SUPPORTING INFORMATION

Flexible Synthesis of Metacycloprodigiosin and Functional Derivatives Thereof

Alois Fürstner* and Helga Krause

Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany

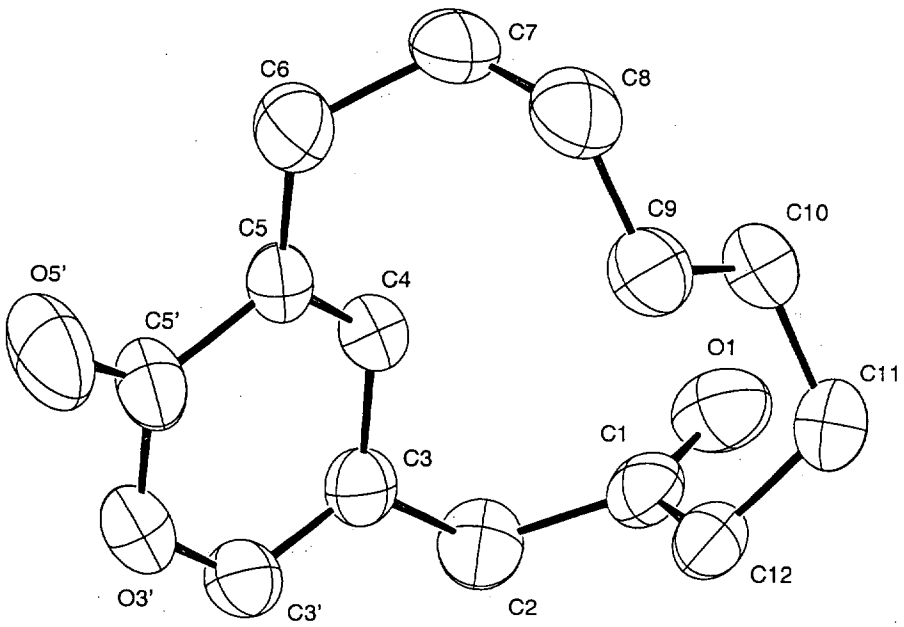
e-mail: fuerstner@mpi-muelheim.mpg.de

Instrumentation and Spectra Formats: NMR: Spectra were recorded on a Bruker AC 200, AMX 300, AMX 400 or DMX 600 spectrometer in $CDCl_3$ unless stated otherwise. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. IR: Nicolet FT-7199, wavenumbers in cm^{-1}. MS: Varian CH-5 (70 eV); HR-MS: Finnigan MAT SSQ 7000 (70 eV). Specific optical rotations: Perkin Elmer 241. Elemental analyses: Dornis & Kolbe, Mülheim.

X-ray structure of compound **14**

Responsible scientist: Dr. Christian W. Lehmann

(lehmann@mpi-muelheim.mpg.de)



The complete set of data has been deposited at the Cambridge Crystallographic Data Center under the deposition number CCDC 127650 and may be obtained free of charge by applying to: „The Director, Cambridge Crystallographic Data Center, 12 Union Road, CB2 1EZ Cambridge, UK.

$C_{14}H_{18}O_3$, M = 234.28 g mol^{-1}, colorless, crystal dimension 0.66 × 0.57 × 0.12 mm, monoclinic C2/c (no. 15), a = 29.981(6),. b = 8.7518(18), c = 9.7499(19) Å, β = 99.32(3) °, V= 2524.5(9) $Å^3$, Z = 8, ρ = 1.233 Mg m^{-3}, λ = 0.71073 Å. X-ray diffraction data were collected using a Nonius KappaCCD area detector diffractometer employing ω-scans to cover reciprocal space up to θ = 27.45 ° with 99.5 % completeness; integration of raw data yielded a total of 28194 reflections, merged into 2881 unique reflections with R_{int} = 0.0619 after applying Lorentz, polarisation and empirical absorption correction.[1] The structure was solved

[1] (a) COLLECT Software, Nonius B.V., Delft, The Netherlands, 1998. (b) Otwinowski, Z., Minor, W., DENZO and SCALEPACK, Program for Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *„Methods in Enzymology, Vol 276: Macromolecular Crystallography Part A"*, Eds. Carter, Jr. C. W., Sweet, R. M., 1997, p. 307-326, Academic Press, New York, USA. (c) Spek, A., PLATON/MULABS, Program for empirical absorption correction, University of Utrecht, The

by direct methods using SHELXS-97,[1] and atomic positions and displacement parameters were refined using full-matrix-least-squares based on F^2 using SHELXL-97.[1] Refinement of 151 parameters using all reflections converged at R = 0.048, wR^2 = 0.146, highest residual electron density peak 0.3 e $Å^{-3}$.

Bond Distances in (Å)

O(1) - C(1)	1.208(2)	O(3') - C(3')	1.358(1)
O(3') - C(5')	1.372(2)	O(5') - C(5')	1.212(2)
C(1) - C(2)	1.519(2)	C(1) - C(12)	1.506(2)
C(2) - C(3)	1.509(2)	C(3) - C(3')	1.337(2)
C(3) - C(4)	1.429(2)	C(4) - C(5)	1.346(2)
C(5) - C(5')	1.448(2)	C(5) - C(6)	1.504(2)
C(6) - C(7)	1.525(2)	C(7) - C(8)	1.507(3)
C(8) - C(9)	1.525(2)	C(9) - C(10)	1.518(2)
C(10) - C(11)	1.527(2)	C(11) - C(12)	1.529(2)

Bond Angles in (°)

C(5') - O(3') - C(3')	122.1(1)	C(12) - C(1) - C(2)	117.7(1)
C(12) - C(1) - O(1)	121.9(1)	C(2) - C(1) - O(1)	120.5(1)
C(3) - C(2) - C(1)	111.3(1)	C(4) - C(3) - C(3')	116.6(1)
C(4) - C(3) - C(2)	120.6(1)	C(3') - C(3) - C(2)	122.8(1)
C(3) - C(3') - O(3')	122.6(1)	C(5) - C(4) - C(3)	122.9(1)
C(6) - C(5) - C(5')	115.8(1)	C(6) - C(5) - C(4)	126.0(1)
C(5') - C(5) - C(4)	118.2(1)	C(5) - C(5') - O(5')	126.1(1)
C(5) - C(5') - O(3')	117.2(1)	O(5') - C(5') - O(3')	116.7(1)
C(7) - C(6) - C(5)	117.8(1)	C(8) - C(7) - C(6)	116.3(2)
C(9) - C(8) - C(7)	117.7(1)	C(10) - C(9) - C(8)	114.1(1)
C(11) - C(10) - C(9)	115.4(1)	C(12) - C(11) - C(10)	114.1(1)
C(11) - C(12) - C(1)	114.4(1)		

Netherlands, 1998. (d) Sheldrick, G.M., SHELXS-97, Program for the solution of crystal structures, University of Göttingen, Germany, 1997. (e) Sheldrick, G. M. *Acta Cryst.* A46 467-473, 1990. (f) Sheldrick, G.M., SHELXL-97, Program for the refinement of crystal structures, University of Göttingen, Germany, 1997.

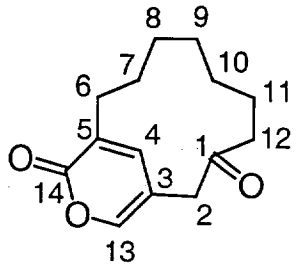
Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) with Standard Deviations in Parentheses. [a)]

Atom	x	y	z	U_{eq}
O(1)	0.3570(1)	0.6659(1)	0.6675(1)	0.064(1)
O(3')	0.2790(1)	0.1665(1)	0.3238(1)	0.055(1)
O(5')	0.3138(1)	-0.0556(1)	0.3399(2)	0.084(1)
C(1)	0.3453(1)	0.6115(1)	0.5535(1)	0.045(1)
C(2)	0.2989(1)	0.5394(2)	0.5156(2)	0.055(1)
C(3)	0.3023(1)	0.3748(2)	0.4725(1)	0.043(1)
C(3')	0.2750(1)	0.3134(1)	0.3648(1)	0.049(1)
C(4)	0.3371(1)	0.2784(1)	0.5429(1)	0.046(1)
C(5)	0.3446(1)	0.1360(2)	0.4998(2)	0.047(1)
C(5')	0.3132(1)	0.0731(2)	0.3853(2)	0.054(1)
C(6)	0.3826(1)	0.0323(2)	0.5616(2)	0.066(1)
C(7)	0.4253(1)	0.1059(2)	0.6399(2)	0.066(1)
C(8)	0.4569(1)	0.1762(2)	0.5521(2)	0.069(1)
C(9)	0.4424(1)	0.3256(2)	0.4773(2)	0.058(1)
C(10)	0.4428(1)	0.4624(2)	0.5732(2)	0.056(1)
C(11)	0.4260(1)	0.6119(2)	0.5023(2)	0.057(1)
C(12)	0.3755(1)	0.6132(2)	0.4443(1)	0.047(1)

[a)] $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$ or U_{iso}

Thermal Parameters (Å) with Standard Deviations in Parentheses

Atom	$U_{1,1}$	$U_{2,2}$	$U_{3,3}$	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$
O(1)	0.081(1)	0.060(1)	0.052(1)	-0.006(1)	0.012(1)	-0.006(1)
O(3')	0.045(1)	0.061(1)	0.056(1)	-0.007(1)	-0.002(1)	-0.010(1)
O(5')	0.071(1)	0.062(1)	0.110(1)	-0.035(1)	-0.012(1)	-0.004(1)
C(1)	0.055(1)	0.033(1)	0.048(1)	0.003(1)	0.008(1)	0.003(1)
C(2)	0.049(1)	0.051(1)	0.067(1)	-0.003(1)	0.014(1)	0.006(1)
C(3)	0.037(1)	0.046(1)	0.047(1)	0.003(1)	0.011(1)	-0.003(1)
C(3')	0.038(1)	0.057(1)	0.052(1)	0.007(1)	0.006(1)	-0.002(1)
C(4)	0.044(1)	0.045(1)	0.046(1)	-0.001(1)	0.001(1)	-0.007(1)
C(5)	0.043(1)	0.041(1)	0.055(1)	-0.001(1)	0.001(1)	-0.008(1)
C(5')	0.044(1)	0.052(1)	0.065(1)	-0.010(1)	0.003(1)	-0.010(1)
C(6)	0.061(1)	0.042(1)	0.089(1)	0.001(1)	-0.010(1)	-0.001(1)
C(7)	0.063(1)	0.053(1)	0.072(1)	0.009(1)	-0.016(1)	0.007(1)
C(8)	0.049(1)	0.064(1)	0.089(1)	0.002(1)	-0.003(1)	0.009(1)
C(9)	0.044(1)	0.065(1)	0.065(1)	0.003(1)	0.008(1)	0.001(1)
C(10)	0.043(1)	0.059(1)	0.061(1)	0.002(1)	-0.001(1)	-0.008(1)
C(11)	0.053(1)	0.053(1)	0.065(1)	0.003(1)	0.010(1)	-0.013(1)
C(12)	0.054(1)	0.040(1)	0.048(1)	0.005(1)	0.008(1)	-0.004(1)



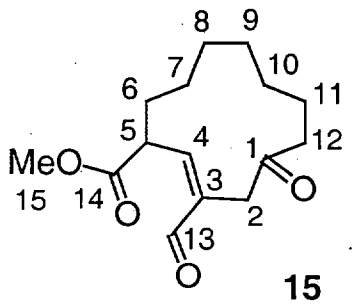
14

Unambiguous assignment of the ^{1}H and ^{13}C NMR data of compound **14** based on COSY, NOESY and $^{13}C,^{1}H$-chemical shift correlated spectra. Arbitrary numbering as shown.

Spectrometer: Bruker DMX 600

Solvent: $CDCl_3$

position	δ_C	δ_H (*J*, Hz)
1	208.5	
2	45.4	3.27 (s)
3	113.5	
4	139.3	7.05 (d, J = 2.5)
5	130.3	
6	30.4	2.55 (t, J = 6.0)
7	22.9	1.66 (m)
8	28.0	1.33 (m)
9	24.9	1.03 (quint., J = 7.4)
10	26.0	1.22 (m)
11	22.3	1.55 (m)
12	36.5	2.35 (t, J = 7.0)
13	147.2	7.34 (d, J = 2.5)
14	162.1	



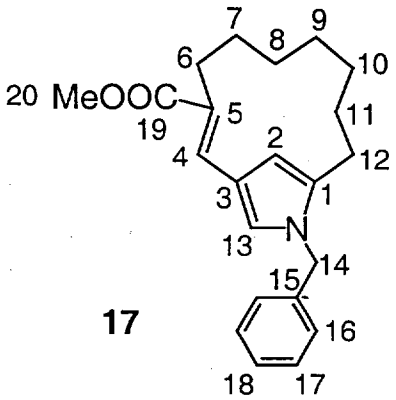
15

Unambiguous assignment of the ^{1}H and ^{13}C NMR data of compound **15** based on COSY, NOESY and ^{13}C,^{1}H-chemical shift correlated spectra. Arbitrary numbering as shown.

Spectrometer: Bruker DMX 600

Solvent: $CDCl_3$

position	δ_C	δ_H (*J*, Hz)
1	206.5	
2	37.4	3.53 (s)
3	138.9	
4	150.6	6.67 (d, J = 10.8)
5	43.4	3.52 (ddd, J = 10.7, 8.4, 5.6)
6	31.2	1.72 (m) and 1.86 (m)
7	24.2	1.10 (m) and 1.35 (m)
8	25.0	1.26 (m)
9	26.0	1.17 (m) and 1.36 (m)
10	25.9	1.32 (m) and 1.42 (m)
11	22.2	1.71 (m) and 1.78 (m)
12	42.6	2.32 (ddd, J = 14.6, 10.2, 3.2)
		2.62 (ddd, J = 14.7, 8.4, 2.9)
13	193.3	9.52 (s)
14	172.9	
15	52.4	3.70 (s)



17

Unambiguous assignment of the ^{1}H and ^{13}C NMR data of compound **17** based on COSY, NOESY and $^{13}C,^{1}H$-chemical shift correlated spectra. Arbitrary numbering as shown.

Spectrometer: Bruker DMX 600

Solvent: CD_2Cl_2

position	δ_C	δ_H (*J*, Hz)
1	133.7	
2	112.1	6.28 (d, J = 1.5)
3	119.5	
4	134.8	7.58 (s)
5	130.6	
6	26.2	2.52 (m)
7	23.8	1.25 (m)
8	27.5	1.28 (m)
9	25.8	1.12 (m)
10	24.5	1.02 (m)
11	25.9	1.60 (m)
12	25.5	2.56 (t, J = 6.5)
13	122.2	6.65 (d, J = 1.5)
14	50.7	4.99 (s)
15	138.5	
16	127.1	7.11 (t, J = 7.3)
17	129.0	7.32 (t, J = 6.2)
18	127.9	7.27 (t, J = 7.3)
19	169.5	
20	51.7	3.71 (s)

Table 1. Characteristic Infrared Absorptions of New Compounds (cm^{-1})

Product	IR
9	2930, 2857, 1736, 1656, 1463, 1471, 1441, 1390, 1361, 1255, 1107, 1085, 1006, 911, 838, 778
10	3065, 2929, 2857, 1744, 1653, 1585, 1463, 1448, 1327, 1312, 1256, 1150, 1108, 1084, 839, 778, 723, 689
11	3531, 3066, 2950, 2928, 2855, 1734, 1585, 1471, 1463, 1447, 1309, 1253, 1223, 1145, 1081, 1005, 839, 778, 757, 720, 690, 597
12	3512, 3444, 3065, 2935, 1730, 1584, 1447, 1396, 1307, 1173, 1143, 1080, 1016, 758, 721, 689, 626, 569
13	3064, 2933, 2858, 1741, 1685, 1628, 1584, 1447, 1308, 1145, 1079, 1054, 721, 688
14	3401, 3087, 3064, 3029, 2932, 2858, 1712, 1648, 1566, 1461, 1446, 1363, 1258, 1149, 1075, 1029, 804, 779, 752, 699
15	1736, 171, 1690, 1643
16	3088, 3063, 3030, 2926, 2853, 1737, 1720, 1515, 1495, 1452, 1368, 1233, 1166, 1021, 954, 816, 729, 700
17	3063, 3029, 2926, 2855, 1700, 1605, 1506, 1497, 1454, 1435, 1356, 1261, 1234, 1162, 1091, 807, 746, 727, 700
18	3323, 3062, 3027, 2961, 2925, 2852, 1731, 1604, 1496, 1453, 1434, 1356, 1154, 1096, 731, 697
19	3497, 2926, 2853, 1733, 1511, 1455, 1436, 1358, 1199, 1164, 1095, 1021, 729, 696
20	3121, 3062, 3031, 2933, 2857, 1740, 1666, 1606, 1507, 1168, 732, 700
21	2924, 2854, 1642, 1561, 1507, 1455, 734, 724

Table 1. ***continued***

Product	IR
22	3088, 3064, 3029, 2925, 2853, 1659, 1606, 1506, 1497, 1454, 1419, 1387, 1354, 1305, 1206, 1183, 1107, 1076, 1029, 897, 815, 728, 696
23	3064, 3029, 2926, 2852, 1606, 1507, 1497, 1455, 1355, 1327, 1299, 1149, 1135, 1075, 1029, 797, 727, 695
24	3064, 3030, 2923, 2853, 1606, 1506, 1497, 1455, 1438, 1354, 1299, 805, 727, 695
25	3088, 3063, 3030, 2929, 2853, 1705, 1612, 1560, 1507, 1454, 1374, 1262, 1178, 1149, 1090, 1038, 848, 809, 730, 697

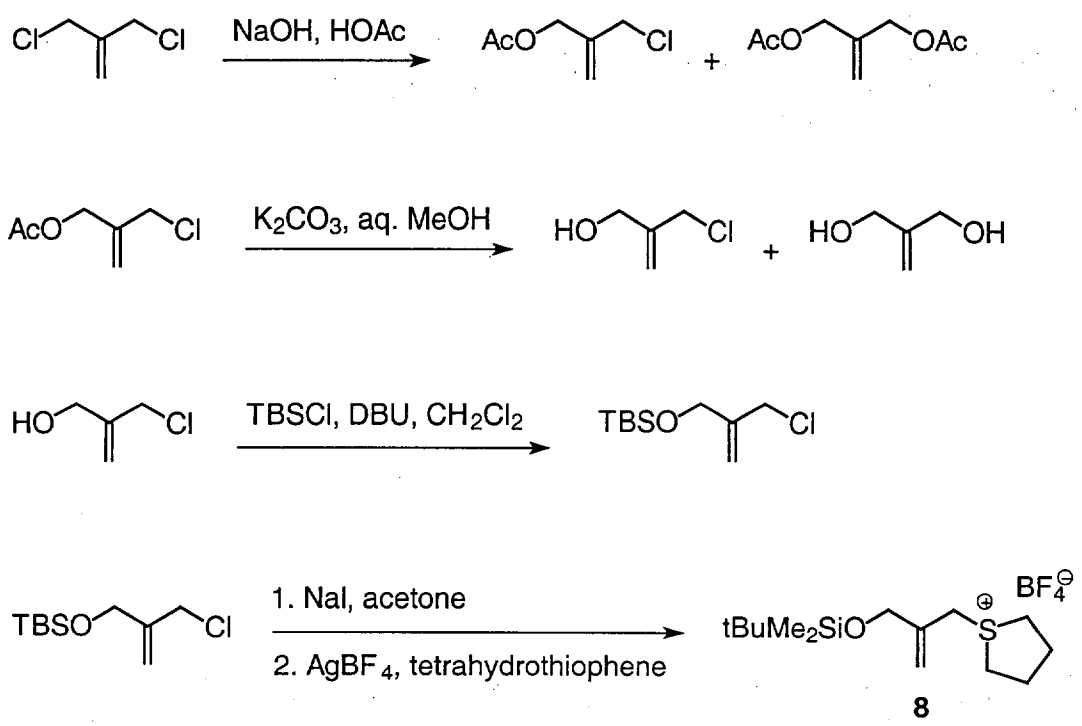
Table 2. MS Data (EI) of New Compounds

Product	*m/z* (rel. intensity)
9	336 (11), 335 (54), 334 (10), 333 (53), 157 (14), 144 (10), 143 (89), 127 (13), 113 (14), 109 (11), 107 (11), 97 (10), 95 (13), 93 (24), 83 (10), 81 (22), 79 (18), 75 (100), 73 (51), 69 (19), 67 (20)
10	469 (13), 468 (30), 467 (100), 199 (18), 143 (22), 77 (15), 75 (18), 73 (13)
11	467 (14), 417 (12), 325 (27), 307 (24), 293 (16), 251 (31), 219 (28), 217 (10), 201 (21), 200 (15), 199 (100), 173 (29), 135 (30), 91 (10), 81 (11), 77 (15), 75 (45), 73 (30), 55 (11)
12	237 (82), 236 (56), 219 (29), 209 (12), 191 (22), 173 (22), 163 (15), 152 (32), 143 (32), 125 (33), 109 (35), 107 (44), 105 (24), 97 (23), 95 (67), 93 (41), 91 (39), 81 (85), 79 (63), 77 (100), 69 (31), 67 (59), 55 (91), 41 (88), 29 (36)
13	376 (2, [M^+]), 236 (14), 235 (100), 234 (96), 207 (11), 191 (19), 161 (10), 137 (33), 136 (10), 125 (18), 124 (11), 123 (17), 121 (11), 119 (11), 109 (11), 107 (14), 105 (15), 97 (12), 95 (24), 94 (10), 93 (15), 91 (19), 81 (28), 79 (26), 77 (50)
14	235 (16), 234 (100, [M^+]), 177 (17), 163 (10), 149 (15), 137 (64), 136 (23), 135 (15), 124 (33), 123 (25), 122 (20), 121 (13), 107 (11), 95 (19), 94 (24), 93 (13), 91 (16), 79 (29), 77 (23), 67 (24), 66 (32), 65 (19), 55 (26), 53 (12), 43 (13), 41 (45), 39 (28), 29 (16), 27 (15)
15	266 (51, [M^+]), 238 (12), 235 (18), 234 (39), 207 (10), 206 (33), 188 (10), 178 (22), 149 (13), 137 (19), 136 (12), 135 (15), 124 (14), 123 (13), 121 (16), 119 (12), 109 (69), 108 (23), 98 (74), 97 (13), 96 (18), 95 (37), 93 (22), 91 (19), 81 (28), 79 (36), 77 (19), 65 (56), 59 (21), 55 (62), 41 (100), 29 (33)
16	398 (14), 397 (55, [M^+]), 355 (22), 338 (31), 326 (9), 240 (12), 199 (18), 91 (100), 43 (10)

Table 2. ***continued***

Product	*m/z* (rel. intensity)
17	338 (22), 337 (91, [M+]), 336 (14), 294 (11), 278 (15), 266 (15), 246 (10), 170 (11), 91 (100)
18	445 (17), 444 (53, [M+]), 353 (11), 343 (14), 302 (20), 301 (45), 289 (14), 288 (60), 91 (100).
19	356 (13), 355 (52, [M+]), 240 (25), 212 (16), 199 (34), 198 (12), 170 (15), 91 (100)
20	354 (12), 353 (50, [M+]), 322 (12), 239 (10), 238 (13), 211 (15), 210 (40), 197 (22), 183 (11), 170 (14), 91 (100)
21	295 (56, [M+]), 267 (14), 224 (15), 211 (11), 210 (33), 197 (15), 183 (10), 170 (17), 91 (100)
22	308 (16), 307 (76, [M+]), 306 (16), 264 (18), 250 (22), 91 (100), 65 (11)
23	310 (23), 309 (100, [M+]), 294 (15), 280 (24), 91 (76)
24	434 (34), 433 (100, [M+]), 432 (12), 307 (11), 306 (29), 292 (11), 91 (93)
25	366 (15), 365 (53, [M+]), 337 (10), 336 (39), 318 (10), 91 (100)

Large Scale Synthesis of Sulfonium Salt 8 [2]



3-Acetoxy-2-chloromethyl-1-propene. A solution of 3-chloro-2-chloromethyl-1-propene (122.0 g, 0.97 mol) is as added over a period of 2 h to a solution of NaOAc (79.0 g, 0.96 mol) in HOAc (300 mL) at 100°C. The resulting mixture is stirred at that temperature for 24 h. For work-up, the reaction is allowed to cool to ambient temperature, the mixture is poured into water (1 L), the aqueous layer is extracted with diethyl ether (1 L in several portions) and the combined organic phases are carefully neutralized with sat. aq. $NaHCO_3$ (ca. 750 mL). Ether is distilled off at normal pressure and the residue is purified by vacuum distillation. This leads to the recovery of unreacted starting material (40.8 g, bp = 53-59 °C/10 mbar) and affords the desired monoacetate (52.6 g, bp = 88-93°C/10 mbar), as well as 3-acetoxy-2-(acetoxymethyl)-1-propene (14.0 g, bp = 116-122°C/10 mbar). The recovered dichloride is used as the starting

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[2] For the preparation of alcohol 3-acetoxy-2-chloromethyl-1-propene by a similar route see: Chalova, O. B.; Christoedova, G. B.; Kiladze, T. K.; Germash, E. V.; Kantor, E. A.; Rakhmankulov, D. L. *Zh. Prikl. Khim.* **1988**, *61*, 934-937; CA: **110**: 38603b.

material for a second substitution under the same conditions, leading to a second crop of monoacetate (16.8 g) and diacetate (6.1 g). Total yield of 3-acetoxy-2-chloromethyl-1-propene: 69.4 g (48 %, 53 % based on recovered starting material. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.35 (s), 5.27 (s) [2H], 4.68 (s, 2H), 4.10 (s, 2H), 2.08 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3, 139.8, 117.7, 64.0, 44.8, 20.6.

2-Chloromethyl-3-hydroxy-1-propene. A solution of acetate 3-acetoxy-2-chloromethyl-1-propene (69.4 g, 0.467 mol) and K_2CO_3 (8.0 g) in MeOH (250 mL) and water (90 mL) is stirred at ambient temperature for 75 min. For work-up, water (100 mL) is added, the aqueous phase is extracted with Et_2O (500 mL in several portions), the combined organic layers are dried over Na_2SO_4 and the solvent is removed by distillation at normal pressure. The crude product thus obtained is purified by distillation in vacuo, providing the title compound (25.6 g, 51 %) as a colorless liquid. bp = 82-82 °C (10 mbar). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.24 (m, 2H), 4.22 (s, 2H), 4.18 (s, 2H), 2.87 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.4, 115.2, 63.0, 45.1.

2-Chloromethyl-3-(*tert*-butyldimethylsilyloxy)-1-propene. To a solution of 2-chloromethyl-3-hydroxy-1-propene (25.37 g, 238.0 mmol) in CH_2Cl_2 (350 mL) is added a solution of *tert*-butyldimethylchlorosilane (38.4 g, 254 mmol) and DBU (39.0 g, 256 mmol) in CH_2Cl_2 (100 mL) over a period of 3 h. After stirring for another 15 min, the reaction is quenched by the addition of aq. sat $NaHCO_3$ (ca. 100 mL), the organic layer is dried over Na_2SO_4, the solvent is evaporated and the residue is purified by distillation, providing the title compound as a colorless liquid (49.33 g, 94%). bp = 53-56 °C (10^{-3} torr). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.21 (s), 5.18 (s) [2H], 4.22 (s, 2H), 4.07 (s, 2H), 0.89 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.5, 114.3, 63.3, 44.9, 25.8, 18.3, -5.4.

1-[2-(((tert-Butyldimethylsilylanyl)oxy)methyl)allyl]tetrahydrothiophenium tetrafluoroborate (8). For the success of this reaction, it is of utmost importance to use only thoroughly dried reagents and solvents (see General). A solution of 2-chloromethyl-3-(*tert*-butyldimethylsilyloxy)-1-propene (5.15 g, 23.3 mmol) and NaI (3.50 g, 23.3 mmol) in acetone (40 mL) is stirred for 16 h at 35°C. Precipitated salts are filtered off under Ar and the residue is washed with acetone (10 mL) in several portions. The combined filtrate is treated

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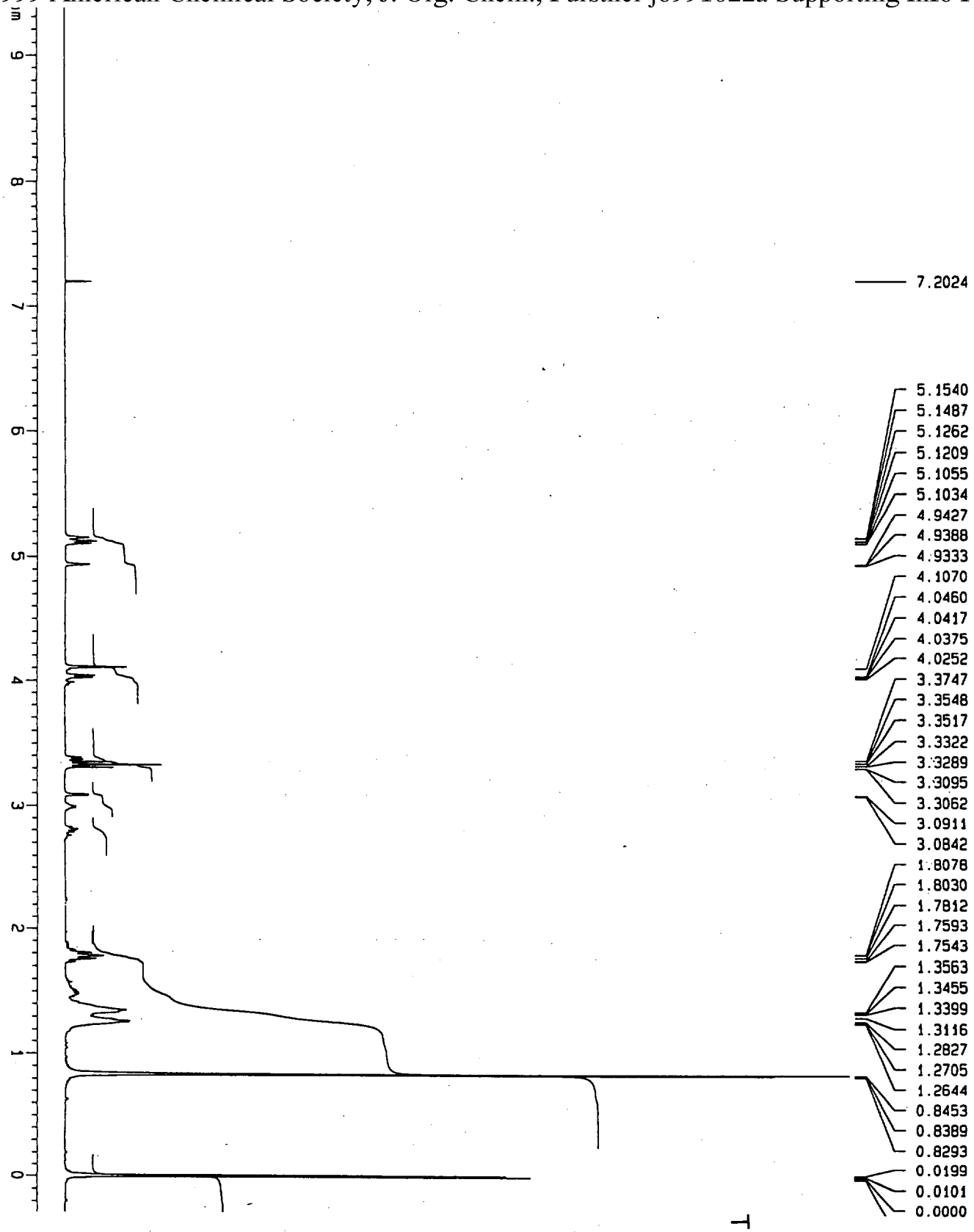
with tetrahydrothiophene (4.11 g, 46.6 mmol) and $AgBF_4$ (4.54 g, 23.3 mmol) and the resulting mixture is stirred in the dark for 1.5 h. The suspension is diluted with CH_2Cl_2 (20 mL), precipitated salts are filtered off and the solvent is evaporated. The residue is suspended in hexane (50 mL) until title compound precipitates in crystalline form. The supernatant hexane is removed via canula and the product dried in vacuo. Colorless crystals (7.62 g, 91%). Mp = 91-92 °C. ^{1}H NMR (200 MHz, THF-d_8): δ 5.55 (d, J = 1.0 Hz, 1H), 5.51 (dd, J = 2.8, 1.5 Hz, 1H), 4.29 (s, 2H), 4.02 (s, 2H), 3.65-3.39 (m, 4H), 2.52-2.22 (m, 4H), 0.95 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (50 MHz, THF-d_8): δ 139.7, 120.8, 65.8, 45.7, 44.2, 29.4, 26.6, 19.3, -5.0. $C_{14}H_{29}BF_4OSSi$: *calcd.*: C, 46.67; H, 8.11; *found*: C, 46.53; H, 8.06.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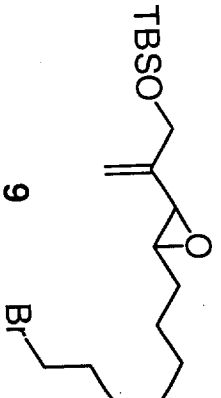
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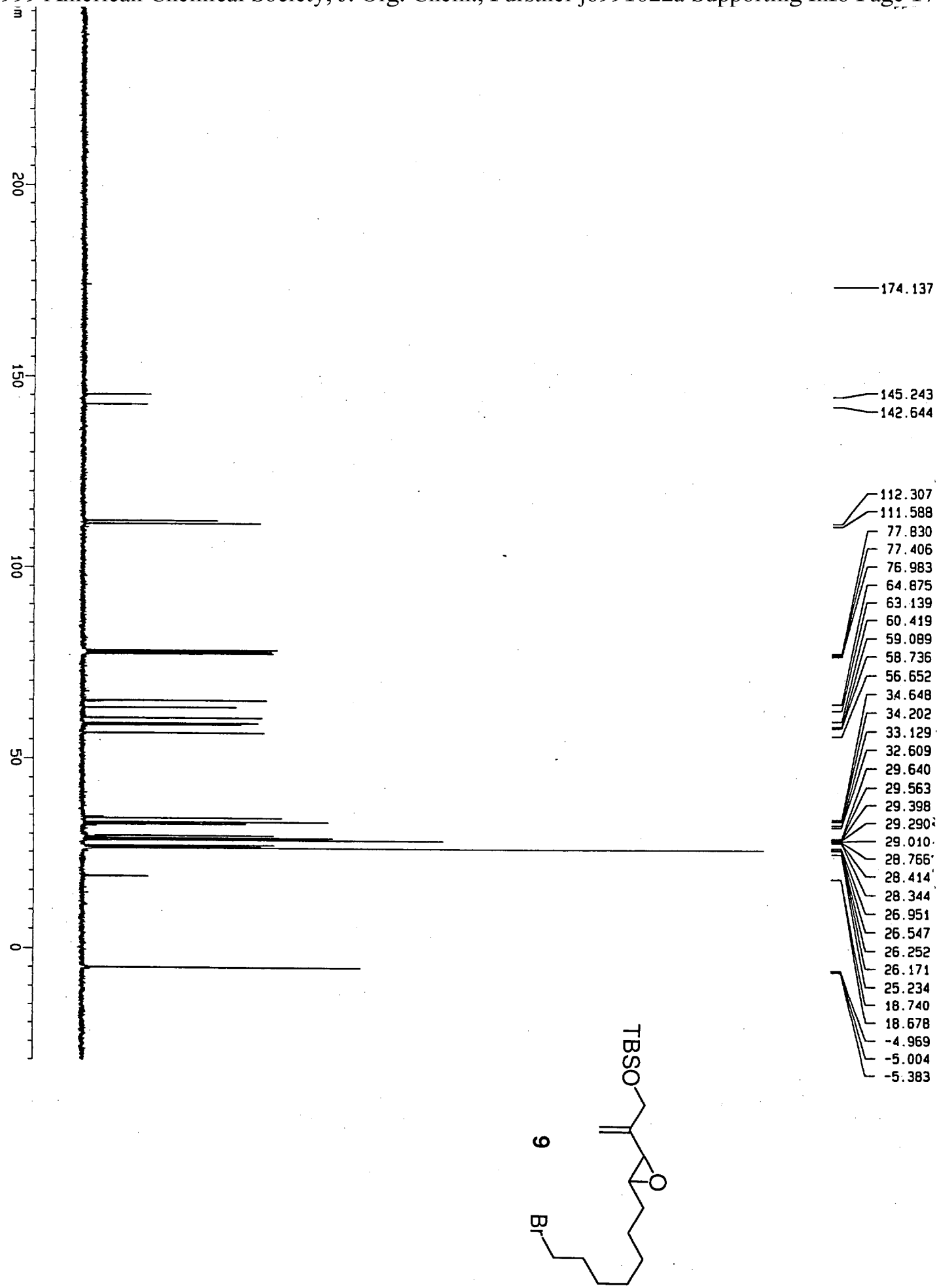
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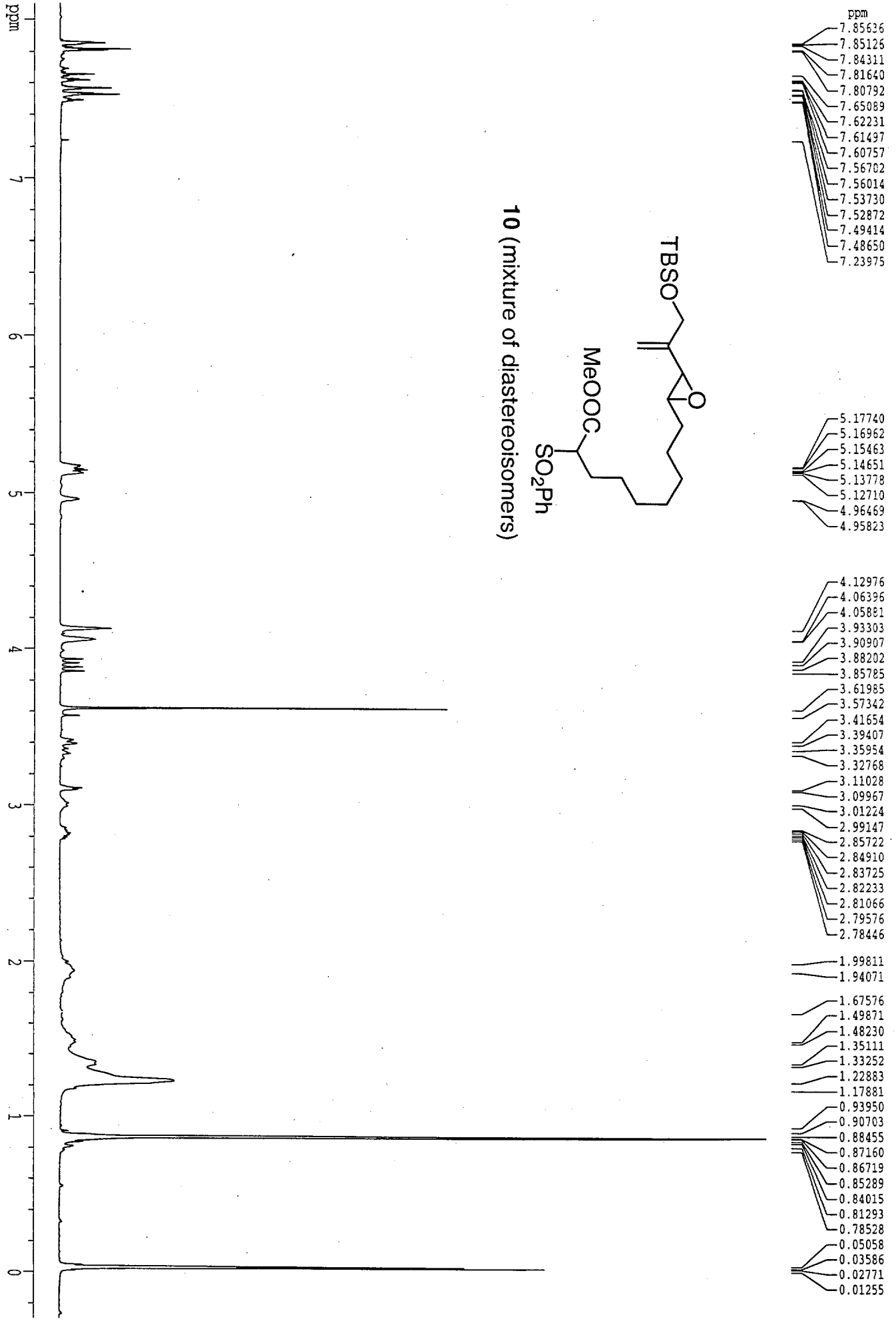

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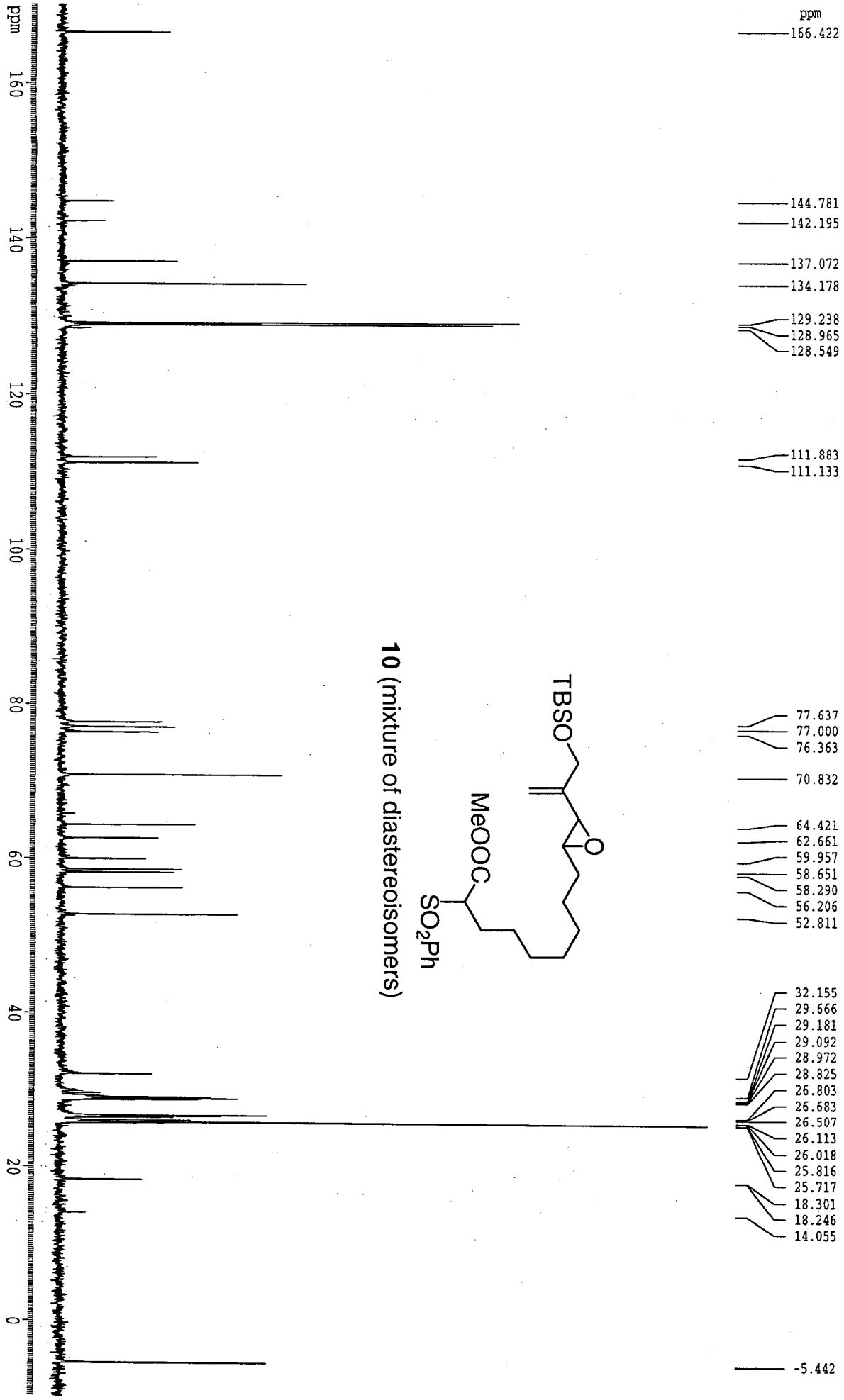

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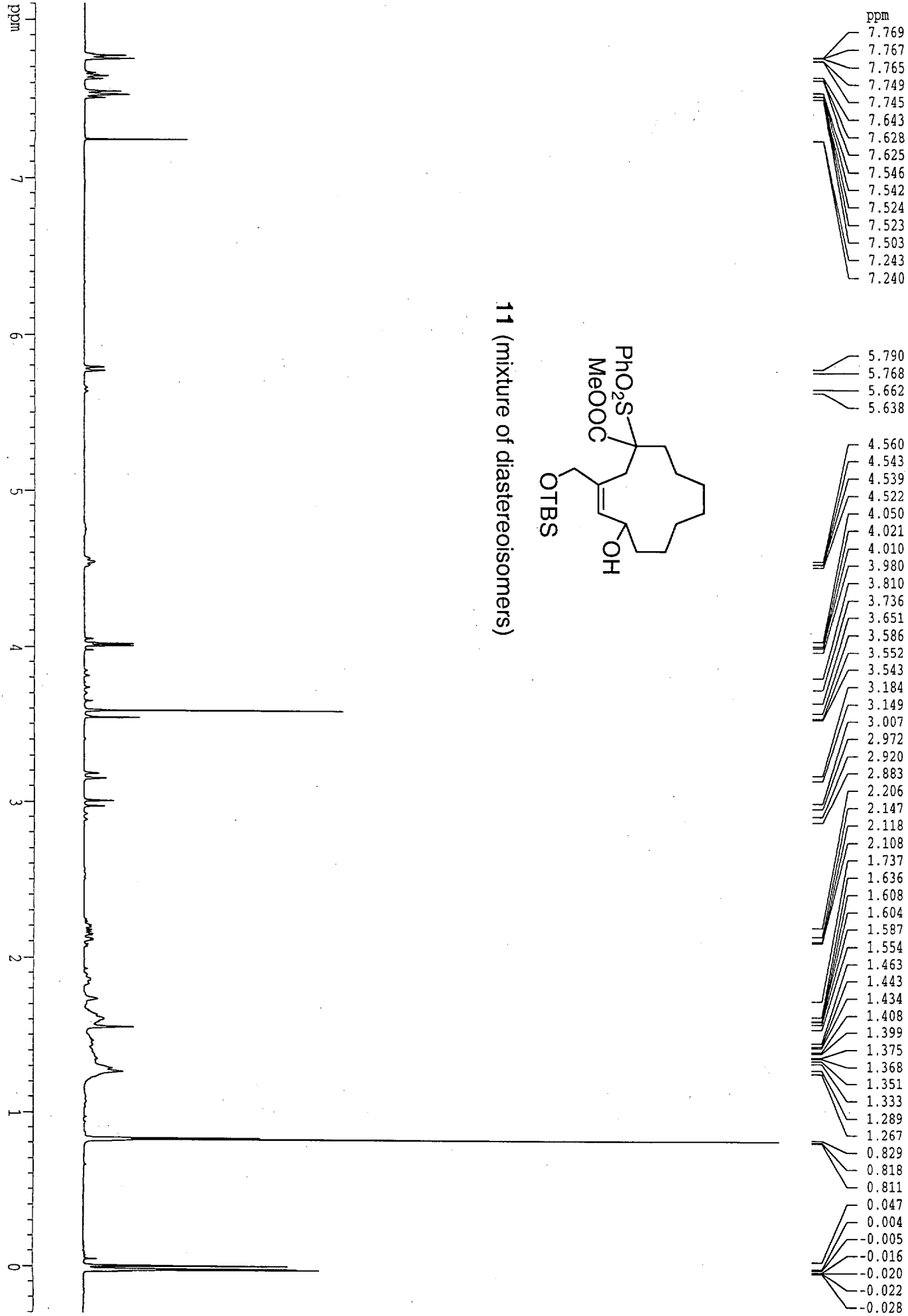

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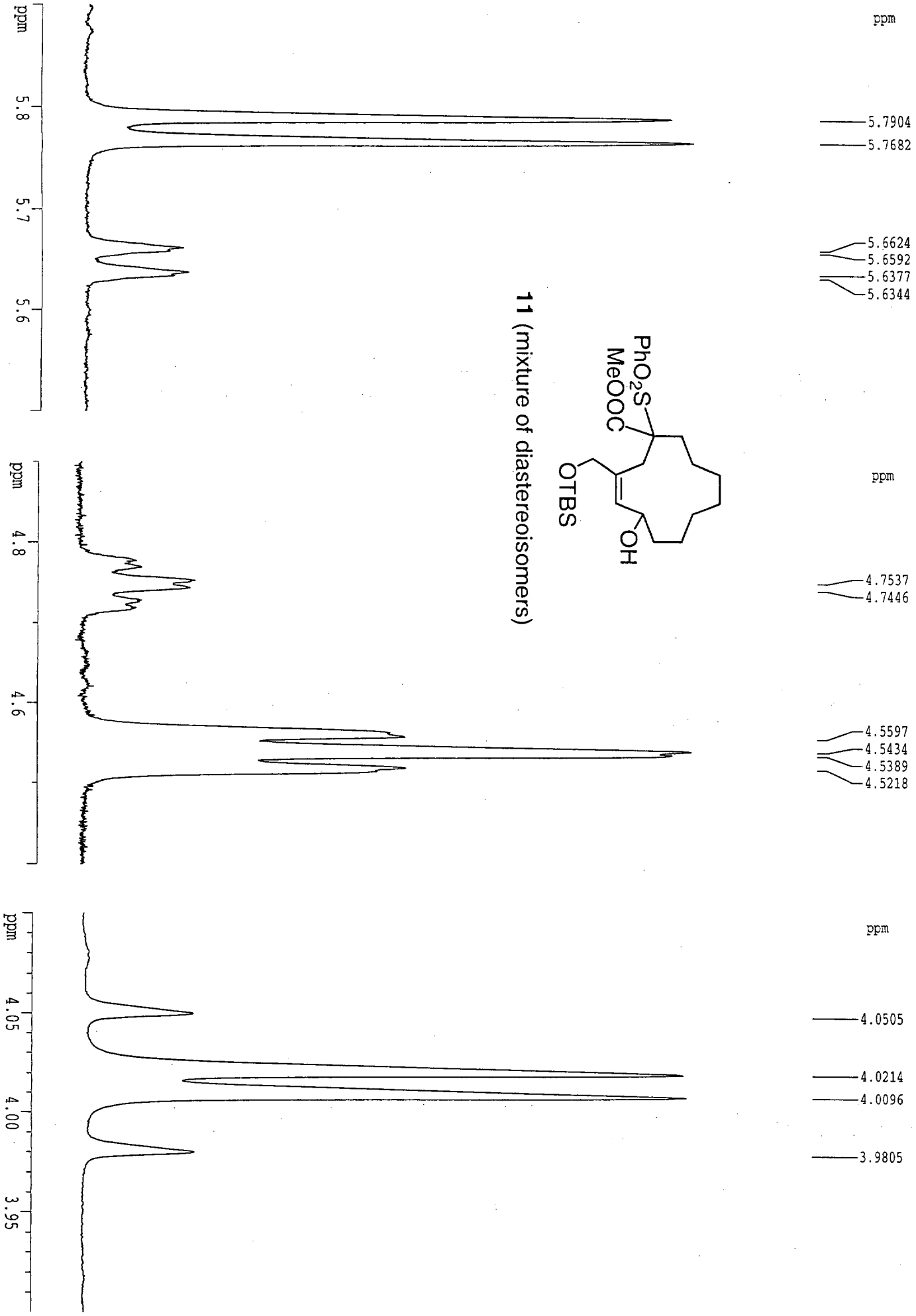

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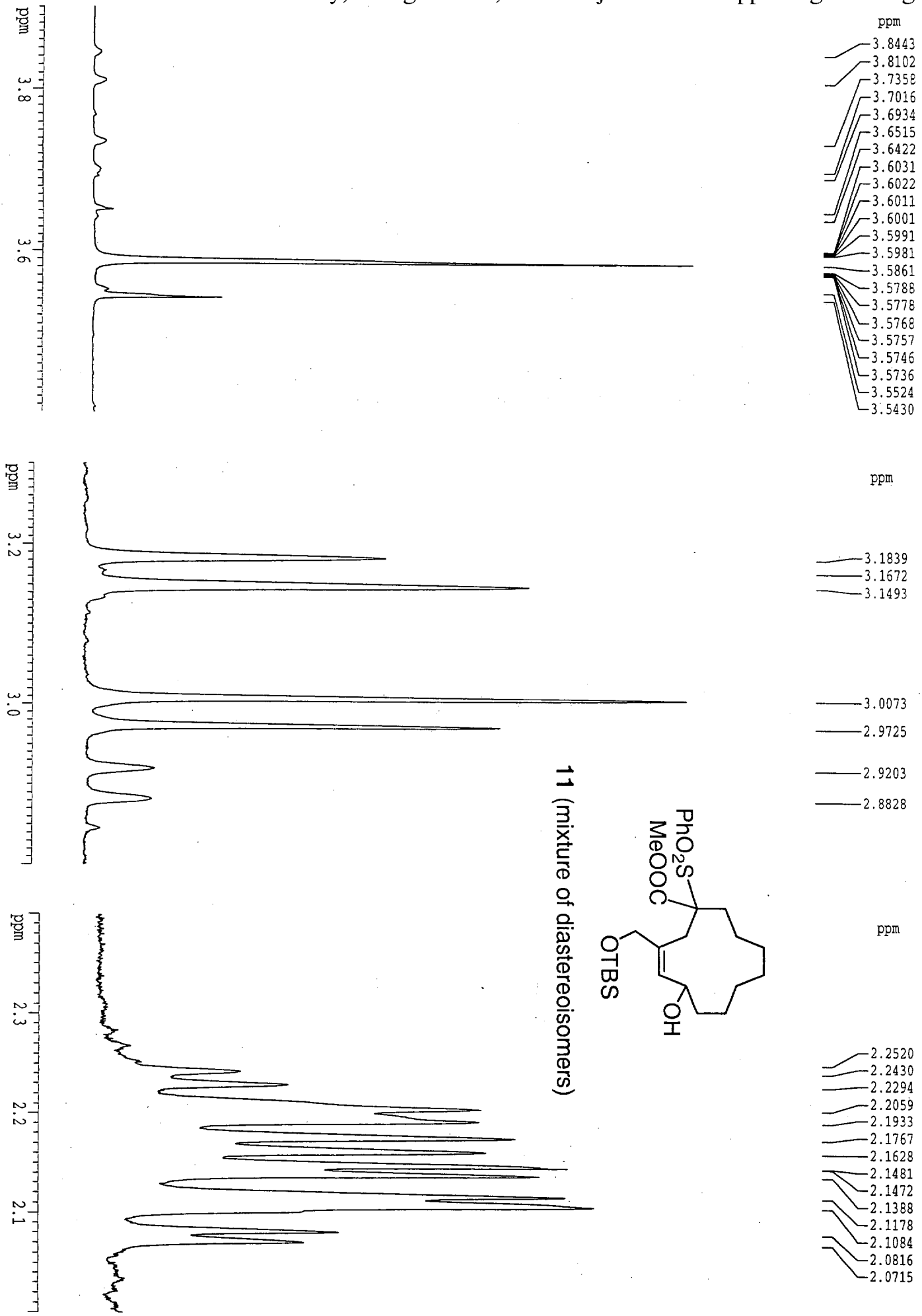

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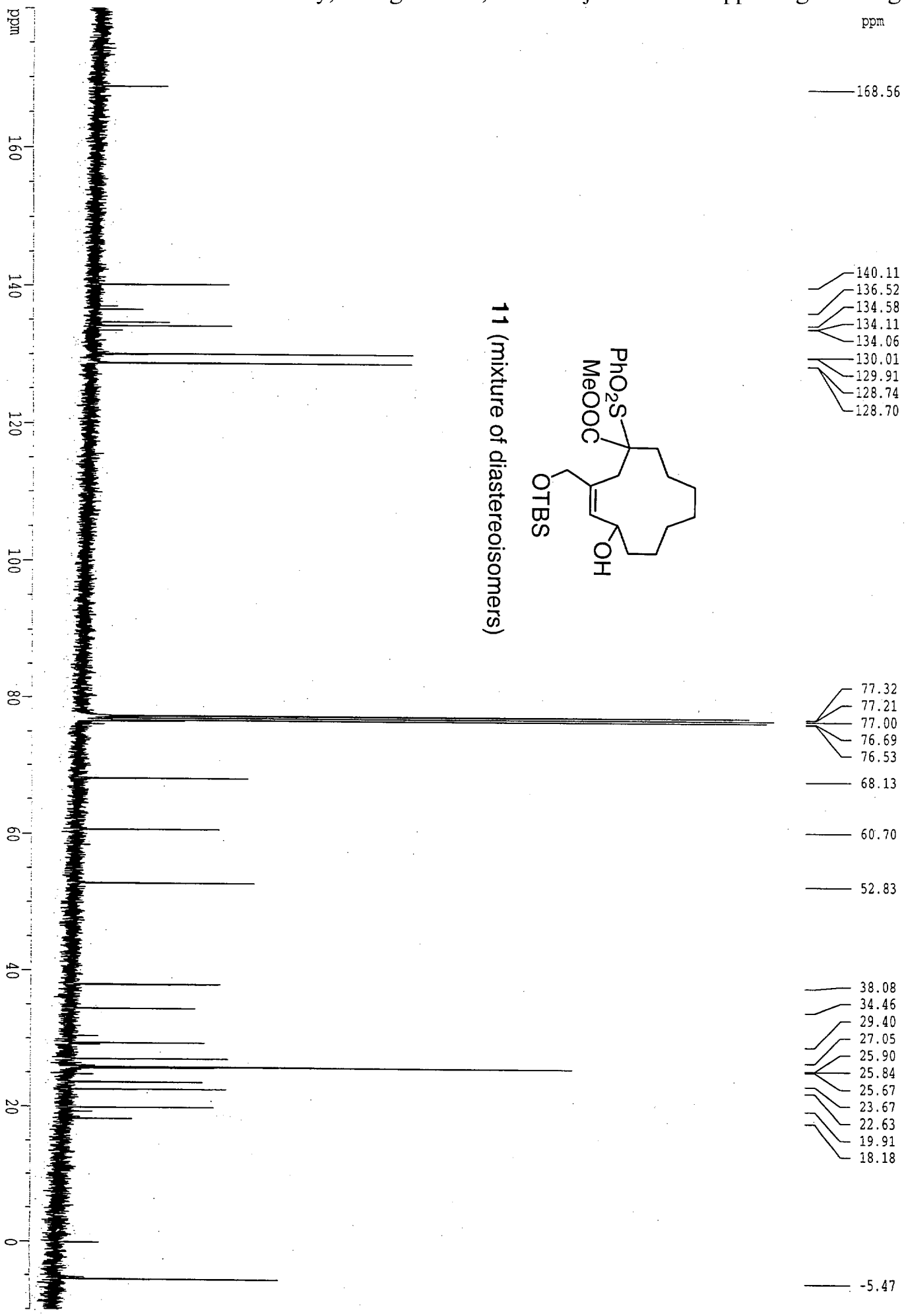

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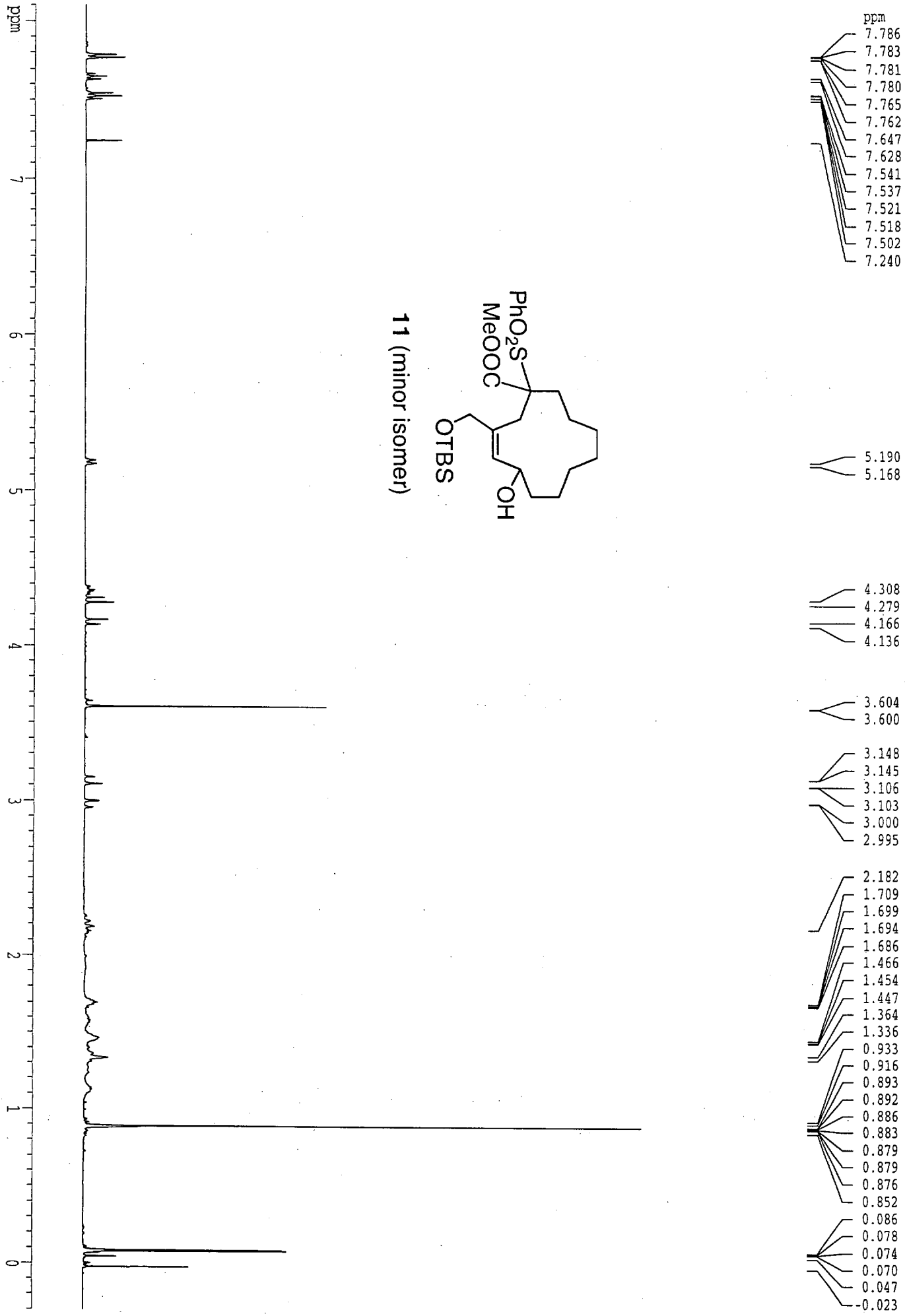

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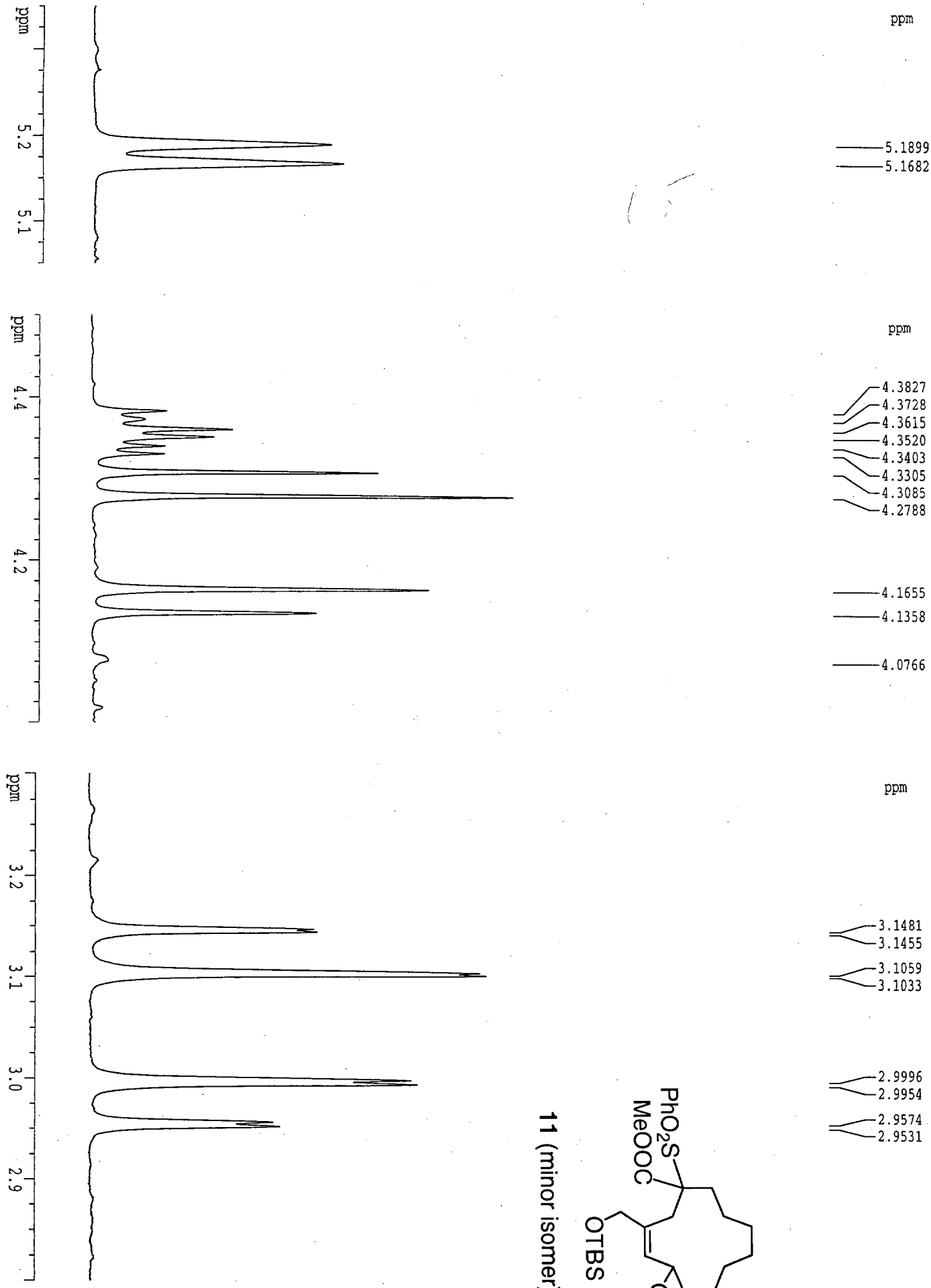

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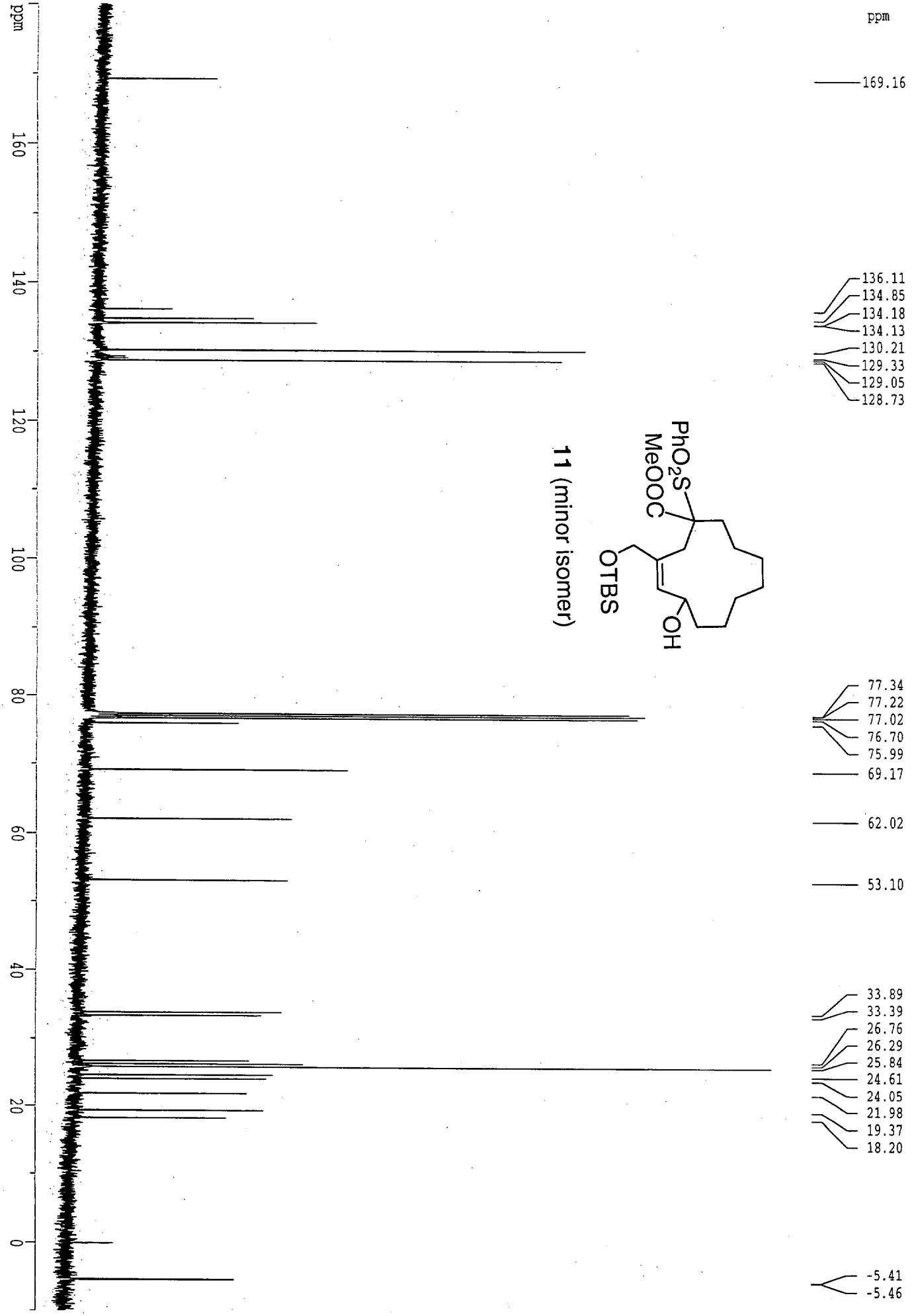

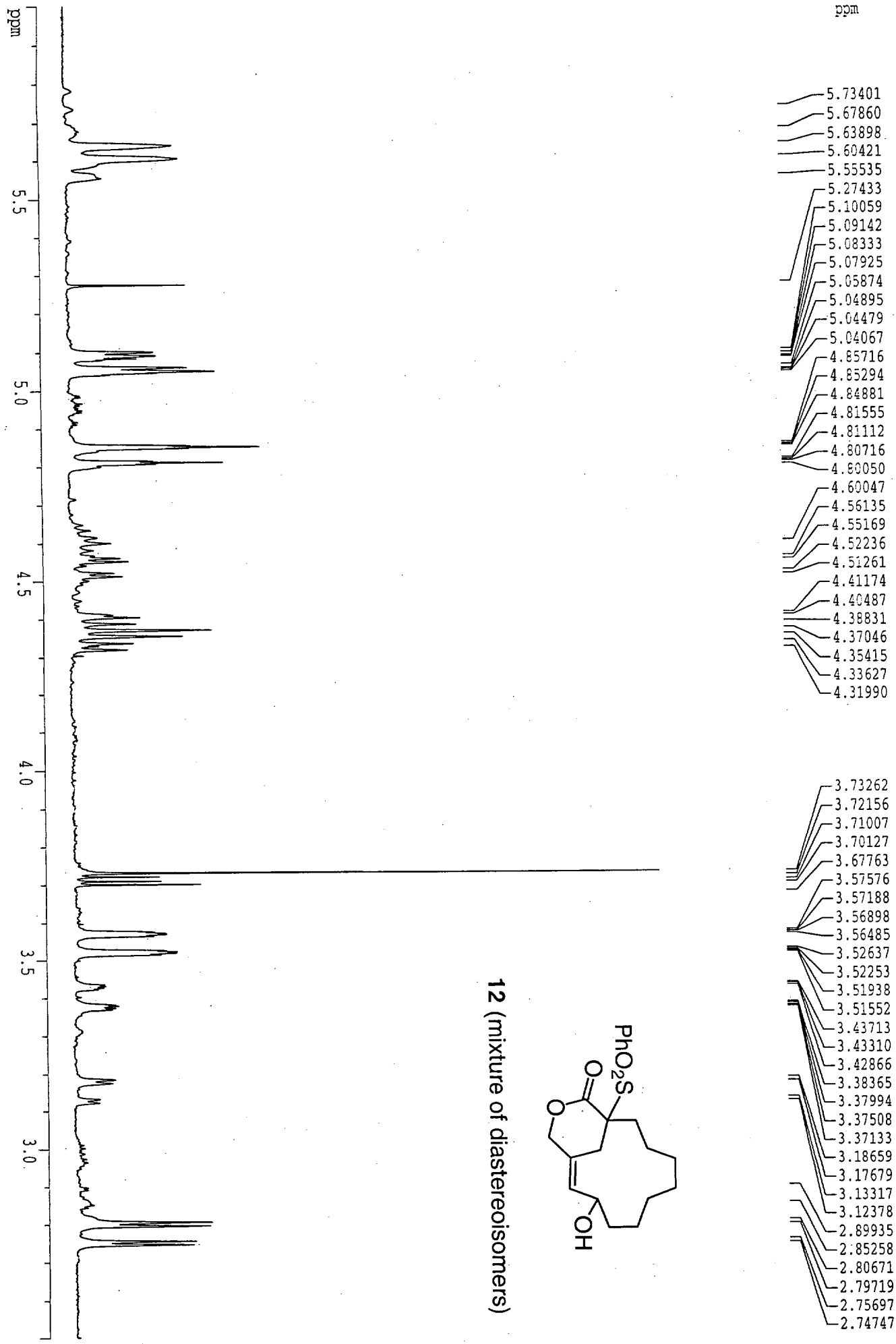

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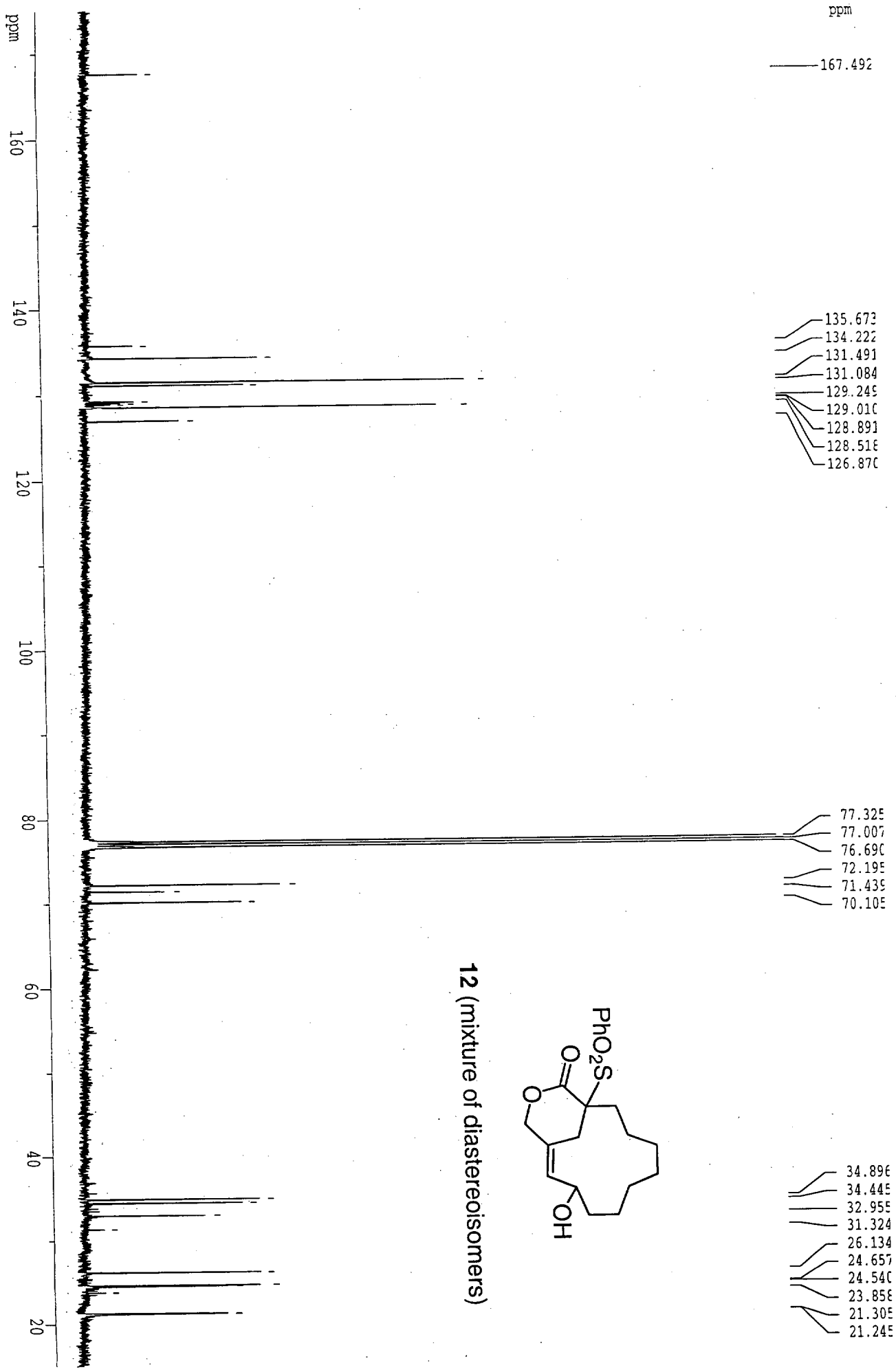

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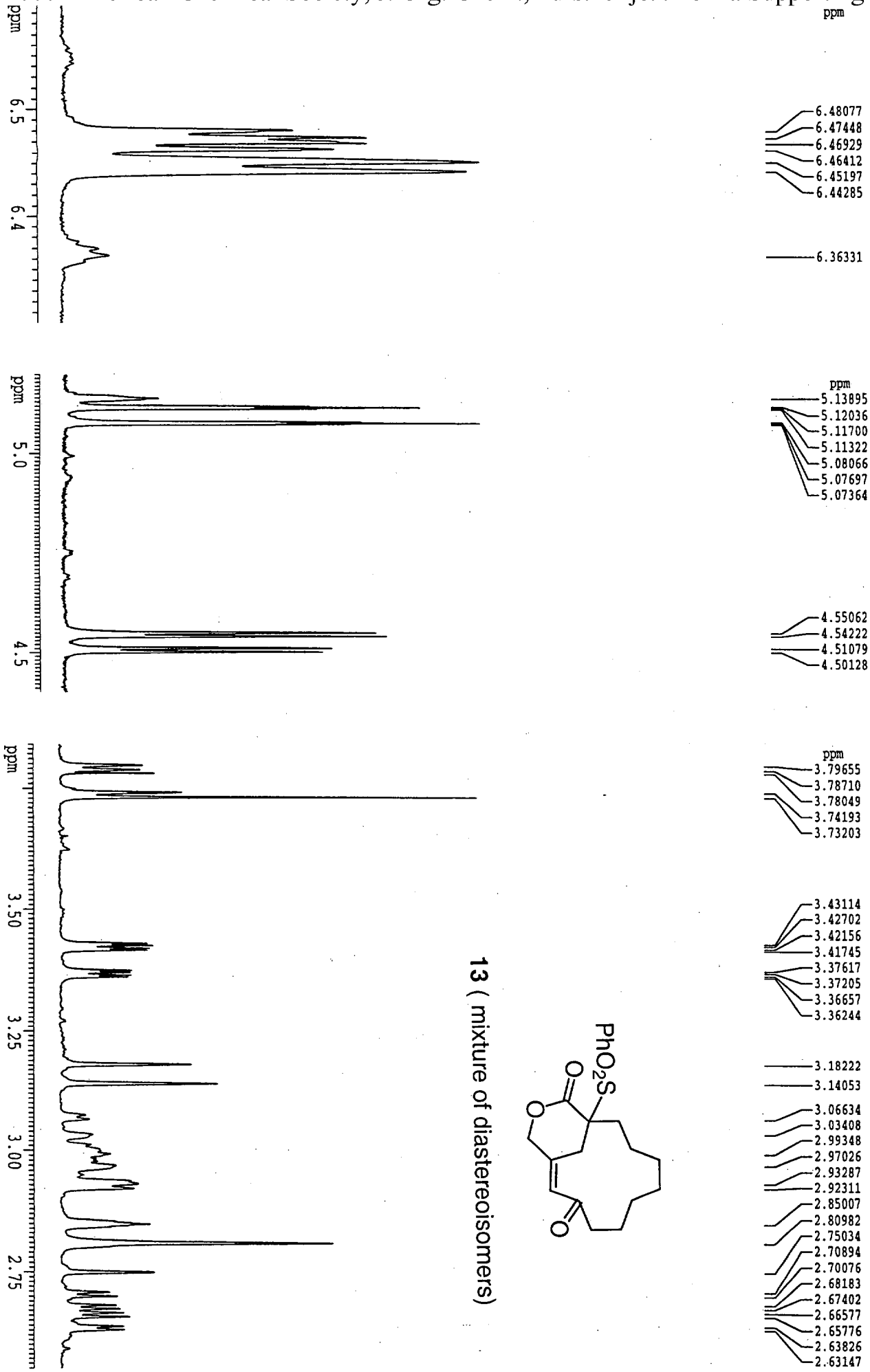

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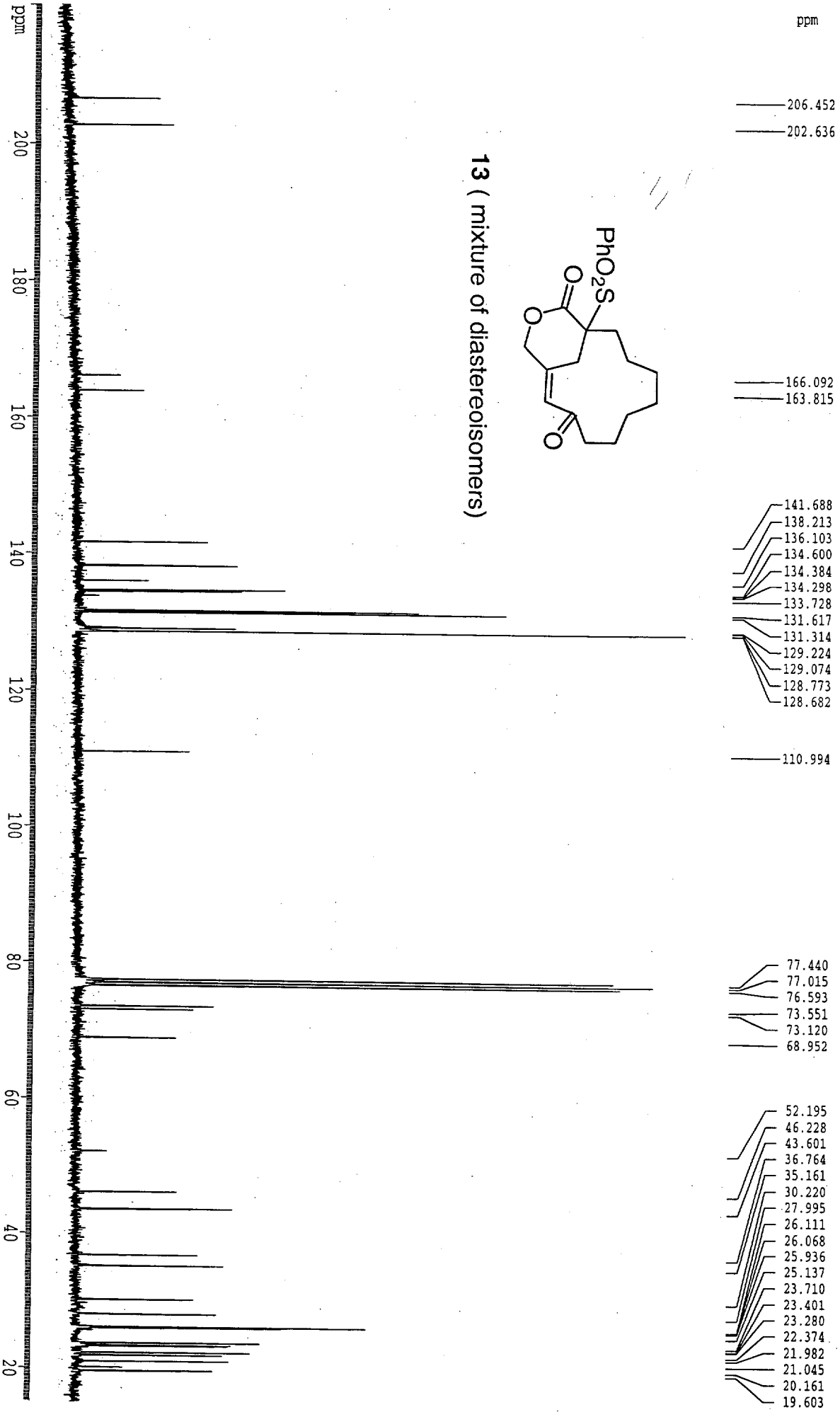

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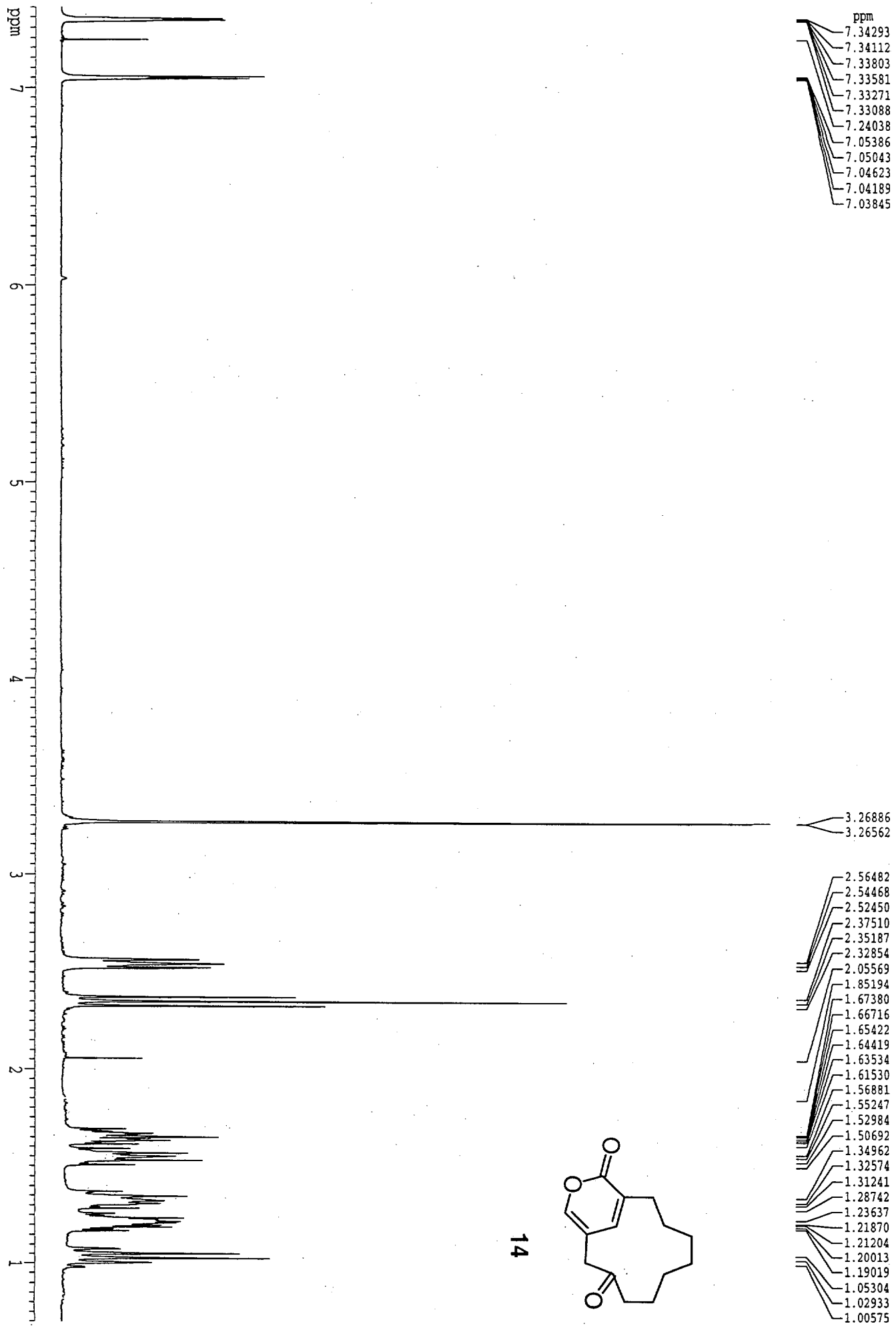

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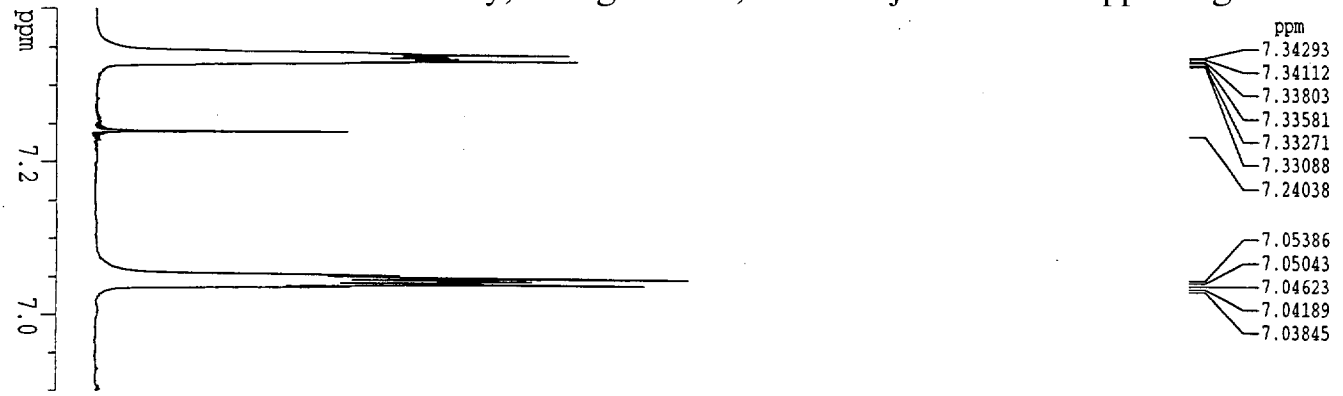

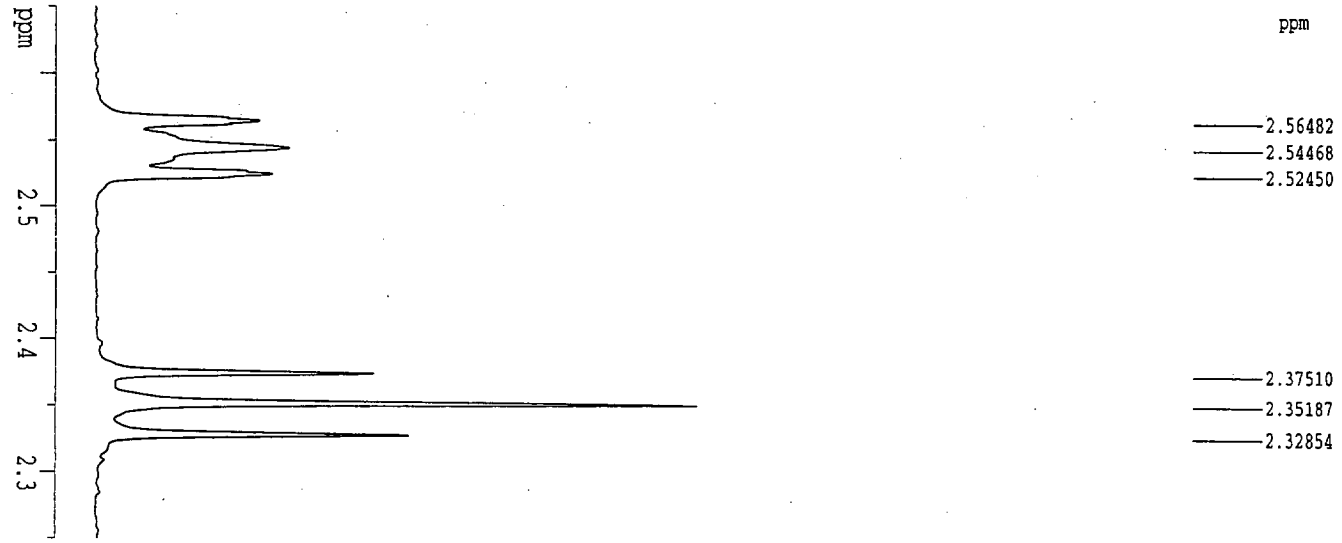

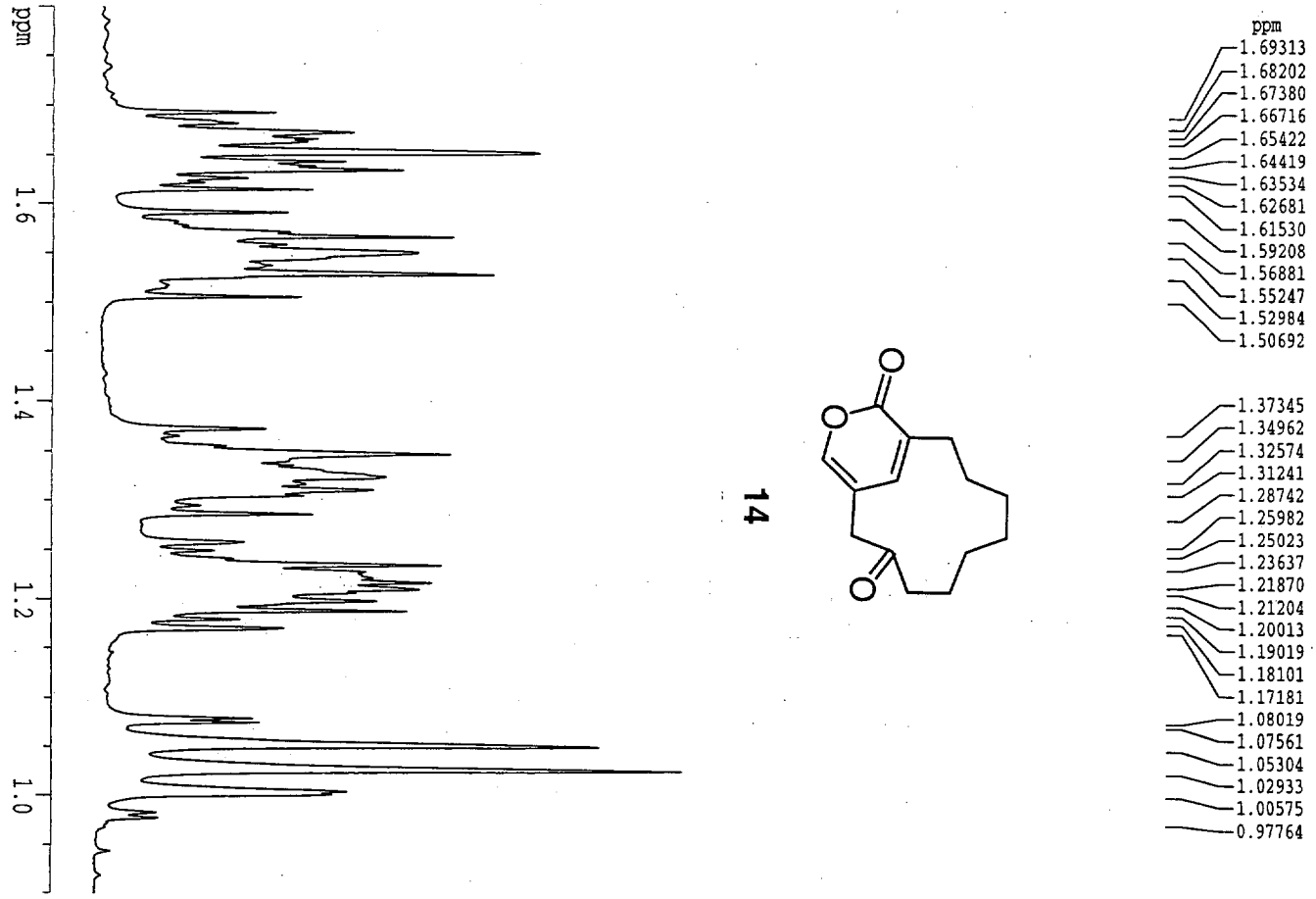

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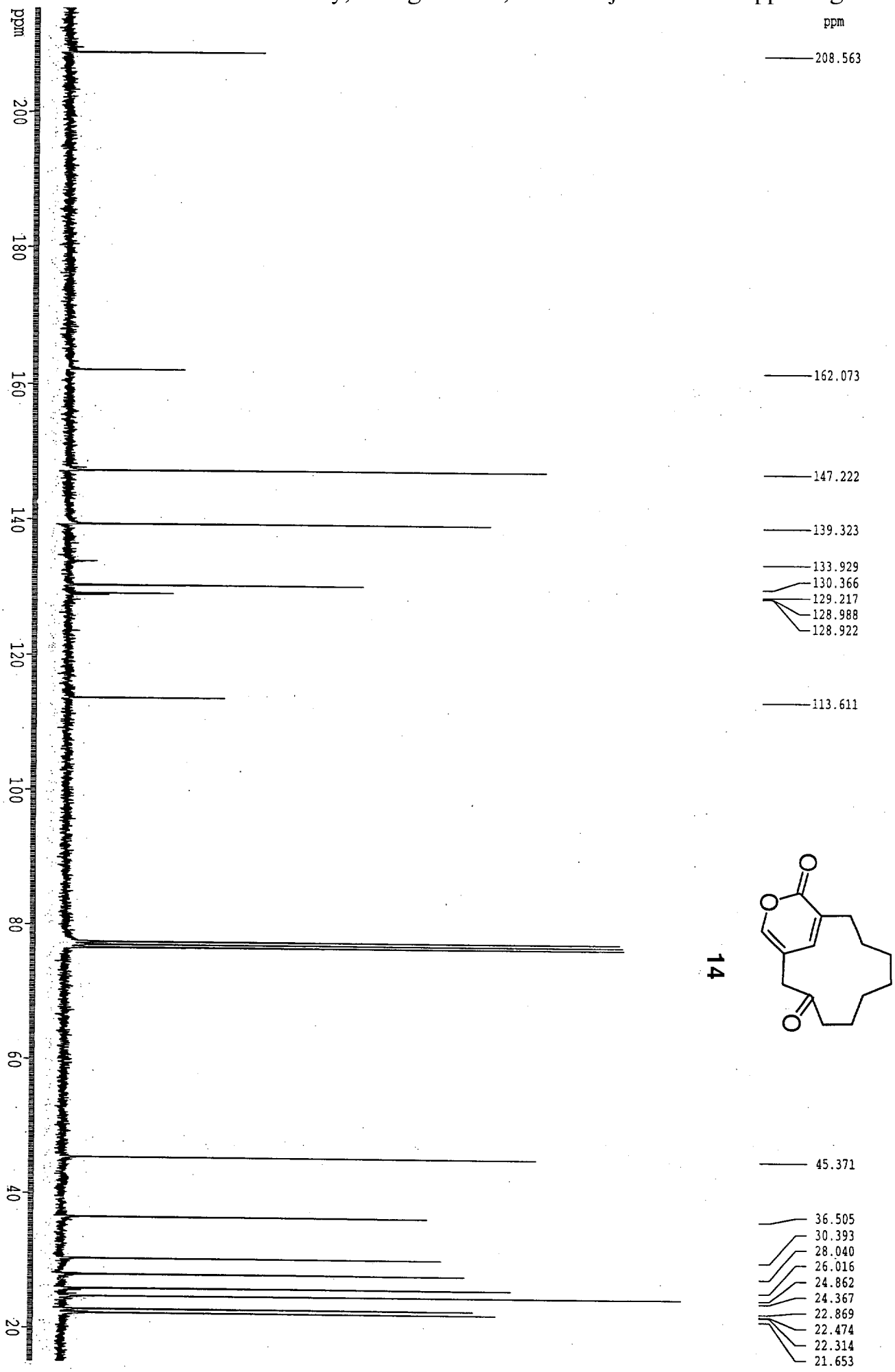

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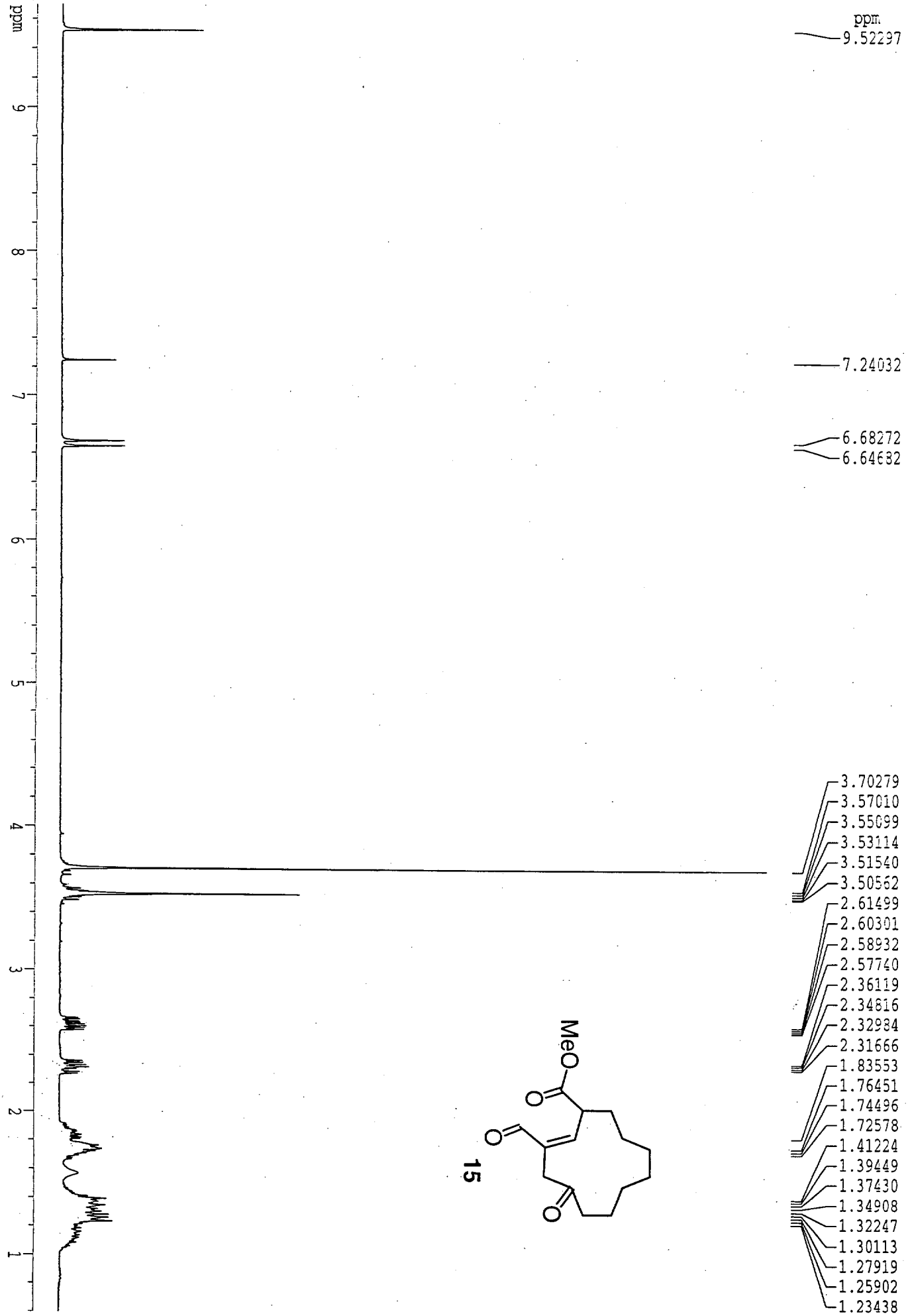

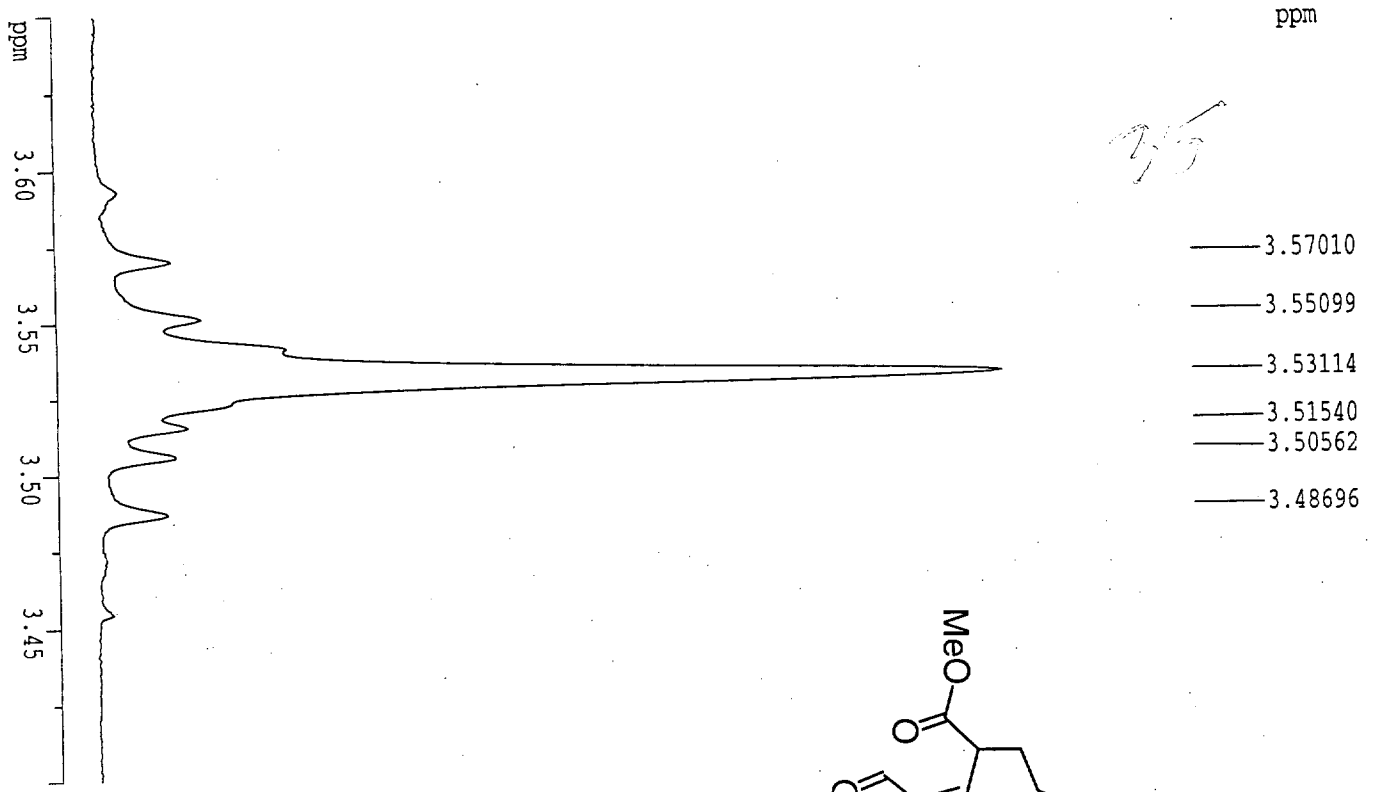
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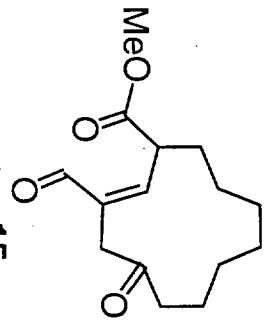
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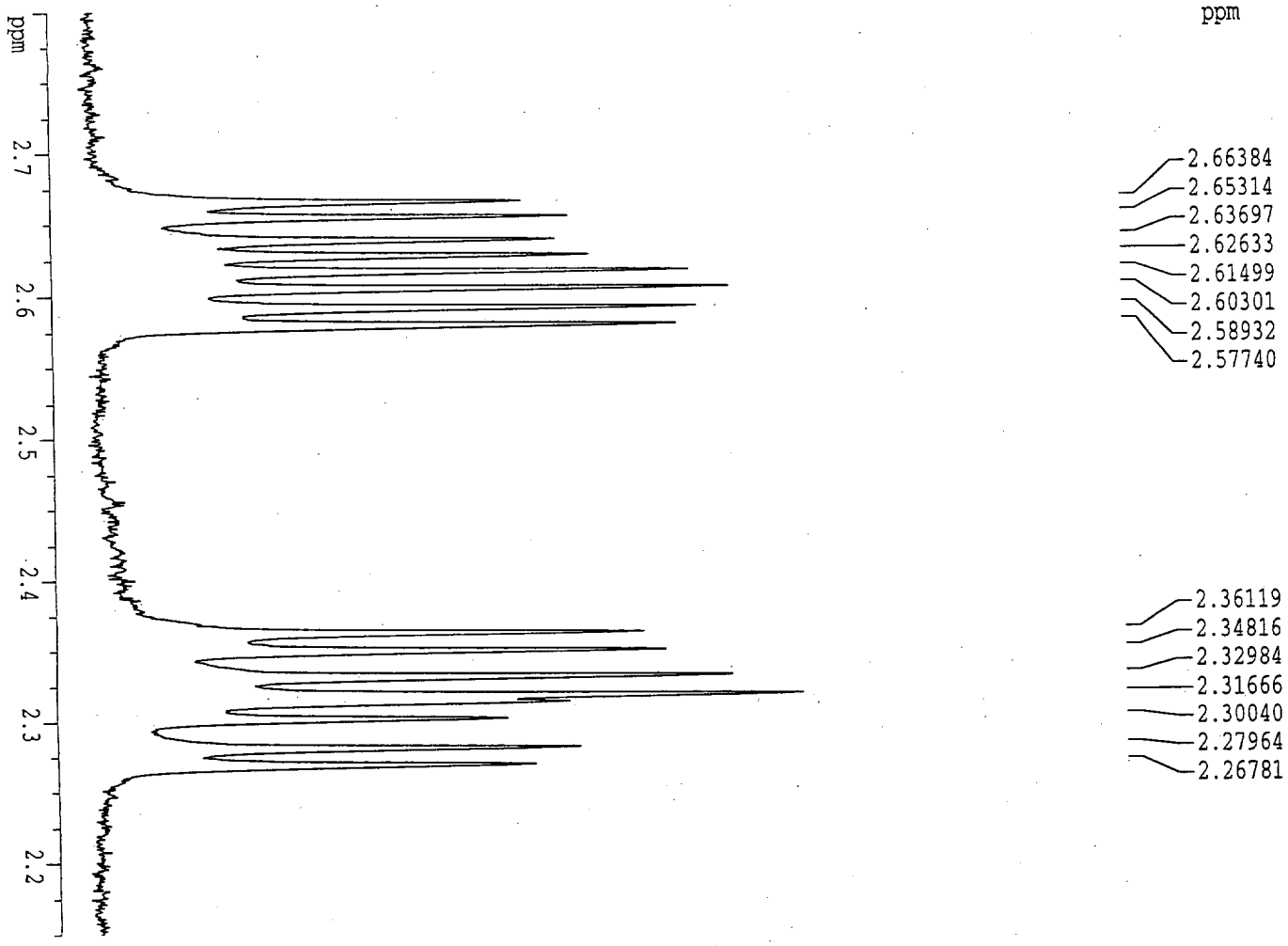
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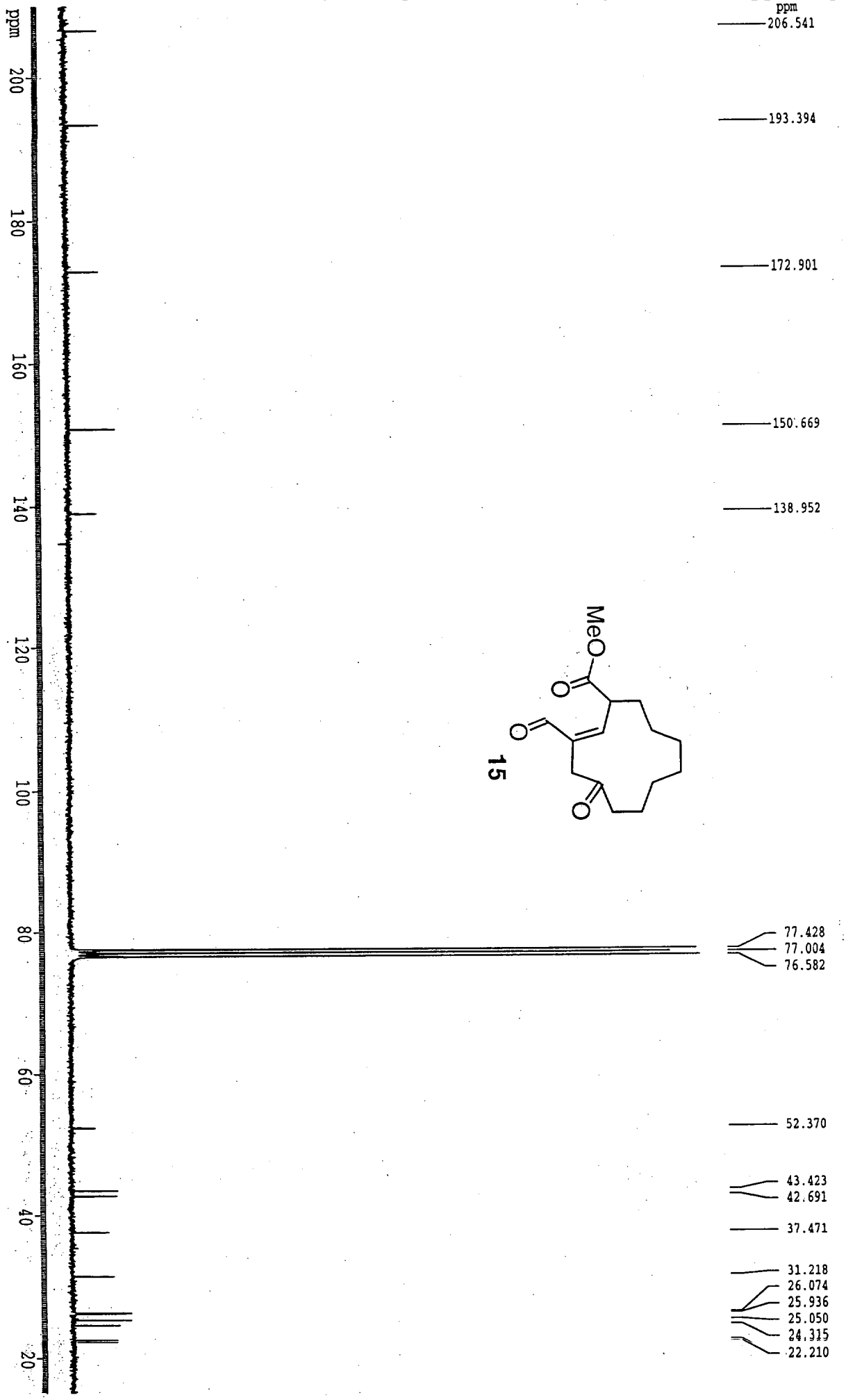
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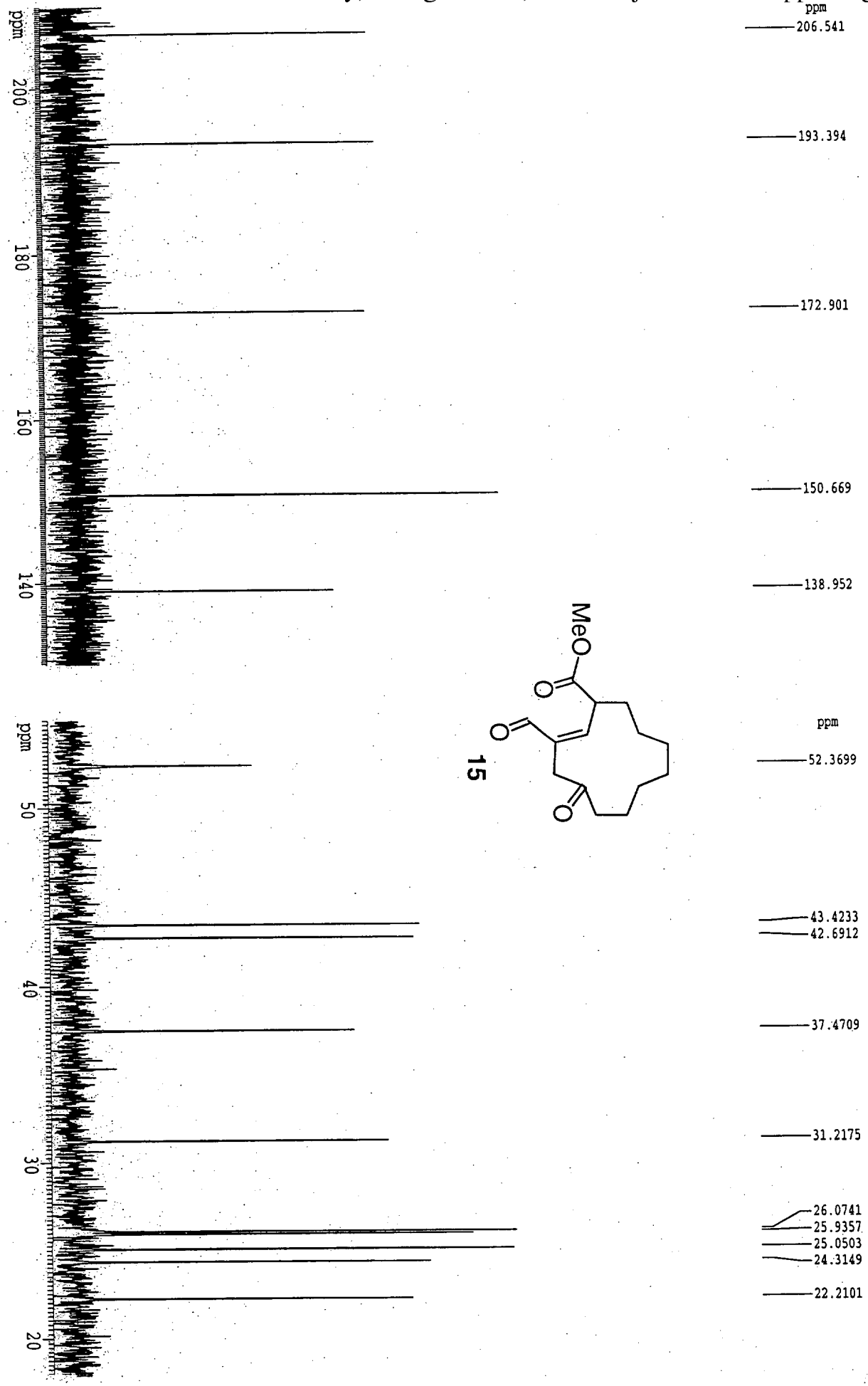
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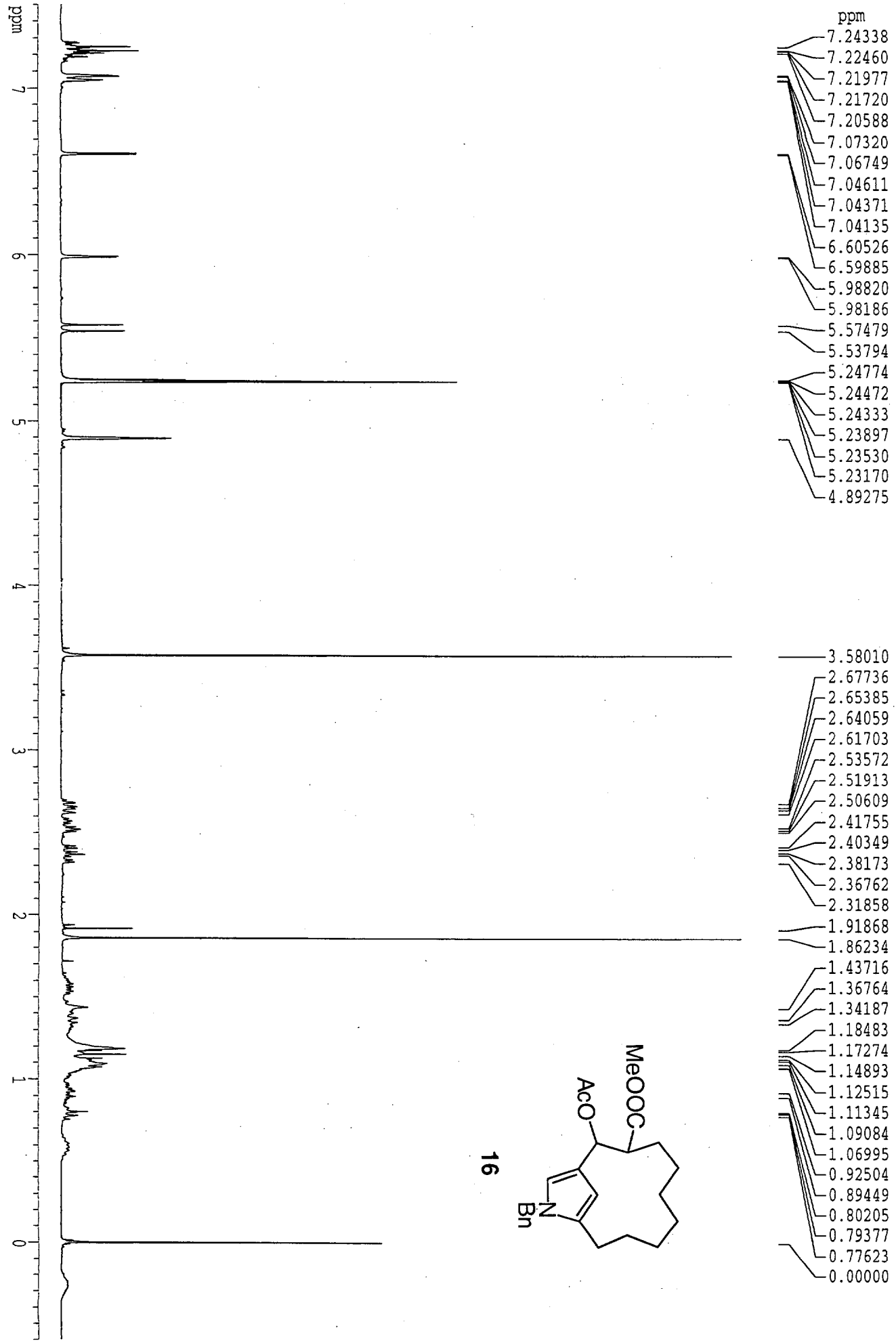
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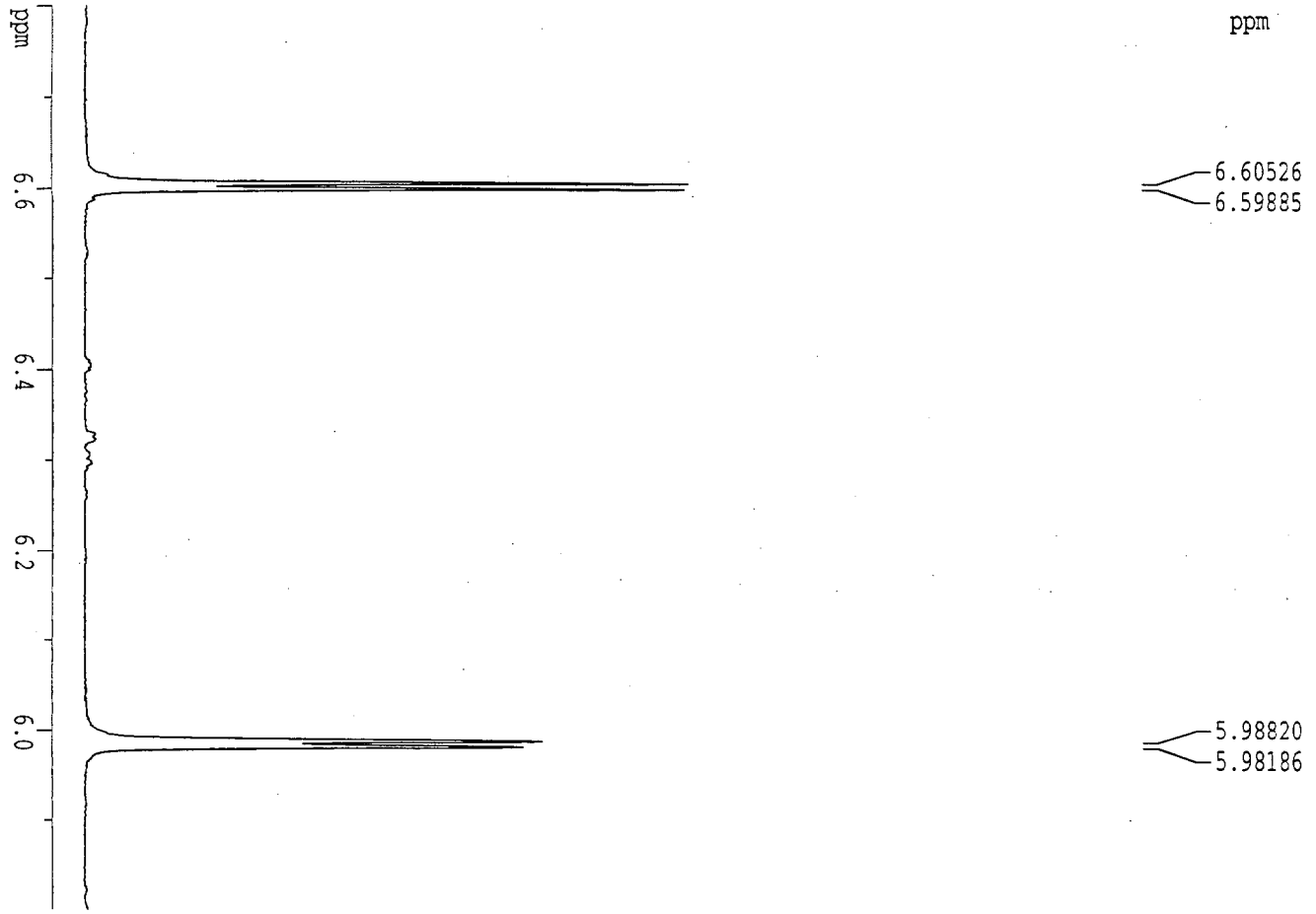

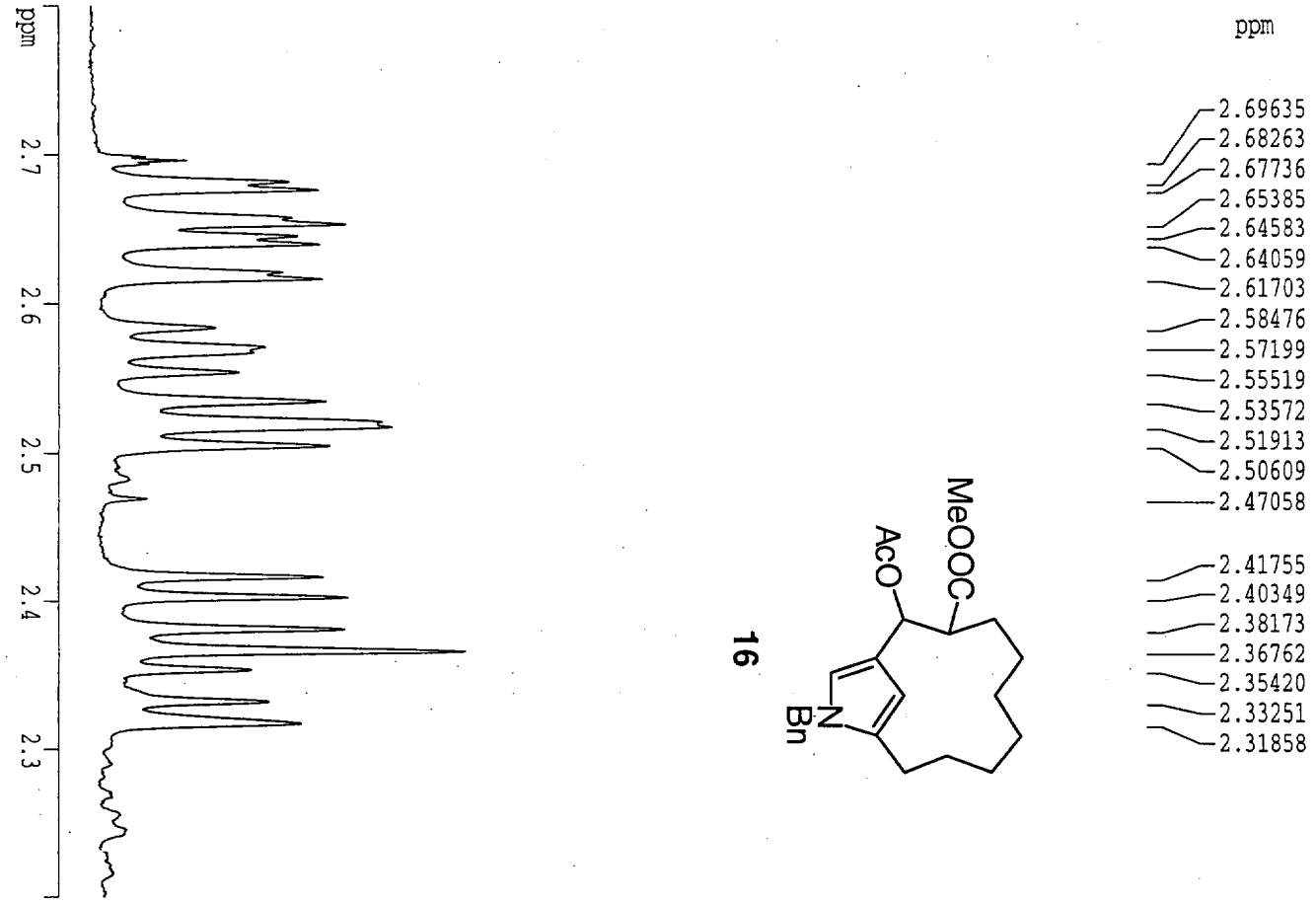

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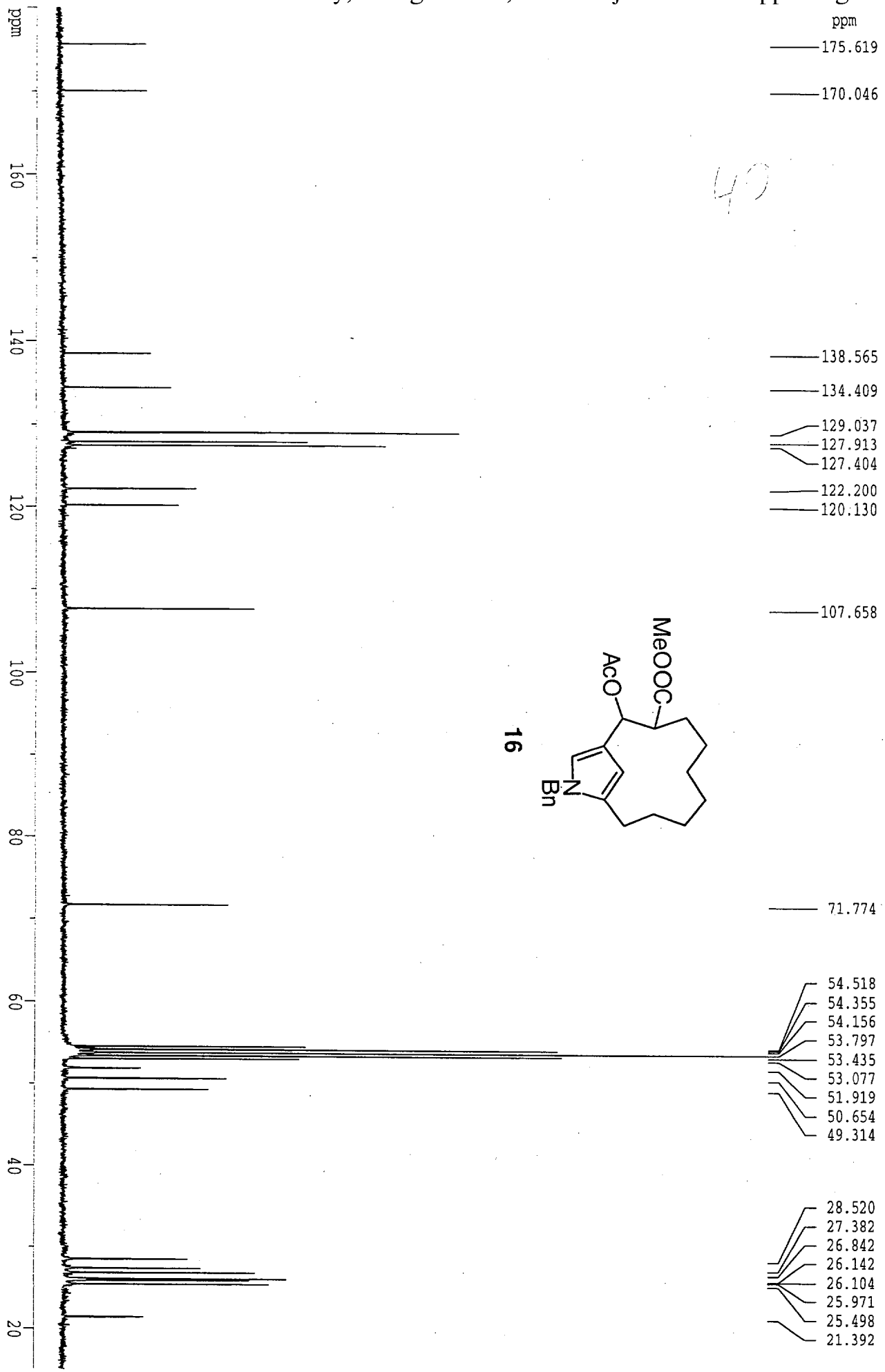
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