C(7)-F(1)	1.350(9)	C(10)-C(11)	1.546(10)
C(11)-C(14)	1.525(10)	C(11)-C(12)	1.540(10)
C(11)-C(13)	1.530(10)	C(14)-C(15)	1.368(10)
C(14)-C(19)	1.414(11)	C(15)-C(16)	1.406(11)
C(16)-C(17)	1.357(11)	C(17)-C(18)	1.388(12)
C(18)-C(19)	1.403(12)	C(20)-C(21)	1.408(11)
C(20)-C(25)	1.425(10)	C(21)-C(22)	1.394(10)
C(21)-C(26)	1.523(10)	C(22)-C(23)	1.386(11)
C(23)-C(24)	1.374(11)	C(24)-C(25)	1.391(10)
C(25)-C(29)	1.495(11)	C(26)-C(28)	1.518(11)
C(26)-C(27)	1.526(11)	C(29)-C(31)	1.527(11)
C(29)-C(30)	1.537(11)	C(32)-C(35)	1.516(10)
C(32)-C(34)	1.516(10)	C(32)-C(33)	1.542(12)
C(33)-F(6)	1.333(10)	C(33)-F(5)	1.332(10)
C(33)-F(4)	1.335(10)		

N(1)-Mo(1)-C(1)	110.5(3)	N(1)-Mo(1)-O(1)	115.2(2)
C(1)-Mo(1)-O(1)	111.2(3)	N(1)-Mo(1)-C(10)	119.7(3)
C(1)-Mo(1)-C(10)	87.2(3)	O(1)-Mo(1)-C(10)	109.7(3)
N(1)-Mo(1)-P(1)	135.2(2)	C(1)-Mo(1)-P(1)	43.9(2)
O(1)-Mo(1)-P(1)	109.2(2)	C(10)-Mo(1)-P(1)	44.9(2)
O(2)-P(1)-C(1)	105.5(3)	O(2)-P(1)-C(10)	106.8(3)
C(1)-P(1)-C(10)	98.0(3)	O(2)-P(1)-Mo(1)	103.4(2)
C(1)-P(1)-Mo(1)	46.6(2)	C(10)-P(1)-Mo(1)	53.4(2)
C(32)-O(1)-Mo(1)	145.3(5)	C(6)-O(2)-P(1)	121.5(4)
C(20)-N(1)-Mo(1)	166.8(5)	C(2)-C(1)-P(1)	120.3(5)

C(2)-C(1)-Mo(1)	149.0(5)	P(1)-C(1)-Mo(1)	89.4(3)
C(3)-C(2)-C(1)	109.9(6)	C(3)-C(2)-C(5)	110.4(7)
C(1)-C(2)-C(5)	107.7(6)	C(3)-C(2)-C(4)	110.2(7)
C(1)-C(2)-C(4)	109.5(6)	C(5)-C(2)-C(4)	109.1(7)
O(2)-C(6)-C(7)	102.2(6)	O(2)-C(6)-C(8)	112.4(6)
C(7)-C(6)-C(8)	109.0(7)	O(2)-C(6)-C(9)	110.3(6)
C(7)-C(6)-C(9)	110.2(7)	C(8)-C(6)-C(9)	112.2(7)
F(3)-C(7)-F(2)	105.7(7)	F(3)-C(7)-F(1)	106.3(7)
F(2)-C(7)-F(1)	105.4(6)	F(3)-C(7)-C(6)	114.3(7)
F(2)-C(7)-C(6)	113.3(7)	F(1)-C(7)-C(6)	111.2(7)
C(11)-C(10)-P(1)	116.1(5)	C(11)-C(10)-Mo(1)	131.5(5)
P(1)-C(10)-Mo(1)	81.7(3)	C(14)-C(11)-C(12)	110.8(6)
C(14)-C(11)-C(13)	112.8(6)	C(12)-C(11)-C(13)	107.6(6)
C(14)-C(11)-C(10)	109.3(6)	C(12)-C(11)-C(10)	110.0(6)
C(13)-C(11)-C(10)	106.1(6)	C(15)-C(14)-C(19)	117.8(7)
C(15)-C(14)-C(11)	121.7(7)	C(19)-C(14)-C(11)	120.5(7)
C(14)-C(15)-C(16)	122.3(8)	C(17)-C(16)-C(15)	119.0(8)
C(16)-C(17)-C(18)	121.1(9)	C(19)-C(18)-C(17)	119.6(8)
C(18)-C(19)-C(14)	120.1(8)	C(21)-C(20)-N(1)	119.0(7)
C(21)-C(20)-C(25)	120.7(7)	N(1)-C(20)-C(25)	120.2(7)
C(22)-C(21)-C(20)	118.5(7)	C(22)-C(21)-C(26)	121.2(7)
C(20)-C(21)-C(26)	120.3(7)	C(23)-C(22)-C(21)	121.4(8)
C(24)-C(23)-C(22)	119.5(8)	C(23)-C(24)-C(25)	122.4(8)
C(24)-C(25)-C(20)	117.5(7)	C(24)-C(25)-C(29)	121.2(7)
C(20)-C(25)-C(29)	121.1(7)	C(28)-C(26)-C(27)	111.3(7)
C(28)-C(26)-C(21)	113.6(7)	C(27)-C(26)-C(21)	110.2(7)
C(25)-C(29)-C(31)	109.6(6)	C(25)-C(29)-C(30)	112.5(7)
C(31)-C(29)-C(30)	111.4(7)	O(1)-C(32)-C(35)	112.5(6)
O(1)-C(32)-C(34)	109.4(6)	C(35)-C(32)-C(34)	111.5(7)
O(1)-C(32)-C(33)	104.9(6)	C(35)-C(32)-C(33)	109.2(7)
C(34)-C(32)-C(33)	109.1(7)	F(6)-C(33)-F(5)	107.2(8)
F(6)-C(33)-F(4)	106.7(8)	F(5)-C(33)-F(4)	108.1(7)
F(6)-C(33)-C(32)	111.4(7)	F(5)-C(33)-C(32)	111.0(7)
F(4)-C(33)-C(32)	112.2(8)		

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 4b.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + \ldots + 2hka^*b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Mo(1)	15(1)	15(1)	16(1)	-1(1)	0(1)	0(1)
P(1)	16(1)	16(1)	18(1)	1(1)	1(1)	1(1)
O(1)	25(3)	14(3)	19(3)	0(2)	3(3)	-3(3)
O(2)	20(3)	20(3)	16(3)	3(2)	-4(2)	-5(3)
N(1)	19(4)	15(4)	17(3)	1(3)	3(3)	-1(3)
C(1)	15(4)	13(4)	19(4)	1(3)	-1(4)	-1(3)
C(2)	18(4)	25(5)	18(4)	1(4)	7(4)	0(4)
C(3)	30(5)	38(6)	27(5)	-1(4)	12(4)	2(5)
C(4)	28(5)	48(7)	35(5)	7(5)	15(4)	1(5)
C(5)	60(7)	30(6)	29(5)	10(4)	11(5)	5(5)
C(6)	11(4)	16(4)	21(4)	1(4)	-2(4)	3(4)
C(7)	25(5)	31(5)	32(5)	3(5)	7(4)	1(4)
C(8)	32(5)	23(5)	34(5)	2(4)	4(4)	8(4)
C(9)	29(5)	31(5)	20(5)	7(4)	-8(4)	-6(4)
C(10)	17(4)	16(4)	16(4)	-2(4)	1(4)	0(4)
C(11)	19(5)	15(4)	21(4)	-1(4)	5(4)	-2(4)
C(12)	29(5)	22(5)	28(5)	-3(4)	-7(4)	-4(4)
C(13)	23(5)	23(5)	42(6)	0(4)	6(4)	-3(4)
C(14)	18(5)	14(4)	22(4)	3(4)	0(4)	-6(4)
C(15)	20(5)	15(4)	28(5)	-4(4)	9(4)	-2(4)
C(16)	30(5)	21(5)	37(6)	-2(4)	1(4)	-2(4)
C(17)	36(5)	24(5)	36(5)	-1(5)	-10(4)	-3(5)
C(18)	52(7)	31(5)	23(5)	5(4)	3(5)	-3(5)
C(19)	37(6)	27(5)	31(5)	5(4)	10(4)	1(5)
C(20)	14(4)	17(5)	19(4)	3(4)	0(4)	-4(4)
C(21)	24(5)	15(4)	25(5)	2(4)	7(4)	-8(4)
C(22)	21(5)	15(4)	26(4)	1(4)	2(4)	9(4)
C(23)	21(5)	23(5)	32(5)	9(4)	-6(4)	5(4)
C(24)	32(5)	38(6)	14(5)	0(4)	-1(4)	-3(5)
C(25)	22(4)	22(5)	15(4)	4(4)	9(4)	-5(4)
C(26)	18(4)	22(4)	22(4)	-5(4)	1(3)	0(4)

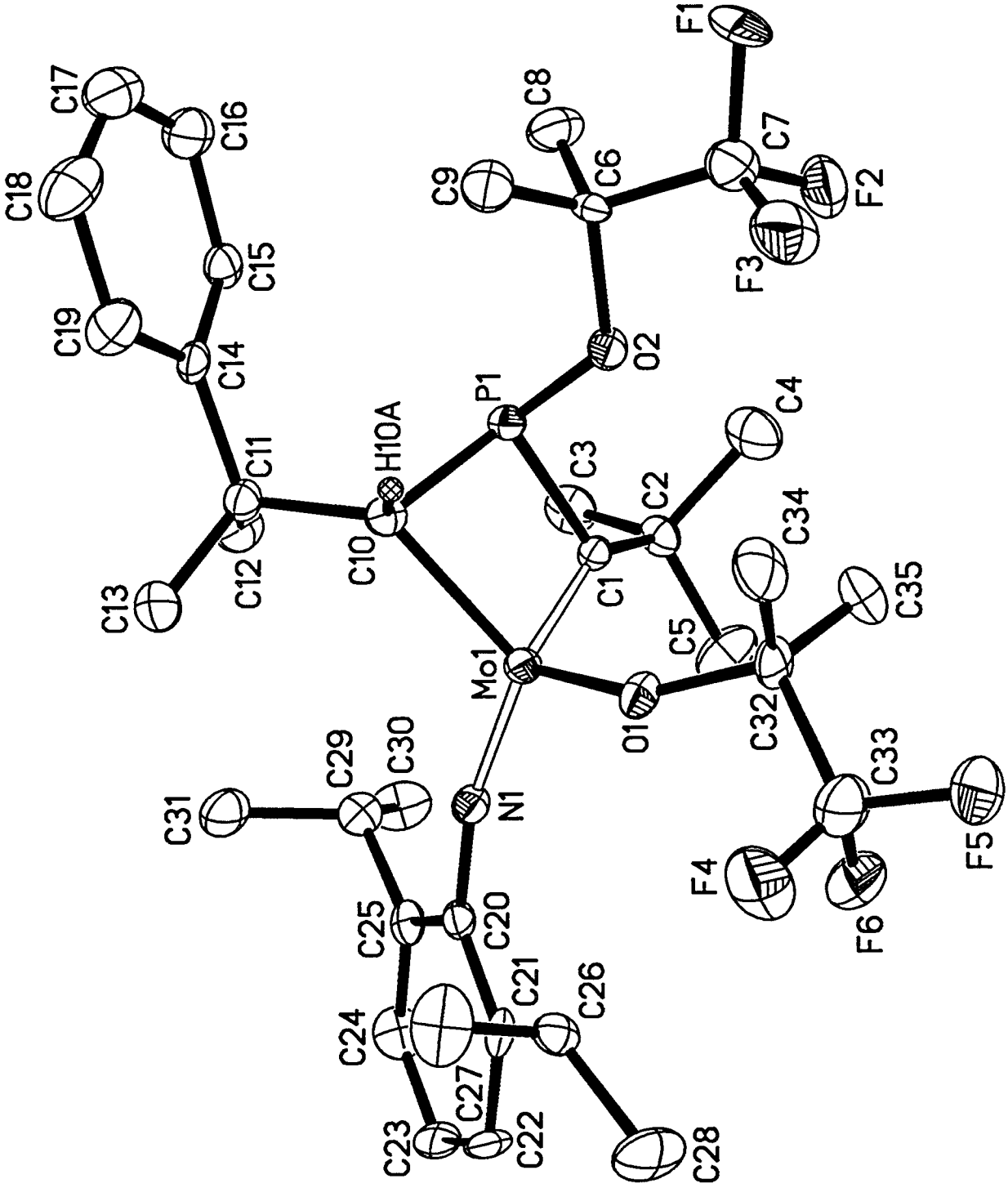
C(27)	59(7)	46(6)	20(5)	-8(4)	14(5)	-14(5)
C(28)	48(6)	30(6)	43(6)	-17(5)	1(5)	11(5)
C(29)	25(5)	25(5)	14(4)	-2(4)	-1(4)	-1(4)
C(30)	49(6)	39(6)	25(5)	-3(4)	9(5)	11(5)
C(31)	34(6)	22(5)	48(6)	-3(5)	-3(5)	-2(4)
C(32)	23(5)	15(5)	25(5)	-9(3)	6(4)	-6(4)
C(33)	38(6)	24(5)	46(7)	-8(5)	0(5)	-4(5)
C(34)	29(5)	37(6)	26(5)	2(4)	-7(4)	-10(5)
C(35)	19(5)	36(6)	28(5)	-6(4)	4(4)	-7(4)
F(1)	21(3)	40(3)	42(3)	6(3)	-17(2)	1(3)
F(2)	30(3)	39(3)	43(3)	8(3)	4(3)	-13(3)
F(3)	37(3)	37(3)	44(3)	-15(3)	-6(2)	0(3)
F(4)	35(3)	46(3)	67(4)	-30(3)	26(3)	-4(3)
F(5)	37(3)	25(3)	92(5)	-21(3)	-3(3)	-8(3)
F(6)	43(4)	29(3)	69(4)	21(3)	-1(3)	0(3)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 4b.

	x	y	z	U(eq)
H(3A)	-1590(9)	1582(5)	3668(4)	46
H(3B)	-1497(9)	2084(5)	3045(4)	46
H(3C)	-162(9)	1650(5)	3446(4)	46
H(4A)	-3369(8)	462(5)	2313(4)	54
H(4B)	-3475(8)	1354(5)	2354(4)	54
H(4C)	-3551(8)	850(5)	2978(4)	54
H(5A)	-1282(10)	-205(5)	2919(4)	59
H(5B)	-1429(10)	171(5)	3595(4)	59
H(5C)	-17(10)	249(5)	3360(4)	59
H(8A)	-3297(9)	2892(4)	1187(4)	46
H(8B)	-4415(9)	2340(4)	1372(4)	46
H(8C)	-4799(9)	2824(4)	710(4)	46
H(9A)	-2166(8)	2547(5)	265(4)	43
H(9B)	-3637(8)	2476(5)	-238(4)	43
H(9C)	-2587(8)	1785(5)	-132(4)	43
H(10A)	-1(8)	1703(4)	885(4)	20
H(12A)	1937(9)	2308(5)	2487(4)	43
H(12B)	554(9)	2794(5)	2375(4)	43
H(12C)	1967(9)	3179(5)	2312(4)	43
H(13A)	2938(8)	1954(5)	1585(4)	45
H(13B)	3040(8)	2813(5)	1383(4)	45
H(13C)	2285(8)	2218(5)	847(4)	45
H(15A)	-826(8)	3457(4)	1737(4)	25
H(16A)	-2236(9)	4342(4)	1072(4)	37
H(17A)	-1860(9)	4625(5)	50(4)	43
H(18A)	-143(10)	4011(5)	-342(4)	44
H(19A)	1193(9)	3077(5)	302(4)	37
H(22A)	5243(7)	-1190(5)	3117(4)	26
H(23A)	6121(8)	-597(5)	4119(4)	33
H(24A)	5197(8)	529(5)	4351(4)	35
H(26A)	2204(8)	-729(5)	1964(3)	25
H(27A)	3581(10)	149(5)	1564(4)	61

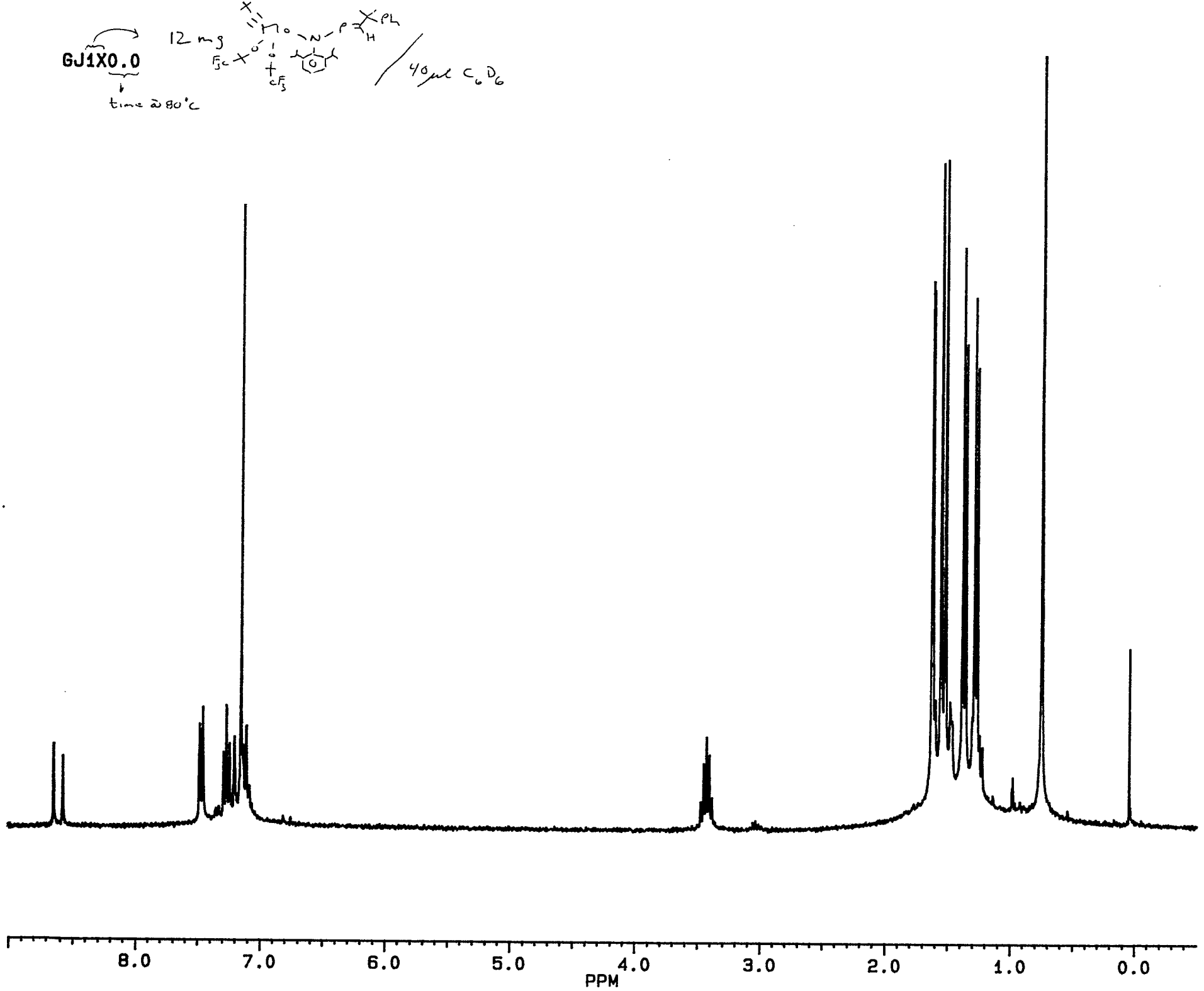
H(27B)	3355(10)	-591(5)	1120(4)	61
H(27C)	4788(10)	-458(5)	1639(4)	61
H(28A)	3148(10)	-1871(5)	2421(4)	63
H(28B)	4517(10)	-1708(5)	2168(4)	63
H(28C)	3083(10)	-1837(5)	1649(4)	63
H(29A)	2261(8)	1446(4)	3341(4)	27
H(30A)	2557(10)	1902(5)	4429(4)	56
H(30B)	3781(10)	1317(5)	4679(4)	56
H(30C)	2239(10)	1023(5)	4405(4)	56
H(31A)	3788(9)	2470(5)	3641(4)	55
H(31B)	4225(9)	1970(5)	3087(4)	55
H(31C)	5057(9)	1902(5)	3837(4)	55
H(34A)	-916(9)	-272(5)	-18(4)	49
H(34B)	-2090(9)	212(5)	196(4)	49
H(34C)	-2368(9)	-647(5)	-8(4)	49
H(35A)	-1859(8)	-695(5)	1749(4)	42
H(35B)	-2952(8)	-908(5)	1086(4)	42
H(35C)	-2671(8)	-48(5)	1288(4)	42

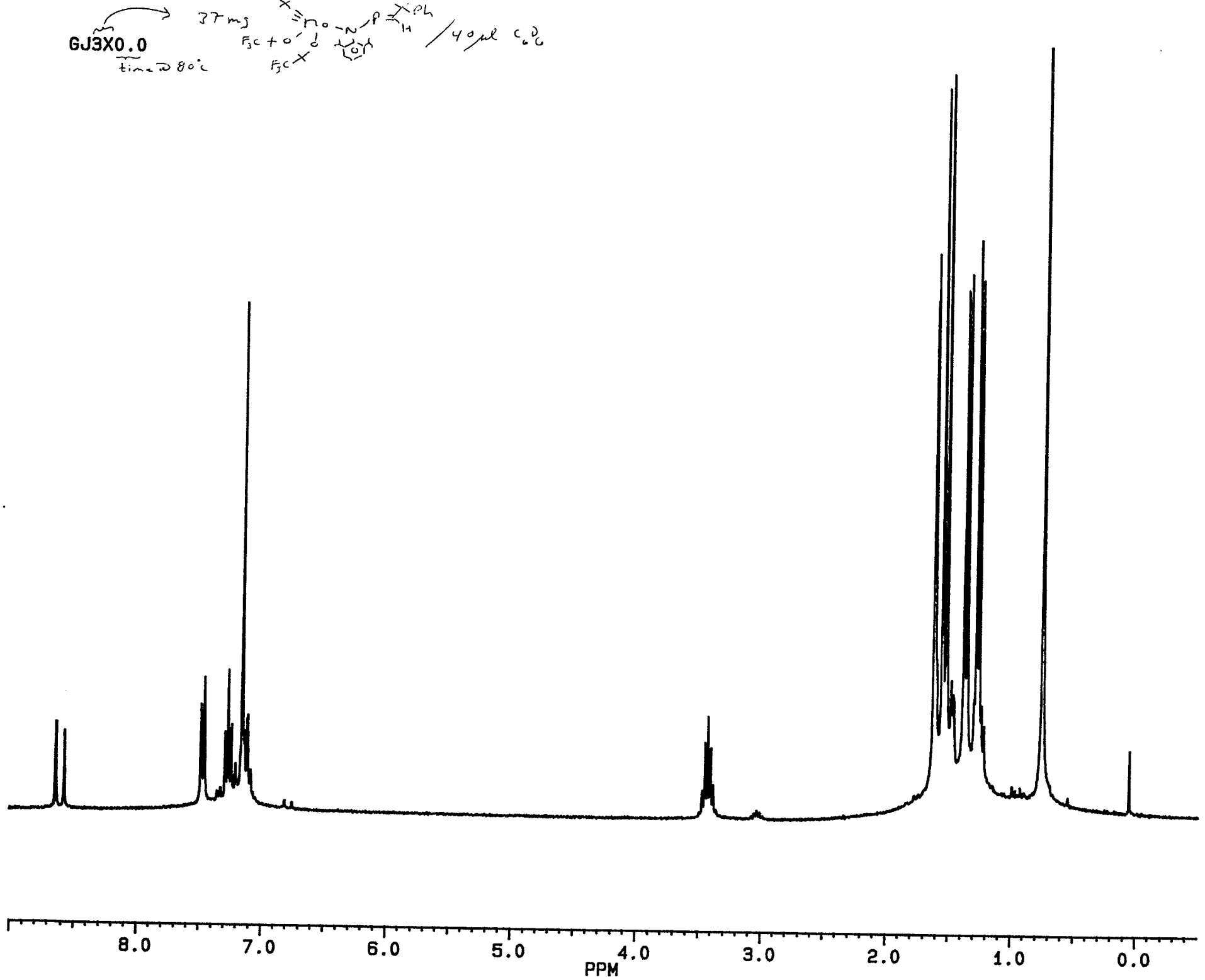
Figure 4. Thermal plot showing complete atomic numbering scheme for **4b**.

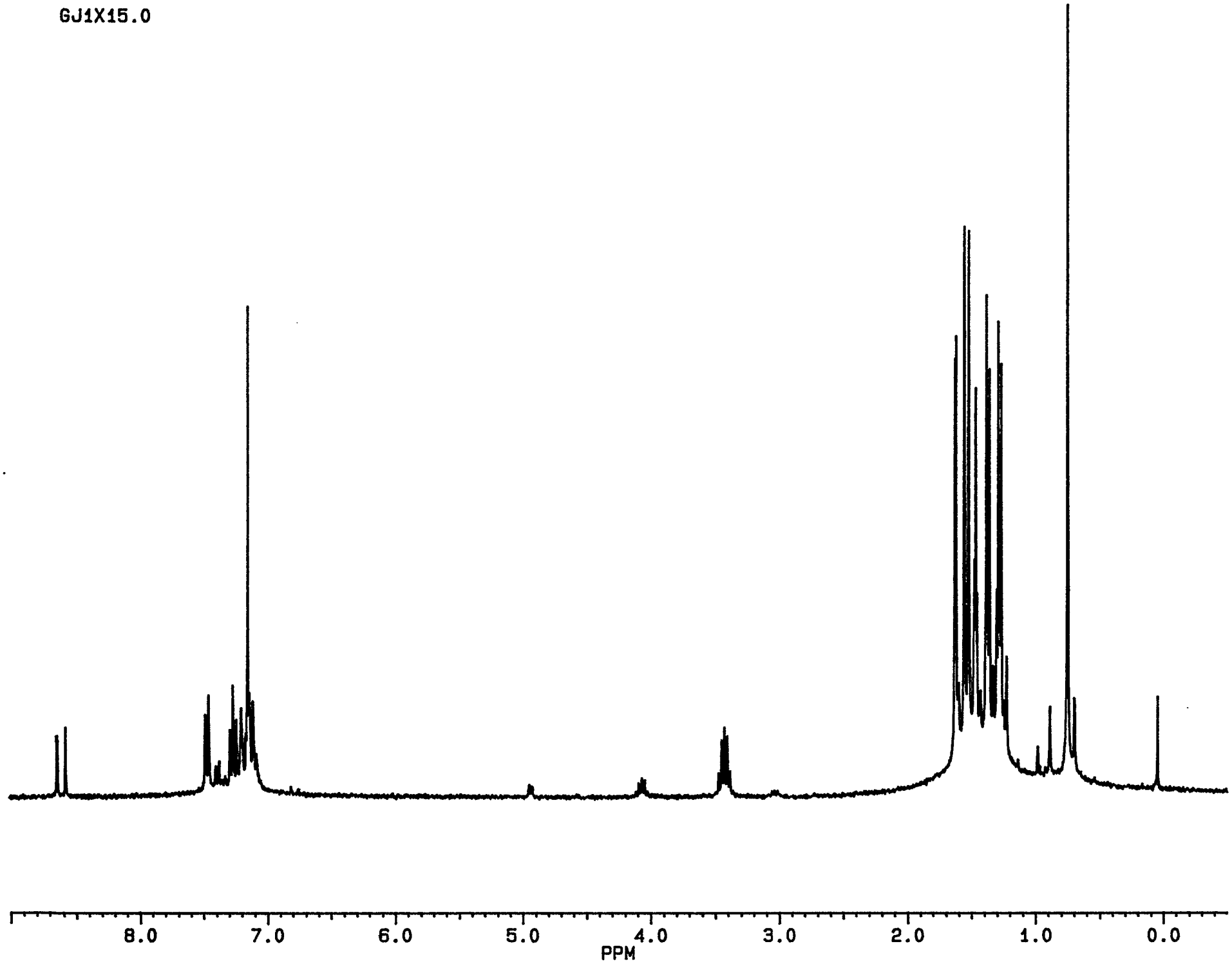

F1
C8
C17
C16
C7
C6
C9
F2
C18
C15
F3
C19
C14
O2
P1
C4
C11
H10A
C3
C2
C34
C10
C12
C1
C35
C13
C5
Mo1
O1
C32
C29
C30
C33
C31
N1
F5
F4
C25
C20
F6
C21
C26
C24
C27
C23
C22
C28

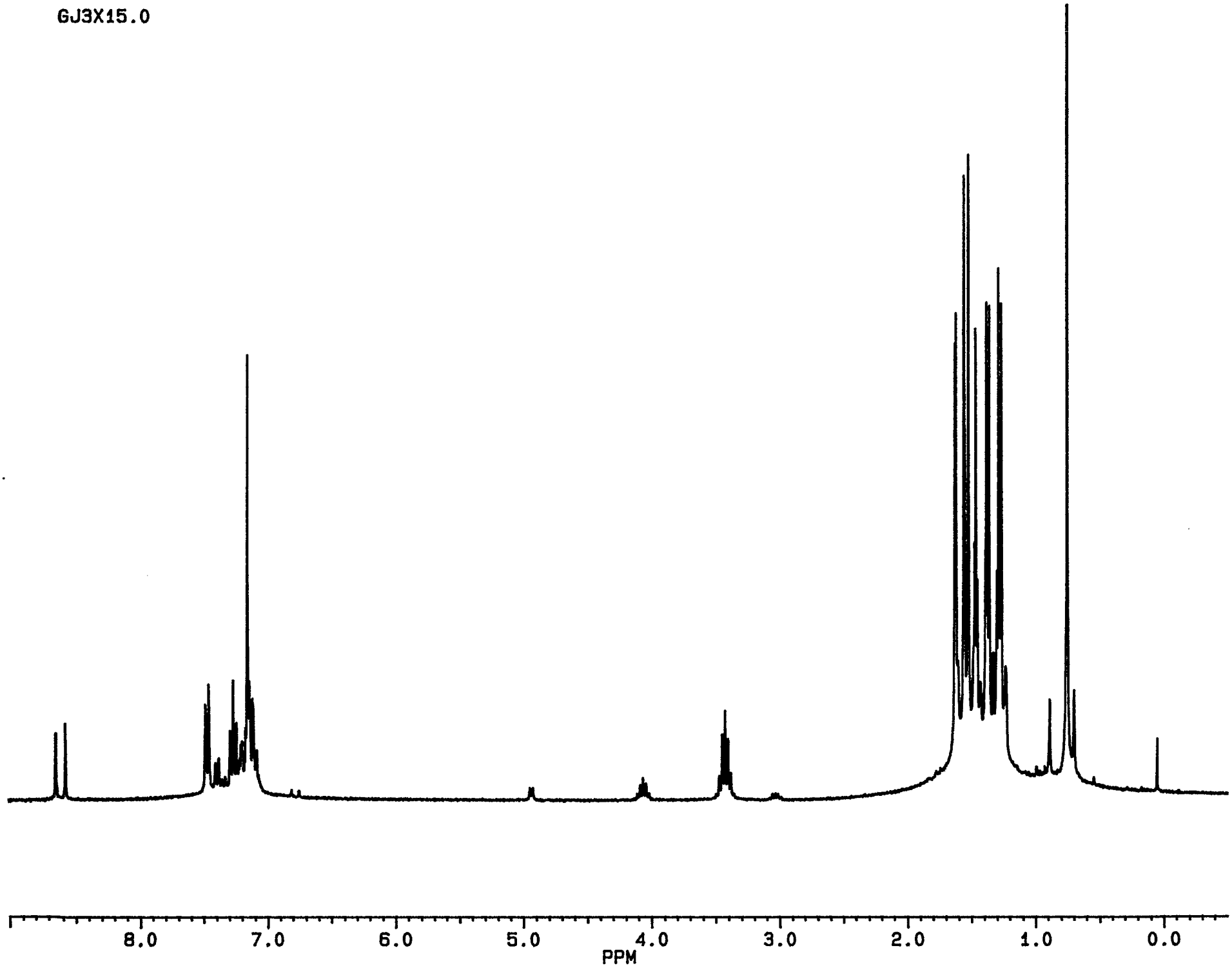
Experimental details and ^1H NMR spectra of concentration studies for the rearrangement of 3b to 4b.

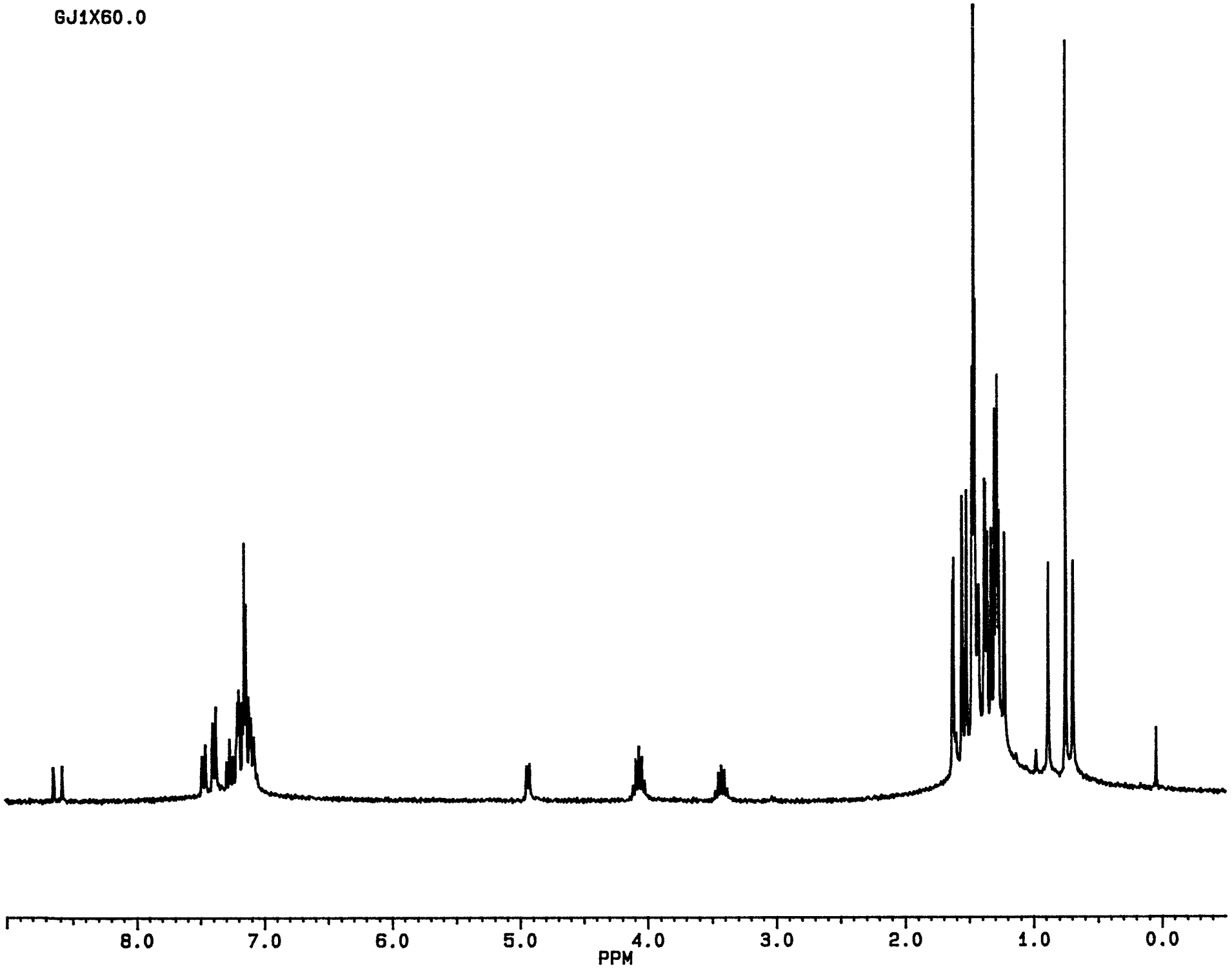
Two NMR tubes were charged with 40 mL of dry C_6D_6 in a helium-filled dry box. One tube was charged with 12 mg (0.016 mmol) of complex **3b**, labeled "1X;" the second tube was charged with 37 mg (0.049 mmol) of complex **3b**, labeled "3X." Both tubes were immersed in an 80 °C oil bath and their ^1H NMR spectra followed at regular intervals. As an example, spectra are labeled as GJ1X15.0, which represents sample 1X at 15 m immersion at 80 °C. The reactions were monitored until all starting **3b** had been converted to complex **4b**.

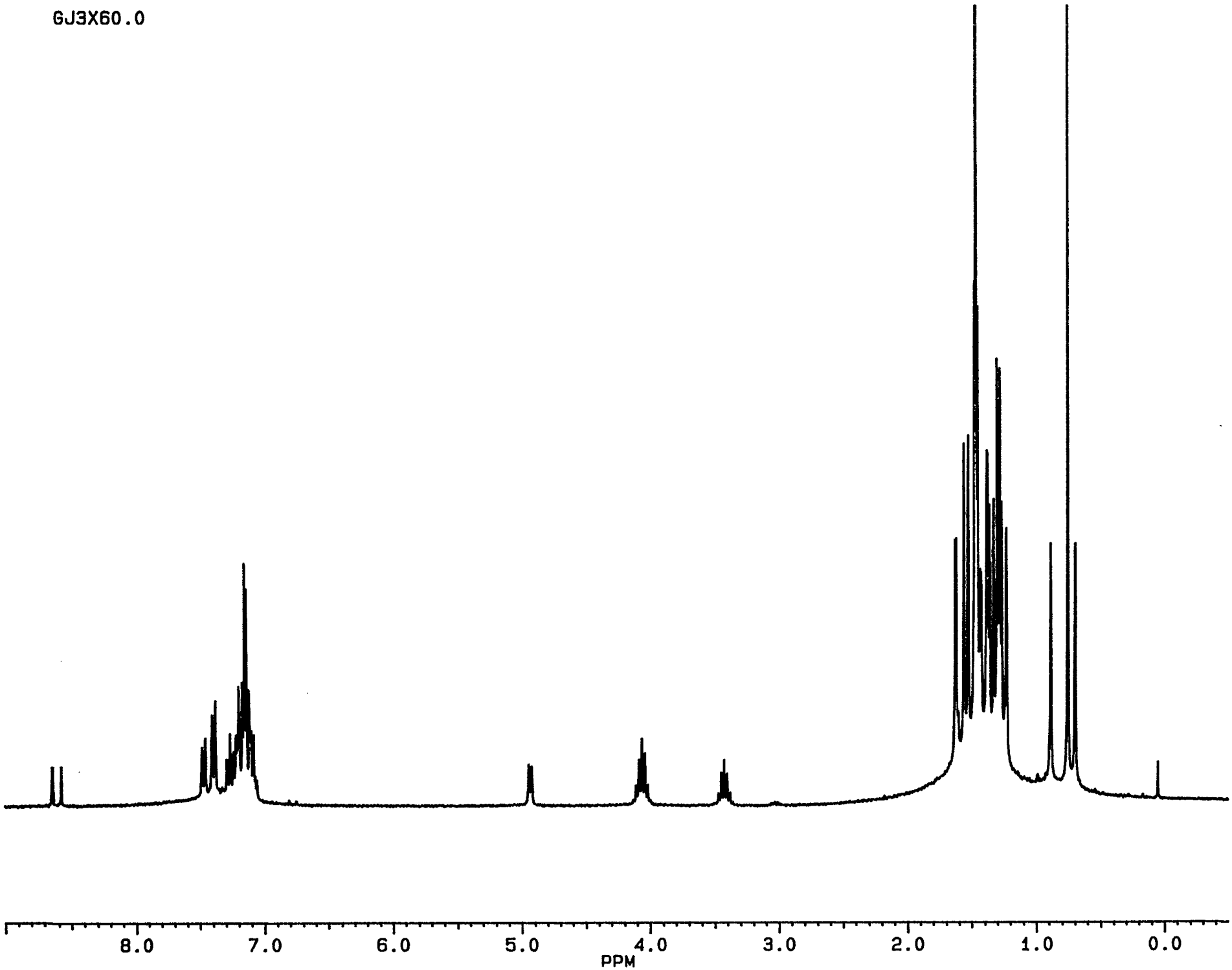


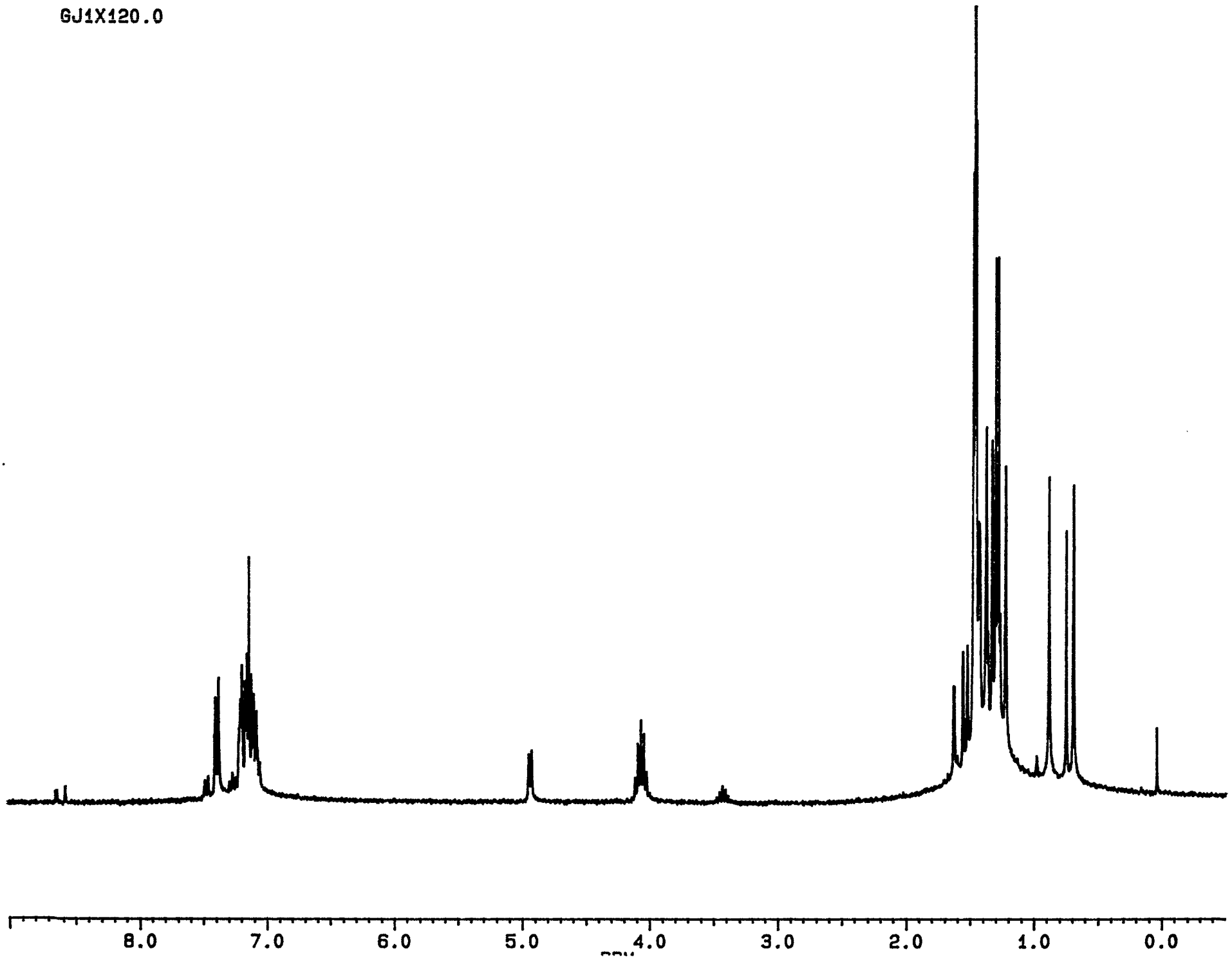


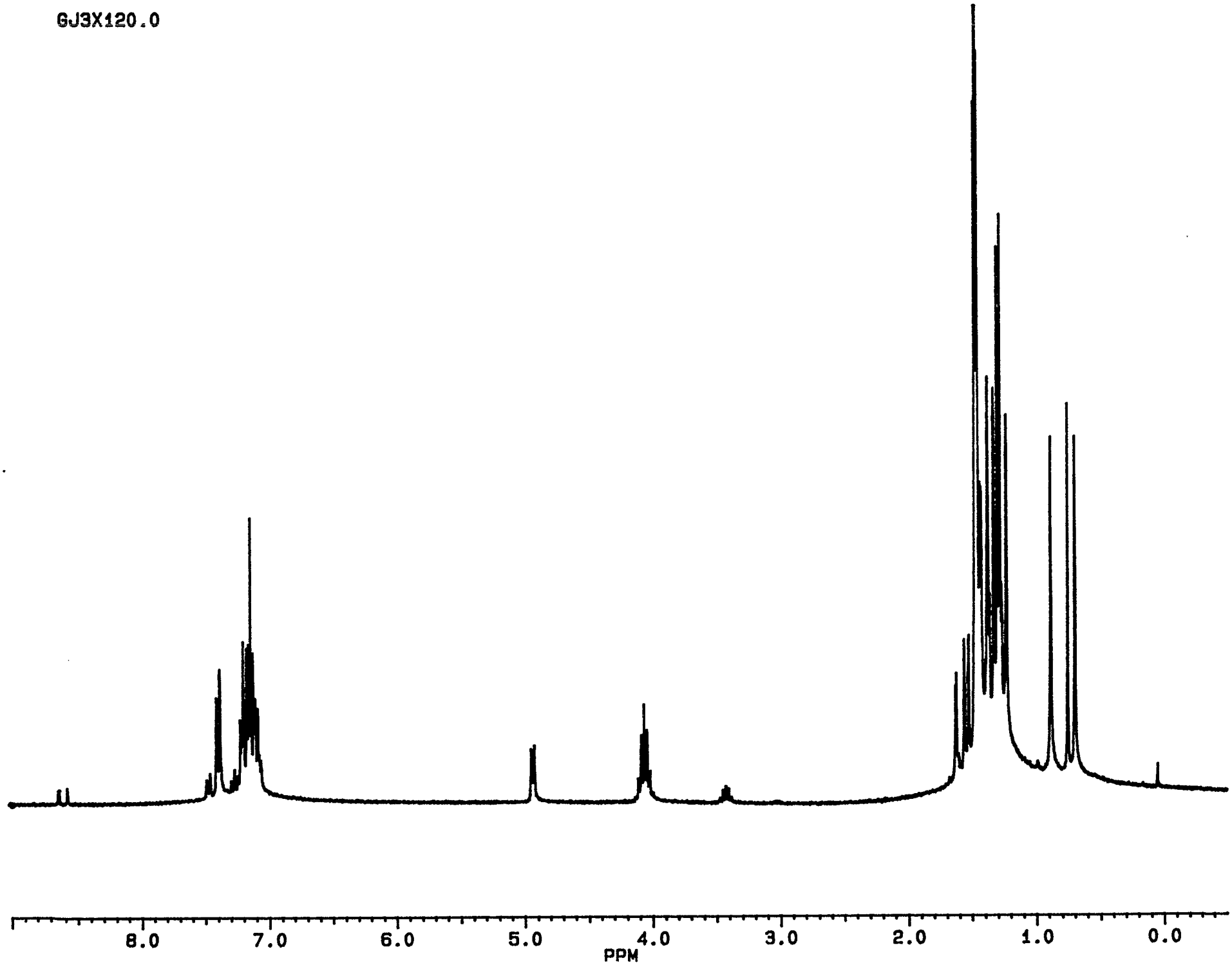


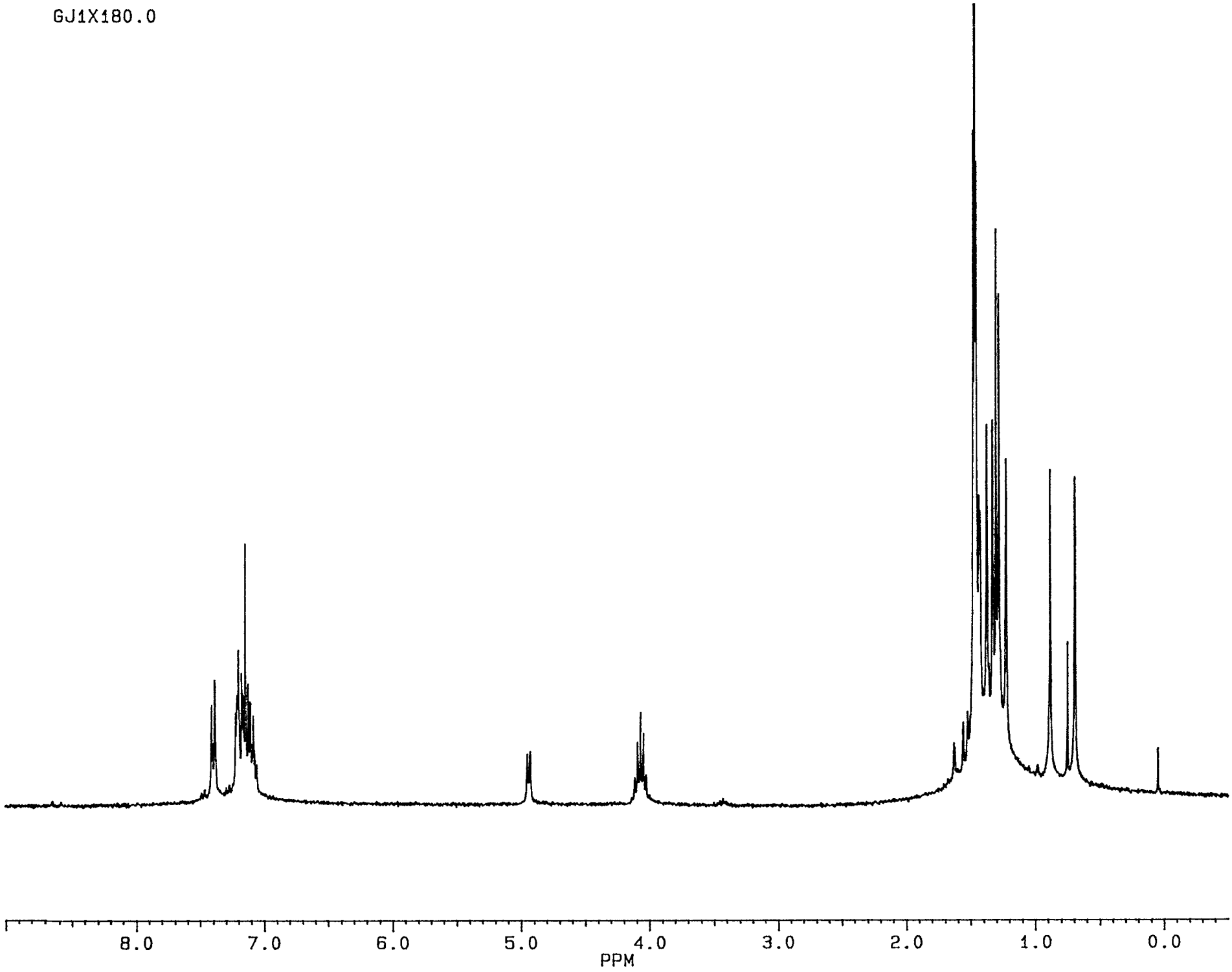


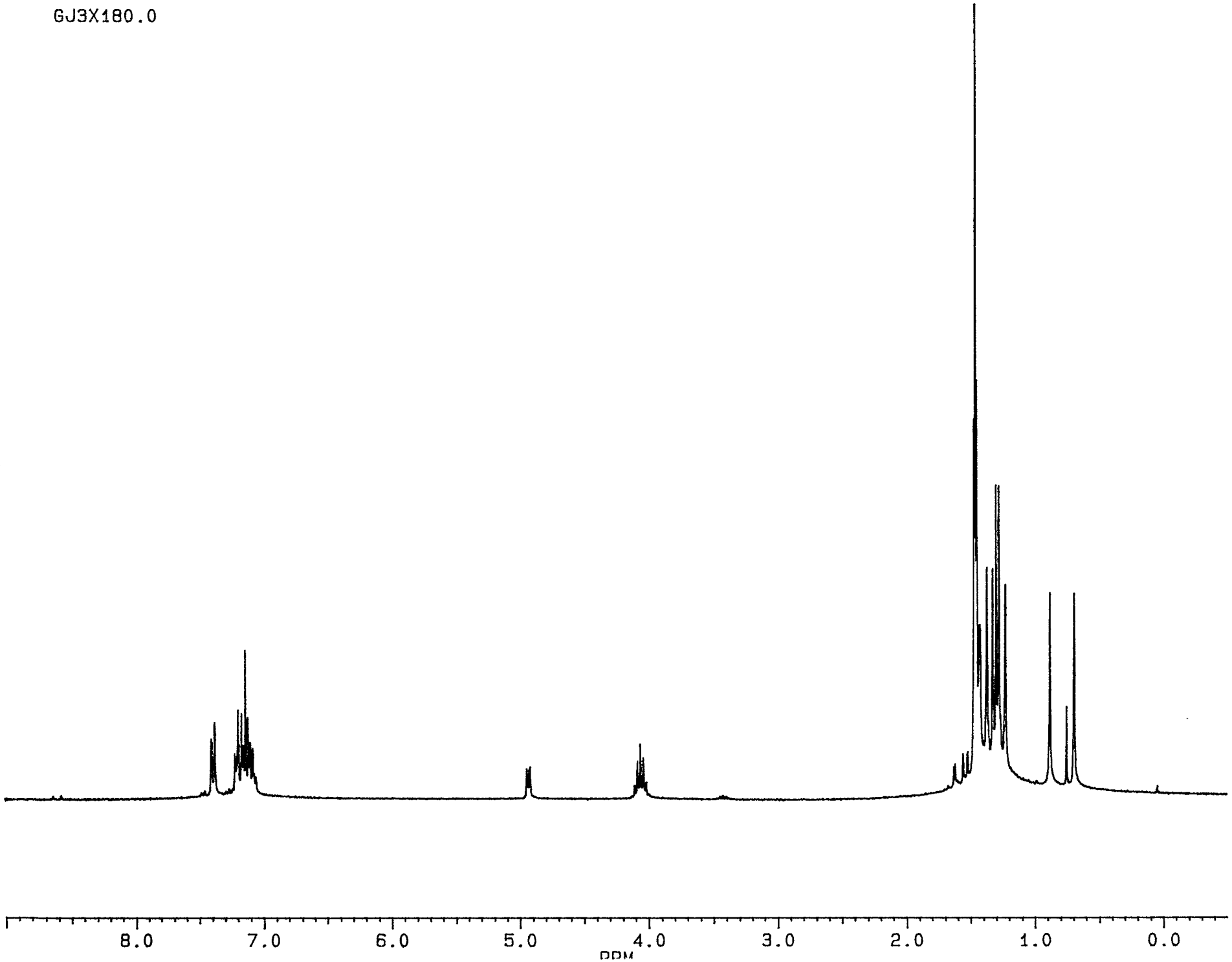












Experimental details and ^{1}H NMR spectra from the reaction of 1b with pivalonitrile.

In a helium-filled dry box, a 25 mL scintillation vial was charged with 0.102 g (0.155 mmol) of alkylidene complex **1b** and approximately 1mL of dry diethyl ether. Upon the addition of 22 μL (0.199 mmol) of pivalonitrile (RN [630-18-2]) at 25 °C, the vial was sealed and stirred at room temperature for 5 h. The reaction mixture was dried under vacuum and the residue dissolved in dry C_6D_6. ^{1}H NMR indicted that there had been no reaction as indicated by the presence of unreacted **1b**.