Supporting Information

PRODAN-conjugated DNA: Synthesis and Photochemical Properties

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Synthetic protocols of ^{PDN}C, ^{PDN}A, and ^{PDN}G

5-[3-(6-Dimethylaminonaphthalen-2-yl)-3-hydroxy-1-propyn-1-yl]-3'*O*,5'*O*-bis(*tert*-butyldimethylsilyl)-2'-deoxycytidine (7). To a solution of 5-iodo-3'*O*,5'*O*-bis(*tert*-butyldimethylsilyl)-2'-deoxycytidine (1.0 g, 1.72 mmol), **2** (320 mg, 1.42 mmol), and triethylamine (780 μL, 5.51 mmol) in DMF (10 mL) were added tetrakis(triphenylphosphine)palladium(0) (398 mg, 0.34 mmol) and copper(I) iodide (131 mg, 0.69 mmol) under nitrogen. The mixture was stirred at room temperature for 3 h. The resulting mixture was concentrated *in vacuo* and diluted ethyl acetate. This solution was washed with 5% (*w/v*) EDTA solution and 5% (*w/v*) sodium bisulfite solution, dried over Na_2SO_4, filtered and evaporated. The crude product was purified by silica gel column chromatography (chloroform-methanol = 50–20 : 1) to yield **7** (890 mg, 1.31 mmol, 92%) as a yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06 (d, 1H, J = 5.1 Hz), 7.77 (s, 1H), 7.68 (d, 1H, J = 9.0 Hz), 7.65 (d, 1H, J = 8.4 Hz), 7.51 (dd, 1H, J = 1.6, 8.4 Hz), 7.16 (dd, 1H, J = 2.6, 9.2 Hz), 6.90 (d, 1H, J = 2.4 Hz), 6.24 (t, 1H, J = 6.2 Hz), 5.93 (brs, 1H), 5.72 (d, 1H, J = 4.0 Hz), 4.35–4.31 (m, 1H), 3.94–3.91 (m, 1H), 3.87 (ddd, 1H, J = 2.7, 6.4, 11.5 Hz), 3.72 (dt, 1H, J = 2.0, 11.4 Hz), 3.05 (s, 6H), 2.44 (ddd, 1H, J = 4.0, 6.0, 13.4 Hz), 2.04–1.96 (m, 1H), 0.87 (s, 9H), 0.81 (s, 9H), 0.05–0.00 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.4, 154.3, 149.0, 143.91, 143.86, 134.9, 133.76, 133.73 128.9, 127.0, 126.31, 126.30, 125.21, 125.15, 124.70, 124.67, 116.77, 116.74, 106.32, 106.26, 96.14, 96.11, 90.1, 88.03, 87.99, 86.76, 86.71, 77.5, 71.4, 65.2, 62.5, 42.5, 40.8, 25.9, 25.7, 18.3, 18.0, –4.6, –4.9, –5.40, –5.43, –5.6; FABMS (NBA/DMSO) *m/z* 679 ($[M + H]^+$), HRMS calcd. for $C_{36}H_{55}O_5N_4Si_2$ ($[M + H]^+$) 679.3706, found 679.3650.

4*N*-(*N*,*N*-Dimethylaminomethylidenyl)-5-[3-(6-dimethylaminonaphthalen-2-yl)-3-hydroxy-1-propyl]-3'*O*,5'*O*-bis(*tert*-butyldimethylsilyl)-2'-deoxycytidine (8). A mixture of **7** (1.68 g, 2.47 mmol) and 10% Pd/C (1.0 g) in ethanol (400 mL) was stirred under hydrogen atmosphere at room temperature for 9 h. The mixture was filtered through celite, washed with methanol and evaporated under reduced pressure. The crude product was purified by silica gel chromatography (ethyl acetate-methanol =

50–10 : 1) to yield the corresponding reduction product (diastereomeric mixture, 1.35 g, 1.98 mmol, 80 %) as a white solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.64 (dd, 1H, J = 2.2, 9.2 Hz), 7.62–7.60 (m, 2H), 7.47 and 7.46 (s×2, total 1H), 7.32 (d, 1H, J = 8.6 Hz), 7.13 (dd, 1H, J = 2.4, 9.2 Hz), 6.89 and 6.88 (s×2, total 1H),6.61 (brs, 2H), 6.28 (t, 1H, J = 6.8 Hz), 4.79 and 4.77 (t×2, total 1H, J = 2.9 Hz), 4.32 and 4.30 (quartet×2, total 1H, J = 3.2 Hz), 3.87 (quartet, 1H, J = 2.7 Hz), 3.78 (dd, 1H, J = 3.1, 11.4 Hz), 3.70 (dt, 1H, J = 2.9, 11.2 Hz), 3.02 (s, 6H), 2.50–2.43 (m, 2H), 2.38–2.31 (m, 1H), 2.04–1.98 (m, 1H), 1.94–1.83 (m, 2H), 0.87 (d, 9H, J = 2.4 Hz), 0.84 (d, 9H, J = 5.7 Hz), 0.04 (t, 6H, J = 3.3 Hz), 0.01 (t, 6H, (d, 9H, J = 5.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.2, 165.0, 155.7, 148.7, 138.29, 138.25, 137.7, 134.6, 128.7, 126.69, 126.67, 126.50, 126.49, 124.19, 124.15, 116.7, 106.4, 106.0, 87.5, 85.82, 85.79, 73.0, 72.8, 71.9, 71.8, 62.8, 62.7, 41.9, 40.8, 38.4, 38.2, 25.9, 25.7, 23.8, 23.7, 18.33, 18.31, 18.0, –4.6, –4.9, –5.43, –5.46, –5.49; FABMS (NBA/PEG/DMSO) *m/z* 683 ($[M + H]^+$), HRMS calcd. for $C_{36}H_{59}O_5N_4Si_2$ ($[M + H]^+$) 683.4019, found 683.4012.

To a solution of the previous reaction product (4.06 g, 5.94 mmol) in DMF (10 mL) was added *N*,*N*-dimethylformamide dimethylacetal (876 μL, 6.54 mmol). The mixture was stirred at 60 ˚C for 3 h. The resulting mixture was evaporated and purified by silica gel column chromatography (chloroform-methanol = 20 : 1) to yield **8** (3.54 g, 4.80 mmol, 81%) as a yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.89 (s, 1H), 7.77 and 7.71 (s×2, total 1H), 7.66 (dd, 1H, J = 2.0, 9.0 Hz), 7.63–7.60 (m, 2H), 7.36–7.31 (m, 1H), 7.15 and 7.14 (dd×2, total 1H, J = 1.1, 9.0 Hz), 6.91 and 6.90 (s×2, total 1H), 6.42 and 6.39 (t×2, total 1H, J = 6.4 Hz), 4.64 and 4.62 (dd×2, total 1H, J = 3.5, 6.2 Hz), 4.41–4.35 (m, 1H), 3.96–3.84 (m, 2H), 3.77 and 3.74 (t×2, total 1H, J = 2.7 Hz), 3.183 and 3.179 (s×2, total 3H), 3.16 and 3.15 (s×2, total 3H), 3.028 and 3.025 (s×2, total 6H), 2.53–2.43 (m, 2H), 2.08–1.97 (m, 2H), 1.87–1.80 (m, 1H), 0.89–0.87 (m, 18H), 0.08–0.06 (m, 12H); ^{13}C NMR($CDCl_3$, 100 MHz) δ 170.4, 158.84, 158.81, 156.0, 148.5, 140.2, 140.0, 138.0, 134.3, 128.69, 128.66, 126.8, 126.4, 124.65, 124.62, 124.06, 124.00. 116.57, 116.55, 113.4, 113.0, 106.5, 87.8, 87.6, 86.4, 86.1, 71.8, 71.7, 71.4, 71.1, 62.8,

62.7, 42.3, 42.2, 41.9, 41.8, 41.2, 40.95, 40.86, 35.72, 35.67, 25.94, 25.93, 25.8, 24.0, 23.7, 18.41, 18.37, 18.0, –4.6, –4.9, –5.4; FABMS (NBA/PEG/DMSO) *m/z* 737 ($[M]^+$), HRMS calcd. for $C_{39}H_{63}O_5N_5Si_2$ ($[M]^+$) 737.4368, found 737.4371.

4*N*-(*N,N*-Dimethylaminomethylidenyl)-5-PRODAN-3'*O*,5'*O*-bis(*tert*-butyldimethylsilyl)-2'-deoxycytidine (9). To a solution of **8** (1.64 g, 2.11 mmol) and molecular sieves (4 Å, 1.0 g) in dichloromethane (20 mL) was added 4-methylmorpholine *N*-oxide (371 mg, 3.17 mmol) and tetrapropylammonium perruthenate (148 mg, 0.42 mmol) at 0 ˚C, and the mixture was stirred at room temperature for 2 h. After diluted with diethyl ether (100 mL), Florisil (60-100 mesh, 500 mg) was added to the solution and the resulting mixture was stirred at room temperature for 15 min. The mixture was filtered through Celite, washed with diethyl ether and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (chloroform-methanol = 50 : 1) to yield **9** (1.18 g, 1.52 mmol, 72 %) as a lemon yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.78 (s, 1H), 8.29 (d, 1H, J = 1.6 Hz), 7.92 (dd, 1H, J = 1.8, 8.6 Hz), 7.76 (d, 1H, J = 9.2 Hz), 7.73 (s, 1H), 7.62 (d, 1H, J = 8.8 Hz), 7.16 (dd, 1H, J = 2.6, 9.2 Hz), 6.86 (d, 1H, J = 2.4 Hz), 6.40 (t, 1H, J = 6.6 Hz), 4.37 (dt, 1H, J = 3.5, 6.2 Hz), 3.93 (q, 1H, J = 3.3 Hz), 3.85 (dd, 1H, J = 3.3, 11.2 Hz), 3.78 (dd, 1H, J = 3.3, 11.4 Hz), 3.42–3.25 (m, 2H), 2.95–2.86 (m, 2H), 3.12 (s, 3H), 3.10 (s, 6H), 3.05 (s, 3H), 2.43 (ddd, 1H, J = 3.5, 6.0, 13.4 Hz), 2.01–1.94 (m, 1H), 0.89 (s, 9H), 0.88 (s, 9H), 0.09 (s, 6H), 0.06 (d, 6H, J = 1.1 Hz); ^{13}C NMR($CDCl_3$, 100 MHz) δ 199.2, 170.4, 157.9, 156.2, 150.2, 139.1, 137.6, 130.6, 129.7, 126.1, 125.1, 124.6, 116.3, 113.4, 105.3, 87.7, 86.1, 71.9, 62.9, 41.9, 41.1, 40.4, 38.6, 35.1, 25.9, 25.8, 24.1, 18.4, 18.0, –4.6, –4.9, –5.3, –5.4; FABMS (NBA/PEG/DMSO) *m/z* 736 ($[M + H]^+$), HRMS calcd. for $C_{39}H_{62}O_5N_5Si_2$ ($[M + H]^+$) 736.4290, found 736.4295.

4-*N*-Acetyl-5-PRODAN-2'-deoxycytidine (10). To a solution of **9** (1.45 g, 1.97 mmol) in methanol (40 mL) was added 28% ammonia (10 mL) at 0 ˚C, and the mixture was stirred at 50 ˚C for 2 h. The resulting mixture was evaporated to yield crude product (1.34 g, 1.97 mmol, *quant.*). To a solution of crude product in pyridine (10 mL) was added acetic acid anhydrous (187 μL, 1.97 mmol) at room

temperature, and the mixture was stirred at 50 ˚C for 4 h. The resulting mixture was diluted with *sat. aq.* NH_4Cl at 0 ˚C, extracted with ethyl acetate. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography (hexane-ethyl acetate = 2 : 1) to yield the acetyl-protected deoxycytidine (1.20 g, 1.67 mmol, 85%) as a lemon yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 13.1 (brs, 1H), 8.34 (s, 1H), 7.96 (s, 1H), 7.78 (d, 1H, J = 8.8 Hz), 7.72 (s, 1H), 7.63 (d, 1H, J = 8.8 Hz), 7.17 (dd, 1H, J = 2.4, 9.3 Hz), 6.87 (d, 1H, J = 2.4 Hz), 6.28 (t, 1H, J = 6.3 Hz), 4.43–4.36 (m, 1H), 3.99–3.95 (m, 1H), 3.87-3.77 (m, 2H), 3.42–3.27 (m, 2H), 3.11 (s, 6H), 2.84 (t, 2H, J = 6.8 Hz), 2.28 (s, 3H), 2.02–1.96 (m, 1H), 0.89 (s, 18H), 0.11 (s, 6H), 0.08 (s, 6H); ^{13}C NMR($CDCl_3$, 100 MHz) δ 199.2, 150.2, 138.2, 137.7, 130.7, 129.9, 126.1, 124.9, 124.5, 116.3, 113.4, 105.2, 88.0, 85.5, 72.2, 63.0, 41.3, 40.3, 37.4, 28.9, 25.9, 25.7, 23.6, 18.4, 17.9, –4.7, –4.9, –5.4; FABMS (NBA/DMSO) *m/z* 722 ($[M + H]^+$), HRMS calcd. for $C_{38}H_{58}O_6N_4Si_2$ ($[M + H]^+$) 722.3895, found 722.4093.

To a solution of the previous reaction product (824 mg, 1.14 mmol) in THF (5 mL) was added TBAF (1 M solution in THF, 2.51 mL, 2.51 mmol). The mixture was stirred at room temperature for 3 h. The resulting mixture was evaporated and purified by silica gel column chromatography (chloroform-methanol = 20 : 1) to yield **10** (539 mg, 1.09 mmol, 96%) as a lemon yellow solid; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.93 (brs, 1H), 8.44 (s, 1H), 8.30 (s, 1H), 7.89 (d, 1H, J = 9.3 Hz), 7.83 (dd, 1H, J = 1.0, 8.8 Hz), 7.67 (d, 1H, J = 8.8 Hz), 7.26 (dd, 1H, J = 2.4, 9.3 Hz), 6.93 (d, 1H, J = 2.4 Hz), 6.12 (t, 1H, J = 6.3 Hz), 5.25 (brs, 1H), 5.14 (brs, 1H), 4.27–4.21 (m, 1H), 4.13–4.04 (m, 1H), 3.84 (quartet, 1H, J = 3.4 Hz), 3.68–3.53 (m, 2H), 3.37–3.27 (m, 3H), 3.05 (s, 6H), 2.76 (t, 1H, J = 7.3 Hz), 2.23 (s, 3H), 2.09–2.03 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 198.1, 150.2, 137.2, 130.6, 130.0, 129.6, 129.0, 126.0, 125.9, 125.5, 124.5, 123.9, 123.7, 123.5, 116.4, 104.7, 87.8, 85.2, 79.2, 69.8, 60.9, 48.6, 37.2, 22.1; FABMS (Glycerol/PEG/DMSO) *m/z* 495 ($[M + H]^+$), HRMS calcd. for $C_{26}H_{31}O_6N_4$ ($[M + H]^+$) 495.2238, found 495.2236.

4-*N*-Acetyl-5-PRODAN-5'*O*-(4,4'-dimethoxytrityl)-2'-deoxycytidine

3'*O*-(2-cyanoethyl)-*N,N*-diisopropylphosphoramidite (11). To a solution of **10** (500 mg, 1.01 mmol) in pyridine (5 mL) was added 4,4'-dimethoxytrityl chloride (411 mg, 1.21 mmol). The mixture was stirred at room temperature for 3 h. The resulting mixture was evaporated and purified by silica gel column chromatography (chloroform-methanol = 50 : 1) to yield the tritylated deoxycytidine (724 mg, 0.91 mmol, 90%) as a lemon yellow solid; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.92 (brs, 1H), 8.26 (s, 1H), 7.89 (s, 1H), 7.82 (d, 1H, J = 9.3 Hz), 7.69 (d, 1H, J = 8.3 Hz), 7.62 (d, 1H, J = 8.8 Hz), 7.35 (d, 2H, J = 7.8 Hz), 7.26–7.21 (m, 7H), 7.12 (t, 1H, J = 7.8 Hz), 6.93 (d, 1H, J = 2.0 Hz), 6.81 (d, 4H, J = 8.8 Hz), 6.16 (t, 1H, J = 6.3 Hz), 5.32 (d, 1H, J = 4.9 Hz), 4.26–4.21 (m, 1H), 3.96 (dd, 1H, J = 4.4, 7.8 Hz), 3.632 (s, 3H), 3.627 (s, 3H), 3.25–3.21 (m, 2H), 3.06 (s, 6H), 2.64–2.52 (m, 1H), 2.34–2.28 (m, 1H), 2.24 (s, 3H), 2.20–2.13 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 197.7, 158.1, 150.1, 144.6, 137.2, 135.4, 135.2, 130.6, 129.8, 129.70, 129.65, 129.5, 127.8, 127.6, 126.7, 125.8, 124.4, 123.8, 116.4, 113.2, 104.7, 86.0, 85.8, 79.2, 70.3, 63.6, 54.9, 37.6, 21.9; FABMS (Glycerol/PEG/DMSO) *m/z* 797 ([M + H]$^+$), HRMS calcd. for $C_{47}H_{49}O_8N_4$ ([M + H]$^+$) 797.3550, found 797.3555.

To a solution of the tritylated deoxycytidine (40 mg, 50.2 μmol) and tetrazole (3.54 mg, 50.2 μmol) in anhydrous acetonitrile (500 μL) was added 2-cyanoethyl tetraisopropylphosphorodiamidite (15.8 μL, 50.2 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The mixture was filtered and used with no further purification.

8-[3-(6-Dimethylaminonaphthalen-2-yl)-3-hydroxy-1-propyn-1-yl]-3'*O*,5'*O*-bis(*tert*-butyldimethylsilyl)-2'-deoxyadenosine (12). To a solution of 8-bromo-3'*O*,5'*O*-bis(*tert*-butyldimethylsilyl)-2'-deoxyadenosine (1.9 g, 3.4 mmol), **2** (700 mg, 3.1 mmol), and triethylamine (1.43 mL, 10 mmol) in DMF (30 mL) was added tetrakis(triphenylphosphine)palladium(0) (718 mg, 0.62 mmol) and copper(I) iodide (240 mg, 1.26 mmol) under nitrogen. The mixture was stirred at room temperature for 17 h. The resulting mixture was concentrated *in vacuo* and diluted ethyl acetate. This solution was washed with 5% (*w/v*) EDTA solution and 5% (*w/v*) sodium bisulfite solution, dried over Na_2SO_4, filtered and evaporated. The crude product

was purified by silica gel column chromatography (chloroform-methanol = 50 : 1) to yield **12** (1.33 g, 1.89 mmol, 61%) as a brown solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (s, 1H), 7.90 (s, 1H), 7.70 (d, 1H, J = 8.8 Hz), 7.66 (dd, 1H, J = 2.0, 8.8 Hz), 7.58 (ddd, 1H, J = 1.6, 5.6, 8.4 Hz), 7.16 (dd, 1H, J = 2.4, 9.2 Hz), 6.89 (d, 1H, J = 2.8 Hz), 6.49 (t, 1H, J = 6.4 Hz), 5.85 (d, 1H, J = 6.8 Hz), 5.82 (brs, 2H), 4.78 (ddd, 1H, J = 3.6, 5.6, 17.6 Hz), 3.97–3.86 (m, 2H), 3.67 (ddd, 1H, J = 2.4, 4.8, 10.4 Hz), 3.46 (quintet, 1H, J = 6.0 Hz), 3.05 (s, 6H), 2.20 (ddd, 1H, J = 4.0, 6.8, 17.2 Hz), 0.89 (s, 9H), 0.83 (s, 9H), 0.10–0.09 (m, 6H), –0.01 (s, 3H), –0.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.0, 153.3, 149.4, 149.1, 135.1, 134.8, 132.5, 129.1, 127.12, 127.07, 126.3, 125.8, 125.6, 124.89, 124.85, 116.7, 106.2, 87.87, 87.84, 85.2, 72.6, 65.1, 65.0, 63.0, 40.8, 37.3, 18.4, 18.0, –4.7, –4.8, –5.4, –5.5; FABMS (NBA/$CHCl_3$) *m/z* 702 ($[M + H]^+$), HRMS calcd. for $C_{37}H_{54}O_4N_6Si_2$ ($[M + H]^+$) 702.3745, found 702.3763.

6*N*-(*N*,*N*-Dimethylaminomethylidenyl)-8-[3-(6-dimethylaminonaphthalen-2-yl)-3-hydroxy-1-propyl]-3'*O*,5'*O*-bis(*tert*-butyldimethylsilyl)-2'-deoxyadenosine (13). A mixture of **12** (1.33 g, 1.89 mmol) and 5% Pd/C (1.5 g) in methanol (50 mL) was stirred under hydrogen atmosphere at room temperature for 2 days. The mixture was filtered through Celite, washed with methanol and evaporated under reduced pressure. The crude product was purified by silica gel chromatography (chloroform-methanol = 50 : 1) to yield the corresponding reduction product (diastereomeric mixture, 604 mg, 0.86 mmol, 45%) as a brown solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.244 and 8.241 (s×2, total 1H), 7.68–7.66 (m, 2H), 7.65 and 7.63 (s×2, total 1H), 7.37 (dd, 1H, J = 1.6, 8.4 Hz), 7.16 (dd, 1H, J = 2.4, 9.2 Hz), 6.91 (d, 1H, J = 2.4 Hz), 6.22 and 6.18 (t×2, total 1H, J = 6.8 Hz), 5.57 (brs, 2h), 4.98 and 4.93 (t×2, total 1H, J = 6.0 Hz), 4.78 and 4.77 (t×2, total 1H, J = 3.6 Hz), 3.93–3.83 (m, 2H), 3.67–3.54 (m, 2H), 3.13–3.07 (m, 2H9, 3.04 (s, 6H), 2.44–2.36 (m, 2H), 2.19–2.11 (m, 1H), 0.62 (d, 9H, J = 2.8 Hz), 0.81 (d, 9H, J = 4.8 Hz), 0.12 (s, 6H), –0.02– –0.06 (m, 6H); FABMS (NBA/$CHCl_3$) *m/z* 707 ($[M + H]^+$), HRMS calcd. for $C_{37}H_{58}O_4N_6Si_2$ ($[M + H]^+$) 707.4136, found 707.4135.

To a solution of the previous reaction product (604 mg, 0.85 mmol) in DMF (5 mL) was added *N*,*N*-dimethylformamide dimethylacetal (6.8 mL, 50 mmol). The mixture was stirred at room

temperature for 6 h. The resulting mixture was evaporated and purified by silica gel column chromatography (chloroform) to yield **13** (diastereomeric mixture, 483 mg, 0.63 mmol, 75%) as a yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.89 (s, 1H), 8.452 and 8.450 (s×2, total 1H), 7.67-7.62 (m, 3H), 7.38 (dt, 1H, J = 1.2, 8.8 Hz), 7.15 (dd, 1H, J = 2.4, 9.2 Hz), 6.91 (d, 1H, J = 2.4 Hz), 6.28 and 6.22 (t×2, total 1H, J = 6.8 Hz), 5.00–4.93 (m, 1H), 4.80–4.75 (m, 1H), 3.92–3.86 (m, 2H), 3.68–3.65 (m, 1H), 3.58 and 3.55 (quintet×2, total 1H, J = 6.8 Hz), 3.24 (s, 3H), 3.19 and 3.18 (s×2, total 3H), 3.16–3.05 (m, 2H), 3.03 (s, 6H), 2.48–2.37 (m, 2H), 2.16 and 2.15 (ddd×2, total 1H, J = 4.0, 6.4, 12.0 Hz), 1.44–1.33 (m, 1H), 0.93 and 0.92 (s×2, total 9H), 0.83 and 0.82 (s×2, total 9H), 0.13 and 0.12 (s×2, total 6H), –0.02 and –0.05 (d×2, total 6H, J = 3.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.4, 158.0, 155.1, 152.7, 151.6, 148.6, 138.1, 138.0, 134.38, 134.35, 130.9, 128.8, 128.7, 126.6, 126.5, 124.9, 124.8, 124.4, 124.1, 116.6, 106.5, 87.4, 84.2, 84.1, 73.6, 73.5, 72.5, 72.4, 68.1, 62.9, 62.8, 41.2, 40.9, 38.7, 37.3, 36.1, 35.7, 35.1, 30.3, 29.7, 28.9, 25.8, 25.0, 24.9, 23.7, 23.0, 18.3, 18.0, 14.0, 10.9, –4.7, –4.8, –5.4, –5.5; FABMS (NBA/$CHCl_3$) *m/z* 762 ($[M + H]^+$), HRMS calcd. for $C_{40}H_{63}O_4N_7Si_2$ ($[M + H]^+$) 762.4558, found 762.4568.

6*N*-(*N*,*N*-Dimethylaminomethylidenyl)-8-PRODAN-2'-deoxyadenosine (14). To a solution of **13** (116 mg, 0.15 mmol) and molecular sieves (4 Å, 75 mg) in dichloromethane (5 mL) was added 4-methylmorpholine *N*-oxide (26 mg, 0.23 mmol) and tetrapropylammonium perruthenate (5 mg, 0.014 mmol) at 0 ˚C, and the mixture was stirred at room temperature for 15 h. After diluted with diethyl ether (50 mL), Florisil (60-100 mesh, 50 mg) was added to the solution and the resulting mixture was stirred at room temperature for 15 min. The mixture was filtered through Celite, washed with diethyl ether and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (chloroform) to yield the PRODAN derivative (37 mg, 0.05 mmol, 32 %) as a lemon yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.85 (s, 1H), 8.45 (s, 1H), 8.44 (d, 1H, J = 1.2 Hz), 7.98 (dd, 1H, J = 2.0, 8.8 Hz), 7.80 (d, 1H, J = 8.8 Hz), 7.64 (d, 1H, J = 8.8 Hz), 7.17 (dd, 1H, J = 2.4, 9.2 Hz), 6.87 (d, 1H, J = 2.4 Hz), 6.44 (t, 1H, J = 7.2 Hz), 4.83 (dt, 1H, J = 3.6, 6.0 Hz), 3.97–3.62 (m, 5H),

3.47–3.41 (m, 2H), 3.20 (s, 3H), 3.11 (s, 6H), 2.99 (s, 3H), 2.27 (ddd, 1H, J = 4.0, 6.8, 13.2 Hz), 0.94 (s, 9H), 0.82 (s, 9H), 0.15 (d, 6H, J = 1.2 Hz), –0.03 (d, 6H, J = 15.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.8, 158.1, 154.5, 152.96, 151.4, 150.3, 137.7, 130.7, 130.3, 130.1, 126.2, 125.3, 125.1, 124.5, 116.3, 105.3, 87.5, 84.1, 72.5, 62.9, 41.0, 40.4, 37.4, 35.5, 35.1, 25.9, 22.7, 18.3, 18.1, –4.6, –4.7, –5.4, –5.5; FABMS (NBA/$CHCl_3$) *m/z* 760 ($[M + H]^+$), HRMS calcd. for $C_{40}H_{61}O_4N_7Si_2$ ($[M + H]^+$) 760.4402, found 760.4403.

To a solution of the PRODAN derivative (37 mg, 0.05 mmol) in THF (500 μL) was added TBAF (1 M solution in THF, 125 μL, 0.13 mmol). The mixture was stirred at room temperature for 3 h. The resulting mixture was evaporated and purified by silica gel column chromatography (chloroform-methanol = 50 : 1) to yield **14** (24 mg, 0.045 mmol, 92%) as a lemon yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.87 (s, 1H), 8.44 (s, 1H), 8.42 (d, 1H, J = 1.6 Hz), 7.95 (dd, 1H, J = 1.6, 8.8 Hz), 7.79 (d, 1H, J = 9.2 Hz), 7.63 (d, 1H, J = 8.8 Hz), 7.16 (dd, 1H, J = 2.4, 7.6 Hz), 6.86 (d, 1H, J = 2.8 Hz), 6.57 (dd, 1H, J = 5.6, 9.6 Hz), 4.84 (dd, 1H, J = 4.4, 5.2 Hz), 4.25 (s, 1H), 4.01 (dd, 1H, J = 1.6, 12.8 Hz), 3.89–3.70 (m, 4H), 3.41–3.25 (m, 3H), 3.23 (s, 3H), 3.11 (s, 6H), 3.04 (s, 3H), 2.37 (dd, 1H, J = 6.8, 13.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.5, 159.0, 158.3, 153.2, 151.8, 151.0, 150.3, 137.8, 130.8, 130.2, 130.0, 126.2, 125.0, 124.4, 116.3, 105.2, 89.5, 86.3, 73.8, 63.6, 41.2, 40.4, 35.5, 35.2, 24.1, 22.4, 20.2, 19.7; FABMS (DTT/TG/$CHCl_3$) *m/z* 532 ($[M + H]^+$), HRMS calcd. for $C_{28}H_{33}O_4N_7$ ($[M + H]^+$) 532.2672, found 532.2683.

6*N*-(*N*,*N*-Dimethylaminomethylidenyl)-8-PRODAN-5'*O*-(4,4'-dimethoxytrityl)-2'-deoxyadenosine 3'*O*-(2-cyanoethyl)-*N*,*N*-diisopropylphosphoramidite (15). To a solution of **14** (49 mg, 0.092 mmol) in pyridine (3 mL) was added 4,4'-dimethoxytrityl chloride (37 mg, 0.11 mmol). The mixture was stirred at room temperature for 3 h. The resulting mixture was evaporated and purified by silica gel column chromatography (chloroform-methanol = 50 : 1) to yield the tritylated compound (38 mg, 0.046 mmol, 49%) as a lemon yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.82 (s, 1H), 8.39 (d, 1H, J = 1.2 Hz), 8.30 (s, 1H), 7.93 (dd, 1H, J = 2.0, 8.8 Hz), 7.74 (d, 1H, J = 9.2 Hz), 7.60 (d, 1H, J = 8.4 Hz), 7.38

(d, 2H, *J* = 7.2 Hz), 7.27 (s, 1H), 7.25 (s, 1H), 7.20–7.10 (m, 5H), 6.83 (d, 1H, *J* = 2.8 Hz), 6.74–6.71 (m, 4H), 6.49 (t, 1H, *J* = 5.6 Hz), 4.93–4.89 (m, 1H), 4.11 (d, 1H, *J* = 4.4 Hz), 3.77–3.73 (m, 2H), 3.702 (s, 3H), 3.698 (s, 3H), 3.66–3.56 (m, 1H), 3.45–3.37 (m, 4H), 3.17 (s, 3H), 3.08 (s, 6H), 2.95 (s, 3H), 2.38 (ddd, 1H, *J* = 4.4, 7.2, 13.6 Hz); FABMS (NBA/$CHCl_3$) *m/z* 834 ($[M + H]^+$), HRMS calcd. for $C_{49}H_{51}O_6N_7$ ($[M + H]^+$) 834.3979, found 834.3984.

To a solution of the tritylated nucleoside (37 mg, 40 μmol) and tetrazole (3.1 mg, 44 μmol) in anhydrous acetonitrile (400 μL) was added 2-cyanoethyl tetraisopropylphosphorodiamidite (15 μL, 48 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The mixture was filtered and used with no further purification.

8-[3-(6-Dimethylaminonaphthalen-2-yl)-3-hydroxy-1-propyn-1-yl]-3'*O*,5'*O*-bis(*tert*-butyldimethylsilyl)-2'-deoxyguanosine (16). To a solution of 8-bromo-3'*O*,5'*O*-bis(*tert*-butyldimethylsilyl)-2'-deoxyguanosine (3.7 g, 6.5 mmol), **2** (1.1 g, 5.0 mmol), and triethylamine (2.3 mL, 16.5 mmol) in DMF (20 mL) was added tetrakis(triphenylphosphine)palladium(0) (1.2 g, 1.0 mmol) and copper(I) iodide (380 mg, 2.0 mmol) under nitrogen. The mixture was stirred at 60 °C for 1 h. The resulting mixture was concentrated *in vacuo* and diluted ethyl acetate. This solution was washed with 5% (*w/v*) EDTA solution and 5% (*w/v*) sodium bisulfite solution, dried over Na_2SO_4, filtered and evaporated. The crude product was purified by silica gel column chromatography (chloroform-methanol = 30 : 1) to yield **16** (3.4 g, 4.7 mmol, 93%) as an orange solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.76 (brs, 1H) 7.87 and 7.83 (s×2, total 1H), 7.68–7.61 (m, 2H), 7.55 (d, 1H, *J* = 8.8 Hz), 7.13 and 7.11 (dd×2, total 1H, *J* = 2.4, 7.3 Hz), 6.89 and 6.87 (d×2, total 1H, *J* = 2.4 Hz), 6.33 (t, 1H, *J* = 6.8 Hz), 6.24 (brs, 2H), 5.80 and 5.77 (s×2, total 1H), 4.58–4.54 (m, 1H), 3.92–3.87 (m, 1H), 3.78–3.73 (m, 1H), 3.68–3.62 (m, 1H),3.30–3.25 (m, 1H), 3.03 and 3.01 (s×2, total 6H), 2.17–2.07 (m, 1H), 0.87–0.82 (m, 18H), 0.09– –0.04 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.1, 153.6, 151.13, 151.09, 148.8, 134.7, 134.3, 133.0, 131.3, 131.1, 129.0, 128.3, 126.8, 126.34, 126.28, 125.44, 125.38, 124.95, 124.90, 117.5, 117.4, 116.7, 116.6, 106.37,

106.32, 95.7, 87.55, 87.48, 84.5, 75.52, 75.42, 72.64, 72.57, 64.77, 64.61, 63.2, 40.78, 40.75, 37.0, 25.84, 25.73, 18.3, 17.9, –4.7, –4.8, -5.37, –5.40; FABMS (NBA/$CHCl_3$) *m/z* 718 ($[M + H]^+$), HRMS calcd. for $C_{37}H_{54}N_6O_5Si_2$ ($[M + H]^+$) 718.3694, found 718.3699.

2*N*-(*N,N*-Dimethylaminomethylidenyl)-8-[3-(6-dimethylaminonaphthalen-2-yl)-3-hydroxy-1-propyl]-3'*O*,5'*O*-bis(*tert*-butyldimethylsilyl)-2'-deoxyguanosine (17). To a solution of **16** (603 mg, 0.84 mmol) and PtO_2 (150 mg) in methanol was stirred under hydrogen atmosphere at room temperature for 12 h. The mixture was filtered through Celite and washed methanol, and the filtrate and washings were combined and evaporated under reduced pressure. The crude product was purified by silica gel chromatography (chloroform-methanol = 50 : 1) to yield the corresponding reduction product (411 mg, 0.57 mmol, 68 %) as an orange solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.82 (brs, 1H) 7.63–7.59 (m, 3H), 7.36 (dd, 1H, *J* = 3.2, 8.5 Hz), 7.11 (dt, 1H, *J* = 2.8, 8.8 Hz), 6.89 (d, 1H, *J* = 2.0 Hz), 6.20 (brs, 1H), 6.05 (dt, 1H, *J* = 6.8, 14.2 Hz), 4.92 (dt, 1H, *J* = 5.6, 15.1 Hz), 4.60–4.52 (m, 1H), 3.83–3.61 (m, 3H), 3.23–3.17 (m, 1H), 3.01 (s, 6H), 2.99–2.90 (m, 2H), 2.38–2.28 (m, 2H), 2.06–2.01 (m, 1H), 0.92–0.83 (m, 18H), 0.095– –0.040 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.4, 152.7, 152.39, 152.34, 150.3, 148.4, 137.98, 137.93, 134.2, 128.6, 126.8, 126.5, 126.4, 124.4, 124.14, 124.08, 116.5, 115.7, 106.49, 106.44, 87.1, 83.68, 83.63, 73.0, 72.18, 72.10, 62.7, 40.9, 40.7, 37.2, 36.1, 25.89, 25.86, 25.78, 25.73, 25.75, 25.70, 24.5, 18.2, 17.9, –4.7, –4.8, –5.5; FABMS (NBA/$CHCl_3$) *m/z* 723 ($[M + H]^+$), HRMS calcd. for $C_{37}H_{58}O_5N_6Si_2$ ($[M + H]^+$) 723.4086, found 723.4085.

To a solution of the previous reaction product (619 mg, 0.86 mmol) in DMF (6 mL) was added *N,N*-dimethylformamide dimethylacetal (126 μL, 0.86 mmol) and the mixture was stirred at 60 °C for 1 h. After evaporation of the solvent, the residue was purified by silica gel chromatography (chloroform-methanol = 50 : 1) to yield **17** (507 mg, 0.65 mmol, 76 %) as an orange solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.82 (brs, 1H), 8.51 and 8.50 (s×2, total 1H), 7.68–7.61 (m, 3H), 7.39 and 7.37 (dd×2, total 1H, *J* = 2.2, 3.8 Hz), 7.16 and 7.14 (d×2, total 1H, *J* = 2.4 Hz), 6.92 and 6.91 (s×2, total 1H), 6.29 (t, 1H, *J* = 7.3 Hz), 4.97–4.92 (m, 1H), 4.52 and 4.49 (quintet×2, total 1H, *J* = 3.4 Hz), 3.89–3.85

(m, 1H), 3.74 (d, 1H, J = 5.9 Hz), 3.71 (d, 1H, J = 5.4 Hz), 3.16 (s, 3H), 3.10 (s, 3H), 3.03 (s, 6H), 3.01–2.91 (m, 2H), 2.49–2.32 (m, 2H), 2.11 and 2.08 (ddd×2, total 1H, J = 2.9, 6.8, 13.2 Hz), 0.91 (d, 9H, J = 2.0 Hz), 0.87 (d, 9H, J = 5.9 Hz), 0.08 (dd, 6H, J = 2.0 5.9 Hz), 0.02 (t, 6H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.8, 157.4, 155.7, 150.9, 150.6, 150.5, 148.3, 138.2, 134.1, 128.6, 126.6, 126.2, 124.50, 124.47, 123.96, 123.93, 118.81, 118.78, 116.4, 106.5, 86.9, 83.2, 73.07, 72.94, 72.0, 62.8, 41.2, 40.8, 38.2, 38.1, 35.75, 35.65, 35.0, 25.7, 25.6, 24.9, 24.8, 18.2, 17.8, –4.7, –4.9, –5.5, –5.6; FABMS (NBA/$CHCl_3$) *m/z* 777 ($[M + H]^+$), HRMS calcd. for $C_{40}H_{63}O_5N_7Si_2$ ($[M + H]^+$) 777.4429, found 777.4438.

2*N*-(*N*,*N*-Dimethylaminomethylidenyl)-8-PRODAN-2'-deoxyguanosine (18). To a solution of **17** (1.64 g, 2.11 mmol) and molecular sieves (4 Å, 1.0 g) in dichloromethane (20 mL) was added 4-methylmorpholine *N*-oxide (371 mg, 3.17 mmol) and tetrapropylammonium perruthenate (148 mg, 0.42 mmol) at 0 ˚C, and the mixture was stirred at room temperature for 2 h. After diluted with diethyl ether (1 L), Florisil (60–100 mesh, 250 mg) was added to the solution and the resulting mixture was stirred at room temperature for 15 min. The mixture was filtered through Celite, washed with diethyl ether and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (chloroform-methanol = 50 : 1) to yield the PRODAN nucleoside (1.18 g, 1.52 mmol, 72 %) as a lemon yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.55 (s, 1H), 8.45 (s, 1H), 8.44 (d, 1H, J = 1.2 Hz), 7.98 (dd, 1H), 7.70 (d, 1H, J = 8.8 Hz), 7.64 (d, 1H, J = 8.8 Hz), 7.17 (dd, 1H, J = 2.4, 9.2 Hz), 6.87 (d, 1H, J = 2.4 Hz), 6.44 (t, 1H, J = 7.2 Hz), 4.63 (quin., 1H, J = 2.4 Hz), 3.62–3.97 (m, 5H), 3.32–3.26 (m, 2H), 3.20 (s, 3H), 3.11 (s, 6H), 2.99 (s, 3H), 2.27 (m, 1H), 0.94 (s, 9H), 0.82 (s, 9H), 0.15 (d, 6H, J = 1.2 Hz), 0.03 (d, 6H, J = 15.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.1, 158.2, 157.3, 156.9, 156.1, 150.7, 148.7, 134.9, 130.8, 130.7, 129.7, 128.7, 127.2, 124.9, 118.9, 117.3, 107.5, 92.3, 72.0, 66.1, 61.3, 43.9, 42.1, 40.3, 40.2, 39.7, 39.6, 25.92, 25.90, 25.88, 25.85, 25.84, 25.81, 18.4, 18.1, 17.8, –5.4, –5.5, –5.6, –5.7; FABMS (NBA/$CHCl_3$) *m/z* 775 ($[M + H]^+$), HRMS calcd. for $C_{40}H_{61}O_5N_7Si_2$ ($[M + H]^+$) 775.4273, found 775.4277.

To a solution of the PRODAN nucleoside (964 mg, 1.24 mmol) in THF (20 mL) was added TBAF (1 M solution in THF, 2.73 mL, 2.73 mmol). The mixture was stirred at room temperature for 2 h. The resulting mixture was evaporated and purified by silica gel column chromatography (chloroform-methanol = 50 : 1) to yield **18** (636 mg, 1.16 mmol, 94%) as a lemon yellow solid; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.3 (brs, 1H), 8.52 (s, 1H), 8.47 (s, 1H), 7.95 (d, 1H, J = 9.3 Hz), 7.85 (d, 1H, J = 8.8 Hz), 7.69 (d, 1H, J = 8.8 Hz), 7.27 (dd, 1H, J = 2.4, 9.3 Hz), 6.95 (s, 1H), 6.31 (t, 1H, J = 7.3 Hz), 5.32 (d, 1H, J = 4.4 Hz), 4.90 (t, 1H, J = 5.9 Hz), 4.44 (dt, 1H, J = 3.9, 10.7 Hz), 3.85–3.81 (m, 1H), 3.70–3.51 (m, 4H), 3.35–3.31 (m, 1H), 3.19–3.14 (m, 2H), 3.11 (s, 3H), 3.06 (s, 6H), 3.01 (s, 3H), 2.19 (ddd, 1H, J = 2.9, 6.4, 12.7 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 197.4, 157.9, 157.2, 156.6, 150.5, 148.7, 137.4, 130.7, 130.0, 129.6, 126.0, 124.5, 123.9, 118.6, 116.5, 104.8, 87.5, 83.3, 71.0, 62.0, 40.7, 39.9, 37.9, 34.6, 34.5, 22.0; FABMS (DTT/TG/$CHCl_3$) *m/z* 548 ($[M + H]^+$), HRMS calcd. for $C_{28}H_{33}O_5N_7$ ($[M + H]^+$) 548.2621, found 548.2624.

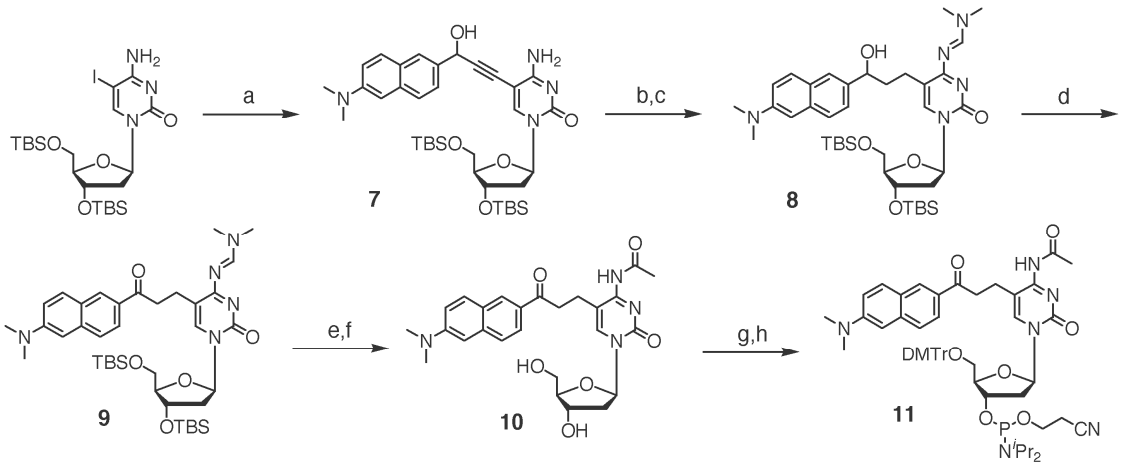
2*N*-(*N*,*N*-Dimethylaminomethylidenyl)-8-PRODAN-5'*O*-(4,4'-dimethoxytrityl)-2'-deoxyguanosine 3'-*O*-(2-cyanoethyl)-*N*,*N*-diisopropylphosphoramidite (19). To a solution of **18** (30 mg, 0.054 mmol) in pyridine (3 mL) was added 4,4'-dimethoxytrityl chloride (22 mg, 0.064 mmol). The mixture was stirred at room temperature for 3 h. The resulting mixture was evaporated and purified by silica gel column chromatography (chloroform-methanol = 50 : 1) to yield the tritylated product (45 mg, 0.053 mmol, 98%) as a lemon yellow solid; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 11.27 (brs, 1H), 8.50 (s, 1H), 8.37 (s, 1H), 7.92 (d, 1H, J = 9.3 Hz), 7.84 (dd, 1H, J = 1.5, 8.3 Hz), 7.68 (d, 1H, J = 8.8 Hz), 7.30–7.12 (m, 10H), 6.95 (d, 1H, J = 2.0 Hz), 6.75 (dd, 4H, J = 8.8, 12.2 Hz), 6.38 (dd, 1H, J = 5.9, 7.3 Hz), 5.37 (d, 1H, J = 4.4 Hz), 4.62–4.56 (m, 1H), 3.89 (dd, 1H, J = 5.4, 8.8 Hz), 3.66 (s, 3H), 3.65 (s, 3H), 3.72–3.52 (m, 2H), 3.23–3.13 (m, 4H), 3.06 (s, 6H), 3.03 (s, 3H), 3.00 (s, 3H), 2.29–2.22 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 197.3, 158.0, 157.9, 157.5, 157.2, 156.2, 150.3, 150.2, 148.9, 144.9, 137.3, 135.64, 135.58, 130.7, 129.9, 129.6, 129.5, 127.6, 126.5, 125.9, 124.6, 123.9, 118.4, 116.4, 113.0, 104.8, 85.2, 85.1, 82.7, 79.2, 70.4, 63.6, 54.9, 40.7, 37.9, 34.6, 34.4, 22.0; FABMS (NBA/$CHCl_3$) *m/z*

850 ([M + H]$^+$), HRMS calcd. for $C_{49}H_{51}O_7N_7$ ([M + H]$^+$) 850.3928, found 850.3948.

To a solution of the tritylated nucleoside (43 mg, 51 μmol) and tetrazole (3.5 mg, 51 μmol) in anhydrous acetonitrile (300 μL) and dichloromethane (200 μL) was added 2-cyanoethyl tetraisopropylphosphorodiamidite (15.8 μL, 51 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The mixture was filtered and used with no further purification.

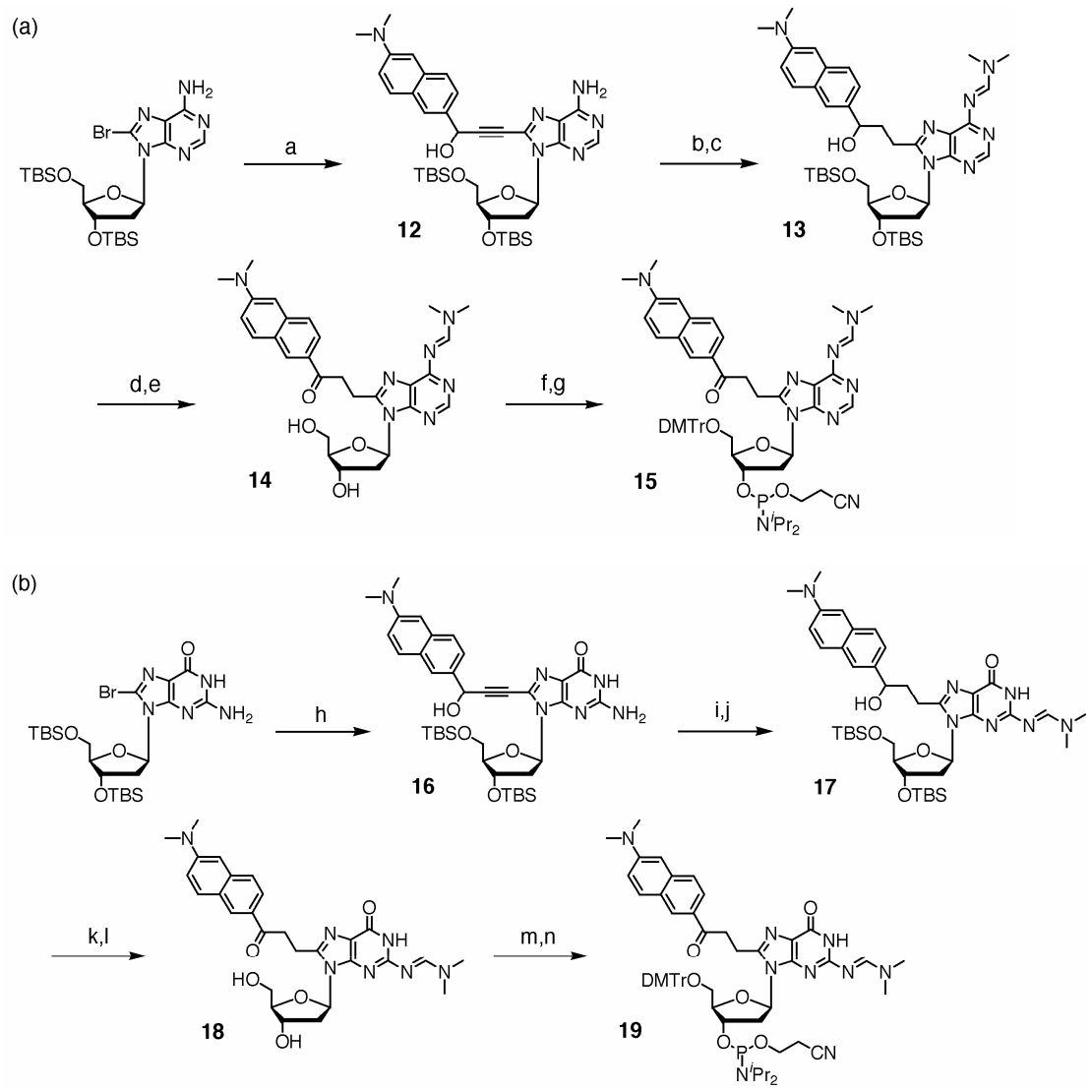
ODN synthesis and characterization. ODNs were synthesized by a conventional phosphoramidite method by using an Applied Biosystems 392 DNA/RNA synthesizer. Commercially available phosphoramidites were used for dA, dG, dC, and dT. The crude mixture after phosphoramidite synthesis was used for ^{PDN}X. Synthesized ODNs were purified by reverse phase HPLC on a 5-ODS-H column (10 × 150 mm, elution with a solvent mixture of 0.1 M triethylamine acetate (TEAA), pH 7.0, linear gradient over 30 min from 5% to 30% acetonitrile at a flow rate of 3.0 mL/min). ODNs containing modified nucleotides were fully digested with calf intestine alkaline phosphatase (50 U/mL), snake venom phosphodiesterase (0.15 U/mL), and P1 nuclease (50 U/mL) at 37 °C for 3 h. Digested solutions were analyzed by HPLC on a CHEMCOBOND 5-ODS-H column (4.6 × 150 mm), elution with a solvent mixture of 0.1 M TEAA, pH 7.0, flow rate of 1.0 mL/min. The concentration of each ODN was determined by comparing peak areas with a standard solution containing dA, dC, dG, and dT at a concentration of 0.1 mM. MALDI–TOF **ODN1(^{PDN}U)**: ([M – H]$^-$) calcd. 4098.81, found 4098.23. **ODN2(^{PDN}U)**: ([M – H]$^-$) calcd. 4128.83, found 4129.04. **ODN1(^{PDN}C)**: ([M – H]$^-$) calcd. 4097.83, found 4097.97. **ODN1(^{PDN}A)**: ([M – H]$^-$) calcd. 4121.85, found 4121.57. **ODN1(^{PDN}G)**: ([M – H]$^-$) calcd. 4137.85, found 4137.95.

Scheme S1[a]



[a] Reagents and conditions: (a) **2**, tetrakis(triphenylphosphine)palladium(0), copper(I) iodide, triethylamine, DMF, room temperature, 3 h, 92%; (b) 10% Pd/C, ethanol, H_2, room temperature, 9 h, 80%; (c) *N*,*N*-dimethylformamide dimethylacetal, DMF, 60 ˚C, 3 h, 81%; (d) tetrapropylammonium perruthenate, 4-methylmorpholine *N*-oxide, 4 Å MS, dichloromethane, room temperature, 4 h, 72%; (e) *conc*. ammonia-methanol (1:4), 50 ˚C, 2 h, then anhydrous acetic acid, pyridine, 50 ˚C, 4 h, 85%; (f) 1 M tetrabutylammonium fluoride, room temperature, 3 h, 96%; (g) 4,4'-dimethoxytrityl chloride, pyridine, room temperature, 3 h, 90%; (h) $(i\mathrm{Pr_2N})_2\mathrm{PO(CH_2)_2CN}$, 1*H*-tetrazole, acetonitrile, room temperature, 30 min.

Scheme S2[a]



[a] Reagents and conditions: (a) **2**, tetrakis(triphenylphosphine)palladium(0), copper(I) iodide, triethylamine, DMF, room temperature, 17 h, 61%; (b) 5% Pd/C, methanol, H_2, room temperature, 2 days, 45%; (c) *N*,*N*-dimethylformamide dimethylacetal, DMF, room temperature, 6 h, 75%; (d) tetrapropylammonium perruthenate, 4-methylmorpholine *N*-oxide, 4 Å MS, dichloromethane, room temperature, 15 h, 32%; (f) 1 M tetrabutylammonium fluoride, room temperature, 3 h, 92%; (g) 4,4'-dimethoxytrityl chloride, pyridine, room temperature, 3 h, 49%; (h) $(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{PO}(\mathrm{CH}_2)_2\mathrm{CN}$, 1*H*-tetrazole, acetonitrile, room temperature, 30 min; (h) **2**, tetrakis(triphenylphosphine)palladium(0), copper(I) iodide, triethylamine, DMF, 60 ˚C, 1 h, 93%; (i) PtO_2, methanol, H_2, room temperature, 12 h, 68%; (j) *N*,*N*-dimethylformamide dimethylacetal, DMF, 60 ˚C, 1 h, 76%; (k) tetrapropylammonium perruthenate, 4-methylmorpholine *N*-oxide, 4 Å MS, dichloromethane, room temperature, 2 h, 72%; (l) 1 M tetrabutylammonium fluoride, room temperature 2 h, 94%; (m) 4,4'-dimethoxytrityl chloride, pyridine, room temperature, 3 h, 98%; (n) $(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{PO}(\mathrm{CH}_2)_2\mathrm{CN}$, 1*H*-tetrazole, acetonitrile, room temperature, 30 min.