SUPPORTING INFORMATION

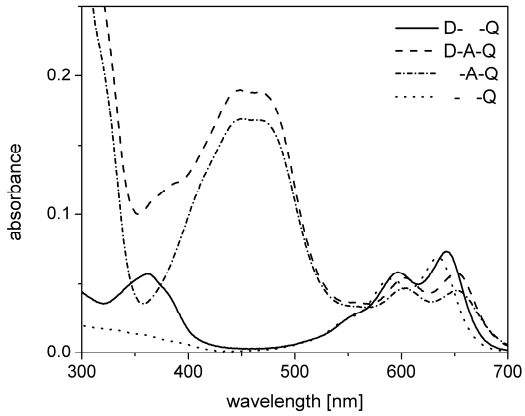

Figure 1SI. Absorption spectra of peptide sequences, with varying quencher behaviour

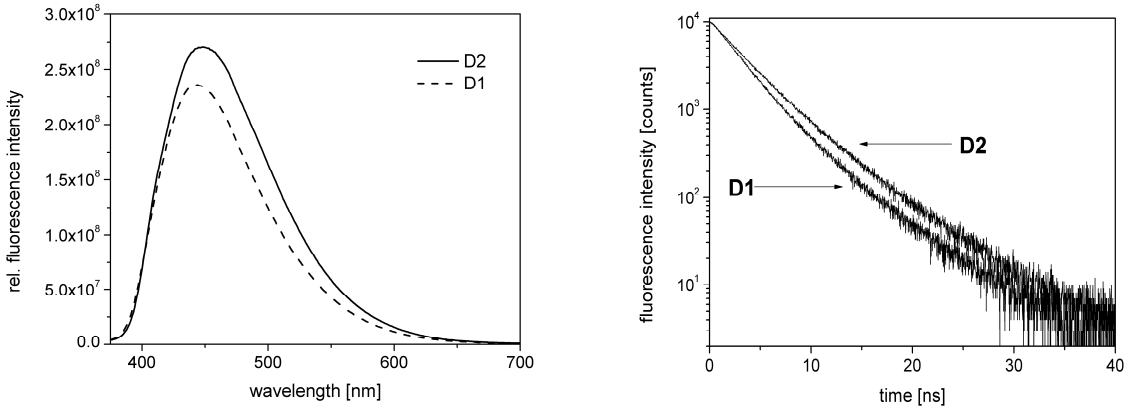

Figure SI2. steady-state (left) and time-resolved (right) fluorescence emission spectra of D-only labelled DNA (D2 - - **26/19** and D1 - - **25/19**)

Synthesis and general characterization:

Oligonucleotide syntheses were carried out on an Expedite™ 8909 Nucleic Acid Synthesis system on a 1 µmol scale using phosphoramidite chemistry and standard protocols. Phosphoramidites as well as nucleosides coupled to solid support (CPG) were obtained from Proligo/Sigma Aldrich. Cleavage of the modified and unmodified oligonucleotides from the solid support and concomitant deprotection was performed by adding a 25% NH_3-solution

followed by vortexing over night at room temperature. After exchanging the counter ion NH_4^+ by K^+, the oligonucleotide samples were desalted by size exclusion chromatography using NAP-10 columns. Purification of the modified oligonucleotides was performed by preparative polyacrylamide-gel electrophoresis (PAGE). Pre-electrophoresis was performed over night at 400 V with tris-borate buffer. Oligonucleotide (5 µL, 1 OD/µL in H_2O) and bromophenol-blue/xylenecyanol- solution (5 µL) were heated to 90°C for 2 min and rapidly cooled to 0°C before being loaded onto the gel. Electrophoretic separation was performed for 18 h at 400 V. The gel was visualized at 366 nm and the bands containing the desired DNA were isolated and cut into small slices. Together with twice the volume of MilliQ water they were extracted over night. After centrifugation, the supernatant was collected and concentrated. Resulting oligonucleotide samples were desalted by size exclusion chromatography on NAP-10 columns.

All oligonucleotides were analyzed by electrophoresis on polyacrylamide gels (20 %) of 0.4 mm thickness. Pre-electrophoresis was performed for 2 h at 500 V with tris-borate running buffer. Oligonucleotide (1 µL, 0.1 OD/µL in H_2O) and bromophenol-blue/xylenecyanol-solution (2 µL) were heated to 90°C for 2 min and rapidly cooled to 0°C before being loaded on the gel. Electrophoretic separations were performed for 2 h at 500 V. Oligonucleotide bands were stained with a solution of 3,3'-diethyl-9-methyl-4,5,4',5'-dibenzothiacarbocyanine bromide (Stains-All, Fluka).

HPLC runs were performed on a Merck/Hitachi system using an EC-125/4-Nucleosil-100-5-C18 (analytical) column. The mobile phase was a gradient of solvent A = 0.1 M $Et_3NH(OAc)$ buffer at pH 7.0 and solvent B = CH_3CN.

Quantification was done by UV-measurements on a Perkin-Elmer-Lambda-35-

UV/VIS spectrometer. ^1H-, ^{13}C- and ^{31}P-NMR-spectra were measured on AC 250, AM 400 and DRX 500 from Bruker as well as a Mercury VX 300 from Varian using $CDCl_3$, CD_3OD

CD_3CN or d-DMSO as solvent. Column chromatography was performed on silica gel type 60 ACC 35-70 µmol.

5'-O-[Bis(4-methoxyphenyl)phenylmethyl]-2'-deoxy-5-{3-{2-[6'',7''-dimethoxy-4''-(trifluoromethyl)-2''-oxoquinolin-1''(2H)-yl]acetamido}prop-1-yn-1-yl}uridine (13)

6,7-Dimethoxy-4-(trifluoromethyl)-2-oxoquinoline-1(2H)-acetic acid (**12**) (174.8 mg, 0.528 mmol, 1.0 equiv.) was dissolved in DMF (10 mL), TBTU [29] (169.8 mg, 0.528 mmol, 1.0 equiv.) and Hünigs base (287.0 mg, 377.6 µL, 2.112 mmol, 4 equiv.) were added and the mixture was stirred for 10 min at room temperature.

5'-O-[Bis(4-methoxyphenyl)phenylmethyl]-2'-deoxy-5-{3-{amino}prop-1-yn-1-yl}uridine (**11**) (400.0 mg, 0.685 mmol, 1.3 equiv.), which was had been dried three times azeotropically with 10 mL anhydrous acetonitrile each was dissolved in 10 mL of DMF and then added to the reaction mixture. The mixture was stirred over night at rt. After removal of DMF under reduced pressure, the residue was purified by short CC (silica gel, 0 - 5% (V/V) MeOH in CH_2Cl_2) yielding 400 mg of the desired compound **13** (82%, 0.446 mmol).

^{1}H-NMR ($CDCl_3$,400 MHz): δ = 2.22-2.58 (m, 2 H, 2'-H), 3.29-3.40 (m, 2 H, 5'-H), 3.74 (m, 6 H, 2× DMT-OMe), 3.87-3.94 (m, 5 H,6''-OMe, N-$\underline{CH_2}$), 3.95 (s, 3 H, 7''-OMe), 4.07-4.13 (m, 1 H, 4'-H), 4.50- 4.56 (m, 1 H, 3'-H), 4.91 (s, 2 H, $\underline{CH_2}$-Carbostyril), 6.30 (t, 1H, 1'-H), 6.78-6.87 (m, 4H, arom. DMT) 6.93 (s, 1 H, 3''-H), 7.03 (s, 1 H, 8''-H), 7.13-7.42 (m, 10H, 9H arom. DMT, 1H 5''-H), 8.03 (s, 1 H, 6-H) ppm.

^{13}C-NMR (CD_3OD, 100 MHz): δ = 30.15, 41.60, 47.35, 55.33, 56.24, 56.45, 63.73, 72.43, 74.29, 86.00, 86.81, 87.11, 89.19, 98.60, 99.39, 106.22, 108.83, 113.43, 117.25, 127.08,

127.96, 128.12, 130.04, 130.09, 135.52, 135.58, 136.50, 143.18, 144.62, 146.07, 149.37, 153.39, 158.69, 158.71, 161.07, 162.07, 166.77 ppm.

MS (EI): m/z (%) = 1790.8 (15) $[2\ M]^+$, 931.0 (33) $[M+35]^+$, 895.2 (100) $[M]^+$.

5'-O-[Bis(4-methoxyphenyl)phenylmethyl]-2'-deoxy-5-{3-{{2-[6'',7''-dimethoxy-4''-(trifluoromethyl)-2''-oxoquinolin-1''(2H)-yl] acetamido}prop-1-yn-1-yl}uridine 3'-[2-cyanoethyl-bis(1-methylethyl)phosphoramidite] (9)

5'-O-[Bis(4-methoxyphenyl)phenylmethyl]-2'-deoxy-5-{3-{2-[6'',7''-dimethoxy-4''-(trifluoromethyl)-2''-oxoquinolin-1''(2H)-yl]acetamido}prop-1-yn-1-yl}uridine (**13**) (160 mg, 0.18 mmol) and diisopropylammonium tetrazolide (23.0 mg, 0.14 mmol, 0.8 equiv.) were dried three times azeotropically with 5 mL of anhydrous acetonitrile each. Under argon, anhydrous CH_2Cl_2 (10 mL) and (2-cyanoethoxy)-bis-(*N*,*N*-diisopropylamino)phosphine (141 mg, 148 µl, 0.47 mmol) were added and stirred for 2.5 h at rt. The reaction was quenched with 10 mL of degassed saturated $NaHCO_3$ solution. The aqueous phase was extracted three times with 10 mL of degassed CH_2Cl_2 each. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure.

The residue was purified by CC (silica gel, 5% (V/V) MeOH in CH_2Cl_2) yielding 196 mg of the desired compound **9** (quantitative, 0.18 mmol).

^{1}H-NMR (CD_3CN, 300 MHz): δ = 1.02-1.30 (m, 12H, 2x CH($\underline{CH_3}$)$_2$), 2.36-2.72 (m, 4H, 2'-H, CH_2CN), 3.22-3.69 (m, 6H, O-$\underline{CH_2}$, 2× C$\underline{H}$(CH_3)$_2$, 5'-H), 3.75 (s, 6 H, 2× DMT-OMe), 3.85-3.93 (m, 8H, 6''-OMe, 7''-OMe, N-$\underline{CH_2}$), 4.09-4.19 (m, 1H, 4'-H), 4.57-4.71 (m, 1H, 3'-H), 4.97 (s, 2 H, CH_2-Carbostyril), 6.10-6.19 (m, 1H, 1'-H), 6.81 (s, 1H, 3''-H), 6.84-6.92

(m, 4H, arom. DMT) 6.95 (s, 1H, 8''-H), 6.98-7.05 (m, 1H, 5''-H), 7.18-7.51 (m, 9H, arom. DMT), 7.89-7.95 (m, 1H, 6-H) ppm.

^{31}P-NMR (CD_3CN, 120 MHz): δ = 149.19 ppm.

2'-Deoxy-5-(octadiynyl)-uridine (15)

A two neck flask was charged with 2'-deoxy-5-iodouridine (**14**) (1.00 g, 2.82 mmol), Pd/C (150 mg, 0.14 mmol, 0.05 equiv.), CuI (110 mg, 0.58 mmol, 0.20 equiv.) and Amberlite IRA-67 (3.00 g). The compounds were dried under high vacuum and afterwards kept under argon. Octadiyne (2.96 g, 27.9 mmol, 10 equiv.) and DMF (28 mL) were added. Through this suspension anhydrous argon was bubbled for 15 minutes and then it was kept under argon. The reaction mixture was stirred at 50°C for 17 h and afterwards cooled to rt. The cooled reaction mixture was filtered over celite and the celite was washed with 50 mL of a mixture of CH_2Cl_2/MeOH (1:1). The solvent of the combined organic phases was removed under reduced pressure and the residue was purified by CC (silica gel, 0-10% (V/V) MeOH in CH_2Cl_2) yielding 730 mg of the desired product **15** (78%, 2.20 mmol).

^{1}H-NMR (CD_3OD, 400 MHz): δ = 1.62-1.78 (m, 4H, 4''-H, 5''-H), 2.22-2.38 (m, 5H, 8''-H, 6''-H, 2'-H), 2.45(t, $J_{3'',4''}$= 6.8, 2H, 3''-H), AB-signal ($\delta_{5'a}$ = 3.77, $\delta_{5'b}$ = 3.85, $J_{A,B}$ = $J_{B,A}$ = 12, additional coupling $J_{5'a,4'}$= 3.6, $J_{5'b,4'}$= 3.2, 2H, 5'-H) 3.95-3.99 (m, 1H, 4'-H), 4.42-4.46 (m, 1H, 3'-H), 6.28 (t, $J_{1',2'}$ = 6.6, 1H, 1'-H), 8.23 (s, 1H, 6-H) ppm.

^{13}C-NMR (100 MHz, inCD_3OD): δ = 18.55, 19.67, 28.62, 28.77, 41.60, 62.61, 69.69, 72.04, 72.82, 84.72, 86.87, 89.06, 94.73, 101.21, 144.23, 151.25, 164.69 ppm.

CHN analysis found (theoretical): C: 61.69 (61.62), H: 5.86 (5.78), N: 8.25 (8.45).

MS [APCI]: m/z (%) = 438.8 (7), 373.8 (5), 332.7 (100) $[M]^+$, 217.0 (25), 96.5(8).

5'-O-[Bis(4-methoxyphenyl)phenylmethyl]-2'-deoxy-5-(octadiynyl)uridine (16)

2'-Deoxy-5-(octadiynyl)-uridine (**15**) (80.0 mg, 0.26 mmol) was dried three times azeotropically with 3 mL of anhydrous pyridine each. Afterwards, it was dissolved in 2 mL of anhydrous pyridine. DMAP (7.33 mg, 0.06 mmol, 0.25 equiv.), NEt_3 (48.7 mg, 0.48 mmol, 2.0 equiv.) and DMT-Cl (97.6 mg, 0.29 mmol, 1.2 equiv.) were added and the reaction mixture was allowed to stir over night at rt. The reaction was quenched with 3 mL of MeOH and the resulting mixture was allowed to stir for an additional 30 min. The solvents were removed under reduced pressure and the residue was purified by CC (silica gel 0-4% (V/V) MeOH in CH_2Cl_2) yielding in 105 mg of the desired compound **16** (65%, 0.17 mmol).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.30-1.44 (m, 4H, 4''-H, 5''-H), 1.88 (t, $^3J_{8'',6''}$ = 2.6, 1H, 8''-H), 2.01(td, $J_{6'',5''}$= 6.8, $J_{6'',8''}$= 2.6, 2H, 6''-H), 2.08-2.12 (m, 2H, 3''-H), 2.22-2.50 (m, 2H, 2'-H), AB-signal ($\delta_{5'a}$ = 3.31, $\delta_{5'b}$ = 3.42, $J_{A,B}$ = $J_{B,A}$ = 10.7, additional coupling $J_{5'a,4'}$= 3.5, $J_{5'b,4'}$= 3.2, 2H, 5´-H), 3.78 (s, 6H, 2× OMe), 4.05-4.08 (m, 1H, 4'-H), 4.48-4.52 (m, 1H, 3'-H), 6.31 (dd, $J_{1',2'a}$= 5.8, $J_{1',2'b}$= 7.6, 1H, 1'-H), 6.81-6.86 (m, 4H, arom. DMT), 7.18-7.45 (m, 9H, arom DMT), 8.00 (s, 1H, 6-H) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ =17.85, 19.03, 27.25, 27.59, 41.49, 55.34, 63.53, 68.52, 71.02, 72.39, 84.23, 85.59, 86.52, 87.10, 94.87, 101.15, 113.40, 127.03, 128.00, 128.11, 130.06, 135.59, 135.64, 141.63, 144.57, 149.33, 158.71, 161.79 ppm.

MS (ESI): m/z (%) = 1941.7 (11), 1394.4 (8), 1290.4 (45) $[2\ M+Na]^+$, 761.1 (23), 657.1 (80) $[M+Na]^+$, 303.2 (100) $[DMT]^+$.

CHN analysis found (theoretical): C: 71.79 (71.91), H: 6.25 (6.03), N: 4.32 (4.41).

1-((2-Azidoethyl)amino)-4-(methylamino)anthraquinone (18)

1-((2-Hydroxyethyl)amino)-4-(methylamino)anthraquinone (Disperse Blue 3) (**17**) (500 mg, 1.69 mmol, 1.0 equiv.) was dissolved in DMF (25 mL) and CBr_4 (559 mg, 1.69 mmol, 1 equiv.), PPh_3 (443 mg, 1.69 mmol, 1.0 equiv.) and NaN_3 (504 mg, 7.77 mmol, 4.6 equiv.) were added and the reaction mixture was stirred over night at rt. Thereafter MeOH (6 mL) was added and the mixture was stirred for additional 15 min. The solvent was evaporated and the residue was purified by CC (silica gel, 0-5% (V/V) MeOH in CH_2Cl_2) yielding in 440 mg of the desired product **18** (81%, 1.37 mmol).

^{1}H-NMR ($CDCl_3$, 400 MH): δ = 3,07 (d, $J_{N\text{-}CH3,\ NH}$ = 5.2, 3H, N-$\underline{CH_3}$), 3.60-3.65 (m, 4H, $\underline{CH_2}$-$\underline{CH_2}$-N_3), 7.20-7.25(m, 2H, 2-H, 3-H), 7.67-7.72(m, 2H, 5-H, 8-H), 8.31-8.36 (m, 2H, 6-H, 7-H), 10.50-10.57 (m, 1H, $\underline{NH}$-CH_3), 10.75-10.83 (m, 1H, $\underline{NH}$-CH_2) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 29.61, 42.07, 51.12, 110.26, 110.89, 122.97, 123.05, 126.15, 126.28, 132.24, 132.42, 134.39, 134.60, 145.27, 147.14, 182.76, 183.38 ppm.

MS ($CI(NH_3)$): m/z (%) 322.1 (100) $[M]^+$, 294.1 (35), 265 (36).

CHN analysis found (theoretical): C: 63.34 (63.54), H: 4.90 (4.71), N: 21.74 (21.79).

5'-O-[Bis(4-methoxyphenyl)phenylmethyl]-2'-deoxy-5-(6-{1-(1-((2-ethyl)amino)-4-(methylamino)anthraquinone)-[1,2,3]-triazol-4-yl]hex-1-yn-1-yl} uridine (36)

Nucleoside **16** (106 mg, 0.17 mmol) was dissolved in a mixture of DMF (4 mL) and H_2O (1.5 mL) Then Hünigs base (279 mg, 367 µL, 2.15 mmol, 13.0 equiv.), quencher **18** (53.6 mg, 0.17 mmol, 1.0 equiv.), $CuSO_4$ (41.7 mg, 0.17 mmol, 1.0 equiv.) and ascorbic acid (294 mg, 1.67 mmol, 10.0 equiv.) were added and the mixture was allowed to stir over night at rt. Afterwards the solvents were removed under reduced pressure. The residue was adsorbed on silica gel and purified by CC (silica gel, 2-10% (V/V) MeOH in CH_2Cl_2) yielding 123 mg of the desired compound **36** (76%, 0.13 mmol).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.32-1.42 (m, 2H, 4''-H), 1.59-1.72 (m, 2H, 5''-H), 2.04-2.10 (m, 2H, 3''-H), 2.26-2.51 (m, 2H, 2'-H), 2.65(t, $J_{6'', 5''}$= 6.9, 2H, 6''-H), 3.07 (d, $J_{\text{N-CH3, NH}}$ = 5.2, 3H, NH-$\underline{CH_3}$), 3.35-3.39 (m, 2H, 5'-H), 3.76 (s, 6H, 2× OMe), 3.87-3.94 (m, 2H, NH-$\underline{CH_2}$-CH_2), 4.05-4.08 (m, 1H, 4'-H), 4.51-4.56 (m, 1H, 3'-H), 4.58-4.63 (m, 2H, NH-CH_2-$\underline{CH_2}$), 6.30-6.35 (m, 1H, 1'-H), 6.78-6.84 (m, 4H, arom. DMT), 7.18-7.45 (m, 11H, 9 H arom. DMT, 2'''-H, 3'''-H), 7.64-7.71 (m, 2H, 5'''-H, 8'''-H), 7.77 (s, 1H, 8''-H), 7.94 (s, 1H, 6-H), 8.26-8.44 (m, 2H,6'''-H, 7'''-H), 10.54-10.63 (m, 1H, $\underline{NH}$-CH_3), 10.92-11.00 (m, 1H, $\underline{NH}$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 19.24, 24.78, 25.13, 27.11, 27.28, 29.53, 37.85, 41.47, 43.02, 45.93, 50.11, 50.25, 55.29, 63.64, 67.49, 70.04, 71.52, 72.26, 76.03, 85.60, 86.30, 86.46, 87.03, 87.08, 88.00, 94.74, 100.87, 109.78, 110.41, 113.34, 113.42, 122.29, 122.46, 122.61, 122.77, 123.48, 126.07, 126.38, 126.98, 127.17, 128.00, 128.05, 128.16, 130.05, 130.07, 130.12, 130.15, 132.22, 132.43, 132.53, 134.19, 134.47, 134.52, 135.60, 135.66,

141.76, 144.40, 144.58, 145.44, 147.22, 148.28, 149.47, 158.65, 158.75, 159.09, 162.39, 176.13, 182.22, 182.38, 182.92 ppm.

MS (ESI): m/z (%) 1931.2 (9) $[2\ M+Na]^+$, 977.7 (100) $[M+Na]^+$, 303.2 (7) $[DMT]^+$.

5'-O-[Bis(4-methoxyphenyl)phenylmethyl]-2´-deoxy-5-{6-[1-(1-((2-ethyl)amino)-4-(methylamino)anthraquinone)-[1,2,3]-triazol-4-yl]hex-1-yn-1-yl}uridine 3'-[2-cyanoethyl-bis(1-methylethyl)phosphoramidite] (10)

Compound **36** (150 mg, 0.16 mmol) and diisopropylammonium tetrazolide (20.0 mg, 0.12 mmol, 0.8 equiv.) were dried three times azeotropically with 5 mL anhydrous acetonitrile each. Under argon, anhydrous CH_2Cl_2 (11 mL) and (2-cyanoethoxy)-bis-(*N*,*N*-diisopropylamino)phosphine (123 mg, 117 µL, 0.4 mmol, 2.6 equiv.) were added and stirred for 2.5 h at rt. The reaction was quenched with 10 mL of degassed saturated $NaHCO_3$ solution. The aqueous phase was extracted three times with 10 mL degassed CH_2Cl_2 each. The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure.

The residue was purified by CC (silica gel, 2% (V/V) MeOH in CH_2Cl_2) yielding in 175 mg of the desired compound **10** (96%, 0.15 mmol).

^{1}H-NMR (CD_3CN, 400 MHz): δ = 1.03-1.19 (m, 12 H, 2× CH($\underline{CH_3}$)$_2$), 1.24-1.29 (m, 2H, 4''-H), 1.46-1.57 (m, 2H, 5''-H), 1.96-2.02 (m, 2H, 3''-H), 2.27-2.55 (m, 4H, 2'-H, CH_2CN), 2.60-2.65 (m, 2H, 6''-H), 3.00-3.03 (m, 3H, N-$\underline{CH_3}$), 3.20-3.30 (m, 2H, 5'-H), 3.52-3.61 (m, 2H, 2× $\underline{CH}(CH_3)_2$), 3.69-3.82 (m, 8H, 2× DMT-OMe, O$\underline{CH_2}$), 3.86-3.93 (m, 2H, NH-$\underline{CH_2}$-CH_2), 4.05-4.08 (m, 1H, 4'-H), 4.51-4.56 (m, 1H, 3'-H), 4.58-4.63 (m, 2H, NH-CH_2-$\underline{CH_2}$), 6.08-6.20 (m, 1H, 1'-H), 6.78-6.84 (m, 4H, arom. DMT), 7.13-7.33 (m, 9H, arom. DMT),

7.37-7.42 (m, 2H, 2’’’-H, 3’’’-H), 7.50-7.51 (m, 1H, 8’’-H), 7.63-7.68 (m, 2H, 5’’’-H, 8’’’-H), 7.76 (s, 1H, 6-H), 8.15-8.24 (m, 2H, 6’’’-H, 7’’’-H), 10.43-10.49 (m, 1H, NH-CH_3), 10.63-10.69 (m, 1H, NH-CH_2) ppm.

^{31}P-NMR (400 MHz, CD_3CN): δ = 153.30 ppm.

MS (ESI): m/z (%) 1178.2 (100) $[M+Na]^+$, 1155.3 (24), 1109.2 (9), 1095.2 (16), 401.2 (27), 303.3 (28) $[DMT]^+$.

5’-O-[Bis(4-methoxyphenyl)phenylmethyl]-2’-deoxy-5-{3{5-[bis[1,10-phenanthrolin-4,7-diylκN, κN´)bis phenyl][4-(7phenyl-1,10-phenanthrolin-4-yl-κN, κN’)]ruthenium(II)chlorid]pentanamid}prop-1-yn-1-yl}uridine (35)

Bis (4,7-diphenyl-1,10-phenanthroline-kN^1,kN^{10})[4-(7-phenyl-1,10-phenanthrolin-4-ylkN^1, kN^{10})benzenepentanoic acid]ruthenium (II) (**33**) (168 mg, 0.13 mmol, 1.0 equiv.) was dissolved in DMF (4 mL). TBTU[29] (43.4 mg, 0.13 mmol, 1.0 equiv.) and Hünigs base (68.4 mg, 90.8 µl, 0.53 mmol, 4.0 equiv.) were added and the mixture stirred for 10 min at rt.

5’-O-[Bis(4-methoxyphenyl)phenylmethyl]-2’-deoxy-5-{3-{{2-acetyl}amino}prop-1-yn-1-yl}uridine **13** (100 mg, 0.17 mmol, 1.3 equiv.) which had been dried three times azeotropically with 5 mL of anhydrous acetonitrile each, was dissolved in 10 mL of DMF and then added to the reaction mixture. The mixture was stirred over night at rt. Thereafter, DMF was removed under reduced pressure. The crude product was dissolved in 10 mL DCM and extracted four times with 10 mL saturated $NaHCO_3$ solution each. The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was used without further purification in the next step.

MS (ESI): m/z (%) 882.0 (100) $[M\text{-}2Cl^{-}\text{-}2H^{+}]^{2+}$, 673.1 (20).

5'-O-[Bis(4-methoxyphenyl)phenylmethyl]-2'-deoxy-5-{3{5-[bis[1,10-phenanthrolin-4,7-diylκN, κN')bis phenyl][4-(7phenyl-1,10-phenanthrolin-4-yl-κN, κN')]ruthenium(II)chlorid]pentanamid}prop-1-yn-1-yl}uridine 3'-[2-cyanoethyl-bis(1-methylethyl)phosphoramidite] (34)

Compound **35** (123 mg, 66.0 µmol) and diisopropylammonium tetrazolide (7.0 mg, 39.0 µmol, 0.6 equiv.) were dried three times azeotropically with 5 mL anhydrous acetonitrile each. Under argon, anhydrous CH_2Cl_2 (8 mL) and (2-cyanoethoxy)-bis-(*N*,*N*-diisopropylamino)phosphine (22.1 mg, 23.0 µl, 70.0 µmol. 1.1 eqiuv.) were added and it was stirred for 2.5 h at rt. Afterwards, the reaction was quenched with 10 mL of degassed saturated $NaHCO_3$ solution and the aqueous phase was extracted three times with 10 mL degassed CH_2Cl_2 each. The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was dried azeotropically with 5 mL of acetonitrile. The product **34** was used directly in the DNA synthesis.

MS (ESI): m/z (%) 1062 (13.29), 990 (100) $[M+O\text{-}2Cl^{-}\text{-}2H^{+}]^{2+}$, 981 (9) $[M\text{-}2Cl^{-}\text{-}2H^{+}]^{2+}$, 898 (20), 672 (32), 417 (13) 303 (12) $[DMT]^{+}$.

Syntheses of the oligonucleotides **19-31**: The modified building blocks (**9**, **10**, **32**) (67 µmol/mL in MeCN) were incorporated into the corresponding oligonucleotide sequences during the automated synthesis using standard DNA synthesis cycles.

The coupling of the hydroxysuccinimide ester of the Ru-complex **33** to the free amino function was carried out in solution. To a solution of the oligo (108 OD, 285 nmol) in a mixture of DMF, 1,4-dioxane and H_2O 1:1:1 (983 µL), Hünigs base (11.2 µL, 65.5 µmol) and

(bathophenanthroline)ruthenium(II) complex hydroxysuccinimide ester (11.2 mg, 8.2 µmol) were added. The mixture was incubated at 25°C in the dark for 24 h. After removal of the solvents, the residue was washed with $CHCl_3$ (3 x 500 µL) to remove excess of Ru-complex (**31-1**).

The modified building block **34** (130 mg, 0.06 mmol) was incorporated manually into the oligonucleotide sequence using 0.7 mL of 0.3 M BMT as activation reagent (**31-2**).

Hybridization: To the DNA strands 20-30 (0.1 OD in 1 µl H_2O) 1.0 eq. of the corresponding complementary DNA-strand 19 or 31 (0.1 OD in 1 µl H_2O) were added and the solvent removed in vacuum. The precipitate was dissolved in phosphate buffer (5 mM, pH 7) and thermal hybridization was performed by heating the sample to 90°C for 2 minutes and then cooling it slowly to room temperature.