Supplementary Material for Organic & Biomolecular Chemistry

Synthesis and photophysical properties of 7-deaza-2'-deoxyadenosines bearing bipyridine ligands and their Ru(II)-complexes in position 7

Milan Vrábel,[a] Radek Pohl,[a] Ivan Votruba,[a] Mohsen Sajadi,[b] Sergey A. Kovalenko,[b] Nikolaus P. Ernsting,[b] and Michal Hocek*[a]

[a] *Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Gilead & IOCB Research Center, Flemingovo nam. 2, CZ-16610 Prague 6, Czech Republic. Fax: +420 220183559; Tel: +420 220183324; E-mail: hocek@uochb.cas.cz*

[b] *Institut für Chemie, Humboldt Universität zu Berlin, Brook-Taylor-Str. 2, D-12489 Berlin, Germany*

Contents:

General Remarks

All cross-coupling reactions were performed under argon atmosphere. Et_3N was degassed in vacuo and stored over molecular sieves under argon. Compounds **1,**[1] **2a,b**, **3a,c,d**, **6a,b**, **7a,c,d**[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 II 600 MHz (600 MHz for ^{1}H and 151 MHz for ^{13}C), Bruker Avance 500 (500 MHz for ^{1}H and 125.8 MHz for ^{13}C) and Bruker Avance 400 (400 for ^{1}H, 100.6 MHz for ^{13}C) spectrometers in DMSO-d_6, acetonitrile-d_3 or acetone-d_6. Chemical shifts (in ppm, δ scale) were referenced to the solvent signal (DMSO-d_6 – 2.5 ppm for ^{1}H NMR and 39.7 ppm for ^{13}C NMR; 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 and acetonitrile-d_3 1.94 ppm for ^{1}H NMR and 1.24 ppm 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).

UV/Vis spectra

The UV-Vis spectra were measured on Varian CARY 100 Bio Spectrophotometer at room temperature. Compounds **4** and **5** were measured as 1.6 x 10^{-5} M solutions in $CHCl_3$. Compounds **8** and **9** were measured as 1.6 x 10^{-5} M solutions in CH_3CN.

Fluorescence measurments

The fluorescence measurements of compounds **4** and **5** were performed on Spectrofluorometer aminco bowman series 2 with 220-850 nm range, Xenon source, excitation and emission wavelength scans, spectral bandwidth 1-16nm, PMT detector, scan rate 3-6000 nm/min, Saya-Namioka grating monochromator. Compounds **4** and **5** were measured as 1.6 x 10^{-4} M solutions in $CHCl_3$.

Stationary absorption and emission spectra of Ru-complexes in acetonitrile (MERCK Uvasol) were obtained with a CARY 300 and SPEX Fluorolog 212, respectively. For measurement of quantum yields, the emission was excited at 430 nm and compared to that from the dye

DCM. The fluorescence band of DCM in acetonitrile (Φ=0.60±0.04)[3] is similar to the emission spectrum of the Ru(II) complexes studied here.

Transient absorption spectra were recorded upon excitation at 403 nm with 40 fs pump pulses. After a variable delay, the transmission of white-light, "supercontinuum" probe pulses was measured in a dual-beam arrangement.[4] The time resolution was 80 fs (fwhm of temporal apparatus function).

Electrochemistry

Voltammetric measurements were performed with an Autolab analyzer (Eco Chemie, The Nederlands) in connection with VA-Stand 663 (Metrohm, Switzerland). Pyrrolitic graphite electrode (PGE) was used as a working electrode (prepared and pretreated as described)[5], Then the electrode was rinsed by deionized water and was placed into the electrochemical cell. Electrochemical responses were measured in a conventional in situ mode (with the analyte dissolved in background electrolyte) initial potential -1.0 V, final potential +1.5 V, pulse amplitude 25 mV, frequency 200 Hz, potential step 5 mV. The measurements were performed at ambient temperature in 0.1M Tris, 0.2M NaCl, pH 7.3 by using an Autolab analyzer (EcoChemie, The Netherlands) in a three-electrode setup (with the PGE as working electrode, Ag/AgCl/3M KCl as reference, and platinum wire as counter-electrode). The voltammograms were baseline corrected by means of a moving average algorithm (GPES 4 software, EcoChemie).

General Procedure for Sonogashira Cross-Coupling Reaction of 7-deaza-7-I-2'-deoxyadenosine (1) with ligands 2a, b

DMF (2.5 ml) and Et_3N (0.35 ml, 2.5 mmol, 10 equiv.) were added to an argon-purged flask containing nucleoside 1 (94 mg, 0.25 mmol), an alkyne 2a, b (0.375 mmol, 1.5 equiv.) and CuI (4.8 mg, 0.025 mmol, 10 mol%). In a separate flask, $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol, 5 mol%), $P(Ph\text{-}SO_3Na)_3$ (18 mg, 0.0313 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 $CHCl_3$ and MeOH (1% to 10%) as eluent.

7-deaza-7-[(2",2'"-bipyridin-6"-yl)ethynyl]-2'-deoxyadenosine (4a)

The product was isolated as white powder 97 mg (91%). M.p. 115-120 °C. ^{1}H NMR (600 MHz, DMSO-d_6): 2.24 (ddd, 1H, J_{gem} = 13.2, $J_{2'b,1'}$ = 6.0, $J_{2'b,3'}$ = 2.8, H-2′b); 2.53 (ddd, 1H, J_{gem} = 13.2, $J_{2'a,1'}$ = 8.0, $J_{2'a,3'}$ = 5.8, H-2′a); 3.55 (ddd, 1H, J_{gem} = 11.7, $J_{5'b,OH}$ = 5.9, $J_{5'b,4'}$ = 4.4, H-5′b); 3.61 (ddd, 1H, J_{gem} = 11.7, $J_{5'a,OH}$ = 5.2, $J_{5'a,4'}$ = 4.6, H-5′a); 3.86 (ddd, 1H, $J_{4',5'}$ = 4.6, 4.4, $J_{4',3'}$ = 2.5, H-4′); 4.39 (m, 1H, $J_{3',2'}$ = 5.8, 2.8, $J_{3',OH}$ = 4.1, $J_{3',4'}$ = 2.5, H-3′); 5.12 (dd, 1H, $J_{OH,5'}$ = 5.9, 5.2, OH-5′); 5.32 (d, 1H, $J_{OH,3'}$ = 4.1, OH-3′); 6.54 (dd, 1H, $J_{1',2'}$ = 8.0, 6.0, H-1′); 6.93 (bs, 2H, NH_2); 7.50 (ddd, 1H, $J_{5''',4'''}$ = 7.4, $J_{5''',6'''}$ = 4.7, $J_{5''',3'''}$ = 1.2, H-5‴); 7.75 (dd, 1H, $J_{5'',4''}$ = 7.7, $J_{5'',3''}$ = 1.1, H-5″); 7.98 (ddd, 1H, $J_{4''',3'''}$ = 8.0, $J_{4''',5'''}$ = 7.4, $J_{4''',6'''}$ = 1.8, H-4‴); 8.01 (dd, 1H, $J_{4'',3''}$ = 8.0, $J_{4'',5''}$ = 7.7, H-4″); 8.04 (s, 1H, H-6); 8.19 (s, 1H, H-2); 8.378 (dd, 1H, $J_{3'',4''}$ = 8.0, $J_{3'',5''}$ = 1.1, H-3″); 8.383 (ddd, 1H, $J_{3''',4'''}$ = 8.0, $J_{3''',5'''}$ = 1.2, $J_{3''',6'''}$ = 0.9, H-3‴); 8.71 (ddd, 1H, $J_{6''',5'''}$ = 4.7, $J_{6''',4'''}$ = 1.8, $J_{6''',3'''}$ = 0.9, H-6‴).^{13}C NMR (151 MHz, DMSO-d_6): 40.16 (CH_2-2′); 62.07 (CH_2-5′); 71.16 (CH-3′); 83.11 (bpy-C≡**C**); 83.59 (CH-1′); 87.88 (CH-4′); 91.76 (bpy-**C**≡C); 93.97 (C-5); 102.51 (C-4a); 120.06 (CH-3″); 120.89 (CH-3‴); 124.84 (CH-5‴); 126.97 (CH-5″); 127.94 (CH-6); 137.78 (CH-4‴); 138.24 (CH-4″); 142.38 (C-6″); 149.62 (CH-6‴); 149.80 (C-7a); 153.25 (CH-2); 154.66 (C-2‴); 155.92 (C-2″); 157.86 (C-4). ESI MS: *m/z* (%) 451.1 (100) [M^+ + Na], 429.1 (93) [M^+ +H], 313.3 (70) [M^+ - dRf]. $C_{23}H_{20}N_6O_3.2H_2O$ (428.44) calcd. C 59.48, H 5.21, N 18.09; found C 59.73, H 4.57, N 17.94. IR (KBr): $\tilde{\nu}$ 3437, 2211, 1631, 1569, 1427, 1094 cm^{-1}. UV/Vis (CH_2Cl_2) λ_{max} (ε) 282 (27724). Fluorescence (CH_2Cl_2): excitation at 351 nm gave emission at 406 nm.

7-deaza-7-[(2",2'"-bipyridin-5"-yl)ethynyl]-2'-deoxyadenosine (4b)

The product was isolated as a yellowish powder 88 mg (82%). M.p. 165-166 °C. ^{1}H NMR (600 MHz, DMSO-d_6): 2.23 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 6.1, $J_{2'b,3'}$ = 2.9, H-2′b); 2.51 (ddd, 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 8.0, $J_{2'a,3'}$ = 5.7, H-2′a); 3.54 and 3.60 (2 × dt, 2H, J_{gem} = 11.8, $J_{5',OH}$ = $J_{5',4'}$ = 4.3, H-5′); 3.85 (td, 1H, $J_{4',5'}$ = 4.3, $J_{4',3'}$ = 2.5, H-4′); 4.37 (m, 1H, $J_{3',2'}$ = 5.7, 2.9, $J_{3',OH}$ = 4.0, $J_{3',4'}$ = 2.5, H-3′); 5.11 (bt, 1H, $J_{OH,5'}$ = 4.3, OH-5′); 5.32 (d, 1H, $J_{OH,3'}$ = 4.0, OH-3′); 6.53 (dd, 1H, $J_{1',2'}$ = 8.0, 6.1, H-1′); 6.83 (bs, 2H, NH_2); 7.48 (ddd, 1H, $J_{5''',4'''}$ = 7.5, $J_{5''',6'''}$ = 4.7, $J_{5''',3'''}$ = 1.2, H-5‴); 7.97 (s, 1H, H-6); 7.97 (ddd, 1H, $J_{4''',3'''}$ = 7.9, $J_{4''',5'''}$ = 7.5, $J_{4''',6'''}$ = 1.7, H-4‴); 8.17 (s, 1H, H-2); 8.17 (dd, 1H, $J_{4'',3''}$ = 8.2, $J_{4'',6''}$ = 2.2, H-4″); 8.41 (ddd, 1H, $J_{3''',4'''}$ = 7.9, $J_{3''',5'''}$ = 1.2, $J_{3''',6'''}$ = 0.9, H-3‴); 8.43 (dd, 1H, $J_{3'',4''}$ = 8.2, $J_{3'',6''}$ = 0.8, H-3″); 8.71 (ddd, 1H, $J_{6''',5'''}$ = 4.7, $J_{6''',4'''}$ = 1.7, $J_{6''',3'''}$ = 0.9, H-6‴); 8.89 (dd, 1H, $J_{6'',4''}$ = 2.2, $J_{6'',3''}$ = 0.8, H-6″).^{13}C NMR (151 MHz, DMSO-d_6): 40.14 (CH_2-2′); 62.09 (CH_2-5′); 71.18 (CH-3′); 83.50 (CH-1′); 87.62 (bpy-C≡**C**); 87.84 (CH-4′); 88.46 (bpy-**C**≡C); 94.54 (C-5); 102.10 (C-4a); 120.12 (CH-3″); 120.27 (C-5″); 120.97 (CH-3‴); 124.72 (CH-5‴); 127.86 (CH-6); 137.70

(CH-4‴); 139.66 (CH-4″); 149.71 (CH-6‴); 149.79 (C-7a); 151.45 (CH-6″); 153.10 (CH-2); 154.07 (C-2″); 154.70 (C-2‴); 157.76 (C-4). ESI MS: *m/z* (%) 451.1 (100) [M^+ + Na], 429.1 (93) [M^+ +H], 313.3 (70) [M^+ - dRf], $C_{23}H_{20}N_6O_3$. H_2O (428.44) calcd. C 61.87, H 4.97, N 18.82; found C 62.28, H 4.72, N 18.71. IR (KBr): $\tilde{\nu}$ 3459, 3393, 2204, 1631, 1572, 1458, 1091 cm^{-1}. UV/Vis (CH_2Cl_2) λ_{max} (ε) 258 (25141). Fluorescence (CH_2Cl_2): excitation at 368 nm gave emission at 427 nm.

General Procedure for Suzuki-Miyaura Cross-Coupling Reactions of 7-deaza-7-I-2'-deoxyadenosine (1) with ligands 3a,c,d

A mixture of H_2O / CH_3CN = 2 / 1 (2.5 ml) was added to an argon-purged flask containing nucleoside **1** (94 mg, 0.25 mmol), a boronate **3a,c,d** (0.3 mmol, 1.2 equiv.) and Cs_2CO_3 (247 mg, 0.75 mmol, 3 equiv.). In a separate flask, $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol, 5 mol%) and $P(Ph\text{-}SO_3Na)_3$ (18 mg, 0.0313 mmol, 2.5 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 were purified by silicagel column chromotagraphy using $CHCl_3$ and MeOH (1% to 10%) as eluent.

7-deaza-7-[(2",2'"-bipyridin-6"-yl)phenyl]-2'-deoxyadenosine (5a)

The product was isolated as white powder 114 mg (95 %). M.p. 135-137 °C. ^{1}H NMR (600 MHz, DMSO-d_6): 2.23 (ddd, 1H, J_{gem} = 13.2, $J_{2'b,1'}$ = 6.1, $J_{2'b,3'}$ = 2.7, H-2′b); 2.60 (ddd, 1H, J_{gem} = 13.2, $J_{2'a,1'}$ = 8.2, $J_{2'a,3'}$ = 5.9, H-2′a); 3.53 (dd, 1H, J_{gem} = 11.7, $J_{5'b,4'}$ = 4.3, H-5′b); 3.60 (dd, 1H, J_{gem} = 11.7, $J_{5'a,4'}$ = 4.5, H-5′a); 3.86 (ddd, 1H, $J_{4',5'}$ = 4.5, 4.3, $J_{4',3'}$ = 2.5, H-4′); 4.39 (bm, 1H, H-3′); 5.10 (bs, 1H, OH-5′); 5.31 (bs, 1H, OH-3′); 6.35 (bs, 2H, NH_2); 6.62 (dd, 1H, $J_{1',2'}$ = 8.2, 6.1, H-1′); 7.50 (ddd, 1H, $J_{5''',4'''}$ = 7.4, $J_{5''',6'''}$ = 4.7, $J_{5''',3'''}$ = 1.1, H-5‴); 7.65 (m, 2H, H-*o*-phenylene); 7.67 (s, 1H, H-6); 8.02 (ddd, 1H, $J_{4''',3'''}$ = 8.0, $J_{4''',5'''}$ = 7.4, $J_{4''',6'''}$ = 1.8, H-4‴); 8.06 (dd, 1H, $J_{4'',5''}$ = 7.9, $J_{4'',3''}$ = 7.7, H-4″); 8.11 (dd, 1H, $J_{5'',4''}$ = 7.9, $J_{5'',3''}$ = 1.0, H-5″); 8.19 (s, 1H, H-2); 8.36 (dd, 1H, $J_{3'',4''}$ = 7.7, $J_{3'',5''}$ = 1.0, H-3″); 8.37 (m, 2H, H-*m*-phenylene); 8.63 (ddd, 1H, $J_{3''',4'''}$ = 8.0, $J_{3''',5'''}$ = 1.1, $J_{3''',6'''}$ = 0.9, H-3‴); 8.72 (ddd, 1H, $J_{6''',5'''}$ = 4.7, $J_{6''',4'''}$ = 1.8, $J_{6''',3'''}$ = 0.9, H-6‴).^{13}C NMR (151 MHz, DMSO-d_6): 39.84 (CH_2-2′); 62.19 (CH_2-5′); 71.29 (CH-3′); 83.27 (CH-1′); 87.66 (CH-4′); 100.45 (C-4a); 116.39 (C-5); 119.32 (CH-3″); 120.59 (CH-5″); 120.94 (CH-3‴); 121.44 (CH-6); 124.59 (CH-5‴); 127.45 (CH-*m*-phenylene); 129.02 (CH-*o*-phenylene); 135.55 (C-*i*-phenylene); 136.97 (C-*p*-phenylene); 137.69 (CH-4‴); 138.75 (CH-4″); 149.55 (CH-6‴); 150.75 (C-7a); 151.62 (CH-2); 155.24 (C-2″); 155.33 (C-6″); 155.52 (C-2‴); 157.31 (C-4). ESI MS: *m/z* (%) 365.4 (100) [M^+ -

dRf], 481.2 (70) [M^+], 503.2 (40) [M^+ + Na]; $C_{27}H_{24}N_6O_3$. H_2O (480.2) calcd. C 65.05, H 5.26, N 16.86; found C 64.95, H 5.12, N 16.77. IR (KBr)$\tilde{\nu}$: 3470, 3393, 1616, 1582, 1430, 1098 cm^{-1}. UV/Vis (CH_2Cl_2) λ_{max} (ε) 291 (30685). Fluorescence (CH_2Cl_2): excitation at 340 nm gave emission at 395 nm.

7-deaza-7-[(1",10"-phenantrolin-2"-yl)phenyl]-2'-deoxyadenosine (5c)

The product was isolated as brownish powder 121 mg (96 %). M.p. 215-218 °C. ^{1}H NMR (600 MHz, DMSO-d_6): 2.24 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 6.0, $J_{2'b,3'}$ = 2.7, H-2′b); 2.62 (ddd, 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 8.3, $J_{2'a,3'}$ = 5.8, H-2′a); 3.55 (ddd, 1H, J_{gem} = 11.7, $J_{5'b,OH}$ = 5.9, $J_{5'b,4'}$ = 4.3, H-5′b); 3.62 (ddd, 1H, J_{gem} = 11.7, $J_{5'a,OH}$ = 5.3, $J_{5'a,4'}$ = 4.5, H-5′a); 3.86 (ddd, 1H, $J_{4',5'}$ = 4.5, 4.3, $J_{4',3'}$ = 2.5, H-4′); 4.40 (m, 1H, $J_{3',2'}$ = 5.8, 2.7, $J_{3',OH}$ = 4.0, $J_{3',4'}$ = 2.5, H-3′); 5.13 (dd, 1H, $J_{OH,5'}$ = 5.9, 5.3, OH-5′); 5.31 (d, 1H, $J_{OH,3'}$ = 4.0, OH-3′); 6.30 (bs, 2H, NH_2); 6.63 (dd, 1H, $J_{1',2'}$ = 8.3, 6.0, H-1′); 7.69 (s, 1H, H-6); 7.71 (m, 2H, H-*o*-phenylene); 7.80 (dd, 1H, $J_{8'',7''}$ = 8.1, $J_{8'',9''}$ = 4.3, H-8″); 7.98 (d, 1H, $J_{6'',5''}$ = 8.8, H-6″); 8.03 (d, 1H, $J_{5'',6''}$ = 8.8, H-5″); 8.19 (s, 1H, H-2); 8.46 (d, 1H, $J_{3'',4''}$ = 8.6, H-3″); 8.51 (dd, 1H, $J_{7'',8''}$ = 8.1, $J_{7'',9''}$ = 1.8, H-7″); 8.57 (m, 2H, H-*m*-phenylene); 8.60 (d, 1H, $J_{4'',3''}$ = 8.6, H-4″); 9.18 (dd, 1H, $J_{9'',8''}$ = 4.3, $J_{9'',7''}$ = 1.8, H-9″).^{13}C NMR (151 MHz, DMSO-d_6): 39.84 (CH_2-2′); 62.21 (CH_2-5′); 71.29 (CH-3′); 83.25 (CH-1′); 87.64 (CH-4′); 100.52 (C-4a); 116.30 (C-5); 120.20 (CH-3″); 121.35 (CH-6); 123.61 (CH-8″); 126.67 (CH-5″); 126.73 (CH-6′); 127.72 (C-4″a); 128.15 (CH-*m*-phenylene); 129.03 (CH-*o*-phenylene); 129.12 (C-6″a); 135.96 (C-*i*-phenylene); 136.54 (CH-7″); 137.33 (C-*p*-phenylene); 137.64 (CH-4″); 145.57 (C-10″b); 145.84 (C-10″a); 150.24 (CH-9″); 150.93 (C-7a); 152.06 (CH-2); 155.46 (C-2″); 157.62 (C-4). ESI MS: *m/z* (%) 1031.1 (100) [2xM^+ + Na], 505.2 (85) [M^+ + H^+], 389.4 (35) [M^+ - dRf]; $C_{29}H_{24}N_6O_3$. H_2O (504.2) calcd. C 66.66, H 5.02, N 16.08; found C 66.37, H 4.75, N 15.82. IR (KBr)$\tilde{\nu}$: 3436, 3368, 1612, 1548, 1450, 1086 cm^{-1}. UV/Vis (CH_2Cl_2) λ_{max} (ε) 283 (45366). Fluorescence (CH_2Cl_2): excitation at 330 nm gave emission at 424 nm.

7-deaza-7-[(4"-(2",2'":6",2'"-terpyridin-1"-yl)phenyl]-2'-deoxyadenosine (5d)

The product was isolated as white powder 109 mg (78 %). M.p. 183-188 °C. ^{1}H NMR (600 MHz, DMSO-d_6): 2.23 (ddd, 1H, J_{gem} = 13.2, $J_{2'b,1'}$ = 6.0, $J_{2'b,3'}$ = 2.7, H-2′b); 2.61 (ddd, 1H, J_{gem} = 13.2, $J_{2'a,1'}$ = 8.4, $J_{2'a,3'}$ = 5.9, H-2′a); 3.54 (ddd, 1H, J_{gem} = 11.6, $J_{5'b,OH}$ = 5.9, $J_{5'b,4'}$ = 4.3, H-5′b); 3.61 (ddd, 1H, J_{gem} = 11.6, $J_{5'a,OH}$ = 5.7, $J_{5'a,4'}$ = 4.5, H-5′a); 3.86 (ddd, 1H, $J_{4',5'}$ = 4.5, 4.3, $J_{4',3'}$ = 2.5, H-4′); 4.39 (m, 1H, $J_{3',2'}$ = 5.9, 2.7, $J_{3',OH}$ = 4.0, $J_{3',4'}$ = 2.5, H-3′); 5.11 (dd, 1H, $J_{OH,5'}$ = 5.9, 5.7, OH-5′); 5.31 (d, 1H, $J_{3',OH}$ = 4.0, OH-3′); 6.30 (bs, 2H, NH_2); 6.63 (dd, 1H, $J_{1',2'}$ = 8.4, 6.0, H-1′); 7.54 (ddd, 2H, $J_{5''',4'''}$ = 7.5, $J_{5''',6'''}$ = 4.8, $J_{5''',3'''}$ = 1.2, H-5‴); 7.67 (s,

1H, H-6); 7.70 (m, 2H, H-*o*-phenylene); 8.04 (m, 2H, H-*m*-phenylene); 8.05 (ddd, 2H, $J_{4''',3'''}$ = 7.9, $J_{4''',5'''}$ = 7.5, $J_{4''',6'''}$ = 1.8, H-4‴); 8.18 (s, 1H, H-2); 8.67 (ddd, 2H, $J_{3''',4'''}$ = 7.9, $J_{3''',5'''}$ = 1.2, $J_{3''',6'''}$ = 0.9, H-3‴); 8.78 (ddd, 2H, $J_{6''',5'''}$ = 4.8, $J_{6''',4'''}$ = 1.8, $J_{6''',3'''}$ = 0.9, H-6‴); 8.78 (s, 2H, H-3″,5″).^{13}C NMR (151 MHz, DMSO-d_6): 39.94 (CH_2-2′); 62.21 (CH_2-5′); 71.29 (CH-3′); 83.21 (CH-1′); 87.64 (CH-4′); 100.41 (C-4a); 116.06 (C-5); 118.00 (CH-3″,5″); 121.20 (CH-3‴); 121.42 (CH-6); 124.83 (CH-5‴); 127.76 (CH-*m*-phenylene); 129.48 (CH-*o*-phenylene); 135.82 (C-*p*-phenylene); 135.94 (C-*i*-phenylene); 137.76 (CH-4‴); 149.39 (C-4″); 149.63 (CH-6‴); 150.98 (C-7a); 152.07 (CH-2); 155.19 (C-2‴); 155.97 (C-2″,6″); 157.60 (C-4). ESI MS: *m/z* (%) 558.2 (100) [M^+], 580.2 (55) [M^+ + Na], 442.4 (20) [M^+ - dRf]; $C_{32}H_{27}N_7O_3$ .H_2O (557.2) calcd. C 66.77, H 5.08, N 17.03; found C 66.64, H 4.91, N 16.80. IR (KBr)$\tilde{}$: 3393, 3305, 1584, 1468, 1095, 792 cm^{-1}. UV/Vis (CH_2Cl_2) λ_{max} (ε) 284 (53746). Fluorescence (CH_2Cl_2): excitation at 343 nm gave emission at 425 nm.

General Procedure for Sonogashira Cross-Coupling Reactions of Ru^{II}complexes 6a,b

A mixture of H_2O / CH_3CN = 2 / 1 (1 ml) was added to an argon-purged flask containing nucleoside **1** (47 mg, 0.125 mmol), an alkyne **6a,b** (0.188 mmol, 1.5 equiv.), CuI (2.4 mg, 0.0125 mmol, 10 mol%) and Et_3N (0.175 ml, 1.25 mmol, 10 equiv.). In a separate flask, $Pd(OAc)_2$ (1.4 mg, 0.00625 mmol, 5 mol%) and $P(Ph\text{-}SO_3Na)_3$ (9 mg, 0.0156 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 products 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 8a

The product was isolated as red powder 66 mg (47 %). M.p. > 300 °C. 1:1 mixture of diastereoisomers ^{1}H NMR (500 MHz, acetone-d_6): 2.46 (ddd, 2H, J_{gem} = 13.3, $J_{2'b,1'}$ = 6.0, $J_{2'b,3'}$ = 2.8, H-2'b); 2.61 and 2.62 (2 × ddd, 2 × 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 7.9, $J_{2'a,3'}$ = 5.6, H-2'a); 3.77, 3.81, 3.84 and 3.89 (4 × dd, 4 × 1H, J_{gem} = 12.0, $J_{5',4'}$ = 3.2, H-5'); 4.07 and 4.10 (2 × td, 2 × 1H, $J_{4',5'}$ = 3.2, $J_{4',3'}$ = 2.5, H-4'); 4.61 (ddd, 2H, $J_{3',2'}$ = 5.6, 2.8, $J_{3',2'a}$ = 2.5, H-3'); 6.59 and 6.62 (2 × dd, 2 × 1H, $J_{1',2'}$ = 7.9, 6.0, H-1'); 6.87 and 6.93 (2 × ddd, 2 × 1H, $J_{5,4}$ = 7.5, $J_{5,6}$ = 5.7, $J_{5,3}$ = 1.4, H-5-bpy); 7.328 and 7.333 (2 × ddd, 2 × 1H, $J_{4,3}$ = 8.2, $J_{4,5}$ = 7.5, $J_{4,6}$ = 1.5, H-4-bpy); 7.48 (ddd, 2H, $J_{5,4}$ = 7.5, $J_{5,6}$ = 5.7, $J_{5,3}$ = 1.4, H-5-bpy); 7.53 (ddd, 2H, $J_{5''',4'''}$ = 7.5, $J_{5''',6'''}$ = 5.7, $J_{5''',3'''}$ = 1.4, H-5'''); 7.555, 7.560, 7.67 and 7.68 (4 × ddd, 4 × 1H, $J_{5,4}$ = 7.6, $J_{5,6}$ =

5.6, $J_{5,3}$ = 1.3, H-5-bpy); 7.728 and 7.731 (2 × s, 2 × 1H, H-6); 7.81 and 7.82 (2 × ddd, 2 × 1H, $J_{6,5}$ = 5.7, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 7.89 (ddd, 2H, $J_{6''',5'''}$ = 5.7, $J_{6''',4'''}$ = 1.5, $J_{6''',3'''}$ = 0.7, H-6'''); 7.91 (dd, 1H, $J_{5'',4''}$ = 7.8, $J_{5'',3''}$ = 1.4, H-5''); 7.92, 7.93, 7.95 and 7.96 (4 × ddd, 4 × 1H, $J_{6,5}$ = 5.7, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 8.15 (ddd, 2H, $J_{4,3}$ = 8.2, $J_{4,5}$ = 7.5, $J_{4,6}$ = 1.5, H-4-bpy); 8.20 (ddd, 2H, $J_{4''',3'''}$ = 8.2, $J_{4''',5'''}$ = 7.5, $J_{4''',6'''}$ = 1.5, H-4'''); 8.22-8.27 (m, 4H, H-4-bpy); 8.29 (dd, 2H, $J_{4'',3''}$ = 8.3, $J_{4'',5''}$ = 7.8, H-4''); 8.39 (bs, 2H, H-2); 8.40 (ddd, 2H, $J_{6,5}$ = 5.7, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 8.45, 8.47, 8.73, 8.74, 8.79 and 8.80 (6 × ddd, 6 × 1H, $J_{3,4}$ = 8.2, $J_{3,5}$ = 1.4, $J_{3,6}$ = 0.7, H-3-bpy); 8.86 (ddd, 2H, $J_{3''',4'''}$ = 8.2, $J_{3''',5'''}$ = 1.4, $J_{3''',6'''}$ = 0.7, H-3'''); 8.87 (dd, 2H, $J_{3'',4''}$ = 8.3, $J_{3'',5''}$ = 1.4, H-3''); 8.94 and 8.95 (2 × bddd, 2 × 1H, $J_{3,4}$ = 8.2, $J_{3,5}$ = 1.4, $J_{3,6}$ = 0.7, H-3-bpy).^{13}C NMR (125.7 MHz, acetone-d_6): 41.90 and 41.98 (CH_2-2'); 63.08 and 63.13 (CH_2-5'); 72.53 (CH-3'); 85.96 and 86.30 (CH-1'); 89.48 (CH-4'); 89.86 (bpy-**C**≡C-); 90.11 and 90.24 (bpy-C≡**C**-); 95.80 and 85.88 (C-5); 102.98 and 103.11 (C-4a); 124.54 and 124.72 (CH-3-bpy), 124.87 (CH-3''); 125.33, 125.43 and 125.72 (CH-3-bpy); 125.97 (CH-3'''); 127.62, 127.91, 128.30, 128.57, 128.89 and 129.03 (CH-5''', CH-5-bpy); 131.03 and 131.11 (CH-6); 135.47 and 135.50 (CH-5''); 136.51 and 136.57 (CH-4-bpy); 138.88, 138.98, 139.12 and 139.24 (CH-4'',4''', CH-4-bpy); 147.91 (CH-2); 148.50 and 148.61 (C-7a); 149.26 and 149.30 (C-6''); 152.07, 152.14, 152.31, 152.35, 152.57, 153.73 and 153.76 (CH-6''' and CH-6-bpy); 154.11 (C-4); 157.81, 157.99, 158.01, 158.27, 158.74 and 158.80 (C-2''', C-2-bpy); 158.98 (C-2''). ESI MS: *m/z* (%) 987.1 (100) [M^+ - PF_6^-], HR MS (TOF ES MS+) calc. 987.1657 found. 987.1691. UV/Vis (CH_3CN) $\lambda_{max}(\varepsilon)$ = 288 (81880), $\lambda(\varepsilon)$ = 448 (14150).

Complex 8b

The product was isolated as red powder 83 mg (59 %). M.p. 140-145 °C. 1:1 mixture of diastereoisomers ^{1}H NMR (600 MHz, acetone-d_6): 2.37 (ddd, 2H, J_{gem} = 13.3, $J_{2'b,1'}$ = 5.9, $J_{2'b,3'}$ = 2.6, H-2'b); 2.645 and 2.649 (2 × ddd, 2 × 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 8.0, $J_{2'a,3'}$ = 5.7, H-2'a); 3.748 and 3.752 (2 × dd, 2 × 1H, J_{gem} = 12.1, $J_{5'b,4'}$ = 3.1, H-5'b); 3.792 and 3.496 (2 × dd, 2 × 1H, J_{gem} = 12.1, $J_{5'a,4'}$ = 3.2, H-5'a); 4.05 (ddd, 2H, $J_{4',5'}$ = 3.2, 3.1, $J_{4',3'}$ = 2.2, H-4'); 4.60 (ddd, 2H, $J_{3',2'}$ = 5.7, 2.6, $J_{3',4'}$ = 2.2, H-3'); 6.54 (dd, 2H, $J_{1',2'}$ = 8.0, 5.9, H-1'); 6.75 (bs, 4H, NH_2); 7.56-7.64 (m, 10H, H-5''' and H-5-bpy); 7.916 and 7.918 (2 × s, 2 × 1H, H-6); 8.01, 8.056 and 8.060 (3 × ddd, 3 × 2H, $J_{6,5}$ = 5.6, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 8.10 (ddd, 2H, $J_{6''',5'''}$ = 5.6, $J_{6''',4'''}$ = 1.5, $J_{6''',3'''}$ = 0.7, H-6'''); 8.11 and 8.12 (2 × dd, 2 × 1H, $J_{6'',4''}$ = 1.8, $J_{6'',3''}$ = 0.7, H-6''); 8.17-8.23 (m, 10H, H-4,6-bpy); 8.252 and 8.254 (2 × ddd, 2 × 1H, $J_{4''',3'''}$ = 8.2, $J_{4''',5'''}$ = 7.6, $J_{4''',6'''}$ = 1.5, H-4'''); 8.28 (s, 2H, H-2); 8.29 (dd, 2H, $J_{4'',3''}$ = 8.5, $J_{4'',6''}$ = 1.8, H-4''); 8.79-8.83 (m, 12H, H-3'', H-3''' and H-3-bpy). ^{13}C NMR (151 MHz, acetone-d_6): 41.83 (CH_2-2´); 63.27 (CH_2-5´); 72.71 (CH-3´); 86.90 (CH-1´); 88.03 (bpy-**C**≡C-); 89.54 (CH-4´); 90.19 (bpy-C≡**C**-); 95.48 (C-5); 103.44 (C-4a); 124.72 (C-5''); 124.82, 125.29, 125.32, 125.39, 125.46 and 125.73 (CH-3'',3''' and CH-3-bpy); 128.74, 128.78 and 128.82 (CH-5''' and CH-5-

bpy); 138.92, 139.00, 139.02, 139.06 and 139.07 (CH-4''' and CH-4-bpy); 140.28 and 140.30 (CH-4''); 149.53 (C-7a); 150.66 (CH-2); 152.58, 152.72, 152.89 and 153.00 (CH-6''' and CH-6-bpy); 154.01 (CH-6''); 156.71 (C-4); 156.81 (C-2''); 157.62, 158.01, 158.11, 158.16 and 158.19 (C-2''' and C-2-bpy). ESI MS: *m/z* (%) 987.1 (100) [M^+ - PF_6^-], HR MS (TOF ES MS+) calc. 987.1657 found. 987.1610. UV/Vis (CH_3CN) $\lambda_{max}(\varepsilon)$ = 287 (98283), $\lambda(\varepsilon)$ = 384 (26536), $\lambda(\varepsilon)$ shoulder = 455 (15720).

General Procedure for Suzuki-Miyaura Cross-Coupling Reactions of Ru^{II} complexes 7a,c,d

A mixture of H_2O / CH_3CN = 2 / 1 (1 ml) was added to an argon-purged flask containing nucleoside **1** (47 mg, 0.125 mmol), a boronate **7a,c,d** (0.15 mmol, 1.2 equiv.) and Cs_2CO_3 (122 mg, 0.375 mmol, 3 equiv.). In a separate flask, $Pd(OAc)_2$ (1.4 mg, 0.00625 mmol, 5 mol%) and $P(Ph\text{-}SO_3Na)_3$ (9 mg, 0.0156 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 this 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 **9a,c,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 9a

The product was isolated as red powder 140 mg (95 %). M.p. 244-249 °C. ^{1}H NMR (500 MHz, acetone-d_6): 2.534 and 2.536 (2 × ddd, 2 × 1H, J_{gem} = 13.4, $J_{2'b,1'}$ = 6.2, $J_{2'b,3'}$ = 3.2, H-2'b); 2.71 and 2.74 (2 × ddd, 2 × 1H, J_{gem} = 13.4, $J_{2'a,1'}$ = 7.5, $J_{2'a,3'}$ = 5.7, H-2'a); 3.88-3.983.89 (m, 4H, H-5'); 4.13 and 4.14 (2 × q, 2 × 1H, $J_{4',5'}$ = $J_{4',3'}$ = 3.0, H-4'); 4.73 (m, 2H, H-3'); 6.30 (bm, 2H, H-*m*-phenylene); 6.81 and 6.82 (2 × dd, 2 × 1H, $J_{1',2'}$ = 7.5, 6.2, H-1'); 6.98 (ddd, 1H, $J_{5,4}$ = 7.6, $J_{5,6}$ = 5.6, $J_{5,3}$ = 1.3, H-5-bpy); 7.02 (bm, 2H, H-*o*-phenylene); 7.09 (ddd, 1H, $J_{5,4}$ = 7.6, $J_{5,6}$ = 5.6, $J_{5,3}$ = 1.3, H-5-bpy); 7.28 (bm, 2H, H-*o*-phenylene); 7.37 and 7.38 (2 × ddd, 2 × 1H, $J_{6,5}$ = 5.6, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 7.41 and 7.43 (2 × ddd, 2 × 1H, $J_{5,4}$ = 7.6, $J_{5,6}$ = 5.6, $J_{5,3}$ = 1.3, H-5-bpy); 7.51 and 7.52 (2 × ddd, 2 × 1H, $J_{5''',4'''}$ = 7.6, $J_{5''',6'''}$ = 5.6, $J_{5''',3'''}$ = 1.3, H-5'''); 7.53 (dd, 1H, $J_{5'',4''}$ = 7.7, $J_{5'',3''}$ = 1.4, H-5''); 7.615 and 7.616 (2 × ddd, 2 × 1H, $J_{5,4}$ = 7.6, $J_{5,6}$ = 5.6, $J_{5,3}$ = 1.3, H-5-bpy); 7.67-7.72 (m, 4H, H-5,6-bpy); 7.78 (ddd, 2H, $J_{4,3}$ = 8.4, $J_{4,5}$ = 7.6, $J_{4,6}$ = 1.5, H-4-bpy); 7.90 (s, 1H, H-6); 7.91 (m, 2H, H-6'''); 7.95 (s, 1H, H-6); 8.078 and 8.082 (2 × ddd, 2 × 1H, $J_{4,3}$ = 8.4, $J_{4,5}$ = 7.6, $J_{4,6}$ = 1.5, H-4-bpy); 8.157 and 8.162 (2 × ddd, 2 × 1H, $J_{6,5}$ = 5.6, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 8.19-8.29 (m, 6H, H-4''' and H-3,4-bpy); 8.33 and 8.34 (2 × ddd, 2 × 1H, $J_{6,5}$ = 5.6, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 8.343 and

8.345 (2 × dd, 2 × 1H, $J_{4'',3''}$ = 8.3, $J_{4'',5''}$ = 7.7, H-4''); 8.36 (ddd, 1H, $J_{3,4}$ = 8.4, $J_{3,5}$ = 1.3, $J_{3,6}$ = 0.7, H-3-bpy); 8.501 and 8.503 (2 × s, 2 × 1H, H-2); 8.637, 8.642, 8.69, 8.716 and 8.722 (5 × ddd, 6H, $J_{3,4}$ = 8.4, $J_{3,5}$ = 1.3, $J_{3,6}$ = 0.7, H-3-bpy); 8.90 (ddd, 2H, $J_{3''',4'''}$ = 8.4, $J_{3''',5'''}$ = 1.3, $J_{3''',6'''}$ = 0.7, H-3'''); 8.94 (dd, 2H, $J_{3'',4''}$ = 8.3, $J_{3'',5''}$ = 1.4, H-3'').^{13}C NMR (125.7 MHz, acetone-d_6): 42.24 and 42.38 (CH_2-2'); 62.96 and 63.07 (CH_2-5'); 72.35 and 72.44 (CH-3'); 85.50 and 85.52 (CH-1'); 89.25 and 89.37 (CH-4'); 100.29 and 100.33 (C-4a); 119.50 and 119.51 (C-5); 124.24 and 124.34 (CH-3-bpy), 124.62 (CH-3''); 124.87 and 124.95 (CH-6); 125.05, 125.14, 125.18, 125.48 and 125.51 (CH-3-bpy); 125.95 (CH-3'''); 127.37, 127.53, 128.16, 128.32 and 128.98 (CH-5''', CH-5-bpy); 129.10, 129.24, 129.42 and 130.30 (CH-*o,m*-phenylene); 130.62 and 130.64 (CH-5''); 133.90 and 133.93 (C-*i*-phenylene); 136.99 (CH-4-bpy); 138.95, 139.08 and 139.27 (CH-4'',4''', CH-4-bpy); 139.31 (C-*p*-phenylene); 143.44 (CH-2); 148.81 (C-7a); 151.90 (CH-6-bpy); 152.50 (C-4); 152.57, 152.84, 152.88, 152.91 and 153.64 (CH-6''' and CH-6-bpy); 157.62, 157.64, 158.09, 158.22, 158.72, 158.74, 158.93 and 159.03 (C-2'', C-2''' and C-2-bpy); 167.16 (C-6'').ESI MS: *m/z* (%) 1039.1 (100) [M^+ - PF_6^-], HR MS (TOF ES MS+) calc. 1039.1970 found. 1039.1986. UV/Vis (CH_3CN) $\lambda_{max}(\varepsilon)$ = 289 (72812), $\lambda(\varepsilon)$ = 450 (12178).

Complex 9c

The product was isolated as red powder 110 mg (73 %). M.p. 252-254 °C. ^{1}H NMR (600 MHz, acetone-d_6): 2.498, 2.506 (2 × ddd, 2 × 1H, J_{gem} = 13.5, $J_{2'b,1'}$ = 6.0, $J_{2'b,3'}$ = 2.7, H-2′b); 2.76, 2.78 (2 × ddd, 2 × 1H, J_{gem} = 13.5, $J_{2'a,1'}$ = 7.9, $J_{2'a,3'}$ = 5.6, H-2′a); 3.89, 3.92 (2 × dd, 2 × 1H, J_{gem} = 12.0, $J_{5',4'}$ = 3.0, H-5′); 3.94 (d, 2H, $J_{5',4'}$ = 3.0, H-5′); 4.14, 4.15 (2 × q, 2 × 1H, $J_{4',3'}$ = $J_{4',5'}$ = 3.0, H-4′); 4.71, 4.72 (2 × ddd, 2 × 1H, $J_{3',2'}$ = 5.6, 2.7, $J_{3',4'}$ = 3.0, H-3′); 6.41 (bd, 2H, J = 7.9, H-*m*-phenylene); 6.775, 6.781 (2 × dd, 2 × 1H, $J_{1',2'}$ = 7.9, 6.0, H-1′); 7.04 (ddd, 1H, $J_{5,4}$ = 7.5, $J_{5,6}$ = 5.6, $J_{5,3}$ = 1.3, H-5-bpy); 7.06, 7.09 (2 × dd, 2 × 1H, J = 7.9, 1.9, H-*o*-phenylene); 7.15 (ddd, 1H, $J_{5,4}$ = 7.5, $J_{5,6}$ = 5.6, $J_{5,3}$ = 1.3, H-5-bpy); 7.33, 7.36 (2 × dd, 2 × 1H, J = 7.9, 1.9, H-*o*-phenylene); 7.417, 7.420 (2 × ddd, 2 × 1H, $J_{5,4}$ = 7.5, $J_{5,6}$ = 5.6, $J_{5,3}$ = 1.3, H-5-bpy); 7.45-7.51 (m, 6H, 2 × H-5,6-bpy); 7.73 (dd, 2H, J = 7.9, 1.9, H-*m*-phenylene); 7.80 (ddd, 2H, $J_{4,3}$ = 8.3, $J_{4,5}$ = 7.5, $J_{4,6}$ = 1.5, H-4-bpy); 7.81-7.83 (m, 2H, H-6-bpy); 7.84 (s, 1H, H-6); 7.858, 7.859 (2 × d, 2 × 1H, $J_{3'',4''}$ = 8.3, H-3''); 7.859, 7.860 (2 × dd, 2 × 1H, $J_{8'',7''}$ = 8.2, $J_{8'',9''}$ = 5.3, H-8''); 7.88 (s, 1H, H-6); 7.89, 7.90 (2 × ddd, 2 × 1H, $J_{6,5}$ = 5.6, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 8.12-8.16 (m, 4H, H-4-bpy); 8.217, 8.219 (2 × ddd, 2 × 1H, $J_{4,3}$ = 8.3, $J_{4,5}$ = 7.5, $J_{4,6}$ = 1.5, H-4-bpy); 8.25, 8.26 (2 × ddd, 2 × 1H, $J_{6,5}$ = 5.6, $J_{6,4}$ = 1.5, $J_{6,3}$ = 0.7, H-6-bpy); 8.28 (dd, 2H, $J_{9'',8''}$ = 5.3, $J_{9'',7''}$ = 1.3, H-9''); 8.32, 8.39 (2 × ddd, 2 × 1H, $J_{3,4}$ = 8.3, $J_{3,5}$ = 1.3, $J_{3,6}$ = 0.7, H-3-bpy); 8.46 (d, 2H, $J_{6'',5''}$ = 8.9, H-6''); 8.48 (s, 2H, H-2); 8.51 (d, 2H, $J_{5'',6''}$ = 8.9,

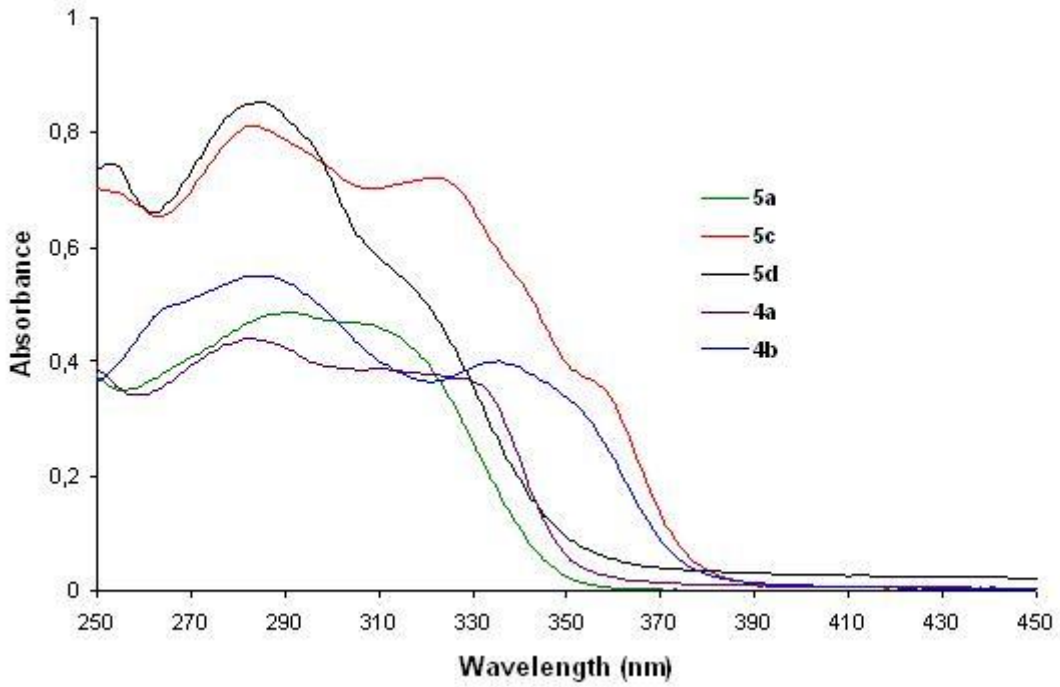
H-5"); 8.68, 8.69, 8.71, 8.72 (4 × ddd, 6H, $J_{3,4}$ = 8.3, $J_{3,5}$ = 1.3, $J_{3,6}$ = 0.7, H-3-bpy); 8.83 (dd, 2H, $J_{7",8"}$ = 8.2, $J_{7",9"}$ = 1.3, H-7"); 8.95 (d, 2H, $J_{4",3"}$ = 8.3, H-4").

^{13}C NMR (151 MHz, acetone-d_6): 42.05, 42.21 (CH_2-2´); 63.19, 63.25 (CH_2-5´); 72.61, 72.66 (CH-3´); 86.03 (CH-1´); 89.32, 89.40 (CH-4´); 100.73, 100.78 (C-4a); 118.82 (C-5); 124.29, 124.39 (CH-3-bpy); 124.74, 124.81 (CH-6); 125.17, 125.28, 125.32 (CH-3-bpy); 126.81 (CH-8"); 127.48, 127.64, 128.07, 128.81 (CH-5-bpy); 128.98, 129.03, 129.12, 129.15, 129.34, 129.38 (CH-5",6" and CH-*o,m*-phenylene); 129.52, 129.55 (CH-3"); 130.06, 130.08 (CH-*m*-phenylene); 131.32 (C-4"a); 132.59 (C-6"a); 134.54 (C-*i*-phenylene); 136.99 (CH-4-bpy); 137.91 (CH-7"); 138.60 (CH-4"); 138.92, 138.94, 138.98 (CH-4-bpy); 139.12 (C-*p*-phenylene); 139.15 (CH-4-bpy); 145.43, 145.53 (CH-2); 148.62 (C-10"b); 149.01 (C-10"a); 149.19 (C-7a); 152.16, 153.04, 153.09, 153.12 (CH-6-bpy); 153.45 (CH-9"); 153.69 (CH-6-bpy); 153.71 (C-4); 157.90, 158.04, 158.40, 158.86 (C-2-bpy); 168.00 (C-2").ESI MS: *m/z* (%) 1063.1 (100) [M^+ - PF_6^-], HR MS (TOF ES MS+) calc. 1063.1970 found. 1063.1976. UV/Vis (CH_3CN) $\lambda_{max}(\varepsilon)$ = 287 (71405), $\lambda(\varepsilon)$ = 448 (9999).

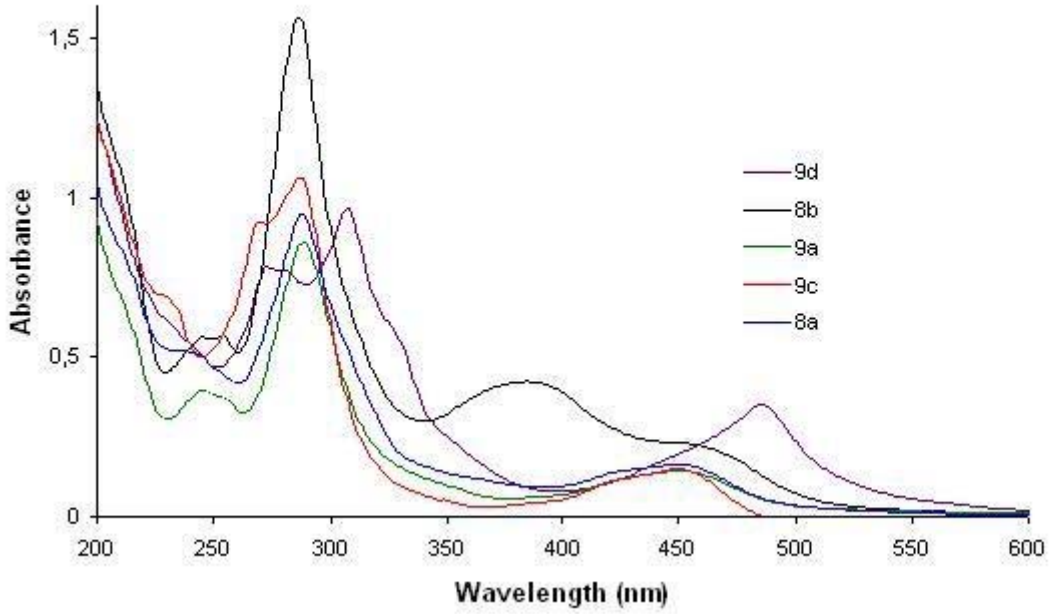
Complex 9d

The product was isolated as red powder 59 mg (76 %). M.p. > 300 °C. ^{1}H NMR (500 MHz, CD_3CN): 2.32 (ddd, 1H, J_{gem} = 13.2, $J_{2'b,1'}$ = 5.9, $J_{2'b,3'}$ = 2.1, H-2'b); 2.89 (ddd, 1H, J_{gem} = 13.2, $J_{2'a,1'}$ = 8.8, $J_{2'a,3'}$ = 5.7, H-2'a); 3.40 (bs, 1H, OH-3'); 3.70 (bd, 1H, J_{gem} = 12.3, H-5'b); 3.79 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'}$ = 2.9, H-5'a); 4.03 (td, 1H, $J_{4',5'}$ = 2.9, $J_{4',3'}$ = 2.0, H-4'); 4.58 (bm, 1H, H-3'); 4.94 (bs, 1H, OH-5'); 5.62 (bs, 2H, NH_2); 6.50 (dd, 1H, $J_{1',2'}$ = 8.8, 5.9, H-1'); 7.15-7.22 (m, 4H, H-5'-tpy, H-5'"); 7.36 (ddd, 2H, $J_{6'",5'"}$ = 5.6, $J_{6'",4'"}$ = 1.4, $J_{6'",3'"}$ = 0.7, H-6'"); 7.44 (ddd, 2H, $J_{6',5'}$ = 5.6, $J_{6',4'}$ = 1.5, $J_{6',3'}$ = 0.7, H-6'-tpy); 7.50 (s, 1H, H-6); 7.89 (m, 2H, H-*o*-phenylene); 7.90-8.00 (m, 4H, H-4'-tpy, H-4'"); 8.25 (s, 1H, H-2); 8.33 (m, 2H, H-*m*-phenylene); 8.44 (t, 1H, $J_{4,3\&5}$ = 8.2, H-4-tpy); 8.50 (ddd, 2H, $J_{3',4'}$ = 8.2, $J_{3',5'}$ = 1.4, $J_{3',6'}$ = 0.8, H-3'-tpy); 8.66 (ddd, 2H, $J_{3'",4'"}$ = 8.2, $J_{3'",5'"}$ = 1.4, $J_{3'",6'"}$ = 0.8, H-3'"); 8.77 (d, 2H, $J_{3\&5,4}$ = 8.2, H-3,5-tpy); 9.06 (s, 2H, H-3",5").^{13}C NMR (125.7 MHz, CD_3CN): 41.05 (CH_2-2'); 63.88 (CH_2-5'); 73.32 (CH-3'); 87.97 (CH-1'); 89.50 (CH-4'); 102.88 (C-4a); 116.58 (C-5); 122.42 (H-3",5"); 124.35 (CH-6); 124.78 (H-3,5-tpy); 125.49 (H-3'-tpy); 125.59 (H-3'"); 128.52 (H-5'" and H-5'-tpy); 129.50 (CH-*m*-phenylene); 130.76 (CH-*o*-phenylene); 136.28 (C-*p*-phenylene); 136.83 (CH-4-tpy); 137.88 (C-*i*-phenylene); 139.12 and 139.15 (CH-4'" and CH-4'-tpy); 148.82 (C-4"); 151.50 (C-7a); 152.78 (CH-2); 153.45 and 153.62 (H-6'" and H-6'-tpy); 156.39 and 156.61 (C-2,6-tpy and C-2",6"); 158.83 (C-4); 159.12 (C-2'-tpy); 159.22 (C-2'"). ESI MS: *m/z* (%) 1037.0 (100) [M^+ - PF_6^-], HR MS (TOF ES MS+) calc. 1037.1814 found. 1037.1826. UV/Vis (CH_3CN) $\lambda_{max}(\varepsilon)$ = 308 (63432), $\lambda(\varepsilon)$ = 273 (51612), $\lambda(\varepsilon)$ = 485 (23048).

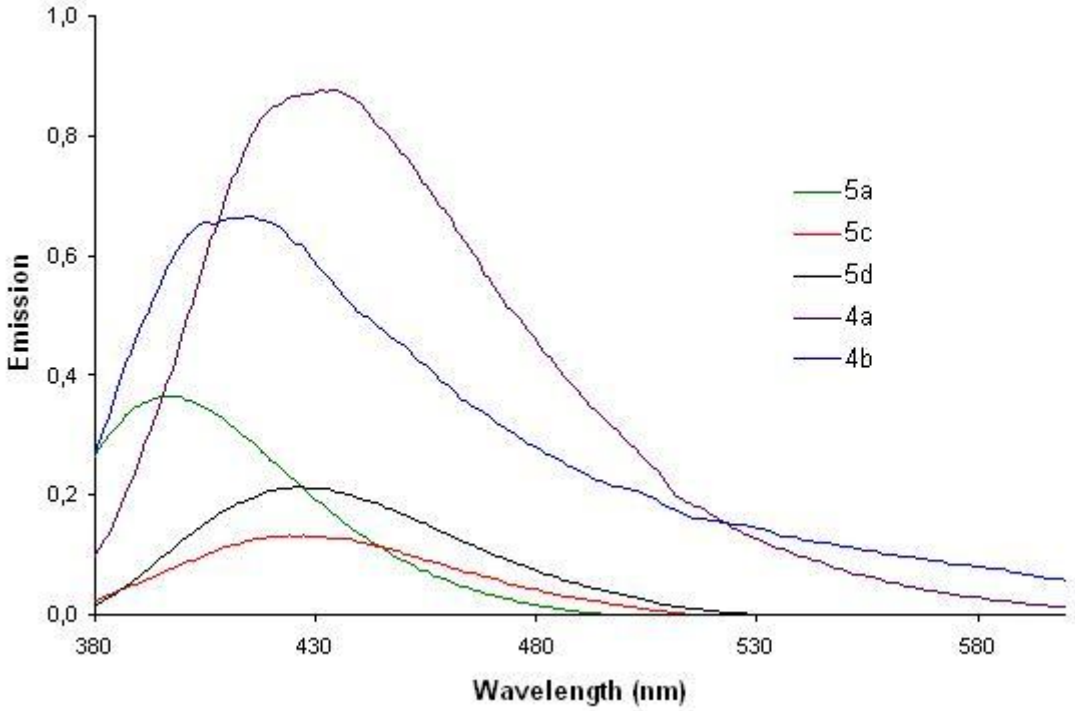
UV-Vis spectra of 7-substituted 7-deaza nucleoside conjugates 4 and 5



UV-Vis spectra of Ru(II) containing 7-deaza nucleoside conjugates 8 and 9



Flurescence spectra of 7-substituted 7-deaza nucleoside conjugates 4 and 5



Absorption and emission spectra of Ru complexes

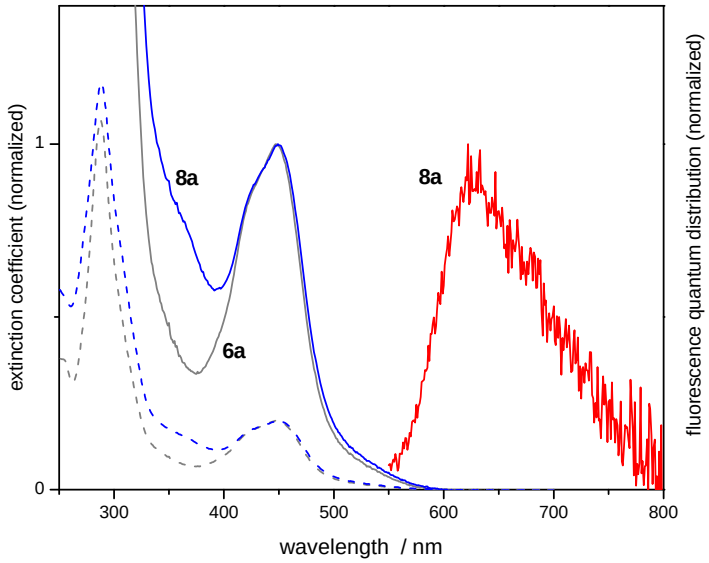


Fig. S1 Absorption and emission spectra of the labeled deaza-adenine **8a** (blue and red lines). The absorption of the Ru(II) complex **6a** alone is shown for comparison (gray). Dashed lines repeat the absorption spectra, but scaled by 0.2. The solvent was acetonitrile throughout.

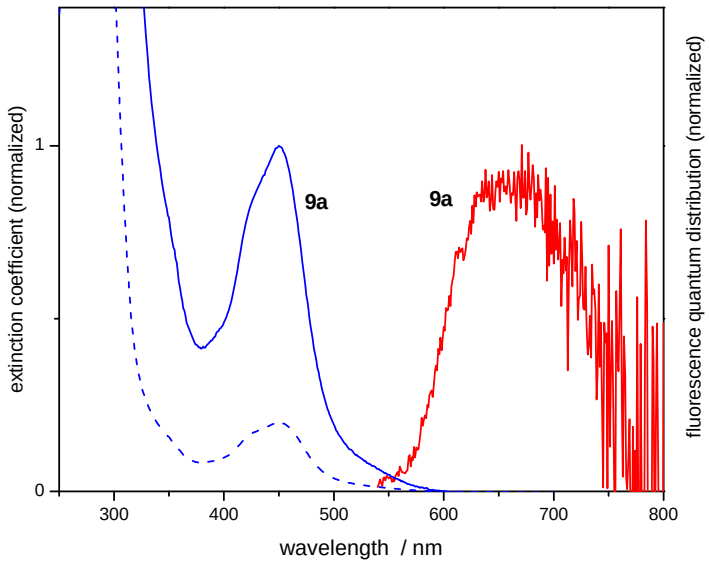


Fig. S2 Absorption and emission spectra of the labelled deaza-adenine **9a**, as in Fig. S1.

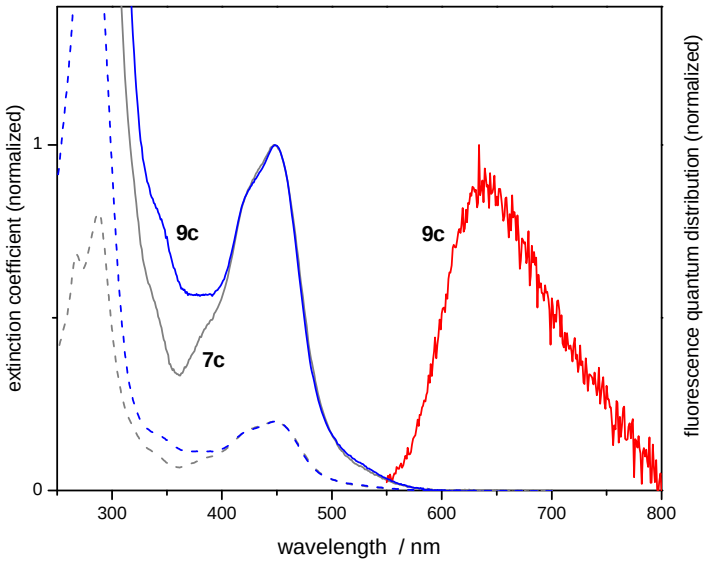


Fig. S3 Absorption and emission spectra of the labelled deaza-adenine **9c** and the absorption of the Ru(II) complex **7c** alone, as in Fig. S1.

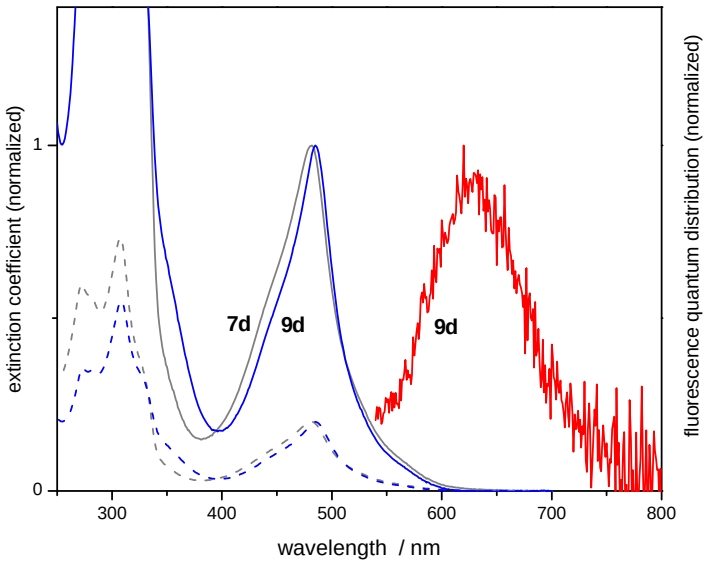


Fig. S4 Absorption and emission spectra of the labelled deaza-adenine **9d** and the absorption of the Ru(II) complex **7d** alone, as in Fig. S1.

Transient absorption spectra of Ru-complexes

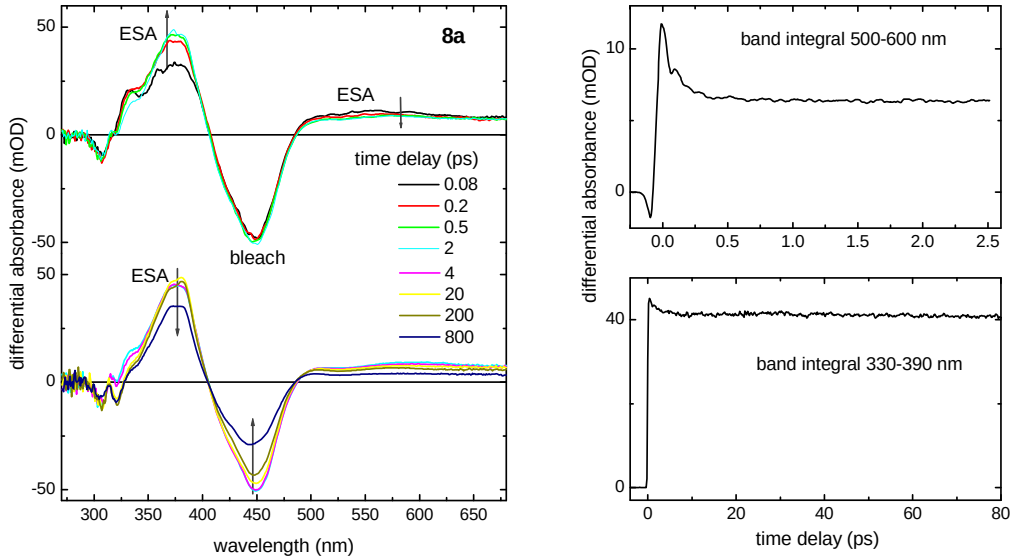


Fig. S5 Transient absorption spectra of **8a** in acetonitrile. Here the excited-state absorption for $\lambda \geq 500$ nm is much smaller compared to *tpy* complex **9d**. Band integral for two different regions are shown at right.

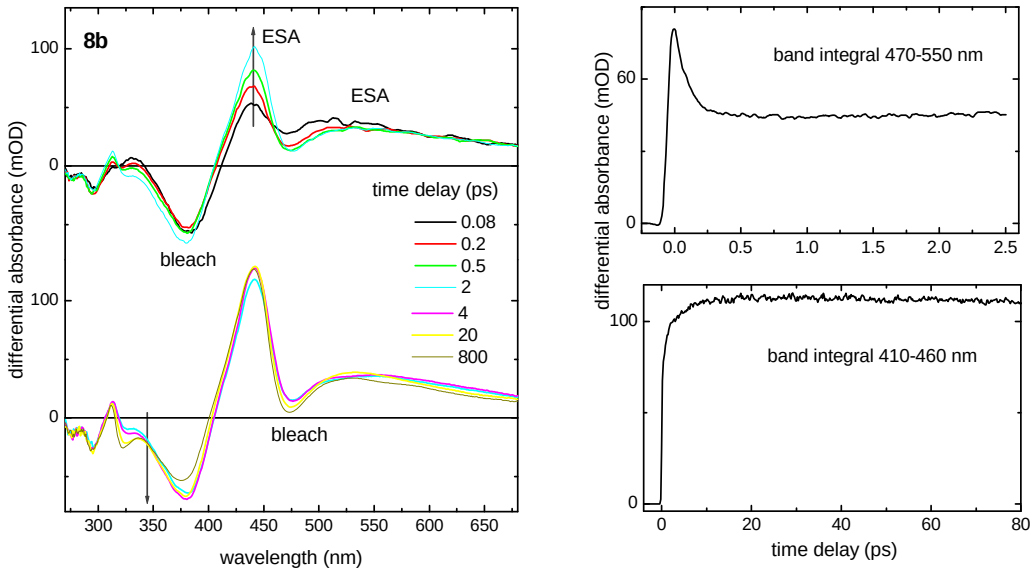


Fig. S6 Transient absorption spectra of **8b** in acetonitrile.

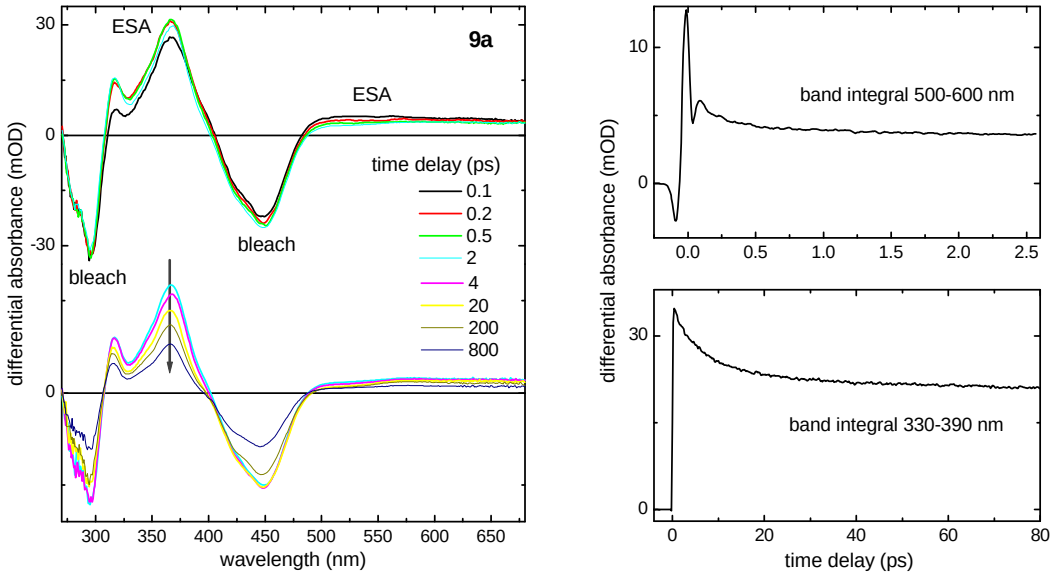


Fig. S7 Transient absorption spectra of **9a** in acetonitrile.

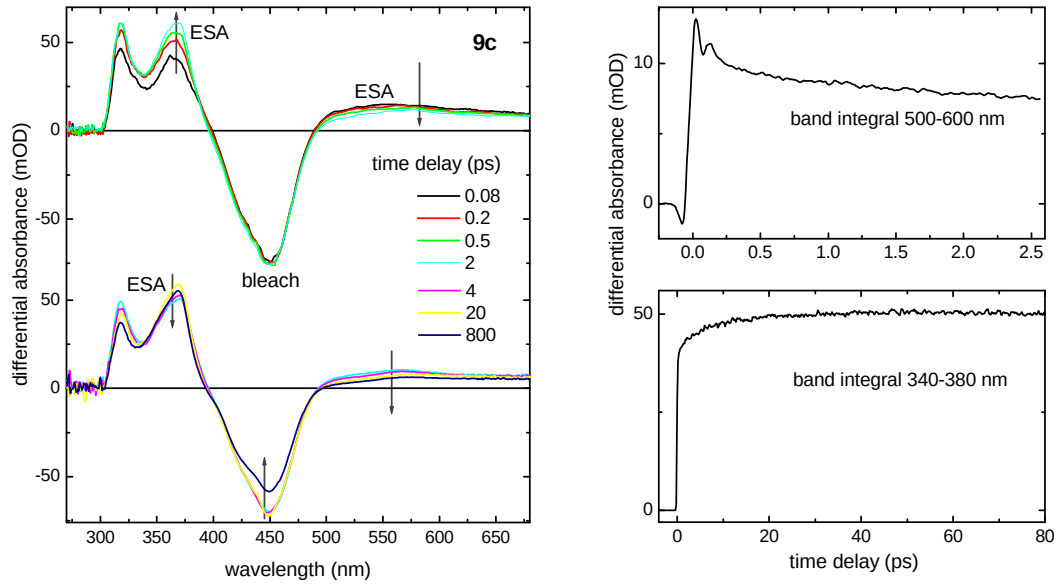
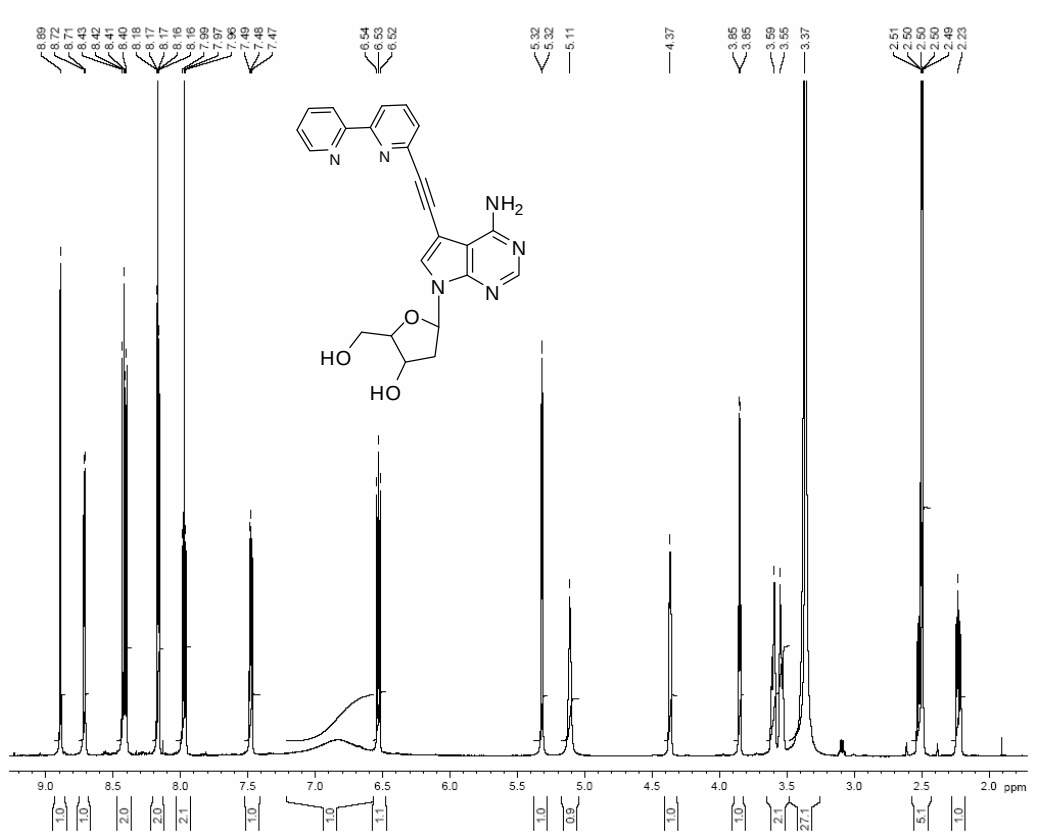
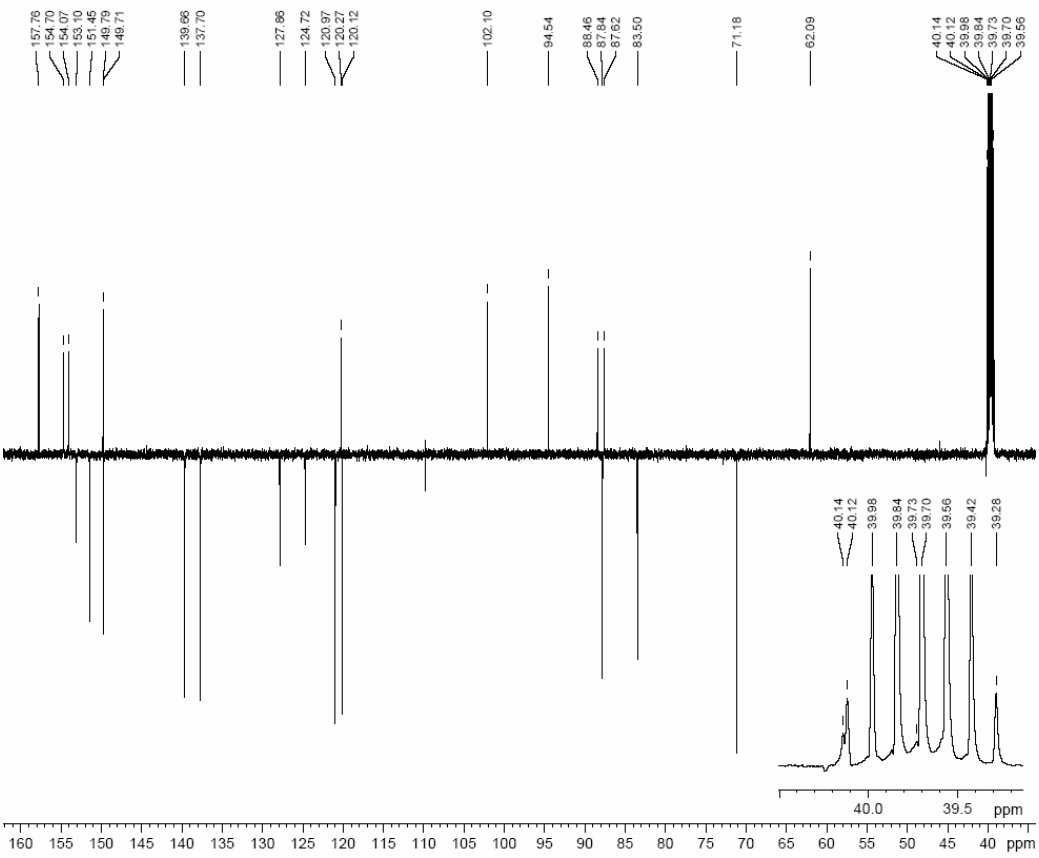


Fig. S8 Transient absorption spectra of **9c** in acetonitrile.

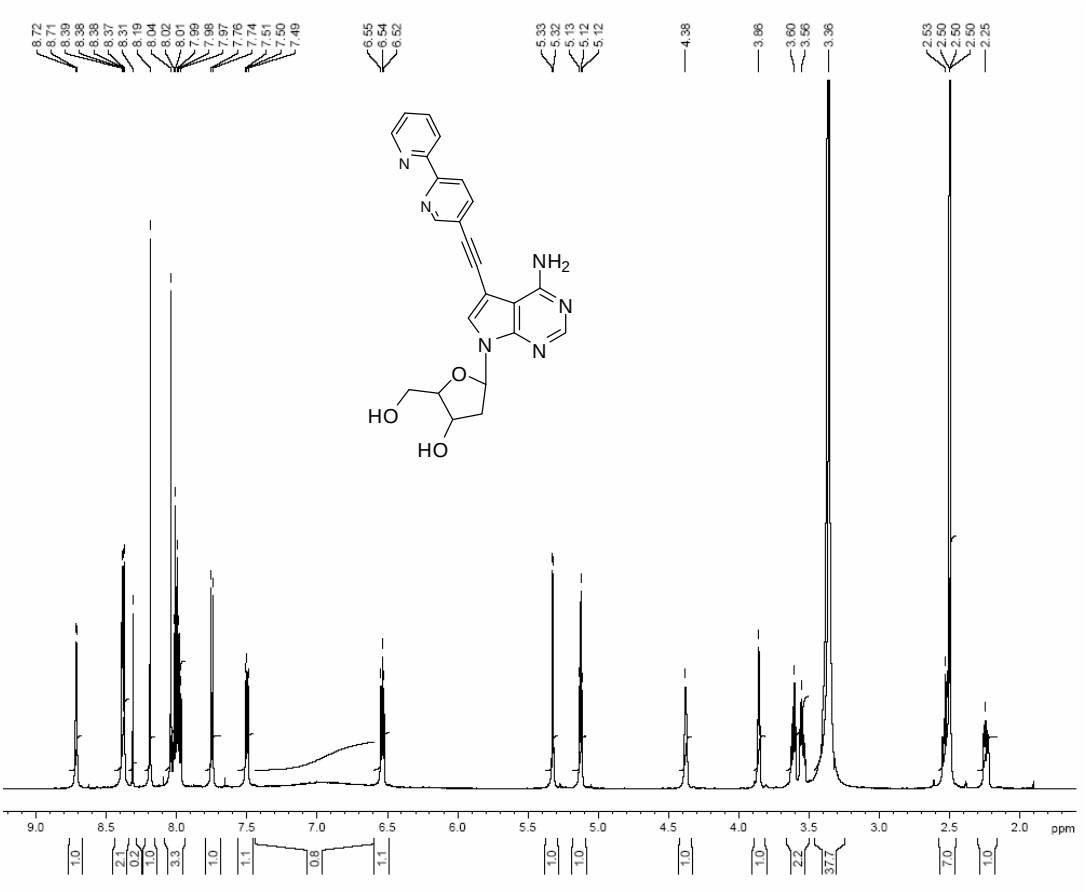
^{1}H and ^{13}C NMR spectra:

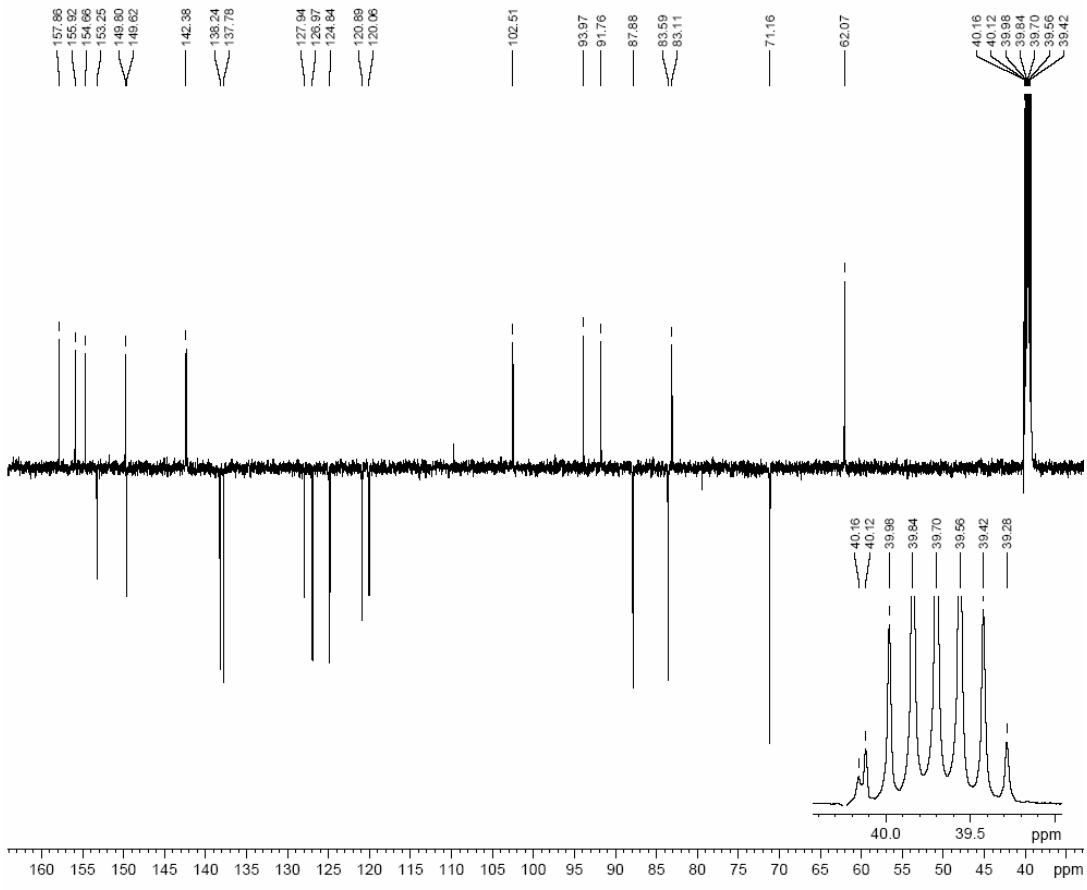
7-deaza-7-[(2",2'"-bipyridin-6"-yl)ethynyl]-2'-deoxyadenosine (4a)



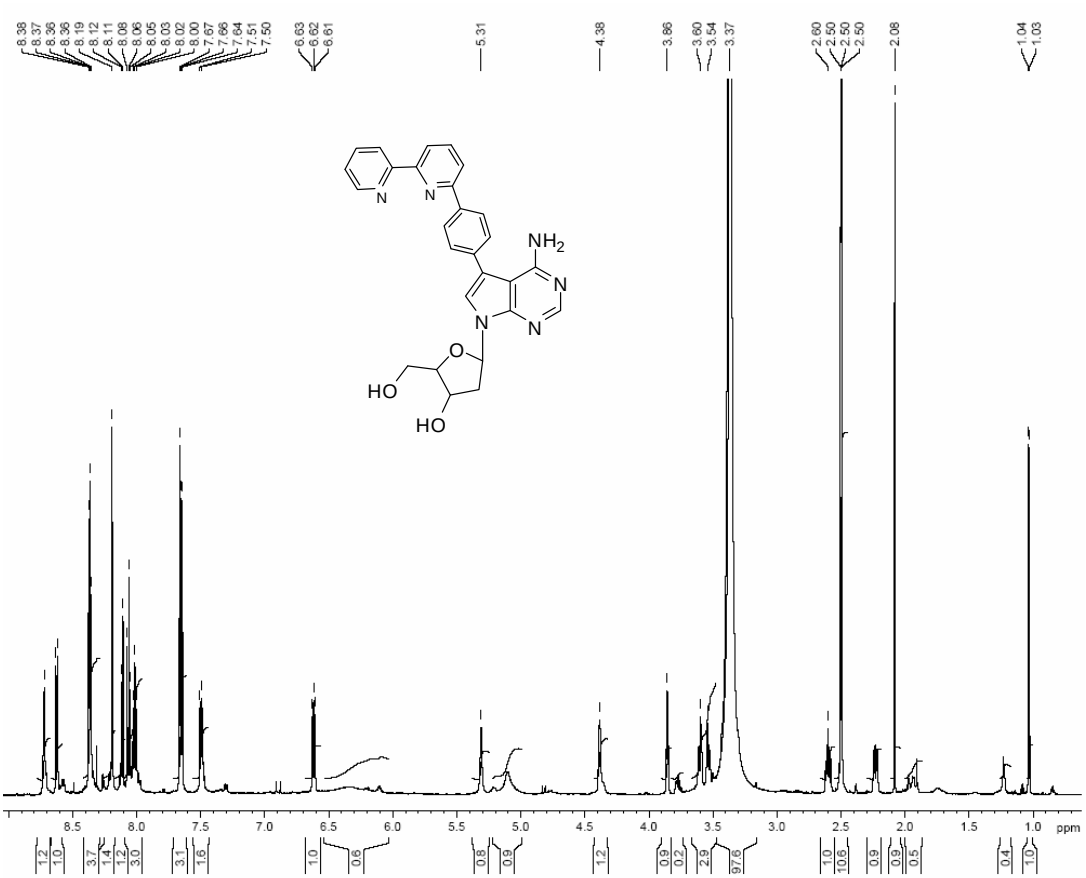


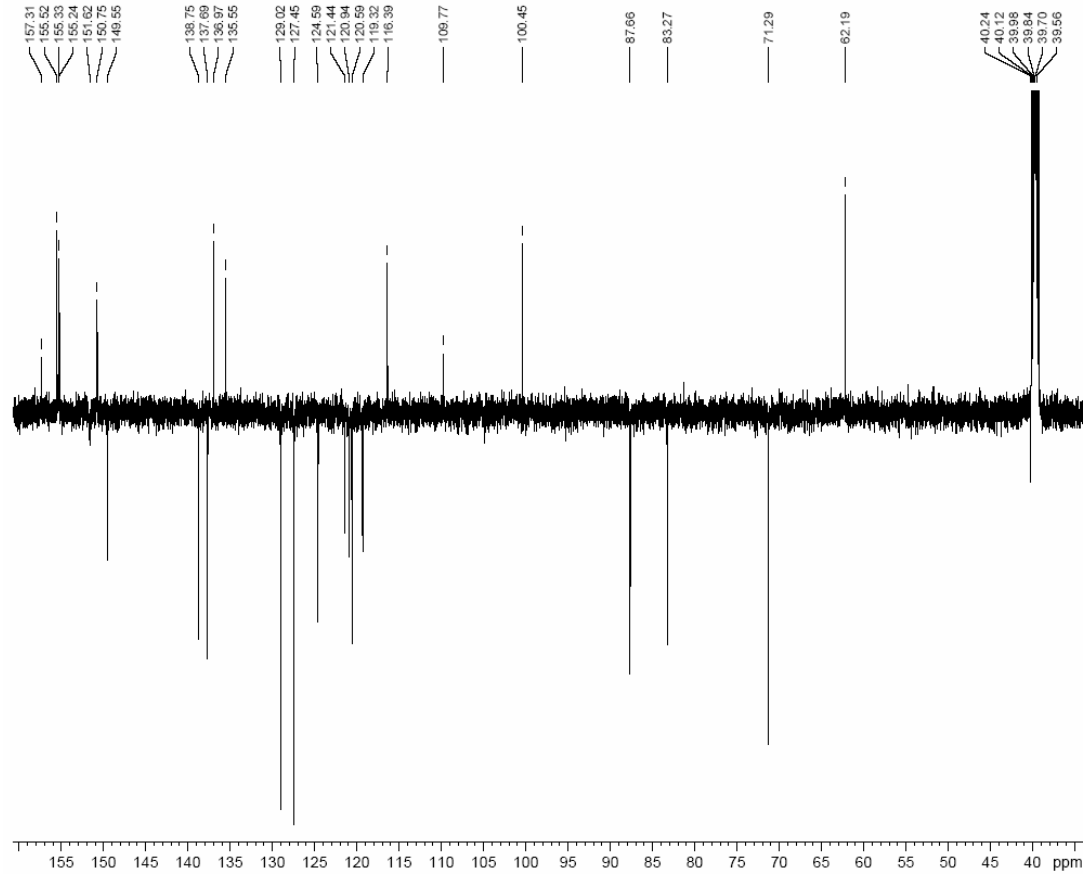
7-deaza-7-[(2",2'"-bipyridin-5"-yl)ethynyl]-2'-deoxyadenosine (4b)



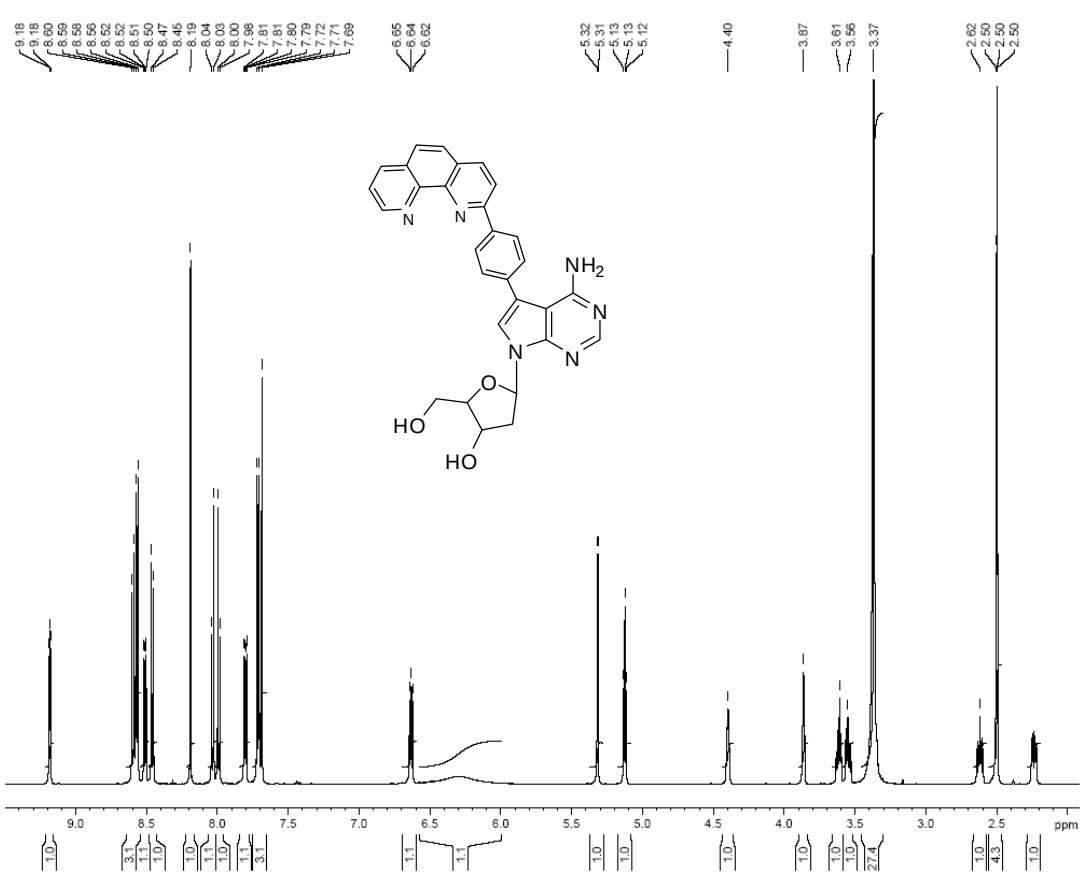


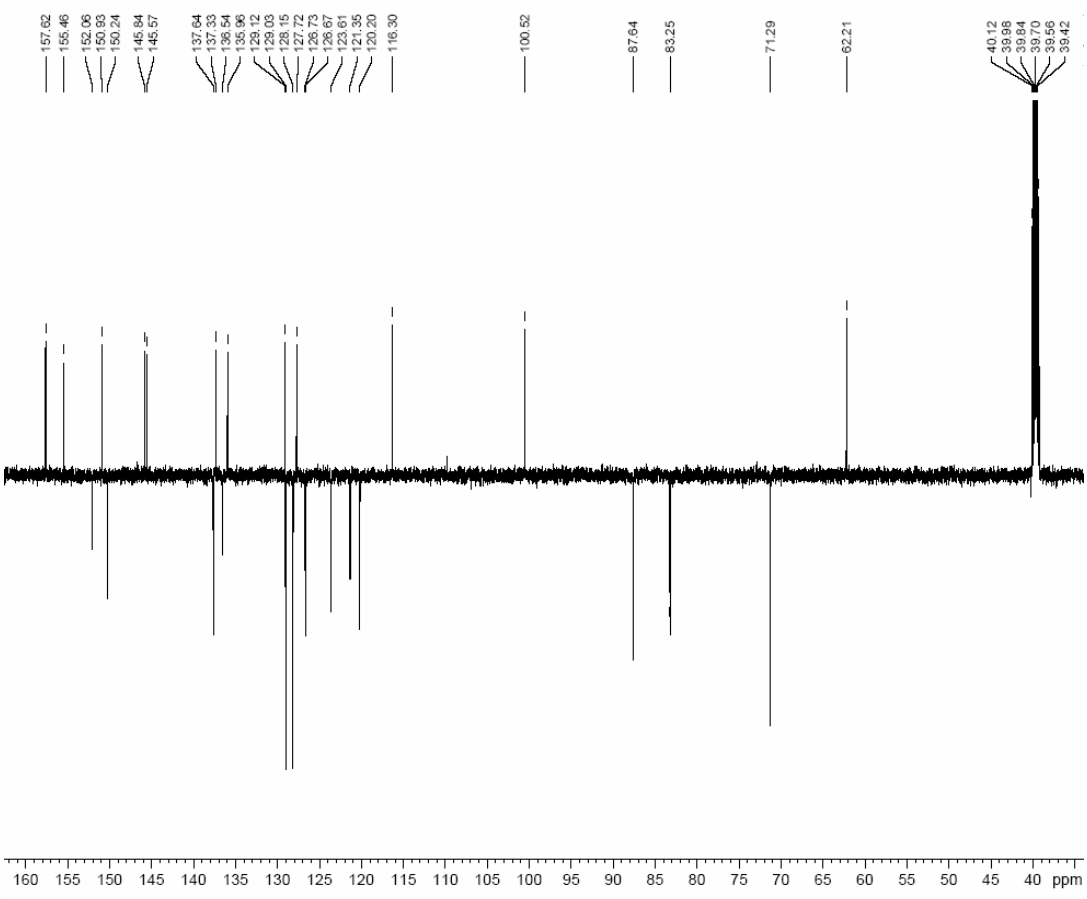
7-deaza-7-[(2",2'"-bipyridin-6"-yl)phenyl]-2'-deoxyadenosine (5a)



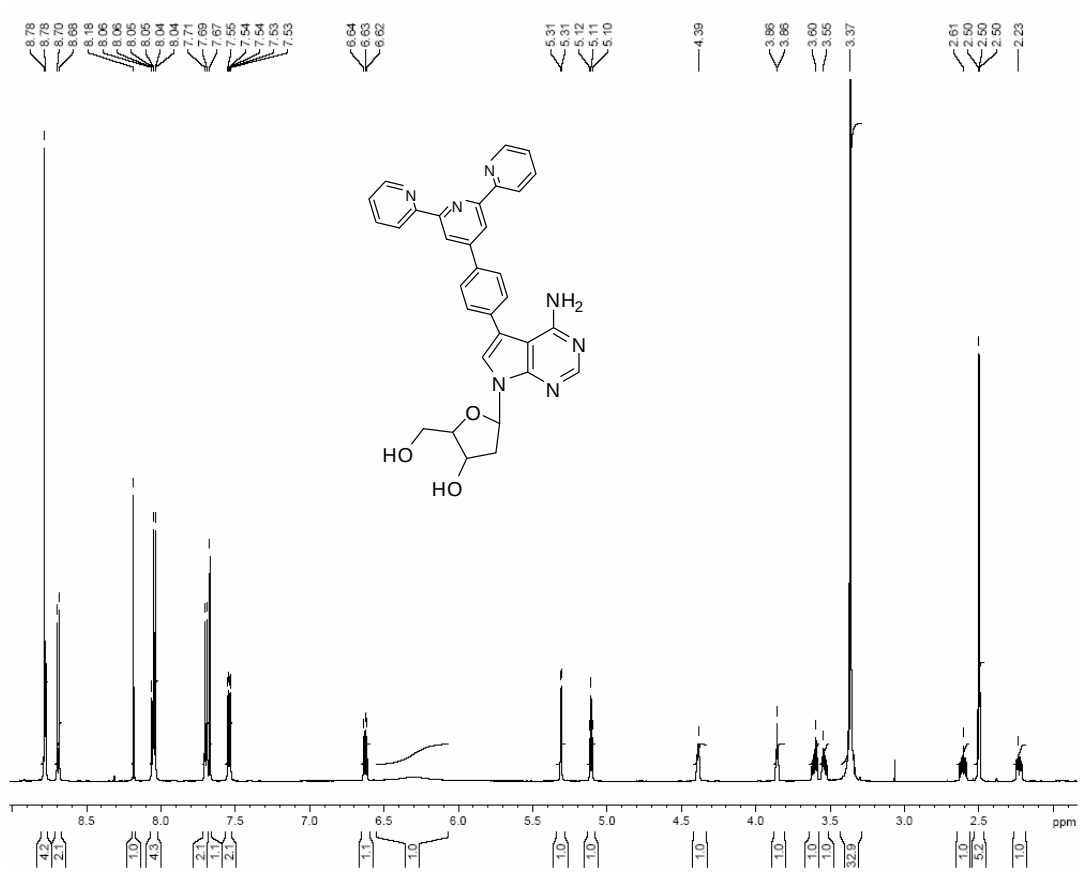


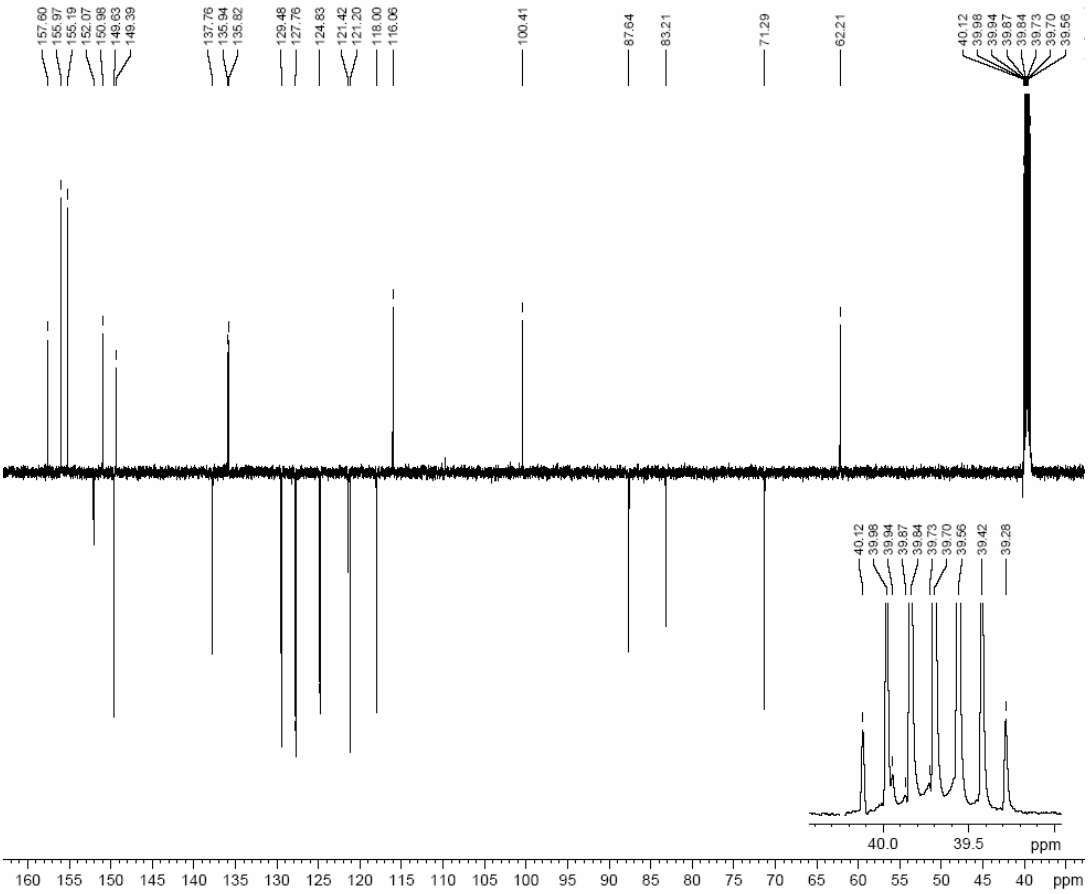
7-deaza-7-[(1",10"-phenantrolin-2"-yl)phenyl]-2'-deoxyadenosine (5c)



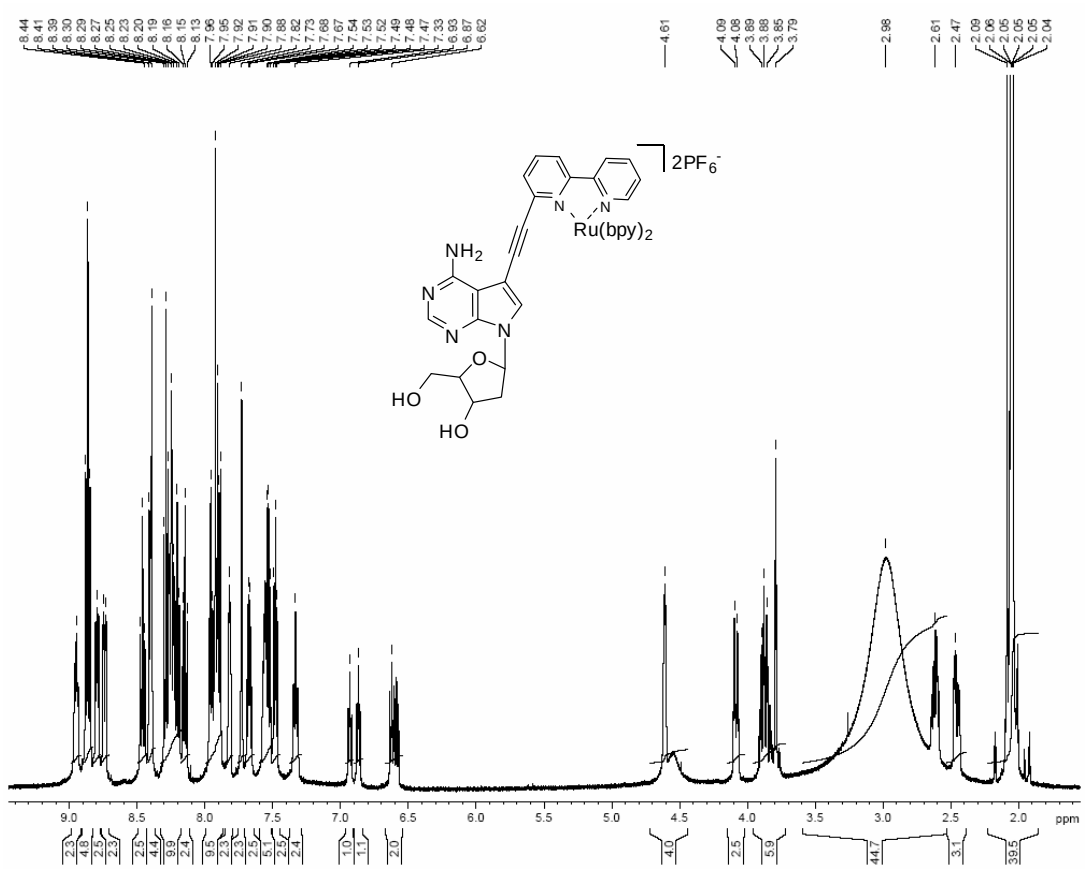


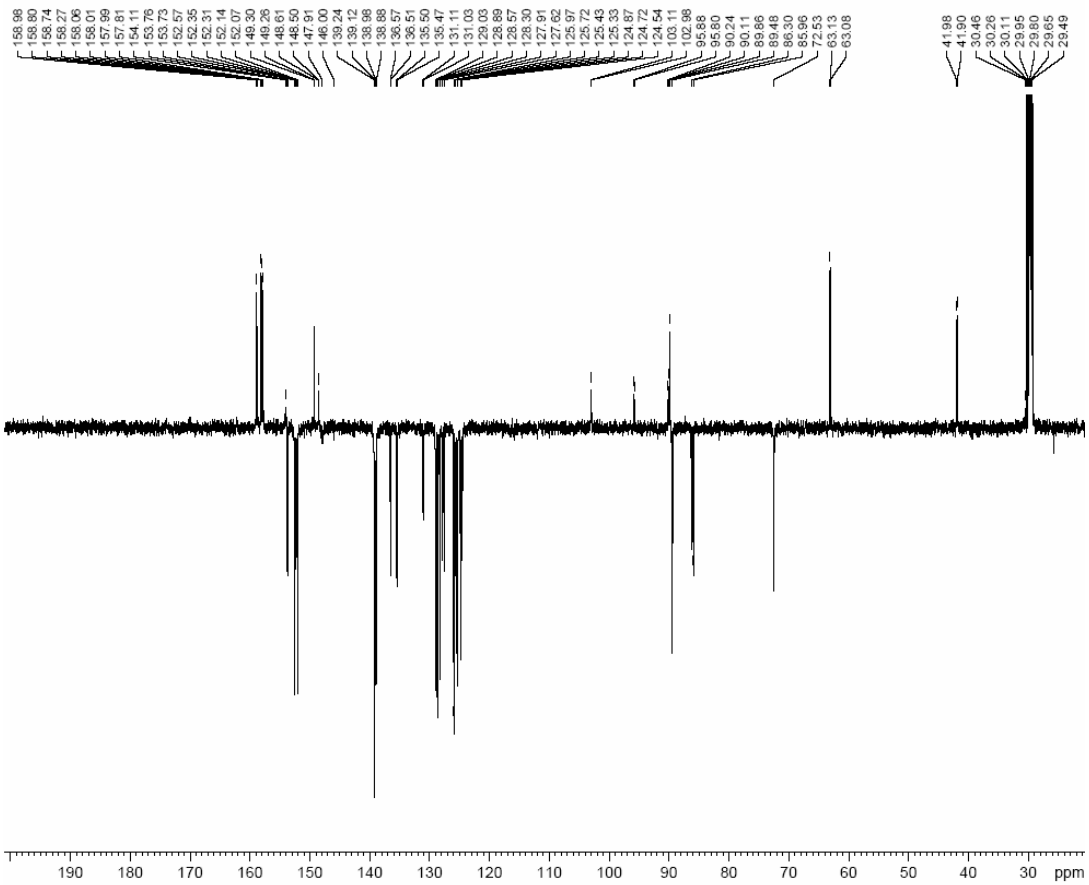
7-deaza-7-[(4"-(2",2'":6",2'"-terpyridin-1"-yl)phenyl]-2'-deoxyadenosine (5d)



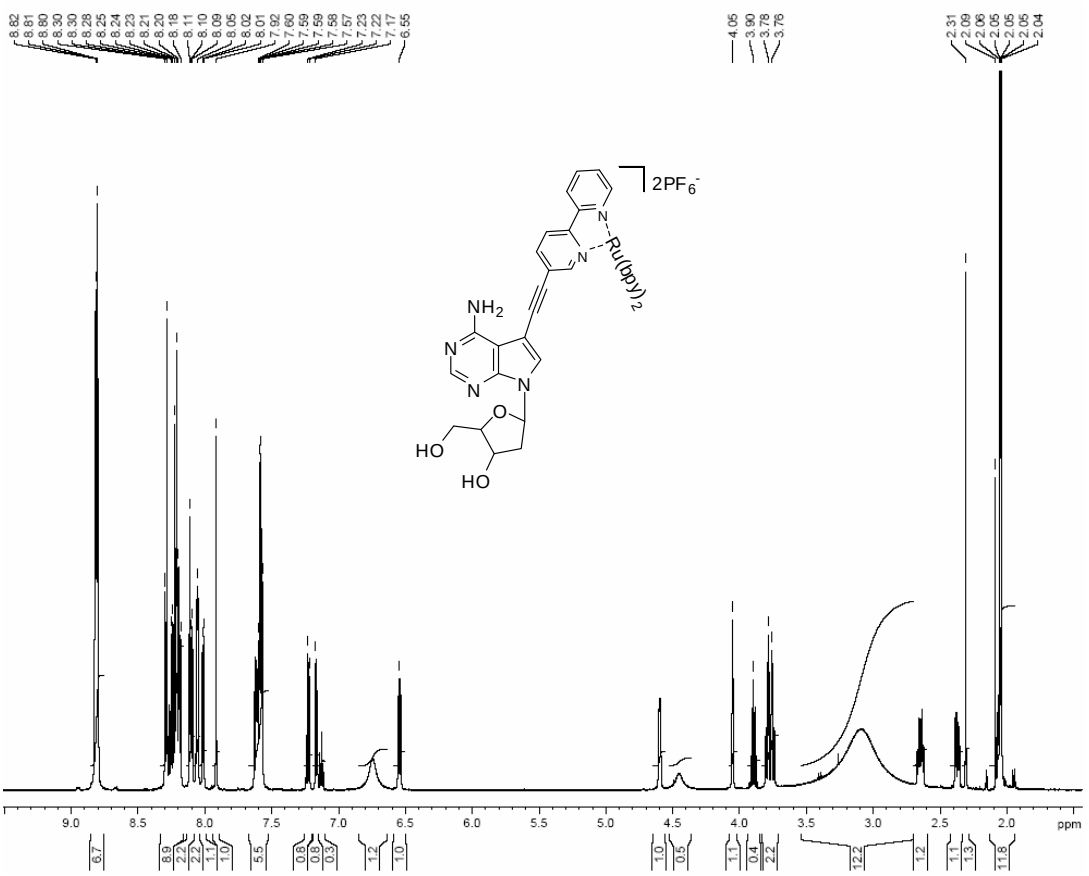


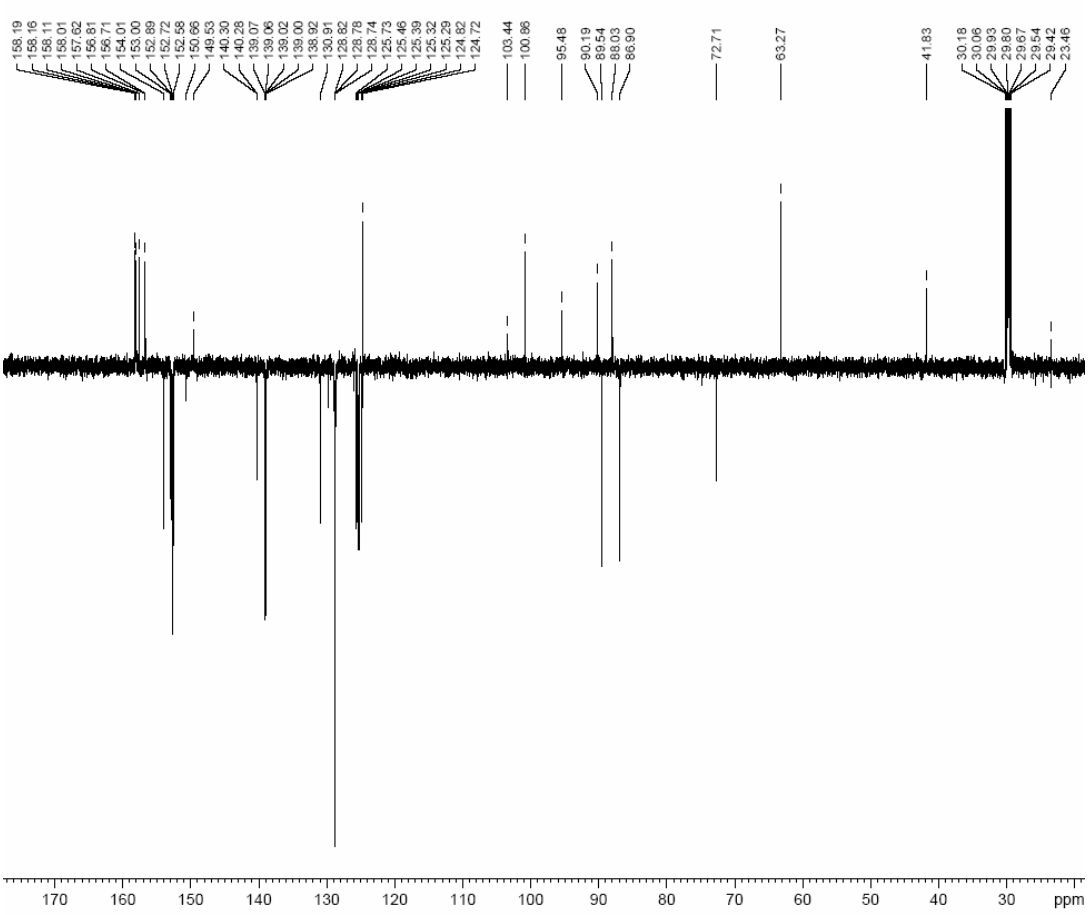
Complex 8a


8.44 8.41 8.39 8.30 8.29 8.27 8.25 8.23 8.20 8.19 8.16 8.15 8.13 7.96 7.95 7.92 7.91 7.90 7.88 7.82 7.73 7.68 7.67 7.54 7.53 7.52 7.49 7.48 7.47 7.33 6.93 6.87 6.62
4.61
4.09 4.06 3.89 3.88 3.85 3.79
2.98
2.61 2.47
2.09 2.06 2.06 2.05 2.05 2.05 2.04
2PF6-
Ru(bpy)2
NH2
HO
HO
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
2.3 4.8 2.5 2.3 2.6 4.4 9.9 2.4 9.5 2.3 2.3 2.5 5.1 2.5 2.4 1.0 1.1 2.0 4.0 2.5 5.9 44.7 3.1 39.5

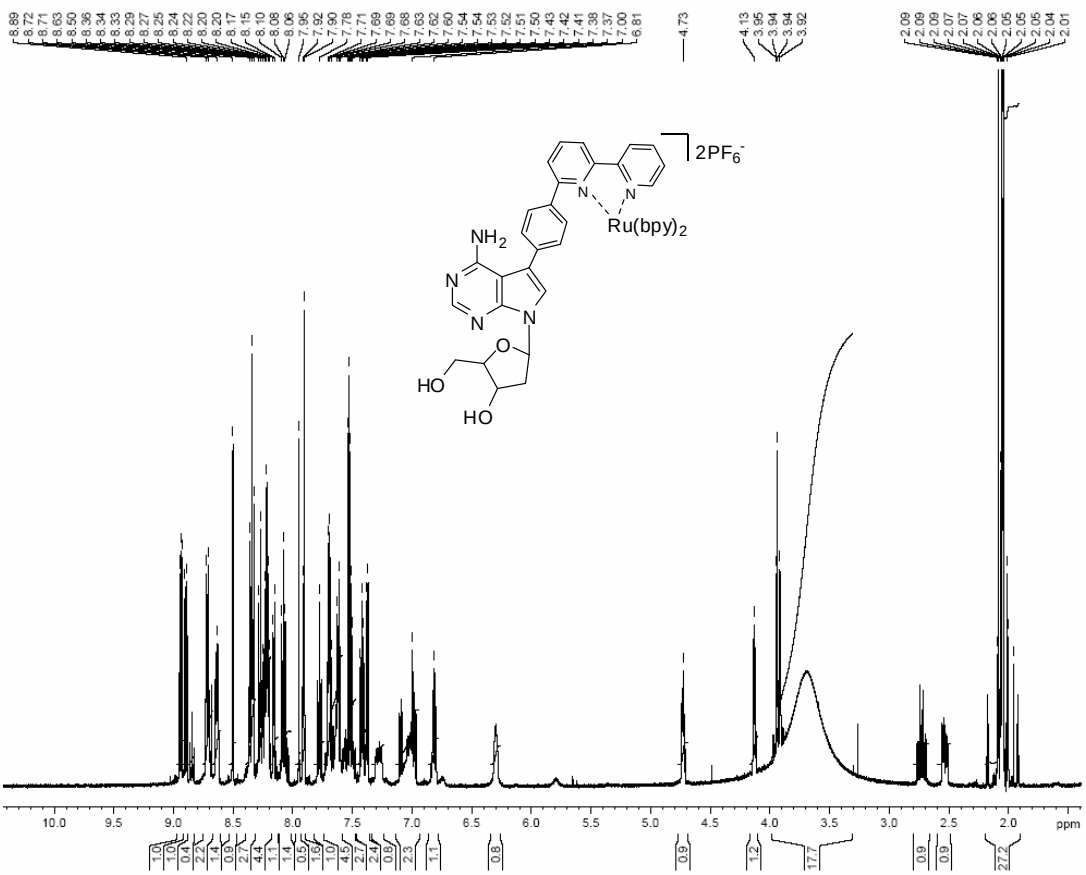

158.98 158.80 158.74 158.27 158.06 158.01 157.99 157.81 154.11 153.76 153.73 152.57 152.35 152.31 152.14 152.07 149.30 149.26 148.61 148.50 147.91 146.00 139.24 139.12 138.98 138.88 136.57 136.51 135.50 135.47 131.11 131.03 129.03 128.89 128.57 128.30 127.91 127.62 125.97 125.72 125.43 125.33 124.87 124.72 124.54 103.11 102.98 95.88 95.80 90.24 90.11 89.86 89.48 86.30 85.96 72.53 63.13 63.08
41.98 41.90
30.46 30.26 30.11 29.95 29.80 29.65 29.49
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

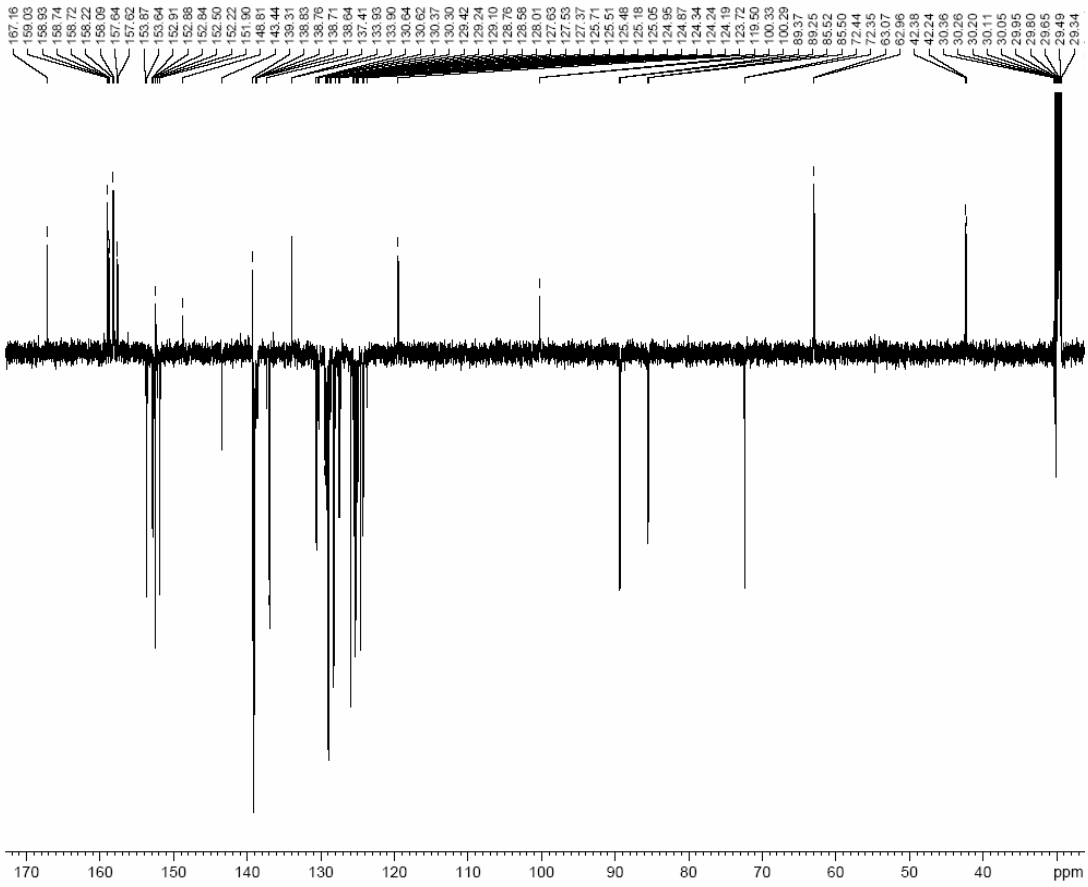
Complex 8b


8.82
8.81
8.80
8.30
8.30
8.28
8.25
8.24
8.23
8.21
8.20
8.18
8.11
8.10
8.09
8.05
8.02
8.01
7.92
7.60
7.59
7.58
7.57
7.23
7.22
7.17
6.55
4.05
3.90
3.78
3.76
2.31
2.09
2.06
2.05
2.05
2.05
2.04
2PF6-
Ru(bpy)2
NH2
HO
HO
ppm

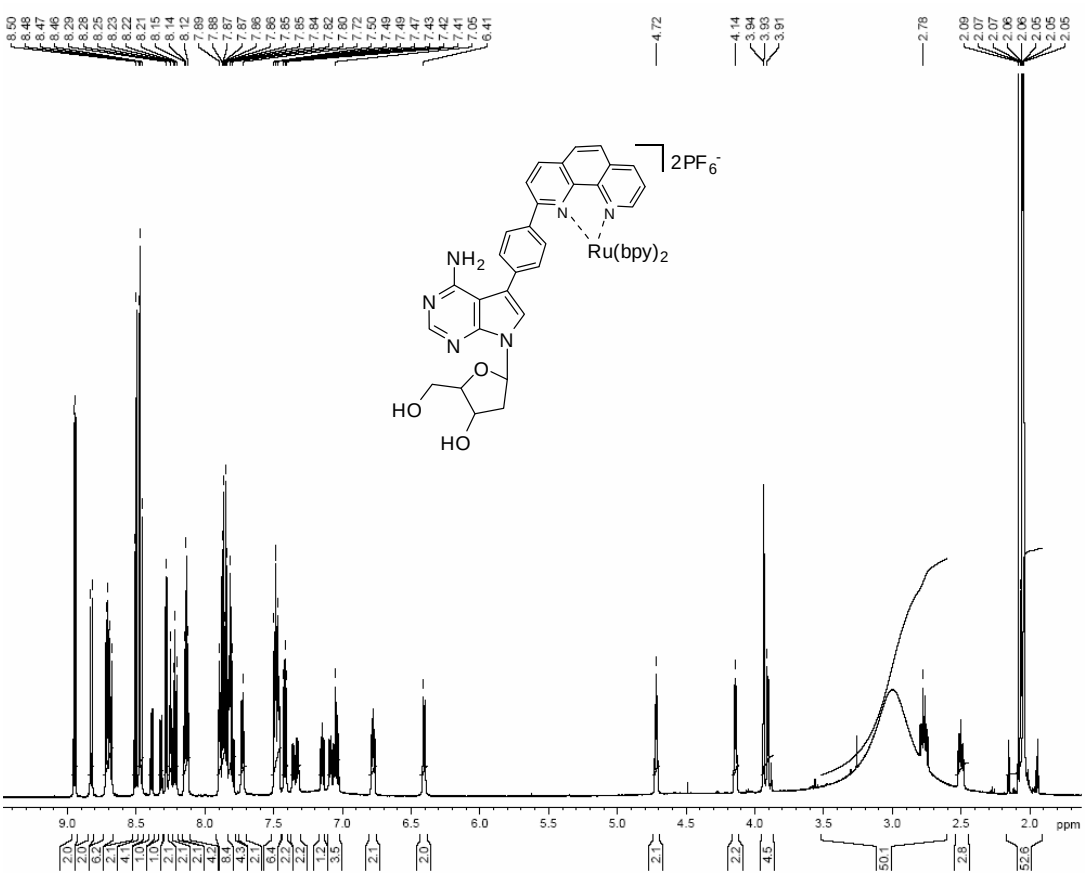

158.19
158.16
158.11
158.01
157.62
156.81
156.71
154.01
153.00
152.89
152.72
152.58
150.66
149.53
140.30
140.28
139.07
139.06
139.02
139.00
138.92
130.91
128.82
128.78
128.74
125.73
125.46
125.39
125.32
125.29
124.82
124.72
103.44
100.86
95.48
90.19
89.54
88.03
86.90
72.71
63.27
41.83
30.18
30.06
29.93
29.80
29.67
29.54
29.42
23.46
ppm

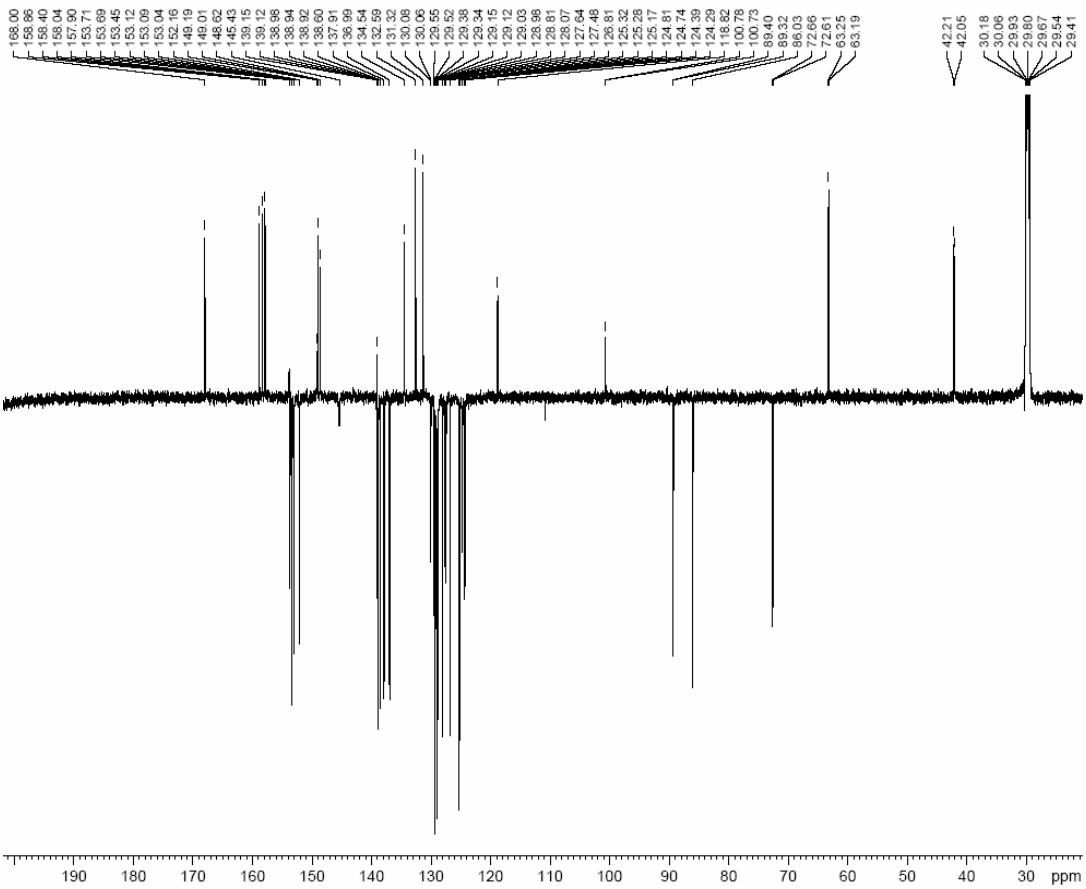
Complex 9a



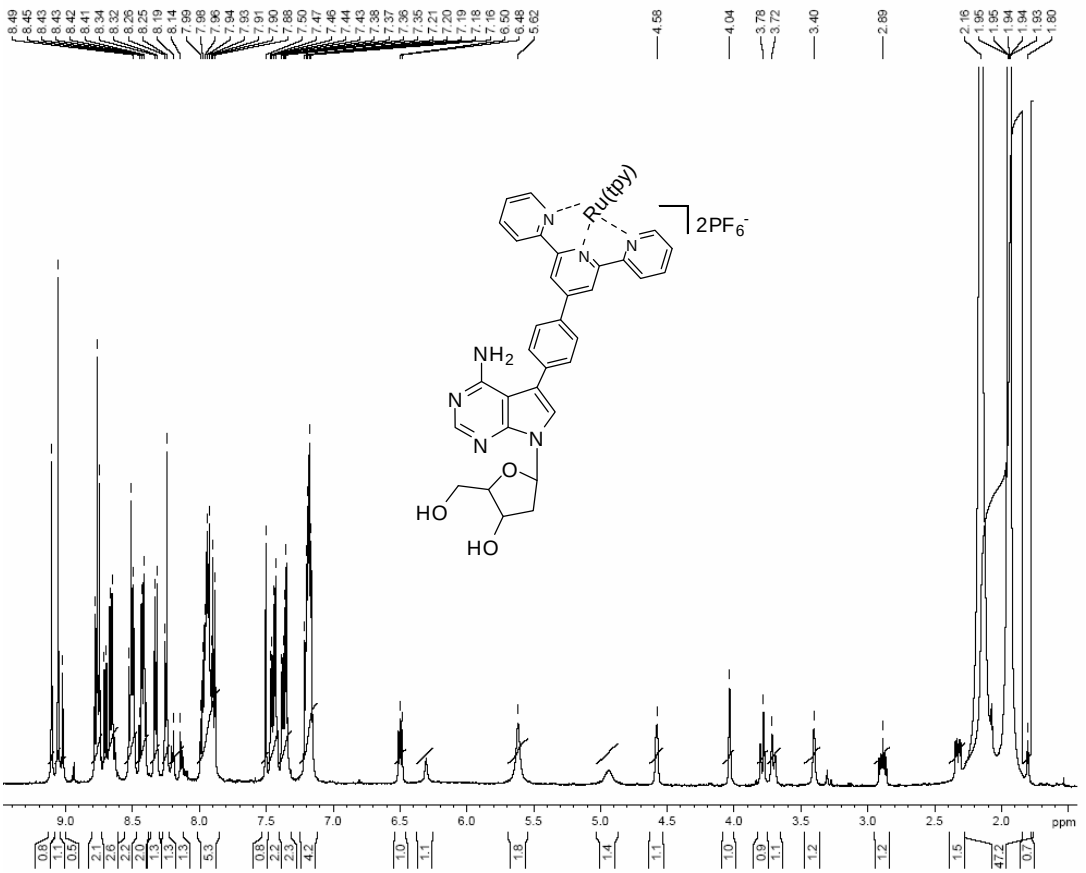


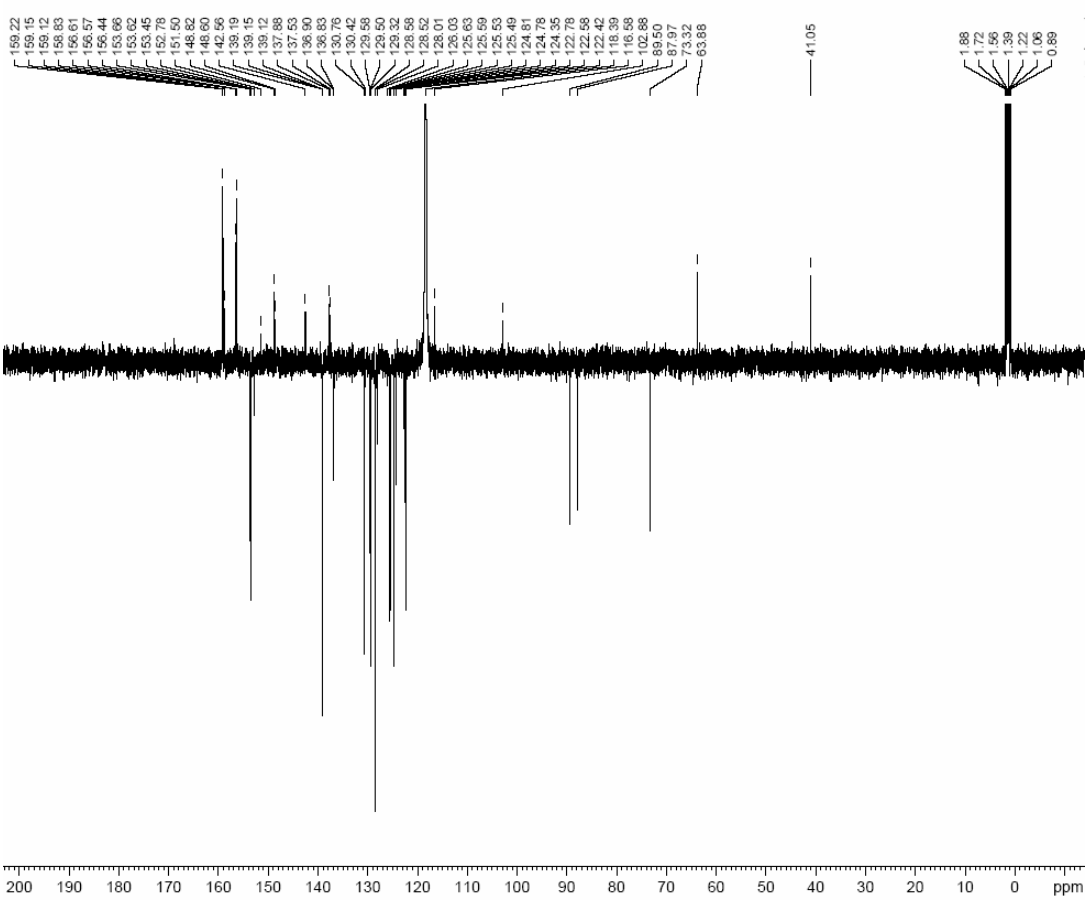
Complex 9c





Complex 9d





[1] P. Čapek, H. Cahová, R. Pohl, M. Hocek, C. Gloeckner, A. Marx, *Chem. Eur. J.,* 2007, **13**, 6196-6203.
[2] M.Vrábel, M. Hocek, L. Havran, M. Fojta, I. Votruba, B. Kepetářová, R. Pohl, L. Rulíšek, L. Zendlová, P. Hobza, I.-h. Shih, E. Mabery, R. Mackman, *Eur. J. Inorg. Chem*., 2007, 1752-1769.
[3] J. Bourson, J. Valeur, *J. Phys. Chem.*, 1989, **93**, 3871-3876.
[4] A. L. Dobryakov, N. P. Ernsting, in: Kühn, O.; Wöste, L.(Eds) *Analysis and Control of Ultrafast Photoinduced Reactions, Springer Series in Chemical Physics*, Vol. 87, Springer, Heidelberg, 2007, pp.689.
[5] (a) M. Fojta, L. Havran, R. Kizek, S. Billova, *Talanta,* 2002, **56**, 867-874; (b) M. Fojta, L. Havran, S. Billova, P. Kostecka, M. Masarik, R. Kizek, *Electroanalysis,* 2003, **15**, 431-440.