

# **A New Route to 2'-*O*-Alkyl-2-thiouridine Derivatives *via* 4-*O*-Protection of the Uracil Base and Hybridization Properties of Oligonucleotides Incorporating These Modified Nucleoside Derivatives**

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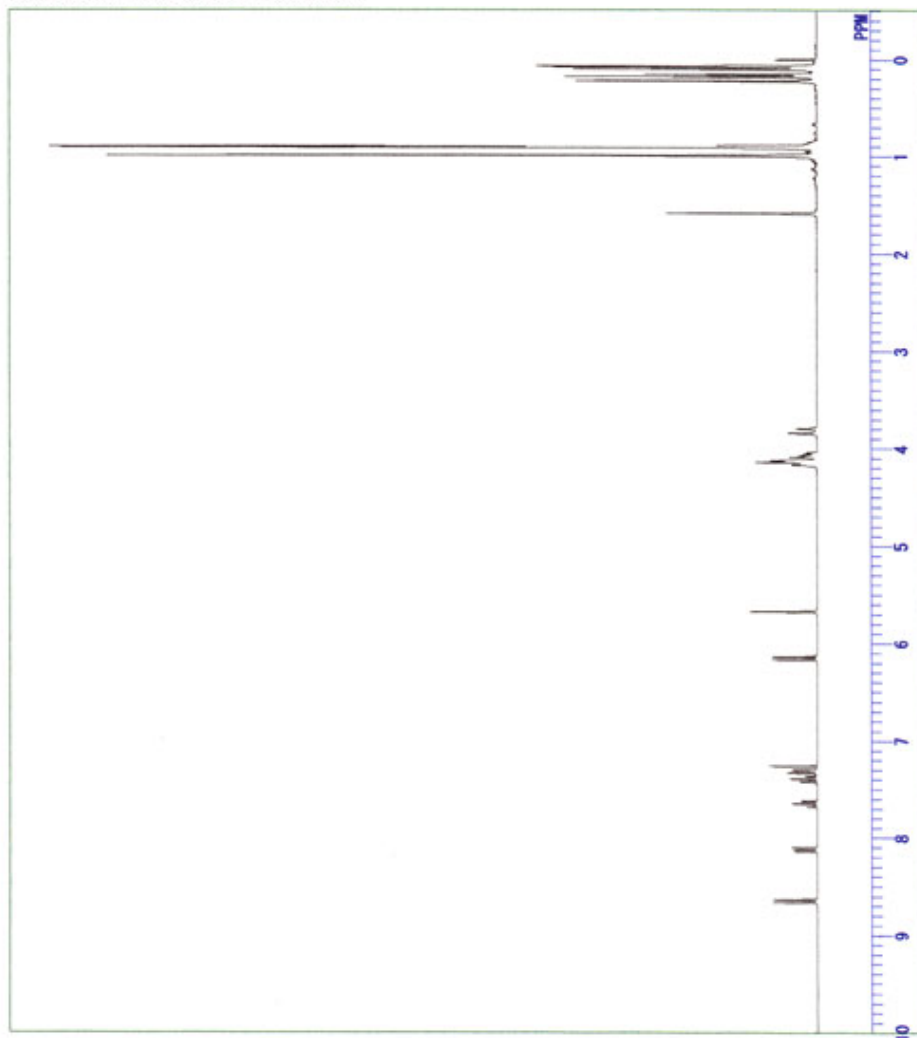
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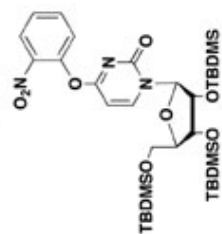
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**General.**  $^1\text{H}$  NMR spectra were recorded at 270 MHz and the chemical shifts were measured from tetramethylsilane (in  $\text{CDCl}_3$ ) as an internal standard or DSS (in  $\text{D}_2\text{O}$ ) as an external standard.  $^{13}\text{C}$  NMR spectra were recorded at 68 MHz and the chemical shifts were measured from  $\text{CDCl}_3$  (77 ppm) as an internal standard or DSS (0 ppm, in  $\text{D}_2\text{O}$ ) as the external standard.  $^{31}\text{P}$  NMR spectra were recorded at 109 MHz and the chemical shifts were measured from 85%  $\text{H}_3\text{PO}_4$  as an external standard. The  $^1\text{H}$ - $^1\text{H}$  coupling constants were measured at 400 MHz at 25 °C. Pyridine was distilled twice from *p*-toluenesulfonyl chloride and  $\text{CaH}_2$  after being refluxed for several hours and stored over molecular sieves 4A. The other dry solvents were purchased and stored over molecular sieves 4A. TLC was performed on precoated glass plates of silica gel. Column chromatography was carried out with silica gel C-200 and C-60. The solid-phase synthesis of oligonucleotides was carried out on a DNA/RNA synthesizer model 392 using normal phosphoramidite protocol. Reversed-phase HPLC was performed using a C18 column with a linear gradient (0-30%) starting from 0.1 M  $\text{NH}_4\text{OAc}$  (pH 7.0) and applying  $\text{CH}_3\text{CN}$  at a flow rate of 1.0 mL/min for 30 min at room temperature. Anion-exchange HPLC was performed on an HPLC apparatus using a FAX column with a linear gradient (0-25%) starting from 25 mM phosphate buffer (pH 6.0) and applying 25 mM phosphate buffer containing 1 M  $\text{NaCl}$  (pH 6.0) at a flow rate of 1.0 mL/min at 50 °C. The MALDI-TOF mass spectrometry was carried out.

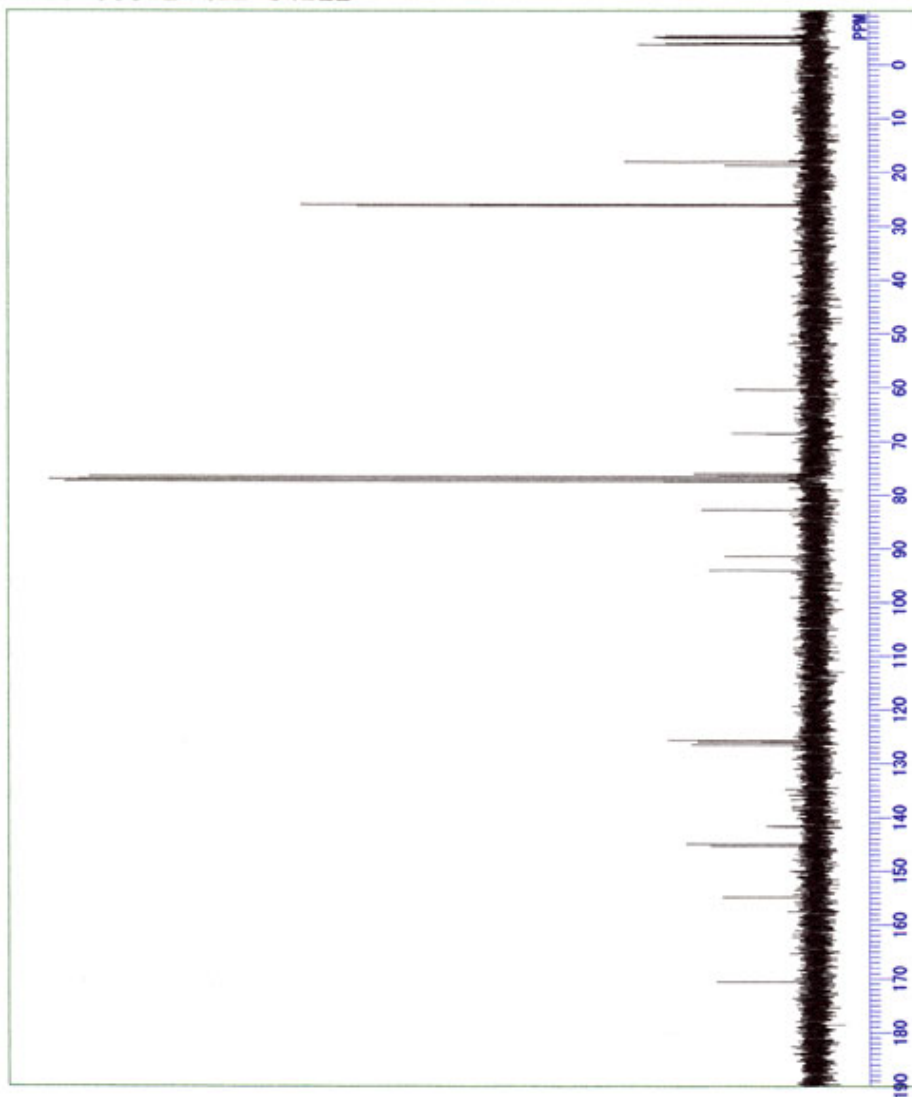
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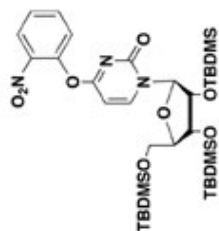
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<sup>13</sup>C NMR spectrum





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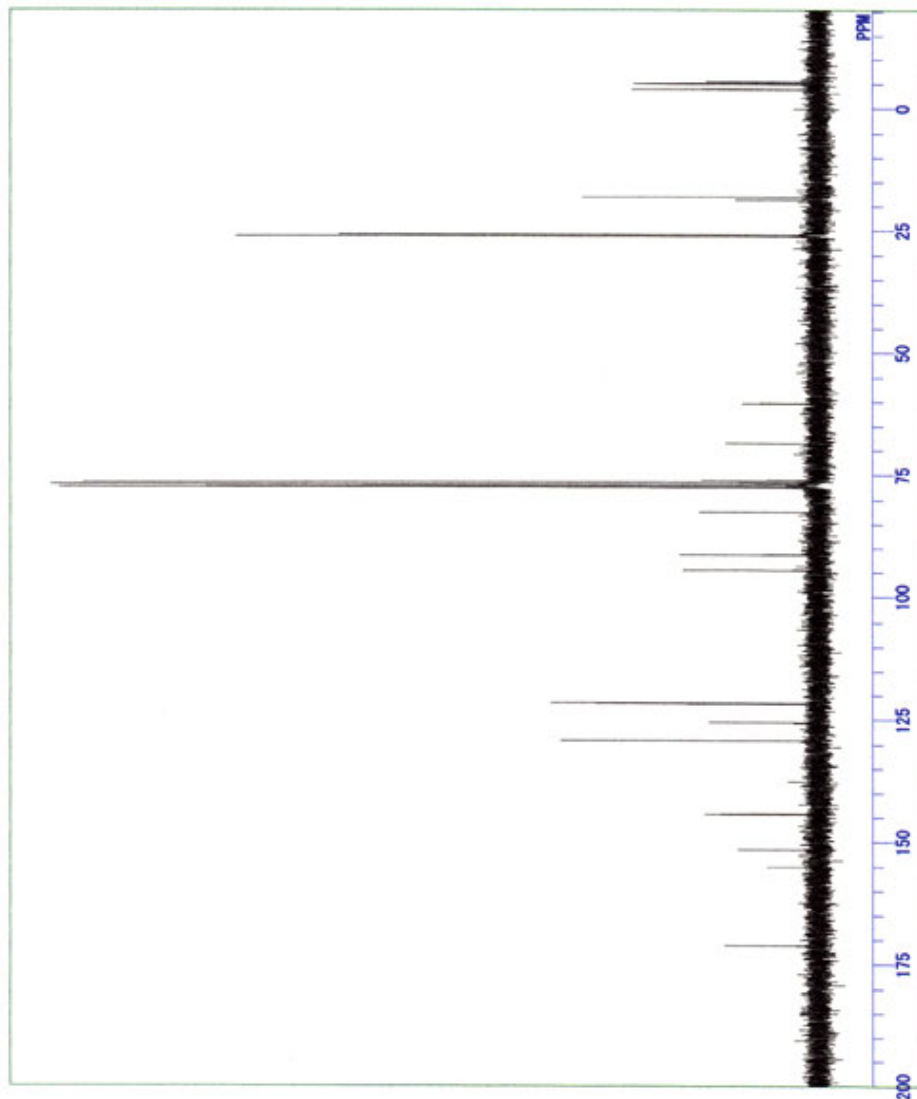
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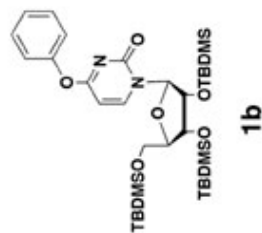
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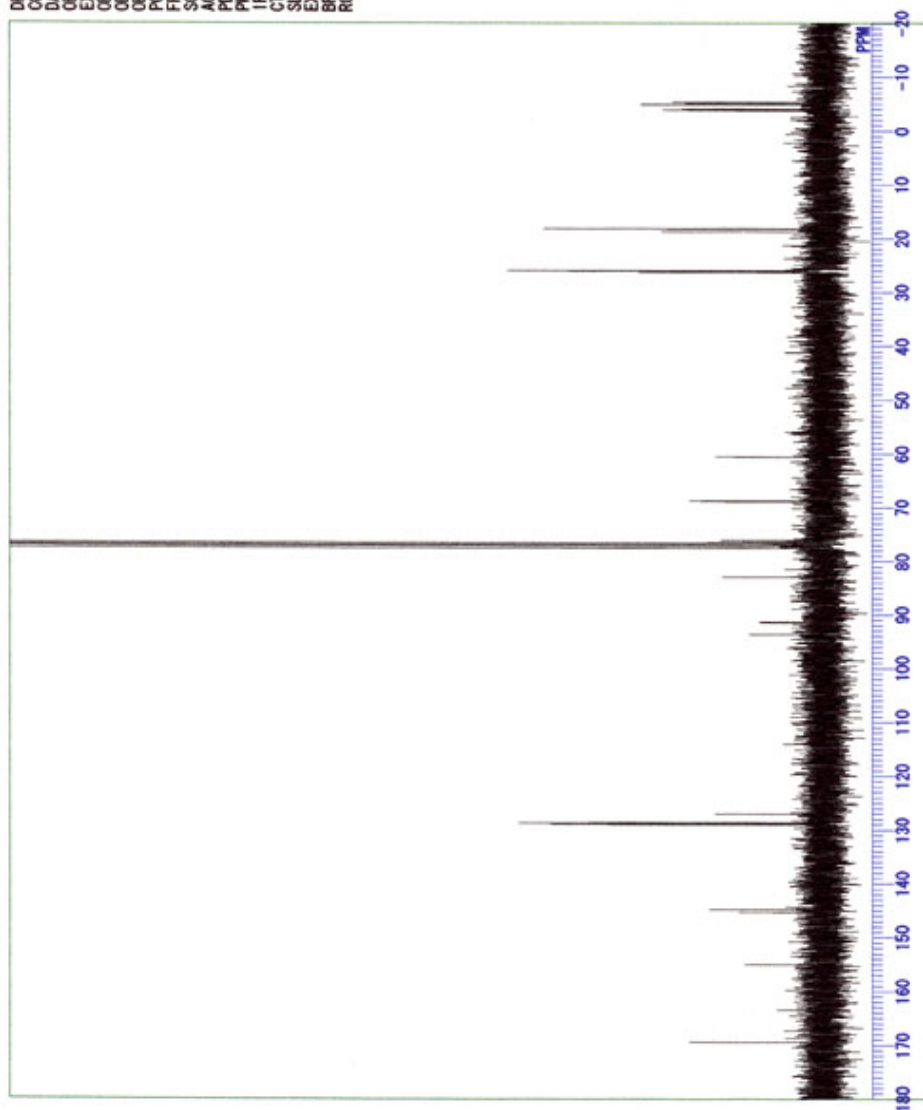
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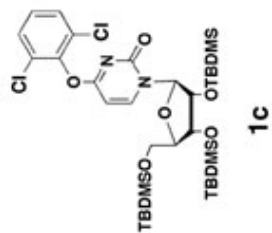




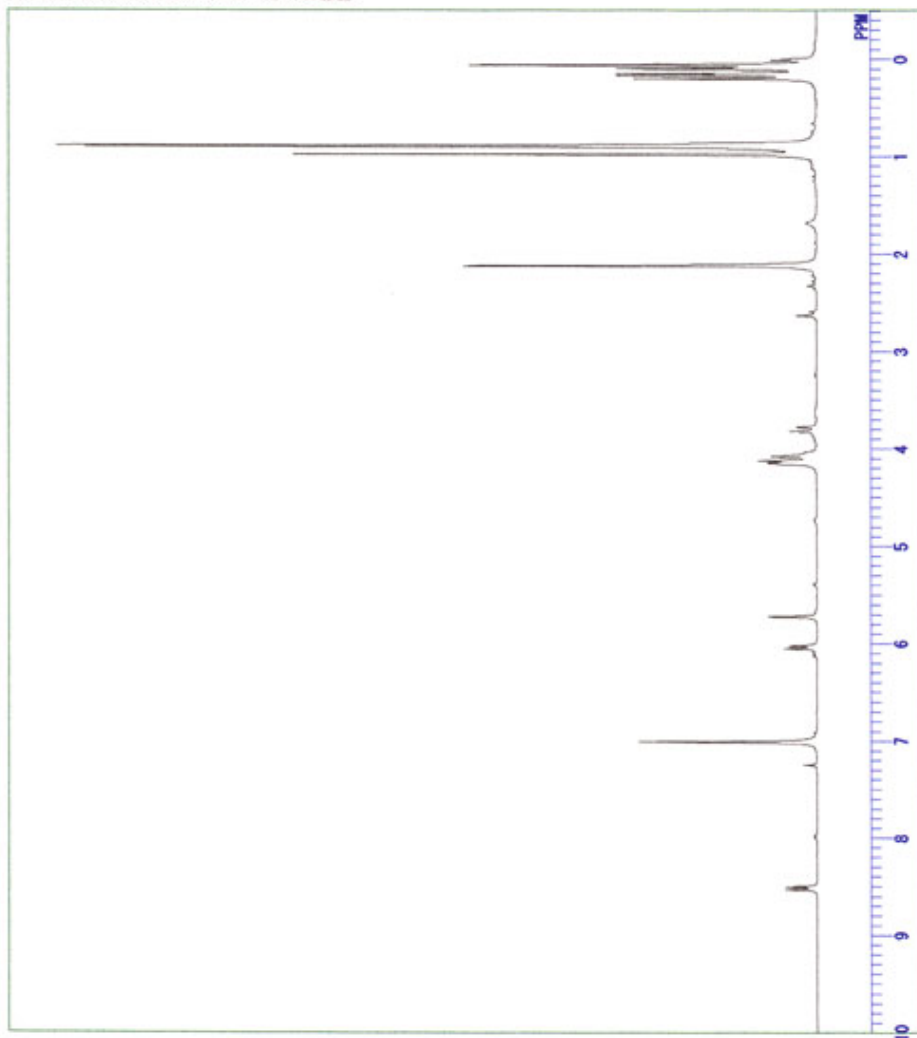
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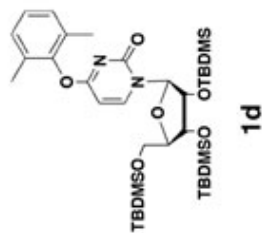
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 RGAIN 14



<sup>1</sup>H NMR spectrum



DF:FILE C:\Nly Documents\Kokamoto\dimethylPh4

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DATIM

ORNUC

EXMDO

ORFRO

ORSET

ORFIN

POINT

FREQD

SCANS

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PD

PW1

IRNUC

CTEMP

SLVNT

EXREF

BF

RGAIN

Tue May 13 14:26:31 2003

13C

BCM

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135.00 KHz

5200.0 Hz

32768

18315.0 Hz

220

1.789 sec

1.211 sec

4.4 us

1H

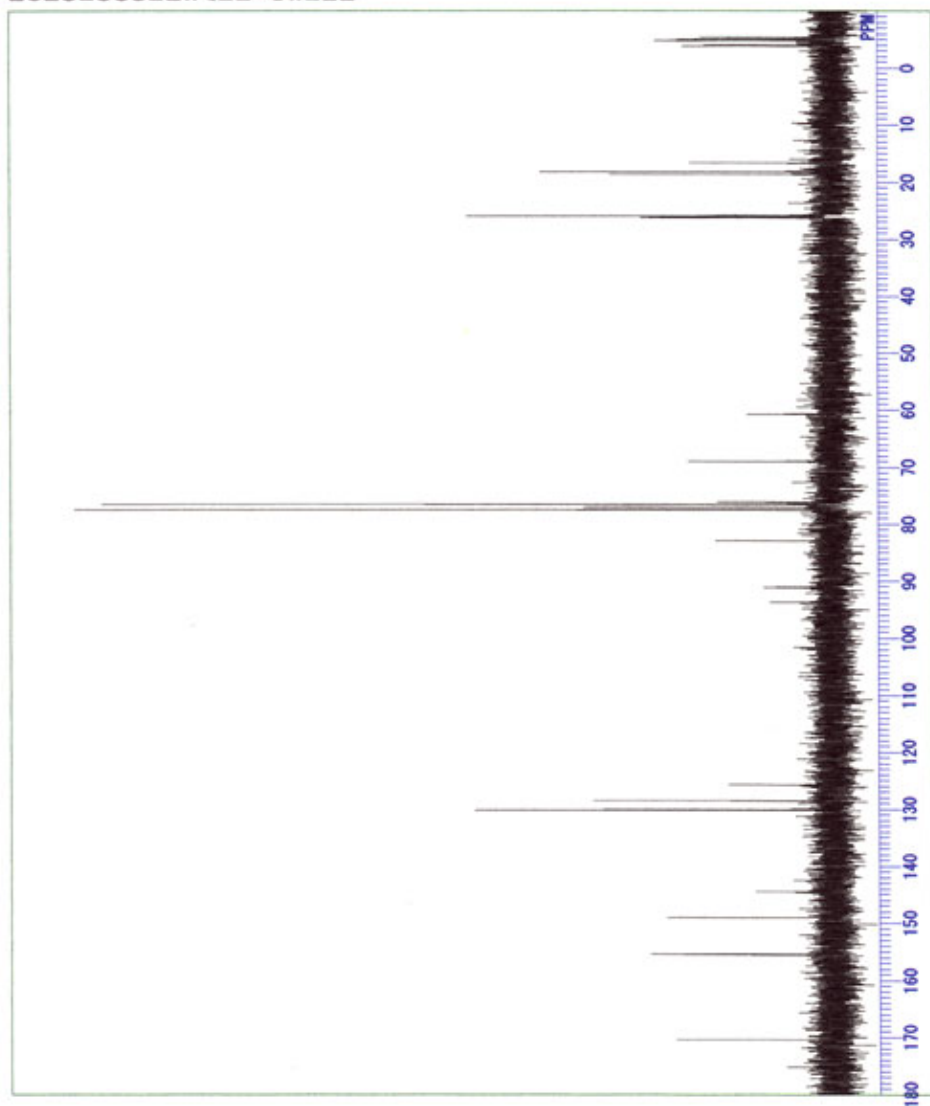
23.2 c

CDCL3

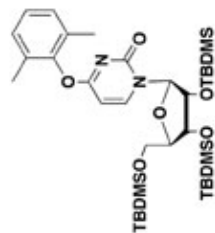
77.00 ppm

0.20 Hz

27



<sup>13</sup>C NMR spectrum



1d

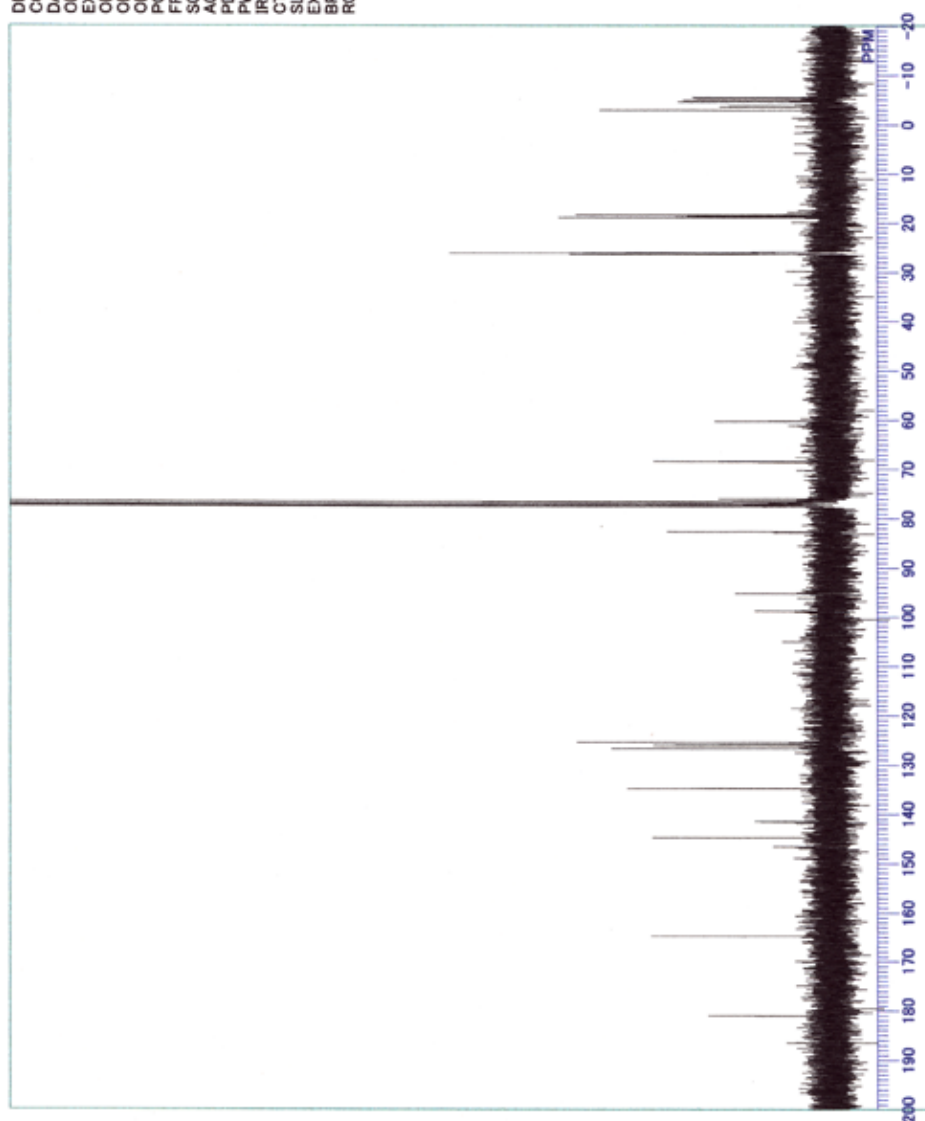


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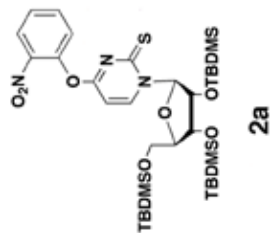
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RGAIN

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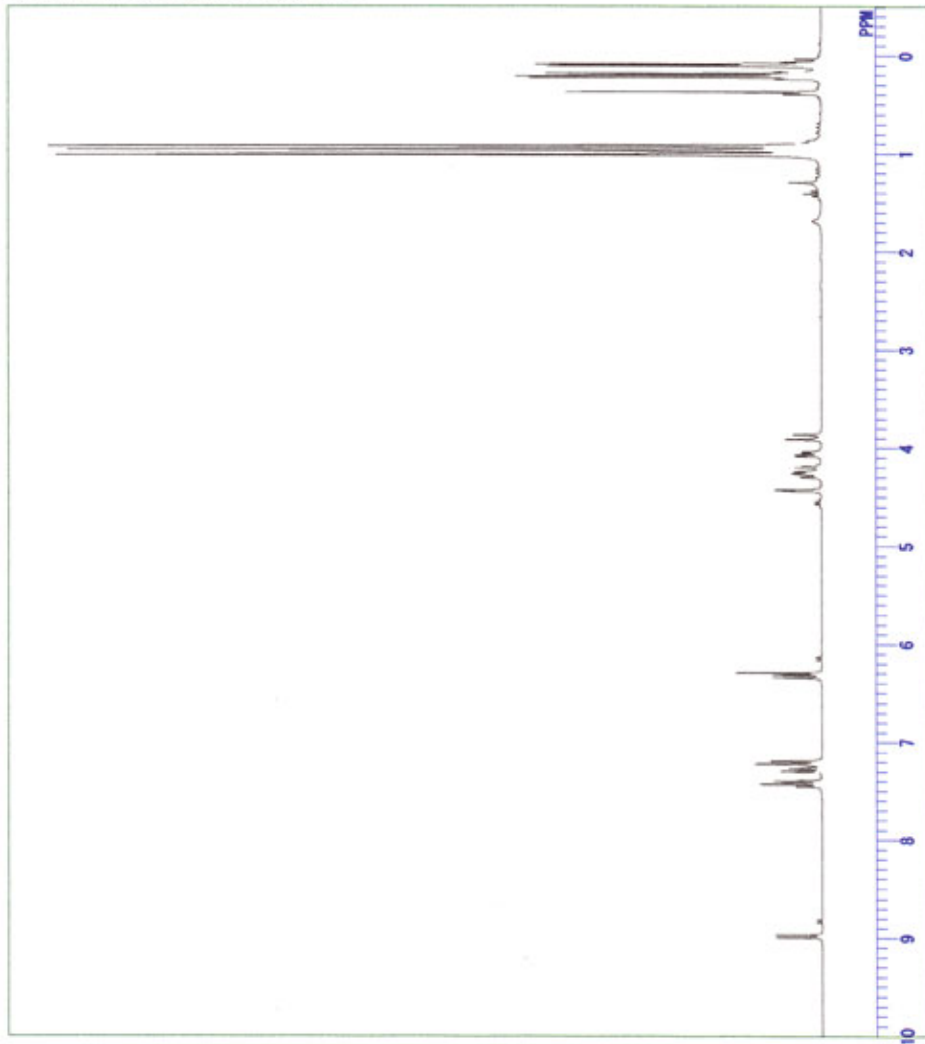


<sup>13</sup>C NMR spectrum

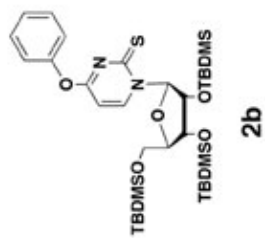


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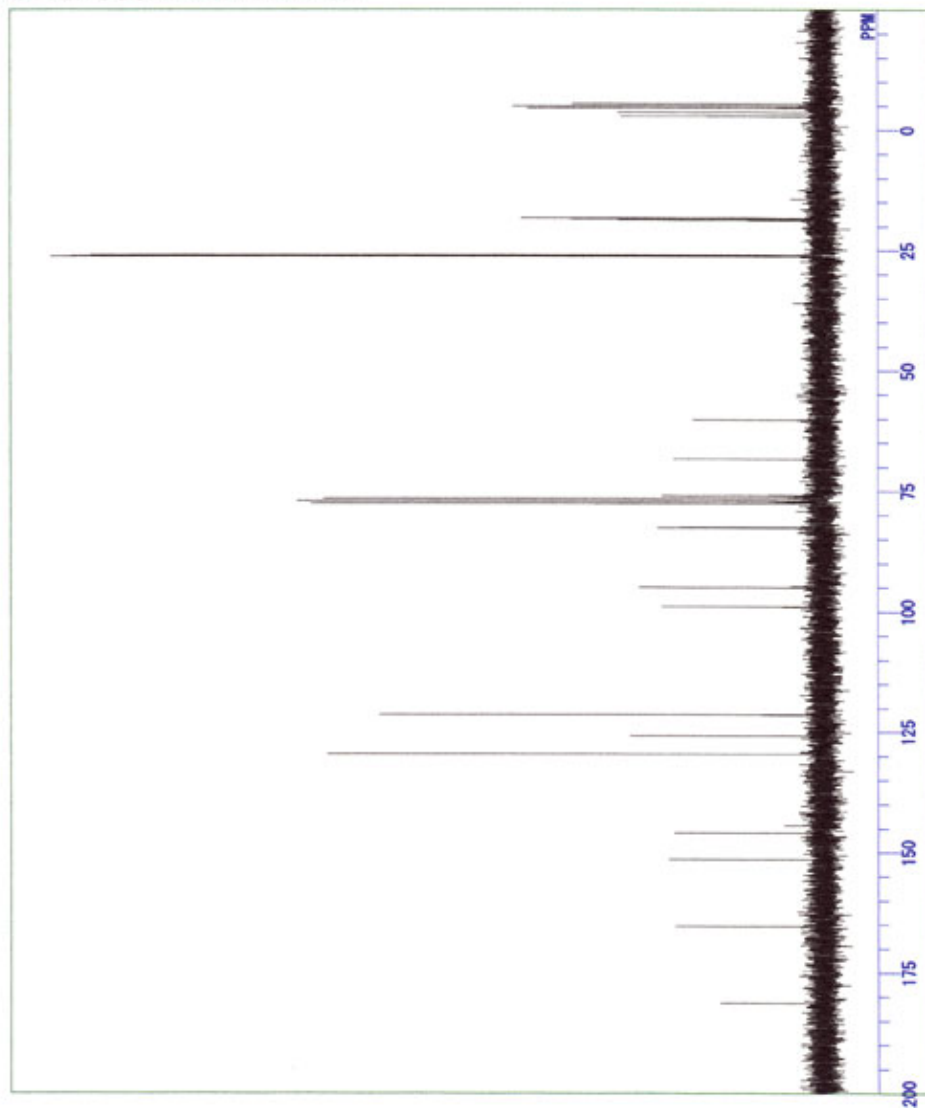


<sup>1</sup>H NMR spectrum

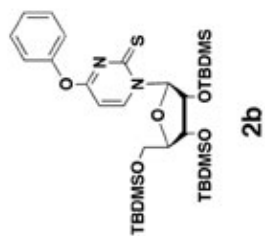


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<sup>13</sup>C NMR spectrum

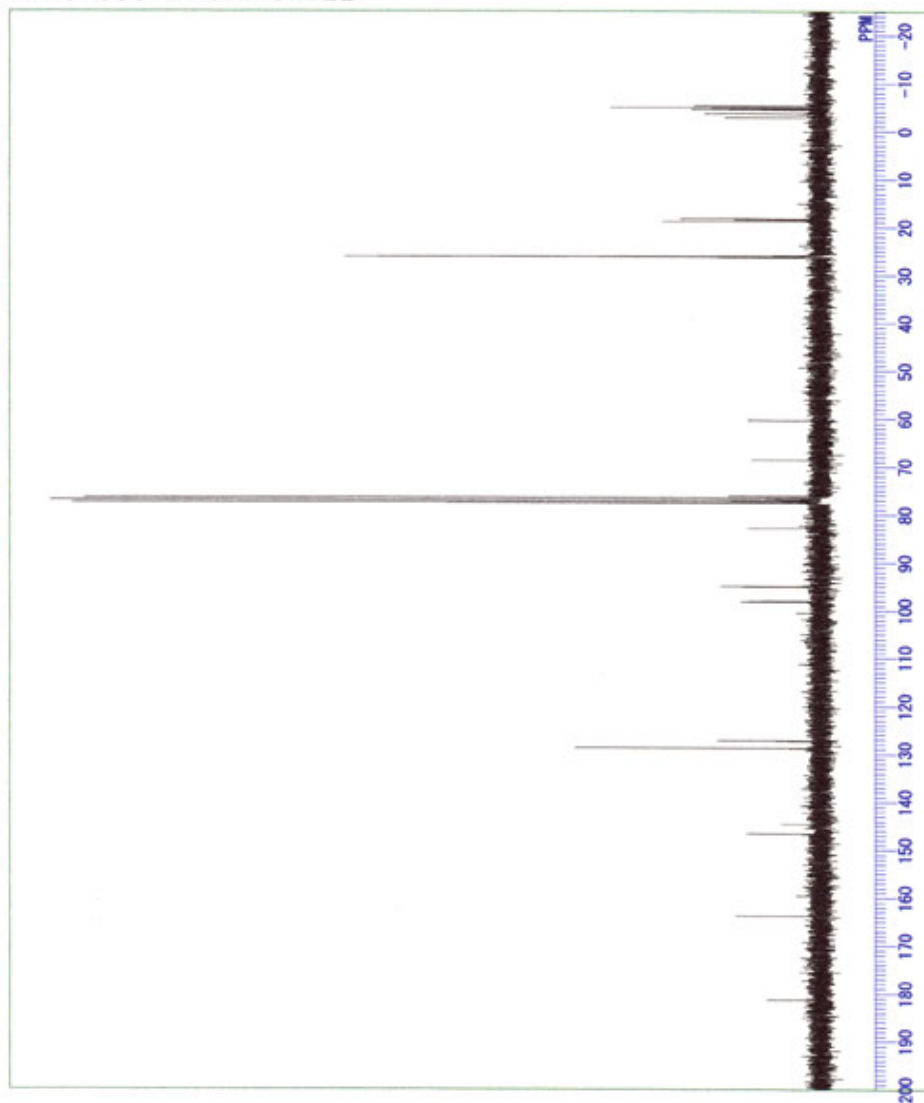




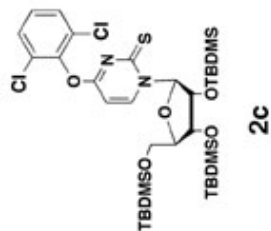


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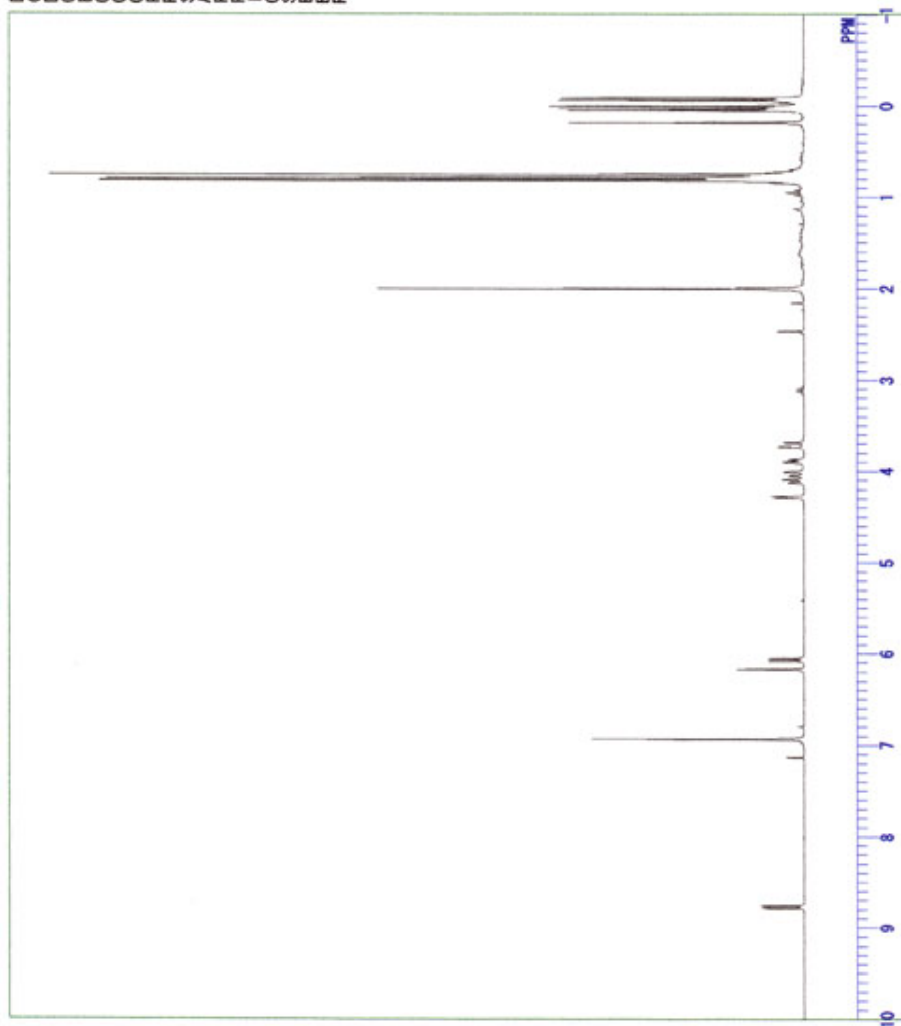
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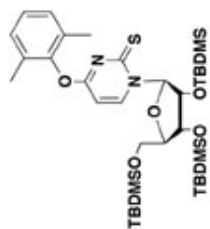
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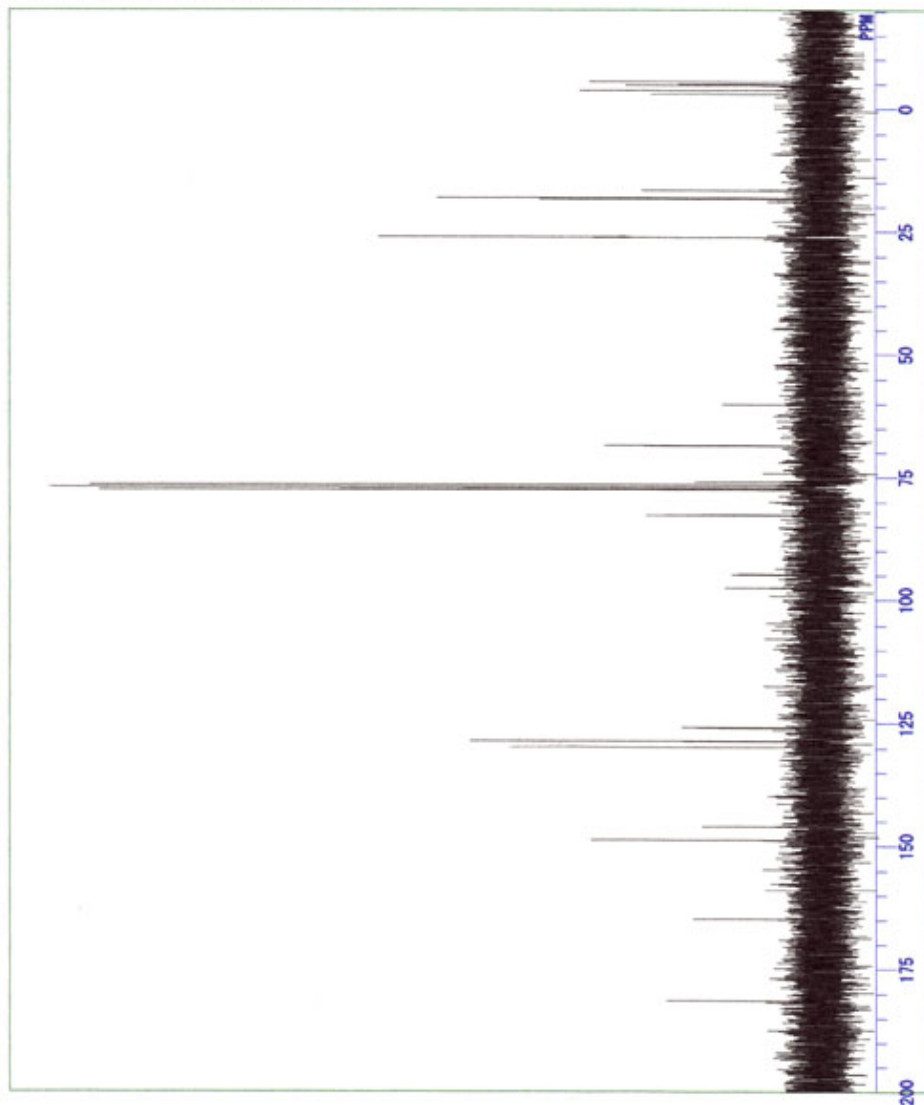


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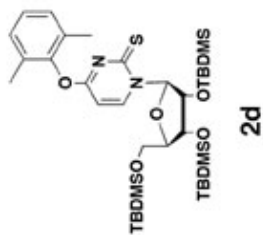


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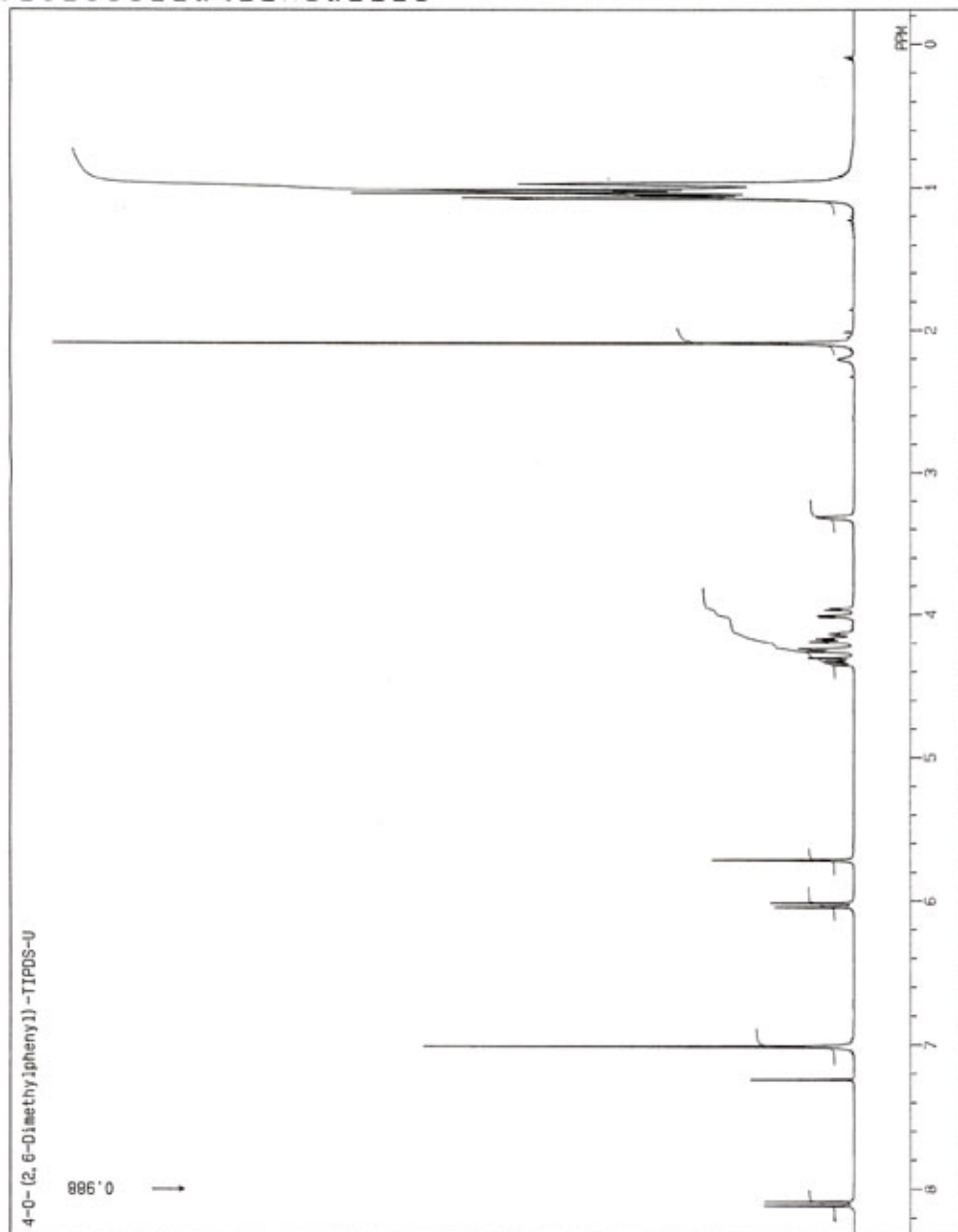
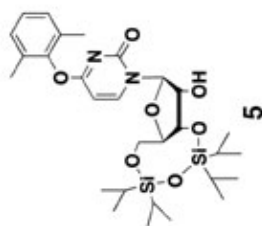


<sup>13</sup>C NMR spectrum



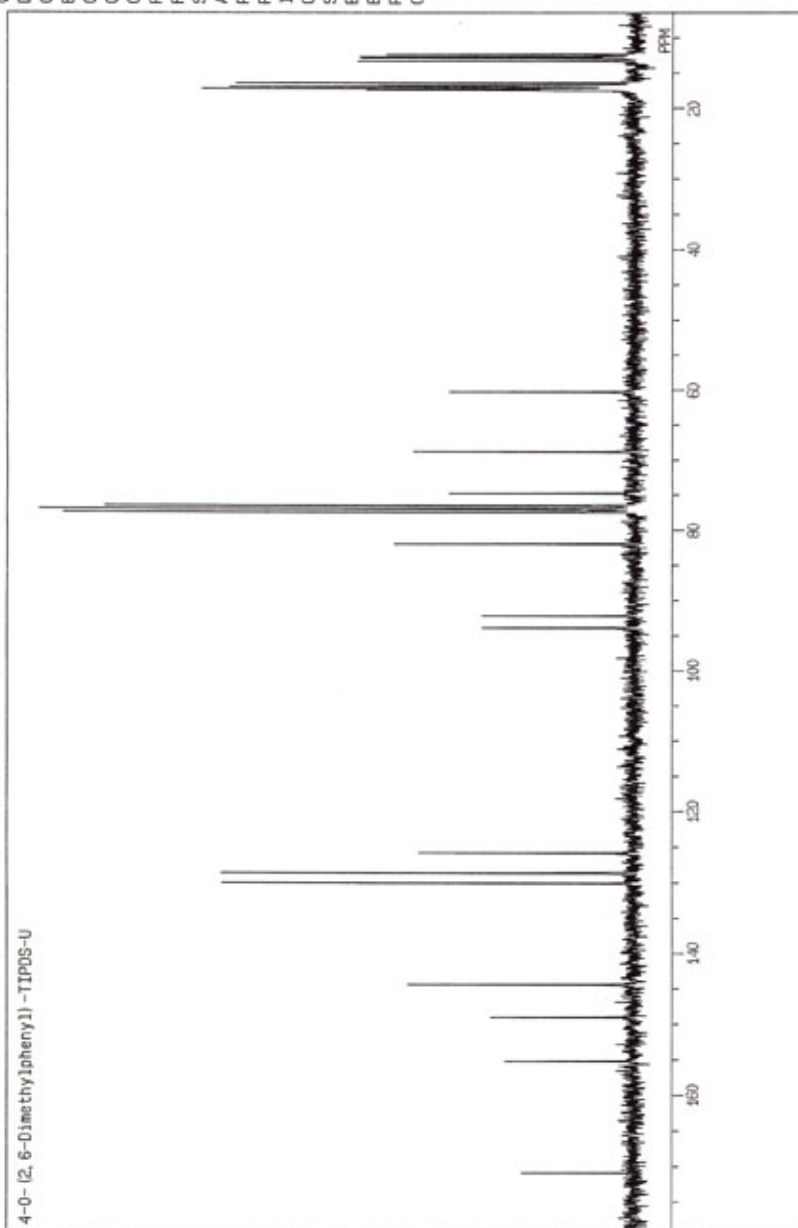
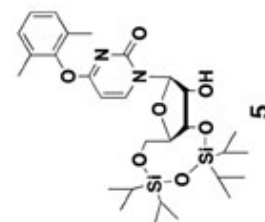
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<sup>1</sup>H NMR spectrum

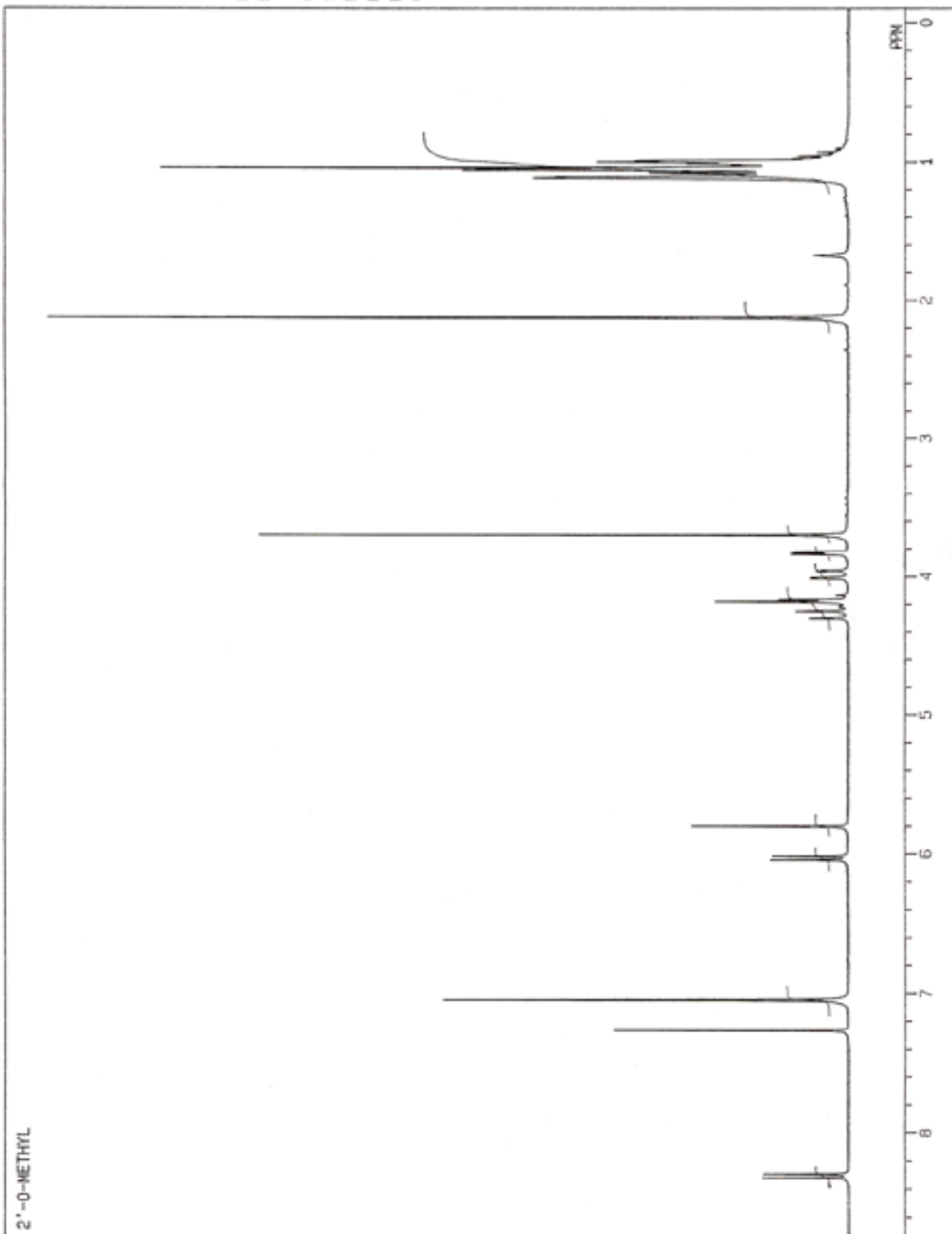


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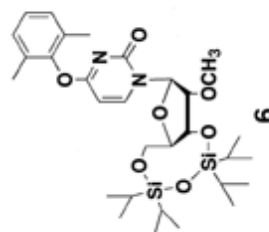
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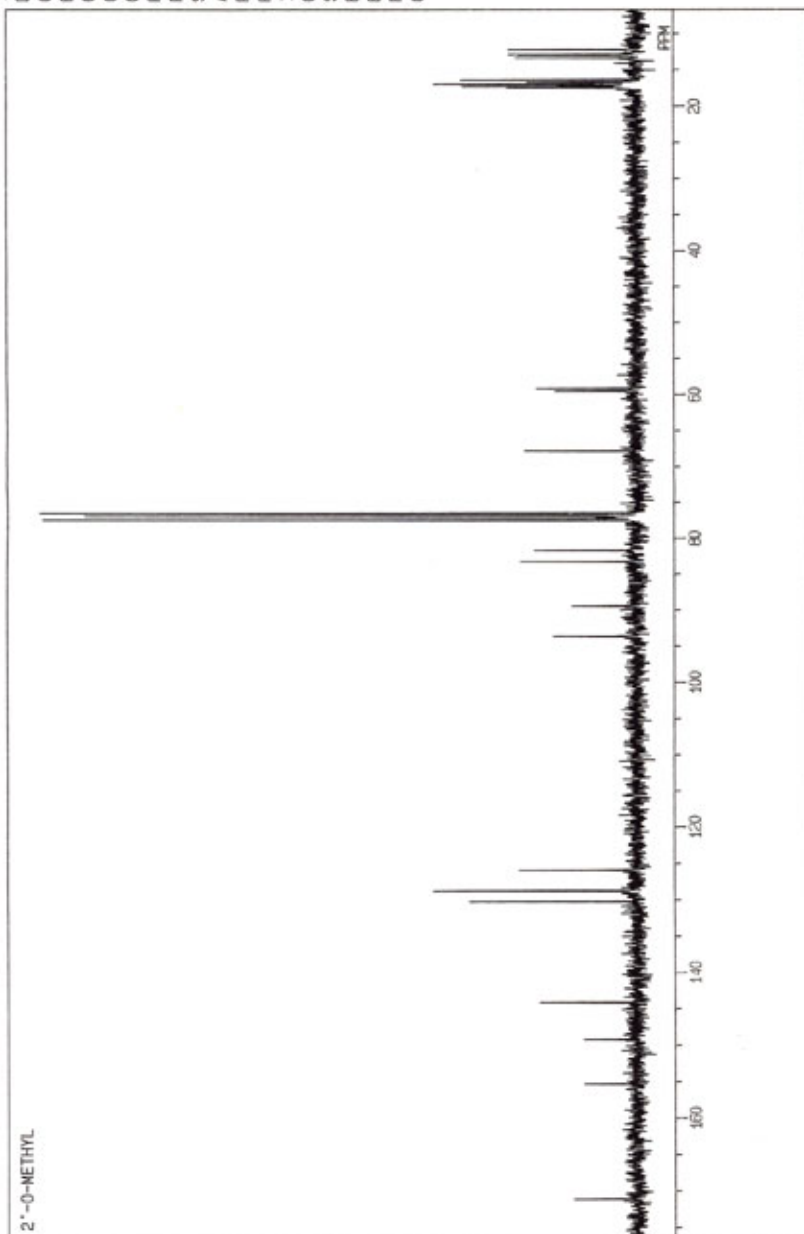
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 IRNUC 1H  
 CTEMP 25.2 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 BF 0.16 Hz  
 RGAIN 20  
 OPERATOR :



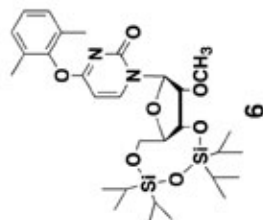
<sup>1</sup>H NMR spectrum



10-JUN-00 01:48:08  
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 OBNUC 13C  
 EXMOD BCM  
 OFR 67.80 MHz  
 OBSET 135.00 kHz  
 OBFIN 5200.0 Hz  
 POINT 32768  
 FREQU 20000.0 Hz  
 SCANS 493  
 ACQTM 0.819 sec  
 PD 2.181 sec  
 PW1 4.4 US  
 IRRUC 1H  
 CTEMP 28.6 c  
 SLVNT CDCL3  
 EXREF 77.00 ppm  
 BF 1.22 Hz  
 RGAIN 24  
 OPERATOR :



<sup>13</sup>C NMR spectrum





4-0- [2, 6-Dimethylphenyl] -TIPDS-s2Um\_1H

OFFICE P2046H

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 (d, 2H, H<sub>A</sub>), 7.15 (d, 2H, H<sub>B</sub>), 6.85 (d, 2H, H<sub>C</sub>), 6.75 (d, 2H, H<sub>D</sub>), 6.65 (d, 2H, H<sub>E</sub>), 6.55 (d, 2H, H<sub>F</sub>), 6.45 (d, 2H, H<sub>G</sub>), 6.35 (d, 2H, H<sub>H</sub>), 6.25 (d, 2H, H<sub>I</sub>), 6.15 (d, 2H, H<sub>J</sub>), 6.05 (d, 2H, H<sub>K</sub>), 5.95 (d, 2H, H<sub>L</sub>), 5.85 (d, 2H, H<sub>M</sub>), 5.75 (d, 2H, H<sub>N</sub>), 5.65 (d, 2H, H<sub>O</sub>), 5.55 (d, 2H, H<sub>P</sub>), 5.45 (d, 2H, H<sub>Q</sub>), 5.35 (d, 2H, H<sub>R</sub>), 5.25 (d, 2H, H<sub>S</sub>), 5.15 (d, 2H, H<sub>T</sub>), 5.05 (d, 2H, H<sub>U</sub>), 4.95 (d, 2H, H<sub>V</sub>), 4.85 (d, 2H, H<sub>W</sub>), 4.75 (d, 2H, H<sub>X</sub>), 4.65 (d, 2H, H<sub>Y</sub>), 4.55 (d, 2H, H<sub>Z</sub>), 4.45 (d, 2H, H<sub>AA'</sub>), 4.35 (d, 2H, H<sub>AB'</sub>), 4.25 (d, 2H, H<sub>AC'</sub>), 4.15 (d, 2H, H<sub>AD'</sub>), 4.05 (d, 2H, H<sub>AE'</sub>), 3.95 (d, 2H, H<sub>AF'</sub>), 3.85 (d, 2H, H<sub>AG'</sub>), 3.75 (d, 2H, H<sub>AH'</sub>), 3.65 (d, 2H, H<sub>AI'</sub>), 3.55 (d, 2H, H<sub>AJ'</sub>), 3.45 (d, 2H, H<sub>AK'</sub>), 3.35 (d, 2H, H<sub>AL'</sub>), 3.25 (d, 2H, H<sub>AM'</sub>), 3.15 (d, 2H, H<sub>AN'</sub>), 3.05 (d, 2H, H<sub>AO'</sub>), 2.95 (d, 2H, H<sub>AP'</sub>), 2.85 (d, 2H, H<sub>AQ'</sub>), 2.75 (d, 2H, H<sub>AR'</sub>), 2.65 (d, 2H, H<sub>AS'</sub>), 2.55 (d, 2H, H<sub>AT'</sub>), 2.45 (d, 2H, H<sub>AU'</sub>), 2.35 (d, 2H, H<sub>AV'</sub>), 2.25 (d, 2H, H<sub>AW'</sub>), 2.15 (d, 2H, H<sub>AX'</sub>), 2.05 (d, 2H, H<sub>AY'</sub>), 1.95 (d, 2H, H<sub>AZ'</sub>), 1.85 (d, 2H, H<sub>BA'</sub>), 1.75 (d, 2H, H<sub>BB'</sub>), 1.65 (d, 2H, H<sub>BC'</sub>), 1.55 (d, 2H, H<sub>BD'</sub>), 1.45 (d, 2H, H<sub>BE'</sub>), 1.35 (d, 2H, H<sub>BF'</sub>), 1.25 (d, 2H, H<sub>BG'</sub>), 1.15 (d, 2H, H<sub>BH'</sub>), 1.05 (d, 2H, H<sub>BI'</sub>), 1.00 (s, 3H, H<sub>CD</sub>), 0.95 (s, 3H, H<sub>CE</sub>), 0.90 (s, 3H, H<sub>CF</sub>), 0.85 (s, 3H, H<sub>CG</sub>), 0.80 (s, 3H, H<sub>CH</sub>), 0.75 (s, 3H, H<sub>CI</sub>), 0.70 (s, 3H, H<sub>CJ</sub>), 0.65 (s, 3H, H<sub>CK</sub>), 0.60 (s, 3H, H<sub>CL</sub>), 0.55 (s, 3H, H<sub>CM</sub>), 0.50 (s, 3H, H<sub>CN</sub>), 0.45 (s, 3H, H<sub>CO</sub>), 0.40 (s, 3H, H<sub>CP</sub>), 0.35 (s, 3H, H<sub>CQ</sub>), 0.30 (s, 3H, H<sub>CR</sub>), 0.25 (s, 3H, H<sub>CS</sub>), 0.20 (s, 3H, H<sub>CT</sub>), 0.15 (s, 3H, H<sub>CU</sub>), 0.10 (s, 3H, H<sub>CV</sub>), 0.05 (s, 3H, H<sub>CW</sub>), 0.00 (s, 3H, H<sub>CD</sub>).

EXMOD NON

OFA

085ET

08FIN

POINT

FREQ

SCANS

ACQTM

PD

PW1

TRANIC 4H

CTEMP

SL VNT COCL

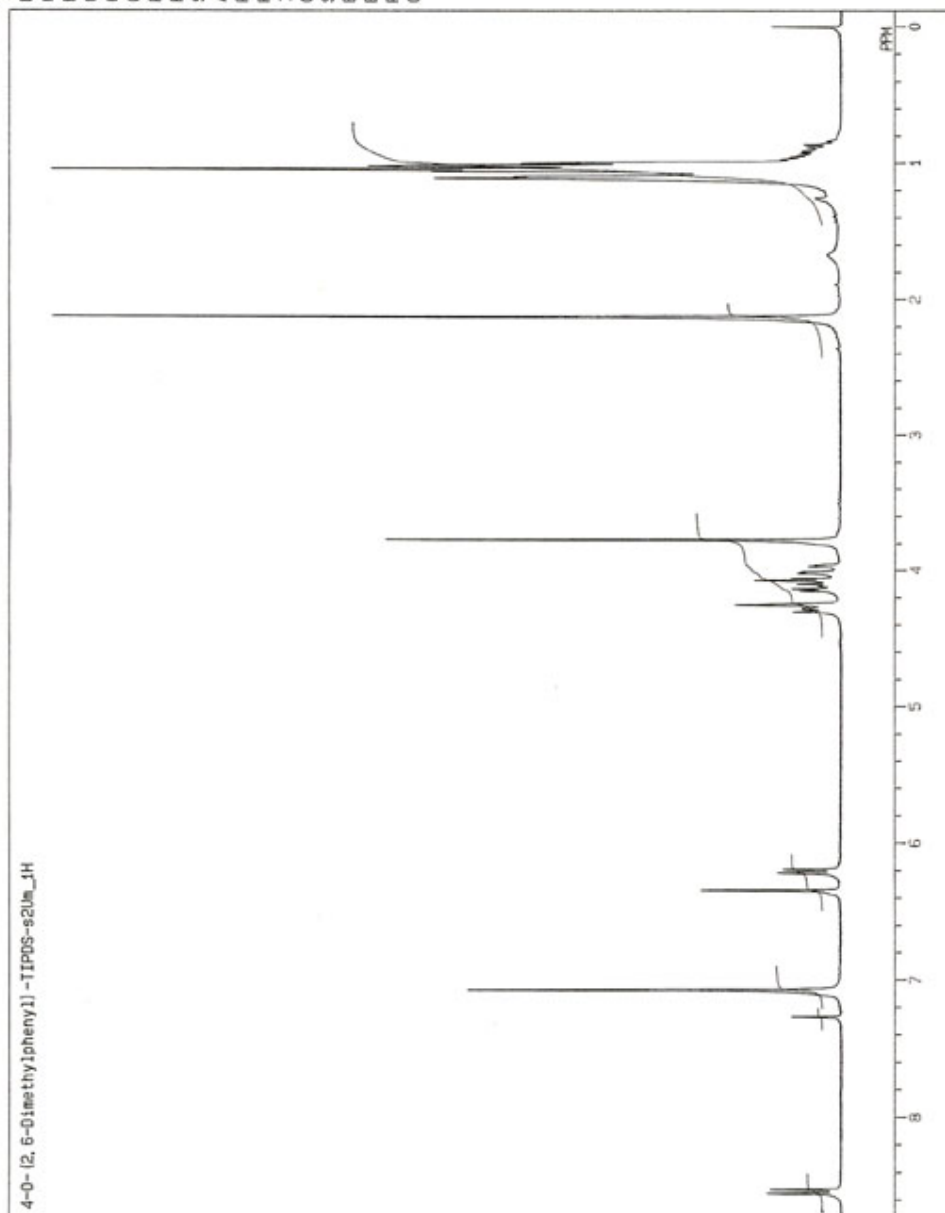
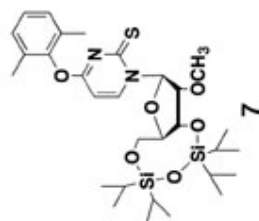
EXAFS

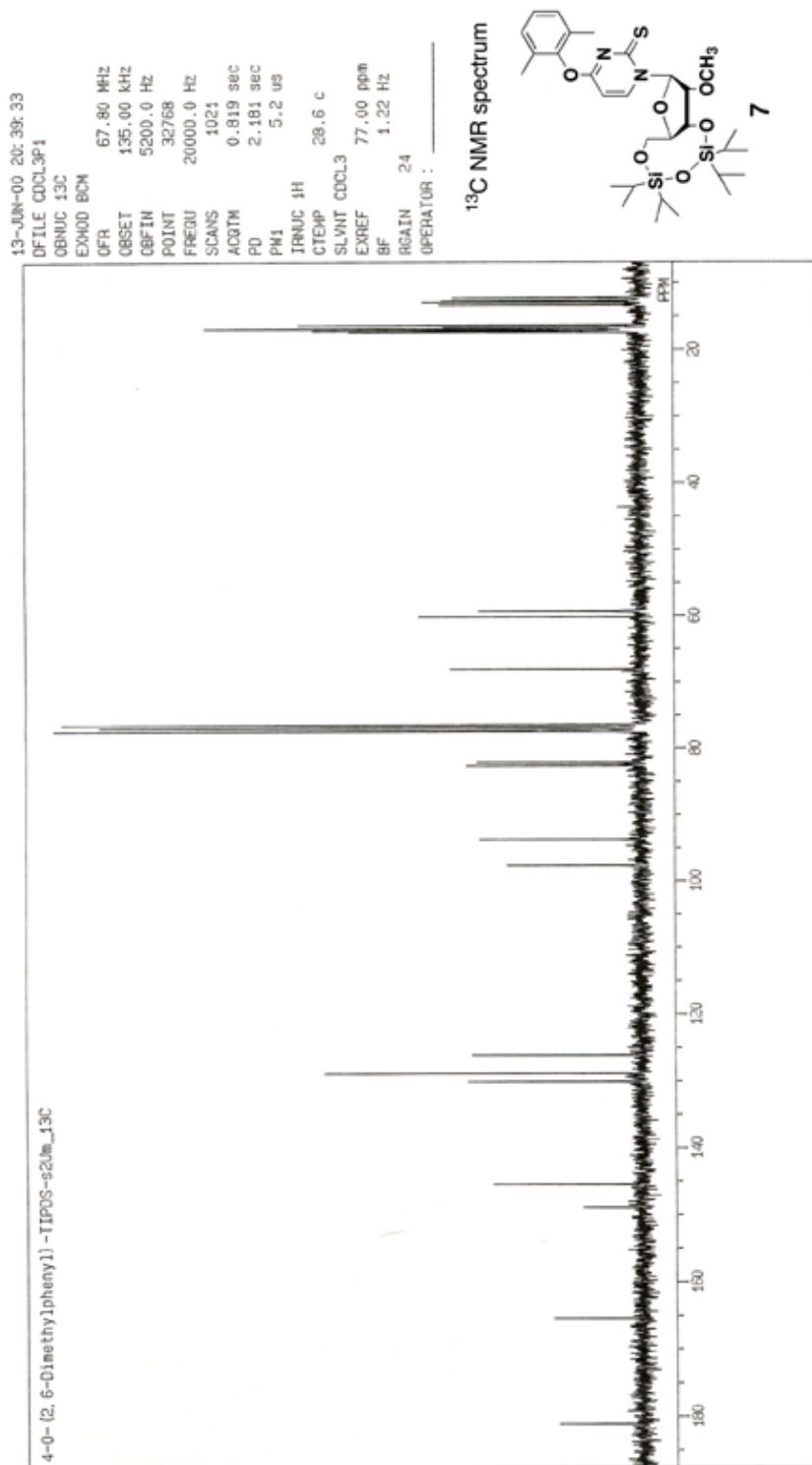
TABLE 1

PGATN 1

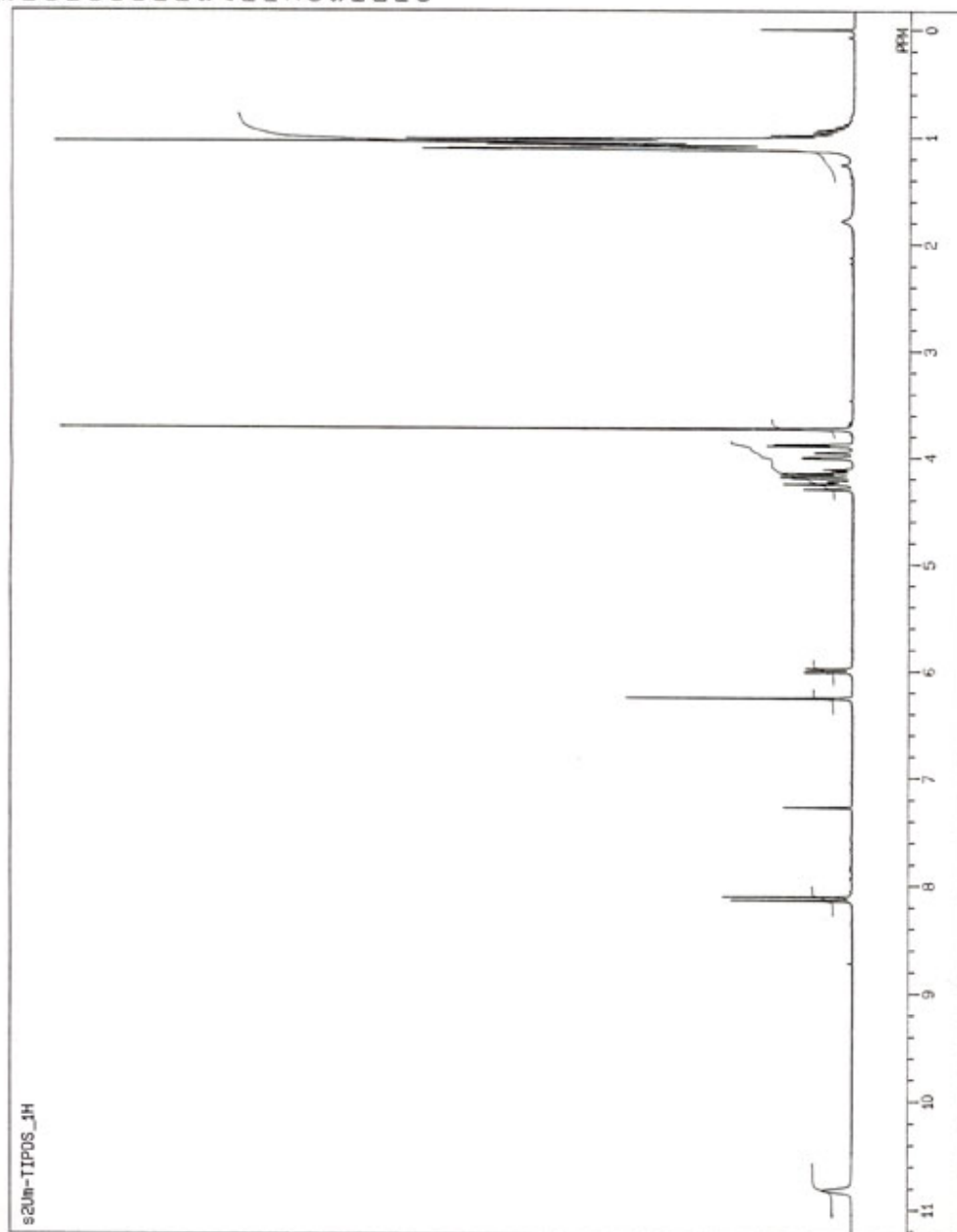
OPERATOR :

REFERENCES:

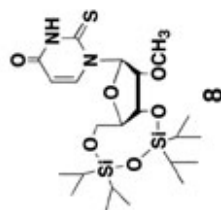
<sup>1</sup>H NMR spectrum



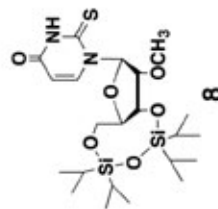
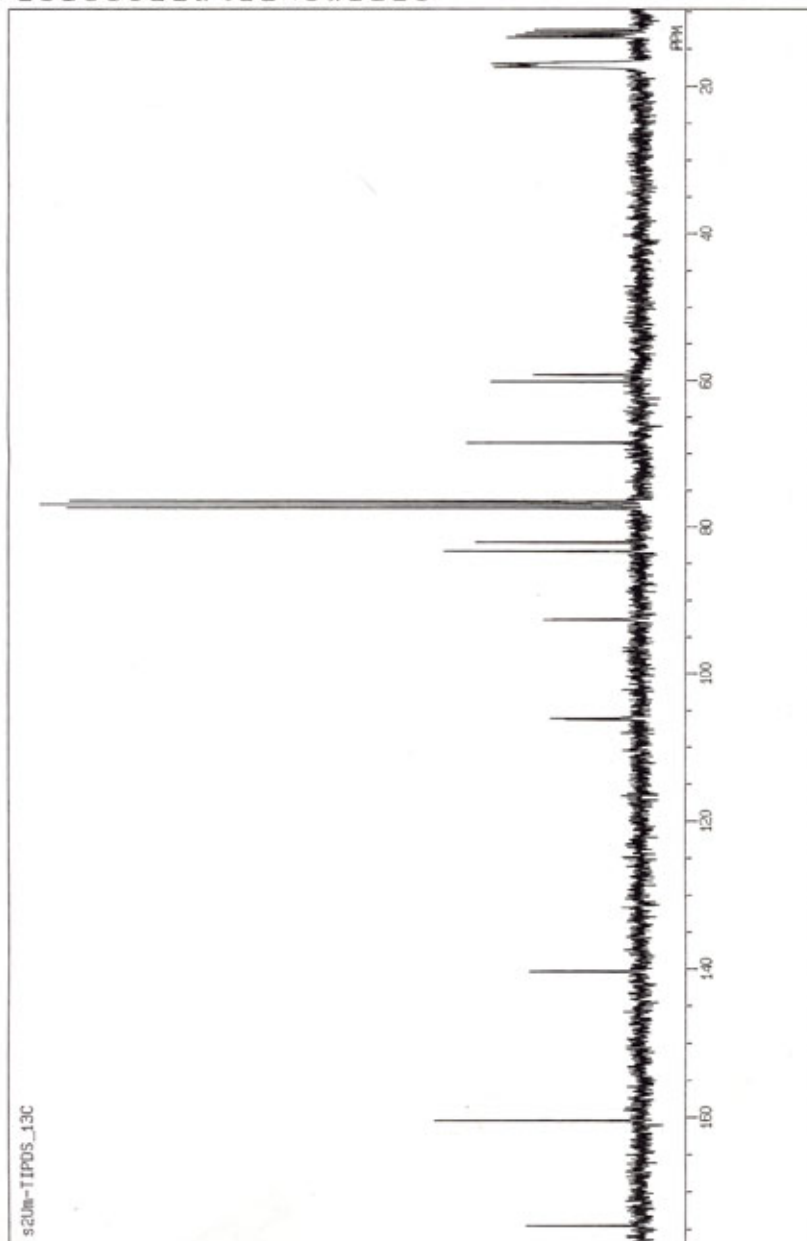
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 EXM00 NON  
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 OBSET 112.00 kHz  
 OFIN 5800.0 Hz  
 POINT 32768  
 FREQ 5405.4 Hz  
 SCANS 16  
 ACQTM 3.031 sec  
 PD 3.969 sec  
 PW1 5.2 us  
 IRNUC 1H  
 CTEMP 24.5 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 BF 0.16 Hz  
 RGAIN 18  
 OPERATOR :



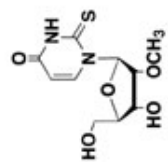
<sup>1</sup>H NMR spectrum



18-JUN-00 11:22:50  
 DF IL ASAI  
 QMUC 13C  
 EXMOD ECH  
 OFR 67.80 MHz  
 OSET 135.00 kHz  
 OFIN 5200.0 Hz  
 POINT 32768  
 FREQU 20000.0 Hz  
 SCANS 765  
 ACQTM 0.819 sec  
 PD 2.181 sec  
 PM1 5.2 us  
 IRMUC 1H  
 CTENP 28.6 c  
 SLVNT CDCL3  
 EXREF 77.00 ppm  
 BF 1.22 Hz  
 RGAIN 24  
 OPERATOR :



<sup>1</sup>H NMR spectrum



3b



C:\WINNMR38\COMMON\DEFAULT.ALS

DFILE C:\WINNMR38\COMMON\DEFAULT.ALS

CONNT Tue Jul 22 16:28:55 2003

OBNUC 13C

EXMDO BOM

OBPRO 67.80 MHz

OBSET 135.00 KHz

OBFIN 5200.0 Hz

POINT 32768

FREQU 18315.0 Hz

SCANS 1480

ACQTM 1.789 sec

PD 1.211 sec

PW1 4.4 us

IRNUC 1H

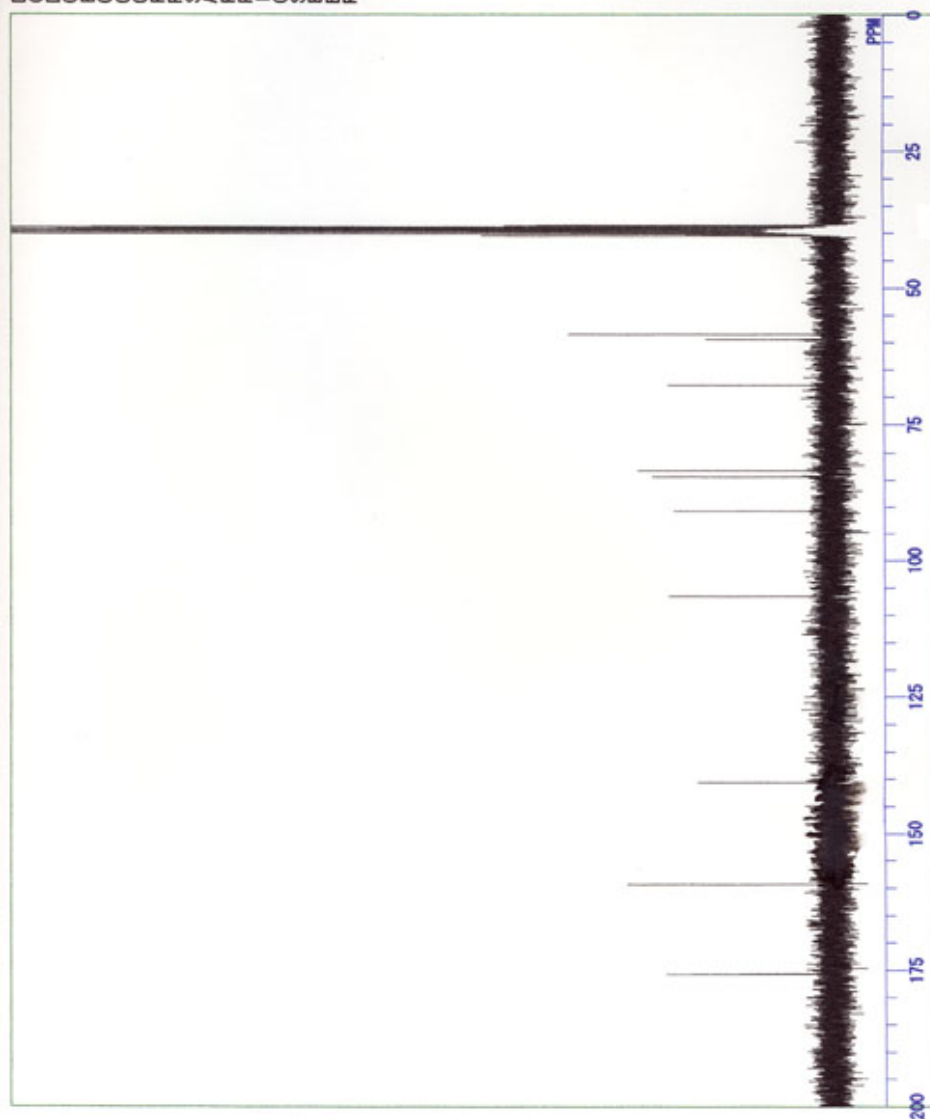
CTEMP 27.2 C

SLVNT DMSO

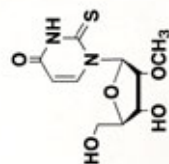
EXREF 39.50 ppm

BF 0.20 Hz

RGAIN 27



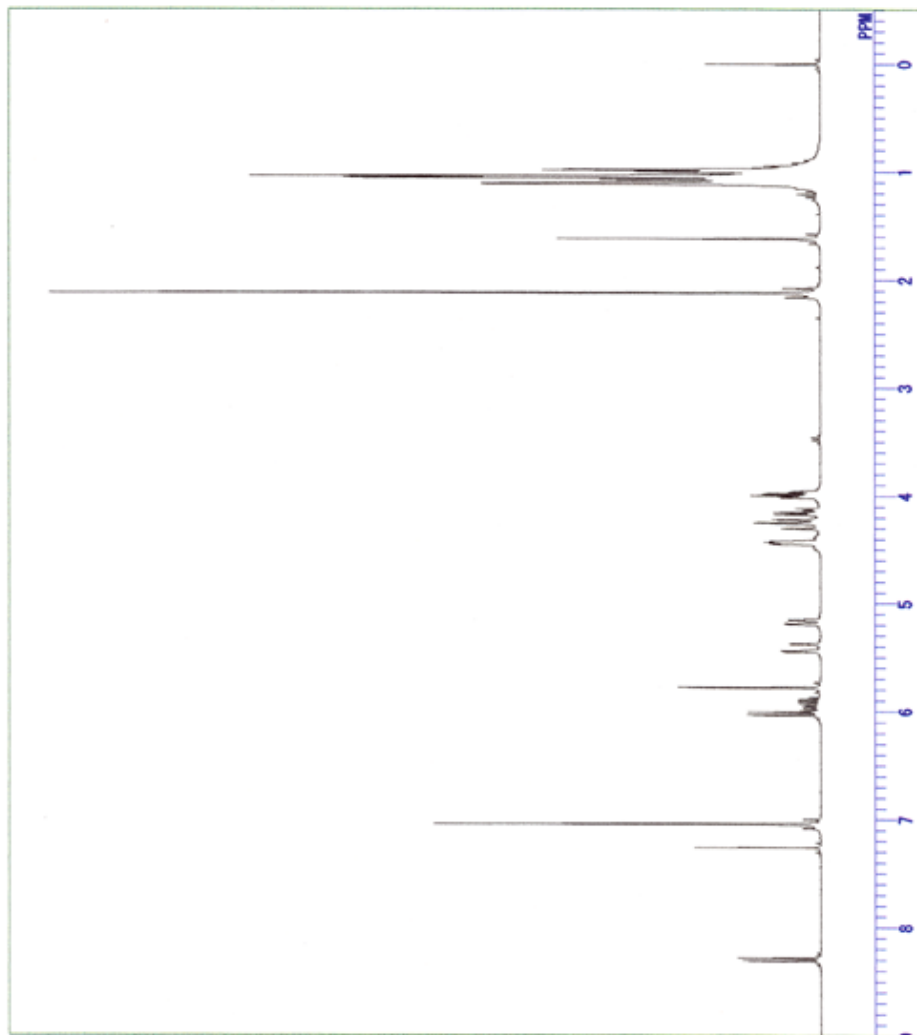
<sup>13</sup>C NMR spectrum



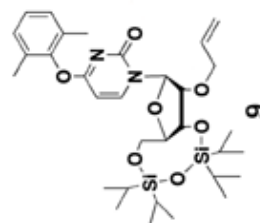
**3b**

C:\My Documents\Kokamoto\2\_6-dimethylPh-2'-  
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 DATUM Wed Sep 26 10:03:11 2001

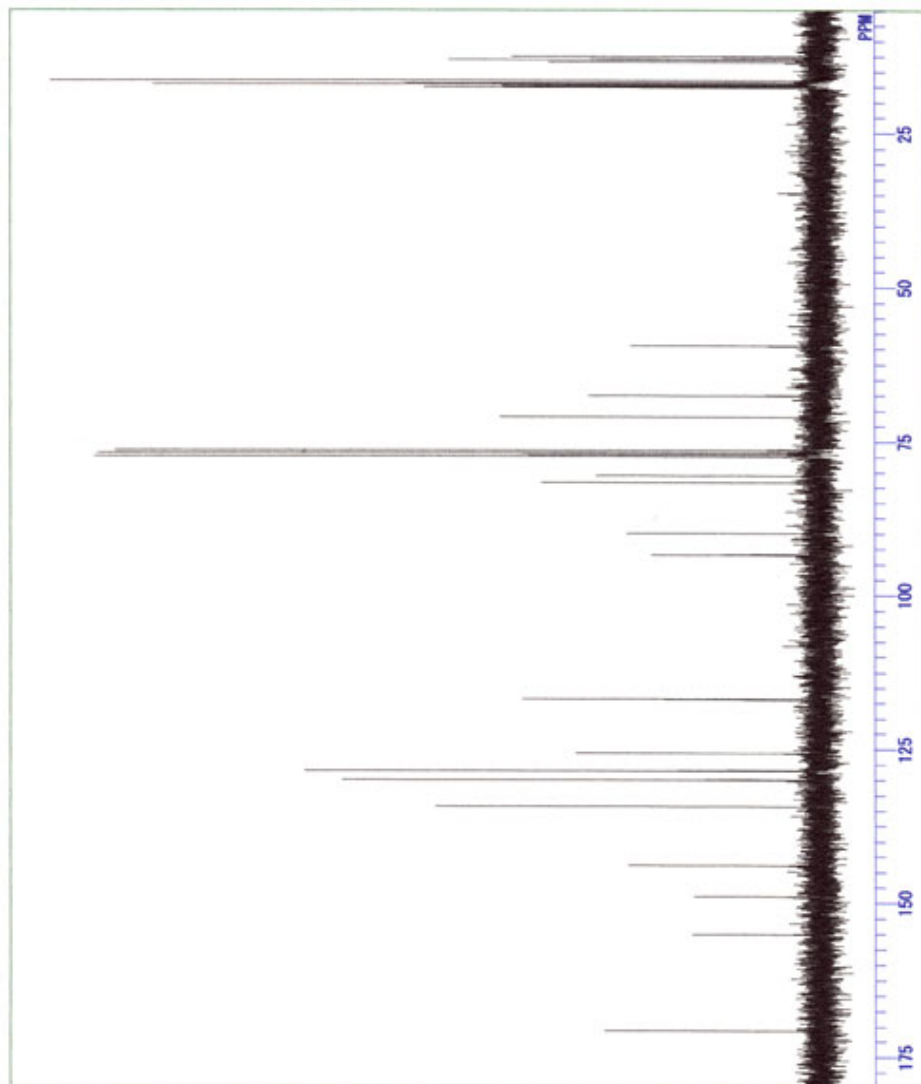
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 COMINT 2'-allyl-4-O-phenyl-TIPDS-U 1H  
 DATUM Wed Sep 26 10:03:11 2001  
 OBNUC 1H  
 EXMOD NON  
 OBFRQ 270.05 MHz  
 OBSET 112.00 KHz  
 OBFTN 5800.0 Hz  
 POINT 16384  
 FREQU 5402.4 Hz  
 SCANS 8  
 ACQTM 3.033 sec  
 PD 0.935 sec  
 PM1 5.1 us  
 1H  
 IRNUC 25.8 c  
 CTMP CDCL3  
 SLVNT 0.00 ppm  
 EXREF 0.20 Hz  
 BF 18  
 RGAIN



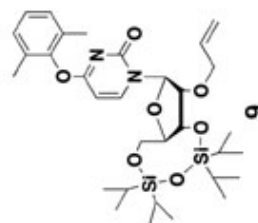
<sup>1</sup>H NMR spectrum



C:\My Documents\Kokamoto\2. 6-diaethy  
 DFILE COMNT  
 DATIM Wed Dec 19 14:36:51 2001  
 C13C  
 EXMOD BCM  
 OBFRQ 67.80 MHz  
 OBSET 135.00 KHz  
 OBFIN 5200.0 Hz  
 POINT 32768  
 FREQ 18315.0 Hz  
 SCANS 312  
 ACQTM 1.789 sec  
 PD 1.211 sec  
 PW 4.4 us  
 IRNUC 1H  
 CTMP 26.2 o  
 CDCL3  
 SLVNT 0.00 ppm  
 EXREF 0.20 Hz  
 BF 32  
 RGAIN



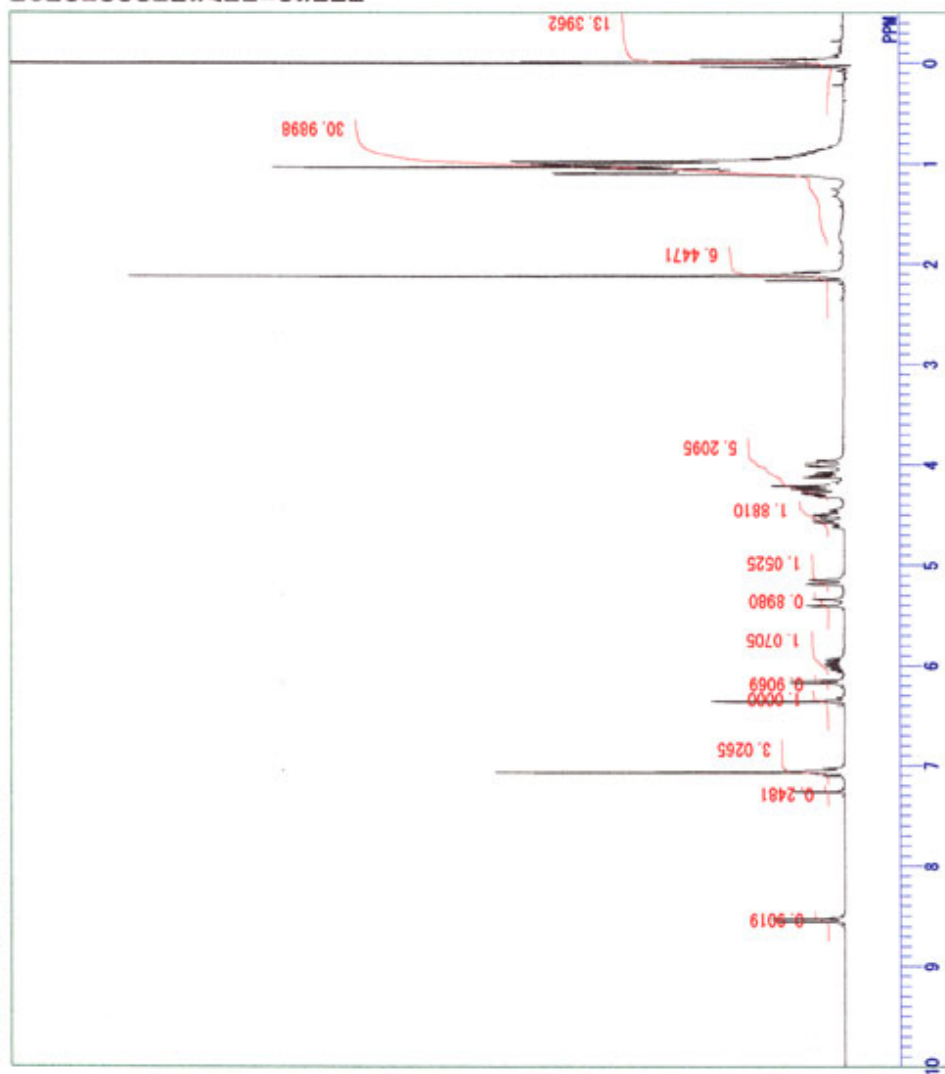
<sup>13</sup>C NMR spectrum



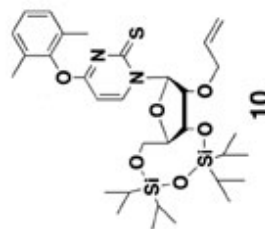


C:\VWINMR8\COMMON\DEFAULT.ALS

D:\FILE C:\VWINMR8\COMMON\DEFAULT.ALS  
 COMPT Wed Dec 19 10:49:52 2001  
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 OSNUC 1H  
 EXMID NON  
 OSFRO 270.05 MHz  
 OSSET 112.00 KHz  
 OSFIN 5800.0 Hz  
 POINT 16384  
 FREQ 5402.4 Hz  
 SCANS 8  
 ACQTM 3.033 sec  
 PD 3.967 sec  
 PM1 5.1 us  
 1H 1H  
 1RNUC 26.7 o  
 CTMP COCL3  
 SLVT 0.00 ppm  
 EXREF 0.20 Hz  
 BF 15  
 RGAIN



<sup>1</sup>H NMR spectrum



DFILE C:\Nly Documents\Yokamoto\2, 6-dimethy

COMPT Wed Dec 19 11:44:17 2001

DATUM 13C

EXMOD BCM

OBFRQ 67.80 MHz

OBSET 135.00 kHz

OBFIN 5200.0 Hz

POINT 32768

FREQD 18315.0 Hz

SCANS 1000

ACQTM 1.789 sec

PD 1.211 sec

PW 4.4 us

IRNUC 1H

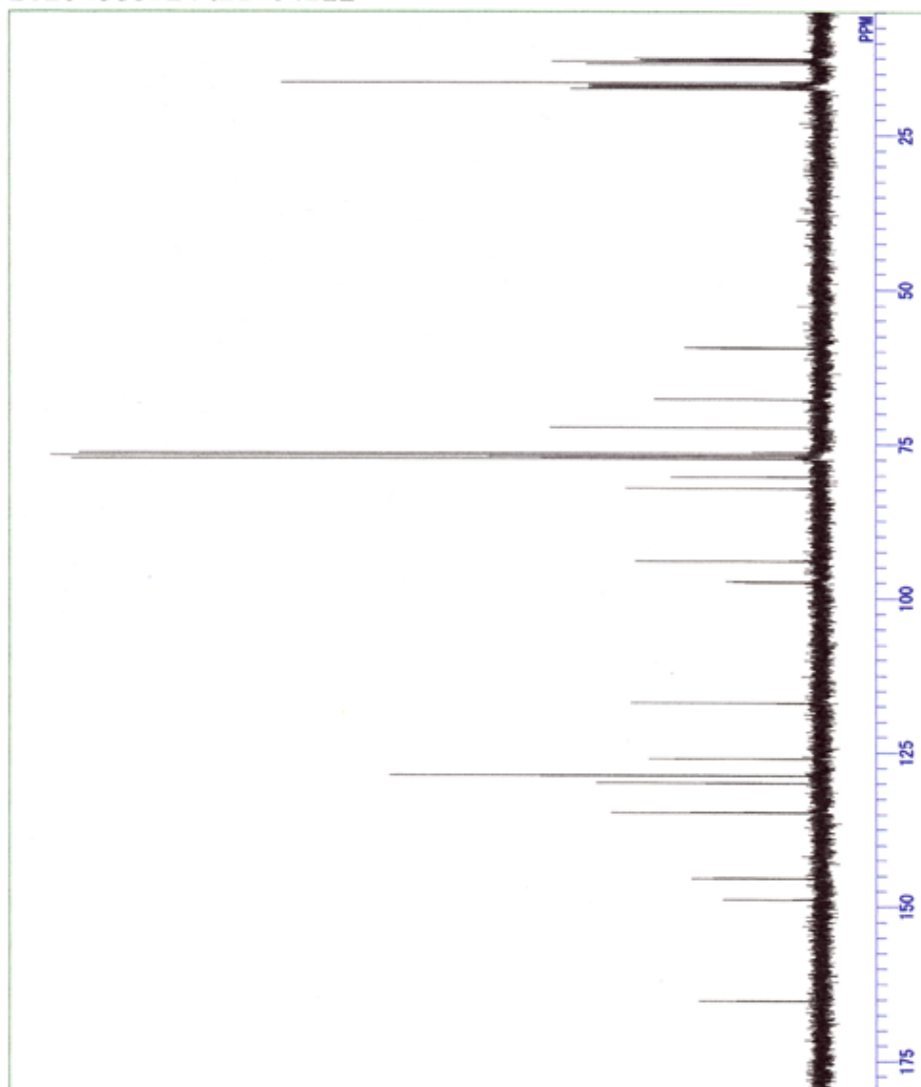
CTEMP 25.2 c

SLVNT CDCl3

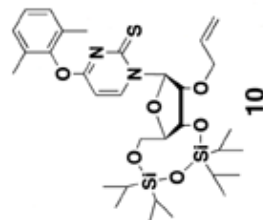
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BF 0.20 Hz

RGAIN 32

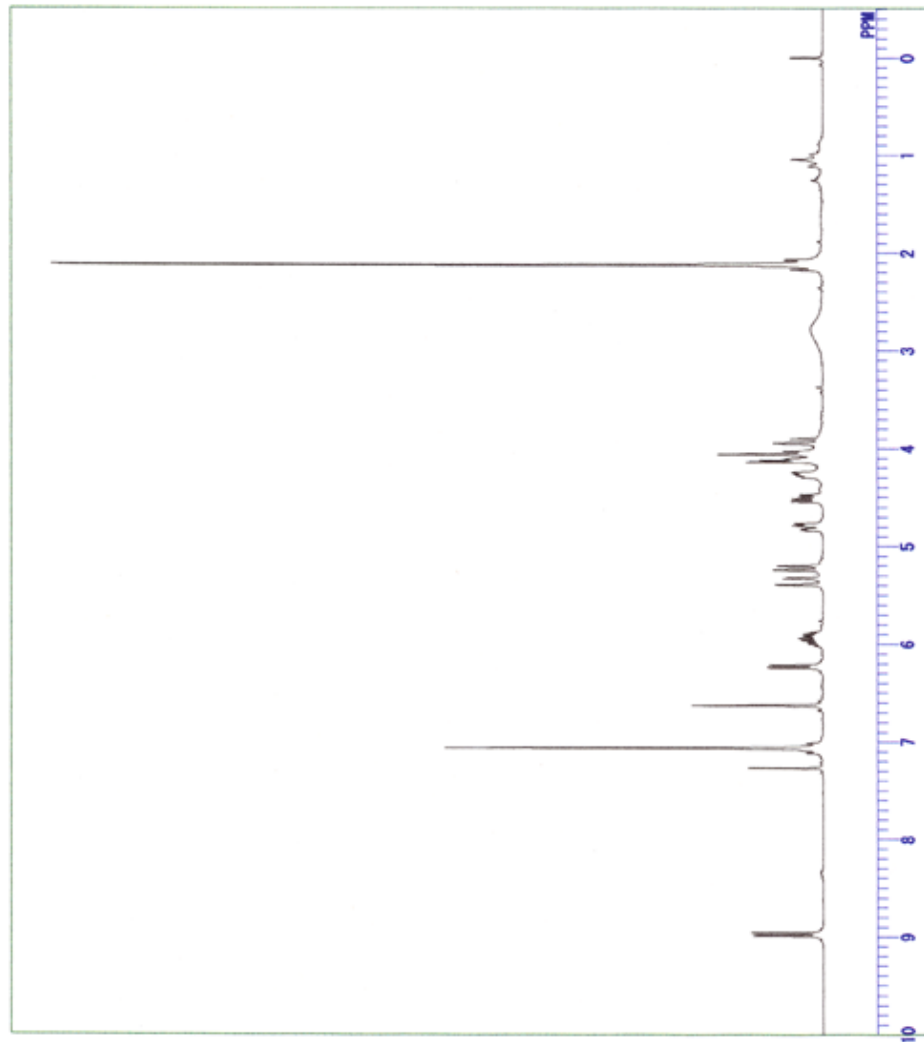


<sup>13</sup>C NMR spectrum

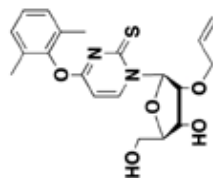


DFILE C:\Nky Documents\Kokamoto\2, 6-dimethyl Ph-2'

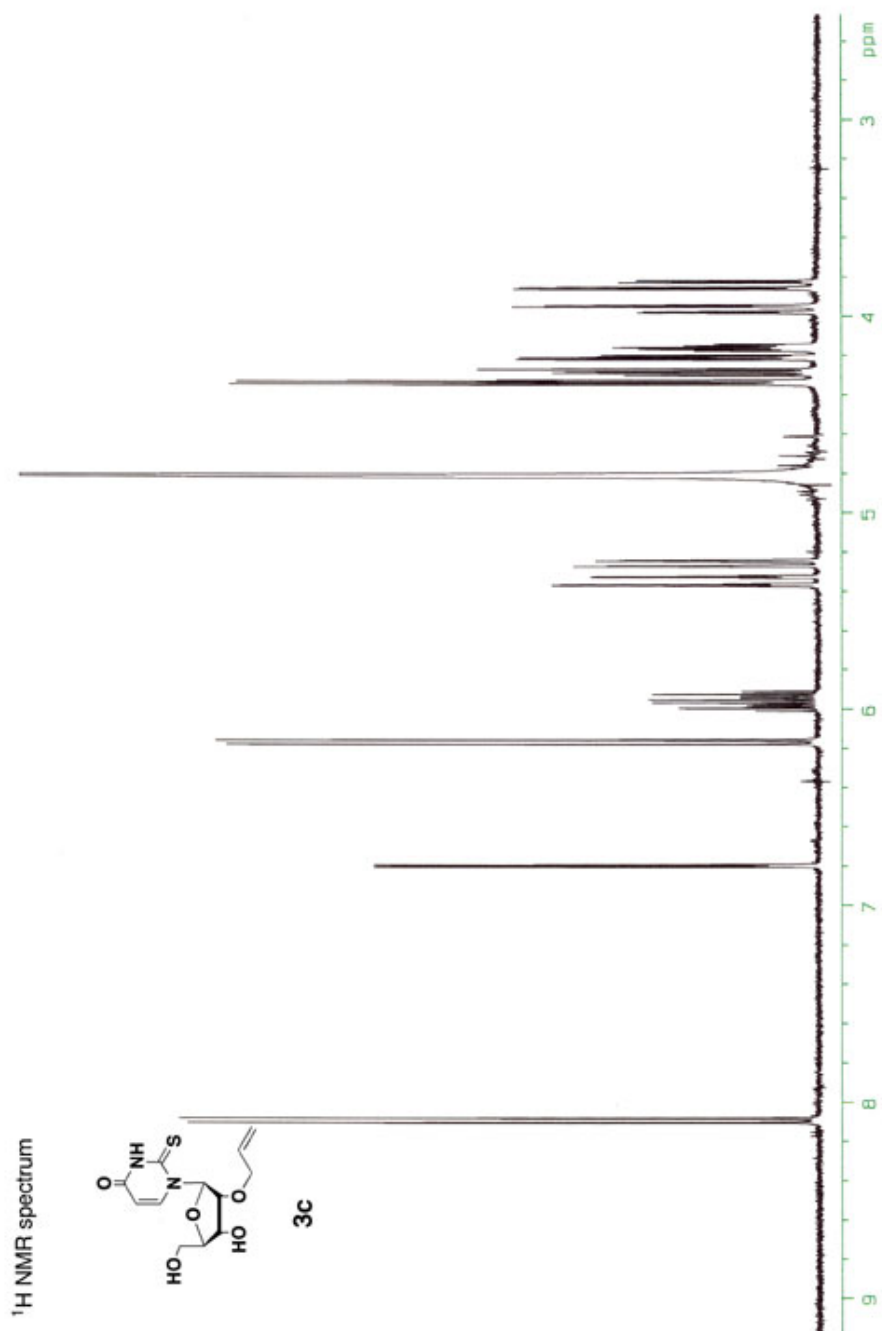
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 DATIM 1H  
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 EXMOD NON  
 OBFRQ 270.05 MHz  
 OBSET 112.00 KHz  
 OBFIN 5800.0 Hz  
 POINT 16384  
 FREQU 5402.4 Hz  
 SCANS 8  
 ACQTM 3.033 sec  
 PD 3.967 sec  
 PVI 5.1 us  
 TRNUC 1H 22.9 c  
 CTEMP CDCL3  
 SLVNT 0.00 ppm  
 EXREF 0.20 Hz  
 BF 18  
 RGAIN



<sup>1</sup>H NMR spectrum



11



C:\My Documents\Kokamoto\2\_6-dimethy

DFILE

COMNT

DATIM Tue Jan 08 15:23:47 2002

OBNUC 13C

EXM30 BCM

OBFRQ 67.80 MHz

OBSET 135.00 KHz

OBFTN 5200.0 Hz

POINT 32768

FREQU 18315.0 Hz

SCANS 1000

ACQTM 1.789 sec

PD 1.211 sec

PW1 4.4 us

IRNUC 1H

CTEMP 23.0 c

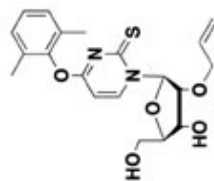
SLVNT CDCL3

EXREF 77.00 ppm

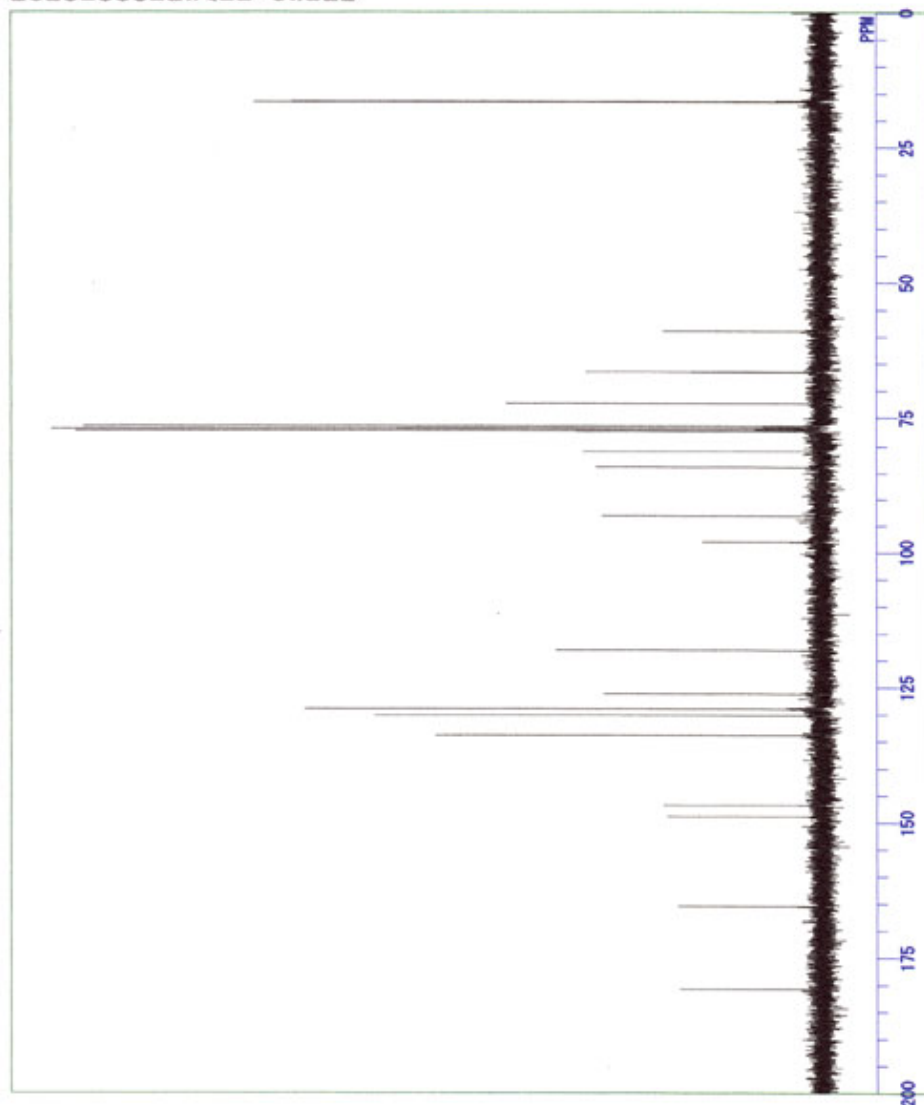
BF 0.20 Hz

RGAIN 32

<sup>13</sup>C NMR spectrum



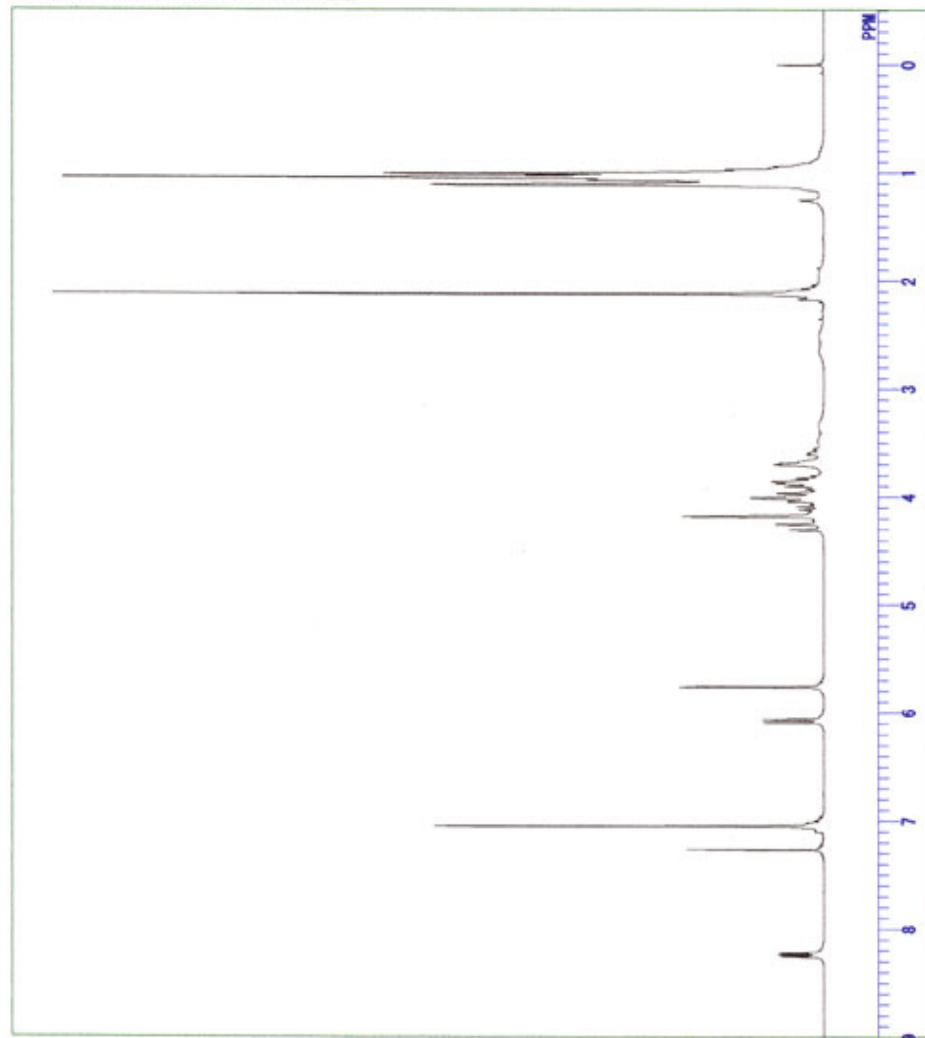
11



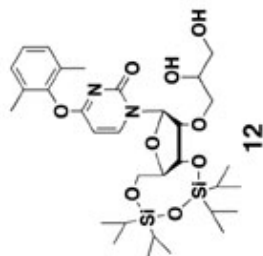


C:\Vky Documents\Yokamoto\2\_6-dimethylPh-2

DEFILE  
 COUNT 1H  
 DATUM 1H  
 EXMOD NON  
 OBFRQ 270.05 MHz  
 OBSET 112.00 KHz  
 OBFIN 5800.0 Hz  
 POINT 16384  
 FREQU 5402.4 Hz  
 SCANS 8  
 ACQTIM 3.032 sec  
 PD 0.935 sec  
 PUL 5.1 us  
 TRNUC 1H  
 CTEMP 24.8 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 BF 0.10 Hz  
 RGAIN 14



<sup>1</sup>H NMR spectrum

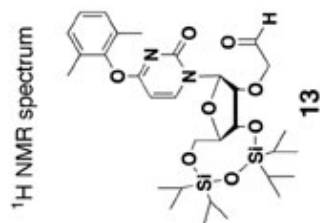
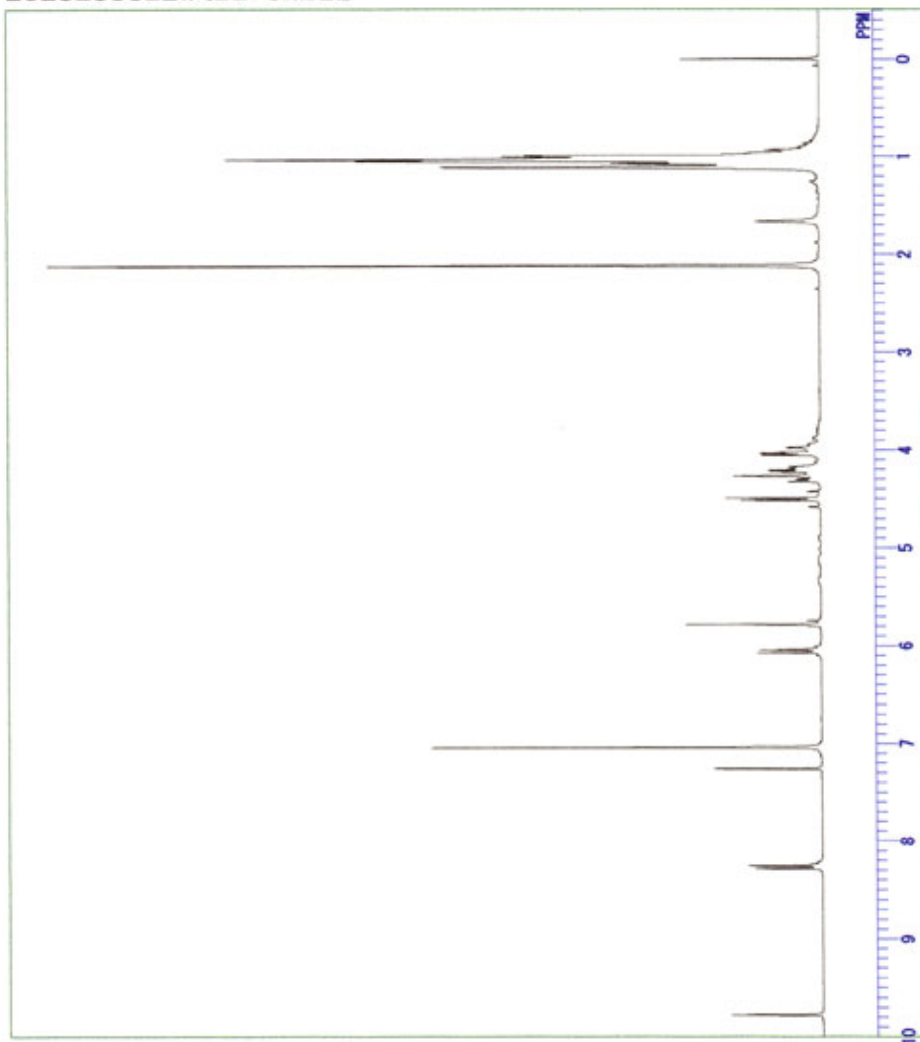




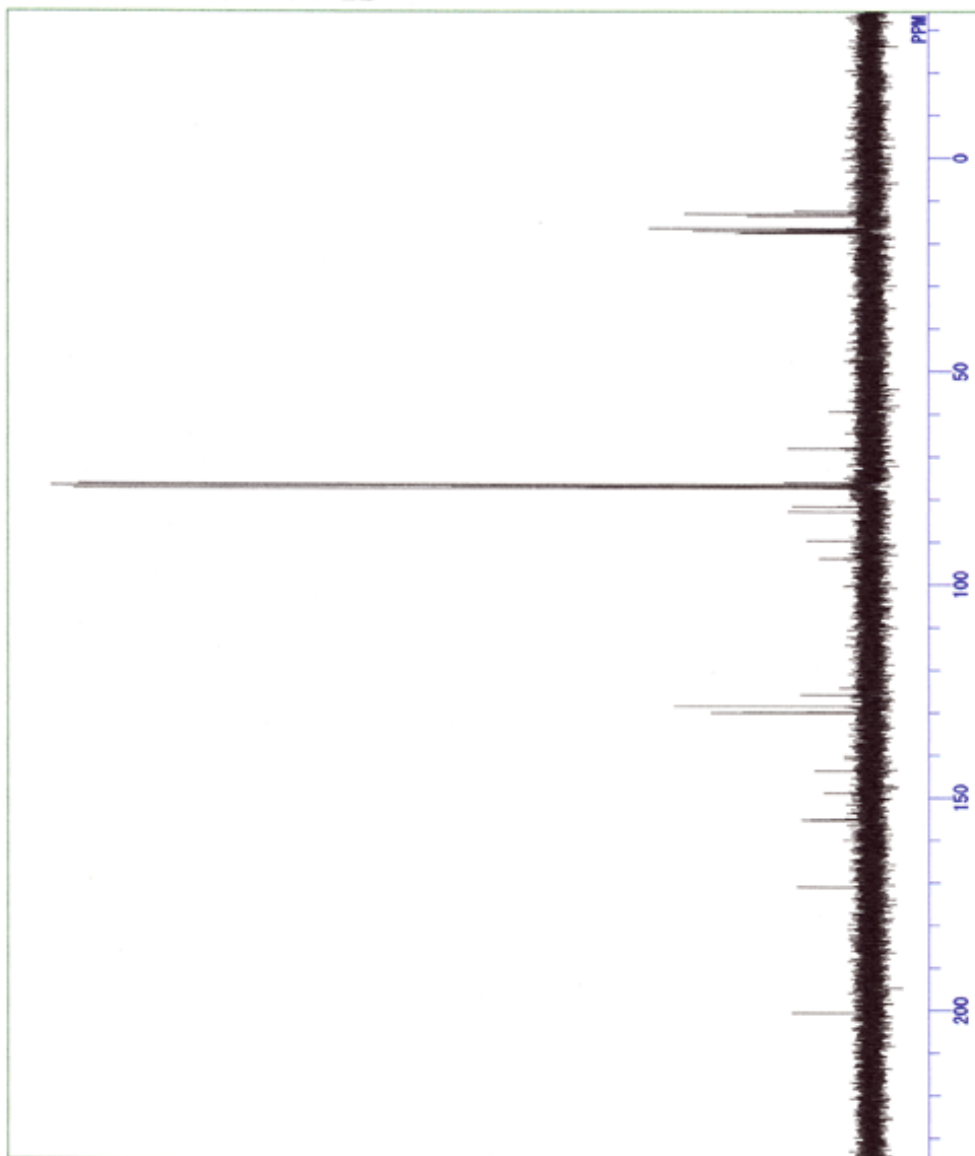


C:\Vily Documents\kokamoto\2\_6-dimethylPh-2'

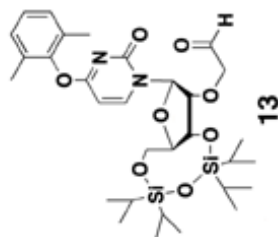
DE FILE  
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 OBFIN 5800.0 Hz  
 POINT 16384  
 FREQU 5402.4 Hz  
 SCANS 16  
 ACQTM 3.033 sec  
 PD 0.935 sec  
 PR 5.1 us  
 IRNUC 1H  
 CTMPC 25.2 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 BF 0.20 Hz  
 RGAIN 16



D:\My Documents\Yokamoto\2\_6-dimethy  
 COMET Wed Oct 10 11:37:12 2001  
 DATUM 13C  
 CENUC BCM  
 EXMOD BCM  
 OBPRO 67.80 MHz  
 OBSET 135.00 KHz  
 OBFIN 5200.0 Hz  
 POINT 32768  
 FREQU 18315.0 Hz  
 SCANS 500  
 ACQTM 1.789 sec  
 PD 1.211 sec  
 PW 4.4 us  
 1H 1H  
 IRNUC 25.4 c  
 CTEMP COOL3  
 SLVNT 77.00 ppm  
 EXREF 0.20 Hz  
 BF 32  
 RGAIN 32

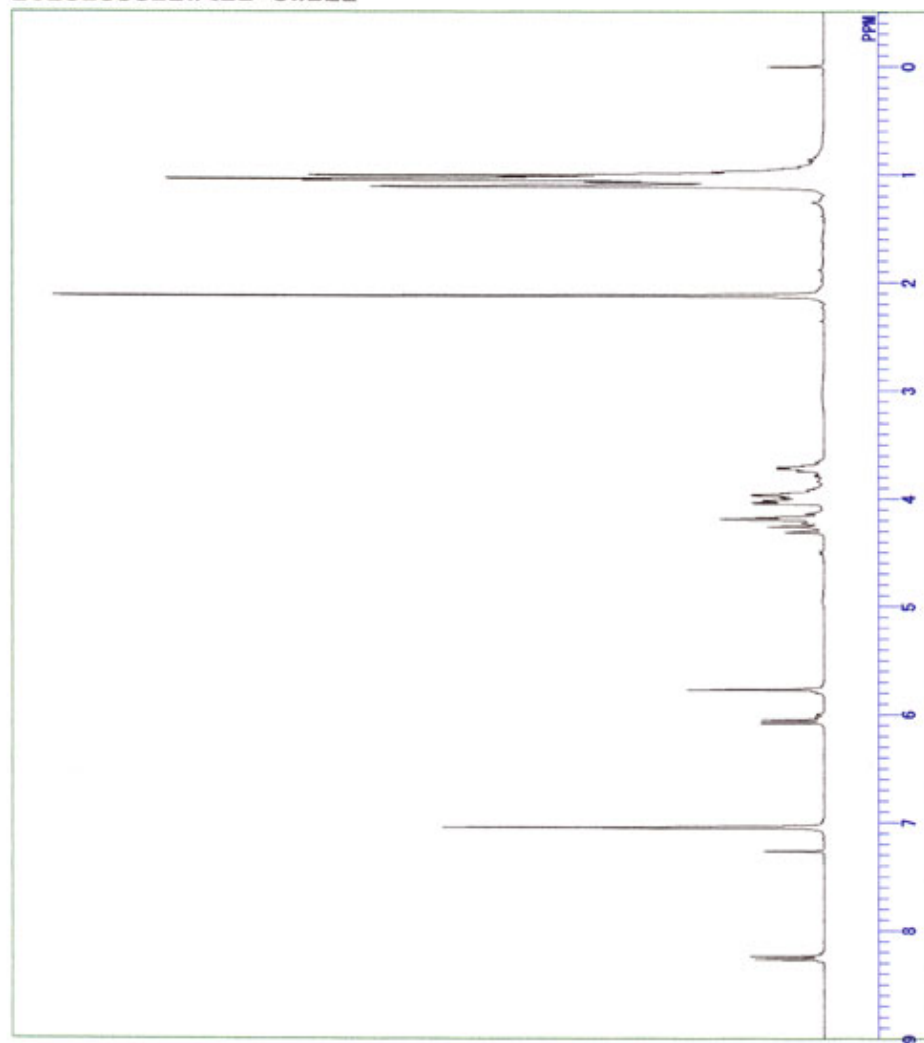


<sup>13</sup>C NMR spectrum

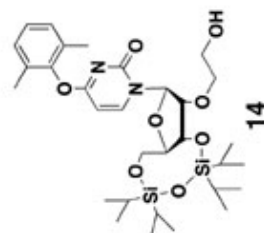


C:\Nky Documents\Kokamoto\2, 6-dimethylPh-2'

DE FILE  
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 OBFIN 5800.0 Hz  
 POINT 16384  
 FREQU 5402.4 Hz  
 SCANS 8  
 ACQTM 3.033 sec  
 PD 0.935 sec  
 PWT 5.1 us  
 1H 26.1 c  
 CTMP C0CL3  
 SLVT 0.00 ppm  
 EXREF 0.00 Hz  
 BF 14  
 RGAIN

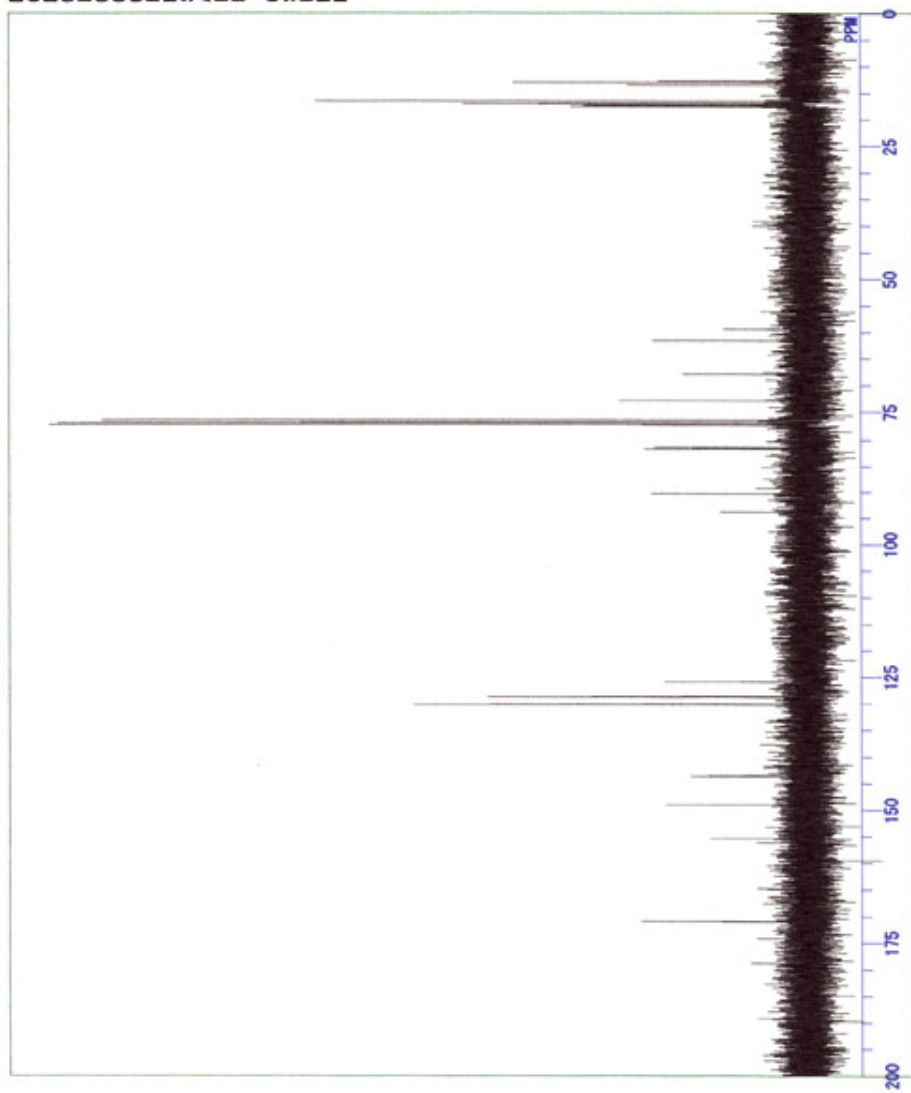
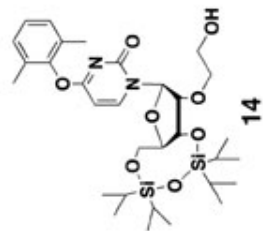


<sup>1</sup>H NMR spectrum



DFILE C:\My Documents\Yokamoto\2\_6-dimethy  
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 DATIN 13C  
 CBNUC BOM  
 EXMDO BCM  
 OBFRO 67.80 MHz  
 OBSFRO 135.00 KHz  
 OBFIN 5200.0 Hz  
 POINT 32768  
 FREQU 18315.0 Hz  
 SCANS 300  
 ACQTM 1.789 sec  
 PD 1.211 sec  
 PM 4.4 us  
 LTRUC 1H 26.0 c  
 CTEMP CDCL3 77.00 ppm  
 SLYNT EXREF 0.00 Hz  
 BF 32  
 RGAIN

<sup>13</sup>C NMR spectrum



DE FILE C:\NW\ Documents\Nokamoto\2, 6-dimethyl\Ph-2'

COMET Tue Feb 05 11:25:42 2002

DATUM 1H

GENUC NON

EXPRO 270.05 MHz

OBFRQ 112.00 KHz

OBSET 5800.0 Hz

POINT 16384

FREQD 5402.4 Hz

SCANS 8

ACQTM 3.033 sec

PD 3.967 sec

PW1 5.1 us

IRNUC 1H

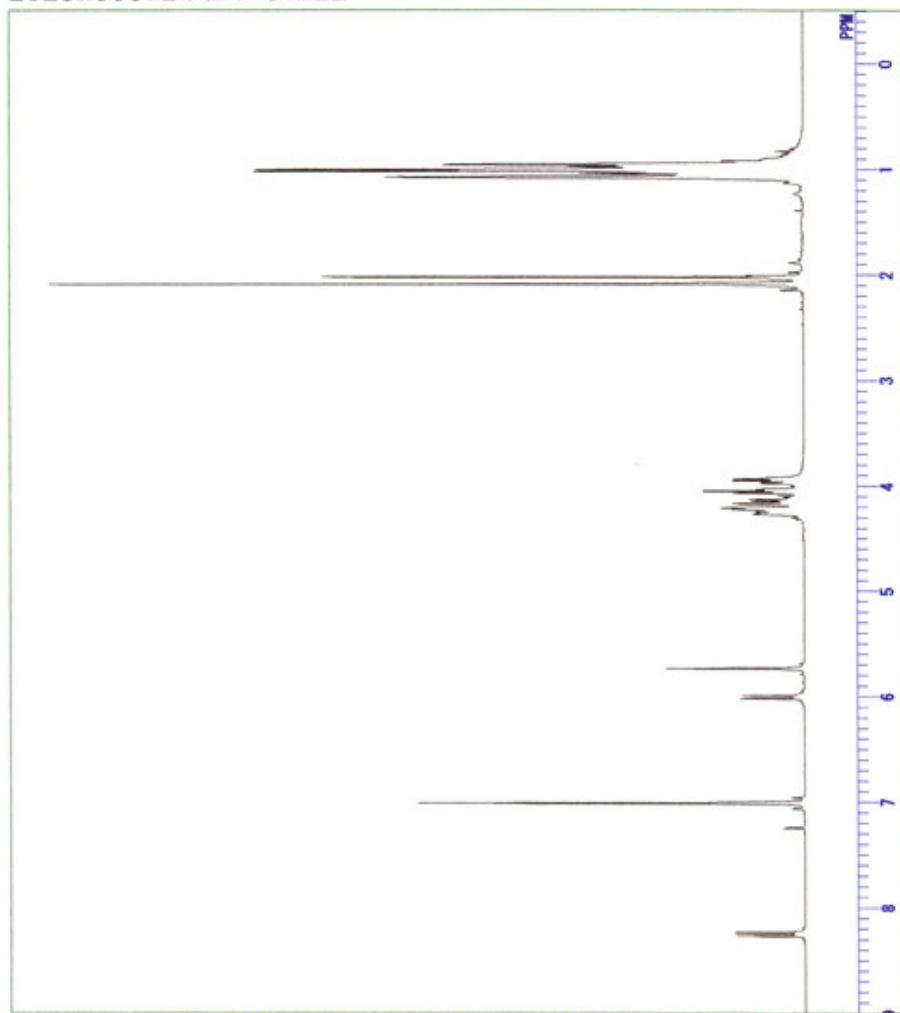
CTEMP 21.0 c

SLVNT CDCL3

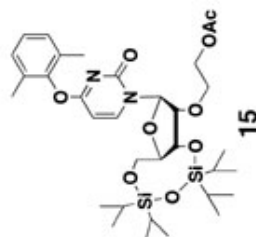
EXREF 7.24 ppm

BF 0.20 Hz

RGAIN 13



<sup>1</sup>H NMR spectrum

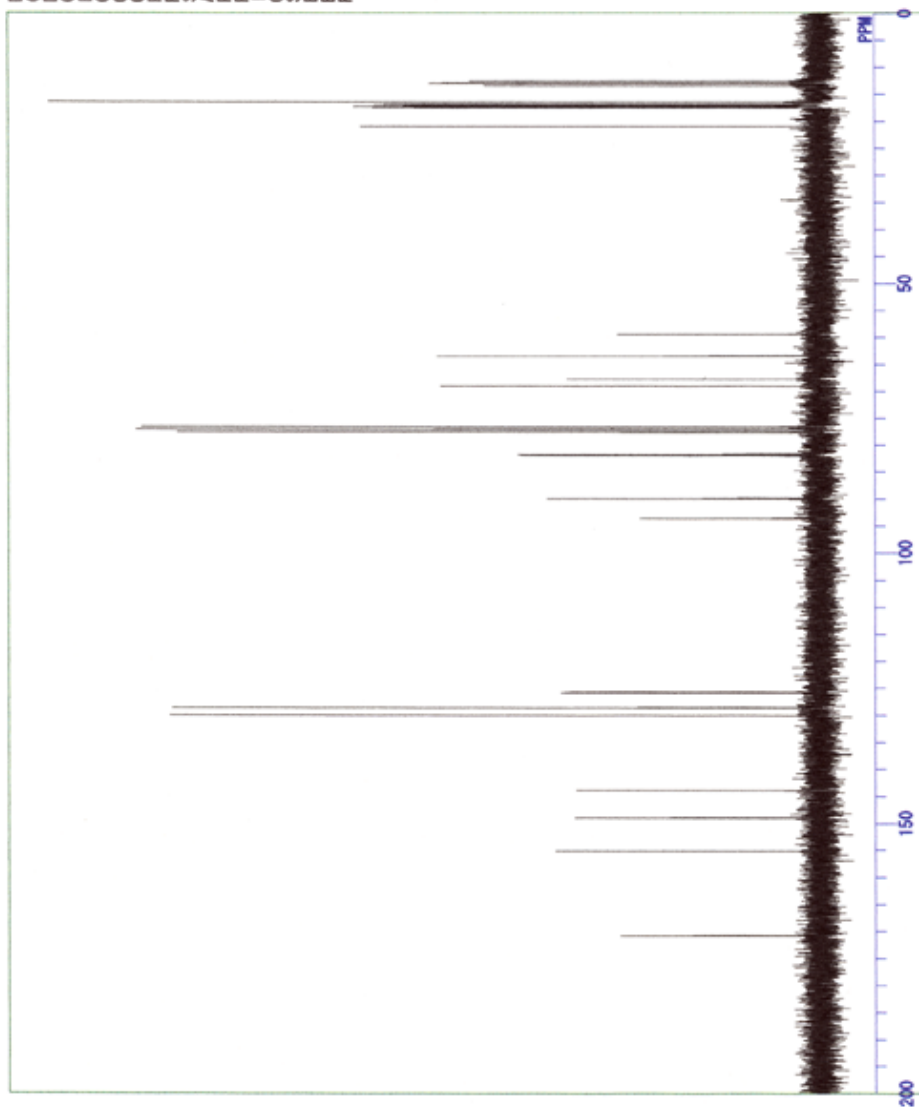




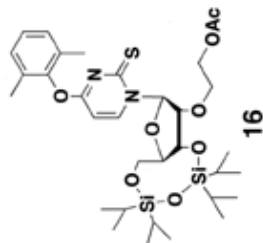


DFILE C:\Nhy Documents\Yokamoto\2, 6-dimethy

COMET  
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OBFIN 5200.0 Hz  
POINT 32768  
FREQU 18315.0 Hz  
SCANS 240  
ACQTM 1.789 sec  
PD 1.211 sec  
PMT 4.4 us  
IRNUC 1H  
CTEMP 21.6 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 0.20 Hz  
RGAIN 32



<sup>13</sup>C NMR spectrum

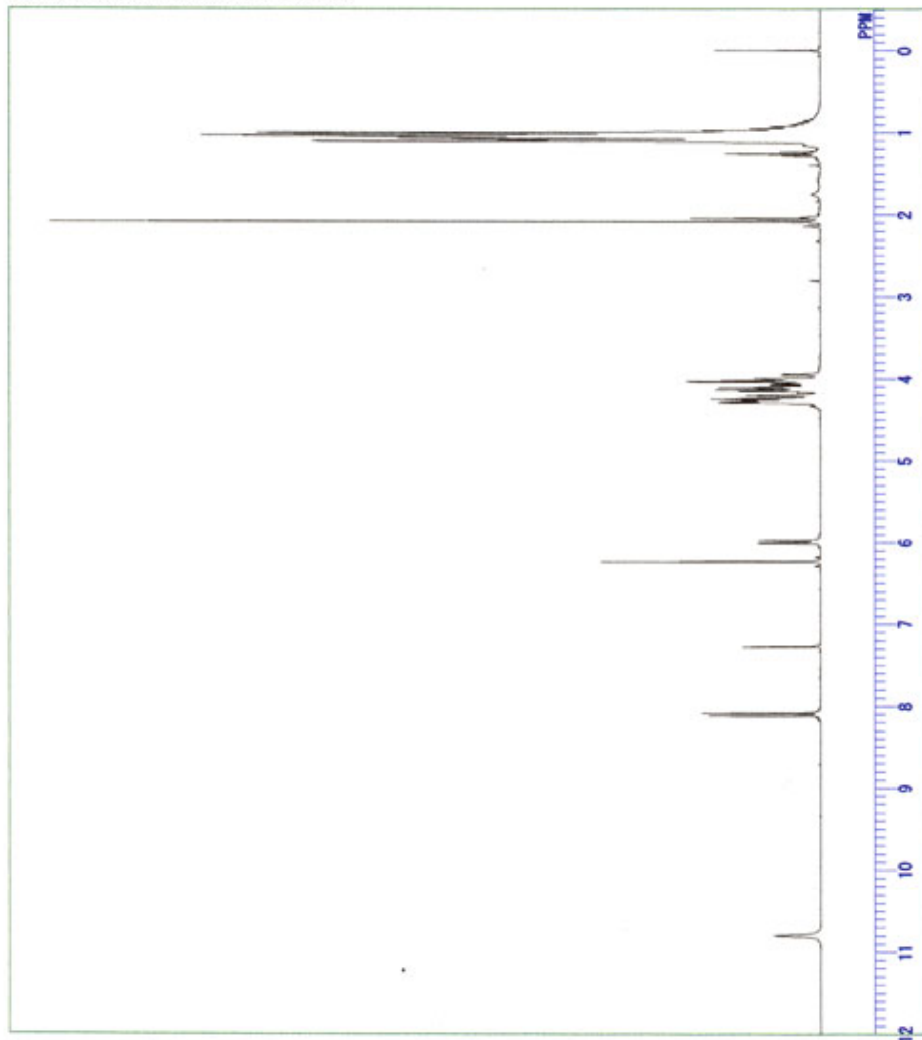


16

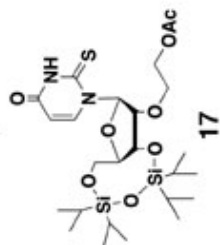


C:\My Documents\kokamoto\2' -CH2CH2OAc-TIPD

DEFILE  
 C:\My Documents\kokamoto\2' -CH2CH2OAc-TIPD  
 DATE: Fri Mar 15 16:38:16 2002  
 CHANNEL 1H  
 EXMOD NON  
 OBFRQ 270.05 MHz  
 OBSET 112.00 KHz  
 OBFIN 5800.0 Hz  
 POINT 16384  
 FREQU 5402.4 Hz  
 SCANS 8  
 ACQTM 3.033 sec  
 PD 3.967 sec  
 PRT 5.1 us  
 TRNUC 1H  
 CTMP 23.5 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 BF 0.10 Hz  
 RGAIN 1.4



<sup>1</sup>H NMR spectrum



```
DFILE  COMINT  DATIM  OBNUC  EXMOD  OBFRO  OBFSE  OBFIN  POINT  FREQU  SCANS  ACOTM  PD  PWI  IRNUC  CTEMP  SLVNT  EXREF  BF  RGA IN
```

DATE TIME PERIOD

GENUG  
EXMOD

DBFRQ  
DBSET

0851  
0852  
0853

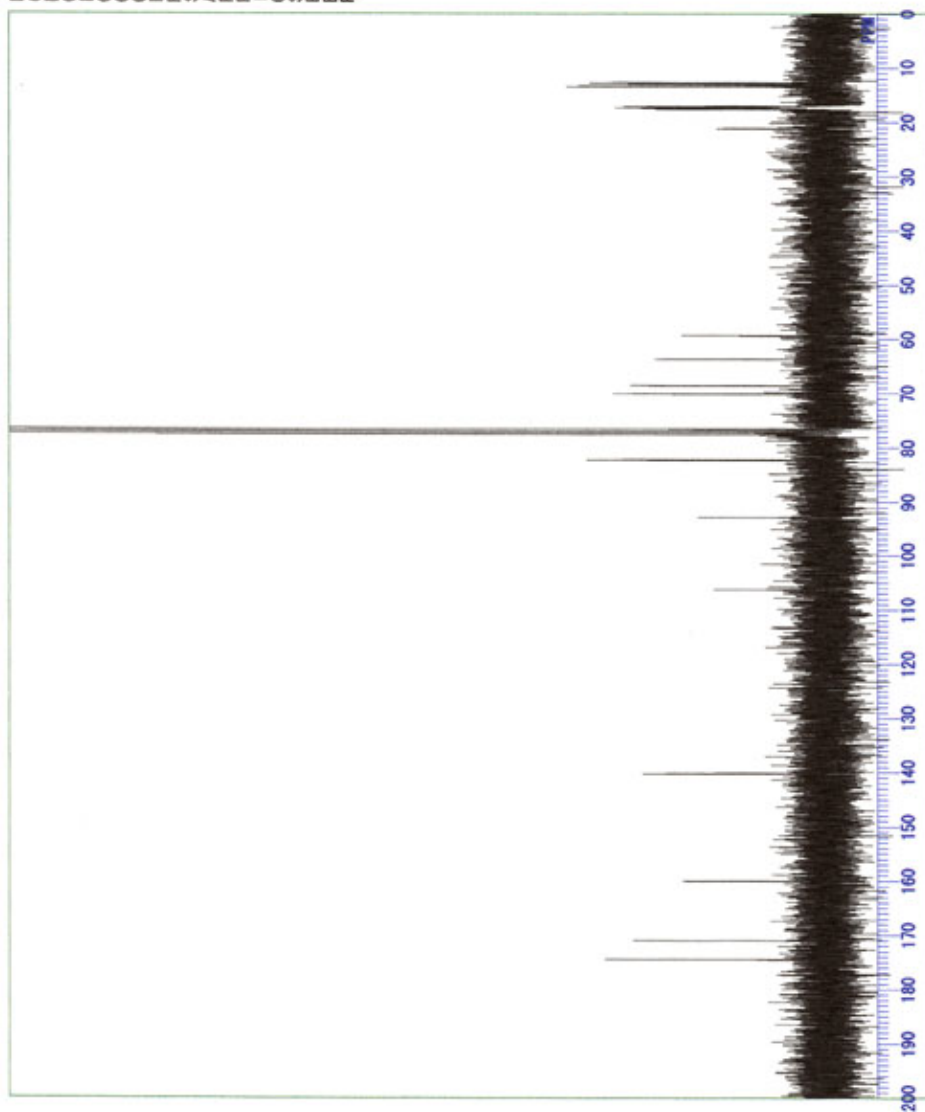
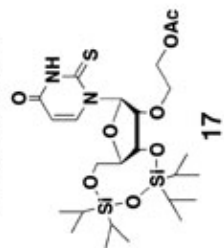
POINT  
FREQUSCAMS  
ACOTM

PD

PWT  
IRNUJCCTEMP  
SI VNT

EXREF  
SLVING

RGAIN

<sup>13</sup>C NMR spectrum

DE FILE C:\Nky Documents\Yokamoto\2' -CH2CH2OAc s2U

DATE Sat Mar 16 22:49:35 2002

NAME 1H

DEMOD NOH

EXMOD 270.05 MHz

OFFREQ 112.00 KHz

OFFSET 5800.0 Hz

POINT 16384

FREQ 5402.4 Hz

SCANS 8

ACQTM 3.033 sec

PD 3.967 sec

PW 5.1 us

PR 1H

IRNUC 24.3 c

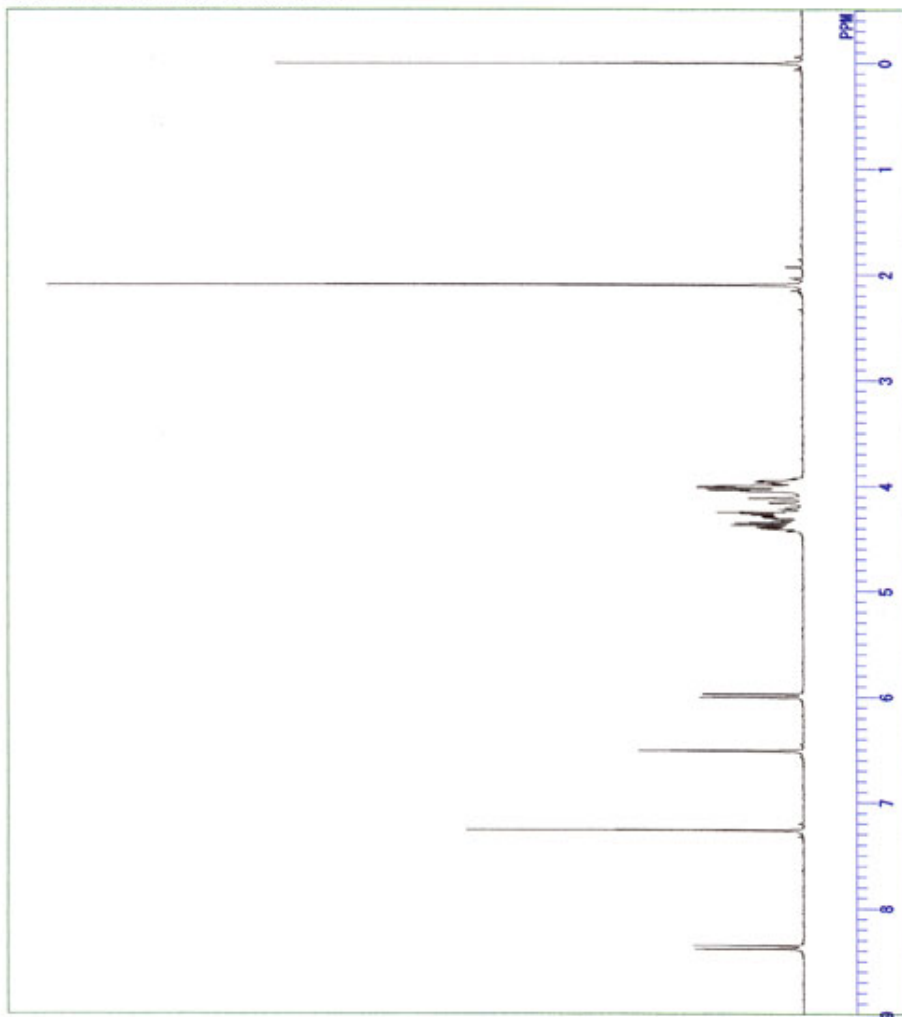
CTEMP CDCL3

SLVNT 0.00 ppm

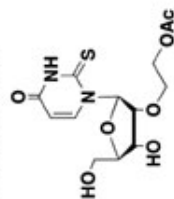
EXREF 0.20 Hz

BF 24

RGAIN



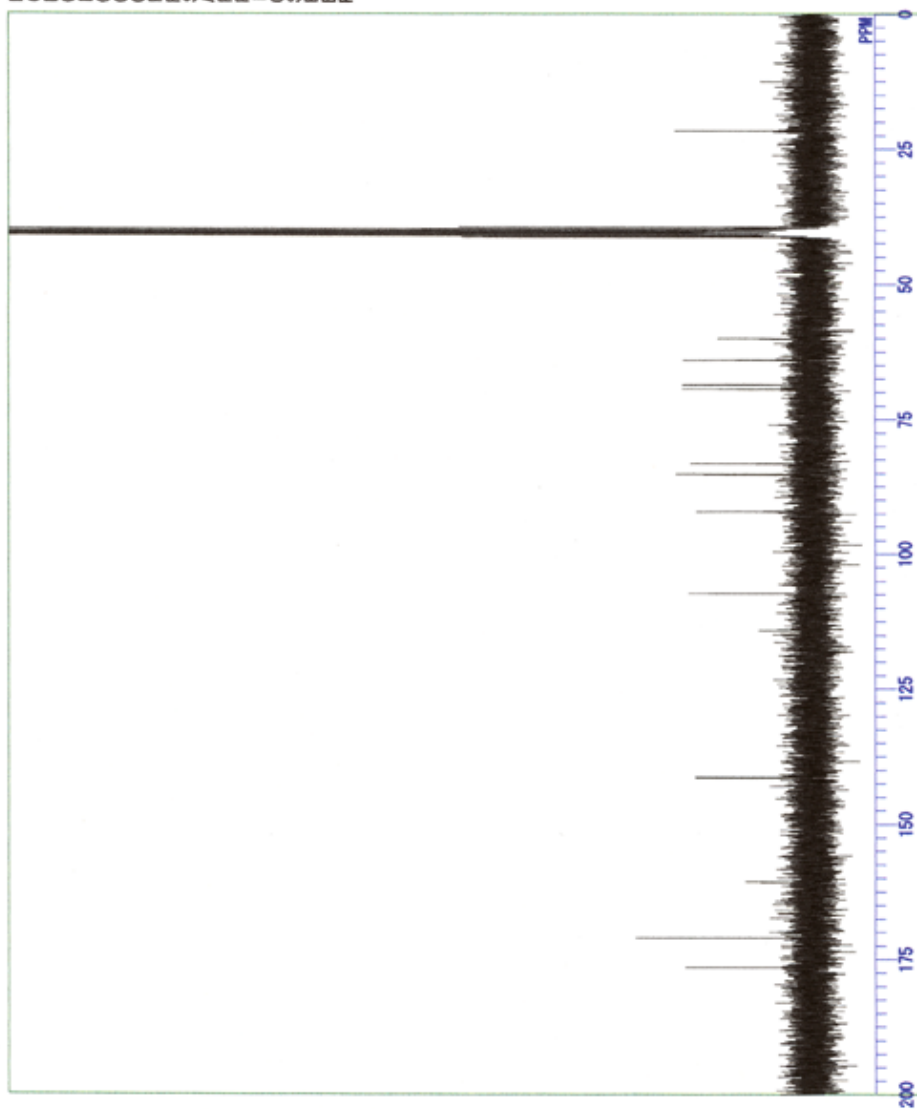
<sup>1</sup>H NMR spectrum



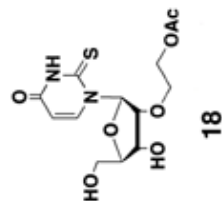
18

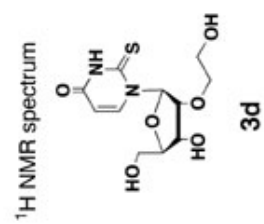
DFILE C:\My Documents\Yokamoto\Y2-CH2CH2O

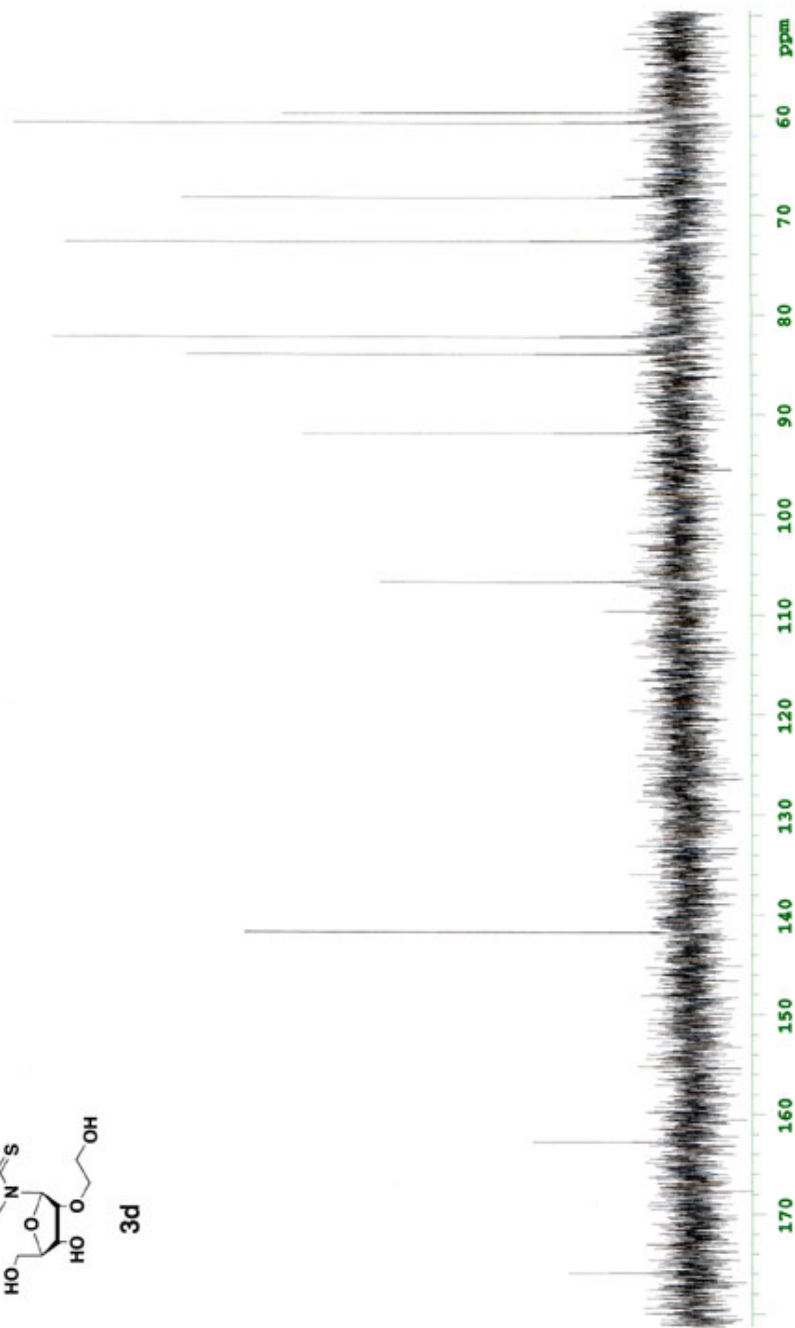
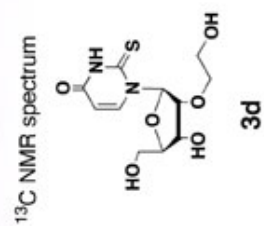
COMINT  
 DATIM Fri May 16 11:36:36 2003  
 CNUC 13C  
 EXM00 BOM  
 OFRO 67.80 MHz  
 OFSET 135.00 KHz  
 OFIN 5200.0 Hz  
 POINT 32768  
 FREQU 18315.0 Hz  
 SCANS 1277  
 ACQTM 1.789 sec  
 PD 1.211 sec  
 PW 4.4 us  
 PWT 1H  
 IRNUC 22.8 c  
 CTMP DMSO  
 SLVNT 77.00 ppm  
 EXREF 0.12 Hz  
 BF 27  
 RGAIN



<sup>13</sup>C NMR spectrum

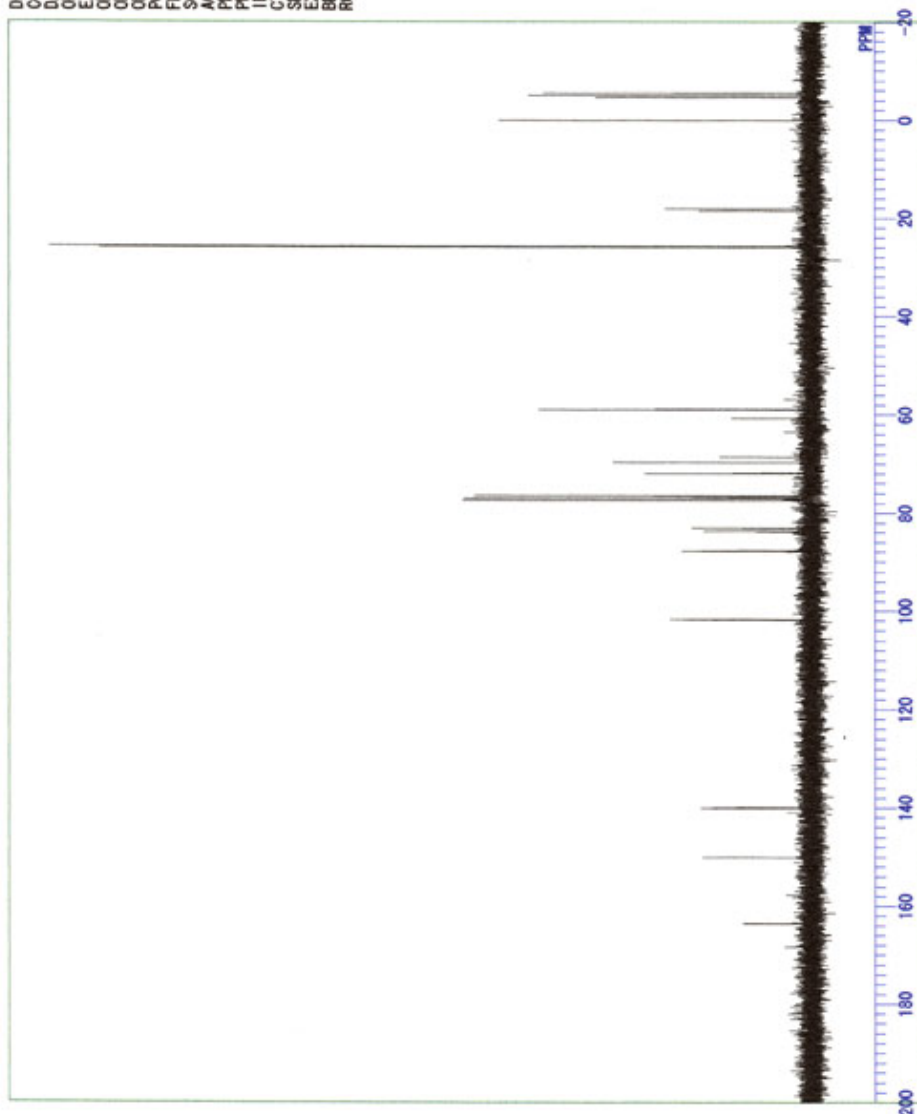




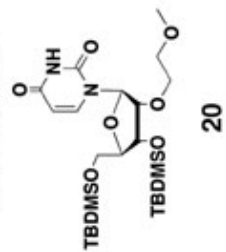




DFILE C:\My Documents\Kokamoto\Vanhydro met  
 CONNT Mon Feb 17 17:57:19 2003  
 DATIM 13C  
 GENUC 13C  
 EXMOD BCM  
 OFREQ 67.80 MHz  
 OBSET 135.00 KHz  
 OFEIN 5200.0 Hz  
 POINT 32768  
 FREQ 18315.0 Hz  
 SCANS 153  
 ACQTM 1.789 sec  
 PD 1.211 sec  
 PW 4.4 us  
 IRNUC 1H  
 CTMP 21.5 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 BF 0.12 Hz  
 RGAIN 27



<sup>13</sup>C NMR spectrum



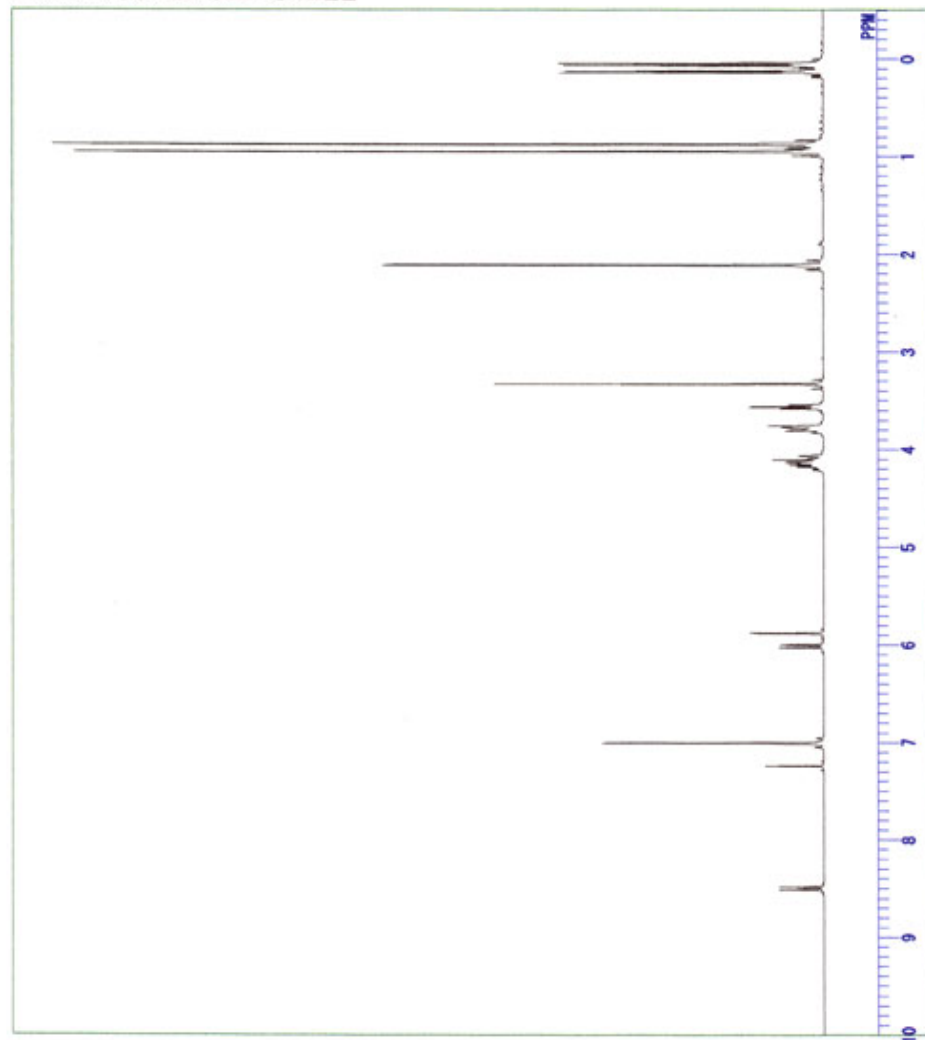


C:\My Documents\kokamoto\hydro method\4-4-

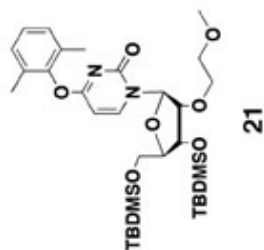
DE FILE  
 COUNT  
 DATIM  
 OBNUC  
 EXMOD  
 OBFRQ  
 OBSET  
 OBFIN  
 POINT  
 FREQU  
 SCANS  
 ACQTM  
 PD  
 PFI  
 TRNUC  
 CTEMP  
 SLVNT  
 EXREF  
 BF  
 RGAIN

Mon Feb 04 14:12:01 2002

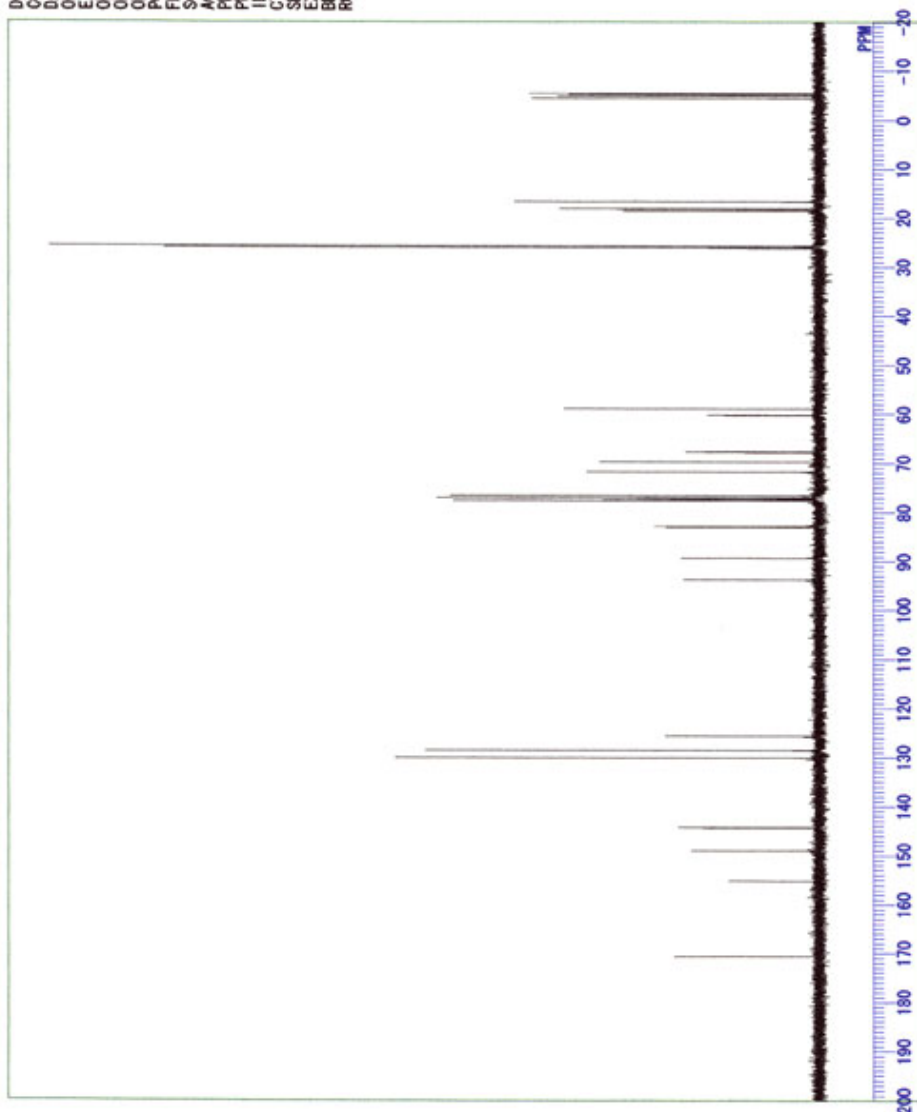
1H  
 270.05 MHz  
 112.00 KHz  
 5800.0 Hz  
 16384  
 5402.4 Hz  
 8  
 3.033 sec  
 3.967 sec  
 5.1 us  
 1H  
 21.6 c  
 CDCL3  
 7.24 ppm  
 0.20 Hz  
 14



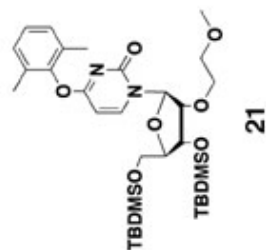
<sup>1</sup>H NMR spectrum



DFILE C:\My Documents\Kokamoto\anhydro met  
 COMMT Mon Feb 04 14:43:02 2002  
 DATIM 13C  
 GBNUC 13C  
 EXMOD BCM  
 OBFRQ 67.80 MHz  
 OBSET 135.00 KHz  
 OBFIN 5300.0 Hz  
 POINT 32768  
 FREQU 18315.0 Hz  
 SCANS 500  
 ACQTM 1.789 sec  
 PD 1.211 sec  
 PW 4.4 us  
 1H  
 IRNUC 21.4 c  
 CTMP CDCL3  
 SLVNT 77.00 ppm  
 EXREF 0.20 Hz  
 BF 32  
 RGAIN



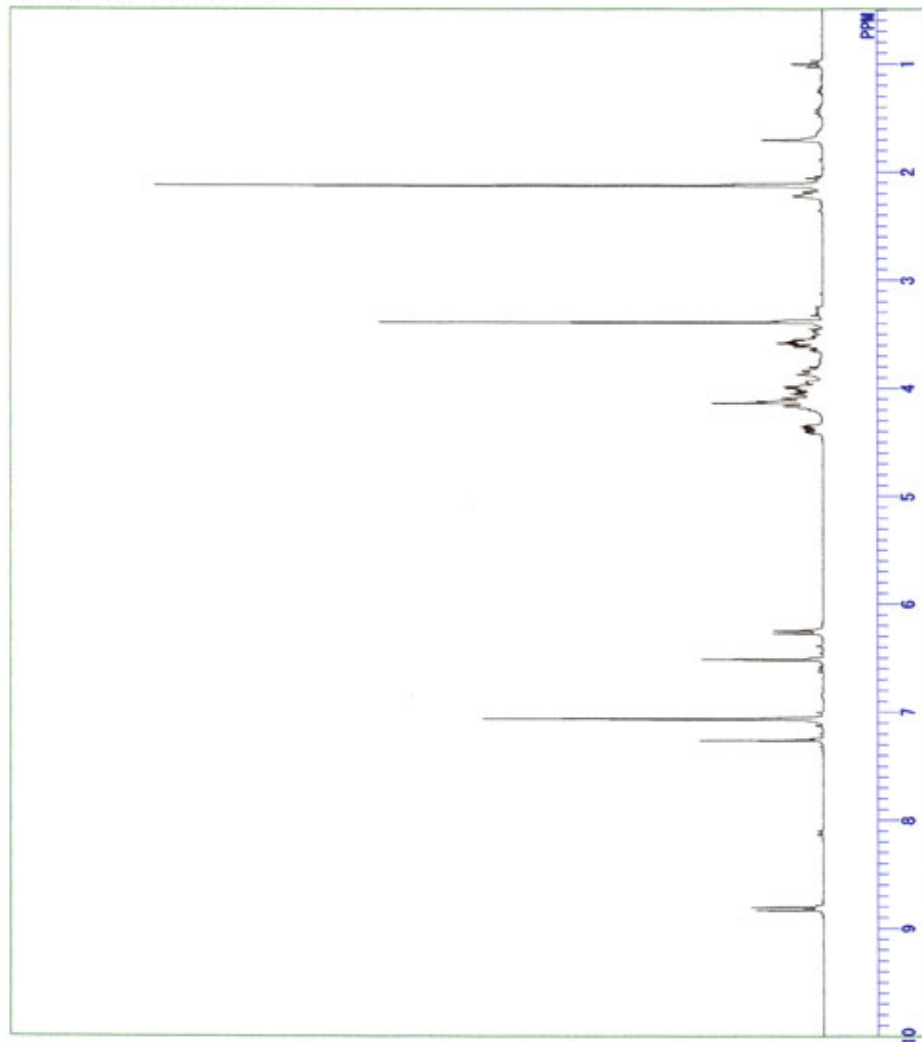
<sup>13</sup>C NMR spectrum



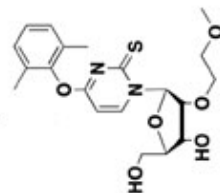
21

DFILE C:\My Documents\Yokamoto\5hydro method\4-1

CONV1  
DAT11 Mon Mar 11 00:53:04 2002  
GENUC 1H  
EXMOD NON  
OBFRQ 270.05 MHz  
OBSET 112.00 KHz  
OBFIN 5800.0 Hz  
POINT 16384  
FREQ 5402.4 Hz  
SCANS 8  
ACQTIM 3.033 sec  
PD 3.967 sec  
PULP 5.1 us  
PR1 1H  
IRNUC 1H  
CTEMP 24.6 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.20 Hz  
RGAIN 16

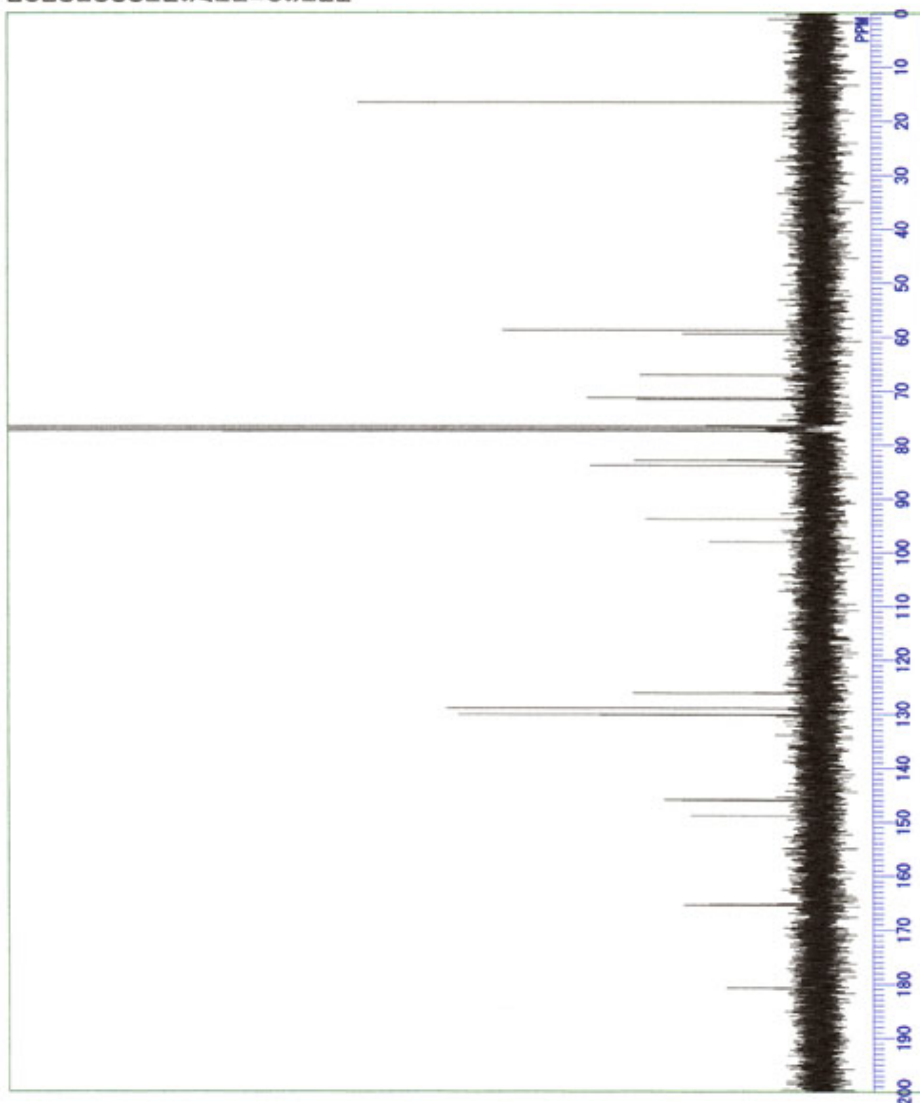


<sup>1</sup>H NMR spectrum

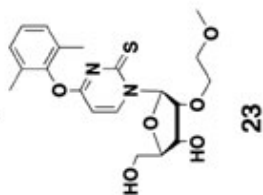


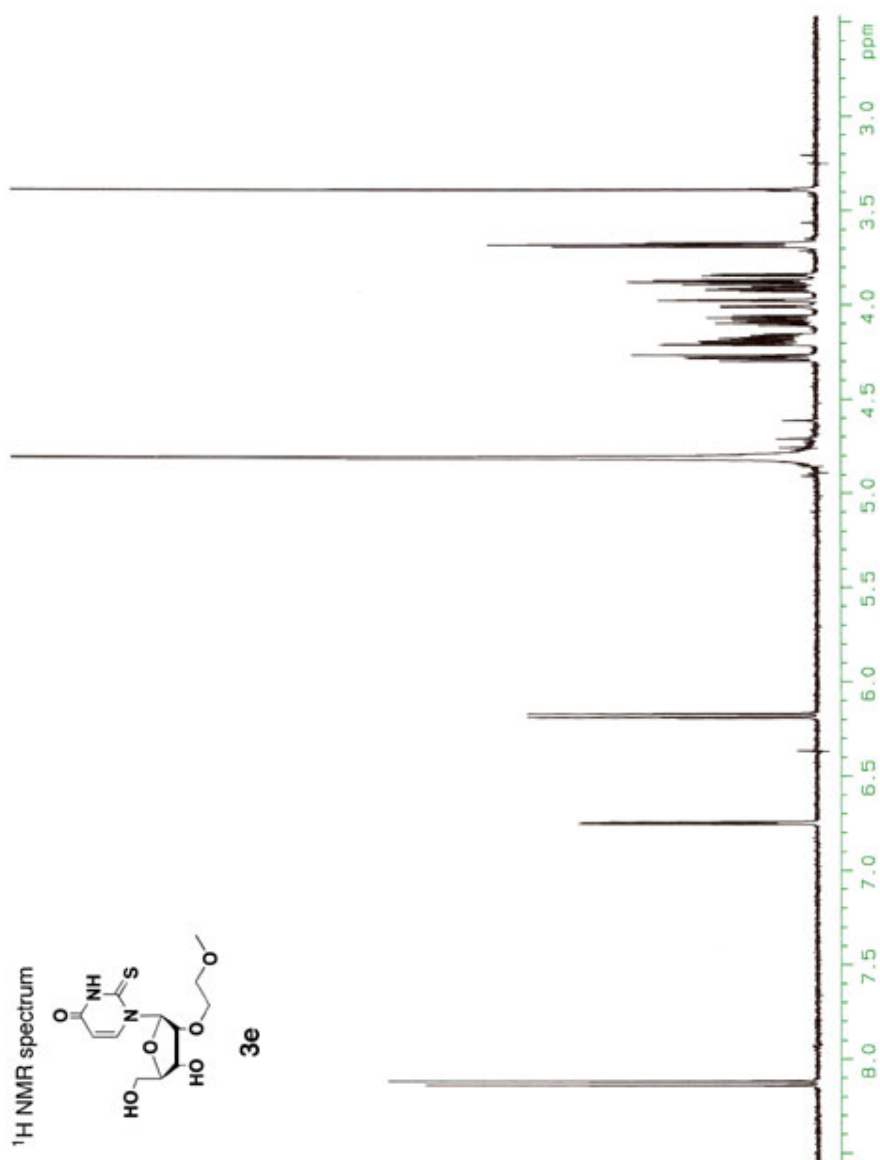
23

C:\My Documents\Kokamoto\2' -MOE-2,6-  
 DF1E COMMT  
 DATIM Sat Jul 26 16:09:35 2003  
 13C  
 EXMOD BCM  
 OBFRQ 67.80 MHz  
 OBSET 135.00 KHz  
 OBFIN 5200.0 Hz  
 POINT 32768  
 FREQ 18315.0 Hz  
 SCANS 1238  
 ACQTM 1.789 sec  
 PD 1.211 sec  
 PWT 4.4 us  
 1H  
 IRNUC 1H  
 CTMP 26.3 o  
 CDCL3  
 SLVT CDCL3  
 EXREF 77.00 ppm  
 RF 0.20 Hz  
 RGAIN 27



<sup>13</sup>C NMR spectrum

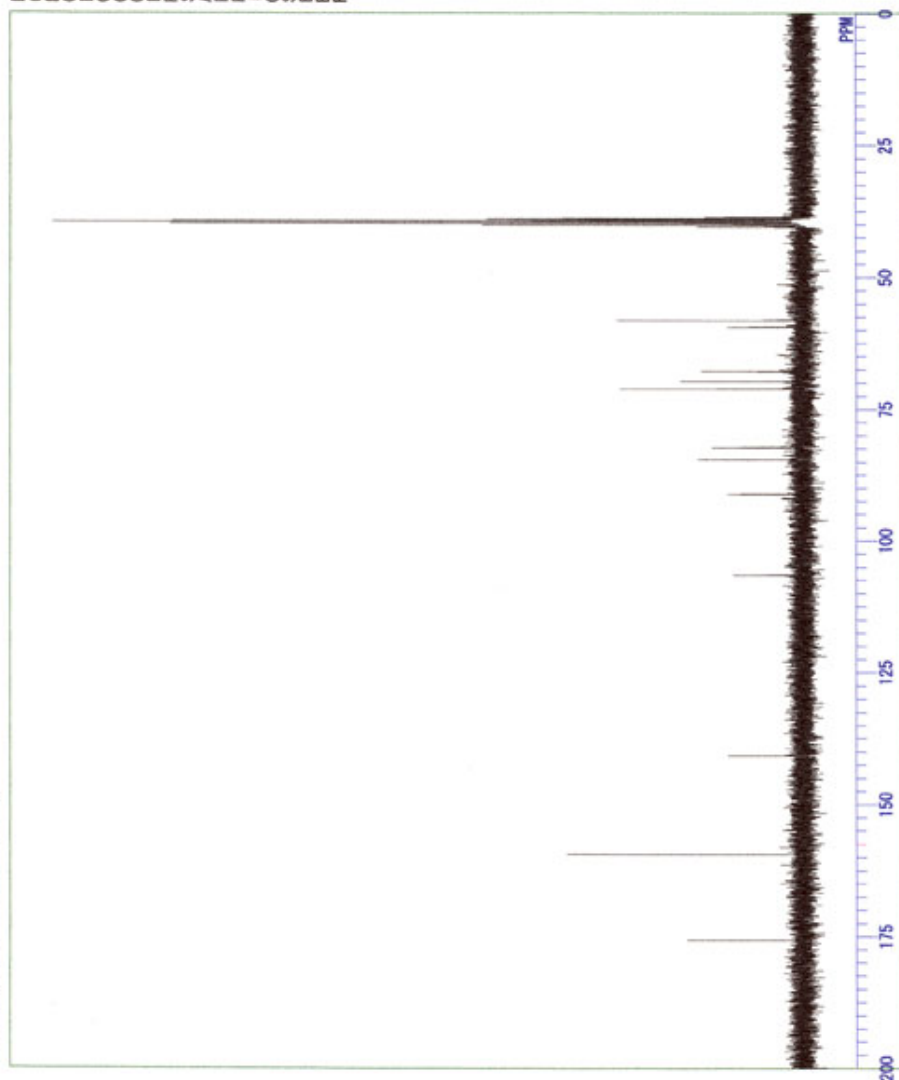




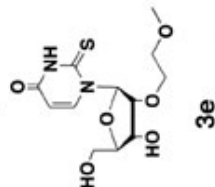
C:\WINNMR98\COMMON\DEFAULT.ALS

DEFILE C:\WINNMR98\COMMON\DEFAULT.ALS

COMPT Mon May 19 10:45:23 2003  
DATIN 13C  
ORNUC 13C  
EXMOD BCM  
ORPRO 67.80 MHz  
ORSET 135.00 KHz  
ORFIN 5200.0 Hz  
POINT 32768  
FREQ 18315.0 Hz  
SCANS 288  
ACQTM 1.789 sec  
PD 1.211 sec  
PWT 4.4 us  
IRNUC 1H  
CTEMP 23.9 o  
SOLVT DMSO  
EXREF 39.50 ppm  
RGAIN 0.20 Hz  
27



<sup>13</sup>C NMR spectrum



DFILE C:\My Documents\Yokamoto\5' DMT-2'-allyl s.

COMPT Mon Apr 28 12:18:09 2003

OBNUC 1H

EXMOD NON

OBFRQ 270.05 MHz

OBSET 112.00 KHz

OBFIN 5800.0 Hz

POINT 16384

FREQ 5402.4 Hz

SCANS 8

ACQTM 3.033 sec

PD 3.967 sec

PW 5.1 us

IRNUC 1H

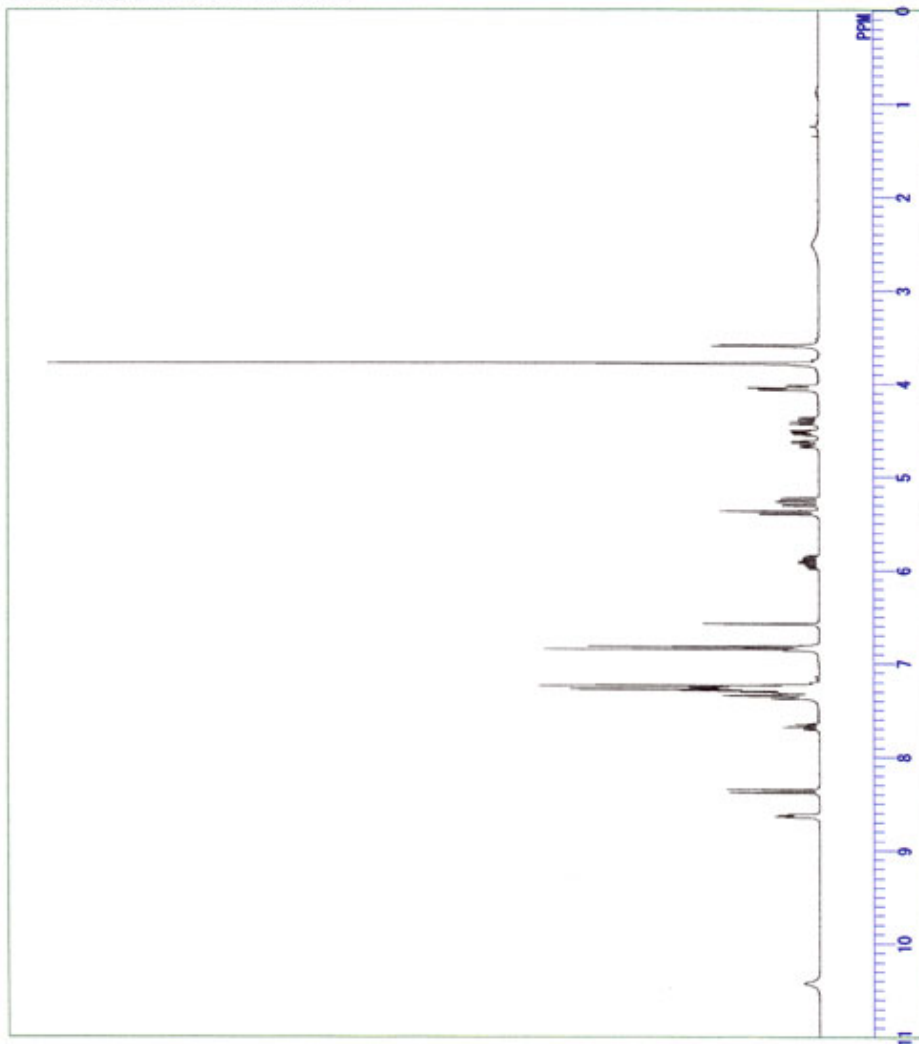
CTEMP 23.4 C

SLVNT CDCL3

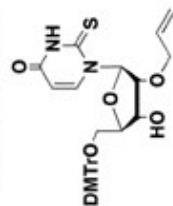
EXREF 7.24 ppm

BF 0.12 Hz

RGAIN 21

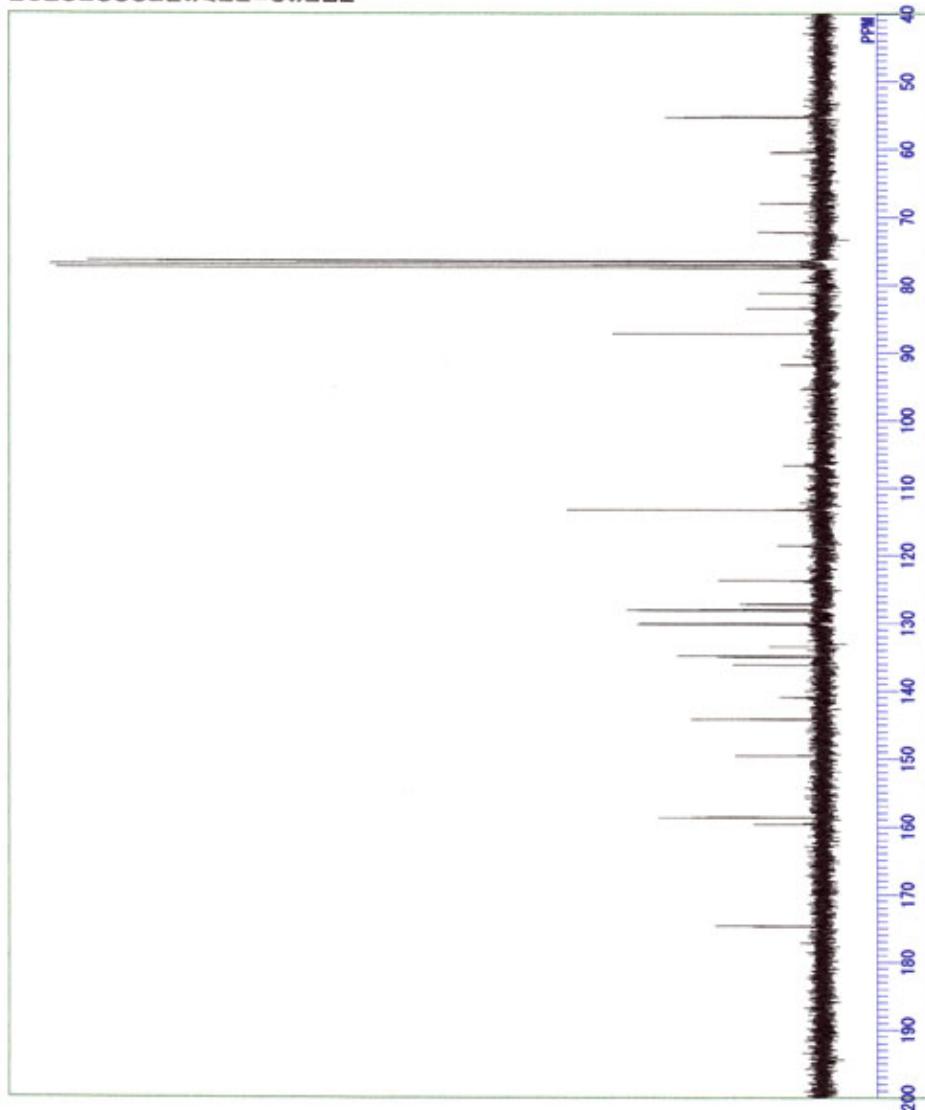


<sup>1</sup>H NMR spectrum

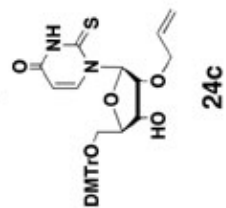


24c

D:\My Documents\Kokamoto\5' DMTr-2' -a  
 COMPT Mon Apr 28 13:07:40 2003  
 DATUM 13C  
 EXM00 BCM 67.80 MHz  
 OBSFQ 135.00 KHz  
 OBSSET 5200.0 Hz  
 OBSF IN 32768  
 POINT 18315.0 Hz  
 FREQ 891  
 SCANS 1.789 sec  
 ACQTM 1.211 sec  
 PD 4.4 us  
 PWT 1H 22.9 c  
 IRRUC SLVNT CDCL3  
 CTMP 77.00 ppm  
 EXREF BF 0.20 Hz  
 RGAIN 27



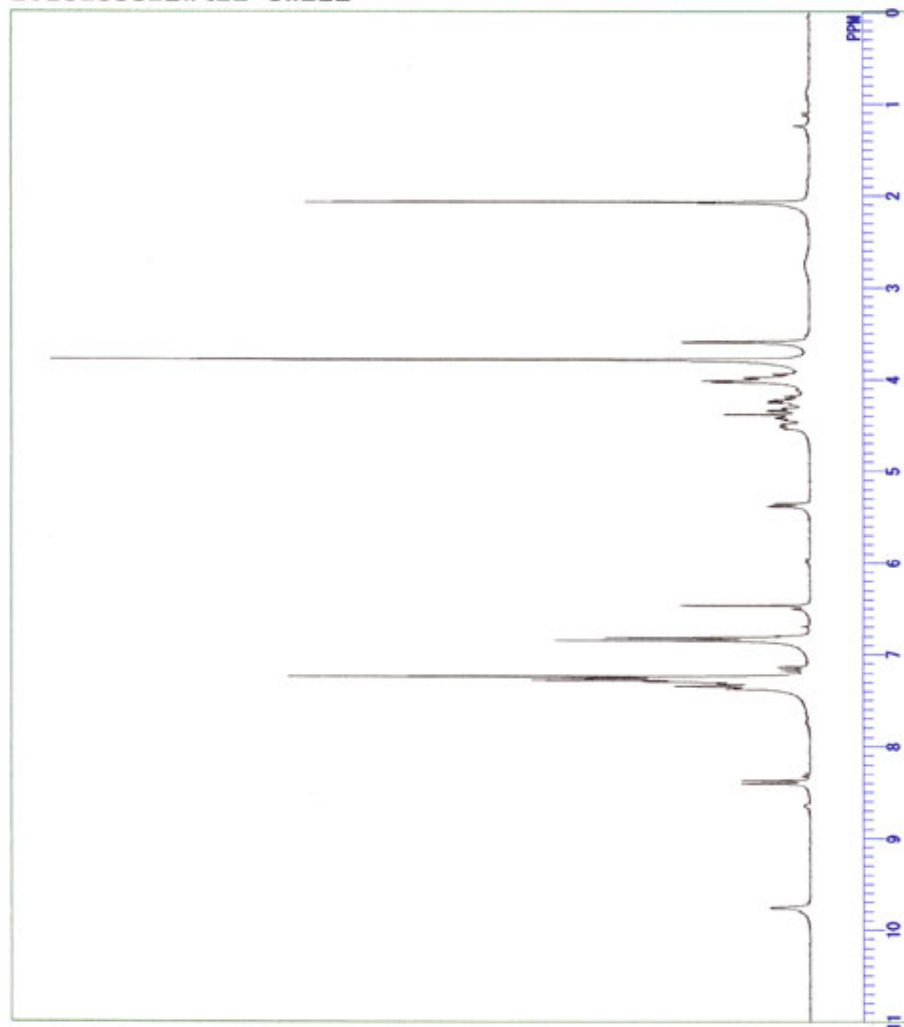
<sup>13</sup>C NMR spectrum



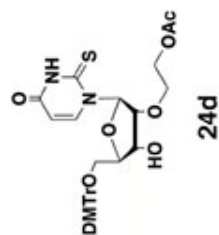


C:\My Documents\kokamoto\5'-DMTr 2'-CH2CH2

DF FILE  
 COUNT  
 DATE Mon Apr 28 15:26:03 2003  
 ORNUC 1H  
 EXMDO NON  
 ORFRO 270.05 MHz  
 ORSET 112.00 KHz  
 ORFIN 5800.0 Hz  
 POINT 16384  
 FREQU 5402.4 Hz  
 SCANS 64  
 ACQTM 3.033 sec  
 PD 3.967 sec  
 PW1 5.1 us  
 IRNUC 1H  
 CTEMP 21.9 c  
 SLVNT CDCL3  
 EXREF 7.24 ppm  
 RF 0.20 Hz  
 RGAIN 25

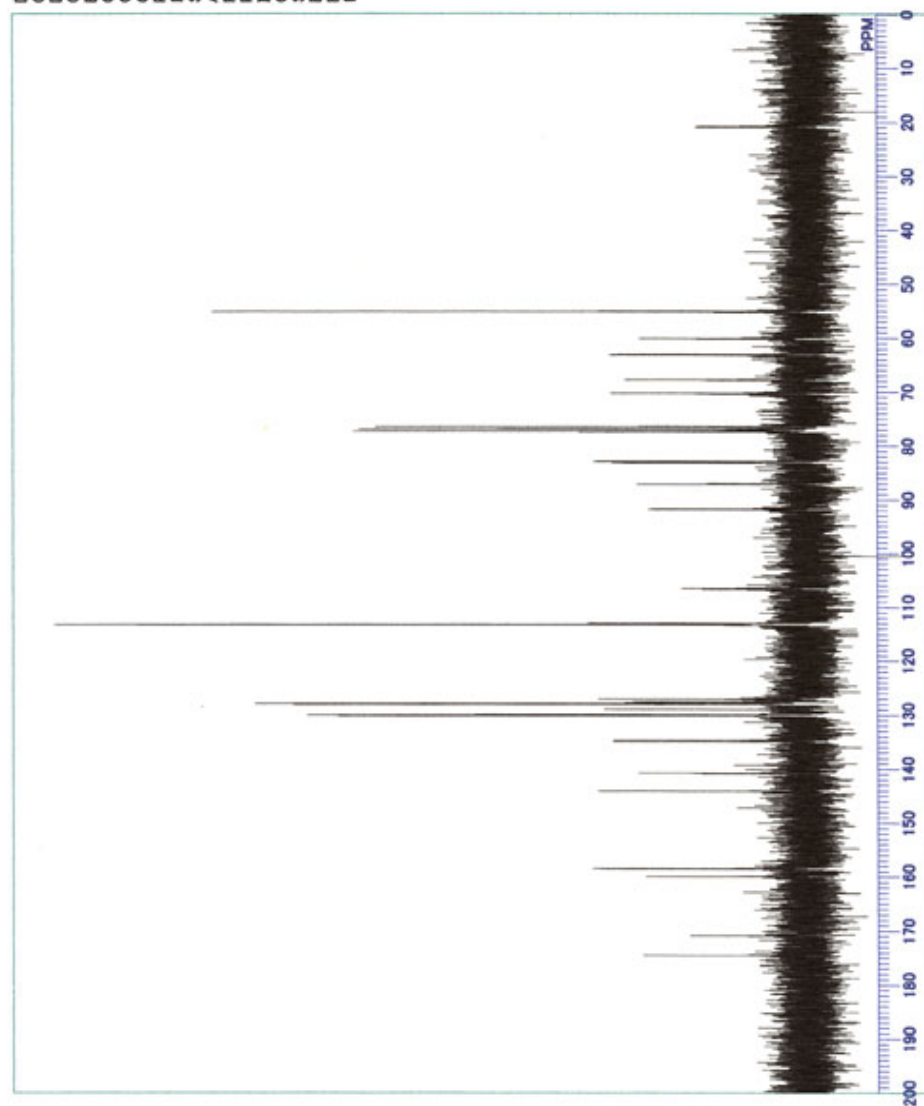


<sup>1</sup>H NMR spectrum

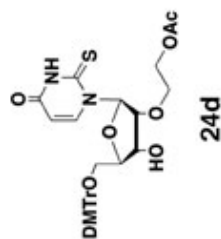


C:\My Documents\Yokamoto\27-O-R 4

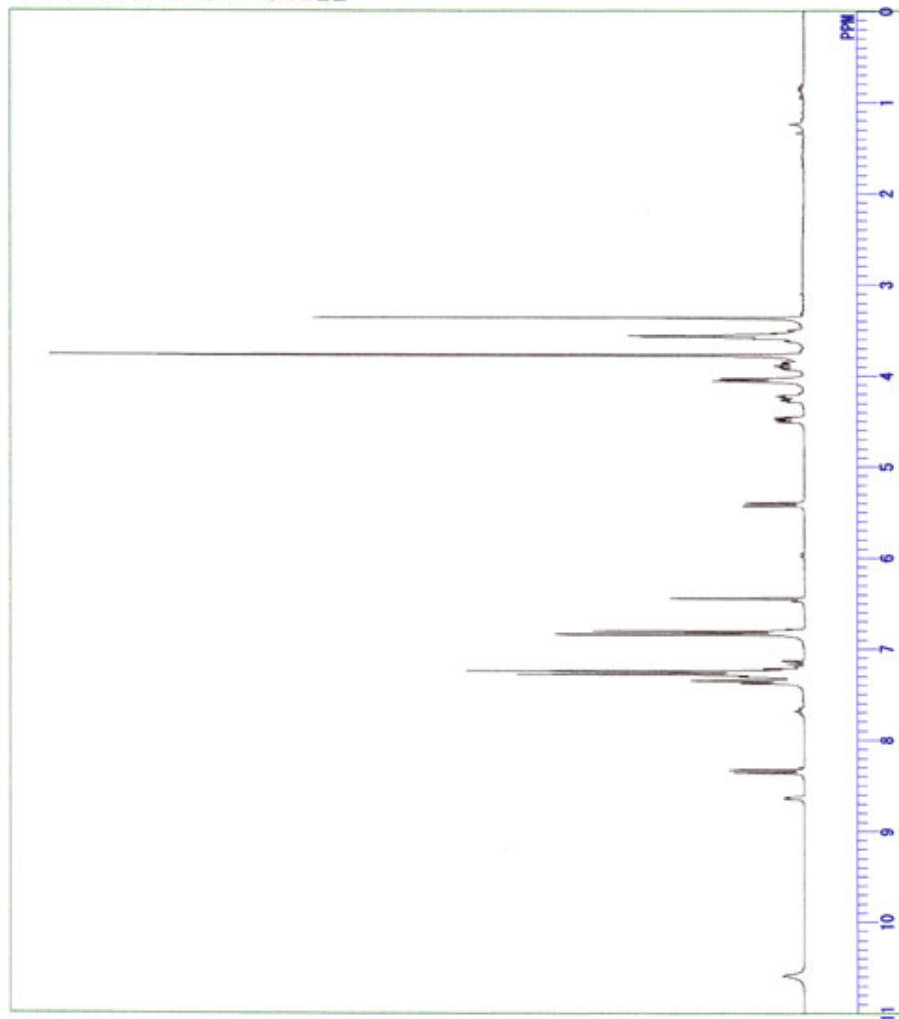
DFILE COMINT  
 DATIM Tue Apr 29 18:45:48 2003  
 13C  
 EXMOD BCM  
 OBFRQ 67.80 MHz  
 OBSET 135.00 KHz  
 OBFIN 5200.0 Hz  
 POINT 32768  
 FREQU 18315.0 Hz  
 SCANS 431  
 ACQTM 1.789 sec  
 PD 1.211 sec  
 PW1 5.2 us  
 1H 23.0 c  
 CDCL3 77.00 ppm  
 EXREF BF 0.12 Hz  
 RGAIN 28



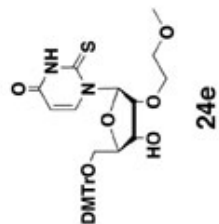
<sup>13</sup>C NMR spectrum



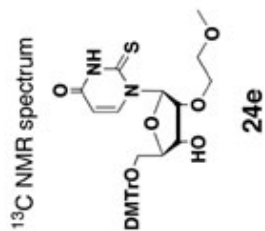
C:\MY Documents\Kamato\5 DMTr-2'-MOE s2U  
 DF FILE  
 COMNT  
 DATIM Wed May 14 17:00:31 2003  
 OBNJC 1H  
 EXMOD NON  
 OFFRQ 270.05 MHz  
 OBSET 112.00 KHz  
 OFEIN 5800.0 Hz  
 POINT 16384  
 FREQD 5402.4 Hz  
 SCANS 8  
 ACQIM 3.033 sec  
 PD 3.967 sec  
 PWT 5.1 us  
 IRNUC 1H  
 CTEMP 22.7 c  
 SLVNT CDCL3  
 EXREF 7.24 ppm  
 BF 0.20 Hz  
 RGAIN 20



<sup>1</sup>H NMR spectrum

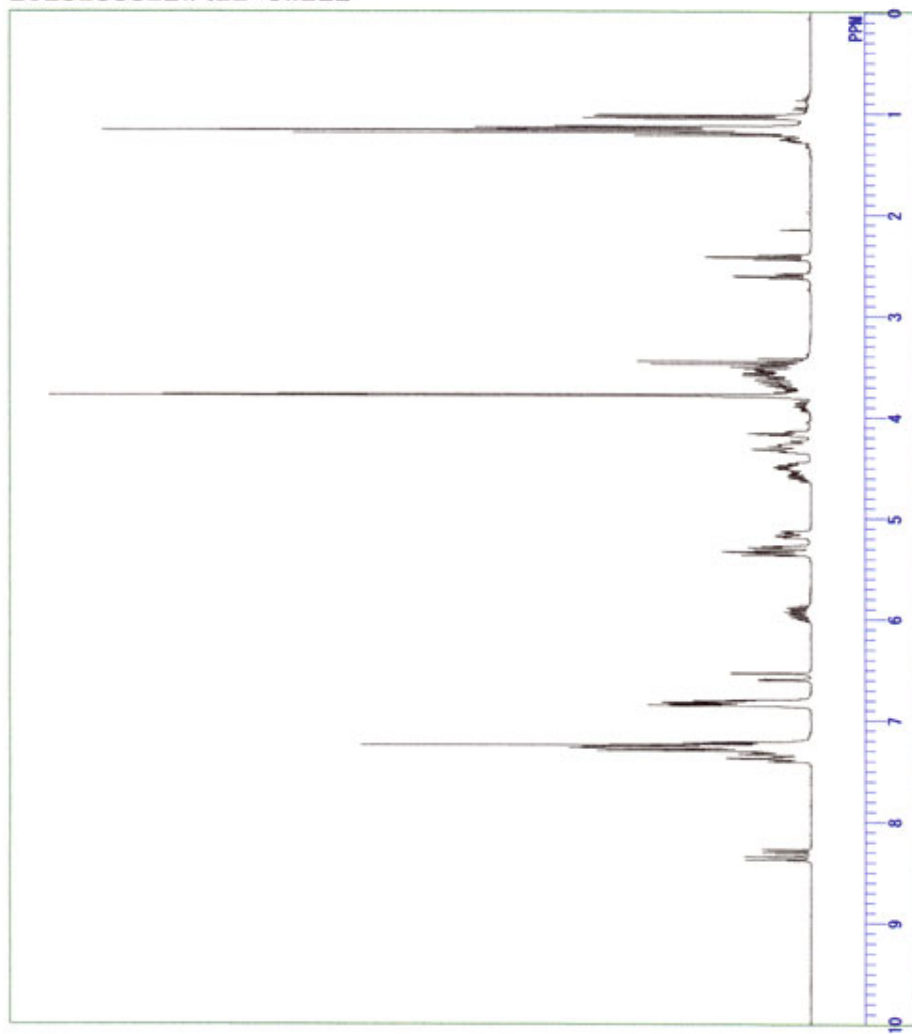


DFILE C:\My Documents\Kokamoto\5' DMTr-2'-M  
 COMMT Wed May 14 17:14:51 2003  
 DATIM 13C  
 OBNUC 67.80 MHz  
 EXMOD 135.00 KHz  
 OBFRQ 5200.0 Hz  
 OBSET 32768  
 OBFIN 18315.0 Hz  
 POINT 208  
 FREQ 1.789 sec  
 SCANS 1.211 sec  
 ACQTM 4.4 us  
 PD 1H  
 PW1 22.8 g  
 IRNUC CDCL3  
 CTMP 77.00 ppm  
 SLVT EXREF 0.20 Hz  
 BF 27  
 RGAIN

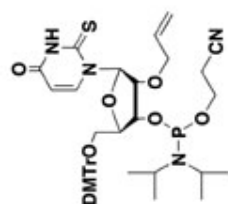


DFILE C:\My Documents\Kokamoto\20 amideV2'-0-

COMET  
 DATIM Sat Aug 02 20:51:58 2003  
 ORNUC 1H  
 EXMOD NON  
 OFPRO  
 OFSET 270.05 MHz  
 OFSET 112.00 KHz  
 OFSET 5800.0 Hz  
 POINT 16384  
 FREQ 5402.4 Hz  
 SCANS 8  
 ACQTIM 3.033 sec  
 PD 3.967 sec  
 PRT 5.1 us  
 IN 1H  
 INUC 34.3 o  
 CTMP  
 SLVIT CQGL3 7.24 ppm  
 EXREF 0.20 Hz  
 BF 20  
 RGAIN



<sup>1</sup>H NMR spectrum

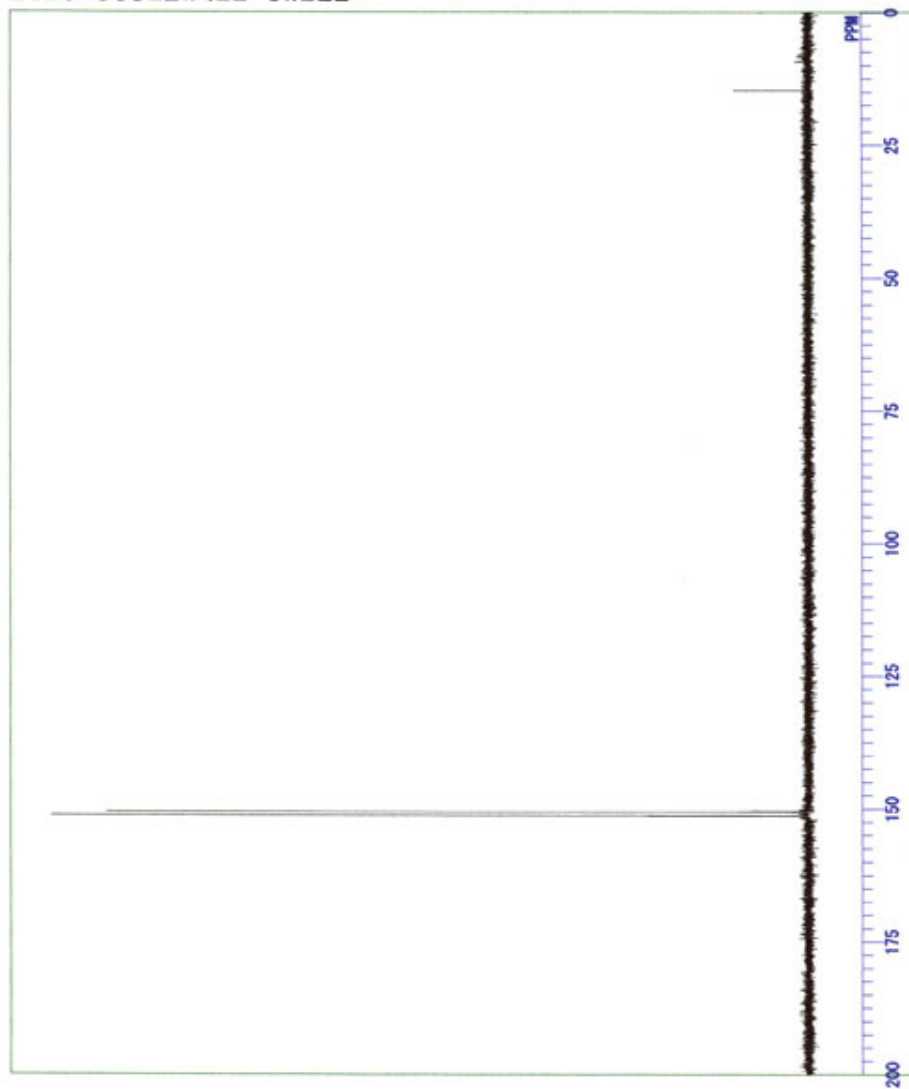


25c

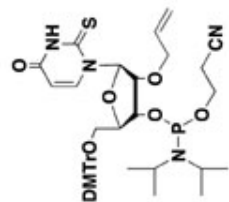
CC(C)N(C(C)C)COP(=O)(OCC#N)OCC1C(OC1COC2=CN=C(NC(=O)O2)S)COC3=CC=CC=C3

**25c**

DFILE C:\My Documents\Kokamoto\20 amide  
 COMINT  
 DATIM Sat Aug 02 20:48:47 2003  
 GENUC 31P  
 EXM00 BCM  
 QBFRQ 109.25 MHz  
 QBSET 121.10 KHz  
 QBFIN 36.4 Hz  
 POINT 32768  
 FREQU 400000.0 Hz  
 SCANS 80  
 ACQIM 0.819 sec  
 PD 5.000 sec  
 PWT 7.1 us  
 TRNUC 1H  
 CTEMP 34.8 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 BF 0.20 Hz  
 RGAIN 31

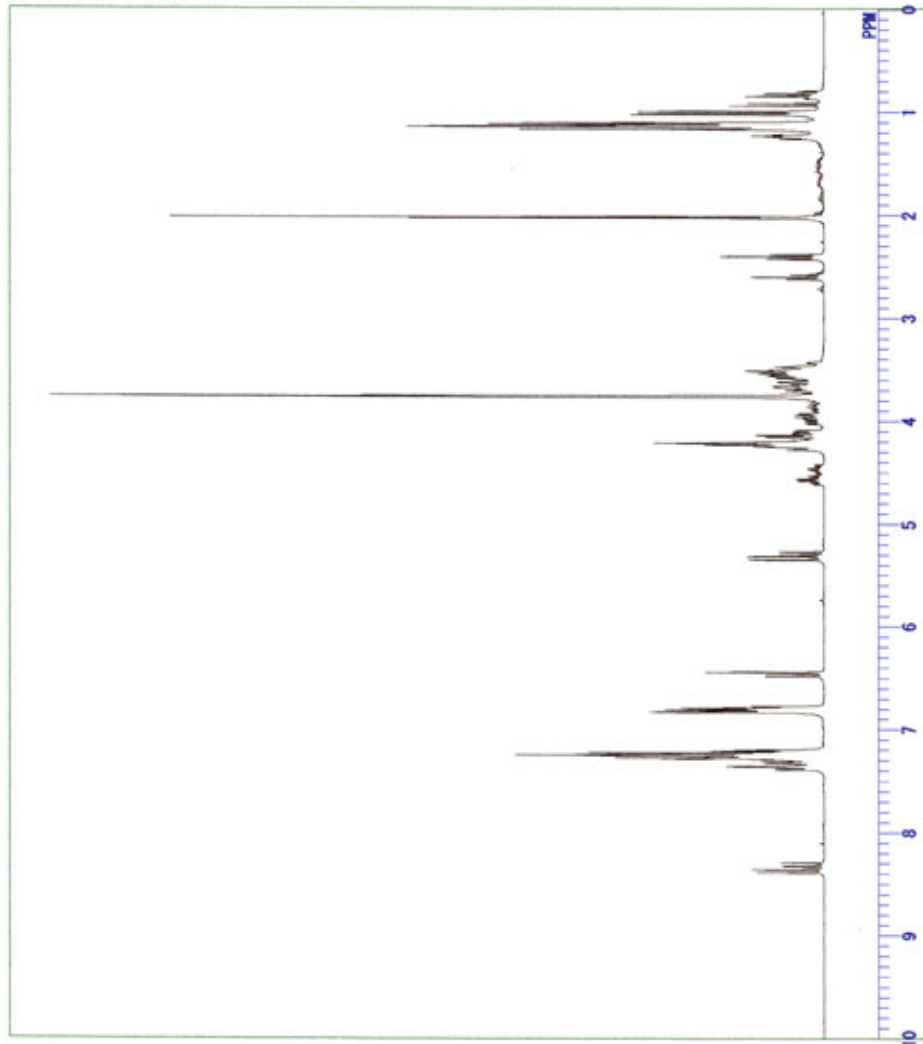


$^{31}\text{P}$  NMR spectrum

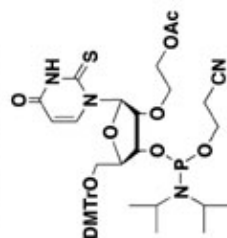


25c

OFILE C:\Nky Documents\Yokamoto\20\2003 2003  
 COMPT Fri Aug 01 20:41:33 2003  
 DATIM TH  
 GENUC TH  
 EXMOD NON  
 OBSFRQ 270.05 MHz  
 OBSSET 112.00 KHz  
 OBSF1N 5800.0 Hz  
 POINT 16384  
 FREQU 5402.4 Hz  
 SCANS 16  
 ACQTM 3.033 sec  
 PD 3.987 sec  
 PWT 5.1 us  
 IRNUC 1H  
 CTMP 32.5 c  
 SLVNT CDCL3  
 EXREF 7.24 ppm  
 BF 0.20 Hz  
 RGAIN 19



<sup>1</sup>H NMR spectrum

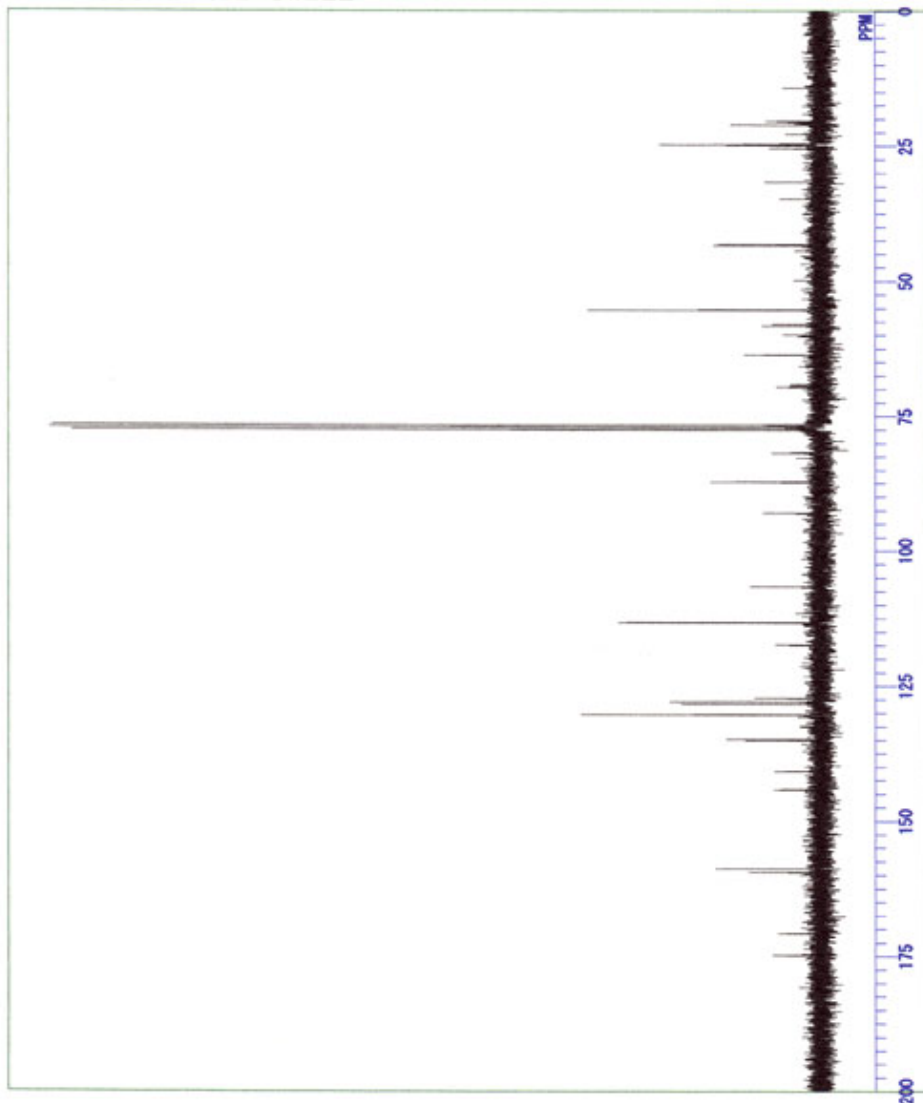


25d

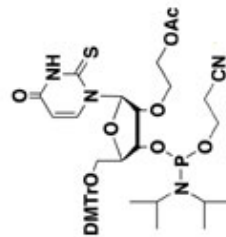


C:\My Documents\Yokamoto\20 anidite

DFILE  
COMNT  
DATIM  
FRI Aug 01 21:30:32 2003  
13C  
OBNUC  
EXMOD  
BOM  
67.80 MHz  
135.00 KHz  
5200.0 Hz  
32768  
18315.0 Hz  
729  
1.789 sec  
1.211 sec  
4.4 us  
1H  
IRNUC  
CTEMP  
CDCL3  
33.5 °  
SLVNT  
EXREF  
BF  
RGAIN  
77.00 ppm  
0.20 Hz  
29



<sup>13</sup>C NMR spectrum



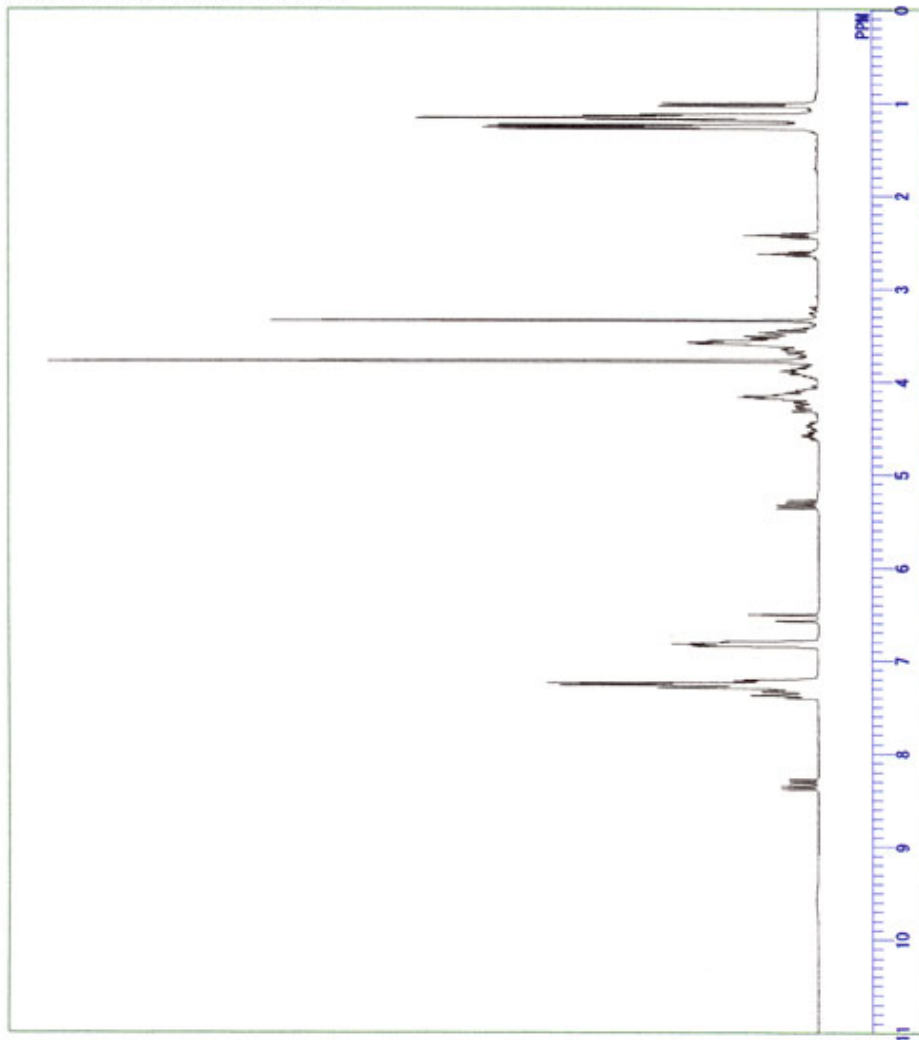
25d

The spectrum shows two distinct signals. The first signal is a triplet centered at approximately 150 ppm, with a peak height of about 1.5 units. The second signal is a quartet centered at approximately 40 ppm, with a peak height of about 1.0 unit. The baseline is flat and noisy, with minor fluctuations around 100 ppm and 175 ppm.

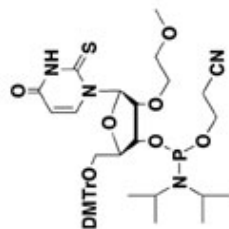
CN(C)C(=O)[C@H]1[C@@H](OC(=O)c2ccccc2)[C@H](OC(=O)c3ccccc3)[C@H](OC(=O)c4ccccc4)[C@H](OP(=O)(c5ccccc5)OC6=CNC(=S)N=C6N)O1

25d

DFILE C:\WINNMR98\COMMON\DEFAULT.ALS  
 COUNT  
 DATIM Fri Aug 08 21:56:23 2003  
 OBNUC 1H  
 EXMOD NON  
 OBFRQ 270.05 MHz  
 OBSET 112.00 KHz  
 OBFIN 5800.0 Hz  
 POINT 16384  
 FREQU 5402.4 Hz  
 SCANS 32  
 ACQTIM 3.033 sec  
 PD 3.967 sec  
 PW 5.1 us  
 IRNUC 1H  
 CTEMP 28.5 C  
 SLVNT CDCL3  
 EXREF 7.24 ppm  
 BF 0.20 Hz  
 RGAIN 21

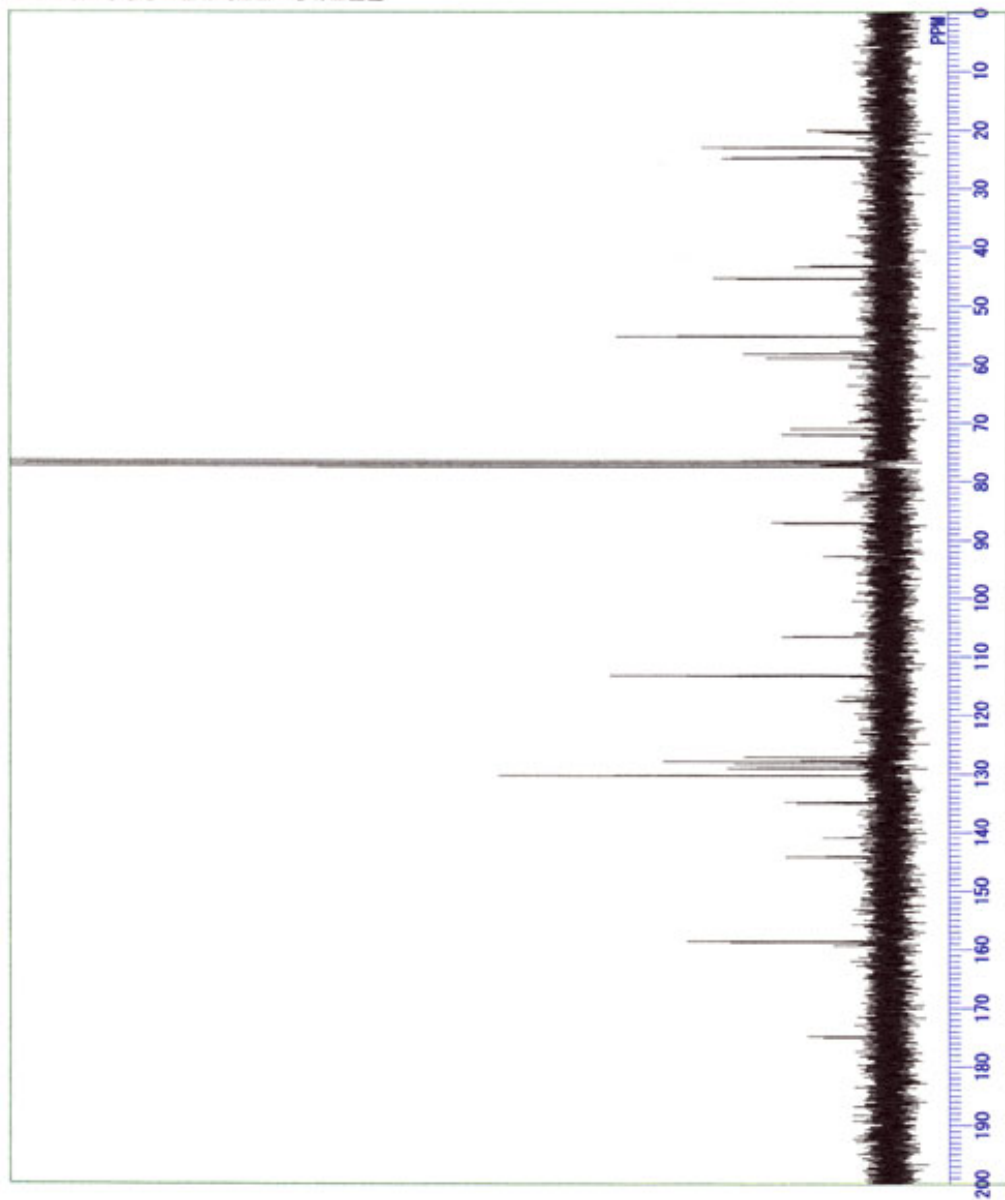


<sup>1</sup>H NMR spectrum

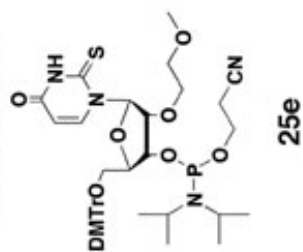


25e

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 DATE Fri Aug 08 23:33:57 2003  
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 EXMOD BCM  
 OBPRO 67.80 MHz  
 OBSET 135.00 KHz  
 OBFTN 5200.0 Hz  
 POINT 32768  
 FREQU 18315.0 Hz  
 SCANS 1859  
 ACQTM 1.789 sec  
 PD 1.211 sec  
 PW1 4.4 us  
 1H  
 IRNUC 28.6 c  
 CTEMP CDCL3  
 SLVNT 77.00 ppm  
 EXREF 0.20 Hz  
 BF 28  
 RGAIN



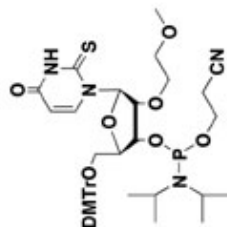
<sup>13</sup>C NMR spectrum



25e

DF:FILE C:\Nly Documents\Kamato\anhydro met  
 COMINT Mon Mar 18 13:02:32 2002  
 DATIM 31P  
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 EXM00 109.25 MHz  
 OBF00 121.10 KHz  
 OBF01 36.4 Hz  
 POINT 32768  
 FREQ0 40000.0 Hz  
 SCANS 76  
 ACQTM 0.819 sec  
 PD 5.000 sec  
 PW1 7.1 us  
 TRNJC 1H  
 CTMP 24.1 c  
 SLVNT CDCL3  
 EXREF 0.00 ppm  
 RF 0.20 Hz  
 RGAIN 26

<sup>31</sup>P NMR spectrum



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