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SUPPORTING INFORMATION

Total Synthesis and Structural Refinement of the Cyclic Tripyrrole Pigment Nonylprodigiosin

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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.

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

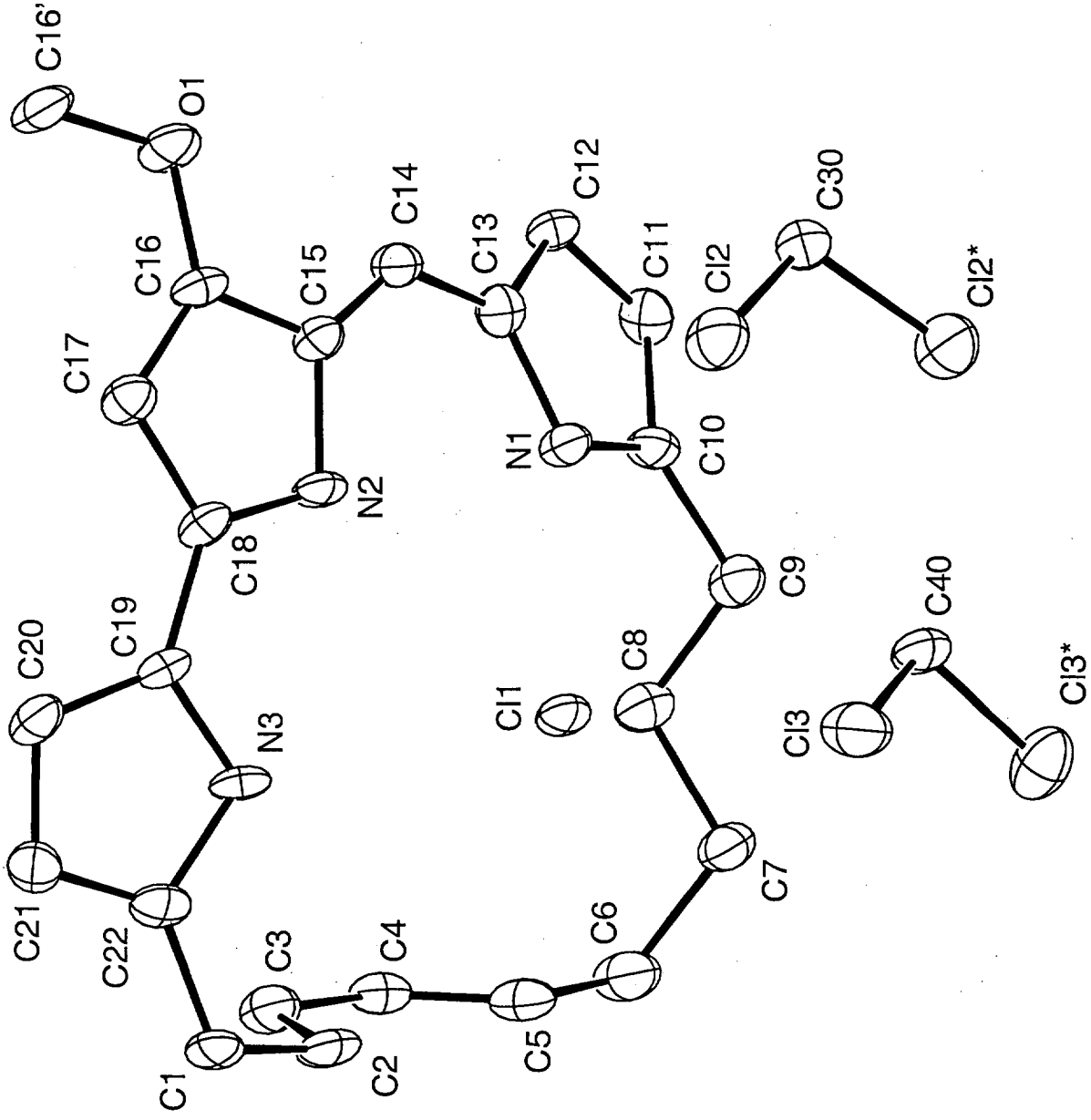
Product	IR
5•HCl	3160, 3121, 2975, 2929, 2858, 1633, 1608, 1552, 1536, 1409, 1372, 1280, 1264, 1181, 1041, 972, 911, 776.
8	3286, 3080, 2978, 2919, 1639, 1546, 1428, 1405, 1136, 1114, 1051, 999, 925, 837, 750, 606.
9	3285, 3078, 2932, 1638, 1546, 1428, 1405, 1301, 1136, 1114, 1044, 994, 912, 842, 749, 606.
10	3386, 3077, 2932, 2858, 1640, 1568, 1439, 1117, 1095, 1025, 992, 912, 884, 787, 714.
11	3386, 3076, 2976, 2931, 2856, 1640, 1568, 1439, 1117, 1094, 1024, 993, 911, 787, 714, 637, 560.
12	3250, 3126, 2934, 2854, 2810, 1631, 1560, 1499, 1424, 1411, 1347, 1189, 1046, 997, 921, 805, 773.
14	3346, 2935, 1675, 1651, 1594, 1578, 1488, 1432, 1357, 1222, 1179, 1044, 1008, 872, 786, 770, 681.
15	3343, 3080, 2975, 2935, 2859, 1630, 1568, 1550, 1485, 1421, 1238, 1216, 1174, 1135, 1085, 1040, 973, 913, 885, 828, 765, 603.
16	3467, 3077, 2979, 2934, 2864, 1741, 1641, 1571, 1495, 1478, 1458, 1408, 1332, 1167, 1128, 1064, 1100, 993, 911, 719.
18•HCl	3435, 3160, 3105, 3059, 2926, 2851, 1605, 1546, 1534, 1375, 1279, 1244, 1178, 1036, 971, 780.

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Table 2. MS Data (EI) of New Compounds

Product	*m/z* (rel. intensity)
8	149 ([M+], 21), 94 (100), 80 (6), 67 (10), 66 (19), 39 (18)
9	163 ([M+], 21), 109 (100), 94 (66), 80 (8), 67 (12), 66 (22), 39 (21)
10	135 ([M+], 15), 93 (16), 81 (21), 80 (100), 53 (15), 39 (10)
11	149 ([M+], 19), 106 (14), 94 (10), 81 (24), 80 (100), 67 (5), 53 (11)
12	177 ([M+], 31), 148 (8), 134 (13), 121 (13), 109 (51), 108 (100), 94 (11), 80 (44), 53 (16)
14	272 ([(M+], 70), 229 (5), 204 (14), 203 (100), 162 (7), 119 (11)
15	404 ([M+], 22), 272 (19), 271 (100), 203 (21), 119 (14), 69 (24), 41 (16)
16	235 ([M+], 2),179 (34), 137 (14), 125 (12), 124 (10), 93 (12), 81 (23), 80 (37), 57 (100), 41 (16)
18·HCl	361 ([M-Cl)+], 100), 346 (12), 318 (14), 279 (16) 266 (13), 104 (28)
4·HCl	363 ([(M-Cl)+], 100), 348 (11), 278 (5), 104 (11)

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Crystal Structure of Compound (*E*)-18·HCl·(CH_2Cl_2)

The complete lists of atomic coordinates, bond length and angles have been deposited with the Cambridge Crystallographic Data Center, Cambridge, U.K., under the deposition number **CCDC 121761** and may be obtained free of charge by applying to: „The Director, Cambridge Crystallographic Data Center, 12 Union Road, CB2 1EZ Cambridge, UK.

Crystal data and structure refinement

Empirical formula	$C_{24}H_{30}Cl_3N_3O$	
Color	dark red	
Formula weight	482.86 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, **C2/c (no.15)**	
Unit cell dimensions	a = 26.091(5) Å	α = 90 °
	b = 8.3912(17) Å	β = 104.99(3) °
	c = 22.571(5) Å	γ = 90 °
Volume	4773.4(17) $Å^3$	
Z, Calculated density	8, 1.344 Mg · m^{-3}	
Absorption coefficient	0.406 mm^{-1}	
F(000)	2032 e	
Crystal size	0.67 x 0.21 x 0.08 mm	
θ range for data collection	1.62 to 27.80 °	
Index ranges	$-29 \le h \le 33$, $-10 \le k \le 9$, $-25 \le l \le 29$	
Reflections collected / unique	21146 / 5173 [R_{int} = 0.2322]	
Completeness to θ = 27.80	91.7%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5173 / 0 / 282	
Goodness-of-fit on F^2	0.933	
Final R indices [I>2σ(I)]	R_1 = 0.0824	wR^2 = 0.1825
R indices (all data)	R_1 = 0.2004	wR^2 = 0.2337
Largest diff. peak and hole	0.982 and -0.646 e · $Å^{-3}$	

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Bond Distances (Å)

CL(2) - C(30)	1.773(1)	CL(3) - C(40)	1.768(2)
O(1) - C(16)	1.340(6)	O(1) - C(16')	1.443(7)
N(1) - C(10)	1.362(7)	N(1) - C(13)	1.402(7)
N(2) - C(15)	1.429(6)	N(2) - C(18)	1.363(7)
N(3) - C(19)	1.396(6)	N(3) - C(22)	1.375(7)
C(1) - C(2)	1.516(8)	C(1) - C(22)	1.499(7)
C(2) - C(3)	1.518(8)	C(3) - C(4)	1.507(8)
C(4) - C(5)	1.329(8)	C(5) - C(6)	1.476(8)
C(6) - C(7)	1.547(8)	C(7) - C(8)	1.523(7)
C(8) - C(9)	1.527(8)	C(9) - C(10)	1.505(7)
C(10) - C(11)	1.388(7)	C(11) - C(12)	1.396(7)
C(12) - C(13)	1.401(7)	C(13) - C(14)	1.420(7)
C(14) - C(15)	1.355(7)	C(15) - C(16)	1.435(7)
C(16) - C(17)	1.369(7)	C(17) - C(18)	1.414(7)
C(18) - C(19)	1.429(7)	C(19) - C(20)	1.384(7)
C(20) - C(21)	1.397(7)	C(21) - C(22)	1.383(7)

Intermolecular Distances between non-H-Atoms in (Å) (less than 3.00)

CL(2) ... CL(2)	2.914(2)	[-x,+y,0.50-z]
CL(3) ... CL(3)	2.932(2)	[-x,+y,1.50-z]

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Bond Angles in (°)

C(16') - O(1) - C(16)	115.2(4)	C(13) - N(1) - C(10)	108.7(4)
C(18) - N(2) - C(15)	108.6(4)	C(22) - N(3) - C(19)	108.7(4)
C(22) - C(1) - C(2)	115.3(4)	C(3) - C(2) - C(1)	113.3(4)
C(4) - C(3) - C(2)	116.0(5)	C(5) - C(4) - C(3)	127.7(5)
C(6) - C(5) - C(4)	126.7(5)	C(7) - C(6) - C(5)	113.7(5)
C(8) - C(7) - C(6)	112.0(4)	C(9) - C(8) - C(7)	113.3(4)
C(10) - C(9) - C(8)	113.5(4)	C(11) - C(10) - C(9)	131.8(5)
C(11) - C(10) - N(1)	108.9(4)	C(9) - C(10) - N(1)	119.3(4)
C(12) - C(11) - C(10)	107.6(5)	C(13) - C(12) - C(11)	107.8(5)
C(14) - C(13) - C(12)	126.1(5)	C(14) - C(13) - N(1)	126.9(5)
C(12) - C(13) - N(1)	107.0(4)	C(15) - C(14) - C(13)	131.3(5)
C(16) - C(15) - C(14)	127.3(5)	C(16) - C(15) - N(2)	104.9(4)
C(14) - C(15) - N(2)	126.9(5)	C(17) - C(16) - C(15)	109.8(4)
C(17) - C(16) - O(1)	130.6(5)	C(15) - C(16) - O(1)	119.5(4)
C(18) - C(17) - C(16)	106.9(5)	C(19) - C(18) - C(17)	127.0(5)
C(19) - C(18) - N(2)	123.0(4)	C(17) - C(18) - N(2)	109.7(4)
C(20) - C(19) - C(18)	129.3(5)	C(20) - C(19) - N(3)	107.5(4)
C(18) - C(19) - N(3)	121.9(4)	C(21) - C(20) - C(19)	107.7(5)
C(22) - C(21) - C(20)	108.3(5)	C(21) - C(22) - C(1)	130.2(5)
C(21) - C(22) - N(3)	107.8(4)	C(1) - C(22) - N(3)	122.0(5)
CL(2)* - C(30) - CL(2)	110.6(4)	CL(3)* - C(40) - CL(3)	112.0(4)

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

Atom	x	y	z	U_{eq}
CL(1)	0.1016(1)	0.8503(1)	0.3917(1)	0.025(1)
CL(2)	0.0183(1)	0.5610(2)	0.1943(1)	0.038(1)
CL(3)	0.0295(1)	-0.0565(2)	0.7029(1)	0.040(1)
O(1)	0.0400(1)	0.1901(4)	0.5093(2)	0.029(2)
N(1)	0.1234(2)	0.5054(5)	0.3498(2)	0.023(3)
N(2)	0.0901(2)	0.5601(5)	0.4735(2)	0.022(3)
N(3)	0.1268(2)	0.8566(5)	0.5373(2)	0.023(3)
C(1)	0.1773(2)	1.1106(6)	0.5695(2)	0.027(3)
C(2)	0.1985(2)	1.1016(6)	0.5131(2)	0.029(4)
C(3)	0.2464(2)	0.9932(7)	0.5212(2)	0.033(4)
C(4)	0.2665(2)	0.9675(6)	0.4651(2)	0.027(3)
C(5)	0.2452(2)	1.0195(6)	0.4085(2)	0.031(4)
C(6)	0.2640(2)	0.9852(7)	0.3535(2)	0.035(4)
C(7)	0.2234(2)	0.8929(6)	0.3032(2)	0.030(4)
C(8)	0.2115(2)	0.7286(6)	0.3250(2)	0.029(3)
C(9)	0.1672(2)	0.6414(6)	0.2789(2)	0.028(3)
C(10)	0.1486(2)	0.4928(6)	0.3043(2)	0.024(3)
C(11)	0.1516(2)	0.3331(6)	0.2895(2)	0.027(3)
C(12)	0.1267(2)	0.2452(6)	0.3267(2)	0.025(3)
C(13)	0.1096(2)	0.3524(6)	0.3652(2)	0.024(3)
C(14)	0.0844(2)	0.3118(6)	0.4117(2)	0.024(3)
C(15)	0.0750(2)	0.3984(6)	0.4585(2)	0.024(3)
C(16)	0.0571(2)	0.3407(6)	0.5095(2)	0.023(3)
C(16')	0.0263(2)	0.1405(6)	0.5644(2)	0.032(4)
C(17)	0.0636(2)	0.4565(6)	0.5536(2)	0.025(3)
C(18)	0.0843(2)	0.5919(6)	0.5306(2)	0.023(3)
C(19)	0.1024(2)	0.7362(6)	0.5628(2)	0.022(3)
C(20)	0.1098(2)	0.7711(6)	0.6244(2)	0.027(3)
C(21)	0.1388(2)	0.9126(6)	0.6364(2)	0.027(3)
C(22)	0.1491(2)	0.9643(6)	0.5825(2)	0.025(3)
C(30)	0.0000	0.4408(9)	0.2500	0.030(5)
C(40)	0.0000	0.0612(9)	0.7500	0.030(5)

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}

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Atomic Fractional Coordinates with Standard Deviations in Parentheses

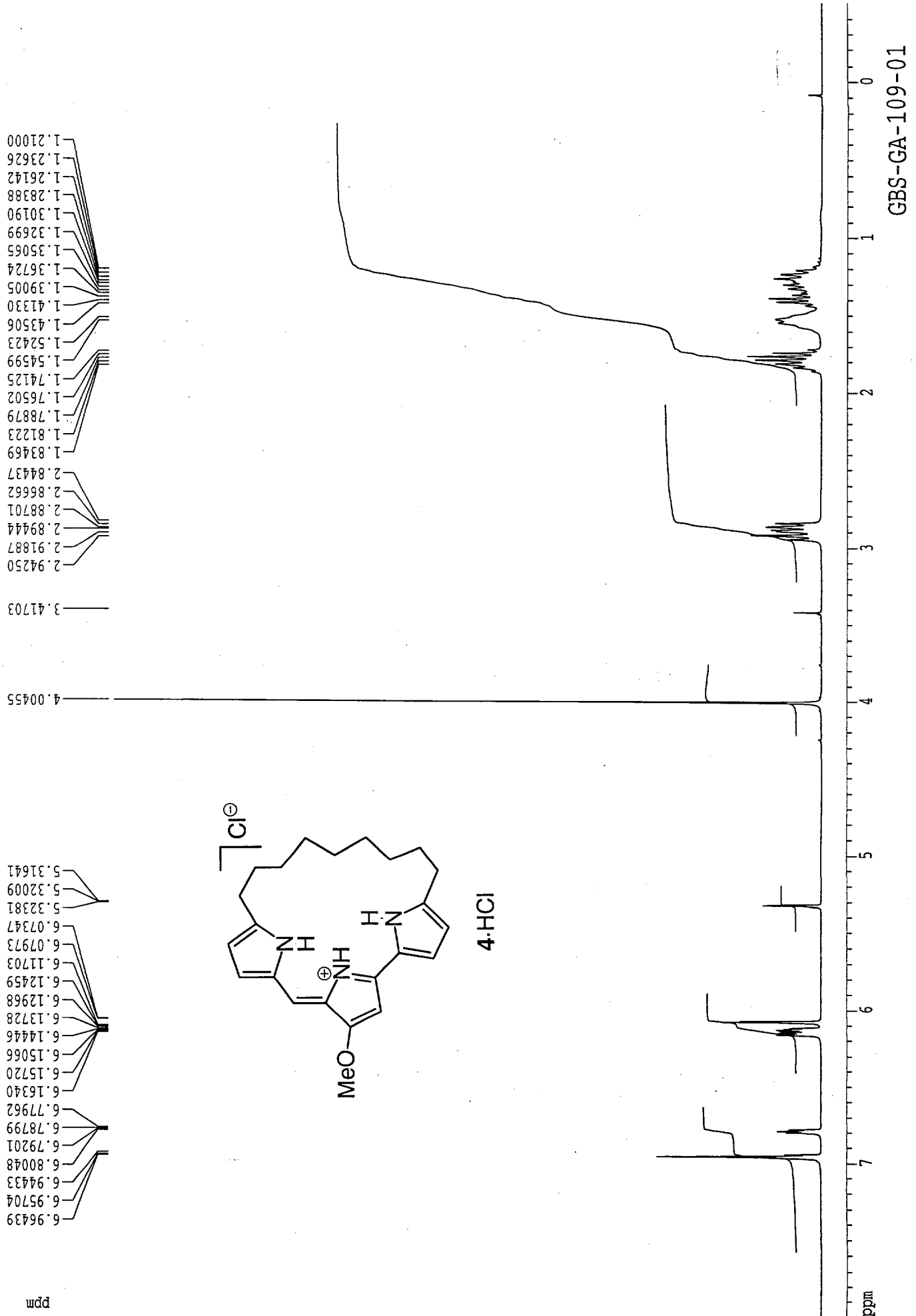
Atom	x	y	z
CL(1)	0.1016(1)	0.8503(1)	0.3917(1)
CL(2)	0.0183(1)	0.5610(2)	0.1943(1)
CL(3)	0.0295(1)	-0.0565(2)	0.7029(1)
O(1)	0.0400(1)	0.1901(4)	0.5093(2)
N(1)	0.1234(2)	0.5054(5)	0.3498(2)
N(2)	0.0901(2)	0.5601(5)	0.4735(2)
N(3)	0.1268(2)	0.8566(5)	0.5373(2)
C(1)	0.1773(2)	1.1106(6)	0.5695(2)
C(2)	0.1985(2)	1.1016(6)	0.5131(2)
C(3)	0.2464(2)	0.9932(7)	0.5212(2)
C(4)	0.2665(2)	0.9675(6)	0.4651(2)
C(5)	0.2452(2)	1.0195(6)	0.4085(2)
C(6)	0.2640(2)	0.9852(7)	0.3535(2)
C(7)	0.2234(2)	0.8929(6)	0.3032(2)
C(8)	0.2115(2)	0.7286(6)	0.3250(2)
C(9)	0.1672(2)	0.6414(6)	0.2789(2)
C(10)	0.1486(2)	0.4928(6)	0.3043(2)
C(11)	0.1516(2)	0.3331(6)	0.2895(2)
C(12)	0.1267(2)	0.2452(6)	0.3267(2)
C(13)	0.1096(2)	0.3524(6)	0.3652(2)
C(14)	0.0844(2)	0.3118(6)	0.4117(2)
C(15)	0.0750(2)	0.3984(6)	0.4585(2)
C(16)	0.0571(2)	0.3407(6)	0.5095(2)
C(16')	0.0263(2)	0.1405(6)	0.5644(2)
C(17)	0.0636(2)	0.4565(6)	0.5536(2)
C(18)	0.0843(2)	0.5919(6)	0.5306(2)
C(19)	0.1024(2)	0.7362(6)	0.5628(2)
C(20)	0.1098(2)	0.7711(6)	0.6244(2)
C(21)	0.1388(2)	0.9126(6)	0.6364(2)
C(22)	0.1491(2)	0.9643(6)	0.5825(2)
C(30)	0.0000	0.4408(9)	0.2500
C(40)	0.0000	0.0612(9)	0.7500

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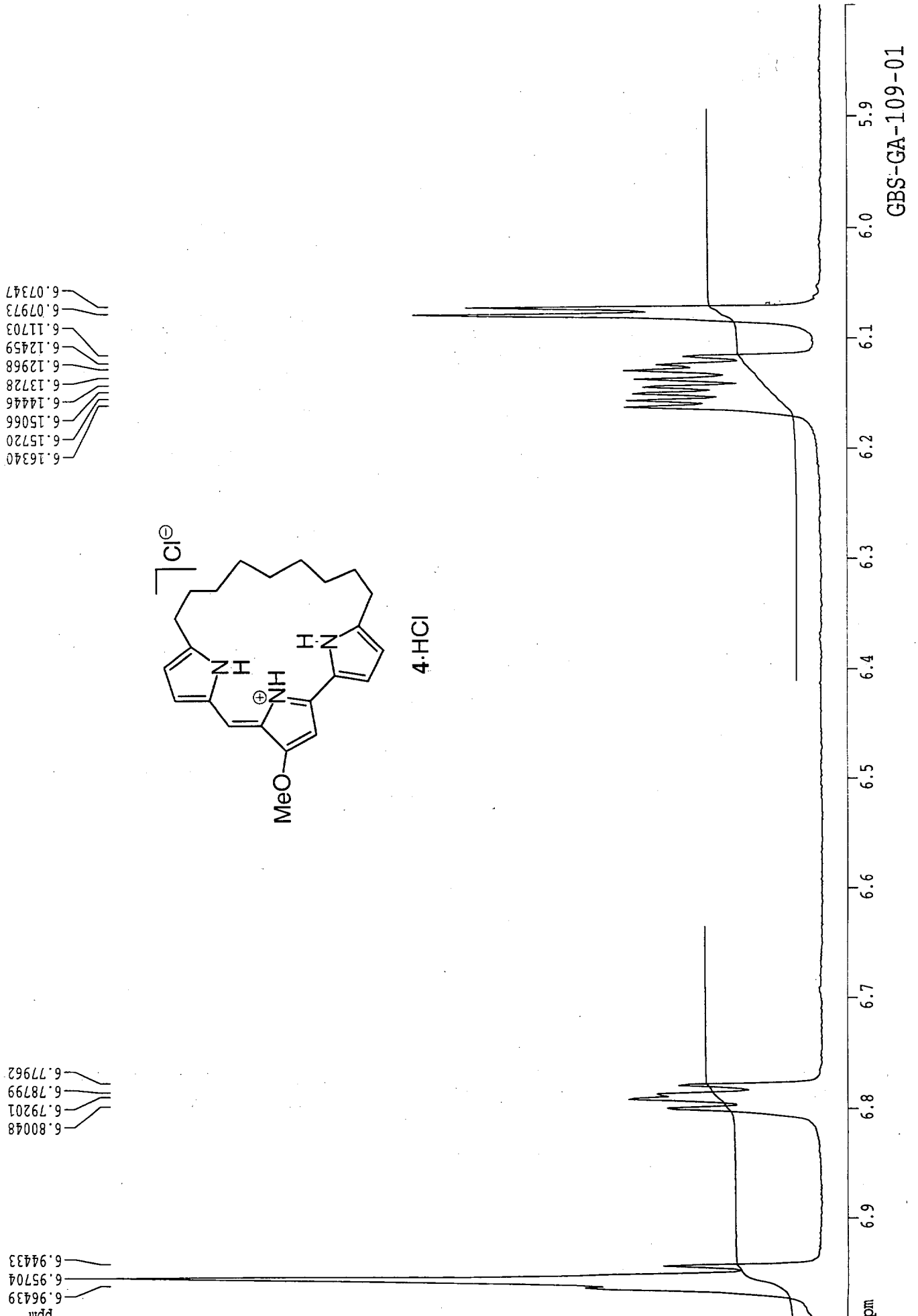
Thermal Parameters (Å) with Standard Deviations in Parentheses

Atom	$U_{1,1}$	$U_{2,2}$	$U_{3,3}$	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$
CL(1)	0.033(1)	0.012(1)	0.029(1)	0.001(1)	0.009(1)	-0.001(1)
CL(2)	0.049(1)	0.035(1)	0.035(1)	-0.001(1)	0.020(1)	0.002(1)
CL(3)	0.052(1)	0.036(1)	0.039(1)	0.008(1)	0.022(1)	0.013(1)
O(1)	0.040(2)	0.014(2)	0.037(2)	0.001(2)	0.016(2)	-0.005(2)
N(1)	0.028(2)	0.017(2)	0.027(2)	0.001(2)	0.009(2)	-0.002(2)
N(2)	0.025(2)	0.009(2)	0.030(2)	0.001(2)	0.005(2)	0.001(2)
N(3)	0.027(2)	0.009(2)	0.036(3)	-0.003(2)	0.010(2)	-0.001(2)
C(1)	0.035(3)	0.010(3)	0.034(3)	-0.003(2)	0.003(3)	0.001(2)
C(2)	0.036(3)	0.011(3)	0.040(3)	0.001(2)	0.009(3)	-0.003(2)
C(3)	0.035(3)	0.022(3)	0.038(3)	0.002(3)	0.004(3)	-0.002(3)
C(4)	0.027(3)	0.017(3)	0.037(3)	-0.003(2)	0.008(3)	-0.003(2)
C(5)	0.032(3)	0.021(3)	0.041(4)	-0.003(3)	0.013(3)	-0.010(3)
C(6)	0.043(4)	0.023(3)	0.041(3)	-0.002(3)	0.016(3)	-0.006(3)
C(7)	0.042(3)	0.021(3)	0.031(3)	0.002(2)	0.014(3)	-0.005(3)
C(8)	0.029(3)	0.021(3)	0.036(3)	0.002(2)	0.008(3)	0.001(3)
C(9)	0.033(3)	0.025(3)	0.028(3)	0.001(3)	0.015(2)	0.001(3)
C(10)	0.031(3)	0.017(3)	0.025(3)	-0.005(2)	0.009(2)	-0.003(2)
C(11)	0.028(3)	0.028(3)	0.026(3)	-0.002(3)	0.010(2)	0.004(3)
C(12)	0.035(3)	0.012(3)	0.028(3)	0.001(2)	0.006(2)	0.002(3)
C(13)	0.021(3)	0.025(3)	0.024(3)	0.001(2)	0.005(2)	0.003(2)
C(14)	0.023(3)	0.018(3)	0.028(3)	0.002(2)	-0.001(2)	-0.002(2)
C(15)	0.027(3)	0.016(3)	0.026(3)	0.002(2)	0.004(2)	0.001(2)
C(16)	0.022(3)	0.012(3)	0.034(3)	0.003(2)	0.008(2)	0.001(2)
C(16')	0.048(4)	0.017(3)	0.037(3)	0.005(3)	0.020(3)	-0.004(3)
C(17)	0.030(3)	0.019(3)	0.028(3)	0.001(2)	0.012(2)	0.003(2)
C(18)	0.027(3)	0.014(3)	0.029(3)	0.004(2)	0.010(2)	0.003(2)
C(19)	0.024(3)	0.013(3)	0.030(3)	0.005(2)	0.009(2)	-0.001(2)
C(20)	0.037(3)	0.018(3)	0.029(3)	0.005(2)	0.014(3)	0.004(3)
C(21)	0.034(3)	0.021(3)	0.026(3)	-0.004(2)	0.008(2)	0.004(3)
C(22)	0.025(3)	0.013(3)	0.035(3)	-0.004(2)	0.007(2)	0.004(2)
C(30)	0.037(5)	0.021(4)	0.030(4)	0.000	0.006(4)	0.000
C(40)	0.041(5)	0.015(4)	0.034(4)	0.000	0.010(4)	0.000

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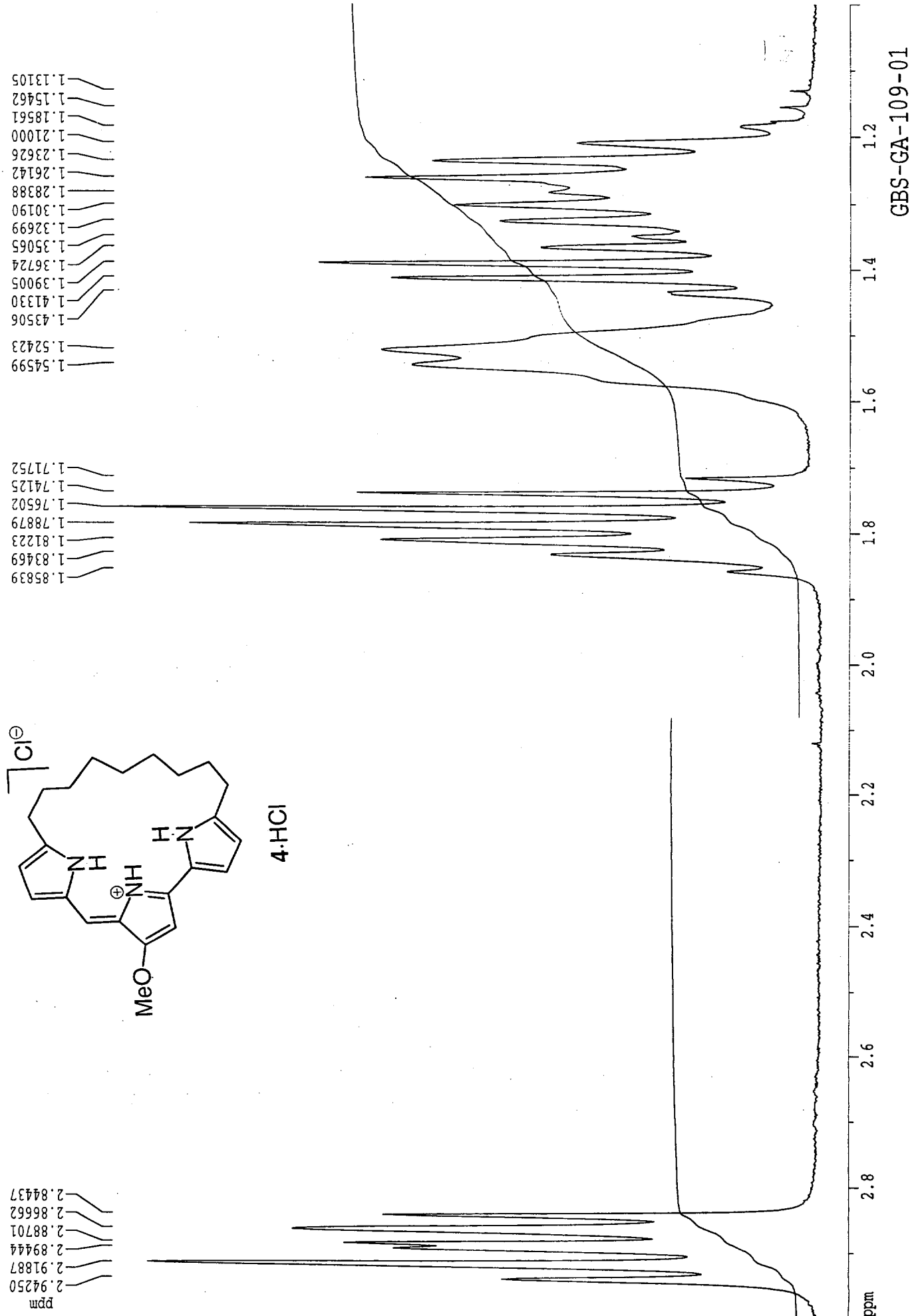


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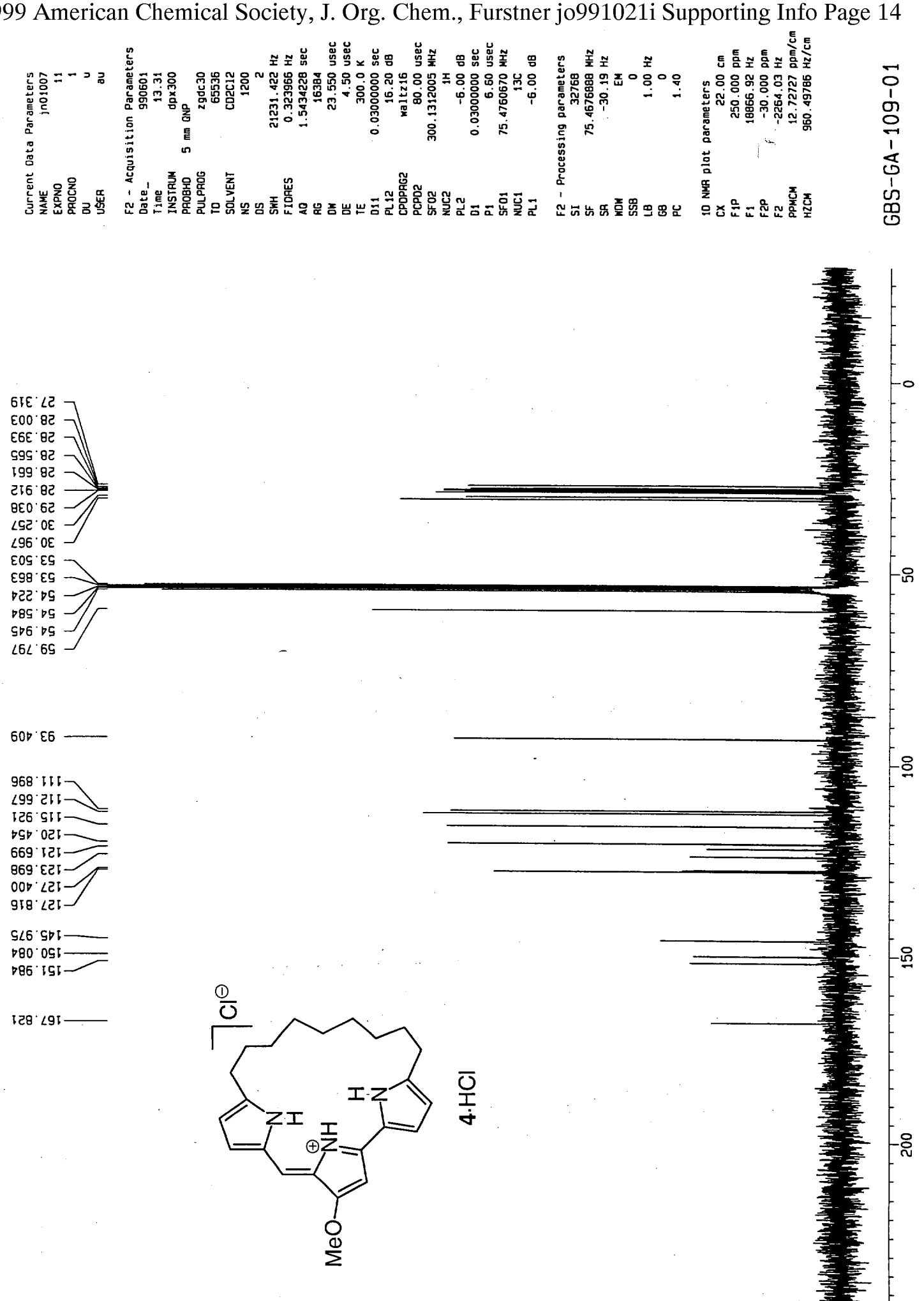


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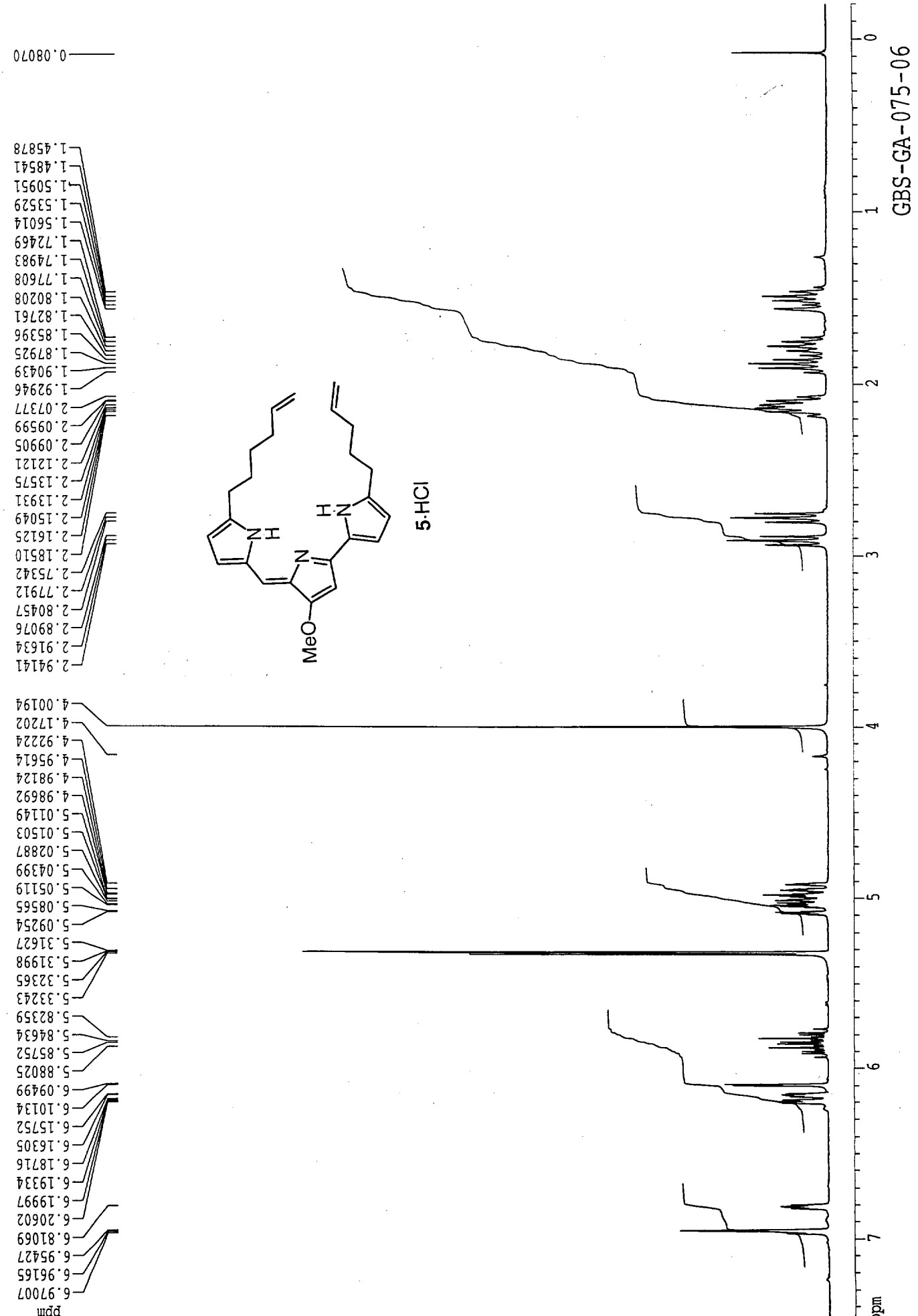
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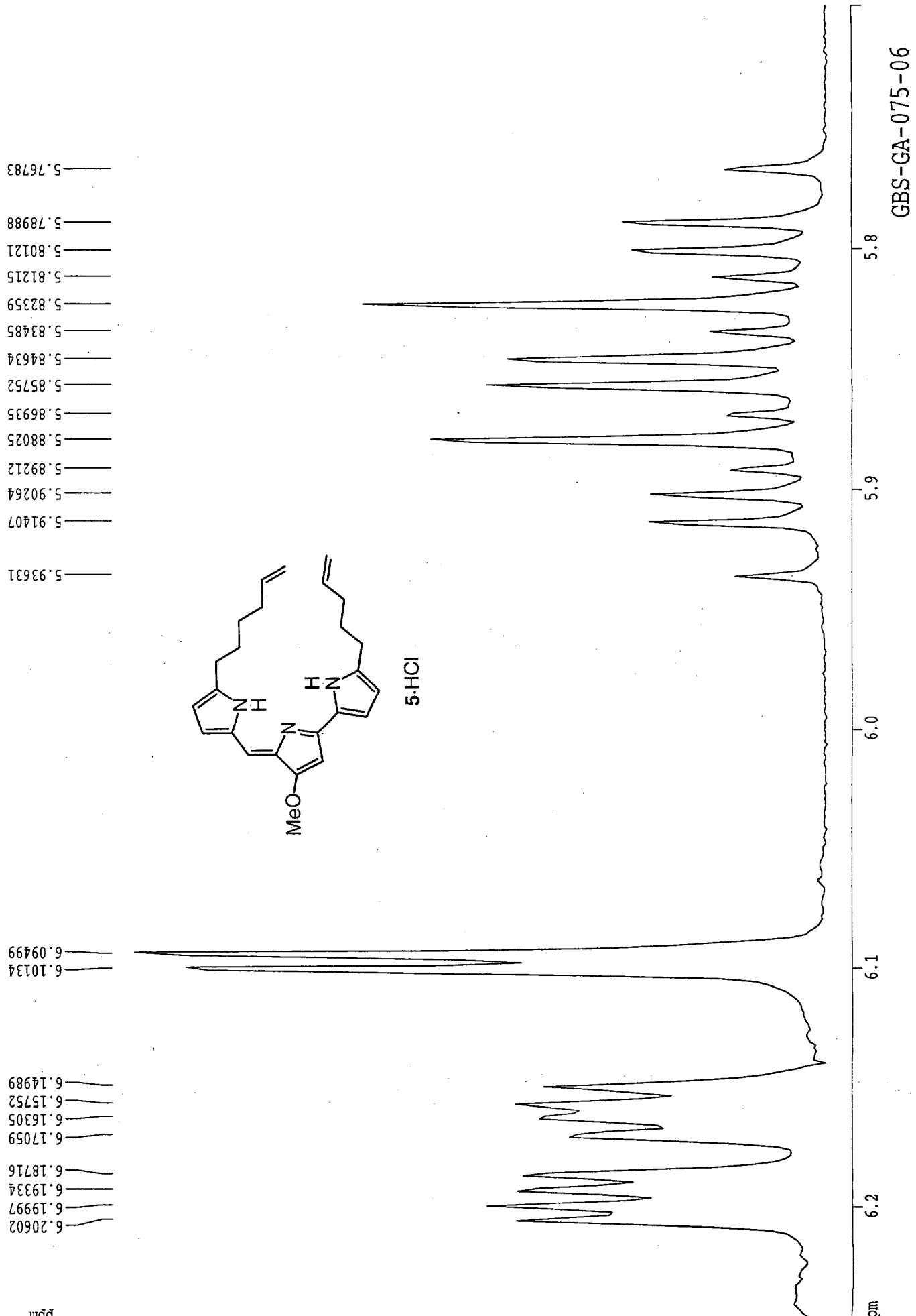
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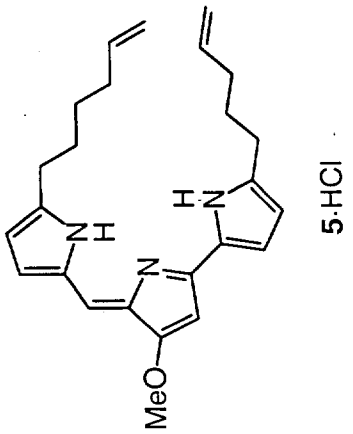
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5·HCl

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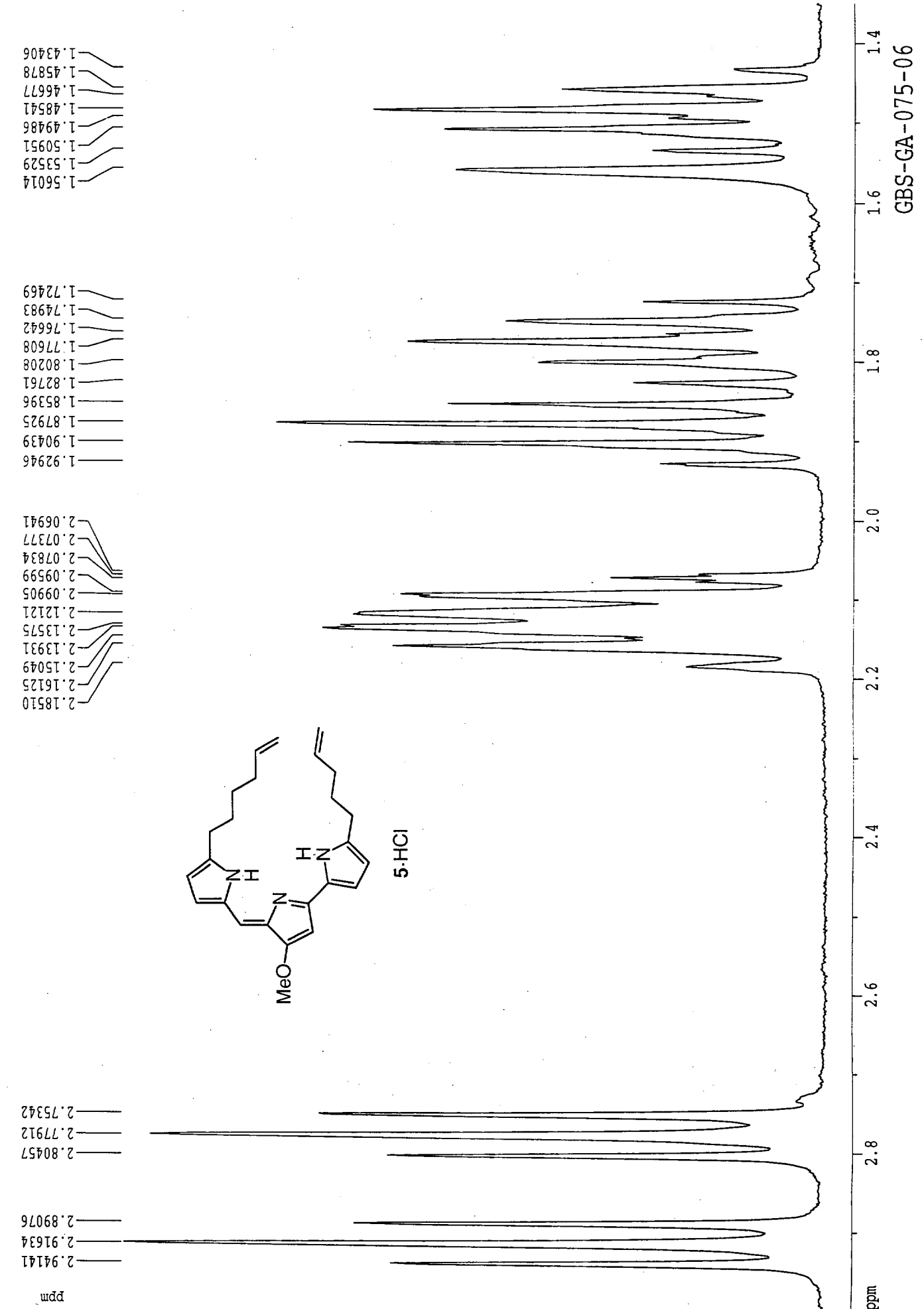
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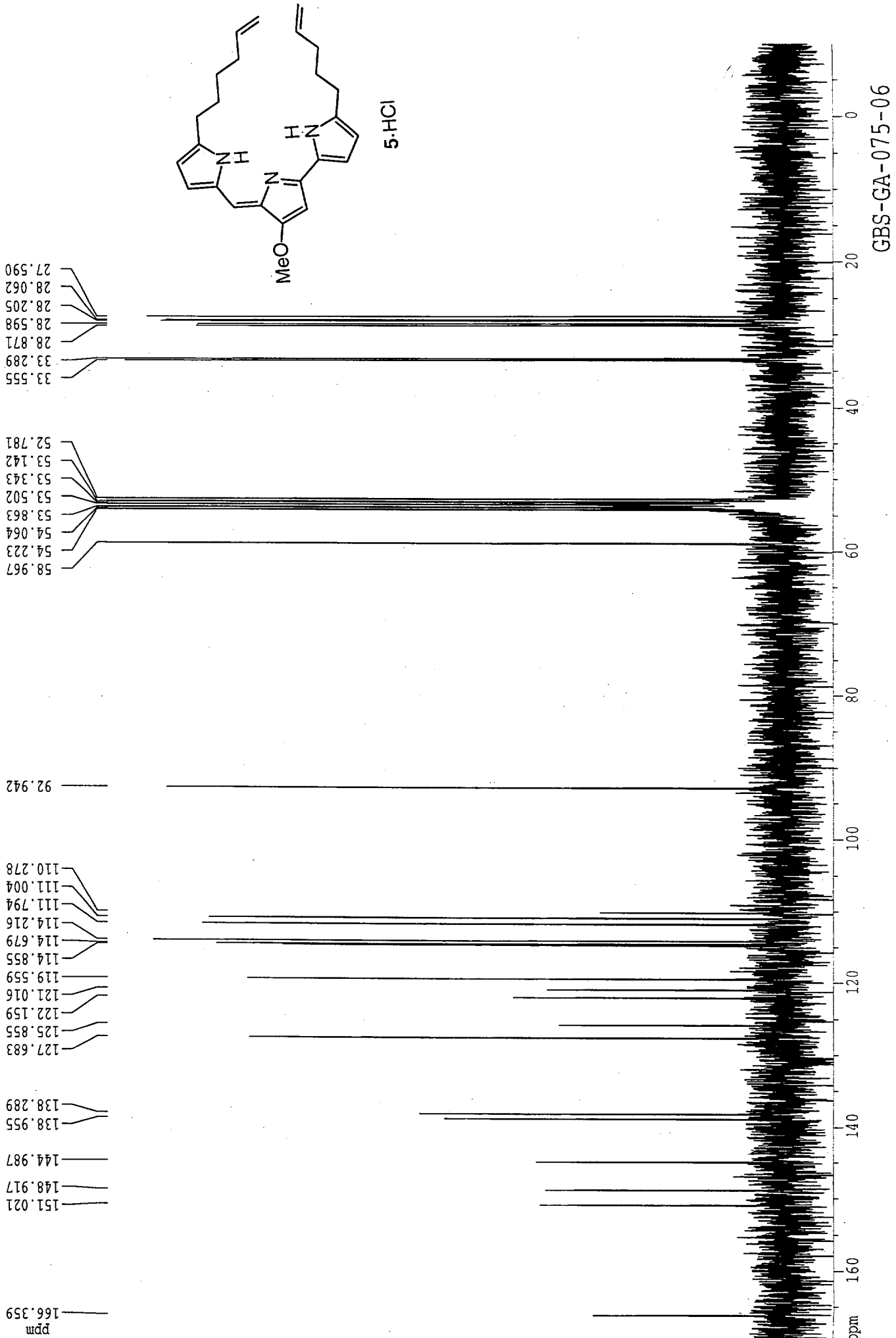
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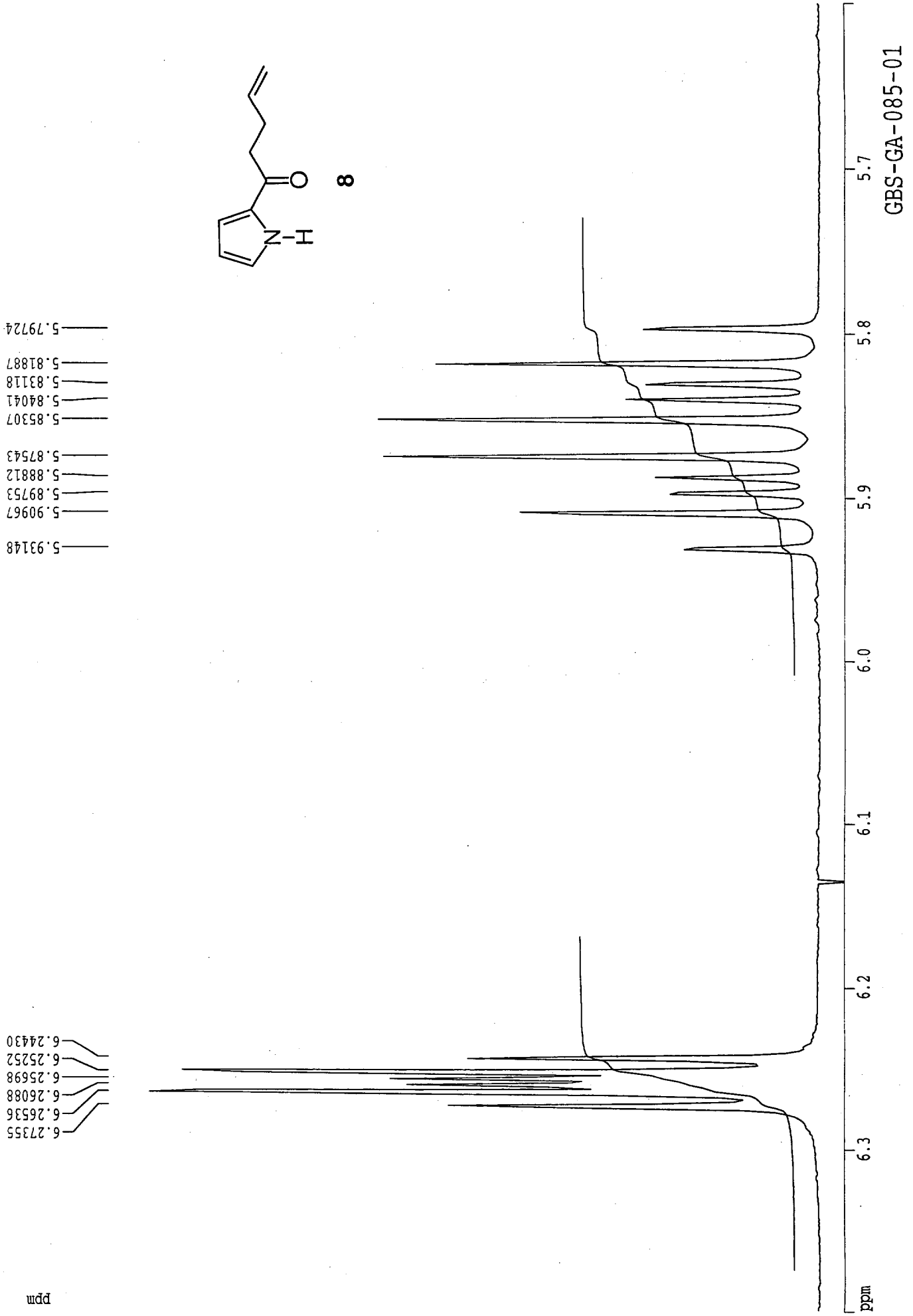
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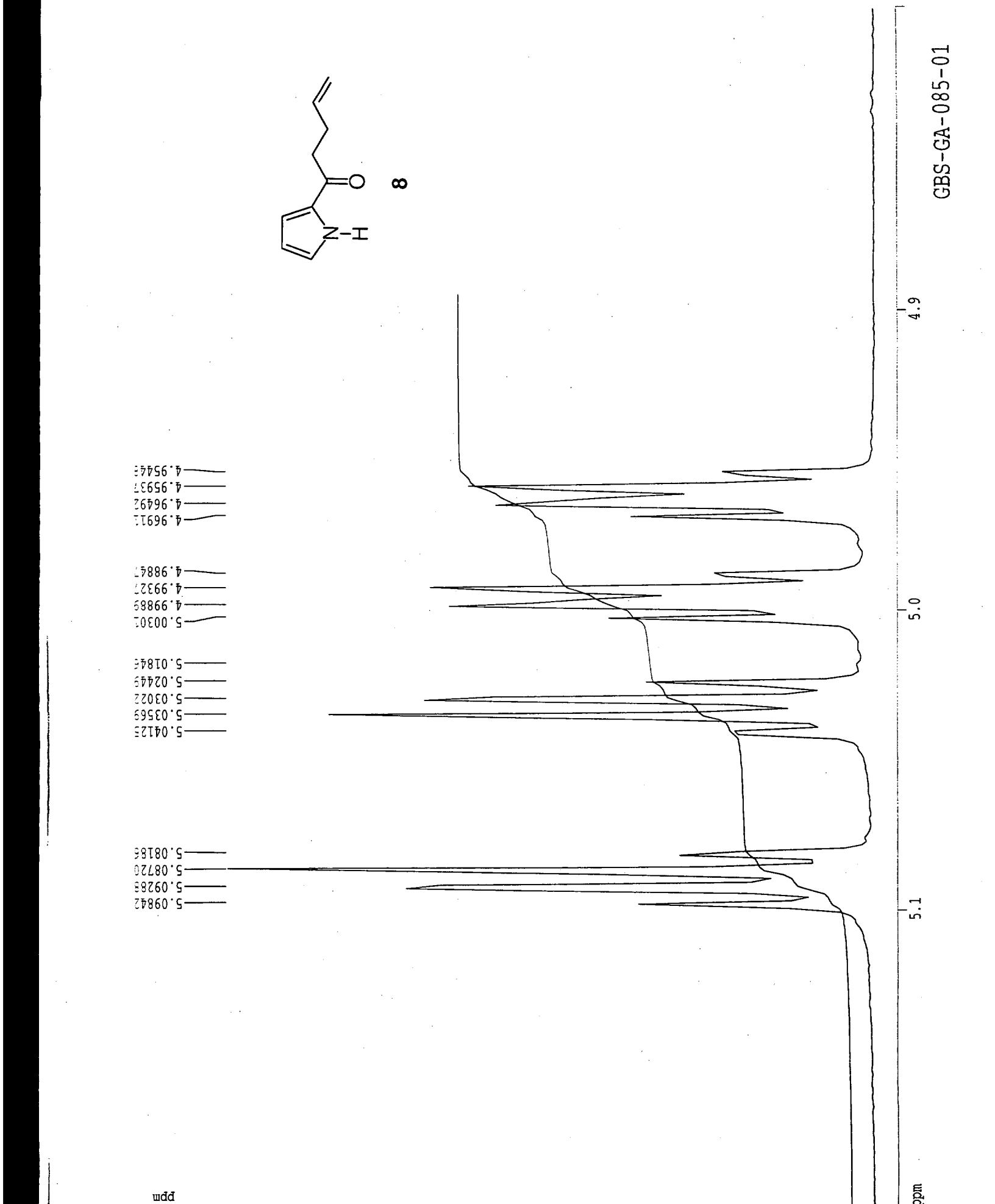
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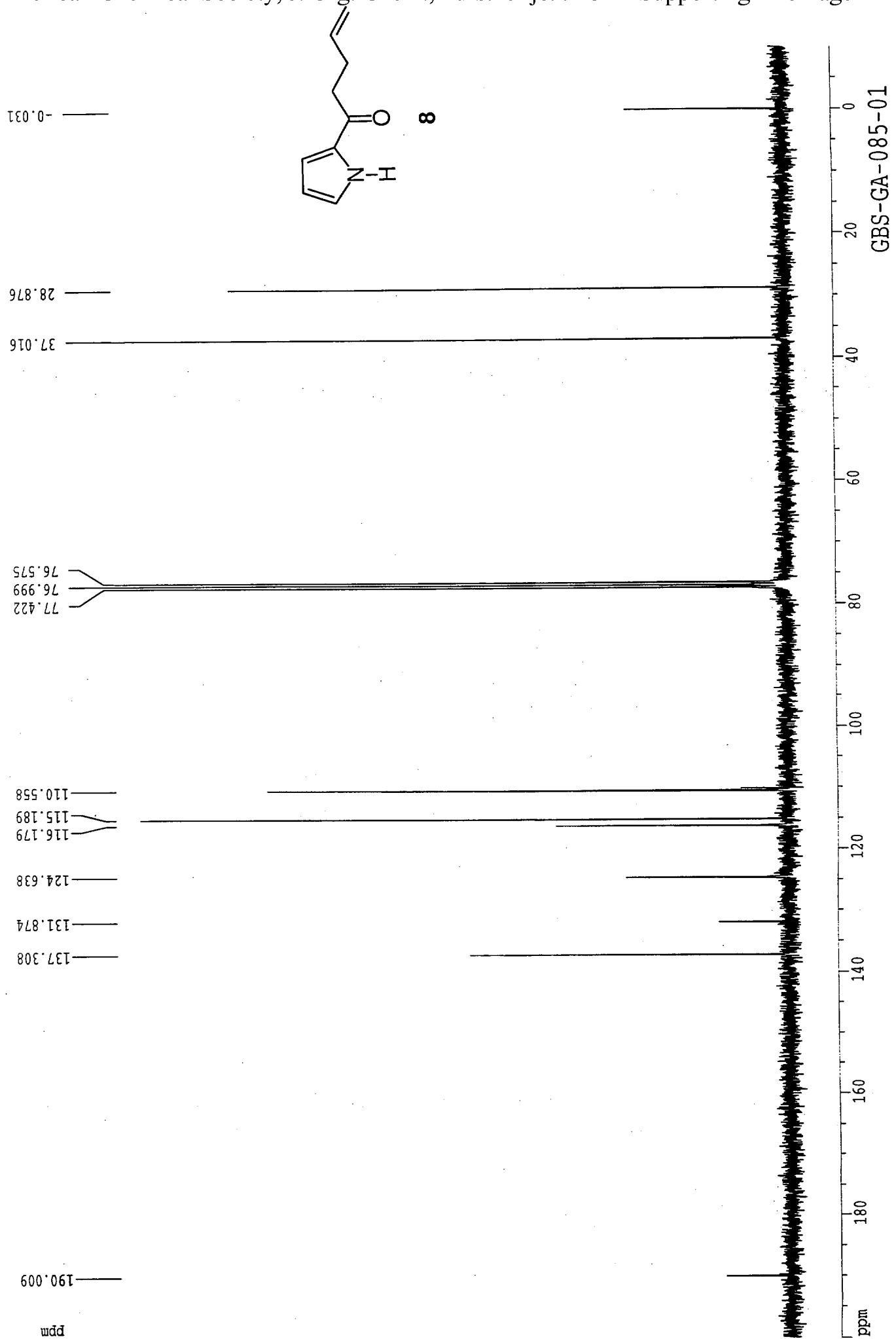
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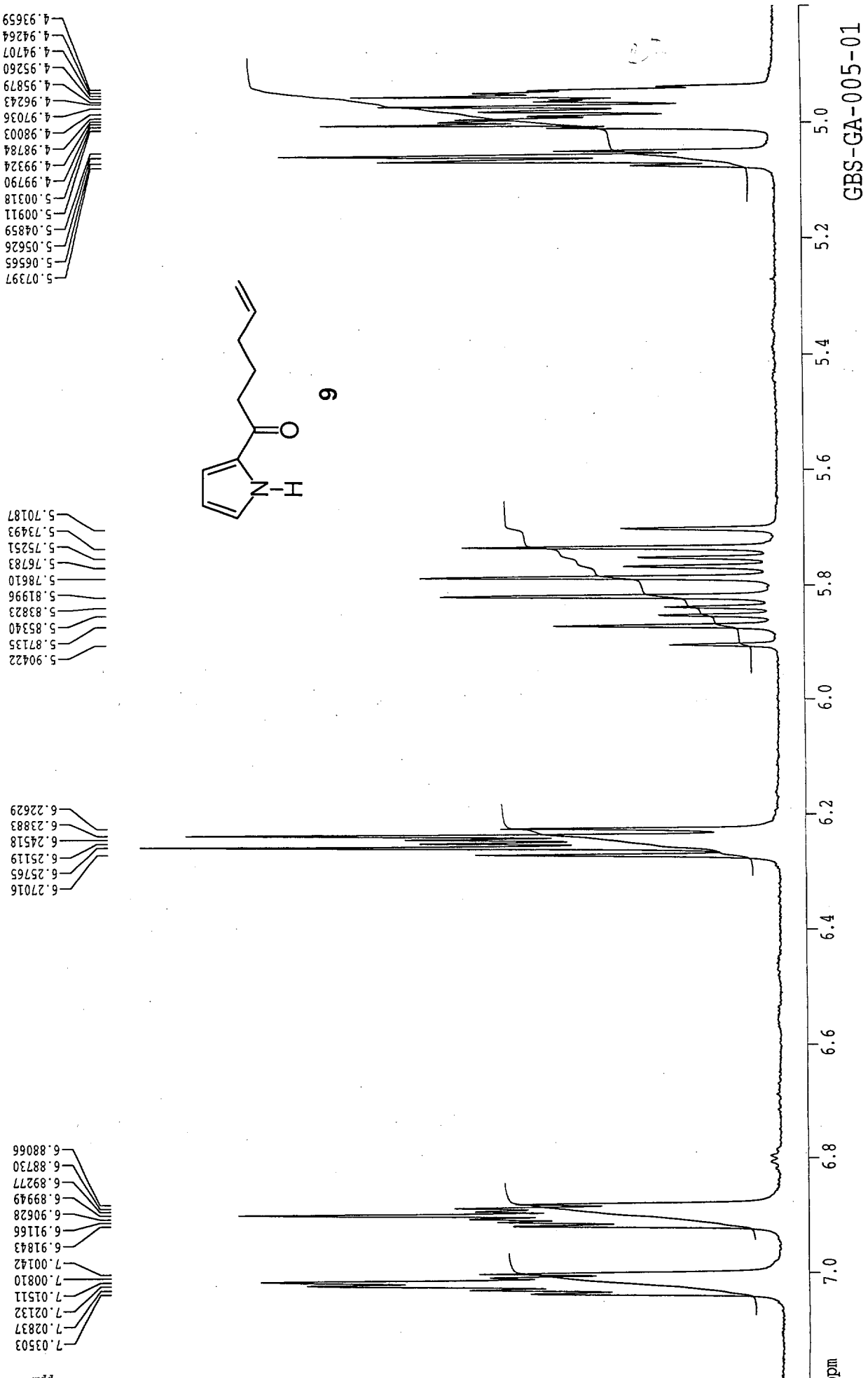
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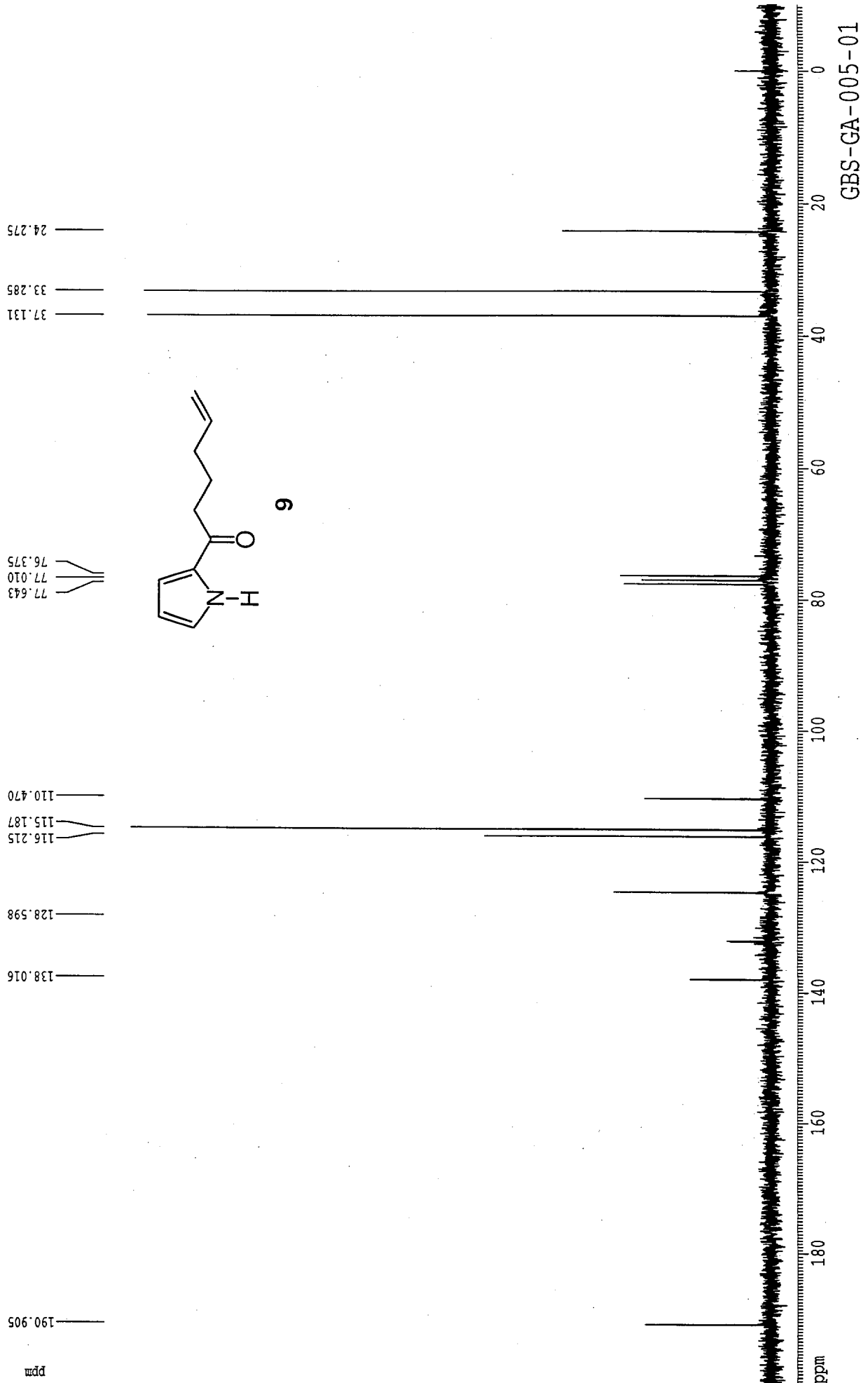
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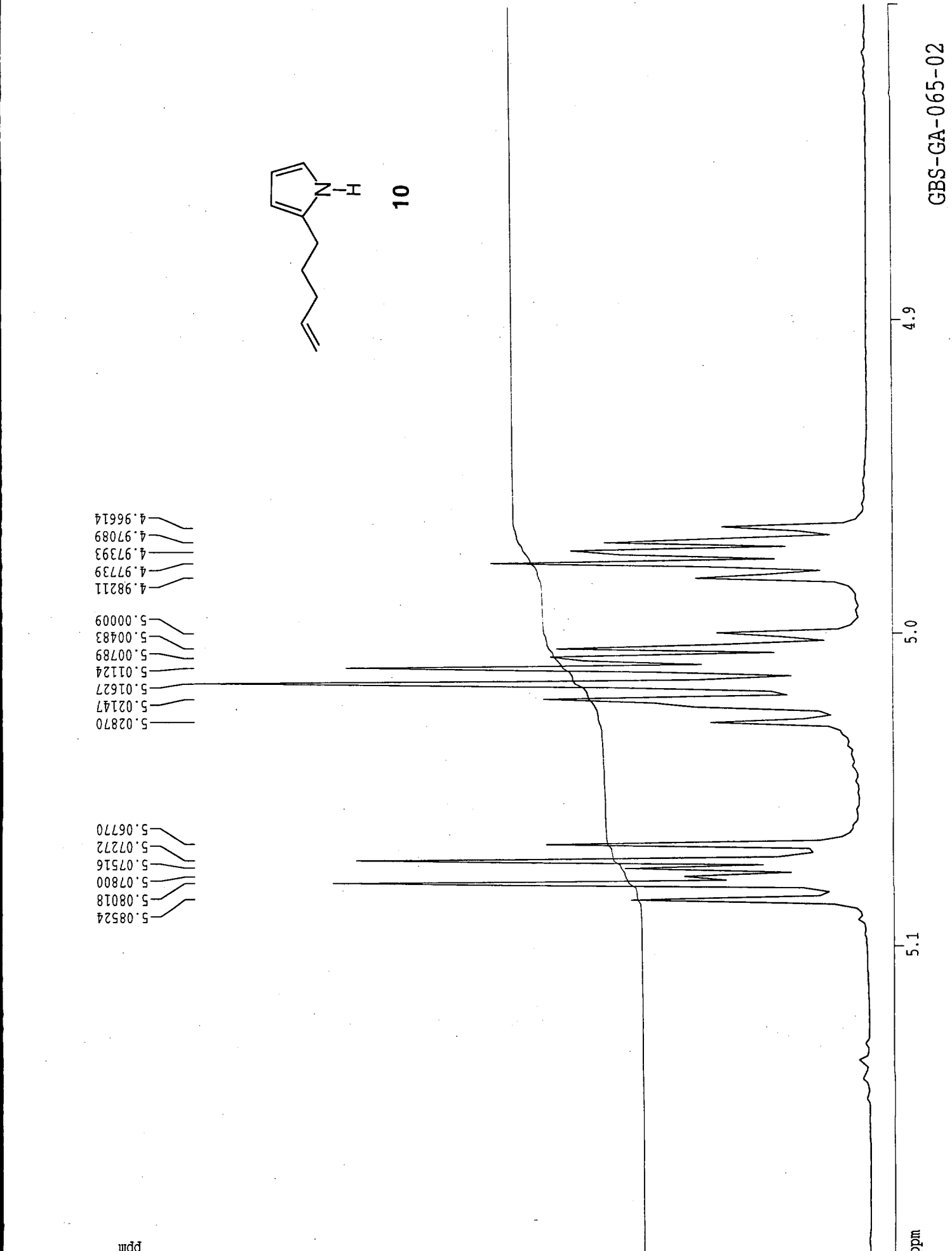
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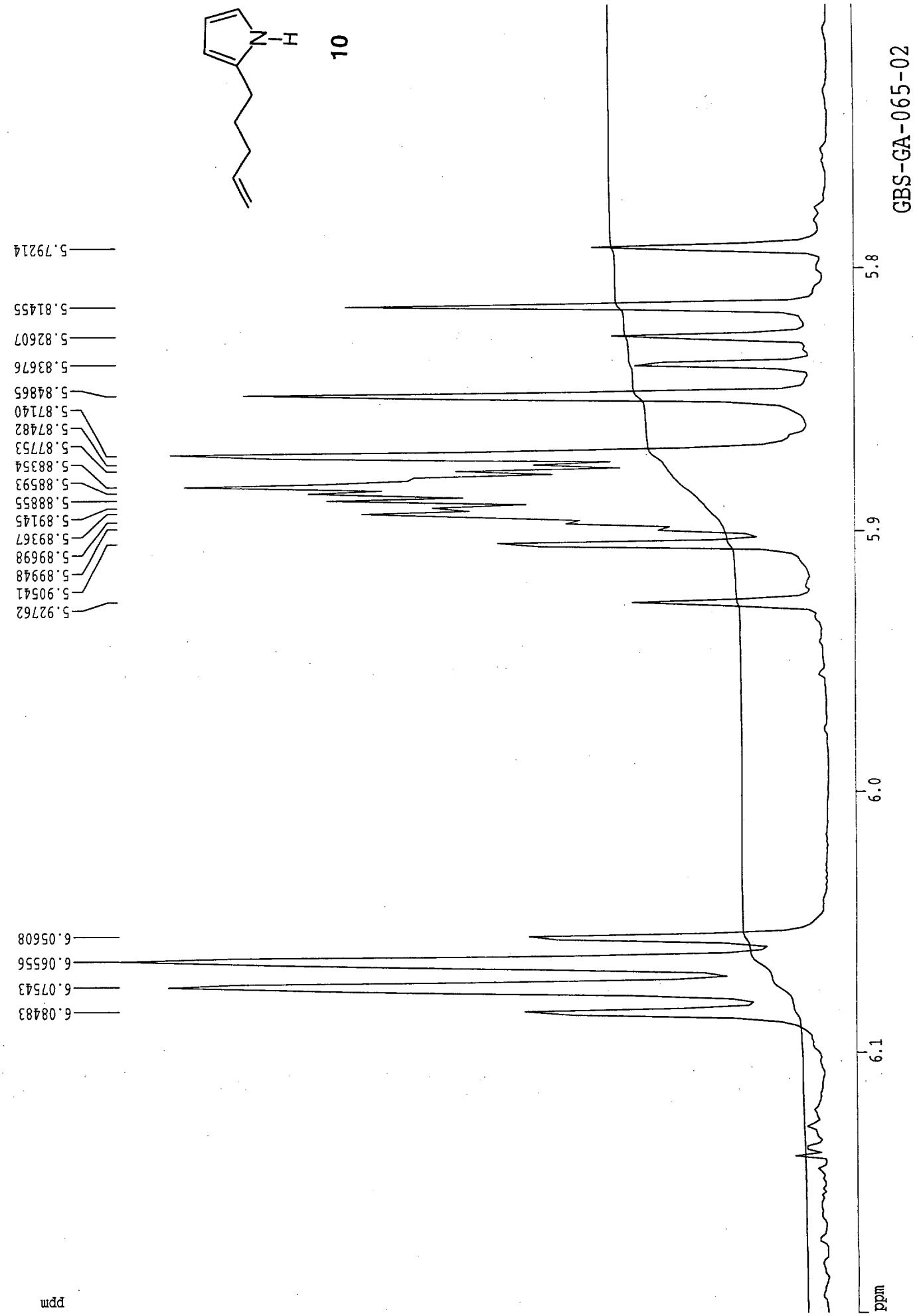
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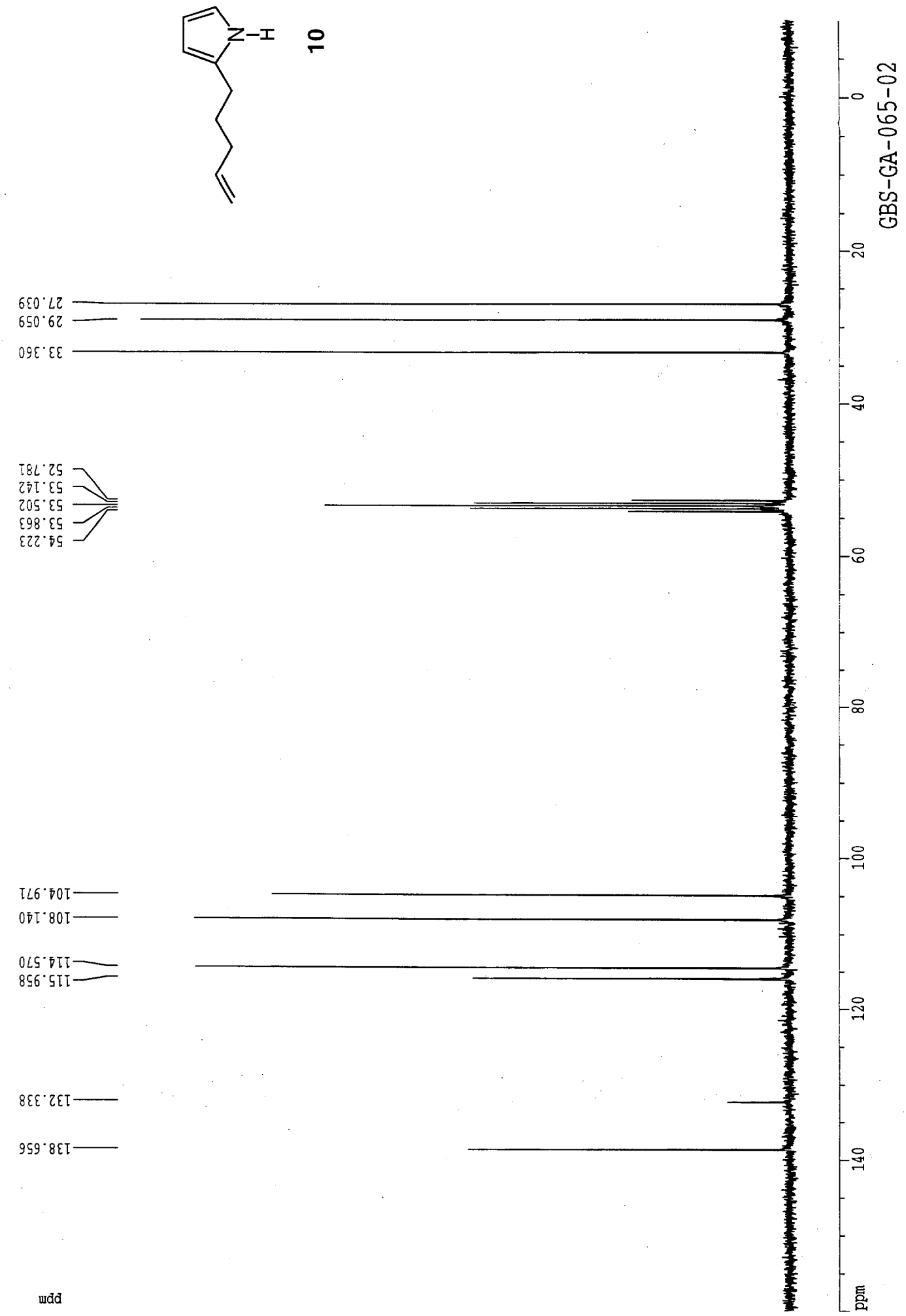
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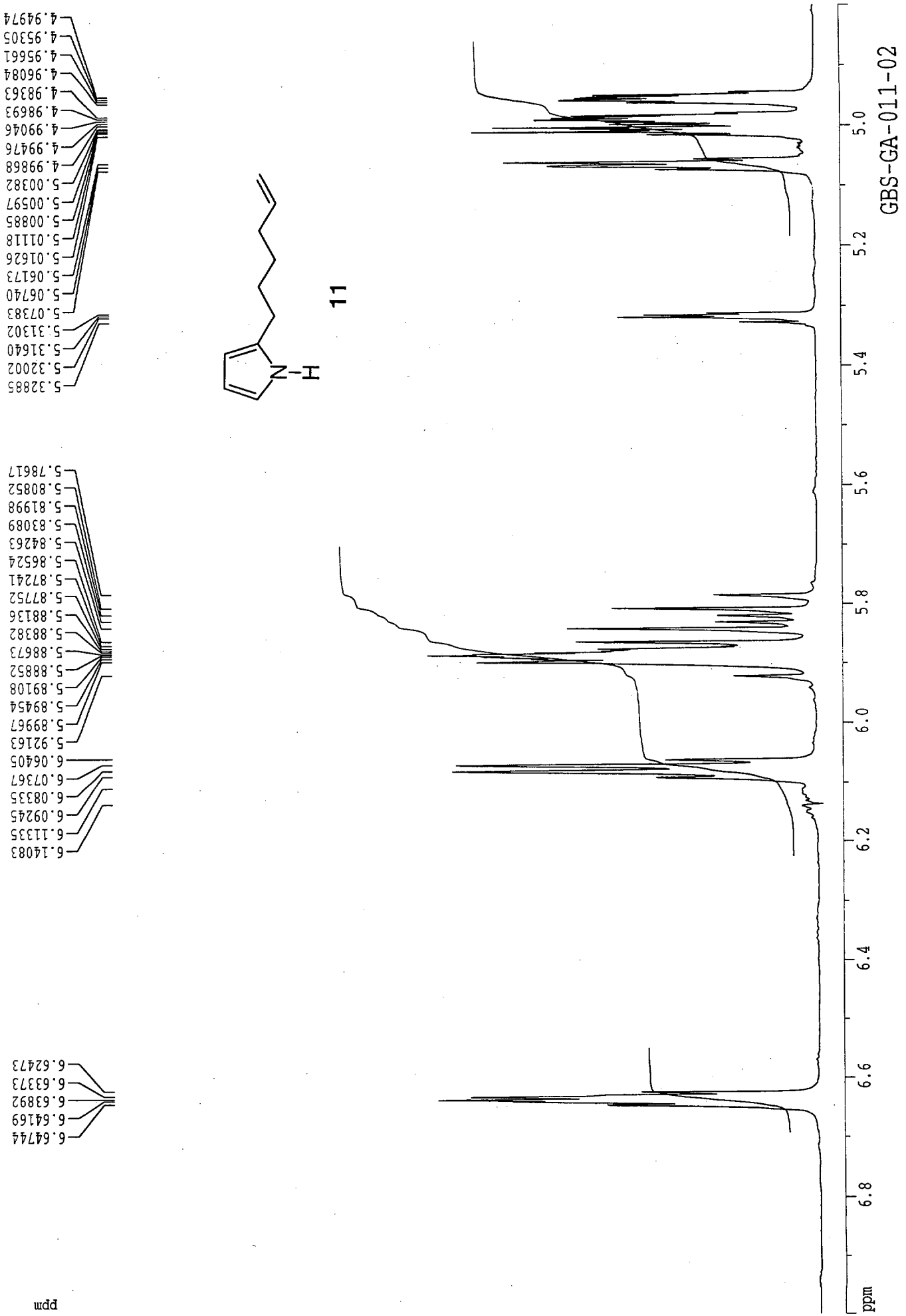
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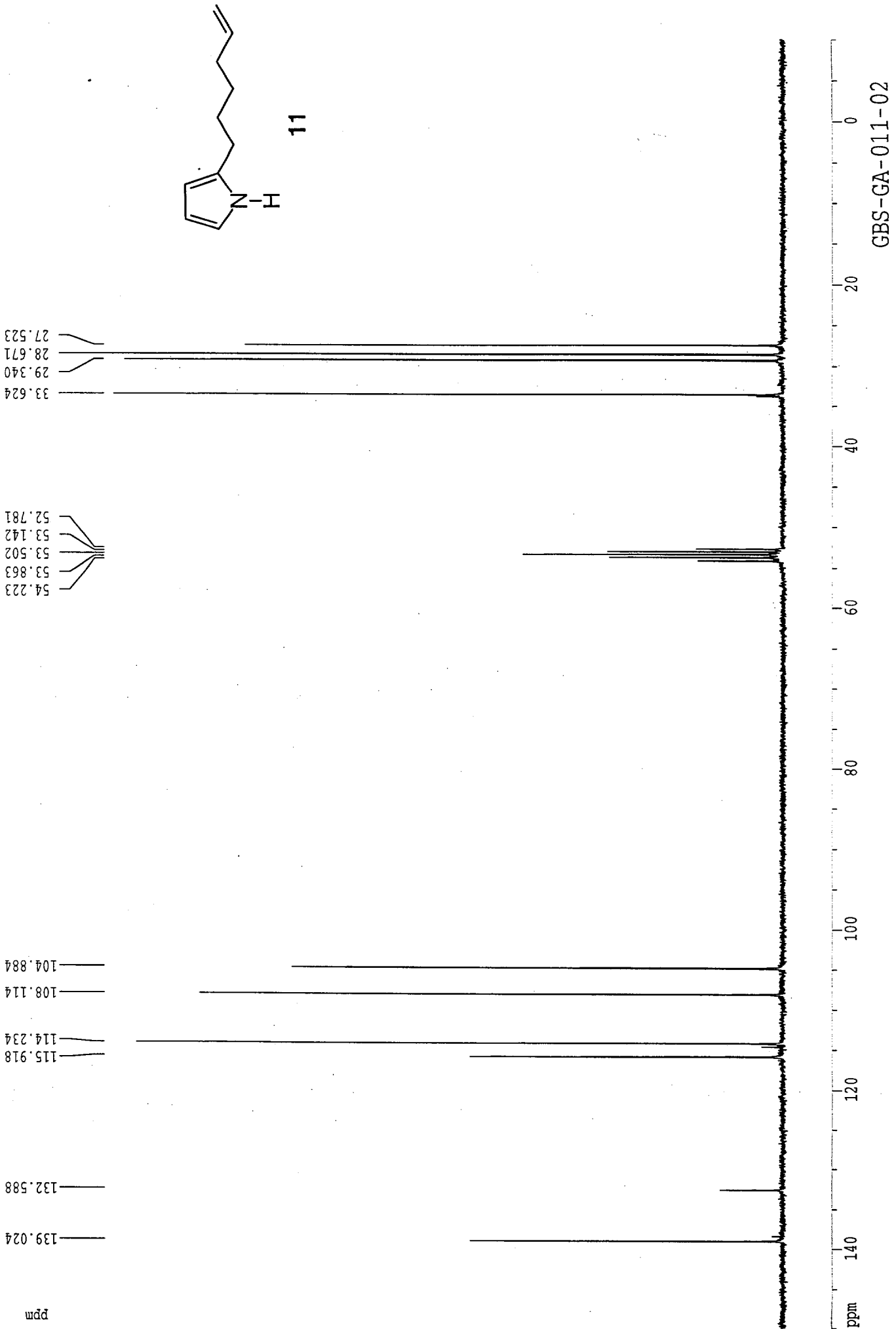
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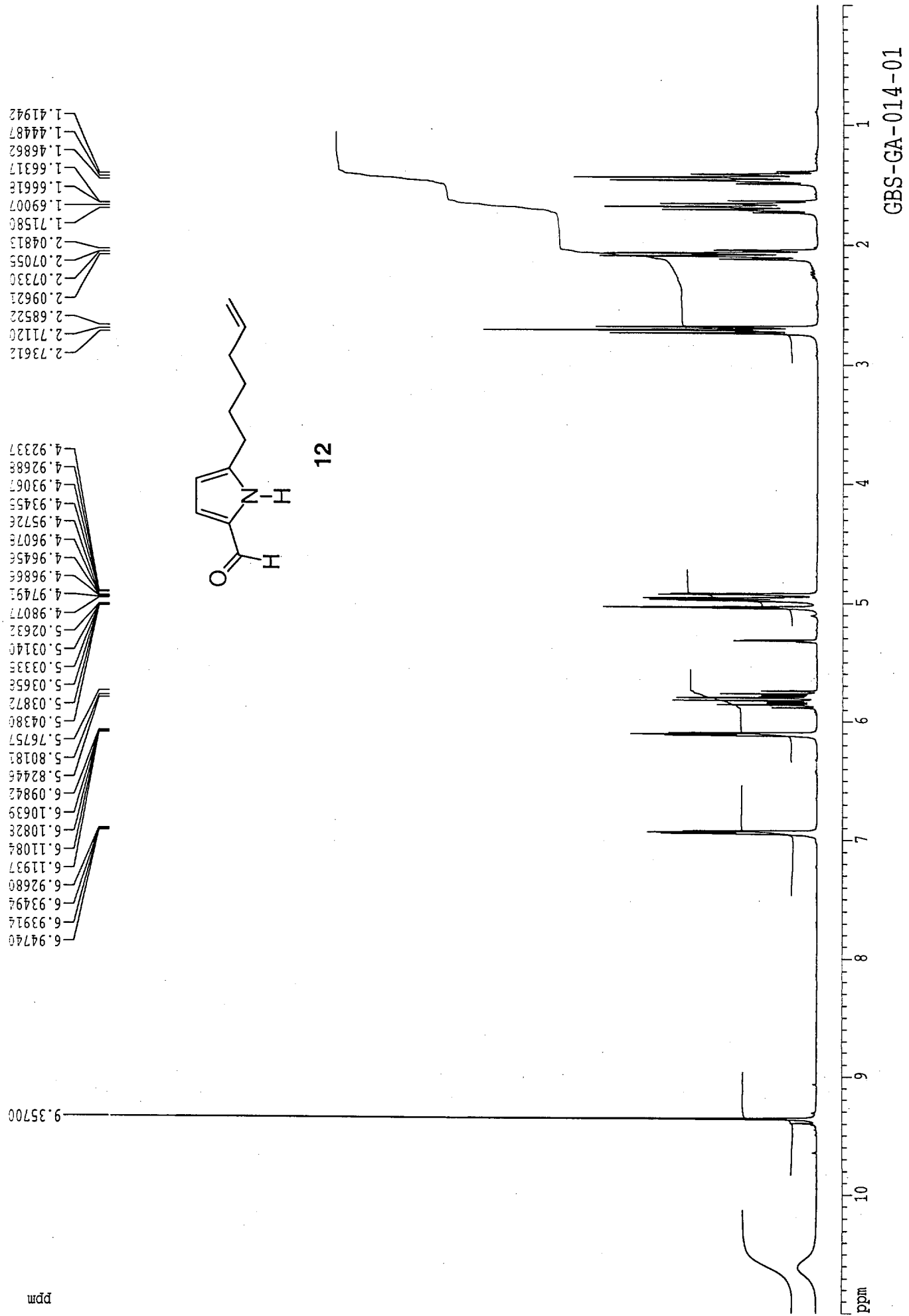
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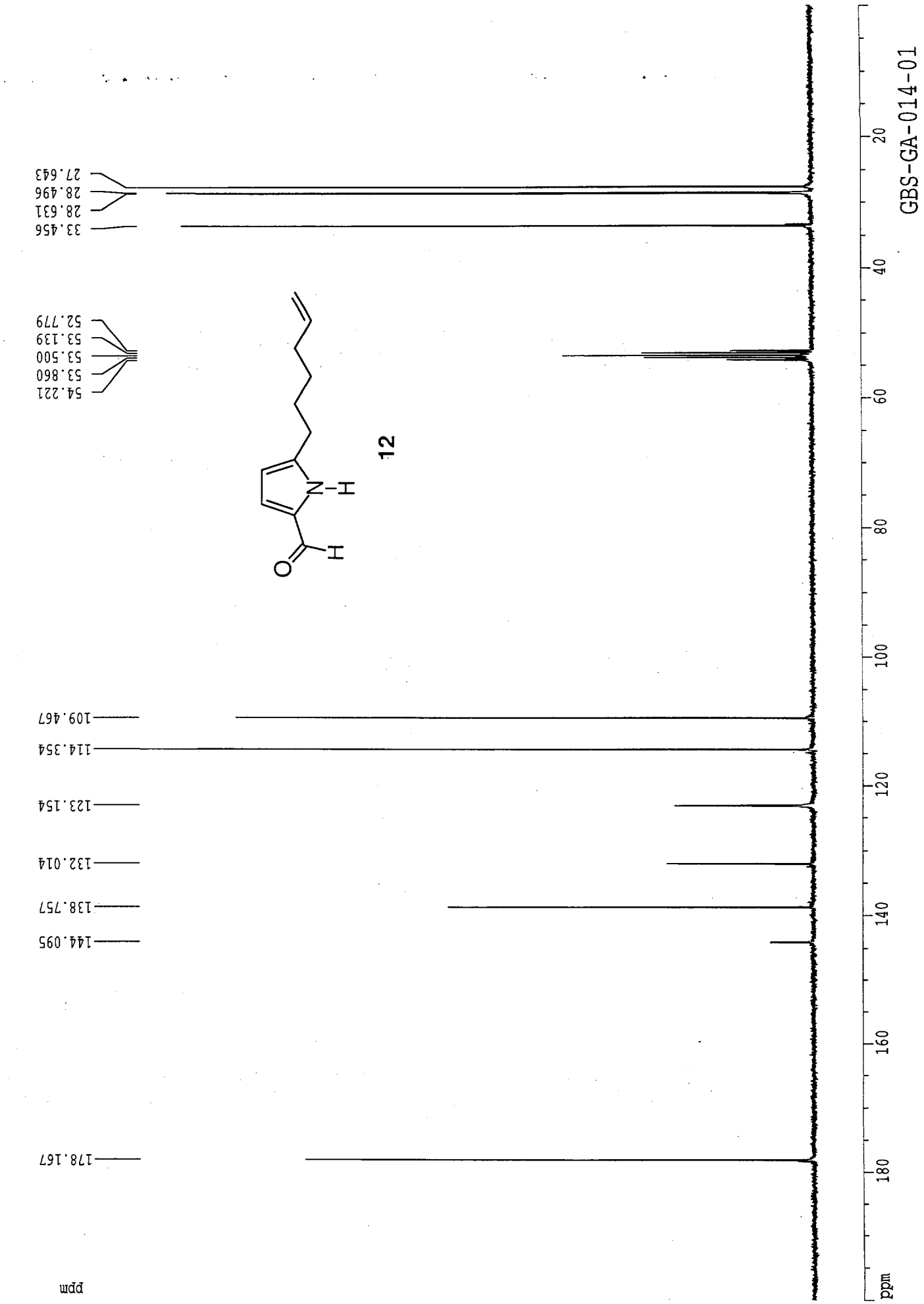
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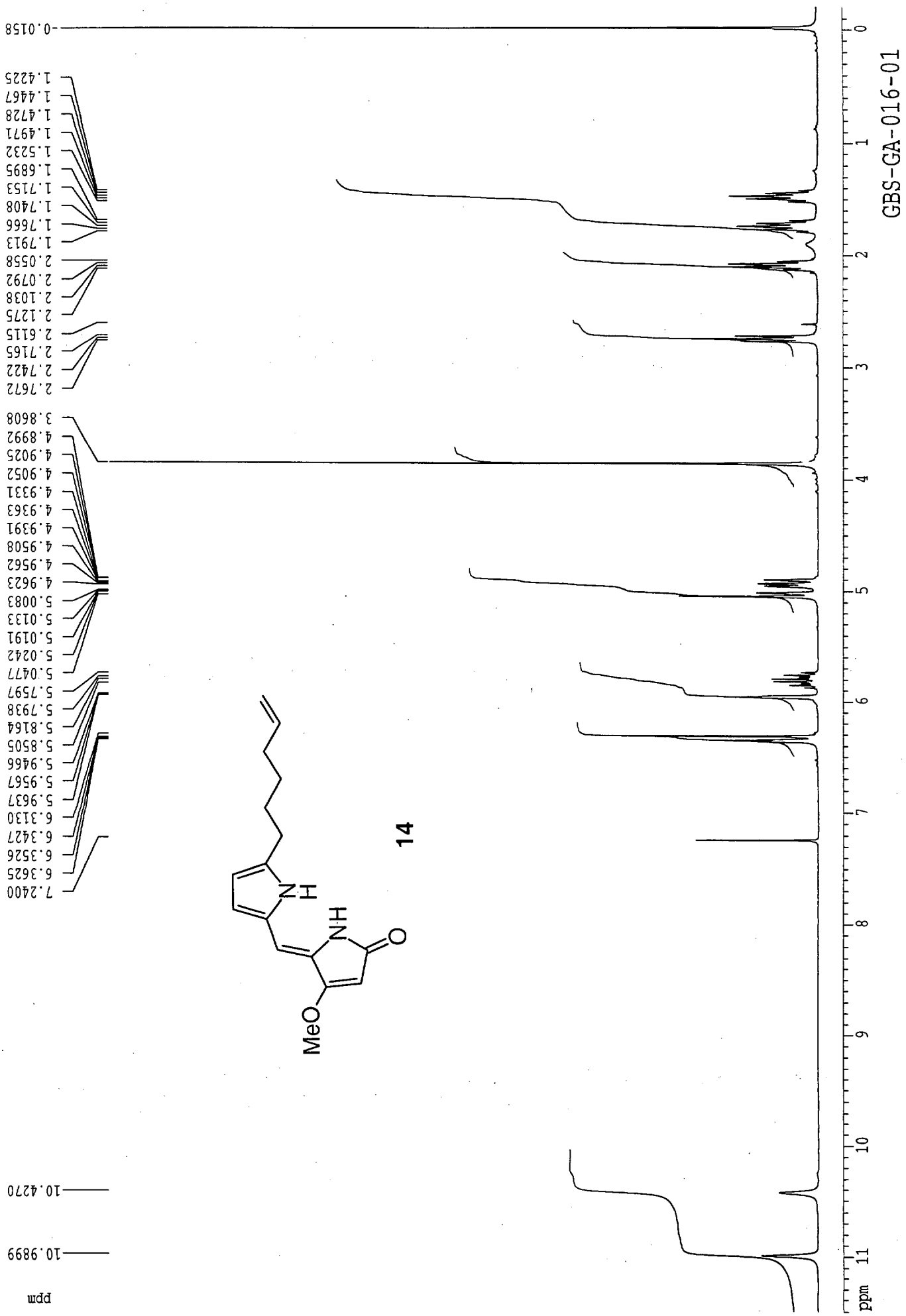
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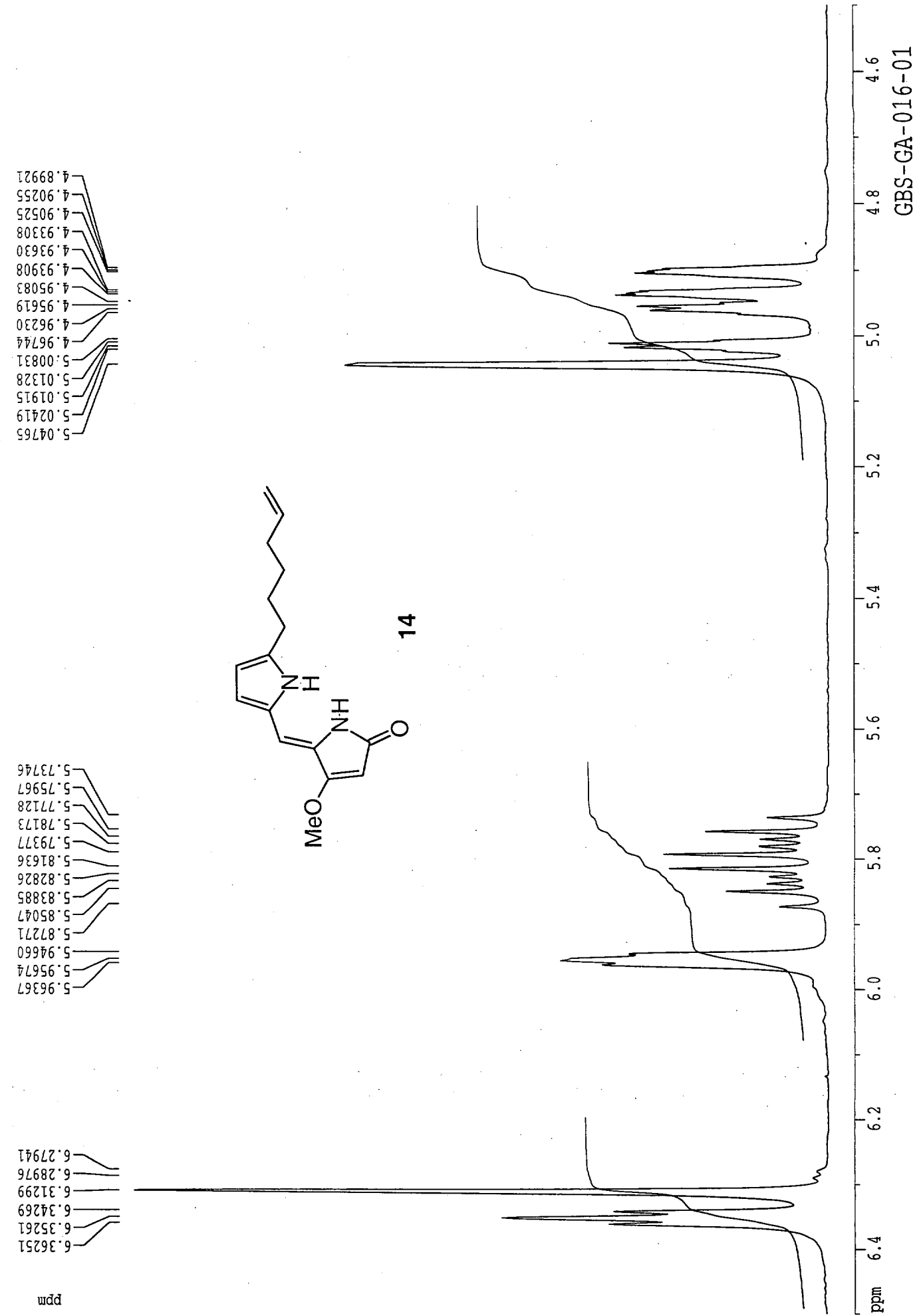
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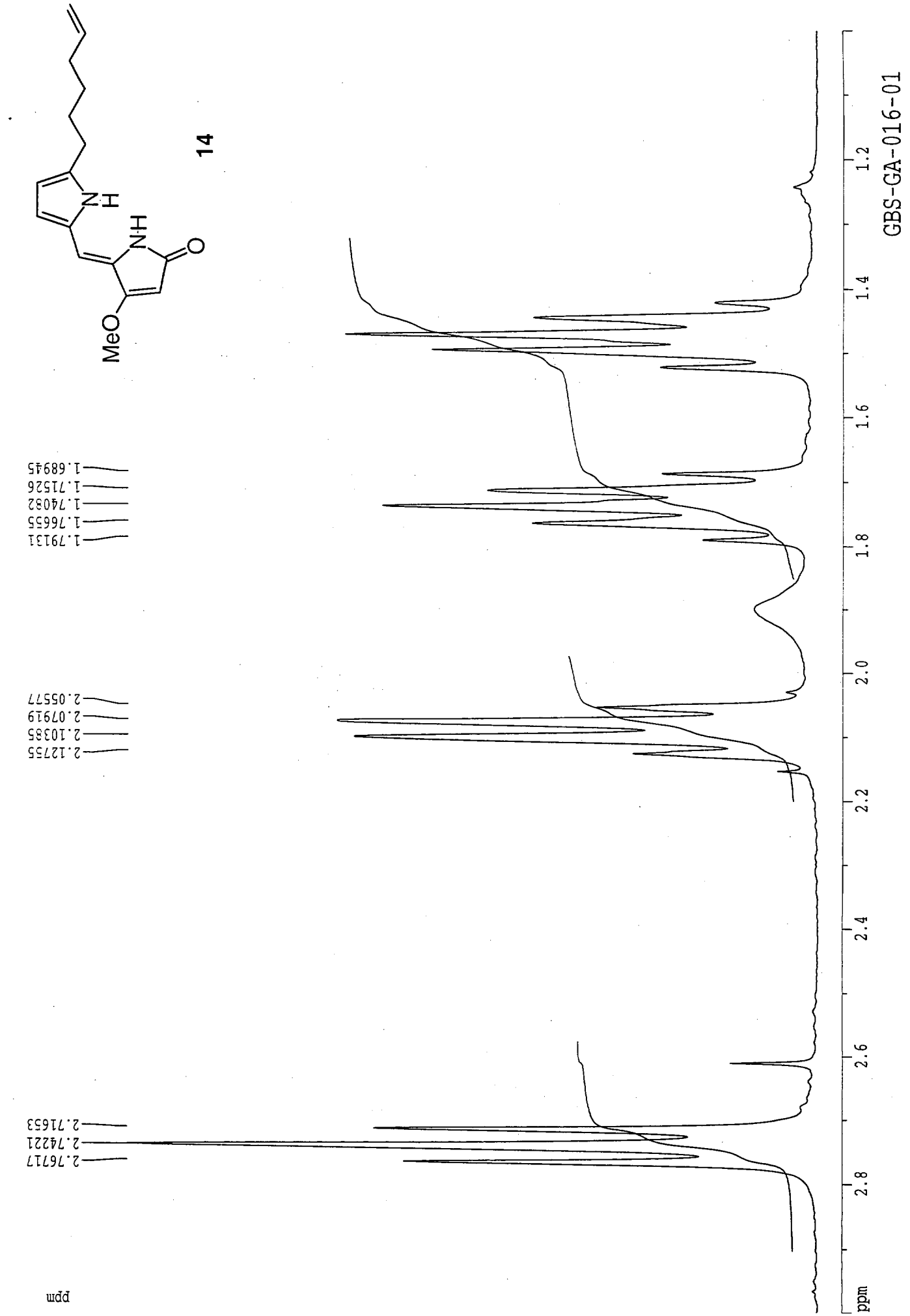
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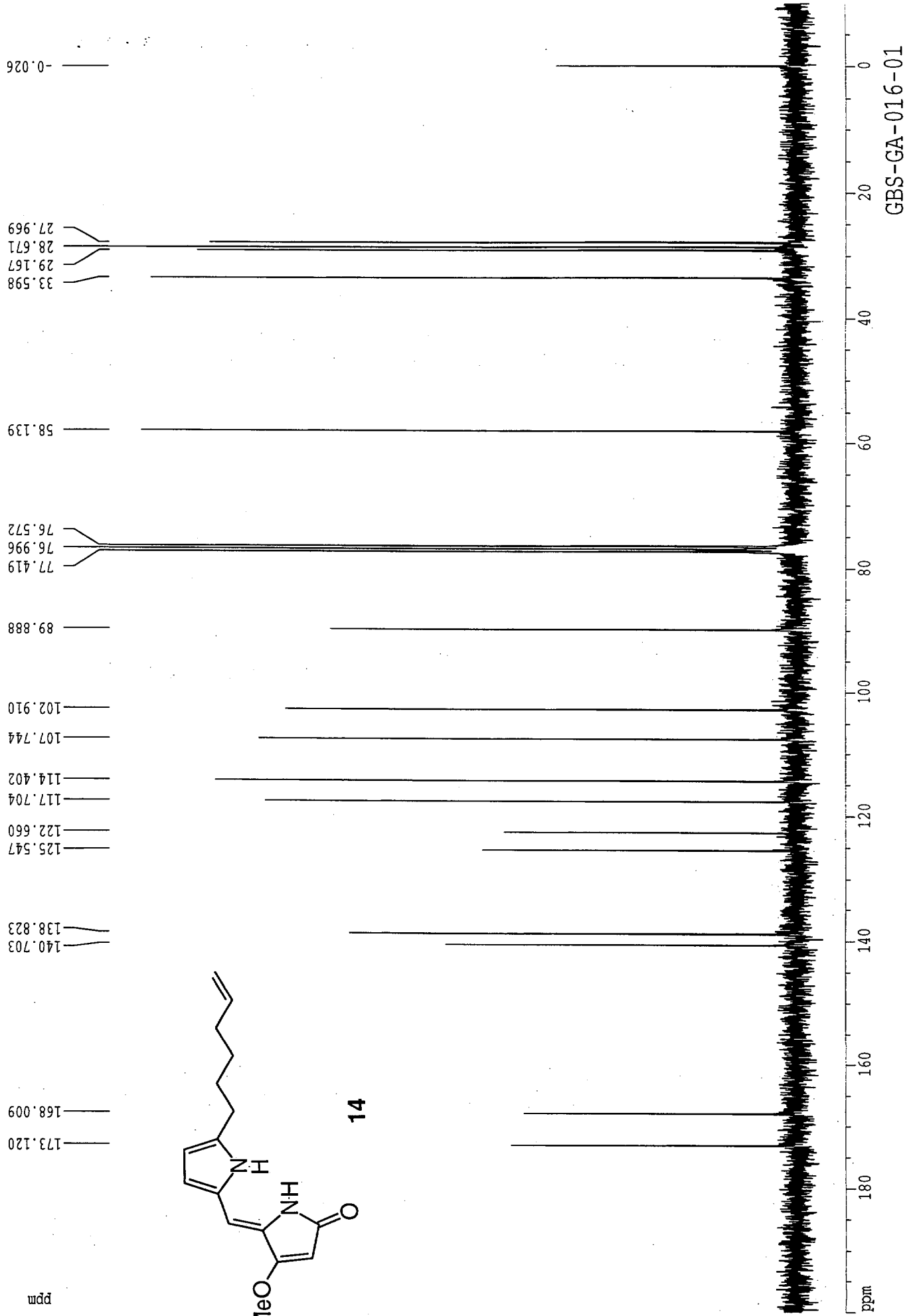
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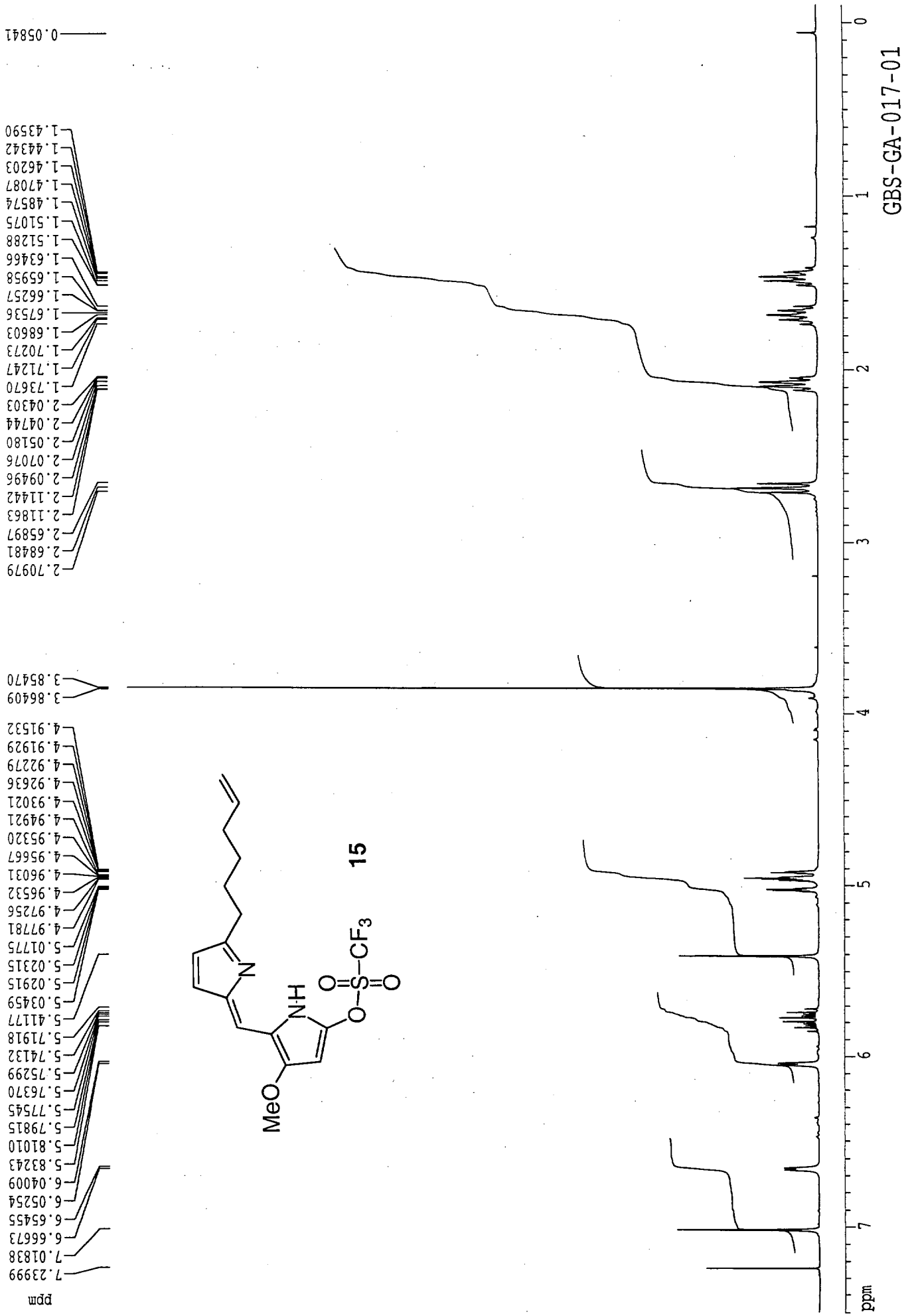
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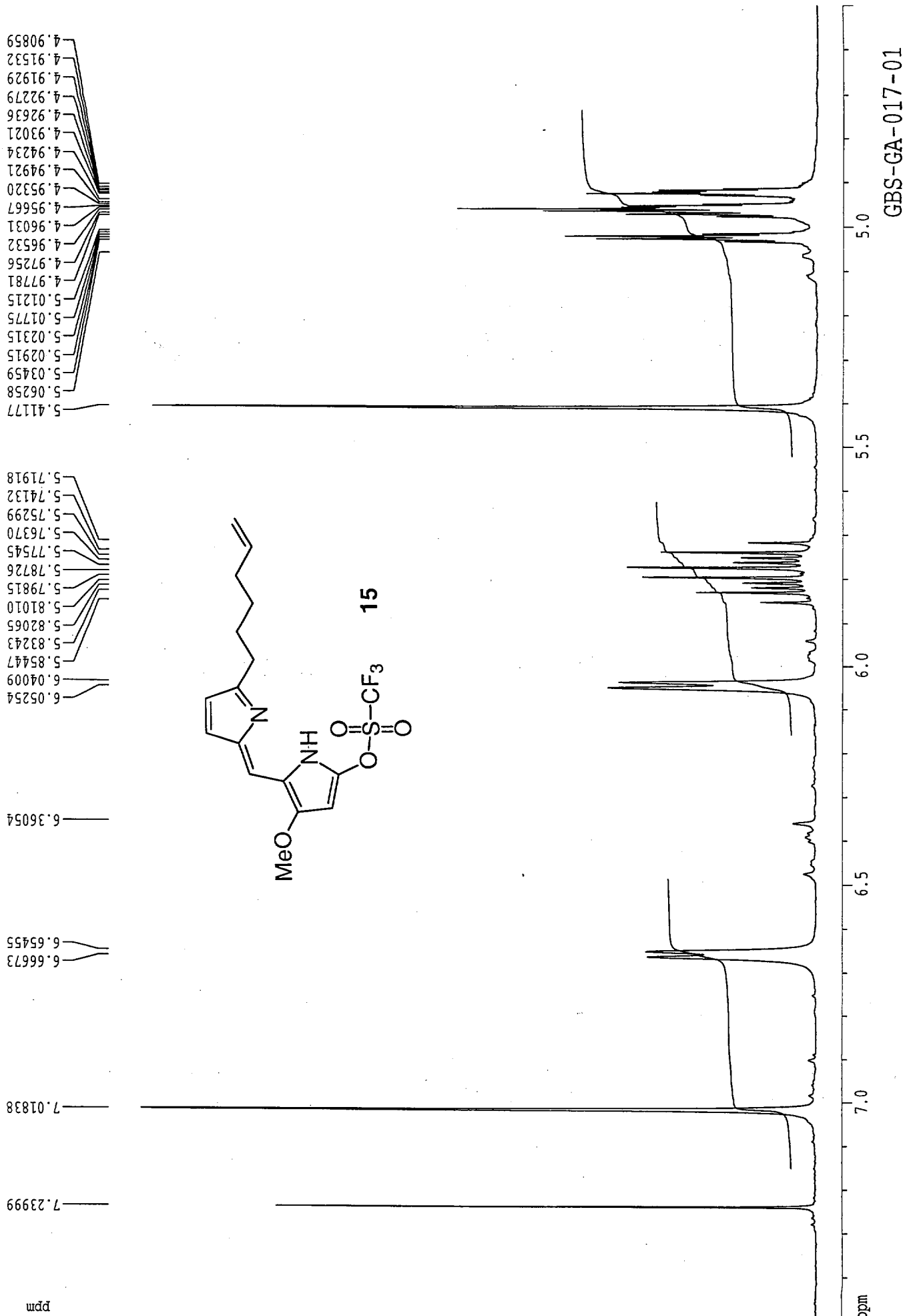
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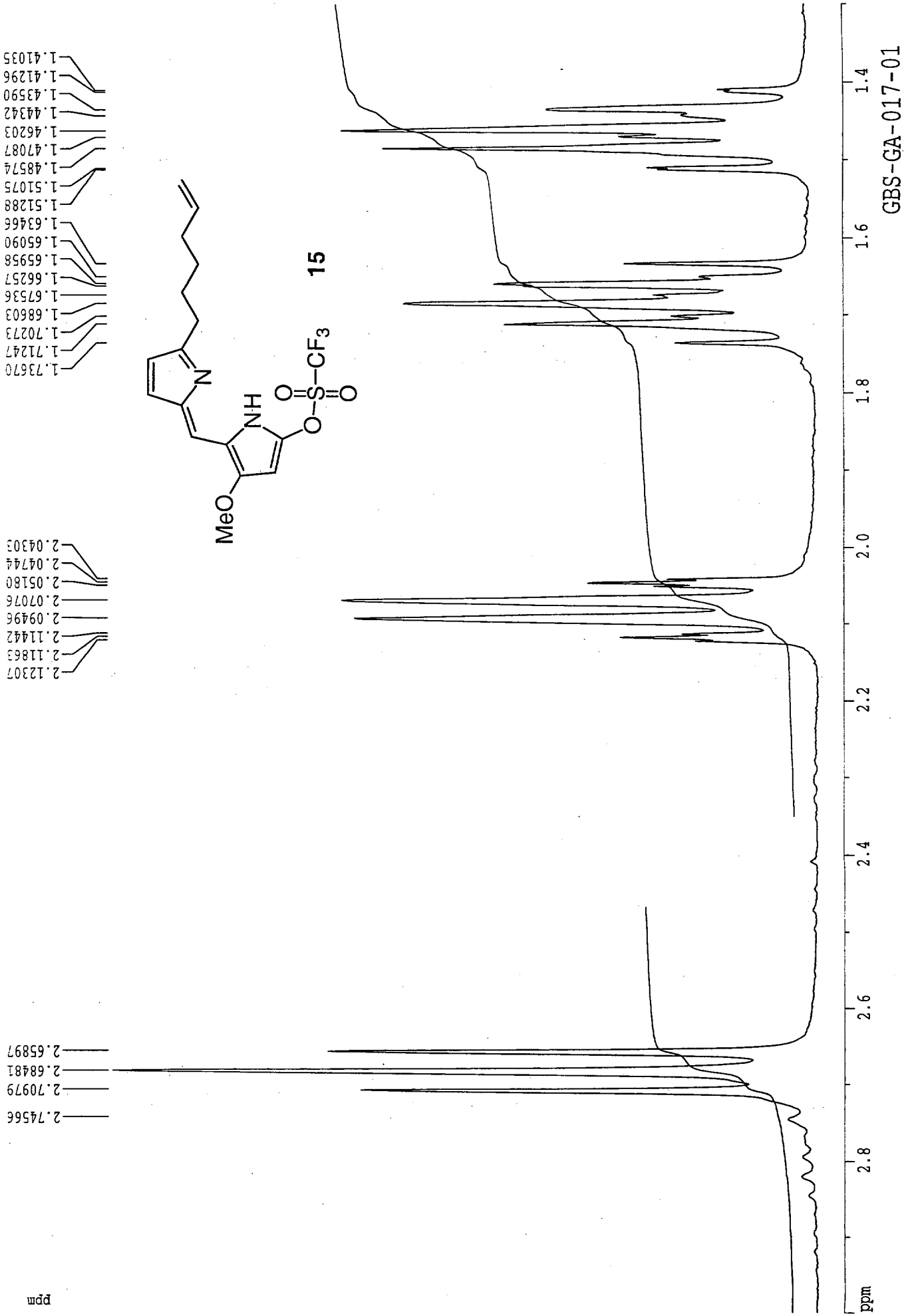
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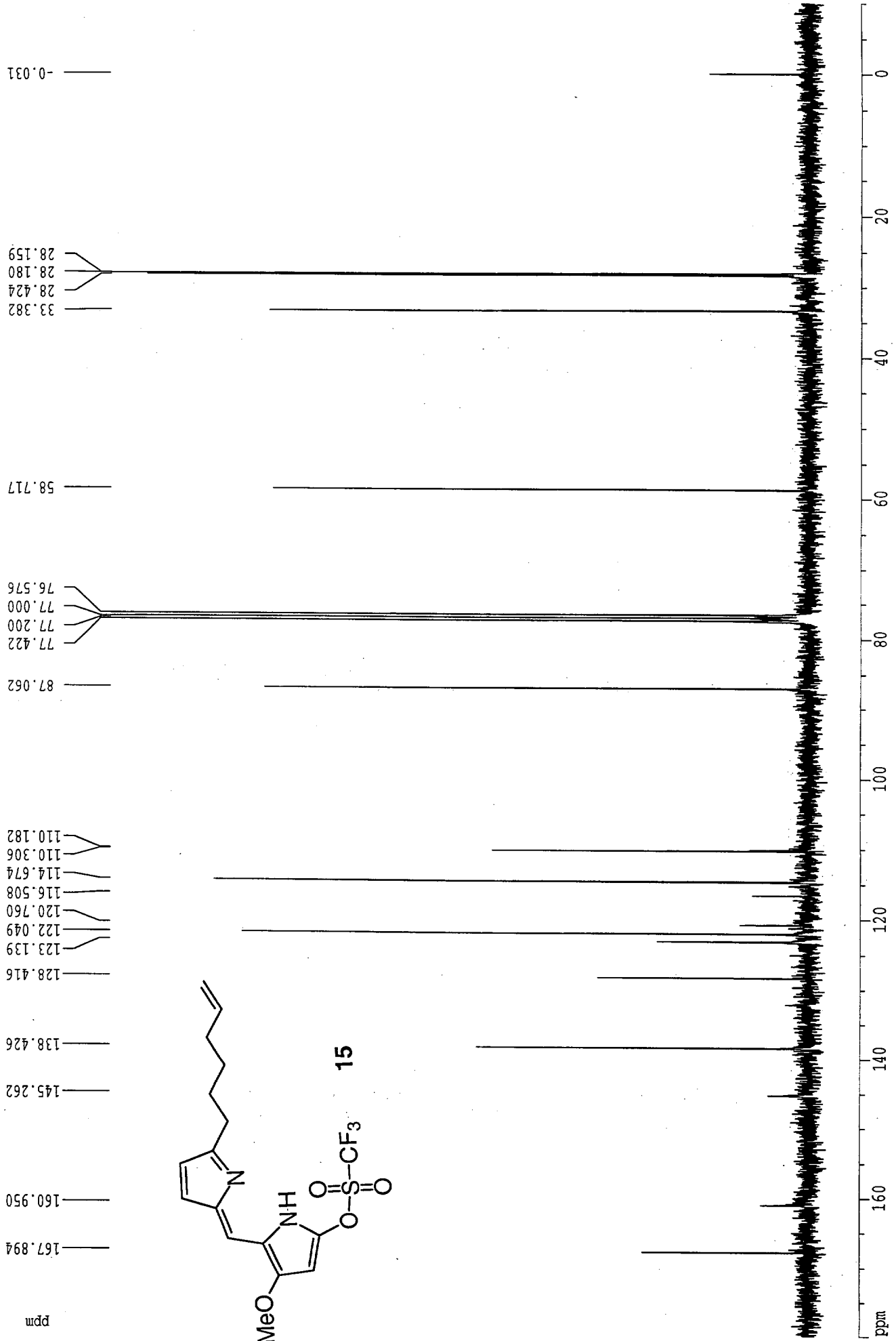
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