Electronic Supplementary Material (ESI) for Dalton Transactions

Kinetics and mechanism of the reactions of Au(III) complexes with some biologically relevant molecules

Ana Djeković, Biljana Petrović, Živadin D. Bugarčić* Ralph Puchta and Rudi van Eldik*

Supporting Information (ESI)

Table S1. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the substitution reaction between $[Au(dien)Cl]^{2+}$ and L-His in 25 mM Hepes buffer (pH = 7.2) in the presence of 10 mM NaCl.

λ/nm	T/K	10^3C_L/M	$10^2k_{obsd}/s^{-1}$
355	288.1	0.4	0.283(5) [a]
		1	0.347(6)
		2	0.481(7)
		3	0.563(5)
		4	0.645(6)
		5	0.759(5)
	298.0	0.4	0.396(6)
		1	0.501(7)
		2	0.742(5)
		3	0.904(6)
		4	1.107(5)
		5	1.284(5)
	310.0	0.4	0.642(7)
		1	0.833(6)
		2	1.110(6)
		3	1.446(5)
		4	1.818(5)
		5	2.158(5)

[a]Number of runs in parenthesis.

Table S2. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the substitution reaction between $[Au(dien)Cl]^{2+}$ and 5'-GMP in 25 mM Hepes buffer (pH = 7.2) in the presence of 10 mM NaCl.

λ/nm	T/K	10^3C_L/M	$10^3k_{obsd}/s^{-1}$
246	288.1	0.4	2.43(6)
		1	2.96(6)
		2	4.01(7)
		3	4.68(5)
		4	5.52(6)
		5	5.96(5)
	298.0	0.4	3.26(6)
		1	3.93(5)
		2	5.11(7)
		3	6.35(5)
		4	7.69(7)
		5	8.99(7)
	309.9	0.4	4.59(7)
		1	6.18(5)
		2	7.99(5)
		3	9.89(5)
		4	12.10(6)
		5	14.62(6)

Table S3. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the substitution reaction between $[Au(dien)Cl]^{2+}$ and 5'-IMP in 25 mM Hepes buffer (pH = 7.2) in the presence of 10 mM NaCl.

λ/nm	T/K	10^3C_L/M	$10^3k_{obsd}/s^{-1}$
353	288.0	0.5	0.422(6)
		1	0.547(6)
		2	0.567(6)
		3	0.727(5)
		4	1.001(6)
		5	1.096(6)
	298.1	0.5	0.914(6)
		1	1.12(5)
		2	1.67(5)
		3	2.06(6)
		4	2.28(7)
		5	2.75(5)
	310.0	0.5	1.84(7)
		1	2.34(6)
		2	3.31(7)
		3	4.08(5)
		4	5.01(7)
		5	6.28(5)

Table S4. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the substitution reaction between $[Au(dien)Cl]^{2+}$ and Ino in 25 mM Hepes buffer (pH = 7.2) in the presence of 10 mM NaCl.

λ/nm	T/K	10^3C_L/M	$10^3k_{obsd}/s^{-1}$
246	288.0	0.4	0.101(5)
		1	0.220(6)
		2	0.271(7)
		3	0.401(5)
		4	0.502(6)
		5	0.584(5)
	298.1	0.4	0.312(6)
		1	0.499(7)
		2	0.821(5)
		3	1.211(6)
		4	1.621(5)
		5	2.003(5)
	310.0	0.4	0.668(7)
		1	1.115(6)
		2	1.889(6)
		3	2.712(5)
		4	3.740(5)
		5	4.663(5)

Table S5. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the substitution reaction between $[Au(terpy)Cl]^{2+}$ and L-His in 25 mM Hepes buffer (pH = 7.2) in the presence of 10 mM NaCl.

λ/nm	T/K	10^3C_L/M	k_{obsd}/s^{-1}
320	288.1	0.5	3.004(5)
		1	3.826(5)
		2	5.712(7)
		3	7.348(7)
		4	8.873(7)
		5	11.156(5)
	298.1	0.5	4.505(5)
		1	6.728(5)
		2	9.580(5)
		3	13.261(6)
		4	16.970(7)
		5	20.804(7)
	310.0	0.5	6.834(7)
		1	10.120(5)
		2	15.692(5)
		3	23.761(5)
		4	30.142(5)
		5	35.790(5)

Table S6. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the substitution reaction between $[Au(terpy)Cl]^{2+}$ and 5'-GMP in 25 mM Hepes buffer (pH = 7.2) in the presence of 10 mM NaCl.

λ/nm	T/K	10^3C_L/M	k_{obsd}/s^{-1}
367	288.2	0.5	0.654(7)
		1	1.598(6)
		2	2.551(7)
		3	3.921(6)
		4	5.186(6)
		5	6.812(6)
	298.1	0.5	1.954(5)
		1	3.106(7)
		2	5.412(5)
		3	7.840(6)
		4	9.961(7)
		5	12.040(7)
	310.0	0.5	4.211(5)
		1	7.912(6)
		2	13.901(5)
		3	19.800(5)
		4	25.782(7)
		5	31.240(5)

Table S7. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the substitution reaction between $[Au(terpy)Cl]^{2+}$ and 5'-IMP in 25 mM Hepes buffer (pH = 7.2) in the presence 10 mM NaCl.

λ/nm	T/K	10^3C_L/M	k_{obsd}/s^{-1}
360	288.0	0.5	2.680(5)
		1	3.445(6)
		2	5.102(7)
		3	7.397(5)
		4	9.191(7)
		5	10.890(6)
	298.1	0.5	3.021(6)
		1	4.137(7)
		2	6.352(7)
		3	7.980(6)
		4	10.122(7)
		5	12.850(5)
	310.1	0.5	3.691(7)
		1	5.157(6)
		2	7.386(6)
		3	10.748(6)
		4	13.930(6)
		5	16.171(6)

Table S8. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the substitution reaction between $[Au(terpy)Cl]^{2+}$ and Ino in 25 mM Hepes buffer (pH = 7.2) in the presence of 10 mM NaCl.

λ/nm	T/K	10^3C_L/M	k_{obsd}/s^{-1}
333	288.0	0.5	0.556(5)
		1	0.996(6)
		2	1.845(7)
		3	3.112(5)
		4	3.737(6)
		5	4.737(5)
	298.1	0.5	0.889(6)
		1	1.684(7)
		2	2.999(5)
		3	4.021(6)
		4	5.331(5)
		5	6.969(5)
	310.0	0.5	1.458(7)
		1	3.027(6)
		2	4.988(6)
		3	7.687(5)
		4	9.505(5)
		5	12.212(5)

Table S9. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the first (k_{obsd1}) and second (k_{obsd2}) steps of the substitution reactions between $[Au(bipy)Cl_2]^+$ and L-His in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl.

λ/nm	T/K	10^3C_L/M	k_{obsd1}/s^{-1}	k_{obsd2}/s^{-1}
295	288.0	0.5	0.087(5)	0.010(5)
		1	0.154(6)	0.018(6)
		2	0.255(6)	0.029(6)
		3	0.329(7)	0.032(7)
		4	0.506(6)	0.049(6)
		5	0.589(6)	0.066(6)
	298.1	0.5	0.157(6)	0.022(6)
		1	0.251(7)	0.031(7)
		2	0,460(7)	0.045(7)
		3	0.689(7)	0.065(7)
		4	0.851(7)	0.078(7)
		5	1.073(5)	0.098(5)
	309.9	0.5	0.267(6)	0.038(6)
		1	0.367(5)	0.052(5)
		2	0.760(5)	0.068(5)
		3	0.927(7)	0.089(7)
		4	1.137(5)	0.109(5)
		5	1.538(5)	0.140(5)

Table S10. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the first (k_{obsd1}) and second (k_{obsd2}) steps of the substitution reactions between $[Au(bipy)Cl_2]^+$ and 5'-GMP in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl.

λ/nm	T/K	10^3C_L/M	k_{obsd1}/s^{-1}	k_{obsd2}/s^{-1}
320	288.2	0.5	0.071(6)	0.031(6)
		1	0.093(7)	0.035(7)
		2	0.279(6)	0.039(6)
		3	0.401(6)	0.045(6)
		4	0.515(5)	0.051(5)
		5	0.580(6)	0.058(6)
	298.0	0.5	0.106(6)	0.044(6)
		1	0.167(7)	0.050(7)
		2	0.337(5)	0.059(5)
		3	0.491(6)	0.068(6)
		4	0.640(5)	0.079(5)
		5	0.761(5)	0.090(5)
	309.9	1	0.211(6)	0.053(6)
		2	0.446(6)	0.079(6)
		3	0.600(5)	0.092(5)
		4	0.710(5)	0.108(5)
		5	0.890(5)	0.129(5)

Table S11. Observed *pseudo*-first order rate constants as a function of nucleophile concentration for the first (k_{obsd1}) and second (k_{obsd2}) steps of the substitution reactions between $[Au(bipy)Cl_2]^+$ and 5'-IMP in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl.

λ/nm	T/K	10^3C_L/M	k_{obsd1}/s^{-1}	k_{obsd2}/s^{-1}
318	298.0	0.5	0.485(6)	0.0766(6)
		1	0.515(5)	0.0800(5)
		2	0.555(6)	0.0805(6)
		3	0.592(6)	0.0874(6)
		4	0.649(6)	0.0929(6)
		5	0.702(7)	0.0950(7)

Table S12. Observed *pseudo*-first order rate constants as a function of nucleophile concentration for the first (k_{obsd1}) and second (k_{obsd2}) steps of the substitution reactions between $[Au(bipy)Cl_2]^+$ and Ino in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl.

λ/nm	T/K	10^3C_L/M	k_{obsd1}/s^{-1}	k_{obsd2}/s^{-1}
318	298.0	0.5	0.286(6)	0.0220(6)
		1	0.301(6)	0.0229(6)
		2	0.355(6)	0.0230(6)
		3	0.381(6)	0.0250(6)
		4	0.422(7)	0.0255(7)
		5	0.465(7)	0.0270(7)

Table S13. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the first (k_{obsd1}) and second (k_{obsd2}) steps of the substitution reactions between $[Au(dach)Cl_2]^+$ and L-His in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl.

λ/nm	T/K	10^3C_L/M	k_{obsd1}/s^{-1}	k_{obsd2}/s^{-1}
290	288.2	0.5	0.088(6)	0.017(6)
		1	0.110(5)	0.019(5)
		2	0.192(7)	0.020(7)
		3	0.207(7)	0.025(7)
		4	0.283(6)	0.027(6)
		5	0.340(6)	0.030(6)
	298.0	0.5	0.118(6)	0.024(6)
		1	0.142(7)	0.026(7)
		2	0.240(5)	0.032(5)
		3	0.320(7)	0.037(7)
		4	0.372(7)	0.040(7)
		5	0.450(5)	0.045(5)
	310.0	0.5	0.141(6)	0.032(6)
		1	0.190(6)	0.037(6)
		2	0.279(6)	0.040(6)
		3	0.356(7)	0.048(7)
		4	0.452(6)	0.051(6)
		5	0.550(7)	0.063(7)

Table S14. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the first (k_{obsd1}) and second (k_{obsd2}) steps of the substitution reactions between $[Au(dach)Cl_2]^+$ and 5'-GMP in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl.

λ/nm	T/K	10^3C_L/M	k_{obsd1}/s^{-1}	k_{obsd2}/s^{-1}
320	288.2	0.5	0.172(7)	0.012(7)
		1	0.201(5)	0.016(5)
		2	0.253(6)	0.018(6)
		3	0.280(7)	0.021(7)
		4	0.351(5)	0.023(5)
		5	0.400(7)	0.033(7)
	298.0	0.5	0.219(7)	0.034(7)
		1	0.251(7)	0.038(7)
		2	0.325(5)	0.042(5)
		3	0.383(6)	0.050(6)
		4	0.450(5)	0.056(5)
		5	0.520(5)	0.062(5)
	310.0	0.5	0.325(7)	0.049(7)
		1	0.377(6)	0.056(6)
		2	0.395(6)	0.061(6)
		3	0.523(6)	0.069(6)
		4	0.592(6)	0.086(6)
		5	0.640(5)	0.090(5)

Table S15. Observed *pseudo*-first order rate constants as a function of nucleophile concentration for the first (k_{obsd1}) and second (k_{obsd2}) steps of the substitution reactions between $[Au(dach)Cl_2]^+$ and 5'-IMP in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl.

λ/nm	T/K	10^3C_L/M	k_{obsd1}/s^{-1}	k_{obsd2}/s^{-1}
310	298.0	0.5	0.007(7)	0.0268(7)
		1	0.010(6)	0.0272(6)
		2	0.017(6)	0.0276(6)
		3	0.022(6)	0.0282(6)
		4	0.026(7)	0.0288(7)
		5	0.035(7)	0.0294(7)

Table S16. Observed *pseudo*-first order rate constants as a function of nucleophile concentration for the first (k_{obsd1}) and second (k_{obsd2}) steps of the substitution reactions between $[Au(dach)Cl_2]^+$ and Ino in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl.

λ/nm	T/K	10^3C_L/M	k_{obsd1}/s^{-1}	$10^{-3}\,k_{obsd2}/s^{-1}$
325	298.0	0.5	0.018(6)	0.121(6)
		1	0.025(5)	0.130(4)
		2	0.032(4)	0.171(4)
		3	0.041(6)	0.210(6)
		4	0.050(6)	0.238(5)
		5	0.066(7)	0.256(7)

Table S17. Rate constants as a function of temperature for the substitution reactions of mono-functional $[Au(dien)Cl]^{2+}$ and $[Au(terpy)Cl]^{2+}$ complexes in 25 mM Hepes buffer (pH = 7.2) and 10 mM NaCl.

	T/K	$k_1/M^{-1}s^{-1}$	$k_{-1}/M^{-1}s^{-1}$ [a]
$[Au(dien)Cl]^{2+}$			
L-His	288.1	1.02 ± 0.03	0.25 ± 0.02
	298.0	1.94 ± 0.05	0.32 ± 0.02
	310.0	3.30 ± 0.04	0.49 ± 0.04
5'-GMP	288.1	0.79 ± 0.01	0.225 ± 0.003
	298.0	1.24 ± 0.02	0.268 ± 0.006
	309,9	2.11 ± 0.02	0.381 ± 0.005
5'-IMP	288.0	0.151 ± 0.002	$(3.0 \pm 0.3) \times 10^{-2}$
	298.1	0.399 ± 0.003	$(8.0 \pm 0.7) \times 10^{-2}$
	310.0	0.954 ± 0.004	$(1.3 \pm 0.4) \times 10^{-1}$
Ino	288.0	0.104 ± 0.006	$(8.9 \pm 0.2)\ 10^{-3}$
	298.1	0.370 ± 0.009	$(1.3 \pm 0.3)\ 10^{-2}$
	310.0	0.874 ± 0.003	$(2.3 \pm 0.4)\ 10^{-2}$
$[Au(terpy)Cl]^{2+}$			
L-His	288.1	$(1.77 \pm 0.03) \times 10^3$	207 ± 10
	298.1	$(3.56 \pm 0.08) \times 10^3$	270 ± 20
	310.0	$(6.55 \pm 0.05) \times 10^3$	347 ± 20
5'-GMP	288.2	$(1.32 \pm 0.01) \times 10^3$	46 ± 6
	298.1	$(2.25 \pm 0.03) \times 10^3$	89 ± 9
	309,9	$(5.97 \pm 0.04) \times 10^3$	171 ± 8
5'-IMP	288.0	$(1.87 \pm 0.04) \times 10^3$	163 ± 3
	298.1	$(2.11 \pm 0.07) \times 10^3$	194 ± 2
	310.1	$(2.84 \pm 0.05) \times 10^3$	218 ± 2
Ino	288.0	$(9.35 \pm 0.02) \times 10^2$	8 ± 1
	298.1	$(1.30 \pm 0.04) \times 10^3$	28 ± 2
	310.0	$(2.33 \pm 0.03) \times 10^3$	46 ± 4

Table S18. Rate constants as a function of temperature for the substitution reactions of mono-functional $[Au(dach)Cl_2]^+$ and $[Au(bipy)Cl_2]^+$ complexes in 25 mM Hepes buffer (pH = 7.2) and 20 mM NaCl.

	T/K	$k_{2,f}/M^{-1}s^{-1}$	$k_{-2,f}/M^{-1}s^{-1}$	$k_{2,s}/M^{-1}s^{-1}$	$k_{-2,s}/s^{-1}$
$[Au(dach)Cl_2]^+$		*First step*		*Second step*	
L-His	288.2	55 ± 2	3.05 ± 0.01	3.0 ± 0.1	0.8 ± 0.2
	298.0	75 ± 2	4.00 ± 0.02	4.6 ± 0.2	1.1 ± 0.3
	310.0	89 ± 4	4.85 ± 0.04	6.4 ± 0.3	1.4 ± 0.3
5'-GMP	288.2	50 ± 2	7.4 ± 0.2	3.9 ± 0.2	0.50 ± 0.02
	298.0	66 ± 2	9.3 ± 0.2	6.2 ± 0.3	1.60 ± 0.05
	310.0	72 ± 4	14.4 ± 0.4	9.3 ± 0.3	2.20 ± 0.04
$[Au(bipy)Cl_2]^+$					
L-His	288.1	(1.12 ± 0.02) x 10^2	1.50 ± 0.03	11.6 ± 0.3	0.15 ± 0.03
	298.1	(2.04 ± 0.06) x 10^2	2.60 ± 0.05	16.7 ± 0.6	0.60 ± 0.05
	309.9	(2.72 ± 0.05) x 10^2	6.50 ± 0.04	21.7 ± 0.05	1.30 ± 0.04
5'-GMP	288.2	121 ± 3	0.50 ± 0.03	5.7 ± 0.3	1.4 ± 0.3
	298.0	149 ± 4	2.0 ± 0.5	10.3 ± 0.4	2.0 ± 0.5
	309,9	162 ± 3	4.2 ± 0.4	16.4 ± 0.4	2.3 ± 0.5

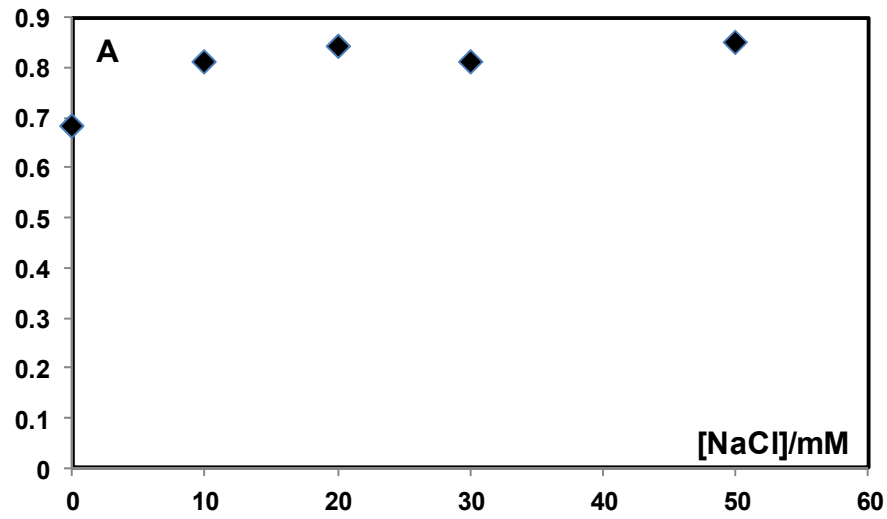

Figure S1. The influence of different chloride concentrations on the absorbance of a solution of $[Au(terpy)Cl]^{2+}$ in 25 mM Hepes buffer (pH = 7.2) at 300 nm.

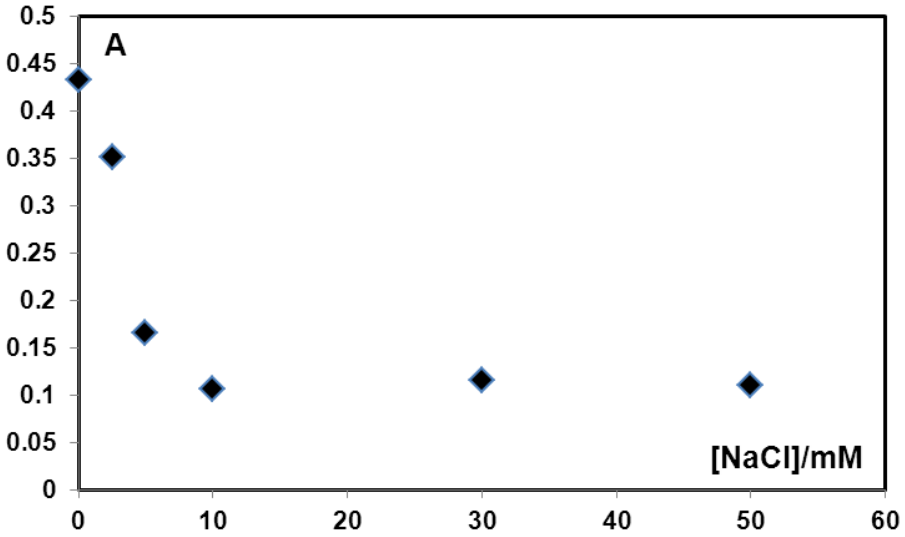

Figure S2. The influence of different chloride concentrations on the absorbance of a solution of $[Au(en)Cl_2]^+$ in 25 mM Hepes buffer (pH = 7.2) at 280 nm.

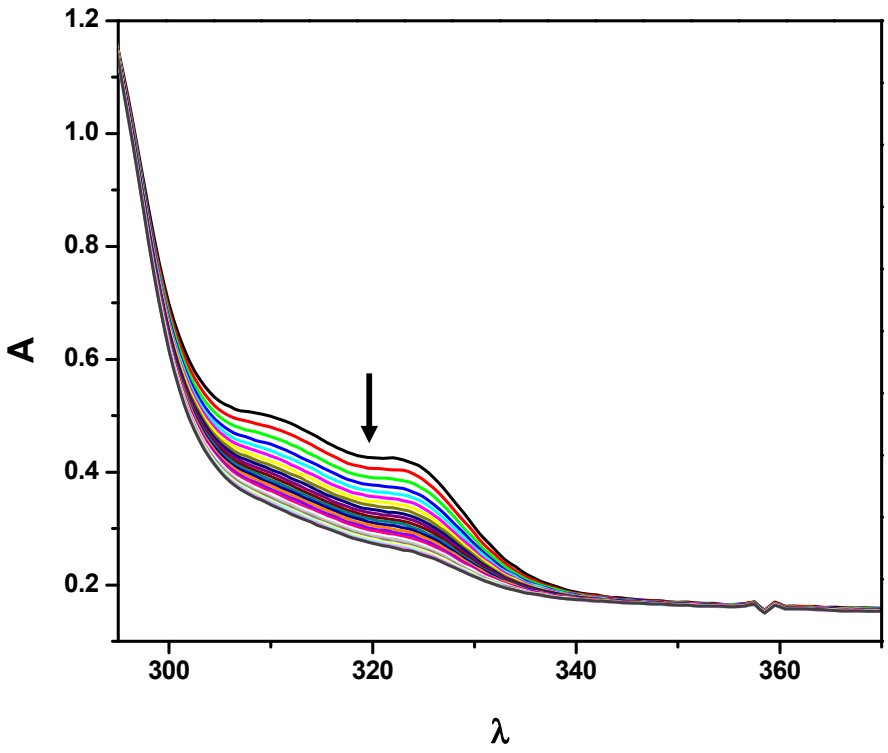

Figure S3. The UV-Vis spectra recorded for the reaction of $[Au(bipy)Cl_2]^+$ (1 x 10^{-4} M) complex with 5'-GMP (4 x 10^{-3} M) as a function of time (Δt = 1 s) at 298 K.

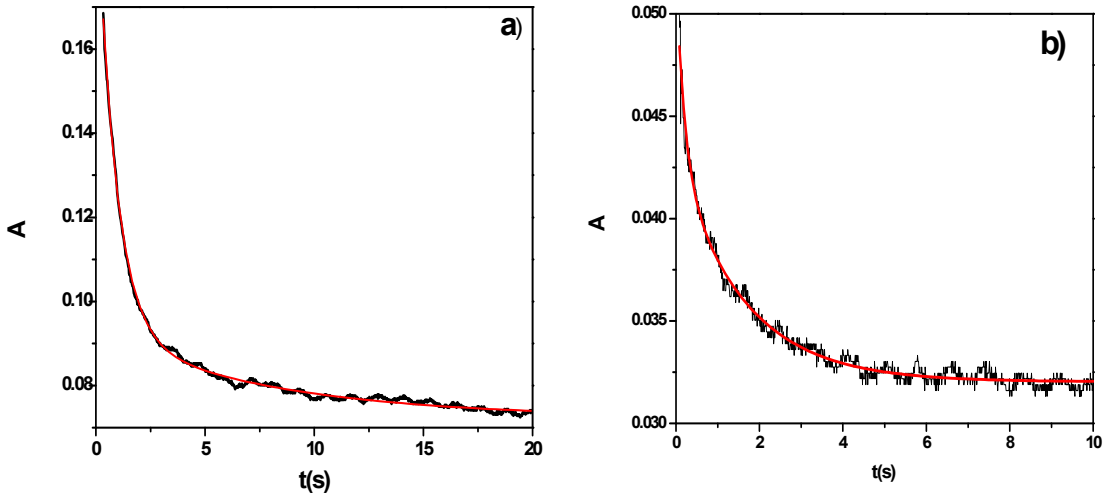

Figure S4. a) Kinetic trace for the reaction between $[Au(bipy)Cl_2]^+$ (1 x 10^{-4} M) and 5'-GMP (3 x 10^{-3} M), T = 298 K, λ = 320 nm; b) Kinetic trace for the reaction between $[Au(dach)Cl_2]^+$ (1 x 10^{-4} M) and 5'-GMP (3 x 10^{-3} M), T = 298 K, λ = 320 nm.

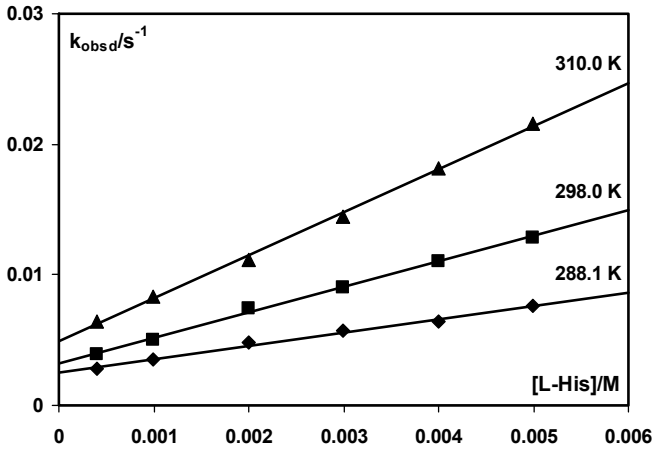

Figure S5. *Pseudo*-first order rate constants, k_{obsd}, as a function of nucleophile concentration and temperature for the substitution reaction between $[Au(dien)Cl]^{2+}$ and L-His in 25 mM Hepes buffer (pH = 7.2) and the presence of 10 mM NaCl.

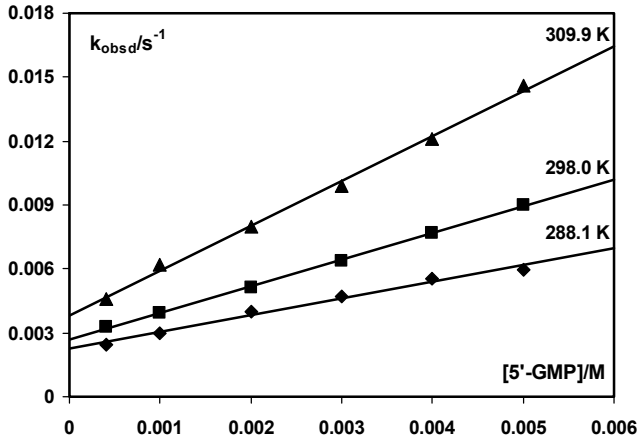

Figure S6. *Pseudo*-first order rate constants, k_{obsd}, as a function of nucleophile concentration and temperature for the substitution reactions between $[Au(dien)Cl]^{2+}$ and 5'-GMP in 25 mM Hepes buffer (pH = 7.2) and the presence of 10 mM NaCl.

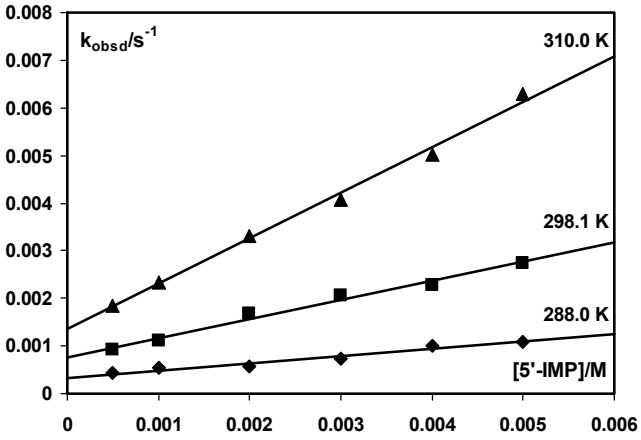

Figure S7. *Pseudo*-first order rate constants, k_{obsd}, as a function of nucleophile concentration and temperature for the substitution reaction between $[Au(dien)Cl]^{2+}$ and 5'-IMP in 25 mM Hepes buffer (pH = 7.2) and the presence of 10 mM NaCl.

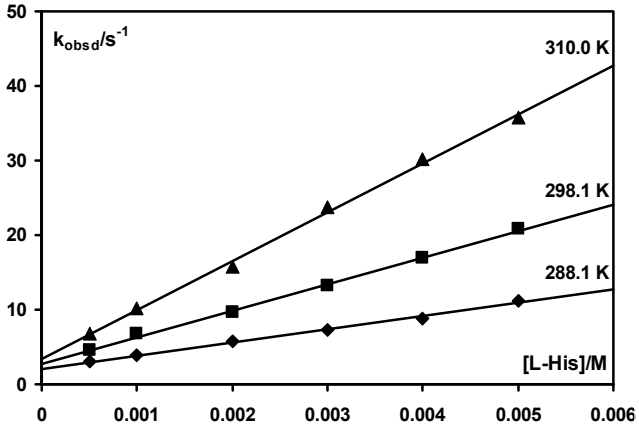

Figure S8. *Pseudo*-first order rate constants, k_{obsd}, as a function of nucleophile concentration and temperature for the substitution reaction between $[Au(terpy)Cl]^{2+}$ and L-His in 25 mM Hepes buffer (pH = 7.2) and the presence of 10 mM NaCl.

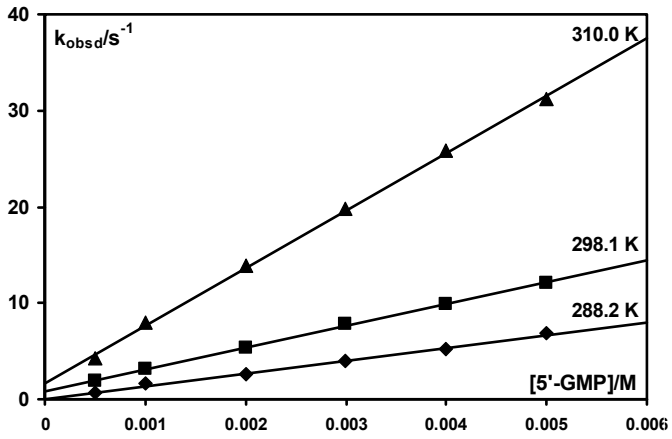

Figure S9. *Pseudo*-first order rate constants, k_{obsd}, as a function of nucleophile concentration and temperature for the substitution reaction between $[Au(terpy)Cl]^{2+}$ and 5'-GMP in 25 mM Hepes buffer (pH = 7.2) and the presence of 10 mM NaCl.

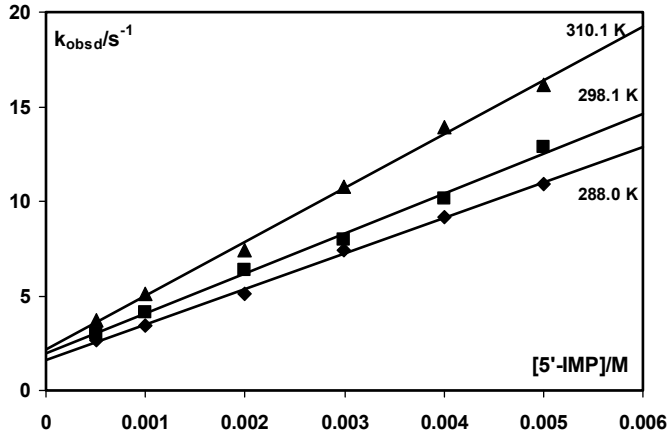

Figure S10. *Pseudo*-first order rate constants, k_{obsd}, as a function of nucleophile concentration and temperature for the substitution reaction between $[Au(terpy)Cl]^{2+}$ and 5'-IMP in 25 mM Hepes buffer (pH = 7.2) and the presence of 10 mM NaCl.

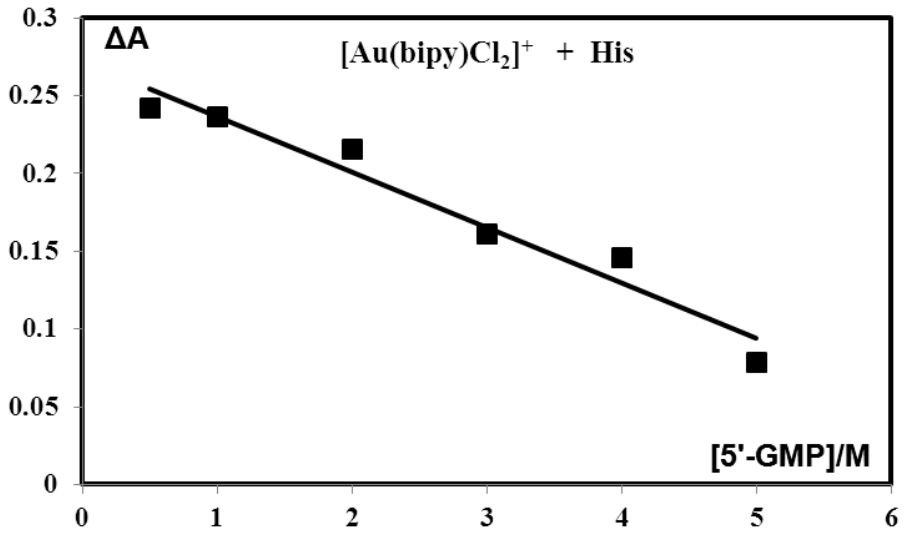

Figure S11. Change in absorbance at 295 nm, ΔAbs, as a function of ligand concentration for the reaction between $[Au(bipy)Cl_2]^+$ and L-Histidine in 25 mM Hepes buffer (pH = 7.2) with the addition of 20 mM NaCl.

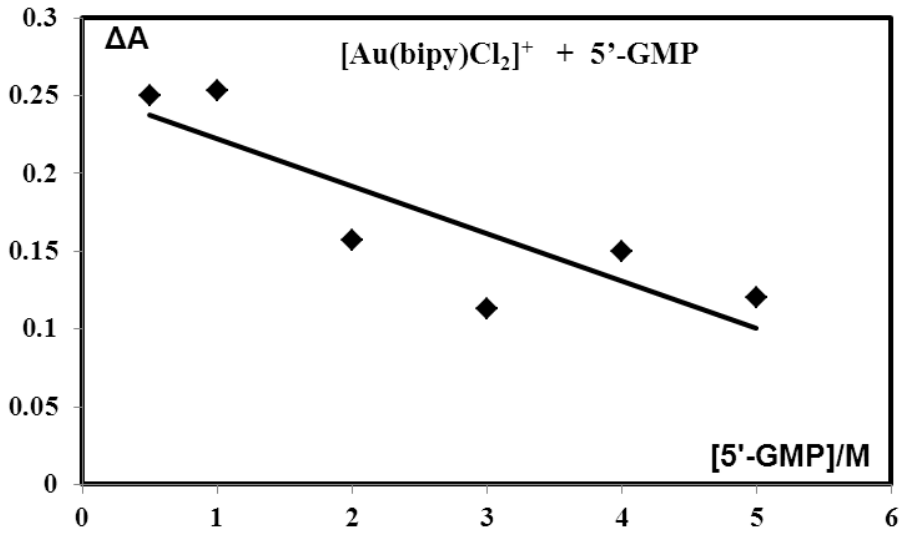

Figure S12. Change of absorbance at 320 nm, ΔAbs, as a function of ligand concentration for the reaction between $[Au(bipy)Cl_2]^+$ and 5'-GMP in 25 mM Hepes buffer (pH = 7.2) with the addition of 20 mM NaCl.

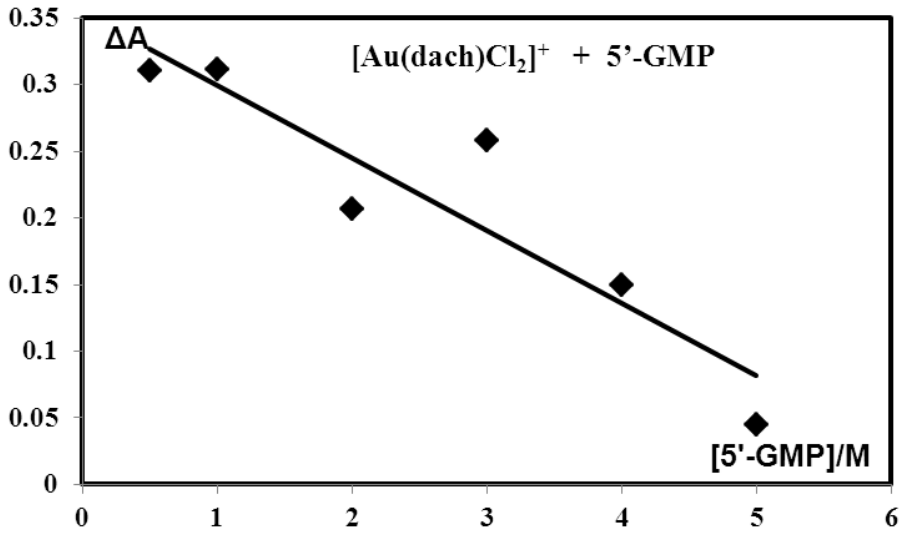

Figure S13. Change in absorbance at 320 nm, ΔAbs, as a function of ligand concentration for the reaction between $[Au(dach)Cl_2]^+$ and 5'-GMP in 25 mM Hepes buffer (pH = 7.2) with the addition of 20 mM NaCl.

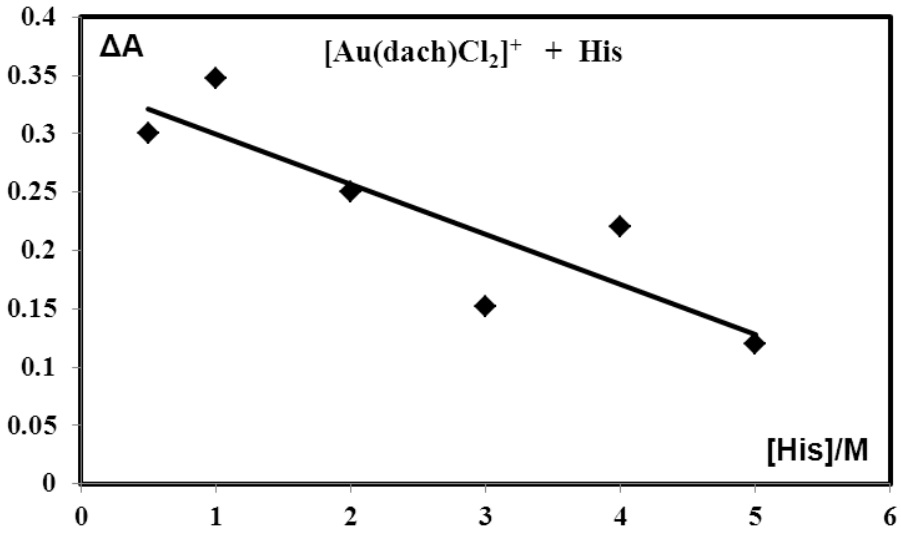

Figure S14. Change in absorbance at 290 nm, ΔAbs, as a function of ligand concentration for the reaction between $[Au(dach)Cl_2]^+$ and L-Histidine in 25 mM Hepes buffer (pH = 7.2) with the addition of 20 mM NaCl.

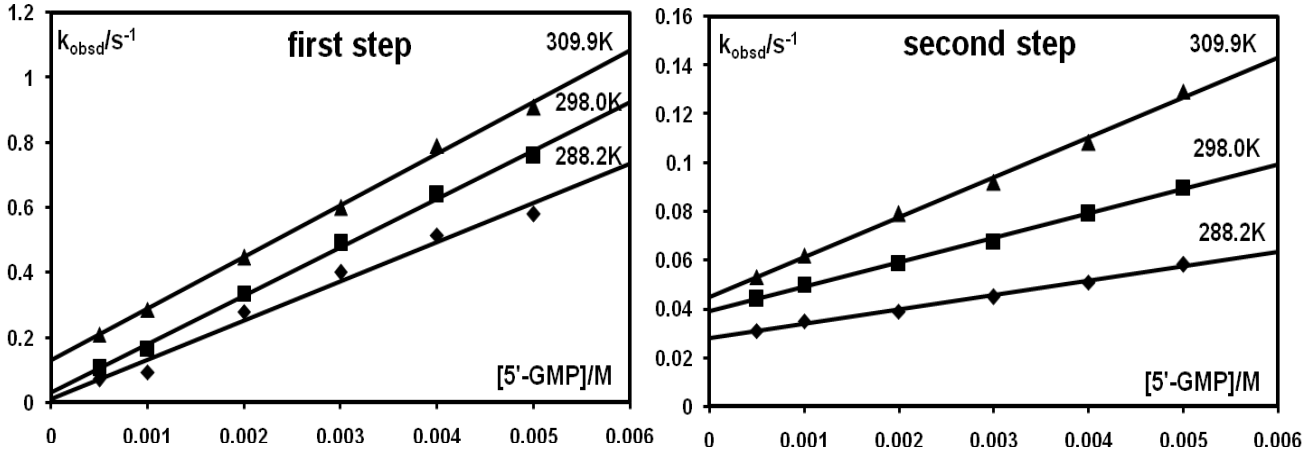

Figure S15. *Pseudo*-first order rate constants for the first (k_{obsd1}) and second (k_{obsd2}) steps of the substitution reactions between $[Au(bipy)Cl_2]^+$ and 5'-GMP as a function of nucleophile concentration and temperature in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl.

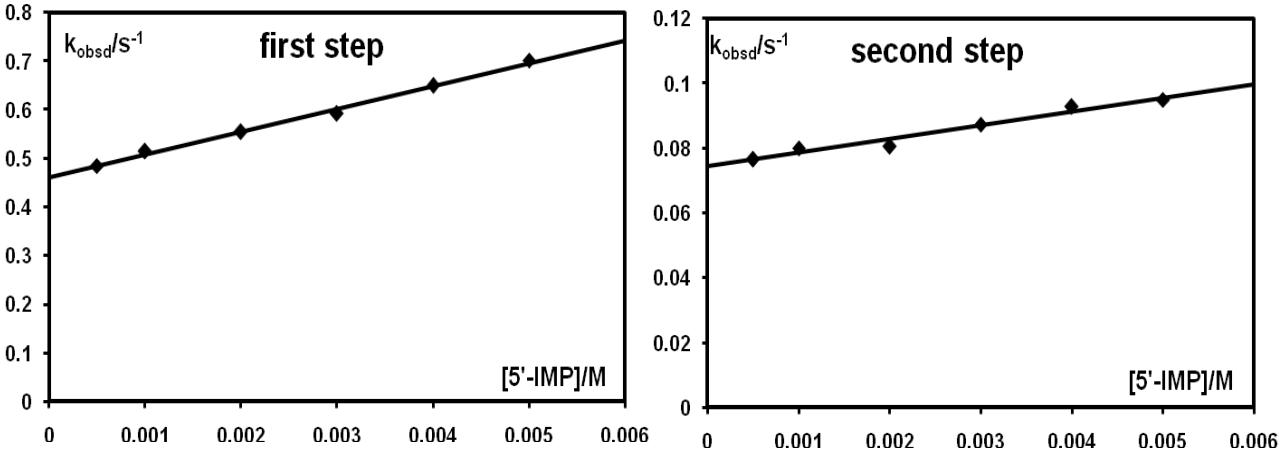

Figure S16. *Pseudo*-first order rate constants for the first (k_{obsd1}) and second (k_{obsd2}) steps of the substitution reactions between $[Au(bipy)Cl_2]^+$ and 5'-IMP as a function of nucleophile concentration at 298 K in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl.

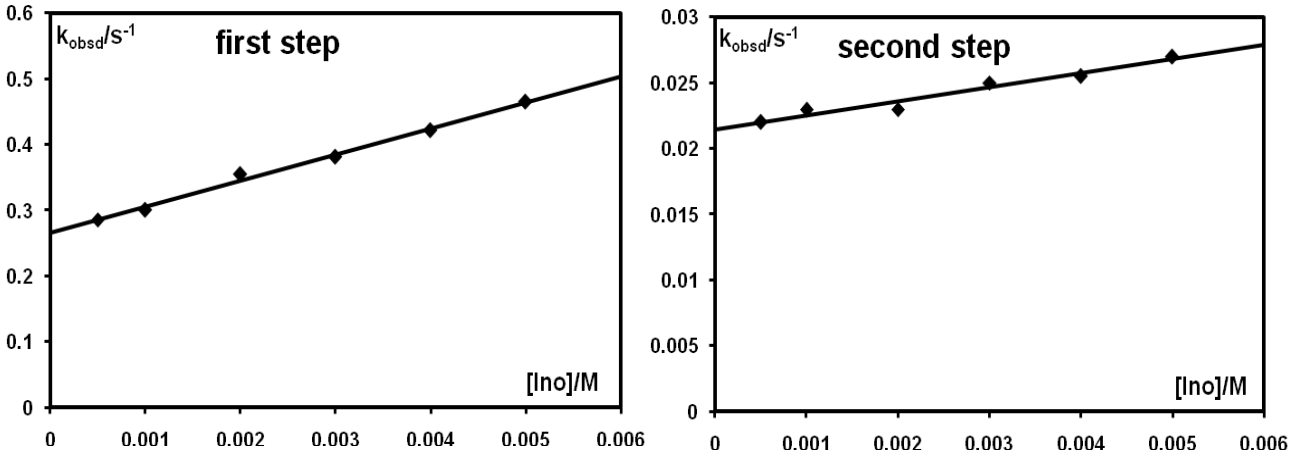

Figure S17. *Pseudo*-first order rate constants for the first (k_{obsd1}) and second (k_{obsd2}) steps of the substitution reactions between $[Au(bipy)Cl_2]^+$ and Ino as a function of nucleophile concentration at 298 K in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl.

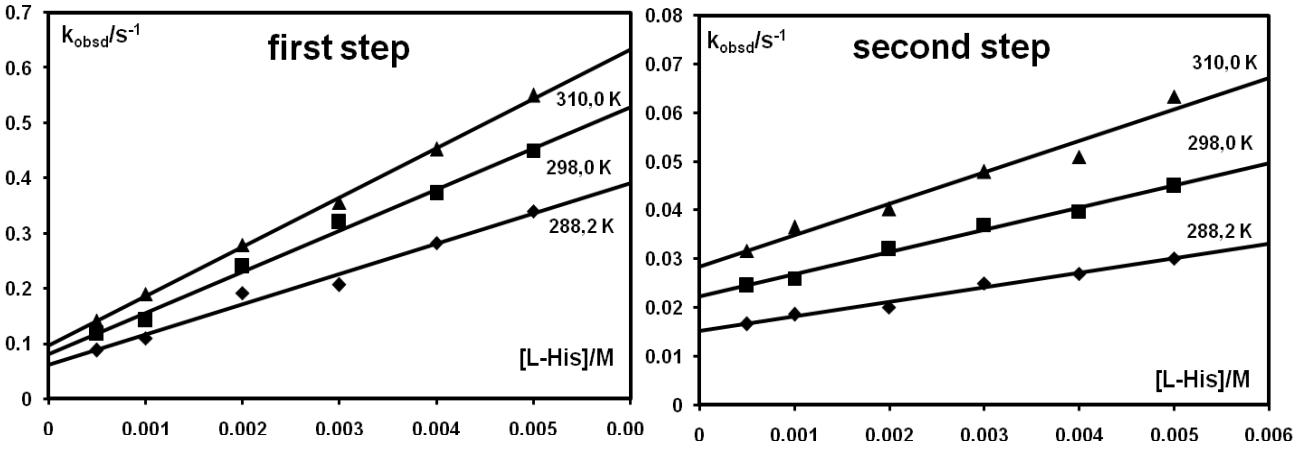

Figure S18. *Pseudo*-first order rate constants for the first (k_{obsd1}) and second (k_{obsd2}) steps of the substitution reactions between $[Au(dach)Cl_2]^+$ and 5'-GMP as a function of nucleophile concentration and temperature in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl.

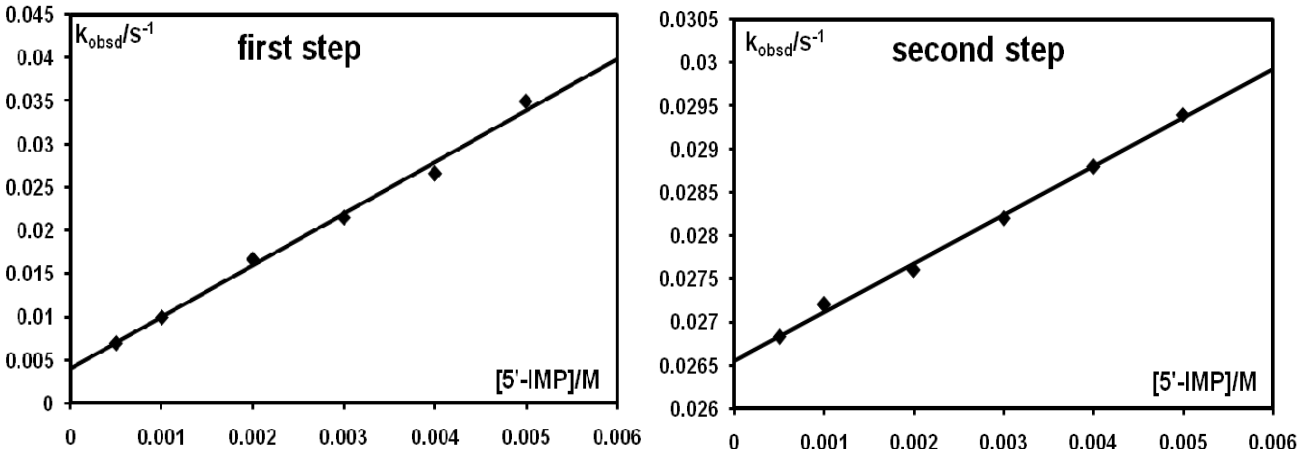

Figure S19. *Pseudo*-first order rate constants for the first (k_{obsd1}) and second (k_{obsd2}) steps of the substitution reactions between $[Au(dach)Cl_2]^+$ and 5'-IMP as a function of nucleophile concentration at 298 K in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl.

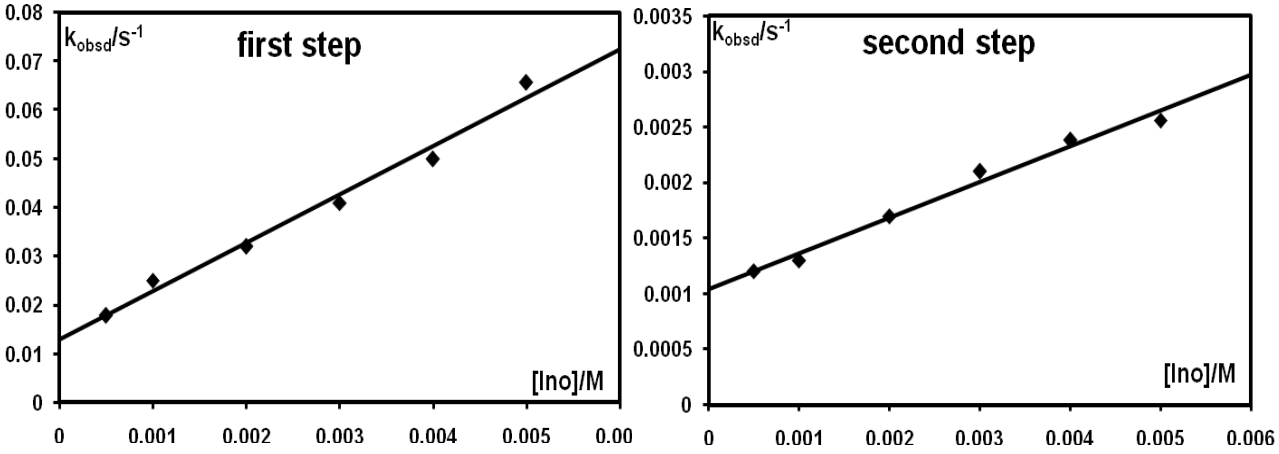

Figure S20. *Pseudo*-first order rate constants for the first (k_{obsd1}) and second (k_{obsd2}) steps of the substitution reactions between $[Au(dach)Cl_2]^+$ and Ino as a function of nucleophile concentration at 298 K in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl.

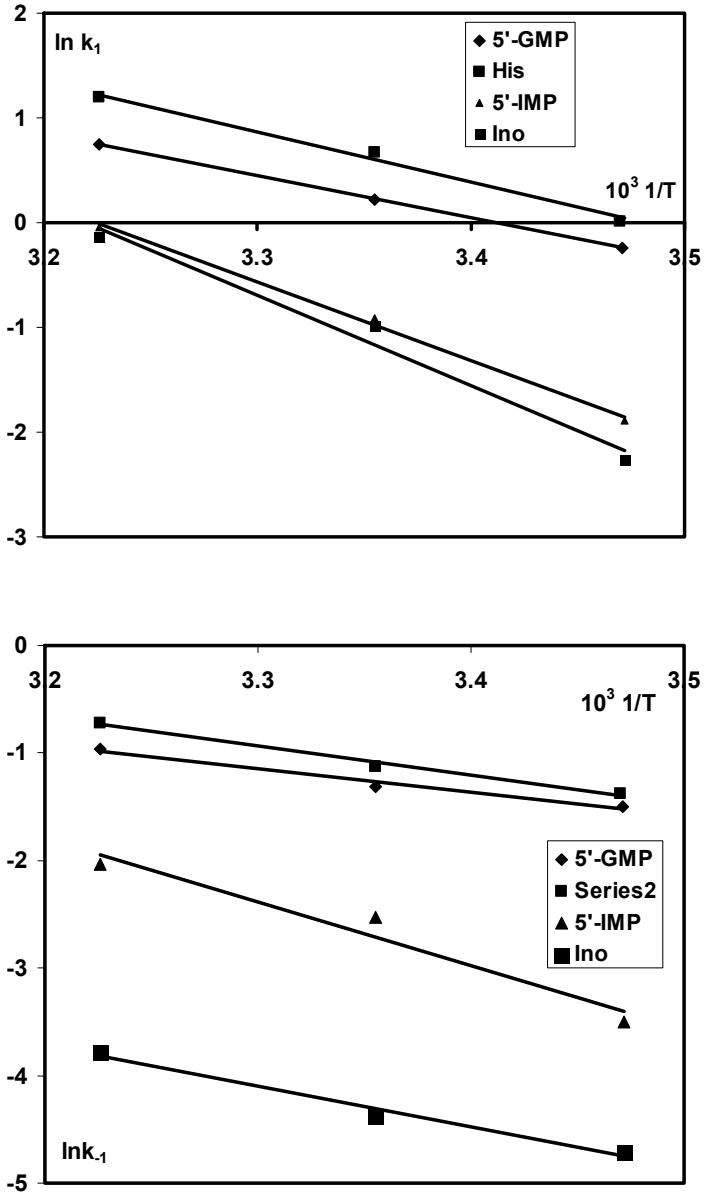

Figure S21. Arrhenius plots for the forward and reverse substitution reactions of $[Au(dien)Cl]^{2+}$ with selected nucleophiles in 25 mM Hepes buffer (pH = 7.2) and 10 mM NaCl.

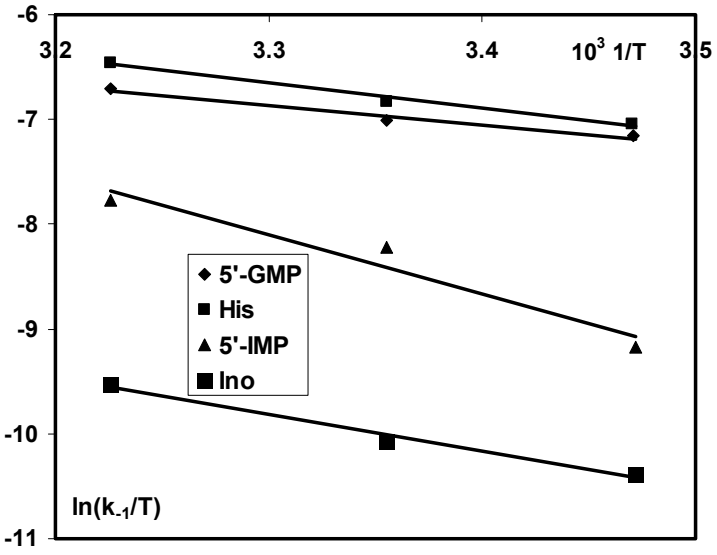

Figure S22. Eyring plots for the forward and reverse substitution reactions of the $[Au(dien)Cl]^{2+}$ complex with selected nucleophiles in 25 mM Hepes buffer (pH = 7.2) and 10 mM NaCl.

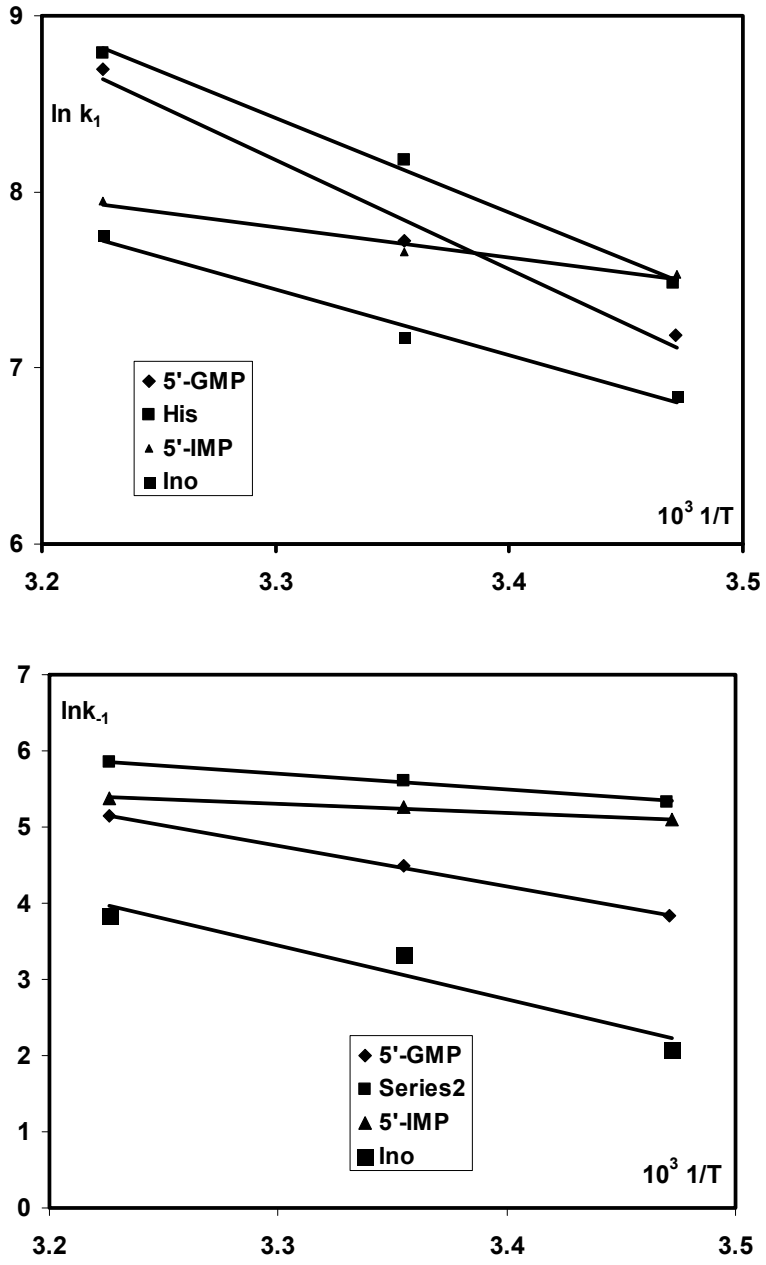

Figure S23. Arrhenius plots for the forward and reverse substitution reactions of the $[Au(terpy)Cl]^{2+}$ complex with selected nucleophiles in 25 mM Hepes buffer (pH = 7.2) and 10 mM NaCl.

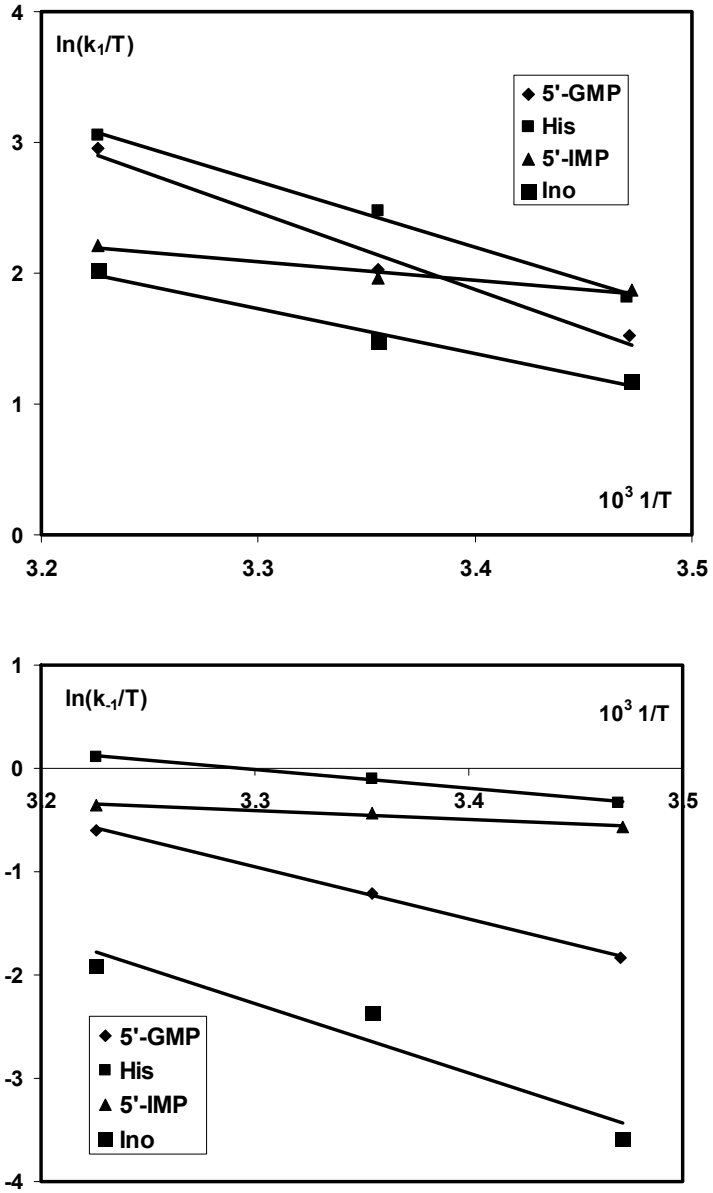

Figure S24. Eyring plots for the forward and reverse substitution reactions of $[Au(terpy)Cl]^{2+}$ complex with selected nucleophiles in 25 mM Hepes buffer (pH = 7.2) and 10 mM NaCl.

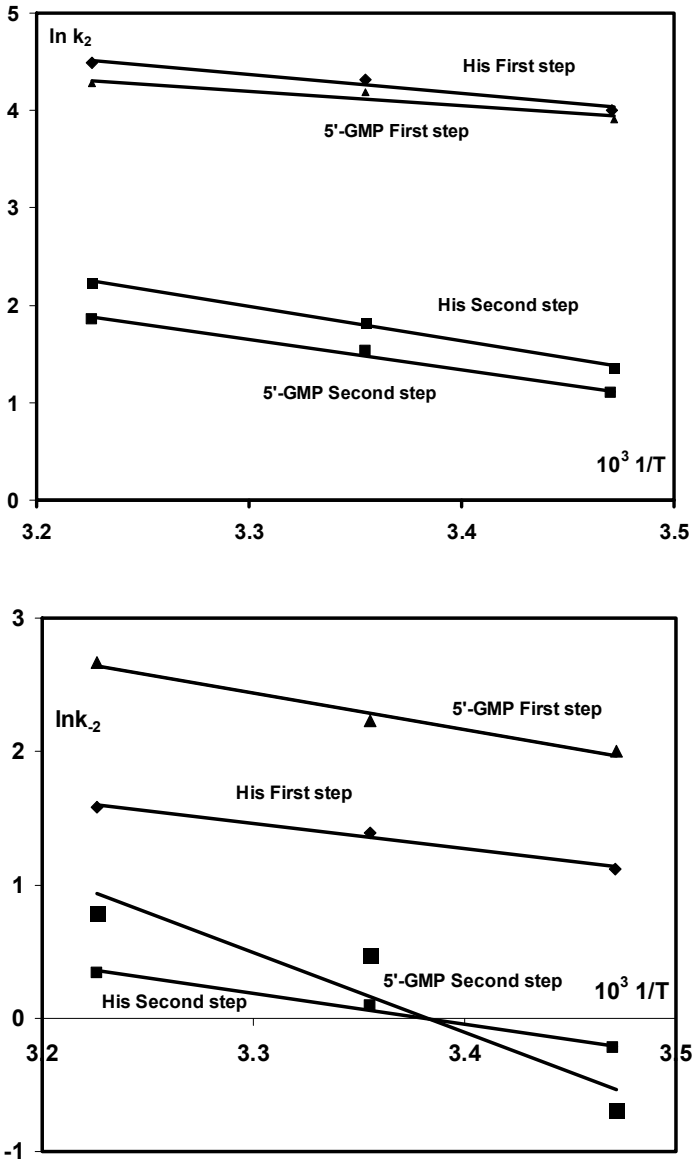

Figure S25. Arrhenius plots for the first and the second steps (both forward and reverse) of the substitution reactions of the $[Au(dach)Cl_2]^{2+}$ complex with His and 5'-GMP in 25 mM Hepes buffer (pH = 7.2) and 20 mM NaCl.

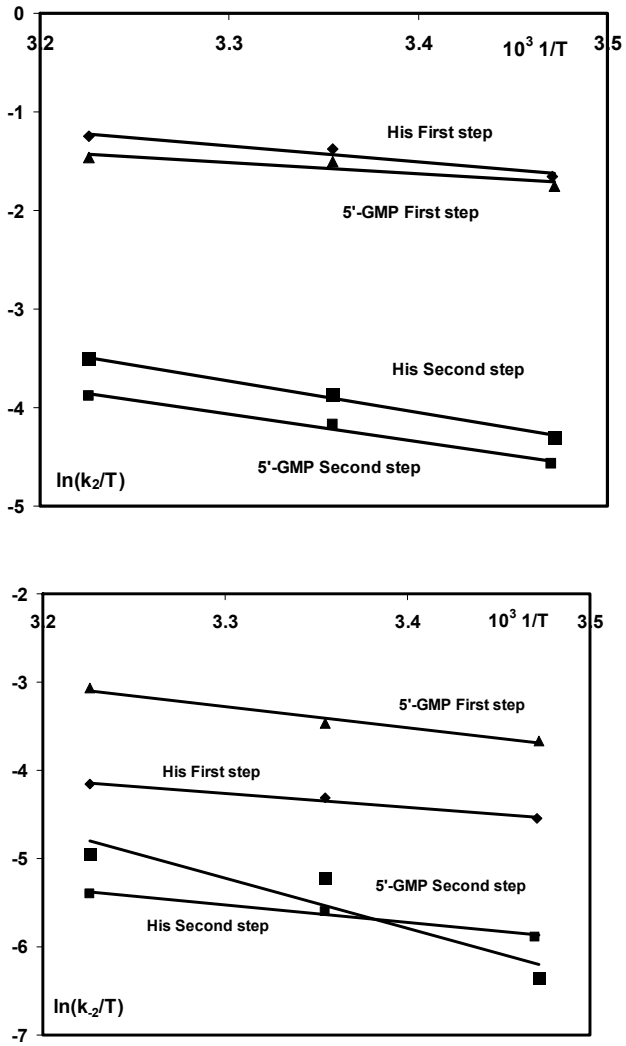

Figure S26. Eyring plots for the first and the second steps (both forward and reverse) of the substitution reactions of the $[Au(dach)Cl_2]^{2+}$ complex with His and 5'-GMP in 25 mM Hepes buffer (pH = 7.2) and 20 mM NaCl.

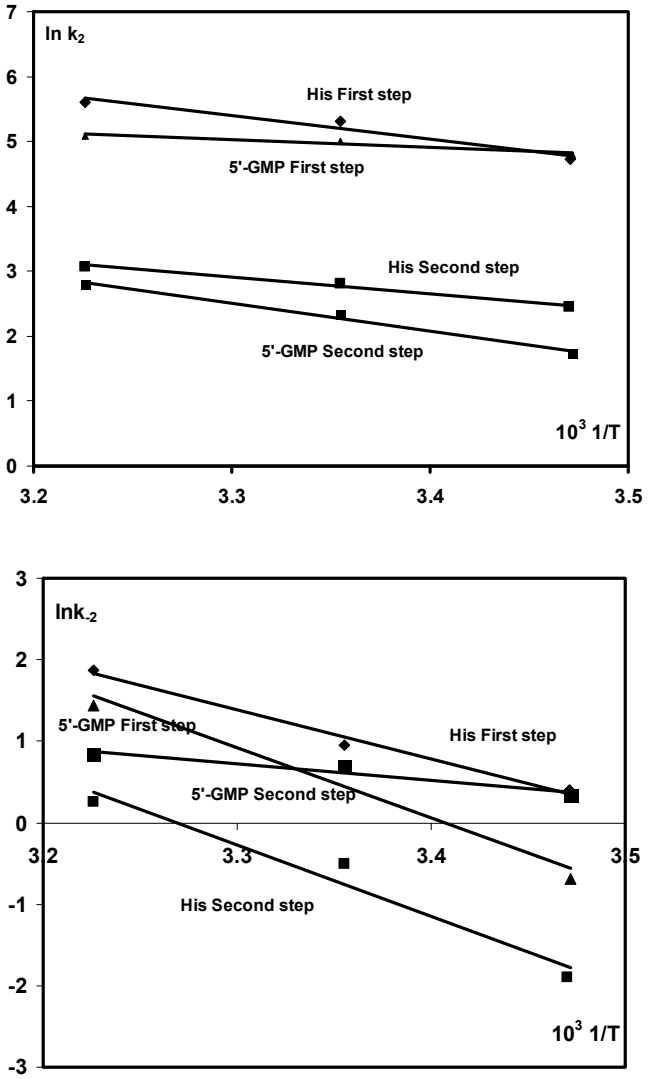

Figure S27. Arrhenius plots for the first and the second steps (both forward and reverse) for the substitution reactions of the $[Au(bipy)Cl_2]^{2+}$ complex with His and 5'-GMP in 25 mM Hepes buffer (pH = 7.2) and 20 mM NaCl.

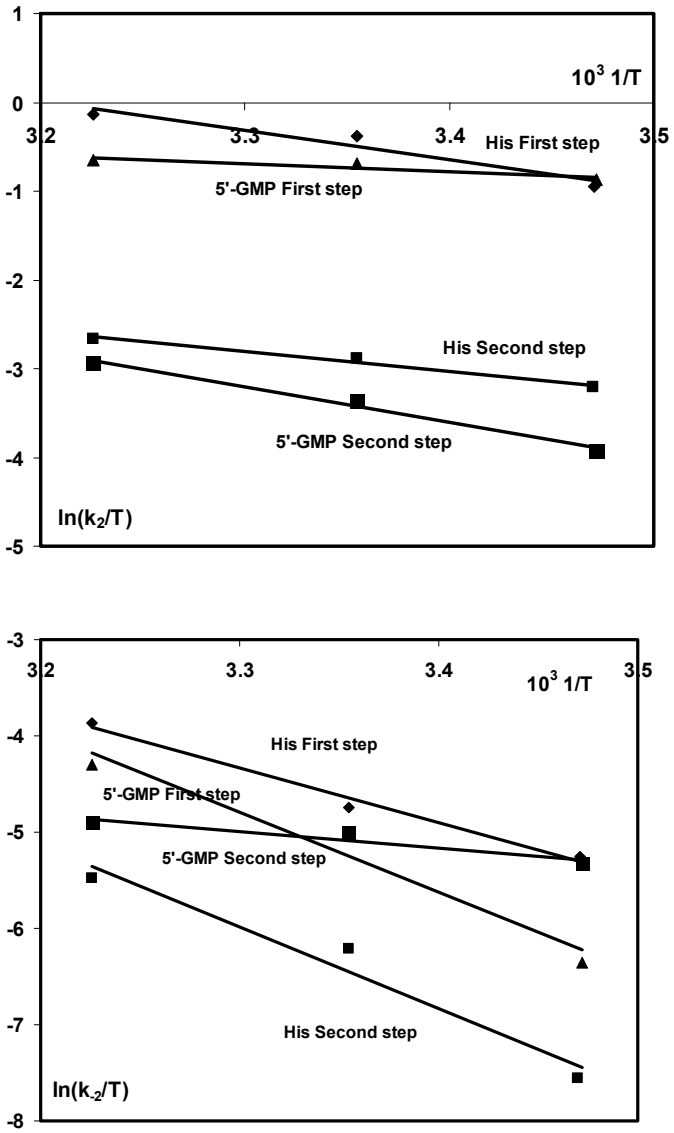

Figure S28. Eyring plots for the first and the second steps (both forward and reverse) of the substitution reactions of the $[Au(bipy)Cl_2]^{2+}$ complex with His and 5'-GMP in 25 mM Hepes buffer (pH = 7.2) and 20 mM NaCl.