Ancillary Ligand and Olefin Substituent Effects on Olefin Dissociation for Cationic Zirconocene Complexes Bearing a Coordinated Pendant Olefin

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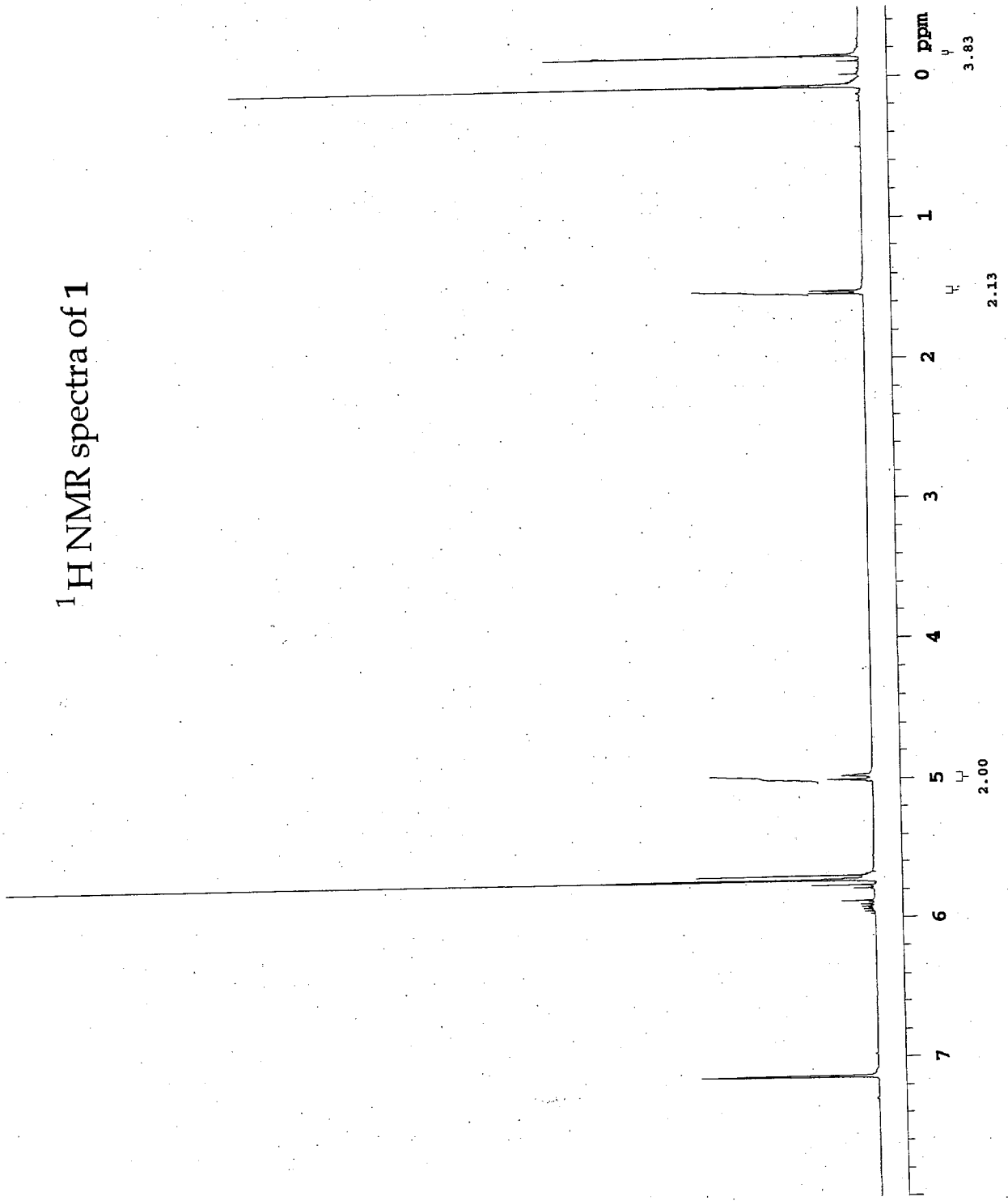
Supporting Information

^{1}H spectra (500 MHz, CD_2Cl_2, -80 °C) for compounds **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12**, **13**, **14**, **16**, **18**

Dynamic ^{1}H spectra (500 MHz, CD_2Cl_2, -10 - +30 °C) for compound **14**

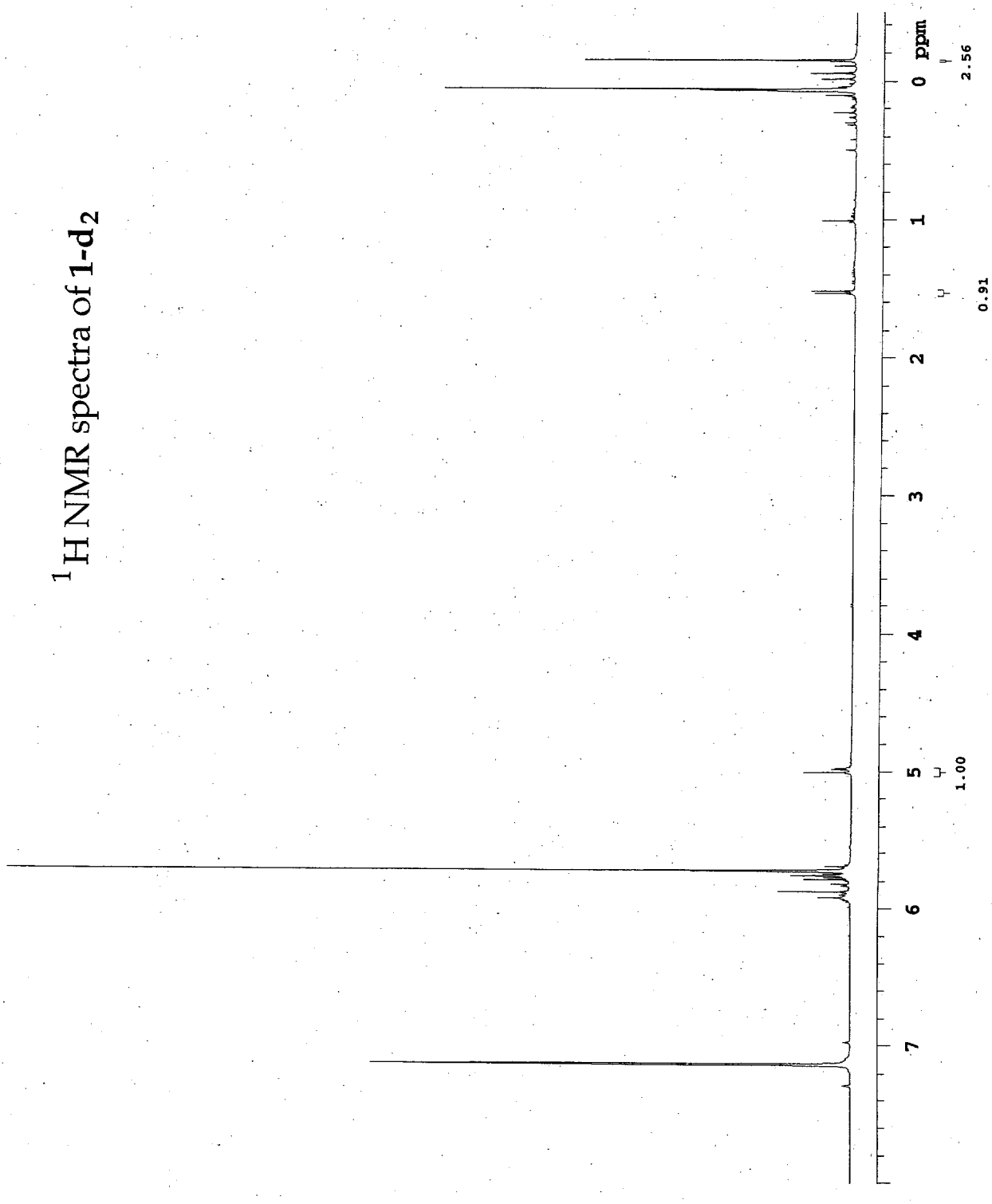
Crystal Structure Analysis of compound **15**

^{1}H NMR spectra of **1**

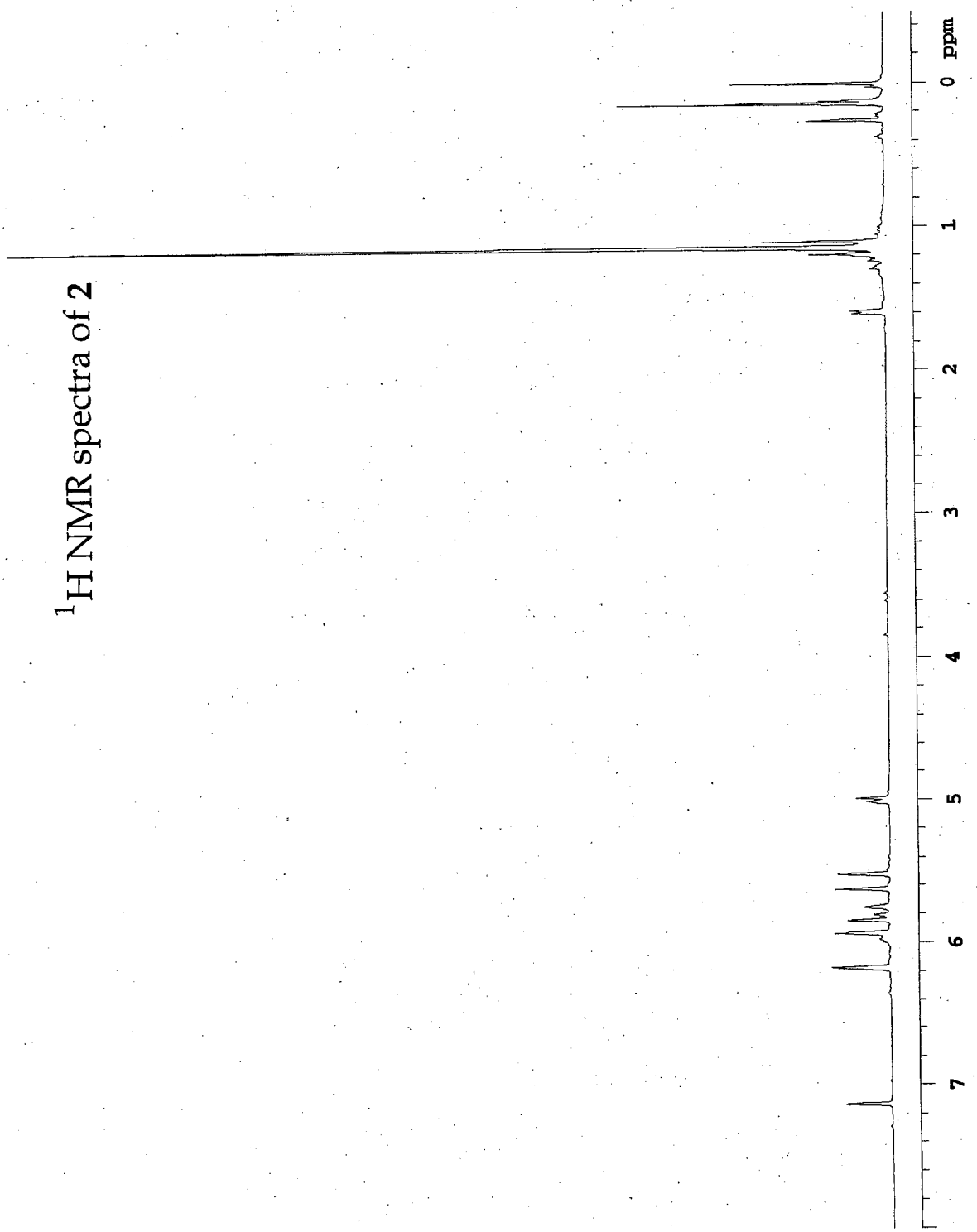


2

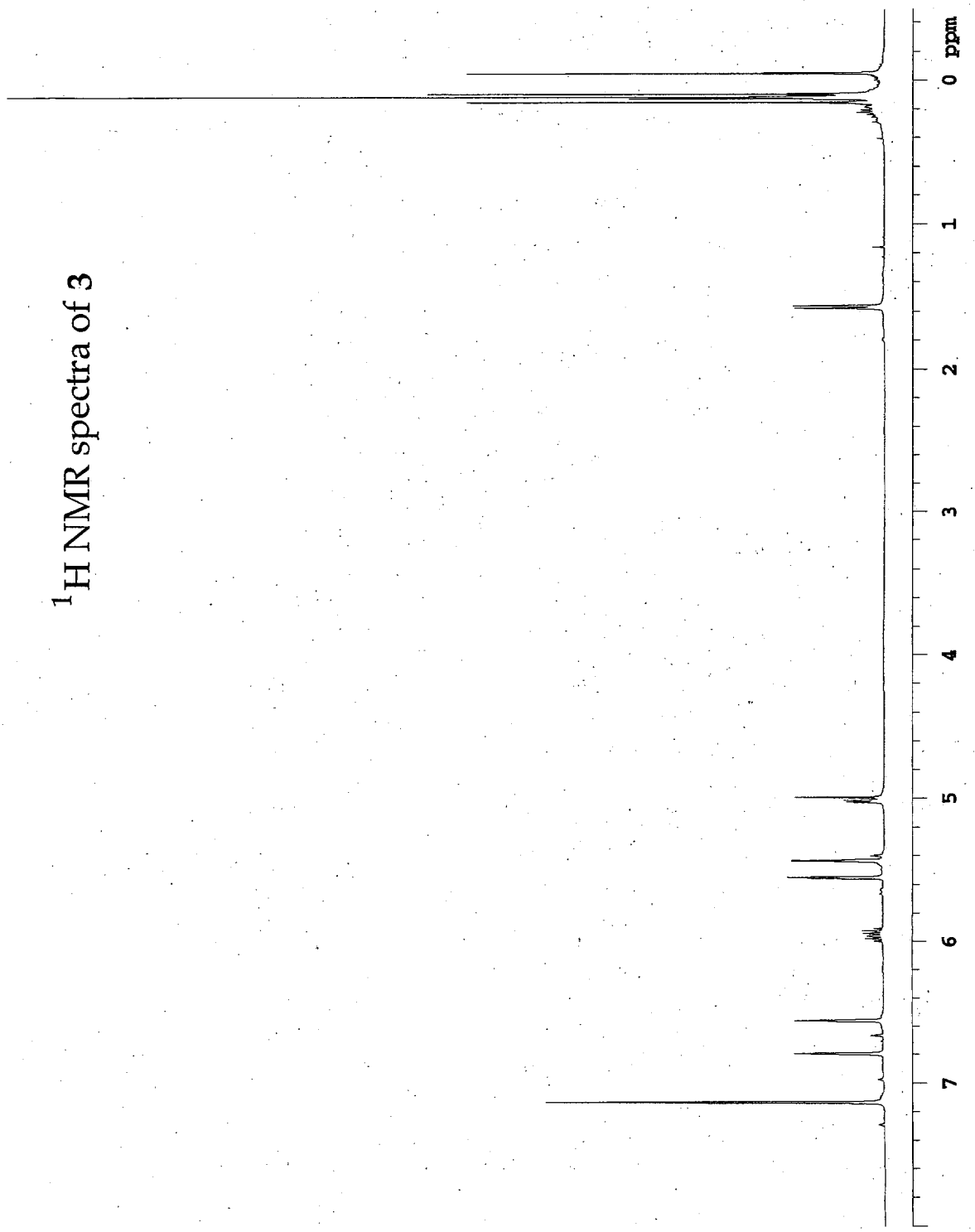
^{1}H NMR spectra of **1-d$_2$**



^{1}H NMR spectra of **2**



^{1}H NMR spectra of **3**



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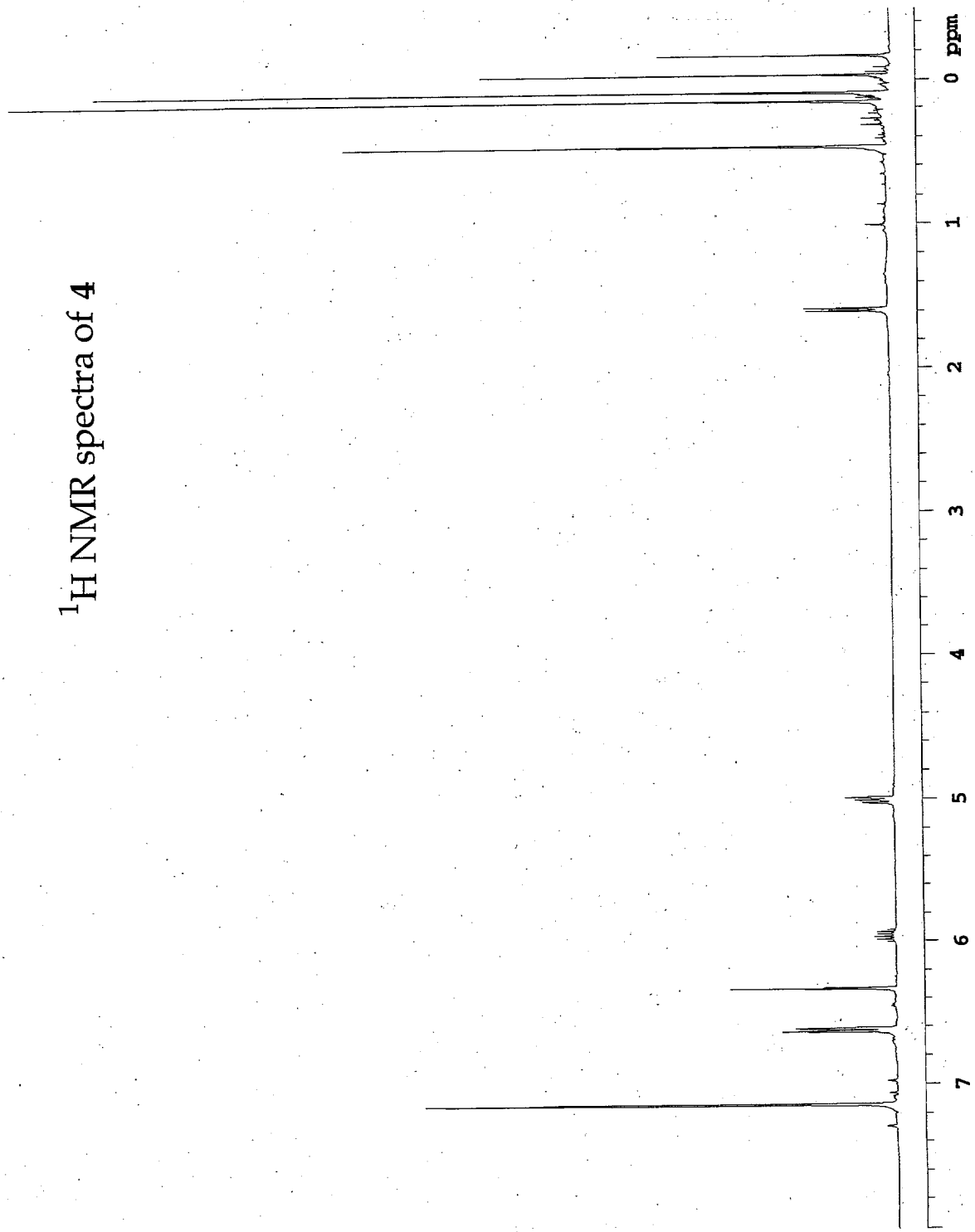
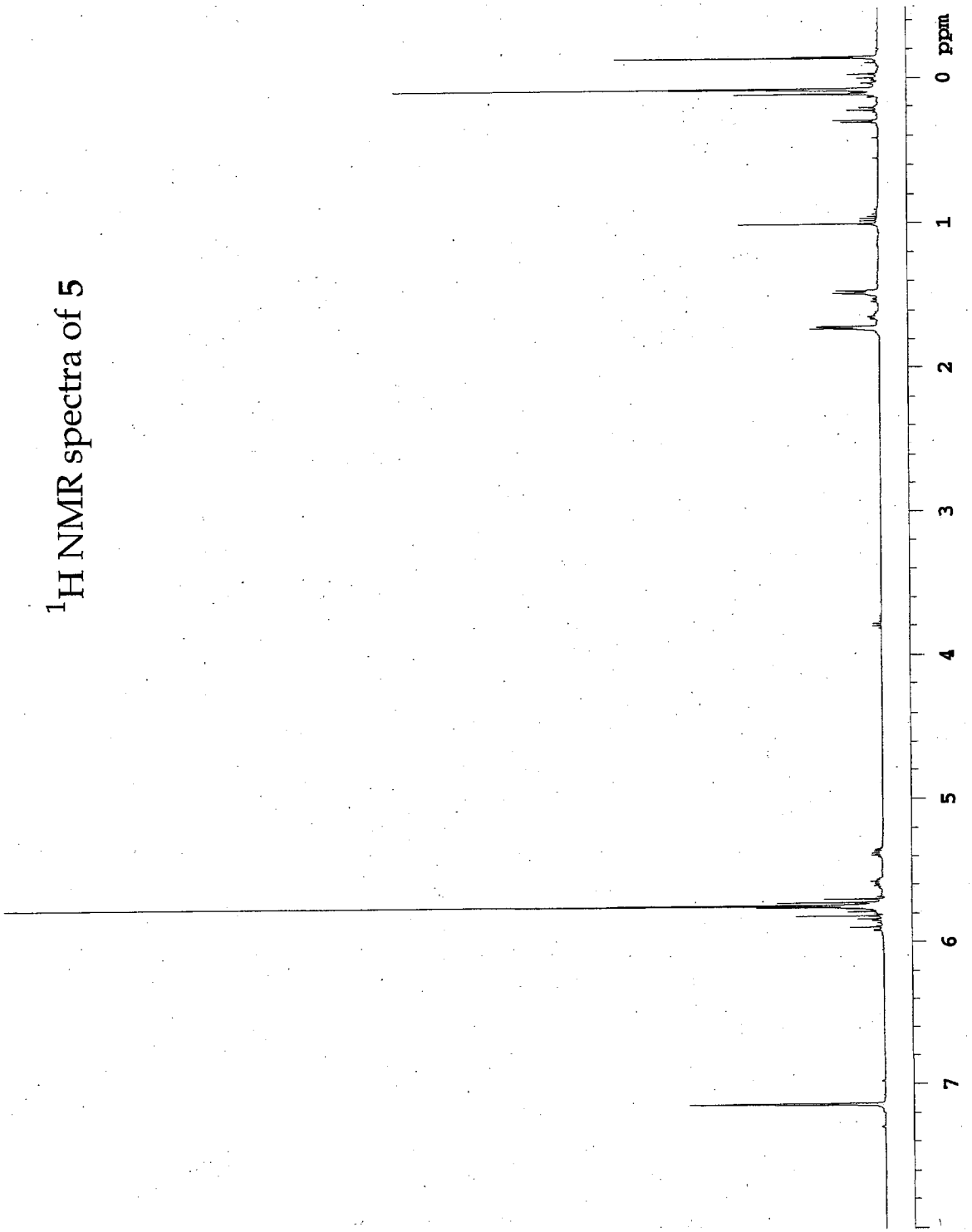
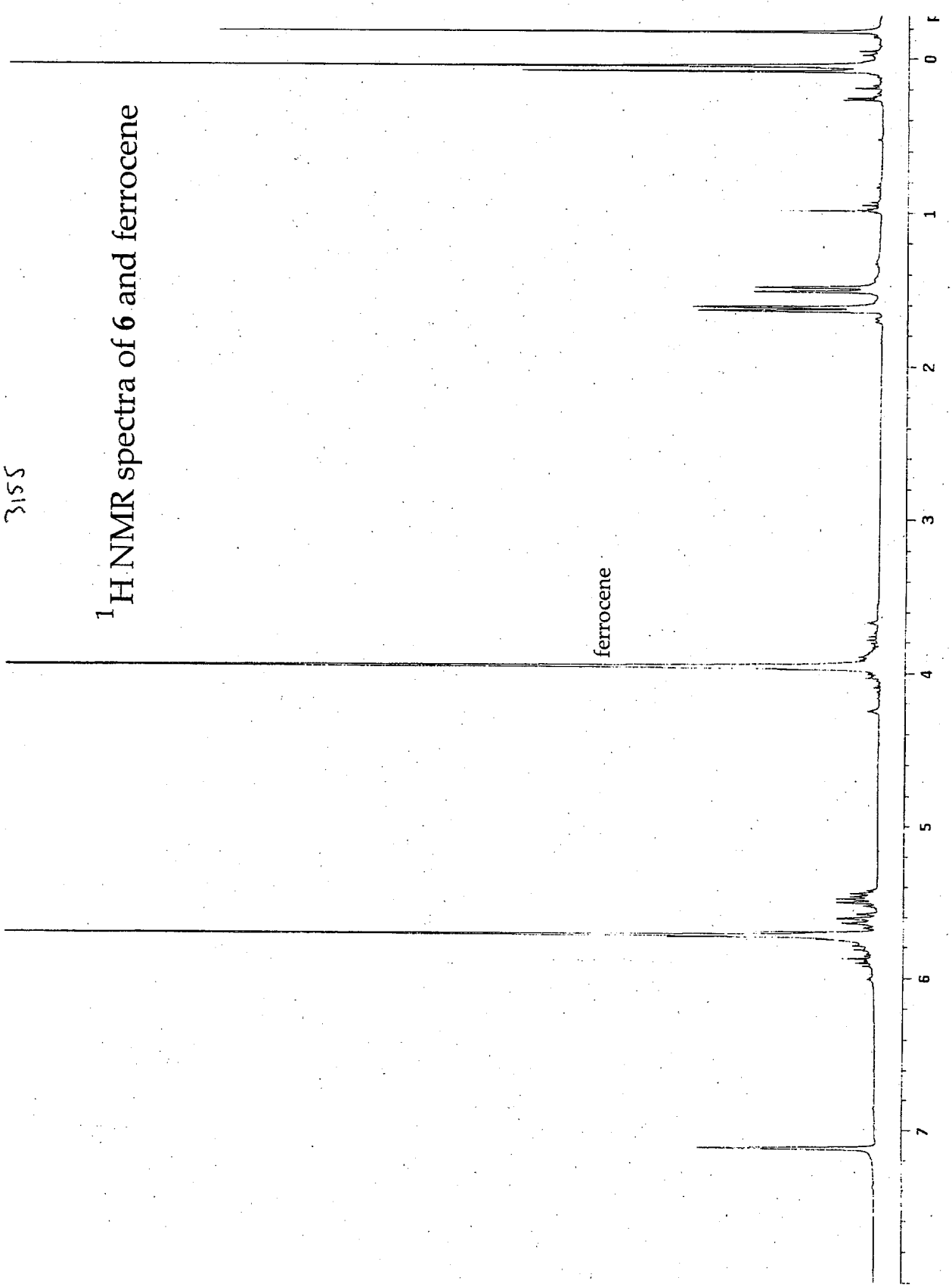
^{1}H NMR spectra of **4**

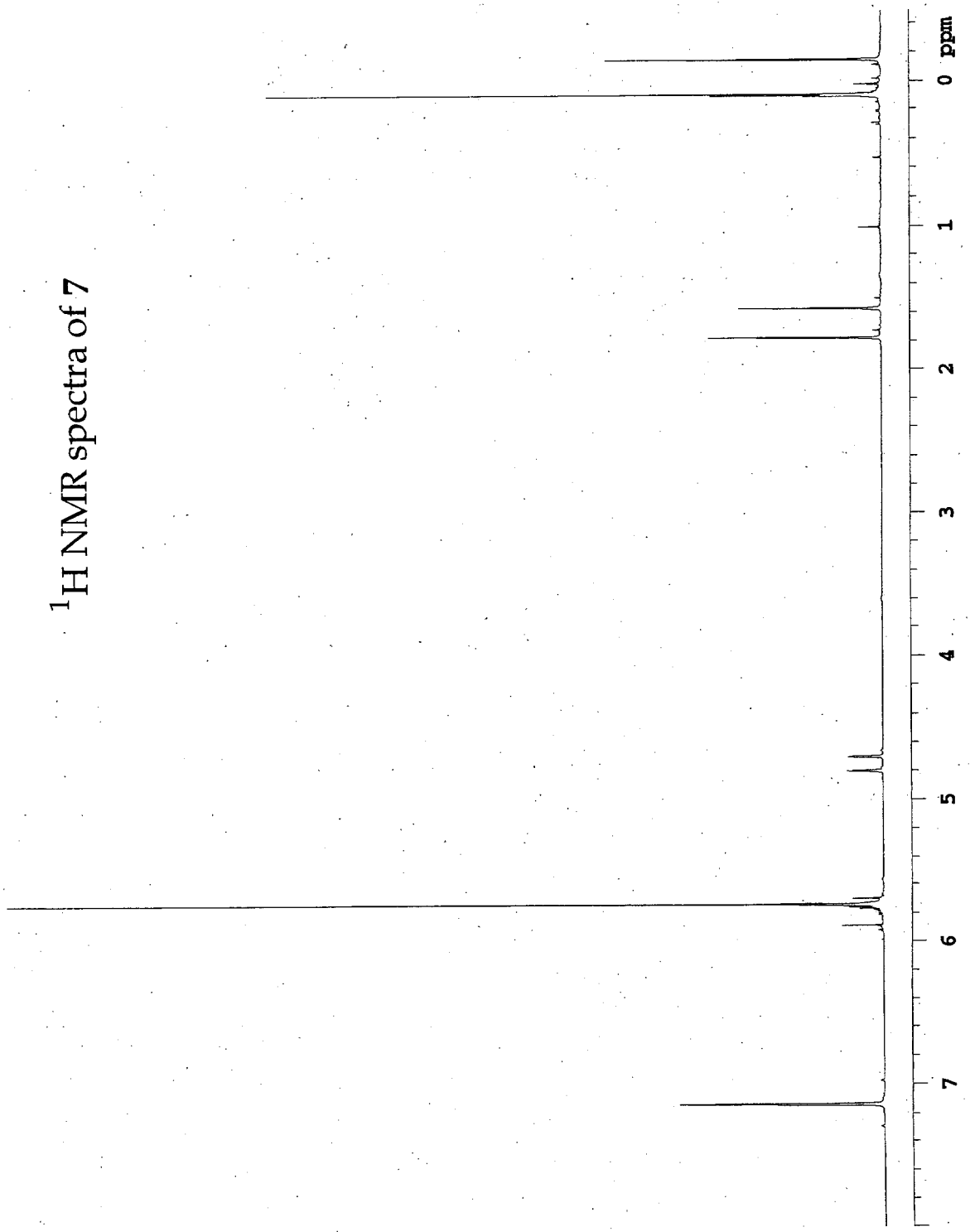


^{1}H NMR spectra of **5**

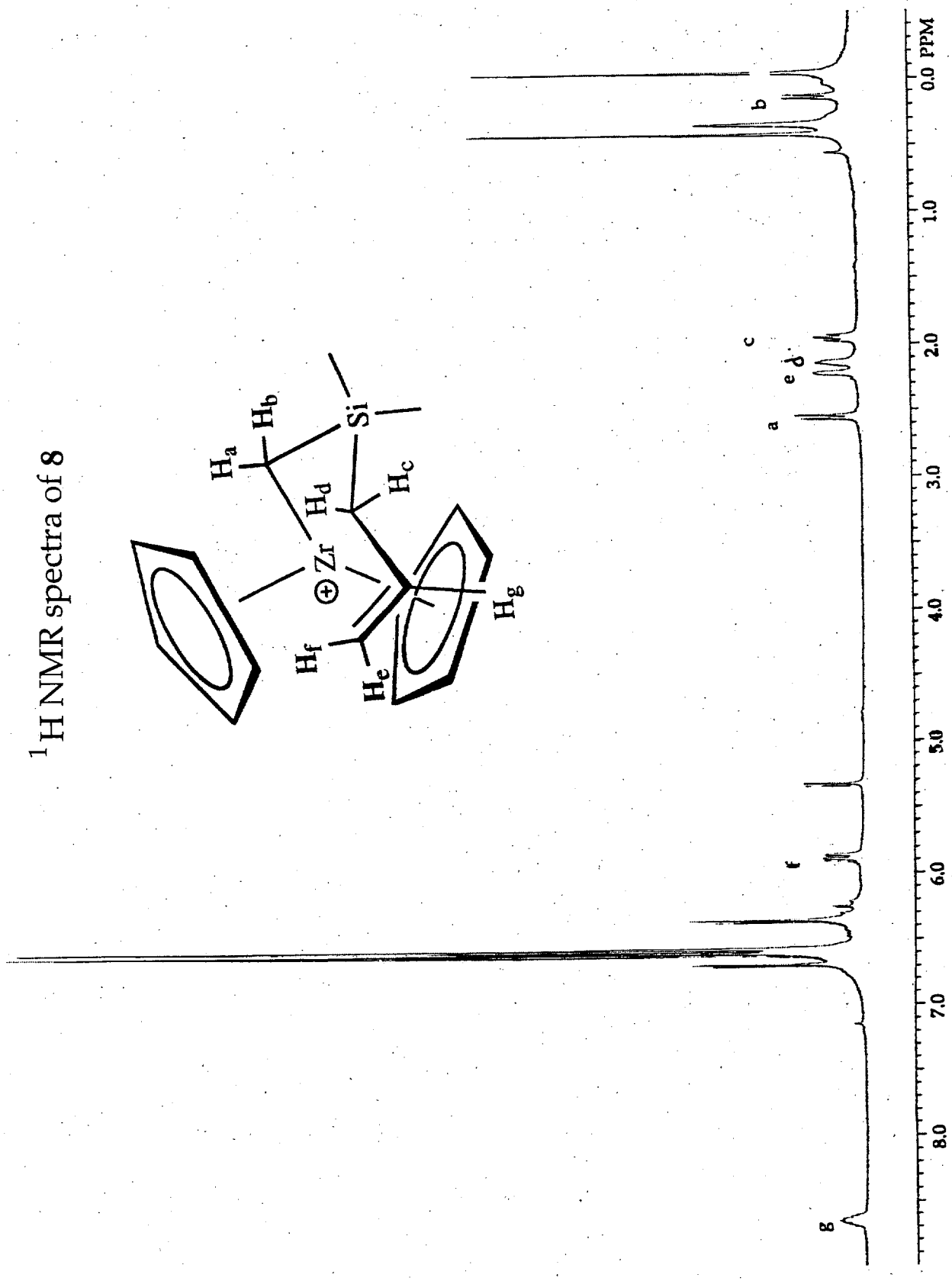



3155
^{1}H NMR spectra of 6 and ferrocene
ferrocene
0
1
2
3
4
5
6
7

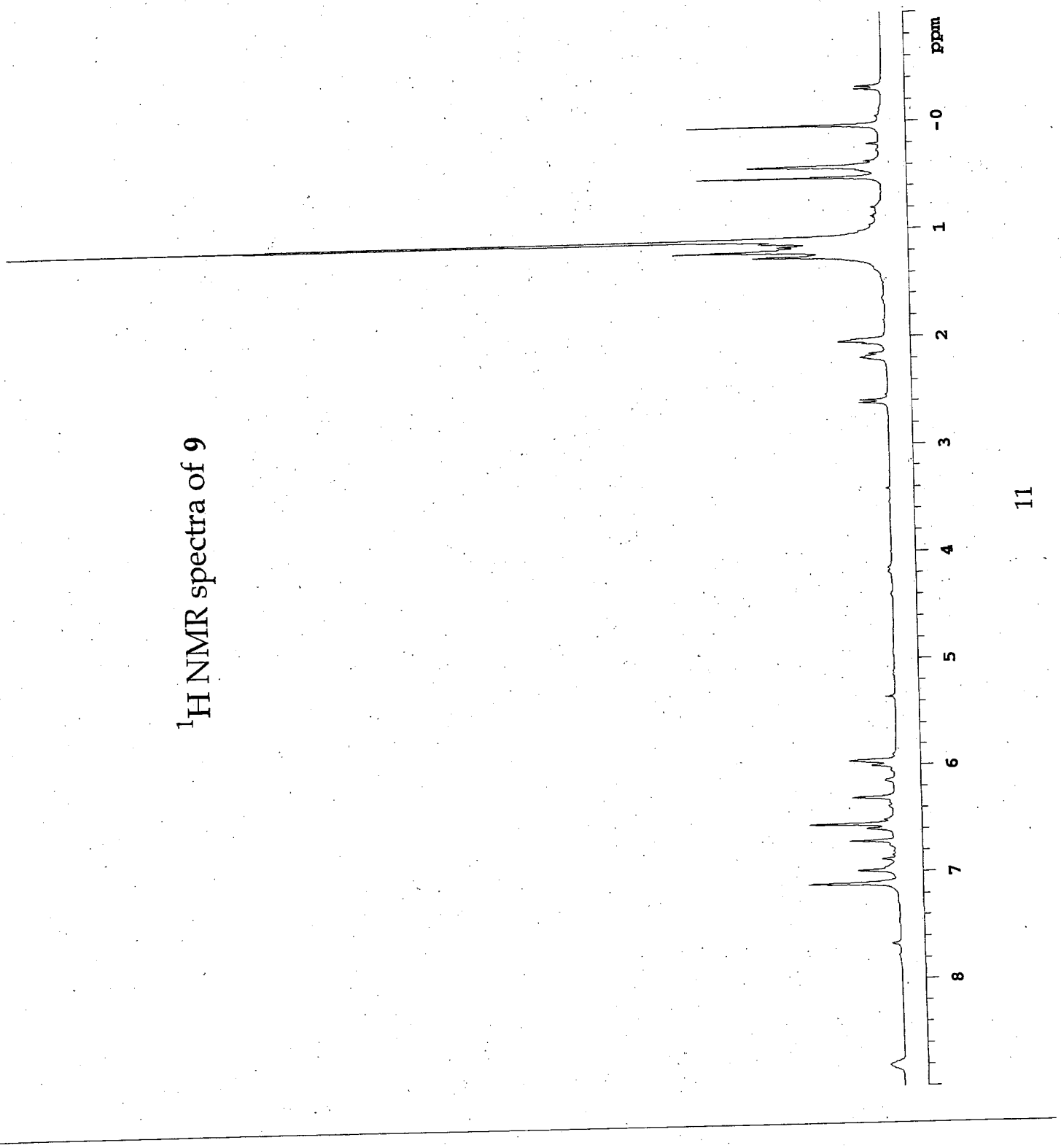
^{1}H NMR spectra of **7**



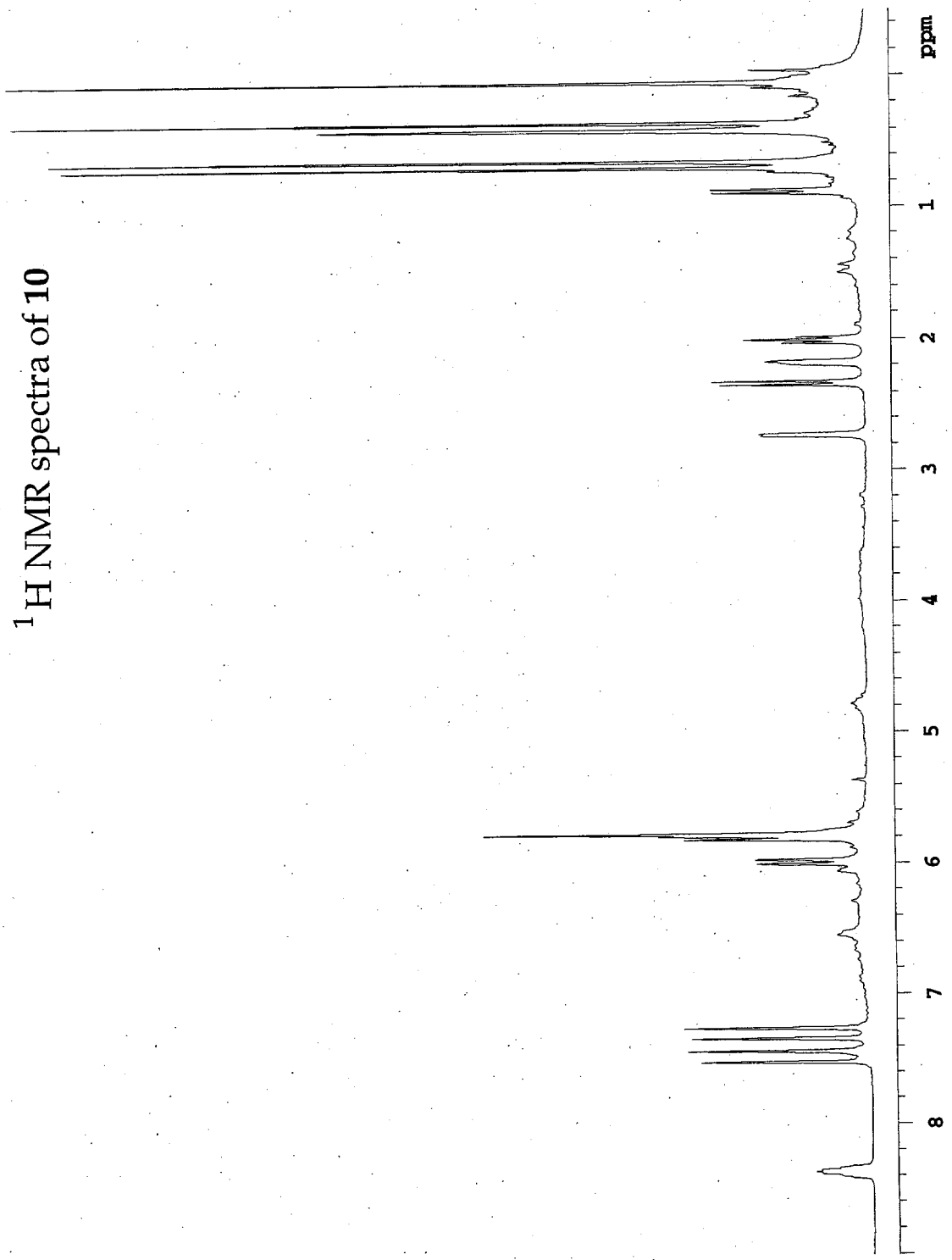
^{1}H NMR spectra of **8**



^{1}H NMR spectra of **9**



^{1}H NMR spectra of **10**



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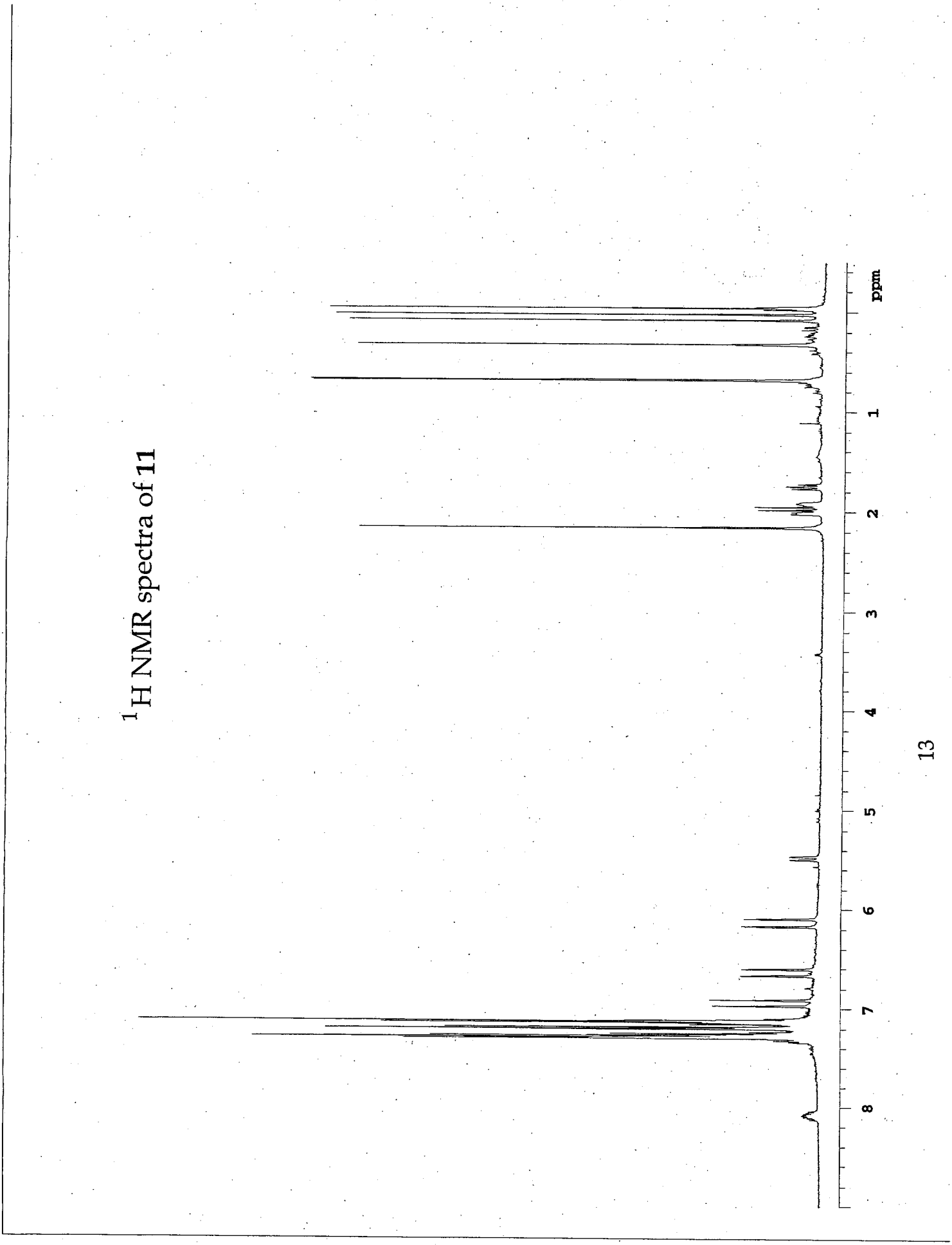
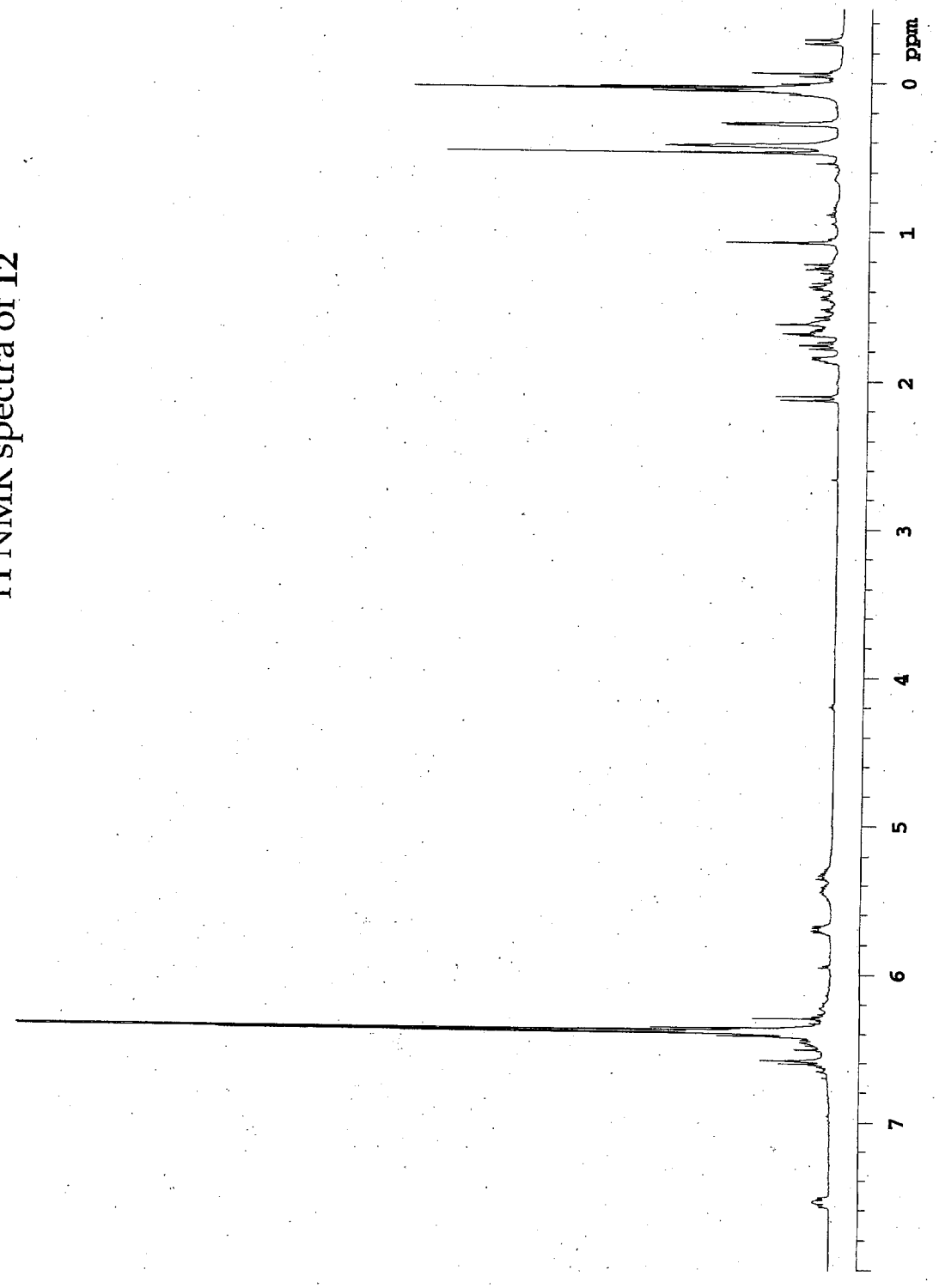
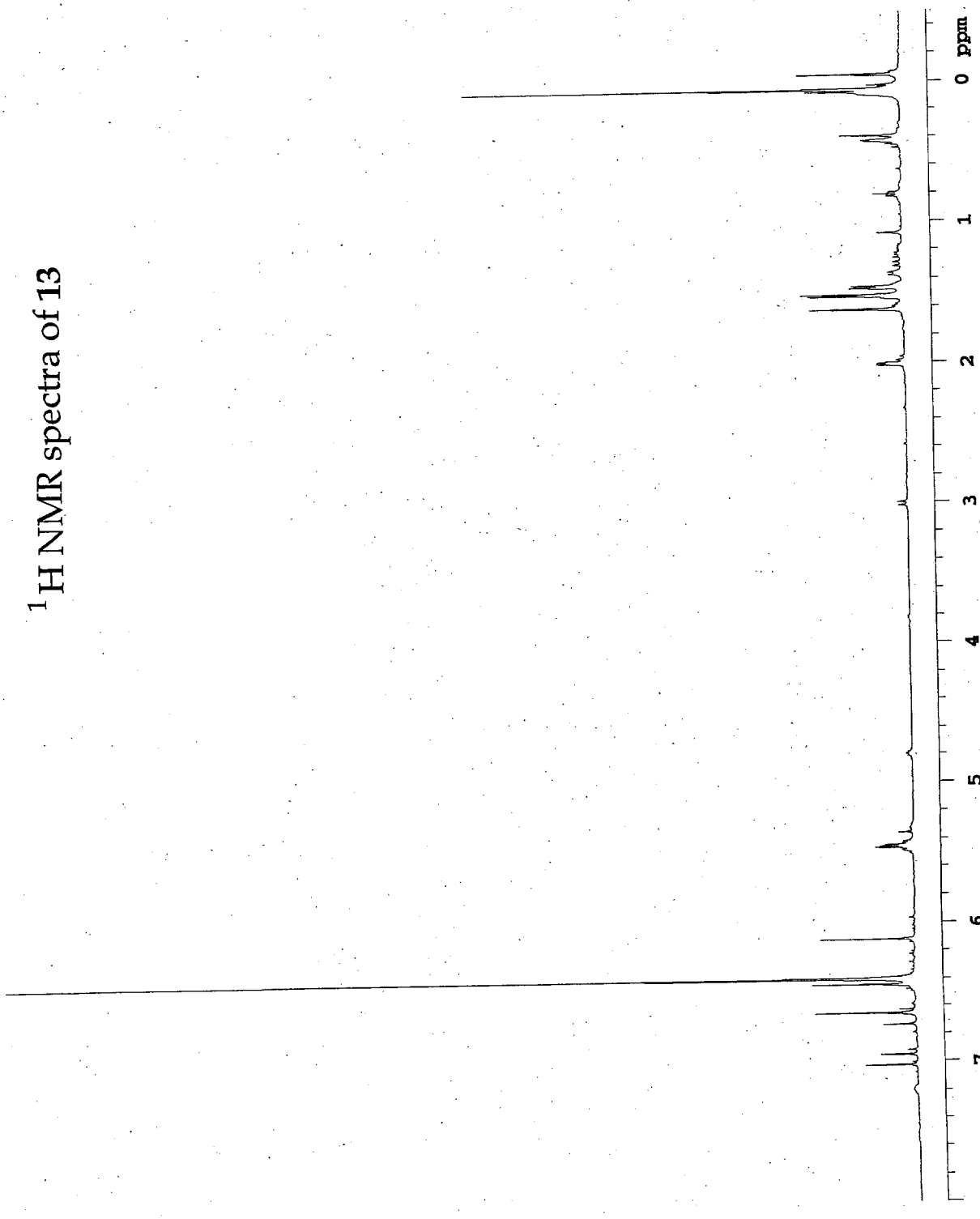
^{1}H NMR spectra of **11**



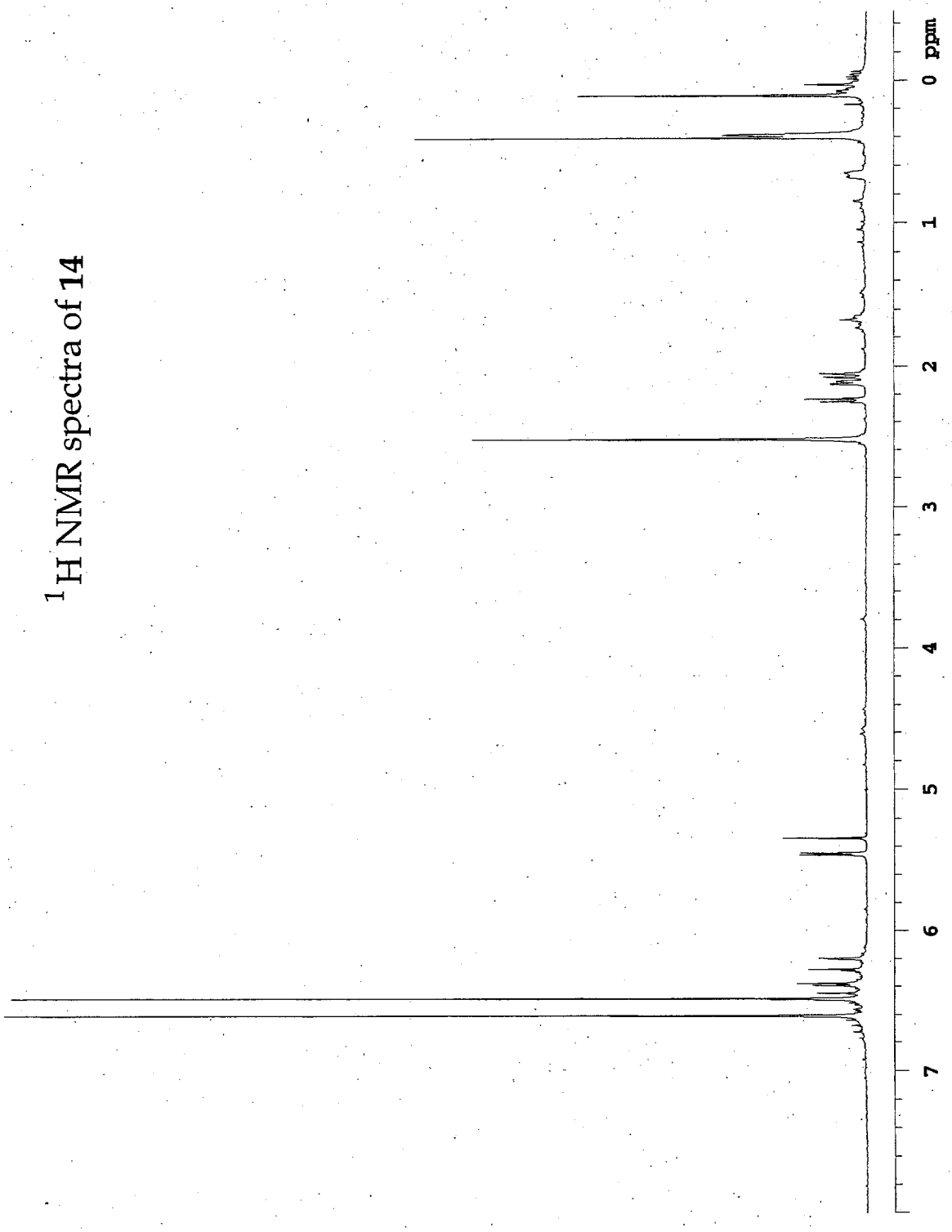
^{1}H NMR spectra of **12**



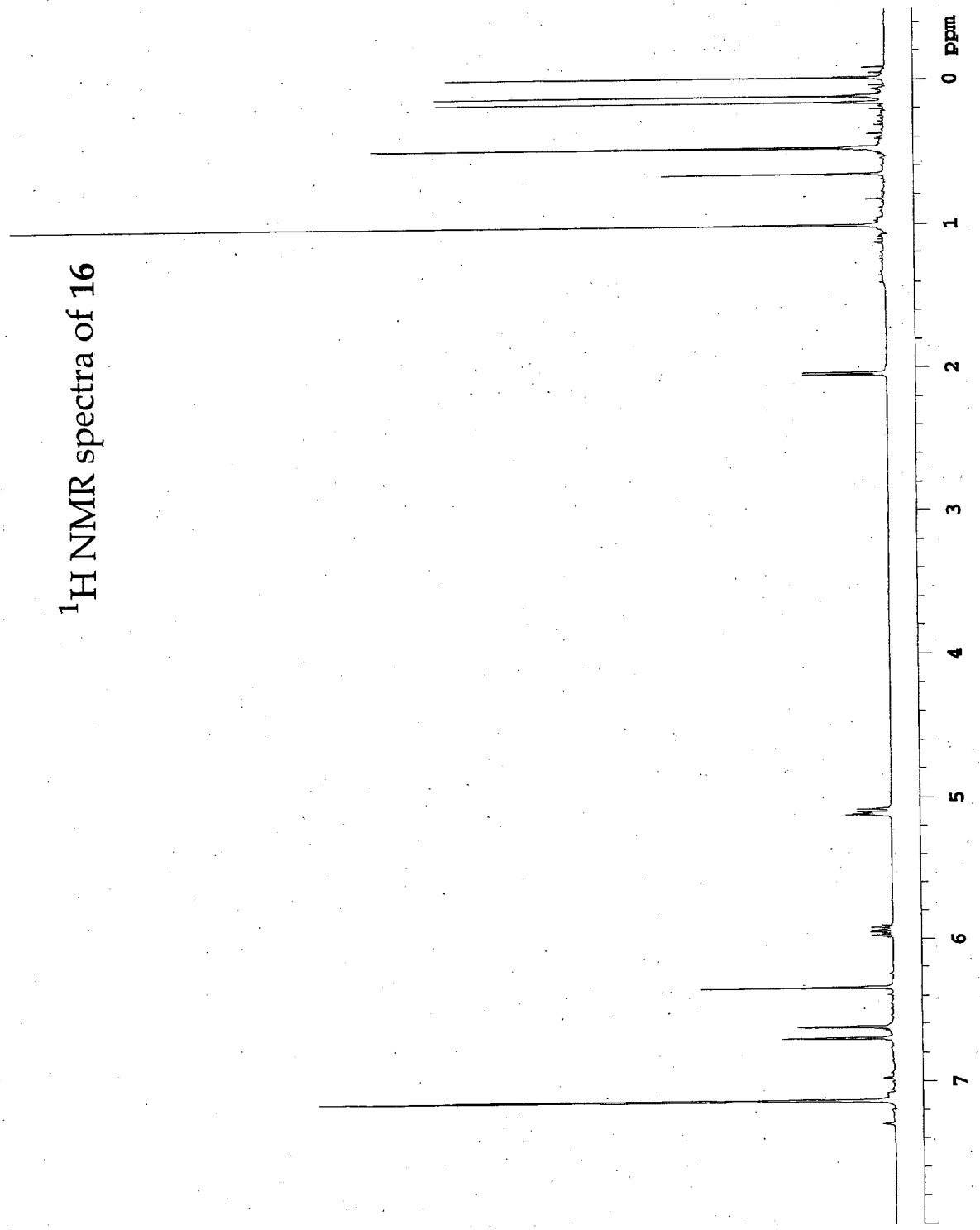
^{1}H NMR spectra of **13**



^{1}H NMR spectra of **14**



^{1}H NMR spectra of **16**



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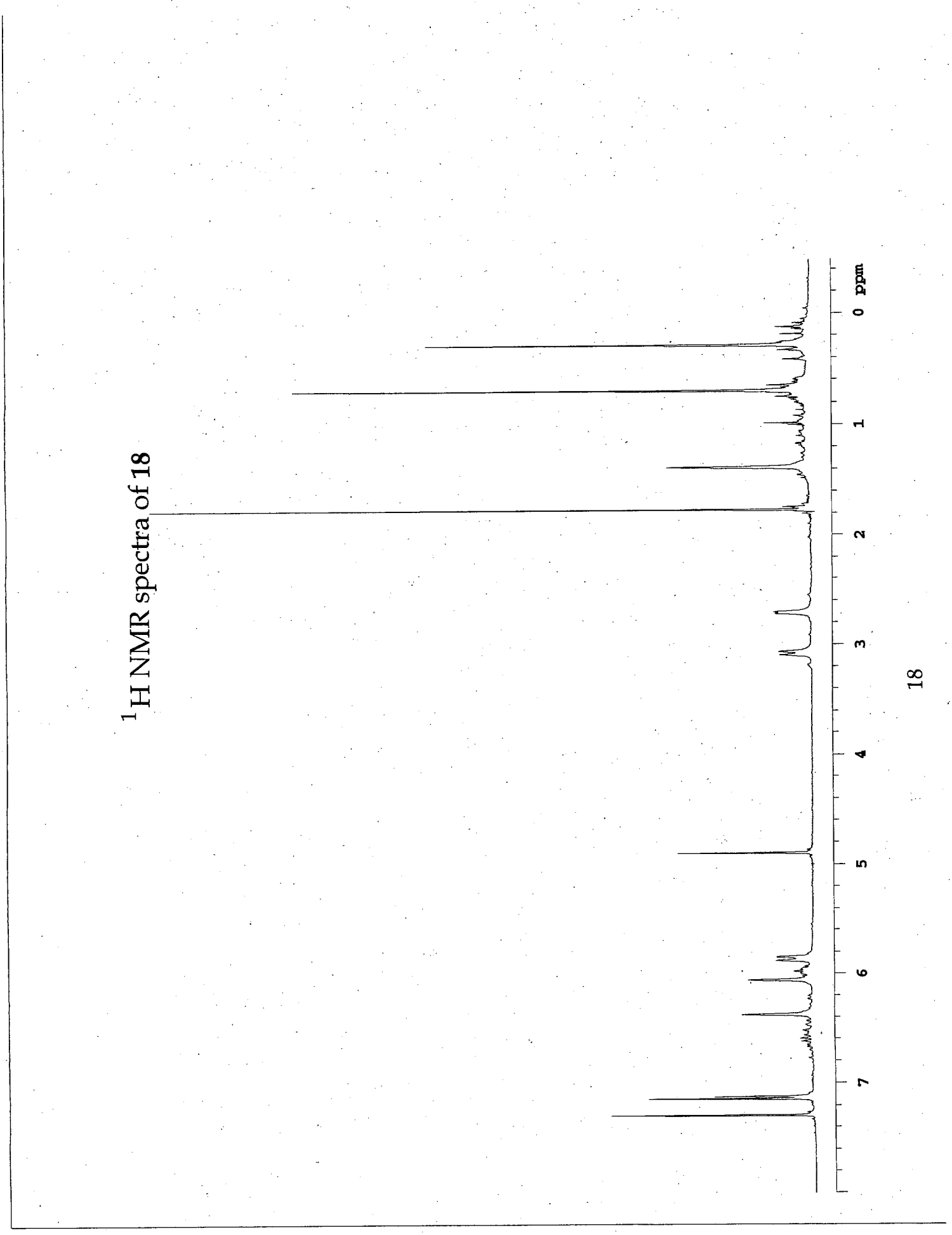
^{1}H NMR spectra of 18



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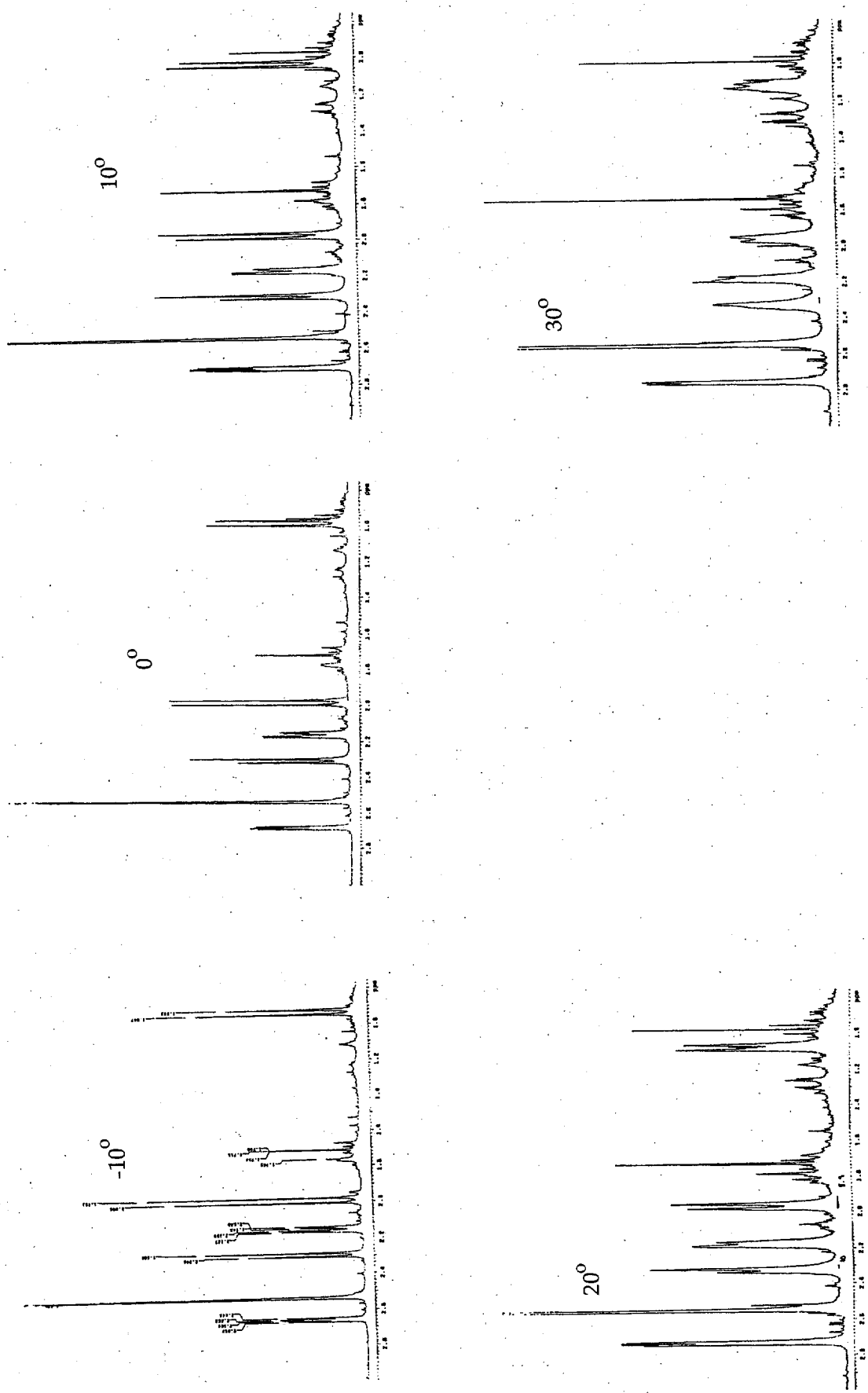
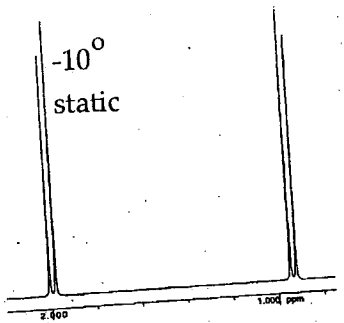
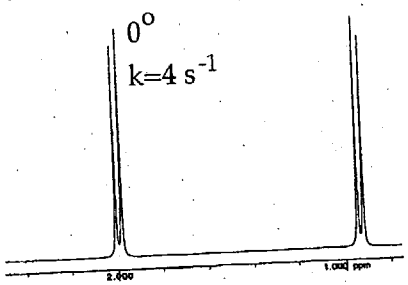
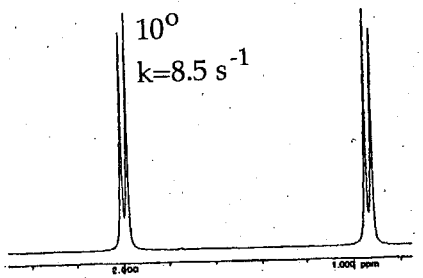
Dynamic spectra of complex **14**

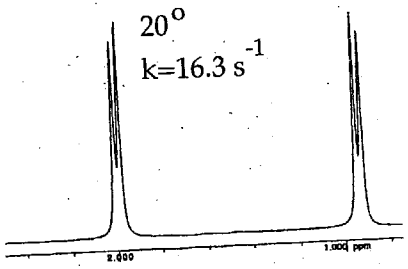


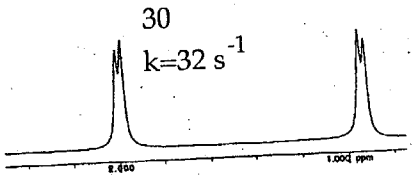
Simulation of alpha protons of olefin tether: complex **14**



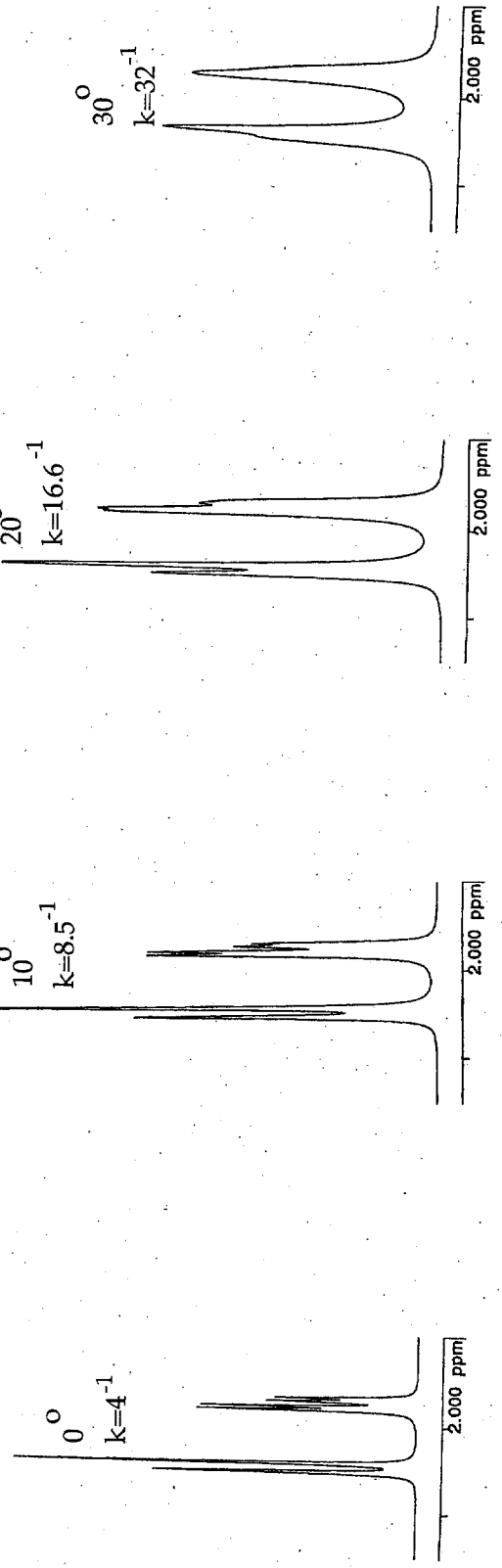








Simulation of allyl protons of olefin tether: complex **14**

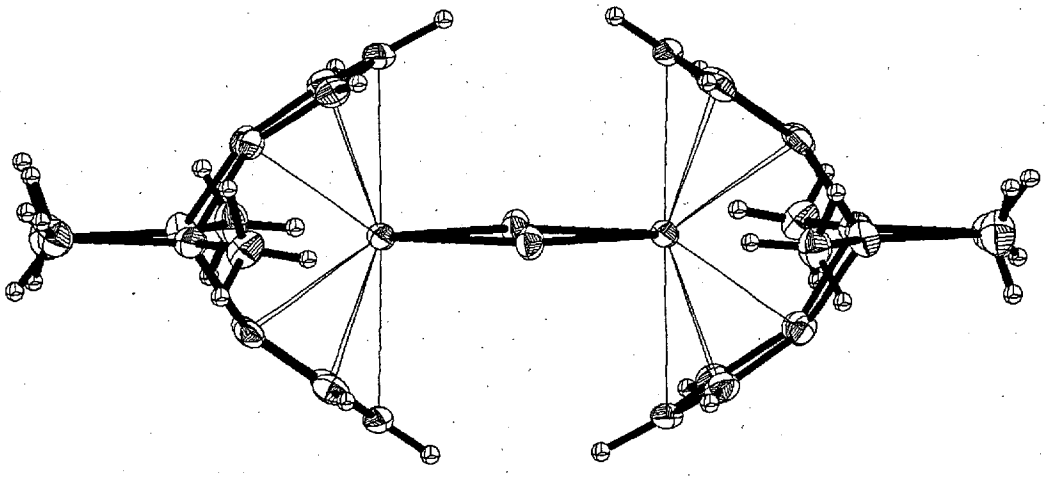


Crystal Structure Analysis of:

$\{[(Me_2Si)_2(C_5H_3)_2Zr]_2(\mu\text{-}Br)_2\}[B(C_6F_5)_4]_2 \bullet 4C_6H_5Br$

(shown below)

Contents



$\{[(Me_2Si)_2(C_5H_3)_2Zr]_2(\mu\text{-}Br)_2\}[B(C_6F_5)_4]_2 \bullet 4C_6H_5Br$

Note: The crystallographic data has been deposited in the Cambridge Database (CCDC). The deposition number is 151303.

Table 1. Crystal data and structure refinement for CGB3.

Empirical formula	$C_{14}H_{18}BrSi_2Zr \bullet BC_{24}F_{20} \bullet 2C_6H_5Br$
Formula weight	1406.66
Crystallization Solvent	Unknown
Crystal Habit	Blade
Crystal size	0.33 x 0.30 x 0.17 mm^3
Crystal color	Red/yellow dichroic

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	CCD area detector
Wavelength	0.71073 Å MoKa
Data Collection Temperature	98(2) K
q range for 12039 reflections used in lattice determination	2.27 to 28.20°
Unit cell dimensions	a = 12.4209(7) Å, a= 111.6510(10)° b = 15.0413(9) Å, b= 99.1430(10)° c = 15.8523(9) Å, g = 107.3110(10)°
Volume	2504.6(3) $Å^3$
Z	2
Crystal system	Triclinic
Space group	P-1
Density (calculated)	1.865 Mg/m^3
F(000)	1372
Data collection program	Bruker SMART
q range for data collection	1.58 to 28.44°
Completeness to q = 28.44°	90.9 %
Index ranges	-15 = h = 15, -19 = k = 19, -21 = l = 20
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.2
Reflections collected	37315
Independent reflections	11472 [R_{int}= 0.0812]
Absorption coefficient	2.772 mm^{-1}
Absorption correction	None
Max. and min. transmission (calculated)	0.6441 and 0.4587

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	11472 / 0 / 806
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.292
Final R indices [I>2s(I), 8069 reflections]	R1 = 0.0453, *w*R2 = 0.0872
R indices (all data)	R1 = 0.0686, *w*R2 = 0.0903
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.003
Average shift/error	0.000
Largest diff. peak and hole	1.584 and -1.566 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for CGB3. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Zr(1)	8697(1)	8700(1)	4079(1)	16(1)
Br(1)	10070(1)	10491(1)	4042(1)	23(1)
Br(2)	7465(1)	4227(1)	832(1)	59(1)
Br(3)	1439(1)	9790(1)	2175(1)	86(1)
Si(1)	6991(1)	7407(1)	1933(1)	24(1)
Si(2)	6856(1)	6449(1)	3654(1)	22(1)
F(22)	5957(2)	630(2)	1632(1)	25(1)
F(23)	4842(2)	-1414(2)	935(2)	36(1)
F(24)	3759(2)	-2258(2)	1985(2)	38(1)
F(25)	3821(2)	-977(2)	3748(2)	34(1)
F(26)	4953(2)	1047(2)	4476(1)	23(1)
F(28)	5584(2)	4127(1)	4449(1)	21(1)
F(29)	6261(2)	5284(2)	6294(1)	25(1)
F(30)	7435(2)	4769(2)	7524(1)	29(1)
F(31)	8023(2)	3093(2)	6825(1)	27(1)
F(32)	7440(2)	1952(2)	4951(1)	21(1)
F(34)	7376(2)	4250(2)	3559(2)	27(1)
F(35)	9581(2)	5096(2)	3543(2)	48(1)
F(36)	10976(2)	3979(2)	3310(2)	52(1)
F(37)	10109(2)	2012(2)	3109(2)	35(1)
F(38)	7939(2)	1149(2)	3125(2)	24(1)
F(40)	6242(2)	2593(2)	1660(1)	25(1)
F(41)	4532(2)	2770(2)	602(1)	31(1)
F(42)	2477(2)	2639(2)	1031(1)	34(1)
F(43)	2185(2)	2341(2)	2583(1)	28(1)
F(44)	3887(2)	2131(2)	3657(1)	22(1)
B(1)	6175(3)	2229(3)	3438(3)	16(1)
C(1)	8269(3)	7238(3)	2589(2)	20(1)
C(2)	8242(3)	6874(3)	3311(2)	20(1)
C(3)	9414(3)	7279(3)	3901(3)	24(1)
C(4)	10175(3)	7894(3)	3580(3)	23(1)
C(5)	9483(3)	7862(3)	2772(3)	23(1)
C(6)	6720(3)	8096(3)	3098(2)	19(1)
C(7)	6665(3)	7699(3)	3804(2)	19(1)
C(8)	6935(3)	8549(3)	4682(3)	21(1)
C(9)	7160(3)	9450(3)	4557(3)	22(1)
C(10)	7025(3)	9181(3)	3591(3)	20(1)
C(11)	7576(4)	8337(4)	1454(3)	29(1)
C(12)	5738(5)	6238(4)	1032(3)	35(1)
C(13)	7233(4)	6459(3)	4829(3)	26(1)
C(14)	5678(4)	5226(3)	2727(3)	27(1)
C(21)	5561(3)	959(3)	3105(2)	16(1)
C(22)	5469(3)	266(3)	2204(2)	19(1)
C(23)	4880(3)	-801(3)	1817(3)	24(1)
C(24)	4329(3)	-1217(3)	2347(3)	25(1)
C(25)	4374(3)	-582(3)	3232(3)	21(1)
C(26)	4977(3)	486(3)	3594(2)	17(1)

C(27)	6434(3)	2945(3)	4589(2)	16(1)
C(28)	6185(3)	3816(3)	4994(2)	17(1)
C(29)	6503(3)	4424(3)	5956(3)	18(1)
C(30)	7108(3)	4181(3)	6586(2)	20(1)
C(31)	7404(3)	3332(3)	6223(2)	20(1)
C(32)	7088(3)	2755(3)	5254(2)	18(1)
C(33)	7515(3)	2644(3)	3328(2)	18(1)
C(34)	8026(3)	3655(3)	3434(3)	22(1)
C(35)	9156(3)	4110(3)	3435(3)	30(1)
C(36)	9865(3)	3556(3)	3317(3)	34(1)
C(37)	9428(3)	2560(3)	3220(3)	27(1)
C(38)	8275(3)	2137(3)	3230(2)	20(1)
C(39)	5177(3)	2383(3)	2736(2)	16(1)
C(40)	5255(3)	2515(3)	1927(2)	19(1)
C(41)	4359(3)	2600(3)	1356(2)	21(1)
C(42)	3341(3)	2553(3)	1572(2)	22(1)
C(43)	3194(3)	2398(3)	2358(2)	20(1)
C(44)	4094(3)	2306(3)	2903(2)	18(1)
C(51)	8591(4)	5260(3)	658(3)	34(1)
C(52)	9750(4)	5658(3)	1223(3)	32(1)
C(53)	10598(4)	6415(3)	1084(3)	37(1)
C(54)	10246(5)	6738(4)	404(3)	41(1)
C(55)	9069(6)	6316(5)	-99(4)	48(2)
C(56)	8257(5)	5621(5)	-11(3)	45(1)
C(61)	1540(4)	9558(3)	941(3)	37(1)
C(62)	525(4)	9076(4)	183(3)	41(1)
C(63)	630(5)	8962(4)	-698(4)	57(2)
C(64)	1727(6)	9320(5)	-799(4)	75(2)
C(65)	2717(5)	9757(5)	-47(4)	78(2)
C(66)	2639(4)	9884(4)	832(4)	47(1)

Table 3. Selected bond lengths [Å] and angles [°] for CGB3.

Zr(1)-Cent(1)	2.156	Cent(1)-Zr(1)-Cen(2)	122.6
Zr(1)-Cent(2)	2.159	Pln(1)-Zr(1)-Pln(2)	111.8
Zr(1)-Pln(1)	2.148	Br(1)#1-Zr(1)-Br(1)	88.901(15)
Zr(1)-Pln(2)	2.148	Zr(1)#1-Br(1)-Zr(1)	91.099(15)
Zr(1)-C(6)	2.386(3)		
Zr(1)-C(7)	2.394(3)		
Zr(1)-C(2)	2.394(3)		
Zr(1)-C(1)	2.402(3)		
Zr(1)-C(3)	2.490(4)		
Zr(1)-C(10)	2.497(4)		
Zr(1)-C(8)	2.507(4)		
Zr(1)-C(5)	2.507(4)		
Zr(1)-C(4)	2.557(4)		
Zr(1)-C(9)	2.570(4)		
Zr(1)-Br(1)#1	2.7314(5)		
Zr(1)-Br(1)	2.7545(5)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+2,-z+1

Table 4. Bond lengths [Å] and angles [°] for CGB3.

Zr(1)-Cent(1)	2.156	C(1)-C(5)	1.434(5)
Zr(1)-Cent(2)	2.159	C(1)-C(2)	1.440(5)
Zr(1)-Pln(1)	2.148	C(2)-C(3)	1.408(5)
Zr(1)-Pln(2)	2.148	C(3)-C(4)	1.409(5)
Zr(1)-C(6)	2.386(3)	C(3)-H(3)	0.99(4)
Zr(1)-C(7)	2.394(3)	C(4)-C(5)	1.400(5)
Zr(1)-C(2)	2.394(3)	C(4)-H(4)	1.03(4)
Zr(1)-C(1)	2.402(3)	C(5)-H(5)	0.95(4)
Zr(1)-C(3)	2.490(4)	C(6)-C(10)	1.419(5)
Zr(1)-C(10)	2.497(4)	C(6)-C(7)	1.453(5)
Zr(1)-C(8)	2.507(4)	C(7)-C(8)	1.402(5)
Zr(1)-C(5)	2.507(4)	C(8)-C(9)	1.395(5)
Zr(1)-C(4)	2.557(4)	C(8)-H(8)	0.88(3)
Zr(1)-C(9)	2.570(4)	C(9)-C(10)	1.399(5)
Zr(1)-Br(1)#1	2.7314(5)	C(9)-H(9)	0.87(4)
Zr(1)-Br(1)	2.7545(5)	C(10)-H(10)	0.94(3)
Br(1)-Zr(1)#1	2.7314(5)	C(11)-H(11A)	0.99(4)
Br(2)-C(51)	1.896(4)	C(11)-H(11B)	0.88(4)
Br(3)-C(61)	1.889(4)	C(11)-H(11C)	0.93(4)
Si(1)-C(12)	1.835(5)	C(12)-H(12A)	0.75(7)
Si(1)-C(11)	1.848(4)	C(12)-H(12B)	0.81(5)
Si(1)-C(1)	1.892(4)	C(12)-H(12C)	1.20(6)
Si(1)-C(6)	1.894(4)	C(13)-H(13A)	1.02(4)
Si(2)-C(13)	1.840(4)	C(13)-H(13B)	0.89(4)
Si(2)-C(14)	1.845(4)	C(13)-H(13C)	0.86(4)
Si(2)-C(2)	1.888(4)	C(14)-H(14A)	0.86(4)
Si(2)-C(7)	1.898(4)	C(14)-H(14B)	1.01(5)
F(22)-C(22)	1.354(4)	C(14)-H(14C)	1.06(4)
F(23)-C(23)	1.344(4)	C(21)-C(26)	1.384(5)
F(24)-C(24)	1.353(4)	C(21)-C(22)	1.384(5)
F(25)-C(25)	1.337(4)	C(22)-C(23)	1.386(5)
F(26)-C(26)	1.350(4)	C(23)-C(24)	1.372(5)
F(28)-C(28)	1.350(4)	C(24)-C(25)	1.357(5)
F(29)-C(29)	1.350(4)	C(25)-C(26)	1.392(5)
F(30)-C(30)	1.334(4)	C(27)-C(28)	1.381(5)
F(31)-C(31)	1.348(4)	C(27)-C(32)	1.394(5)
F(32)-C(32)	1.353(4)	C(28)-C(29)	1.372(5)
F(34)-C(34)	1.356(4)	C(29)-C(30)	1.374(5)
F(35)-C(35)	1.351(4)	C(30)-C(31)	1.379(5)
F(36)-C(36)	1.341(4)	C(31)-C(32)	1.374(5)
F(37)-C(37)	1.335(4)	C(33)-C(38)	1.373(5)
F(38)-C(38)	1.356(4)	C(33)-C(34)	1.395(5)
F(40)-C(40)	1.346(4)	C(34)-C(35)	1.366(5)
F(41)-C(41)	1.348(4)	C(35)-C(36)	1.371(6)
F(42)-C(42)	1.333(4)	C(36)-C(37)	1.372(5)
F(43)-C(43)	1.344(4)	C(37)-C(38)	1.388(5)
F(44)-C(44)	1.361(4)	C(39)-C(40)	1.382(5)
B(1)-C(33)	1.656(5)	C(39)-C(44)	1.392(5)
B(1)-C(27)	1.658(5)	C(40)-C(41)	1.387(5)
B(1)-C(39)	1.659(5)	C(41)-C(42)	1.350(5)
B(1)-C(21)	1.663(5)	C(42)-C(43)	1.378(5)

C(43)-C(44)	1.374(5)
C(51)-C(52)	1.384(6)
C(51)-C(56)	1.418(7)
C(52)-C(53)	1.414(6)
C(52)-H(52)	1.14(4)
C(53)-C(54)	1.398(6)
C(53)-H(53)	1.09(4)
C(54)-C(55)	1.370(7)
C(54)-H(54)	1.09(4)
C(55)-C(56)	1.286(7)
C(55)-H(55)	0.68(3)
C(56)-H(56)	0.75(4)
C(61)-C(66)	1.369(6)
C(61)-C(62)	1.375(6)
C(62)-C(63)	1.376(6)
C(62)-H(62)	1.02(4)
C(63)-C(64)	1.366(7)
C(63)-H(63)	0.94(4)
C(64)-C(65)	1.356(8)
C(64)-H(64)	0.92(4)
C(65)-C(66)	1.358(7)
C(65)-H(65)	0.82(4)
C(66)-H(66)	0.94(4)

Cent(1)-Zr(1)-Cen(2)	122.6
Pln(1)-Zr(1)-Pln(2)	111.8
C(6)-Zr(1)-C(7)	35.40(11)
C(6)-Zr(1)-C(2)	79.74(12)
C(7)-Zr(1)-C(2)	68.16(12)
C(6)-Zr(1)-C(1)	68.30(12)
C(7)-Zr(1)-C(1)	78.55(12)
C(2)-Zr(1)-C(1)	34.95(12)
C(6)-Zr(1)-C(3)	113.19(12)
C(7)-Zr(1)-C(3)	96.40(12)
C(2)-Zr(1)-C(3)	33.45(12)
C(1)-Zr(1)-C(3)	55.88(13)
C(6)-Zr(1)-C(10)	33.70(11)
C(7)-Zr(1)-C(10)	56.11(12)
C(2)-Zr(1)-C(10)	113.43(12)
C(1)-Zr(1)-C(10)	97.15(12)
C(3)-Zr(1)-C(10)	146.87(12)
C(6)-Zr(1)-C(8)	55.84(12)
C(7)-Zr(1)-C(8)	33.16(12)
C(2)-Zr(1)-C(8)	95.74(12)
C(1)-Zr(1)-C(8)	111.71(12)
C(3)-Zr(1)-C(8)	114.30(13)
C(10)-Zr(1)-C(8)	53.78(12)
C(6)-Zr(1)-C(5)	96.45(12)
C(7)-Zr(1)-C(5)	112.44(12)
C(2)-Zr(1)-C(5)	56.03(12)
C(1)-Zr(1)-C(5)	33.89(12)
C(3)-Zr(1)-C(5)	53.96(13)
C(10)-Zr(1)-C(5)	115.50(13)
C(8)-Zr(1)-C(5)	145.59(13)
C(6)-Zr(1)-C(4)	123.66(12)
C(7)-Zr(1)-C(4)	123.45(12)
C(2)-Zr(1)-C(4)	55.30(12)
C(1)-Zr(1)-C(4)	55.36(12)
C(3)-Zr(1)-C(4)	32.39(12)
C(10)-Zr(1)-C(4)	147.59(13)
C(8)-Zr(1)-C(4)	146.67(12)
C(5)-Zr(1)-C(4)	32.09(12)
C(6)-Zr(1)-C(9)	54.97(12)
C(7)-Zr(1)-C(9)	54.72(12)
C(2)-Zr(1)-C(9)	122.87(12)
C(1)-Zr(1)-C(9)	123.23(13)
C(3)-Zr(1)-C(9)	146.18(13)
C(10)-Zr(1)-C(9)	32.02(12)
C(8)-Zr(1)-C(9)	31.87(11)
C(5)-Zr(1)-C(9)	147.46(13)
C(4)-Zr(1)-C(9)	178.17(12)
C(6)-Zr(1)-Br(1)#1	139.56(9)
C(7)-Zr(1)-Br(1)#1	110.08(8)
C(2)-Zr(1)-Br(1)#1	110.13(9)
C(1)-Zr(1)-Br(1)#1	140.00(9)
C(3)-Zr(1)-Br(1)#1	84.14(9)
C(10)-Zr(1)-Br(1)#1	120.48(9)
C(8)-Zr(1)-Br(1)#1	83.83(9)
C(5)-Zr(1)-Br(1)#1	122.02(9)
C(4)-Zr(1)-Br(1)#1	90.99(9)
C(9)-Zr(1)-Br(1)#1	89.84(9)
C(6)-Zr(1)-Br(1)	109.42(9)
C(7)-Zr(1)-Br(1)	140.00(9)
C(2)-Zr(1)-Br(1)	138.92(9)
C(1)-Zr(1)-Br(1)	109.56(9)
C(3)-Zr(1)-Br(1)	121.01(9)
C(10)-Zr(1)-Br(1)	83.89(9)
C(8)-Zr(1)-Br(1)	123.01(9)
C(5)-Zr(1)-Br(1)	82.93(9)
C(4)-Zr(1)-Br(1)	89.64(9)
C(9)-Zr(1)-Br(1)	92.01(9)
Br(1)#1-Zr(1)-Br(1)	88.901(15)
Zr(1)#1-Br(1)-Zr(1)	91.099(15)
C(12)-Si(1)-C(11)	111.7(2)
C(12)-Si(1)-C(1)	118.1(2)
C(11)-Si(1)-C(1)	108.94(19)
C(12)-Si(1)-C(6)	115.7(2)
C(11)-Si(1)-C(6)	110.01(19)
C(1)-Si(1)-C(6)	90.47(15)
C(12)-Si(1)-Zr(1)	148.71(18)
C(11)-Si(1)-Zr(1)	99.52(14)
C(1)-Si(1)-Zr(1)	48.43(10)
C(6)-Si(1)-Zr(1)	47.92(10)
C(13)-Si(2)-C(14)	113.9(2)
C(13)-Si(2)-C(2)	110.2(2)
C(14)-Si(2)-C(2)	114.10(18)
C(13)-Si(2)-C(7)	109.06(18)
C(14)-Si(2)-C(7)	117.00(19)

C(2)-Si(2)-C(7)	90.25(15)
C(13)-Si(2)-Zr(1)	101.32(15)
C(14)-Si(2)-Zr(1)	144.78(15)
C(2)-Si(2)-Zr(1)	47.59(11)
C(7)-Si(2)-Zr(1)	47.62(10)
C(33)-B(1)-C(27)	101.0(3)
C(33)-B(1)-C(39)	113.1(3)
C(27)-B(1)-C(39)	113.6(3)
C(33)-B(1)-C(21)	115.0(3)
C(27)-B(1)-C(21)	113.5(3)
C(39)-B(1)-C(21)	101.3(3)
C(5)-C(1)-C(2)	106.6(3)
C(5)-C(1)-Si(1)	122.9(3)
C(2)-C(1)-Si(1)	125.0(3)
C(5)-C(1)-Zr(1)	77.1(2)
C(2)-C(1)-Zr(1)	72.20(19)
Si(1)-C(1)-Zr(1)	95.48(15)
C(3)-C(2)-C(1)	107.2(3)
C(3)-C(2)-Si(2)	126.2(3)
C(1)-C(2)-Si(2)	122.0(3)
C(3)-C(2)-Zr(1)	77.0(2)
C(1)-C(2)-Zr(1)	72.85(19)
Si(2)-C(2)-Zr(1)	96.80(15)
C(2)-C(3)-C(4)	109.6(3)
C(2)-C(3)-Zr(1)	69.5(2)
C(4)-C(3)-Zr(1)	76.4(2)
C(2)-C(3)-H(3)	127(2)
C(4)-C(3)-H(3)	123(2)
Zr(1)-C(3)-H(3)	119(2)
C(5)-C(4)-C(3)	107.6(3)
C(5)-C(4)-Zr(1)	72.0(2)
C(3)-C(4)-Zr(1)	71.2(2)
C(5)-C(4)-H(4)	129(2)
C(3)-C(4)-H(4)	123(2)
Zr(1)-C(4)-H(4)	118(2)
C(4)-C(5)-C(1)	109.0(3)
C(4)-C(5)-Zr(1)	75.9(2)
C(1)-C(5)-Zr(1)	69.1(2)
C(4)-C(5)-H(5)	127(2)
C(1)-C(5)-H(5)	124(2)
Zr(1)-C(5)-H(5)	122(2)
C(10)-C(6)-C(7)	106.5(3)
C(10)-C(6)-Si(1)	125.8(3)
C(7)-C(6)-Si(1)	122.8(3)
C(10)-C(6)-Zr(1)	77.5(2)
C(7)-C(6)-Zr(1)	72.61(19)
Si(1)-C(6)-Zr(1)	95.97(14)
C(8)-C(7)-C(6)	106.8(3)
C(8)-C(7)-Si(2)	124.9(3)
C(6)-C(7)-Si(2)	123.6(3)
C(8)-C(7)-Zr(1)	77.9(2)
C(6)-C(7)-Zr(1)	71.99(19)
Si(2)-C(7)-Zr(1)	96.54(15)
C(9)-C(8)-C(7)	109.6(3)
C(9)-C(8)-Zr(1)	76.5(2)
C(7)-C(8)-Zr(1)	69.0(2)
C(9)-C(8)-H(8)	129(2)
C(7)-C(8)-H(8)	121(2)
Zr(1)-C(8)-H(8)	120(2)
C(8)-C(9)-C(10)	108.2(3)
C(8)-C(9)-Zr(1)	71.6(2)
C(10)-C(9)-Zr(1)	71.1(2)
C(8)-C(9)-H(9)	125(2)
C(10)-C(9)-H(9)	127(2)
Zr(1)-C(9)-H(9)	123(2)
C(9)-C(10)-C(6)	108.9(3)
C(9)-C(10)-Zr(1)	76.8(2)
C(6)-C(10)-Zr(1)	68.8(2)
C(9)-C(10)-H(10)	131.5(19)
C(6)-C(10)-H(10)	119.6(19)
Zr(1)-C(10)-H(10)	118(2)
Si(1)-C(11)-H(11A)	110(2)
Si(1)-C(11)-H(11B)	108(2)
H(11A)-C(11)-H(11B)	106(3)
Si(1)-C(11)-H(11C)	105(2)
H(11A)-C(11)-H(11C)	107(3)
H(11B)-C(11)-H(11C)	121(3)
Si(1)-C(12)-H(12A)	111(5)
Si(1)-C(12)-H(12B)	105(3)
H(12A)-C(12)-H(12B)	137(6)
Si(1)-C(12)-H(12C)	104(2)
H(12A)-C(12)-H(12C)	78(5)
H(12B)-C(12)-H(12C)	115(4)
Si(2)-C(13)-H(13A)	106(2)
Si(2)-C(13)-H(13B)	112(2)
H(13A)-C(13)-H(13B)	107(3)
Si(2)-C(13)-H(13C)	112(2)
H(13A)-C(13)-H(13C)	114(3)
H(13B)-C(13)-H(13C)	106(3)
Si(2)-C(14)-H(14A)	104(3)
Si(2)-C(14)-H(14B)	121(2)
H(14A)-C(14)-H(14B)	114(4)
Si(2)-C(14)-H(14C)	109(2)
H(14A)-C(14)-H(14C)	99(3)
H(14B)-C(14)-H(14C)	107(3)
C(26)-C(21)-C(22)	113.4(3)
C(26)-C(21)-B(1)	126.5(3)
C(22)-C(21)-B(1)	119.6(3)
F(22)-C(22)-C(21)	119.5(3)
F(22)-C(22)-C(23)	115.8(3)
C(21)-C(22)-C(23)	124.7(3)
F(23)-C(23)-C(24)	120.8(3)
F(23)-C(23)-C(22)	120.5(3)
C(24)-C(23)-C(22)	118.7(3)
F(24)-C(24)-C(25)	120.7(3)
F(24)-C(24)-C(23)	119.6(3)
C(25)-C(24)-C(23)	119.7(3)
F(25)-C(25)-C(24)	120.2(3)

F(25)-C(25)-C(26)	120.1(3)	F(41)-C(41)-C(40)	119.2(3)
C(24)-C(25)-C(26)	119.8(3)	C(42)-C(41)-C(40)	120.6(3)
F(26)-C(26)-C(21)	121.3(3)	F(42)-C(42)-C(41)	121.0(3)
F(26)-C(26)-C(25)	114.9(3)	F(42)-C(42)-C(43)	119.9(3)
C(21)-C(26)-C(25)	123.8(3)	C(41)-C(42)-C(43)	119.1(3)
C(28)-C(27)-C(32)	113.4(3)	F(43)-C(43)-C(44)	120.9(3)
C(28)-C(27)-B(1)	127.0(3)	F(43)-C(43)-C(42)	120.1(3)
C(32)-C(27)-B(1)	119.2(3)	C(44)-C(43)-C(42)	119.0(3)
F(28)-C(28)-C(29)	114.7(3)	F(44)-C(44)-C(43)	116.3(3)
F(28)-C(28)-C(27)	121.0(3)	F(44)-C(44)-C(39)	119.1(3)
C(29)-C(28)-C(27)	124.2(3)	C(43)-C(44)-C(39)	124.7(3)
F(29)-C(29)-C(28)	120.5(3)	C(52)-C(51)-C(56)	121.5(4)
F(29)-C(29)-C(30)	119.3(3)	C(52)-C(51)-Br(2)	117.0(3)
C(28)-C(29)-C(30)	120.2(3)	C(56)-C(51)-Br(2)	121.5(3)
F(30)-C(30)-C(29)	121.0(3)	C(51)-C(52)-C(53)	117.3(4)
F(30)-C(30)-C(31)	120.7(3)	C(51)-C(52)-H(52)	106(2)
C(29)-C(30)-C(31)	118.2(3)	C(53)-C(52)-H(52)	136(2)
F(31)-C(31)-C(32)	120.9(3)	C(54)-C(53)-C(52)	119.9(4)
F(31)-C(31)-C(30)	119.4(3)	C(54)-C(53)-H(53)	120(2)
C(32)-C(31)-C(30)	119.8(3)	C(52)-C(53)-H(53)	120(2)
F(32)-C(32)-C(31)	116.3(3)	C(55)-C(54)-C(53)	118.1(5)
F(32)-C(32)-C(27)	119.6(3)	C(55)-C(54)-H(54)	119(2)
C(31)-C(32)-C(27)	124.1(3)	C(53)-C(54)-H(54)	123(2)
C(38)-C(33)-C(34)	112.8(3)	C(56)-C(55)-C(54)	125.0(5)
C(38)-C(33)-B(1)	127.3(3)	C(56)-C(55)-H(55)	124(3)
C(34)-C(33)-B(1)	119.5(3)	C(54)-C(55)-H(55)	110(3)
F(34)-C(34)-C(35)	116.4(3)	C(55)-C(56)-C(51)	118.2(5)
F(34)-C(34)-C(33)	118.8(3)	C(55)-C(56)-H(56)	124(3)
C(35)-C(34)-C(33)	124.8(4)	C(51)-C(56)-H(56)	117(3)
F(35)-C(35)-C(34)	120.9(4)	C(66)-C(61)-C(62)	121.9(4)
F(35)-C(35)-C(36)	119.6(4)	C(66)-C(61)-Br(3)	118.2(3)
C(34)-C(35)-C(36)	119.5(4)	C(62)-C(61)-Br(3)	119.9(4)
F(36)-C(36)-C(35)	121.0(4)	C(61)-C(62)-C(63)	118.3(5)
F(36)-C(36)-C(37)	120.0(4)	C(61)-C(62)-H(62)	120(2)
C(35)-C(36)-C(37)	119.0(4)	C(63)-C(62)-H(62)	122(2)
F(37)-C(37)-C(36)	119.8(3)	C(64)-C(63)-C(62)	119.7(5)
F(37)-C(37)-C(38)	121.2(3)	C(64)-C(63)-H(63)	119(3)
C(36)-C(37)-C(38)	119.0(4)	C(62)-C(63)-H(63)	122(3)
F(38)-C(38)-C(33)	121.4(3)	C(65)-C(64)-C(63)	120.9(6)
F(38)-C(38)-C(37)	113.8(3)	C(65)-C(64)-H(64)	113(3)
C(33)-C(38)-C(37)	124.8(3)	C(63)-C(64)-H(64)	126(3)
C(40)-C(39)-C(44)	113.3(3)	C(64)-C(65)-C(66)	120.7(6)
C(40)-C(39)-B(1)	126.9(3)	C(64)-C(65)-H(65)	123(3)
C(44)-C(39)-B(1)	119.6(3)	C(66)-C(65)-H(65)	116(3)
F(40)-C(40)-C(39)	120.8(3)	C(65)-C(66)-C(61)	118.5(5)
F(40)-C(40)-C(41)	115.8(3)	C(65)-C(66)-H(66)	126(3)
C(39)-C(40)-C(41)	123.3(3)	C(61)-C(66)-H(66)	116(3)
F(41)-C(41)-C(42)	120.1(3)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+2,-z+1

Table 5. Anisotropic displacement parameters ($Å^2 x 10^4$) for CGB3. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	153(2)	145(2)	198(2)	87(2)	49(1)	57(2)
Br(1)	215(2)	183(2)	217(2)	57(2)	-13(2)	64(2)
Br(2)	410(3)	519(3)	683(4)	164(3)	241(3)	67(3)
Br(3)	996(5)	633(4)	417(3)	221(3)	117(3)	-335(4)
Si(1)	217(6)	231(6)	222(6)	106(5)	31(4)	49(5)
Si(2)	218(6)	167(5)	296(6)	121(5)	94(5)	64(5)
F(22)	242(12)	254(12)	250(12)	112(10)	116(9)	76(10)
F(23)	355(14)	243(12)	324(13)	4(11)	108(11)	69(11)
F(24)	349(14)	151(12)	502(15)	72(11)	114(11)	5(10)
F(25)	346(14)	254(13)	438(14)	208(11)	183(11)	41(11)
F(26)	245(12)	209(11)	243(12)	123(10)	105(9)	62(9)
F(28)	203(11)	202(11)	253(11)	117(9)	48(9)	105(9)
F(29)	276(12)	195(11)	260(12)	67(10)	77(9)	104(10)
F(30)	314(13)	290(13)	196(11)	55(10)	38(9)	108(10)
F(31)	250(12)	311(13)	228(12)	127(10)	-19(9)	108(10)
F(32)	191(11)	209(11)	246(11)	106(9)	21(9)	108(9)
F(34)	223(12)	190(11)	445(14)	173(10)	112(10)	100(10)
F(35)	287(14)	235(13)	990(20)	351(14)	233(14)	52(11)
F(36)	187(13)	433(16)	1070(20)	455(16)	293(14)	95(11)
F(37)	185(12)	372(14)	669(17)	323(13)	219(11)	170(11)
F(38)	157(11)	186(11)	465(14)	209(10)	122(10)	75(9)
F(40)	217(12)	359(13)	289(12)	204(10)	132(9)	145(10)
F(41)	340(13)	373(14)	238(12)	194(11)	65(10)	123(11)
F(42)	283(13)	447(15)	304(13)	188(11)	-16(10)	194(11)
F(43)	121(11)	402(14)	341(13)	160(11)	56(9)	131(10)
F(44)	159(11)	299(12)	230(11)	151(10)	82(9)	76(9)
B(1)	150(20)	170(20)	190(20)	96(18)	54(17)	70(17)
C(1)	210(20)	132(18)	185(19)	11(15)	63(15)	51(16)
C(2)	200(20)	110(18)	260(20)	65(16)	72(16)	50(15)
C(3)	250(20)	170(20)	310(20)	104(18)	73(18)	119(17)
C(4)	170(20)	180(20)	330(20)	71(18)	93(17)	93(17)
C(5)	250(20)	200(20)	250(20)	83(18)	134(17)	87(17)
C(6)	100(18)	178(19)	270(20)	98(17)	40(15)	42(15)
C(7)	119(18)	179(19)	280(20)	117(17)	81(15)	44(15)
C(8)	180(20)	260(20)	270(20)	176(19)	102(17)	105(17)
C(9)	170(20)	150(20)	310(20)	64(18)	73(17)	77(16)
C(10)	128(19)	210(20)	310(20)	163(18)	61(16)	71(16)
C(11)	280(20)	290(30)	210(20)	100(20)	30(20)	50(20)
C(12)	340(30)	280(30)	330(30)	120(20)	0(20)	70(20)
C(13)	360(30)	190(20)	270(20)	130(20)	140(20)	90(20)
C(14)	260(20)	200(20)	340(30)	140(20)	90(20)	53(19)
C(21)	93(17)	172(19)	230(20)	99(16)	18(14)	66(15)
C(22)	109(18)	240(20)	230(20)	130(17)	49(15)	53(16)
C(23)	180(20)	230(20)	240(20)	34(18)	44(16)	88(17)
C(24)	160(20)	160(20)	400(20)	96(19)	61(18)	44(16)
C(25)	147(19)	210(20)	300(20)	150(18)	68(16)	49(16)
C(26)	143(18)	180(19)	220(20)	106(16)	72(15)	66(15)

C(27)	118(18)	144(18)	221(19)	104(16)	55(15)	38(15)
C(28)	118(18)	167(19)	260(20)	137(17)	41(15)	45(15)
C(29)	127(18)	145(19)	280(20)	87(17)	77(15)	56(15)
C(30)	149(19)	210(20)	162(19)	46(16)	26(15)	9(16)
C(31)	125(18)	220(20)	230(20)	119(17)	2(15)	49(16)
C(32)	109(18)	126(18)	270(20)	88(16)	15(15)	23(15)
C(33)	147(19)	200(20)	175(19)	87(16)	24(15)	45(16)
C(34)	162(19)	220(20)	300(20)	120(18)	55(16)	83(17)
C(35)	220(20)	200(20)	510(30)	210(20)	102(19)	52(17)
C(36)	140(20)	350(20)	580(30)	290(20)	155(19)	34(18)
C(37)	170(20)	310(20)	420(30)	220(20)	113(18)	123(18)
C(38)	150(19)	200(20)	280(20)	145(17)	78(16)	53(16)
C(39)	113(18)	139(18)	199(19)	66(15)	30(14)	44(15)
C(40)	153(19)	182(19)	240(20)	112(16)	69(16)	52(16)
C(41)	260(20)	200(20)	123(18)	77(16)	24(16)	59(17)
C(42)	200(20)	210(20)	200(20)	76(16)	-25(16)	99(17)
C(43)	141(19)	200(20)	230(20)	69(17)	45(15)	83(16)
C(44)	190(20)	145(19)	193(19)	66(16)	49(15)	56(16)
C(51)	290(20)	320(20)	330(20)	60(20)	125(19)	110(20)
C(52)	300(20)	310(20)	290(20)	90(20)	86(19)	130(20)
C(53)	370(30)	350(30)	290(20)	50(20)	40(20)	160(20)
C(54)	550(30)	310(30)	450(30)	170(20)	180(20)	240(20)
C(55)	660(40)	540(40)	360(30)	240(30)	50(30)	410(30)
C(56)	210(30)	680(40)	250(30)	20(30)	-30(20)	190(30)
C(61)	390(30)	300(20)	430(30)	210(20)	100(20)	120(20)
C(62)	230(20)	450(30)	420(30)	200(20)	40(20)	10(20)
C(63)	400(30)	750(40)	420(30)	250(30)	20(30)	80(30)
C(64)	660(40)	780(40)	440(40)	70(30)	270(30)	-30(30)
C(65)	340(30)	800(50)	550(40)	-180(30)	240(30)	-60(30)
C(66)	310(30)	420(30)	480(30)	20(20)	40(20)	160(20)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for CGB3.

	x	y	z	U_{iso}
H(3)	9690(30)	7190(30)	4480(30)	41(12)
H(4)	11060(40)	8320(30)	3940(30)	47(12)
H(5)	9750(30)	8180(30)	2390(20)	27(11)
H(8)	6950(30)	8470(20)	5210(20)	7(9)
H(9)	7350(30)	10070(30)	5010(20)	24(11)
H(10)	7130(30)	9590(20)	3260(20)	7(8)
H(11A)	6950(40)	8540(30)	1220(30)	40(12)
H(11B)	8110(30)	8910(30)	1930(30)	32(12)
H(11C)	7780(30)	7970(30)	930(20)	16(10)
H(12A)	5730(60)	5770(50)	1100(50)	120(30)
H(12B)	5260(40)	6450(30)	850(30)	48(16)
H(12C)	6160(50)	5840(40)	440(40)	84(17)
H(13A)	7560(30)	5900(30)	4750(20)	28(11)
H(13B)	6600(30)	6290(30)	5020(20)	22(11)
H(13C)	7700(30)	7070(30)	5270(30)	23(11)
H(14A)	5660(40)	4790(30)	2960(30)	42(14)
H(14B)	4870(40)	5200(30)	2450(30)	51(14)
H(14C)	5990(30)	4910(30)	2150(30)	30(11)
H(52)	9770(40)	5190(30)	1640(30)	47(12)
H(53)	11530(40)	6750(30)	1500(30)	48(13)
H(54)	10840(40)	7380(30)	330(30)	58(14)
H(55)	8990(30)	6450(30)	-460(20)	10(12)
H(56)	7620(40)	5400(30)	-280(30)	28(13)
H(62)	-280(40)	8780(30)	270(30)	34(11)
H(63)	-30(40)	8600(30)	-1250(30)	43(13)
H(64)	1880(40)	9310(30)	-1350(30)	40(13)
H(65)	3390(40)	9980(30)	-80(30)	44(14)
H(66)	3280(40)	10230(30)	1390(30)	47(13)