Asymmetric Reactions of 2-Methoxy-1,4-benzoquinones with Styrenyl Systems: Enantioselective Syntheses of 8-Aryl-3-methoxybicyclo[4.2.0]oct-3-en-2,5-diones, 7-Aryl-3-hydroxybicyclo[3.2.1]oct-3-en-2,8-diones, 2-Aryl-6-methoxy-2,3-dihydrobenzofuran-5-ols and Pterocarpans

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SUPPORTING INFORMATION

IR and mass spectral data:

(+)-**12**: IR (CH_2Cl_2) 3438, 1775, 1681; EIMS: *m/z* (relative intensity) 336 ($(M+2)^+$, 3), 334 (M^+, 3), 132 (100), 117 (61), 115 (34), 91 (21).

allyl ether of **6a**: IR ($CHCl_3$) 2945, 2920, 2860, 1615, 1605, 1590, 1485, 1460, 1440, 1410, 1370, 1325, 1250, 1160, 1110, 1020, 980, 930, 890, 850; UV λ (ε_{max}) 231 (11837), 287 (5178), 297 (5167); EIMS *m/z* (relative intensity) 357 (M^+, 15), 356 (60), 316 (10), 315 (30), 284 (15), 283 (50), 268 (10), 255 (15), 252 (20), 151 (10), 69 (20).

(+)-**16**: IR ($CHCl_3$) 3535, 3030, 2945, 2920, 2830, 1620, 1600, 1455, 1430, 1325, 1245, 1150, 1135, 1105, 1020, 1000, 930, 850, 820; UV λ (ε_{max}) 241 (8383), 288 (5819), 304 (6340); EIMS *m/z* (relative intensity) 357 (M^+, 20), 356 (85), 341 (15), 205 (25), 203 (30), 192 (75), 187 (25), 173 (75), 165 (25), 151 (60), 115 (20), 91 (20), 84 (50), 69 (25).

(-)-**24**: IR (CH_2Cl_2) 2944, 2855, 1694, 1655, 1604, 1513, 1463, 1365, 1192, 1118, 1068, 1035, 1006, 857, 833; EIMS: *m/z* (relative intensity) 312 (M^+, 2), 174 (100), 173 (33), 143 (24), 69 (24).

(-)-**26**: IR (CH_2Cl_2) 2946, 2848, 1693, 1654, 1603, 1513, 1462, 1366, 1224, 1184, 1118, 1068, 1035, 1007, 858, 834; EIMS: *m/z* (relative intensity) 326 (M^+, 2), 188 (100), 160 (30), 159 (24), 69 (23), 49 (28).

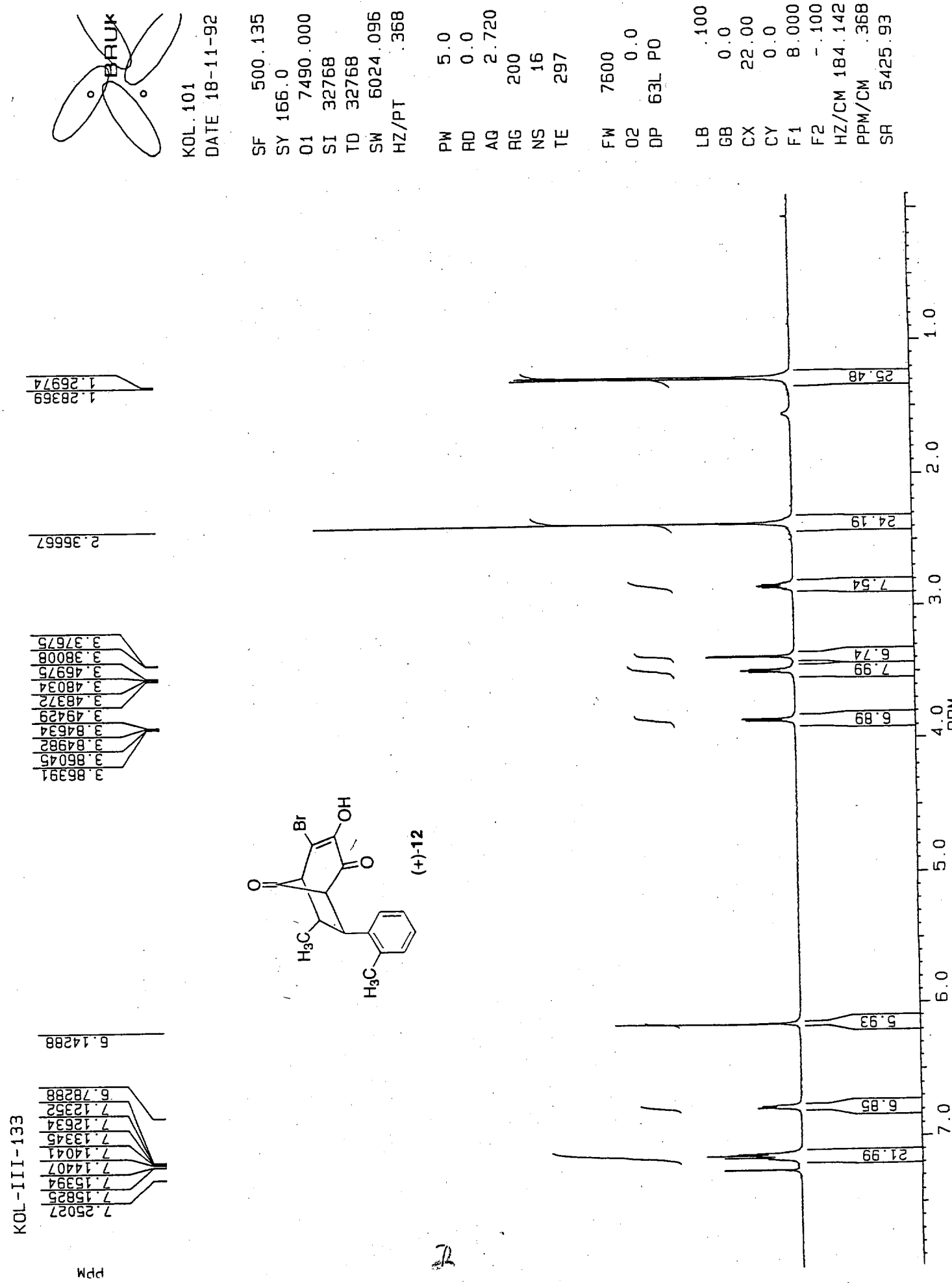
(-)-**29**: IR (CH_2Cl_2) 2930, 1694, 1660, 1601, 1513, 1459, 1358, 1252, 1162, 799; EIMS: *m/z* (relative intensity) 340 (M^+, 2), 202 (71), 174 (33), 86 (28), 84 (47), 51 (26), 49 (100).

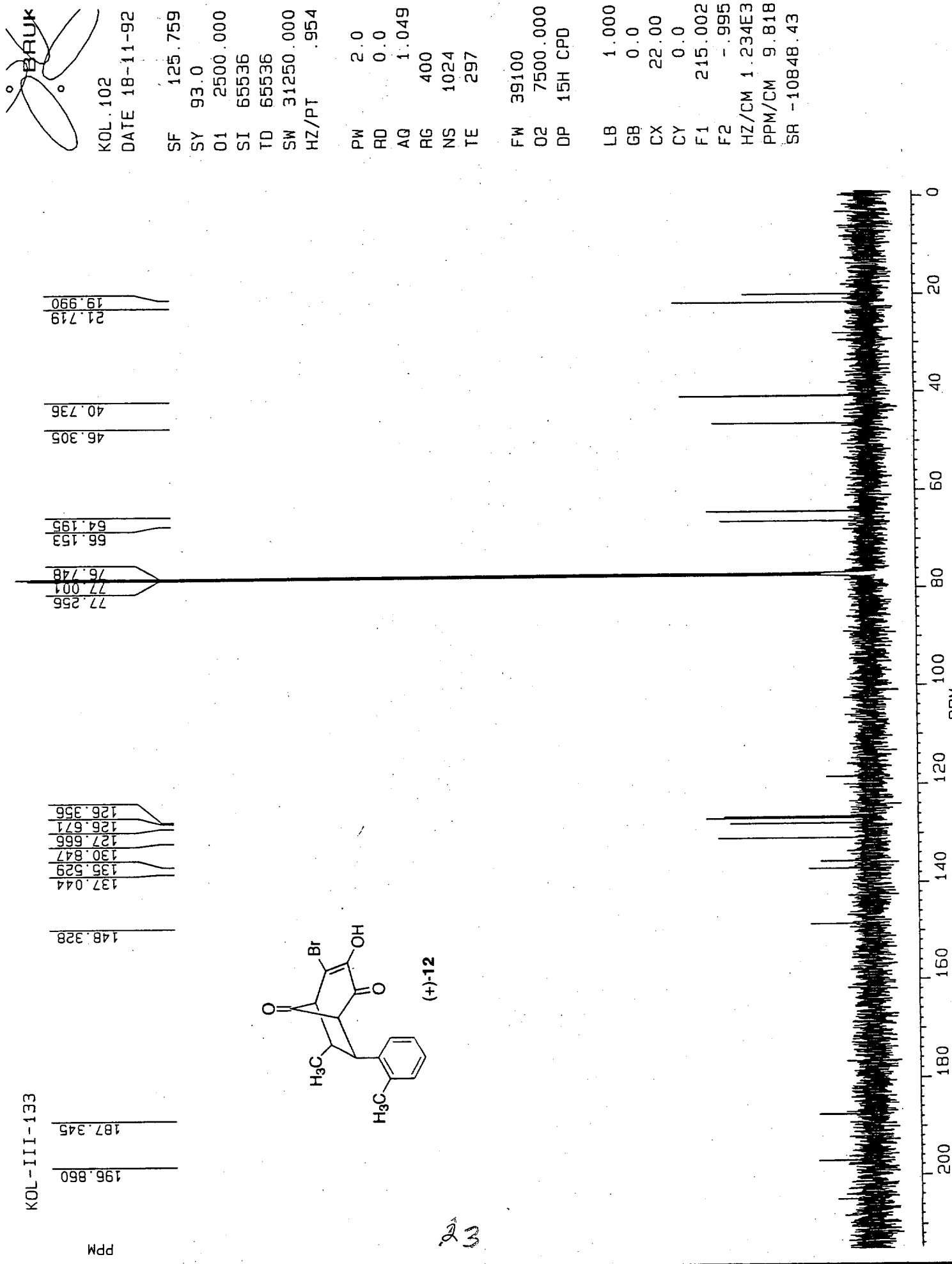
(3a*R*,3b*R*,7*S*,7a*R*,7b*S*)-7-hydroxy-6-methoxy-7b-(4-methoxyphenyl)-1,2,3, 3a,3b,7,7a,7b-octahydro-cyclopenta[3,4]cyclobuta-[1,2]benzen-4-one: IR ($CHCl_3$) 3432, 2989, 2901, 1621, 1510, 1459, 1367, 1297, 1111, 1002, 948, 871; EIMS *m/z* (relative intensity) 314 (M^+, 0.2), 198 (3), 174 (100), 159 (13), 143 (18), 84 (19), 49 (31).

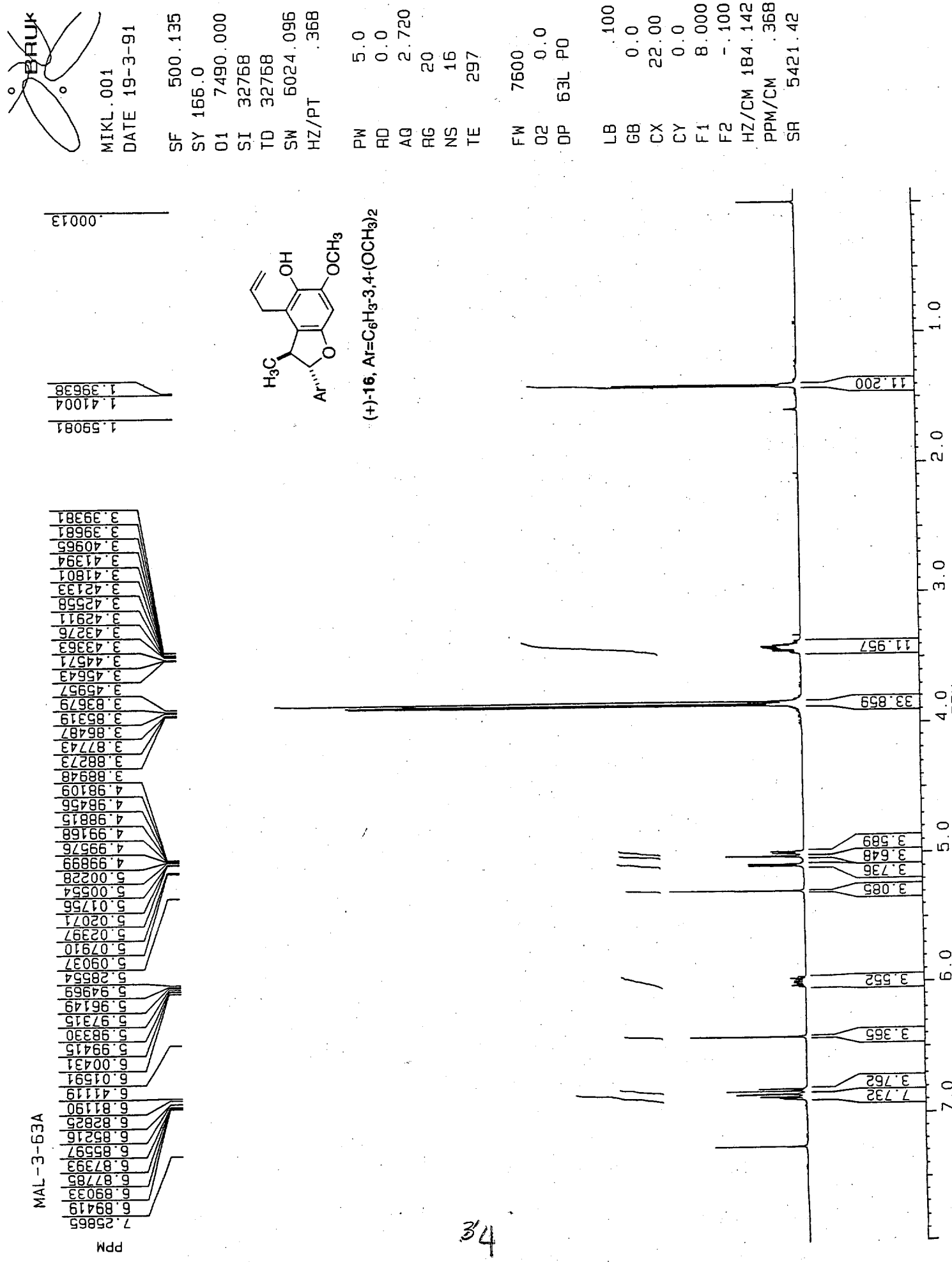
(4*S*,4a*R*,4b*R*,9a*S*,9b*R*)-4-hydroxy-3-methoxy-4b-[4-methoxyphenyl]-4,4a, 4b,5,6,7,8,9,9a,9b-decahydro-benzo[3,4]cyclobuta[1,2]cyclohepten-1-one: IR ($CHCl_3$) 3541, 2929, 2854, 1646, 1611, 1510, 1457, 1401, 1372, 1302, 1170, 997, 832.

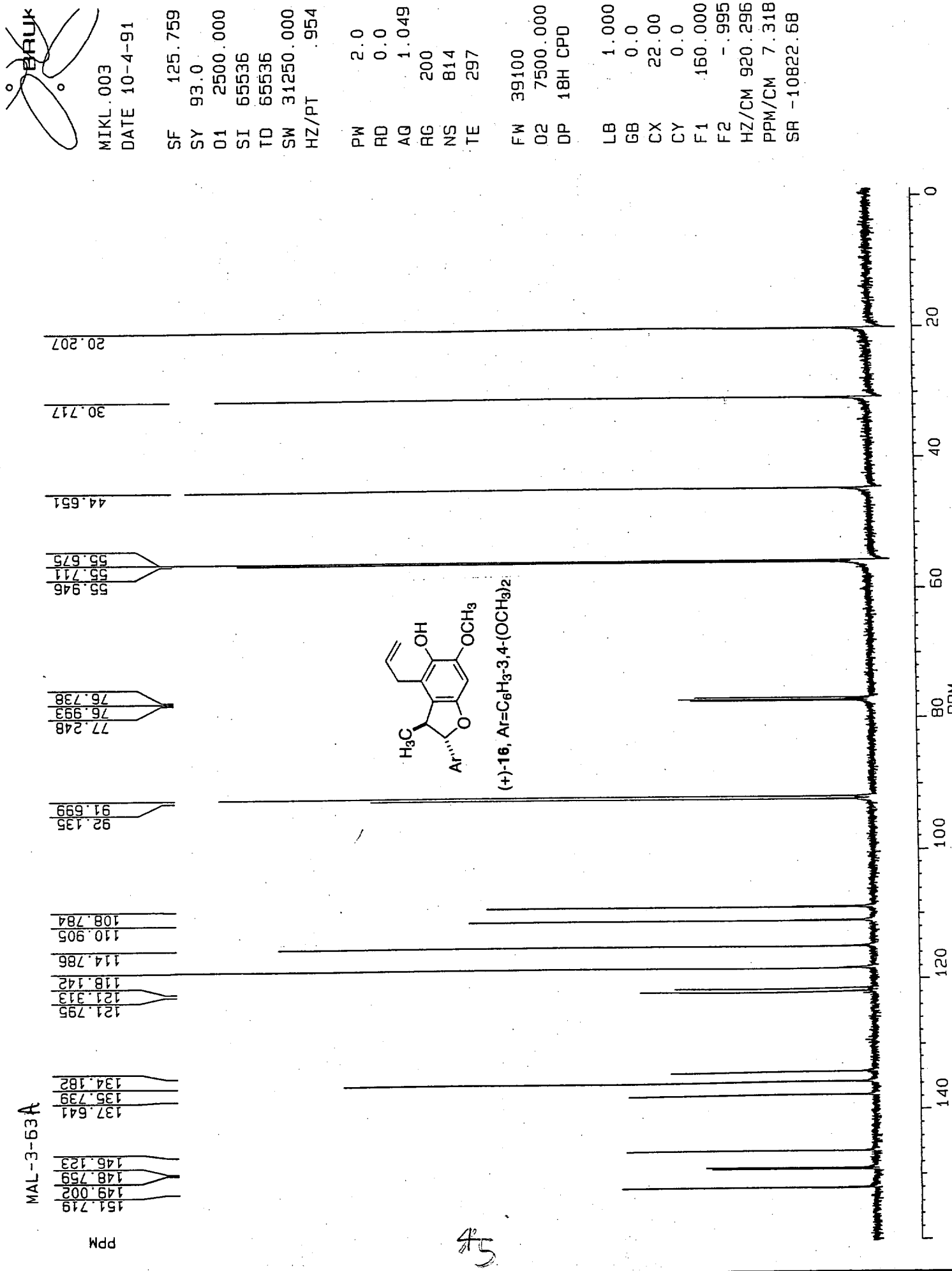
(-)-**32**: IR ($CHCl_3$) 3428, 2931, 2856, 1737, 1638, 1606, 1513, 1459, 1397, 1304, 1247, 1180, 1113, 833; FAB *m/z* (relative intensity) 540 (M^+, 100), 542 (M^++2, 100).

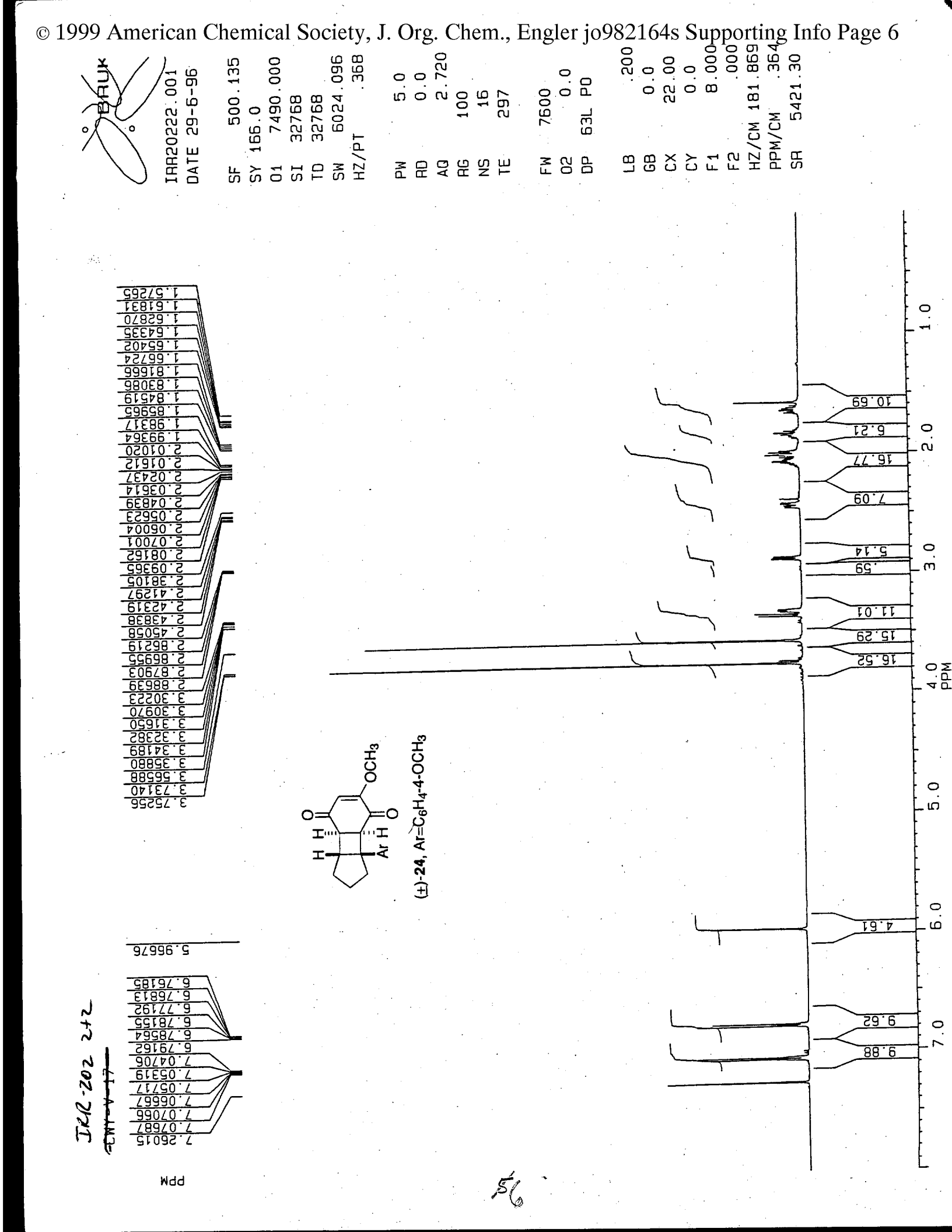
(+)-**33**: IR (CH_2Cl_2) 2938, 1738, 1604, 1502, 1336, 1194, 1169, 1137, 1098, 1069, 1033, 1011, 944, 837; EIMS: *m/z* (relative intensity) 496 (M^++2, 53), 494 (M^+, 56), 311 (29), 185 (100), 183 (93), 157 (48), 155 (48), 115 (32), 91 (33), 76 (61), 75 (43), 69 (33), 50 (34), 49 (35).











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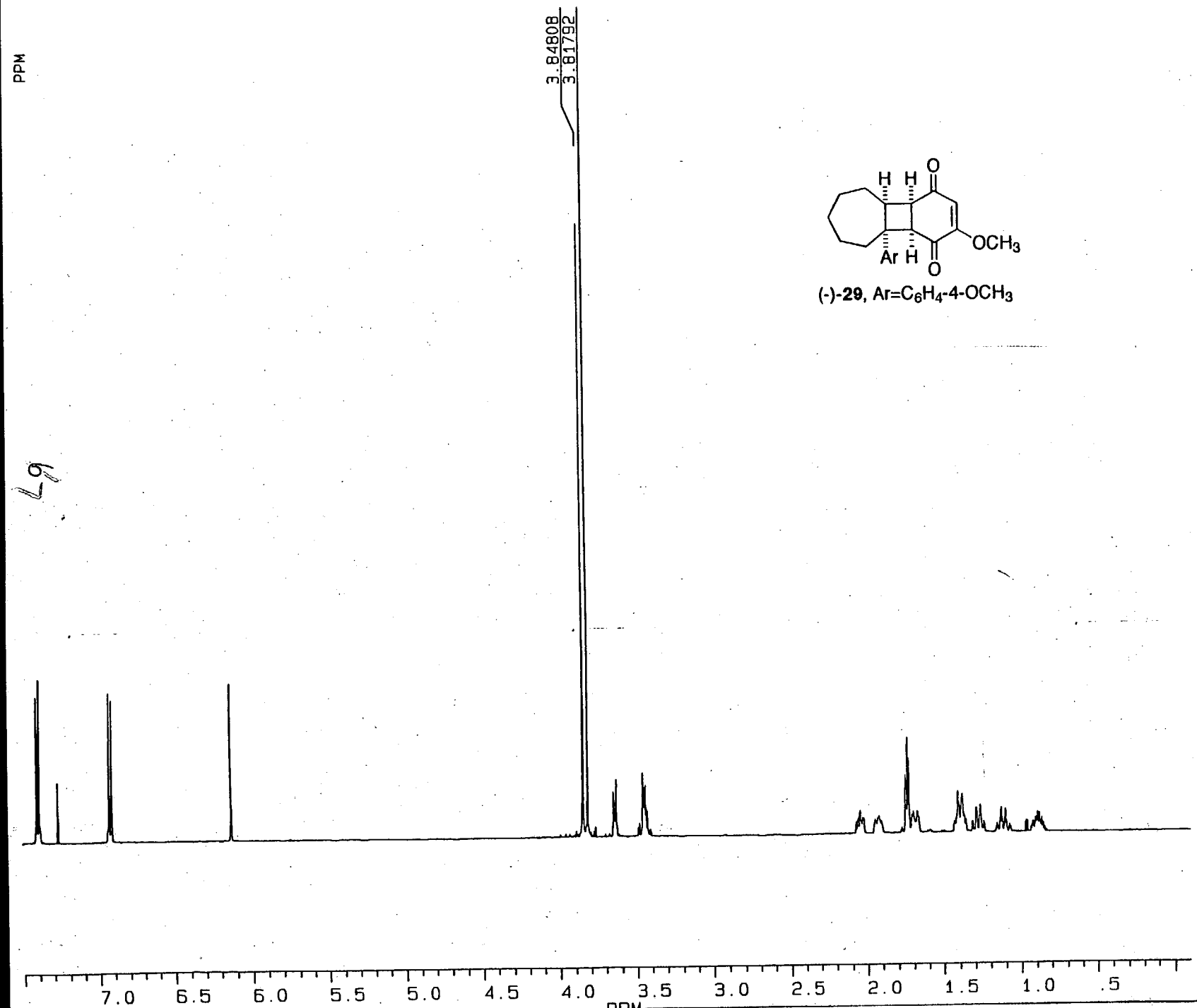
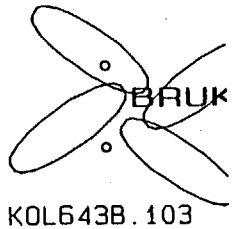


(-)-**29**, Ar=C_6H_4-4-OCH_3



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DATE 14-10-94

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FW	7600
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KOL-VI-43B

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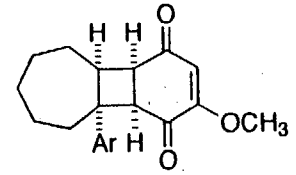

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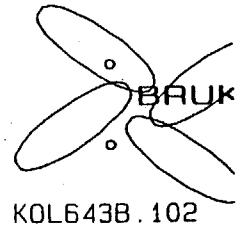

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NS	256
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FW	39100
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LB	.500
GB	0.0
CX	22.00
CY	0.0
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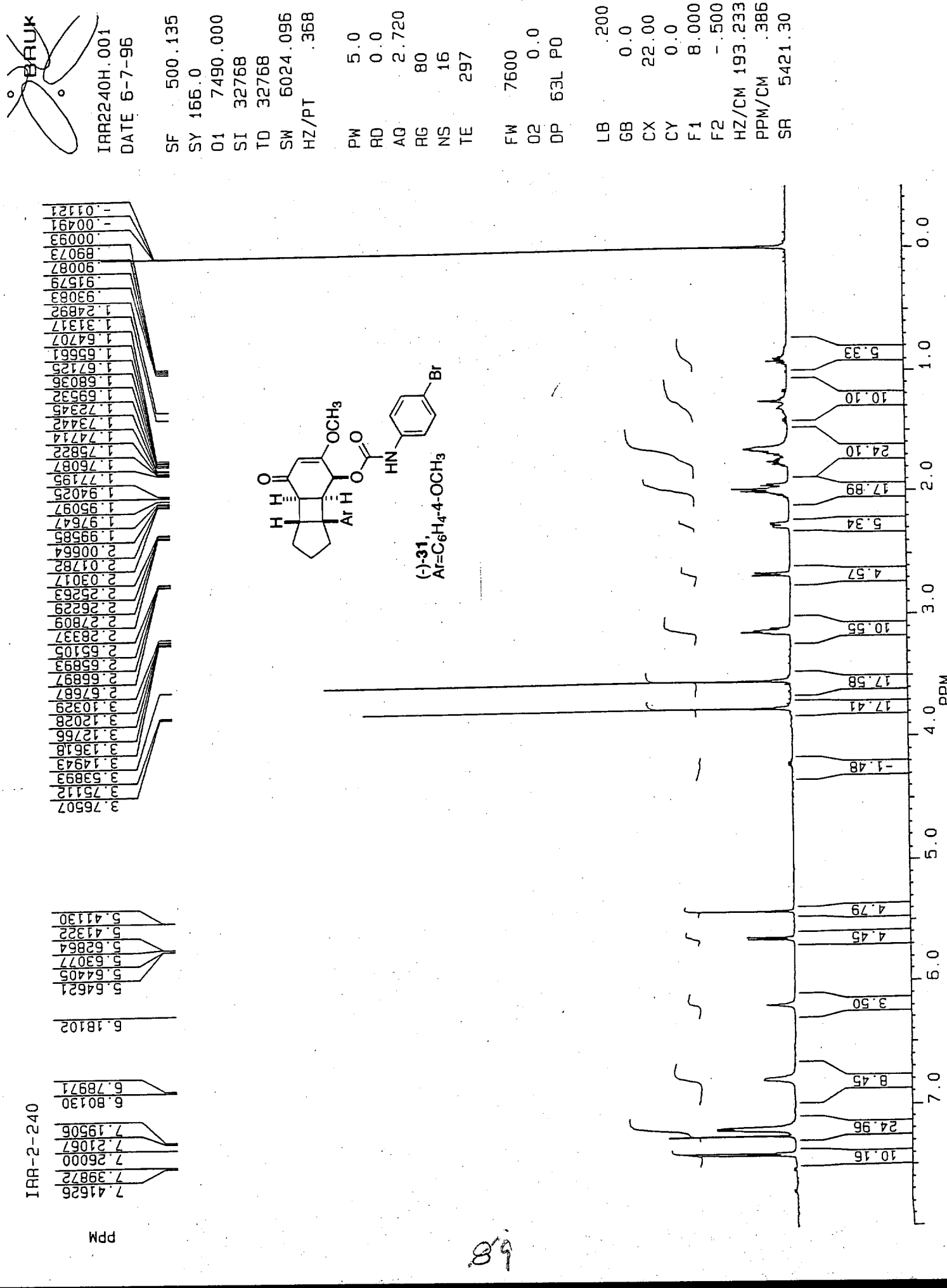

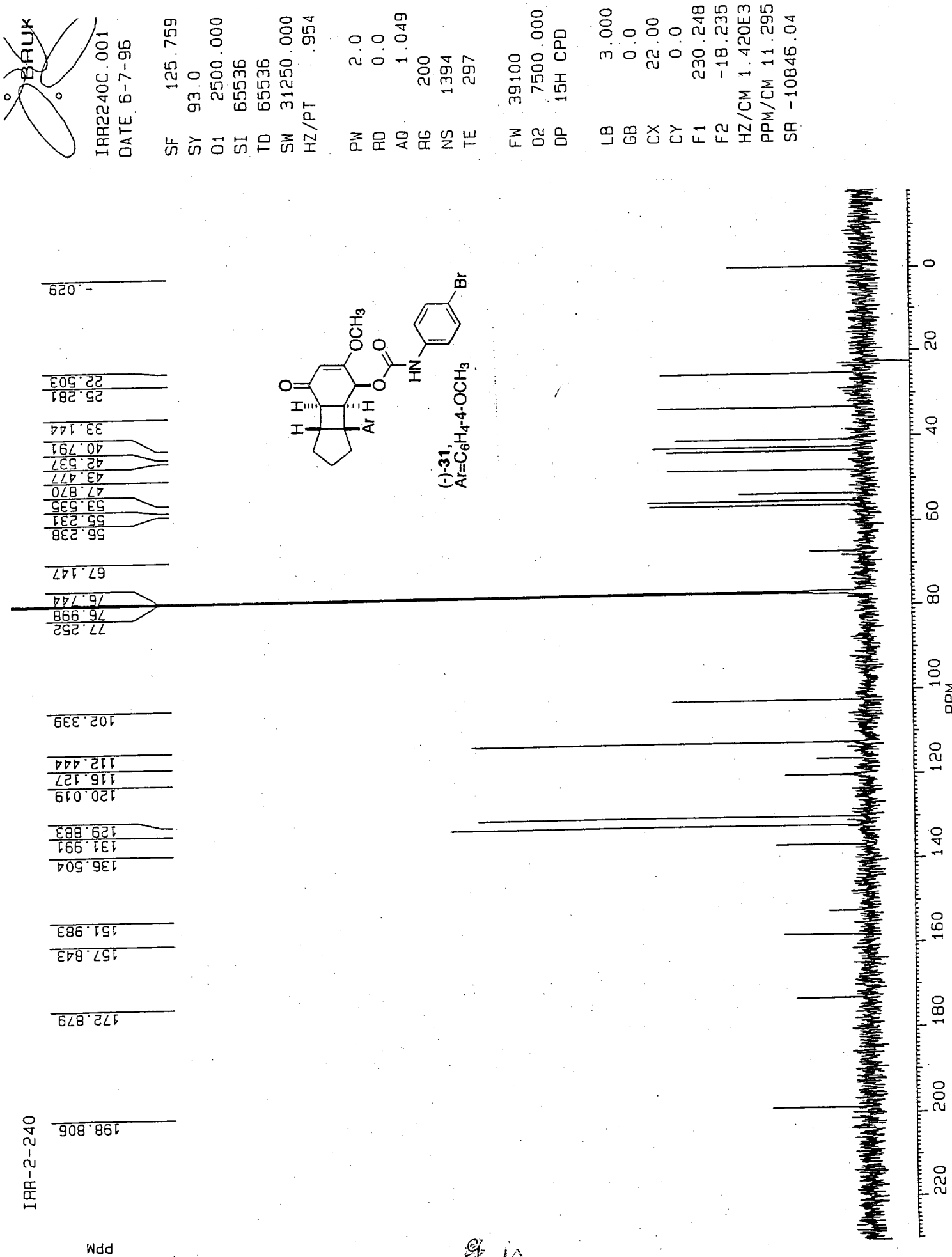

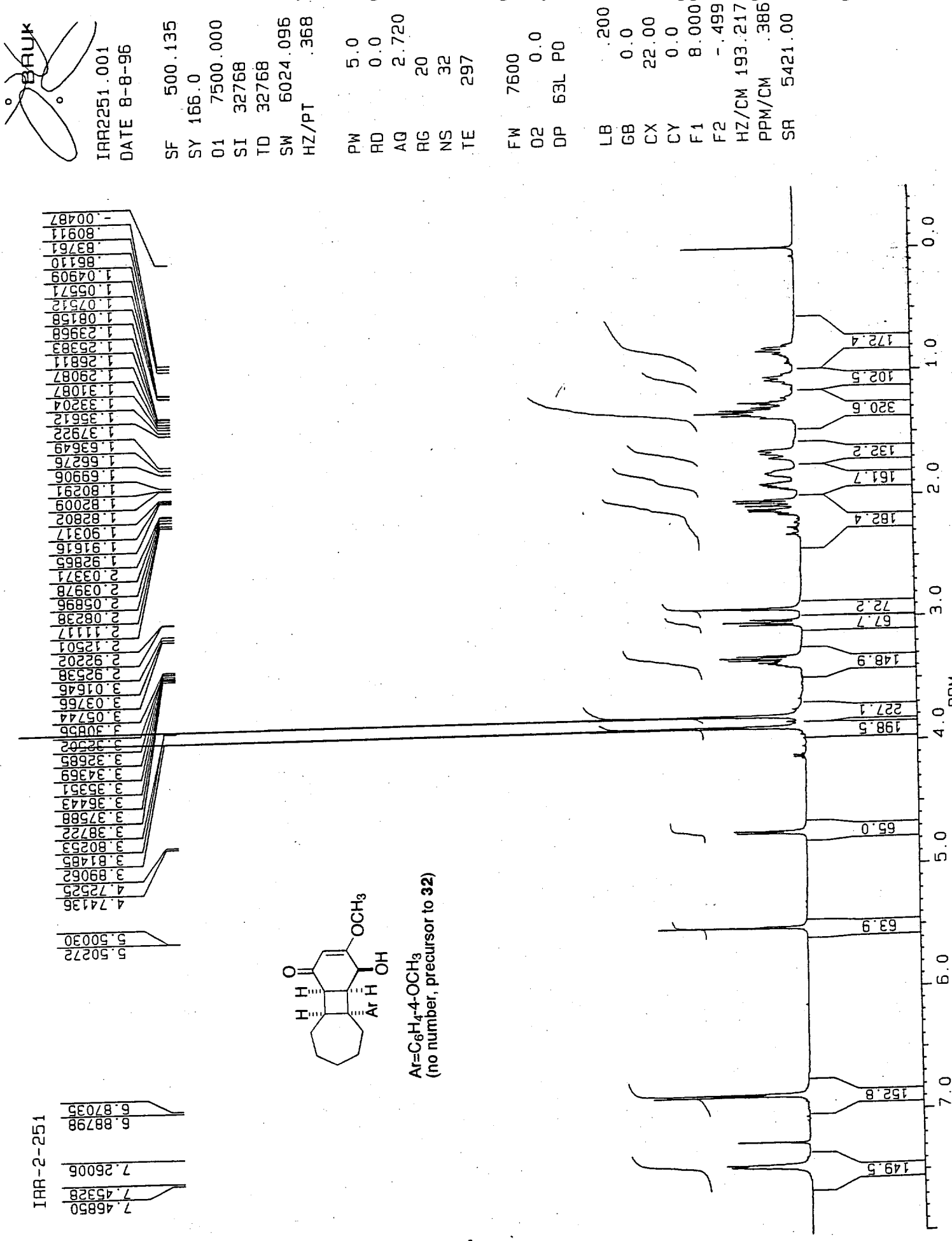

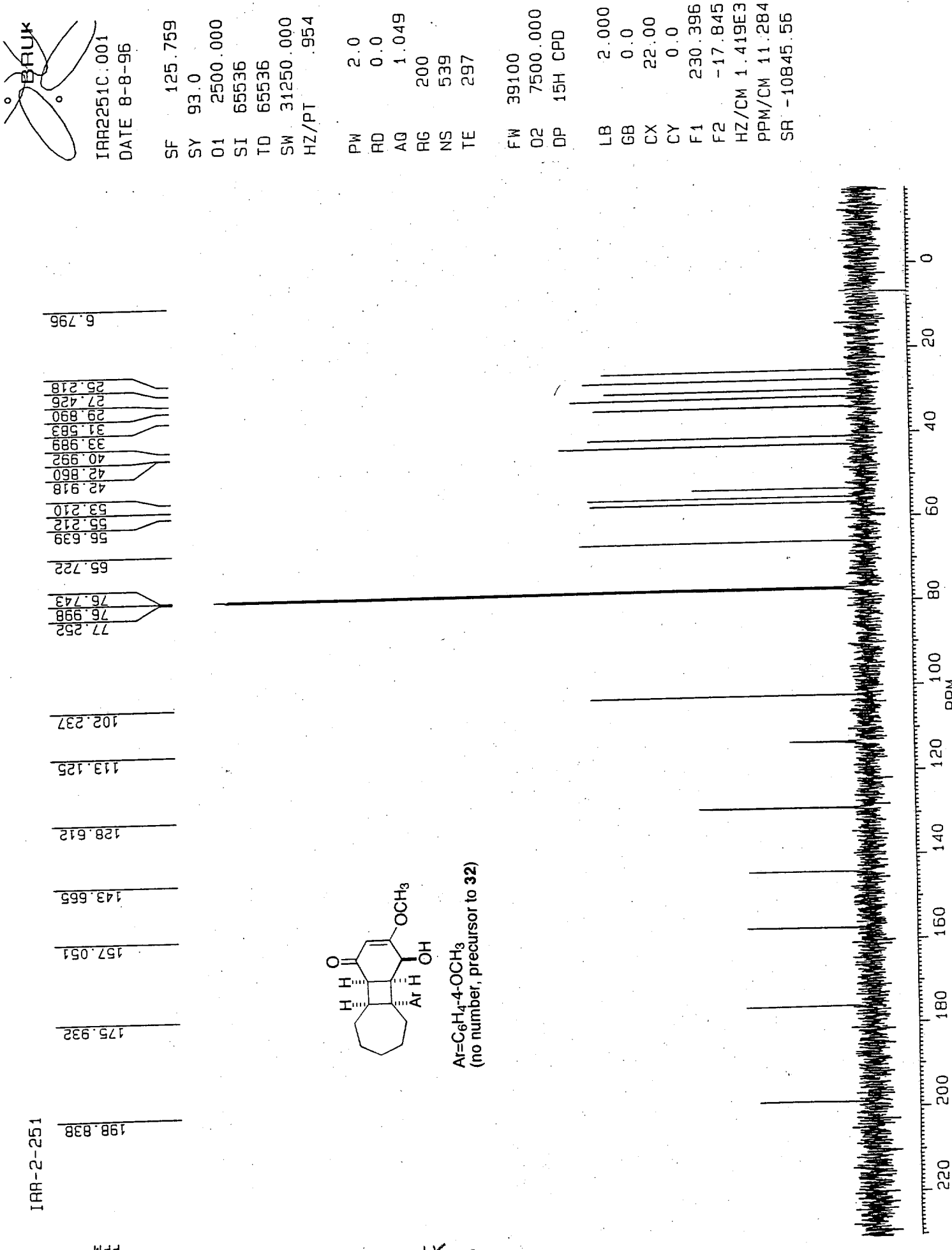

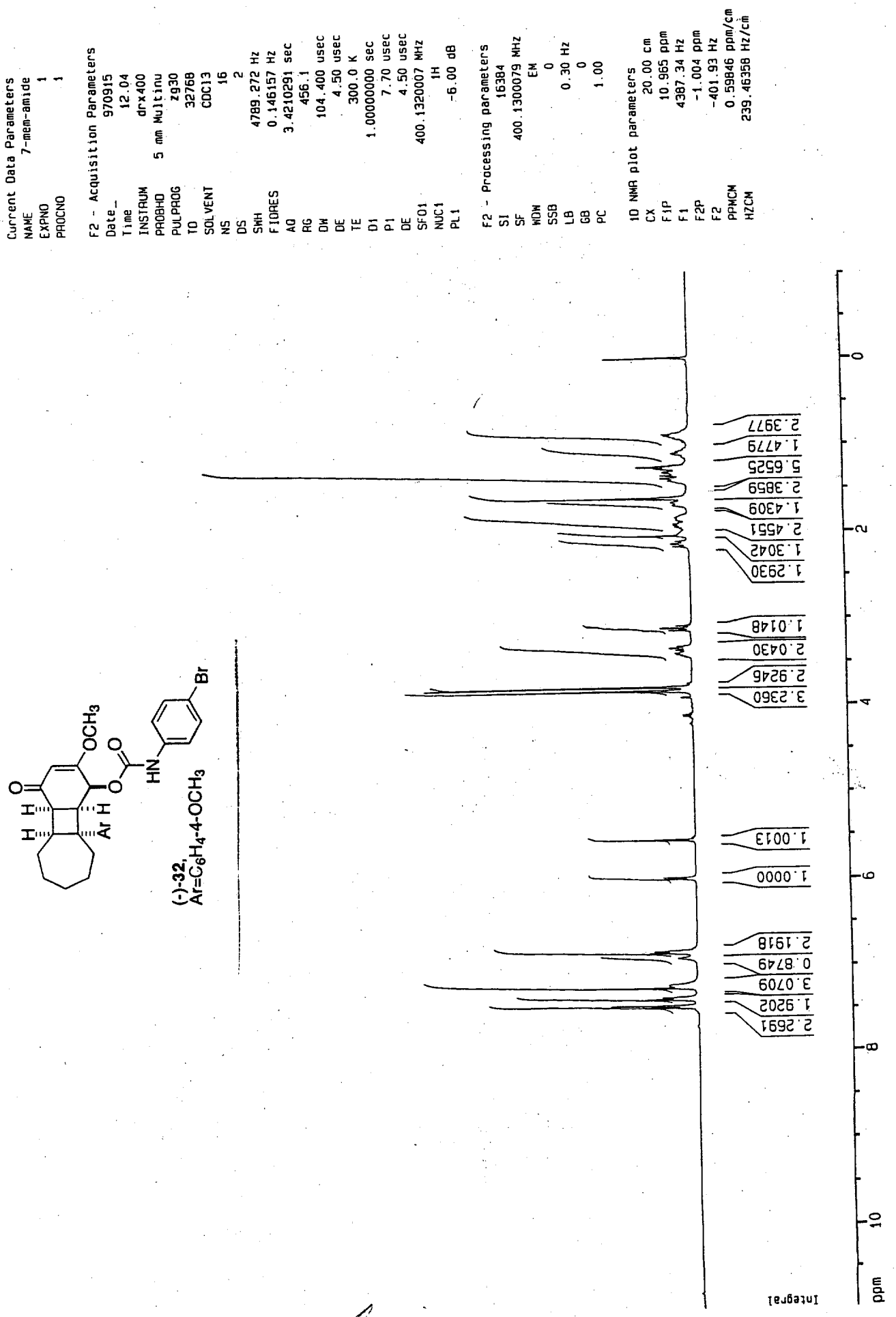

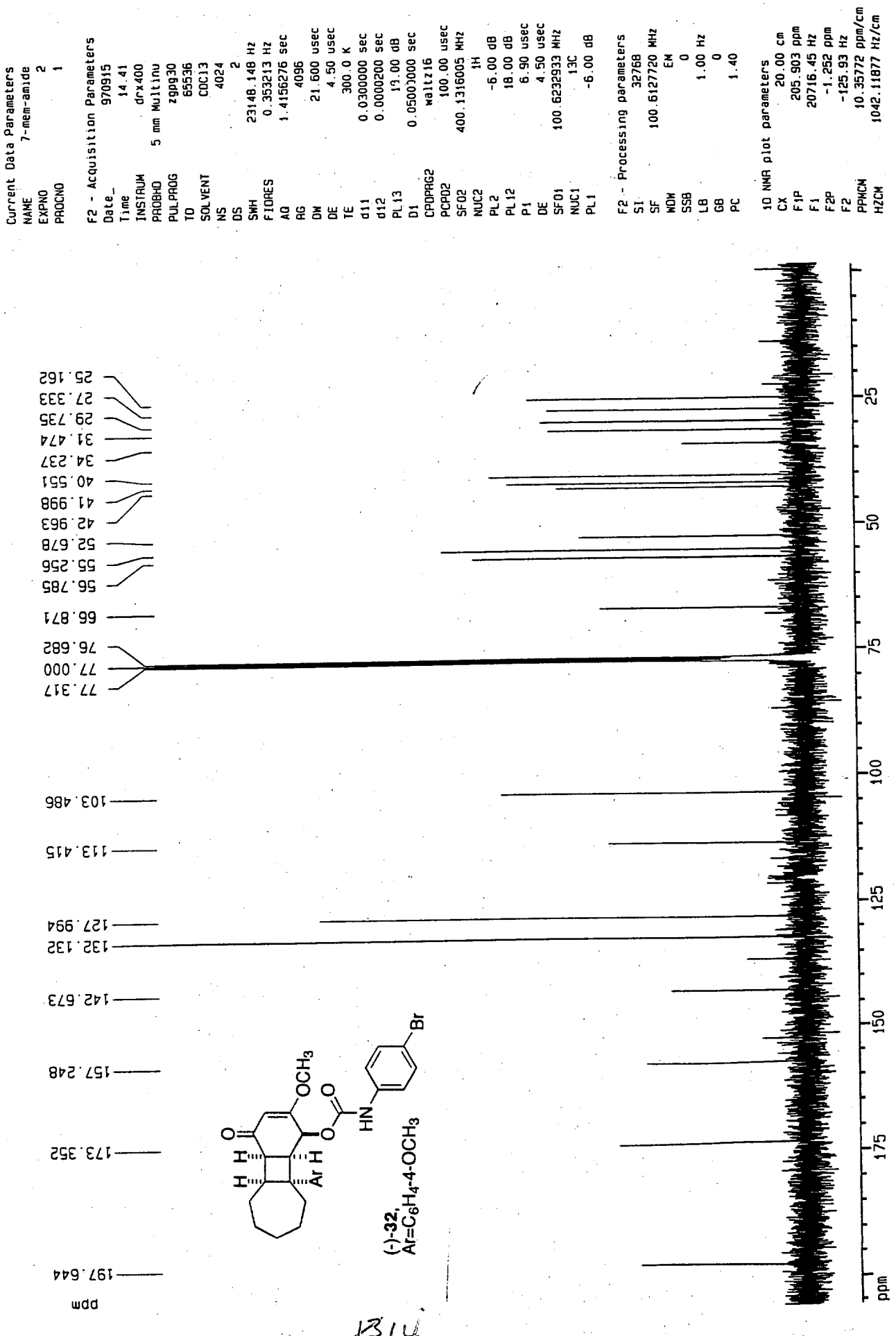

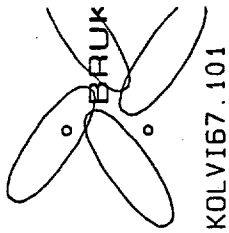

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AQ	2.720
RG	80
NS	16
TE	297
FW	7600
O2	0.0
DP	63L PO
LB	.100
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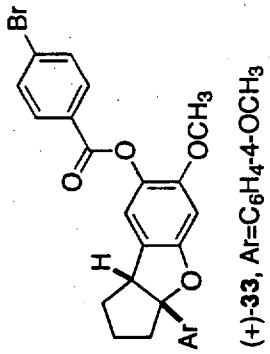

(+)-**33**, Ar=C_6H_4-4-OCH_3

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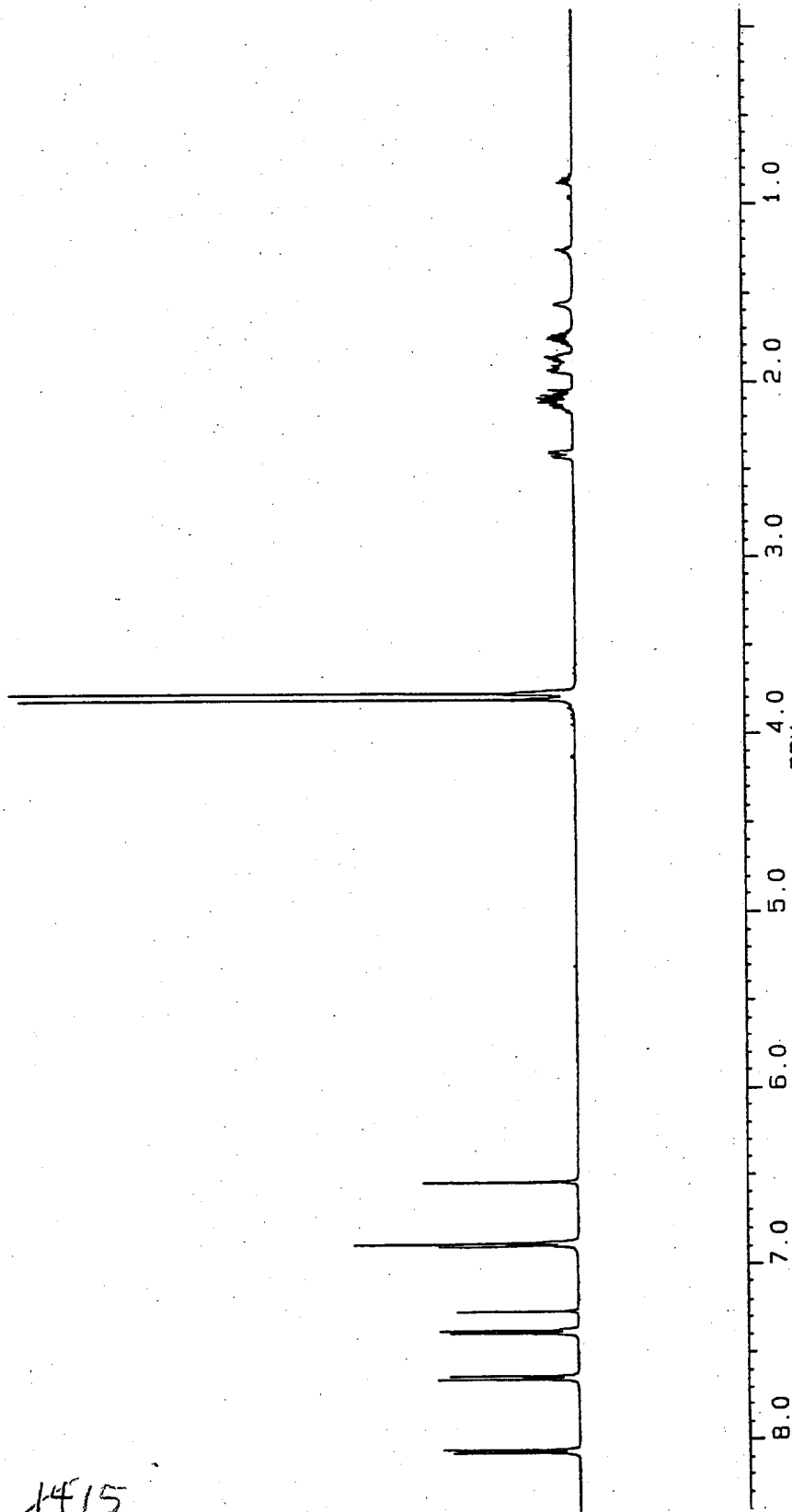
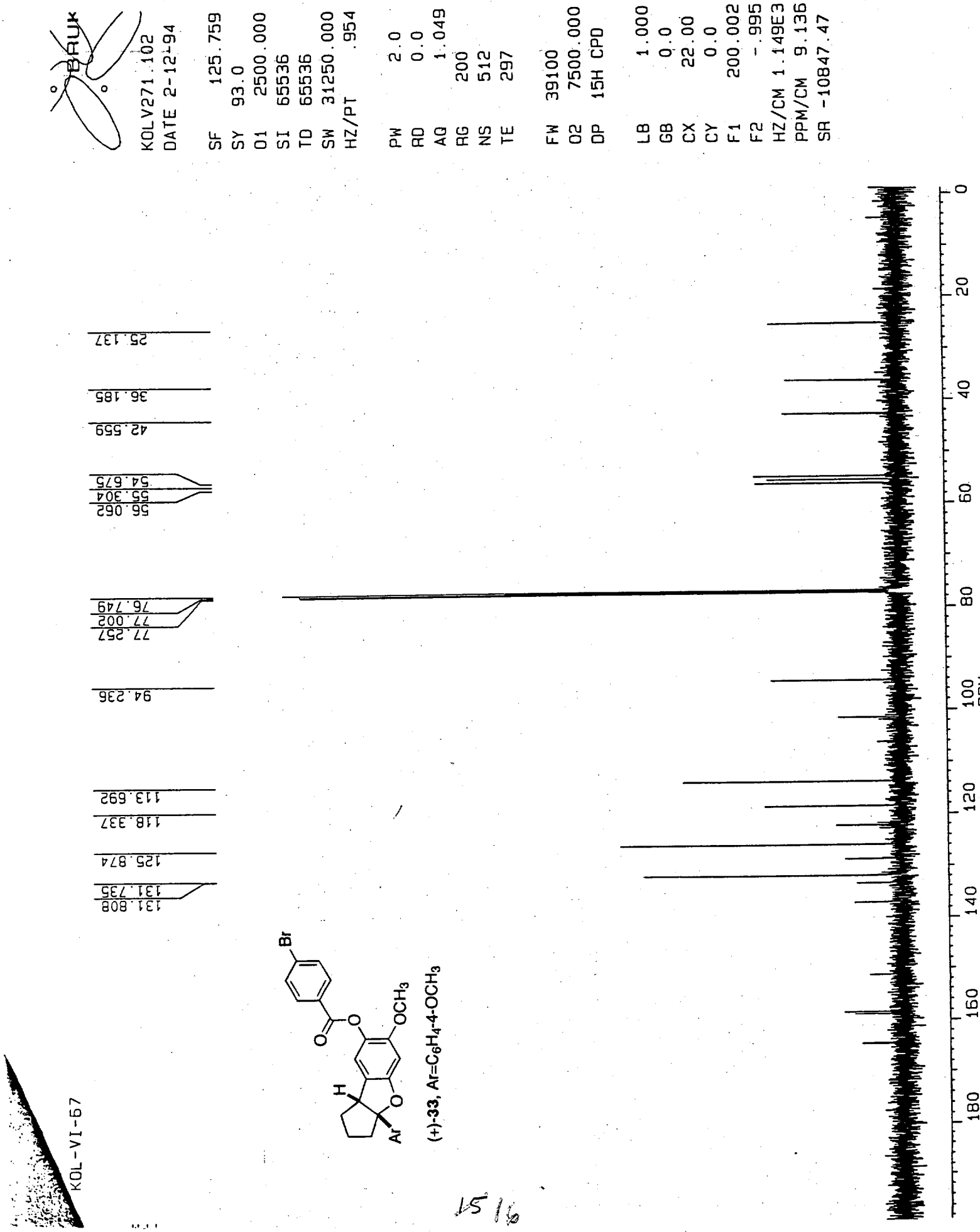


KOL-VI-67

1415

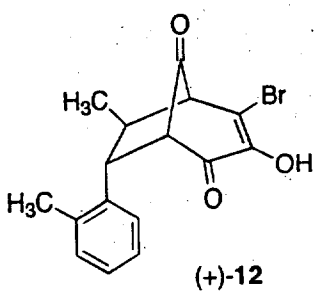


Ref. No.: Crystal-136

X-RAY STRUCTURE REPORT

for

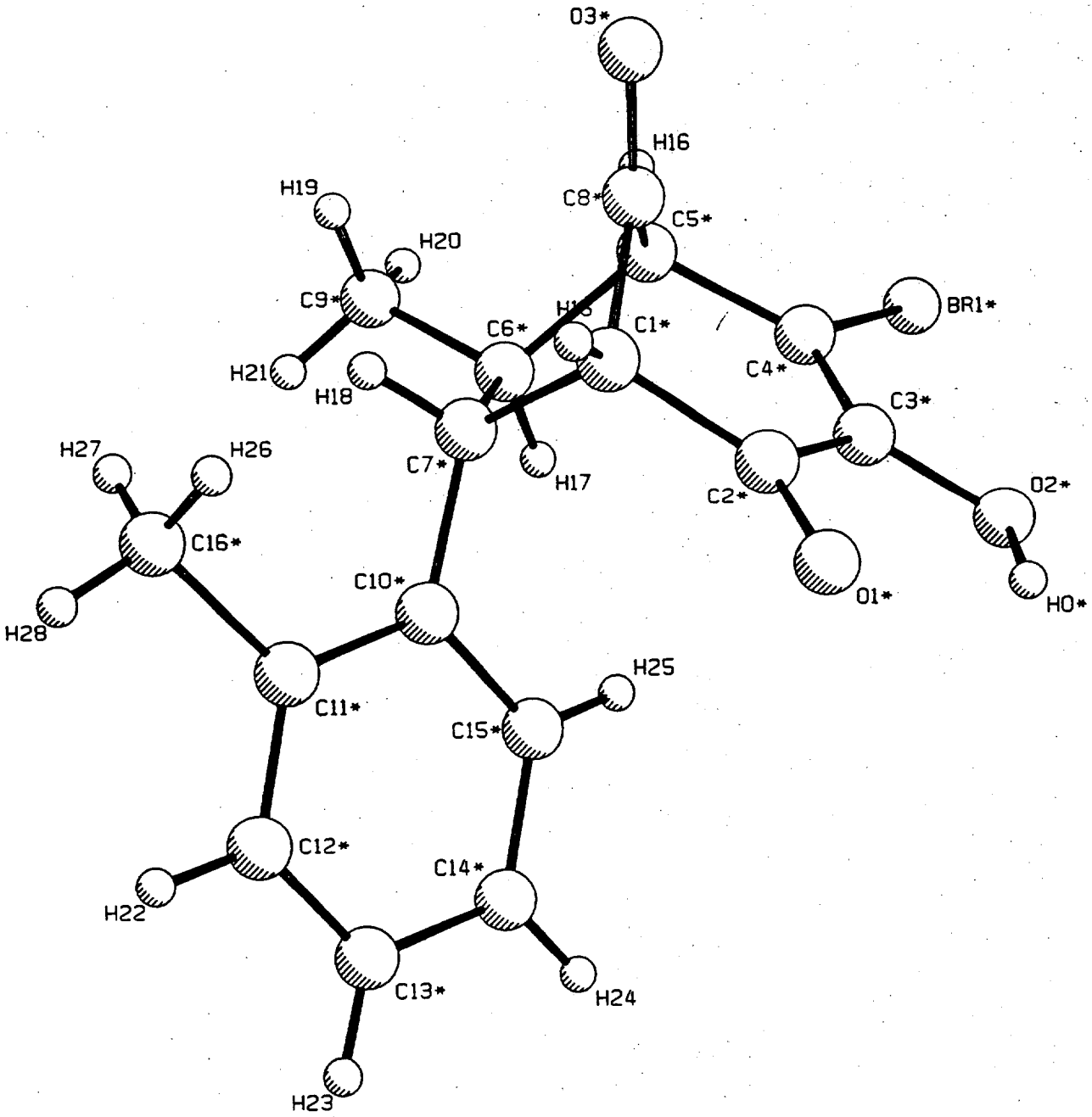
Prof. T. Engler



(+)-12

18-NOV-92

crustal-136



17 18

TABLE OF CONTENTS

INTRODUCTION

The absolute configuration of the molecule has been determined by using the anomalous dispersion effects of the Br- atoms. The refinement results are:

	Correct structure	Enantiomorph
R-factor	0.044	0.051
wR-factor	0.066	0.076
Goodness of fit	1.22	1.89

According to the Hamilton's R-factor test [W. C. Hamilton, Acta Crypt. 18, 502-570 (1965)], the correct structure gives significantly better fit to the data than its enantiomorph structure at the 99.5 % significant level.

Two independent molecules are in an asymmetric unit. One has no-* and the other has * on the atom name. 1920

EXPERIMENTAL

DATA COLLECTION

A colorless needle crystal of $C_{16}H_{15}BrO_3$ having approximate dimensions of 0.150 X 0.200 X 0.500 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Cu Kα radiation and a 12KW rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $58.96 < 2\theta < 68.55°$ /corresponded to an orthorhombic cell with dimensions:

a = 16.251 (1)Å
b = 22.854 (2)Å
c = 7.7685 (4)Å
V = 2885.4 (3)Å^3

For Z = 8 and F.W. = 335.20, the calculated density is 1.543 g/cm^3. Based on the systematic absences of:

h00: h ≠ 2n
0k0: k ≠ 2n
00l: l ≠ 2n

and the successful solution and refinement of the structure, the space group was determined to be:

$P2_12_12_1$ (#19)

The data were collected at a temperature of 23 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 112.6°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.36° with a take-off angle of 6.0°. Scans of (1.73 + 0.30 tan θ)° were made at a speed of 32.0°/min (in omega). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 285.0 mm.

DATA REDUCTION

A total of 2225 reflections was collected. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for Cu Kα is 39.4 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.72 to 1.00. The data were corrected for Lorentz and polarization effects.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods[3]. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement[4] was based on 1981 observed reflections ($I > 3.00\sigma(I)$) and 361 variable parameters and converged (largest parameter shift was 0.02 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.044$$

$$R_w = [(\Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2)]^{1/2} = 0.066$$

The standard deviation of an observation of unit weight[5] was 1.22. The weighting scheme was based on counting statistics and included a factor ($p = 0.10$) to downweight the intense reflections. Plots of $\Sigma \, w \, (|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.34 and -0.76 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[6]. Anomalous dispersion effects were included in Fcalc[7]; the values for Δf′ and Δf″ were those of Cromer[8]. All calculations were performed using the TEXSAN[9] crystallographic software package of Molecular Structure Corporation.

References

(1) PLUTO:
Motherwell,S. & Clegg,W.; PLUTO. Program for plotting molecular and crystal structures. Univ. of Cambridge, England (1978).

(2) ORTEP:
Johnson,C.K.; ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee (1976).

(3) Structure Solution Methods:
MITHRIL
Gilmore,C.J.; MITHRIL - an integrated direct methods computer program. J. Appl. Cryst. 17, 42-46, Univ. of Glasgow, Scotland, (1984).
DIRDIF
Beurskens,P.T.; DIRDIF: Direct Methods for Difference Structures - an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1 Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.

(4) Least-Squares:
Function minimized: $\Sigma\, w\,(|Fo| - |Fc|)^2$
where: $w = 4Fo^2/\sigma^2(Fo^2)$
$\sigma^2(Fo^2) = [S^2(C+R^2B) + (pFo^2)^2]/Lp^2$
S = Scan rate
C = Total Integrated Peak Count
R = Ratio of Scan Time to background counting time.
B = Total Background Count
Lp = Lorentz-polarization factor
p = p-factor

(5) Standard deviation of an observation of unit weight:

$$[\Sigma\, w(|Fo| - |Fc|)^2/(No - Nv)]^{1/2}$$

where: No = number of observations
Nv = number of variables

(6) Cromer,D.T. & Waber,J.T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(7) Ibers,J.A. & Hamilton,W.C.; Acta Crystallogr., 17, 781 (1964).

(8) D.T. Cromer, "International Tables for X-ray Crystallography", Vol/ IV, The Kynoch Press, Birmingham, England, Table 2.3.1 (1974).

(9) TEXSAN - TEXRAY Structure Analysis Package, Molecular Structure Corporation (1985).

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{16}H_{15}BrO_3$
Formula Weight	335.20
Crystal Color, Habit	colorless, needle
Crystal Dimensions (mm)	0.150 X 0.200 X 0.500
Crystal System	orthorhombic
No. Reflections Used for Unit Cell Determination (2θ range)	25 (59.0 - 68.6°)
Omega Scan Peak Width at Half-height	0.36
Lattice Parameters:	a = 16.251 (1)Å b = 22.854 (2)Å c = 7.7685 (4)Å V = 2885.4 (3)Å^3
Space Group	$P2_12_12_1$ (#19)
Z value	8
D_{calc}	1.543 g/cm^3
F_{000}	1360
$\mu_{(CuK\alpha)}$	39.41 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC5R
Radiation	CuKα (λ = 1.54178 Å)
Temperature	23°C
Attenuators	Zr foil (factors: 4.1, 14.5, 54.4)
Take-off Angle	6.0°

Detector Aperture	6.0 mm horizontal 6.0 mm vertical
Crystal to Detector Distance	40 cm
Scan Type	ω-2θ
Scan Rate	32.0°/min (in omega) (2 rescans)
Scan Width	(1.73 + 0.30 tanθ)°
$2\theta_{max}$	112.6°
No. of Reflections Measured	Total: 2225
Corrections	Lorentz-polarization Absorption (trans. factors: 0.72 - 1.00)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least-squares Weights	$4Fo^2/\sigma^2(Fo^2)$
p-factor	0.10
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	1981
No. Variables	361
Reflection/Parameter Ratio	5.49
Residuals: R; R_w	0.044; 0.066
Goodness of Fit Indicator	1.22
Max Shift/Error in Final Cycle	0.02
Maximum Peak in Final Diff. Map	0.34 $e^-/Å^3$
Minimum Peak in Final Diff. Map	-0.76 $e^-/Å^3$

Positional parameters for crystal-136

atom	x	y	z
Br(1)	0.69060(6)	0.10001(4)	0.2224(1)
O(1)	0.4157(3)	0.0610(3)	0.522(1)
O(2)	0.5072(4)	0.0760(3)	0.2360(8)
O(3)	0.6385(4)	0.0220(3)	0.7857(9)
C(1)	0.5252(5)	0.0889(4)	0.712(1)
C(2)	0.4845(5)	0.0773(4)	0.539(1)
C(3)	0.5412(5)	0.0835(3)	0.391(1)
C(4)	0.6214(5)	0.0940(3)	0.415(1)
C(5)	0.6557(5)	0.1033(4)	0.587(1)
C(6)	0.6322(5)	0.1665(3)	0.657(1)
C(7)	0.5469(5)	0.1553(3)	0.745(1)
C(8)	0.6110(5)	0.0632(3)	0.703(1)
C(9)	0.6939(7)	0.1891(5)	0.778(1)
C(10)	0.4814(5)	0.1991(4)	0.704(1)
C(11)	0.4338(5)	0.2253(4)	0.833(1)
C(12)	0.3772(6)	0.2689(4)	0.786(1)
C(13)	0.3660(6)	0.2867(4)	0.624(2)
C(14)	0.4150(7)	0.2625(4)	0.491(2)
C(15)	0.4705(7)	0.2192(4)	0.538(1)
C(16)	0.4375(6)	0.2047(6)	1.013(1)
H(1)	0.4942	0.0720	0.8054
H(2)	0.7133	0.0965	0.5893
H(3)	0.6255	0.1929	0.5641
H(4)	0.5573	0.1588	0.8653

Positional parameters for crystal-136

atom	x	y	z
H(5)	0.7029	0.1616	0.8663
H(6)	0.7444	0.1951	0.7159
H(7)	0.6760	0.2251	0.8236
H(8)	0.3461	0.2876	0.8750
H(9)	0.3259	0.3167	0.5970
H(10)	0.4121	0.2763	0.3749
H(11)	0.5028	0.2017	0.4513
H(12)	0.4020	0.2268	1.0807
H(13)	0.4221	0.1642	1.0158
H(14)	0.4928	0.2080	1.0531
H(0)	0.4602	0.0585	0.2199
Br(1*)	0.25372(6)	0.14325(4)	0.2561(1)
O(1*)	0.1289(3)	-0.0167(2)	0.6318(9)
O(2*)	0.1748(4)	0.0240(2)	0.3247(8)
O(3*)	0.3166(3)	0.1017(2)	0.8415(7)
C(1*)	0.1756(4)	0.0673(3)	0.793(1)
C(2*)	0.1599(4)	0.0316(3)	0.636(1)
C(3*)	0.1862(4)	0.0571(3)	0.466(1)
C(4*)	0.2194(4)	0.1105(3)	0.463(1)
C(5*)	0.2280(5)	0.1468(3)	0.625(1)
C(6*)	0.1418(4)	0.1689(3)	0.694(1)
C(7*)	0.1138(4)	0.1187(3)	0.817(1)
C(8*)	0.2524(4)	0.1032(3)	0.764(1)
C(9*)	0.1481(6)	0.2264(4)	0.779(1)
C(10*)	0.0232(4)	0.0995(3)	0.812(1)

Positional parameters for crystal-136

atom	x	y	z
C(11*)	-0.0232(5)	0.0926(4)	0.958(1)
C(12*)	-0.1034(6)	0.0741(4)	0.945(2)
C(13*)	-0.1396(5)	0.0608(4)	0.797(2)
C(14*)	-0.0964(6)	0.0671(5)	0.646(2)
C(15*)	-0.0144(5)	0.0888(4)	0.651(1)
C(16*)	0.0156(7)	0.1052(6)	1.139(1)
H(15)	0.1798	0.0433	0.8943
H(16)	0.2665	0.1783	0.6132
H(17)	0.1044	0.1719	0.5999
H(18)	0.1233	0.1333	0.9290
H(19)	0.1849	0.2220	0.8757
H(20)	0.1685	0.2539	0.7027
H(21)	0.0955	0.2369	0.8211
H(22)	-0.1334	0.0703	1.0492
H(23)	-0.1948	0.0473	0.7968
H(24)	-0.1209	0.0569	0.5392
H(25)	0.0142	0.0960	0.5461
H(26)	0.0610	0.0784	1.1555
H(27)	0.0345	0.1436	1.1449
H(28)	-0.0243	0.0976	1.2255
H(0*)	0.1534	-0.0174	0.3735

U values for crystal-136

ATOM	U11	U22	U33	U12	U13	U23
Br(1)	0.0691(6)	0.0771(6)	0.0531(6)	-0.0167(4)	0.0199(5)	-0.0095(5)
O(1)	0.041(3)	0.090(5)	0.104(6)	-0.019(3)	0.012(4)	-0.015(4)
O(2)	0.063(3)	0.073(4)	0.049(3)	-0.023(3)	-0.021(3)	-0.001(3)
O(3)	0.079(4)	0.069(4)	0.065(4)	0.007(3)	0.003(4)	0.026(4)
C(1)	0.045(4)	0.049(4)	0.065(6)	-0.003(3)	0.016(4)	0.004(4)
C(2)	0.051(5)	0.046(5)	0.070(6)	0.005(4)	-0.001(5)	-0.009(5)
C(3)	0.037(4)	0.041(4)	0.059(5)	0.001(3)	-0.004(4)	-0.005(4)
C(4)	0.052(5)	0.039(4)	0.042(4)	0.001(3)	0.002(4)	-0.003(4)
C(5)	0.037(4)	0.055(5)	0.055(5)	0.001(3)	-0.007(4)	-0.007(4)
C(6)	0.057(5)	0.045(4)	0.051(5)	-0.008(4)	-0.007(4)	-0.002(4)
C(7)	0.051(4)	0.056(4)	0.029(4)	-0.008(3)	0.005(4)	0.001(4)
C(8)	0.064(5)	0.045(4)	0.041(5)	-0.006(4)	-0.003(4)	0.005(4)
C(9)	0.100(7)	0.082(6)	0.058(6)	-0.029(6)	-0.009(6)	-0.013(6)
C(10)	0.057(5)	0.047(4)	0.053(5)	-0.002(4)	0.004(4)	-0.013(4)
C(11)	0.054(5)	0.057(5)	0.070(6)	-0.019(4)	0.010(5)	-0.016(5)
C(12)	0.064(5)	0.060(5)	0.075(7)	0.002(4)	0.019(5)	-0.012(5)
C(13)	0.061(6)	0.066(6)	0.11(1)	0.013(5)	0.009(7)	0.002(7)

U values for crystal-136

ATOM	U11	U22	U33	U12	U13	U23
C(14)	0.093(7)	0.049(5)	0.078(7)	0.009(5)	0.001(6)	-0.007(5)
C(15)	0.087(6)	0.050(5)	0.043(5)	0.010(5)	0.000(5)	0.002(4)
C(16)	0.054(6)	0.14(1)	0.071(7)	-0.016(6)	0.017(6)	-0.039(7)
H(1)	0.0248					
H(2)	0.0360					
H(3)	0.0127					
H(4)	0.0361					
H(5)	0.1900					
H(6)	0.1317					
H(7)	0.1247					
H(8)	0.1431					
H(9)	0.1202					
H(10)	0.0998					
H(11)	0.1900					
H(12)	0.1900					
H(13)	0.1323					
H(14)	0.1900					
H(0)	0.0330					

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U values for crystal-136

ATOM	U11	U22	U33	U12	U13	U23
Br(1*)	0.0796(6)	0.0595(5)	0.0421(5)	-0.0106(4)	0.0093(5)	0.0095(4)
O(1*)	0.061(3)	0.034(3)	0.089(5)	-0.009(3)	0.036(3)	0.015(3)
O(2*)	0.058(3)	0.052(3)	0.063(4)	0.001(3)	0.002(3)	-0.014(3)
O(3*)	0.048(3)	0.058(3)	0.047(3)	0.003(3)	0.002(3)	0.004(3)
C(1*)	0.040(4)	0.047(4)	0.042(5)	0.009(3)	0.012(4)	0.015(4)
C(2*)	0.017(3)	0.049(5)	0.056(5)	0.006(3)	0.011(3)	0.012(4)
C(3*)	0.042(4)	0.039(4)	0.039(4)	0.005(3)	0.001(4)	-0.003(3)
C(4*)	0.036(4)	0.039(4)	0.038(4)	0.003(3)	0.006(3)	-0.001(3)
C(5*)	0.041(4)	0.047(4)	0.046(5)	-0.008(3)	0.002(4)	-0.002(4)
C(6*)	0.039(4)	0.041(4)	0.046(5)	0.005(3)	-0.004(3)	-0.003(4)
C(7*)	0.041(4)	0.049(4)	0.038(4)	0.008(3)	-0.001(3)	-0.006(3)
C(8*)	0.031(4)	0.044(4)	0.048(4)	0.010(3)	-0.004(4)	-0.008(4)
C(9*)	0.070(5)	0.064(5)	0.065(6)	0.014(4)	-0.003(5)	-0.010(5)
C(10*)	0.030(3)	0.047(4)	0.043(4)	0.008(3)	0.005(3)	-0.001(4)
C(11*)	0.043(4)	0.057(5)	0.061(5)	0.019(4)	0.010(4)	0.011(5)
C(12*)	0.058(6)	0.062(6)	0.083(7)	0.015(5)	0.019(6)	0.019(6)
C(13*)	0.039(4)	0.071(6)	0.10(1)	0.000(4)	-0.020(6)	0.030(6)
C(14*)	0.064(6)	0.077(7)	0.072(7)	0.012(5)	-0.025(6)	-0.018(6)

U values for crystal-136

ATOM	U11	U22	U33	U12	U13	U23
C(15*)	0.041(4)	0.070(6)	0.056(5)	0.011(4)	-0.013(4)	-0.015(5)
C(16*)	0.075(7)	0.16(1)	0.047(6)	0.008(7)	0.020(5)	-0.010(7)
H(15)	0.0784					
H(16)	0.0127					
H(17)	0.0615					
H(18)	0.0419					
H(19)	0.0463					
H(20)	0.1900					
H(21)	0.1900					
H(22)	0.1069					
H(23)	0.0706					
H(24)	0.1287					
H(25)	0.0414					
H(26)	0.0838					
H(27)	0.1887					
H(28)	0.0581					
H(0*)	0.1086					

Intramolecular Distances

atom	atom	distance	atom	atom	distance
BR1	C4	1.874(8)	C11	C16	1.48(2)
O1	C2	1.19(1)	C12	C13	1.34(2)
O2	C3	1.33(1)	C12	H8	0.959
O2	H0	0.873	C13	C14	1.42(2)
O3	C8	1.22(1)	C13	H9	0.968
C1	C2	1.52(1)	C14	C15	1.39(1)
C1	C7	1.58(1)	C14	H10	0.958
C1	C8	1.51(1)	C15	H11	0.945
C1	H1	0.961	C16	H12	0.928
C2	C3	1.48(1)	C16	H13	0.959
C3	C4	1.34(1)	C16	H14	0.952
C4	C5	1.47(1)	BR1*	C4*	1.858(8)
C5	C6	1.59(1)	O1*	C2*	1.213(9)
C5	C8	1.48(1)	O2*	C3*	1.344(9)
C5	H2	0.949	O2*	H0*	1.077
C6	C7	1.57(1)	O3*	C8*	1.205(8)
C6	C9	1.47(1)	C1*	C2*	1.49(1)
C6	H3	0.947	C1*	C7*	1.56(1)
C7	C10	1.49(1)	C1*	C8*	1.51(1)
C7	H4	0.955	C1*	H15	0.959
C9	H5	0.942	C2*	C3*	1.51(1)
C9	H6	0.961	C3*	C4*	1.34(1)
C9	H7	0.943	C4*	C5*	1.51(1)
C10	C11	1.40(1)	C5*	C6*	1.58(1)
C10	C15	1.38(1)	C5*	C8*	1.52(1)
C11	C12	1.40(1)	C5*	H16	0.957

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Distances (cont)

atom	atom	distance	atom	atom	distance
C6*	C7*	1.56(1)			
C6*	C9*	1.47(1)			
C6*	H17	0.952			
C7*	C10*	1.54(1)			
C7*	H18	0.945			
C9*	H19	0.964			
C9*	H20	0.927			
C9*	H21	0.946			
C10*	C11*	1.37(1)			
C10*	C15*	1.42(1)			
C11*	C12*	1.37(1)			
C11*	C16*	1.57(2)			
C12*	C13*	1.32(2)			
C12*	H22	0.950			
C13*	C14*	1.38(2)			
C13*	H23	0.949			
C14*	C15*	1.42(1)			
C14*	H24	0.948			
C15*	H25	0.951			
C16*	H26	0.966			
C16*	H27	0.931			
C16*	H28	0.948			

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles

atom	atom	atom	angle	atom	atom	atom	angle
C3	O2	H0	123.38	C7	C6	H3	109.44
C2	C1	C7	113.8(7)	C9	C6	H3	110.03
C2	C1	C8	106.9(7)	C1	C7	C6	106.6(6)
C2	C1	H1	111.60	C1	C7	C10	116.8(6)
C7	C1	C8	100.0(6)	C1	C7	H4	105.90
C7	C1	H1	112.54	C6	C7	C10	115.5(6)
C8	C1	H1	111.28	C6	C7	H4	104.93
O1	C2	C1	124(1)	C10	C7	H4	105.96
O1	C2	C3	122(1)	O3	C8	C1	127.6(8)
C1	C2	C3	113.6(7)	O3	C8	C5	128.1(8)
O2	C3	C2	115.6(7)	C1	C8	C5	104.1(7)
O2	C3	C4	123.3(8)	C6	C9	H5	109.73
C2	C3	C4	121.1(8)	C6	C9	H6	108.29
BR1	C4	C3	119.2(7)	C6	C9	H7	109.68
BR1	C4	C5	119.2(5)	H5	C9	H6	109.20
C3	C4	C5	121.5(8)	H5	C9	H7	110.77
C4	C5	C6	110.6(7)	H6	C9	H7	109.12
C4	C5	C8	106.2(7)	C7	C10	C11	122.1(9)
C4	C5	H2	111.51	C7	C10	C15	120.6(8)
C6	C5	C8	103.7(7)	C11	C10	C15	117.2(8)
C6	C5	H2	112.44	C10	C11	C12	118.4(9)
C8	C5	H2	111.92	C10	C11	C16	121(1)
C5	C6	C7	102.3(6)	C12	C11	C16	120.2(9)
C5	C6	C9	111.9(8)	C11	C12	C13	123.6(9)
C5	C6	H3	110.34	C11	C12	H8	118.18
C7	C6	C9	112.6(8)	C13	C12	H8	118.19

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles (cont)

atom	atom	atom	angle	atom	atom	atom	angle
C12	C13	C14	119.4(9)	O2*	C3*	C4*	123.9(7)
C12	C13	H9	120.71	C2*	C3*	C4*	118.9(7)
C14	C13	H9	119.89	BR1*	C4*	C3*	120.2(6)
C13	C14	C15	117(1)	BR1*	C4*	C5*	118.1(5)
C13	C14	H10	121.96	C3*	C4*	C5*	121.7(7)
C15	C14	H10	121.10	C4*	C5*	C6*	112.1(6)
C10	C15	C14	124.5(9)	C4*	C5*	C8*	104.8(6)
C10	C15	H11	117.23	C4*	C5*	H16	113.23
C14	C15	H11	118.27	C6*	C5*	C8*	101.4(6)
C11	C16	H12	109.50	C6*	C5*	H16	111.73
C11	C16	H13	108.32	C8*	C5*	H16	112.83
C11	C16	H14	108.74	C5*	C6*	C7*	103.4(6)
H12	C16	H13	110.53	C5*	C6*	C9*	112.1(6)
H12	C16	H14	111.18	C5*	C6*	H17	109.09
H13	C16	H14	108.52	C7*	C6*	C9*	113.5(7)
C3*	O2*	H0*	104.64	C7*	C6*	H17	109.60
C2*	C1*	C7*	113.5(6)	C9*	C6*	H17	109.01
C2*	C1*	C8*	108.3(6)	C1*	C7*	C6*	107.1(6)
C2*	C1*	H15	111.72	C1*	C7*	C10*	113.6(6)
C7*	C1*	C8*	98.1(6)	C1*	C7*	H18	105.69
C7*	C1*	H15	112.42	C6*	C7*	C10*	118.4(6)
C8*	C1*	H15	111.94	C6*	C7*	H18	104.72
O1*	C2*	C1*	126.1(7)	C10*	C7*	H18	106.24
O1*	C2*	C3*	116.6(8)	O3*	C8*	C1*	128.6(7)
C1*	C2*	C3*	117.3(6)	O3*	C8*	C5*	126.8(6)
O2*	C3*	C2*	117.2(6)	C1*	C8*	C5*	104.3(5)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles (cont)

atom	atom	atom	angle	atom	atom	atom	angle
C6*	C9*	H19	107.51	C11*	C16*	H28	109.14
C6*	C9*	H20	109.92	H26	C16*	H27	109.75
C6*	C9*	H21	108.56	H26	C16*	H28	108.27
H19	C9*	H20	110.21	H27	C16*	H28	111.29
H19	C9*	H21	108.66				
H20	C9*	H21	111.86				
C7*	C10*	C11*	122.9(8)				
C7*	C10*	C15*	118.9(7)				
C11*	C10*	C15*	118.2(7)				
C10*	C11*	C12*	120(1)				
C10*	C11*	C16*	119.9(8)				
C12*	C11*	C16*	120.0(9)				
C11*	C12*	C13*	124(1)				
C11*	C12*	H22	117.05				
C13*	C12*	H22	119.33				
C12*	C13*	C14*	119.4(8)				
C12*	C13*	H23	119.83				
C14*	C13*	H23	120.81				
C13*	C14*	C15*	119.4(9)				
C13*	C14*	H24	120.49				
C15*	C14*	H24	120.14				
C10*	C15*	C14*	119.2(9)				
C10*	C15*	H25	121.03				
C14*	C15*	H25	119.77				
C11*	C16*	H26	107.94				
C11*	C16*	H27	110.37				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Torsion or Conformation Angles

(1)	(2)	(3)	(4)	angle	(1)	(2)	(3)	(4)	angle
BR1	C4	C3	O2	1(1)	C3	C2	C1	C8	-38.1(9)
BR1	C4	C3	C2	178.9(6)	C3	C4	C5	C6	-75(1)
BR1	C4	C5	C6	102.5(7)	C3	C4	C5	C8	37(1)
BR1	C4	C5	C8	-145.5(5)	C4	C5	C6	C7	87.6(7)
O1	C2	C1	C7	-114(1)	C4	C5	C6	C9	-151.6(8)
O1	C2	C1	C8	136.8(9)	C5	C6	C7	C10	-134.4(7)
O1	C2	C3	O2	8(1)	C5	C8	C1	C7	-46.9(8)
O1	C2	C3	C4	-170.5(9)	C6	C7	C1	C8	29.3(9)
O2	C3	C2	C1	-177.4(8)	C6	C7	C10	C11	-131.1(8)
O2	C3	C4	C5	178.5(7)	C6	C7	C10	C15	43(1)
O3	C8	C1	C2	-114(1)	C7	C6	C5	C8	-25.9(8)
O3	C8	C1	C7	127.0(9)	C7	C10	C11	C12	175.8(7)
O3	C8	C5	C4	116.1(9)	C7	C10	C11	C16	-9(1)
O3	C8	C5	C6	-127.2(9)	C7	C10	C15	C14	-175.6(8)
C1	C2	C3	C4	5(1)	C8	C1	C7	C10	160.3(8)
C1	C7	C6	C5	-2.8(8)	C8	C5	C6	C9	94.9(8)
C1	C7	C6	C9	-123.1(8)	C9	C6	C7	C10	105.3(8)
C1	C7	C10	C11	102.3(9)	C10	C11	C12	C13	0(1)
C1	C7	C10	C15	-83(1)	C10	C15	C14	C13	-1(2)
C1	C8	C5	C4	-70.0(8)	C11	C10	C15	C14	-1(1)
C1	C8	C5	C6	46.6(8)	C11	C12	C13	C14	-2(2)
C2	C1	C7	C6	-84.3(8)	C12	C11	C10	C15	1(1)
C2	C1	C7	C10	47(1)	C12	C13	C14	C15	2(2)
C2	C1	C8	C5	71.9(8)	C13	C12	C11	C16	-175(1)
C2	C3	C4	C5	-4(1)	C15	C10	C11	C16	177(1)
C3	C2	C1	C7	71.3(9)	BR1*	C4*	C3*	O2*	0(1)

The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

Torsion or Conformation Angles (cont)

(1)	(2)	(3)	(4)	angle	(1)	(2)	(3)	(4)	angle
BR1*	C4*	C3*	C2*	179.3(5)	C3*	C4*	C5*	C6*	-70.0(9)
BR1*	C4*	C5*	C6*	108.1(6)	C3*	C4*	C5*	C8*	39.1(9)
BR1*	C4*	C5*	C8*	-142.8(5)	C4*	C5*	C6*	C7*	89.5(7)
O1*	C2*	C1*	C7*	-104.5(8)	C4*	C5*	C6*	C9*	-147.9(7)
O1*	C2*	C1*	C8*	147.7(7)	C5*	C6*	C7*	C10*	-138.3(7)
O1*	C2*	C3*	O2*	-1.5(9)	C5*	C8*	C1*	C7*	-50.3(7)
O1*	C2*	C3*	C4*	178.9(6)	C6*	C7*	C1*	C8*	35.1(8)
O2*	C3*	C2*	C1*	177.6(6)	C6*	C7*	C10*	C11*	-131.9(8)
O2*	C3*	C4*	C5*	177.8(7)	C6*	C7*	C10*	C15*	48(1)
O3*	C8*	C1*	C2*	-117.6(8)	C7*	C6*	C5*	C8*	-21.8(7)
O3*	C8*	C1*	C7*	124.2(8)	C7*	C10*	C11*	C12*	-178.7(8)
O3*	C8*	C5*	C4*	114.8(8)	C7*	C10*	C11*	C16*	1(1)
O3*	C8*	C5*	C6*	-128.5(7)	C7*	C10*	C15*	C14*	175.7(8)
C1*	C2*	C3*	C4*	-2.0(9)	C8*	C1*	C7*	C10*	167.8(6)
C1*	C7*	C6*	C5*	-8.3(8)	C8*	C5*	C6*	C9*	100.8(8)
C1*	C7*	C6*	C9*	-129.9(7)	C9*	C6*	C7*	C10*	100.0(8)
C1*	C7*	C10*	C11*	101.1(9)	C10*	C11*	C12*	C13*	2(1)
C1*	C7*	C10*	C15*	-79.3(9)	C10*	C15*	C14*	C13*	5(2)
C1*	C8*	C5*	C4*	-70.5(7)	C11*	C10*	C15*	C14*	-5(1)
C1*	C8*	C5*	C6*	46.2(7)	C11*	C12*	C13*	C14*	-2(2)
C2*	C1*	C7*	C6*	-79.0(7)	C12*	C11*	C10*	C15*	2(1)
C2*	C1*	C7*	C10*	53.6(9)	C12*	C13*	C14*	C15*	-1(2)
C2*	C1*	C8*	C5*	67.8(7)	C13*	C12*	C11*	C16*	-178(1)
C2*	C3*	C4*	C5*	-3(1)	C15*	C10*	C11*	C16*	-179(1)
C3*	C2*	C1*	C7*	76.6(8)					
C3*	C2*	C1*	C8*	-31.3(8)					

The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.