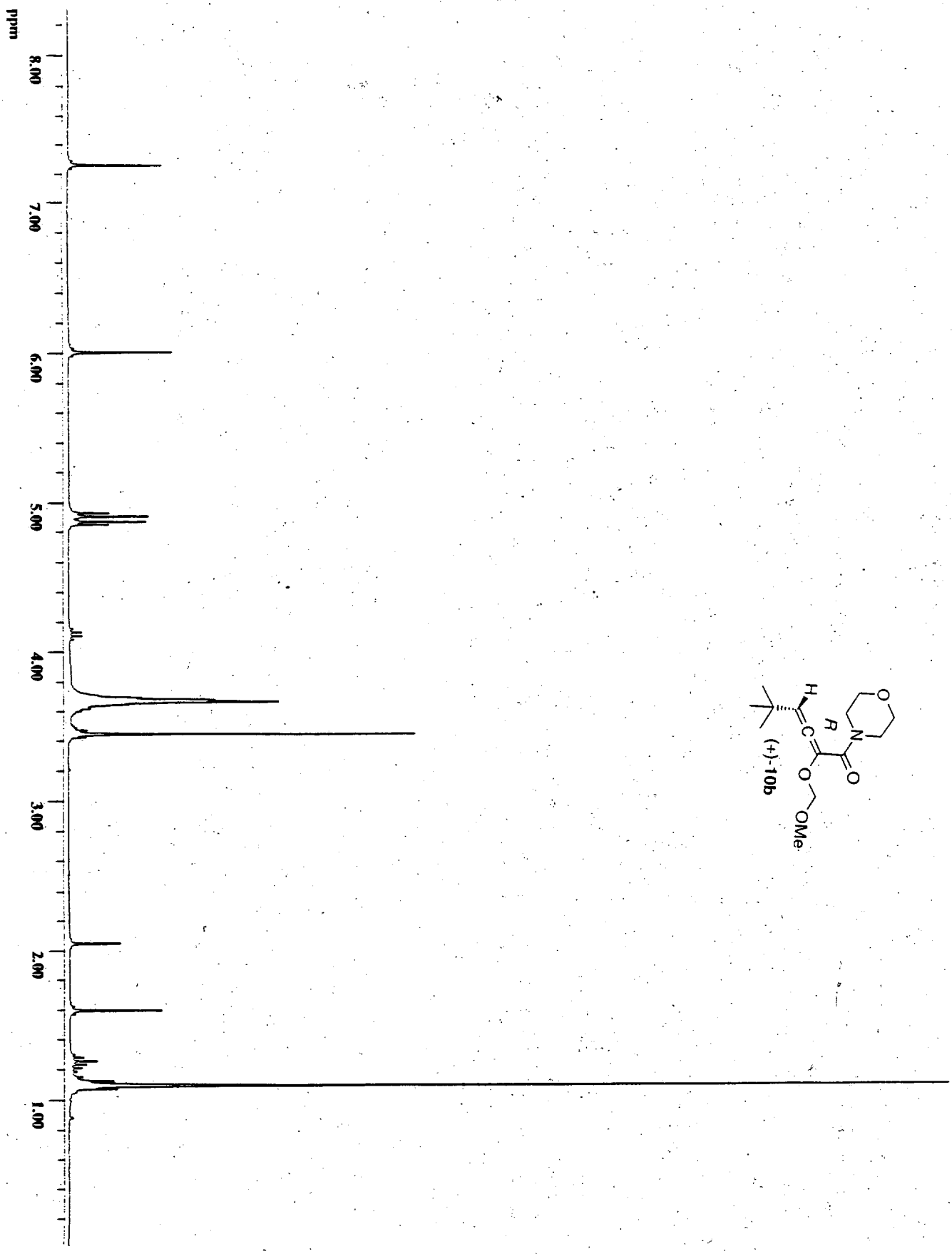
Preparation of (-)-12b. A solution of 170 mg (0.54 mmol) of the TBS ether of (*E*)-3-iodobut-2-en-3-ol in 5 mL of THF was treated with 0.63 mL of a solution of *t*-BuLi (1.70 M, 1.07 mmol) at -78 °C. After 30 min a solution of 110 mg (0.41 mmol, 98% ee, $[\alpha]_D$ +68° (c 2.5, CH_2Cl_2)) of allene (+)-**10b** was transferred to the solution of the anion by cannula. After 30 min the reaction was quenched with satd aq KH_2PO_4 and extracted with a mixture of ether and hexane. The combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated. Flash column chromatography on silica gel provided 85 mg of cyclopentenone (-)-**12b** as an oil (95% ee, 64% yield): tlc R_f = 0.44 (10% EtOAc in hexanes); $[\alpha]_D$ -56° (c 2.5, CH_2Cl_2); R_f = 0.44 (10% EtOAc in hexanes); IR (neat) 3340 (br), 1690, 1670, 1620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.20 (s, 1H), 5.53 (s, 1H), 3.71 (AB dq, 2H), 2.99 (ddt, *J* = 4.4, 1.0, 1.0 Hz, 1H), 1.98 (d, *J* = 1.0 Hz, 3H), 1.28 (s, 9H), 0.85 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.13 (C=O), 152.02 (C=<u>C</u>H), 151.10 (HO<u>C</u>=C), 135.17 (<u>C</u>=CH), 132.81 (=<u>C</u>-CH_3), 64.55 (OCH_2), 47.31 (OCH_2<u>C</u>H), 33.39 (=C-<u>C</u>(CH_3)$_3$), 29.82 (=C-C(<u>C</u>H_3)$_3$), 25.82 (SiC(<u>C</u>H_3)$_3$), 18.16 (Si<u>C</u>(CH_3)$_3$), 11.95 (=C-<u>C</u>H_3), -5.52 ($SiCH_3$); mass spectrum *m/z* 324(M^+, 6), 309(12), 267(100); hrms calcd for $C_{18}H_{32}O_3Si$ 324.2122, found 324.2124.

Preparation of (-)-15b. A solution of 13 mg (0.047 mmol) of (-)-**12b** in 2 mL of CH_2Cl_2 was treated with 20 μL (3 equiv) of (*S*)-α-methylbenzyl isocyanate and 10 μL of triethylamine at 0 °C for 1 h. The reaction mixture was partitioned between ether and water. The ether extracts were washed with brine, dried (Na_2SO_4) and evaporated. Flash column chromatography on silica gel produced carbamate (-)-**15b** as a solid (18 mg, 90% yield): mp 131-132 °C; $[\alpha]_D$ -99° (c 5, CH_2Cl_2); tlc R_f = 0.34 (15% EtOAc in hexanes); IR (neat) 3300, 1750, 1700, 1270 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36-7.24 (m, 5H), 6.14 (s, 1H), 5.35 (d, *J* = 7.3 Hz, 1H), 4.88 (m, 1H), 3.75 (AB dq, 2H), 3.09 (br, 1H), 1.95 (s, 3H), 1.55 (d, *J* = 7.5 Hz, 3H), 1.27 (s, 9H), 0.85 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.10 (C-<u>C</u>=O), 152.77 (N<u>C</u>=O), 151.83 (O-<u>C</u>=C), 151.43 (O=C-C=<u>C</u>H), 148.82 (=<u>C</u>-C(CH_3)-N), 143.04 (O-C=<u>C</u>-CH_3), 132.78 (O=C-<u>C</u>=CH), 128.68 (HC=CH-CH=), 127.43 (HC=CH-CH=), 125.99 (HC=CH-CH=), 64.41 (OCH_2), 51.09 (N-<u>C</u>-CH_3), 47.76 (OCH_2-<u>C</u>H), 33.33 (=C-<u>C</u>(CH_3)$_3$), 29.70 (=C-C(<u>C</u>H_3)$_3$), 25.75 (SiC(<u>C</u>H_3)$_3$), 22.23 (N-C-<u>C</u>H_3), 18.09 (Si<u>C</u>(CH_3)$_3$), 12.94 (=C-<u>C</u>H_3), -5.57 ($SiCH_3$), -5.64 ($SiCH_3$).

Preparation of (-)-16. A solution of 300 mg of *p*-dibromobenzene (1.27 mmol) in 3 mL of THF was treated at -78 °C with 0.60 mL of a solution of *t*-BuLi in pentane (1.70 M, 1.02 mmol) dropwise. After 1 h a solution of 110 mg of amide (-)-**10b** (93% ee, $[\alpha]_D$ -68° (c 5, CH_2Cl_2)) in 3 mL THF was transferred to the solution of the anion by cannula. After 30 min the reaction was quenched with aq satd $NaHCO_3$. The reaction was extracted 3x with ether. The organic extracts were washed with brine, dried (Na_2SO_4) and evaporated. Flash column chromatography on silica gel provided 100 mg of ketone

(-)-**16** as a yellow solid (72% yield): mp 74-76 °C; $[\alpha]_D$ -176° (c 5, CH_2Cl_2); tlc R_f = 0.32 (10% EtOAc in hexanes); IR (neat) 1940, 1660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 6.03 (s, 1H), 4.98 (AB q, 2H), 3.47 (s, 3H), 0.99 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.20 (C=O), 189.11 (=C=), 136.10 (C-C=O), 130.78 (=CH-CH=), 130.26 (=CH-CH=), 128.62 (C-Br), 126.55 (C=C=CH), 119.81 (C=C=CH), 94.20 (OCH_2O), 56.16 (OCH_3), 34.58 ($C(CH_3)_3$), 29.10 ($C(CH_3)_3$).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6.00
5.00
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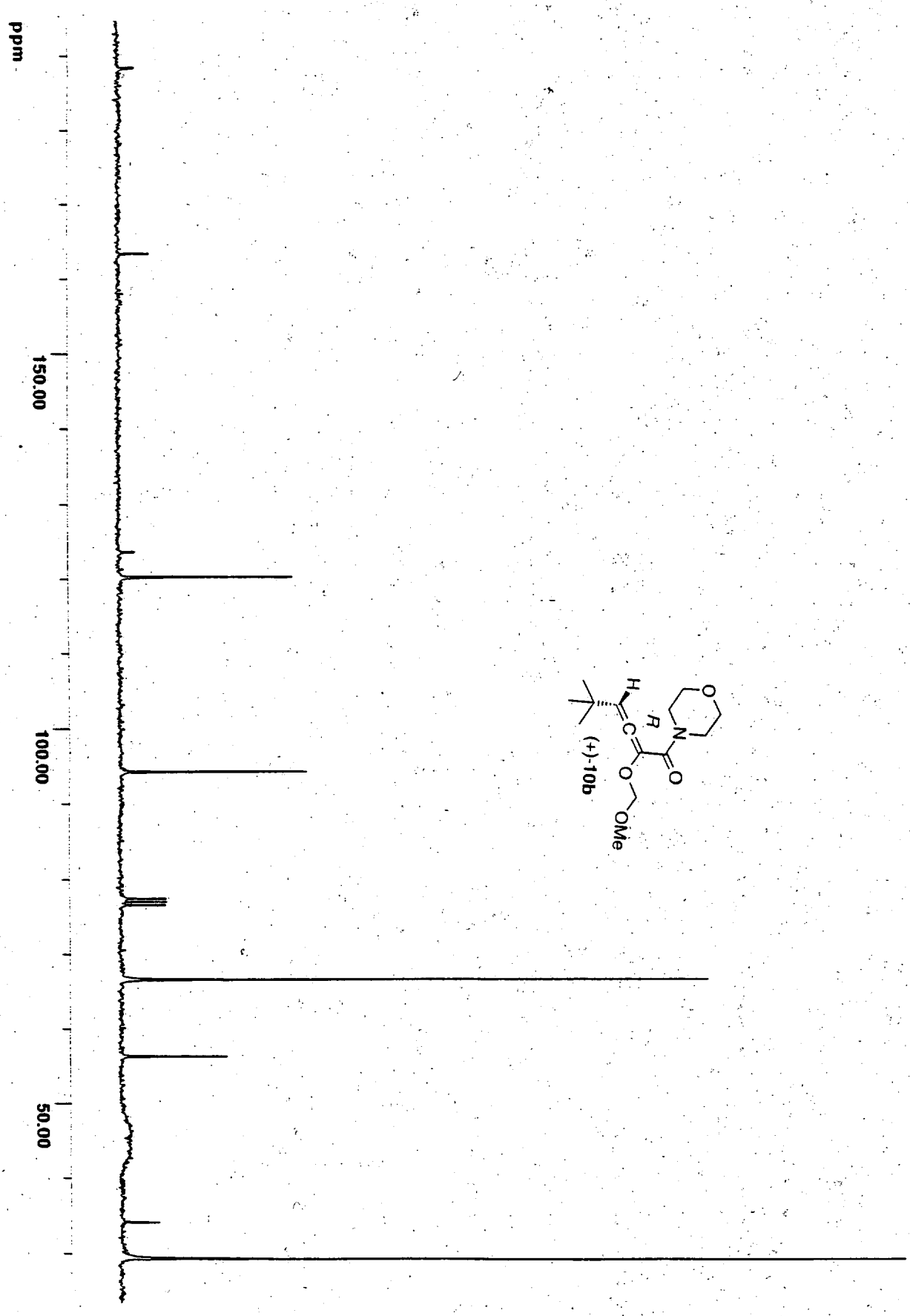
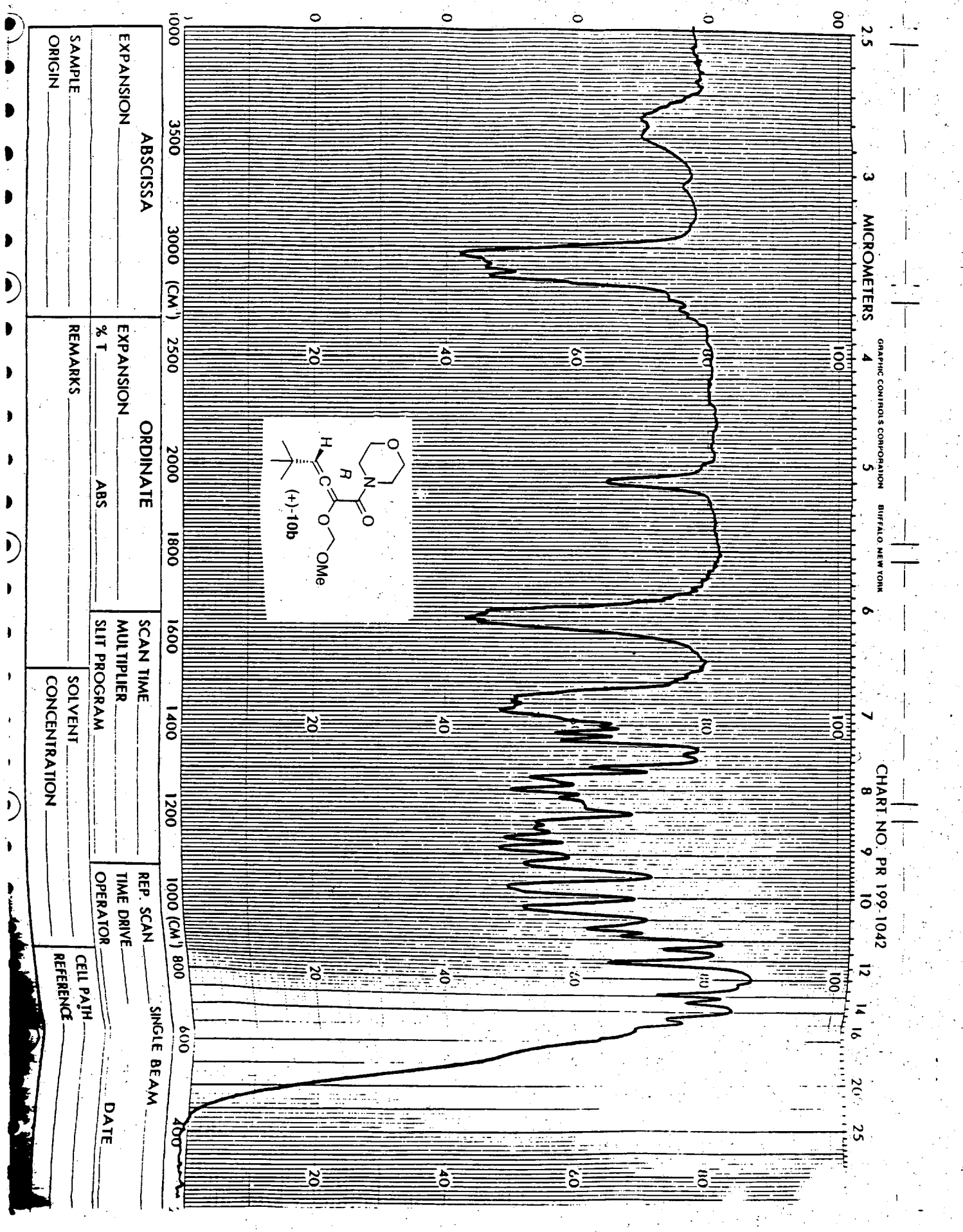
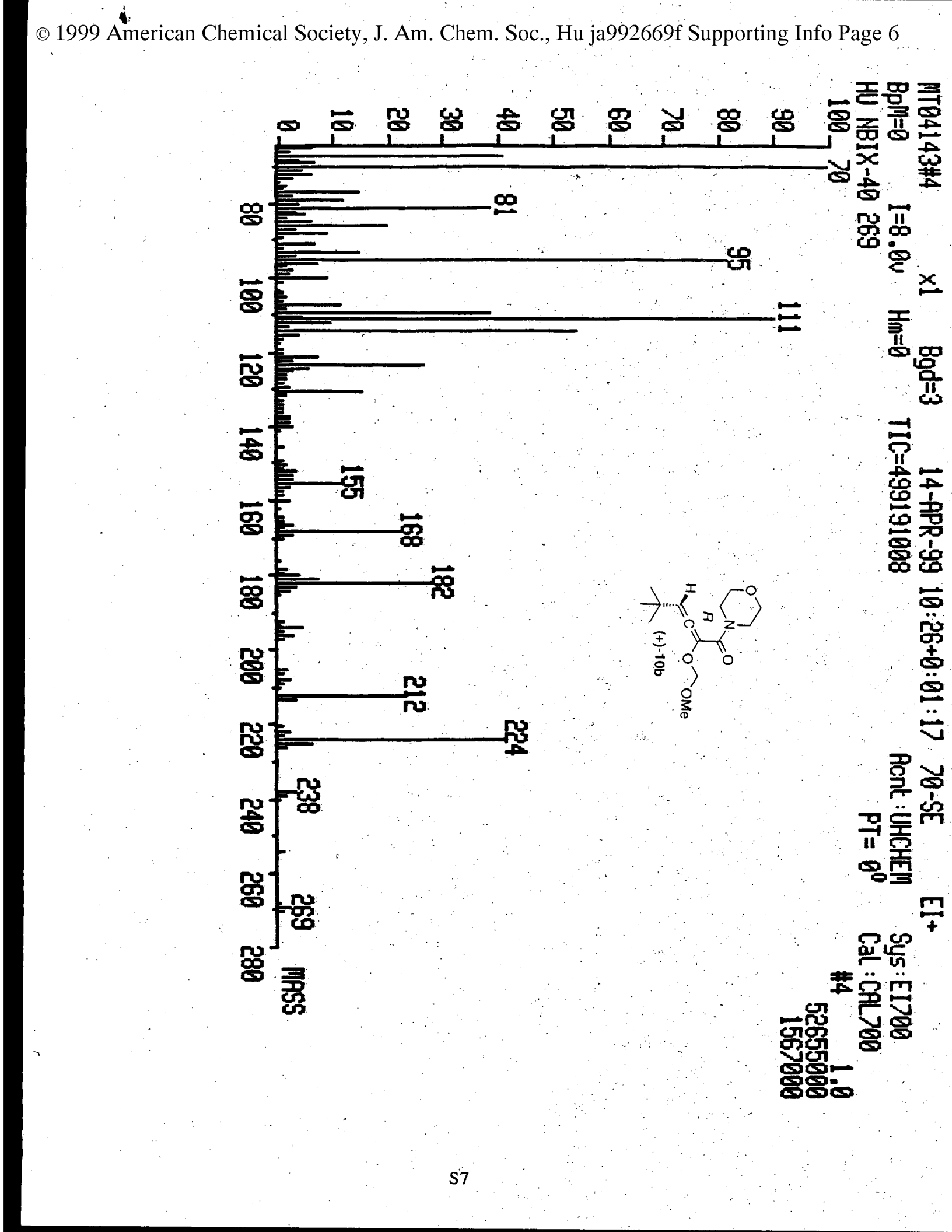
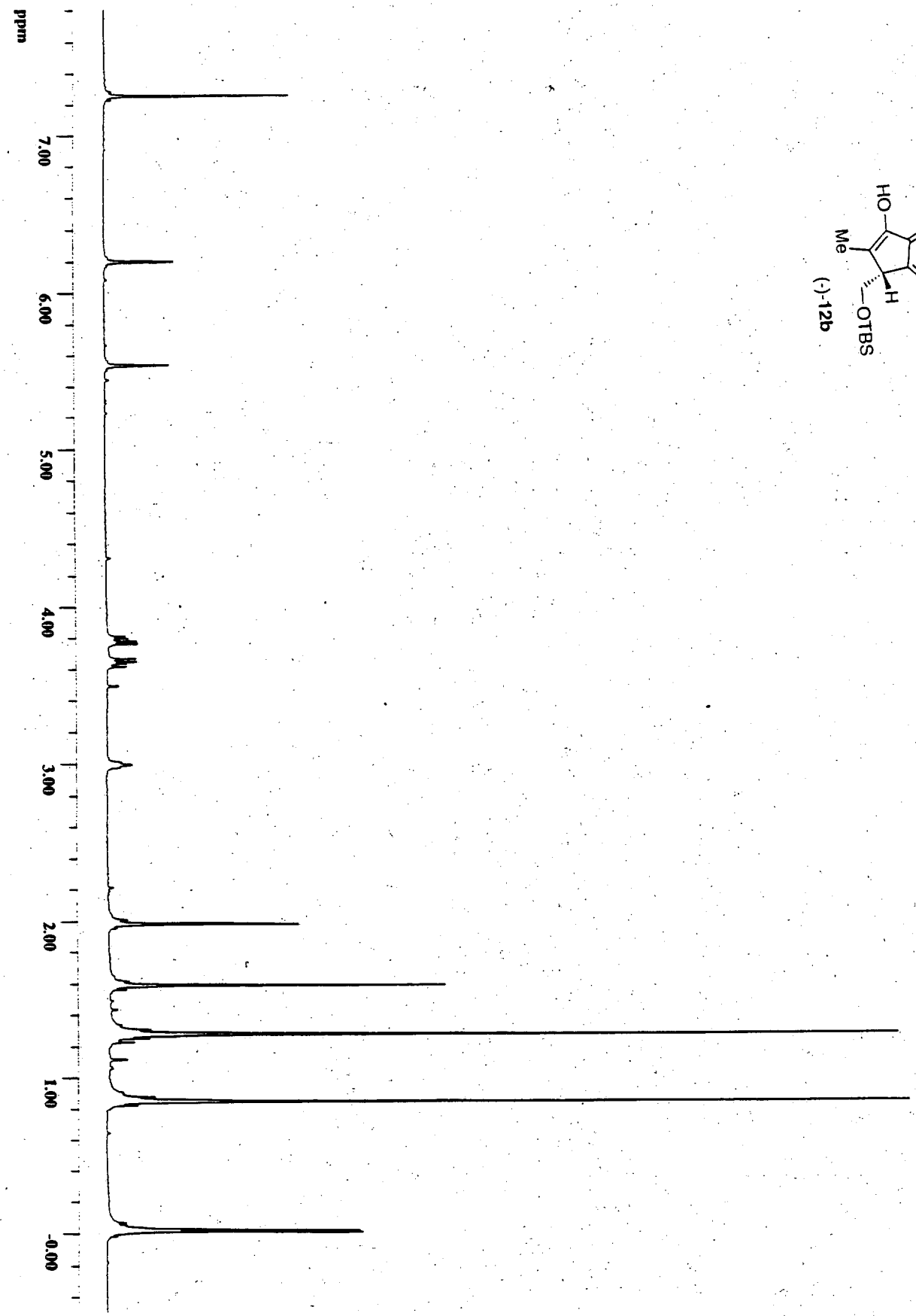
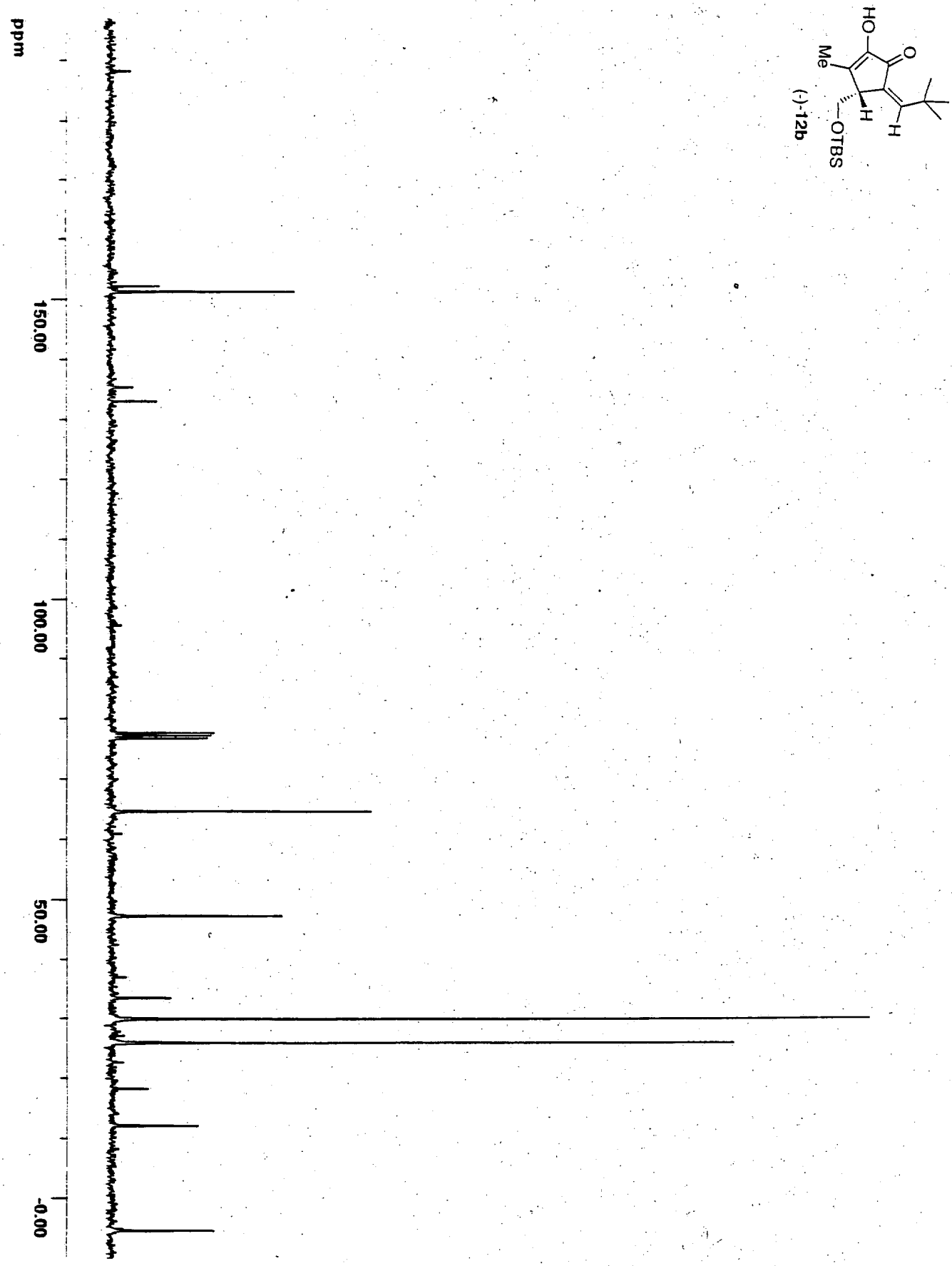
3.00
2.00
1.00
(+)-10b
OMe







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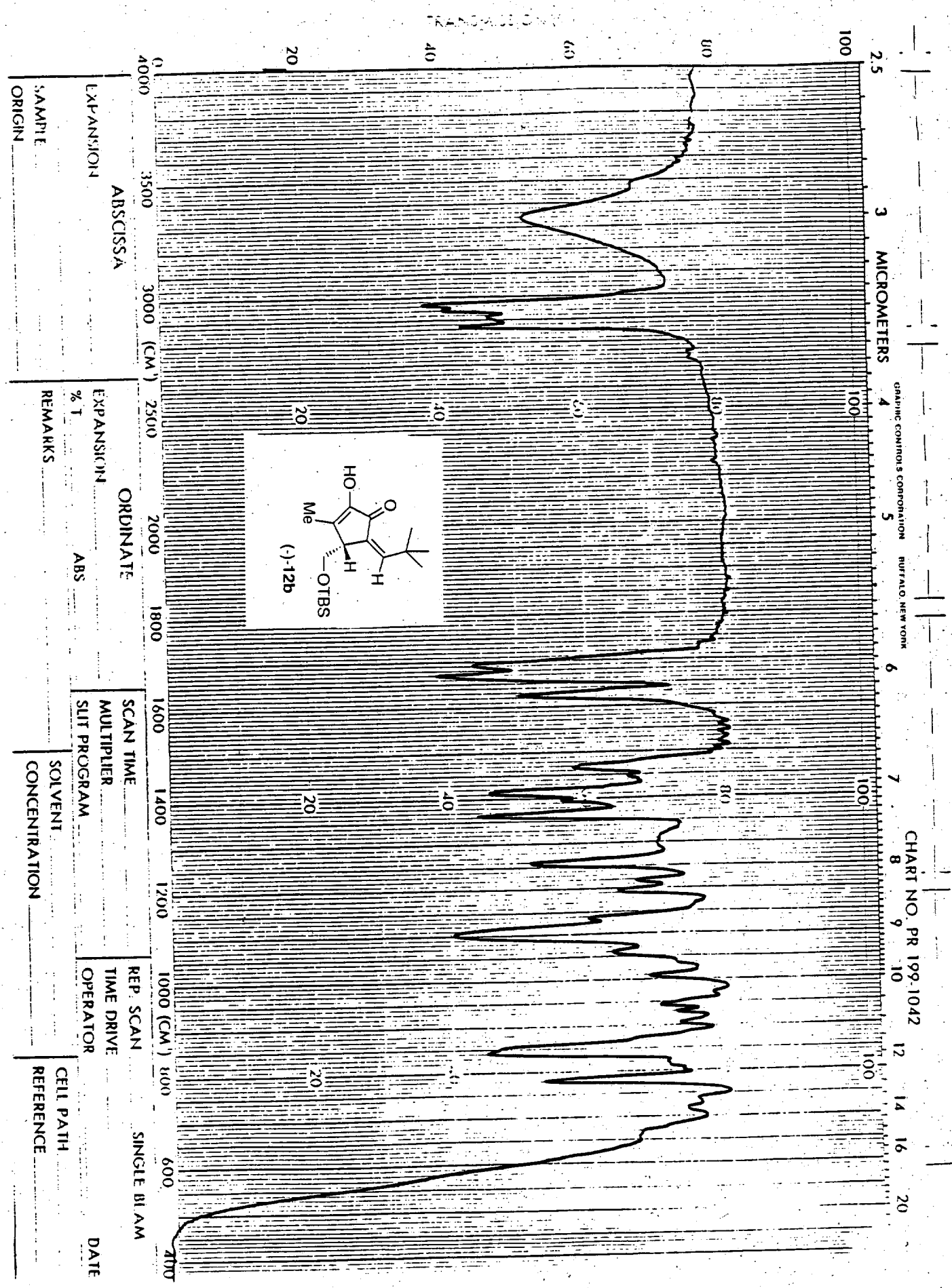
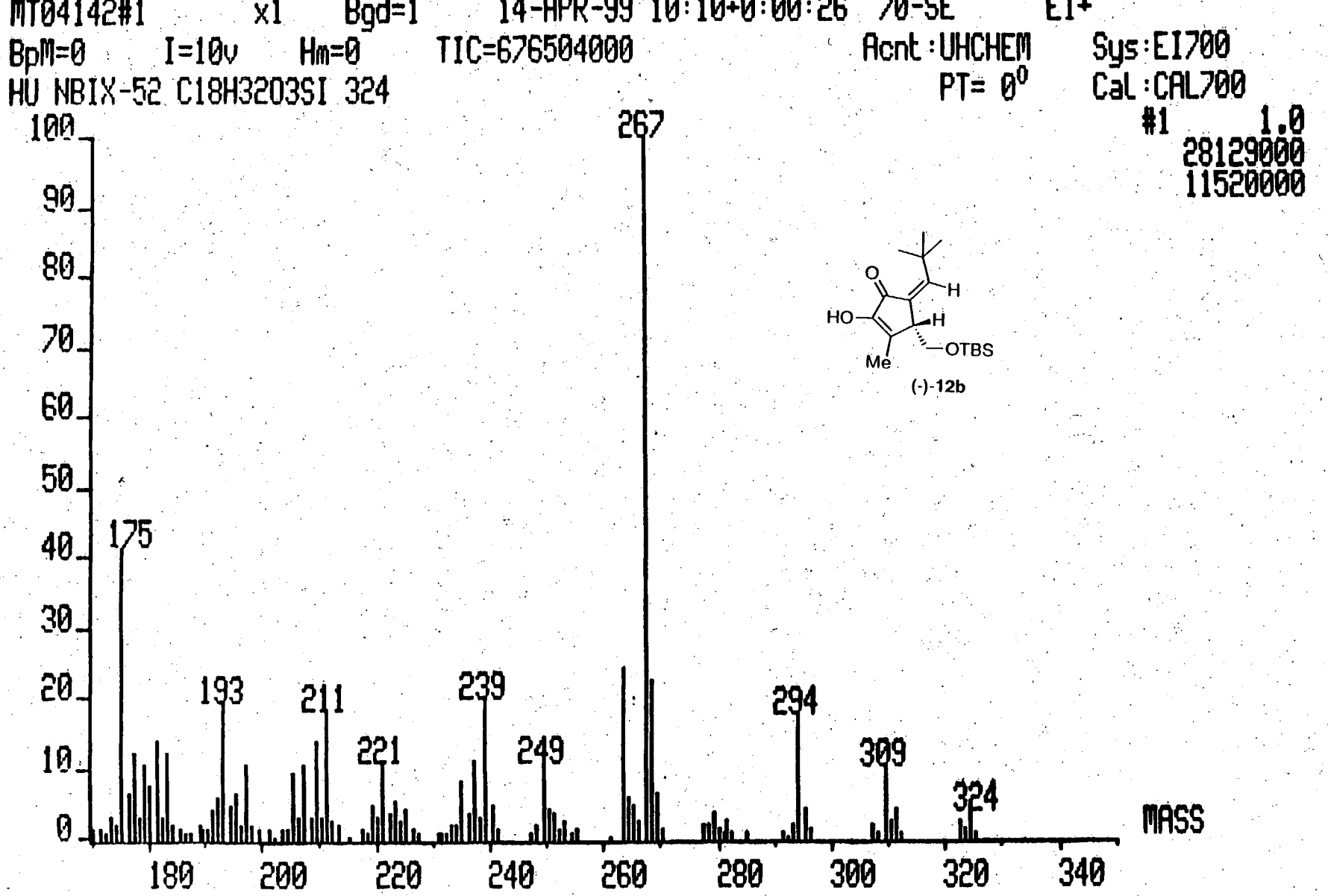
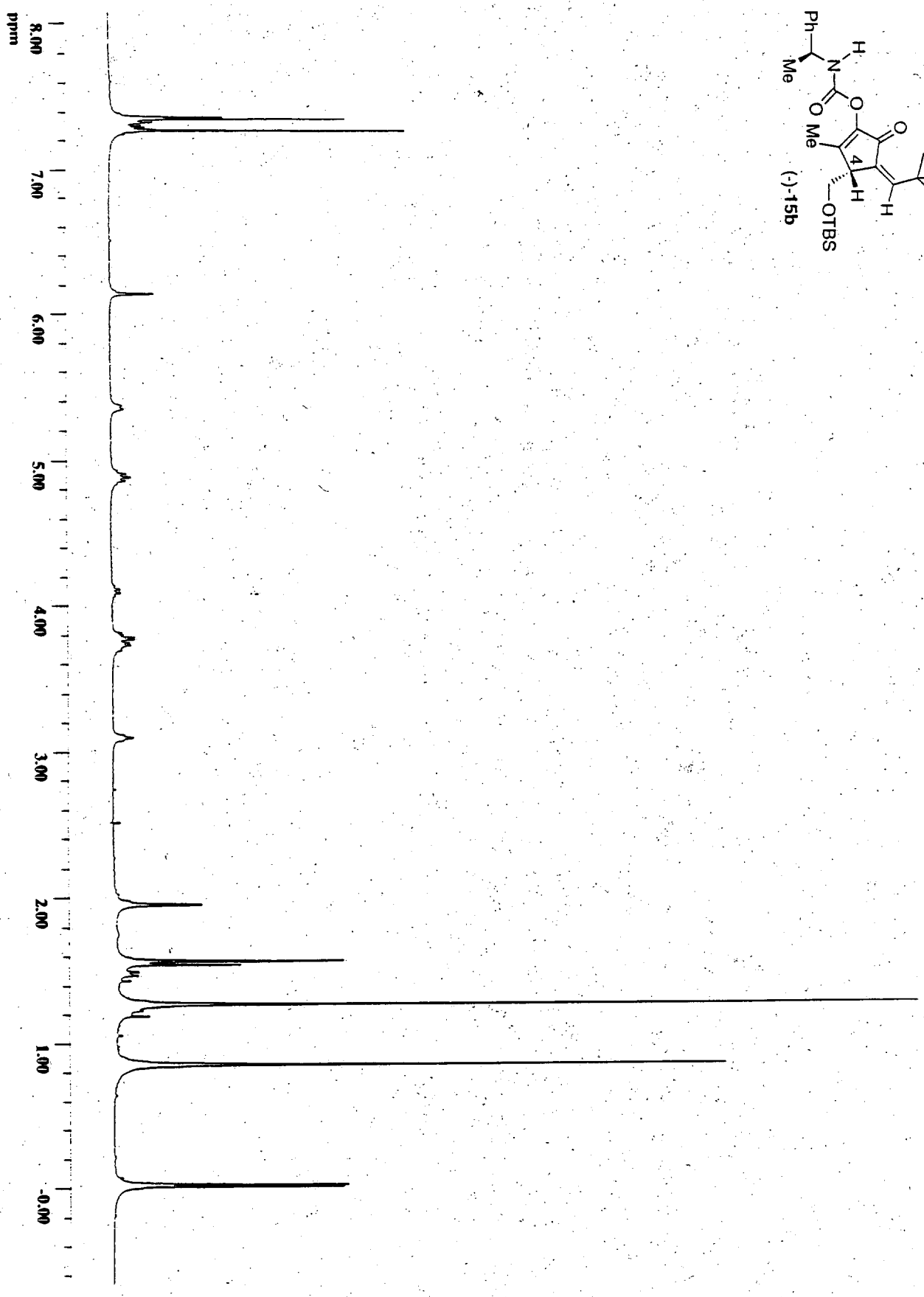
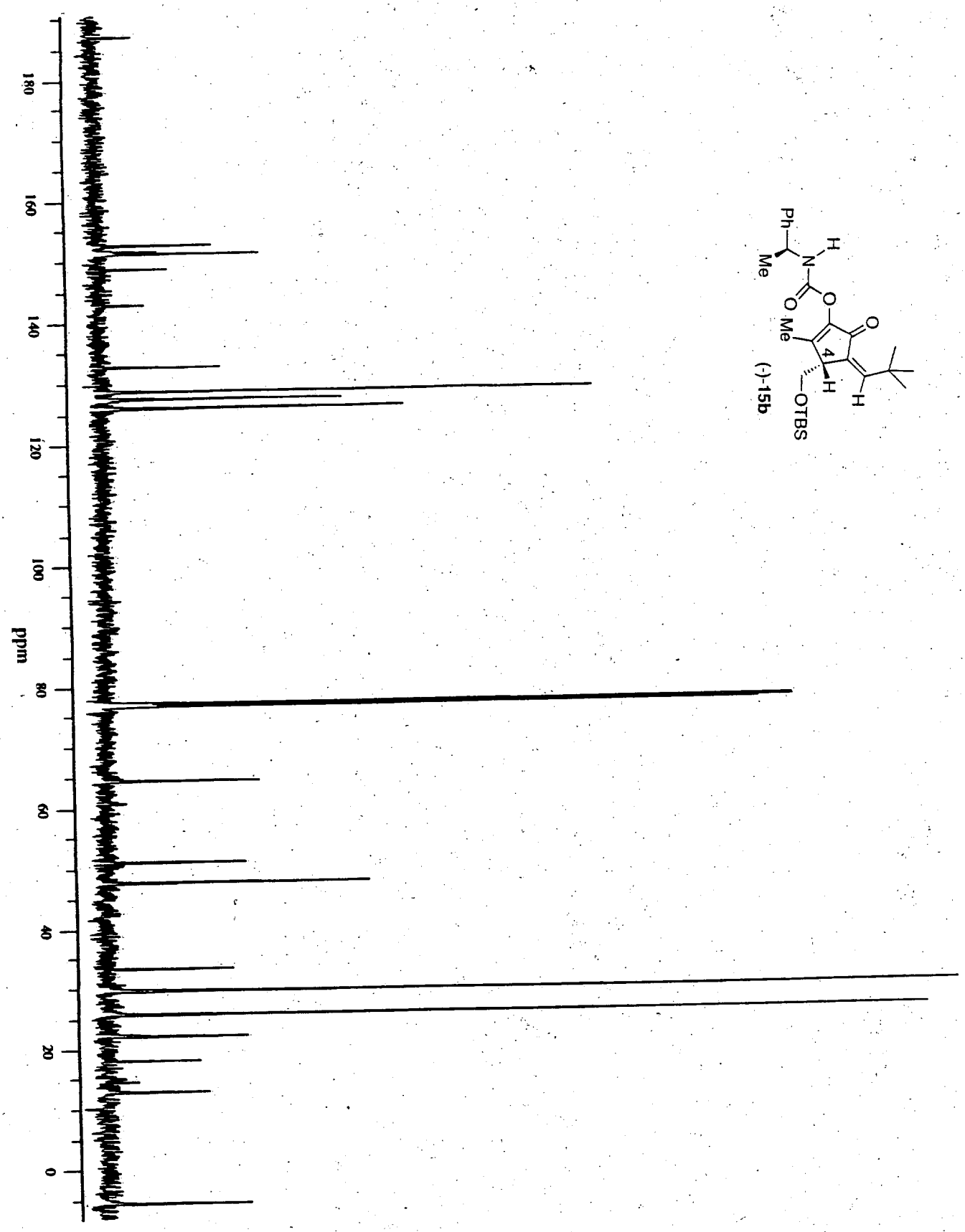
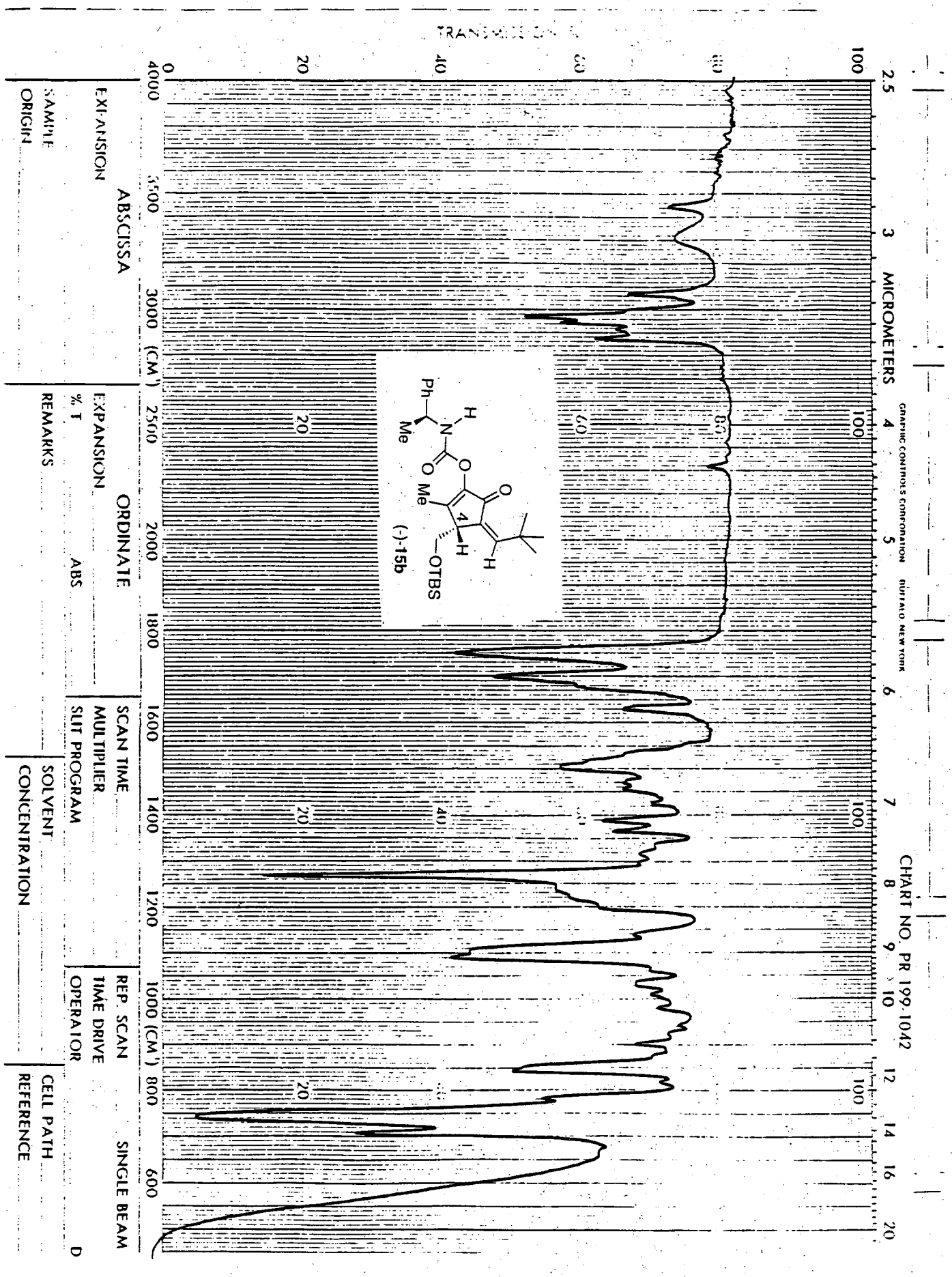
H
H
OTBS
(-)-12b

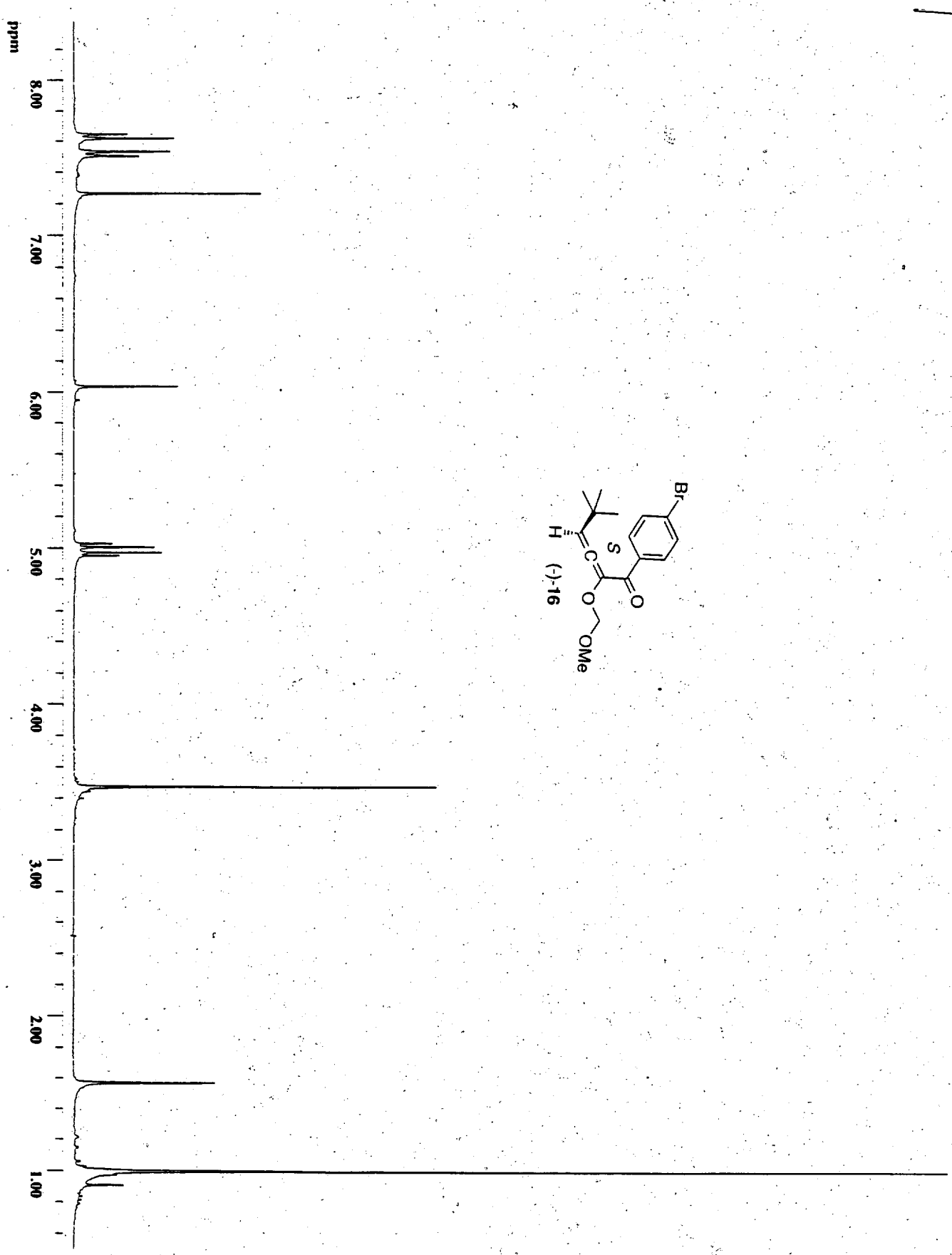


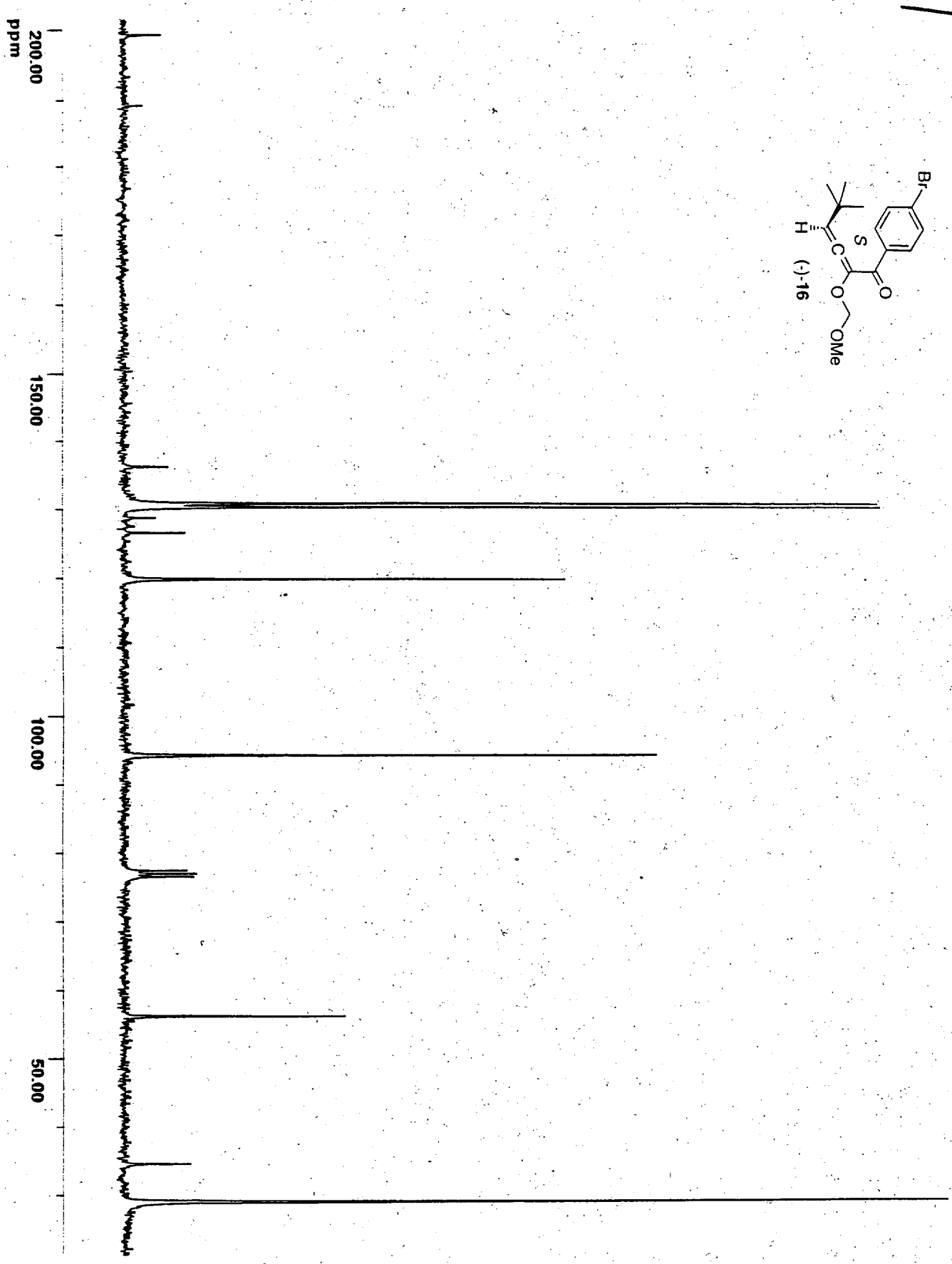


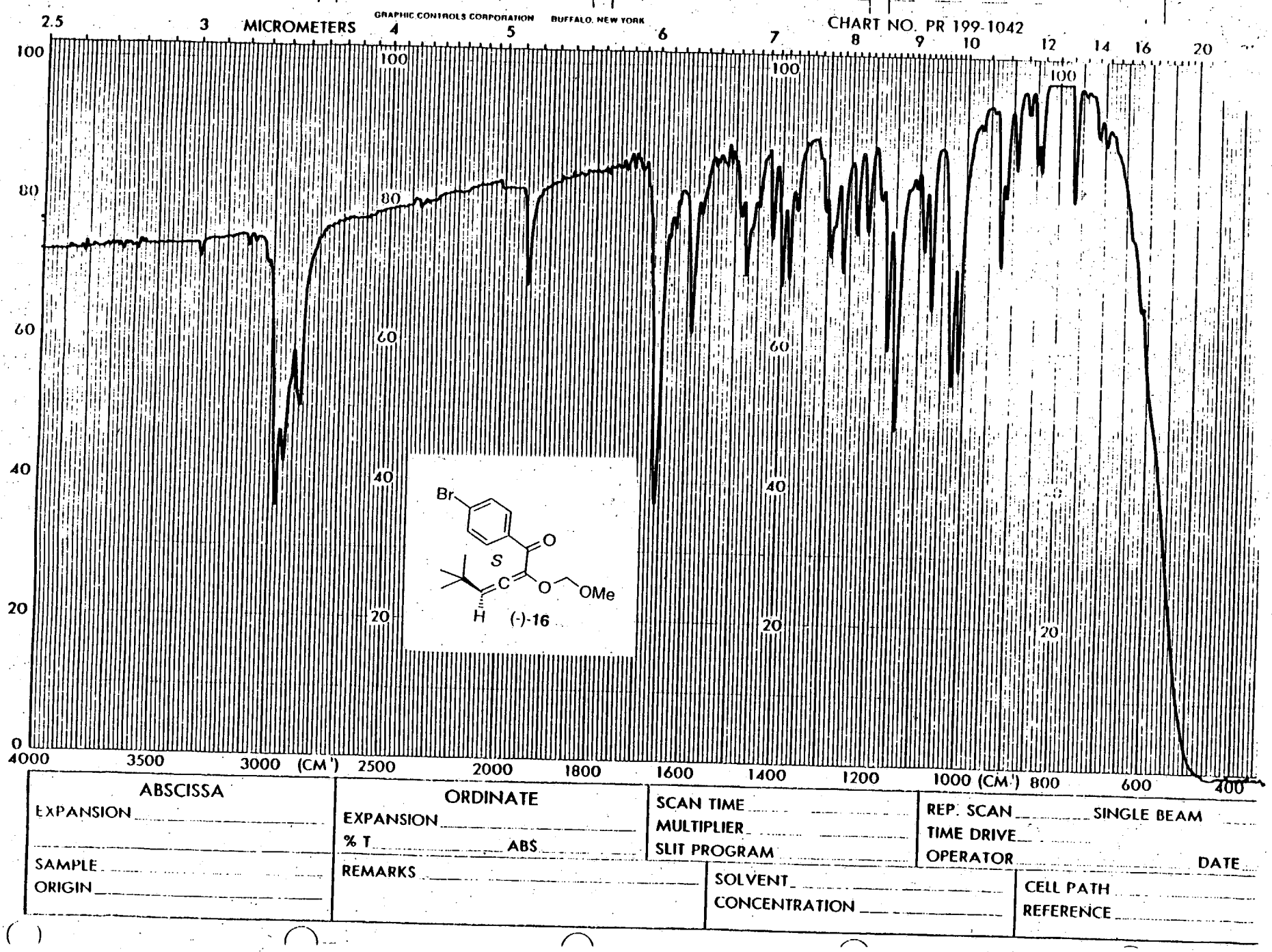


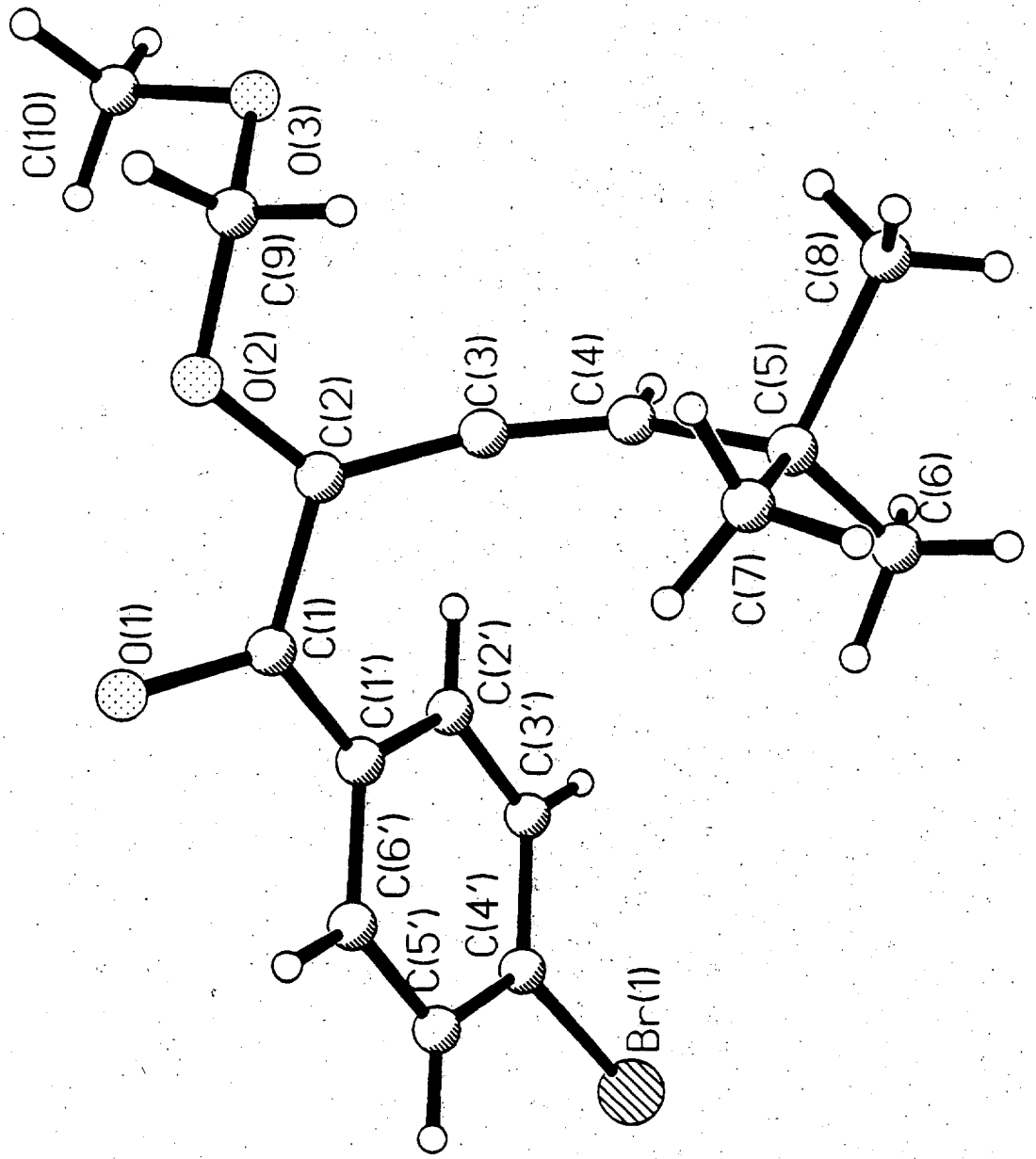








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C(9)
O(2)
C(2)
C(3)
C(4)
C(5)
C(8)
C(6)
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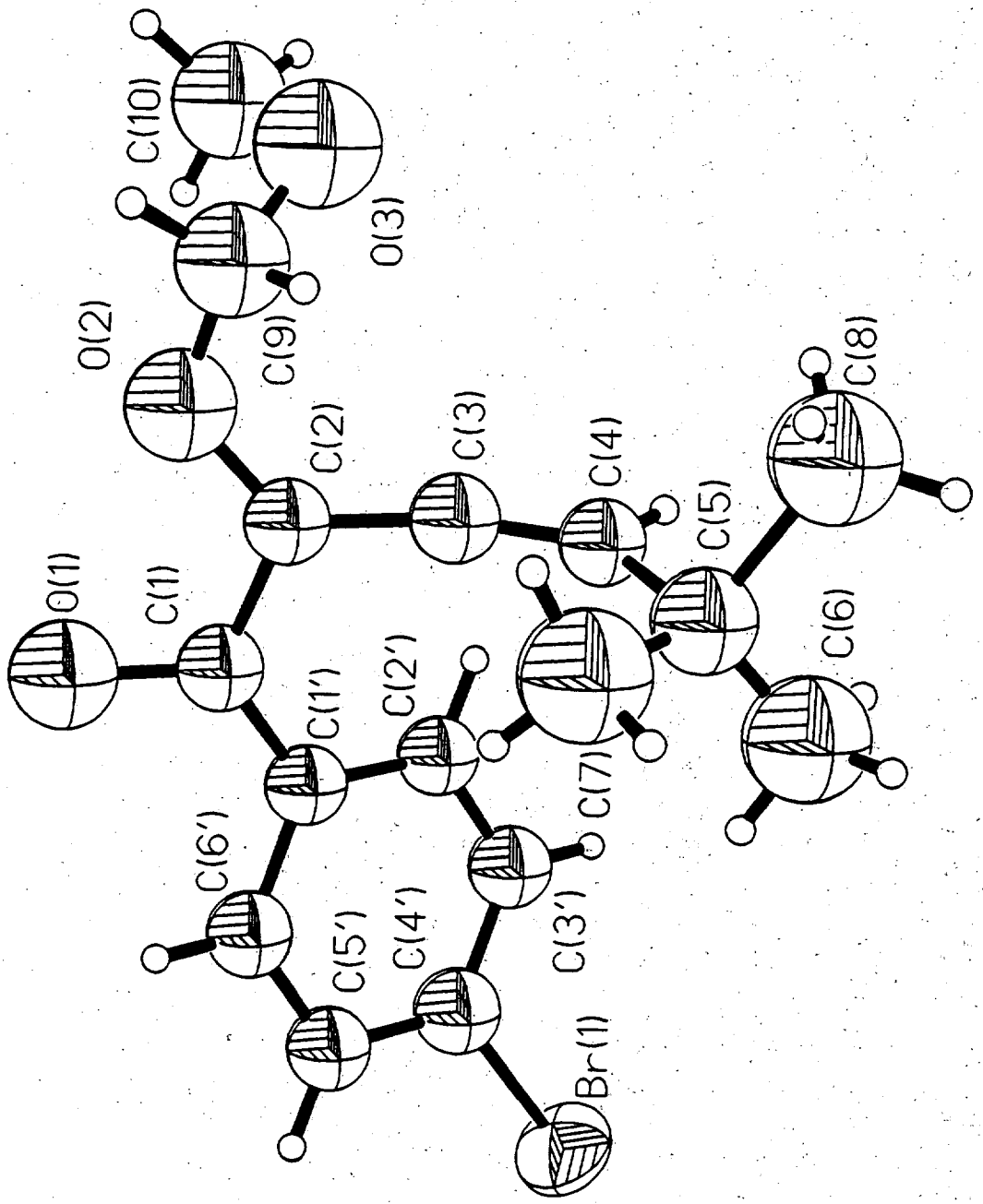
C(3')
C(6')
C(5')
C(4')
Br(1)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O(3)
O(2)
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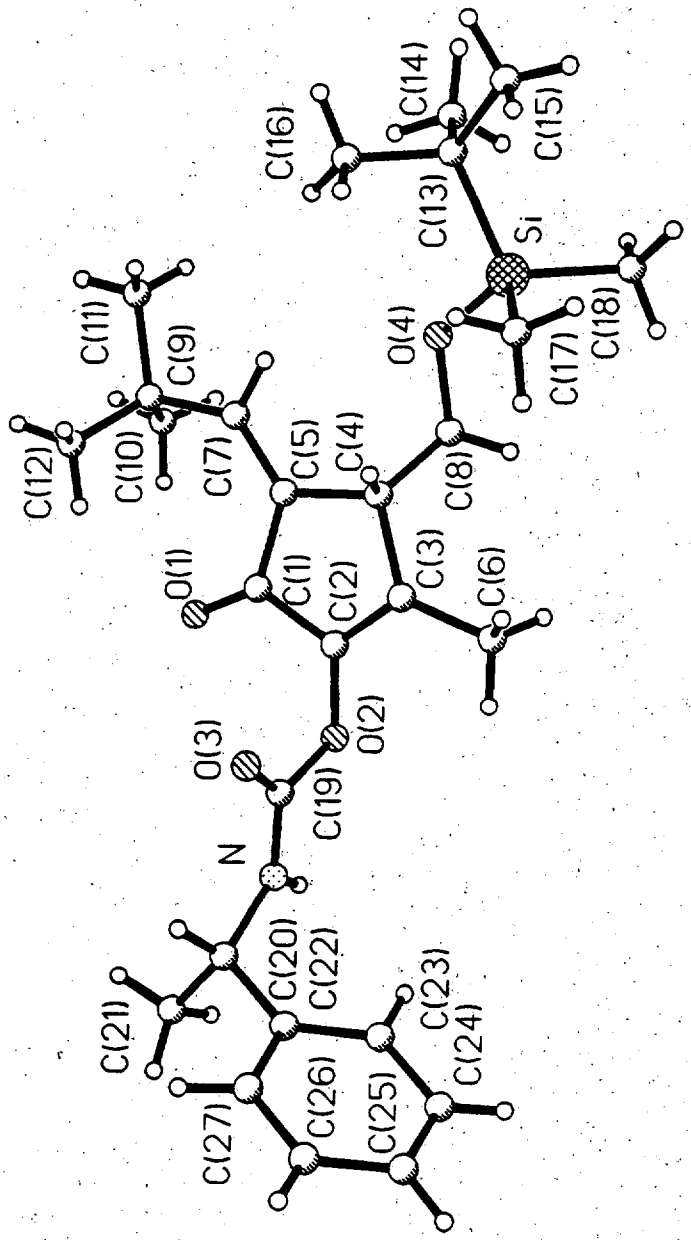
C(6')
C(5')
C(4')
C(3')
Br(1)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C(1)
C(2)
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C(6)
O(3)
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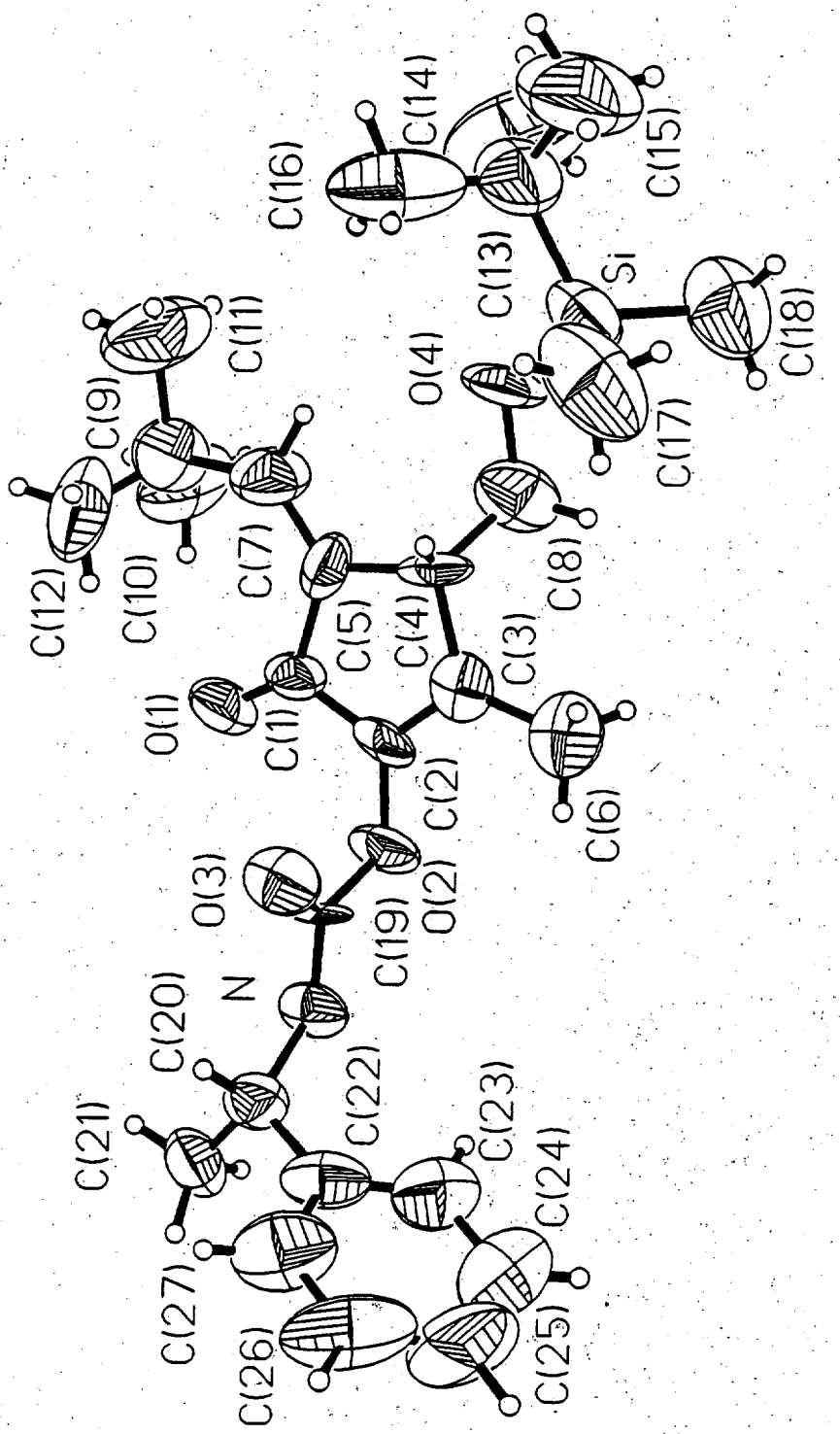
C(23)
C(21)
C(24)
C(26)
C(25)
C(27)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C(8)
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C(4)
C(3)
O(1)
C(1)
C(2)
C(6)
O(3)
O(2)
C(19)
C(20)
N
C(21)
C(22)
C(23)
C(24)
C(27)
C(26)
C(25)

Data Collection and Structure Refinement for (-)-**16**

A clear, yellow needle was mounted on a glass fiber with epoxy cement at room temperature. A Nicolet P3 diffractometer, using graphite monochromated Mo Kα radiation, was used to determine unit-cell parameters and for data collection. During data collection, the intensities of three check reflections were monitored every 97 reflections and showed a small decrease in intensity. The data were corrected for Lorentz and polarization effects using the SHELXL system. An absorption correction was applied using two ψ -scans.

This structure was solved using a Patterson map generated by SHELX-86 software. The bromine atom and most of the non-hydrogen atoms along the backbone of the system were found in the initial map. The rest of the atoms in the system were found in subsequent Fourier difference maps. Atoms in the phenyl ring were restrained to a hexagonal shape with fixed distances. In the final model only the bromine atom was refined anisotropically. Hydrogen atoms were included at calculated positions and refined with fixed thermal parameters. After the final cycle of refinement, the largest remaining peak was 0.286 eÅ^{-3} near Br and the FLAK parameter, which indicates the absolute configuration, was -0.01(5). Final parameters are given in tables 1-5.

Crystal Data for (-)-**16**: Dimensions 0.2 x 0.2 x 1.0 mm, Monoclinic, $P2_1$, a = 11.40(2) Å b = 6.61(1) Å c = 11.41(2) Å β = 97.07(1)° V = 853(3) Å^3, z = 2, Nicolet P3 using graphite monochromated Mo Kα radiation. A total of 2605 reflections were measured, and 1210 unique ($2\theta<45°$, r_{int} = 0.1561) were used in refinement. Solved by Patterson methods and refined by full-matrix least squares on F^2 that converged to R_1 = 0.0800 ($I>2\sigma$), R_1 = 0.1860 (all data), wR^2 = 0.1769 ($I>2\sigma$), wR^2 = 0.2196 (all data), absolute structure parameter -0.01(5).

Data Collection and Structure Refinement for (-)-**15b**

A clear, colorless needle was cut from a cluster, and mounted on a glass fiber with epoxy cement at room temperature. A Nicolet P3 diffractometer, using graphite monochromated Mo Kα radiation, was used to determine unit-cell parameters and for data collection. During data collection, the intensities of three check reflections were monitored every 97 reflections and showed no decreases in intensity. The data were corrected for Lorentz and polarization effects using the SHELXL system. An absorption correction was applied using one ψ -scan.

This structure was solved by direct methods using SHELX-86 software using all E values greater than 1.1. Refinement was carried out using SHELX-93 software. The initial solution located the silicon atom, the five-membered ring, and its links to both the silicon atom and the six-membered ring. The rest of the atoms in the system were located from subsequent Fourier difference maps. In the final model, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions (except methyl hydrogens which were refined as rigid rotors) and refined with a fixed thermal parameter. After the final cycle of refinement, the largest remaining peak was 0.15 eÅ^{-3} near C94) and the FLAK parameter which indicates the absolute configuration was 0.4(8). Thus the absolute configuration of this molecule was determined by using the known absolute configuration (*S*) at C(20). Final parameters are given in tables 6-10.

Crystal Data for (-)-**15b**: Dimensions 0.13 x 0.13 x 1.0 mm, Orthorhombic, $P2_12_12$, a = 15.65(2) Å b = 29.43(4) Å c = 6.833(8) Å V = 3147(7) Å^3, z = 4, Nicolet P3 using graphite monochromated Mo Kα radiation. A total of 2652 reflections were measured, and 1862 unique ($2\theta<35°$, r_{int} = 0.1284) were used in refinement. Solved by direct methods and refined by full-matrix least squares on F^2 that converged to R_1 = 0.0713 ($I>2\sigma$), R_1 = 0.1257 (all data), wR^2 = 0.1740 ($I>2\sigma$), wR^2 = 0.1989 (all data), absolute structure parameter 0.4(8).

Table 1. Crystal data and structure refinement for (-)-16.

Empirical formula	$C_{16}H_{19}BrO_3$
Formula weight	339.22
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 11.40(2) Å a = 90 ° b = 6.610(13) Å b = 97.070(10) ° c = 11.41(2) Å c = 90 °
Volume	853(3) $Å^3$
Z	2
Density (calculated)	1.320 Mg/m^3
Absorption coefficient	2.412 mm^{-1}
F(000)	348
Crystal size	1 x 0.2 x 0.2 mm
Theta range for data collection	1.80 to 22.49 °
Index ranges	-9 \ h \ 9, -7 \ k \ 7, -12 \ M \ 12
Reflections collected	2605
Independent reflections	1210 (R_{int} = 0.1561)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1019 / 0 / 77
Goodness-of-fit on F^2	0.922
Final R indices [I>2r(I)]	R1 = 0.0800, wR2 = 0.1769
R indices (all data)	R1 = 0.1860, wR2 = 0.2196
Absolute structure parameter	-0.01(5)
Largest diff. peak and hole	0.286 and -0.397 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for (-)-16. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Br(1)	2321(3)	0	8442(2)	89(1)
C(4')	3655(11)	-1711(19)	8427(8)	65(6)
C(5')	3566(11)	-3719(20)	8066(8)	58(5)
C(6')	4582(14)	-4877(14)	8048(7)	58(4)
C(1')	5686(11)	-4026(20)	8390(8)	54(5)
C(2')	5774(10)	-2018(20)	8751(8)	55(5)
C(3')	4759(13)	-860(14)	8769(8)	60(5)
C(1)	6696(22)	-5305(35)	8293(12)	57(5)
O(1)	6641(20)	-7234(27)	8551(10)	89(5)
C(2)	7876(24)	-4676(34)	7965(12)	54(6)
O(2)	8736(23)	-5991(24)	8200(11)	89(5)
C(3)	7953(25)	-2765(29)	7457(13)	58(5)
C(4)	7839(22)	-1138(30)	6929(13)	54(5)
C(5)	7495(30)	-666(37)	5601(15)	75(7)
C(6)	6617(33)	684(43)	5432(18)	112(10)
C(7)	7292(29)	-2564(44)	4938(16)	111(9)
C(8)	8708(27)	495(43)	5203(17)	112(9)
C(9)	9822(33)	-5547(40)	7903(18)	90(8)
O(3)	10612(26)	-4218(25)	8555(15)	117(7)
C(10)	10865(25)	-4827(66)	9752(13)	101(7)

Table 3. Bond lengths [Å] and angles [°] for (-)-16.

Br(1)-C(4')	1.897(10)	C(4')-C(5')	1.39
C(4')-C(3')	1.39	C(5')-C(6')	1.39
C(6')-C(1')	1.39	C(1')-C(2')	1.39
C(1')-C(1)	1.44(2)	C(2')-C(3')	1.39
C(1)-O(1)	1.31(3)	C(1)-C(2)	1.50(3)
C(2)-O(2)	1.31(3)	C(2)-C(3)	1.40(3)
O(2)-C(9)	1.35(4)	C(3)-C(4)	1.23(2)
C(4)-C(5)	1.55(3)	C(5)-C(6)	1.34(4)
C(5)-C(7)	1.47(3)	C(5)-C(8)	1.69(4)
C(9)-O(3)	1.40(3)	O(3)-C(10)	1.42(2)

C(5')-C(4')-C(3')	120.0	C(5')-C(4')-Br(1)	122.9(8)
C(3')-C(4')-Br(1)	117.1(9)	C(6')-C(5')-C(4')	120.0
C(1')-C(6')-C(5')	120.0	C(2')-C(1')-C(6')	120.0
C(2')-C(1')-C(1)	123.5(14)	C(6')-C(1')-C(1)	116.4(14)
C(1')-C(2')-C(3')	120.0	C(2')-C(3')-C(4')	120.0
O(1)-C(1)-C(1')	120(2)	O(1)-C(1)-C(2)	113(2)
C(1')-C(1)-C(2)	127(2)	O(2)-C(2)-C(3)	127(2)
O(2)-C(2)-C(1)	116(2)	C(3)-C(2)-C(1)	117(2)
C(2)-O(2)-C(9)	119(2)	C(4)-C(3)-C(2)	170(3)
C(3)-C(4)-C(5)	131(2)	C(6)-C(5)-C(7)	115(3)
C(6)-C(5)-C(4)	112(2)	C(7)-C(5)-C(4)	110(2)
C(6)-C(5)-C(8)	106(2)	C(7)-C(5)-C(8)	109(2)
C(4)-C(5)-C(8)	104(2)	O(2)-C(9)-O(3)	123(2)
C(9)-O(3)-C(10)	112(2)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for (-)-16. The anisotropic displacement factor exponent takes the form: $-2p^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Br(1)	56(4)	90(2)	125(2)	21(2)	26(1)	23(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (-)-16.

	x	y	z	U(eq)
H(5')	2827(12)	-4289(29)	7838(12)	80
H(6')	4522(19)	-6221(15)	7806(11)	80
H(2')	6513(12)	-1448(29)	8980(12)	80
H(3')	4818(19)	484(14)	9011(12)	80
H(4)	7983(22)	-3(30)	7407(13)	80
H(6A)	6787(40)	1803(68)	5962(65)	80
H(6B)	5890(30)	57(49)	5580(76)	80
H(6C)	6543(74)	1162(125)	4632(33)	80
H(7A)	6738(78)	-3383(100)	5295(69)	80
H(7B)	8026(29)	-3282(92)	4950(92)	80
H(7C)	6981(117)	-2268(46)	4137(34)	80
H(8A)	8489(33)	1791(76)	4865(74)	80
H(8B)	9042(52)	-321(82)	4633(68)	80
H(8C)	9279(47)	674(133)	5886(25)	80
H(9A)	9701(33)	-5025(40)	7103(18)	80
H(9B)	10235(33)	-6825(40)	7868(18)	80
H(10A)	10148(30)	-5247(180)	10043(37)	80
H(10B)	11204(114)	-3712(103)	10216(25)	80
H(10C)	11415(93)	-5933(167)	9808(21)	80

Table 6. Crystal data and structure refinement for (-)-15b.

Identification code	huaa
Empirical formula	$C_{27}H_{41}NO_4Si$
Formula weight	471.70
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12$
Unit cell dimensions	a = 15.65(2) Å a = 90 ° b = 29.43(4) Å b = 90 ° c = 6.833(8) Å c = 90 °
Volume	3147(7) $Å^3$
Z	4
Density (calculated)	0.995 Mg/m^3
Absorption coefficient	0.101 mm^{-1}
F(000)	1024
Crystal size	1 x .13 x .13 mm
Theta range for data collection	1.90 to 17.16 °
Index ranges	-12 \ h \ 12, -24 \ k \ 24, -5 \ M \ 5
Reflections collected	2652
Independent reflections	1862 (R_{int} = 0.1284)
Absorption correction	Psi-scans
Max. and min. transmission	0.995 and 0.938
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1711 / 0 / 308
Goodness-of-fit on F^2	0.908
Final R indices [I>2r(I)]	R1 = 0.0713, wR2 = 0.1740
R indices (all data)	R1 = 0.1257, wR2 = 0.1989
Absolute structure parameter	0.4(8)
Largest diff. peak and hole	0.156 and -0.174 $eÅ^{-3}$

Table 7. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for (-)-15b. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Si	7574(4)	2264(2)	3926(6)	90(2)
O(1)	6732(8)	336(4)	-2281(16)	80(4)
O(2)	4978(9)	638(4)	-1629(19)	72(3)
O(3)	5115(8)	1032(4)	-4539(16)	79(4)
O(4)	7559(7)	1742(3)	3133(15)	91(3)
C(1)	6572(16)	690(7)	-1389(26)	63(5)
C(2)	5705(17)	857(7)	-915(26)	55(4)
C(3)	5708(12)	1255(7)	159(25)	60(5)
C(4)	6612(12)	1389(6)	694(25)	67(5)
C(5)	7160(14)	1020(7)	-342(26)	65(5)
C(6)	4917(11)	1523(5)	810(21)	90(5)
C(7)	8031(15)	1027(5)	-340(27)	92(6)
C(8)	6798(12)	1469(6)	2820(26)	99(6)
C(9)	8699(14)	708(9)	-1166(40)	127(9)
C(10)	8625(10)	220(6)	-166(31)	143(8)
C(12)	8639(13)	672(7)	-3303(35)	169(11)
C(11)	9580(12)	894(6)	-479(39)	205(13)
C(13)	8742(14)	2419(8)	3975(39)	125(8)
C(14)	9209(14)	2109(8)	5401(38)	217(14)
C(15)	8862(14)	2923(7)	4465(33)	202(11)
C(16)	9137(14)	2344(7)	1938(38)	187(12)
C(17)	6947(15)	2645(6)	2215(24)	170(9)
C(18)	7091(12)	2322(6)	6438(21)	144(8)
C(19)	4781(11)	723(7)	-3605(35)	64(6)
N	4169(10)	445(4)	-4234(20)	63(4)
C(20)	3785(12)	472(6)	-6205(26)	66(4)
C(21)	3631(9)	-26(6)	-7024(20)	91(5)
C(22)	2966(15)	741(7)	-6336(45)	83(6)
C(23)	2418(24)	786(7)	-4741(42)	129(7)
C(24)	1641(26)	1034(11)	-4895(52)	163(11)
C(25)	1402(22)	1213(13)	-6613(76)	198(18)
C(26)	1945(25)	1191(9)	-8237(49)	144(11)
C(27)	2689(19)	945(8)	-8060(43)	113(7)

Table 8. Bond lengths [Å] and angles [°] for (-)-15b.

Si-O(4)	1.629(10)	Si-C(13)	1.89(2)
Si-C(18)	1.88(2)	Si-C(17)	1.89(2)
O(1)-C(1)	1.23(2)	O(2)-C(2)	1.40(2)
O(2)-C(19)	1.41(2)	O(3)-C(19)	1.23(2)
O(4)-C(8)	1.45(2)	C(1)-C(2)	1.48(2)
C(1)-C(5)	1.52(2)	C(2)-C(3)	1.38(2)
C(3)-C(4)	1.51(2)	C(3)-C(6)	1.53(2)
C(4)-C(8)	1.50(2)	C(4)-C(5)	1.56(2)
C(5)-C(7)	1.36(2)	C(7)-C(9)	1.51(2)
C(9)-C(12)	1.47(3)	C(9)-C(11)	1.56(2)
C(9)-C(10)	1.60(3)	C(13)-C(16)	1.54(2)
C(13)-C(14)	1.52(3)	C(13)-C(15)	1.53(2)
C(19)-N	1.33(2)	N-C(20)	1.48(2)
C(20)-C(22)	1.51(2)	C(20)-C(21)	1.59(2)
C(22)-C(23)	1.39(3)	C(22)-C(27)	1.39(2)
C(23)-C(24)	1.42(3)	C(24)-C(25)	1.34(3)
C(25)-C(26)	1.40(3)	C(26)-C(27)	1.38(3)

O(4)-Si-C(13)	104.3(8)	O(4)-Si-C(18)	112.5(7)
C(13)-Si-C(18)	110.5(10)	O(4)-Si-C(17)	110.2(7)
C(13)-Si-C(17)	111.8(11)	C(18)-Si-C(17)	107.6(8)
C(2)-O(2)-C(19)	115.6(13)	C(8)-O(4)-Si	125.6(10)
O(1)-C(1)-C(2)	125(2)	O(1)-C(1)-C(5)	131(2)
C(2)-C(1)-C(5)	104(2)	C(3)-C(2)-O(2)	125(2)
C(3)-C(2)-C(1)	113(2)	O(2)-C(2)-C(1)	121(2)
C(2)-C(3)-C(4)	111(2)	C(2)-C(3)-C(6)	126(2)
C(4)-C(3)-C(6)	124(2)	C(8)-C(4)-C(3)	117(2)
C(8)-C(4)-C(5)	116(2)	C(3)-C(4)-C(5)	102.9(14)
C(7)-C(5)-C(1)	128(2)	C(7)-C(5)-C(4)	123(2)
C(1)-C(5)-C(4)	109(2)	C(5)-C(7)-C(9)	133(2)
O(4)-C(8)-C(4)	112.8(14)	C(12)-C(9)-C(7)	112(2)
C(12)-C(9)-C(11)	113(2)	C(7)-C(9)-C(11)	106(2)
C(12)-C(9)-C(10)	111(2)	C(7)-C(9)-C(10)	110(2)
C(11)-C(9)-C(10)	105(2)	C(16)-C(13)-C(14)	108(2)
C(16)-C(13)-C(15)	107(2)	C(14)-C(13)-C(15)	112(2)
C(16)-C(13)-Si	110(2)	C(14)-C(13)-Si	110(2)
C(15)-C(13)-Si	111(2)	O(3)-C(19)-N	126(2)
O(3)-C(19)-O(2)	123(2)	N-C(19)-O(2)	111(2)
C(19)-N-C(20)	124(2)	N-C(20)-C(22)	115(2)
N-C(20)-C(21)	109.4(14)	C(22)-C(20)-C(21)	109.6(14)
C(23)-C(22)-C(27)	116(2)	C(23)-C(22)-C(20)	122(3)
C(27)-C(22)-C(20)	123(3)	C(22)-C(23)-C(24)	121(3)
C(25)-C(24)-C(23)	120(3)	C(24)-C(25)-C(26)	121(3)
C(25)-C(26)-C(27)	118(3)	C(26)-C(27)-C(22)	124(2)

Table 9. Anisotropic displacement parameters [$Å^2 \times 10^3$] for (-)-15b. The anisotropic displacement factor exponent takes the form: $-2p^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Si	123(5)	87(4)	59(3)	-13(3)	-2(4)	-27(4)
O(1)	87(9)	82(8)	72(8)	-24(8)	-11(7)	-24(8)
O(2)	75(10)	106(9)	36(9)	6(7)	-23(7)	-29(8)
O(3)	89(9)	79(8)	68(8)	10(7)	-7(7)	-22(7)
O(4)	82(8)	84(8)	106(8)	-32(7)	-35(8)	-37(7)
C(1)	58(17)	78(15)	53(13)	-5(12)	0(15)	-35(19)
C(2)	75(21)	72(15)	19(11)	7(11)	-15(14)	-25(16)
C(3)	77(19)	64(13)	39(10)	27(11)	-3(12)	11(14)
C(4)	39(13)	96(14)	66(14)	5(11)	-29(11)	-24(12)
C(5)	46(15)	84(15)	65(12)	0(12)	15(14)	17(16)
C(6)	105(15)	90(12)	74(11)	28(11)	22(13)	-11(12)
C(7)	73(16)	75(15)	128(17)	-19(13)	-8(16)	-21(15)
C(8)	110(17)	93(14)	94(16)	1(12)	-36(14)	11(13)
C(9)	75(17)	142(22)	164(22)	-76(21)	-22(17)	55(19)
C(10)	72(15)	121(17)	237(24)	-8(19)	-13(16)	46(12)
C(12)	157(23)	131(18)	220(27)	-87(20)	122(22)	-52(16)
C(11)	73(16)	190(21)	353(38)	-113(27)	-5(22)	10(14)
C(13)	142(21)	116(18)	119(17)	-23(17)	25(18)	-64(15)
C(14)	131(21)	273(31)	248(30)	126(30)	-79(21)	-23(20)
C(15)	212(25)	202(24)	190(23)	-43(23)	-8(22)	-115(20)
C(16)	147(21)	148(20)	265(35)	10(23)	-61(26)	-67(17)
C(17)	275(27)	141(17)	94(13)	-6(15)	-12(18)	-19(18)
C(18)	191(21)	132(15)	110(16)	-10(13)	24(14)	-11(15)
C(19)	27(13)	84(16)	82(23)	-43(17)	-18(13)	-27(12)
N	72(10)	80(10)	38(10)	22(8)	-13(9)	-20(9)
C(20)	61(14)	86(14)	52(15)	7(12)	-8(11)	-3(11)
C(21)	96(13)	115(15)	62(10)	-30(12)	-20(10)	47(12)
C(22)	77(20)	84(13)	87(18)	24(17)	-33(21)	-13(12)
C(23)	89(22)	184(21)	115(24)	-8(16)	-21(23)	11(19)
C(24)	96(29)	228(30)	165(32)	-16(26)	5(23)	15(24)
C(25)	96(27)	242(36)	256(49)	-71(38)	-56(33)	88(22)
C(26)	115(24)	103(17)	213(37)	57(19)	-87(27)	22(17)
C(27)	102(23)	108(16)	128(23)	46(15)	-30(17)	-1(16)

Table 10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (-)-15b.

	x	y	z	U(eq)
H(4)	6733(12)	1674(6)	71(25)	80
H(6A)	4419(12)	1401(15)	177(76)	80
H(6B)	4983(22)	1837(7)	459(87)	80
H(6C)	4852(25)	1498(18)	2204(24)	80
H(7)	8272(15)	1275(5)	392(27)	80
H(8A)	6858(12)	1178(6)	3446(26)	80
H(8B)	6324(12)	1626(6)	3397(26)	80
H(10A)	8124(27)	68(11)	-644(78)	80
H(10B)	8584(42)	255(6)	1228(31)	80
H(10C)	9121(24)	43(10)	-480(89)	80
H(12A)	8114(24)	524(21)	-3650(35)	80
H(12B)	9113(26)	498(18)	-3788(36)	80
H(12C)	8652(42)	971(7)	-3870(36)	80
H(11A)	9643(22)	1203(10)	-904(88)	80
H(11B)	10028(12)	713(16)	-1032(91)	80
H(11C)	9612(20)	882(20)	923(40)	80
H(14A)	9673(30)	2273(10)	5991(77)	80
H(14B)	9428(35)	1850(13)	4713(41)	80
H(14C)	8820(18)	2010(19)	6401(64)	80
H(15A)	9447(18)	3008(9)	4252(100)	80
H(15B)	8715(44)	2975(8)	5811(45)	80
H(15C)	8498(37)	3103(7)	3641(81)	80
H(16A)	9710(19)	2460(21)	1923(47)	80
H(16B)	8801(27)	2500(19)	973(40)	80
H(16C)	9146(40)	2025(7)	1646(54)	80
H(17A)	7280(22)	2704(19)	1062(53)	80
H(17B)	6820(41)	2926(12)	2862(44)	80
H(17C)	6424(24)	2497(12)	1852(79)	80
H(18A)	7401(27)	2135(18)	7344(27)	80
H(18B)	6505(16)	2228(20)	6402(28)	80
H(18C)	7123(38)	2634(7)	6850(44)	80
H(0)	3987(10)	238(4)	-3449(20)	80
H(20)	4206(12)	618(6)	-7010(26)	80
H(21A)	3239(35)	-14(7)	-8103(69)	80
H(21B)	3397(40)	-213(8)	-6007(37)	80
H(21C)	4165(12)	-152(10)	-7456(88)	80
H(23)	2610(24)	665(7)	-3512(42)	80
H(24)	1297(26)	1073(11)	-3798(52)	80
H(25)	868(22)	1370(13)	-6757(76)	80
H(26)	1793(25)	1354(9)	-9404(49)	80
H(27)	3022(19)	890(8)	-9215(43)	80