Supplementary Material (ESI) for Chemical Communications

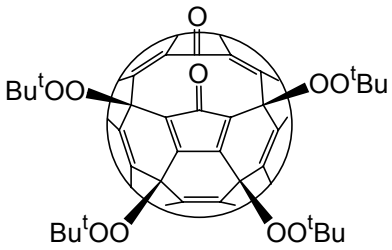
Controlled regio- and chemo-selective addition of isothiocyanate to the dione moiety of a cage-opened fullerene-mixed peroxide derivative

Xiaobing Yanga,c, Liangbing Gan,*a,b and Zheming Wang

All the reagents were used as received. CH_2Cl_2 used for reactions were distilled from P_2O_5, other solvents were used as received. Reactions were carried out under lab light in air at r.t. except indicated. Chromatographic purifications were carried out with 200-300 mesh silica gel. The NMR spectra were recorded on a Bruker ARX 400 (^1H, 400 MHz, ^{13}C, 100 MHz) spectrometer at 298 K. ESI-MS spectra were recorded on a LCQ Decaxp Plus Spectrometer with $CHCl_3/CH_3OH$ or $CDCl_3/CH_3OH$ as the solvent.

Caution: a large amount of peroxide is involved in some of the reactions, care must be taken to avoid possible explosion.

Preparation and characterization of fullerene dione 1.



1

Preparation and characterization data of **1** can be found in Huang, S. H., Wang, F. D., Gan, L. B., Yuan, Gu, Zhou, Jiang, Zhang, S. W. *Org. Lett*. **2006**, *8*, 277-279.

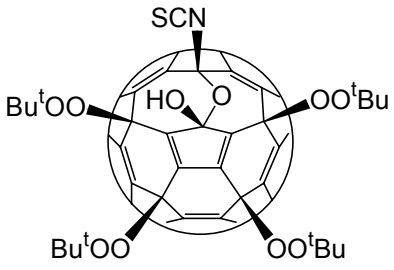
Formation of compound 1 from compound 3

Compound **3** (28 mg) was dissolved in 7 ml new distilled CH_2Cl_2 and stirred at room temperature. Then Al_2O_3 (140 mg) was added. Progress of the reaction was monitored by TLC. When **3** was nearly consumed (2 h), The residue was chromatographed on a silica gel column eluting with DCM gave the only band, **1** (22 mg, yield: 82.7%).

Preparation of 2:

Method A: see manuscript.

Method B: Compound **1** (60 mg, 0.054 mmol) was dissolved in 6 ml freshly distilled CH_2Cl_2 and stirred at room temperature in dark. Then TMSNCS (152 μL, 0.54 mmol) and silica gel (120 mg) were added. Progress of the reaction was monitored by TLC. After being stirred for 3 days, the residue was chromatographed on a silica gel column. Eluting with DCM gave compound **3** (14 mg, yield: 20%) as the first band, the second band was the main product **2** (49 mg, yield: 71%).



4

Preparation of 4:

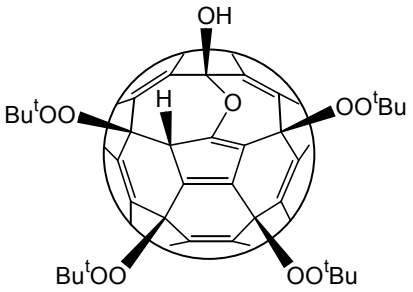
Method A: Compound **3** (44 mg) was dissolved in 44 mL freshly distilled CH_2Cl_2 and stirred at room temperature. Progress of the reaction was monitored by TLC. After being stirred for 3 h, the solution was directly chromatographed on a silica gel column. Eluting with DCM gave the only product, **4** (30 mg, yield: 68%).

Method B: To a stirred solution of compound **3** (18 mg) in freshly distilled CH_2Cl_2 (4 mL) was added excess $ZnCl_2$ (20 equiv.,

42 mg) at 30°C in dark. After being stirred for 3 h, the solution was directly chromatographed on a silica gel column. Eluting with DCM gave trace **1** as the first band, the second band was the main product **3** (16 mg, yield: 89%).

Method C: To a stirred solution of compound **1** (50 mg, 0.045 mmol) in freshly distilled CH_2Cl_2 (10 mL) was added TMSNCS (126 μL, 0.9 mmol) and $ZnCl_2$ (60 mg, 0.45 mmol) at 30°C in dark. After being stirred for 2 h, the solution was directly chromatographed on a silica gel column. Eluting with DCM/petroleum ether (2:1) gave the main product **4** (30 mg, yield: 57%) as the first band. Then the eluting solvent was changed to DCM/EtOAc (30:1).The red band was collected and evaporated to give the compound **3** (7 mg, yield: 13%).

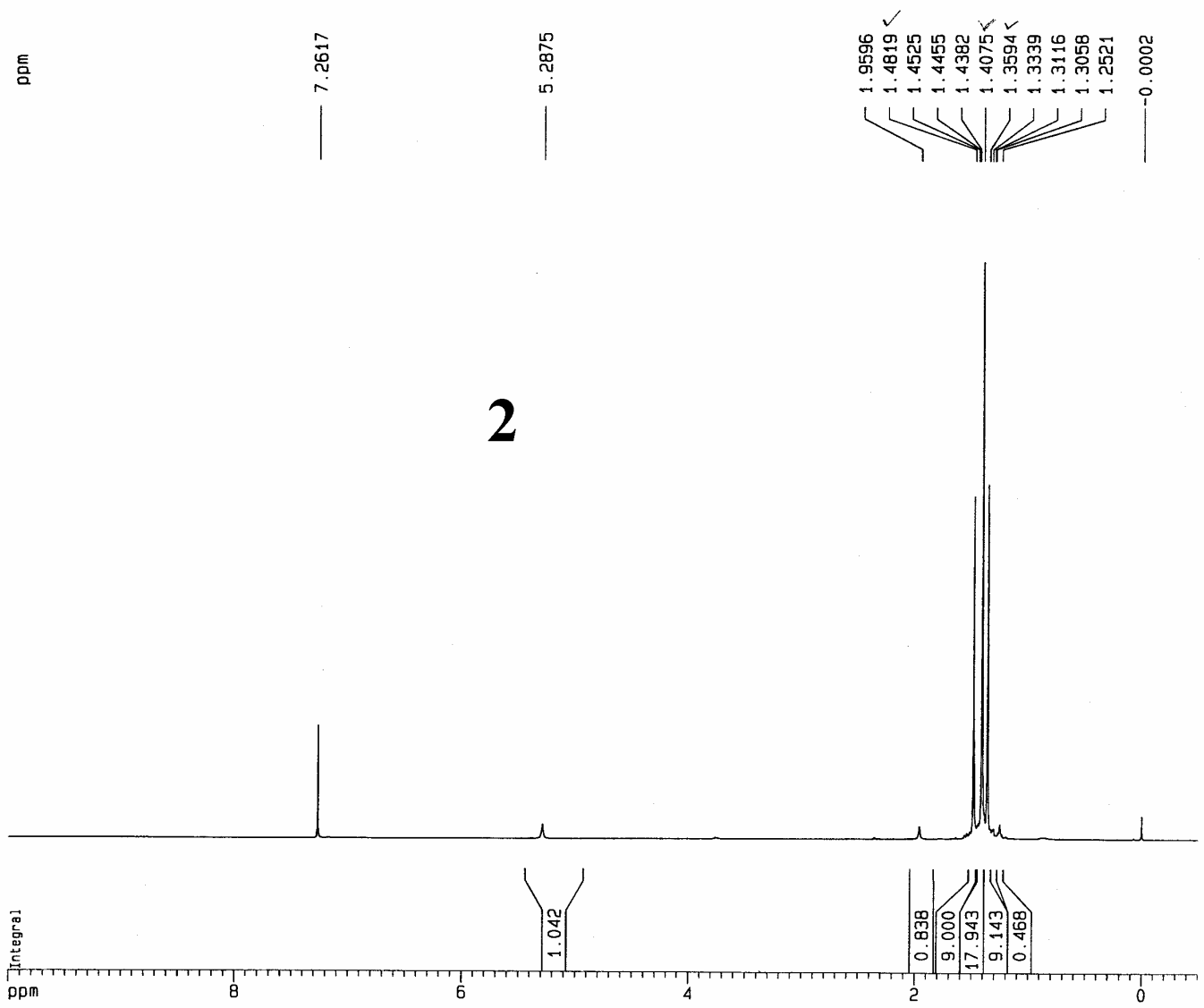
^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 4.990 (1H, OH), 1.477 (s, 18H), 1.457 (s, 18H). ^{13}C-NMR ($CDCl_3$, 100 MHz) all signals represent 2C except noted. δ: 162.20, 149.68, 148.89, 148.84, 148.72, 148.52, 148.43, 148.24, 148.21 (1C), 148.07, 147.16, 147.13, 147.07 (1C), 146.59, 146.55, 145.77, 145.72, 145.10, 144.89, 144.78 (4C), 144.07, 143.49, 143.08, 142.97, 141.58, 141.56, 139.75, 132.21, 106.58 (1C-OH), 95.17 (1C-NCS), 87.94, 82.48 (2*C*-$(CH_3)_3$), 81.91 (2*C*-$(CH_3)_3$), 79.00, 26.77 ($6CH_3$), 26.70 ($6CH_3$). FT-IR (microscope): 3535, 2979, 2931, 2870, 1979, 1752, 1473, 1455, 1421, 1387, 1364, 1304, 1244, 1230, 1192, 1159, 1105, 1087, 1058, 1042, 1021, 1003, 972, 910, 870, 853, 783, 758, 733. (+) ESI-MS (VGPlatform II): m/z (rel intens) 1185 (100) [M+NH_4^+], (-) ESI-MS (VGPlatform II): m/z (rel intens) 1166 (51) [M-H^+], calculated for $C_{77}H_{37}NO_{10}S$ MW = 1167. (-) HR-MS (Bruker apex-IV FT-MS): $C_{77}H_{36}NO_{10}S$ (M - 1) calcd 1166.2065, found 1166.2038.



5

Preparation of 5: Compound **2** (45 mg, 0.039 mmol) was dissolved in 9 mL freshly distilled CH_2Cl_2 and stirred at room temperature in dark. Then Ph_3P (15 mg, 0.058 mmol) was added. Progress of the reaction was monitored by TLC. When **2** was completely consumed, the residue was chromatographed on a silica gel column. Eluting with DCM gave compound **5** (33 mg, yield: 77%) as the only band.

^{1}H-NMR (CS_2 : $CDCl_3$ / 1 : 1, 400 MHz) δ: 4.932 (1H, H), 4.608 (1H, OH), 1.369 (s, 18H), 1.357 (s, 9H), 1.348 (s, 9H). ^{13}C-NMR (CS_2 : $CDCl_3$ / 1 : 1, 100 MHz) all signals represent 1C except noted. δ: 160.36, 150.68, 149.85, 149.46, 149.11, 149.02, 148.92, 148.65, 148.57, 148.25, 148.03, 147.98, 147.97 (2C), 147.94, 147.91, 147.87, 147.73 (2C), 147.67, 147.65, 147.60, 147.06, 147.02, 146.75, 146.54, 146.30, 145.84, 145.79, 145.75, 145.72, 145.17, 143.99, 143.87, 143.79, 143.75, 143.60, 143.41, 143.24, 143.14, 142.86, 142.31, 142.20, 142.16, 141.83, 141.72, 140.85, 140.71 (2C), 140.65, 139.90, 138.88, 137.48, 129.17, 106.82 (1C-OH), 88.77, 84.75, 81.65, 81.41 (1*C*-$(CH_3)_3$), 81.30 (1*C*-$(CH_3)_3$), 81.20 (1*C*-$(CH_3)_3$), 81.09 (1*C*-$(CH_3)_3$), 78.86, 56.58 (1C-H), 26.89 ($3CH_3$), 26.78 ($6CH_3$) , 26.77 ($3CH_3$). FT-IR (microscope): 3321, 2979, 2931, 2259, 1648, 1603, 1518, 1472, 1454, 1387, 1364, 1338, 1310, 1261, 1243, 1190, 1154, 1106, 1055, 1014, 977, 909, 872, 732. (+) ESI-MS (VGPlatform II): m/z (rel intens) 1059 (100) [M-BuOH+Na^+], 1076 (48) [M-BuOH+K^+], (-) ESI-MS (VGPlatform II): m/z (rel intens) 1067 (100) [M-BuOH +MeO^-], calculated for $C_{76}H_{38}O_{10}$ MW = 1110.

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PROCNO                     1

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F2 - Processing parameters
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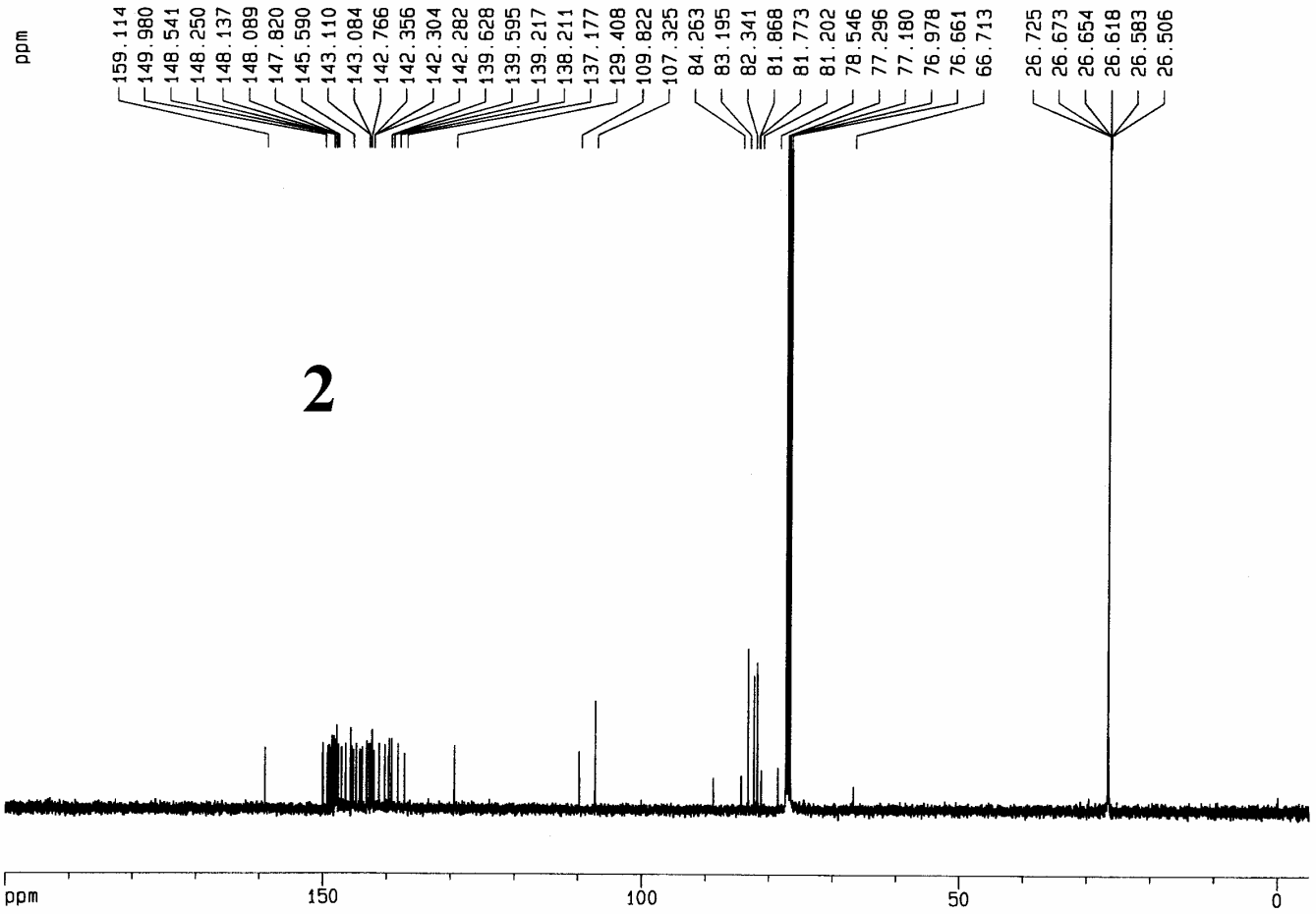

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EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

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1D NMR plot parameters

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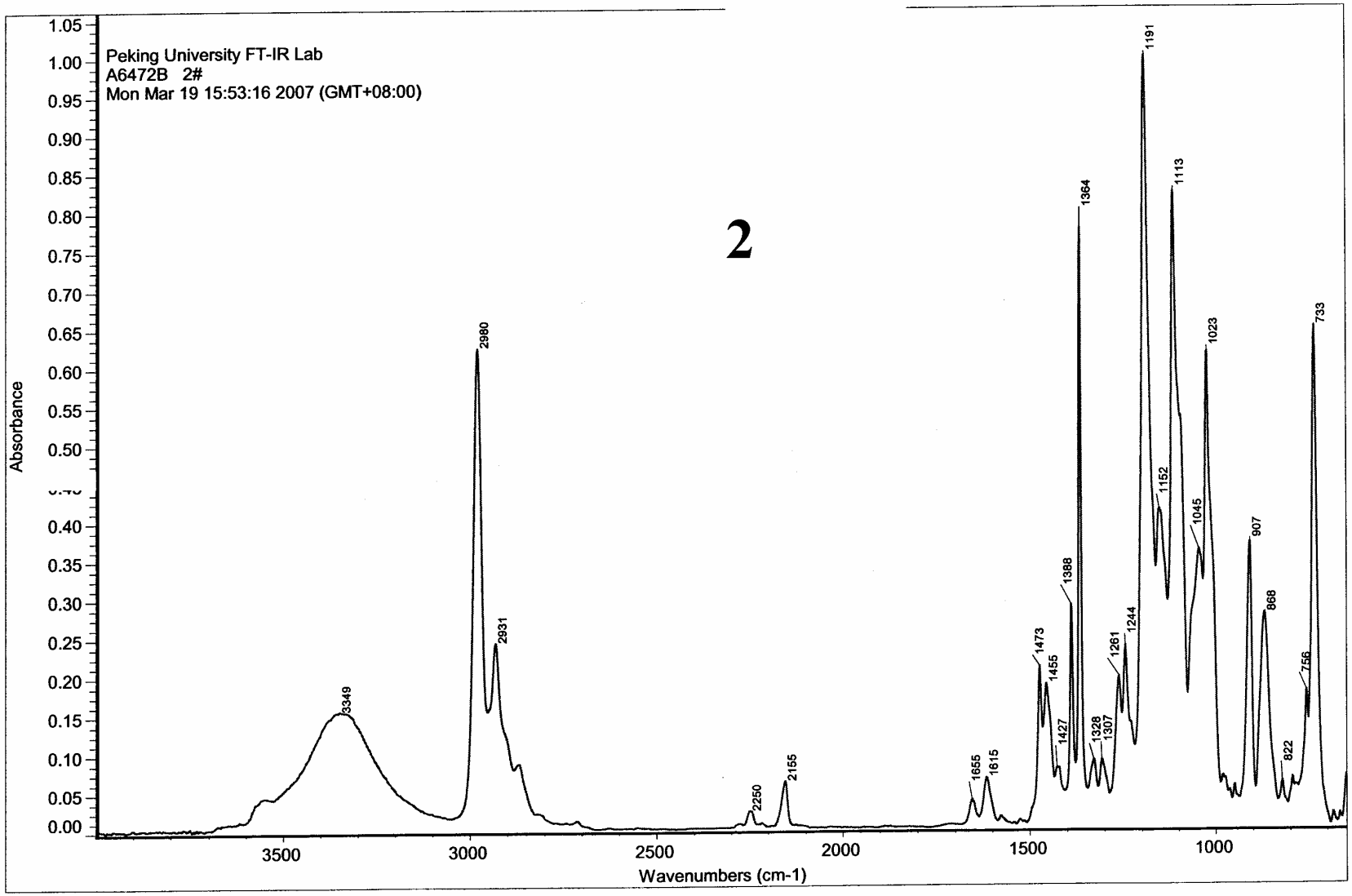

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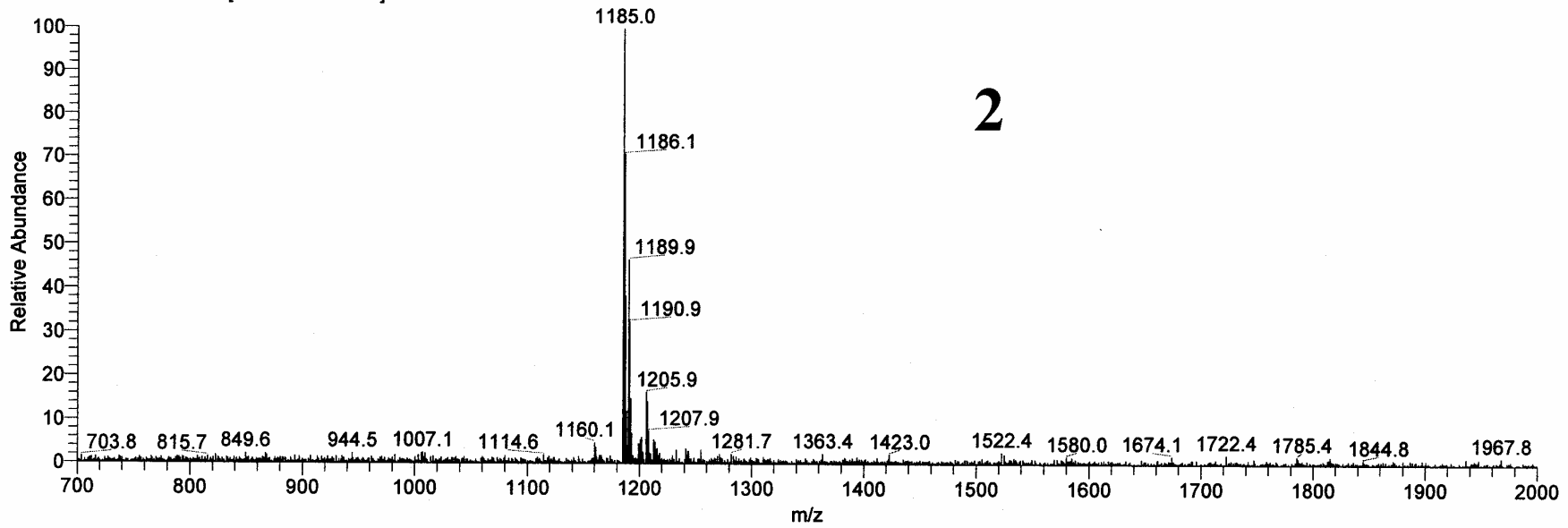

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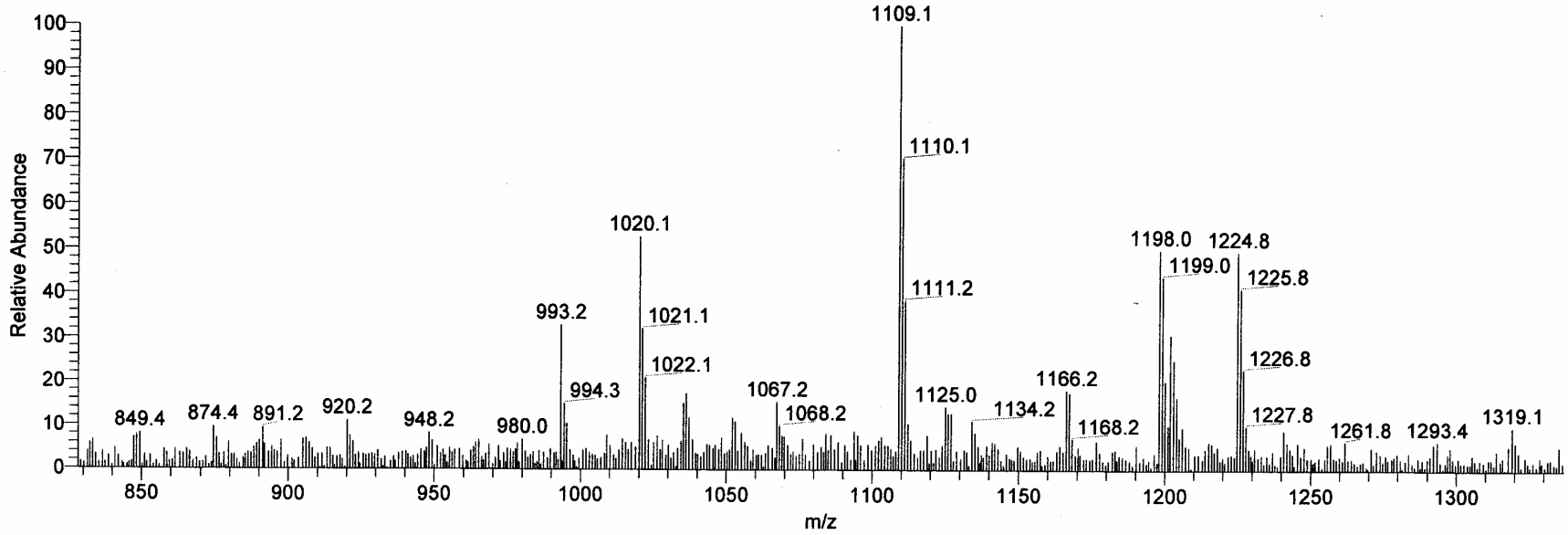

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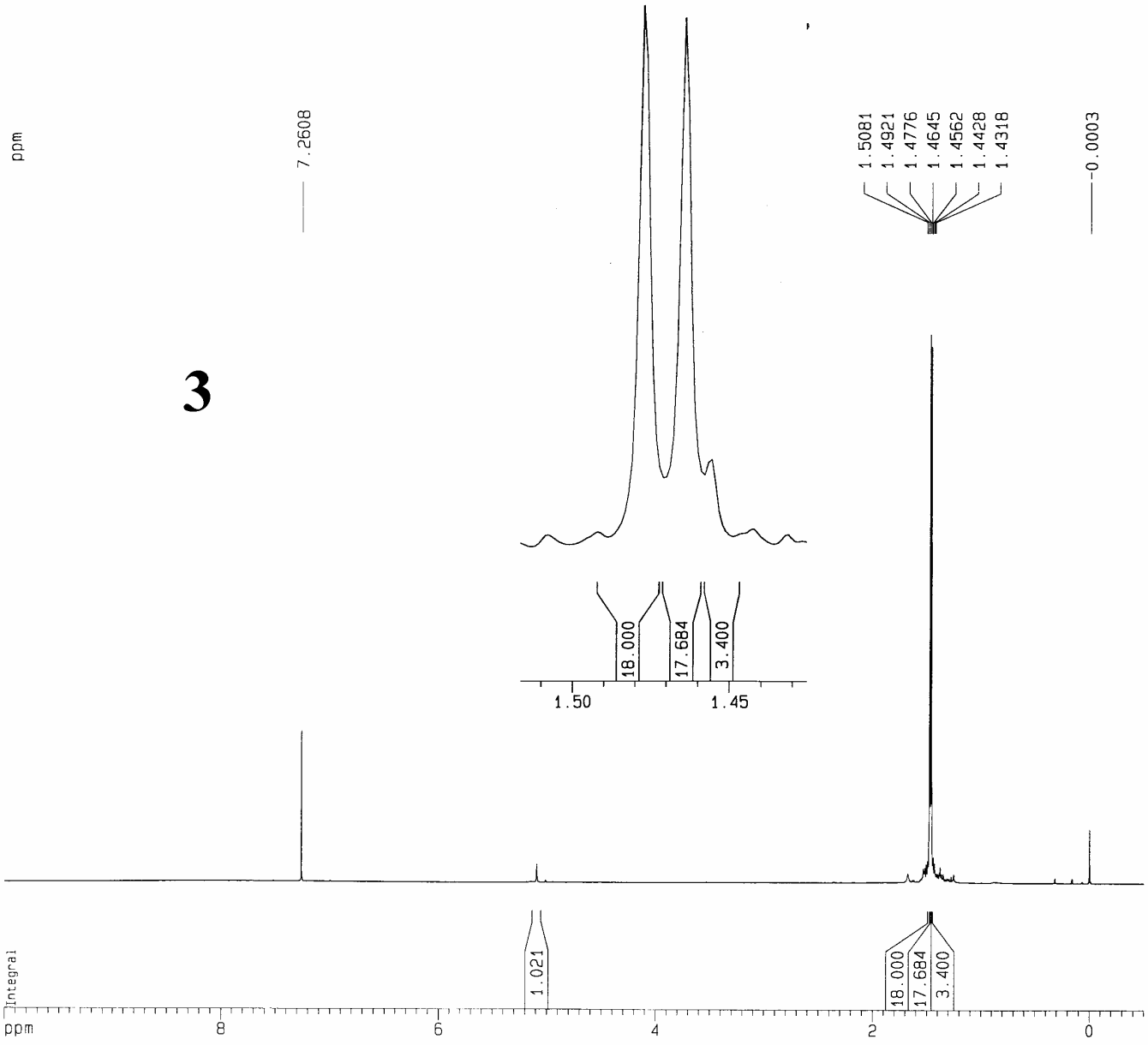

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PROCNO	1

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F2 - Processing parameters

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1D NMR plot parameters

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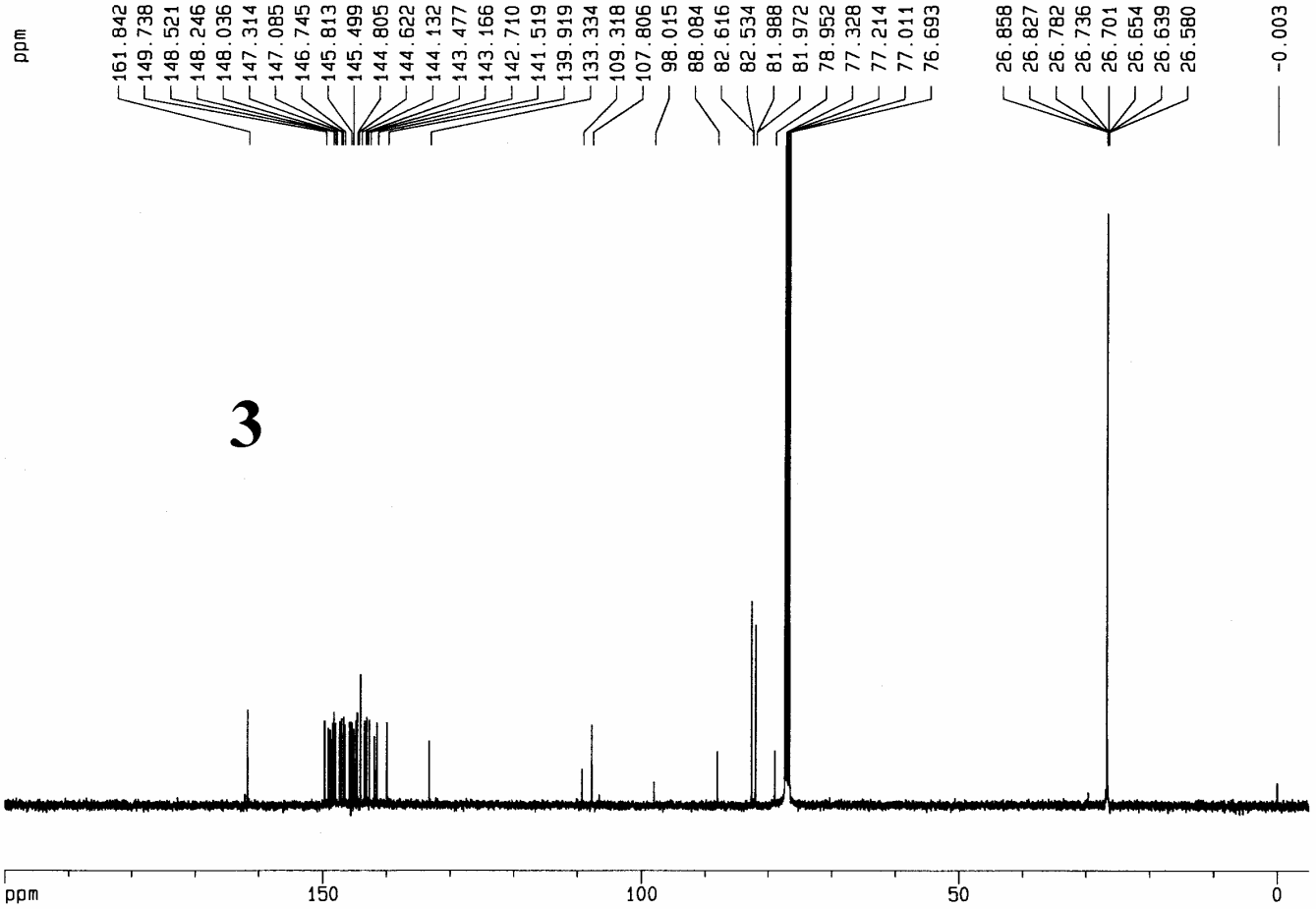

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EXPNO	1
PROCNO	1

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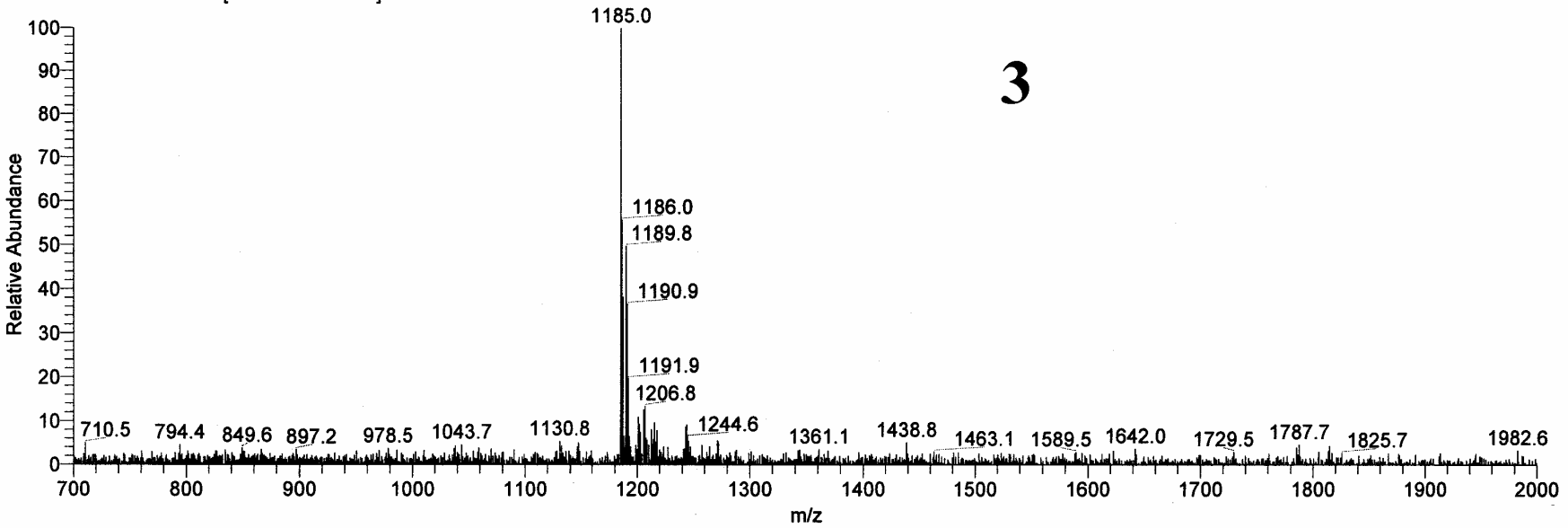

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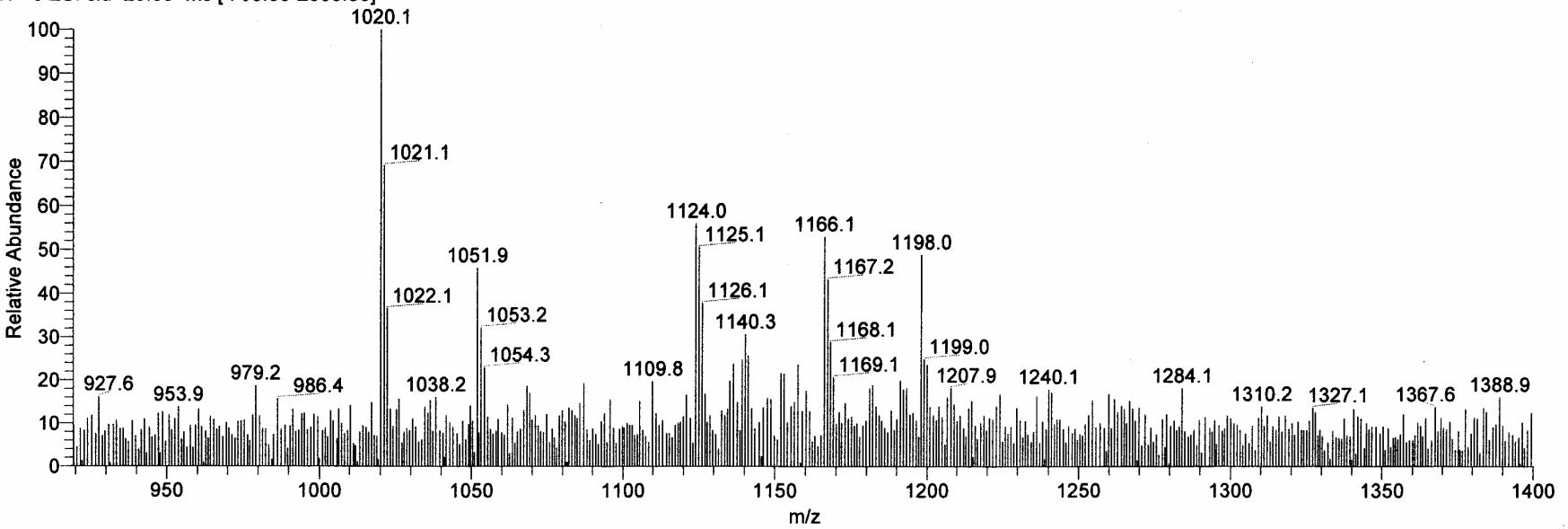

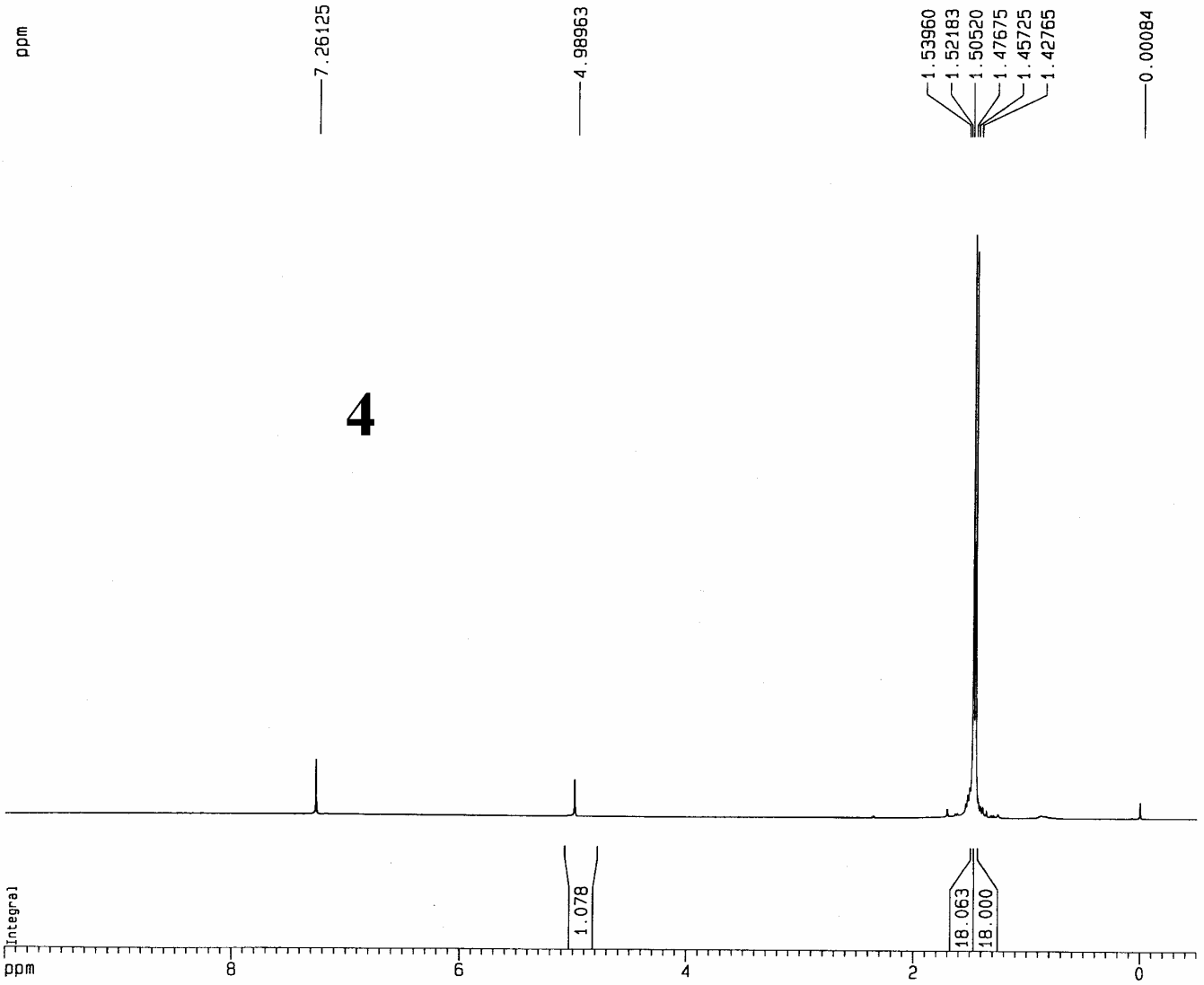

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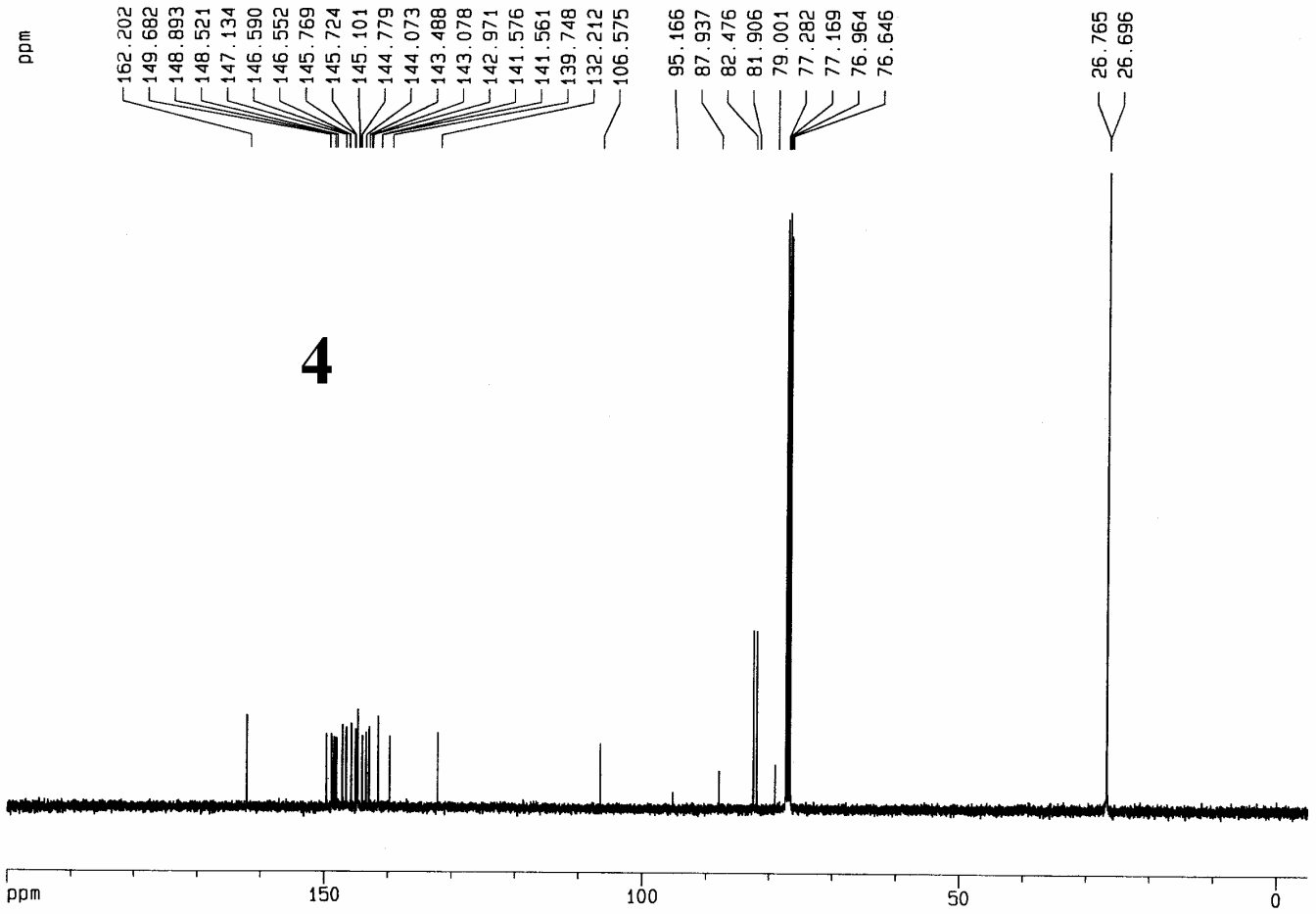

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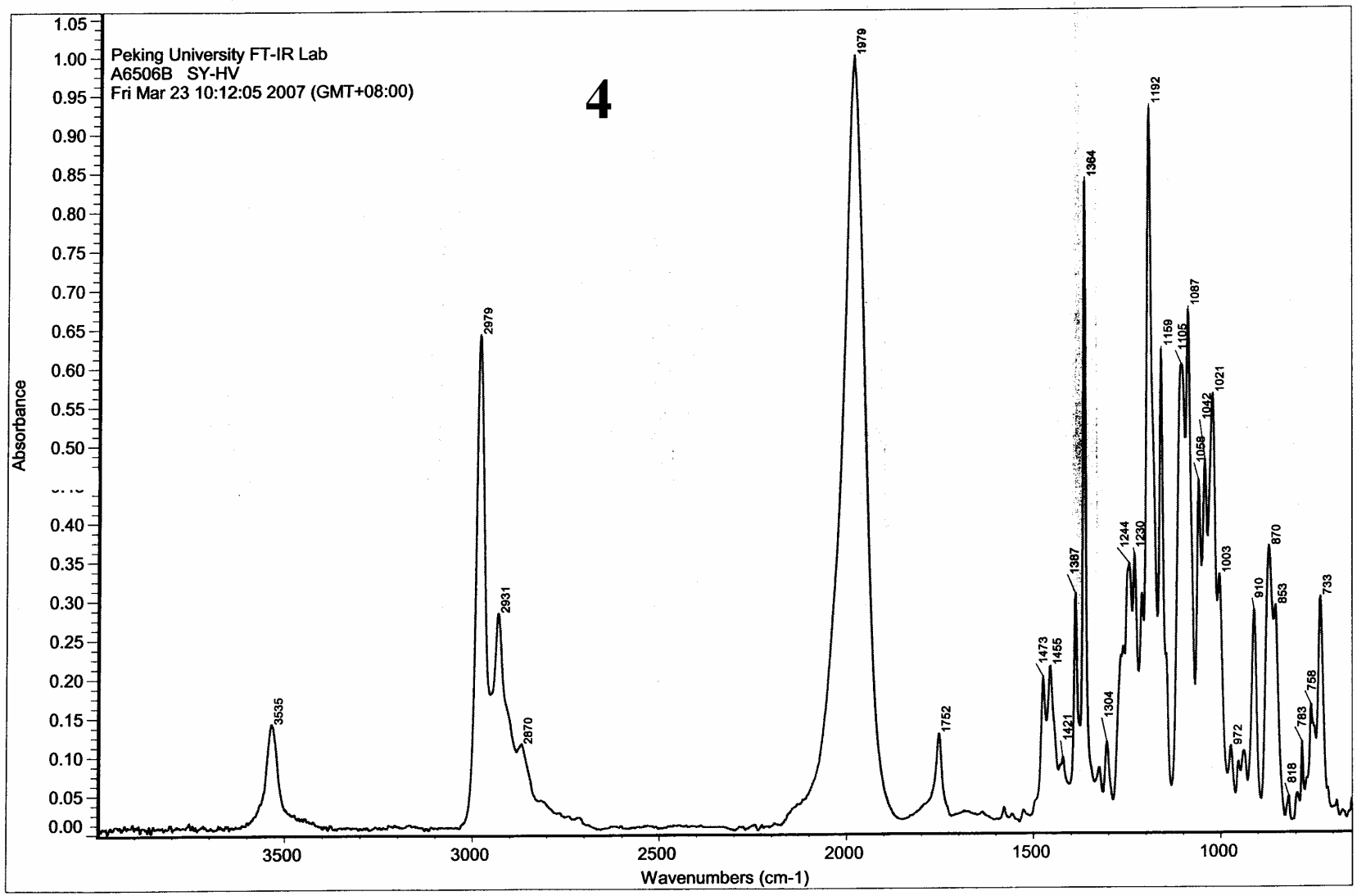
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Fri Mar 23 10:12:05 2007 (GMT+08:00)
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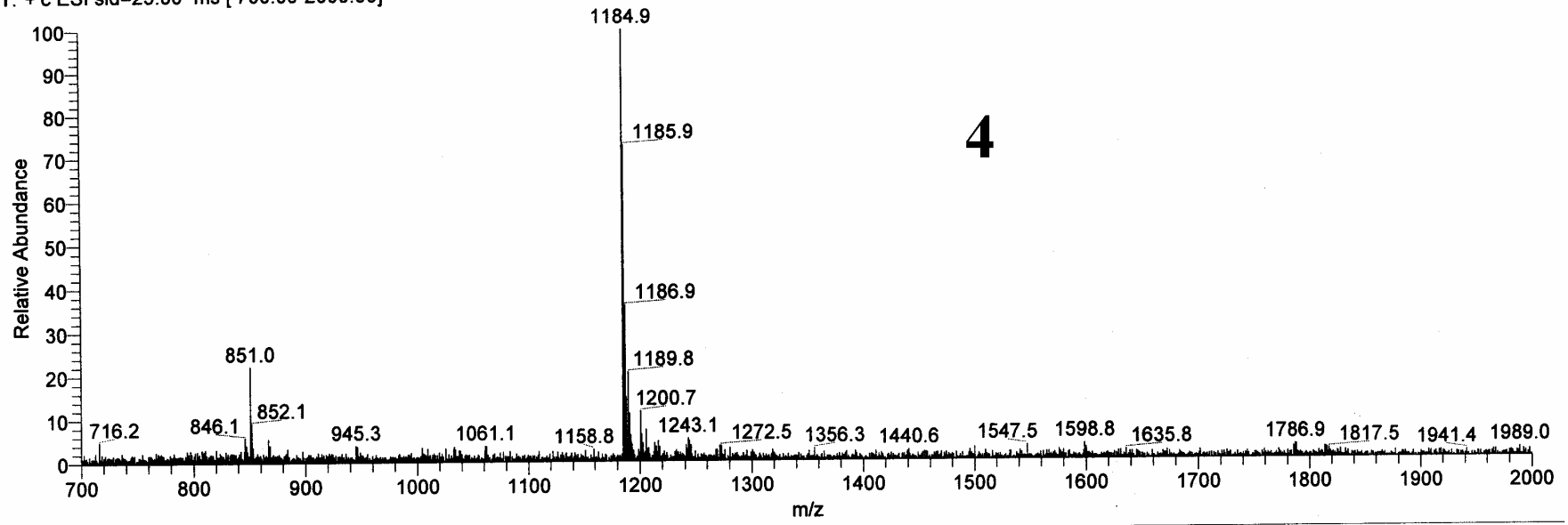

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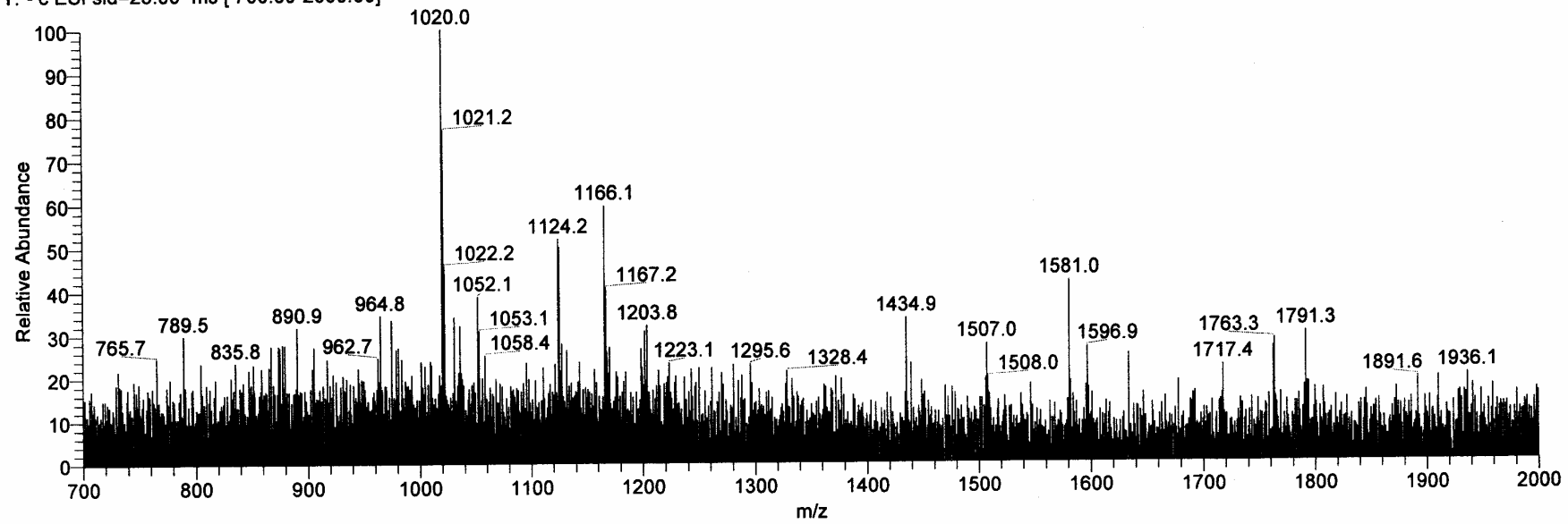

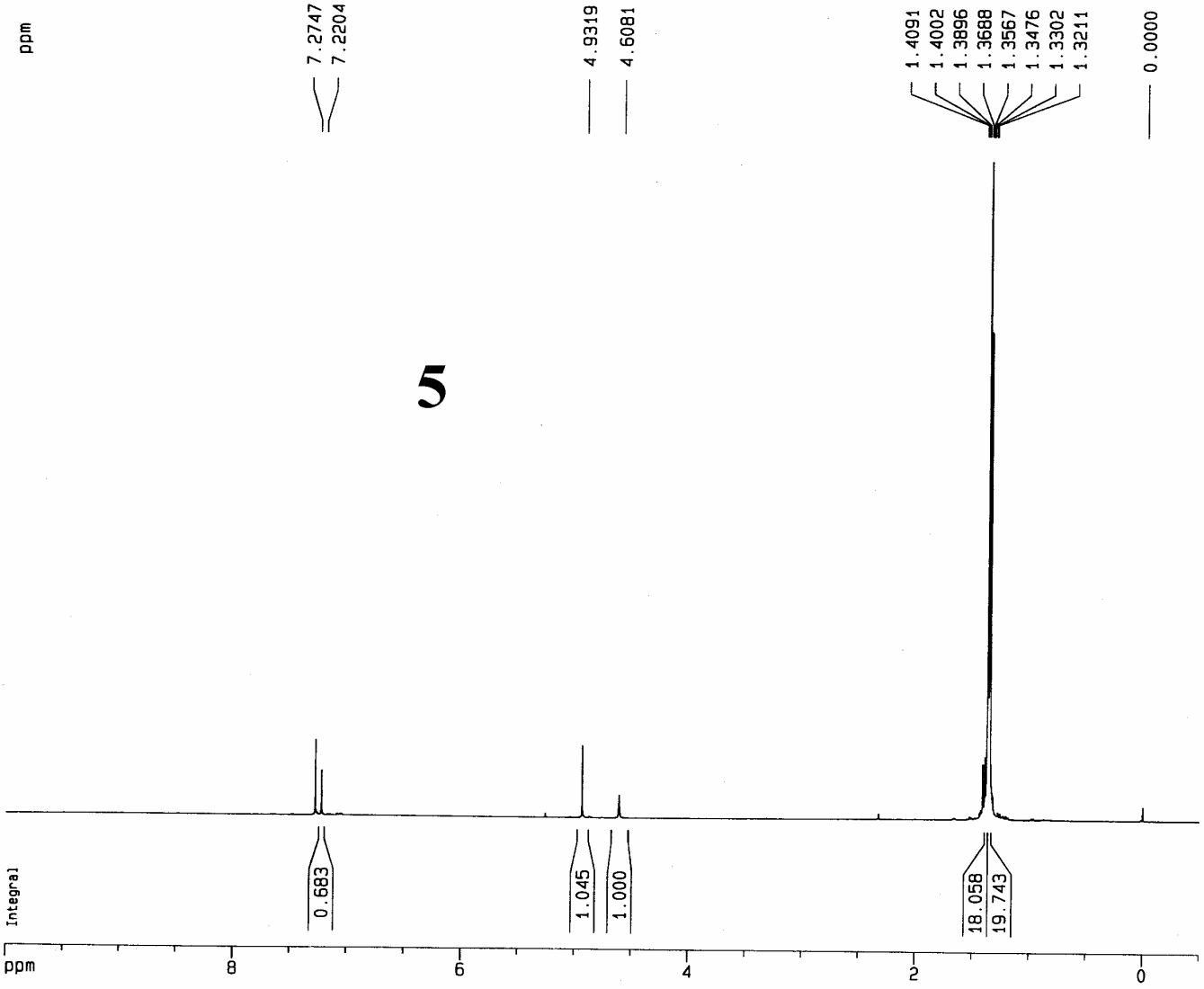

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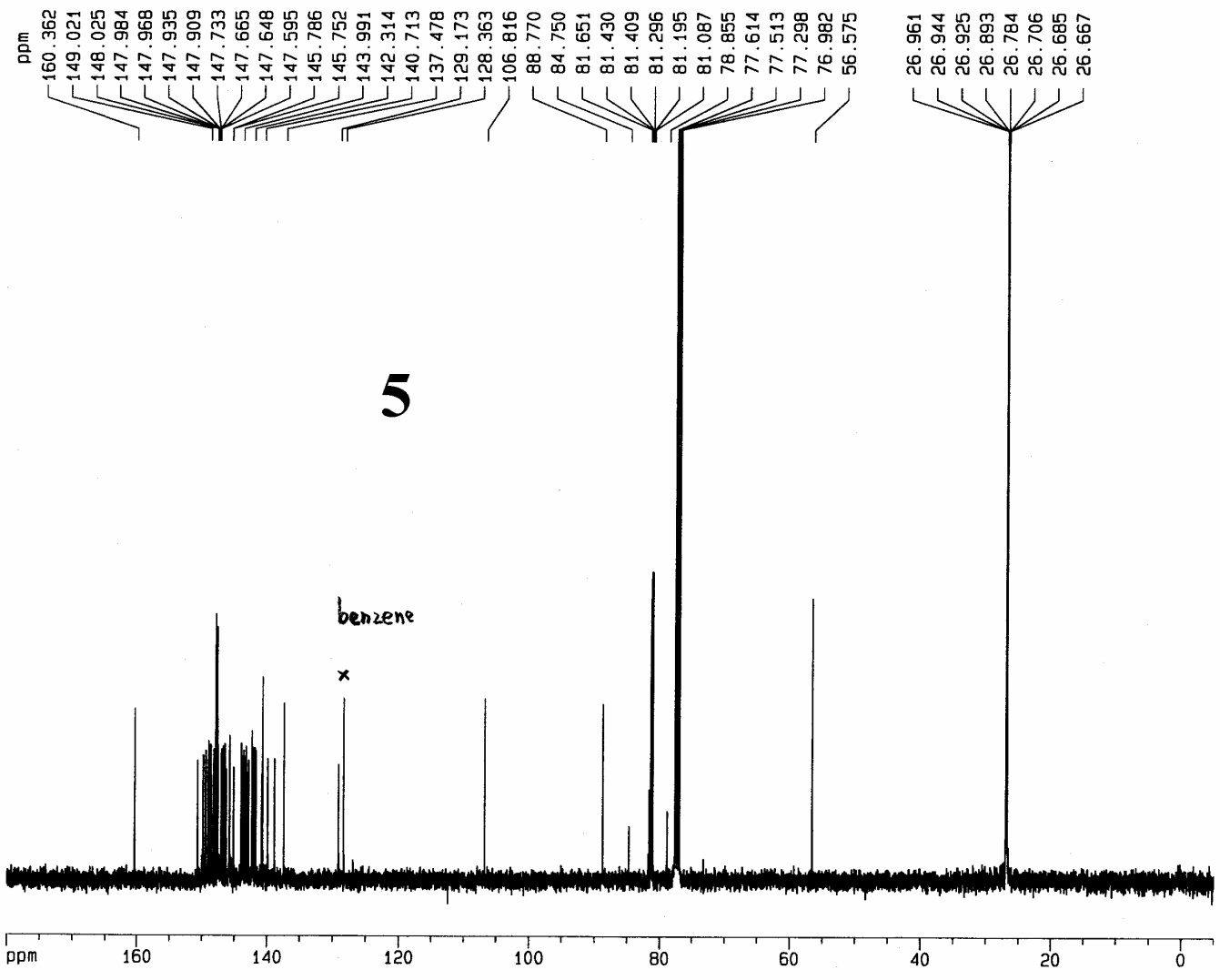

Current Data Parameters

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PROCNO	1

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TE	300.0 K
D12	0.00002000 sec
DL5	22.20 dB
CPDPRG	waltz16
P31	100.00 usec
D1	2.00000000 sec
P1	2.50 usec
DE	25.71 usec
SFO1	100.6240000 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters

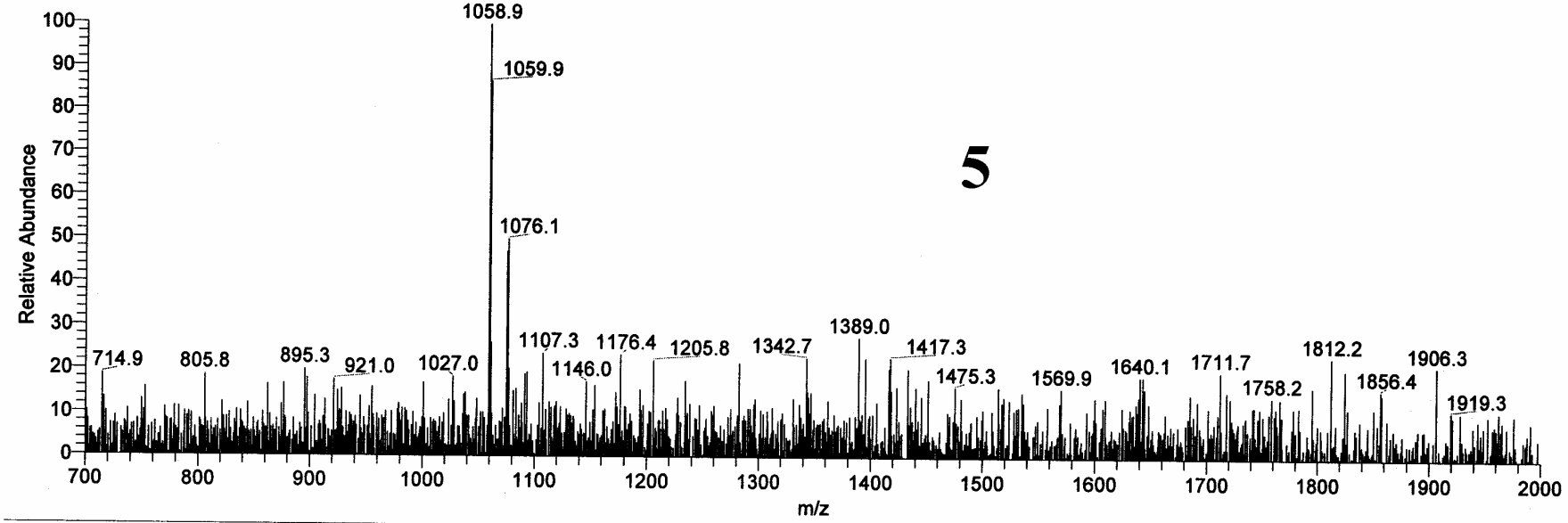
SI	32768
SF	100.6127747 MHz
WDW	EM
SSB	0
LB	0.50 Hz
GB	0
PC	0.30

1D NMR plot parameters

CX	20.00 cm
F1P	180.000 ppm
F1	18110.30 Hz
F2P	-5.000 ppm
F2	-503.07 Hz
PPMCM	9.25000 ppm/cm
HZCM	930.66827 Hz/cm

C:\Xcalibur\...\ZHOU JIANG\Gan2007041015 04/10/2007 05:28:39 PM

Gan2007041015 #12-13 RT: 0.28-0.30 AV: 2 NL: 3.16E7
T: + c ESI sid=25.00 ms [700.00-2000.00]



5

Gan2007041015 #33-37 RT: 0.70-0.81 AV: 5 NL: 7.79E6
T: - c ESI Full ms [700.00-2000.00]