Asymmetric aldol reaction via memory of chirality

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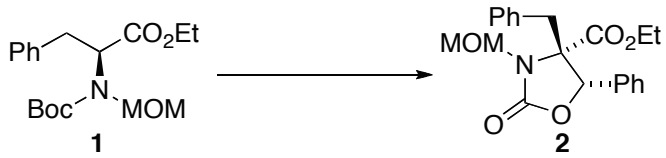
Electronic Supplementary Information

General Procedure. ^{1}H NMR were measured in $CDCl_3$ solution and referenced from TMS (0.00 ppm) using JEOL ECX-400 or JEOL AL-400 (400 MHz) spectrophotometers, unless otherwise noted. ^{13}C NMR were measured in $CDCl_3$ solution and referenced to $CDCl_3$ (77.5 ppm) using JEOL ECX-400 or JEOL AL-400 (100 MHz) spectrophotometers, unless otherwise noted. Chemical shifts are reported in ppm. When peak multiplicities are reported, the following abbreviations are used: s, singlet; d, doublet; t, triplet, q, quartet; m, multiplet; br, broadened. IR spectra were recorded on JASCO FT/IR-4200 spectrometer. Mass spectra were obtained on JEOL JMS-700. Elemental analyses were performed with CHN J-science-lab. Microcoder JM10. Optical rotations were determined on HORIBA SEPA-200. Melting points were measured with Yanagimoto Micro Melting Point Apparatus PM-500 and are uncorrected. Enantiomeric excess was determined by HPLC analysis using Shimadzu LC-10AS liquid chromatograph with Chiralpak AD-H or Chiralcel OD-H as chiral stationary phase. Flash column chromatography was performed on Silica Gel (SilicaFlash® $60F_{245}$) and compounds were visualized with UV light and *p*-anisaldehyde stain, phosphomolybdic acid stain or ninhydrin stain. Preparative thin layer chromatography was performed on precoated plates (0.5 mm, silica gel Merck Kieselgel $60F_{245}$) and visualized with UV light. All reactions were conducted in oven-dried glassware under argon atmosphere. Dehydrated solvents were purchased from Kanto Kagaku or Wako Chemicals and pre-treated with activated MS4Å for 1 day or longer.

General Procedure for Table 1



Procedure I

KHMDS (1.1 eq.) was added to a solution of **1** (1.0 eq.) in toluene/THF at –78 ˚C. After being stirred for 30 min, benzaldehyde (3.0 eq) was added dropwise at same temperature. The resulting mixture was stirred for 2.5 hr and poured into sat. NH_4Cl aq. and extracted with AcOEt. The extracts were washed with sat. $NaHCO_3$ aq. and brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was purified through flash silica gel column chromatography (hexane/Et_2O=1/1) to give an oil, which was further purified by PTLC (hexane/1,4-dioxane=4/1) to obtain **2**.

Procedure II

A solution of **1** (1.0 eq.) was added to a solution of benzaldehyde (3.0 eq.) and KHMDS (1.1 eq.) in toluene/THF at the temperature shown in Table 1. After being stirred for 10 min, the mixture was poured into sat. NH_4Cl aq. and extracted with AcOEt. The extracts were washed with sat. $NaHCO_3$ aq. and brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was purified through flash silica gel column chromatography (hexane/Et_2O=1/1) to give an oil, which was further purified by PTLC (hexane/1,4-dioxane=4/1) to obtain **2**.

Procedure III

Benzaldehyde (0.13 mL, 1.25 mmol) was added to a mixture of **1** (84 mg, 0.25 mmol) in toluene (1.5 mL) at rt and the mixture was cooled to the temperature shown in Table 1. KHMDS (0.37-0.41 M in toluene, 1.83-2.02 mL, 0.75 mmol) was added to this solution and the resulting mixture was stirred for the time shown in Table 1 at same temperature. The reaction mixture was poured into sat. NH_4Cl aq. and extracted with AcOEt. The

extracts were washed with sat. $NaHCO_3$ aq. and brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was purified through flash silica gel column chromatography (hexane/Et_2O=1/1) to give an oil, which was further purified by PTLC (hexane/1,4-dioxane=4/1) to obtain **2**.

2:**(4*S*, 5*S*)-Ethyl 4-benzyl-3-(methoxymethyl)-2-oxo-5-phenyloxazolidine-4-carboxylate**

Colorless oil; $[\alpha]_D^{20}$ +2.8 (*c* 1.0, $CHCl_3$, 87% ee); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.26 (m, 10H), 5.38 (s, 1H), 4.83 (ABq, $\Delta\upsilon_{AB}$=0.32 Hz *J*=11.6 Hz, 2H), 3.71 (q, *J*=7.2 Hz, 2H), 3.52 (ABq, $\Delta\upsilon_{AB}$=0.031 Hz *J*=15.6 Hz, 2H), 3.47 (s, 3H), 0.94 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 158.5, 134.4, 134.3, 131.4, 129.3, 129.2, 128.6, 128.0, 126.3, 78.9, 76.3, 73.1, 62.4, 57.6, 37.4, 13.8; IR (neat) cm^{-1}: 2935, 1774, 1739, 1496, 1455, 1374, 1233, 1078, 1028, 744, 701; MS (EI) *m/z* (rel intensity) 369 (M^+, 5), 338 (10), 296 (40), 278 (100), 220 (20), 202 (40), 158 (20), 130 (20), 91 (60); HRMS (EI) *m/z* Calcd for $C_{21}H_{23}NO_5$ (M^+): 369.1576 Found 369.1581; Anal. Calcd for $C_{21}H_{23}NO_5$: C, 68.28; H, 6.28; N, 3.79 Found: C, 68.02; H, 6.36; N, 3.77; HPLC conditions: Daicel Chiralcel OD-H, hexane:2-propanol=95:5, flow 0.5 mL/min, t_R=32 (4*R*,5*R*), 37 (4*S*,5*S*) min.

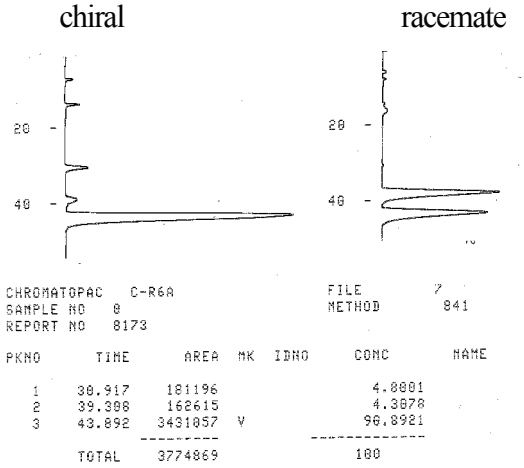
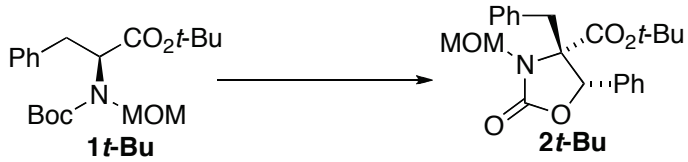


Table 1, entry 13



To a solution of **1*t*-Bu** (91 mg, 0.25 mmol) and benzaldehyde (0.13 mL, 1.25 mmol) in *t*-BuOMe (1.5 mL) was added dropwise KHMDS (0.37 M in PhMe, 2.02 mL, 0.75 mmol) at –50 ˚C. After being stirred for 12 hr, the reaction mixture was poured into sat. NH_4Cl aq. and the resulting mixture was extracted with AcOEt. The extracts were washed with sat. $NaHCO_3$ aq. and brine, and dried over Na_2SO_4, filtered and concentrated. The residue was chromatographed on silica gel (hexane/Et_2O=1/1) to give an oil, which was further purified by PTLC (hexane/1,4-dioxane=4/1) to give **2*t*-Bu** (31 mg, 31%, 89% ee).

2*t*-Bu:***tert*-Butyl 4-benzyl-3-(methoxymethyl)-2-oxo-5-phenyloxazolidine-4-carboxylate**

Colorless oil; $[\alpha]_D^{20}$ +1.9 (*c* 1.0, $CHCl_3$, 86% ee); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.30 (m, 10H), 5.38 (s, 1H), 4.82 (ABq, $\Delta\upsilon_{AB}$=0.27 Hz *J*=11.6 Hz, 2H), 3.50 (s, 2H), 3.48 (s, 3H) 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 158.7, 135.0, 134.7, 131.5, 129.3, 129.1, 128.8, 128.0, 126.4, 83.8, 78.6, 76.4, 73.0, 57.8, 38.1, 27.6. IR (neat) cm^{-1}: 2930, 1771, 1732, 1454, 1370, 1251, 1081, 1040, 745, 701. MS (EI) *m/z* (rel intensity) 397 (M^+, 1), 306 (60), 296 (100), 250 (60), 220 (30), 174 (25), 130 (20), 91 (40), 57 (10); HRMS (EI) *m/z* Calcd for $C_{23}H_{27}NO_5$ (M^+): 397.1889 Found 397.1875; Anal. Calcd for $C_{23}H_{27}NO_5$: C, 69.50; H, 6.85; N, 3.52%. Found: C, 69.29; H, 7.02; N, 3.49%; HPLC conditions: Daicel Chiralcel OJ-H, hexane: 2-propanol=85:15, flow 0.6 mL/min, t_R=14 (major), 22 (minor) min.

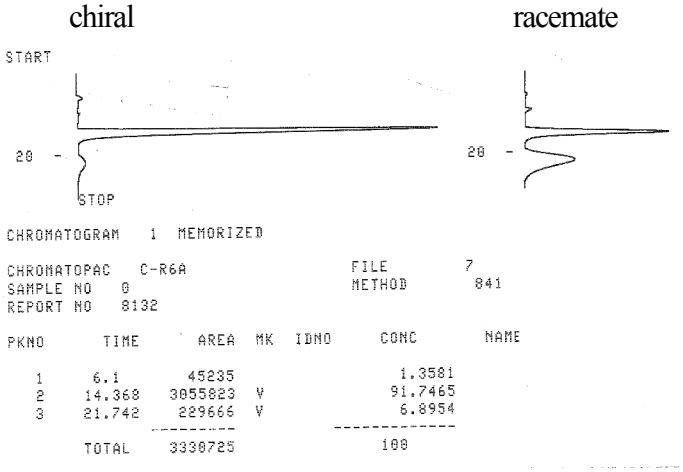
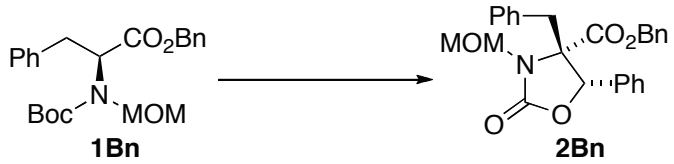


Table 1, entry 14



To a solution of **1Bn** (100 mg, 0.25 mmol) and benzaldehyde (0.13 mL, 1.25 mmol) in *t*-BuOMe (1.50 mL) was added dropwise KHMDS (0.30 M in PhMe, 2.50 mL, 0.75 mmol) at –50 ˚C. After being stirred for 12 hr, the reaction mixture was poured into sat. NH_4Cl aq. and the resulting mixture was extracted with AcOEt. The extracts were washed with sat. $NaHCO_3$ aq. and brine, and dried over Na_2SO_4, filtered and concentrated. The residue was chromatographed on silica gel (hexane/Et_2O=1/1) to give an oil, which was further purified by PTLC (hexane/1,4-dioxane=4/1) to give **2Bn** (106 mg, 99%, 82% ee).

2Bn:**Benzyl 4-benzyl-3-(methoxymethyl)-2-oxo-5-phenyloxazolidine-4-carboxylate**

Colorless oil; $[\alpha]_D^{20}$ +22 (*c* 1.0, $CHCl_3$, 91% ee); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.24 (m, 13H), 7.12-7.09 (m, 2H), 5.39 (s, 1H), 4.80 (ABq, $\Delta\upsilon_{AB}$=0.33 Hz *J*=11.6 Hz, 2H), 4.63 (ABq, $\Delta\upsilon_{AB}$=0.035 Hz *J*=12.4 Hz, 2H) 3.52 (ABq, $\Delta\upsilon_{AB}$=0.024 Hz *J*=15.6 Hz, 2H) 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 158.5, 134.6, 134.2, 134.2, 131.5, 129.4, 129.3, 128.9, 128.8, 128.8, 128.1, 126.4, 79.1, 76.4, 73.4, 68.3, 57.7, 37.4; IR (neat) cm^{-1}: 3064, 2934, 1770, 1742, 1455, 1374, 1078, 910, 698; MS (EI) *m/z* (rel intensity) 431 (M^+, 1), 400 (5), 340 (100), 296 (60), 220 (50), 130 (20); HRMS (EI) *m/z* Calcd for $C_{26}H_{25}NO_5$ (M^+): 431.1733 Found 431.1725 Anal. Calcd for $C_{26}H_{25}NO_5$: C, 72.37; H, 5.84; N, 3.25%. Found: C, 72.13; H, 5.90; N, 3.06%; HPLC conditions: Daicel Chiralcel OD-H, hexane: 2-propanol=90:10, flow 0.6 mL/min, t_R=27 (major), 33 (minor) min.

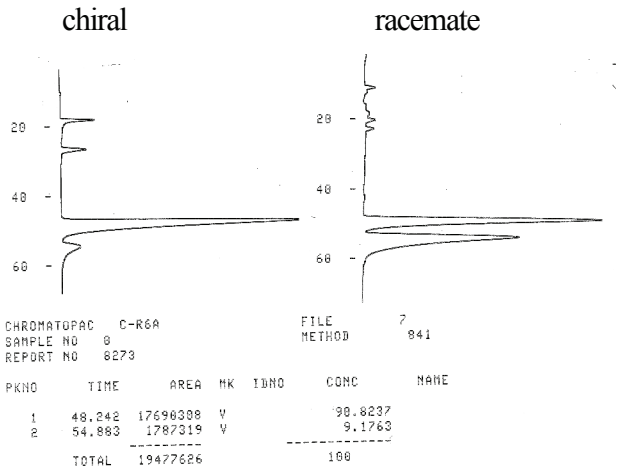
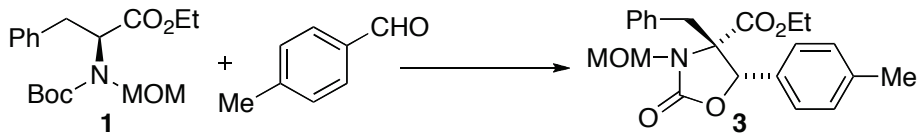


Table 2, entry 2



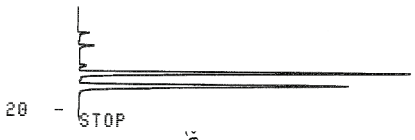
p-Tolualdehyde (0.15 mL, 1.25 mmol) was added to a solution of **1** (84 mg, 0.25 mmol) in *t*-BuOMe (1.5 mL) and the mixture was cooled to –60 ˚C and KHMDS (0.40 M in toluene, 1.88 mL, 0.75 mmol) was added slowly. After being stirred for 12 hr at same temperature, the reaction mixture was poured into sat. NH_4Cl aq. and extracted with AcOEt and the extracts were washed with sat. $NaHCO_3$ aq. and brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was purified through flash silica gel column chromatography (hexane/AcOEt=7/1) to give an oil, which was further purified by PTLC (hexane/AcOEt=3/1) to give **3** (65 mg, 67%, 88% ee).

3:**Ethyl 4-benzyl-3-(methoxymethyl)-2-oxo-5-*p*-tolyloxazolidine-4-carboxylate**

Colorless oil; $[\alpha]_D^{20}$ –9.9 (*c* 1.1, $CHCl_3$, 86% ee); ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 -7.31 (m, 5H), 7.15 (s, 4H), 5.34 (s, 1H), 4.82 (ABq, $\Delta\upsilon_{AB}$=0.32 Hz *J*=11.5 Hz, 2H), 3.75 (q, *J*=7.3 Hz, 2H), 3.49 (ABq, $\Delta\upsilon_{AB}$=0.034 Hz *J*=15.6 Hz, 2H), 3.46 (s, 3H), 2.33 (s, 3H), 0.98 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 158.8, 139.3, 134.5, 131.6, 131.4, 129.4, 129.3, 128.1, 126.4, 79.2, 76.5, 73.3, 62.5, 57.7, 37.5, 21.6, 14.0; IR (neat) cm^{-1}: 2930, 1773, 1740, 1373, 1232, 1039, 704; MS (EI) *m/z* (rel intensity) 383 (M^+, 5), 351 (10), 310 (20), 292 (100), 234 (20), 216 (90), 144 (30), 91 (50); HRMS (EI) *m/z* Calcd for $C_{22}H_{25}NO_5$ (M^+): 383.1733 Found 383.1739 Anal. Calcd for $C_{22}H_{25}NO_5$: C, 68.91; H, 6.57; N, 3.65 Found C, 68.70; H, 6.53; N, 3.56; HPLC conditions: Daicel Chiralcel OD-H, hexane:2-propanol=93:7, flow 0.8 mL/min, t_R=13 (minor), 16 (major) min.

chiral

racemate



CHROMATOPAC C-R6A
SAMPLE NO 0
REPORT NO 1099

FILE 0
METHOD 841

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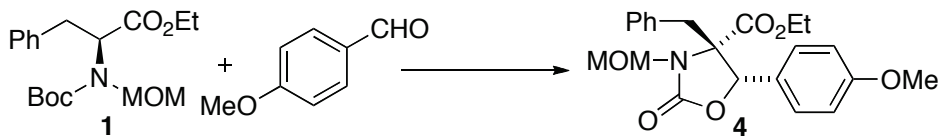
Table 2, entry 3



p-Anisaldehyde (0.15 mL, 1.25 mmol) was added to a solution of **1** (84 mg, 0.25 mmol) in *t*-BuOMe (1.5 mL) and the mixture was cooled to –60 ˚C and KHMDS (0.38 M in toluene, 1.97 mL, 0.75 mmol) was added slowly. After being stirred for 6 hr at same temperature, the reaction mixture was poured into sat. NH_4Cl aq. and extracted with AcOEt and the extracts were washed with sat. $NaHCO_3$ aq. and brine, and dried over Na_2SO_4,

filtered, and concentrated. The residue was purified through flash silica gel column chromatography (hexane/AcOEt=7/1) to give an oil, which was further purified by PTLC (hexane/1,4-dioxane=4/1) to obtain **4** (66 mg, 66%, 88% ee).

4:**Ethyl 4-benzyl-3-(methoxymethyl)-5-(4-methoxyphenyl)-2-oxooxazolidine-4-carboxylate**

Colorless oil; $[\alpha]_D^{20}$ –14 (*c* 1.1, $CHCl_3$, 87% ee); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.30 (m, 5H), 7.18 (d, *J*=8.8 Hz, 2H), 6.86 (d, *J*=8.8 Hz, 2H), 5.33 (s, 1H), 4.82 (ABq, $\Delta\upsilon_{AB}$=0.32 Hz *J*=11.2 Hz, 2H), 3.78 (s, 3H), 3.77 (q, *J*=7.2 Hz, 2H), 3.48 (ABq, $\Delta\upsilon_{AB}$=0.031 Hz *J*=15.6 Hz, 2H), 3.46 (s, 3H), 1.01 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 160.4, 158.6, 134.4, 131.5, 129.2, 128.0, 127.8, 126.2, 114.0, 79.1, 76.4, 73.3, 62.5, 57.6, 55.6, 37.5, 14.0; IR (neat) cm^{-1}: 2935, 1769, 1741, 1516, 1254, 1032, 704; MS (EI) *m/z* (rel intensity) 399 (M^+, 40), 308 (100), 264 (90), 232 (90), 191 (30), 151 (30), 135 (20); HRMS (EI) *m/z* Calcd for $C_{22}H_{25}NO_6$ (M^+): 399.1682 Found 399.1681; Anal. Calcd for $C_{22}H_{25}NO_6$: C, 66.15; H, 6.31; N, 3.51 Found C, 65.85; H, 6.38; N, 3.28; HPLC conditions: Daicel Chiralpak AD-H, hexane:2-propanol=85:15, flow 1.0 mL/min, t_R=33 (minor), 40 (major) min.

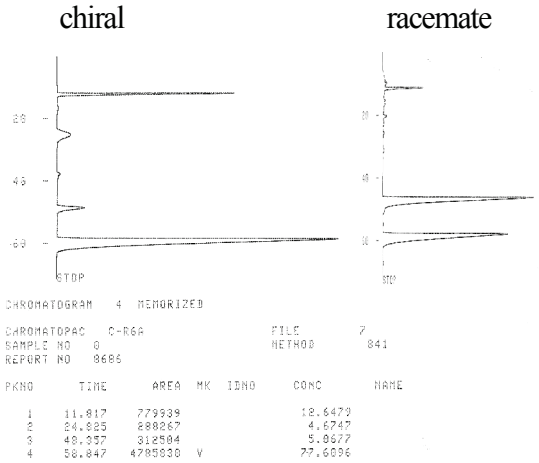
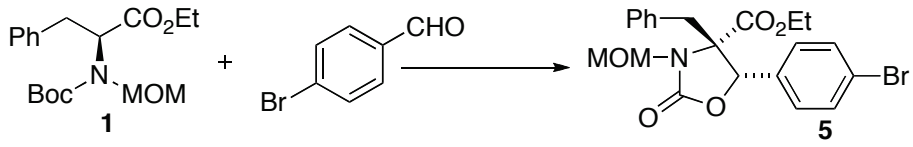


Table 2, entry 4



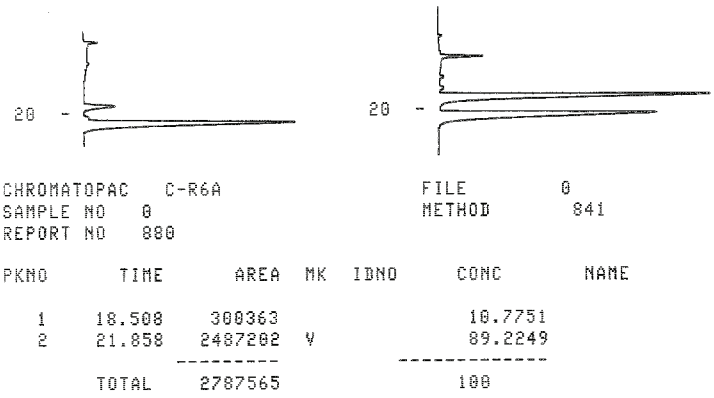
A mixture of **1** (84 mg, 0.25 mmol) and *p*-bromobenzaldehyde (231 mg, 1.25 mmol) was dissolved in toluene (4.5 mL) and the resulting mixture was cooled to –50 ˚C. KHMDS (0.37 M in *t*-BuOMe, 2.03 mL, 0.75 mmol) was added dropwise slowly to this solution. After being stirred for 6 hr at same temperature, the reaction mixture was poured into sat. NH_4Cl aq. and extracted with AcOEt. The extracts were washed with sat. $NaHCO_3$ aq. and brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was purified through flash silica gel column chromatography (hexane/1,4-dioxane=5/1) to give an oil, which was further purified by PTLC (hexane/AcOEt=3/1) to obtain **5** (72 mg, 64%, 78% ee).

5:**Ethyl 4-benzyl-5-(4-bromophenyl)-3-(methoxymethyl)-2-oxooxazolidine-4-carboxylate**

Colorless oil; $[\alpha]_D^{20}$ –23 (*c* 1.1, $CHCl_3$, 78% ee); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J*=8.2 Hz, 2H), 7.42-7.33 (m, 5H), 7.12 (d, *J*=8.2 Hz, 2H), 5.32 (s, 1H), 4.83 (ABq, $\Delta\upsilon_{AB}$=0.30 Hz *J*=11.4 Hz, 2H), 3.77 (q, *J*=6.8 Hz, 2H), 3.49 (ABq, $\Delta\upsilon_{AB}$=0.024 Hz *J*=15.6 Hz, 2H), 3.42 (s, 3H), 0.99 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 158.3, 134.2, 133.6, 131.9, 131.5, 129.4, 128.3, 128.1, 123.5, 78.4, 76.4, 72.9, 62.7, 57.8, 37.5, 14.0; IR (neat) cm^{-1}: 2935, 1773, 1739, 1373, 1232 1081, 1040, 704; MS (EI) *m/z* (rel intensity) 449

(M^+, ^{81}Br, 3), 447 (M^+, ^{79}Br, 3), 376 (15), 374 (20), 358 (95), 356 (100), 282 (20), 280 (20), 91 (80); HRMS (EI) *m/z* Calcd for $C_{21}H_{22}BrNO_5$ (M^+): 447.0681 Found 447.0682; Anal. Calcd for $C_{21}H_{22}BrNO_5$: C, 56.26; H, 4.95; N, 3.12 Found C, 56.51; H, 5.17; N, 3.06; HPLC conditions: Daicel Chiralcel OD-H, hexane: 2-propanol=90:10, flow 0.7 mL/min, t_R=18 (minor), 22 (major) min.

chiral racemate



CHROMATOPAC C-R6A
SAMPLE NO 0
REPORT NO 880

FILE 0
METHOD 841

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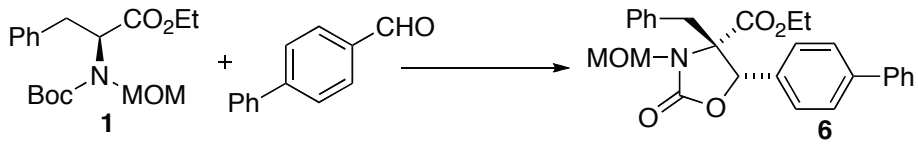
Table 2, entry 5

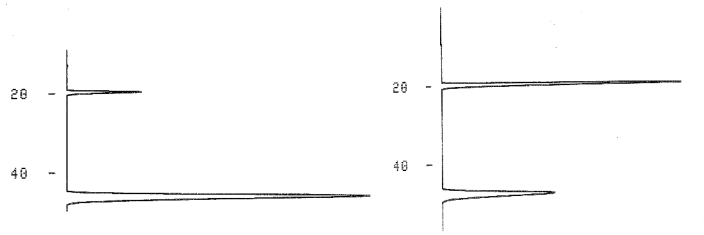


A mixture of **1** (84 mg, 0.25 mmol) and *p*-phenylbenzaldehyde (228 mg, 1.25 mmol) was dissolved in toluene (4.5 mL) and the resulting mixture was cooled to –50 ˚C. KHMDS (0.37 M in *t*-BuOMe, 2.03 mL, 0.75 mmol) was added slowly. After being stirred for 12 hr at same temperature, the reaction mixture was poured into sat. NH_4Cl aq. and extracted with AcOEt. The extracts were washed with sat. $NaHCO_3$ aq. and brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was purified through flash silica gel column chromatography (hexane/AcOEt=6/1) to give an oil, which was further purified by PTLC (hexane/AcOEt=4/1) to obtain **6** (106 mg, 95%, 80% ee).

6:**Ethyl 4-benzyl-5-(biphenyl-4-yl)-3-(methoxymethyl)-2-oxooxazolidine-4-carboxylate**

Colorless oil; $[\alpha]_D^{20}$ –58 (*c* 1.0, $CHCl_3$, 85% ee); ^1H NMR (400 MHz, $CDCl_3$): δ 7.59-7.55 (m, 4H), 7.47-7.32 (m, 10H), 5.43 (s, 1H), 4.85 (ABq, $\Delta\upsilon_{AB}$=0.31 Hz *J*=11.4 Hz, 2H), 3.75 (q, *J*=7.3 Hz, 2H), 3.54 (ABq, $\Delta\upsilon_{AB}$=0.043 Hz *J*=15.1 Hz, 2H), 3.48 (s, 3H), 0.95 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 158.6, 142.3, 140.6, 134.4, 133.5, 131.6, 129.4, 129.3, 128.2, 128.1, 127.5, 127.4, 126.9, 79.0, 76.5, 73.3, 62.6, 57.8, 37.6, 14.0; IR (neat) cm^{-1}: 2933, 1772, 1739, 1373, 1233, 1082, 1038, 764, 700; MS (EI) *m/z* (rel intensity) 445 (M^+, 10), 354 (100), 310 (20), 278 (95), 165 (30), 91 (40); HRMS (EI) *m/z* Calcd for $C_{27}H_{27}NO_5$ (M^+): 445.1889 Found 445.1882; Anal. Calcd for $C_{27}H_{27}NO_5$: C, 72.79; H, 6.11; N, 3.14 Found C, 72.59; H, 6.30; N, 3.06; HPLC conditions: Daicel Chiralpak AD-H, hexane:2-propanol=80:20, flow 1.0 mL/min, t_R=20 (minor), 47 (major) min.

chiral racemate



CHROMATOPAC C-R6A FILE
SAMPLE NO 0 METHOD 841
REPORT NO 1034

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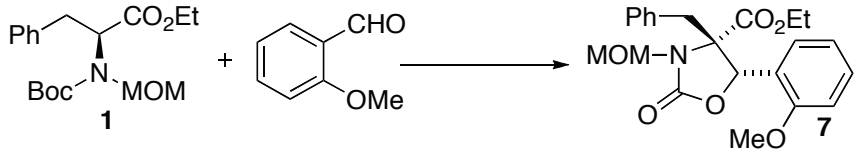
2	46.075	11606530			89.7933	
	TOTAL	12925832			100	

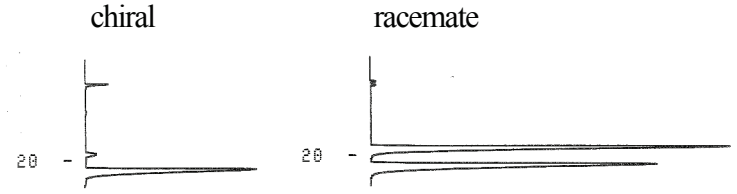
Table 2, entry 6



o-Anisaldehyde (0.15 mL, 1.25 mmol) was added to a solution of **1** (84 mg, 0.25 mmol) in *t*-BuOMe (1.5 mL) and the mixture was cooled to –50 ˚C and KHMDS (0.44 M in toluene, 1.70 mL, 0.75 mmol) was added slowly. After being stirred for 12 hr at same temperature, the reaction mixture was poured into sat. NH_4Cl aq. and extracted with AcOEt. The extracts were washed with sat. $NaHCO_3$ aq. and brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was purified through flash silica gel column chromatography (hexane/AcOEt=7/1) to give an oil, which was further purified by PTLC (hexane/1,4-dioxane=7/1) to obtain **7** (67 mg, 67%, 89% ee).

7:**Ethyl 4-benzyl-3-(methoxymethyl)-5-(2-methoxyphenyl)-2-oxooxazolidine-4-carboxylate**

Colorless oil; $[\alpha]_D^{20}$ +9.0 (*c* 1.1, $CHCl_3$, 89% ee); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J*=7.2 Hz, 2H), 7.39-7.26 (m, 5H), 6.95 (t, *J*=8.2 Hz, 1H), 6.87 (d, *J*=8.2 Hz, 1H), 5.86 (s, 1H), 4.81 (ABq, $\Delta\upsilon_{AB}$=0.31 Hz *J*=11.6 Hz, 2H), 3.91 (s, 3H), 3.61 (q of ABq, $\Delta\upsilon_{AB}$=0.095 Hz J_{AB}=10.8 Hz, J_{AX}=7.2 Hz, 2H), 3.55 (ABq, $\Delta\upsilon_{AB}$=0.27 Hz *J*=15.4 Hz, 2H), 3.42 (s, 3H), 0.92 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 158.7, 156.7, 135.1, 131.6, 130.3, 129.0, 127.8, 127.8, 124.2, 120.9, 110.5, 76.3, 75.3, 73.0, 62.3, 57.7, 55.6, 37.6, 13.9; IR (neat) cm^{-1}: 2937, 1768, 1738, 1495, 1378, 1250, 1036, 756, 704; MS (EI) *m/z* (rel intensity) 399 (M^+, 10), 368 (10), 308 (100), 276 (10), 264 (10), 232 (40), 151 (20), 135 (10); HRMS (EI) *m/z* Calcd for $C_{22}H_{25}NO_6$ (M^+): 399.1682 Found 399.1675; Anal. Calcd for $C_{22}H_{25}NO_6$: C, 66.15; H, 6.31; N, 3.51 Found C, 66.00; H, 6.31; N, 3.39; HPLC conditions: Daicel Chiralcel OD-H, hexane:2-propanol=95: 5, flow 0.8 mL/min, t_R=20 (minor), 23 (major) min.



CHROMATOPAC C-R6A FILE 0
SAMPLE NO 0 METHOD 841
REPORT NO 940

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
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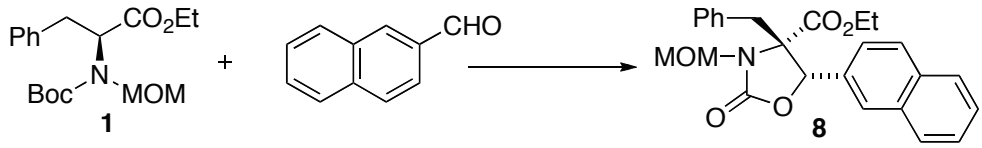
2	19.158	57656	V		5.4654	
3	22.475	948395	V		89.9015	
	TOTAL	1054926			100	

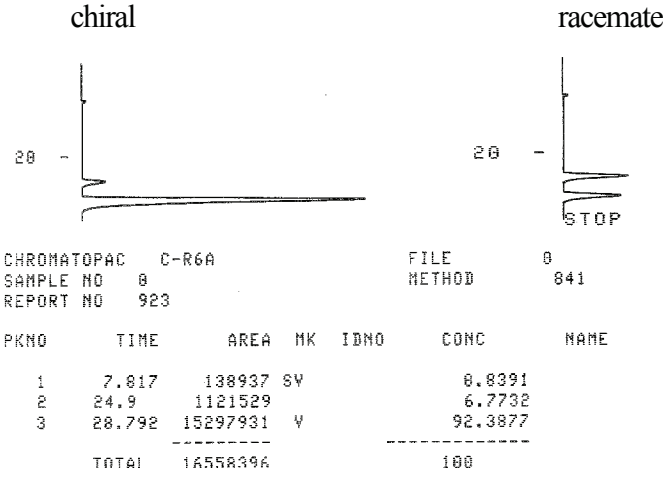
Table 2, entry 7



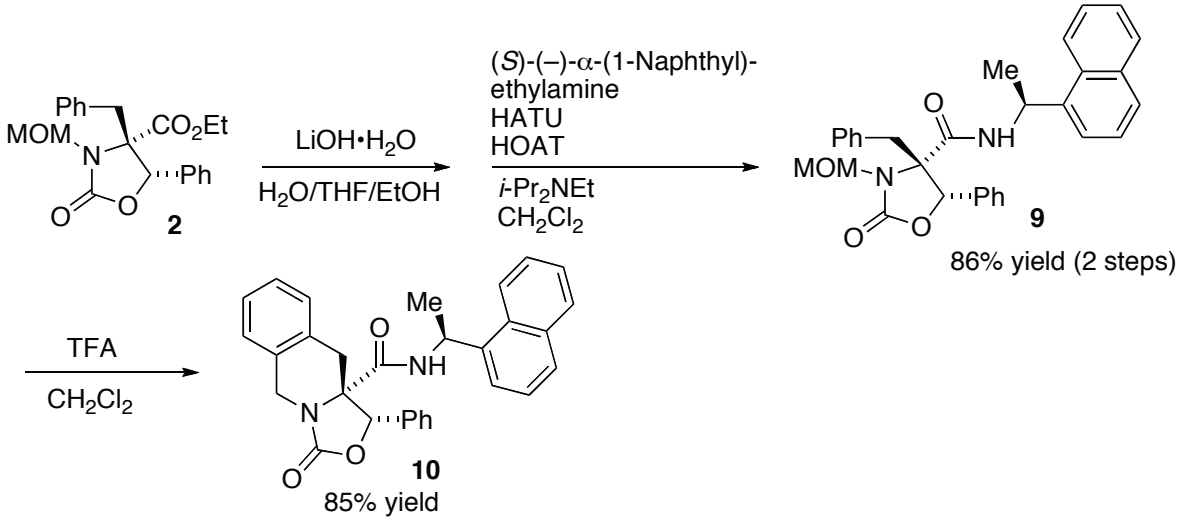
A mixture of **1** (84 mg, 0.25 mmol) and 2-naphthaldehyde (195 mg, 1.25 mmol) was dissolved in toluene (4.5 mL) and the resulting mixture was cooled to –50 ˚C. KHDMS (0.37 M in *t*-BuOMe, 2.03 mL, 0.75 mmol) was added slowly to this solution. After being stirred for 6 hr at same temperature, the reaction mixture was poured into sat. NH_4Cl aq. and extracted with AcOEt. The extracts were washed with sat. $NaHCO_3$ aq. and brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was purified through flash silica gel column chromatography (hexane/AcOEt=3/1) to give an oil, which was further purified by PTLC (hexane/1,4-dioxane=5/1) to obtain **8** (46 mg, 44%, 86% ee).

8:**Ethyl 4-benzyl-3-(methoxymethyl)-5-(naphthalen-2-yl)-2-oxooxazolidine-4-carboxylate**

Colorless oil; $[\alpha]_D^{20}$ –59 (*c* 1.0, $CHCl_3$, 86% ee); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.78 (m, 3H), 7.72 (s, 1H), 7.52-7.47 (m, 4H), 7.44-7.32 (m, 4H), 5.56 (s, 1H), 4.86 (ABq, $\Delta\upsilon_{AB}$=0.32 Hz *J*=11.6 Hz, 2H), 3.60 (q, *J*=7.2 Hz, 2H), 3.57 (ABq, $\Delta\upsilon_{AB}$=0.087 Hz *J*=15.6 Hz, 2H), 3.48 (s, 3H), 0.79 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 158.7, 134.5, 133.7, 133.1, 131.8, 131.6, 129.4, 128.5, 128.5, 128.2, 128.1, 127.1, 127.1, 126.1, 123.6, 79.3, 76.5, 73.3, 62.6, 57.8, 37.8, 13.8; IR (neat) cm^{-1}: 2934, 1771, 1739, 1376, 1227, 1083, 1040, 704; MS (EI) *m/z* (rel intensity) 419 (M^+, 30), 284 (20), 270 (20), 252 (60), 91 (60); HRMS (EI) *m/z* Calcd for $C_{25}H_{25}NO_5$ (M^+): 419.1733 Found 419.1749; Anal. Calcd for $C_{25}H_{25}NO_5$: C, 71.58; H, 6.01; N, 3.34 Found C, 71.48; H, 6.12; N, 3.24; HPLC conditions: Daicel Chiralcel OD-H, hexane:2-propanol=90:10, flow 0.5 mL/min, t_R=25 (minor), 29 (major) min.



Determination of Absolute configuration



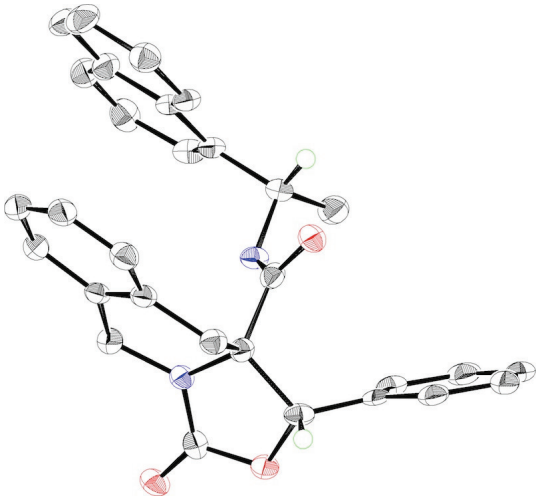
LiOH•H_2O (82 mg, 1.95 mmol) was added to a solution of **2** (239 mg, 0.65 mmol, 85% ee) in H_2O/EtOH/THF (18 mL, 1/1/1, v/v/v) at 0 ˚C. The resulting mixture was warmed to 50 ˚C and stirred for 3 hr. After being cooled to rt, the mixture was diluted with AcOEt and 1 M HCl was added. The aqueous layer was extracted with AcOEt and the extracts were washed with brine and dried over Na_2SO_4, filtered, and concentrated. The residue was dissolved in CH_2Cl_2 (6.5 mL) and cooled to 0 ˚C. To this solution were added *O*-(7-azabenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HATU, 373 mg, 0.98 mmol), 1-hydroxy-7-benzotriazole (HOAT, 133 mg, 0.98 mmol), (*S*)-(–)-α-(1-naphthyl)ethylamine (0.21 mL, 1.30 mmol), and *i*-Pr_2NEt (0.34 mL, 1.95 mL), successively. After being stirred at rt for 48 hr, the mixture was diluted with AcOEt and washed with aqueous 10% citric acid solution, sat. $NaHCO_3$ aq., and brine and dried over Na_2SO_4, filtered, and concentrated. The residue was purified through flash silica gel column chromatography (hexane/AcOEt=4/1) to give **9** (277 mg, 89%). Trifluoroacetic acid (6 mL) was added to a solution of **9** (200 mg, 0.40 mmol) in CH_2Cl_2 (2.0 mL) at 0 ˚C. The resulting mixture was refluxed for 2 hr. After removal of volatiles, the residue was purified through flash silica gel column chromatography (hexane/AcOEt=3/1) to give **10** (157 mg, 85%) as colorless crystals.

10:(1*S*,10*aS*)-*N*-((*S*)-1-(naphthalen-1-yl)ethyl)-3-oxo-1-phenyl-3,5,10,10a-tetrahydro-1H-oxazolo[3,4-b]-isoquinoline-10a-carboxamide

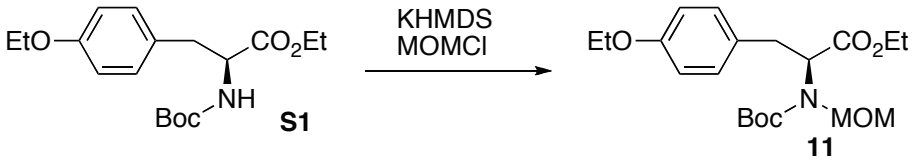
Colorless crystal; mp. 210-213 ˚C (recrystallized from 1,4-dioxane/petroleum ether) $[\alpha]_D^{20}$ +15.0 (*c* 0.39, $CHCl_3$, >99% ee); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J*=8.3 Hz, 1H), 7.73 (d, *J*=8.3 Hz, 1H), 7.46-7.43 (m,

3H), 7.39-7.31 (m, 4H), 7.25-7.21 (m, 2H), 7.18-7.14 (m, 3H), 6.91-6.87 (m, 1H), 6.62 (d, *J*=7.8 Hz, 1H), 5.84 (br d, *J*=7.8 Hz, 1H), 5.54 (s, 1H), 5.22 (dq, *J*=7.3 Hz, 6.8 Hz, 1H), 4.64 (d, *J*=17.0 Hz, 1H), 4.06 (d, *J*=14.7 Hz, 1H), 3.59 (d, *J*=17.0 Hz, 1H), 3.08 (d, *J*=14.7 Hz, 1H), 0.80 (d, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 158.7, 136.8, 135.3, 134.1, 131.3, 131.2, 130.1, 130.0, 129.7, 129.2, 129.1, 127.7, 127.6, 127.1, 126.7, 126.6, 126.1, 125.3, 123.1, 123.0, 84.1, 68.4, 45.09, 44.0, 18.2; IR (neat) cm^{-1}: 2925, 1754, 1668, 1401, 1220, 1004, 776; MS (EI) *m/z* (rel intensity) 431 (M^+, 20), 264 (80), 263 (40), 220 (100), 218 (30), 155 (20); HRMS (EI) *m/z* Calcd for $C_{30}H_{26}N_2O_3$ (M^+): 462.1943 Found 462.1941.

Crystal data for **10**+[1/2 1,4-dioxane], found $C_{32}H_{30}N_2O_4$, FW=506.58, T=103 (2) K, Wavelength 0.71069 Å Crystal system triclinic, Space group *P*1 (#1), Unit cell dimensions a=9.1521 (3) Å α=97.7195 (13)°. b=14.3285 (4) Å β=97.2737 (19)°. c=20.2138 (6) Å γ=89.468 (2)°. Volume=2605.51 (14) $Å^3$, *Z*=4, Density (calculated)=1.291 Mg/m^3, Absorption coefficient=0.085 mm^{-1}, F (000)=1072, Crystal size=0.35 x 0.10 x 0.05 mm^3, Reflections collected 23140, Independent reflections 17122 [R (int)=0.0499], Completeness to theta=25.50° 99.4 %, Final R indices [I>2sigma (I)] R_1=0.0551, wR_2=0.1210 R indices (all data) R_1=0.0762, wR_2=0.1297. CCDC 867310 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request/cif.



Preparation of precursor **11**



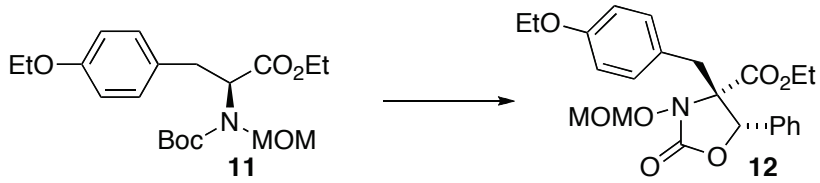
KHMDS (0.32 M in THF, 8.31 mL, 2.66 mmol) was added dropwise slowly to a solution of known **S1** (1.0 g, 2.96 mmol) at –78 ˚C. The resulting mixture was stirred for 30 min and MOMCl (0.90 mL, 11.8 mmol) was added slowly. After being stirred for 17 hr, the reaction mixture was poured into sat. NH_4Cl aq. and extracted with AcOEt. The extracts were washed with sat. $NaHCO_3$ aq. and brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was purified through flash silica gel column chromatography (hexane/1,4-dioxane=20/1) to give **11** (870 mg, 86%, >99% ee).

A 2/3 mixture of rotamers of **11:(*S*)-Ethyl 2-(*tert*-butoxycarbonyl(methoxymethyl)amino)-3-(4-ethoxyphenyl)propanoate**

Colorless oil; $[\alpha]_D^{20}$ –127 (*c* 0.96, $CHCl_3$, >99% ee); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09, 7.06 (two d, *J*=8.7

Hz and *J*=8.7 Hz, ratio=2:3, 2H), 6.80 (d, *J*=8.7 Hz, 2H), 4.73, 4.60 (two d, *J*=11.0 Hz and *J*=11.0 Hz, ratio=3:2, 2H), 4.27-4.12 (m, 2.4 H), 4.07 (dd, *J*=11.0 Hz, 5.0 Hz, 3/5 H), 4.02-3.97 (m, 12/5 H), 3.81 (d, *J*=11.0 Hz, 3/5H), 3.32, 3.28 (two d, *J*=5.0 Hz and *J*=5.0 Hz, ratio=2:3, 1H), 3.25-3.06 (m, 1H), 3.23, 3.17 (two s, ratio=3:2, 3H), 1.49, 1.48 (two s, ratio=3:2, 9H), 1.40 (t, *J*=7.3 Hz, 3H), 1.30, 1.25 (two t, *J*=7.3 Hz and *J*=7.3 Hz, ratio=3:2, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 158.0 and 157.9 (rotamer), 155.3 and 154.7 (rotamer), 130.6, 130.4 and 130.2 (rotamer), 114.9 and 114.7 (rotamer), 81.5 and 81.1 (rotamer), 79.8, 63.7, 61.1 and 61.4 (rotamer), 61.2 and 60.9 (rotamer), 56.2 and 55.8 (rotamer), 35.7 and 34.8 (rotamer), 28.6, 15.2, 14.5; IR (neat) cm^{-1}: 2930, 1740, 1705, 1512, 1243, 1175, 1091, 913, 863; MS (EI) *m/z* (rel intensity) 381 (M^+, 10), 276 (10), 250 (20), 220 (100), 135 (90), 107 (50), 57 (50); HRMS (EI) *m/z* Calcd for $C_{20}H_{31}NO_6$ (M^+): 381.2151 Found 381.2160 Anal. Calcd for $C_{20}H_{31}NO_6$: C, 62.97; H, 8.91; N, 3.67 Found C, 62.88; H, 8.22; N, 3.85; HPLC conditions: Daicel Chiralcel OD-H, hexane:2-propanol=98:2, flow 0.4 mL/min, t_R=18 (*R*), 20 (*S*) min.

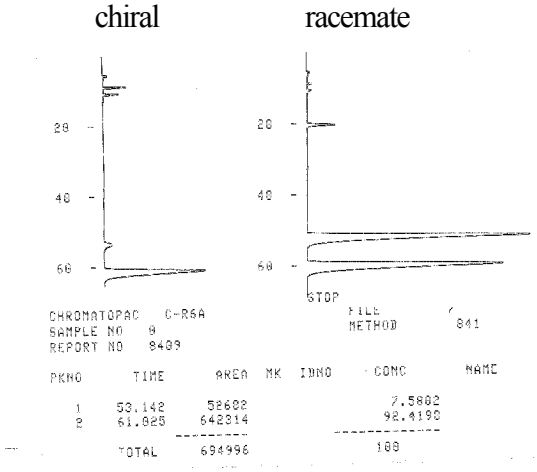
Procedure for aldol reaction between **11** and benzaldehyde



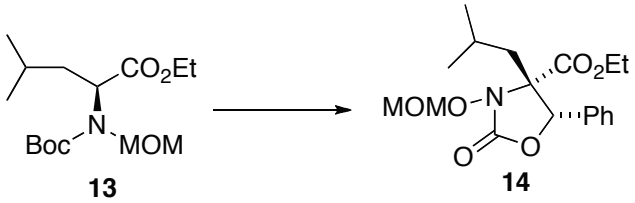
Benzaldehyde (0.13 mL, 1.25 mmol) was added to a solution of **11** (95 mg, 0.25 mmol) in *t*-BuOMe (1.5 mL) and the mixture was cooled to – 40 ˚C and KHMDS (0.39 M in toluene, 1.92 mL, 0.75 mmol) was added dropwise slowly. After being stirred for 6 hr at same temperature, the reaction mixture was poured into sat. NH_4Cl aq. and extracted with AcOEt. The extracts were washed with sat. $NaHCO_3$ aq. and brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was purified through flash silica gel column chromatography (hexane/Et_2O=1/1) to give an oil, which was further purified by PTLC (hexane/1,4-dioxane=4/1) to obtain **12** (98 mg, 95%, 85% ee).

12:**Ethyl 4-(4-ethoxybenzyl)-3-(methoxymethyl)-2-oxo-5-phenyloxazolidine-4-carboxylate**

Colorless oil; $[\alpha]_D^{20}$ –6.6 (*c* 1.2, $CHCl_3$, 91% ee); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.30 (m, 5H), 7.09 (ABq, $\Delta\upsilon_{AB}$=0.37 Hz *J*=8.4 Hz, 4H), 5.39 (s, 1H), 4.82 (ABq, $\Delta\upsilon_{AB}$=0.32 Hz *J*=11.4 Hz, 2H), 4.04 (q, *J*=7.2 Hz, 2H), 3.70 (q, *J*=7.6 Hz, 2H), 3.46 (s, 3H), 3.44 (ABq, $\Delta\upsilon_{AB}$=0.043 Hz *J*=15.6 Hz, 2H), 1.42 (t, *J*=7.2 Hz, 3H), 0.93 (t, *J*=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 158.8, 158.6, 134.6, 132.5, 129.3, 128.7, 126.4, 125.9, 115.1, 79.0, 76.3, 73.3, 63.8, 62.4, 57.6, 36.7, 15.2, 13.9; IR (neat) cm^{-1}: 2934, 1770, 1739, 1513, 1248, 913, 733; MS (EI) *m/z* (rel intensity) 413 (M^+, 20), 382 (5), 278 (10), 202 (5), 135 (100), 107 (60); HRMS (EI) *m/z* Calcd for $C_{23}H_{27}NO_6$ (M^+): 413.1838 Found 413.1844; Anal. Calcd for $C_{23}H_{27}NO_6$: C, 66.81; H, 6.58; N, 3.39 Found C, 66.80; H, 6.68; N, 3.34; HPLC conditions: Daicel Chiralpak AD-H, hexane: 2-propanol=90:10, flow 0.6 mL/min, t_R=53 (minor), 59 (major) min.



Procedure for aldol reaction between **13** and benzaldehyde

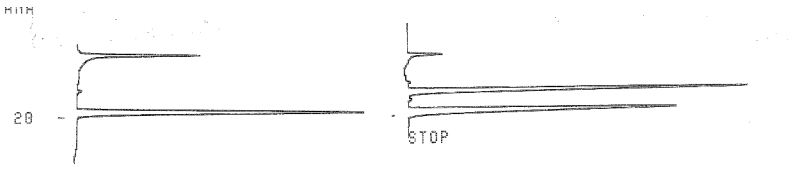


Benzaldehyde (0.13 mL, 1.25 mmol) was added to a solution of **13** (76 mg, 0.25 mmol) in *t*-BuOMe (1.5 mL) and the mixture was cooled to –40 ˚C and KHMDS (0.44 M in toluene, 1.70 mL, 0.75 mmol) was added dropwise slowly. After being stirred for 12 hr at same temperature, the reaction mixture was poured into sat. NH_4Cl aq. and extracted with AcOEt. The extracts were washed with sat. $NaHCO_3$ aq. and brine, and dried over Na_2SO_4, filtered, and concentrated. The residue was purified through flash silica gel column chromatography (hexane/AcOEt=6/1) to give an oil, which was further purified by PTLC (hexane/1,4-dioxane=4/1) to obtain **14** (70 mg, 83%, 94% ee).

14:**Ethyl 4-isobutyl-3-(methoxymethyl)-2-oxo-5-phenyloxazolidine-4-carboxylate**

Colorless oil; $[\alpha]_D^{20}$ +19 (*c* 1.2, $CHCl_3$, 98% ee); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.30 (m, 5H), 5.58 (s, 1H), 4.74 (ABq, $\Delta\upsilon_{AB}$=0.29 Hz *J*=11.8 Hz, 2H), 3.61 (q of ABq, $\Delta\upsilon_{AB}$=0.080 Hz J_{AB}=10.8 Hz, J_{AX}=7.2 Hz, 2H), 3.42 (s, 3H), 2.08 (d of ABq, $\Delta\upsilon_{AB}$=0.18 Hz *J*=15.2 Hz, J_{AX}=6.0 Hz, 2H), 2.05 (br sept, *J*= 6.0 Hz, 1H), 1.20 (d, *J*=6.0 Hz, 3H), 1.04 (d, *J*=6.0 Hz, 3H), 0.87 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 158.8, 134.5, 129.5, 128.8, 126.4, 80.2, 76.0, 73.2, 62.2, 57.4, 40.3, 25.9, 24.5, 23.6, 13.9; IR (neat) cm^{-1}: 2960, 2940, 1772, 1740, 1455, 1374, 1229, 1082, 1029, 751, 697; MS (EI) *m/z* (rel intensity) 335 (M^+, <1), 304 (1), 278 (1), 262 (100), 232 (10), 218 (10), 186 (15); HRMS (EI) *m/z* Calcd for $C_{18}H_{25}NO_5$ (M^+): 335.1733 Found 335.1736; Anal. Calcd for $C_{18}H_{25}NO_5$: C, 64.46; H, 7.51; N, 4.18 Found C, 64.46; H, 7.64; N, 4.27; HPLC conditions: Daicel Chiralcel OD-H, hexane:2-propanol=90:10, flow 0.5 mL/min, t_R=14 (minor), 19 (major) min.

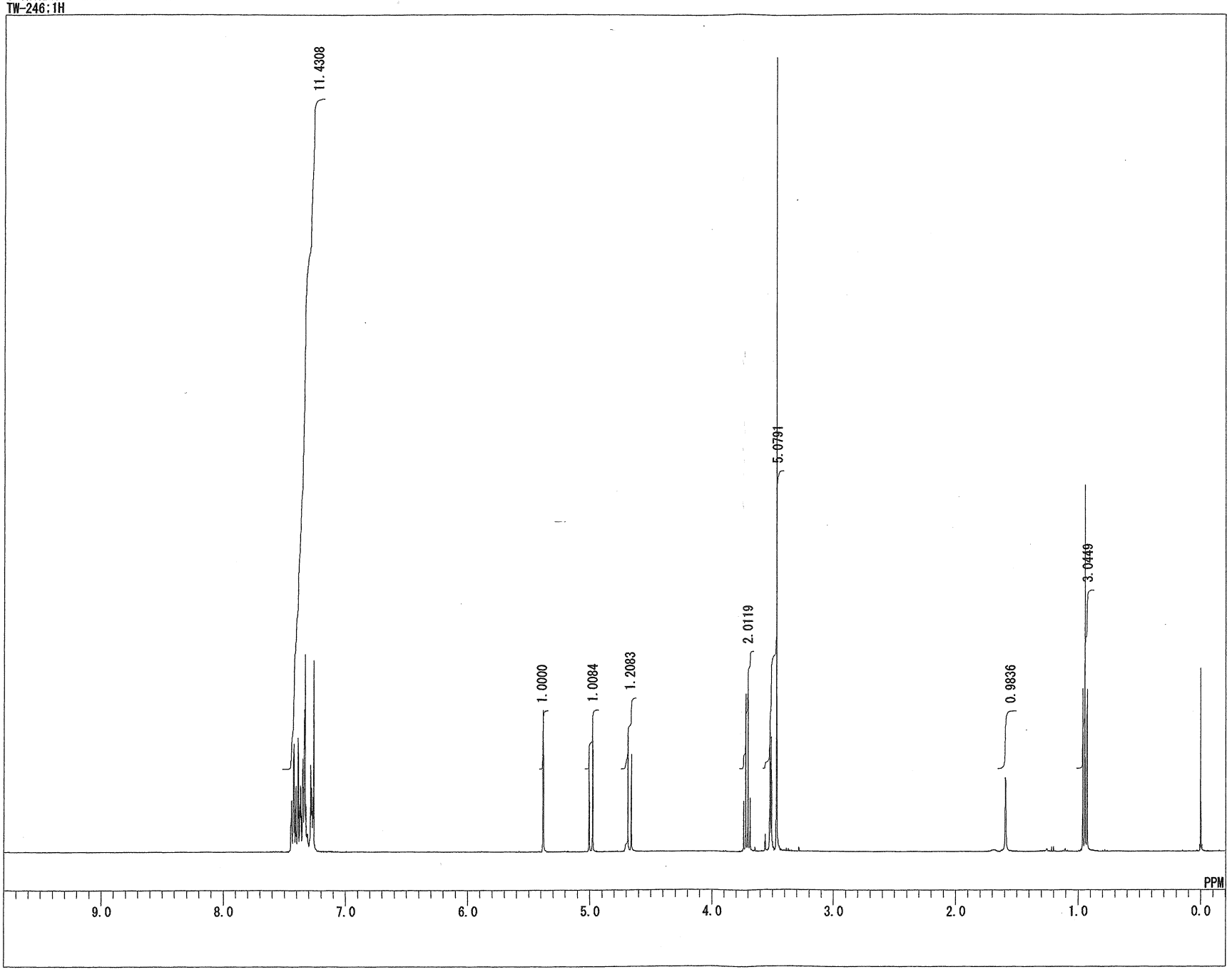
chiral racemate



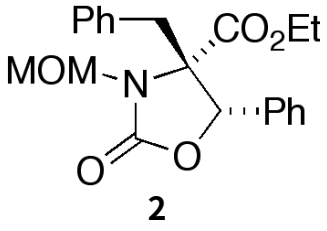
CHROMATOPAC C-R6A FILE 7
SAMPLE NO 0 METHOD 841
REPORT NO 8416

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	6.683	111042			22.748	
2	14.533	4945			1.0129	
3	19.05	372153			76.2391	
	TOTAL	488140			100	

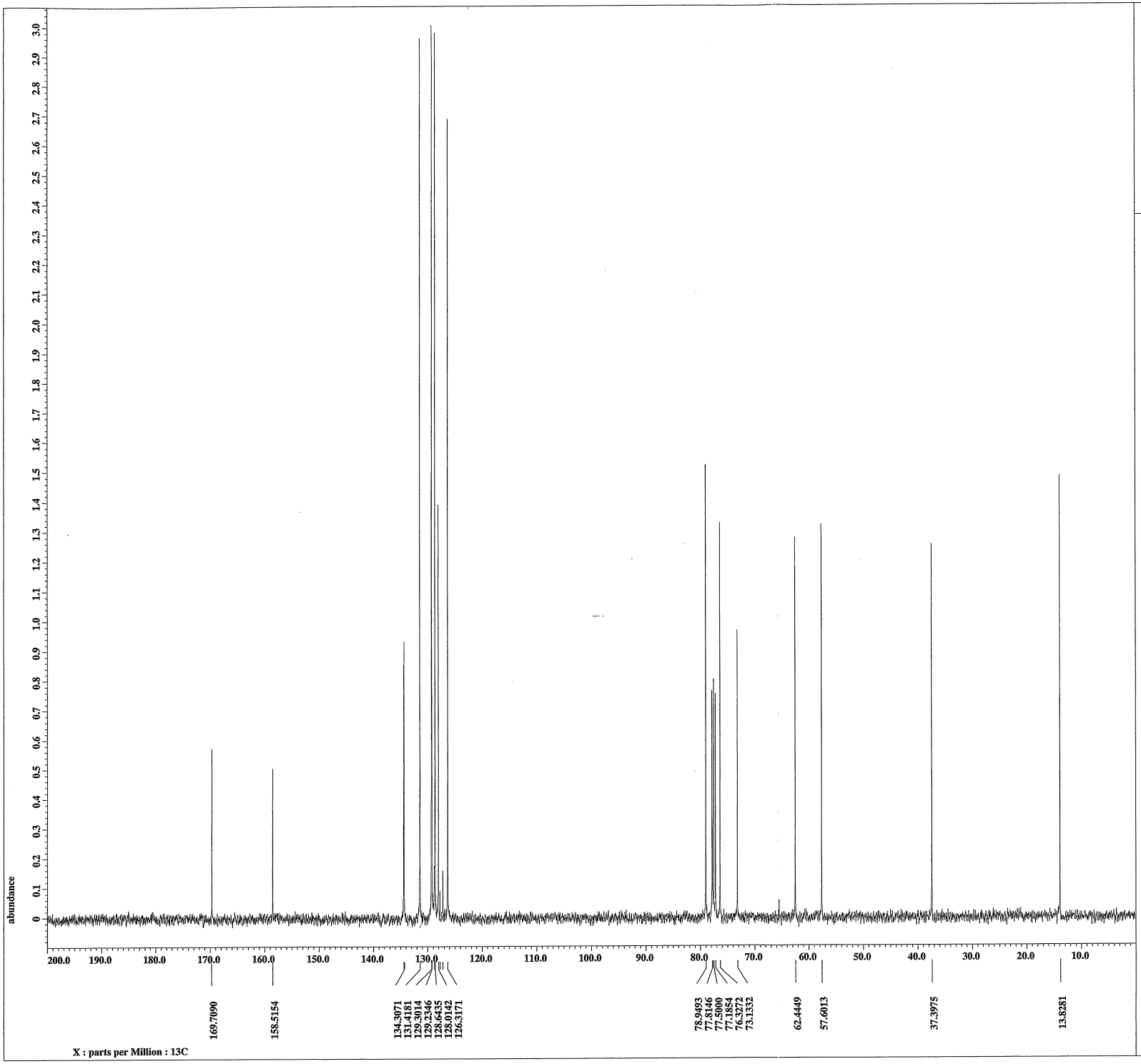
C:¥WINNMR98¥DATA¥tw246h.als
TW-246;1H




```
DFILE   C:¥WINNMR98¥DATA¥tw246h.als
COMNT   TW-246;1H
DATIM   Wed Jul 27 09:28:46 2005
OBNUC   1H
EXMOD   NON
OBFRQ       395.75 MHz
OBSET       124.00 KHz
OBFIN     10277.0 Hz
POINT       32768
FREQU       7936.5 Hz
SCANS          16
ACQTM       4.129 sec
PD         10.000 sec
PW1         5.0 us
IRNUC   1H
CTEMP       21.8 c
SLVNT   CDCL3
EXREF       0.00 ppm
BF          0.00 Hz
RGAIN          19
```

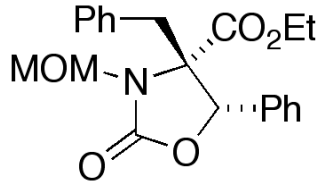


2



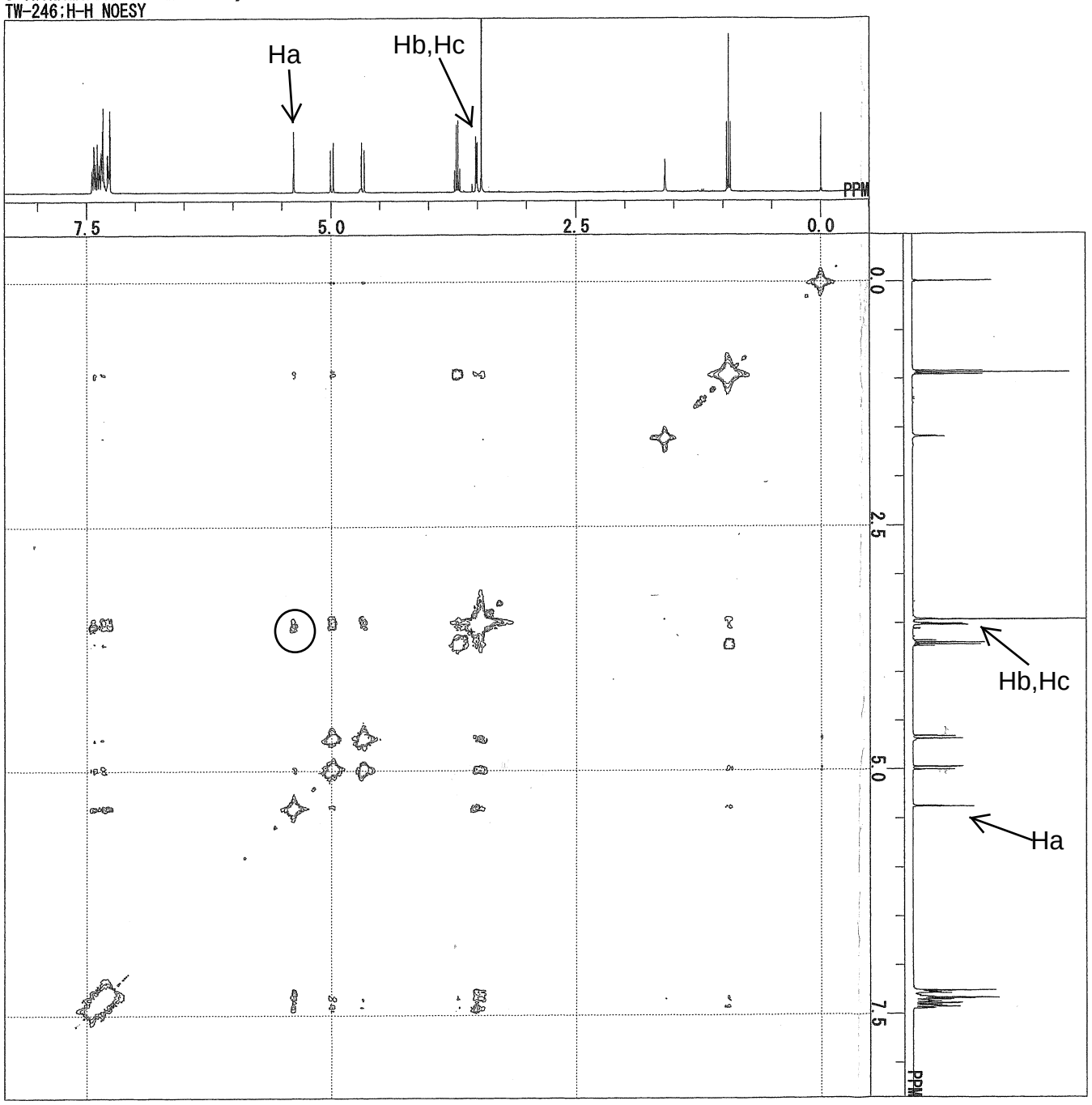

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: 13C No2-1.jdf
```

```
Filename            = 13C No2-3.jdf
Author              = delta
Experiment          = single_pulse_dec
Sample_id           = S#767267
Solvent             = CHLOROFORM-D
Creation_time       = 22-MAR-2007 16:06:00
Revision_time       = 22-MAR-2007 21:25:12
Current_time        = 22-MAR-2007 21:25:40

Content             = single pulse decouple
Data_format         = 1D COMPLEX
Dim_size            = 26214
Dim_title           = 13C
Dim_units           = [ppm]
Dimensions          = X
Site                = ECX 400P
Spectrometer        = DELTA2_NMR

Field_strength      = 9.389766[T] (400[MHz]
X_acq_duration      = 1.04333312[s]
X_domain            = 13C
X_freq              = 100.52530333[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_resolution        = 0.95846665[Hz]
X_sweep             = 31.40703518[kHz]
Irr_domain          = 1H
Irr_freq            = 399.78219838[MHz]
Irr_offset          = 5[ppm]
Clipped             = FALSE
Mod_return          = 1
Scans               = 53
Total_scans         = 53

X_90_width          = 10.2[us]
X_acq_time          = 1.04333312[s]
X_angle             = 30[deg]
X_atn               = 3.8[dB]
X_pulse             = 3.4[us]
Irr_atn_dec         = 19.8[dB]
Irr_atn_noe         = 19.8[dB]
Irr_noise           = WALTZ
Decoupling          = TRUE
Initial_wait        = 1[s]
Noe                 = TRUE
Noe_time            = 2[s]
Recvr_gain          = 58
Relaxation_delay    = 2[s]
Repetition_time     = 3.04333312[s]
Temp_get            = 18.5[dC]
```

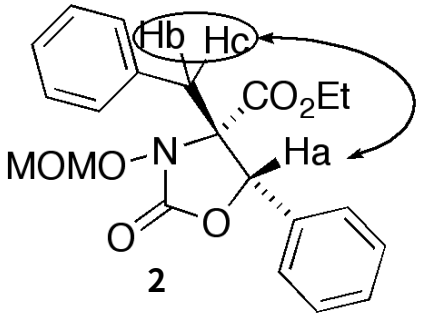


2

C:¥WINNMR98¥DATA¥tw246noesy.ALS
TW-246;H-H NOESY

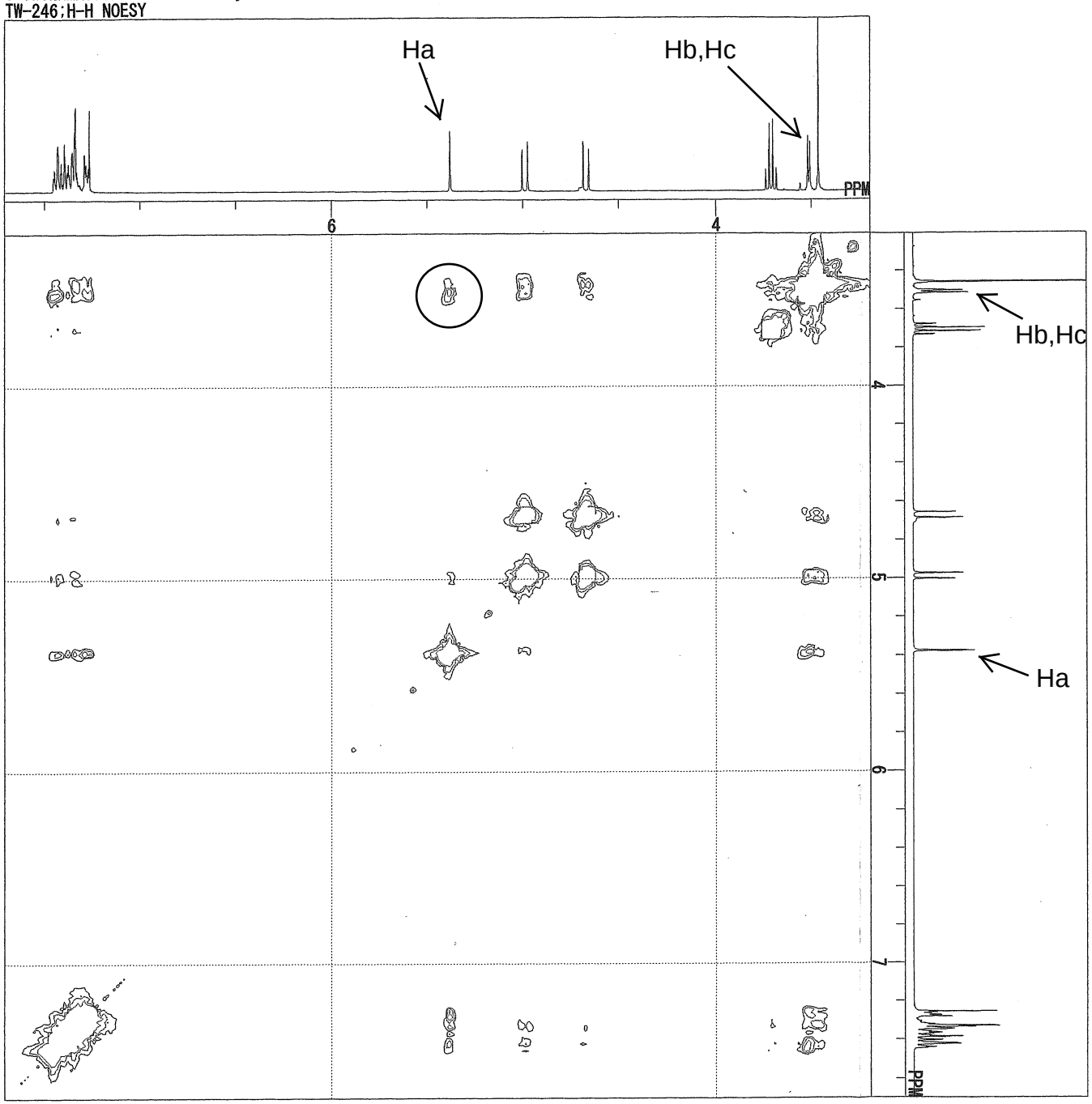



```
DFILE  C:¥WINNMR98¥DATA¥tw246noesy.ALS
COMNT  TW-246;H-H NOESY
DATIM  Wed Jul 27 13:29:18 2005
EXMOD  VNOENH
OBNUC  1H
OBFRQ       395.75 MHz
OBSET       134.00 KHz
OBFIN         77.4 Hz
POINT          512
FREQU       3500.1 Hz
CLPNT          512
TODAT          256
CLFRQ       3496.5 Hz
SCANS           16
ACQTM        0.146 sec
PD           1.500 sec
PW1           12.4 us
PW2           12.4 us
PW3           10.0 us
PI1           0.286 ms
PI2           0.286 ms
PI3         1000.00 ms
IRNUC  1H
CTEMP         21.6 c
SLVNT  CDCL3
EXREF         0.00 ppm
CLEXR         0.00 ppm
RGAIN           18
OBATN          511
LOOP1            1
```

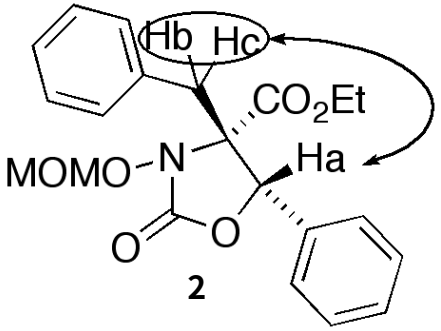


2

C:¥WINNMR98¥DATA¥tw246noesy.ALS
TW-246;H-H NOESY

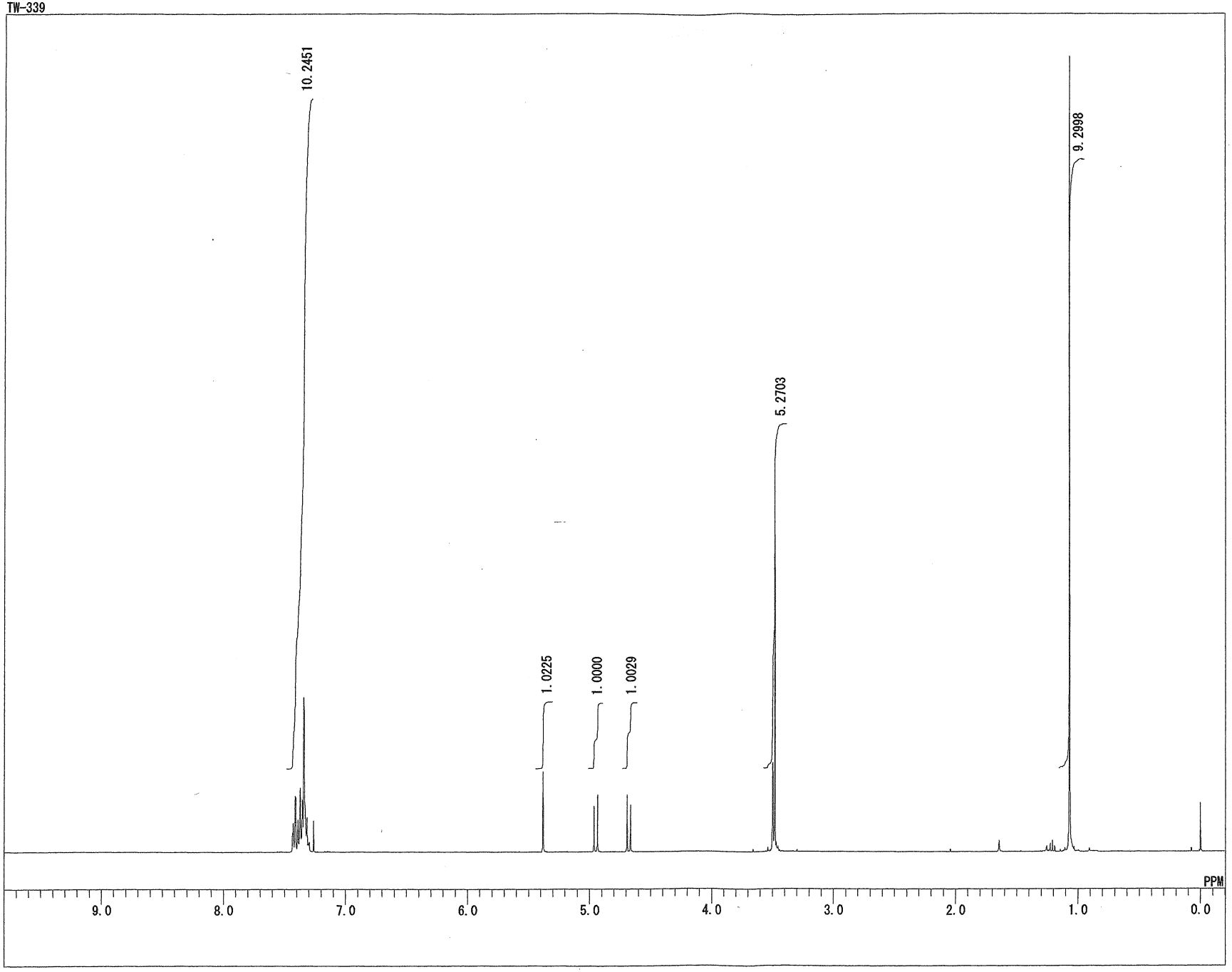


DFILE	C:¥WINNMR98¥DATA¥tw246noesy.ALS	
COMNT	TW-246;H-H NOESY	
DATIM	Wed Jul 27 13:29:18 2005	
EXMOD	VNOENH	
OBNUC	1H	
OBFRQ	395.75	MHz
OBSET	134.00	KHz
OBFIN	77.4	Hz
POINT	512	
FREQU	3500.1	Hz
CLPNT	512	
TODAT	256	
CLFRQ	3496.5	Hz
SCANS	16	
ACQTM	0.146	sec
PD	1.500	sec
PW1	12.4	us
PW2	12.4	us
PW3	10.0	us
PI1	0.286	ms
PI2	0.286	ms
PI3	1000.00	ms
IRNUC	1H	
CTEMP	21.6	c
SLVNT	CDCL3	
EXREF	0.00	ppm
CLEXR	0.00	ppm
RGAIN	18	
OBATN	511	
LOOP1	1	

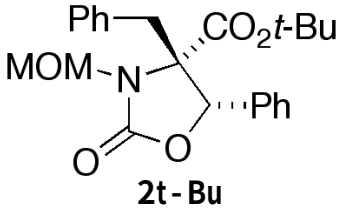


2

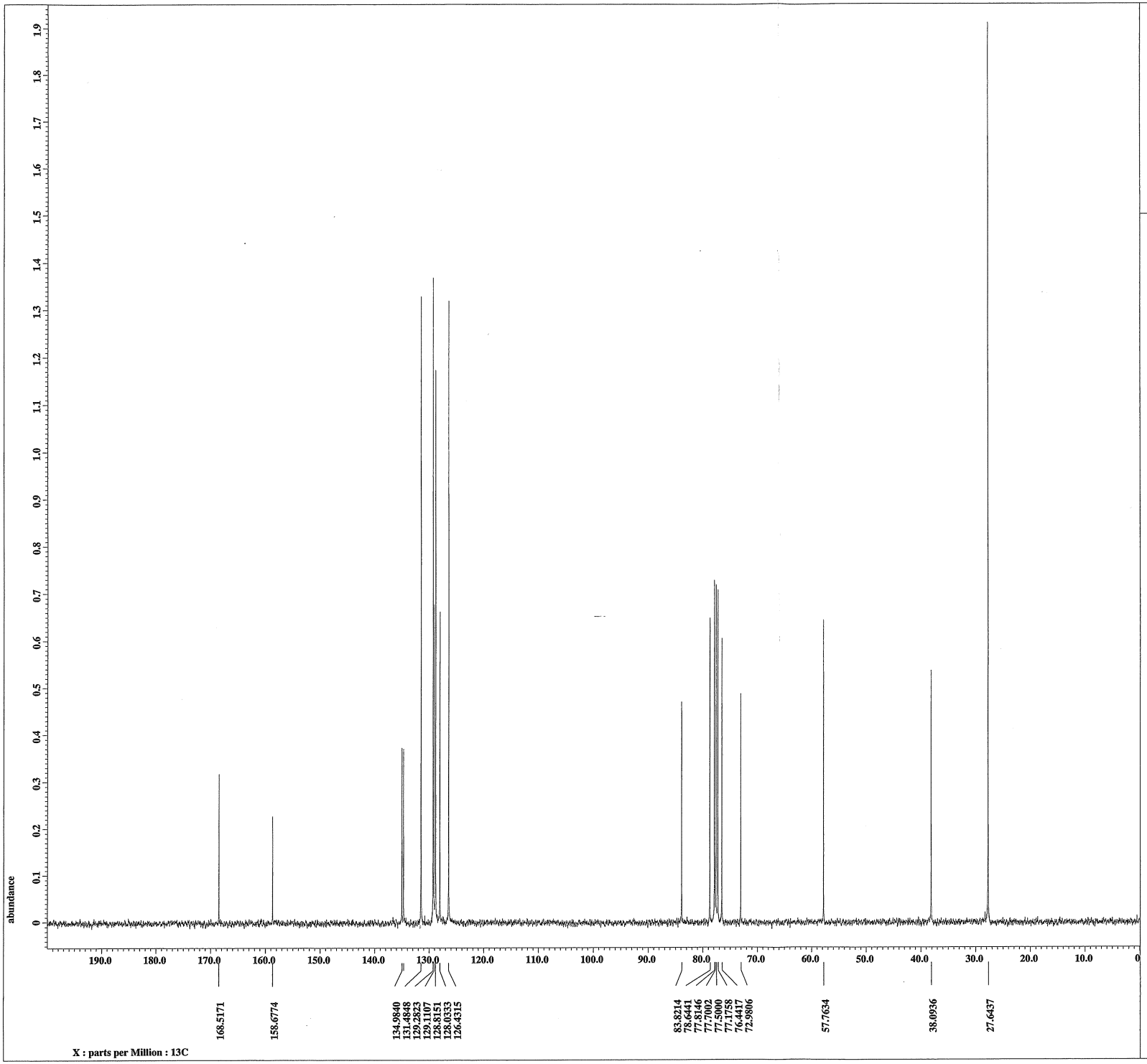
C:¥WINNMR98¥DATA¥tw339.als
TW-339



DFILE	C:¥WINNMR98¥DATA¥tw339.als
COMNT	TW-339
DATIM	Thu Feb 23 10:21:39 2006
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.0 Hz
POINT	32768
FREQU	7936.5 Hz
SCANS	16
ACQTM	4.129 sec
PD	10.000 sec
PW1	5.0 us
IRNUC	1H
CTEMP	19.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.00 Hz
RGAIN	15

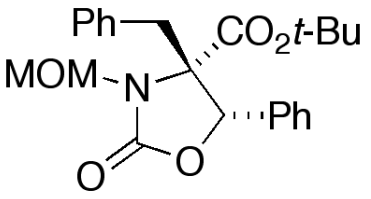


2t-Bu

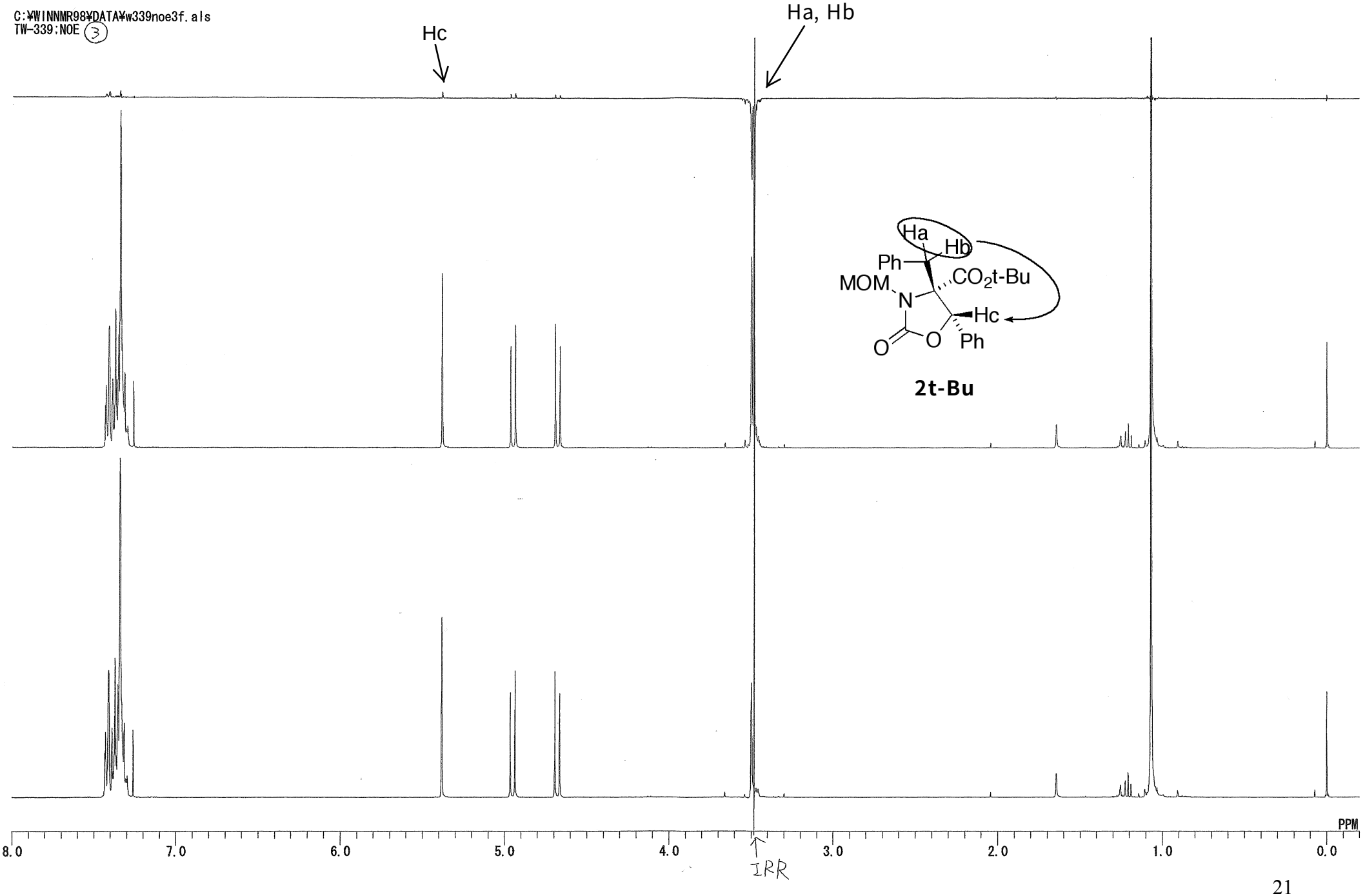



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: TW-786 13C-1.jdf
```

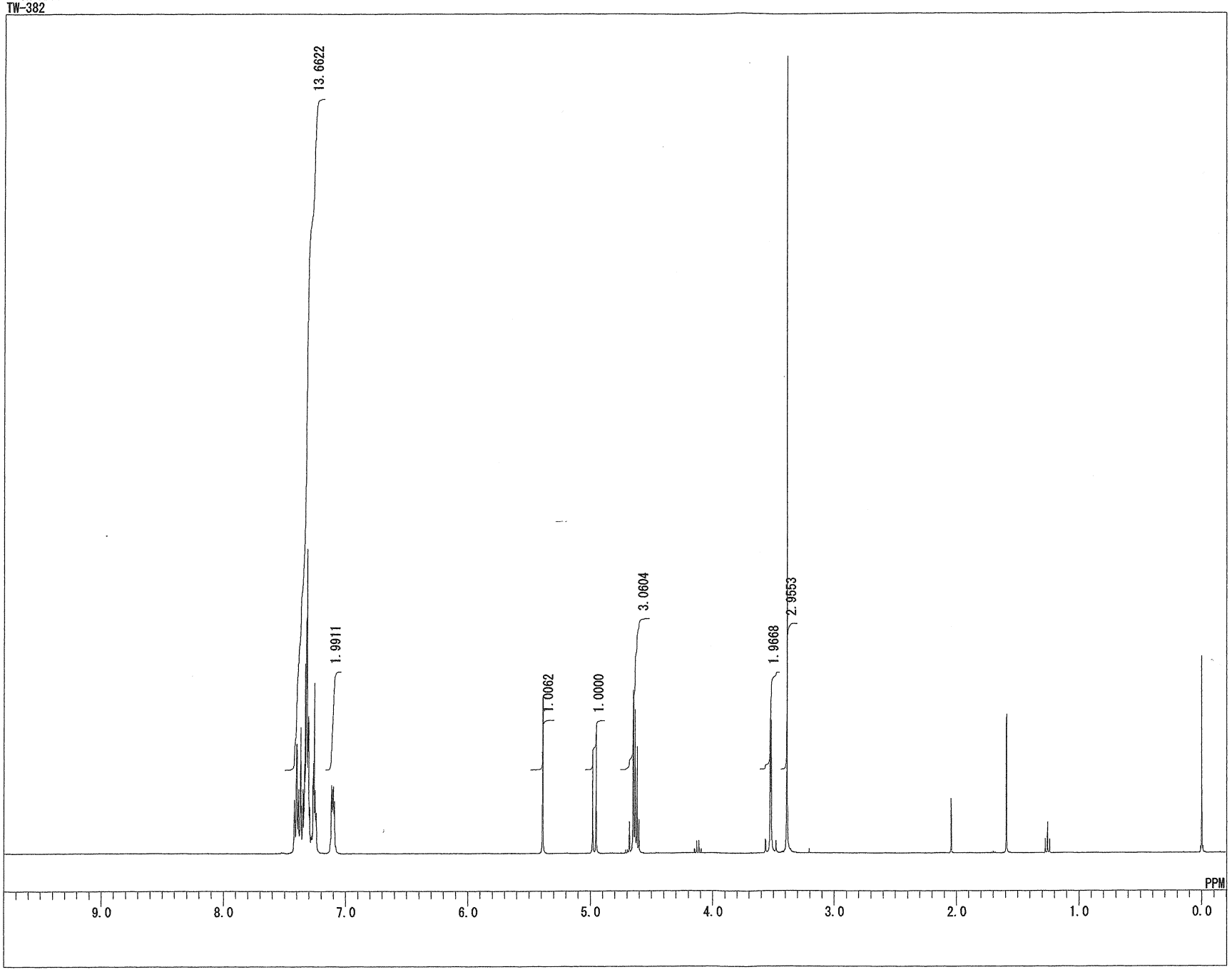
```
Filename          = TW-786 13C-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#6581
Solvent           = CHLOROFORM-D
Creation_time     = 27-MAR-2007 19:05:26
Revision_time     = 28-MAR-2007 00:25:02
Current_time      = 28-MAR-2007 00:25:40

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 236
Total_scans       = 236

X_90_width        = 10.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 3.8[dB]
X_pulse           = 3.4[us]
Irr_atn_dec       = 19.8[dB]
Irr_atn_noe       = 19.8[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 56
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 17.7[dC]
```



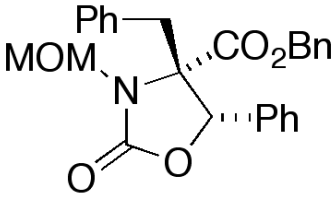
2t - Bu



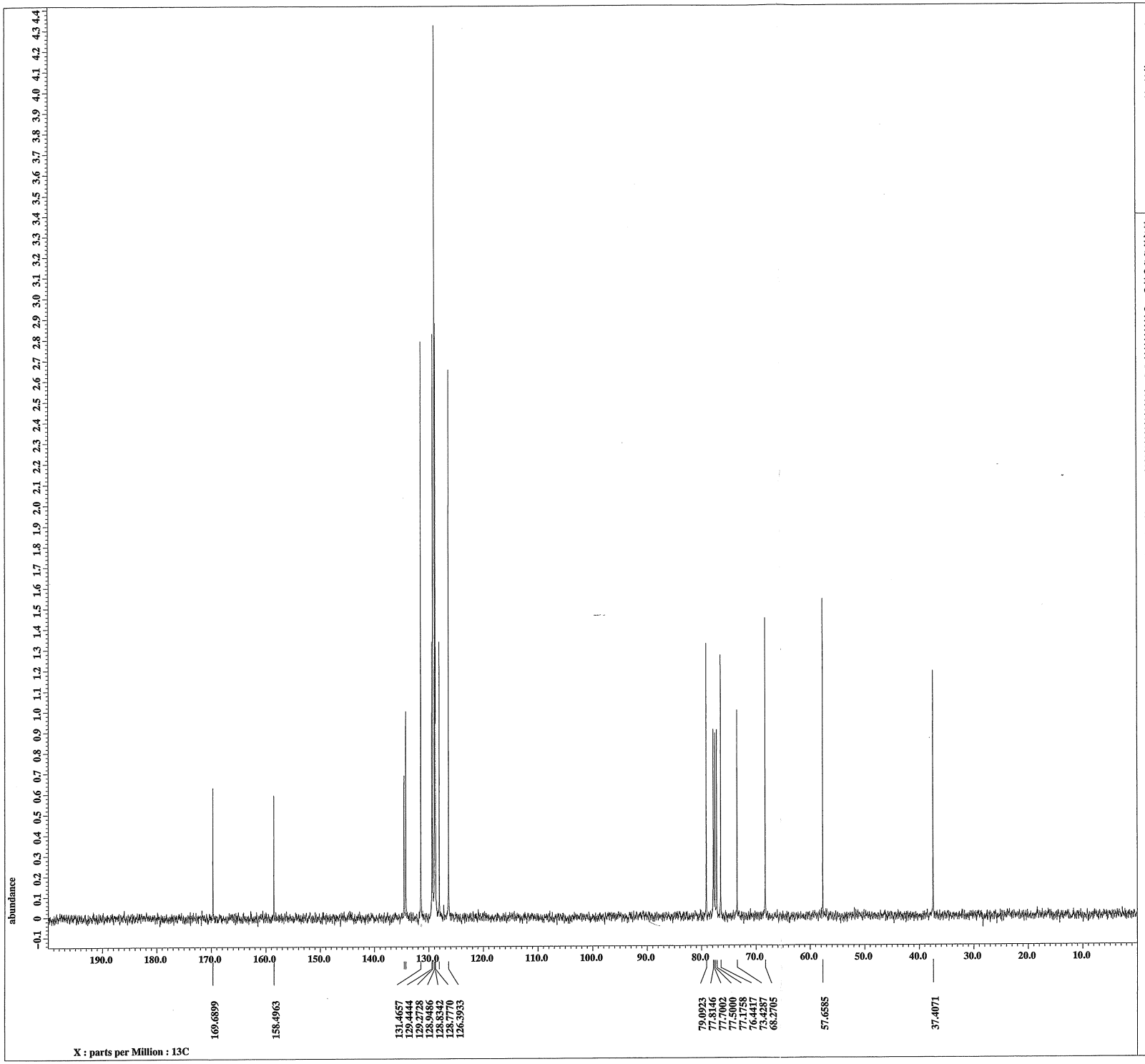
C:¥WINNMR98¥DATA¥tw382.als
TW-382



DFILE	C:¥WINNMR98¥DATA¥tw382.als
COMNT	TW-382
DATIM	Thu Feb 23 14:07:31 2006
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.0 Hz
POINT	32768
FREQU	7936.5 Hz
SCANS	16
ACQTM	4.129 sec
PD	10.000 sec
PW1	5.0 us
IRNUC	1H
CTEMP	20.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.00 Hz
RGAIN	18

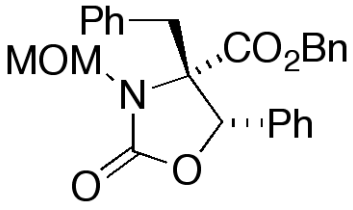


2Bn

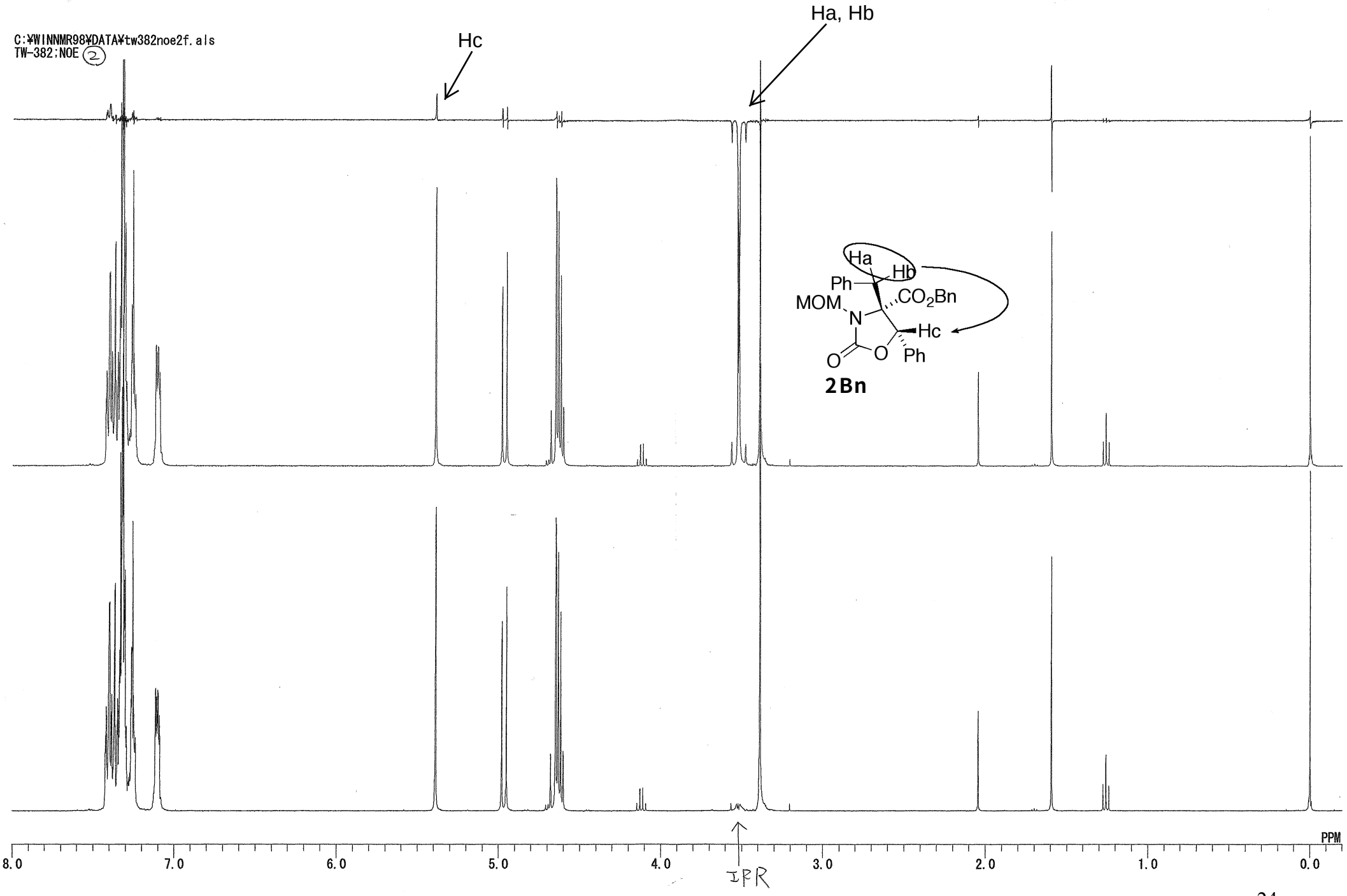



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: 13C No4-1.jdf
```

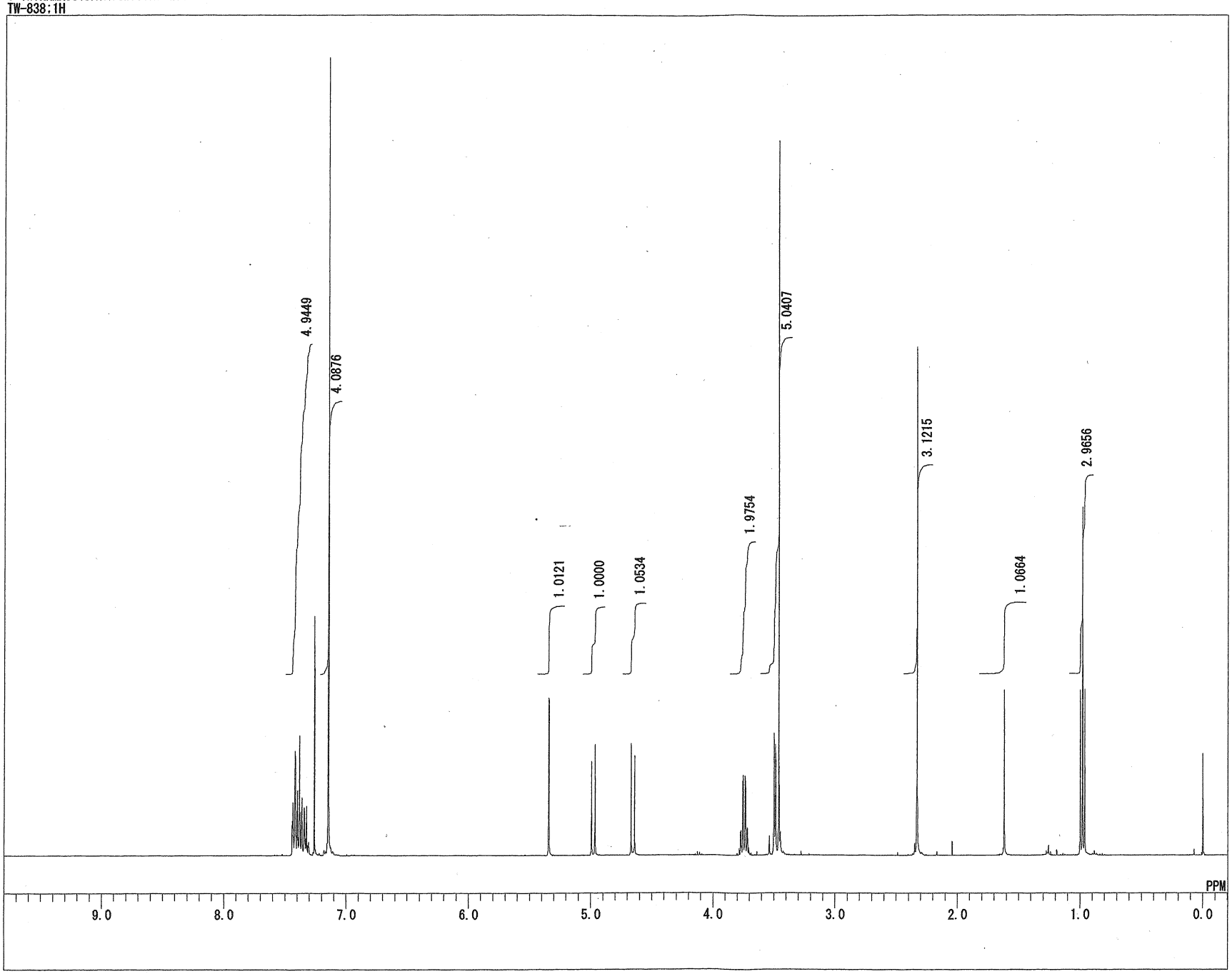
```
Filename            = 13C No4-4.jdf
Author              = delta
Experiment          = single_pulse_dec
Sample_id           = S#653972
Solvent             = CHLOROFORM-D
Creation_time       = 22-MAR-2007 12:58:10
Revision_time       = 22-MAR-2007 18:18:30
Current_time        = 22-MAR-2007 18:20:39

Content             = single pulse decouple
Data_format         = 1D COMPLEX
Dim_size            = 26214
Dim_title           = 13C
Dim_units           = [ppm]
Dimensions          = X
Site                = ECX 400P
Spectrometer        = DELTA2_NMR

Field_strength      = 9.389766[T] (400[MHz]
X_acq_duration      = 1.04333312[s]
X_domain            = 13C
X_freq              = 100.52530333[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_resolution        = 0.95846665[Hz]
X_sweep             = 31.40703518[kHz]
Irr_domain          = 1H
Irr_freq            = 399.78219838[MHz]
Irr_offset          = 5[ppm]
Clipped             = TRUE
Mod_return          = 1
Scans               = 52
Total_scans         = 52

X_90_width          = 10.2[us]
X_acq_time          = 1.04333312[s]
X_angle             = 30[deg]
X_atn               = 3.8[dB]
X_pulse             = 3.4[us]
Irr_atn_dec         = 19.8[dB]
Irr_atn_noe         = 19.8[dB]
Irr_noise           = WALTZ
Decoupling          = TRUE
Initial_wait        = 1[s]
Noe                 = TRUE
Noe_time            = 2[s]
Recvr_gain          = 60
Relaxation_delay    = 2[s]
Repetition_time     = 3.04333312[s]
Temp_get            = 18.2[dC]
```



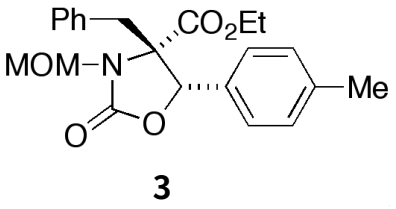
2Bn



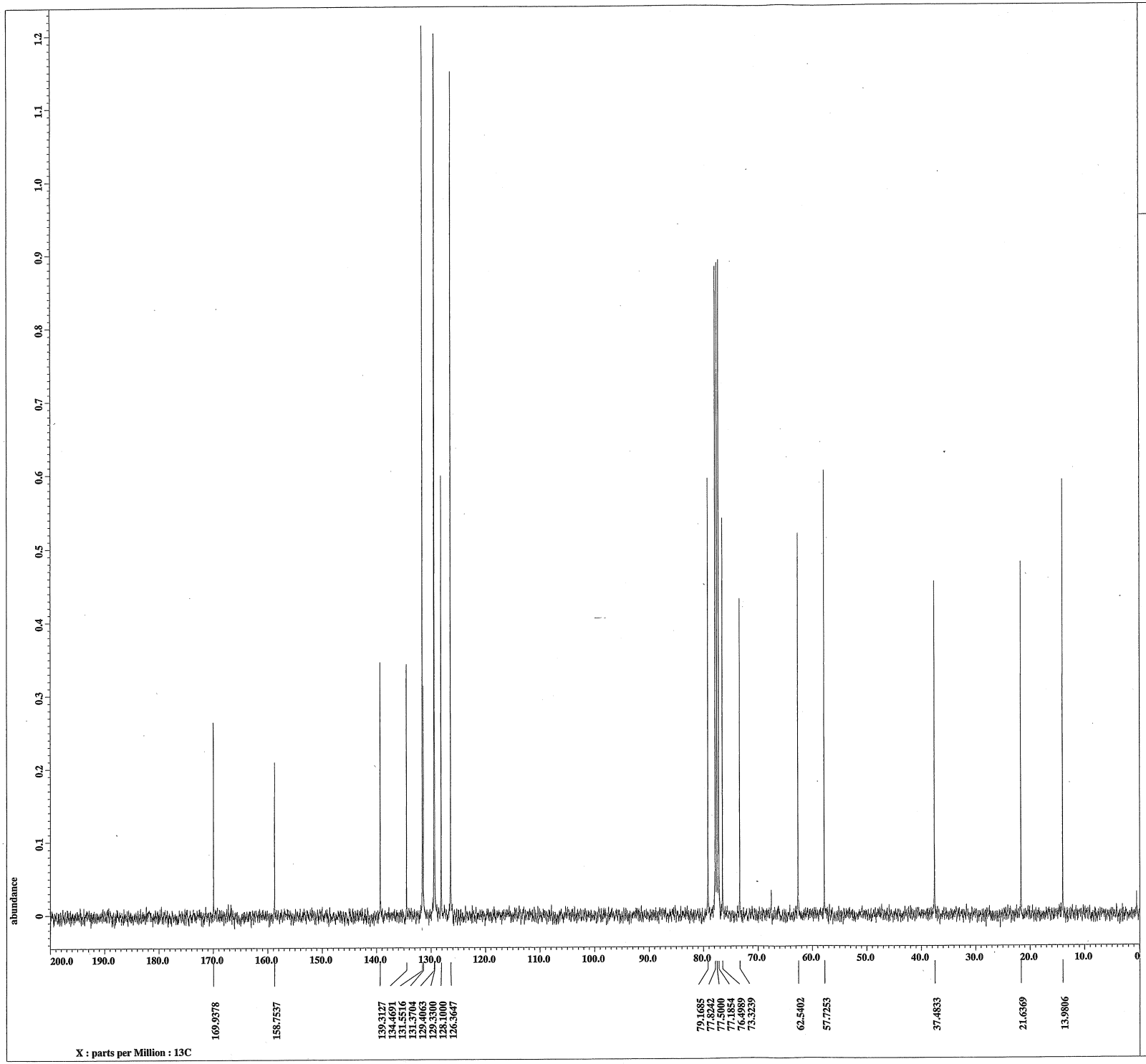
C:¥WINNMR98¥DATA¥tw838hf.als
TW-838:1H




```
DFILE   C:¥WINNMR98¥DATA¥tw838hf.als
COMNT   TW-838:1H
DATIM   Thu Jun 28 09:22:18 2007
OBNUC   1H
EXMOD   NON
OBFRQ       395.75 MHz
OBSET       124.00 KHz
OBFIN     10277.0 Hz
POINT       32768
FREQU       7936.5 Hz
SCANS          16
ACQTM       4.129 sec
PD         10.000 sec
PW1          5.0 us
IRNUC   1H
CTEMP        21.8 c
SLVNT   CDCL3
EXREF        0.00 ppm
BF           0.00 Hz
RGAIN          17
```

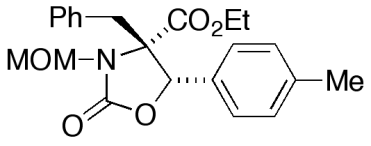


3



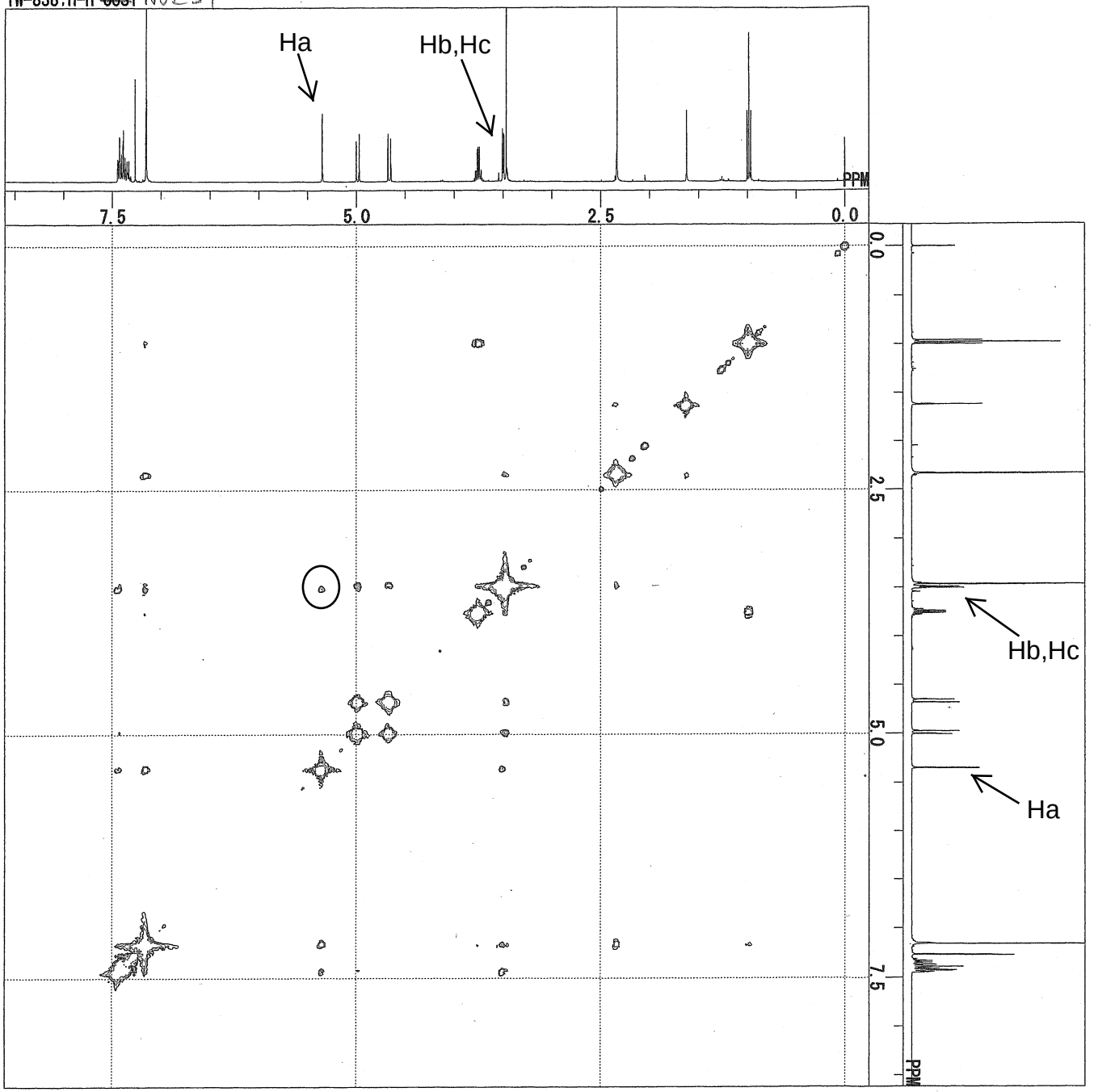

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: TW-830 pure 13C-1.jdf
```

```
Filename          = TW-830 pure 13C-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#419704
Solvent           = CHLOROFORM-D
Creation_time     = 23-MAY-2007 06:36:00
Revision_time     = 23-MAY-2007 11:56:47
Current_time      = 23-MAY-2007 11:57:13

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 267
Total_scans       = 267

X_90_width        = 10.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 3.8[dB]
X_pulse           = 3.4[us]
Irr_atn_dec       = 19.8[dB]
Irr_atn_noe       = 19.8[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 60
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 18.2[dC]
```

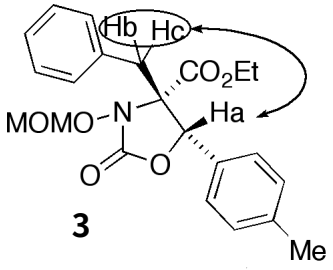


3

C:¥WINNMR98¥DATA¥tw838noesy.ALS
TW-838;H-H ~~COSY~~ NOESY

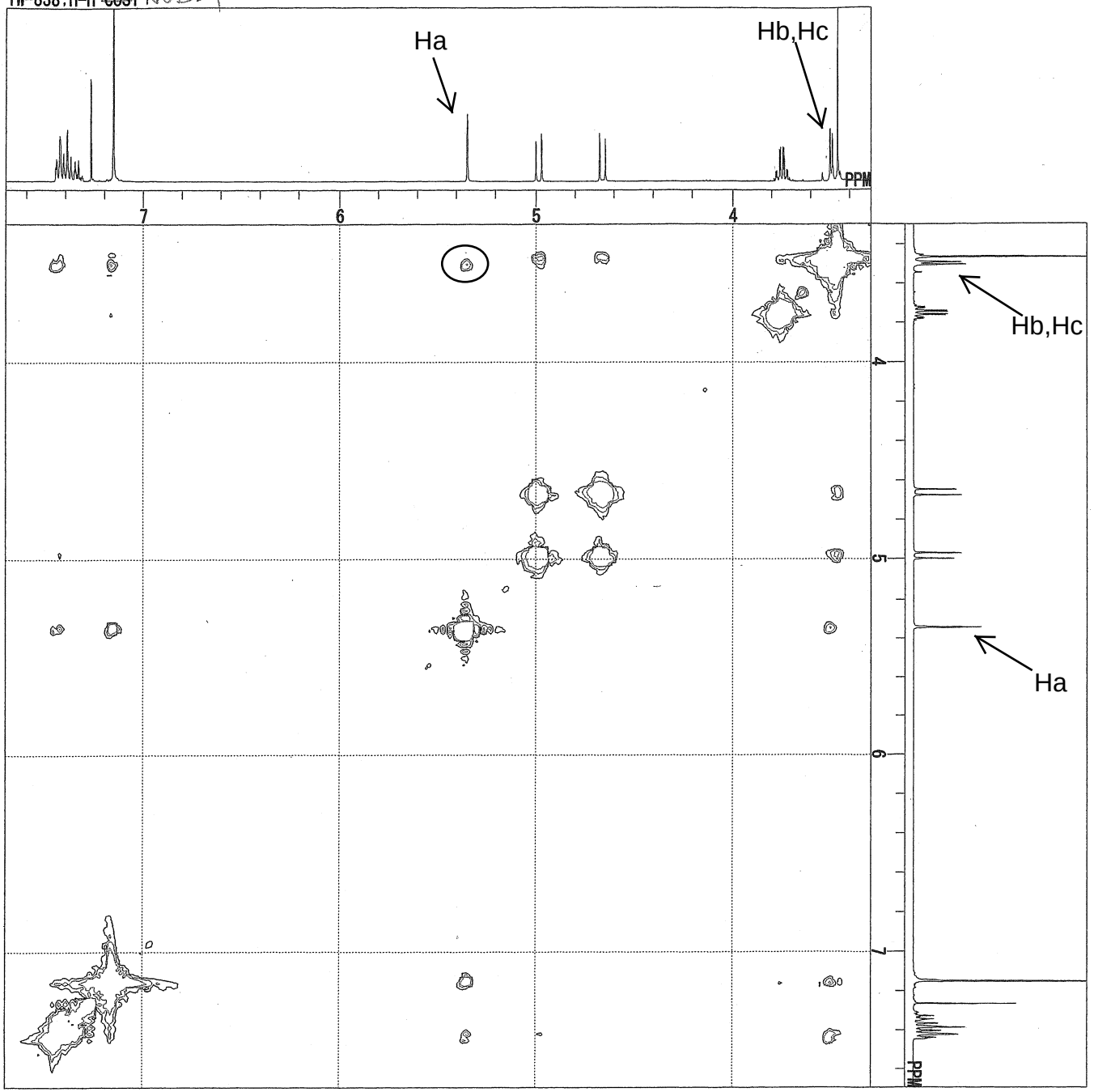



```
DFILE   C:¥WINNMR98¥DATA¥tw838noesy.ALS
COMNT   TW-838;H-H ~~COSY~~ NOESY
DATIM   Thu Jun 28 13:05:26 2007
EXMOD   VNOENH
OBNUC   1H
OBFRQ       395.75 MHz
OBSET       134.10 KHz
OBFIN         77.0 Hz
POINT          512
FREQU       3500.1 Hz
CLPNT          512
TODAT          256
CLFRQ       3496.5 Hz
SCANS          16
ACQTM        0.146 sec
PD           1.500 sec
PW1           12.6 us
PW2           12.6 us
PW3           10.0 us
PI1           0.286 ms
PI2           0.286 ms
PI3         1000.00 ms
IRNUC   1H
CTEMP         21.6 c
SLVNT   CDCL3
EXREF         0.00 ppm
CLEXR         0.00 ppm
RGAIN          16
OBATN          511
LOOP1            1
```

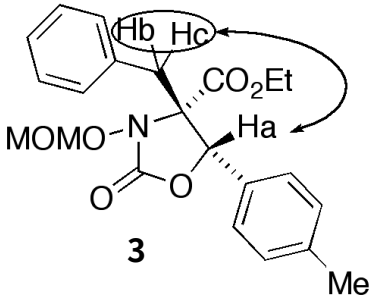


3

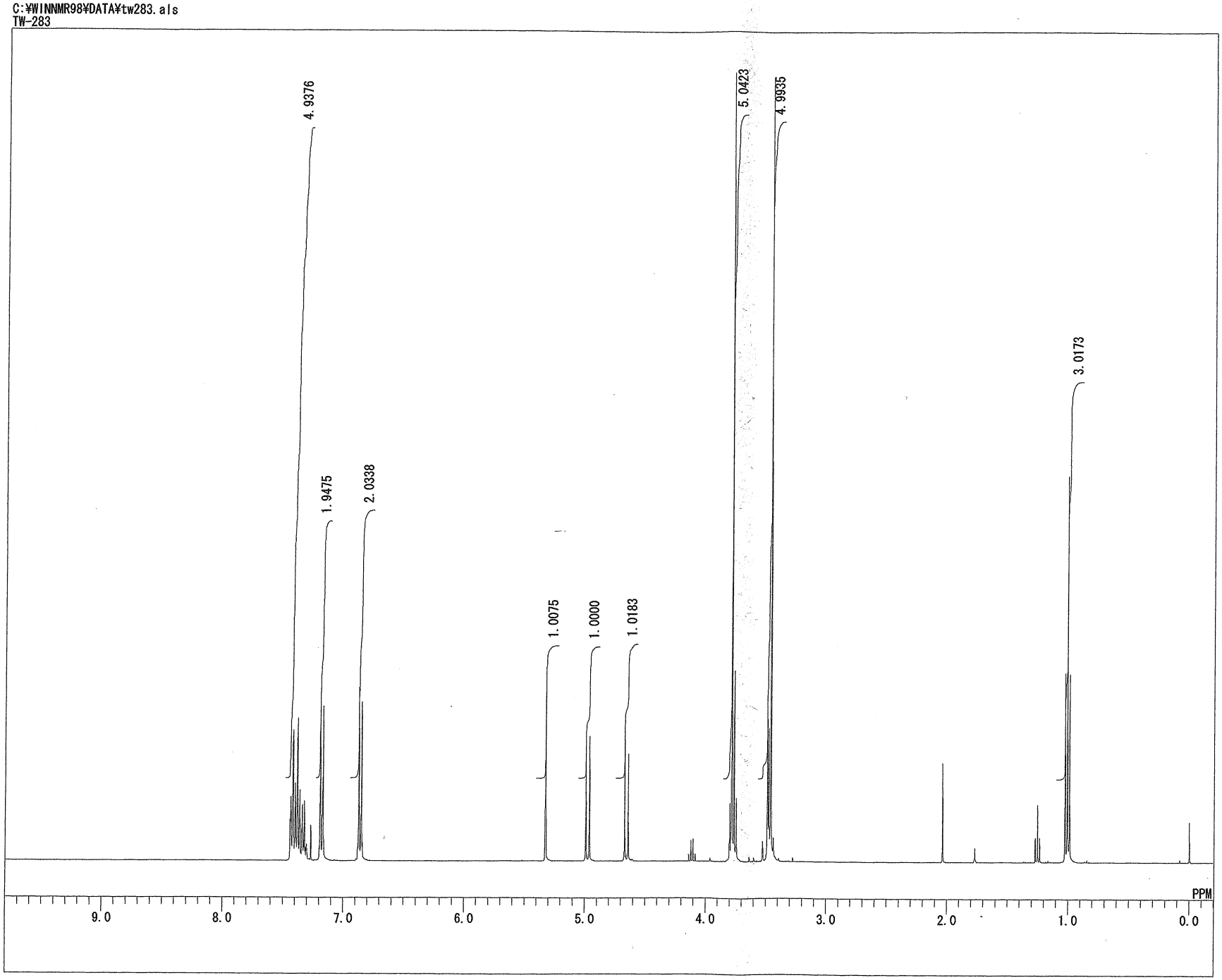
C:¥WINNMR98¥DATA¥tw838noesy.ALS
TW-838;H-H COSY NOESY



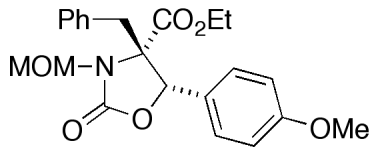
DFILE	C:¥WINNMR98¥DATA¥tw838noesy.ALS
COMNT	TW-838;H-H COSY NOESY
DATIM	Thu Jun 28 13:05:26 2007
EXMOD	VNOENH
OBNUC	1H
OBFRQ	395.75 MHz
OBSET	134.10 KHz
OBFIN	77.0 Hz
POINT	512
FREQU	3500.1 Hz
CLPNT	512
TODAT	256
CLFRQ	3496.5 Hz
SCANS	16
ACQTM	0.146 sec
PD	1.500 sec
PW1	12.6 us
PW2	12.6 us
PW3	10.0 us
PI1	0.286 ms
PI2	0.286 ms
PI3	1000.00 ms
IRNUC	1H
CTEMP	21.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
CLEXR	0.00 ppm
RGAIN	16
OBATN	511
LOOP1	1



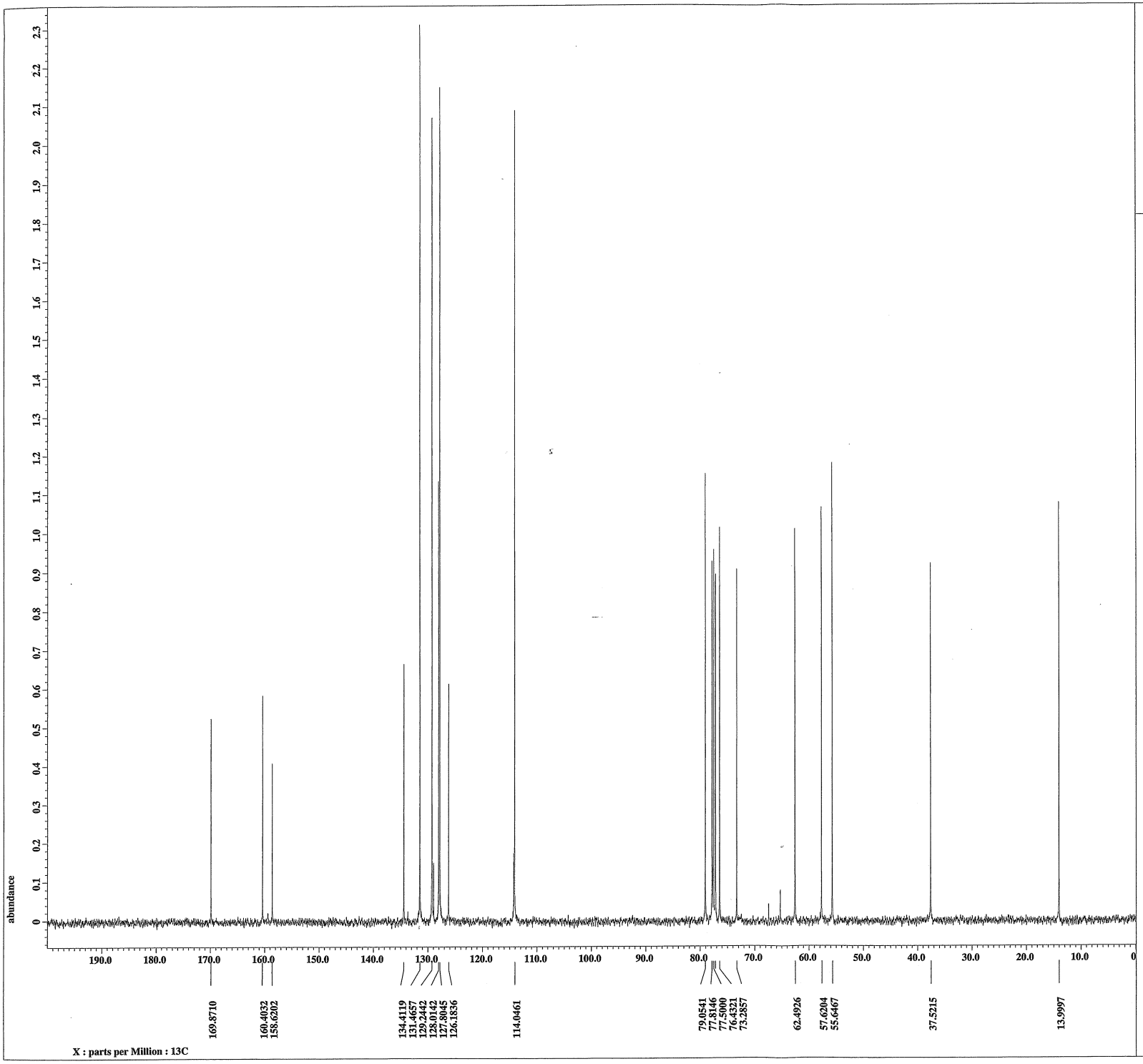
3




```
DFILE   C:¥WINNMR98¥DATA¥tw283.als
COMNT   TW-283
DATIM   Tue Mar 14 14:31:18 2006
OBNUC   1H
EXMOD   NON
OBFRQ       395.75 MHz
OBSET       124.00 KHz
OBFIN     10277.0 Hz
POINT       32768
FREQU       7936.5 Hz
SCANS          16
ACQTM       4.129 sec
PD         10.000 sec
PW1         5.0 us
IRNUC   1H
CTEMP       20.0 c
SLVNT   CDCL3
EXREF       0.00 ppm
BF          0.00 Hz
RGAIN          13
```

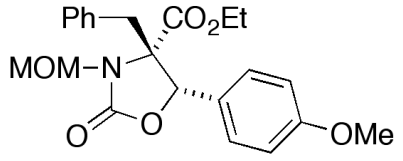


4

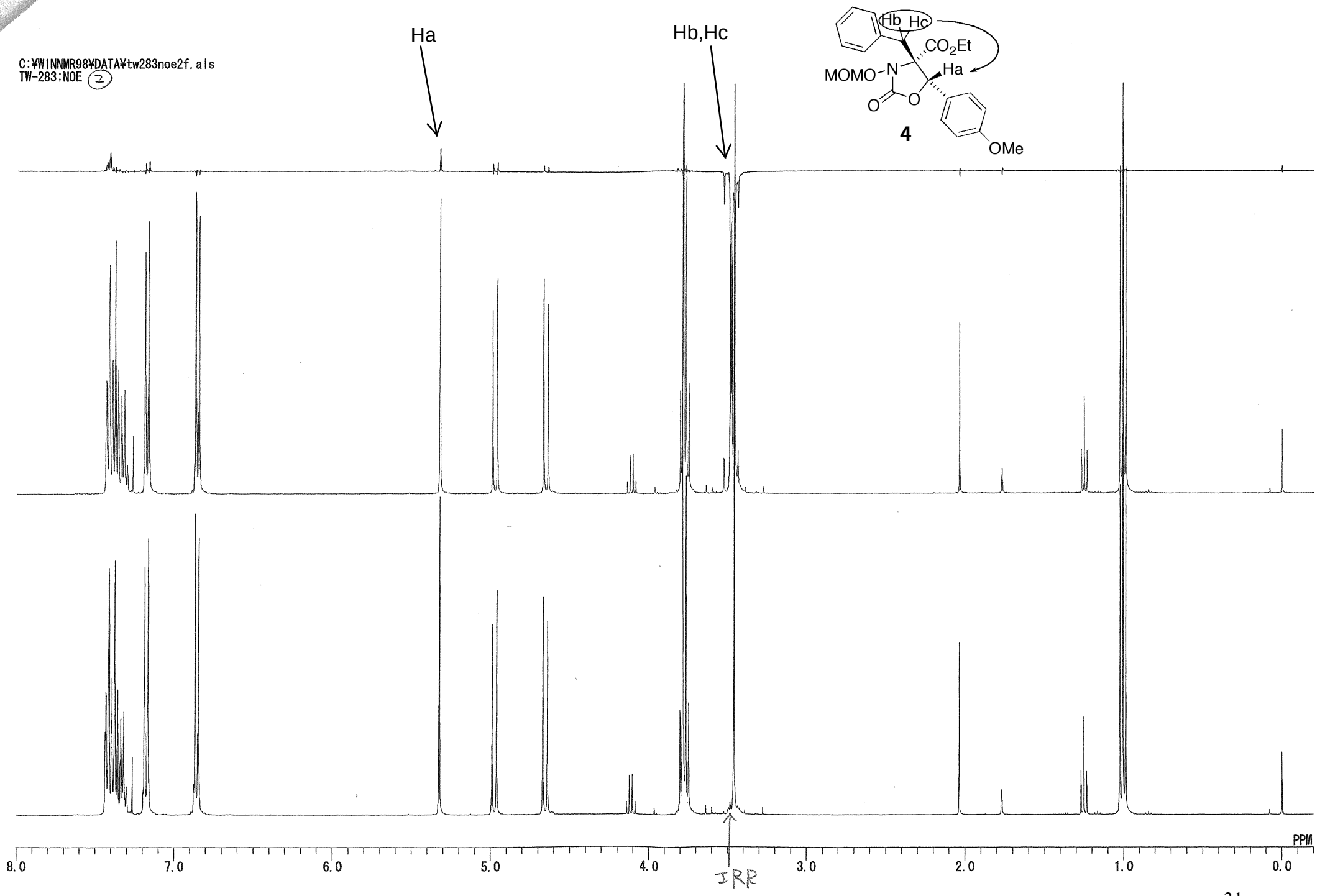


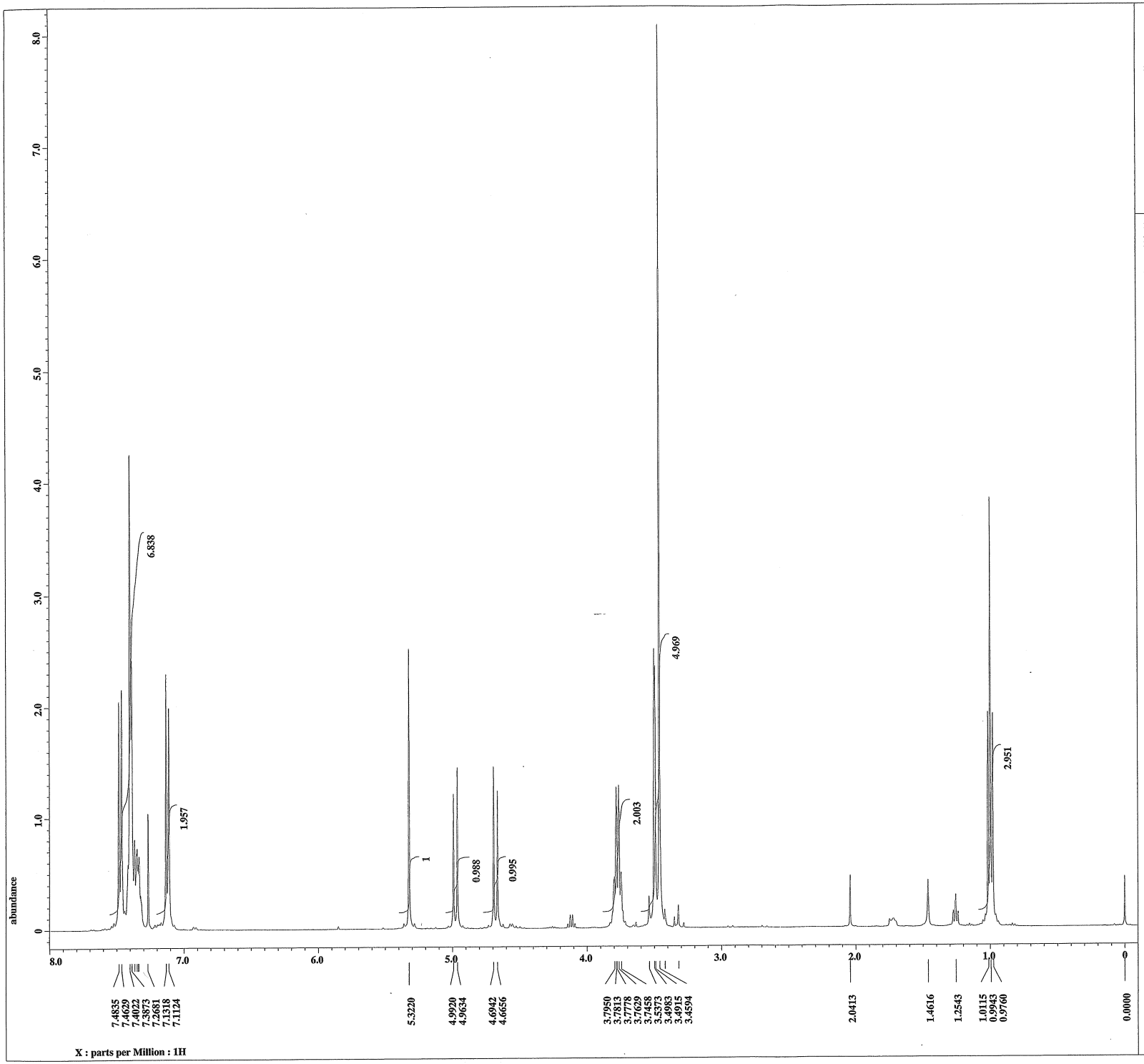

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: 13C No9, p-OMe-1.jdf
```

```
Filename          = 13C No9, p-OMe-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#601764
Solvent           = CHLOROFORM-D
Creation_time     = 11-APR-2007 11:33:56
Revision_time     = 11-APR-2007 16:53:22
Current_time      = 11-APR-2007 16:53:38

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 180
Total_scans       = 180

X_90_width        = 10.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 3.8[dB]
X_pulse           = 3.4[us]
Irr_atn_dec       = 19.8[dB]
Irr_atn_noe       = 19.8[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 19[dC]
```



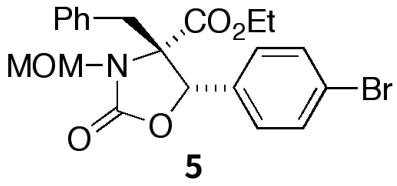
4


C:¥WINNMR98¥DATA¥tw283noe2f.als
TW-283;NOE (2)
Ha
Hb,Hc
Hb Hc
CO2Et
MOMO-N
Ha
O
O
4
OMe
PPM
8.0
7.0
6.0
5.0
4.0
IRR
3.0
2.0
1.0
0.0

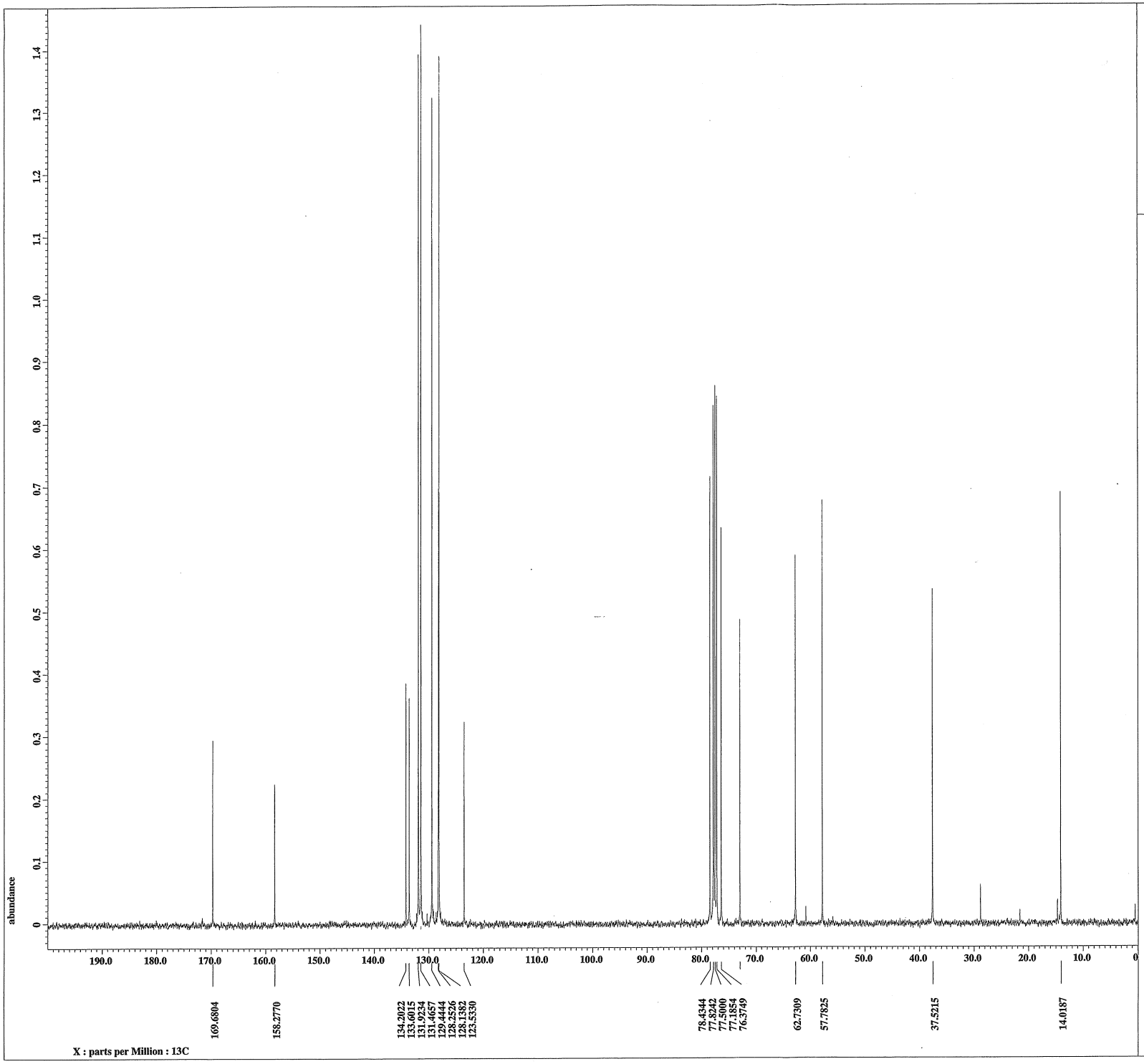



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: TW-800 APTLC-2.jdf
```

```
Filename          = TW-800 APTLC-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#638334
Solvent           = CHLOROFORM-D
Creation_time     = 13-APR-2007 12:26:40
Revision_time     = 13-APR-2007 17:49:41
Current_time      = 13-APR-2007 17:49:51

Content           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 2.18365952[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.45794685[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 10.6[us]
X_acq_time        = 2.18365952[s]
X_angle           = 45[deg]
X_atn             = 0.3[dB]
X_pulse           = 5.3[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 5[s]
Repetition_time   = 7.18365952[s]
Temp_get          = 17.5[dC]
```

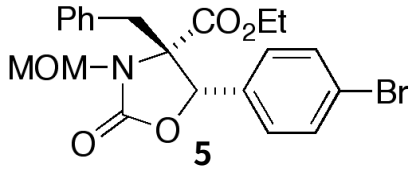


5



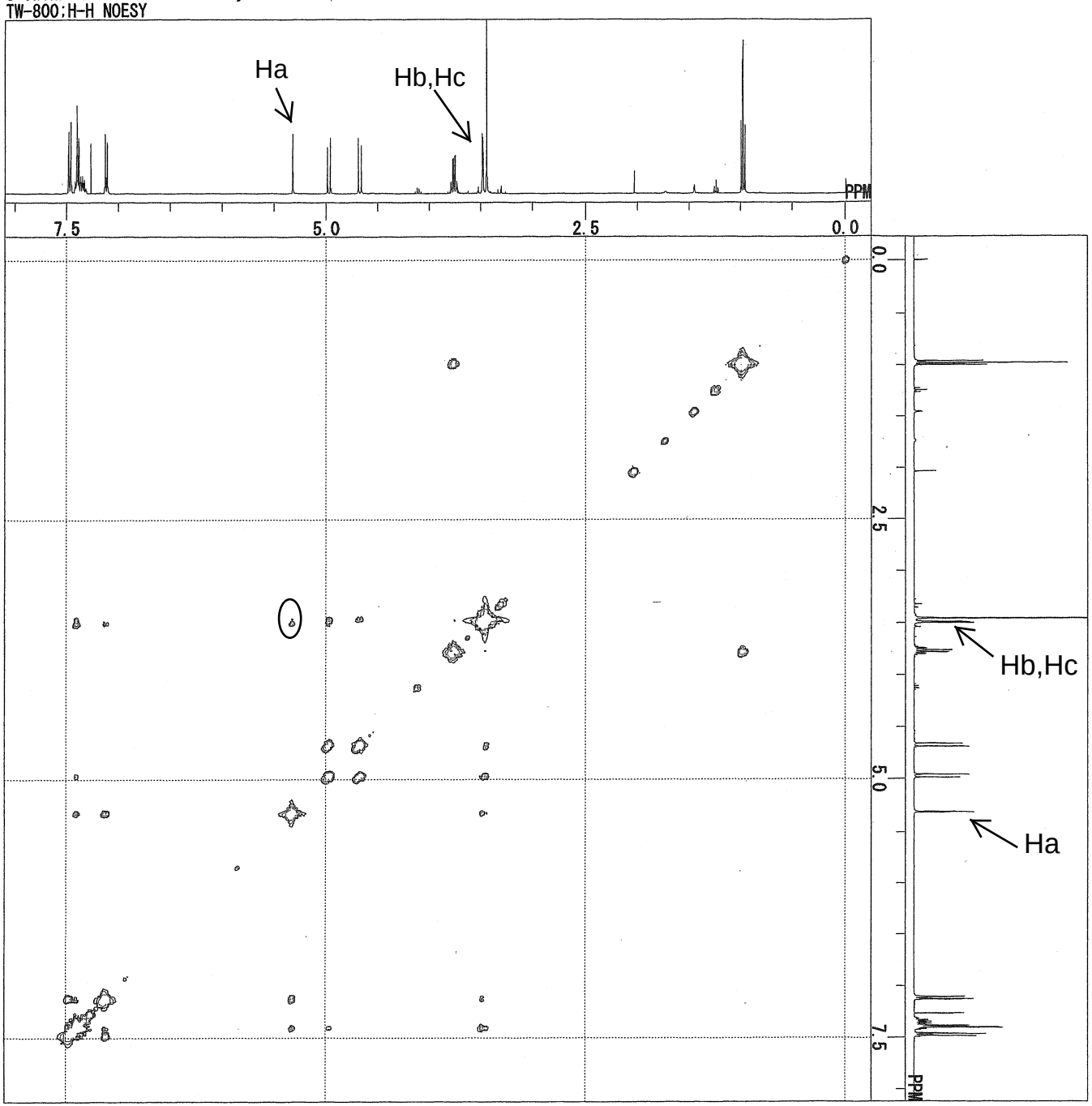

```
----- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: TW-800 APTLC 13C-1.jdf
```

```
Filename            = TW-800 APTLC 13C-4.jd
Author              = delta
Experiment          = single_pulse_dec
Sample_id           = S#642831
Solvent             = CHLOROFORM-D
Creation_time       = 13-APR-2007 13:26:07
Revision_time       = 13-APR-2007 20:17:04
Current_time        = 13-APR-2007 20:17:22

Content             = single pulse decouple
Data_format         = 1D COMPLEX
Dim_size            = 26214
Dim_title           = 13C
Dim_units           = [ppm]
Dimensions          = X
Site                = ECX 400P
Spectrometer        = DELTA2_NMR

Field_strength      = 9.389766[T] (400[MHz]
X_acq_duration      = 1.04333312[s]
X_domain            = 13C
X_freq              = 100.52530333[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_resolution        = 0.95846665[Hz]
X_sweep             = 31.40703518[kHz]
Irr_domain          = 1H
Irr_freq            = 399.78219838[MHz]
Irr_offset          = 5[ppm]
Clipped             = TRUE
Mod_return          = 1
Scans               = 1000
Total_scans         = 1000

X_90_width          = 10.2[us]
X_acq_time          = 1.04333312[s]
X_angle             = 30[deg]
X_atn               = 3.8[dB]
X_pulse             = 3.4[us]
Irr_atn_dec         = 19.8[dB]
Irr_atn_noe         = 19.8[dB]
Irr_noise           = WALTZ
Decoupling          = TRUE
Initial_wait        = 1[s]
Noe                 = TRUE
Noe_time            = 2[s]
Recvr_gain          = 60
Relaxation_delay    = 2[s]
Repetition_time     = 3.04333312[s]
Temp_get            = 19.2[dC]
```

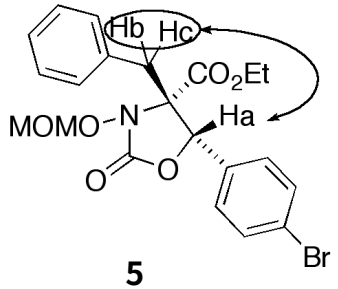


5

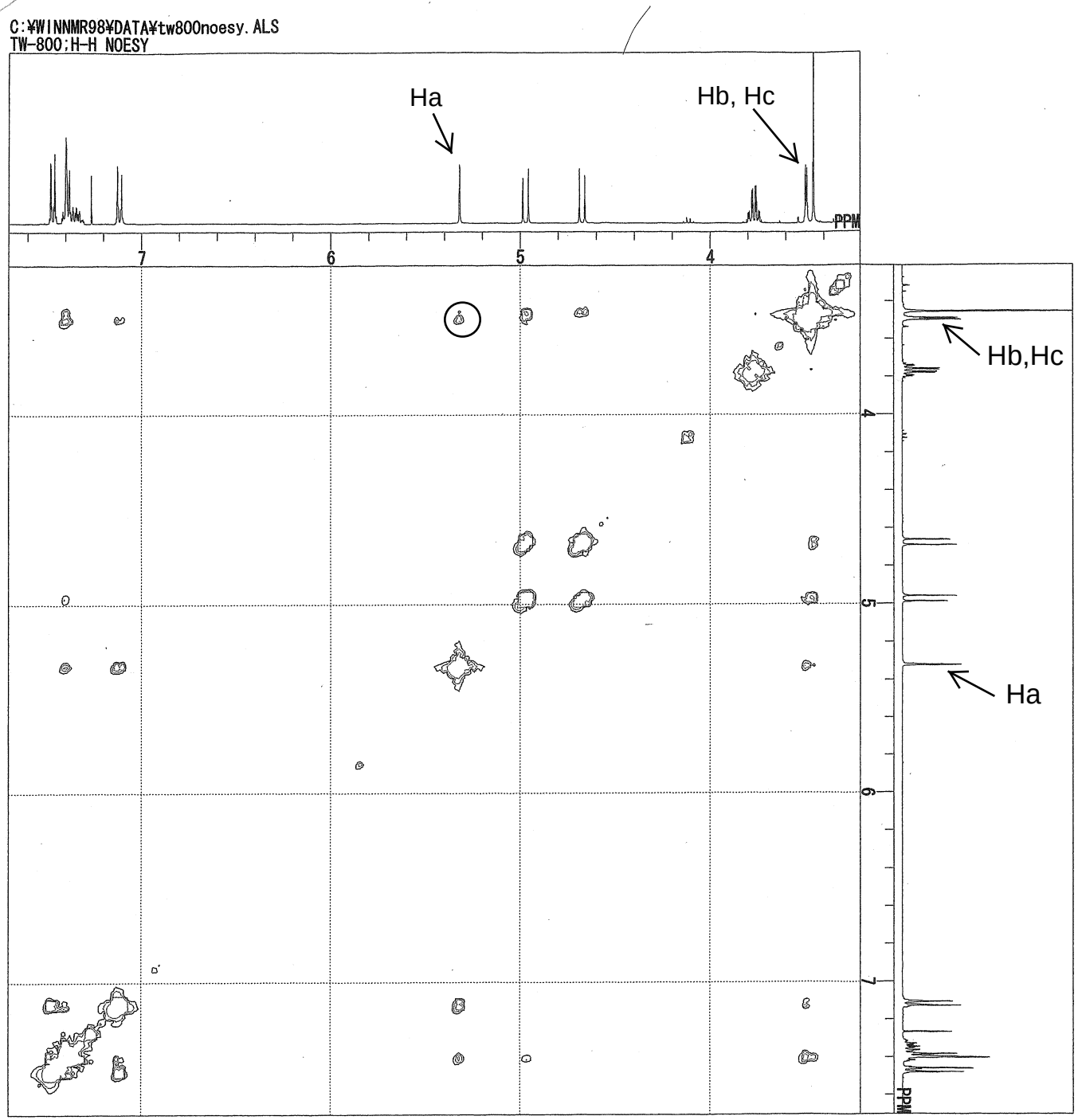
C:¥WINNMR98¥DATA¥tw800noesy.ALS
TW-800;H-H NOESY



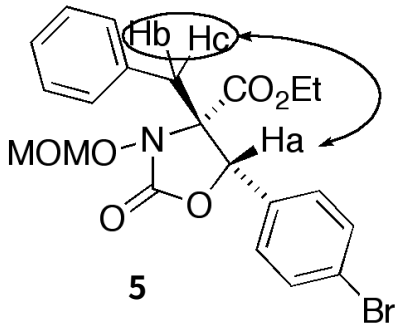

```
DFILE  C:¥WINNMR98¥DATA¥tw800noesy.ALS
COMNT  TW-800;H-H NOESY
DATIM  Wed Apr 18 15:47:57 2007
EXMOD  VNOENH
OBNUC  1H
OBFRQ       395.75 MHz
OBSET       134.00 KHz
OBFIN         76.9 Hz
POINT          512
FREQU       3300.3 Hz
CLPNT          512
TODAT          256
CLFRQ       3300.3 Hz
SCANS           16
ACQTM        0.155 sec
PD           1.500 sec
PW1           12.8 us
PW2           12.8 us
PW3           10.0 us
PI1          0.303 ms
PI2          0.303 ms
PI3       1500.00 ms
IRNUC  1H
CTEMP        21.2 c
SLVNT  CDCL3
EXREF         0.00 ppm
CLEXR         0.00 ppm
RGAIN           11
OBATN          511
LOOP1            1
```



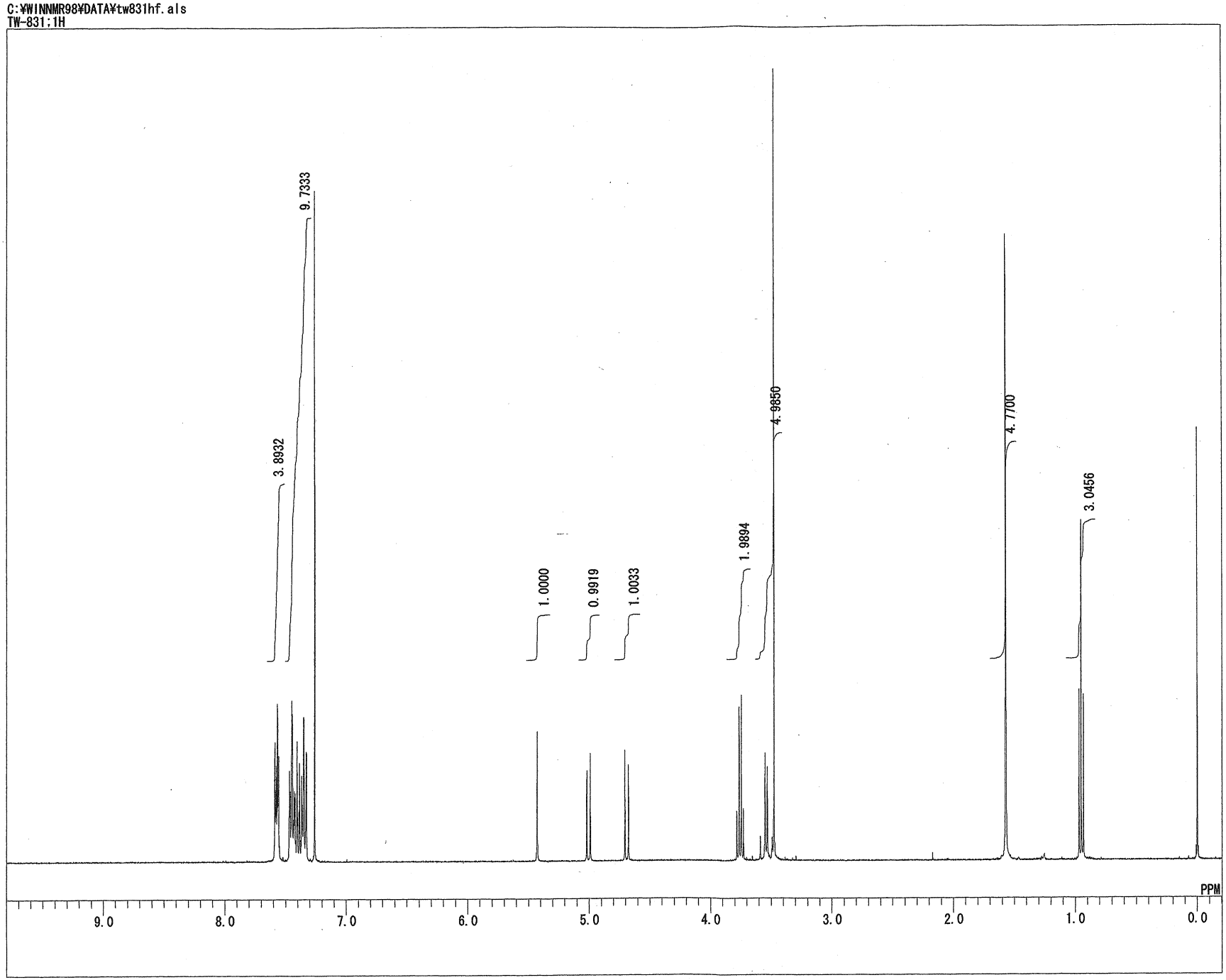
5

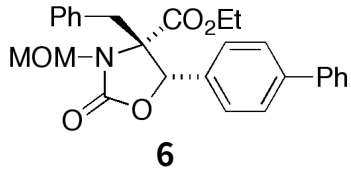



```
DFILE   C:¥WINNMR98¥DATA¥tw800noesy.ALS
COMNT   TW-800;H-H NOESY
DATIM   Wed Apr 18 15:47:57 2007
EXMOD   VNOENH
OBNUC   1H
OBFRQ       395.75 MHz
OBSET       134.00 KHz
OBFIN         76.9 Hz
POINT          512
FREQU       3300.3 Hz
CLPNT          512
TODAT          256
CLFRQ       3300.3 Hz
SCANS           16
ACQTM        0.155 sec
PD           1.500 sec
PW1           12.8 us
PW2           12.8 us
PW3           10.0 us
PI1          0.303 ms
PI2          0.303 ms
PI3       1500.00 ms
IRNUC   1H
CTEMP        21.2 c
SLVNT   CDCL3
EXREF         0.00 ppm
CLEXR         0.00 ppm
RGAIN           11
OBATN          511
LOOP1            1
```

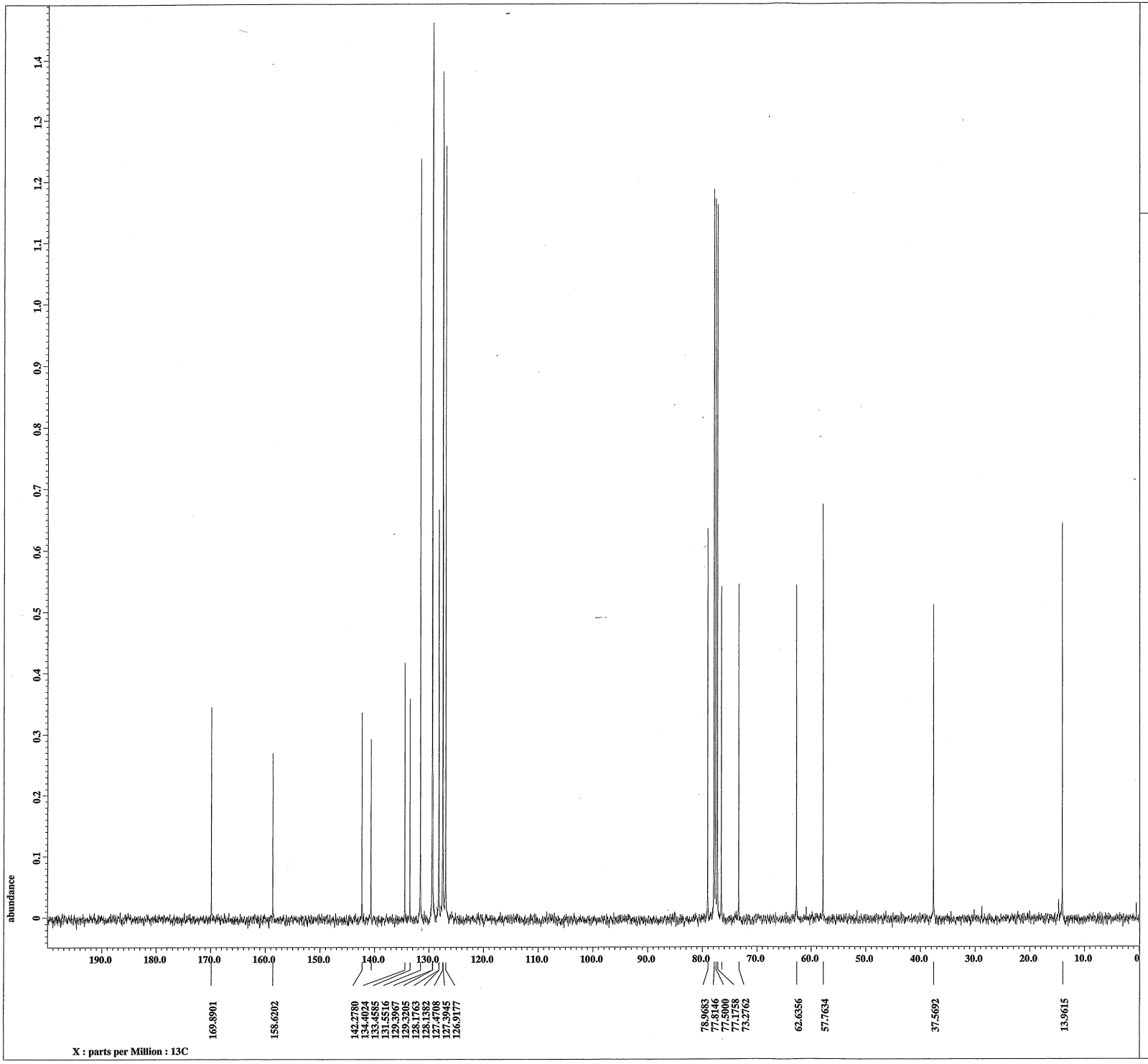


5


C:¥WINNMR98¥DATA¥tw831hf.als
TW-831;1H
DFILE C:¥WINNMR98¥DATA¥tw831hf.als
COMNT TW-831;1H
DATIM Wed Jun 27 12:20:26 2007
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.0 Hz
POINT 32768
FREQU 7936.5 Hz
SCANS 16
ACQTM 4.129 sec
PD 10.000 sec
PW1 5.0 us
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.00 Hz
RGAIN 22
3.8932
9.7333
1.0000
0.9919
1.0033
1.9894
4.9850
4.7700
3.0456
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

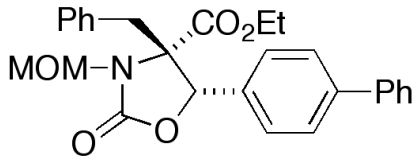

Ph
CO2Et
MOM–N
Ph
O
O

6



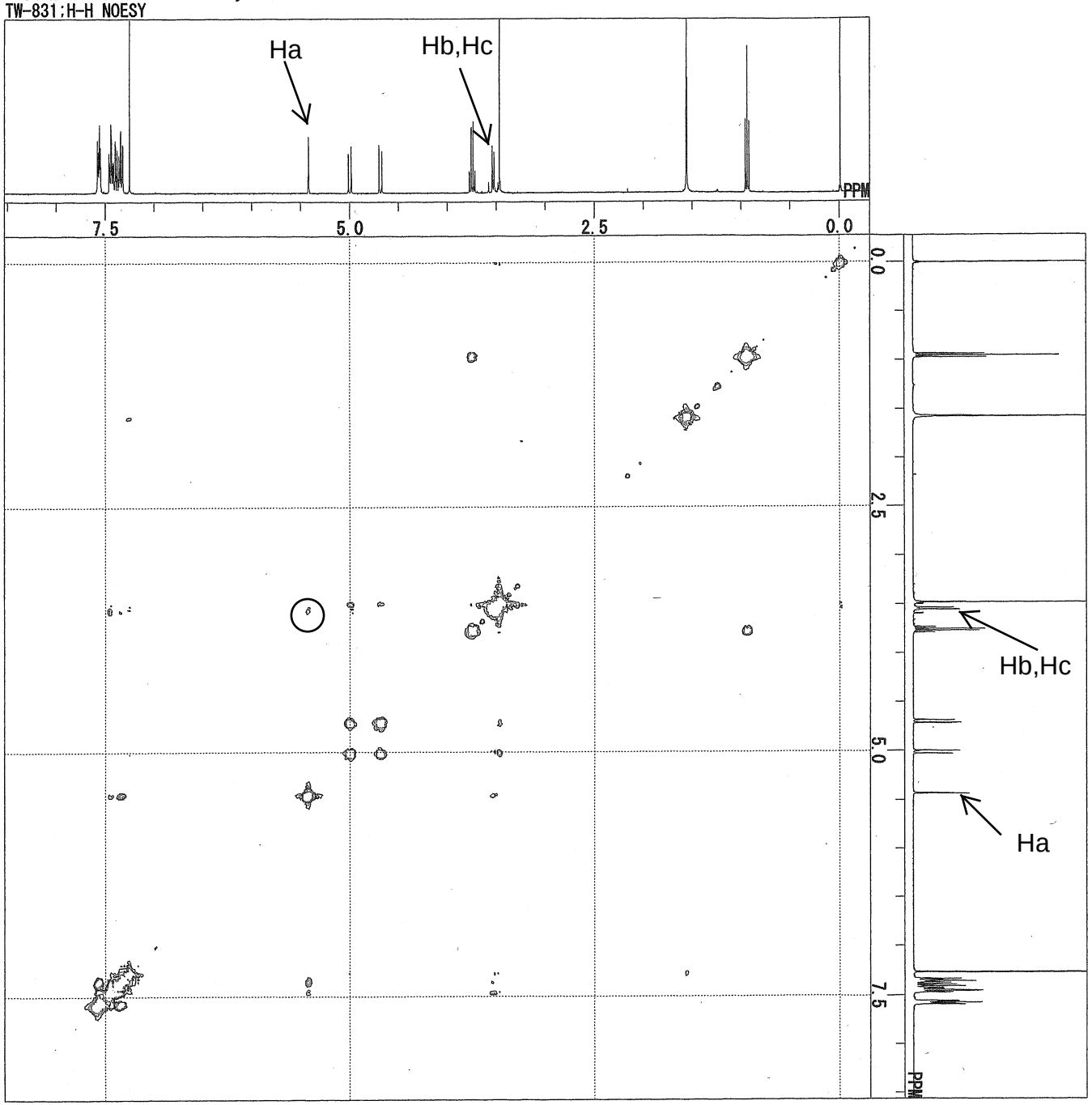

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: TW-831 13C-1.jdf
```

```
Filename            = TW-831 13C-3.jdf
Author              = delta
Experiment          = single_pulse_dec
Sample_id           = S#505725
Solvent             = CHLOROFORM-D
Creation_time       = 21-MAY-2007 09:06:37
Revision_time       = 21-MAY-2007 14:27:22
Current_time        = 21-MAY-2007 14:28:00

Content             = single pulse decouple
Data_format         = 1D COMPLEX
Dim_size            = 26214
Dim_title           = 13C
Dim_units           = [ppm]
Dimensions          = X
Site                = ECX 400P
Spectrometer        = DELTA2_NMR

Field_strength      = 9.389766[T] (400[MHz]
X_acq_duration      = 1.04333312[s]
X_domain            = 13C
X_freq              = 100.52530333[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_resolution        = 0.95846665[Hz]
X_sweep             = 31.40703518[kHz]
Irr_domain          = 1H
Irr_freq            = 399.78219838[MHz]
Irr_offset          = 5[ppm]
Clipped             = TRUE
Mod_return          = 1
Scans               = 421
Total_scans         = 421

X_90_width          = 10.2[us]
X_acq_time          = 1.04333312[s]
X_angle             = 30[deg]
X_atn               = 3.8[dB]
X_pulse             = 3.4[us]
Irr_atn_dec         = 19.8[dB]
Irr_atn_noe         = 19.8[dB]
Irr_noise           = WALTZ
Decoupling          = TRUE
Initial_wait        = 1[s]
Noe                 = TRUE
Noe_time            = 2[s]
Recvr_gain          = 60
Relaxation_delay    = 2[s]
Repetition_time     = 3.04333312[s]
Temp_get            = 17.4[dC]
```

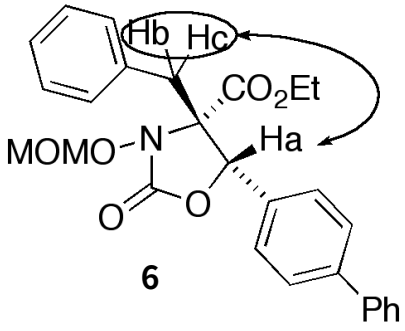


6

C:¥WINNMR98¥DATA¥tw831noesy.ALS
TW-831;H-H NOESY

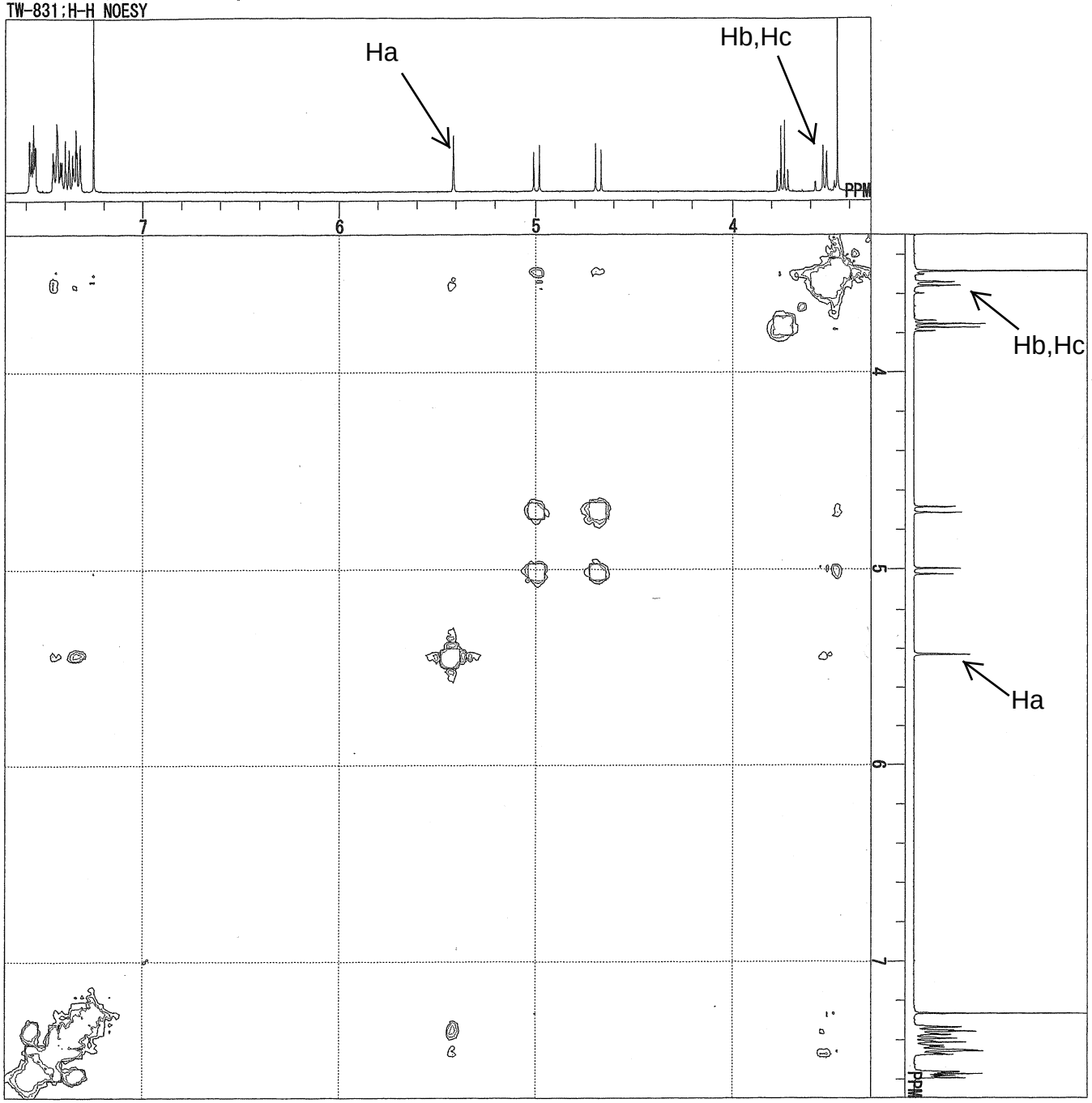



```
DFILE  C:¥WINNMR98¥DATA¥tw831noesy.ALS
COMNT  TW-831;H-H NOESY
DATIM  Wed Jun 27 14:02:00 2007
EXMOD  VNOENH
OBNUC  1H
OBFRQ        395.75 MHz
OBSET        134.10 KHz
OBFIN          56.1 Hz
POINT           512
FREQU        3500.1 Hz
CLPNT           512
TODAT           256
CLFRQ        3496.5 Hz
SCANS             8
ACQTM         0.146 sec
PD            1.500 sec
PW1            12.6 us
PW2            12.6 us
PW3            10.0 us
PI1           0.286 ms
PI2           0.286 ms
PI3         1000.00 ms
IRNUC  1H
CTEMP         21.6 c
SLVNT  CDCL3
EXREF          0.00 ppm
CLEXR          0.00 ppm
RGAIN            21
OBATN           511
LOOP1             1
```

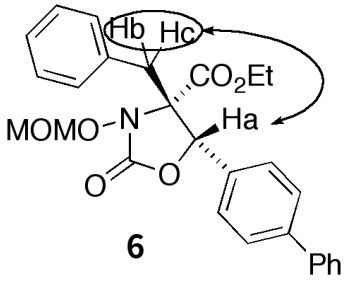


6

C:¥WINNMR98¥DATA¥tw831noesy.ALS
TW-831;H-H NOESY

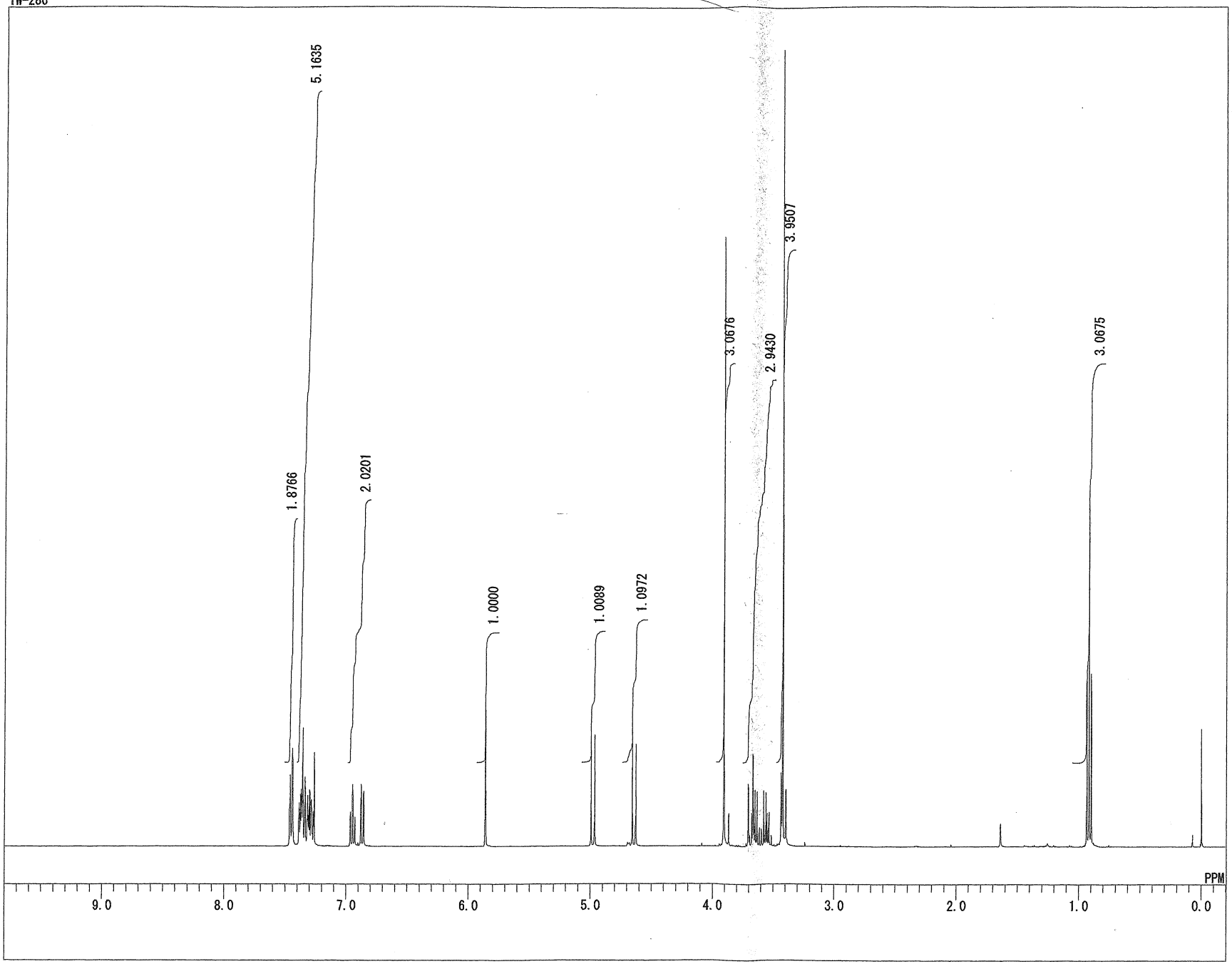



```
DFILE  C:¥WINNMR98¥DATA¥tw831noesy.ALS
COMNT  TW-831;H-H NOESY
DATIM  Wed Jun 27 14:02:00 2007
EXMOD  VNOENH
OBNUC  1H
OBFRQ        395.75 MHz
OBSET        134.10 KHz
OBFIN          56.1 Hz
POINT           512
FREQU        3500.1 Hz
CLPNT           512
TODAT           256
CLFRQ        3496.5 Hz
SCANS             8
ACQTM         0.146 sec
PD            1.500 sec
PW1            12.6 us
PW2            12.6 us
PW3            10.0 us
PI1           0.286 ms
PI2           0.286 ms
PI3         1000.00 ms
IRNUC  1H
CTEMP         21.6 c
SLVNT  CDCL3
EXREF          0.00 ppm
CLEXR          0.00 ppm
RGAIN            21
OBATN           511
LOOP1             1
```

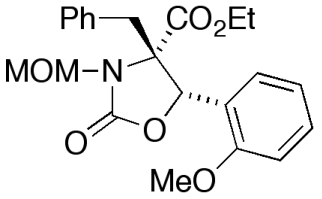


6

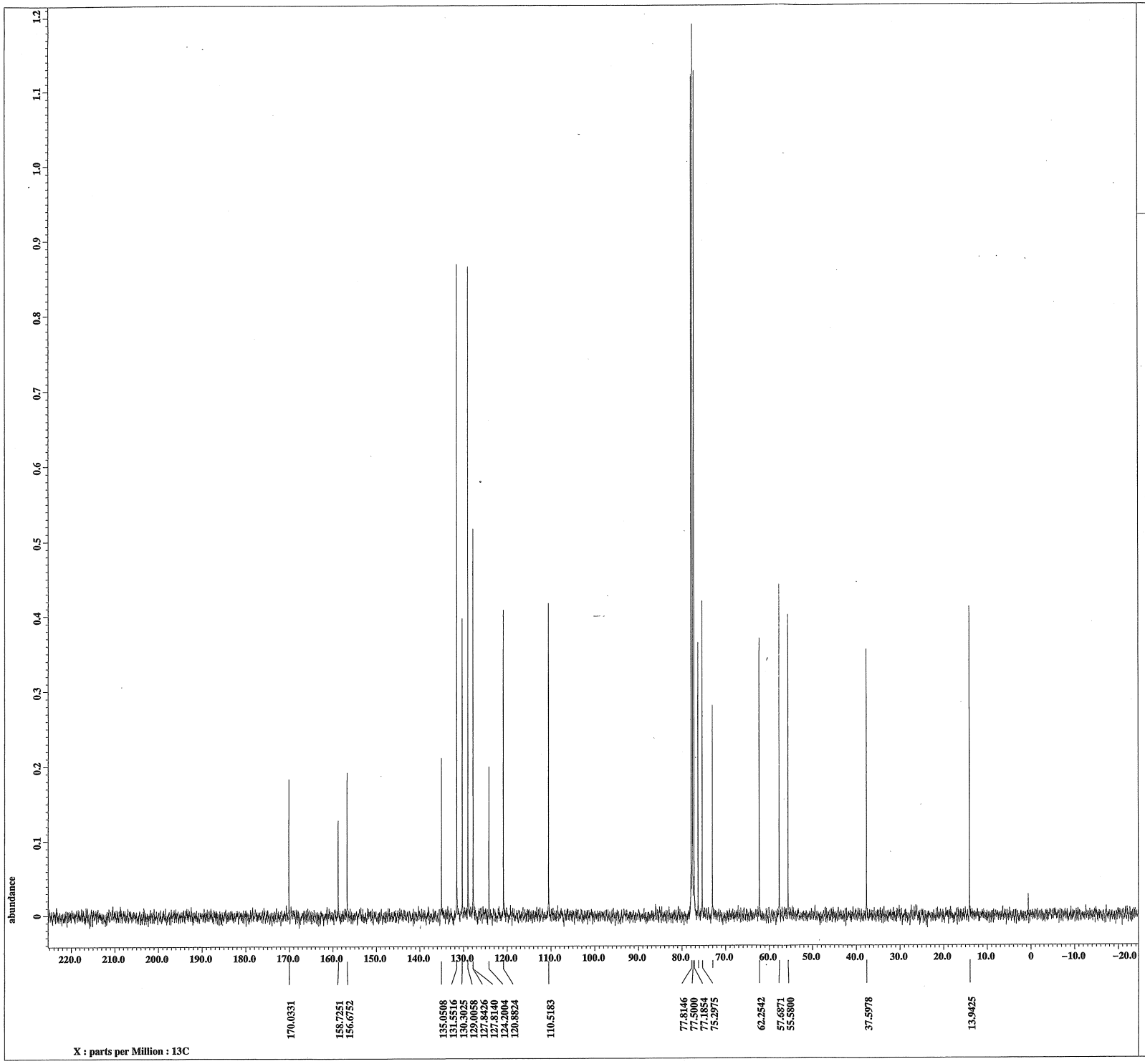
C:¥WINNMR98¥DATA¥tw286.als
TW-286




```
DFILE   C:¥WINNMR98¥DATA¥tw286.als
COMNT   TW-286
DATIM   Wed Mar 15 11:04:36 2006
OBNUC   1H
EXMOD   NON
OBFRQ       395.75 MHz
OBSET       124.00 KHz
OBFIN     10277.0 Hz
POINT       32768
FREQU      7936.5 Hz
SCANS          16
ACQTM       4.129 sec
PD         10.000 sec
PW1         5.0 us
IRNUC   1H
CTEMP       19.6 c
SLVNT   CDCL3
EXREF       0.00 ppm
BF          0.00 Hz
RGAIN          17
```

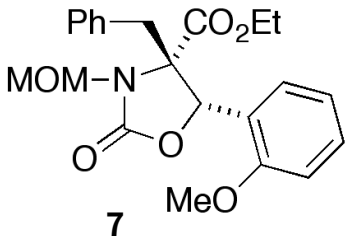


7

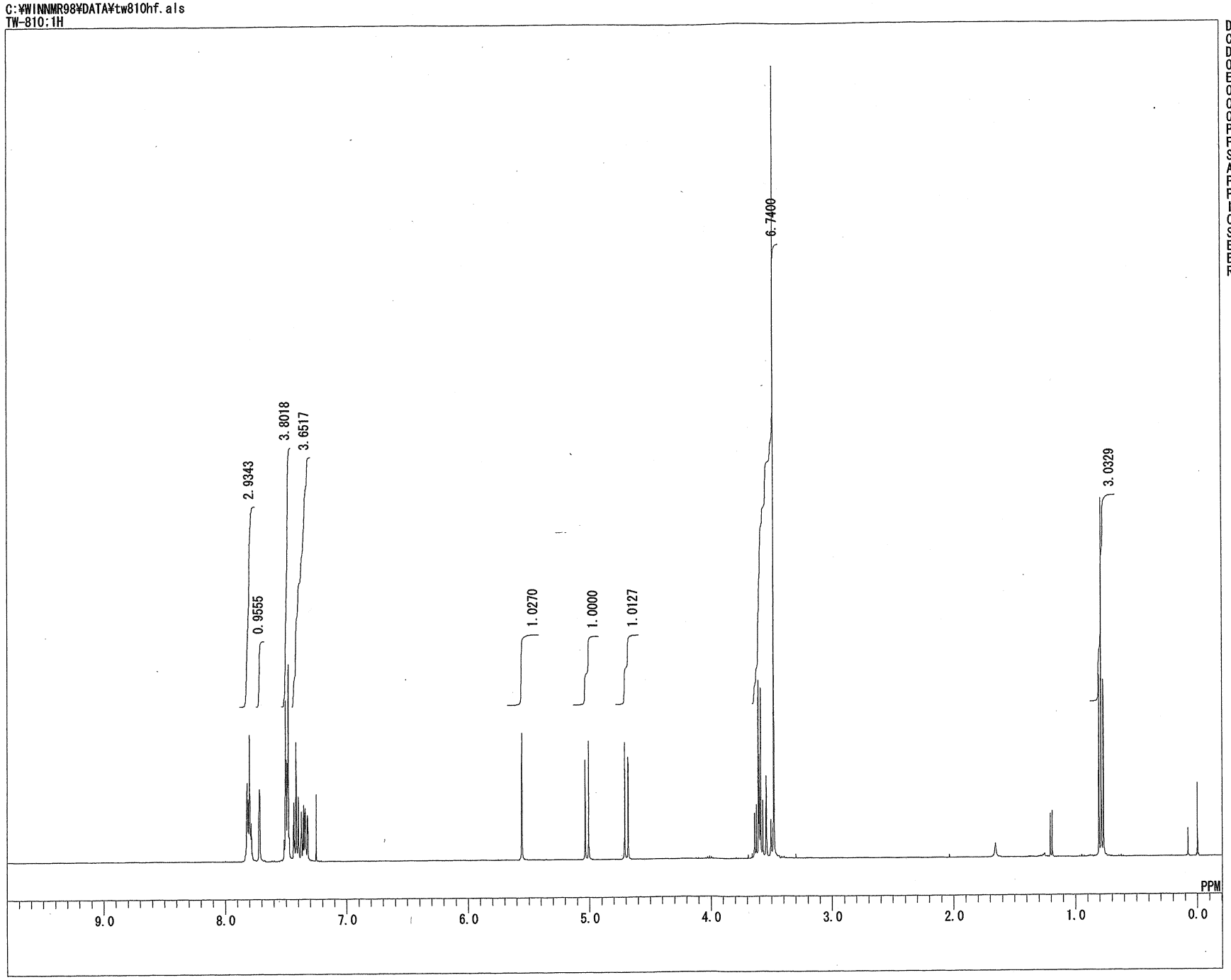



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: 13C No12, o-OMe-1.jdf
```

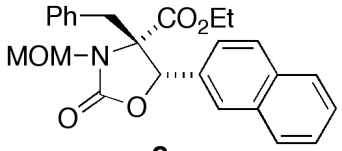
```
Filename          = 13C No12, o-OMe-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#802030
Solvent           = CHLOROFORM-D
Creation_time     = 20-APR-2007 17:17:27
Revision_time     = 20-APR-2007 22:42:01
Current_time      = 20-APR-2007 22:42:33

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 342
Total_scans       = 342

X_90_width        = 10.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 3.8[dB]
X_pulse           = 3.4[us]
Irr_atn_dec       = 19.8[dB]
Irr_atn_noe       = 19.8[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 60
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 17.9[dC]
```



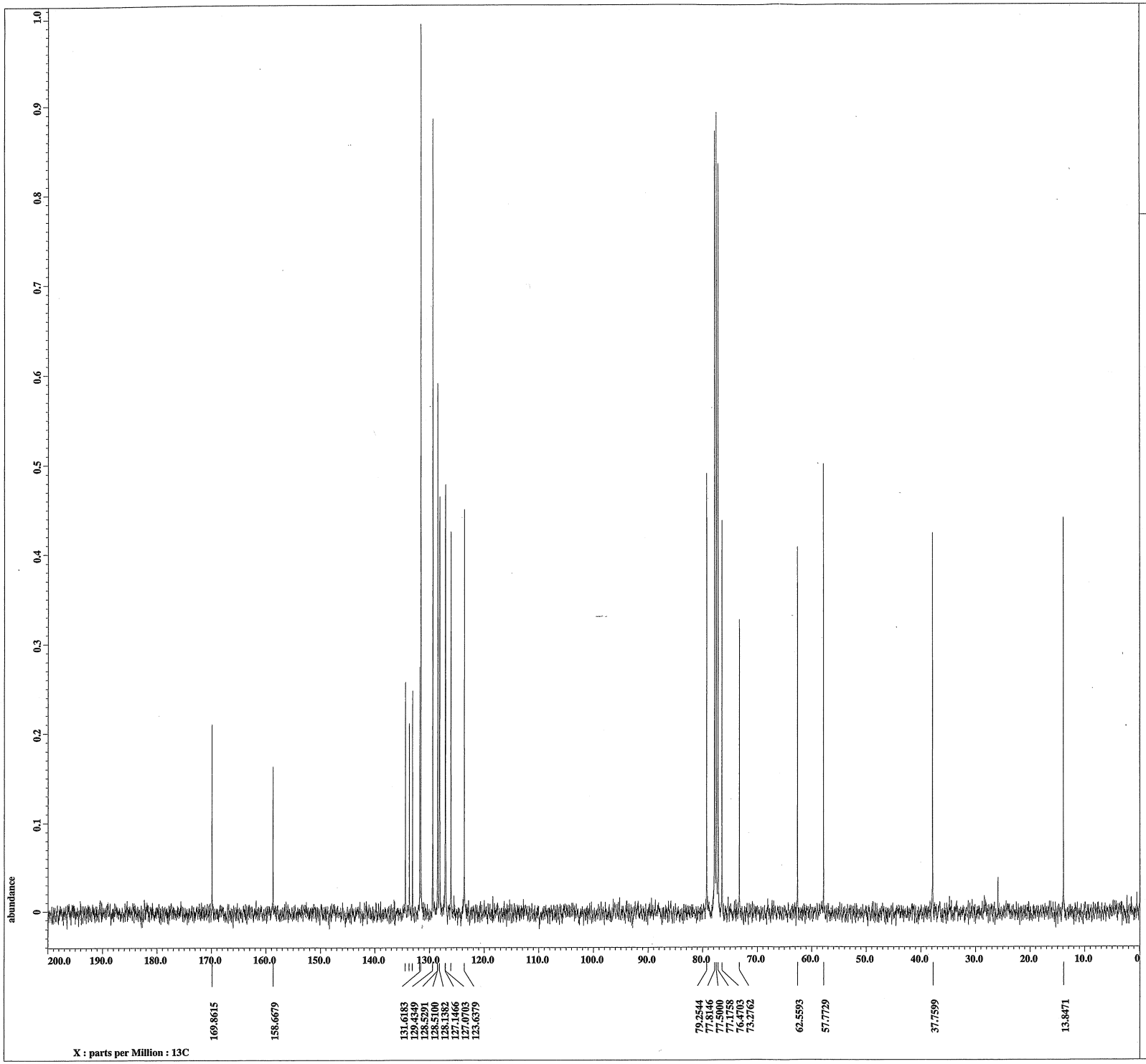
7




```
DFILE   C:¥WINNMR98¥DATA¥tw810hf.als
COMNT   TW-810:1H
DATIM   Fri May 11 10:39:26 2007
OBNUC   1H
EXMOD   NON
OBFRQ        395.75 MHz
OBSET        124.00 KHz
OBFIN      10277.0 Hz
POINT        32768
FREQU        7936.5 Hz
SCANS           16
ACQTM          4.129 sec
PD            10.000 sec
PW1            5.0 us
IRNUC   1H
CTEMP          21.7 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             0.00 Hz
RGAIN            16
```

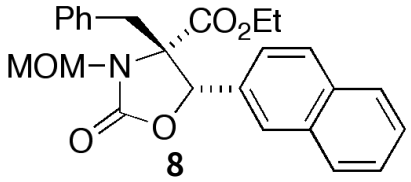


8



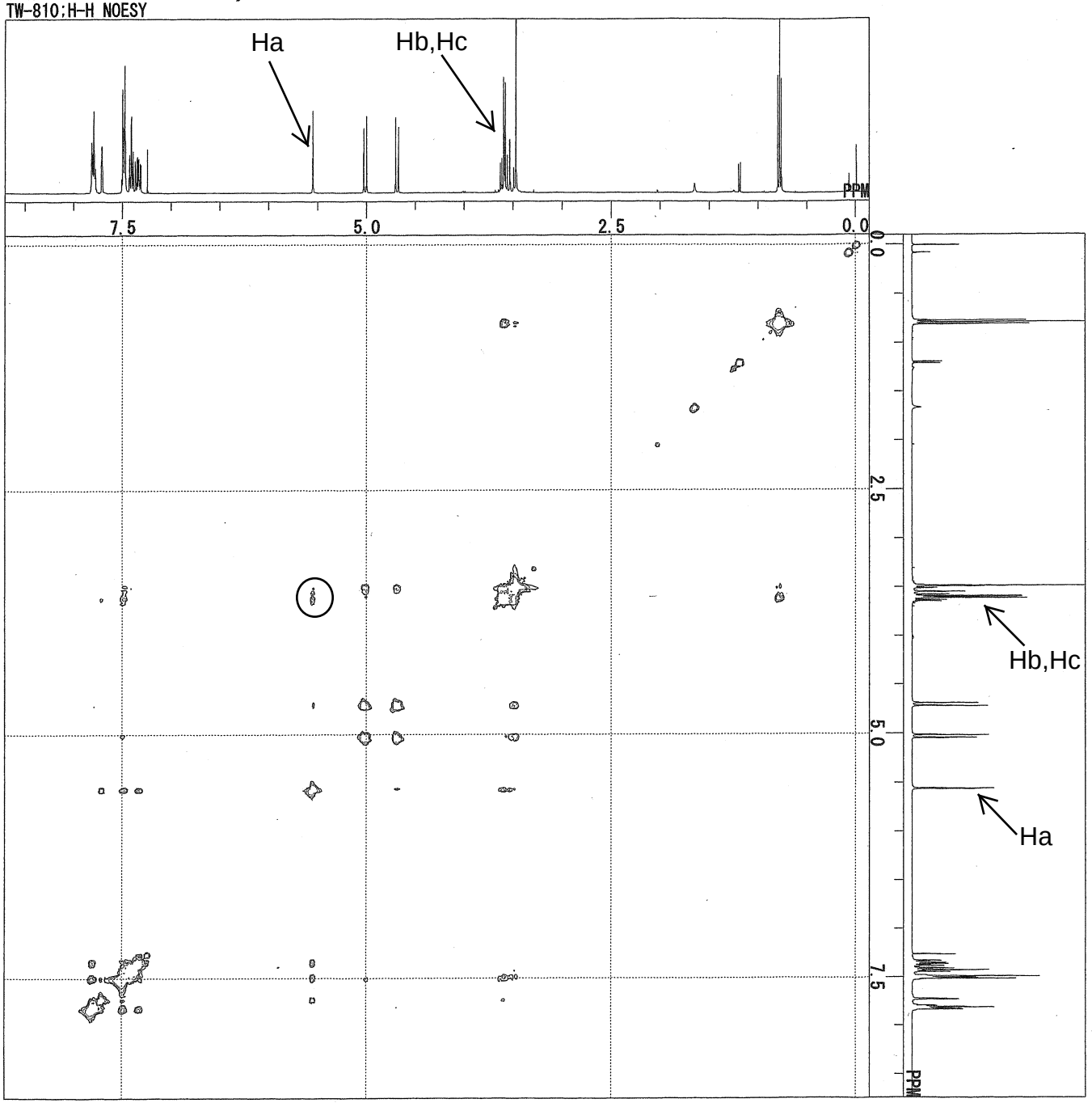

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: TW-810 13C-1.jdf
```

```
Filename          = TW-810 13C-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#489646
Solvent           = CHLOROFORM-D
Creation_time     = 15-MAY-2007 08:26:47
Revision_time     = 15-MAY-2007 13:47:18
Current_time      = 15-MAY-2007 13:47:49

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 152
Total_scans       = 152

X_90_width        = 10.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 3.8[dB]
X_pulse           = 3.4[us]
Irr_atn_dec       = 19.8[dB]
Irr_atn_noe       = 19.8[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 18[dC]
```

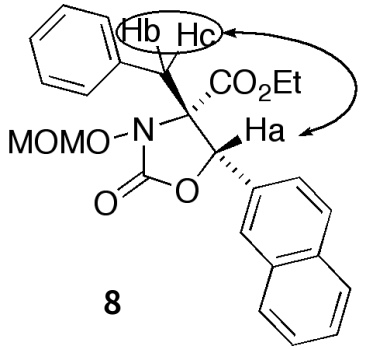


8

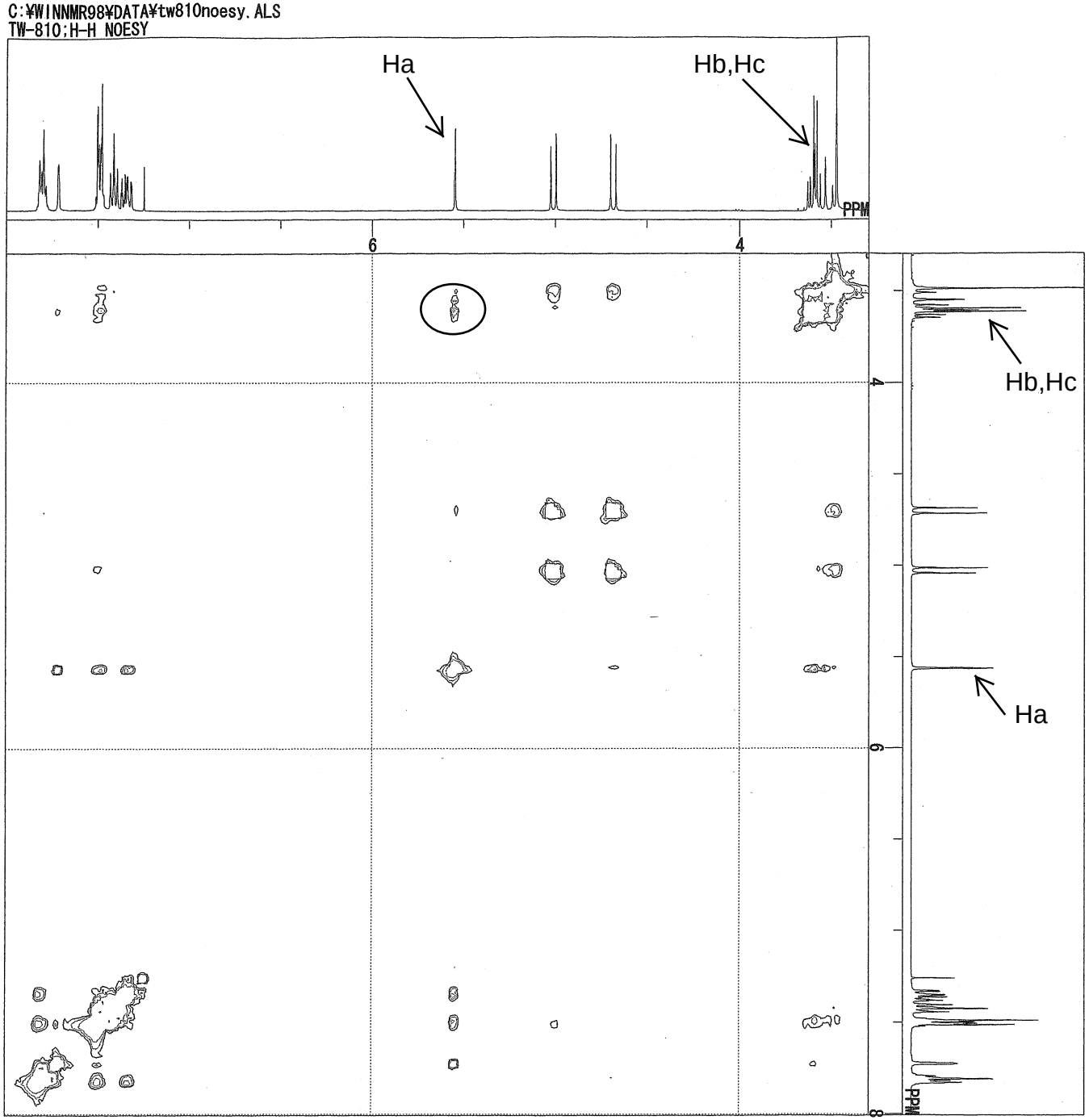
C:¥WINNMR98¥DATA¥tw810noesy.ALS
TW-810;H-H NOESY



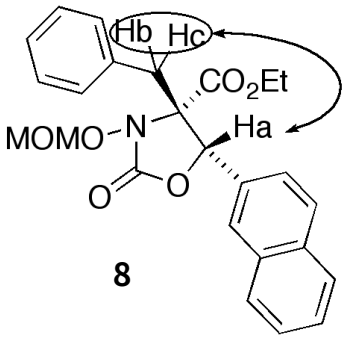

```
DFILE  C:¥WINNMR98¥DATA¥tw810noesy.ALS
COMNT  TW-810;H-H NOESY
DATIM  Fri May 11 13:20:41 2007
EXMOD  VNOENH
OBNUC  1H
OBFRQ        395.75 MHz
OBSET        134.20 KHz
OBFIN          27.1 Hz
POINT           512
FREQU        3500.1 Hz
CLPNT           512
TODAT           256
CLFRQ        3496.5 Hz
SCANS             8
ACQTM         0.146 sec
PD            1.500 sec
PW1            12.6 us
PW2            12.6 us
PW3            10.0 us
PI1           0.286 ms
PI2           0.286 ms
PI3        1500.00 ms
IRNUC  1H
CTEMP         21.7 c
SLVNT  CDCL3
EXREF          0.00 ppm
CLEXR          0.00 ppm
RGAIN            15
OBATN           511
LOOP1             1
```



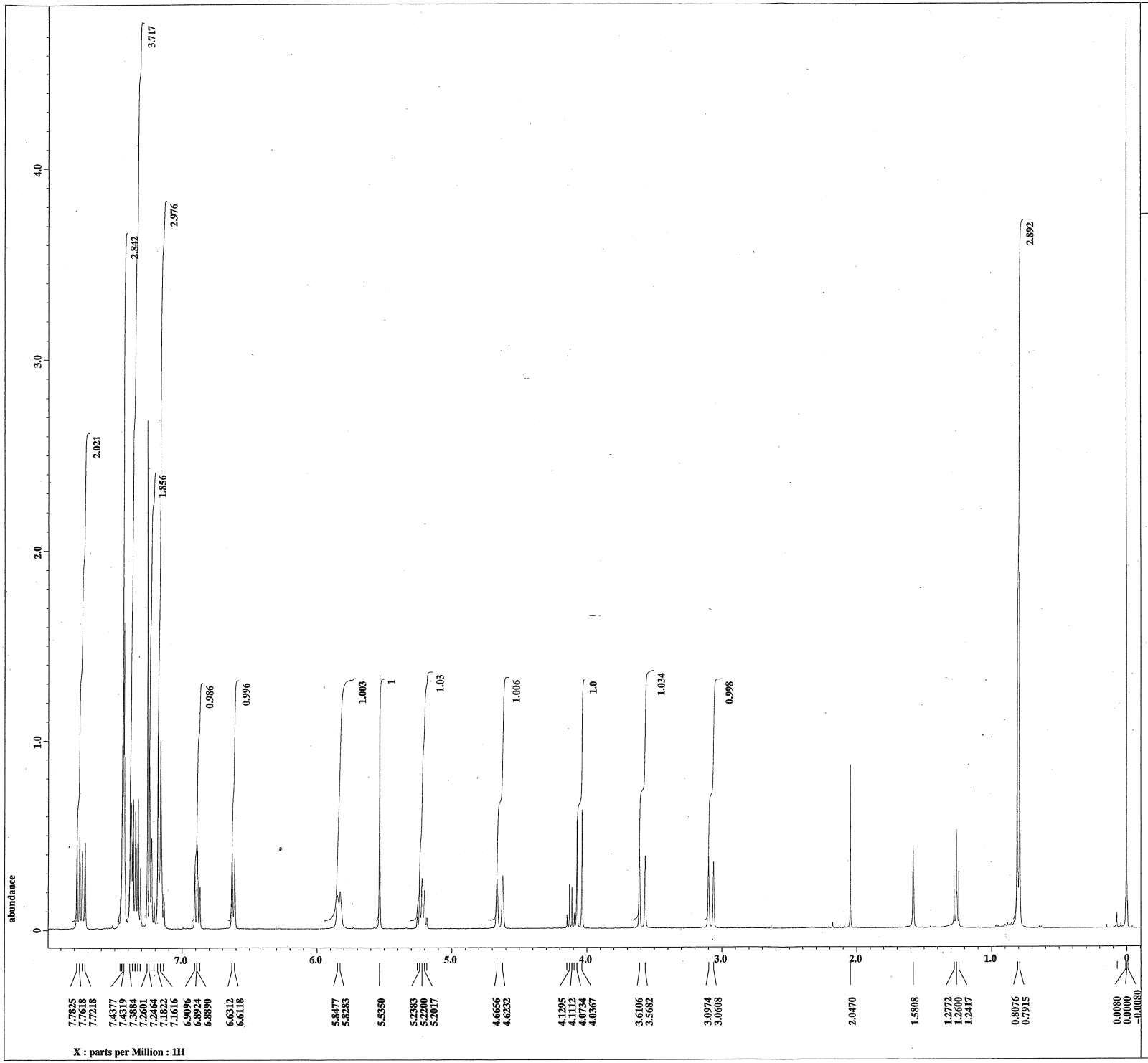
8




```
DFILE  C:¥WINNMR98¥DATA¥tw810noesy.ALS
COMNT  TW-810;H-H NOESY
DATIM  Fri May 11 13:20:41 2007
EXMOD  VNOENH
OBNUC  1H
OBFRQ        395.75 MHz
OBSET        134.20 KHz
OBFIN          27.1 Hz
POINT           512
FREQU        3500.1 Hz
CLPNT           512
TODAT           256
CLFRQ        3496.5 Hz
SCANS             8
ACQTM         0.146 sec
PD            1.500 sec
PW1            12.6 us
PW2            12.6 us
PW3            10.0 us
PI1           0.286 ms
PI2           0.286 ms
PI3         1500.00 ms
IRNUC  1H
CTEMP          21.7 c
SLVNT  CDCL3
EXREF          0.00 ppm
CLEXR          0.00 ppm
RGAIN            15
OBATN           511
LOOP1             1
```

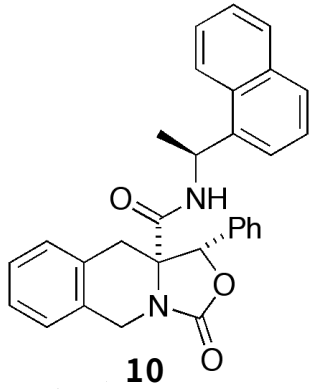


8

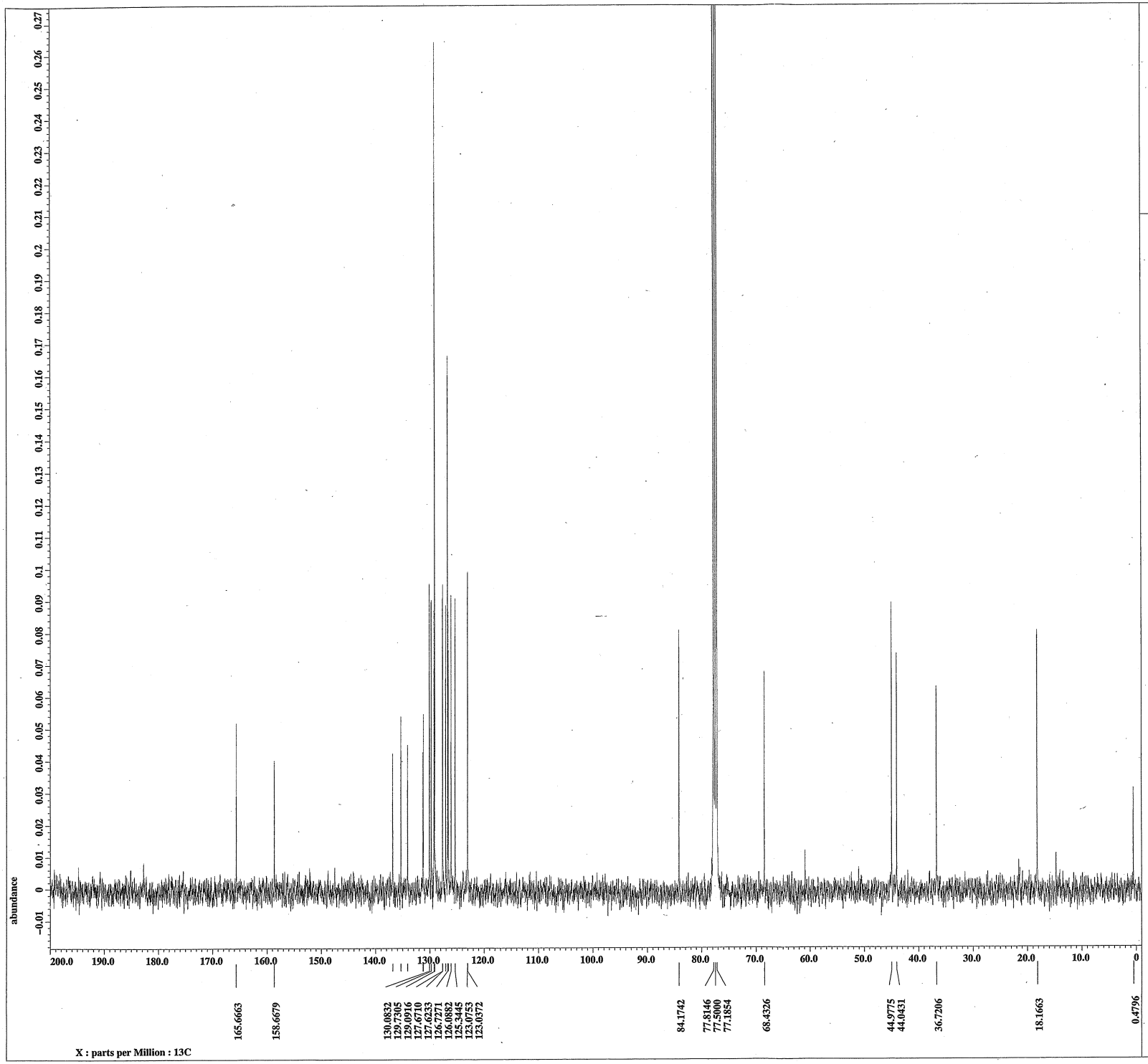



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: TW-1086 for data3-1.jdf
```

```
Filename          = TW-1086 for data3-4.j
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#14992
Solvent           = CHLOROFORM-D
Creation_time     = 29-JAN-2009 17:57:44
Revision_time     = 30-JAN-2009 00:40:14
Current_time      = 30-JAN-2009 00:44:06

Content           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 2.18365952[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.45794685[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 10.6[us]
X_acq_time        = 2.18365952[s]
X_angle           = 45[deg]
X_atn             = 0.3[dB]
X_pulse           = 5.3[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 5[s]
Repetition_time   = 7.18365952[s]
Temp_get          = 18.9[dC]
```

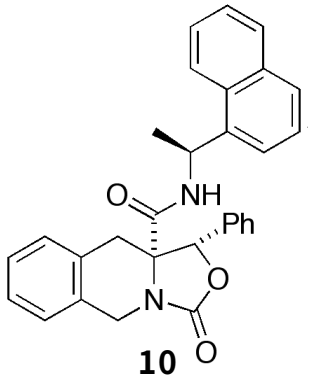


10

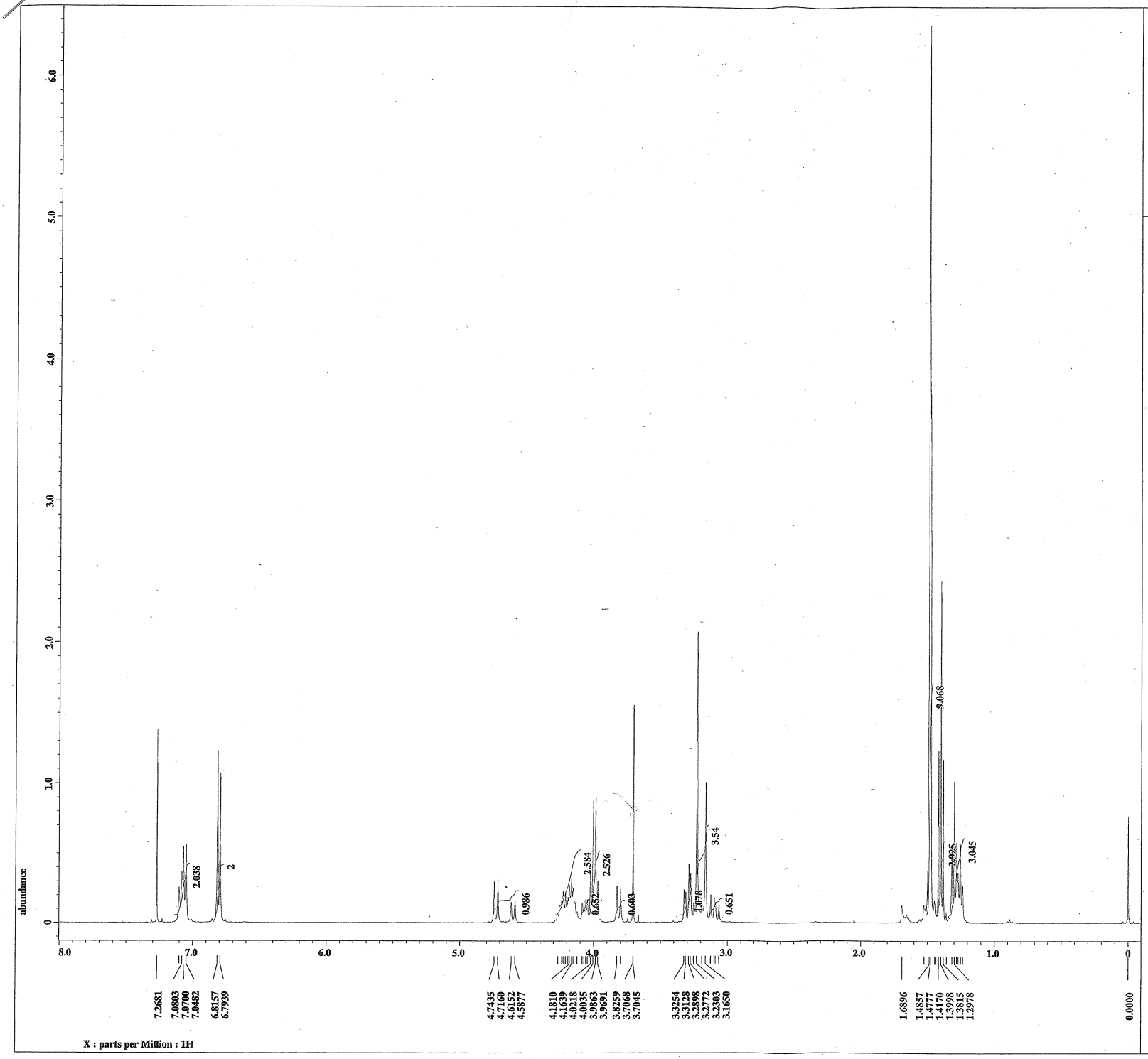



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: TW-1086 13C-1.jdf
```

```
Filename          = TW-1086 13C-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#39570
Solvent           = CHLOROFORM-D
Creation_time     = 29-JAN-2009 19:51:01
Revision_time     = 30-JAN-2009 02:21:41
Current_time      = 30-JAN-2009 02:22:24

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 1434
Total_scans       = 1434

X_90_width        = 10.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 3.8[dB]
X_pulse           = 3.4[us]
Irr_atn_dec       = 19.8[dB]
Irr_atn_noe       = 19.8[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 60
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 19.8[dC]
```

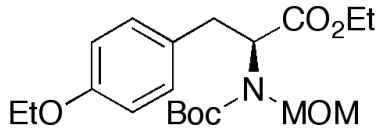


10

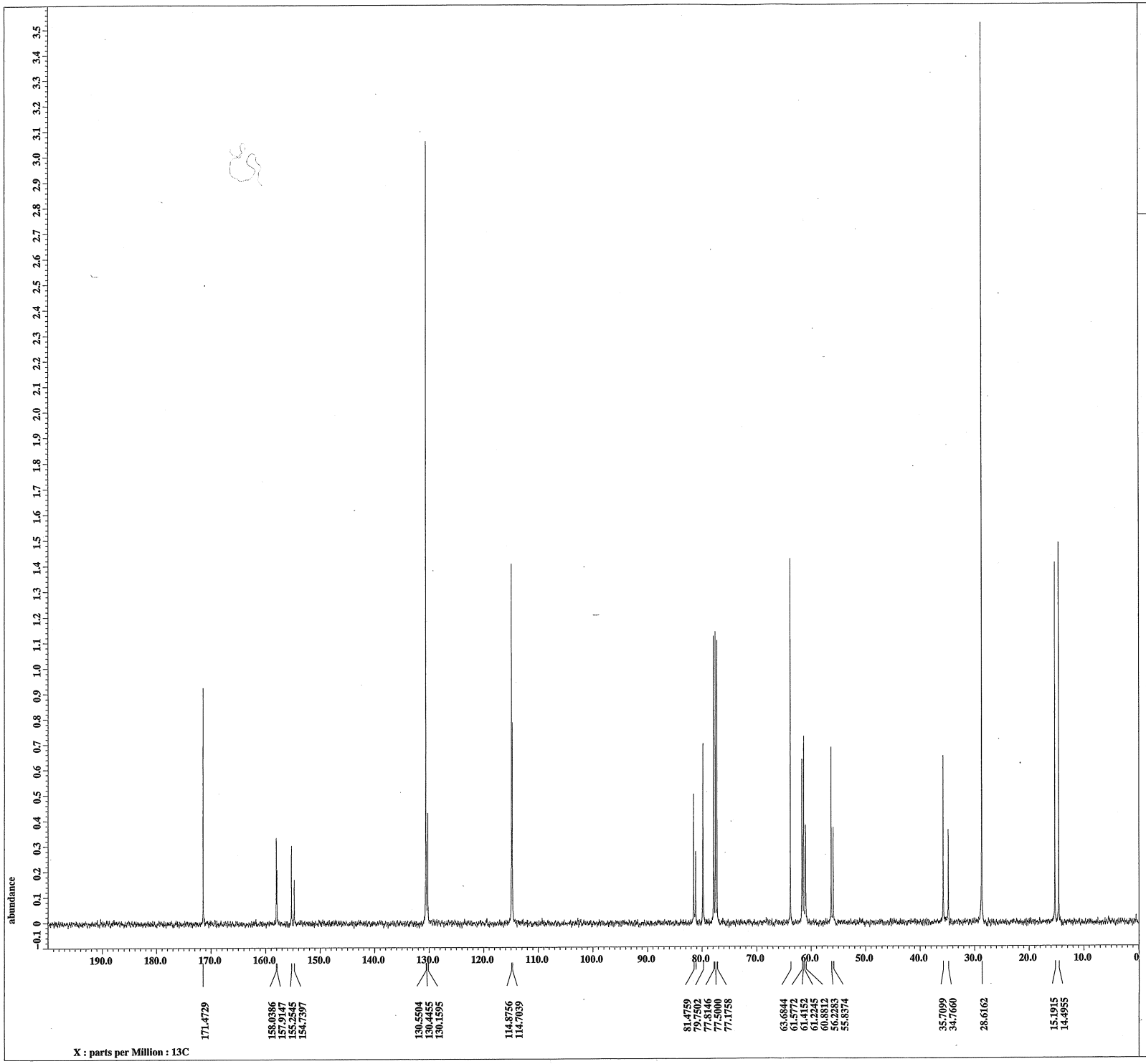



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: TW-784-1.jdf
```

```
Filename          = TW-784-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#537714
Solvent           = CHLOROFORM-D
Creation_time     = 27-MAR-2007 09:40:34
Revision_time     = 27-JAN-2009 19:50:27
Current_time      = 27-JAN-2009 19:50:38

Content           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 2.18365952[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.45794685[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 10.6[us]
X_acq_time        = 2.18365952[s]
X_angle           = 45[deg]
X_atn             = 0.3[dB]
X_pulse           = 5.3[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 5[s]
Repetition_time   = 7.18365952[s]
Temp_get          = 17.9[dC]
```

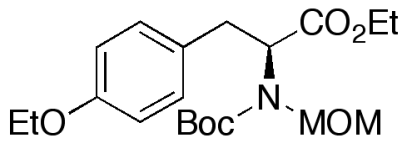


11



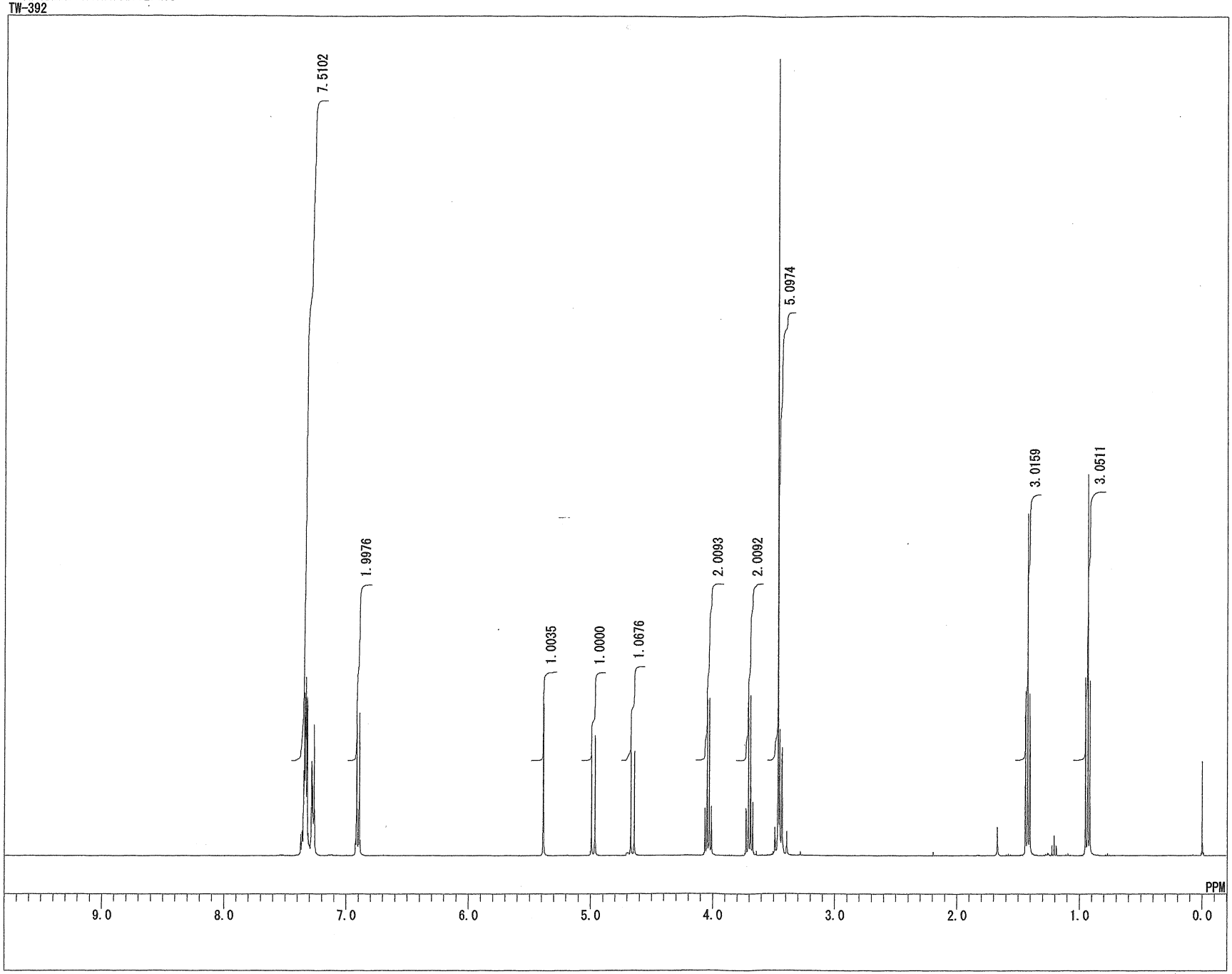

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: 13C No5-1.jdf
```

```
Filename          = 13C No5-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#830307
Solvent           = CHLOROFORM-D
Creation_time     = 20-APR-2007 17:57:28
Revision_time     = 20-APR-2007 23:17:45
Current_time      = 20-APR-2007 23:18:36

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 200
Total_scans       = 200

X_90_width        = 10.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 3.8[dB]
X_pulse           = 3.4[us]
Irr_atn_dec       = 19.8[dB]
Irr_atn_noe       = 19.8[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 60
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 18.3[dC]
```

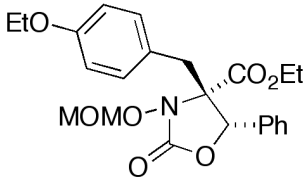


11

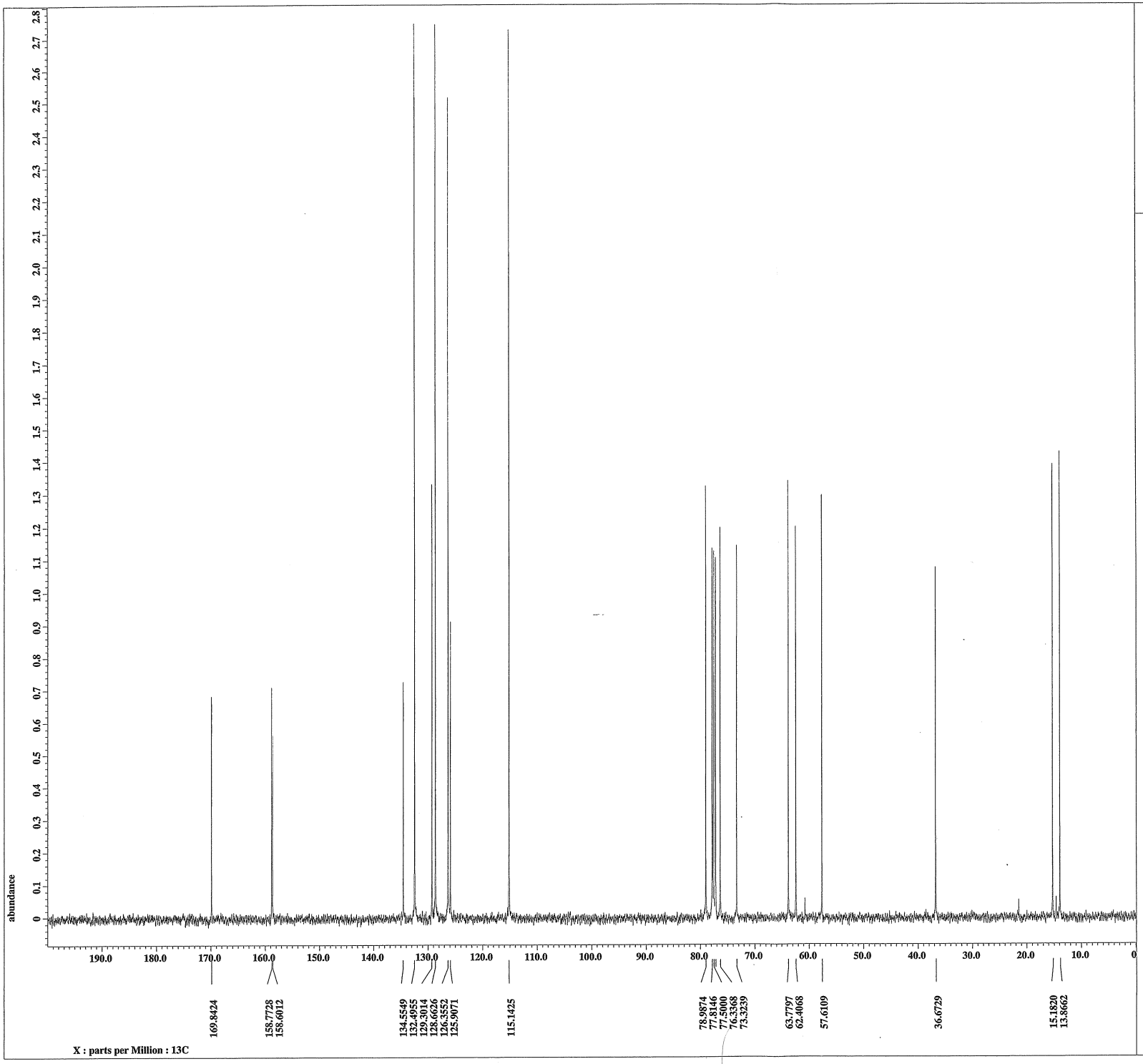
C:¥WINNMR98¥DATA¥tw392.als
TW-392




```
DFILE   C:¥WINNMR98¥DATA¥tw392.als
COMNT   TW-392
DATIM   Thu Feb 23 14:49:47 2006
OBNUC   1H
EXMOD   NON
OBFRQ       395.75 MHz
OBSET       124.00 KHz
OBFIN     10277.0 Hz
POINT       32768
FREQU      7936.5 Hz
SCANS          16
ACQTM       4.129 sec
PD         10.000 sec
PW1         5.0 us
IRNUC   1H
CTEMP       20.2 c
SLVNT   CDCL3
EXREF       0.00 ppm
BF          0.00 Hz
RGAIN          16
```

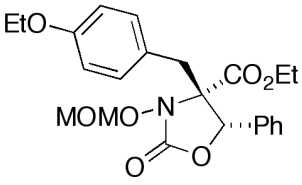


12

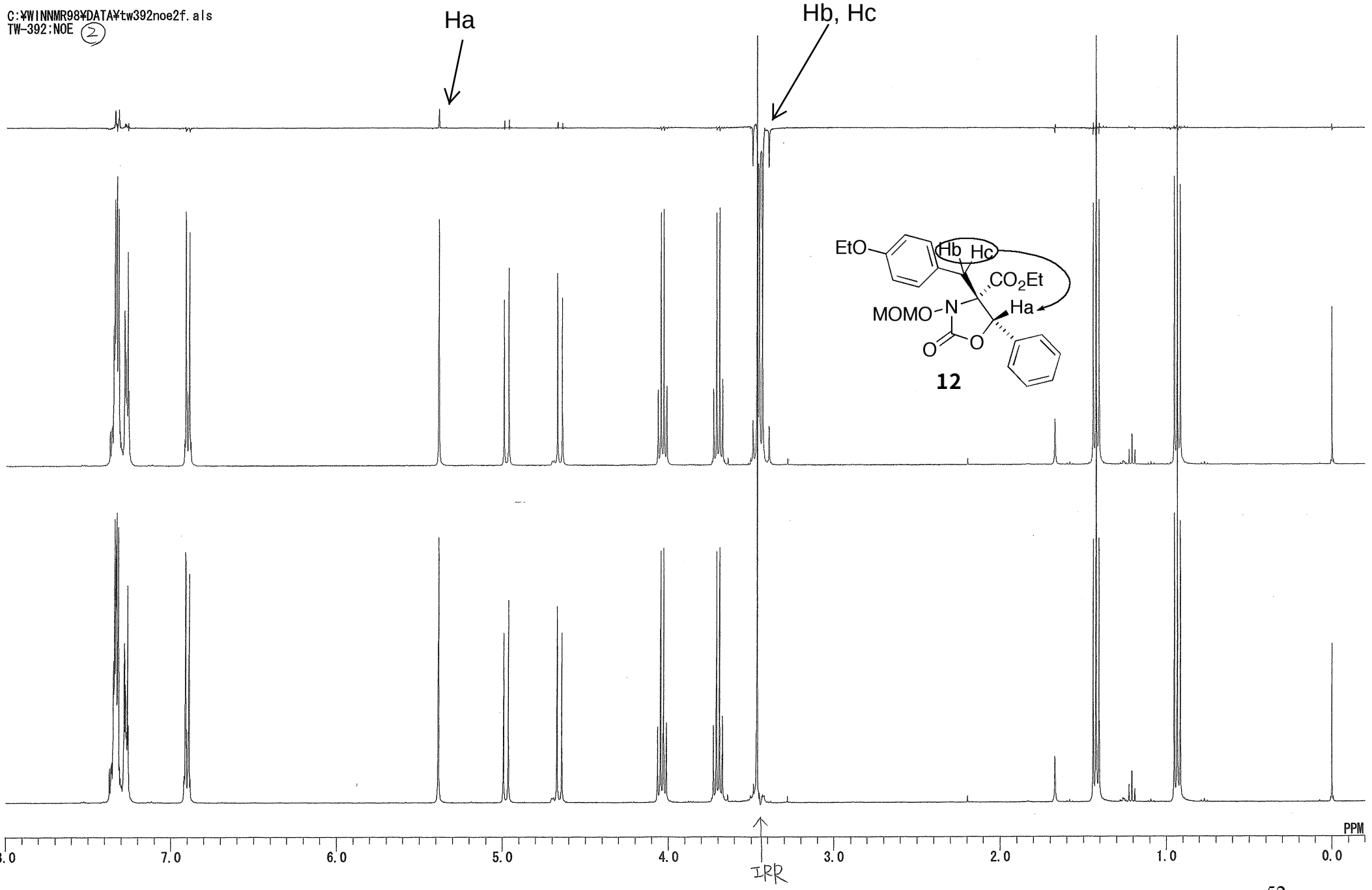



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: TW-788 13C-1.jdf
```

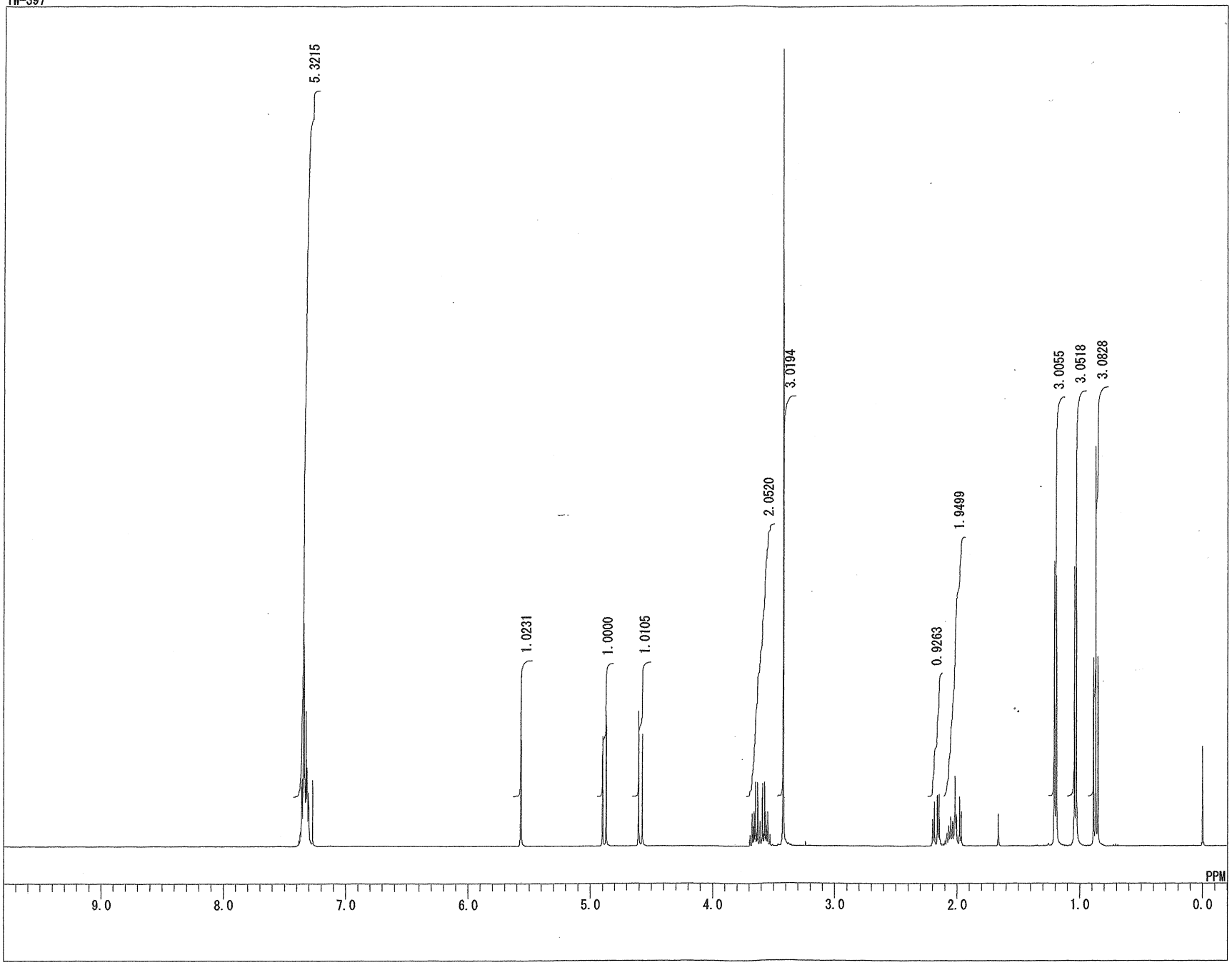
```
Filename            = TW-788 13C-3.jdf
Author              = delta
Experiment          = single_pulse_dec
Sample_id           = S#776531
Solvent             = CHLOROFORM-D
Creation_time       = 28-MAR-2007 16:25:02
Revision_time       = 28-MAR-2007 21:44:03
Current_time        = 28-MAR-2007 21:47:20

Content             = single pulse decouple
Data_format         = 1D COMPLEX
Dim_size            = 26214
Dim_title           = 13C
Dim_units           = [ppm]
Dimensions          = X
Site                = ECX 400P
Spectrometer        = DELTA2_NMR

Field_strength      = 9.389766[T] (400[MHz]
X_acq_duration      = 1.04333312[s]
X_domain            = 13C
X_freq              = 100.52530333[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_resolution        = 0.95846665[Hz]
X_sweep             = 31.40703518[kHz]
Irr_domain          = 1H
Irr_freq            = 399.78219838[MHz]
Irr_offset          = 5[ppm]
Clipped             = FALSE
Mod_return          = 1
Scans               = 129
Total_scans         = 129

X_90_width          = 10.2[us]
X_acq_time          = 1.04333312[s]
X_angle             = 30[deg]
X_atn               = 3.8[dB]
X_pulse             = 3.4[us]
Irr_atn_dec         = 19.8[dB]
Irr_atn_noe         = 19.8[dB]
Irr_noise           = WALTZ
Decoupling          = TRUE
Initial_wait        = 1[s]
Noe                 = TRUE
Noe_time            = 2[s]
Recvr_gain          = 60
Relaxation_delay    = 2[s]
Repetition_time     = 3.04333312[s]
Temp_get            = 17.9[dC]
```



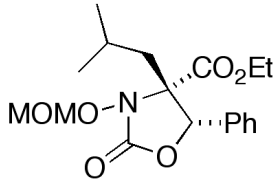
12



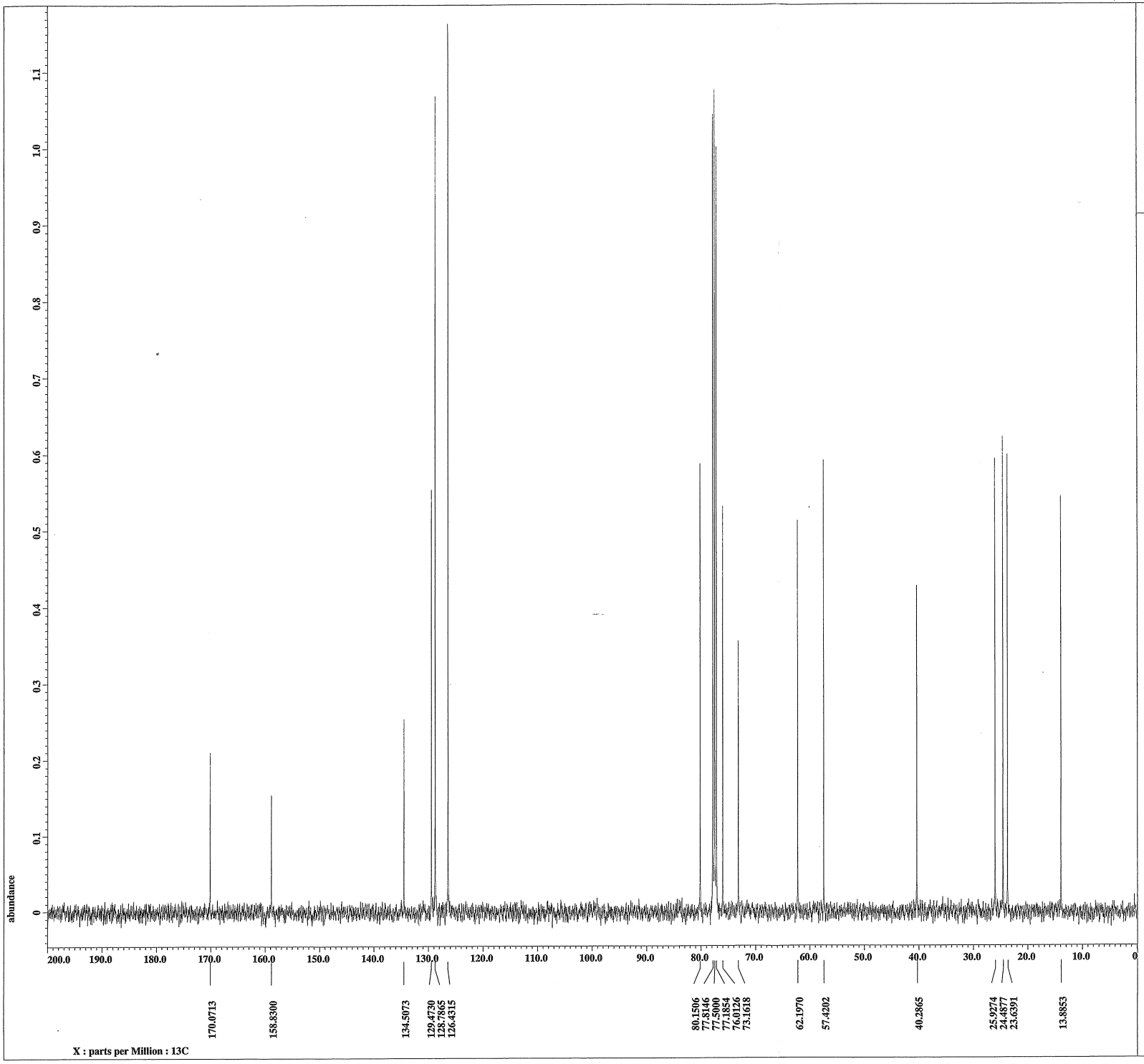
C:¥WINNMR98¥DATA¥tw397.als
TW-397




```
DFILE   C:¥WINNMR98¥DATA¥tw397.als
COMNT   TW-397
DATIM   Thu Feb 23 16:42:05 2006
OBNUC   1H
EXMOD   NON
OBFRQ       395.75 MHz
OBSET       124.00 KHz
OBFIN     10277.0 Hz
POINT       32768
FREQU       7936.5 Hz
SCANS          16
ACQTM        4.129 sec
PD          10.000 sec
PW1          5.0 us
IRNUC   1H
CTEMP        20.0 c
SLVNT   CDCL3
EXREF         0.00 ppm
BF            0.00 Hz
RGAIN          16
```

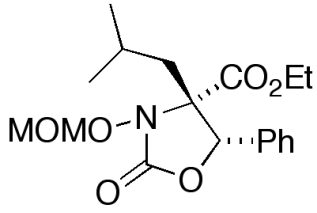


14

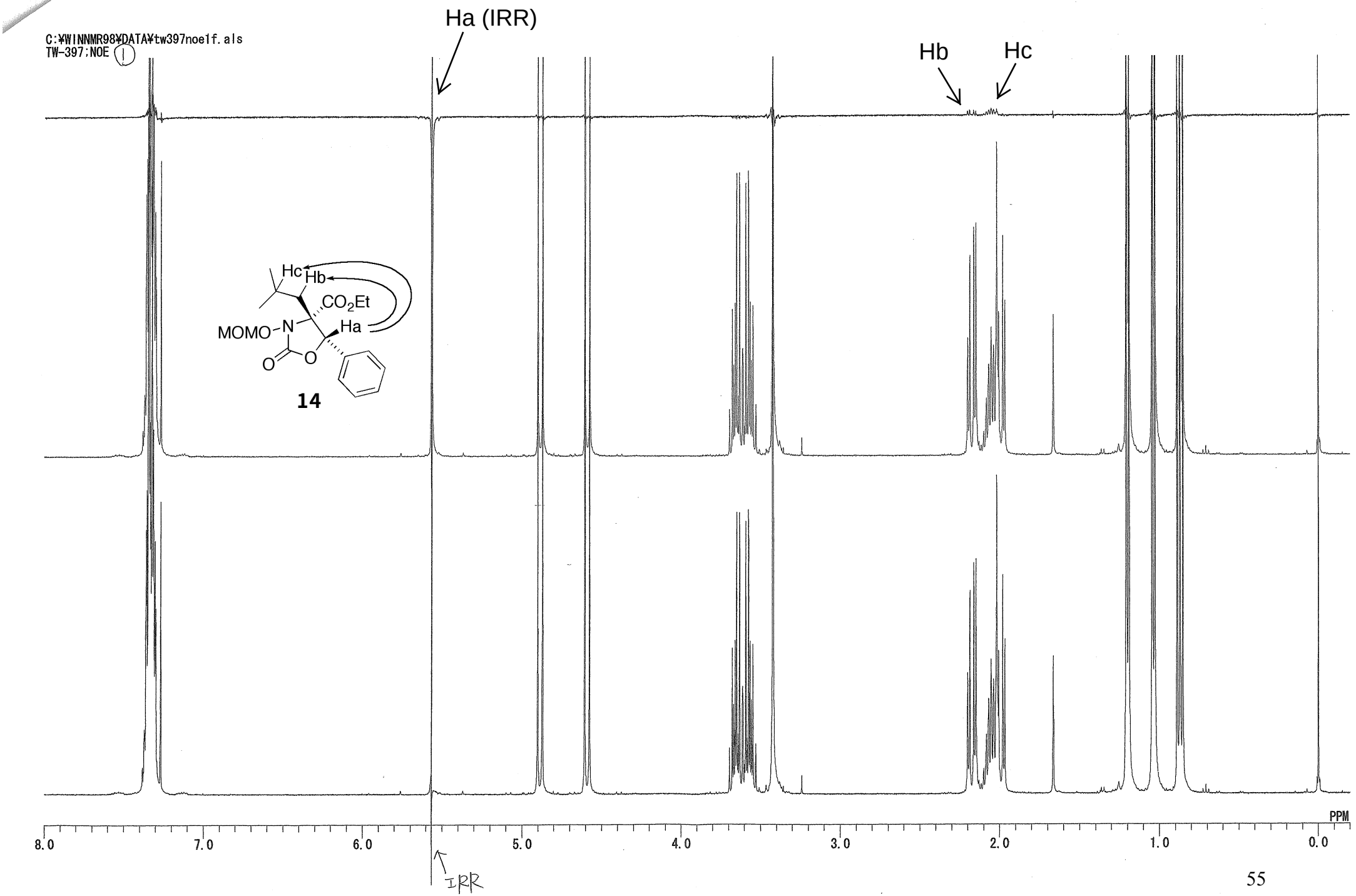


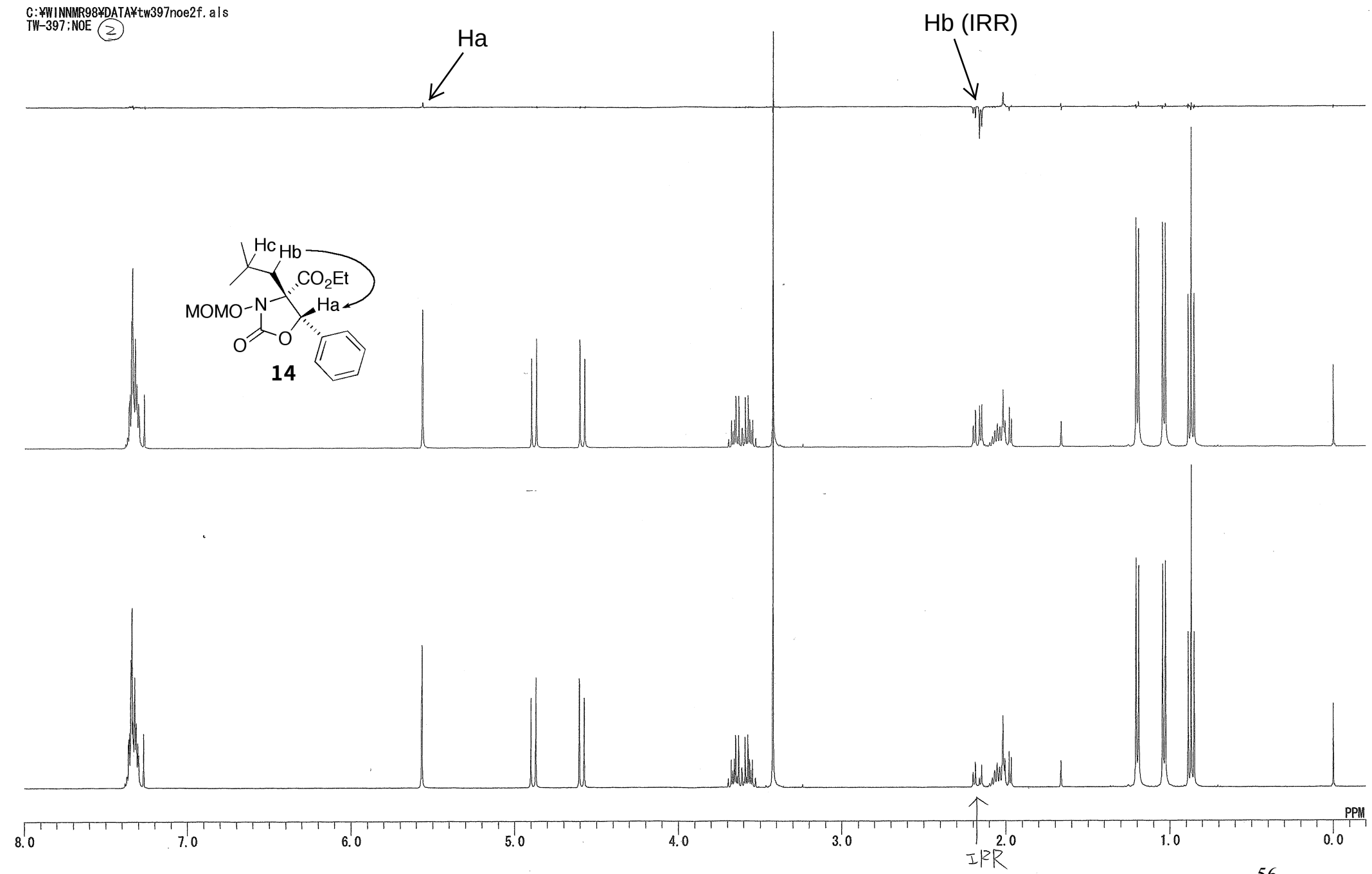

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: 13C No7-1.jdf
```

```
Filename          = 13C No7-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#803039
Solvent           = CHLOROFORM-D
Creation_time     = 27-MAR-2007 17:14:07
Revision_time     = 27-MAR-2007 22:33:30
Current_time      = 27-MAR-2007 22:33:49

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400P
Spectrometer      = DELTA2_NMR

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 203.0
Total_scans       = 203.0

X_90_width        = 10.2[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 3.8[dB]
X_pulse           = 3.4[us]
Irr_atn_dec       = 19.8[dB]
Irr_atn_noe       = 19.8[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 60
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 17.8[dC]
```



14


C:¥WINNMR98¥DATA¥tw397noe1f.als
TW-397:NOE
Ha (IRR)
Hb
Hc
Hc
Hb
CO2Et
MOMO-N
Ha
O
O
14
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
IRR


C:¥WINNMR98¥DATA¥tw397noe2f.als
TW-397;NOE (2)
Ha
Hb (IRR)
Hc
Hb
CO2Et
MOMO-N
Ha
O
O
14
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
IRR