Asymmetric Organocatalytic Desymmetrization of 4,4-Disubstituted Cyclohexadienones at High-Pressure: A New Powerful Strategy for the Synthesis of Highly Congested Chiral Cyclohexenones

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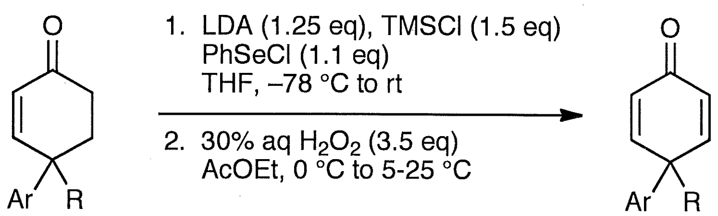
General.

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen or argon. All melting points were measured on a Yanagimoto MP-S3 micro-melting point apparatus and are uncorrected. The NMR spectra were recorded on a JEOL ECA-500 (500 MHz for ^{1}H NMR analysis and 125.8 MHz for ^{13}C NMR analysis) instrument in $CDCl_3$ unless otherwise stated and are reported in parts per million (δ) downfield from TMS as an internal standard. Mass spectral analyses were performed on a JEOL JMS-700/MStation mass spectrometer. The infrared spectra were measured with a JASCO FTIR-460plus Fourier Transform Infrared Spectrophotometer and are reported in wave-numbers (cm^{-1}). Optical rotations were measured on a JASCO DIP-370 polarimeter. HPLC analyses were carried out using a Hitachi L-6200 HPLC system.

Thin-layer chromatography (TLC) was conducted using Merck Kieselgel 60F-254 plates (0.25 mm). Kanto Chemicals silica gel 60N (spherical, neutral 63–210 μm) and Merck alumina (90 active, neutral 70–230 μm) were used for column chromatography.

Catalysts **A** and **B** are known and prepared following the literature procedure.[1] The starting cyclohexenones were prepared from α,α'–disubstituted acetaldehydes and methyl vinyl ketone via Robinson-type annulation.[2] 4-Methyl-4-trichloromethylcyclohexadienone **1g** was prepared from *p*-cresol following the literature procedure.[3] Cyclohexenone (*R*)-**8** was prepared following the literature procedure,[2] and used after recrystallization from hexane. The ee of this compound was determined by chiral HPLC analysis (Chiralpak AD column, 0.46 × 25 cm, hexane/*i*-PrOH = 99 : 1, 0.3 cm^3/min): R_t (*S*) = 25.4 min; R_t (*R*) = 29.2 min (our previous data[2] for the assignment of (*S*)- and (*R*)-isomers should be corrected).

General Procedure for the Synthesis of Cyclohexadienones (1).[4]

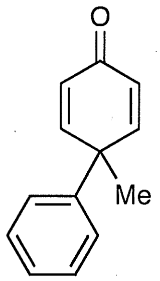


1

To a solution of *i*-Pr_2NH (6.25 mmol) in THF (6 mL) was slowly added *n*-BuLi (6.25 mmol) at –78 °C under Ar. The mixture was stirred for 20 min before a solution of cyclohexenone (5.0 mmol) in THF (6 mL) was introduced. After stirring at 0 °C for 30 min, TMSCl (7.5 mmol) was added in one portion and the resulting mixture stirred at rt for 1 h before PhSeCl (5.5 mmol) in THF (5.5 mL) was introduced with stirring at rt. After stirring for 45 min, the mixture was quenched by addition of 10% aq HCl (7.5 mL) followed by stirring for another 1.5 h. The mixture was then extracted with Et_2O, and the combined extracts were washed with brine, dried (Na_2SO_4), and concd. Purification by column chromatography on silica gel (hexane/AcOEt) gave the crude product as a pale yellow oil.

To a solution of this crude product (3.3 mmol) in AcOEt (45 mL) was added dropwise 30% aq H_2O_2 (3.5 eq) at 0 °C, and the mixture was stirred at 5-25 °C for 60 min. The reaction was quenched by addition of sat. aq $NaHCO_3$ (22 mL) and sat. aq $Na_2S_2O_3$, and extracted with AcOEt. The combined extracts were dried (Na_2SO_4) and concd. Purification by column chromatography on alumina (eluted with hexane/AcOEt) and recrystallization from hexane gave the cyclohexadienone **1**.[5]

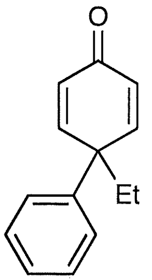
4-Methyl-4-phenylcyclohexadienone (1a).



1a

67% yield; colorless solid, mp 53–55 °C (lit.[6] 53–55 °C); R_f 0.36 (hexane / AcOEt = 5 : 1).
FTIR (KBr) ν 1682, 1666, 1630, 1607, 1450, 1403, 1393, 1364 cm^{-1}.
^1H NMR (500 MHz, $CDCl_3$) δ 1.69 (3H, s), 6.28 (2H, d, J = 10.0 Hz), 6.92 (2H, d, J = 10.0 Hz), 7.26–7.36 (5H, m).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ 23.80, 44.95, 126.28 (×2), 126.90 (×2), 127.53, 128.92 (×2), 139.80, 155.37 (×2), 185.85.

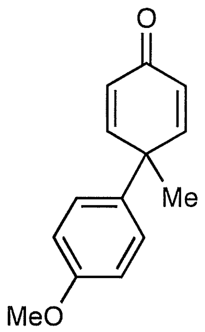
4-Ethyl-4-phenylcyclohexadienone (1b).



1b

50% yield; colorless solid, mp 43–45 °C; R_f 0.27 (hexane / AcOEt = 5 : 1).
FTIR (KBr) ν 1665, 1626, 1595, 1489, 1456, 1444, 1398 cm^{-1}.
^1H NMR (500 MHz, $CDCl_3$) δ 0.89 (3H, t, J = 7.5 Hz), 2.16 (2H, q, J = 7.5 Hz), 6.36 (2H, d, J = 10.5 Hz), 6.87 (2H, d, J = 10.5 Hz), 7.24–7.35 (5H, m).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ 8.89, 30.08, 49.44, 126.50 (×2), 127.41, 128.71 (×2), 128.88 (×2), 139.93, 154.10 (×2), 186.13.

4-Methyl-4-(4-methoxyphenyl)cyclohexadienone (1c).



1c

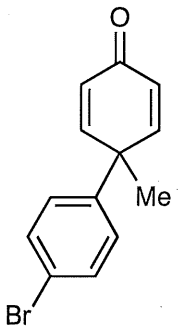
35% yield; colorless solid, mp 55–57 °C; R_f 0.16 (hexane / AcOEt = 5 : 1).

FTIR (KBr) ν 1666, 1624, 1607, 1509, 1458, 1401 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.65 (3H, s), 3.78 (3H, s), 6.24 (2H, d, J = 10.0 Hz), 6.85–6.87 (2H, m), 6.88 (2H, d, J = 10.0 Hz), 7.19–7.21 (2H, m).

^{13}C NMR (125.8 MHz, $CDCl_3$) δ 23.83, 44.32, 55.22, 114.22 (×2), 126.57 (×2), 127.38 (×2), 131.46, 155.66 (×2), 158.86, 185.85.

4-Methyl-4-(4-bromophenyl)cyclohexadienone (1d).



1d

45% yield; colorless solid, mp 59–60 °C; R_f 0.19 (hexane / AcOEt = 5 : 1).

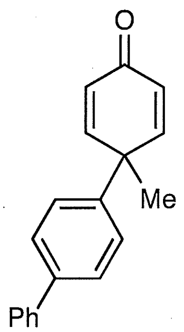
FTIR (KBr) ν 1661, 1619, 1591, 1508, 1448, 1391 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67 (3H, s), 6.27 (2H, d, J = 10.0 Hz), 6.86 (2H, d, J = 10.0 Hz), 7.15–7.17 (2H, m), 7.46 (2H, d, J = 8.5 Hz).

^{13}C NMR (125.8 MHz, $CDCl_3$) δ 23.82, 44.56, 121.66, 127.21 (×2), 128.11 (×2), 132.02 (×2), 139.02, 154.58 (×2), 185.52.

HRMS Calcd for $C_{13}H_{11}BrO$ + H 263.0072, found 263.0077.

4-Methyl-4-(4,4'-biphenyl)cyclohexadienone (1e).

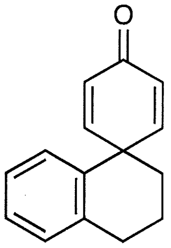


1e

15% yield; colorless solid, mp 111–113 °C; R_f 0.20 (hexane / AcOEt = 5 : 1).

FTIR (KBr) ν 1665, 1622, 1597, 1484, 1448, 1398 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.74 (3H, s), 6.32 (2H, d, J = 10.0 Hz), 6.96 (2H, d, J = 10.0 Hz), 7.35–7.39 (3H, m), 7.45 (2H, t, J = 7.5 Hz), 7.57 (4H, dd, J = 7.5, 5.5 Hz).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ 23.90, 44.79, 126.77 (×2), 127.00 (×2), 127.06 (×2), 127.50, 127.65 (×2), 128.80 (×2), 138.81, 140.25, 140.56, 155.25 (×2), 185.85.
HRMS Calcd for $C_{19}H_{16}O$ + H 261.1279, found 261.1282.

3',4'-Dihydro-2'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalen]-4-one.



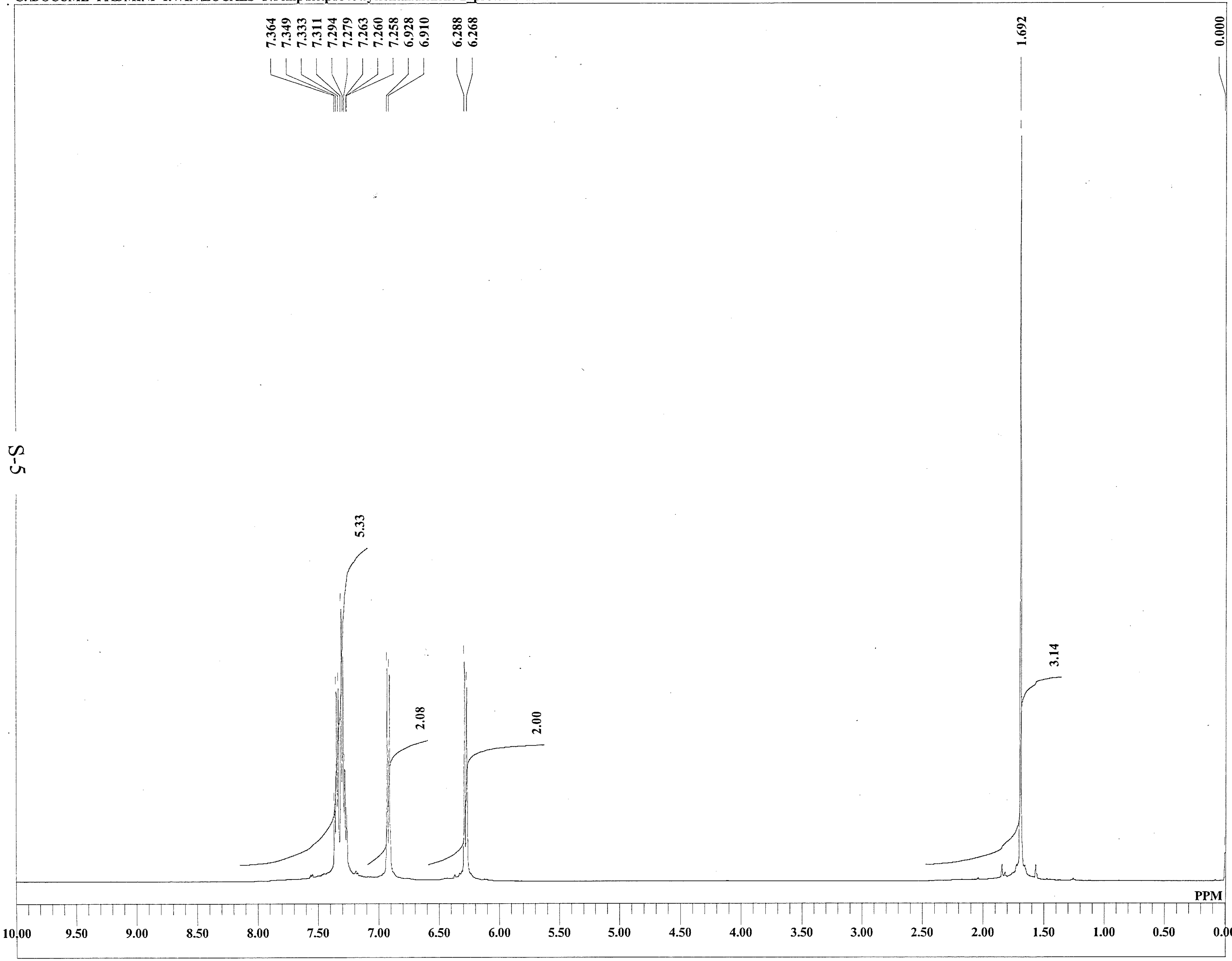
1f

86% yield; colorless solid; mp 150–151 °C (lit.[7] 144–146 °C); R_f 0.26 (hexane / AcOEt = 5 : 1).
FTIR (KBr) ν 1662, 1621, 1487, 1445, 1400 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.97–2.02 (4H, m), 2.91–2.93 (2H, m), 6.28 (2H, d, J = 10.0 Hz), 6.95 (1H, d, J = 8.0 Hz), 7.02 (2H, d, J = 10.0 Hz), 7.07–7.11 (1H, m), 7.16–7.17 (2H, m).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ 19.23, 29.58, 34.21, 44.74, 126.34, 126.79 (×2), 127.49, 128.79, 130.23, 133.39, 136.46, 155.31 (×2), 186.16.

References

(1) M. Moritaka, N. Miyamae, K. Nakano, Y. Ichikawa and H. Kotsuki, *Synlett,* 2012, **23**, 2554–2558.
(2) Y. Inokoishi, N. Sasakura, K. Nakano, Y. Ichikawa and H. Kotsuki, *Org. Lett.*, 2010, **12**, 1616–1619.
(3) (a) Z. Wang, *Comprehensive Organic Name Reactions and Reagents*, John Wiley & Sons: New York, 2010; Vol. 3, pp 3178–3182; (b) M. S. Newman and A. G. Pinkus, *J. Org. Chem.*, 1954, **19**, 978–984.
(4) (a) H. Plieninger and W. Gramlich, *Chem. Ber.*, 1978, **111**, 1944–1957; (b) D. Crich, Q. Yao and G. F. Filzen, *J. Am. Chem. Soc.*, 1995, **117**, 11455–11470.
(5) Yields were not optimized.
(6) H. E. Zimmerman and G. Jones, II, *J. Am. Chem. Soc.*, 1970, **92**, 2753–2761.
(7) S. Rousseaux, J. García-Fortanet, M. A. D. A. Sanchez and S. L. Buchwald, *J. Am. Chem. Soc.*, 2011, **133**, 9282–9285.

single_pulse



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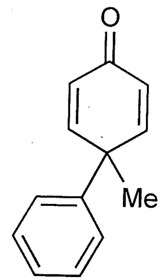

1a
^{1}H NMR
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

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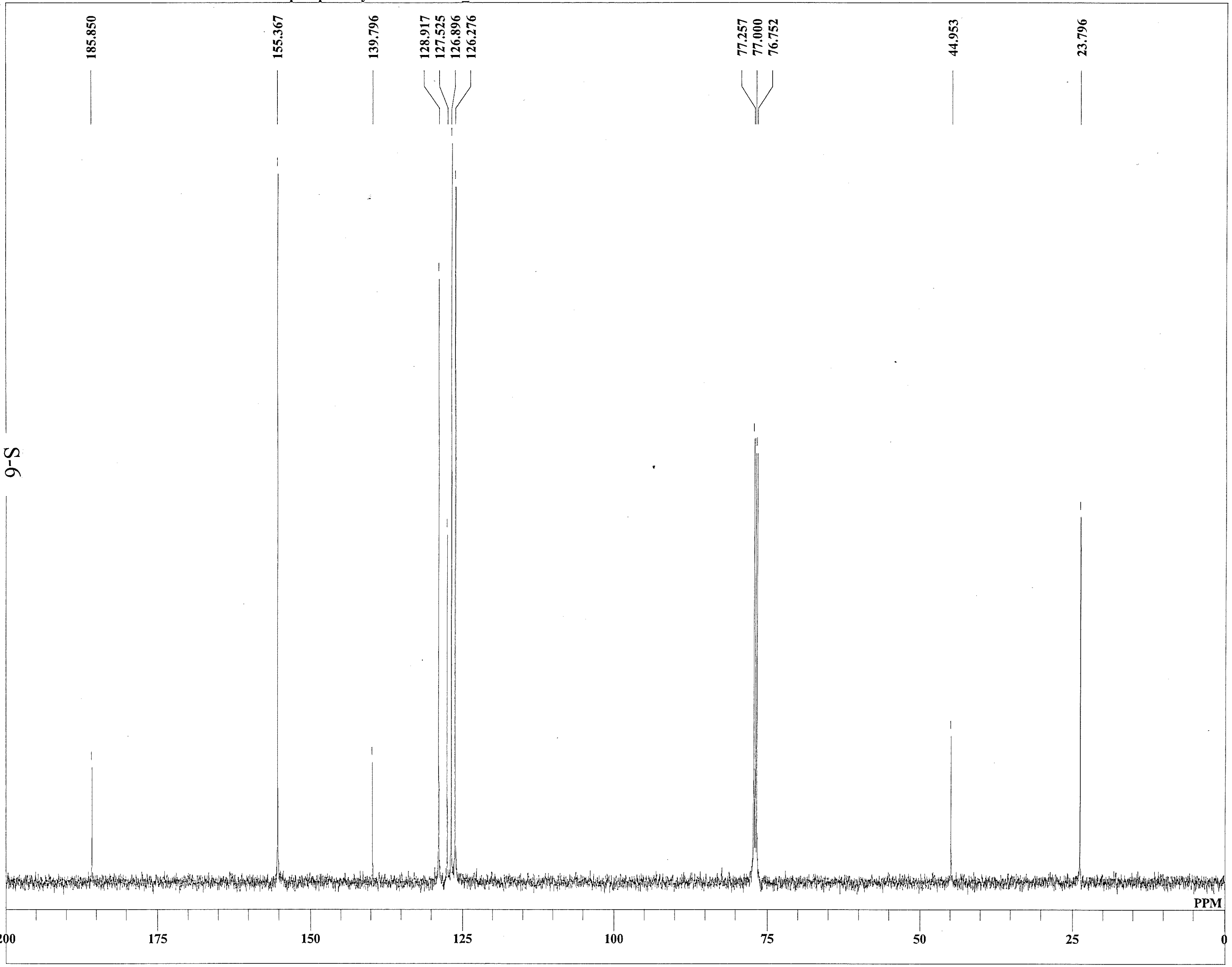

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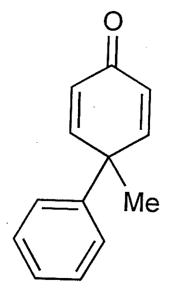

1a

^{13}C NMR

(125 MHz, $CDCl_3$)

single_pulse

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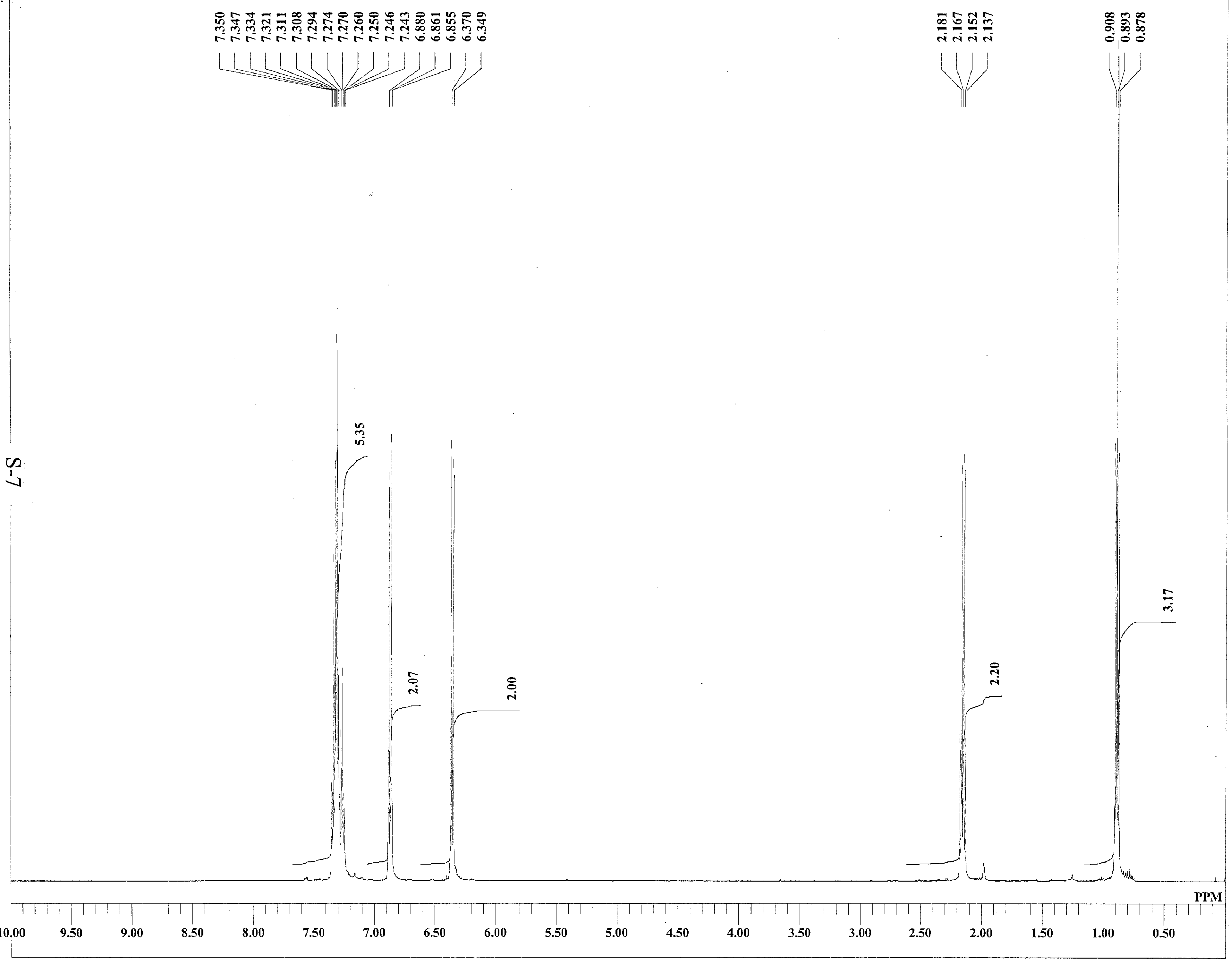

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PD	5.0000 sec
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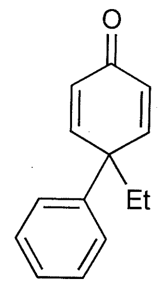
RGAIN	30



1b

^{1}H NMR

(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

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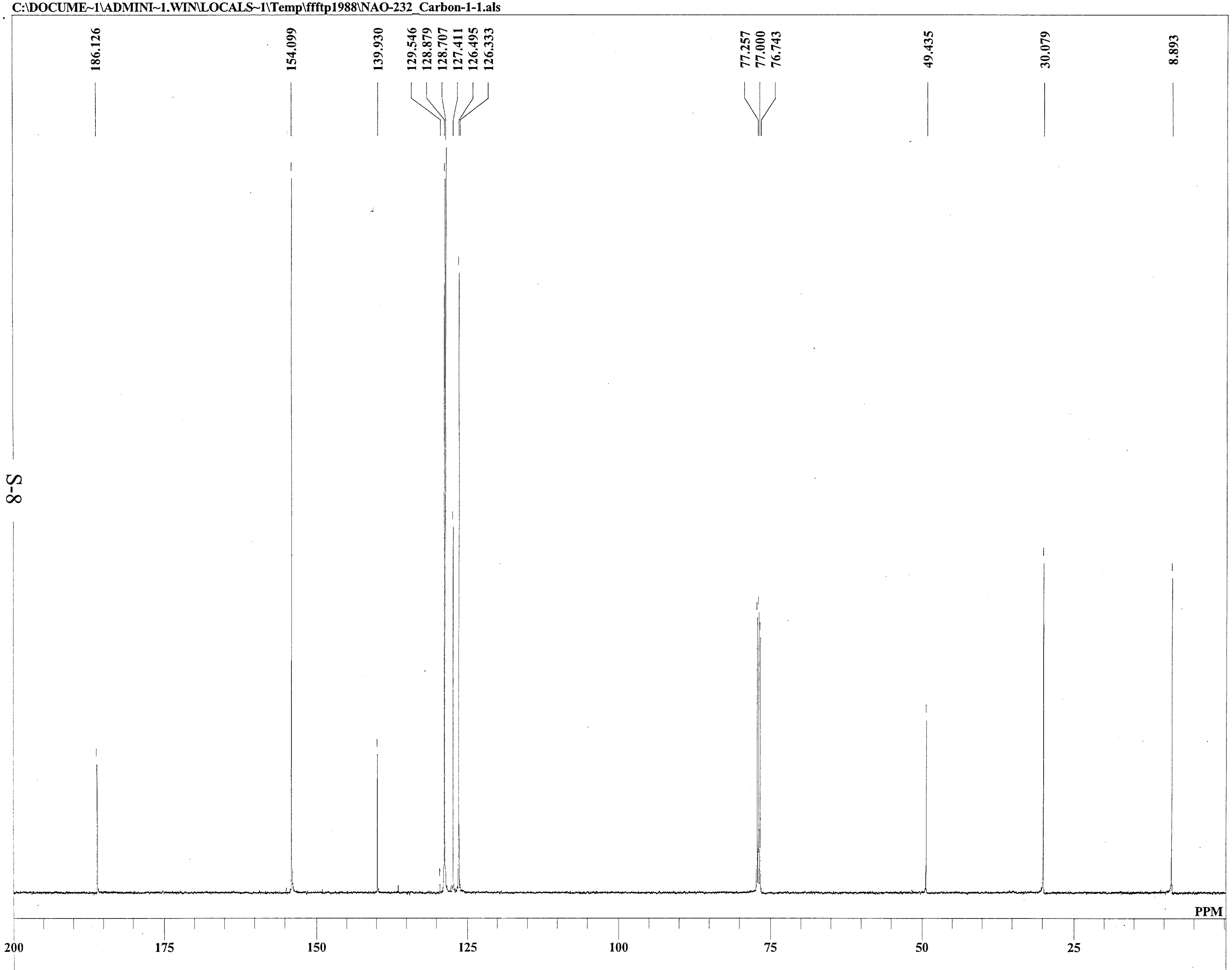

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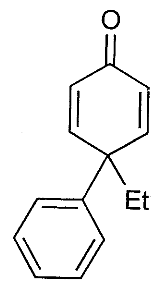
RGAIN	60



1b
^{13}C NMR
(125 MHz, $CDCl_3$)

single_pulse

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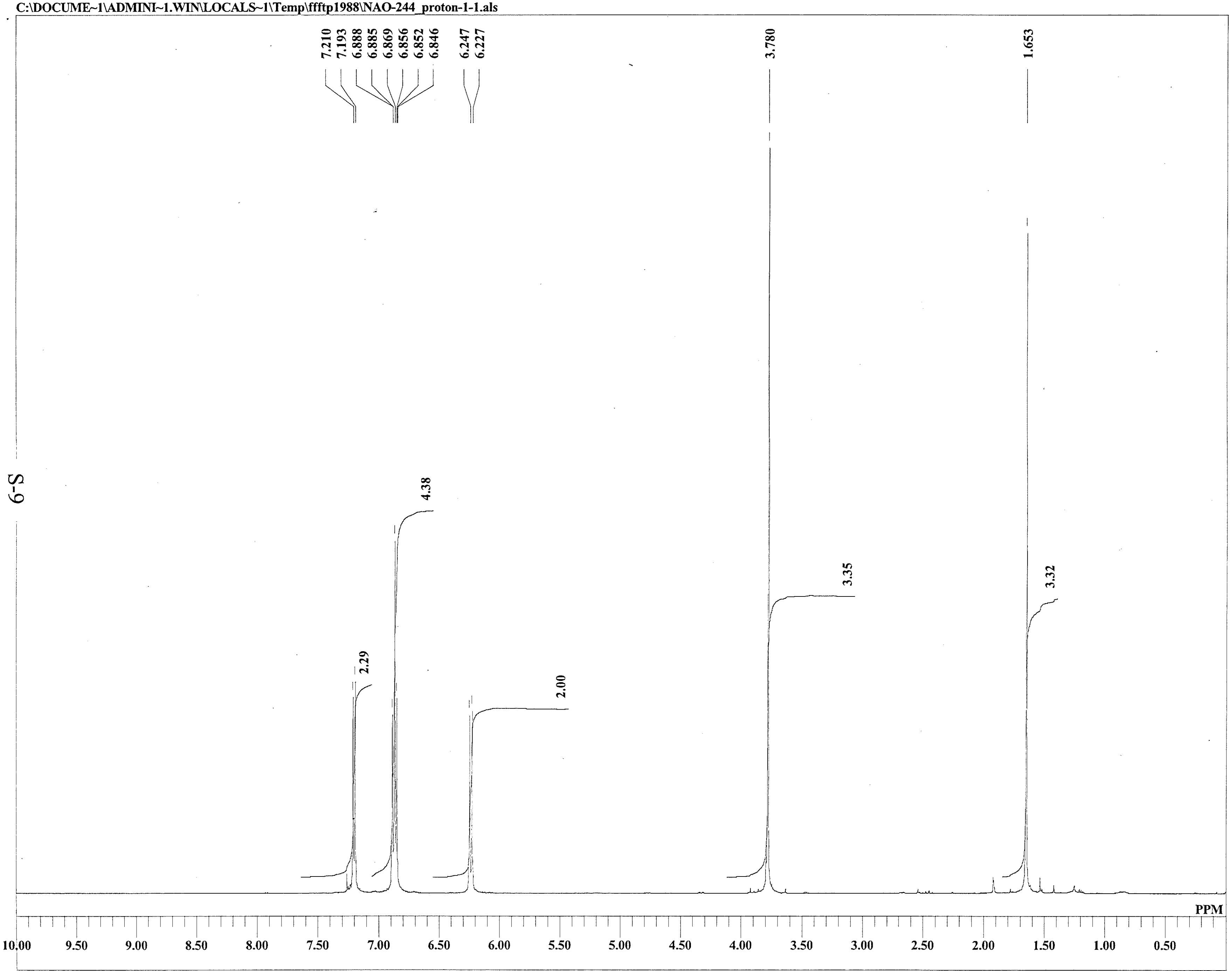

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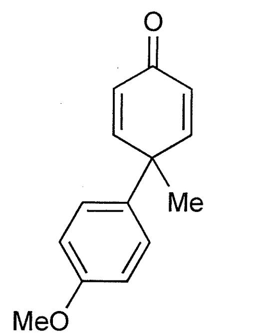
RGAIN	30



1c

^{1}H NMR

(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

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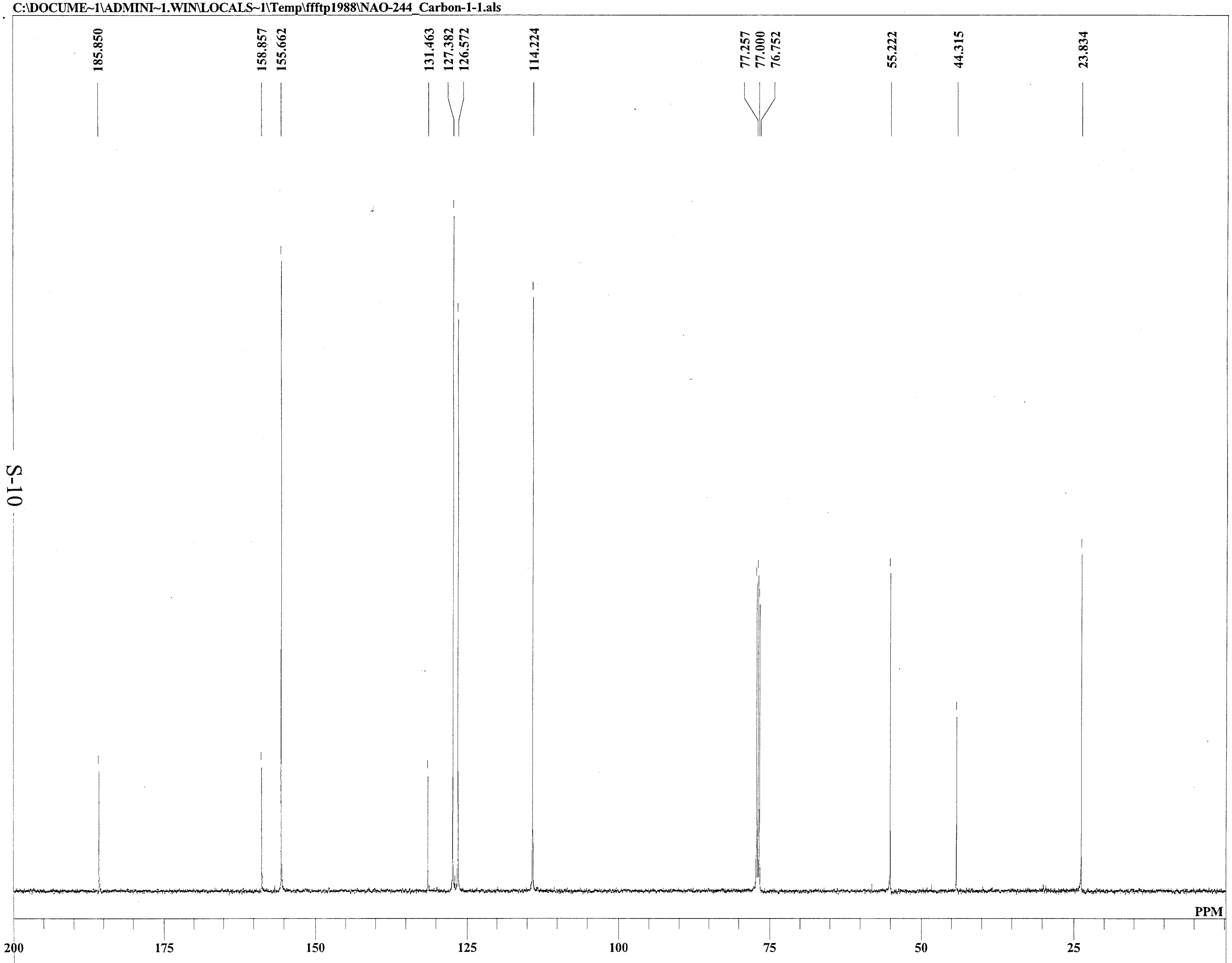

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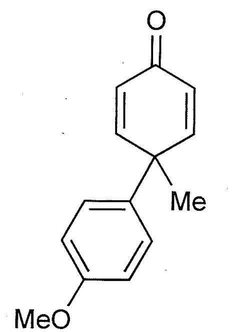
RGAIN	58



1c

^{13}C NMR

(125 MHz, $CDCl_3$)

single_pulse

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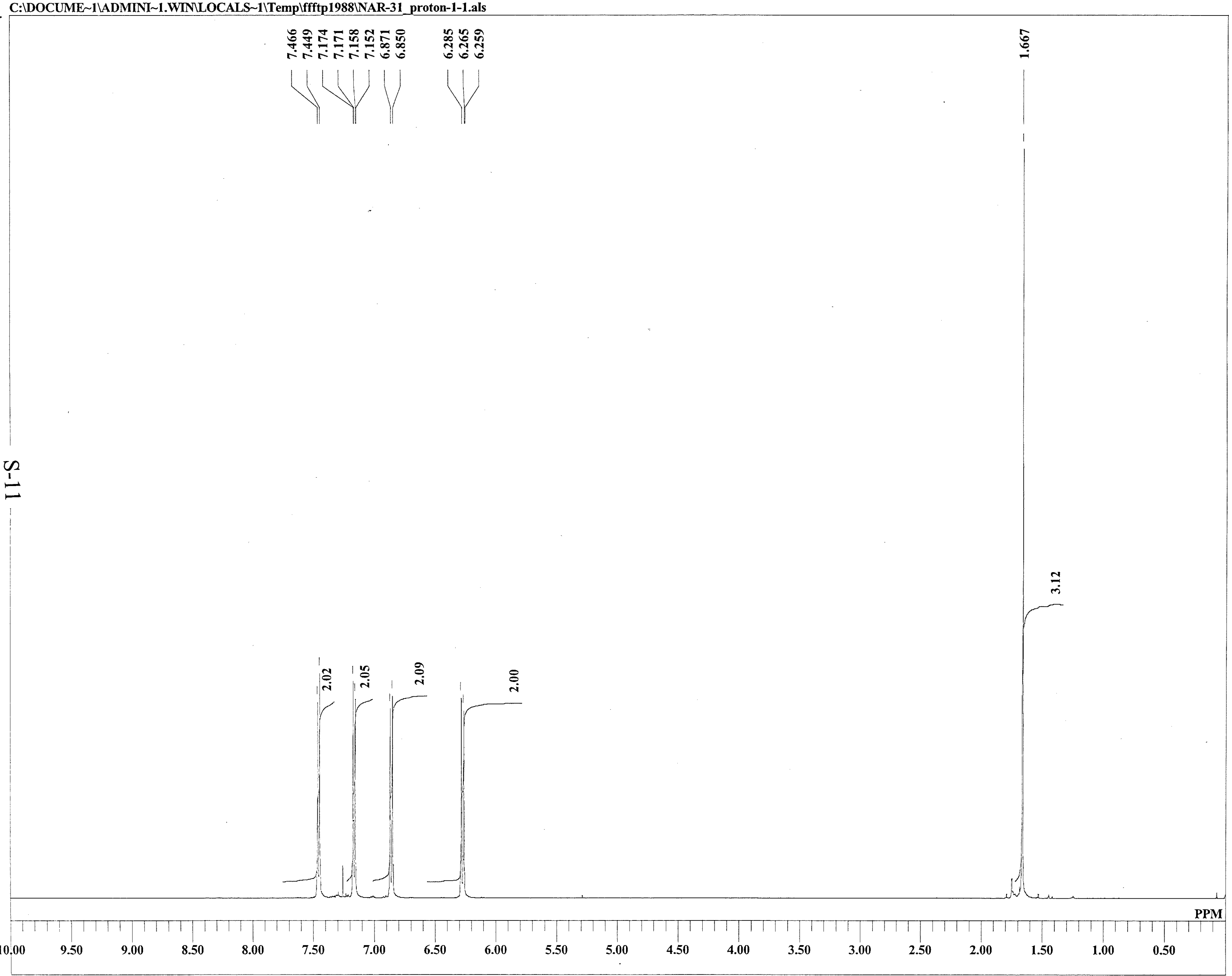

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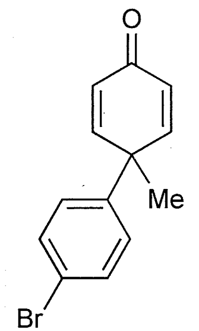

1d

^{1}H NMR

(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

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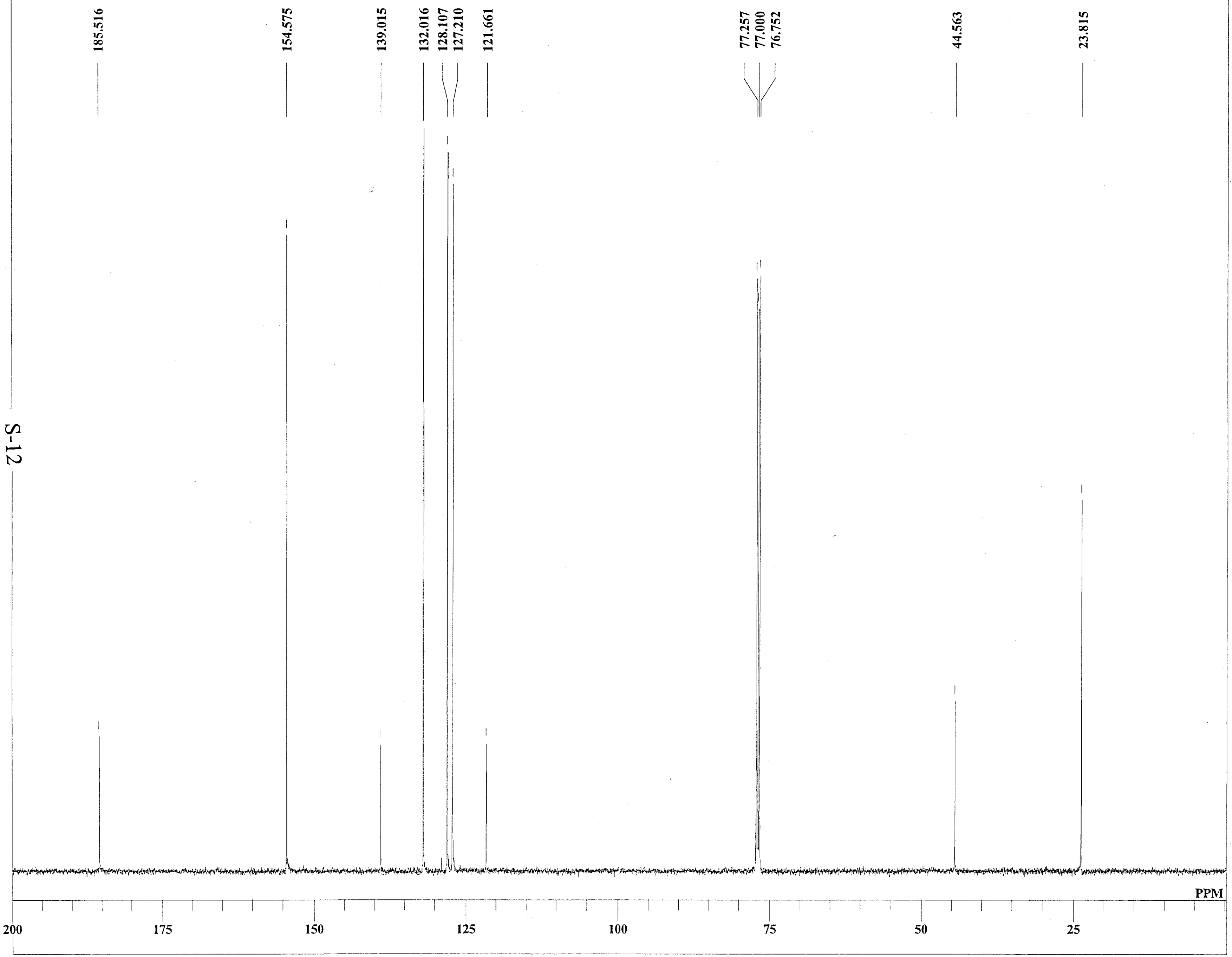

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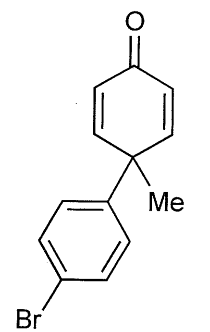
RGAIN	58



1d

^{13}C NMR

(125 MHz, $CDCl_3$)

single_pulse

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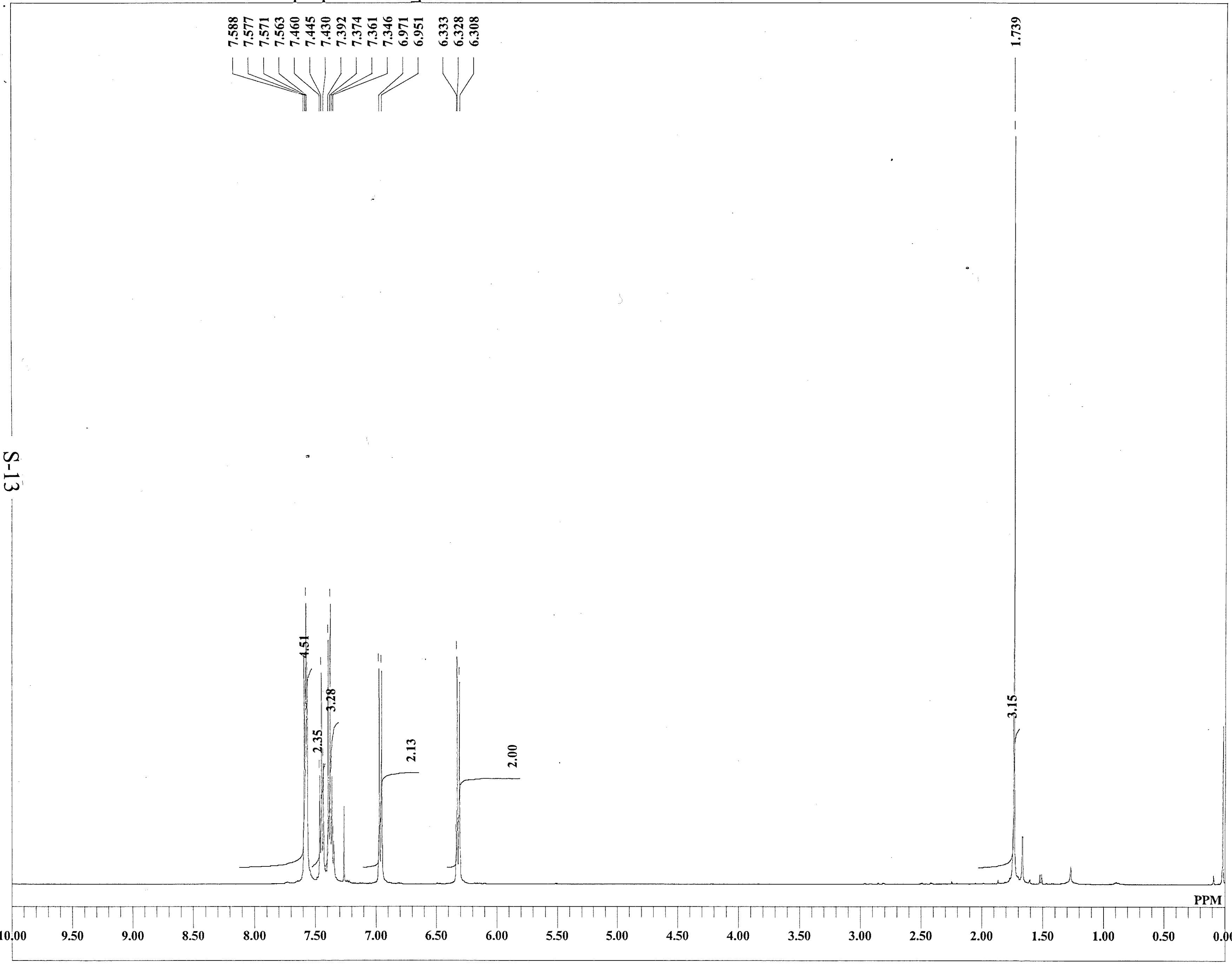

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SCANS	8
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PD	5.0000 sec
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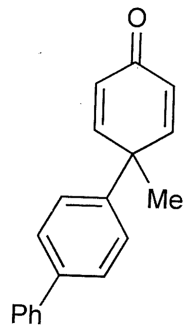
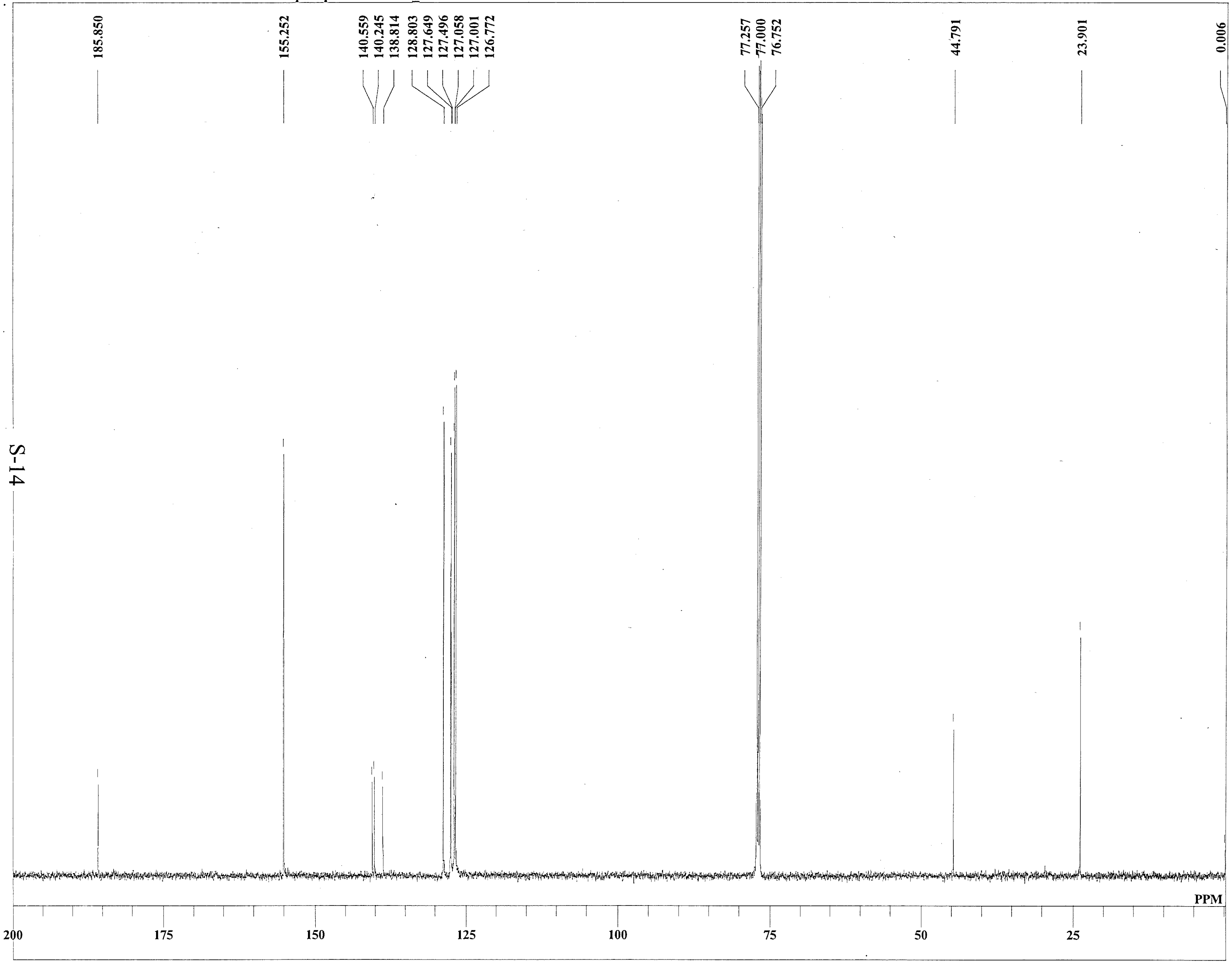
RGAIN	40



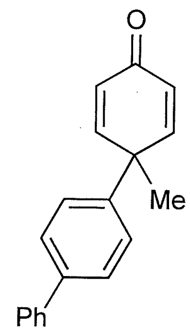
1e
^{1}H NMR
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1988\NAO-247_Carbon-1-1.als



DFILE	NAO-247_Carbon-1-1.als
COMNT	single pulse decoupled gated NOE
DATIM	2012-07-31 20:12:15
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26224
FREQU	31446.54 Hz
SCANS	512
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	23.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



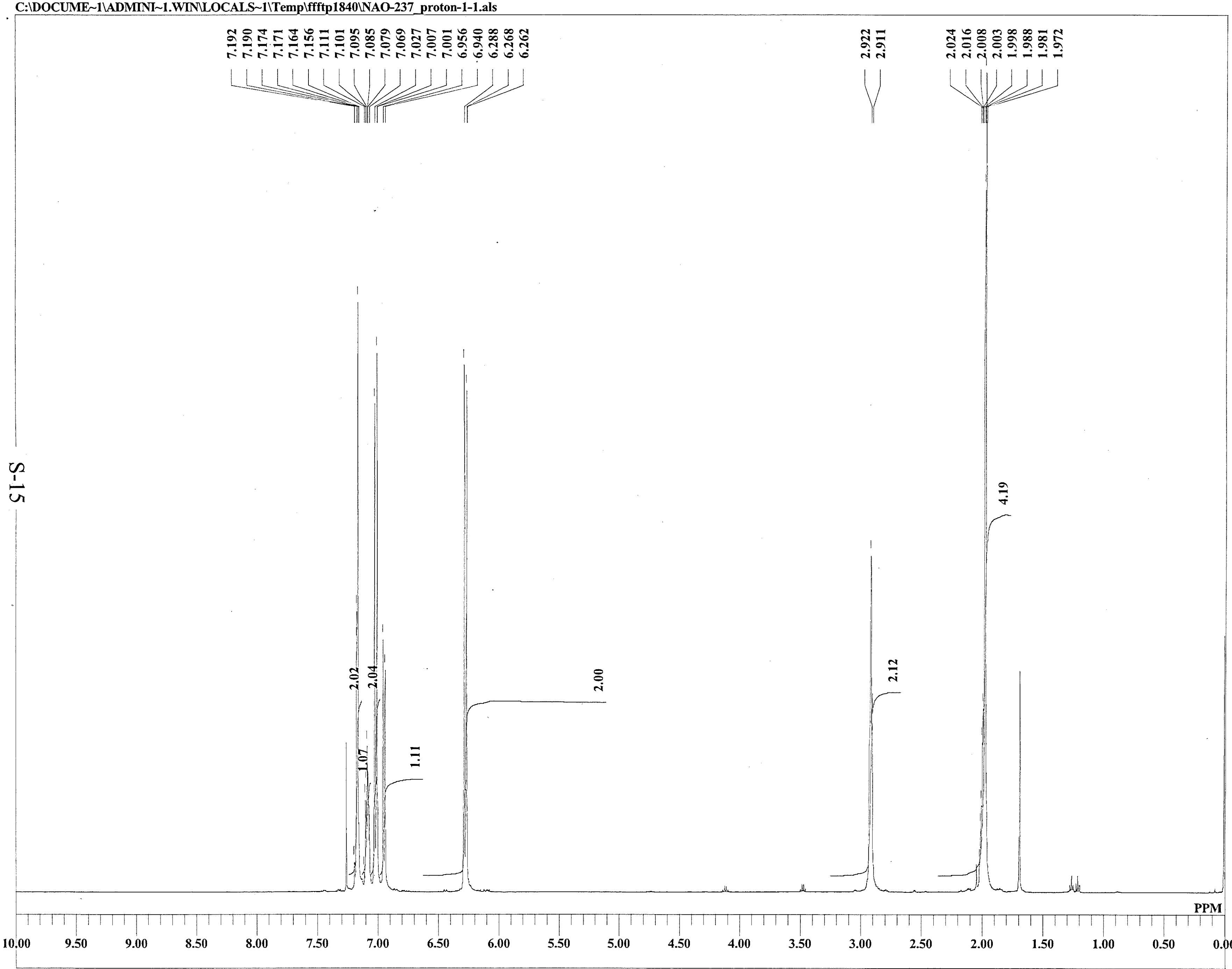
1e

^{13}C NMR

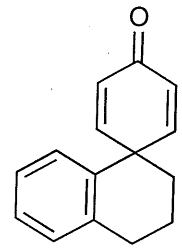
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1840\NAO-237_proton-1-1.als



DFILE	NAO-237_proton-1-1.als
COMNT	single_pulse
DATIM	2012-08-12 15:49:59
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	22.6 c
SLVNT	CDCL3
EXREF	12.51 ppm
BF	0.12 Hz
RGAIN	40



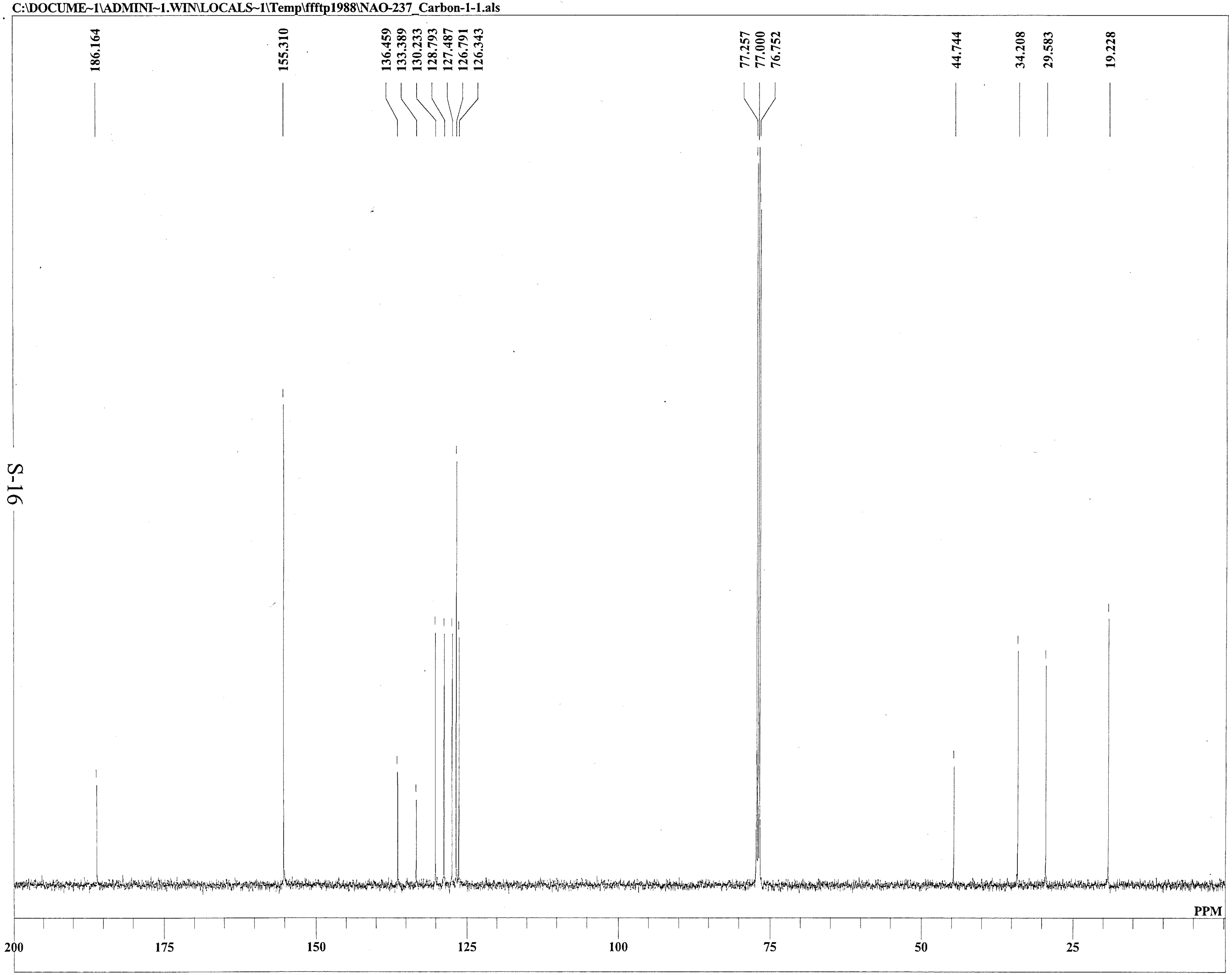
1f

^{1}H NMR

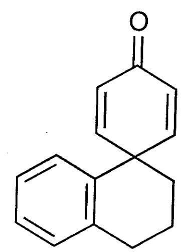
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1988\NAO-237_Carbon-1-1.als



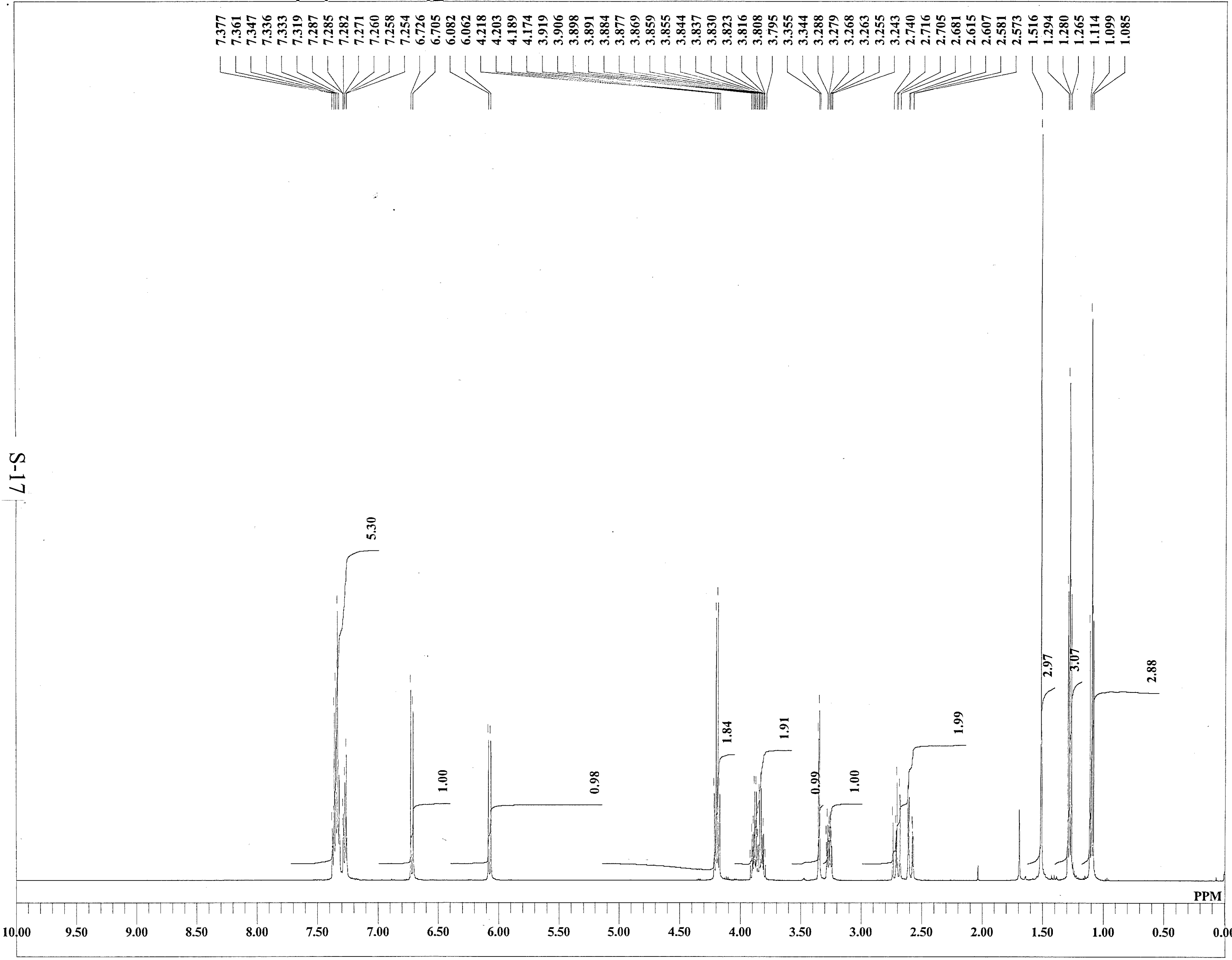
DFILE	NAO-237_Carbon-1-1.als
COMNT	single pulse decoupled gated NOE
DATIM	2012-08-12 15:58:20
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26224
FREQU	31446.54 Hz
SCANS	256
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	23.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



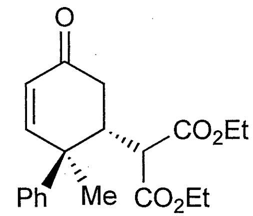
1f
^{13}C NMR
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1840\MYY-830-up_proton-1-1.als



DFILE	MYY-830-up_proton-1-1.als
COMNT	single_pulse
DATIM	2012-07-28 15:55:23
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	22.4 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	34



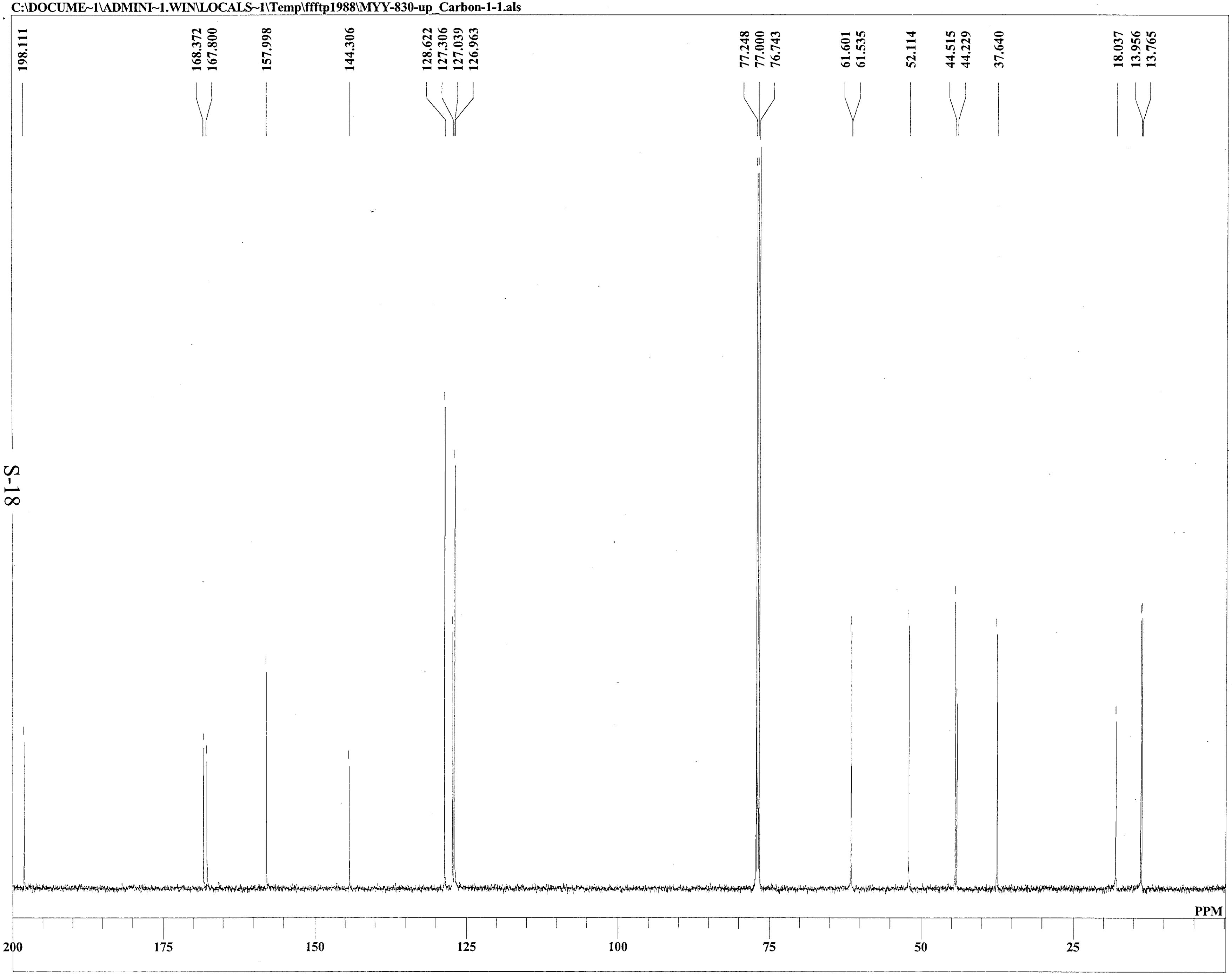
3a

^1H NMR

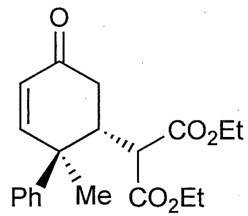
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1988\MYY-830-up_Carbon-1-1.als



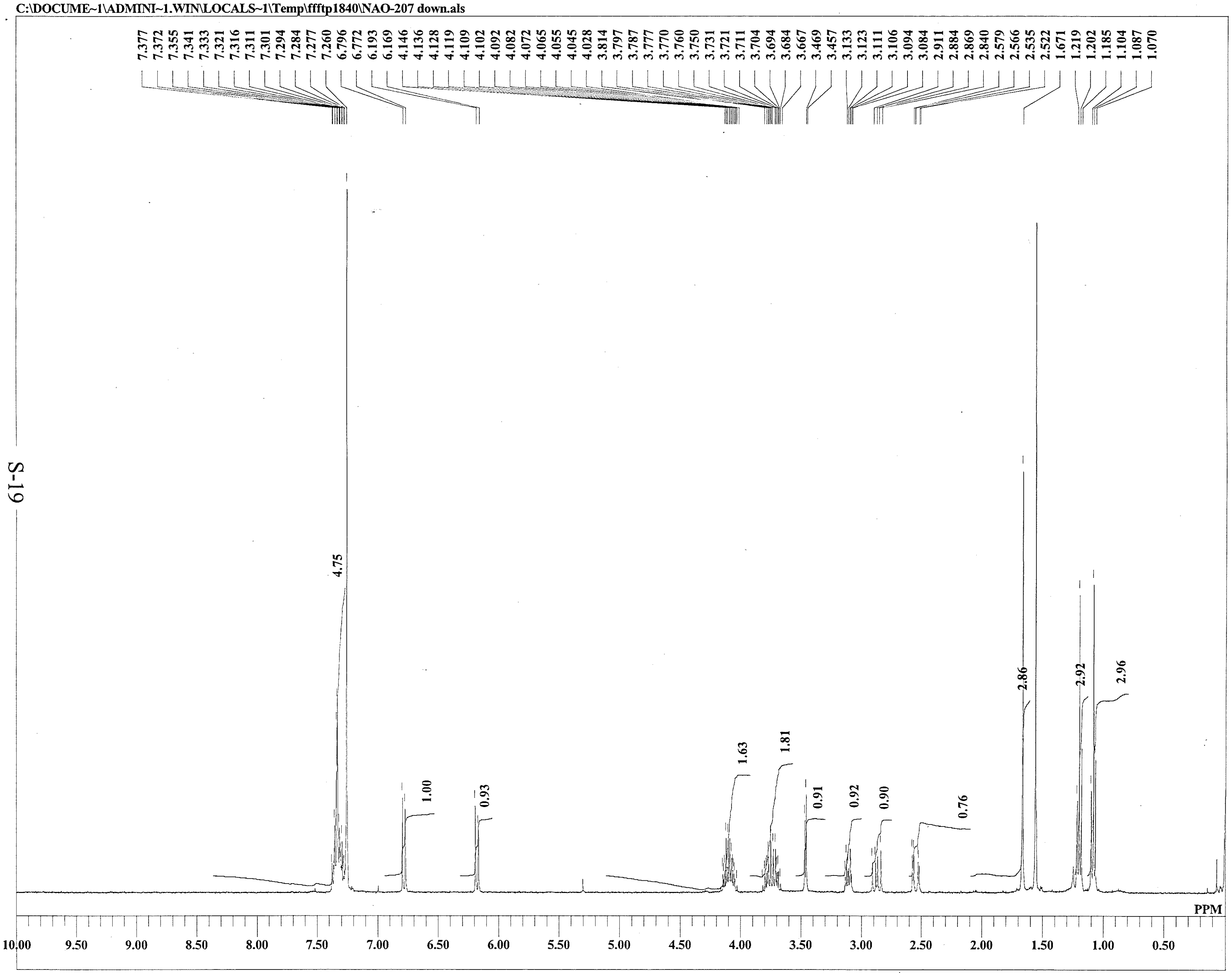
DFILE	MYY-830-up_Carbon-1-1.als
COMNT	single pulse decoupled gated NOE
DATIM	2012-07-28 16:02:42
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26224
FREQU	31446.54 Hz
SCANS	512
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



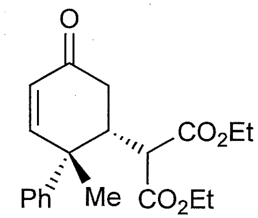
3a

^{13}C NMR

(125 MHz, $CDCl_3$)



DFILE	NAO-207 down.als
COMNT	
DATIM	Sat Jan 21 21:45:47 2012
OBNUC	1H
EXMOD	non
OBFRQ	399.65 MHz
OBSET	0.00 KHz
OBFIN	134300.00 Hz
POINT	8192
FREQU	7993.60 Hz
SCANS	16
ACQTM	1.0248 sec
PD	5.9752 sec
PW1	4.45 usec
IRNUC	1H
CTEMP	18.6 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	28



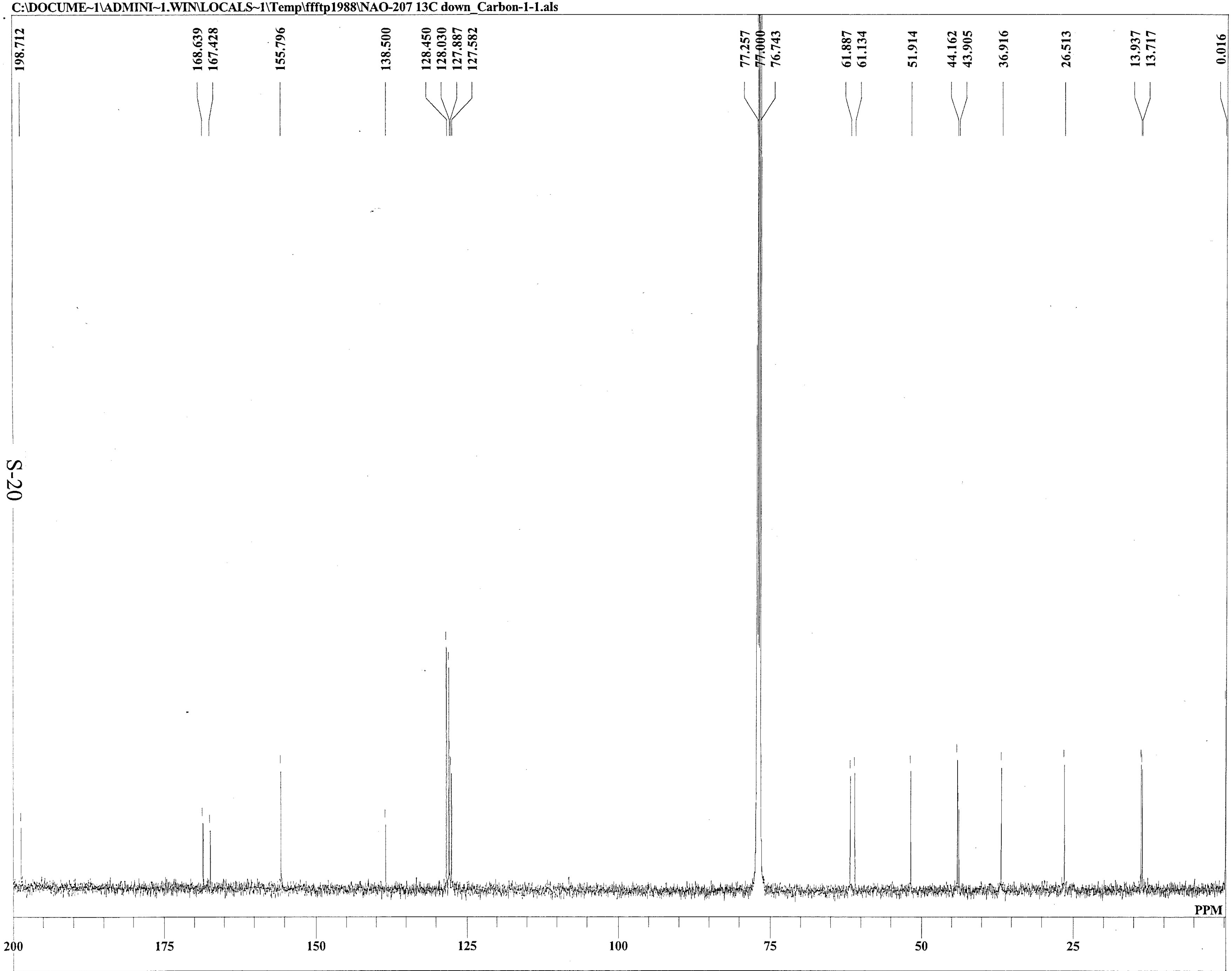
4a

^1H NMR

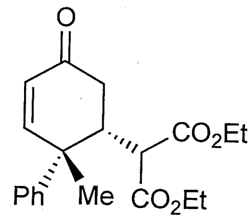
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1988\NAO-207 13C down_Carbon-1-1.als



DFILE	NAO-207 13C down_Carbon-1-1.als
COMNT	single pulse decoupled gated NOE
DATIM	2012-02-05 00:51:11
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26224
FREQU	31446.54 Hz
SCANS	11264
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	17.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	54



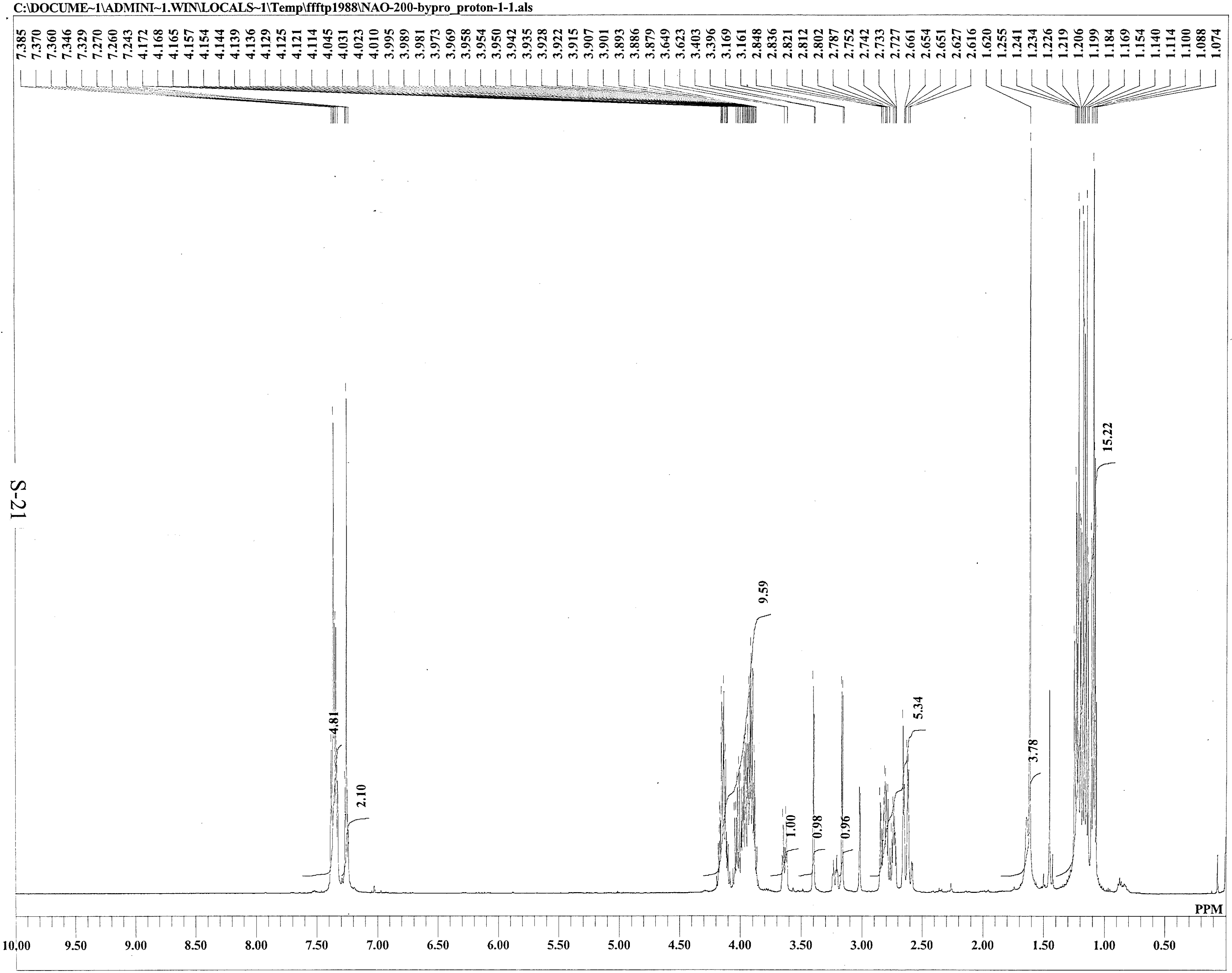
4a

^{13}C NMR

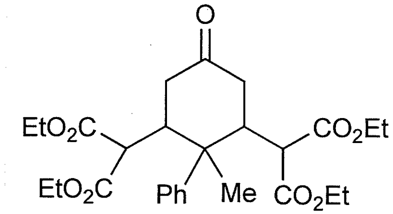
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1988\NAO-200-bypro_proton-1-1.als



DFILE	NAO-200-bypro_proton-1-1.als
COMNT	single_pulse
DATIM	2012-10-22 21:33:21
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	19.4 c
SLVNT	CDCL3
EXREF	12.51 ppm
BF	0.12 Hz
RGAIN	38



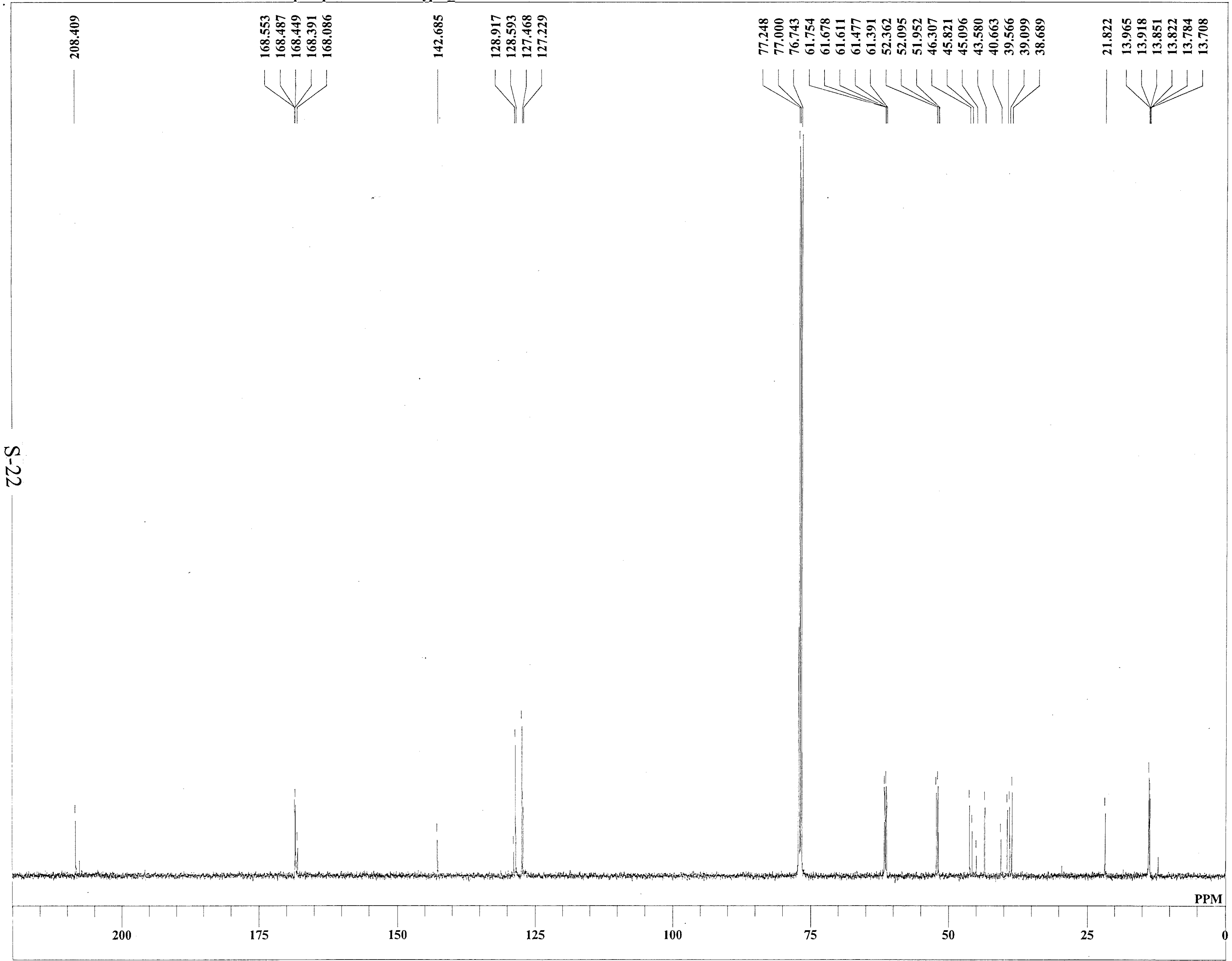
5

^1H NMR

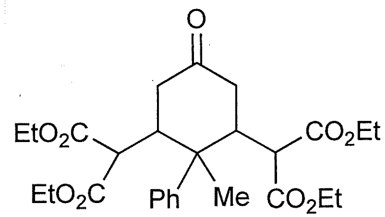
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1988\NAO-200-bypro_Carbon-1-1.als



DFILE	NAO-200-bypro_Carbon-1-1.als
COMNT	single pulse decoupled gated NOE
DATIM	2012-10-22 21:40:45
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26224
FREQU	31446.54 Hz
SCANS	512
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	19.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

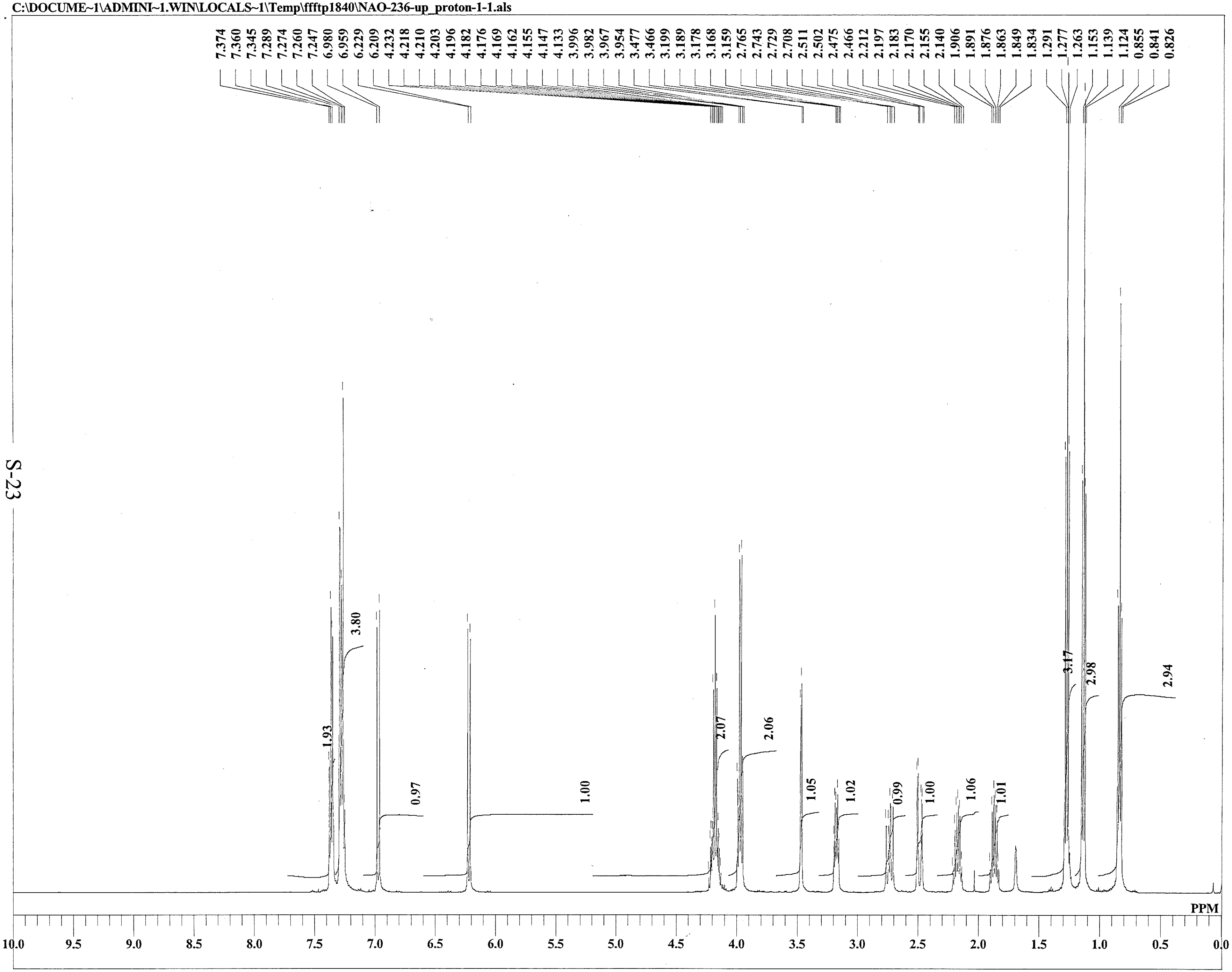


5

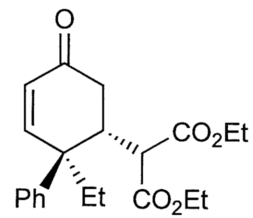
^{13}C NMR

(125 MHz, $CDCl_3$)

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1840\NAO-236-up_proton-1-1.als



DFILE	NAO-236-up_proton-1-1.als
COMNT	
DATIM	2012-07-19 09:25:55
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	22.1 c
SLVNT	CDCL3
EXREF	12.51 ppm
BF	0.12 Hz
RGAIN	34



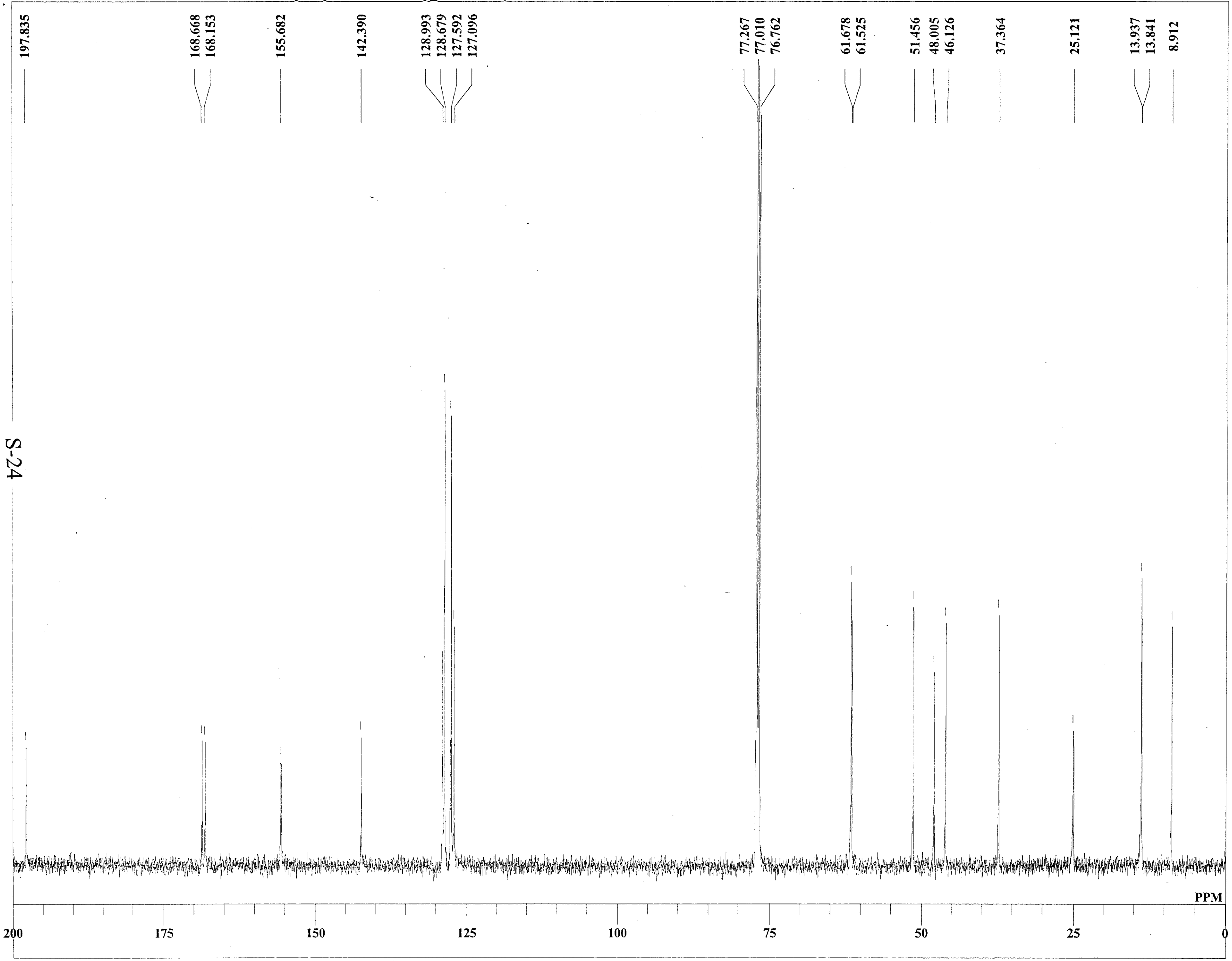
3b

^1H NMR

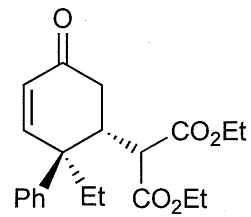
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1988\NAO-236-up_Carbon-1-1.jdf



DFILE	NAO-236-up_Carbon-1-1.jdf
COMNT	single pulse decoupled gated NOE
DATIM	2012-07-19 09:29:27
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32780
FREQU	39308.18 Hz
SCANS	512
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	22.9 c
SLVNT	NONE
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



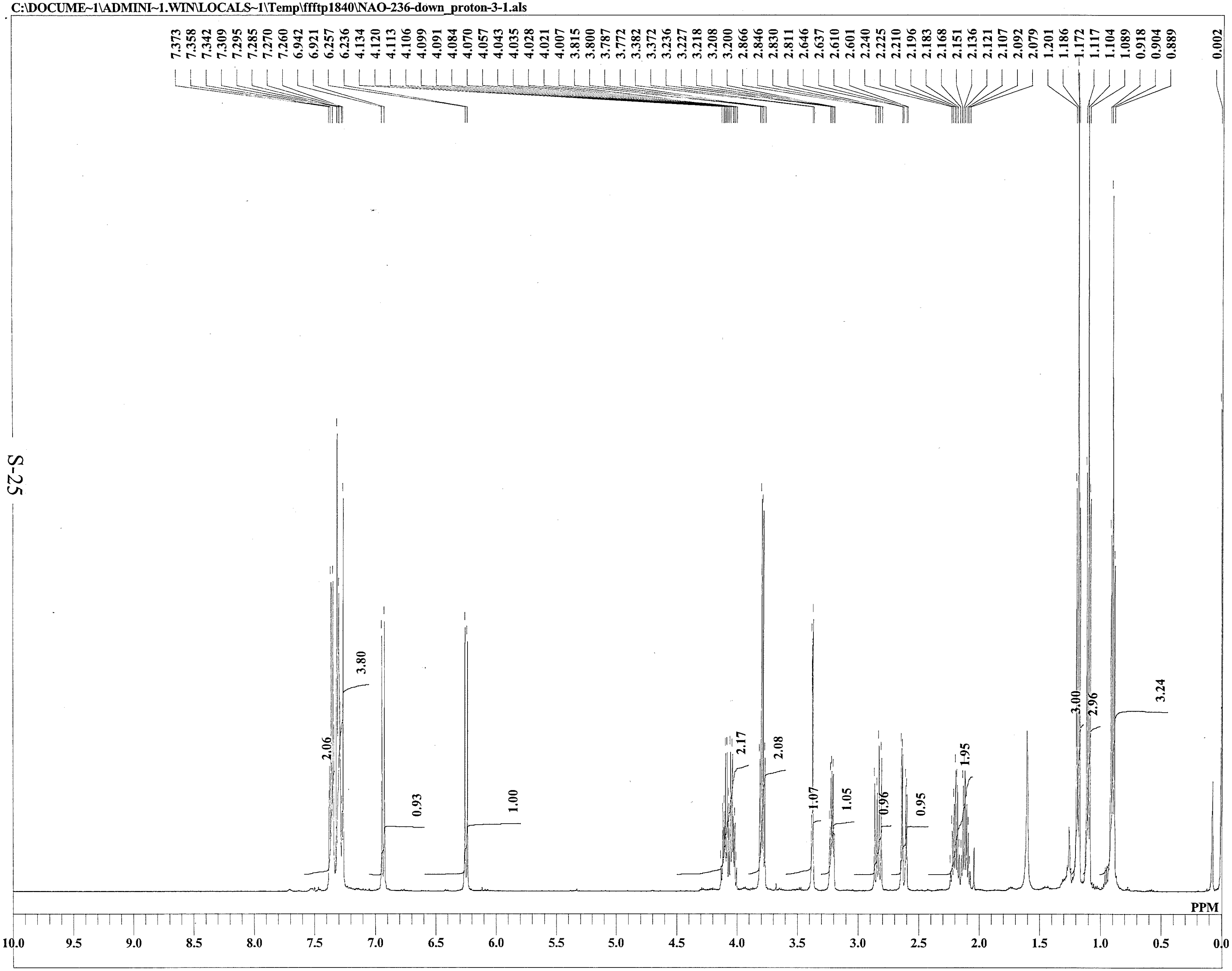
3b

^{13}C NMR

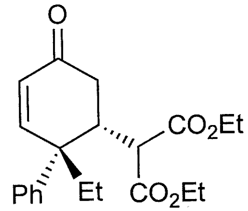
(125 MHz, $CDCl_3$)

NAO-236-syn

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1840\NAO-236-down_proton-3-1.als



DFILE	NAO-236-down_proton-3-1.als
COMNT	NAO-236-syn
DATIM	2012-08-07 23:31:08
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	23.4 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	44



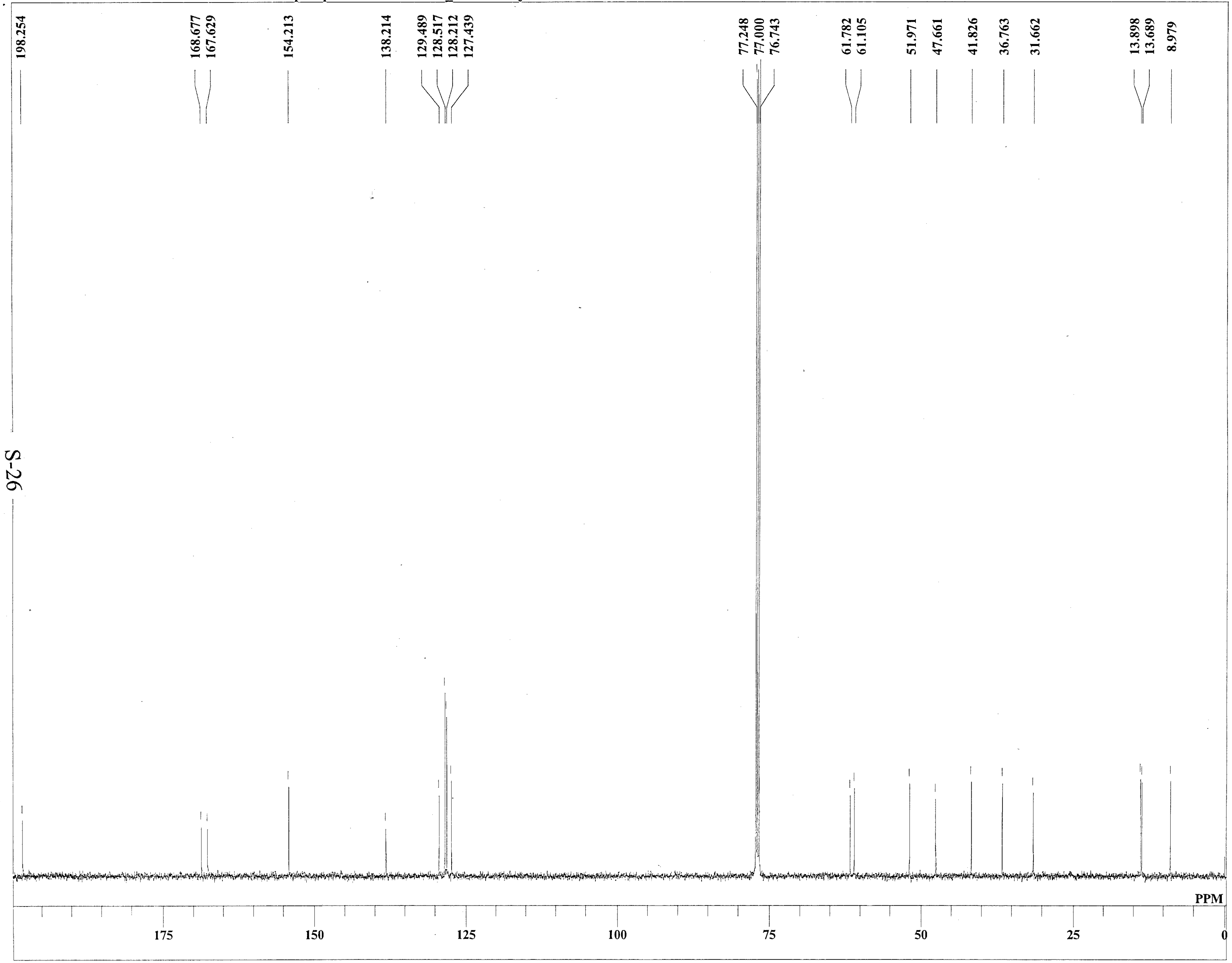
4b

^{1}H NMR

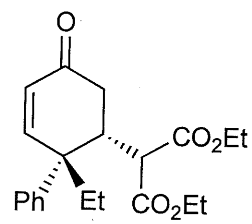
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1988\NAO-236-down_Carbon-1-1.jdf



DFILE	NAO-236-down_Carbon-1-1.jdf
COMNT	single pulse decoupled gated NOE
DATIM	2012-08-07 23:38:60
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32780
FREQU	39308.18 Hz
SCANS	512
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	24.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	58



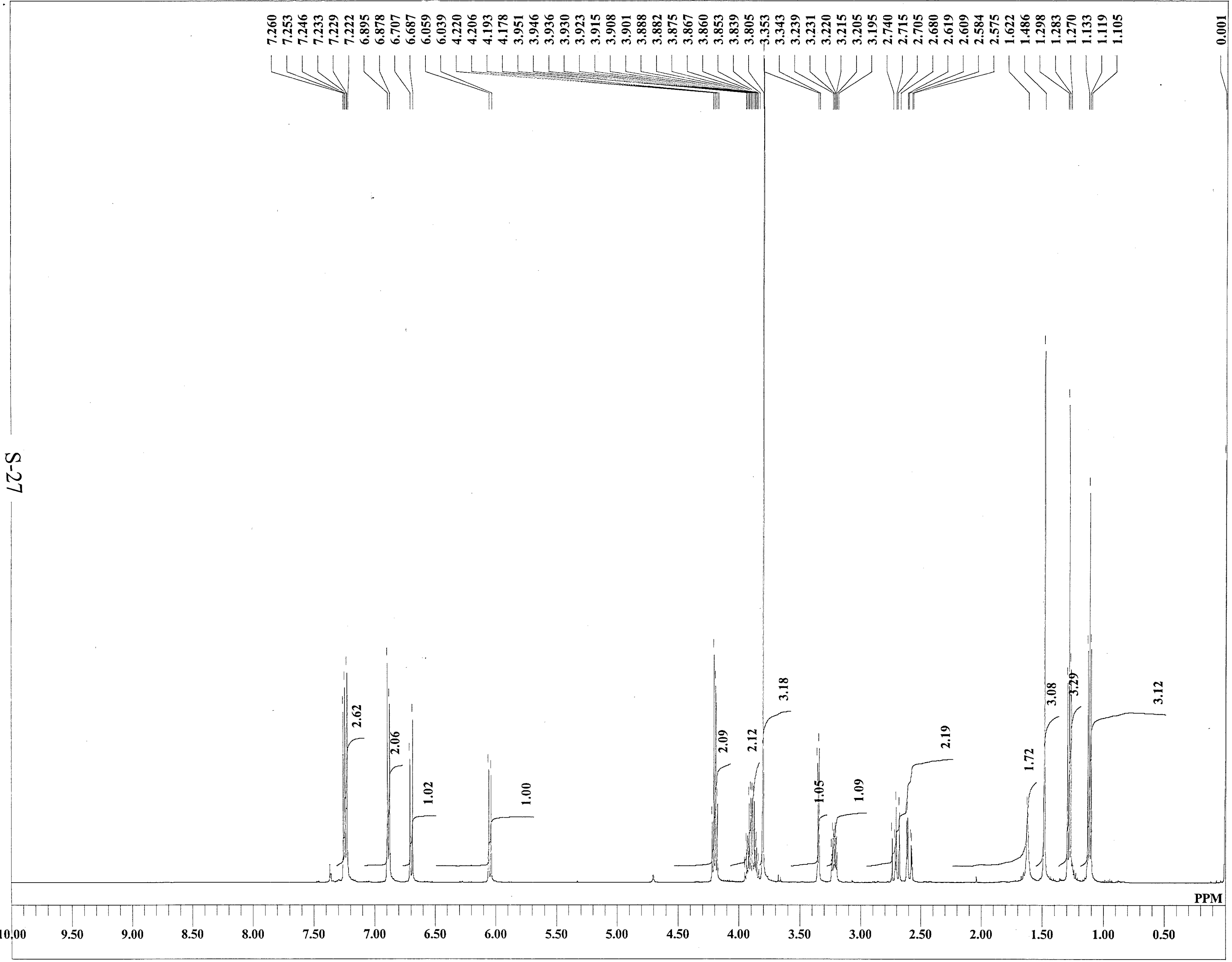
4b

^{13}C NMR

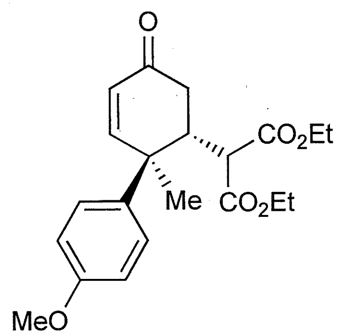
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-245-up_proton-4-1.als



DFILE	NAO-245-up_proton-4-1.als
COMNT	single_pulse
DATIM	2012-07-25 00:09:03
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	22.8 c
SLVNT	CDCL3
EXREF	12.51 ppm
BF	0.12 Hz
RGAIN	42



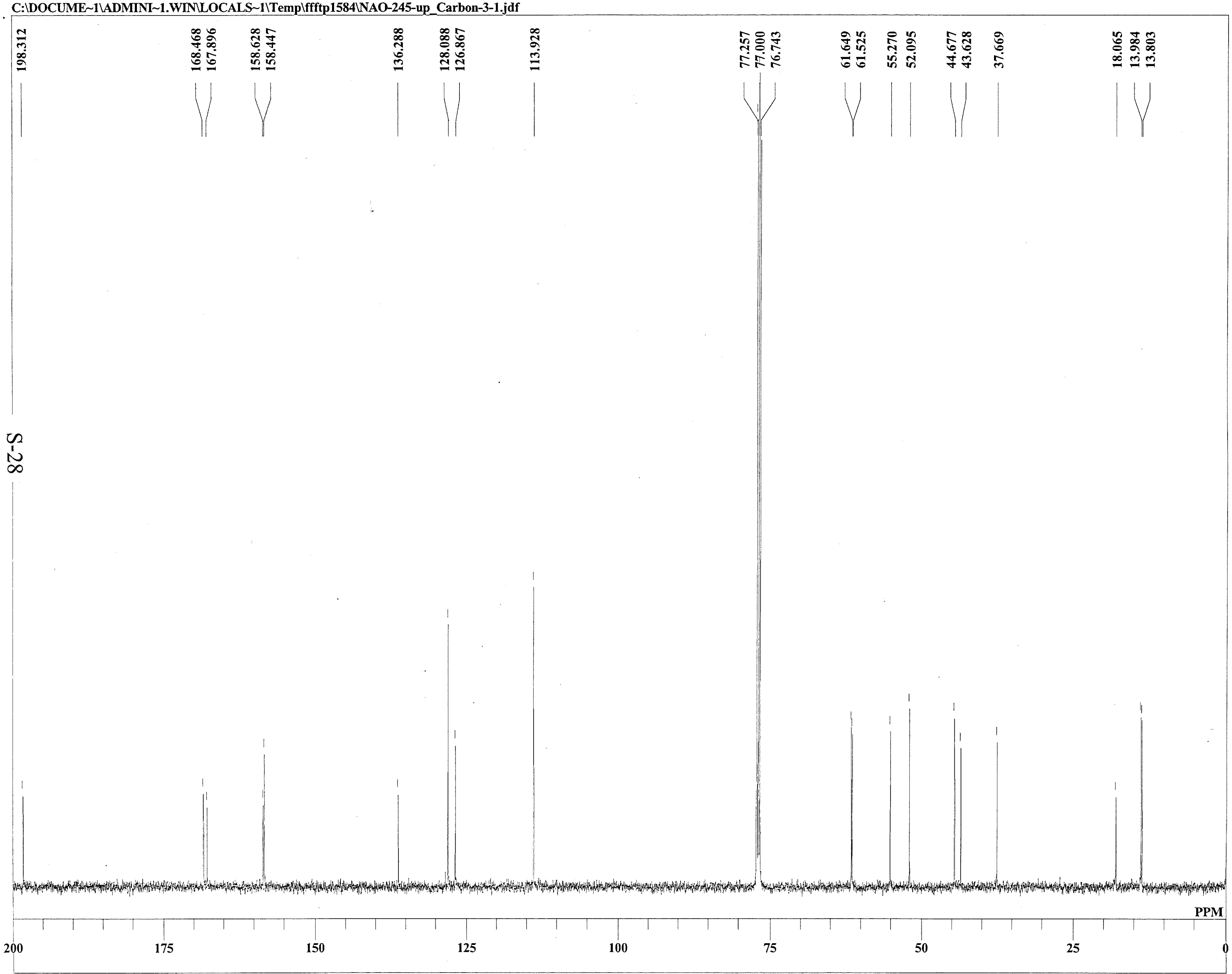
3c

^1H NMR

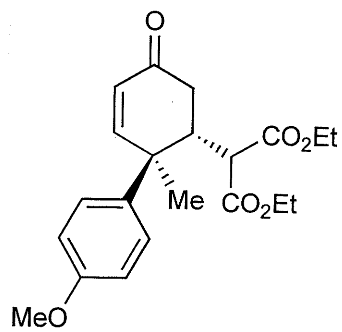
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-245-up_Carbon-3-1.jdf



DFILE	NAO-245-up_Carbon-3-1.jdf
COMNT	single pulse decoupled gated NOE
DATIM	2012-07-24 22:31:60
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32780
FREQU	39308.18 Hz
SCANS	256
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	22.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



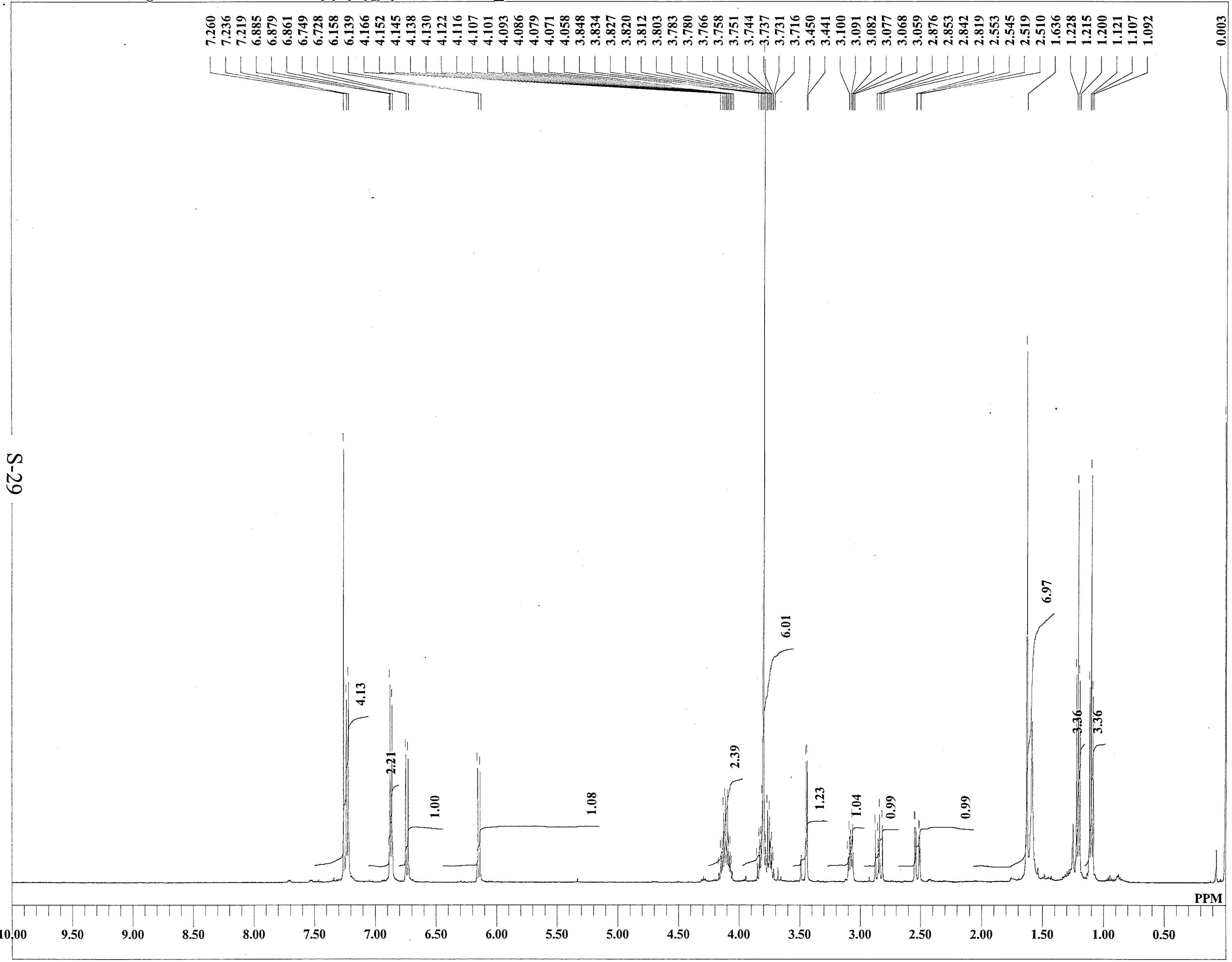
3c

^{13}C NMR

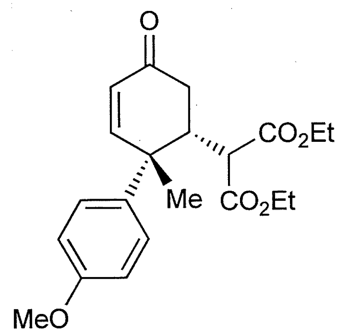
(125 MHz, $CDCl_3$)

single_pulse

C:\Documents and Settings\Administrator.WIN-CRYST\ffXfNfgfbfv\NAO-245-down_proton-5-1.als



DFILE	NAO-245-down_proton-5-1.als
COMNT	single_pulse
DATIM	2012-08-30 11:55:45
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	22.3 c
SLVNT	CDCL3
EXREF	12.51 ppm
BF	0.12 Hz
RGAIN	48



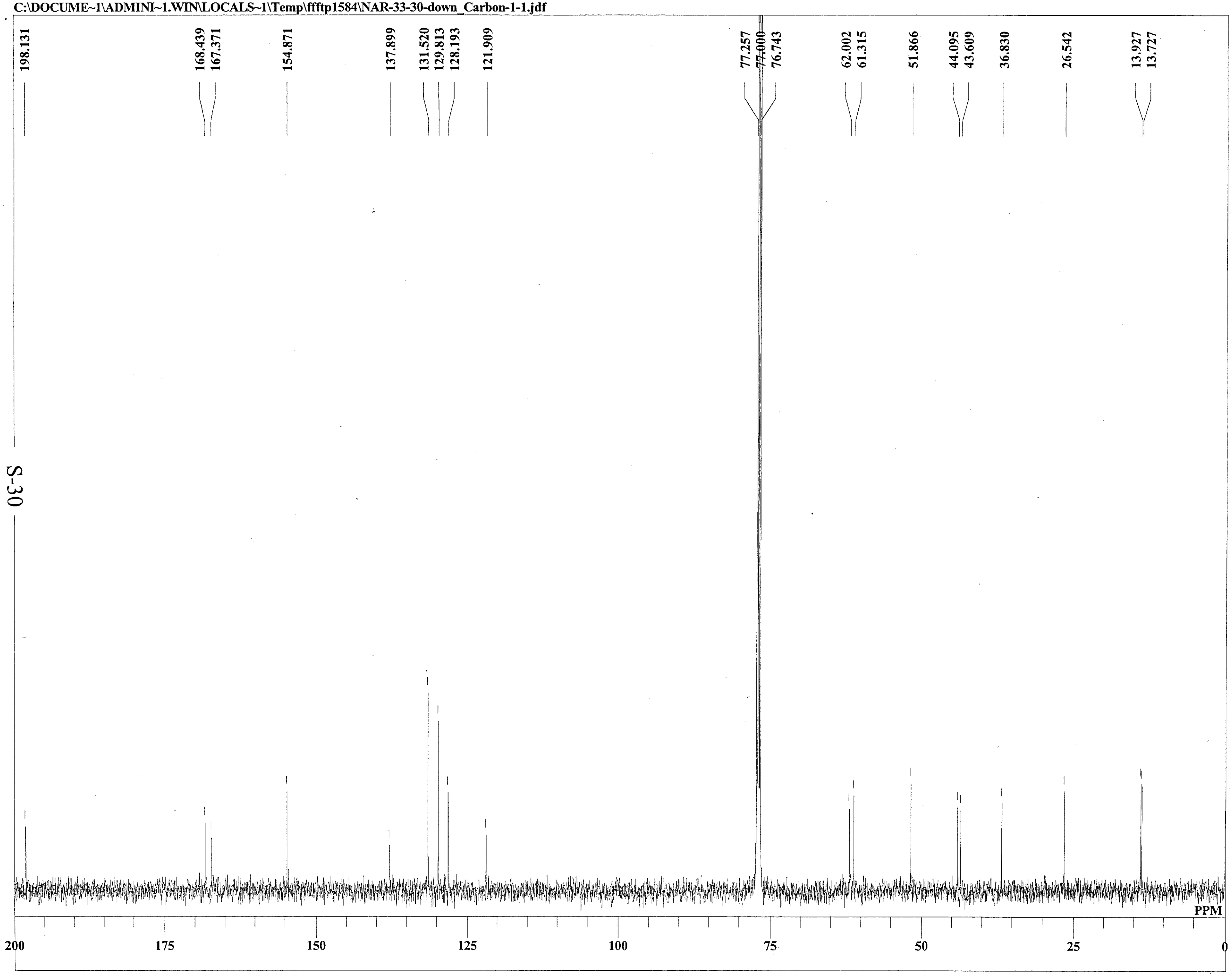
4c

^1H NMR

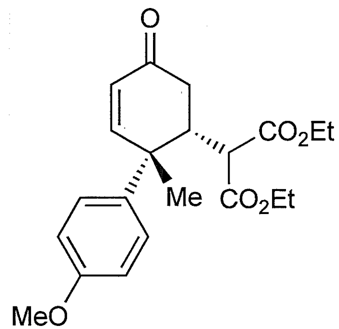
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAR-33-30-down_Carbon-1-1.jdf



DFILE	NAR-33-30-down_Carbon-1-1.jdf
COMNT	single pulse decoupled gated NOE
DATIM	2012-08-22 20:41:05
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32780
FREQU	39308.18 Hz
SCANS	1024
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	23.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	56



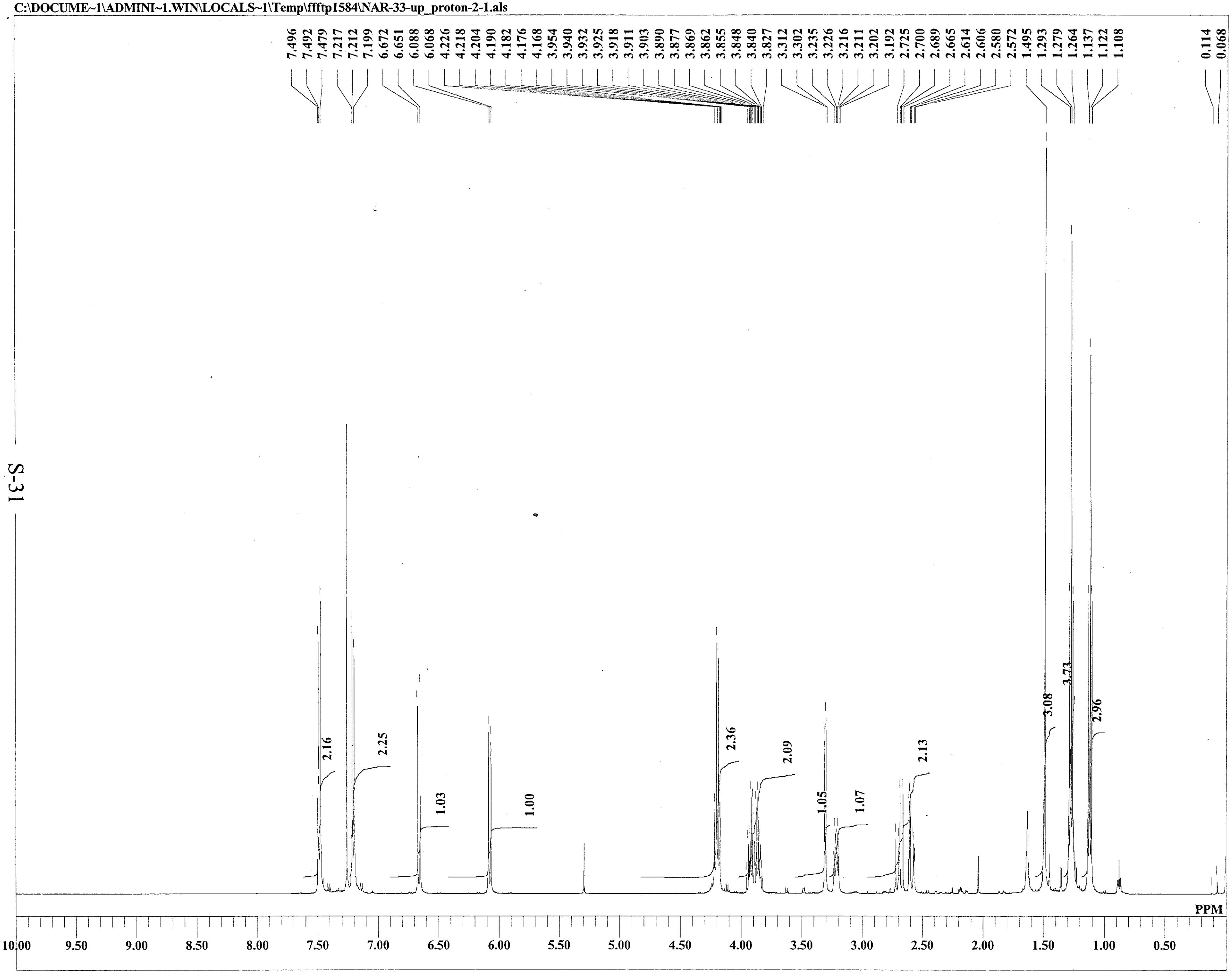
4c

^{13}C NMR

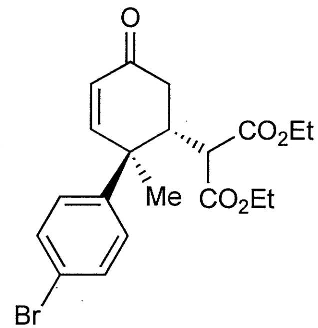
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAR-33-up_proton-2-1.als



DFILE NAR-33-up_proton-2-1.als
COMNT single_pulse
DATIM 2012-09-28 22:44:38
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13120
FREQU 7507.51 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 4.68 usec
IRNUC 1H
CTEMP 20.4 c
SLVNT CDCL3
EXREF 12.51 ppm
BF 0.12 Hz
RGAIN 40



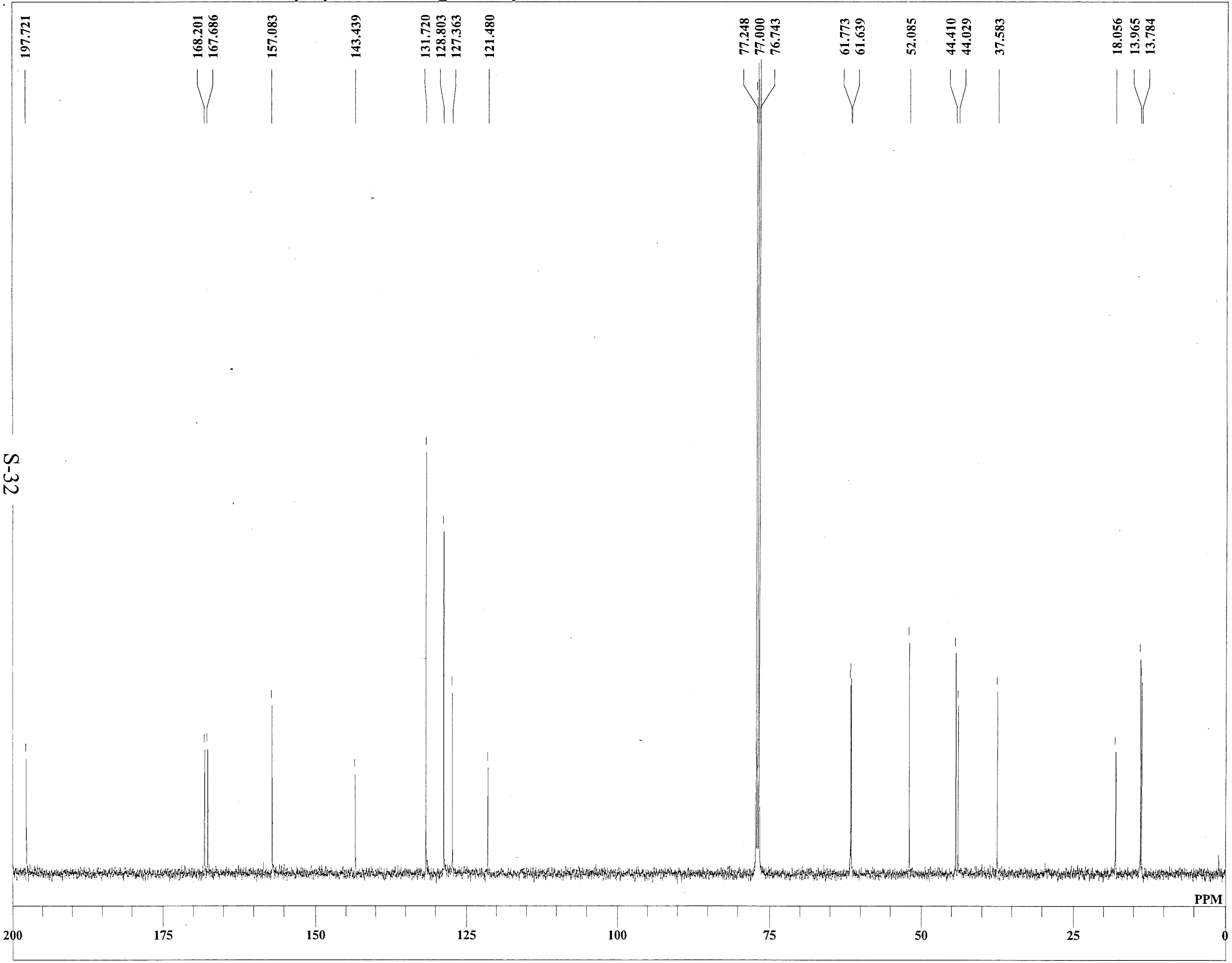
3d

^1H NMR

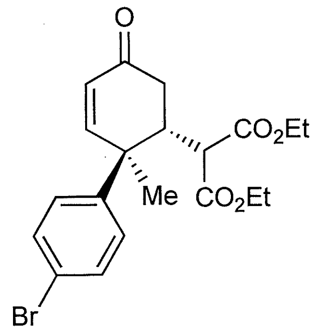
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAR-33-12-13_Carbon-1-1.jdf



DFILE	NAR-33-12-13_Carbon-1-1.jdf
COMNT	single pulse decoupled gated NOE
DATIM	2012-08-22 20:13:16
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32780
FREQU	39308.18 Hz
SCANS	256
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	23.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



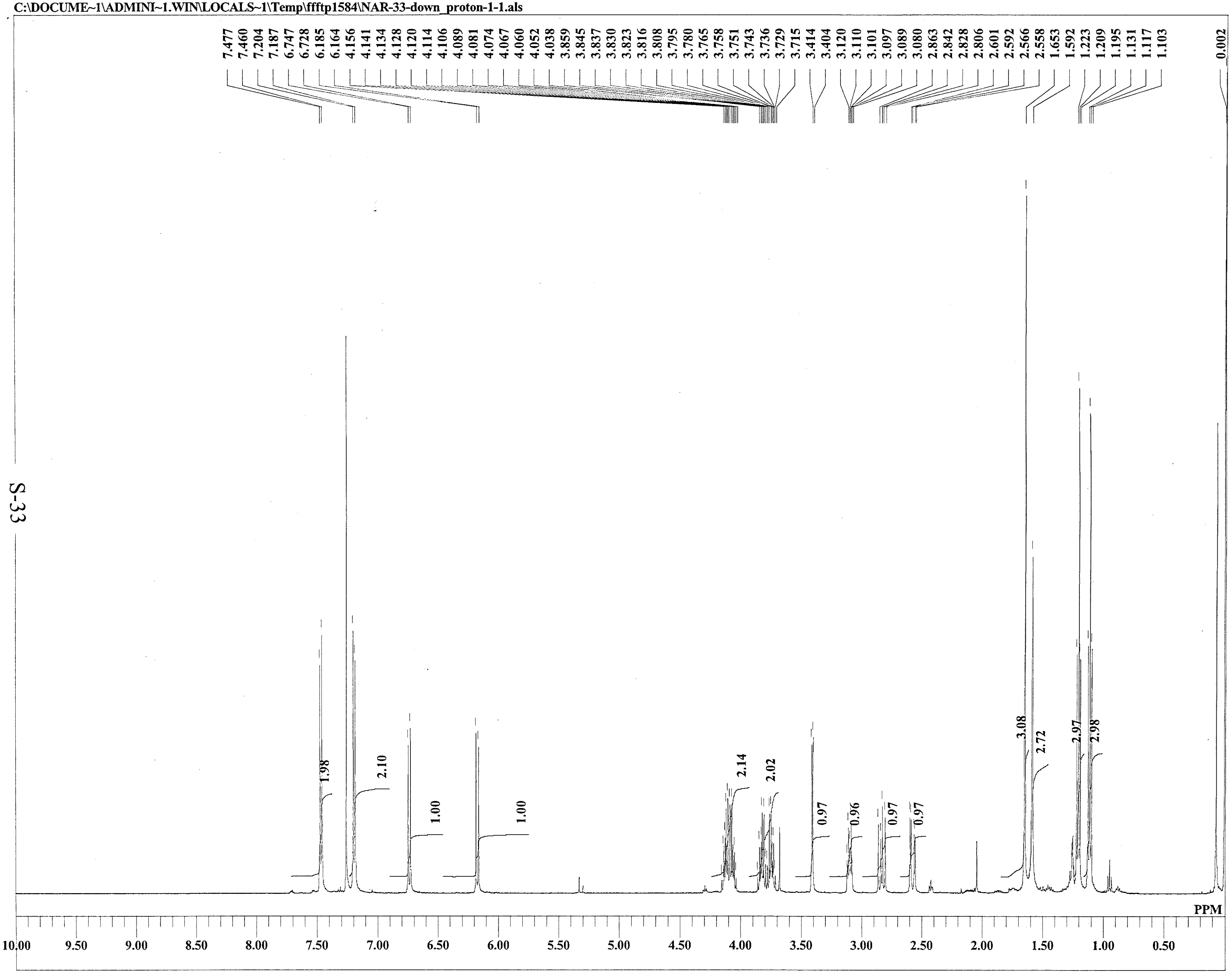
3d

^{13}C NMR

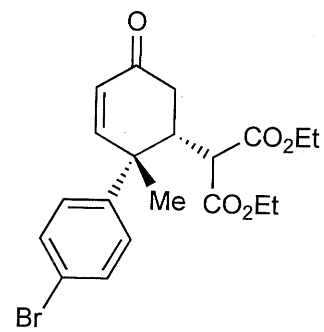
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAR-33-down_proton-1-1.als



DFILE	NAR-33-down_proton-1-1.als
COMNT	single_pulse
DATIM	2012-09-29 09:32:22
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	20.2 c
SLVNT	CDCL3
EXREF	12.51 ppm
BF	0.12 Hz
RGAIN	50



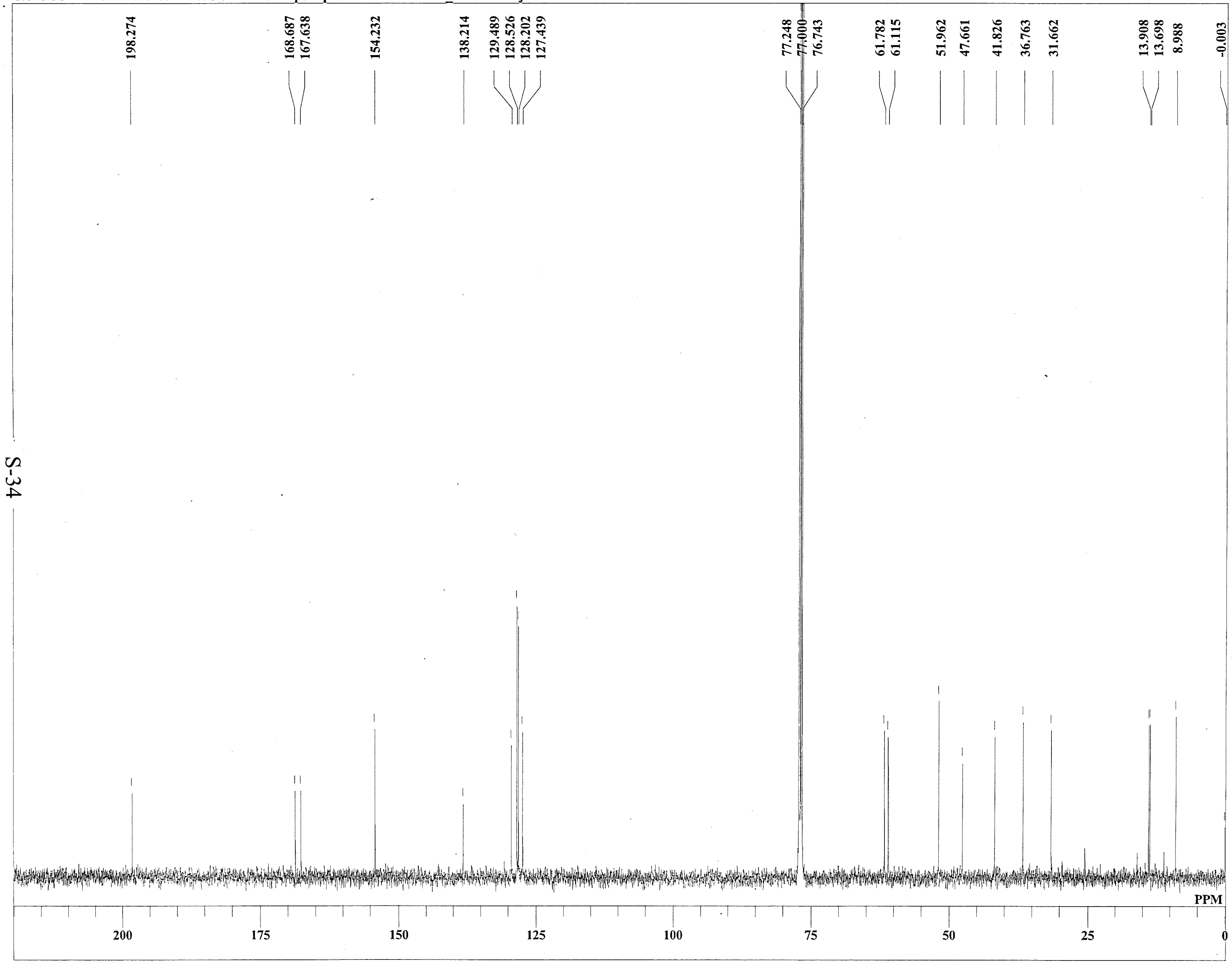
4d

^1H NMR

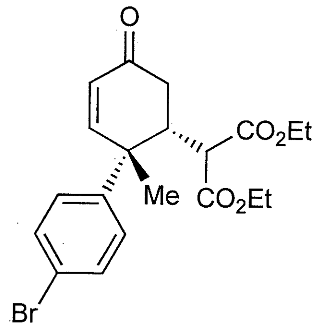
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-245-down_Carbon-1-1.jdf



DFILE	NAO-245-down_Carbon-1-1.jdf
COMNT	single pulse decoupled gated NOE
DATIM	2012-07-24 22:59:07
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32780
FREQU	39308.18 Hz
SCANS	512
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	22.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	58



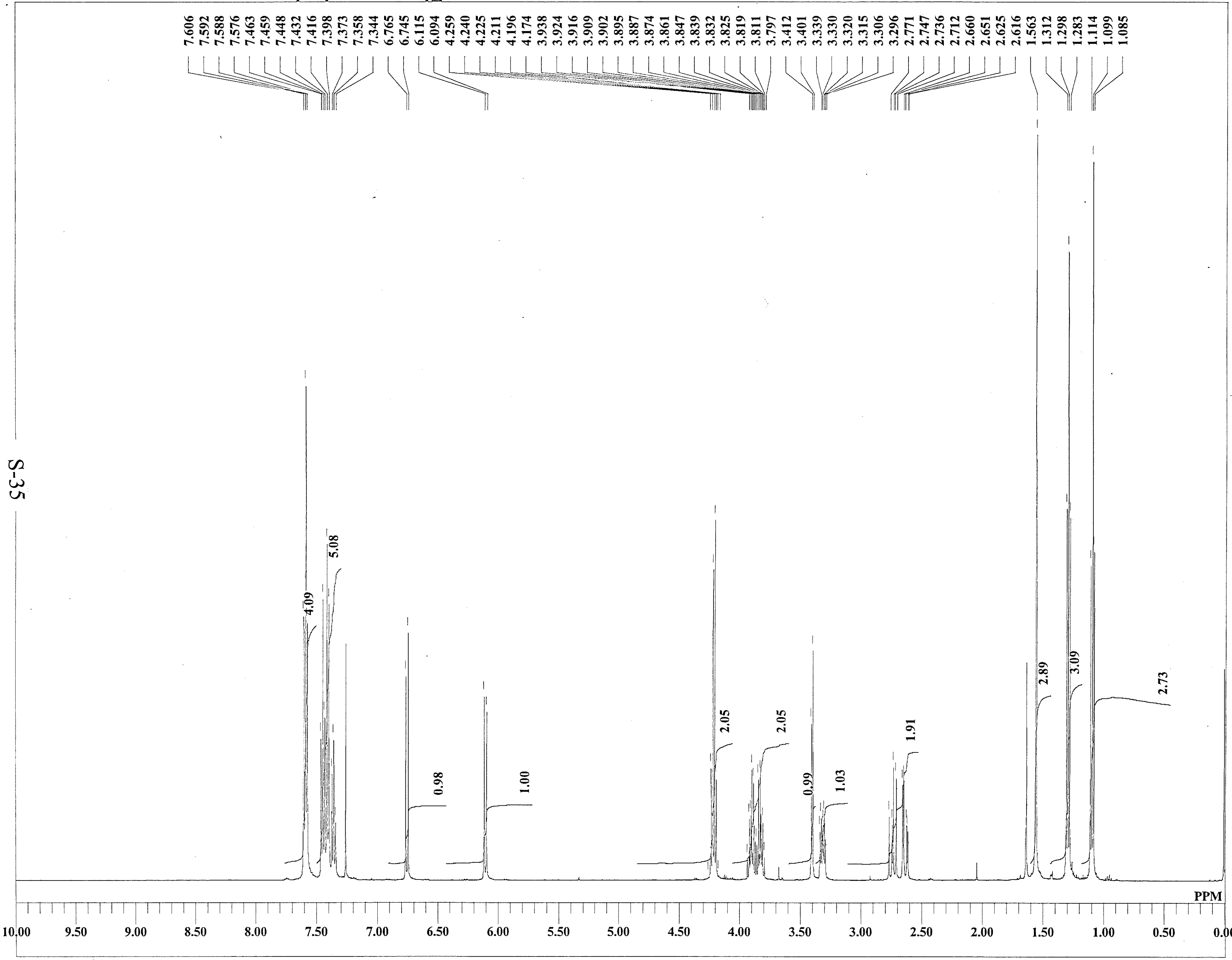
4d

^{13}C NMR

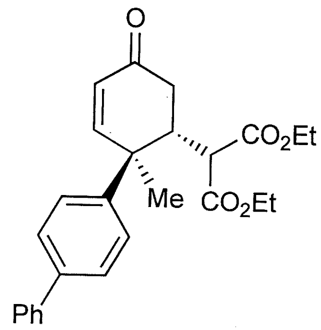
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-251-up_proton-2-1.als



DFILE	NAO-251-up_proton-2-1.als
COMNT	single_pulse
DATIM	2012-08-29 15:19:59
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	38



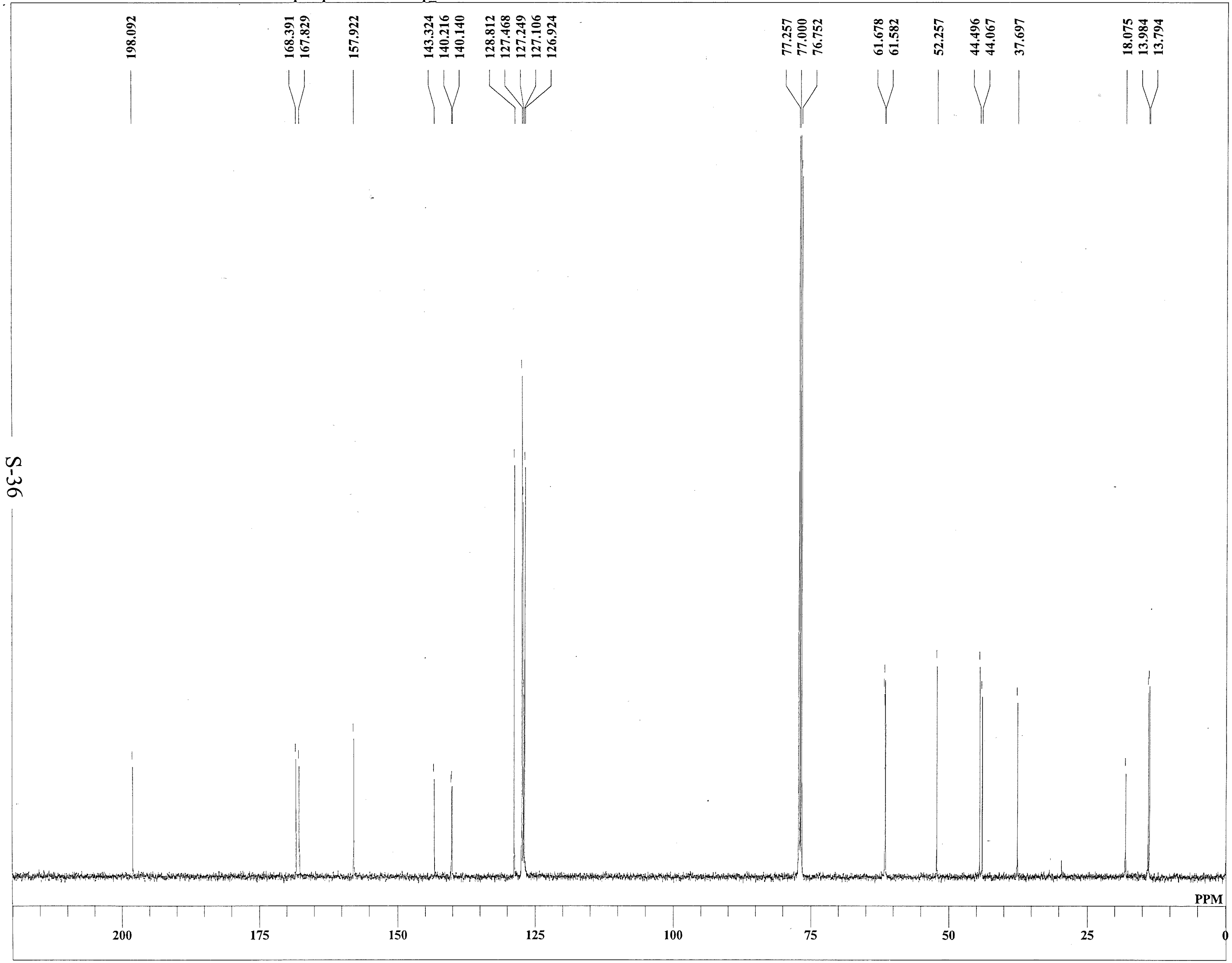
3e

^1H NMR

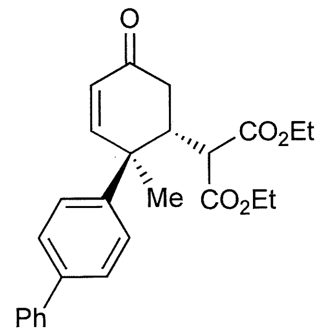
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-251-up_Carbon-1-1.als



DFILE	NAO-251-up_Carbon-1-1.als
COMNT	single pulse decoupled gated NOE
DATIM	2012-08-01 20:05:21
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26224
FREQU	31446.54 Hz
SCANS	512
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	23.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	58



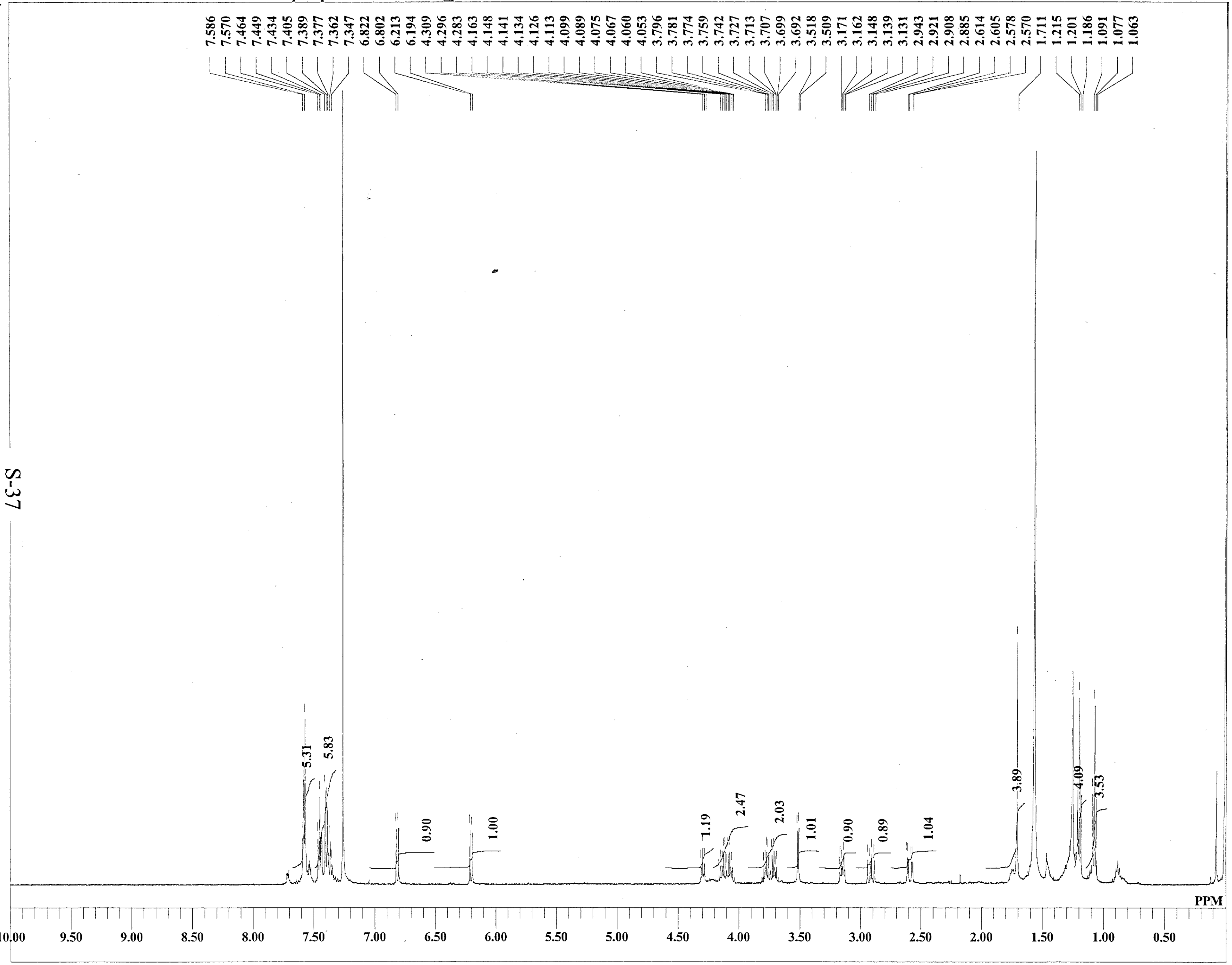
3e

^{13}C NMR

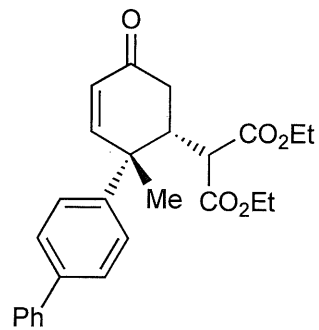
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-251-down_proton-4-1.als



DFILE	NAO-251-down_proton-4-1.als
COMNT	single_pulse
DATIM	2012-10-07 18:23:51
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	20.0 c
SLVNT	CDCL3
EXREF	12.51 ppm
BF	0.12 Hz
RGAIN	54

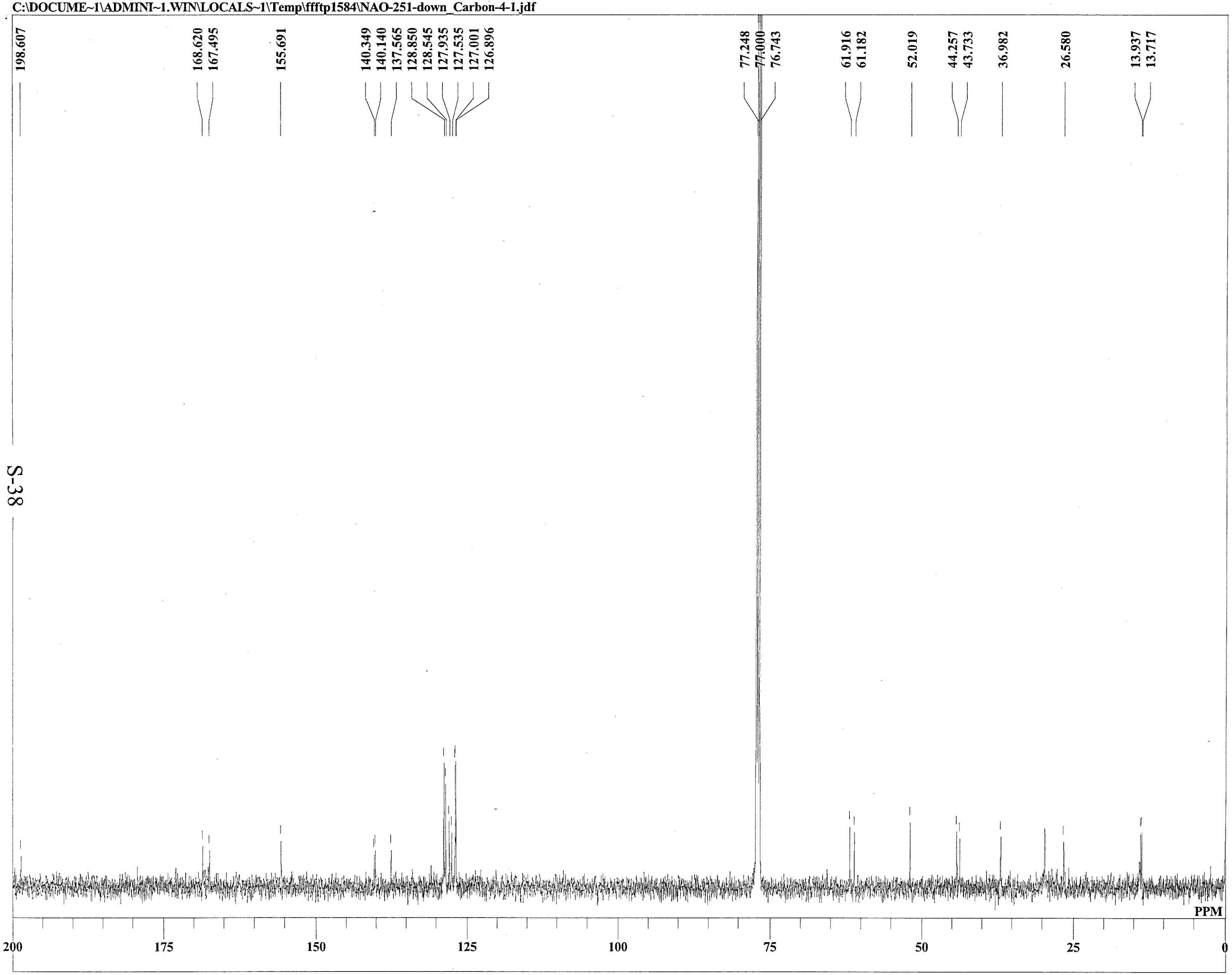


4e

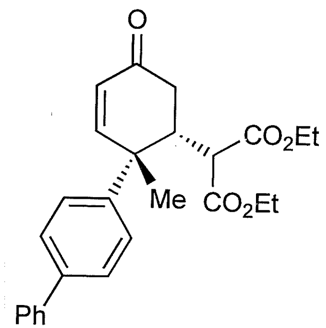
^1H NMR

(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE



DFILE	NAO-251-down_Carbon-4-1.jdf
COMNT	single pulse decoupled gated NOE
DATIM	2012-10-07 11:24:26
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32780
FREQU	39308.18 Hz
SCANS	2048
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



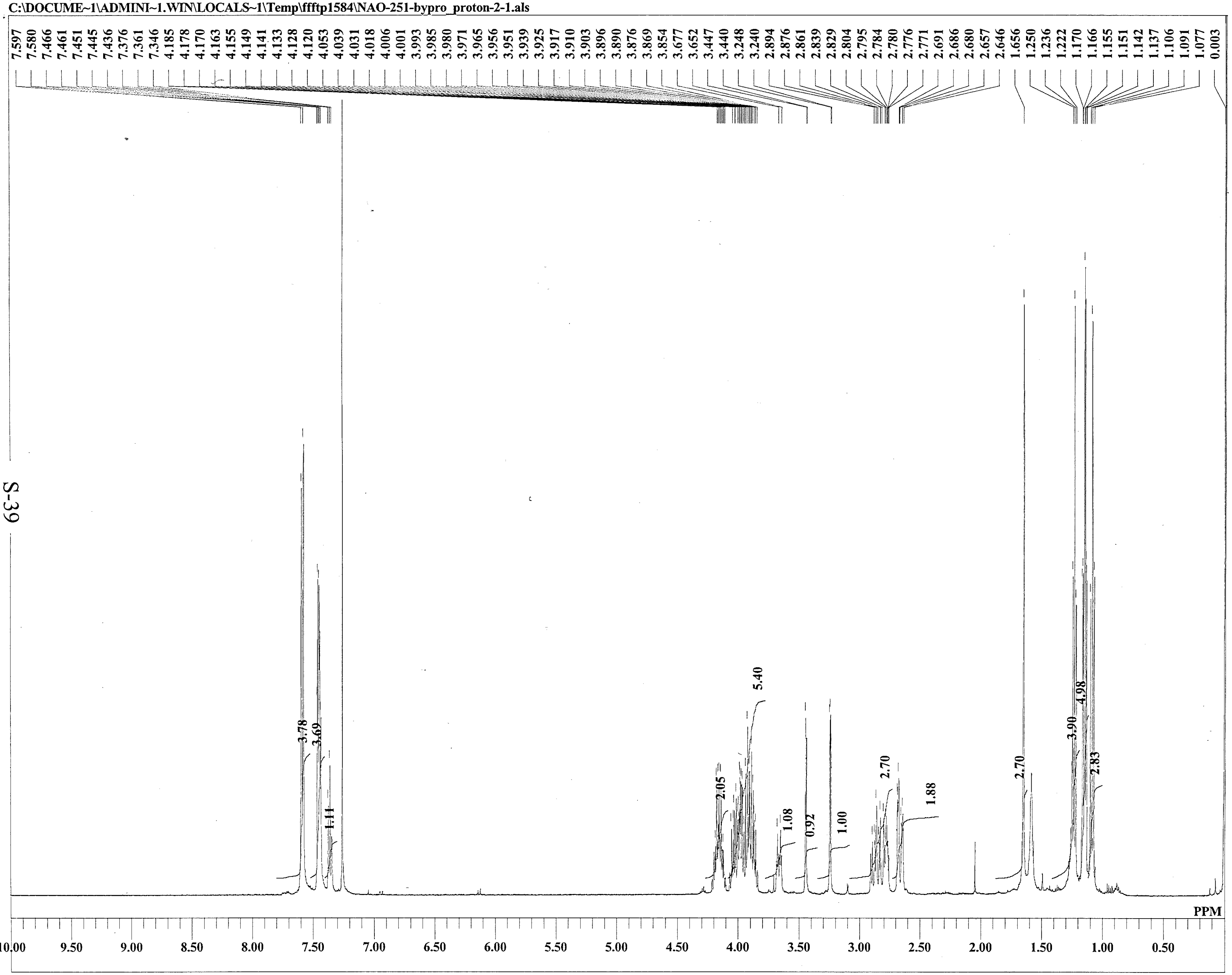
4e

^{13}C NMR

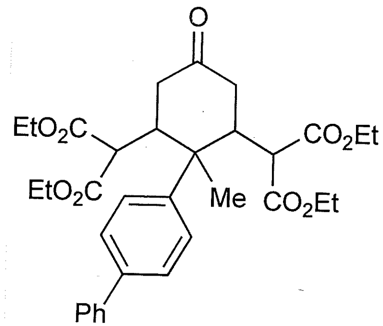
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-251-bypro_proton-2-1.als



DFILE	NAO-251-bypro_proton-2-1.als
COMNT	single_pulse
DATIM	2012-10-24 21:03:04
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	18.5 c
SLVNT	CDCL3
EXREF	12.51 ppm
BF	0.12 Hz
RGAIN	48



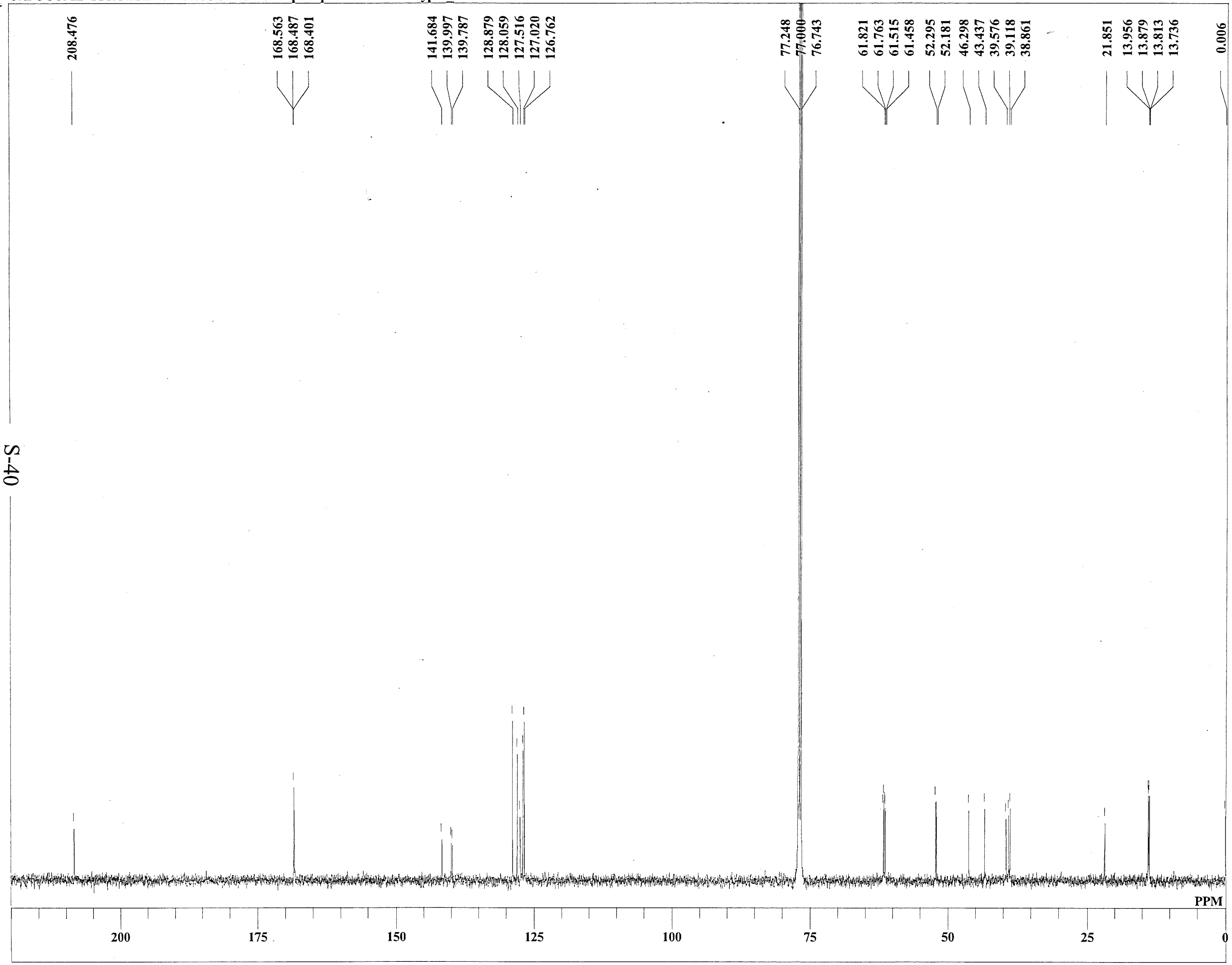
6

^1H NMR

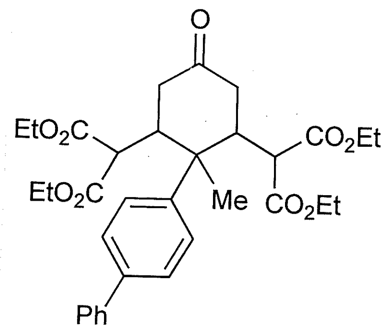
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-251-bypro_Carbon-2-1.als



DFILE	NAO-251-bypro_Carbon-2-1.als
COMNT	single pulse decoupled gated NOE
DATIM	2012-10-24 21:12:02
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26224
FREQU	31446.54 Hz
SCANS	1024
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	18.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



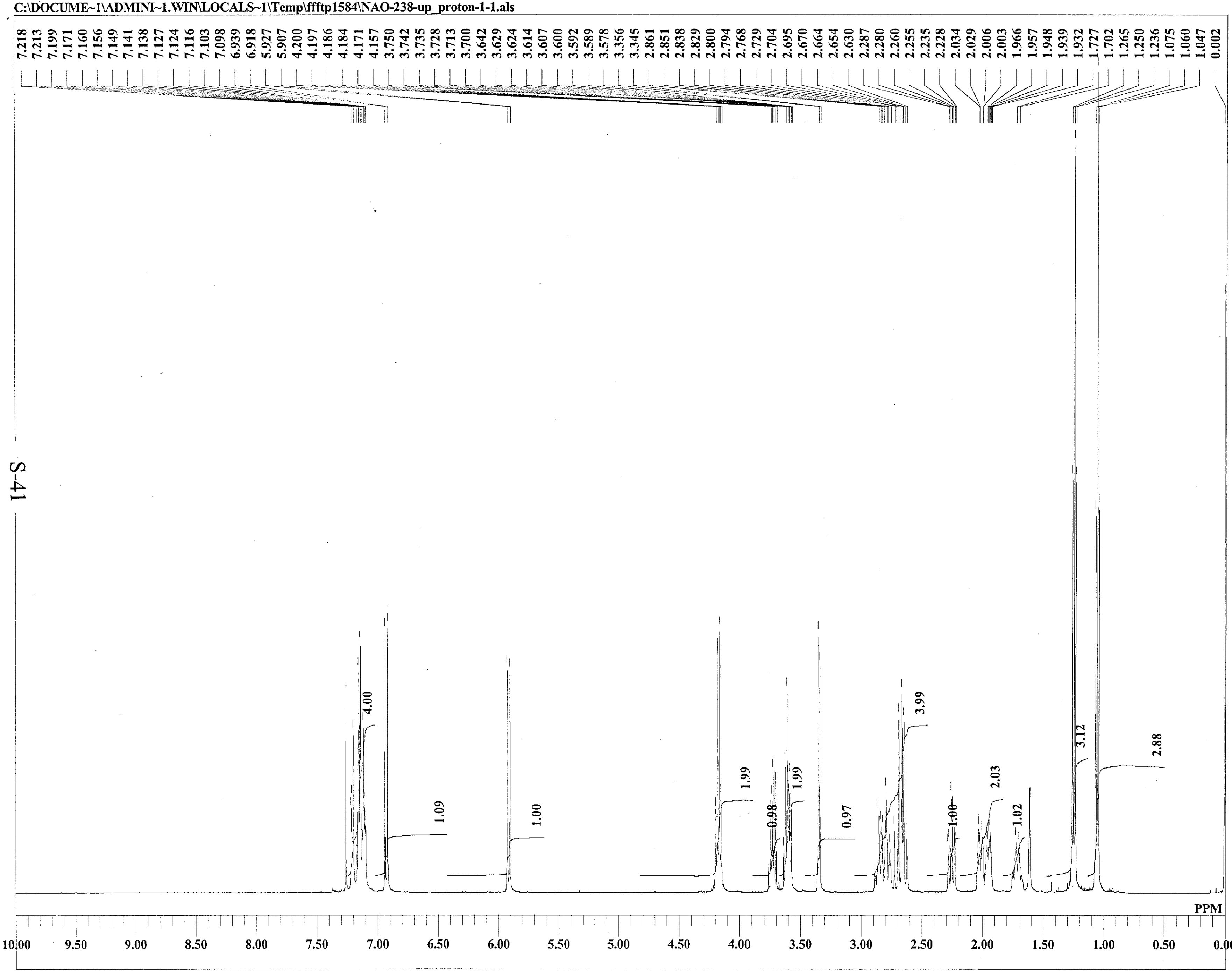
6

^{13}C NMR

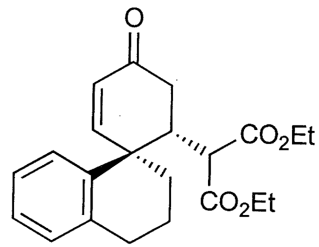
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-238-up_proton-1-1.als



DFILE	NAO-238-up_proton-1-1.als
COMNT	single_pulse
DATIM	2012-07-24 23:30:27
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	22.5 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	40



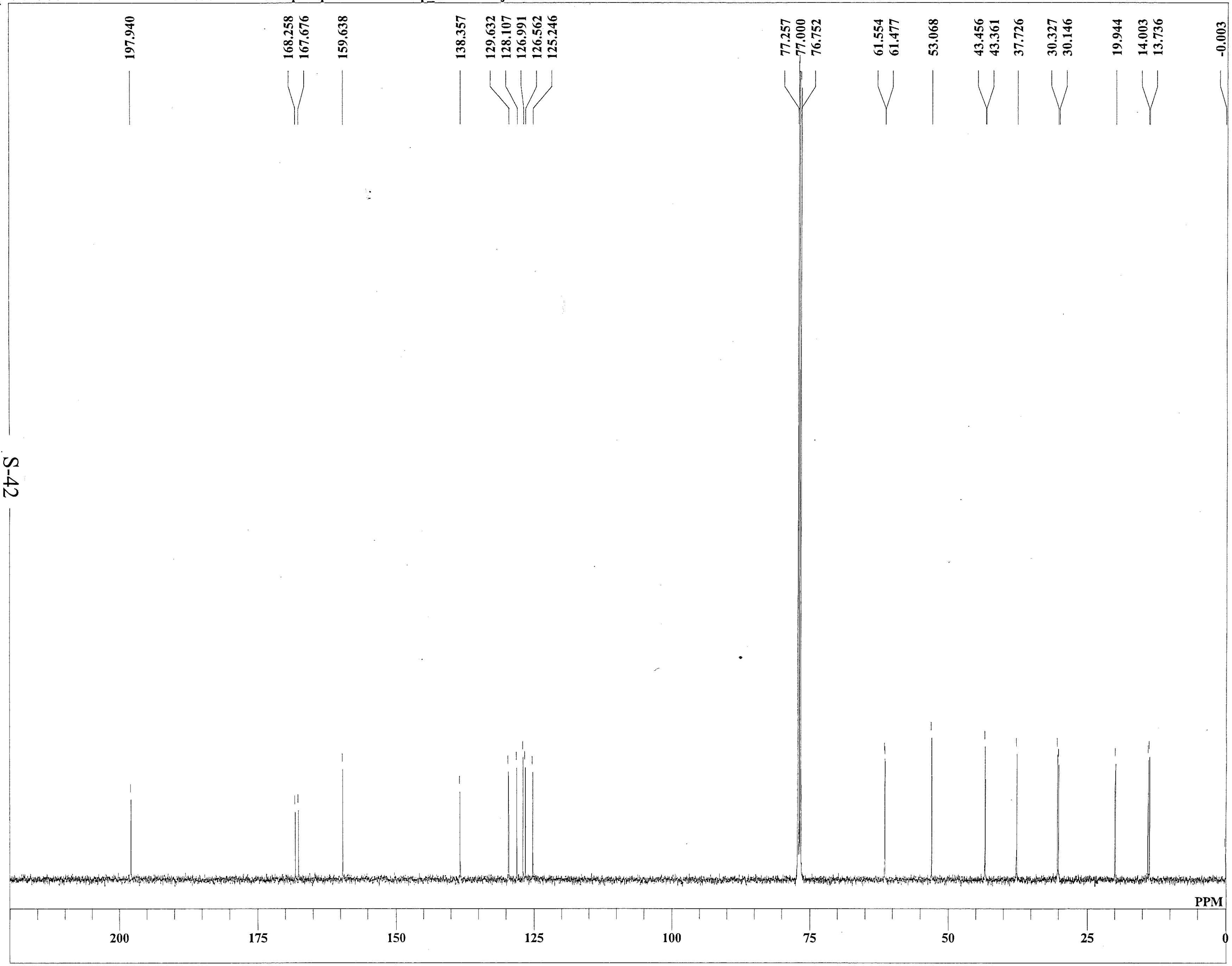
3f

^1H NMR

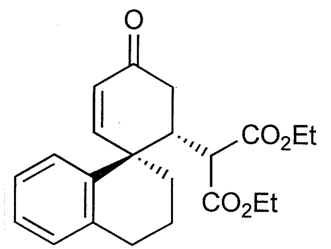
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-238-up_Carbon-1-1.jdf



DFILE	NAO-238-up_Carbon-1-1.jdf
COMNT	single pulse decoupled gated NOE
DATIM	2012-07-24 23:37:58
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32780
FREQU	39308.18 Hz
SCANS	512
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	56



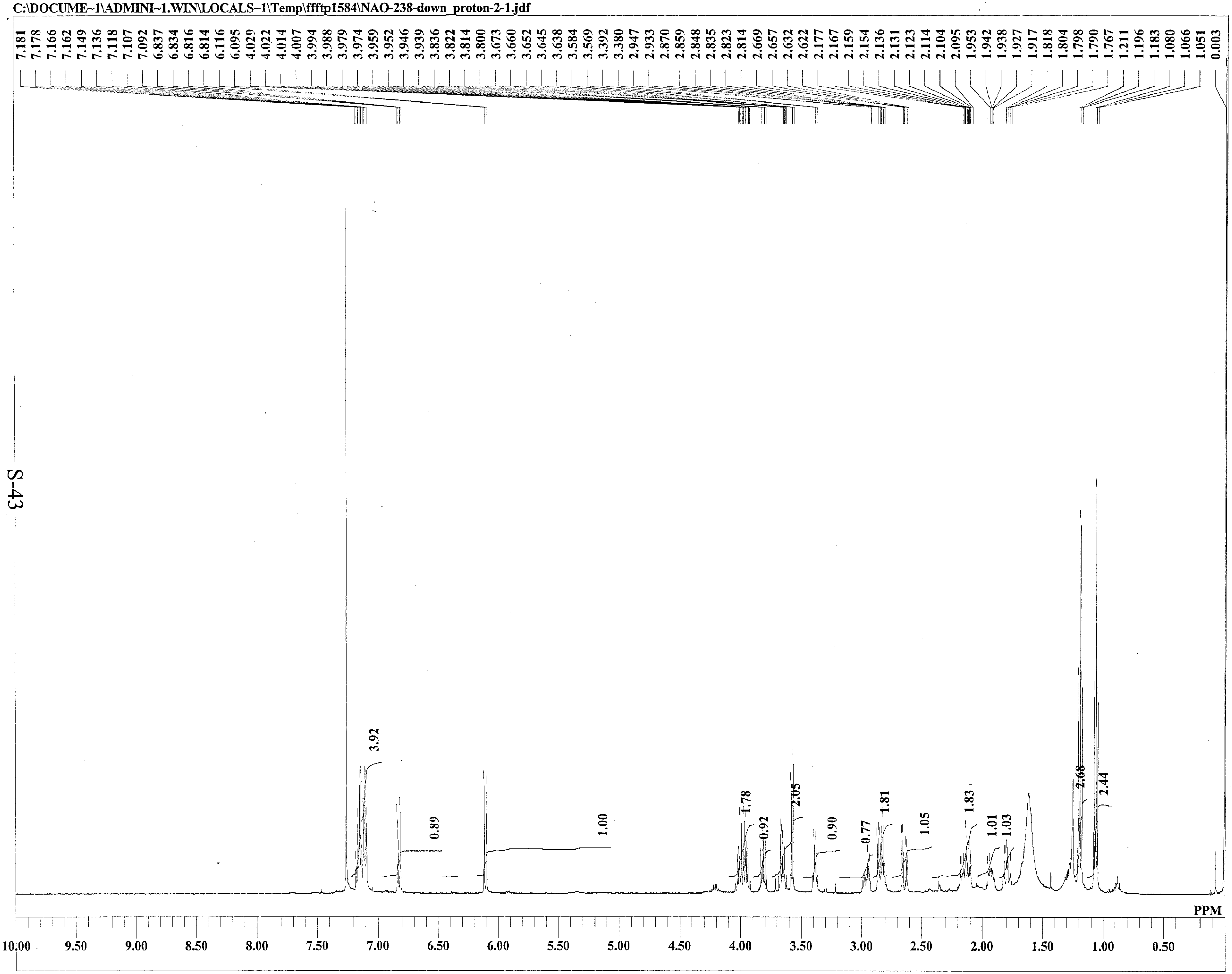
3f

^{13}C NMR

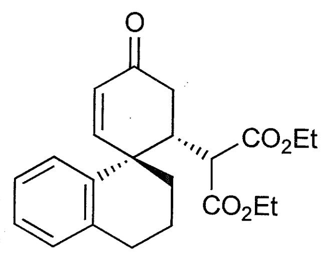
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-238-down_proton-2-1.jdf



DFILE	NAO-238-down_proton-2-1.jdf
COMNT	single_pulse
DATIM	2012-10-16 23:08:26
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	16400
FREQU	9384.38 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	20.1 c
SLVNT	CDCL3
EXREF	12.51 ppm
BF	0.12 Hz
RGAIN	50



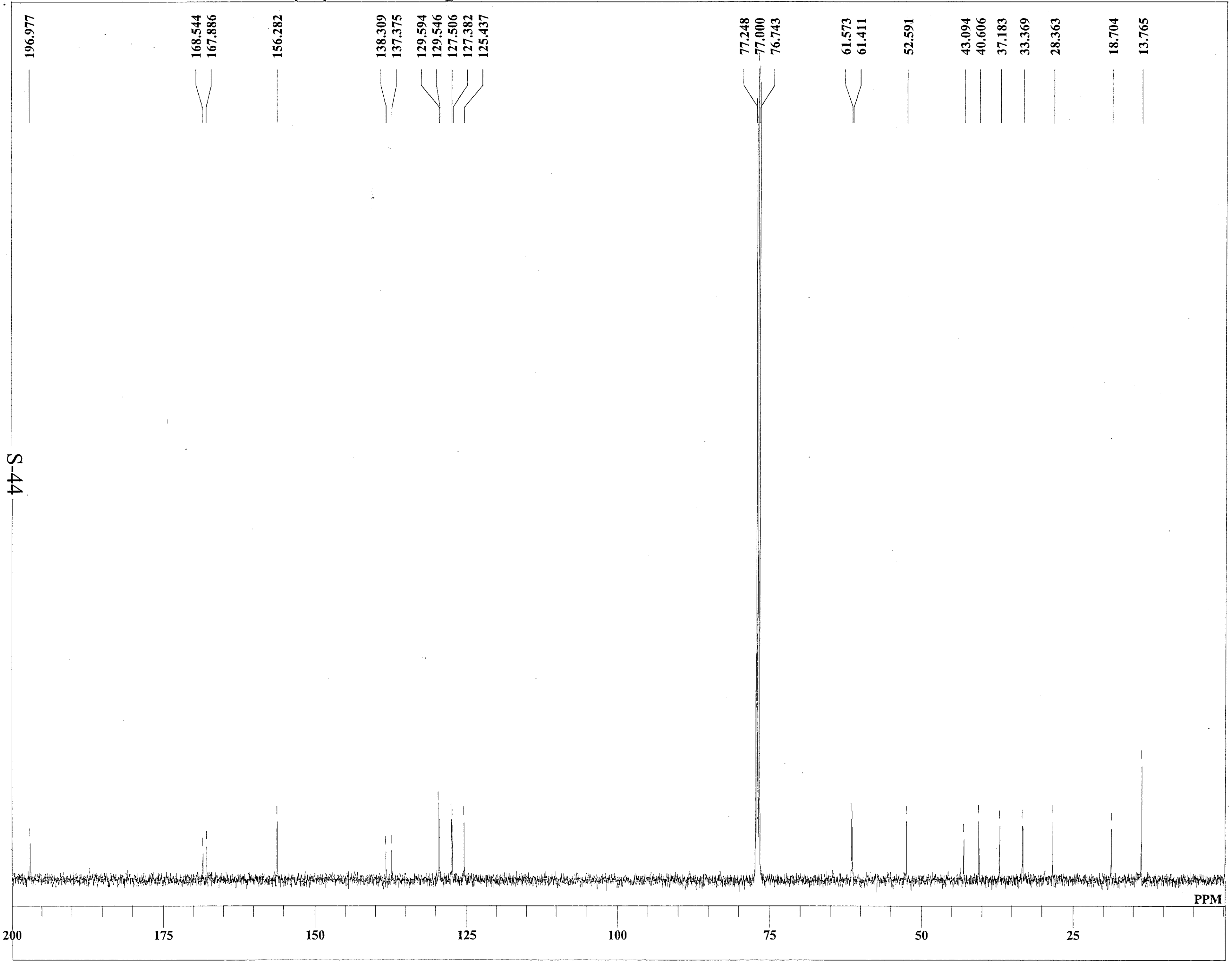
4f

^1H NMR

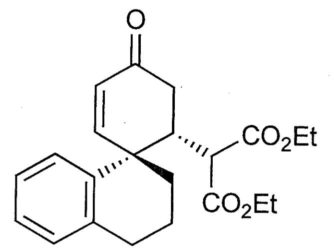
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-238-down_Carbon-1-1.als



DFILE	NAO-238-down_Carbon-1-1.als
COMNT	single pulse decoupled gated NOE
DATIM	2012-10-07 17:22:46
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26224
FREQU	31446.54 Hz
SCANS	1024
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	20.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



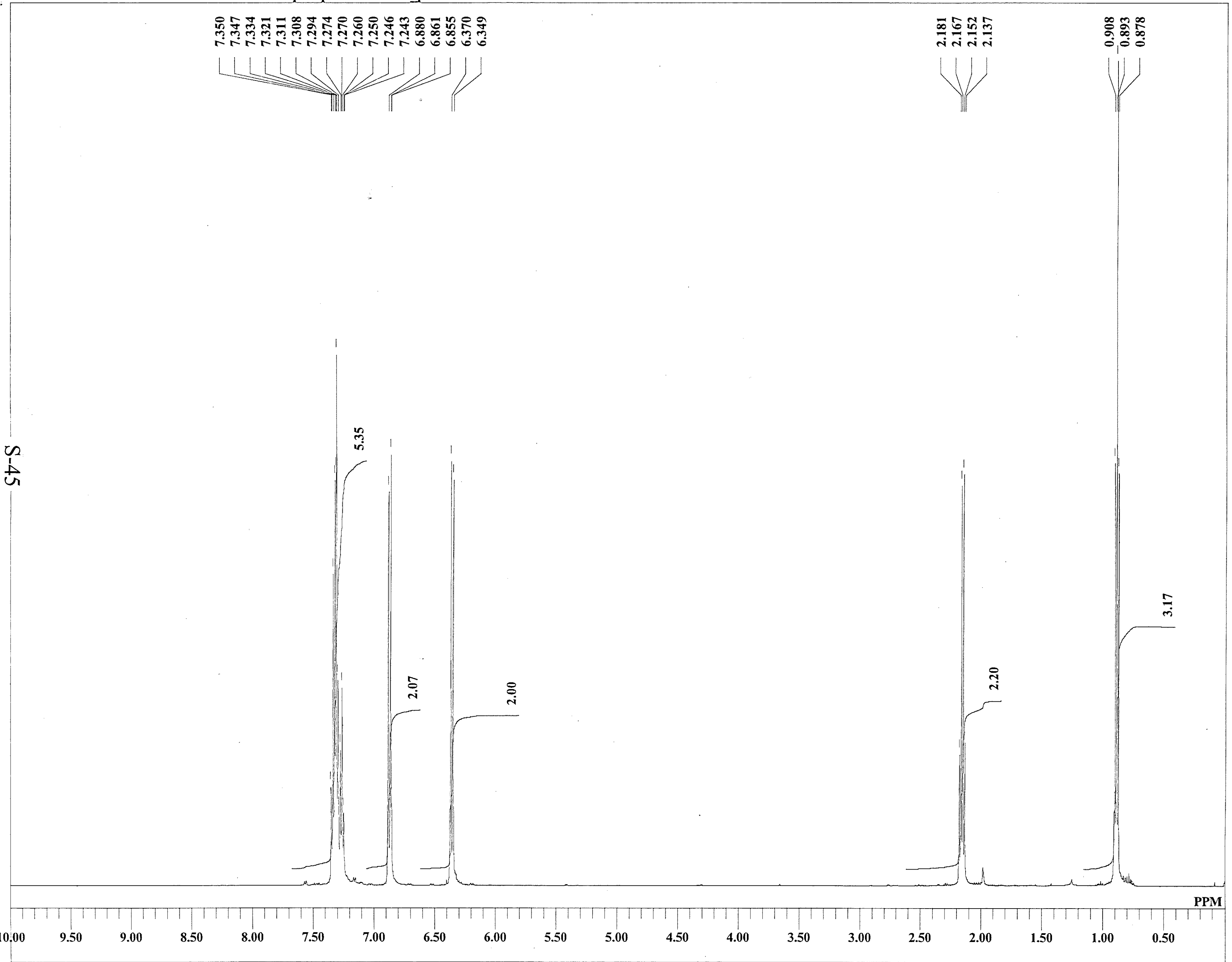
4f

^{13}C NMR

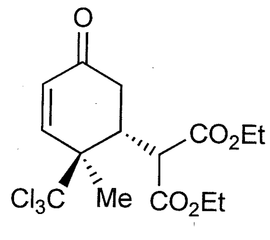
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-232_proton-1-1.als



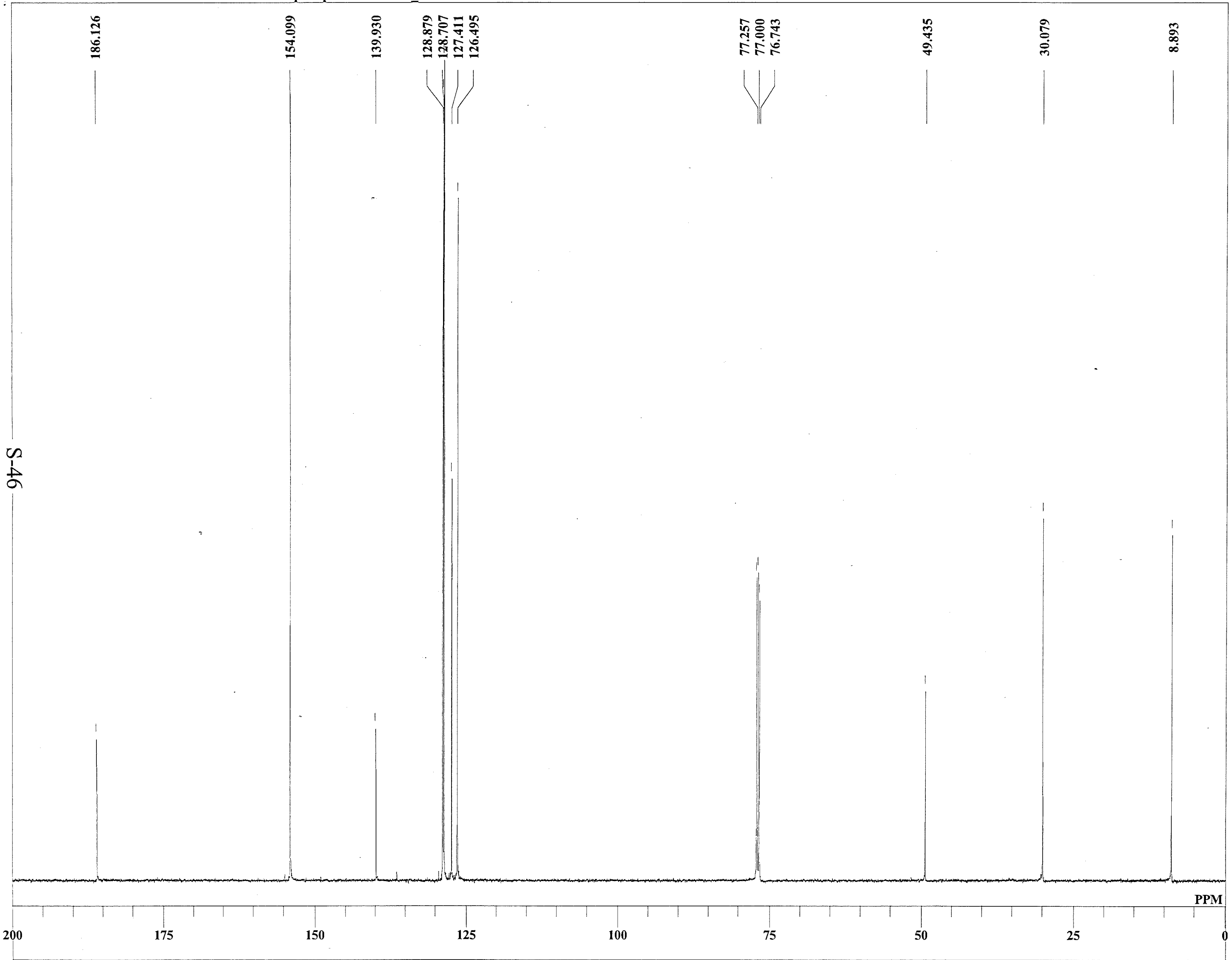
DFILE	NAO-232_proton-1-1.als
COMNT	single_pulse
DATIM	2012-08-29 14:40:50
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	30



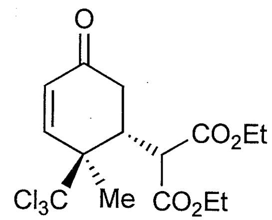
3g
^1H NMR
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-232_Carbon-1-1.als



DFILE	NAO-232_Carbon-1-1.als
COMNT	single pulse decoupled gated NOE
DATIM	2012-08-29 14:48:18
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26224
FREQU	31446.54 Hz
SCANS	512
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	22.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



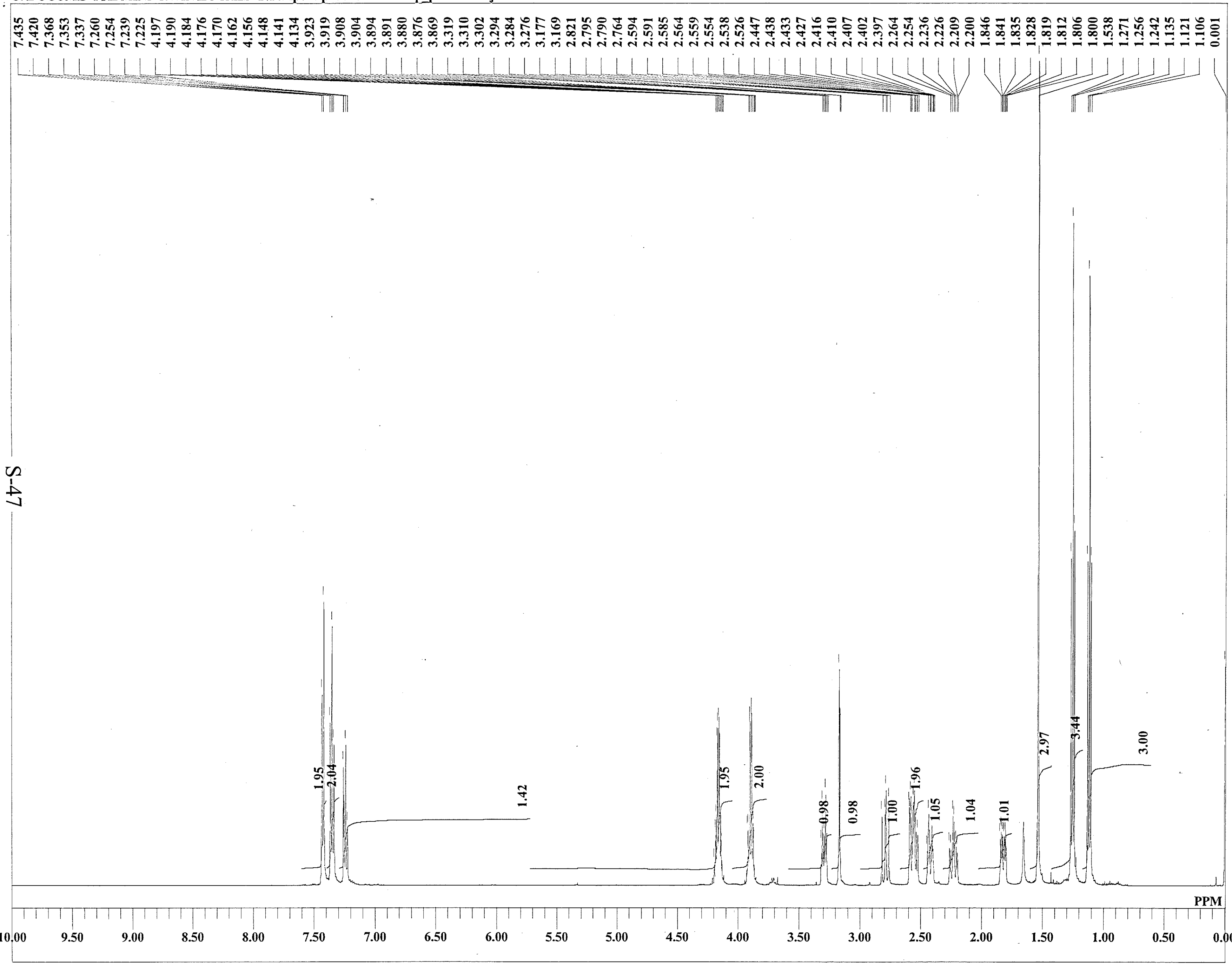
3g

^{13}C NMR

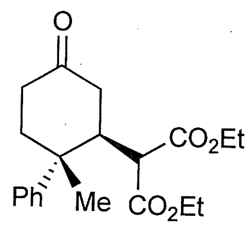
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAR-26-up_proton-1-1.jdf



DFILE	NAR-26-up_proton-1-1.jdf
COMNT	single_pulse
DATIM	2012-08-24 14:59:23
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	16400
FREQU	9384.38 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	22.9 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	38



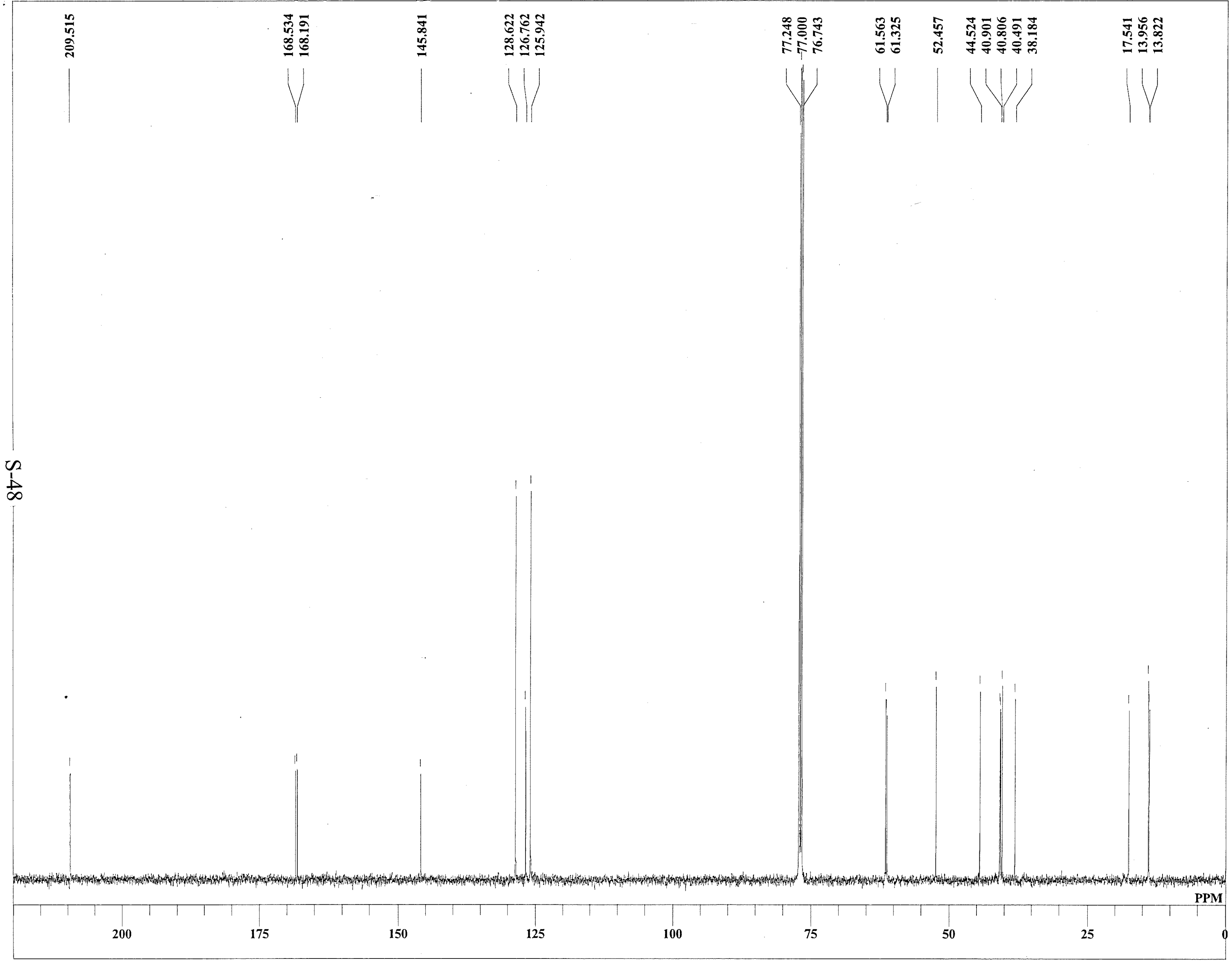
(3*S*,4*R*)-**9**

^{1}H NMR

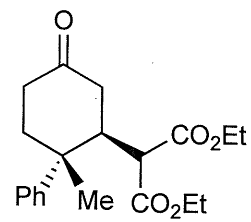
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1840\NAR-26-up_Carbon-1-1.jdf



DFILE	NAR-26-up_Carbon-1-1.jdf
COMNT	single pulse decoupled gated NOE
DATIM	2012-08-25 09:29:17
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32780
FREQU	39308.18 Hz
SCANS	256
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	22.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



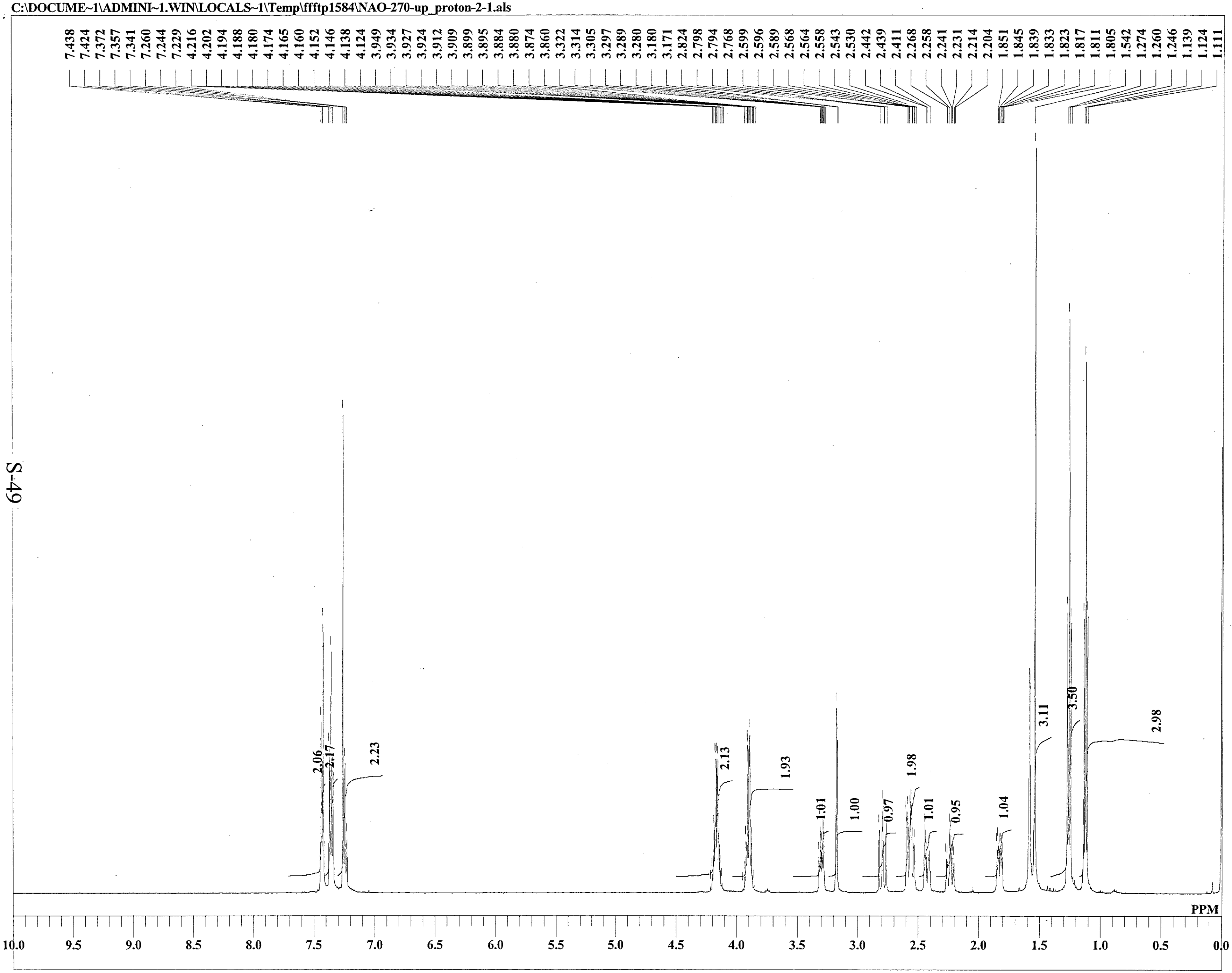
(3*S*,4*R*)-**9**

^{13}C NMR

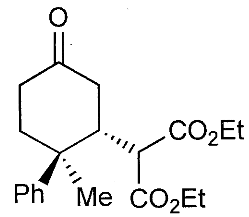
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-270-up_proton-2-1.als



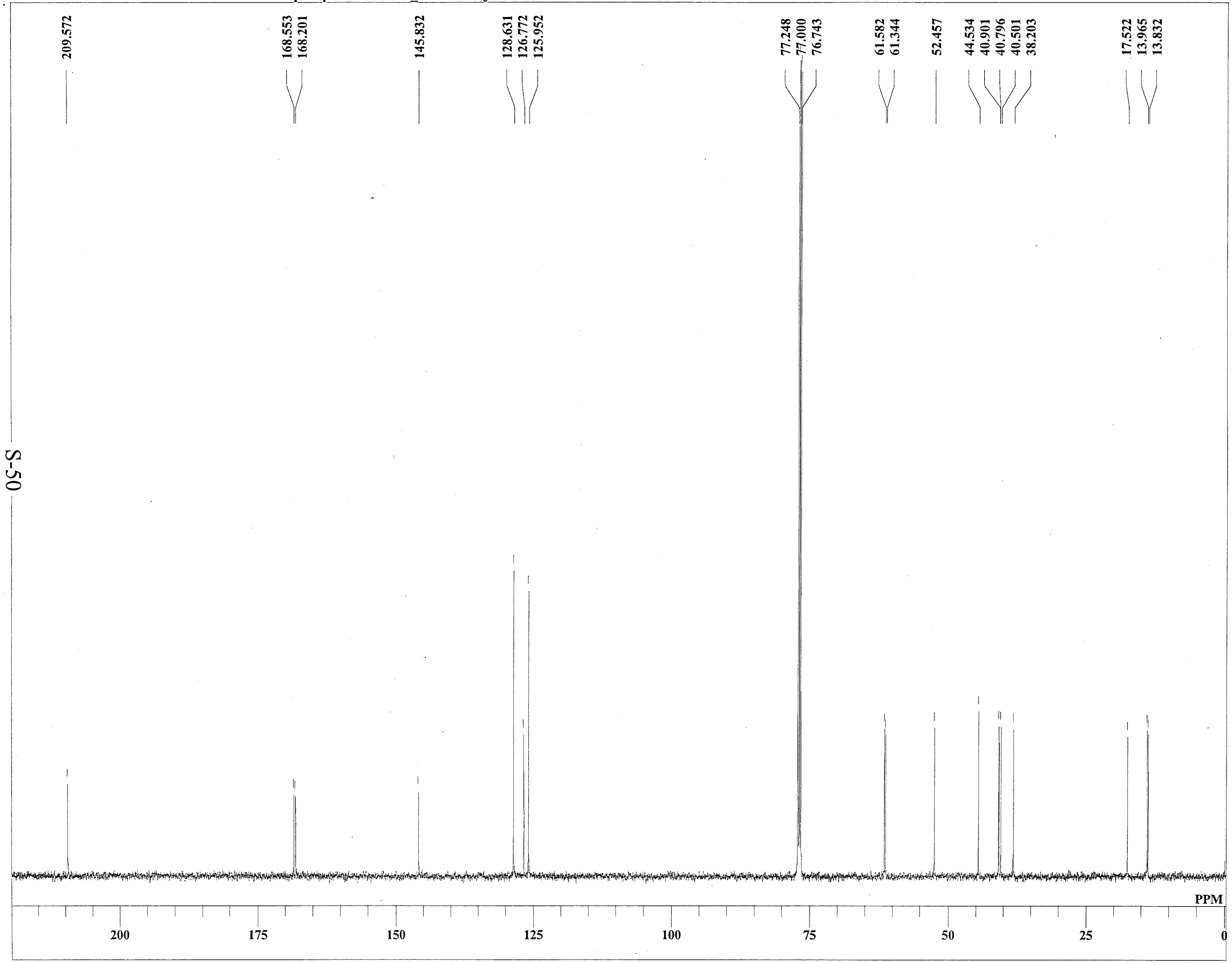
DFILE	NAO-270-up_proton-2-1.als
COMNT	single_pulse
DATIM	2012-07-10 14:56:26
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	22.9 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	48



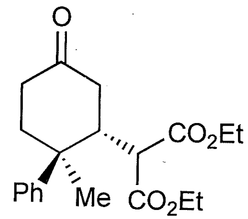
(3*R*,4*S*)-**7**
^{1}H NMR
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1584\NAO-254_Carbon-1-1.jdf



DFILE	NAO-254_Carbon-1-1.jdf
COMNT	single pulse decoupled gated NOE
DATIM	2012-06-02 18:21:03
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32780
FREQU	39308.18 Hz
SCANS	512
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	19.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	58



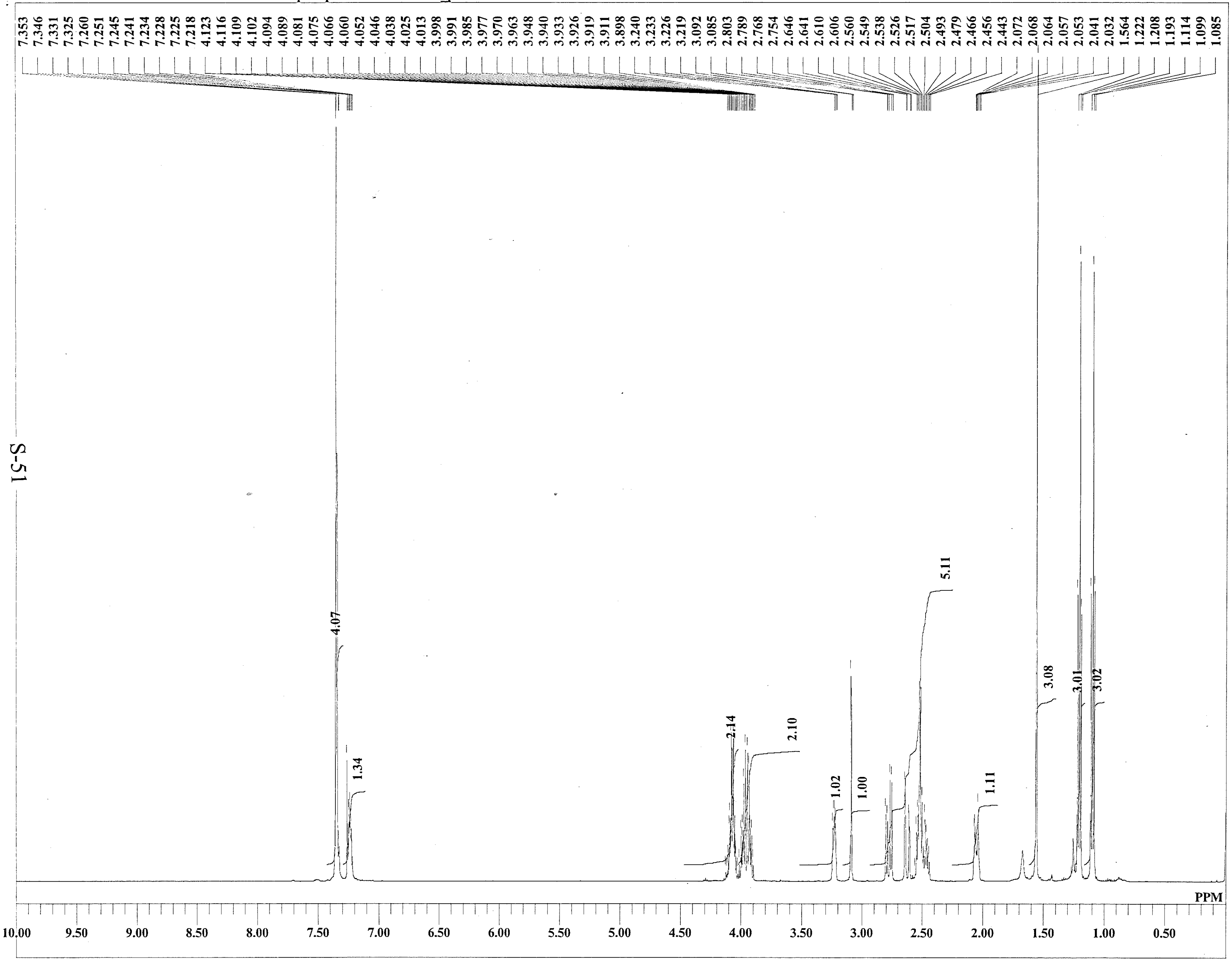
(3*R*,4*S*)-**7**

^{13}C NMR

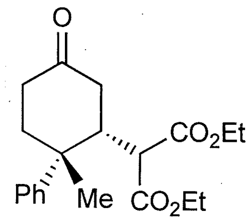
(125 MHz, $CDCl_3$)

single_pulse

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1988\NAR-25-down_proton-1-1.als



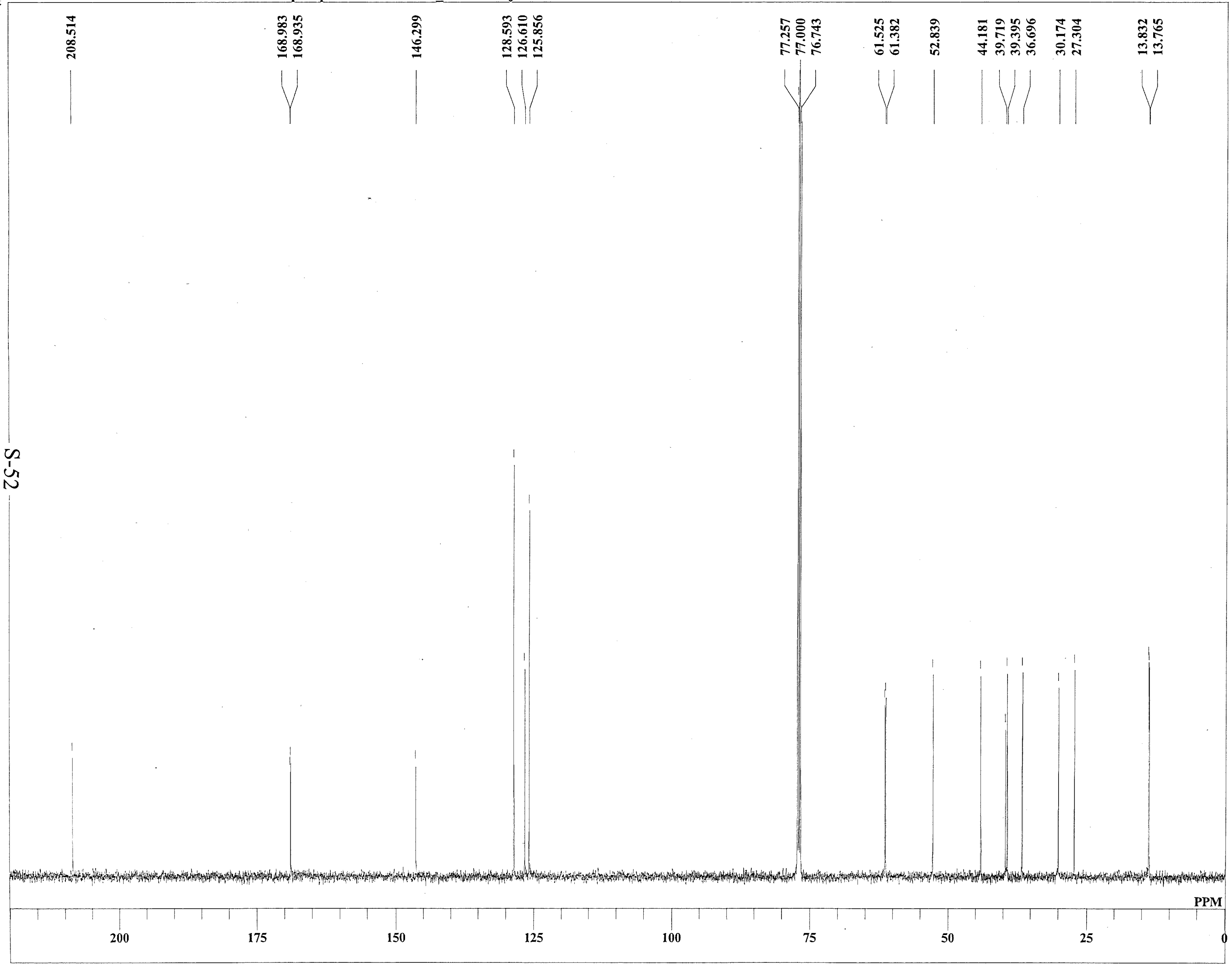
DFILE	NAR-25-down_proton-1-1.als
COMNT	single_pulse
DATIM	2012-08-24 18:21:20
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13120
FREQU	7507.51 Hz
SCANS	8
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	4.68 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	36



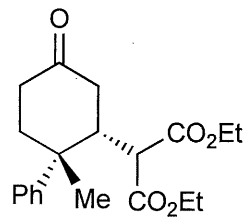
(3*R*,4*R*)-**11**
^{1}H NMR
(500 MHz, $CDCl_3$)

single pulse decoupled gated NOE

C:\DOCUME~1\ADMINI~1.WIN\LOCALS~1\Temp\ffftp1988\NAR-25-down_Carbon-1-1.jdf



DFILE	NAR-25-down_Carbon-1-1.jdf
COMNT	single pulse decoupled gated NOE
DATIM	2012-08-25 13:10:12
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32780
FREQU	39308.18 Hz
SCANS	256
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	2.72 usec
IRNUC	1H
CTEMP	22.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	58



(3*R*,4*R*)-**11**

^{13}C NMR

(125 MHz, $CDCl_3$)