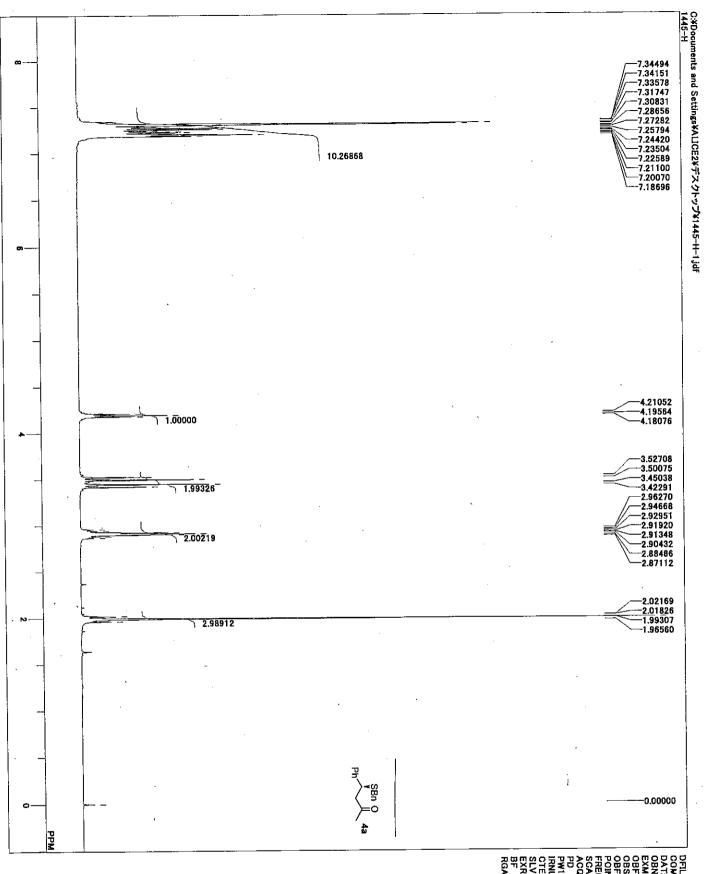
## Chiral-Sc Catalyzed Asymmetric Michael Addition/Protonation of Thiols with Enones in Water

Taku Kitanosono, Masaru Sakai, Masaharu Ueno, and Shu Kobayashi\*

Department of Chemistry, School of Science and Graduate School of Pharmaceutical Sciences, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

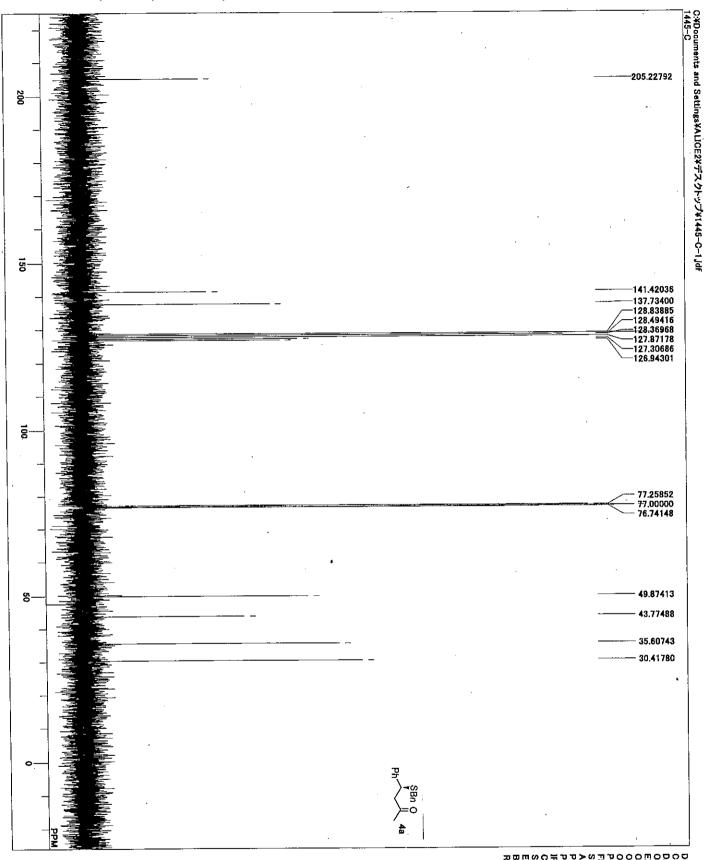
## Copies of <sup>1</sup>H and <sup>13</sup>C NMR Spectra

	Products <b>8aH/8aD</b> ( <b>Table 7, Entry 2</b> )
6.	Deuterium Kinetic Isotope Effect Experiments
5.	Desulfurization of protonated products <b>9p</b> S-86
4.	Protonations 8a-8r S-50
3.	Michael additions and protonations 6a-6f S-38
2.	$\alpha,\beta$ -Unsaturated ketones $7g, 7h, 7o$ S-32
1.	Michael reactions of thiols 4a-40 S-2

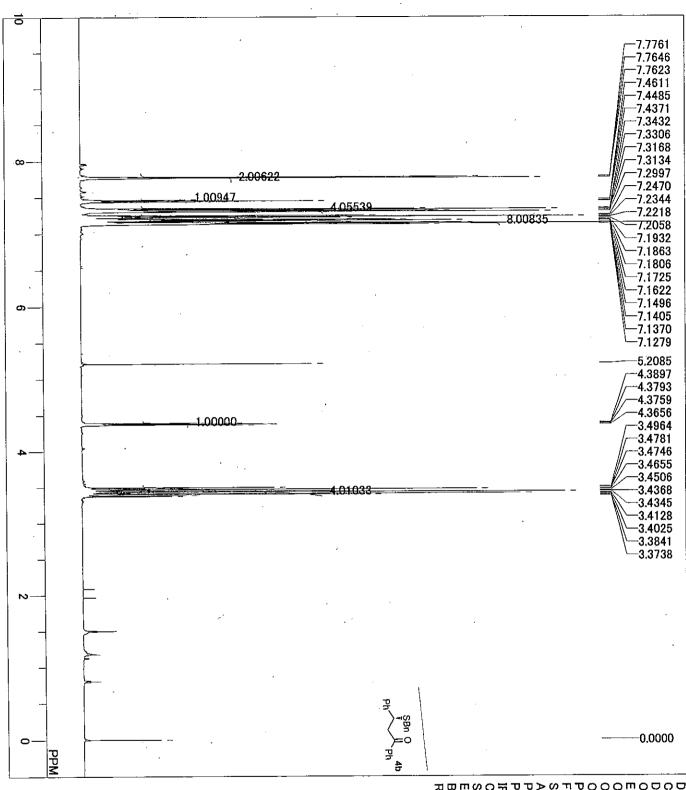


DFILE CXDocuments and Settings¥ALIGE2¥₹⊼./
COMNT 1445-H
DATIM 17-01-2011 18:02:42

OBNUC 1H
EXMOD 1H NMR.ex2
OBFRQ 495.13 MHz
OBFRI 16.4 Hz
OBFIN 16.84
FREQU 986.78 Hz
SCANS 8
ACQTM 1.7642 sec
PD 5.0000 sec
PM1 5.80 usec
IRNUC 1H
SLYNT CDCL3
EXREF CDCL3
EXREF CD0.00 ppm
BF 0.12 Hz
RGAIN 32

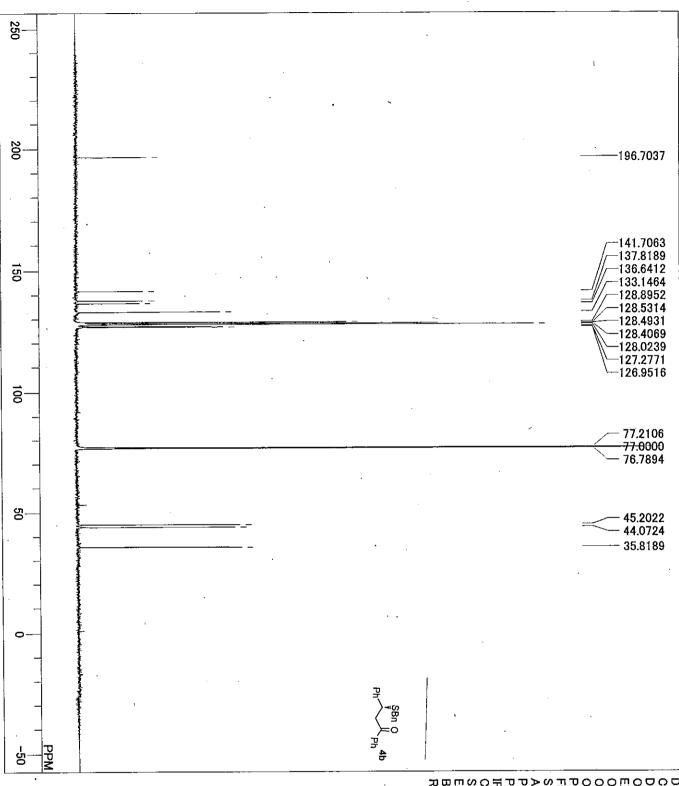


DFILE CAME TO THE PRICE TO THE



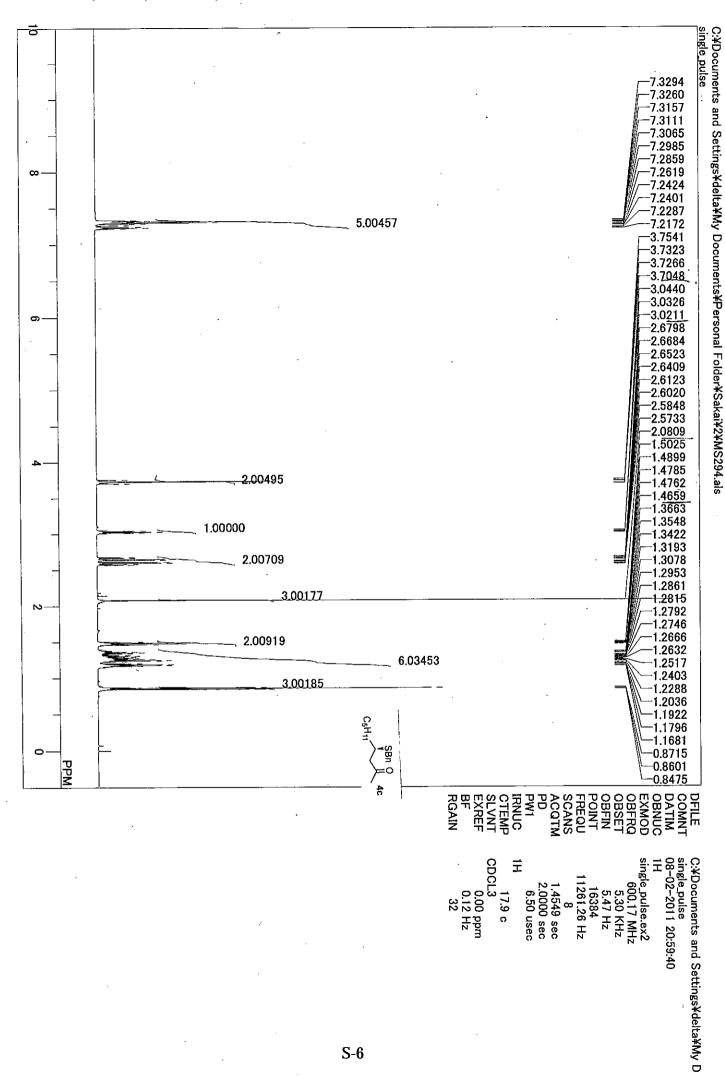
DFILE C:\*Documents and S COMNIT 17-02-2011 22:03:54 OBNUC 1H Single pulse.ex2 600.17 MHz 5.00 KHz 5.00 KHz 5.00 KHz 5.00 KHz 5.00 KHz 5.00 KHz 600.17 MHz 5.00 KHz 5.00 KHz 6.00 KHz 6.00 KHz 6.00 Sec PU 16.50 usec FD 18.4 c SLVNT CDCL3 EXREF 0.00 ppm BF 0.12 Hz 7.00 SCOMNIT 18.4 c SLVNT CDCL3 EXREF 0.00 ppm BF 0.12 Hz 7.000 SCOMNIT CDCL3 EXREF 0.00 ppm 0.12 Hz

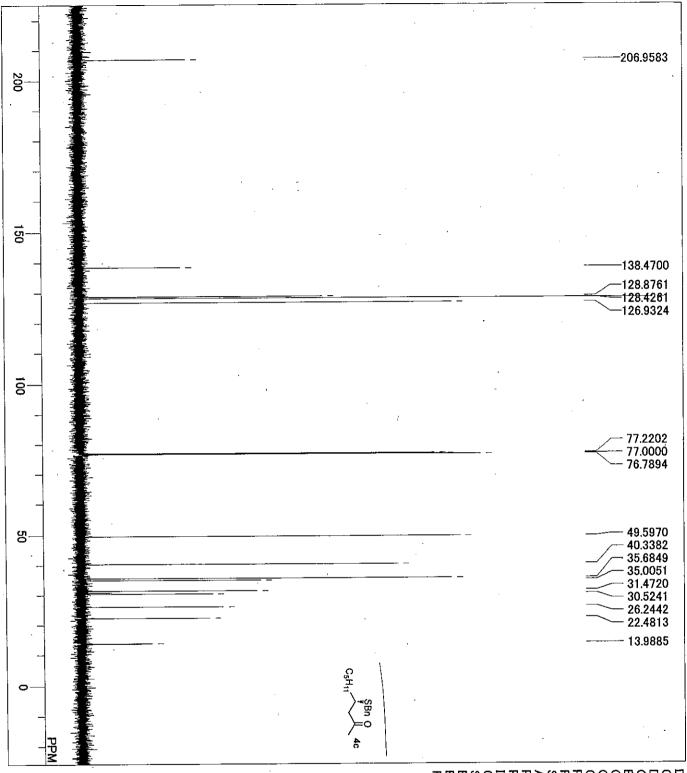
C:¥Documents and Settings¥delta¥My D



DFILE C:¥Documents and S COMNT 17-02-2011 10:17:37 OBNUC 13C 150.92 MHz OBFRQ 150.92 MHz OBFRQ 150.92 MHz OBFRQ 17.4 Hz OBFIN 17.4 Hz OBFIN 1024 SCANS ACQTM 0.6921 sec PD 2.0000 sec PW1 2.87 usec IRNUC 1H 19.9 c SLVNT CDCL3 EXREF 0.12 Hz RGAIN 60

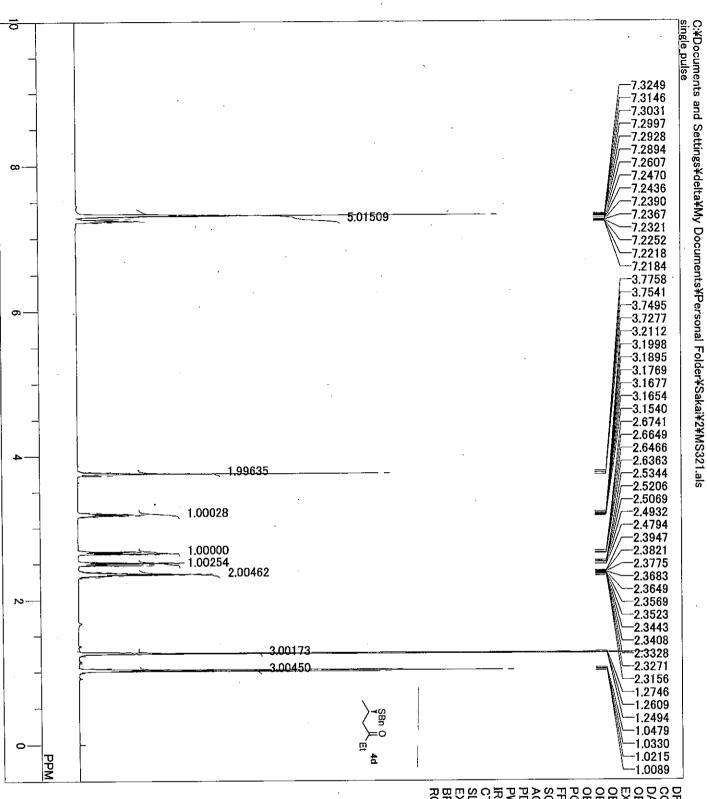
C:¥Documents and Settings¥delta¥デス!





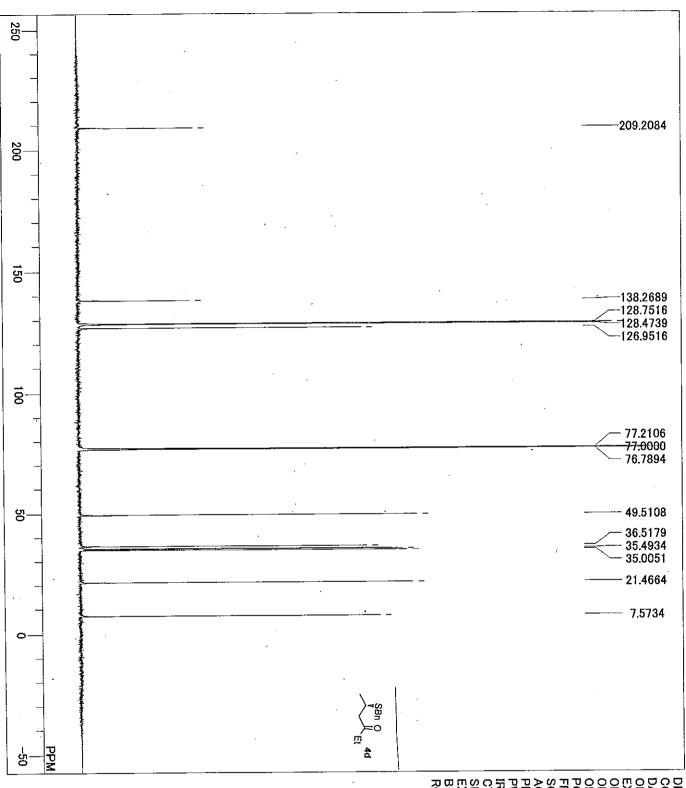
DFILE
COMNT
DATIM
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBSET
OBSIT
POINT
FREQU
SCANS
ACQTM
PD
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

0.6921 sec 2.0000 sec 17348.49 Hz 32768 2.87 usec

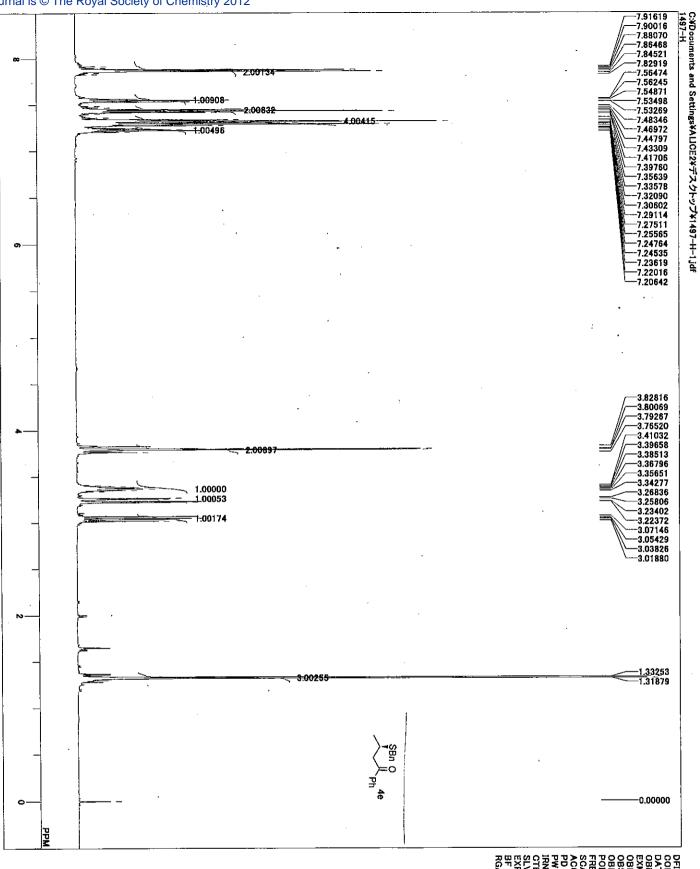


DFILE C:\*Do
COMNIT single
COMNIT 16-02
COBNUC 1H
EXMOD single
COBFIN
POINT
FREQUU
SCANS
ACQTM 1
PD
PD
SLVNT CDCL
EXREF
BF
RGAIN

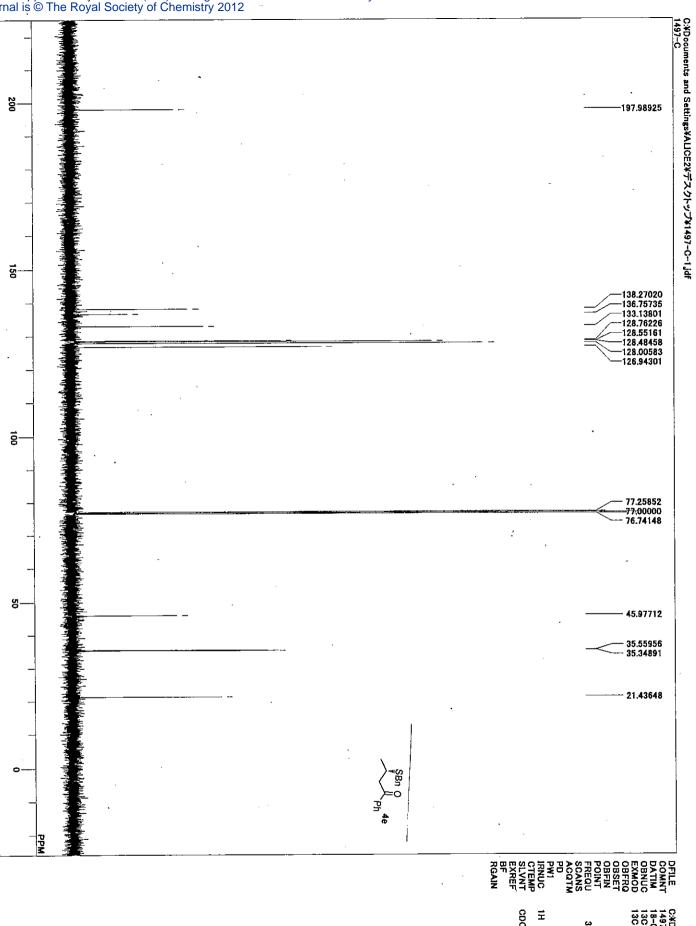
single\_pulse.ex2
600.17 MHz
600.17 MHz
5.47 Hz
13107
9008.87 Hz
8
1.4549 sec
2.0000 sec
6.50 usec
1H
17.6 c
CDCL3
0.000 ppm
0.12 Hz
34



DFILE C:\(\pi\)Documents and S. COMNT
COMNT
DATIM
DATIM
16-02-2011 12:33:59
OBNUC
13C
EXMOD
Single pulse dec
OBFRQ
150.92 MHz
OBSET
0852T
0852T
0852T
0852T
1.74 Hz
POINT
40961
FREQU
1024
ACQTM
ACQTM
0.6921 sec
PD
2.87 usec
IRNUC
IRNUC
IH
CTEMP
CTEMP
SCANI
BF
0.12 Hz
0.12 Hz
0.12 Hz
0.12 Hz



DFILE COMMIT DATIMI DATIMI DESCRIPTION DES C.\*Documents and Settings\*ALICE2\*デス:
1497-H
18-02-2011 13:30:34
1H
NMR.ex2
495.13 MHz
495.13 MHz
4,38 KHz
9,64 Hz
16384
9286.78 Hz
8
1.7642 sec
5.0000 sec
5.80 usec



DFILE C\*Documents and Settings\*ALICE2\*\*\*\*\footnote{\pi\_{\text{COMNT}}} 1497-C

DATIM 18-02-2011 13:51:06

OBNUC 13C

EXMOD 13C NMR.ex2

OBFRQ 124.51 MHz

OBSET 3.45 KHz

OBFIN 6.00 Hz

POINT 32768

FREQU 3412

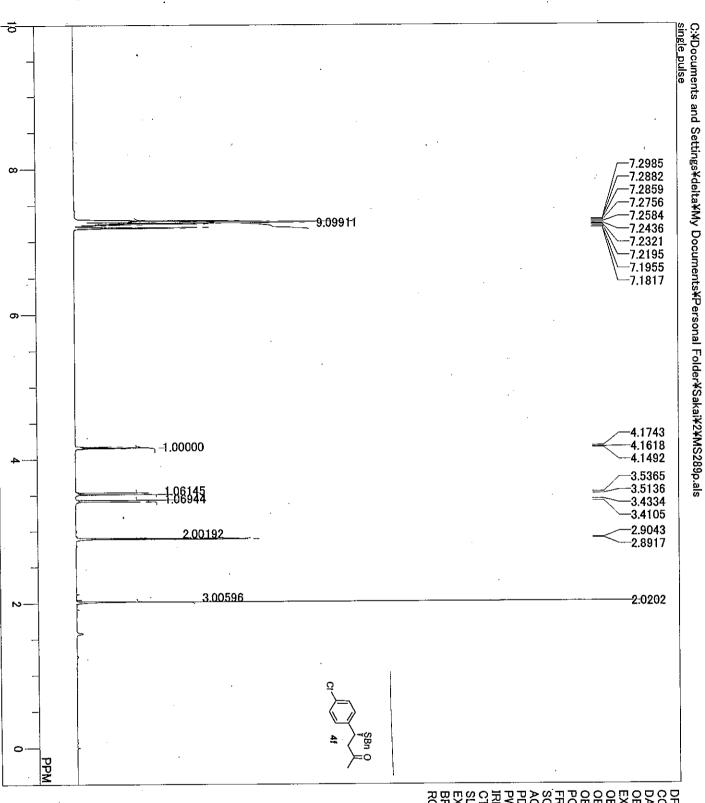
SCANS 412

AGGTM 0.8389 sec

PW1 3.67 usec

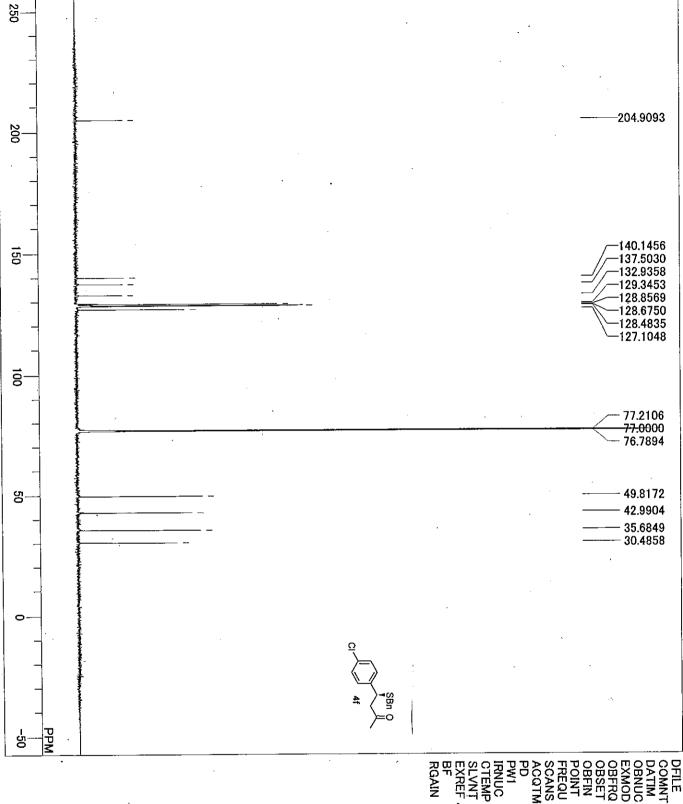
IRNUC 1H

18.9 c

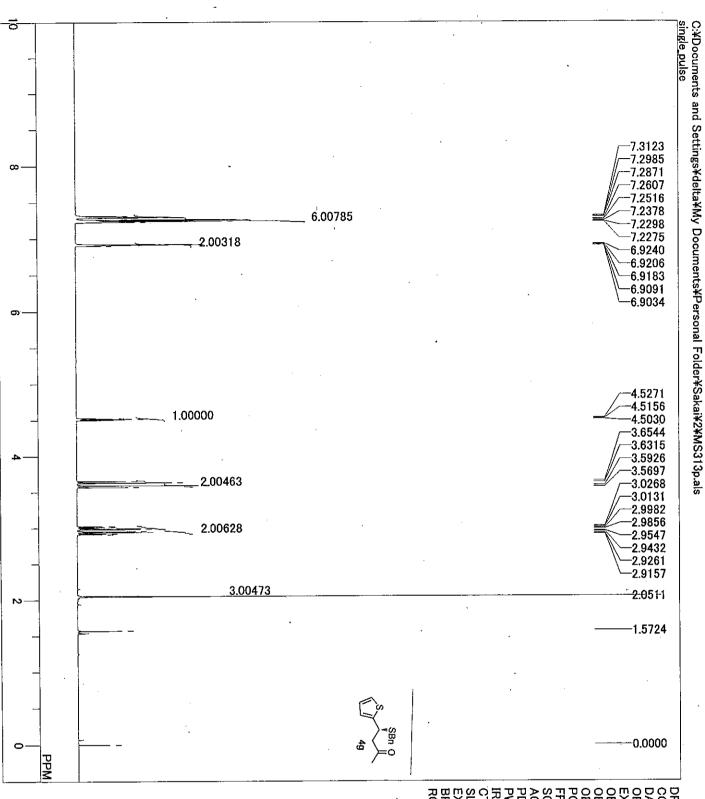


DFILE C.\*
COMNT Sing DATIM 15OBNUC 1H
EXMOD Sing OBFRQ OBSET OBSIN POINT FREQU SCANS ACQTM PD PW1 IRNUC 1H
CTEMP SLVNT CD EXREF BF RGAIN

single pulse.ex2 600.17 MHz 5.30 KHz 5.47 Hz 13107 9008.87 Hz 8 1.4549 sec 2.0000 sec 6.50 usec 1H 18.0 c CDCL3 0.00 ppm 0.12 Hz C:¥Documents and Settings¥delta¥My D single\_pulse 15-02-2011 05:24:44



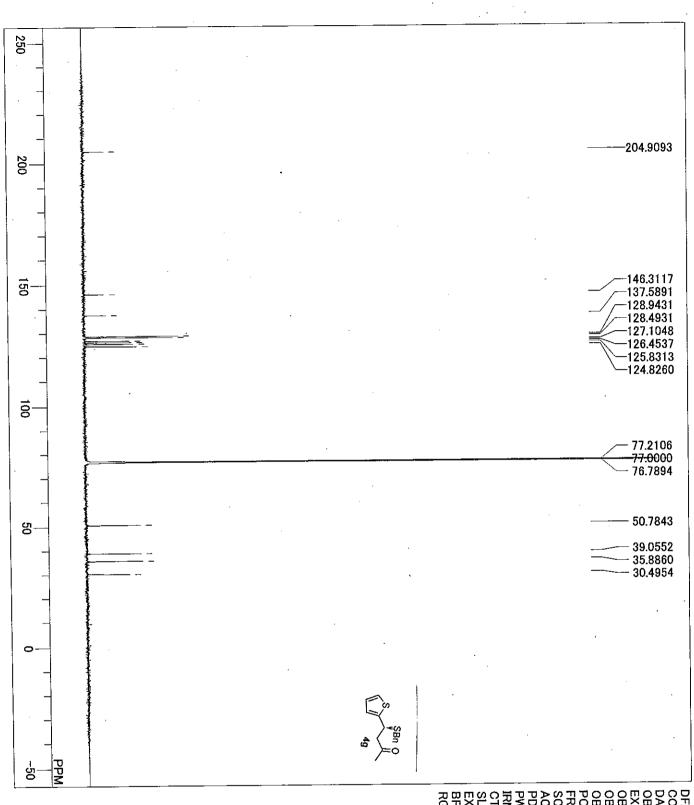
16-02-2011 09:51:12 13C



DFILE C:XI
COMNIT Sing
DATIM 16-1
OBNUC 1H
EXMOD Sing
OBSET

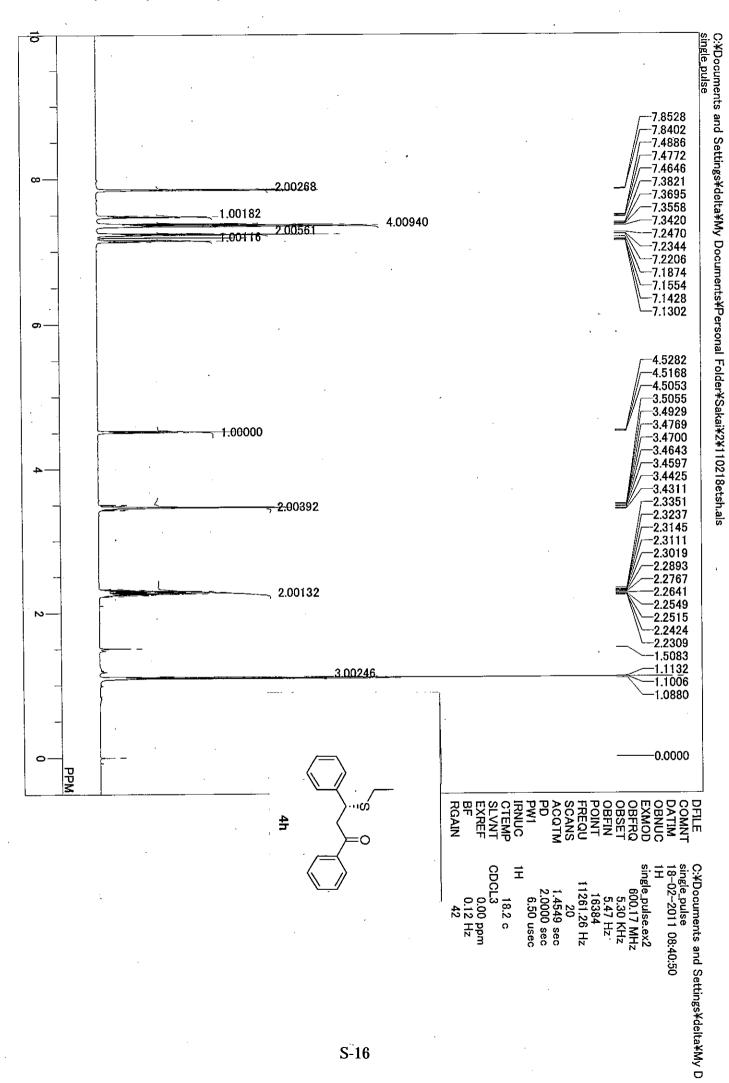
single\_pulse.ex2 600.17 MHz 5.30 KHz 5.47 Hz 13107 9008.87 Hz 8 1.4549 sec 2.0000 sec 6.50 usec 1H 17.8 c CDCL3 0.000 ppm 0.12 Hz

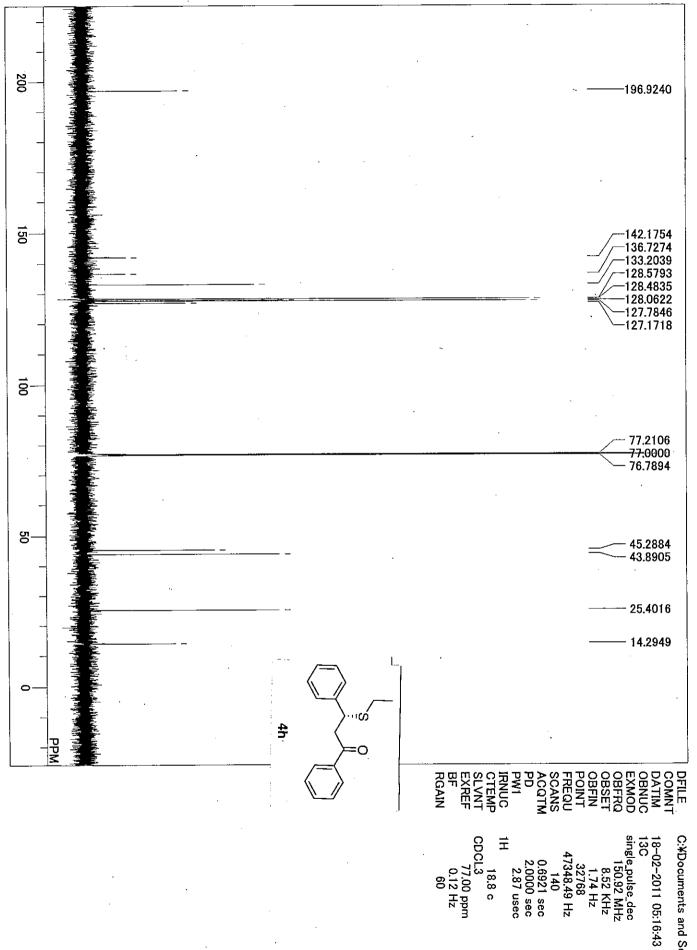
C:\(\foatings\)\(\text{delta}\)\(\text{My D}\)
single\_pulse
16-02-2011 02:44:54

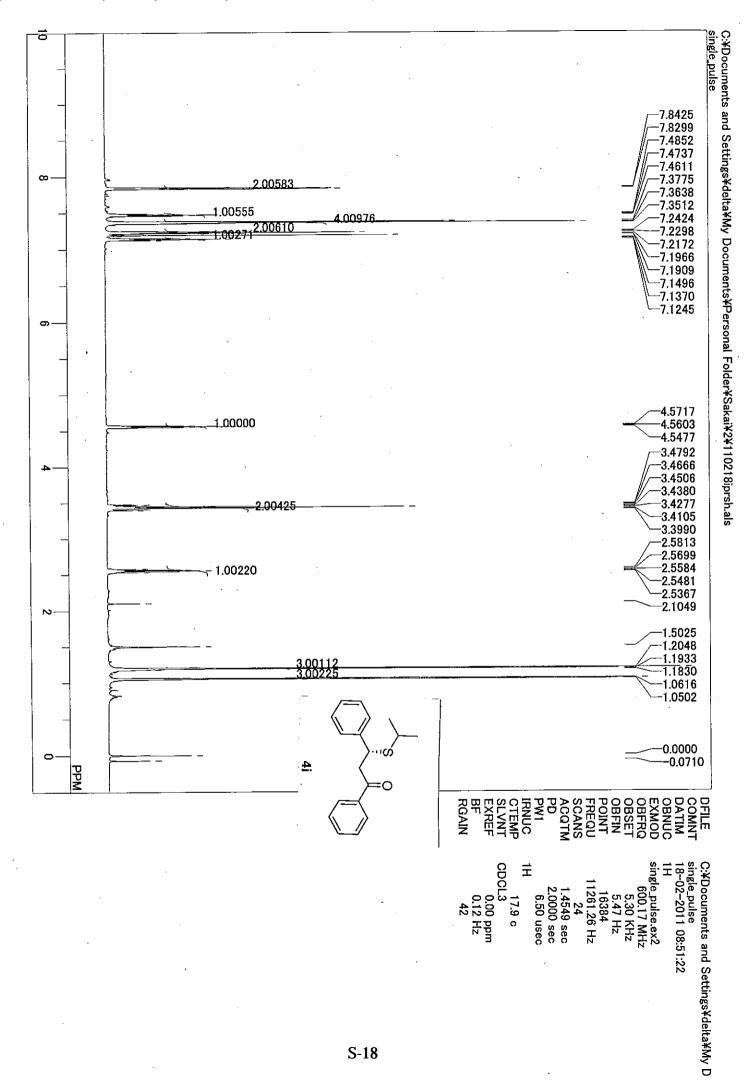


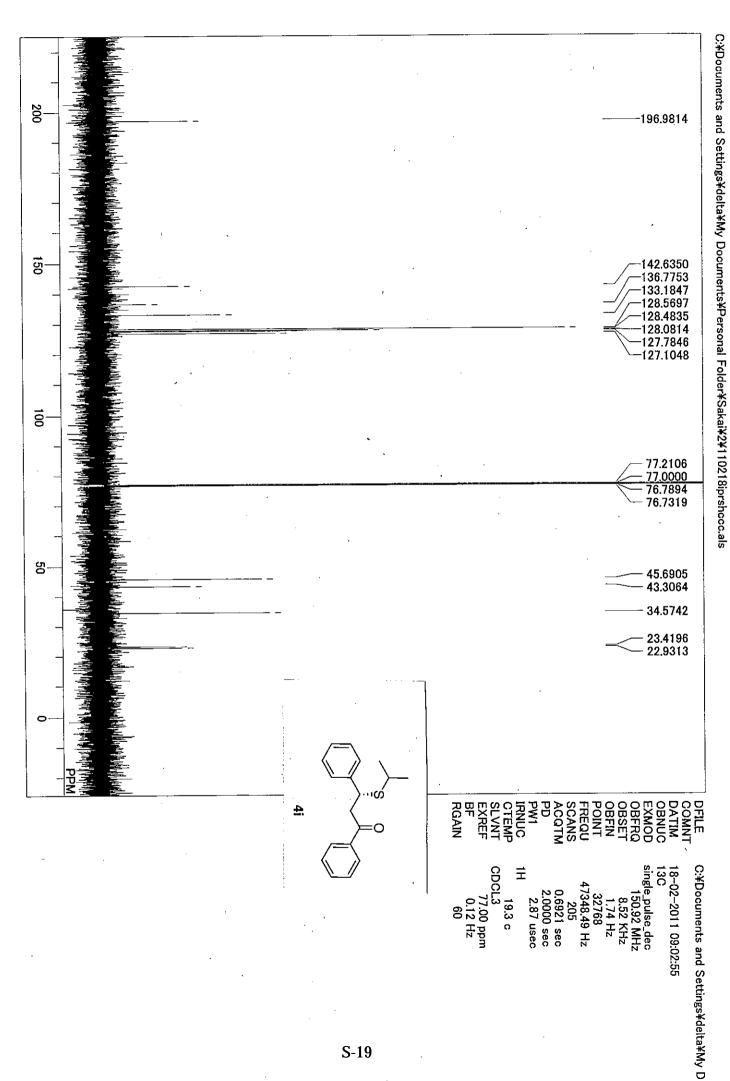
DFILE C:#Documents and Seconnt COMNT 16-02-2011 13:28:06 OBNUC 13C Single pulse\_dec OBFRQ 150.92 MHz OBSET 1.74 Hz OBFIN 40961 FREQU 504NS 0.6921 sec PD 2.87 usec PW1 19.8 c CTEMP CTEMP SLVNT CDCL3 EXREF 77.00 ppm BF 0.12 Hz RGAIN

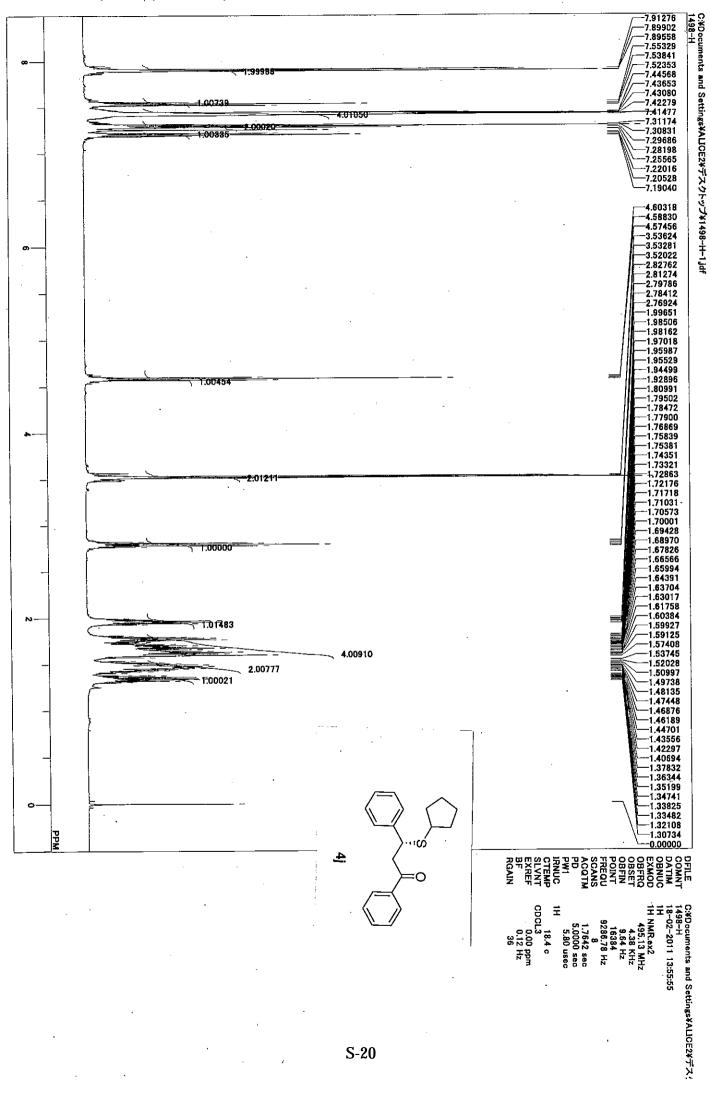
C:¥Documents and Settings¥delta¥My D

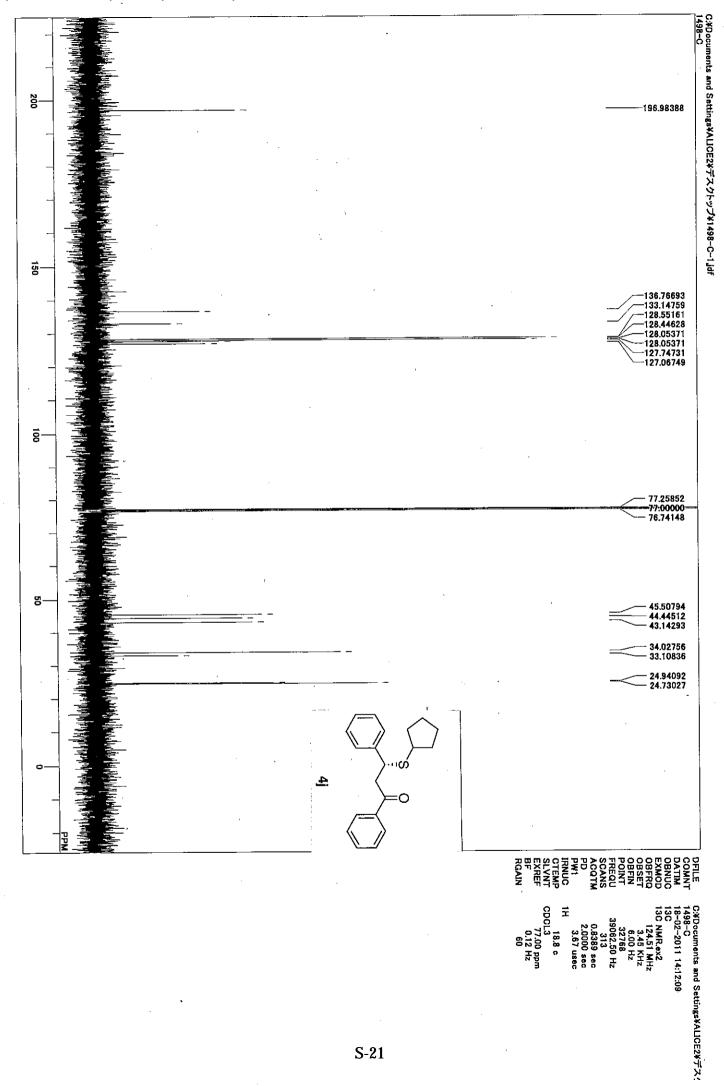


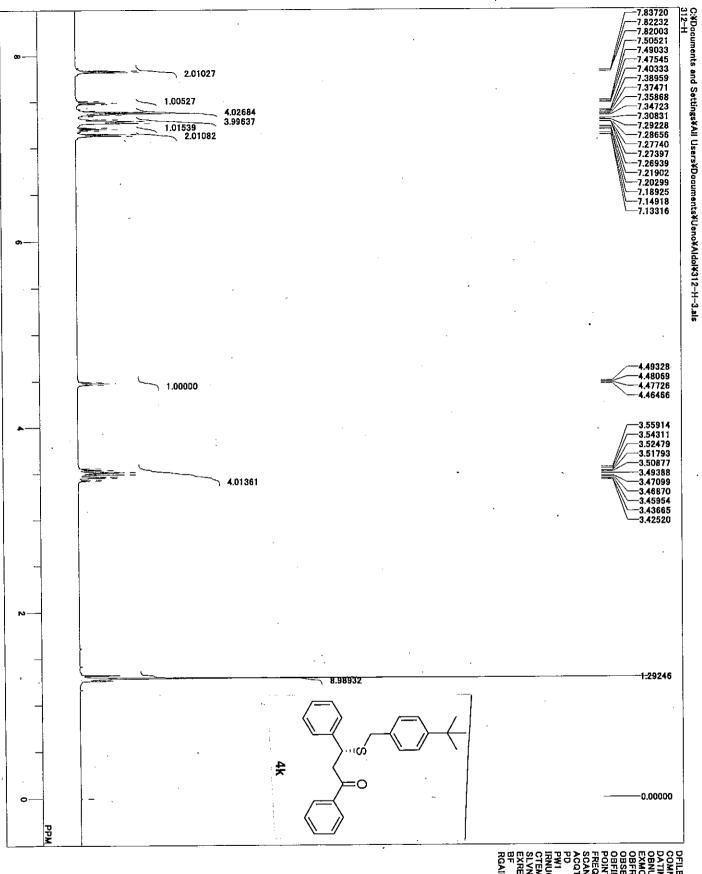


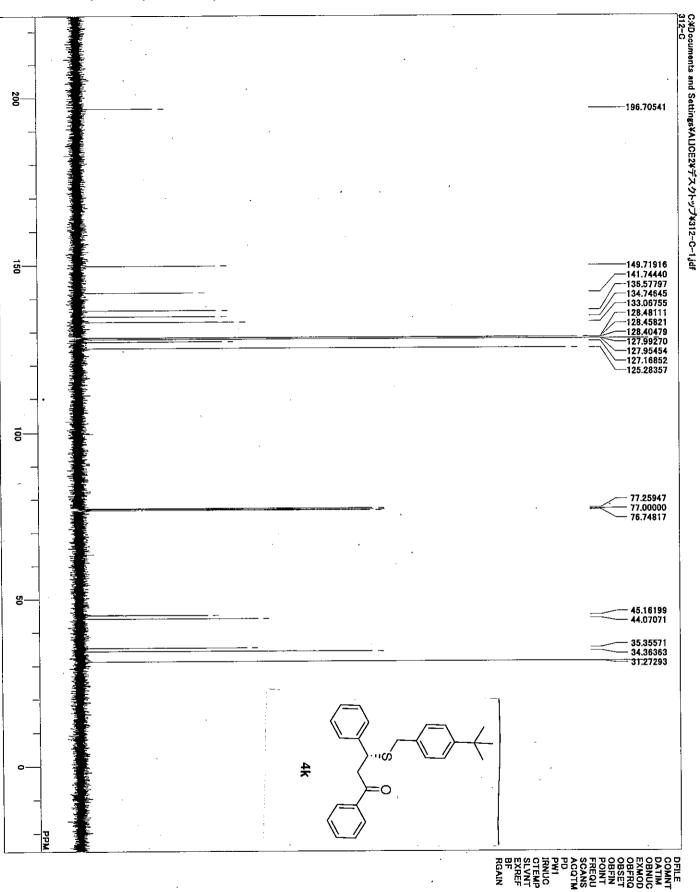




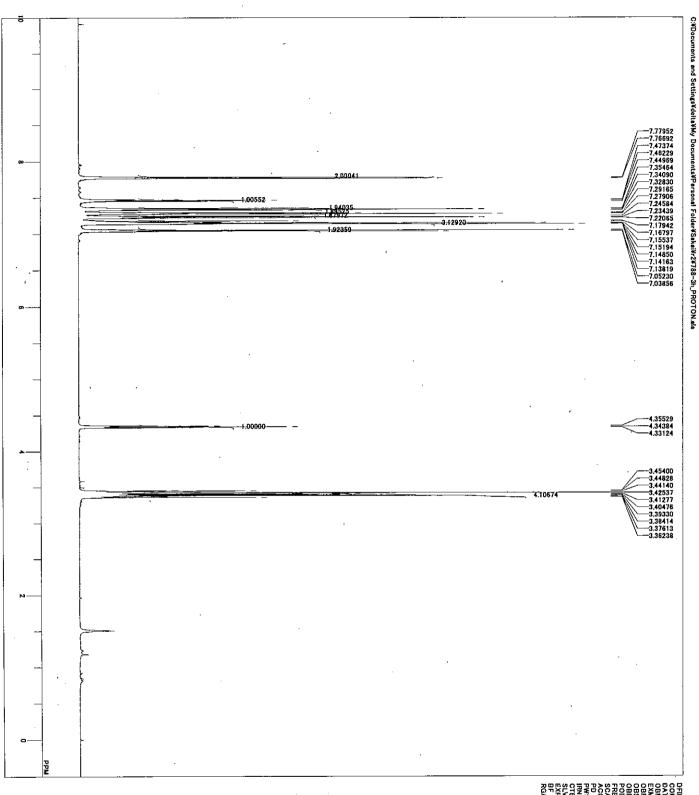


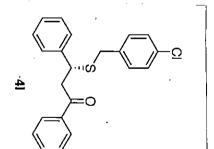




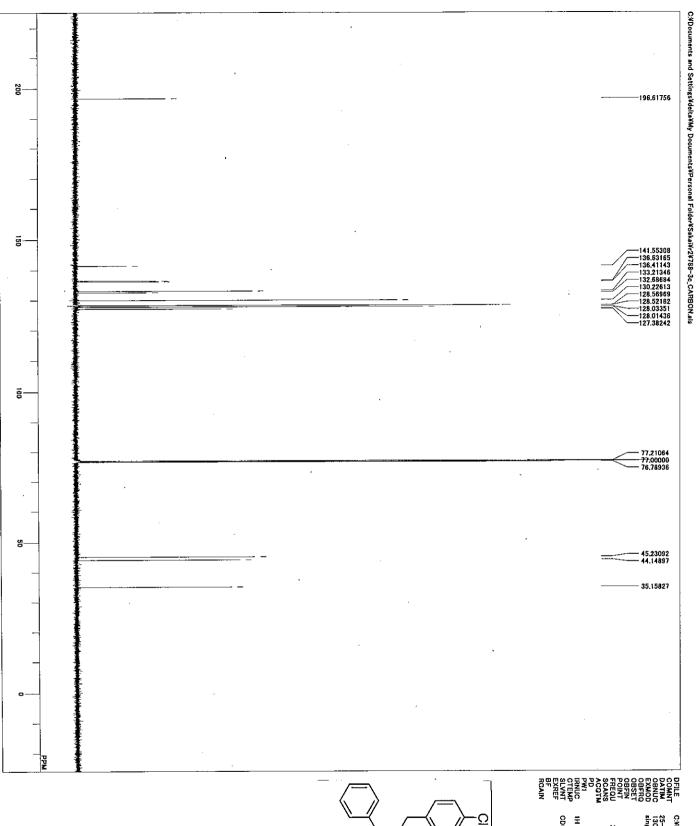


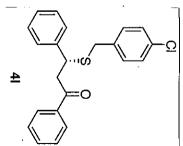
CXDocuments and Settings¥ALICE2¥₹X!
312-C
18-C2-2011 15:48:17
13C
13C
13C
13C
13C
14X:1 MHz
14.51 MHz
15.00 Hz
27.68
3173.25 Hz
421
1.0525 sec
2.000 sec
3.67 usec
1H
18.8 c
CDCL3
77.00 ppm
0.12 Hz





DFILE
CXDocuments and SettingsVdoltaVMy DocumentsVPersonal FolderVSakaiV/2
DATIM
25-11-2011 13:13:49
DATIM
25-11-2011 13:13:49
EXMOD
single pulse e-2
DBFIC
530 KHz
OBSRT
530 KHz
OBSRT
1317
SAV Hz
POINT
13107
FREDU
9008.87 Hz
SCANS
16
ACQTM
4,0000 sec
PM1
6,50 usec
IRNUC
IRNUC
11
49.3 c
SLWH
CDCL3
SLWH
A9.3 c
SLWH
CDCL3
SLWH
A9.3 c
SLWH
CDCL3
SLWH
CDC





C.VDocuments and SattingsVdeltaVMy DocumentsVParsonal FolderVSakaVV.2

W 25-11-2011 14:01:02

W 125-11-2011 14:01:02

U 136 KHz

U 150.92 MHz

U 150.92 MHz

U 174 Hz

174 Hz

174 Hz

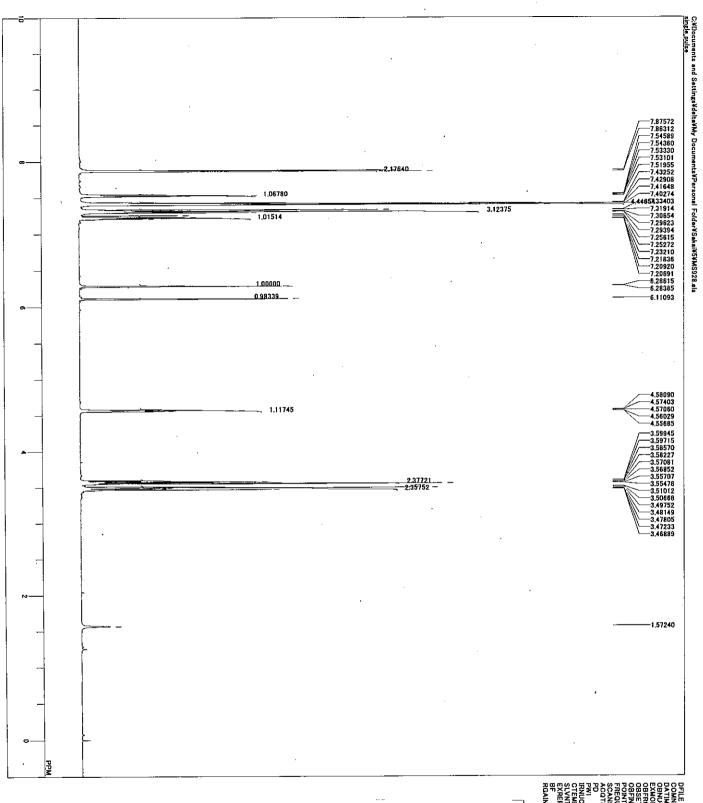
174 Hz

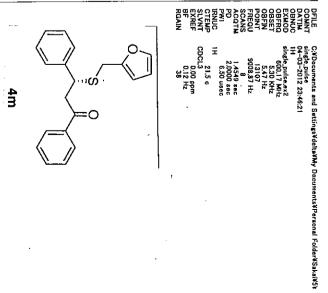
175 Hz

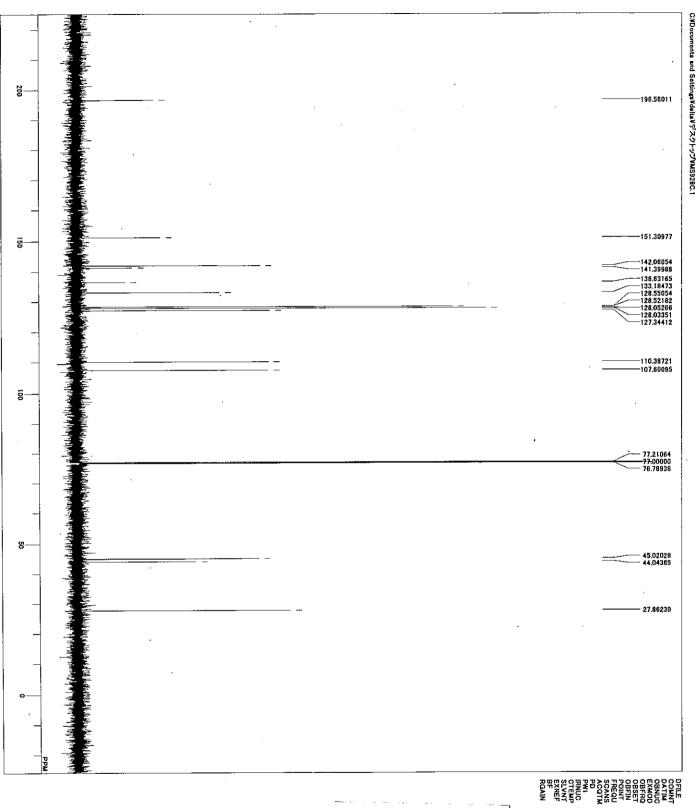
187 WH

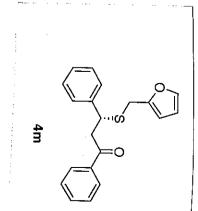
188 10921 sec

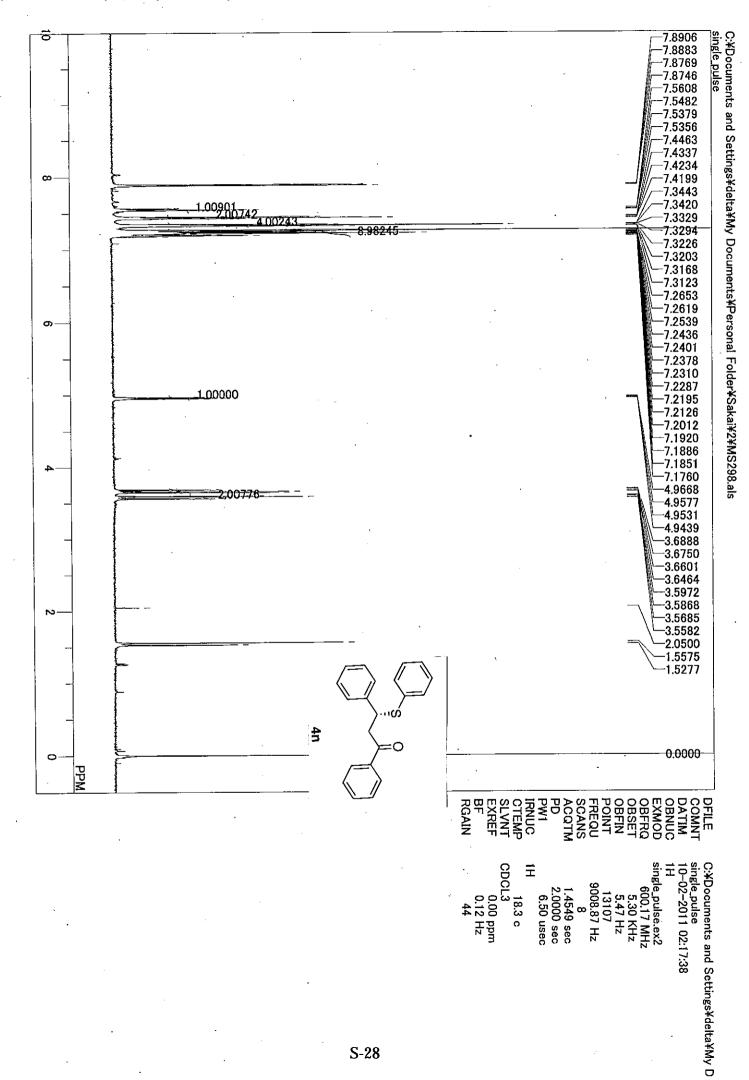
2,0000 sec

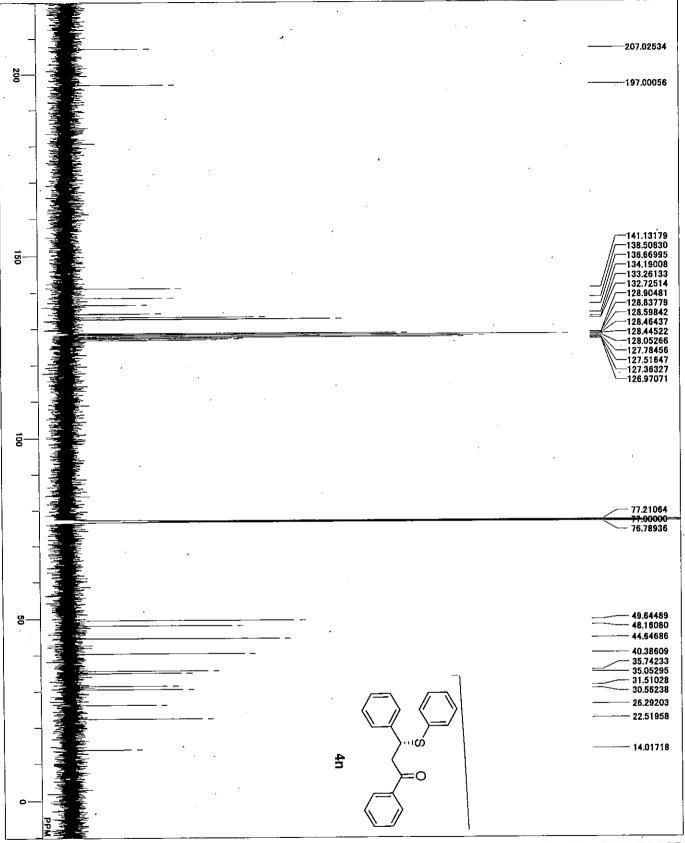








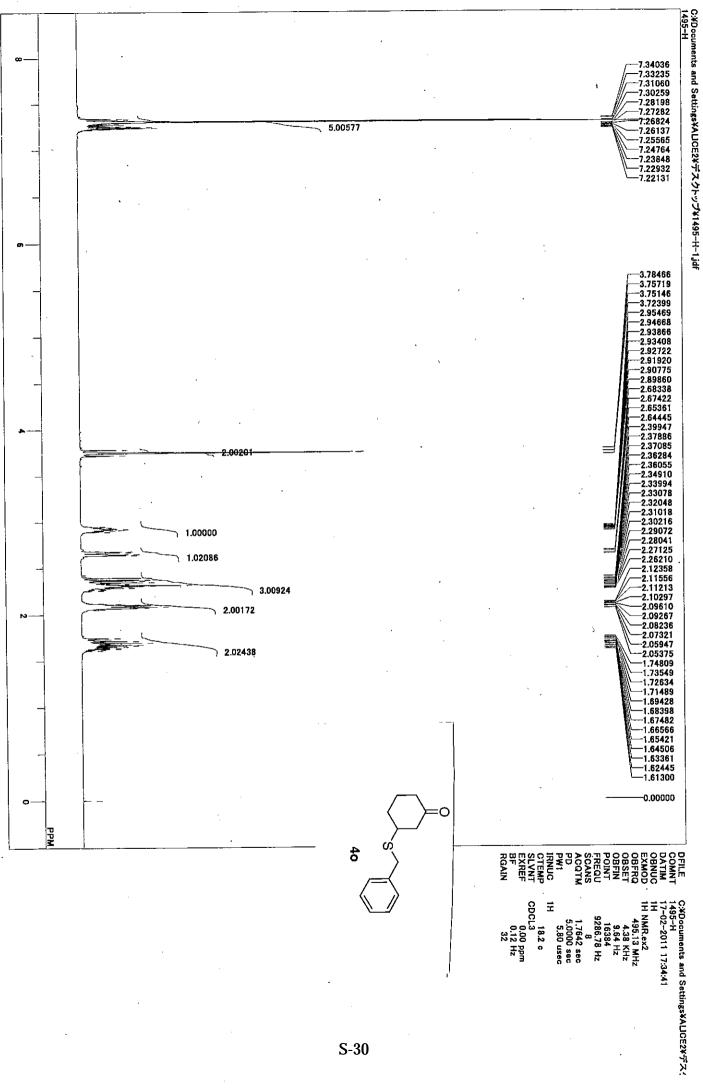


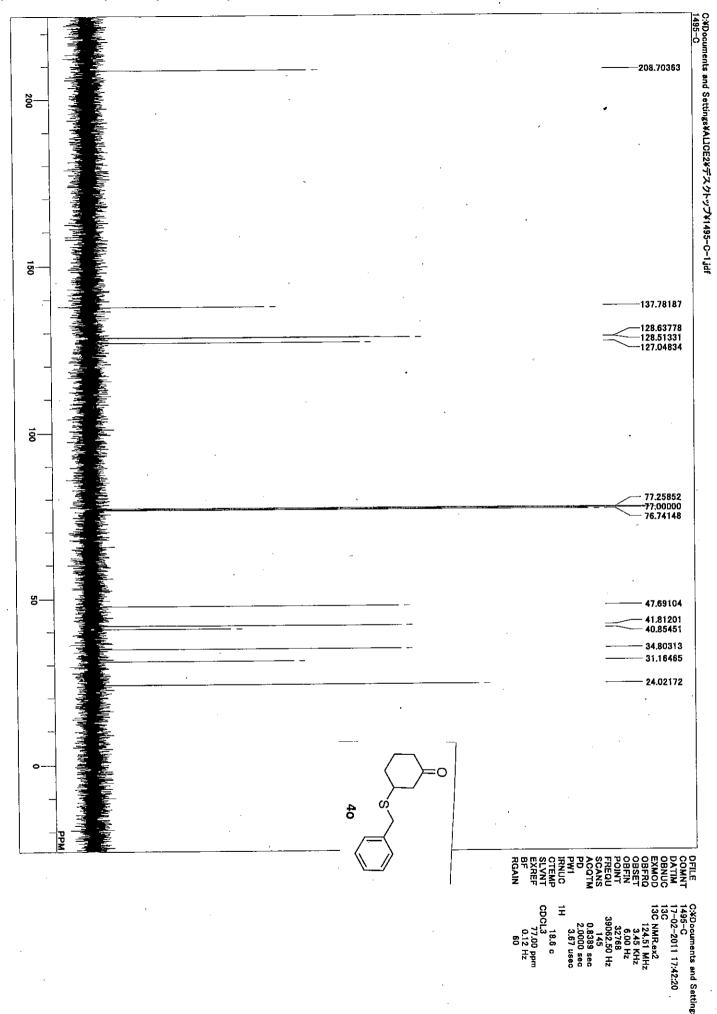


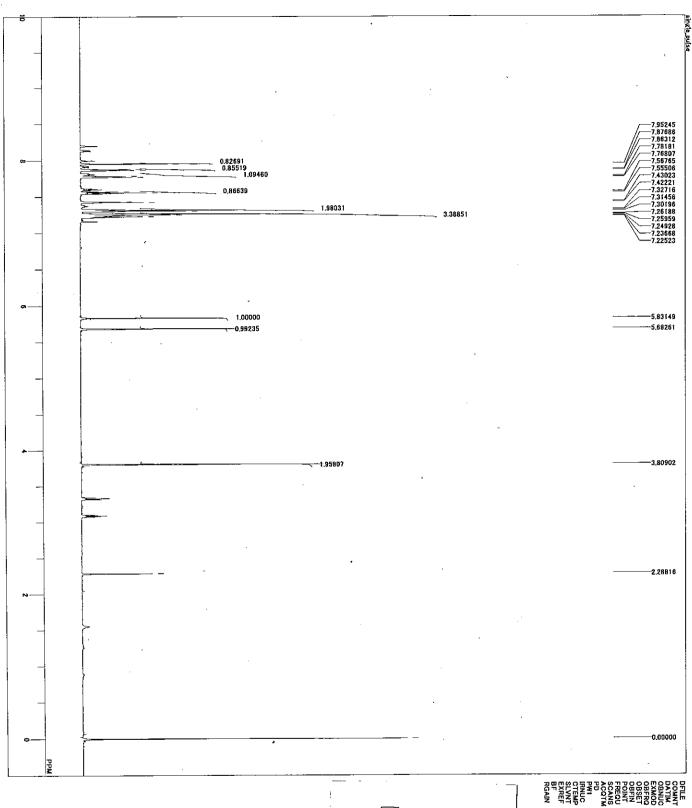
DFILE
COMMIT
DATIM
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DBNUG
DBFRQ
OBSET
OBSIN
OBSIN
PONT
FREQU

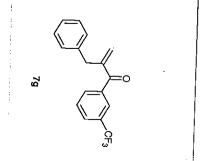
18-02-2011 17:36:05
13C
13C
13C
150.92 MHz
150.92 MHz
8.52 KHz
17.74 Hz
327:68
47348.49 Hz
9999
0.6921 sec
2.0000 sec
2.87 usec
1H
19.0 c
CDCL3
77.00 ppm
0.12 Hz
60

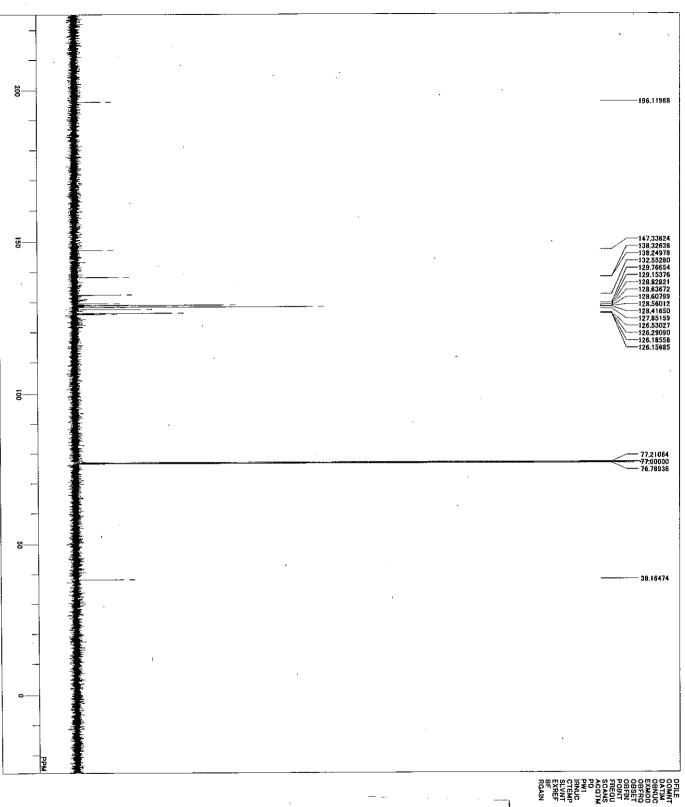
C:¥Documents and Settings¥AUCE2¥デス!

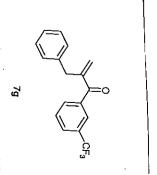




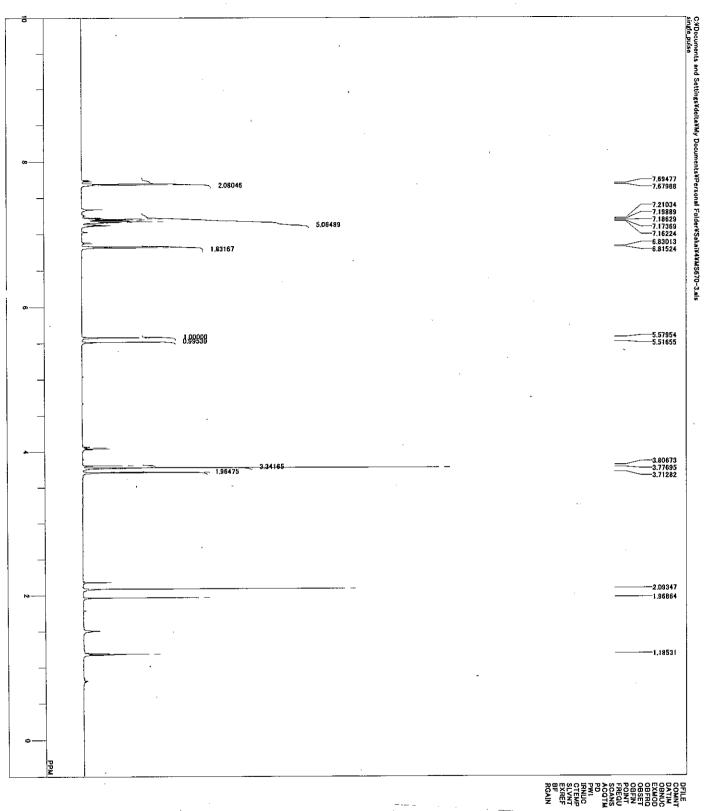


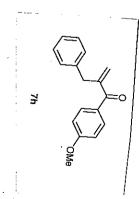


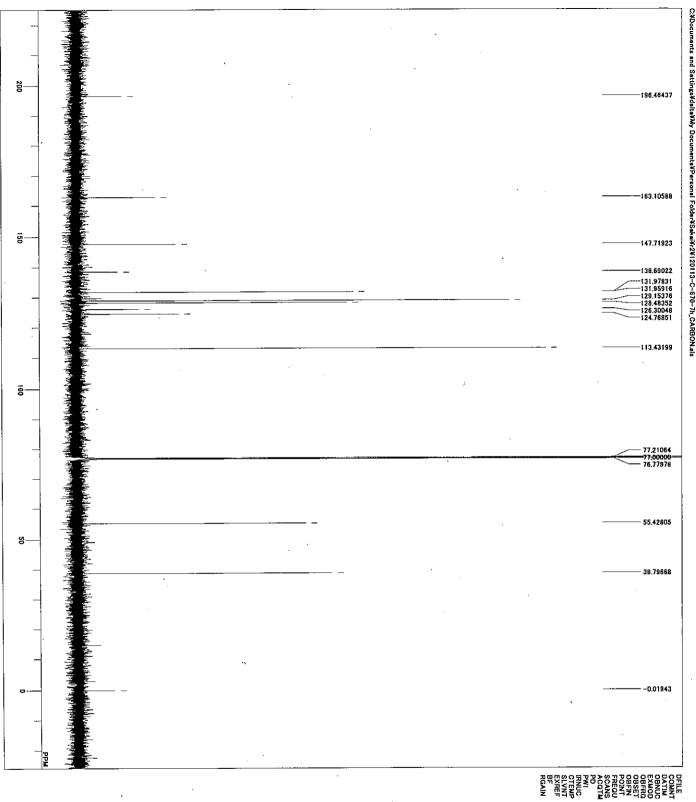


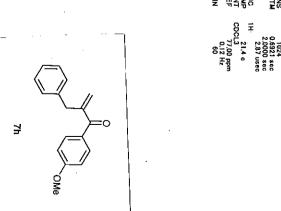


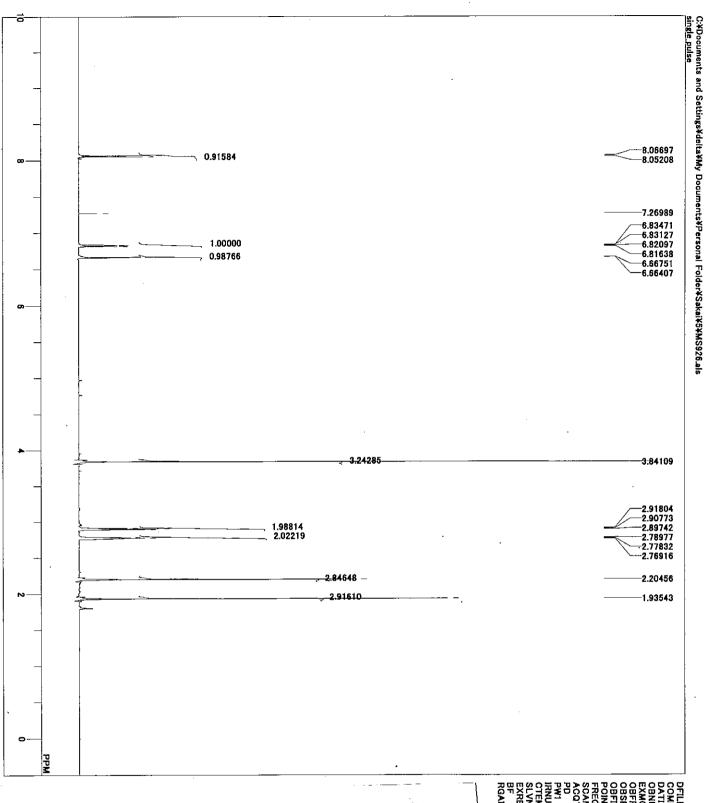
NT 12-D1-2012 23:49:59
JC 13C
JGC plise\_dec
150.92 MHz
150.92 MHz
150.92 MHz
174 Hz
174 Hz
174 Hz
174 Hz
174 Hz
175 Hz
176 Hz
177 177 177 Hz
17

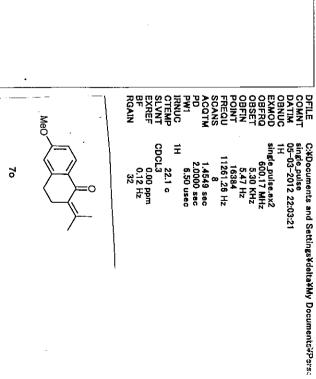


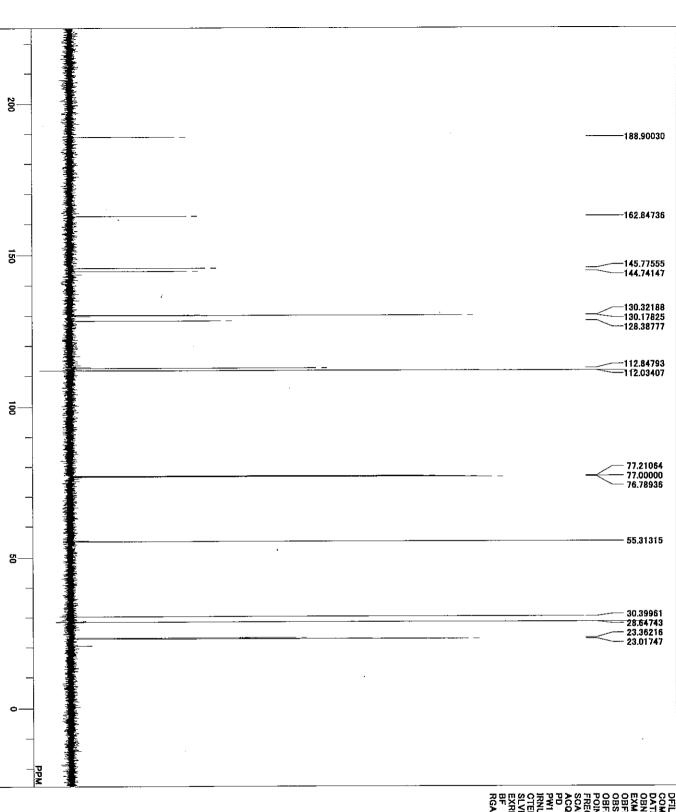


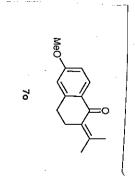






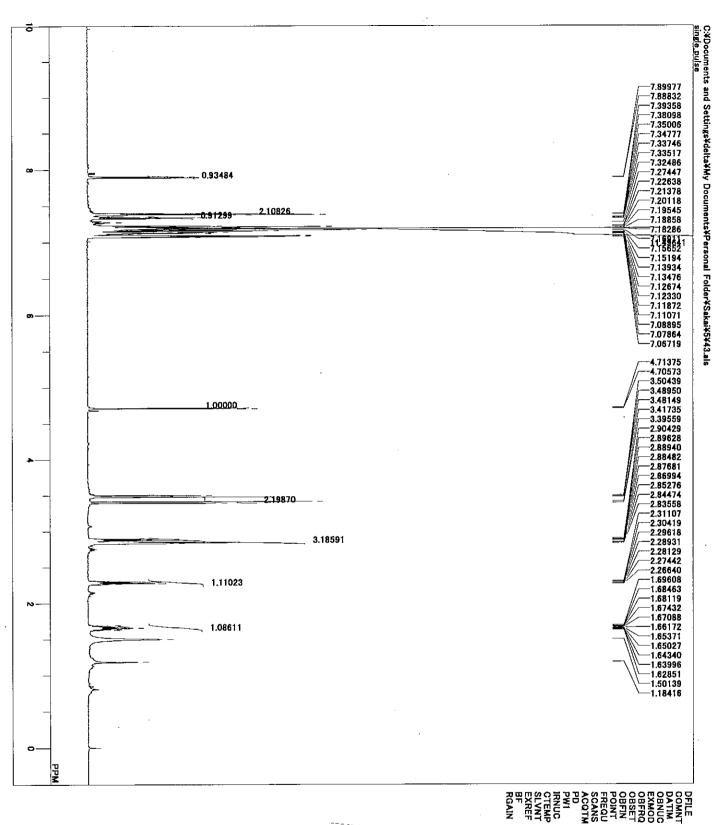


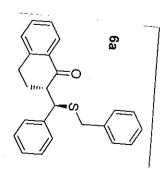




C:¥Documents and Settings¥delta¥My Documents¥Pers:

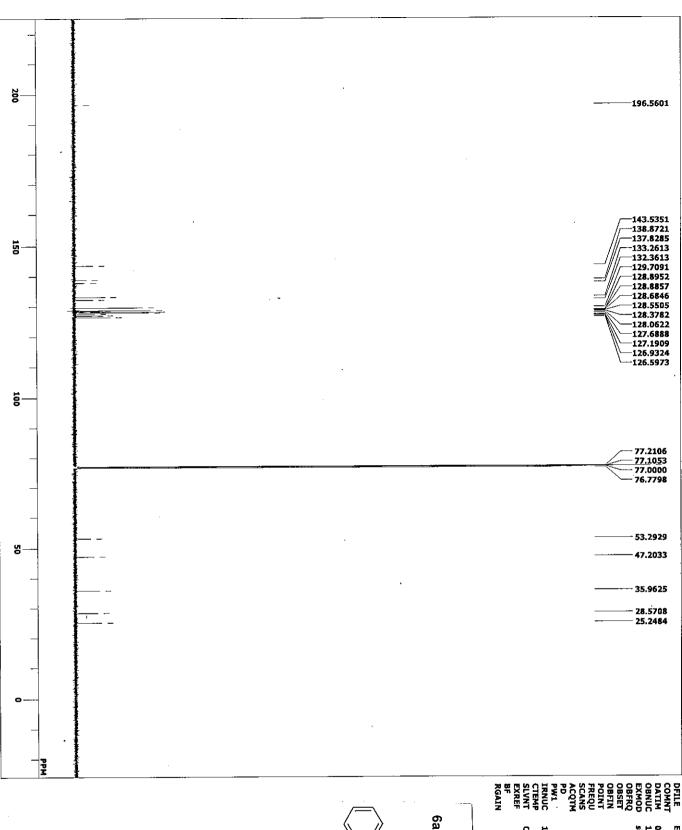
C:\(\partial Documents \) and Settings\(\partial delta\) Ams Documents\(\partial Personal Folder\) Sakai\(\partial S\) Fins 926C.als

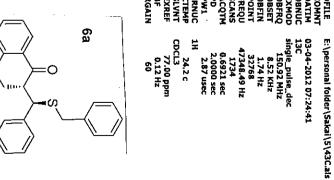




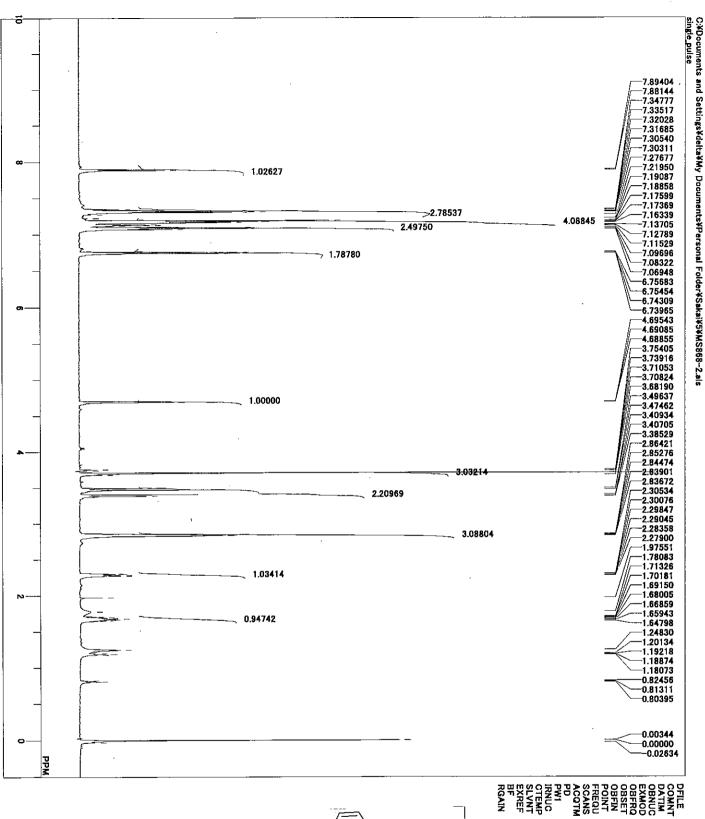
WNT single\_pulse
WNT 03-04-2012 06:04:46
VUC 1H

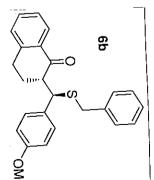
AOD single\_pulse.ex2
600.17 MHz
5.47 Hz
FIN 5.47 Hz
FIN 16:384
FIN 16:384
FIN 16:49 sec
FIN 1.4549 sec
FIN 2.0000 sec



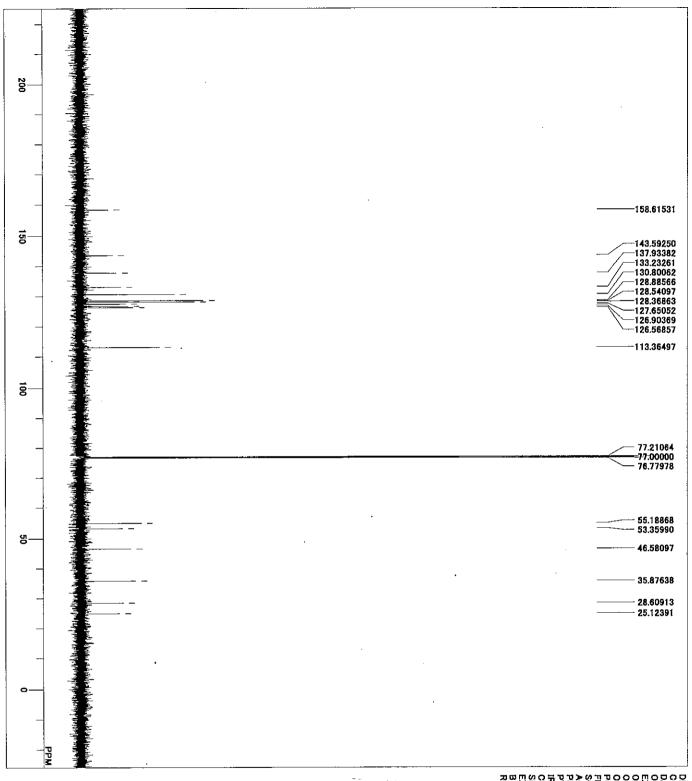


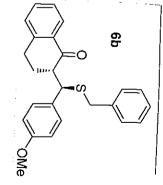
E:\personal folder\Sakai\5\43C.als

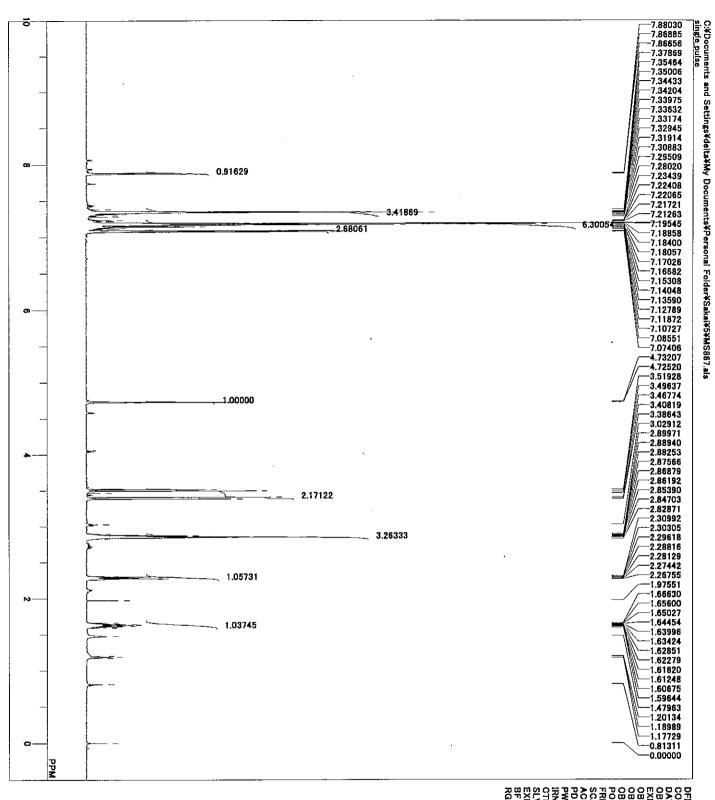


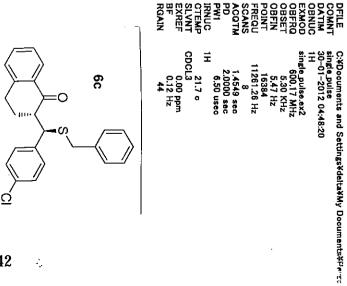


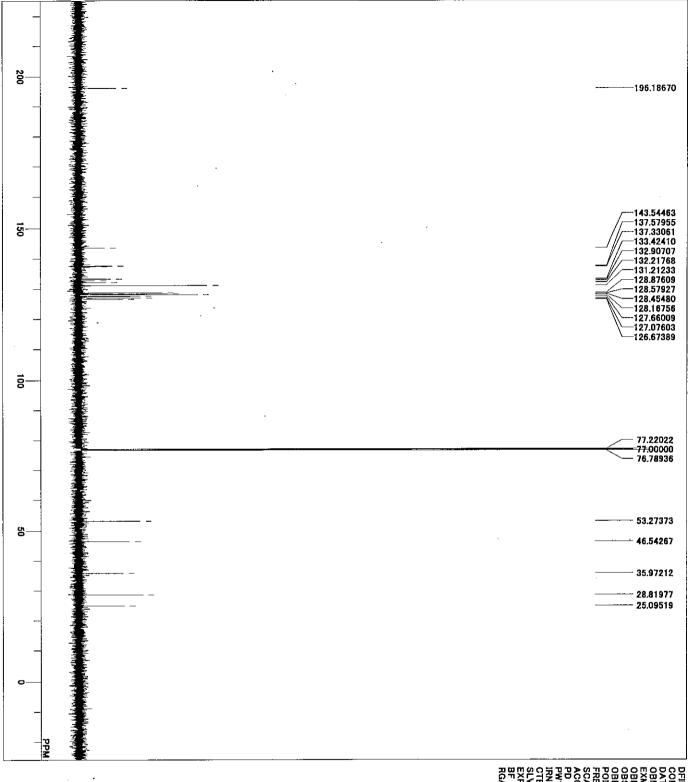
E C: XDocuments and Settings \( \) \text{delta\text{YMy Documents\text{YP}} \) \( \)

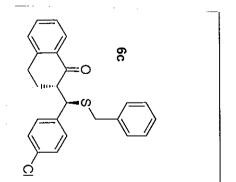


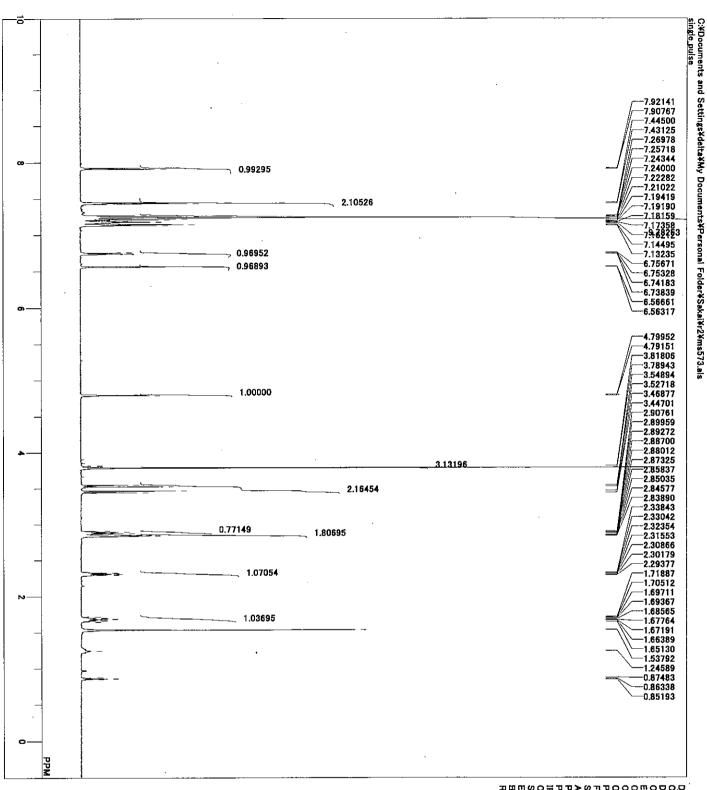


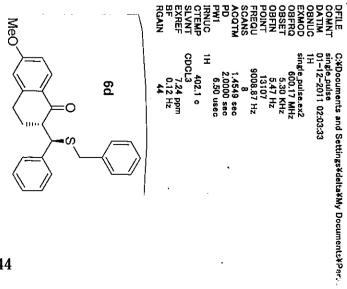


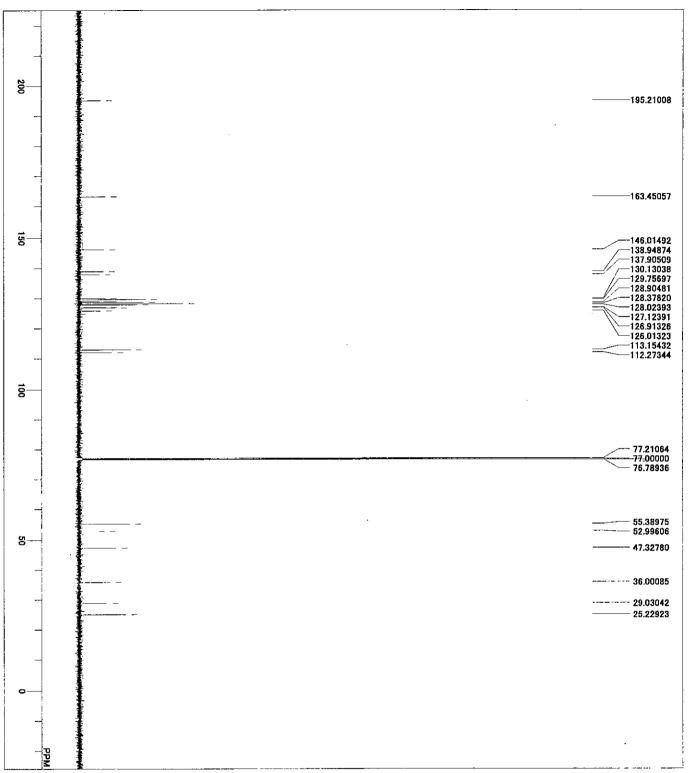


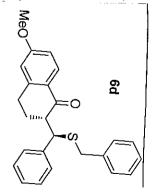




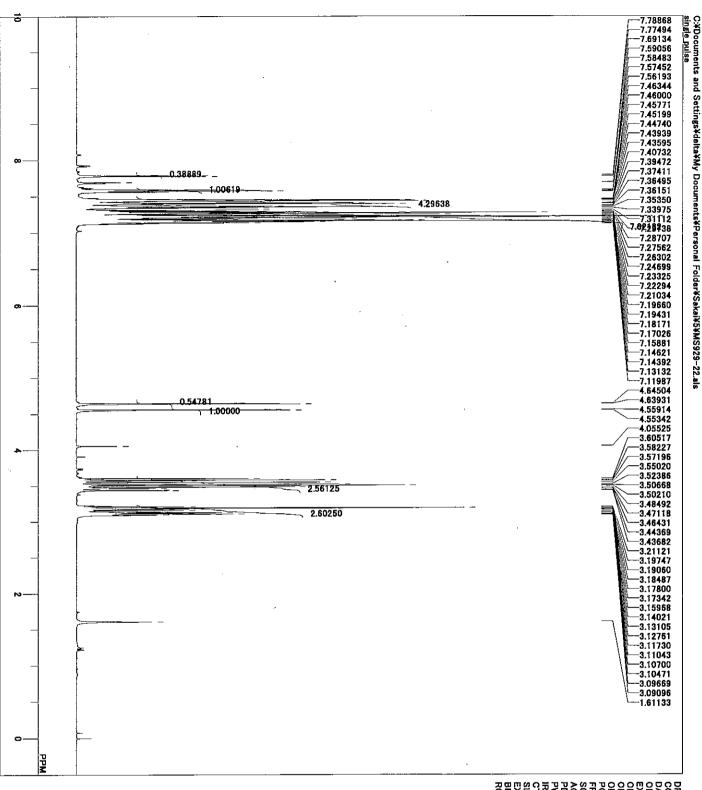


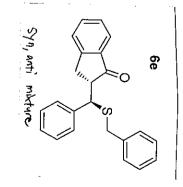






DFILE
CONTINU
DATIM
DATIM
DATIM
OBNUG
DEFRO
OBFRO
OBSET
OBFIN
OBFIN
POINT
FREQU
FREG
FREQU
FREQU OWDocuments and SettingsKdoltakデスクーツンドウト 12-12-2011 10:27.41 13C

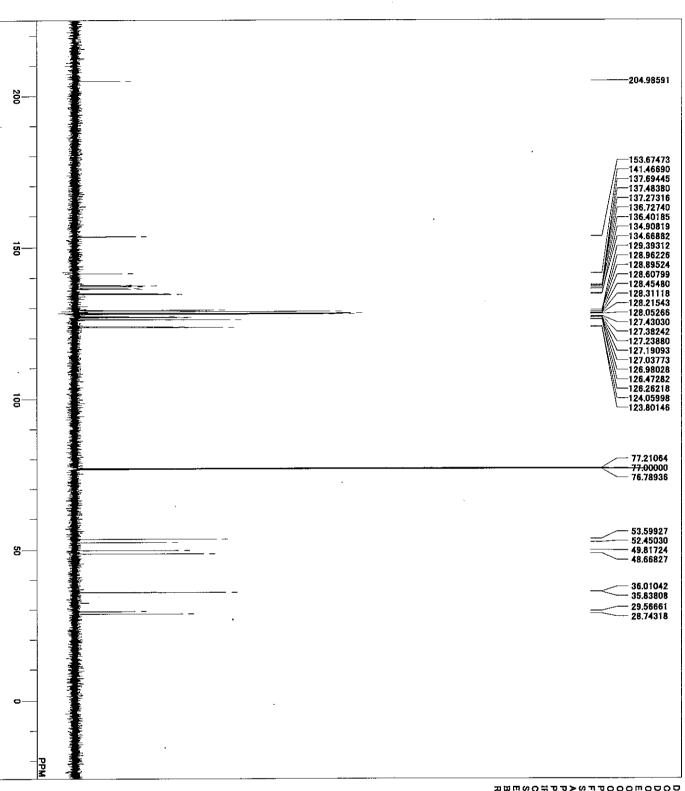


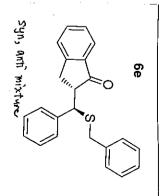


DFILE C: ADocuments and Settings V delta V My Documents V Pers:
COMNT single pulse
DATIM 05-03-2012 22:18:49

OBNUC 1H

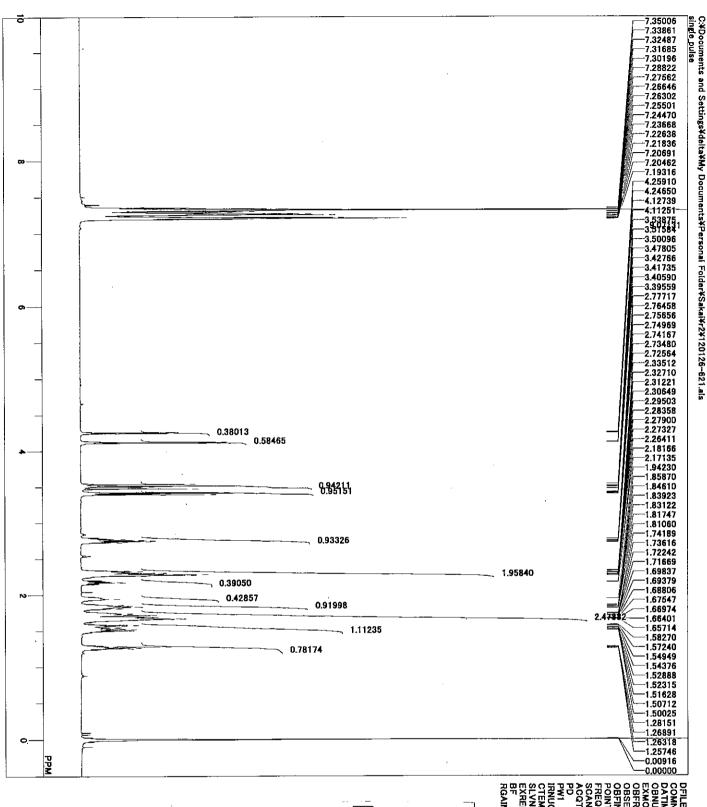
EXMOD single pulse ex 2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 116384
FREQUU 11261.26 Hz
SCANS 8
ACQTM 1.4549 sec
PM1 6.50 usec
IRNUC 1H
CTEMP 22.3 c
SLVNT 0.00 ppm
BF 0.12 Hz
RGAIN 38

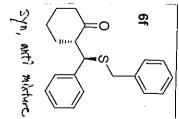




DFILE
COMDOCUMENTS and Settings
COMNT
COMNT
DATIM
DATIM
O5-03-2012 22:31:41
OBNUC
EXMOD
Single-pulse dec
OBFRQ
OBSET
OBSET
OBSET
FREQU
COMPONT
OBSET
O

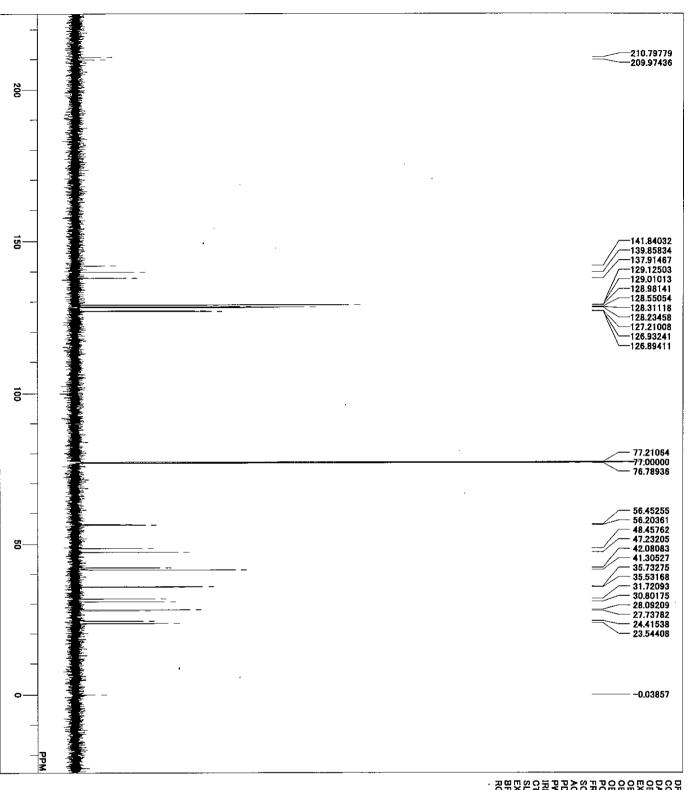
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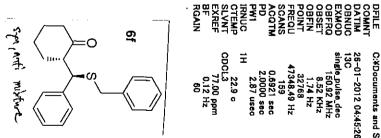




DFILE
CWDocuments and (
single\_pulse\_pulse
DATIM
14-2012 04:36:0

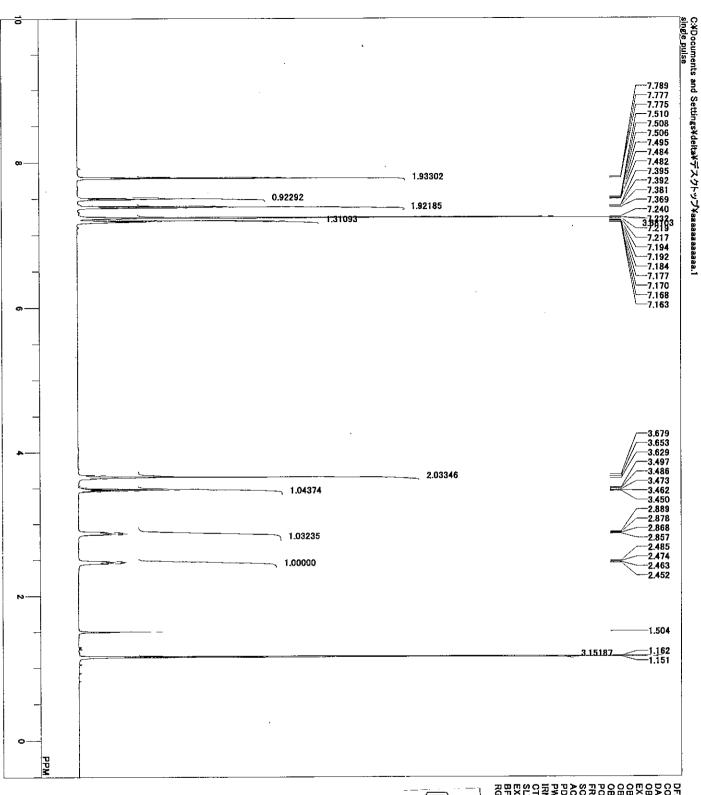
OBNUC
Single\_pulse.ex2
600.17 MHz
600.17 MHz
COBFRQ
OBFRQ
DATIM
15.30 KHz
5.30 KHz
5.30 KHz
16384
FREQU
16384
FREQU
FREQU
1626.26 Hz
SCANS
ACQTM
1.4549 sec
PD
2.0000 sec
PM1
CTEMP
CTEMP
21.7 c
SLVNT
CDCL3
EXREF
0.00 ppm
BF
RGAIN
38

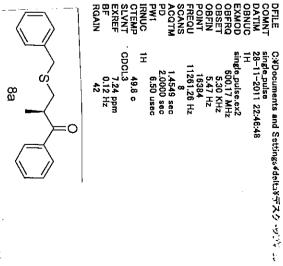


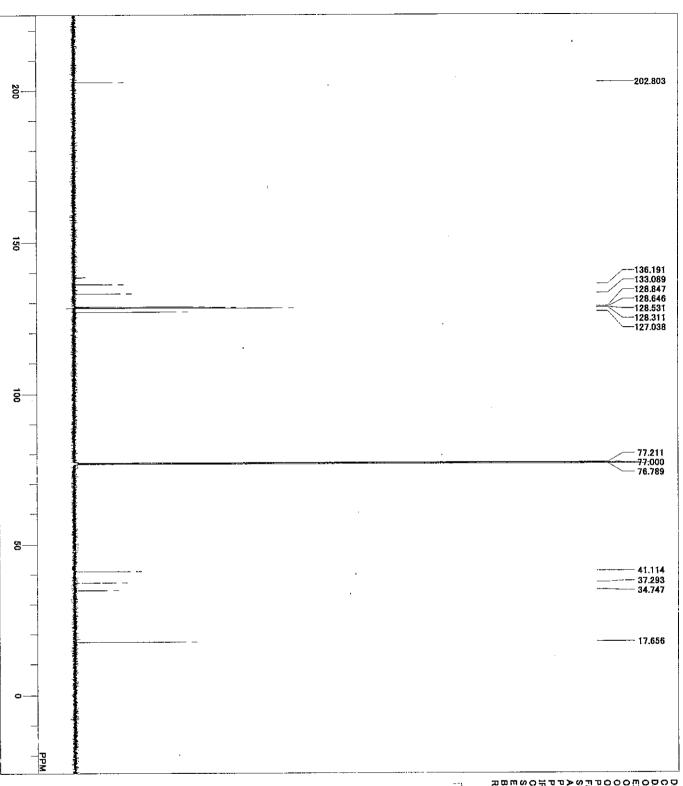


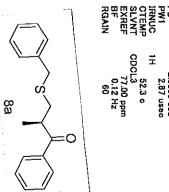
26-01-2012 04:45:26 13C

C:\Documents and Settings\delta\My Documents\Personal Folder\Sakai\r2\120126-621c.als

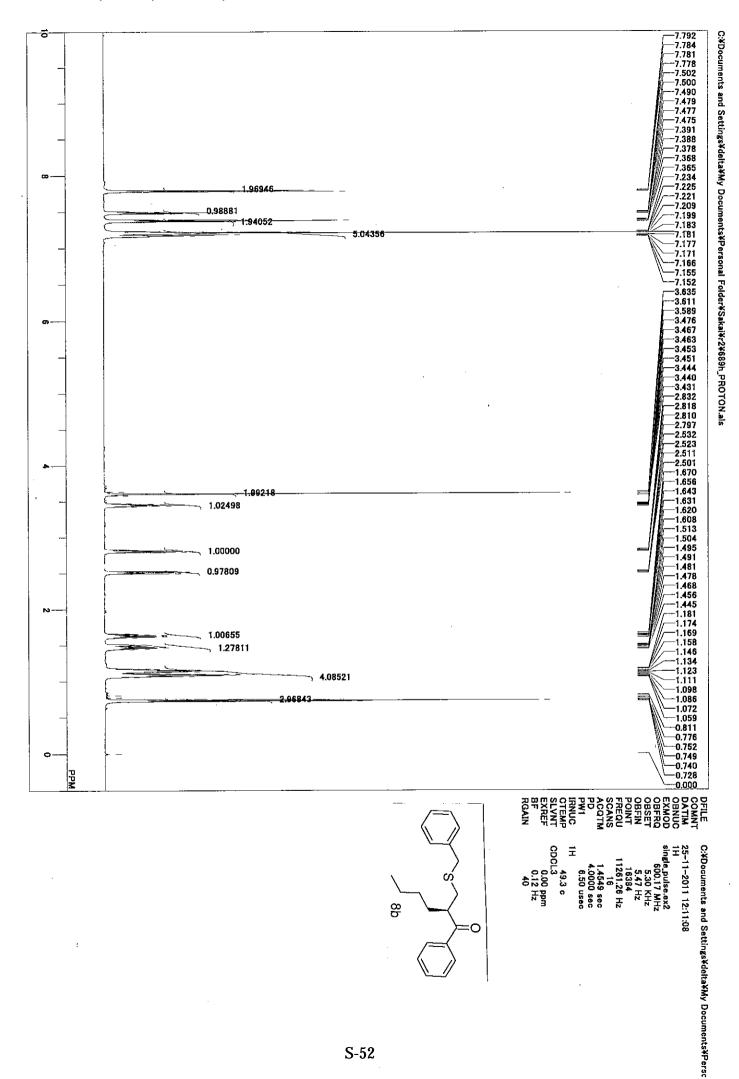


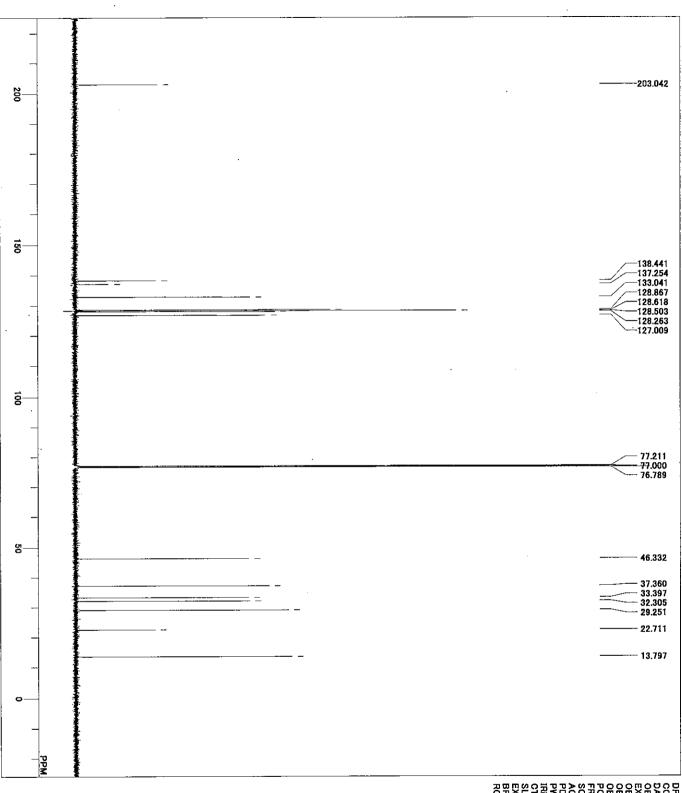


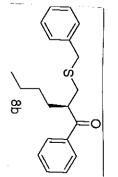




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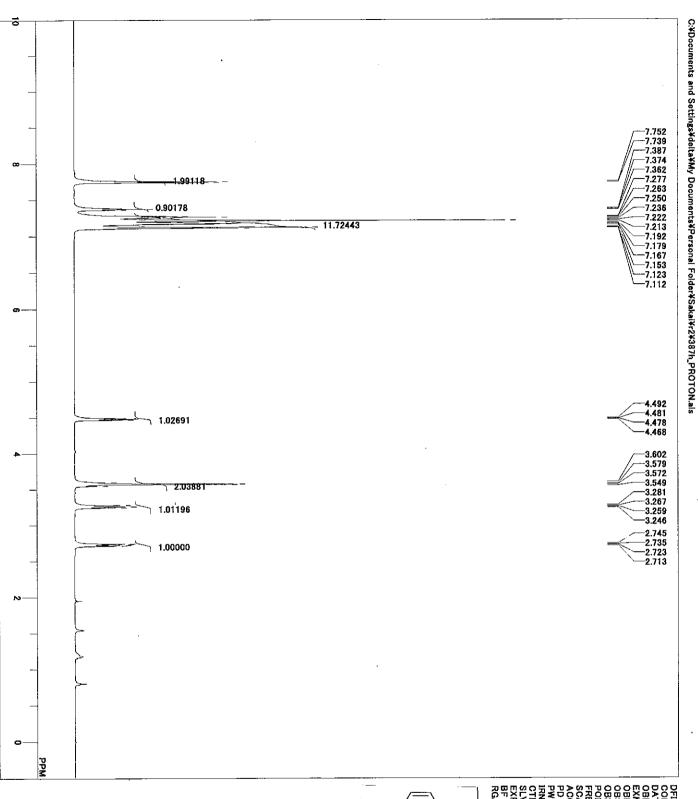


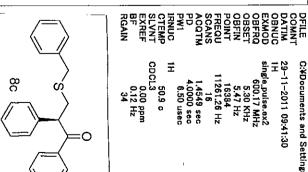


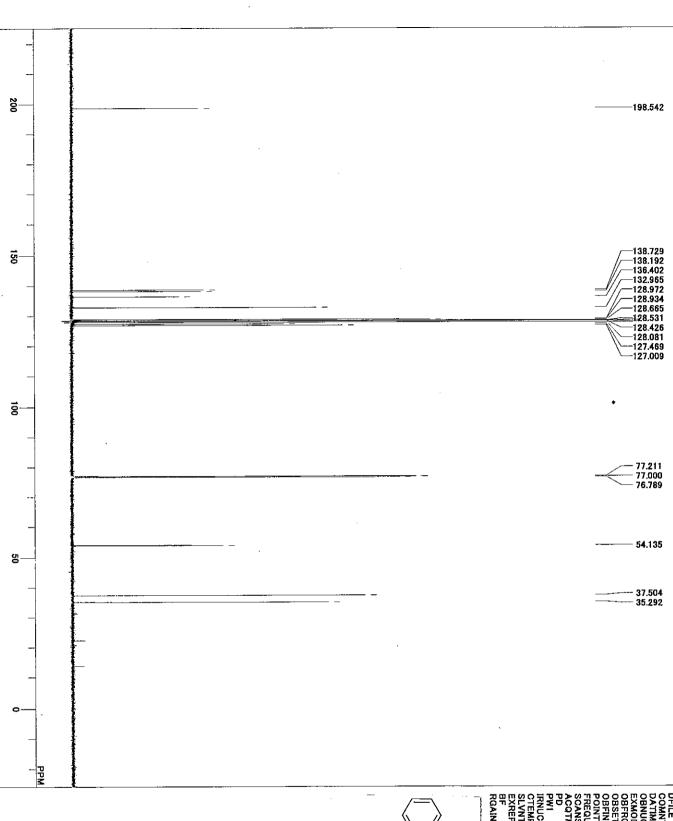


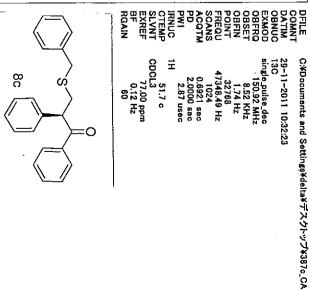
DFILE C:\*Documents and Sett COMNT 25-11-2011 12:58:01 DATIM 25-11-2011 12:58:01 OBNUC 13C Single-puise\_dec OBFRQ 150.92 MHz OBSET 150.92 MHz OBSET 32:768 FREQU 47348.49 Hz SCANS 1024 ACGTM 0.6921 sec PD 2.0000 sec PM1 2.87 usec IRNUC 1H 2.87 usec IRNUC 1H 50.0 c SLVNT 57.00 ppm BF CDC13 CDC13 CDC2 Hz CDC14 CDC2 Hz CDC14 CDC2 Hz CDC14 CDC2 Hz CDC15 CDC15 CDC2 Hz CDC15 CD

C:¥Documents and Settings¥delta¥My Documents¥Personal Folder¥Sakai¥r2¥689c\_CARBON.als

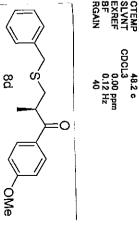








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PFILE C: #Documents and Settings #delta #My Documents #Persc

DMNT 14

BBFRQ 600.17 MHz

BBFRQ 600.17 MHz

BBFRQ 600.17 MHz

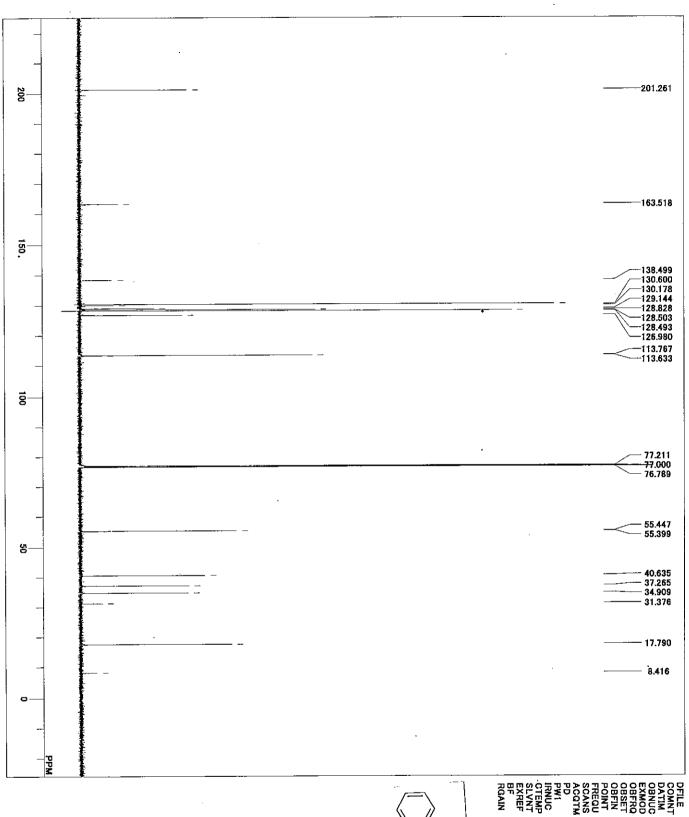
BSET 5.30 KHz

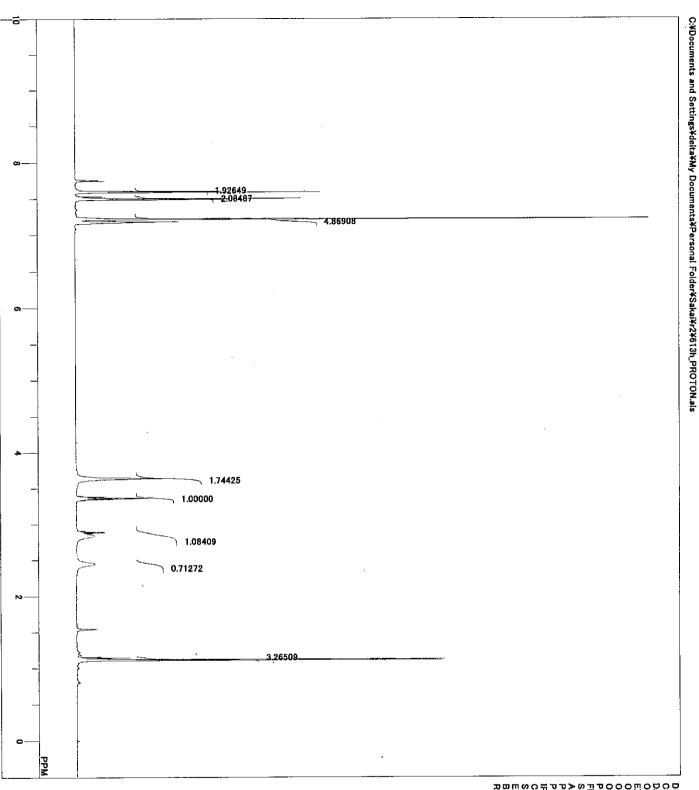
BBFRQ 617 MHz

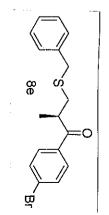
COINT 16384

REQU 11261.26 Hz

CCANS 16

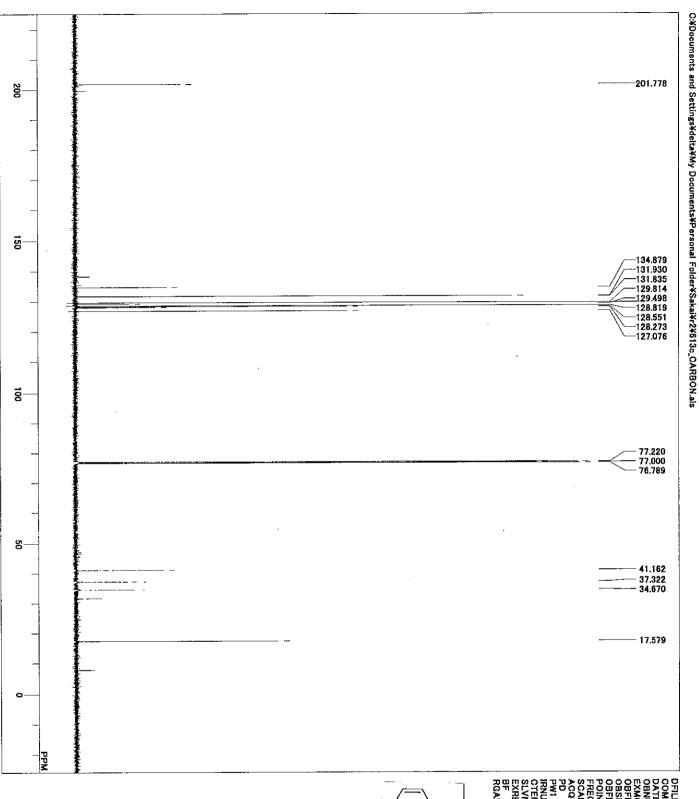


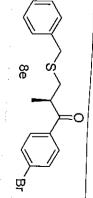




DFILE C:#Documents and Second To ATIM 29-11-2011 10:42:40
DATIM 19-11-2011 10:42:40
DATIM 19-11-2011 10:42:40
DBNUC single-pulse-ex2
DBFRQ Single-pulse-ex2
DBFRQ Single-pulse-ex2
DBFRQ Single-pulse-ex2
DBFRQ Single-pulse-ex2
DBFRQ Single-pulse-ex2
DBFRQ 11:261:26 Hz
SCANS 1.4549 sec
PD 1.4549 sec
PD 4.0000 sec
PD 4.0000 sec
DFRUUC 19-000 sec

C:\Documents and Settings\delta\My Documents\Perso





DFILE C:WDocuments and SettingsVdeltaVMy DocumentsXPers/
COMNTI
DATIM 29-11-2011 11:29:33

DBNUC 13C

EXMOD single\_pulse\_dec

OBFRQ 150.92 MHz

OBFIN 1.74 Hz

POINT 32768

FREQU 47348.49 Hz

SCANS 1024

ACQTM 0.6921 sec

PW1 2.87 usec

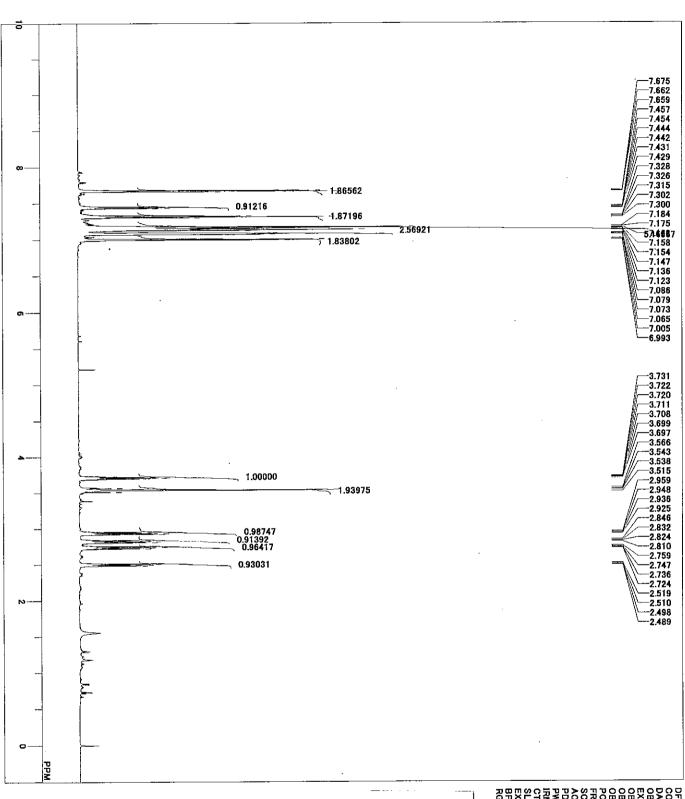
IRNUC 1H

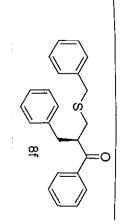
EXREF 77.00 ppm

BF 77.00 ppm

BF 0.12 Hz

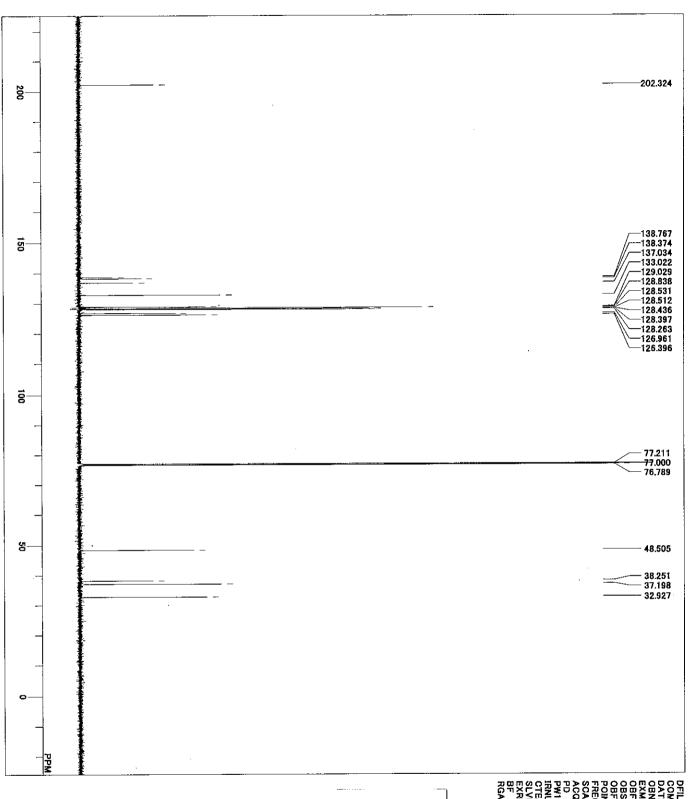
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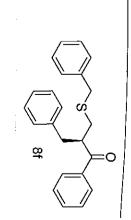




DFILE C.\*Documents and St. COMMIT 22-11-2011 10:25:38 OBNUC 1H EXAMOD Single\_pulse.ex2 600:17 MHz OBSET 5.30 KHz OBSET 16384 FREQU 11261:26 Hz SCANS 1649 sec PD 4,0000 sec PW1 6.50 usec IRNUC 1H 48.3 c SLYNT CDCL3 EXEREF 0.00 ppm BF 0.12 Hz

C※Documents and Settings¥delta¥デスクトップ¥656h\_PR 22-11-2011 10:25:38 C:¥Documents and Settings¥delta¥デスクトップ¥656h\_PROTON.1

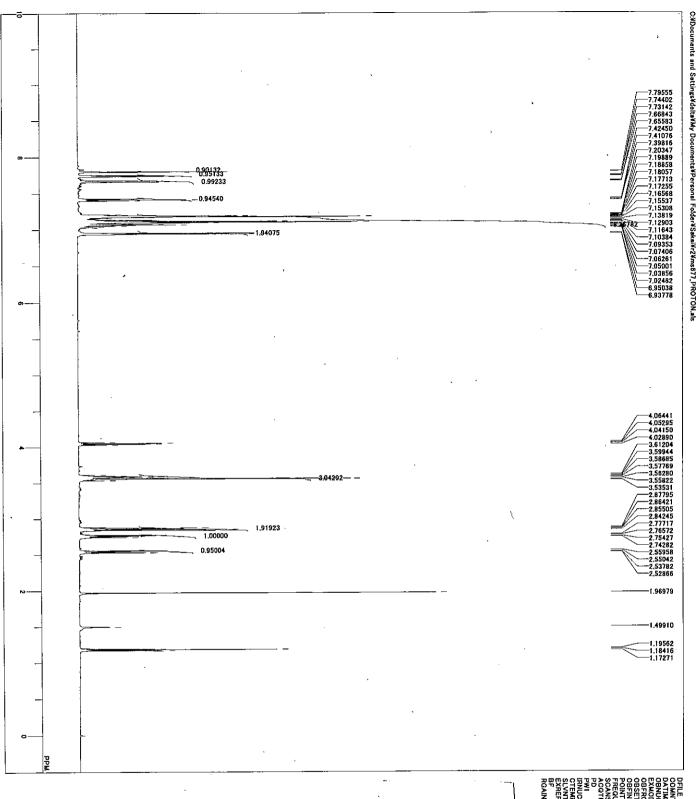


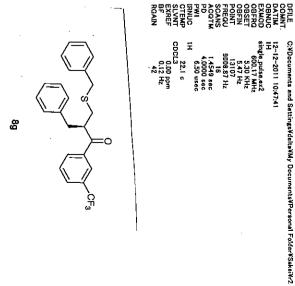


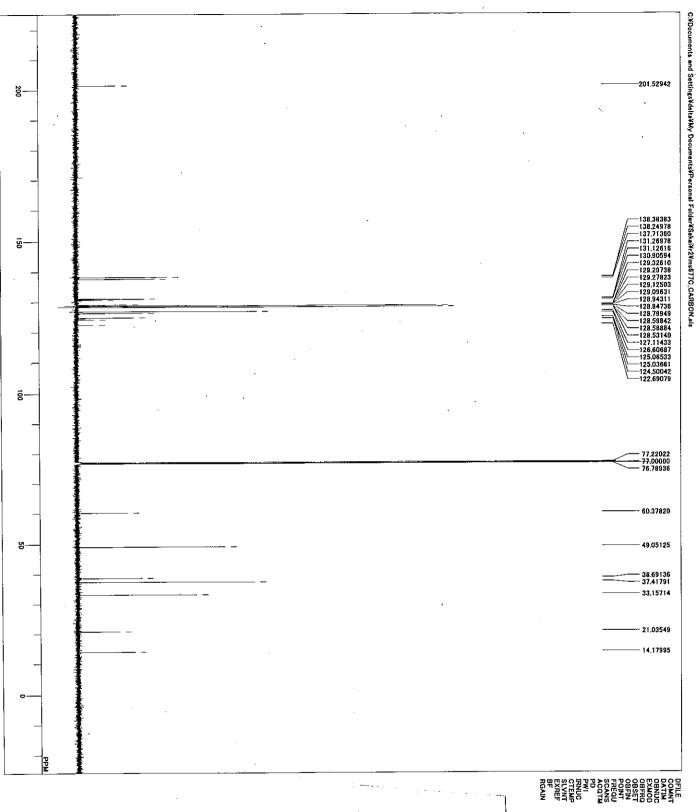
DFILE C: W Documents and Se COMMI 22—11—2011 11:12:32 OBNUC single pulse dec OBFRQ 150.92 MHz OBSET 8.52 KHz OBSET 1.74 Hz OBSET 1.74 Hz OBSET 1.74 Hz OBSET 1.72 Hz OBSET 2.76 Hz OBSET 2.70 OBSET 2.7

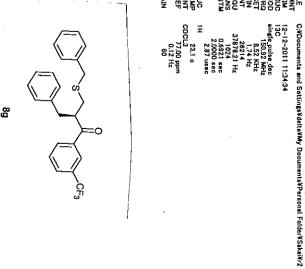
C:XDocuments and SettingsYdeltaXMy DocumentsXPersc

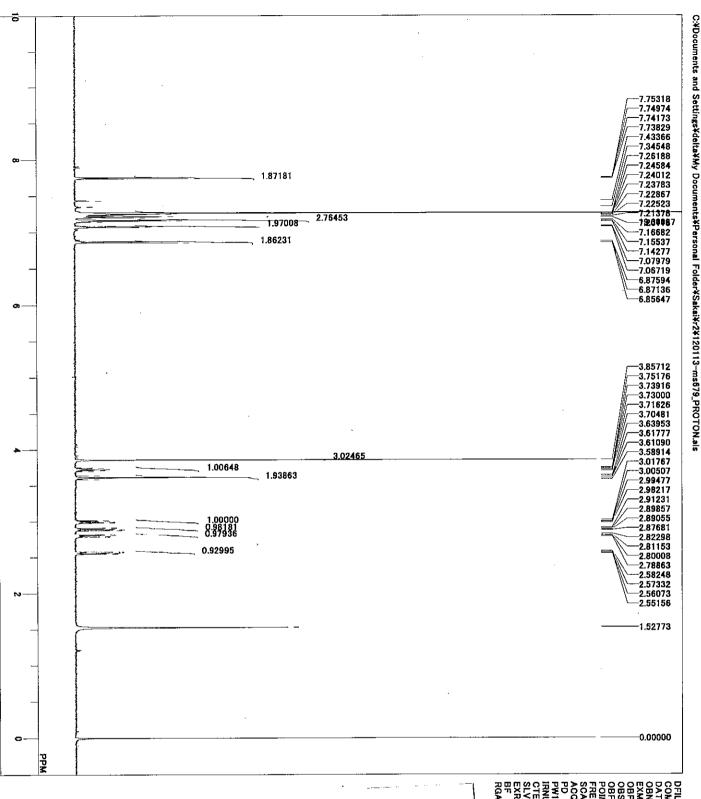
C:\Documents and Settings\delta\My Documents\Personal Folder\Sakai\r2\656c\_CARBON.als

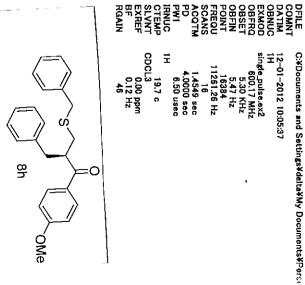


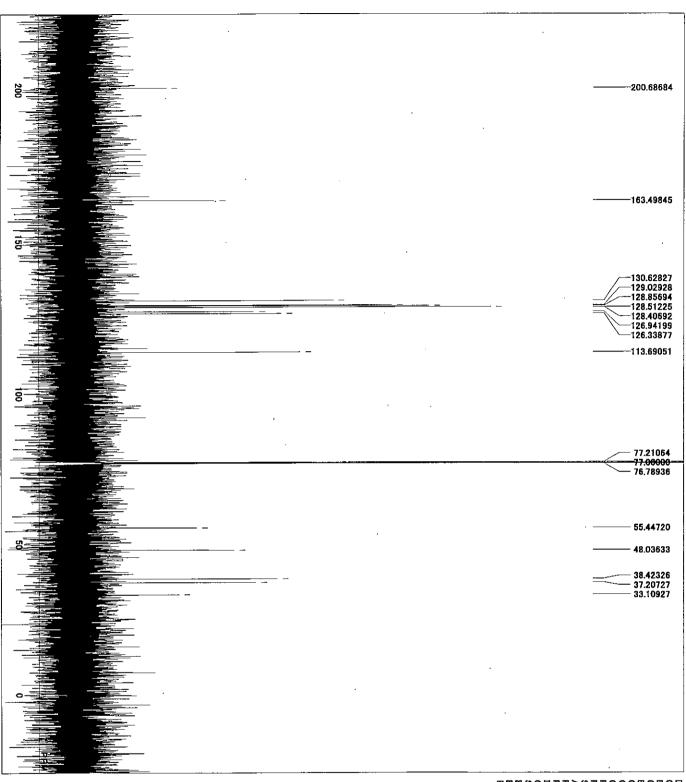


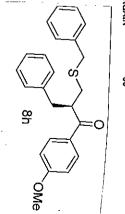




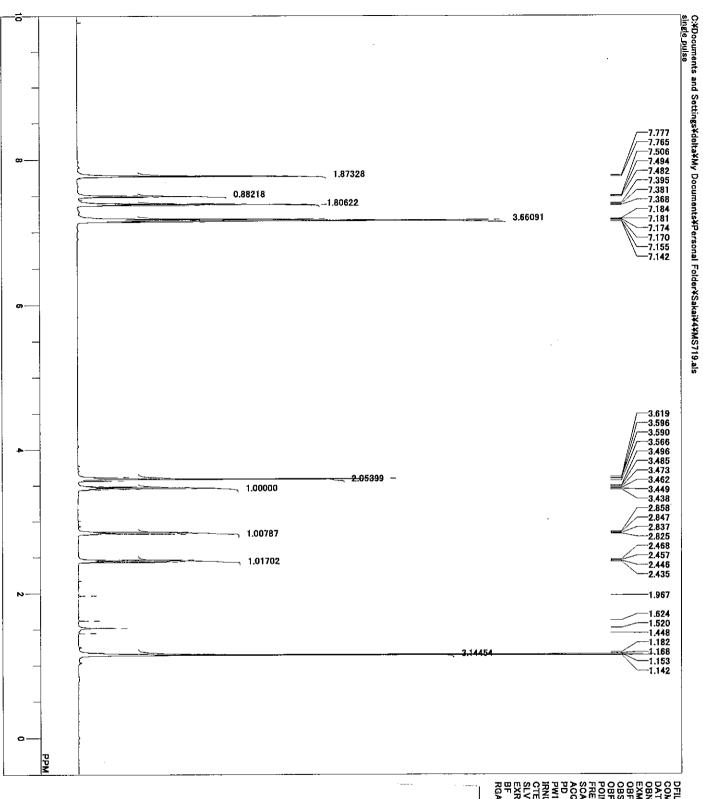


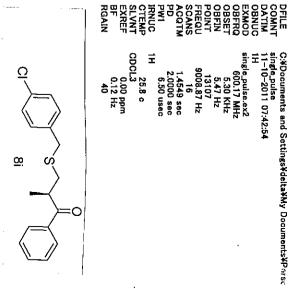


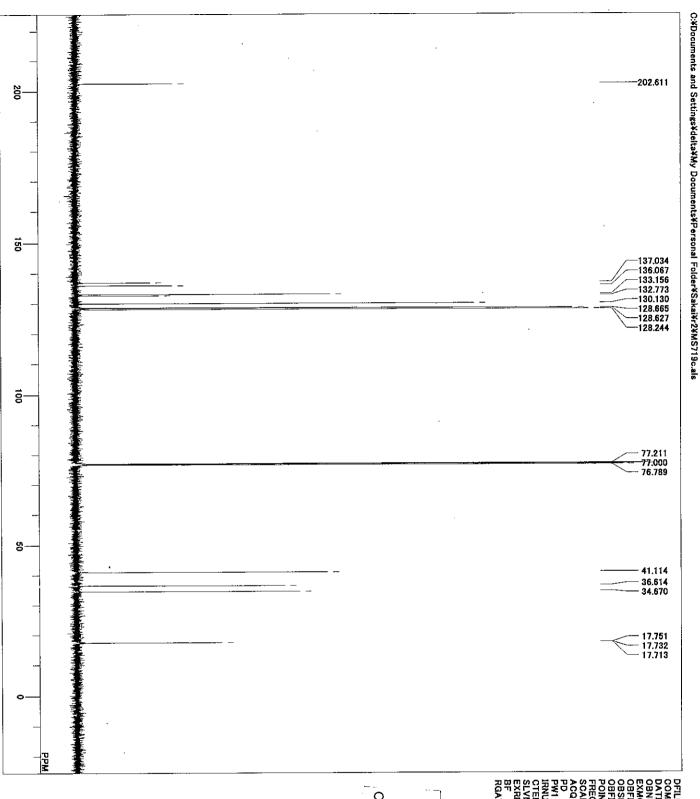


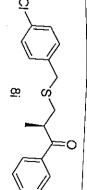


C:¥Documents and Settings¥delta¥My Documents¥Personal Folder¥Sakai¥r2¥120116-ms679.als



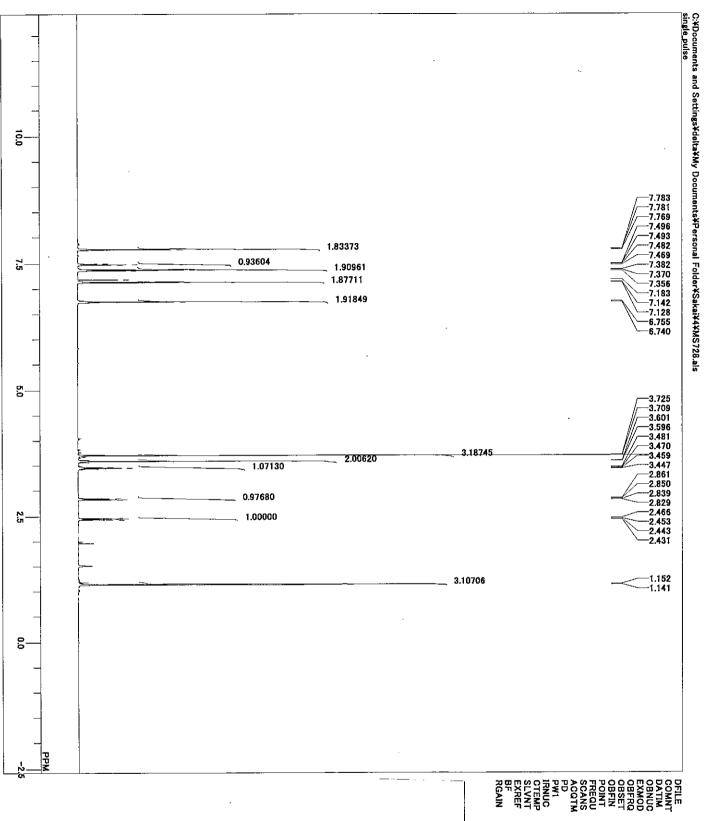


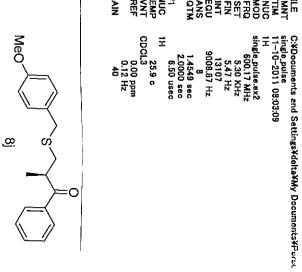


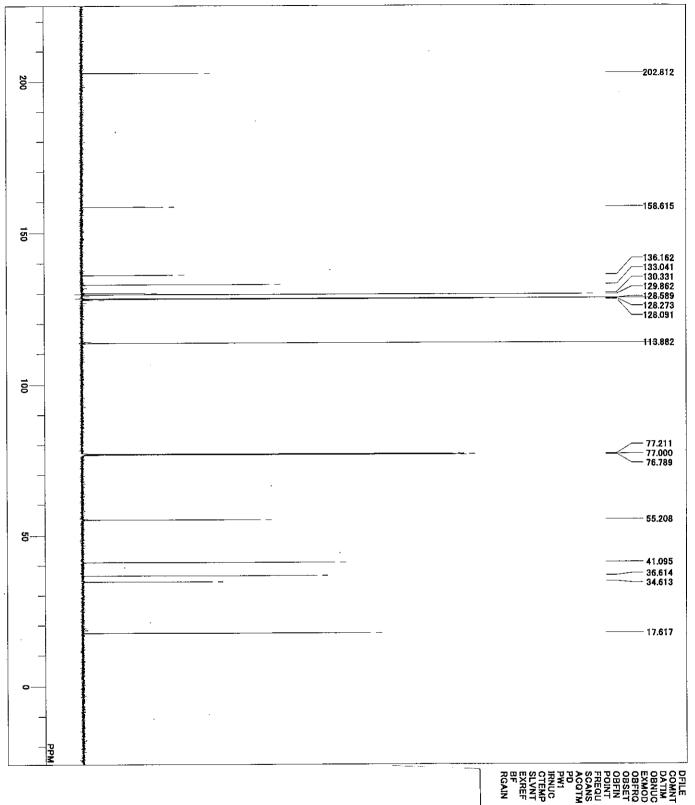


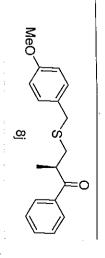
DFILE C:\*Documents and Set COMINT 25-11-2011 22:37:56 COMINT 25-11-2011 22:37:56 COMING DIVISION DIVISIONI DI LI CALINI DI LI CALIN

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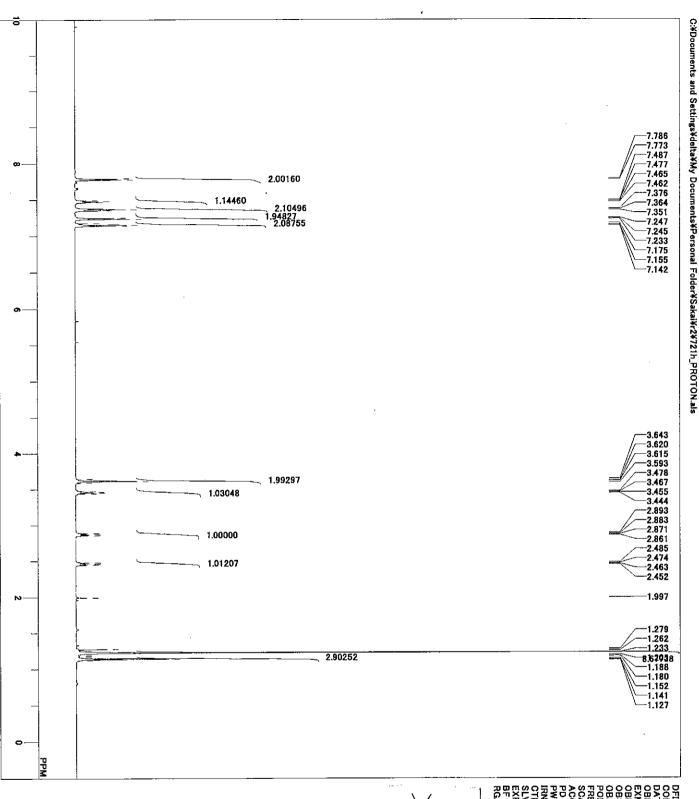


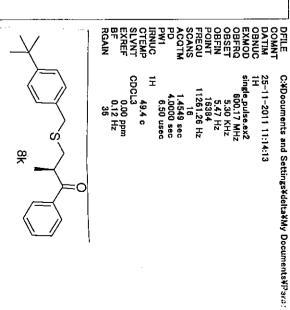


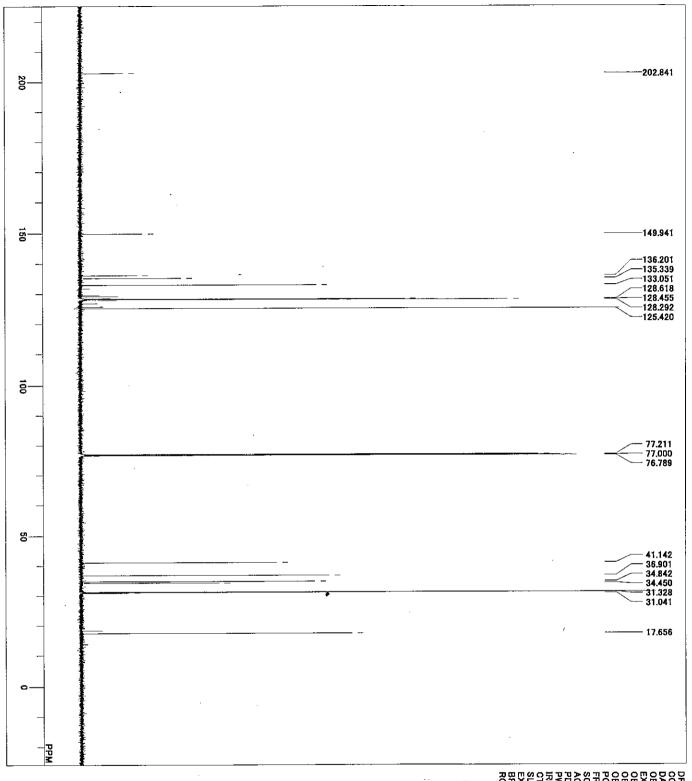


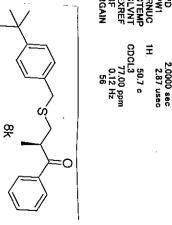
DG 13C
D single pulse deco
DD 174 Hz
174 8.52 KHz
4 32768
Hz
1024
D 1024
D 1024
D 1026
D 1026
D 1027
D 1027
D 1027
D 1028
D 1028
D 1029

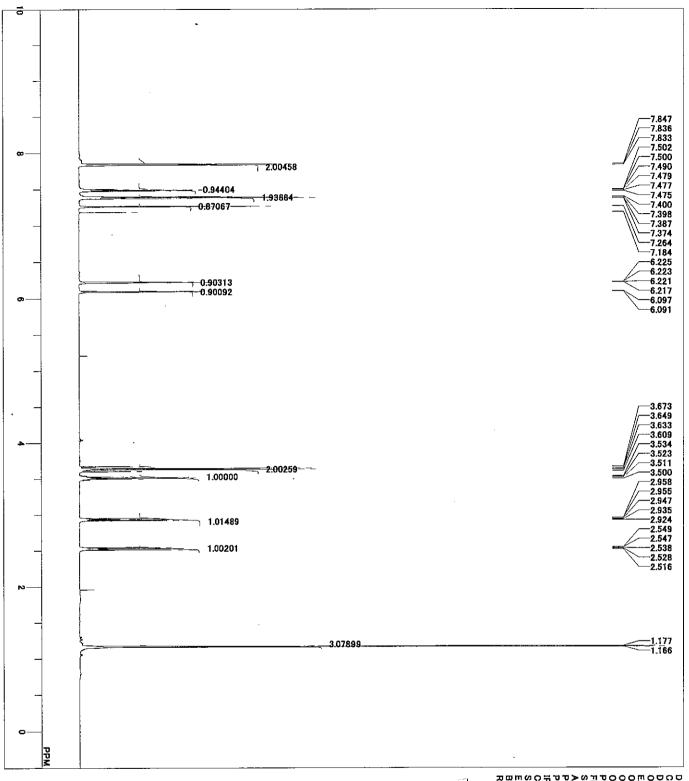
C※Documents and SettingsYdelta¥デスクトップ¥727c,C/. 25-11-2011 11:04:33 13C

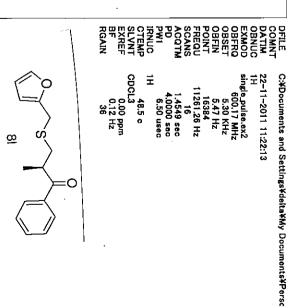


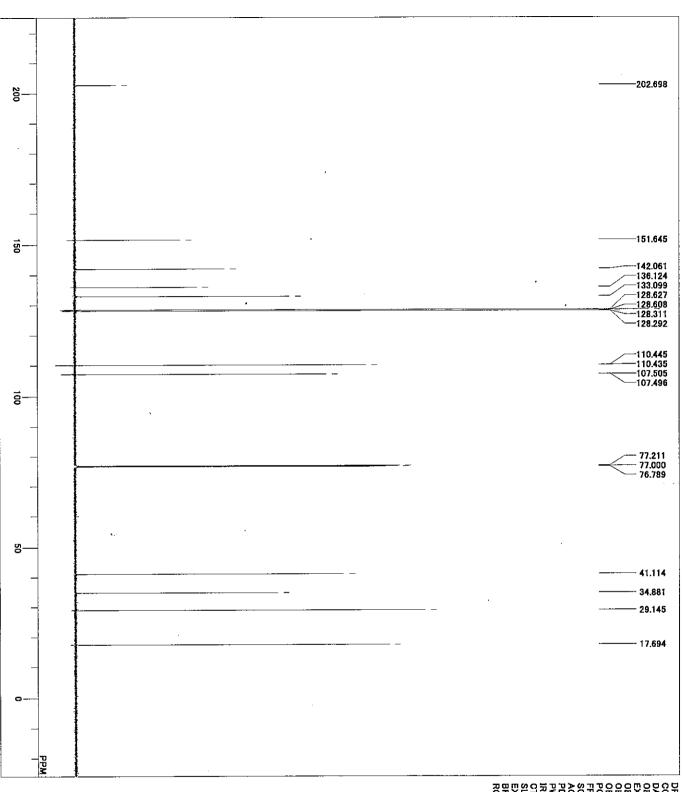


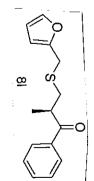




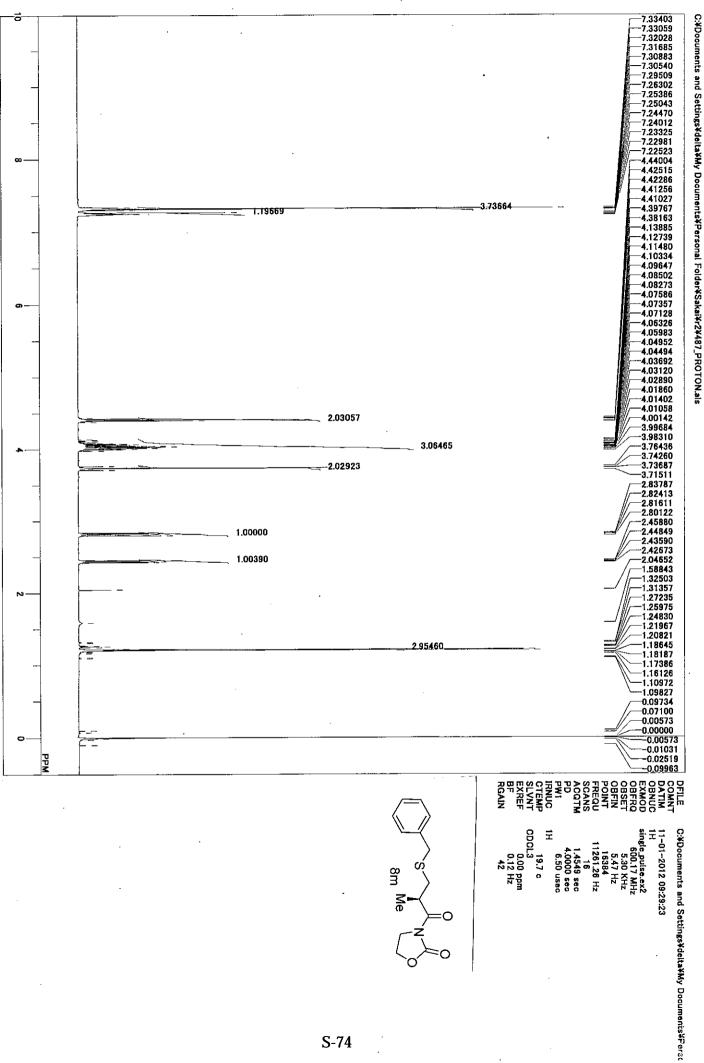


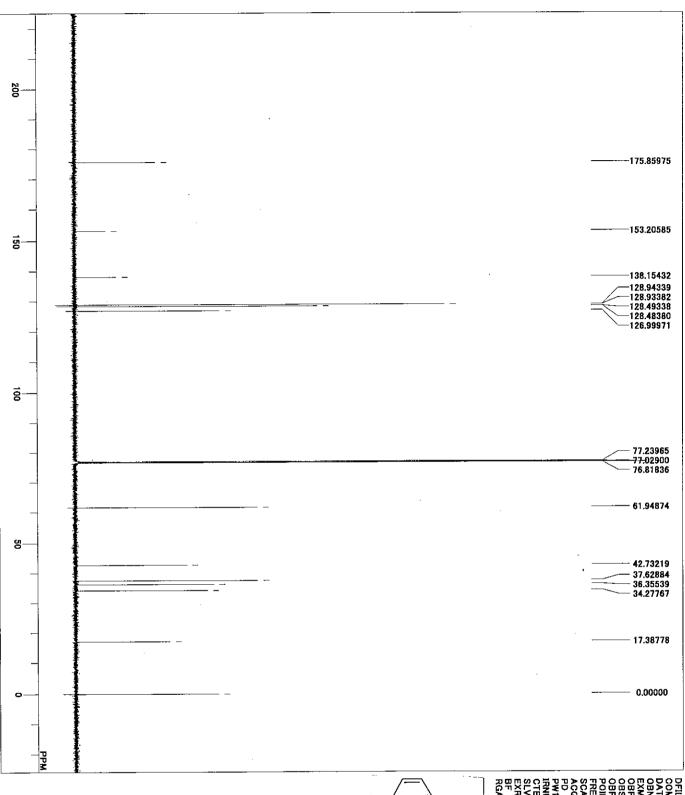


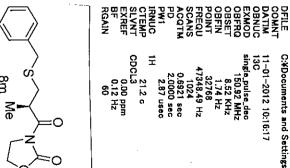




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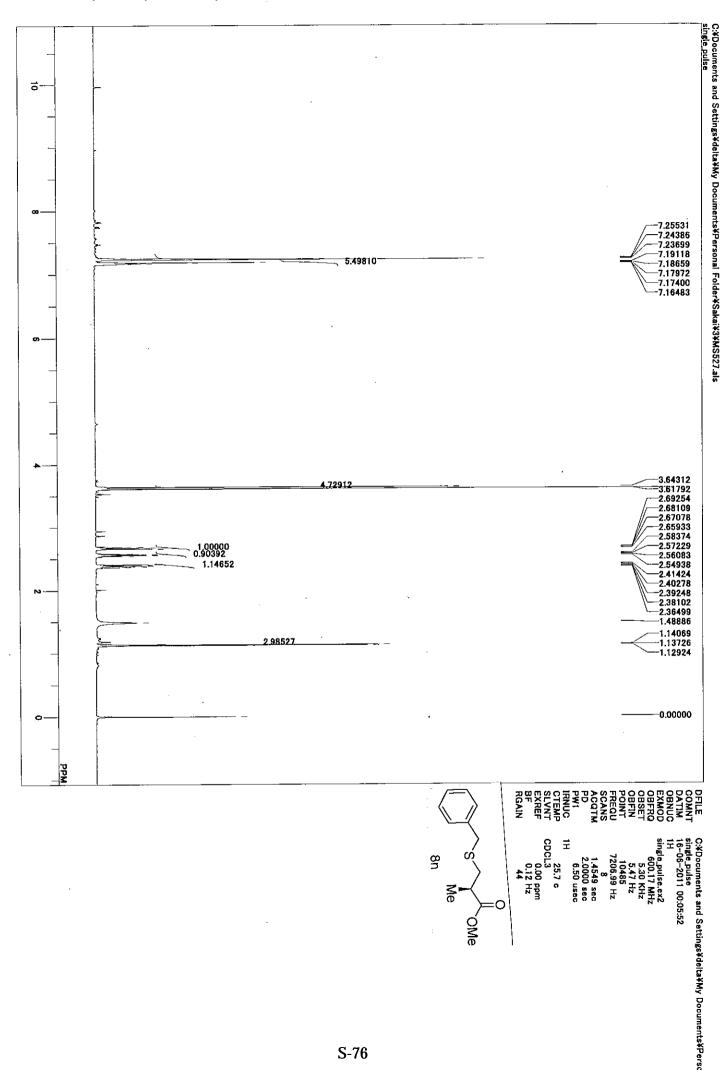


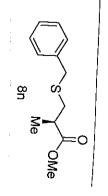




11-01-2012 10:16:17 13C

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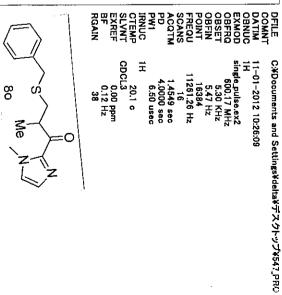




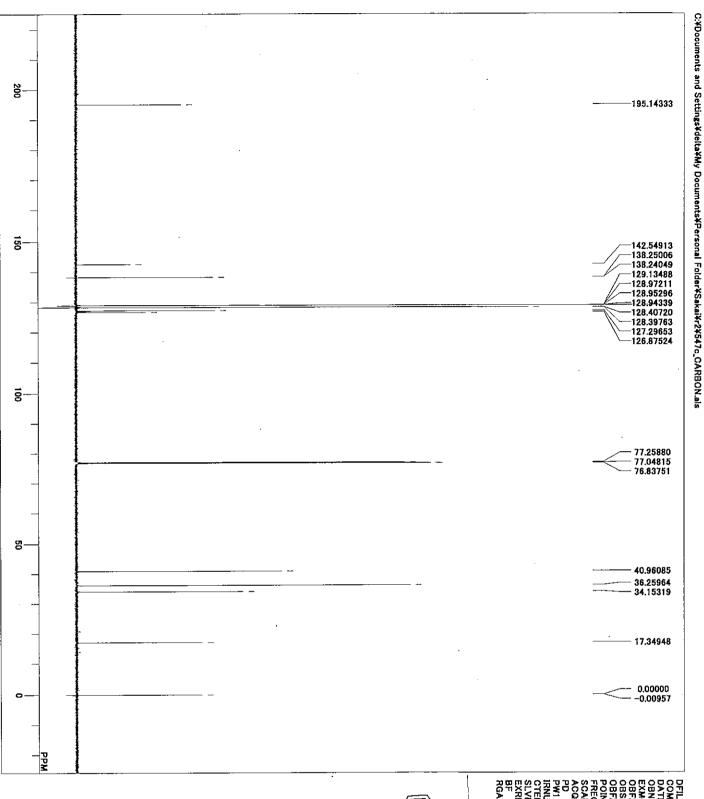
DFILE C: ADocuments and Settings
COMNIT
DATIM 13C
DBNUC 13C
DBNUC 150.92 MHz
OBSET 150.92 MHz
OBSET 1.74 Hz
OBSET 32768
FREQU 47348.49 Hz
SCANS 1024
ACGTM 0.6921 sec
PD 2.0000 sec
PMI 2.87 usec
IRNUC 1H
EXECULA 1.70
BFI 102.4
CTEMP CDCL3
EXPER 0.00 ppm
BF 0.12 Hz
EXPER 0.00 ppm
BF 0.12 Hz

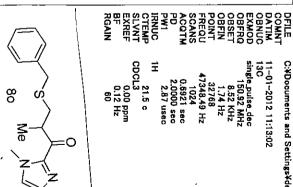
EXPER 0.12 Hz

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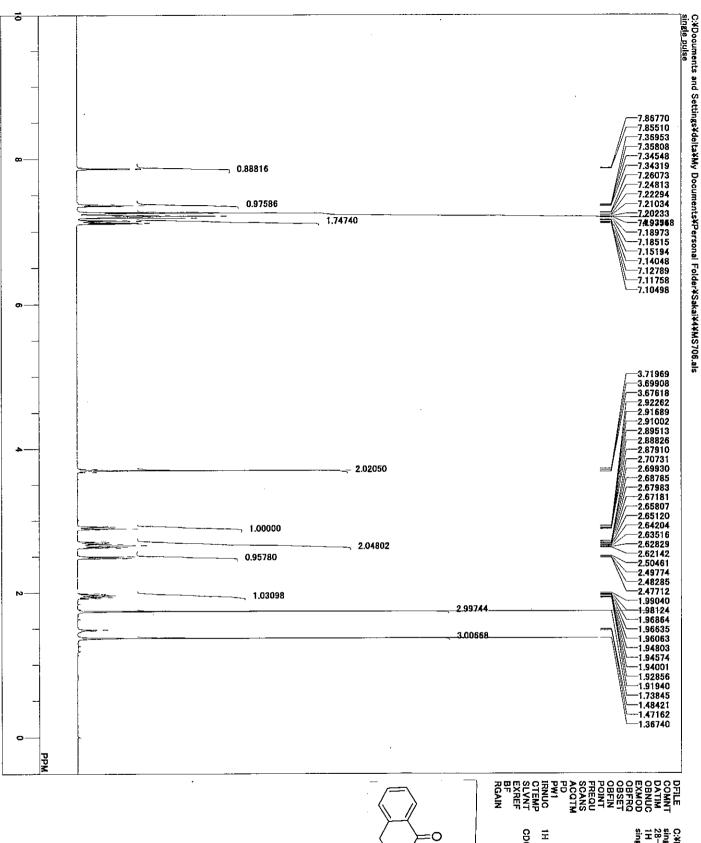


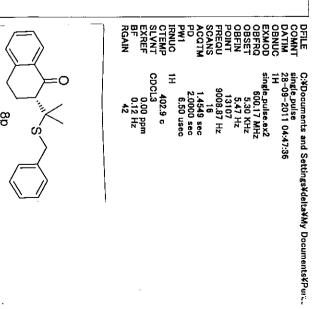
C:¥Documents and Settings¥delta¥デスクトップ¥547\_PROTON.1

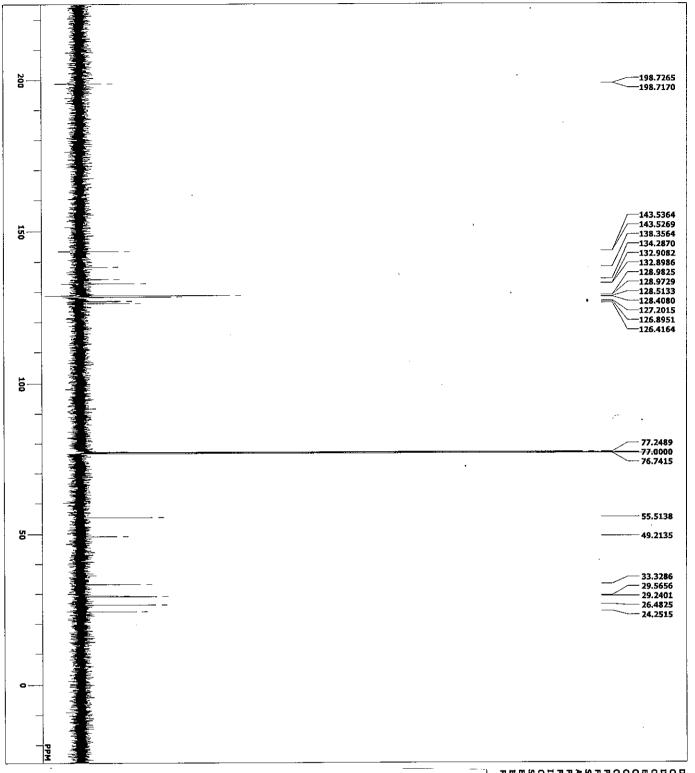


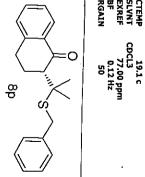


11-01-2012 11:13:02 13C







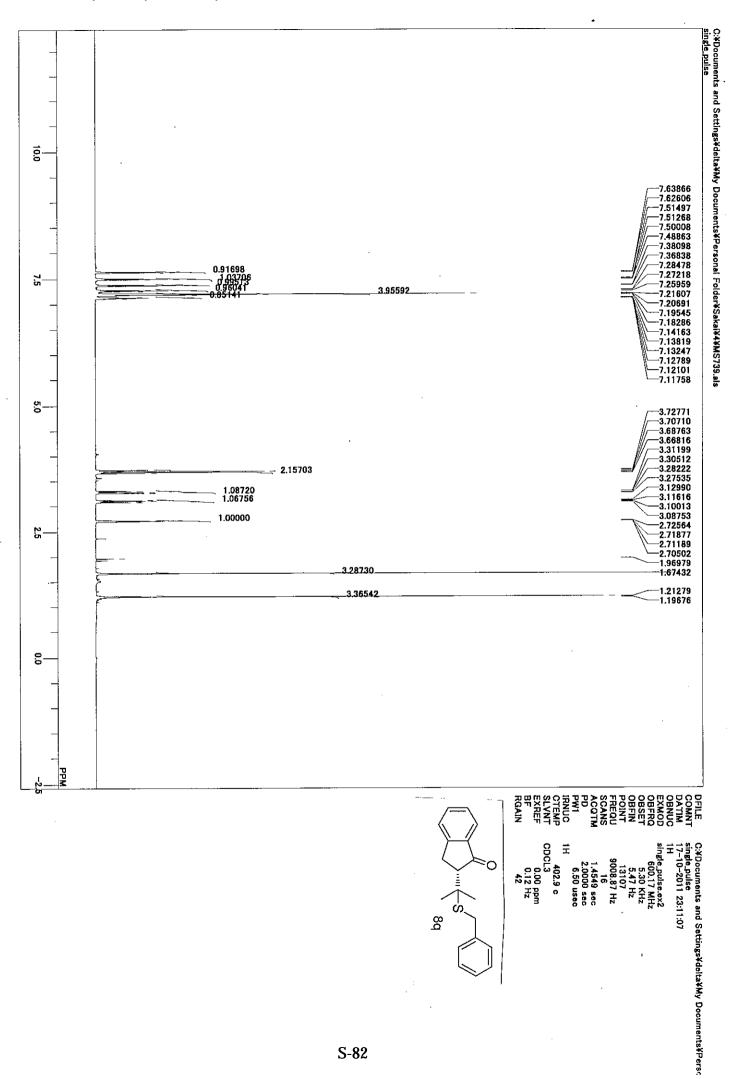


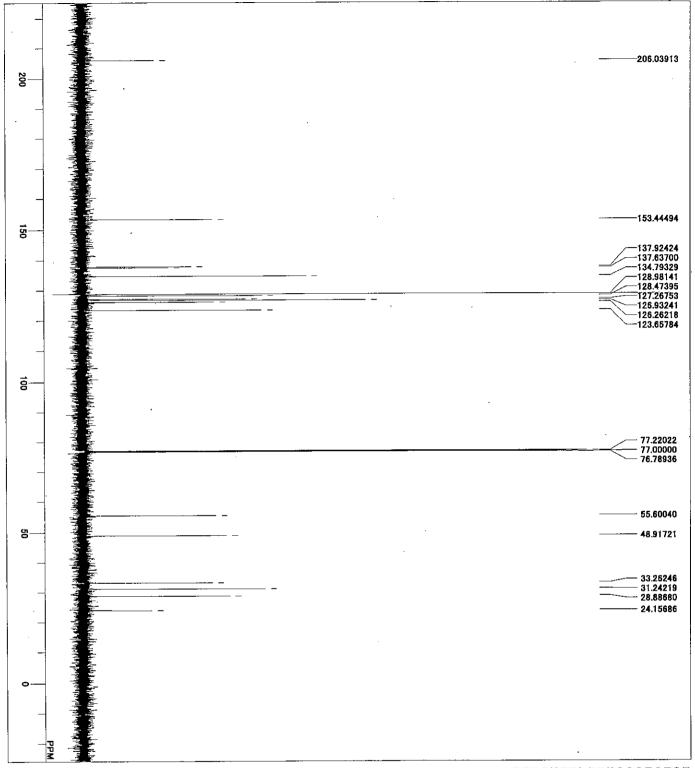
DFILE D:\Documents and Settings\Kobayashilab\Desktop\120109\
COMMT
DATIM 09-01-2012 19:17:03

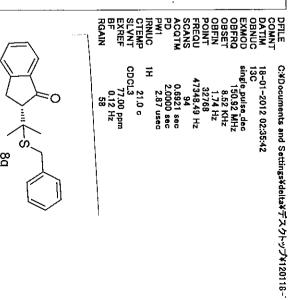
OBNUC 13C
EXMOD 13C NMR.ex2
EXMOD 13C NMR.ex2
OBERQ 124.51 MHz
OBSET 3.45 KHz
OBINT 32768
FREQU 39062.50 Hz
SCANS 204
ACQTM 0.8389 sec
PM1 3.67 usec
IRNUC 1H
EXMED 19.1 c
SLANT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz

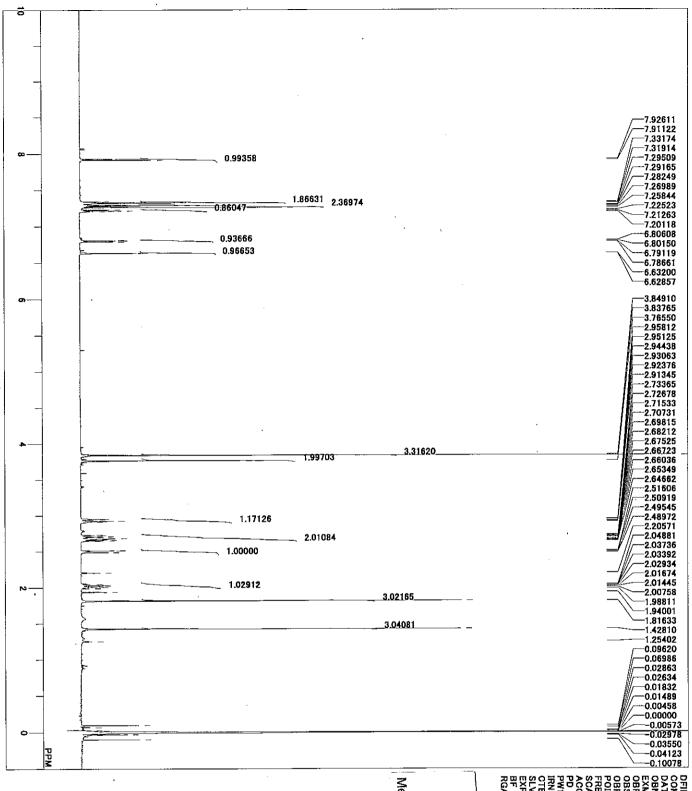
FGAIN 50

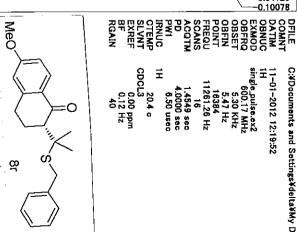
O. Con



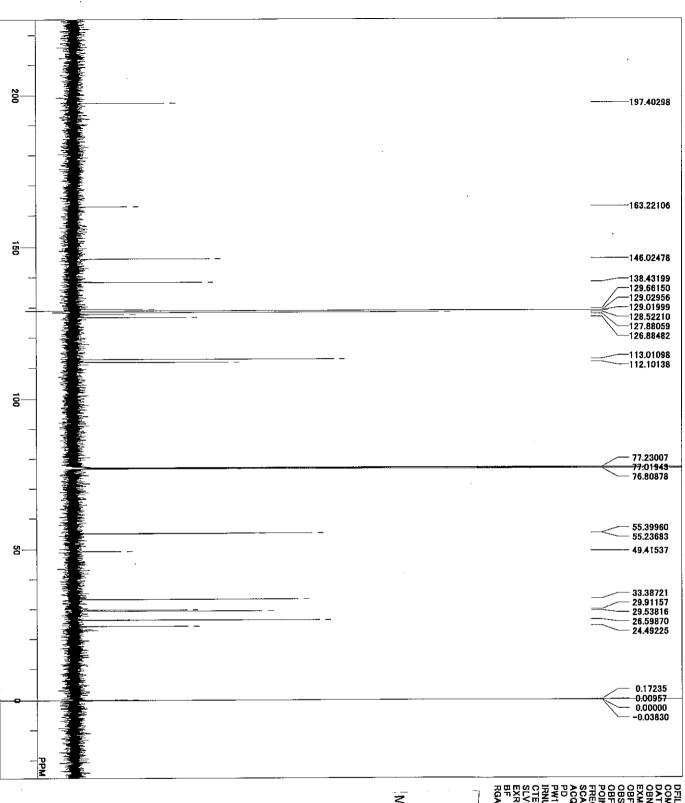


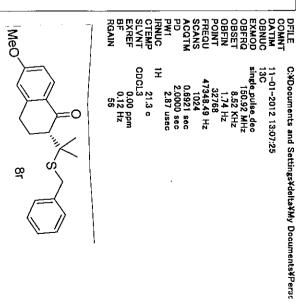




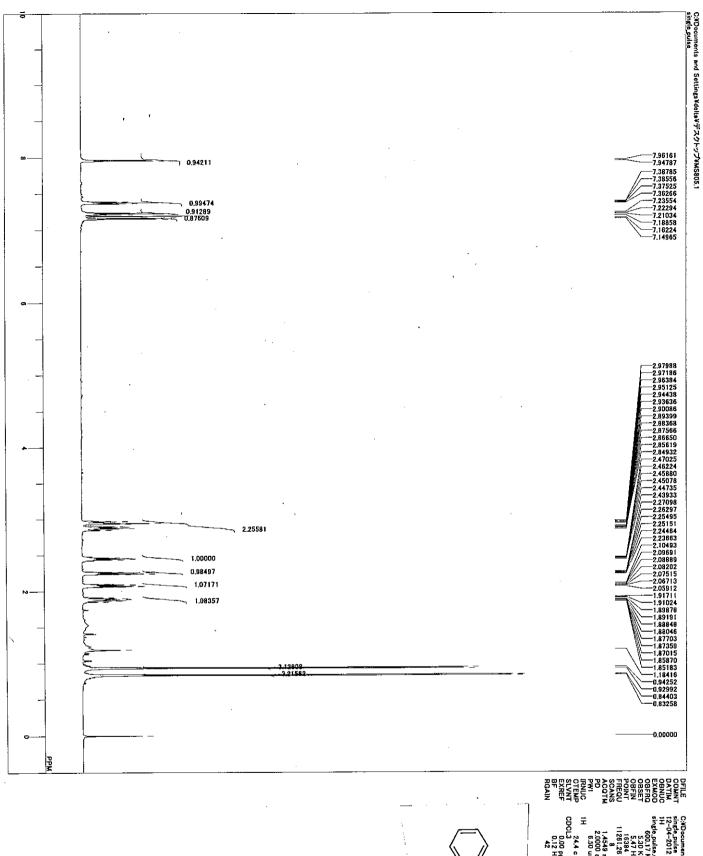


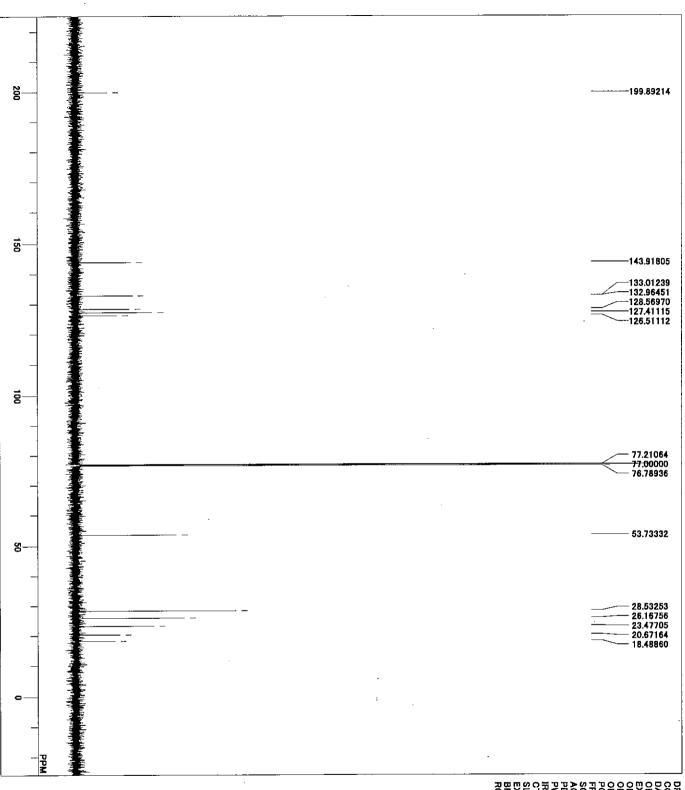
C:¥Documents and Settings¥delta¥My Documents∜Fersc

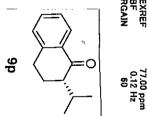




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