Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis of 2-hydroxymalonic acid derivatives via tandem oxidation and rearrangement by singlet oxygen

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1. General Information

All dry solvents were obtained from Kanto Kagaku Co., Ltd. Other chemicals used were of reagent grade and were obtained from Aldrich Chemical Co., Tokyo Kasei Kogyo Co., Ltd. and Wako Pure Chemical Industries, Ltd. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL ECA 500 spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) or JEOL AL 400 spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) at room temperature in $CDCl_3$ as a solvent. Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal Me_4Si. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100TD and are reported as m/z (M+Na+, relative intensity). Thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (MERCK, silica gel F-254, 0.5 mm). Flash column chromatography was preformed with Kanto silica gel 60N (Spherical, Neutral, 40-50 mm) and Biotage Isolera® automated chromatography system using normal phase cartridges with YMC*GEL SIL (YMC Co., Ltd., 25 μm). IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Irradiation of visible light was performed with a 22 W fluorescent lamp (daylight color lamp, EFR25ED 22W from Panasonic Co., Ltd. as shown detailed in the bellow (Figure S-1 and Figure S-2)).

Figure S-1. The appearance of the fluorescent lamps

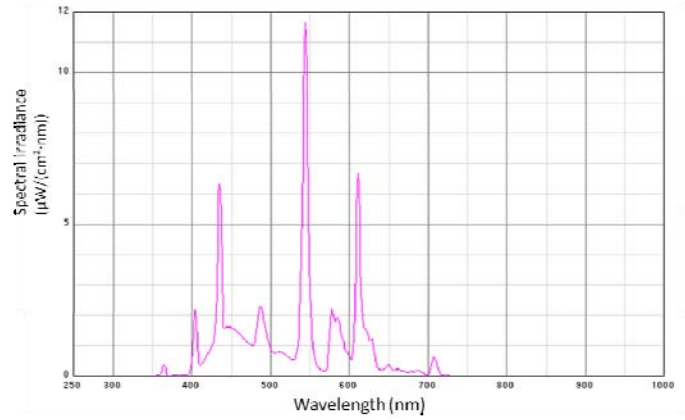


Figure S-2. The wavelength of the fluorescent lamp

2. Materials

Methyl 3-(4-nitrophenyl)-3-oxopropanoate (**1e**) were prepared from ethyl 3-(4-nitrophenyl)-3-oxopropanoate according to the literature.[1] **1j** was prepared from amine according to the literature.[2]

3. General Experimental Procedure

A dry methanol solution (5 mL) of **1a** (0.3 mmol), methylene blue (2.0 mol%) and $Ca(OH)_2$ (0.1 equiv) in a Pyrex test tube (diameter: 15mm, height: 145mm) equipped with an O_2 balloon, was irradiated with stirring condition for 10 h with four 22 W fluorescent lamps, which was set from the test tube in the distance of 80 mm. The crude product was analyzed by ^{1}H NMR with 1,1,2,2-tetrachloroethane as the internal standard for determination of the NMR yields. The reaction mixture was concentrated under the reduced pressure. The pure product **2a** was obtained in 80% yield (49.0 mg) after column chromatography.

4. Synthesis of Methyl 3-n-butyl-2-hydroxy-3-oxopropanoate (3a)

A dry methanol solution (5 mL) of **1a** (0.3 mmol), methylene blue (2.0 mol%), $Ca(OH)_2$ (0.1 equiv) and $P(OEt)_3$ (1.0 equiv) in a Pyrex test tube equipped with an O_2 balloon, was irradiated with stirring condition for 10 h with four 22 W fluorescent lamps, which was set from the test tube in the distance of 80 mm. The reaction mixture was concentrated under the reduced pressure. This reaction was performed three times, then methyl 3-*n*-butyl-3,3-dimethoxy-2-hydroxypropanoate was obtained (total 30.6 mg) after column chromatography. A chloroform solution (3 mL) of this product and TFA (0.1 equiv) in flask was stirred for 10 minutes at 0 ºC. The reaction mixture was concentrated under the reduced pressure. **3a** was obtained in 4% yield (6.7 mg) after column chromatography.

5. Spectral Data of Compounds

Dimethyl 2-butyl-2-hydroxymalonate (2a)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 6H), 3.82 (s, 1H), 2.05-2.01 (m, 2H), 1.35-1.25 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 79.0, 53.3, 34.6, 25.2, 22.5, 13.8.

R_f = 0.20 (hexane:ether = 3:1).

Yield: 80% (49.0 mg)

Dimethyl 2-ethyl-2-hydroxymalonate (2b) [4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 6H), 2.07 (q, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 79.4, 53.3, 28.1, 7.4.

HRMS: *m*/*z* (DART) calcd for $C_7H_{13}O_5$ $[M+H]^+$: 177,0763 found 177.0770.

IR (ATR): 3941, 2959, 1735, 1438, 1225, 1156, 1119, 1089, 1006, 803 (cm^{-1}).

R_f = 0.20 (hexane:ether = 3:1).

Yield: 60% (31.8 mg)

Dimethyl 2-hydroxy-2-propylmalonate (2c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 6H), 3.73 (s, 1H), 2.03-1.99 (m , 2H), 1.36-1.30 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 79.0, 53.3, 36.9, 16.5, 13.9.

HRMS: *m*/*z* (DART) calcd for $C_8H_{15}O_5$ $[M+H]^+$: 191.0919, found 191.0913.

IR (ATR): 3505, 2980, 2960, 1738, 1723, 1428, 1294, 1249, 1215, 1117, 935, 806, 599 (cm^{-1}).

R_f = 0.20 (hexane:ether = 3:1).

Yield: 79% (45.2 mg)

Dimethyl 2-hydroxy-2-isopropylmalonate (2d)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 6H), 3.66 (s, 1H), 2.65 (sep, *J* = 6.8 Hz, 1H), 0.92 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 82.3, 53.3, 33.4, 16.4.

R_f = 0.20 (hexane:ether = 3:1).

Yield: 82% (47.0 mg)

Dimethyl 2-hydroxy-2-(4-nitrophenyl)malonate (2e)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 9.2 Hz, 2H), 7.89 (d, *J* = 9.2 Hz, 2H), 4.50 (s, 1H), 3.88 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 148.0, 142.1, 128.0, 123.0, 79.6, 54.2.

R_f = 0.30 (hexane:ethyl acetate = 3:2).

Yield: 74% (60.1 mg)

Dimethyl 2-hydroxy-2-(pylydine-3-yl)malonate (2f)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.56 (d, *J* = 4.5, 1H), 8.00 (dt, *J* = 8.3, 1.9 Hz, 1H), 7.30 (dd, *J* = 8.3, 4.8 Hz, 1H), 3.82 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 149.4, 148.2, 134.7,132.0, 122.9, 78.8, 54.0.

R_f = 0.32 (hexane:ethyl acetate = 1:3).

Yield: 34% (25.9 mg)

Methyl 2-hydroxy-2-methyl-3-(dimethylamino)-3-oxopropanoate (2g)

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 (s, 1H), 3.81 (s, 3H), 3.03 (s,3H), 2.96 (s, 3H), 1.63 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 170.2, 75.1, 53.0, 37.2, 22.9.

HRMS: *m*/*z* (DART) calcd for $C_7H_{14}NO_4$ $[M+H]^+$: 176.0922, found 176.0919.

IR (ATR): 3512, 2925, 1740, 1636, 1396, 1257, 1157, 1088, 970 (cm^{-1}).

R_f = 0.50 (hexane:ethyl acetate = 2:1).

Yield: 59% (31.2 mg)

Methyl 2-hydroxy-2-methyl-3-(diethylamino)-3-oxopropanoate (2h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 (s, 1H), 3.72 (s, 3H) 3.36-3.32 (m, 2H), 3.21-3.15 (m, 2H), 1.54 (s, 3H), 1.09-1.05 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 169.5, 75.1, 52.8, 41.4, 41.0, 23.0, 13.3, 12.1.

HRMS: *m*/*z* (DART) calcd for $C_9H_{18}NO_4$ $[M+H]^+$: 204.1235, found 204.1229.

IR (ATR): 3348, 2938, 1740, 1630, 1251, 1118, 980, 795 (cm^{-1}).

R_f = 0.50 (hexane:ethyl acetate = 1:1).

Yield: 72% (44.0 mg)

Methyl 2-hydroxy-2-methyl-3-(4-morpholinyl)-3-oxopropanoate (2i)

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.60 (s, 1H), 3.81 (s, 3H), 3.75-3.45 (m, 8H), 1.63 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 168.7, 75.5, 66.6, 66.2, 53.1, 46.3, 43.7, 23.4.

HRMS: *m*/*z* (DART) calcd for $C_9H_{16}NO_5$ $[M+H]^+$: 218.1028, found 218.1028.

IR (ATR): 3461, 3284, 2970, 1741, 1637, 1432, 1266, 1235, 1109, 1031, 969, 835 (cm^{-1}).

R_f = 0.50 (hexane:ethyl acetate = 1:2).

Yield: 68% (44.2 mg)

Methyl 2-hydroxy-2-methyl-3-(1-indolinyl)-3-oxopropanoate (2j)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 1H), 7.25-7.19 (m, 2H), 7.09-7.06 (t, *J* =7.5 Hz, 1H), 4.55 (s, 1H), 4.14 (dd, *J* =10.9, 8.0, 1H), 3.97-3.92 (m, 1H), 3.81 (s, 3H), 3.12 (t, *J* = 8.0 Hz, 2H), 1.73 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 167.6, 143.1, 131.2, 127.5, 124.7, 124.5, 117.9, 53.3, 47.9, 28.6, 23.1.

HRMS: *m*/*z* (DART) calcd for $C_{13}H_{16}NO_4$ $[M+H]^+$: 250.1079, found 250.1069.

IR (ATR): 3383, 3013, 1747, 1640, 1480, 1410, 1162, 1080, 750 (cm^{-1}).

R_f = 0.46 (hexane:ethyl acetate = 2:1).

Yield: 75% (65.0 mg)

Methyl 3-*n*-butyl-2-hydroxy-3-oxopropanoate (3a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.80 (s, 1H), 3.83 (s, 1H), 2.77-2.56 (m, 2H), 1.66-1.56 (m, 2H), 1.38-1.25 (m, 2H), 0.91 (t, *J* = 2.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 204.4, 168.8, 77.6, 53.1, 38.3, 25.4, 22.1, 13.7.

HRMS: *m*/*z* (DART) calcd for $C_8H_{15}O_4$ $[M+H]^+$: 175.0970, found 175.0972.

IR (ATR): 3441, 2960, 2875, 1727, 1439, 1210, 1170, 1123, 972 (cm^{-1})

R_f = 0.40 (hexane:ethyl acetate = 3:1).

Yield: 4% (6.7 mg)

6. References

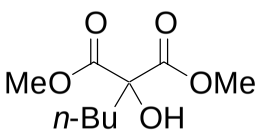
(1) Rappoprot, Z.; Gazit, A. *J. Org. Chem.* **1986**, *51*, 4112.

(2) Hengzhen, Q.; Zhanhui, Y.; Jiaxi, X. *Synthesis* **2011**, 5, 723.

(3) Kanai, N.; Nakayama, H.; Tada, N.; Itoh, A. *Org. Lett.* **2010**, 12, 1948.

(4) Ciufolini, M.; Rohrschange, F. WO1998004557 A1 19980205.

(5) Chuang, G.-J.; Wang, W.; Lee, E.; Ritter, T. *J. Am. Chem. Soc.* **2011**, 133, 1760.



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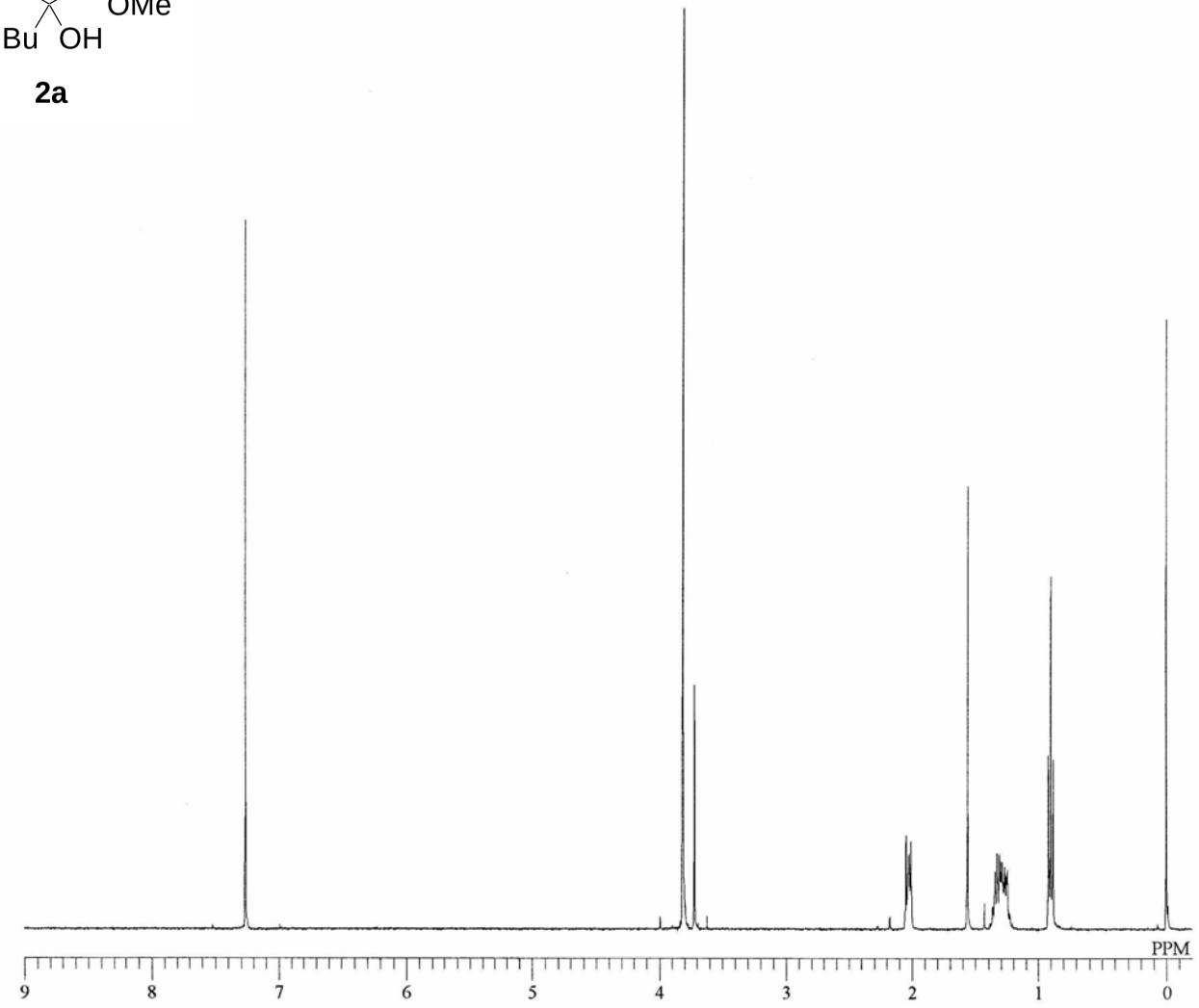

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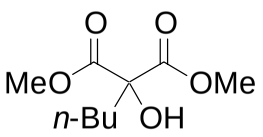

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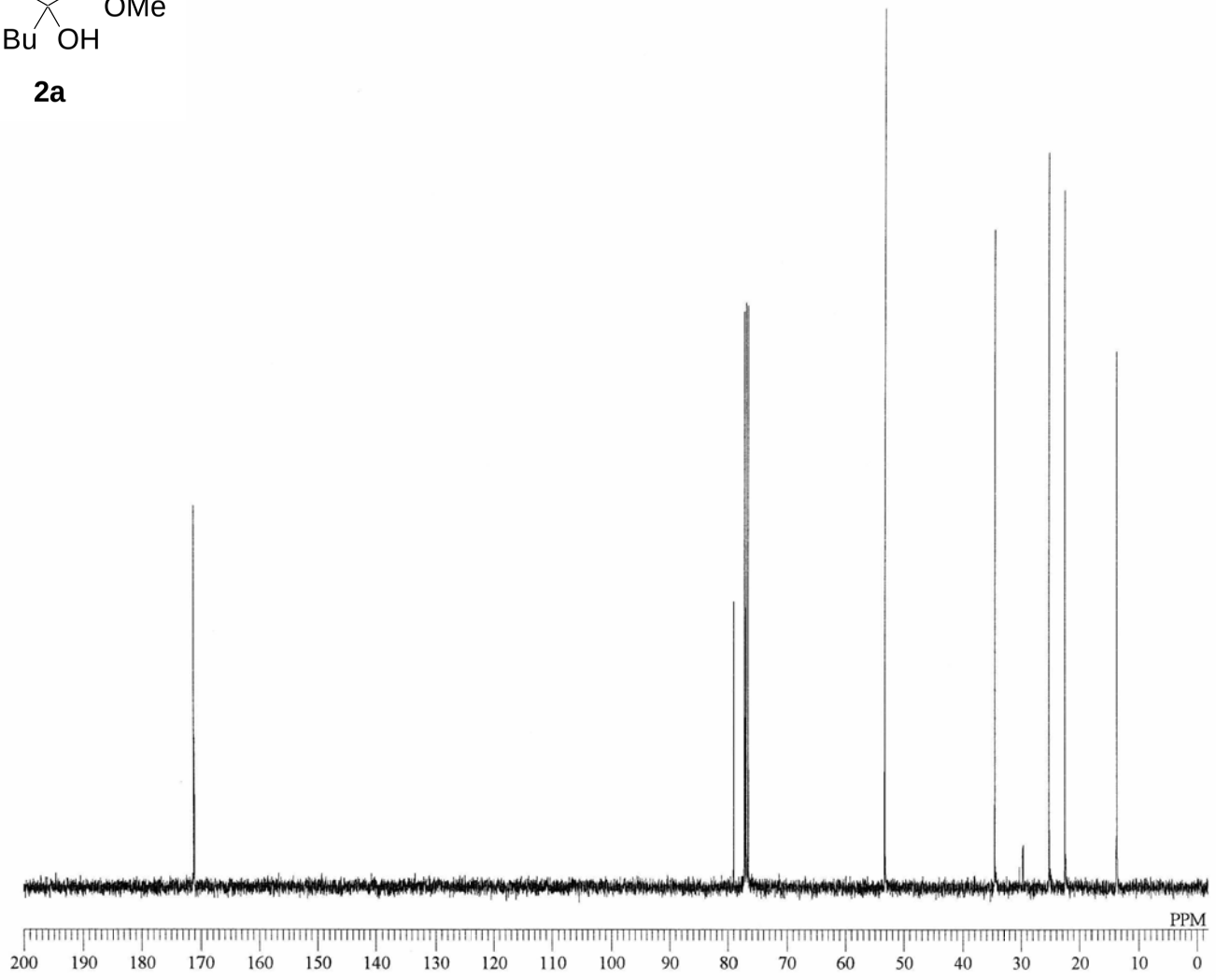

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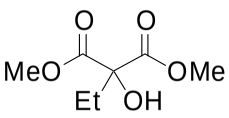

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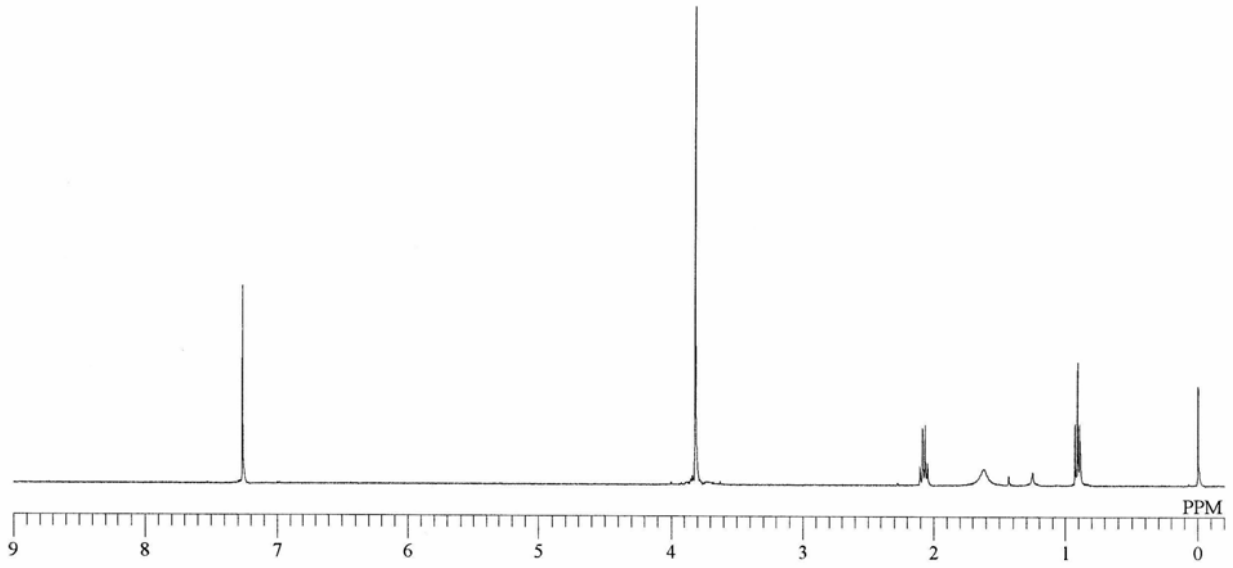

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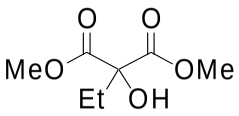

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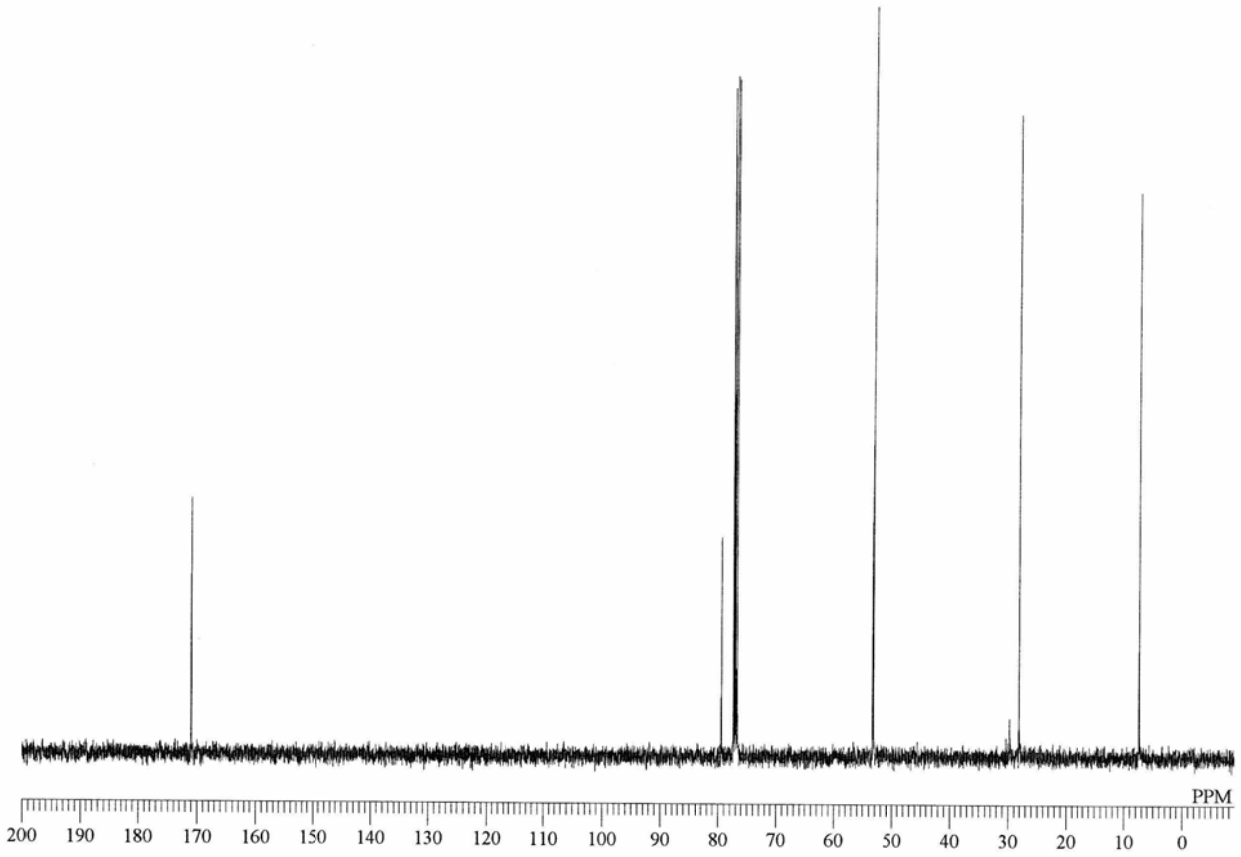

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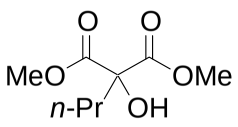

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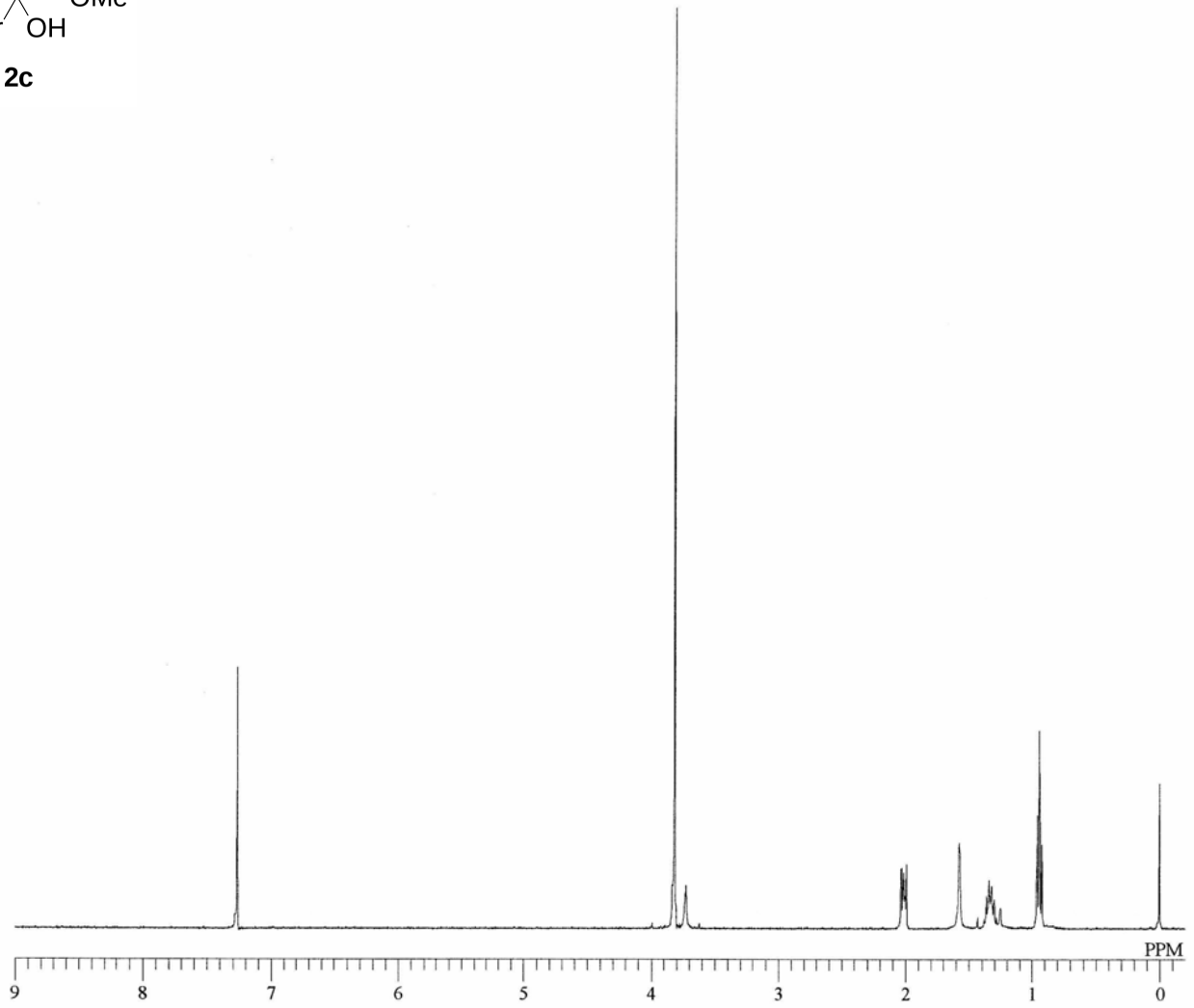

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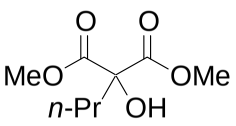

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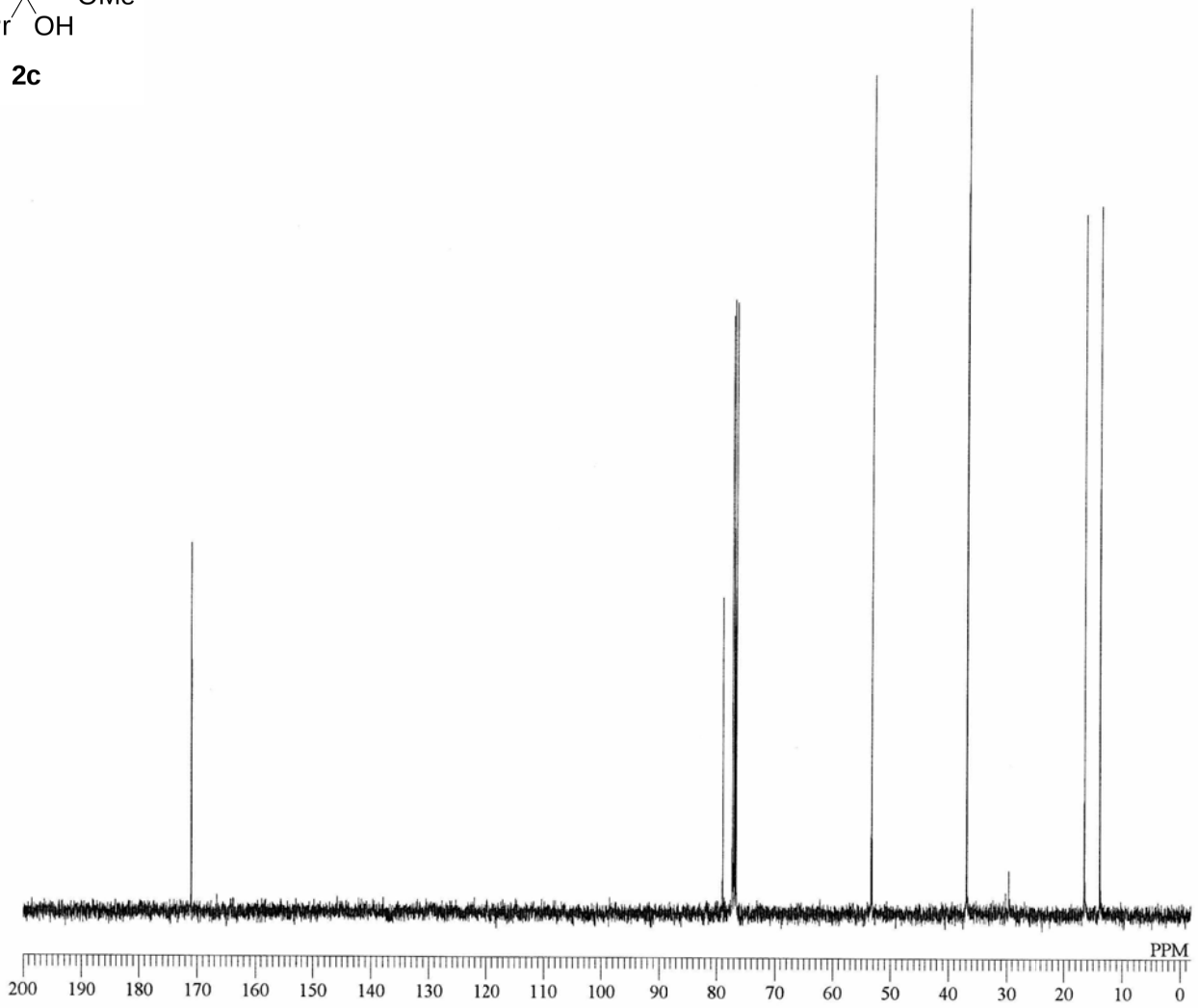

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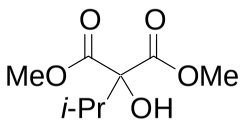
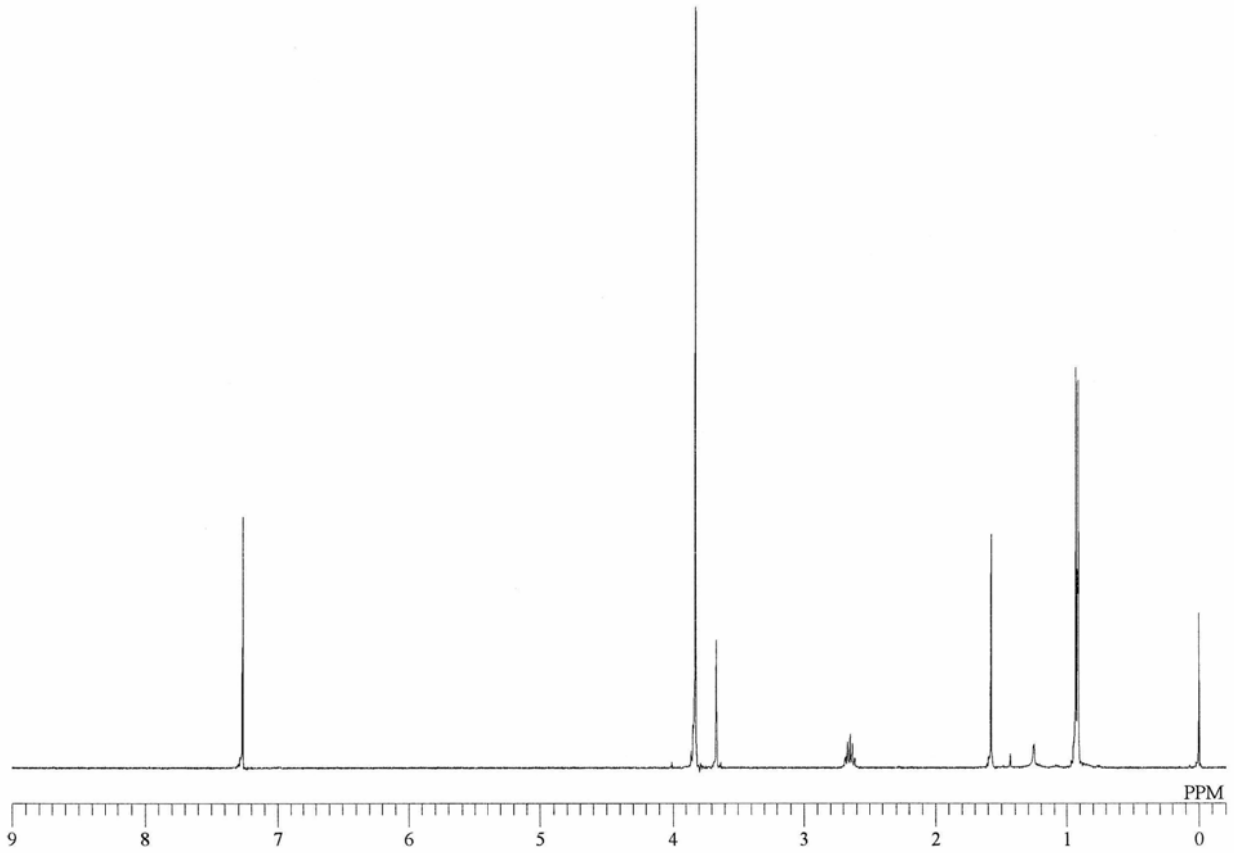
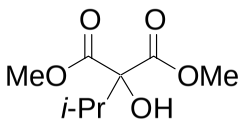


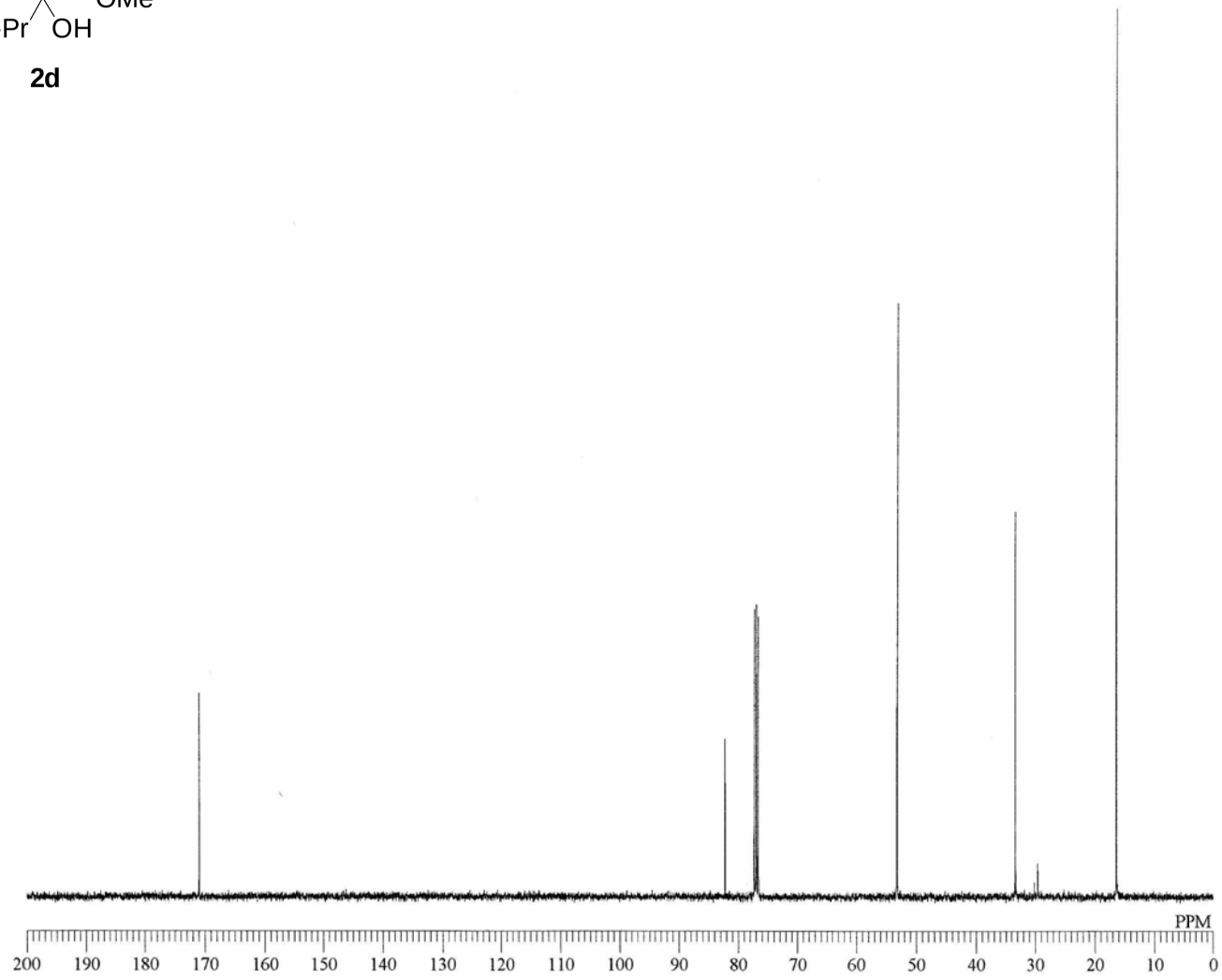
2d



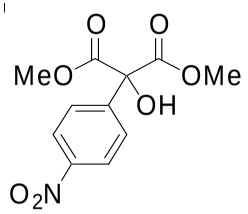
MENUF	NON
OBNUC	1H
OFR	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
PW1	8.00 usec
DEADT	71.90 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	16384
SPO	16384
TIMES	4
DUMMY	1
FREQU	7912.96 Hz
FLT	3950 Hz
DELAY	50.60 usec
ACQTM	2.0705 sec
PD	4.9290 sec
ADBIT	16
RGAIN	19
BF	0.12 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	NON
EXPCM	NON:Single.coupled:PW
IRNUC	1H
IFR	395.75 MHz
IRSET	124.00 KHz
IRFIN	10277.00 Hz
IRRPW	45 usec
IRATN	511
DFILE	AO-351e.als
SF	TH5ATFG2_
LKSET	12.90 KHz
LKFIN	104.0 Hz
LKLEV	180
LGAIN	22
LKPHS	120
LKSIG	883
CSPED	14 Hz
FILDC	
FILDF	



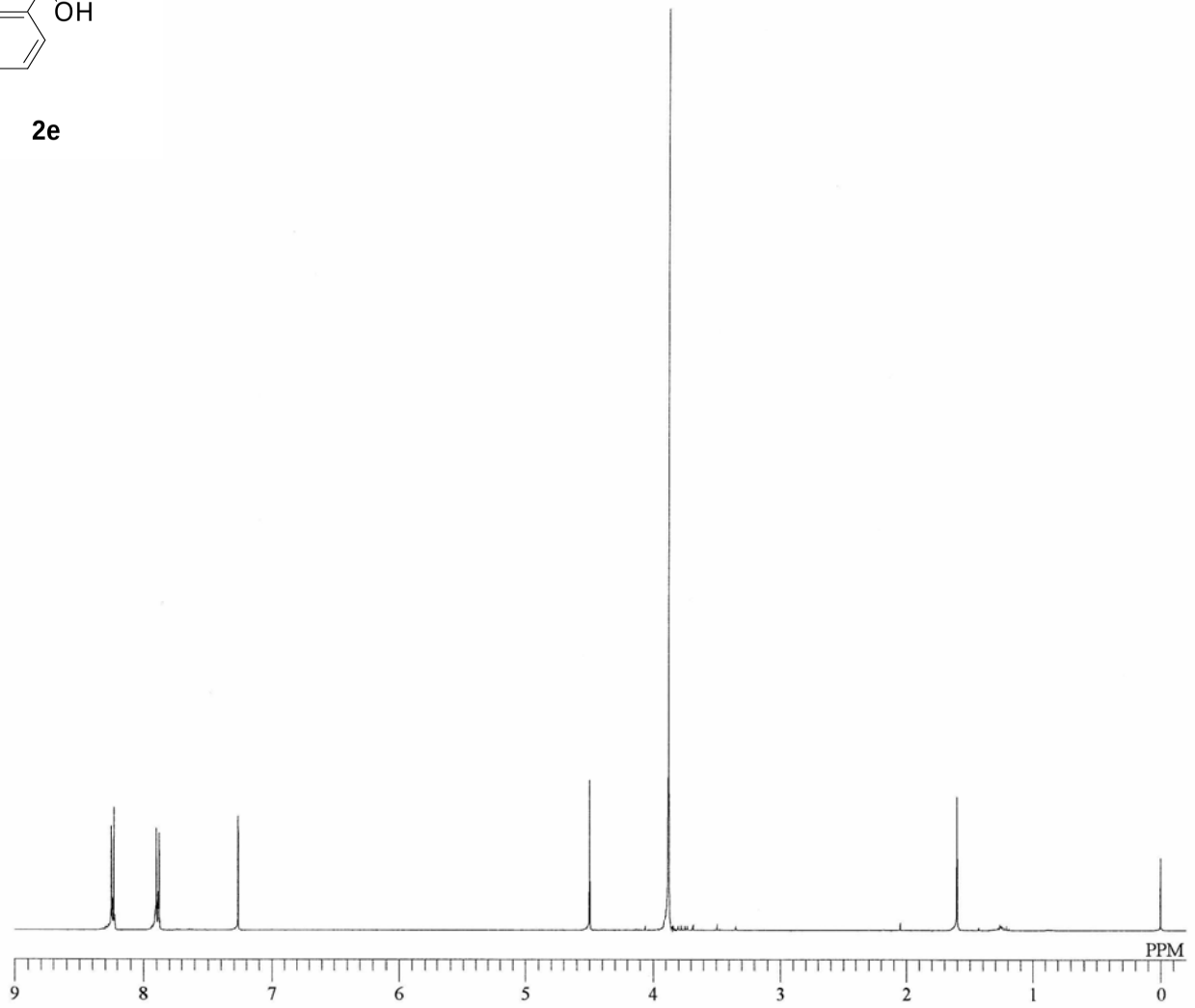
2d



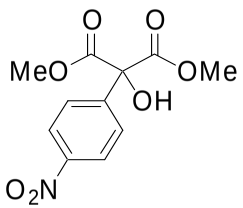
MENUF	BCM
OBNUC	13C
OFR	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
PW1	6.00 usec
DEADT	19.40 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	32768
SPO	32768
TIMES	256
DUMMY	1
FREQU	26845.64 Hz
FLT	13400 Hz
DELAY	14.90 usec
ACQTM	1.2206 sec
PD	1.7790 sec
ADBIT	16
RGAIN	24
BF	1.20 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	BCM
EXPCM	Bilevel.complete.decoupl
IRNUC	1H
IFR	395.75 MHz
IRSET	124.00 KHz
IRFIN	10277.00 Hz
IRRPW	45 usec
IRATN	511
DFILE	AO-351e 13C.als
SF	TH5ATFG2_
LKSET	12.90 KHz
LKFIN	104.0 Hz
LKLEV	180
LGAIN	23
LKPHS	120
LKSIG	1030
CSPED	13 Hz
FILDC	
FILDF	



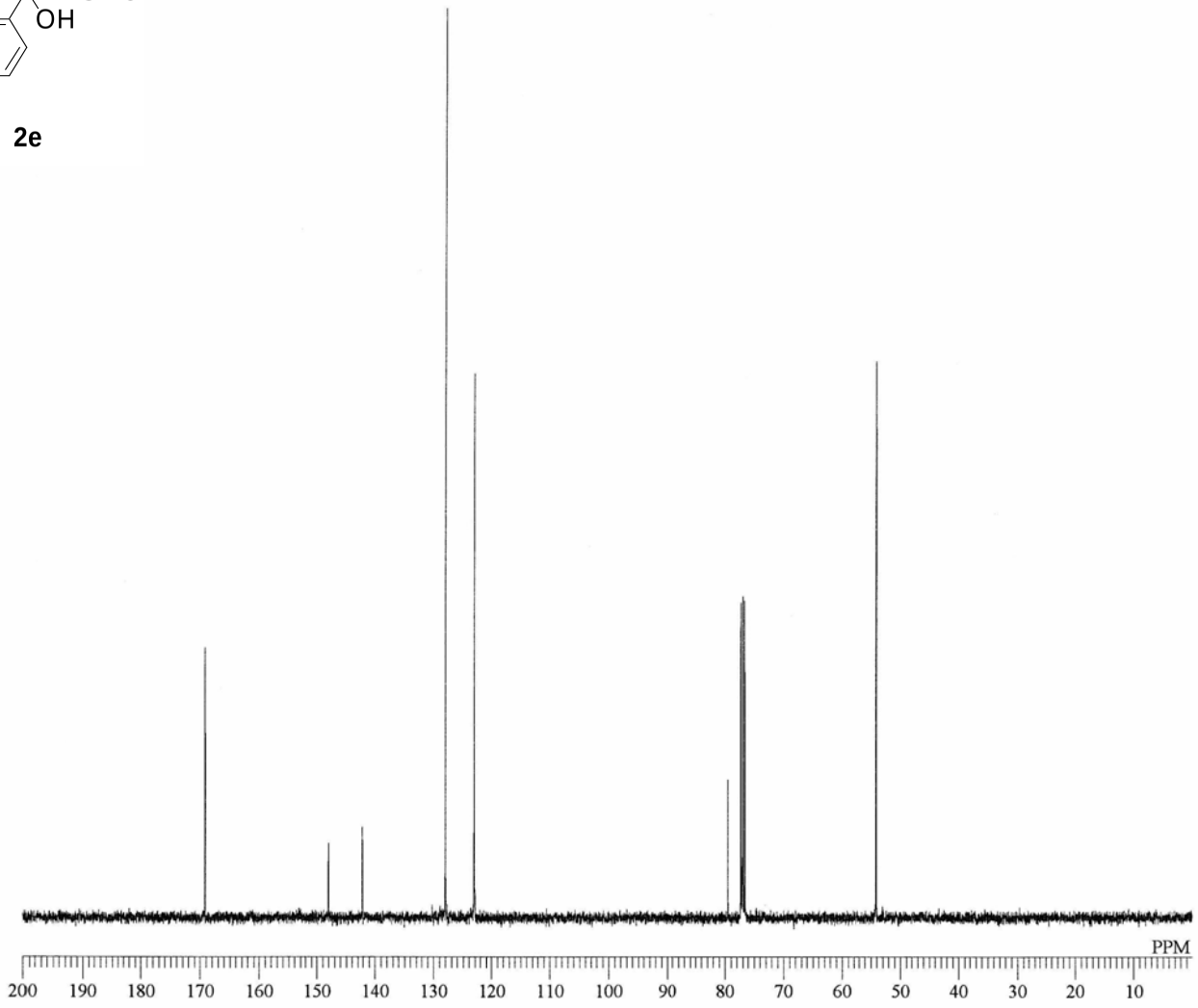
2e



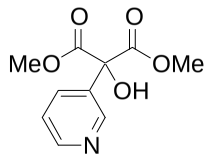
MENUF	NON
OBNUC	1H
OFR	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
PW1	8.00 usec
DEADT	71.90 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	16384
SPO	16384
TIMES	8
DUMMY	1
FREQU	7912.96 Hz
FLT	3950 Hz
DELAY	50.60 usec
ACQTM	2.0705 sec
PD	4.9290 sec
ADBIT	16
RGAIN	16
BF	0.12 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	NON
EXPCM	NON:Single.coupled:PW
IRNUC	1H
IFR	395.75 MHz
IRSET	124.00 KHz
IRFIN	10277.00 Hz
IRRPW	45 usec
IRATN	511
DFILE	AO-369 Fr6-10.als
SF	TH5ATFG2_1AO-369 Fr
LKSET	12.90 KHz
LKFIN	104.0 Hz
LKLEV	180
LGAIN	22
LKPHS	120
LKSIG	1064
CSPED	16 Hz
FILDC	
FILDF	



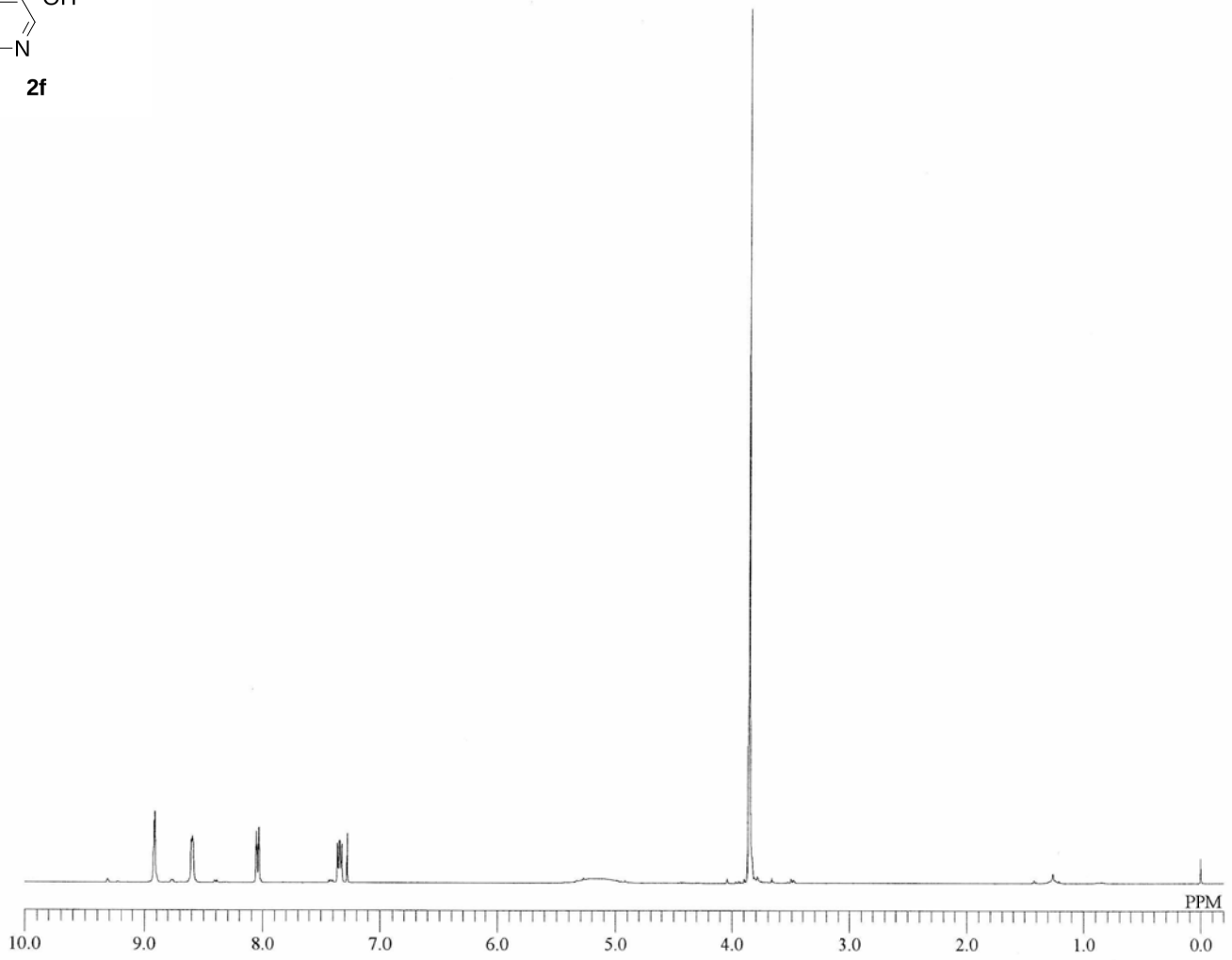
2e



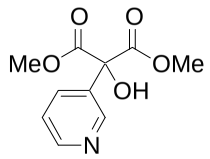
MENUF	BCM
OBNUC	13C
OFR	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
PW1	6.00 usec
DEADT	19.40 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	32768
SPO	32768
TIMES	256
DUMMY	1
FREQU	26845.64 Hz
FLT	13400 Hz
DELAY	14.90 usec
ACQTM	1.2206 sec
PD	1.7790 sec
ADBIT	16
RGAIN	25
BF	1.20 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	BCM
EXPCM	Bilevel.complete.decoupl
IRNUC	1H
IFR	395.75 MHz
IRSET	124.00 KHz
IRFIN	10277.00 Hz
IRRPW	45 usec
IRATN	511
DFILE	AO-369 Fr6-10 13C.als
SF	TH5ATFG2_1AO-369 F1
LKSET	12.90 KHz
LKFIN	104.0 Hz
LKLEV	180
LGAIN	22
LKPHS	120
LKSIG	893
CSPED	13 Hz
FILDC	
FILDF	



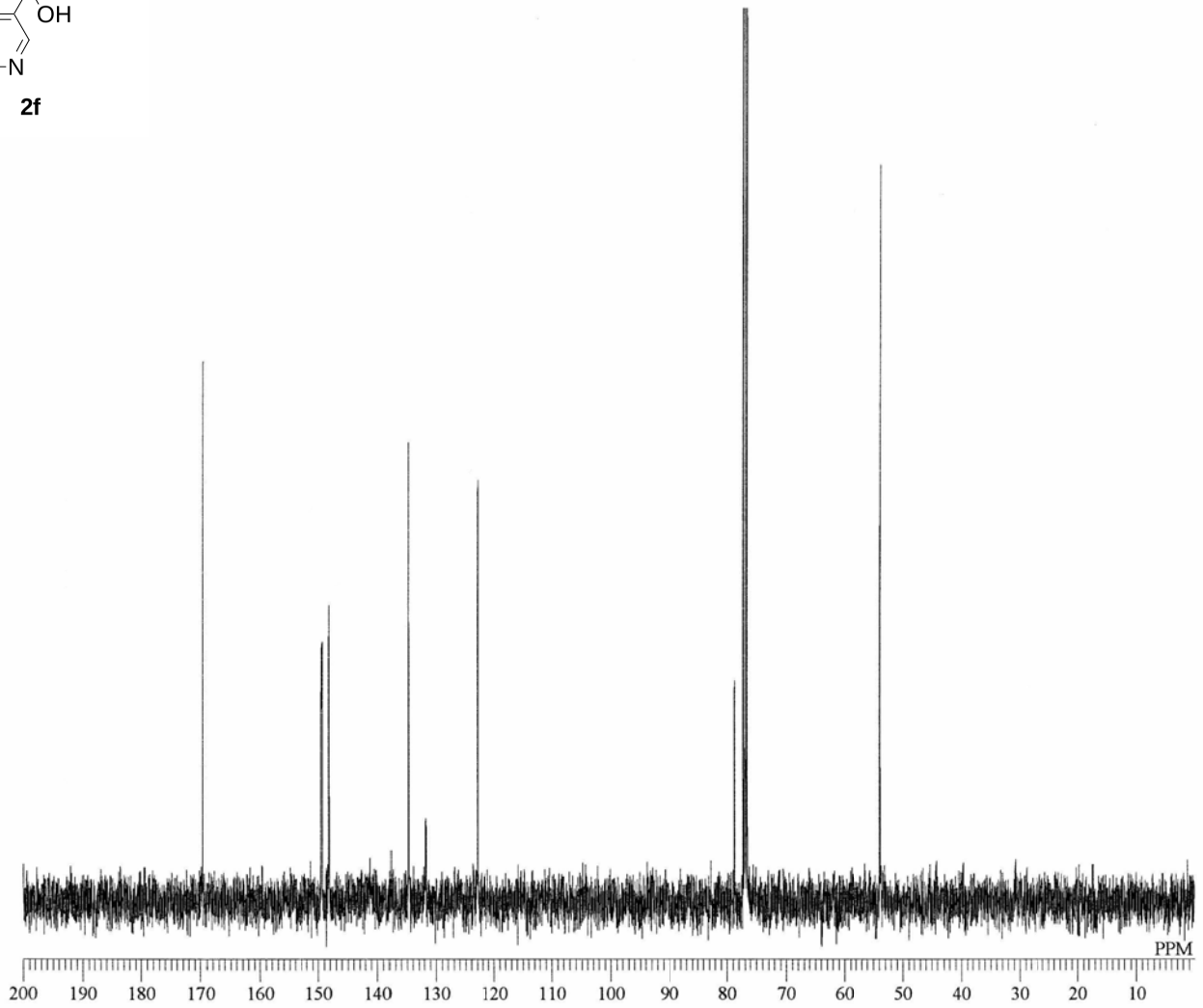
2f



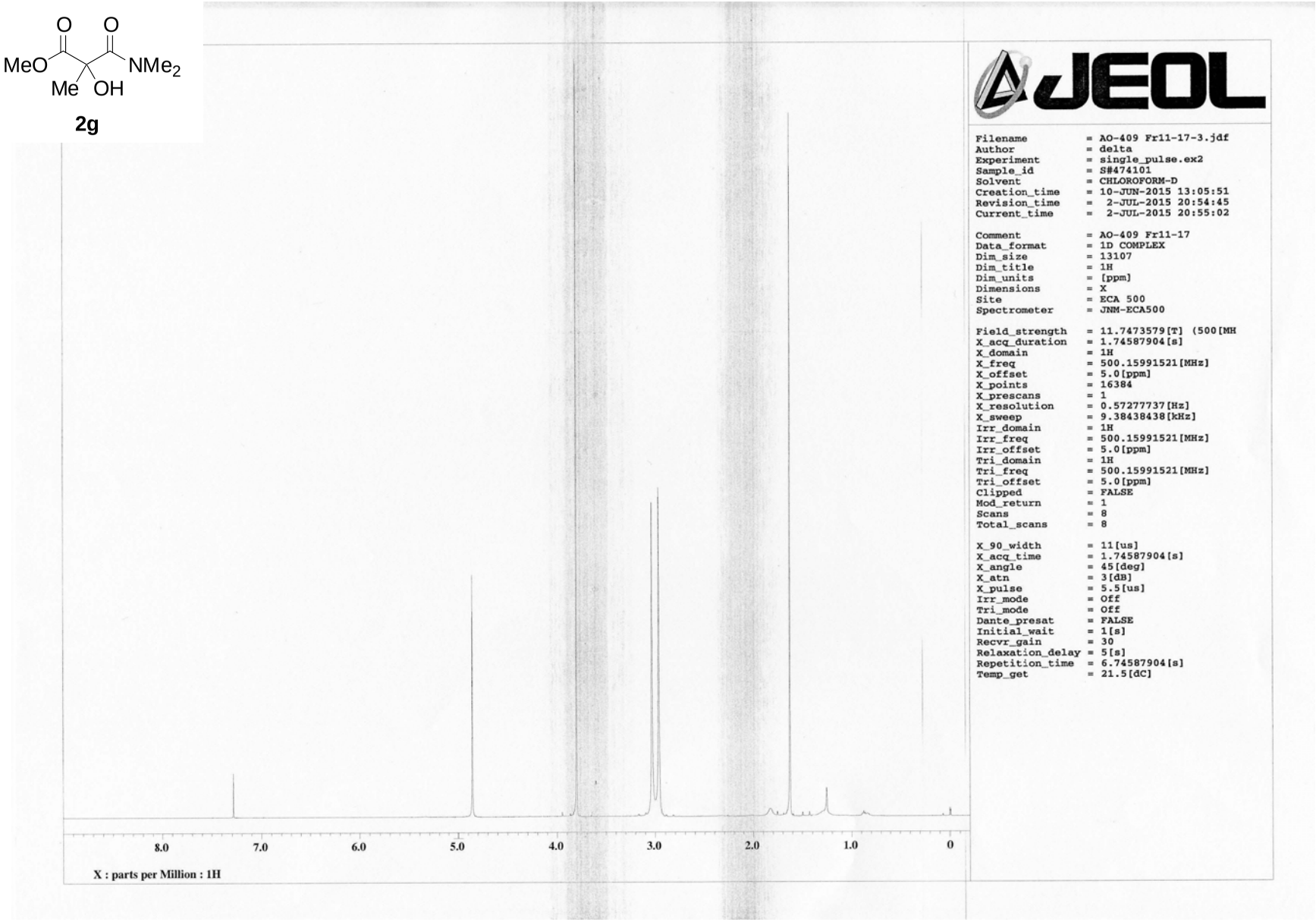
MENUF	non
OBNUC	1H
OFR	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
PW1	8.00 usec
DEADT	71.90 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	16384
SPO	16384
TIMES	32
DUMMY	1
FREQU	7912.96 Hz
FLT	3950 Hz
DELAY	50.60 usec
ACQTM	2.0705 sec
PD	4.9290 sec
ADBIT	16
RGAIN	14
BF	0.12 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	NON
EXPCM	NON:Single.coupled:PW1
IRNUC	1H
IFR	395.75 MHz
IRSET	124.00 KHz
IRFIN	10277.00 Hz
IRRPW	45 usec
IRATN	511
DFILE	_DEFAULT.ALS
SF	TH5ATFG2_
LKSET	12.90 KHz
LKFIN	104.0 Hz
LKLEV	180
LGAIN	22
LKPHS	110
LKSIG	855
CSPED	15 Hz
FILDC	
FILDF	



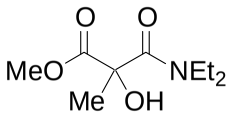
2f



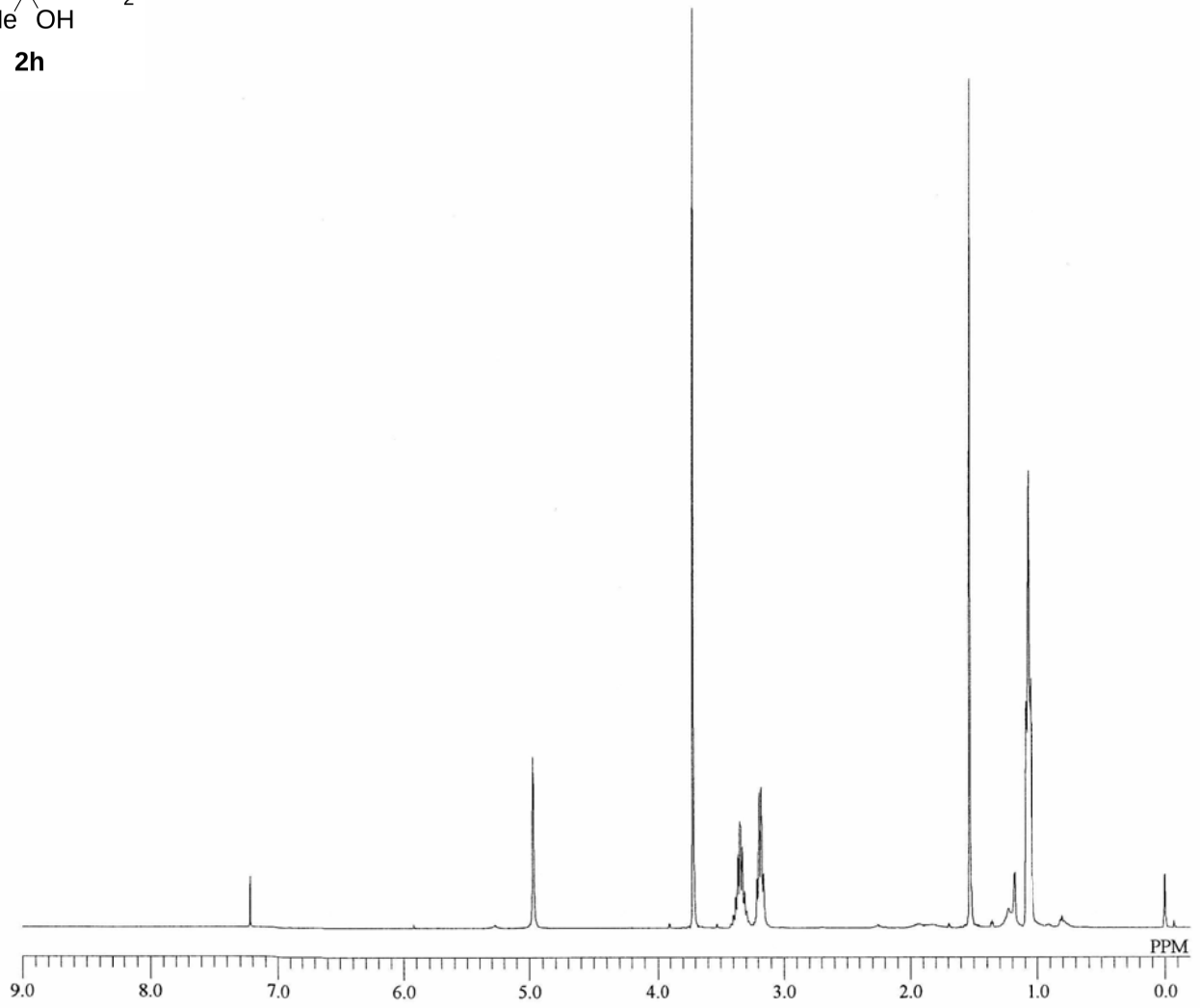
MENUF	BCM
OBNUC	13C
OFR	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
PW1	6.00 usec
DEADT	19.40 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	32768
SPO	32768
TIMES	256
DUMMY	1
FREQU	26845.64 Hz
FLT	13400 Hz
DELAY	14.90 usec
ACQTM	1.2206 sec
PD	1.7790 sec
ADBIT	16
RGAIN	24
BF	1.20 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	BCM
EXPCM	Bilevel.complete.decoupl
IRNUC	1H
IFR	395.75 MHz
IRSET	124.00 KHz
IRFIN	10277.00 Hz
IRRPW	45 usec
IRATN	511
DFILE	AO-358-2 Fr5.6 13C.als
SF	TH5ATFG2_
LKSET	12.90 KHz
LKFIN	104.0 Hz
LKLEV	180
LGAIN	22
LKPHS	120
LKSIG	767
CSPED	13 Hz
FILDC	
FILDF	


MeO
O
O
NMe2
Me
OH
2g
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H
JEOL
Filename = AO-409 Fr11-17-3.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#474101
Solvent = CHLOROFORM-D
Creation_time = 10-JUN-2015 13:05:51
Revision_time = 2-JUL-2015 20:54:45
Current_time = 2-JUL-2015 20:55:02
Comment = AO-409 Fr11-17
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 1.74587904[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5.0[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.57277737[Hz]
X_sweep = 9.38438438[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Tri_domain = 1H
Tri_freq = 500.15991521[MHz]
Tri_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 11[us]
X_acq_time = 1.74587904[s]
X_angle = 45[deg]
X_atn = 3[dB]
X_pulse = 5.5[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 30
Relaxation_delay = 5[s]
Repetition_time = 6.74587904[s]
Temp_get = 21.5[dC]

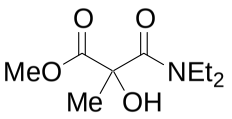
JEOL
Filename = AO-409 fr11-17 13C-3.
Author = delta
Experiment = single_pulse_dec
Sample_id = S#475589
Solvent = CHLOROFORM-D
Creation_time = 10-JUN-2015 13:13:25
Revision_time = 2-JUL-2015 21:02:00
Current_time = 2-JUL-2015 21:02:04
Comment = AO-409 fr11-17 13C
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 128
Total_scans = 128
X_90_width = 10[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 5.5[dB]
X_pulse = 3.33333333[us]
Irr_atn_dec = 21.4479[dB]
Irr_atn_noe = 21.4479[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 = 2.83361792[s]
Temp_get = 21.7[dC]
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
X : parts per Million : 13C



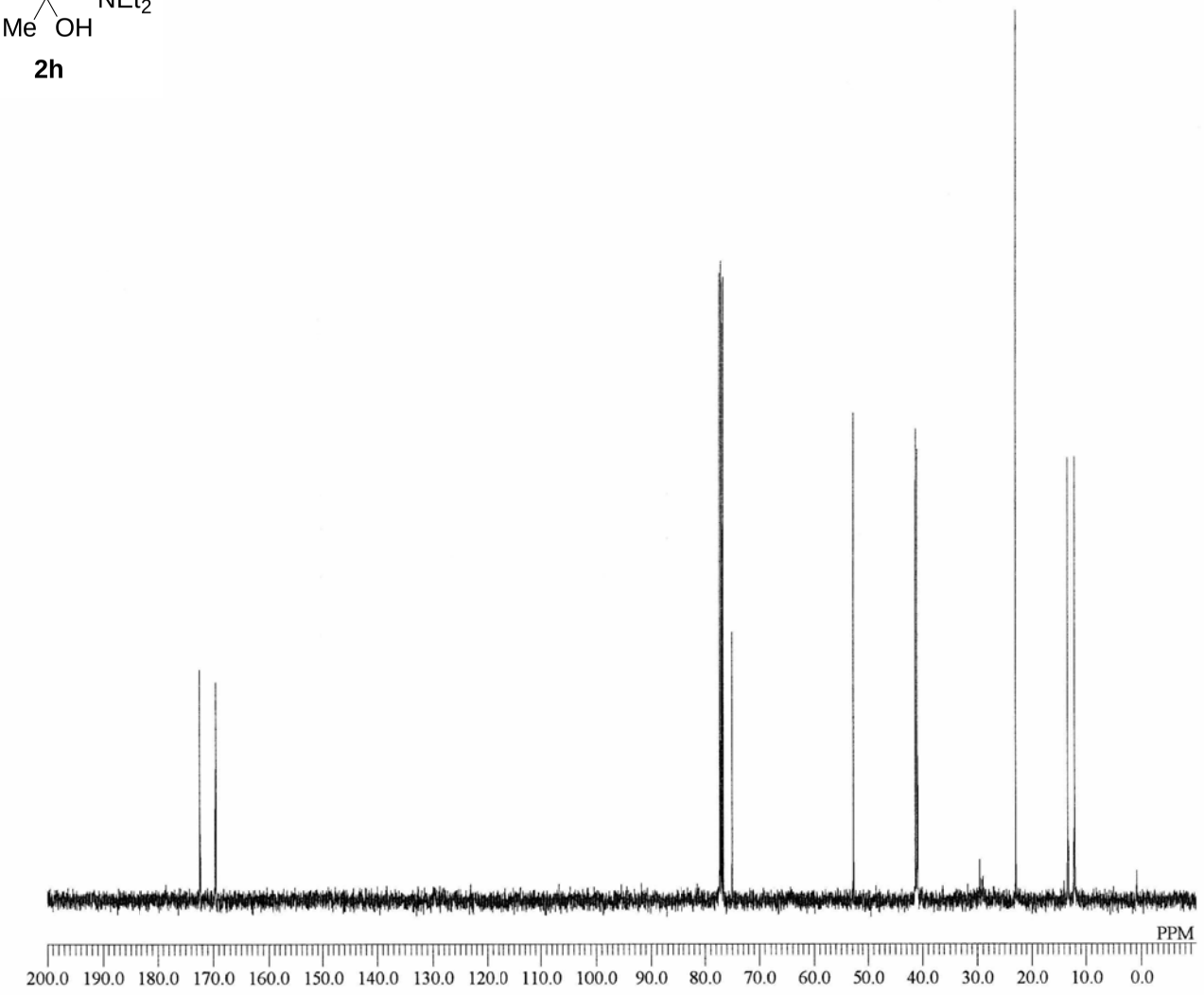
2h



MENUF	NON
OBNUC	1H
OFR	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
PW1	8.00 usec
DEADT	71.90 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	16384
SPO	16384
TIMES	8
DUMMY	1
FREQU	7912.96 Hz
FLT	3950 Hz
DELAY	50.60 usec
ACQTM	2.0705 sec
PD	4.9290 sec
ADBIT	16
RGAIN	10
BF	0.12 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	NON
EXPCM	NON:Single.coupled:PW
IRNUC	1H
IFR	395.75 MHz
IRSET	124.00 KHz
IRFIN	10277.00 Hz
IRRPW	45 usec
IRATN	511
DFILE	AO-413 Fr1-8.als
SF	TH5ATFG2_
LKSET	12.90 KHz
LKFIN	104.0 Hz
LKLEV	180
LGAIN	22
LKPHS	110
LKSIG	885
CSPED	13 Hz
FILDC	
FILDF	

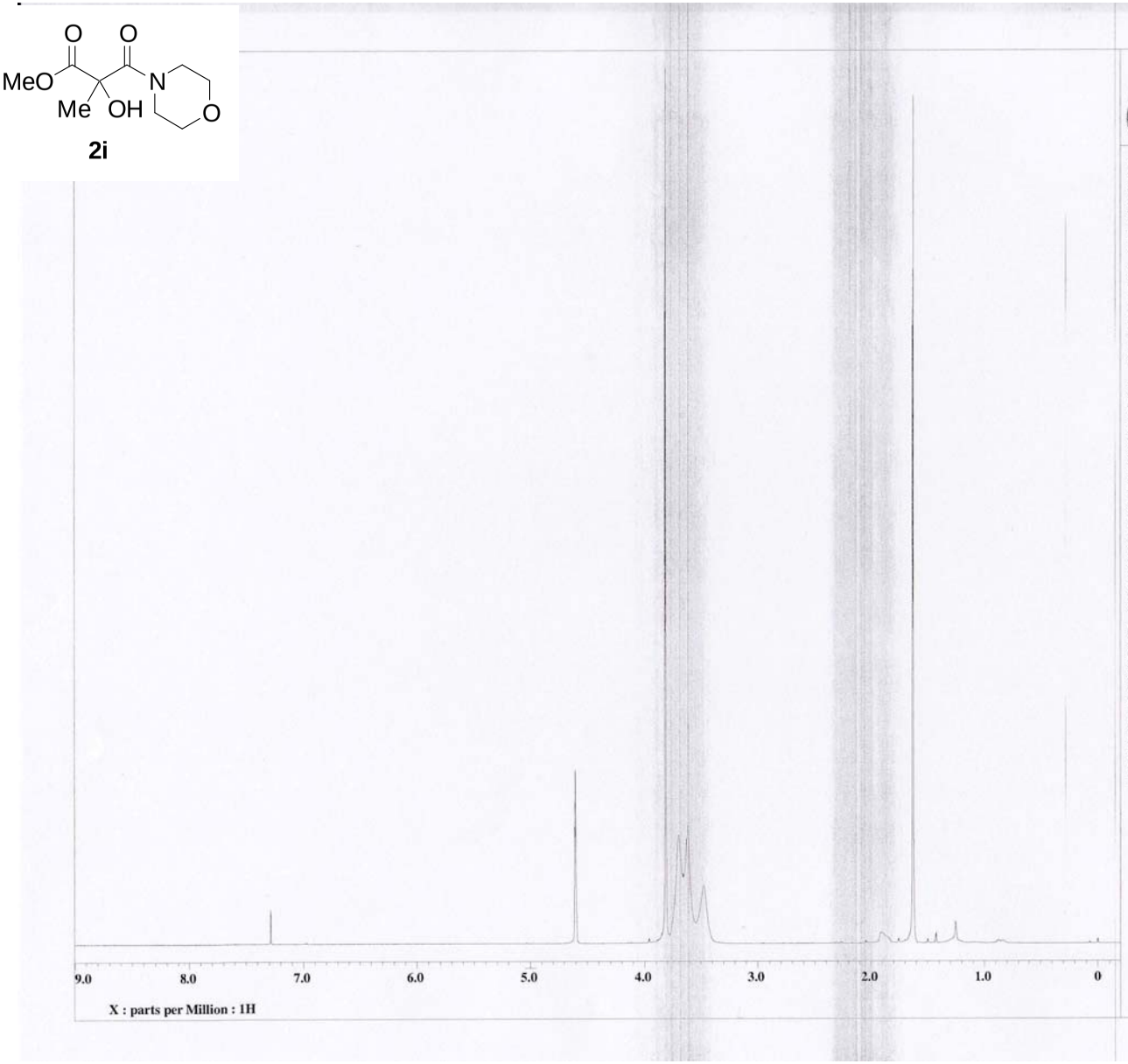


2h

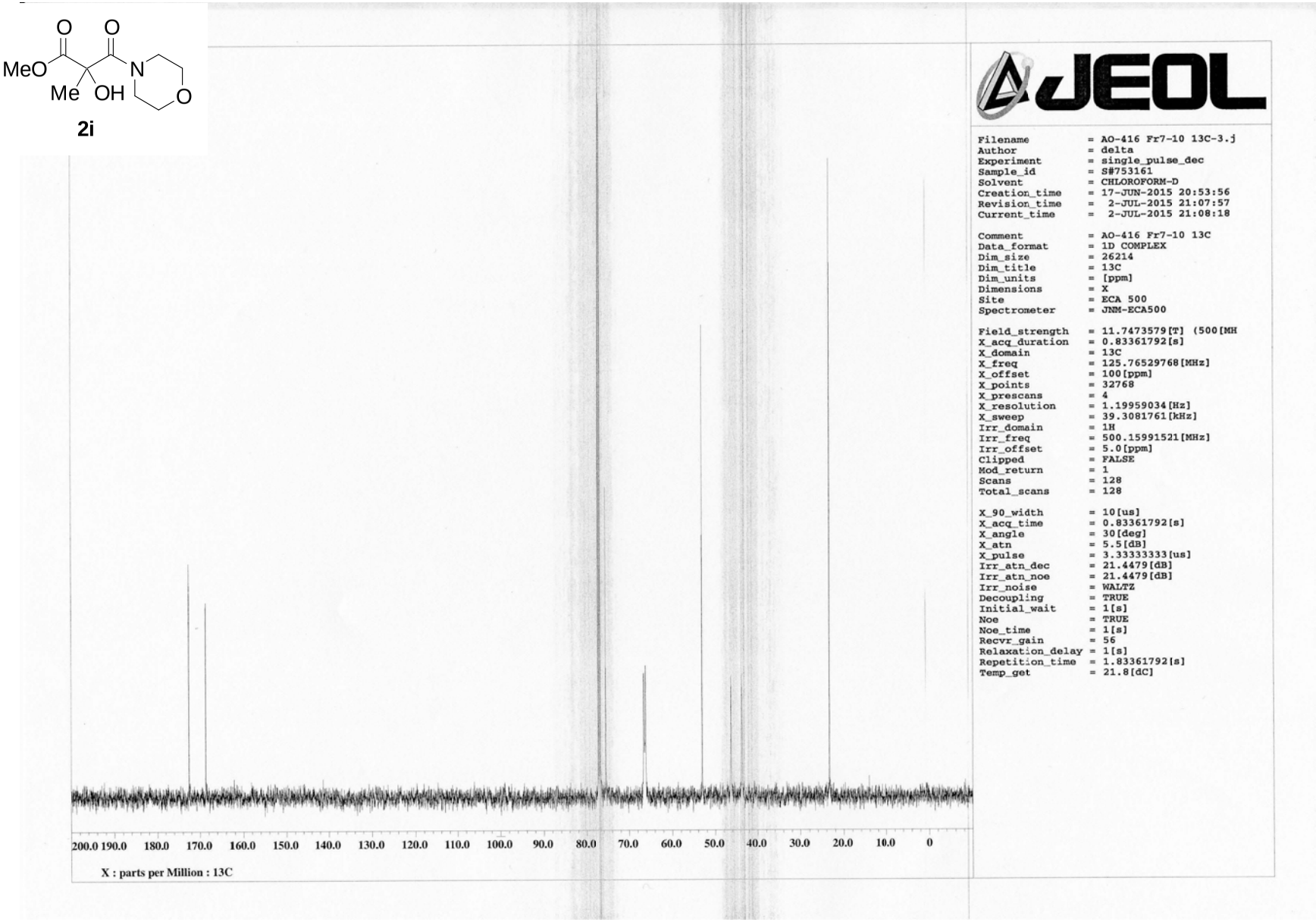


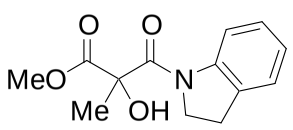
MENUF	BCM
OBNUC	13C
OFR	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
PW1	6.00 usec
DEADT	19.40 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	32768
SPO	32768
TIMES	256
DUMMY	1
FREQU	26845.64 Hz
FLT	13400 Hz
DELAY	14.90 usec
ACQTM	1.2206 sec
PD	1.7790 sec
ADBIT	16
RGAIN	24
BF	1.20 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	BCM
EXPCM	Bilevel.complete.decoupl
IRNUC	1H
IFR	395.75 MHz
IRSET	124.00 KHz
IRFIN	10277.00 Hz
IRRPW	45 usec
IRATN	511
DFILE	AO-413 Fr1-8 13C.als
SF	TH5ATFG2_
LKSET	12.90 KHz
LKFIN	104.0 Hz
LKLEV	180
LGAIN	22
LKPHS	110
LKSIG	774
CSPED	17 Hz
FILDC	
FILDF	

2i

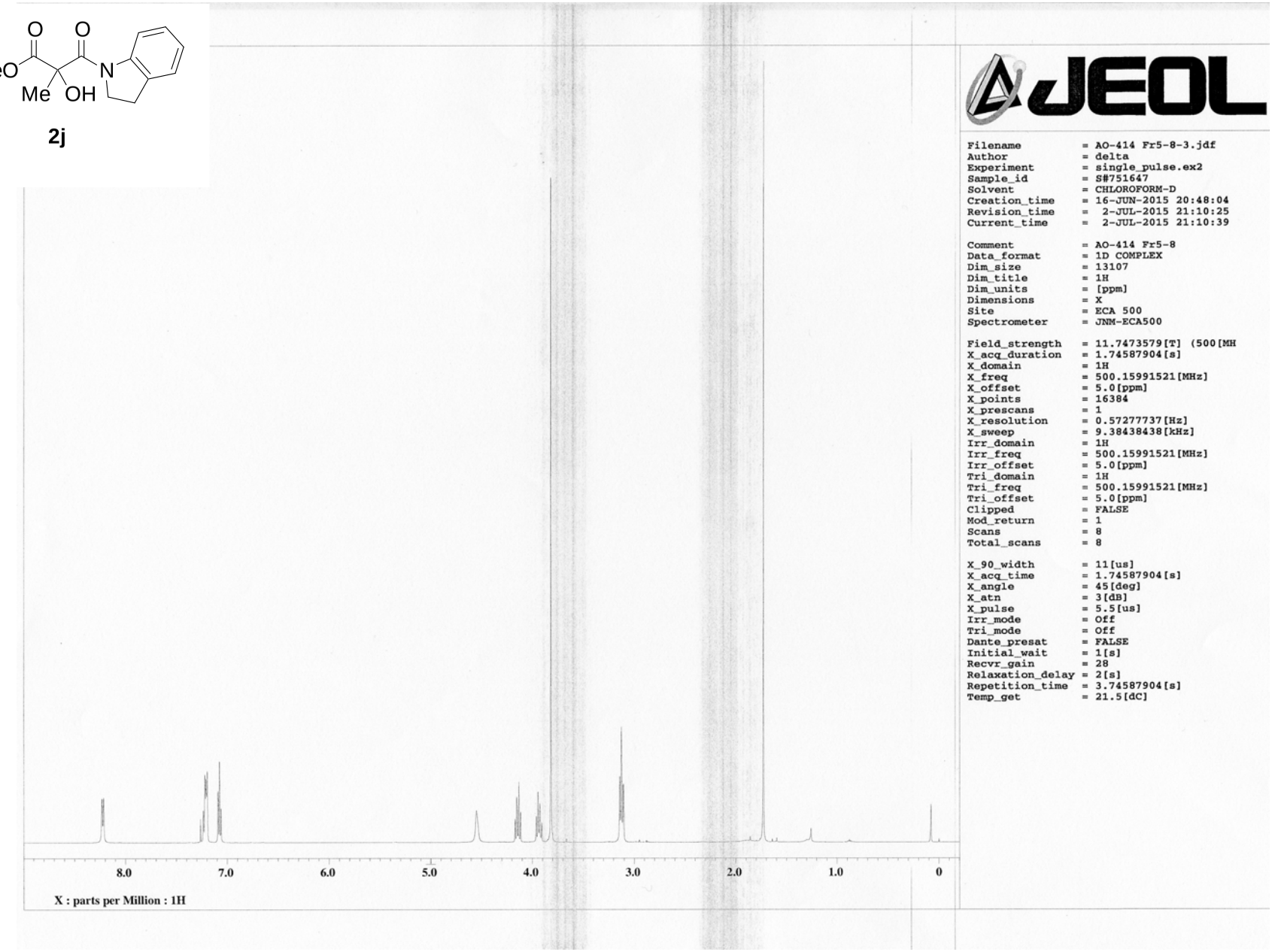



```
Filename          = AO-416 Fr7-10-3.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#752505
Solvent           = CHLOROFORM-D
Creation_time     = 17-JUN-2015 20:49:23
Revision_time     =  2-JUL-2015 21:06:26
Current_time      =  2-JUL-2015 21:06:47

Comment           = AO-416 Fr7-10
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 11[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 3[dB]
X_pulse           = 5.5[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Repetition_time   = 3.74587904[s]
Temp_get          = 21.5[dC]
```

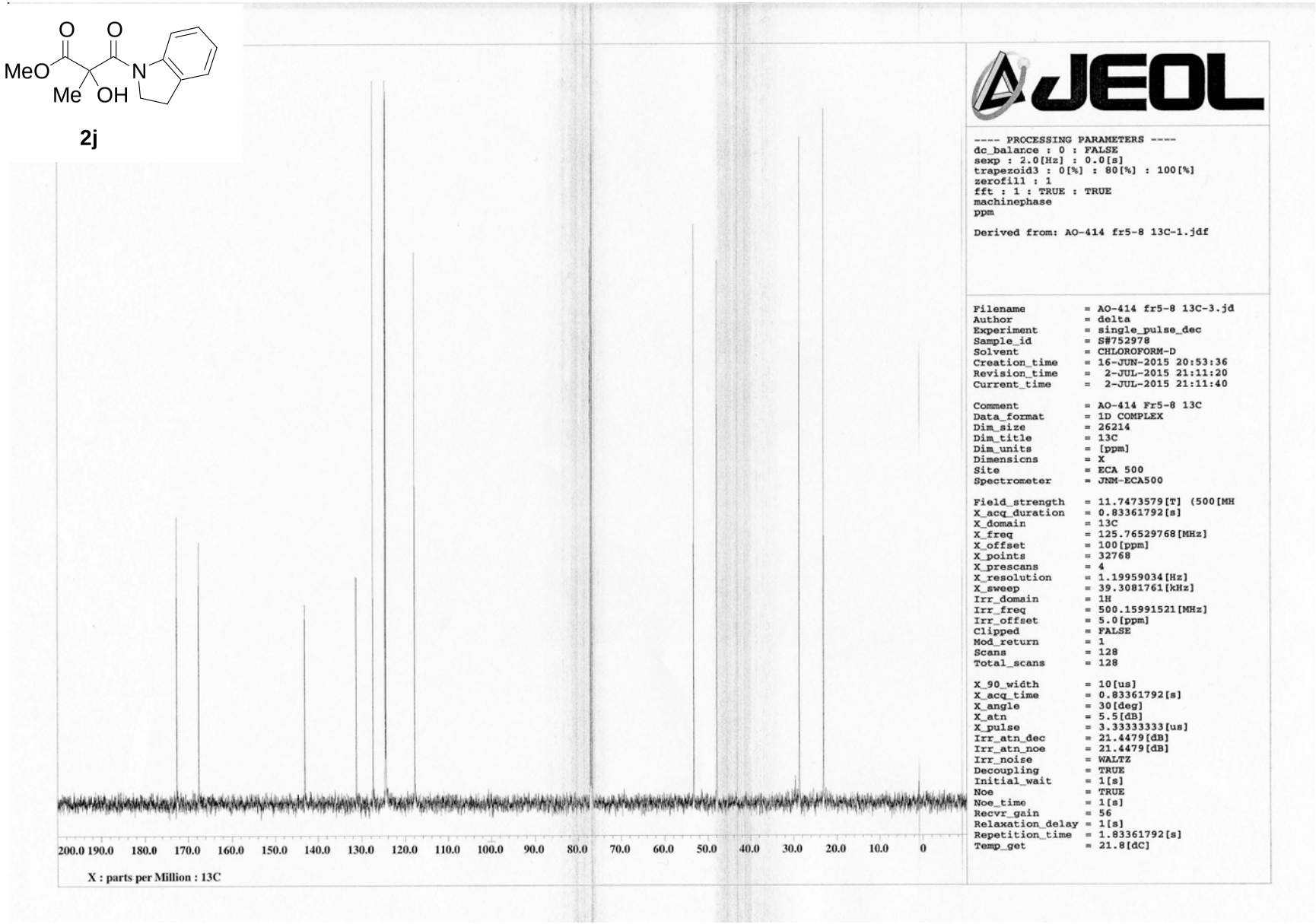

MeO
Me
OH
N
O
O
O
2i
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : 13C
JEOL
Filename = AO-416 Fr7-10 13C-3.j
Author = delta
Experiment = single_pulse_dec
Sample_id = S#753161
Solvent = CHLOROFORM-D
Creation_time = 17-JUN-2015 20:53:56
Revision_time = 2-JUL-2015 21:07:57
Current_time = 2-JUL-2015 21:08:18
Comment = AO-416 Fr7-10 13C
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 128
Total_scans = 128
X_90_width = 10[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 5.5[dB]
X_pulse = 3.33333333[us]
Irr_atn_dec = 21.4479[dB]
Irr_atn_noe = 21.4479[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 1[s]
Recvr_gain = 56
Relaxation_delay = 1[s]
Repetition_time = 1.83361792[s]
Temp_get = 21.8[dC]

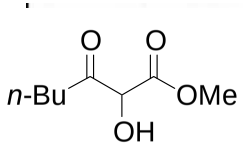


2j

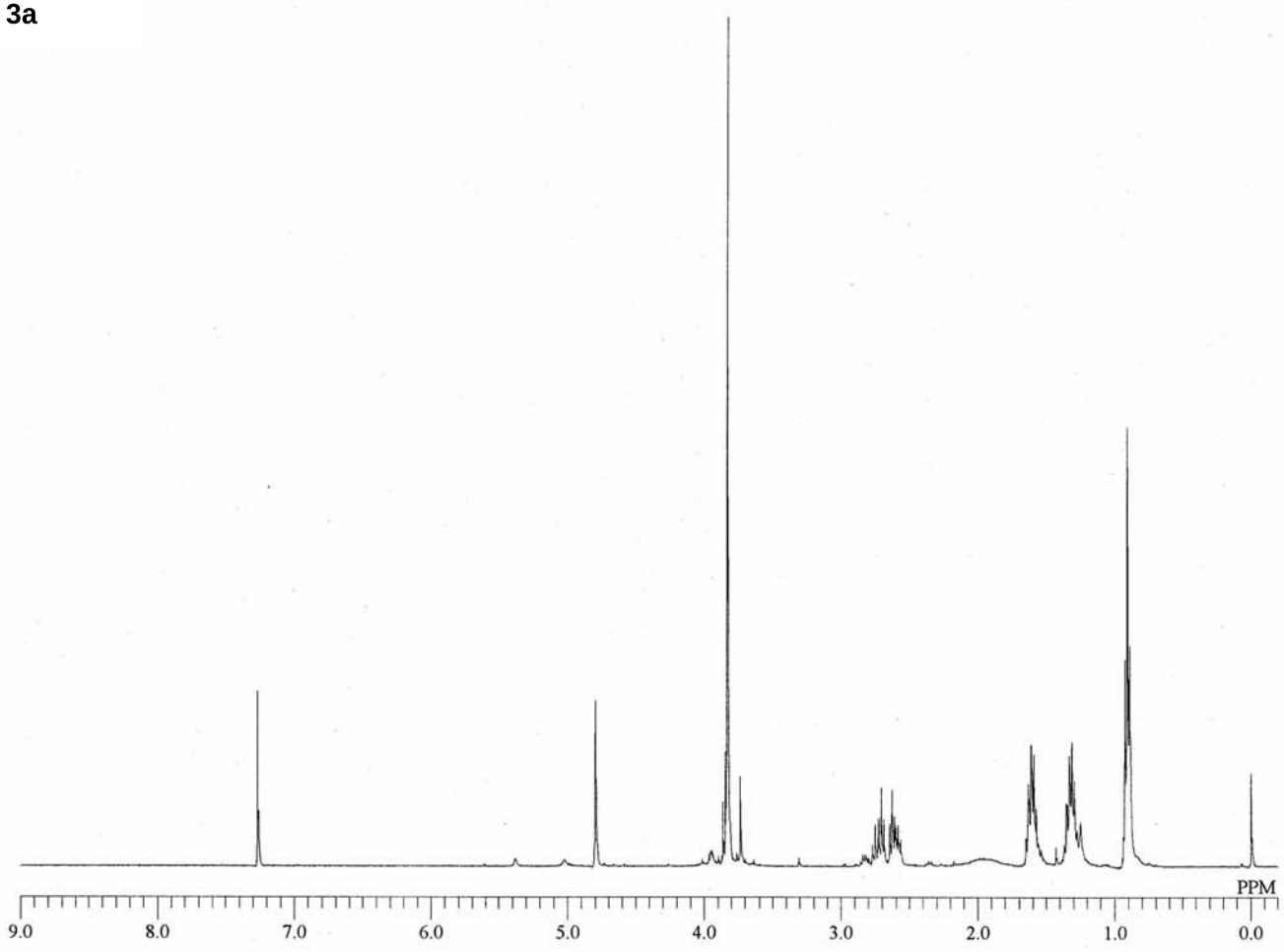



```
Filename          = AO-414 Fr5-8-3.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#751647
Solvent           = CHLOROFORM-D
Creation_time     = 16-JUN-2015 20:48:04
Revision_time     =  2-JUL-2015 21:10:25
Current_time      =  2-JUL-2015 21:10:39

Comment           = AO-414 Fr5-8
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 11[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 3[dB]
X_pulse           = 5.5[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 28
Relaxation_delay  = 2[s]
Repetition_time   = 3.74587904[s]
Temp_get          = 21.5[dC]
```

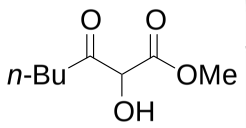

MeO
O
O
N
Me
OH
2j
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
X : parts per Million : 13C
JEOL
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: AO-414 fr5-8 13C-1.jdf
Filename = AO-414 fr5-8 13C-3.jd
Author = delta
Experiment = single_pulse_dec
Sample_id = S#752978
Solvent = CHLOROFORM-D
Creation_time = 16-JUN-2015 20:53:36
Revision_time = 2-JUL-2015 21:11:20
Current_time = 2-JUL-2015 21:11:40
Comment = AO-414 Fr5-8 13C
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = JNM-ECA500
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 128
Total_scans = 128
X_90_width = 10[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 5.5[dB]
X_pulse = 3.33333333[us]
Irr_atn_dec = 21.4479[dB]
Irr_atn_noe = 21.4479[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 1[s]
Recvr_gain = 56
Relaxation_delay = 1[s]
Repetition_time = 1.83361792[s]
Temp_get = 21.8[dC]



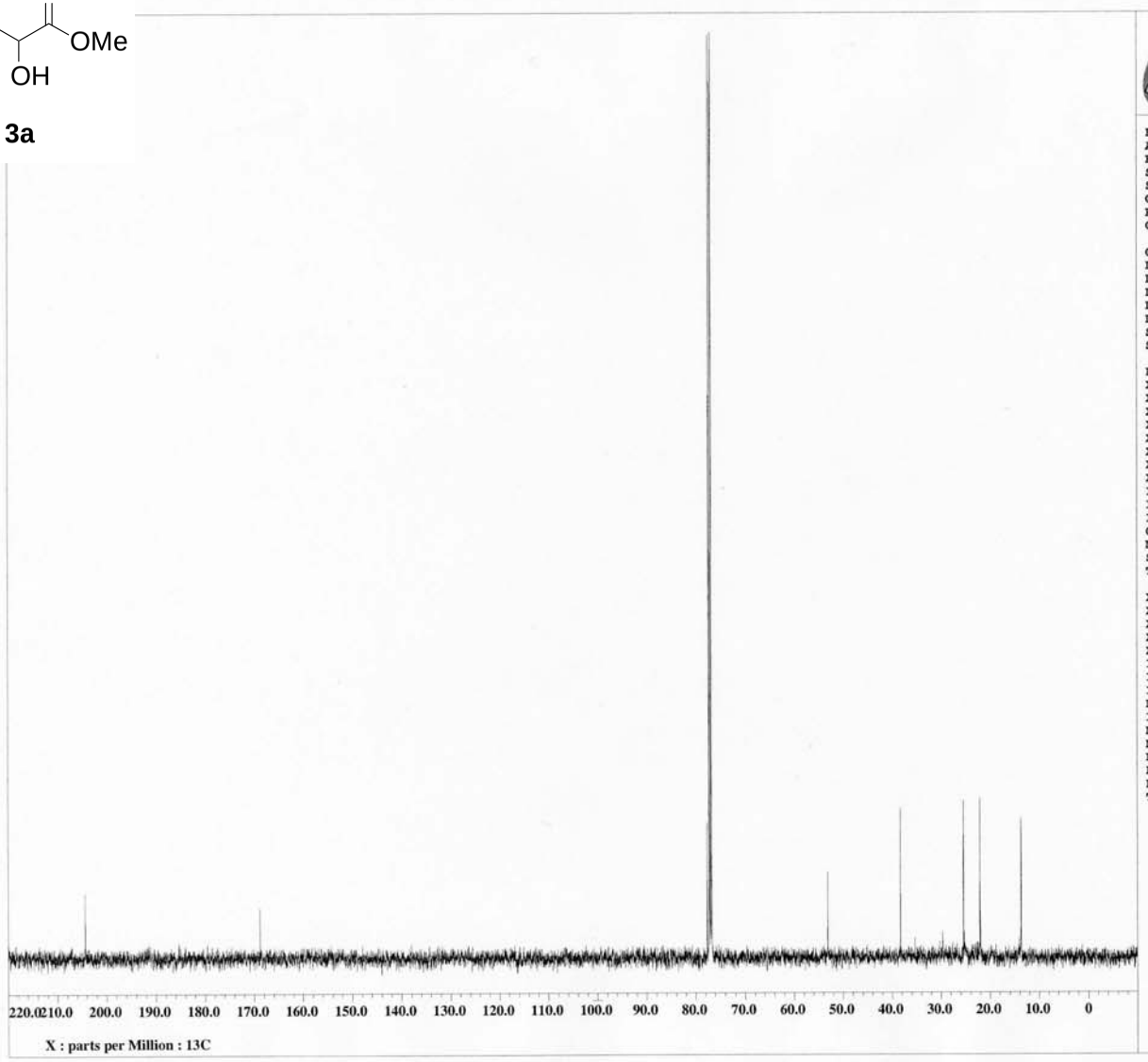
3a



MENUF	NON
OBNUC	1H
OFR	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
PW1	8.00 usec
DEADT	71.90 usec
PREDL	0.20000 msec
IWT	1.0000 sec
POINT	16384
SPO	16384
TIMES	8
DUMMY	1
FREQU	7912.96 Hz
FLT	3950 Hz
DELAY	50.60 usec
ACQTM	2.0705 sec
PD	4.9290 sec
ADBIT	16
RGAIN	15
BF	0.12 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	NON
EXPCM	NON:Single.coupled:PW
IRNUC	1H
IFR	395.75 MHz
IRSET	124.00 KHz
IRFIN	10277.00 Hz
IRRPW	45 usec
IRATN	511
DFILE	AO-445-1-Fr6.7.als
SF	TH5ATFG2_1AO-445-1·
LKSET	12.90 KHz
LKFIN	104.0 Hz
LKLEV	180
LGAIN	23
LKPHS	110
LKSIG	794
CSPED	15 Hz
FILDC	
FILDF	



3a



JEOL

```
Filename          = AO-445 Fr7-14 13C-3.j
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#482672
Solvent           = CHLOROFORM-D
Creation_time     = 11-SEP-2015 13:23:41
Revision_time     = 14-SEP-2015 15:31:31
Current_time      = 14-SEP-2015 15:31:54

Comment           = AO-445 Fr7-14 13C
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 128
Total_scans       = 128

X_90_width        = 10[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 5.5[dB]
X_pulse           = 3.33333333[us]
Irr_atn_dec       = 21.4479[dB]
Irr_atn_noe       = 21.4479[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   = 2.83361792[s]
Temp_get          = 21.7[dC]
```