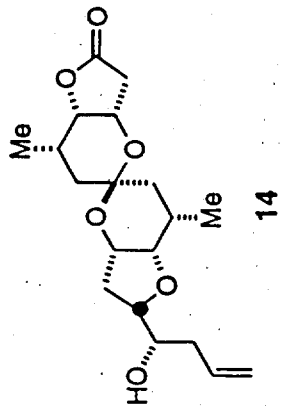
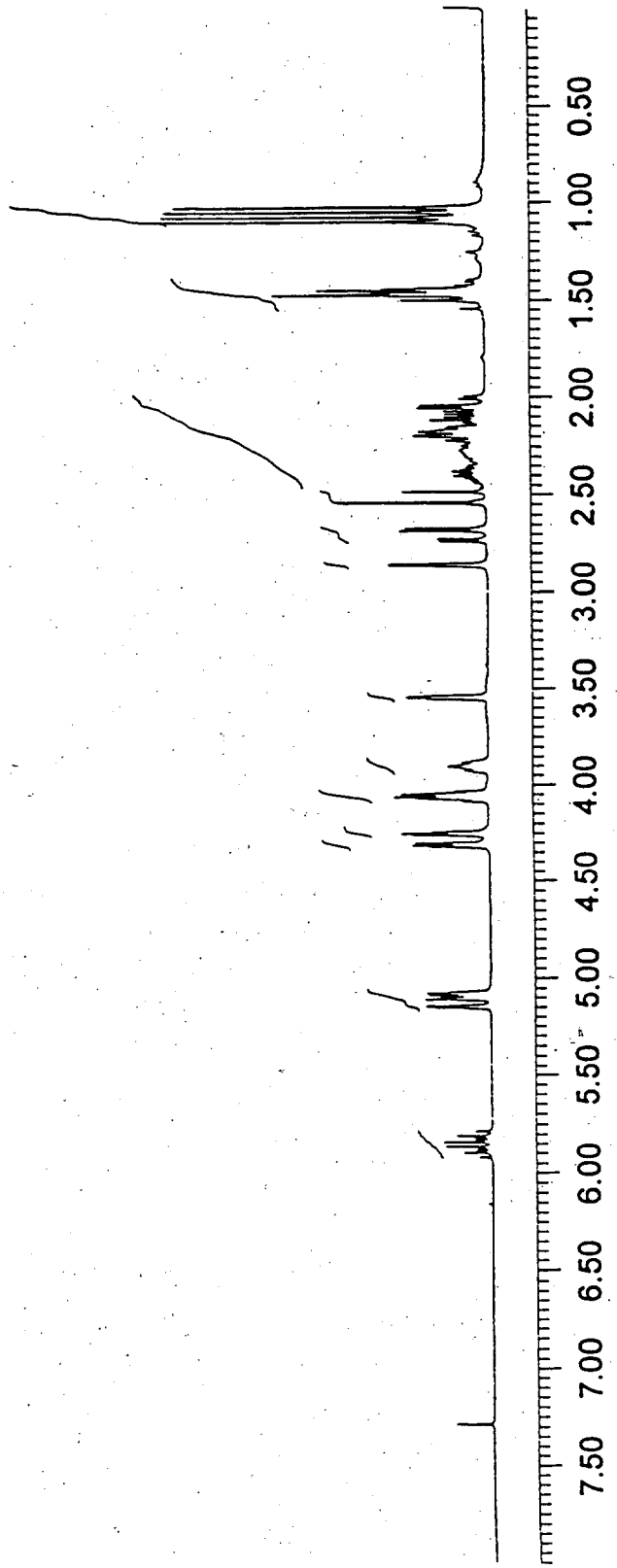
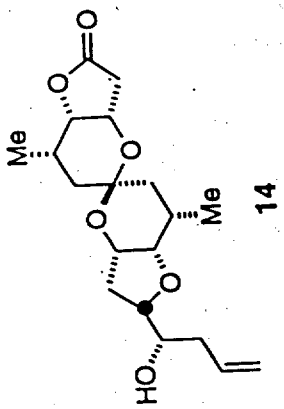
JOC The Journal of Organic Chemistry

J. Org. Chem., 1998, 63(20), 6770-6771, DOI:10.1021/jo981181e

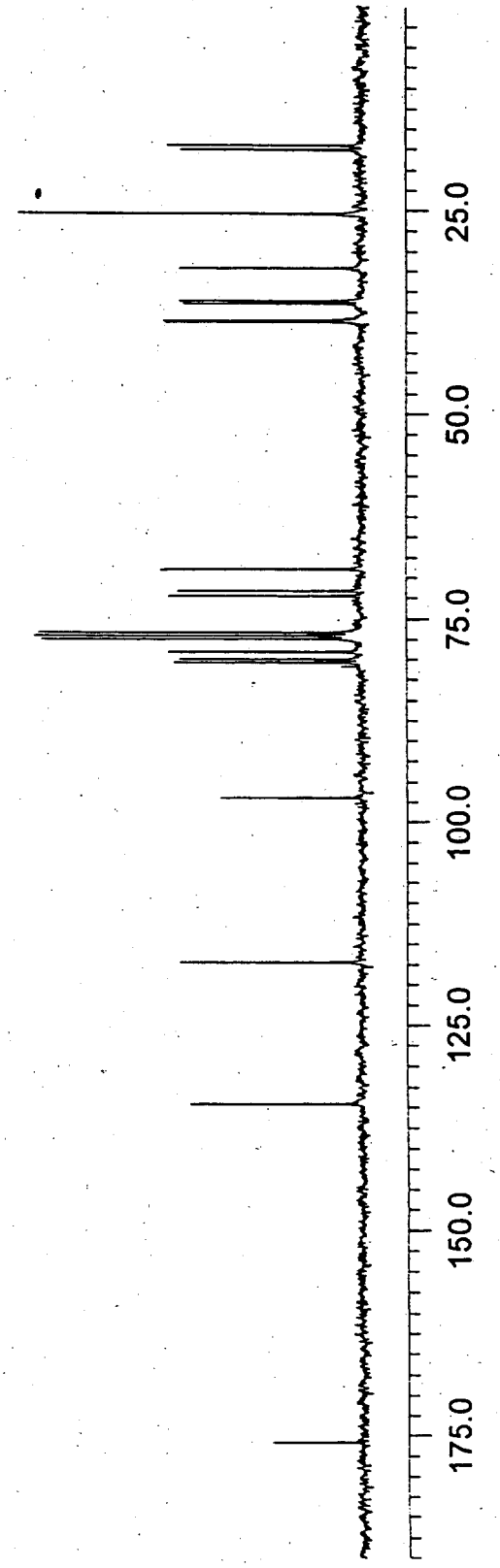


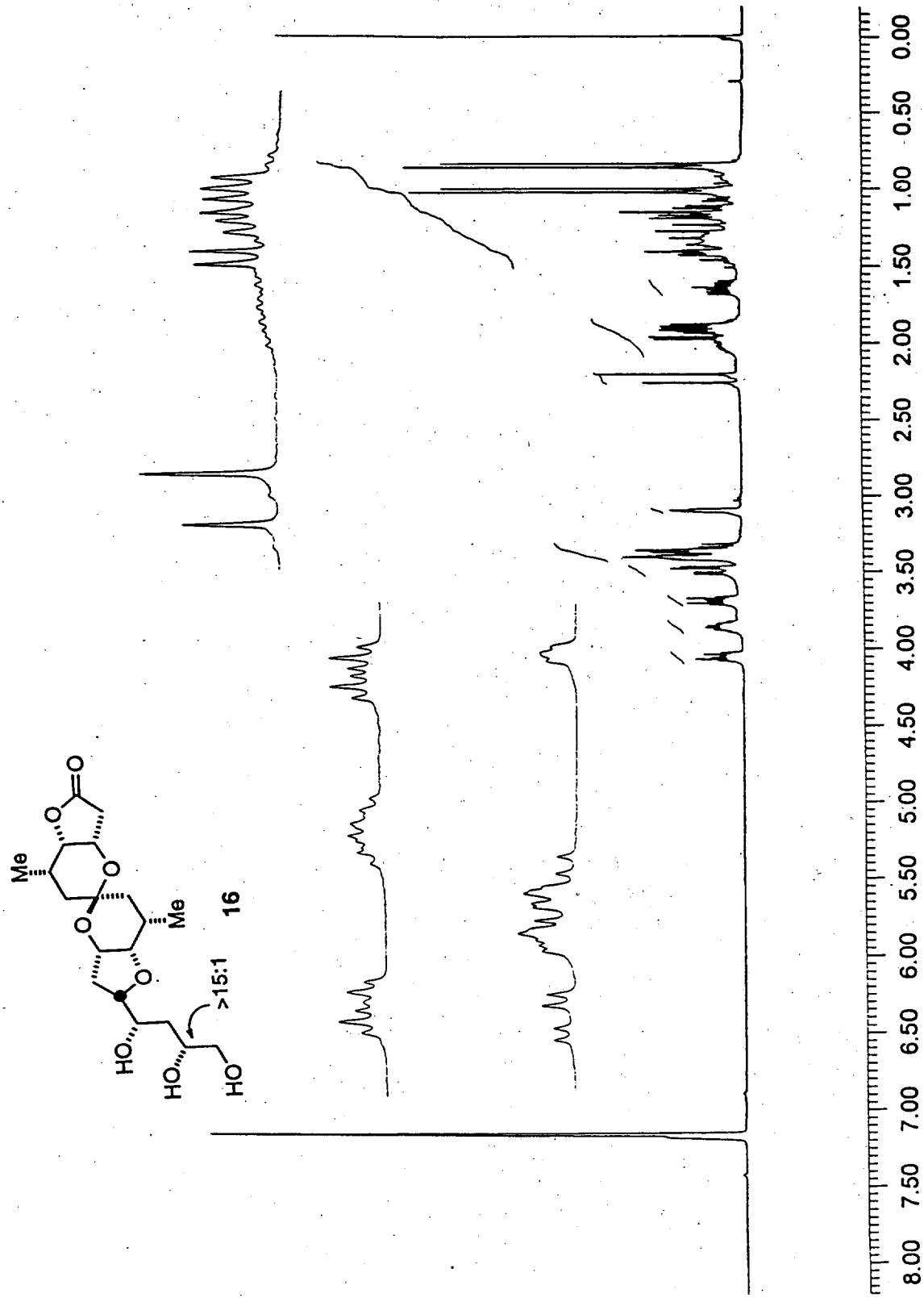
14

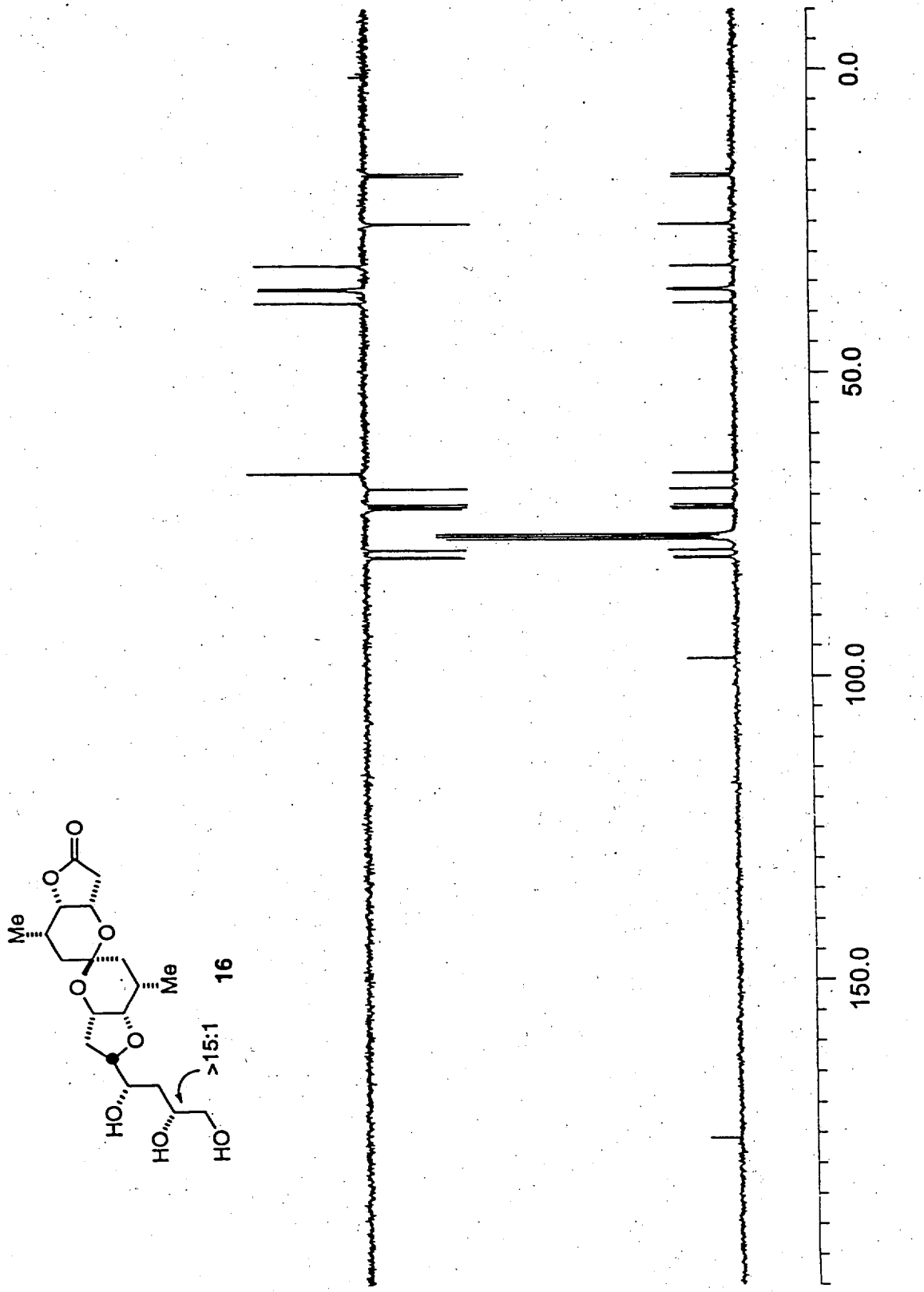


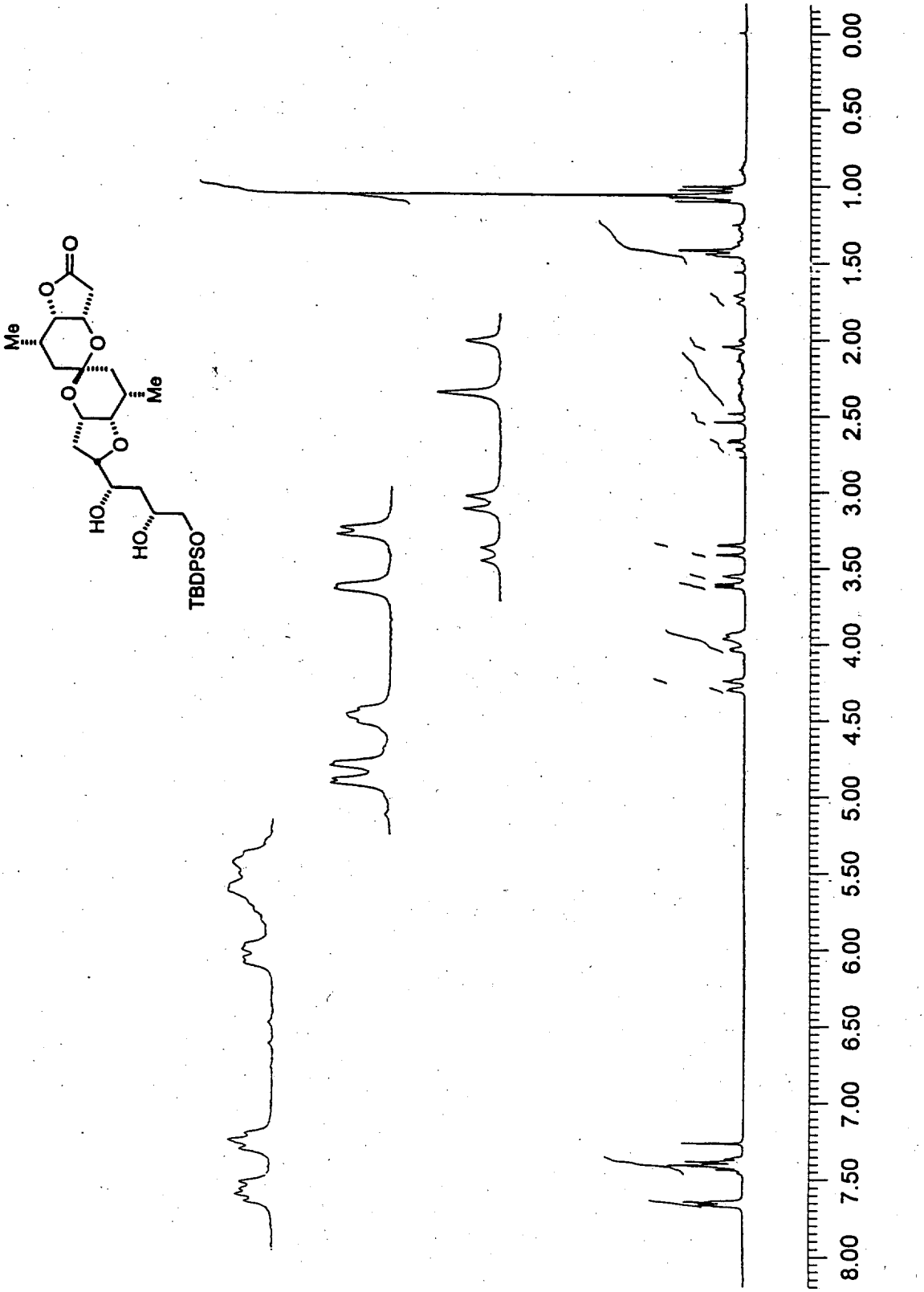


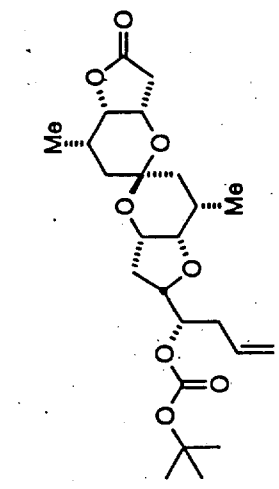
14

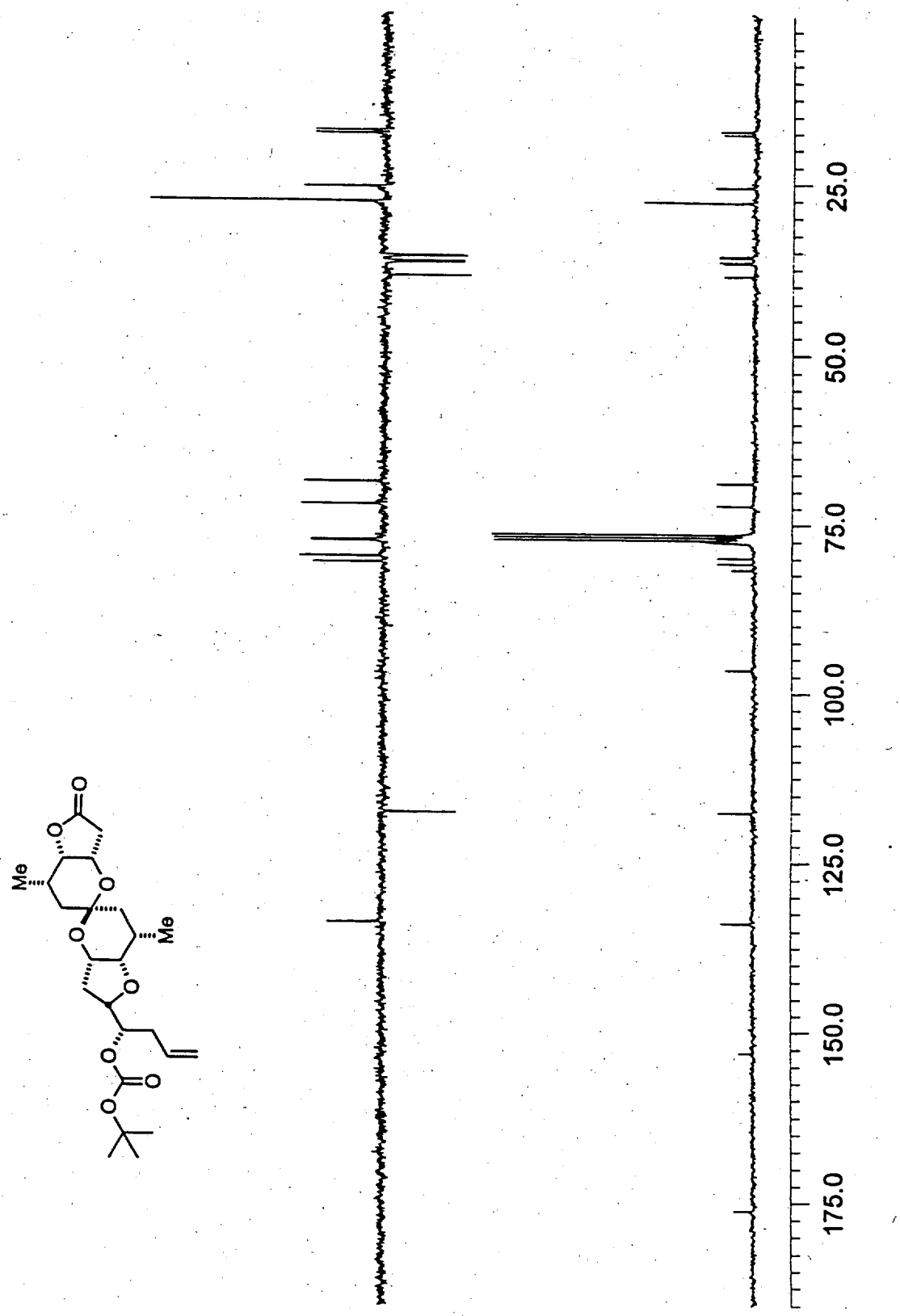


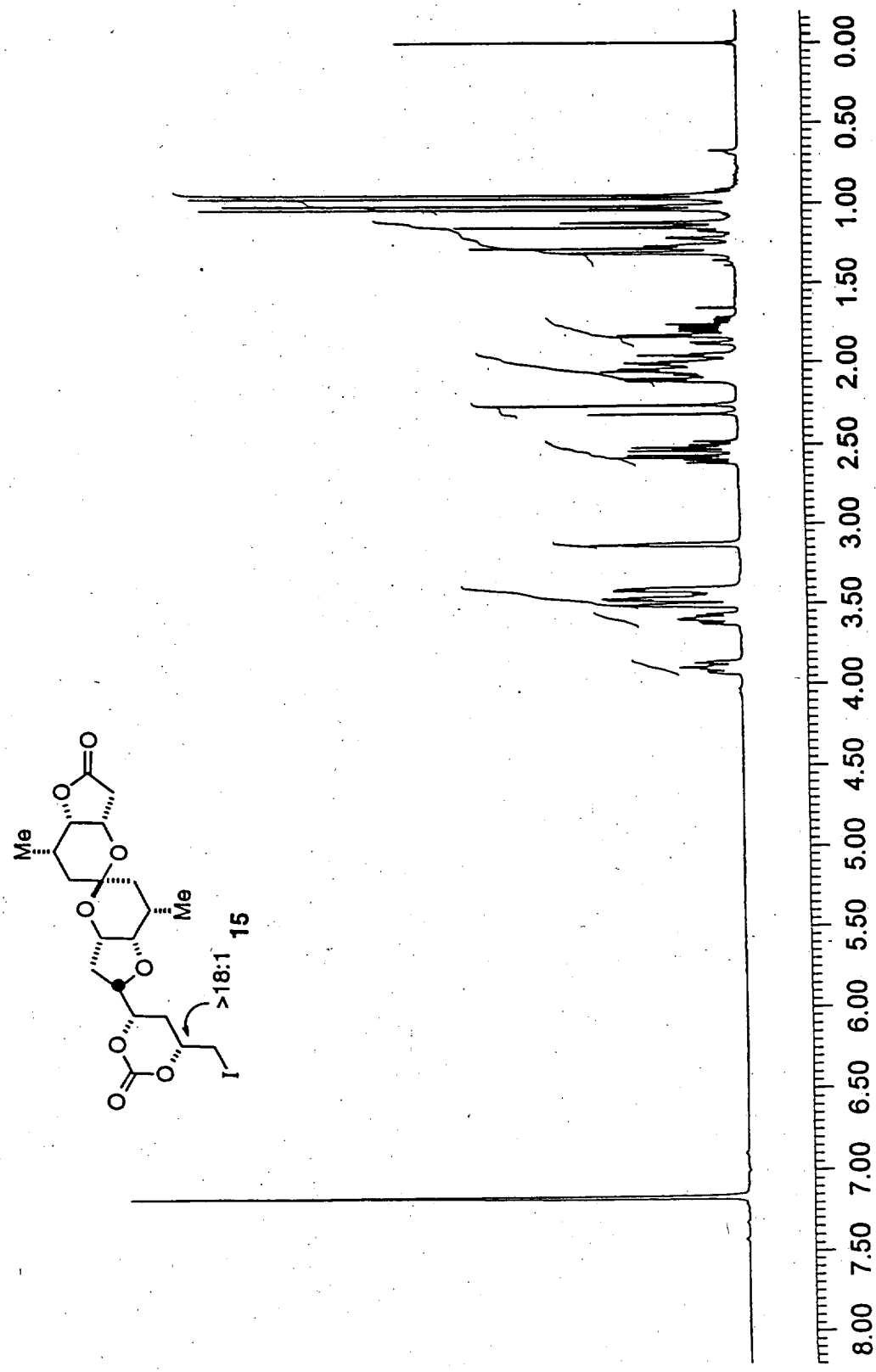


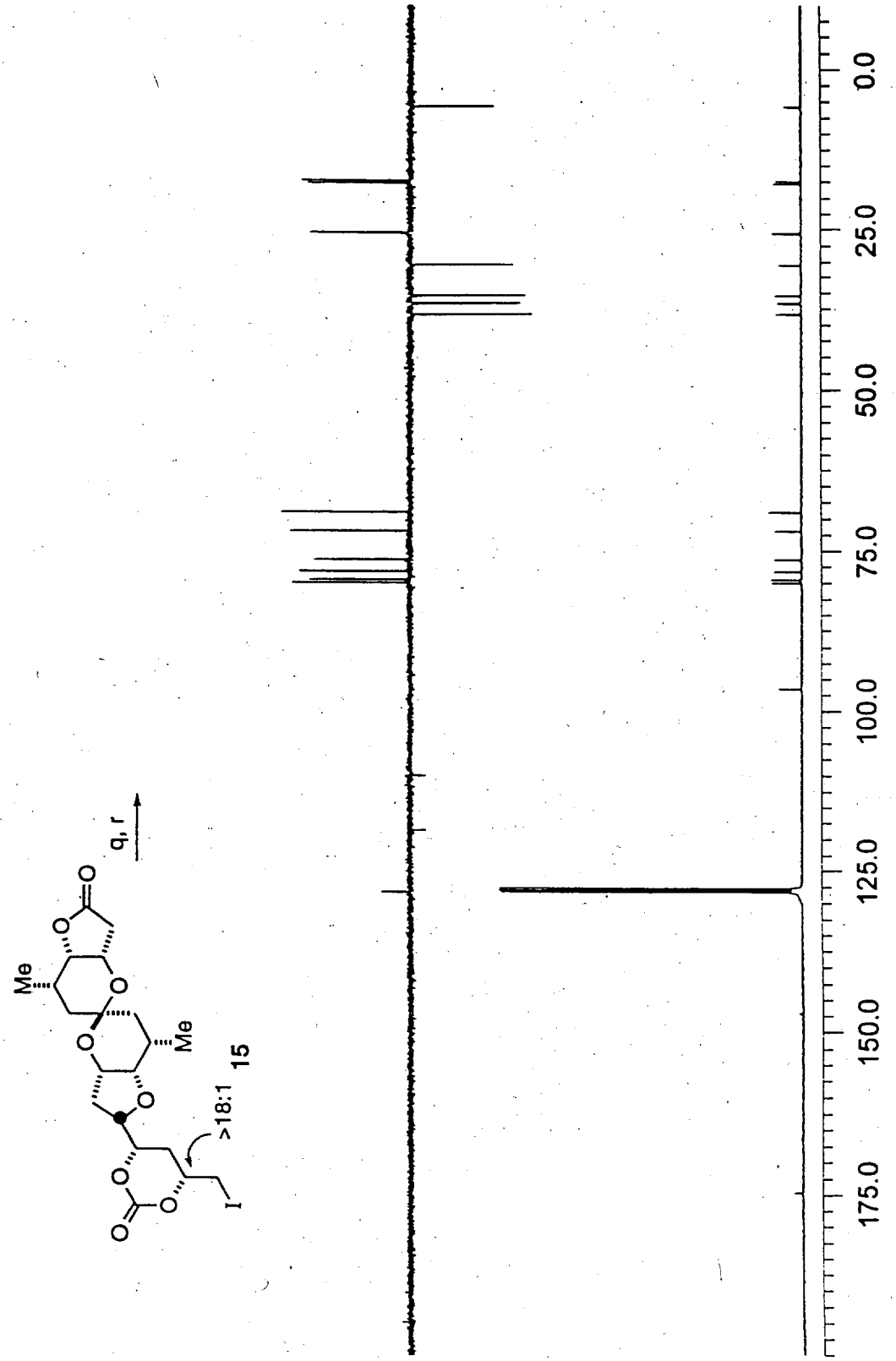


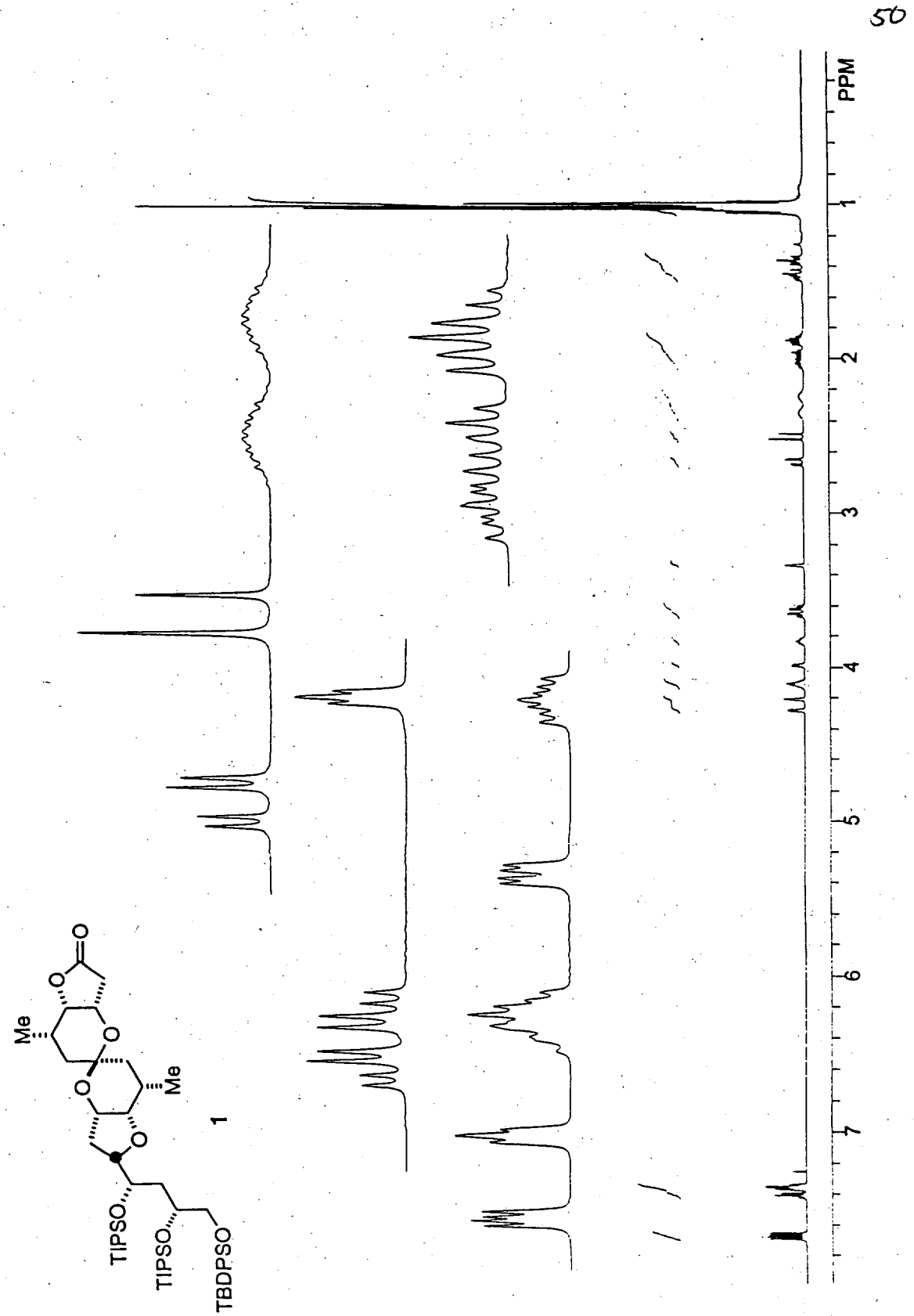




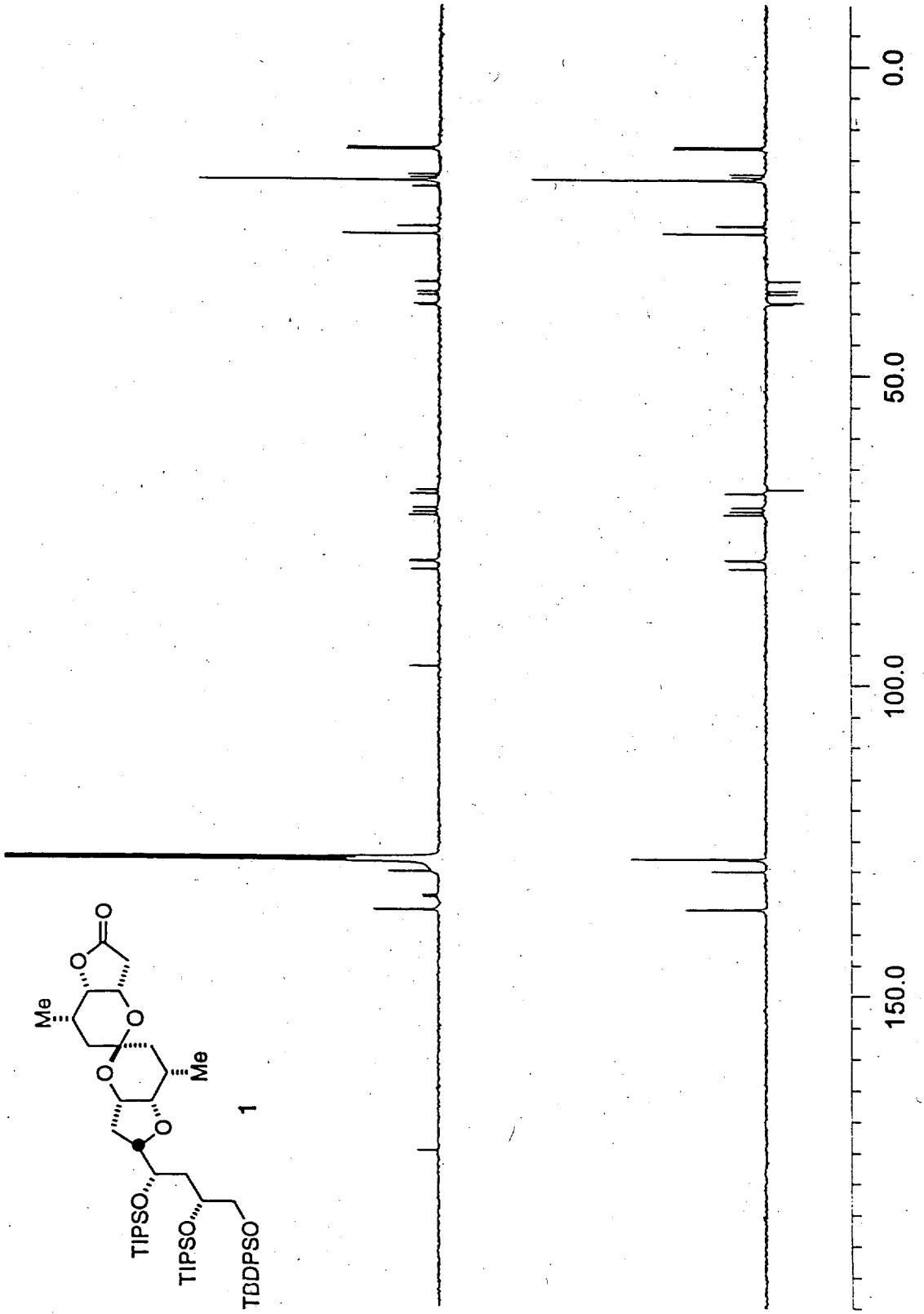








50



Crystallographic Data for 12

Figure 1: X-Ray Crystal Structure of Bis(lactone) 12

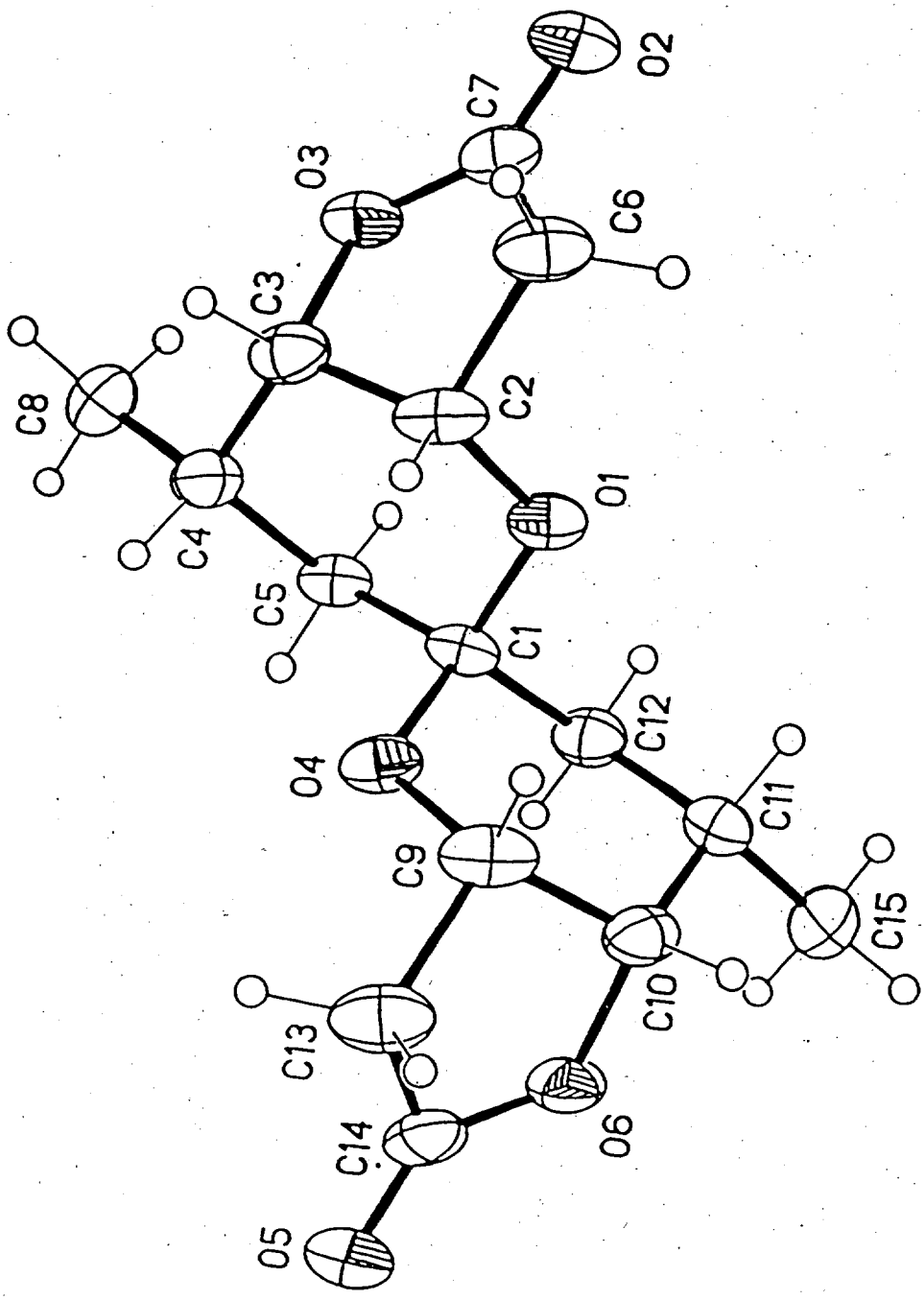


Figure 2: Unit Cell for Bis(lactone) 12

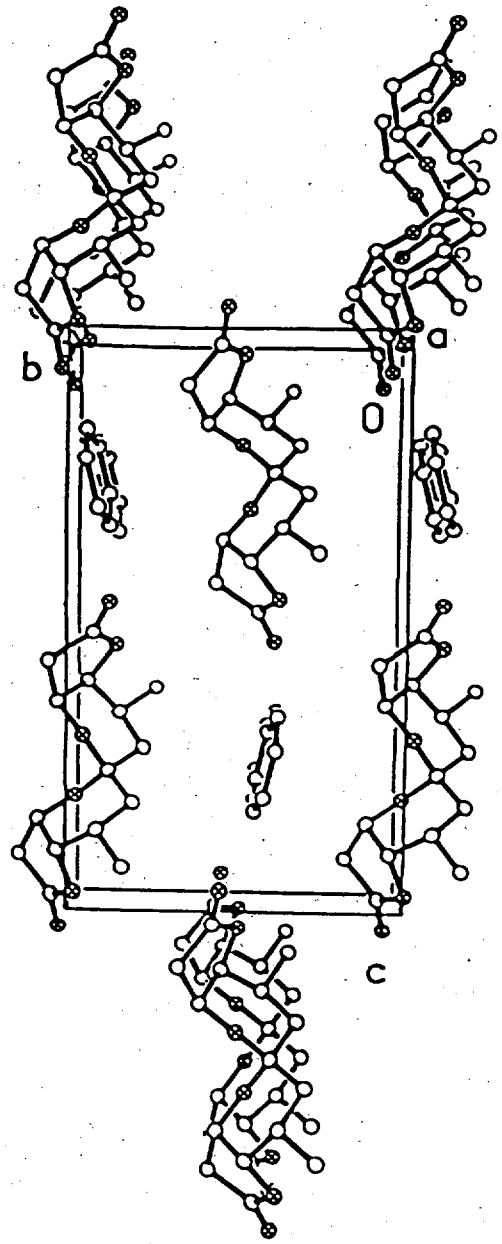


Table 1. Crystal Data and Structure Refinement for 12

Identification code	98093
Empirical formula	$(C_{15}H_{20}O_6)$ (C_6H_6)
Formula weight	374.42
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 6.4618(4) Å $\alpha = 90^o$
	b = 9.3221(2) Å $\beta = 97.336(2)^o$
	c = 16.2081(10) Å $\gamma = 90^o$
Volume	968.34(9) $Å^3$
Z	2
Density (calculated)	1.284 Mg/m^3
Wavelength	0.71073 Å
Temperature	153(2) K
F(000)	400
Absorption coefficient	0.094 mm^{-1}
Absorption correction	Empirical
Max. and min. transmission	0.833 and 0.585
θ range for data collection	2.53 to 29.14°
Reflections collected	4815
Independent reflections	2546 (R_{int} = 0.0289)
Data / restraints / parameters	2546 / 1 (space group) / 244
wR(F^2 all data)	wR2=0.1267
R(F obsd data)	R1 = 0.0575
Goodness-of-fit on F^2	1.091
Observed data [I>2σ(I)]	2018
Absolute structure parameter	-2.2(15) (not reliable)
Largest diff. peak and hole	0.204 and -0.222 $eÅ^{-3}$
Largest and mean Δ / esd	0.001 and 0.000
Absolute structure parameter	-2.2(15)

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$] for 136. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	0.4418(5)	0.3908(3)	0.23483(18)	0.0270(7)
O(1)	0.5412(4)	0.4915(2)	0.18676(12)	0.0292(6)
C(2)	0.4061(6)	0.5999(3)	0.14634(18)	0.0323(8)
C(3)	0.2143(6)	0.5364(4)	0.09566(19)	0.0343(8)
C(4)	0.1062(6)	0.4148(4)	0.1361(2)	0.0345(8)
C(5)	0.2687(5)	0.3130(3)	0.18096(18)	0.0274(7)
C(6)	0.5224(6)	0.6620(4)	0.07964(19)	0.0363(8)
C(7)	0.4654(6)	0.5612(4)	0.0078(2)	0.0322(8)
O(2)	0.5524(4)	0.5418(3)	-0.05242(14)	
	0.0414(7)			
O(3)	0.2924(4)	0.4874(3)	0.01917(13)	0.0339(6)
C(8)	-0.0483(6)	0.3353(5)	0.0748(2)	0.0473(10)
O(4)	0.3461(4)	0.4640(2)	0.29748(12)	0.0293(6)
C(9)	0.4838(6)	0.5466(4)	0.35569(19)	0.0358(8)
C(10)	0.6711(6)	0.4610(4)	0.39374(19)	0.0346(8)
C(11)	0.7735(6)	0.3661(4)	0.3349(2)	0.0361(8)
C(12)	0.6093(6)	0.2904(3)	0.27441(19)	0.0299(8)
C(13)	0.3652(7)	0.5697(4)	0.4290(2)	0.0426(10)
C(14)	0.4173(6)	0.4368(4)	0.48004(19)	0.0373(9)
O(5)	0.3286(4)	0.3867(3)	0.53405(14)	0.0478(7)
O(6)	0.5887(4)	0.3737(3)	0.45774(13)	0.0356(6)
C(15)	0.9270(6)	0.2583(5)	0.3804(2)	0.0503(11)
C(16)	-0.1327(7)	0.8826(5)	0.2830(2)	0.0521(11)
C(17)	0.0471(7)	0.8766(5)	0.3378(2)	0.0504(11)
C(18)	0.2356(6)	0.9043(4)	0.3104(2)	0.0406(9)
C(19)	0.2438(6)	0.9394(4)	0.2280(2)	0.0365(9)
C(20)	0.0651(7)	0.9441(4)	0.1736(2)	0.0397(10)
C(21)	-0.1255(6)	0.9173(4)	0.2007(2)	0.0443(10)

Table 3. Bond Lengths [Å] and Angles [°] for 12

C(1)-O(1)	1.424(4)	C(1)-O(4)	1.428(4)
C(1)-C(12)	1.511(4)	C(1)-C(5)	1.513(4)
O(1)-C(2)	1.438(4)	C(2)-C(6)	1.509(5)
C(2)-C(3)	1.517(5)	C(3)-O(3)	1.470(4)
C(3)-C(4)	1.523(5)	C(4)-C(8)	1.510(5)
C(4)-C(5)	1.529(4)	C(6)-C(7)	1.504(5)
C(7)-O(2)	1.201(4)	C(7)-O(3)	1.345(4)
O(4)-C(9)	1.435(4)	C(9)-C(13)	1.509(5)
C(9)-C(10)	1.514(5)	C(10)-O(6)	1.471(4)
C(10)-C(11)	1.513(5)	C(11)-C(12)	1.523(5)
C(11)-C(15)	1.533(6)	C(13)-C(14)	1.504(5)
C(14)-O(5)	1.201(4)	C(14)-O(6)	1.344(5)
C(16)-C(17)	1.371(6)	C(16)-C(21)	1.379(6)
C(17)-C(18)	1.373(6)	C(18)-C(19)	1.382(5)
C(19)-C(20)	1.361(5)	C(20)-C(21)	1.382(6)
O(1)-C(1)-O(4)	109.9(2)	O(1)-C(1)-C(12)	107.0(3)
O(4)-C(1)-C(12)	110.2(2)	O(1)-C(1)-C(5)	110.6(2)
O(4)-C(1)-C(5)	106.5(3)	C(12)-C(1)-C(5)	112.6(3)
C(1)-O(1)-C(2)	115.0(2)	O(1)-C(2)-C(6)	105.5(3)
O(1)-C(2)-C(3)	112.3(3)	C(6)-C(2)-C(3)	102.1(2)
O(3)-C(3)-C(2)	103.5(3)	O(3)-C(3)-C(4)	111.0(3)
C(2)-C(3)-C(4)	116.4(3)	C(8)-C(4)-C(3)	112.5(3)
C(8)-C(4)-C(5)	111.4(3)	C(3)-C(4)-C(5)	110.0(3)
C(1)-C(5)-C(4)	112.9(3)	C(7)-C(6)-C(2)	102.7(3)
O(2)-C(7)-O(3)	121.2(3)	O(2)-C(7)-C(6)	129.0(4)
O(3)-C(7)-C(6)	109.8(3)	C(7)-O(3)-C(3)	109.7(3)
C(1)-O(4)-C(9)	115.8(3)	O(4)-C(9)-C(13)	105.0(3)
O(4)-C(9)-C(10)	112.4(3)	C(13)-C(9)-C(10)	102.4(3)
O(6)-C(10)-C(11)	110.4(3)	O(6)-C(10)-C(9)	103.7(3)
C(11)-C(10)-C(9)	116.3(3)	C(10)-C(11)-C(12)	110.6(3)
C(10)-C(11)-C(15)	112.8(3)	C(12)-C(11)-C(15)	111.1(3)
C(1)-C(12)-C(11)	112.9(3)	C(14)-C(13)-C(9)	102.4(3)
O(5)-C(14)-O(6)	120.8(4)	O(5)-C(14)-C(13)	128.9(4)

O(6)-C(14)-C(13)	110.3(3)	C(14)-O(6)-C(10)	109.4(3)
C(17)-C(16)-C(21)	120.4(4)	C(16)-C(17)-C(18)	119.7(4)
C(17)-C(18)-C(19)	120.1(4)	C(20)-C(19)-C(18)	119.9(4)
C(19)-C(20)-C(21)	120.4(3)	C(16)-C(21)-C(20)	119.4(4)

Table 4. Anisotropic Displacement Parameters [Å^2 x 10^3] for 12

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2U_{11} + ... + 2hka^*b^*U_{12}]$

	U11	U22	U33	U23	U13	U12
C(1)	40(2)	23(2)	20(2)	1(1)	10(1)	1(1)
O(1)	41(2)	24(1)	23(1)	3(1)	5(1)	-1(1)
C(2)	58(2)	19(2)	20(2)	0(1)	8(2)	8(2)
C(3)	44(2)	33(2)	26(2)	3(1)	6(2)	15(2)
C(4)	36(2)	43(2)	24(2)	4(2)	5(2)	6(2)
C(5)	39(2)	23(2)	21(2)	0(1)	6(2)	1(1)
C(6)	60(2)	21(2)	27(2)	2(1)	3(2)	-4(2)
C(7)	44(2)	27(2)	25(2)	5(1)	2(2)	6(2)
O(2)	57(2)	43(1)	27(1)	1(1)	14(1)	-3(1)
O(3)	45(2)	37(1)	20(1)	1(1)	7(1)	2(1)
C(8)	35(2)	68(3)	36(2)	5(2)	-4(2)	-4(2)
O(4)	45(2)	22(1)	20(1)	-2(1)	3(1)	5(1)
C(9)	62(3)	22(2)	24(2)	-2(1)	7(2)	-6(2)
C(10)	40(2)	38(2)	25(2)	5(1)	0(2)	-16(2)
C(11)	36(2)	46(2)	27(2)	9(2)	7(2)	-7(2)
C(12)	39(2)	25(2)	27(2)	3(1)	7(2)	4(1)
C(13)	66(3)	35(2)	27(2)	-6(2)	7(2)	1(2)
C(14)	45(2)	49(2)	18(2)	-7(1)	-1(2)	-5(2)
O(5)	50(2)	69(2)	27(1)	6(1)	12(1)	-2(2)
O(6)	40(2)	43(1)	24(1)	9(1)	4(1)	-8(1)
C(15)	36(2)	71(3)	43(2)	16(2)	1(2)	4(2)

C(16) 47(2)	55(3)	56(3)	10(2)	14(2)	-1(2)
C(17) 61(3)	60(3)	32(2)	10(2)	11(2)	22(2)
C(18) 40(2)	40(2)	39(2)	-6(2)	-6(2)	14(2)
C(19) 40(2)	28(2)	44(2)	-1(1)	15(2)	3(2)
C(20) 61(3)	30(2)	30(2)	-4(1)	10(2)	1(2)
C(21) 42(2)	41(2)	46(2)	-3(2)	-11(2)	
-3(2)					

Table 5. Hydrogen Coordinates and Isotropic Displacement Parameters [Å^2] for 12

	x	y	z	U(eq)
H(2)	0.3693	0.6747	0.1862	0.039
H(3)	0.1108	0.6150	0.0810	0.041
H(4)	0.0269	0.4582	0.1790	0.041
H(5A)	0.1987	0.2466	0.2162	0.033
H(5B)	0.3302	0.2549	0.1391	0.033
H(6A)	0.4755	0.7610	0.0652	0.044
H(6B)	0.6748	0.6623	0.0973	0.044
H(8A)	-0.1251	0.2658	0.1046	0.057
H(8B)	0.0264	0.2847	0.0346	0.057
H(8C)	-0.1466	0.4037	0.0454	0.057
H(9)	0.5250	0.6392	0.3312	0.043
H(10)	0.7780	0.5287	0.4217	0.042
H(11)	0.8551	0.4299	0.3014	0.043
H(12A)	0.6784	0.2444	0.2301	0.036
H(12B)	0.5434	0.2138	0.3044	0.036
H(13A)	0.4133	0.6573	0.4603	0.051

H(13B)	0.2132	0.5771	0.4110	0.051
H(15A)	1.0065	0.2117	0.3403	0.060
H(15B)	0.8495	0.1856	0.4076	0.060
H(15C)	1.0231	0.3086	0.4224	0.060
H(16)	-0.2630	0.8628	0.3018	0.063
H(17)	0.0413	0.8533	0.3945	0.060
H(18)	0.3606	0.8994	0.3481	0.049
H(19)	0.3741	0.9601	0.2093	0.044
H(20)	0.0715	0.9660	0.1168	0.048
H(21)	-0.2504	0.9227	0.1629	0.053

Table 6. Torsion Angles [°] for 12

O4-C1-O1-C2	-58.2(3)	C12-C1-O1-C2	-177.9(2)
C5-C1-O1-C2	59.1(3)	C1-O1-C2-C6	-162.4(2)
C1-O1-C2-C3	-52.1(3)	O1-C2-C3-O3	-78.7(3)
C6-C2-C3-O3	33.8(3)	O1-C2-C3-C4	43.3(4)
C6-C2-C3-C4	155.8(3)	O3-C3-C4-C8	-48.2(4)
C2-C3-C4-C8	-166.2(3)	O3-C3-C4-C5	76.6(3)
C2-C3-C4-C5	-41.4(4)	O1-C1-C5-C4	-56.5(3)
O4-C1-C5-C4	62.9(3)	C12-C1-C5-C4	-176.2(3)
C8-C4-C5-C1	172.8(3)	C3-C4-C5-C1	47.3(4)
O1-C2-C6-C7	85.7(3)	C3-C2-C6-C7	-31.8(3)
C2-C6-C7-O2	-160.4(4)	C2-C6-C7-O3	19.1(4)
O2-C7-O3-C3	-177.7(3)	C6-C7-O3-C3	2.8(4)

C2-C3-O3-C7	-23.4(3)	C4-C3-O3-C7	-149.0(3)
O1-C1-O4-C9	-59.7(3)	C12-C1-O4-C9	58.0(3)
C5-C1-O4-C9	-179.5(2)	C1-O4-C9-C13	-161.5(3)
C1-O4-C9-C10	-50.9(3)	O4-C9-C10-O6	-78.9(3)
C13-C9-C10-O6	33.3(3)	O4-C9-C10-C11	42.4(4)
C13-C9-C10-C11	154.6(3)	O6-C10-C11-C12	76.2(3)
C9-C10-C11-C12	-41.5(4)	O6-C10-C11-C15	-49.0(4)
C9-C10-C11-C15	-166.7(3)	O1-C1-C12-C11	63.6(3)
O4-C1-C12-C11	-55.9(3)	C5-C1-C12-C11	-174.7(3)
C10-C11-C12-C1	47.9(4)	C15-C11-C12-C1	174.0(3)
O4-C9-C13-C14	86.4(3)	C10-C9-C13-C14	-31.2(4)
C9-C13-C14-O5	-161.5(4)	C9-C13-C14-O6	18.6(4)
O5-C14-O6-C10	-177.1(3)	C13-C14-O6-C10	2.7(4)
C11-C10-O6-C14	-148.2(3)	C9-C10-O6-C14	-23.0(3)
C21-C16-C17-C18	-0.4(7)	C16-C17-C18-C19	0.5(6)
C17-C18-C19-C20	-1.1(6)	C18-C19-C20-C21	1.5(5)
C17-C16-C21-C20	0.9(7)	C19-C20-C21-C16	-1.4(6)

Experimental

A colorless plate-shaped crystal of dimensions 0.60 x 0.25 x 0.10 mm was selected for structural analysis. Intensity data for this compound were collected using a Siemens SMART ccd area detector [1] mounted on a Siemens P4 diffractometer equipped with graphite-monochromated Mo Ka radiation (Λ = 0.71073 Å). The sample was cooled to 153 (2) K. The intensity data, which nominally covered one and a half hemispheres of reciprocal space, were measured as a series of ø oscillation frames each of 0.4° for 60 sec / frame. The

detector was operated in 512 x 512 mode and was positioned 5.26 cm from the sample. Coverage of unique data was 95.4 % complete to at least 25° in θ. Cell parameters were determined from a non-linear least-squares fit of 2522 peaks in the range $3.0 < \theta < 25.0$. The first 50 frames were repeated at the end of data collection and yielded a total of 120 peaks showing a variation of 0.12 % during the data collection. A total of 4815 data were measured in the range $2.53 < \theta < 29.4°$. The data were corrected for absorption by the empirical method(2) giving minimum and maximum transmissions of 0.585 and 0.833. The data were merged to form a set of 2546 independent data with $R_{int} = 0.0289$.

The monoclinic space group $P2_1$ was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2(3). Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. A total of 244 parameters were refined against 1 restraint and 2546 data to give $wR(F^2) = 0.1267$ and $S = 1.091$ for weights of $w = 1/[\sigma^2(F^2) + (0.710\ P)^2]$, where $P = [F_o^2 + 2F_c^2] / 3$. The final R(F) was 0.0575 for the 2018 observed, $[F > 4\sigma(F)]$, data. The largest shift/su was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 0.204 and -0.222, respectively. The absolute structure was determined by refinement of the Flack parameter(4). The polar axis restraints were taken from Flack and Schwarzenbach(5).

Comment

The displacement ellipsoids were drawn at the 50% probability level.

Acknowledgment

The authors thank the National Science Foundation (grant CHE-9310428) and the University of Wisconsin for funds to purchase the x-ray instrument and computers. This structure was determined by Randy K. Hayashi.

References

(1) (a) Data Collection: SMART Software Reference Manual (1994). Siemens Analytical X-ray Instruments, 6300 Enterprise Dr., Madison, WI 53719-1173, USA.

(b) Data Reduction: SAINT Software Reference Manual (1995). Siemens Analytical X-ray Instruments, 6300 Enterprise Dr., Madison, WI 53719-1173, USA.

(2) G.M. Sheldrick (1996). SADABS. Program for Empirical Absorption Correction of Area Detector Data. University of Gottingen, Germany.

(3) (a) G.M. Sheldrick (1994). SHELXTL Version 5 Reference Manual. Siemens Analytical X-ray Instruments, 6300 Enterprise Dr., Madison, WI 53719-1173, USA.

(b) International Tables for Crystallography, Vol C, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2, Kluwer: Boston (1995).

(4) H.D. Flack, Acta Cryst. A39, 876-881 (1983).

(5) H.D. Flack and D. Schwarzenbach, Acta Cryst. A44, 499-506 (1998).