Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Synthesis and Properties of 1-(3-Dihydroxyboryl-2,3-dideoxyribosyl)pyrimidines"

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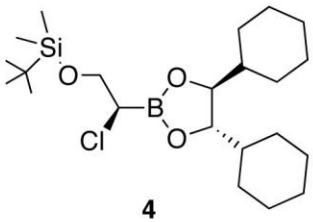
Supporting Information

NMR spectra (in $CDCl_3$ if not otherwise specified); plots of cytotoxicity data and degradation of β-14b and β-14c.



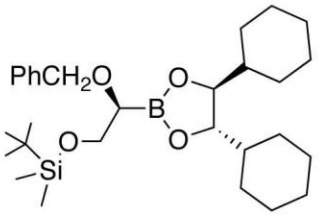
4

300-MHz ^{1}H-NMR ($CDCl_3$)

Purified TBSOCH2CHOBnB S,S'-DICH
ED

expl s2pul

SAMPLE		SPECIAL	
date	Dec 3 2008	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	3602.3	pw90	9.800
at	1.998	alfa	20.000
np	14394	FLAGS	
fb	not used	il	n
bs	16	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		fn	not used
tn	H1	DISPLAY	
sfrq	300.144	sp	-300.4
tof	1.3	wp	3602.3
tpwr	57	rfl	300.4
pw	4.900	rfp	0
DECOUPLER		rp	45.9
dn	C13	lp	-49.9
dof	0	PLOT	
dm	nnn	wc	250
dmm	c	sc	0
dpwr	39	vs	82
dmf	13100	th	14
		ai cdc ph	



5

300-MHz ^{1}H-NMR ($CDCl_3$)

Benzyloxy boronate 13C

exp3 s2pul

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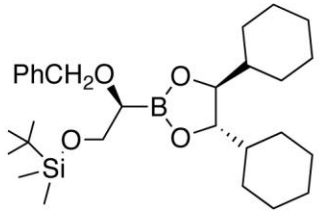
date	Jun 18 2009	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	18867.9	pw90	9.700
at	1.815	alfa	20.000
np	68492	FLAGS	
fb	10400	il	n
bs	16	in	n
d1	1.000	dp	y
nt	20000	hs	nn
ct	13328	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	not used
sfrq	75.479	DISPLAY	
tof	737.5	sp	-1106.8
tpwr	57	wp	13560.4
pw	4.850	rfl	6963.0
DECOUPLER		rfp	5828.6
dn	H1	rp	51.0
dof	0	lp	-250.7
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	37	sc	0
dmf	9100	vs	134
		th	6
		nm no ph	



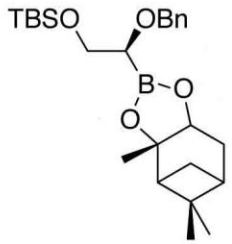
5

75-MHz ^{13}C-NMR ($CDCl_3$)

Transesterified
TBSOCH2CHOBn pinanediol boronate

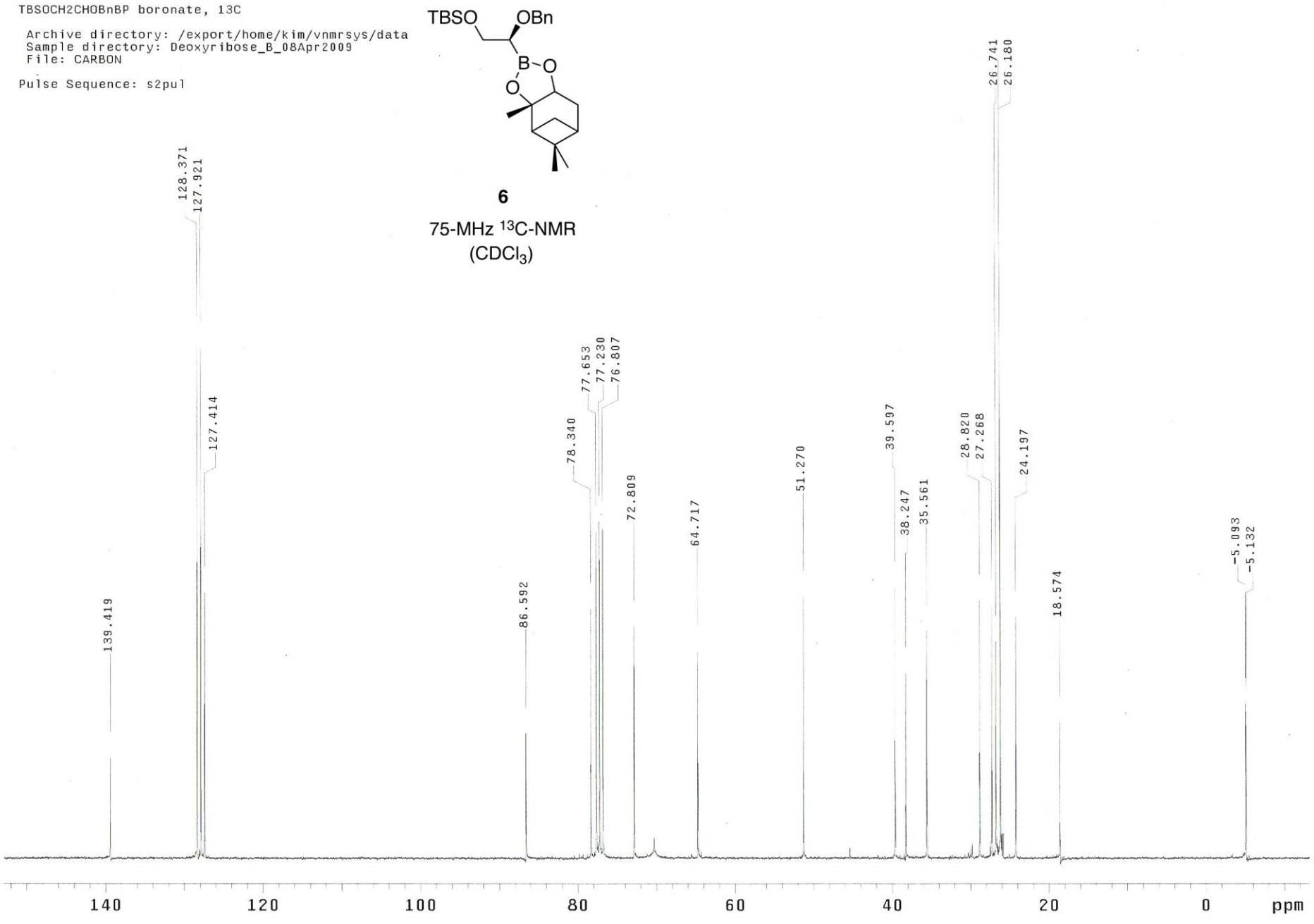
expl s2pul

SAMPLE		SPECIAL	
date	Dec 3 2008	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	3602.3	pw90	9.800
at	1.998	alfa	20.000
np	14394	FLAGS	
fb	not used	il	n
bs	16	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		fn	not used
tn	H1	DISPLAY	
sfrq	300.144	sp	-299.5
tof	1.3	wp	3602.3
tpwr	57	rfl	299.5
pw	4.900	rfp	0
DECOUPLER		rp	44.9
dn	C13	lp	-50.5
dof	0	PLOT	
dm	nnn	wc	250
dmm	c	sc	0
dpwr	39	vs	89
dmf	13100	th	3
		ai cdc ph	



6

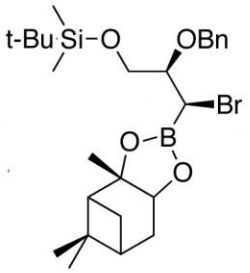
300-MHz ^{1}H-NMR
($CDCl_3$)



TBSOCH2CHOBnCHBrB+P
Purified, 170mg

exp1 std1h

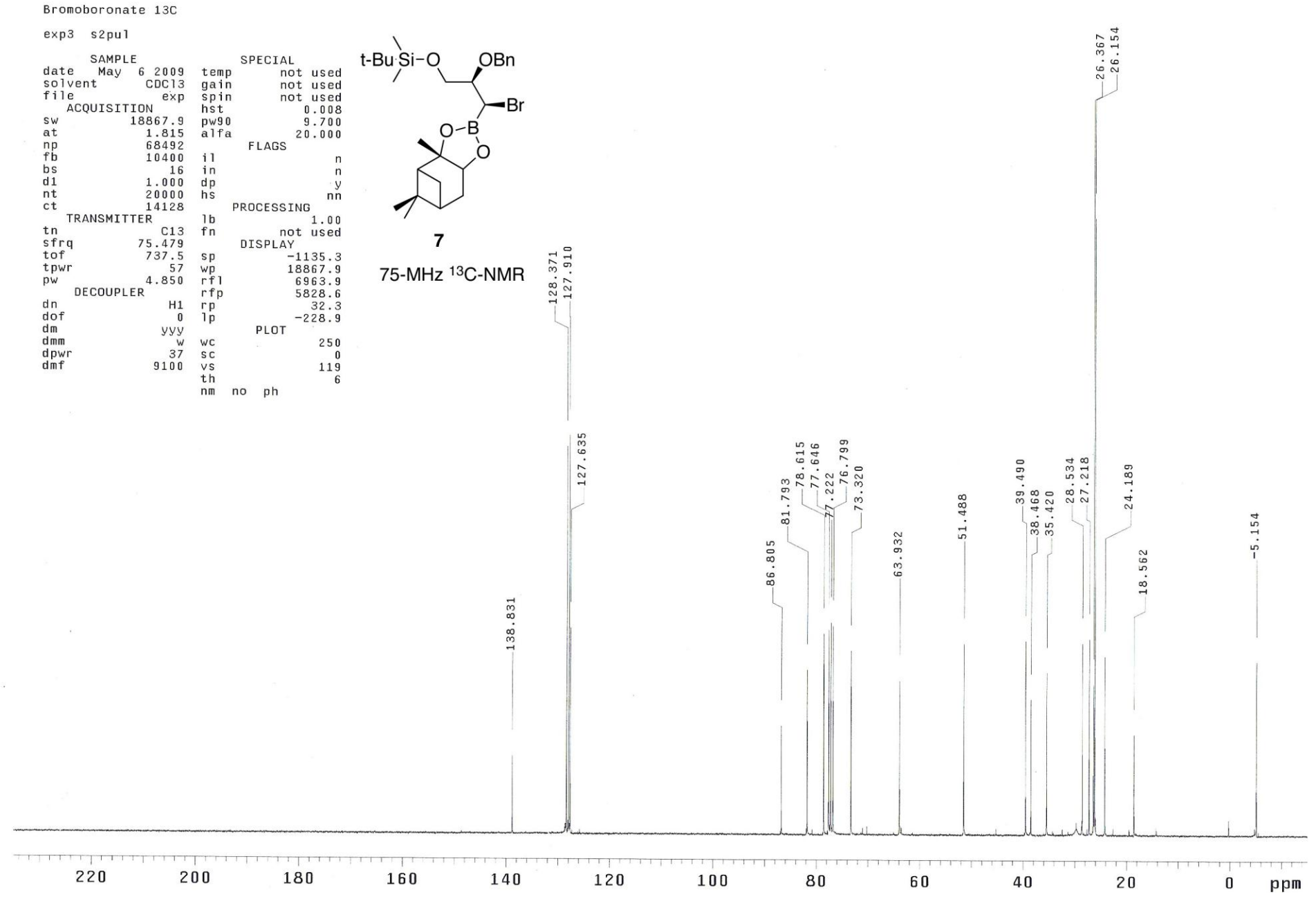
SAMPLE		DEC. & VT	
date	Jan 17 2009	dfrq	300.144
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	300.144	dm	nnn
tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	4	fn	not used
tpwr	57		
pw	4.5	werr	
d1	1.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-102.9		
wp	2621.5		
vs	148		
sc	0		
wc	250		
hzmm	10.49		
is	695.93		
rfl	753.2		
rfp	0		
th	5		
ins	2.000		
nm cdc ph			



7

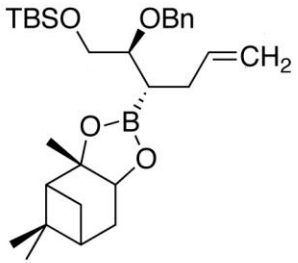
300-MHz ^{1}H-NMR

Solvent is $CDCl_3$ if not otherwise specified.



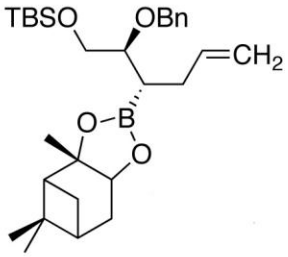
```
Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 22.0 C / 295.1 K
INOVA-500  "nmrc500b"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 8 repetitions
OBSERVE    H1, 499.8560475 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec
```



8
500-MHz ^{1}H-NMR
($CDCl_3$)

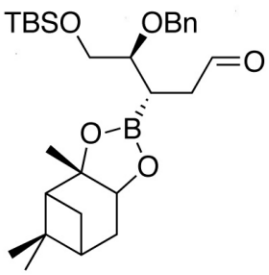
SAMPLE		SPECIAL	
date	Apr 4 2009	temp	22.0
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	30165.9	pw90	10.300
at	1.300	alfa	10.000
np	78460	FLAGS	
fb	17000	il	n
bs	64	in	n
d1	4.000	dp	y
nt	20000	hs	nn
ct	15488	PROCESSING	
TRANSMITTER		lb	0.50
tn	C13	fn	not used
sfrq	125.703	DISPLAY	
tof	1883.8	sp	-1217.1
tpwr	55	wp	20215.7
pw	5.150	fl	1257.2
DECOUPLER		fp	0
dn	H1	rp	-47.5
dof	0	lp	-203.5
dm	yyy	PLOT	
dmm	c	wc	250
dpwr	43	sc	0
dmf	9940	vs	117
		th	9
		nm	cdc ph



8

125-MHz ^{13}C-NMR

($CDCl_3$)



9

300-MHz ^{1}H-NMR

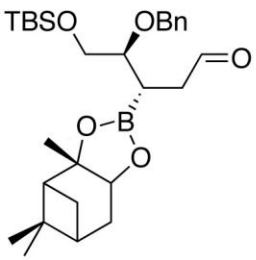
($CDCl_3$)

11

aldehyde boronate, 13C

Archive directory: /export/home/kim/vnmrsys/data
Sample directory: Ribose_B_C_15Feb2009
File: CARBON

Pulse Sequence: s2pul



9

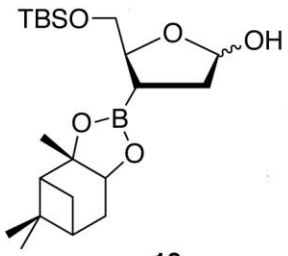
75-MHz ^{13}C-NMR

($CDCl_3$)

Ribose boronate
latter fraction

exp1 std1h

SAMPLE		DEC. & VT	
date	Feb 16 2009	dfrq	300.144
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	300.144	dm	nnn
tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	4	fn	not used
tpwr	57		
pw	4.5	werr	
d1	1.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-234.9		
wp	2827.2		
vs	153		
sc	0		
wc	250		
hzmm	11.31		
is	75.30		
rfl	752.6		
rfp	0		
th	3		
ins	1.000		
nm cdc ph			



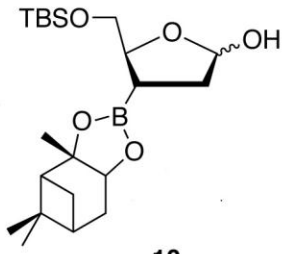
10

300-MHz ^{1}H-NMR

Ribose boronate
Made on 2/15/09

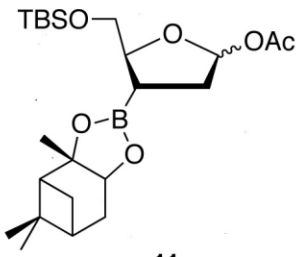
exp3 s2pul

SAMPLE		SPECIAL	
date	Feb 15 2009	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	18867.9	pw90	9.700
at	1.815	alfa	20.000
np	68492	FLAGS	
fb	10400	il	n
bs	16	in	n
d1	1.000	dp	y
nt	20000	hs	nn
ct	20000	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	not used
sfrq	75.479	DISPLAY	
tof	737.5	sp	-1133.5
tpwr	57	wp	18867.9
pw	4.850	rfl	6962.1
DECOUPLER		rfp	5828.6
dn	H1	rp	-16.3
dof	0	lp	-219.2
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	37	sc	0
dmf	9100	vs	289
		th	2
		ai	no ph



10

75-MHz ^{13}C-NMR



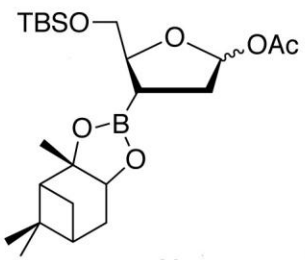
11

300-MHz ^{1}H-NMR

Deoxyribose boronate
Acylated, w/o Thymine

exp3 s2pul

SAMPLE		SPECIAL	
date	Apr 9 2009	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	18867.9	pw90	9.700
at	1.815	alfa	20.000
np	68492	FLAGS	
fb	10400	il	n
bs	16	in	n
d1	1.000	dp	y
nt	20000	hs	nn
ct	14512	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	not used
sfrq	75.479	DISPLAY	
tof	737.5	sp	-1134.1
tpwr	57	wp	18867.9
pw	4.850	rfl	6962.7
DECOUPLER		rfp	5828.6
dn	H1	rp	35.2
dof	0	lp	-223.1
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	37	sc	0
dmf	9100	vs	153
		th	3
		nm	no ph



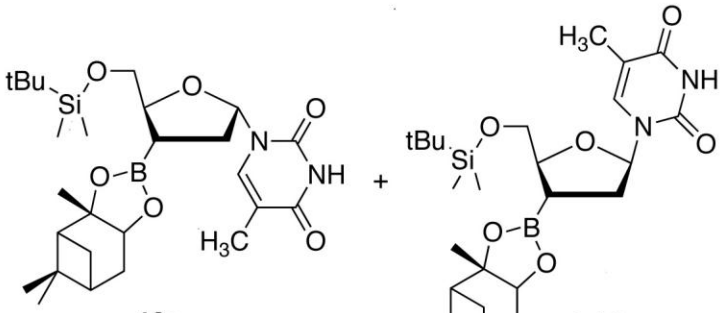
11

75-MHz ^{13}C-NMR

Silyated Thymidine boronate
ab mixture

exp1 std1h

SAMPLE		DEC. & VT	
date	May 7 2009	dfrq	300.144
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	300.144	dm	nnn
tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	4	fn	not used
tpwr	57		
pw	4.5	werr	
d1	1.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-216.5		
wp	3344.9		
vs	152		
sc	0		
wc	250		
hzmm	13.38		
is	159.04		
rfl	754.0		
rfp	0		
th	2		
ins	1.000		
nm cdc ph			

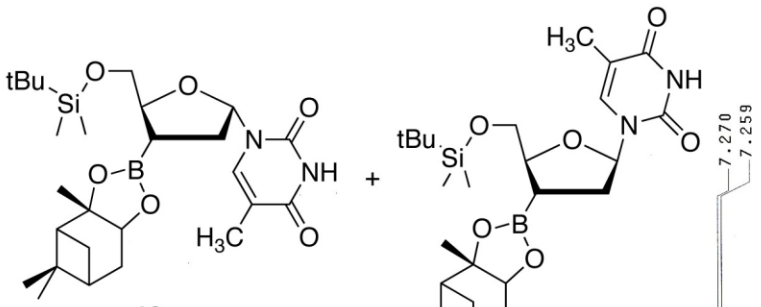


α-12a

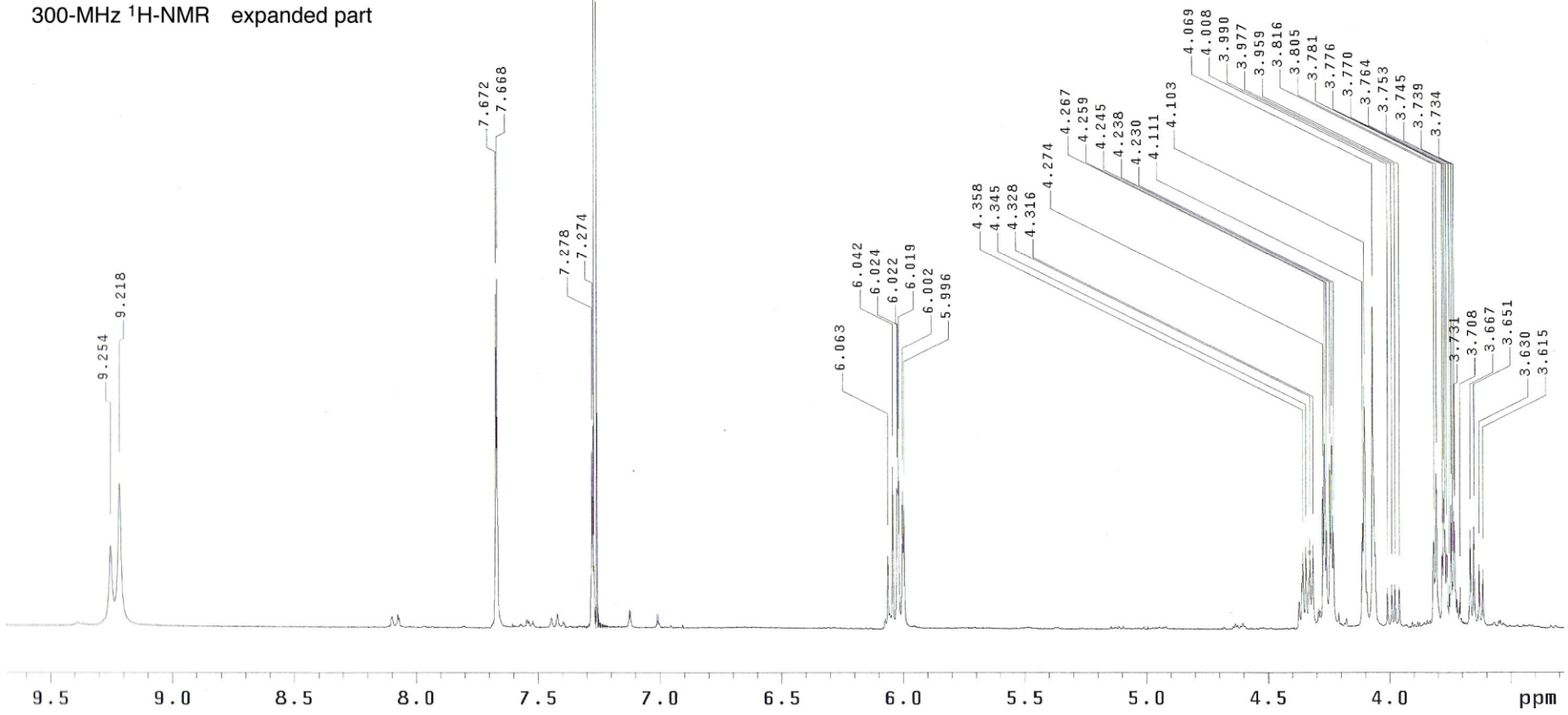
+

β-12a

300-MHz ^{1}H-NMR



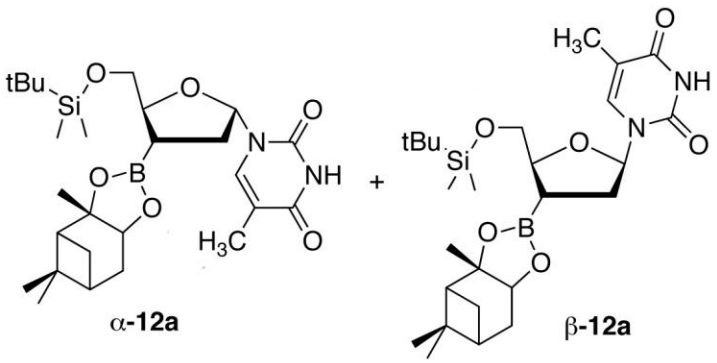
300-MHz ^{1}H-NMR expanded part



Silylated Thymidine BPab 13C

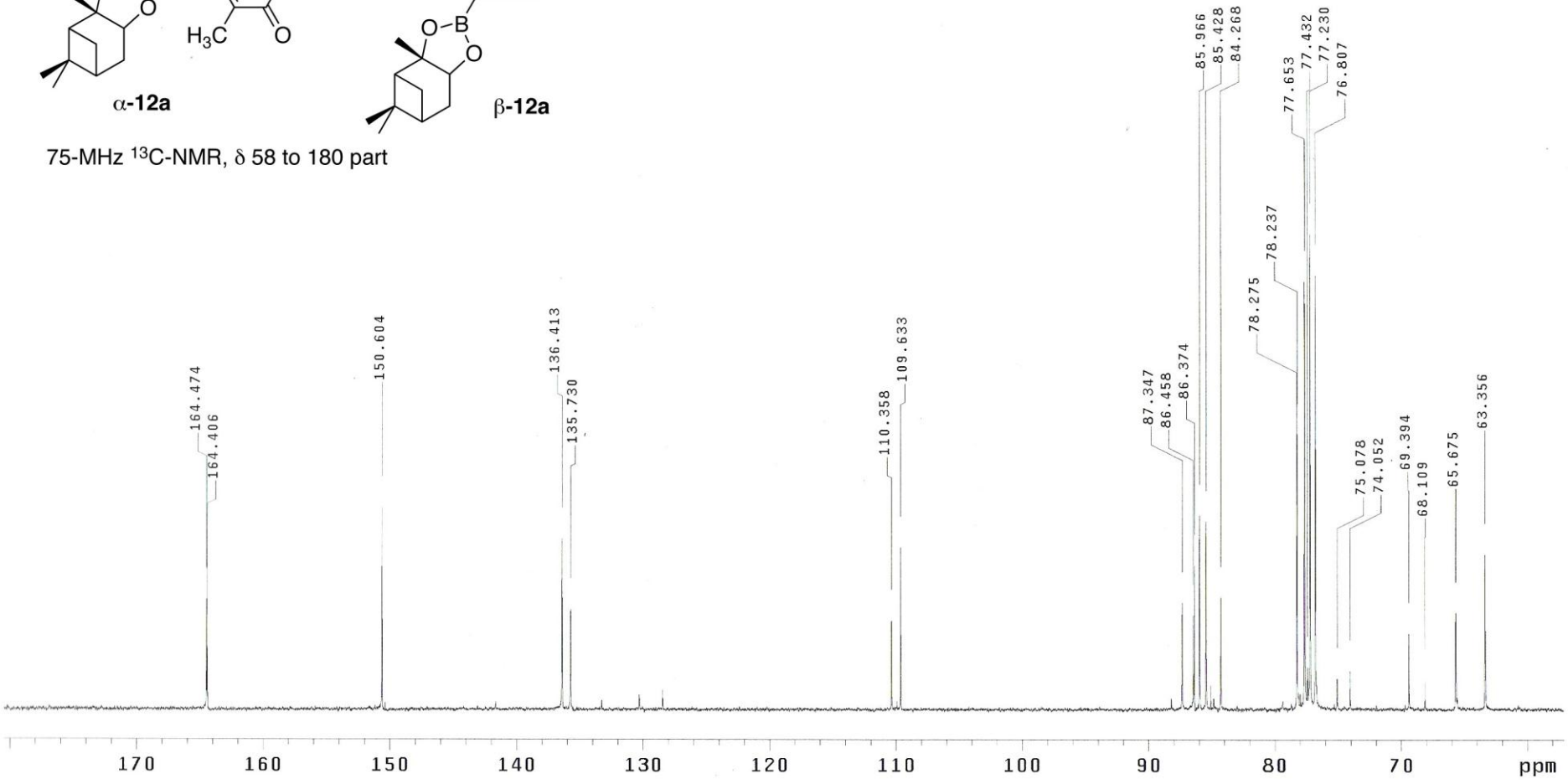
Archive directory: /export/home/kim/vnmrsys/data
Sample directory: Deoxyribose_B_08Apr2009
File: CARBON

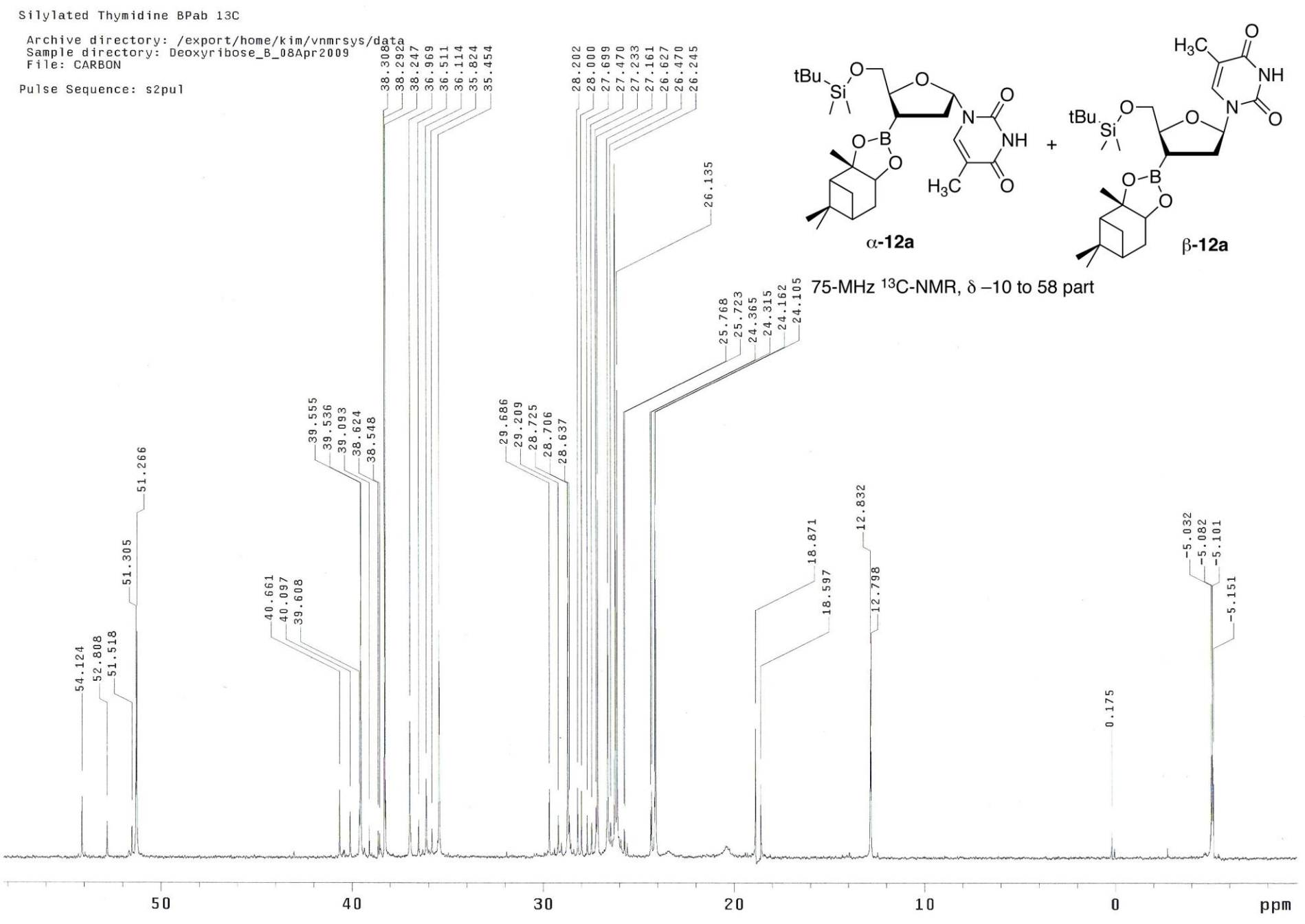
Pulse Sequence: s2pul



α-12a β-12a

75-MHz ^{13}C-NMR, δ 58 to 180 part

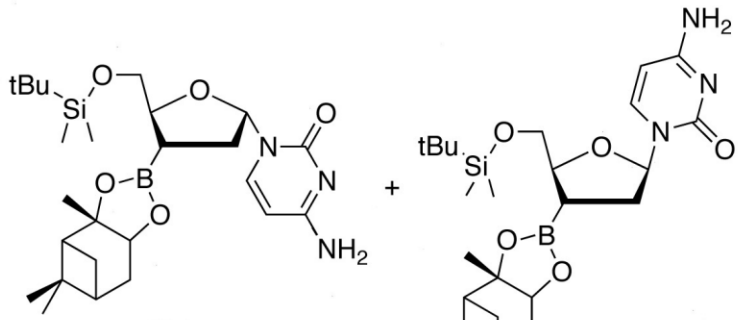




Silated cytidine boronate

exp5 s2pul

SAMPLE		SPECIAL	
date	Oct 13 2009	temp	not used
solvent	CD3OD	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	4803.1	pw90	9.800
at	1.998	alfa	20.000
np	19192	FLAGS	
fb	not used	il	n
bs	4	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		fn	not used
tn	H1	DISPLAY	
sfrq	300.145	sp	-899.8
tof	1.3	wp	4803.1
tpwr	57	rfl	899.8
pw	4.900	rfp	0
DECOUPLER		rp	66.2
dn	C13	lp	-63.8
dof	0	PLOT	
dm	nnn	wc	250
dmm	c	sc	0
dpwr	39	vs	48
dmf	13100	th	14
		ai cdc ph	



α-12d

+

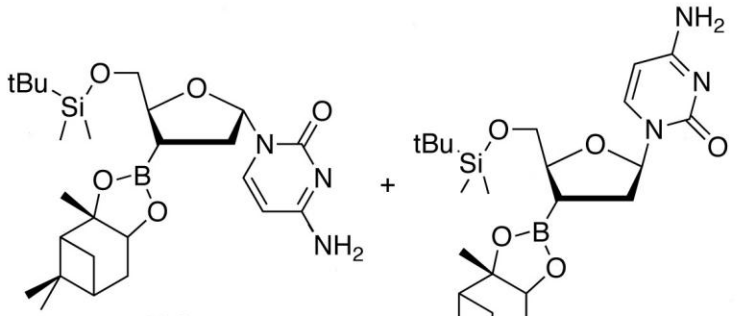
β-12d

300 MHz ^{1}H NMR
in CD_3OD

Silated cytidine boronate

Archive directory: /export/home/kim/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul



α-12d

β-12d

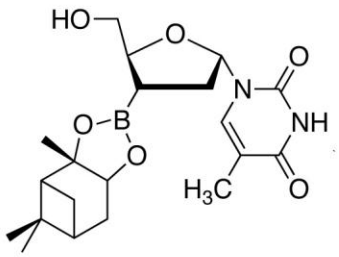
300 MHz ^{1}H NMR
in CD_3OD

expanded part

Deoxythymidine boronate
b fraction, TMSBr treated

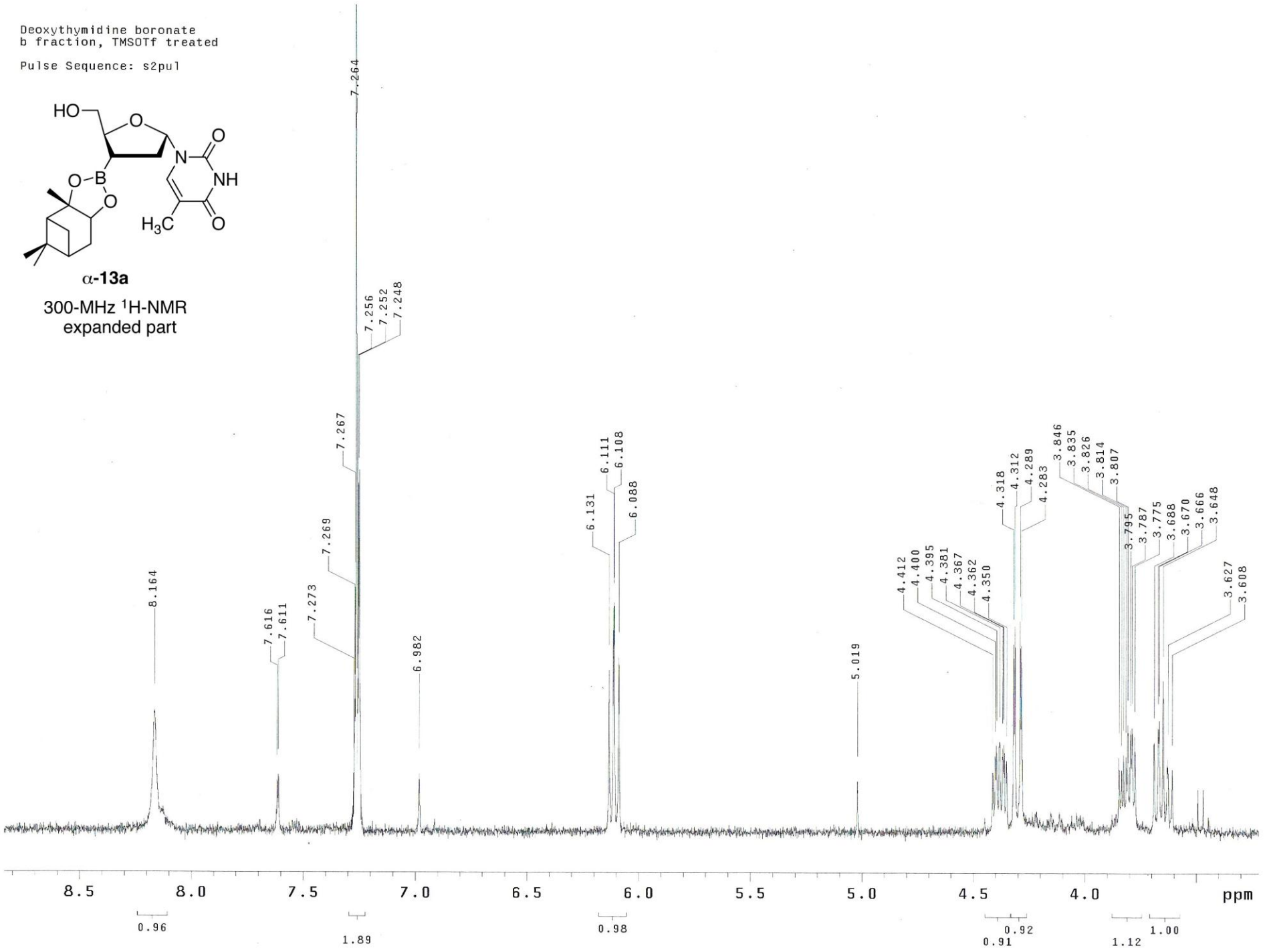
exp1 std1h

SAMPLE		DEC. & VT	
date	Apr 21 2009	dfrq	300.144
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	300.144	dm	nnn
tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	4	fn	not used
tpwr	57		
pw	4.5	werr	
d1	1.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-128.5		
wp	2926.8		
vs	158		
sc	0		
wc	250		
hzmm	11.71		
is	114.53		
rfl	752.3		
rfp	0		
th	4		
ins	1.000		
nm cdc ph			



α-13a

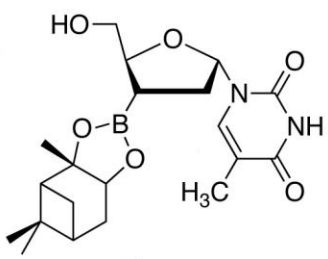
300-MHz ^{1}H-NMR



Thymidine boronat, 13C
Thymidine BP2_C

exp3 s2pul

SAMPLE		SPECIAL	
date	Apr 30 2009	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	18867.9	pw90	9.700
at	1.815	alfa	20.000
np	68492	FLAGS	
fb	10400	il	n
bs	16	in	n
d1	1.000	dp	y
nt	20000	hs	nn
ct	14128	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	not used
sfrq	75.479	DISPLAY	
tof	737.5	sp	-1106.2
tpwr	57	wp	15394.3
pw	4.850	rfl	6962.4
DECOUPLER		rfp	5828.6
dn	H1	rp	31.6
dof	0	lp	-216.0
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	37	sc	0
dmf	9100	vs	162
		th	5
		nm	no ph



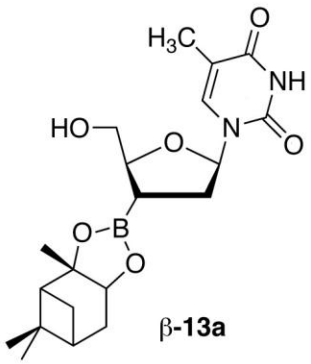
α-13a

75-MHz ^{13}C-NMR

Thymidine boronate
Thymidine BP_Hab

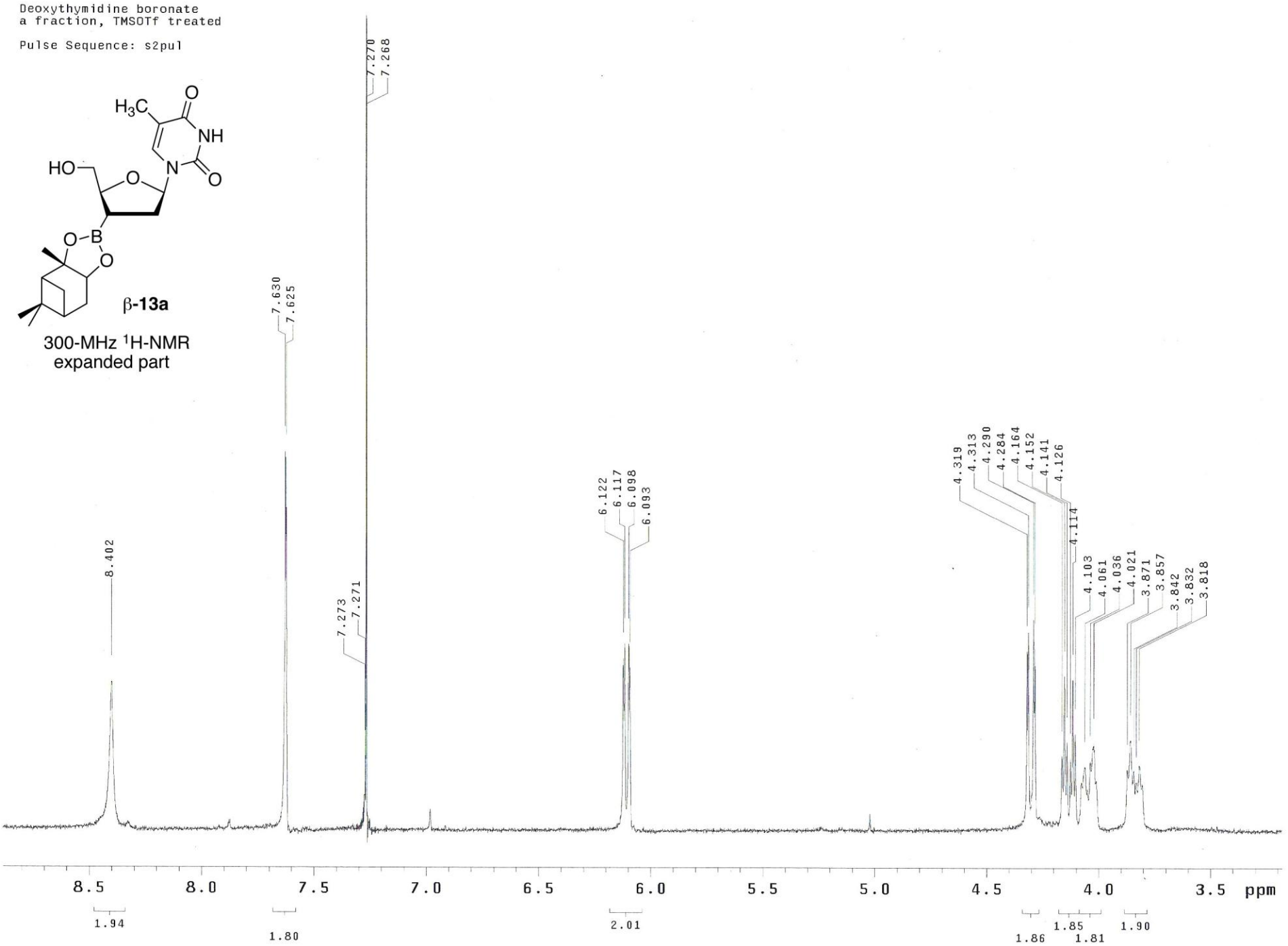
exp1 std1h

SAMPLE		DEC. & VT	
date	Apr 27 2009	dfrq	300.144
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	300.144	dm	nnn
tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	4	fn	not used
tpwr	57		
pw	4.5	werr	
d1	1.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-118.6		
wp	3092.7		
vs	162		
sc	0		
wc	250		
hzmm	12.37		
is	114.53		
rfl	749.0		
rfp	0		
th	4		
ins	1.000		
nm cdc ph			



β-13a

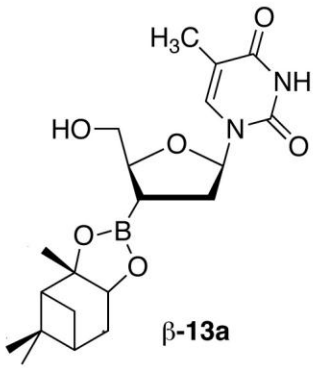
300-MHz ^{1}H-NMR



Thymidine boronat, 13C
Thymidine BP_Ca

exp3 s2pul

SAMPLE		SPECIAL	
date	Apr 24 2009	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	18867.9	pw90	9.700
at	1.815	alfa	20.000
np	68492	FLAGS	
fb	10400	il	n
bs	16	in	n
d1	1.000	dp	y
nt	20000	hs	nn
ct	15952	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	not used
sfrq	75.479	DISPLAY	
tof	737.5	sp	-1135.3
tpwr	57	wp	18867.9
pw	4.850	rfl	6963.9
DECOUPLER		rfp	5828.6
dn	H1	rp	47.2
dof	0	lp	-251.3
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	37	sc	0
dmf	9100	vs	133
		th	8
		nm	no ph



β-13a

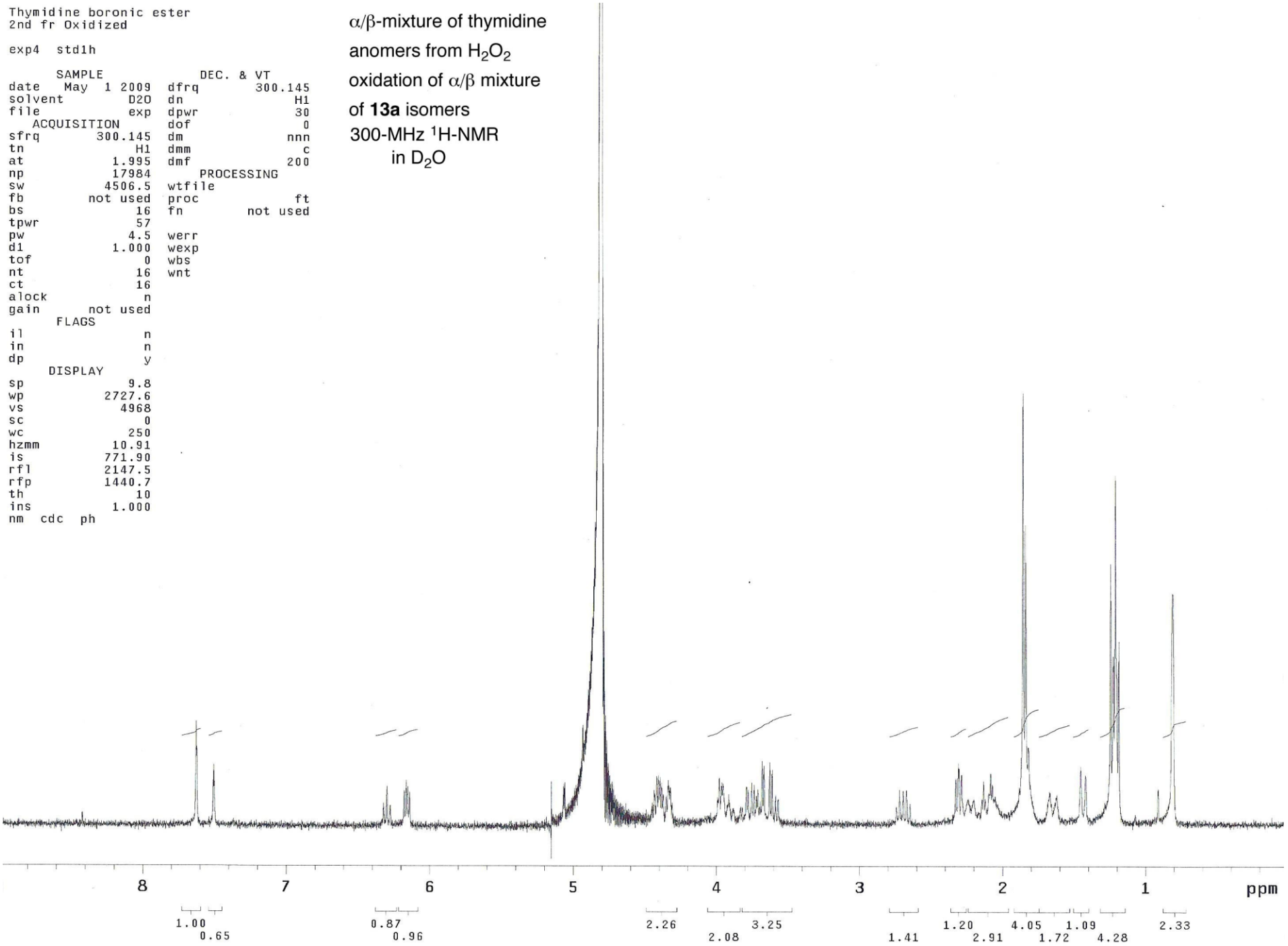
75-MHz ^{13}C-NMR

Thymidine boronic ester
2nd fr Oxidized

exp4 std1h

SAMPLE		DEC. & VT	
date	May 1 2009	dfrq	300.145
solvent	D2O	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	300.145	dm	nnn
tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	16	fn	not used
tpwr	57		
pw	4.5	werr	
d1	1.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	9.8		
wp	2727.6		
vs	4968		
sc	0		
wc	250		
hzmm	10.91		
is	771.90		
rfl	2147.5		
rfp	1440.7		
th	10		
ins	1.000		
nm cdc ph			

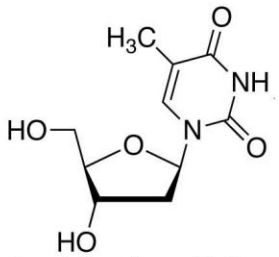
α/β-mixture of thymidine anomers from H_2O_2 oxidation of α/β mixture of **13a** isomers
300-MHz ^{1}H-NMR in D_2O



Thymidine boronic ester
1st fr Oxidized

exp4 std1h

SAMPLE		DEC. & VT	
date	May 1 2009	dfrq	300.145
solvent	D2O	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	300.145	dm	nnn
tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	16	fn	not used
tpwr	57		
pw	4.5	werr	
d1	1.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	58.4		
wp	2548.6		
vs	2341		
sc	0		
wc	250		
hzmm	10.19		
is	290.02		
rfl	2148.3		
rfp	1443.7		
th	5		
ins	1.000		
nm cdc ph			



thymidine from H_2O_2 oxidation of β-**13a**

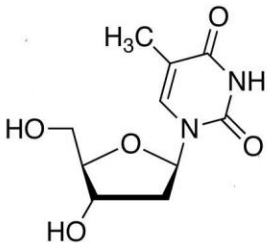
300-MHz ^{1}H-NMR in D_2O

Thymidine in D2O
standard

exp4 std1h

SAMPLE		DEC. & VT	
date	Apr 1 2009	dfrq	300.145
solvent	D2O	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	300.145	dm	nnn
tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	16	fn	not used
tpwr	57		
pw	4.5	werr	
d1	1.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	291.1		
wp	2446.5		
vs	1863		
sc	0		
wc	250		
hzmm	9.79		
is	500.00		
rfl	2148.1		
rfp	1443.7		
th	20		
ins	1.000		

nm cdc ph



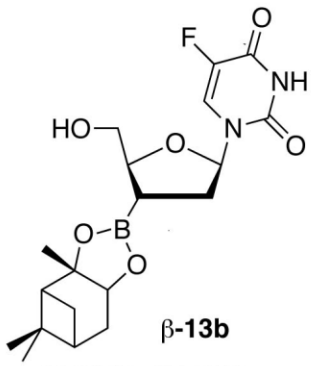
thymidine authentic sample

300-MHz ^{1}H-NMR in D_2O

Fluorouridine boronate
PLC purified, 30mg

exp1 std1h

SAMPLE		DEC. & VT	
date	Jul 4 2009	dfrq	300.144
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	300.144	dm	nnn
tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	4	fn	not used
tpwr	57		
pw	4.5	werr	
d1	1.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-177.4		
wp	3313.8		
vs	151		
sc	0		
wc	250		
hzmm	13.26		
is	82.22		
rfl	751.2		
rfp	0		
th	4		
ins	2.000		
nm cdc ph			



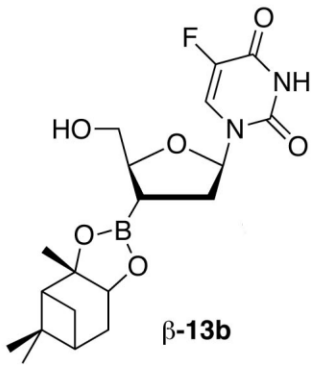
β-13b

300-MHz ^{1}H-NMR

FUridine Boronic ester, B11

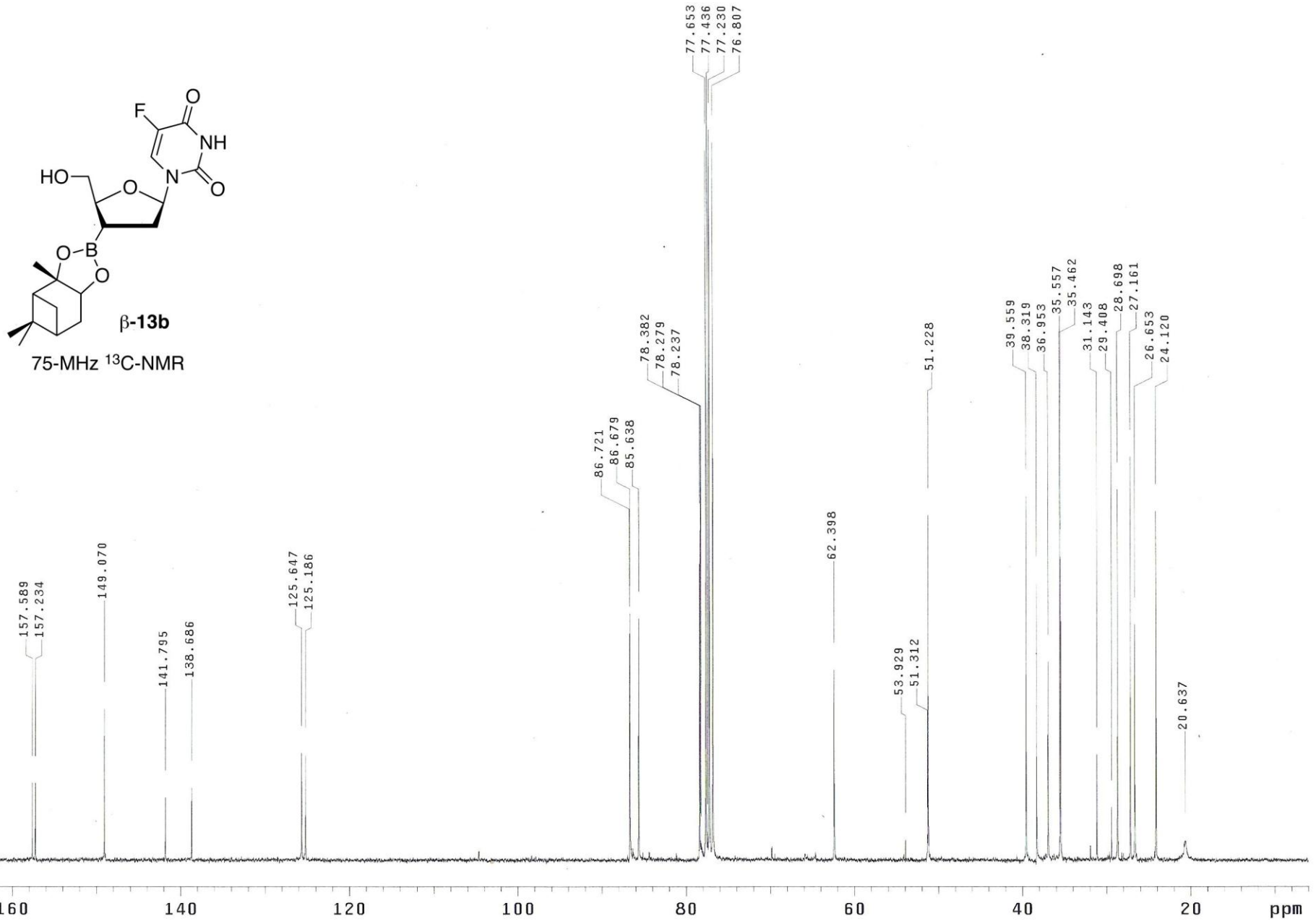
exp3 s2pul

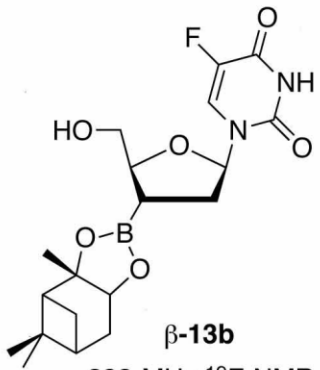
SAMPLE		DEC. & VT	
date	Jul 13 2009	dfrq	499.859
solvent	CDCl3	dn	H1
file	/net/work6/da~	dpwr	43
ta/NMRC300/matteso~		dof	0
n/Tommy_Kim_Folder~		dm	nyy
/Uridine_B11/Furid~		dmm	w
ine_BP_std.fid		dmf	9940
ACQUISITION		dseq	
sfrq	160.377	dres	1.0
tn	B11	homo	n
at	0.200	temp	22.0
np	10000	DEC2	
sw	25000.0	dfrq2	0
fb	14000	dn2	
bs	32	dpwr2	1
tpwr	57	dof2	0
pw	5.5	dm2	n
d1	1.000	dmm2	c
tof	7915.4	dmf2	9900
nt	1000	dseq2	
ct	1000	dres2	1.0
alock	n	homo2	n
gain	not used	DEC3	
FLAGS		dfrq3	0
il	n	dn3	
in	n	dpwr3	1
dp	y	dof3	0
hs	nn	dm3	n
DISPLAY		dmm3	c
sp	-9564.2	dmf3	9900
wp	24998.5	dseq3	
vs	664	dres3	1.0
sc	0	homo3	n
wc	250	PROCESSING	
hzmm	99.99	lb	7.80
is	500.00	wtfile	
rfl	9565.7	proc	ft
rfp	0	fn	32768
th	7	math	f
ins	100.000		
nm cdc ph		werr	
		wexp	
		wbs	
		wnt	



β-13b

160-MHz ^{11}B-NMR





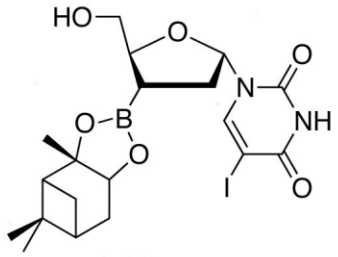
β-**13b**

282-MHz ^{19}F-NMR

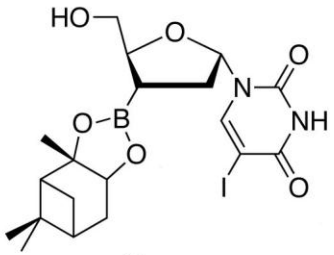
IUridine
2nd fraction
after PLC

exp1 std1h

SAMPLE		DEC. & VT	
date	Sep 2 2009	dfrq	300.144
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	300.144	dm	nnn
tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	4	fn	not used
tpwr	57		
pw	4.5	werr	
d1	1.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-82.8		
wp	3139.1		
vs	157		
sc	0		
wc	250		
hzmm	12.56		
is	129.66		
rfl	746.3		
rfp	0		
th	3		
ins	1.000		
nm cdc ph			

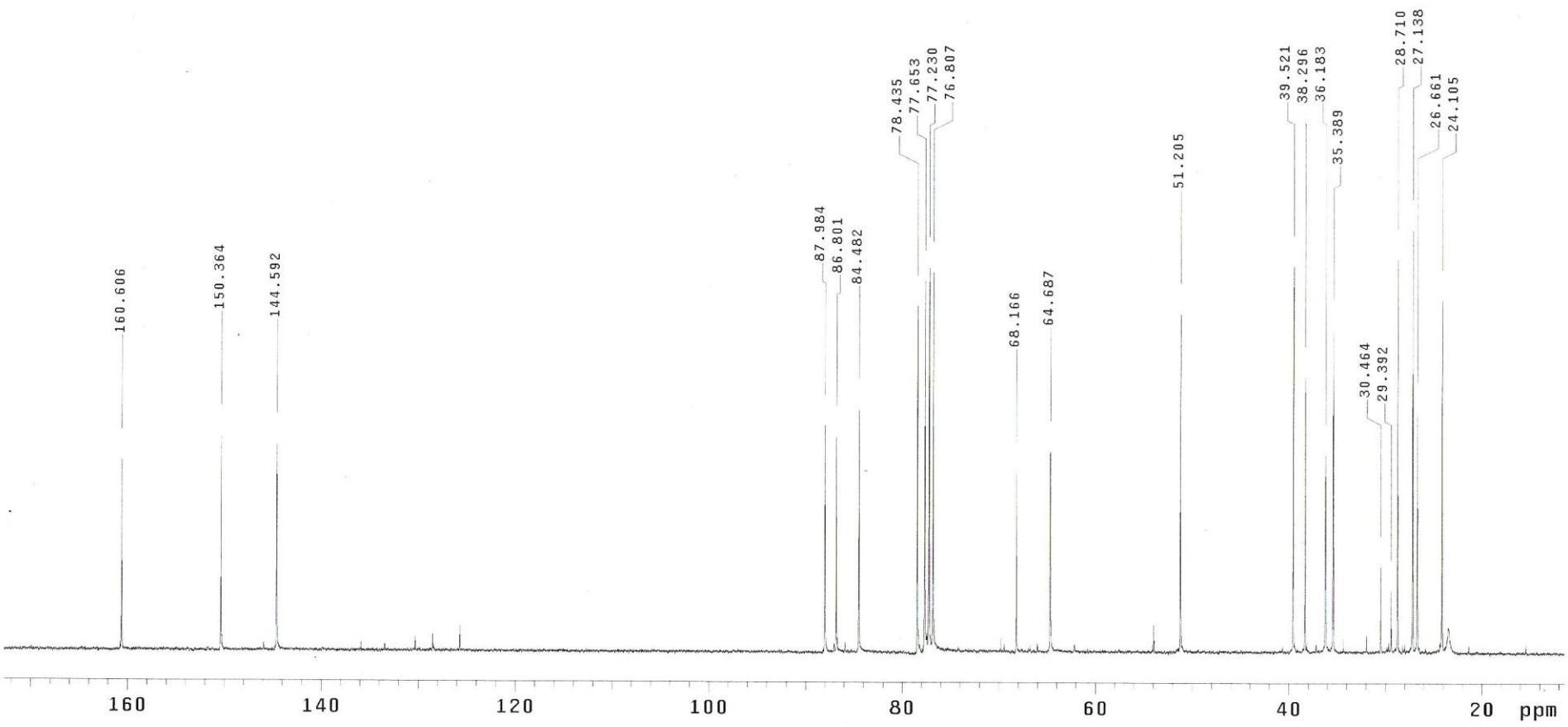


α-13c
300-MHz ^{1}H-NMR



α-13c

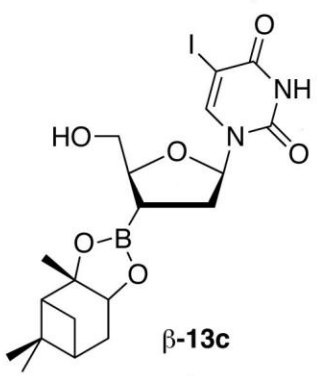
75-MHz ^{13}C-NMR



IUridine
first fraction
after PLC

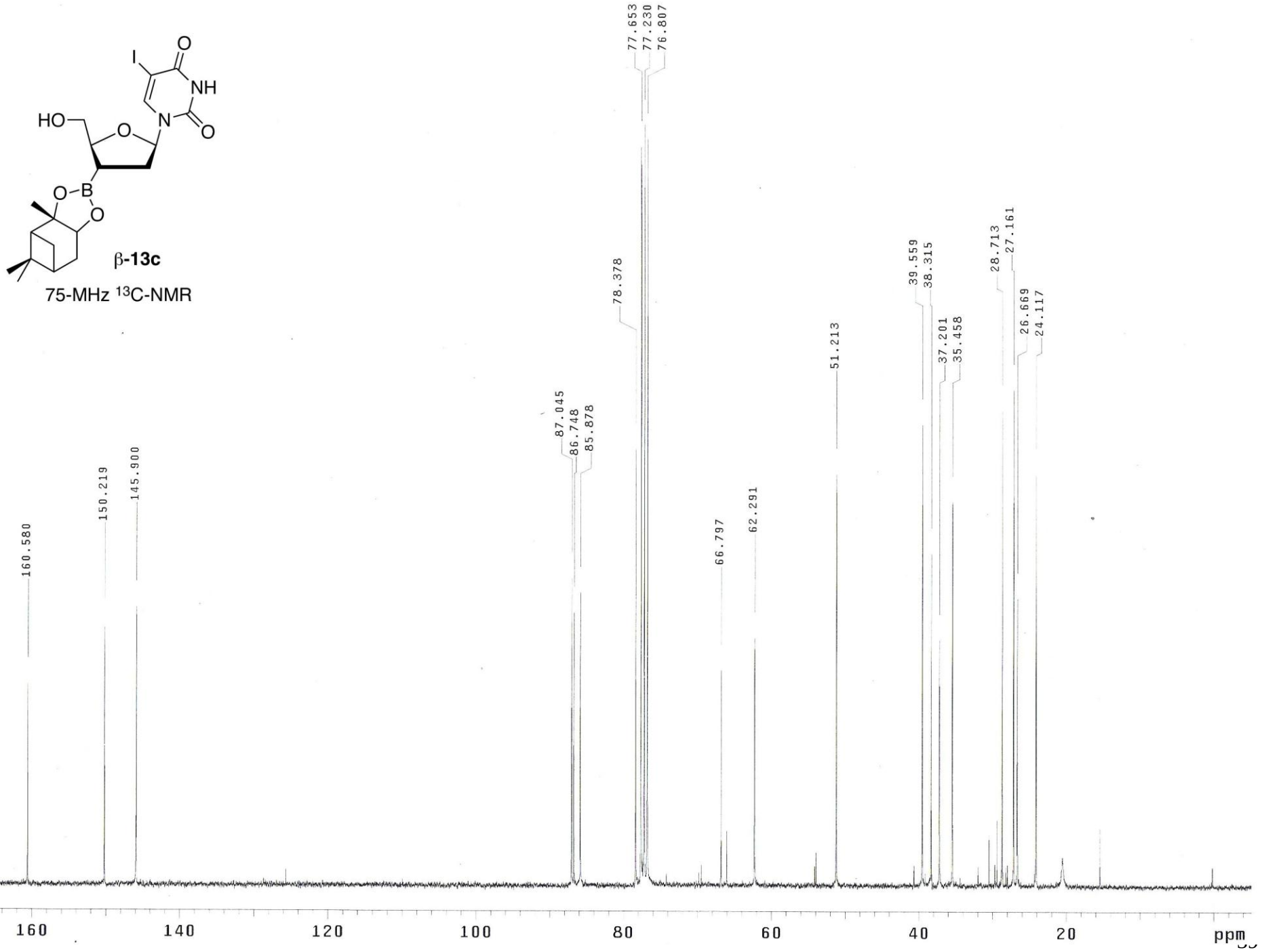
exp1 std1h

SAMPLE		DEC. & VT	
date	Sep 1 2009	dfrq	300.144
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	300.144	dm	nnn
tn	H1	dmm	c
at	1.995	dmf	200
np	17984	PROCESSING	
sw	4506.5	wtfile	
fb	not used	proc	ft
bs	4	fn	not used
tpwr	57		
pw	4.5	werr	
d1	1.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-170.5		
wp	3165.8		
vs	157		
sc	0		
wc	250		
hzmm	12.66		
is	129.66		
rfl	747.9		
rfp	0		
th	3		
ins	1.000		
nm cdc ph			



β-13c

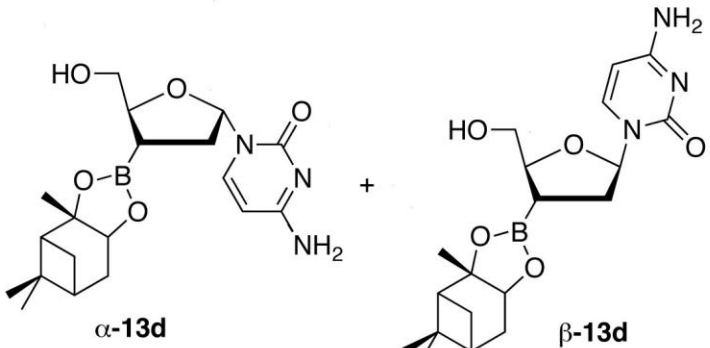
300-MHz ^{1}H-NMR



Desilated cytidine boronate
HCl salt

exp5 s2pul

SAMPLE		SPECIAL	
date	Oct 13 2009	temp	not used
solvent	CD3OD	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	4803.1	pw90	9.800
at	1.998	alfa	20.000
np	19192	FLAGS	
fb	not used	il	n
bs	4	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		fn	not used
tn	H1	DISPLAY	
sfrq	300.145	sp	-899.8
tof	1.3	wp	4803.1
tpwr	57	rfl	899.8
pw	4.900	rfp	0
DECOUPLER		rp	62.3
dn	C13	lp	-60.2
dof	0	PLOT	
dm	nnn	wc	250
dmm	c	sc	0
dpwr	39	vs	126
dmf	13100	th	15
		ai cdc ph	



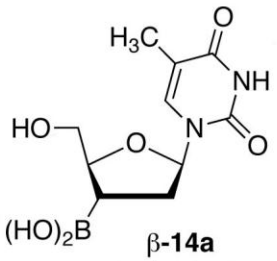
α-13d + β-13d

300-MHz ^{1}H-NMR
in CD_3OD

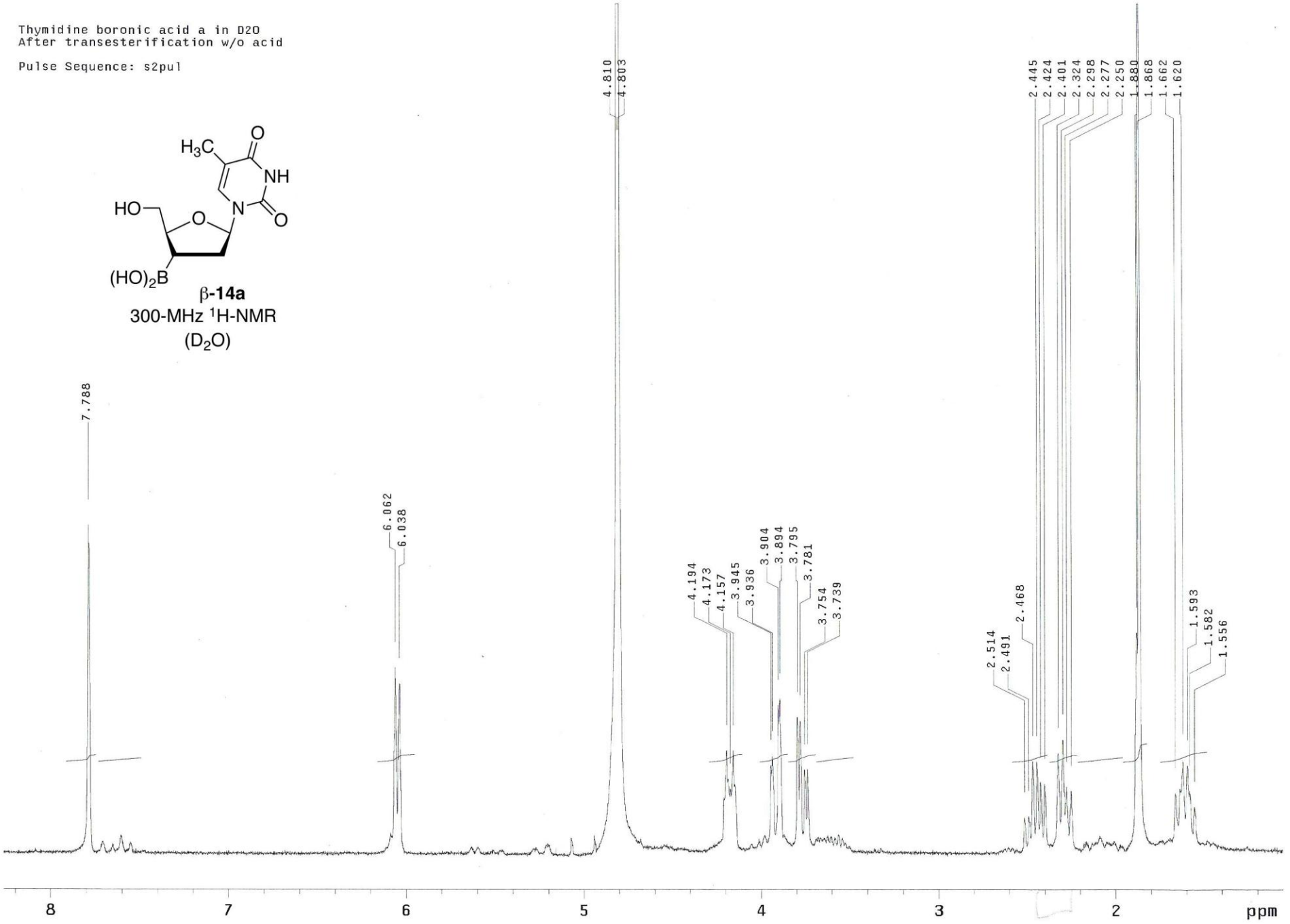
3-DeoxyThymidine boronic acid
2nd batch
3DO_Thymidine_BOH_H

exp5 s2pul

SAMPLE		SPECIAL	
date	May 12 2009	temp	not used
solvent	CD3OD	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	4803.1	pw90	9.800
at	1.998	alfa	20.000
np	19192	FLAGS	
fb	not used	il	n
bs	4	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		fn	not used
tn	H1	DISPLAY	
sfrq	300.145	sp	225.9
tof	1.3	wp	2440.4
tpwr	57	rfl	898.7
pw	4.900	rfp	0
DECOUPLER		rp	67.2
dn	C13	lp	-51.8
dof	0	PLOT	
dm	nnn	wc	250
dmm	c	sc	0
dpwr	39	vs	113
dmf	13100	th	3
		ai cdc ph	



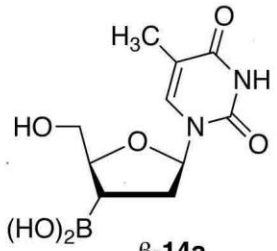
β-**14a**
300-MHz ^{1}H-NMR
in CD_3OD



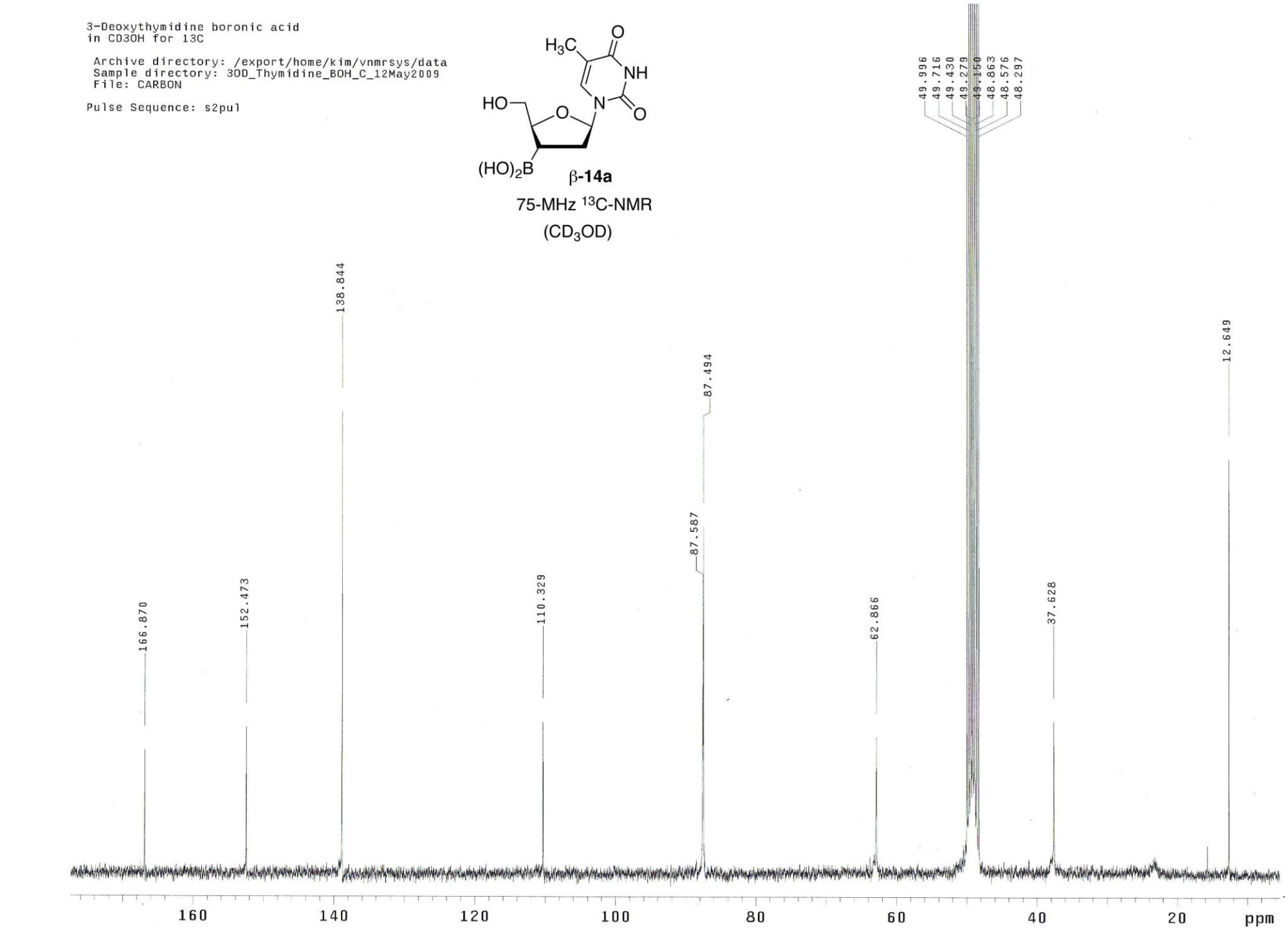
b-Thymidine boronic acid, 11B

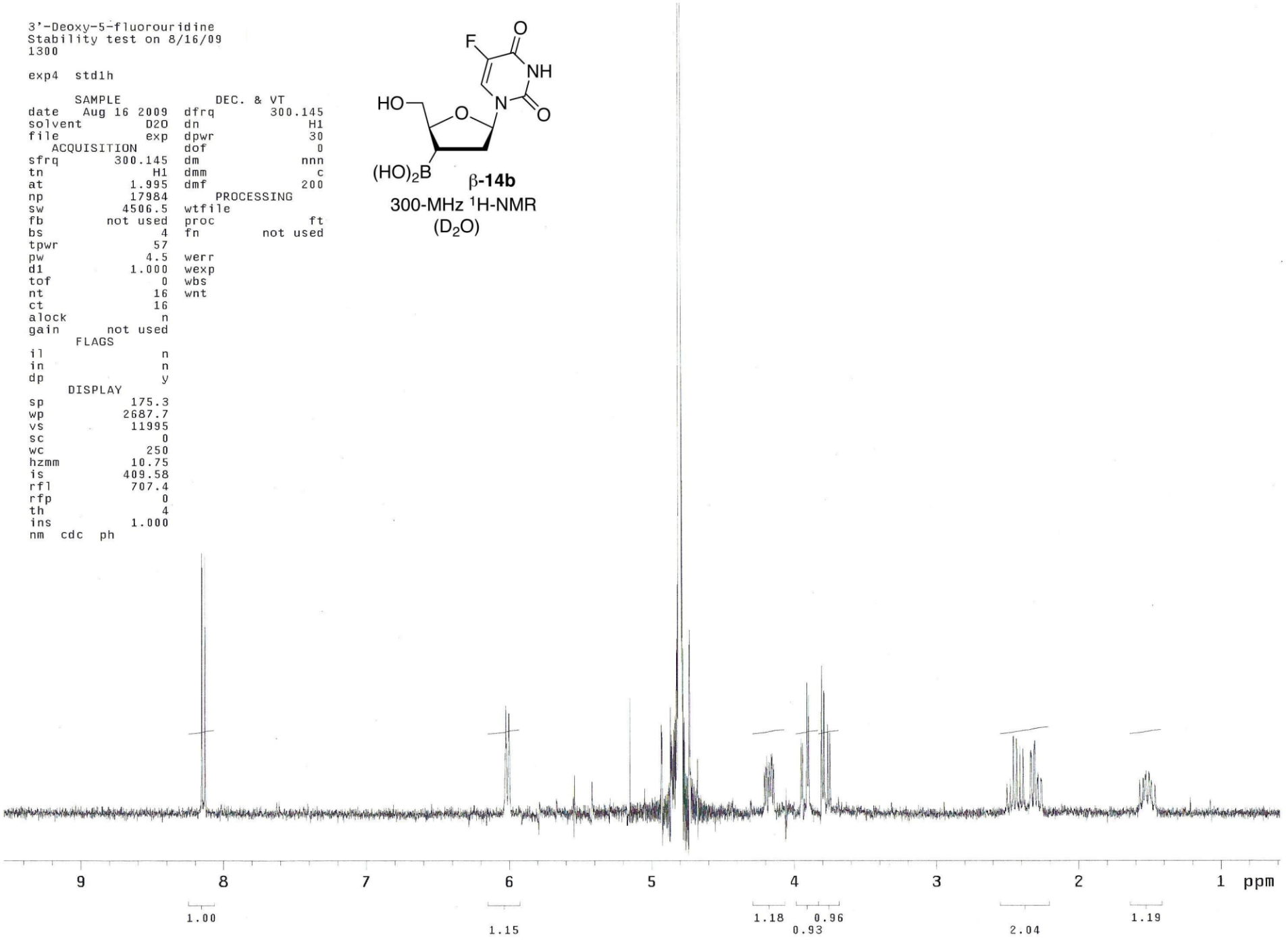
exp3 s2pul

SAMPLE		DEC. & VT	
date	Jul 13 2009	dfrq	499.861
solvent	CD3OD	dn	H1
file	exp	dpwr	43
ACQUISITION		dof	0
sfrq	160.377	dm	nyy
tn	B11	dmm	w
at	0.200	dmf	9940
np	10000	dseq	
sw	25000.0	dres	1.0
fb	14000	homo	n
bs	32	temp	22.0
tpwr	57	DEC2	
pw	5.5	dfrq2	0
d1	1.000	dn2	
tof	7915.4	dpwr2	1
nt	1000	dof2	0
ct	672	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	9900
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-9448.2	dpwr3	1
wp	24998.5	dof3	0
vs	140	dm3	n
sc	0	dmm3	c
wc	250	dmf3	9900
hzmm	99.99	dseq3	
is	500.00	dres3	1.0
rfl	9449.8	homo3	n
rfp	0	PROCESSING	
th	6	lb	7.80
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	32768
		math	f
		werr	
		wexp	
		wbs	
		wnt	



β-**14a**
160-MHz ^{11}B-NMR
(CD_3OD)

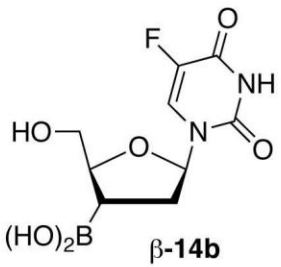




FUridine boronic acid, 11B

exp3 s2pul

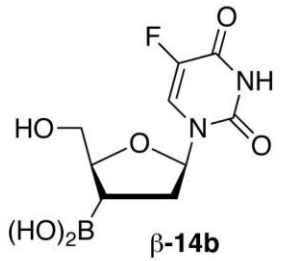
SAMPLE		DEC. & VT	
date	Jul 13 2009	dfrq	499.861
solvent	CD3OD	dn	H1
file	exp	dpwr	43
ACQUISITION		dof	0
sfrq	160.377	dm	nyy
tn	B11	dmm	w
at	0.200	dmf	9940
np	10000	dseq	
sw	25000.0	dres	1.0
fb	14000	homo	n
bs	32	temp	22.0
tpwr	57	DEC2	
pw	5.5	dfrq2	0
d1	1.000	dn2	
tof	7915.4	dpwr2	1
nt	1000	dof2	0
ct	128	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	9900
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-9446.7	dpwr3	1
wp	24998.5	dof3	0
vs	218	dm3	n
sc	0	dmm3	c
wc	250	dmf3	9900
hzmm	99.99	dseq3	
is	500.00	dres3	1.0
rfl	9448.2	homo3	n
rfp	0	PROCESSING	
th	6	lb	7.80
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	32768
		math	f
		werr	
		wexp	
		wbs	
		wnt	



β-**14b**

160-MHz ^{11}B-NMR

(CD_3OD)



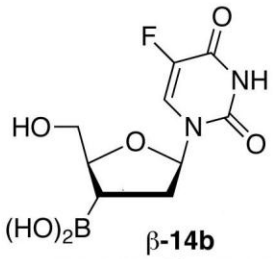
β-**14b**

75-MHz ^{13}C-NMR
(CD_3OD)

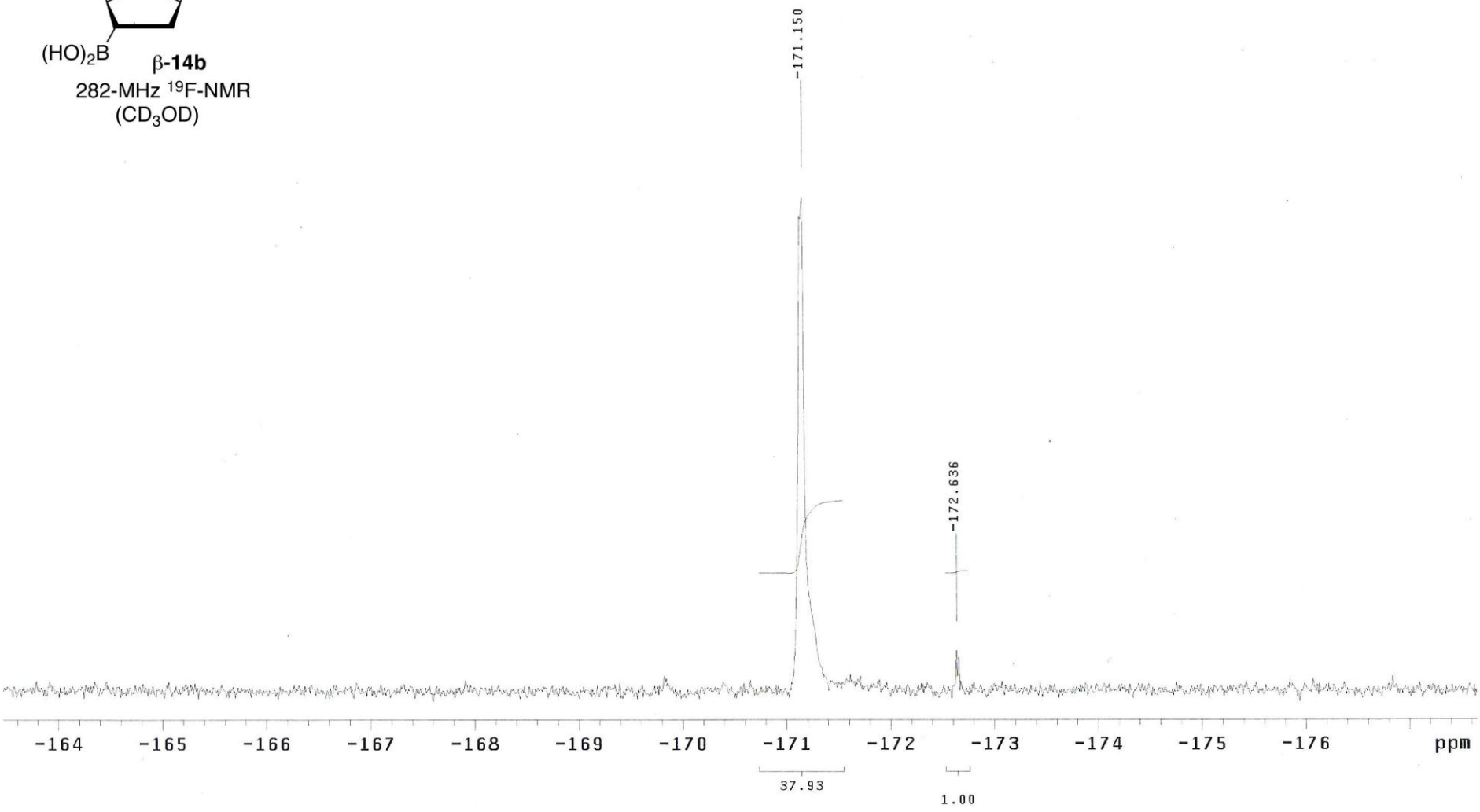
FUridine_BOH_F

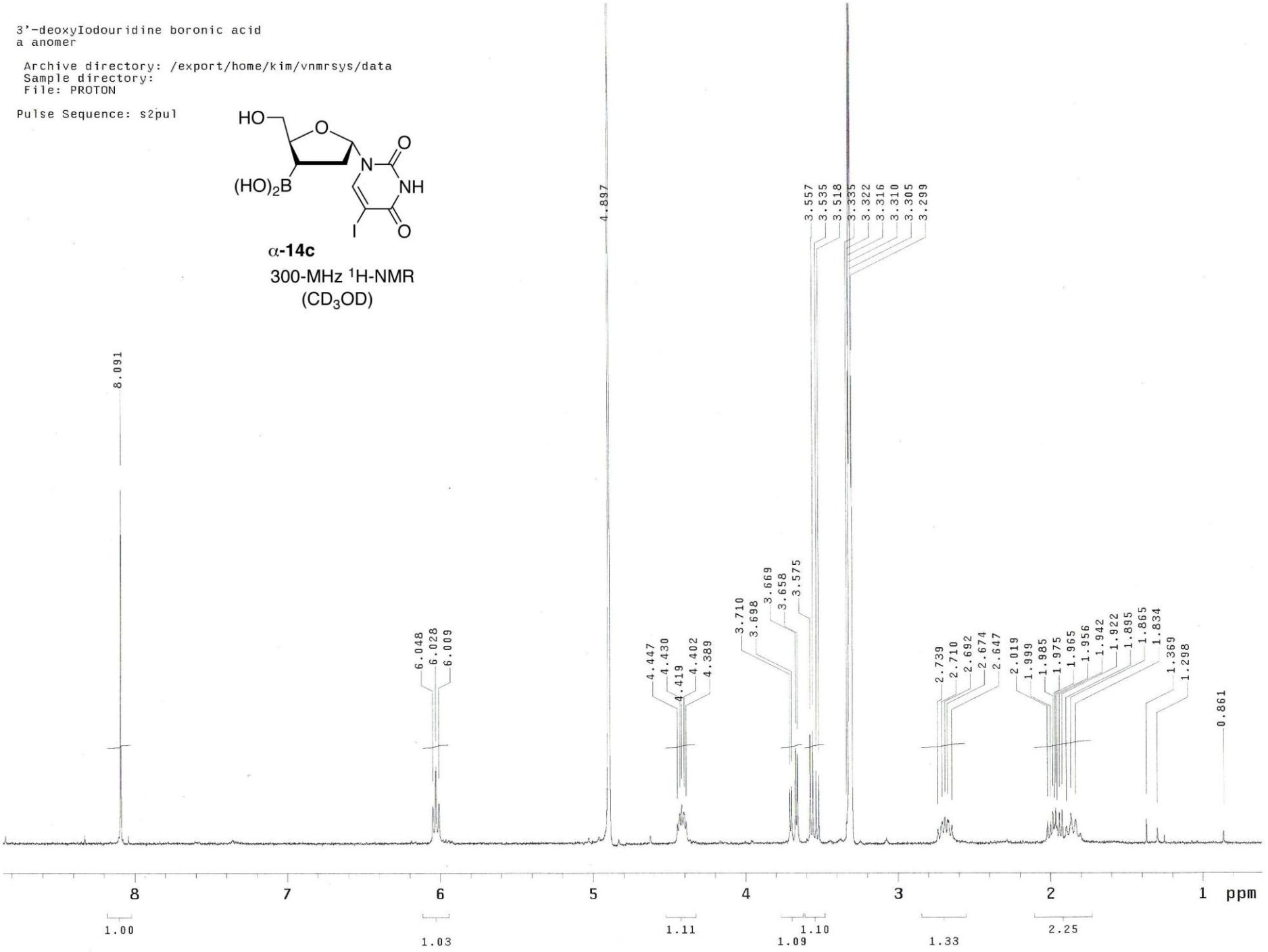
Archive directory: /export/home/kim/vnmrsys/data
Sample directory: FUridine_BOHF_07Jul2009

Pulse Sequence: s2pul



β-**14b**
282-MHz ^{19}F-NMR
(CD_3OD)

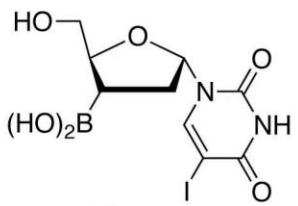




IUridine_aBOH_C

Archive directory: /export/home/kim/vnmrsys/data
Sample directory: IUridine_aBOH_C_12Sep2009
File: CARBON

Pulse Sequence: s2pul



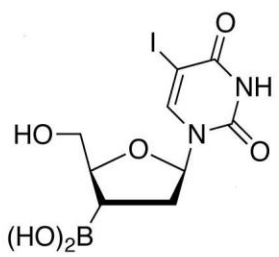
α-14c

75-MHz ^{13}C-NMR
(CD_3OD)

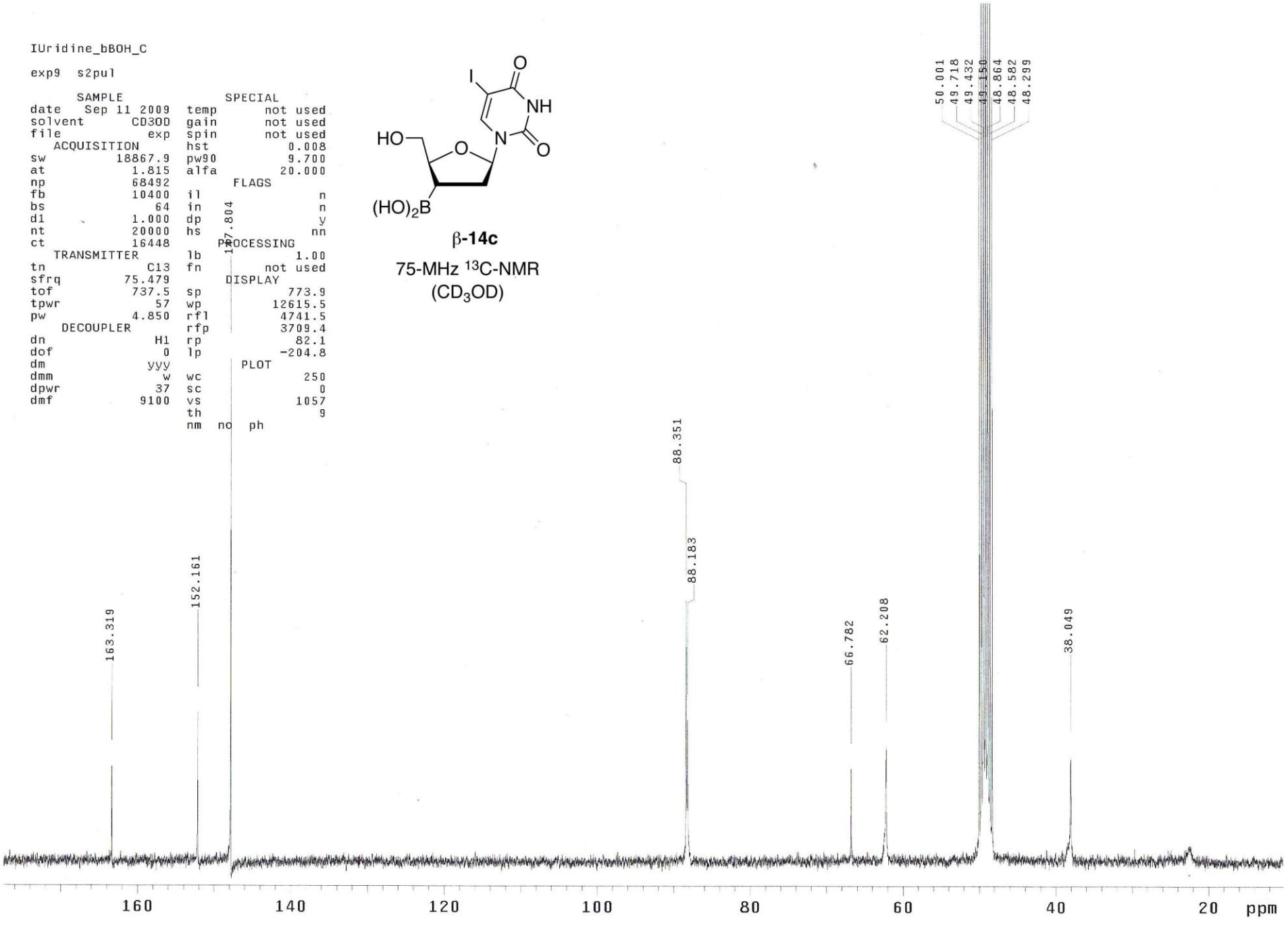
3'-deoxyIodouridine boronic acid
b anomer

exp5 s2pul

SAMPLE		SPECIAL	
date	Sep 11 2009	temp	not used
solvent	CD3OD	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	4803.1	pw90	9.800
at	1.998	alfa	20.000
np	19192	FLAGS	
fb	not used	il	n
bs	4	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		fn	not used
tn	H1	DISPLAY	
sfrq	300.145	sp	466.3
tof	1.3	wp	2334.3
tpwr	57	rfl	1892.1
pw	4.900	rfp	993.5
DECOUPLER		rp	60.6
dn	C13	lp	-58.7
dof	0	PLOT	
dm	nnn	wc	250
dmm	c	sc	0
dpwr	39	vs	1567
dmf	13100	th	6
		ai cdc ph	



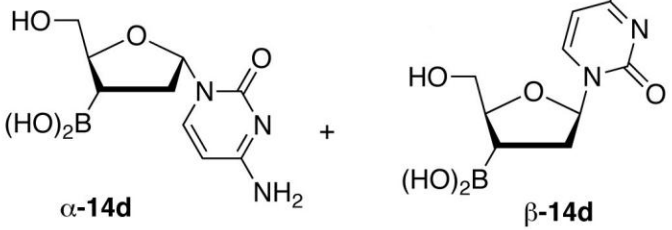
β-14c
300-MHz ^{1}H-NMR
(CD_3OD)



After PLC, Cytidine boronic ester
fraction 4
CD3OD:D2O=2:1

Archive directory: /export/home/kim/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul

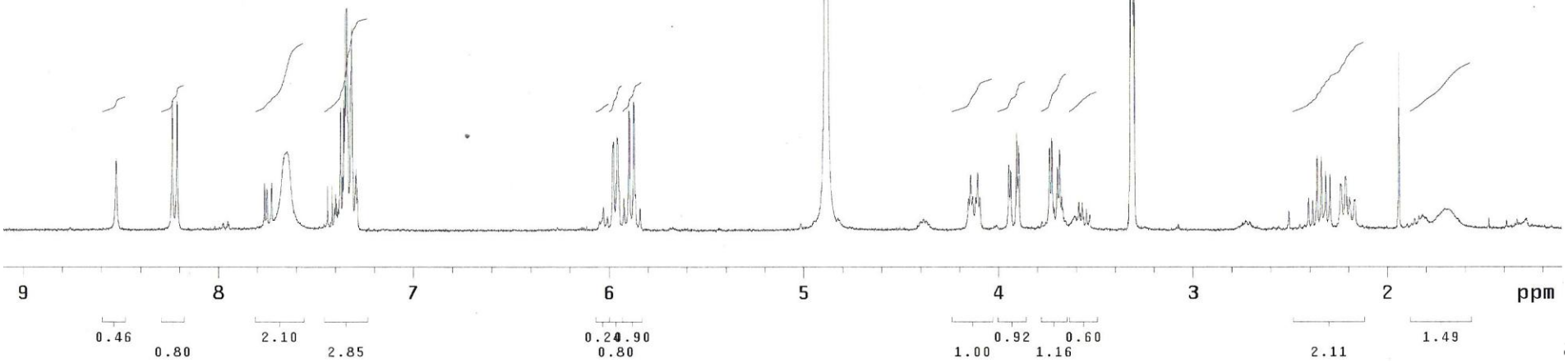


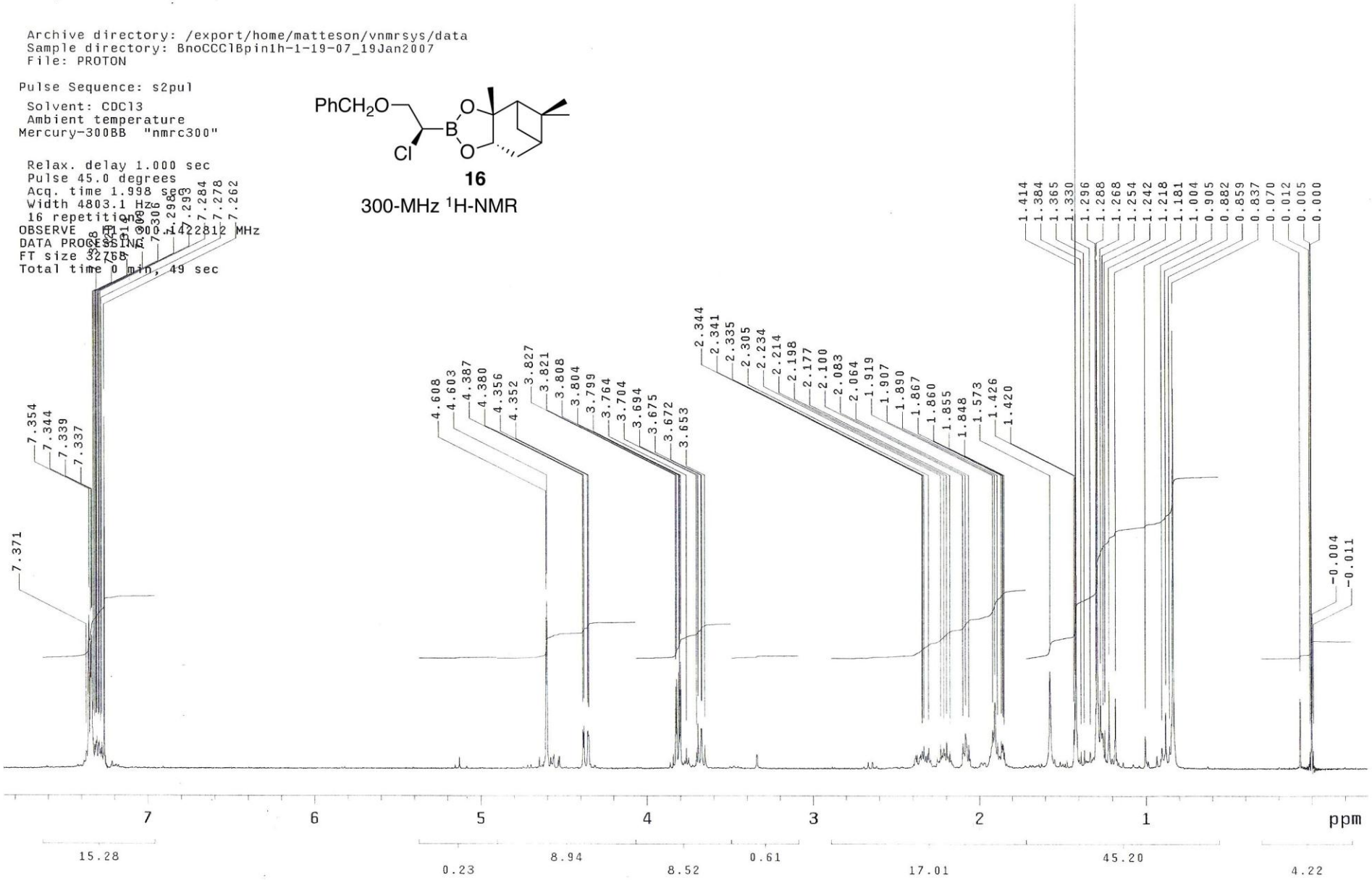
α-14d

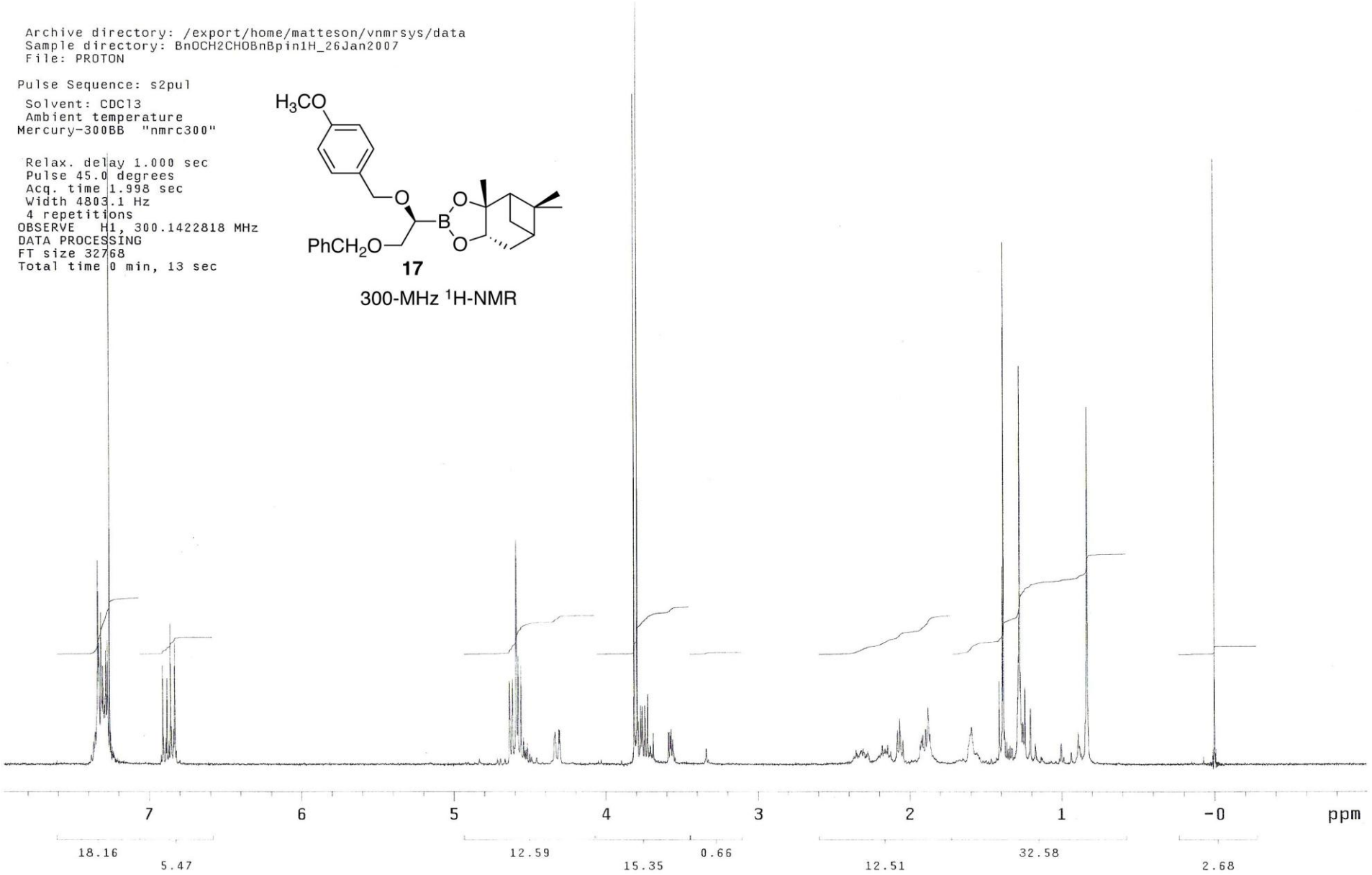
+

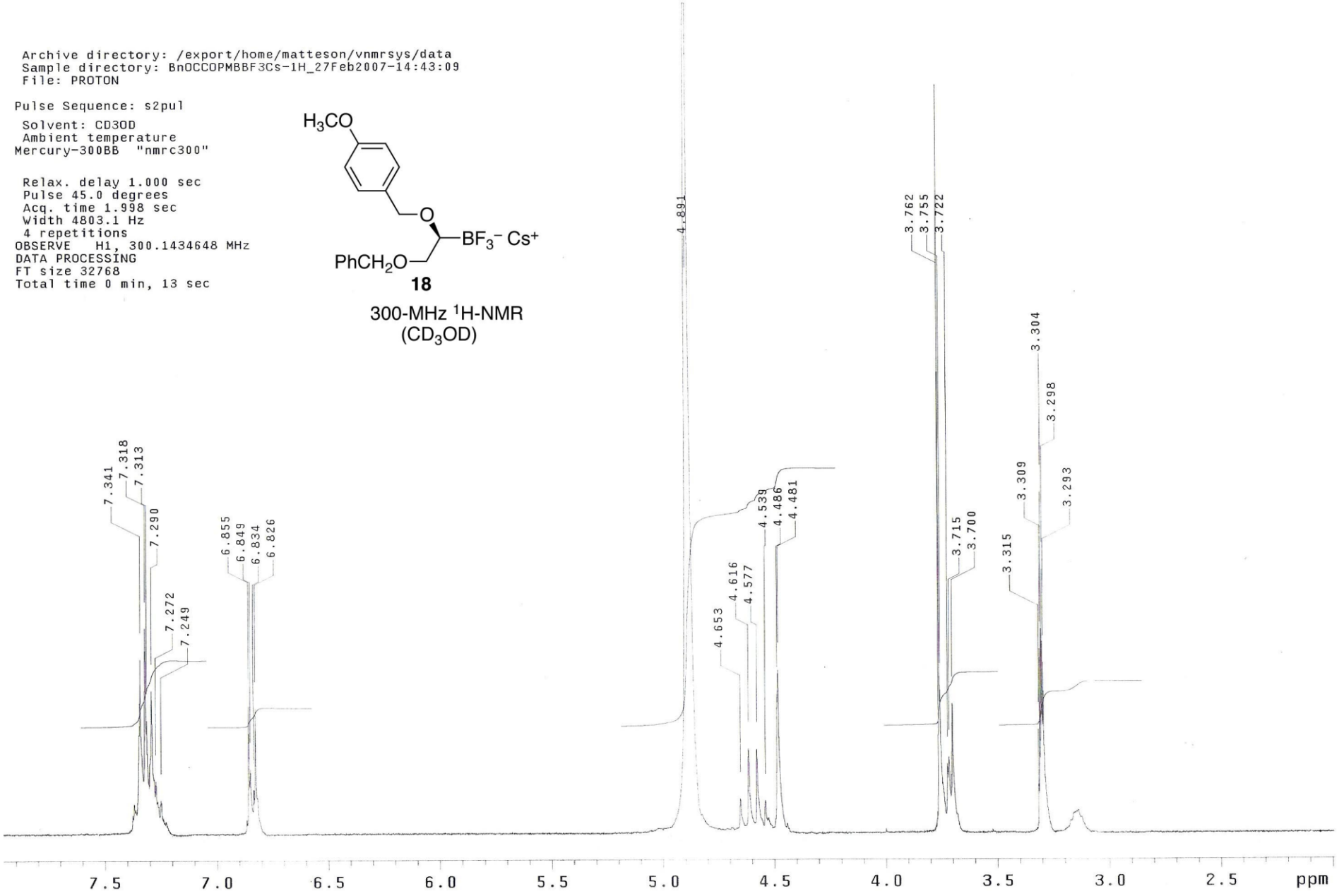
β-14d

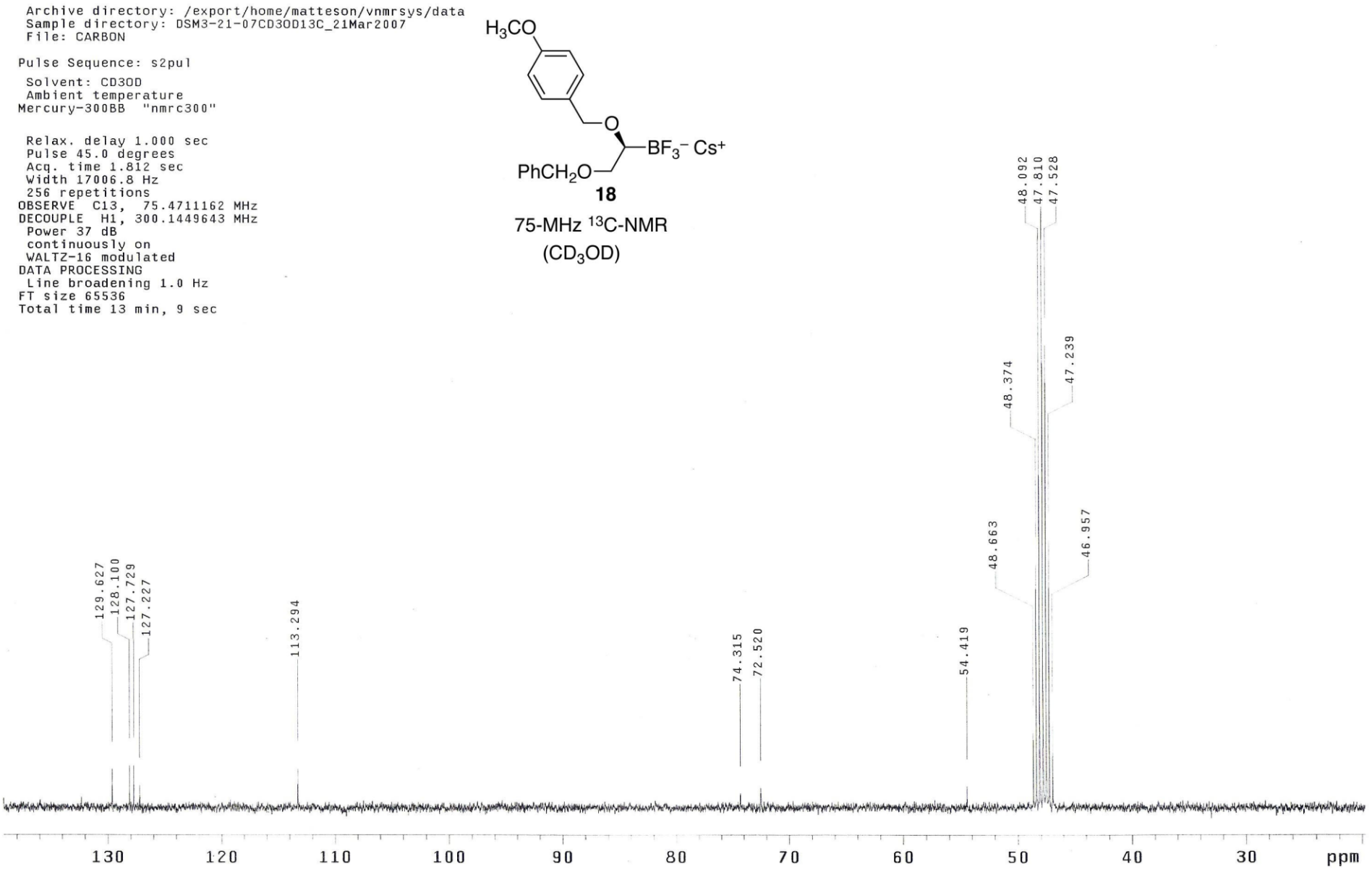
300-MHz ^{1}H-NMR (CD_3OD:D_2O 2:1)

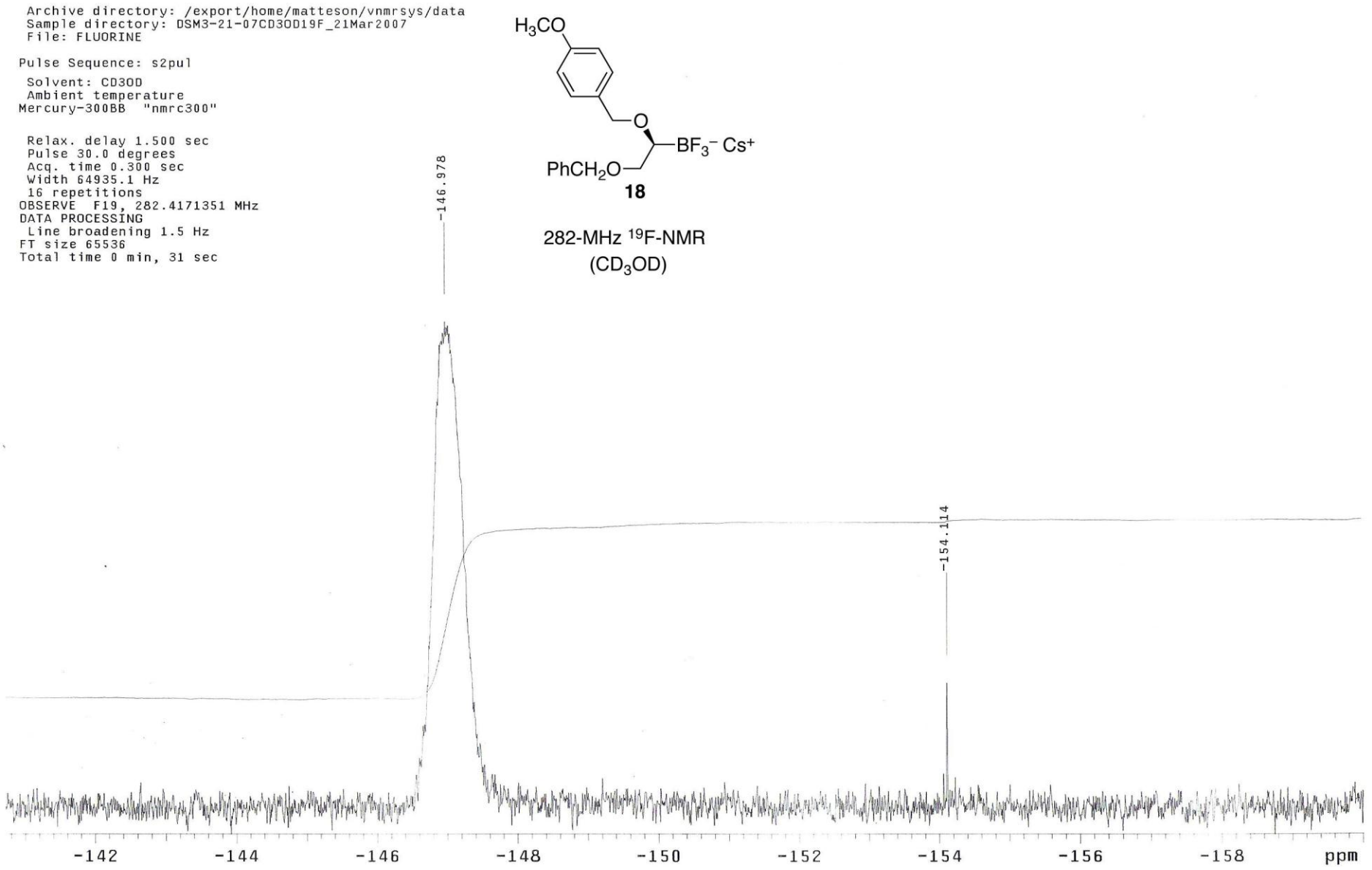










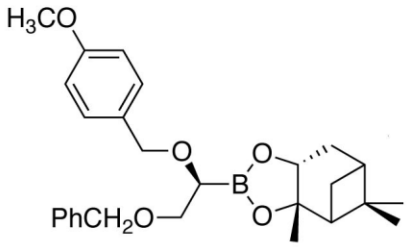


STANDARD 1H OBSERVE

Archive directory: /export/home/matteson/vnmrsys/data
Sample directory: BnOCC(OPMB)B+PD1H_03Apr2007
File: PROTON

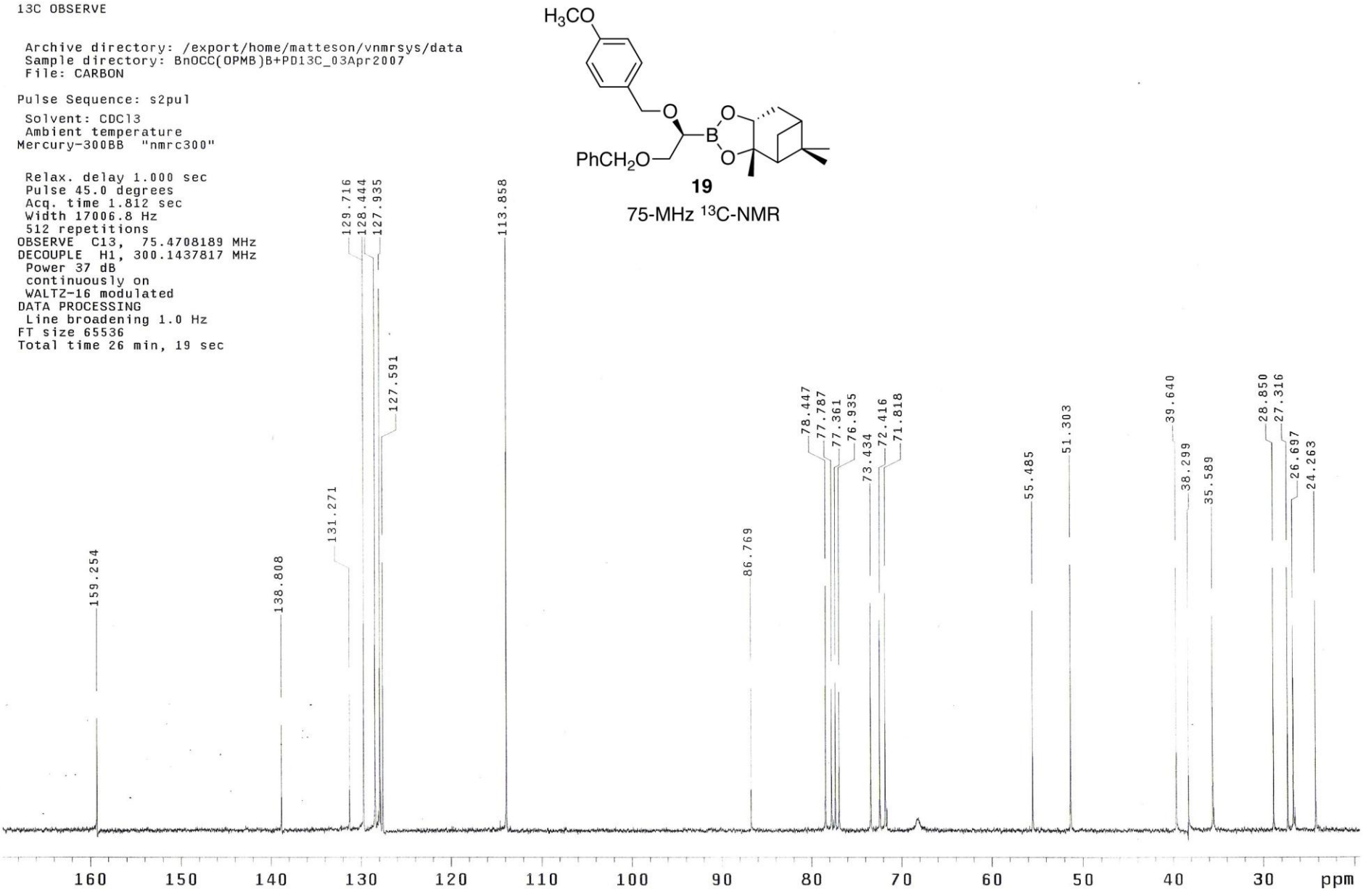
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "nmrc300"

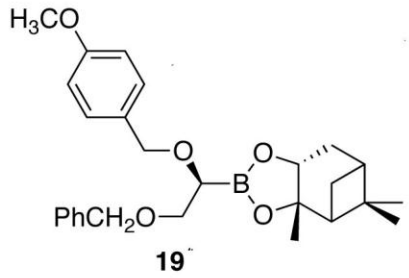
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4803.1 Hz
4 repetitions
OBSERVE H1, 300.1422879 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 13 sec



19

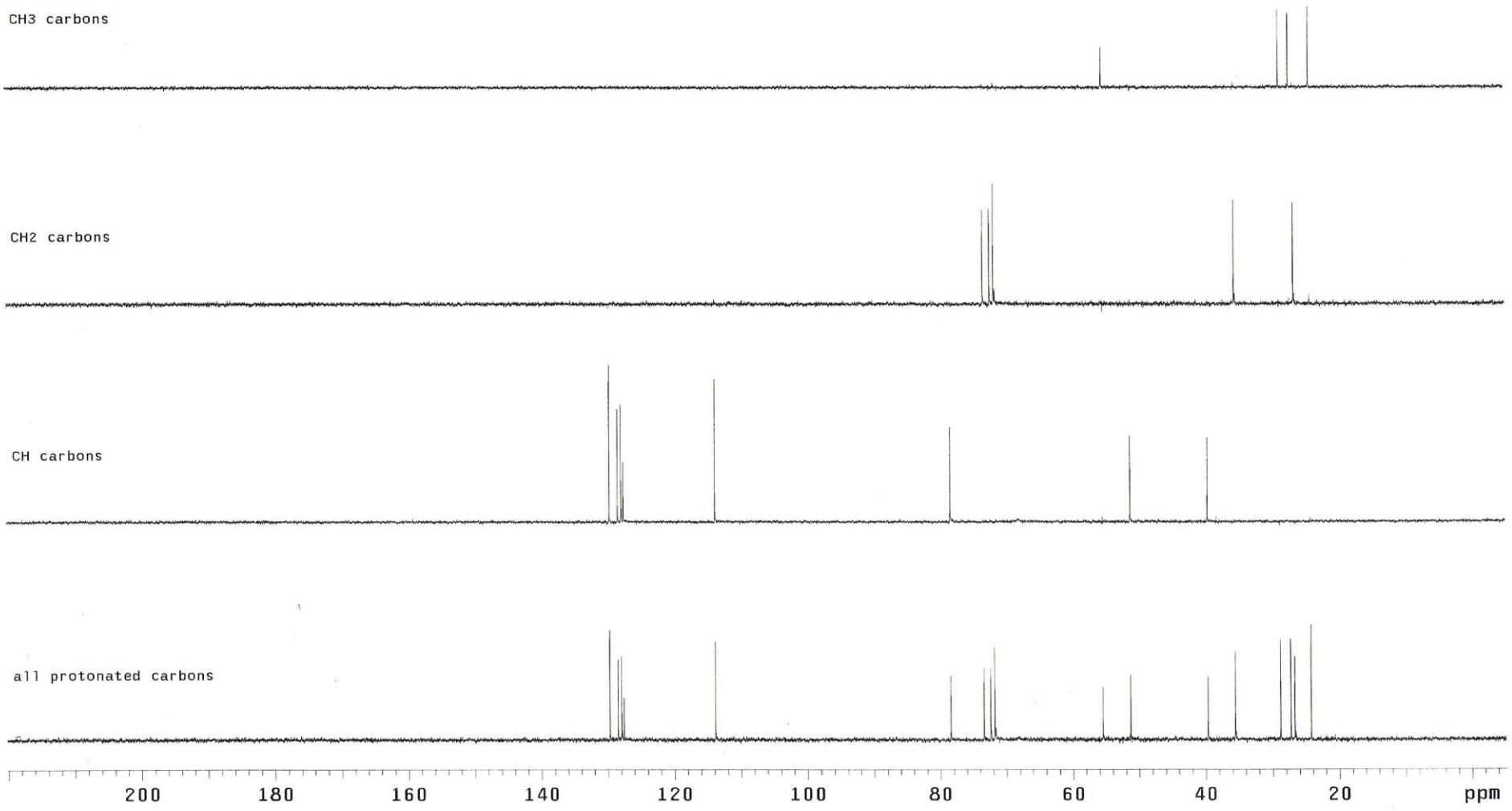
300-MHz ^{1}H-NMR

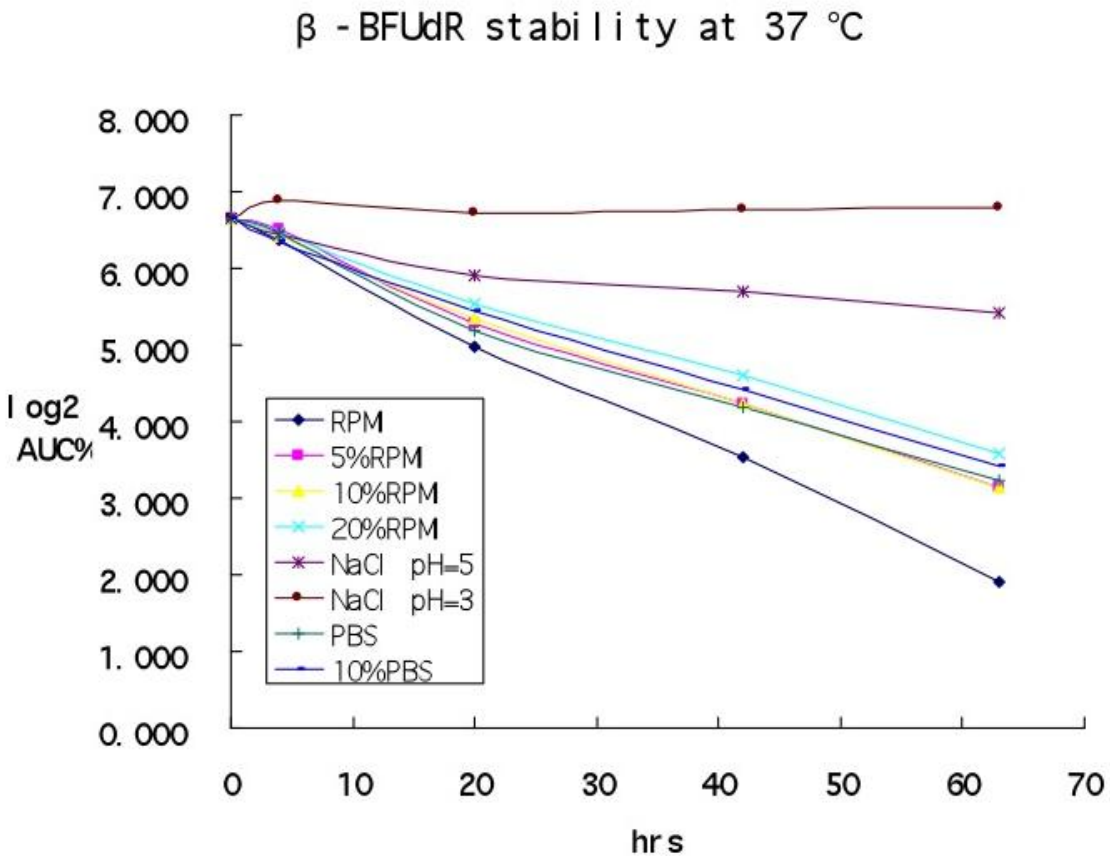




19

DEPT NMR



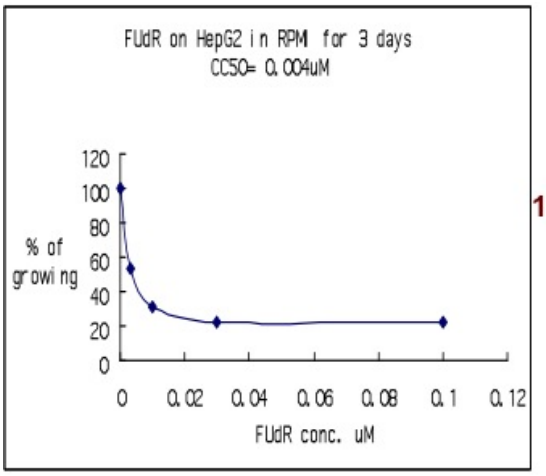


AUC = area under curve, integrated HPLC signal. RPM is RPMI-1640, 10%RPM is 10% bovine fetal serum/90% RPMI-1640, PBS is phosphate, BFUdR is **β-14b**.

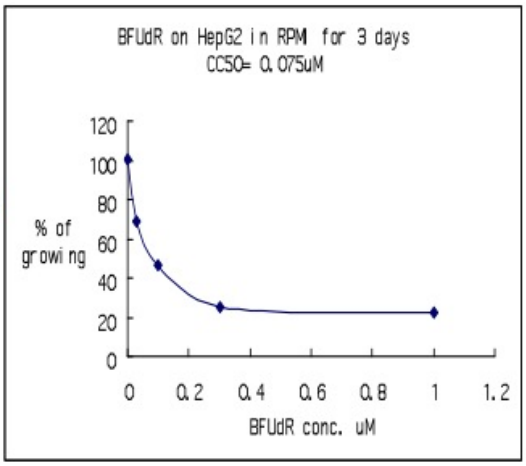
Half life of β-BFUdR in different conditions at 37 ℃

condition	T1/2(hrs)
RPMI pH=7.4	13.4
5 % FBS-RPMI pH=7.4	17.7
10 % FBS-RPMI pH=7.4	18.0
20 % FBS-RPMI pH=7.4	20.6
150 mM Nacl pH=5	54.1
150 mM Nacl pH=3	stable
PBS pH=7.4	18.3
10 % FBS-PBS pH=7.4	19.8

RPMI	y = -0.0747x + 6.612
	R2 = 0.9983
5%FBS-RPMI	y = -0.0564x + 6.6142
	R2 = 0.9933
10%FBS-RPMI	y = -0.0556x + 6.5915
	R2 = 0.9973
20%FBS-RPMI	y = -0.0485x + 6.6214
	R2 = 0.9976
150mM Nacl pH=5	y = -0.0185x + 6.4973
	R2 = 0.9268
150Mm Nacl pH=3	stable
PBS	y = -0.0545x + 6.5508
	R2 = 0.9861
10%FBS-PBS	y = -0.0506x + 6.5558
	R2 = 0.997



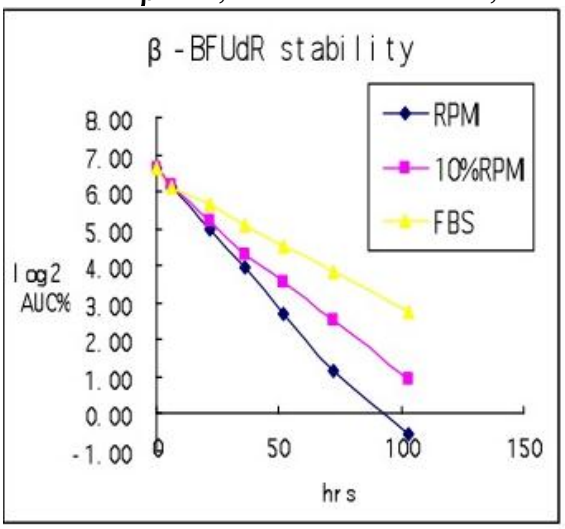
19 fold

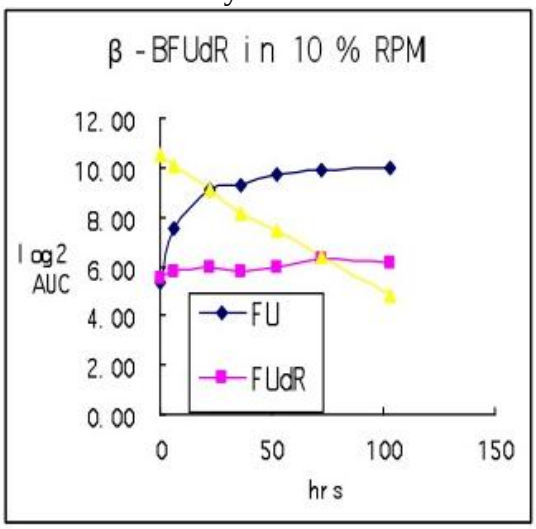


	β-BFUdR in 10% RPMI		
hrs	FU%	FUdR%	β-BFUdR%
0	4.6	3.0	92.4
4	10.9	5.5	83.6
20	45.3	6.9	47.8
42	69.3	7.6	23.0
63	81.7	7.7	10.5

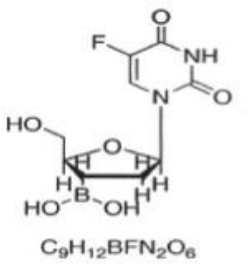
In 63 hrs, about 5% β-BFUdR was converted into FUdR, which might explain the phenomenon that the cytotoxicity of β-BFUdR is about 5% of FUdR.

BFUdR is **β-14b**, FU is 5-fluorouracil, FUdR is 5-fluoro-2´-deoxyuridine.



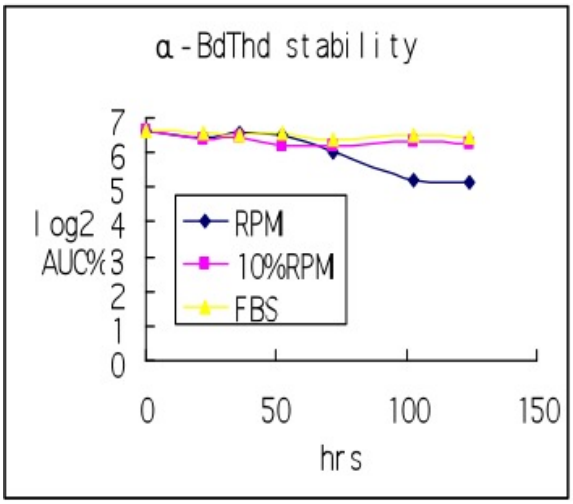


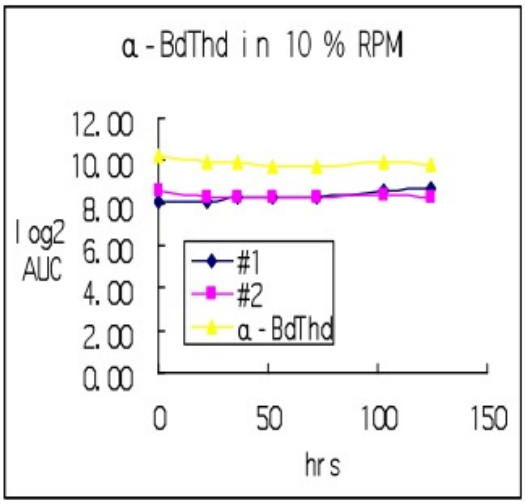
β-BFUdR	RPMI	10 % RPMI	FBS
T1/2 (hrs)	14.1	18.3	27.3



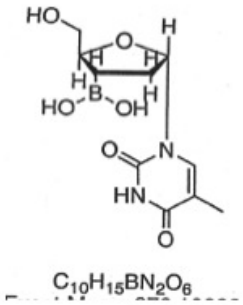
$C_9H_{12}BFN_2O_6$

β-BFUdR





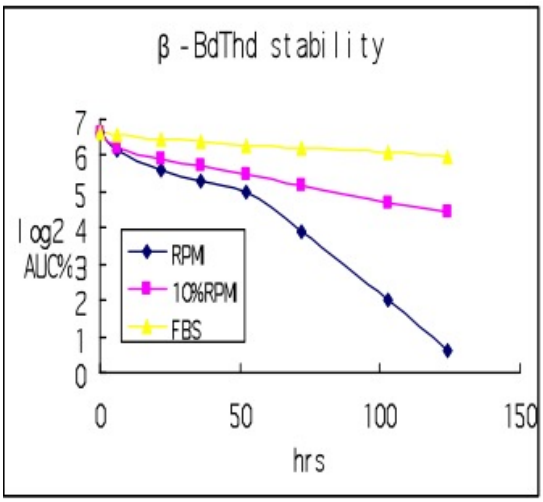
α-BdThd	RPMI	10 % RPMI	FBS
T1/2(hrs)	72.5	454.5	769.2

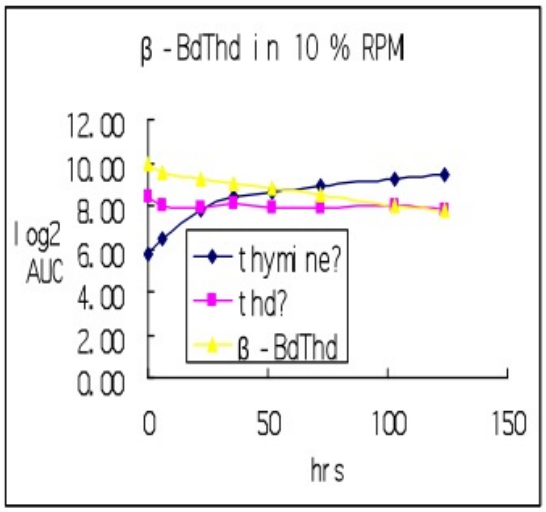


$C_{10}H_{15}BN_2O_6$

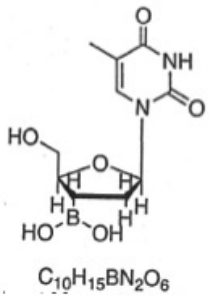
α-BdThd

BdThd is **14a**, Thd is thymidine.



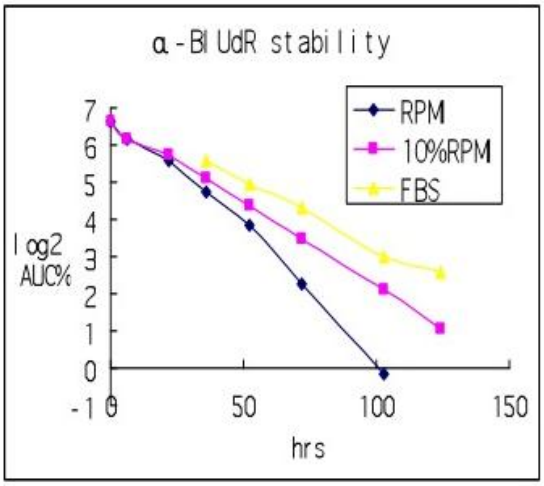


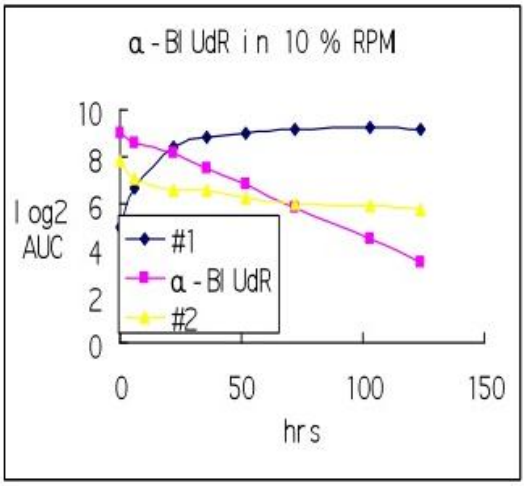
β-BdThd	RPMI	10 % RPMI	FBS
T1/2 (hrs)	21.8	61.3	192.3



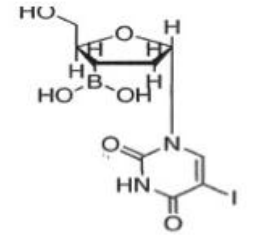
$C_{10}H_{15}BN_2O_6$

β-BdThd





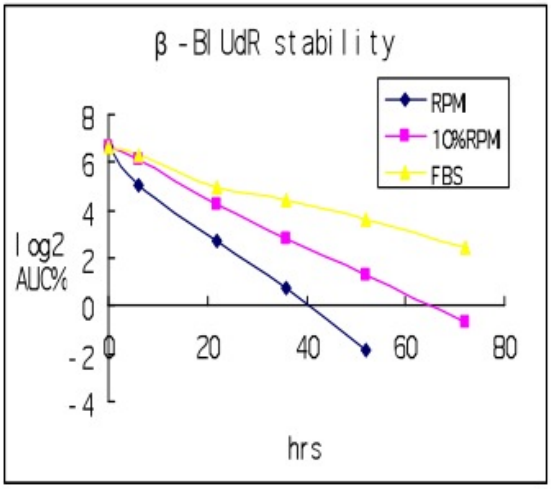
α-BIUdR	RPMI	10 % RPMI	FBS
T1/2(hrs)	15.5	22.6	28.3

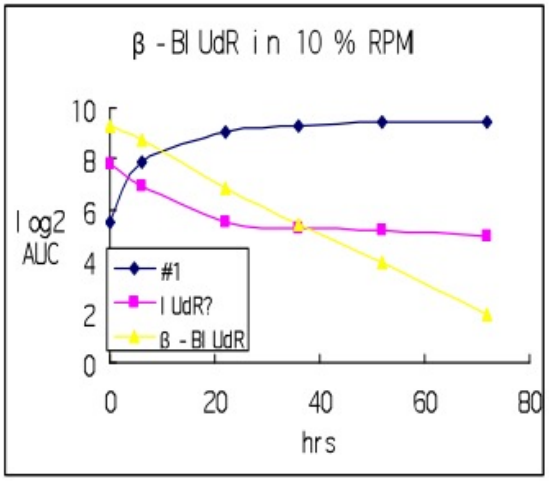


$C_9H_{12}BIN_2O_6$

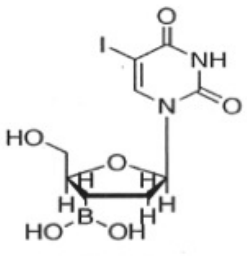
α-BIUdR

BIUdR is **14c**, IUdR is 5-iodo-2´-deoxyuridine.



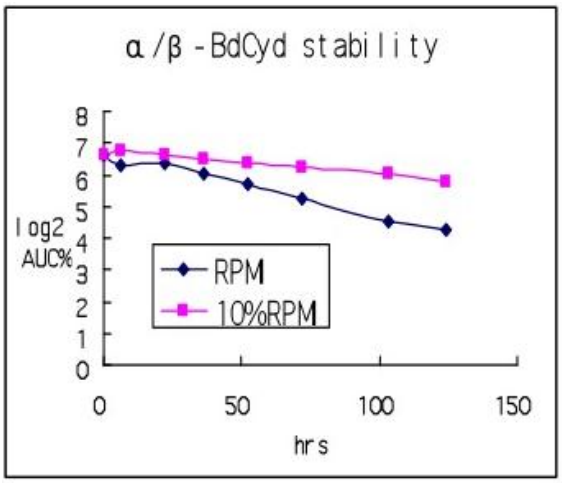


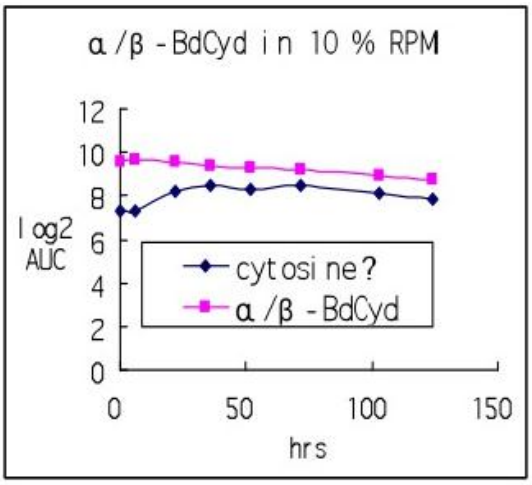
β-BIUdR	RPMI	10 % RPMI	FBS
T1/2(hrs)	6.4	9.7	17.5



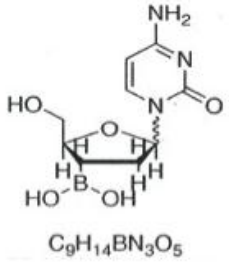
$C_9H_{12}BIN_2O_6$

β-BIUdR





α/β-BdCyd	RPMI	10 % RPMI	FBS
T1/2 (hrs)	51.8	138.9	400.0



$C_9H_{14}BN_3O_5$

α/β-BdCyd

BdCyd is **14d**.

Stability of the compounds at 37 ℃			
T1/2(hrs)	RPMI	10 % RPMI	FBS
β-BFUdR	14.1	18.3	27.3
α-BdThd	72.5	454.5	769.2
β-BdThd	21.8	61.3	192.3
α-BIUdR	15.5	22.6	28.3
β-BIUdR	6.4	9.7	17.5
α/β-BdCyd	51.8	138.9	400.0
IUdR	769.2	625.0	166.7
FUdR	stable	stable	