

## Electronic Supplementary Material (ESI)

# 4'-C-Trifluoromethyl Modified Oligodeoxynucleotides: Synthesis, Biochemical Studies, and Cellular Uptake Properties<sup>#,†</sup>

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### TABLE OF CONTENTS

Figure S1. NMR spectra of new compounds. (Page S2)

Figure S2. MS spectra of synthesized ODNs. (Pages S29)

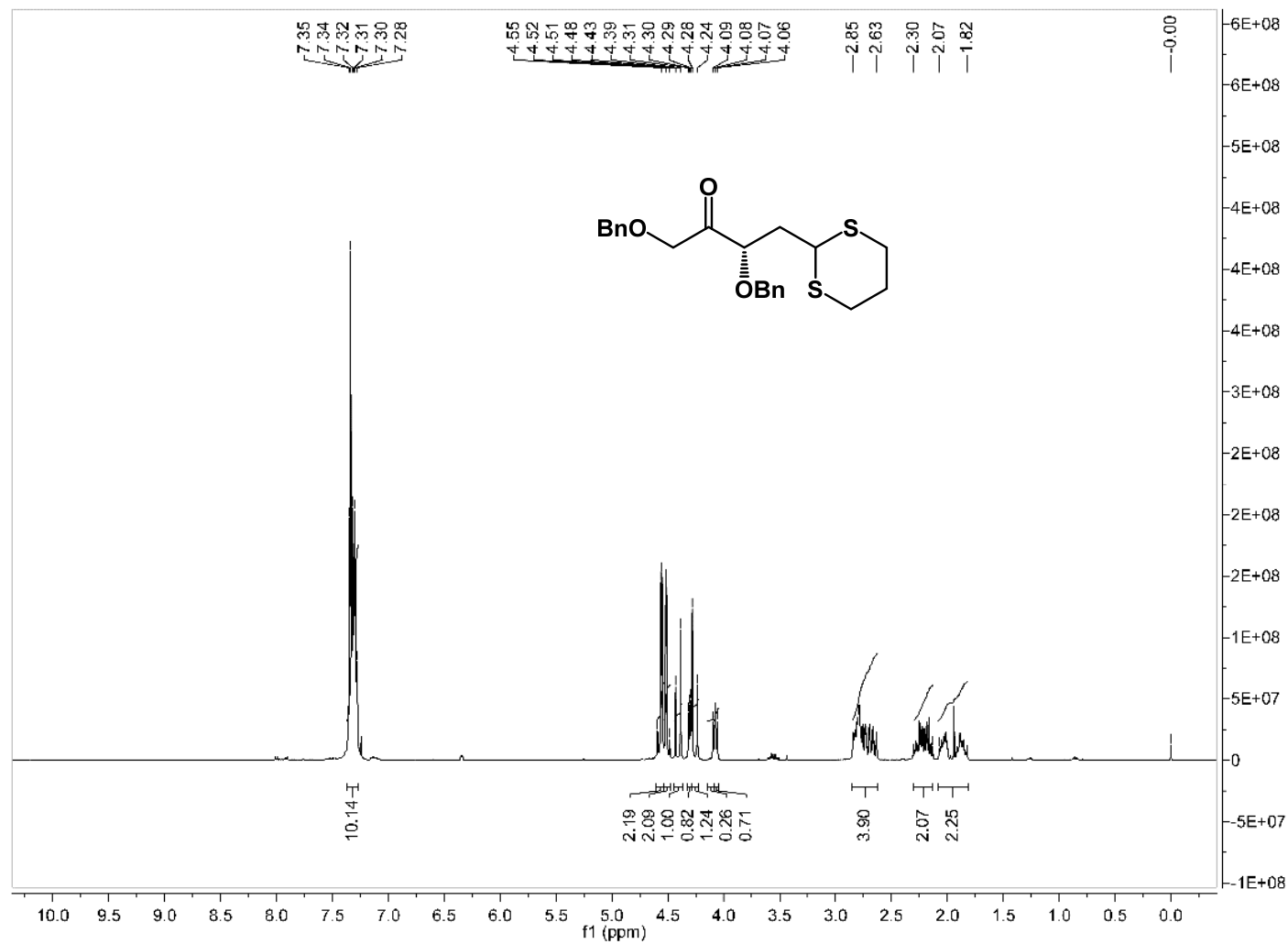
Figure S3. Melting Curves of ODN/DNA and ODN/RNA duplexes. (Page S33)

Figure S4. Circular dichroism spectroscopy of ODNs/DNA duplexes and ODNs/RNA duplexes. (Page S34)

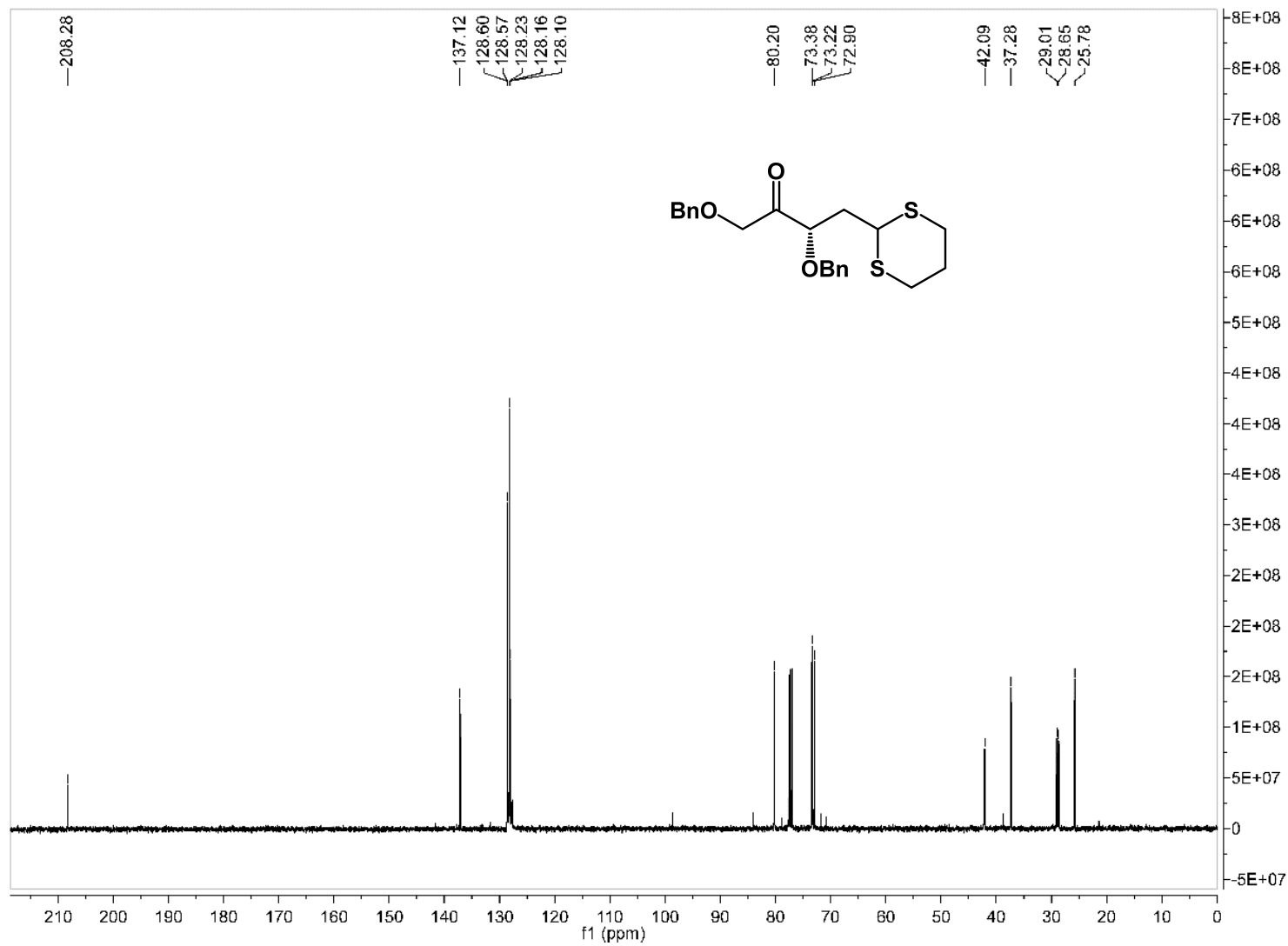
Figure S5. Flow Cytometry analysis of cell permeability of ODNs. (Page S35)

**Figure S1. NMR Spectra of new compounds.**

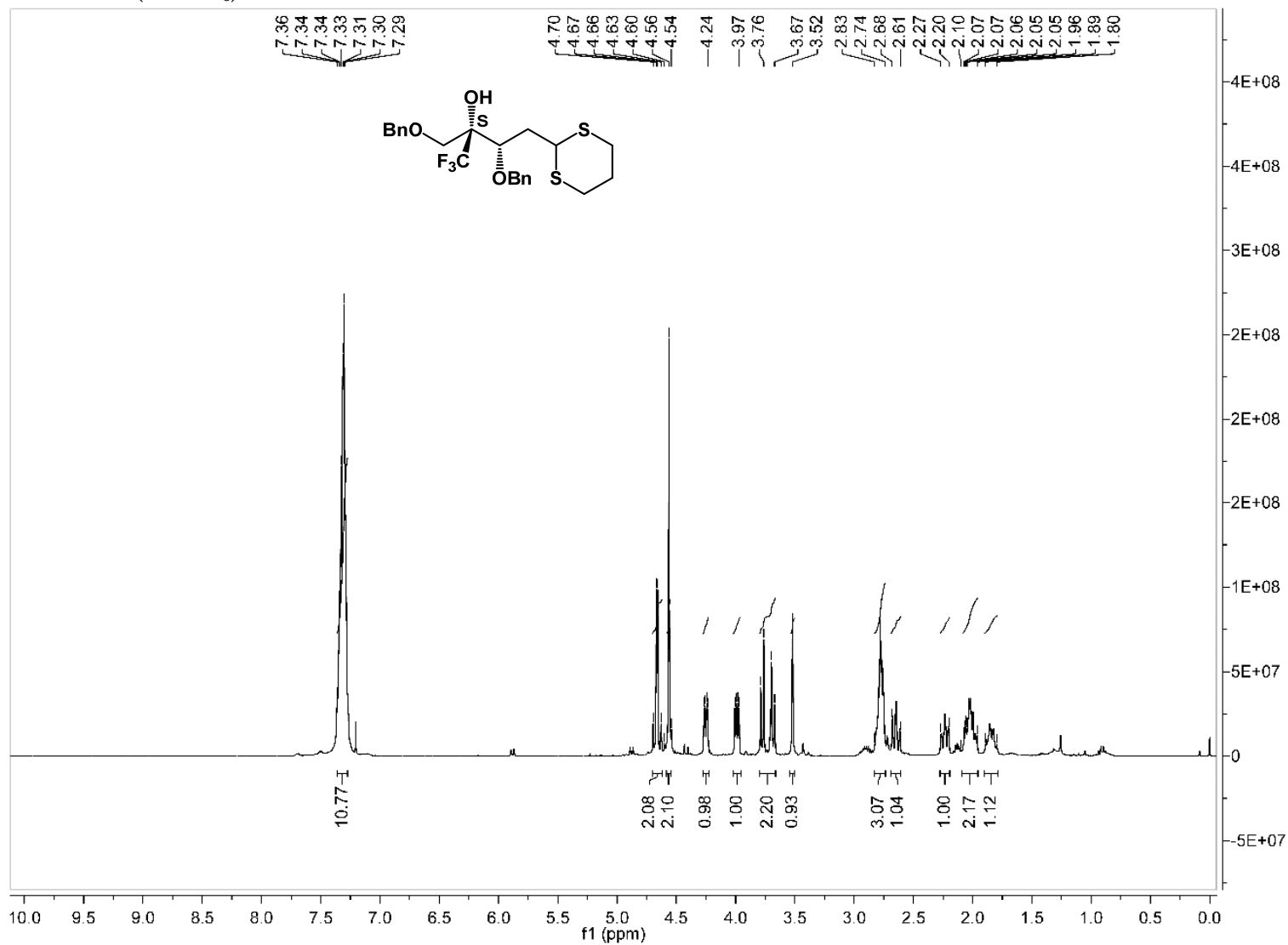
(A)  $^1\text{H}$  NMR spectrum of **2** (in  $\text{CDCl}_3$ ):



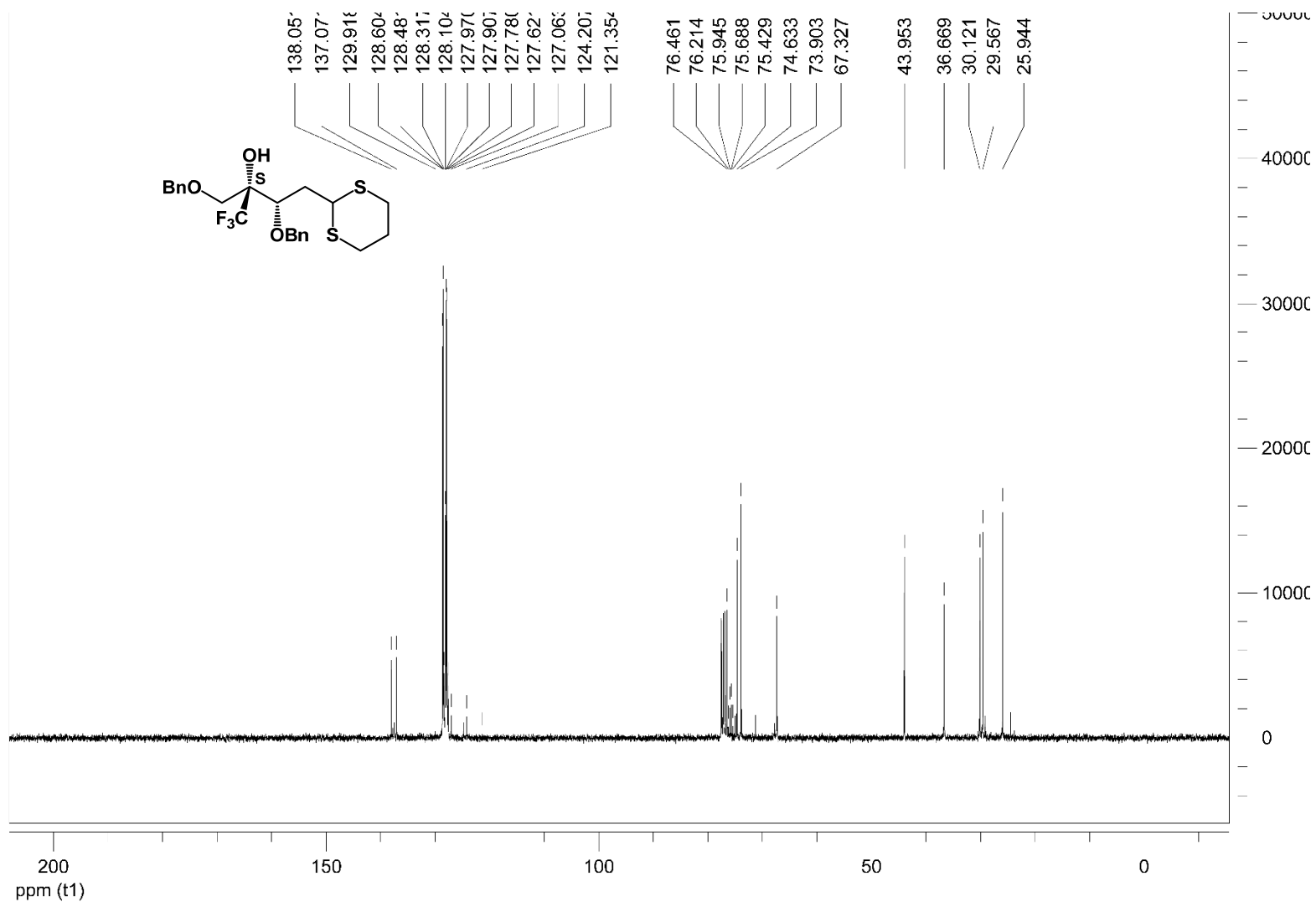
(B)  $^{13}\text{C}$  NMR spectrum of **2** (in  $\text{CDCl}_3$ ):



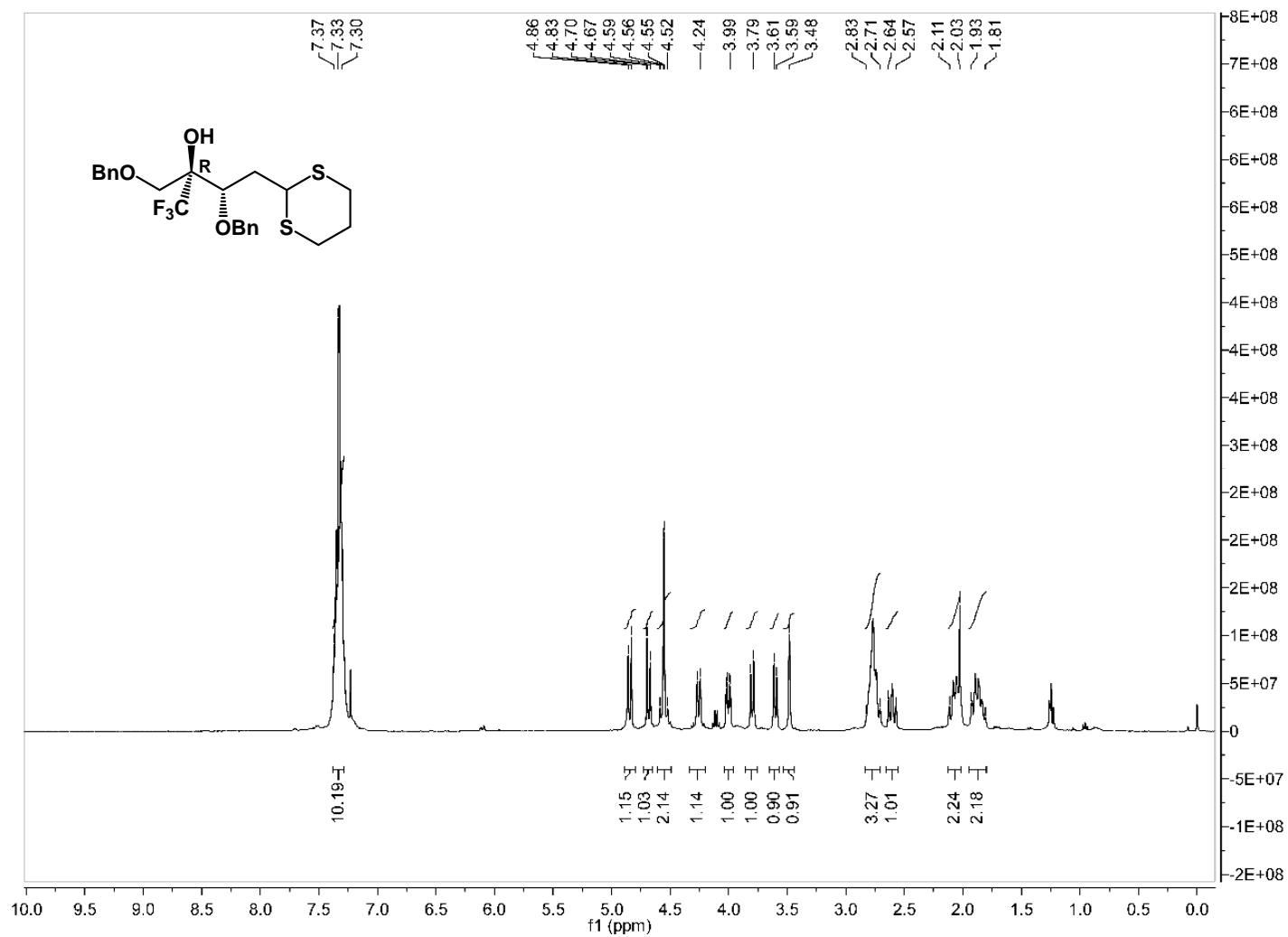
(C) <sup>1</sup>H NMR spectrum of **3b** (in CDCl<sub>3</sub>):



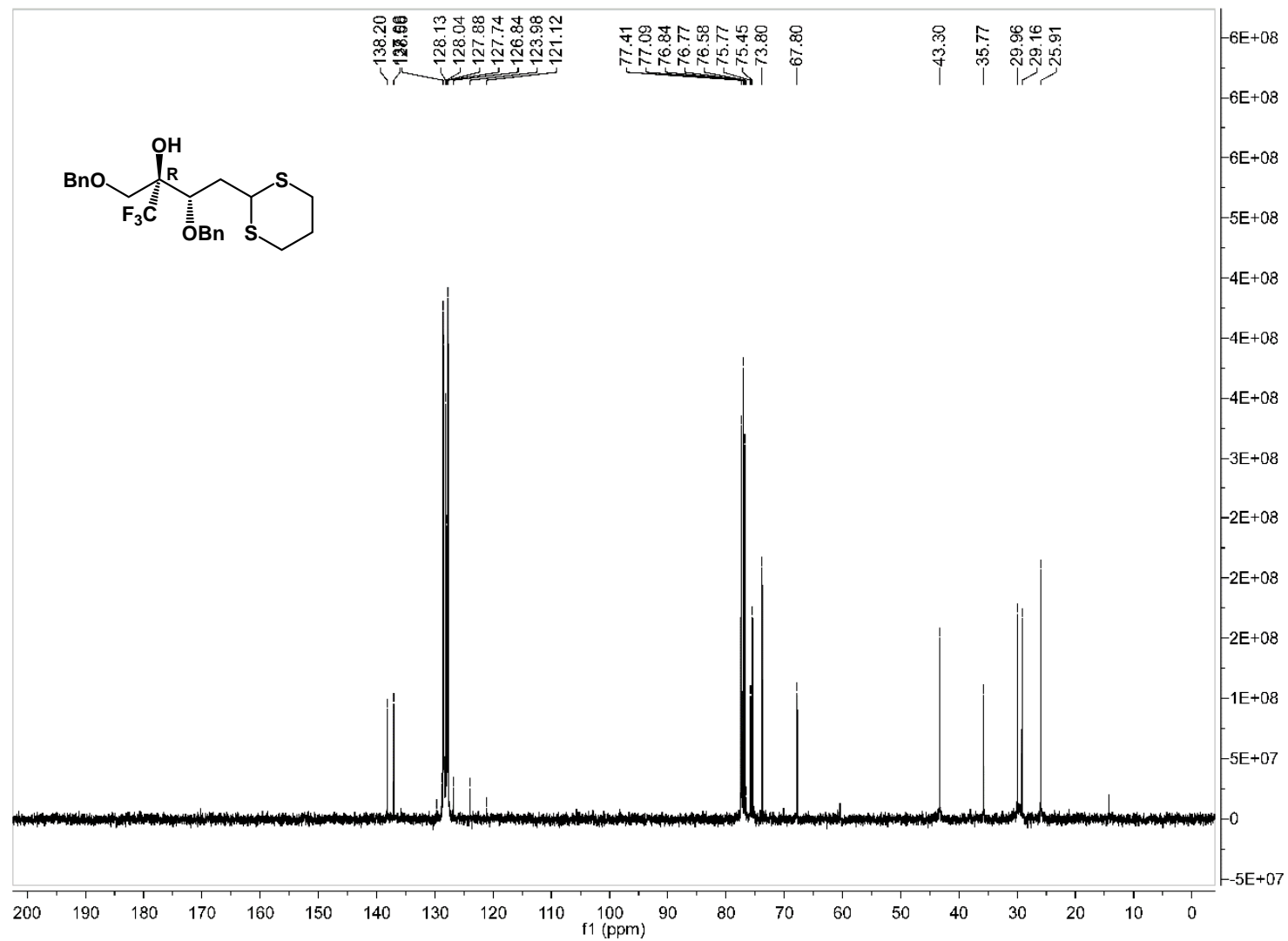
(D)  $^{13}\text{C}$  NMR spectrum of **3b** (in  $\text{CDCl}_3$ ):



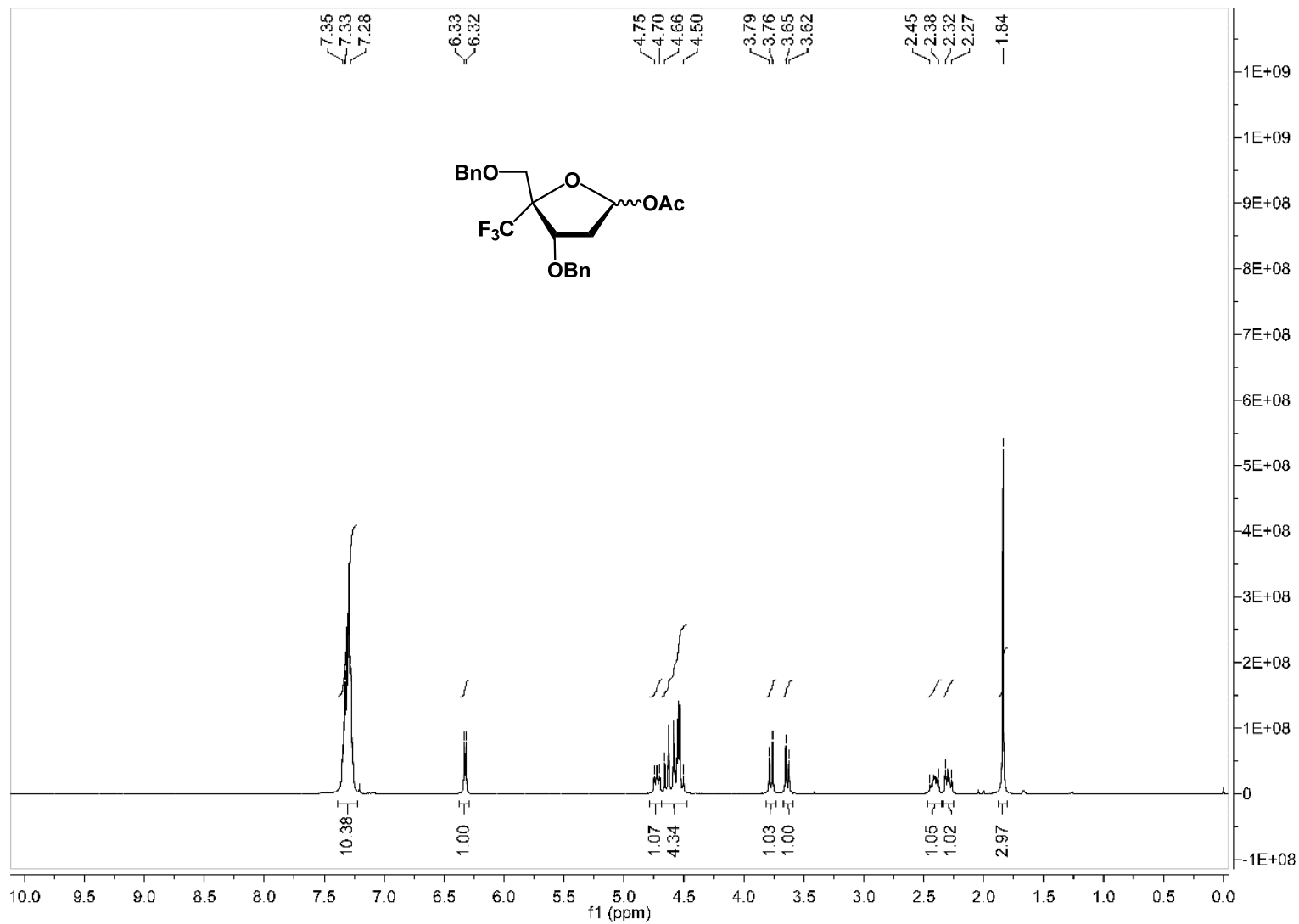
(E)  $^1\text{H}$  NMR spectrum of **3a** (in  $\text{CDCl}_3$ ):



(F)  $^{13}\text{C}$  NMR spectrum of 3a (in  $\text{CDCl}_3$ ):

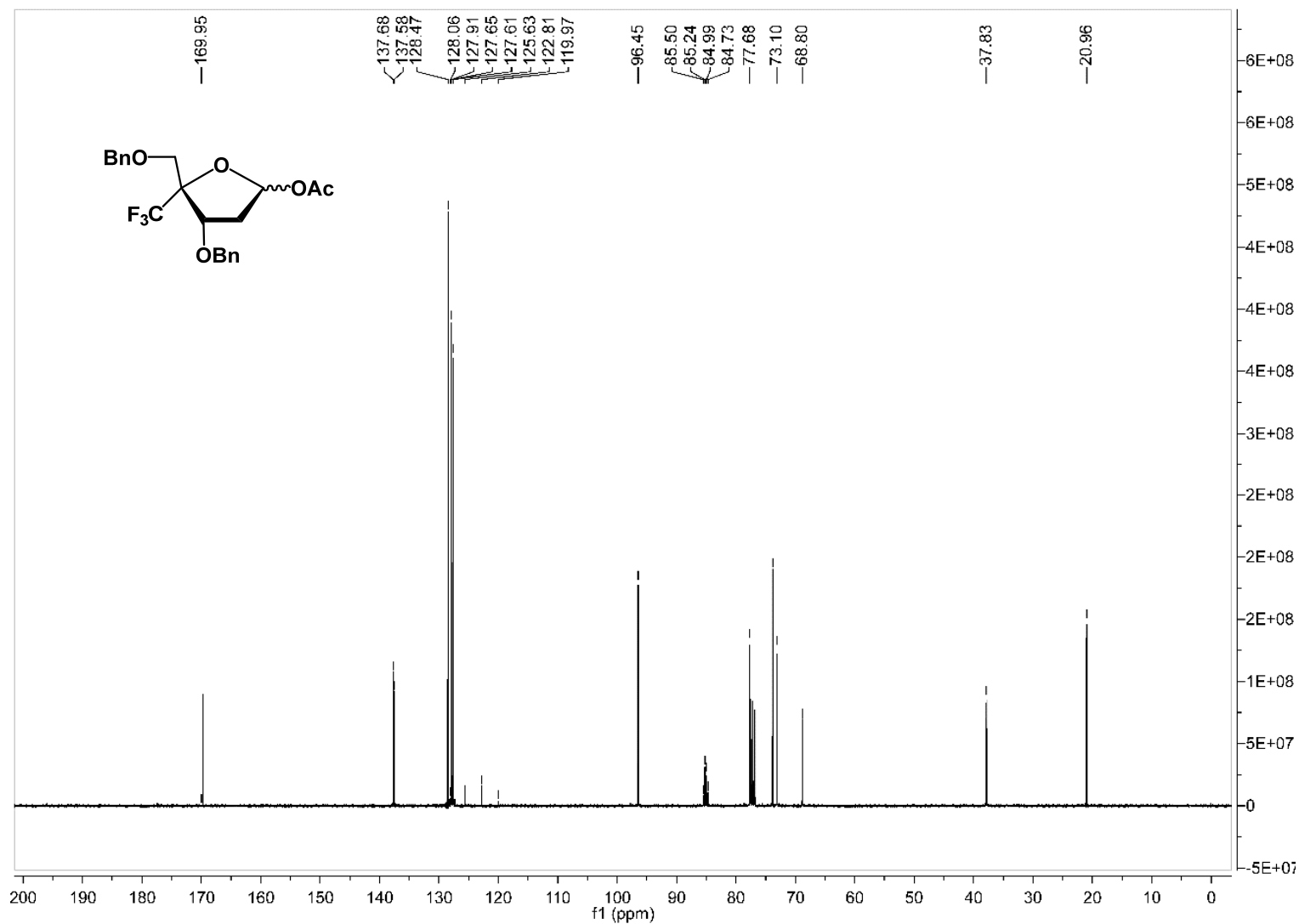


(G)  $^1\text{H}$  NMR spectrum of 4 (in  $\text{CDCl}_3$ ):

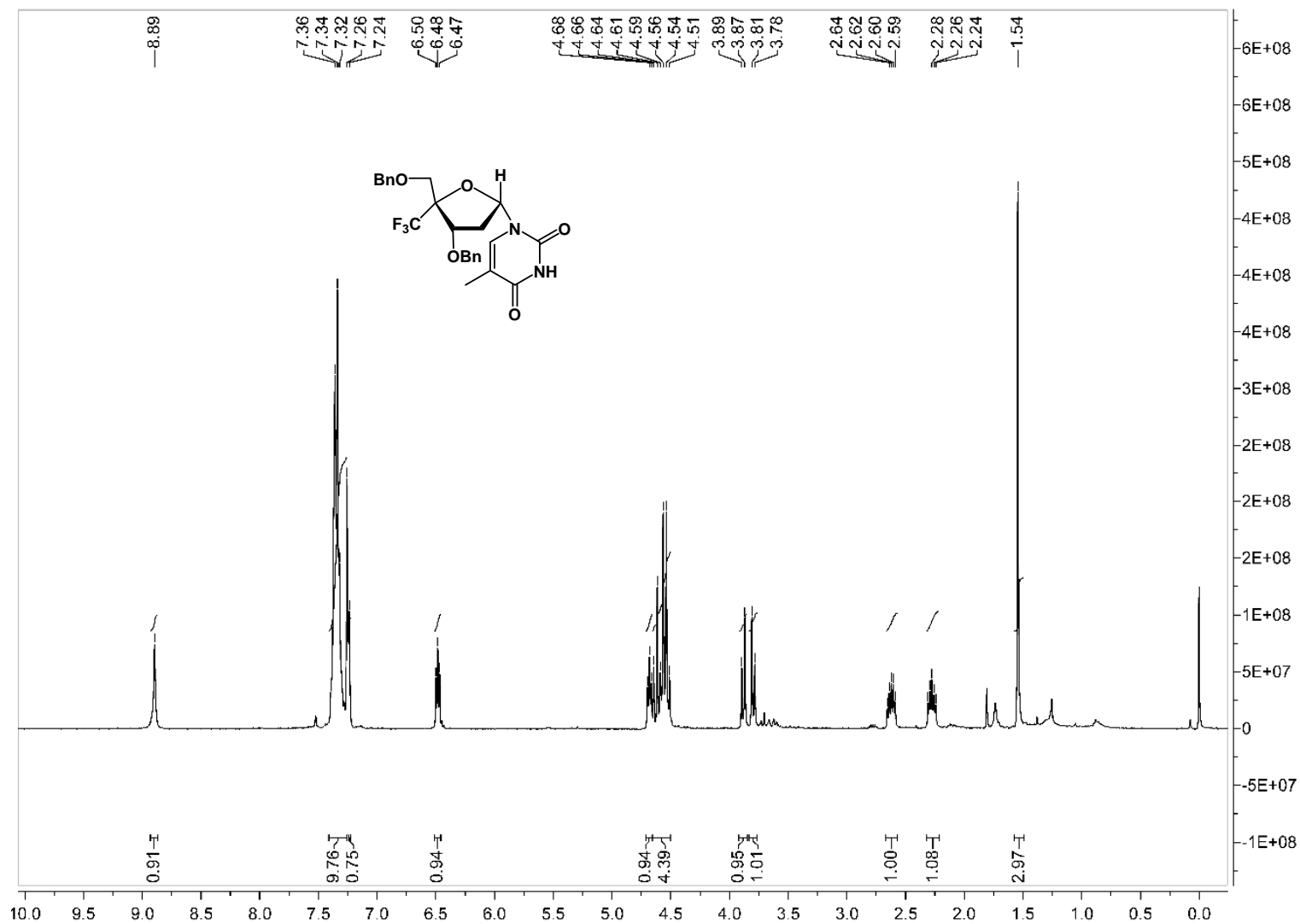




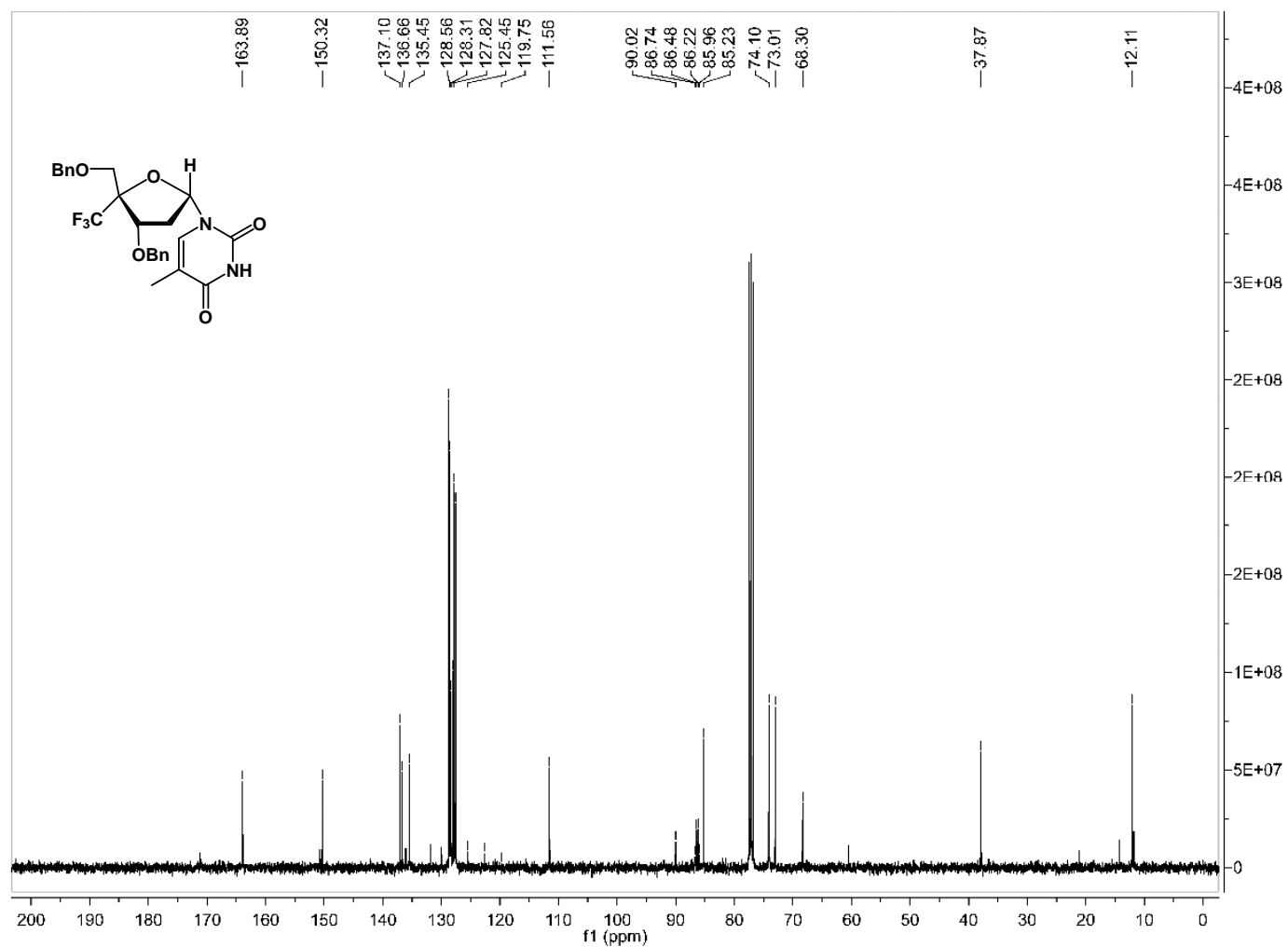
(H)  $^{13}\text{C}$  NMR spectrum of 4 (in  $\text{CDCl}_3$ ):



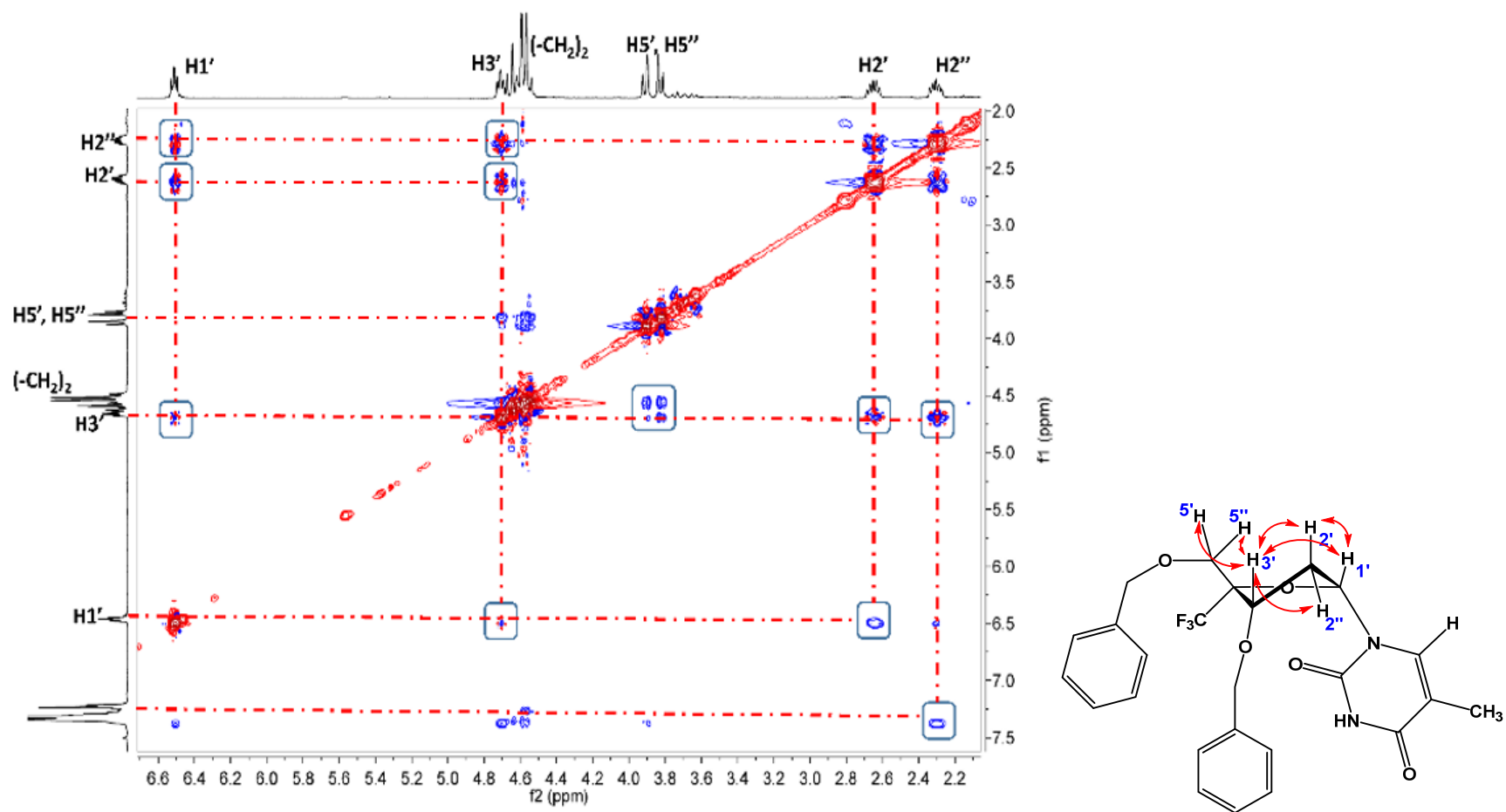
(I)  $^1\text{H}$  NMR spectrum of **5a** (in  $\text{CDCl}_3$ ):



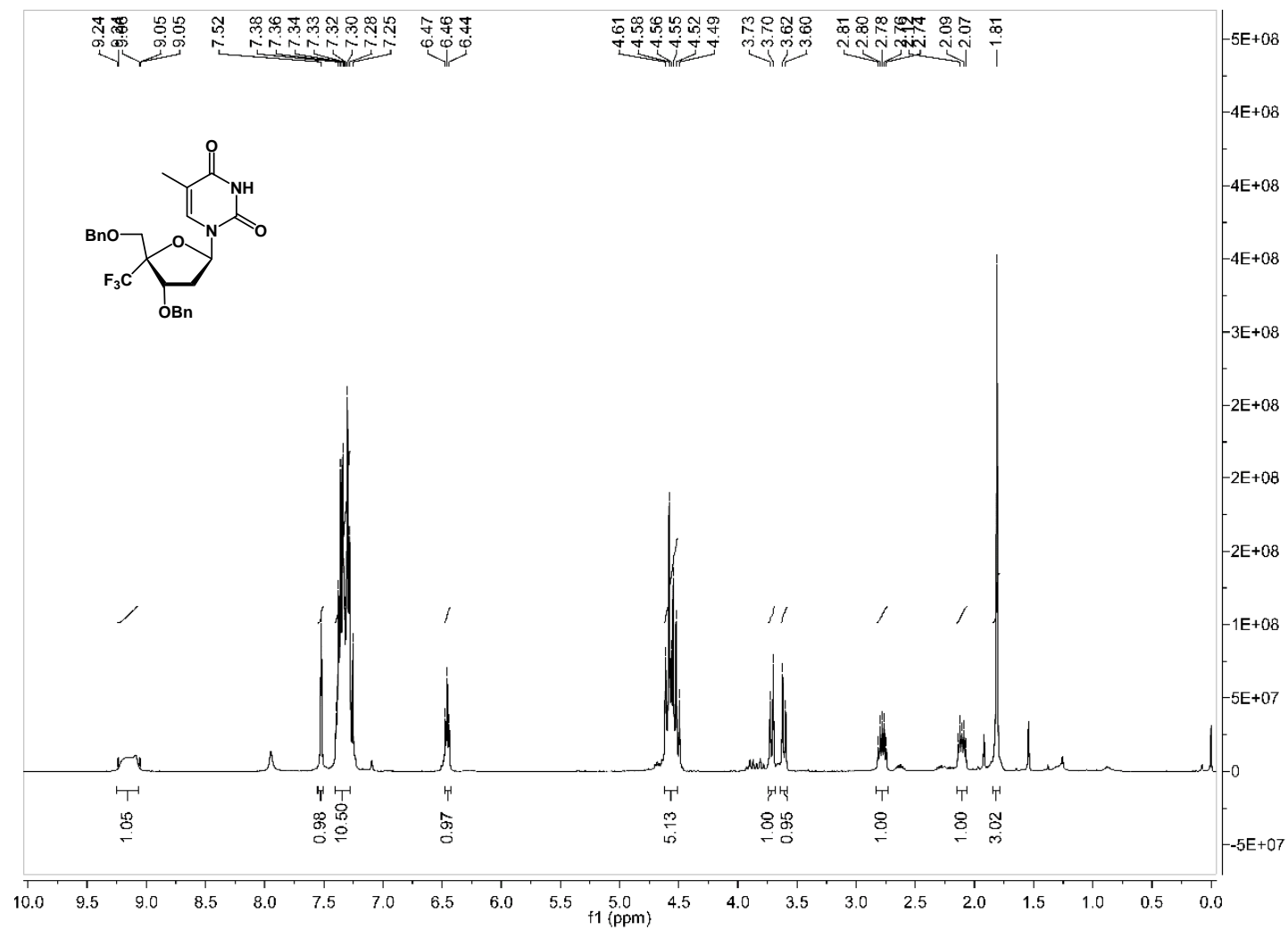
(J)  $^{13}\text{C}$  NMR spectrum of **5a** (in  $\text{CDCl}_3$ ):



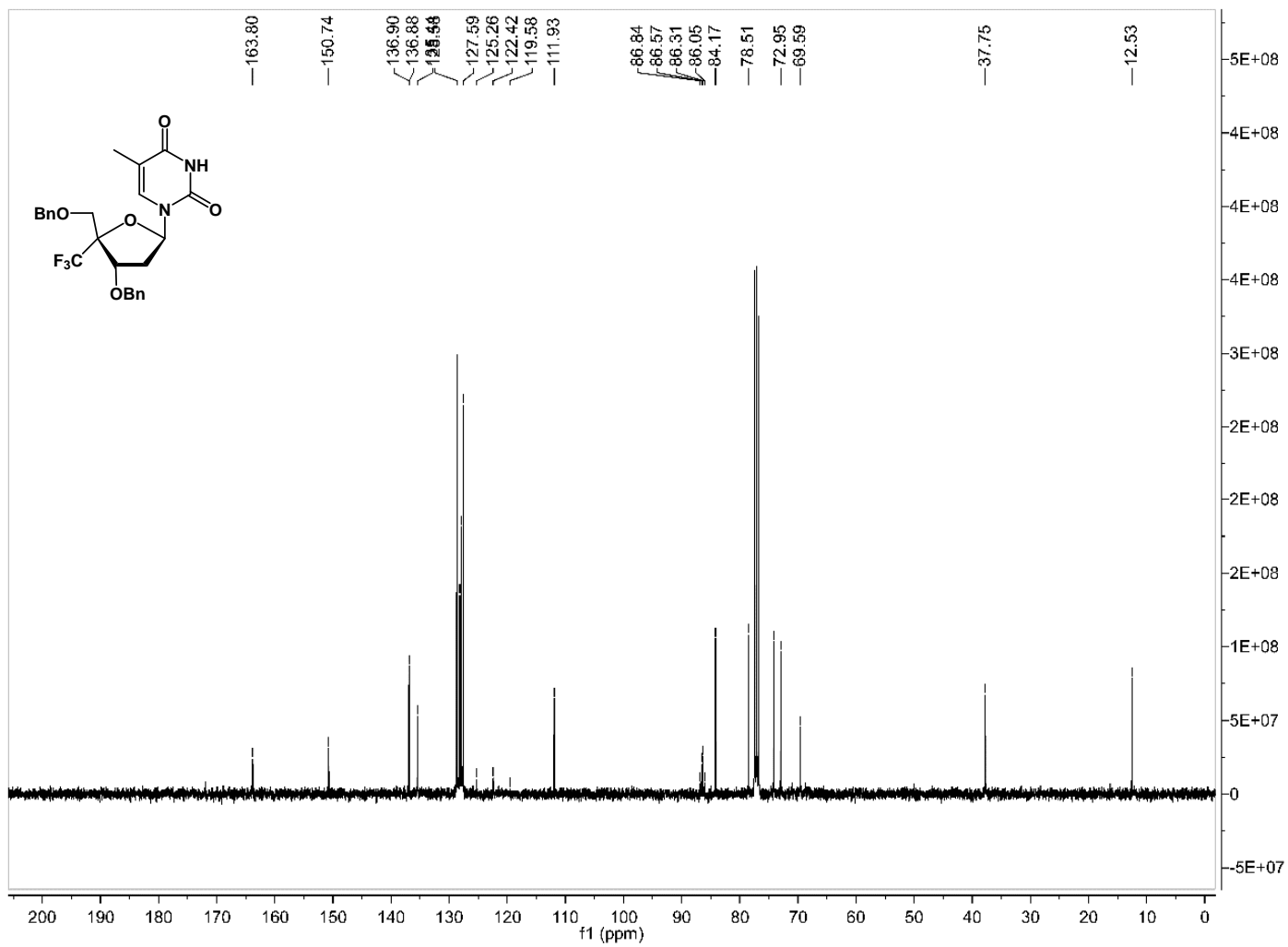
(K) NOESY NMR spectrum of 5a (in CDCl<sub>3</sub>):



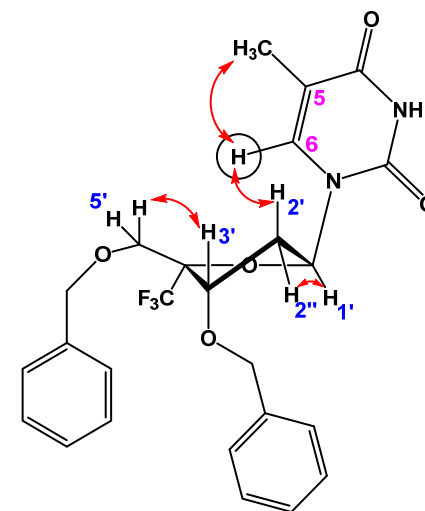
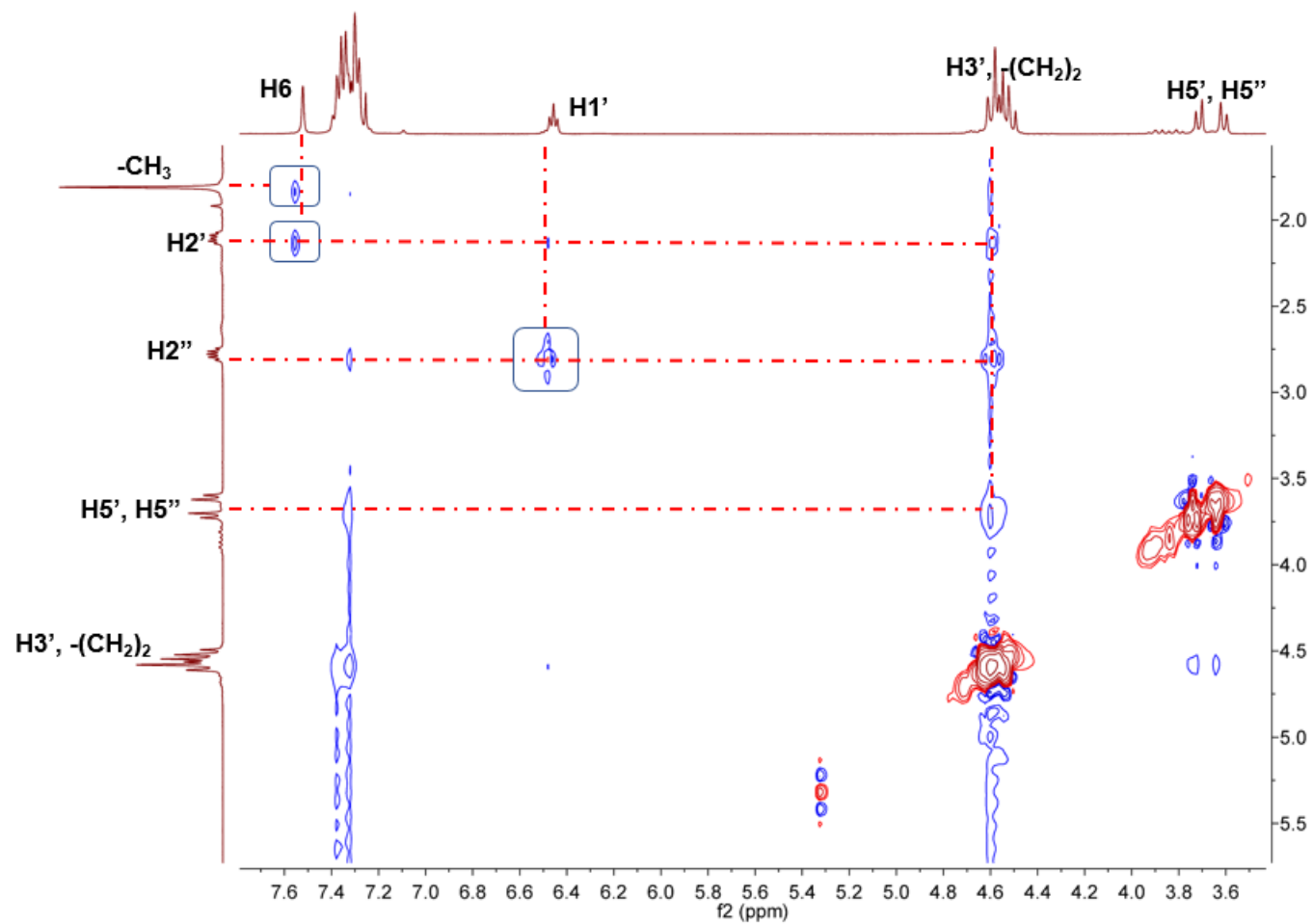
(L) <sup>1</sup>H NMR spectrum of **5b** (in CDCl<sub>3</sub>):



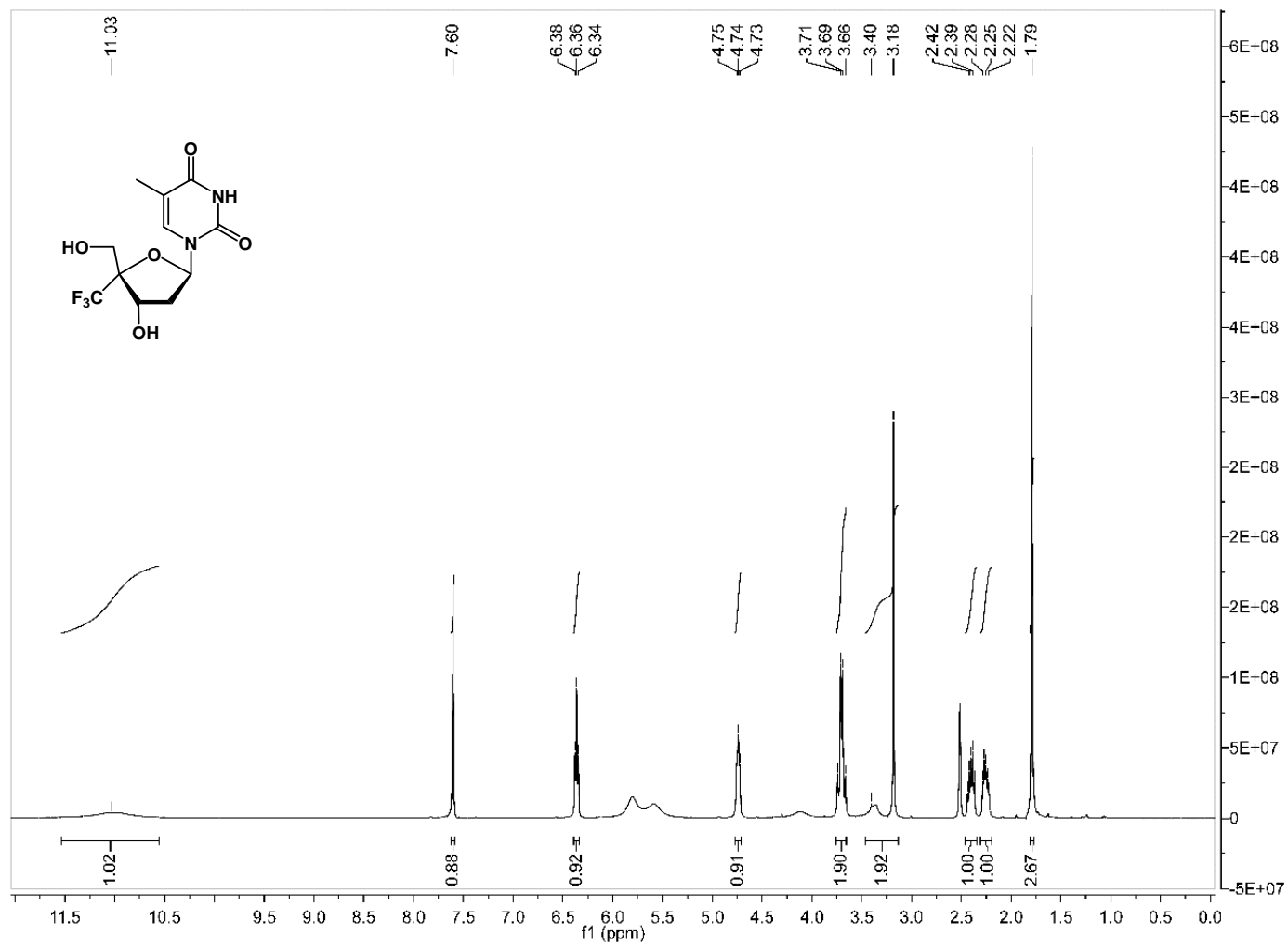
(M)  $^{13}\text{C}$  NMR spectrum of **5b** (in  $\text{CDCl}_3$ ).



(N) NOESY spectrum of **5b** (in CDCl<sub>3</sub>):

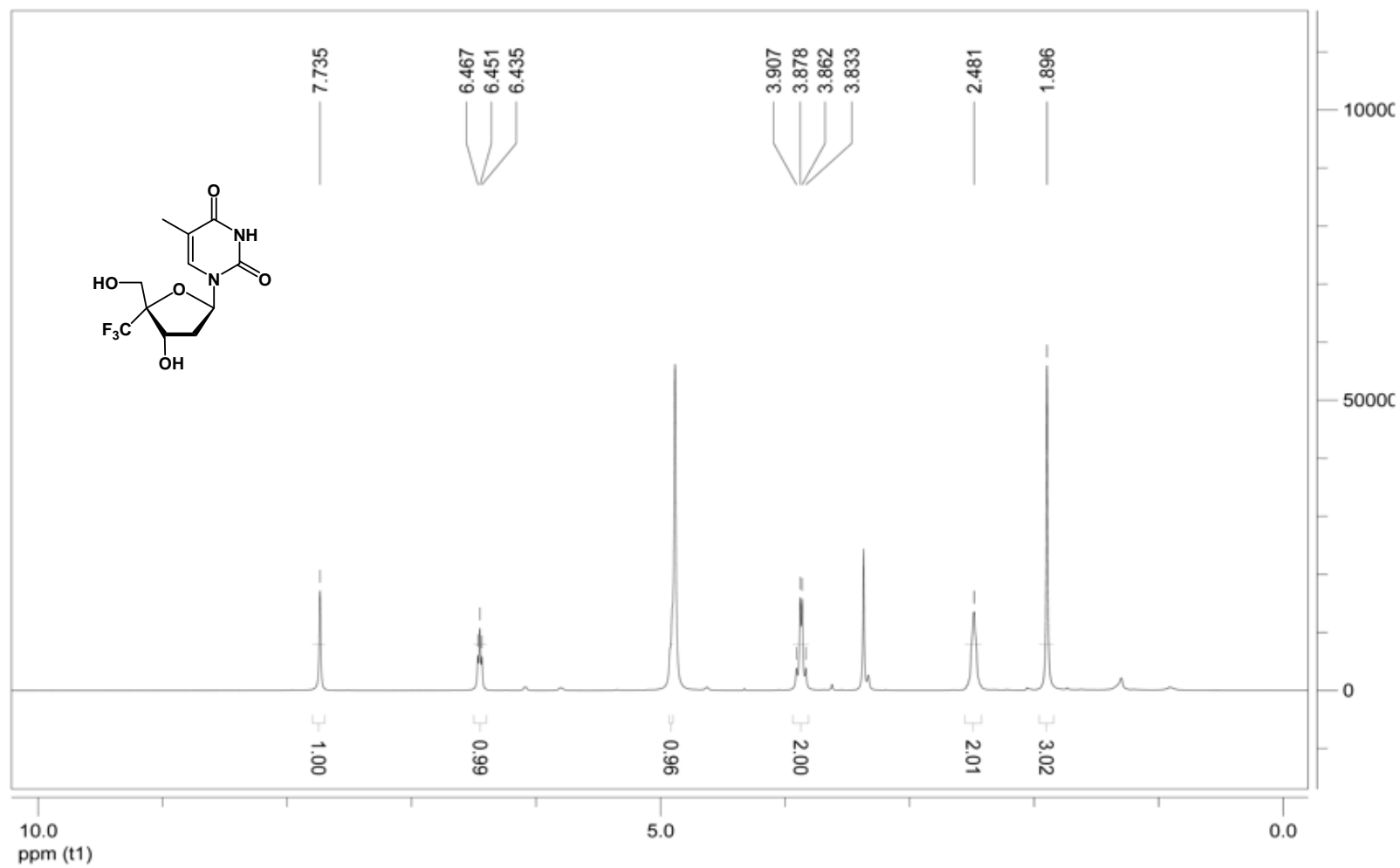


(O)  $^1\text{H}$  NMR spectrum of 6 in  $d_6$ -DMSO:

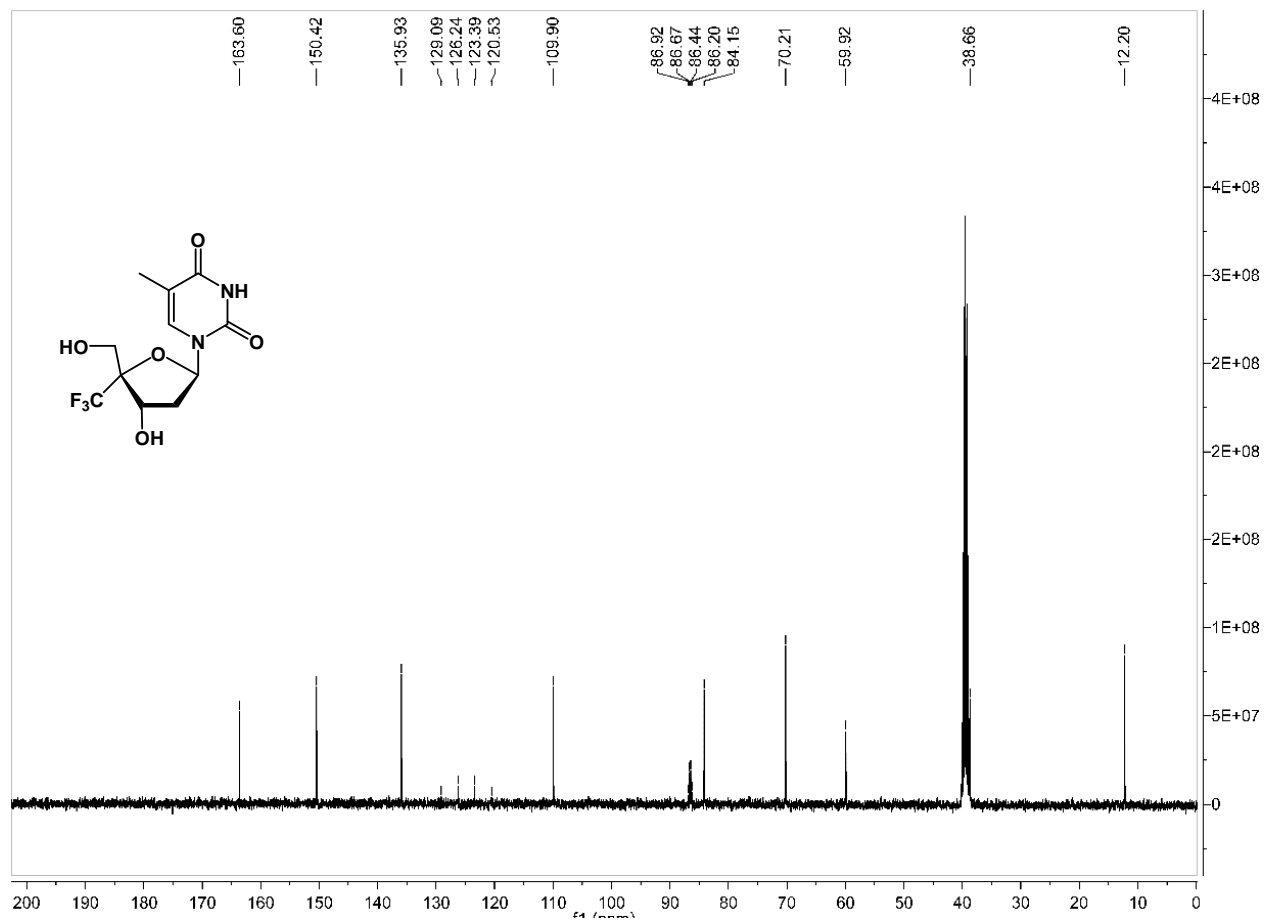




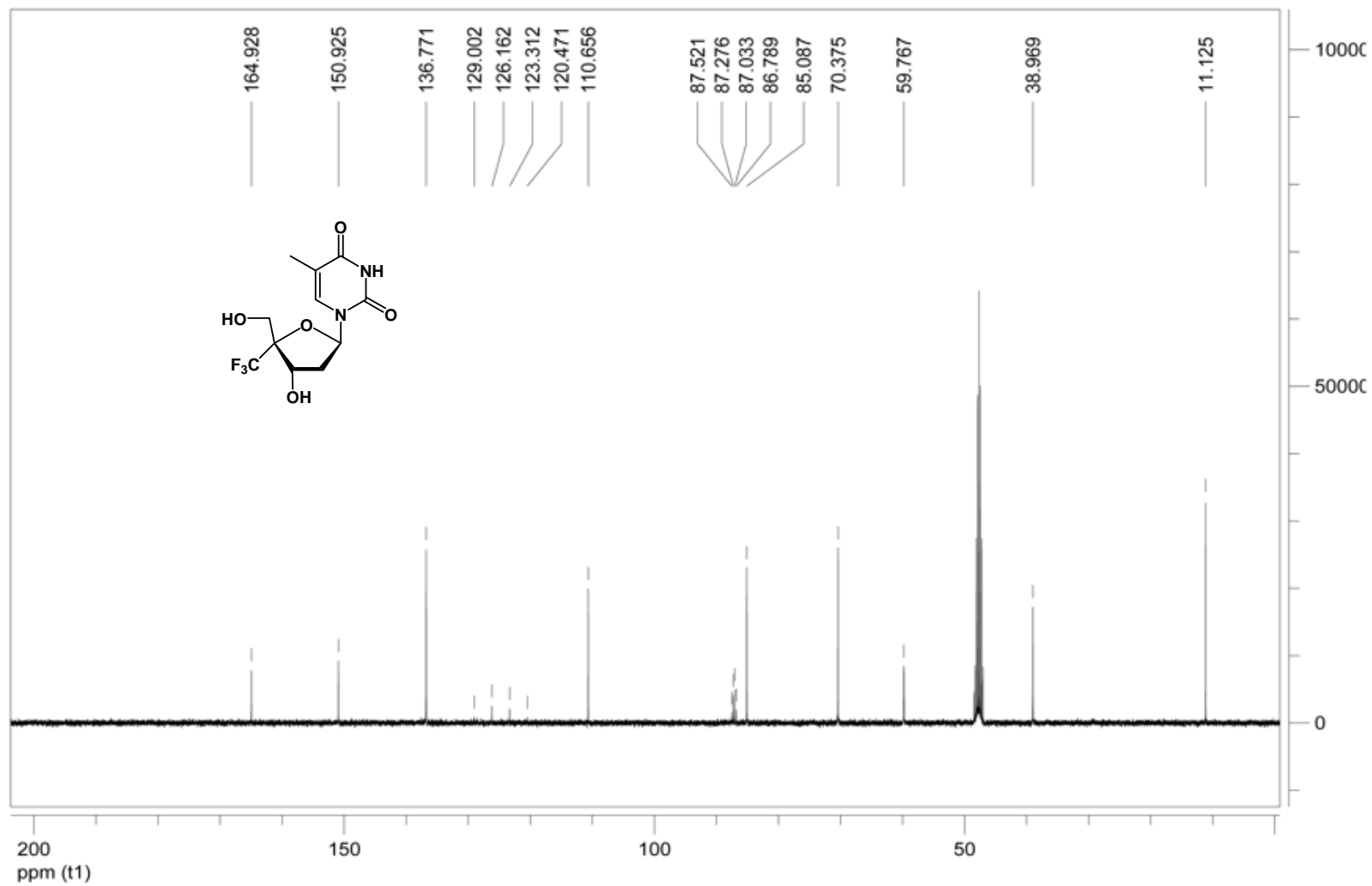
<sup>1</sup>H NMR spectrum of 6 in CD<sub>3</sub>OD:



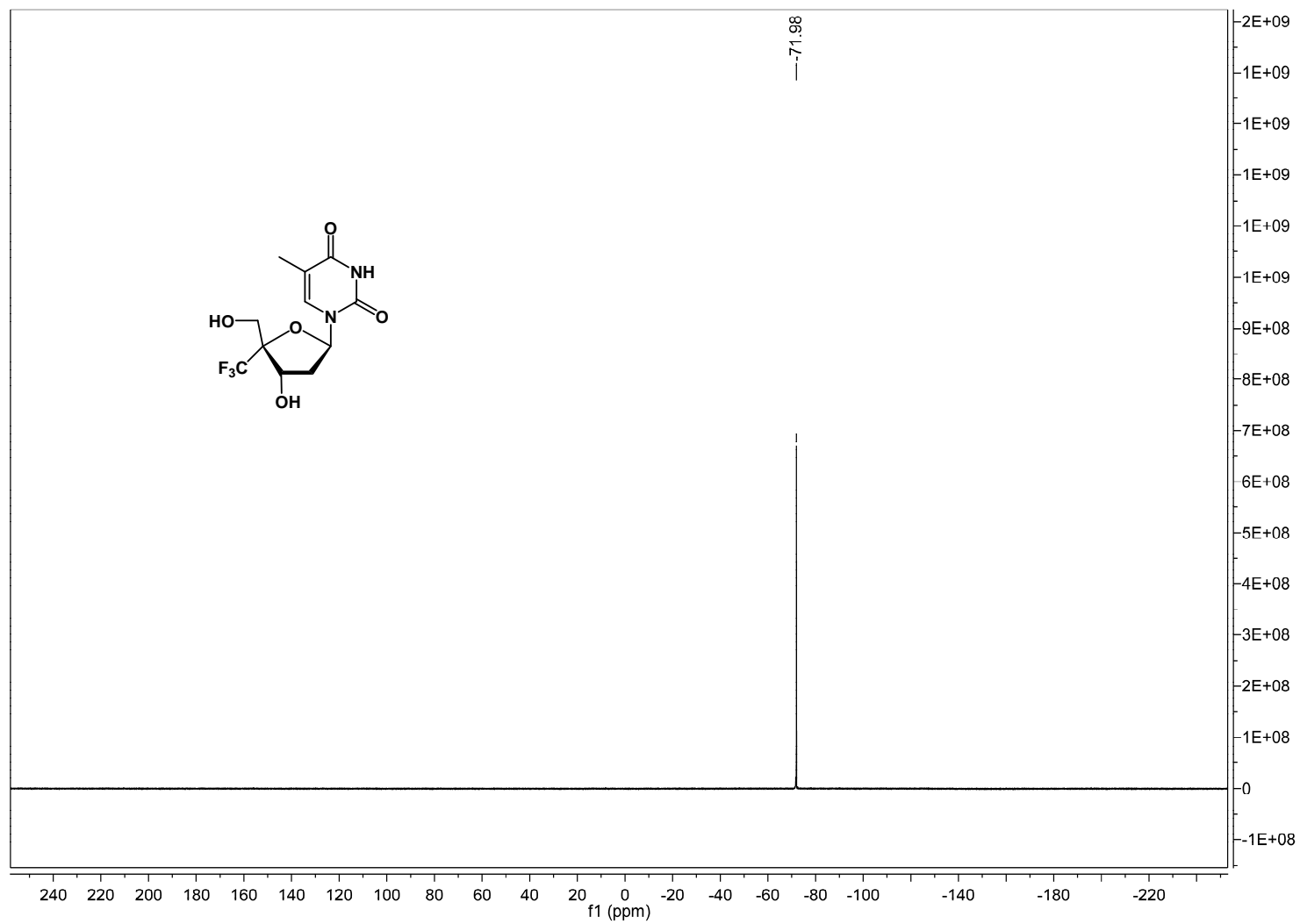
(P)  $^{13}\text{C}$  NMR spectrum of 6 in  $d_6$ -DMSO:



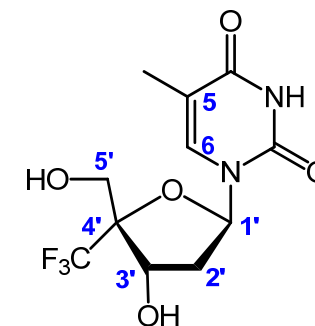
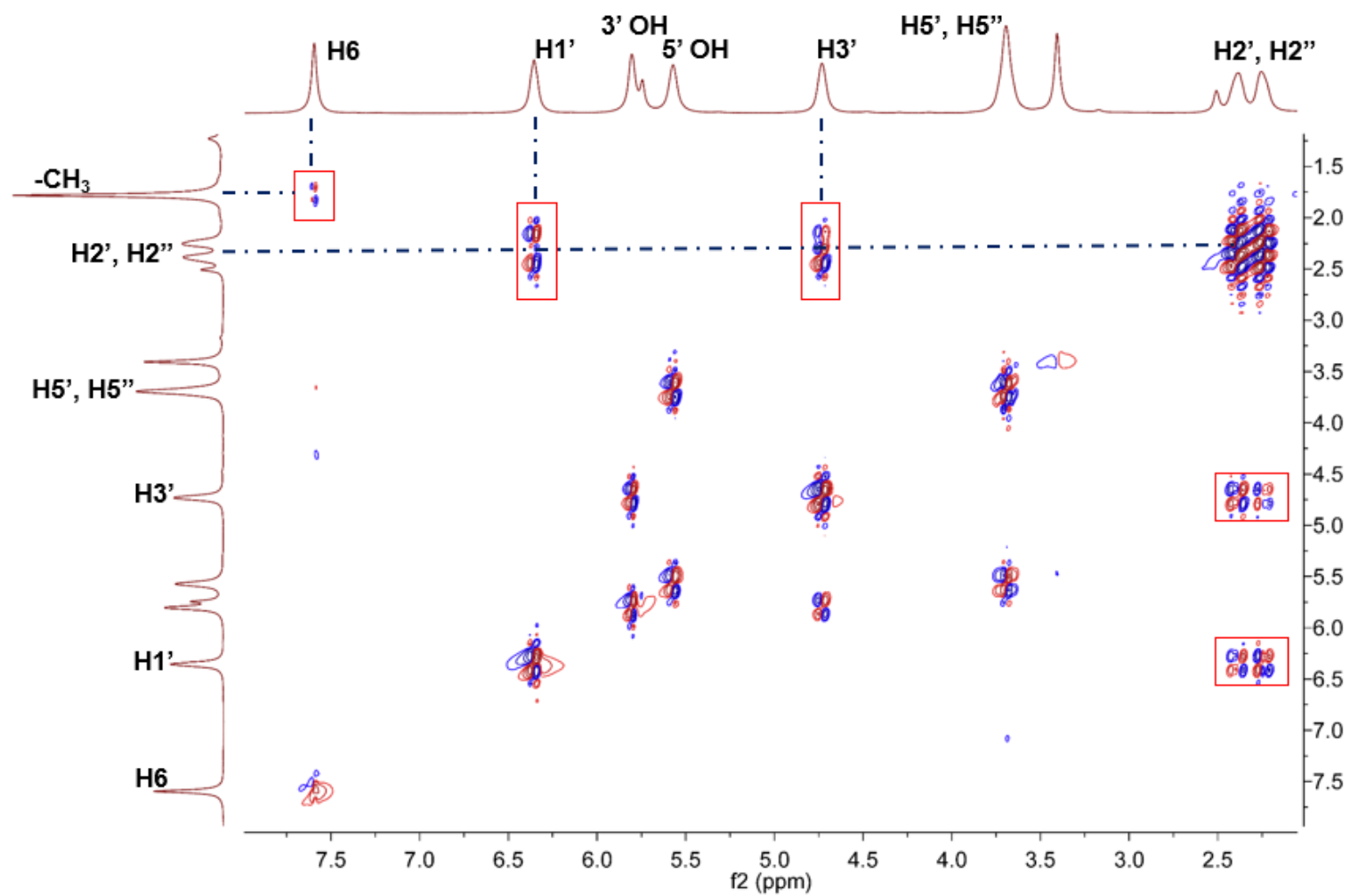
<sup>13</sup>C NMR spectrum of 6 in CD<sub>3</sub>OD:



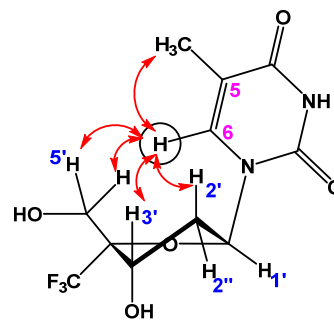
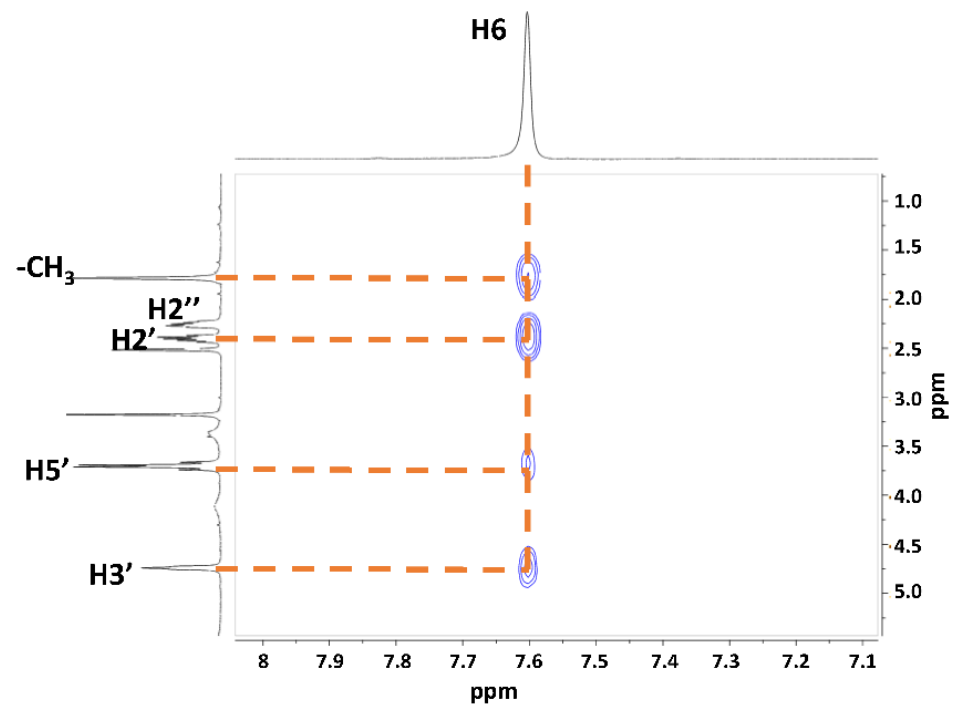
(Q)  $^{19}\text{F}$  NMR spectrum of 6 (in  $d_6$ -DMSO):



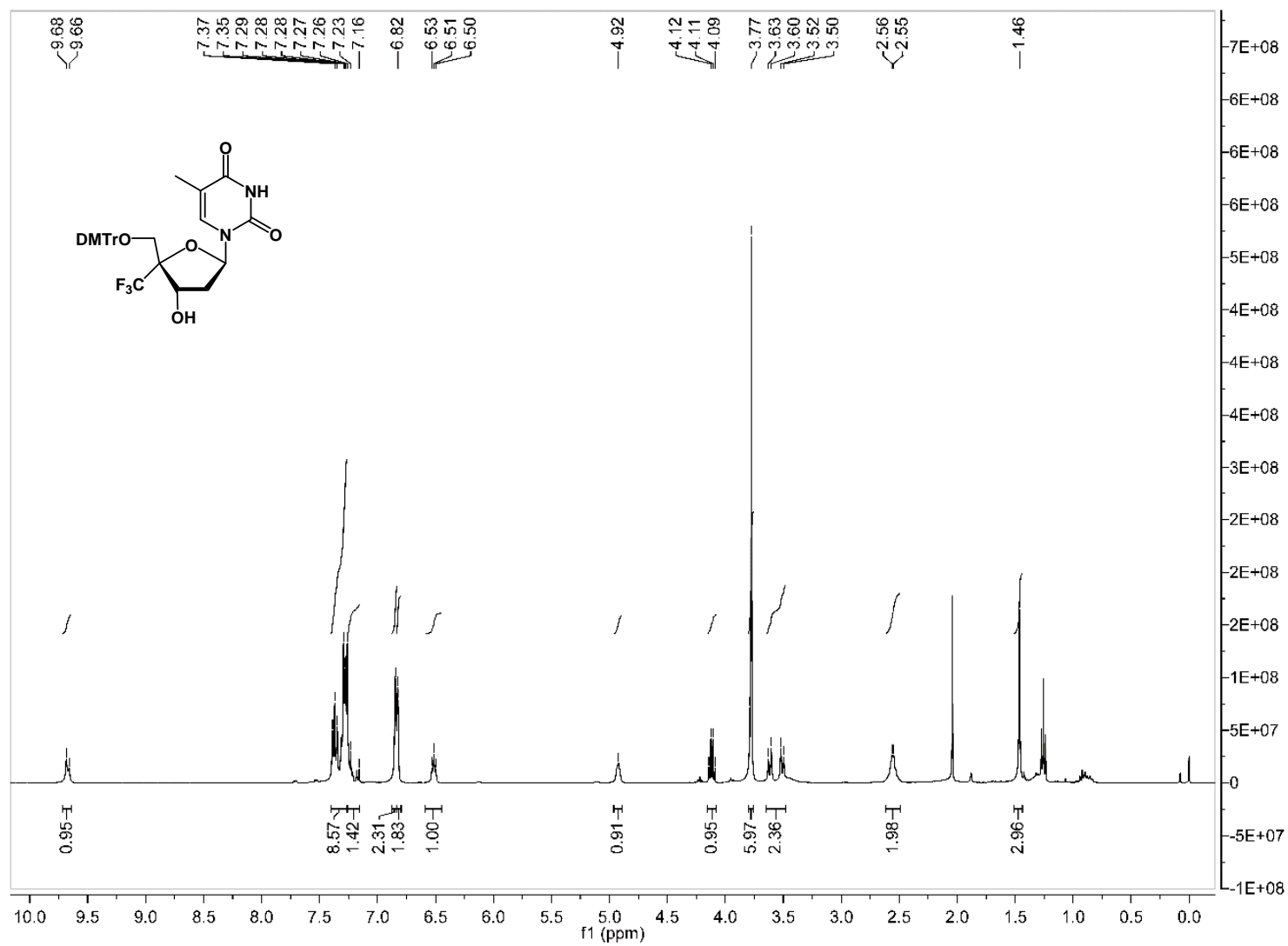
(R) COSY NMR spectrum of 6 (in  $d_6$ -DMSO):



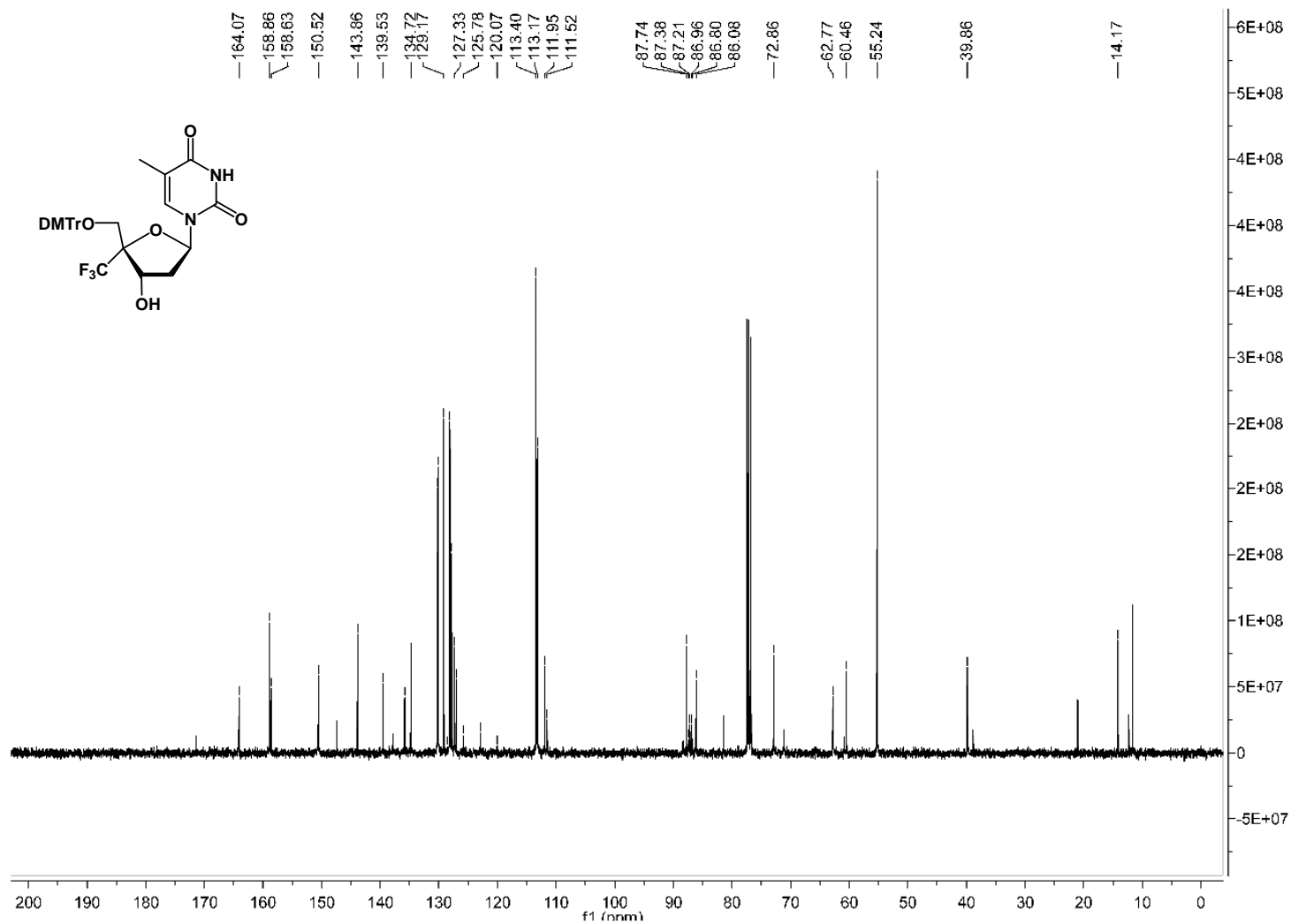
(S) NOESY NMR spectrum of 6 (in  $d_6$ -DMSO):



(T)  $^1\text{H}$  NMR spectrum of 7 (in  $\text{CDCl}_3$ ):

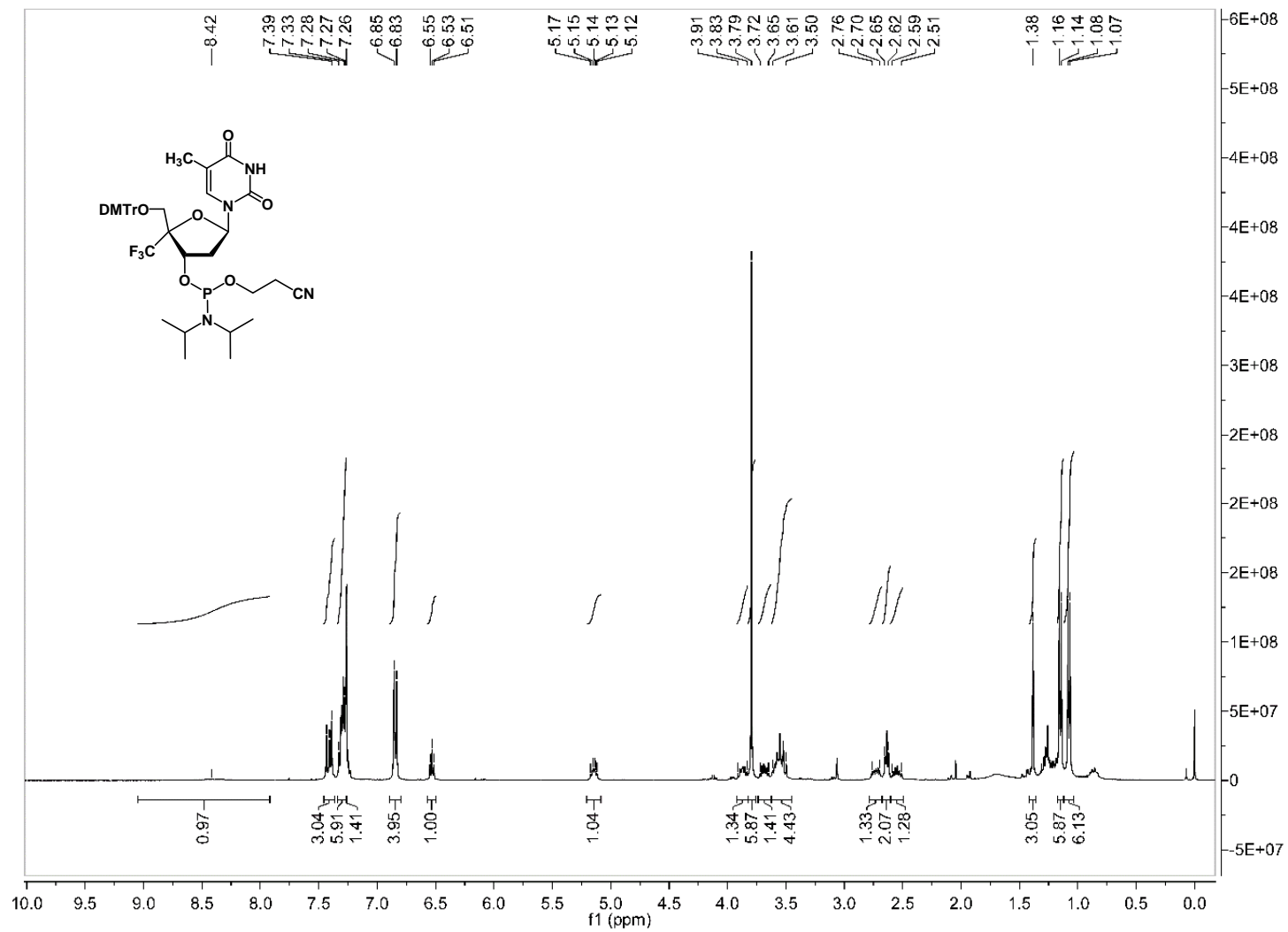


(U)  $^{13}\text{C}$  NMR spectrum of 7 (in  $\text{CDCl}_3$ ):

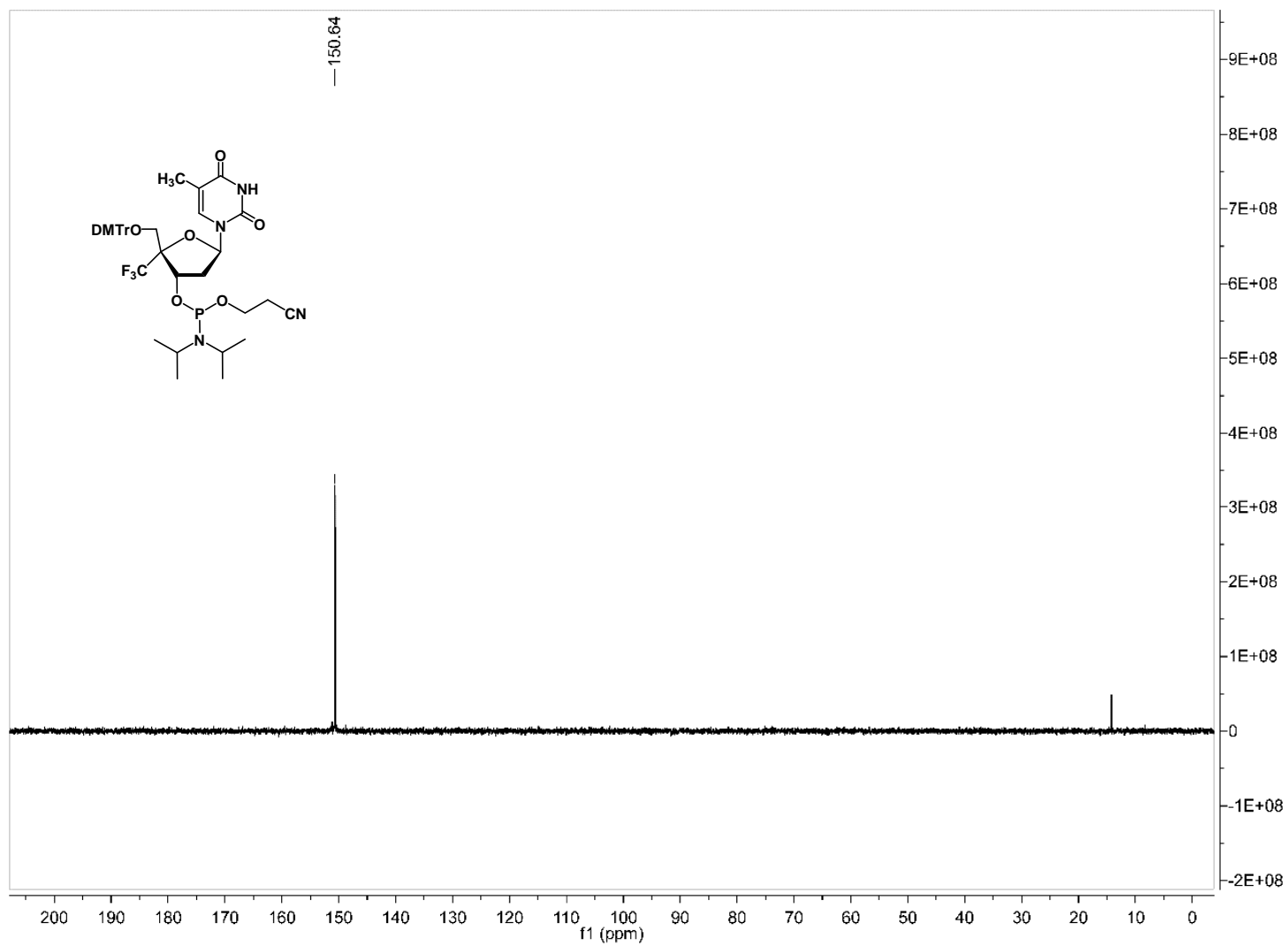




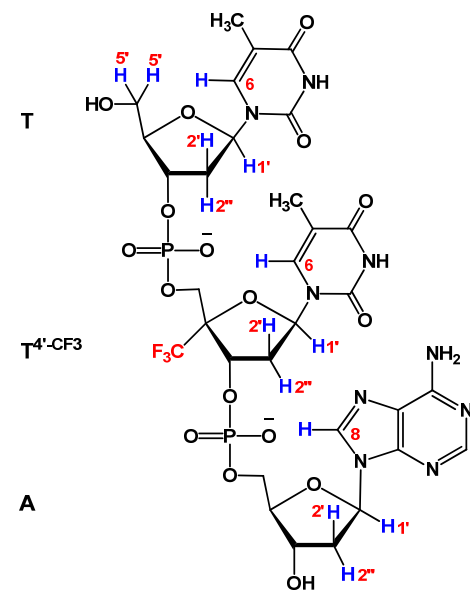
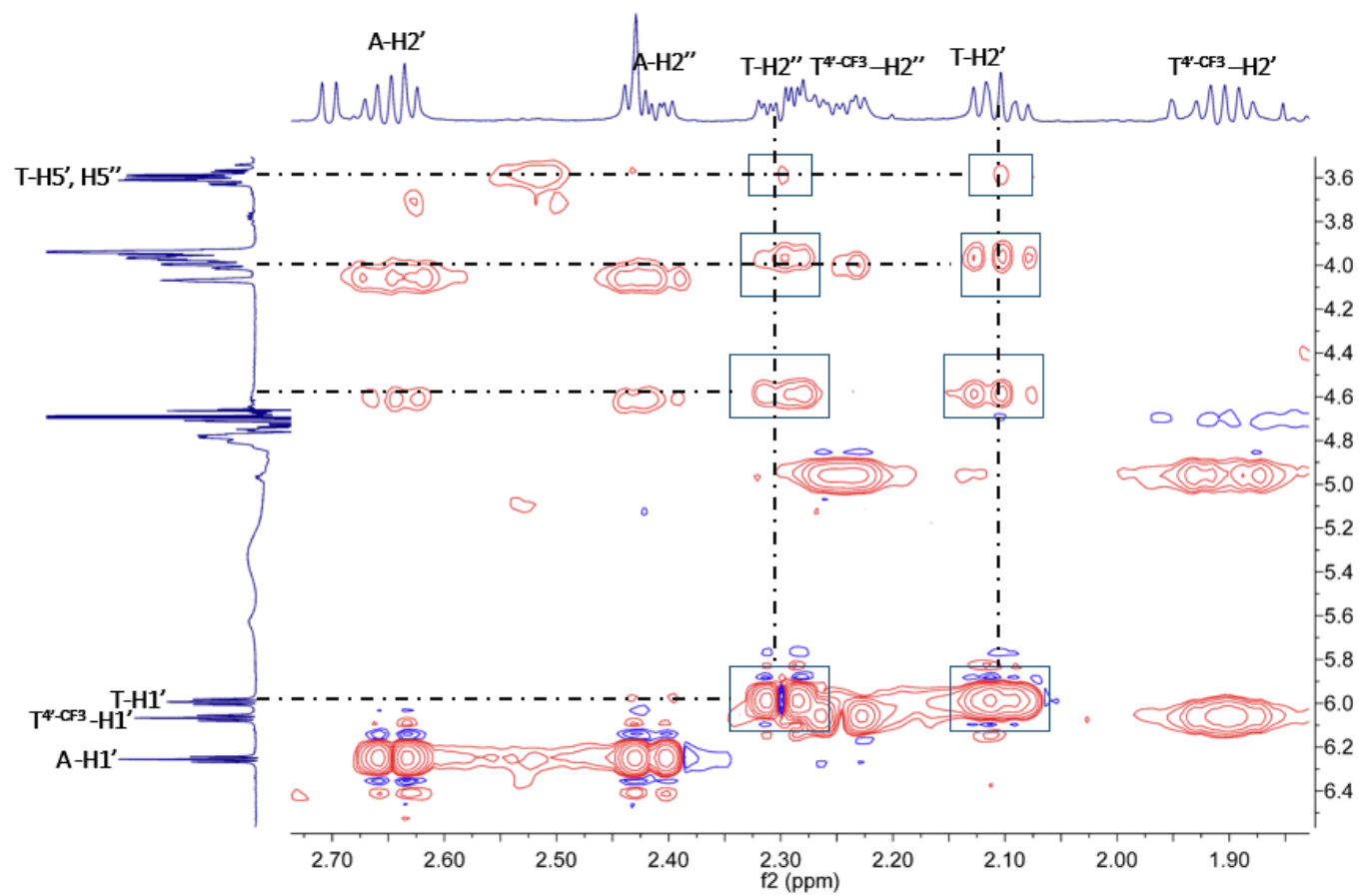
(V)  $^1\text{H}$  NMR spectrum of **8** (in  $\text{CDCl}_3$ ):



(W)  $^{31}\text{P}$  NMR spectrum of **8** (in  $\text{CDCl}_3$ ):



(X) 2D TOSCY NMR of oligo 5'-d[TT<sup>4'-CF3</sup>A] (600 MHz, 0.6 mM of oligo in 10% D<sub>2</sub>O/H<sub>2</sub>O).



(Y) 2D NOESY NMR of oligo 5'-d[TT<sup>4'-CF3</sup>A] (600 MHz, 0.6 mM of oligo in 10% D<sub>2</sub>O/H<sub>2</sub>O).

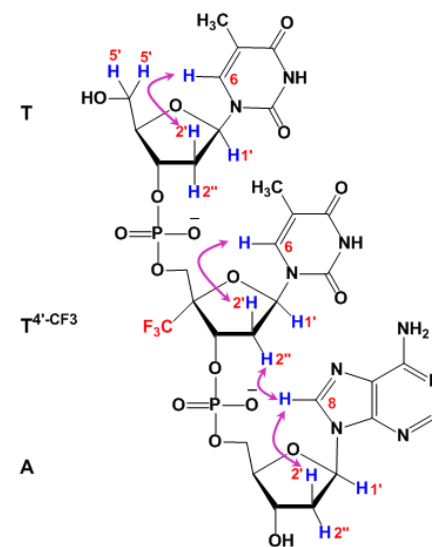
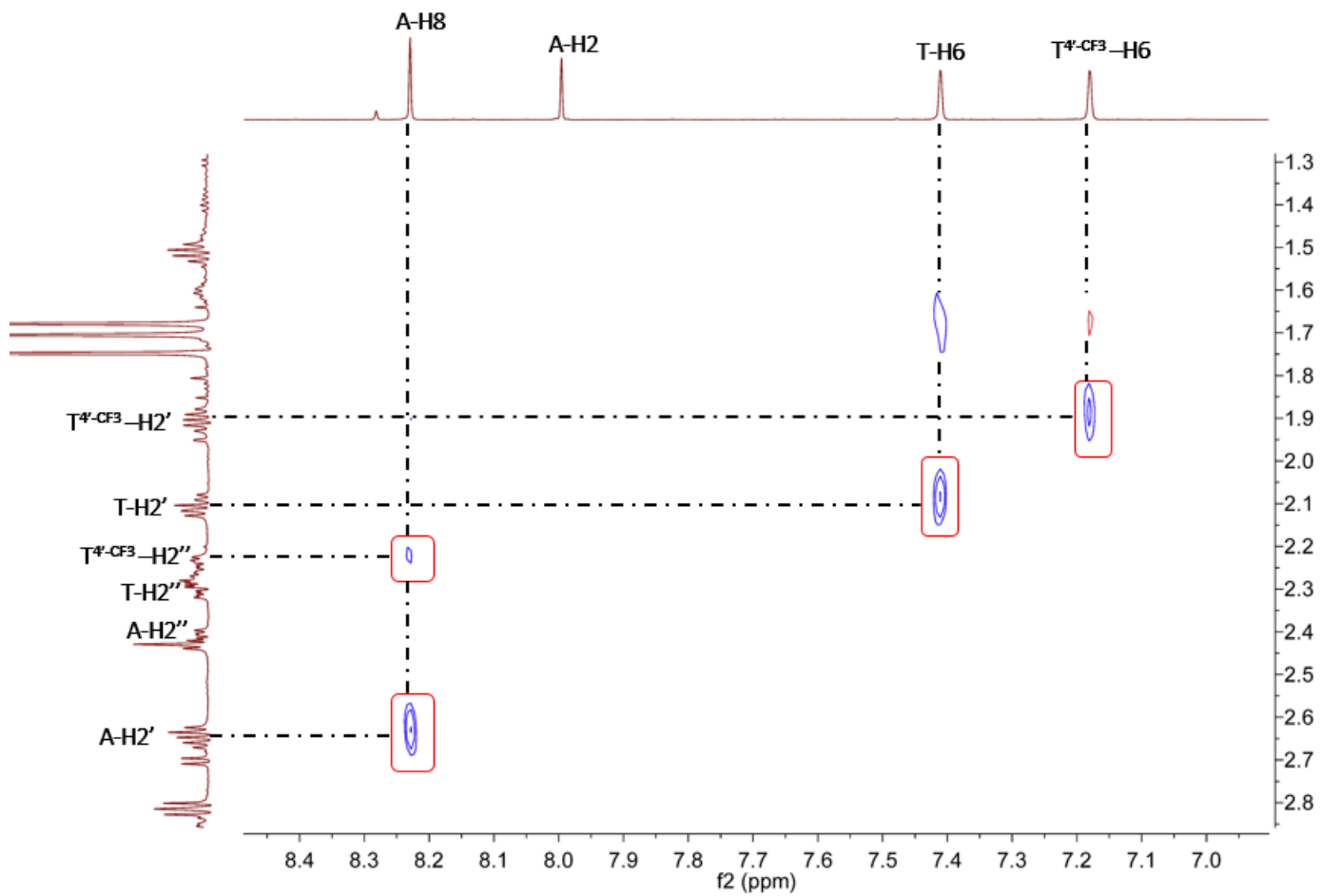
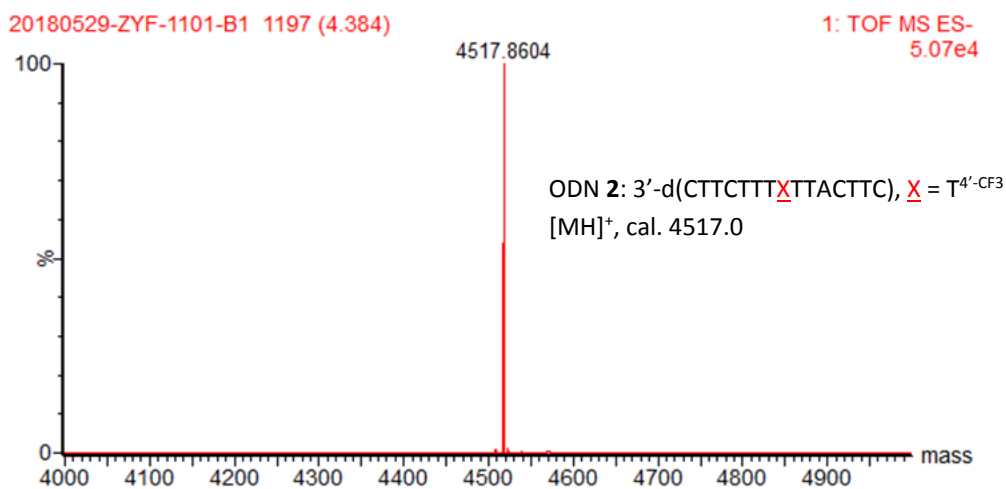
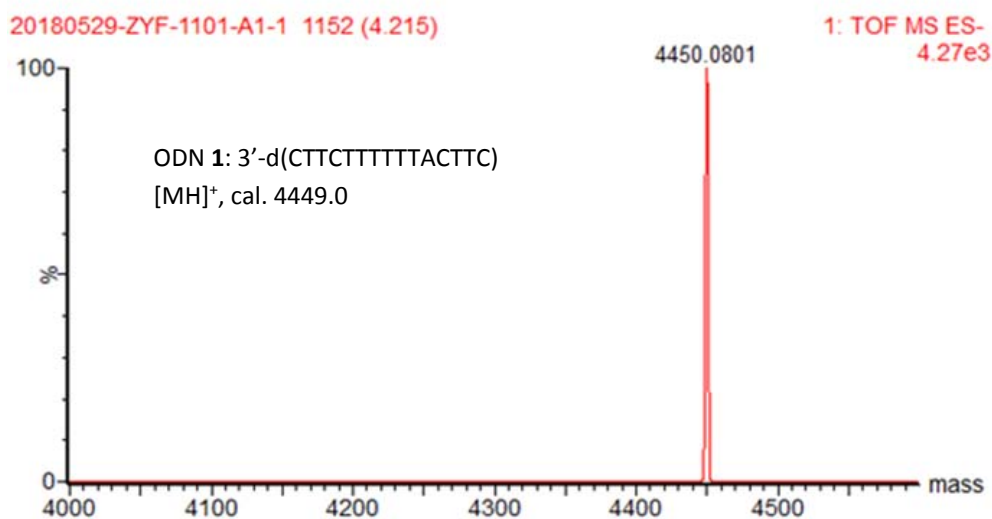
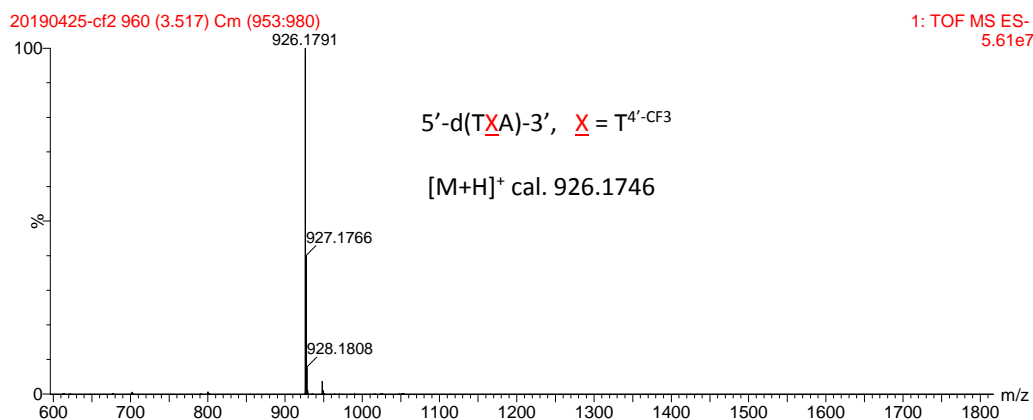
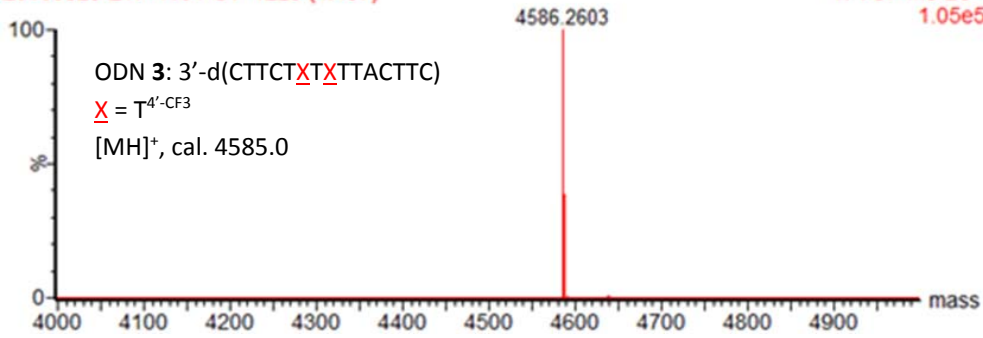


Figure S2. MS spectra of oligos.



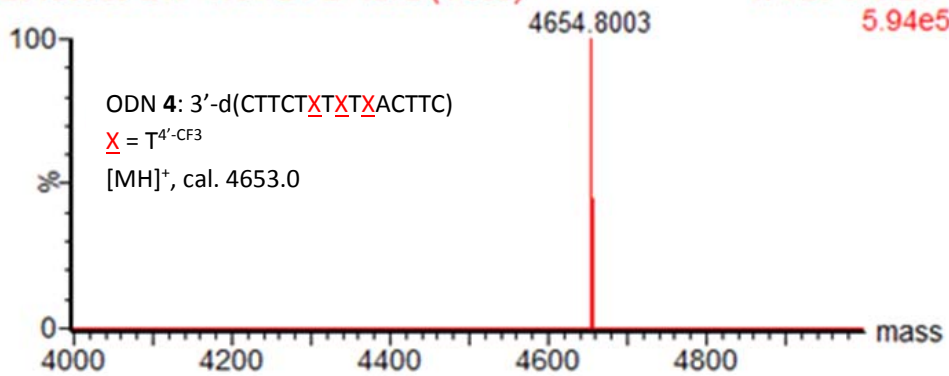
20180529-ZYF-1101-C1 1229 (4.497)

1: TOF MS ES-  
1.05e5



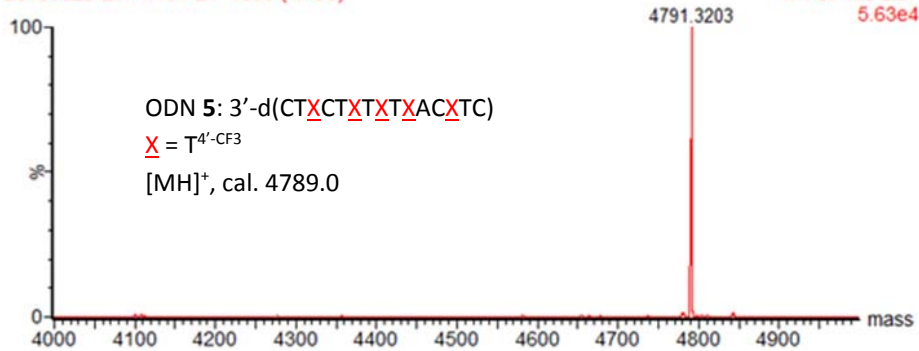
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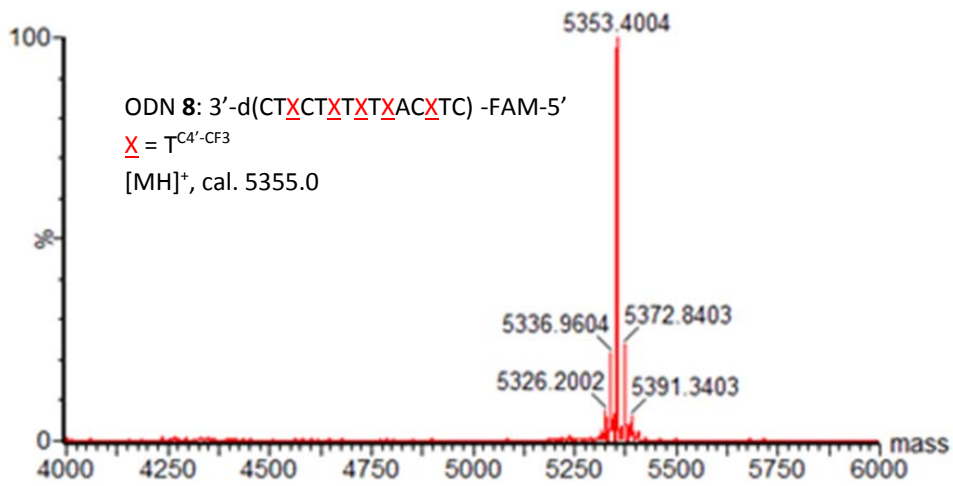
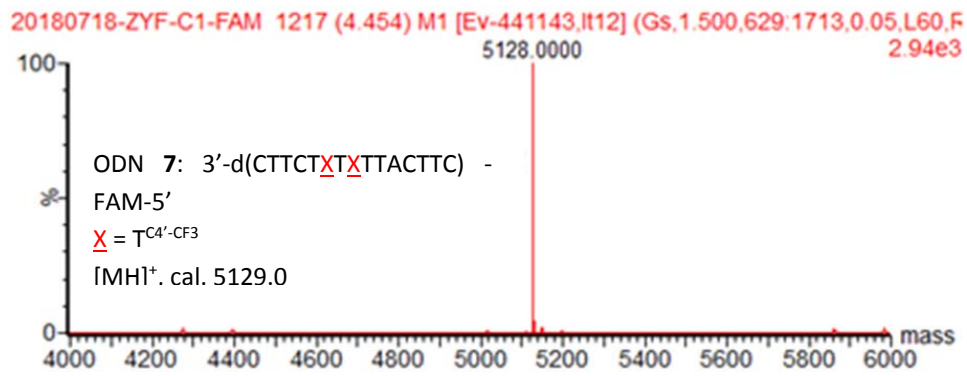
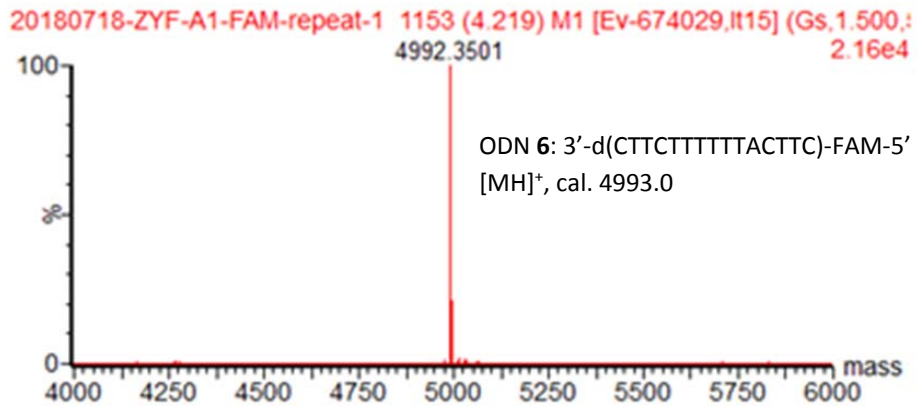
1: TOF MS ES-  
5.94e5

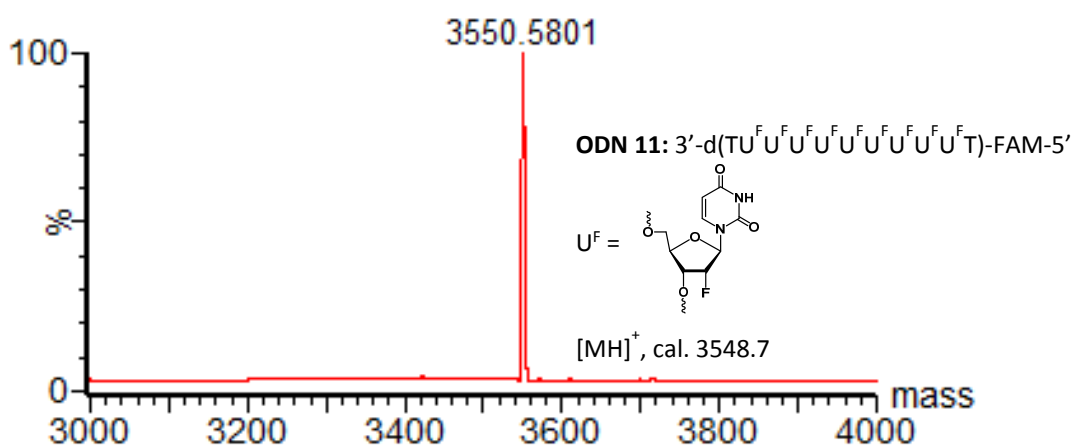
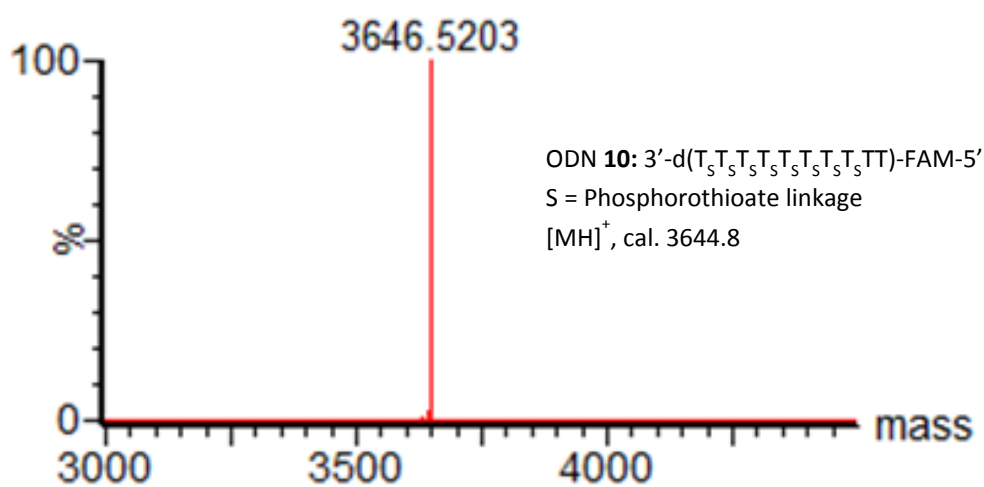
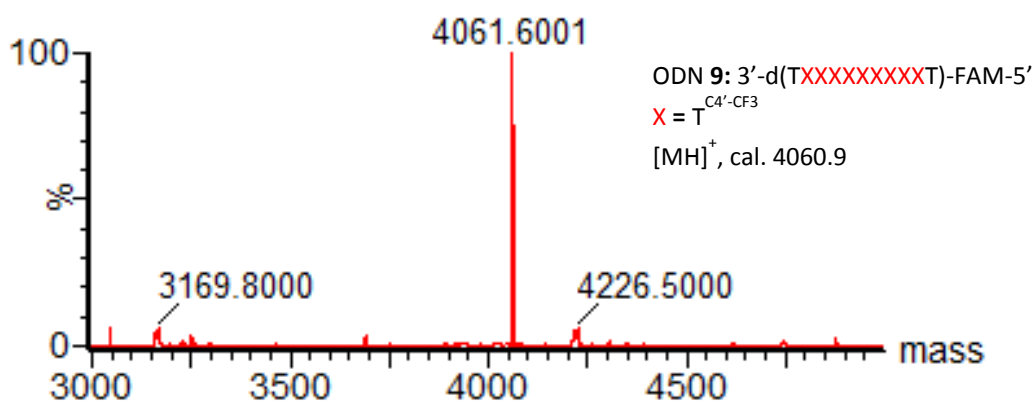


20180529-ZYF-1101-E1 1309 (4.790)

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5.63e4

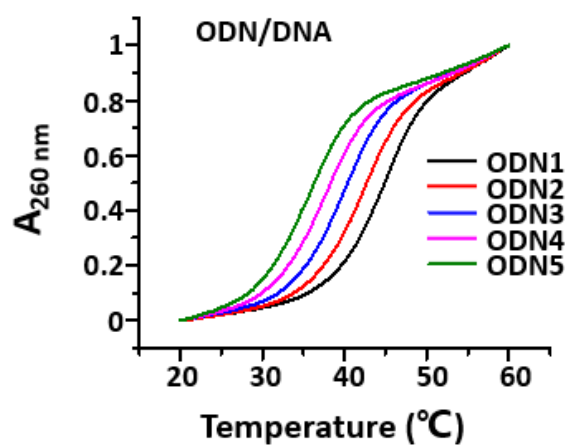








(A)



(B)

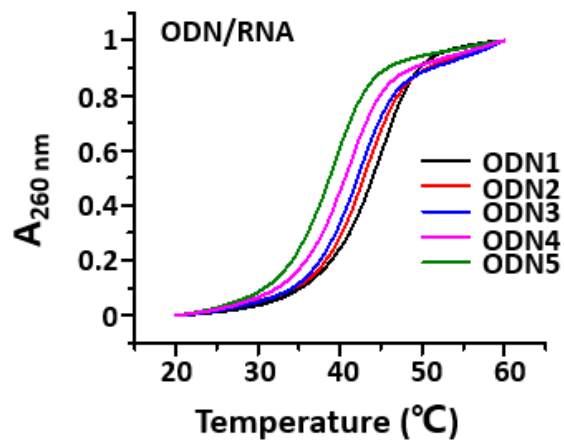


Figure S3. Melting Curves of ODN/DNA and ODN/RNA duplexes.

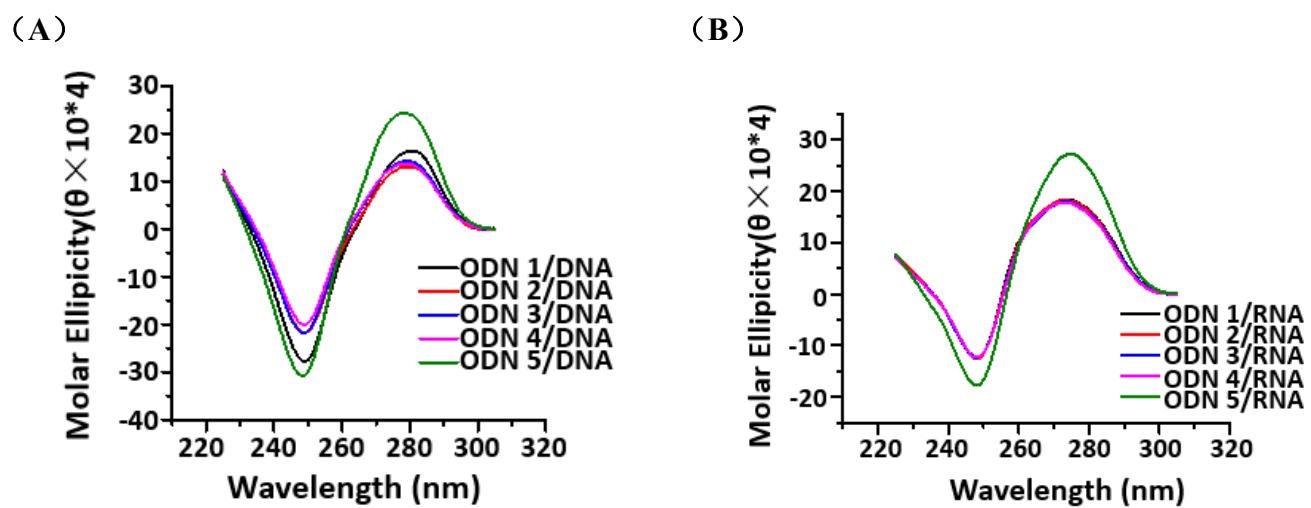


Figure S4. Circular dichroism spectroscopy of ODNs/DNA duplexes and ODNs/RNA duplexes.

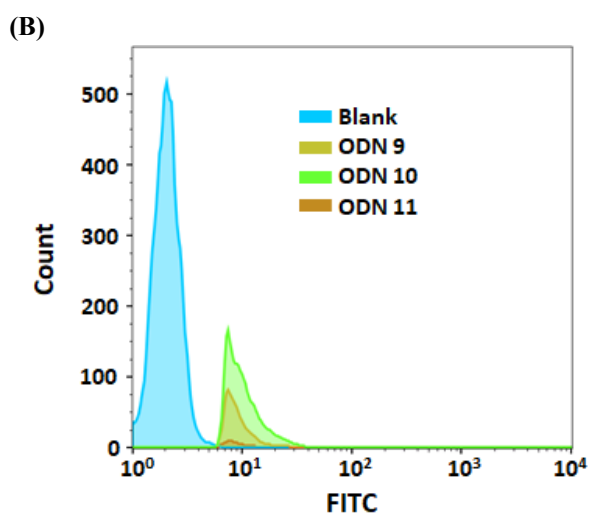
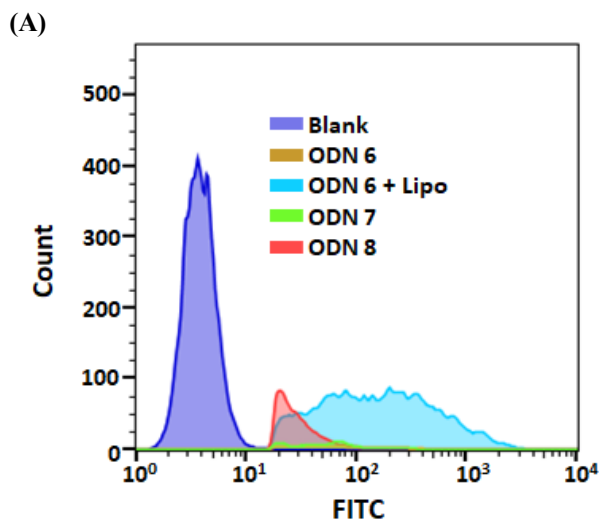


Figure S5. Flow Cytometry analysis of cell permeability of ODNs.