

Palladacycle-Catalyzed Cyclopropanation of Bicyclic Alkenes with Propiolates

Dong-Liang Mo,^a Teng Yuan,^a Chang-Hua Ding,^{*a} Li-Xin Dai,^a Xue-Long Hou^{*a,b}

xlhou@sioc.ac.cn; dingch@sioc.ac.cn

^aState Key Laboratory of Organometallic Chemistry, ^bShanghai-Hong Kong Joint Laboratory in Chemical Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Ling Ling Road, Shanghai, 200032, China.

Table of Contents

1. ORTEP drawing, Crystal data, and Atomic coordinates of the compound 3a	S-2
2. ORTEP drawing, Crystal data, and Atomic coordinates of the compound 4	S-5
3. NMR Spectra of compounds 3a-3o, 4, and 5.....	S-8

1 ORTEP drawing, Crystal data, and Atomic coordinates of the compound 3a

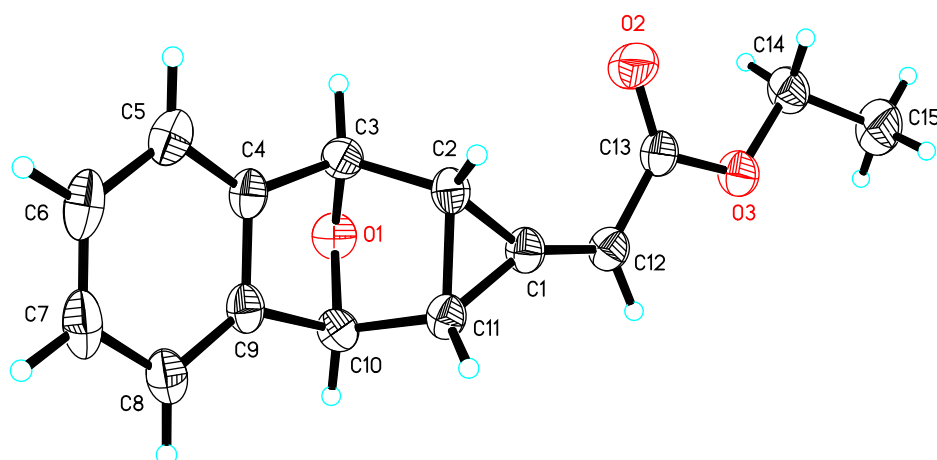


Table 1. Crystal data and structure refinement for cd2836.

Identification code	cd2836
Empirical formula	C15 H14 O3
Formula weight	242.26
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.471(6) Å alpha = 77.390(14) deg. b = 9.498(7) Å beta = 70.626(13) deg. c = 9.667(7) Å gamma = 86.718(14) deg.
Volume	631.4(8) Å ³
Z, Calculated density	2, 1.274 Mg/m ³
Absorption coefficient	0.088 mm ⁻¹
F(000)	256

Crystal size	0.445 x 0.306 x 0.286 mm
Theta range for data collection	2.20 to 26.50 deg.
Limiting indices	$-9 \leq h \leq 7$, $-10 \leq k \leq 11$, $-12 \leq l \leq 10$
Reflections collected / unique	3595 / 2556 [R(int) = 0.0722]
Completeness to theta = 26.50	97.8 %
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.7523
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2556 / 0 / 164
Goodness-of-fit on F^2	0.975
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0612, wR2 = 0.1487
R indices (all data)	R1 = 0.0777, wR2 = 0.1599
Largest diff. peak and hole	0.256 and -0.282 e. $\text{\AA}^{-3}$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd2836.
 $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	4486(2)	7868(1)	2306(1)	51(1)
O(2)	-593(2)	10474(2)	2294(2)	73(1)
O(3)	393(2)	12331(1)	348(2)	57(1)
C(1)	3183(3)	10406(2)	2449(2)	47(1)
C(2)	2702(3)	9340(2)	3865(2)	45(1)
C(3)	3036(3)	7750(2)	3749(2)	47(1)
C(4)	4151(3)	7123(2)	4788(2)	47(1)
C(5)	3713(3)	6209(2)	6181(2)	59(1)
C(6)	5169(4)	5876(2)	6796(3)	68(1)
C(7)	6944(4)	6450(2)	6068(3)	70(1)
C(8)	7379(3)	7396(2)	4678(2)	57(1)
C(9)	5964(3)	7703(2)	4050(2)	46(1)
C(10)	5845(3)	8663(2)	2613(2)	46(1)
C(11)	4718(3)	9986(2)	3066(2)	45(1)
C(12)	2608(3)	11303(2)	1430(2)	48(1)
C(13)	660(3)	11294(2)	1444(2)	47(1)
C(14)	-1445(3)	12398(2)	156(3)	61(1)
C(15)	-1553(4)	13777(3)	-878(3)	84(1)

2 ORTEP drawing, Crystal data, and Atomic coordinates of the compound 4

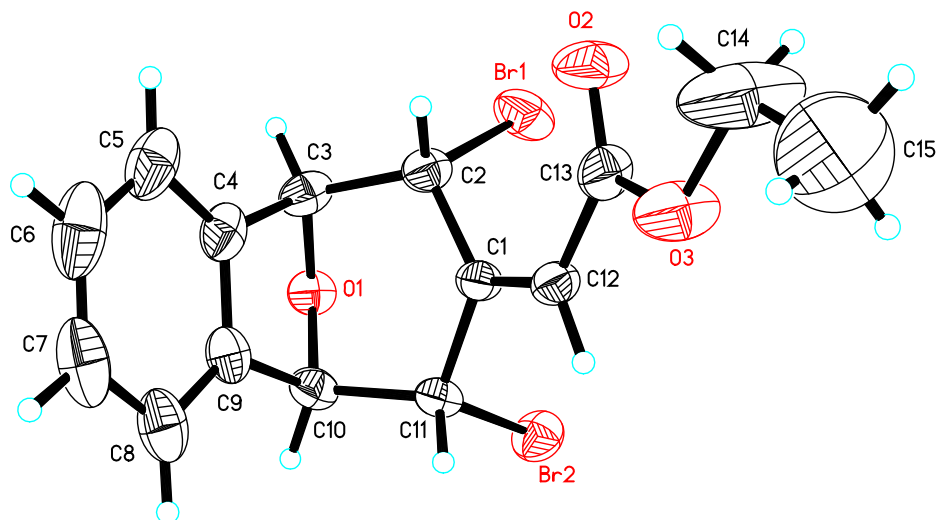


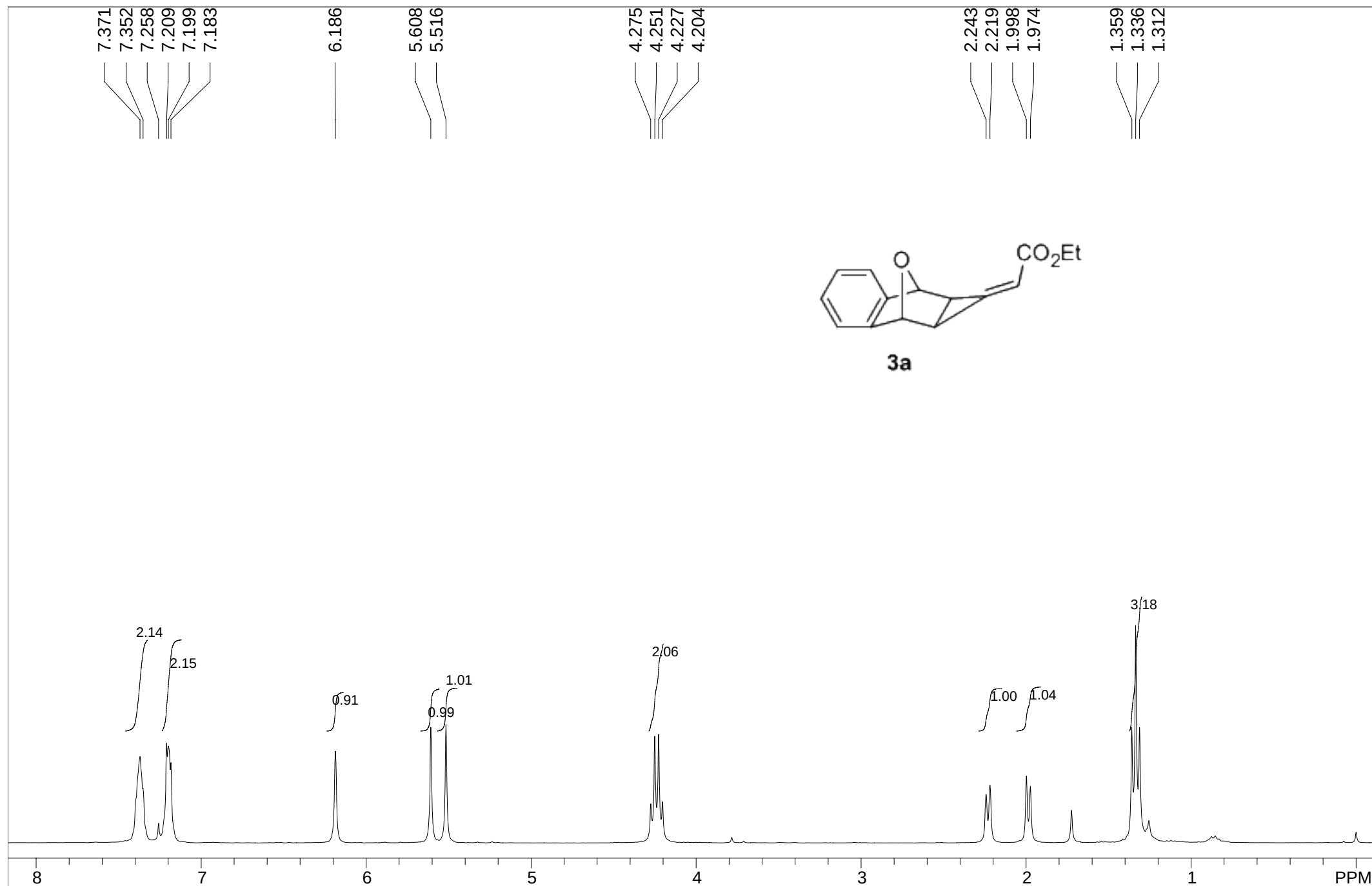
Table 1. Crystal data and structure refinement for cd28274.

Identification code	cd28274
Empirical formula	C15 H14 Br2 O3
Formula weight	402.08
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 11.033(2) Å alpha = 90 deg. b = 10.0044(18) Å beta = 95.223(4) deg. c = 14.451(3) Å gamma = 90 deg.
Volume	1588.4(5) Å ³
Z, Calculated density	4, 1.681 Mg/m ³
Absorption coefficient	5.107 mm ⁻¹

F(000)	792
Crystal size	0.425 x 0.391 x 0.297 mm
Theta range for data collection	2.23 to 27.00 deg.
Limiting indices	$-8 \leq h \leq 14$, $-12 \leq k \leq 12$, $-18 \leq l \leq 18$
Reflections collected / unique	9146 / 3443 [R(int) = 0.0447]
Completeness to theta = 27.00	99.4 %
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.3665
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3443 / 1 / 178
Goodness-of-fit on F^2	0.820
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0409, wR2 = 0.0913
R indices (all data)	R1 = 0.0870, wR2 = 0.0989
Extinction coefficient	0.0117(7)
Largest diff. peak and hole	0.573 and -0.387 e. $\text{\AA}^{-3}$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd28274.
 $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

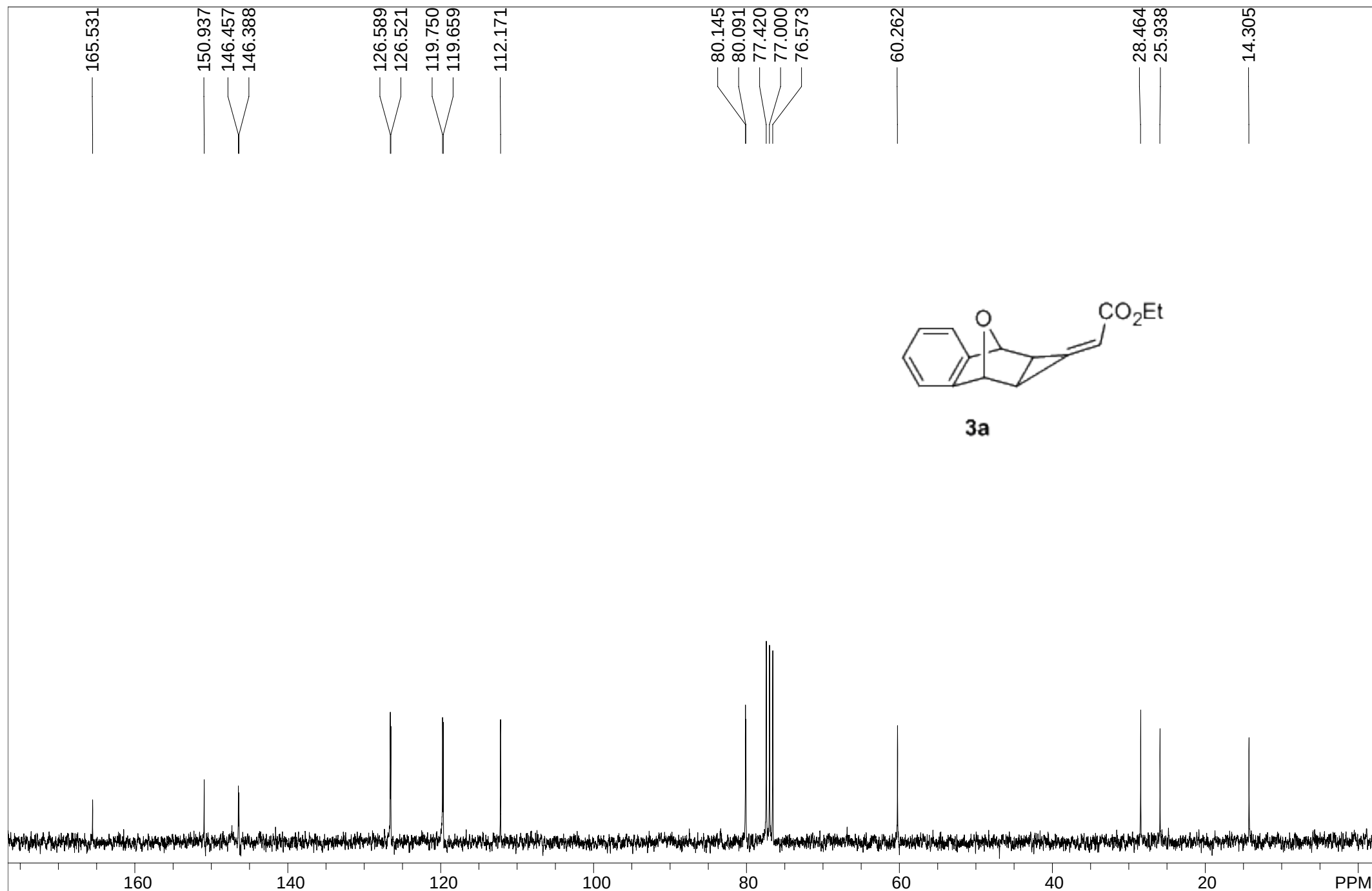
	x	y	z	$U(\text{eq})$
Br (1)	4848 (1)	-1576 (1)	6770 (1)	76 (1)
Br (2)	2936 (1)	31 (1)	8548 (1)	64 (1)
O (1)	1894 (3)	-1054 (3)	6563 (2)	49 (1)
O (2)	5885 (3)	1551 (4)	5865 (3)	89 (1)
O (3)	5795 (4)	3522 (4)	6529 (3)	98 (1)
C (1)	3649 (4)	959 (4)	6802 (3)	42 (1)
C (2)	3813 (4)	-189 (4)	6157 (3)	50 (1)
C (3)	2591 (4)	-789 (5)	5796 (3)	54 (1)
C (4)	1868 (5)	302 (5)	5281 (4)	56 (1)
C (5)	1870 (5)	735 (6)	4381 (4)	79 (2)
C (6)	1131 (7)	1814 (8)	4129 (5)	100 (2)
C (7)	447 (6)	2437 (7)	4743 (5)	89 (2)
C (8)	474 (5)	2003 (5)	5656 (4)	73 (2)
C (9)	1190 (4)	916 (5)	5901 (3)	51 (1)
C (10)	1476 (4)	235 (4)	6816 (3)	48 (1)
C (11)	2547 (4)	944 (4)	7354 (3)	43 (1)
C (12)	4352 (4)	2032 (4)	6870 (3)	47 (1)
C (13)	5417 (5)	2296 (5)	6355 (3)	61 (1)
C (14)	6885 (8)	3876 (7)	6052 (6)	179 (5)
C (15)	7244 (10)	5162 (10)	6354 (7)	181 (5)



STANDARD 1H OBSERVE;blank line

USER: -- DATE: Dec 22 2007

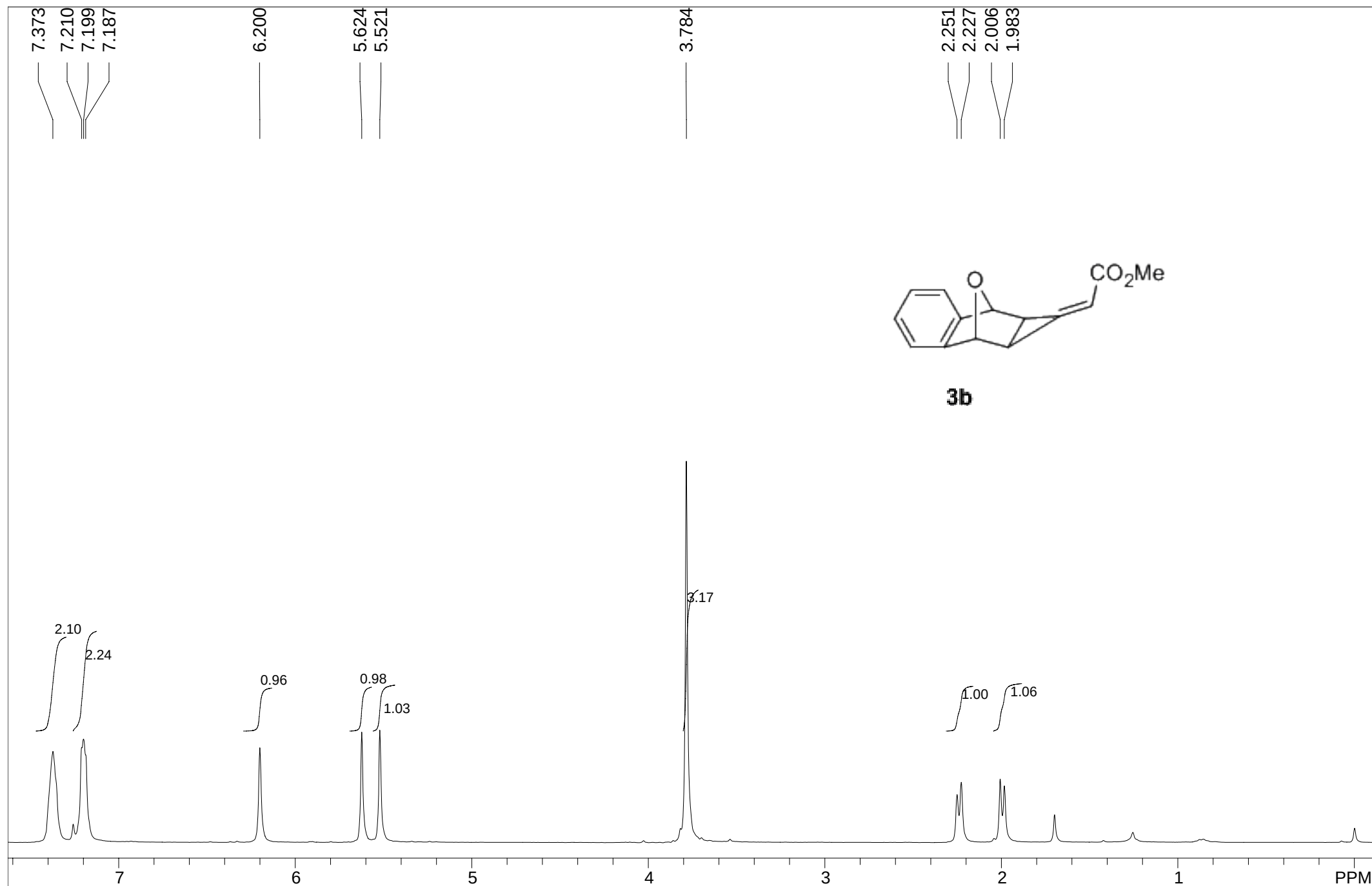
F1: 300.029	F2: 75.449	SW1: 4803		OF1: 1799.9		PTS1d: 9592 , 16384	
EX: s2pul	PW: 4.2 us	PD: 1.0 sec		NA: 4	LB: 2.0	Nuts - \$mdl-3-16-a-H.fid	



mdl-3-16-a-C

USER: -- DATE: Dec 22 2007

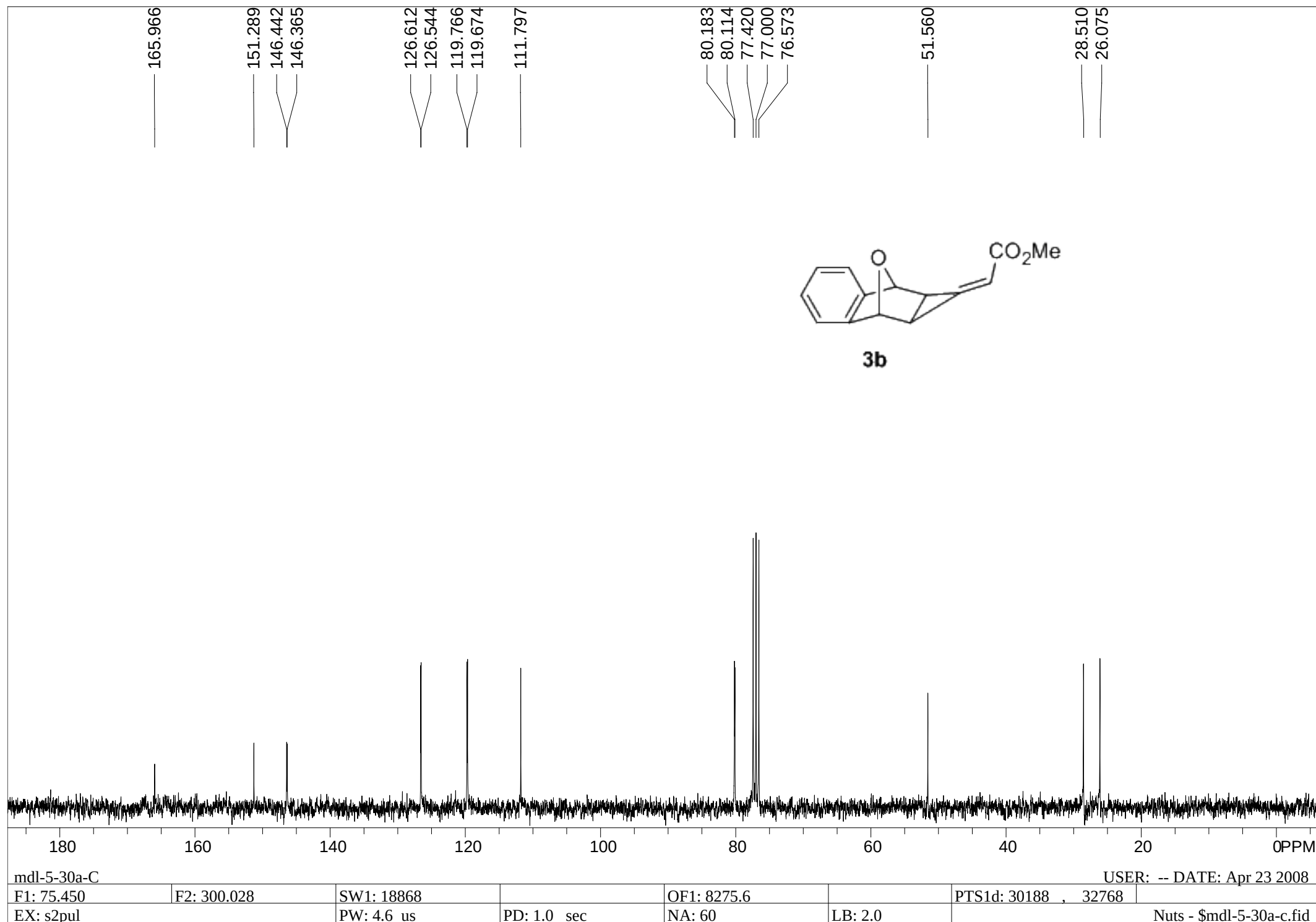
F1: 75.450	F2: 300.028	SW1: 18868		OF1: 8275.0		PTS1d: 30188 , 32768	
EX: s2pul	PW: 4.6 us	PD: 1.0 sec		NA: 46	LB: 2.0	Nuts - \$mdl-3-16-a-C.fid	

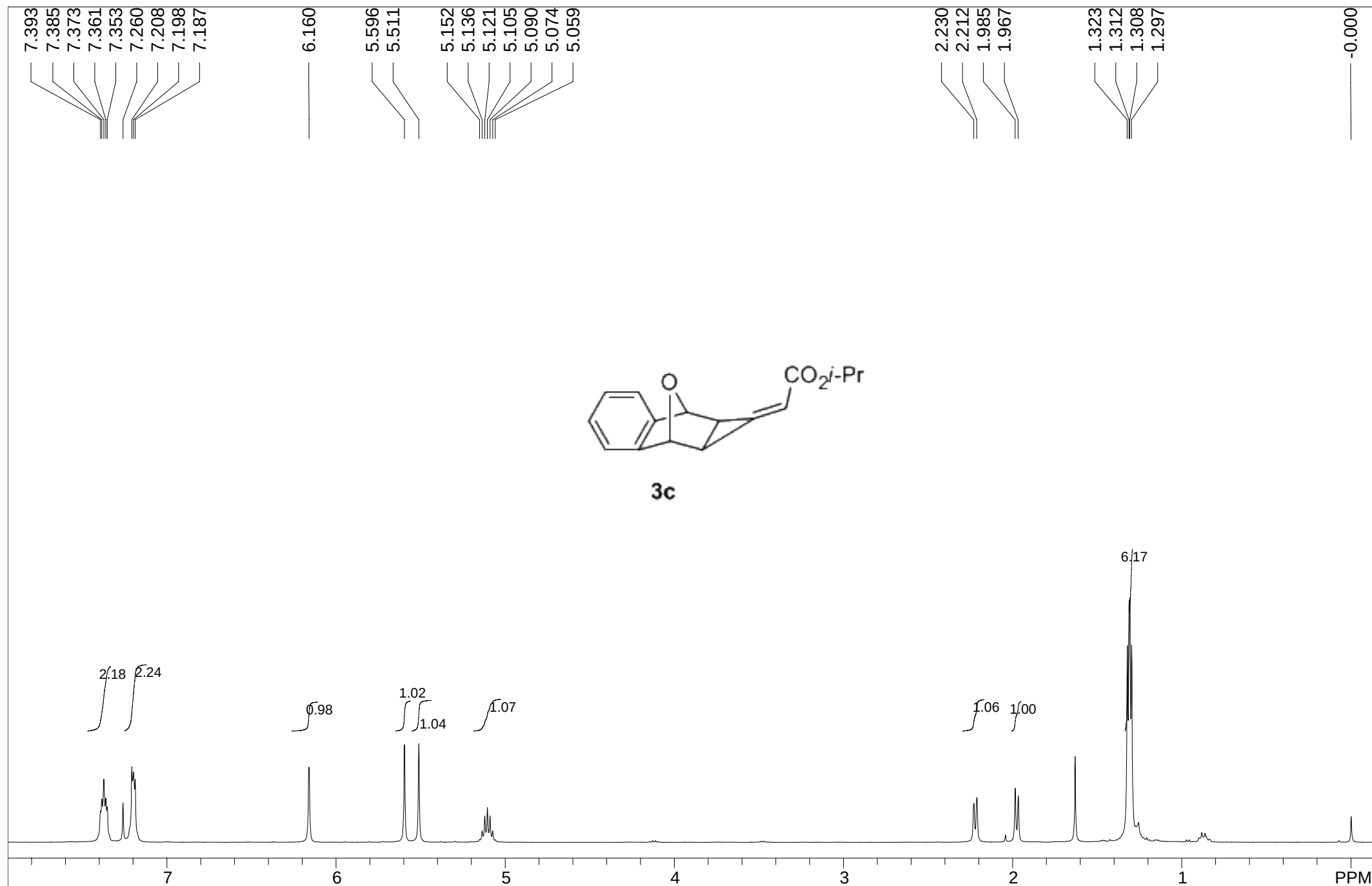


STANDARD 1H OBSERVE;blank line

USER: -- DATE: Apr 23 2008

F1: 300.028	F2: 300.028	SW1: 5602		OF1: 1510.6		PTS1d: 11169 , 16384	
EX: s2pul	PW: 4.0 us	PD: 1.0 sec		NA: 4	LB: 2.0	Nuts - \$mdl-5-35a-H.fid	

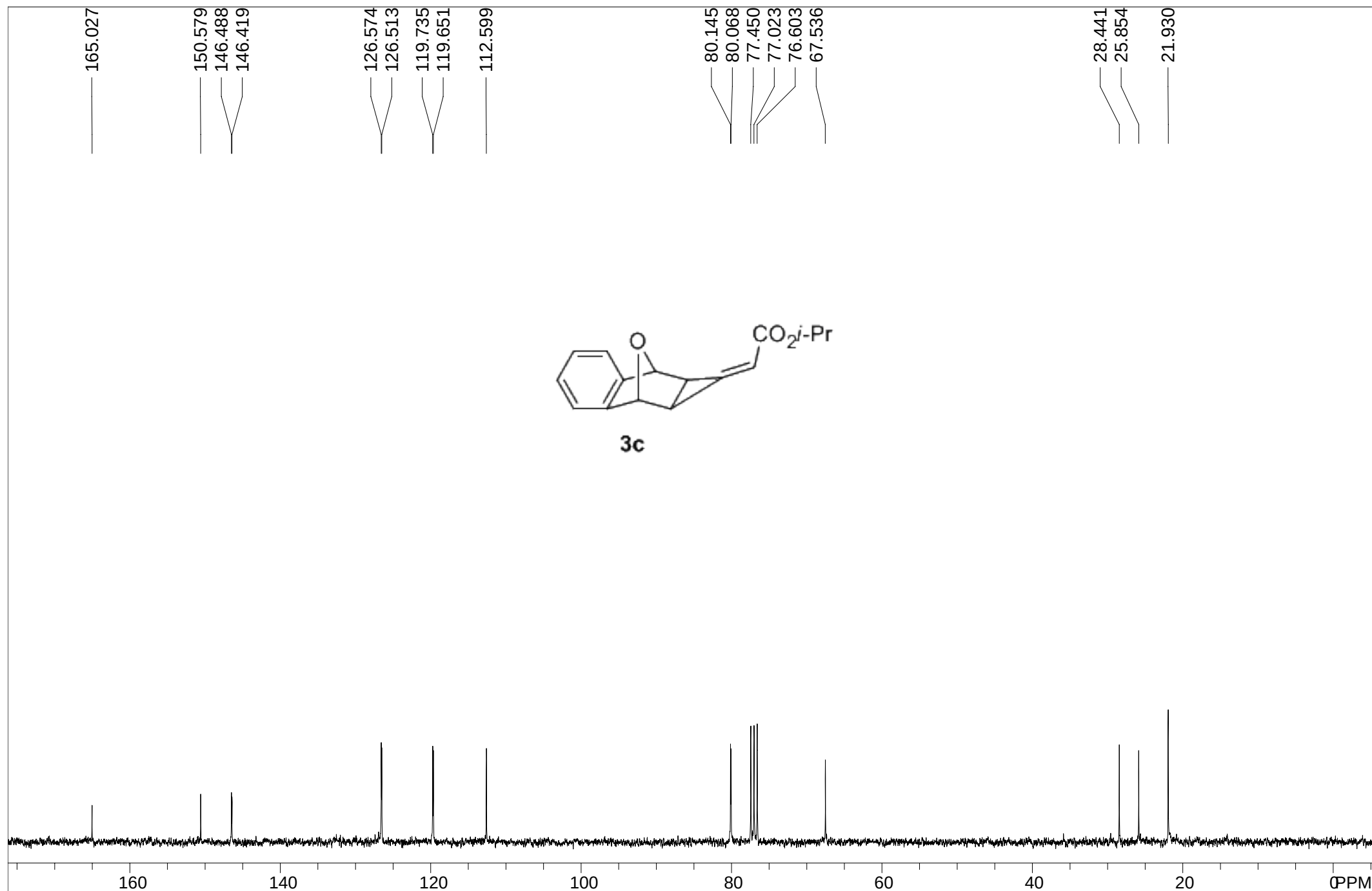




Std proton;blank line

USER: -- DATE: Oct 16 2008

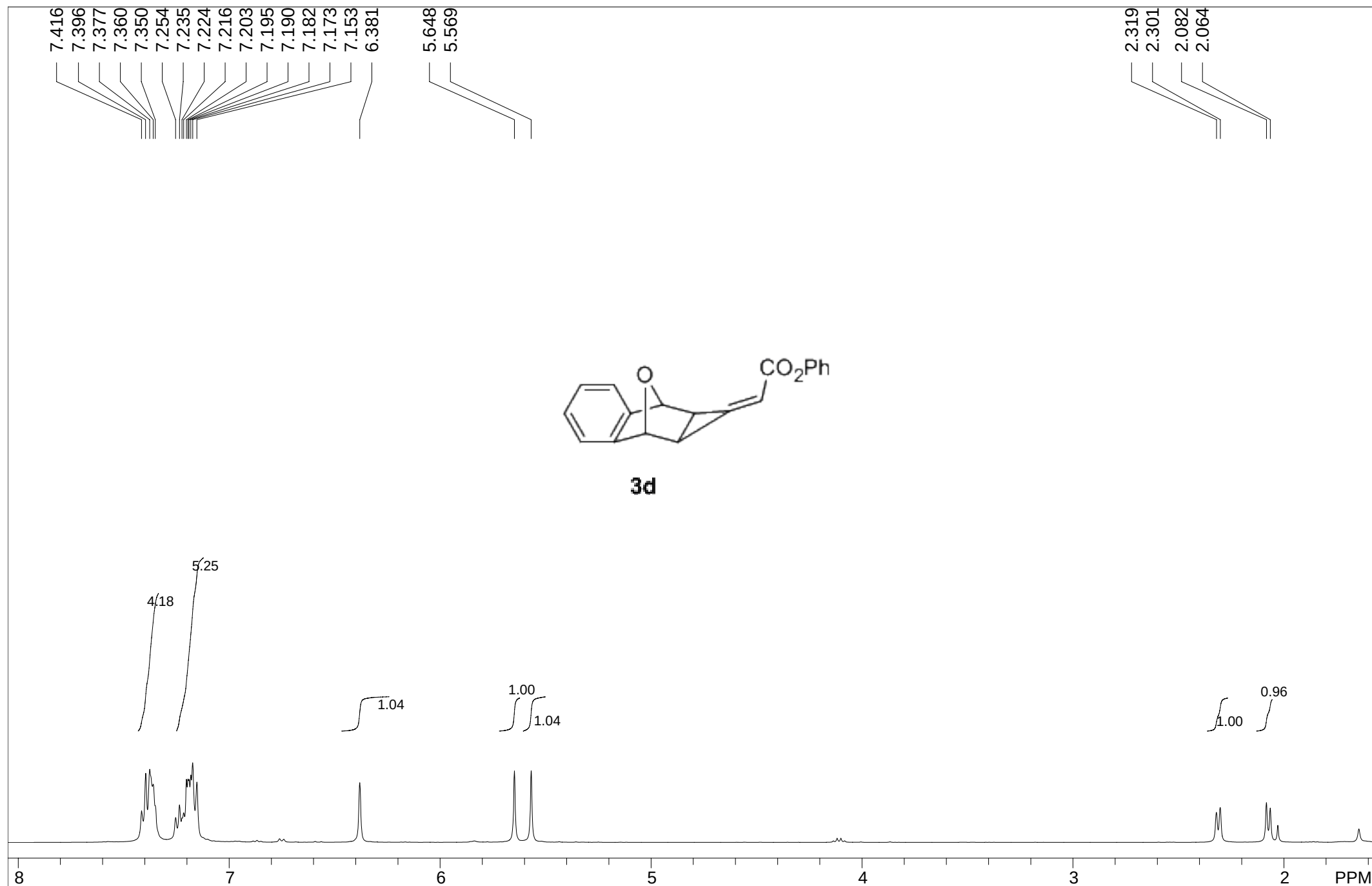
F1: 400.038	F2: 100.598	SW1: 6614		OF1: 2901.0		PTS1d: 18519 , 32768	
EX: s2pul		PW: 6.9 us	PD: 1.0 sec	NA: 40	LB: 2.0	Nuts - \$mdl-7-53-H.fid	



wwq-14-79

USER: -- DATE: Oct 27 2008

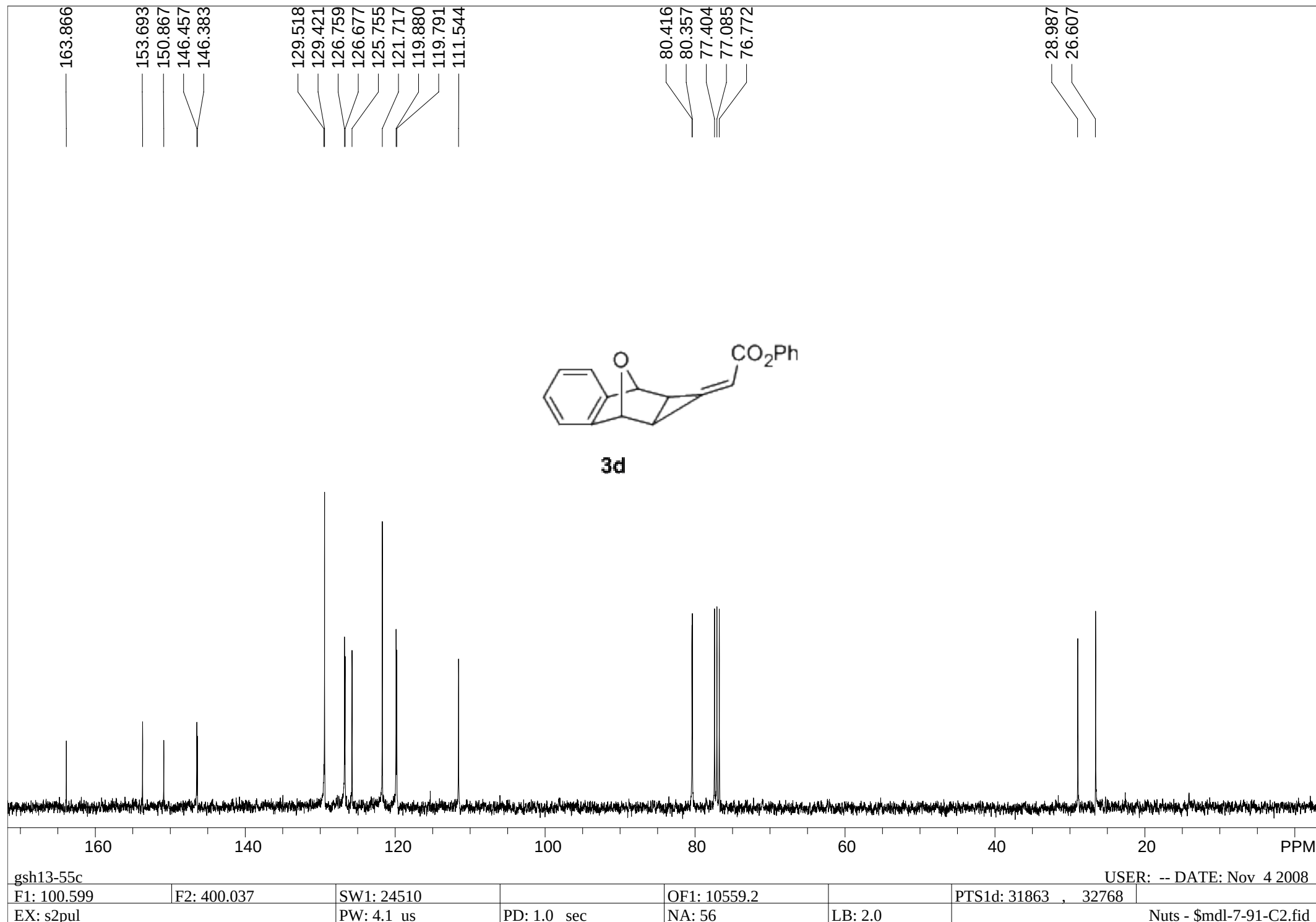
F1: 75.450	F2: 300.028	SW1: 18868		OF1: 8275.6		PTS1d: 30188 , 32768	
EX: s2pul	PW: 4.6 us	PD: 1.0 sec		NA: 56	LB: 2.0	Nuts - \$mdl-7-68b-C2.fid	

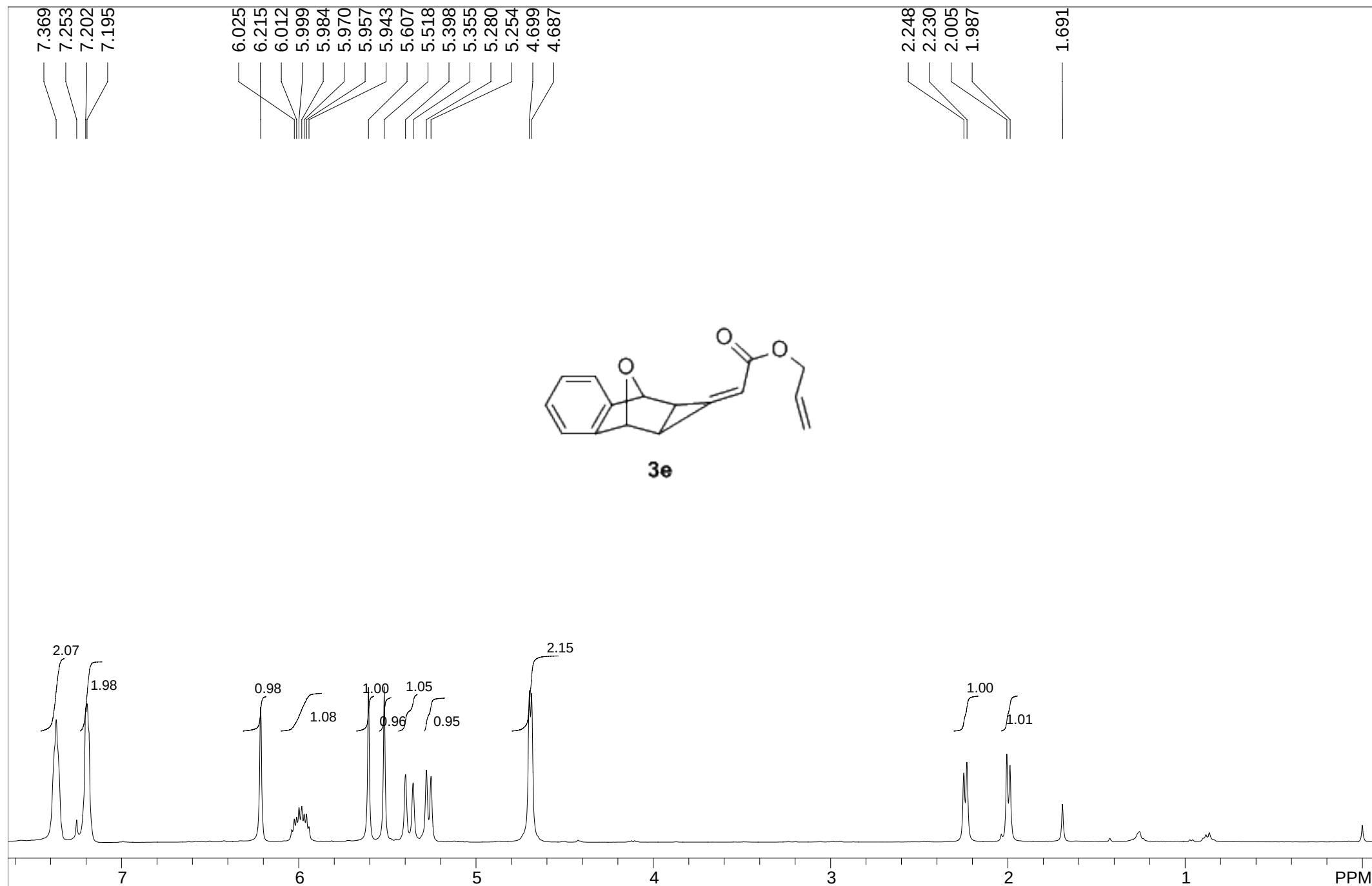


Std proton;blank line

USER: -- DATE: Nov 4 2008

F1: 400.037	F2: 100.598	SW1: 6410		OF1: 2386.8		PTS1d: 17949 , 32768	
EX: s2pul	PW: 6.9 us	PD: 5.0 sec		NA: 8	LB: 2.0	Nuts - \$mdl-7-91-H.fid	

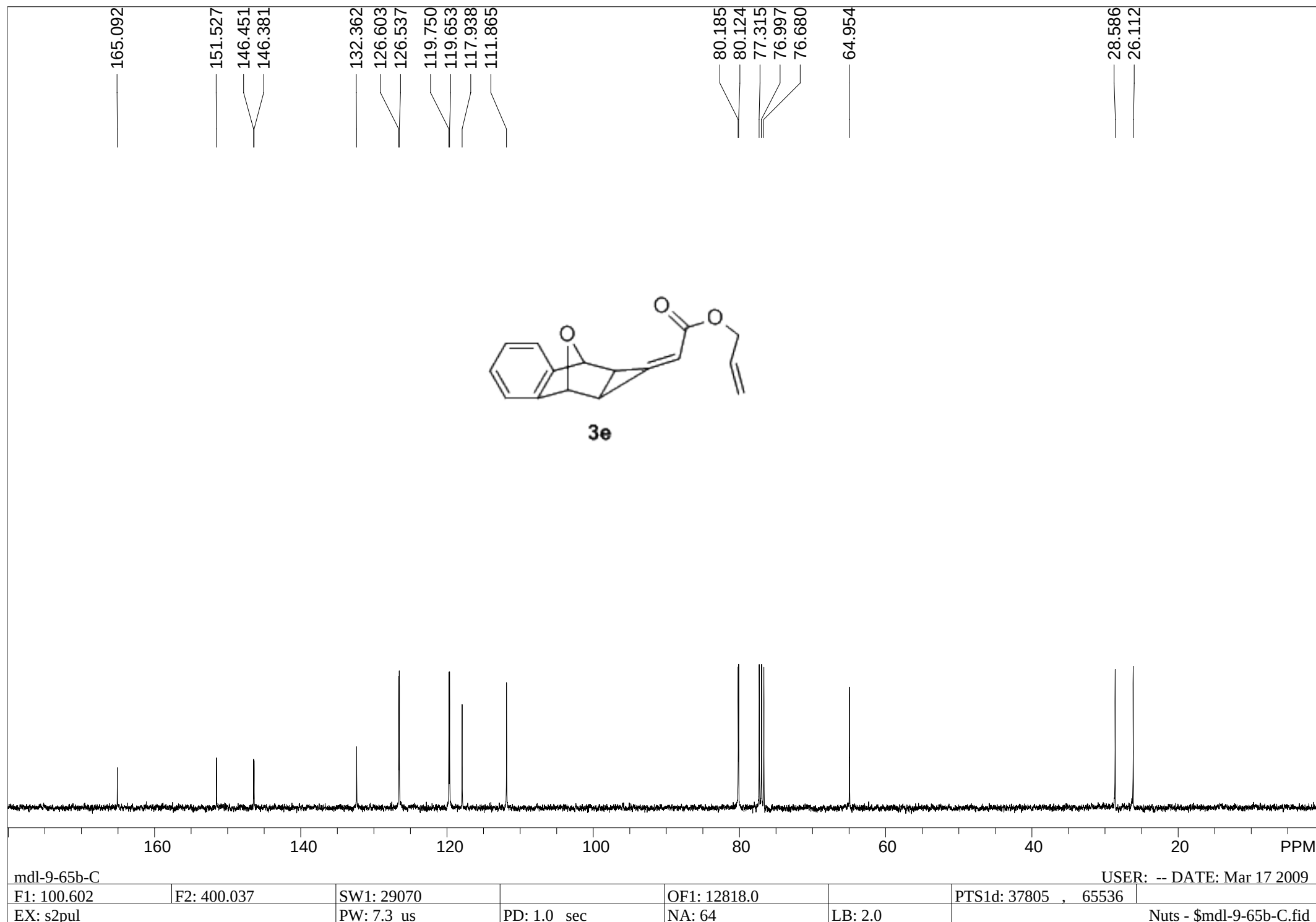


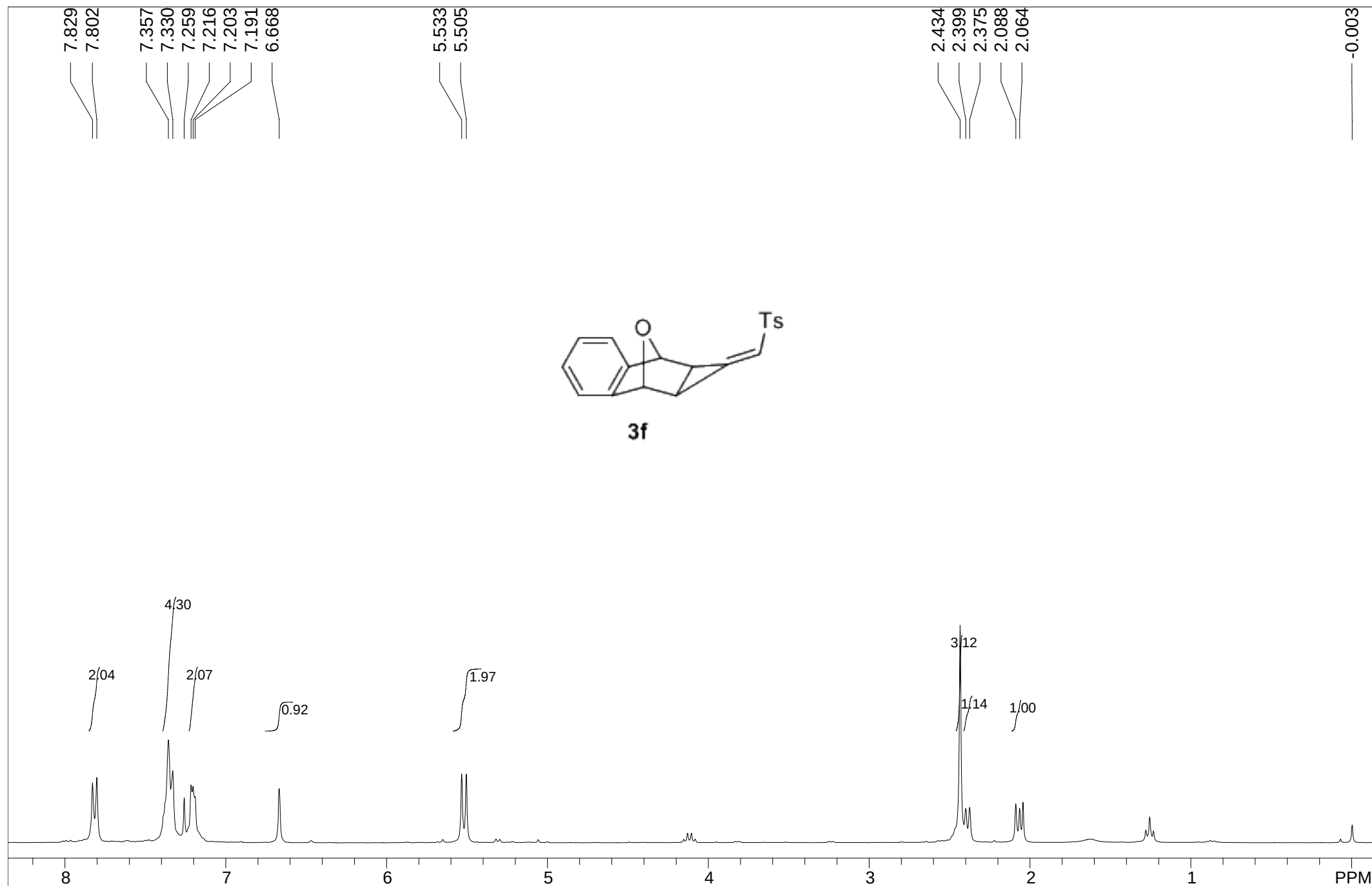


fxp-8-23-1h;blank line

USER: -- DATE: Mar 17 2009

F1: 400.037	F2: 100.598	SW1: 7225		OF1: 2798.8		PTS1d: 21677 , 32768	
EX: s2pul		PW: 4.4 us	PD: 1.0 sec	NA: 18	LB: 2.0	Nuts - \$mdl-9-65b-H.fid	

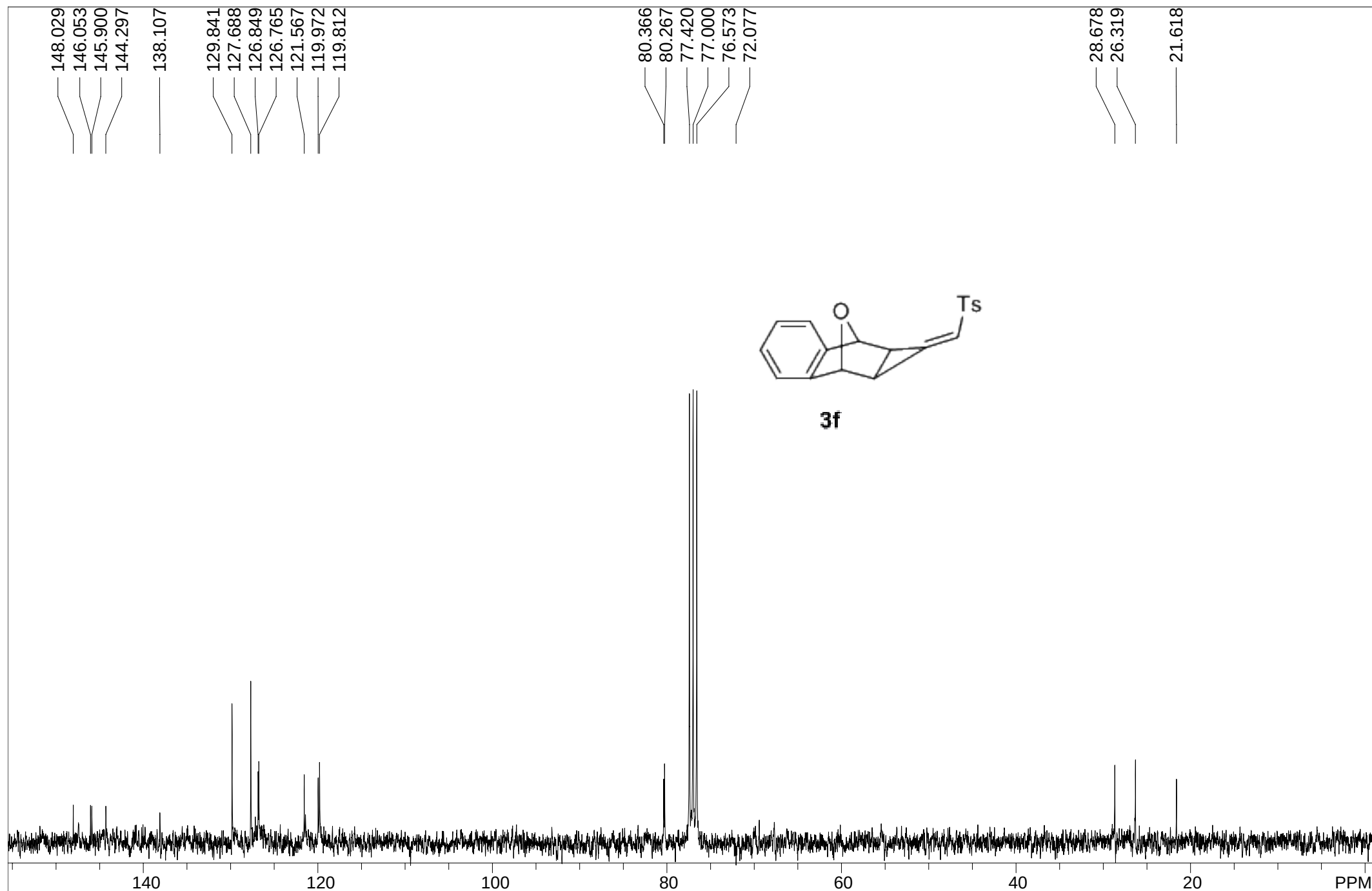




STANDARD 1H OBSERVE;blank line

USER: -- DATE: Mar 5 2008

F1: 300.028	F2: 300.028	SW1: 5602		OF1: 1510.6		PTS1d: 11169 , 16384	
EX: s2pul	PW: 4.0 us	PD: 1.0 sec		NA: 4	LB: 2.0	Nuts - \$mdl-4-18a.fid	



mdl-4-18aC

USER: -- DATE: Mar 6 2008

F1: 75.450

F2: 300.028

SW1: 18868

OF1: 8277.3

PTS1d: 30188 , 32768

EX: s2pul

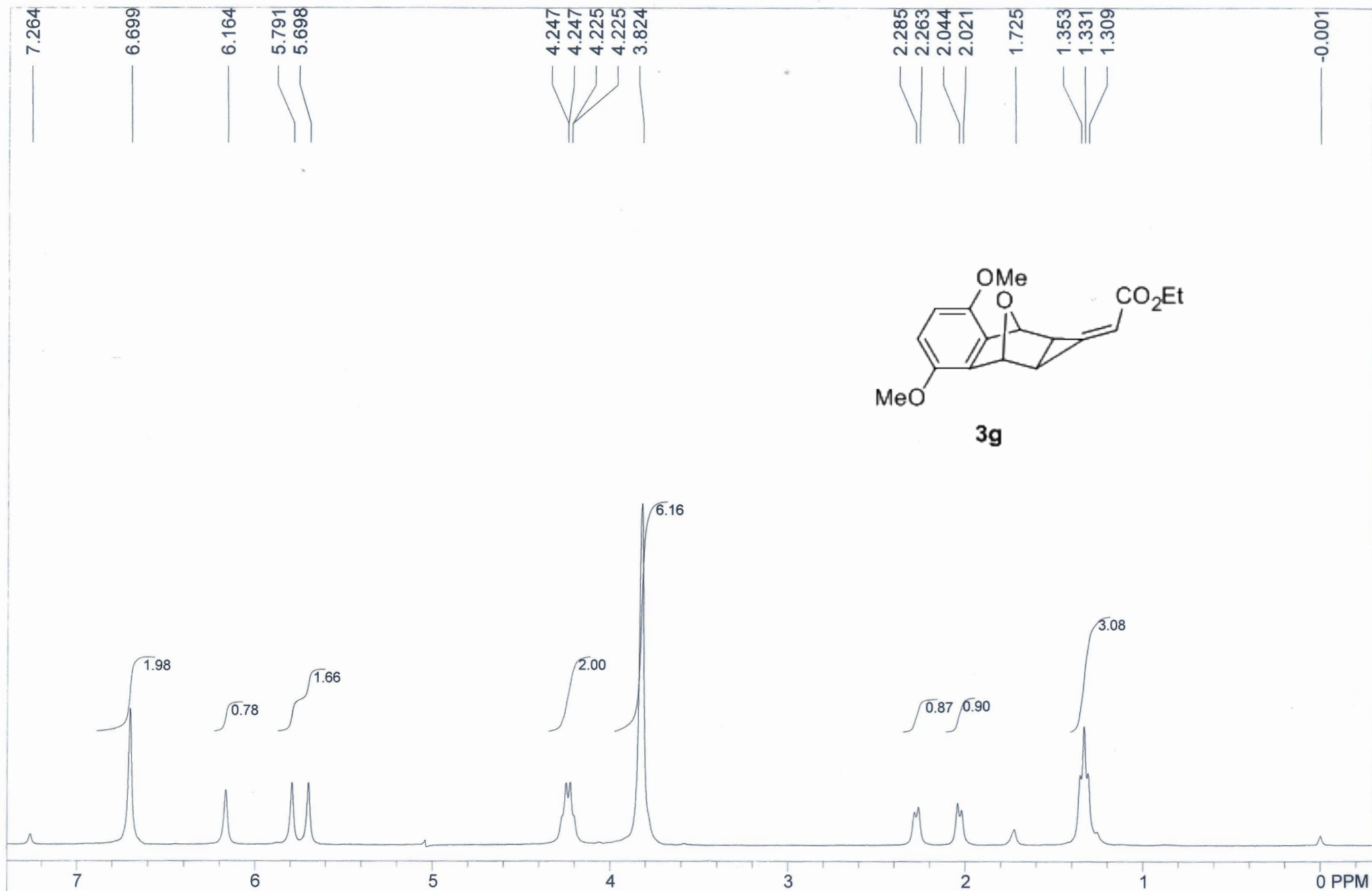
PW: 4.6 us

PD: 1.0 sec

NA: 118

LB: 2.0

Nuts - \$mdl-4-18AC.fid



STANDARD 1H OBSERVE;blank line

USER: -- DATE: Jun 26 2008

F1: 300.028

F2: 300.028

SW1: 4507

OF1: 1511.7

PTS1d: 9004 , 16384

EX: s2pul

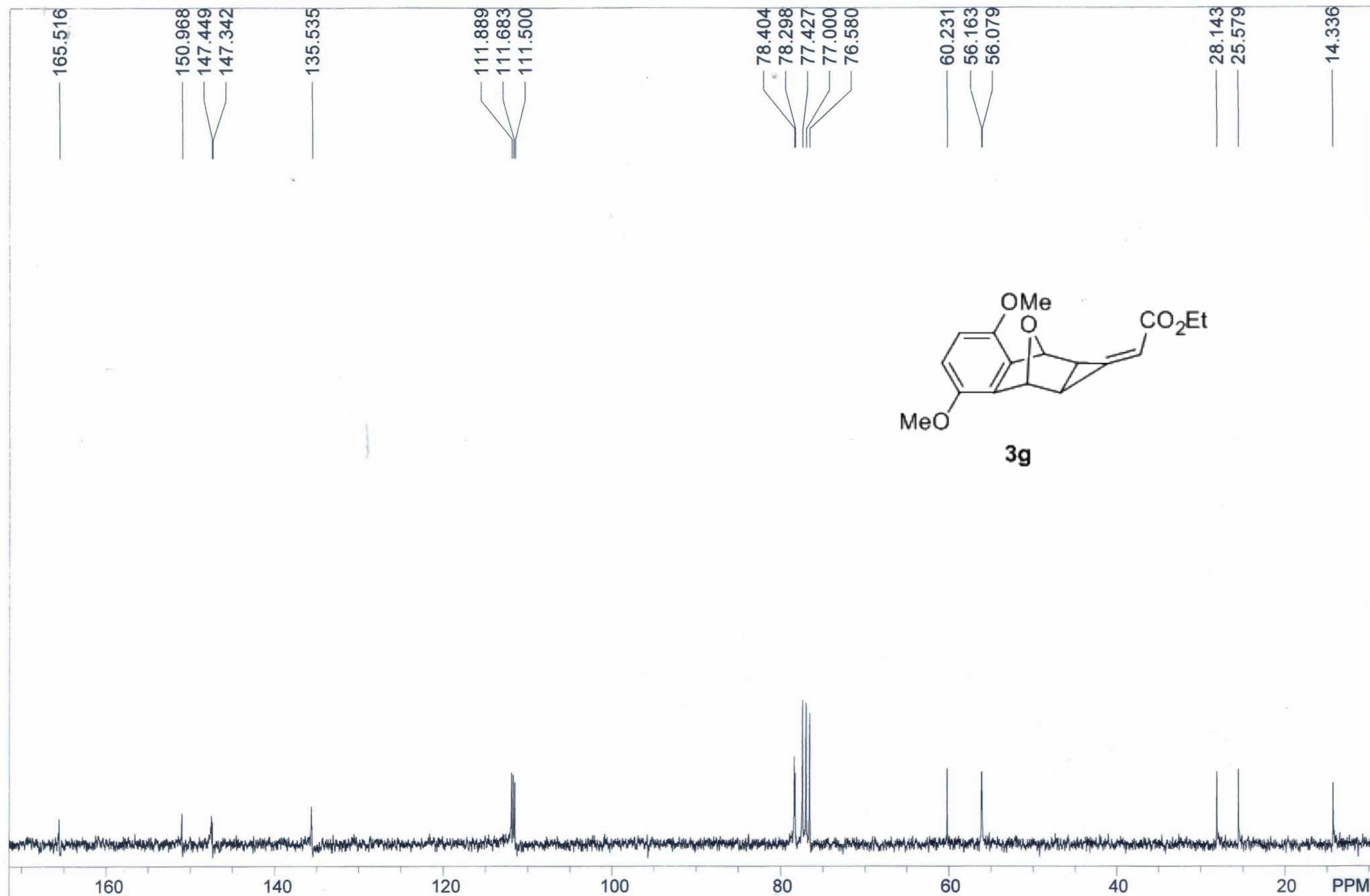
PW: 4.0 us

PD: 1.0 sec

NA: 2

LB: 2.0

Nuts - \$mdl-6-39H.fid



mdl-6-27b-C

F1: 75.450

F2: 300.028

SW1: 18868

PW: 4.6 us

PD: 1.0 sec

OF1: 8276.7

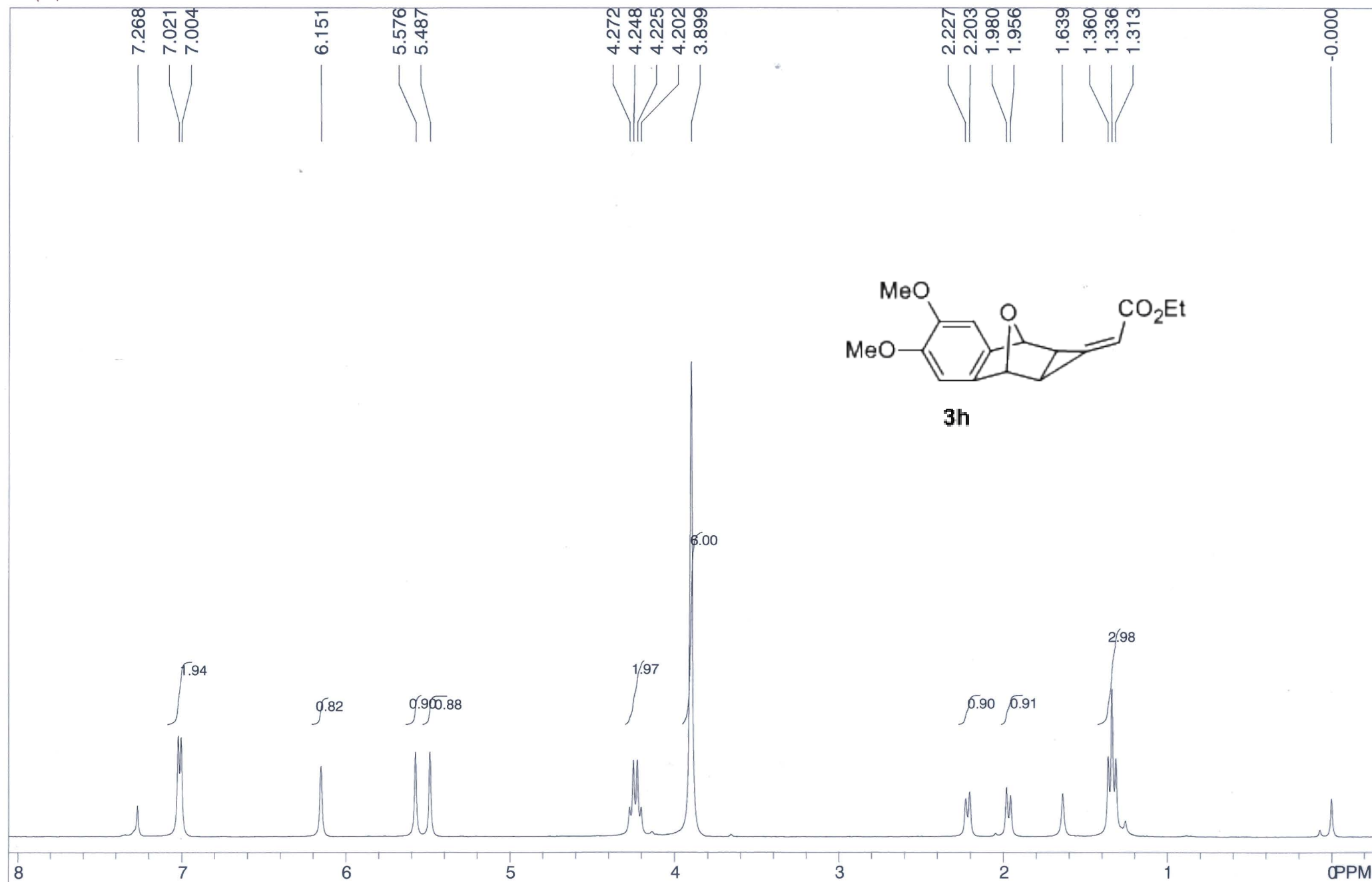
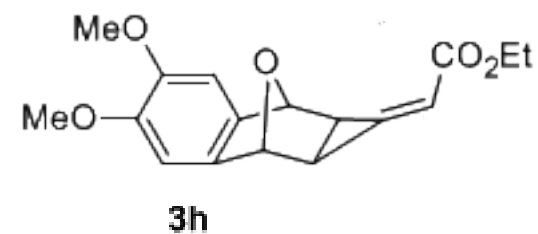
NA: 69

LB: 2.0

PTS1d: 30188 , 32768

USER: -- DATE: Jun 26 2008

Nuts - \$mdl-6-39C.fid



STANDARD 1H OBSERVE;blank line

USER: -- DATE: Jul 14 2010

F1: 300.029

F2: 300.028

SW1: 4902

OF1: 2041.7

PTS1d: 9776 , 16384

EX: s2pul

PW: 4.2 us

PD: 1.0 sec

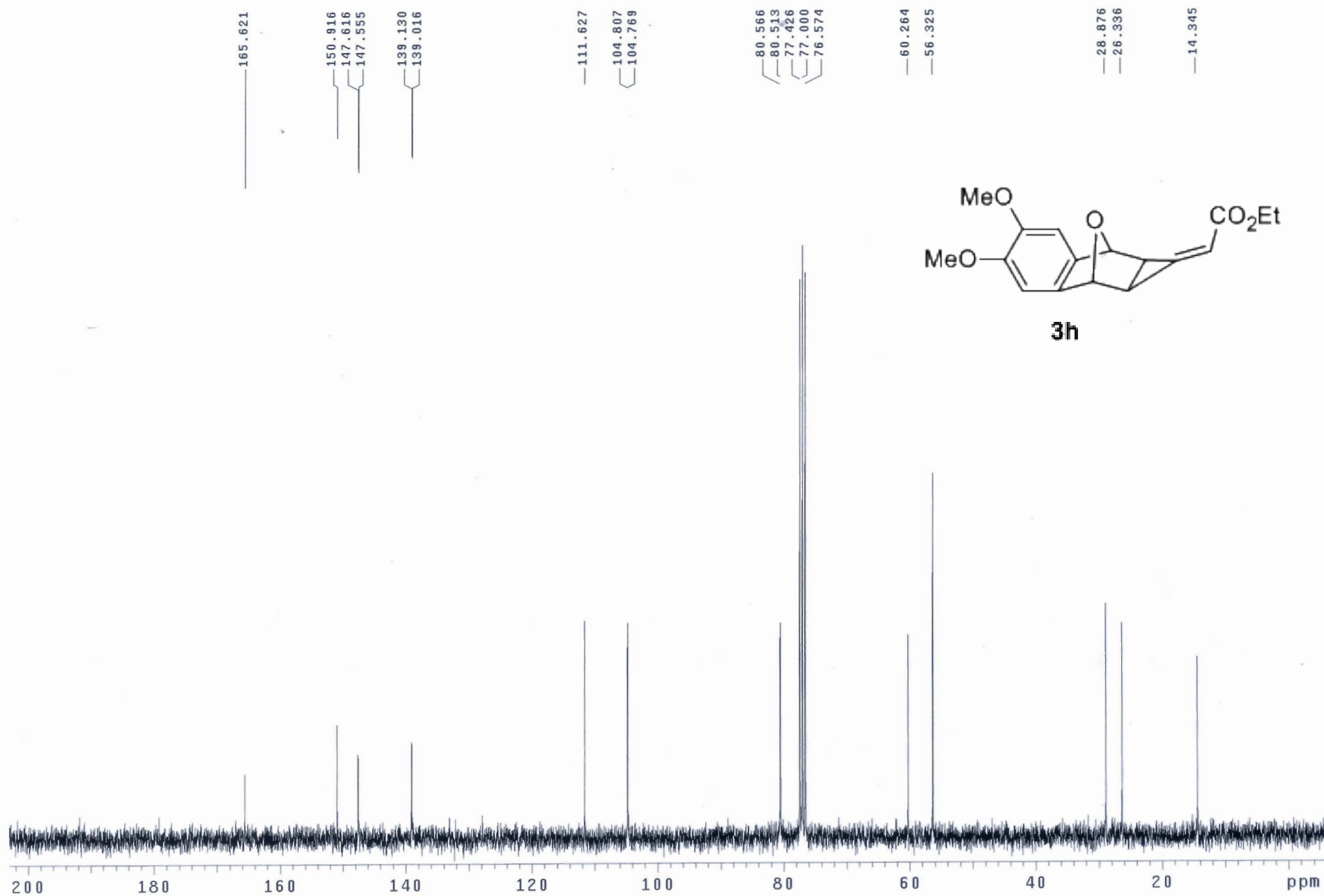
NA: 12

LB: 2.0

Nuts - \$mdl-13-47b-H.fid

md1-13-47b-C

Pulse Sequence: s2pu1



7.630
7.613
7.263

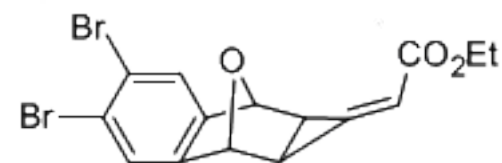
6.195

5.539
5.453

4.265
4.248
4.230
4.213

2.241
2.225
2.001
1.984

1.349
1.331
1.314



3i

2.02

1.04

1.00
1.00

2.01

1.00
1.10

3.07

8

7

6

5

4

3

2

1

0 PPM

:blank line

USER: -- DATE: Jun 18 2011

F1: 400.031

F2: 100.597

SW1: 6831

OF1: 2608.8

PTS1d: 17758 , 32768

EX: s2pul

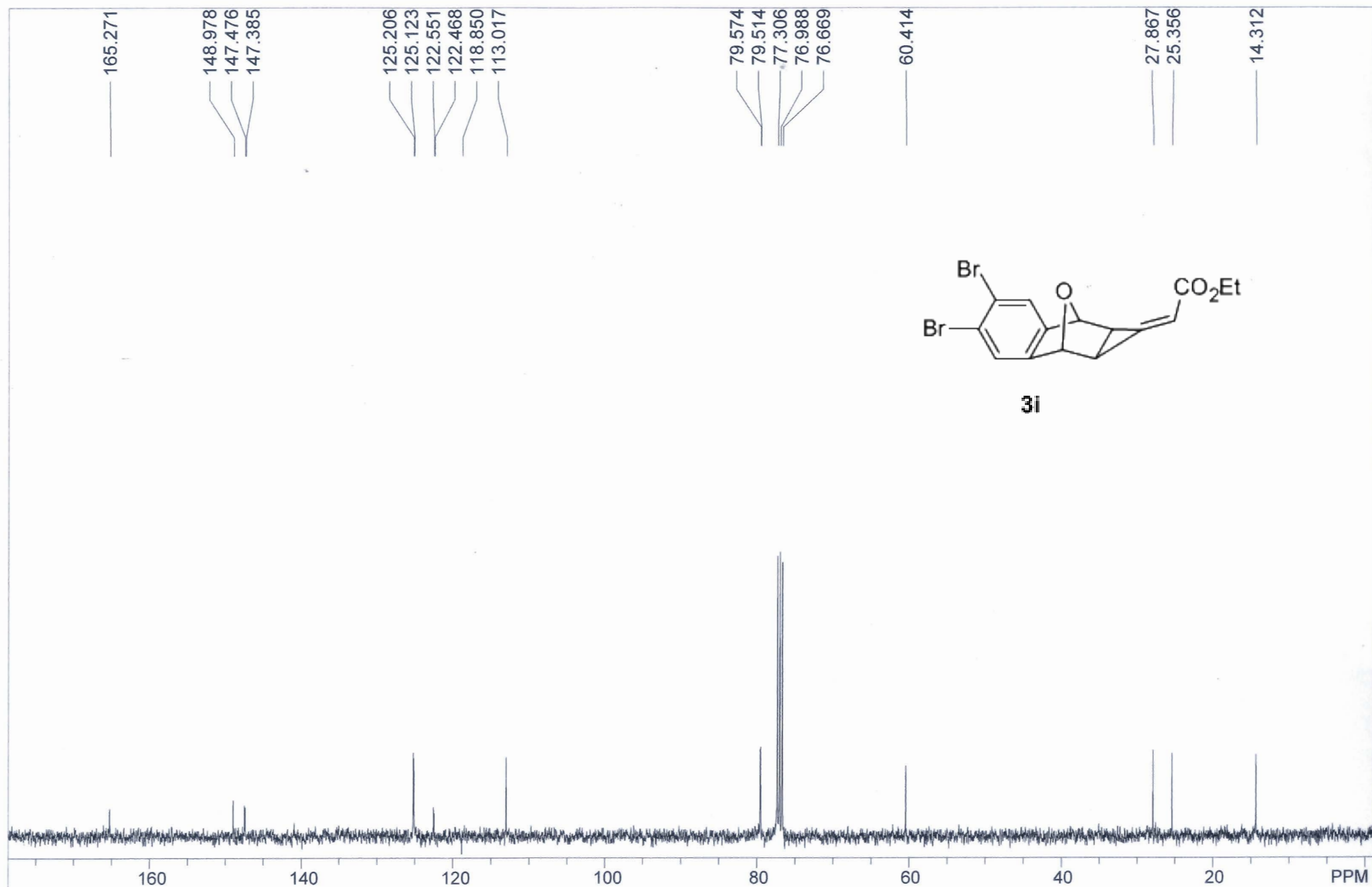
PW: 10.3 us

PD: 1.0 sec

NA: 4

LB: 2.0

Nuts - \$mdl-16-14b-H.fid



sk-8-0616-1-c13

USER: -- DATE: Jun 18 2011

F1: 100.598

F2: 400.031

SW1: 25000

OF1: 10320.9

PTS1d: 32500 , 32768

EX: s2pul

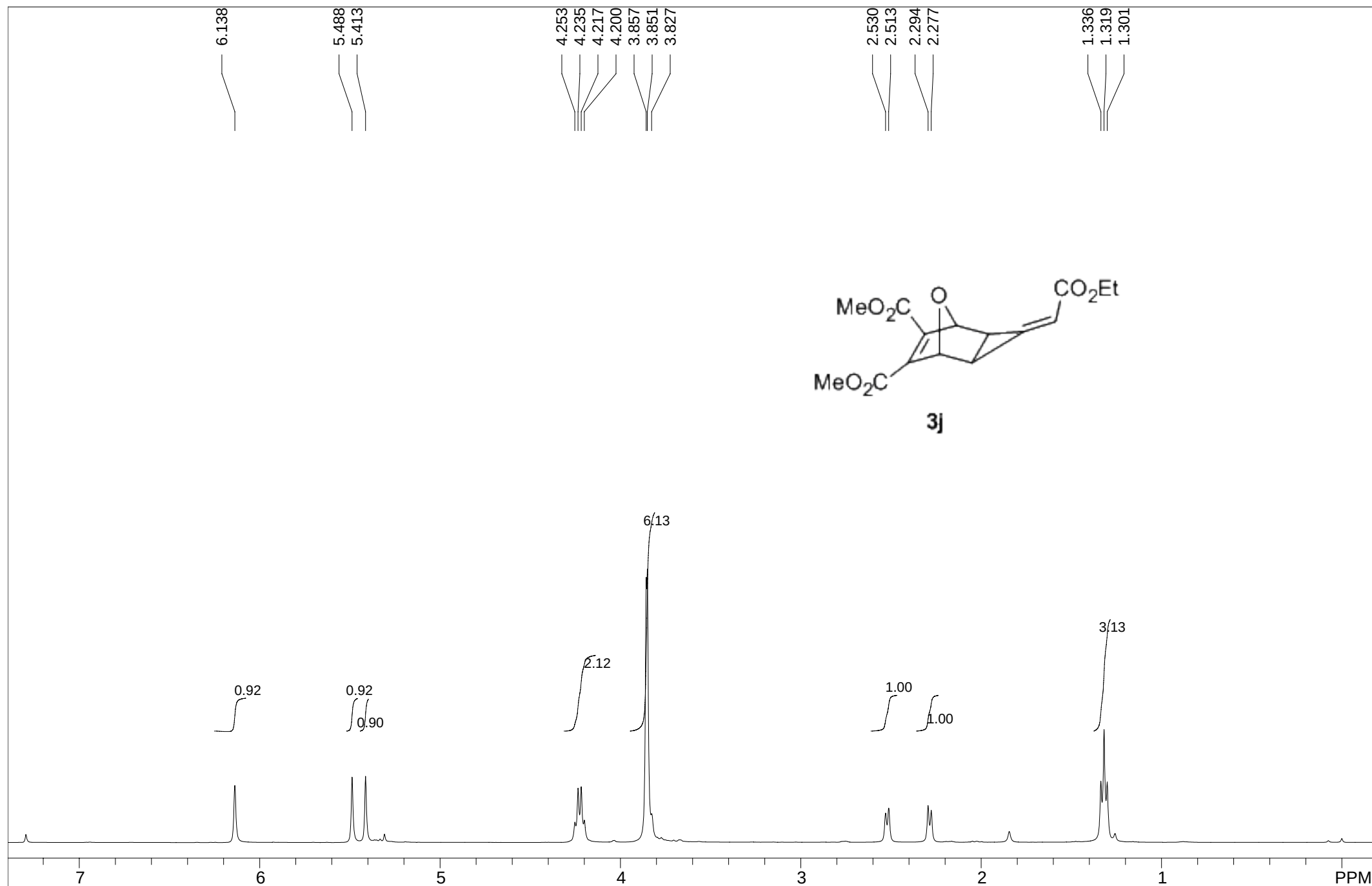
PW: 7.3 us

PD: 1.0 sec

NA: 80

LB: 2.0

Nuts - \$mdl-16-14b-C.fid

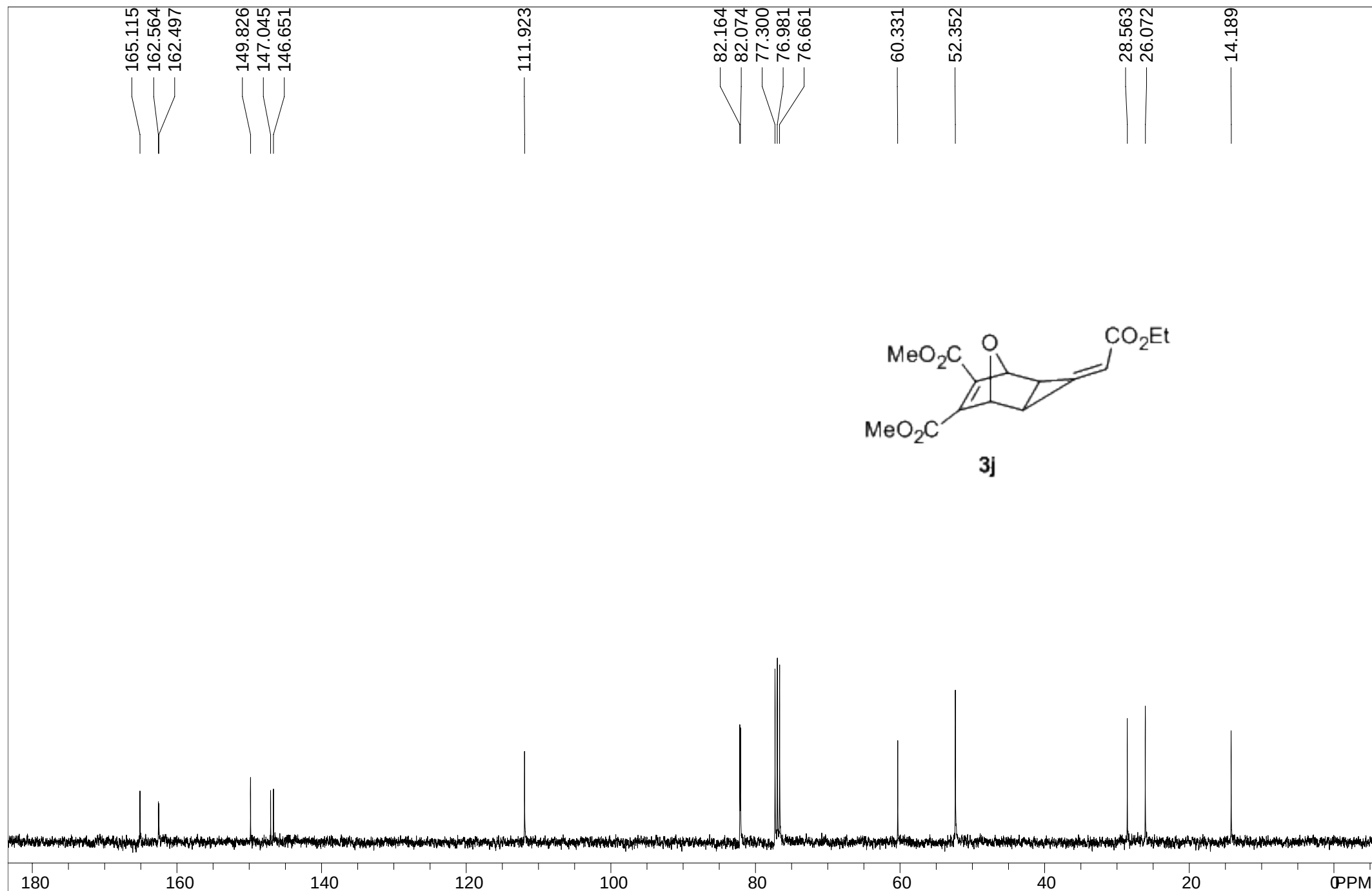


Std proton;blank line

USER: -- DATE: Oct 28 2008

F1: 400.037	F2: 100.598	SW1: 6831	OF1: 2615.9	PTS1d: 18443 , 32768
EX: s2pul	PW: 6.9 us	PD: 5.0 sec	NA: 6	LB: 2.0

Nuts - \$mdl-7-73-H.fid



dxw-7-79-2c

USER: -- DATE: Oct 28 2008

F1: 100.599

F2: 400.037

SW1: 24510

OF1: 10553.3

PTS1d: 31875 , 32768

EX: s2pul

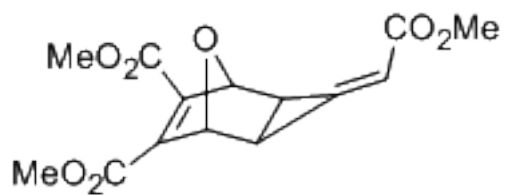
PW: 4.1 us

PD: 1.0 sec

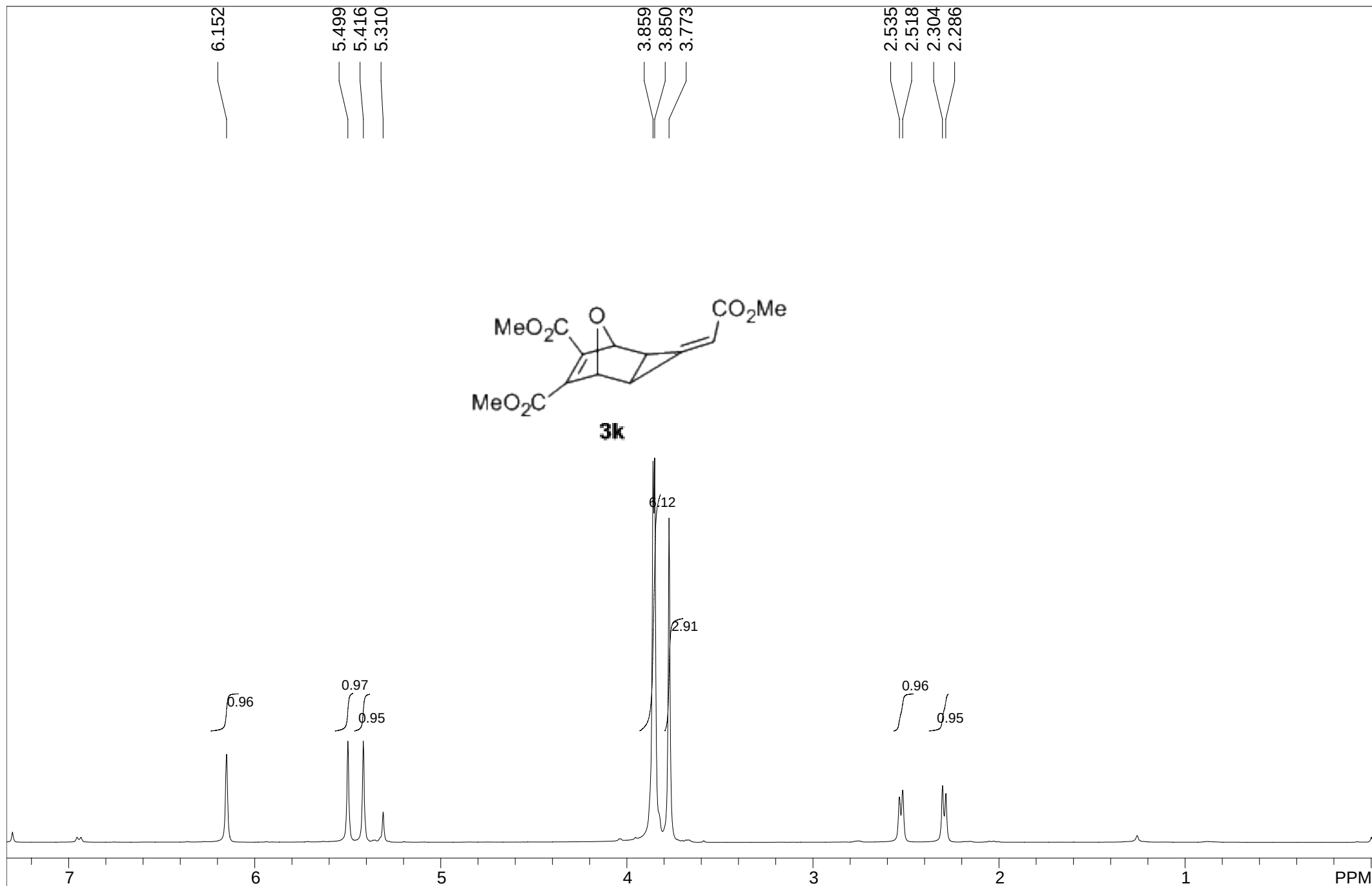
NA: 36

LB: 2.0

Nuts - \$mdl-7-73-C2.fid



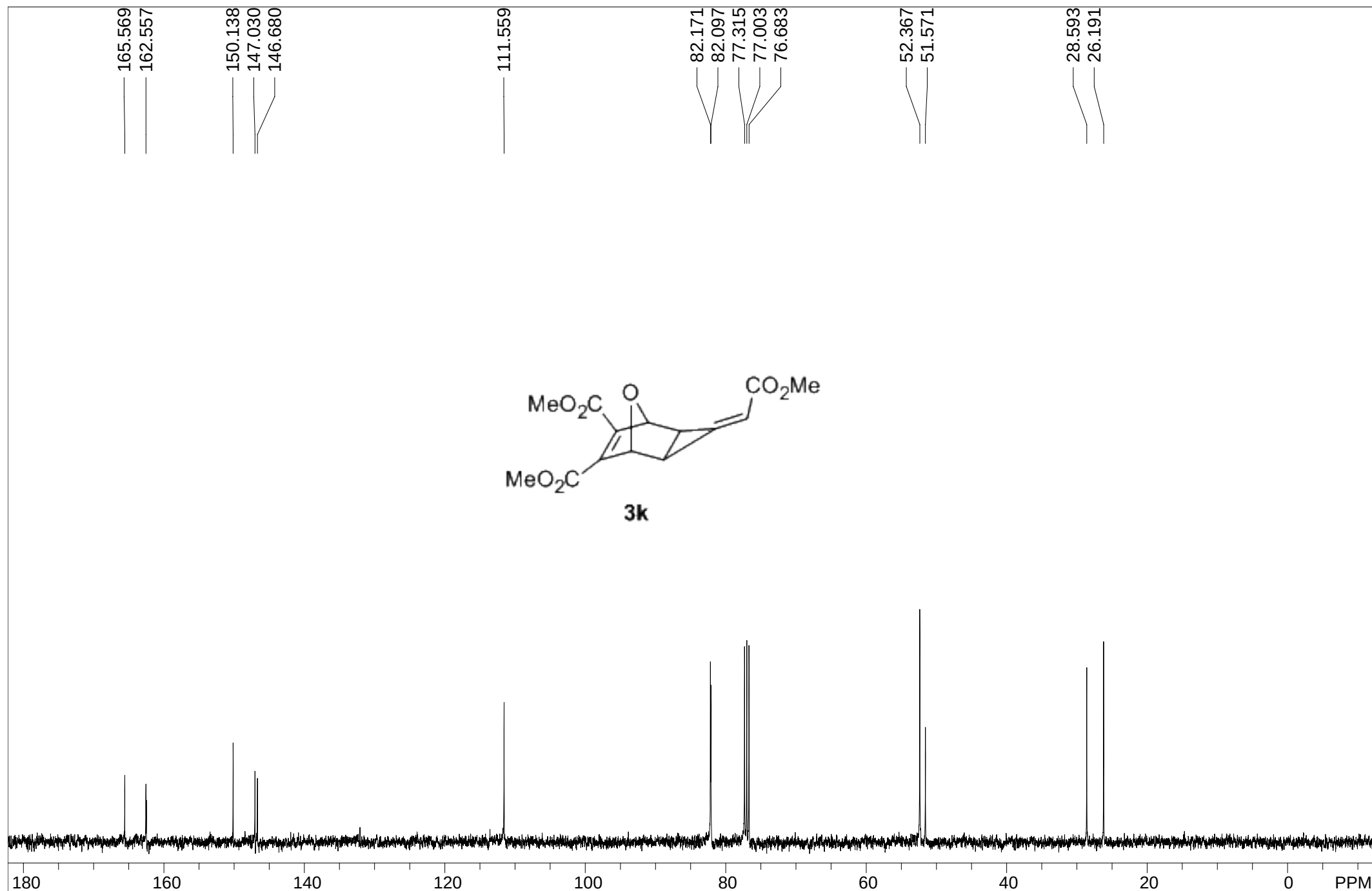
3k



Std proton;blank line

USER: -- DATE: Oct 28 2008

F1: 400.037	F2: 100.598	SW1: 6831	PD: 5.0 sec	OF1: 2618.2	NA: 6	PTS1d: 18443 , 32768	Nuts - \$mdl-7-74-H.fid
EX: s2pul	PW: 6.9 us			LB: 2.0			



dxw-7-79-2c

USER: -- DATE: Oct 28 2008

F1: 100.599

F2: 400.037

SW1: 24510

OF1: 10553.3

PTS1d: 31875 , 32768

EX: s2pul

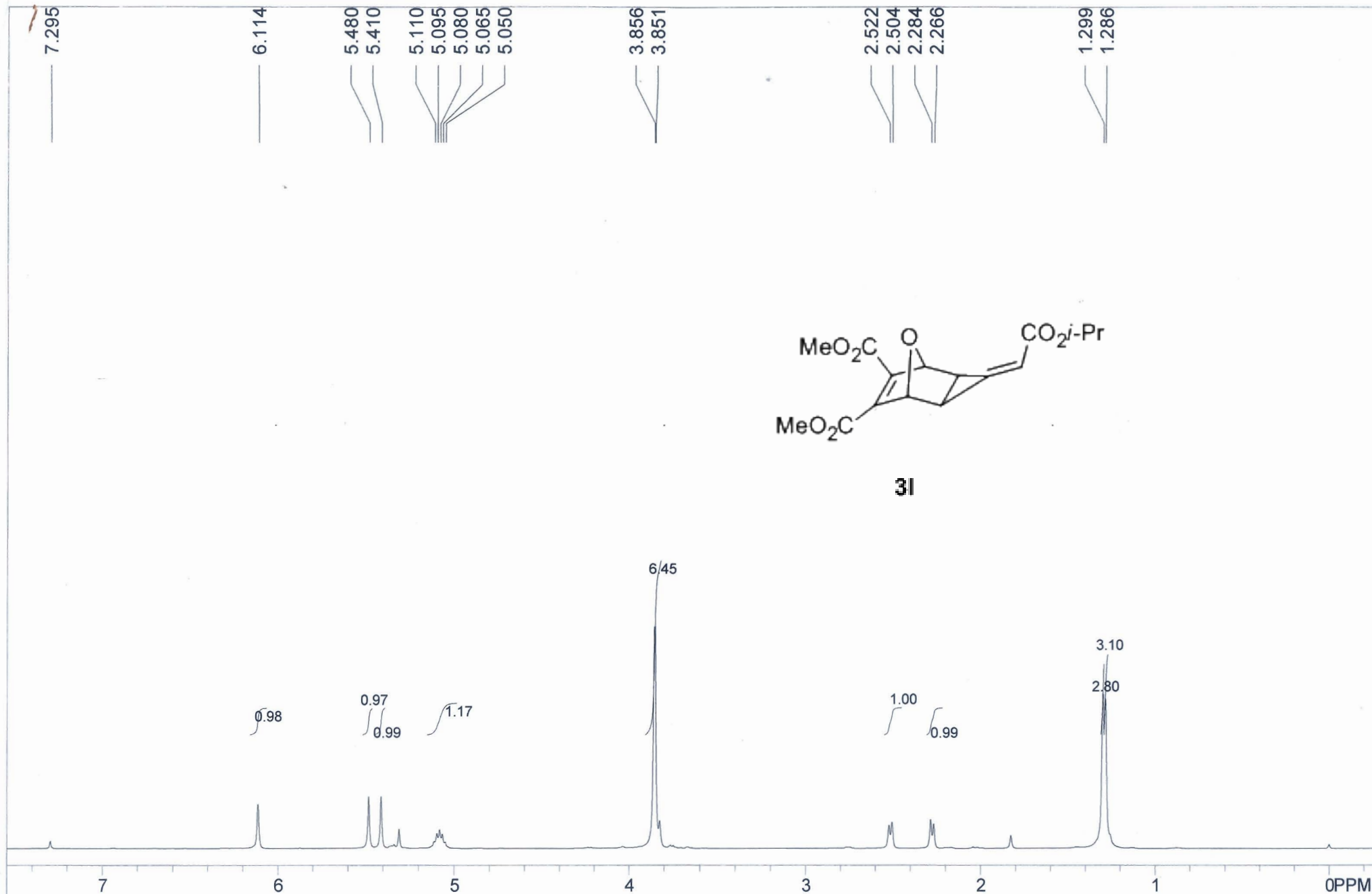
PW: 4.1 us

PD: 1.0 sec

NA: 40

LB: 2.0

Nuts - \$mdl-7-74-C2.fid



Std proton;blank line

USER: -- DATE: Oct 28 2008

F1: 400.037

F2: 100.598

SW1: 6831

OF1: 2615.4

PTSId: 18443 , 32768

EX: s2pul

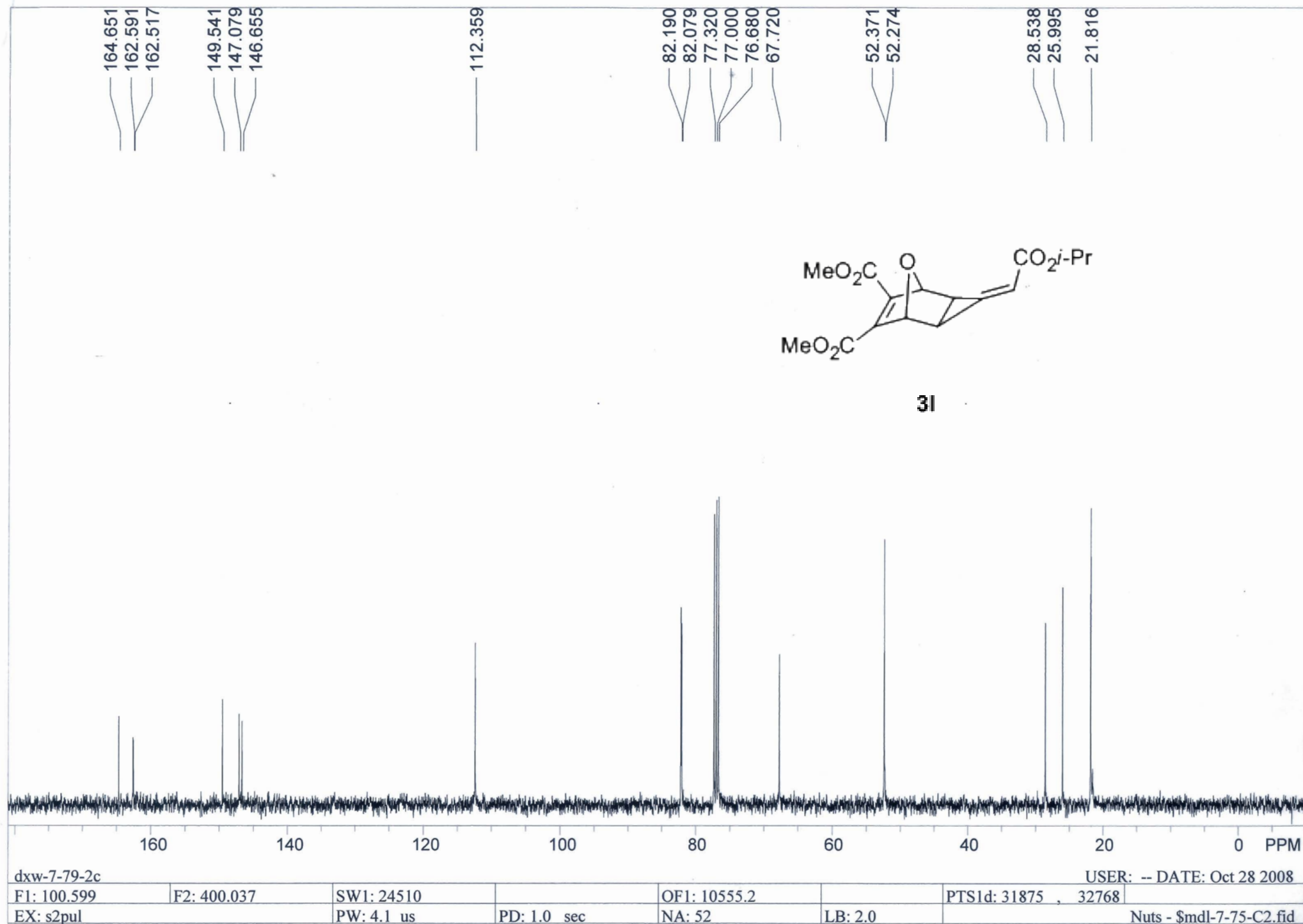
PW: 6.9 us

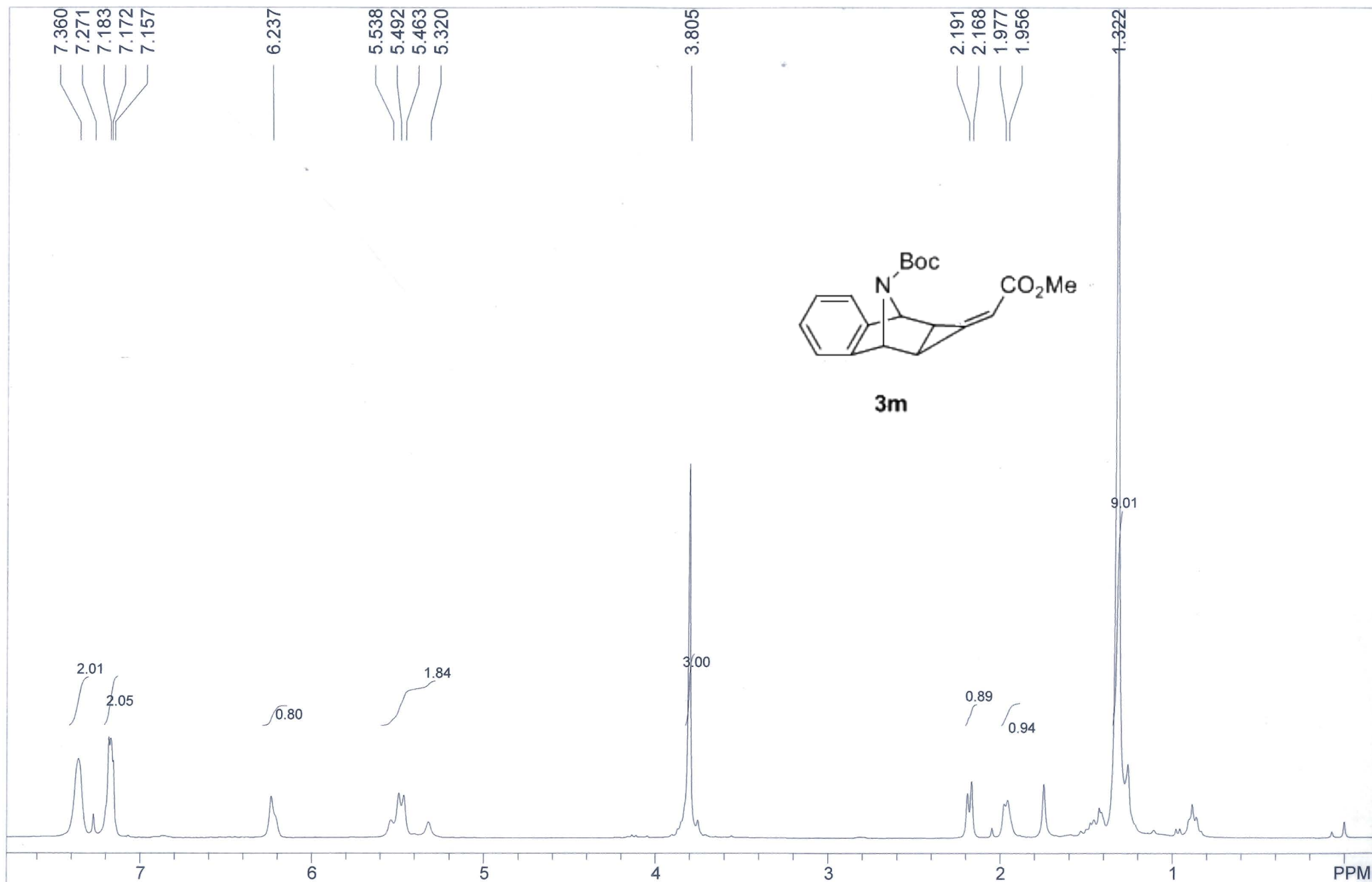
PD: 5.0 sec

NA: 6

LB: 2.0

Nuts - \$mdl-7-75-H.fid





;blank line

USER: -- DATE: Jun 15 2011

F1: 300.029

F2: 300.028

SW1: 6010

OF1: 2180.2

PTS1d: 12019 , 16384

EX: s2pul

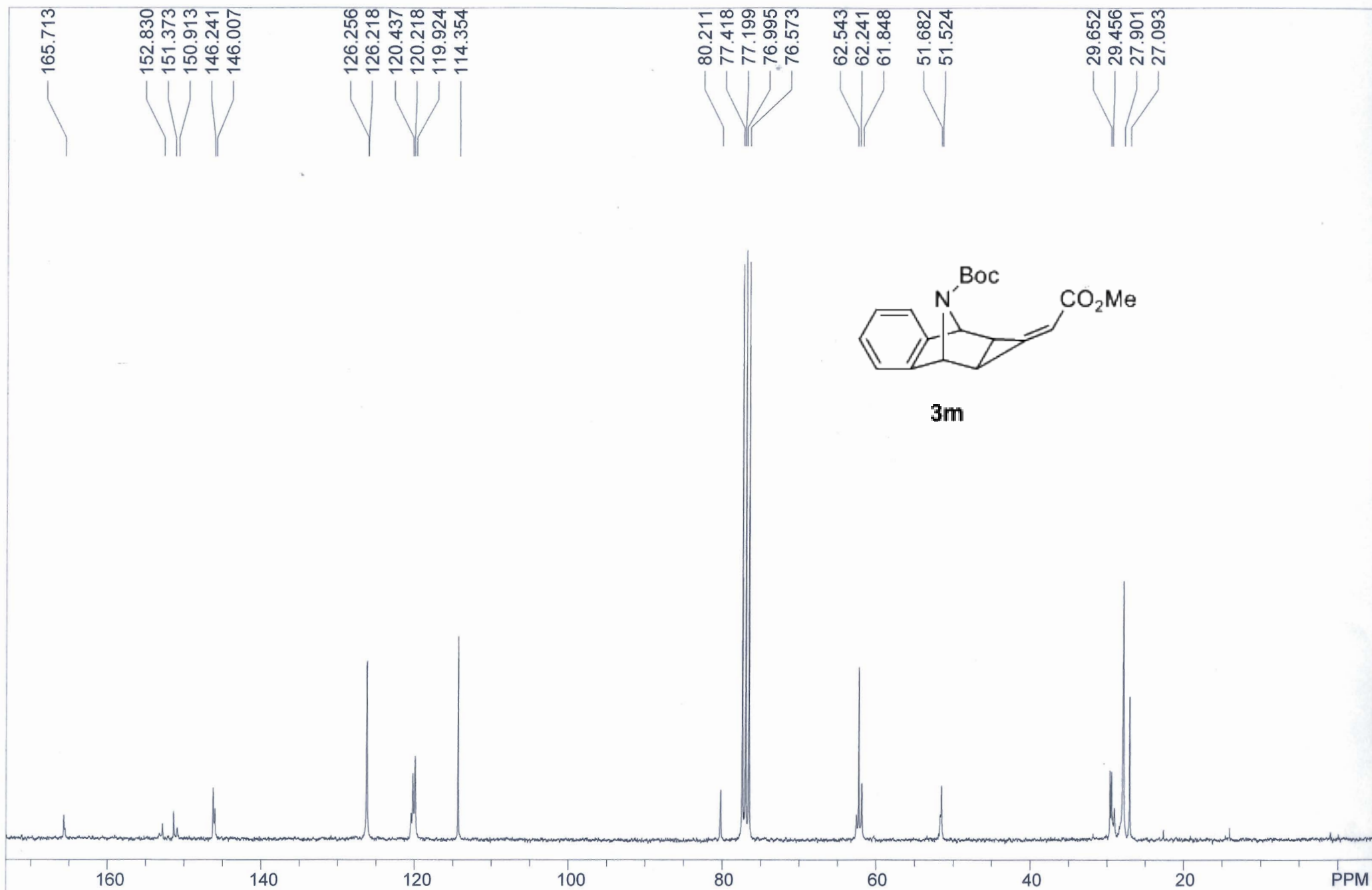
PW: 4.2 us

PD: 1.0 sec

NA: 20

LB: 2.0

Nuts - \$mdl-16-2-H.fid



mdl-16-8a-C

USER: -- DATE: Jun 16 2011

F1: 75.450

F2: 300.028

SW1: 18657

OF1: 7821.1

PTS1d: 24254 , 32768

EX: s2pul

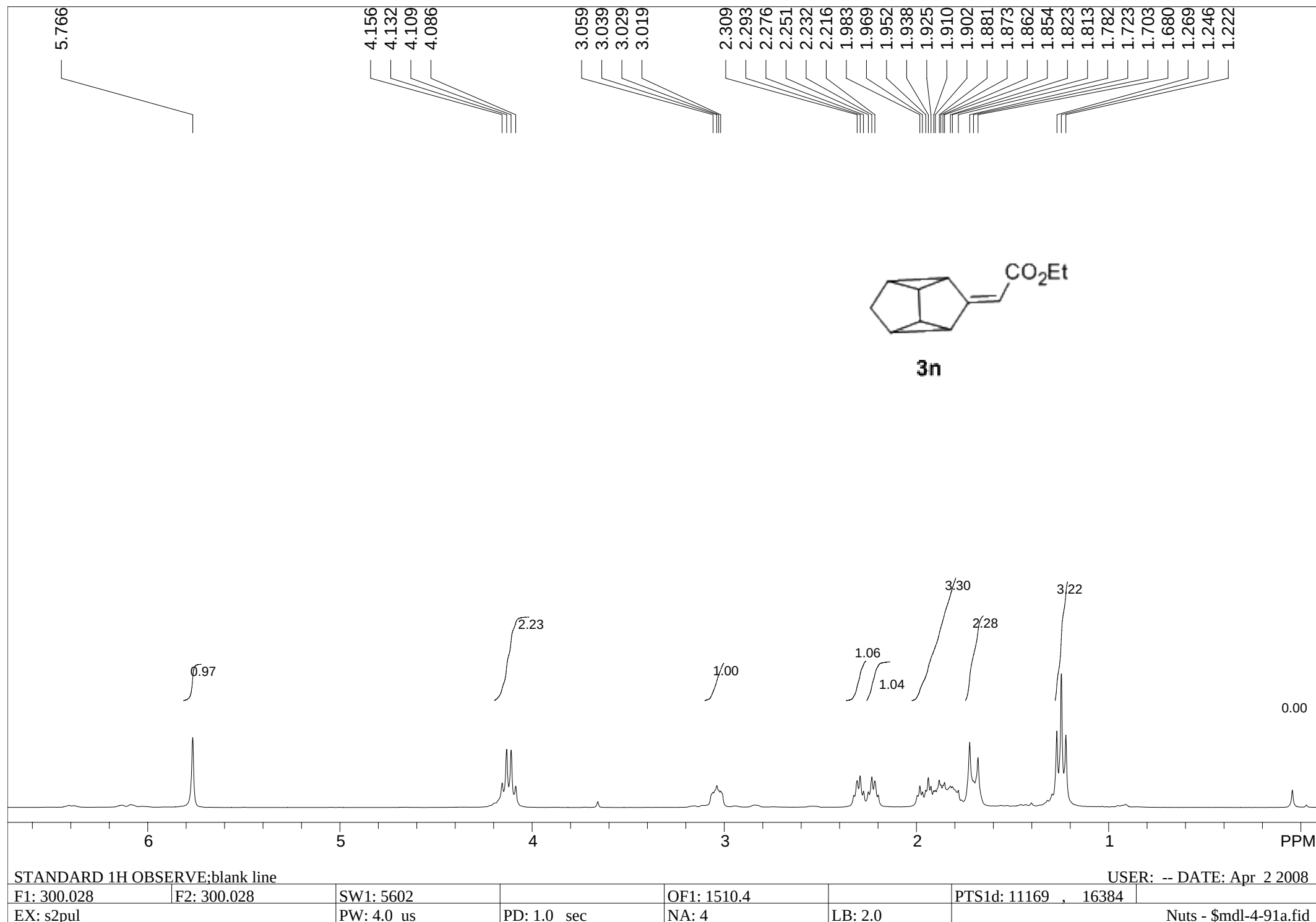
PW: 4.6 us

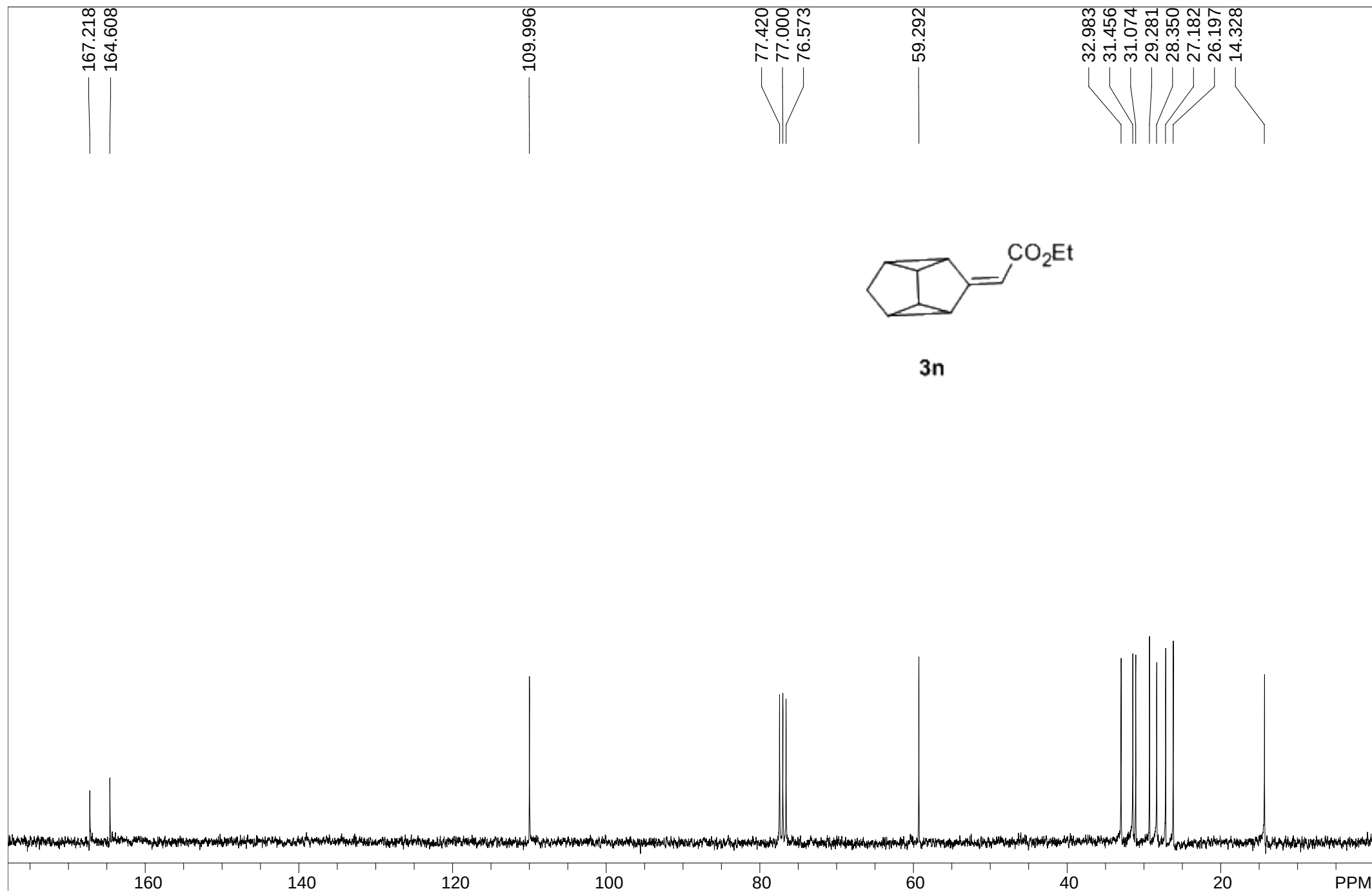
PD: 1.0 sec

NA: 10696

LB: 2.0

Nuts - \$mdl-16-2-CC.fid





mdl-4-91a

USER: -- DATE: Apr 3 2008

F1: 75.450

F2: 300.028

SW1: 18868

OF1: 8276.1

PTS1d: 30188 , 32768

EX: s2pul

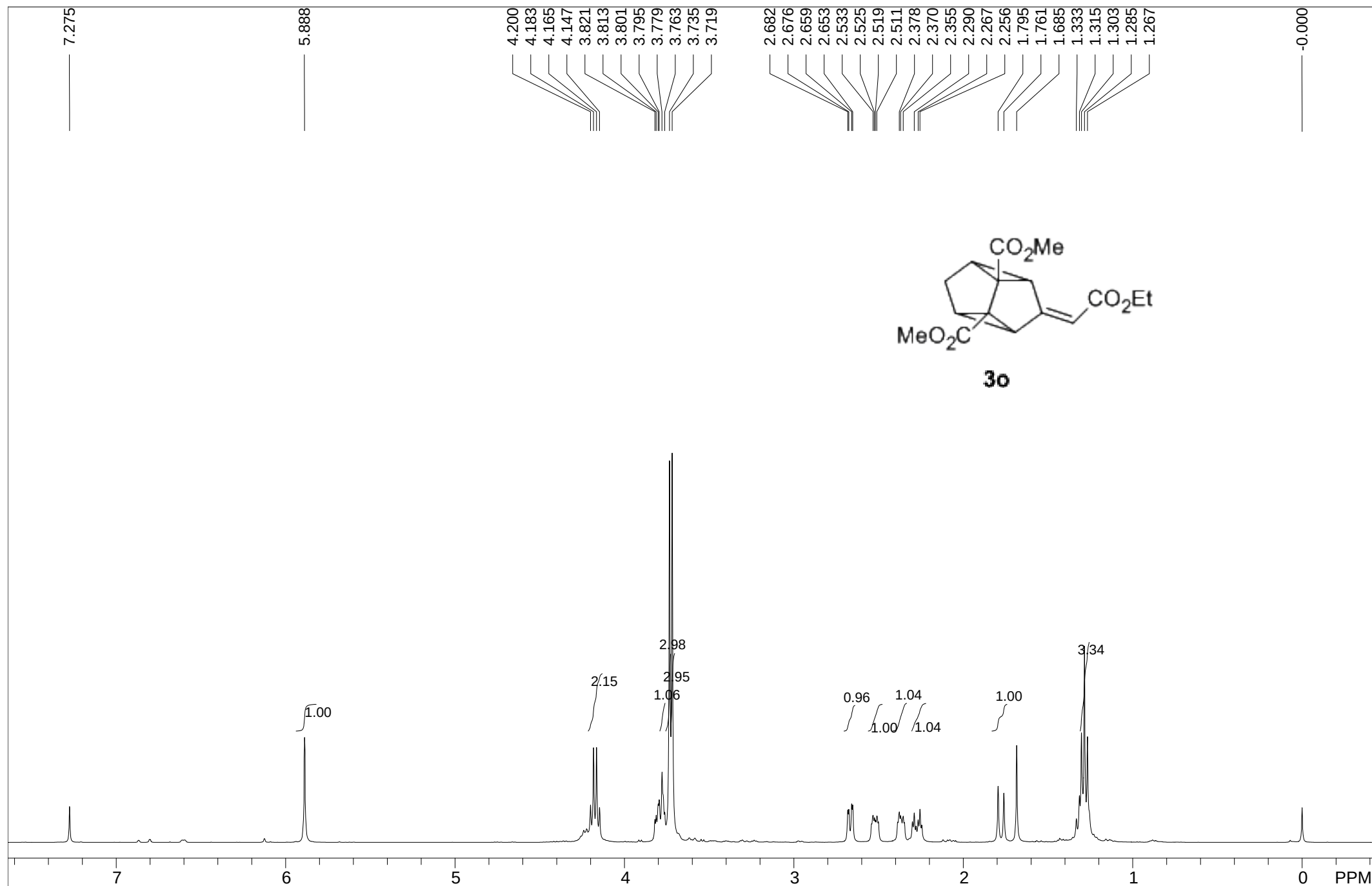
PW: 4.6 us

PD: 1.0 sec

NA: 108

LB: 2.0

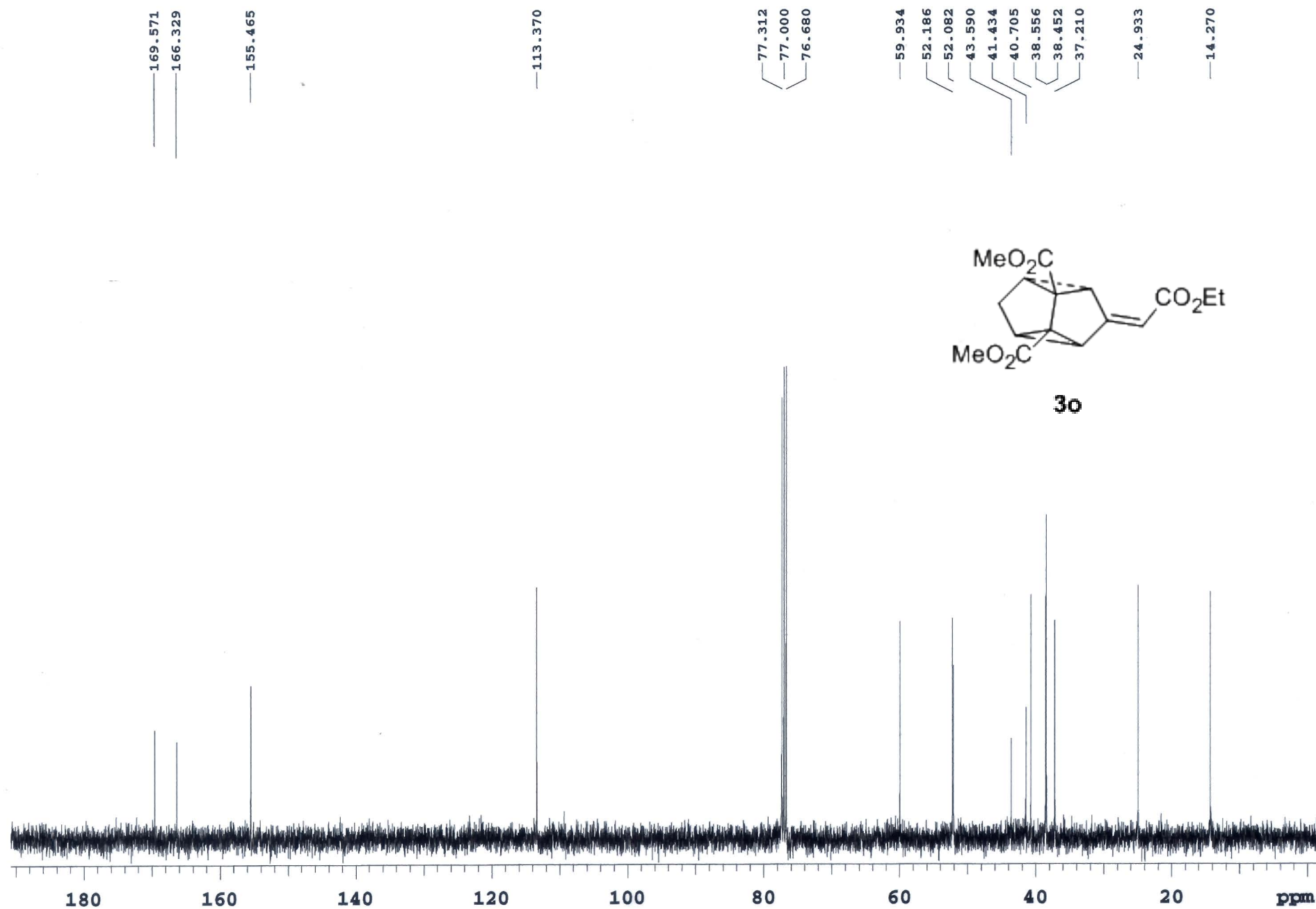
Nuts - \$mdl-4-91a-C.fid

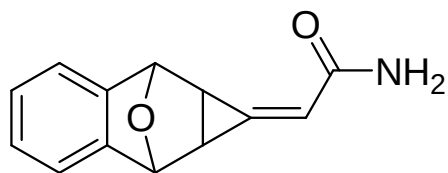


;blank line

USER: -- DATE: Jul 15 2009

F1: 400.037	F2: 100.599	SW1: 7225	PD: 1.0 sec	OF1: 2406.8	NA: 12	PTS1d: 21677 , 32768	Nuts - \$mdl-9-58-H.fid
EX: s2pul	PW: 4.4 us			LB: 2.0			

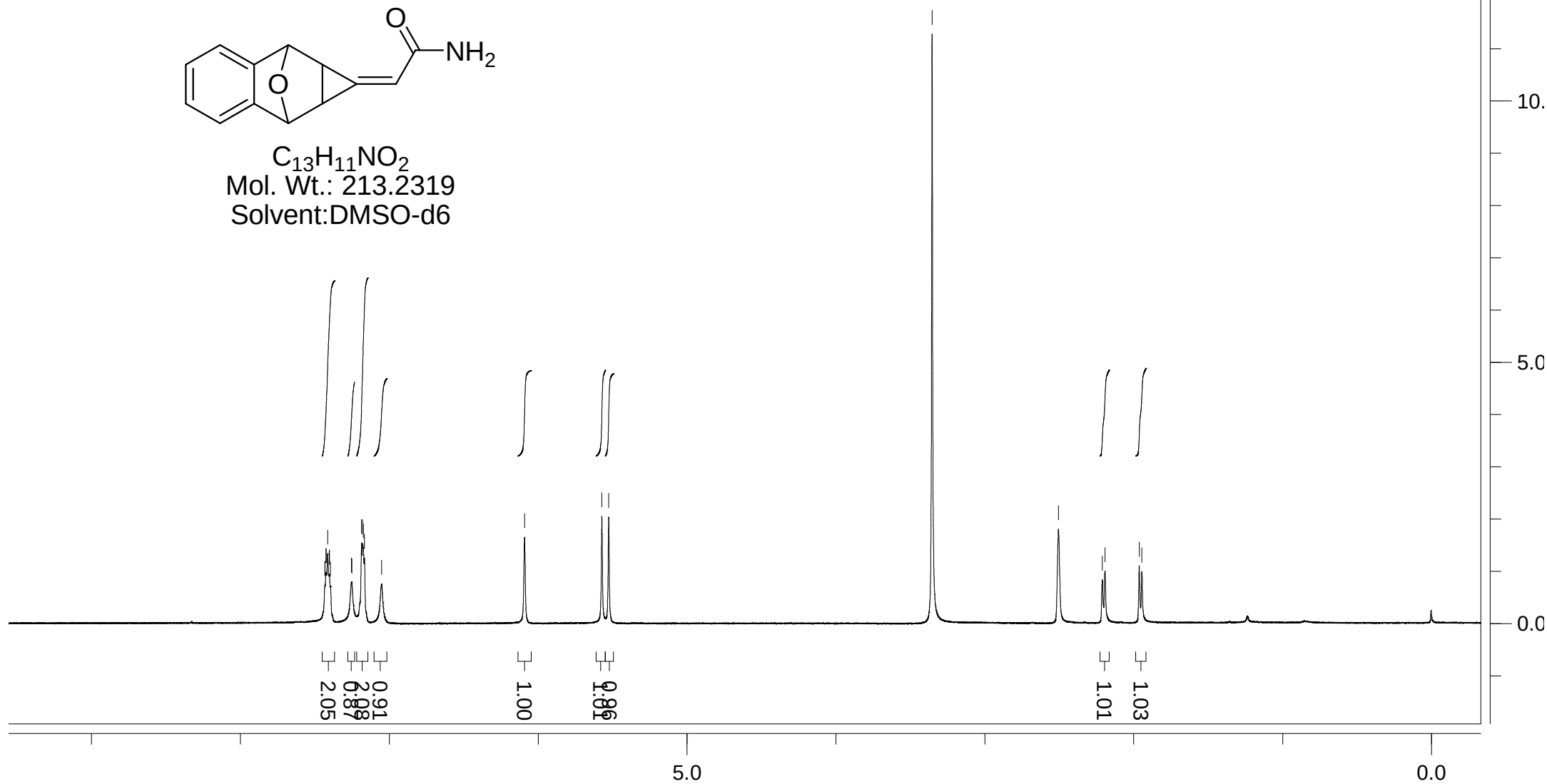


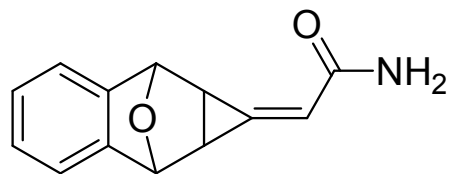


$C_{13}H_{11}NO_2$
 Mol. Wt.: 213.2319
 Solvent: DMSO-d6

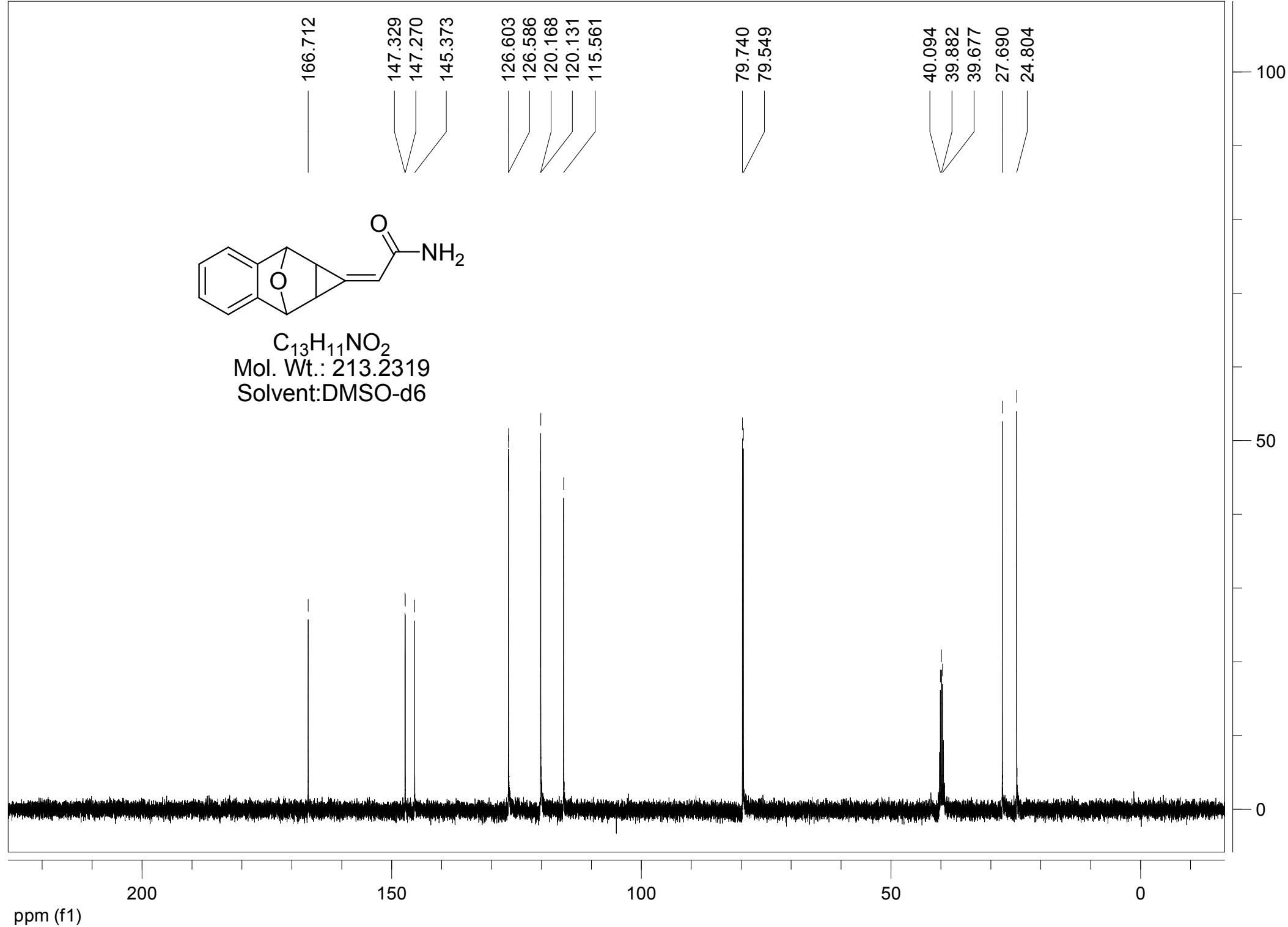
7.433
 7.431
 7.425
 7.424
 7.414
 7.403
 7.402
 7.395
 7.254
 7.251
 7.186
 7.178
 7.175
 7.166
 7.052
 6.091
 5.572
 5.526

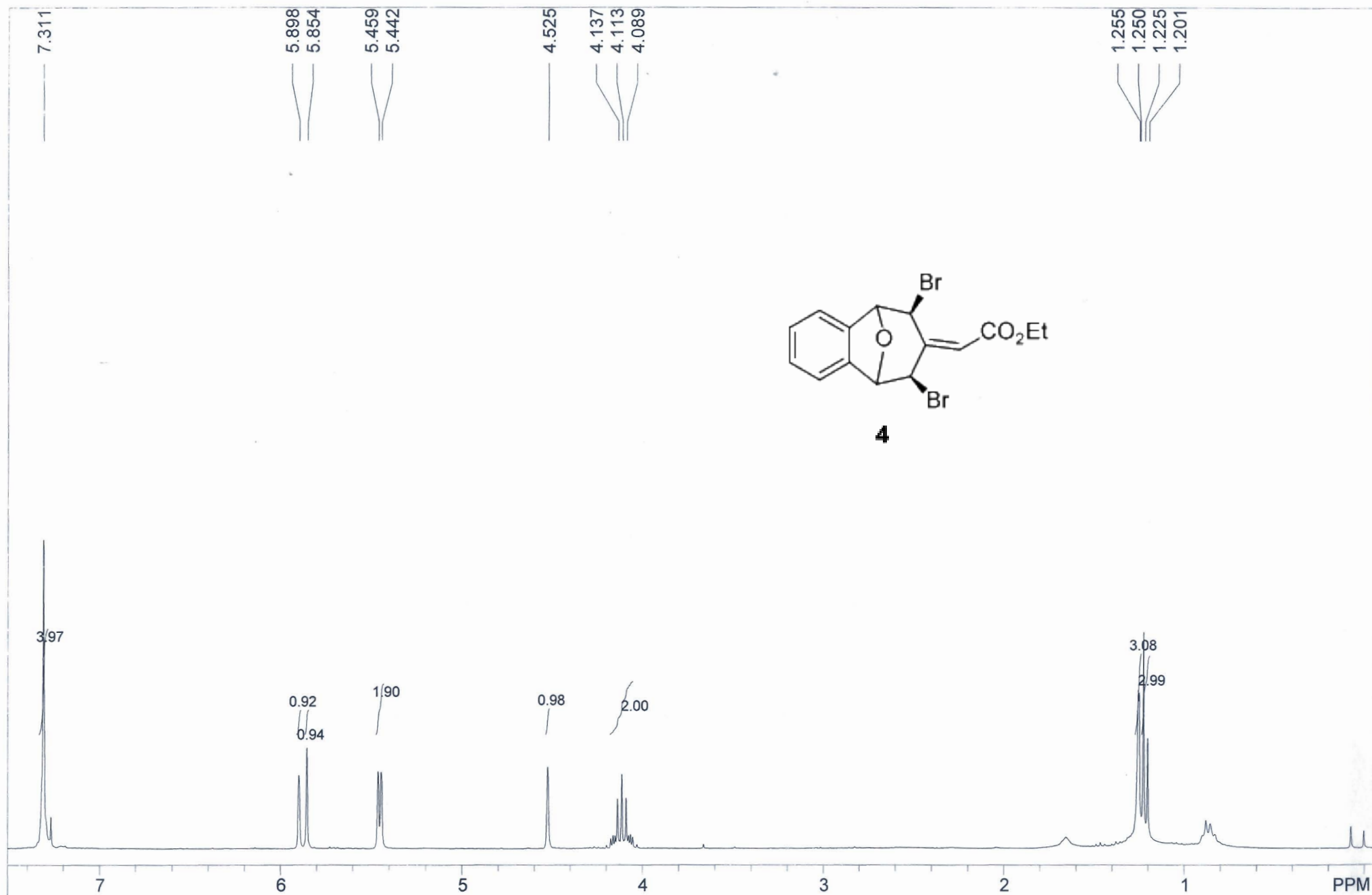
3.354
 2.505
 2.211
 2.193
 1.963
 1.945





$\text{C}_{13}\text{H}_{11}\text{NO}_2$
 Mol. Wt.: 213.2319
 Solvent: DMSO-d₆





STANDARD 1H OBSERVE:blank line

USER: -- DATE: May 27 2008

F1: 300.028

F2: 300.028

SW1: 5602

OF1: 1513.3

PTS1d: 11169 , 16384

EX: s2pul

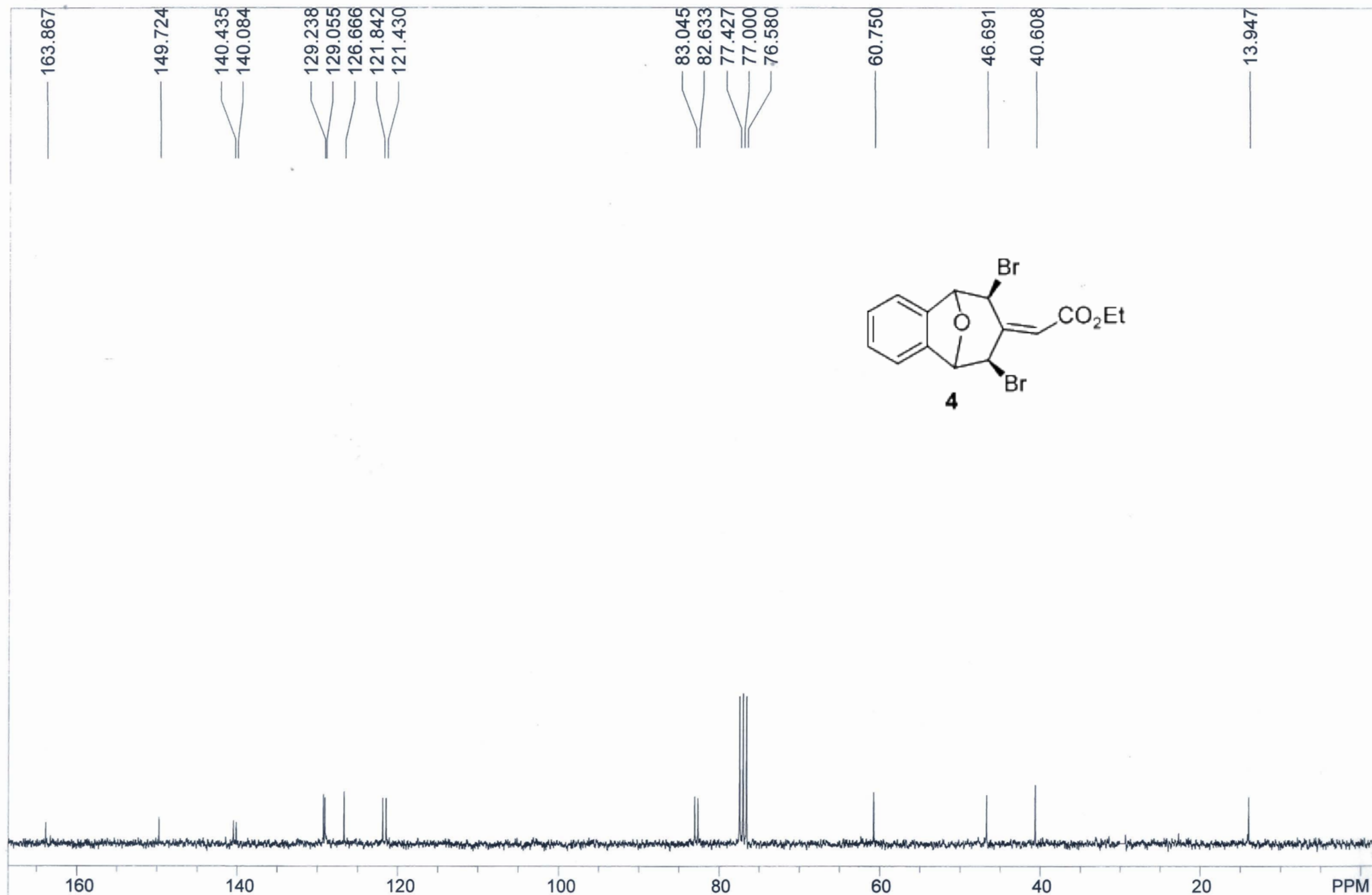
PW: 4.0 us

PD: 1.0 sec

NA: 24

LB: 0.0

Nuts - \$mdl-5-97a.fid



zbh-6-31-1C

USER: -- DATE: May 27 2008

F1: 75.450

F2: 300.028

SW1: 18868

OF1: 8277.3

PTS1d: 30188 , 32768

EX: s2pul

PW: 4.6 us

PD: 1.0 sec

NA: 99

LB: 2.0

Nuts - \$mdl-5-97a-C.fid

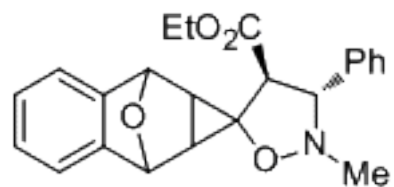
7.441
7.423
7.390
7.371
7.360
7.343
7.322
7.313
7.293
7.262
7.166
7.157
7.154
7.145

5.273
5.244

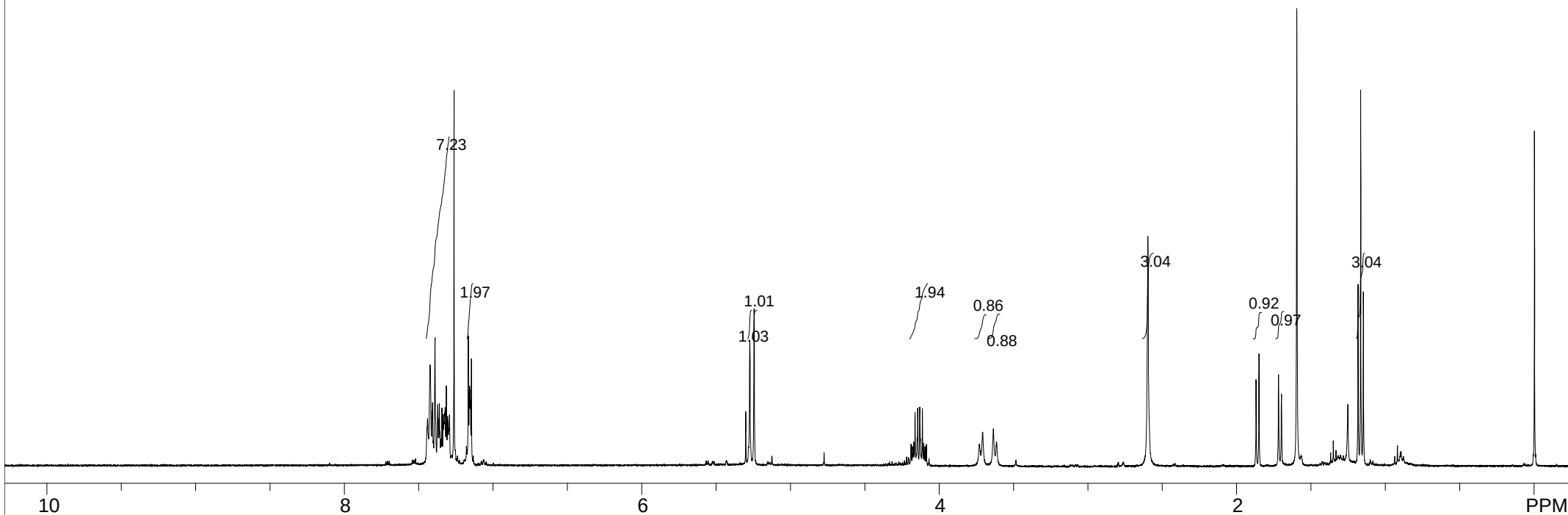
4.188
4.180
4.161
4.144
4.130
4.112
4.095
4.085
3.729
3.707
3.636
3.614
2.597

1.870
1.851
1.719
1.699
1.185
1.167
1.149

0.000



5a



Std proton;blank line

USER: -- DATE: Jul 20 2013

F1: 400.032 F2: 100.597

SW1: 7225

OF1: 2807.7

PTS1d: 32768

EX: s2pul

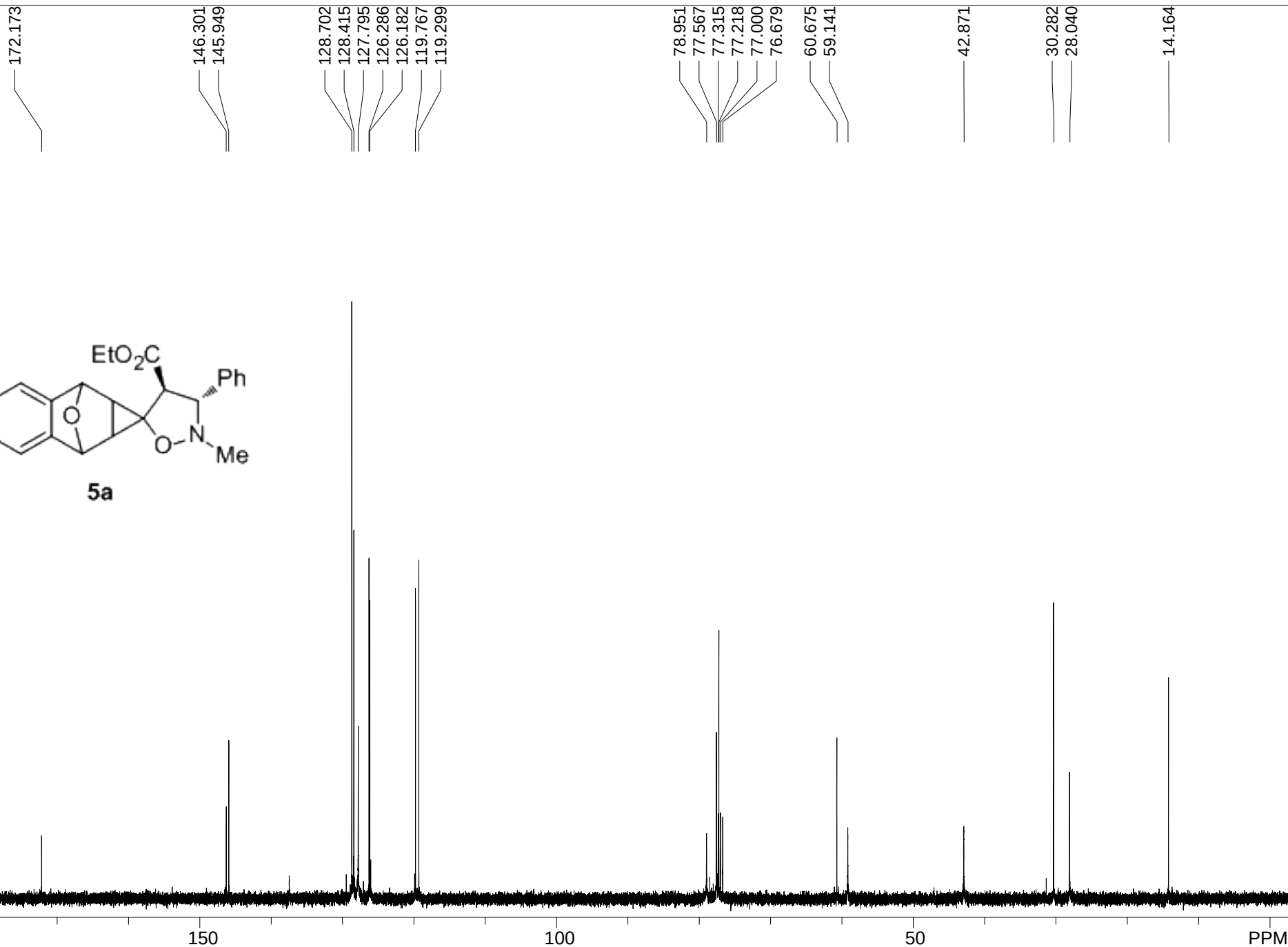
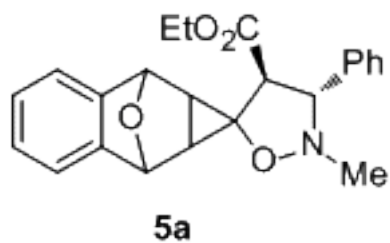
PW: 10.4 usec

PD: 1.0 sec

NA: 4

LB: 0.0

Nuts - \$yt-01-32a.fid



Std carbon;blank line

USER: -- DATE: Aug 27 2013

F1: 100.598	F2: 400.031	SW1: 24510		OF1: 10556.9		PTS1d: 65536	
EX: s2pul		PW: 9.5 usec	PD: 1.0 sec	NA: 364	LB: 0.0	Nuts - \$yt-01-39-222C.fid	

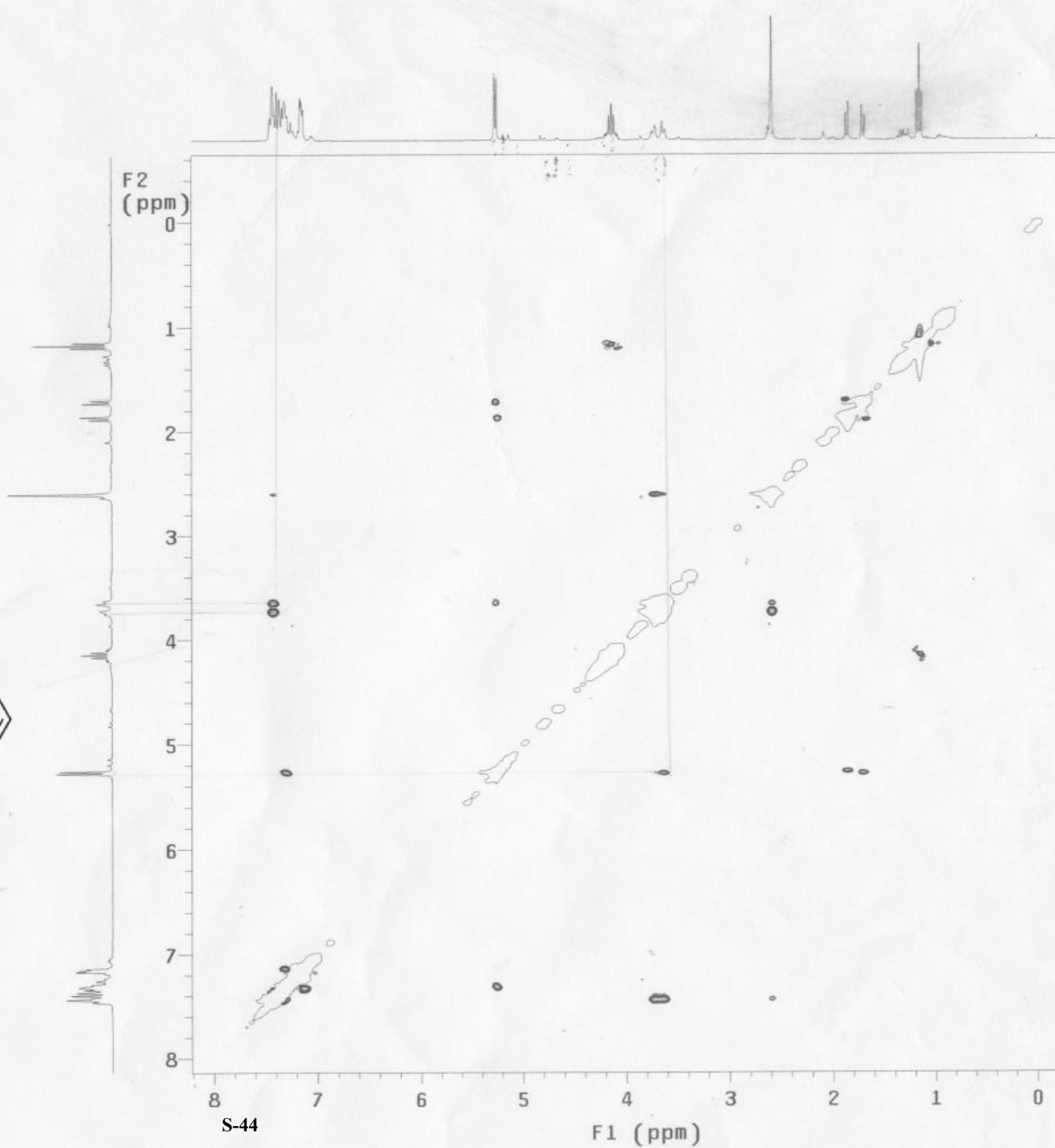
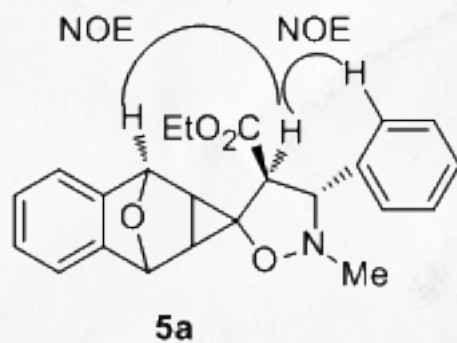
e Name:

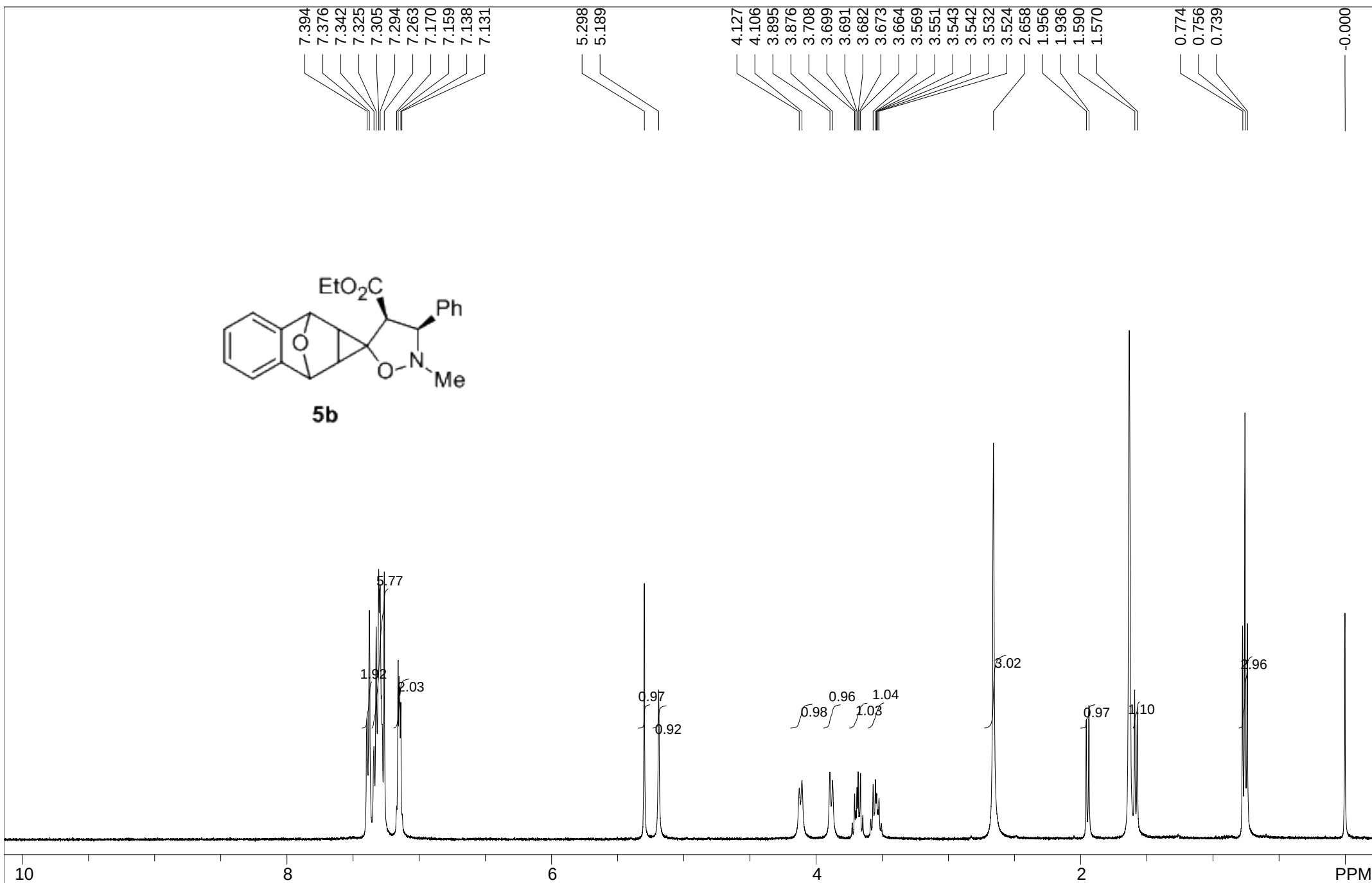
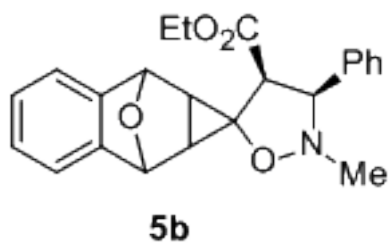
ve directory:
port/home/omc/vnmrsys/data
e directory:
01-39q_24Aug2013
le: NOESY

Sequence: NOESY
t: CDC13
ollected on: Aug 24 2013

or: omc
600 "OMC-NMR600"

. delay 2.000 sec
g 0.800 sec
time 0.142 sec
3597.1 Hz
dth 3597.1 Hz
petitions
28 increments
E H1, 300.0268154 MHz
ROCESSING
apodization 0.066 sec
A PROCESSING
apodization 0.033 sec
e 2048 x 2048
time 4 hr, 56 min





Std proton;blank line

USER: -- DATE: Sep 9 2013

F1: 400.032 F2: 100.597

SW1: 7225

OF1: 2809.5

PTS1d: 32768

EX: s2pul

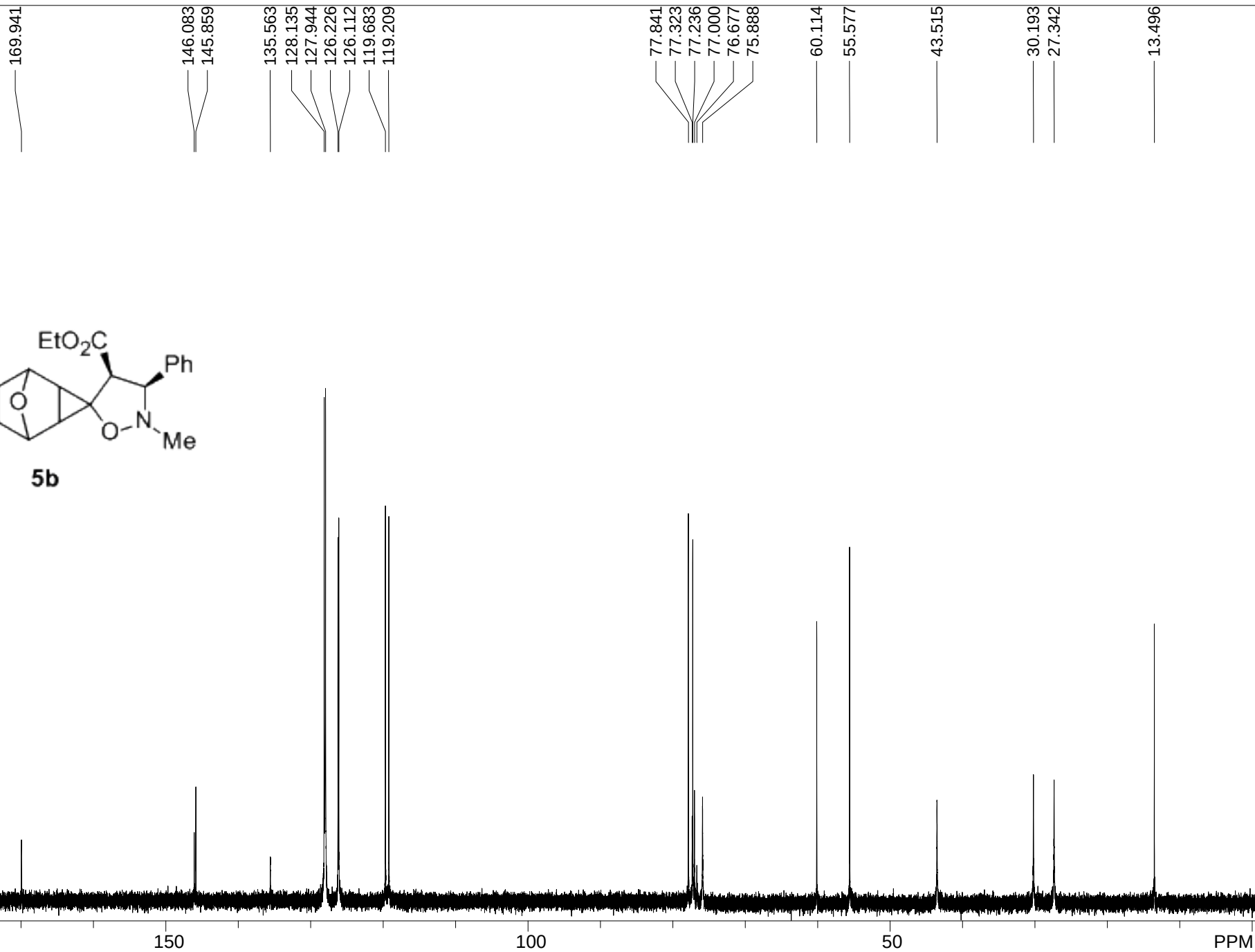
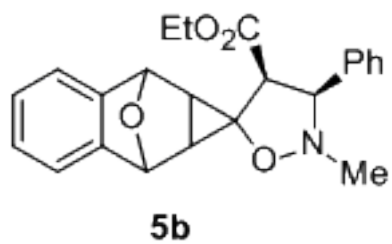
PW: 10.0 usec

PD: 1.0 sec

NA: 8

LB: 0.0

Nuts - \$yt-01-62b1-h.fid



Std carbon;blank line

USER: -- DATE: Sep 9 2013

F1: 100.598	F2: 400.031	SW1: 24510		OF1: 10524.7		PTS1d: 65536	
EX: s2pul		PW: 9.5 usec	PD: 1.0 sec	NA: 244	LB: 0.0	Nuts - \$yt-01-62b1-c.fid	

Pulse Sequence: NOESY

Operator: omcl

VNMRS-400 "Agilent-NMR"

Relax. delay 2.000 sec

Mixing 0.800 sec

Acq. time 0.142 sec

Width 3597.1 Hz

2D Width 3597.1 Hz

32 repetitions

2 x 128 increments

OBSERVE H1, 300.0268138 MHz

DATA PROCESSING

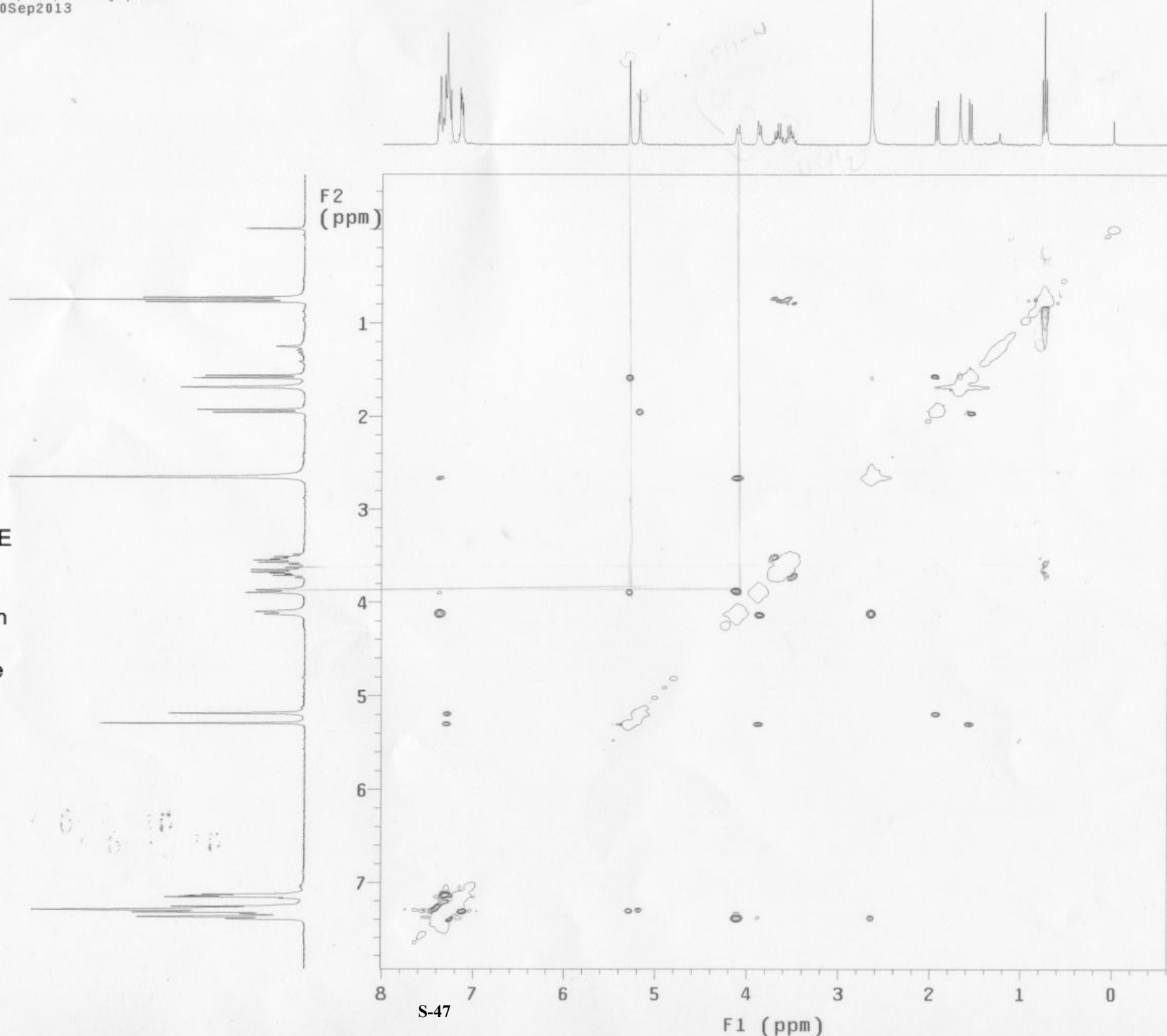
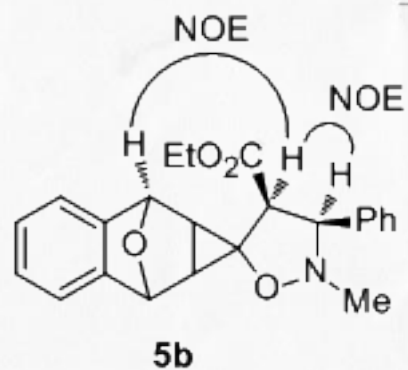
Gauss apodization 0.066 sec

F1 DATA PROCESSING

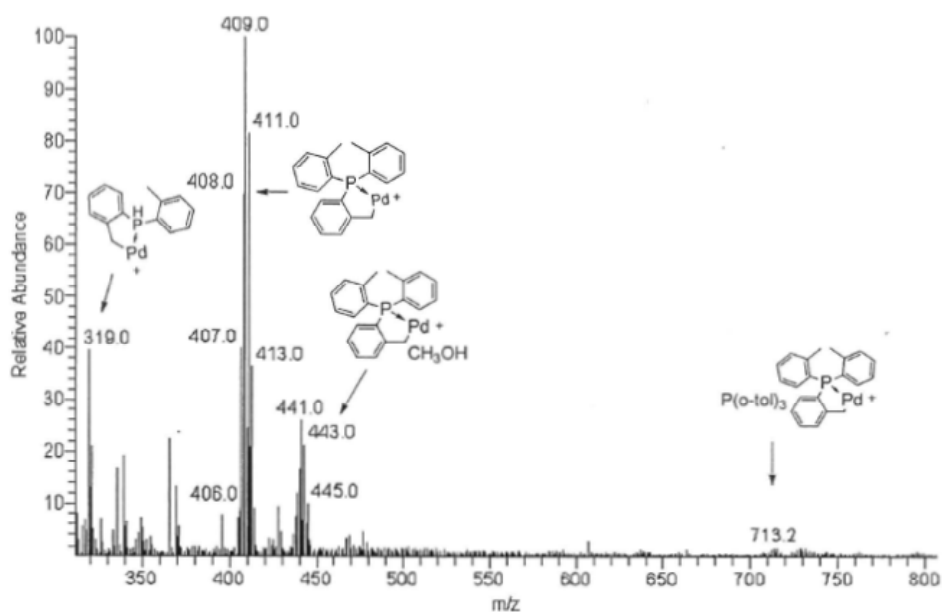
Gauss apodization 0.033 sec

FT size 2048 x 2048

Total time 4 hr, 56 min



1. The Mass spectrum (ESI) of **Sample A** (Figure 2)



2. The Mass spectrum of the reaction completed (**Sample D**, Figure 2)

