**SUPPLEMENTARY INFORMATION.**

**DNA synthesis and irradiation:**

The DNA oligonucleotide 5'-GCGTTT$^{Br}$dUXGAC-3' (1 μmol scale) was synthesized on an *Äkta Oligopilot 10* (*Amersham Biosciences)* DNA synthesizer using ultra-mild phosphoramidites and an Ac-dC-Q-CPG 500 solid support (Glen Research). An elongated coupling protocol was applied for the coupling of the modified bases. The capping was achieved with $Pac_2O$. After automated synthesis ODNs were cleaved from the solid support with 50 mM potassium carbonate in MeOH (50 mM) within three hours at RT. The slurry was concentrated *in vacuo* and the crude ODNs were redissolved in water. Analytics and purification were performed using a *Waters* system equipped with 3 μm $C_{18}$-*reversed phase* Nucleodur columns from *Machery-Nagel*. Eluting buffers were buffer A (0.1 M $NHEt_3OAc$ in $H_2O$) and buffer B (0.1 M $NHEt_3OAc$ in $H_2O$/MeCN 20/80). The elution was monitored at 260 nm. The product was analyzed by MALDI-TOF (Figure 1A). A 1 μM solution of the single strand was irradiated for 45 minutes at 10 °C with a 340 nm longpass filter (Fig 2.) in 150 mM NaCl, 10 mM Tris/HCl-buffer (pH 7.4) after purging it with argone for 40 minutes.

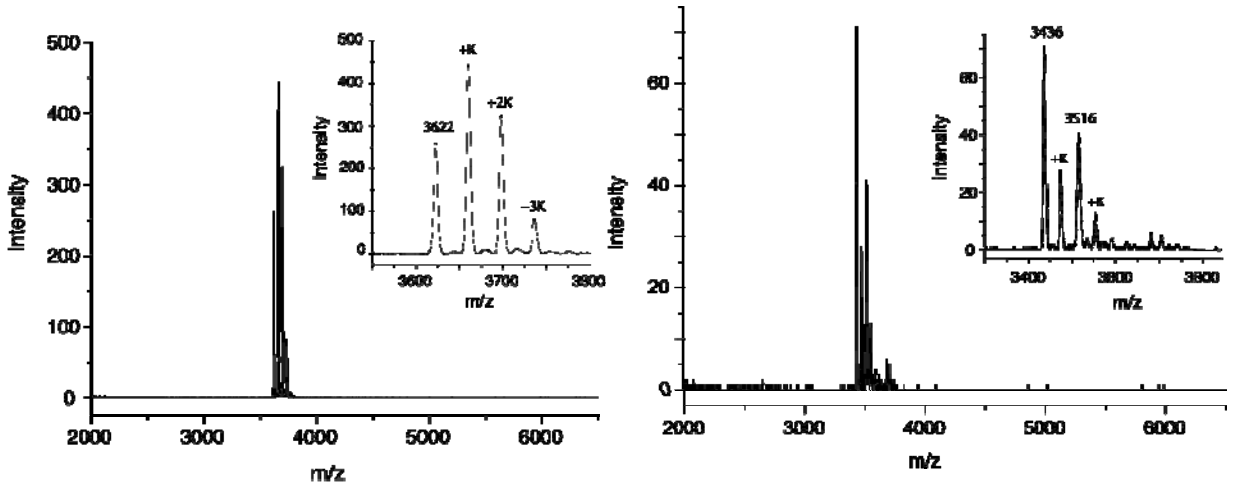



Fig. 1. A) MALDI-TOF analysis of the educt single strand 5'-GCGTTT$^{Br}$dUXGAC-3' where $^{Br}$dU is 5-Br-dU and X is Donor **1**. The strand has an exact mass of 3620 Daltons. B) After 45 minutes of irradiation no educt strand is left and two masses dominate the MALDI-TOF

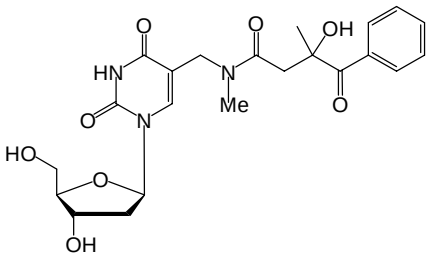
spectra. The main peak at 3436 D corresponds to the debrominated strand and the peak at 3516 D shows Donor cleavage and no debromination.

| λ in nm | 280 | 290 | 300 | 310 | 320 | 330 | 340 | 350 | 360 | 370 | 380 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| k (λ) | 6 | 3.7 | 2.20 | 1.03 | 0.47 | 0.21 | 0.096 | 0.047 | 0.026 | 0.018 | 0.016 |
| λ in nm | 390 | 400 | 410 | 420 | 430 | 440 | 450 | 460 | 470 | 480 | 490 |
| k (λ) | 0.011 | 0.010 | 0.010 | 0.010 | 0.010 | 0.010 | 0.010 | 0.010 | 0.009 | 0.008 | 0.009 |
| λ in nm | 500 | 510 | 520 | 530 | 540 | 550 | 560 | 570 | 580 | 590 | 600 |
| k (λ) | 0.010 | 0.011 | 0.014 | 0.018 | 0.023 | 0.029 | 0.037 | 0.046 | 0.055 | 0.066 | 0.077 |
| λ in nm | 610 | 620 | 630 | 640 | 650 | 660 | 670 | 680 | 690 | 700 | 710 |
| k (λ) | 0.089 | 0.101 | 0.113 | 0.125 | 0.136 | 0.147 | 0.158 | 0.168 | 0.177 | 0.186 | 0.190 |
| λ in nm | 720 | 730 | 740 | 750 | 760 | 780 | 800 | 820 | 840 | 860 | 880 |
| k (λ) | 0.20 | 0.20 | 0.20 | 0.20 | 0.21 | 0.21 | 0.21 | 0.20 | 0.190 | 0.180 | 0.175 |

Figure 2. Absorption coefficients k(λ) of the applied filter (russian C3C17, 3 mm thickness)

Experimental data for compounds **1**-**14**:

Chemicals were purchased from Sigma-Aldrich, Fluka or ACROS and used without further purification. Solvents used were of reagent grade and purified by usual methods. Reactions were monitored on Merck Silica 60 F254 TLC plates. Detection was done by irradiation with UV light (254 nm) and staining with *p*-anisaldehyde solution in ethanol or with a 0.05 M solution of $KMnO_4$ (in 1 M NaOH). Flash column chromatography was performed on Silica 60 (Merck, 230-400 mesh). NMR spectra were recorded on the following spectrometers: *Varian Oxford 200, Bruker AC 300, Varian XL 400* and *Bruker AMX 600*. The chemical shifts (δ) are given in ppm, the coupling constants (*J*) in Hz. Mass spectra were recorded on the following machines: Finnigan MAT 95 (EI), *Bruker Autoflex II* (MALDI-Tof) and Thermo Finnigan LTQ-FT (ESI-ICR).

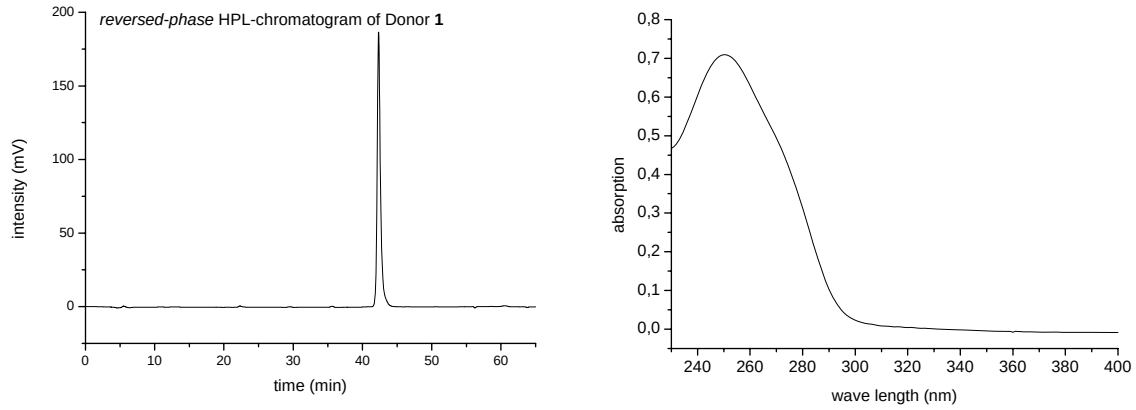



Synthesis of single electron donor **1**:

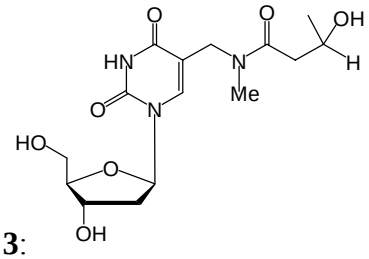
**5** (698 mg, 0.74 mmol) was solved in pyridine (6 mL) and cooled to 0 °C. HF·pyridine (70% HF, 22.2 mmol, 533 µL) was added dropwise. The reaction was stirred for 18 h at 22 °C and finally quenched with $Me_3SiOMe$ (10.2 mL, 74 mmol). After 30 min the solvents were removed *in vacuo* and the residual was chromatographically ($SiO_2$, $CH_2Cl_2$:MeOH, 22:3) purified. Yield: 335 mg (98%). Colorless foam. 4 Diastereoisomers in the ratio 18:18:32:32.

$^1$H-NMR (600 MHz, $CDCl_3$) δ: 1.50 (*s*, Me), 1.51 (*s*, Me), 1.52 (*s*, Me), 1.53 (*s*, Me), 2.04-2.35 (*m*), 2.47-2.61 (*m*), 2.82 (*s*, N-Me), 2.833 (*s*, N-Me), 3.07 (*s*, N-Me), 3.08 (*s*, N-Me), 3.34-3.42 (*m*), 3.53-3.63 (*m*), 3.71-3.73 (*m*), 3.78-3.84 (*m*), 3.87-3.89 (*m*), 3.98-4.00 (*m*), 4.07-4.10 (*m*), 4.16-4.18 (*m*), 4.24-4.33, 4.43-4.54 (*m*), 6.16-6.20 (*m*, 2 x H1'), 6.30 (*t*, H1'), 6.39 (*t*, H1'), 7.33-7.38 (*m*, Ph), 7.42-7.48 (*m*), 7.81 (*s*, H6), 7.83 (*s*, H6), 7.85 (*s*, H6), 7.92

(*s*, H6), 8.14-8.16 (*m*), 10.09 (*s*, 2 x NH), 10.23-10.24 (*m*, 2 x NH); $^{13}$C-NMR (150 MHz, $CDCl_3$) δ: 26.30, 26.46, 26.49, 26.51, 33.69, 33.85, 36.64, 36.68, 40.38, 40.50, 40.60, 40.99, 43.13, 43.35, 43.52, 43.80, 43.90, 44.03, 46.38, 46.48, 61.72, 61.93 (2x), 62.17 71.30, 71.33, 71.38, 71.84, 79.27, 79.30, 79.39 (2x), 85.54, 85.87, 85.98, 86.06, 87.40, 87.45 (2x), 87.54, 108.79, 108.98, 109.58, 109.71, 127.98 (2x), 128.06 (4x), 128.09 (2x), 130.19 (4x), 162.65 (4x), 132.70 (4x), 134.72 (4x), 137.29, 137.64, 139.64 , 140.13, 150.44 (2x), 150.48, 150.58, 163.13, 163.18, 163.72, 163.77, 172.89 ,173.06 (2x) ,173.29 ,204.90 ,205.09, 205.15, 205.34; MS (ESI): calc. for $[C_{22}H_{28}N_3O_8+H]^+$: 462.1876; found: 462.1853.



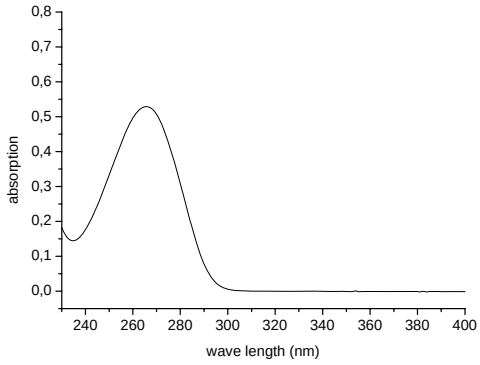

Left: UV-spectr. of **1**: 70 µM in MeOH:$H_2O$ 1:4, $\lambda_{max}$ = 251 nm, $\varepsilon_{260nm}$ = 10120 $M^{-1}cm^{-1}$, $\varepsilon_{340nm}$ = 37 $M^{-1}cm^{-1}$; Right: HPLC (Merck Hitachi, CC 250/4 Nucleosil 100-5 C18) of **1**, gradient: 100% to 25% 0.1 M $NEt_3$/AcOH in $H_2O$ and 75% 0.1 M $NEt_3$/AcOH in MeOH/$H_2O$ 80/20 in 45 min.

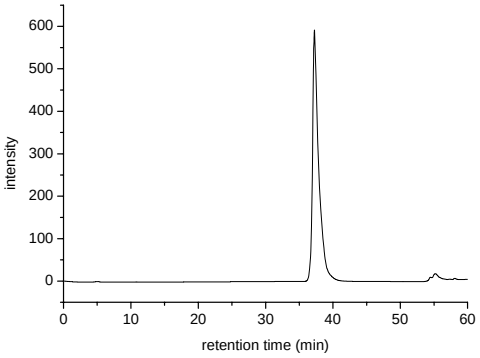


Synthesis of reference molecule **3**:

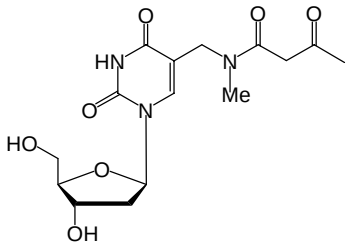
The same deprotection- and work-up procedures as described for **1** were applied to the corresponding 3',5'-TBDPS-ether **14** (214 mg, 0.26 mmol). Yield: 68 mg (74%). Colorless solid. 4 Diastereoisomers in the ratio of about 17:17:33:33.

$^{1}$H-NMR (400 MHz, $CD_3OD$) δ: 1.21 (*s*, 2 x $CH_3$), 1.22 (*s*, 2 x $CH_3$), 2.15-2.33 (*m*, 4 x H2'), 2.46 (*ddd*, *J* = 2.27, 4.44, 15.46 Hz, $CH_2$), 2.58 (*ddd*, *J* = 2.40, 8.17, 15.51 Hz, $CH_2$), 2.63 (*dt*, *J* = 3.17, 4.53 Hz, $CH_2$), 2.71 (*ddd*, *J* = 4.14, 8.00, 15.41 Hz, $CH_2$), 2.87 (*s*, 2 x N-$CH_3$), 3.11 (*s*, 2 x N-CH3), 3.69-3.81 (*m*, 4 x H5'), 3.90-3.94 (*m*, 4 x H4'), 4.15-4.41 (*m*, 4 x (H3', $CH_2$, CH)), 6.25-6.30 (*m*, 4 x H1'), 7.88 (*s*, H6), 7.90 (*s*, H6), 8.01 (*s*, H6), 8.03 (*s*, H6). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 21.91 (4x), 32.06, 32.09, 35.54, 35.55, 39.95 (2x), 40.20, 40.28, 41.26, 41.28, 41.58, 41.59, 43.76, 43.78, 46.28 (2x), 61.22, 61.29, 61.52, 61.55, 64.47, 64.50, 64.75, 64.76, 70.74, 70.83, 70.94, 70.98, 85.17, 85.02, 85.25, 85.29, 87.64 (2x), 87.69 (2x), 109.00 (2x), 109.61, 109.62, 138.70, 138.79, 138.88, 138.94, 150.64 (4x), 163.55, 163.57, 164.01 (2x), 173.02, 173.05, 173.10, 173.12; MS (ESI): calc. for $[C_{15}H_{24}N_3O_7+H]^+$: 358.1614; found: 358.1614.



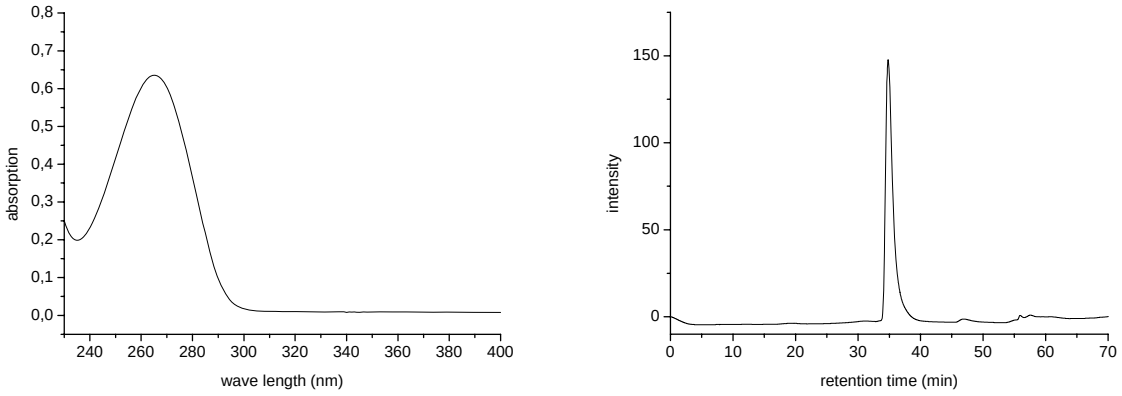

Left: UV-absorption of **3**: 70 μM in MeOH:$H_2O$ 1:4, $\lambda_{max}$ = 266 nm, $\varepsilon_{260nm}$ = 7090 $M^{-1}cm^{-1}$; Right: *reversed-phase* HPLC (Merck Hitachi, CC 250/4 Nucleosil 100-5 C18) of **3**, gradient: 100% to 96% 0.1 M $NEt_3$/AcOH in $H_2O$ and 4% 0.1 M $NEt_3$/AcOH in $CH_3CN/H_2O$ 80/20 in 45 min.



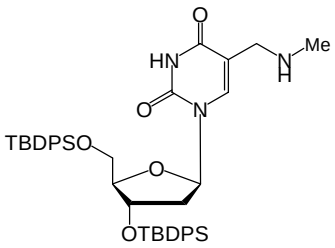

Synthesis of reference molecule **4**:

The same deprotection- and work-up procedures as described for **1** were applied to the corresponding 3',5'-TBDPS-ether **15** (247 mg, 0.3 mmol). Yield: 85 mg (81%). Colorless solid. 2 Conformational isomers in the ratio of about 35:65.

$^{1}$H-NMR (400 MHz, $CD_3OD$) δ: 2.21 (*s*, Me), 2.22 (*s*, Me), 2.23–2.26 (*m*, 2 x H2', 2 x H2''), 2.85 (*s*, NMe), 3.02 (*s*, NMe), 3.28-3.30 (*m*, 2 x $CH_2$), 3.68–3.82 (*m*, 2 x H5', 2 x H5''), 3.88–3.94 (*m*, 2 x H4'), 4.09-4.23 (*m*, 2 x $NCH_2$), 4.33–4.42 (*m*, 2 x H3'), 6.24–6.29 (*m*, 2 x H1'), 7.86 (*s*, H6), 8.06 (*s*, H6); $^{13}$C-NMR (100 MHz, $CD_3OD$) δ: 28.96, 28.99, 31.68, 35.83, 39.62, 40.22, 43.78, 46.83, 47.90 (2x), 61.25, 61.71, 70.68, 70.96, 85.02, 85.30, 87.55, 87.64, 108.56, 109.34, 138.85, 139.45, 150.59, 150.66, 163.61, 163.92, 168.71, 168.92, 203.69, 204.04; MS (ESI): calc. for $[C_{15}H_{22}N_3O_7+H]^+$: 356.1458; found: 358.1456.




Left: UV-absorption: 70 μM in MeOH:$H_2O$ 1:4, $\lambda_{max}$ = 265 nm, $\varepsilon_{260nm}$ = 8770 $M^{-1}cm^{-1}$; right: *reversed-phase* HPLC, gradient: 100% to 96% 0.1 M $NEt_3$/AcOH in $H_2O$ and 4% 0.1 M $NEt_3$/AcOH in $CH_3CN/H_2O$ 80/20 in 45 min.

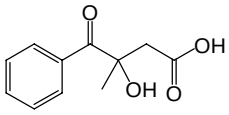



Synthesis of secondary amine **5**:

A solution of 3'- and 5'-TBDPS protected bromo-thymidine[1] (1.9 g, 2.38 mmol) was solved in dry DMF and saturated with $MeNH_2$ at 0 °C. The solution was stirred for 16 h at 22 °C and was finally diluted with AcOEt. The organic phase was washed three times with $H_2O$, dried over $MgSO_4$, concentrated *in vacuo* and chromatographically purified ($SiO_2$, $CH_2Cl_2$: MeOH 15:1). Yield: 1.158 mg (64%). Colorless solid.

$^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.93 (*s*, 9 H, $^t$Bu), 1.08 (*s*, 9 H, $^t$Bu), 1.90 – 2.00 (*m*, 1 H, H2'), 2.15 (*s*, 3 H, Me), 2.34 (*ddd*, *J* = 13.0, 5.2, 1.2 Hz, 1 H, H2''), 3.07 (*dd*, *J* = 11.2, 2.2 Hz, 2 H, $NCH_2$), 3.34 (*dd*, *J* = 11.5, 2.2 Hz, 1 H, H5'), 3.77 (*dd*, *J* = 11.4, 2.2 Hz, 1 H, H5''), 4.00 (*s*, 1 H, H4'), 4.55 (*d*, *J* = 5.5 Hz, 1 H, H3'), 5.63 (*bs*, 1 H, NH), 6.57 (*dd*, *J* = 9.2, 5.4 Hz, 1 H, H1'), 7.30 – 7.65 (*m*, 21 H, H6, 20 x CH(Ph));

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 19.01, 19.29, 26.89 (3x), 26.91 (3x), 34.93, 41.29, 47.75, 63.93, 73.83, 84.93, 87.78, 112.06, 127.87 (2x), 127.90 (4x), 127.91 (2x), 129.98 (2x), 130.01 ,130.03, 132.23, 133.04, 133.06, 133.17, 135.15 (2x), 135.43 (2x), 135.65 (2x), 135.71 (2x), 137.30, 150.38, 163.72; MS (ESI): calc. for $[C_{43}H_{54}N_3O_5Si_2+H]^+$: 748.3602; found: 748.3610.

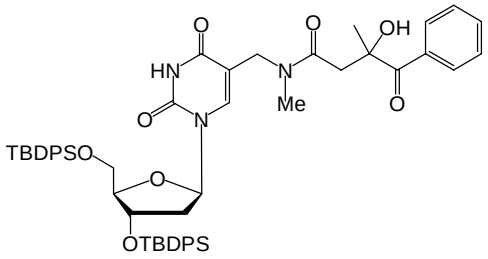



Synthesis of carbonic acid **6**:

A suspension of 11 (1.5 g, 7.72 mmol) and TEMPO (84 mg, 0.54 mmol) in $CH_3CN$ (40 mL) and 1 M phosphate-buffer (29 mL, pH 6.8) was heated to 35 °C. 20% of an aqueous $NaClO_2$-solution (80% (techn.), 1.75 g, 15.45 mmol in 7.8 mL $H_2O$), followed by 20% of an aqueous NaOCl-solution (13% in $H_2O$, 90 µL in 3.81 mL $H_2O$) were added dropwise. The residuals

$NaClO_2$- and NaOCl-solutions were added synchronically within 2 hours. After 29 h at 35 °C the yellow solution was diluted with 60 mL $H_2O$ and the pH was adjusted to 8 with 2 N NaOH. A cooled aqueous solution of $Na_2SO_3$ (2.3 g in 40 mL H2O) was added and the solution was warmed to 22 °C. After 1 h the suspension was washed with TBME and then acidified to pH 3 with 2 N HCl. The suspension was extracted with TBME, the organic phase washed with water, then dried over $MgSO_4$ and concentrated *in vacuo*. Yield: 1.41 g (88%). Colorless oil.

$^1$H-NMR (400 MHz, $CDCl_3$) δ: 1.21 (*s*, 3 H, Me), 2.72 (*d*, *J* = 17.06 Hz, 1 H, $CH_2$), 3.31 (*d*, *J* = 16.98 Hz, 1 H, $CH_2$), 7.44-7.50 (*m*, 2 H, CH), 7.55-7.65 (*m*, 1 H, CH), 8.18-8.21 (*m*, 1 H, CH); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 26.53, 44.00, 78.40, 128.27 (2x), 128.45, 130.13 (2x), 132.93, 177.3, 202.6; MS (ESI): calc. for $[C_{11}H_{11}O_4\text{-}H]^-$: 207.0657; found: 207.0665.

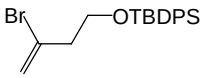



Synthesis of **7**:

A solution of HBTU (287 mg, 0.76 mmol), $NEt(^iPr)_2$ (132 µL, 0.76 mmol) and **6** (143 mg, 0.69 mmol) in dry DMF (8 mL) was stirred at 22 °C. After 30 min a solution of **5** (536 mg, 0.72 mmol) in dry DMF (8 mL) was added and the mixture was heated to 50 °C. After 16 hours AcOEt was added. The organic phase was washed with water three times, dried over $MgSO_4$ and concentrated *in vacuo*. The residual was chromatographically purified ($SiO_2$, $^i$hexanes:AcOEt 1:1). Yield: 580 mg (86%). Colorless solid. 4 Diastereoisomers in the ratio 18:18:32:32.

$^1$H-NMR (600 MHz, $CDCl_3$) δ: 0.87 (*s*, $CH_3$), 0.88 (*s*, $CH_3$), 0.94 (*s*, $CH_3$), 0.9 (*s*, $CH_3$), 1.07 (*s*, $CH_3$), 1.09 (*s*, $CH_3$), 1.11 (*s*, 2 x $CH_3$), 1.52 (*s*, $CH_3$), 1.53 (*s*, $CH_3$), 1.54 (*s*, $CH_3$), 1.55 (*s*,

$CH_3$), 1.74-1.79 (*m*), 1.97-2.03 (*m*), 2.16-2.21 (*m*), 2.26-2.34 (*m*), 2.39-2.45 (*m*), 2.44 (*s*, $NCH_3$), 2.50 (*s*, $NCH_3$), 2.70-2.74 (*m*, $CH_2$), 3.06 (*s*, $NCH_3$), 3.16 (*s*, $NCH_3$), 3.21-3.38 (*m*), 3.43-3.46 (*m*), 3.48-3.56 (*m*), 3.74-3.76 (*m*), 3.85-3.90 (*m*), 3.98-4.03 (*m*), 4.08-4.16 (*m*), 4.30 (*d*, *J* = 5.34 Hz, H3'), 4.47 (*d*, *J* = 5.50 Hz, H3'), 4.57 (*d*, *J* = 5.90 Hz, H3'),4.59 (*d*, *J* = 5.62 Hz, H3'), 6.37 (*dd*, *J* = 8.71, 5.38 Hz, H1'), 6.42 (*dd*, *J* = 8.80, 5.40 Hz, H1'), 6.50 (*dd*, *J* = 8.14, 5.78 Hz, H1'), 6.56 (*dd*, *J* = 8.73, 5.43 Hz, H1'), 7.22-7.69 (*m*), 8.18-8.22 (*m*), 9.66 (*bs*, 2 x NH), 9.79 (*bs*, 2 x NH); $^{13}$C-NMR (150 MHz, $CDCl_3$) δ: 19.01, 19.03, 19.06, 19.07, 19.09, 19.12, 19.34, 19.39, 26.51, 26.52 (2x), 26.57, 26.82 (4x), 26.83 (4x), 26.89 (4x), 26.93 (11x), 26.96, 31.79, 32.15, 36.76, 37.17, 40.44, 40.67, 40.77, 41.02, 42.48, 42.49, 42.60, 42.99, 44.31, 44.40, 45.84, 46.08, 63.87 (2x), 63.95 (2x), 73.51, 73.92, 73.95, 74.00, 79.45, 79.58, 79.67, 79.80, 85.26, 85.28, 85.38, 85.85, 87.85 (2x), 87.93, 88.90, 108.95, 109.12, 109.87, 109.89, 127.68-135.72 (96x), 137.85, 138.75, 139.89, 140.86, 150.12 (2x), 150.23 (2x), 162.78 (2x), 163.71, 163.97, 172.78, 173.09, 173.23, 173.25; MS (ESI): calc. for $[C_{54}H_{64}N_3O_8Si_2+H]^+$: 938.4232; found: 938.4250.

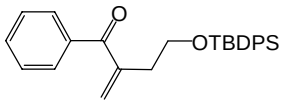



Synthesis of vinylbromide **8**:

A solution of commercially available 3-Bromo-3-buten-1-ol (5 g, 33 mmol), TBDPS-Cl (11.819 g, 43 mmol) and imidazole (6.33 g, 93 mmol) in dry DMF (36 mL) was stirred at 22 °C for 18 hours. The reaction was quenched by the addition of saturated $NaHCO_3$-solution. The mixture was diluted with isohexane. The organic phase was washed with water three times, dried over $MgSO_4$ and concentrated *in vacuo*. The residual was chromatographically purified ($SiO_2$, isohexanes:AcOEt 95:5). Yield: 12.339 g (96%). Colorless oil.

$^1$H-NMR (300 MHz, $CDCl_3$) δ: 1.14 (*s*, 9 H), 2.72 (*td*, *J* = 0.98, 6.21, 6.23 Hz, 2 H), 3.92 (*t*, *J* = 6.21 Hz, 2 H), 5.56 (*d*, *J* = 1.57 Hz, 1 H), 5.68-5.69 (*m*, 1 H), 7.36-7.60 (*m*, 6 H), 7.75-7.79

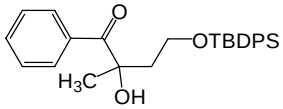
(*m*, 4 H). $^{13}$C-NMR (75 MHz, $CDCl_3$) δ: 19.37, 26.92 (3x), 44.64, 61.54, 118.63, 127.79 (4x), 129.78 (2x), 130.96, 133.71 (2x), 135.70 (4x); MS (EI): calc. for $[C_{20}H_{25}{}^{79}BrOSi\text{-}{}^{t}Bu]^+$: 331.0154; found: 331.0110.




Synthesis of ketone **9**:

A solution of vinylbromid **8** (1 g, 2.57 mmol), $PhB(OH)_2$ (626 mg, 5.14 mmol), $CsCO_3$ (2.51 g, 7.7 mmol) and PEPPSI-IPr (52 mg, 77 μmol) in PhCl (13 mL) was heated to 80 °C while a steady stream of CO was bubbling through it. After 4 hours the reaction mixture was filtered through a pad of Celite, concentrated *in vacuo* and the residual was chromatographically purified ($SiO_2$, isohexane:AcOEt 96:4). Yield: 757 mg (71%). Colorless oil.

$^1$H-NMR (300 MHz, $CDCl_3$) δ: 1.02 (*s*, 9 H, $CH_3$), 2.73 (*td*, *J* = 6.21, 0.79 Hz, 2 H, $CH_2$), 3.85 (*t*, *J* = 6.24 Hz, 2 H, $CH_2$), 5.67 (*d*, *J* = 0.62 Hz, 1 H, =$CH_2$), 5.93 (*m*, 1 H, =$CH_2$), 7.32-7.44 (*m*, 8 H), 7.50-7.56 (*m*, 1 H), 7.64-7.67 (*m*, 4 H), 7.76-7.80 (*m*, 2 H); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ: 19.21, 26.82 (3x), 35.72, 62.55, 127.55, 127.66 (4x), 128.14 (2x), 129.63 (2x), 129.71 (2x), 132.17, 133.73 (2x), 135.58 (4x), 137.81, 145.39, 198.08; MS (ESI): calc. for $[C_{27}H_{30}O_2Si+H]^+$: 415.2088; found: 415.2077.

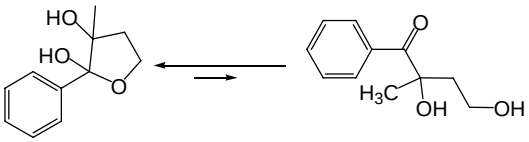



Synthesis of α–hydroxyl-ketone **9**:

A solution of ketone **8** (51 mg, 0.12 mmol) in $^{i}$PrOH (1 mL) was added to a cooled (0 °C) suspension of $Mn(dpm)_3$ (3.7 mg, 6μmol) in $^{i}$PrOH (250 μL). $PhSiH_3$ (30 μL, 0.25 mmol) was added and $O_2$ was bubbled through for 45 min at 0 °C. Then $P(OEt)_3$ (24 μL, 0.14 mmol) was added. After 1 hour at 0 °C the reaction was quenched by the addition of a saturated solution of $Na_2S_2O_3$. The mixture was extracted with $Et_2O$, the organic phase was washed,

dried over $MgSO_4$ and concentrated *in vacuo*. The residual was chromatographically purified ($SiO_2$, isohexane:AcOEt 96:4). Yield: 34 mg (64%). Colorless oil.

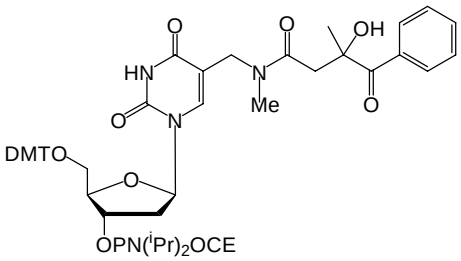
$^1$H-NMR (300 MHz, $CDCl_3$) δ: 0.87 (*s*, 9 H, $CH_3$), 1.59 (*s*, 3 H, $CH_3$), 2.03-2.12 (*m*, 1 H, $CH_2$), 2.39-2.48 (*m*, 1 H, $CH_2$), 3.80-3.85 (*m*, 2 H, $CH_2$), 5.05 (*s*, 1 H, OH), 7.26-7.58 (*m*, 22 H), 8.13-8.17 (*m*, 3 H); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ: 18.86, 26.58 (3x), 28.24, 42.07, 61.21, 79.72, 127.70, 127.76, 128.18, 129.76, 129.82, 130.15 (3x), 132.64 (2x), 132.67, 135.03 (2x), 135.46 (2x), 135.52 (2x), 135.56, 204.87; MS (ESI): calc. for $[C_{27}H_{32}O_3Si+H]^+$: 433,2193; found: 433.2181.




Synthesis of glycol **11**:

Following the procedure of *M. Newcomb*[2], α–hydroxy-ketone **9** (2.0 g, 6.5 mmol) was dissolved in dry THF (35 mL) and stirred under nitrogen atmosphere. Then a solution of 1 M TBAF in THF (13 mL, 13 mmol) was added dropwise over 5 minutes. After stirring 20 minutes at 22 °C the reaction mixture was diluted with EtOAc (50 mL) and washed with saturated $NaHCO_3$ aqueous solution, water and brine (each 20 mL). The organic phase was then dried over $MgSO_4$ and concentrated *in vacuo*. Yield: 1.1 g (86 %). Colorless solid.

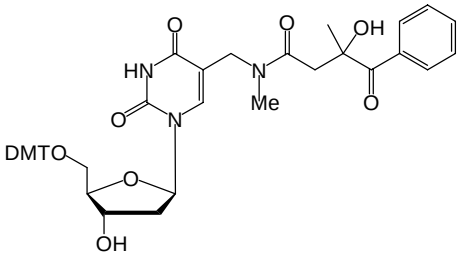
$^1$H-NMR (300 MHz, DMSO-d6) δ: 1.18 (*s*, 3 H, $CH_3$), 1.88 (*ddd*, *J* = 2.4, 7.36, 12.05 Hz, 1 H, $CH_2$), 2.28 (*dt*, *J* = 9.45, 12.03 Hz, 1 H, $CH_2$), 3.93 (*ddd*, *J* = 2.39, 7.62, 9.87 Hz, 1 H, $CH_2$), 4.06 (*dt*, *J* = 7.48, 9.16 Hz, 1 H, $CH_2$), 4.15 (*s*, 1 H, OH), 5.98 (*s*, 1 H, OH), 7.22-7.31 (*m*, 3 H, CH(arom.)), 7.48-7.51 (*m*, 2 H, CH(arom.)). $^{13}$C-NMR (75 MHz, DMSO-d6) δ: 21.66, 39.30, 64.37, 79.78, 106.92, 127.04 (2x), 127.46, 128.32 (2x), 141.56; MS (ESI): calc. for $[C_{11}H_{14}O_3+Cl]^-$: 229.0637; found: 229.0636.




Synthesis of phosphoramidite **12**:

$^{i}Pr_2NH_2$-tetrazolate (54 mg, 0.316 mmol) and P(N $^{i}Pr_2)_2$OCE (100 µL, 0.316 mmol) were added to a cooled (0 °C) solution of **13** (120 mg, 0.158 mmol) in $CH_2Cl_2$ (2.5 ml). After 2.5 hours at 22 °C the reaction was concentrated *in vacuo* and chromatographically purified ($SiO_2$, $CH_2Cl_2$:MeOH 9:1 + 1% pyridine). Yield: 114 mg (75%). Slightly yellow solid.

$^{31}$P-NMR (81 MHz, $CDCl_3$) δ: 149.6-150.5 (*m*); MS (ESI): calc. for $[C_{52}H_{62}N_5O_{11}\text{-}H]^-$: 963.4111; found: 963.4095.

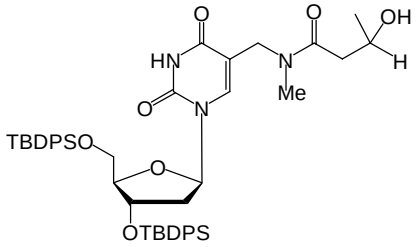



Synthesis of **13**:

Amide **1** (321 mg, 0.7 mmol) was coevaporated with pyridine three times, then solved in pyridine (4 mL) and 3 Å molsieves were added. After 1 hour a solution of DMT-OTf (629 mg, 1.39 mmol) in 2.5 ml pyridine (mixture also stored over 3 Å molsieves) was added. After 4 hours at 22 °C the reaction was quenched by the addition of MeOH, concentrated *in vacuo* and chromatographically purified ($SiO_2$, $CH_2Cl_2$→$CH_2Cl_2$:MeOH 24:1 + 1% pyridine). Yield: 474 mg (89%). Slightly yellow solid. 4 Diastereoisomers in the ratio of 19:19:31:31.

$^{1}$H-NMR (600 MHz, $CDCl_3$) δ: 1.48 (*s*), 1.50 (*s*), 1.52 (*s*), 1.53 (*s*), 1.94-2.05 (*m*), 2.13-2.17 (*m*), 2.2-2.37 (*m*), 2.43-2.47 (*m*), 2.51-2.58 (*m*), 2.61-2.65 (*m*), 3.01 (*s*), 3.12 (*s*), 3.21-3.47 (*m*), 3.72 (*s*), 3.72 (*s*), 3.80-3.87 (*m*), 3.92-4.07 (*m*), 4.40-4.43 (*m*), 4.54-4.58 (*m*), 5.79 (*s*), 5.91 (*s*), 6.01 (*s*), 6.13 (*s*), 6.18 (*t*, *J* = 6.22 Hz), 6.27 (*t*, *J* = 6.42 Hz), 6.37 (*t*,

*J* = 6.62 Hz), 6.42 (*t*, *J* = 6.5 Hz), 6.74-6.78 (*m*), 7.11-7.61 (*m*), 8.17-8.21 (*m*), 9.85 (*bs*), 10.12 (*bs*); $^{13}$C-NMR (150 MHz, $CDCl_3$) δ: 26.58, 26.61, 26.66, 26.71, 32.24, 32.60, 36.89, 37.22, 39.94, 40.14, 40.18, 40.57, 42.45, 42.78 (2x), 43.00, 44.23, 44.58, 46.04, 46.34, 55.33 (2x), 55.35, 55.36, 63.90, 63.95, 64.01, 64.07, 71.42, 71.71, 72.05, 72.07, 79.64, 79.72, 79.76, 79.91, 84.93, 85.22, 85.47 (2x), 85.51, 85.66, 85.75, 86.14, 86.66, 86.67, 86.85, 86.93, 109.22, 109.28, 110.07, 110.21, 113.28, 113.29, 113.36, 113.38, 123.98 (16x), 126.95-136.02, 137.73, 138.95, 139.75, 141.16, 144.43, 144.48, 144.77, 144.79, 150.26, 150.41, 150.43, 150.52, 158.60, 158.62, 158.63, 158.65, 158.79 (2x), 158.81, 158.82, 162.89, 162.92, 163.54, 163.84, 173.03, 173.36, 173.41, 173.49, 204.26, 204.74, 204.87, 204.92; MS (ESI): calc. for $[C_{43}H_{45}N_3O_{10}\text{-}H]^-$: 762.3032; found: 762.3026.

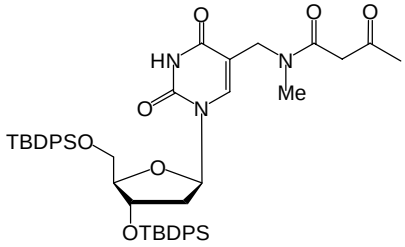



Synthesis of β-hydroxyl-amide **14**:

A solution of HBTU (54 mg, 0.14 mmol), $NEt(iPr)_2$ (27 μL, 0.14 mmol) and 3-hydroxy-butyric acid (13 μL, 0.13mmol) in DMF (1.5 mL) was stirred at 22 °C. After 30 min a solution of amine **5** (100 mg, 0.13 mmol) in DMF (1.5 mL) was added and the mixture was heated to 45 °C. After 24 h the reaction was diluted with AcOEt, washed with water and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residual was chromatographically purified ($SiO_2$, isohexanes:AcOEt 5:3). Yield: 104 mg (93%). Colorless foam. 4 Diastereoisomers.

$^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.93-0.94 (*m*), 1.06-1.07 (*m*), 1.09 (s), 1.16-1.21 (*m*), 1.87-1.99 (*m*), 2.16-2.23 (*m*), 2.30-2.46 (*m*), 2.69-2.74 (*m*), 2.80-2.84 (*m*), 2.97 (s), 3.02-3.06 (*m*), 3.34-3.51 (*m*), 3.66-3.71 (*m*), 3.76-3.99 (*m*), 4.03-4.04 (*m*, 2 x H4'), 4.06-4.07 (*m*, 2 x H4'), 4.08-4.24 (*m*), 4.45-4.48 (*m*, 2 x H3'), 4.55-4.57 (*m*, 2 x H3'), 6.37-6.41 (*m*, 2 x H1'), 6.46-

6.05 (*m*, 2 x H1'), 7.25-7.66 (*m*), 7.74 (*s*), 7.77 (*s*), 9.48 (*bs*), 9.67 (*bs*); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 18.98 (2x), 19.01 (2x), 19.19 (2x), 19.41, 19.42, 22.12 (2x), 22.21, 22.26, 26.87 (18x), 26.96 (6x), 31.25, 31.27, 36.55, 36.54, 40.61, 40.64, 40.93, 41.02, 41.08 (2x), 41.41, 41.58, 44.36, 44.49, 45.69, 45.76, 63.74, 63.77, 63.94, 64.02, 64.09 (2x), 64.42 (2x), 73.43, 73.57, 73.76, 73.92, 84.98, 85.16, 85.51, 85.66, 87.74, 87.83, 87.90, 87.98, 109.10, 109.16, 110.10, 110.13, 127.73-135.68 (96x), 138.45, 138.54, 140.70, 140.77, 150.02, 150.05 (2x), 150.08, 162.59, 162.61, 163.69, 163.71, 172.84, 172.88, 173.05, 173.08; MS (ESI): calc. for $[C_{47}H_{60}N_3O_7Si_2+H]^+$: 834.3970; found: 834.3981.




Synthesis of β-keto-amide **15**:

Amine **5** (150 mg, 0.2 mmol), EDC (43 mg, 0.22 mmol) and HOBt (33 mg, 0.24 mmol) were solved in DMF (2 mL). A solution of 3-oxo-butanoic acid[9] (42 mg, 0.4 mmol) in DMF (1.5 mL) was added dropwise at 0 °C. After 24 h at 22 °C the mixture was diluted with AcOEt, washed with water/brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residual was chromatographically purified ($SiO_2$, isoxexane:AcOEt 5:3 -> 1:1). Yield: 175 mg (63%). Colorless foam. Two conformational isomers in the ratio 6:4.

$^1$H-NMR (400 MHz, $CDCl_3$) δ: 0.92 (*s*, *t*Bu), 1.05 (*s*, *t*Bu), 1.08 (*s*, *t*Bu), 1.86-1.98 (*m*), 2.10 ($CH_3$), 2.20 ($CH_3$), 2.31-2.42 (*m*), 2.90 (*s*, 2 x $CH_3$), 3.19 (*d*), 3.40-3.45 (*m*), 3.65 (*dd*), 3.77-4.07 (*m*), 4.45 (*d*, H3'), 4.54 (*d*, H3'), 6.37 (*dd*, H1'), 6.44-6.48 (*m*, H1'), 7.24-7.69 (*m*), 9.34 (*bs*, NH), 9.59 (*bs*, NH); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ: 19.19 (2x), 19.37, 19.61, 27.04 (3x), 27.07 (6x), 27.15 (3x), 30.25, 30.49, 37.28 (2x), 40.80, 41.64, 44.76, 46.88, 49.91, 50.37,

63.93, 64.24, 73.71, 74.05, 85.27, 85.79, 88.01, 88.14, 109.24, 109.98, 127.93-135.88 (48x), 138.90, 140.41, 150.19, 150.27, 162.99, 163.75, 167.06, 167.43, 202.43, 202.43; MS (ESI): calc. for $[C_{47}H_{58}N_3O_7Si_2+H]^+$: 832.3813; found: 832.3827.

[1]S. Hong, M. M. Greenberg, *Org. Lett.*, 2004, **6**, *26*, 5011-5013.

[2]L. Xu, J. Jin, M. Lal, P. Daublain and M. Newcomb, *Org. Lett.*, 2007, **9**, *9*, 1837-1840.