Electronic Supplementary Information

Dinuclear Ni_2-Schiff base complex-catalyzed asymmetric 1,4-addition of β-keto esters to nitroethylene toward γ^2-amino acid synthesis

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Experimental Section

General:

Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. NMR spectra were recorded on JEOL JNM-LA500 spectrometers, operating at 500 MHz for ^{1}H NMR and 125.65 MHz for ^{13}C NMR. Chemical shifts in $CDCl_3$ were reported in the scale relative to $CHCl_3$ (7.26 ppm for ^{1}H NMR) for ^{1}H NMR and $CDCl_3$ (77.0 ppm for ^{13}C NMR) as an internal reference. Column chromatography was performed with silica gel Merck 60 (230-400 mesh ASTM). Optical rotations were measured on a JASCO P-1010 polarimeter. ESI mass spectra were measured on a Waters ZQ4000 spectrometer (for LRMS), and JEOL JMS-T100LC AccuTOF spectrometer (for HRMS). The enantiomeric excess (ee) was determined by HPLC analysis. HPLC was performed on JASCO HPLC systems consisting of the following: pump, PU-2080 plus; detector, UV-2075 plus, measured at 220 and 254 nm; column, DAICEL CHIRALPAK AS-H, AD-H and OD-H ; mobile phase, hexane-2-propanol. Dry ethyl acetate and toluene were purchased from Kanto. β-Keto esters[S1, S2] and nitroethylene[S3] were prepared by following the same procedures as described in literatures.

References:

[S1] C. Palomo, M. Oiarbide, J. M. García, P. Bañuelos, J. M. Odriozola, J. Razkin and A. Linden, *Org. Lett.* 2008, **10**, 2637.

[S2] T. B. Poulsen, L. Bernardi, M. Bell and K. A. Jørgensen, *Angew. Chem., Int. Ed.* 2006, **45**, 6551.

[S3] Y. Chi, L. Guo, N. A. Kopf and S. H. Gellman, *J. Am. Chem. Soc*. 2008, **130**, 5608.

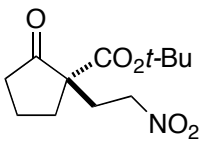
Preparation of Ni_2-Schiff Base 1 Complex:

To a solution of (*R*,*R*)-Schiff base ligand **1** (400 mg, 0.76 mmol) in EtOH (7.6 mL), was added $Ni(OAc)_2 \bullet 4H_2O$ (378 mg, 1.52 mmol), and the mixture was stirred for 12 h under reflux. After cooling down to room temperature, H_2O (1.0 mL) was added to the mixture. The precipitate (Ni_2/Schiff base **1** complex) was collected by filtration. Then, the solid was washed with diethyl ether and EtOH. The solid was dried under reduced pressure at 50 ºC to afford the Ni_2-Schiff base **1** complex (417 mg) as a dark yellow solid. The complex was used for the asymmetric reaction without further purification, and was stored under Ar at room temperature.

General Procedure for Catalytic Asymmetric 1,4-Addition of β-Keto Esters to Nitroethylene Using a Ni_2-Schiff Base 1 Catalyst:

To a stirred solution of the Ni_2/Schiff base **1** catalyst (3.19 mg, 5 μmol) in ethyl acetate (912 μL) was added β-keto ester **2a** (36.8 mg, 0.20 mmol). To the mixture at 40 °C was added 0.24 mmol nitroethylene (stock solution in toluene [nitroethylene] = 2.73 M), and the resulting solution was stirred for 5 h. The mixture was diluted with diethyl ether, and the precipitate was removed by filtration through a pad of celite. After the filtrate was concentrated under reduced pressure, the residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 20/1) to give **3a** (47.7 mg, 92% yield) as a colorless oil.

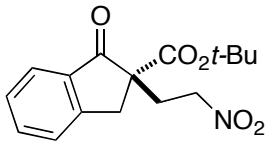
(*S*)-*tert*-butyl 1-(2-nitroethyl)-2-oxocyclopentanecarboxylate (3a):



colorless oil; IR (neat) ν 2977, 1748, 1721, 1555, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (s, 9H), 1.83-1.91 (m, 1H), 1.92-2.12 (m, 2H), 2.23-2.36 (m, 2H), 2.38-2.50 (m, 3H), 4.46 (ddd, *J* = 5.8, 9.2, 15.0 Hz, 1H), 4.69 (ddd, *J* = 6.1, 9.2, 15.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.7, 27.7, 30.4, 34.6, 37.6, 58.2, 71.6, 82.9, 169.7, 214.1; LRMS(ESI): *m/z* 280 $[M+Na]^+$; HRMS calcd. for $C_{12}H_{19}NO_5Na^+$ $[M+Na]^+$: 280.1161, found: 280.1162, $[\alpha]_D^{21.7}$ −15.2 (*c* 2.05, $CHCl_3$); HPLC (DAICEL CHIRALPAK AS-H, hexane/2-propanol = 20/1, flow 1.0 mL/min, detection at 220 nm) t_R 11.3 min (minor)

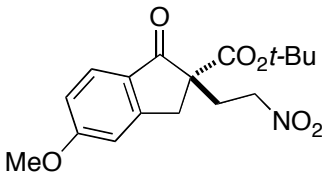
and 12.5 min (major).

(*S*)-*tert*-butyl 2-(2-nitroethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3b):



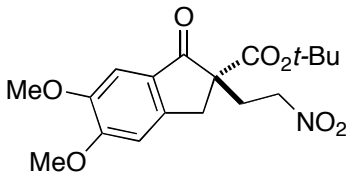
colorless oil; IR (neat) ν 3398, 2494, 1737, 1709, 1553, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (s, 9H), 2.51-2.65 (m, 2H), 3.03 (d, *J* = 17.1 Hz, 1H), 3.63 (d, *J* = 17.1 Hz, 1H), 4.62 (ddd, *J* = 6.1, 9.2, 15.3 Hz, 1H), 4.71 (ddd, *J* = 6.1, 9.2, 15.3 Hz, 1H), 7.42 (dd, *J* = 7.4, 7.8 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.64 (dd, *J* = 7.4, 7.8 Hz, 1H) , 7.76 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 27.7, 31.4, 38.1, 58.5, 71.8, 82.9, 124.9, 126.3, 128.1, 134.6, 135.7, 152.2, 169.3, 201. 5; LRMS(ESI): *m/z* 328 $[M+Na]^+$; HRMS calcd. for $C_{16}H_{19}NO_5Na^+$ $[M+Na]^+$: 328.1161, found: 328.1164; $[\alpha]_D^{21.7}$ +35.7 (*c* 2.37, $CHCl_3$), HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol = 20/1, flow 1.0 mL/min, detection at 254 nm) t_R 11.3 min (minor) and 12.4 min (major).

(*S*)-*tert*-butyl
5-methoxy-2-(2-nitroethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3c):



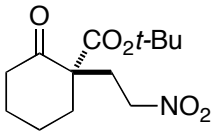
colorless oil; IR (neat) ν 3405, 2929, 1731, 1703, 1600, 1369 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (s, 9H), 2.48-2.63 (m, 2H), 2.95 (d, *J* = 17.4 Hz, 1H), 3.57 (d, *J* = 17.4 Hz, 1H), 3.89 (s, 3H), 4.60 (ddd, *J* = 5.9, 9.2, 15.3 Hz, 1H), 4.66 (ddd, *J* = 6.1, 9.2, 15.3 Hz, 1H), 6.89 (s, *1*H), 6.93 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 28.0, 31.9, 38.2, 56.0, 59.1, 72.1, 83.0, 109.7, 116.4, 126.9, 127.9, 155.6, 166.3, 169.7 , 199.7 ; ESI-MS *m/z* 358 $[M+Na]^+$; HRMS calcd. for $C_{17}H_{21}NO_6Na$ $[M+Na]^+$:358.1267, found 358.1265; $[\alpha]_D^{24.3}$ +64.8 (*c* 1.84, $CHCl_3$); HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol = 20/1, flow 1.0 mL/min, detection at 254 nm) t_R 21.5 min (minor) and 29.3 min (major).

(*S*)-*tert*-butyl
5,6-dimethoxy-2-(2-nitroethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3d):



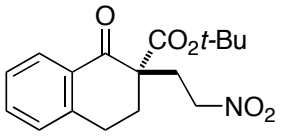
colorless oil; IR (neat) ν 2977, 1730, 1698, 1554, 1369 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (s, 9H), 2.50-2.64 (m, 2H), 2.92 (d, *J* = 17.0 Hz, 1H), 3.52 (d, *J* = 17.0 Hz, 1H), 3.90 (s, 3H), 3.97 (s, 3H), 4.55-4.63 (m, 1H), 4.63-4.72 (m, 1H), 6.87 (s, 1H), 7.15 (s, 1H),; ^{13}C NMR ($CDCl_3$) δ 27.7, 31.7, 37.8, 56.1, 56.3, 58.9, 71.9, 82.7, 105.0, 107.1, 127.3, 147.9, 150.0, 156.3, 169.6, 199.9; ESI-MS *m/z* 388 $[M+Na]^+$; HRMS calcd. for $C_{18}H_{23}NO_7Na$ $[M+Na]^+$: 388.1372, found 388.1370; $[\alpha]_D^{24.1}$ +50.1 (*c* 3.20, $CHCl_3$); HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol = 20/1, flow 1.0 mL/min, detection at 254 nm) t_R 32.5 min (minor) and 46.0 min (major).

(*S*)-*tert*-butyl 1-(2-nitroethyl)-2-oxocyclohexanecarboxylate (3e):



colorless oil; ^1H NMR ($CDCl_3$) δ 1.48 (s, 9H), 1.55-1.72 (m, 3H), 1.73-1.84 (m, 1H), 2.00-2.12 (m, 1H), 2.26 (ddd, *J* = 5.9, 9.5, 14.4 Hz ,1H), 2.39-2.63 (m, 4H), 4.34 (ddd, *J* = 5.5, 9.5, 14.9 Hz ,1H), 4.62 (ddd, *J* = 5.9, 9.5, 14.9 Hz ,1H); ^{13}C NMR ($CDCl_3$) δ 22.2, 27.1, 27.6, 31.7, 36.8, 40.5, 59.6, 71.5, 83.2, 169.8, 207.0; ESI-MS *m/z* 294 $[M+Na]^+$; HRMS calcd. for $C_{13}H_{21}NO_5Na$ $[M+Na]^+$: 294.1317, found 294.1322; $[\alpha]_D^{23.2}$ –97.1 (*c* 0.92, $CHCl_3$); HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol = 99/1, flow 1.0 mL/min, detection at 220 nm) t_R 14.5 min (minor) and 16.9 min (major).

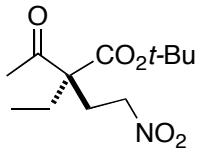
(*S*)-*tert*-butyl 2-(2-nitroethyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3f):



colorless oil; IR (neat) ν 2978, 1726, 1688, 1555, 1369 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (s, 9H), 2.10 (ddd, *J* = 5.0, 11.0, 16.0, 1H), 2.47-2.56 (m, 2H), 2.56-2.66 (m, 1H), 2.90-3.02 (m, 1H), 3.03-3.15 (m, 1H), 4.54 (ddd, *J* = 5.5, 10.0, 15.0 Hz ,1H), 4.81 (ddd, *J* = 6.0, 9.5, 15.0 Hz ,1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.32 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.48 (dd, *J* = 7.6, 7.6 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.1, 27.8, 31.7, 32.8, 56.5, 72.2, 83.5, 127.1, 127.9, 128.8, 132.3, 133.8, 142.4, 170.2 , 195.4; ESI-MS *m/z* 342 $[M+Na]^+$; HRMS calcd. for $C_{17}H_{21}NO_5Na$ $[M+Na]^+$: 342.1317, found 342.1313; $[\alpha]_D^{20.8}$ –63.6 (*c* 1.09, $CHCl_3$); HPLC (DAICEL CHIRALPAK AD-H,

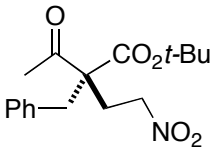
hexane/2-propanol = 20/1, flow 1.0 mL/min, detection at 254 nm) t_R 10.1 min (major) and 11.3 min (minor).

(*S*)-*tert*-butyl 2-acetyl-2-ethyl-4-nitrobutanoate (3g):



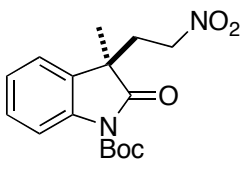
colorless oil; IR (neat) ν 2977, 1710, 1557, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, *J* = 7.8 Hz, 3H), 1.47 (s, 9H), 0.84 (q, *J* = 7.8 Hz, 2H), 2.17 (s, 3H), 2.42 (ddd, *J* = 6.5, 10.0, 15.5 Hz, 1H), 2.54 (ddd, *J* = 5.5, 9.5, 15.5 Hz, 1H), 4.27-4.45 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 8.1, 25.8, 26.5, 27.8, 28.2, 62.6, 71.8, 83.2, 170.2, 204.3; ESI-MS *m/z* 282 $[M+Na]^+$; HRMS calcd. for $C_{12}H_{21}NO_5Na$ $[M+Na]^+$: 282.1317, found 282.1313; $[\alpha]_D^{23.6}$ –23.0 (*c* 0.77, $CHCl_3$); HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol = 99/1, flow 0.5 mL/min, detection at 220 nm) t_R 21.8 min (minor) and 23.0 min (major).

(*S*)-*tert*-butyl 2-acetyl-2-benzyl-4-nitrobutanoate (3h):



colorless oil; IR (neat) ν 2979, 1710, 1556, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (s, 9H), 2.23 (s, 3H), 2.32-2.50 (m, 2H), 3.19 (d, *J* = 14.6 Hz, 1H), 3.22 (d, *J* = 14.6 Hz, 1H), 4.25-4.45 (m, 2H), 7.09 (brd, *J* = 6.7 Hz, 2H), 7.24-7.31 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 27.0, 27.5, 29.1, 38.9, 63.1, 71.4, 83.4, 100.3, 127.2, 128.4, 129.6, 134.6, 169.5, 203.7 ; ESI-MS *m/z* 344 $[M+Na]^+$; HRMS calcd. for $C_{17}H_{23}NO_5Na$ $[M+Na]^+$: 344.1474, found 344.1466; $[\alpha]_D^{24.4}$ -3.6 (*c* 0.645, $CHCl_3$); HPLC (DAICEL CHIRALPAK OD-H, hexane/2-propanol = 99/1, flow 1.0 mL/min, detection at 220 nm) t_R 26.6 min (minor) and 40.1 min (major).

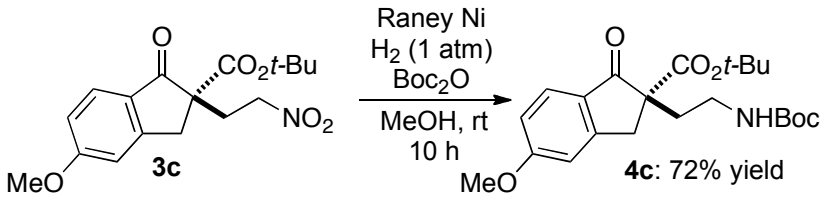
(*R*)-*tert*-butyl 3-methyl-3-(2-nitroethyl)-2-oxoindoline-1-carboxylate (3i):



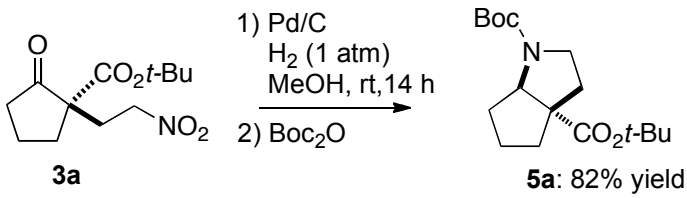
colorless oil; IR (neat) ν 2979, 1791, 1762, 1732, 1556, 1349 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (s, 3H), 1.65 (s, 9H), 2.55 (ddd, *J* = 5.8, 10.0, 15.8 Hz, 1H), 2.66 (ddd, *J* = 5.8, 10.0, 15.8 Hz, 1H), 4.12 (ddd, *J* = 5.8, 10.0, 15.8 Hz, 1H), 4.29 (ddd, *J* = 5.8, 10.0, 15.8 Hz, 1H), 7.18-7.24 (m, 2H), 7.30-7.38 (m, 1H), 7.86 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) 24.6, 28.1, 35.0, 46.5, 71.1, 84.9, 115.4, 122.4, 125.0, 129.0, 130.5, 138.8, 148.9, 177.5; ESI-MS *m/z* 343 $[M+Na]^+$; HRMS calcd. for $C_{18}H_{20}NO_5Na$ $[M+Na]^+$:343.1270, found 343.1267; $[\alpha]_D^{21.4}$ –20.2 (*c* 1.28, $CHCl_3$); HPLC (DAICEL CHIRALPAK AD-H,

hexane/2-propanol = 9/1, flow 1.0 mL/min, detection at 254 nm) t_R 5.0 min (major) and 5.4 min (minor).

Tranformation of 1,4-Adducts (Scheme 1):



(*S*)-*tert*-butyl 2-(2-((*tert*-butoxycarbonyl)amino)ethyl)-5-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (4c): To a solution of **3c** (41.5 mg, 0.124 mmol) in methanol (0.62 mL) were added Raney-Ni (10 mg) and Boc_2O (81.2 mg, 0.372 mmol). The reaction mixture was stirred at room temperature under hydrogen atmosphere (1 atm) for 10 h. The mixture was filtered through a pad of celite, and the Raney-Ni and the celite were washed with dichloromethane. The combined organic solvents were evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 5/1) to give **4c** in 72% yield as a colorless solid (36.3 mg, 0.090 mmol); IR (neat) ν 2977, 1704, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (s, 9H), 1.37 (s, 9H), 1.94-2.06 (m, 1H), 2.18-2.32 (m, 1 H), 3.00-3.27 (m, 3H), 3.57 (d, *J* = 17.0 Hz, 1H), 3.87 (s, 3 H), 4.67 (brs, 1H), 6.84-6.93 (m, 2 H), 7.65 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 28.0, 28.6, 34.6, 36.8, 37.2, 55.9, 60.5, 79.4, 82.1, 109.6, 116.1, 126.6, 128.4, 155.9, 156.4, 166.0, 170.3; ESI-MS *m/z* 428 $[M+Na]^+$; HRMS calcd. for $C_{22}H_{31}NO_6Na$ $[M+Na]^+$:428.2049, found 428.2050; $[\alpha]_D^{23.4}$ +75.6 (*c* 2.29, $CHCl_3$)

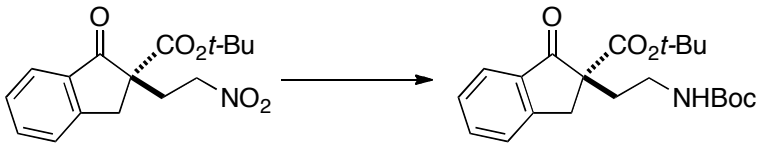


(3a*S*,6a*R*)-di-*tert*-butyl hexahydrocyclopenta[*b*]pyrrole-1,3a(2*H*)-dicarboxylate (5a): To a suspension of **3a** (25.8 mg, 0.10 mmol) in methanol (0.5 mL) was added Pd/C (8.2 mg) at room temperature. The reaction mixture was stirred under hydrogen atmosphere (1 atm) for 14 h at room temperature. Then, Boc_2O (32.7 mg, 0.15 mmol) was added and the mixture was stirred for another 1.5 h at room temperature. Then the

mixture was filtered through a pad of celite and washed with dichloromethane. The filtrate was concentrated under reduced pressure and purified by silica gel column chromatography (hexane/ethyl acetate = 20/1) to give **5a** in 83% yield as a colorless oil (26.0 mg, 0.083 mmol) ; IR (neat) ν 2975, 1723, 1698 cm^{-1}; ^1H NMR ($CDCl_3$ at 45 °C) δ 1.44 (s, 9H), 1.45 (s, 9H), 1.59-1.85 (m, 5H), 1.90-2.02 (m, 1H), 2.03-2.14 (m, 1H), 2.25 (brm, 1H), 3.28-3.40 (m, 1H), 3.56 (brm, 1H), 4.25 (brm, 1H); ^{13}C NMR ($CDCl_3$) δ 25.4, 28.2, 28.8, 29.9, 34.8, 37.1, 46.5, 46.7, 66.5, 79.4, 80.9, 154.4, 175.5; ESI-MS *m/z* 334 $[M+Na]^+$; HRMS calcd. for $C_{17}H_{29}NO_4Na$ $[M+Na]^+$:334.1994, found 334.1996; $[\alpha]_D^{23.1}$ –61.1 (*c* 1.29, $CHCl_3$)

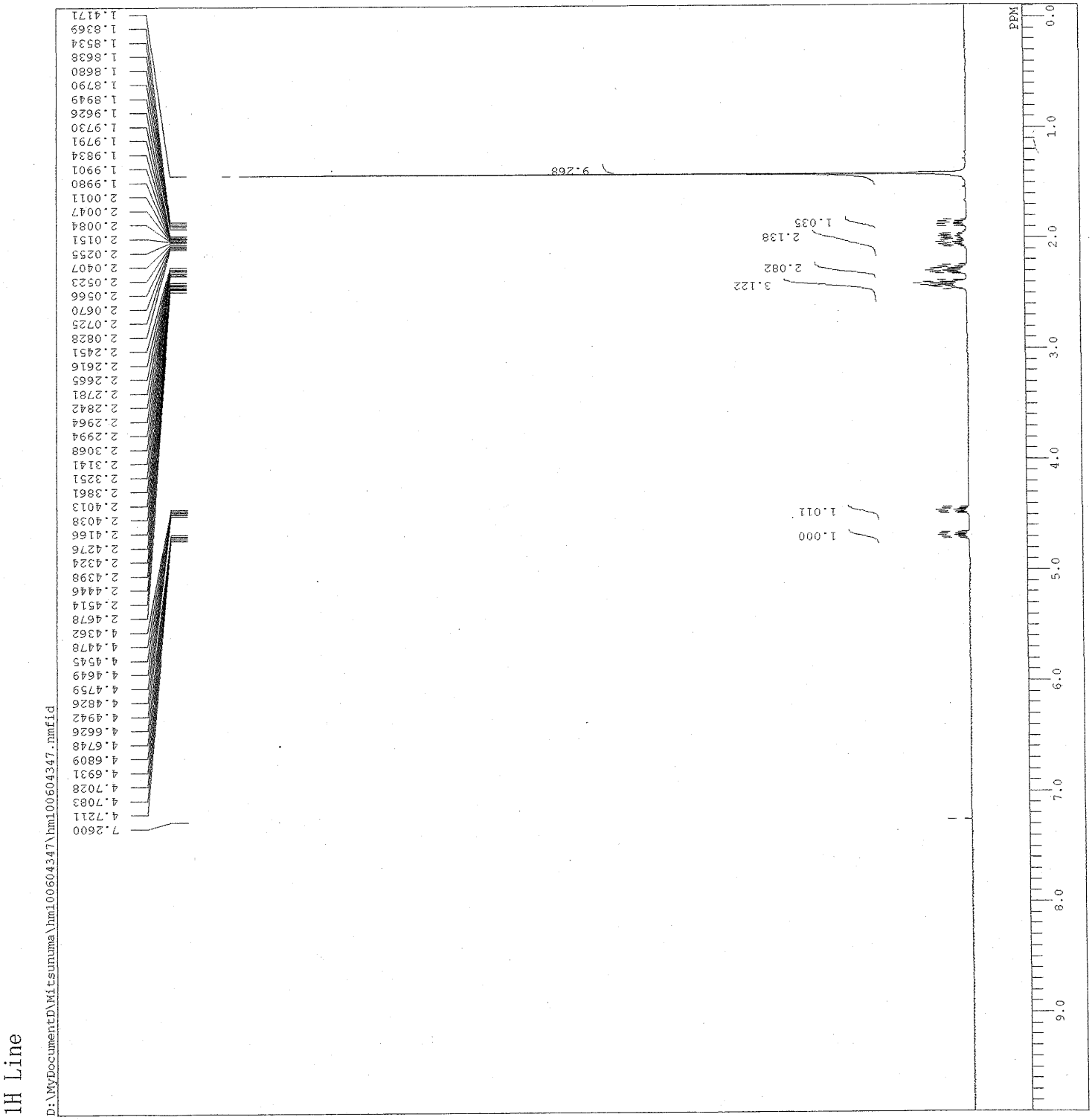
Determination of Absolute Configuration:

The absolute configuration of **3b** was determined by comparing with the reported data[S4] after conversion **2b** into corresponding γ^2-amino ester **4b** (in a similar conditions as Scheme 1). Those of others were assigned by analogy.



3b **4b** (known compound)

[S4] T. A. Moss, B. Alonso, D. R. Fenwick and D. J. Dixon, *Angew. Chem., Int. Ed.,* 2010, **49**, 568.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OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 12
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.90 usec
IRNUC 1H
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SLVNT CDCL3
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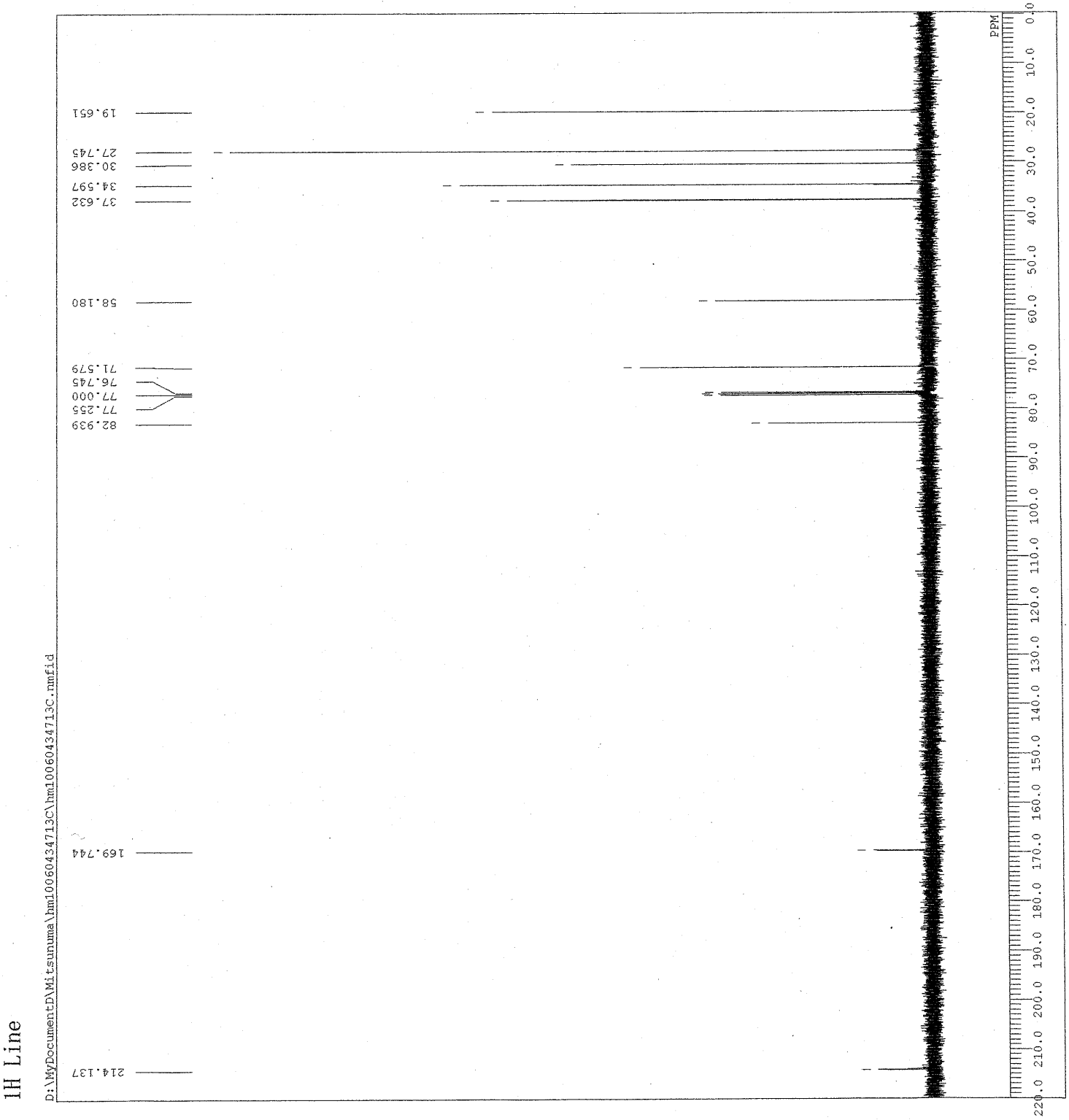
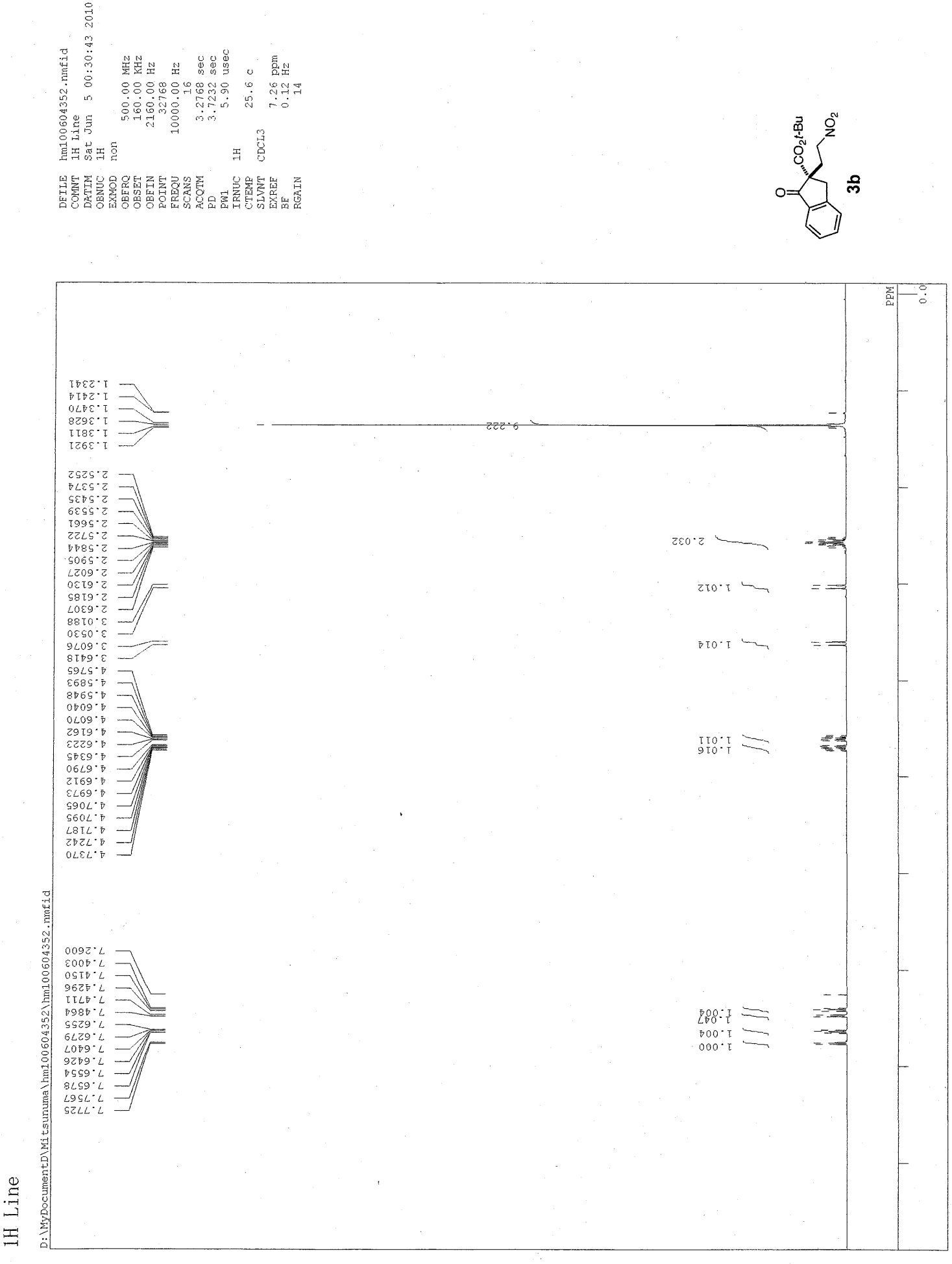
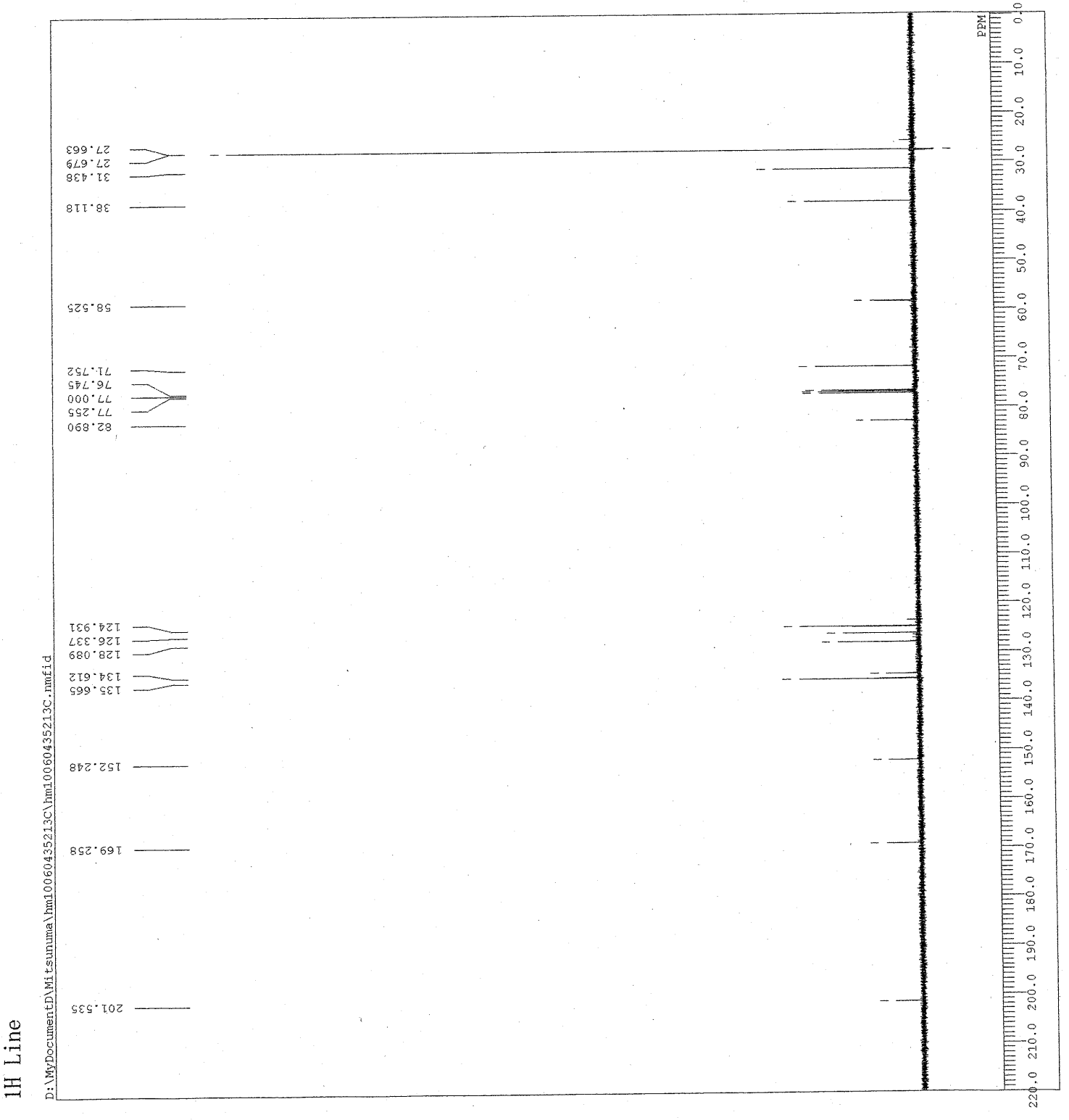
9.268
3.122
2.082
2.138
1.035
1.011
1.000
PPM
3a


1H Line
D:\MyDocumentD\Mitsunuma\hm1006043471 3C\hm1006043471 3C.nmfid
DFILE hm1006043471 3C.nmfid
COMNT 1H Line
DATIM Fri Jun 4 22:49:01 2010
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 63
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 5.12 usec
IRNUC 1H
CTEMP 27.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.01 Hz
RGAIN 30
19.651
27.745
30.386
34.597
37.632
58.180
71.579
76.745
77.000
77.255
82.939
169.744
214.137
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
210.0
220.0
O
CO2t-Bu
NO2
3a


DFILE hm100604352.nmfid
COMNT 1H Line
DATIM Sat Jun 5 00:30:43 2010
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.90 usec
IRNUC 1H
CTEMP 25.6 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 14
CO2t-Bu
NO2
O
3b
1H Line
D:\MyDocument\Mitsunuma\hm100604352\hm100604352.nmfid
PPM
0.0

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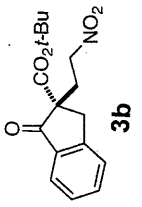
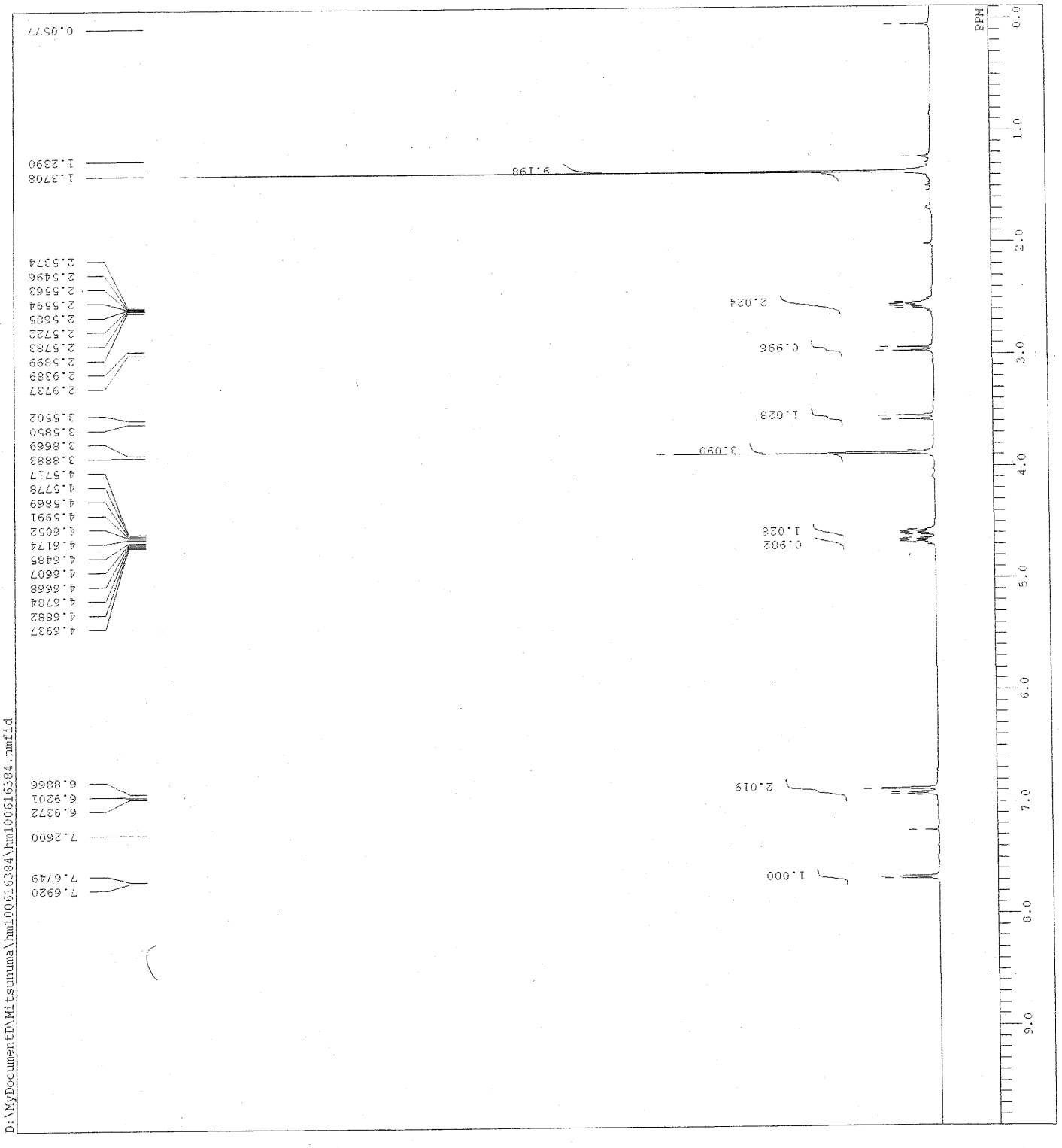
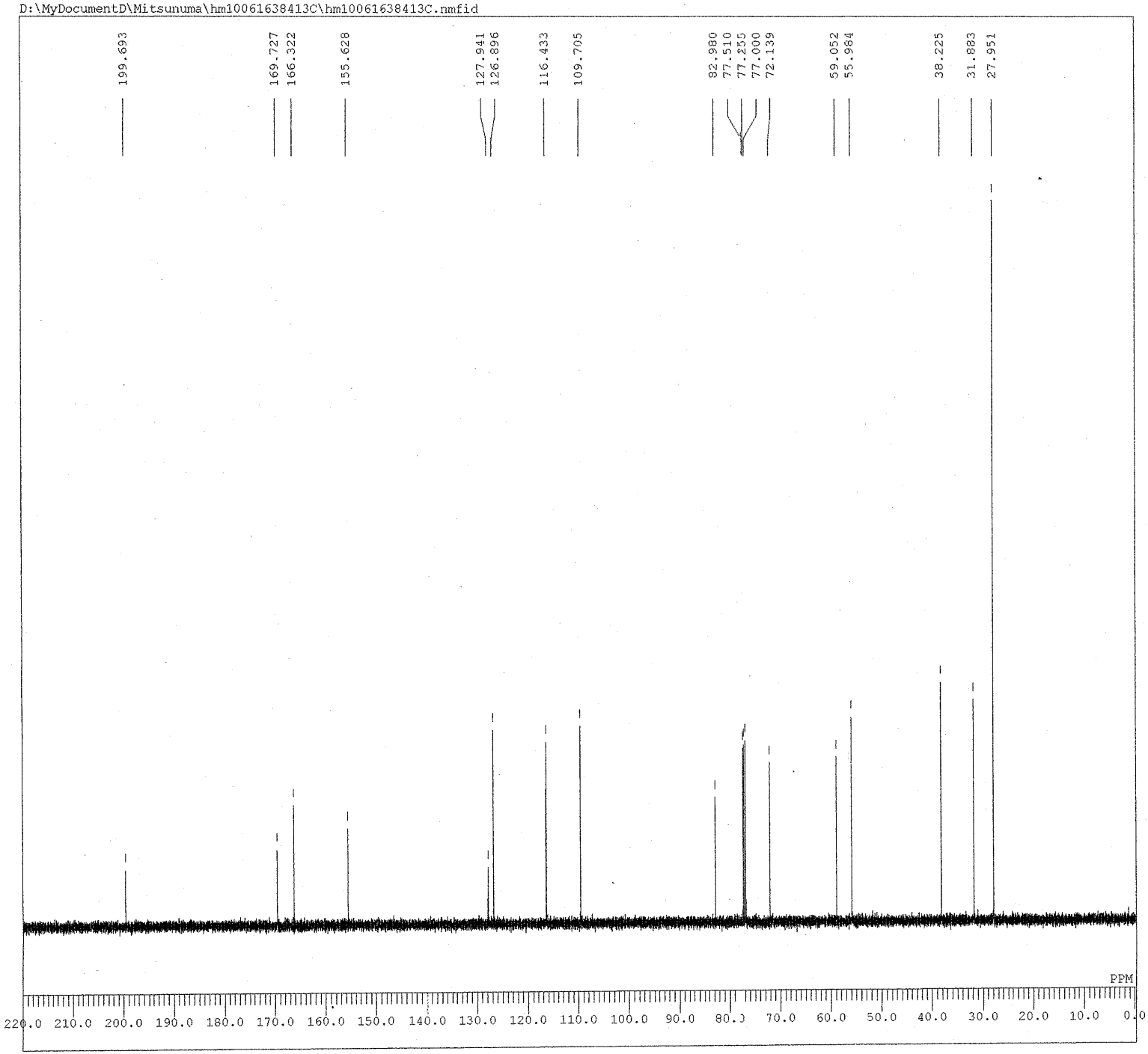
COMNT  1H Line
DATIM  Sat Jun  5 00:37:22 2010
OBNUC  13C
EXMOD  bcm
OBFRQ      125.65 MHz
OBSET      120.00 KHz
OBFIN     7958.00 Hz
POINT       32768
FREQU    33898.30 Hz
SCANS         104
ACQTM      0.9667 sec
PD         2.0333 sec
PW1           5.12 usec
IRNUC  1H
CTEMP     27.0 c
SLVNT  CDCL3
EXREF     77.00 ppm
BF         0.01 Hz
RGAIN        30
```



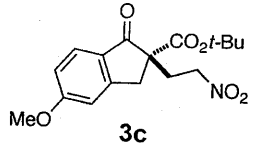

1H Line
D:\MyDocumentD\Mitsunuma\hm1006163841hm1006163841.nmfid
DFILE hm1006163841.nmfid
COMNT 1H Line
DATIM Wed Jun 16 02:24:59 2010
ONUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 12
ACQTM 3.2768 sec
PD 3.7232 sec
FW1 5.90 usec
IFNUC 1H
CTEMP 28.1 c
SLVNT CDCL3
EXREF 7.26 ppm
EP 1.00 Hz
RGAIN 15
0.0577
1.2390
1.3708
2.5374
2.5496
2.5563
2.5594
2.5685
2.5722
2.5783
2.5899
2.9389
2.9737
3.5502
3.5850
3.8669
3.8883
4.5717
4.5778
4.5869
4.5991
4.6052
4.6174
4.6485
4.6607
4.6668
4.6784
4.6882
4.6937
6.8866
6.9201
6.9372
7.2600
7.6749
7.6920
9.198
2.024
0.996
1.028
3.090
0.982
1.028
2.019
1.000
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
CO2t-Bu
NO2
O
MeO
3c

1H Line

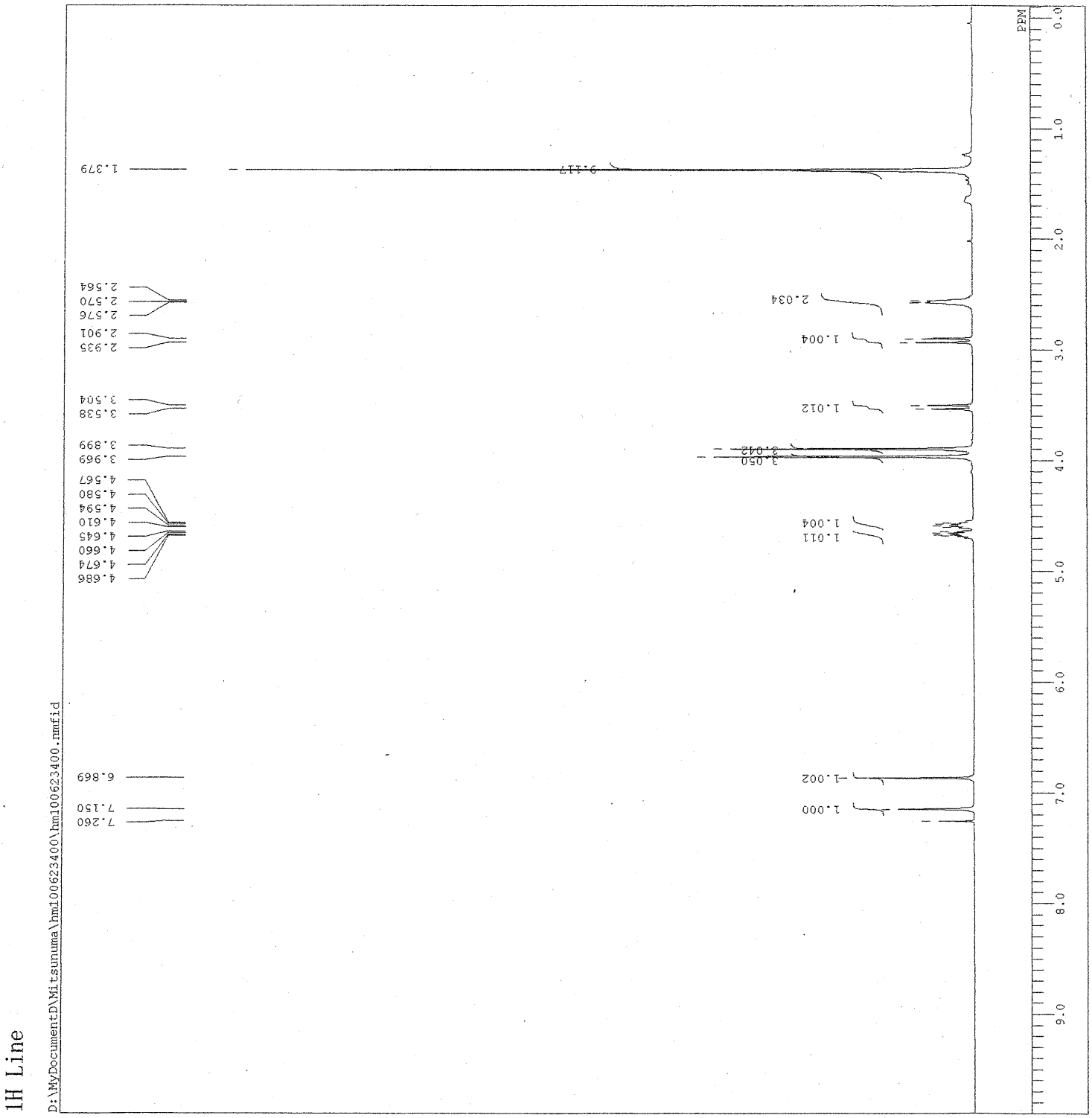
D:\MyDocumentD\Mitsunuma\hm10061638413C\hm10061638413C.nmfid

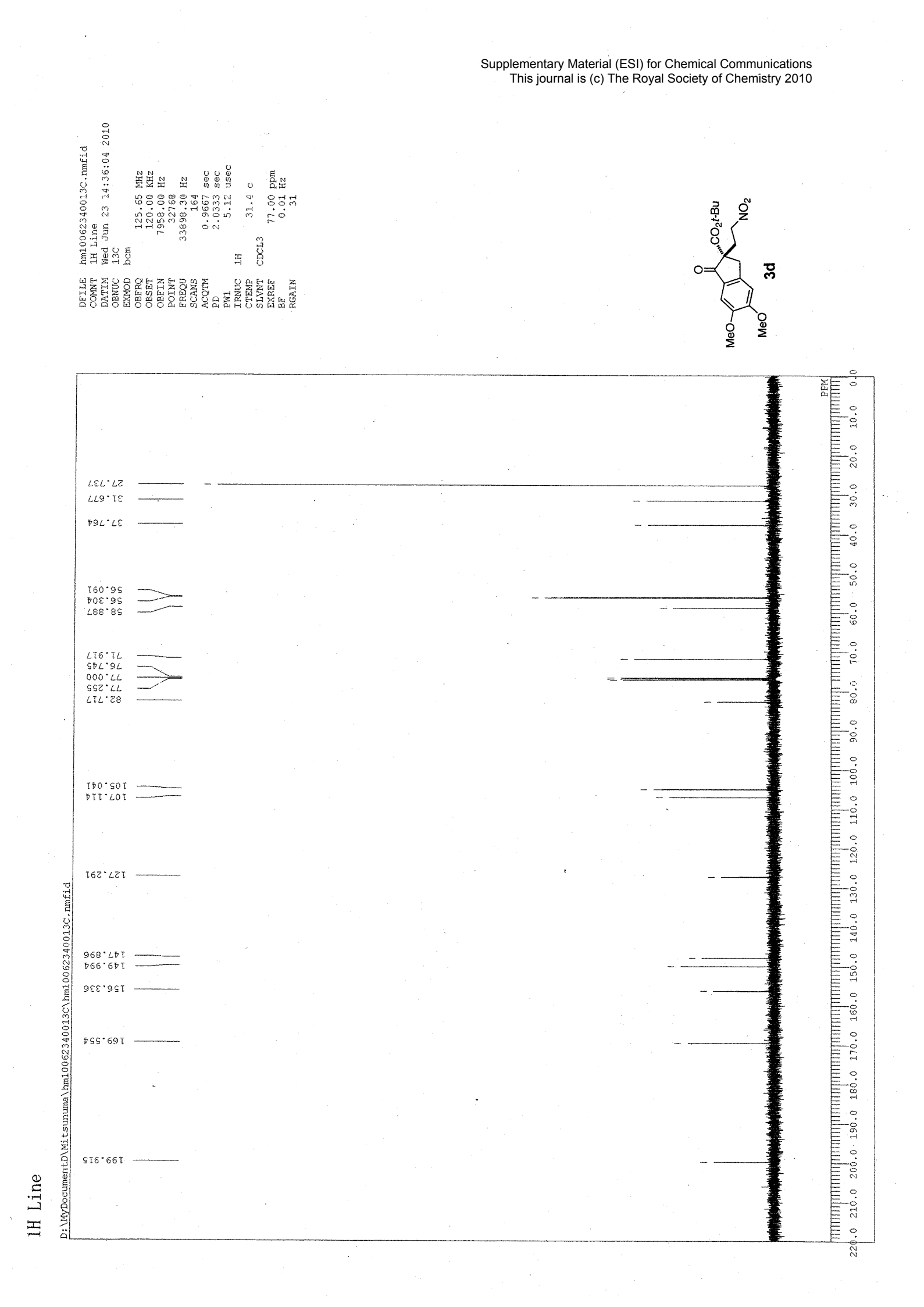


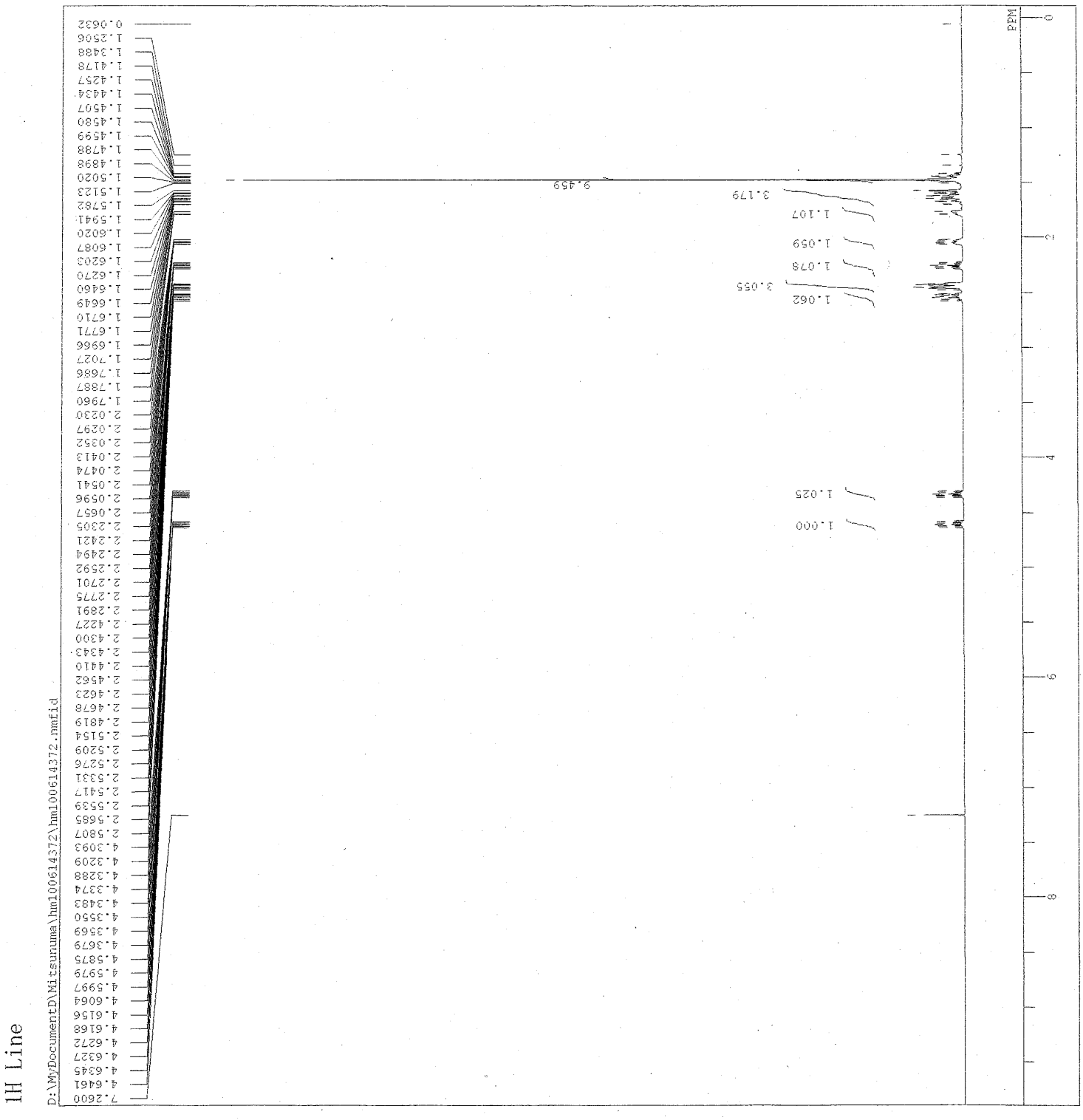
DFILE	hm10061638413C.nmfid
COMNT	1H Line
DATIM	Wed Jun 16 02:32:10 2010
OBNUC	13C
EXMOD	bcm
OBFRQ	125.65 MHz
OBSET	120.00 KHz
OBFIN	7958.00 Hz
POINT	32768
FREQU	33898.30 Hz
SCANS	120
ACQTM	0.9667 sec
PD	2.0333 sec
PW1	5.12 usec
IRNUC	1H
CTEMP	29.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.01 Hz
RGAIN	30

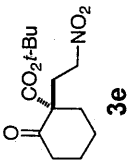


3c


1H Line
D:\MyDocumentDV\Mitsunuma\hm100623400\hm100623400.nmfid
DFILE hm100623400.nmfid
COMNT 1H Line
DATIM Wed Jun 23 14:26:34 2010
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.90 usec
IRNUC 1H
CTEMP 30.0 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 1.00 Hz
RGAIN 16
CO2t-Bu
NO2
MeO
MeO
3d
PPM

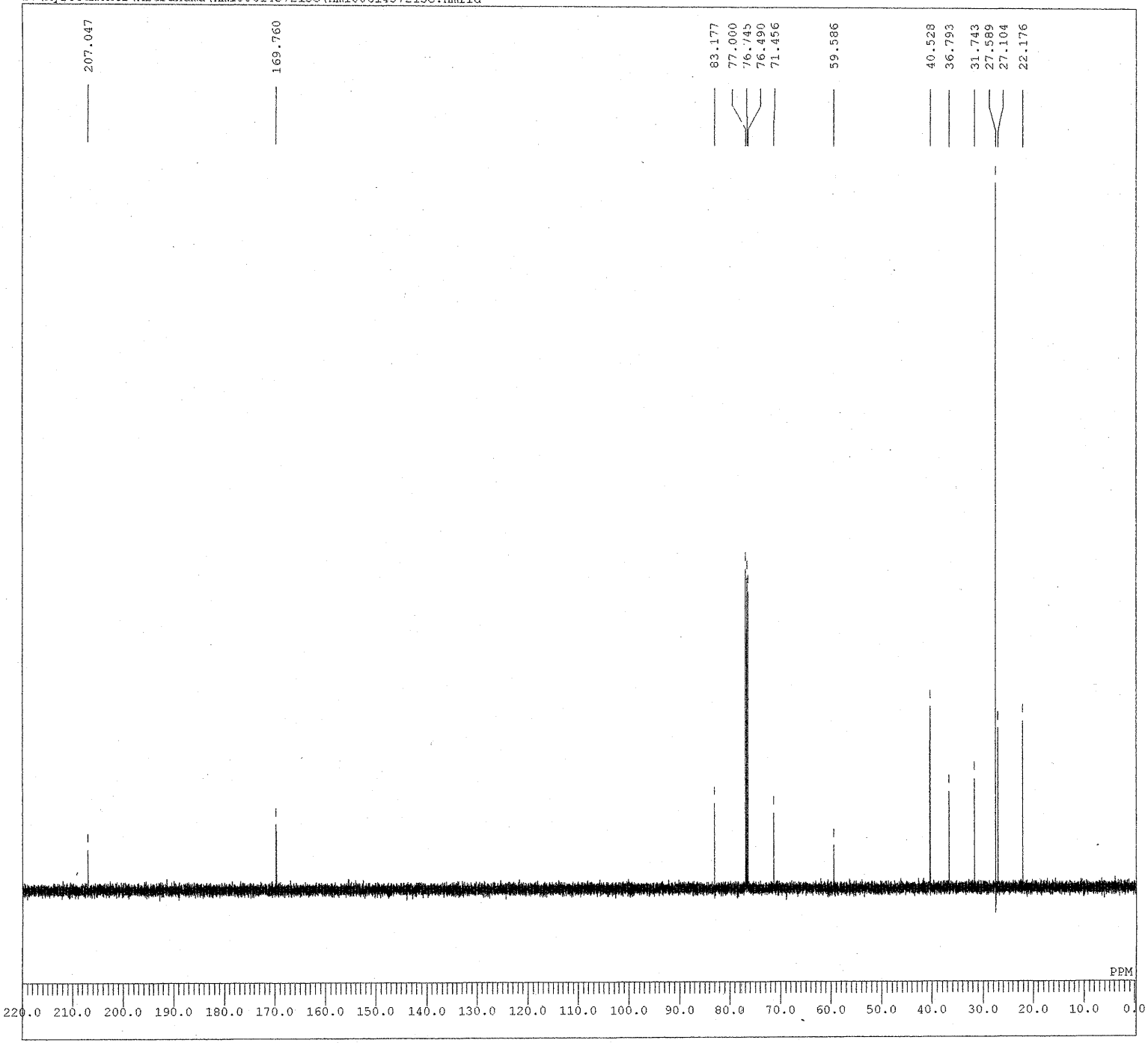

DFILE hm1006234001 3C.nmfid
COMNT 1H Line
DATIM Wed Jun 23 14:36:04 2010
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 164
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 5.12 usec
IRNUC 1H
CTEMP 31.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.01 Hz
RGAIN 31
CO2t-Bu
NO2
MeO
MeO
3d
1H Line
D:\MyDocumentD\Mitsunuma\hm1006234001 3C\hm1006234001 3C.nmfid
199.915
169.554
156.336
149.994
147.896
127.291
107.114
105.041
82.717
77.255
77.000
76.745
71.917
58.887
56.304
56.091
37.764
31.677
27.737
PPM


DFILE hm100614372.nmfid
COMNT 1H Line
DATIM Mon Jun 14 18:41:39 2010
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
FD 3.7232 sec
PW1 5.90 usec
IRNUC 1H
CTEMP 28.7 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 18
9.459
3.179
1.107
1.059
1.078
3.055
1.062
1.025
1.000
PPM
0
2
4
6
8
D:\MyDocument\Mitsunuma\hm100614372\hm100614372.nmfid
1H Line

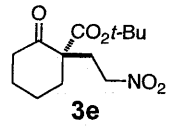

CO2t-Bu
NO2
O
3e

1H Line

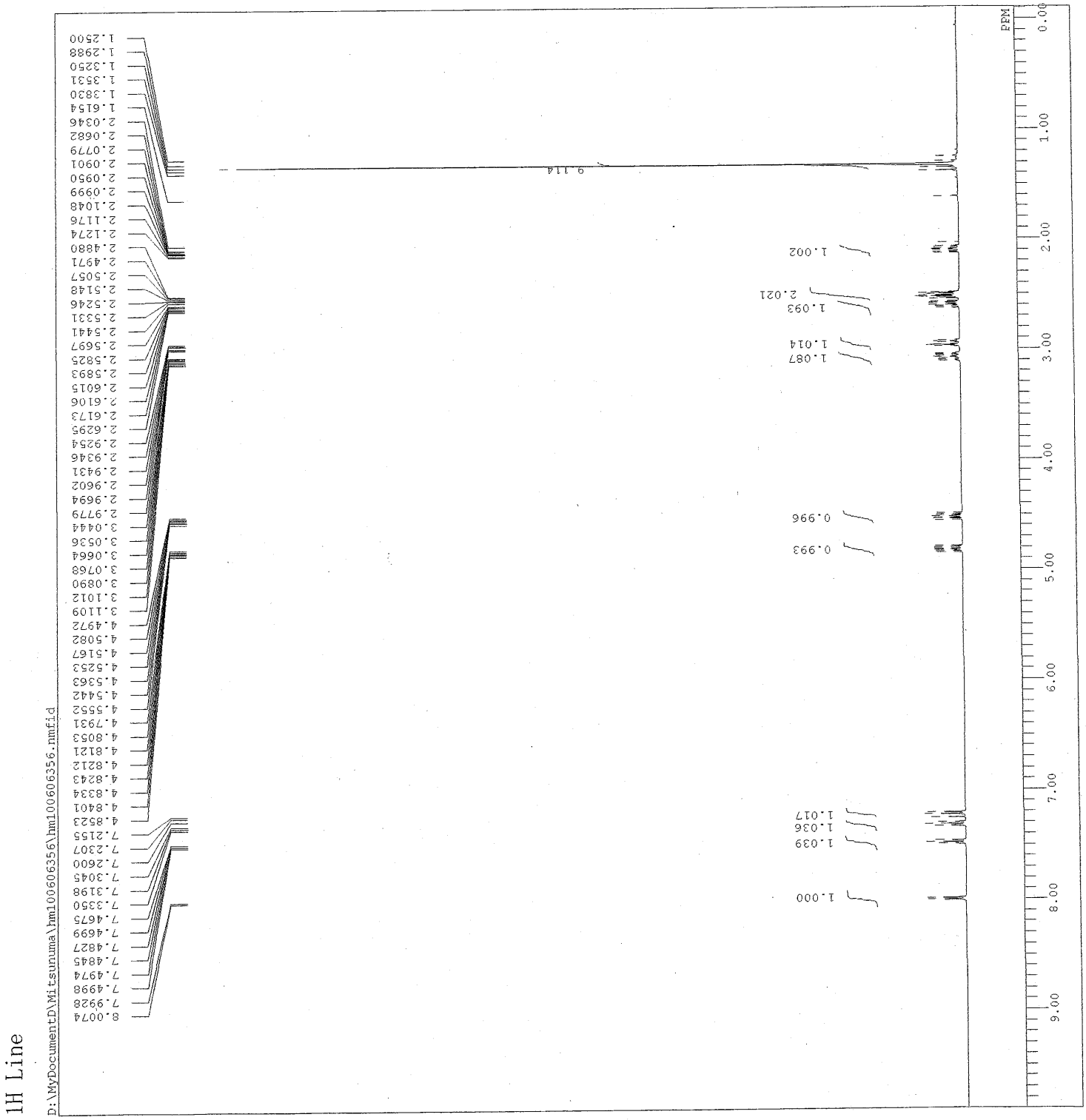
D:\MyDocumentD\Mitsunuma\hm10061437213C\hm10061437213C.nmfid

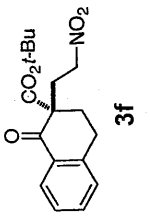


DFILE	hm10061437213C.nmfid
COMNT	1H Line
DATIM	Mon Jun 14 18:59:19 2010
OBNUC	13C
EXMOD	bcm
OBFRQ	125.65 MHz
OBSET	120.00 KHz
OBFIN	7958.00 Hz
POINT	32768
FREQU	33898.30 Hz
SCANS	300
ACQTM	0.9667 sec
PD	2.0333 sec
PW1	5.12 usec
IRNUC	1H
CTEMP	30.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.01 Hz
RGAIN	31

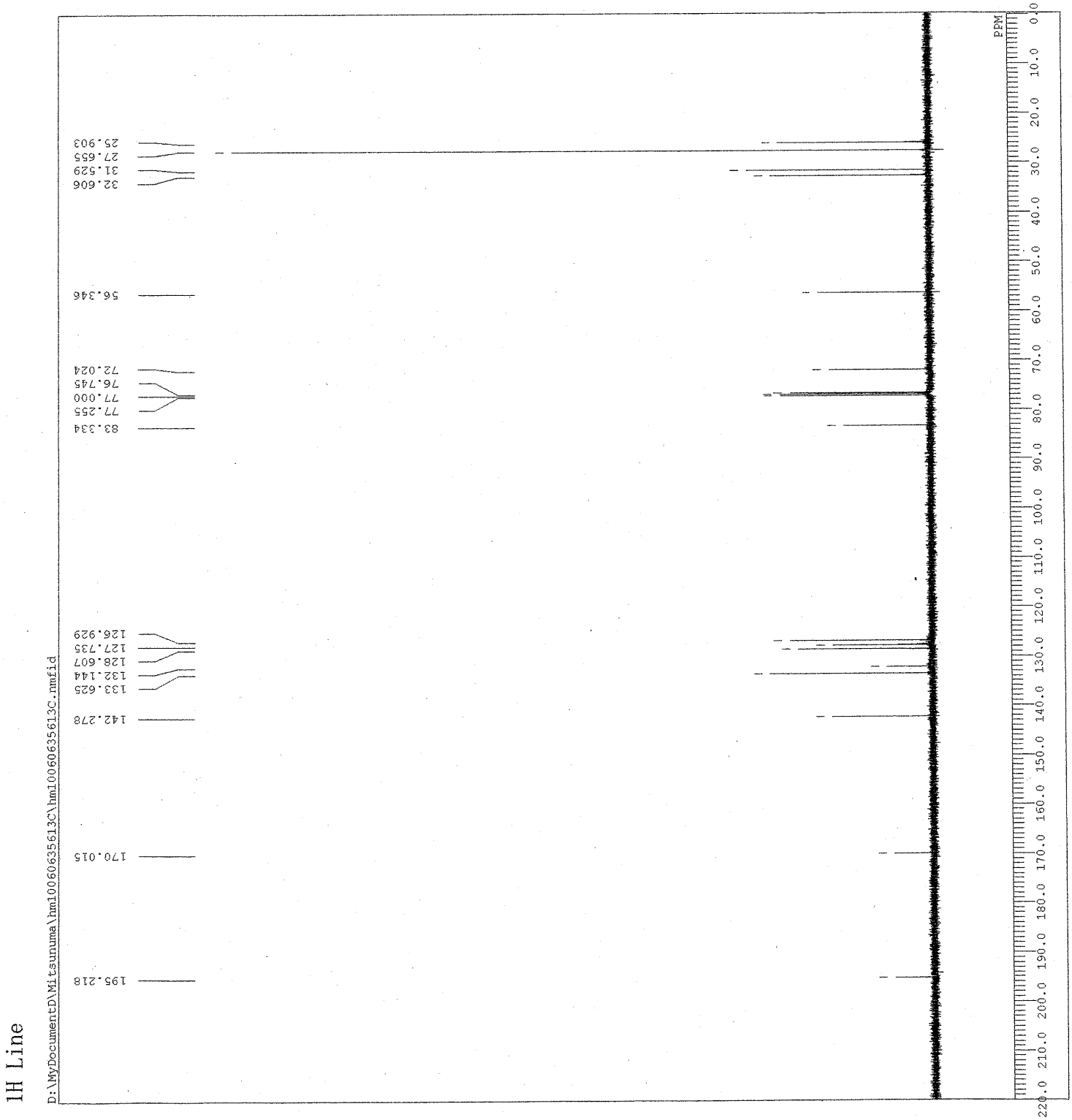


3e


1H Line
D:\MyDocuments\Mitsunuma\hm100606356\hm100606356.nmfid
DFILE hm100606356.nmfid
COMNT 1H Line
DATIM Sun Jun 6 01:34:40 2010
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 kHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 12
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.90 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 16
8.0074
7.9928
7.4998
7.4974
7.4845
7.4827
7.4699
7.4675
7.3350
7.3198
7.3045
7.2600
7.2307
7.2155
4.8523
4.8401
4.8334
4.8243
4.8212
4.8121
4.8053
4.7931
4.5552
4.5442
4.5363
4.5253
4.5167
4.5082
4.4972
3.1109
3.1012
3.0890
3.0768
3.0664
3.0536
3.0444
2.9779
2.9694
2.9602
2.9431
2.9346
2.9254
2.6295
2.6173
2.6106
2.6015
2.5893
2.5825
2.5697
2.5441
2.5331
2.5246
2.5148
2.5057
2.4971
2.4880
2.1274
2.1176
2.1048
2.0999
2.0950
2.0901
2.0779
2.0682
2.0346
1.6154
1.3830
1.3531
1.3250
1.2988
1.2500
9.114
1.002
2.021
1.093
1.014
1.087
0.996
0.993
1.000
1.039
1.036
1.017
PPM
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00


CO2t-Bu
NO2
O

3f


1H Line
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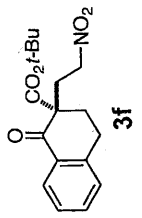
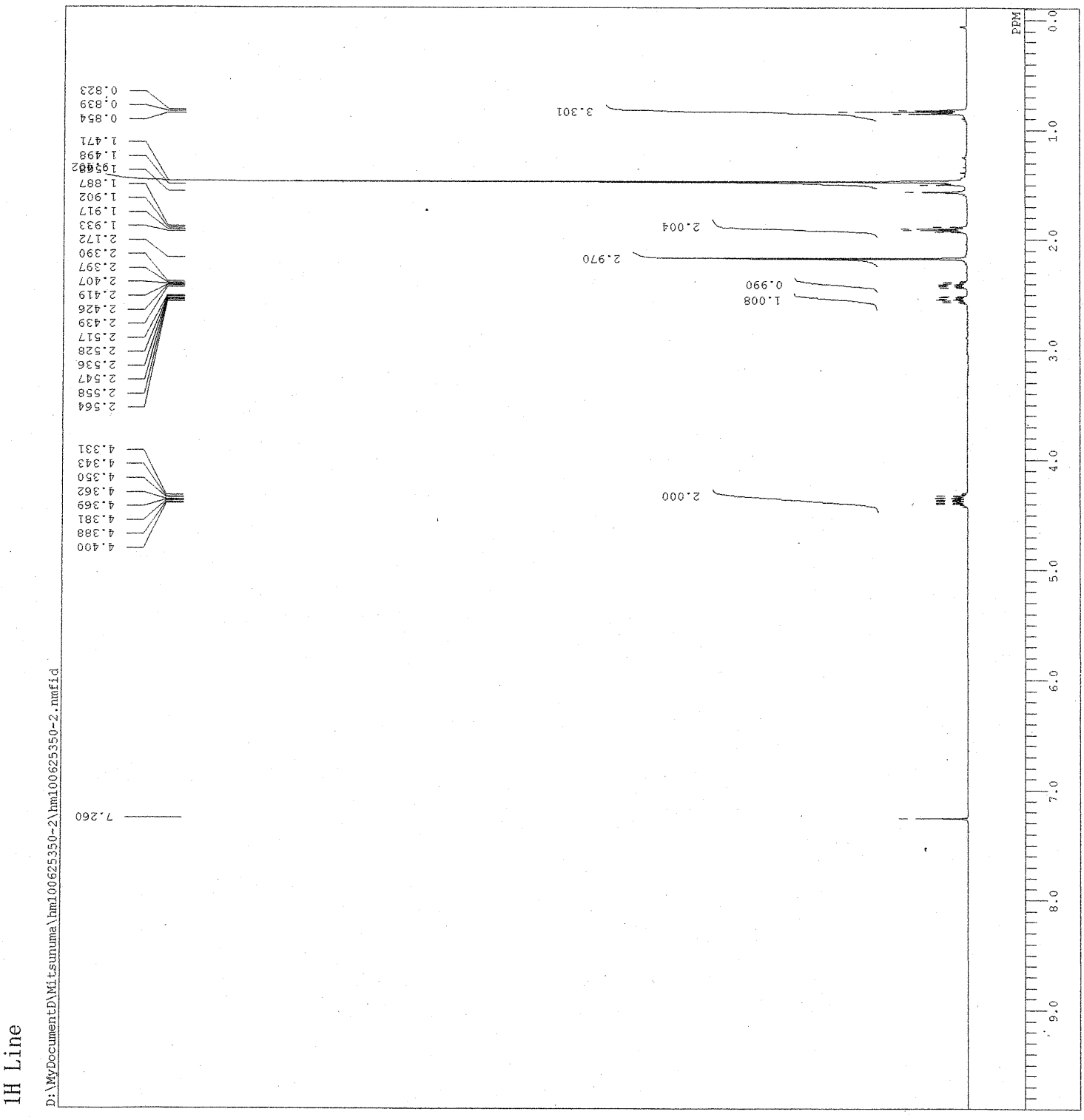
DFILE hm100606356l3C.nmfid
COMNT 1H Line
DATIM Sun Jun 6 01:43:56 2010
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 136
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 5.12 usec
IRNUC 1H
CTEMP 26.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.01 Hz
RGAIN 30
195.218
170.015
142.278
133.625
132.144
128.607
127.735
126.929
83.334
77.255
77.000
76.745
72.024
56.346
32.606
31.529
27.655
25.903
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0


O
CO2t-Bu
NO2
3f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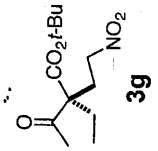
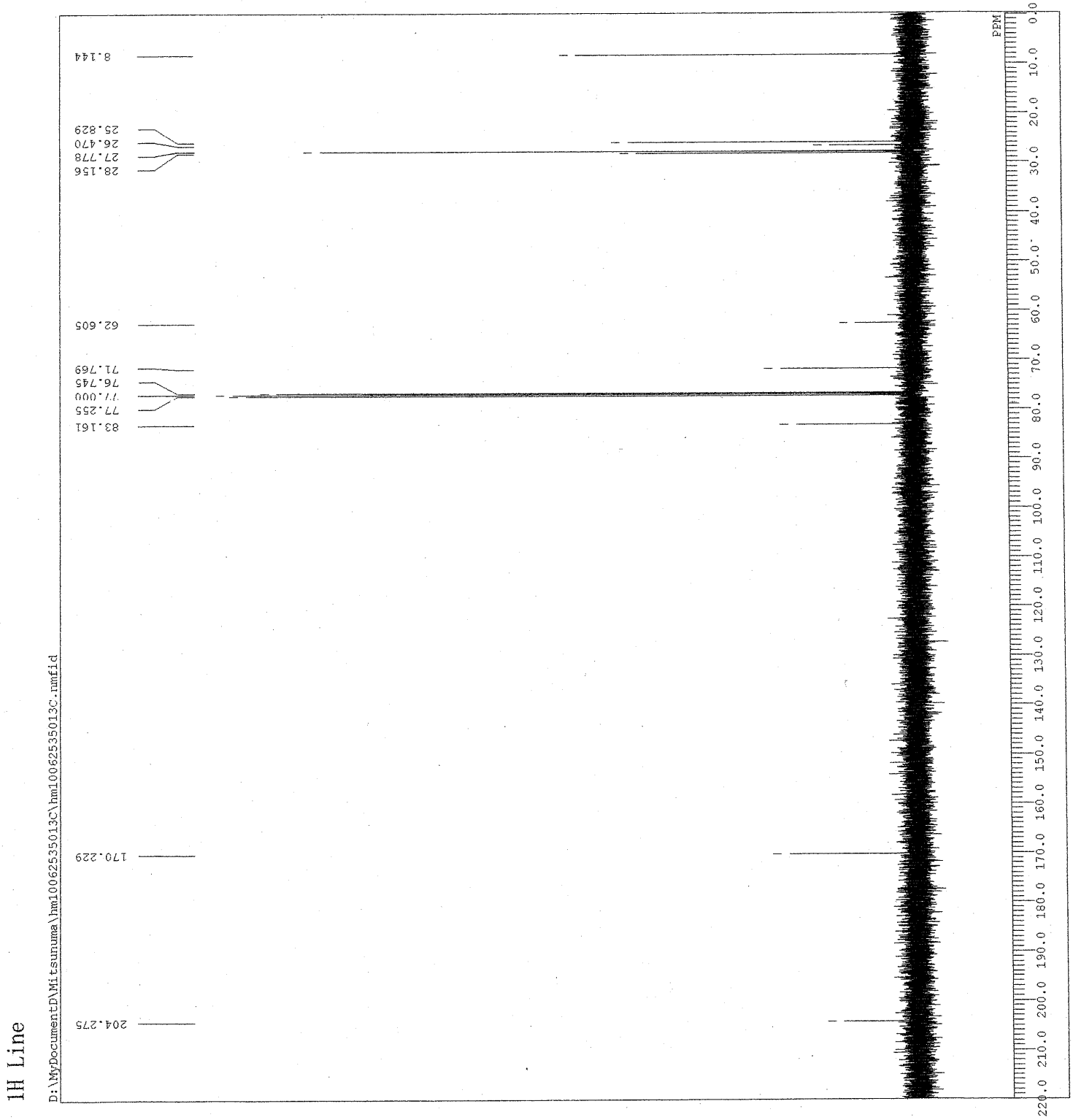
DFILE hm100625350-2.nmfid
COMNT 1H Line
DATIM Fri Jun 25 06:14:44 2010
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.90 usec
IRNUC 1H
CTEMP 28.2 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 19
7.260
4.400
4.388
4.381
4.369
4.362
4.350
4.343
4.331
2.564
2.558
2.547
2.536
2.528
2.517
2.439
2.426
2.419
2.407
2.397
2.390
2.172
1.933
1.917
1.902
1.887
1.498
1.471
0.854
0.839
0.823
3.301
2.004
2.970
0.990
1.008
2.000
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


CO2t-Bu
NO2
3g


1H Line
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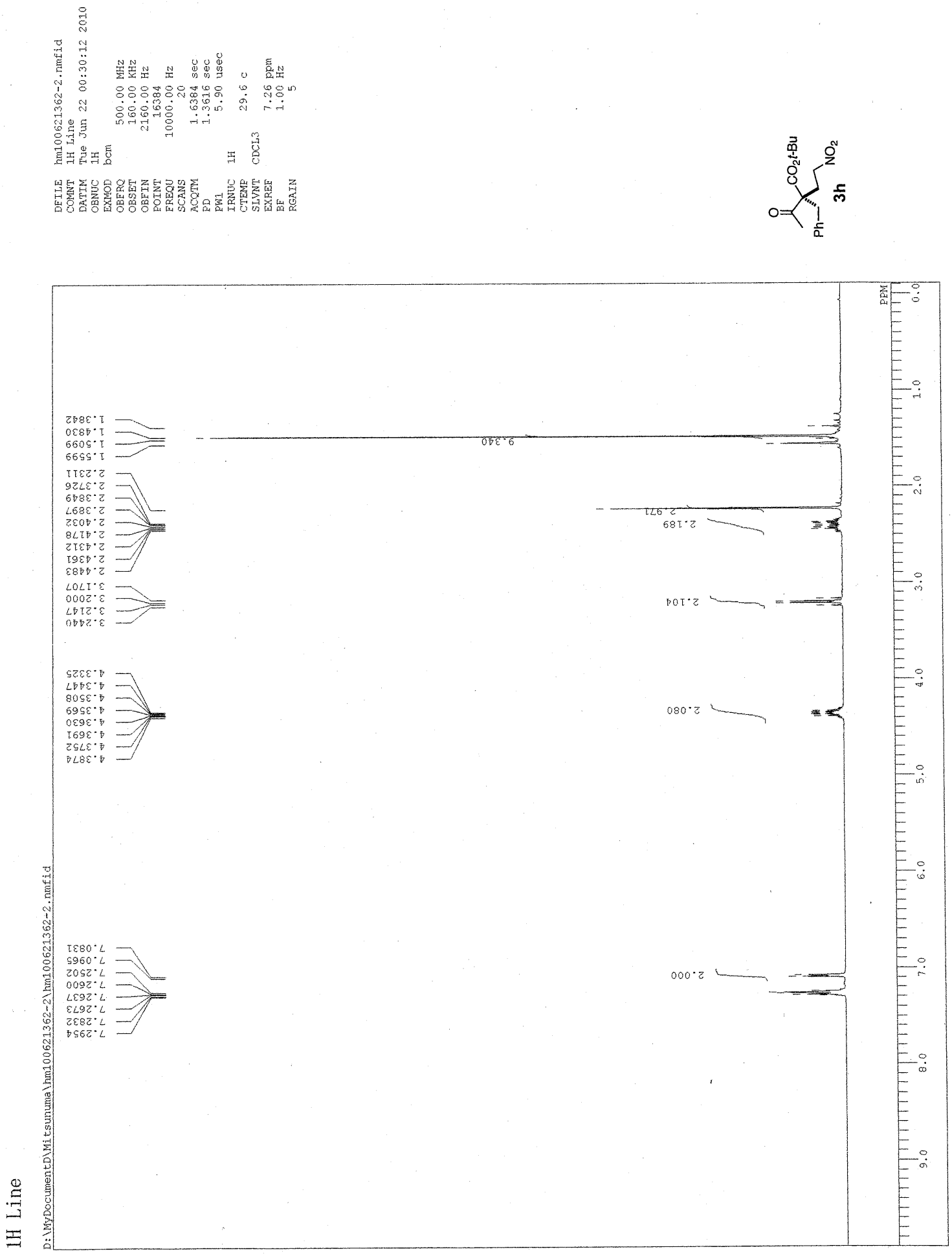
DFILE hm1006253513C.nmfid
COMNT 1H Line
DATIM Fri Jun 25 01:44:18 2010
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 200
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 5.12 usec
IRNUC 1H
CTEMP 29.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.01 Hz
RGAIN 31
8.144
25.829
26.470
27.778
28.156
62.605
71.769
76.745
77.000
77.255
83.161
170.229
204.275
PPM
3g


1H Line
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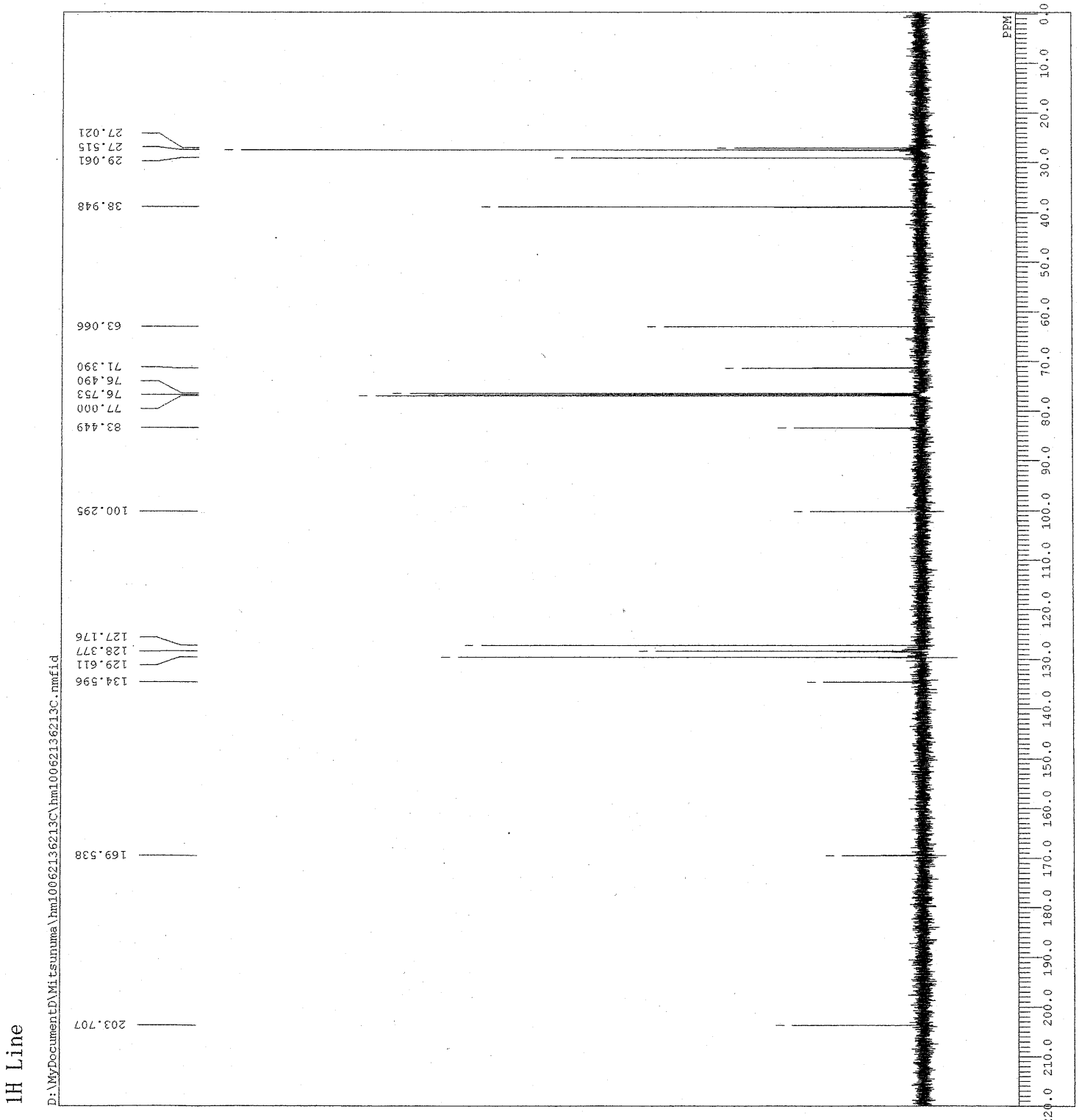
DFILE hm100621362-2.nmfid
COMNT 1H Line
DATIM Tue Jun 22 00:30:12 2010
OBNUC 1H
EXMOD bcm
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 16384
FREQU 10000.00 Hz
SCANS 20
ACQTM 1.6384 sec
PD 1.3616 sec
PW1 5.90 usec
IRNUC 1H
CTEMP 29.6 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 1.00 Hz
RGAIN 5
CO2t-Bu
NO2
Ph
O
3h
PPM
9.340
2.971
2.189
2.104
2.080
2.000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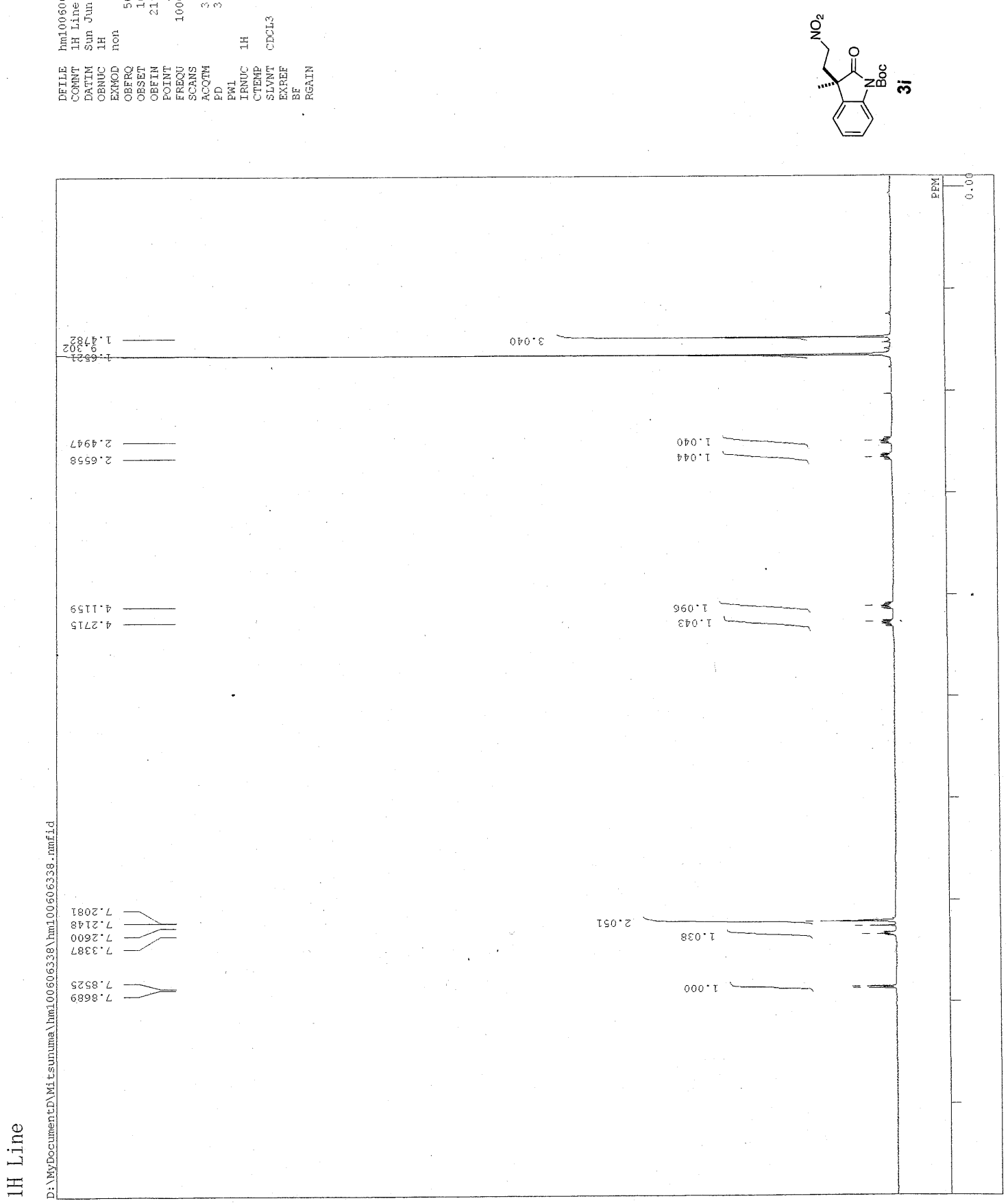
DFILE hm100621362l3C.nmfid
COMNT 1H Line
DATIM Mon Jun 21 23:50:24 2010
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 16384
FREQU 33898.30 Hz
SCANS 288
ACQTM 0.4833 sec
PD 2.5167 sec
PW1 5.12 usec
IRNUC 1H
CTEMP 31.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.01 Hz
RGAIN 5
27.021
27.515
29.061
38.948
63.066
71.390
76.490
76.753
77.000
83.449
100.295
127.176
128.377
129.611
134.596
169.538
203.707
PPM
CO2t-Bu
NO2
Ph
O
3h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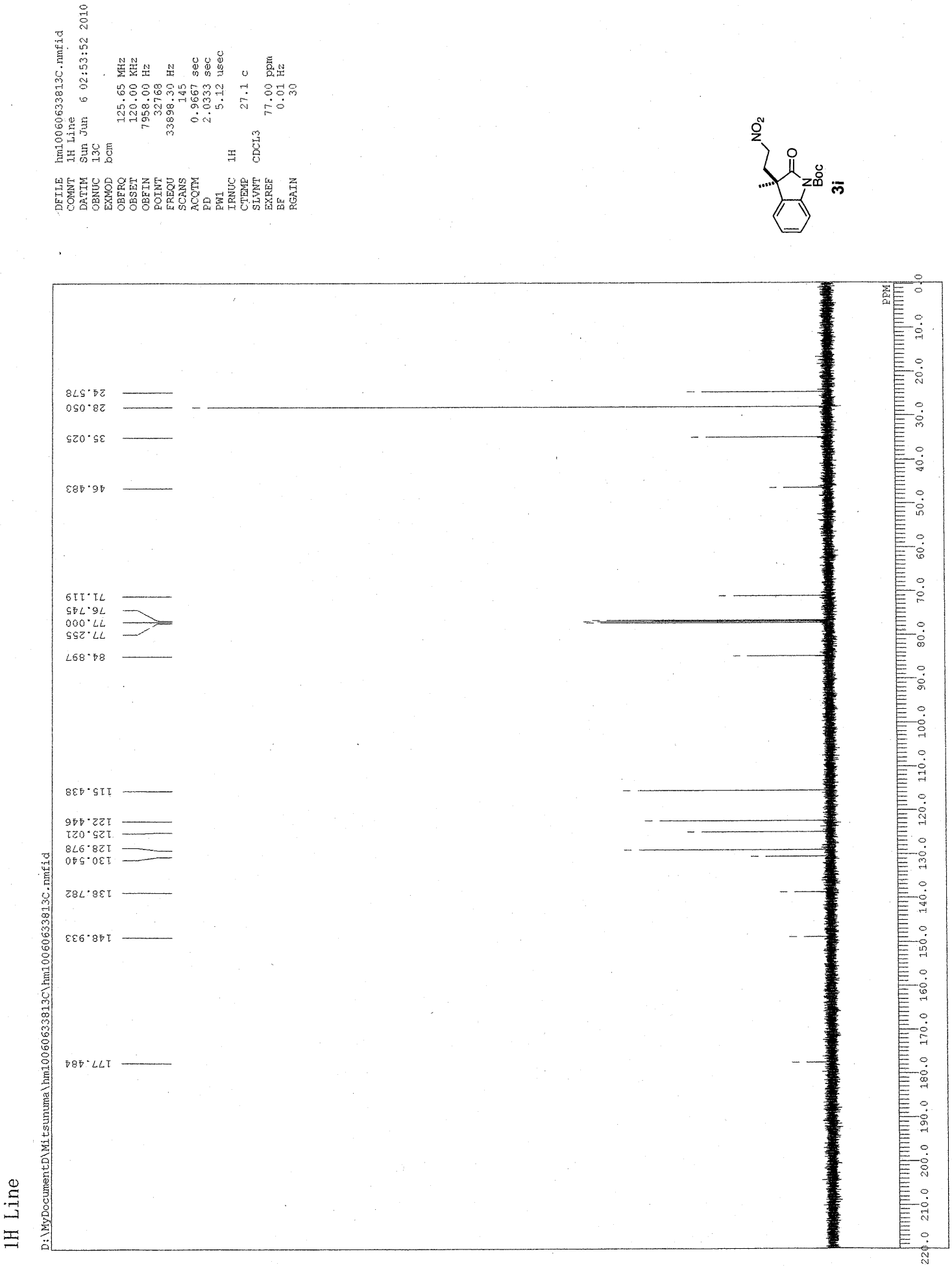
D:\MyDocumentD\Mitsunuma\hm100606338\hm100606338.nmfid
DFILE hm100606338.nmfid
COMNT 1H Line
DATIM Sun Jun 6 02:45:19 2010
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
FD 3.7232 sec
PW1 5.90 usec
IRNUC 1H
CTEMP 25.8 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 17
NO2
O
N
Boc
3i
PPM
0.00
7.8689
7.8525
7.3387
7.2600
7.2148
7.2081
4.2715
4.1159
2.6558
2.4947
1.4782
1.4652
3.040
2.051
1.044
1.040
1.043
1.096
1.038
1.000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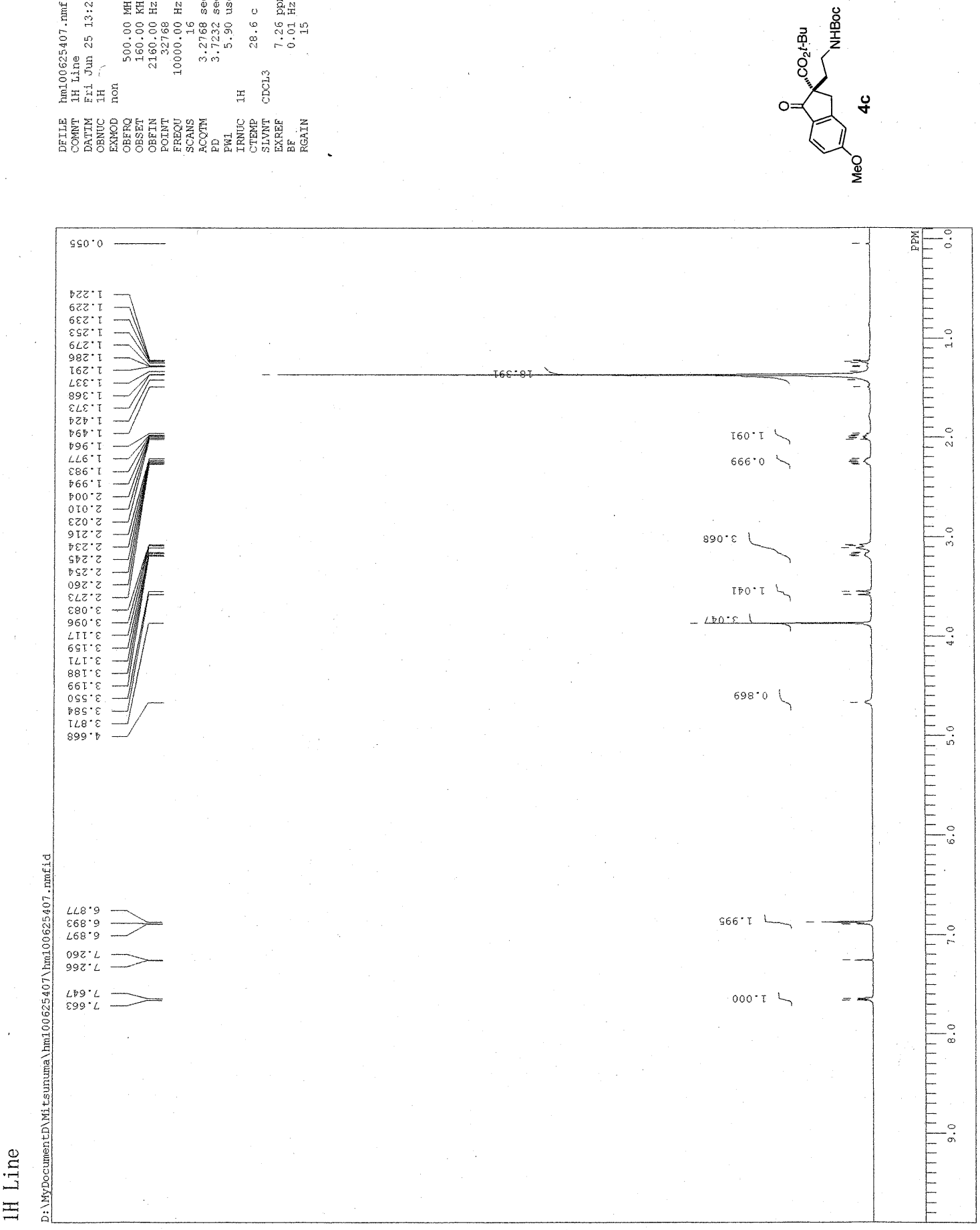
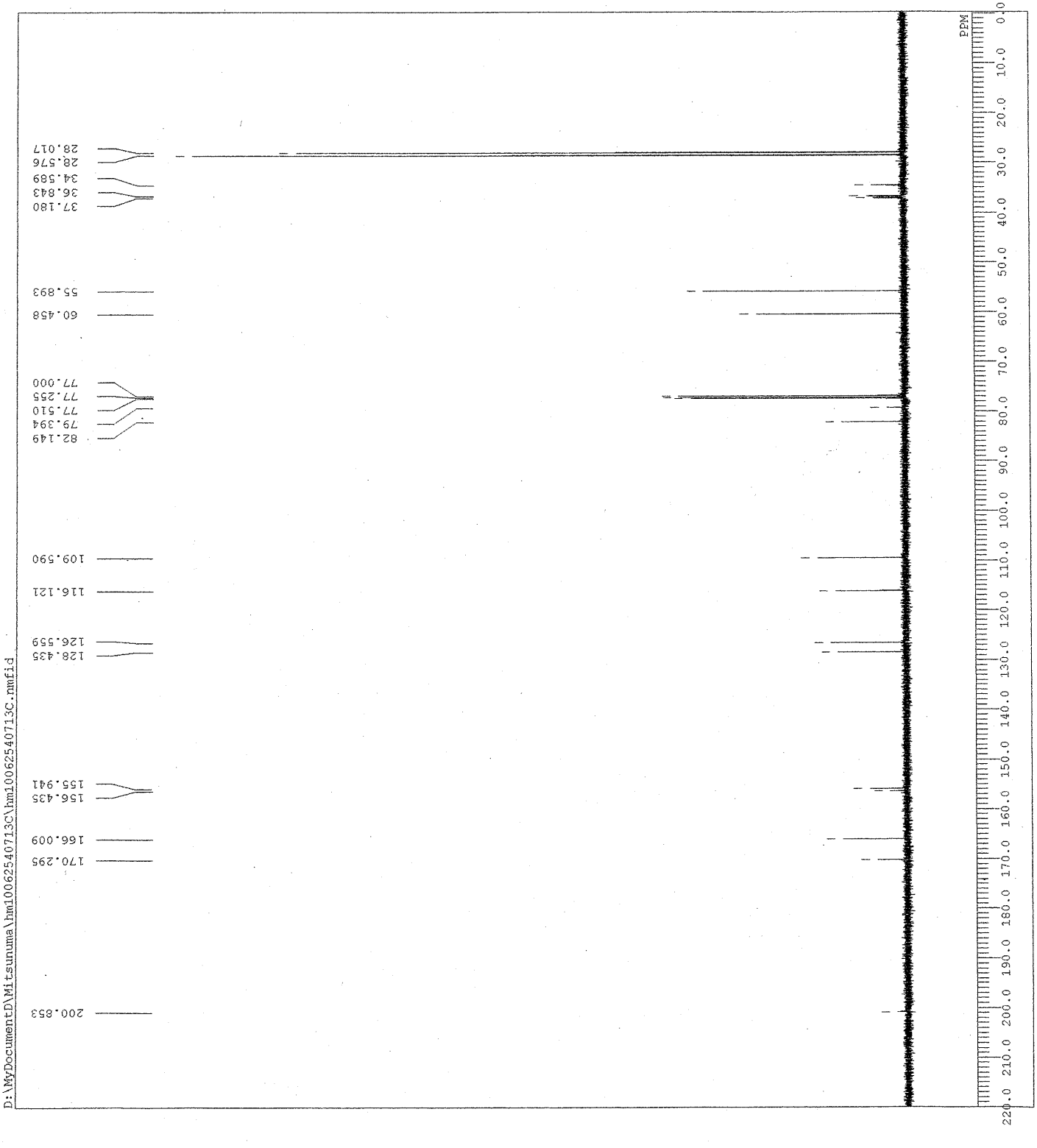
DFILE hm1006063813C.nmfid
COMNT 1H Line
DATIM Sun Jun 6 02:53:52 2010
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 145
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 5.12 usec
IRNUC 1H
CTEMP 27.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.01 Hz
RGAIN 30
24.578
28.050
35.025
46.483
71.119
76.745
77.000
77.255
84.897
115.438
122.446
125.021
128.978
130.540
138.782
148.933
177.484
PPM
NO2
O
N
Boc
3i


1H Line
D:\MyDocumentD\Mitsunuma\hm100625407\hm100625407.nmfid
DFILE hm100625407.nmfid
COMNT 1H Line
DATIM Fri Jun 25 13:27:20 2010
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 16
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.90 usec
IRNUC 1H
CTEMP 28.6 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.01 Hz
RGAIN 15
CO2t-Bu
NHBoc
MeO
4c
PPM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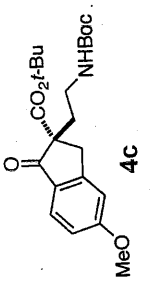
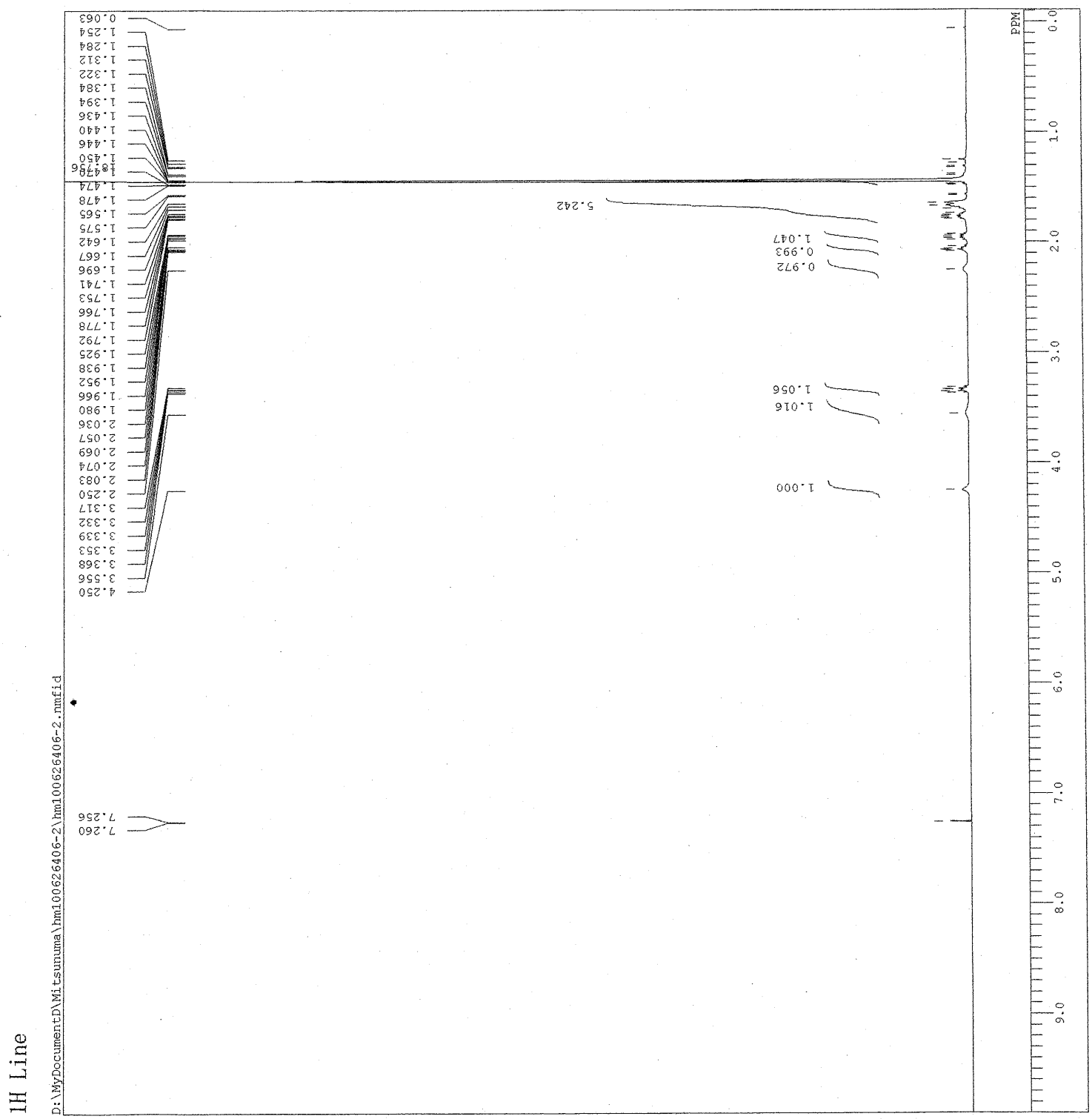
DFILE hm1006254071 3C.nmfid
COMNT 1H Line
DATIM Fri Jun 25 13:48:26 2010
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 120.00 KHz
OBFIN 7958.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 400
ACQTM 0.9667 sec
PD 2.0333 sec
PW1 5.12 usec
IRNUC 1H
CTEMP 30.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.01 Hz
RGAIN 30
200.853
170.295
166.009
156.435
155.941
128.435
126.559
116.121
109.590
82.149
79.394
77.510
77.255
77.000
60.458
55.893
37.180
36.843
34.589
28.576
28.017
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
210.0
220.0


NHBoc
CO2t-Bu
O
MeO
4c


1H Line
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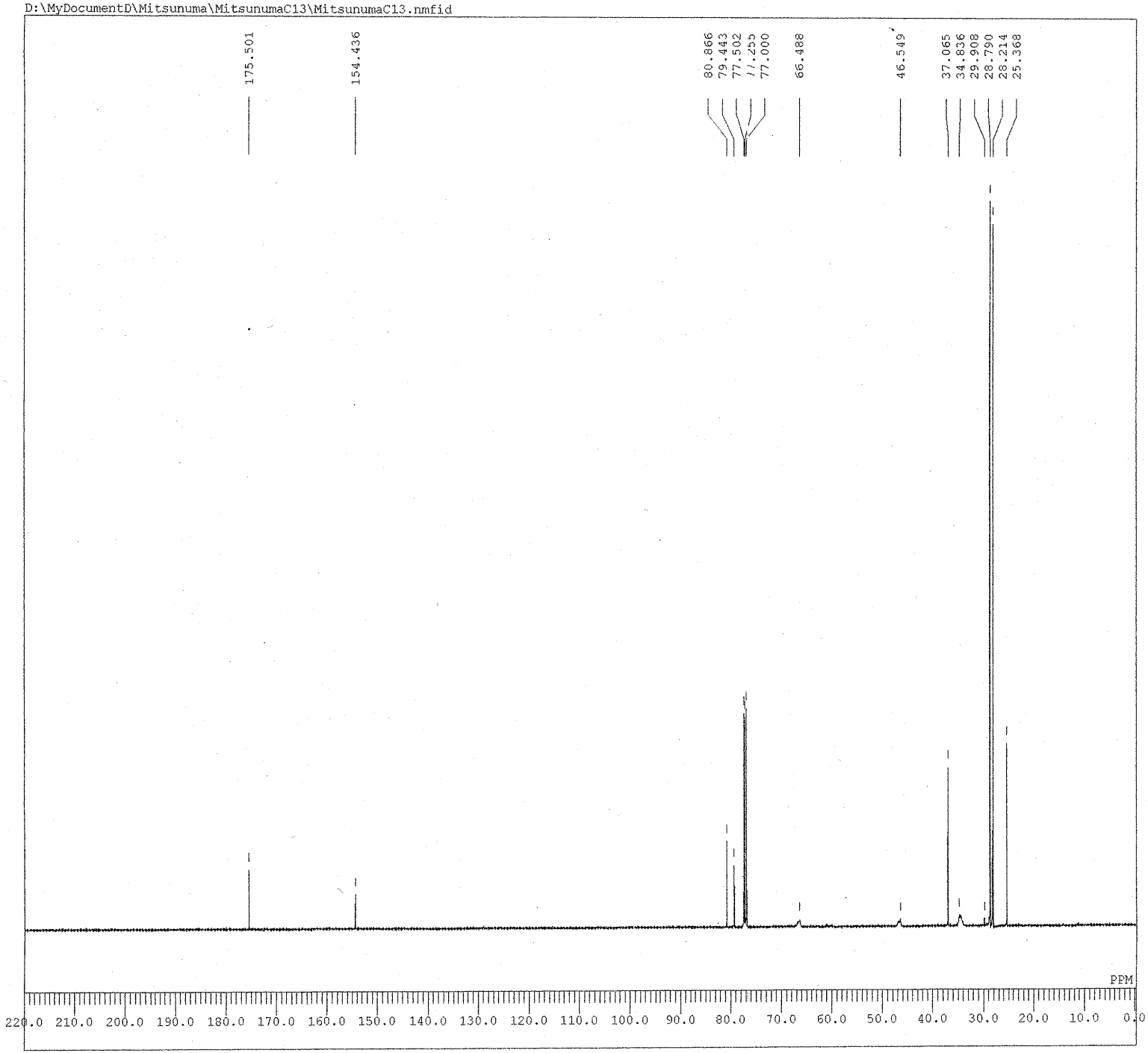
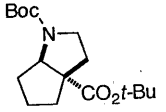
DFILE hm100626406-2.nmfid
COMNT 1H Line
DATIM Sat Jun 26 13:59:28 2010
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 160.00 KHz
OBFIN 2160.00 Hz
POINT 32768
FREQU 10000.00 Hz
SCANS 20
ACQTM 3.2768 sec
PD 3.7232 sec
PW1 5.90 usec
IRNUC 1H
CTEMP 45.0 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.01 Hz
RGAIN 15
Boc
CO2t-Bu
5a
PPM

1H Line

D:\MyDocumentD\Mitsunuma\MitsunumaC13\MitsunumaC13.nmfid



DFILE	MitsunumaC13.nmfid
COMNT	1H Line
DATIM	Sun Jun 27 13:34:41 2010
OBNUC	13C
EXMOD	bcm
OBFRQ	125.65 MHz
OBSET	120.00 KHz
OBFIN	7958.00 Hz
POINT	32768
FREQU	33898.30 Hz
SCANS	16011
ACQTM	0.9667 sec
PD	2.0333 sec
PW1	5.12 usec
IRNUC	1H
CTEMP	45.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.01 Hz
RGAIN	31



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