Electronic Supplementary Information (ESI)

Studies on the reactions of $[AuCl_4]^-$ with different nucleophiles in aqueous solution

Mirjana D. Đurović[a], Ralph Puchta[b], Živadin D. Bugarčić[a,*] and Rudi van Eldik[b,*]

[a]*Department of Chemistry, Faculty of Science, University of Kragujevac, R. Domanovića 12, P O Box 60, 34000 Kragujevac, Serbia*

[b]*Inorganic Chemistry, Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Egerlandstr. 1, 91058 Erlangen, Germany*

Table S1. Observed pseudo-first-order rate constants as a function of nucleophile concentration and temperature for the reaction between $[AuCl_4]^-$ and thiourea in 0.4 M NaCl aqueous solution

T(K)	10^3 C_{tu}/M	10^{-2} k_{obsd}/s^{-1}
287.9	2	0.36(5)[a]
	4	0.64(5)
	6	0.88(5)
	8	1.15(5)
	10	1.36(5)
298.3	2	0.54(5)
	4	1.11(5)
	6	1.60(5)
	8	2.04(5)
	10	2.50(5)
310.0	2	0.81(5)
	4	1.58(5)
	6	2.58(5)
	8	3.30(5)
	10	3.77(5)

[a] Number of runs in parentheses

Table S2. Observed pseudo-first-order rate constants as a function of nucleophile concentration and temperature for the reaction between $[AuCl_4]^-$ and iodide in 0.4 M NaCl aqueous solution

T(K)	10^3 C_{I^-}/M	10^{-2} k_{obsd}/s^{-1}
287.9	2	2.55(5)
	4	2.87(5)
	6	3.25(5)
	8	3.61(5)
	10	4.04(5)
298.2	2	2.69(5)
	4	3.31(5)
	6	3.80(5)
	8	4.18(5)
	10	4.68(5)
310.1	2	2.85(5)
	4	3.73(5)
	6	4.34(5)
	8	4.81(5)
	10	-

Table S3. Observed pseudo-first-order rate constants as a function of nucleophile concentration and temperature for the reaction between $[AuCl_4]^-$ and pyridine in 0.4 M NaCl aqueous solution

T(K)	10^3 C_{py}/M	k_{obsd}/s^{-1}
288.0	2	0.15(5)
	4	0.25(5)
	6	0.34(5)
	8	0.45(5)
	10	0.50(5)
298.3	2	0.30(5)
	4	0.51(5)
	6	0.71(5)
	8	0.91(5)
	10	1.06(5)
310.2	2	0.59(5)
	4	0.95(5)
	6	1.36(5)
	8	1.72(5)
	10	1.98(5)

Table S4. Observed pseudo-first-order rate constants as a function of nucleophile concentration and temperature for the reaction between $[AuCl_4]^-$ and bromide in 0.4 M NaCl aqueous solution

T(K)	10^3 C_{Br^-}/M	10^1 k_{obsd}/s^{-1}
288.2	2	0.64(5)
	4	0.87(5)
	6	1.30(5)
	8	1.48(5)
	10	1.88(5)
298.2	2	1.58(5)
	4	2.07(5)
	6	2.75(5)
	8	3.52(5)
	10	3.94(5)
310.2	2	3.09(5)
	4	4.48(5)
	6	5.69(5)
	8	6.62(5)
	10	7.41(5)

Table S5. Observed pseudo-first-order rate constants as a function of nucleophile concentration and temperature for the reaction between $[AuCl_4]^-$ and nitrite in 0.4 M NaCl aqueous solution

T(K)	$10^3\ C_{NO2^-}/M$	$10^2\ k_{obsd}/s^{-1}$
288.6	2	2.3(5)
	4	2.4(5)
	6	2.68(5)
	8	2.85(5)
	10	3.36(5)
298.6	2	8.75(5)
	4	9.58(5)
	6	10.06(5)
	8	10.50(5)
	10	11.24(5)
310.0	2	13.88(5)
	4	14.58(5)
	6	15.27(5)
	8	16.45(5)
	10	17.19(5)

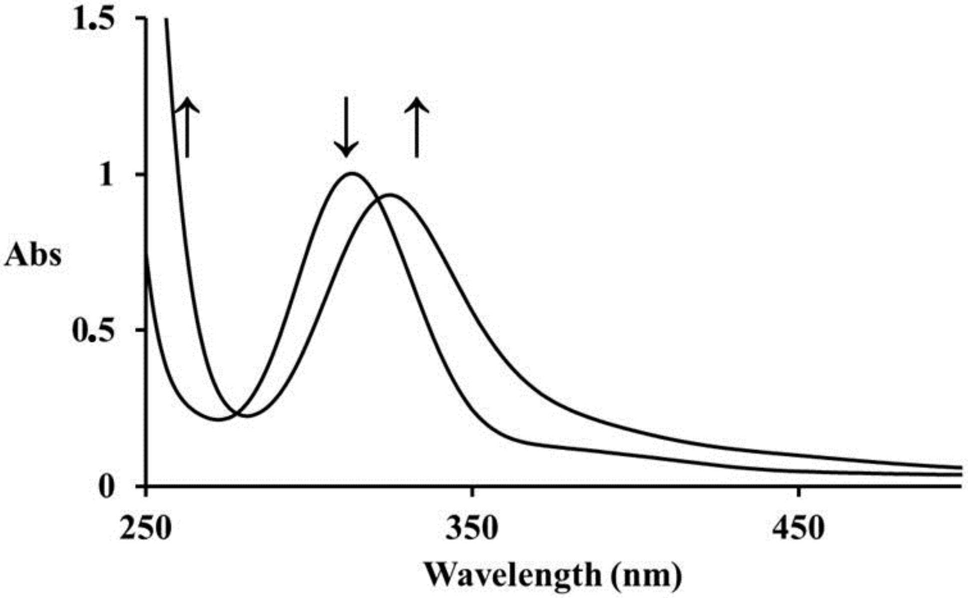

Figure S1. Spectral changes observed during the reaction of 2 x 10^{-4} M $[AuCl_4]^-$ with 4x10^{-3} M Br^-, in 0.4 M NaCl aqueous solution; the arrows show the reaction progress before and after mixing (without changes after 2 h).

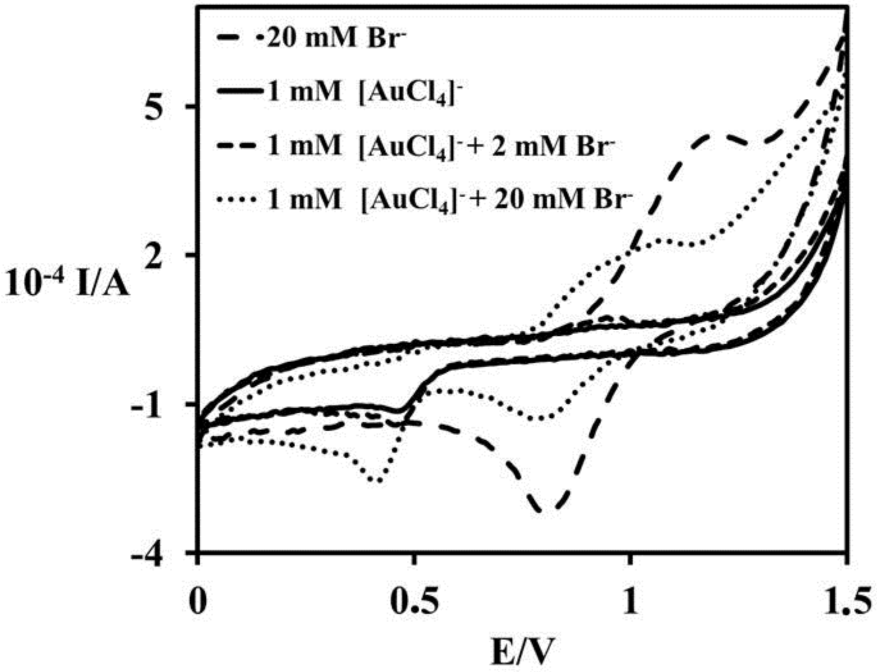

Figure S2. Cyclic voltammograms recorded during the first minute of the reaction between 1 mM $[AuCl_4]^-$ and different concentrations of Br^-, in 0.4 M NaCl aqueous solution; GCE; $E = 0.1$ V s^{-1}.

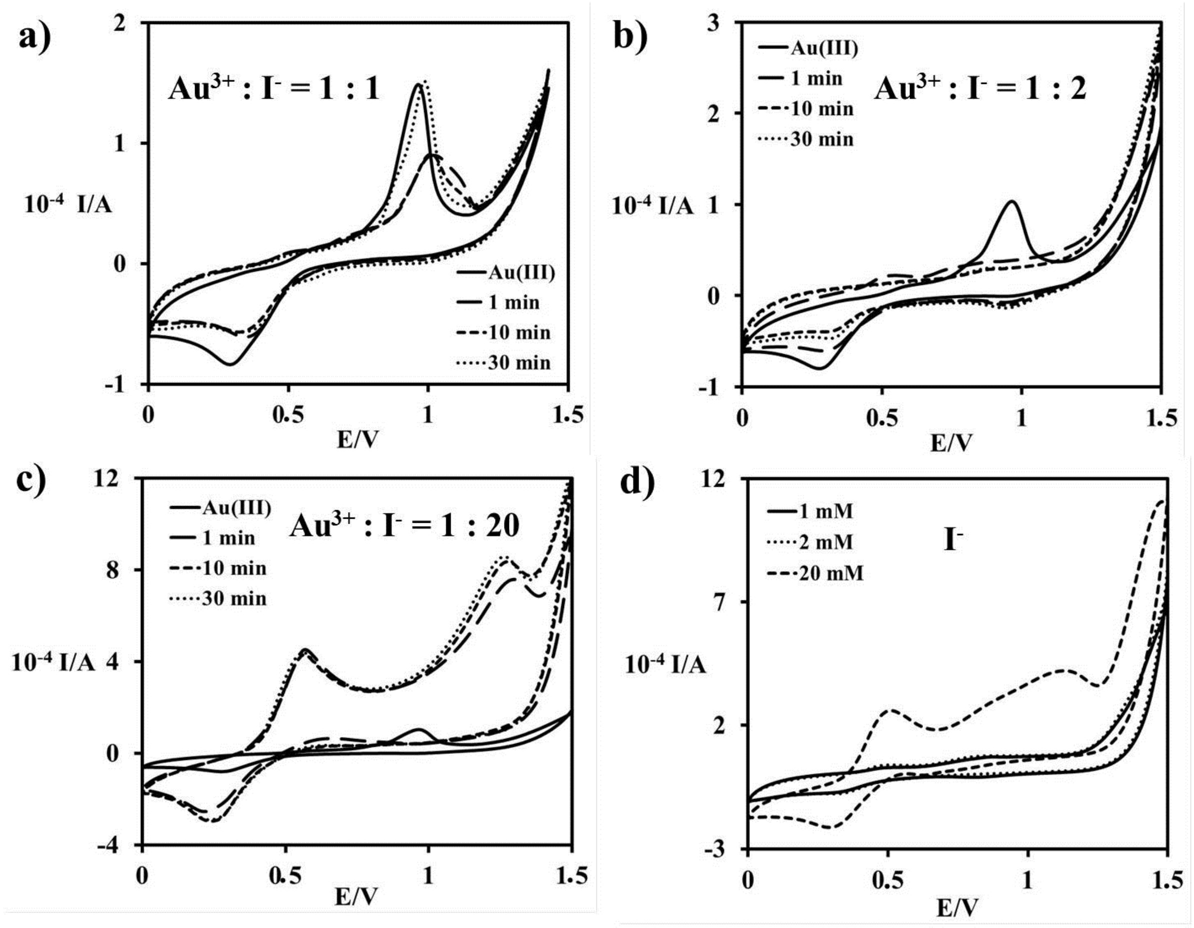

Figure S3. Cyclic voltammograms recorded for different $[AuCl_4]^-$:I^- molar ratios (a), b), c)) compared to free I^- (d), in 0.4 M NaCl aqueous solution; GCE; E = 0.1 V s^{-1}.

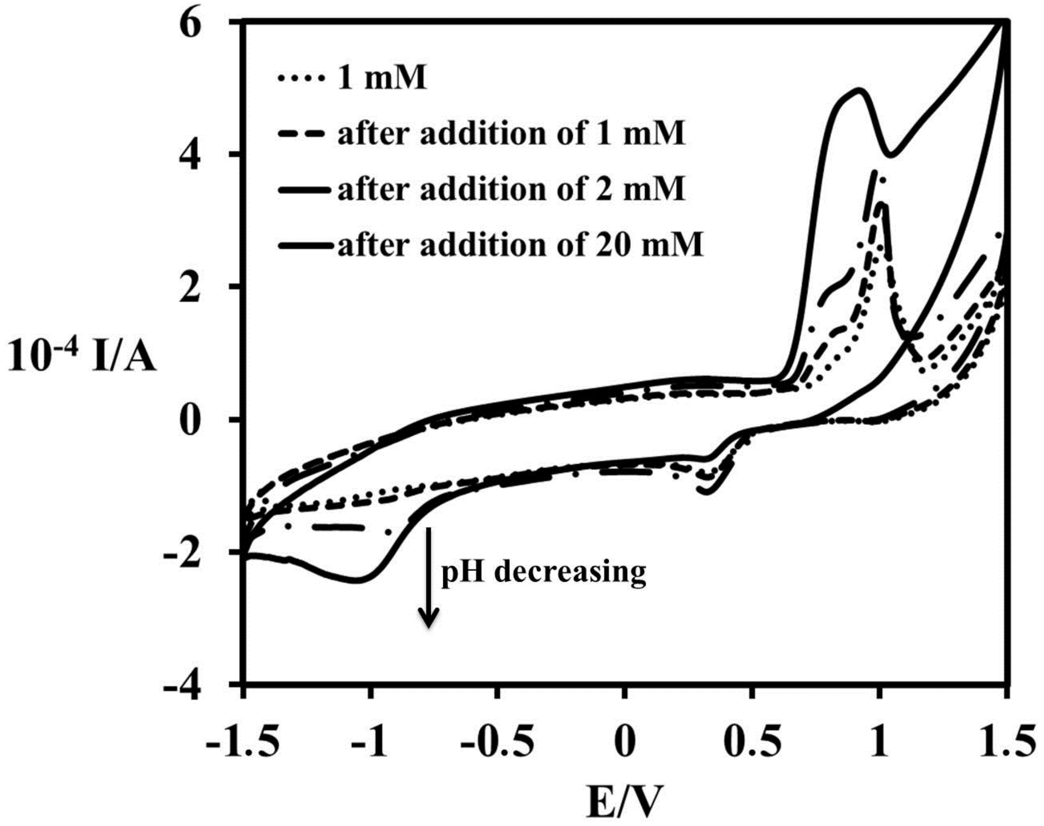

Figure S4. Cyclic voltamograms recorded for 1 mM $[AuCl_4]^-$ and 1 min after addition of different concentrations of NO_2^- in 0.4 M NaCl, GCE, E = 0.1 V s^{-1}. Evidence for H_3O^+ formation as a side product of the redox reaction.

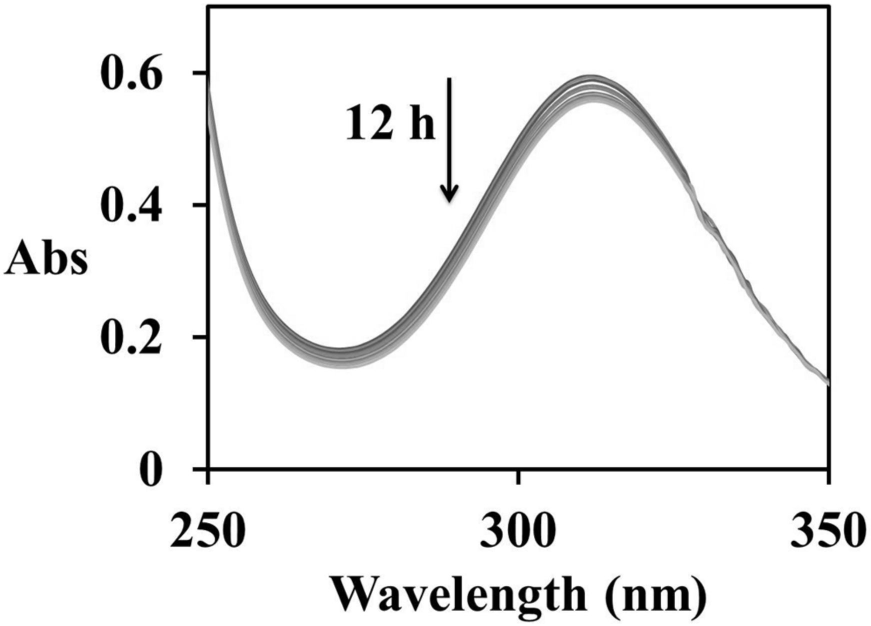

Figure S5. UV-Vis spectral changes observed for the reaction of $[AuCl(OH)_3]^-$ and DMSO (1:1), in 0.4 M NaCl, at room temperature; indication of gold(III) time-dependent instability. No evidence for substitution reaction, nor for Au^0 formation.

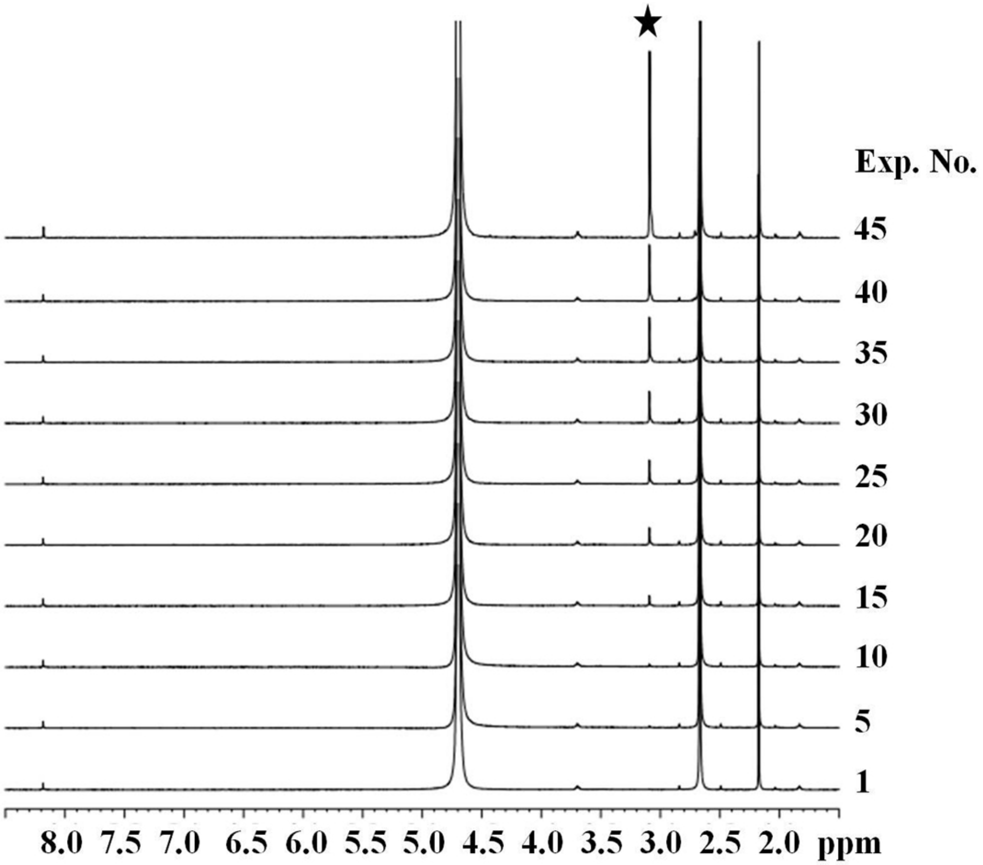

Figure S6. Expanded ^{1}H NMR spectra recorded for the reaction of $[AuCl_4]^-$ and DMSO in a 10:1 molar ratio in D_2O; recorded during 30 h; T = 298.2 K; * is dimethylsulfone.

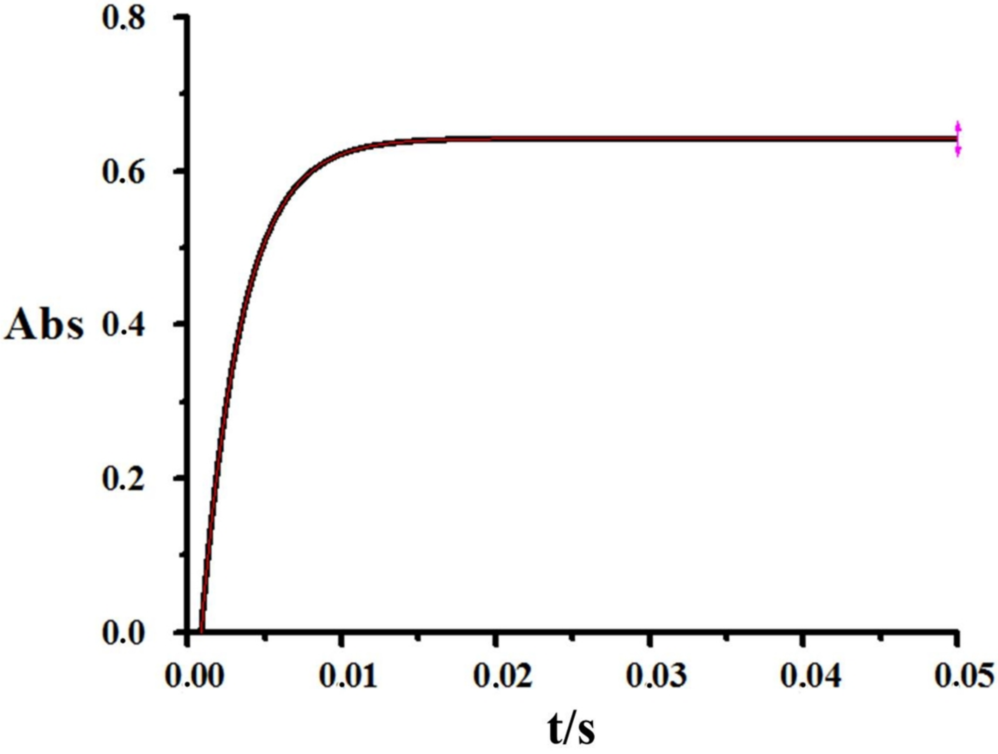

Figure S7. Kinetic trace fitted to a double exponential function for the reaction of 1 x 10^{-4} M $[AuCl_4]^-$ and 2 x 10^{-3} M I^-; T = 298 K; λ = 380 nm.

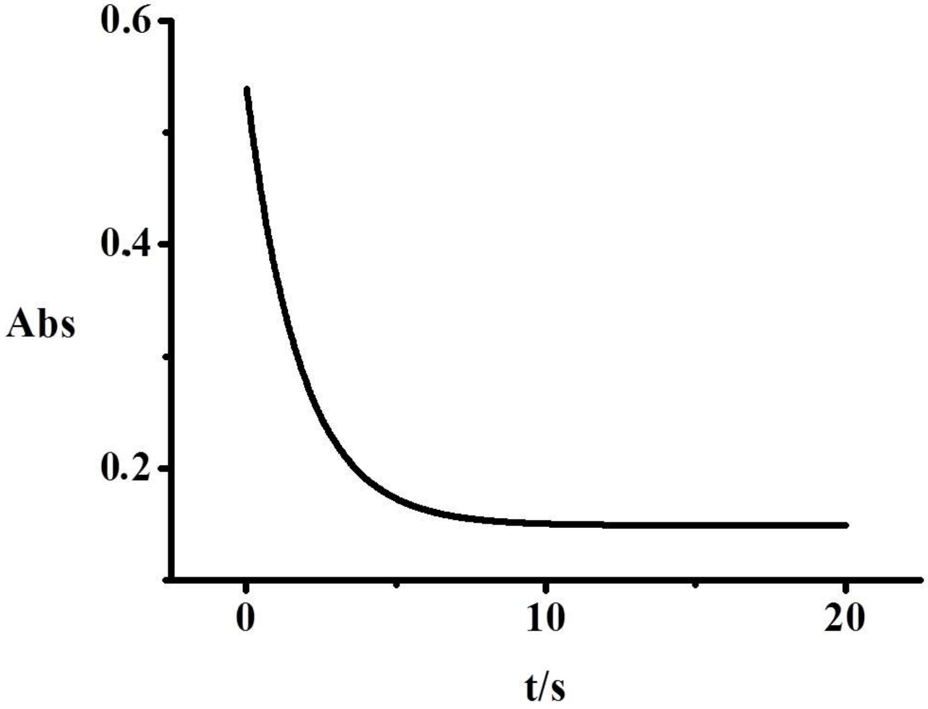

Figure S8. Typical kinetic trace for the reaction of 1 × 10^{-4} M $[AuCl_4]^-$ with the sixty-fold excess of py, T = 298.3 K, λ = 310 nm.