

## **Supporting Information**

**for**

### **Synthesis and Optical Resolution of Aminophosphines with Axially Chiral C(aryl)–N(amine) Bonds for Use as Ligands in Asymmetric Catalysis**

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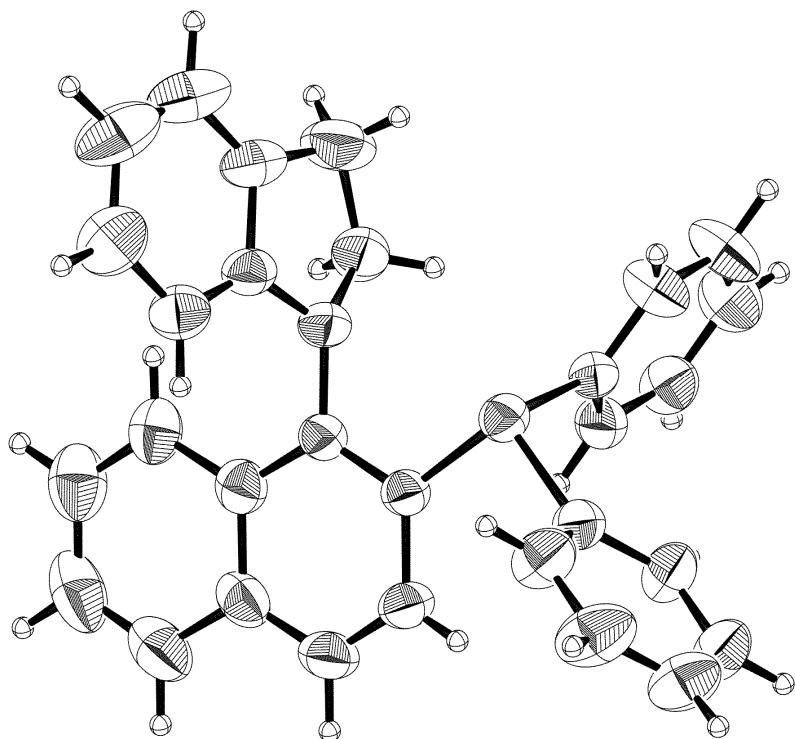


Figure S1. ORTEP drawing of ( $\pm$ )-**1a**.

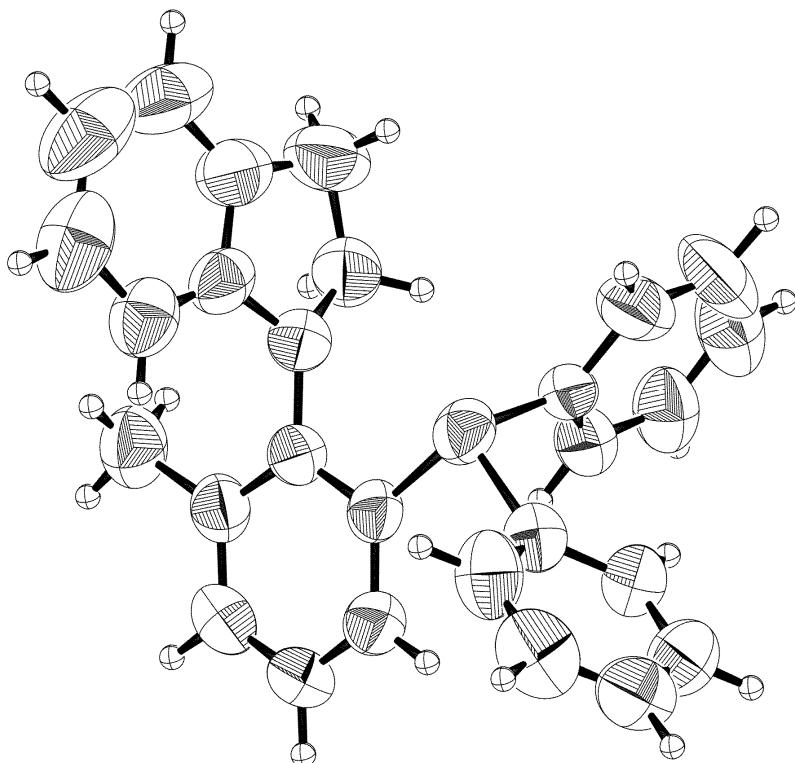


Figure S2. ORTEP drawing of ( $\pm$ )-**1b**.

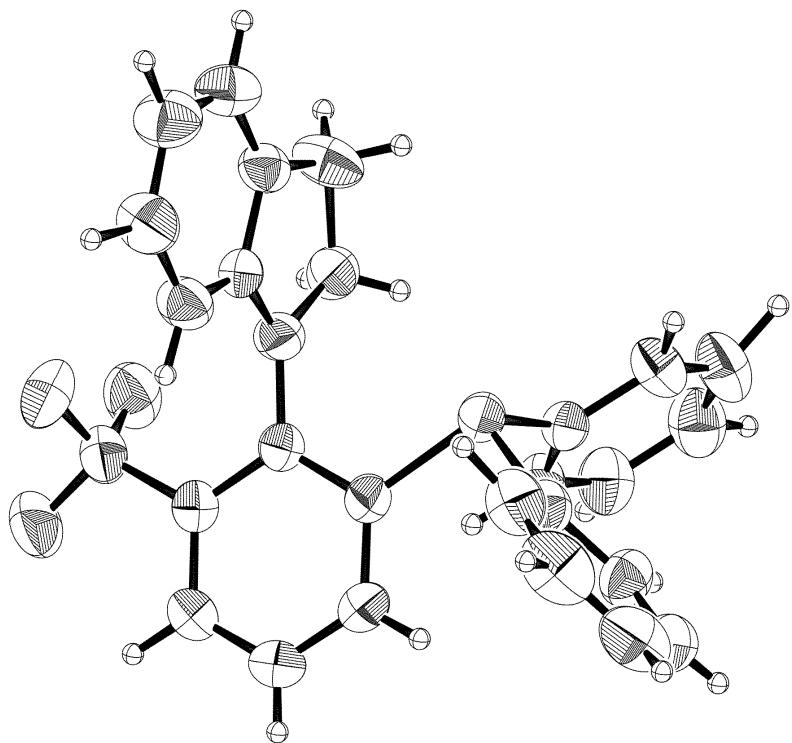


Figure S3. ORTEP drawing of ( $\pm$ )-**1c**.

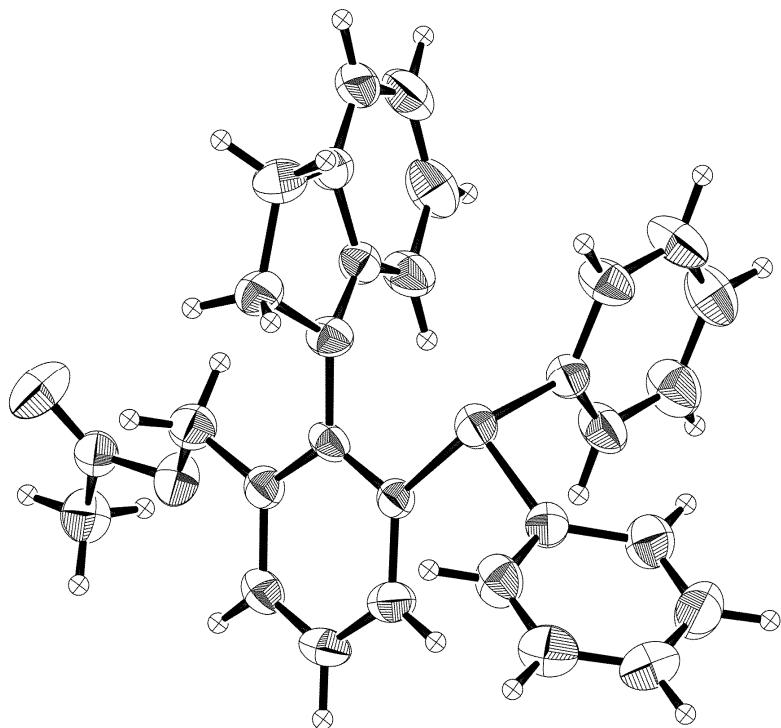


Figure S4. ORTEP drawing of ( $\pm$ )-**1d**.

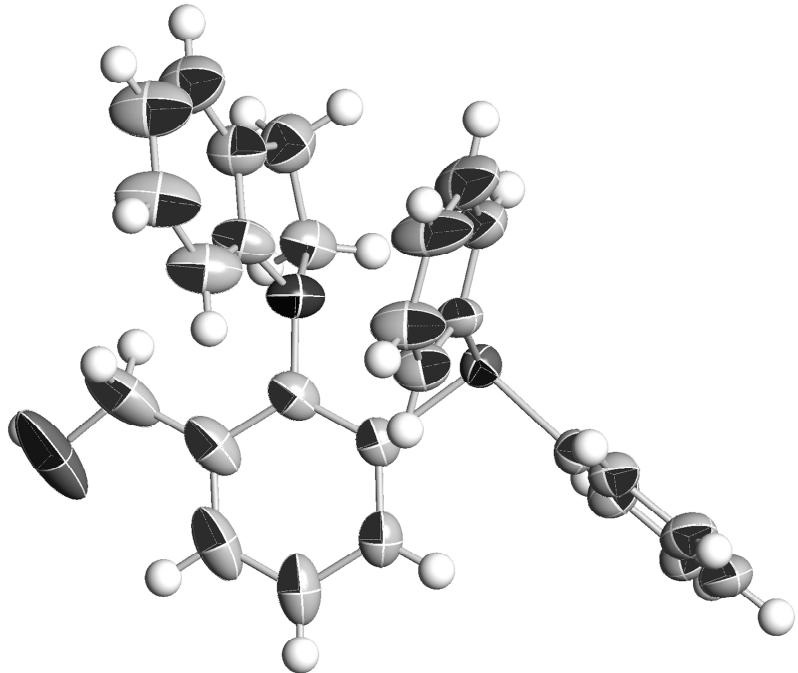


Figure S5. ORTEP drawing of **9**.

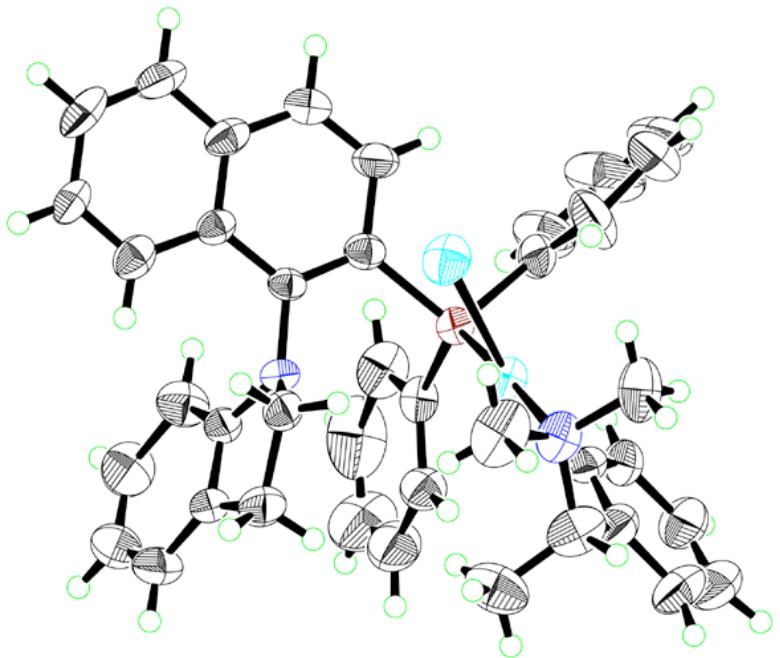


Figure S6. ORTEP drawing of (aR,S)-(-)-**12a**.

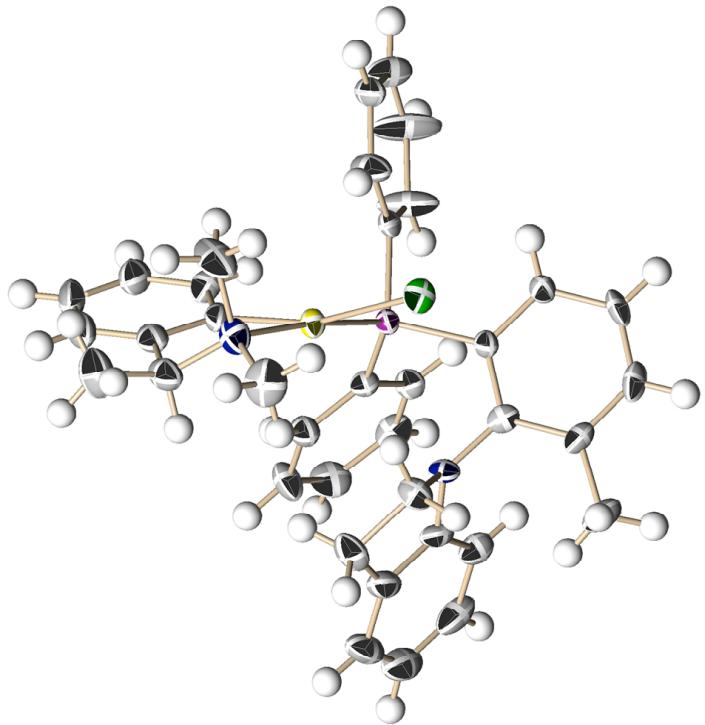


Figure S7. ORTEP drawing of (a*S,S*)-(+)-**11b**.

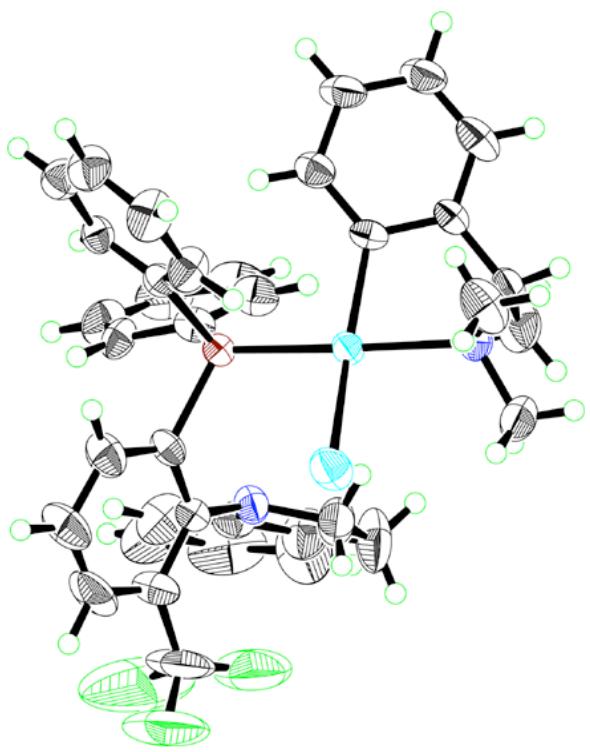


Figure S8. ORTEP drawing of (aR,S)-(-)-**12c**.

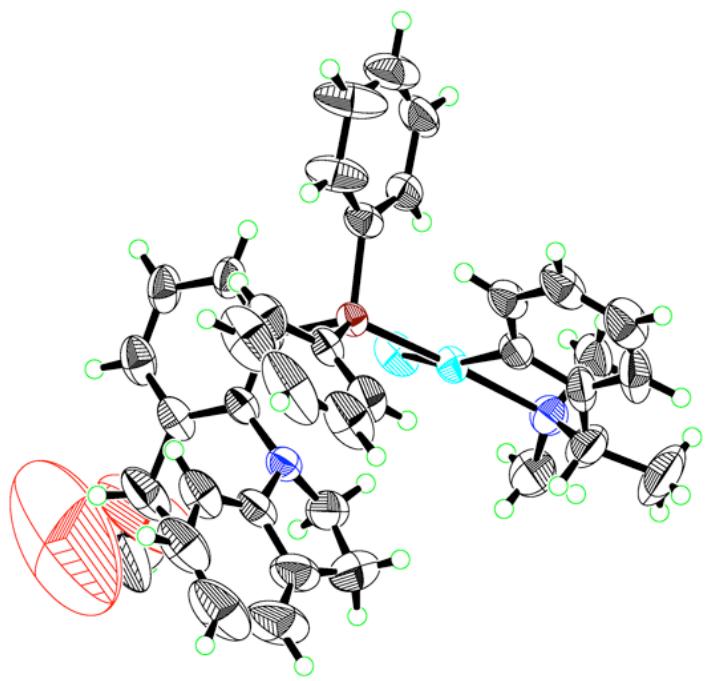
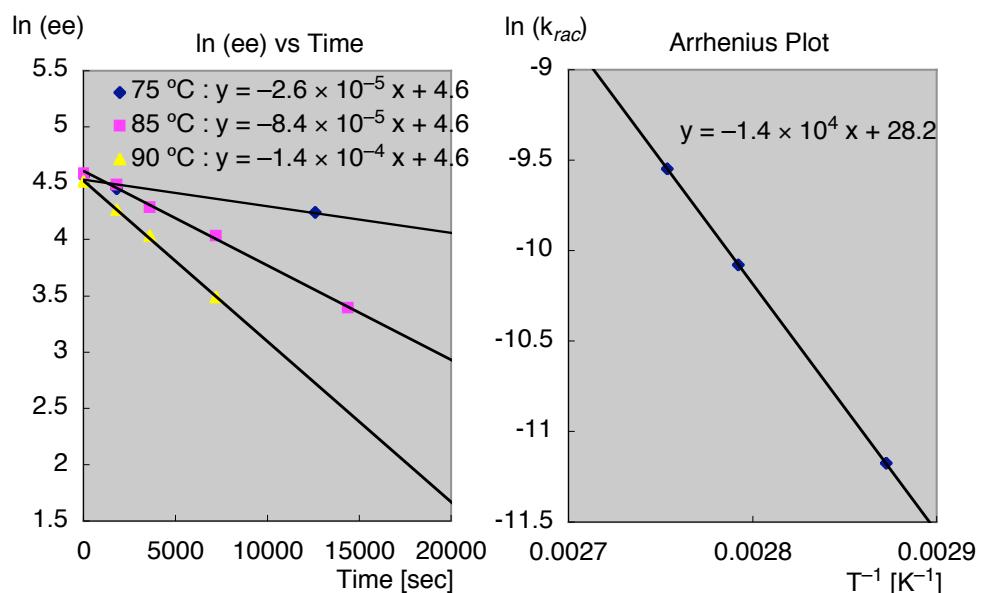


Figure S9. ORTEP drawing of (aS,S)-(+)-**11d**.

Figure S10. Thermal racemization of optically active **1a**

Time (sec)	E.e. (%) at 75 °C	E.e. (%) at 85 °C	E.e. (%) at 90 °C
0	95.72	98.32	91.34
1800		88.74	71.08
3600		72.92	56.36
5600	85.88		
7200		56.34	32.68
12600	69.48		
14400		29.72	

E.e. was determined by chiral HPLC (Daicel CHIRALCEL® OJ, 0.46  $\phi$   $\times$  25 cm, hexane : ethanol ethanol = 90 : 10, 0.50 mL/min, UV 254 nm) analysis.

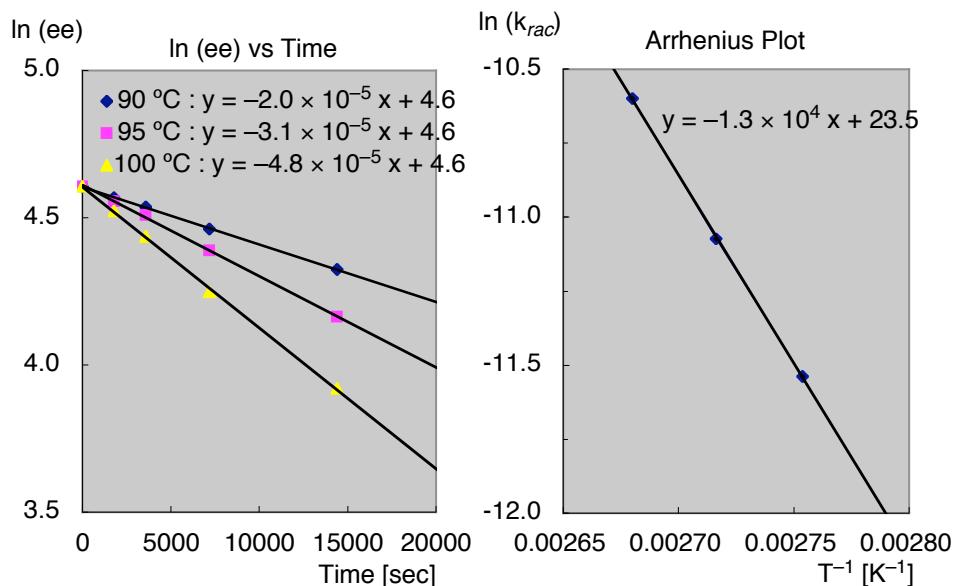


Thermodynamic parameter at 25 °C	<b>1a</b>
Half-life (day)	211.4
$\Delta H$ (kcal/mol)	26.6
$\Delta S$ (cal/mol·K)	-4.5
$\Delta G$ (kcal/mol)	28.0

Figure S11. Thermal racemization of optically active **1b**

Time (sec)	E.e. (%) at 90 °C	E.e. (%) at 95 °C	E.e. (%) at 100 °C
0	100	100	100
1800	96.26	95.24	92.13
3600	93.31	90.72	84.42
7200	86.59	80.57	69.95
14400	75.49	64.23	50.45

E.e. was determined by chiral HPLC (Daicel CHIRALPAK® AD-H, 0.46  $\phi \times 25$  cm  $\times$  2, hexane : ethanol = 99.7 : 0.3, 0.20 mL/min, UV 254 nm) analysis.

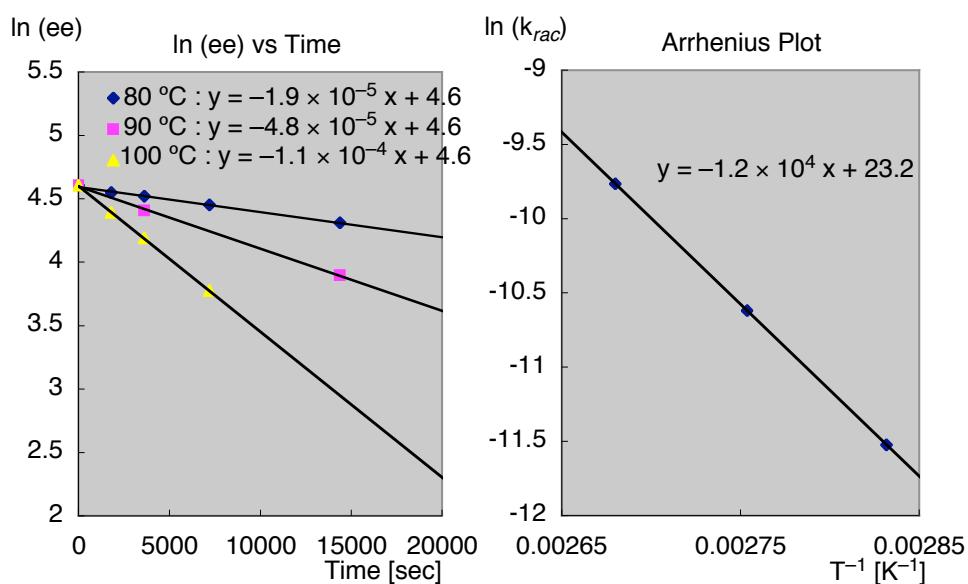


Thermodynamic parameter at 25 °C	<b>1b</b>
Half-life (day)	853.4
$\Delta H$ (kcal/mol)	24.7
$\Delta S$ (cal/mol·K)	-13.9
$\Delta G$ (kcal/mol)	28.8

Figure S12. Thermal racemization of optically active **1c**

Time (sec)	E.e. (%) at 80 °C	E.e. (%) at 90 °C	E.e. (%) at 100 °C
0	100	100	100
1800	94.58		80.64
3600	91.80	82.12	66.00
7200	85.82		43.60
14400	74.54	49.16	

E.e. was determined by chiral HPLC (Daicel CHIRALPAK® AD-H, 0.46  $\phi \times 25$  cm  $\times$  2, hexane : ethanol = 99.7 : 0.3, 0.20 mL/min; UV 254 nm) analysis.

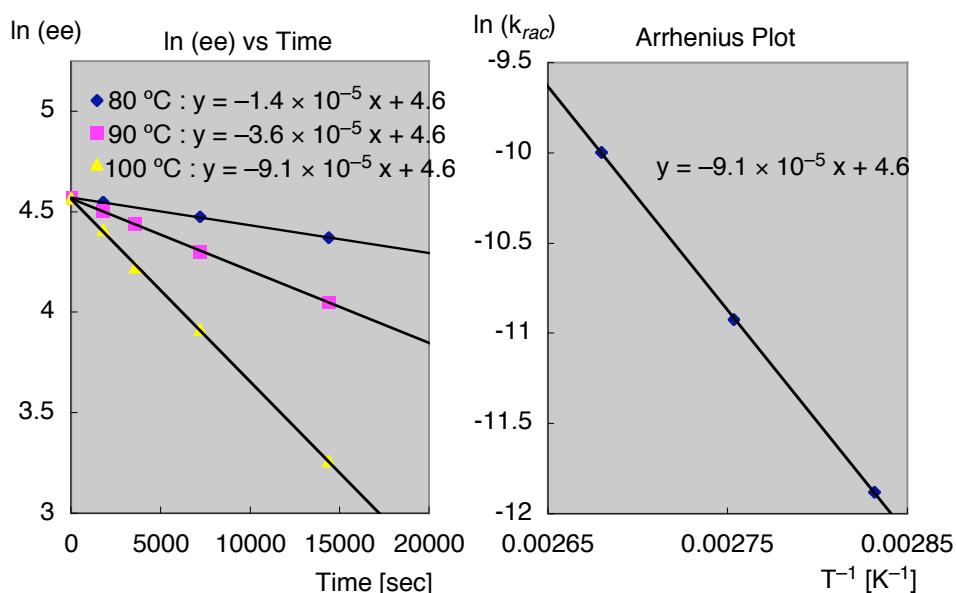


Thermodynamic parameter at 25 °C	<b>1c</b>
Half-life (day)	172.6
$\Delta H$ (kcal/mol)	22.4
$\Delta S$ (cal/mol·K)	-18.2
$\Delta G$ (kcal/mol)	27.9

Figure S13. Thermal racemization of optically active **1d**

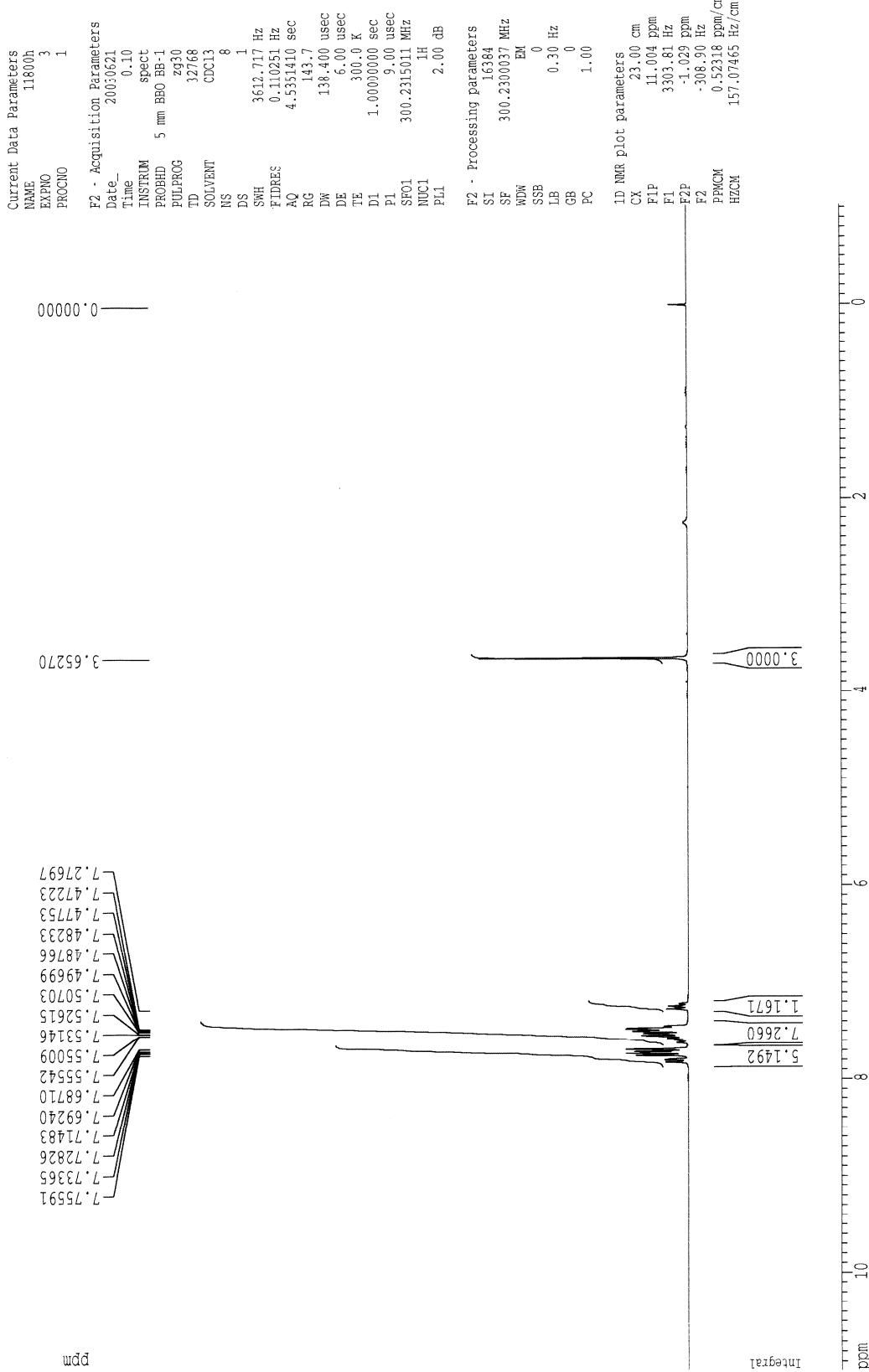
Time (sec)	E.e. (%) at 80 °C	E.e. (%) at 90 °C	E.e. (%) at 100 °C
0	96.54	96.53	96.36
1800	94.52	90.32	82.28
3600		84.47	68.38
7200	87.79	73.76	49.94
14400	79.17	57.54	26.02

E.e. was determined by chiral HPLC (Daicel CHIRALCEL® OD-H, 0.46  $\phi$   $\times$  25 cm, hexane : ethanol = 99 : 1, 0.20 mL/min; UV 254 nm) analysis.

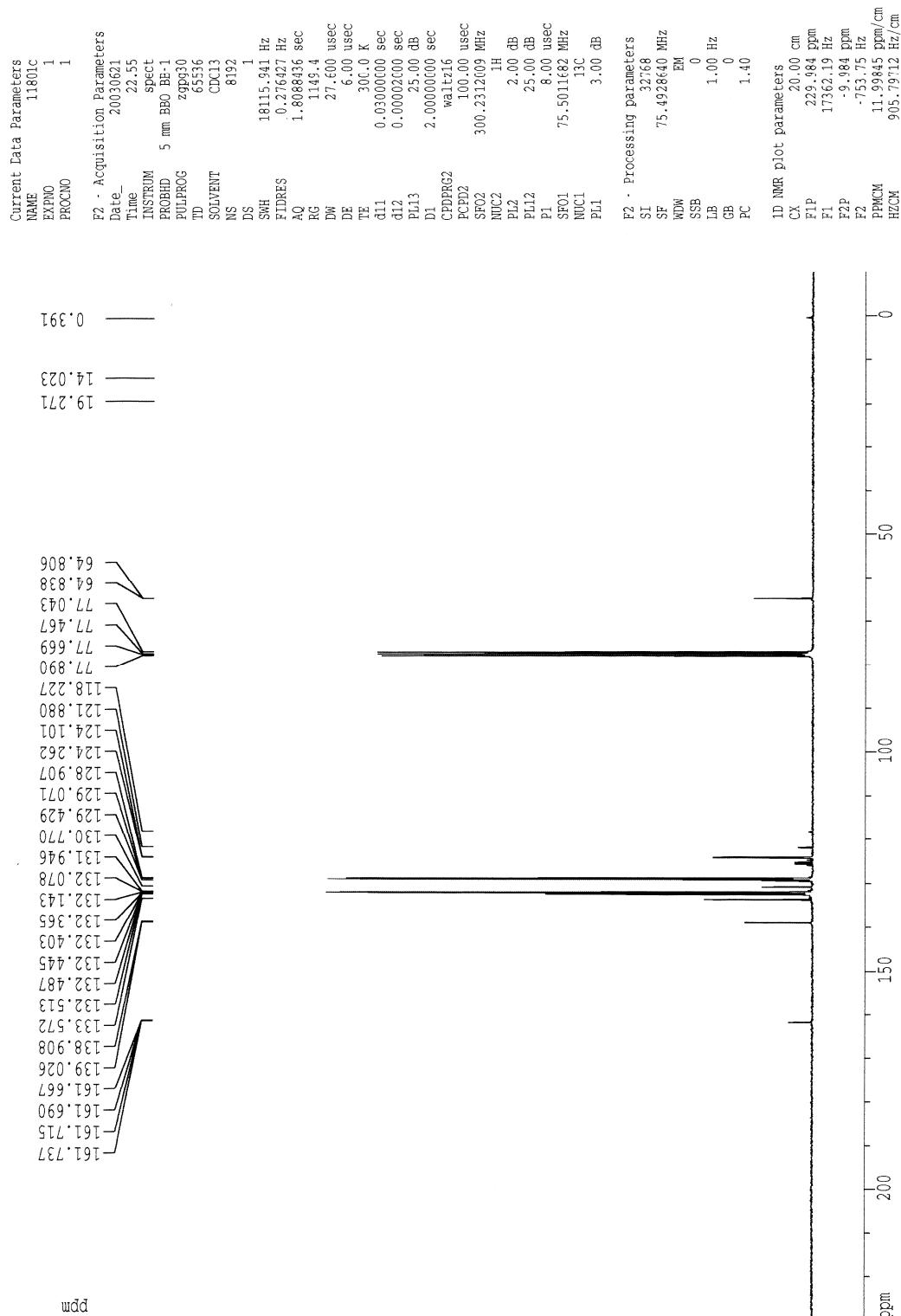


Thermodynamic parameter at 25 °C	<b>1d</b>
Half-life (day)	377.4
$\Delta H$ (kcal/mol)	24.0
$\Delta S$ (cal/mol·K)	-14.4
$\Delta G$ (kcal/mol)	28.3

<sup>1</sup>H NMR of **2c**



<sup>13</sup>C NMR of **2c**



### <sup>31</sup>P NMR of 2c

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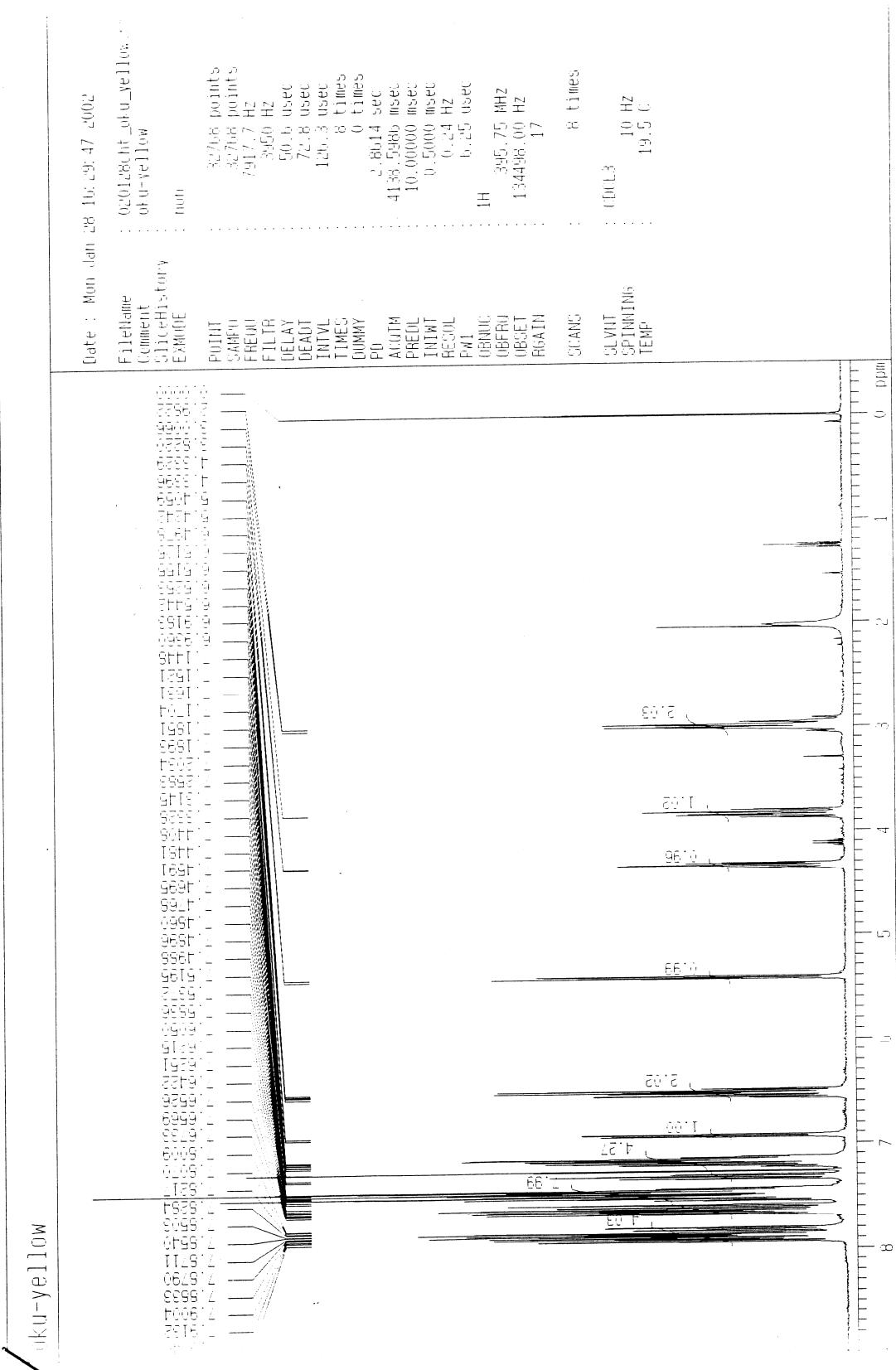
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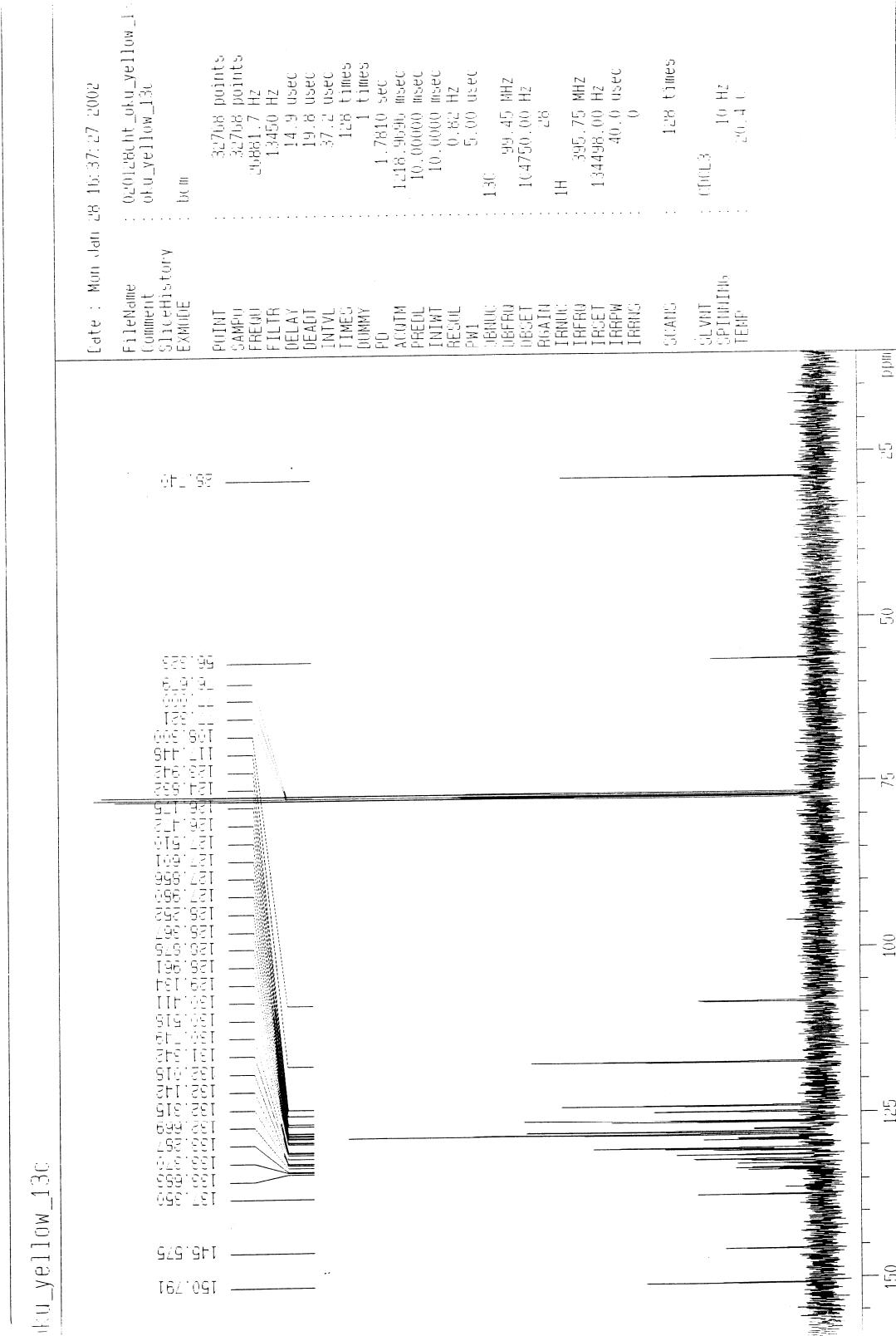
— 26.9956 —

ddd

<sup>1</sup>H NMR of 3a



<sup>13</sup>C NMR of 3a



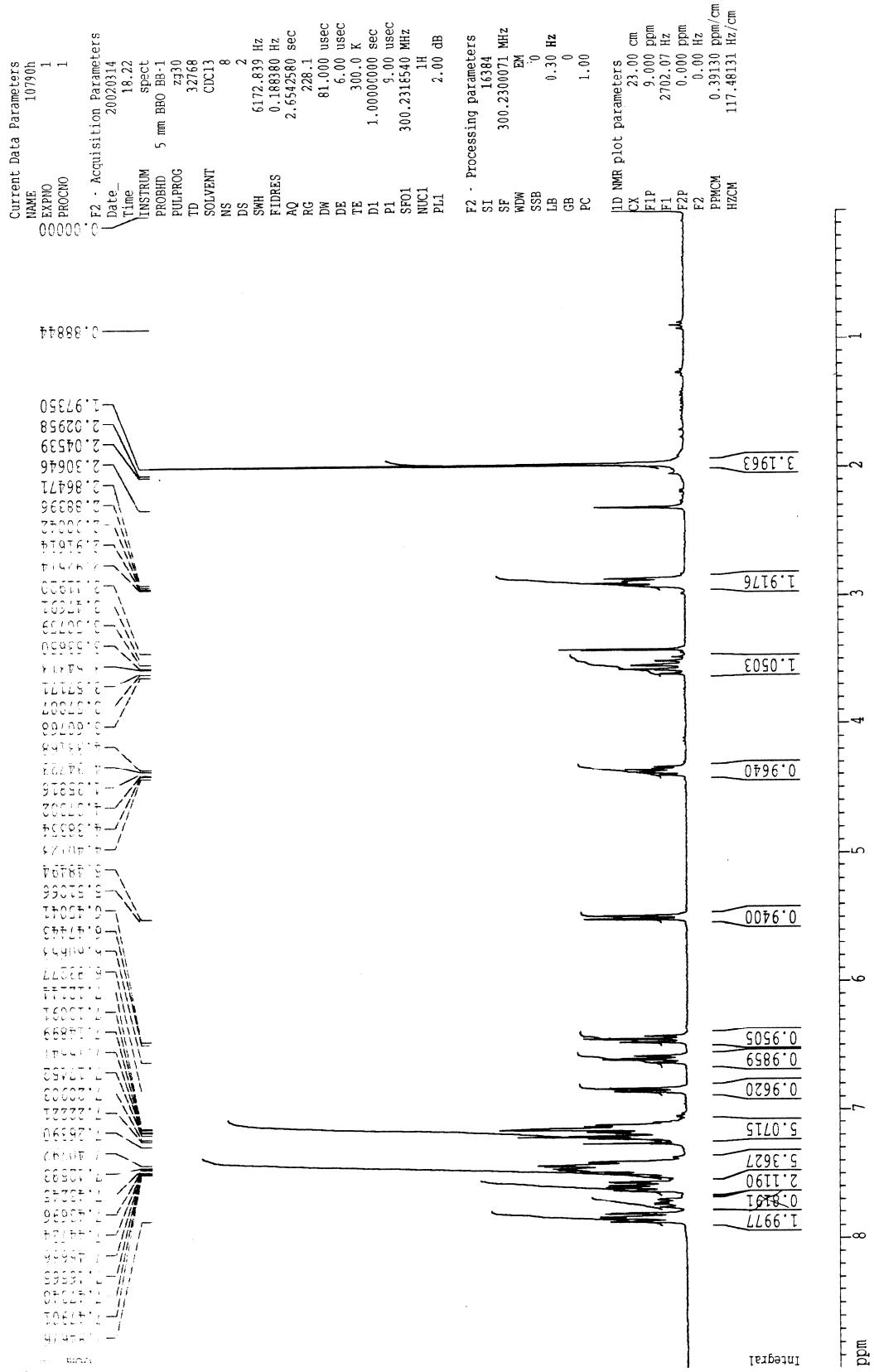
<sup>31</sup>P NMR of **3a**

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HZCM	3759.39844 Hz/cm

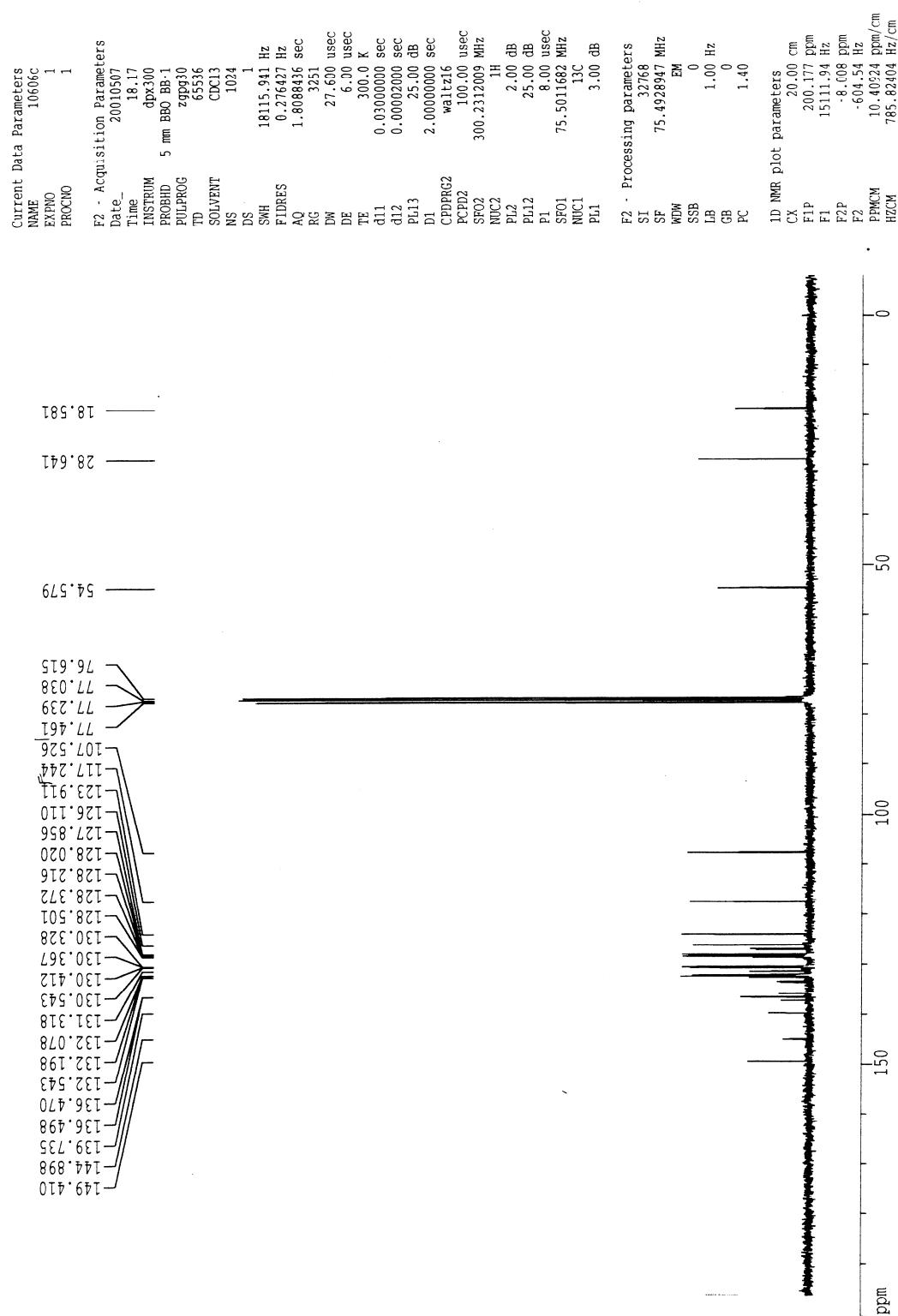
25,8445

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### <sup>1</sup>H NMR of **3b**



<sup>13</sup>C NMR of **3b**

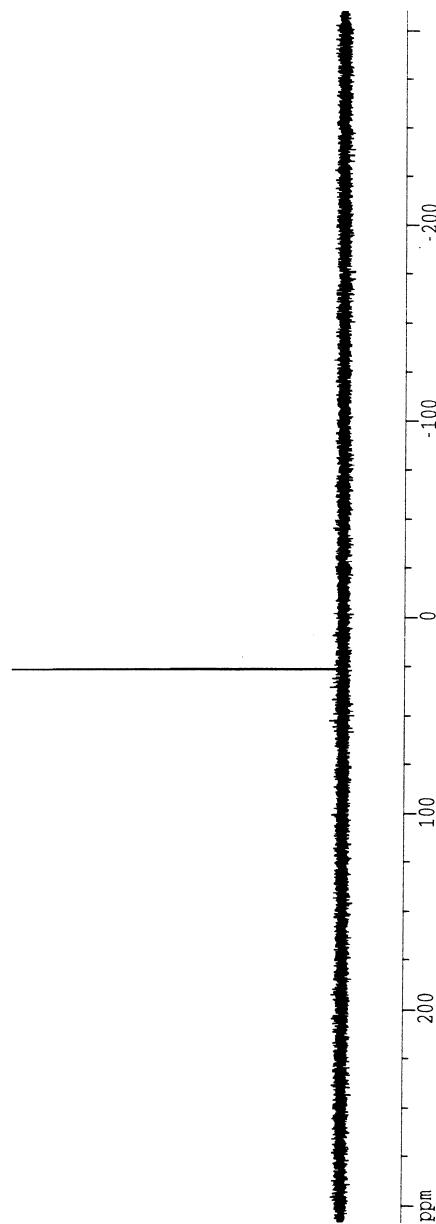


<sup>31</sup>P NMR of **3b**

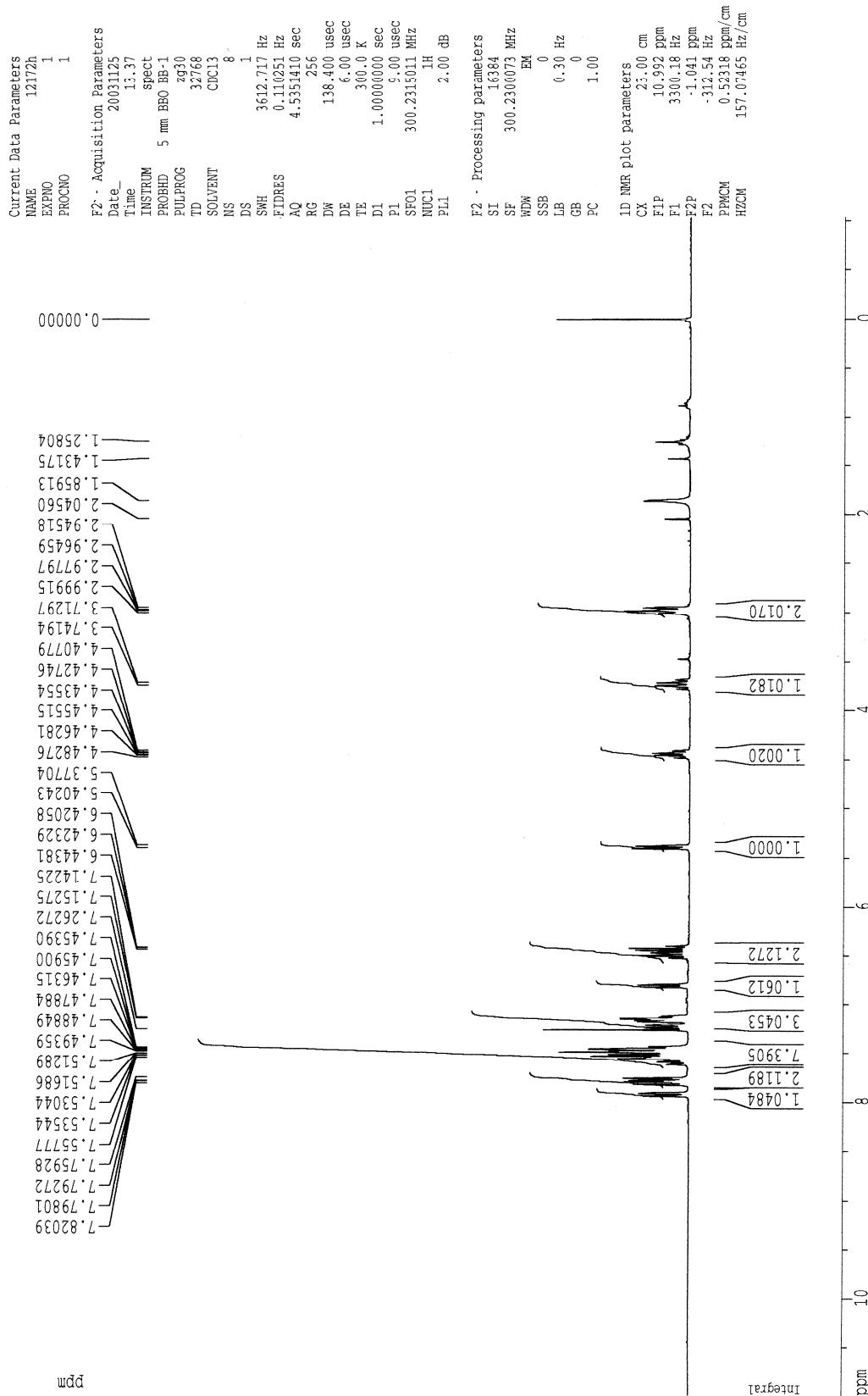
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—26.2760—

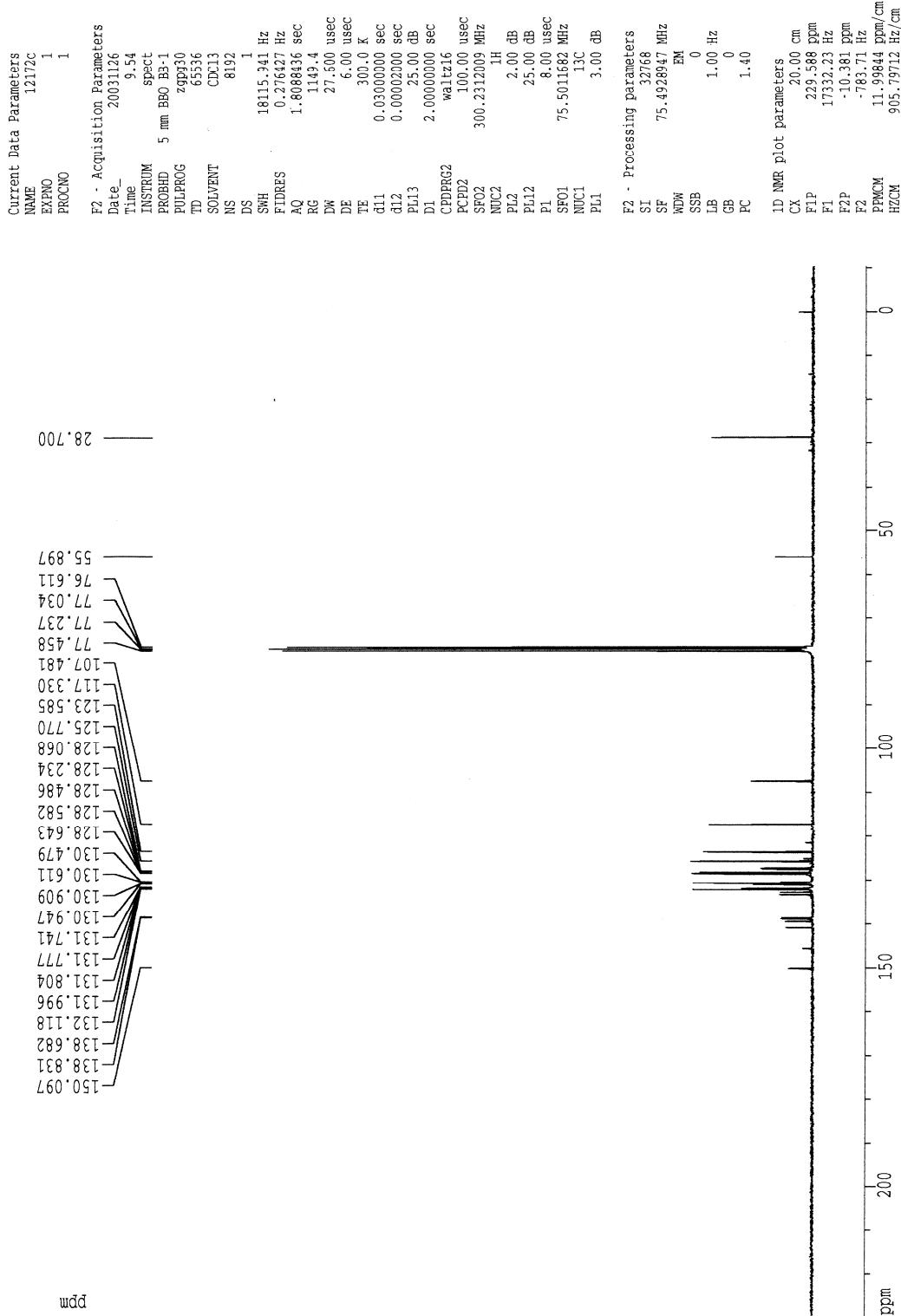
ddd



<sup>1</sup>H NMR of **3c**

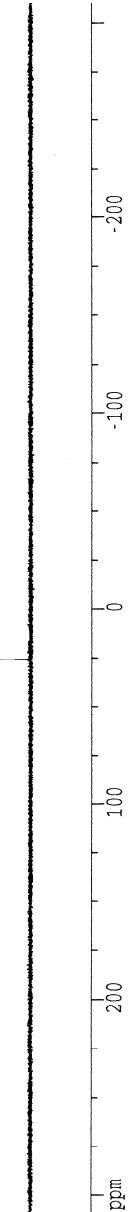


<sup>13</sup>C NMR of **3c**



<sup>31</sup>P NMR of **3c**

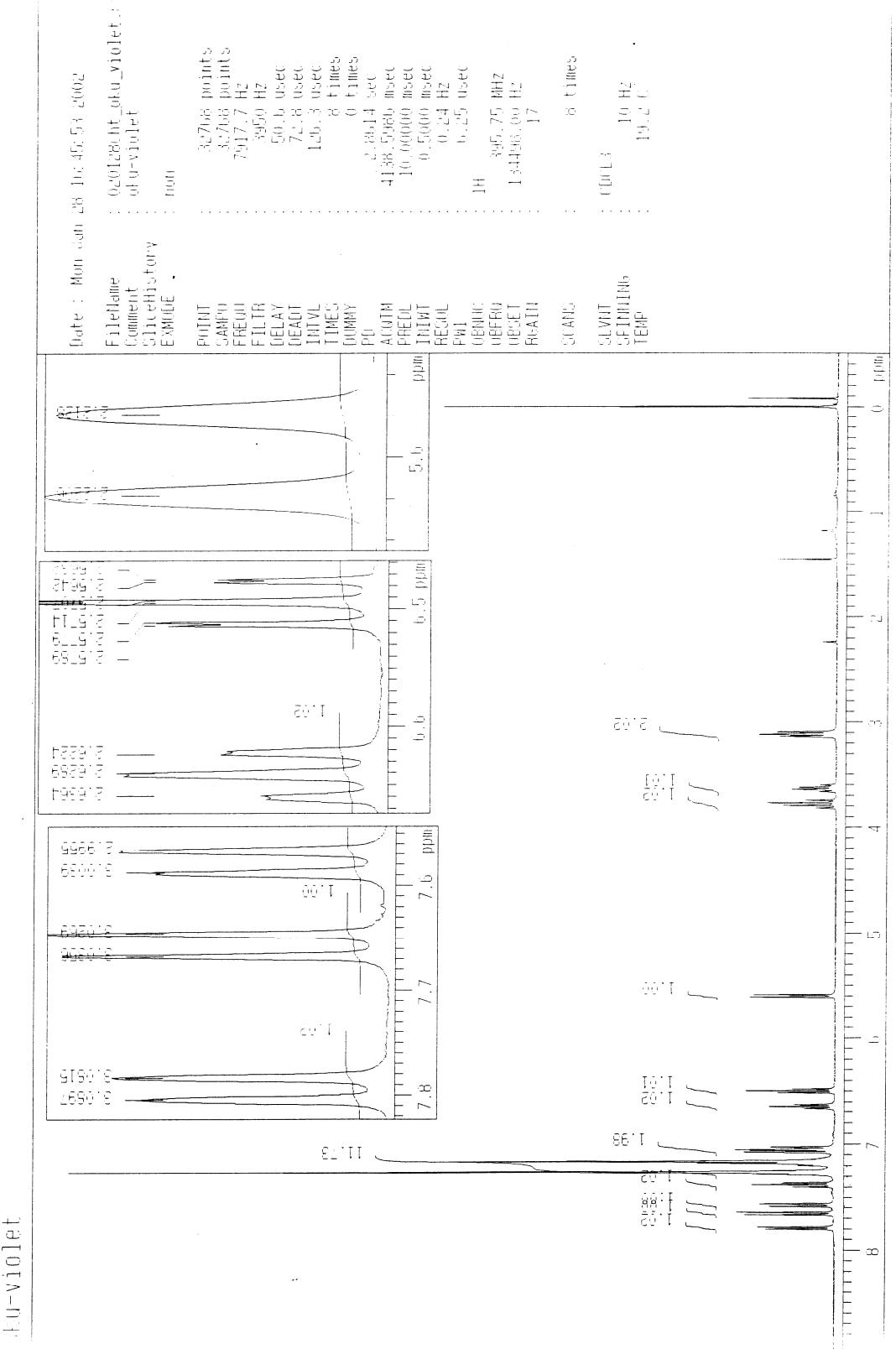
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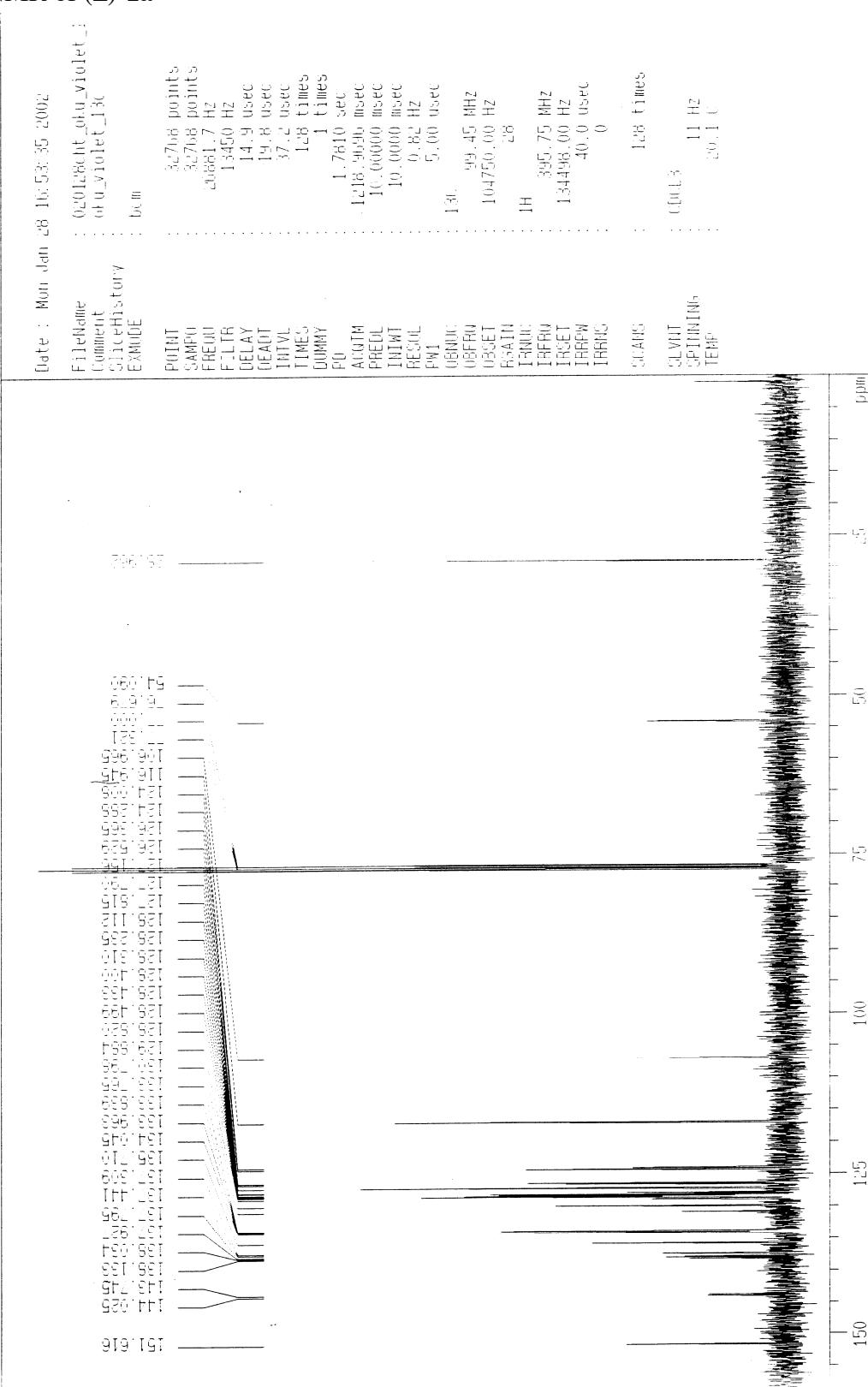
— 25,8676 —

ddd

<sup>1</sup>H NMR of ( $\pm$ )-**1a**



<sup>13</sup>C NMR of ( $\pm$ )-1a



<sup>31</sup>P NMR of (+)-1a

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NUC1	31P
PL1	3.00 dB

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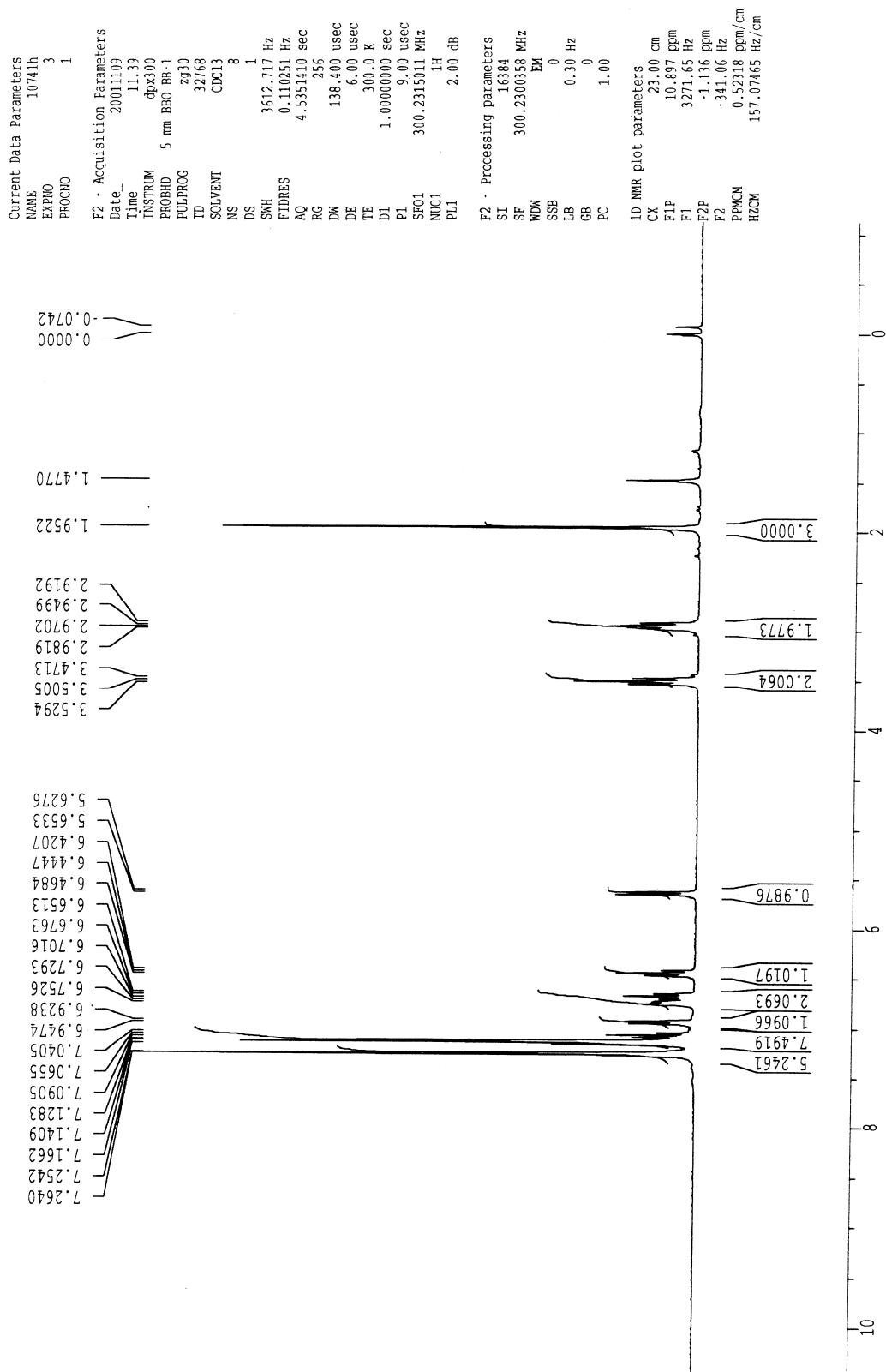
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HZCM	3759.39844 Hz/cm

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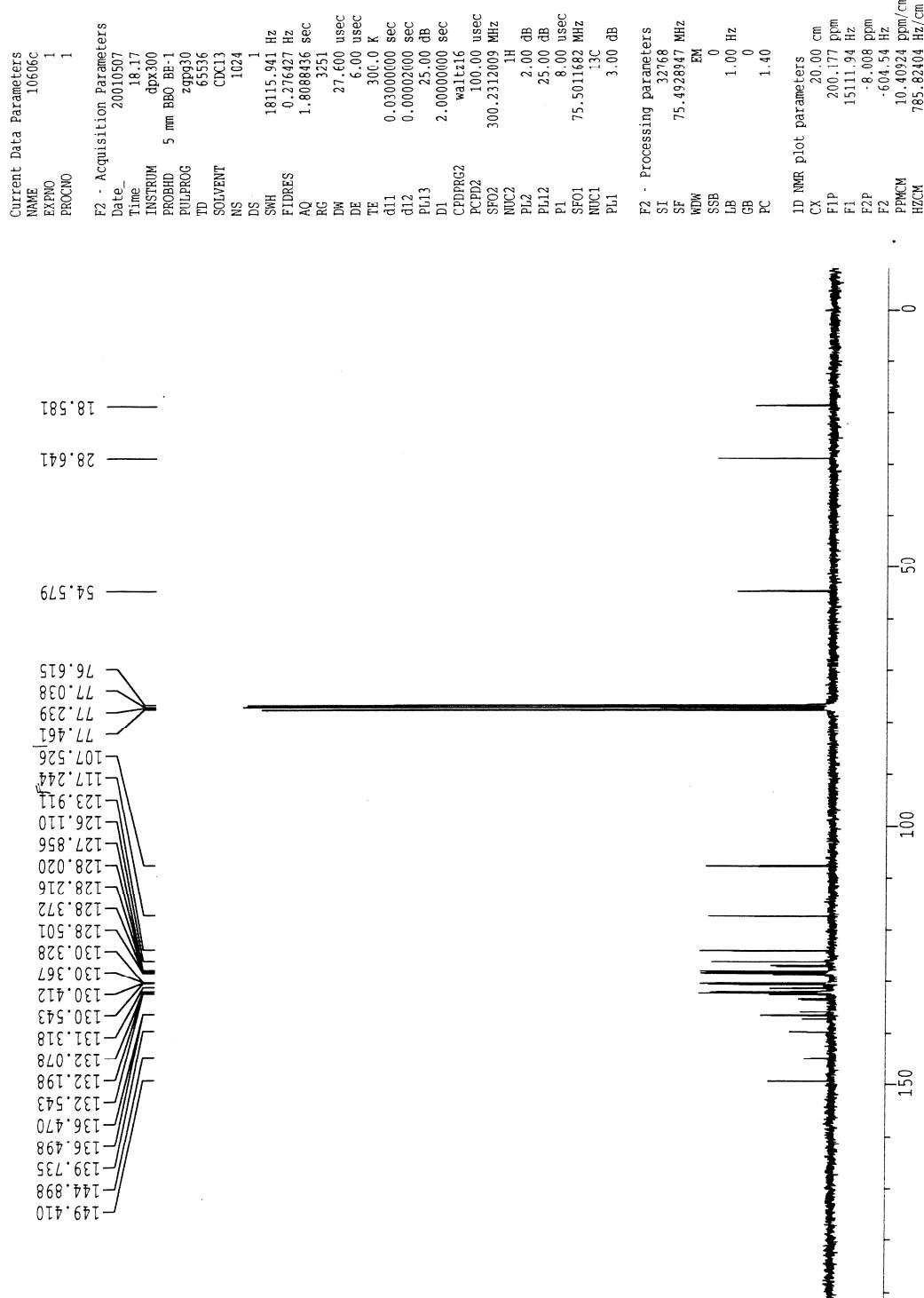
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<sup>1</sup>H NMR of ( $\pm$ )-**1b**



<sup>13</sup>C NMR of ( $\pm$ )-**1b**

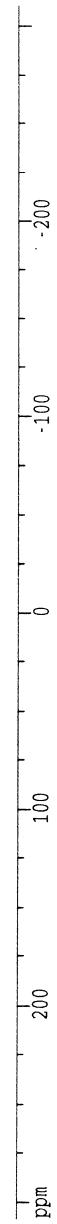


<sup>31</sup>P NMR of (+)-**1b**

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NUC2 1H  
PL2 2.00 dB  
PL12 25.00 dB  
P1 8.00 usec  
SF01 121.5351820 MHz  
NUC1 31P  
PL1 3.00 dB

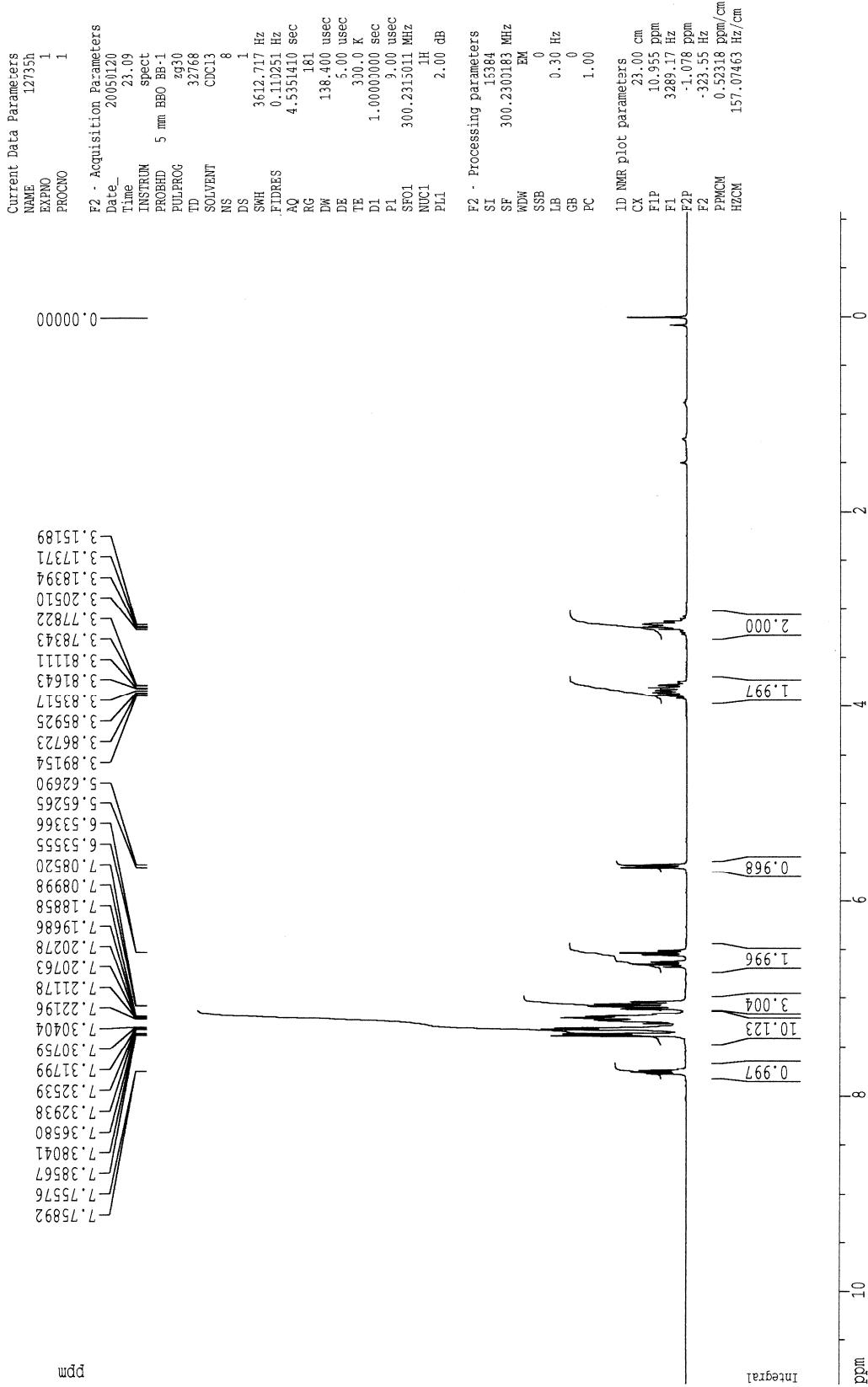
F2 - Processing parameters  
SI 32768  
SF 121.5352115 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
FC 1.00



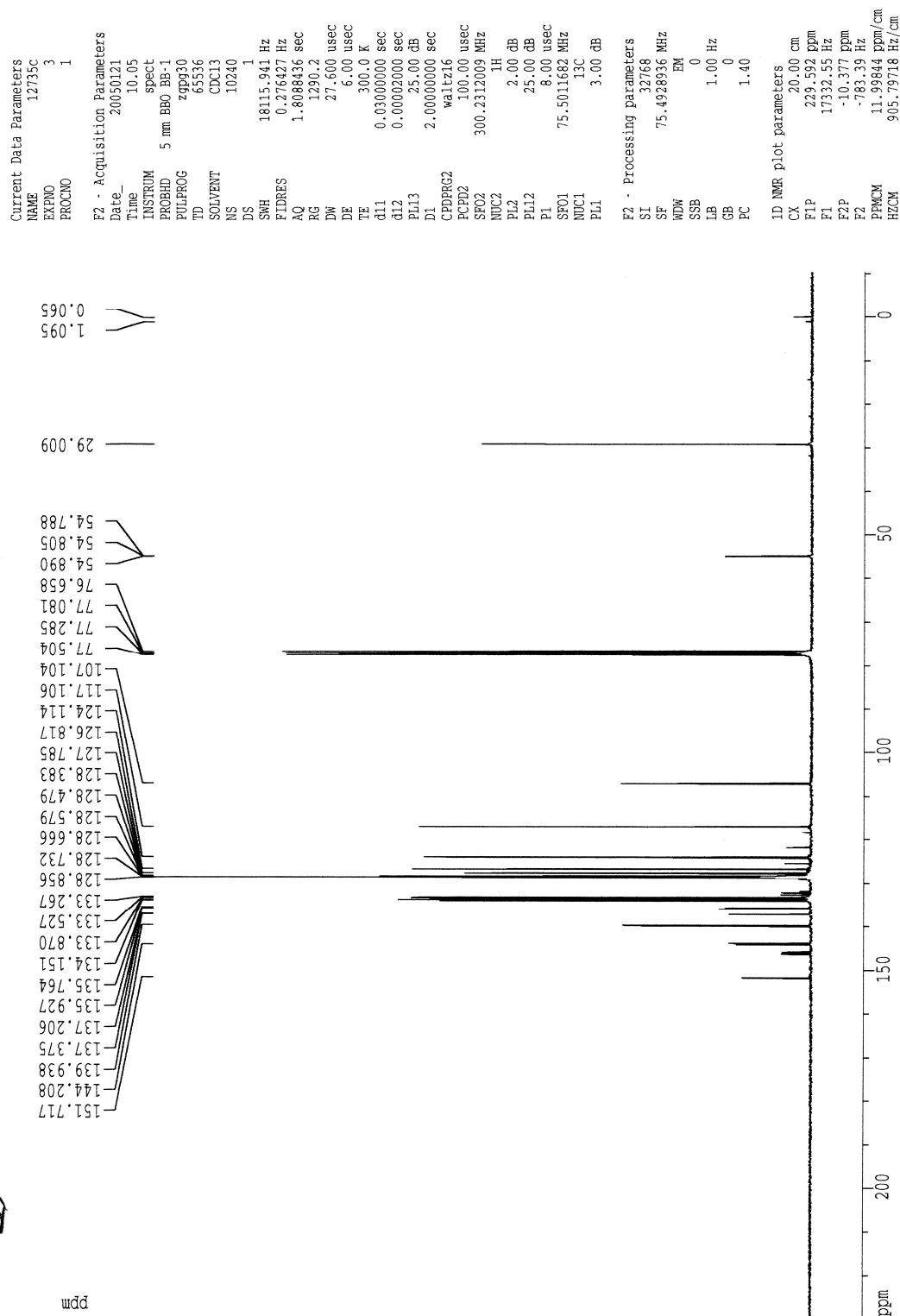
-14.122

ddd

<sup>1</sup>H NMR of ( $\pm$ )-**1c**



<sup>13</sup>C NMR of ( $\pm$ )-**1c**



**<sup>31</sup>P NMR of ( $\pm$ )-1c**

Current Data Parameters  
NAME 117059  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters  
Date 2003026  
Time 17:05  
INSTRUM spect  
PROBHD 5 mm BBO BB-1  
PULPROG zgpp30  
TD 6536  
SOLVENT CDCl<sub>3</sub>  
NS 8  
DS 1  
SWH 75187.969 Hz  
FIDRES 1.147277 Hz  
AQ 0.455844 sec  
RG 2895.3  
DW 6.650 usec  
DE 6.00 usec  
TE 300.0 K  
d11 0.0300000 sec  
d12 0.0000200 sec  
PL1 3 25.00 dB  
D1 8.0000000 sec  
CPDPRG2 waltz16  
FCPD2 100.00 usec  
SF02 300.2312009 MHz  
NUC2 1H  
PL2 2.00 dB  
PL12 25.00 dB  
P1 8.00 usec  
SF01 121.5351320 MHz  
NUC1 31P  
PL1 3.00 dB

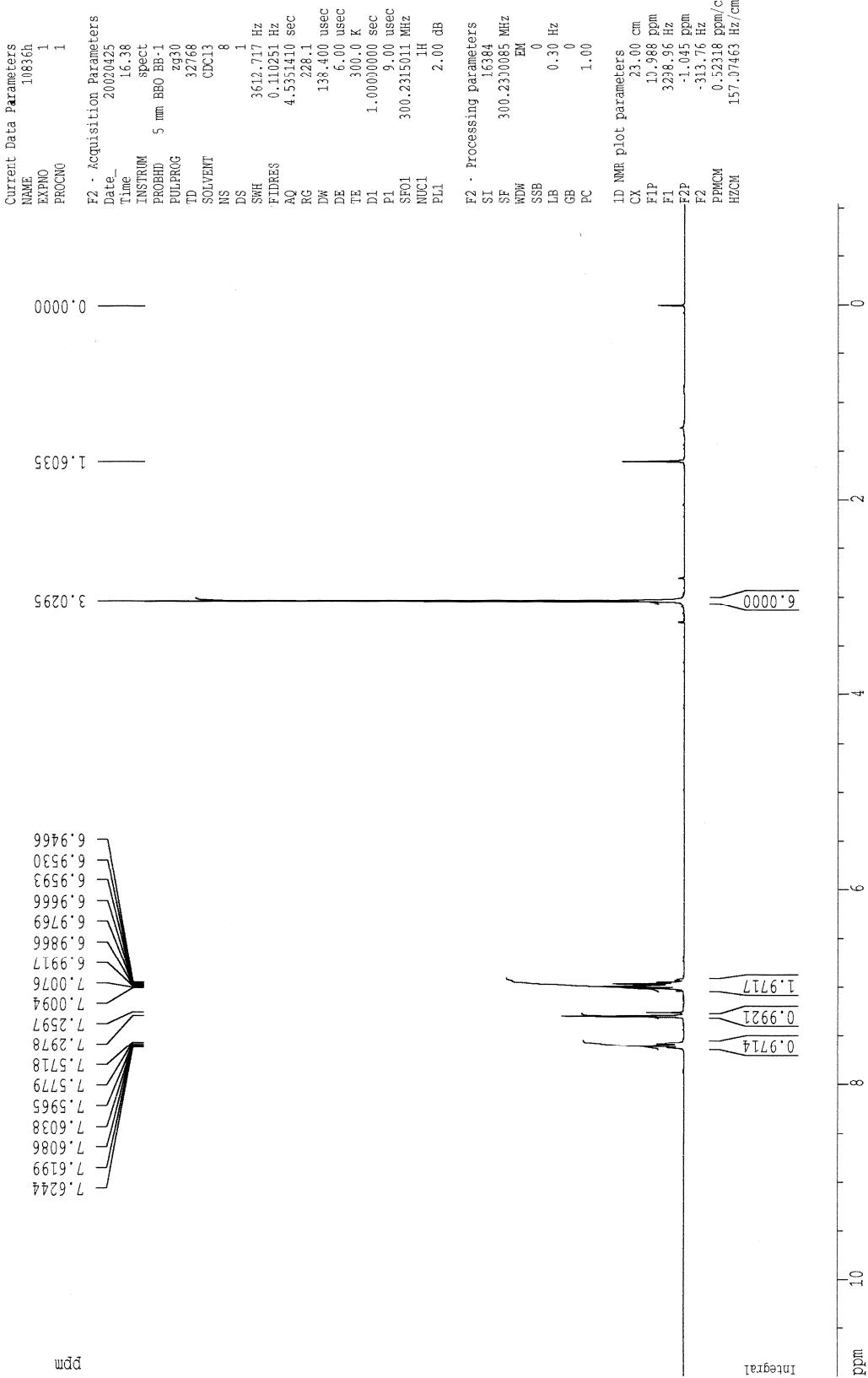
F2 - Processing parameters  
SI 32768  
SF 121.535215 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.00

1D NMR plot parameters  
CX 20.00 cm  
F1P 308.389 ppm  
F1 37514.50 Hz  
F2P -310.062 ppm  
F2 -3763.47 Hz  
PPM0H 30.93257 ppm/cm  
HZCM 3759.39344 Hz/cm

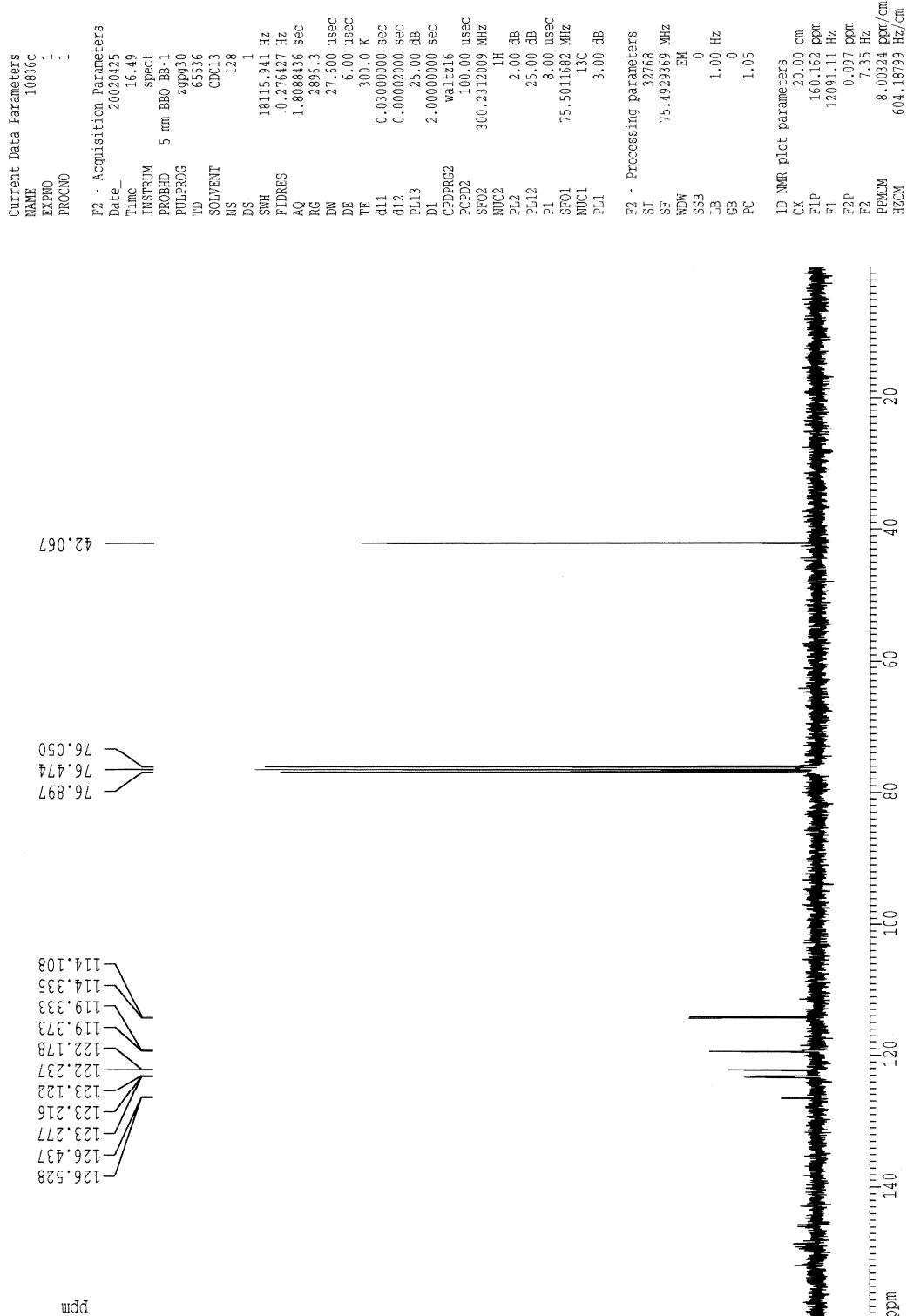
— -17.932 —

ddd

<sup>1</sup>H NMR of **5**

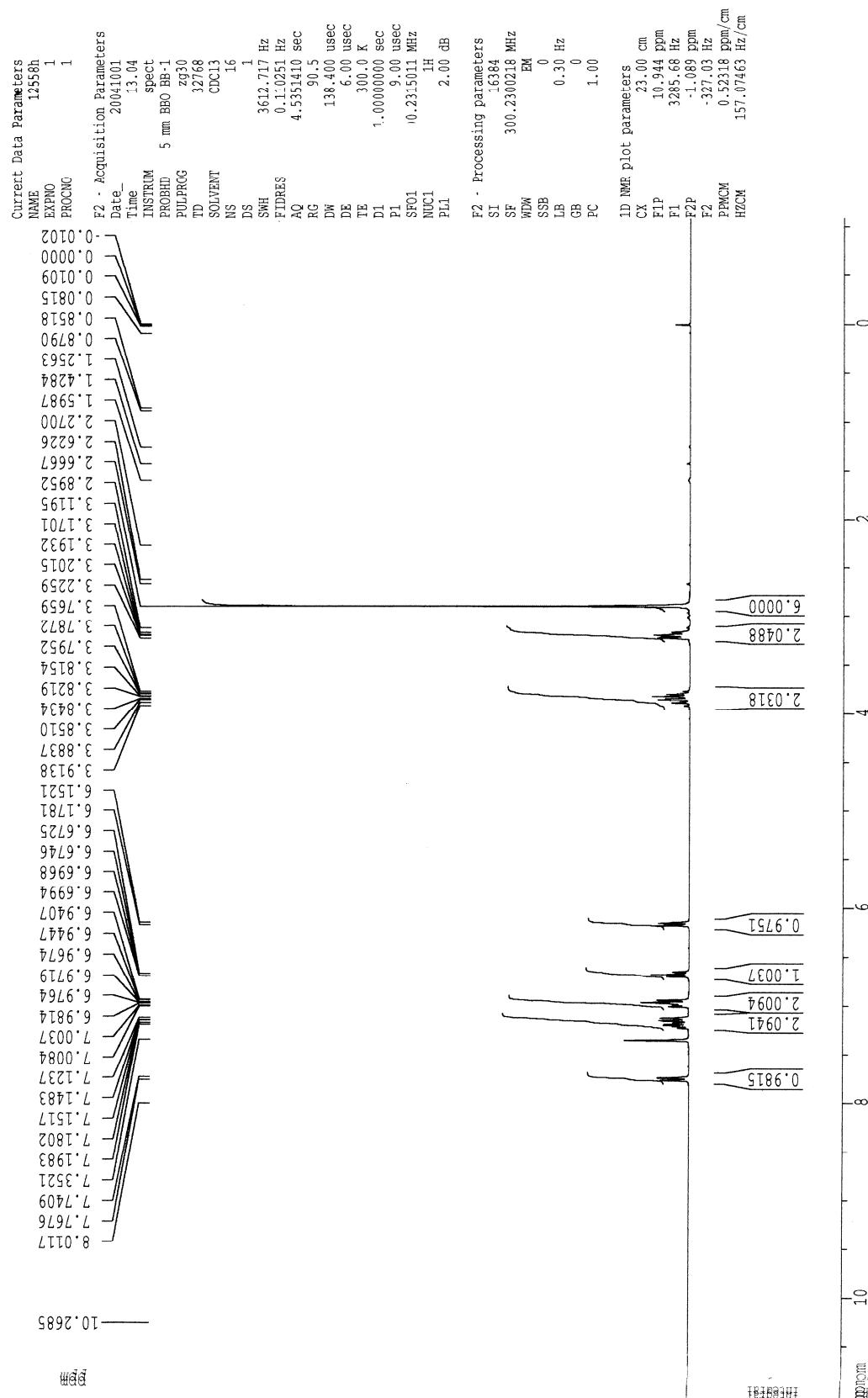


<sup>13</sup>C NMR of **5**

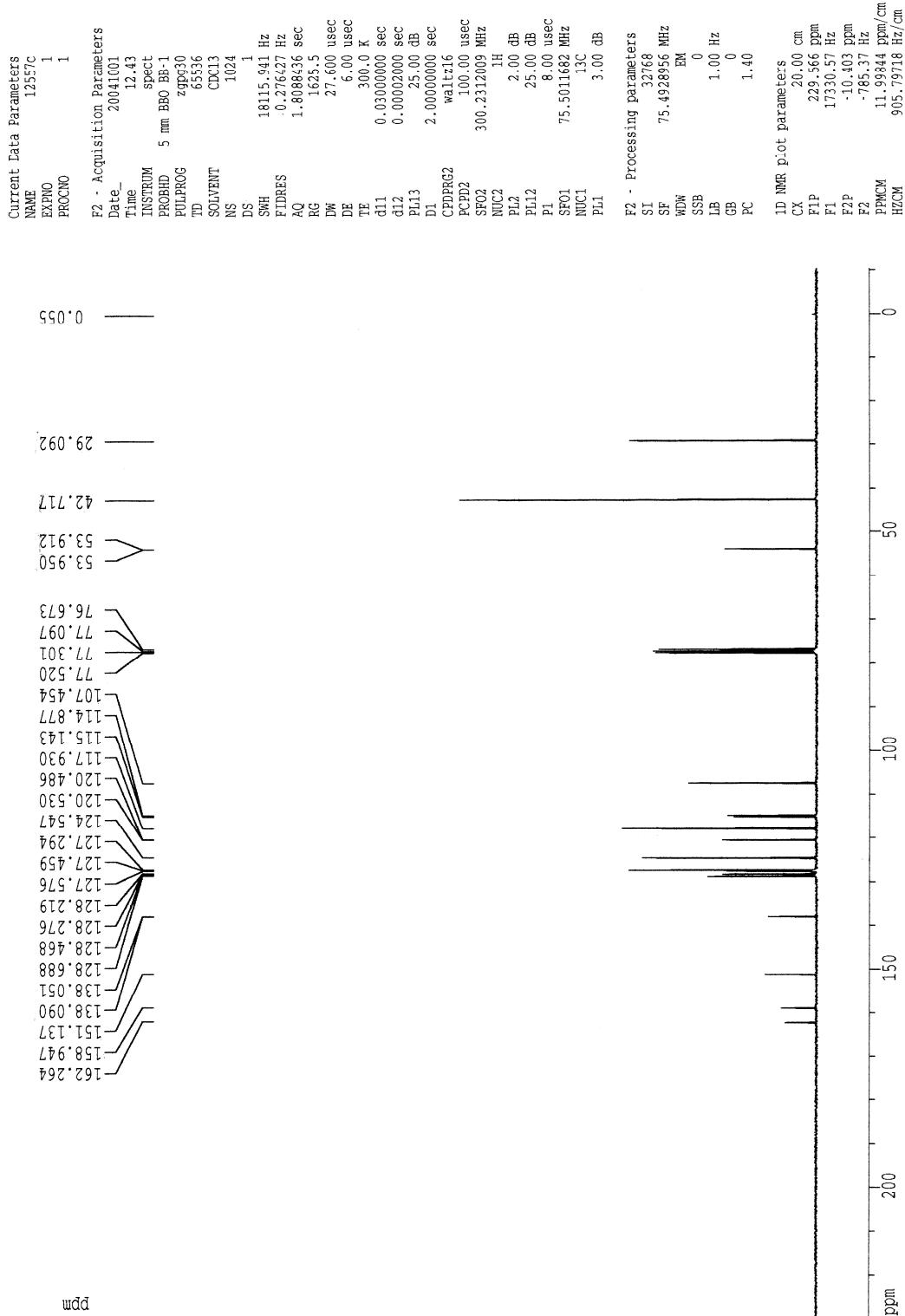


ppm

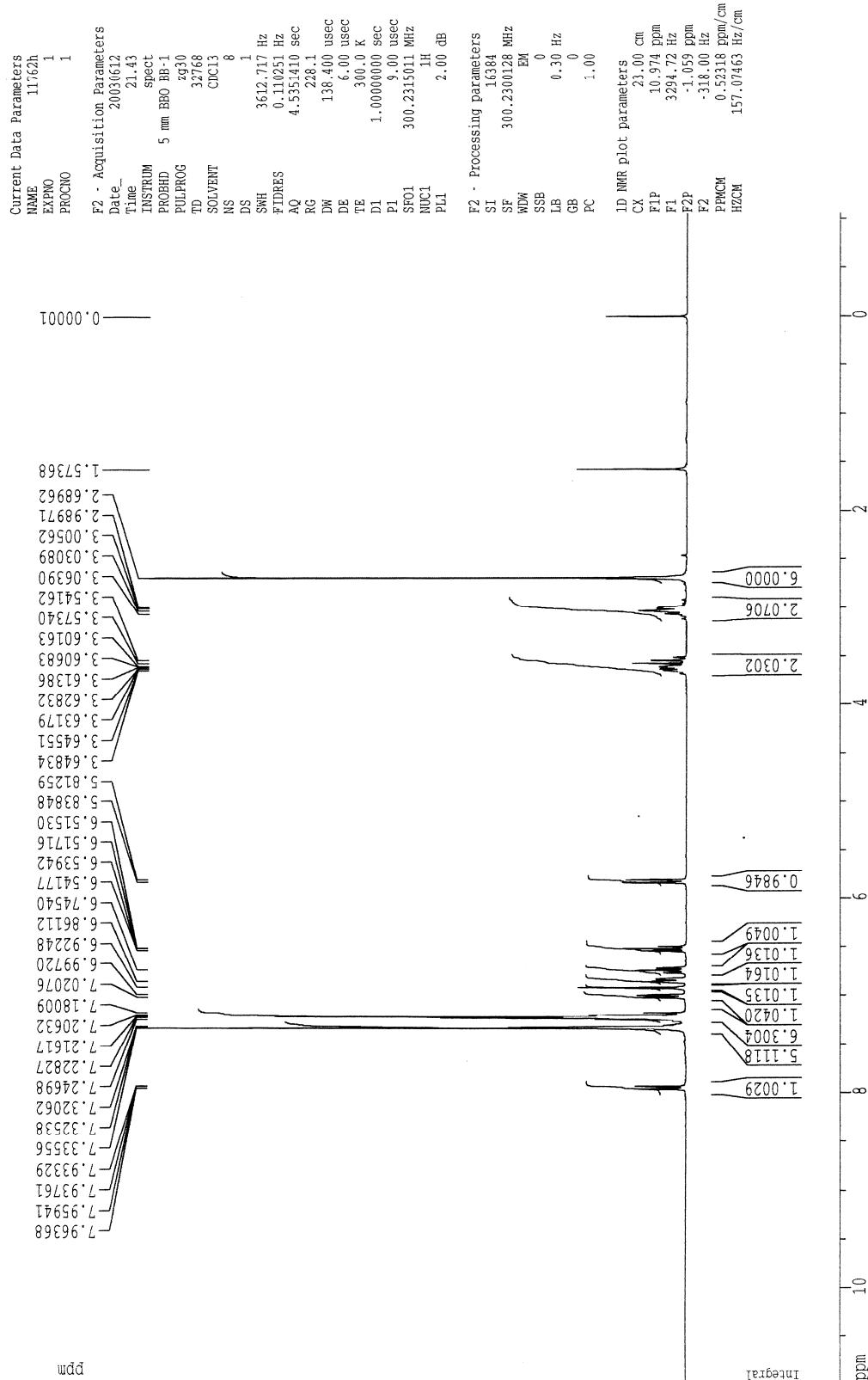
<sup>1</sup>H NMR of **6**



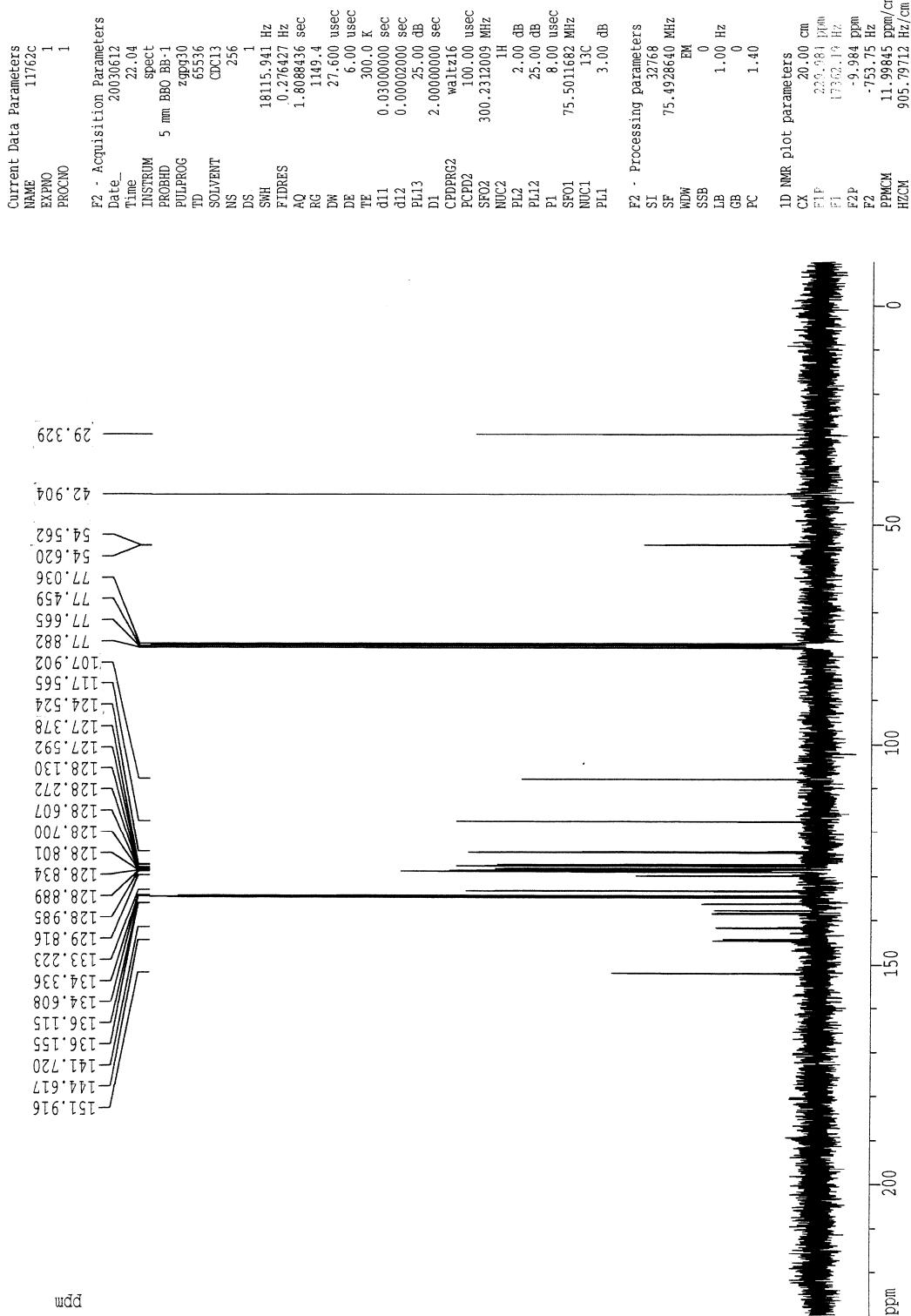
<sup>13</sup>C NMR of **6**



<sup>1</sup>H NMR of 7



<sup>13</sup>C NMR of 7



<sup>31</sup>P NMR of 7

Current Data Parameters  
NAME 1172p  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters

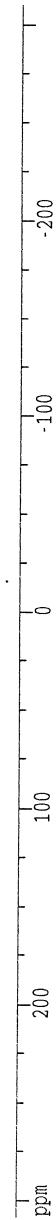
Date\_ 20030612  
Time 22.14  
INSTRUM spect  
PROBHD 5 mm BBO BB-1  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 8  
DS 1  
SWH 75187.969 Hz  
FIDRES 1.147277 Hz  
AQ 0.4958644 sec  
RG 2896.3  
DW 6.650 usec  
DE 6.00 usec  
TE 300.0 K  
d1 0.0300000 sec  
d11 0.0300000 sec  
d12 0.0002000 sec  
PL1 3  
D1 25.00 dB  
CPDPG2 8.0000000 sec  
CPD22 100.00 usec  
SF02 300.231209 MHz  
NUC2 <sup>1</sup>H  
PL2 2.00 GB  
PL12 25.00 dB  
P1 8.00 usec  
SF01 121.5551820 MHz  
NUC1 31P  
PL1 3.00 dB

F2 - Processing parameters

SI 32768  
SF 121.5552715 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.00

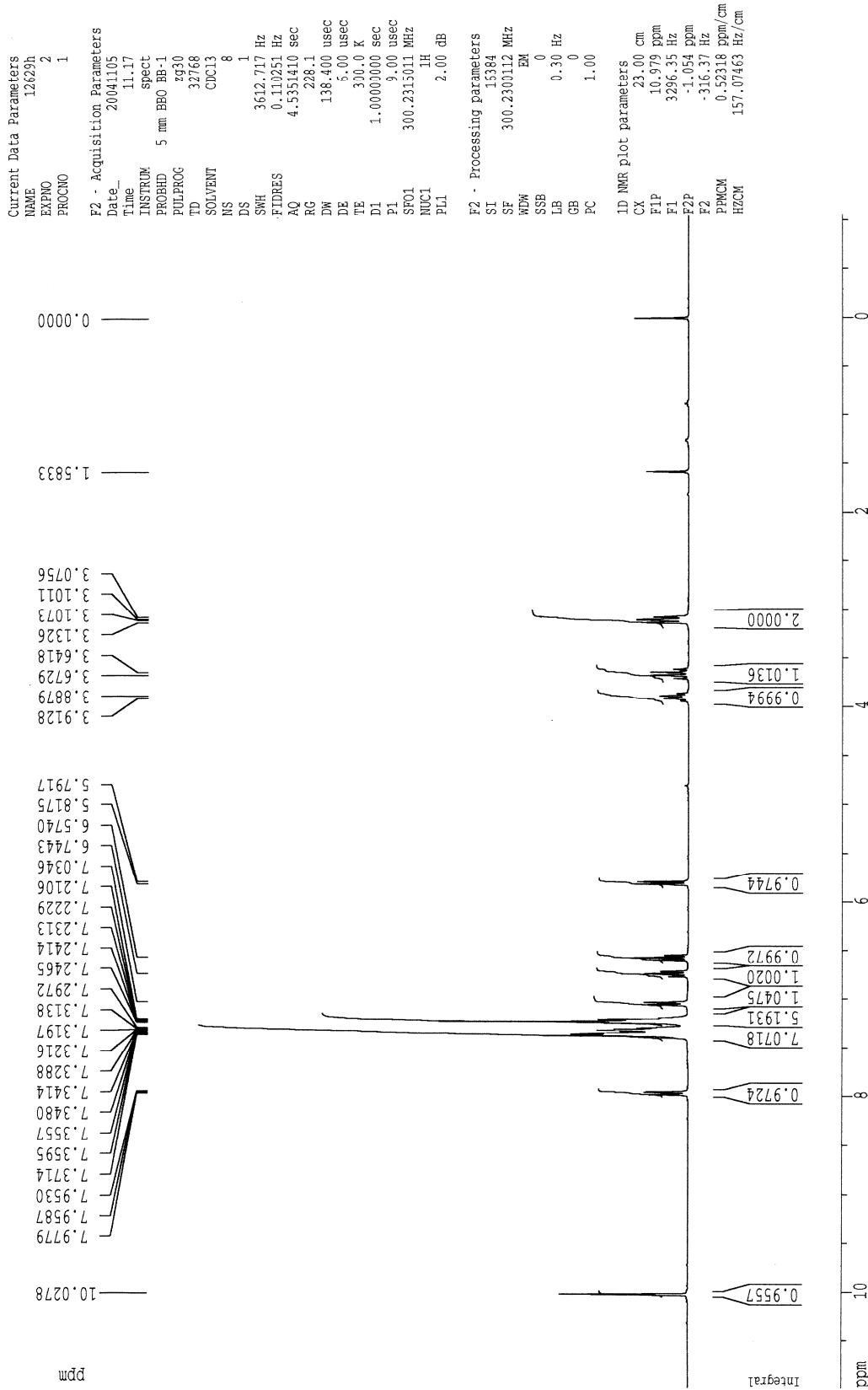
1D NMR Plot parameters

CX 20.00 cm  
F1P 308.589 ppm  
F1 37504.50 Hz  
F2P 310.062 ppm  
F2 -37683.47 Hz  
PNORM 30.92257 ppm/cm  
HZCM 3759.39844 Hz/cm

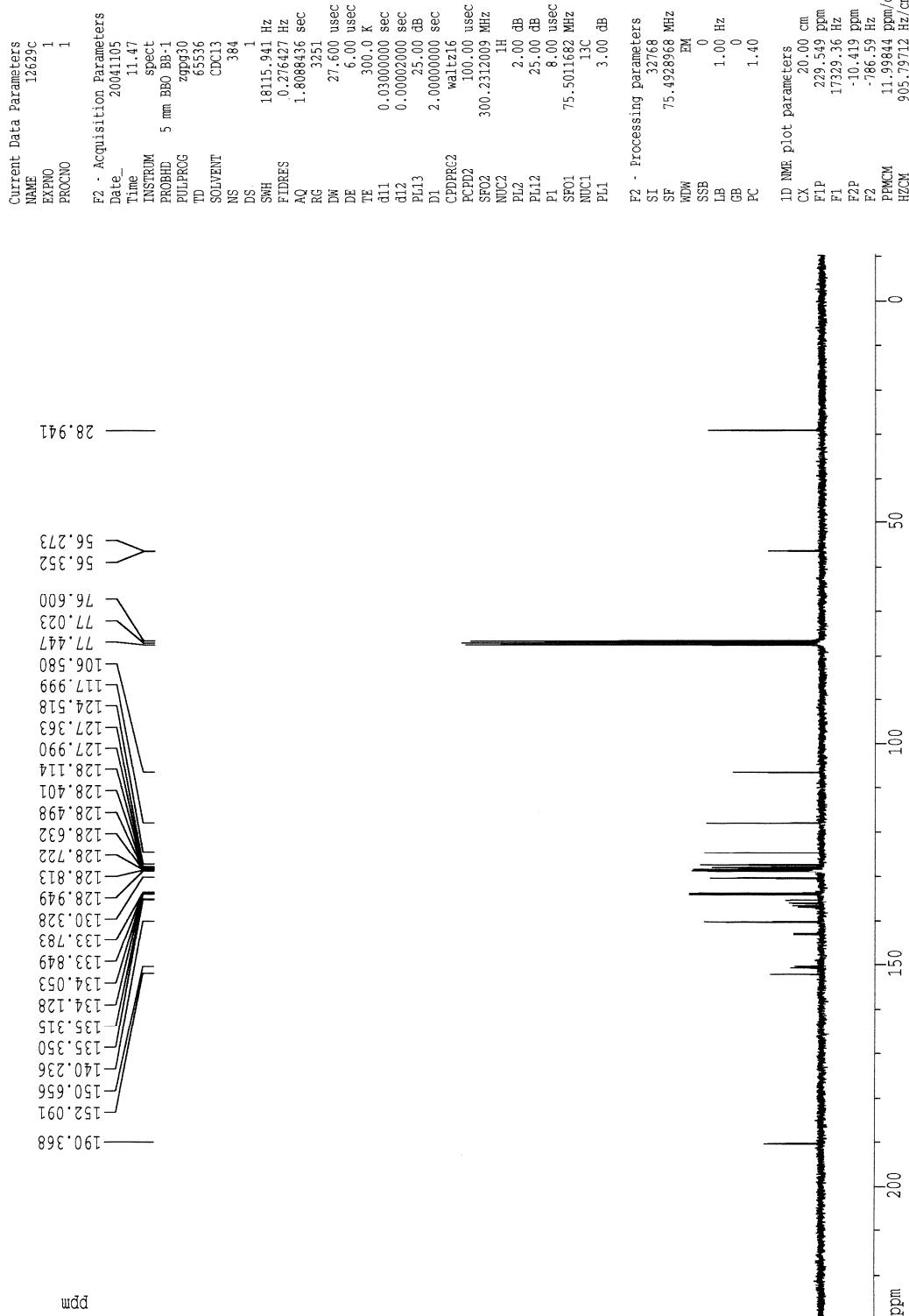


wdd

### <sup>1</sup>H NMR of **8**



<sup>13</sup>C NMR of **8**



<sup>31</sup>P NMR of **8**

Current Data Parameters

NAME	11704p
EXPTN	1
PRCNO	1

F2 - Acquisition Parameters

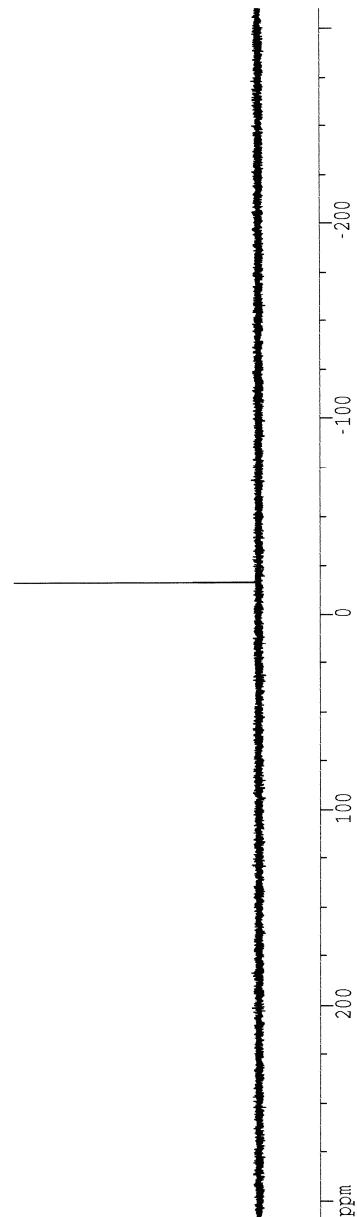
Date	20030526
Time	15:51
INSTRUM	5 mm BBO 3B-1 spect
PROBDHD	2g930
PULPROG	65336
TD	CDCl <sub>3</sub>
SOLVENT	NS
RG	8
DW	75187.969 Hz
SWH	1.147277 Hz
FLDRES	0.4558644 sec
AQ	2895.3
RG	6.650 usec
DE	6.00 usec
TE	300.0 K
d11	0.03000000 sec
d12	0.0002000 sec
PL13	0.0000000 sec
D1	25.00 dB
CPDRG2	walt16
FCP12	100.00 usec
SFO2	300.23212009 MHz
NUC2	<sup>1</sup> H
PL2	2.00 dB
PL12	25.00 dB
P1	8.00 usec
SFO1	121.5351820 MHz
NUC1	<sup>31</sup> P
PL1	3.00 dB

F2 - Processing parameters

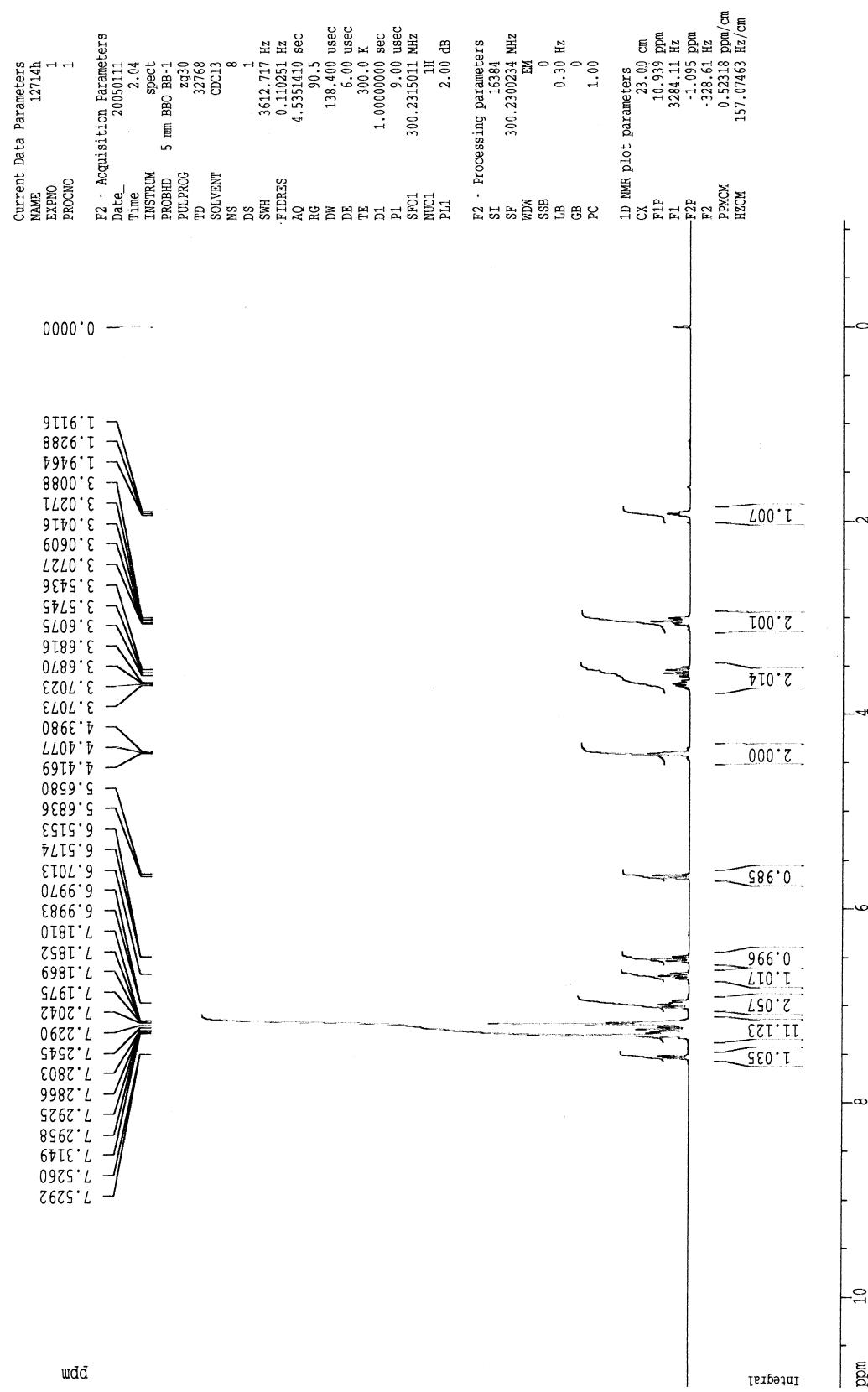
SI	32768
SF	121.535215 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

-16.219

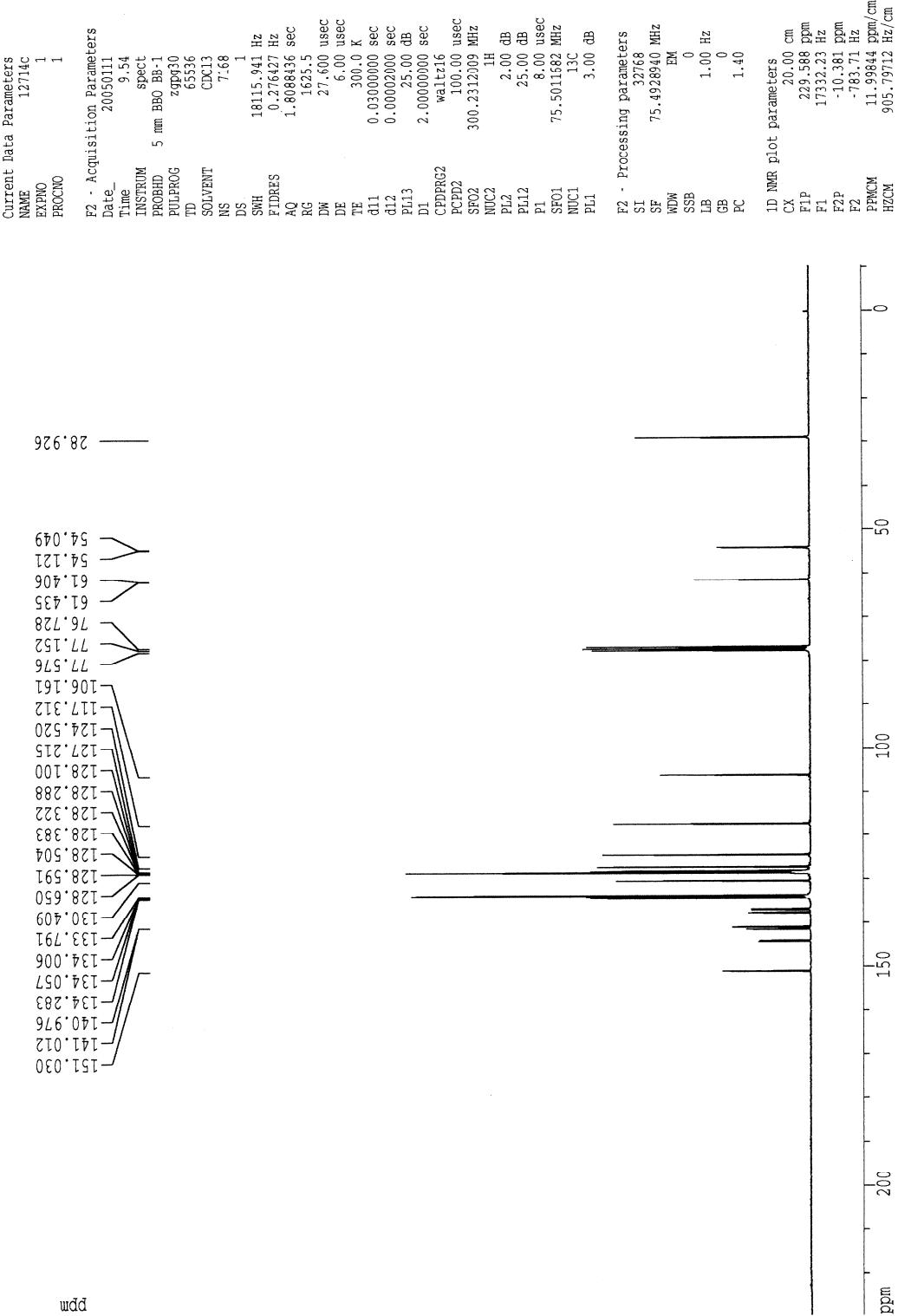
dd



<sup>1</sup>H NMR of **9**



<sup>13</sup>C NMR of **9**



### <sup>31</sup>P NMR of **9**

Current Data Parameters  
NAME 1211p  
EXPNO 1  
PRCNO 1

F2 - Acquisition Parameters  
Date\_ 20050111  
Time 2.14  
INSTRUM spect  
PROBID 5 mm BB6 BB-1  
PULPROG zgpg30  
TD 6536  
SOLVENT CDC13  
NS 16  
DS 1  
SWH 38535.645 Hz  
FIDRES 0.589007 Hz  
AQ 0.893795 sec  
RG 369.1  
DW 12.975 usec  
DE 6.00 usec  
TE 300.0 K  
d11 0.0300000 sec  
d12 0.0000200 sec  
PL13 25.00 dB  
D1 8.0000000 sec  
CPDPG2 waltz16  
PCPD2 100.00 usec  
SF02 300.231209 MHz  
NUC2 1H  
PL2 2.00 dB  
PL12 25.00 dB  
P1 8.00 usec  
SF01 121.5355820 MHz  
NUC1 3J1P  
PL1 3.00 dB

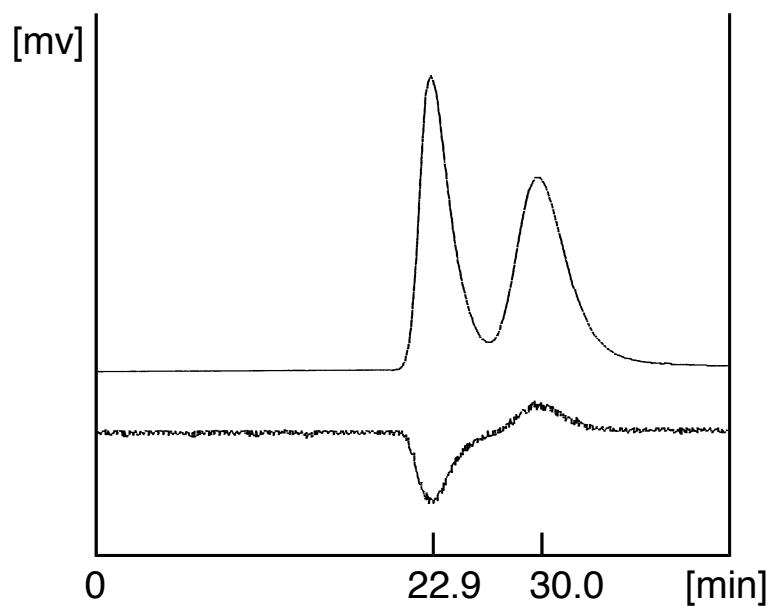
F2 - Processing parameters  
SI 32768  
SF 121.5352715 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.00

1D NMR plot parameters  
CX 20.00 cm  
F1P 157.801 ppm  
F1 19178.34 Hz  
F2P -159.273 ppm  
F2 -1957.30 Hz  
PPCM 15.83369 ppm/cm  
HZCM 1326.78210 Hz/cm

-15.275

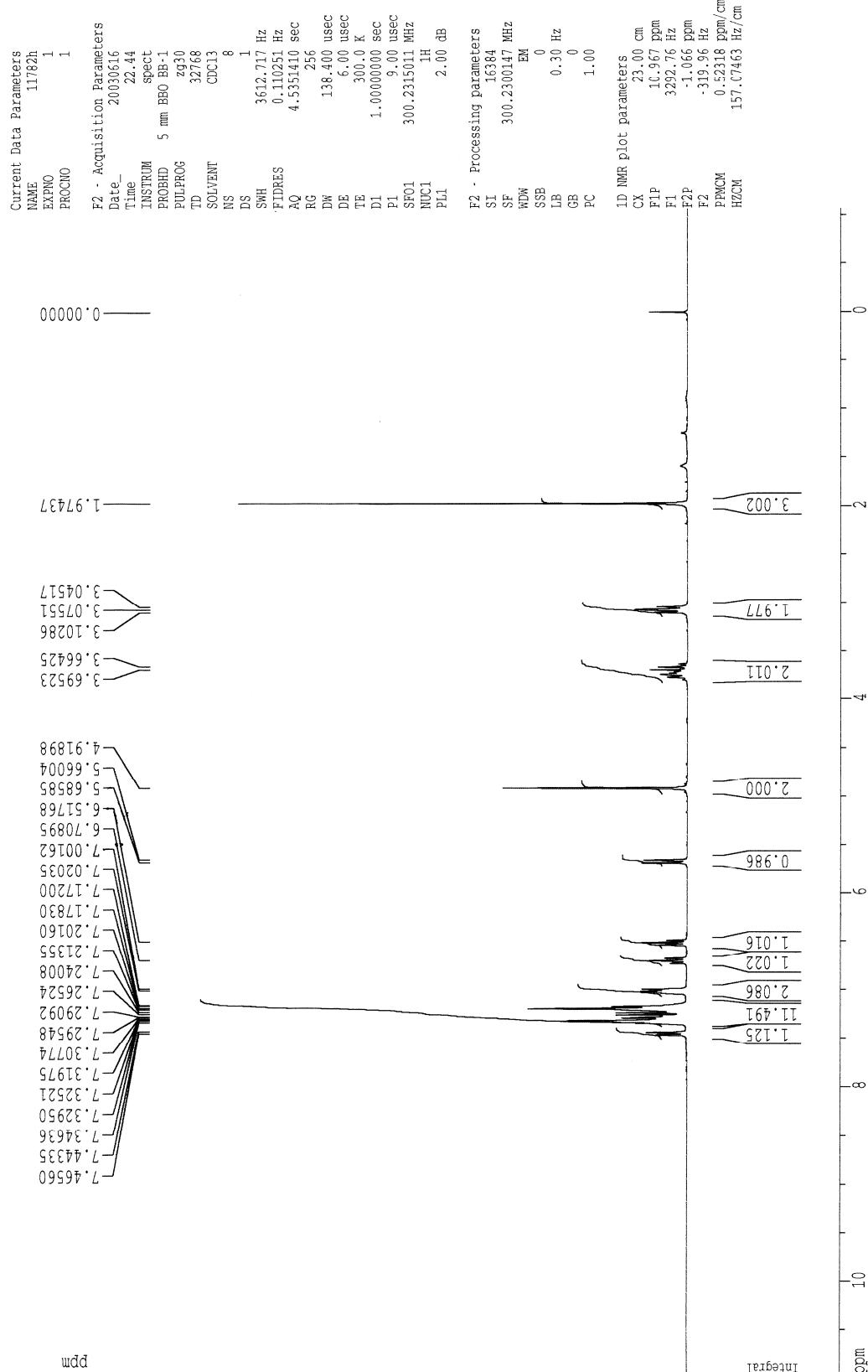
ddd

Chiral phase HPLC–UV (254 nm) and –CD (254 nm) chart of **9**

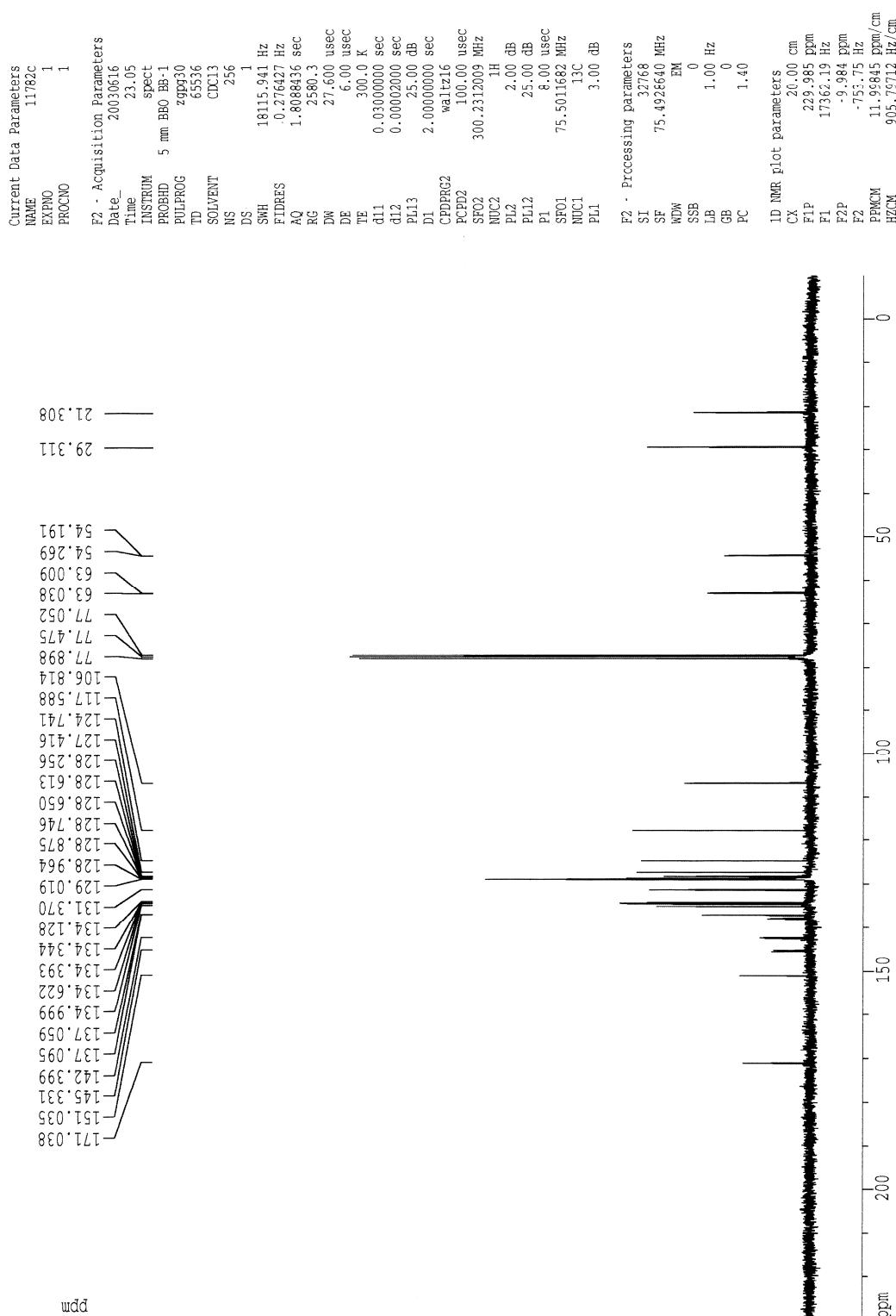


Daicel Chiralcel OJ<sup>®</sup>, hexane : ethanol=99 : 1, 0.3 mL/min

### <sup>1</sup>H NMR of ( $\pm$ )-**1d**



<sup>13</sup>C NMR of ( $\pm$ )-**1d**



<sup>31</sup>P NMR of (+)-**1d**

Current Data Parameters

NAME	11783p
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

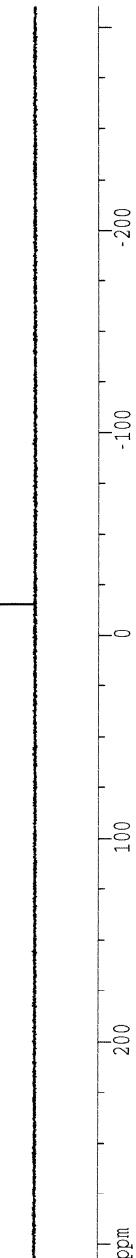
Date	20030616
Time	23:15
INSTRUM	spect
PROBHD	5 mm BBO BB-1
PULPROG	zpg30
TD	65536
SOLVENT	CDCl <sub>3</sub>
NS	8
DS	1
SWH	75187.969 Hz
EDDRES	1.147277 Hz
AQ	0.435644 sec
RG	2896.3
DW	6.650 usec
DE	6.00 usec
TE	300.0 K
d11	0.03000000 sec
d12	0.00000000 sec
PL13	25.00 dB
D1	8.00000000 sec
CPDPFG2	waltz16
PCPD2	100.00 usec
SFO2	300.2312009 MHz
NUC2	1H
PL2	2.00 dB
PL12	25.00 dB
P1	8.00 usec
SFO1	121.5351820 MHz
NUC1	31P
PL1	3.00 dB

F2 - Processing parameters

SI	32768
SF	121.5352715 MHz
NW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

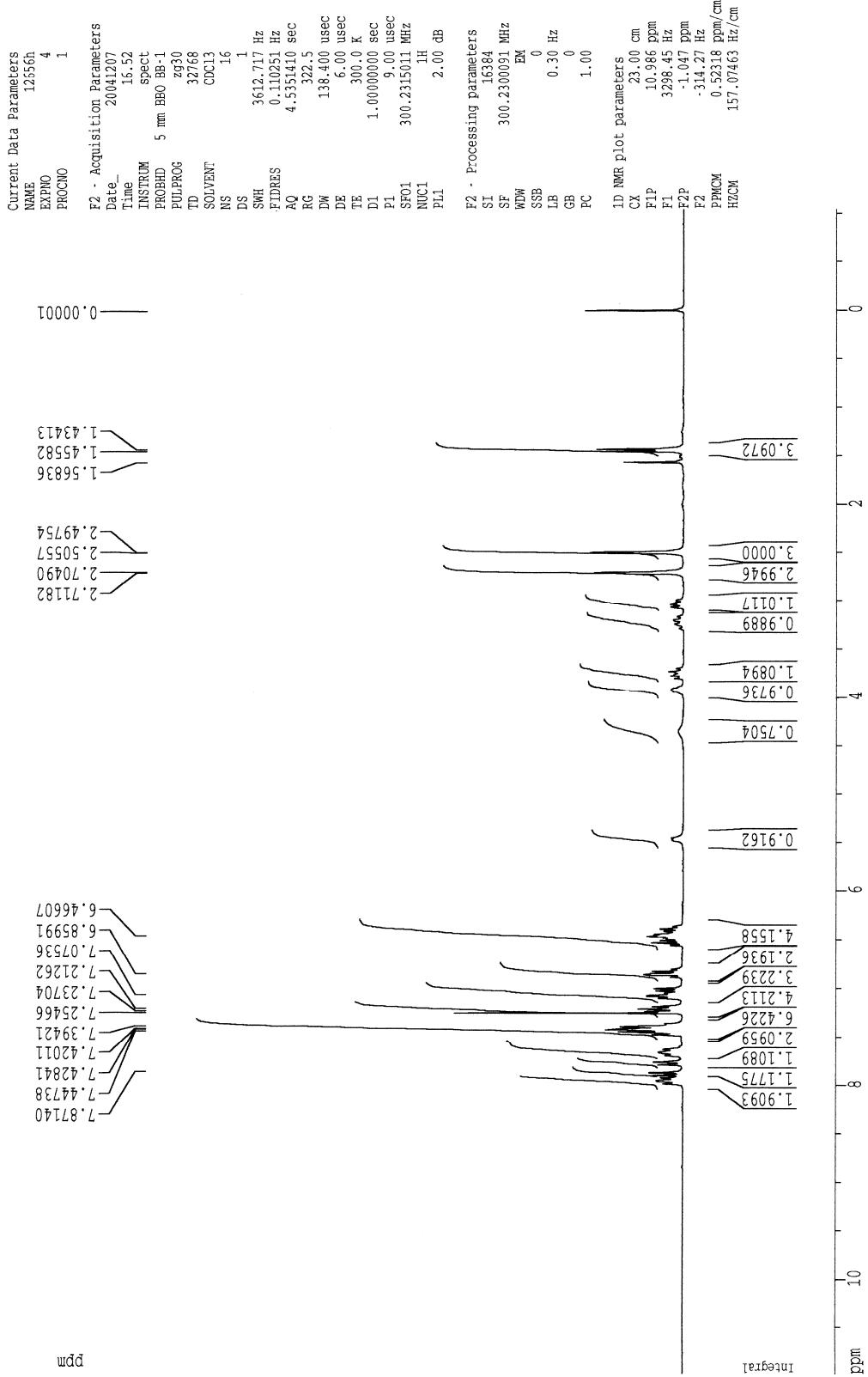
1D NMR plot parameters

CX	20.00 cm
F1P	308.589 ppm
F1	37504.50 Hz
F2P	-310.062 ppm
F2	-37683.47 Hz
PPCM	30.9257 ppm/cm
HZCM	3759.39844 Hz/cm

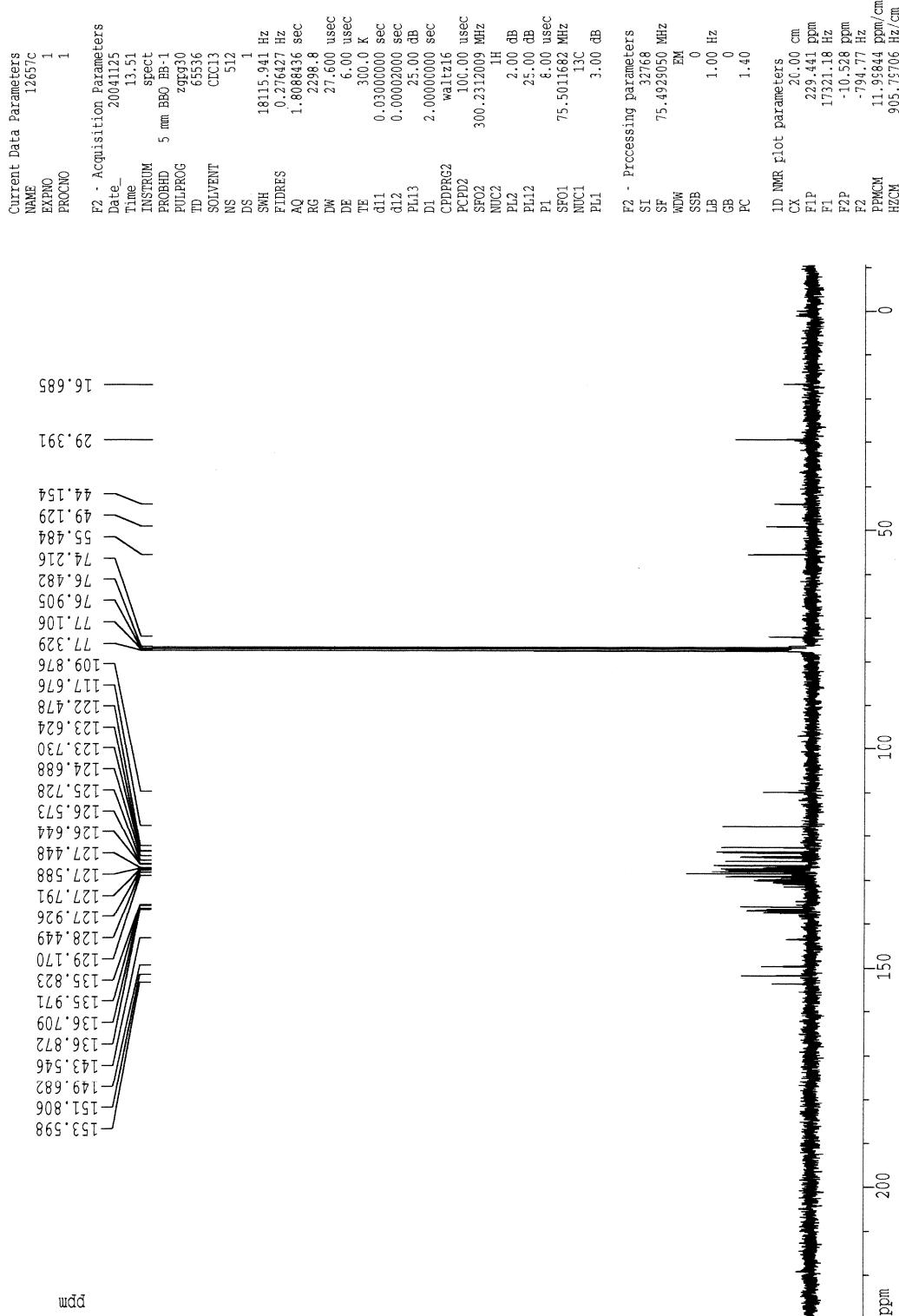


ddd

<sup>1</sup>H NMR of (aS,S)-(+)-11a



<sup>13</sup>C NMR of (aS,S)-(+)-**11a**



<sup>31</sup>P NMR of (aS,S)-(+)-**11a**

Current data Parameters

NAME	12656p
EXPN0	1
PROCN0	1

F2 - Acquisition Parameters

Date	20041122
Time	13:05
INSTRUM	spect
PROBHD	5 mm BBO B3-1
PULPROG	zdp30
TD	65536
SOLVENT	CDC13
NS	8
DS	1
SWH	75187.369 Hz
FLDRES	1.117277 Hz
AQ	0.439844 sec
RG	349.1
DW	6.550 usec
DE	6.00 usec
TE	300.0 K
d1	0.0300000 sec
d12	0.0000200 sec
PL13	25.00 dB
D1	8.0000000 sec
CDDPRG2	waltz16
PCPD2	100.00 usec
SP02	300.231209 MHz
NUC2	1H
PL2	2.00 dB
PL12	25.00 dB
P1	8.00 usec
SP01	121.531320 MHz
NUC1	31P
PL1	3.00 dB

F2 - Processing parameters

SI	32768
SF	121.5352715 MHz
NW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

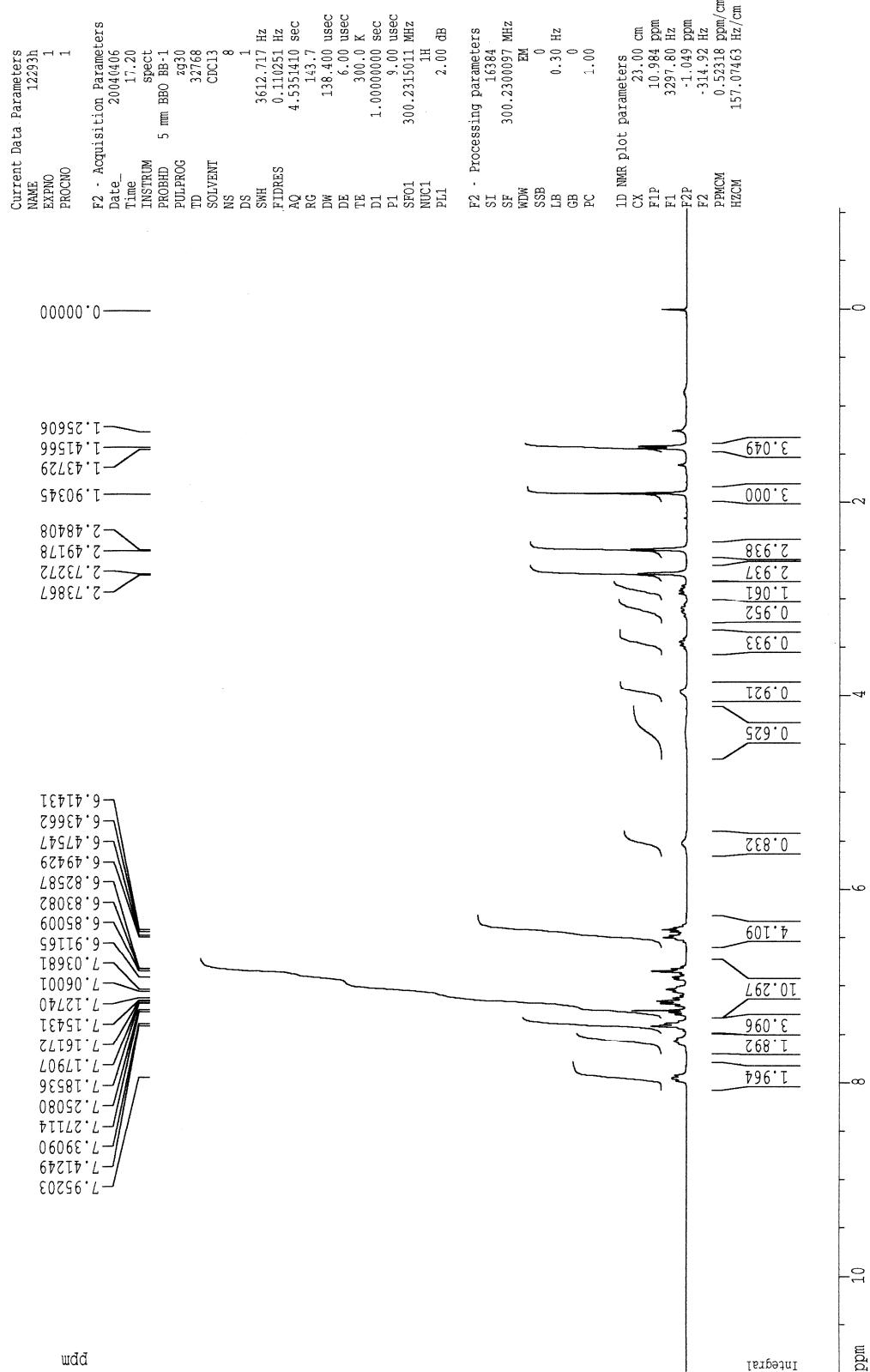
1D NMR plot parameters

CX	20.00 cm
F1P	308.389 ppm
F1	37504.49 Hz
F2P	-310.362 ppm
F2	-37633.48 Hz
PPMCM	30.33257 ppm/cm
HzCM	3754.49244 Hz/cm

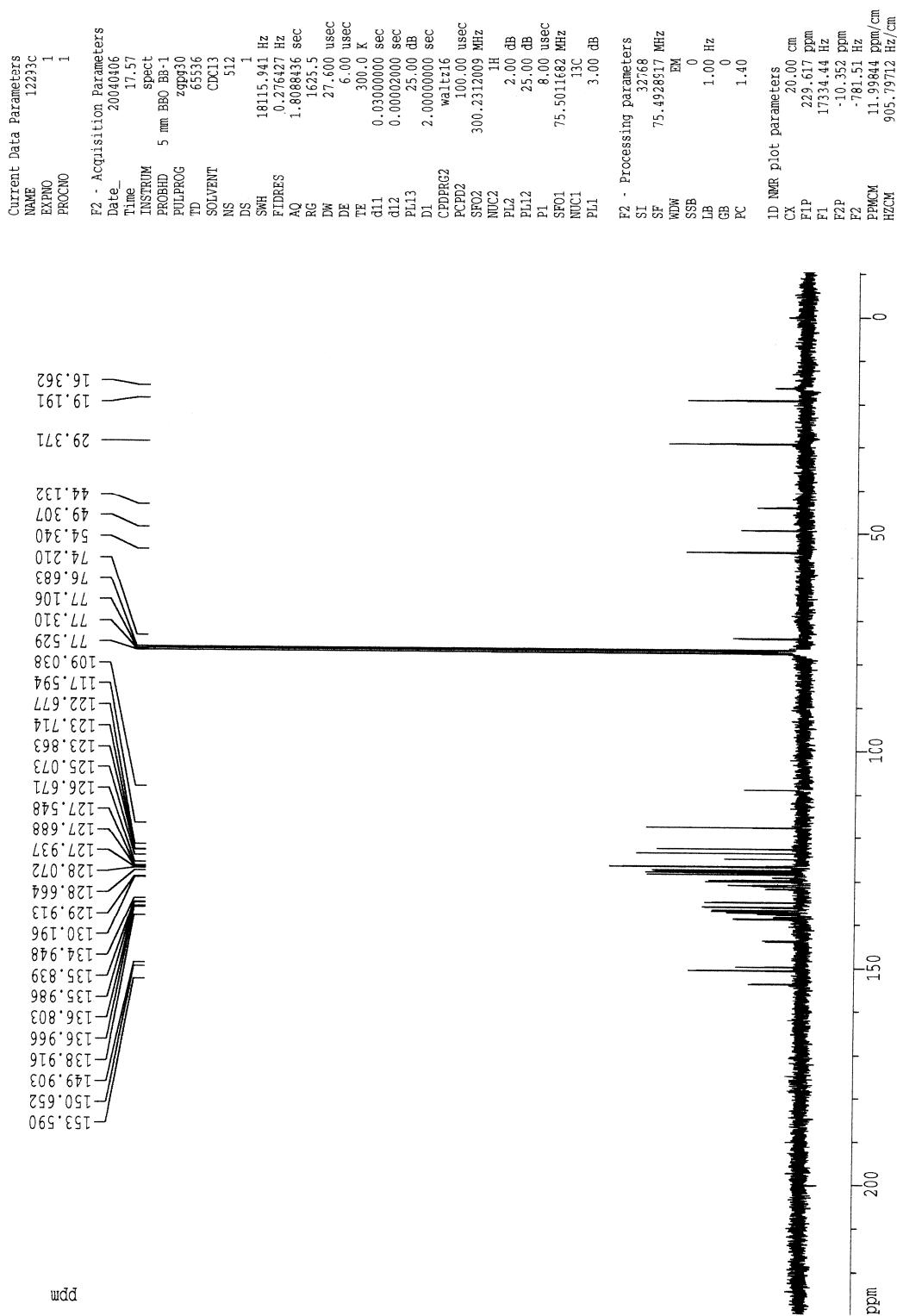
—33.2657—

ddd

<sup>1</sup>H NMR of (aS,S)-(+)-**11b**



<sup>13</sup>C NMR of (aS,S)-(+)-**11b**



<sup>31</sup>P NMR of (aS,S)-(+)-**11b**

Current Data Parameters  
NAME 122890  
EXPNO 1  
PROCNO 1

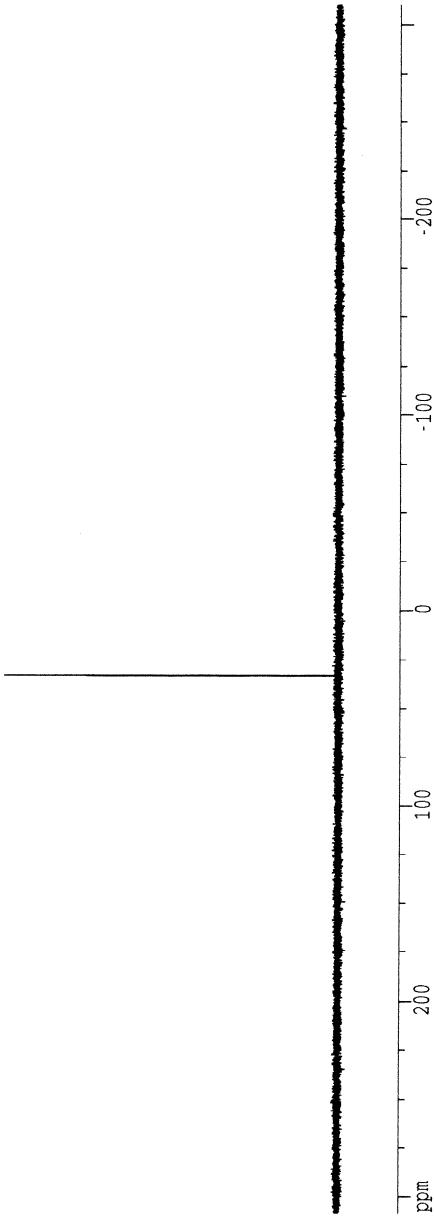
F2 - Acquisition Parameters

Date 2004/05/05  
Time 11:45  
INSTRUM spect  
PROBHD 5 mm BB0 BB-1  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 8  
DS 1  
SWH 75187.968 Hz  
FIDRES 1.141277 Hz  
AQ 0.455644 sec  
RG 2896.3  
DW 6.650 usec  
DE 6.00 usec  
TE 300.0 K  
d11 0.03000000 sec  
d12 0.00002000 sec  
PL13 25.00 dB  
D1 8.0000000 sec  
CPDPG2 w1,z16  
FCPD2 100.00 usec  
SFQ2 300.2312009 MHz  
NUC2 1H  
PL2 2.00 dB  
PL12 25.00 dB  
P1 8.00 usec  
SFQ1 121.5551820 MHz  
NUC1 31P  
PL1 3.00 dB

F2 - Processing parameters

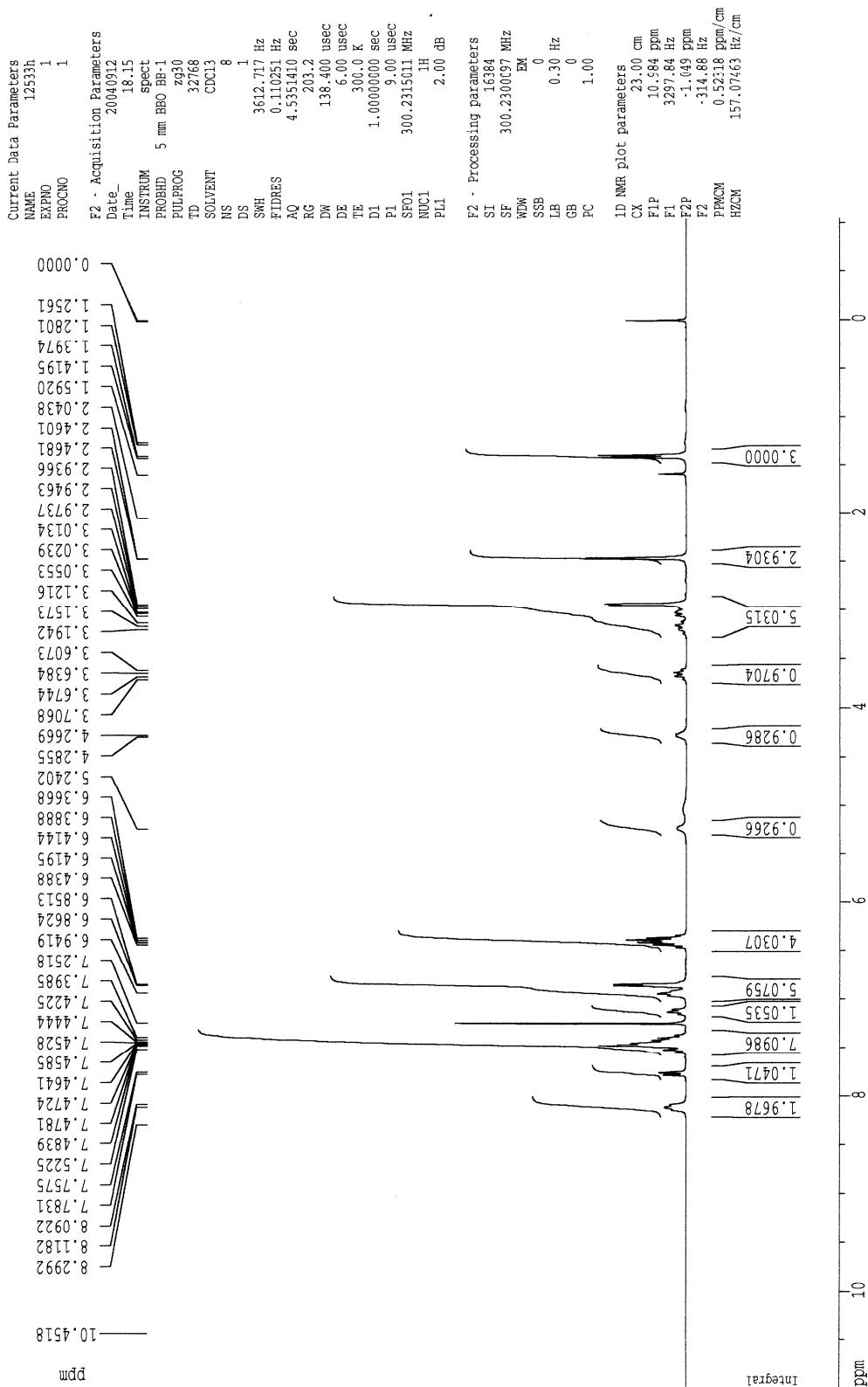
SI 32768  
SF 121.5552715 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.00

1D NMR plot parameters  
CX 21.00 cm  
F1P 308.589 ppm  
F1 3704.50 Hz  
F2P 0 Hz  
F2 -370.062 ppm  
F2 -3768.47 Hz  
PPCM 30.93257 ppm/cm  
HZCM 3759.39844 Hz/cm

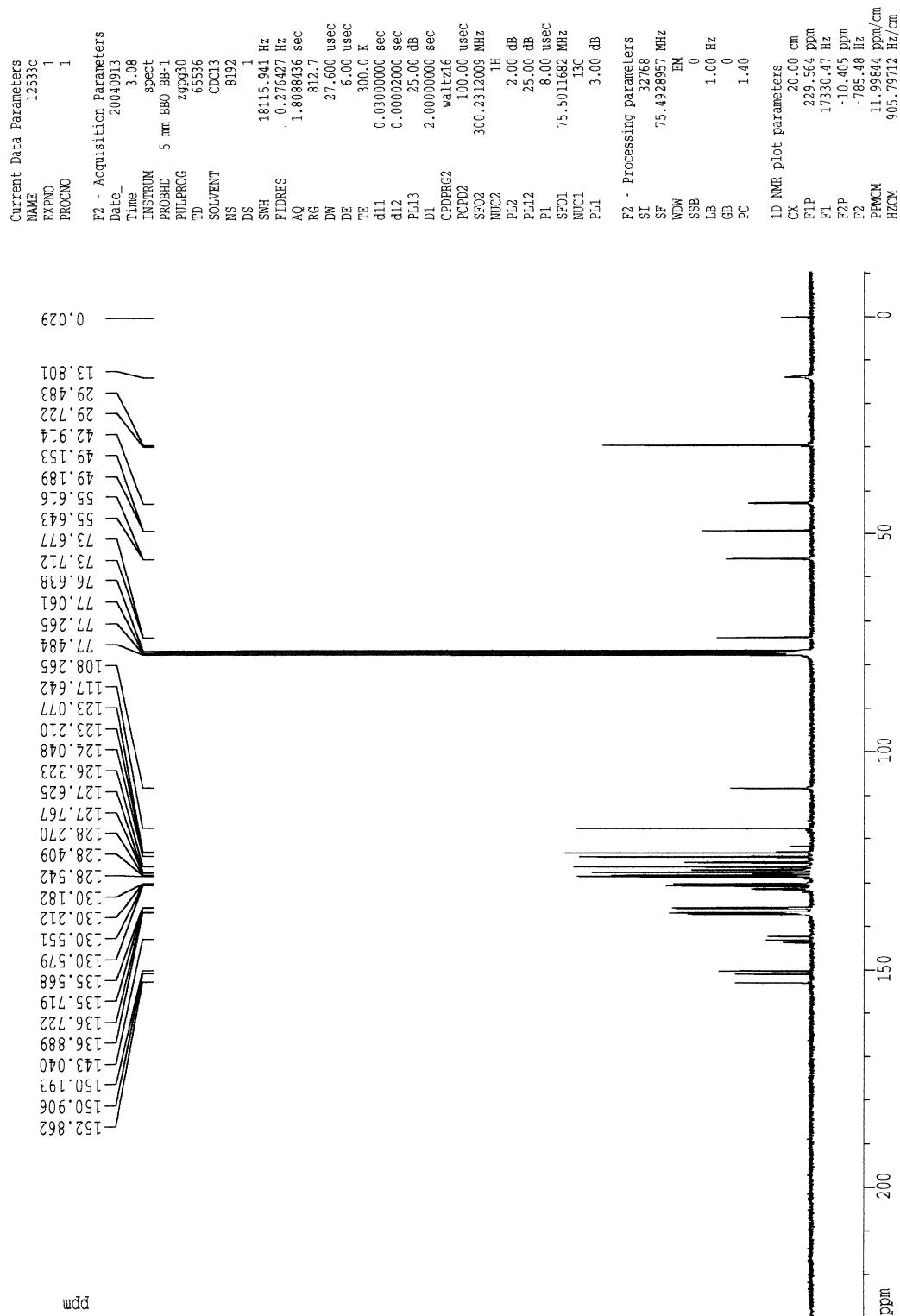


ddd

<sup>1</sup>H NMR of (aS,S)-(+)-11c



<sup>13</sup>C NMR of (aS,S)-(+)-**11c**



**<sup>31</sup>P NMR of (aS,S)-(+) -11c**

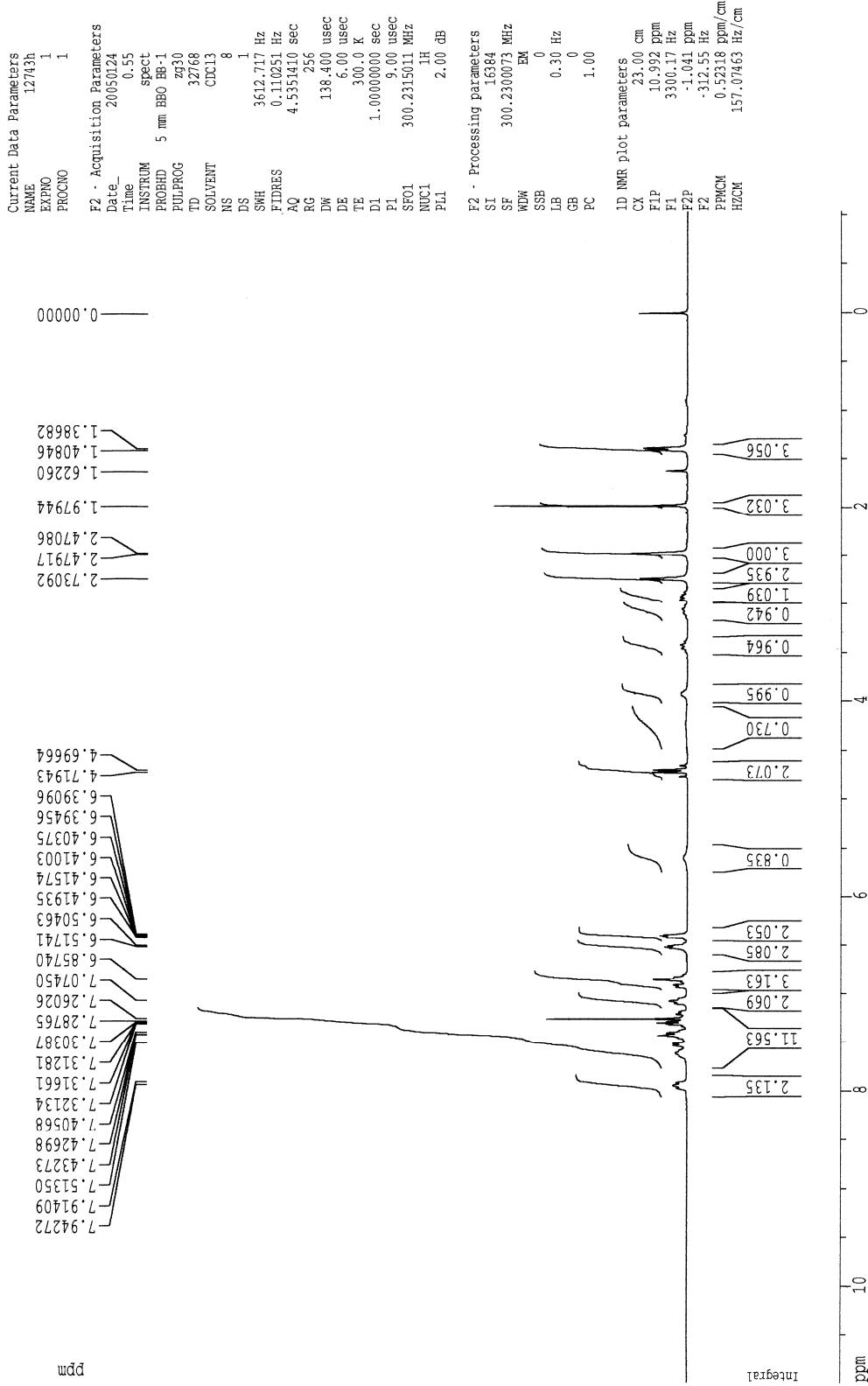
Current Data Parameters	
NAME	1533p
EXPNO	2
PROCNO	1
F2 - Acquisition Parameters	
Date_	20040912
Time	18.04
INSTRUM	spect
PROBHD	5 mm B30 BB-1
PULPROG	zprg30
TD	65536
SOLVENT	CDC13
NS	8
DS	1
SWH	75187.959 Hz
FLDRES	1.142377 Hz
AQ	0.4338644 sec
RG	2896.3
DW	6.650 usec
DE	6.00 usec
TE	300.0 K
dt1	0.0000000 sec
dt2	0.00002000 sec
PL1.3	25.00 dB
D1	8.0000000 sec
CPDPG2	Walzt16
CPDPD2	100.00 usec
SF02	300.2312009 MHz
NDC2	<sup>1</sup> H
PL1.2	2.00 dB
PL2	25.00 dB
PL	8.00 usec
SFO1	121.5351820 MHz
NDC1	<sup>31</sup> IP
PL1	3.00 dB
F2 - Processing parameters	
SI	32768
SF	121.5332715 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00
1D NMR plot parameters	
CX	20.00 cm
F1P	308.569 ppm
F1	37504.50 Hz
F2P	-310.062 ppm
F2	-37683.47 Hz
PPCM	30.93257 ppm/cm
HZCM	3759.39844 Hz/cm



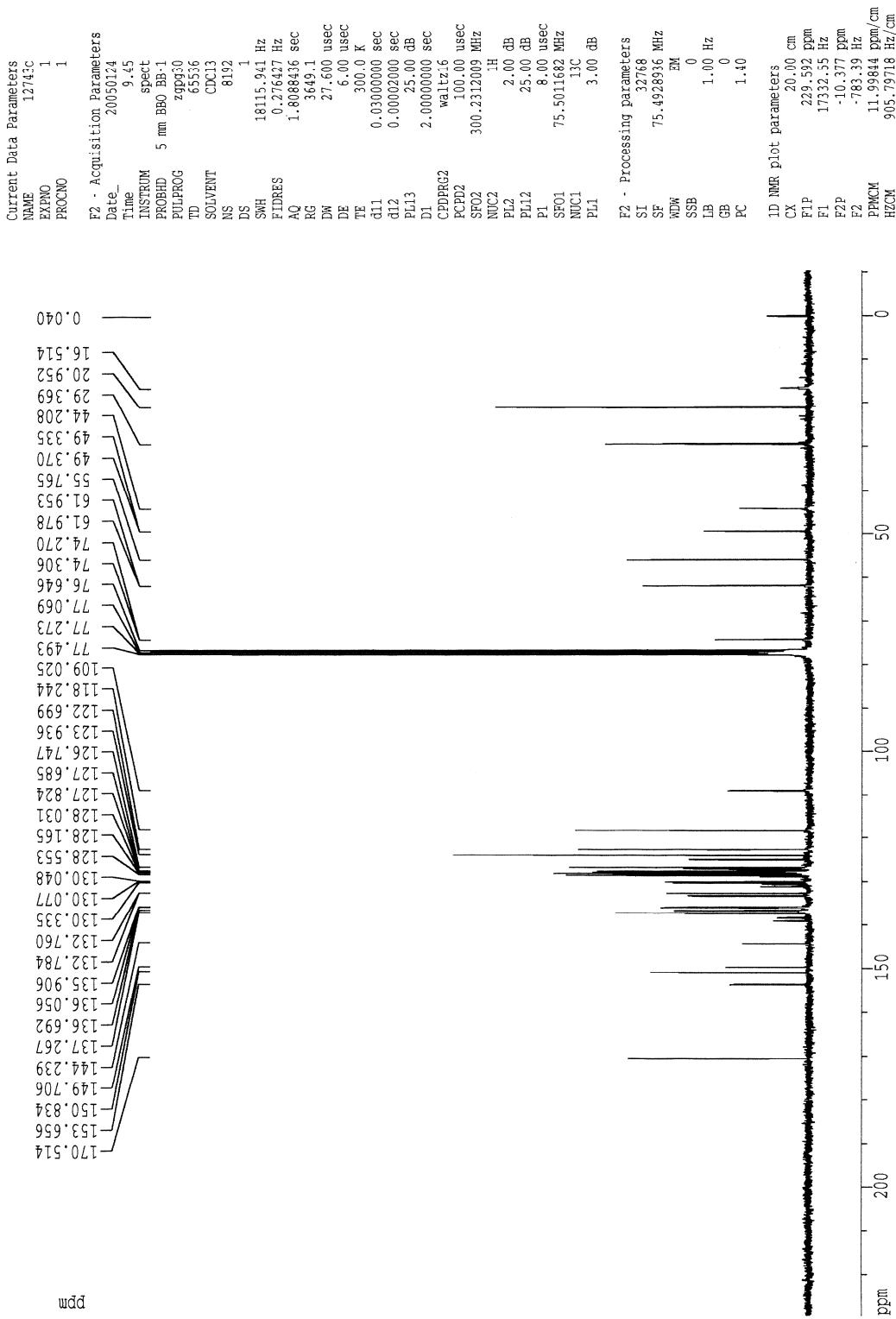
—33,9248

ddd

<sup>1</sup>H NMR of (aS,S)-(+)-**11d**



<sup>13</sup>C NMR of (aS,S)-(+)-**11d**



**<sup>31</sup>P NMR of (aS,S)-(+)-11d**

Current Data Parameters  
NAME 12280P  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters

Date 20040331  
Time 15.53  
INSTRUM spect  
PROBHD 5 mm BBO BB-1  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 8  
DS 1  
SWH 75187.968 Hz  
FIDRES 1.147277 Hz  
AQ 0.455644 sec  
RG 2856.3  
DW 6.650 usec  
DE 5.00 usec  
TE 300.0 K  
d1 0.03000000 sec  
d11 0.00002000 sec  
d12 0.00002000 sec  
PL13 25.00 dB  
D1 8.0000000 sec  
CPDPRG2 waltz16  
PCPD2 100.00 usec  
SF02 300.231209 MHz  
NUC2 1H  
PL2 2.00 dB  
PL12 25.00 dB  
P1 8.00 usec  
SF01 121.5551820 MHz  
NUC1 31P  
PL1 3.00 dB

F2 - Processing parameters

SI 32768  
SF 121.5552715 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.00

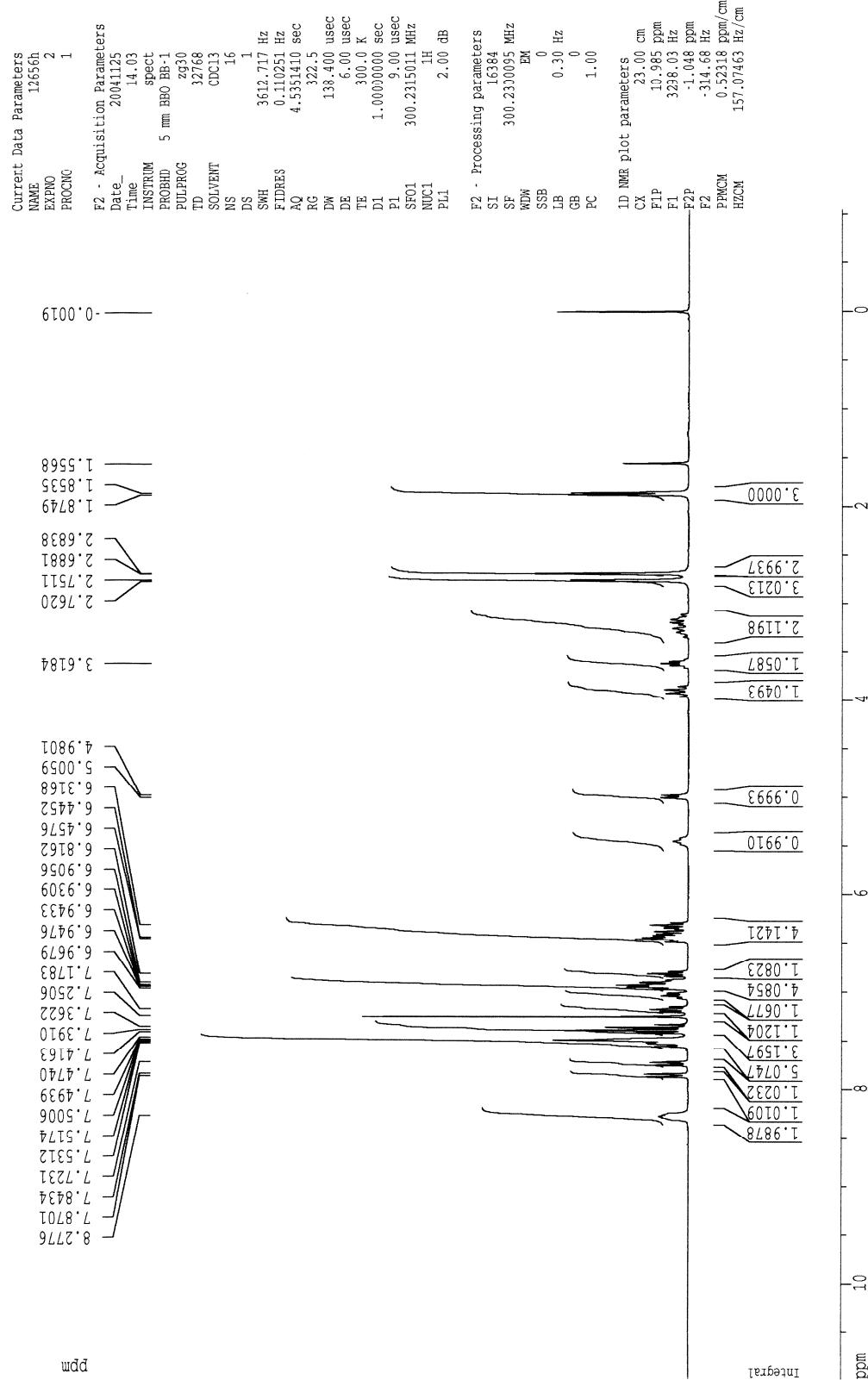
1D NMR Dplot parameters

CX 20.00 cm  
F1P 308.589 ppm  
F1 37504.50 Hz  
F2P 0  
F2 -310.062 ppm  
F2 -37683.47 Hz  
PPCM 30.91257 ppm/cm  
HZCM 3759.39844 Hz/cm

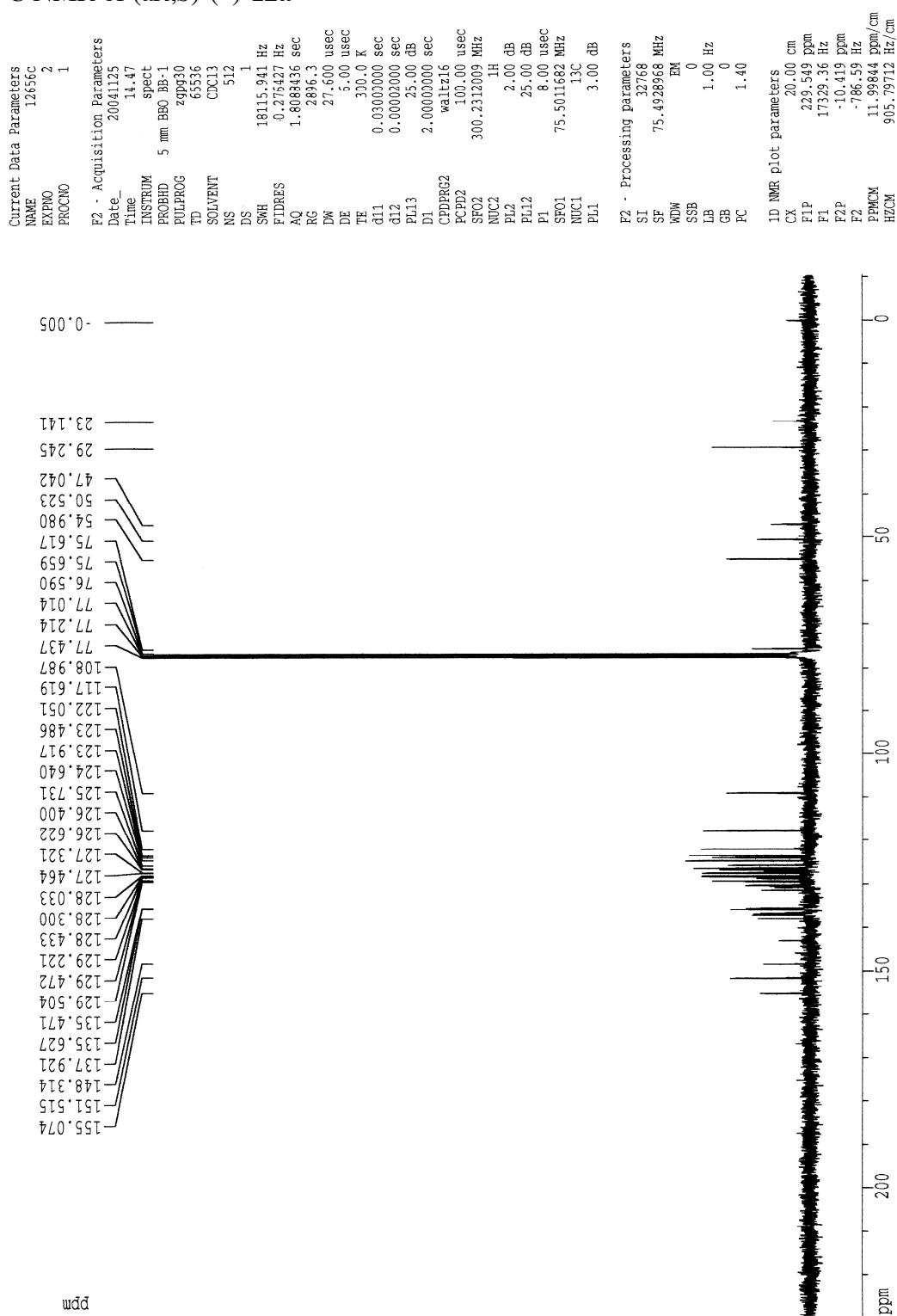


ddd

<sup>1</sup>H NMR of (aR,S)-(-)-**12a**



<sup>13</sup>C NMR of (aR,S)-(-)-**12a**



<sup>31</sup>P NMR of (aR,S)-(-)-**12a**

Current Data Parameters

NAME	12657p
EXPT0	1
PROCNO	1

F2 - Acquisition Parameters

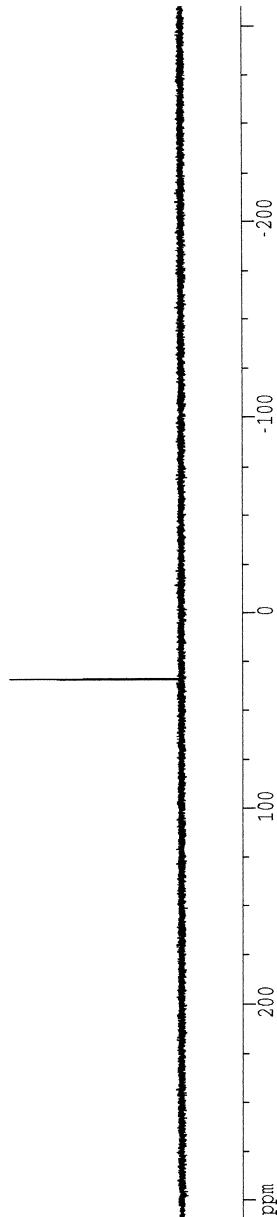
date	20041122
time	13.10
INSTRUM	spect
PROBHD	5 mm BBO BB-1
FULLPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	8
DS	1
SWH	75187.969 Hz
FIDRES	1.147277 Hz
AQ	0.4398344 sec
RG	3649.1
DW	6.750 usec
DE	6.00 usec
TE	300.0 K
d11	0.03000000 sec
d12	0.00002000 sec
PL13	25.00 dB
D1	8.0000000 sec
CPDRG2	wait:16
PCPD2	100.00 usec
SP02	300.2312009 MHz
NUC2	1H
PL2	2.00 dB
PL12	25.00 dB
P1	8.00 usec
SP01	121.5351820 MHz
NUC1	31P
PL1	3.00 dB

F2 - Processing parameters

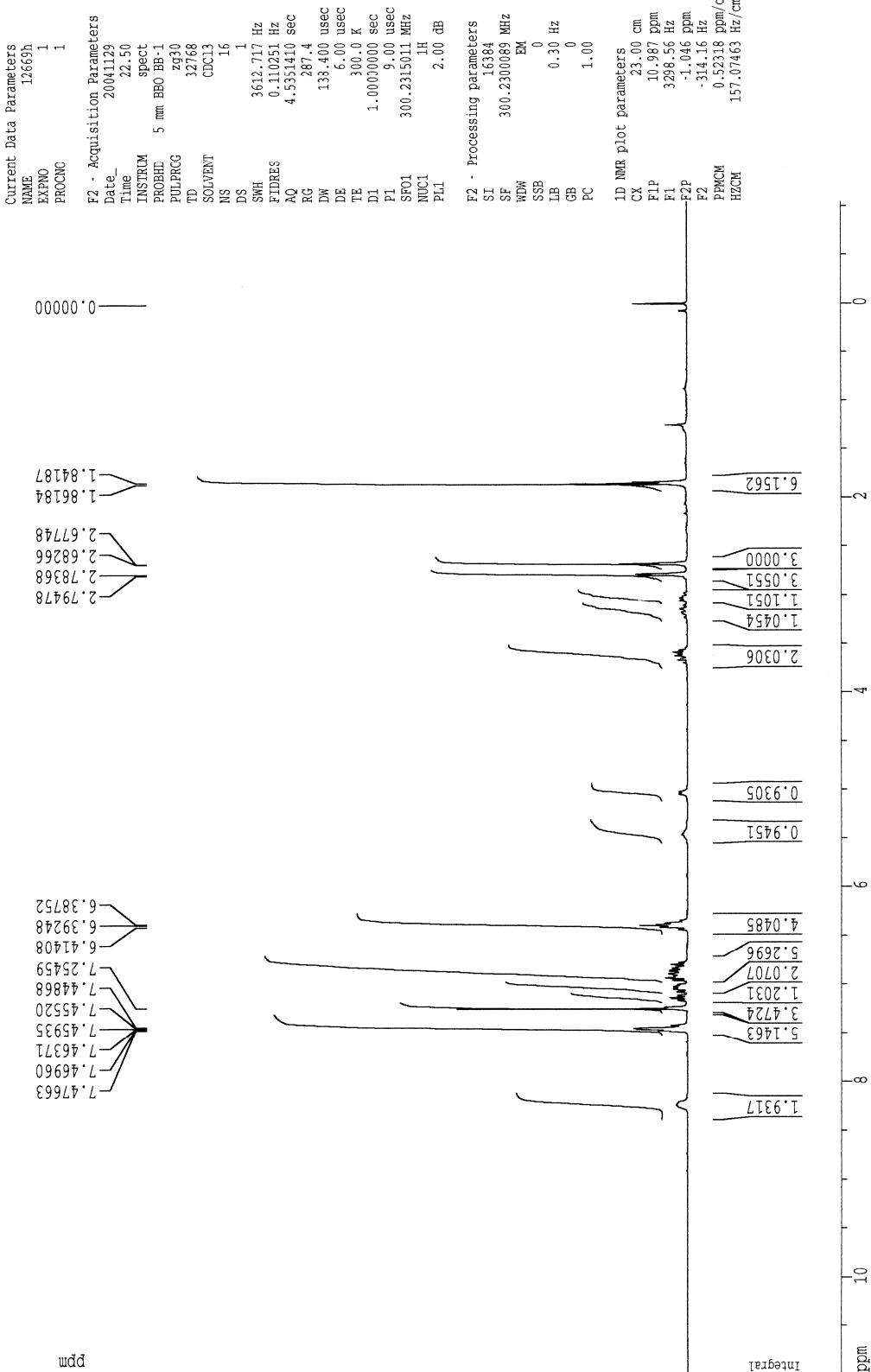
SI	32768
SF	121.5332715 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

—34.4070

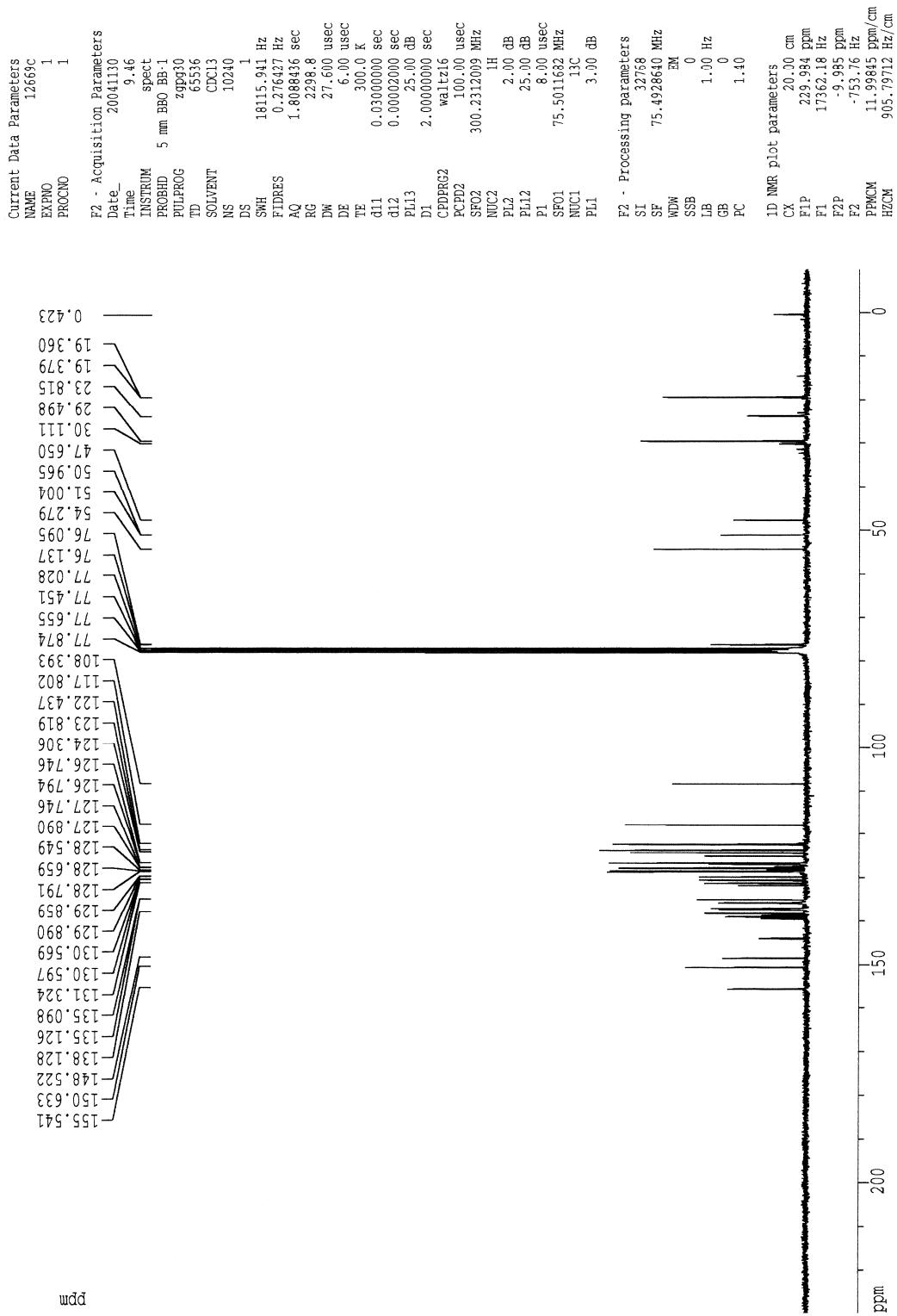
ddd



<sup>1</sup>H NMR of (aR,S)-(-)-12b



<sup>13</sup>C NMR of (aR,S)-(-)-**12b**



<sup>31</sup>P NMR of (aR,S)-(-)-**12b**

Current Data Parameters  
NAME 12295p  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters

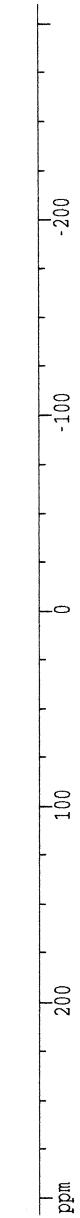
Date 20140407  
Time 18:04  
INSTRUM spect  
PROBHD 5 mm BBO BB-1  
PULPROG zgpp30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 8  
DS 1  
SWH 7518.969 Hz  
FIDRES 1.14727 Hz  
AQ 0.43844 sec  
RG 3251  
DW 6.150 usec  
DE 6.00 usec  
TE 300.0 K  
d11 0.0300000 sec  
d12 0.0000200 sec  
PL13 25.00 dB  
D1 8.0000000 sec  
CPDPRG2 wait:16  
PCPD2 100.00 usec  
SP02 300.231209 MHz  
NUC2 1H  
PL2 2.00 dB  
PL12 25.00 dB  
P1 8.00 usec  
SP01 121.5351820 MHz  
NUC1 31P  
PL1 3.00 dB

F2 - Processing parameters

SI 32768  
SF 121.5352715 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.00

1D NMR plot parameters

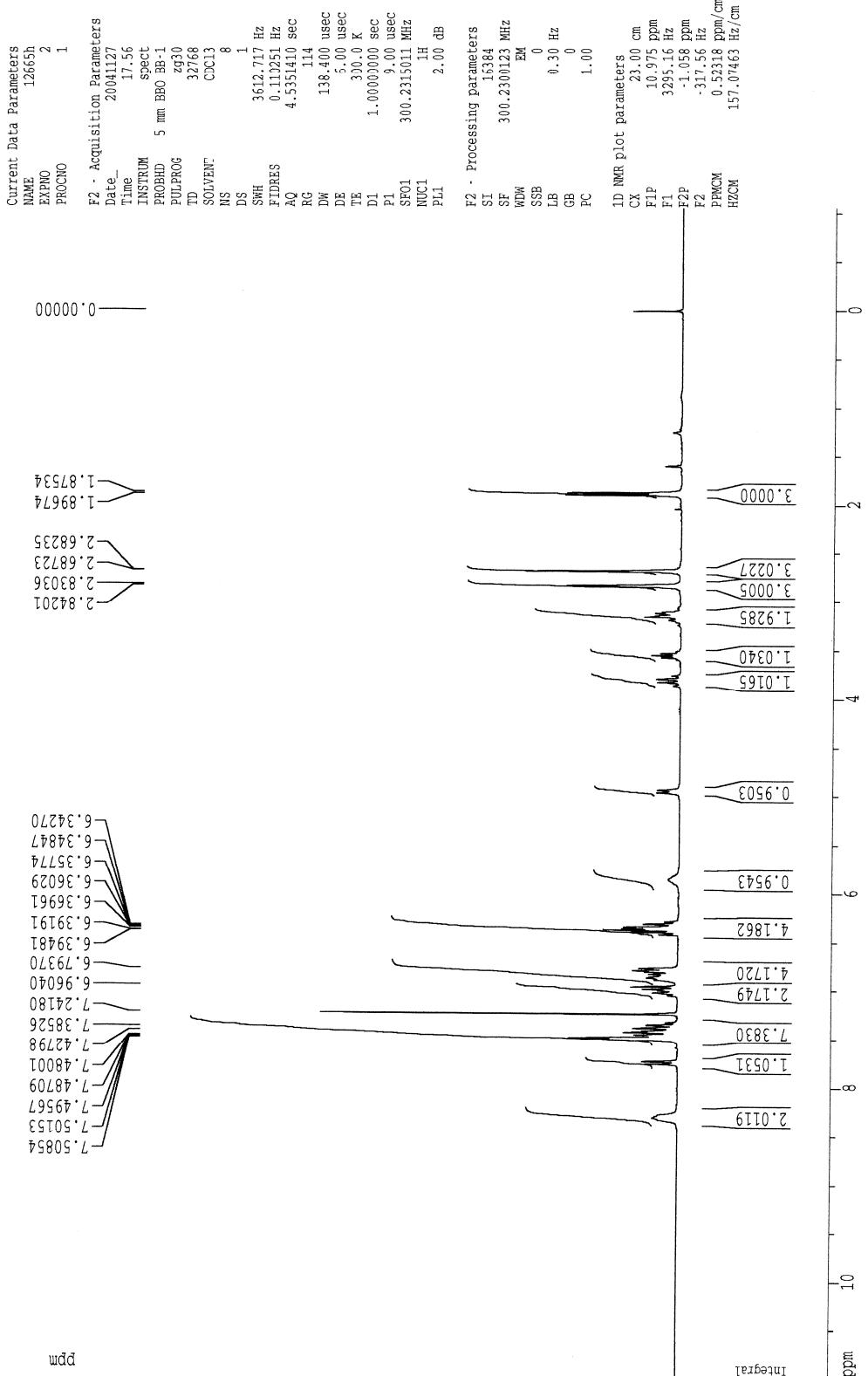
CX 20.00 cm  
F1P 308.569 ppm  
F1 37594.50 Hz  
F2P 0  
F2 -310.062 ppm  
F2 -31683.47 Hz  
PPM 30.33257 ppm/cm  
HZZM 37593.39844 Hz/cm



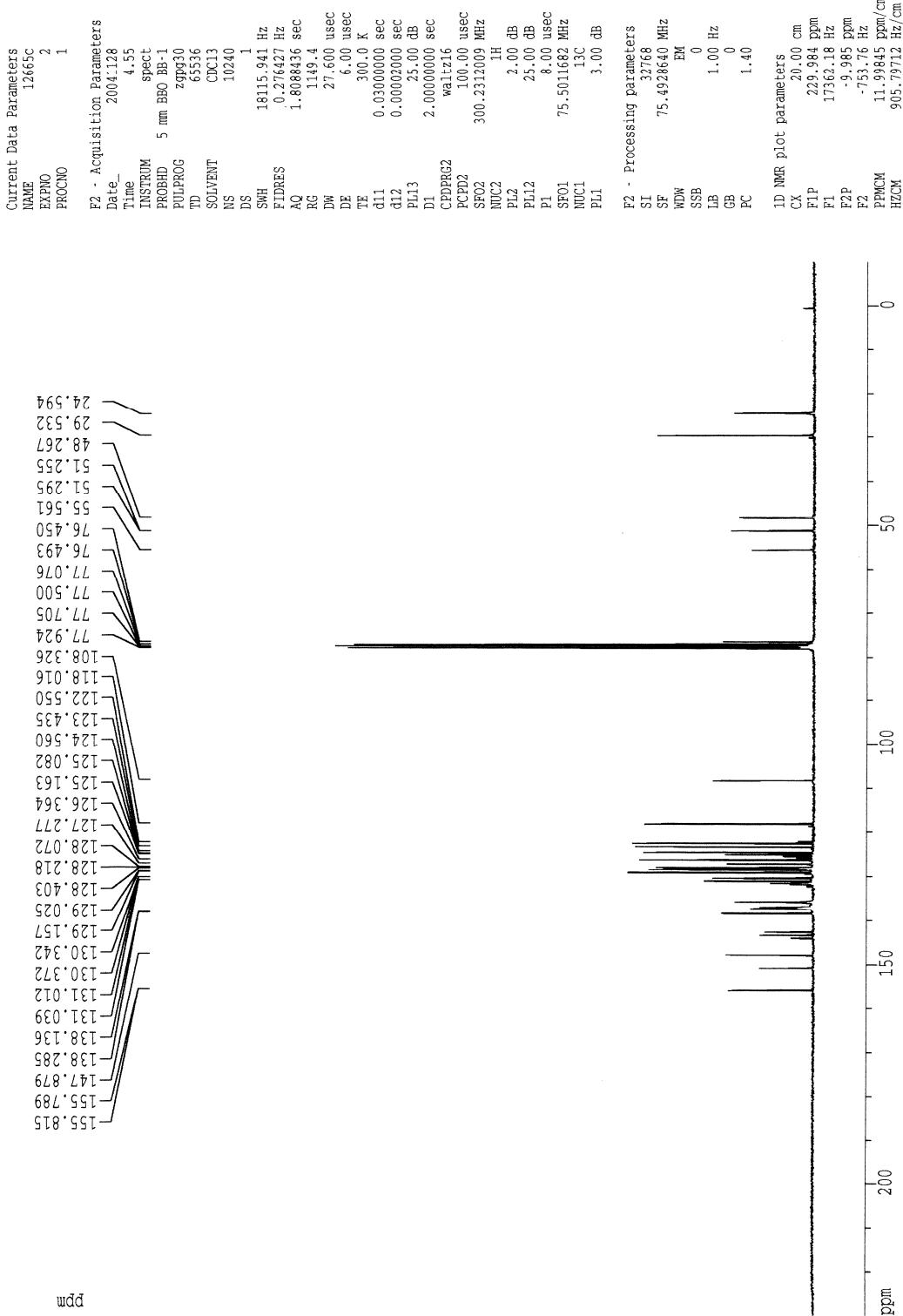
—34.0764—

ddd

<sup>1</sup>H NMR of (aR,S)-(-)-**12c**



<sup>13</sup>C NMR of (aR,S)-(-)-**12c**



<sup>31</sup>P NMR of (aR,S)-(-)-**12c**

Current Data Parameters

NAME	1263P
EXPTNO	1
PROCNO	1

F2 - Acquisition Parameters

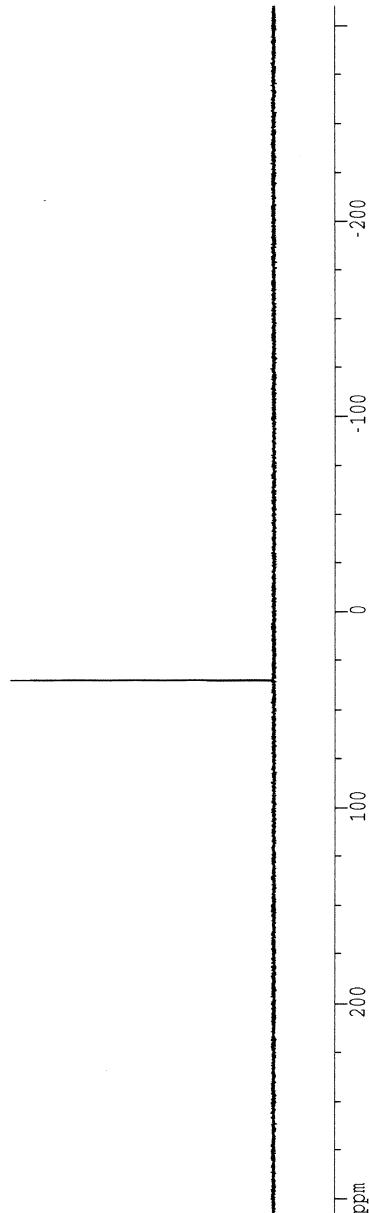
Date	2004/11/25
Time	22:56
INSTRUM	Spect
PROBID	5 mm BBO BB-1
PULPROG	zg3g30
TD	65536
SOVLENT	CDC13
NS	8
DS	1
SWH	75187.959 Hz
FIDRES	1.147277 Hz
AQ	0.435644 sec
RG	3699.1
DW	6.650 usec
DE	6.00 usec
TE	300.0 K
dt	0.0300000 sec
dd	0.0000200 sec
dl1	0.0000000 sec
dl2	0.0000000 sec
PL13	25.00 dB
D1	8.0000000 sec
CPDPR2	waltz16
PCPD2	100.00 usec
SF02	300.231203 MHz
NUC1	1H
NUC2	
PL2	2.00 dB
PL12	25.00 dB
P1	8.00 usec
SFO1	121.5354820 MHz
NUC1	31P
PL1	3.00 dB

F2 - Processing parameters

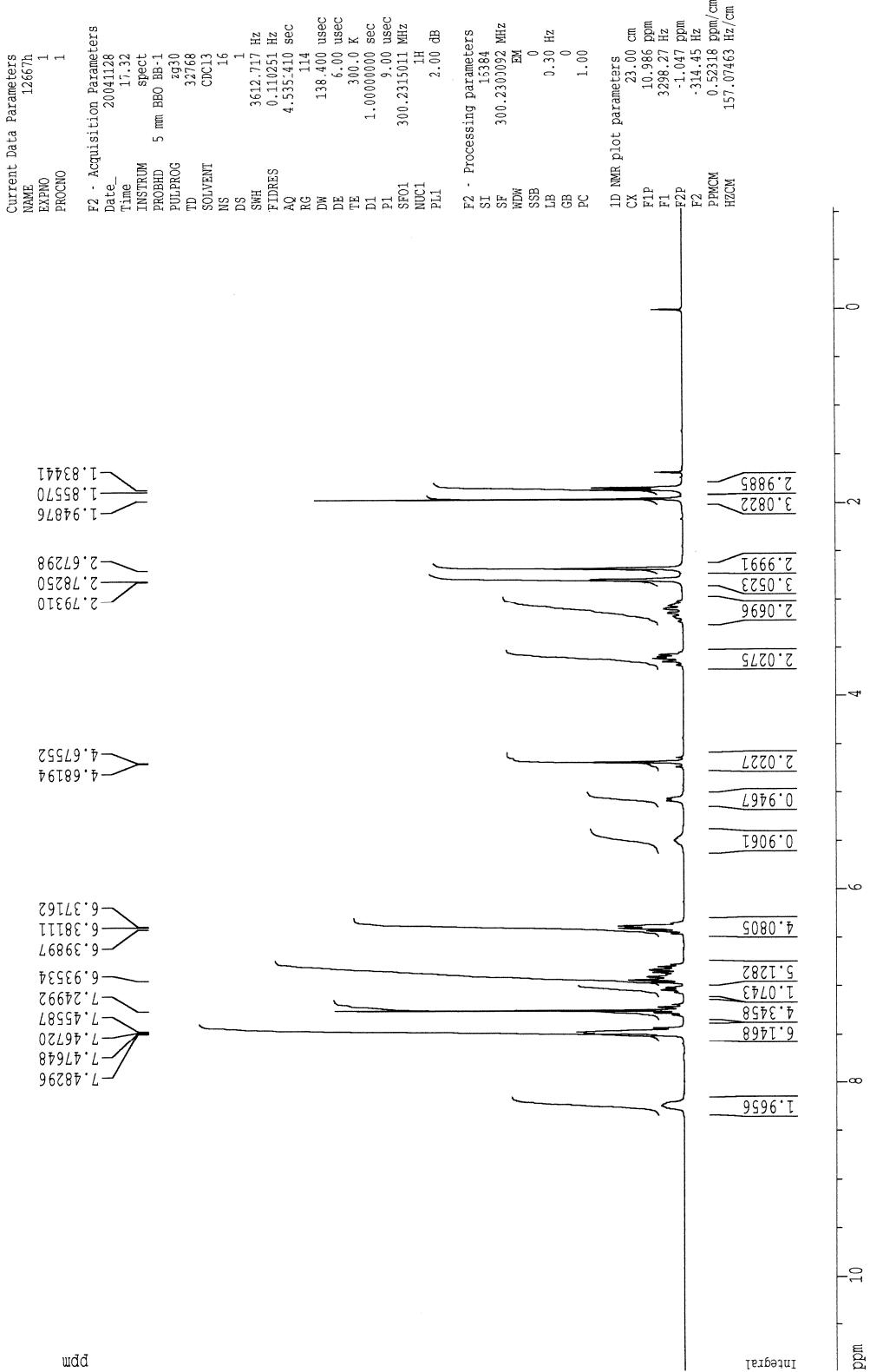
CX	20.00 cm
SI	32768
SF	121.5352715 MHz
NDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

—34.9260

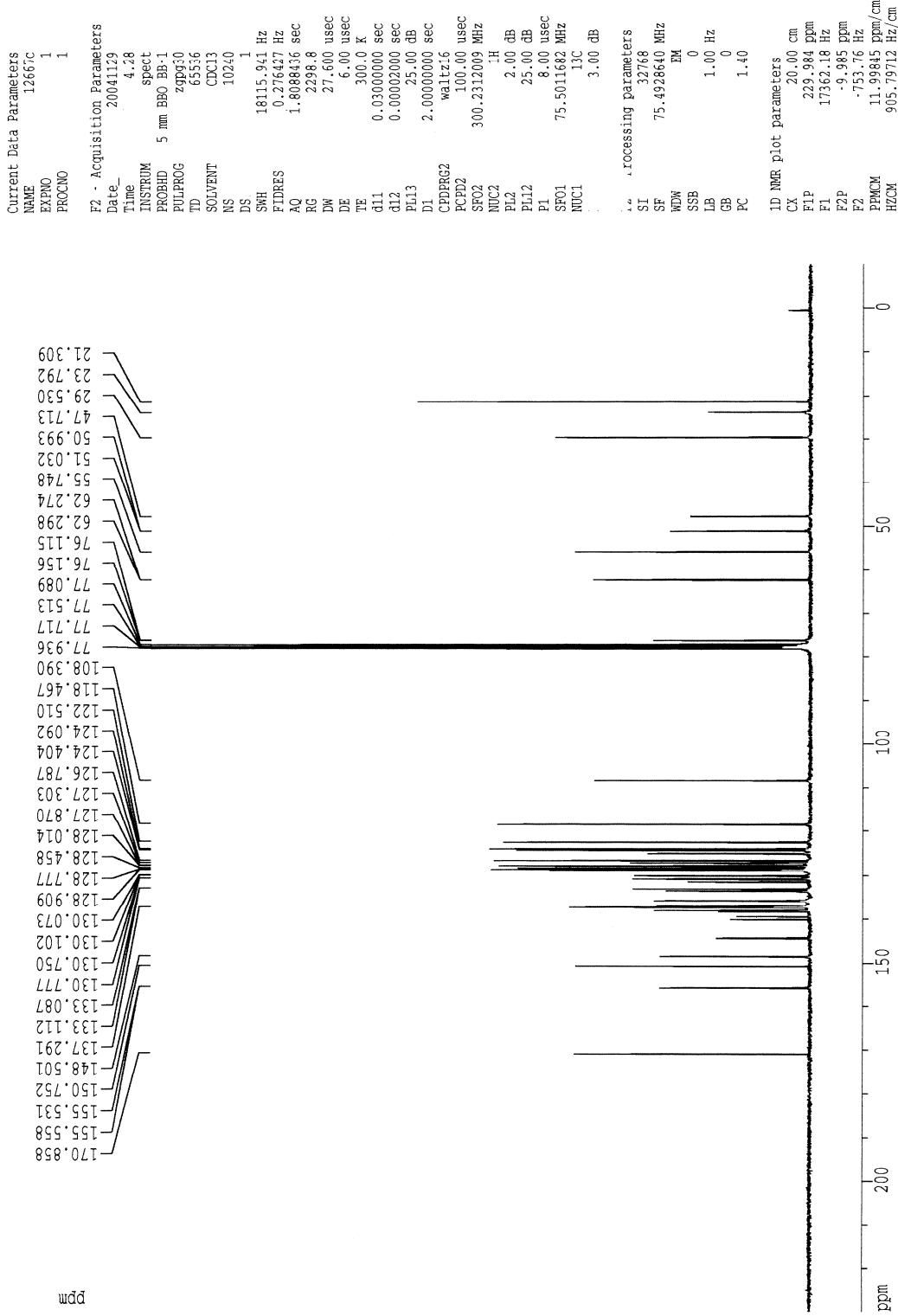
ddd



<sup>1</sup>H NMR of (aR,S)-(-)-**12d**



<sup>13</sup>C NMR of (aR,S)-(-)-**12d**

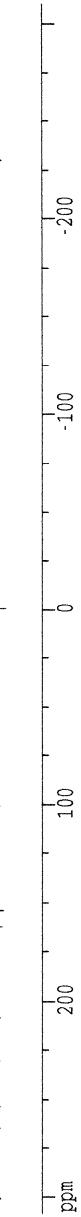


<sup>31</sup>P NMR of (aR,S)-(-)-**12d**

Current Data Parameters  
NAME 12281p  
EXPNO 1  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 2004/03/31  
Time\_ 16:13  
INSTRUM spect  
PROBID 5 mm BBO BB-1  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl<sub>3</sub>  
NS 32  
DS 1  
SWH 75187.969 Hz  
ETDRGS 1.147277 Hz  
AQ 0.435644 sec  
RG 2896.3  
DW 6.650 usec  
DE 6.00 usec  
TE 300.0 K  
d11 0.0300000 sec  
d12 0.0000000 sec  
PL13 0.0000000 sec  
D1 8.0000000 sec  
CPDPG2 waltz16  
PCPD2 100.00 usec  
SF02 300.231209 MHz  
NUC2 1H  
PL2 2.00 dB  
PL12 25.00 dB  
P1 8.00 usec  
SF01 121.5351820 MHz  
NUC1 31P  
PL1 3.00 dB

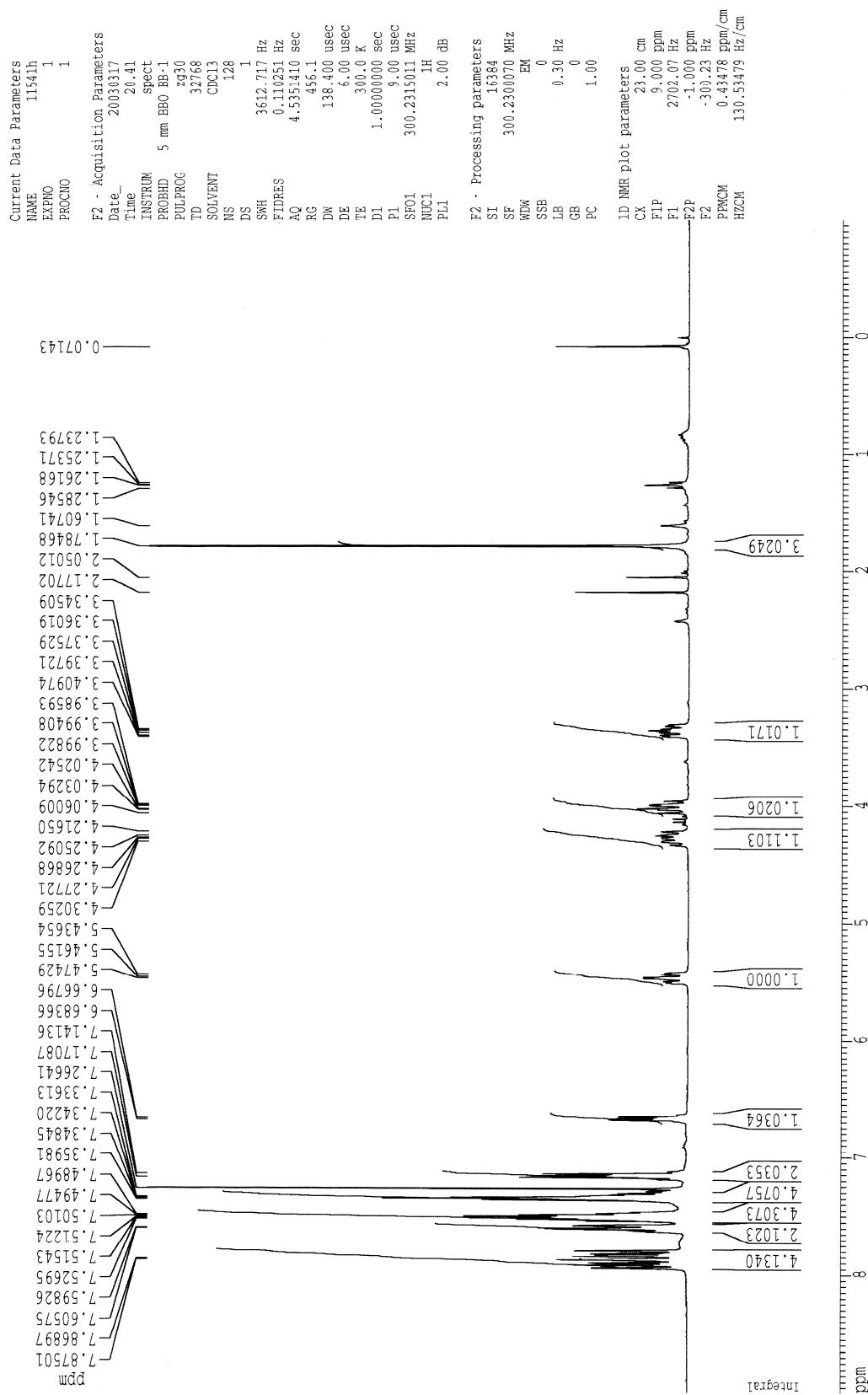
F2 - Processing parameters  
SI 32768  
SF 121.5352715 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.00  
  
1D NMR plot parameters  
CX 20.00 cm  
F1P 308.589 ppm  
F1 37504.50 Hz  
F2P -310.062 ppm  
F2 -37683.47 Hz  
PPCM 30.93257 ppm/cm  
HZCM 3759.33844 Hz/cm



34.1952

ddd

### <sup>1</sup>H NMR of ( $\pm$ )-13

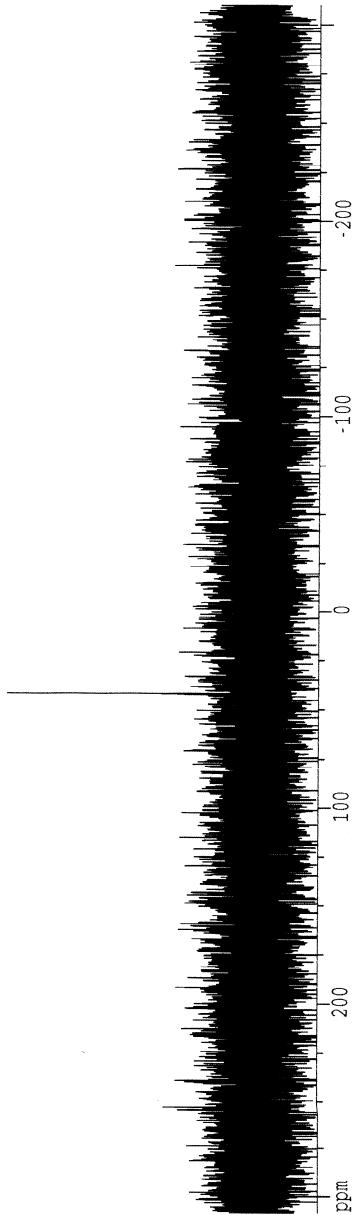


### <sup>31</sup>P NMR of (+)-13

Current Data Parameters  
NAME 1154p  
EXPNO 1  
PROCNO 1

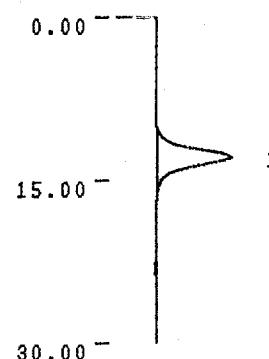
F2 - Acquisition Parameters  
Date\_ 20130313  
Time 21:27  
INSTRUM spect  
PROBHD 5 mm BBO BB-1  
PULPROG zgpp30  
TD 65336  
SOLVENT CDCl3  
NS 16  
DS 1  
SWH 75187.469 Hz  
FIDRES 1.147277 Hz  
AQ 0.43864 sec  
RG 3251  
DW 6.650 usec  
DE 6.00 usec  
TE 300.0 K  
d1 0.0300000 sec  
d11 0.0000200 sec  
d12 0.0000200 sec  
PL13 25.00 dB  
D1 8.000000 sec  
CPDRG2 waltz16  
FCPD2 100.00 usec  
SFO2 300.2312019 MHz  
NUC2 1H  
PL2 2.00 dB  
PL12 25.00 dB  
P1 8.00 usec  
SFO1 121.5351820 MHz  
NUC1 31P  
PL1 3.00 dB

F2 - Processing parameters  
SI 32768  
SF 121.5352715 MHz  
MW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.00



dd

Chiral phase HPLC chart of (aS)-(+)-**1a**



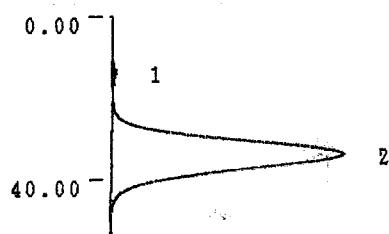
Conc.Level:0 Calc.Method:0(Area%) PA:1.00000 PB:1.00000

NO.	NAME	RT	AREA	MARK	CONC	HEIGHT
1		12.869	10165300		100.0000	90774
	TOTAL		10165300		100.0000	90774

>99%ee

Daicel CHIRALCEL® OJ (0.46  $\phi$  × 25 cm, hexane : ethanol = 90 : 10, 0.50 mL/min, UV 254 nm)

Chiral phase HPLC chart of (aR)-(-)-**1a**



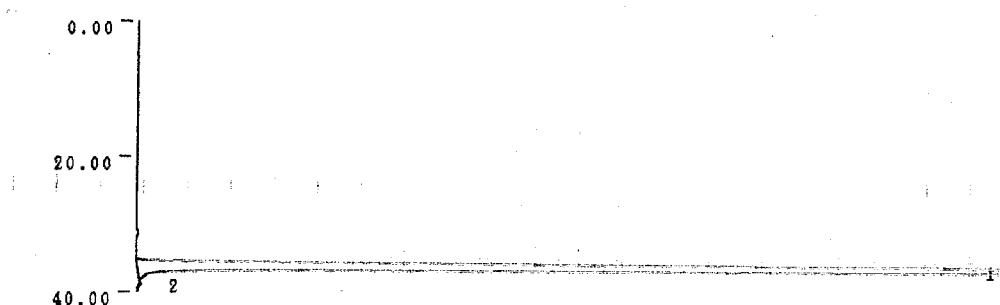
Conc.Level:0 Calc.Method:0(Area%) PA:1.00000 PB:1.00000

NO.	NAME	RT	AREA	MARK	CONC	HEIGHT
1		13.792	158391		0.4309	896
2		33.952	36597200		99.5690	70933
	TOTAL		36755591		100.0000	71829

99.1%ee

Daicel CHIRALCEL® OJ (0.46  $\phi$  × 25 cm, hexane : ethanol = 90 : 10, 0.50 mL/min, UV 254 nm)

Chiral phase HPLC chart of (aS)-(+)-**1b**

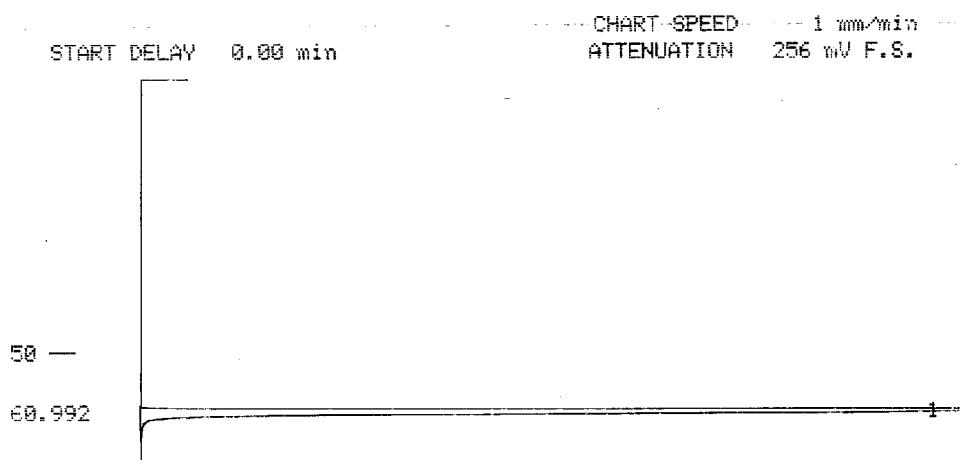


Conc.Level:0	Calc.Method:0(Area%)	PA:1.00000	PB:1.00000			
NO.	NAME	RT	AREA	MARK	CONC	HEIGHT
1		35.962	47614500		99.9559	1356132
2		38.810	20969		0.0440	700
TOTAL			47635469		100.0000	1356832

>99%ee

Daicel CHIRALPAK® AD-H × 2 (0.46  $\phi$  × 25 cm × 2, hexane : ethanol = 99.7 : 0.3, 0.25 mL/min, UV 254 nm)

Chiral phase HPLC chart of (aR)-(-)-**1b**



-- % CALCULATION RESULT --

TEST DATA

WINDOW = 0 %	SCALE FACTOR = 1.0000	PEAK AREA			
PEAK#	RT(min)	AREA	HEIGHT	MK	AREAX%
1	60.992	19486453	444199		100.0000
TOTAL		19486453	444199		100.0000

>99%ee

Daicel CHIRALPAK® AD-H × 2 (0.46  $\phi$  × 25 cm × 2, hexane : ethanol = 99.7 : 0.3, 0.15 mL/min, UV 254 nm)

Chiral phase HPLC chart of (aS)-(-)-**1c**



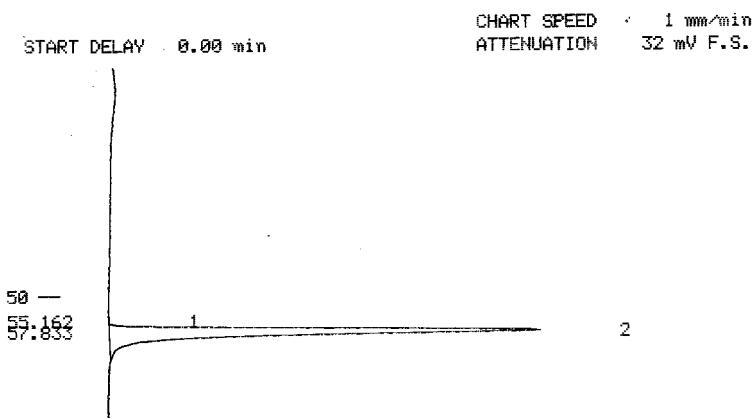
Conc.Level:0 Calc.Method:0(Area%) PA:1.00000 PB:1.00000

NO.	NAME	RT	AREA	MARK	CONC	HEIGHT
1		32.144	35339400		100.0000	658496
	TOTAL		35339400		100.0000	658496

>99%ee

Daicel CHIRALPAK® AD-H × 2 (0.46  $\phi$  × 25 cm × 2, hexane : ethanol = 99.7 : 0.3, 0.25 mL/min, UV 254 nm)

Chiral phase HPLC chart of (aR)-(+)-**1c**



-- % CALCULATION RESULT --

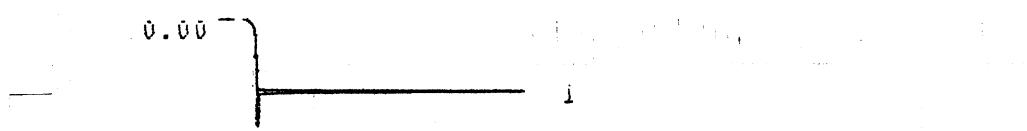
TEST-DATA

WINDOW	SCALE FACTOR	PEAK AREA			
PEAK#	RT(min)	AREA	HEIGHT	MK	AREA%
1	55.162	748	19		3.9630E-02
2	57.833	1886377	18233		99.9604
TOTAL		1887125	18252		100.0000

>99%ee

Daicel CHIRALPAK® AD-H × 2 (0.46  $\phi$  × 25 cm × 2, hexane : ethanol = 99.7 : 0.3, 0.15 mL/min, UV 254 nm)

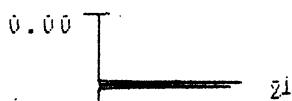
Chiral phase HPLC chart of (aS)-(-)-**1d**



Conc.Level:0 Calc.Method:0(Area%) PA:1.00000 PB:1.00000

NO.	NAME	RT	AREA	MARK	CONC	HEIGHT
1		15.317	2904540		100.0000	137200
	TOTAL		2904540		100.0000	137200

>99%ee



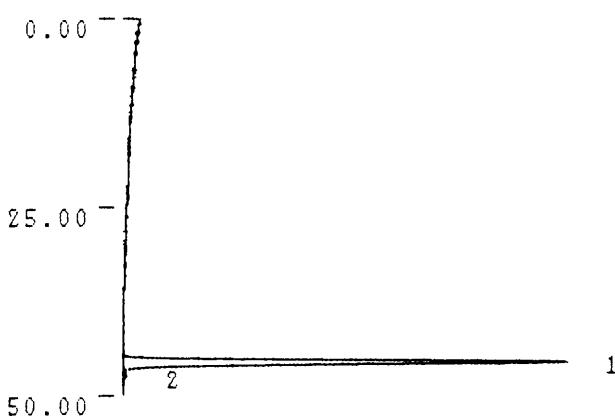
Conc.Level:0 Calc.Method:0(Area%) PA:1.00000 PB:1.00000

NO.	NAME	RT	AREA	MARK	CONC	HEIGHT
1		14.485	1406530		50.5419	72906
2		15.386	1376370		49.4581	66864
	TOTAL		2782900		100.0000	139770

(±)-**1d**

Daicel CHIRALCEL® OD (0.46  $\phi$  × 25 cm, hexane : ethanol = 99 : 1, 0.40 mL/min, UV 254 nm)

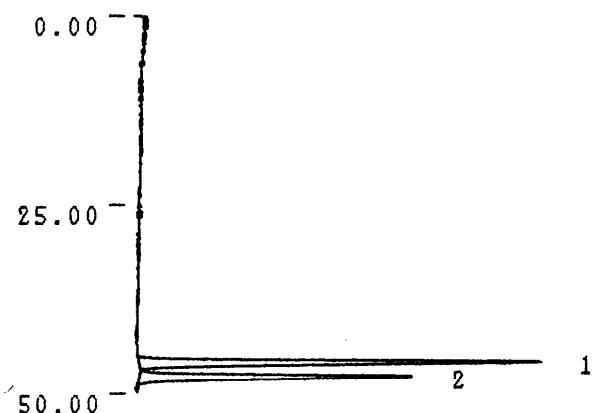
Chiral phase HPLC chart of (aR)-(+)-**1d**



Conc.Level:0 Calc.Method:0(Area%) PA:1.00000 PB:1.00000

NO.	NAME	RT	AREA	MARK	CONC	HEIGHT
1		45.472	2372450		99.5991	58361
2		47.408	9548		0.4008	243
	TOTAL		2381998		100.0000	58604

99.2%ee



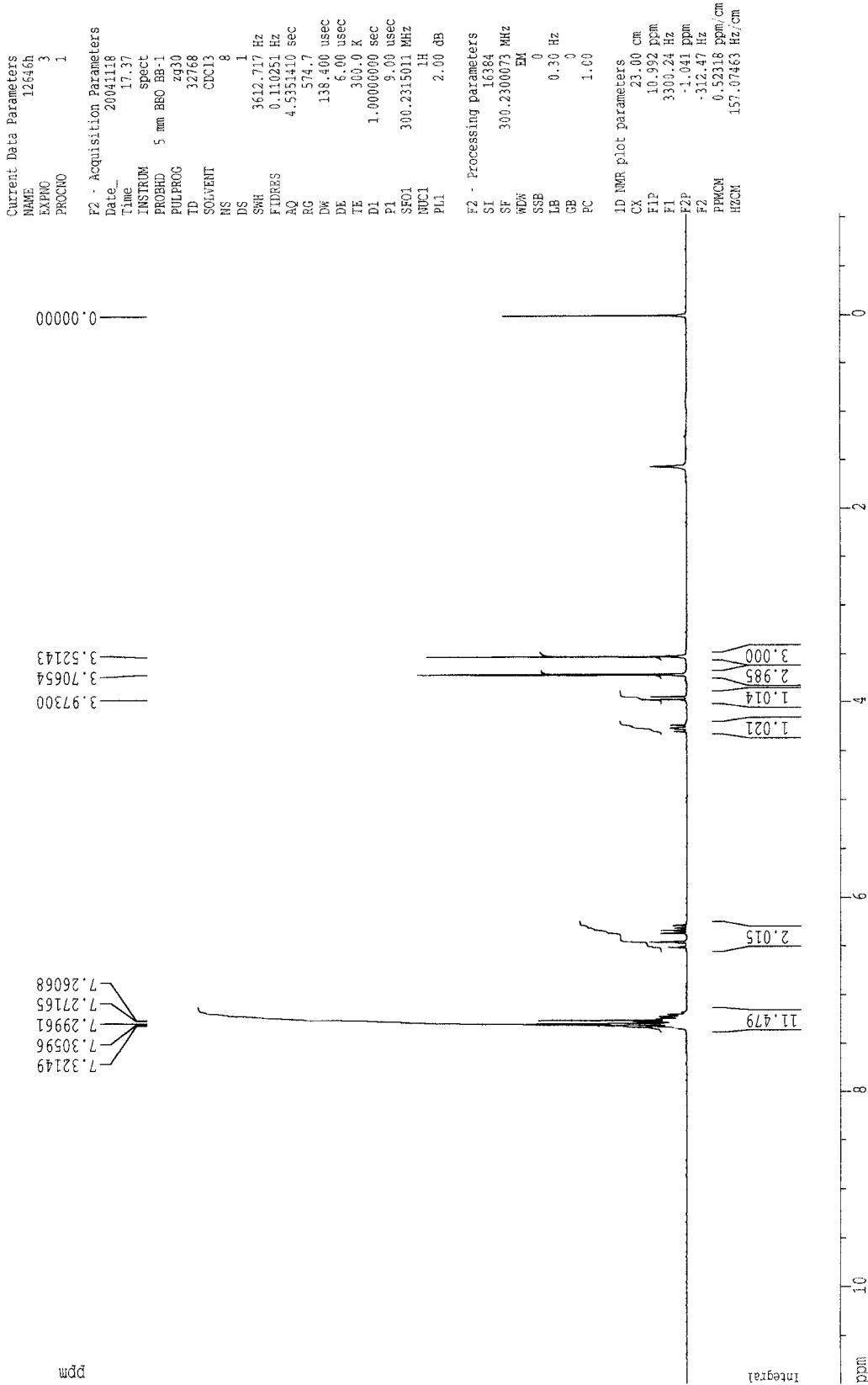
Conc.Level:0 Calc.Method:0(Area%) PA:1.00000 PB:1.00000

NO.	NAME	RT	AREA	MARK	CONC	HEIGHT
1		45.824	2113320		58.4558	52665
2		47.818	1501920		41.5441	35708
	TOTAL		3615240		100.0000	88373

(±)-**1d**

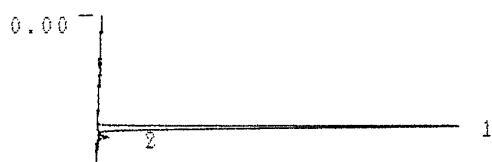
Daicel CHIRALCEL® OD+OD-H (0.46  $\phi$  × 25 cm × 2, hexane : ethanol = 99 : 1, 0.25 mL/min, UV 254 nm)

<sup>1</sup>H NMR of (*R*)-**16**



Chiral phase HPLC chart of (*R*)-**16** (Table 1, entry 4)

Name:123            08:07 OCT. 21, 2004    Sample:027    ATTN:32    POS1:0



ono.Level:0 Calc.Method:0(Area%) PA:1.00000 PB:1.00000

D.	NAME	RT	AREA	MARK	CONC	HEIGHT
1		25.744	3963330		97.5914	98528
2		28.005	37813		2.4085	2785

95% ee

Daicel CHIRALCEL® OD-H (0.46  $\phi$   $\times$  25 cm, hexane : *i*-PrOH = 99 : 1, 0.40 mL/min, UV 254 nm).