The Supporting Information to:

4'-*C*-[(4-Trifluoromethyl-1*H*-1,2,3-triazol-1-yl)methyl]thymidine as a Sensitive ^{19}F NMR-sensor for the Detection of Oligonucleotide Secondary Structures

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Contents:

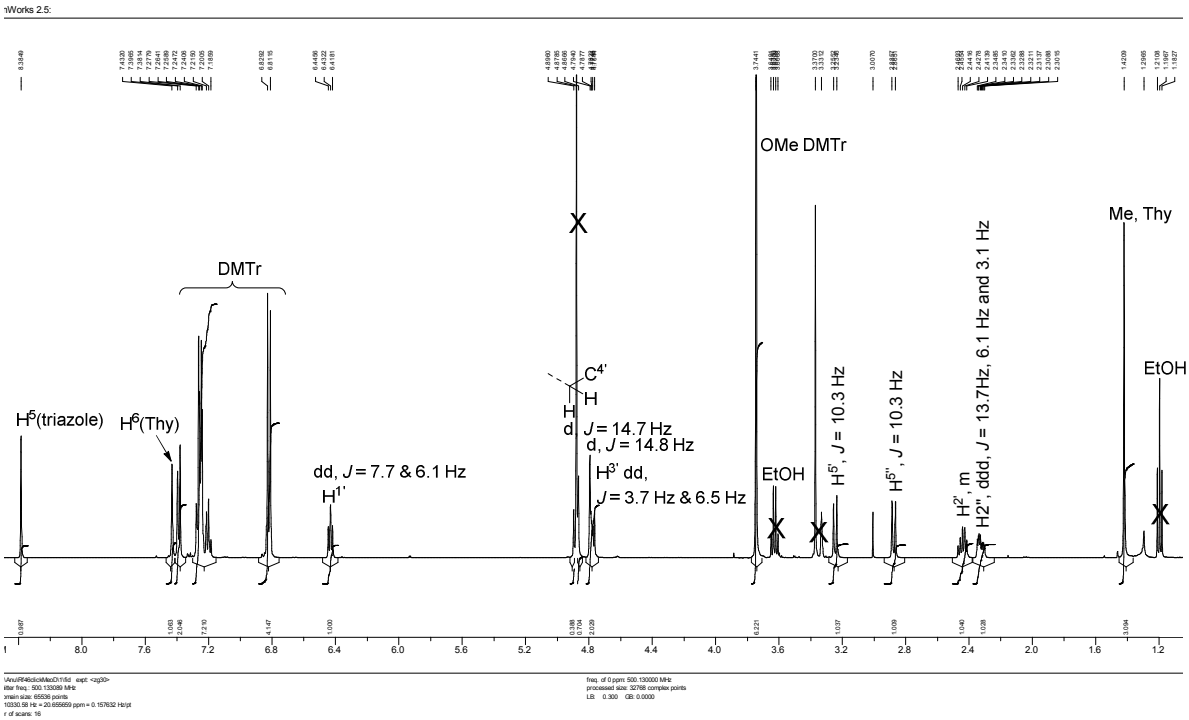


Figure S1. ^{1}H NMR (500 MHz, MeOD) spectrum of **11.**

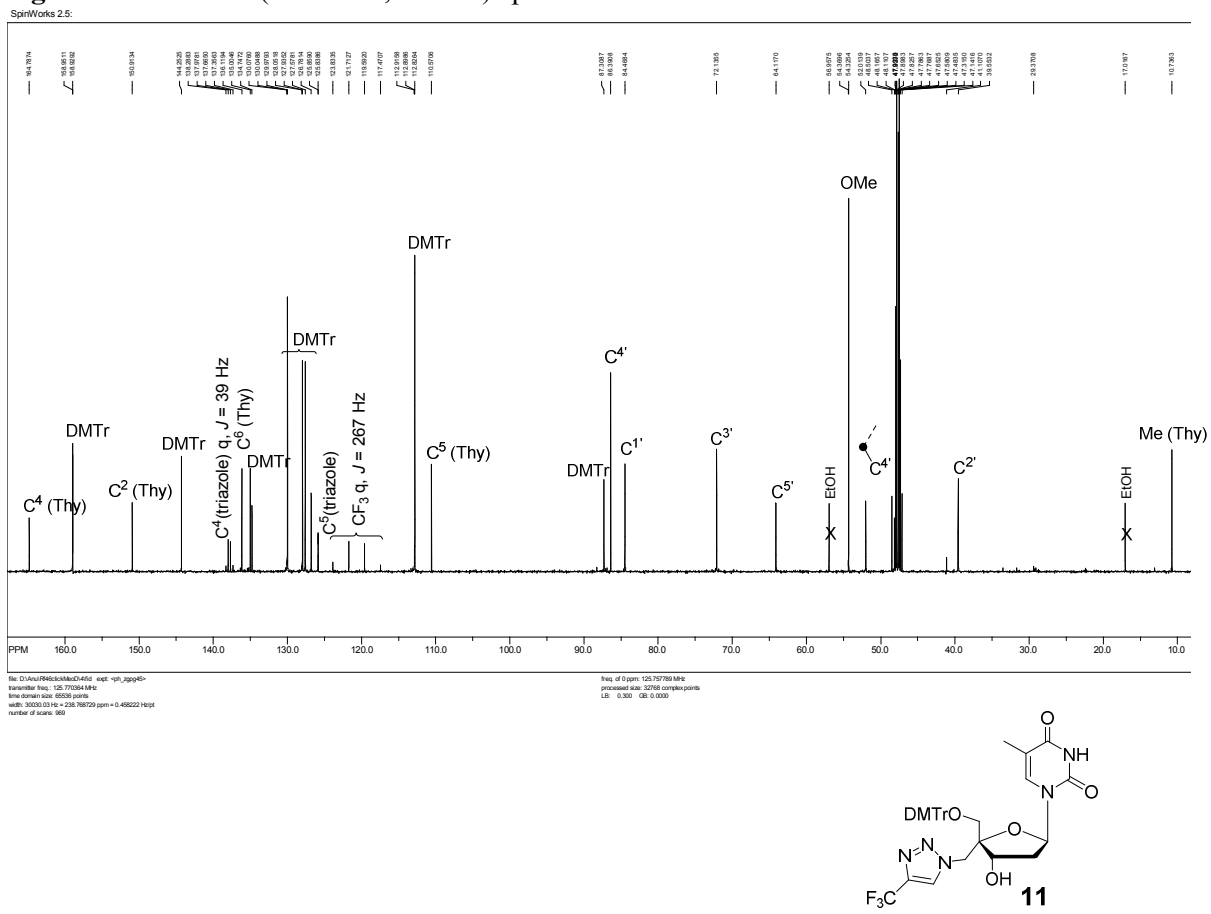
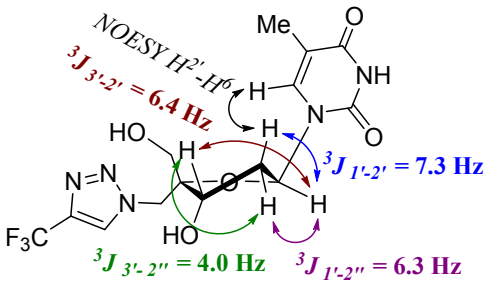


Figure S2. ^{13}C NMR (125 MHz, MeOD) spectrum of **11.**



%S = $^{3}J_{H1'-H2'}$ x 100 / 10.1 => 72%

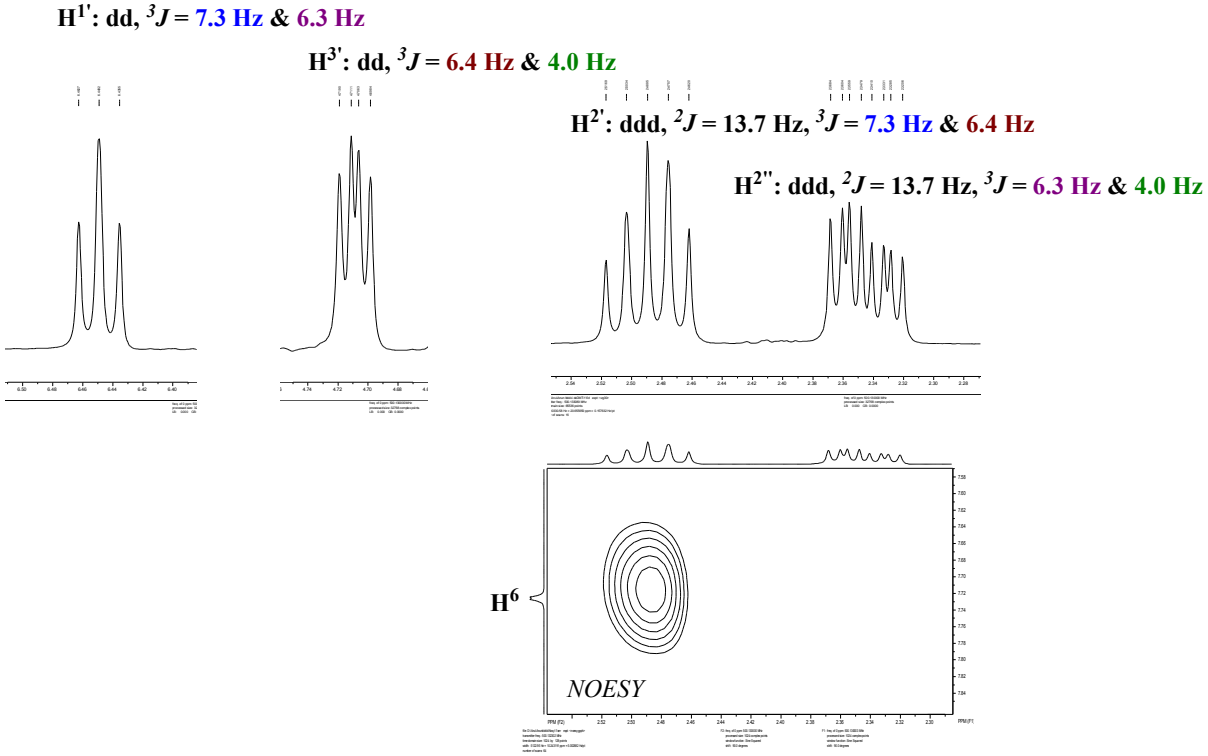


Figure S3. Sugar buckering of 4'-*C*-[(4-trifluoromethyl-1*H*-1,2,3-triazol-1-yl)methyl]thymidine. The sugar puckering of 4'-*C*-[(4-trifluoromethyl-1*H*-1,2,3-triazol-1-yl)methyl]thymidine was additionally determined for the fully exposed nucleoside. An aliquot of **11** was detritylated and the resulted 4'-*C*-[(4-trifluoromethyl-1*H*-1,2,3-triazol-1-yl)methyl]thymidine was analyzed by ^{1}H NMR and 1D-NOESY. DNA-type S-form (72%) is favoured according to the optimized Karplus relation for nucleosides (Davies, D. B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1978**, *12*, 135.). The corresponding coupling constants for H$^{1'}$ are 7.7 Hz and 6.1 Hz for **11** and 6.7 Hz (average) for **12**.

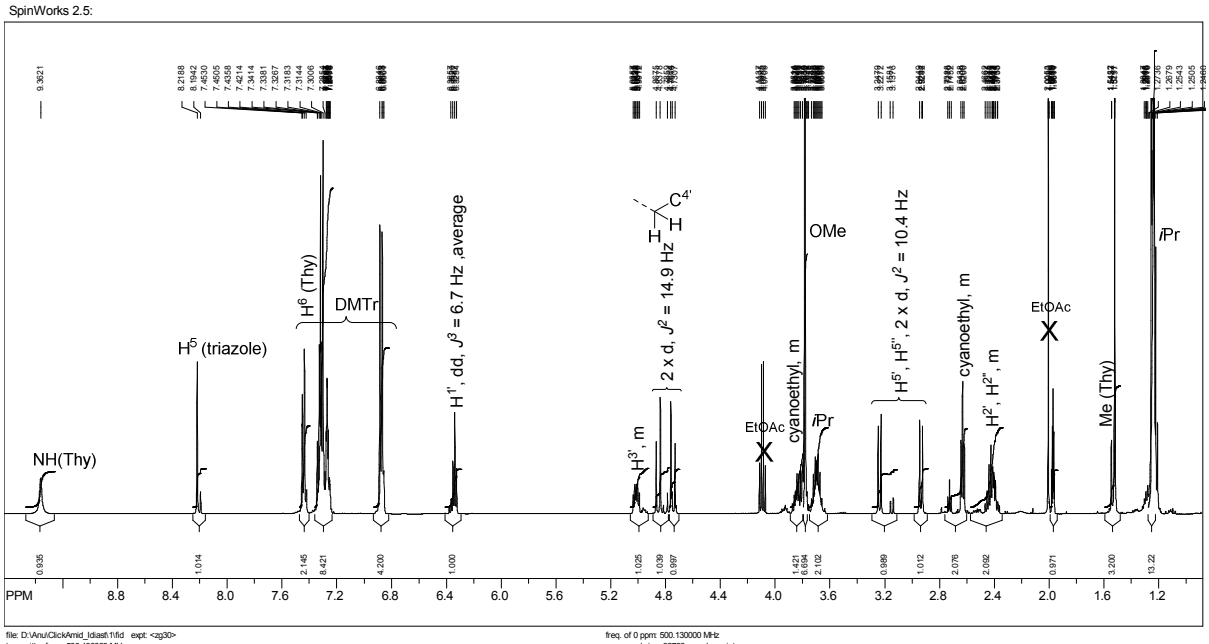


Figure S4, ^{1}H NMR (500 MHz, CD_3CN) spectrum of **12**

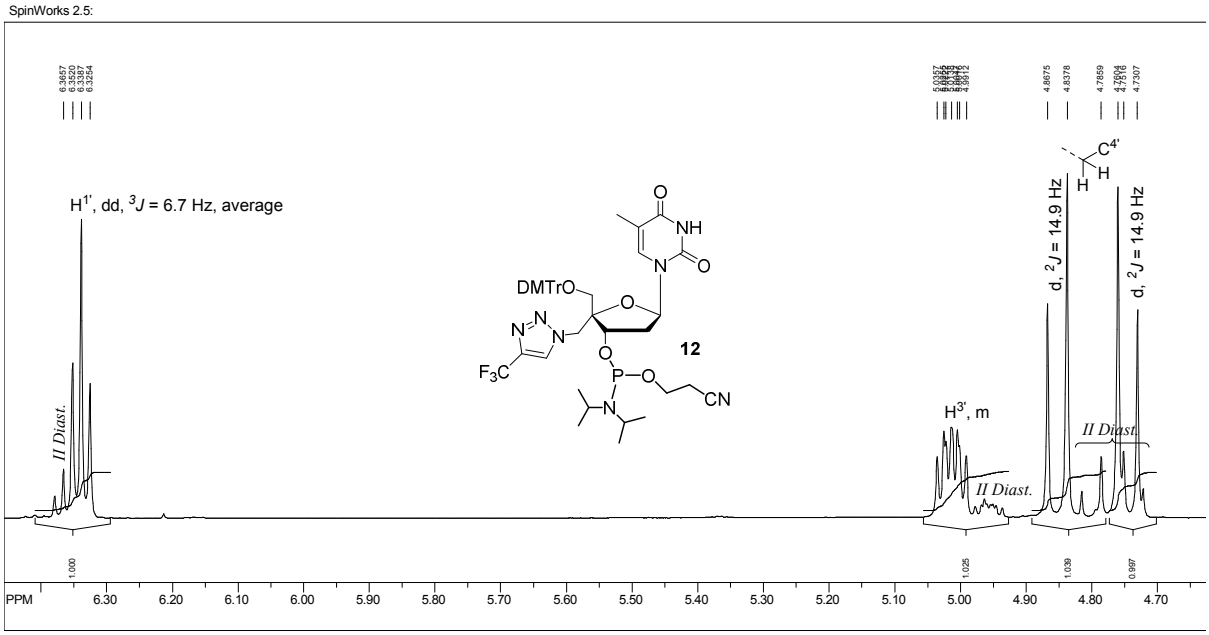


Figure S5. The same spectrum as above.

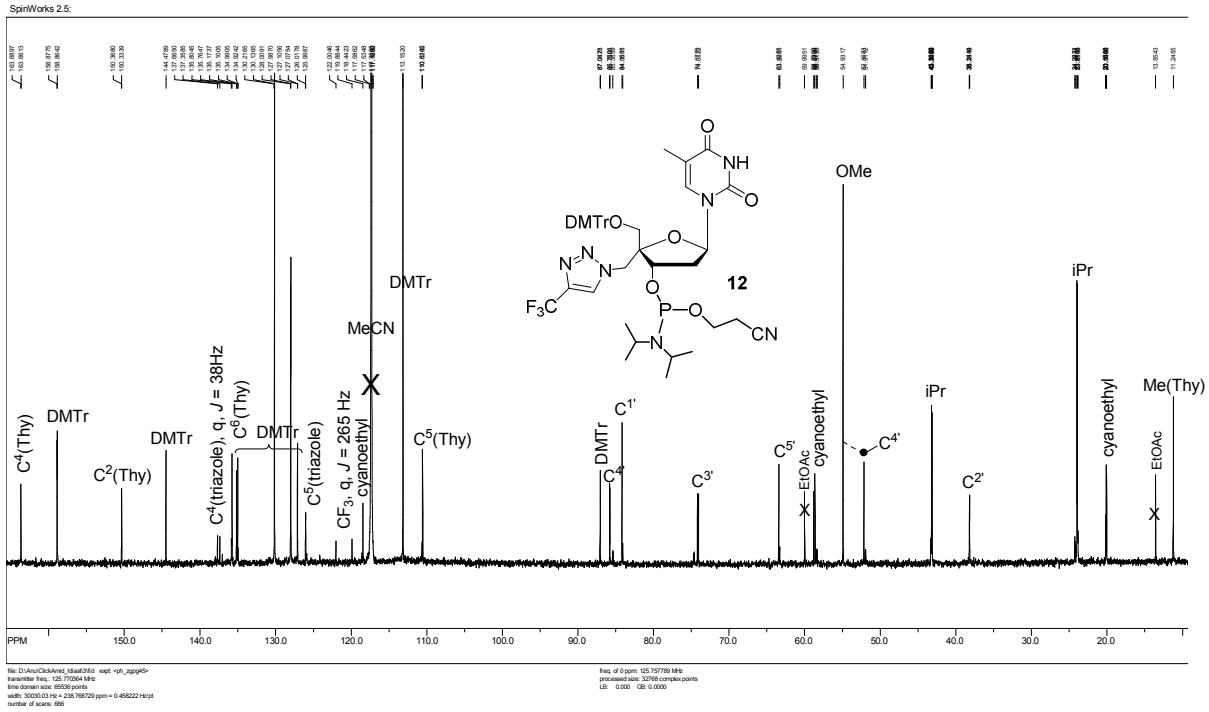


Figure S6. ^{13}C NMR (125 MHz, CD_3CN) spectrum of **12**

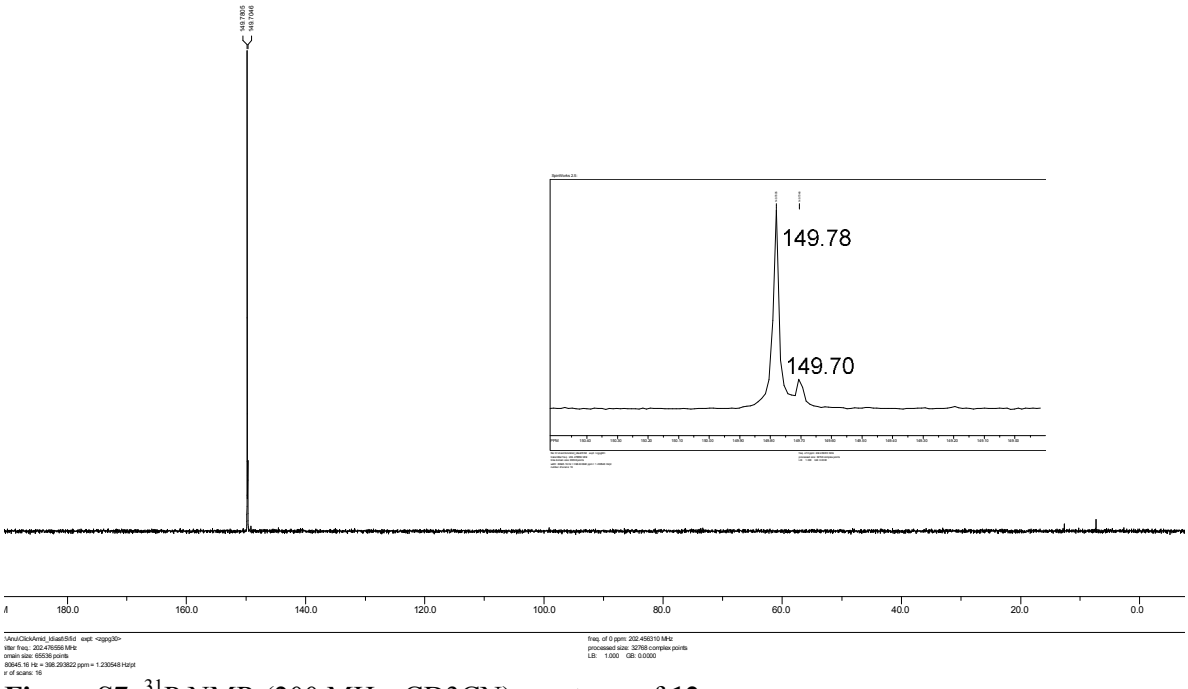


Figure S7. ^{31}P NMR (200 MHz, CD3CN) spectrum of **12**

Notation to the spectra in **Figures S4-7:** One of the phosphoramidite diastereomers **12** was isolated (mainly) in order to facilitate interpretation of the NMR signals.

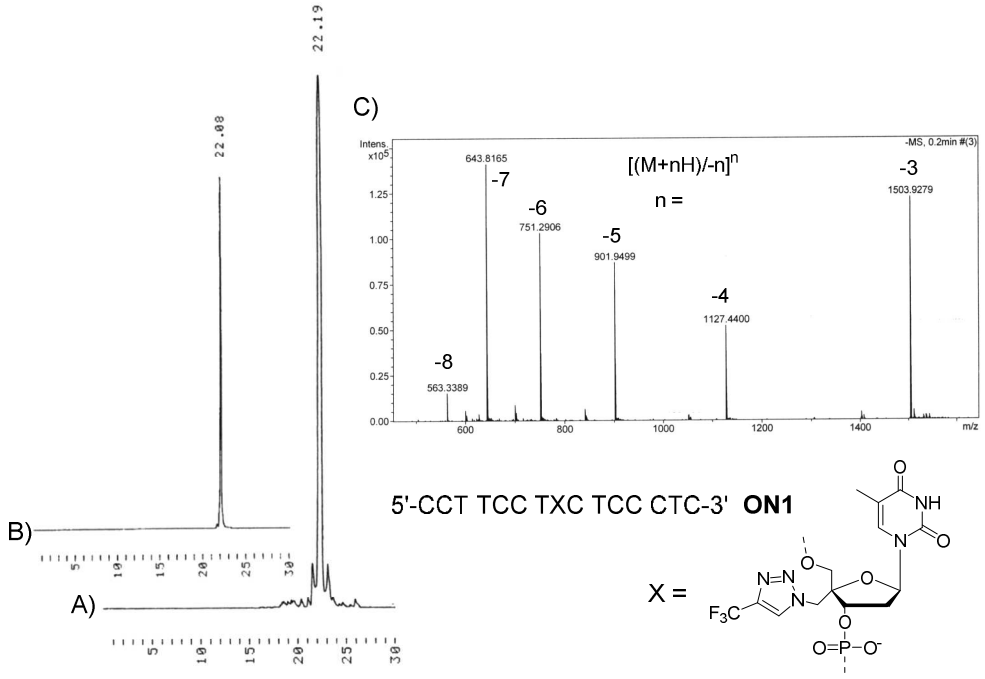


Figure S8. RP-HPLC profiles of A) crude and B) homogenized **ON1** mixture and C) MS (ESI-TOF) spectrum of **ON1**.

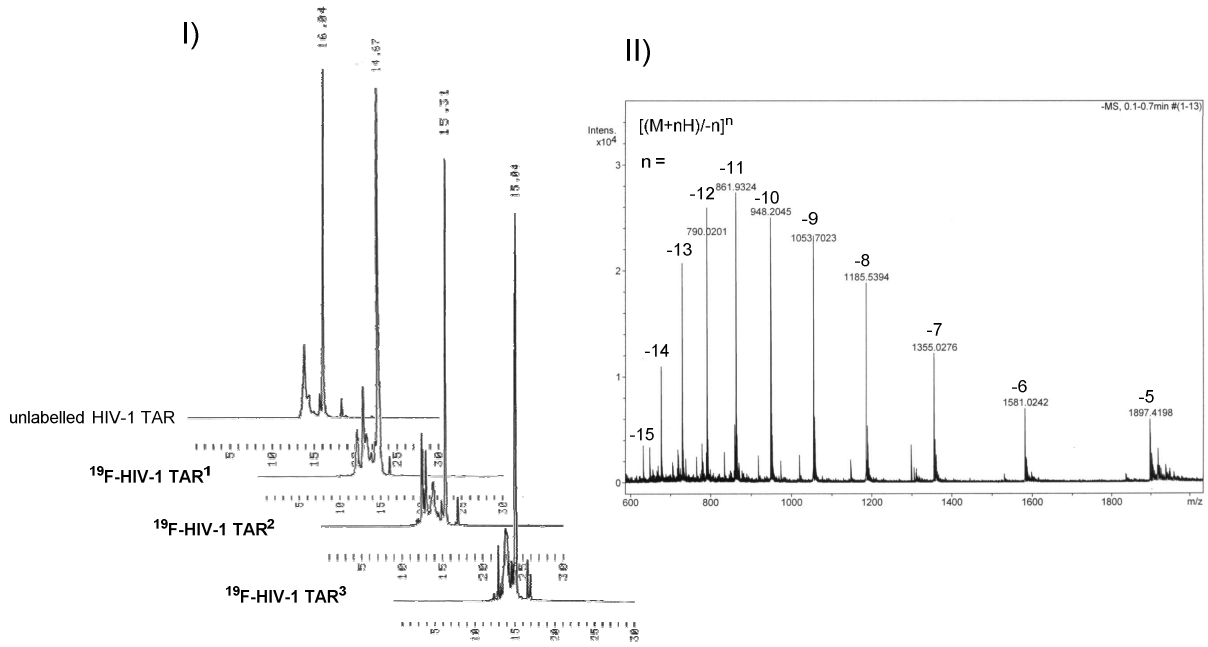
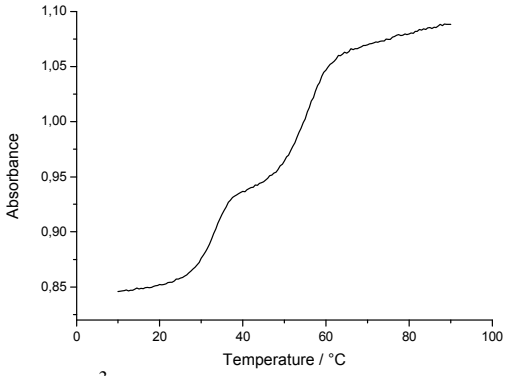


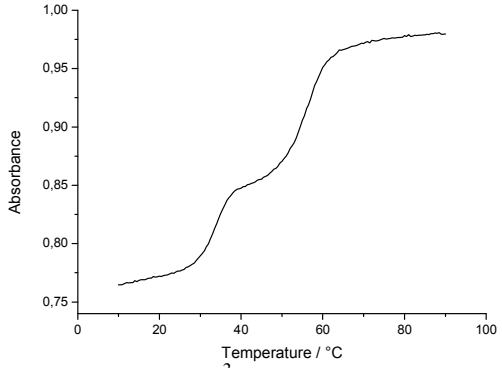
Figure S9. I) RP HPLC profiles of the crude product mixtures of HIV-1-TAR models. The efficiency of the synthesis of the labelled sequences in comparison to that of the unlabelled sequence demonstrated. II) MS (ESI-TOF) spectrum of **^{19}F-HIV-1 TAR(3)** as an example. RP HPLC conditions: A semipreparative column (C-18, 250 × 10 mm, 5 μm), flow rate 3.0 mL min^{-1}, a linear gradient from 0 to 90% acetonitrile in aqueous 0.1 mol L^{-1} triethylammonium acetate (0-25 min), then continued with 90% acetonitrile in aqueous 0.1 mol L^{-1} triethylammonium acetate (25-30 min), detection at 260 nm.

(a)



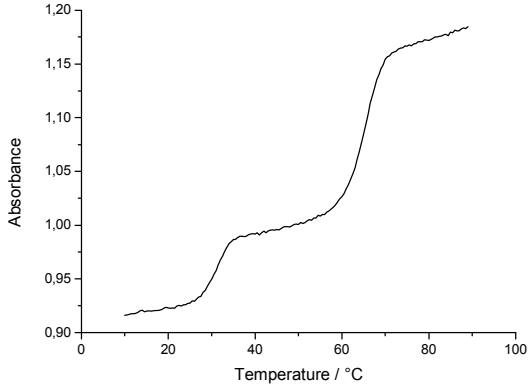
T_m^3 = 32.9 °C
T_m^2 = 54.9 °C

(b)



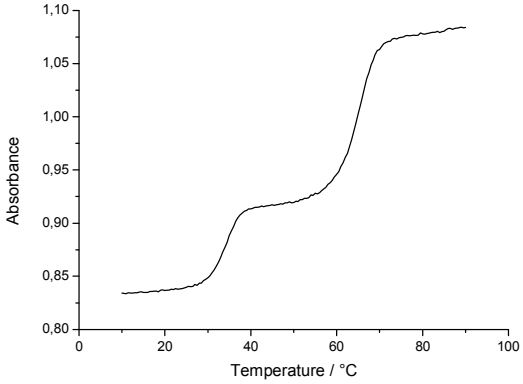
T_m^3 = 33.5 °C
T_m^2 = 55.5 °C

(c)



T_m^3 = 31.0 °C
T_m^2 = 65.0 °C

(d)



T_m^3 = 33.7 °C
T_m^2 = 64.5 °C

Figure S10. The recorded UV-melting profiles for the triplexes: (a) **ON1**/**ON2**/**ON3**-triplex, (b) Reference DNA-triplex (X = T), (c) **ON1**/**ON4**/**ON5** triplex, (d) Reference DNA triplex (X = T). 2 μmol L^{-1} of each oligonucleotide in 10 mmol L^{-1} sodium phosphate buffer (pH 6) containing 0.1 mol L^{-1} NaCl and 2 mmol L^{-1} $MgCl_2$

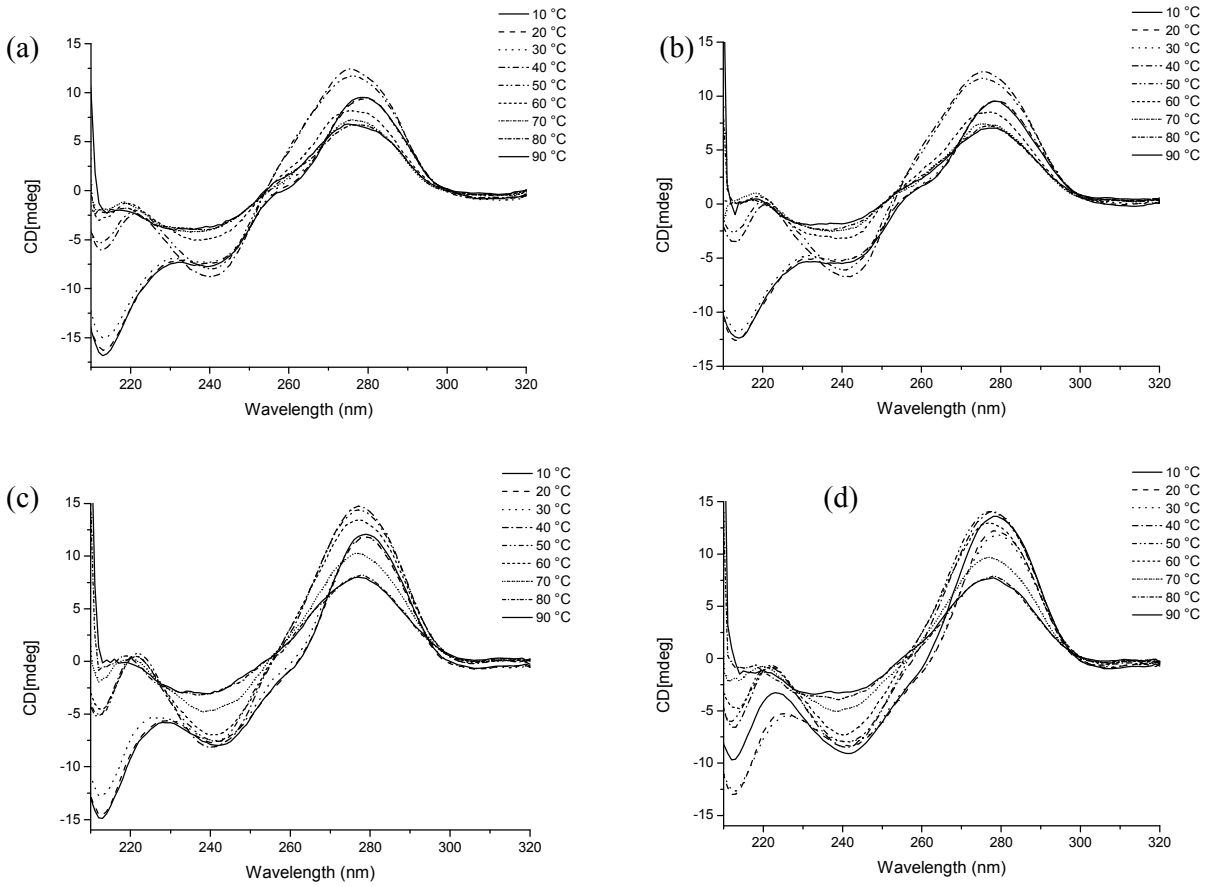


Figure S11. The CD spectra of the triplexes. (a) **ON1**/**ON2**/**ON3**-triplex, (b) Reference DNA-triplex (X = T), (c) **ON1**/**ON4**/**ON5** triplex, (d) Reference DNA triplex (X = T). 2 μmol L^{-1} of each oligonucleotide in 10 mmol L^{-1} sodium phosphate buffer (pH 6) containing 0.1 mol L^{-1} NaCl and 2 mmol L^{-1} $MgCl_2$.

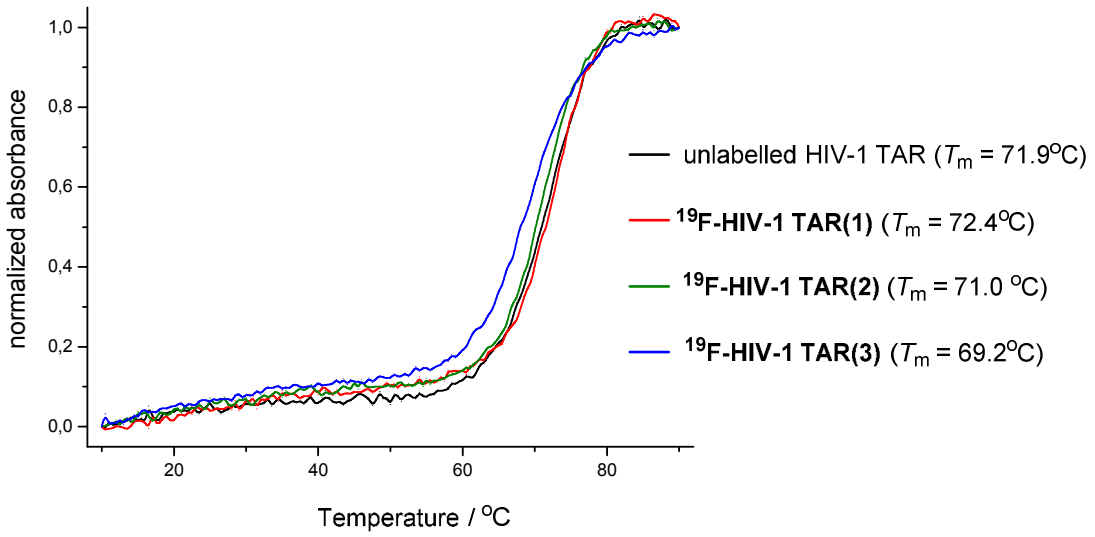


Figure S12. The recorded UV-melting profiles for the HIV-1 TAR models 2 μmol L^{-1} of each oligonucleotide in 10 mmol L^{-1} sodium cacodylate (pH 7) containing 0.1 mol L^{-1} NaCl.