SUPPORTING INFORMATION

Photochemical Reactivity of 1-Substituted-1-aza-1,4-dienes Promoted by Electron-Acceptor Sensitizers. Di-π-methane Rearrangements and Alternative Reactions via Radical-cation Intermediates

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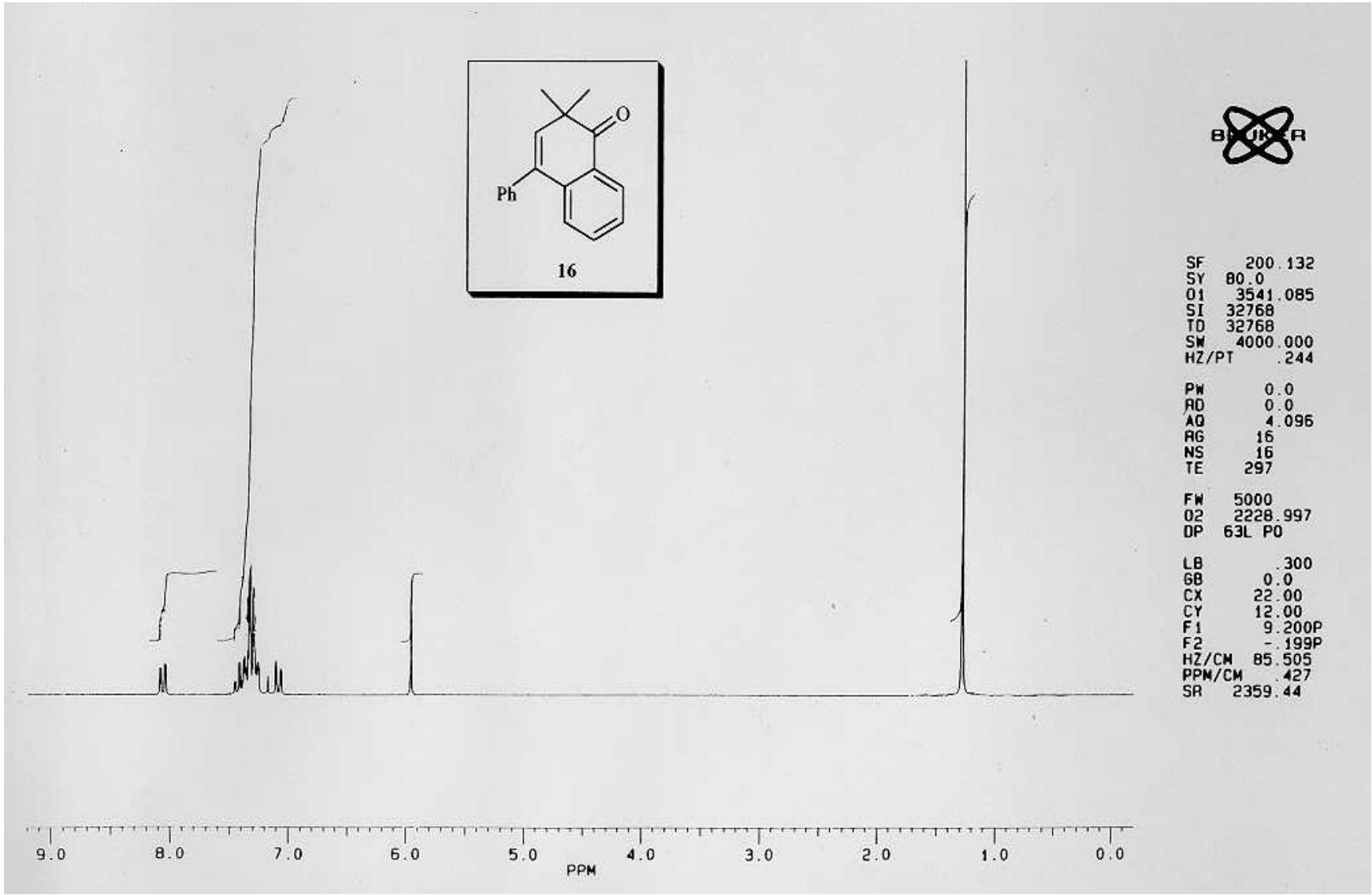
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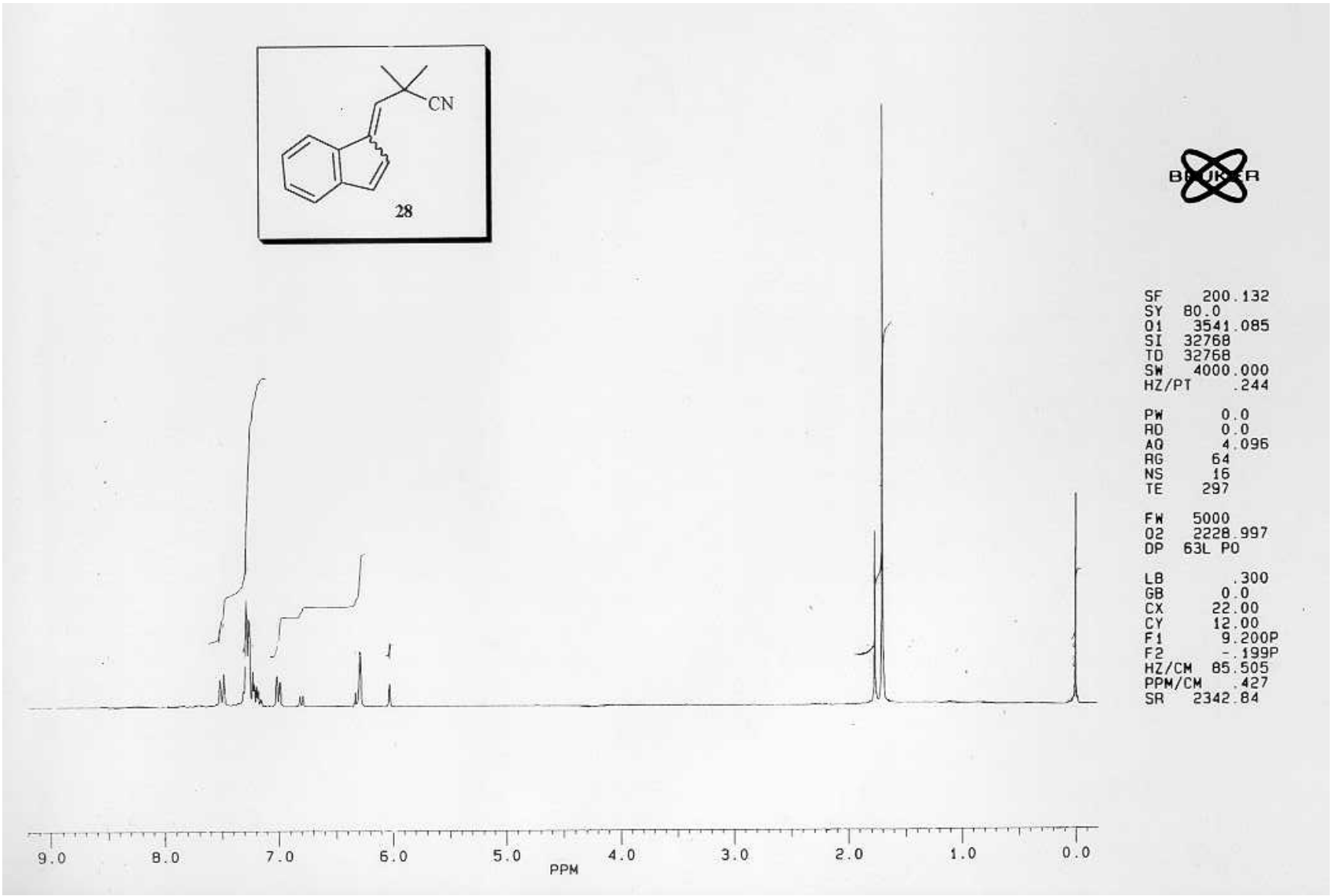
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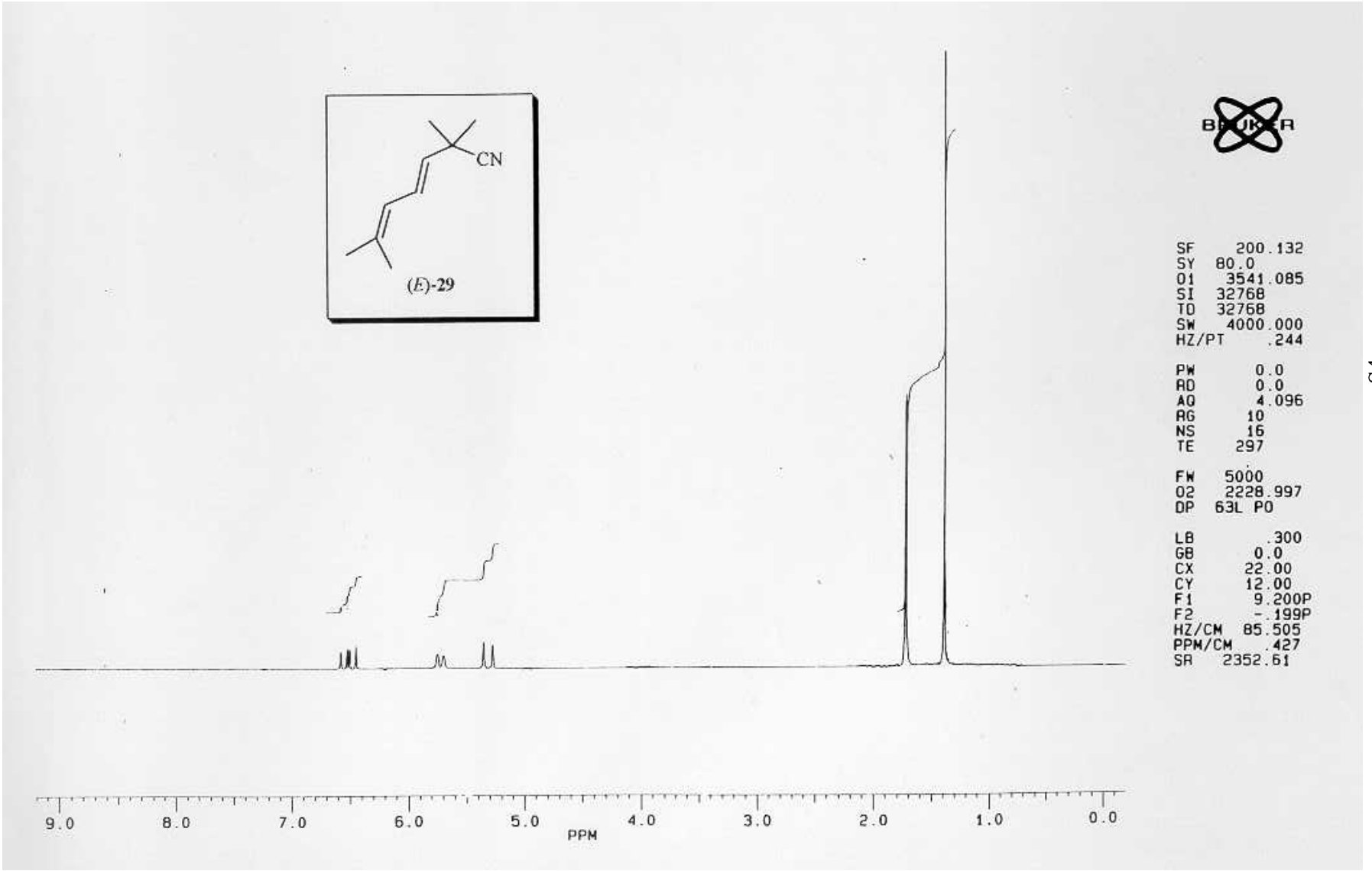
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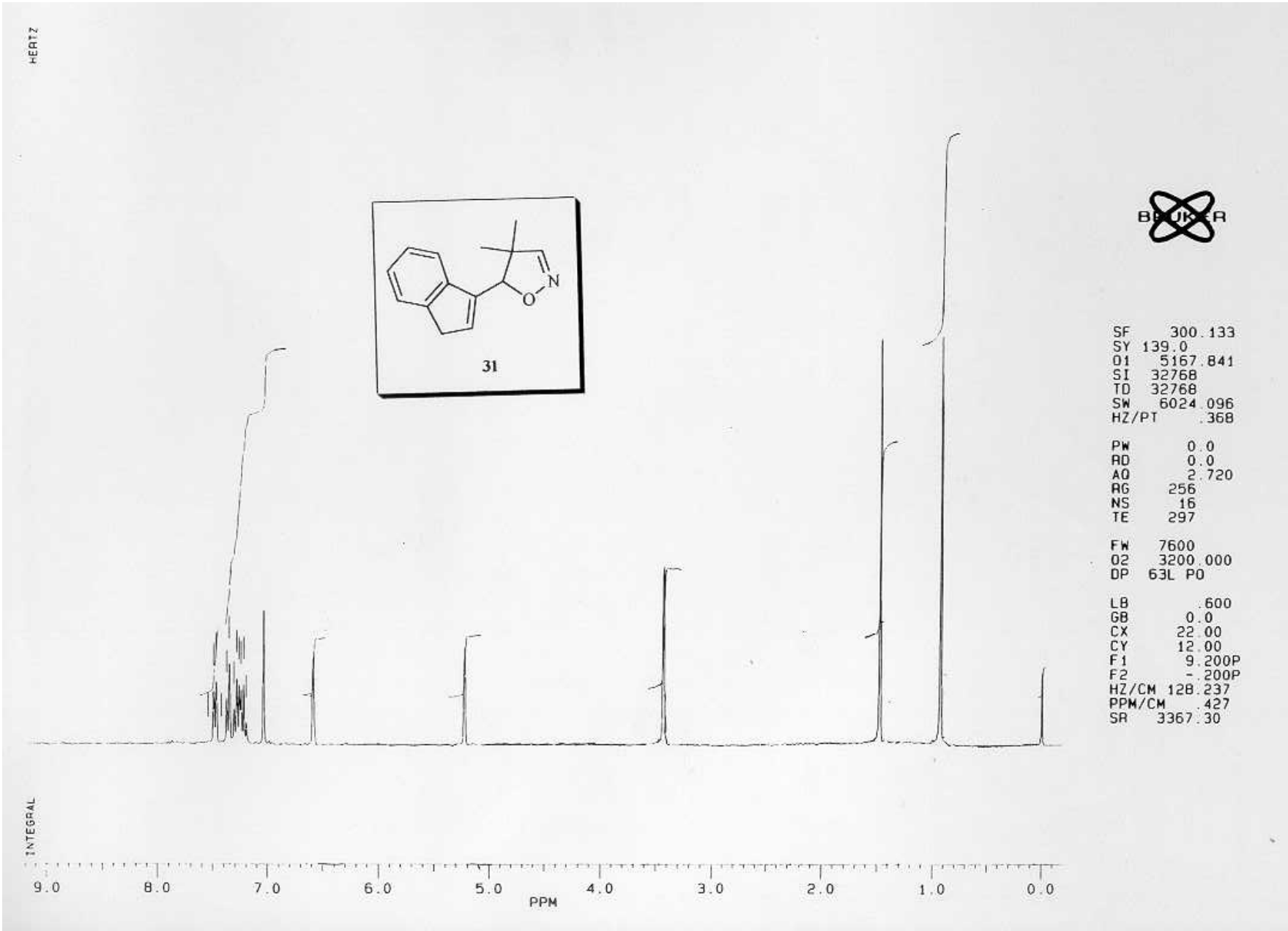
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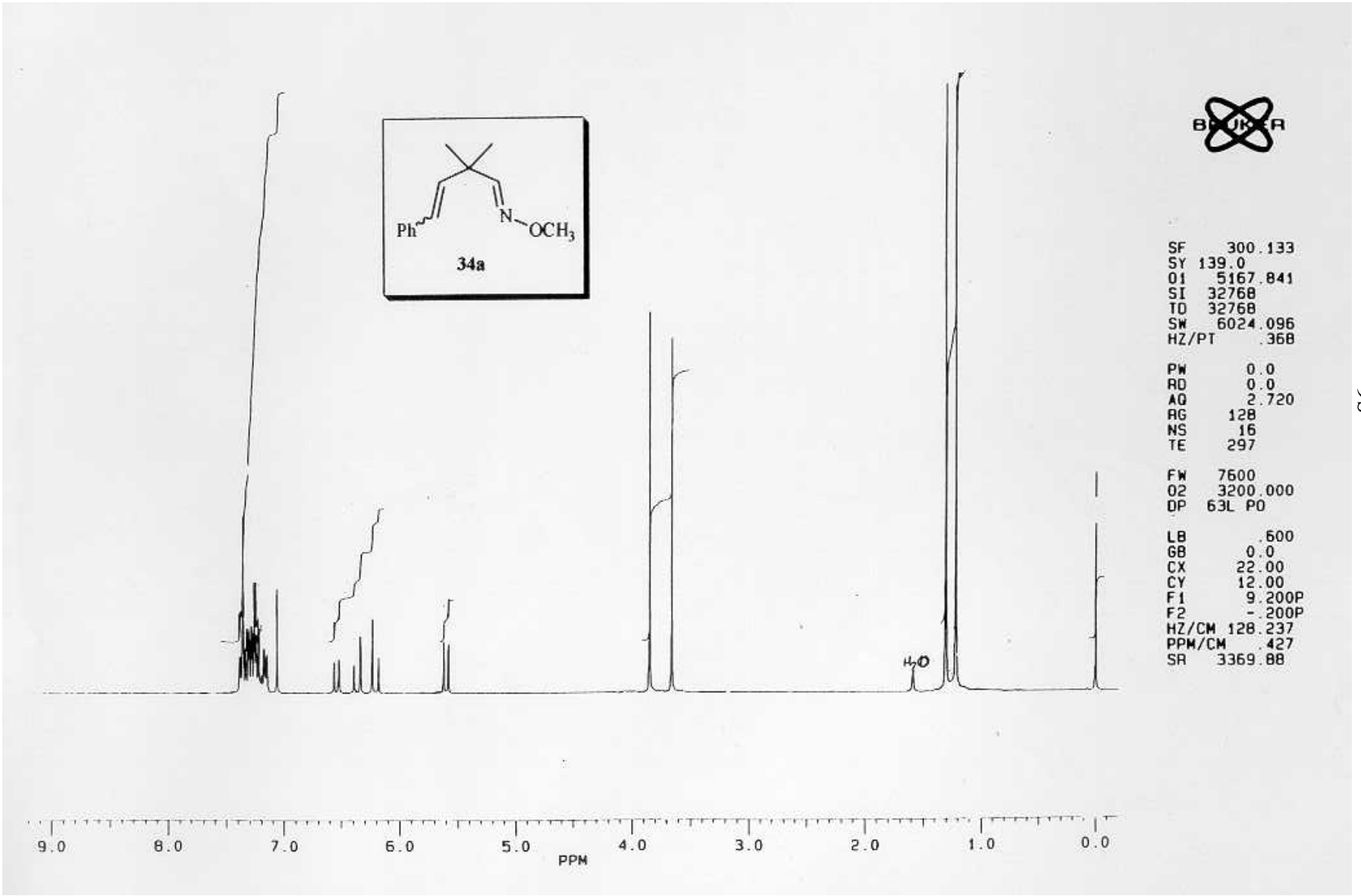
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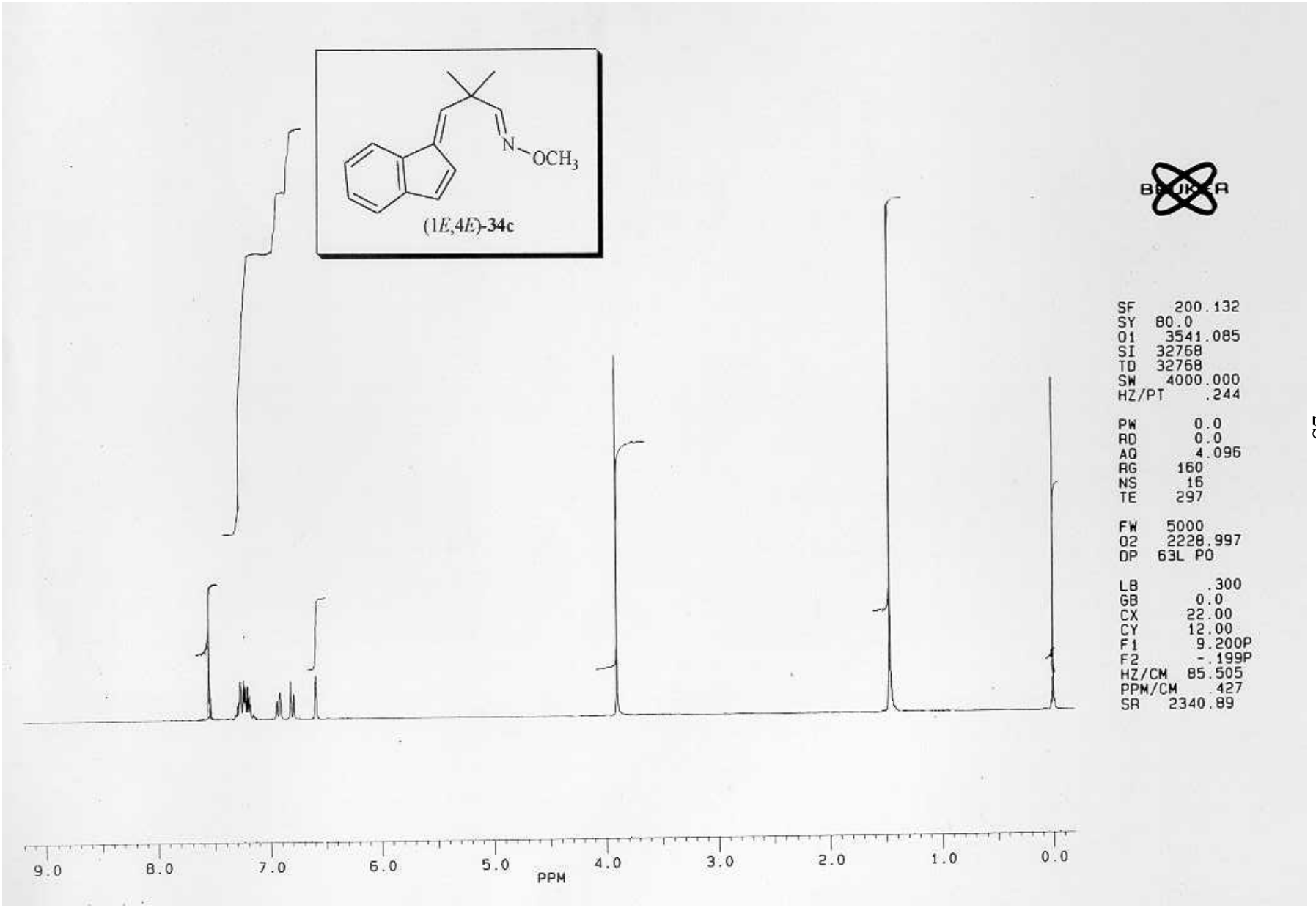
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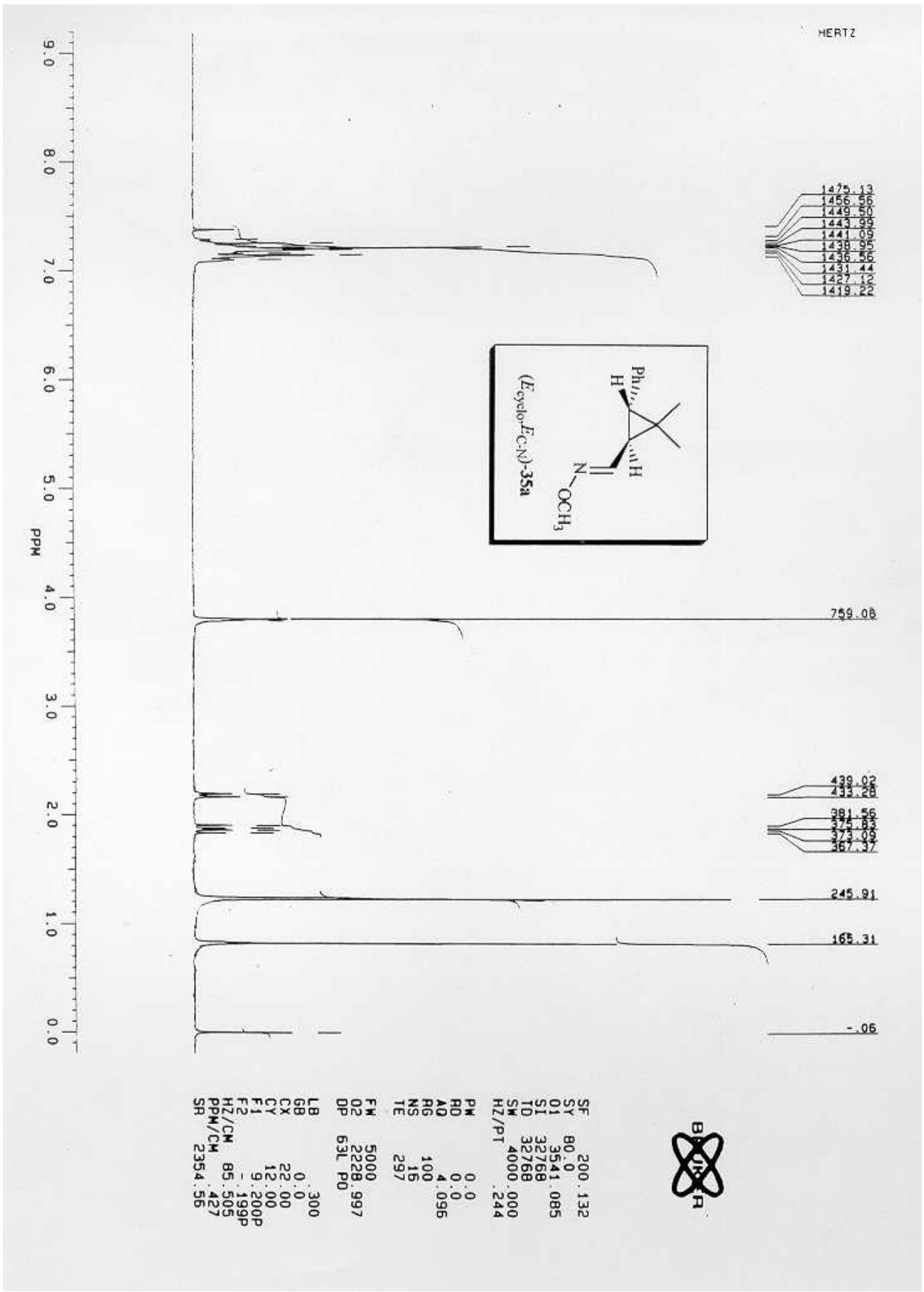
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1449.50
1443.99
1441.09
1438.95
1436.56
1431.44
1427.12
1419.22
759.08
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375.83
373.09
367.37
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-.06
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H
H
N
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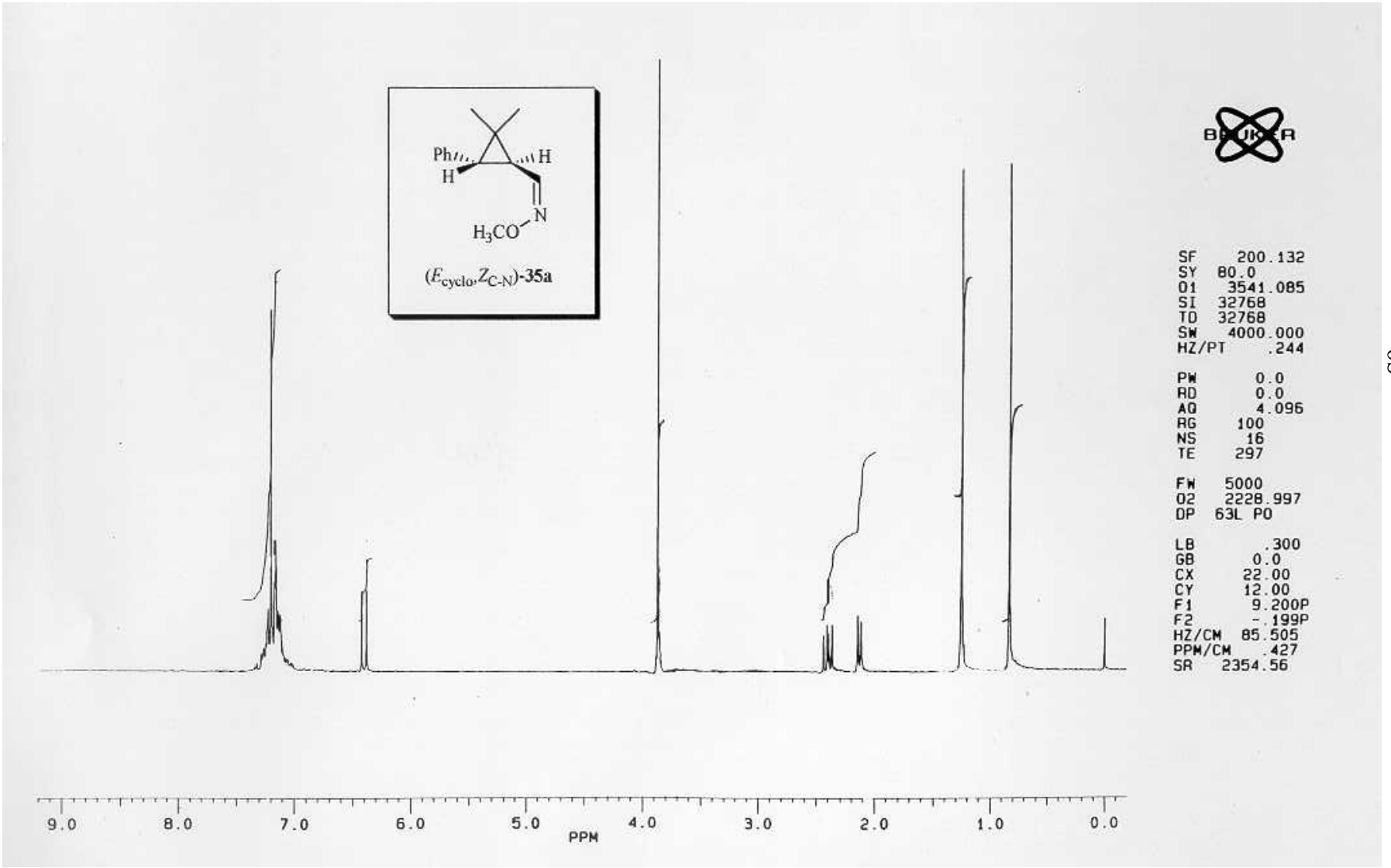
BRUKER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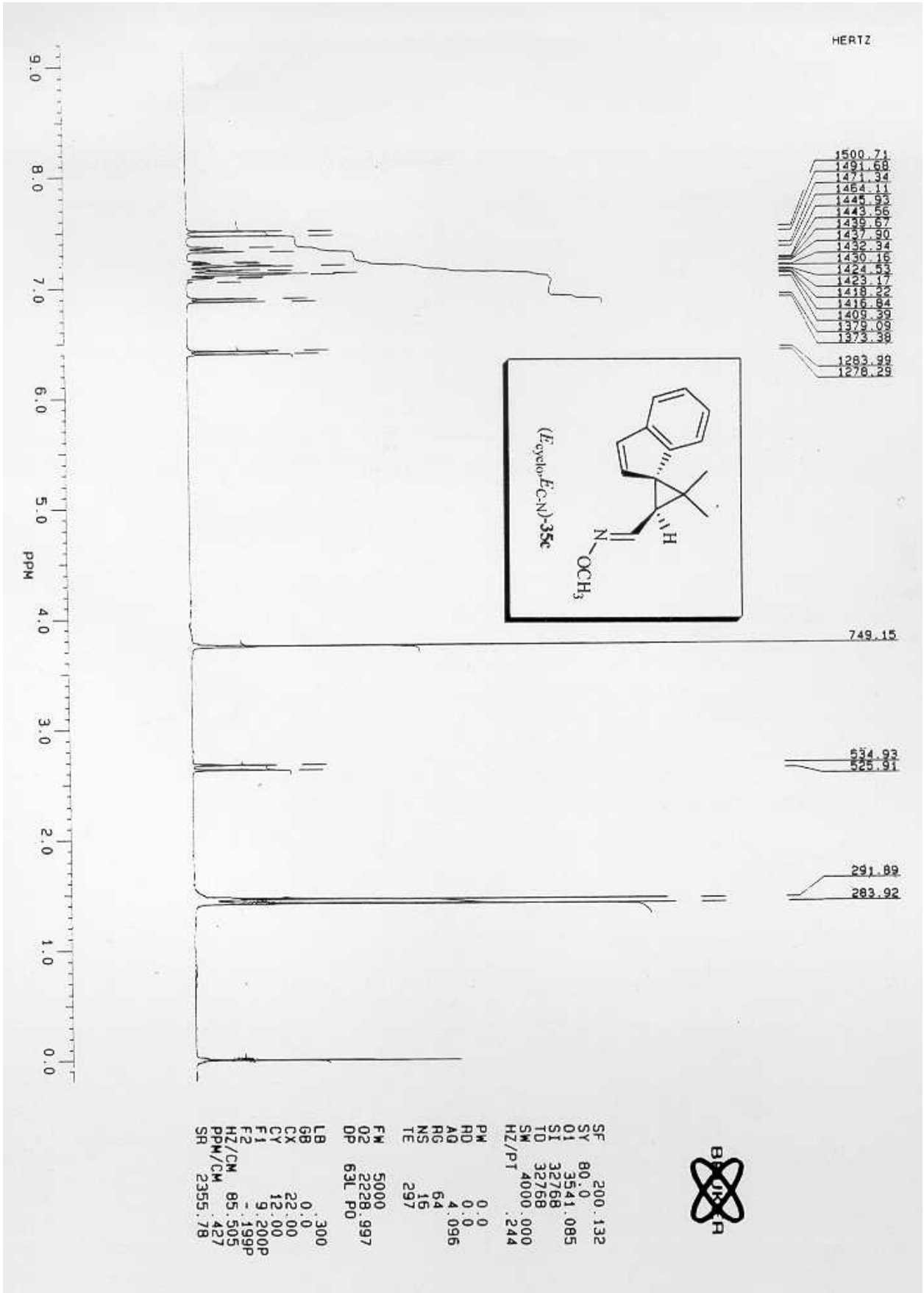
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1418.22
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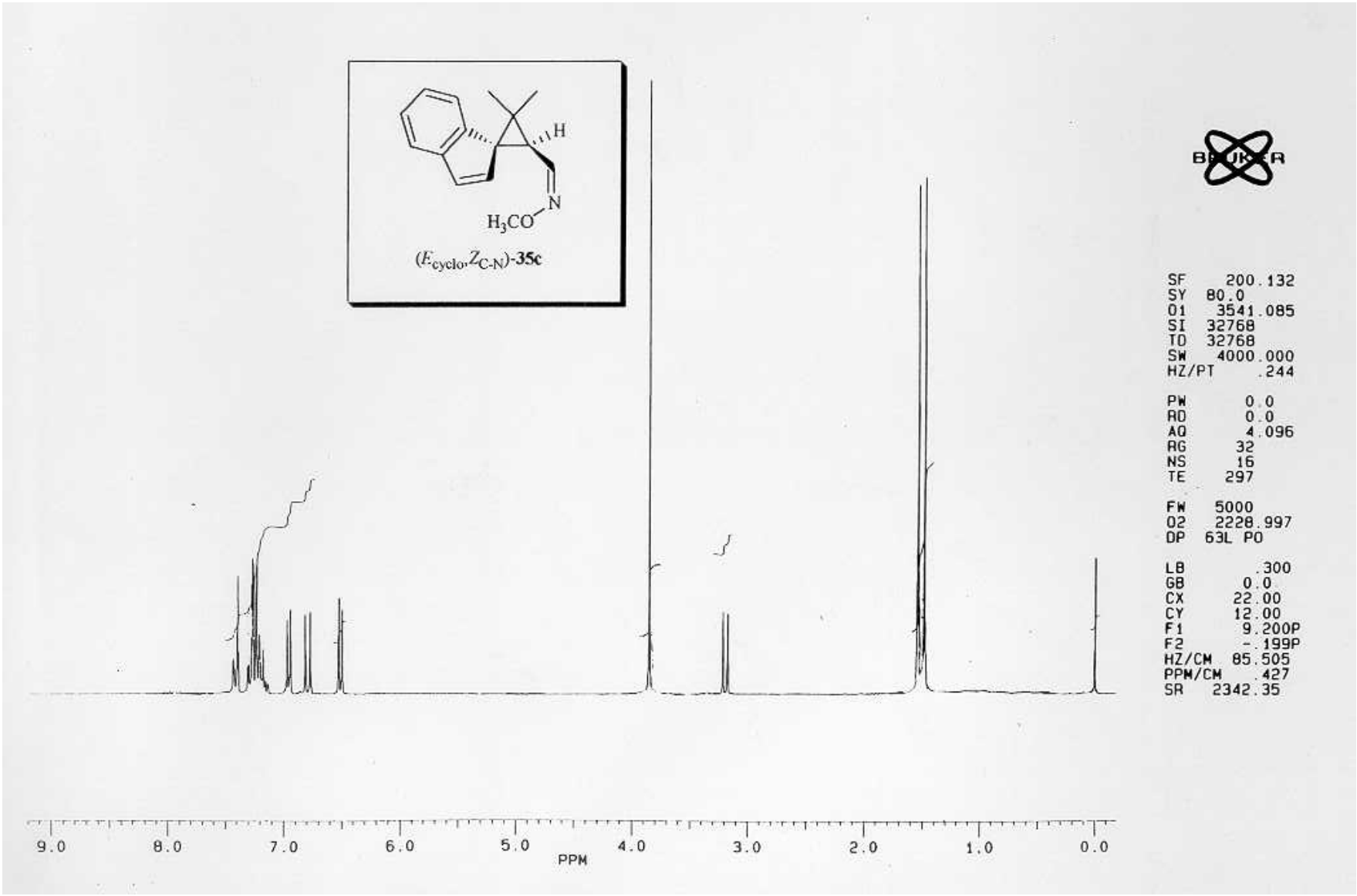
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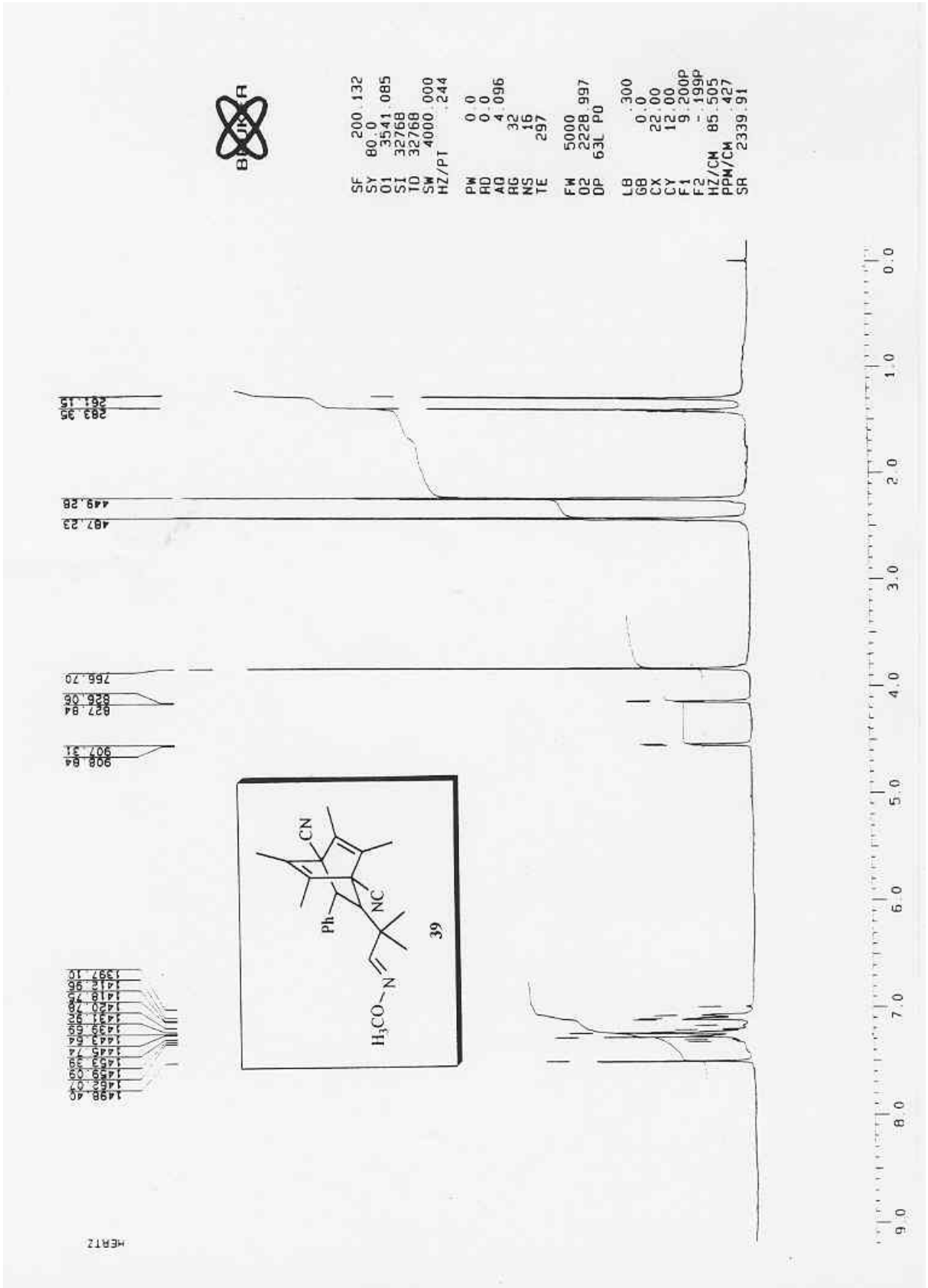
CN
Ph
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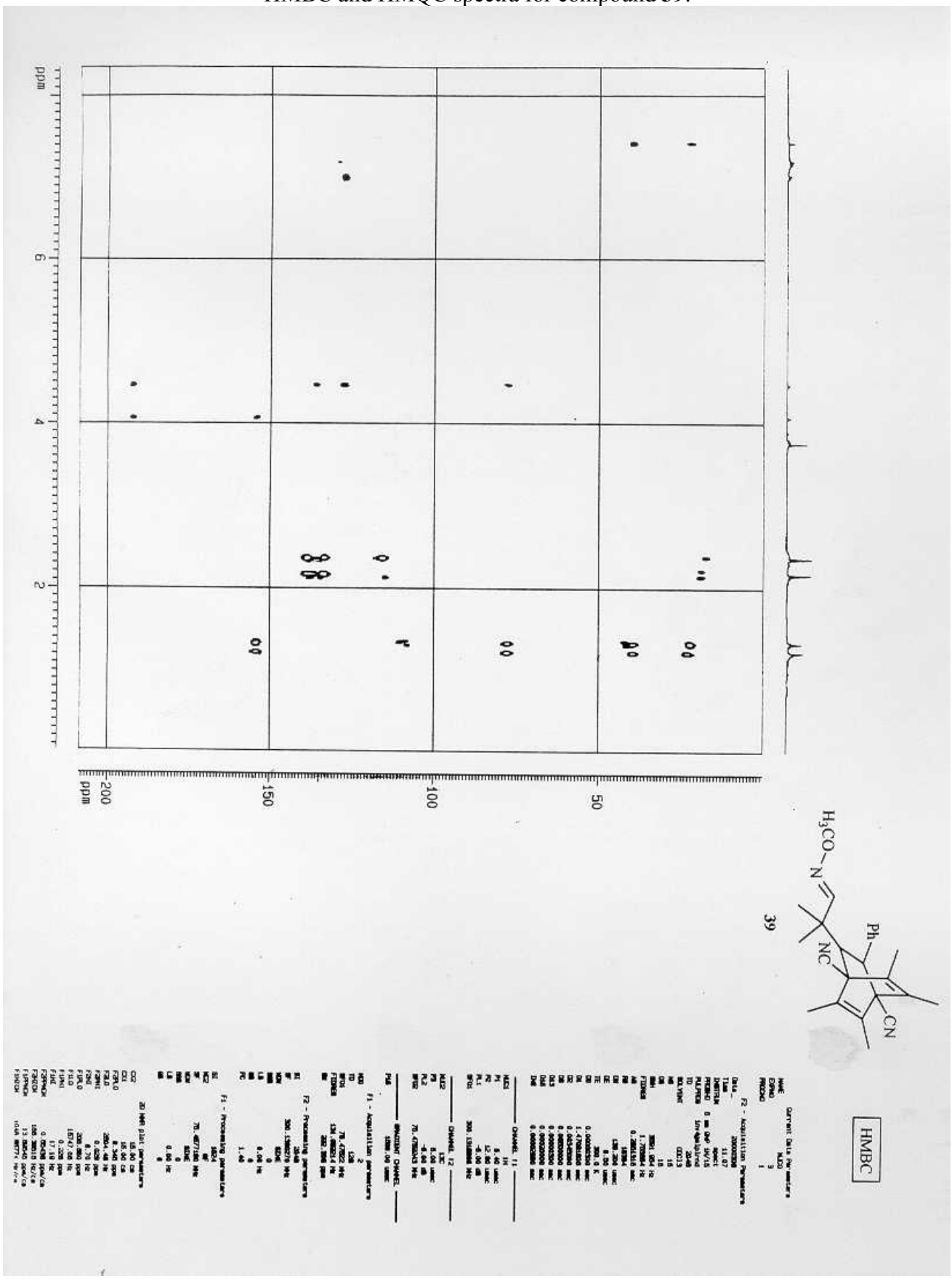
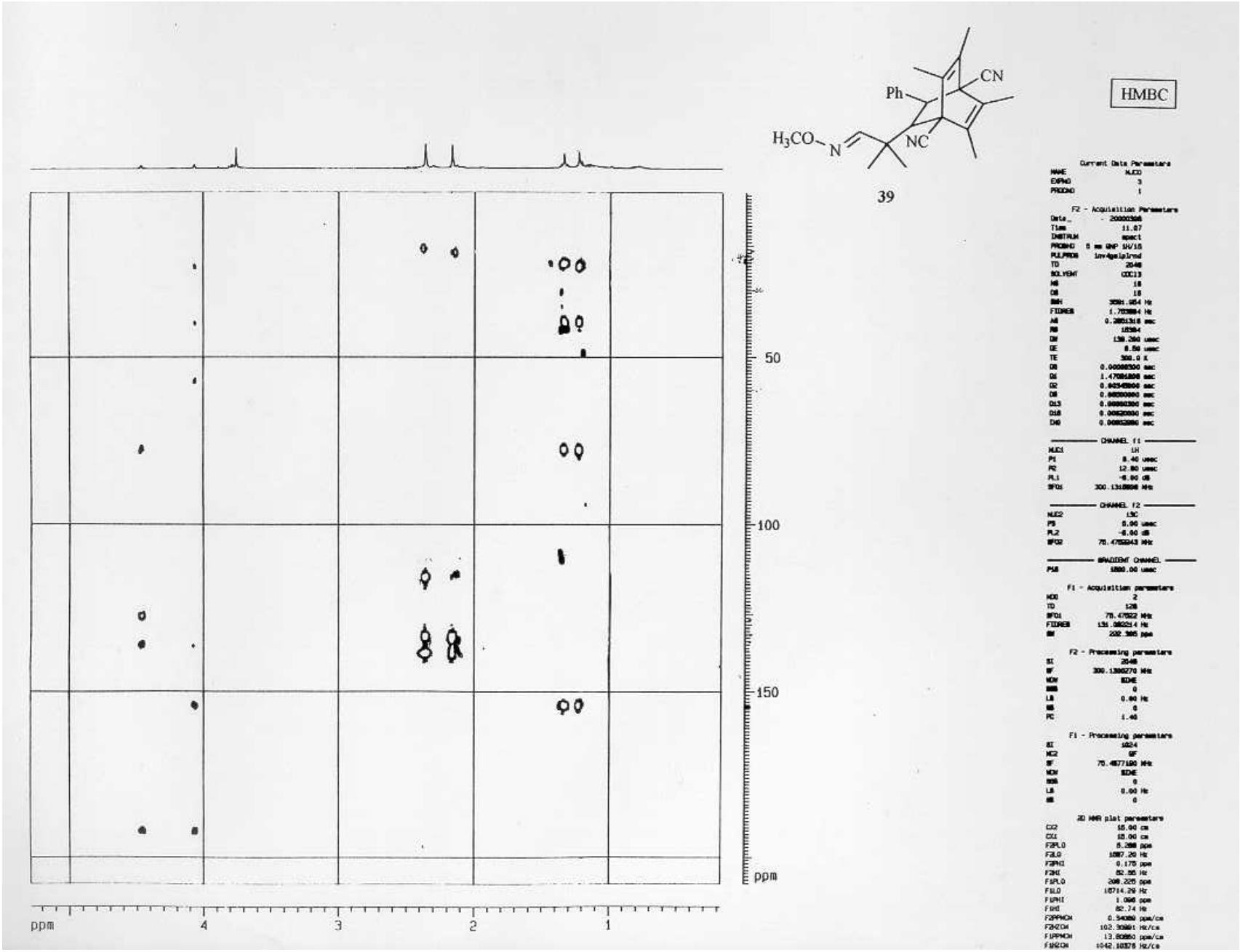
H_3CO
N
39

HMBC and HMQC spectra for compound **39**.

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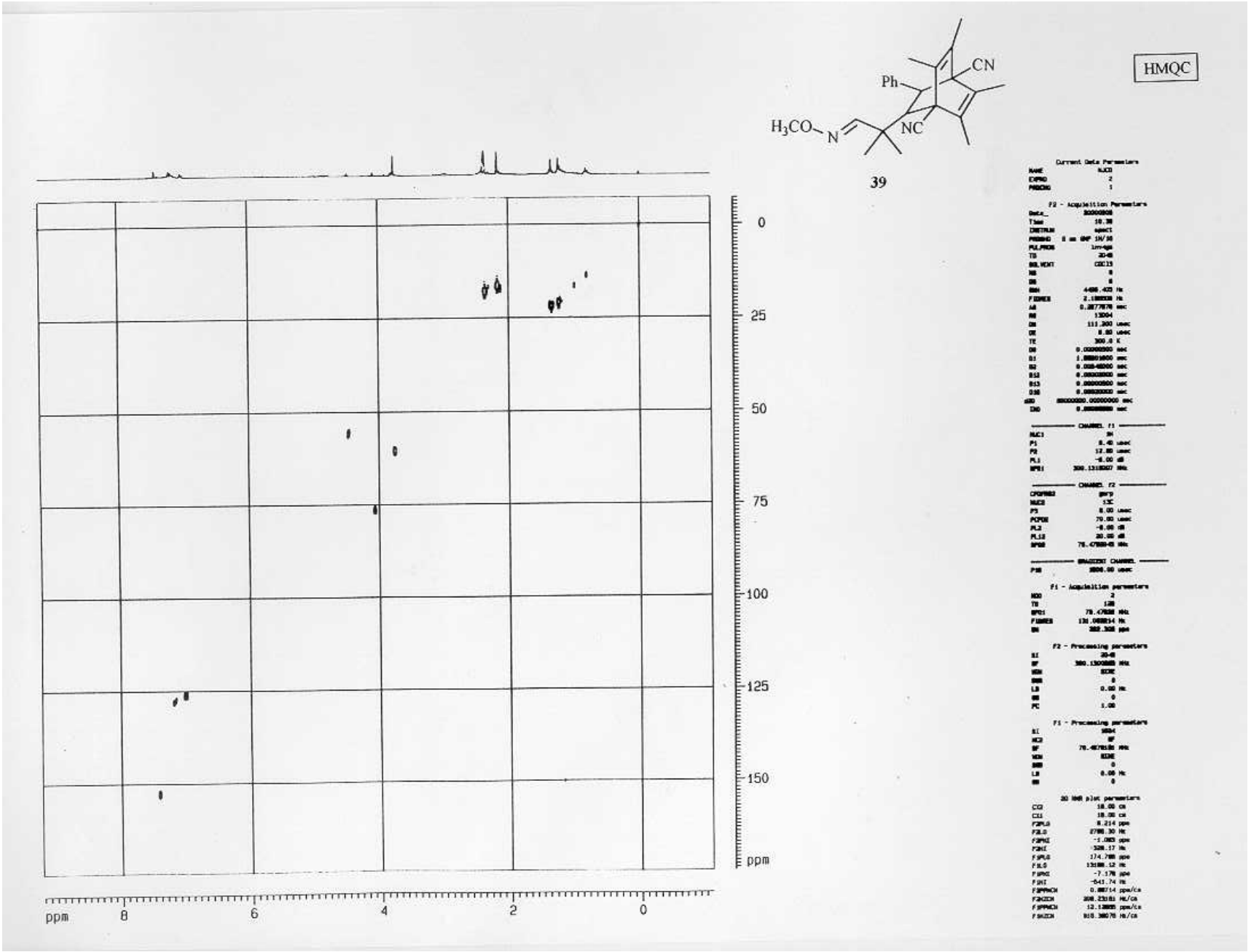
ppm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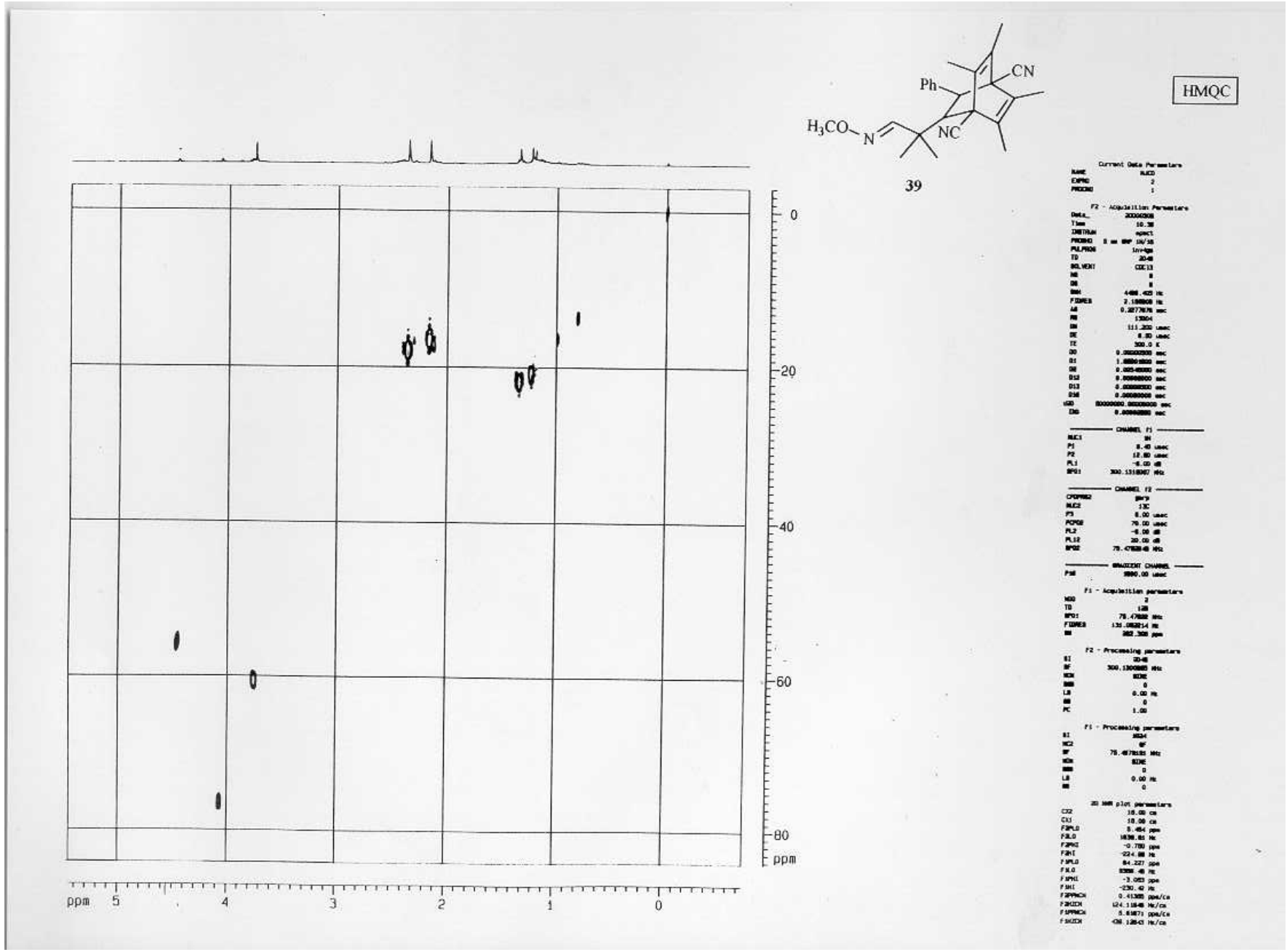
ppm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NC
H_3CO
N
39
HMQC
ppm
5
4
3
2
1
0
0
20
40
60
80
ppm

X-Ray crystallographic data for compound 36.

TABLE 1. EXPERIMENTAL DATA

CRYSTAL DATA

Empirical formula	C31 H25 N3 O
Formula weight	455.54
Crystal system, space group	Triclinic, P-1
Unit cell determination	Least-squares fit from 58 reflections (2 <α <35)
Unit cell dimensions	a = 14.516(2)A;α = 112.040(10) b = 10.9320(10)A;β = 81.04(2) c = 8.0860(10)A; γ= 99.650(10)
Volume	1166.5(2) A^3
Formula units per cell, Z,	2
Calculated density	1.297 Mg/m
Absorption coefficient	0.622 mm^{-1}
F(000)	480
Crystal size	0.22x 0.11 x 0.02 mm

DATA COLLECTION

Four circle difractometer	Seifert XRS 3000S. Bisecting geometry Graphite oriented monochromator
w-20 scans	
Theta range for data collection	3.10 to 66.82 deg.
Temperature	293(2) K
Wavelength	Cu K ,1.54180 A
Limiting indices	0<=h<=17, -12<=k<=12, -9<=l<=9
Reflections collected / unique	3913 / 3913 [R(int) = 0.0000]
Observed reflections	2971
2 starndard reflections monitored	every 90 min
Intensity variation	none

SOLUTION AND REFINEMENT

Solution	Direct methods
Refinement method	Full-matrix least-squares on F
Data / restraints / parameters	3913 / 0 / 339
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.1122
R indices (all data)	R1 = 0.0606, wR2 = 0.1285
Extinction coefficient	0.0327(18)
Largest diff. peak and hole	0.160 and -0.189 e.A
w-sheme	w=1/[o (F)+ (0.0816P)] were P=(F + 2F)/3
H- parameters	riding model
Computers and programs	VAX 6410, SIR97[1], SHELX97[2], PARTS[3], Atomic Scattering Factors from International Tables for X-Ray Crystallography

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

	x	y	z	U(eq)
N(1)	7972(1)	582(2)	-216(2)	39(1)
C(2)	8770(1)	1463(2)	605(3)	39(1)
C(3)	9368(2)	2218(2)	-573(3)	51(1)
C(4)	8711(2)	2902(2)	-1130(3)	52(1)
C(5)	7826(2)	2394(2)	-1340(3)	45(1)
C(6)	7409(1)	1126(2)	-1046(3)	41(1)
C(7)	6418(1)	1433(2)	-54(3)	38(1)
C(8)	6198(2)	2370(2)	-883(3)	43(1)
C(9)	7023(2)	2947(2)	-1582(3)	47(1)
C(10)	6995(2)	3885(3)	-2347(3)	62(1)
C(11)	6129(2)	4221(3)	-2425(4)	72(1)
C(12)	5314(2)	3645(3)	-1758(4)	68(1)
C(13)	5331(2)	2719(2)	-973(3)	56(1)
O(14)	8265(1)	-658(1)	-1462(2)	56(1)
C(15)	7671(2)	-1714(2)	-1080(4)	68(1)
C(16)	9823(2)	1185(3)	-2274(4)	73(1)
C(17)	10164(2)	3222(3)	375(4)	71(1)
C(18)	8375(1)	2309(2)	2627(3)	34(1)
C(19)	7650(1)	1341(2)	3247(2)	32(1)
C(20)	7919(2)	509(2)	3973(3)	38(1)
C(21)	7276(2)	-474(2)	4340(3)	44(1)
C(22)	6355(2)	-610(2)	4001(3)	46(1)
C(23)	6075(2)	232(2)	3303(3)	42(1)
C(24)	6714(1)	1204(2)	2898(2)	32(1)
C(25)	6408(1)	2096(2)	2058(2)	32(1)
C(26)	6993(1)	3457(2)	2646(2)	31(1)
C(27)	7934(1)	3562(2)	2921(2)	33(1)
C(28)	8433(2)	4823(2)	3557(3)	43(1)
C(29)	8029(2)	5951(2)	3843(3)	51(1)
C(30)	7107(2)	5835(2)	3522(3)	53(1)
C(31)	6593(1)	4600(2)	2944(3)	42(1)
C(32)	9169(1)	2681(2)	3730(3)	45(1)
N(33)	9781(1)	2944(2)	4579(3)	68(1)
C(34)	5413(1)	2272(2)	2714(3)	42(1)
N(35)	4630(1)	2353(2)	3145(3)	67(1)

Table 2. GEOMETRICAL FEATURES

a) Bond lengths [A]

N(1)-O(14)	1.4388(19)
N(1)-C(2)	1.448(3)
N(1)-C(6)	1.450(2)
C(2)-C(3)	1.561(3)
C(2)-C(18)	1.615(3)
C(3)-C(4)	1.515(3)
C(3)-C(17)	1.532(4)
C(3)-C(16)	1.551(3)
C(4)-C(5)	1.321(3)
C(5)-C(9)	1.470(3)
C(5)-C(6)	1.505(3)
C(6)-C(7)	1.558(3)
C(7)-C(8)	1.514(3)
C(7)-C(25)	1.584(3)
C(8)-C(13)	1.395(3)
C(8)-C(9)	1.398(3)
C(9)-C(10)	1.390(3)
C(10)-C(11)	1.384(4)
C(11)-C(12)	1.376(4)
C(12)-C(13)	1.387(4)
O(14)-C(15)	1.422(3)
C(18)-C(32)	1.476(3)
C(18)-C(19)	1.529(2)
C(18)-C(27)	1.533(2)
C(19)-C(20)	1.385(3)
C(19)-C(24)	1.403(2)
C(20)-C(21)	1.390(3)
C(21)-C(22)	1.379(3)
C(22)-C(23)	1.384(3)
C(23)-C(24)	1.391(3)
C(24)-C(25)	1.531(2)
C(25)-C(34)	1.478(3)
C(25)-C(26)	1.527(2)
C(26)-C(31)	1.389(3)
C(26)-C(27)	1.396(2)
C(27)-C(28)	1.392(3)
C(28)-C(29)	1.380(3)
C(29)-C(30)	1.379(3)
C(30)-C(31)	1.377(3)
C(32)-N(33)	1.140(3)
C(34)-N(35)	1.144(3)

b) Bond angles [ ]

O(14)-N(1)-C(2)	110.24(14)
O(14)-N(1)-C(6)	110.74(15)
C(2)-N(1)-C(6)	115.83(16)
N(1)-C(2)-C(3)	114.11(17)
N(1)-C(2)-C(18)	105.85(14)
C(3)-C(2)-C(18)	118.85(16)
C(4)-C(3)-C(17)	110.7(2)
C(4)-C(3)-C(16)	109.1(2)
C(17)-C(3)-C(16)	107.4(2)
C(4)-C(3)-C(2)	108.01(17)

C(17)-C(3)-C(2)	113.3(2)
C(16)-C(3)-C(2)	108.32(18)
C(5)-C(4)-C(3)	120.9(2)
C(4)-C(5)-C(9)	131.4(2)
C(4)-C(5)-C(6)	122.95(19)
C(9)-C(5)-C(6)	104.89(18)
N(1)-C(6)-C(5)	116.93(18)
N(1)-C(6)-C(7)	115.70(16)
C(5)-C(6)-C(7)	103.66(16)
C(8)-C(7)-C(6)	100.22(16)
C(8)-C(7)-C(25)	112.40(15)
C(6)-C(7)-C(25)	113.64(15)
C(13)-C(8)-C(9)	120.0(2)
C(13)-C(8)-C(7)	129.3(2)
C(9)-C(8)-C(7)	110.72(17)
C(10)-C(9)-C(8)	120.9(2)
C(10)-C(9)-C(5)	130.3(2)
C(8)-C(9)-C(5)	108.82(18)
C(11)-C(10)-C(9)	118.4(3)
C(12)-C(11)-C(10)	120.9(3)
C(11)-C(12)-C(13)	121.4(2)
C(12)-C(13)-C(8)	118.4(3)
C(15)-O(14)-N(1)	108.52(16)
C(32)-C(18)-C(19)	108.08(15)
C(32)-C(18)-C(27)	108.86(16)
C(19)-C(18)-C(27)	109.42(14)
C(32)-C(18)-C(2)	106.80(15)
C(19)-C(18)-C(2)	105.70(14)
C(27)-C(18)-C(2)	117.60(15)
C(20)-C(19)-C(24)	119.72(17)
C(20)-C(19)-C(18)	121.04(16)
C(24)-C(19)-C(18)	118.91(16)
C(19)-C(20)-C(21)	120.83(19)
C(22)-C(21)-C(20)	119.56(19)
C(21)-C(22)-C(23)	120.07(19)
C(22)-C(23)-C(24)	121.05(19)
C(23)-C(24)-C(19)	118.75(17)
C(23)-C(24)-C(25)	120.82(16)
C(19)-C(24)-C(25)	120.43(15)
C(34)-C(25)-C(26)	108.68(15)
C(34)-C(25)-C(24)	107.74(15)
C(26)-C(25)-C(24)	110.16(14)
C(34)-C(25)-C(7)	104.54(15)
C(26)-C(25)-C(7)	112.38(15)
C(24)-C(25)-C(7)	113.00(14)
C(31)-C(26)-C(27)	119.47(16)
C(31)-C(26)-C(25)	120.56(16)
C(27)-C(26)-C(25)	119.96(15)
C(28)-C(27)-C(26)	118.62(17)
C(28)-C(27)-C(18)	121.51(16)
C(26)-C(27)-C(18)	119.77(15)
C(29)-C(28)-C(27)	121.35(19)
C(30)-C(29)-C(28)	119.61(19)
C(31)-C(30)-C(29)	119.9(2)
C(30)-C(31)-C(26)	121.00(19)
N(33)-C(32)-C(18)	178.7(2)
N(35)-C(34)-C(25)	176.5(2)

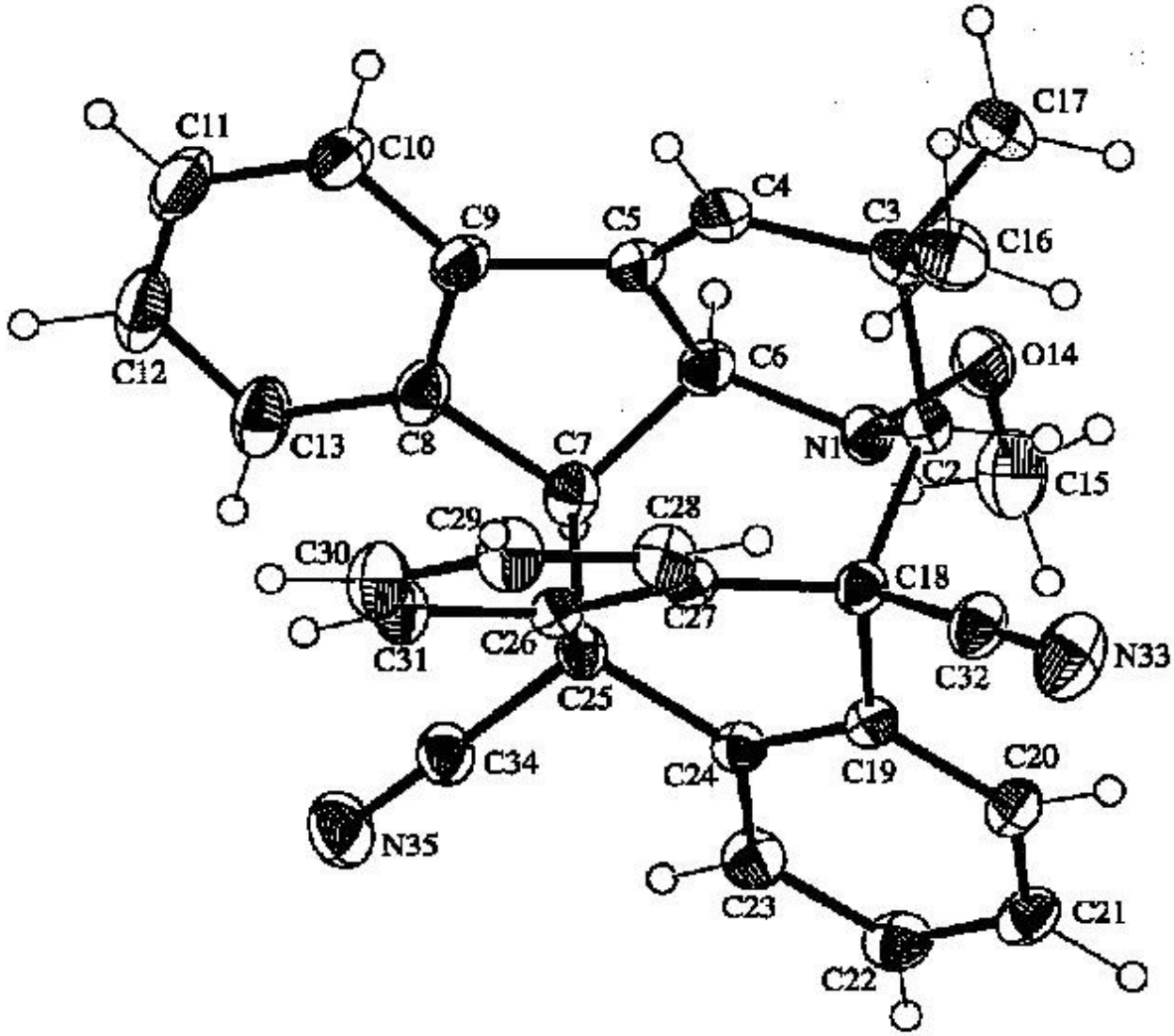
Table 4. Anisotropic displacement parameters (A^2 x 10^3) for fin.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	48(1)	34(1)	34(1)	8(1)	-2(1)	16(1)
C(2)	34(1)	44(1)	43(1)	20(1)	3(1)	12(1)
C(3)	40(1)	63(1)	58(1)	35(1)	14(1)	17(1)
C(4)	55(1)	59(1)	52(1)	35(1)	13(1)	18(1)
C(5)	53(1)	52(1)	35(1)	22(1)	5(1)	19(1)
C(6)	52(1)	42(1)	30(1)	11(1)	-5(1)	13(1)
C(7)	41(1)	35(1)	39(1)	9(1)	-13(1)	5(1)
C(8)	55(1)	41(1)	36(1)	9(1)	-16(1)	12(1)
C(9)	65(1)	51(1)	33(1)	17(1)	-3(1)	21(1)
C(10)	85(2)	67(2)	49(1)	32(1)	3(1)	30(1)
C(11)	106(2)	76(2)	54(2)	31(1)	-11(2)	43(2)
C(12)	82(2)	70(2)	63(2)	17(1)	-29(1)	33(2)
C(13)	60(1)	55(1)	56(2)	12(1)	-27(1)	14(1)
O(14)	73(1)	44(1)	49(1)	7(1)	3(1)	27(1)
C(15)	79(2)	39(1)	83(2)	12(1)	-16(2)	10(1)
C(16)	68(2)	95(2)	71(2)	47(2)	34(1)	43(2)
C(17)	43(1)	86(2)	95(2)	54(2)	7(1)	0(1)
C(18)	30(1)	37(1)	38(1)	17(1)	-6(1)	2(1)
C(19)	35(1)	31(1)	30(1)	11(1)	-4(1)	3(1)
C(20)	49(1)	33(1)	34(1)	12(1)	-8(1)	7(1)
C(21)	65(1)	32(1)	37(1)	14(1)	-7(1)	7(1)
C(22)	56(1)	35(1)	49(1)	21(1)	2(1)	0(1)
C(23)	39(1)	38(1)	49(1)	18(1)	-3(1)	-2(1)
C(24)	35(1)	29(1)	32(1)	11(1)	-2(1)	2(1)
C(25)	26(1)	33(1)	37(1)	12(1)	-5(1)	2(1)
C(26)	33(1)	31(1)	31(1)	11(1)	-4(1)	2(1)
C(27)	33(1)	33(1)	33(1)	13(1)	-4(1)	2(1)
C(28)	40(1)	37(1)	51(1)	16(1)	-9(1)	-5(1)
C(29)	53(1)	32(1)	64(2)	15(1)	-12(1)	-3(1)
C(30)	60(1)	30(1)	69(2)	15(1)	-12(1)	6(1)
C(31)	40(1)	35(1)	52(1)	14(1)	-8(1)	6(1)
C(32)	39(1)	46(1)	57(1)	25(1)	-13(1)	-1(1)
N(33)	50(1)	74(1)	92(2)	42(1)	-35(1)	-12(1)
C(34)	34(1)	43(1)	52(1)	21(1)	-4(1)	4(1)
N(35)	39(1)	80(1)	91(2)	43(1)	3(1)	11(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for fin.

	x	y	z	U(eq)
H(2)	9193(9)	876(13)	726(4)	47
H(4)	8954(6)	3760(20)	-1344(6)	62
H(6)	7303(3)	415(15)	-2300(30)	49
H(7)	5968(10)	613(18)	-378(7)	46
H(10)	7591(17)	4309(12)	-2833(14)	75
H(11)	6098(2)	4840(20)	-2932(18)	87
H(12)	4673(18)	3909(8)	-1844(4)	82
H(13)	4731(16)	2308(11)	-480(14)	67
H(15A)	7685(10)	-1597(11)	210(20)	103
H(15B)	7898(9)	-2588(15)	-1880(20)	103
H(15C)	7008(11)	-1706(12)	-1300(30)	103
H(16A)	9327(9)	500(16)	-2899(18)	110
H(16B)	10271(13)	756(16)	-1922(7)	110
H(16C)	10163(13)	1638(8)	-3087(19)	110
H(17A)	10566(11)	3583(16)	-488(16)	106
H(17B)	10548(11)	2773(9)	840(20)	106
H(17C)	9894(5)	3959(16)	1390(20)	106
H(20)	8596(15)	618(3)	4241(6)	46
H(21)	7481(5)	-1082(14)	4849(12)	52
H(22)	5910(12)	-1284(18)	4247(7)	56
H(23)	5422(16)	141(3)	3093(6)	51
H(28)	9083(16)	4911(3)	3805(7)	52
H(29)	8400(9)	6840(20)	4278(11)	61
H(30)	6825(8)	6610(20)	3701(6)	64
H(31)	5914(15)	4523(3)	2732(6)	50

ORTEP Diagram



Cell-packing Diagram