Experimental Details

General:

All chemicals were purchased from Sigma-Aldrich unless noted otherwise and used without further purification. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc.

UV-Vis experiments were carried out using an Agilent 8453 single beam UV-Visible spectrophotometer. To a solution of the metal salts ($HAuCl_4 .3H_2O$, K_2PtCl_4, $AgNO_3$ or $CuCl_2$) at a concentration of 5 mM in water, the boranephosphonate DNA was added such that **bpT$_2$** and **bpT$_{21}$** were at final concentrations of 200 μM and 2.5 μM respectively. Absorbance spectra were then recorded at various time intervals. For experiments at 55 ^oC, the cuvette was incubated at that temperature in an incubating oven. Photographs were also taken of the cuvettes at various time intervals using a Fujifilm digital camera.

NMR spectra were recorded on a Bruker Avance-III 300 spectrophotometer at 300 MGHz in solvents mentioned in various experiments. Typically, $HAuCl_4$ was dissolved in D_2O, methanol, or n-butanol at a final concentration of 10 mM and **bpT$_2$** was added from a stock solution in the same solvent such that the final concentration of the dimer was 2 mM and the final volume was 500 μL. The solution was left at room temperature overnight. For the methanol and butanol reactions 50 μL of D_2O was added before recording the ^{31}P and ^{11}B $\{^1H\}$ NMR. Long accumulation times (several hours) were required to obtain acceptable signal to noise. ^{11}B $\{^1H\}$ NMR was recorded using a quartz NMR tube.

ESI-MS spectra were recorded using a Waters SYNAPT G2 High Definition Mass Spectrometry System with a triple quadrupole time-of-flight mass spectrometer (qTOF-MS). To a solution of $HAuCl_4$ at a concentration of 5 mM, **bpT$_2$** was added to a final concentration of 200 μM and incubated overnight at room temperature. This solution was diluted 10 to 25 times in HPLC grade methanol and filtered through 0.2 μm PVDF micro-spin centrifugal filters (Life Sciences Product, Inc., Frederick, CO) before injection. The spectra for **bpT$_2$** and the reaction in water were recorded in the negative mode whereas those in methanol and n-butanol were recorded in the positive mode.

Transmission Electron Microscopy was carried out using a CM100 transmission electron microscope (FEI, Inc., Hillsboro, OR) operating at 80KV. 400 mesh carbon coated gold grids (Electron Microscopy Sciences) were used. These were cleaned by plasma treatment prior to use. Samples were prepared by adding 4 μL of the solution containing metal nanoparticles (made using identical concentrations as used for the UV-Vis experiments described above) to the grid, waiting for 5 minutes and then removing the excess liquid using a Kimwipe. The grid was subsequently air-dried and used for imaging.

Synthesis of Boranephosphonate Oligodeoxyribonucleotides.

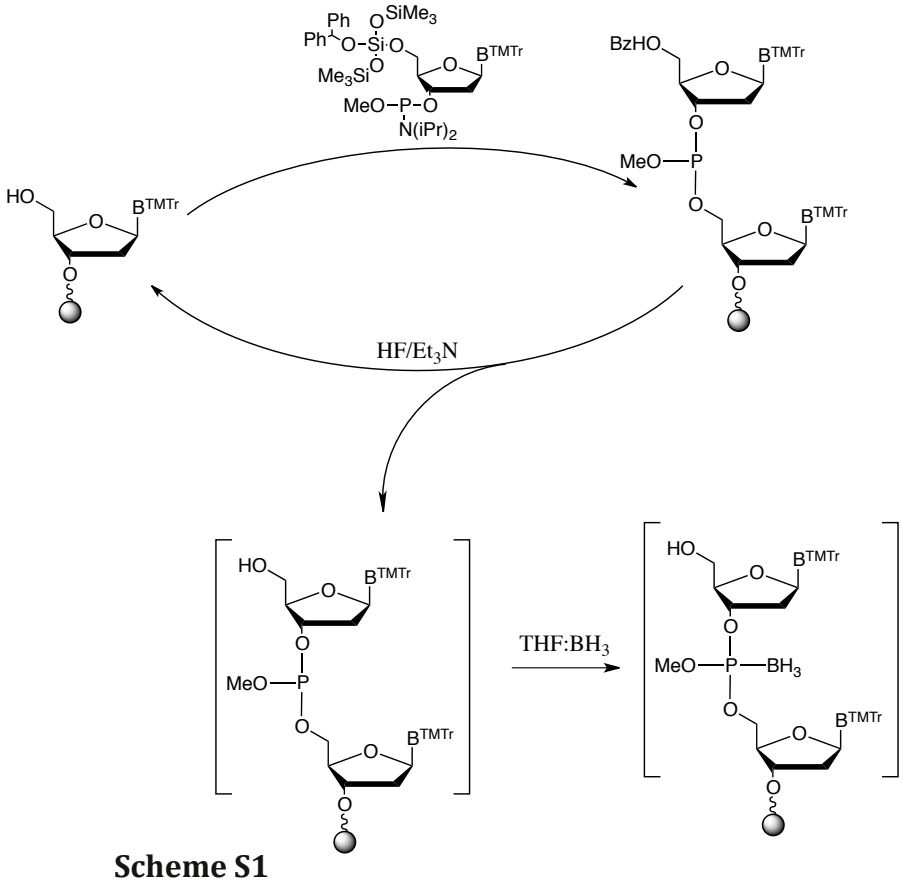
bpT$_{21}$: Our group has published the synthesis of mixed sequence boranephosphonate DNA using 5′-*O*-[benzhydroxy*bis*(trimethylsilyloxy)]silyl and N-trimethoxytrityl protected phosphoramidites.[1] The synthesis of fully modified

boranephosphonate oligomers as used here was a variation of this approach (Scheme S1) that generated higher yields. Briefly, the DNA strand was first synthesized on the solid support as the P(III) triester using the previously described synthesis cycle but with the boronation step omitted. Boronation was completed as a single step at the end by treatment of the solid support bound oligomer with a 0.025 M solution of BH_3 in THF for 45 s. Deprotection and cleavage from the support was carried out as before. **bpT$_{21}$** was purified by gel electrophoresis using a 20% denaturing polyacrylamide gel. Oligomers were verified by MALD-TOF mass spectrometry (Expected: 6179.7 Da; Found: 6183.7).

Synthesis of Oligonucleotide containing *O*-methylphosphate triesters.

Synthesis of boranephosphonate containing decadeoxythymidine precursor (Figure S8a): Synthesis was carried out using 5'-dimethoxytrityl-2'-deoxythymidine, 3'[(methyl)-(N,N-diisopropyl)]phosphoramidite (Glen Research) on a 0.2 μmole scale with standard reagents for DNA synthesis. For the last coupling cycle the oxidation was replaced by a boronation step using a 0.025M solution of a borane-THF complex in anhydrous THF. In addition the acid deprotection step was omitted to leave the 5' DMT group intact. Next after removal of the methyl protection on the phosphate, the oligomers were cleaved from the solid support using 37% aqueous ammonia (2h, room temperature). The DMT group improved the solubility of the oligomers in methanol as well as allowed purification on a Sep-pak II column after reaction with $HAuCl_4$ in methanol.

Conversion to O-methylphosphate triester (Figure 8b): The entire amount of boranephosphonate containing oligodeoxynucleotide obtained from a 0.2 μmole synthesis (described above) was evaporated to dryness and re-dissolved in a 200-300 μL of freshly made 25mM $HAuCl_4$ in methanol by sonicating the mixture for a few minutes. This mixture was incubated over night at room temperature then evaporated to dryness in a speedvac and re-dissolved in 2mL of water. This mixture was filtered through a 0.2 μm PVDF micro-spin centrifugal filter and subjected to DMT on/of purification using a Poly-Pak II cartridge (Glen Research). The manufacturer's protocol was followed with the exception of omitting the ammonia washing steps.



Scheme S1

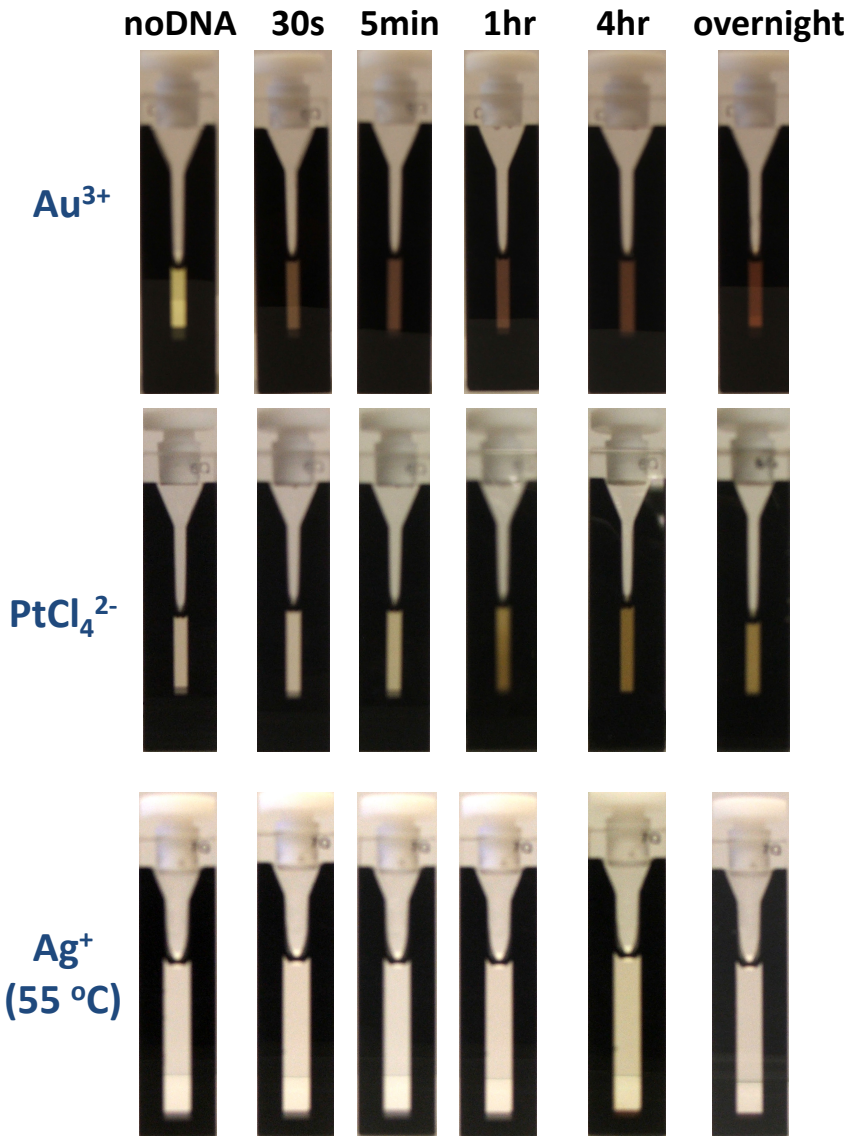


Figure S1 Reduction of $AuCl_4^-$ and $PtCl_4^{2-}$ at room temperature or Ag^+ at 55 °C by **bpT$_2$**. **bpT$_2$** was added at a final concentration of 200 μM to solutions containing the metal ions at 5mM.

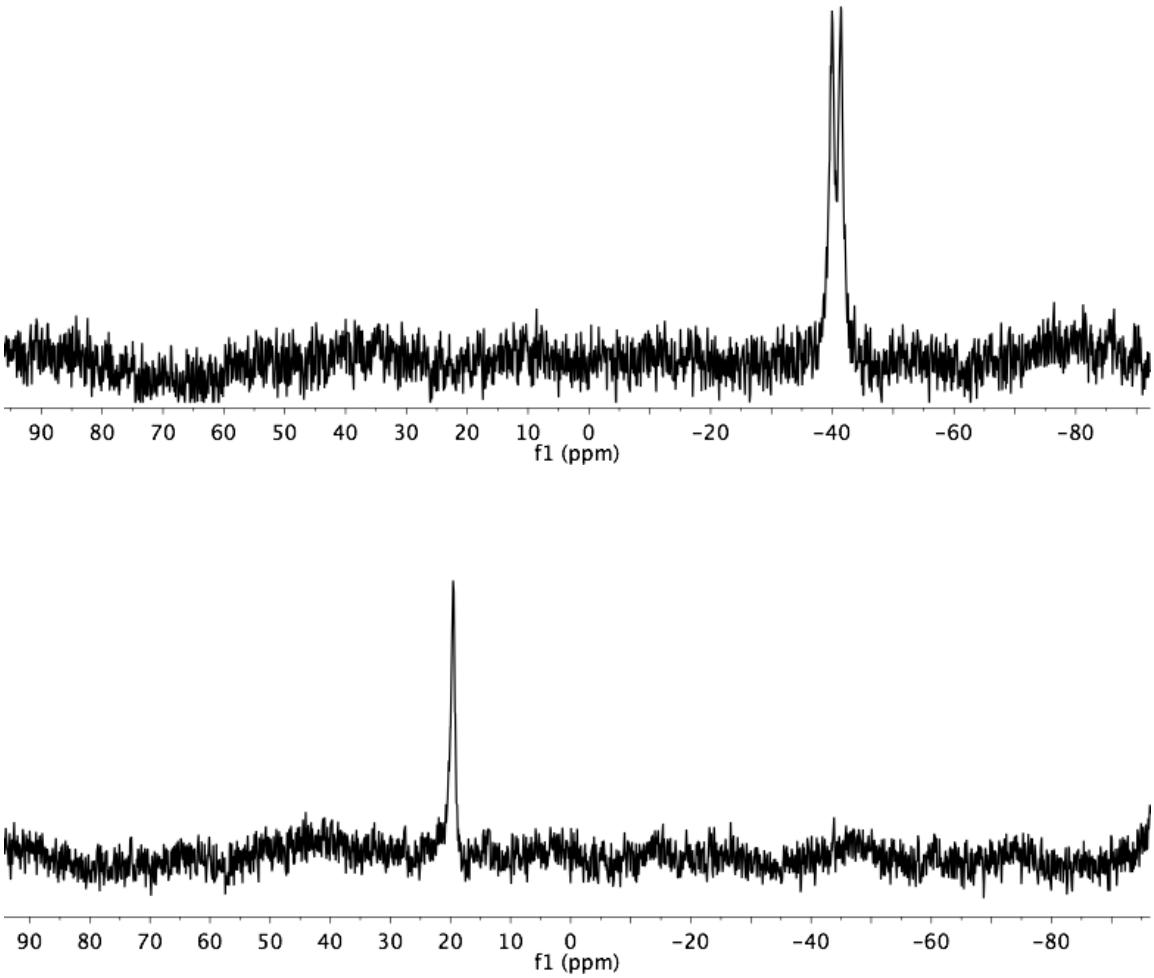


Figure S2. ^{11}B $\{^{1}H\}$ NMR of the (top) boranephosphonate dimer (**bpT$_2$)** and the (bottom) product mixture upon reduction of $AuCl_4^-$ in D_2O.

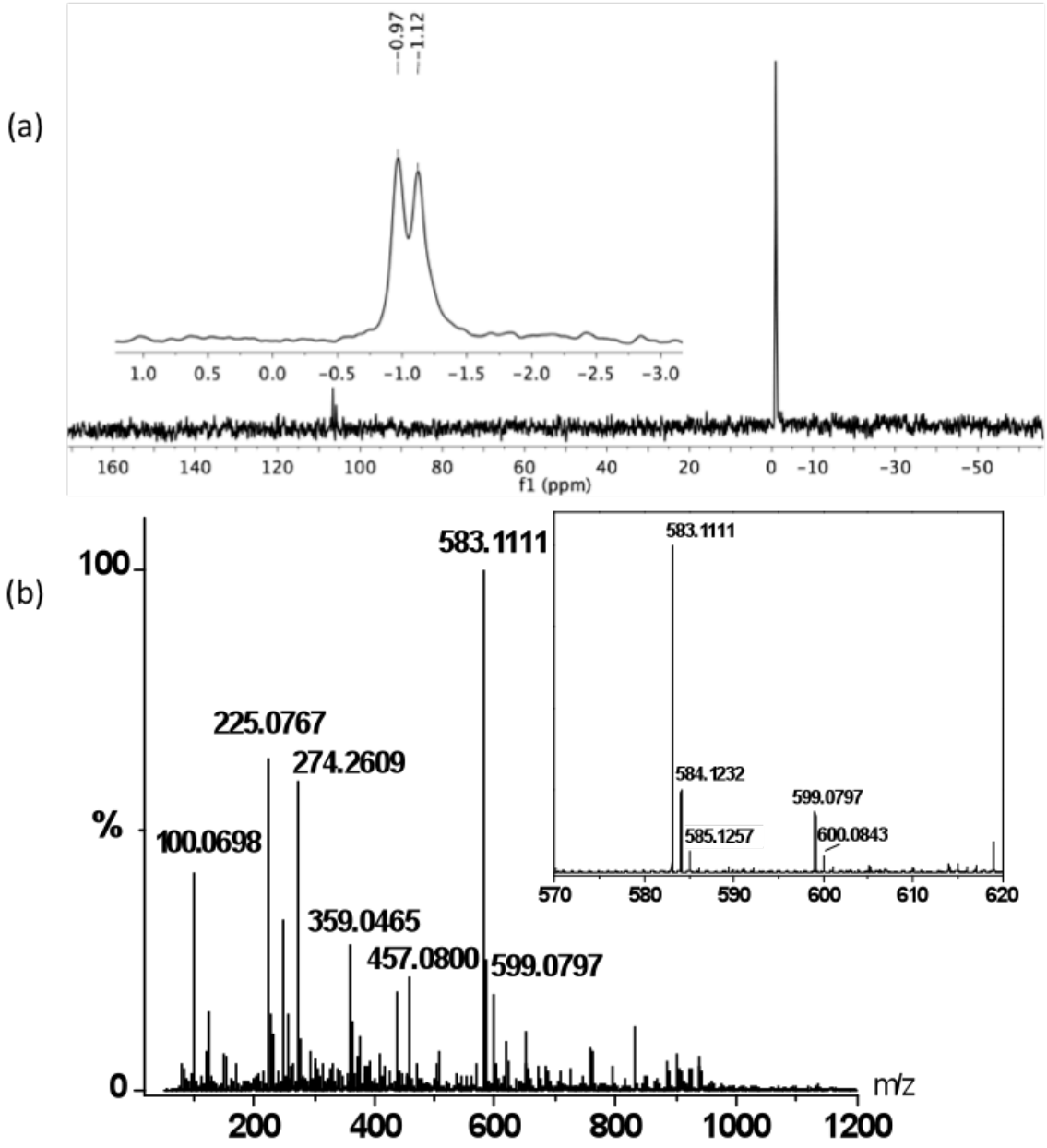


Figure S3. (top) ^{31}P NMR spectrum of the product mixture following reduction of $AuCl_4^-$ by **bpT$_2$** in methanol. The inset shows an expansion of the peak which demonstrates the formation of the two diastereomers of the *O*-methylphosphate dinucleotide. (bottom) ESI-MS of the same mixture showing the detection of *O*-methylphosphate dithymidine adducts with Na^+ and K^+. Theoretical m/z: [M+H]: 561.1, [M + Na]: 583.1, [M+K]: 599.1

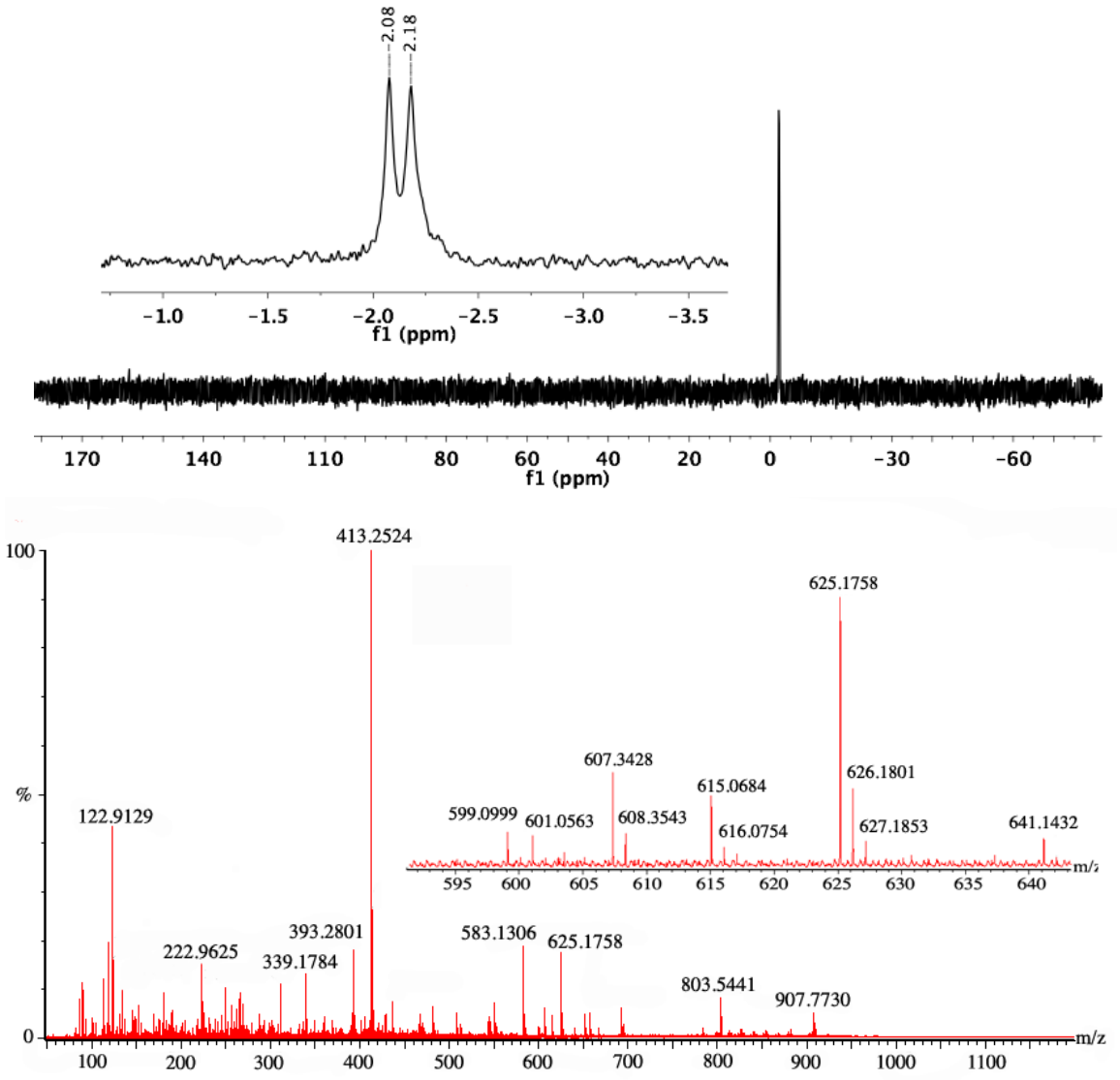


Figure S4. (Top) ^{31}P NMR spectrum of the product mixture following reduction of $AuCl_4^-$ ions by **bpT$_2$** in n-butanol. The inset shows an expansion of the peak which demonstrates the formation of the two diastereomers of the *O*-(n-buty)lphosphate dinucleotide. (bottom) ESI-MS of the same mixture showing the detection of *O*-(n-butyl) phosphate dithymidine adducts with Na^+ and K^+. Theoretical m/z: [M+H]: 603.20, [M + Na]: 625.19, [M+K]: 641.16

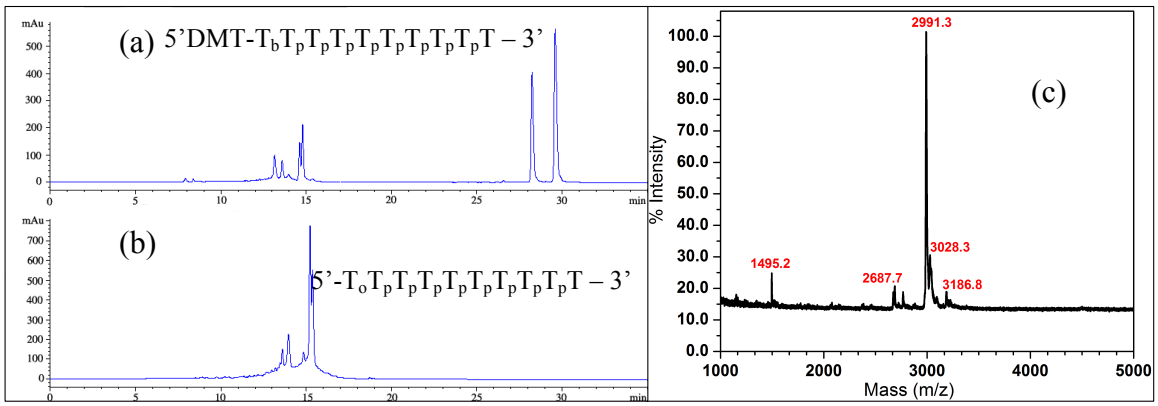


Figure S5. (a) HPLC chromatogram of 5'-DMT- decathymidine containing a single boranephosphonate linkage (sequence shown in inset where p denotes a phosphate linkage and b denotes a boranephosphonate linkage) (b) chromatogram obtained after reaction with $HAuCl_4$ in methanol followed by DMT on/off purification. The inset shows the resulting sequence containing a single *O*-methylphosphate triester linkage denoted as 'o' (c) MALDI-TOF MS of the product obtained after DMT on/off purification. Theoretical m/z: $[M\text{-}H^+]^-$: 2991.5; $[M\text{-}2H^+]^{2-}$: 1495.2. The peak at 2687.7 Da corresponds to a T9 oligomer.

REFERENCES

1. H. B. McCuen, M. S. Noe, A. B. Sierzchala, A. P. Higson, and Caruthers, M. H. *J. Am. Chem Soc.* 2006, **128**, 8138.