Supporting Material

Copies of ^{1}H NMR spectra of **6A**, **6D**, **6E**, **7A**, **7D**, **7E**, **10**, **11**, **19**, (-)-**24** and (+)-**24**, and X-ray structural information of the racemic *N*-Boc derivative **28** (19 pages).

Utility of a Diene-Tricarbonyliron Complex as a Mobile Chiral Auxiliary: Regio- and Stereocontrolled Functionalization of Acyclic Diene Ligands

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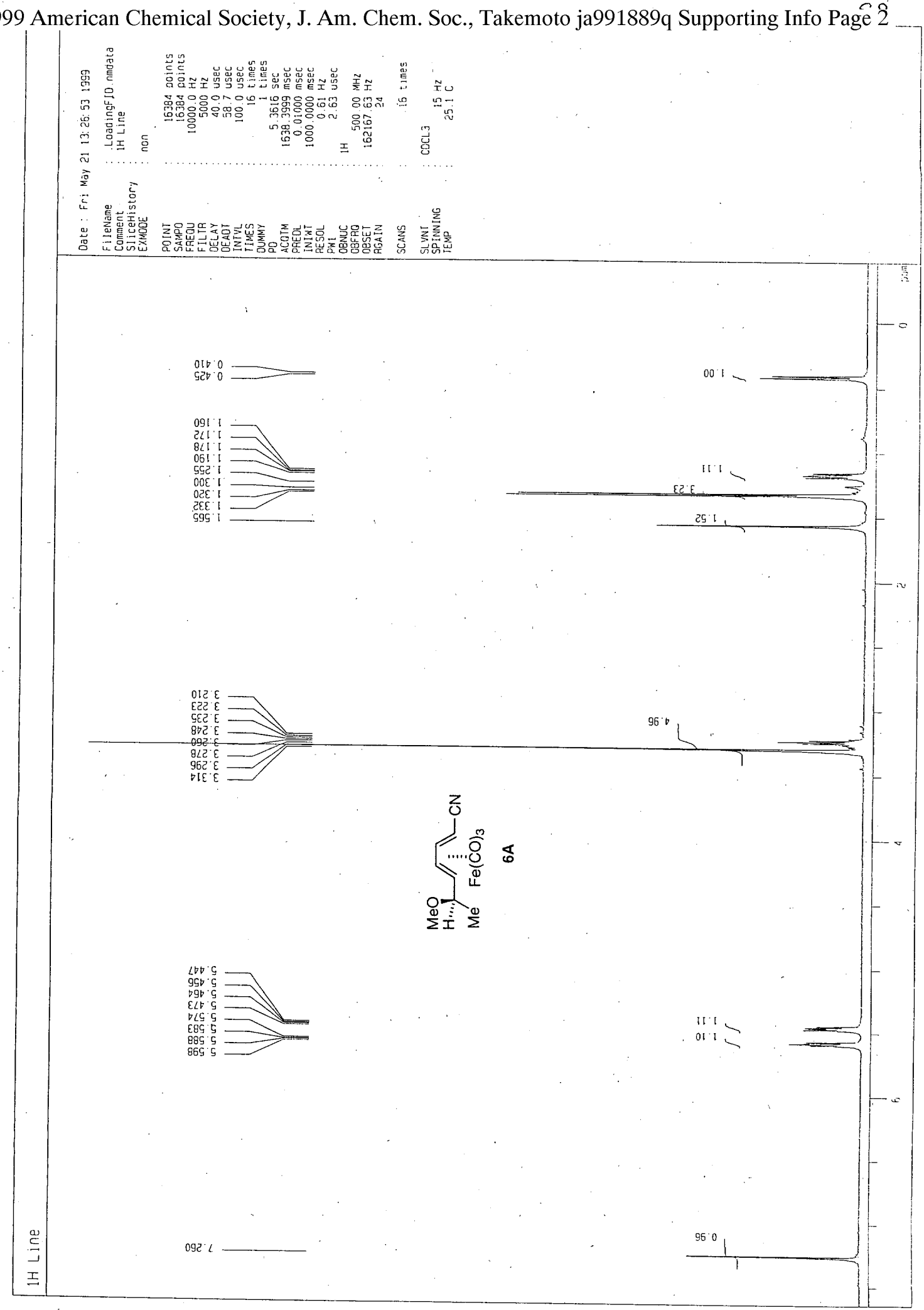
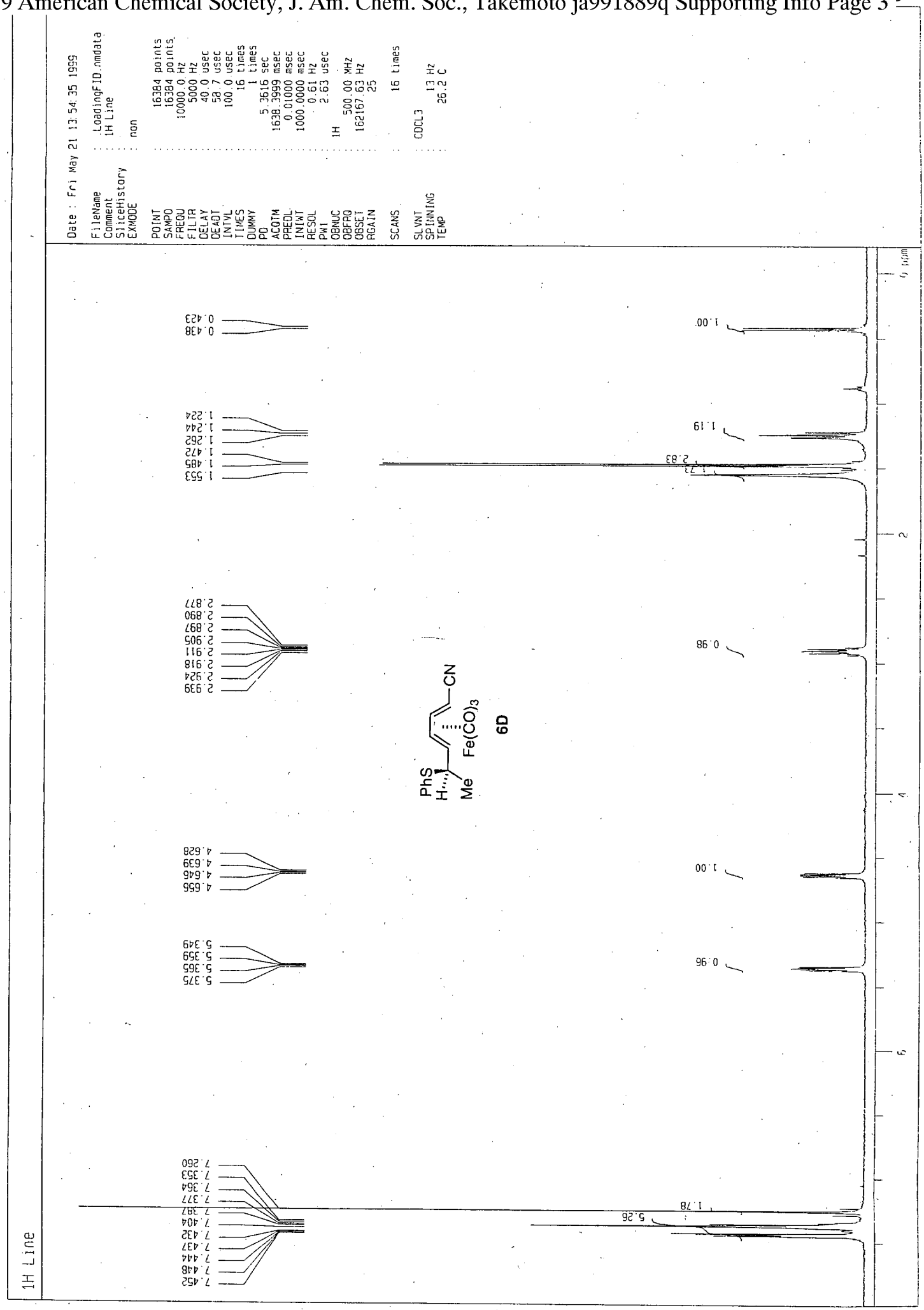
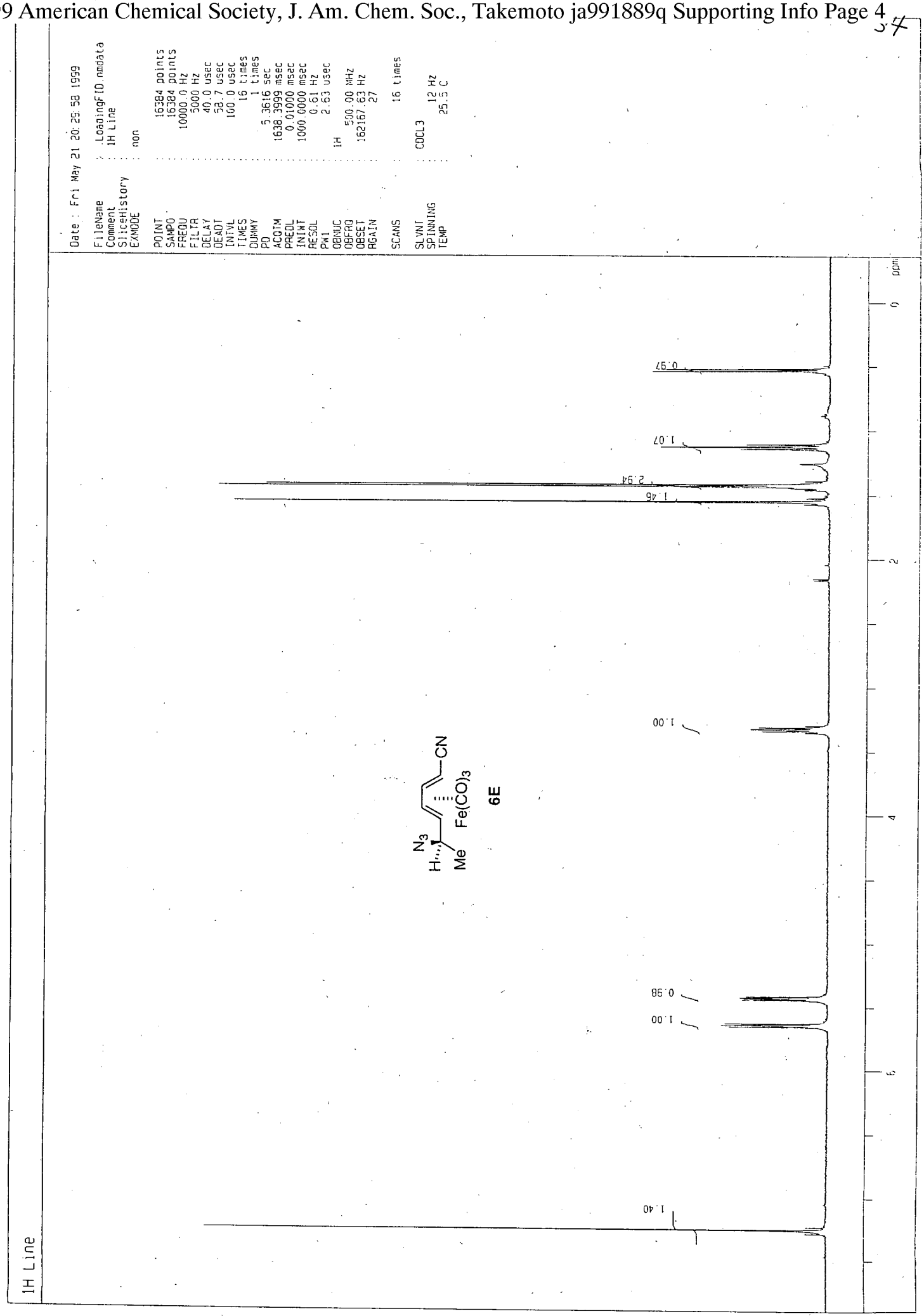
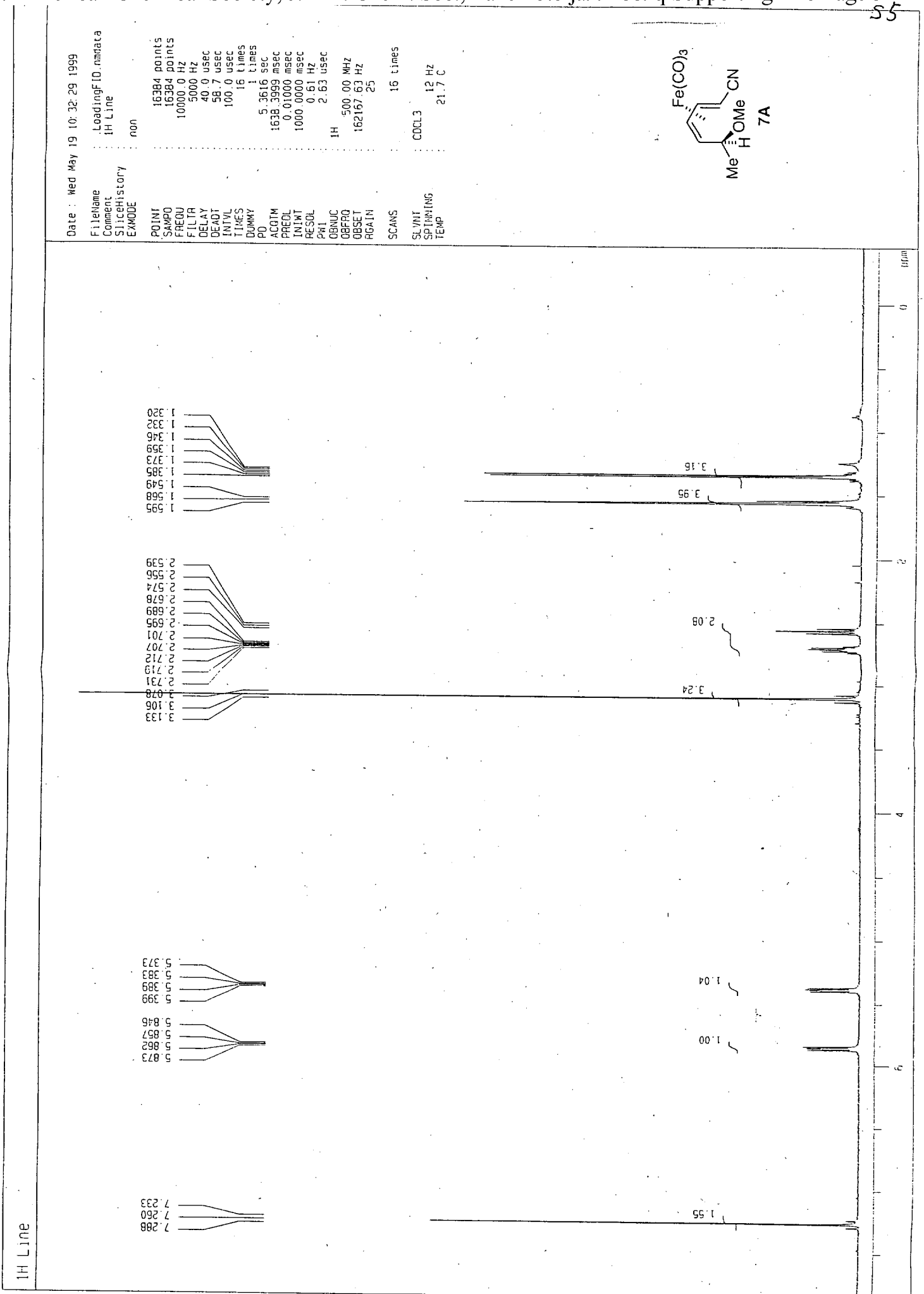
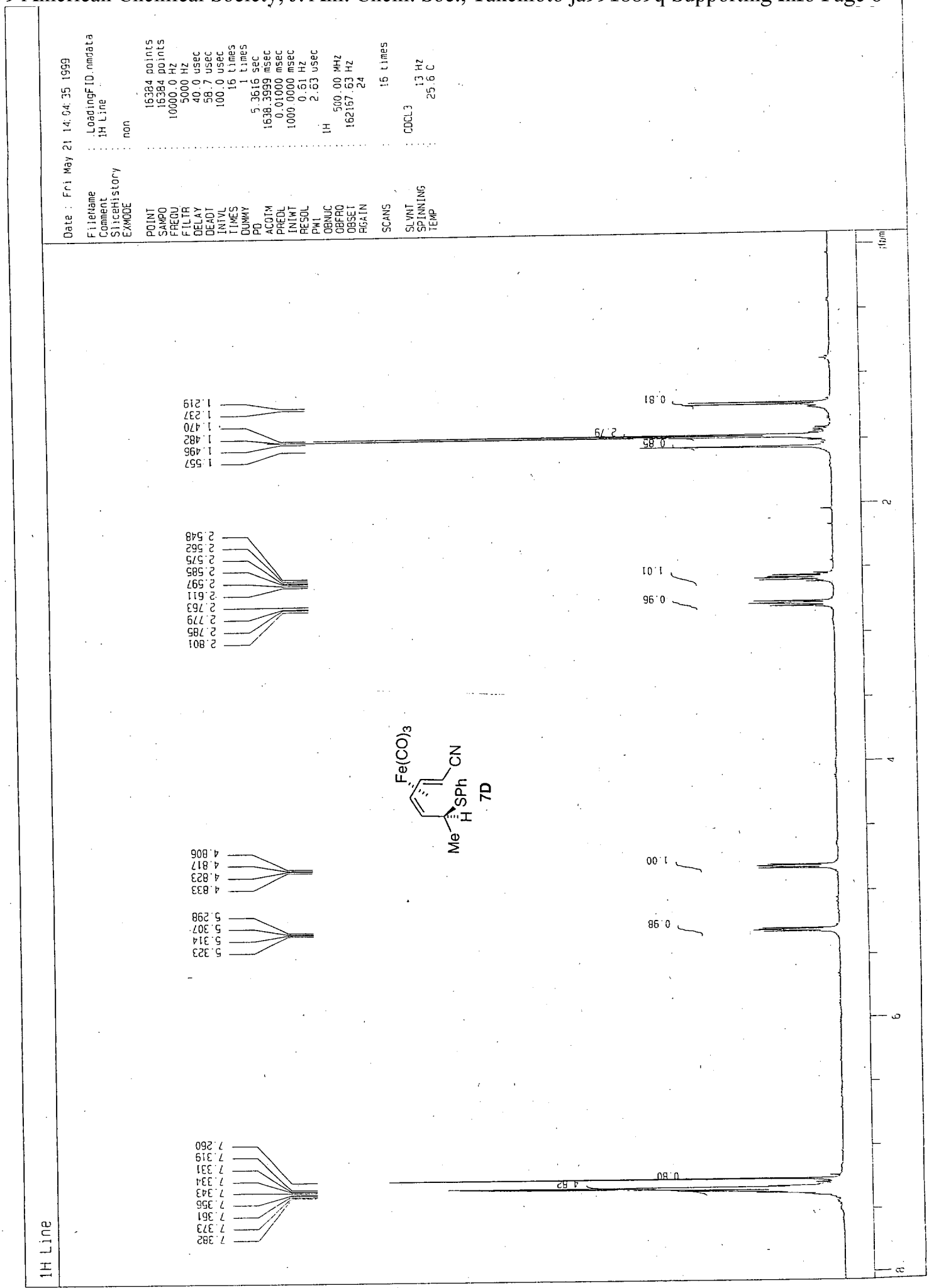
(2*RS*,5*SR*,6*SR*,17*SR*,8*SR*,2*E*,4*E*)-Tricarbonyliron[(η^4-2-5)-8-(tert-butoxycarbonylamino)-6-ethylthio-7-methoxynona-2,4-dienenitrile] 28. A mixture of **19** (86.8 mg, 0.213 mmol), 10% Pd/C (15 mg), Boc_2O (50 ul, 0.217 mmol), and dry MeOH (1.5 ml) was vigorously stirred at room temperature under a medium–pressured hydrogen atmosphere (5 atm) for 40 h. The reaction mixture was filtered off through a pad of celite and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexane/AcOEt = 4/1) to give **19** (16.4 mg, 19%), 28 (20.3 mg, 20%), and **20** (31.3 mg, 35%). **28**; yellow crystals: mp 108 °C (petroleum ether/benzene); ^{1}H NMR ($CDCl_3$) δ 0.60 (d, 1H, J = 7.3 Hz), 1.09 (d, 3H, J = 6.7 Hz), 1.24-1.30 (m, 4H), 1.46 (s, 9H), 2.61 (dq, 1H, J = 4.9, 7.3 Hz) 2.67 (m, 1H), 2.78 (m, 1H), 3.44 (m, 1H), 3.48 (s, 3H), 3.99 (dq, 1H, J = 7.9, 6.7 Hz), 4.60 (br, 1H), 5.33-5.57 (m, 2H); ^{13}C NMR (77.5 MHz, $CDCl_3$) δ 14.4, 16.3, 24.1, 26.0, 28.3, 48.3, 49.1, 60.3, 64.2, 79.6, 81.4, 87.2, 88.2, 121.3, 154.9, 207.9; IR (KBr) 3361, 2220, 2062, 2000, 1701 cm^{-1}; MS (EI) *m/z* (%) 425 (M^++1–2CO, 0.6), 397 (M^++1–3CO, 1.4), 132 (100).

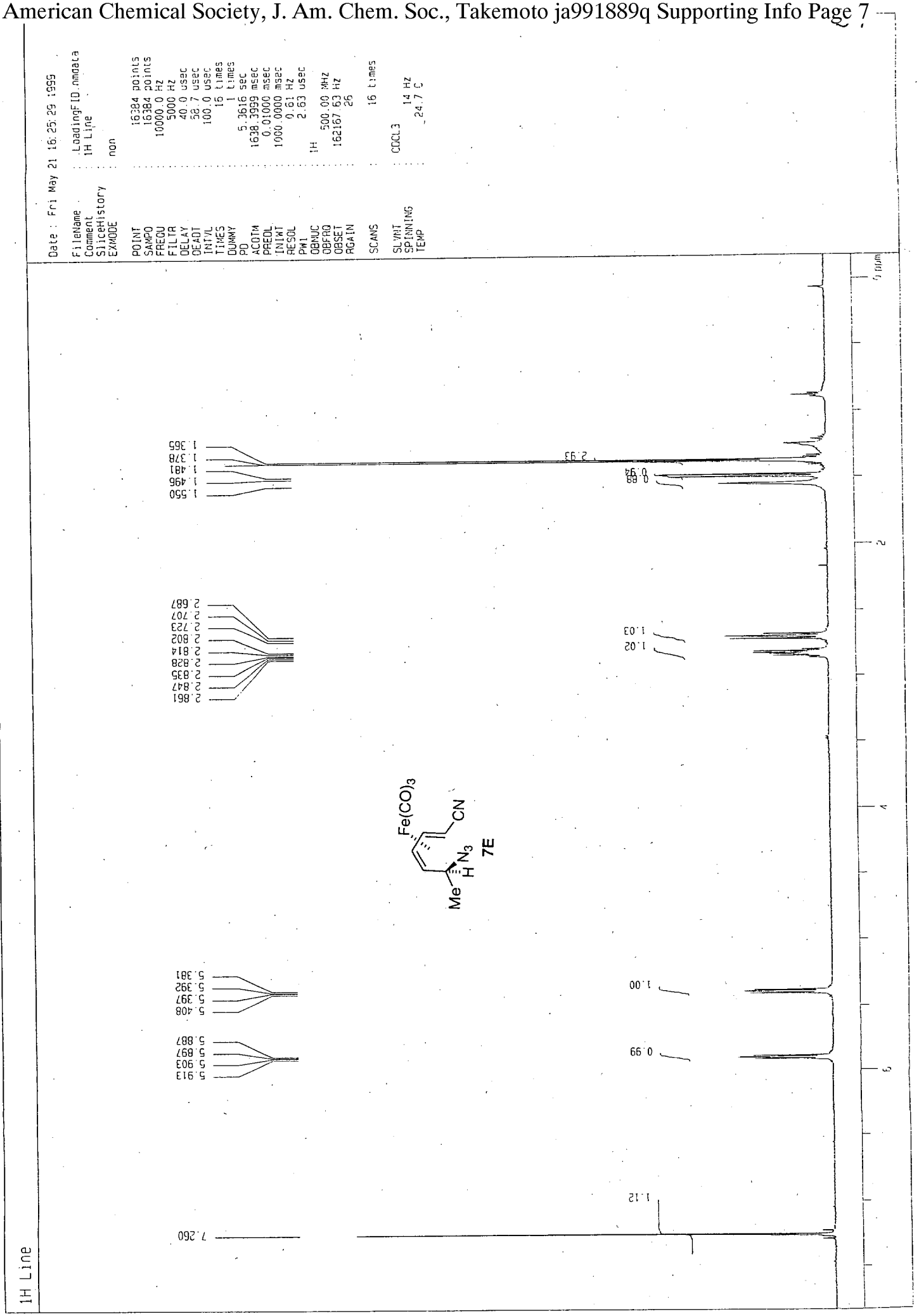


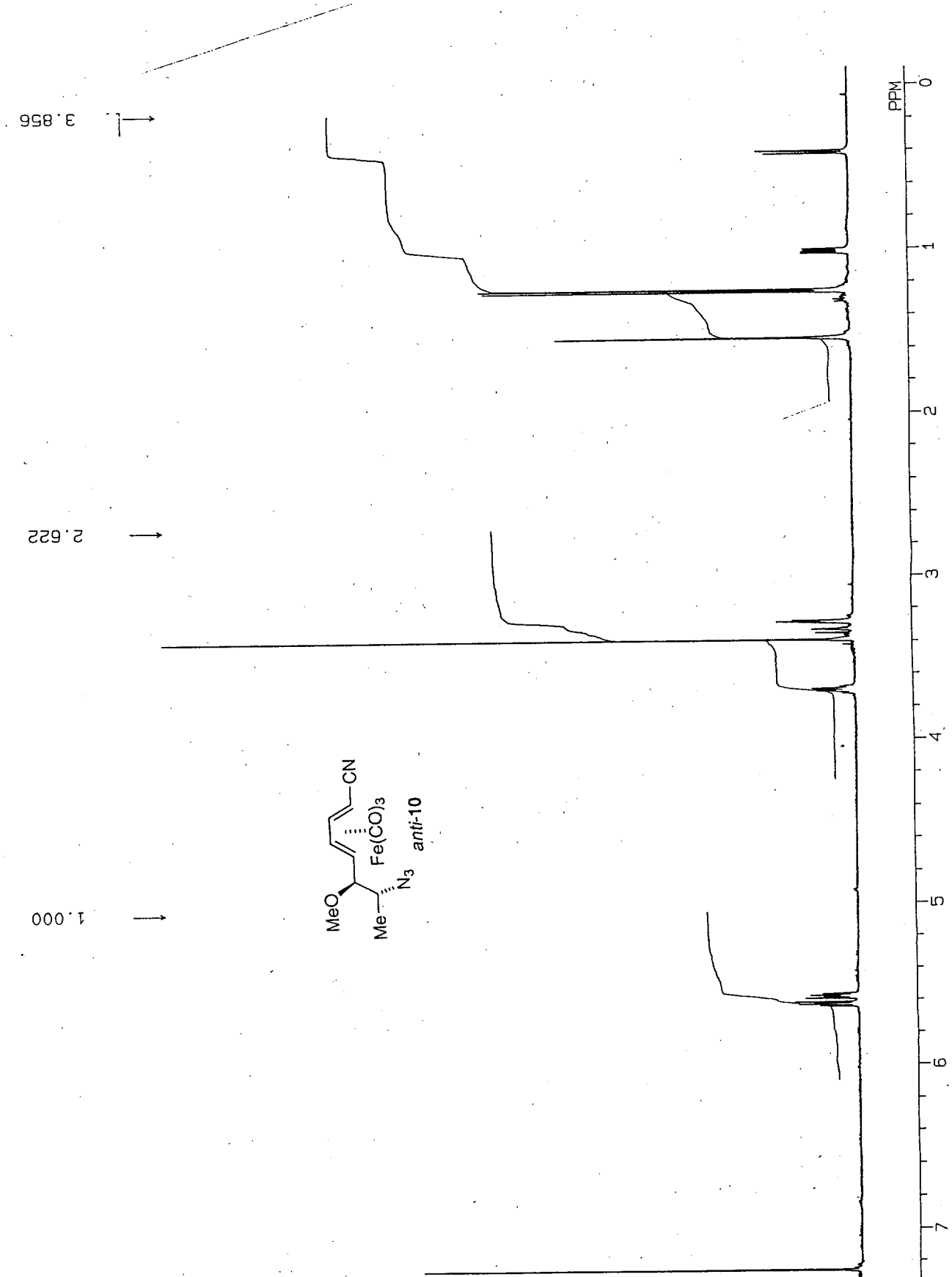








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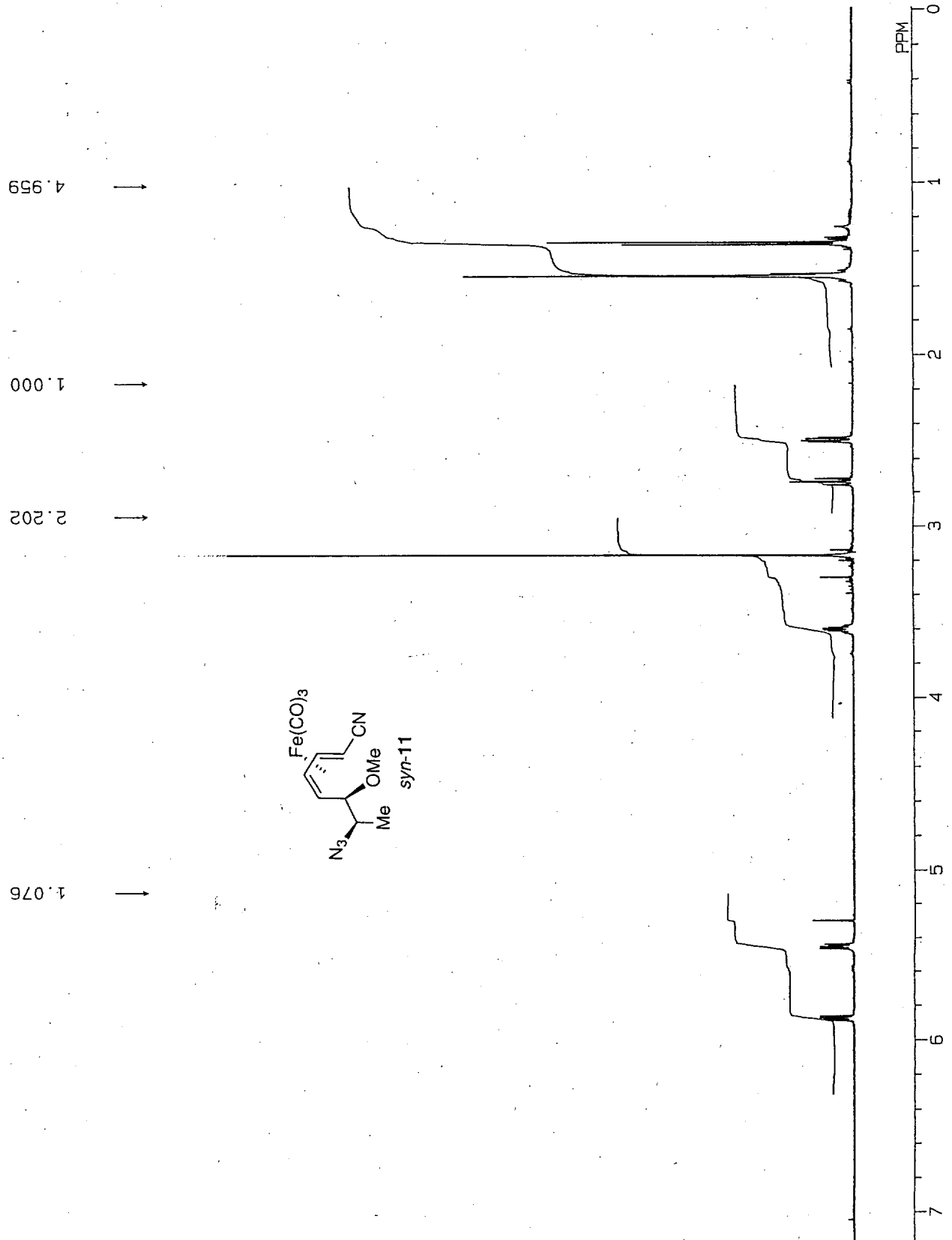
6
7



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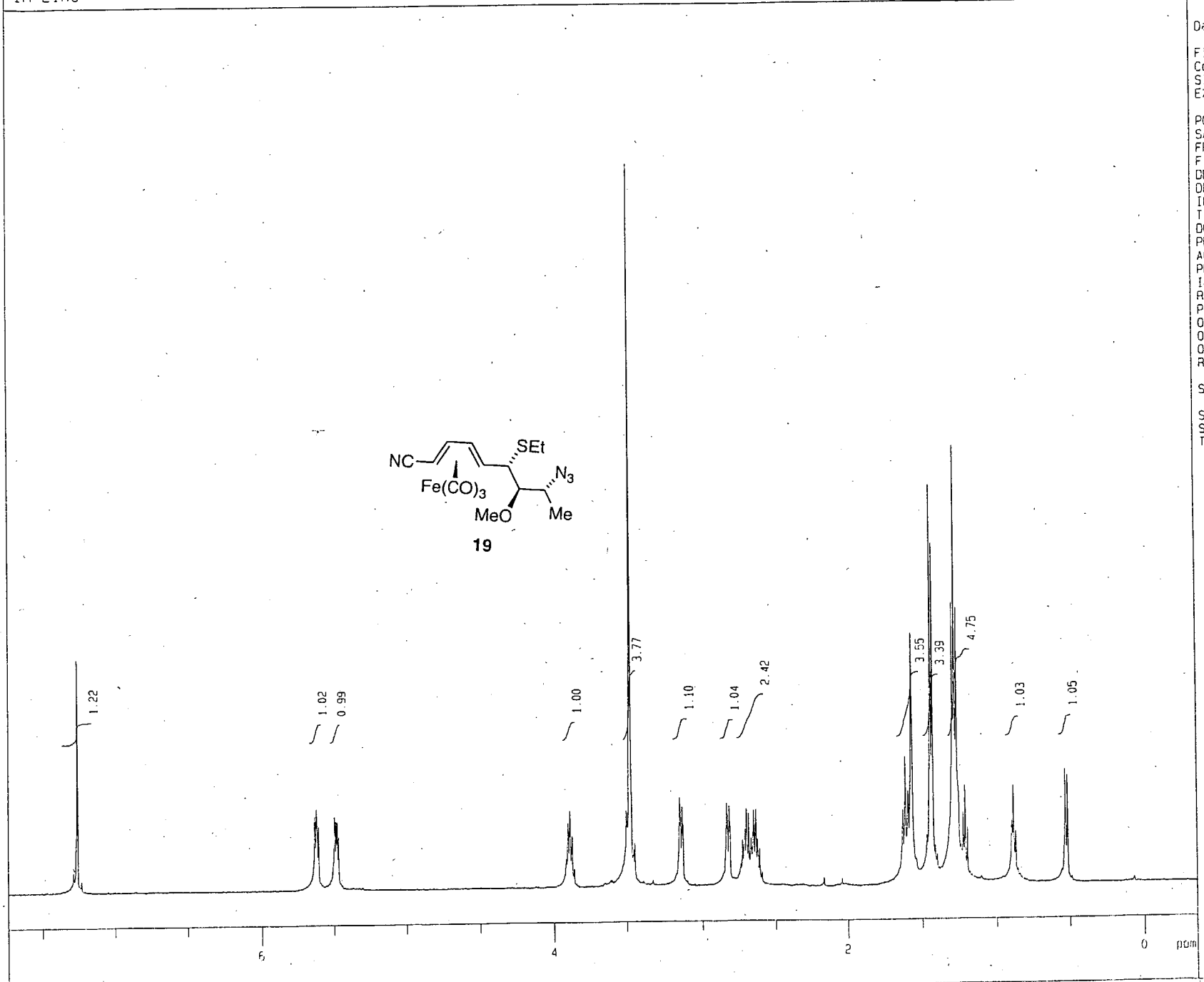

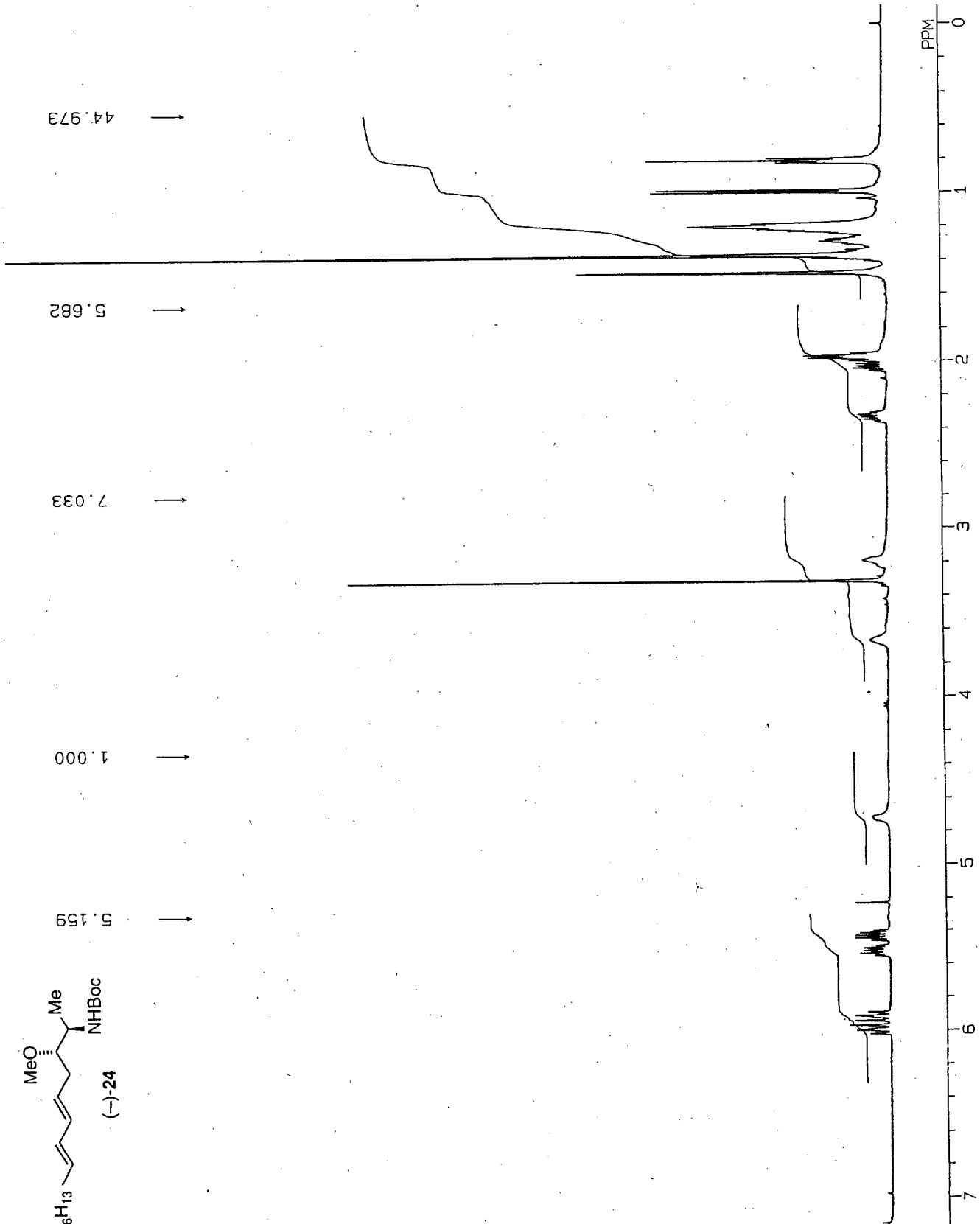

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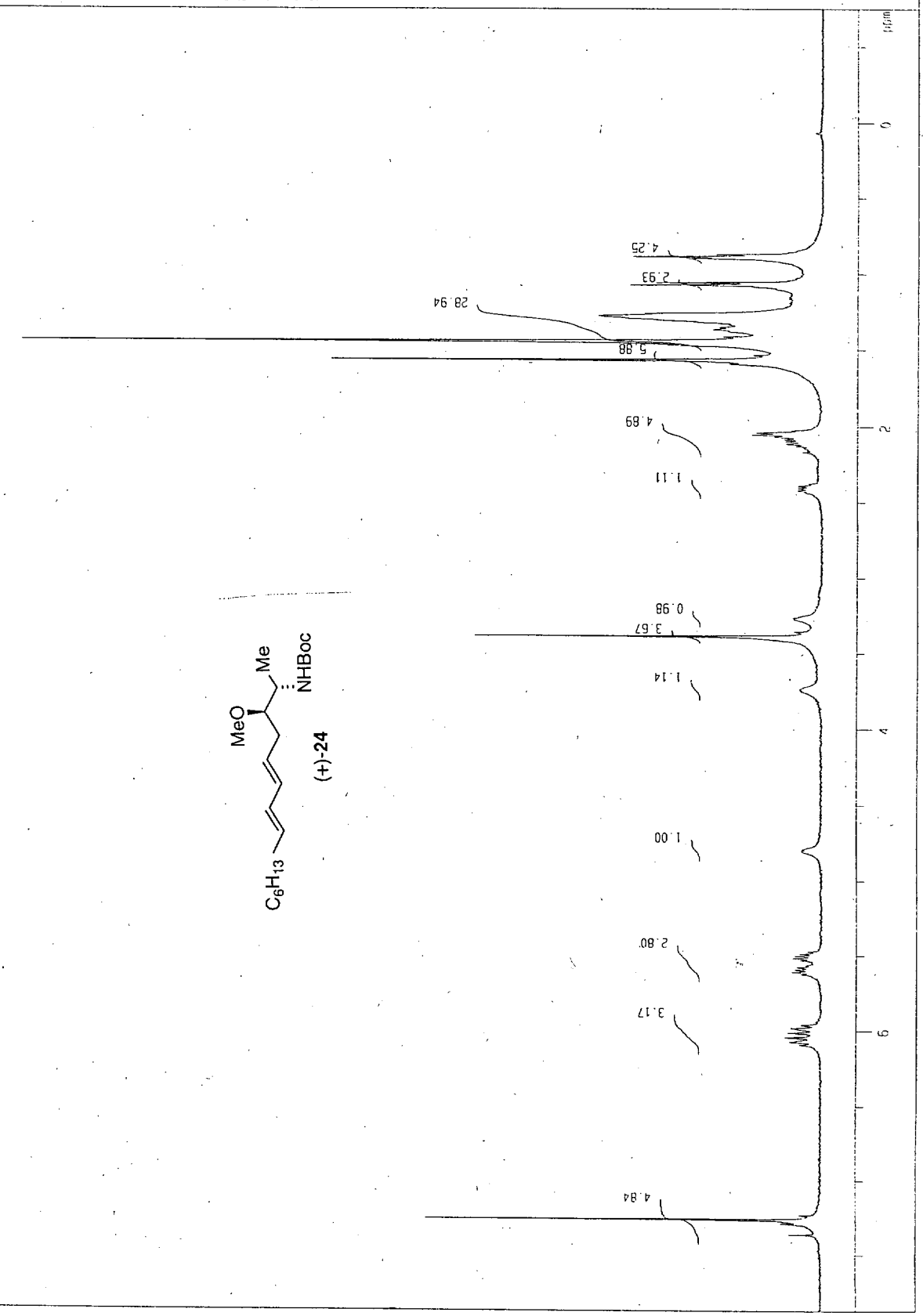


Table 1. Crystal data and structure refinement for 1.

Identification code	mnf2
Empirical formula	C20 H28 Fe N2 O6 S
Formula weight	480.35
Temperature	293(2) K
Wavelength	1.54180 A
Crystal system	monoclinic
Space group	P21/C
Color of crystal	yellow
Unit cell dimensions	a = 12.508(2) A alpha = 90 deg. b = 9.745(2) A beta = 100.710(10) deg. c = 19.6560(10) A gamma = 90 deg.
Volume	2354.1(6) A^3
Z	4
Density (calculated)	1.355 Mg/m^3
Absorption coefficient	6.279 mm^-1
F(000)	1008
Crystal size	0.02 x 0.02 x 0.5 mm3
Theta range for data collection	3.60 to 60.13 deg.
Index ranges	0<=h<=14, -10<=k<=0, -22<=l<=21
Reflections collected	3675
Independent reflections	3496 [R(int) = 0.0276]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3496 / 0 / 325
Goodness-of-fit on F^2	0.085
Final R indices [I>2sigma(I)]	R1 = 0.0735, wR2 = 0.1532
R indices (all data)	R1 = 0.1346, wR2 = 0.1994
Largest diff. peak and hole	0.466 and -0.317 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe	7343(1)	942(1)	3857(1)	50(1)
S(1)	6014(2)	4416(3)	3073(1)	64(1)
C(1)	8371(9)	-1755(11)	3421(6)	74(3)
C(2)	8086(8)	-362(9)	3215(4)	60(2)
C(3)	6976(7)	-39(9)	2938(4)	56(2)
C(4)	6712(7)	1350(9)	2823(4)	52(2)
C(5)	7545(7)	2327(9)	3005(4)	49(2)
C(6)	7338(7)	3867(8)	2941(4)	51(2)
C(7)	7492(6)	4350(8)	2196(4)	48(2)
C(8)	8605(6)	4056(8)	2025(3)	40(2)
C(9)	8654(9)	4519(11)	1282(5)	60(2)
C(10)	6349(8)	5360(10)	3876(5)	68(3)
C(11)	5346(10)	5823(14)	4094(7)	87(4)
C(12)	5946(8)	4598(14)	1285(6)	73(3)
C(13)	10200(6)	4029(8)	2955(4)	45(2)
C(14)	11746(7)	4523(9)	3900(4)	52(2)
C(15)	12295(10)	5891(12)	4122(6)	75(3)
C(16)	12552(9)	3519(11)	3709(6)	72(3)
C(17)	11166(11)	3962(17)	4446(5)	93(4)
C(18)	6320(8)	1859(10)	4191(5)	63(2)
C(19)	7075(8)	-468(10)	4377(5)	62(2)
C(20)	8568(10)	1560(12)	4397(6)	80(3)
O(1)	6663(4)	3719(6)	1716(3)	56(2)
O(2)	10223(5)	2794(6)	3048(3)	65(2)
O(3)	10959(4)	4912(6)	3287(3)	52(1)
O(4)	5660(7)	2313(8)	4460(4)	99(3)
O(5)	6895(7)	-1342(8)	4721(4)	96(2)
O(6)	9337(8)	1901(12)	4748(4)	130(4)
N(1)	8630(9)	-2825(10)	3574(6)	99(3)
N(2)	9460(5)	4701(6)	2508(3)	47(2)

Table 4. Bond lengths [A] and angles [deg] for 1.

Fe-C(19)	1.781(10)
Fe-C(18)	1.783(12)
Fe-C(20)	1.798(13)
Fe-C(3)	2.021(8)
Fe-C(4)	2.077(8)
Fe-C(2)	2.123(9)
Fe-C(5)	2.202(8)
S(1)-C(6)	1.805(9)
S(1)-C(10)	1.809(9)
C(1)-N(1)	1.117(13)
C(1)-C(2)	1.442(14)
C(2)-C(3)	1.428(12)
C(3)-C(4)	1.402(12)
C(4)-C(5)	1.407(11)
C(5)-C(6)	1.524(11)
C(6)-C(7)	1.583(10)
C(7)-O(1)	1.407(9)
C(7)-C(8)	1.520(10)
C(8)-N(2)	1.437(9)
C(8)-C(9)	1.539(11)
C(10)-C(11)	1.469(14)
C(12)-O(1)	1.404(11)
C(13)-O(2)	1.217(9)
C(13)-N(2)	1.325(9)
C(13)-O(3)	1.356(9)
C(14)-O(3)	1.458(9)
C(14)-C(16)	1.502(14)
C(14)-C(17)	1.504(13)
C(14)-C(15)	1.525(13)
C(18)-O(4)	1.148(11)
C(19)-O(5)	1.136(11)
C(20)-O(6)	1.125(13)
C(19)-Fe-C(18)	87.2(4)
C(19)-Fe-C(20)	98.6(4)
C(18)-Fe-C(20)	101.9(5)
C(19)-Fe-C(3)	96.5(4)
C(18)-Fe-C(3)	120.4(4)
C(20)-Fe-C(3)	135.5(4)
C(19)-Fe-C(4)	129.1(4)
C(18)-Fe-C(4)	95.5(4)
C(20)-Fe-C(4)	129.8(4)
C(3)-Fe-C(4)	40.0(3)
C(19)-Fe-C(2)	91.7(4)
C(18)-Fe-C(2)	160.4(4)
C(20)-Fe-C(2)	97.6(5)
C(3)-Fe-C(2)	40.2(3)
C(4)-Fe-C(2)	70.2(3)
C(19)-Fe-C(5)	165.9(4)
C(18)-Fe-C(5)	99.4(4)
C(20)-Fe-C(5)	92.2(4)
C(3)-Fe-C(5)	69.4(3)
C(4)-Fe-C(5)	38.3(3)
C(2)-Fe-C(5)	77.9(3)
C(6)-S(1)-C(10)	101.9(4)
N(1)-C(1)-C(2)	177.3(13)

C(3)-C(2)-C(1)	119.1(9)
C(3)-C(2)-Fe	66.0(5)
C(1)-C(2)-Fe	120.6(7)
C(4)-C(3)-C(2)	117.2(8)
C(4)-C(3)-Fe	72.2(5)
C(2)-C(3)-Fe	73.7(5)
C(3)-C(4)-C(5)	118.1(8)
C(3)-C(4)-Fe	67.8(5)
C(5)-C(4)-Fe	75.7(5)
C(4)-C(5)-C(6)	122.6(8)
C(4)-C(5)-Fe	66.1(4)
C(6)-C(5)-Fe	128.7(6)
C(5)-C(6)-C(7)	108.7(6)
C(5)-C(6)-S(1)	115.2(6)
C(7)-C(6)-S(1)	108.5(5)
O(1)-C(7)-C(8)	111.1(6)
O(1)-C(7)-C(6)	106.9(6)
C(8)-C(7)-C(6)	115.0(6)
N(2)-C(8)-C(7)	111.8(6)
N(2)-C(8)-C(9)	110.0(7)
C(7)-C(8)-C(9)	110.8(7)
C(11)-C(10)-S(1)	109.8(8)
O(2)-C(13)-N(2)	125.6(7)
O(2)-C(13)-O(3)	124.1(7)
N(2)-C(13)-O(3)	110.2(7)
O(3)-C(14)-C(16)	110.1(7)
O(3)-C(14)-C(17)	110.0(8)
C(16)-C(14)-C(17)	112.1(10)
O(3)-C(14)-C(15)	102.0(7)
C(16)-C(14)-C(15)	110.7(8)
C(17)-C(14)-C(15)	111.5(9)
O(4)-C(18)-Fe	171.5(8)
O(5)-C(19)-Fe	178.1(9)
O(6)-C(20)-Fe	177.4(11)
C(12)-O(1)-C(7)	116.5(7)
C(13)-O(3)-C(14)	122.5(6)
C(13)-N(2)-C(8)	124.4(6)

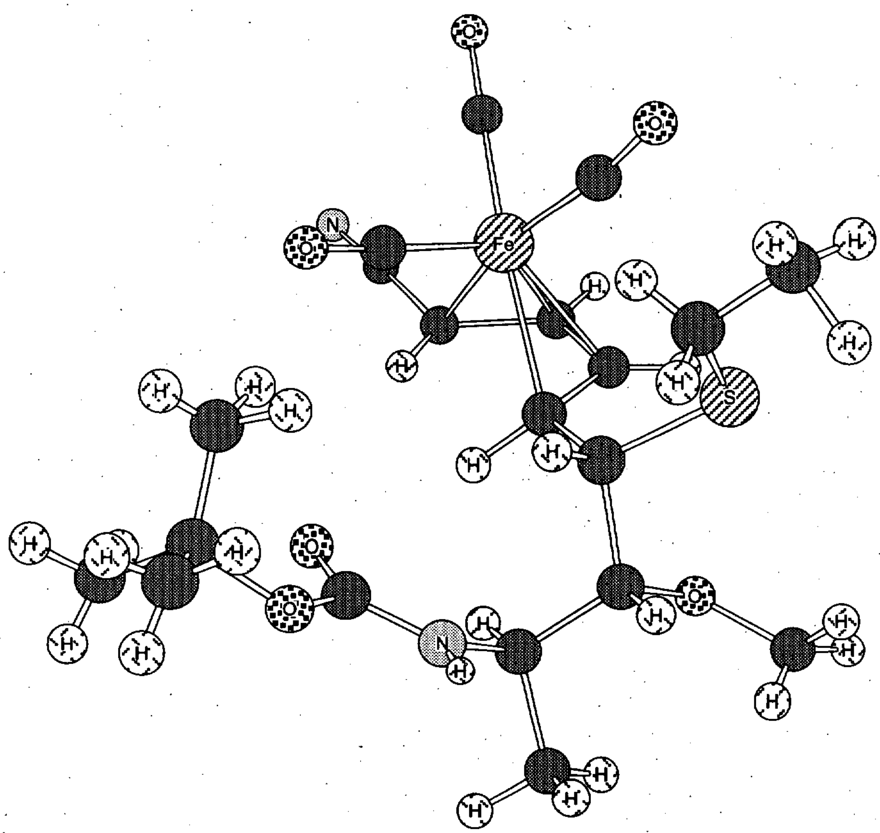
Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters (A^2 x 10^3) for 1.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Fe	61(1)	50(1)	40(1)	-1(1)	12(1)	-8(1)
S(1)	58(1)	79(2)	53(1)	-13(1)	8(1)	10(1)
C(1)	86(8)	60(7)	78(7)	-3(6)	23(6)	3(6)
C(2)	81(7)	45(5)	59(5)	-2(4)	22(5)	-3(5)
C(3)	66(6)	55(5)	47(5)	-14(4)	14(4)	-2(5)
C(4)	58(5)	58(5)	39(4)	-2(4)	4(4)	1(4)
C(5)	53(5)	54(5)	37(4)	6(4)	3(4)	7(4)
C(6)	76(6)	45(5)	27(4)	-2(3)	-2(4)	-1(4)
C(7)	46(5)	41(4)	49(5)	6(4)	-10(4)	0(4)
C(8)	49(5)	34(4)	34(4)	-3(3)	-1(3)	3(3)
C(9)	82(7)	52(5)	44(5)	2(4)	4(5)	2(5)
C(10)	81(7)	62(6)	63(6)	-21(5)	18(5)	-15(5)
C(11)	80(8)	95(9)	92(9)	-33(7)	31(7)	3(7)
C(12)	48(6)	94(9)	67(7)	9(6)	-19(5)	7(6)
C(13)	43(5)	47(5)	42(4)	-1(4)	-2(4)	2(4)
C(14)	49(5)	65(6)	38(4)	7(4)	-3(4)	-18(4)
C(15)	78(8)	71(7)	66(7)	-7(6)	-15(6)	-23(6)
C(16)	70(7)	57(6)	84(8)	16(6)	2(6)	-2(5)
C(17)	92(9)	136(12)	49(6)	19(7)	12(6)	-46(8)
C(18)	70(6)	53(6)	62(6)	12(5)	6(5)	-20(5)
C(19)	74(6)	58(6)	56(5)	-12(5)	19(5)	-13(5)
C(20)	97(8)	82(8)	69(7)	16(6)	37(6)	-18(7)
O(1)	55(3)	58(4)	48(3)	-1(3)	-5(3)	0(3)
O(2)	83(4)	40(4)	63(4)	14(3)	-10(3)	-7(3)
O(3)	56(3)	46(3)	49(3)	3(3)	-9(3)	-7(3)
O(4)	131(7)	80(5)	102(6)	0(5)	66(5)	10(5)
O(5)	140(7)	74(5)	80(5)	19(4)	36(5)	-14(5)
O(6)	117(7)	196(11)	69(5)	12(6)	-3(5)	-87(7)
N(1)	116(8)	55(6)	131(9)	17(6)	38(7)	10(6)
N(2)	47(4)	34(3)	54(4)	-3(3)	-3(3)	-2(3)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 1.

	x	y	z	U(eq)
H(2)	8617(8)	317(9)	3261(4)	72
H(3)	6451(7)	-723(9)	2837(4)	67
H(4)	6006(7)	1618(9)	2633(4)	63
H(5)	8249(7)	2021(9)	3170(4)	58
H(6)	7888(7)	4330(8)	3285(4)	61
H(7)	7374(6)	5344(8)	2166(4)	58
H(8)	8723(6)	3061(8)	2052(3)	48
H(9A)	9421(84)	4302(107)	1201(51)	91
H(9B)	8635(82)	5480(116)	1288(52)	91
H(9C)	8070(85)	4161(110)	979(54)	91
H(10A)	6760(8)	4778(10)	4232(5)	82
H(10B)	6796(8)	6147(10)	3814(5)	82
H(11A)	5574(105)	6404(140)	4457(68)	131
H(11B)	4633(107)	5562(142)	3976(68)	131
H(11C)	5101(101)	6670(134)	3626(65)	131
H(12A)	5330(97)	4175(120)	989(59)	110
H(12B)	6364(98)	5166(132)	1166(64)	110
H(12C)	5491(97)	5130(131)	1466(61)	110
H(15A)	11662(97)	6387(127)	4237(60)	113
H(15B)	12734(97)	6181(129)	3813(61)	113
H(15C)	12885(97)	5733(125)	4442(62)	113
H(16A)	13067(94)	3816(124)	3452(59)	108
H(16B)	12161(93)	2723(127)	3607(58)	108
H(16C)	13150(95)	3345(119)	4103(60)	108
H(17A)	10485(110)	4621(146)	4515(66)	139
H(17B)	11622(110)	3845(152)	4807(69)	139
H(17C)	10634(114)	3210(146)	4368(67)	139
H(2A)	9494(5)	5582(6)	2507(3)	56



X-ray structure of **19** drawn by CS Chem3D