Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Intermolecular Rhodium-Catalyzed Carbometallation–Heck-Type Reaction in Water

Takuya Kurahashi, Hiroshi Shinokubo,* and Atsuhiro Osuka

Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan and PRESTO, Japan Science and Technology Agency (JST)

E-mail: hshino@kuchem.kyoto-u.ac.jp

Table of Contents

Instrumentation and Materials

^{1}H NMR spectra were measured on a JEOL ECA-600 (600 MHz) and JEOL EX-400 (400 MHz) spectrometers. The chemical shifts of ^{1}H NMR are expressed in parts per million downfield relative to the internal tetramethylsilane (δ = 0 ppm) or chloroform (δ = 7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. ^{13}C NMR spectra were measured on a JEOL ECA-600 (150 MHz) spectrometers with tetramethylsilane as an internal standard (δ = 0 ppm) or chloroform-*d* (δ = 77.0 ppm). Chemical shift values are given in parts per million downfield relative to the internal standard. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer. GC-MS analyses were performed with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. Elemental analyses were carried out at Elemental Analysis Center of Kyoto University. Melting points were determined using a Yanako Micro Melting Point Apparatus. TLC analyses were performed by means of Merck Kieselgel 60 F254 and column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). X-ray data were taken on a Rigaku. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Pure water was obtained with Millipore Direct-Q system. Degassed water was used for all reactions.

General Procedure

A mixture of phenylboronic acid (**1a**, 24 mg, 0.2 mmol), $[RhOH(cod)]_2$ (1.8 mg, 0.004 mmol), 5-decyne (**2a**, 14 mg, 0.1 mmol), and methyl acrylate (**3a**, 17 mg, 0.2 mmol) in water (1 mL) was sonicated for a few minutes to form a stable emersion. The emersion was stood for 12 h at ambient temperature (Figure S1). The resulting mixture was diluted with ether (10 mL). The aqueous layer was extracted with ether (twice). The combined organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude product was purified by silica-gel chromatography (hexane/ether = 20:1) to give **6aaa** as colorless oil (24 mg, 81% yield).

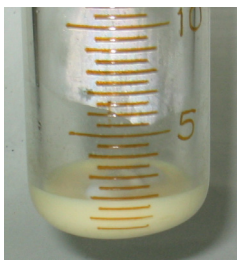


Figure S1

4-Butyl-5-phenylnona-2,4-dienoic acid methyl ester (6aaa)

Yield: 81%. Colorless oil.

TLC: R_f 0.23 (hexane/ether 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 6.8 Hz, 3H), 0.98 (t, *J* = 6.8 Hz, 3H), 1.28 (m, 4H), 1.47 (m, 4H), 2.38 (t, *J* = 8.0 Hz, 2H), 2.52 (t, *J* = 8.0 Hz, 2H), 3.66 (s, 3H), 5.85 (d, *J* = 16.1 Hz, 1H), 7.09–7.11 (m, 2H), 7.24–7.37 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 14.1, 22.9, 23.2, 28.1, 30.5, 31.5, 35.3, 51.4, 115.8, 127.3, 128.1, 129.1, 133.0, 141.5, 145.4, 151.0, 168.2.

IR (neat) 3060, 2956, 1717, 1616, 1271, 1167, 700 cm^{-1}.

EIMS (70 eV) *m/z* 302 (M^++2, 6), 301 (M^++1, 12), 300 (M^+, 63), 167 (100).

Anal. Calcd for $C_{20}H_{28}O_2$: C, 79.96; H, 9.39. Found: C, 79.73; H, 9.40.

4-Butyl-5-(*p*-tolyl)nona-2,4-dienoic acid methyl ester (6baa)

Yield: 66%. Colorless oil.

TLC: R_f 0.21 (hexane/ether 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, *J* = 6.8 Hz, 3H), 0.97 (t, *J* = 6.8 Hz, 3H), 1.26 (m, 4H), 1.44 (m, 4H), 2.36 (s, 3H), 2.39 (t, *J* = 7.6 Hz, 2H), 2.50 (t, *J* = 7.6 Hz, 2H), 3.66 (s, 3H), 5.85 (d, *J* = 16.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 16.0 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 13.9, 14.0, 21.2, 22.8, 23.1, 28.0, 30.5, 31.4, 35.2, 51.2, 115.4, 128.7, 129.0, 132.8, 136.9, 138.4, 145.6, 151.1, 168.2.

IR (neat) 2956, 1717, 1616, 1279, 1166, 822 cm^{-1}.

EIMS (70 eV) *m/z* 316 (M^++2, 3), 315 (M^++1, 22), 314 (M^+, 98), 143 (100).

Anal. Calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62. Found: C, 80.33; H, 9.83.

4-Butyl-5-(4-methoxyphenyl)nona-2,4-dienoic acid methyl ester (6caa)

Yield: 50%. Colorless oil.

TLC: R_f 0.32 (hexane/ether 10 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H), 1.22 (m, 4H), 1.44 (m, 4H), 2.37 (t, *J* = 7.6 Hz, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 3.66 (s, 3H), 3.83 (s, 3H), 5.83 (d, *J* = 15.6 Hz, 1H), 6.87 (d, *J* = 11.2 Hz, 2H), 7.03 (d, *J* = 11.2 Hz, 2H), 7.30 (d, *J* = 15.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 13.9, 14.0, 22.8, 23.1, 28.1, 30.6, 31.3, 35.2, 51.3, 55.2, 113.4, 115.4, 130.3, 132.7, 133.6, 145.6, 150.3, 158.8, 168.3.

IR (neat) 2956, 1719, 1610, 1248, 1166, 834 cm^{-1}.

EIMS (70 eV) *m/z* 332 (M^++2, 5), 331 (M^++1, 25), 330 (M^+, 100), 273 (31).

Anal. Calcd for $C_{21}H_{30}O_3$: C, 76.33; H, 9.15. Found: C, 76.48; H, 9.29.

4-Butyl-5-(4-trifluoromethylphenyl)nona-2,4-dienoic acid methyl ester (6daa)

Yield: 72%. Colorless oil.

TLC: R_f 0.22 (hexane/ether 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H), 1.27 (m, 4H), 1.45 (m, 4H), 2.41 (t, *J* = 7.2 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 3.67 (s, 3H), 5.89 (d, *J* = 16.0 Hz, 1H), 7.14 (d, *J* = 16.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 13.8, 14.0, 22.8, 23.1, 28.0, 30.3, 31.4, 35.0, 116.8, 124.1 (q, *J* = 263 Hz), 125.1, 129.3 (q, *J* = 31.5 Hz), 129.4, 133.9, 144.2, 145.3, 145.3, 148.9, 167.9.

^{19}F NMR (564 MHz, $CDCl_3$) δ –63.4.

IR (neat) 2957, 1717, 1616, 1323, 1166, 845 cm^{-1}.

EIMS (70 eV) *m/z* 370 (M^++2, 28), 369 (M^++1, 24), 368 (M^+, 98), 57 (100).

HRMS Calcd for $C_{21}H_{27}FO_2$: M^+ 368.1963. Found: *m/z* 368.1965.

4-Butyl-5-naphthalen-2-yl-nona-2,4-dienoic acid methyl ester (6eaa)

Yield: 45%. Colorless oil.

TLC: R_f 0.11 (hexane/ether 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H), 1.23 (m, 4H), 1.47 (m, 4H), 2.42 (t, *J* = 8.4 Hz, 2H), 2.55 (t, *J* = 8.4 Hz, 2H), 3.55 (s, 3H), 5.83 (d, *J* = 15.6 Hz, 1H), 7.18–7.26 (m, 2H), 7.42–7.50 (m, 3H), 7.75–7.80 (m, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 13.9, 14.0, 22.8, 23.1, 28.1, 30.5, 31.5, 35.3, 51.3, 116.1, 125.9, 126.2, 127.2, 127.6, 127.7, 128.0, 128.0, 132.5, 133.0, 133.3, 138.9, 145.1, 150.8.

IR (neat) 2956, 1717, 1616, 1277, 1166, 750 cm^{-1}.

EIMS (70 eV) *m/z* 352 (M^++2, 10), 351 (M^++1, 41), 350 (M^+, 100), 291 (89).

Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 81.95; H, 8.75.

5-Phenyl-4-propylocta-2,4-dienoic acid methyl ester (6aba)

Yield: 61%. Colorless oil.

TLC: R_f 0.21 (hexane/ether 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H), 1.31 (m, 2H), 1.55 (m, 2H), 2.41 (t, *J* = 5.6 Hz, 2H), 2.53 (t, *J* = 5.6 Hz, 2H), 3.67 (s, 3H), 5.87 (d, *J* = 16.0 Hz, 1H), 7.10–7.13 (m, 2H), 7.26–7.38 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 14.3, 21.5, 22.4, 30.2, 37.4, 51.3, 115.9, 127.2, 128.0, 129.1, 132.6, 141.3, 145.2, 150.8, 168.1.

IR (neat) 3060, 2959, 1717, 1616, 1267, 1167, 701 cm^{-1}.

EIMS (70 eV) *m/z* 274 (M^++2, 2), 275 (M^++1, 19), 274 (M^+, 77), 167 (100).

HRMS Calcd for $C_{18}H_{24}O_2$: M^+ 272.1776. Found: *m/z* 272.1772.

4-Pentyl-5-phenyldeca-2,4-dienoic acid methyl ester (6aca)

Yield: 53%. Colorless oil.

TLC: R_f 0.26 (hexane/ether 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H), 1.25 (m, 6H), 1.38 (m, 4H), 1.46 (m, 2H), 2.38 (t, *J* = 5.6 Hz, 2H), 2.50 (t, *J* = 5.6 Hz, 2H), 3.65 (s, 3H), 5.84 (d, *J* = 16.0 Hz, 1H), 7.09–7.10 (m, 2H), 7.26–7.36 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 13.9, 14.1, 22.4, 22.6, 27.9, 28.2, 29.0, 31.9, 32.2, 35.4, 51.3, 115.7, 127.2, 128.0, 128.0, 129.1, 132.9, 141.4, 145.3, 150.9, 168.1.

IR (neat) 2955, 1717, 1616, 1271, 1165, 702 cm^{-1}.

EIMS (70 eV) *m/z* 330 (M^++2, 5), 329 (M^++1, 21), 328 (M^+, 100), 155 (98).

Anal. Calcd for $C_{20}H_{28}O_2$: C, 80.44; H, 9.82. Found: C, 80.22; H, 9.68.

4-Hexyl-5-phenylundeca-2,4-dienoic acid methyl ester (6ada)

Yield: 57%. Colorless oil.

TLC: R_f 0.14 (hexane/ether 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H), 1.25–1.44 (m, 16H), 2.38 (t, *J* = 8.0 Hz, 2H), 2.50 (t, *J* = 8.0 Hz, 2H), 3.65 (s, 3H), 5.84 (d, *J* = 18.8 Hz, 1H), 7.07–7.10 (m, 2H), 7.23–7.36 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 14.1, 22.5, 22.7, 28.2, 28.3, 29.2, 29.4, 29.7, 31.6, 31.7, 35.4, 51.3, 115.7, 127.2, 128.0, 129.1, 133.0, 141.4, 145.3, 151.0, 168.2.

IR (neat) 2928, 1717, 1616, 1269, 1116, 701 cm^{-1}.

EIMS (70 eV) *m/z* 358 (M^++2, 8), 357 (M^++1, 19), 356 (M^+, 63), 85 (100).

Anal. Calcd for $C_{24}H_{36}O_2$: C, 80.85; H, 10.18. Found: C, 81.06; H, 10.08.

4,5-Diphenyl-5-(*p*-tolyl)penta-2,4-dienoic acid methyl ester (6bea)

Yield: 31%. Colorless solid.

TLC: R_f 0.17 (hexane/ether 20 : 1).

Mp: 187.2 °C (hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.65 (s, 3H), 5.62 (d, *J* = 16.0 Hz, 1H), 6.88–6.90 (m, 2H), 7.02–7.22 (m, 12H), 7.75 (d, *J* = 16.0 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 21.3, 51.4, 121.1, 127.0, 127.0, 127.3, 128.1, 128.8, 131.0, 131.1, 131.1, 136.6, 138.2, 138.4, 139.5, 142.2, 146.7, 149.9, 168.1.

IR (neat) 2962, 1717, 1616, 1288, 1172, 698 cm^{-1}.

EIMS (70 eV) *m/z* 356 (M^++2, 8), 355 (M^++1, 19), 354 (M^+, 84), 295 (100).

HRMS Calcd for $C_{25}H_{22}O_2$: M^+ 354.1620. Found: *m/z* 354.1624.

Crystallographic data for this structure has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-612527. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

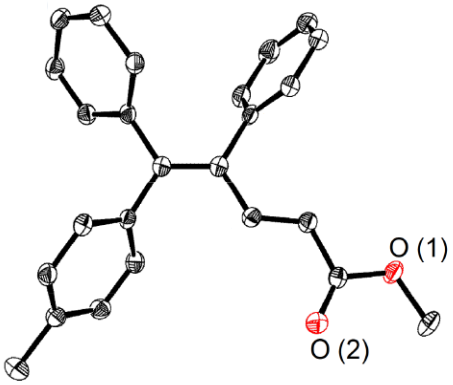
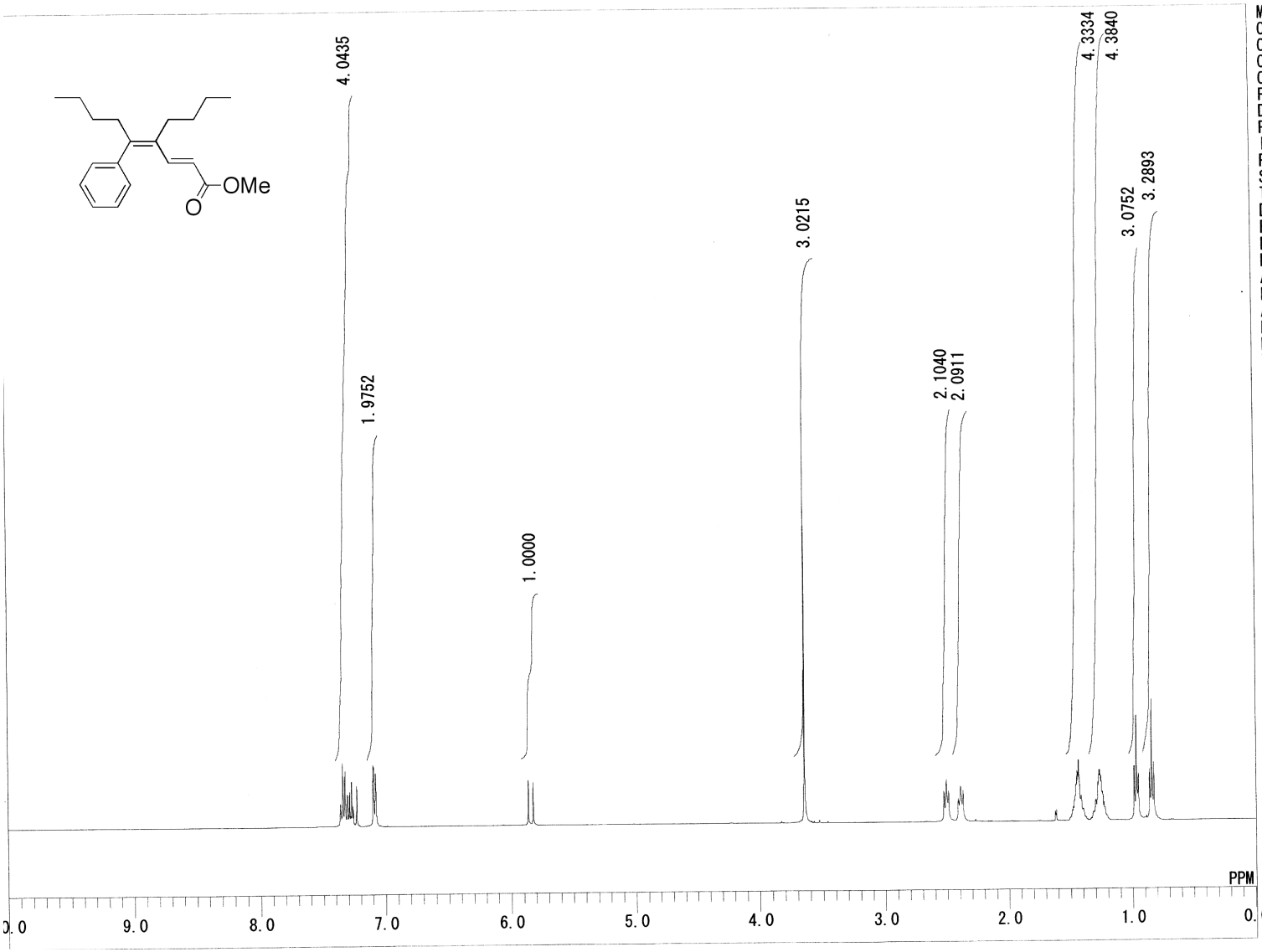
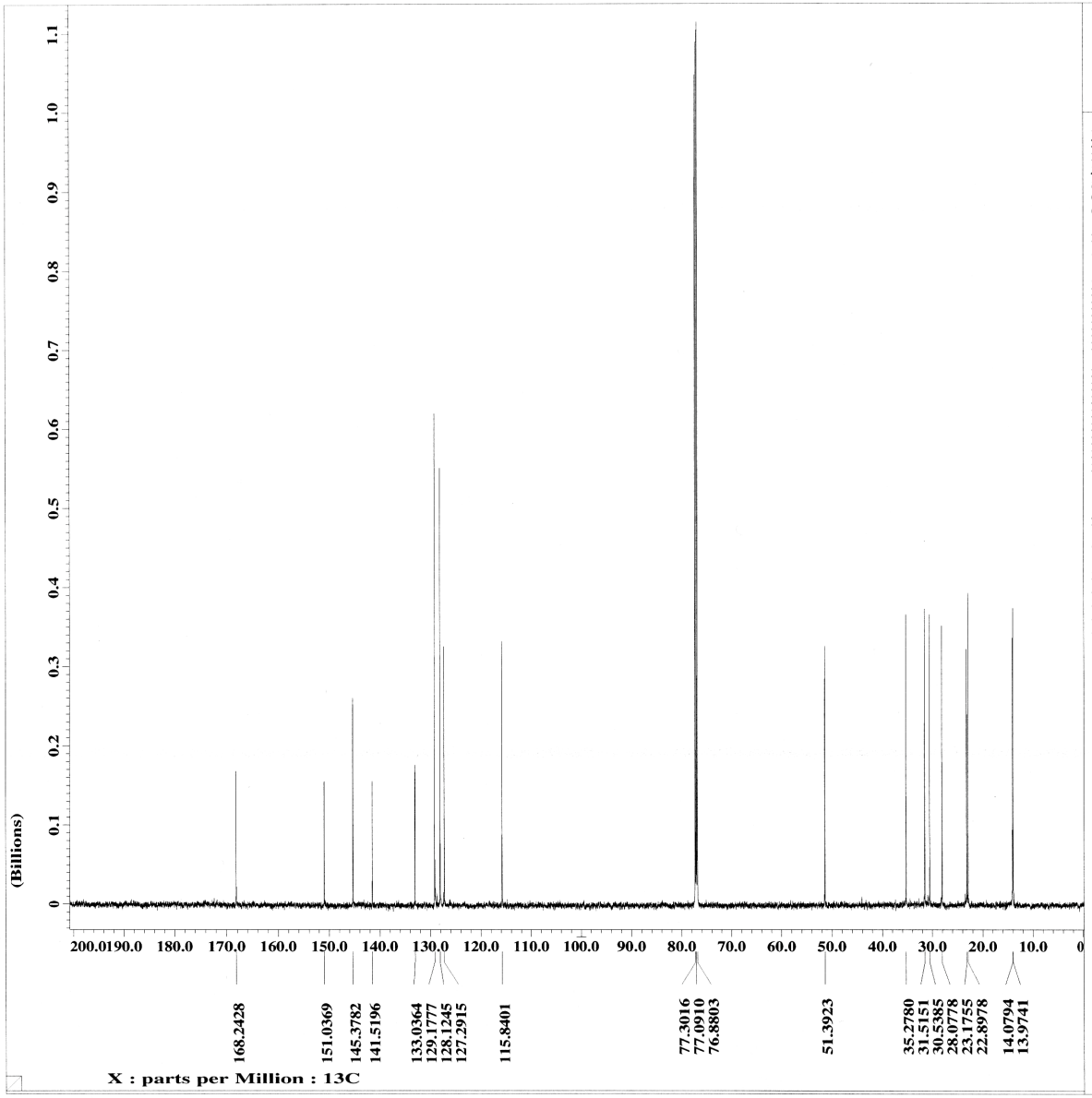


Figure S2. ORTEP Drawing of **6bea**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are 50% probability level.

C:¥WINNMR98¥COMMON¥_DEFAULT.ALS

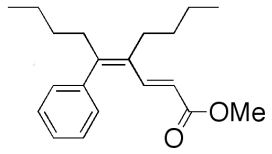


MENUF	1HNON
OBNUC	1H
OFR	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.0 Hz
PW1	6.8 us
DEADT	71.6 us
PREDL	0.2000 ms
IWT	1.0 sec
POINT	32768
SPO	16000
TIMES	8
DUMMY	1
FREQU	8000.0 Hz
FLT	4000 Hz
DELAY	50.0 us
ACQTM	2.000 sec
PD	1.500 sec
ADBIT	16.00
RGAIN	14
BF	0.12 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	NON
EXPCM	NON:Single.cou
IRNUC	1H
IFR	399.65 MH
IRSET	124.00 KH
IRFIN	10500.0 Hz
IRRPW	450 us
IRATN	511
DFILE	C:¥WINNMR98¥CO
SF	RESO
LKSET	61.60 KH
LKFIN	79.0 Hz
LKLEV	180
LGAIN	20
LKPHS	263
LKSIG	968
CSPED	10 Hz
FILDC	
FILDF	

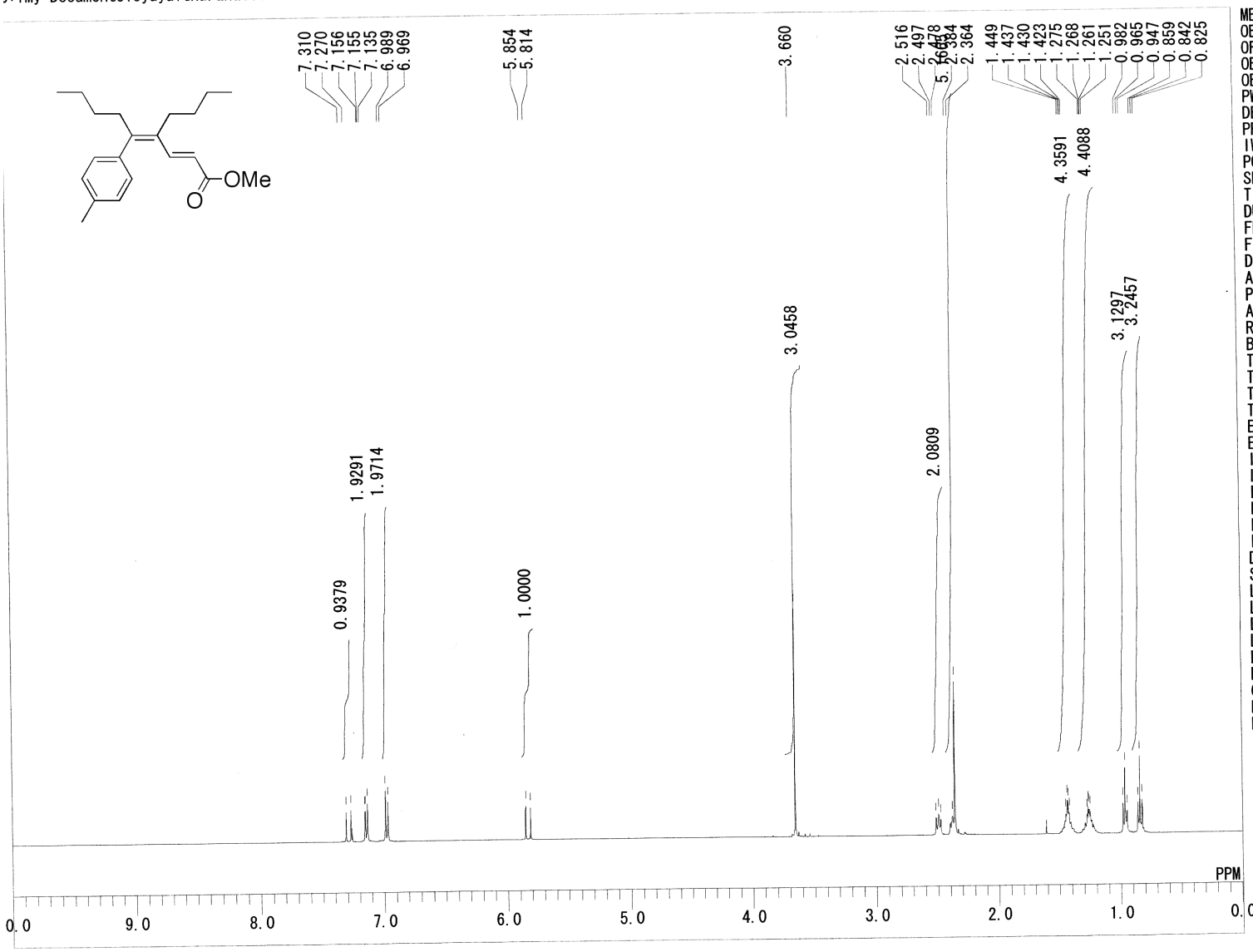


JEOL

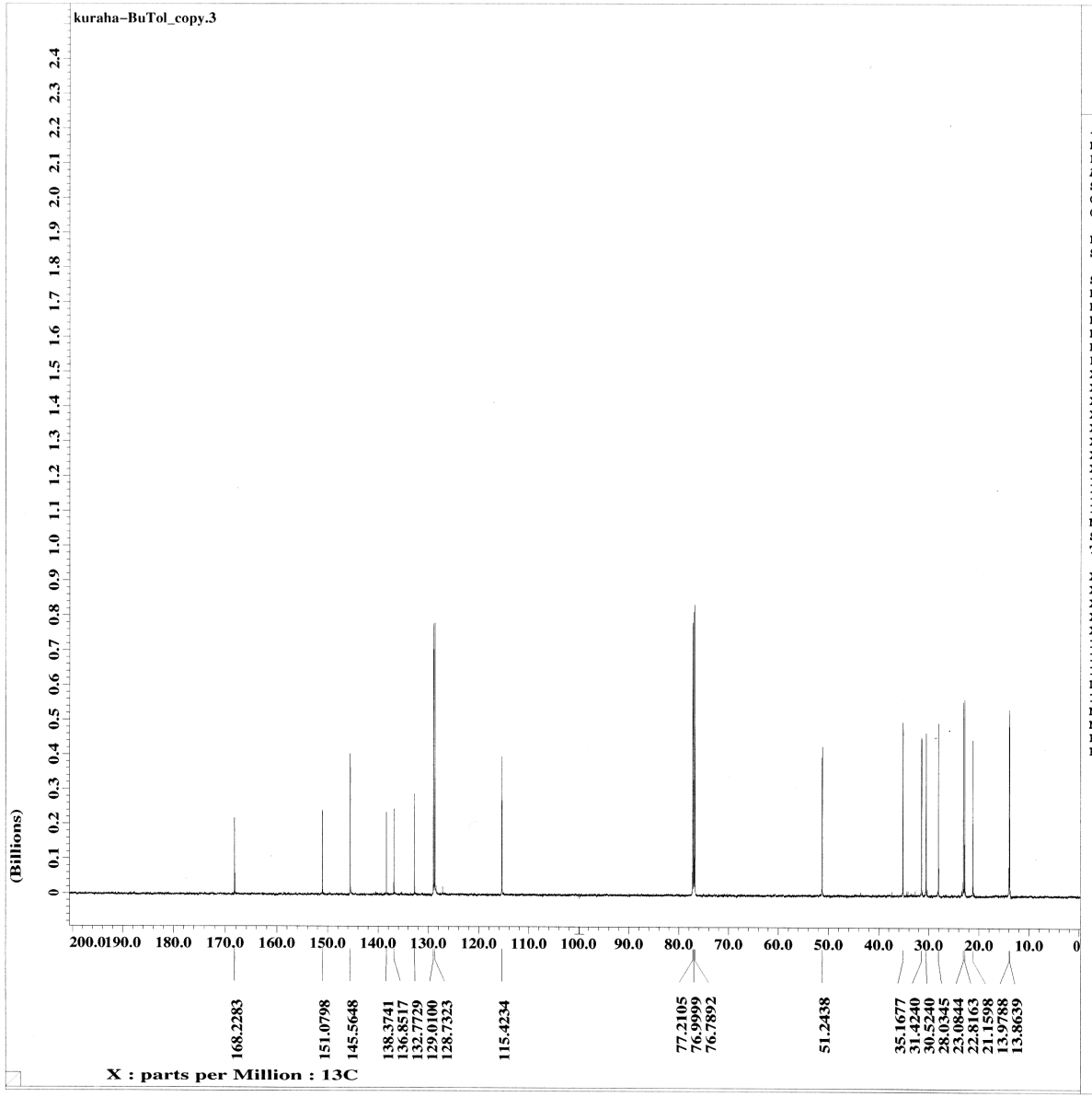
```
---- ACQUISITION PARAMETERS ----
Derived from: a.2
File Name          = a.4
Author             = delta
Sample ID          = S#685246
Content            = single pulse decouple
Creation Date      = 23-FEB-2006 19:38:40

Revision Date      = 23-FEB-2006 19:56:20
Spec Site          = ECA600

Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 14.09636928[T] (600[M
X_acq_duration     = 0.69206016[s]
X_domain           = 13C
X_freq             = 150.91343039[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 1.44496109[Hz]
X_sweep            = 47.34848485[kHz]
Irr_domain         = 1H
Irr_freq           = 600.1723046[MHz]
Irr_offset         = 5[ppm]
Mod_return         = 1
Scans              = 1000
Total_scans        = 1000

X_90_width         = 11.2[us]
X_acq_time         = 0.69206016[s]
X_angle            = 30[deg]
X_atn              = 7.6[dB]
X_pulse            = 3.73333333[us]
Irr_atn_dec        = 18[dB]
Irr_atn_noe        = 18[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Relaxation_delay   = 2[s]
Repetition_time    = 2.69206016[s]
```



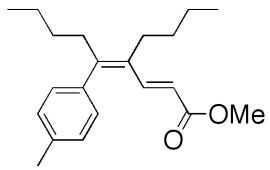
C:¥My Documents¥syuyu¥tkuraha030305¥BuTol2.als

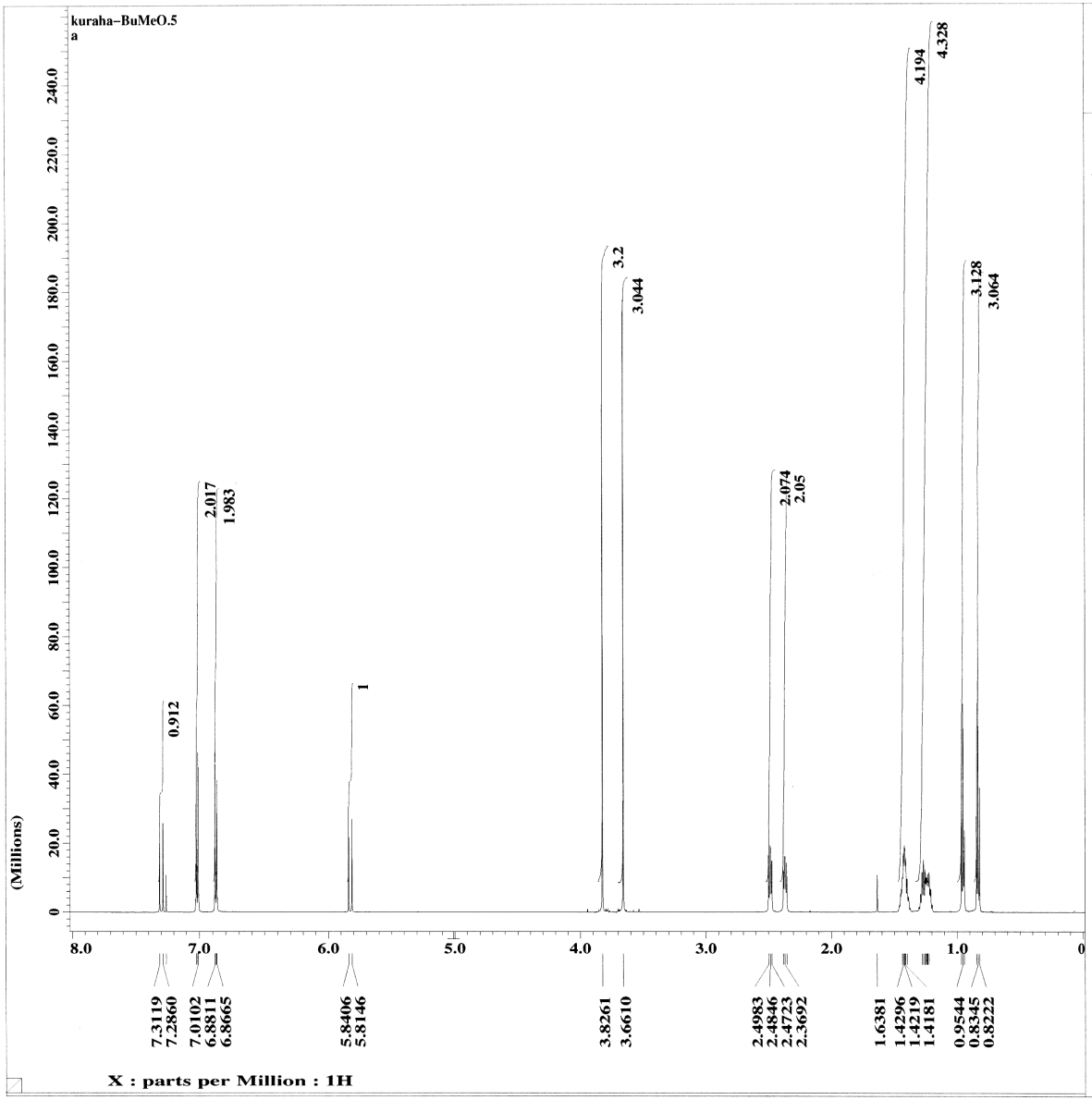


MENUF	1HNON
OBNUC	1H
OFR	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.0 Hz
PW1	6.8 us
DEADT	71.6 us
PREDL	0.2000 ms
IWT	1.0 sec
POINT	32768
SPO	16000
TIMES	8
DUMMY	1
FREQU	8000.0 Hz
FLT	4000 Hz
DELAY	50.0 us
ACQTM	2.000 sec
PD	1.500 sec
ADBIT	16.00
RGAIN	14
BF	0.12 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	NON
EXPCM	NON:Single.coup
IRNUC	1H
IFR	399.65 MHz
IRSET	124.00 KHz
IRFIN	10500.0 Hz
IRRPW	450 us
IRATN	511
DFILE	C:¥My Documents
SF	RESO
LKSET	61.60 KHz
LKFIN	79.0 Hz
LKLEV	200
LGAIN	22
LKPHS	263
LKSIG	857
CSPED	11 Hz
FILDC	
FILDF	



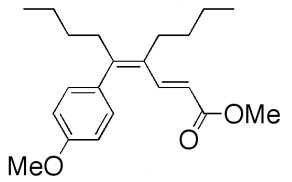

```
---- ACQUISITION PARAMETERS ----
Derived from: kuraha-BuTol_copy.1
File Name          = kuraha-BuTol_copy.3
Author             = delta
Sample ID          = S#762641
Content            =
Creation Date      =  2-MAR-2006 21:34:22

Revision Date      =  2-MAR-2006 21:45:18
Spec Site          = ECA600

Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 14.09636928[T]  (600[M
X_acq_duration     = 0.69206016[s]
X_domain           = 13C
X_freq             = 150.91343039[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 1.44496109[Hz]
X_sweep            = 47.34848485[kHz]
Irr_domain         = 1H
Irr_freq           = 600.1723046[MHz]
Irr_offset         = 5[ppm]
Mod_return         = 1
Scans              = 702
Total_scans        = 702

X_90_width         = 11.2[us]
X_acq_time         = 0.69206016[s]
X_angle            = 30[deg]
X_atn              = 7.6[dB]
X_pulse            = 3.73333333[us]
Irr_atn_dec        = 18[dB]
Irr_atn_noe        = 18[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Relaxation_delay   = 2[s]
Repetition_time    = 2.69206016[s]
```

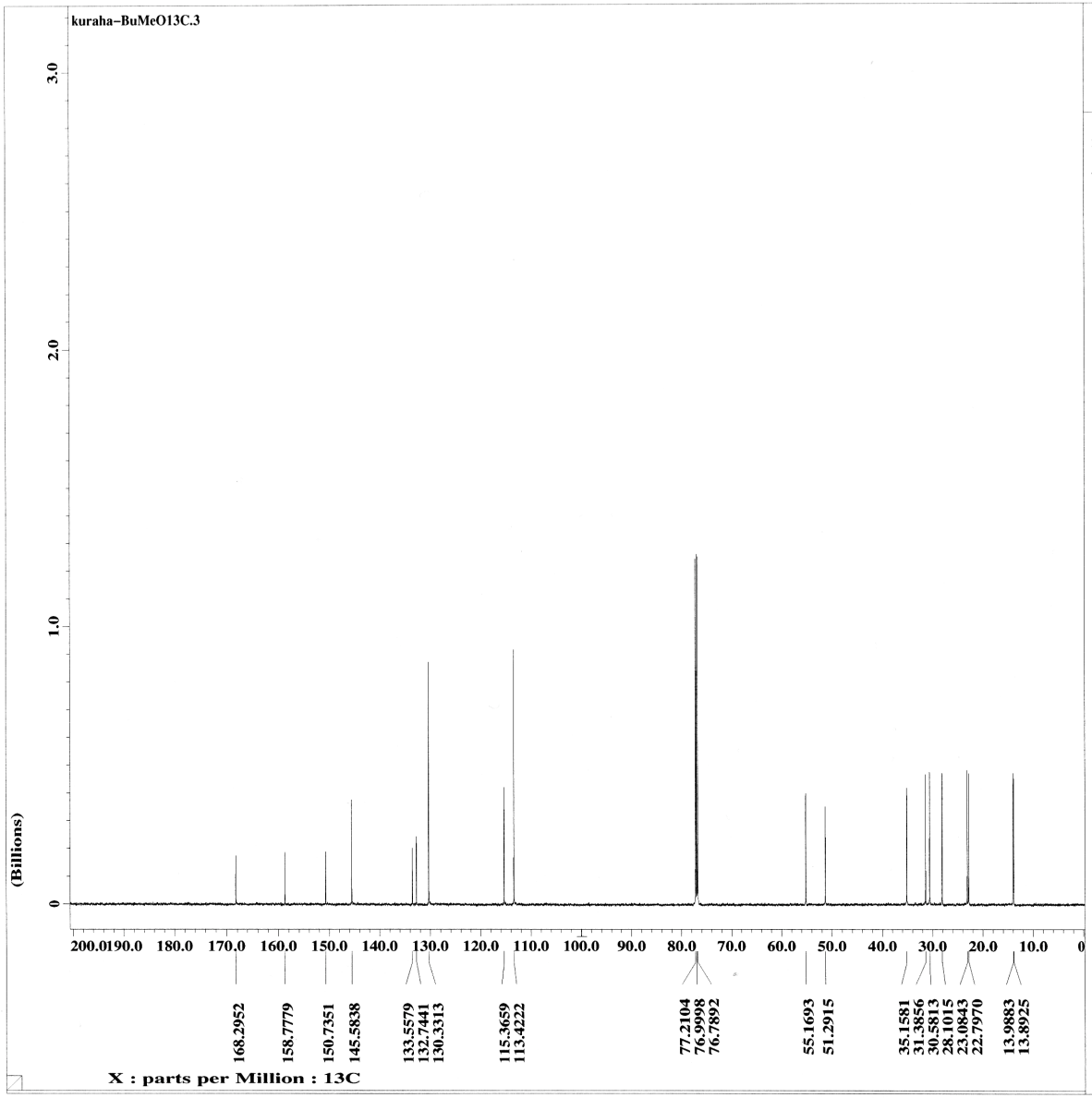





JEOL

```
---- ACQUISITION PARAMETERS ----
Derived from: kuraha-BuMeO.1
File Name          = kuraha-BuMeO.5
Author             = delta
Sample ID          = S#488848
Content            = a
Creation Date      =  1-MAR-2006 13:27:04

Revision Date      =  1-MAR-2006 13:39:16
Spec Site          = ECA600

Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 1H
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 14.09636928[T]  (600[M
X_acq_duration     = 2.18103808[s]
X_domain           = 1H
X_freq             = 600.1723046[MHz]
X_offset           = 5[ppm]
X_points           = 32768
X_prescans         = 1
X_resolution       = 0.45849727[Hz]
X_sweep            = 15.02403846[kHz]
Irr_domain         = 1H
Irr_freq           = 600.1723046[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 1H
Tri_freq           = 600.1723046[MHz]
Tri_offset         = 5[ppm]
Mod_return         = 1
Scans              = 16
Total_scans        = 16

X_90_width         = 12.3[us]
X_acq_time         = 2.18103808[s]
X_angle            = 45[deg]
X_atn              = 2.8[dB]
X_pulse            = 6.15[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Initial_wait       = 1[s]
Relaxation_delay   = 1.5[s]
Repetition_time    = 3.68103808[s]
```



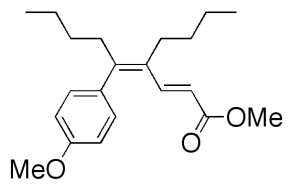


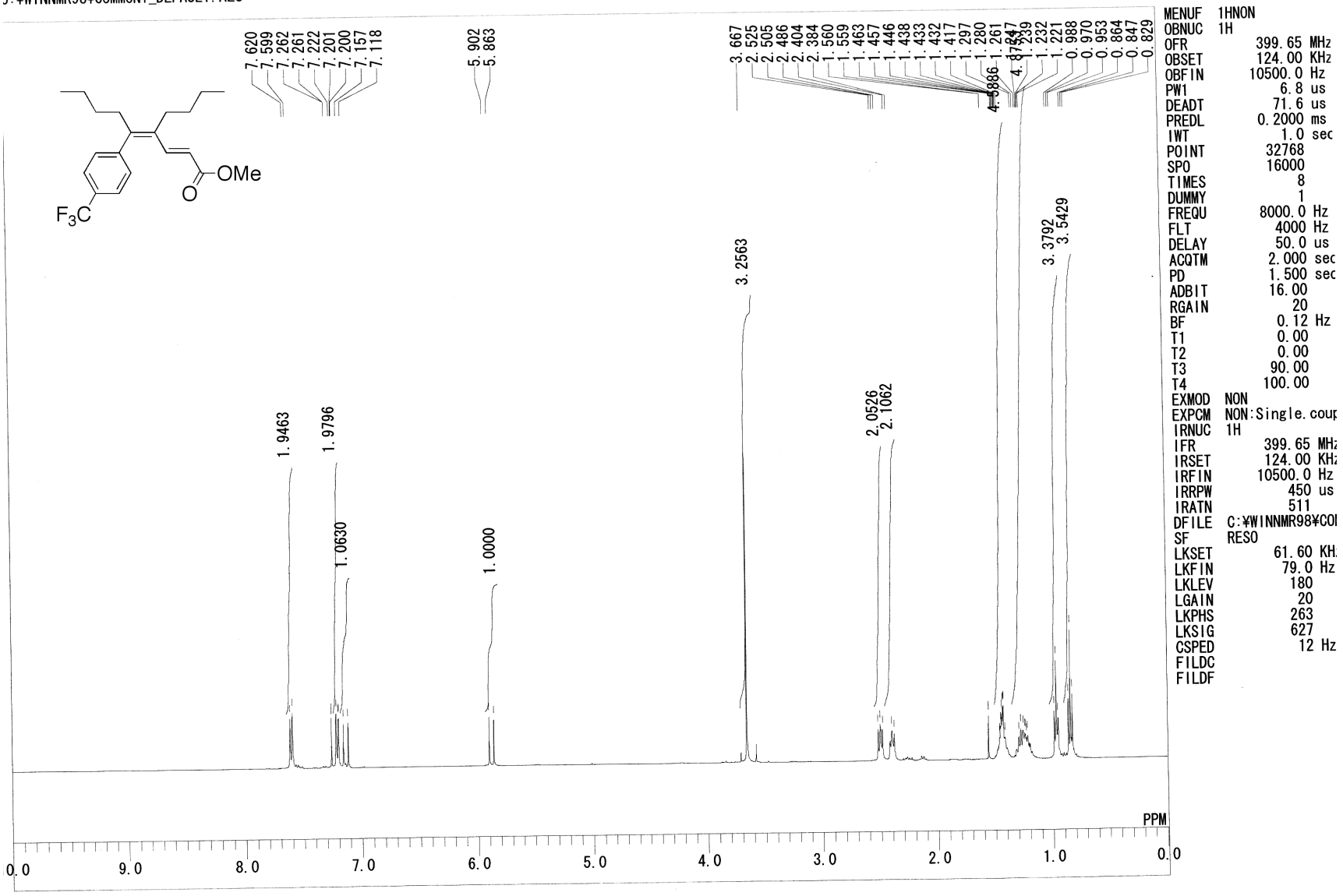
---- ACQUISITION PARAMETERS ----
Derived from: kuraha-BuMeO13C.1
File Name = kuraha-BuMeO13C.3
Author = delta
Sample ID = S#489842
Content =
Creation Date = 1-MAR-2006 14:14:12

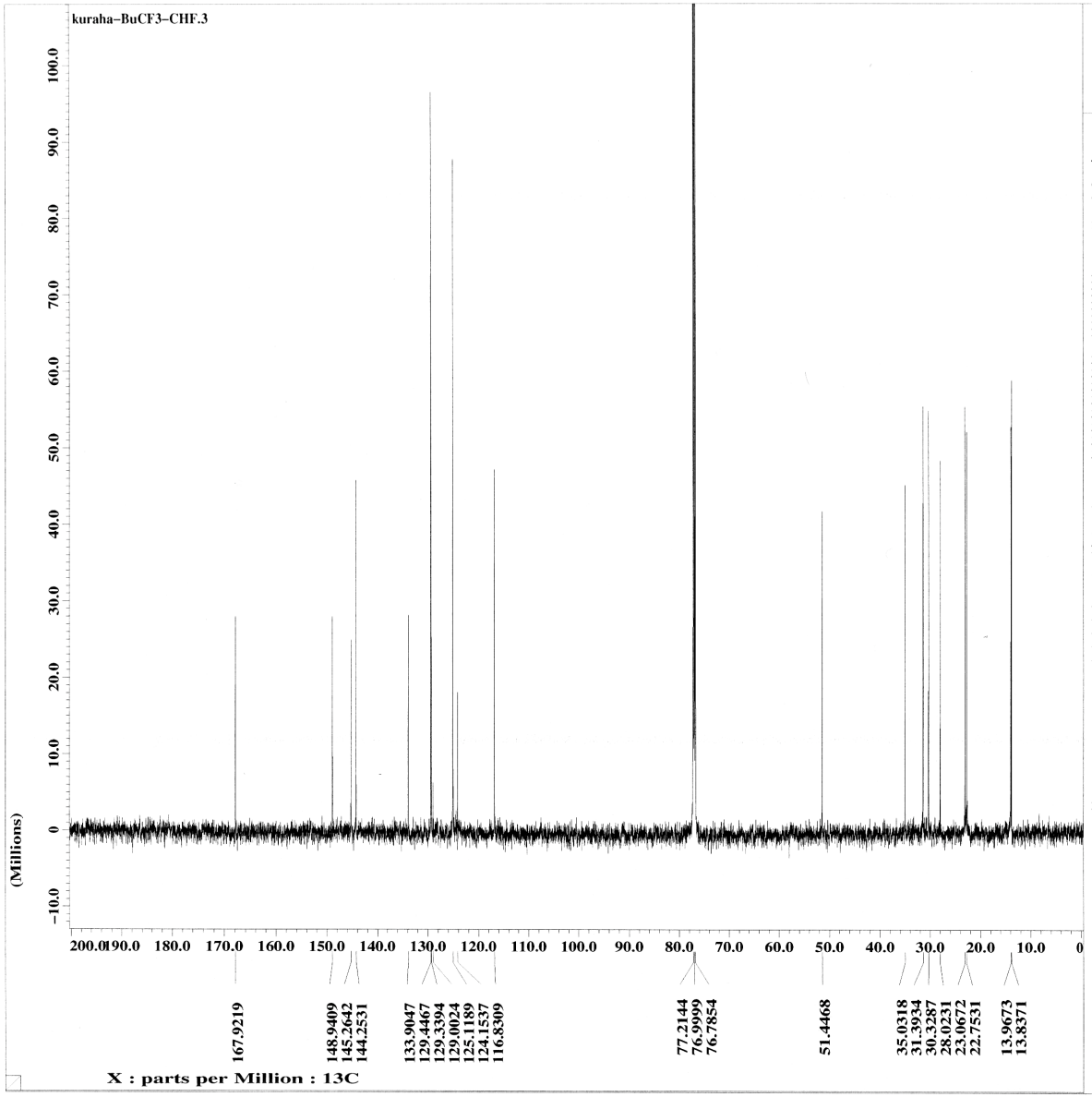
Revision Date = 1-MAR-2006 14:25:14
Spec Site = ECA600

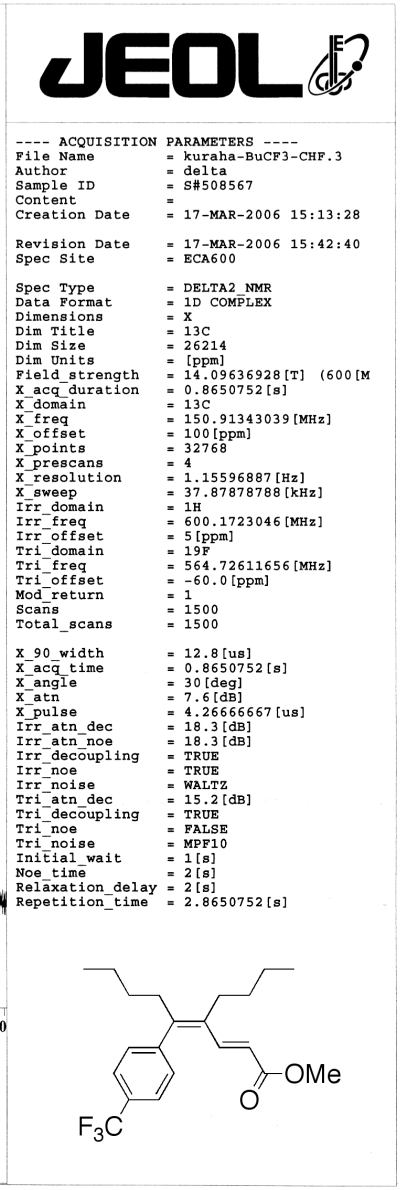
Spec Type = DELTA2_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 13C
Dim Size = 26214
Dim Units = [ppm]
Field_strength = 14.09636928[T] (600[M
X_acq_duration = 0.69206016[s]
X_domain = 13C
X_freq = 150.91343039[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.44496109[Hz]
X_sweep = 47.34848485[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Mod_return = 1
Scans = 1000
Total_scans = 1000

X_90_width = 11.2[us]
X_acq_time = 0.69206016[s]
X_angle = 30[deg]
X_atn = 7.6[dB]
X_pulse = 3.73333333[us]
Irr_atn_dec = 18[dB]
Irr_atn_noe = 18[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Relaxation_delay = 2[s]
Repetition_time = 2.69206016[s]



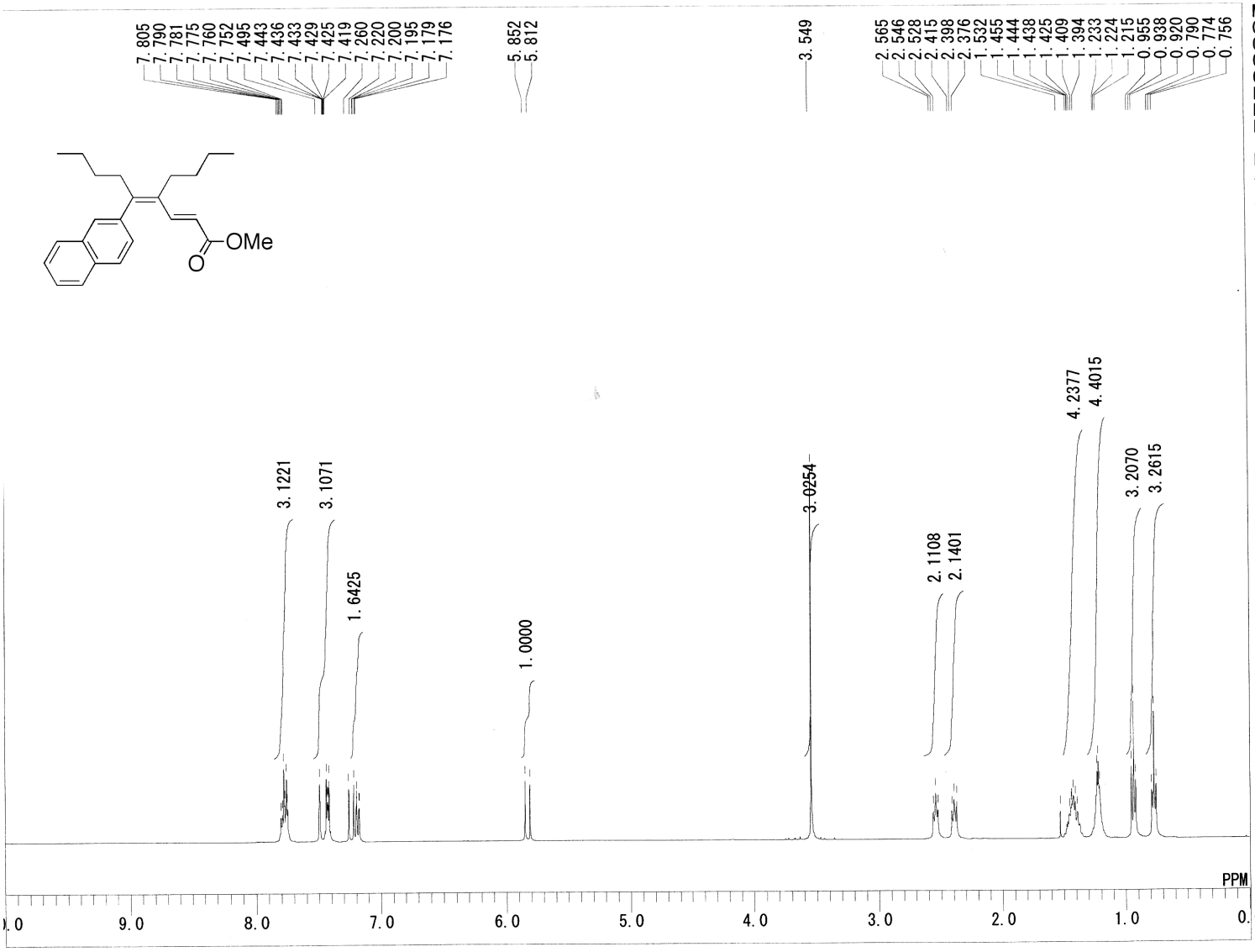

C:¥WINNMR98¥COMMON¥_DEFAULT.ALS
7.620
7.599
7.262
7.261
7.222
7.201
7.200
7.157
7.118
5.902
5.863
3.667
2.525
2.505
2.486
2.404
2.384
2.560
1.559
1.463
1.457
1.446
1.438
1.433
1.432
1.417
1.297
1.280
1.261
1.239
1.232
1.221
0.988
0.970
0.953
0.864
0.847
0.829
OMe
O
F3C
1.9463
1.9796
1.0630
1.0000
3.2563
2.0526
2.1062
3.3792
3.5429
PPM
0.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
MENUF 1HNON
OBNUC 1H
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
PW1 6.8 us
DEADT 71.6 us
PREDL 0.2000 ms
IWT 1.0 sec
POINT 32768
SPO 16000
TIMES 8
DUMMY 1
FREQU 8000.0 Hz
FLT 4000 Hz
DELAY 50.0 us
ACQTM 2.000 sec
PD 1.500 sec
ADBIT 16.00
RGAIN 20
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD NON
EXPCM NON:Single.coup
IRNUC 1H
IFR 399.65 MHz
IRSET 124.00 KHz
IRFIN 10500.0 Hz
IRRPW 450 us
IRATN 511
DFILE C:¥WINNMR98¥COM
SF RESO
LKSET 61.60 KH
LKFIN 79.0 Hz
LKLEV 180
LGAIN 20
LKPHS 263
LKSIG 627
CSPED 12 Hz
FILDC
FILDF



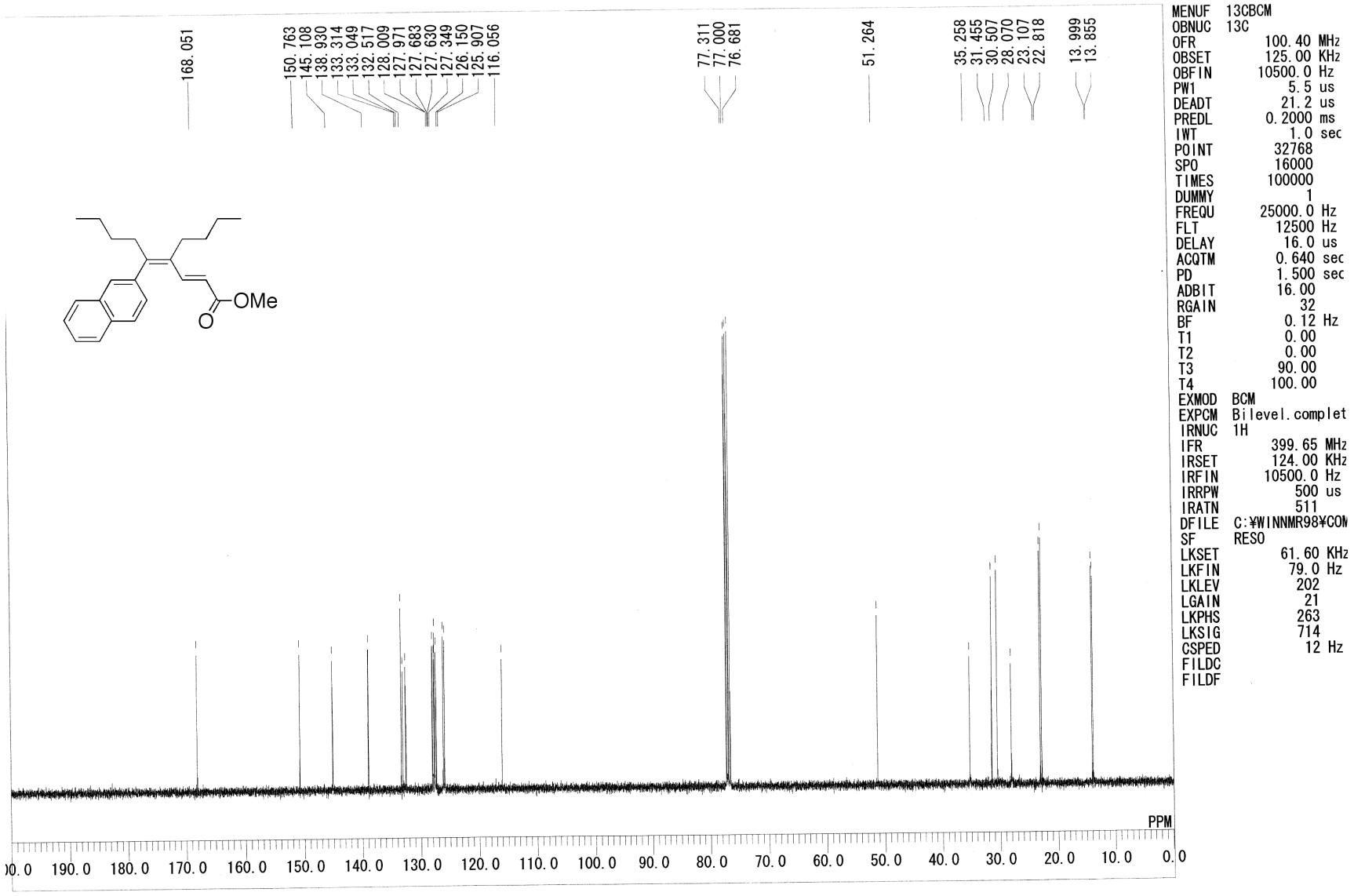


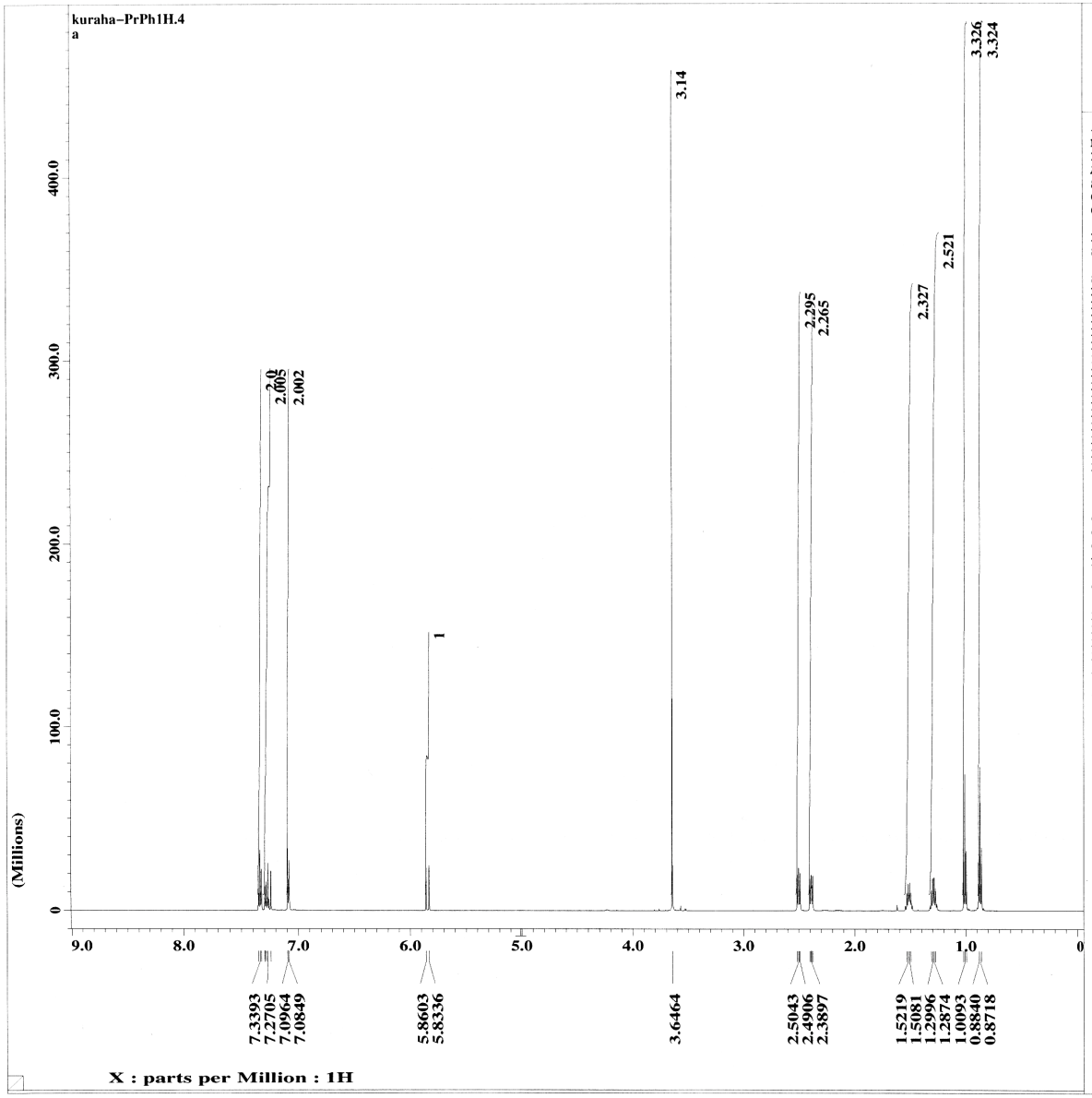
```
---- ACQUISITION PARAMETERS ----
File Name          = kuraha-BuCF3-CHF.3
Author             = delta
Sample ID          = S#508567
Content            =
Creation Date      = 17-MAR-2006 15:13:28

Revision Date      = 17-MAR-2006 15:42:40
Spec Site          = ECA600

Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 14.09636928[T]  (600[M
X_acq_duration     = 0.8650752[s]
X_domain           = 13C
X_freq             = 150.91343039[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 1.15596887[Hz]
X_sweep            = 37.87878788[kHz]
Irr_domain         = 1H
Irr_freq           = 600.1723046[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 19F
Tri_freq           = 564.72611656[MHz]
Tri_offset         = -60.0[ppm]
Mod_return         = 1
Scans              = 1500
Total_scans        = 1500

X_90_width         = 12.8[us]
X_acq_time         = 0.8650752[s]
X_angle            = 30[deg]
X_atn              = 7.6[dB]
X_pulse            = 4.26666667[us]
Irr_atn_dec        = 18.3[dB]
Irr_atn_noe        = 18.3[dB]
Irr_decoupling     = TRUE
Irr_noe            = TRUE
Irr_noise          = WALTZ
Tri_atn_dec        = 15.2[dB]
Tri_decoupling     = TRUE
Tri_noe            = FALSE
Tri_noise          = MPF10
Initial_wait       = 1[s]
Noe_time           = 2[s]
Relaxation_delay   = 2[s]
Repetition_time    = 2.8650752[s]
```

):¥WINNMR98¥COMMON¥_DEFAULT.ALS



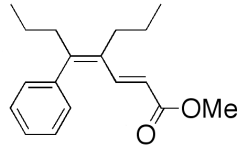
MENUF	1HNON
OBNUC	1H
OFR	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.0 Hz
PW1	6.8 us
DEADT	71.6 us
PREDL	0.2000 ms
IWT	1.0 sec
POINT	32768
SPO	16000
TIMES	8
DUMMY	1
FREQU	8000.0 Hz
FLT	4000 Hz
DELAY	50.0 us
ACQTM	2.000 sec
PD	1.500 sec
ADBIT	16.00
RGAIN	16
BF	0.12 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	NON
EXPCM	NON:Single.coup
IRNUC	1H
IFR	399.65 MHz
IRSET	124.00 KHz
IRFIN	10500.0 Hz
IRRPW	450 us
IRATN	511
DFILE	C:¥WINNMR98¥COM
SF	RESO
LKSET	61.60 KHz
LKFIN	79.0 Hz
LKLEV	202
LGAIN	21
LKPHS	263
LKSIG	717
CSPED	13 Hz
FILDC	
FILDF	

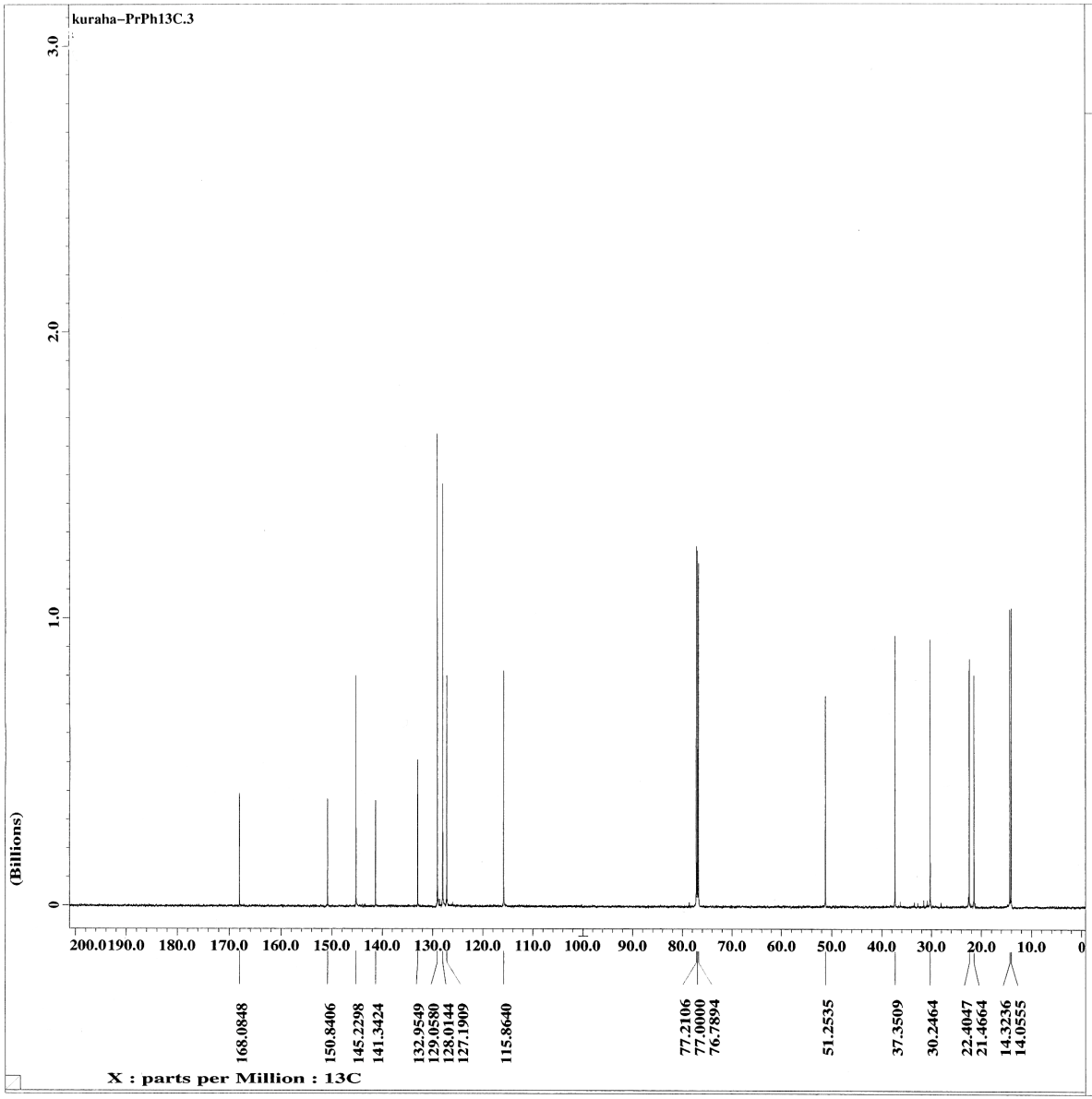

C:¥WINNMR98¥COMMON¥_DEFAULT.ALS
168.051
150.763
145.108
138.930
133.314
133.049
132.517
128.009
127.971
127.683
127.630
127.349
126.150
125.907
116.056
77.311
77.000
76.681
51.264
35.258
31.455
30.507
28.070
23.107
22.818
13.999
13.855
OMe
O
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
MENUF 13CBCM
OBNUC 13C
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
PW1 5.5 us
DEADT 21.2 us
PREDL 0.2000 ms
IWT 1.0 sec
POINT 32768
SPO 16000
TIMES 100000
DUMMY 1
FREQU 25000.0 Hz
FLT 12500 Hz
DELAY 16.0 us
ACQTM 0.640 sec
PD 1.500 sec
ADBIT 16.00
RGAIN 32
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD BCM
EXPCM Bilevel.complet
IRNUC 1H
IFR 399.65 MHz
IRSET 124.00 KHz
IRFIN 10500.0 Hz
IRRPW 500 us
IRATN 511
DFILE C:¥WINNMR98¥COM
SF RESO
LKSET 61.60 KHz
LKFIN 79.0 Hz
LKLEV 202
LGAIN 21
LKPHS 263
LKSIG 714
CSPED 12 Hz
FILDC
FILDF

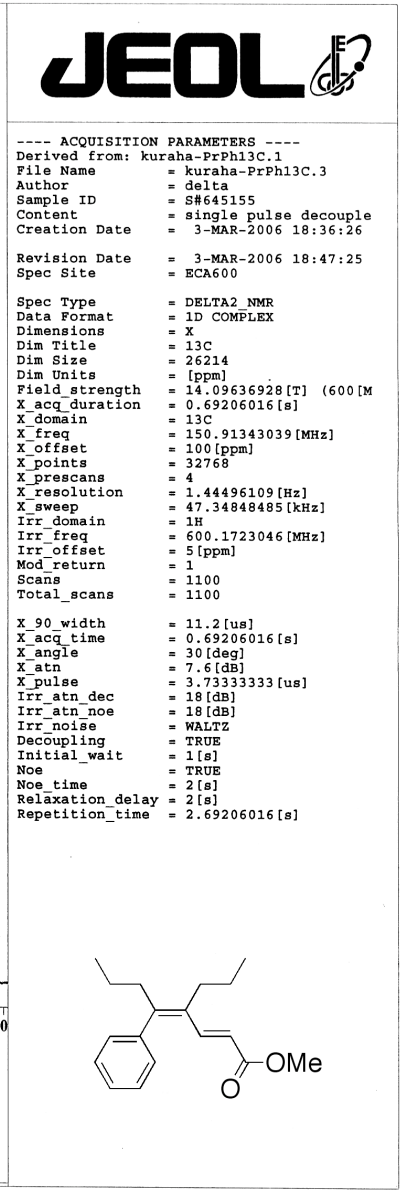


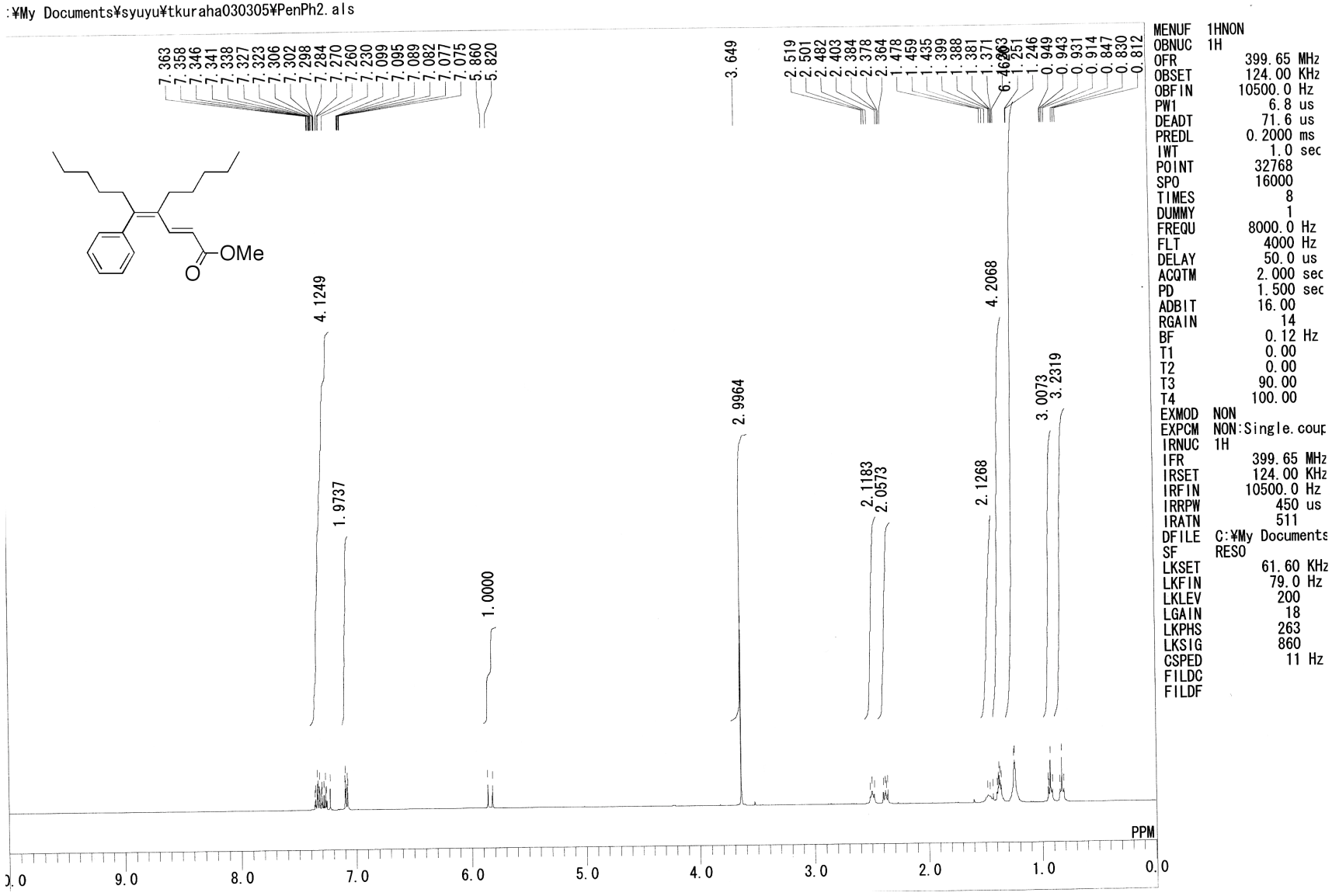
JEOL

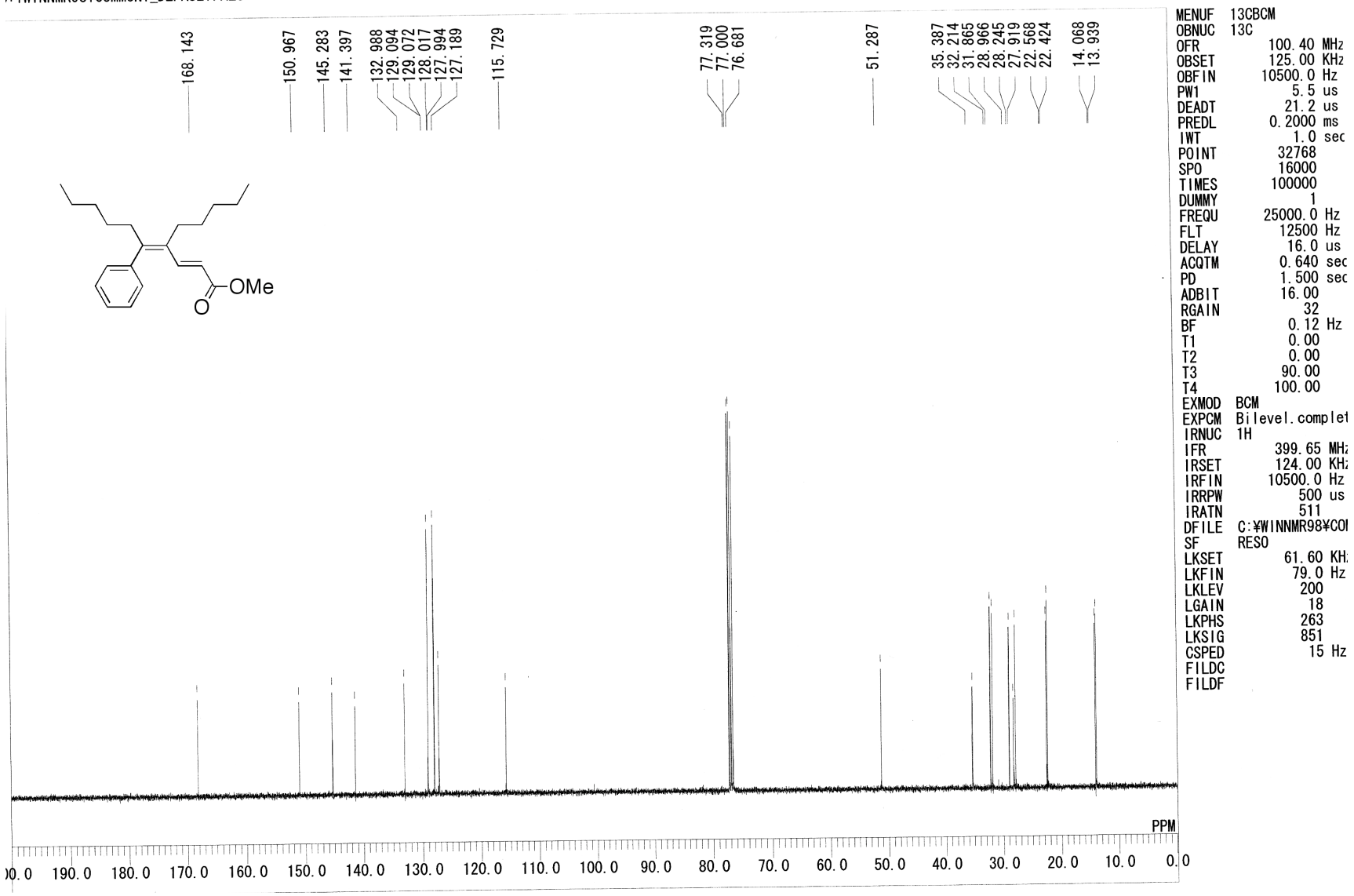
```
---- ACQUISITION PARAMETERS ----
Derived from: kuraha-PrPh1H.1
File Name         = kuraha-PrPh1H.4
Author            = delta
Sample ID         = S#629437
Content           = a
Creation Date     =  3-MAR-2006 17:21:07

Revision Date     =  3-MAR-2006 17:34:00
Spec Site         = ECA600

Spec Type         = DELTA2_NMR
Data Format       = 1D COMPLEX
Dimensions        = X
Dim Title         = 1H
Dim Size          = 26214
Dim Units         = [ppm]
Field_strength    = 14.09636928[T]  (600[M
X_acq_duration    = 2.18103808[s]
X_domain          = 1H
X_freq            = 600.1723046[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.45849727[Hz]
X_sweep           = 15.02403846[kHz]
Irr_domain        = 1H
Irr_freq          = 600.1723046[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 600.1723046[MHz]
Tri_offset        = 5[ppm]
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 12.3[us]
X_acq_time        = 2.18103808[s]
X_angle           = 45[deg]
X_atn             = 2.8[dB]
X_pulse           = 6.15[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Relaxation_delay  = 1.5[s]
Repetition_time   = 3.68103808[s]
```

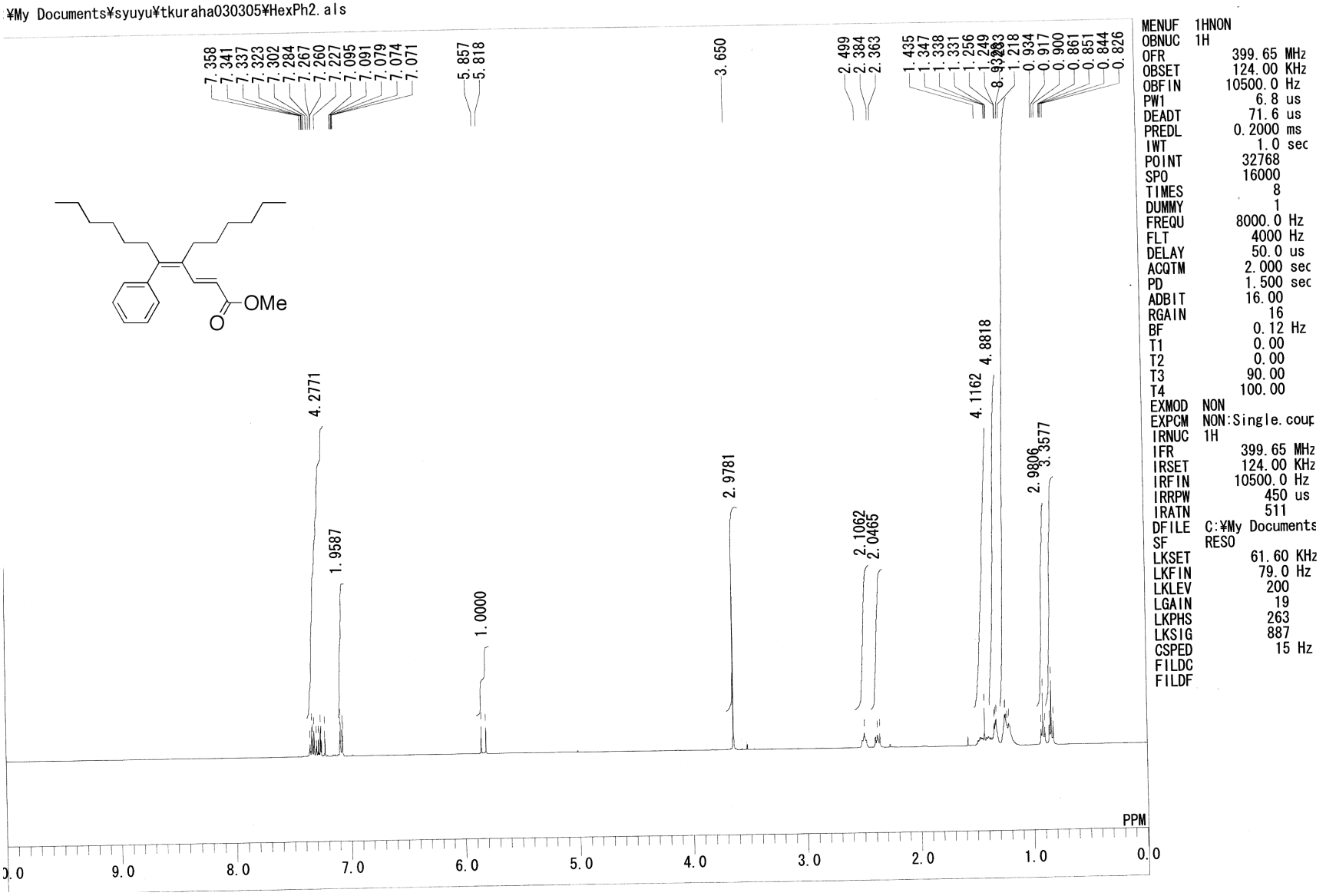



kuraha-PrPh13C.3
(Billions)
3.0
2.0
1.0
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
168.0848
150.8406
145.2298
141.3424
132.9549
129.0580
128.0144
127.1909
115.8640
77.2106
77.0000
76.7894
51.2535
37.3509
30.2464
22.4047
21.4664
14.3236
14.0555
X : parts per Million : 13C

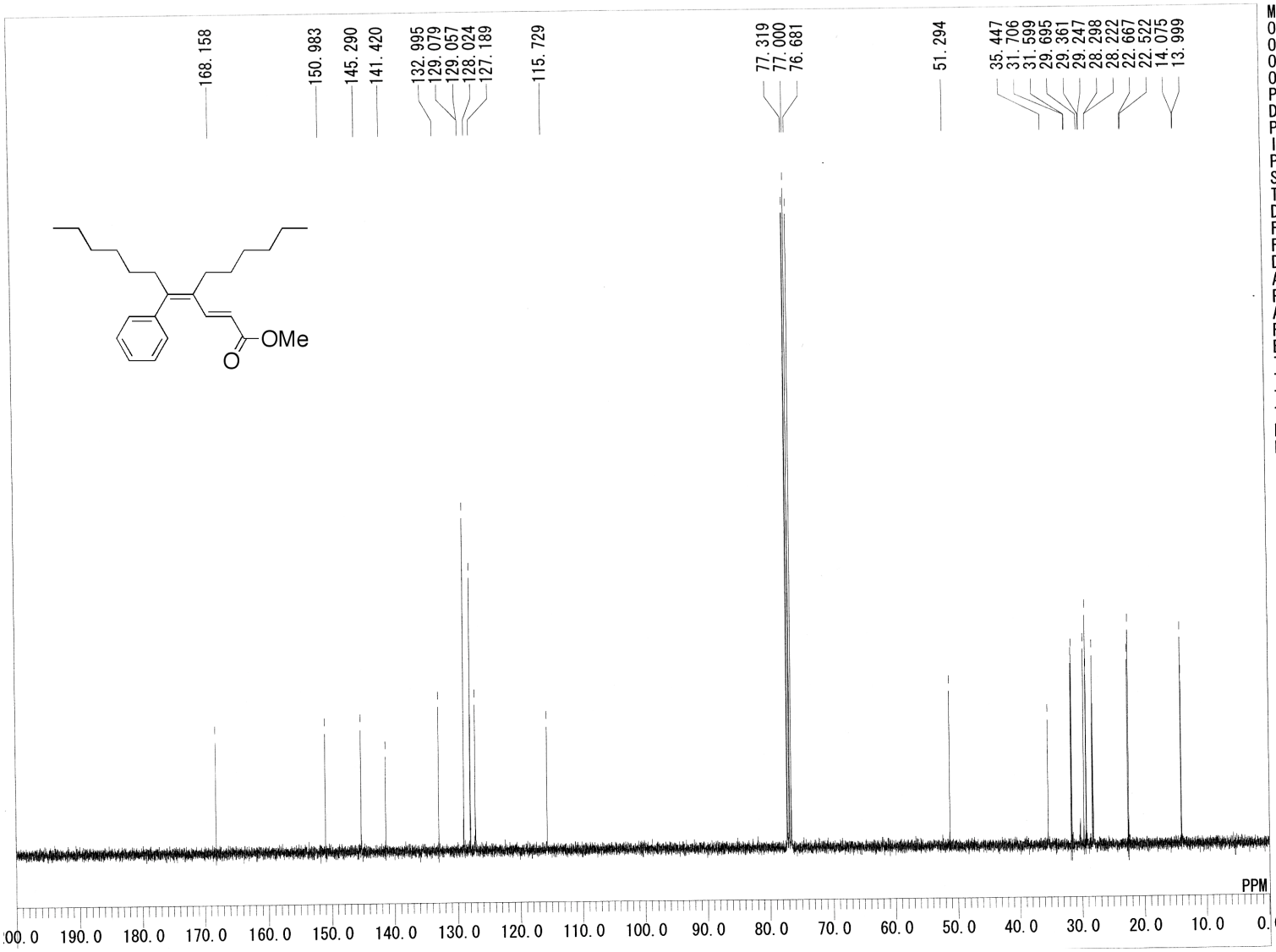

---- ACQUISITION PARAMETERS ----
Derived from: kuraha-PrPh13C.1
File Name = kuraha-PrPh13C.3
Author = delta
Sample ID = S#645155
Content = single pulse decouple
Creation Date = 3-MAR-2006 18:36:26
Revision Date = 3-MAR-2006 18:47:25
Spec Site = ECA600
Spec Type = DELTA2_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 13C
Dim Size = 26214
Dim Units = [ppm]
Field_strength = 14.09636928[T] (600[M
X_acq_duration = 0.69206016[s]
X_domain = 13C
X_freq = 150.91343039[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.44496109[Hz]
X_sweep = 47.34848485[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Mod_return = 1
Scans = 1100
Total_scans = 1100
X_90_width = 11.2[us]
X_acq_time = 0.69206016[s]
X_angle = 30[deg]
X_atn = 7.6[dB]
X_pulse = 3.73333333[us]
Irr_atn_dec = 18[dB]
Irr_atn_noe = 18[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Relaxation_delay = 2[s]
Repetition_time = 2.69206016[s]
OMe
O


:¥My Documents¥syuyu¥tkuraha030305¥PenPh2.als
7.363
7.358
7.346
7.341
7.338
7.327
7.323
7.306
7.302
7.298
7.284
7.270
7.260
7.230
7.099
7.095
7.089
7.082
7.077
7.075
5.860
5.820
3.649
2.519
2.501
2.482
2.403
2.384
2.378
2.364
1.478
1.459
1.435
1.399
1.388
1.381
1.371
1.263
1.251
1.246
0.949
0.943
0.931
0.914
0.847
0.830
0.812
OMe
O
4.1249
1.9737
1.0000
2.9964
2.1183
2.0573
2.1268
4.2068
3.0073
3.2319
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
MENUF 1HNON
OBNUC 1H
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
PW1 6.8 us
DEADT 71.6 us
PREDL 0.2000 ms
IWT 1.0 sec
POINT 32768
SPO 16000
TIMES 8
DUMMY 1
FREQU 8000.0 Hz
FLT 4000 Hz
DELAY 50.0 us
ACQTM 2.000 sec
PD 1.500 sec
ADBIT 16.00
RGAIN 14
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD NON
EXPCM NON:Single.coup
IRNUC 1H
IFR 399.65 MHz
IRSET 124.00 KHz
IRFIN 10500.0 Hz
IRRPW 450 us
IRATN 511
DFILE C:¥My Documents
SF RESO
LKSET 61.60 KHz
LKFIN 79.0 Hz
LKLEV 200
LGAIN 18
LKPHS 263
LKSIG 860
CSPED 11 Hz
FILDC
FILDF

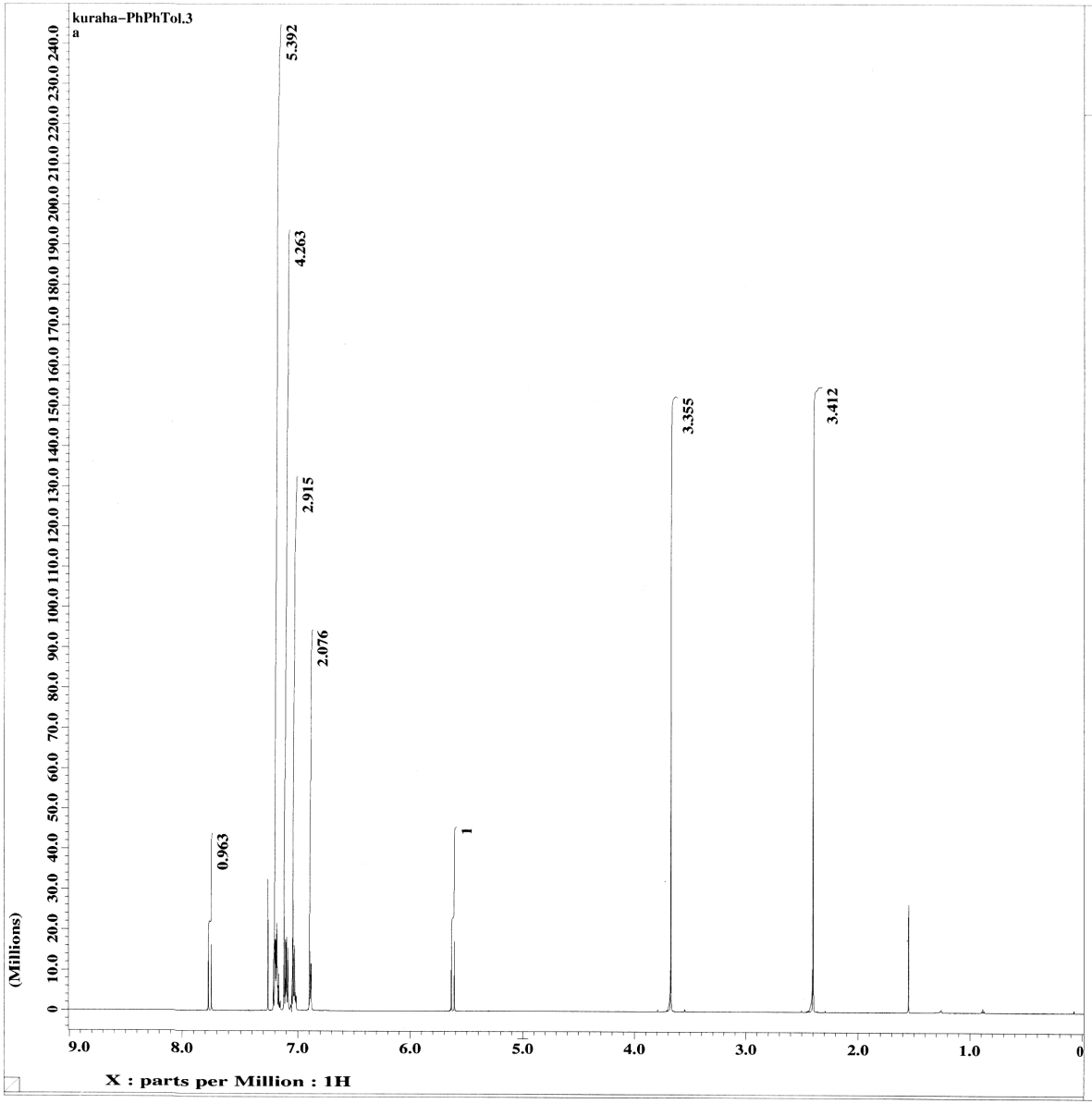

C:¥WINNMR98¥COMMON¥_DEFAULT.ALS
168.143
150.967
145.283
141.397
132.988
129.094
129.072
128.017
127.994
127.189
115.729
77.319
77.000
76.681
51.287
35.387
32.214
31.865
28.966
28.245
27.919
22.568
22.424
14.068
13.939
OMe
O
PPM
0.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
MENUF 13CBCM
OBNUC 13C
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
PW1 5.5 us
DEADT 21.2 us
PREDL 0.2000 ms
IWT 1.0 sec
POINT 32768
SPO 16000
TIMES 100000
DUMMY 1
FREQU 25000.0 Hz
FLT 12500 Hz
DELAY 16.0 us
ACQTM 0.640 sec
PD 1.500 sec
ADBIT 16.00
RGAIN 32
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD BCM
EXPCM Bilevel.complet
IRNUC 1H
IFR 399.65 MHz
IRSET 124.00 KHz
IRFIN 10500.0 Hz
IRRPW 500 us
IRATN 511
DFILE C:¥WINNMR98¥COM
SF RESO
LKSET 61.60 KHz
LKFIN 79.0 Hz
LKLEV 200
LGAIN 18
LKPHS 263
LKSIG 851
CSPED 15 Hz
FILDC
FILDF


¥My Documents¥syuyu¥tkuraha030305¥HexPh2.als
7.358
7.341
7.337
7.323
7.302
7.284
7.267
7.260
7.227
7.095
7.091
7.079
7.074
7.071
5.857
5.818
3.650
2.499
2.384
2.363
1.435
1.347
1.338
1.331
1.256
1.249
1.218
0.934
0.917
0.900
0.861
0.851
0.844
0.826
OMe
O
4.2771
1.9587
1.0000
2.9781
2.1062
2.0465
4.1162
4.8818
2.9806
3.3577
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
MENUF 1HNON
OBNUC 1H
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
PW1 6.8 us
DEADT 71.6 us
PREDL 0.2000 ms
IWT 1.0 sec
POINT 32768
SPO 16000
TIMES 8
DUMMY 1
FREQU 8000.0 Hz
FLT 4000 Hz
DELAY 50.0 us
ACQTM 2.000 sec
PD 1.500 sec
ADBIT 16.00
RGAIN 16
BF 0.12 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD NON
EXPCM NON:Single.coup
IRNUC 1H
IFR 399.65 MHz
IRSET 124.00 KHz
IRFIN 10500.0 Hz
IRRPW 450 us
IRATN 511
DFILE C:¥My Documents
SF RESO
LKSET 61.60 KHz
LKFIN 79.0 Hz
LKLEV 200
LGAIN 19
LKPHS 263
LKSIG 887
CSPED 15 Hz
FILDC
FILDF

C:¥WINNMR98¥COMMON¥_DEFAULT.ALS



MENUF	13CBCM
OBNUC	13C
OFR	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.0 Hz
PW1	5.5 us
DEADT	21.2 us
PREDL	0.2000 ms
IWT	1.0 sec
POINT	32768
SPO	16000
TIMES	88888888
DUMMY	1
FREQU	25000.0 Hz
FLT	12500 Hz
DELAY	16.0 us
ACQTM	0.640 sec
PD	1.500 sec
ADBIT	16.00
RGAIN	32
BF	0.12 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	BCM
EXPCM	Bilevel.comple
IRNUC	1H
IFR	399.65 MH
IRSET	124.00 KH
IRFIN	10500.0 Hz
IRRPW	500 us
IRATN	511
DFILE	C:¥WINNMR98¥CO
SF	RESO
LKSET	61.60 KH
LKFIN	79.0 Hz
LKLEV	200
LGAIN	19
LKPHS	263
LKSIG	895
CSPED	14 Hz
FILDC	
FILDF	

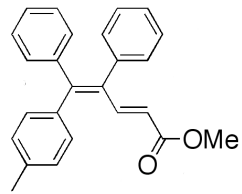


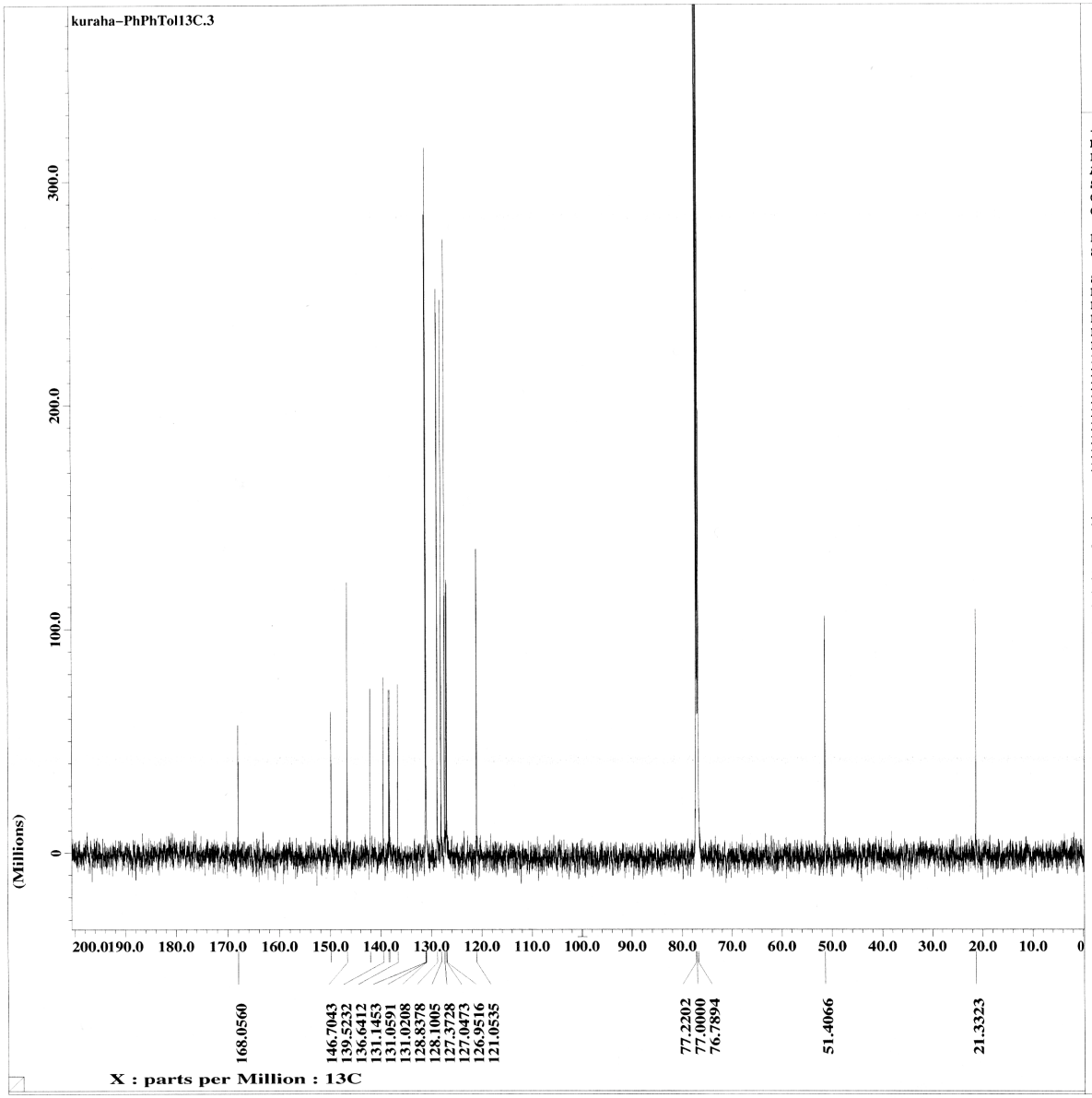
---- ACQUISITION PARAMETERS ----
Derived from: kuraha-PhPhTol.1
File Name = kuraha-PhPhTol.3
Author = delta
Sample ID = S#567952
Content = a
Creation Date = 2-MAR-2006 15:38:23

Revision Date = 2-MAR-2006 15:49:15
Spec Site = ECA600

Spec Type = DELTA2_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 1H
Dim Size = 26214
Dim Units = [ppm]
Field_strength = 14.09636928[T] (600[M
X_acq_duration = 2.18103808[s]
X_domain = 1H
X_freq = 600.1723046[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 1
X_resolution = 0.45849727[Hz]
X_sweep = 15.02403846[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 600.1723046[MHz]
Tri_offset = 5[ppm]
Mod_return = 1
Scans = 16
Total_scans = 16

X_90_width = 12.3[us]
X_acq_time = 2.18103808[s]
X_angle = 45[deg]
X_atn = 2.8[dB]
X_pulse = 6.15[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Relaxation_delay = 1.5[s]
Repetition_time = 3.68103808[s]





JEOL

```
---- ACQUISITION PARAMETERS ----
Derived from: kuraha-PhPhTol13C.1
File Name          = kuraha-PhPhTol13C.3
Author             = delta
Sample ID          = S#568878
Content            =
Creation Date      =  2-MAR-2006 17:10:15

Revision Date      =  2-MAR-2006 17:24:50
Spec Site          = ECA600

Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 14.09636928[T]  (600[M
X_acq_duration     = 0.69206016[s]
X_domain           = 13C
X_freq             = 150.91343039[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 1.44496109[Hz]
X_sweep            = 47.34848485[kHz]
Irr_domain         = 1H
Irr_freq           = 600.1723046[MHz]
Irr_offset         = 5[ppm]
Mod_return         = 1
Scans              = 2000
Total_scans        = 2000

X_90_width         = 11.2[us]
X_acq_time         = 0.69206016[s]
X_angle            = 30[deg]
X_atn              = 7.6[dB]
X_pulse            = 3.73333333[us]
Irr_atn_dec        = 18[dB]
Irr_atn_noe        = 18[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Relaxation_delay   = 2[s]
Repetition_time    = 2.69206016[s]
```