

SUPPORTING INFORMATION

Synthesis and structural studies of S-type/N-type-locked/frozen nucleoside analogues and their incorporation in RNA-selective, nuclease resistant 2'-5'linked oligonucleotides

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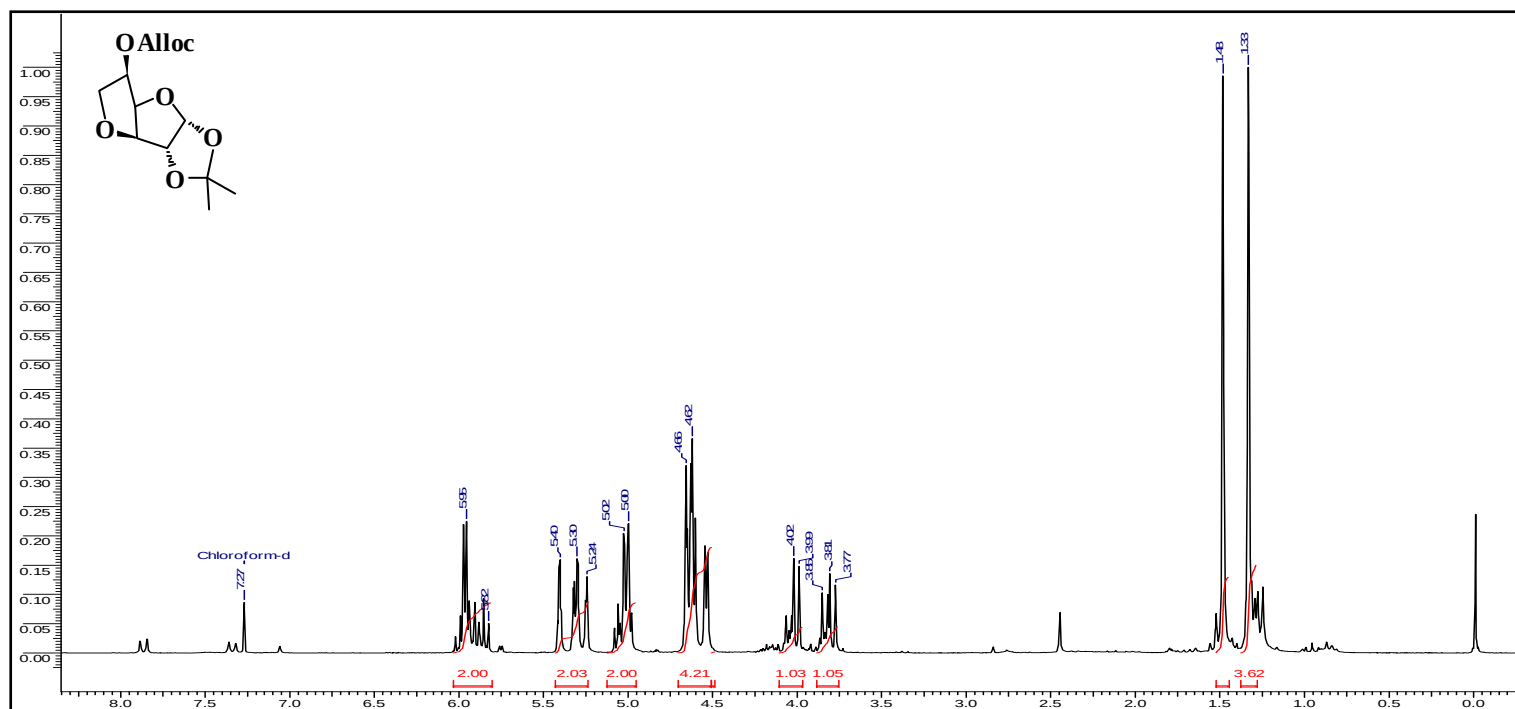
Table 1. Chemical shift value of S and N-type locked and frozen nucleoside (CD₃OD)

Entry	Compound	1'	2'	3'	4'	5a'	5a''	5b' 6a'	5b'' 6a''	H5	H6
1	(U ^S , I)	6.33	4.04	4.97	-----	3.65	3.74	4.42	4.74	5.67	7.60
2	(U ^N , II)	5.95	4.33	4.36	4.68	4.45	-----	3.72	3.97	5.72	7.95
3	(^t U ^F , III)	5.74	4.37	4.94	4.29	3.77	3.75	---	---	6.06	7.96
4	(^x U ^F , IV)	5.83	4.42	4.96	4.37	3.95	3.92	---	---	5.70	7.65

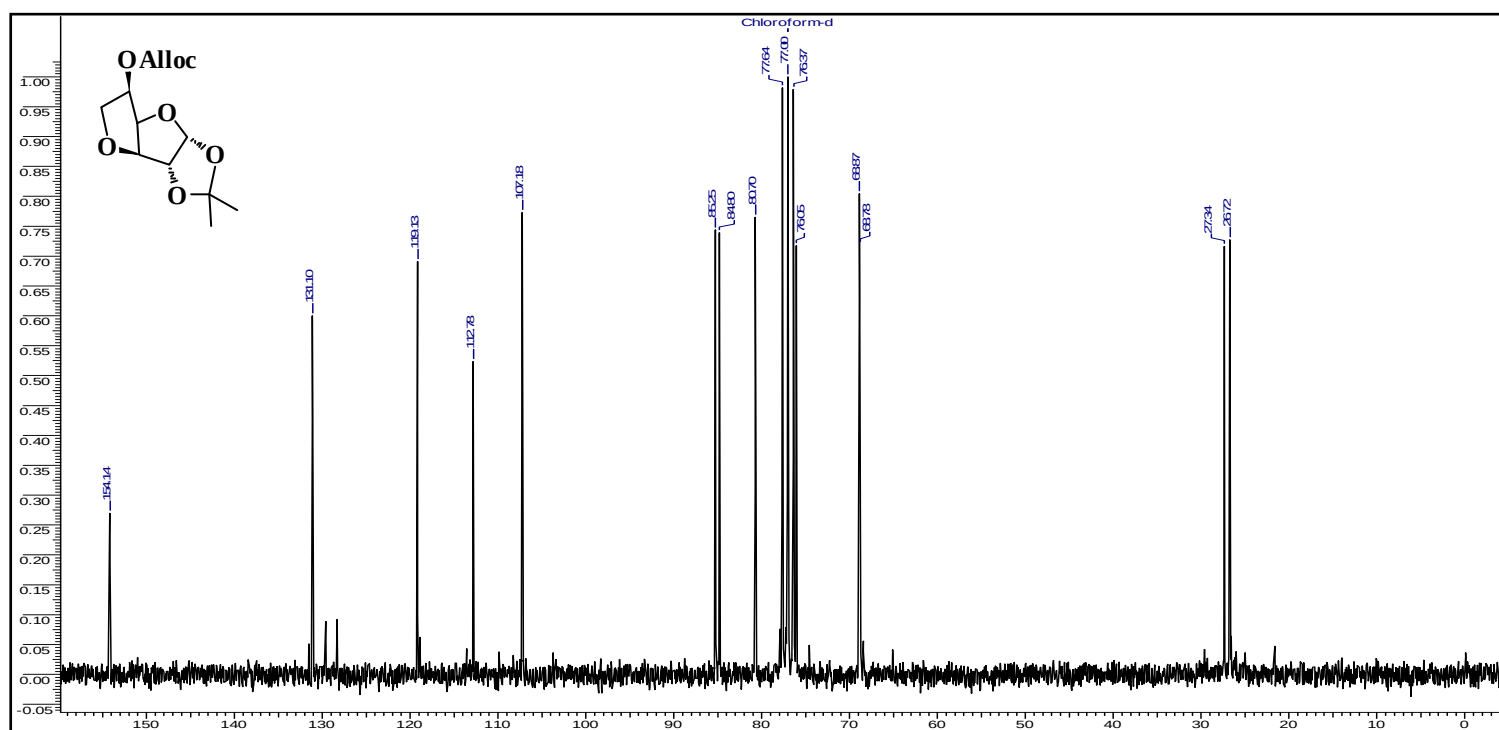
Table 2. ³J_{HH} ¹H NMR coupling constant of S and N-type locked and frozen nucleoside

Entry	Compound	1'2'	2'3'	3'4'	4'5'	4'5'' (5'6a')	5a'5a'' (5'6a'')	5b'5b'' (6'a6a'')	2'F	3'F	4'F	5,6
1	(U ^S , I)	7.39	4.61	----	----	---	12.44	7.96	----	----	----	8.0
2	(U ^N , II)	3.4	1.81	4.18	4.89	6.9	6.3	9.04	----	-----	-----	8.1
3	(^t U ^F , III)	7.71	4.5	0.76	2.65	3.0	12.0	---	23.4	54.4	27.1	8.08
4	(^x U ^F , IV)	1.01	1.01	2.5	5.92	6.19	11.7	----	13.6	54.7	36.63	8.09

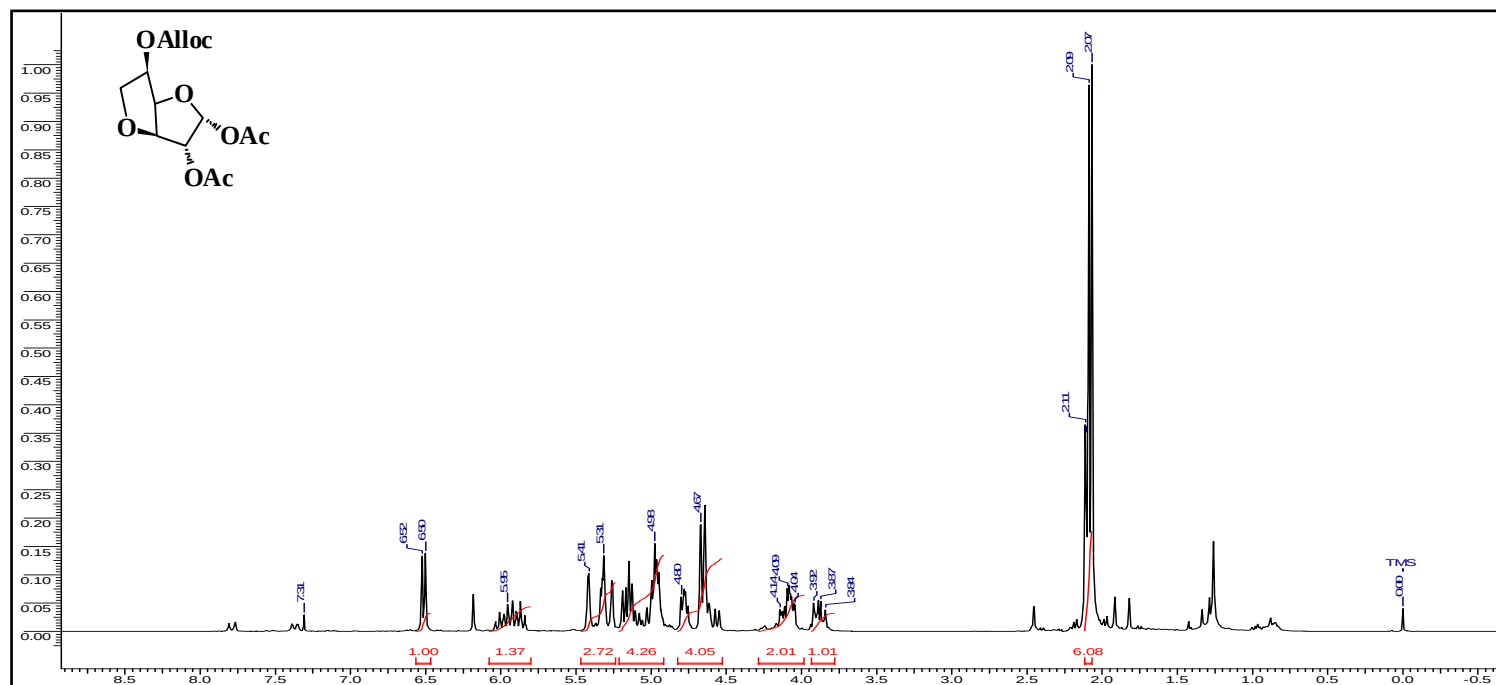
^1H NMR (CDCl_3 , 200MHz) Compound 2



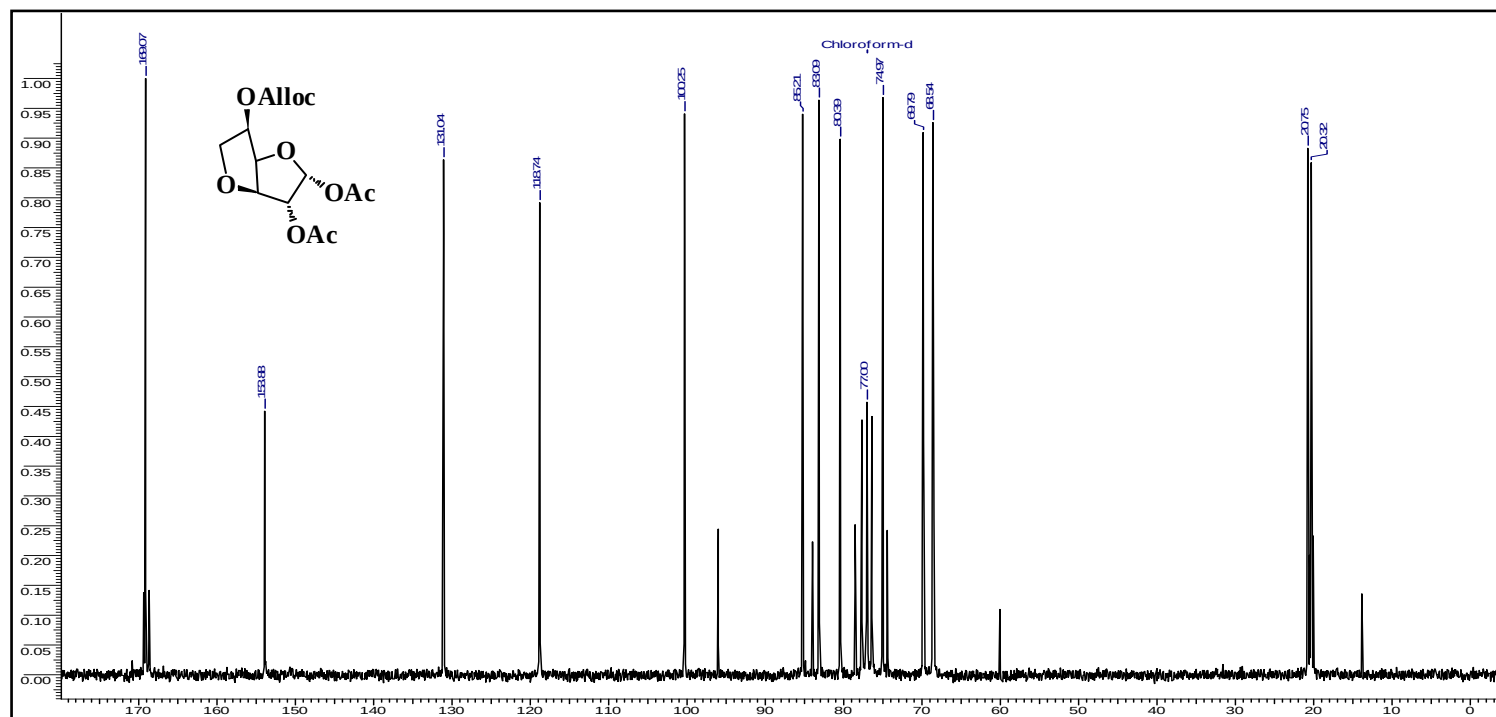
^{13}C NMR (CDCl_3 , 50MHz) Compound 2



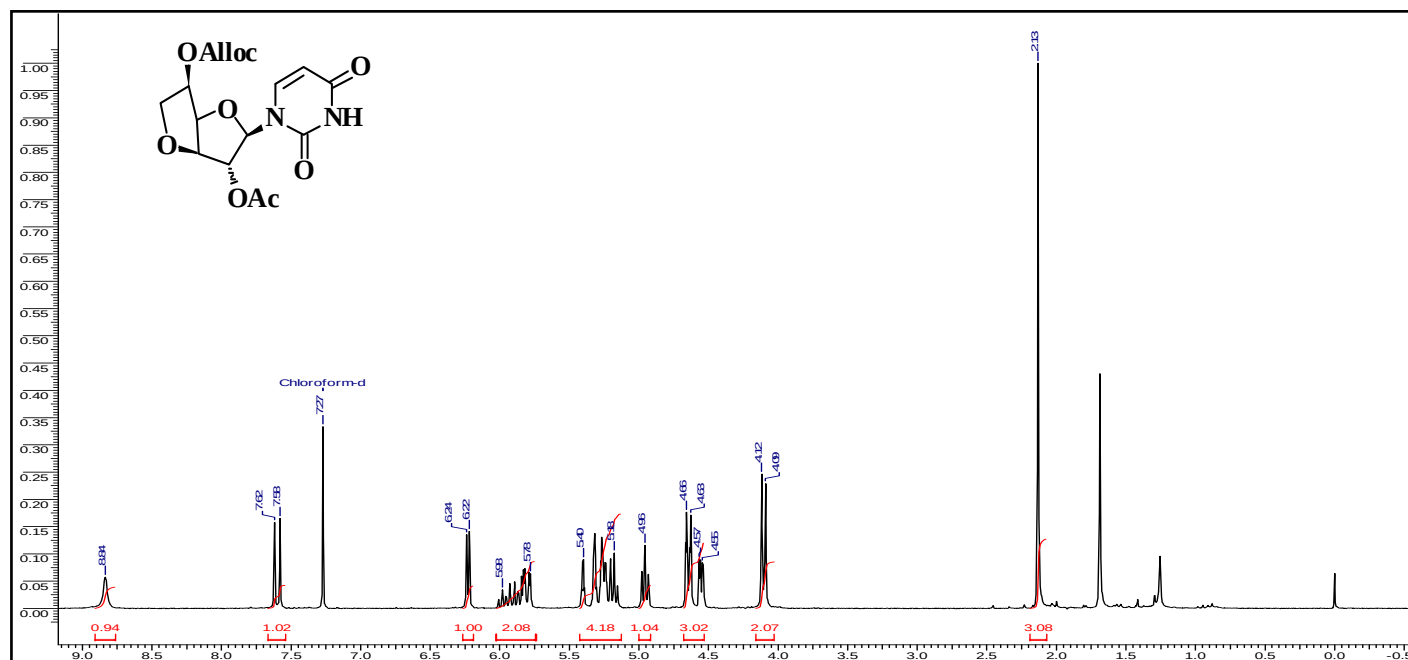
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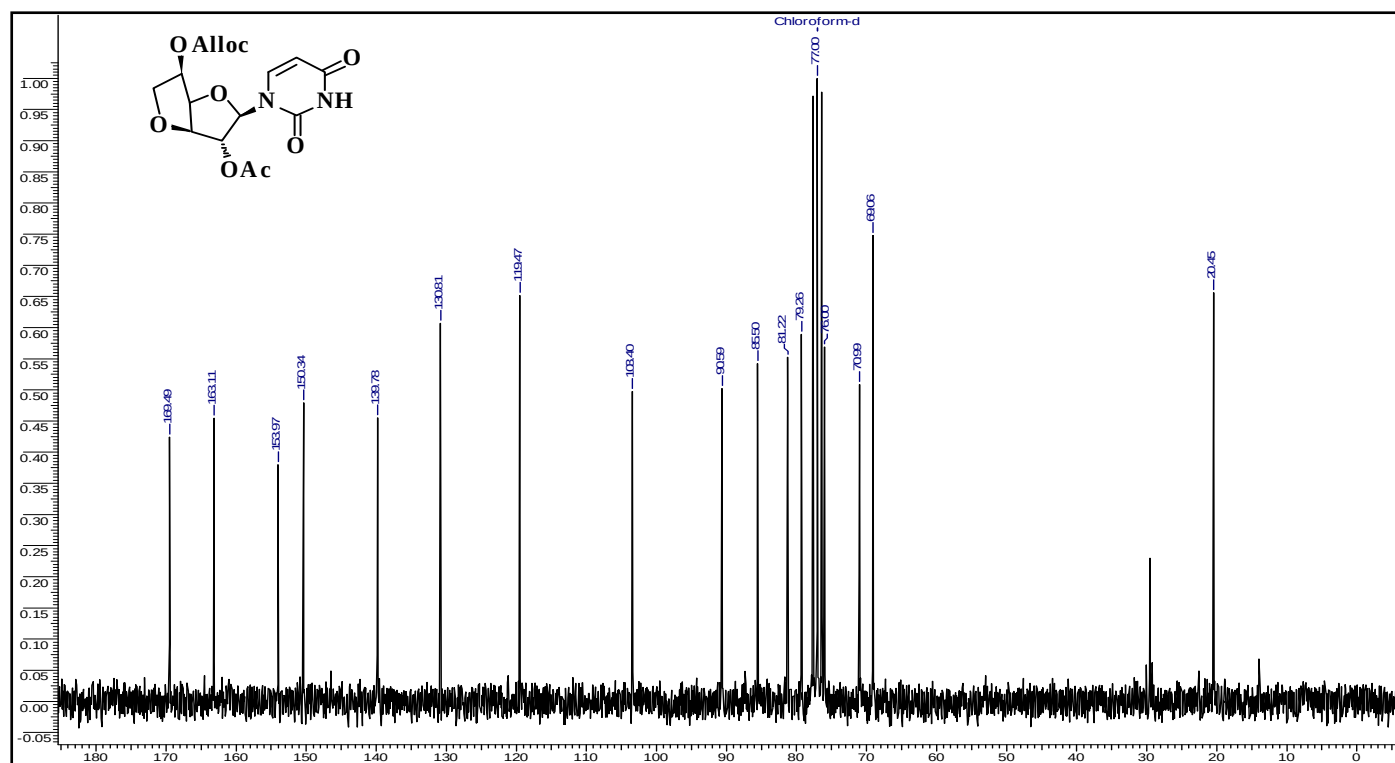
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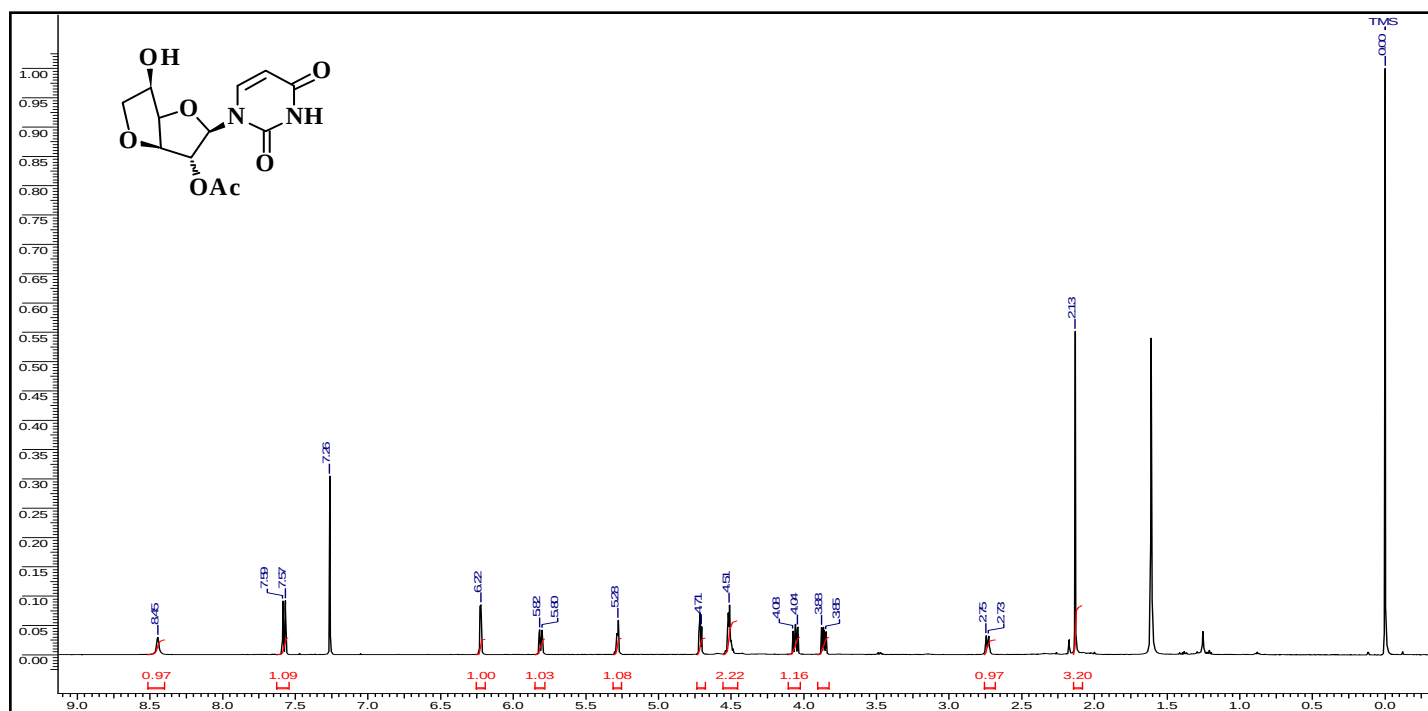
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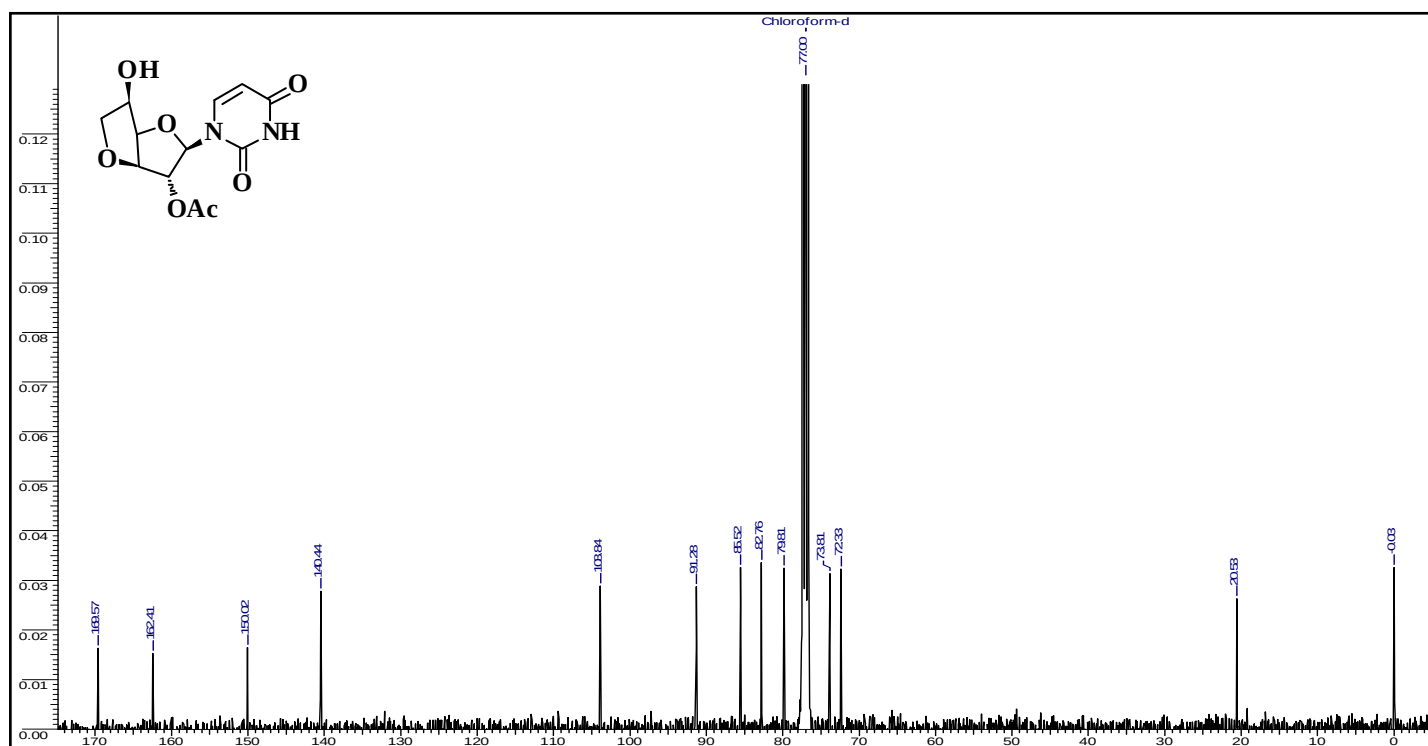
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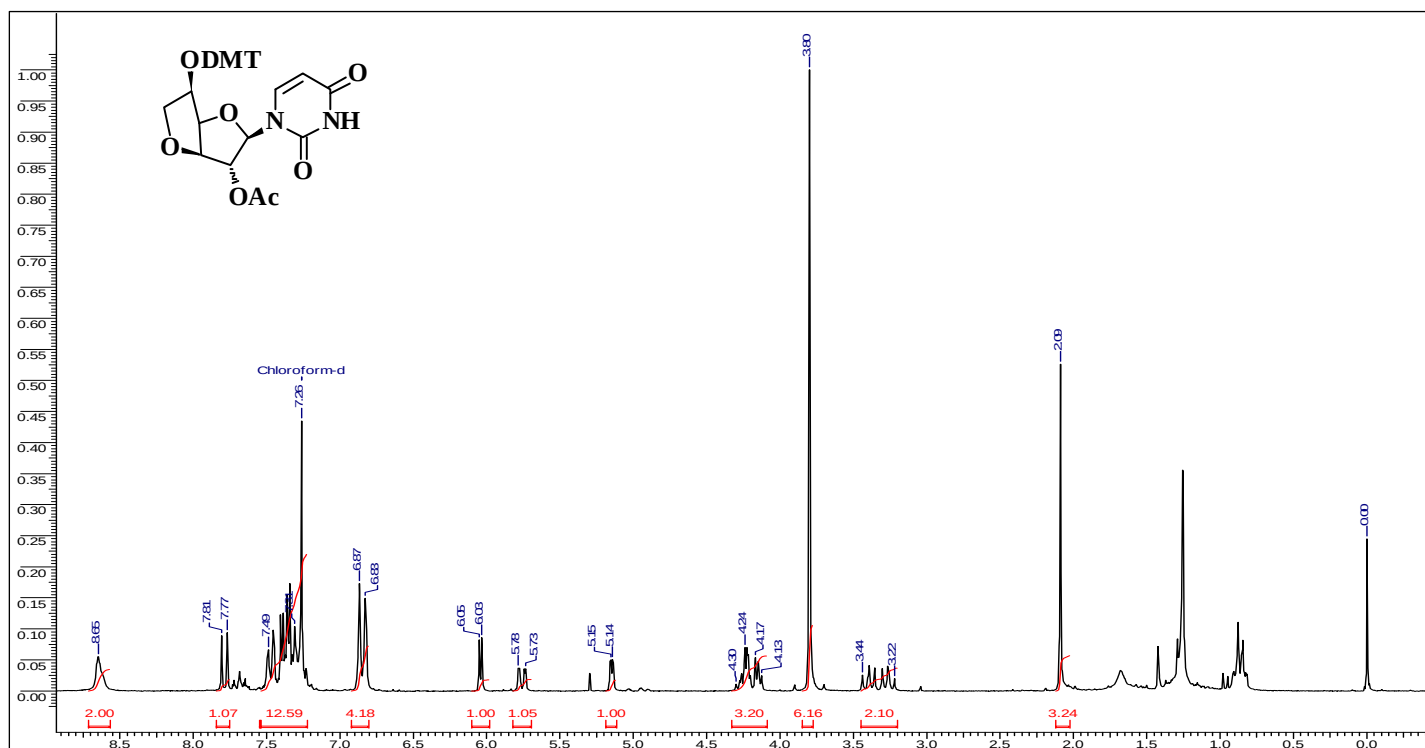
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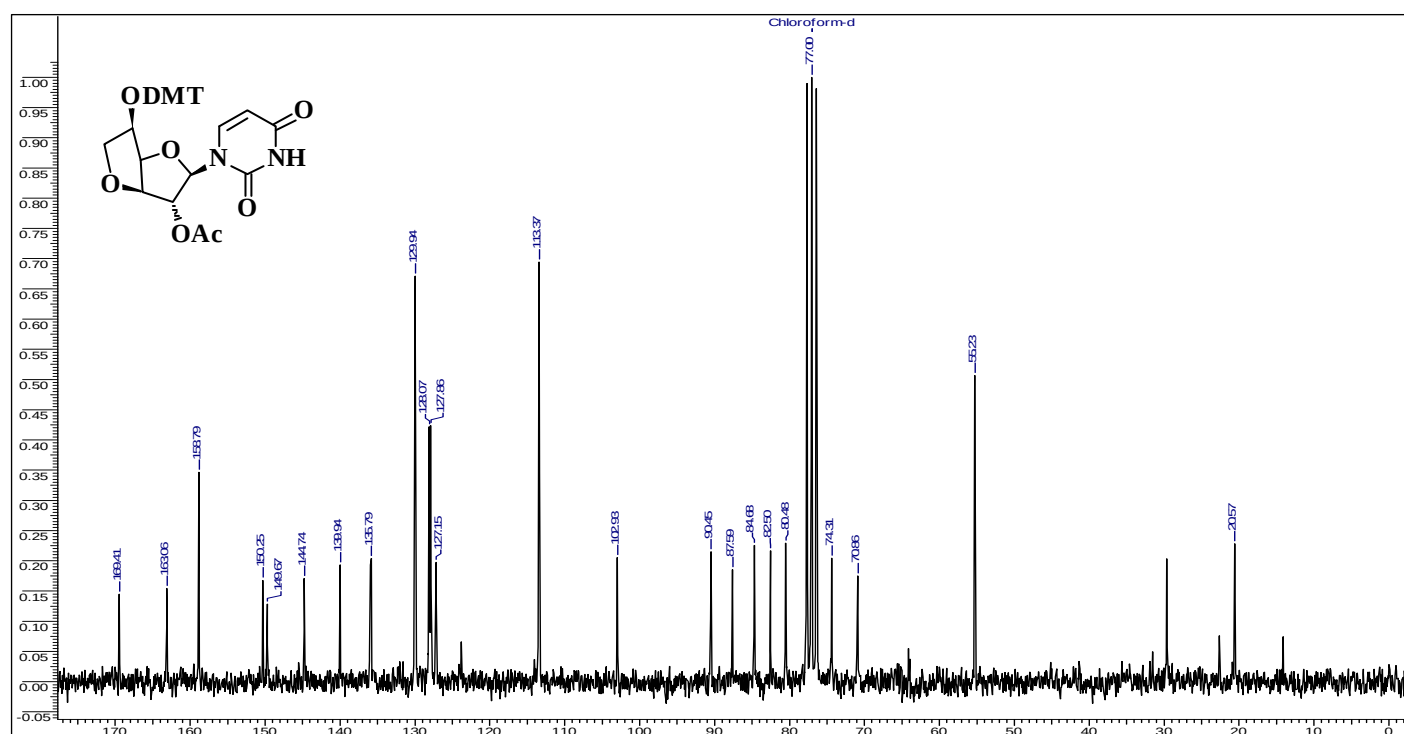
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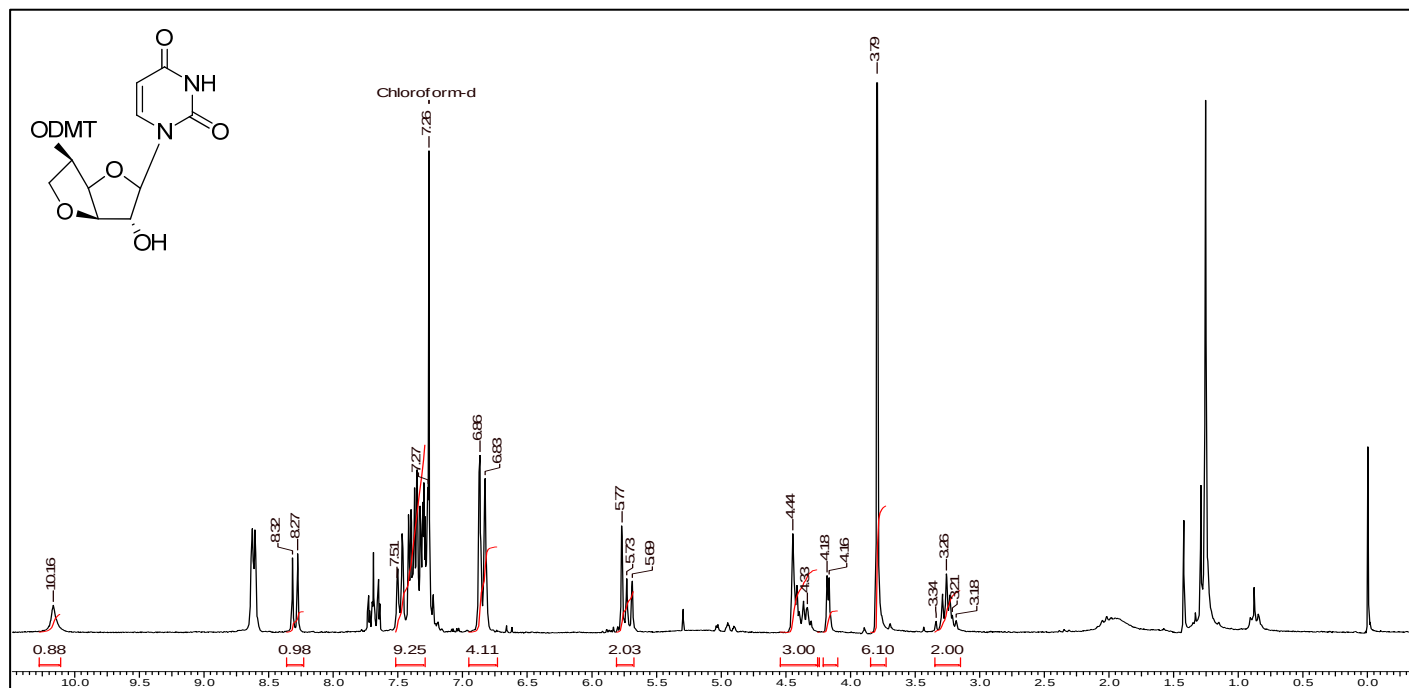
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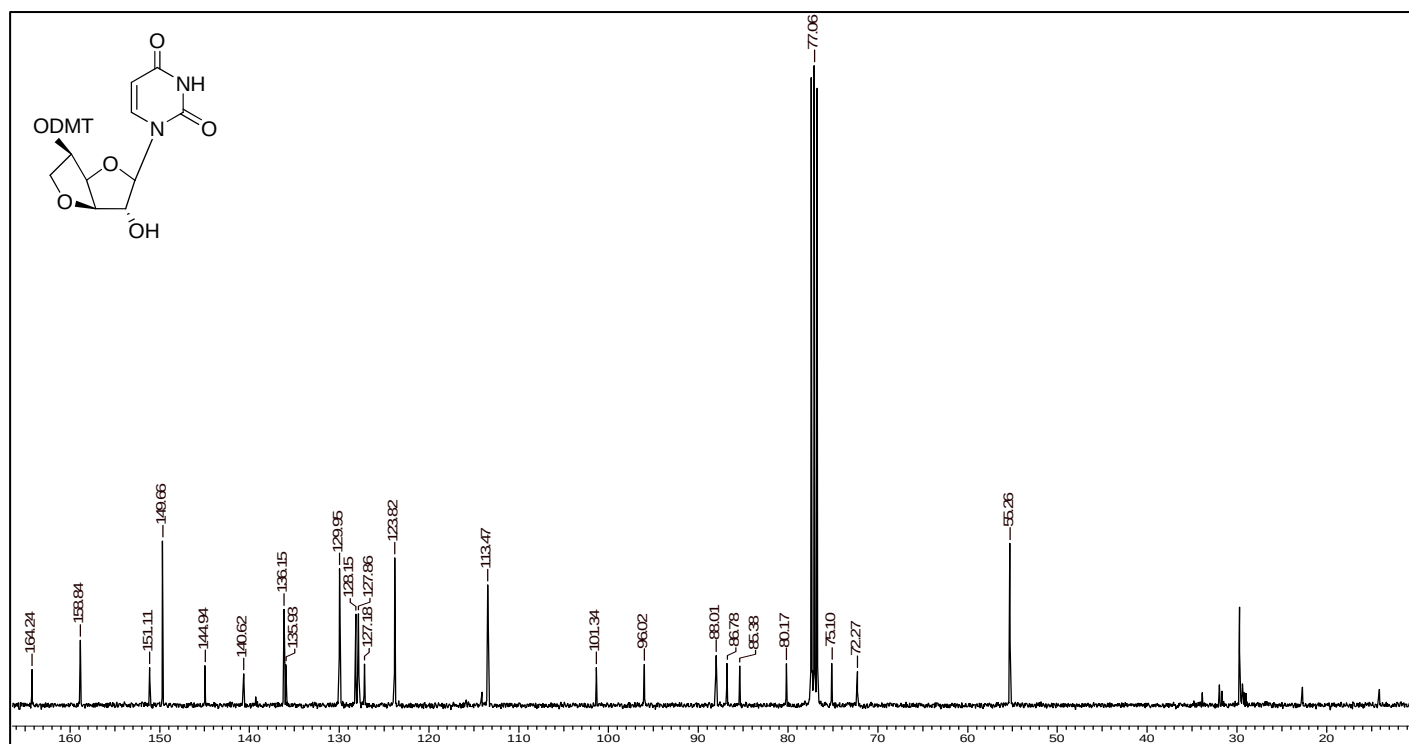
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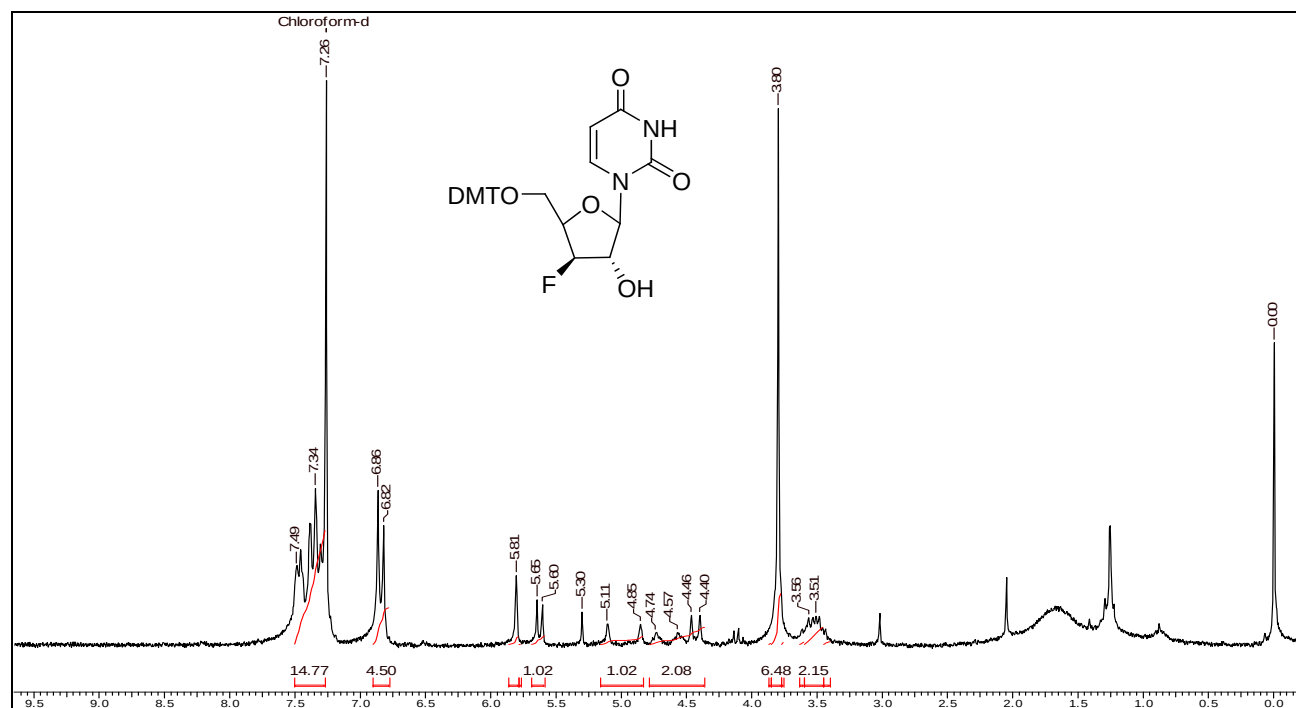
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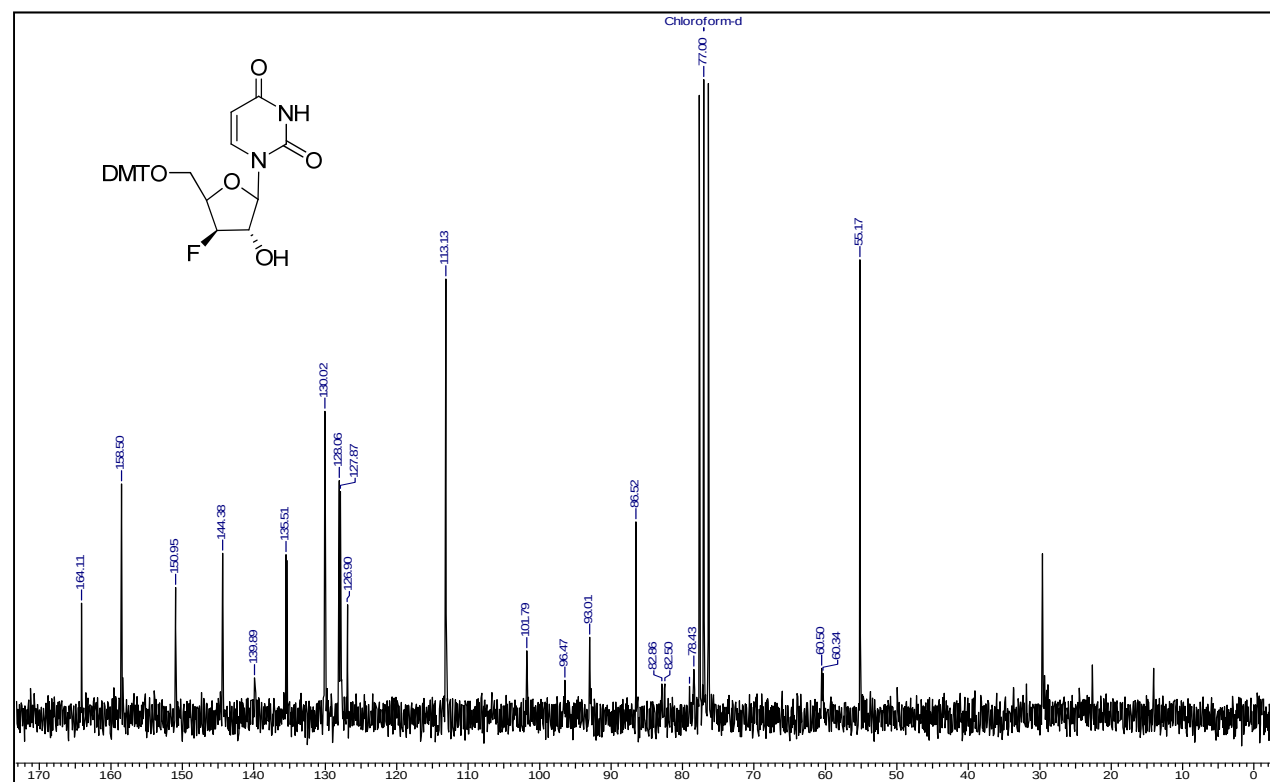
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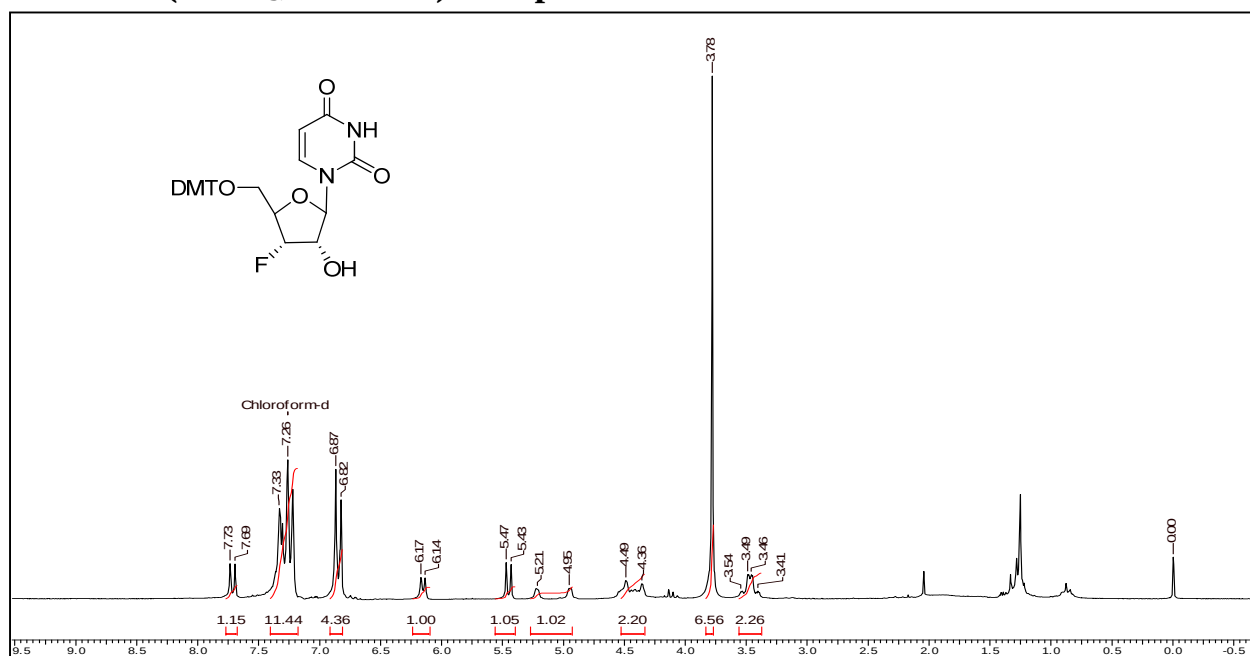
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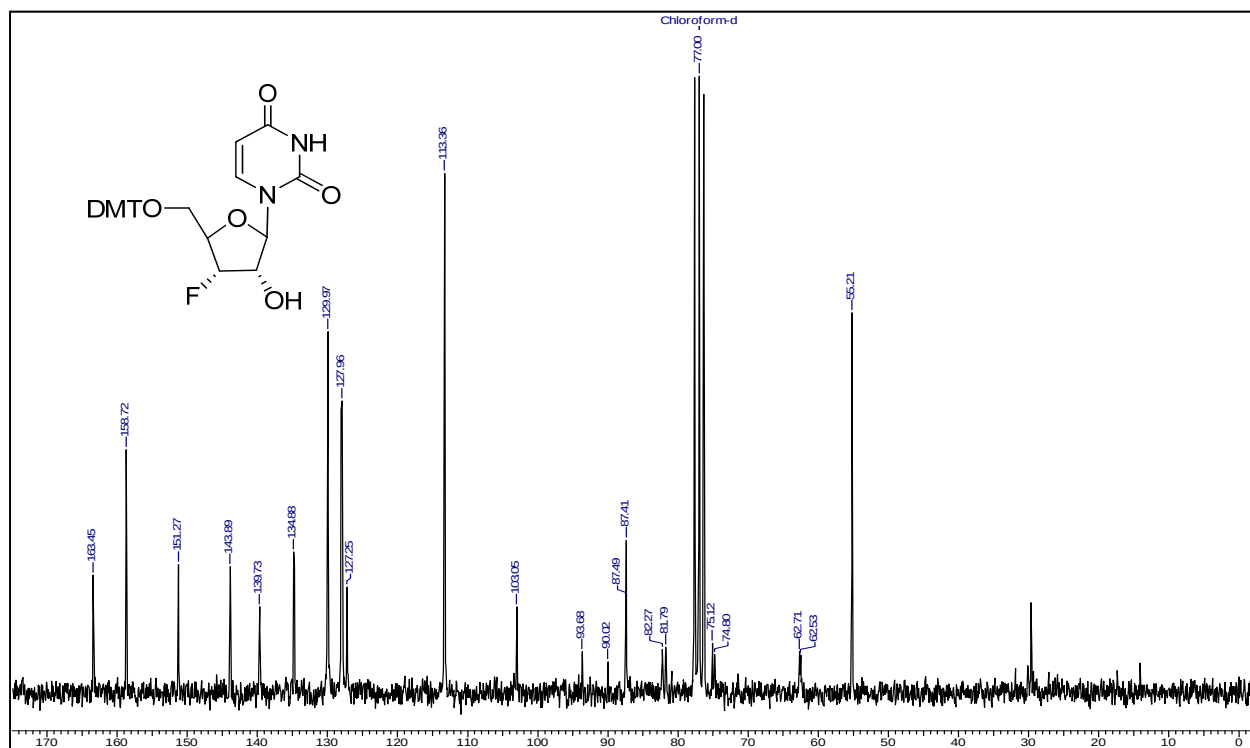
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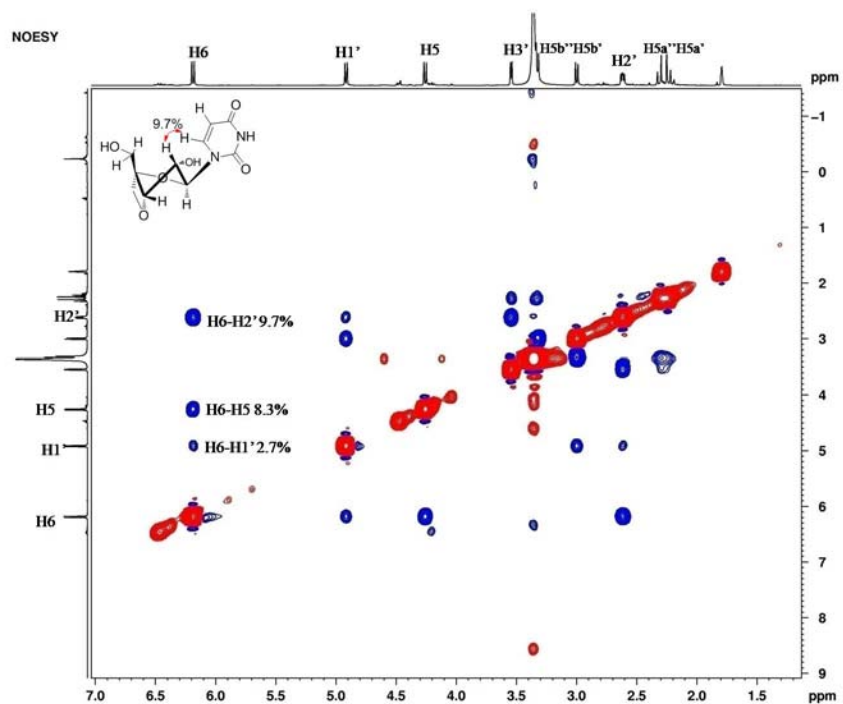
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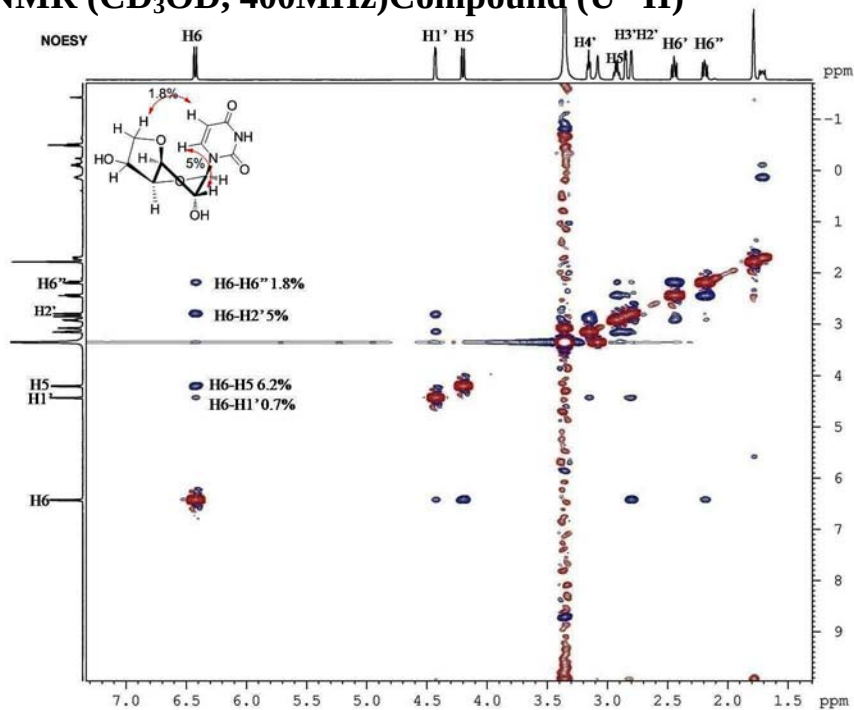
¹³C NMR (CDCl₃, 50MHz) Compound 10b



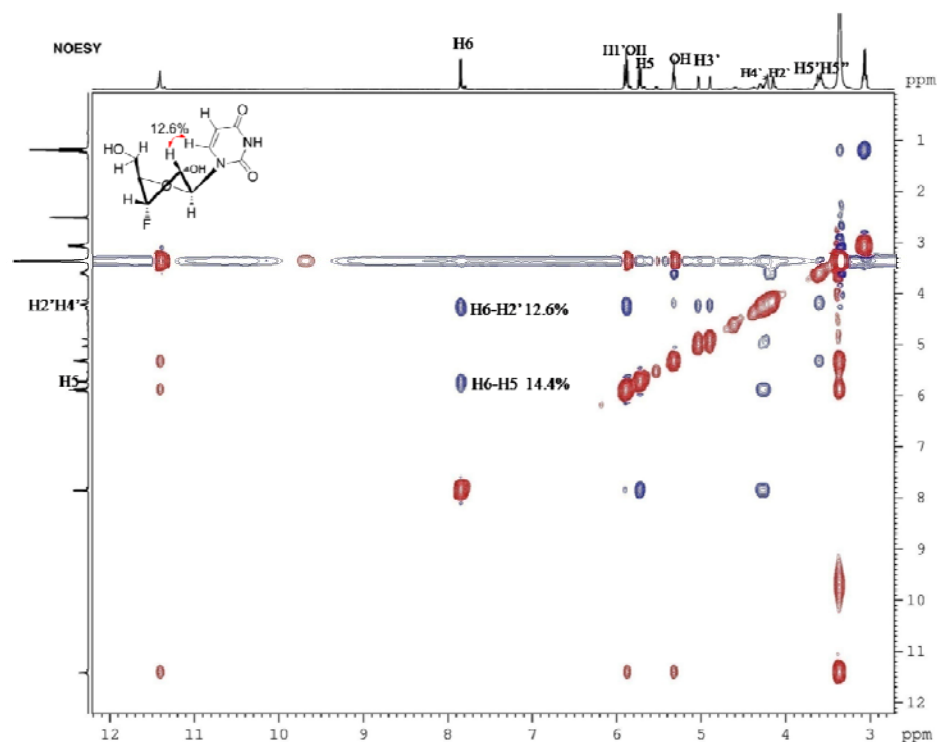
NOESY NMR (CD₃OD, 400MHz)Compound (U^S I)



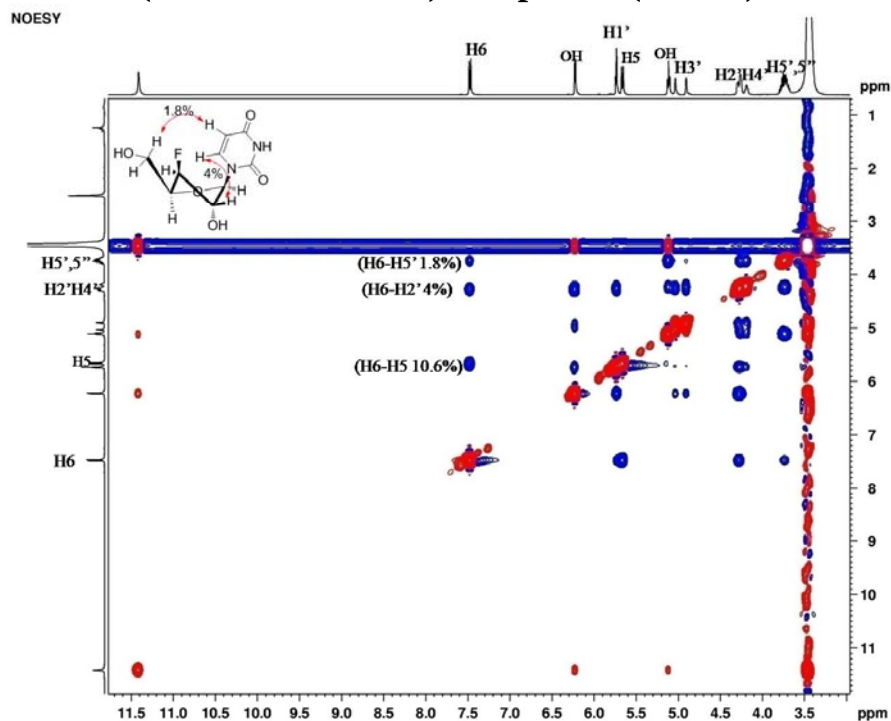
NOESY NMR (CD₃OD, 400MHz)Compound (U^N II)



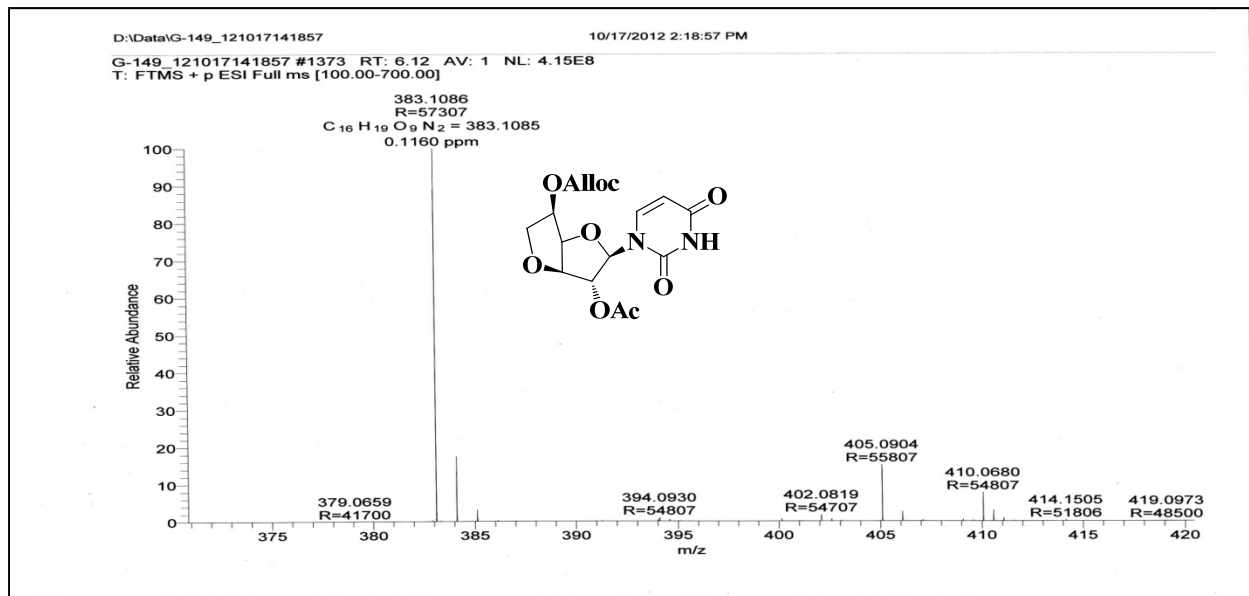
NOESY NMR (CD₃OD, 400MHz)Compound (^rU^F III)



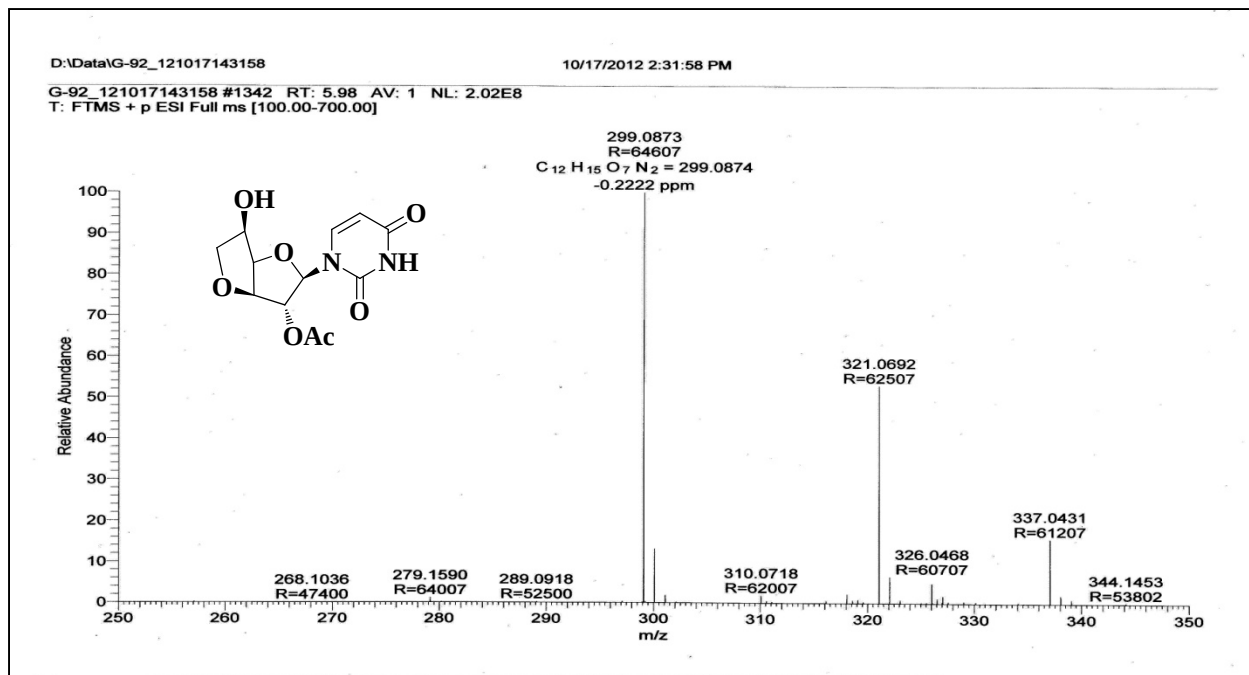
NOESY NMR (CD₃OD, 400MHz)Compound (^xU^F IV)



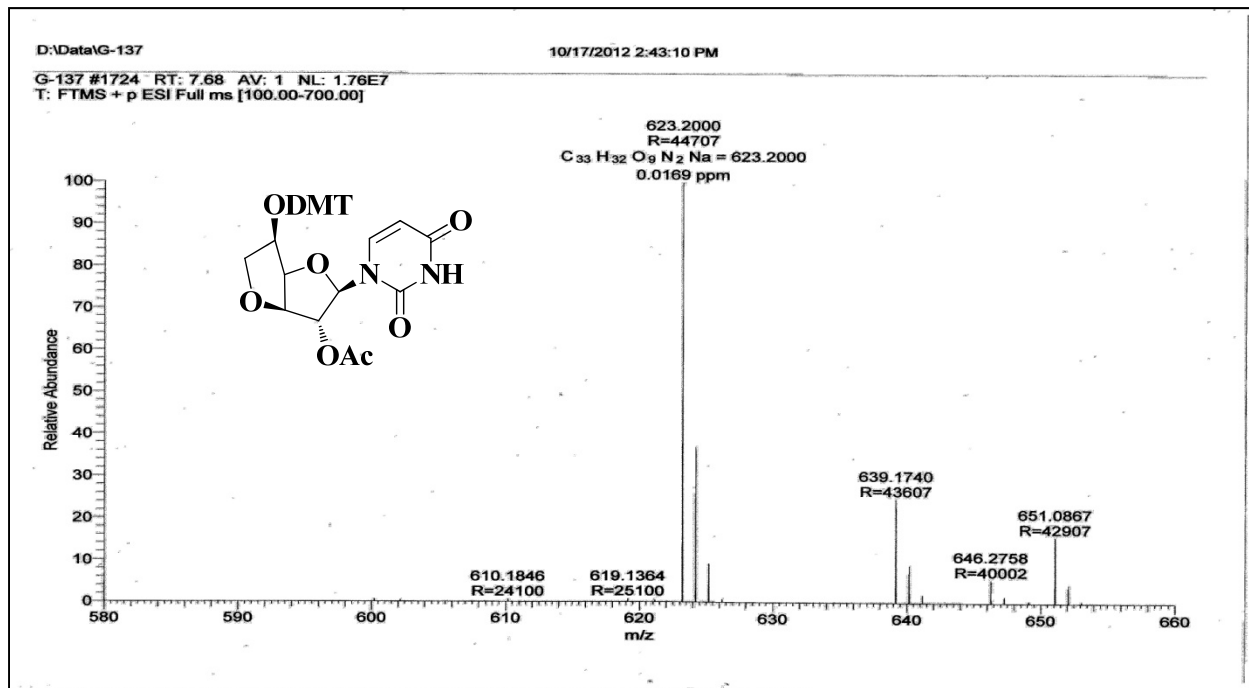
HRMS spectrum of Compound 4



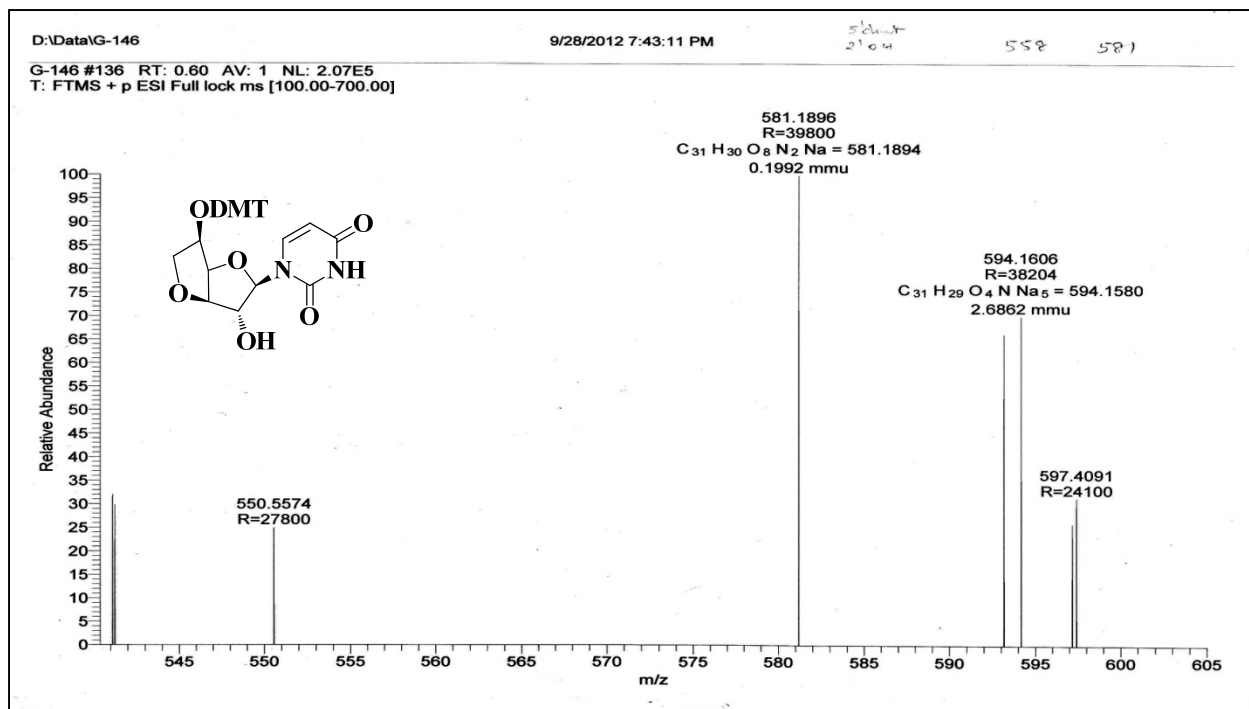
HRMS spectrum of Compound 5



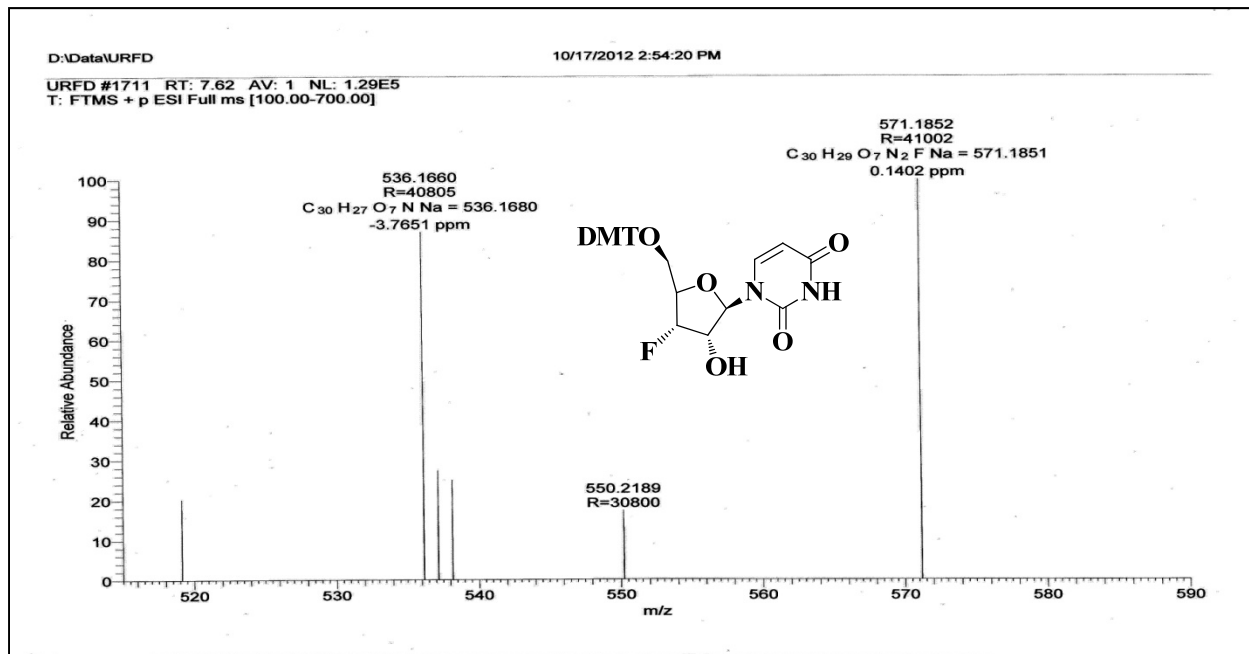
HRMS spectrum of Compound 6



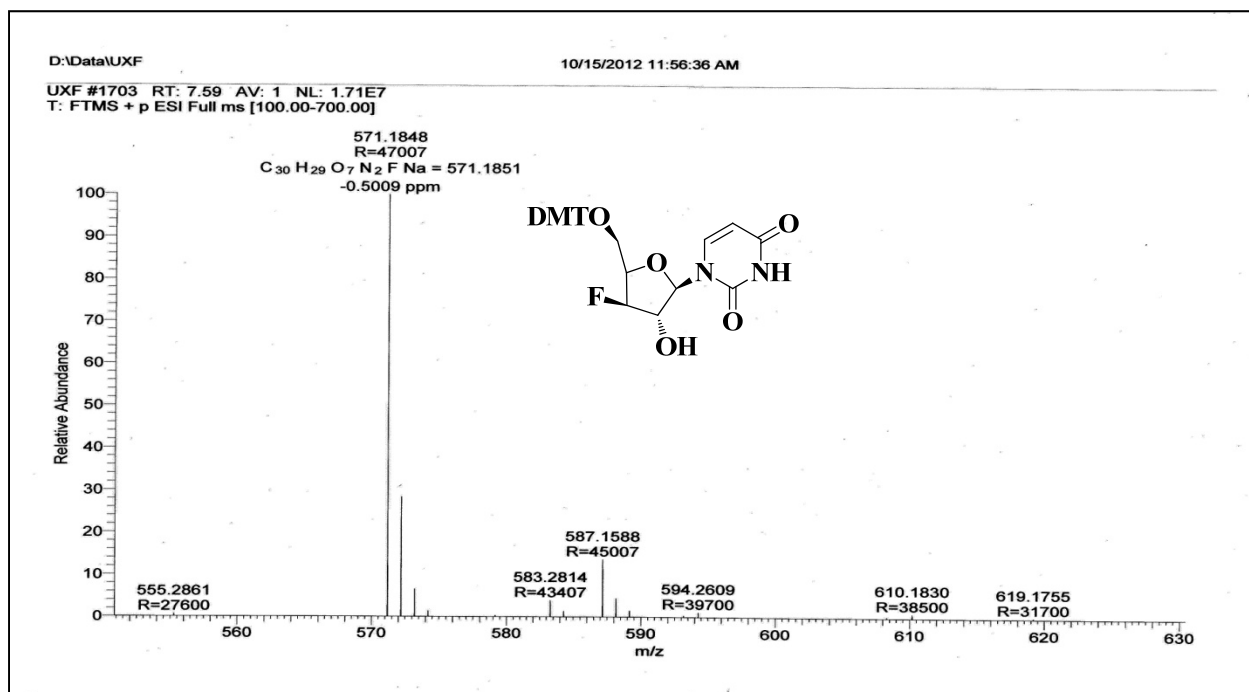
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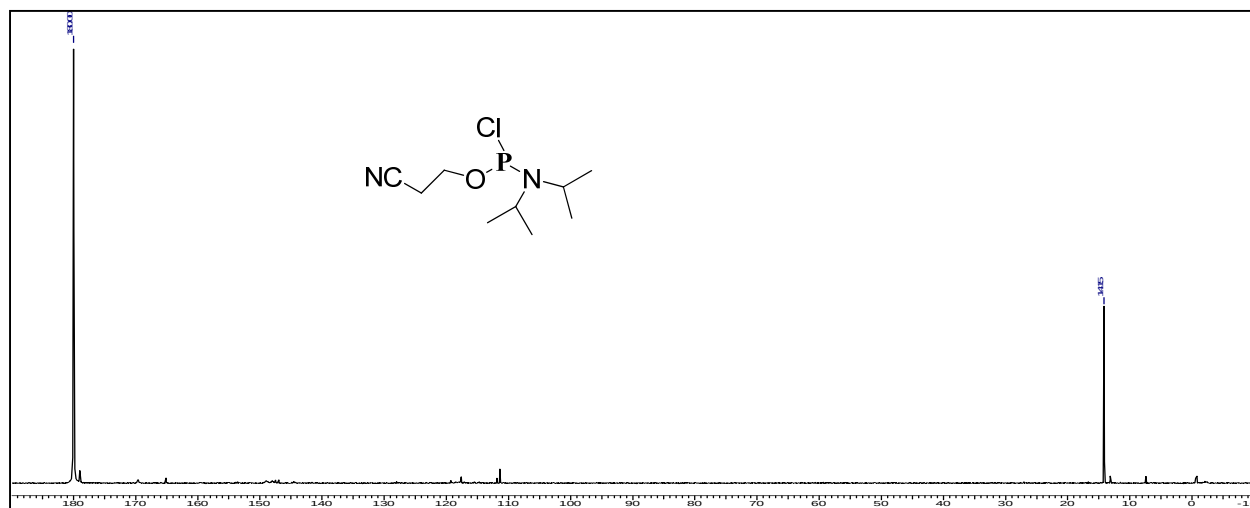
HRMS spectrum of Compound 10a



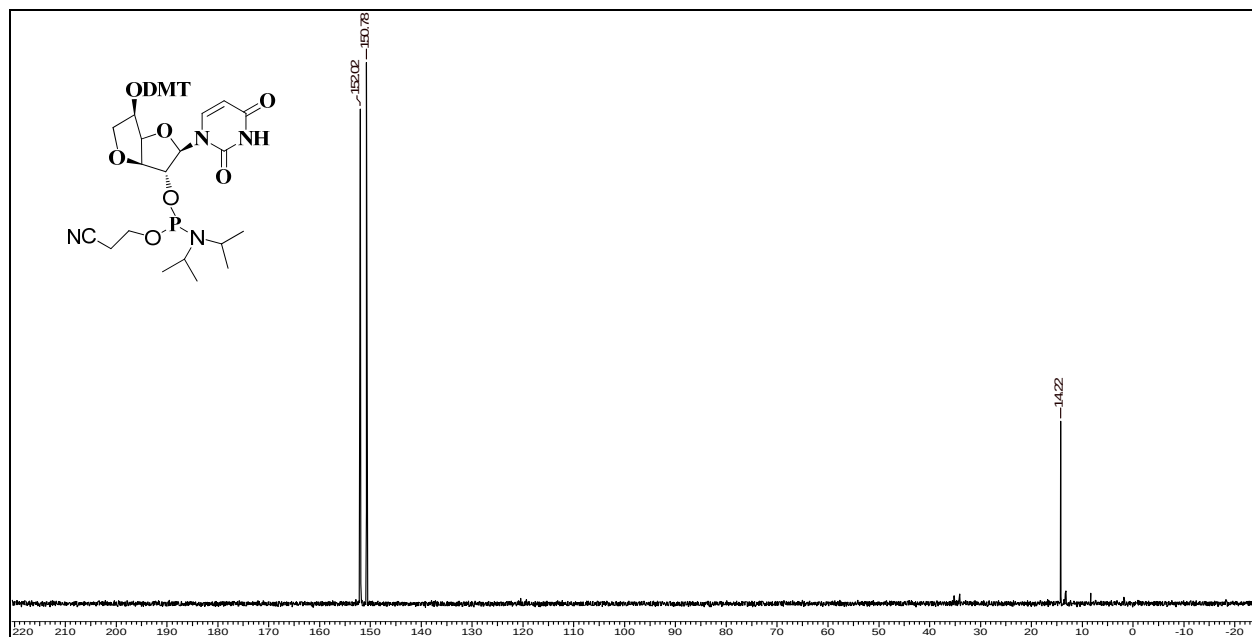
HRMS spectrum of Compound 10b



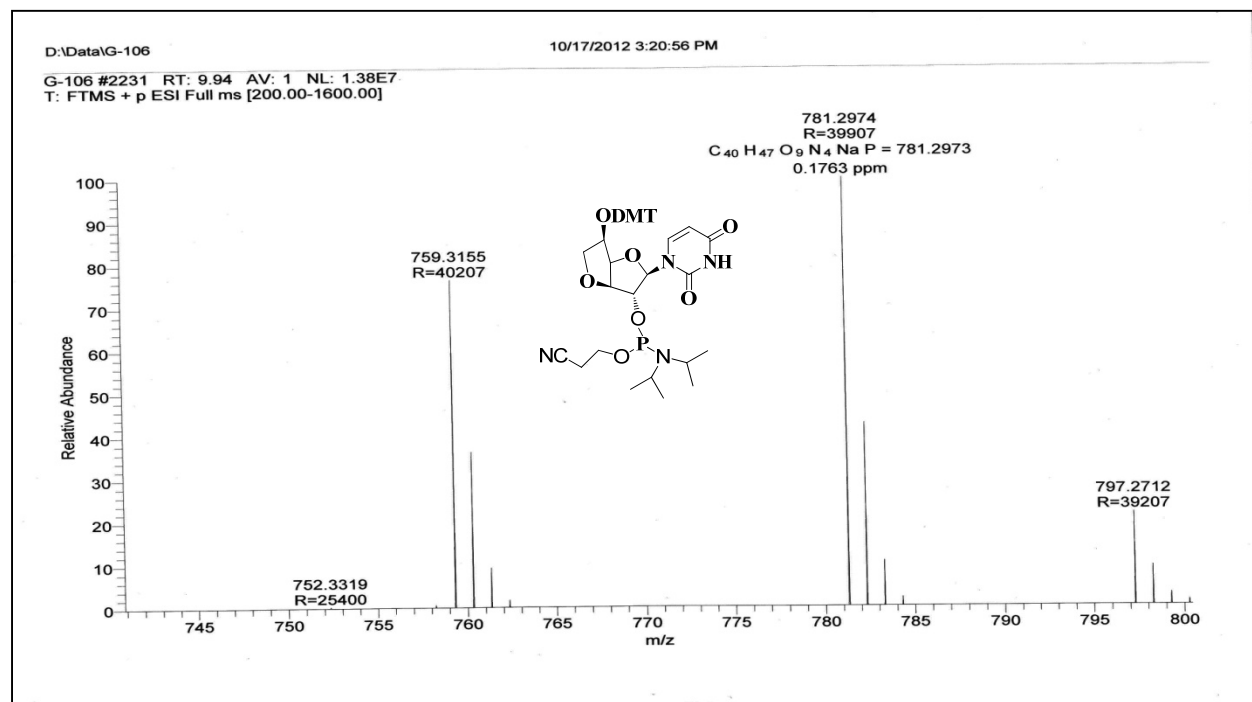
^{31}P NMR (CDCl_3 , 50MHz) Amidite reagent:



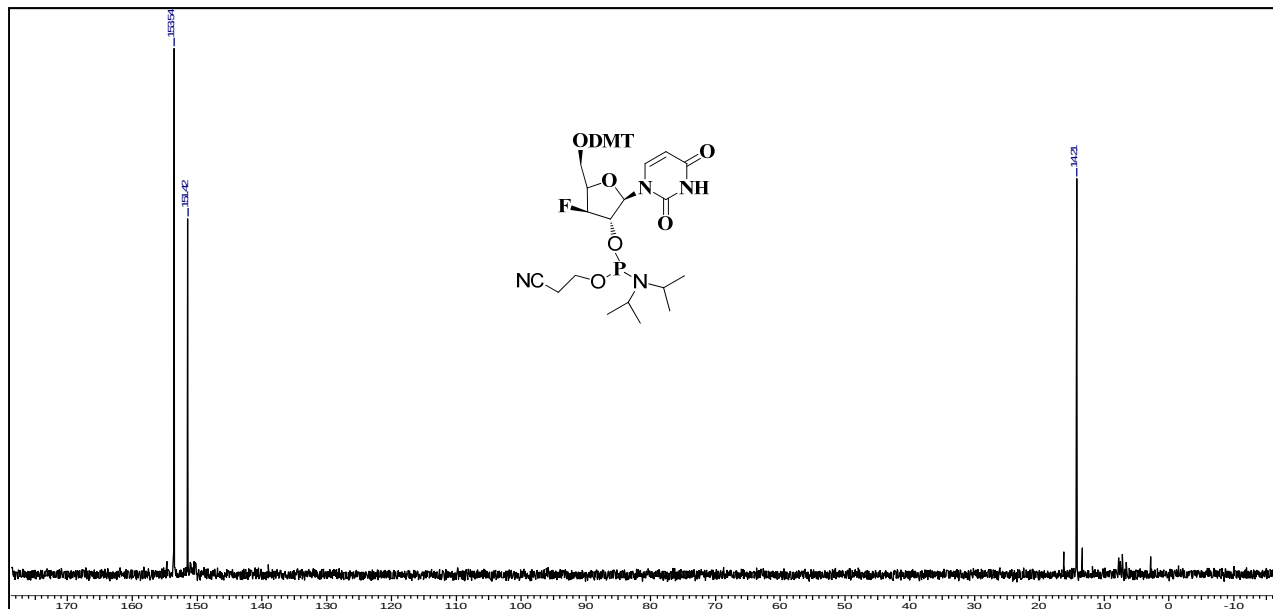
³¹P NMR (CDCl₃, 50MHz) Compound 8



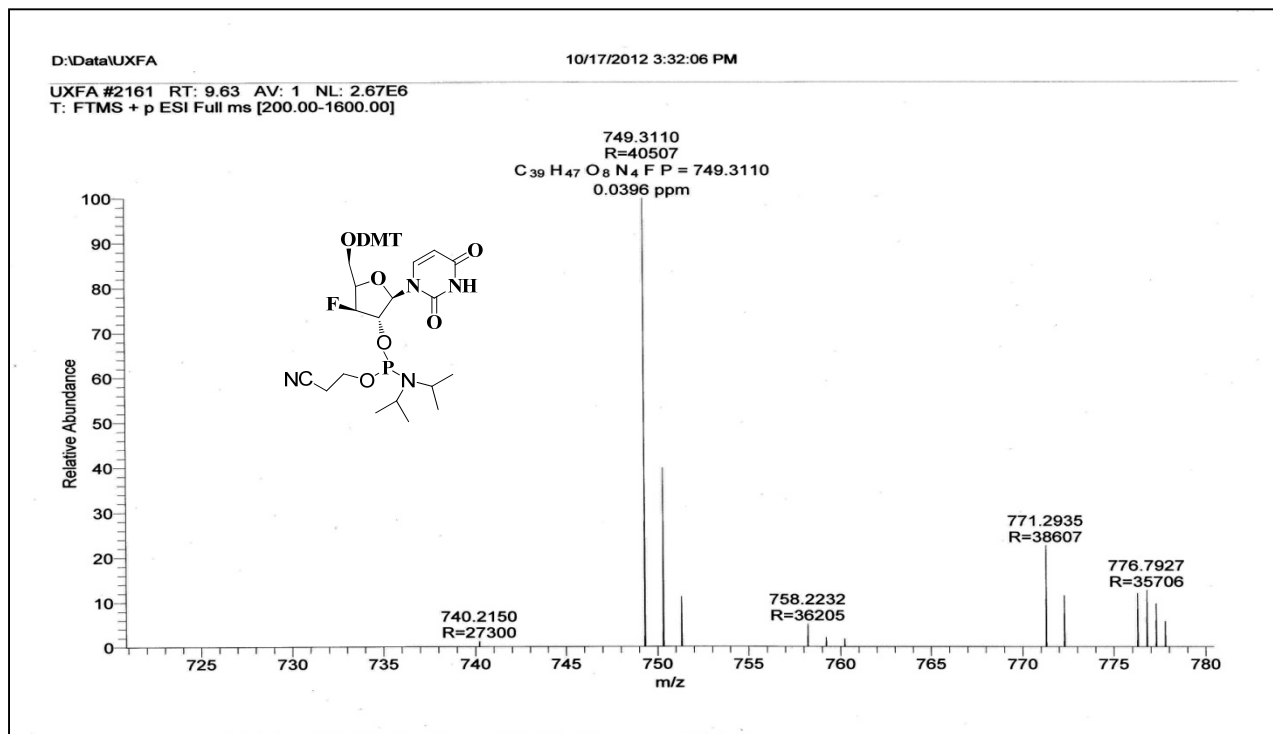
HRMS spectrum of Compound 8



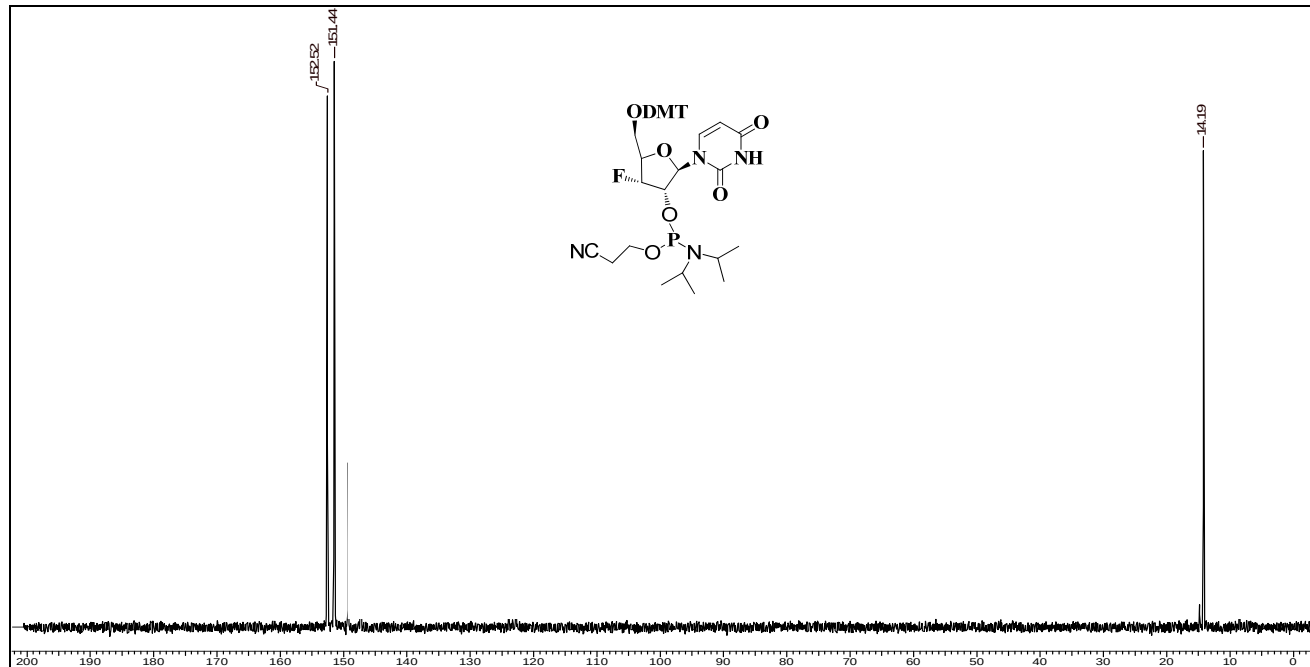
³¹P NMR (CDCl₃, 50MHz) Compound 11a



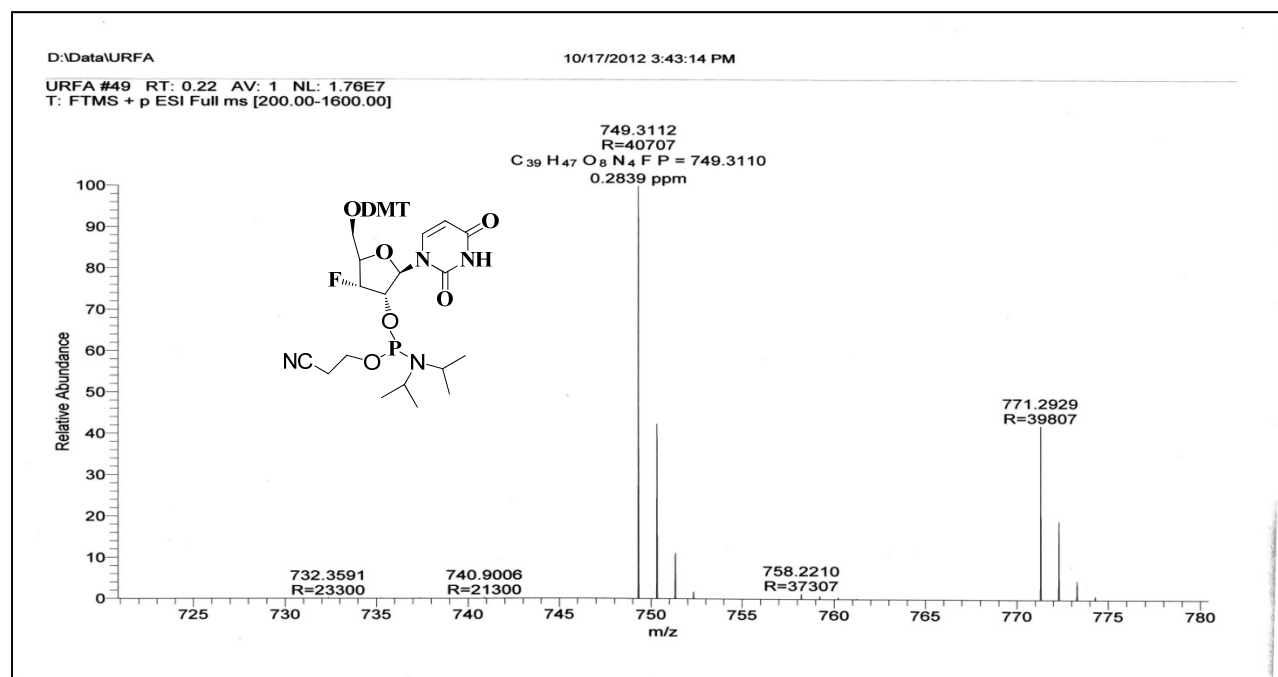
HRMS spectrum of Compound 11a



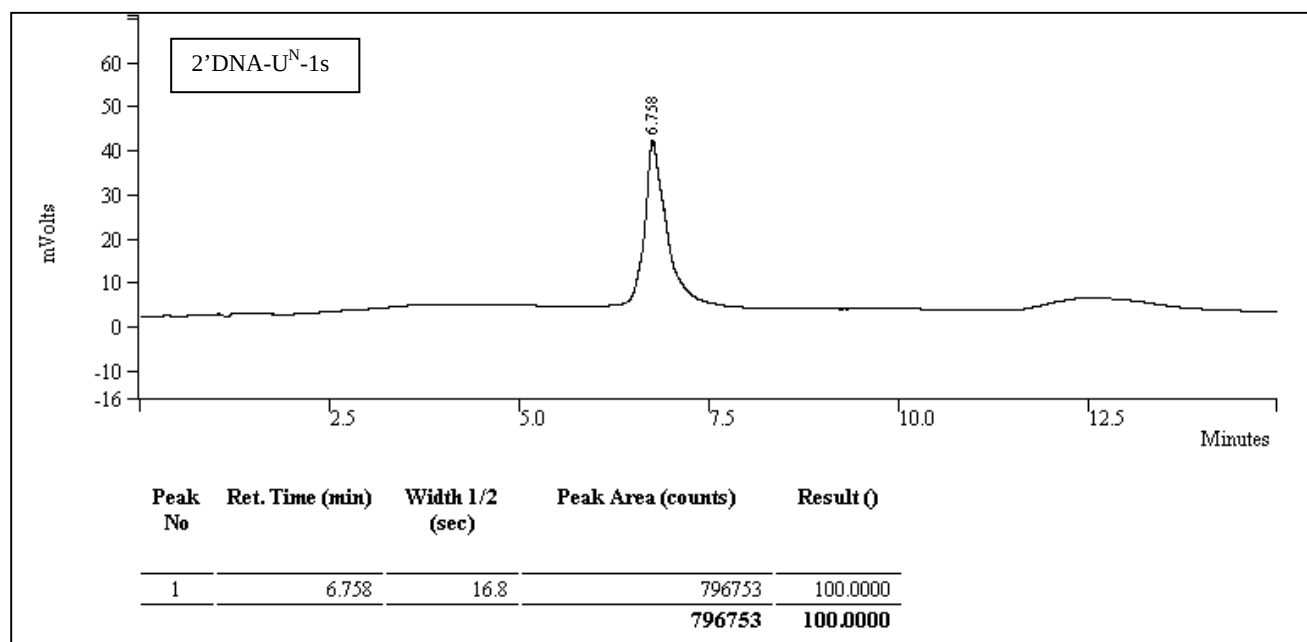
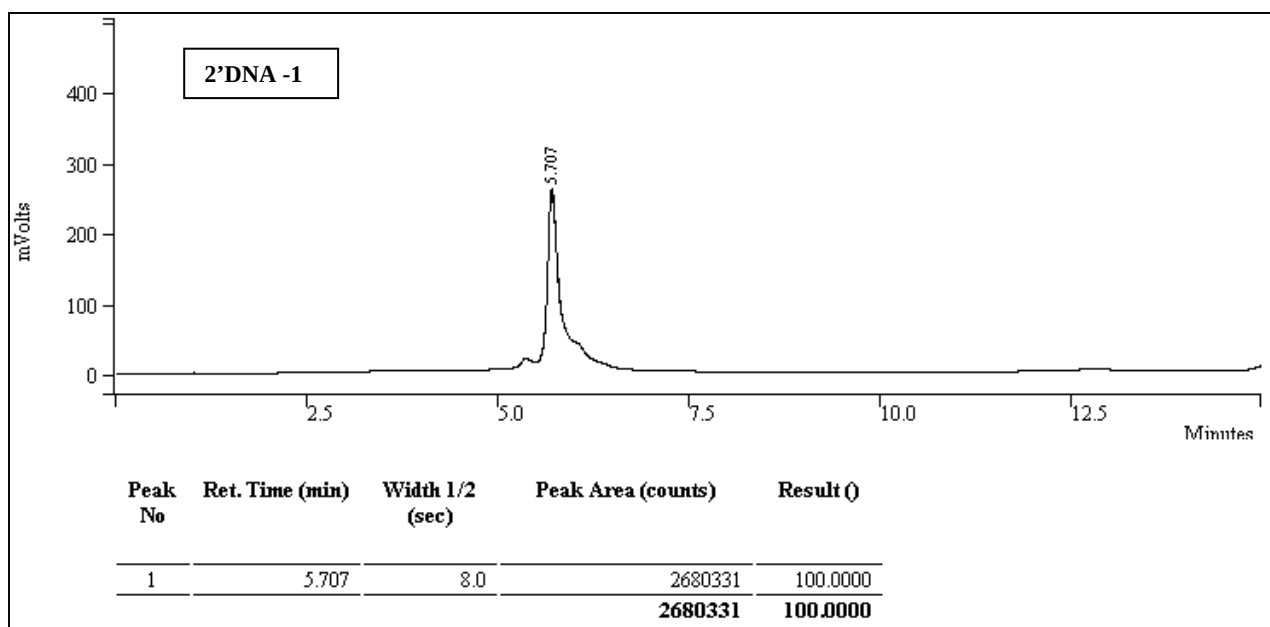
³¹P NMR (CDCl₃, 50MHz) Compound 11b

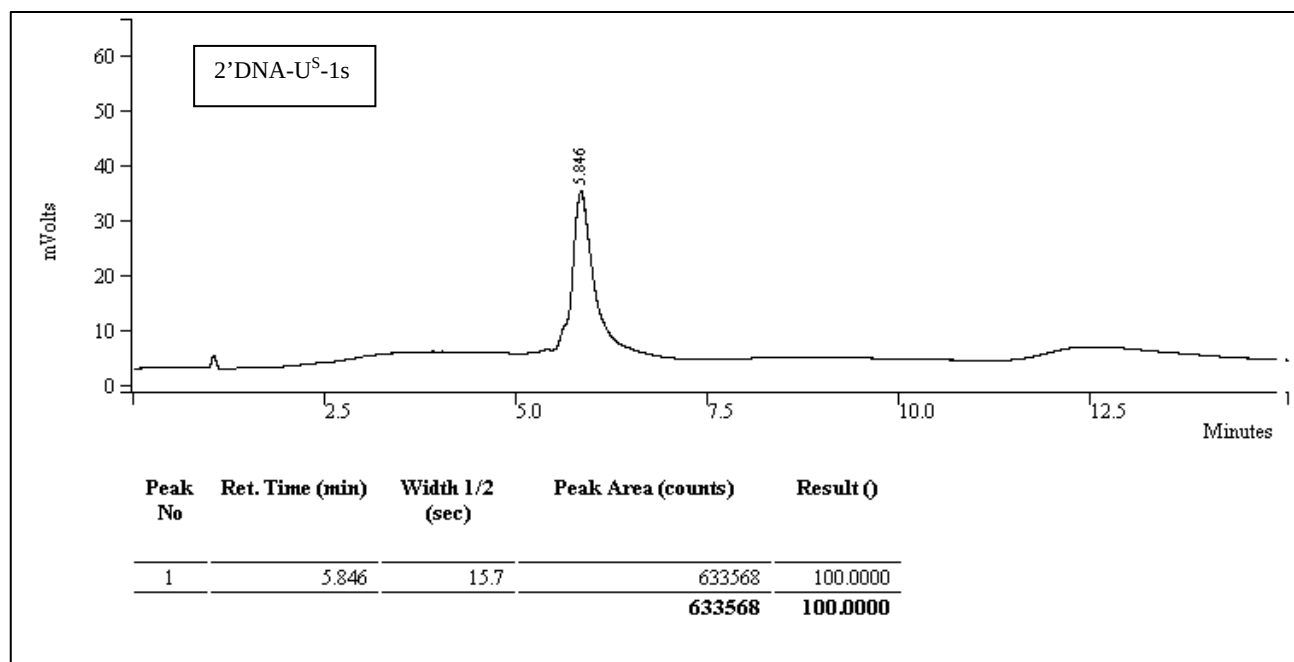
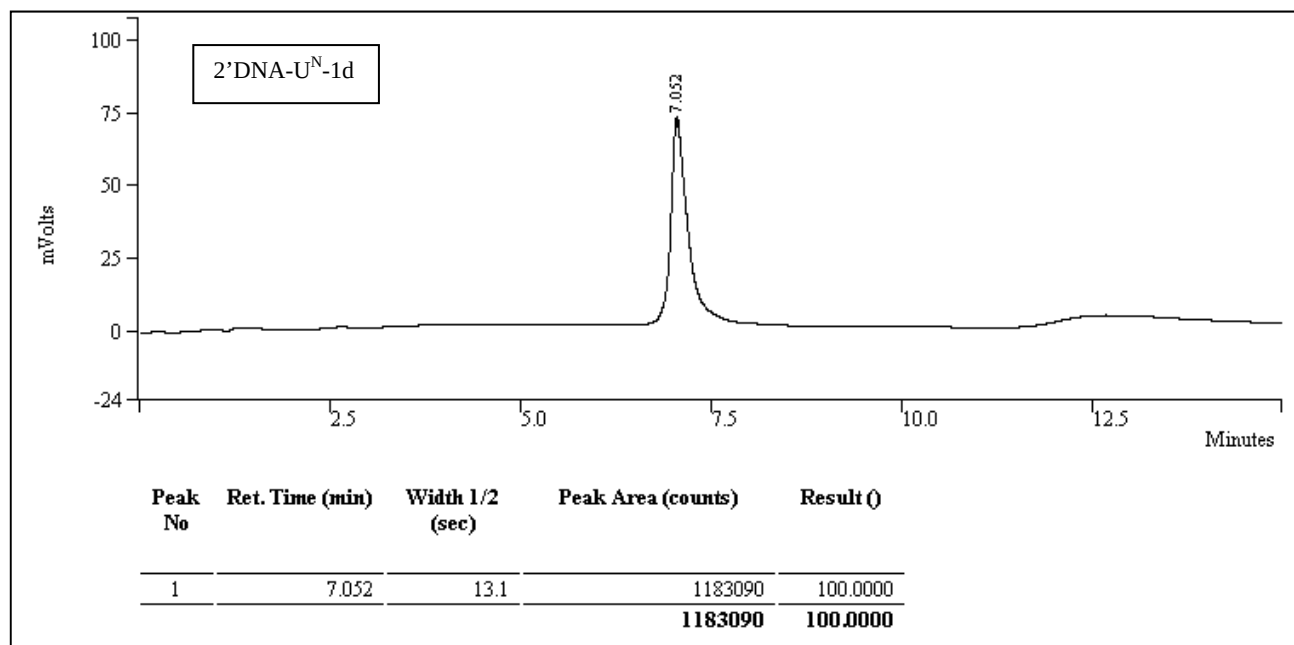


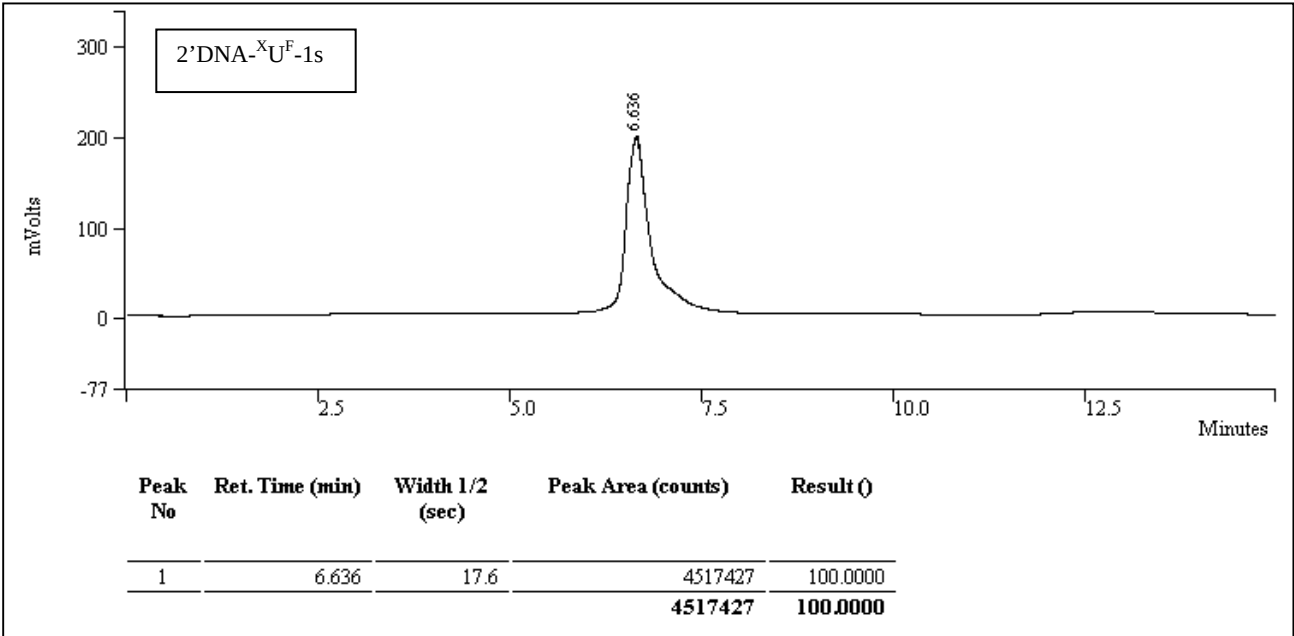
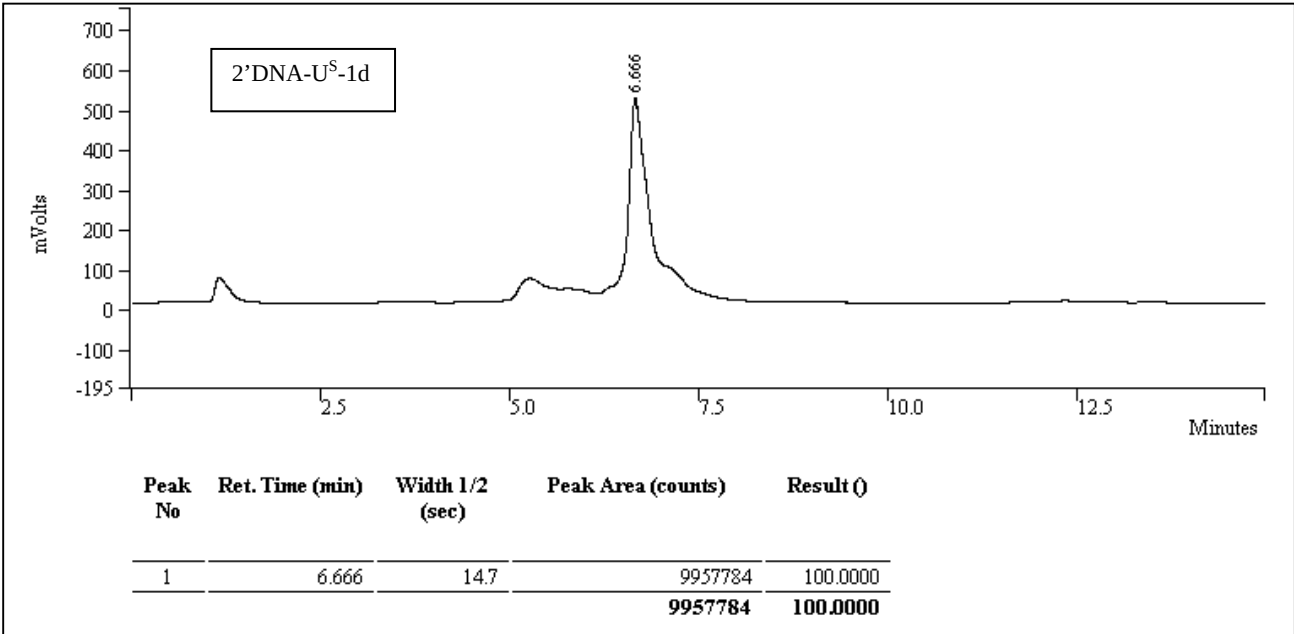
HRMS spectrum of Compound 11b

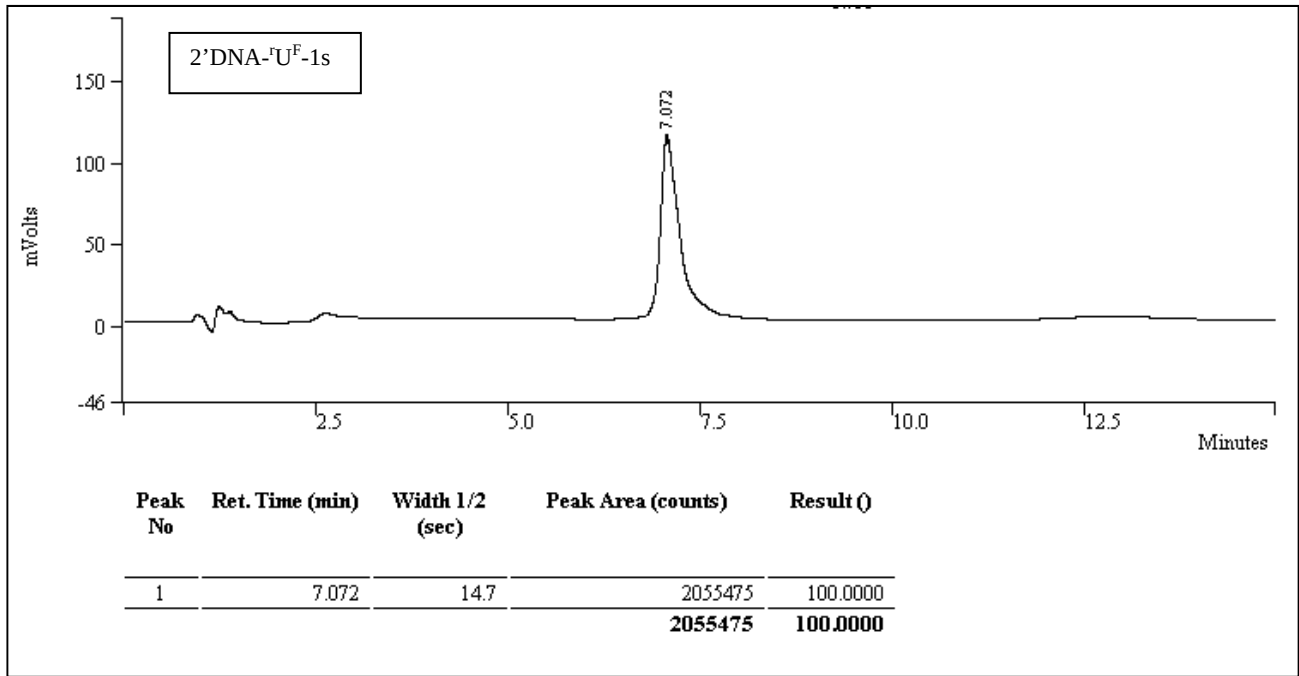
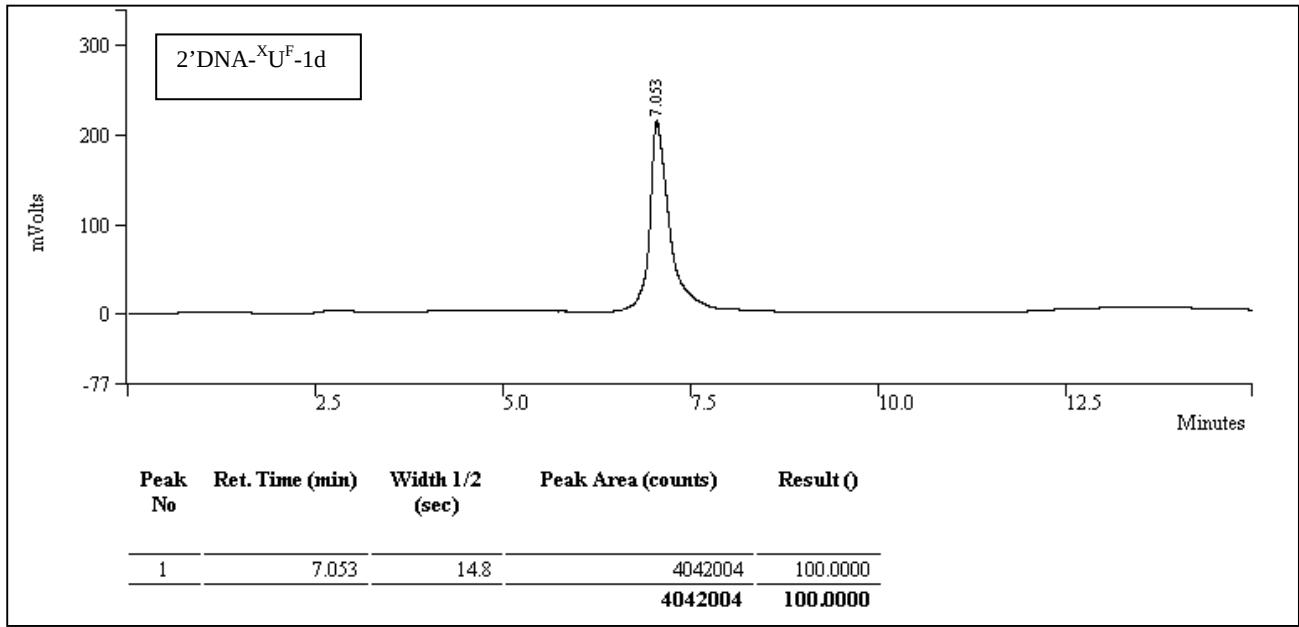


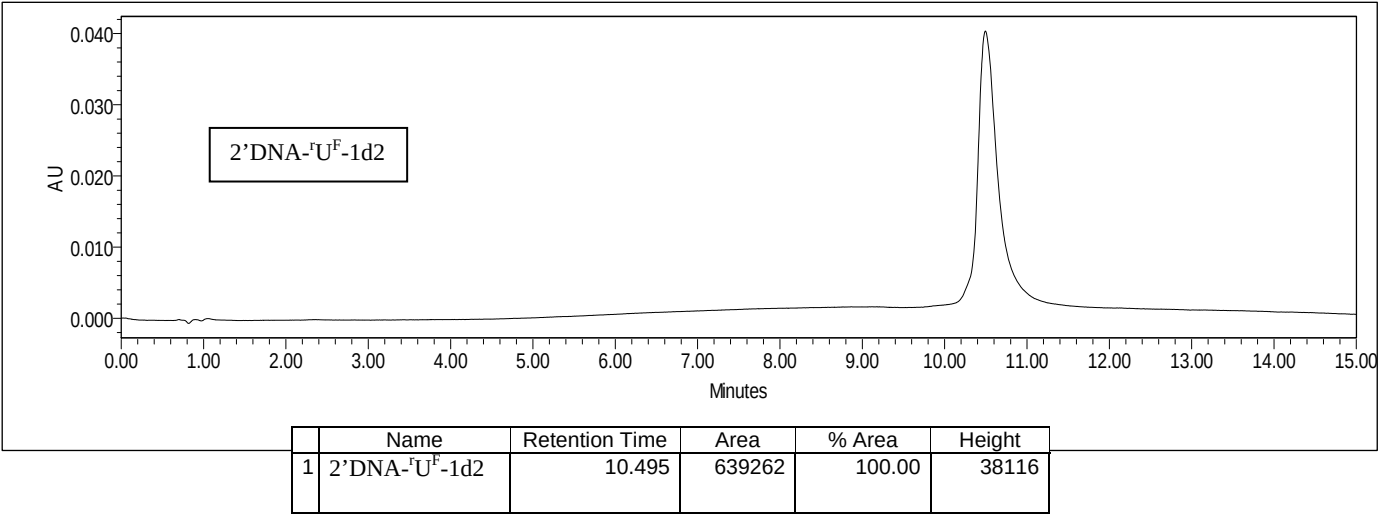
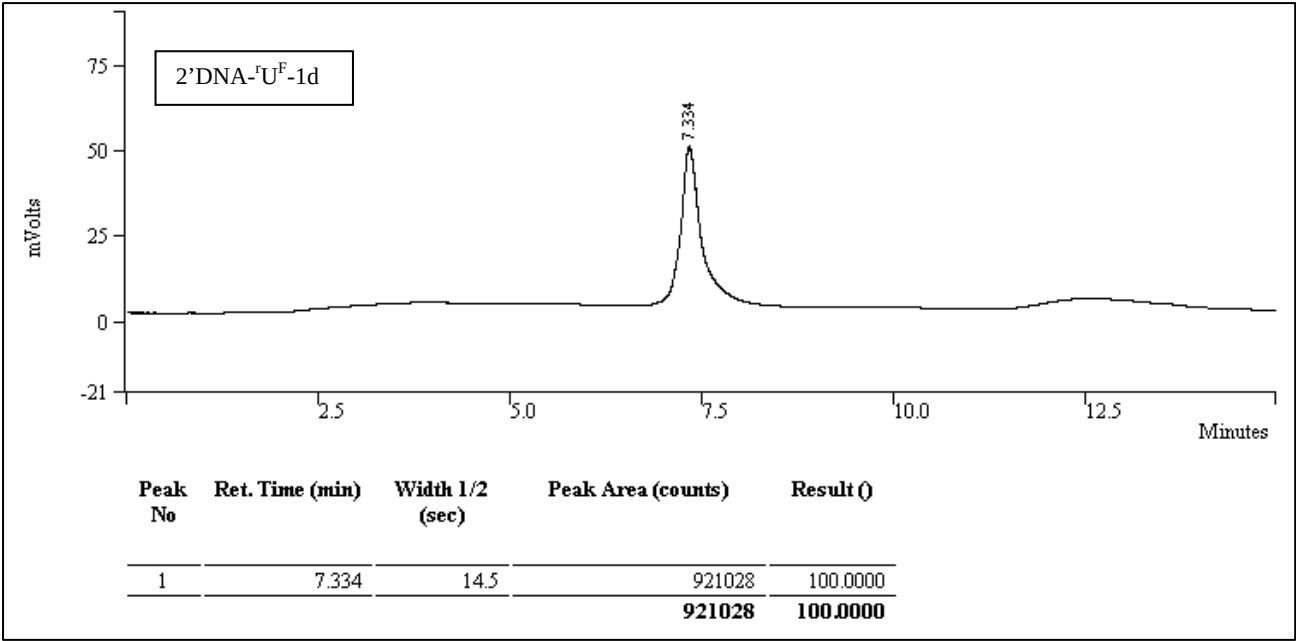
HPLC chromatograms of purified synthesized 2'-oligomers

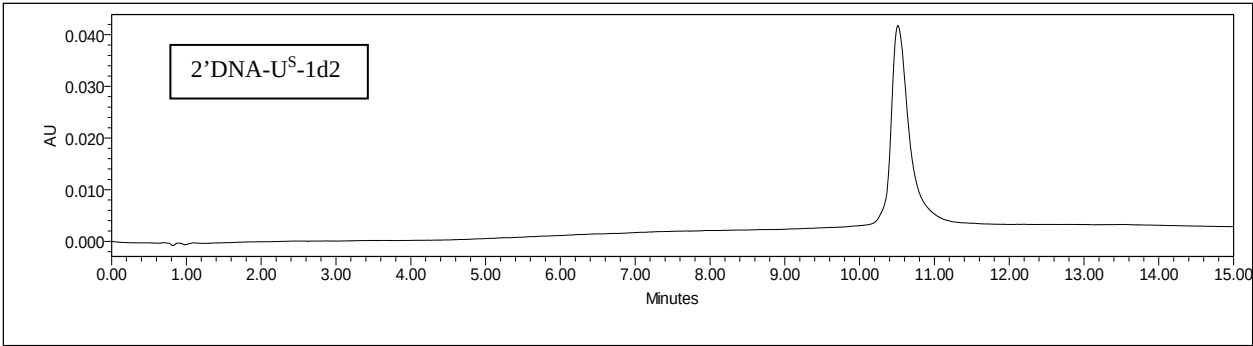




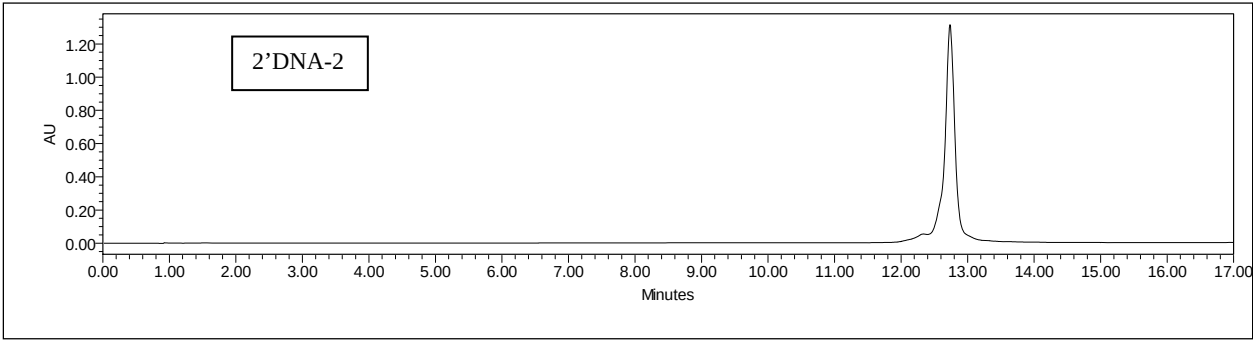




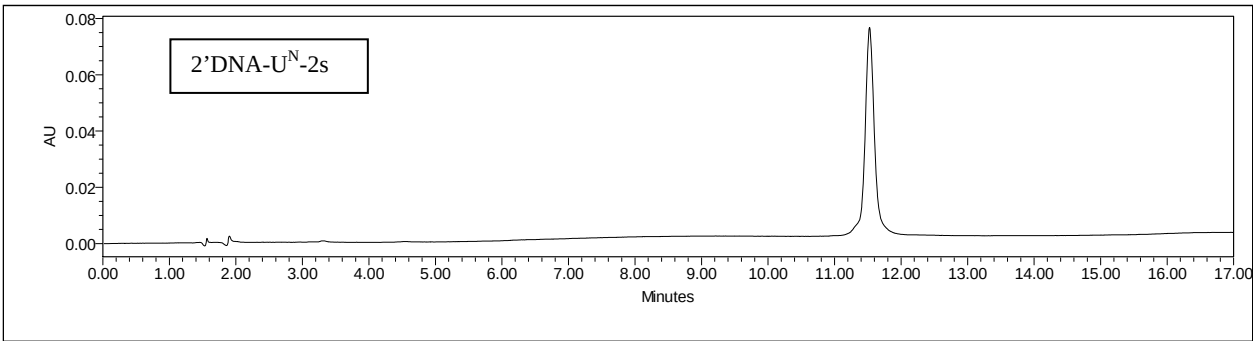




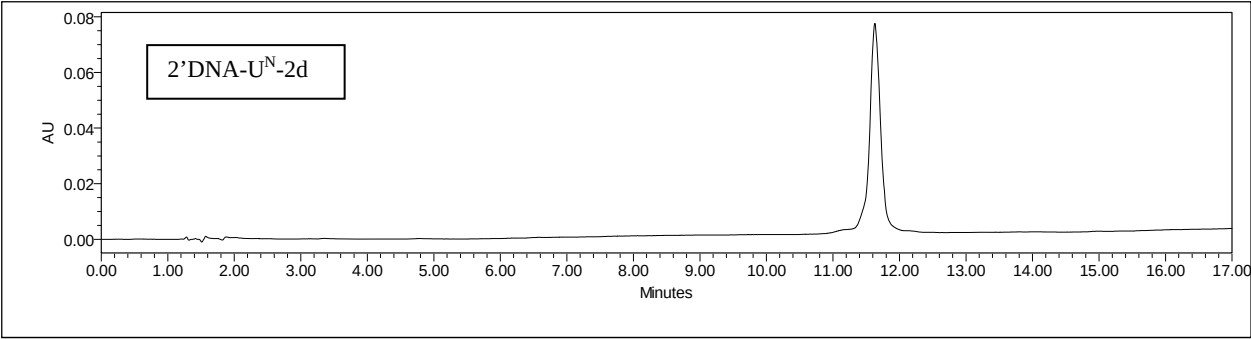
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1	2'DNA-U ^S -1d2	10.512	575826	100.00	37111



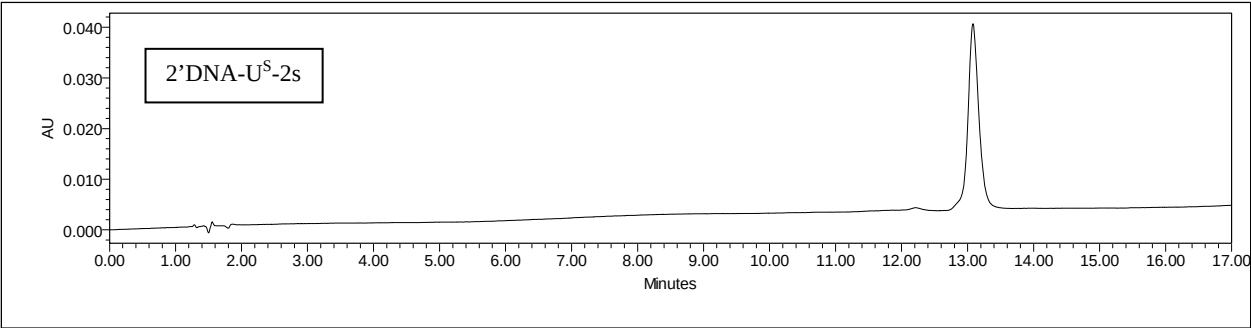
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1	2'DNA-2	12.737	12002211	100.00	1252638



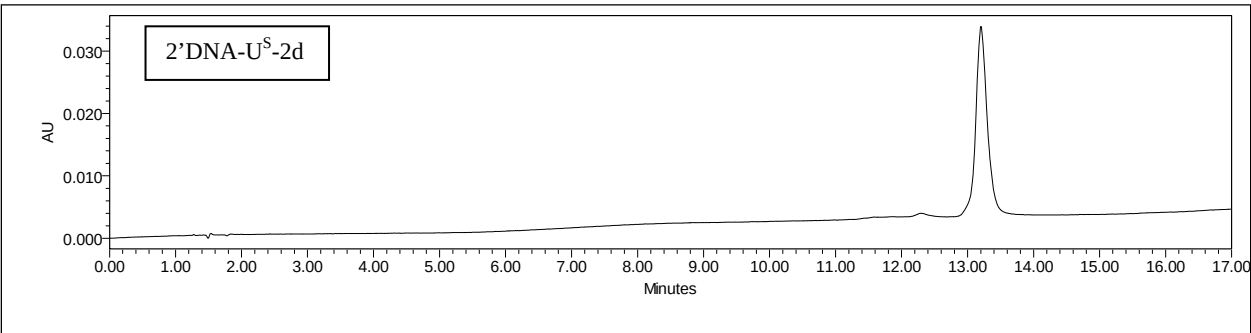
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1	2'DNA-U ^N -2s	11.527	617781	100.00	70686



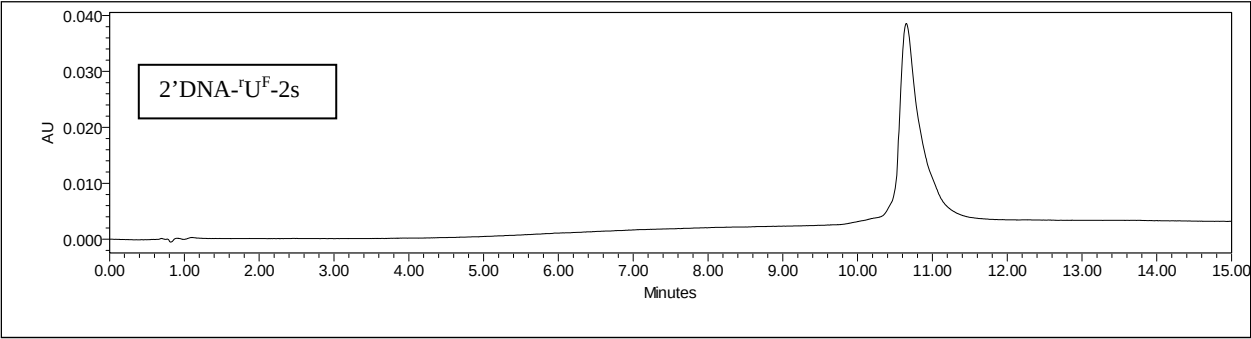
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1	2'DNA-U ^N -2d	11.631	737416	100.00	71396



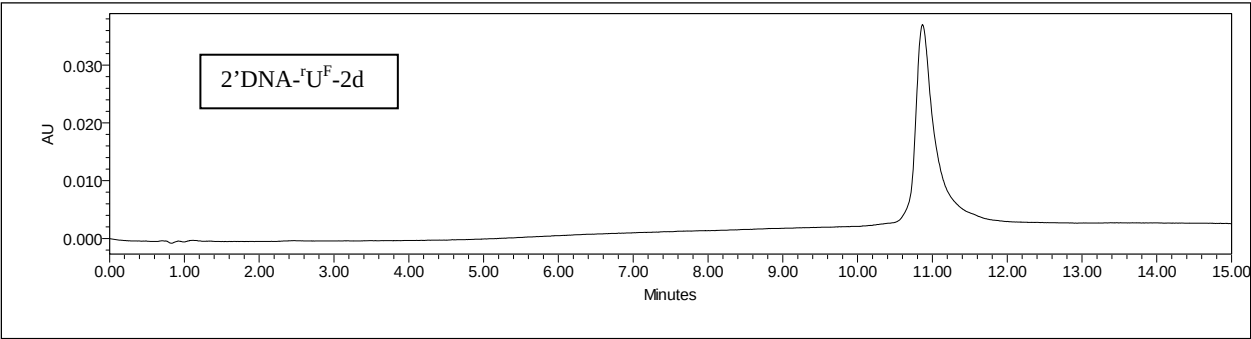
	Name	Retention Time	Area	% Area	Height
1	2'DNA-U ^S -2s	13.082	391008	100.00	35787



	Name	Retention Time	Area	% Area	Height
1	2'DNA-U ^S -2d	13.203	330838	100.00	29326

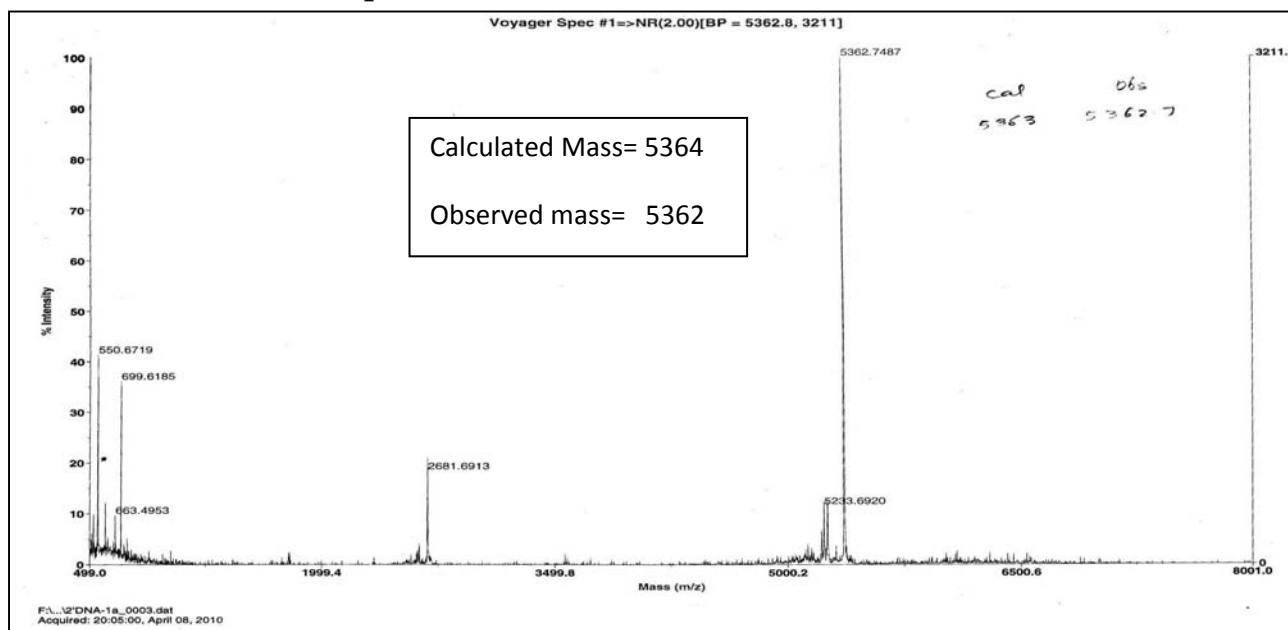


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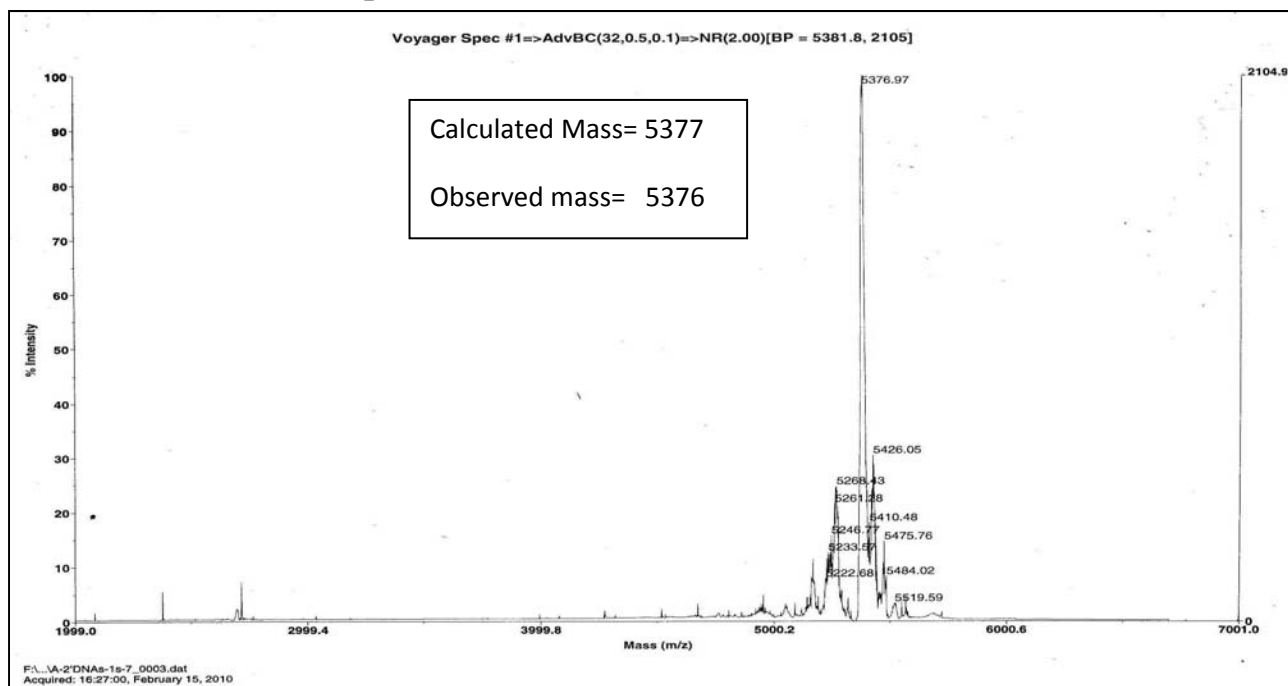


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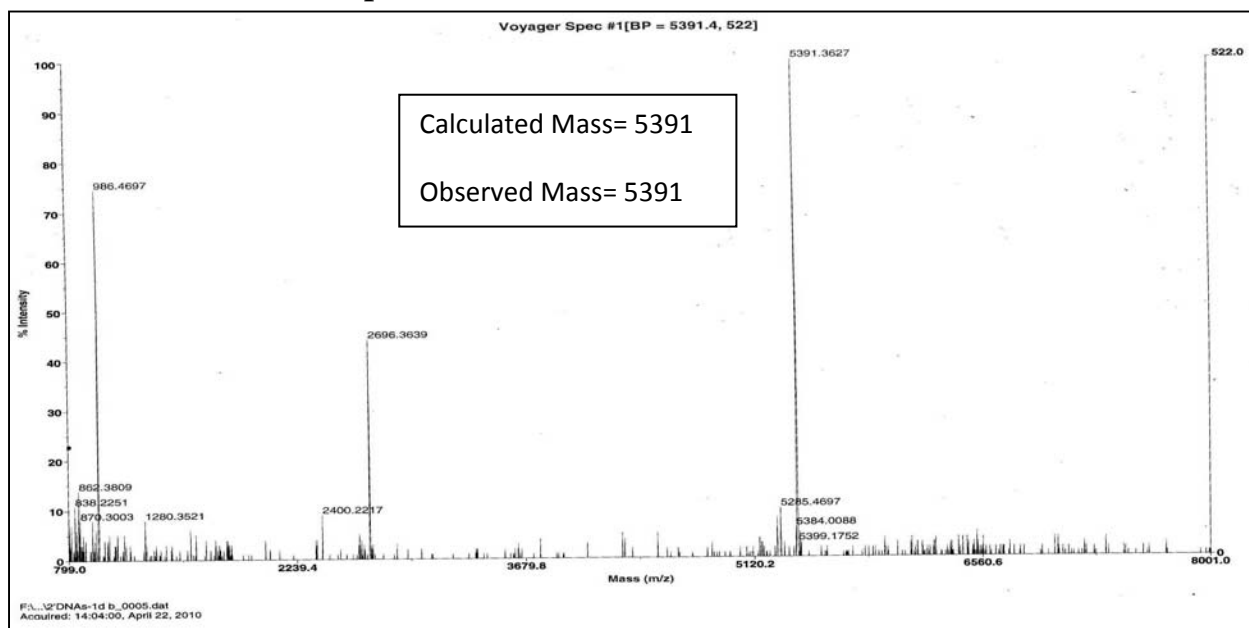
MALDI-TOF mass spectrum of 2'DNA-1



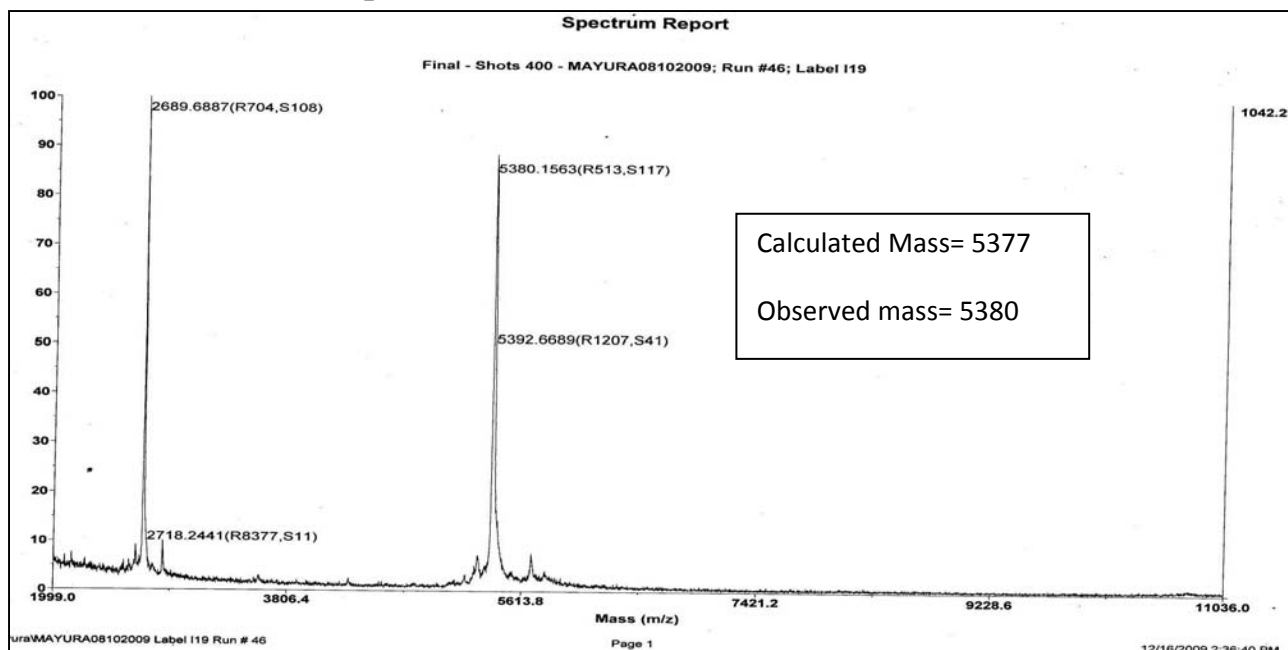
MALDI-TOF mass spectrum of 2'DNA-U^N-1s



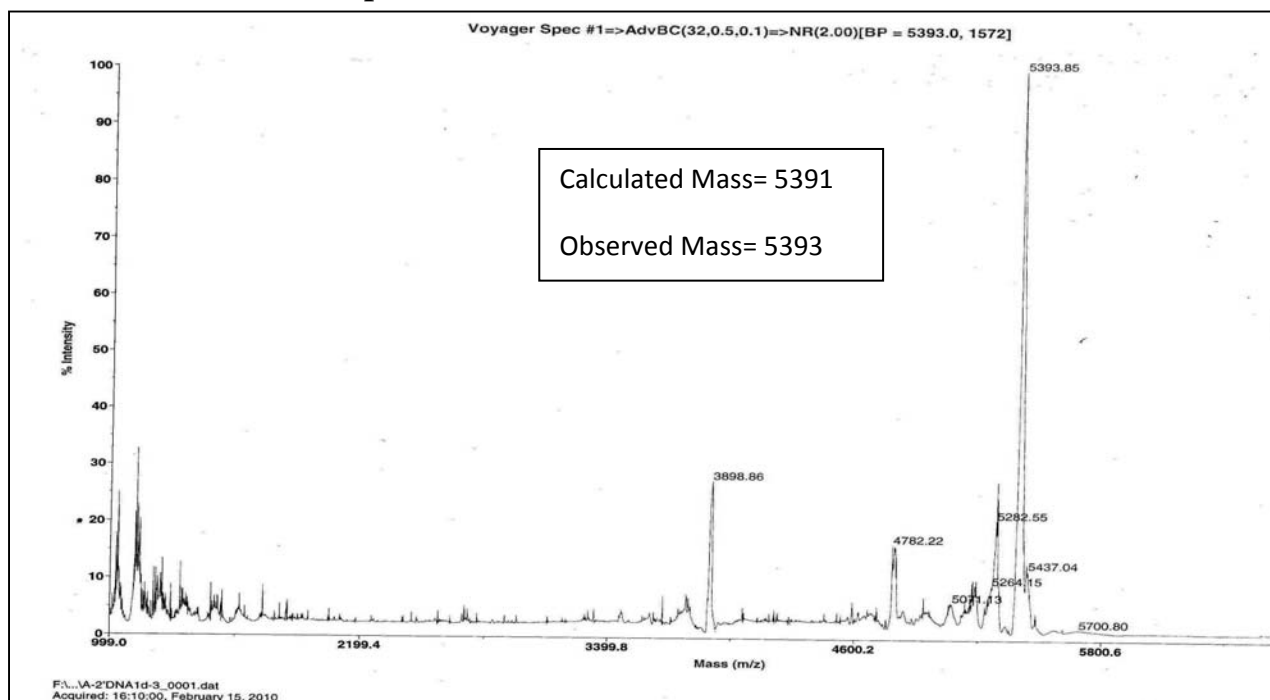
MALDI-TOF mass spectrum of 2'DNA-U^N-1d



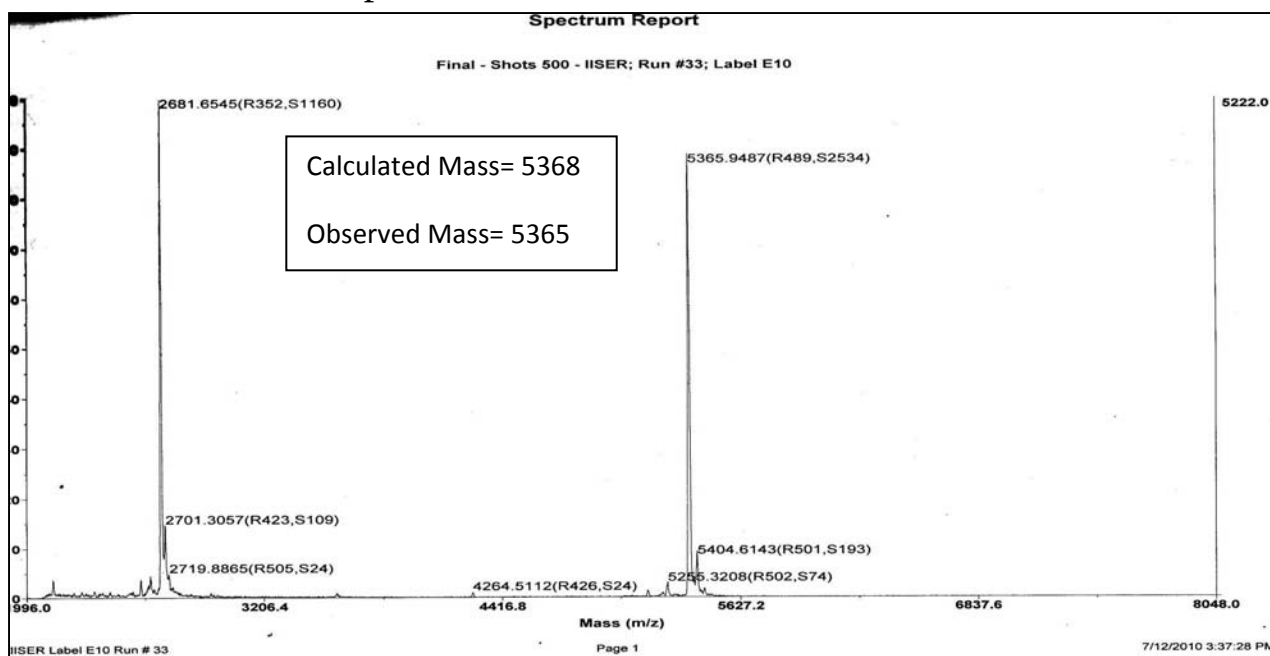
MALDI-TOF mass spectrum of 2'DNA-U^S-1s



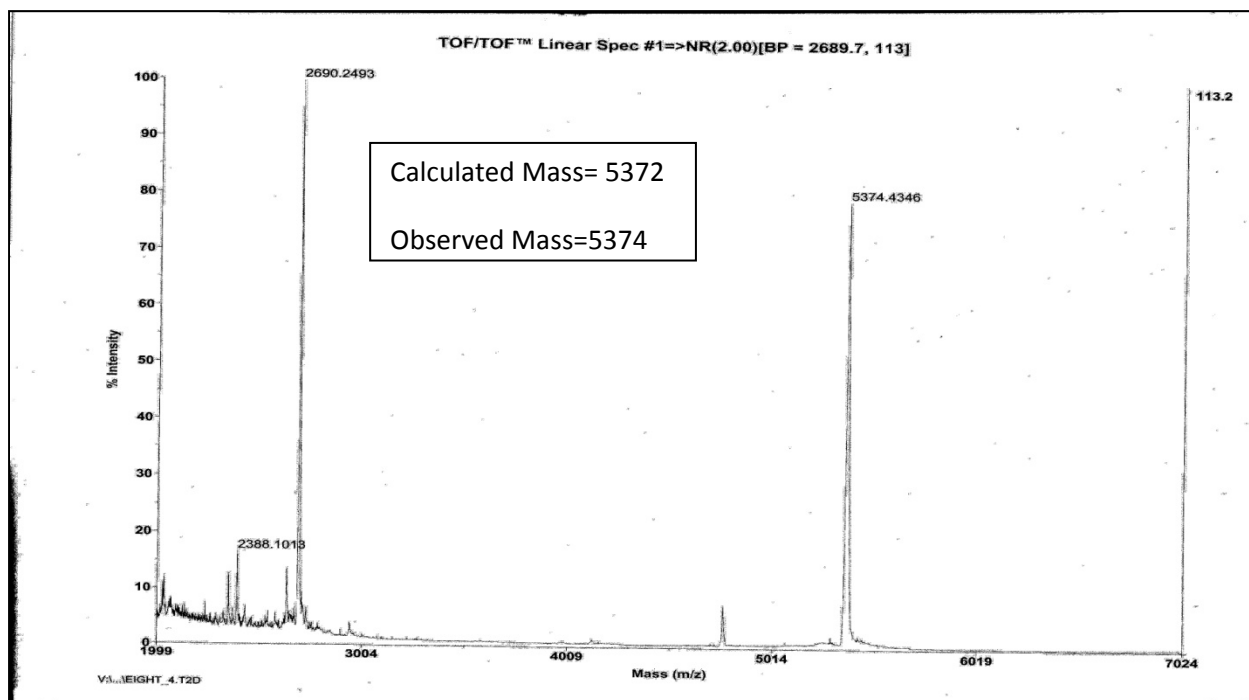
MALDI-TOF mass spectrum of 2'DNA-U^S-1d



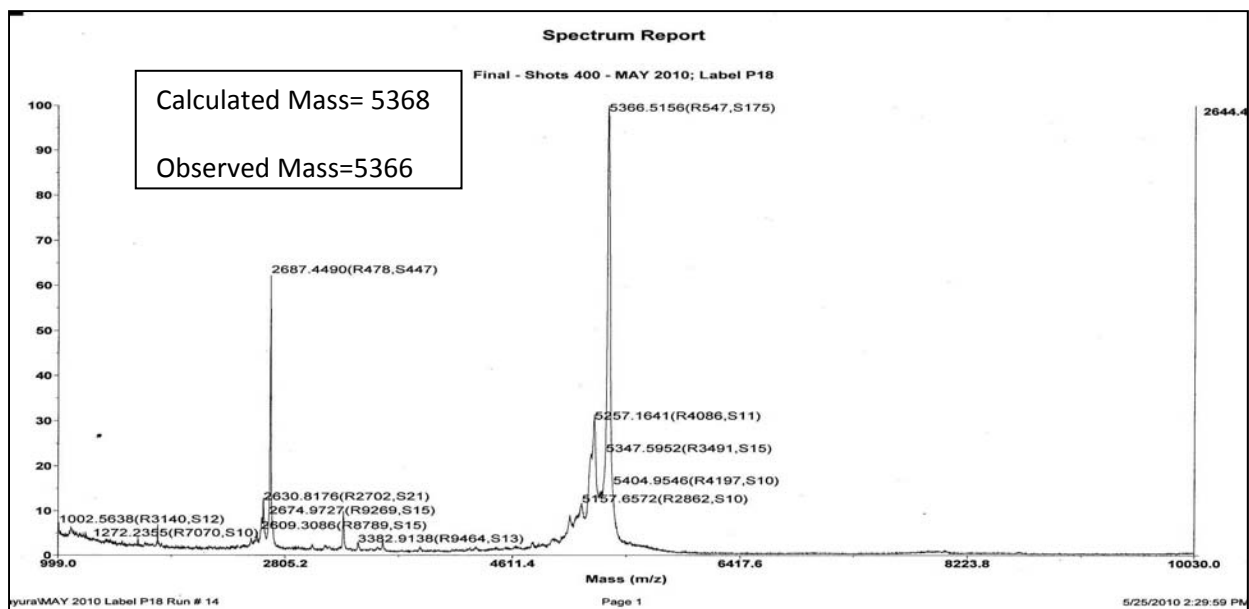
MALDI-TOF mass spectrum of 2'DNA-^XU^F-1s



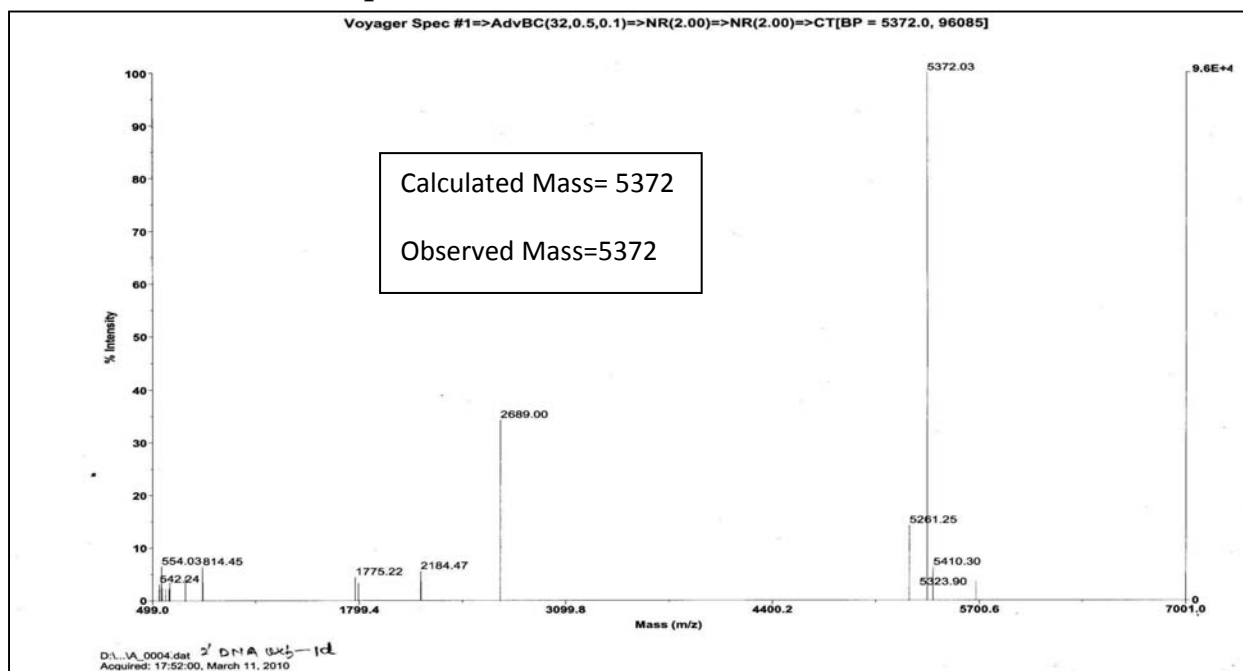
MALDI-TOF mass spectrum of 2'DNA-^XU^F-1d



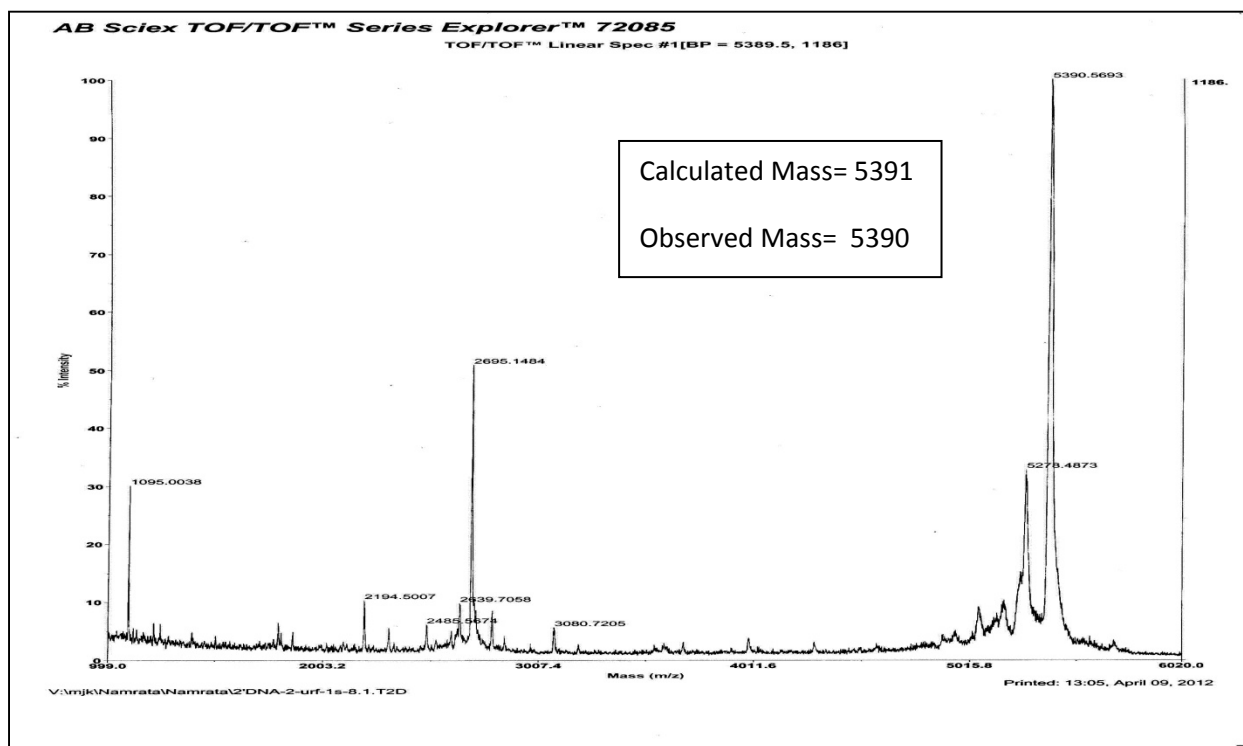
MALDI-TOF mass spectrum of 2'DNA-^rU^F-1s



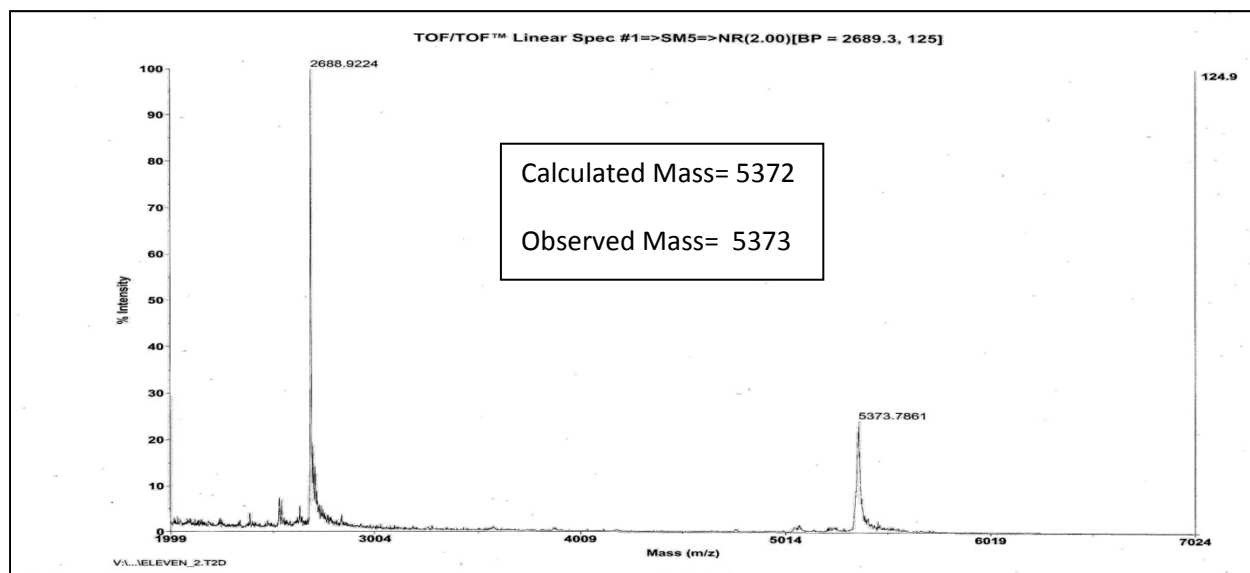
MALDI-TOF mass spectrum of 2'DNA-rU^F-1d



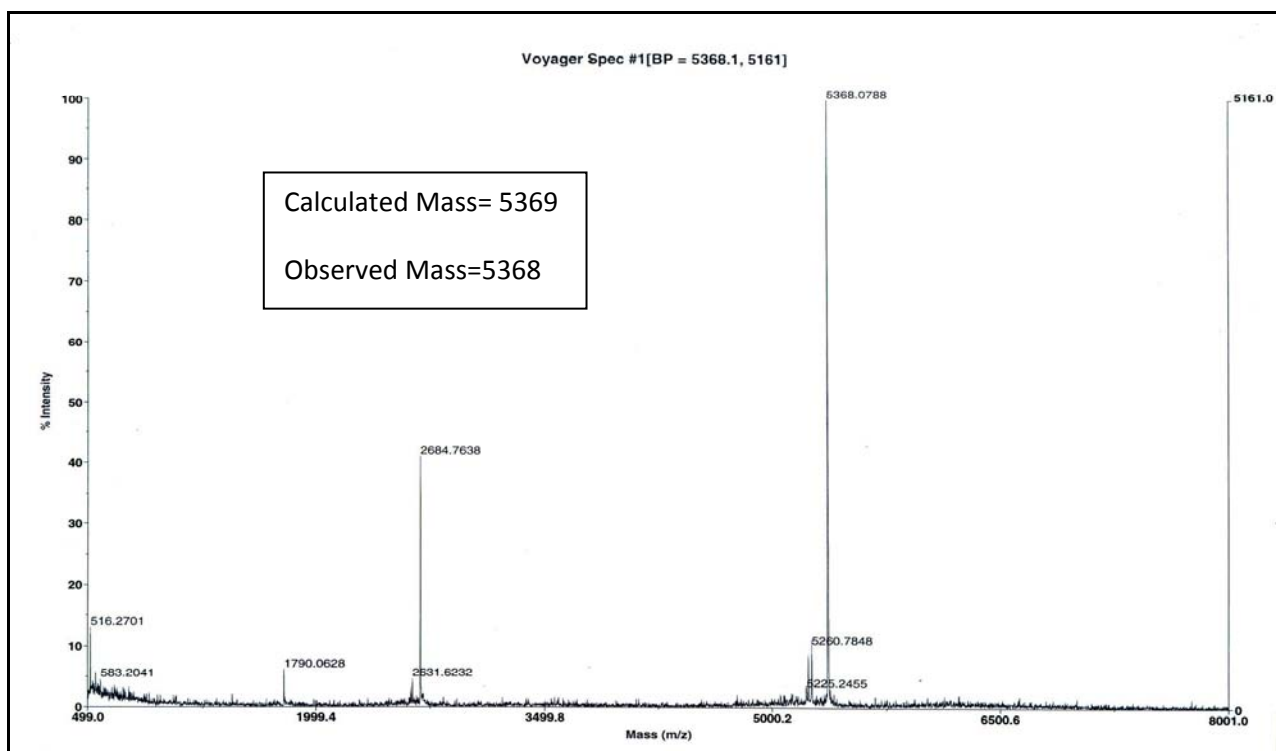
MALDI-TOF mass spectrum of 2'DNA-U^S-1d2



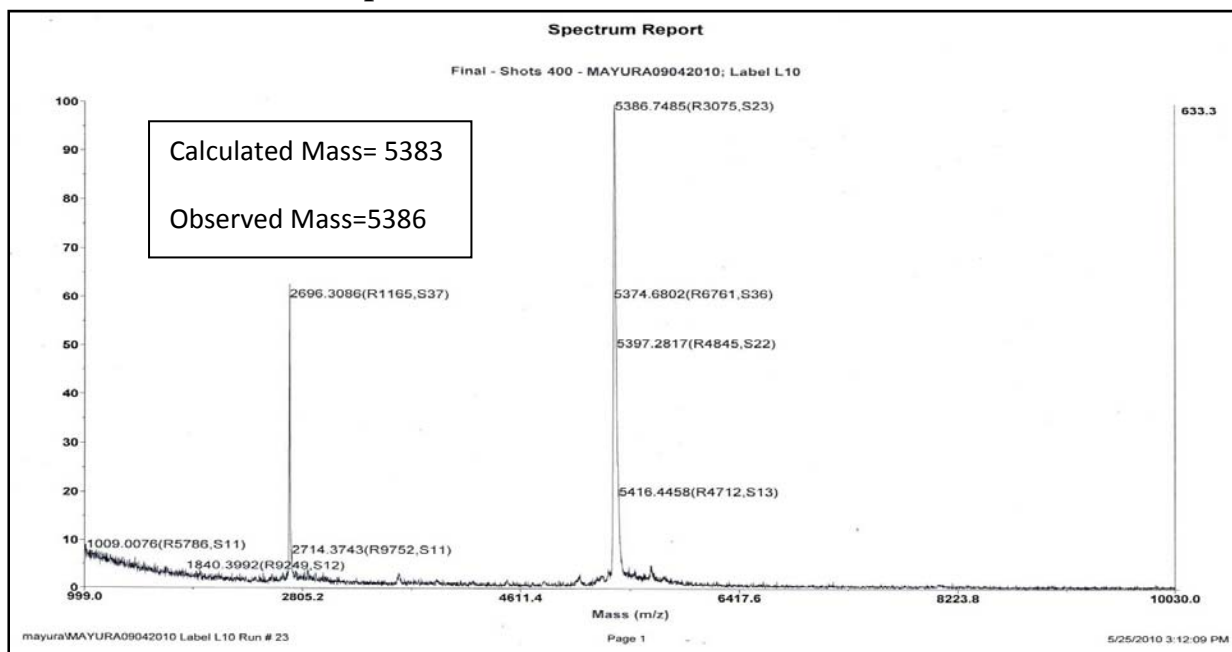
MALDI-TOF mass spectrum of 2'DNA-rU^F-1d2



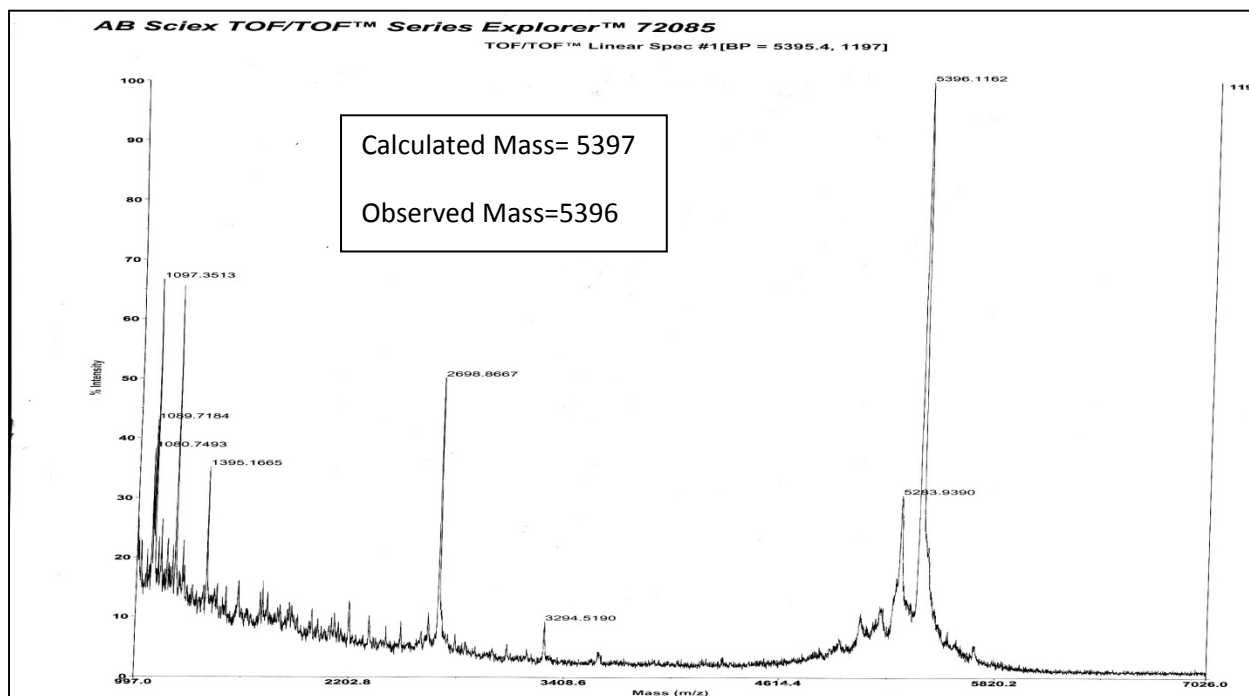
MALDI-TOF mass spectrum of 2'DNA-2



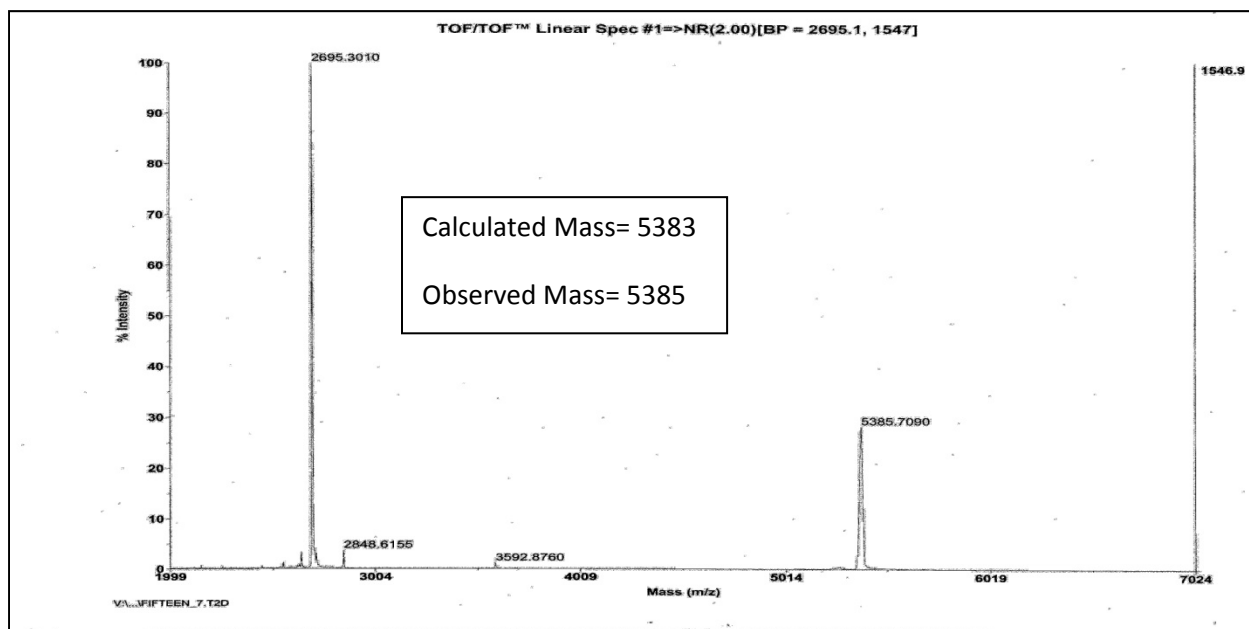
MALDI-TOF mass spectrum of 2'DNA-U^N-2s



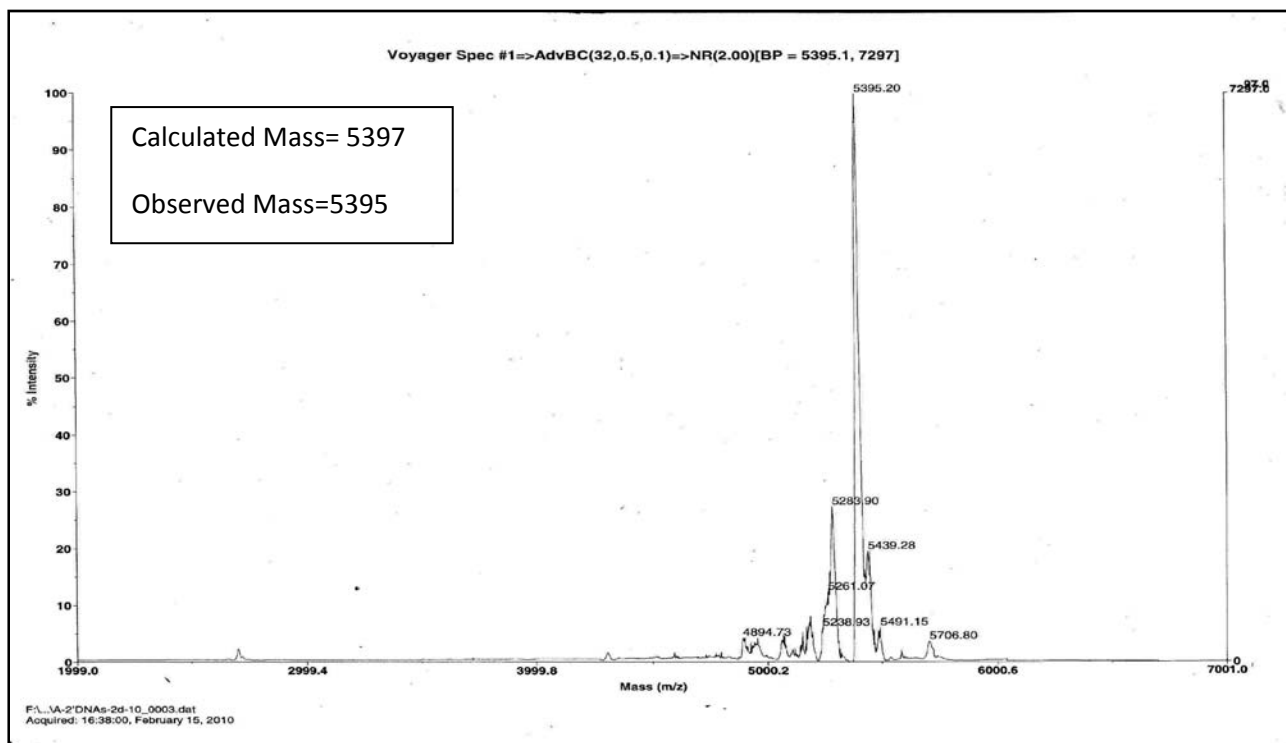
MALDI-TOF mass spectrum of 2'DNA-U^N-2d



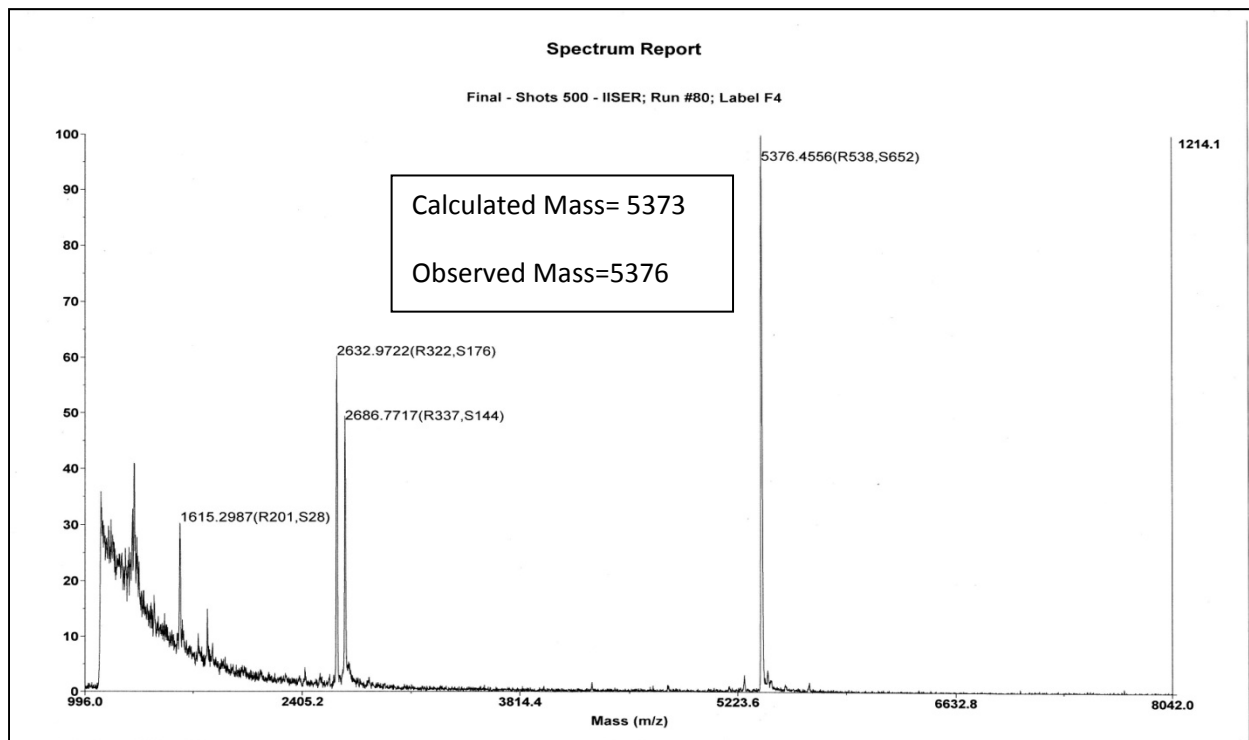
MALDI-TOF mass spectrum of 2'DNA-U^S-2s



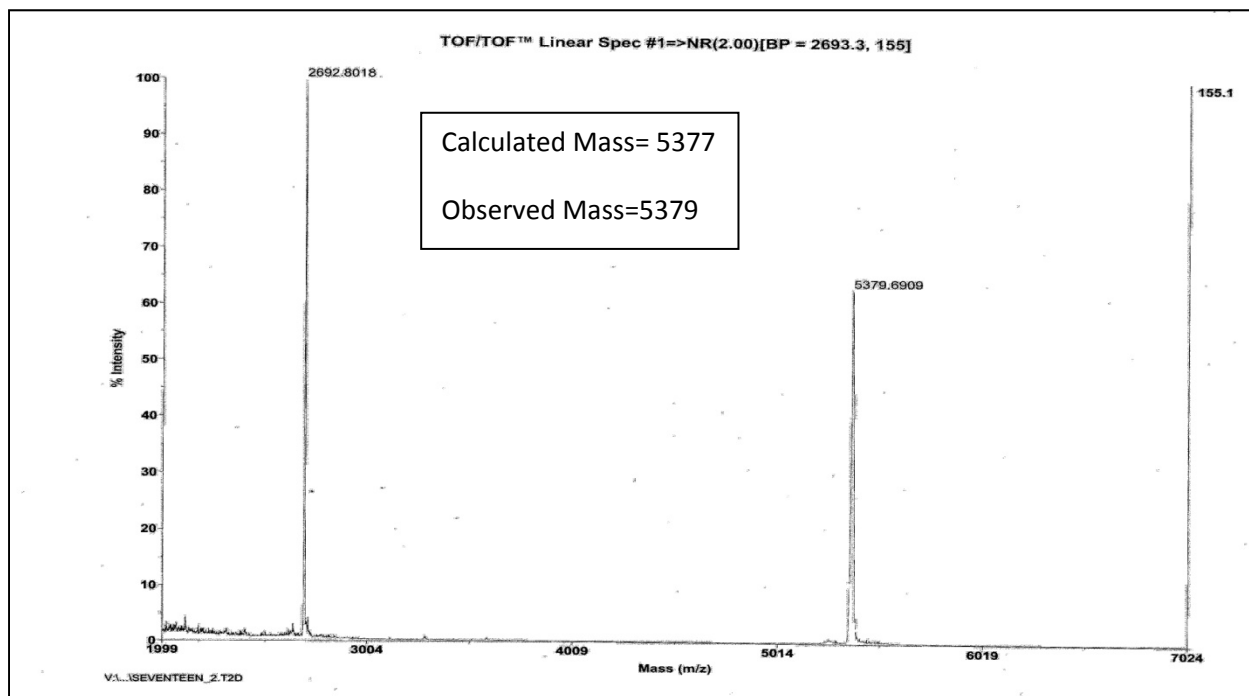
MALDI-TOF mass spectrum of 2'DNA-U^S-2d



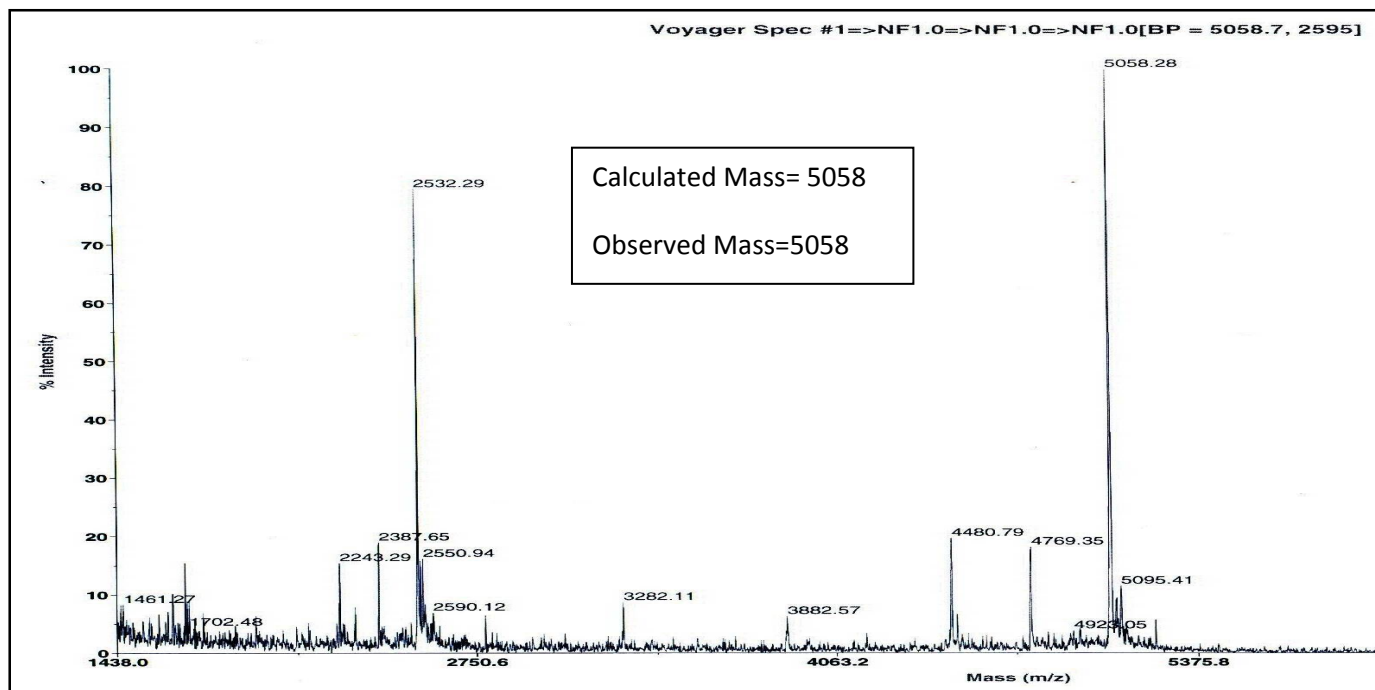
MALDI-TOF mass spectrum of 2'DNA-^rU^F-2s



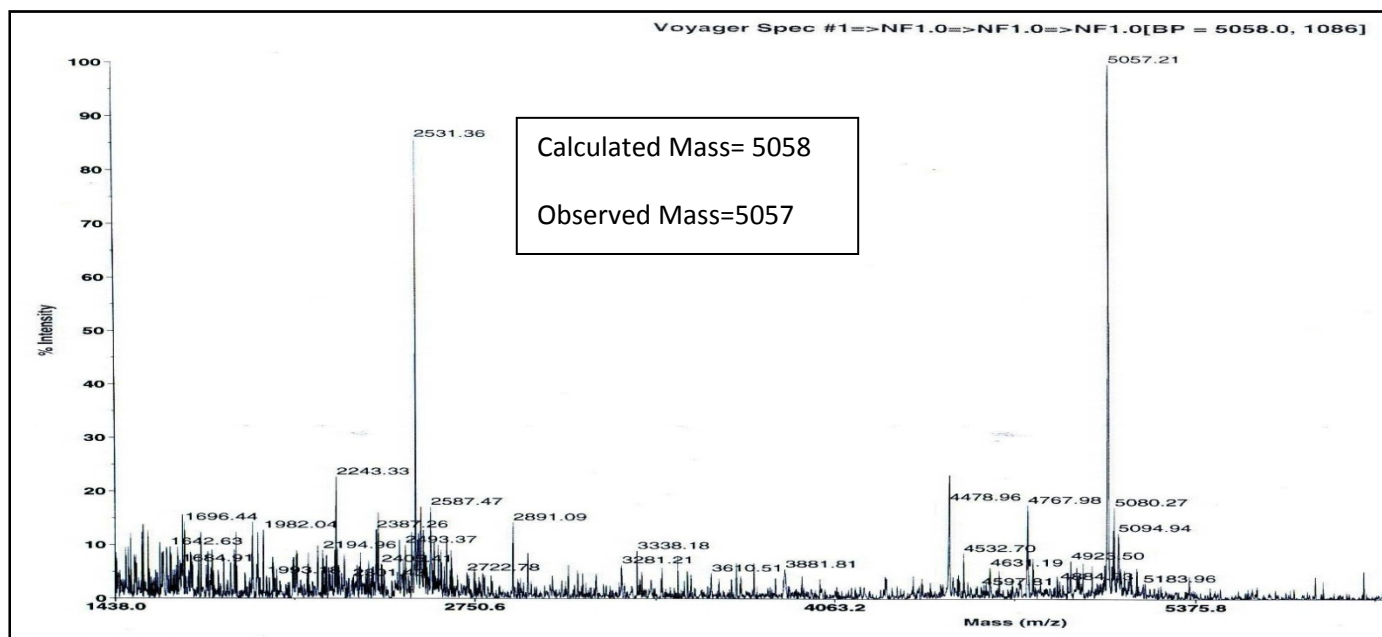
MALDI-TOF mass spectrum of 2'DNA-^rU^F-2d



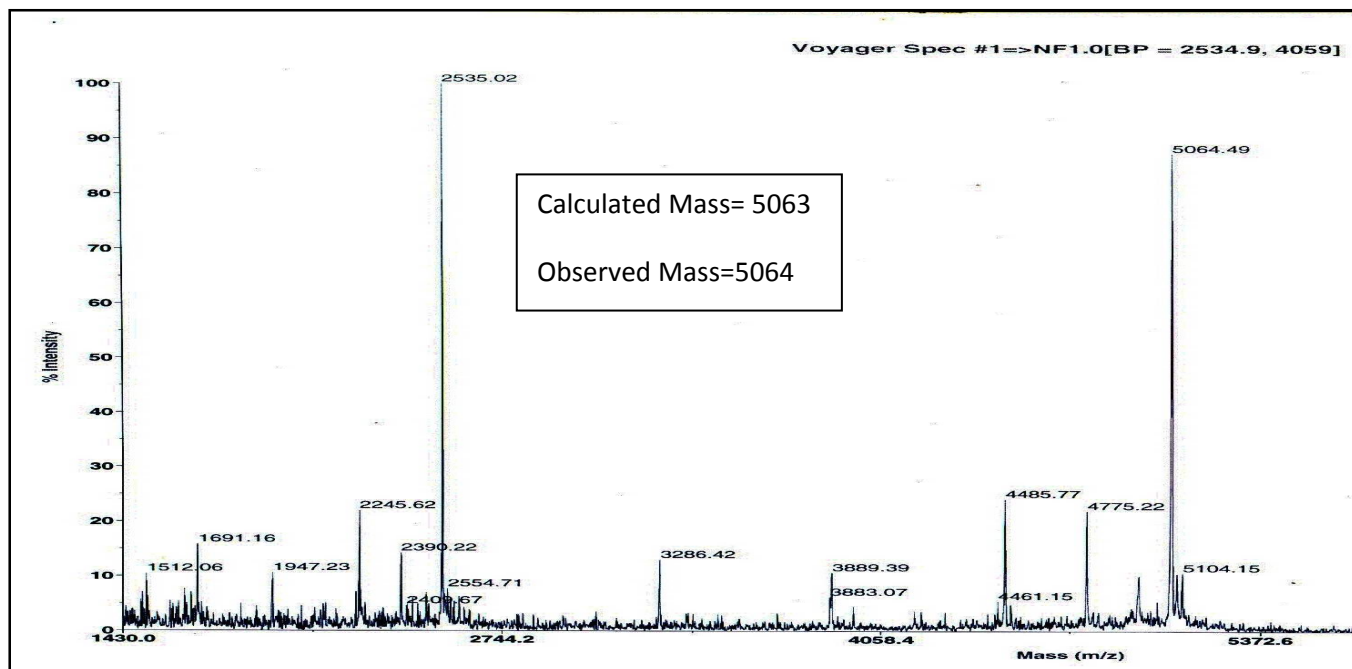
MALDI-TOF mass spectrum of 2'DNA-^XU^F-1d with deletion of the 2'terminal Adenosine-5'-phosphate.



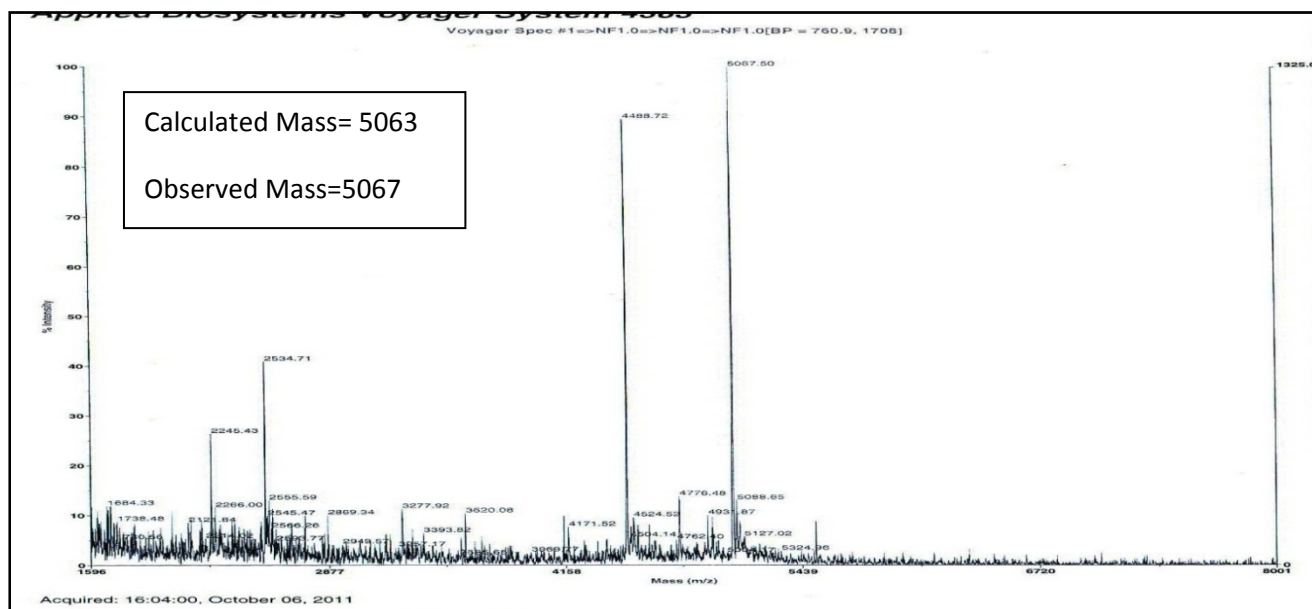
MALDI-TOF mass spectrum of 2'DNA-^rU^F-1d with deletion of the 2'terminal Adenosine-5'-phosphate



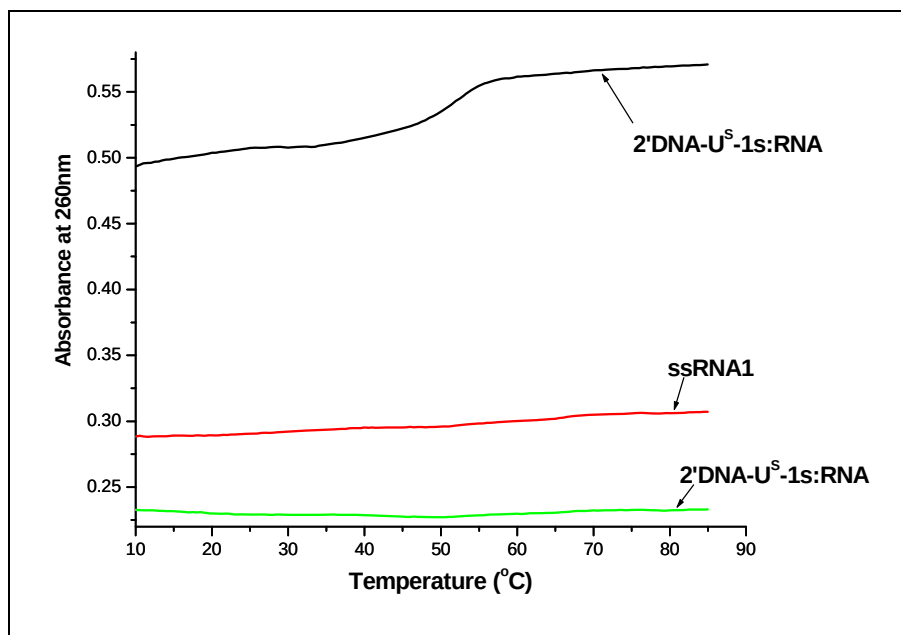
MALDI-TOF mass spectrum of 2'DNA-U^N-1s with deletion of the 2'terminal Adenosine-5'phosphate.



MALDI-TOF mass spectrum of 2'DNA-U^S-1s with deletion of the 2'terminal Adenosine-5'phosphate.

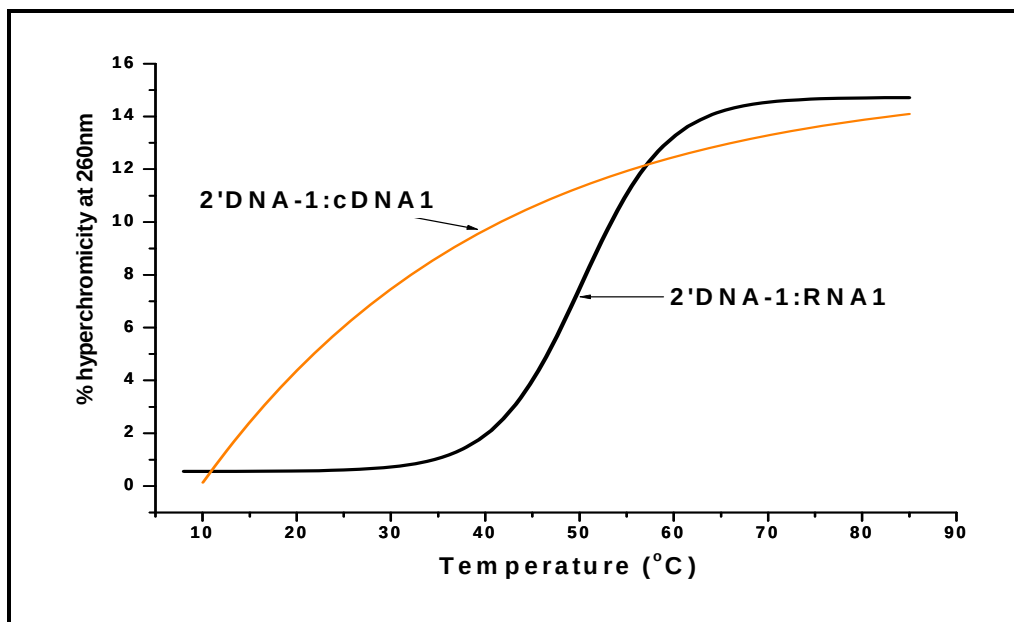


Representative UV-melting of single-stranded 2'DNA-U^S-1s, complementary single-stranded RNA1 and 2'DNA-U^S-1s:RNA1 complex.

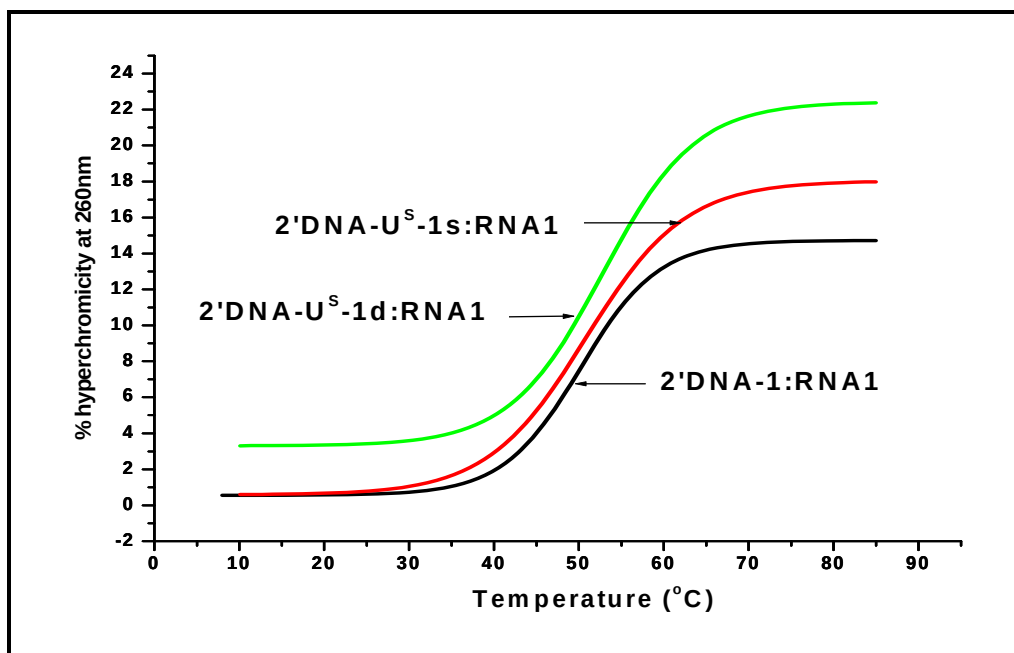


UV-Melting Plots

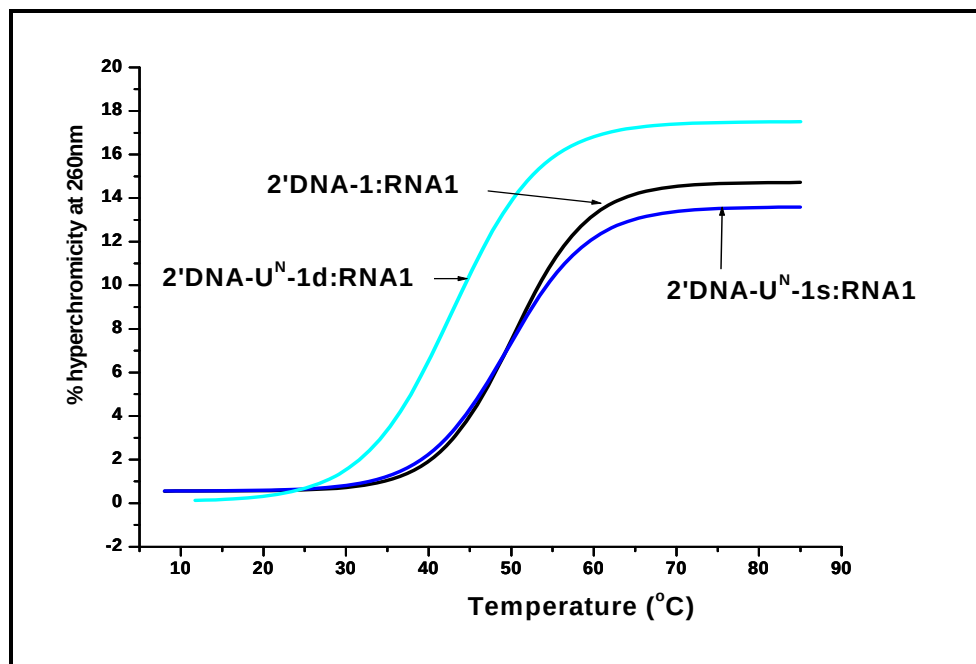
UV-melting plots of complexes of 2'DNA-1 with complementary RNA1 and complementary cDNA1



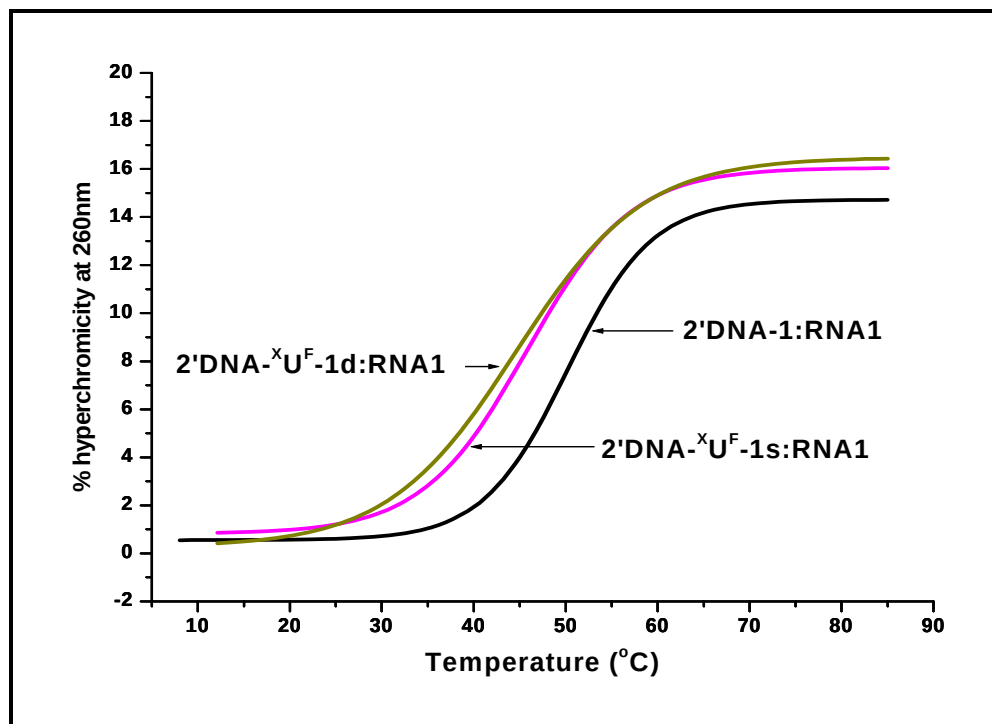
UV-melting plots of complexes of 2'DNA-1, 2'DNA-U^S-1s and 2'DNA-U^S-1d with complementary RNA1



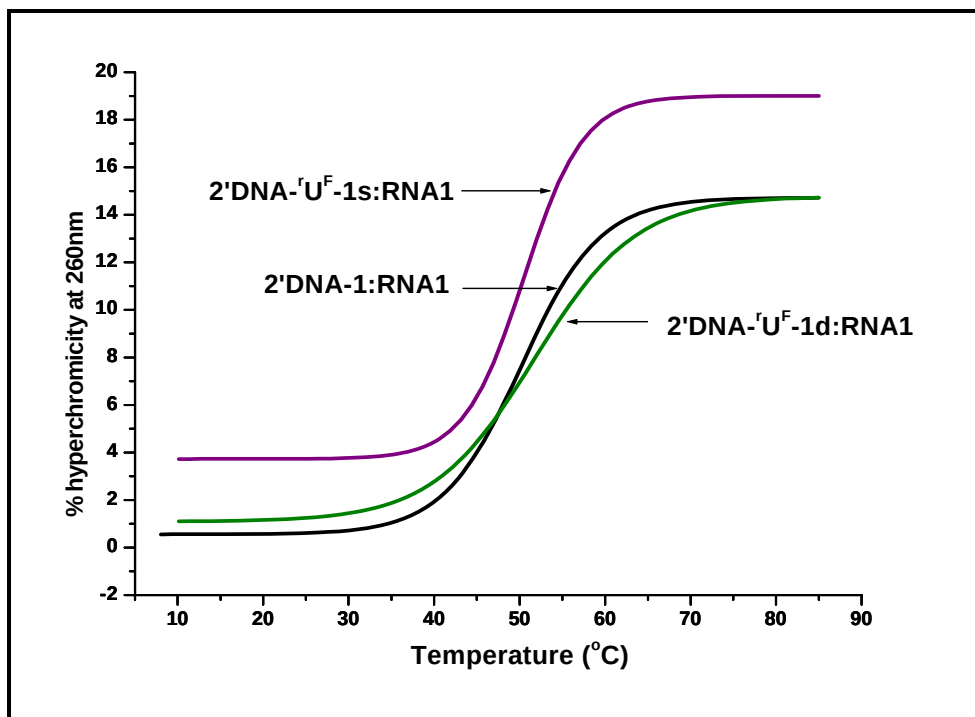
UV-melting plots of complexes of 2'DNA-1, 2'DNA- U^N -1s and 2'DNA- U^N -1d with complementary RNA1



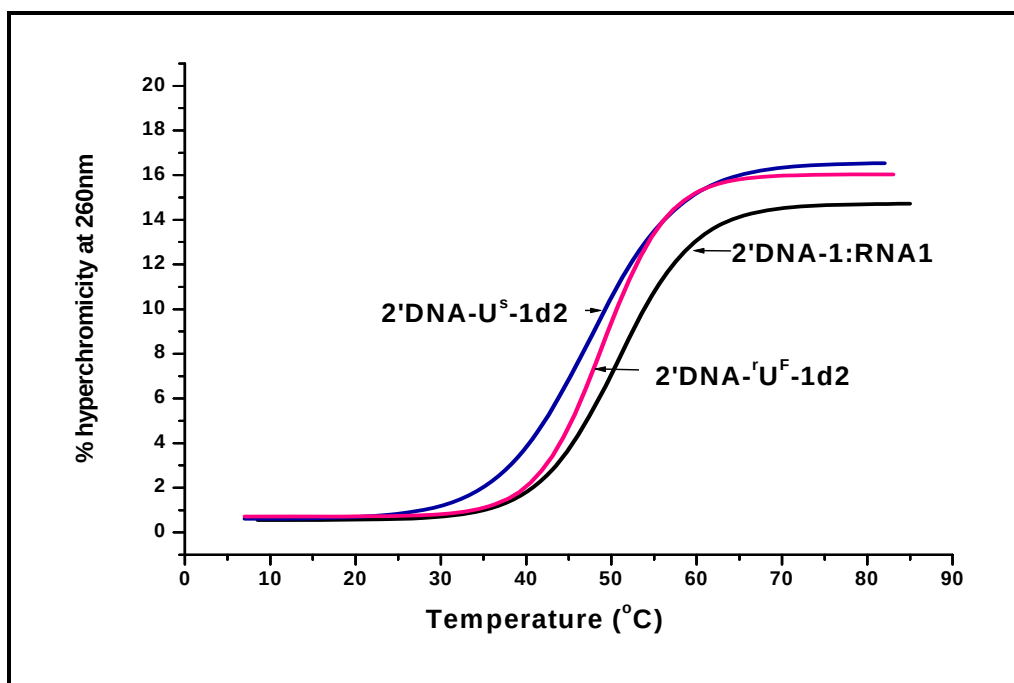
UV-melting plots of complexes of 2'DNA-1, 2'DNA- $^xU^F$ -1s and 2'DNA- $^xU^F$ -1d with complementary RNA1



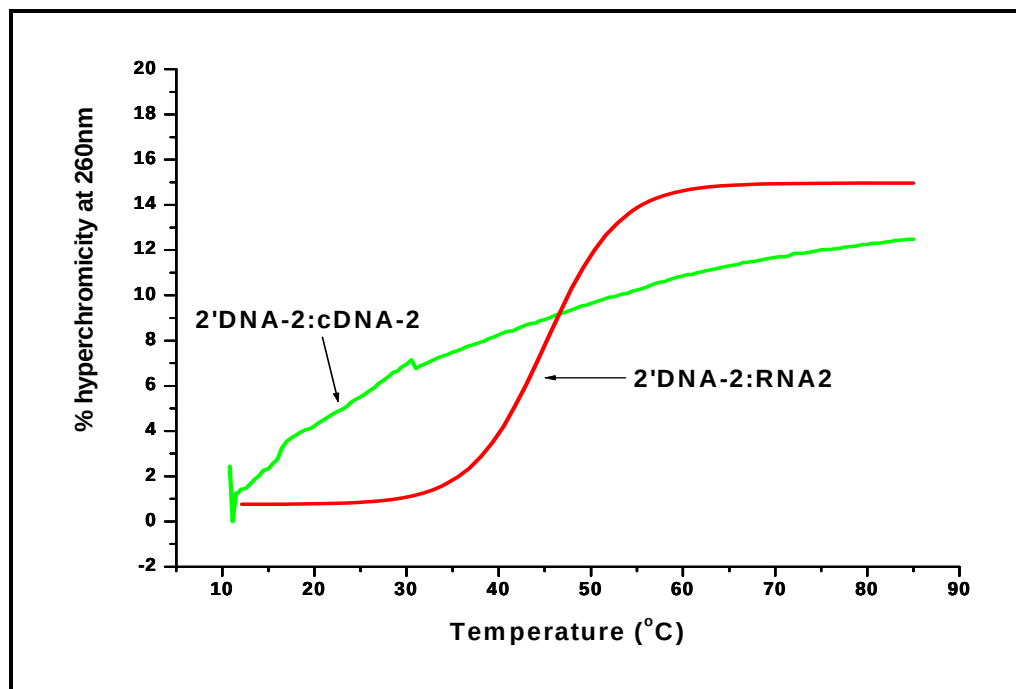
UV-melting plots of complexes of 2'DNA-1, 2'DNA-^rU^F-1s and 2'DNA-^rU^F-1d with complementary RNA1



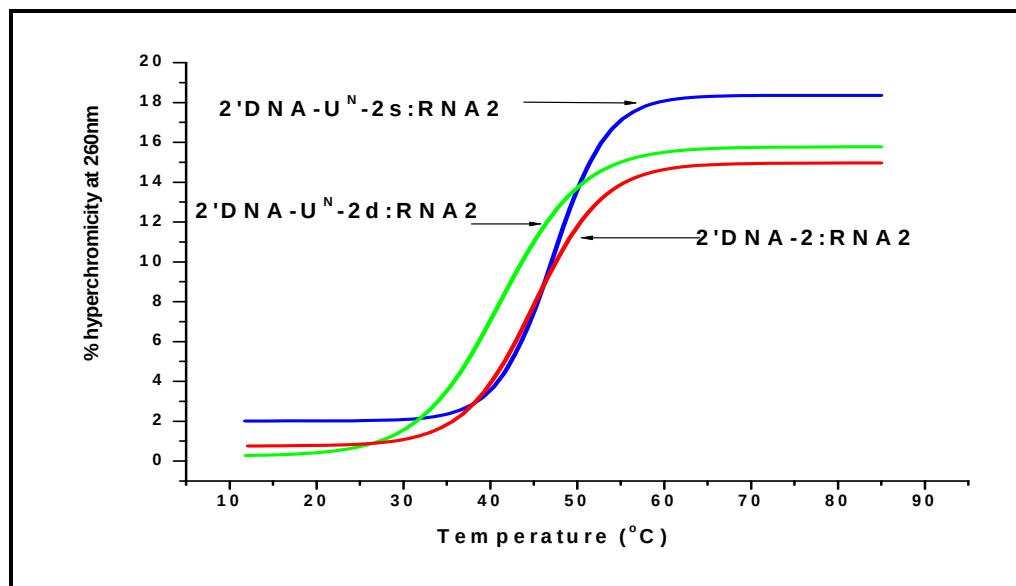
UV-melting plots of complexes of 2'DNA-1, 2'DNA-^rU^F-1d2 and 2'DNA-U^S-1d2 with complementary RNA1



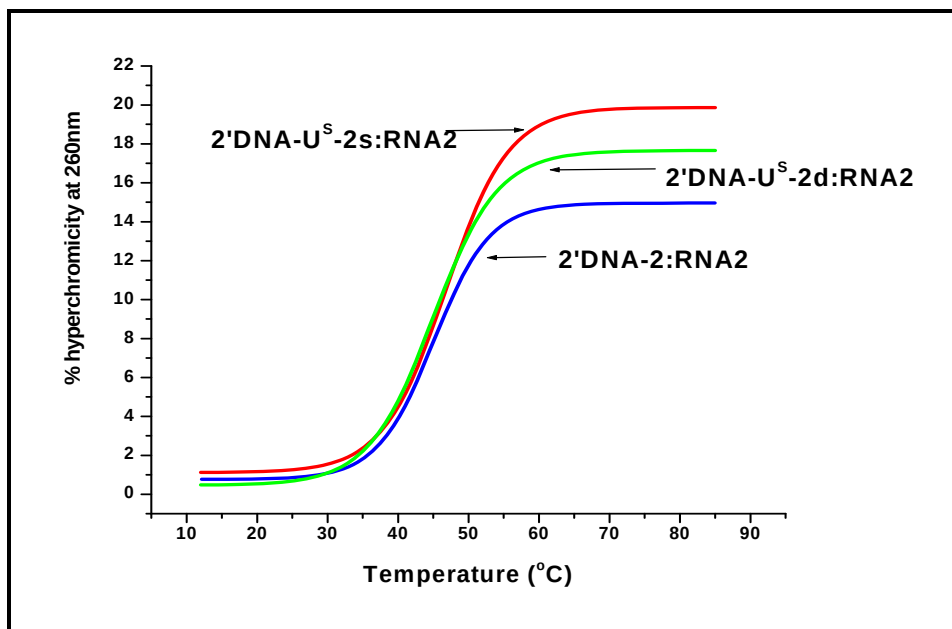
UV-melting plots of complexes of 2'DNA-2 with complementary RNA2 and complementary cDNA-2



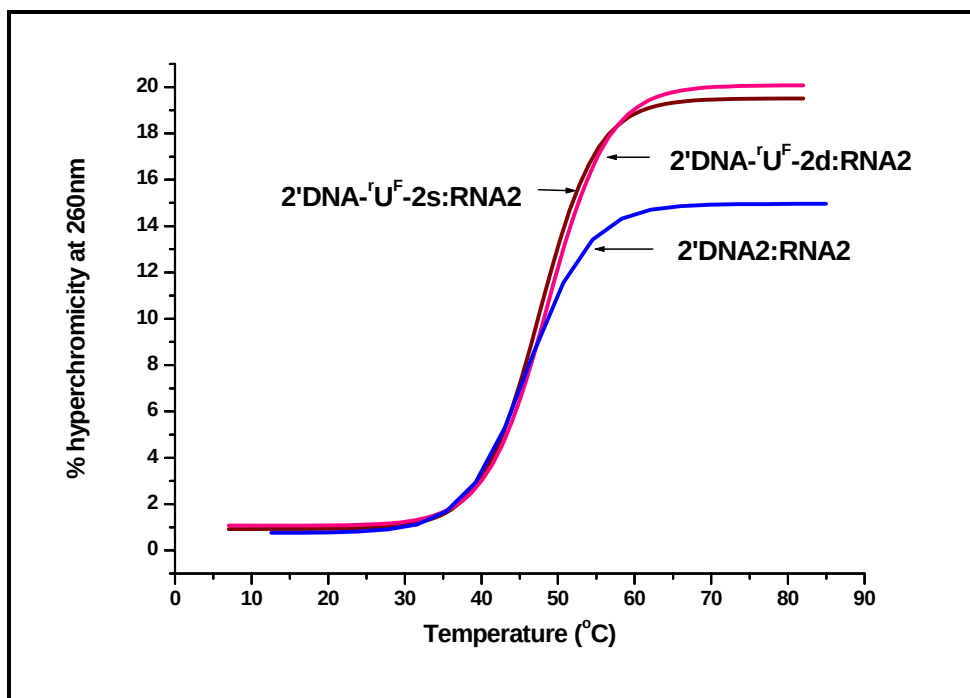
UV-melting plots of complexes of 2'DNA-2, 2'DNA-U^N-2s and 2'DNA-U^N-2d with complementary RNA2



UV-melting plots of complexes of 2'DNA-2, 2'DNA-U^S-2s and 2'DNA-U^S-2d with complementary RNA2

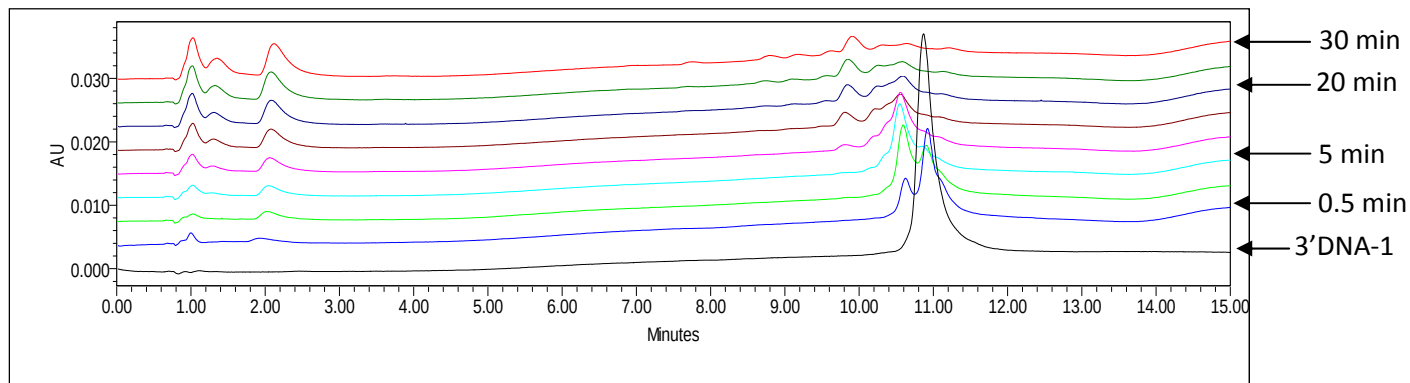


UV-melting plots of complexes of 2'DNA-1, 2'DNA-^rU^F-2s and 2'DNA-^rU^F-2d with complementary RNA2

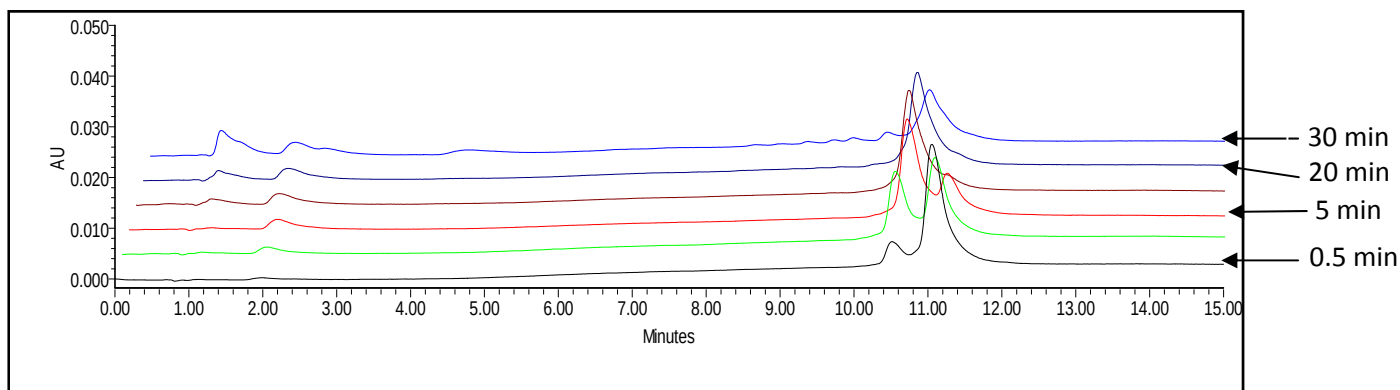


❖ Representative RP-HPLC at several time-points for SVPDE study of
3'DNA-1, 2'DNA-1, and 2'DNA-3 (5'GAAGGGCTTCTTCCTTA**T**2')

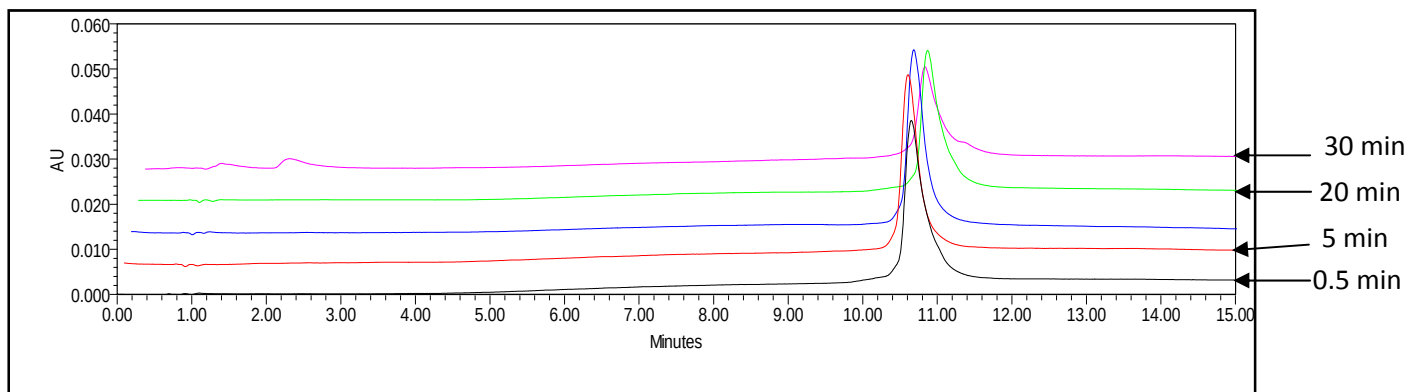
3'DNA-1



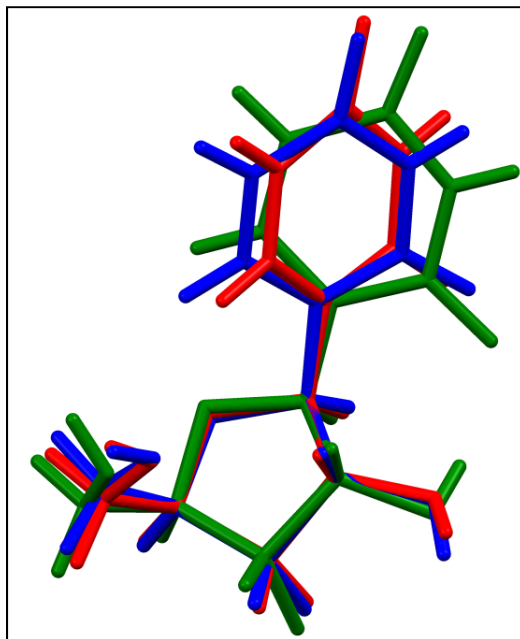
2'DNA-1



2'DNA-3



- ❖ **X-Ray Crystal Structure Overlay diagram of three form of 3'-deoxy-3'-ribofluorouridine ($^rU^F$, III):(Red=MolA, , Blue=molB, Green=MolC)**



- ❖ **ORTEP Drawing for compound 3'-deoxy-3'-xylofluorouridine($^xU^F$, IV):**

