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Synthesis of 2'-deoxyadenosine nucleosides bearing bipyridine-type ligands and their Ru-complexes in position 8 through cross-coupling reactions

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Complete experimentral part and characterization data

General Remarks

All cross-coupling reactions were performed under argon atmosphere. Et_3N and $Et(iPr)_2N$ was degassed in vacuo and stored over molecular sieves under argon. Compounds **1a,b** [lit.[1]], **2a,b**, **3a-d**, **10a,b**, **11a-d**, [lit.[2]], were prepared according to the literature procedures. Other chemicals were purchased from commercial suppliers and used as received. NMR spectra were recorded on Bruker Avance 500 (500 MHz for ^{1}H and 125.8 MHz for ^{13}C) and Bruker Avance 400 (^{1}H at 400, ^{13}C at 100.6 MHz) spectrometers in $CDCl_3$, DMSO-d_6 or acetone-d_6. Chemical shifts (in ppm, δ scale) were referenced to TMS (for ^{1}H NMR spectra in $CDCl_3$) and/or to the solvent signal ($CDCl_3$ – 7.26 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR; DMSO-d_6 – 2.5 ppm for ^{1}H NMR and 39.7 ppm for ^{13}C NMR;.and actone-d_6 – 2.05 ppm for ^{1}H NMR and 29.8 ppm (CD_3 group from acetone-d_6) for ^{13}C NMR); coupling constants (*J*) are given in Hz. The assignment of proton and carbon signals was based on H,H-COSY, H,C-HSQC and H,C-HMBC experiments. Melting points were determined on a Kofler block and are uncorrected. Mass spectra were measured on a ZAB-EQ (VG Analytical) spectrometer using FAB (ionization by Xe, accelerating voltage 8 kV, glycerol matrix) or on LCQ classic spectrometer using electrospray ionization (ESI).

General Procerude for Sonogashira Cross-Coupling Reactions (protected nucleosides):

DMF (1.5 ml) and Et_3N (0.35 ml, 2.5 mmol, 10 equiv.) were added to an argon-purged flask containing nucleoside **1b** (158 mg, 0.25 mmol), an alkyne **2a-c** (0.375 mmol, 1.5 equiv.), $PdCl_2$ (2.2 mg, 0.0125 mmol, 5 mol%), dppf (1,1'-bis-diphenylphosphino-ferrocene) (7 mg, 0.0125 mmol, 5 mol%) and CuI (4.8 mg, 0.025 mmol, 10 mol%). The reaction mixture was stired at 80°C until complete consumption of the strating material. The solvent was then evaporated in vacuo. The products were purified by silicagel column chromotagraphy (pre-equilibrated with 1 % Et_3N in hexanes) using a AcOEt/hexanes (1:4 to 1:1) as eluent.

5'-*O*-DMTr-8-[(2",2'"-bipyridine-6"-yl)ethynyl]-2'-deoxyadenosine (5a)

The product was isolated as white powder 115 mg (63 %). M.p. 134-138 °C. ^{1}H NMR (500 MHz, DMSO-d_6): 2.40 (ddd, 1H, J_{gem} = 13.4, $J_{2'b,1'}$ = 7.7, $J_{2'b,3'}$ = 5.3, H-2'b); 3.17 (dd, 1H, J_{gem} = 10.2, $J_{5'b,4'}$ = 3.8, H-5'b); 3.27 (dd, 1H, J_{gem} = 10.2, $J_{5'a,4'}$ = 6.9, H-5'a); 3.30 (ddd, 1H, J_{gem} = 13.4, $J_{2'a,3'}$ = 7.3, $J_{2'a,1'}$ = 5.8, H-2'a); 3.67 (s, 6H, OCH_3); 4.01 (ddd, 1H, $J_{4',5'}$ = 6.9, 3.8, $J_{4',3'}$ = 5.1, H-4'); 4.76 (dq, 1H, $J_{3',2'}$ = 7.3, 5.3, $J_{3',4'}$ = 5.1, $J_{3',OH}$ = 5.0, H-3'); 5.42 (d, 1H, $J_{OH,3'}$ = 5.0, OH-3'); 6.64 (dd, 1H, $J_{1',2'}$ = 7.7, 5.8, H-1'); 6.66 and 6.69 (2 × m, 2 × 2H, H-*m*-C_6H_4-DMTr); 7.06 (m, 4H, H-*o*-C_6H_4-DMTr); 7.10-7.16 (m, 3H, H-*m*+*p*-C_6H_5-DMTr); 7.23 (m, 2H, H-*o*-C_6H_5-DMTr); 7.51 (ddd, 1H, $J_{5'",4'"}$ = 7.5, $J_{5'",6'"}$ = 4.8, $J_{5'",3'"}$ = 1.2, H-5'"); 7.63 (bs, 2H, NH_2); 7.70 (dd, 1H, $J_{5",4"}$ = 7.7, $J_{5",3"}$ = 1.1, H-5"); 7.93 (td, 1H, $J_{4'",3'"}$ = 8.0, $J_{4'",5'"}$ = 7.5, $J_{4'",6'"}$ = 1.7, H-4'"); 8.06 (t, 1H, $J_{4",3"}$ = 8.0, $J_{4",5"}$ = 7.7, H-4"); 8.13 (s, 1H, H-2); 8.35 (dt, 1H, $J_{3'",4'"}$ = 8.0, $J_{3'",5'"}$ = 1.2, $J_{3'",6'"}$ = 0.9, H-3'"); 8.51 (dd, 1H, $J_{3",4"}$ = 8.0, $J_{3",5"}$ = 1.1, H-3"); 8.74 (ddd, 1H, $J_{6'",5'"}$ = 4.8, $J_{6'",4'"}$ = 1.7, $J_{6'",3'"}$ = 0.9, H-6'"); ^{13}C NMR (125.8 MHz, DMSO-d_6): 37.86 (CH_2-2'); 55.09 and 55.10 (OCH_3); 64.06 (CH_2-5'); 70.89 (CH-3'); 77.36 (pur-**C**≡C-); 84.02 (CH-1'); 85.35 (C-DMTr); 85.94 (CH-4'); 93.37 (bpy-**C**≡C-); 113.04 and 113.07 (CH-*m*-C_6H_4-DMTr); 119.57 (C-5); 120.98 (CH-3'"); 121.48 (CH-3"); 124.96 (CH-5'"); 126.57 and 127.73 (CH-C_6H_5-DMTr); 128.28 (CH-5"); 129.71 and 129.74 (CH-*o*-C_6H_4-DMTr); 132.16 (C-8); 135.64 and 135.82 (C-*i*-C_6H_4-DMTr); 137.72 (CH-4'"); 138.48 (CH-4"); 140.29 (C-6"); 145.10 (C-*i*-C_6H_5-DMTr); 149.07 (C-4); 149.61 (CH-6'"); 154.15 (CH-2); 154.27 (C-2'"); 156.27 (C-6 and C-2"); 158.01 and 158.04 (C-*p*-C_6H_4-DMTr); FAB MS: *m/z* (%) 303.3 (40) [DMTr], 754.2 (100) [M^+ + Na]; HR MS (FAB) calc. 732.2934 found. 732.2933.

5'-*O*-DMTr-8-[(2",2'"-bipyridin-5"-yl)ethynyl]-2'-deoxyadenosine (5b)

The product was isolated as white powder 132 mg (72 %). M. p. 129-135 °C; ^{1}H NMR (400 MHz, DMSO-d_6): 2.37 (ddd, 1H, J_{gem} = 13.1, $J_{2'b,3'}$ = 7.6, $J_{2'b,1'}$ = 5.4, H-2'b); 3.13 (dd, 1H, J_{gem} = 10.0, $J_{5'b,4'}$ = 3.8, H-5'b); 3.19 (dd, 1H, J_{gem} = 10.0, $J_{5'a,4'}$ = 6.6, H-5'a); 3.29 (ddd, 1H, J_{gem} = 13.1, $J_{2'a,1'}$ = 7.2, $J_{2'a,3'}$ = 5.6, H-2'a); 3.676 and 3.680 (2 × s, 2 × 3H, OCH_3); 4.01 (ddd, 1H, $J_{4',5'}$ = 6.6, 3.8, $J_{4',3'}$ = 5.6, H-4'); 4.64 (dq, 1H, $J_{3',2'}$ = 7.6, 5.6, $J_{3',4'}$ = 5.6, $J_{3',OH}$ = 5.1, H-3'); 5.41 (d, 1H, $J_{OH,3'}$ = 5.1, OH-3'); 6.63 (dd, 1H, $J_{1',2'}$ = 7.2, 5.4, H-1'); 6.71 and 6.75 (2 × m, 2 × 2H, H-*m*-C_6H_4-DMTr); 7.09-7.20 (m, 7H, H-*o*-C_6H_4-DMTr and H-*m*+*p*-C_6H_5-DMTr); 7.28 (m, 2H, H-*o*-C_6H_5-DMTr); 7.53 (ddd, 1H, $J_{5''',4'''}$ = 7.5, $J_{5''',6'''}$ = 4.7, $J_{5''',3'''}$ = 1.2, H-5'''); 7.61 (bs, 2H, NH_2); 8.02 (td, 1H, $J_{4''',3'''}$ = 7.9, $J_{4''',5'''}$ = 7.5, $J_{4''',6'''}$ = 1.8, H-4'''); 8.09 (s, 1H, H-2); 8.13 (t, 1H, $J_{4'',3''}$ = 8.3, $J_{4'',6''}$ = 2.2, H-4''); 8.46 (dt, 1H, $J_{3''',4'''}$ = 7.9, $J_{3''',5'''}$ = 1.2, $J_{3''',6'''}$ = 1.0, H-3'''); 8.48 (dd, 1H, $J_{3'',4''}$ = 8.3, $J_{3'',6''}$ = 1.0, H-3''); 8.76 (ddd, 1H, $J_{6''',5'''}$ = 4.7, $J_{6''',4'''}$ = 1.8, $J_{6''',3'''}$ = 1.0, H-6'''); 8.88 (dd, 1H, $J_{6'',4''}$ = 2.2, $J_{6'',3''}$ = 1.0, H-6''); ^{13}C NMR (100.6 MHz, DMSO-d_6): 37.62 (CH_2-2'); 55.10 (OCH_3); 64.11 (CH_2-5'); 70.89 (CH-3'); 83.28 (pur-**C**≡C-); 84.28 (CH-1'); 85.35 (C-DMTr); 85.92 (CH-4'); 91.40 (bpy-**C**≡C-); 113.08 and 113.11 (CH-*m*-C_6H_4-DMTr); 117.65 (C-5''); 119.67 (C-5); 120.27 (CH-3''); 121.25 (CH-3'''); 125.06 (CH-5'''); 126.62 (CH-*p*-C_6H_5-DMTr); 127.76 (CH-*o,m*-C_6H_5-DMTr); 129.76 (CH-*o*-C_6H_4-DMTr); 132.60 (C-8); 135.68 and 135.93 (C-*i*-C_6H_4-DMTr); 137.78 (CH-4'''); 140.34 (CH-4''); 145.12 (C-*i*-C_6H_5-DMTr); 148.97 (C-4); 149.80 (CH-6'''); 151.97 (CH-6''); 153.98 (CH-2); 154.29 (C-2'''); 155.58 (C-2''); 156.22 (C-6); 158.06 and 158.08 (C-*p*-C_6H_4-DMTr); FAB MS: *m/z* (%) 303.0 (100) [DMTr], 314 (30) [M^+ - DMTrdRf], 732 (10) [M^+]; HR MS (FAB) calc. 732.2934 found. 732.2924.

5'-*O*-DMTr-8-[(1'',10''-phenantrolin-2''-yl)ethynyl]-2'-deoxyadenosine (5c)

The product was isolated as brownish powder 60 mg (32 %). M. p. 152-156 °C; ^{1}H NMR (400 MHz, DMSO-d_6): 2.45 (ddd, 1H, J_{gem} = 13.5, $J_{2'b,1'}$ = 7.6, $J_{2'b,3'}$ = 5.7, H-2'b); 3.18 (dd, 1H, J_{gem} = 10.1, $J_{5'b,4'}$ = 3.9, H-5'b); 3.24 (dd, 1H, J_{gem} = 10.1, $J_{5'a,4'}$ = 6.1, H-5'a); 3.41 (ddd, 1H, J_{gem} = 13.5, $J_{2'a,3'}$ = 6.9, $J_{2'a,1'}$ = 5.2, H-2'a); 3.64 and 3.65 (2 × s, 6H, OCH_3); 4.04 (td, 1H, $J_{4',5'}$ = 6.1, 3.9, $J_{4',3'}$ = 5.0, H-4'); 5.13 (bp, 1H, $J_{3',2'}$ = 6.9, 5.7, $J_{3',4'}$ = 5.0, $J_{3',OH}$ = 4.9, H-3'); 5.79 (d, 1H, $J_{OH,3'}$ = 4.9, OH-3'); 6.59 and 6.63 (2 × m, 2 × 2H, H-*m*-C_6H_4-DMTr); 6.67 (dd, 1H, $J_{1',2'}$ = 7.6, 5.2, H-1'); 7.05 (m, 4H, H-*o*-C_6H_4-DMTr); 7.06-7.12 (m, 3H, H-*m*+*p*-C_6H_5-DMTr); 7.21 (m, 2H, H-*o*-C_6H_5-DMTr); 7.66 (bs, 2H, NH_2); 7.85 (dd, 1H, $J_{8'',7''}$ = 8.0, $J_{8'',9''}$ = 4.3, H-8''); 8.01 (d, 1H, $J_{3'',4''}$ = 8.2, H-3''); 8.05 (d, 1H, $J_{5'',6''}$ = 8.7, H-5''); 8.12 (d, 1H, $J_{6'',5''}$ = 8.7, H-6''); 8.13 (s, 1H, H-2); 8.57 (dd, 1H, $J_{7'',8''}$ =

8.0, $J_{7",9"}$ = 1.8, H-7"); 8.62 (d, 1H, $J_{4",3"}$ = 8.2, H-4"); 9.09 (dd, 1H, $J_{9",8"}$ = 4.3, $J_{9",7"}$ = 1.8, H-9"); ^{13}C NMR (100.6 MHz, DMSO-d_6): 37.51 (CH_2-2'); 55.09 (OCH_3); 63.71 (CH_2-5'); 70.66 (CH-3'); 79.00 (pur-**C**≡C-); 84.03 (CH-1'); 85.26 (C-DMTr); 85.79 (CH-4'); 94.07 (phen-**C**≡C-); 112.96 and 113.00 (CH-*m*-C_6H_4-DMTr); 119.72 (C-5); 124.17 (CH-8"); 126.45 (CH-3"); 126.55 (CH-5" and CH-*p*-C_6H_5-DMTr); 127.66 and 127.75 (CH-*o*+*m*-C_6H_5-DMTr); 128.45 (C-4"a); 128.51 (CH-6"); 129.17 (C-6"a); 129.66 and 129.75 (CH-*o*-C_6H_4-DMTr); 132.17 (C-8); 135.73 and 135.79 (C-*i*-C_6H_4-DMTr); 136.81 (CH-7"); 137.36 (CH-4"); 140.49 (C-2"); 144.78 (C-10"a); 145.13 (C-*i*-C_6H_5-DMTr); 149.25 (C-10"b); 149.25 (C-4); 150.51 (C-9"); 154.22 (CH-2); 156.31 (C-6); 157.95 and 158.00 (C-*p*-C_6H_4-DMTr); FAB MS: *m/z* (%) 303.1 (100) [DMTr], 338.1 (30) [M^+ - DMTrdRf], 778.4 (10) [M^+ + Na], HR MS (TOF MS ES+) calc. 756.2934 found 756.2947.

***N*^{6}-benzoyl-5'-*O*-DMTr-8-[(2",2'"-bipyridin-6"-yl)ethynyl]-2'-deoxyadenosine (4a)**

A solution of **5a** (0.5 g, 0.68 mmol) in dry pyridine (10 ml) was cooled to 0°C. TMSCl (0.45 ml, 5 equiv.) was added and the mixture was stired for 2 hours during which the temperature rises the room temperature. Then the reaction mixture was cooled to 0°C and BzCl (0.4 ml, 5 equiv.) was added. The reaction mixture was stired for 4 hours at room temperature and then MeOH (15 ml) was added. The solvents were evaporated under vacuum. The crude product was extracted in $CHCl_3$ and purified by silica gel collumn chromatography (pre-equilibrated with 1 % Et_3N) using AcOEt and hexanes as eluent. The corresponding fractions were collected and the solvent was evaporated. The di-benzoylated intermediate (280 mg, 44 %) was then disolved in 25 ml of EtOH and 1 M NH_4OH (2 ml) was added and the mixture was stired at r.t. until complete consumption of the starting material. The mono-benzoylated product **4a** was purified by silica gel collumn chromatography (pre-equilibrated with 1 % Et_3N) using AcOEt/hexanes (1:6 to 1:1) as eluent (189 mg, 76 % for second step, 33% overal from **5a**). **4a**: M. p. 132-135 °C; ^{1}H NMR (400 MHz, DMSO-d_6): 2.49 (overlapped with DMSO, H-2'b); 3.19 (dd, 1H, J_{gem} = 10.2, $J_{5'b,4'}$ = 3.7, H-5'b); 3.29-3.35 (m, 2H, H-2'a and H-5'a); 3.66 (s, 6H, OCH_3); 4.08 (ddd, 1H, $J_{4',5'}$ = 6.9, 3.7, $J_{4',3'}$ = 5.0, H-4'); 4.80 (bm, 1H, H-3'); 5.50 (bd, 1H, OH-3'); 6.67 and 6.70 (2 × m, 2 × 2H, H-*m*-C_6H_4-DMTr); 6.78 (dd, 1H, $J_{1',2'}$ = 7.5, 5.7, H-1'); 7.05-7.16 (m, 7H, H-*o*-C_6H_4-DMTr and H-*m*+*p*-C_6H_5-DMTr); 7.24 (m, 2H, H-*o*-C_6H_5-DMTr); 7.51 (ddd, 1H, $J_{5'",4'"}$ = 7.5, $J_{5'",6'"}$ = 4.7, $J_{5'",3'"}$ = 1.2, H-5'"); 7.58 (m, 2H, H-*m*-Bz); 7.67 (m, 1H, H-*p*-Bz); 7.78 (dd, 1H, $J_{5",4"}$ = 7.7, $J_{5",3"}$ = 1.1, H-5"); 7.91 (td, 1H, $J_{4'",3'"}$ = 8.0, $J_{4'",5'"}$

= 7.5, $J_{4''',6'''}$ = 1.8, H-4'''); 8.05-8.10 (m, 3H, H-4'' and H-*o*-Bz); 8.37 (dt, 1H, $J_{3''',4'''}$ = 8.0, $J_{3''',5'''}$ = 1.2, $J_{3''',6'''}$ = 0.9, H-3'''); 8.53 (dd, 1H, $J_{3'',4''}$ = 8.1, $J_{3'',5''}$ = 1.1, H-3''); 8.69 (s, 1H, H-2); 8.74 (ddd, 1H, $J_{6''',5'''}$ = 4.7, $J_{6''',4'''}$ = 1.8, $J_{6''',3'''}$ = 0.9, H-6'''); ^{13}C NMR (100.6 MHz, DMSO-d_6): 38.00 (CH_2-2'); 55.09 (OCH_3); 64.12 (CH_2-5'); 70.92 (CH-3'); 77.59 (pur-**C**≡C-); 84.38 (CH-1'); 85.39 (C-DMTr); 86.15 (CH-4'); 94.78 (bpy-**C**≡C-); 113.06 (CH-*m*-C_6H_4-DMTr); 121.06 (CH-3'''); 121.87 (CH-3''); 125.00 (CH-5'''); 125.41 (C-5); 126.62 (CH-*p*-C_6H_5-DMTr); 127.73 (CH-*o*+*m*-C_6H_5-DMTr); 128.60 (CH-5''); 128.67 (CH-*m*-Bz); 128.82 (CH-*o*-Bz); 129.72 (CH-*o*-C_6H_4-DMTr); 132.80 (CH-*p*-Bz); 133.43 (C-*i*-Bz); 135.54 (C-8 and C-*i*-C_6H_4-DMTr); 135.81 (C-*i*-C_6H_4-DMTr); 137.72 (CH-4'''); 138.55 (CH-4''); 139.82 (C-6''); 145.04 (C-*i*-C_6H_5-DMTr); 149.60 (CH-6'''); 151.06 (C-6); 151.51 (C-4); 152.84 (CH-2); 154.17 (C-2'''); 156.39 (C-2''); 158.04 (C-*p*-C_6H_4-DMTr); 166.00 (CO); FAB MS: *m/z* (%) 303.1 (100) [DMTr], 418.2 (30) [M^+ - DMTrdRf], 858.4 (25) [M^+ + Na]; HR MS (FAB) calc. 836.3197 found. 836.3181.

N^6-benzoyl-5'-*O*-DMTr-8-[(2'',2'''-bipyridin-5''-yl)ethynyl]-2'-deoxyadenosine (4b)

This compound was prepared in the same way as **4a** The reaction of **5b** (0.5 g, 0.68 mmol) gave **4b** (278 mg, 49 %). M. p. 128-133 °C; ^{1}H NMR (400 MHz, DMSO-d_6): 2.47 (ddd, J_{gem} = 13.4, $J_{2'b,1'}$ = 7.6, $J_{2'b,3'}$ = 5.5, H-2'b); 3.16 (dd, 1H, J_{gem} = 10.0, $J_{5'b,4'}$ = 3.7, H-5'b); 3.22-3.30 (m, 2H, H-2'a and H-5'a); 3.67 and 3.68 (2 × s, 2 × 3H, OCH_3); 4.07 (ddd, 1H, $J_{4',5'}$ = 6.6, 3.7, $J_{4',3'}$ = 5.2, H-4'); 4.68 (dq, 1H, $J_{3',2'}$ = 6.6, 5.5, $J_{3',4'}$ = 5.2, $J_{3',OH}$ = 5.1, H-3'); 5.47 (d, 1H, $J_{OH,3'}$ = 5.1, OH-3'); 6.69-6.79 (m, 5H, H-1' and H-*m*-C_6H_4-DMTr); 7.10-7.20 (m, 7H, H-*o*-C_6H_4-DMTr and H-*m*+*p*-C_6H_5-DMTr); 7.28 (m, 2H, H-*o*-C_6H_5-DMTr); 7.51 (ddd, 1H, $J_{5''',4'''}$ = 7.6, $J_{5''',6'''}$ = 4.8, $J_{5''',3'''}$ = 1.2, H-5'''); 7.57 (m, 2H, H-*m*-Bz); 7.67 (m, 1H, H-*p*-Bz); 8.02 (td, 1H, $J_{4''',3'''}$ = 7.9, $J_{4''',5'''}$ = 7.6, $J_{4''',6'''}$ = 1.8, H-4'''); 8.07 (m, 2H, H-*o*-Bz); 8.20 (dd, 1H, $J_{4'',3''}$ = 8.3, $J_{4'',6''}$ = 2.2, H-4''); 8.46 (dt, 1H, $J_{3''',4'''}$ = 7.9, $J_{3''',5'''}$ = 1.2, $J_{3''',6'''}$ = 0.9, H-3'''); 8.49 (dd, 1H, $J_{3'',4''}$ = 8.4, $J_{3'',6''}$ = 1.0, H-3''); 8.66 (s, 1H, H-2); 8.76 (ddd, 1H, $J_{6''',5'''}$ = 4.8, $J_{6''',4'''}$ = 1.8, $J_{6''',3'''}$ = 0.9, H-6'''); 8.94 (dd, 1H, $J_{6'',4''}$ = 2.2, $J_{6'',3''}$ = 1.0, H-6''); 11.38 (bs, 1H, NH); ^{13}C NMR (100.6 MHz, DMSO-d_6): 37.77 (CH_2-2'); 55.11 (OCH_3); 64.15 (CH_2-5'); 70.91 (CH-3'); 82.60 (pur-**C**≡C-); 84.69 (CH-1'); 85.40 (C-DMTr); 86.13 (CH-4'); 93.16 (bpy-**C**≡C-); 113.11 and 113.14 (CH-*m*-C_6H_4-DMTr); 117.14 (C-5''); 120.27 (CH-3''); 121.35 (CH-3'''); 125.15 (CH-5'''); 125.58 (C-5); 126.68 (CH-*p*-C_6H_5-DMTr); 127.74 and 127.77 (CH-*o,m*-C_6H_5-DMTr); 128.67 (CH-*m*-Bz); 128.80 (CH-*o*-Bz); 129.73 and 129.80 (CH-*o*-C_6H_4-DMTr); 132.80 (CH-*p*-Bz); 133.36

(C-*i*-Bz); 135.59 and 135.93 (C-*i*-C_6H_4-DMTr); 136.09 (C-8); 137.80 (CH-4'''); 140.70 (CH-4''); 145.07 (C-*i*-C_6H_5-DMTr); 149.82 (CH-6'''); 150.91 (C-6); 151.45 (C-4); 152.29 (CH-6'' and CH-2); 154.22 (C-2'''); 155.95 (C-2''); 158.10 (C-*p*-C_6H_4-DMTr); 165.85 (CO); FAB MS: *m/z* (%) 303.1 (100) [DMTr], 418.1 (20) [M^+ - DMTrdRf], 836 (10) [M^+]; HR MS (FAB) calc. 836.3197 found. 836.3207.

General Procerude for Suzuki-Miyaura Cross-Coupling Reactions (protected nucleosides):

DMF (2 ml) was added to an argon-purged flask containing nucleoside **1b** (158 mg, 0.25 mmol), a boronate **3a-d** (0.3 mmol, 1.2 equiv.), $PdCl_2$ (4.4 mg, 0.025 mmol, 10 mol%), dppf (1,1′-bis-diphenylphosphino-ferrocene) (14 mg, 0.025 mmol, 10 mol%) and K_2CO_3 (138 mg, 1 mmol, 4 equiv.). The reaction mixture was then stired at 90 °C until complete consumption of the strating material. The solvent was evaporated in vacuo. The products were purified by silicagel column chromotagraphy (preequilibrated with 1% Et_3N in hexanes) using AcOEt/hexanes (1:4 to 1:1) as eluent.

5'-*O*-DMTr-8-[(2'',2'''-bipyridin-6''-yl)phenyl]-2'-deoxyadenosine (6a)

The product was isolated as white powder 114 mg (58 %). M. p. 139-146 °C; ^{1}H NMR (500 MHz, DMSO-d_6): 2.20 (ddd, 1H, J_{gem} = 13.0, $J_{2'b,1'}$ = 7.5, $J_{2'b,3'}$ = 4.7, H-2'b); 3.23 (dd, 1H, J_{gem} = 10.1, $J_{5'b,4'}$ = 6.0, H-5'b); 3.27 (dd, 1H, J_{gem} = 10.1, $J_{5'a,4'}$ = 4.8, H-5'a); 3.50 (ddd, 1H, J_{gem} = 13.0, $J_{2'a,3'}$ = 6.3, $J_{2'a,1'}$ = 6.3, H-2'a); 3.71 (s, 6H, OCH_3); 4.02 (dt, 1H, $J_{4',5'}$ = 6.0, 4.8, $J_{4',3'}$ = 4.8, H-4'); 4.70 (dq, 1H, $J_{3',2'}$ = 6.3, 4.7, $J_{3',4'}$ = 4.8, $J_{3',OH}$ = 4.7, H-3'); 5.31 (d, 1H, $J_{OH,3'}$ = 4.7, OH-3'); 6.26 (dd, 1H, $J_{1',2'}$ = 7.5, 6.3, H-1'); 6.77 and 6.80 (2 × m, 2 × 2H, H-*m*-C_6H_4-DMTr); 7.16 (m, 1H, H-*p*-C_6H_5-DMTr); 7.19-7.24 (m, 6H, H-*o*-C_6H_4-DMTr and H-*m*-C_6H_5-DMTr); 7.36 (m, 4H, H-*o*-C_6H_5-DMTr and NH_2); 7.51 (ddd, 1H, $J_{5''',4'''}$ = 7.5, $J_{5''',6'''}$ = 4.8, $J_{5''',3'''}$ = 1.2, H-5'''); 7.99 (m, 2H, H-*o*-phenylene); 8.00 (s, 1H, H-2); 8.03 (td, 1H, $J_{4''',3'''}$ = 8.0, $J_{4''',5'''}$ = 7.5, $J_{4''',6'''}$ = 1.8, H-4'''); 8.11 (t, 1H, $J_{4'',5''}$ = 7.9, $J_{4'',3''}$ = 7.7, H-4''); 8.18 (dd, 1H, $J_{5'',4''}$ = 7.9, $J_{5'',3''}$ = 1.1, H-5''); 8.42 (dd, 1H, $J_{3'',4''}$ = 7.7, $J_{3'',5''}$ = 1.1, H-3''); 8.48 (m, 2H, H-*m*-phenylene); 8.65 (dt, 1H, $J_{3''',4'''}$ = 8.0, $J_{3''',5'''}$ = 1.2, $J_{3''',6'''}$ = 1.0, H-3'''); 8.74 (ddd, 1H, $J_{6''',5'''}$ = 4.8, $J_{6''',4'''}$ = 1.8, $J_{6''',3'''}$ = 1.0, H-6'''); ^{13}C NMR (125.8 MHz, DMSO-d_6): 36.42 (CH_2-2'); 55.15 and 55.17 (OCH_3); 63.90 (CH_2-5'); 71.24 (CH-3'); 84.91 (CH-1'); 85.41 (C-DMTr); 86.02 (CH-4'); 113.14 and 113.19 (CH-*m*-C_6H_4-DMTr); 119.34 (C-5); 119.83 (CH-3''); 120.99 and 121.02 (CH-3''' and CH-5''); 124.62 (CH-5'''); 126.68 (CH-*p*-C_6H_6-DMTr); 127.05 (CH-*m*-phenylene); 127.82 and

127.86 (CH-*o*+*m*-C_6H_5-DMTr); 129.81 and 129.91 (CH-*o*-C_6H_4-DMTr); 130.19 (CH-*o*-phenylene); 130.78 (C-*i*-phenylene); 135.90 and 135.93 (C-*i*-C_6H_4-DMTr); 137.63 (CH-4'''); 138.85 (CH-4''); 139.86 (C-*p*-phenylene); 145.25 (C-*i*-C_6H_5-DMTr); 149.53 (CH-6'''); 150.41 (C-4); 150.60 (C-8); 152.36 (CH-2); 154.67 (C-6''); 155.36 and 155.37 (C-2'' and C-2'''); 156.21 (C-6); 158.11 and 158.16 (C-*p*-C_6H_4-DMTr); FAB MS: *m/z* (%) 303.1 (100) [DMTr], 366.2 (40) [M^+ - DMTrdRf], 784.3 [M^+], 806.4 (35) [M^+ + Na]; HR MS (TOF ES MS+) calc. 784.3247 found. 784.3262.

5'-*O*-DMTr-8-[(2'',2'''-bipyridin-5''-yl)phenyl]-2'-deoxyadenosine (6b)

The product was isolated as white powder 96 mg (49 %). M. p. 128-133 °C; ^{1}H NMR (600 MHz, DMSO-d_6): 2.20 (ddd, 1H, J_{gem} = 13.5, $J_{2'b,1'}$ = 7.6, $J_{2'b,3'}$ = 4.7, H-2'b); 3.22 (dd, 1H, J_{gem} = 10.1, $J_{5'b,4'}$ = 6.1, H-5'b); 3.28 (dd, 1H, J_{gem} = 10.1, $J_{5'a,4'}$ = 4.7, H-5'a); 3.52 (ddd, 1H, J_{gem} = 13.5, $J_{2'a,3'}$ = 6.4, $J_{2'a,1'}$ = 5.8, H-2'a); 3.706 and 3.714 (2 × s, 2 × 3H, OCH_3); 4.03 (ddd, 1H, $J_{4',5'}$ = 6.1, 4.7, $J_{4',3'}$ = 4.0, H-4'); 4.73 (m, 1H, $J_{3',2'}$ = 6.4, 4.7, $J_{3',OH}$ = 4.6, $J_{3',4'}$ = 4.0, H-3'); 5.33 (d, 1H, $J_{OH,3'}$ = 4.6, OH-3'); 6.25 (dd, 1H, $J_{1',2'}$ = 7.6, 5.8, H-1'); 6.76 and 6.80 (2 × m, 2 × 2H, H-*m*-C_6H_4-DMTr); 7.16 (m, 1H, H-*p*-C_6H_5-DMTr); 7.19-7.23 (m, 6H, H-*o*-C_6H_4-DMTr and H-*m*-C_6H_5-DMTr); 7.35 (m, 2H, H-*o*-C_6H_5-DMTr); 7.38 (bs, 2H, NH_2); 7.49 (ddd, 2H, $J_{5''',4'''}$ = 7.5, $J_{5''',6'''}$ = 4.7, $J_{5''',3'''}$ = 1.2, H-5'''); 7.97-8.01 (m, 4H, H-2, H-*o*-phenylene and H-4'''); 8.07 (m, 2H, H-*m*-phenylene); 8.38 (dd, 1H, $J_{4'',3''}$ = 8.2, $J_{4'',6''}$ = 2.3, H-4''); 8.46 (ddd, 1H, $J_{3''',4'''}$ = 7.9, $J_{3''',5'''}$ = 1.2, $J_{3''',6'''}$ = 0.9, H-3'''); 8.53 (dd, 1H, $J_{3'',4''}$ = 8.2, $J_{3'',6''}$ = 0.8, H-3''); 8.73 (ddd, 1H, $J_{6''',5'''}$ = 4.7, $J_{6''',4'''}$ = 1.8, $J_{6''',3'''}$ = 0.9, H-6'''); 9.15 (dd, 1H, $J_{6'',4''}$ = 2.3, $J_{6'',3''}$ = 0.8, H-6''); ^{13}C NMR (151 MHz, DMSO-d_6): 36.33 (CH_2-2'); 55.17 and 55.18 (OCH_3); 63.89 (CH_2-5'); 71.28 (CH-3'); 84.98 (CH-1'); 85.41 (C-DMTr); 86.08 (CH-4'); 113.15 and 113.20 (CH-*m*-C_6H_4-DMTr); 119.38 (C-5); 120.74 (CH-3'' and CH-3'''); 124.58 (CH-5'''); 126.69 (CH-*p*-C_6H_6-DMTr); 127.32 (CH-*m*-phenylene); 127.86 (CH-*o*+*m*-C_6H_5-DMTr); 129.81 and 129.93 (CH-*o*-C_6H_4-DMTr); 129.96 (C-*i*-phenylene); 130.45 (CH-*o*-phenylene); 134.88 (C-5''); 135.58 (CH-4''); 135.92 (C-*i*-C_6H_4-DMTr); 137.64 (CH-4'''); 138.25 (C-*p*-phenylene); 145.27 (C-*i*-C_6H_5-DMTr); 147.59 (CH-6''); 149.66 (CH-6'''); 150.39 and 150.54 (C-4 and C-8); 152.36 (CH-2); 154.82 (C-2''); 155.21 (C-2'''); 156.21 (C-6); 158.11 and 158.117 (C-*p*-C_6H_4-DMTr). ESI MS: *m/z* (%) 303.1 (80) [DMTr], 784.2 (10) [M^+], 806.2 (10) [M^+ + Na]; HR MS (TOF ES MS+) calc. 784.3247 found. 784.3284.

5'-*O*-DMTr-8-[(1'',10''-phenantrolin-2''-yl)phenyl]-2'-deoxyadenosine (6c)

The product was isolated as white powder 119 mg (59 %). M. p. 177-182 °C; ^{1}H NMR (500 MHz, DMSO-d_6): 2.22 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 7.4, $J_{2'b,3'}$ = 4.6, H-2'b); 3.23 (dd, 1H, J_{gem} = 10.1, $J_{5'b,4'}$ = 5.9, H-5'b); 3.30 (dd, 1H, J_{gem} = 10.1, $J_{5'a,4'}$ = 4.8, H-5'a); 3.52 (dt, 1H, J_{gem} = 13.3, $J_{2'a,3'}$ = 6.5, $J_{2'a,1'}$ = 6.5, H-2'a); 3.71 and 3.72 (2 × s, 2 × 3H, OCH_3); 4.04 (dt, 1H, $J_{4',5'}$ = 5.9, 4.8, $J_{4',3'}$ = 4.8, H-4'); 4.70 (dq, 1H, $J_{3',2'}$ = 6.5, 4.6, $J_{3',4'}$ = 4.8, $J_{3',OH}$ = 4.7, H-3'); 5.30 (d, 1H, $J_{OH,3'}$ = 4.7, OH-3'); 6.29 (dd, 1H, $J_{1',2'}$ = 7.4, 6.5, H-1'); 6.78 and 6.82 (2 × m, 2 × 2H, H-*m*-C_6H_4-DMTr); 7.17 (m, 1H, H-*p*-C_6H_5-DMTr); 7.20-7.25 (m, 6H, H-*o*-C_6H_4-DMTr and H-*m*-C_6H_5-DMTr); 7.37 (m, 4H, H-*o*-C_6H_5-DMTr and NH_2); 7.82 (dd, 1H, $J_{8",7"}$ = 8.1, $J_{8",9"}$ = 4.3, H-8"); 8.01 (s, 1H, H-2); 8.02 (d, 1H, $J_{6",5"}$ = 8.9, H-6"); 8.05 (m, 2H, H-*o*-phenylene); 8.06 (d, 1H, $J_{5",6"}$ = 8.9, H-5"); 8.51 (d, 1H, $J_{3",4"}$ = 8.6, H-3"); 8.53 (dd, 1H, $J_{7",8"}$ = 8.1, $J_{7",9"}$ = 1.8, H-7"); 8.65 (d, 1H, $J_{4",3"}$ = 8.6, H-4"); 8.67 (m, 2H H-*m*-phenylene); 9.19 (dd, 1H, $J_{9",8"}$ = 4.3, $J_{9",7"}$ = 1.8, H-9"); ^{13}C NMR (125.8 MHz, DMSO-d_6): 36.45 (CH_2-2'); 55.13 and 55.14 (OCH_3); 63.89 (CH_2-5'); 71.24 (CH-3'); 84.90 (CH-1'); 85.41 (C-DMTr); 85.96 (CH-4'); 113.14 and 113.18 (CH-*m*-C_6H_4-DMTr); 119.35 (C-5); 120.43 (CH-3"); 123.62 (CH-8"); 126.56 (CH-5"); 126.65 (CH-6"); 127.05 (CH-*p*-C_6H_6-DMTr); 127.69 (CH-*m*-phenylene); 127.79 and 127.85 (CH-*o*+*m*-C_6H_5-DMTr); 127.95 (C-4"a); 129.08 (C-6"a); 129.78 and 129.88 (CH-*o*-C_6H_4-DMTr); 130.18 (CH-*o*-phenylene); 130.98 (C-*i*-phenylene); 135.91 (C-*i*-C_6H_4-DMTr); 136.49 (CH-7"); 137.74 (CH-4"); 140.25 (C-*p*-phenylene); 145.22 (C-*i*-C_6H_5-DMTr); 145.55 (C-10"b); 145.79 (C-10"a); 150.23 (CH-9"); 150.44 and 150.59 (C-4 and C-8); 152.34 (CH-2); 154.76 (C-2"); 156.20 (C-6); 158.10 and 158.14 (C-*p*-C_6H_4-DMTr); FAB MS: *m/z* (%) 303.2 (50) [DMTr], 390.2 (10) [M^+ - DMTrdRf], 830.6 (40) [M^+ + Na]; HR MS (TOF ES MS+) calc. 808.3247 found. 808.3256.

5'-*O*-DMTr-8-[(4"-(2",2'":6",2'"-terpyridin-1"-yl)phenyl]-2'-deoxyadenosine (6d)

The product was isolated as white powder 142 mg (66 %). M. p. 173-177 °C; ^{1}H NMR (600 MHz, DMSO-d_6): 2.21 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 7.5, $J_{2'b,3'}$ = 4.7, H-2'b); 3.22 (dd, 1H, J_{gem} = 10.1, $J_{5'b,4'}$ = 6.3, H-5'b); 3.28 (dd, 1H, J_{gem} = 10.1, $J_{5'a,4'}$ = 4.7, H-5'a); 3.49 (ddd, 1H, J_{gem} = 13.3, $J_{2'a,3'}$ = 6.7, $J_{2'a,1'}$ = 5.9, H-2'a); 3.70 and 3.71 (2 × s, 2 × 3H, OCH_3); 4.03 (dt, 1H, $J_{4',5'}$ = 6.3, 4.7, $J_{4',3'}$ = 3.8, H-4'); 4.69 (dq, 1H, $J_{3',2'}$ = 6.7, 4.7, $J_{3',OH}$ = 4.7, $J_{3',4'}$ = 3.8, H-3'); 5.34 (d, 1H, $J_{OH,3'}$ = 4.7, OH-3'); 6.28 (dd, 1H, $J_{1',2'}$ = 7.5, 5.9, H-1'); 6.77 and 6.81 (2 × m, 2 × 2H, H-*m*-C_6H_4-DMTr); 7.16 (m, 1H, H-*p*-C_6H_5-DMTr); 7.20-7.23 (m, 6H, H-*o*-C_6H_4-DMTr and H-*m*-C_6H_5-DMTr); 7.36 (m, 2H, H-*o*-C_6H_5-DMTr); 7.41 (bs, 2H, NH_2); 7.55 (ddd, 2H, $J_{5'",4'"}$ = 7.5, $J_{5'",6'"}$ = 4.7, $J_{5'",3'"}$ = 1.1, H-5'"); 8.01 (s, 1H, H-

2); 8.04 (m, 2H, H-*o*-phenylene); 8.06 (ddd, 2H, $J_{4''',3'''}$ = 7.9, $J_{4''',5'''}$ = 7.5, $J_{4''',6'''}$ = 1.8, H-4'''); 8.16 (m, 2H, H-*m*-phenylene); 8.70 (dt, 2H, $J_{3''',4'''}$ = 7.9, $J_{3''',5'''}$ = 1.1, $J_{3''',6'''}$ = 0.9, H-3'''); 8.78 (ddd, 2H, $J_{6'''5'''}$ = 4.7, $J_{6'''4'''}$ = 1.8, $J_{6'''3'''}$ = 0.9, H-6'''); 8.81 (s, 2H, H-3",5"); ^{13}C NMR (151 MHz, DMSO-d_6): 36.53 (CH_2-2'); 55.18 and 55.19 (OCH_3); 63.93 (CH_2-5'); 71.25 (CH-3'); 84.91 (CH-1'); 85.45 (C-DMTr); 86.01 (CH-4'); 113.18 and 113.22 (CH-*m*-C_6H_4-DMTr); 118.14 (CH-3",5"); 119.40 (C-5); 121.24 (CH-3'''); 124.90 (CH-5'''); 126.73 (CH-*p*-C_6H_6-DMTr); 127.54 (CH-*m*-phenylene); 127.88 and 127.90 (CH-*o*+*m*-C_6H_5-DMTr); 129.84 and 129.94 (CH-*o*-C_6H_4-DMTr); 130.71 (CH-*o*-phenylene); 131.06 (C-*i*-phenylene); 135.93 and 135.95 (C-*i*-C_6H_4-DMTr); 137.78 (CH-4'''); 139.07 (C-*p*-phenylene); 145.25 (C-*i*-C_6H_5-DMTr); 148.84 (C-4"); 149.63 (CH-6'''); 150.37 (C-4); 150.46 (C-8); 152.46 (CH-2); 155.08 (C-2'''); 156.08 (C-2",6"); 156.27 (C-6); 158.14 and 158.18 (C-*p*-C_6H_4-DMTr); TOF MS ES+: *m/z* (%) 861.4 (100), HR MS (TOF MS ES+) calc. 861.3513 found 861.3539

General Procerude for Sonogashira Cross-Coupling Reactions (unprotected nucleosides):

DMF (1 ml) and Et(*i*Pr)$_2$N (0.22 ml, 1.25 mmol, 10 equiv.) were added to an argon-purged flask containing nucleoside **7** (41 mg, 0.125 mmol), an alkyne **2a-b** (0.188 mmol, 1.5 equiv.) and CuI (2.4 mg, 0.0125 mmol, 10 mol%). In a separate flask, $Pd(OAc)_2$ (1.4 mg, 0.00625 mmol, 5 mol%) and P(Ph-$SO_3Na)_3$ (8.9 mg, 0.0156 mmol, 2.5 equiv. to Pd) were combined, evacuated and purged with argon followed by addition of DMF (0.5 ml). This solution of catalyst was added through a syringe to the reaction mixture which was then stirred at 75 °C until complete consumption of the strating material. The solvent was evaporated in vacuo. The products were purified by silicagel column chromotagraphy using MeOH/$CHCl_3$ (1% to 20%) as eluent.

8-[(2",2'"-bipyridin-6"-yl)ethynyl]-2'-deoxyadenosine (8a)

The product was isolated as white powder 51 mg (96 %). M.p. 210-214 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 2.32 (ddd, 1H, J_{gem} = 13.4, $J_{2'b,1'}$ = 6.6, $J_{2'b,3'}$ = 2.8, H-2'b,); 3.19 (ddd, 1H, J_{gem} = 13.4, $J_{2'a,1'}$ = 7.9, $J_{2'a,3'}$ = 6.3, H-2'a); 3.56 (ddd, 1H, J_{gem} = 11.8, $J_{5'b,OH}$ = 7.5, $J_{5'b,4'}$ = 5.2, 1H, H-5'b); 3.72 (dt, 1H, J_{gem} = 11.8, $J_{5'a,OH}$ = $J_{5'a,4'}$ = 4.6, H-5'a); 3.94 (ddd, 1H, $J_{4',5'}$ = 5.2, 4.6, $J_{4',3'}$ = 2.9, 1H, H-4'); 4.56 (dddd, 1H, $J_{3',2'}$ = 6.3, 2.8, $J_{3',OH}$ = 4.2, $J_{3',4'}$ = 2.0, H-3'); 5.26 (dd, $J_{OH,5'}$ = 7.5, 4.6, 1H, OH-5'); 5.39 (d, $J_{OH,3'}$ = 4.2, OH-3'); 6.59 (dd, $J_{1',2'}$ = 7.9, 6.6, 1H, H-1'); 7.52 (ddd, $J_{5'''4'''}$ = 7.5, $J_{5'''6'''}$ = 4.8, $J_{5'''3'''}$ = 1.2, 1H, H-5'''); 7.71

(bs, 2H, NH_2); 7.87 (dd, $J_{5'',4''}$ = 7.7, $J_{5'',3''}$ = 1.0, 1H, H-5''); 7.99 (ddd, $J_{4''',3'''}$ = 8.0, $J_{4''',5'''}$ = 7.5, $J_{4''',6'''}$ = 1.8, 1H, H-4'''); 8.11 (dd, $J_{4'',3''}$ = 8.1, $J_{4'',5''}$ = 7.7, 1H, H-4''); 8.21 (s, 1H, H-2); 8.43 (ddd, $J_{3''',4'''}$ = 8.0, $J_{3''',5'''}$ = 1.2, $J_{3''',6'''}$ = 0.9, 1H, H-3'''); 8.51 (dd, $J_{3'',4''}$ = 8.1, $J_{3'',5''}$ = 1.0, 1H, H-3''); 8.73 (ddd, $J_{6''',5'''}$ = 4.8, $J_{6''',4'''}$ = 1.8, $J_{6''',3'''}$ = 0.9, 1H, H-6'''). ^{13}C NMR (100.6 MHz, DMSO-d_6): 38.07 (CH_2-2'); 62.39 (CH_2-5'); 71.41 (CH-3'); 77.69 (pur-**C**≡C-); 85.10 (CH-1'); 88.53 (CH-4'); 93.51 (bpy-**C**≡C-); 119.92 (C-5); 121.05 (CH-3'''); 121.70 (CH-3''); 124.98 (CH-5'''); 128.47 (CH-5''); 132.23 (C-8); 137.76 (CH-4'''); 138.64 (CH-4''); 140.23 (C-6''); 148.90 (C-4); 149.62 (CH-6'''); 153.99 (C-2'''); 154.28 (CH-2); 156.41 (C-6); 156.42 (C-2''); ESI MS: *m/z* (%) 452.1 (100) [M^+ + Na], 314.3 (10) [M^+ - dRf], $C_{22}H_{19}N_7O_3.1/2H_2O$ (429.43) calcd. C 60.27, H 4.60, N 22.36; found C 60.13, H 4.33, N 22.21; IR (KBr): 3414, 3186, 2229,1652, 1572, 1427, 1336, 1102, 779 .

8-[(2'',2'''-bipyridin-5''-yl)ethynyl]-2'-deoxyadenosine (8b)

The product was isolated as yellowish powder 48 mg (90 %). M.p. > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 2.31 (ddd, 1H, J_{gem} = 13.4, $J_{2'b,1'}$ = 6.7, $J_{2'b,3'}$ = 3.1, H-2'b); 3.16 (ddd, 1H, J_{gem} = 13.4, $J_{2'a,1'}$ = 7.5, $J_{2'a,3'}$ = 6.1, H-2'a); 3.52 (ddd, 1H, J_{gem} = 11.9, $J_{5'b,OH}$ = 7.5, $J_{5'b,4'}$ = 5.0, H-5'b); 3.69 (dt, 1H, J_{gem} = 11.9, $J_{5'a,OH}$ = $J_{5'a,4'}$ = 4.6, H-5'a); 3.92 (td, 1H, $J_{4',5}$ = 5.0, 4.6 $J_{4',3'}$ = 3.1, H-4'); 4.54 (ddt, 1H, $J_{3',2'}$ = 6.1, 3.1, $J_{3',OH}$ = 4.6, $J_{3',4'}$ = 3.1, H-3'); 5.29 (dd, 1H, $J_{OH,5'}$ = 7.5, 4.6, OH-5'); 5.38 (d, 1H, $J_{OH,3'}$ = 4.6, OH-3'); 6.58 (dd, 1H, $J_{1',2'}$ = 7.5, 6.7, H-1'); 7.51 (ddd, 1H, $J_{5''',4'''}$ = 7.5, $J_{5''',6'''}$ = 4.7, $J_{5''',3'''}$ = 1.2, H-5'''); 7.69 (bs, 2H, NH_2); 8.00 (ddd, 1H, $J_{4''',3'''}$ = 8.0, $J_{4''',5'''}$ = 7.5, $J_{4''',6'''}$ = 1.8, H-4'''); 8.20 (s, 1H, H-2); 8.27 (dd, 1H, $J_{4'',3''}$ = 8.3, $J_{4'',6''}$ = 2.3, H-4''); 8.44 (dd, 1H, $J_{3''',4'''}$ = 8.0, $J_{3''',5'''}$ = 1.2, $J_{3''',6'''}$ = 0.9, H-3'''); 8.51 (dd, 1H, $J_{3'',4''}$ = 8.3, $J_{3'',6''}$ = 1.0, H-3''); 8.74 (ddd, 1H, $J_{6''',5'''}$ = 4.7, $J_{6''',4'''}$ = 1.8, $J_{6''',3'''}$ = 0.9, H-6'''); 9.00 (dd, 1H, $J_{6'',4''}$ = 2.3, $J_{6'',3''}$ = 1.0, H-6''). ^{13}C NMR (100.6 MHz, DMSO-d_6): 38.09 (CH_2-2'); 62.32 (CH_2-5'); 71.33 (CH-3'); 82.64 (pur-**C**≡C-); 85.19 (CH-1'); 88.48 (CH-4'); 91.64 (bpy-**C**≡C-); 117.57 (C-5''); 119.94 (C-5); 120.34 (CH-3''); 121.26 (CH-3'''); 125.04 (CH-5'''); 132.54 (C-8); 137.73 (CH-4'''); 140.50 (CH-4''); 148.82 (C-4); 149.77 (CH-6'''); 152.09 (CH-6''); 153.84 (C-2'''); 154.28 (CH-2); 155.68 (C-2''); 156.37 (C-6); ESI MS: *m/z* (%) 452.1 (90) [M^+ + Na], 314.3 (15) [M^+ - dRf], $C_{22}H_{19}N_7O_3$. H_2O (429.43) calcd. C 59.05, H 4.73, N 21.91; found C 59.02, H 4.67, N 21.56; IR (KBr): 3392, 3180, 2285, 1645, 1572, 1332, 1103, 797.

General Procerude for Suzuki-Miyaura Cross-Coupling Reactions (unprotected nucleosides):

A mixture of H_2O / CH_3CN = 2 / 1 (1 ml) was added to an argon-purged flask containing nucleoside **7** (83 mg, 0.25 mmol), a boronate **3a-d** (0.3 mmol, 1.2 equiv.) and Cs_2CO_3 (247 mg, 0.75 mmol, 3 equiv.). H_2O / CH_3CN = 2 / 1 (1 ml) was added to the argon purged reaction mixture. In a separate flask, $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol, 5 mol%) and $P(Ph\text{-}SO_3Na)_3$ (17.5 mg, 0.0313 mmol, l2.5 equiv. to Pd) were combined, evacuated and purged with argon followed by addition of H_2O / CH_3CN = 2 / 1 (0.5 ml). The mixture of catalyst was then injected to the reaction mixture and the reaction mixture was stired at 80°C until complete consumption of the strating material. The solvent was evaporated in vacuo. Products **9a,c,d** were purified by silicagel column chromotagraphy using MeOH/$CHCl_3$ (1% to 20%) as eluent. Product **9b** was purified by HPLC on silicagel (25x250 mm column) using a linear gradient of MeOH in $CHCl_3$ (1% to 20%).

8-[(2",2'"-bipyridin-6"-yl)phenyl]-2'-deoxyadenosine (9a)

The product was isolated as white powder 112 mg (93 %). M.p. 166-168 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 2.20 (ddd, 1H, J_{gem} = 13.2, $J_{2'b,1'}$ = 6.2, $J_{2'b,3'}$ = 2.4, H-2'b); 3.36 (ddd, 1H, J_{gem} = 13.2, $J_{2'a,1'}$ = 8.5, $J_{2'a,3'}$ = 5.6, H-2'a); 3.56 (ddd, 1H, J_{gem} = 11.9, $J_{5'b,OH}$ = 8.2, $J_{5'b,4'}$ = 4.5, H-5'b); 3.73 (dt, 1H, J_{gem} = 11.9, $J_{5'a,OH}$ = $J_{5'a,4'}$ = 4.2, H-5'a); 3.90 (ddd, 1H, $J_{4',5'}$ = 4.5, 4.2, $J_{4',3'}$ = 2.2, H-4'); 4.49 (dddd, 1H, $J_{3',2'}$ = 5.6, 2.4, $J_{3',OH}$ = 4.1, $J_{3',4'}$ = 2.2, H-3'); 5.26 (d, 1H, $J_{OH,3'}$ = 4.1, OH-3'); 5.54 (dd, 1H, $J_{OH,5'}$ = 8.2, 4.2, OH-5'); 6.25 (dd, 1H, $J_{1',2'}$ = 8.5, 6.2, H-1'); 7.51 (ddd, 1H, $J_{5'",4'"}$ = 7.5, $J_{5'",6'"}$ = 4.7, $J_{5'",3'"}$ = 1.2, H-5'"); 7.51 (bs, 2H, NH_2); 7.91 (m, 2H, H-*o*-phenylene); 8.02 (ddd, 1H, $J_{4'",3'"}$ = 8.0, $J_{4'",5'"}$ = 7.5, $J_{4'",6'"}$ = 1.8, H-4'"); 8.10 (dd, 1H, $J_{4",5"}$ = 8.0, $J_{4",3"}$ = 7.8, H-4"); 8.17 (s, 1H, H-2); 8.18 (dd, 1H, $J_{5",4"}$ = 8.0, $J_{5",3"}$ = 1.1, H-5"); 8.41 (dd, 1H, $J_{3",4"}$ = 7.8, $J_{3",5"}$ = 1.1, H-3"); 8.49 (m, 2H, H-*m*-phenylene); 8.65 (ddd, 1H, $J_{3'",4'"}$ = 8.0, $J_{3'",5'"}$ = 1.2, $J_{3'",6'"}$ = 0.9, H-3'"); 8.73 (ddd, 1H, $J_{6'",5'"}$ = 4.7, $J_{6'",4'"}$ = 1.8, $J_{6'",3'"}$ = 0.9, H-6'"); ^{13}C NMR (100.6 MHz, DMSO-d_6): 37.65 (CH_2-2'); 62.69 (CH_2-5'); 71.83 (CH-3'); 86.12 (CH-1'); 88.76 (CH-4'); 119.61 (C-5) 120.06 (CH-3"); 121.17 and 121.21 (CH-3'" and CH-5"); 124.79 (CH-5'"); 127.30 (CH-*m*-phenylene); 130.33 (CH-*o*-phenylene); 130.52 (C-*i*-phenylene); 137.83 (CH-4'"); 139.05 (CH-4"); 140.19 (C-*p*-phenylene); 149.67, 150.35 and 150.54 (C-4, C-8 and CH-6'"); 152.44 (CH-2); 154.78 (CH-6"); 155.48 and 155.53 (C-2" and C-2'"); 156.51 (C-6); ESI MS: *m/z* (%) 366.4 (100) [M^+ - dRf], 504.2 (60) [M^+ + Na]; $C_{26}H_{23}N_7O_3.1/2H_2O$ (481.51) calcd. C 63.66, H 4.93, N 19.99; found C 63.57, H 4.78, N 19.72; IR (KBr): 3400, 3187, 2297, 1639, 1582, 1430, 1091, 781.

8-[(2",2'"-bipyridin-5"-yl)phenyl]-2'-deoxyadenosine (9b)

The product was isolated as white powder 46 mg (38 %). M.p. 162-168 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 2.19 (ddd, 1H, J_{gem} = 13.2, $J_{2'b,1'}$ = 6.3, $J_{2'b,3'}$ = 2.2, H-2'b); 3.38 (ddd, 1H, J_{gem} = 13.2, $J_{2'a,1'}$ = 8.4, $J_{2'a,3'}$ = 5.6, H-2'a); 3.56 (ddd, 1H, J_{gem} = 11.9, $J_{5'b,OH}$ = 8.1, $J_{5'b,4'}$ = 4.5, H-5'b); 3.73 (dt, 1H, J_{gem} = 11.9, $J_{5'a,OH}$ = $J_{5'a,4'}$ = 4.2, H-5'a); 3.92 (ddd, 1H, $J_{4',5'b}$ = 4.5, $J_{4',5'a}$ = 4.2, $J_{4',3'}$ = 2.1, H-4'); 4.50 (dddd, 1H, $J_{3',2'}$ = 5.6, 2.2, $J_{3',OH}$ = 4.1, $J_{3',4'}$ = 2.1, H-3'); 5.27 (d, 1H, $J_{OH,3'}$ = 4.1, OH-3'); 5.53 (dd, 1H, $J_{OH,5'}$ = 8.1, 4.2, OH-5'); 6.25 (dd, 1H, $J_{1',2'}$ = 8.4, 6.3, H-1'); 7.48 (ddd, 1H, $J_{5'",4'"}$ = 7.5, $J_{5'",6'"}$ = 4.8, $J_{5'",3'"}$ = 1.3, H-5'"); 7.48 (bs, 2H, NH_2); 7.89 (m, 2H, H-*o*-phenylene); 7.98 (ddd, 1H, $J_{4'",3'"}$ = 7.9, $J_{4'",5'"}$ = 7.5, $J_{4'",6'"}$ = 1.8, H-4'"); 8.07 (m, 2H, H-*m*-phenylene); 8.18 (s, 1H, H-2); 8.37 (dd, 1H, $J_{4",3"}$ = 8.4, $J_{4",6"}$ = 2.5, H-4"); 8.46 (ddd, 1H, $J_{3'",4'"}$ = 7.9, $J_{3'",5'"}$ = 1.3, $J_{3'",6'"}$ = 1.0, H-3'"); 8.52 (dd, 1H, $J_{3",4"}$ = 8.2, $J_{3",6"}$ = 0.8, H-3"); 8.73 (ddd, 1H, $J_{6'",5'"}$ = 4.8, $J_{6'",4'"}$ = 1.8, $J_{6'",3'"}$ = 1.0, H-6'"); 9.14 (dd, 1H, $J_{6",4"}$ = 2.5, $J_{6",3"}$ = 0.8, H-6"); ^{13}C NMR (100.6 MHz, DMSO-d_6): 37.33 (CH_2-2'); 62.54 (CH_2-5'); 71.69 (CH-3'); 85.94 (CH-1'); 88.65 (CH-4'); 119.53 (C-5); 120.73 (CH-3" and CH-3'"); 124.52 (CH-5'"); 127.32 (CH-*m*-phenylene); 129.66 (C-*i*-phenylene); 130.41 (CH-*o*-phenylene); 134.82 (C-5"); 135.55 (CH-4"); 137.57 (CH-4'"); 138.36 (C-*p*-phenylene); 147.59 (CH-6"); 149.61 (CH-6'"); 150.23 (C-4 and C-8); 152.28 (CH-2); 154.84 (C-2"); 155.00 (C-2'"); 156.42 (C-6); ESI MS: *m/z* (%) 366.5 (100) [M^+ - dRf], 504.2 (65) [M^+ + Na]; $C_{26}H_{23}N_7O_3.1/2H_2O$ (481.51) calcd. C 63.66, H 4.93, N 19.99; found C 63.30, H 4.84, N 19.47; IR (KBr): 3409, 3189, 3060, 2299, 1640, 1461, 1093, 798.

8-[(1",10"-phenantrolin-2"-yl)phenyl]-2'-deoxyadenosine (9c)

The product was isolated as white powder 120 mg (95 %). M.p. 202-204 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 2.23 (ddd, 1H, J_{gem} = 13.1, $J_{2'b,1'}$ = 6.2, $J_{2'b,3'}$ = 2.0, H-2'b); 3.36 (ddd, 1H, J_{gem} = 13.1, $J_{2'a,1'}$ = 8.5, $J_{2'a,3'}$ = 5.6, H-2'a); 3.57 (ddd, 1H, J_{gem} = 12.0, $J_{5'b,OH}$ = 8.2, $J_{5'b,4'}$ = 4.3, H-5'b); 3.73 (dt, 1H, J_{gem} = 12.0, $J_{5'a,OH}$ = $J_{5'a,4'}$ = 4.0, H-5'a); 3.92 (ddd, 1H, $J_{4',5'}$ = 4.3, 4.0, $J_{4',3'}$ = 2.2, H-4'); 4.49 (dddd, 1H, $J_{3',2'}$ = 5.6, 2.0, $J_{3',OH}$ = 4.2, $J_{3',4'}$ = 2.2, H-3'); 5.27 (d, 1H, $J_{OH,3'}$ = 4.2, OH-3'); 5.57 (dd, 1H, $J_{OH,5'}$ = 8.2, 4.0, OH-5'); 6.28 (dd, 1H, $J_{1',2'}$ = 8.5, 6.2, H-1'); 7.52 (bs, 2H, NH_2); 7.82 (dd, 1H, $J_{8",7"}$ = 8.0, $J_{8",9"}$ = 4.3, H-8"); 7.98 (m, 2H H-*o*-phenylene); 8.02 (d, 1H, $J_{6",5"}$ = 8.8, H-6"); 8.06 (d, 1H, $J_{5",6"}$ = 8.8, H-5"); 8.18 (s, 1H, H-2); 8.52 (d, 1H, $J_{3",4"}$ = 8.5, H-3"); 8.53 (dd, 1H, $J_{7",8"}$ = 8.1, $J_{7",9"}$ = 1.8, H-7"); 8.65 (d, 1H, $J_{4",3"}$ = 8.5, H-4"); 8.68 (m, 2H, H-*m*-phenylene); 9.19 (dd, 1H, $J_{9",8"}$ = 4.3, $J_{9",7"}$ = 1.8, H-9"); ^{13}C NMR (100.6 MHz, DMSO-d_6): 37.81 (CH_2-2');

62.82 (CH_2-5'); 71.96 (CH-3'); 86.24 (CH-1'); 88.90 (CH-4'); 119.80 (C-5); 120.77 (CH-3''); 123.95 (CH-8''); 126.87 (CH-5''); 127.37 (CH-6''); 128.08 (CH-*m*-phenylene); 128.27 (C-4''a); 129.39 (C-6''a); 130.48 (CH-*o*-phenylene); 130.98 (C-*i*-phenylene); 136.83 (CH-7''); 138.06 (CH-4''); 140.66 (C-*p*-phenylene); 145.83 (C-10''b); 146.05 (C-10''a); 150.54 (CH-9''); 150.61 (C-8); 152.60 (C-4); 155.02 (C-2''); 156.73 (C-6); ESI MS: *m/z* (%) 506.2 (100) [$M^+ + H^+$], 528.2 (70) [M^+ + Na]; $C_{28}H_{23}N_7O_3$. H_2O (505.19) calcd. C 64.24, H 4.81, N 18.73; found C 64.10, H 4.54, N 18.60; IR (KBr): 3401, 3174, 2342, 1637, 1489, 1090,737.

8-[(4''-(2'',2''':6'',2'''-terpyridin-1''-yl)phenyl]-2'-deoxyadenosine (9d)

The product was isolated as white powder 129 mg (95 %). M.p. 192-198 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 2.20 (ddd, 1H, J_{gem} = 13.2, $J_{2'b,1'}$ = 6.2, $J_{2'b,3'}$ = 2.2, H-2'b); 3.36 (ddd, 1H, J_{gem} = 13.2, $J_{2'a,1'}$ = 8.4, $J_{2'a,3'}$ = 6.1, H-2'a); 3.57 (ddd, 1H, J_{gem} = 11.8, $J_{5'b,OH}$ = 8.1, $J_{5'b,4'}$ = 4.6, H-5'b); 3.73 (dt, 1H, J_{gem} = 11.8, $J_{5'a,OH}$ = $J_{5'a,4'}$ = 4.1, H-5'a); 3.92 (ddd, 1H, $J_{4',5'}$ = 4.6, 4.1, $J_{4',3'}$ = 2.3, H-4'); 4.50 (dddd, 1H, $J_{3',2'}$ = 6.1, 2.2, $J_{3',OH}$ = 4.3, $J_{3',4'}$ = 2.3, H-3'); 5.27 (d, 1H, $J_{OH,3'}$ = 4.3, OH-3'); 5.53 (dd, 1H, $J_{OH,5'}$ = 8.1, 4.1, OH-5'); 6.28 (dd, 1H, $J_{1',2'}$ = 8.4, 6.2, H-1'); 7.55 (bs, 2H, NH_2); 7.55 (ddd, 2H, $J_{5''',4'''}$ = 7.5, $J_{5''',6'''}$ = 4.7, $J_{5''',3'''}$ = 1.2, H-5'''); 7.96 (m, 2H, H-*o*-phenylene); 8.05 (ddd, 2H, $J_{4''',3'''}$ = 8.0, $J_{4''',5'''}$ = 7.5, $J_{4''',6'''}$ = 1.8, H-4'''); 8.18 (m, 2H, H-*m*-phenylene); 8.18 (s, 1H, H-2); 8.70 (ddd, 2H, $J_{3''',4'''}$ = 8.0, $J_{3''',5'''}$ = 1.2, $J_{3''',6'''}$ = 0.9, H-3'''); 8.78 (ddd, 2H, $J_{6''',5'''}$ = 4.7, $J_{6''',4'''}$ = 1.8, $J_{6''',3'''}$ = 0.9, H-6'''); 8.82 (s, 2H, H-3'',5''); ^{13}C NMR (100.6 MHz, DMSO-d_6): 37.75 (CH_2-2'); 62.77 (CH_2-5'); 71.91 (CH-3'); 86.17 (CH-1'); 88.90 (CH-4'); 118.52 (CH-3'',5''); 119.81 (C-5); 121.46 (CH-3'''); 125.09 (CH-5'''); 127.81 (CH-*m*-phenylene); 130.92 (CH-*o*-phenylene); 131.01 (C-*i*-phenylene); 137.98 (CH-4'''); 139.40 (C-*p*-phenylene); 149.00 (C-4''); 149.85 (CH-6'''); 150.34 (C-8); 150.56 (C-4); 152.64 (CH-2); 155.31 (C-2'''); 156.32 (C-2'',6''); 156.73 (C-6); ESI MS: *m/z* (%) 581.2 (100) [M^+ + Na]; $C_{31}H_{26}N_8O_3$ .H_2O (558.21) calcd. C 64.57, H 4.89, N 19.43; found C 64.23, H 4.81, N 19.30; IR (KBr): 3401, 3062, 2295, 1637, 1585, 1039, 792.

General Procerude for Sonogashira Cross-Coupling Reactions (Ru^{II} complexes):

A mixture of H_2O / CH_3CN = 2 / 1 (1 ml) was added to an argon-purged flask containing nucleoside 7 (53 mg, 0.16 mmol), an alkyne **10a-b** (0.24 mmol, 1.5 equiv.), CuI (3 mg, 0.016 mmol, 10 mol%) and Et(*i*Pr)$_2$N (0.28 ml, 1.6 mmol, 10 equiv.). In a separate flask, $Pd(OAc)_2$ (1.8 mg, 0.008 mmol, 5 mol%) and P(Ph-$SO_3Na)_3$ (11 mg, 0.02 mmol, 2.5

equiv. to Pd) were combined, evacuated and purged with argon followed by an addition of H_2O / CH_3CN = 2 / 1 (0.5 ml). This catalyst solution was then injected to the reaction mixture which was further stirred at 75°C until complete consumption of the strating material. The solvent was evaporated in vacuo. The product was purified by silicagel column chromotagraphy using a mixture of CH_3CN / H_2O / sat. KNO_3 = 10 / 1 / 0.1 as eluent. The products were isolated as PF_6^- salt by precipitation from water solution by addition of sat. NH_4PF_6.

Complex 12a

The product was isolated as orange powder 29 mg (16 %). M.p. > 300 °C. Mixture of two diastereoisomers 5:2. NMR spectra of the major isomer: ^{1}H NMR (600 MHz, acetone-d_6): 2.25 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 6.0, $J_{2'b,3'}$ = 1.6, H-2′b); 3.0.8 (ddd, 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 8.7, $J_{2'a,3'}$ = 5.6, H-2′a); 3.60 (bdd, 1H, J_{gem} = 12.5, $J_{5'b,4'}$ = 2.5, H-5′b); 3.73 (dd, 1H, J_{gem} = 12.5, $J_{5'a,4}$ = 2.5, H-5′a); 3.94 (td, 1H, $J_{4',5'}$ = 2.5, $J_{4',3'}$ = 1.5, H-4′); 4.48 (bs, 1H, OH-3′); 4.67 (bd, 1H, $J_{3',2'a}$ = 5.6, H-3′); 5.53 (bs, 1H, OH-5′); 6.24 (dd, 1H, $J_{1',2'}$ = 8.7, 6.0, H-1′); 6.89 (ddd, 1H, $J_{5,4}$ = 7.6, $J_{5,6}$ = 5.6, $J_{5,3}$ = 1.3, H-5-bpy); 6.99 (bs, 2H, NH_2); 7.50 (ddd, 1H, $J_{5,4}$ = 7.6, $J_{5,6}$ = 5.6, $J_{5,3}$ = 1.3, H-5-bpy); 7.55 (ddd, 1H, $J_{4,3}$ = 8.3, $J_{4,5}$ = 7.6, $J_{4,6}$ = 1.5, H-4-bpy); 7.58, 7.59, 7.77 (3 × ddd, 3 × 1H, $J_{5,4}$ = 7.6, $J_{5,6}$ = 5.6, $J_{5,3}$ = 1.3, H-5''' and H-5-bpy); 7.89, 7.91, 7.92, 7.93 (4 × ddd, 4 × 1H, $J_{6,5}$ = 5.6, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6''' and H-6-bpy); 8.06 (dd, 1H, $J_{5'',4''}$ = 7.8, $J_{5'',3''}$ = 1.3, H-5''); 8.19 (ddd, 1H, $J_{4,3}$ = 8.3, $J_{4,5}$ = 7.6, $J_{4,6}$ = 1.5, H-4-bpy); 8.20 (s, 1H, H-2); 8.24, 8.25 (2 × ddd, 2 × 1H, $J_{4,3}$ = 8.3, $J_{4,5}$ = 7.6, $J_{4,6}$ = 1.5, H-4-bpy); 8.31 (ddd, 1H, $J_{4''',3'''}$ = 8.3, $J_{4''',5'''}$ = 7.6, $J_{4''',6'''}$ = 1.5, H-4'''); 8.33 (dd, 1H, $J_{4'',3''}$ = 8.3, $J_{4'',5''}$ = 7.8, H-4''); 8.58 (ddd, 1H, $J_{3,4}$ = 8.3, $J_{3,5}$ = 1.3, $J_{3,6}$ = 0.7, H-3-bpy); 8.66 (ddd, 1H, $J_{6,5}$ = 5.6, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 8.80, 8.83, 8.85 (3 × ddd, 3 × 1H, $J_{3,4}$ = 8.3, $J_{3,5}$ = 1.3, $J_{3,6}$ = 0.7, H-3-bpy); 8.91 (ddd, 1H, $J_{3''',4'''}$ = 8.3, $J_{3''',5'''}$ = 1.3, $J_{3''',6'''}$ = 0.7, H-3'''); 8.94 (dd, 1H, $J_{3'',4''}$ = 8.3, $J_{3'',5''}$ = 1.3, H-3''). ^{13}C NMR (151 MHz, acetone-d_6): 40.03 (CH_2-2′); 63.81 (CH_2-5′); 73.15 (CH-3′); 86.53 (pur-**C**≡C-); 87.82 (CH-1′); 90.16 (bpy-**C**≡C-); 90.73 (CH-4′); 121.09 (C-5); 124.89, 125.21, 125.55, 125.63, 125.71 (CH-3'', CH-3-bpy); 126.30 (CH-3'''); 128.40, 128.60, 128.77, 129.02, 129.38 (CH-5''', CH-5-bpy); 132.52 (C-8); 135.86 (CH-5''); 137.85 (CH-4-bpy); 139.07, 139.18, 139.21, 139.28, 139.40 (CH-4'',4''', CH-4-bpy); 147.29 (C-6''); 149.31 (C-4); 152.12, 152.47, 152.57, 152.77, 154.05 (CH-6''', CH-6-bpy); 154.69 (CH-2); 157.71, 157.75, 157.98, 158.01, 158.11, 158.68 (C-6, C-2''', C-2-bpy); 159.75 (C-2''). ESI MS: *m/z* (%) 988.0 (100) [M^+ - PF_6^-], 842.2 (15) [M^+ - $2PF_6^-$], 726.1 (25) [M^+ - dRf, -$2PF_6^-$],

$C_{42}H_{35}F_{12}N_{11}O_3P_2Ru.H_2O$ (1132.8) calcd. C 43.83, H 3.24, N 13.39; found C 43.63, H 3.21, N 12.89.

General Procerude for Suzuki-Miyaura Cross-Coupling Reactions (Ru^{II} complexes):

A mixture of H_2O / CH_3CN = 2 / 1 (1 ml) was added to an argon-purged flask containing nucleoside 7 (53 mg, 0.16 mmol), a boronate **11a-d** (0.192 mmol, 1.2 equiv.) and Cs_2CO_3 (158 mg, 0.48 mmol, 3 equiv.). In a separate flask, $Pd(OAc)_2$ (1.8 mg, 0.008 mmol, 5 mol%) and $P(Ph\text{-}SO_3Na)_3$ (11 mg, 0.02 mmol, 2.5 equiv. to Pd) were combined evacuated and purged with argon followed by an addition of H_2O / CH_3CN = 2/1 (0.5 ml). The solution of catalyst was injected to the reaction mixture which was then stirred at 80°C until complete consumption of the starting material. The solvent was evaporated in vacuo. The products **13a-d** were purified by silicagel column chromotagraphy using a mixture of CH_3CN / H_2O / sat. KNO_3 = 10 / 1 / 0.1 as eluent. The products were isolated as PF_6^- salt by precipitation from water solution by addition of sat. NH_4PF_6.

Complex 13a

The product was isolated as orange powder 104 mg (55 %). M.p. 243 - 251 °C. Mixture of diastereoisomers 1:1. ^{1}H NMR (600 MHz, acetone-d_6): 2.33, 2.47 (2 × dd, 2 × 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 5.4, H-2′b); 3.30, 3.38 (2 × ddd, 2 × 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 10.1, $J_{2'a,3'}$ = 4.9, H-2′a); 3.69 (bm, 2H, H-5′b); 3.82, 3.85 (2 × dd, 2 × 1H, J_{gem} = 12.3, $J_{5'a,4}$ = 2.3, H-5′a); 4.20, 4.28 (2 × t, 2 × 1H, $J_{4',5'}$ = 2.3, H-4′); 4.70, 4.77 (2 × d, 2 × 1H, $J_{3',2'a}$ = 4.9, H-3′); 4.79, 5.10 (2 × bs, 2 × 1H, OH-3′); 6.03 (bs, 1H, OH-5′); 6.22, 6.26 (2 × dd, 2 × 1H, $J_{1',2'}$ = 10.1, 5.4, H-1′); 6.31, 6.35 (2 × dd, 2 × 1H, J = 8.0, 1.8, H-*m*-phenylene); 6.38 (bs, 1H, OH-5′); 6.98 (bs, 4H, NH_2); 7.05, 7.13 (2 × ddd, 2 × 1H, $J_{5,4}$ = 7.6, $J_{5,6}$ = 5.6, $J_{5,3}$ = 1.3, H-5-bpy); 7.16, 7.20 (2 × dd, 2 × 1H, J = 8.0, 1.8, H-*o*-phenylene); 7.40-7.46 (m, 4H, 2 × H-5-bpy, H-*o*-phenylene); 7.46, 7.51 (2 × ddd, 2 × 1H, $J_{6,5}$ = 5.6, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 7.53, 7.54 (2 × ddd, 2 × 1H, $J_{5''',4'''}$ = 7.6, $J_{5''',6'''}$ = 5.6, $J_{5''',3'''}$ = 1.3, H-5'''); 7.59, 7.62 (2 × dd, 2 × 1H, $J_{5'',4''}$ = 7.7, $J_{5'',3''}$ = 1.4, H-5''); 7.64, , 7.66 (2 × ddd, 2 × 1H, $J_{5,4}$ = 7.6, $J_{5,6}$ = 5.6, $J_{5,3}$ = 1.3, H-5-bpy); 7.69-7.75 (m, 6H, 2 × H-6''', 2 × H-5-bpy, 2 × H-*m*-phenylene); 7.79, 7.81, 8.08, 8.09 (4 × ddd, 4 × 1H, $J_{4,3}$ = 8.2, $J_{4,5}$ = 7.6, $J_{4,6}$ = 1.5, H-4-bpy); 8.19 (s, 2H, H-2); 8.20-8.25 (m, 6H, 2 × H-4,6-bpy, 2 × H-4'''); 8.25, 8.29 (2 × ddd, 2 × 1H, $J_{6,5}$ = 5.6, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 8.30, 8.32 (2 × ddd, 2 × 1H, $J_{4,3}$ = 8.2, $J_{4,5}$ = 7.6, $J_{4,6}$ = 1.5, H-4-bpy); 8.37 (dd, 2H, $J_{4'',3''}$ = 8.3, $J_{4'',5''}$ = 7.7, H-4''); 8.37, 8.39, 8.64, 8.71, 8.72, 8.81, 8.85 (7 × ddd, 8H, $J_{3,4}$ = 8.3, $J_{3,5}$ = 1.3, $J_{3,6}$ = 0.7, H-3-bpy); 8.90,

8.91 (2 × ddd, 2 × 1H, $J_{3''',4'''}$ = 8.3, $J_{3''',5'''}$ = 1.3, $J_{3''',6'''}$ = 0.7, H-3'''); 8.96, 8.97 (2 × dd, 2 × 1H, $J_{3'',4''}$ = 8.3, $J_{3'',5''}$ = 1.4, H-3''). ^{13}C NMR (151 MHz, acetone-d_6): 39.22, 39.90 (CH_2-2′); 64.09, 64.12 (CH_2-5′); 73.68, 73.89 (CH-3′); 87.79, 87.94 (CH-1′); 90.73, 90.87 (CH-4′); 120.94 (C-5); 124.21, 124.41 (CH-3-bpy); 124.62, 124.72 (CH-3''); 125.07, 125.24, 125.26, 125.55, 125.58, 125.89 (CH-3''', CH-3-bpy); 127.54, 127.68, 128.12, 128.16 (CH-5-bpy); 128.31, 128.35, 128.62 (CH-5-bpy, CH-5''', CH-*m*-phenylene); 128.99, 129.05, 129.07 (CH-5-bpy); 129.54, 129.59, 130.08, 130.18 (CH-*o*-phenylene); 130.85, 130.89, 130.96 (CH-*o*-phenylene, CH-5''); 131.04, 131.05 (C-*i*-phenylene); 137.49, 137.57 (CH-4-bpy); 138.93, 138.96, 139.02, 139.07, 139.08, 139.14 (CH-4''', CH-4-bpy); 139.30 (CH-4''); 141.05, 141.08 (C-*p*-phenylene); 150.57 (C-8); 150.89, 150.99 (C-4); 151.78, 151.81, 152.48, 152.51, 152.83, 153.06, 153.09, 153.42, 153.48 (CH-6''', CH-6-bpy); 157.43, 157.45, 157.46, 157.99, 158.12, 158.15, 158.73, 158.77, 158.81, 158.90, 158.92 (C-6, C-2''', C-2-bpy); 166.73, 166.78 (C-2''). ESI MS: *m/z* (%) 1040.2 (100) [M^+ - PF_6^-], 894.2 (15) [M^+ - $2PF_6^-$], 777.3 (5) [M^+ - dRf, -$2PF_6^-$], $C_{46}H_{39}F_{12}N_{11}O_3P_2Ru.H_2O$ (1184.9) calcd. C 45.93, H 3.44, N 12.81; found C 45.98, H 3.44, N 12.67.

Complex 13b

The product was isolated as orange powder 163 mg (86 %). M.p. 256-260 °C. Mixture of diastereoisomers 1:1. ^{1}H NMR (600 MHz, acetone-d_6): 2.28, 3.28 (2 × m, 2 × 2H, H-2′); 3.66, 3.81 (2 × dd, 2 × 2H, J_{gem} = 12.6, $J_{5',4'}$ = 2.5, H-5′); 4.07 (m, 2H, H-4′); 4.65 (bd, 2H, $J_{3',2'a}$ = 5.1, H-3′); 6.28 (dd, 2H, $J_{1',2'}$ = 9.5, 5.6, H-1′); 6.91 (bs, 4H, NH_2); 7.56-7.66 (m, 10H, H-5''' and H-5-bpy); 7.69, 7.71 (2 × m, 2 × 2H, H-*m*-phenylene); 7.77, 7.78 (2 × m, 2 × 2H, H-*o*-phenylene); 8.04-8.29 (m, 24H, H-2, H-6'', H-4''',6''' and H-4,6-bpy); 8.56, 8.58 (2 × dd, 2 × 1H, $J_{4'',3''}$ = 8.4, $J_{4'',6''}$ = 2.1, H-4''); 8.77-8.90 (m, 10H, H-3''' and H-3-bpy); 8.91, 8.94 (2 × d, 2 × 1H, $J_{3'',4''}$ = 8.4, H-3''). ^{13}C NMR (151 MHz, acetone-d_6): 39.68, 39.74 (CH_2-2′); 64.02 (CH_2-5′); 73.51 (CH-3′); 87.89, 87.92 (CH-1′); 90.54 (CH-4′); 120.88 (C-5); 125.21, 125.27, 125.33, 125.44, 125.48 (CH-3'',3''' and CH-3-bpy); 128.04, 128.34, 128.36, 128.53, 128.69, 128.72, 128.78 (CH-5''', CH-5-bpy and CH-*m*-phenylene); 131.22 (CH-*o*-phenylene); 131.53, 131.81 (C-*i*-phenylene); 136.61, 136.89 (CH-4''); 137.08, 137.34 (C-*p*-phenylene); 138.90 (CH-4''' and CH-4-bpy); 139.81, 139.85 (C-5''); 149.98, 150.23 (CH-6''); 150.86, 151.02 (C-8); 152.60, 152.64, 152.76, 152.99, 153.05, 153.08 (CH-2, C-4,6, CH-6''' and CH-6-bpy); 157.03, 157.17 (C-2''); 157.39, 157.80, 157.97, 158.10, 158.22 (C-2''' and C-2-bpy). ESI MS: *m/z* (%) 1040.2 (100) [M^+ -

PF_6^-], 924.1 (30) [M^+ - dRf, -PF_6^-], $C_{46}H_{39}F_{12}N_{11}O_3P_2Ru.H_2O$ (1184.9) calcd. C 45.93, H 3.44, N 12.81; found C 46.07, H 3.49, N 12.34.

Complex 13c

The product was isolated as orange powder 155 mg (80 %). M.p. 264 - 270 °C. Mixture of diastereoisomers 1:1. ^{1}H NMR (600 MHz, acetone-d_6): 2.35, 2.49 (2 × dd, 2 × 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 5.4, H-2′b); 3.32, 3.41 (2 × ddd, 2 × 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 10.1, $J_{2'a,3'}$ = 5.0, H-2′a); 3.69, 3.72 (2 × ddd, 2 × 1H, J_{gem} = 12.6, $J_{5'b,OH}$ = 11.4, $J_{5'b,4'}$ = 2.5, H-5′b); 3.83, 3.86 (2 × ddd, 2 × 1H, J_{gem} = 12.6, $J_{5'a,4}$ = $J_{5'a,OH}$ = 2.0, H-5′a); 4.20, 4.30 (2 × dd, 2 × 1H, $J_{4',5'}$ = 2.5, 2.0, H-4′); 4.69 (d, 1H, $J_{OH,3'}$ = 2.9, OH-3′); 4.71, 4.78 (2 × dd, 2 × 1H, $J_{3',2'a}$ = 5.0, $J_{3',OH}$ = 2.9, H-3′); 5.00 (d, 1H, $J_{OH,3'}$ = 2.9, OH-3′); 6.04 (dd, 1H, $J_{OH,5'}$ = 11.4, 2.0, OH-5′); 6.26, 6.30 (2 × dd, 2 × 1H, $J_{1',2'}$ = 10.1, 5.4, H-1′); 6.36 (dd, 1H, $J_{OH,5'}$ = 11.4, 2.0, OH-5′); 6.45, 6.47 (2 × dd, 2 × 1H, J = 7.8, 1.8, H-*m*-phenylene); 6.92, 6.93 (2 × bs, 2 × 2H, NH_2); 7.10, 7.18 (2 × ddd, 2 × 1H, $J_{5,4}$ = 7.6, $J_{5,6}$ = 5.6, $J_{5,3}$ = 1.3, H-5-bpy); 7.24, 7.29 (2 × dd, 2 × 1H, J = 7.8, 1.8, H-*o*-phenylene); 7.44, 7.46 (2 × ddd, 2 × 1H, $J_{5,4}$ = 7.6, $J_{5,6}$ = 5.6, $J_{5,3}$ = 1.3, H-5-bpy); 7.47-7.52 (m, 5H, H-*o*-phenylene and 4 × H-5-bpy); 7.53 (dd, 1H, J = 7.8, 1.8, H-*o*-phenylene); 7.55, 7.62 (2 × ddd, 2 × 1H, $J_{6,5}$ = 5.6, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 7.81-7.86 (m, 6H, 2 × H-4,6-bpy and 2 × H-*m*-phenylene); 7.86, 7.87 (2 × dd, 2 × 1H, $J_{8",7"}$ = 8.4, $J_{8",9"}$ = 5.3, H-8"); 7.91, 7.93 (2 × d, 2 × 1H, $J_{3",4"}$ = 8.3, H-3"); 7.98, 8.00 (2 × ddd, 2 × 1H, $J_{6,5}$ = 5.6, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 8.11-8.16 (m, 4H, H-4-bpy); 8.17 (ddd, 1H, $J_{6,5}$ = 5.6, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 8.196, 8.198 (2 × s, 2 × 1H, H-2); 8.22 (ddd, 1H, $J_{6,5}$ = 5.6, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 8.24, 8.26 (2 × ddd, 2 × 1H, $J_{4,3}$ = 8.2, $J_{4,5}$ = 7.6, $J_{4,6}$ = 1.5, H-4-bpy); 8.29, 8.30 (2 × dd, 2 × 1H, $J_{9",8"}$ = 5.3, $J_{9",7"}$ = 1.3, H-9"); 8.41 (ddd, 2H, $J_{3,4}$ = 8.2, $J_{3,5}$ = 1.3, $J_{3,6}$ = 0.7, H-3-bpy); 8.47 (d, 2H, $J_{6",5"}$ = 8.9, H-6"); 8.52 (d, 2H, $J_{5",6"}$ = 8.9, H-5"); 8.67, 8.68, 8.69, 8.71, 8.78, 8.82 (6 × ddd, 6 × 1H, $J_{3,4}$ = 8.2, $J_{3,5}$ = 1.3, $J_{3,6}$ = 0.7, H-3-bpy); 8.824, 8.826 (2 × dd, 2 × 1H, $J_{7",8"}$ = 8.4, $J_{7",9"}$ = 1.3, H-7"); 8.97 (d, 2H, $J_{4",3"}$ = 8.3, H-4"). ^{13}C NMR (151 MHz, acetone-d_6): 39.29, 39.97 (CH_2-2′); 64.11, 64.15 (CH_2-5′); 73.72, 73.98 (CH-3′); 87.81, 88.00 (CH-1′); 90.75, 90.90 (CH-4′); 121.01 (C-5); 124.26, 124.48, 125.16, 125.25, 125.27, 125.37, 125.39 (CH-3-bpy); 126.86 (CH-8"); 127.68, 127.81, 128.07, 128.10 (CH-5-bpy); 128.40, 128.72 (CH-*m*-phenylene); 128.87, 128.89, 129.00, 129.02 (CH-5-bpy); 129.14, 129.16 (CH-6"); 129.29, 129.30 (CH-5"); 129.51, 129.55 (CH-*o*-phenylene); 129.80, 129.82 (CH-3"); 130.01 (CH-*o*-phenylene); 130.19 (CH-*m*-phenylene); 130.86 (CH-*o*-phenylene); 131.31, 131.33, 131.36, 131.40 (C-4"a and C-*i*-

phenylene); 132.58, 132.59 (C-6"a); 137.61, 137.69 (CH-4-bpy); 137.92 (CH-7"); 138.63, 138.66 (CH-4"); 138.93, 139.02, 139.10, 139.18 (CH-4-bpy); 141.10, 141.15 (C-*p*-phenylene); 148.64, 148.76 (C-10"b); 148.89, 148.91 (C-10"a); 150.60, 150.63 (C-8); 150.98, 151.08 (C-4); 152.10, 152.14, 152.75 (CH-6-bpy); 152.90, 152.92 (CH-2); 153.09, 153.32, 153.36 (CH6-bpy); 153.41, 153.42 (CH-9"); 153.53, 153.61 (CH-6"); 157.49, 157.52 (C-6); 157.76, 157.77, 157.99, 158.37, 158.89, 158.91 (C-2-bpy); 167.58, 167.63 (C-2"). ESI MS: *m/z* (%) 1064.1 (100) [M^+ - PF_6^-], 948.1 (20) [M^+ - dRf, -PF_6^-], $C_{46}H_{39}F_{12}N_{11}O_3P_2Ru.H_2O$ (1208.9) calcd. C 46.99, H 3.37, N 12.56; found C 47.01, H 3.38, N 12.09.

Complex 13d

The product was isolated as orange powder 99 mg (52 %). M.p. > 300 °C. ^{1}H NMR (600 MHz, acetone-d_6): 2.30 (ddd, 1H, J_{gem} = 13.7, $J_{2'b,1'}$ = 5.7, $J_{2'b,3'}$ = 1.2, H-2'b); 3.38 (ddd, 1H, J_{gem} = 13.7, $J_{2'a,1'}$ = 9.5, $J_{2'a,3'}$ = 5.4, H-2'a); 3.70 (ddd, 1H, J_{gem} = 12.3, $J_{5'b,OH}$ = 11.1, $J_{5'b,4'}$ = 2.4, H-5'b); 3.86 (ddd, 1H, J_{gem} = 12.3, $J_{5'a,OH}$ = 2.4, $J_{5'a,4'}$ = 2.3, H-5'a); 4.14 (td, 1H, $J_{4',5'}$ = 2.4, $J_{4',3'}$ = 1.0, H-4'); 4.54 (d, 1H, $J_{OH,3'}$ = 3.1, OH-3'); 4.71 (m, 1H, H-3'); 6.08 (dd, 1H, $J_{OH,5'}$ = 11.1, 2.3, OH-5'); 6.46 (dd, 1H, $J_{1',2'}$ = 9.5, 5.7, H-1'); 6.94 (bs, 2H, NH_2); 7.32-7.39 (m, 4H, H-5'-tpy, H-5'"); 7.76 (ddd, 2H, $J_{6'",5'"}$ = 5.7, $J_{6'",4'"}$ = 1.5, $J_{6'",3'"}$ = 0.7, H-6'"); 7.83 (ddd, 2H, $J_{6',5'}$ = 5.7, $J_{6',4'}$ = 1.5, $J_{6',3'}$ = 0.7, H-6'-tpy); 8.08-8.15 (m, 6H, H-4'-tpy, H-4'" and H-*o*-phenylene); 8.57 (m, 2H, H-*m*-phenylene); 8.62 (t, 1H, $J_{4,3\&5}$ = 8.3, H-4-tpy); 8.85 (ddd, 2H, $J_{3',4'}$ = 8.1, $J_{3',5'}$ = 1.4, $J_{3',6'}$ = 0.8, H-3'-tpy); 9.11 (ddd, 2H, $J_{3'",4'"}$ = 8.1, $J_{3'",5'"}$ = 1.4, $J_{3'",6'"}$ = 0.8, H-3'"); 9.12 (d, 2H, $J_{3\&5,4}$ = 8.3, H-3,5-tpy); 9.58 (s, 2H, H-3",5"); ^{13}C NMR (151 MHz, acetone-d_6): 39.86 (CH_2-2'); 64.10 (CH_2-5'); 73.60 (CH-3'); 88.09 (CH-1'); 90.73 (CH-4'); 120.98 (C-5); 122.53 (H-3",5"); 124.81 (H-3,5-tpy); 125.45 (H-3'-tpy); 125.70 (H-3'"); 128.62 and 128.68 (H-5'" and H-5'-tpy); 128.97 (CH-*m*-phenylene); 131.53 (CH-*o*-phenylene); 132.73 (C-*i*-phenylene); 137.07 (CH-4-tpy); 139.11, 139.14 and 139.19 (C-*p*-phenylene, CH-4'" and CH-4'-tpy); 148.01 (C-4"); 150.93 (C-8); 151.18 (C-4); 153.03 (CH-2); 153.45 and 153.54 (H-6'" and H-6'-tpy); 156.39 (C-2,6-tpy); 156.83 (C-2",6"); 157.57 (C-6); 159.19 (C-2'-tpy); 159.31 (C-2'"). ESI MS: *m/z* (%) 1037.9 (100) [M^+ - PF_6^-], 892.1 (15) [M^+ - 2PF_6^-], $C_{46}H_{37}F_{12}N_{11}O_3P_2Ru.H_2O$ (1182.9) calcd. C 46.01, H 3.27, N 12.83; found C 46.15, H 3.29, N 12.62.

Complex 15

A mixture of H_2O / CH_3CN = 2 / 1 (1 ml) was added to an argon-purged flask containing 8-bromo-dATP **14** (used as 3x Et_3N salt and dihydrate) (40 mg, 0.044 mmol), boronate **13d** (86 mg, 0.088 mmol, 2 equiv.), and Cs_2CO_3 (43 mg, 0.13 mmol, 3 equiv.). In a separate flask, $Pd(OAc)_2$ (0.5 mg, 0.0022 mmol, 5 mol%) and $P(Ph\text{-}SO_3Na)_3$ (6.1 mg, 0.011 mmol, 5 equiv. to Pd) were combined, evacuated and purged with argon followed by an addition of H_2O / CH_3CN = 2/1 (0.5 ml). The solution of catalyst was injected to the reaction mixture which was then stirred at 80°C for 1 hour. The solvent was evaporated in vacuo. The product **15** was purified by RP HPLC using a linear gradient of 0.1 M TEAB (triethylammonium bicarbonate) in H_2O to 0.1 M TEAB in H_2O/MeOH (1:1) as eluent. The product was isolated after lyofilization as red powder 30 mg (39 %) (isolated as 2x Et_3N salt). ^{1}H NMR (500 MHz, D_2O): 1.25 (t, 18H, J_{vic} = 7.3, CH_3CH_2N); 2.30 (bm, 1H, H-2'b); 3.15 (q, 12H, J_{vic} = 7.3, CH_3CH_2N); 3.30 (bm, 1H, H-2'a); 4.34-4.43 (m, 2H, H-4' and H-5'b); 4.48 (bm, 1H, H-5'a); 4.82 (bm, 1H, H-3'); 6.25 (bt, 1H, $J_{1',2'}$ = 6.5, H-1'); 6.89 (bm, 2H, H-5'''); 7.21 (bt, 2H, $J_{5',4'}$ = 7.5, $J_{5',6'}$ = 5.4, H-5'-tpy); 7.38 (bd, 2H, $J_{6''',5'''}$ = 5.4, H-6'''); 7.44 (bd, 2H, $J_{6',5'}$ = 5.4, H-6'-tpy); 7.61 (bs, 1H, H-2); 7.73 (bt, 2H, $J_{4''',3'''}$ = 8.2, $J_{4''',5'''}$ = 7.5, H-4'''); 7.81 (bm, 2H, H-*o*-phenylene); 7.93 (bm, 2H, H-*m*-phenylene); 8.04 (bt, 2H, $J_{4',3'}$ = 8.2, $J_{4',5'}$ = 7.5, H-4'-tpy); 8.37 (t, 1H, $J_{4,3\&5}$ = 8.4, H-4-tpy); 8.45 (bd, 2H, $J_{3''',4'''}$ = 8.2, H-3'''); 8.62 (bd, 2H, $J_{3',4'}$ = 8.2, H-3'-tpy); 8.72 (bs, 2H, H-3",5"); 8.75 (d, 2H, $J_{3\&5,4}$ = 8.4, H-3,5-tpy); ^{31}P NMR (162 MHz, D_2O): -22.30 (t, J = 21, 20, P_β); -11.06 (d, J = 20, P_α); -6.30 (d, J = 21, P_γ); ESI MS: *m/z* (%) = 1132.0 (100) [M^+ - $2PF_6^-$].

X-ray diffraction

X-ray crystallographic analysis of single crystals of **9c** (yellowish, 0.17 x 0.19 x 0.63 mm) and **13c** (red, 0.18 x 0.28 x 0.71 mm) was performed with Xcalibur X-ray diffractometr with $Cu_{K\alpha}$ (λ=1.54184 Å), data collected at 150K. Both structures were solved by direct methods with SIR92[3] and refined by full-matrix least-squares methods based on F with CRYSTALS.[4]

Crystal data for 9c: $C_{28}H_{23}N_7O_3$, $C_{28}H_{22}N_7O_3$, triclinic, space group *P1*, a = 10.790(4), b = 10.800(3), c = 13.163(4) Å, α = 96.79(3), β = 106.00(3), γ = 105.90(3)°, V = 1386.6(9) Å^3, Z = 1, M = 1010.06, 5801 reflections measured, 5801 independent reflections. Final R = 0.0576, wR = 0.0920 for 2973 reflections with $I > 1.8\sigma(I)$ and 685 parameters. Hydrogen atoms were located in a difference map, but those attached to carbon atoms were repositioned geometrically and then refined with riding constraints. Hydrogen atom on

O55 has not been found. All non-hydrogen atoms were refined anisotropically. The methanol solvent molecules were not modelled and the disordered density was taken into account using the SQUEEZE/PLATON procedure.[5]

Crystal data for 13c: $C_{48}H_{38}N_{11}O_3Ru$, $C_{48}H_{37}N_{11}O_3$ Ru, 4(F_6P), triclinic, space group *P1*, a = 13.291(5), b = 13.669(5), c = 16.242(5) Å, α = 89.02(3), β = 71.32(3), γ = 89.82(4)°, V = 2794.9(18) Å^3, Z = 1, M = 2414.80, 21182 reflections measured, 21182 independent reflections. Final R = 0.0585, wR = 0.0778 for 14870 reflections with $I > 2\sigma(I)$ and 1358 parameters. Hydrogen atoms were located in a difference map, but those attached to carbon atoms were repositioned geometrically and then refined with riding constraints. Hydrogen atoms on oxygen atoms have not been found except the one attached to O16. Six fluorine atoms on one of the hexafluorophosphate anions had to be refined isotropically due to unresolved disorder. All other atoms were refined anisotropically in both cases. The methanol solvent molecules were not modelled and the disordered density was taken into account using the SQUEEZE/PLATON procedure. [5]

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