Electronic Supplementary Information for:

Kinetics and mechanism of the reaction of cyanocobalamin with potassium hydroxide in non-aqueous media

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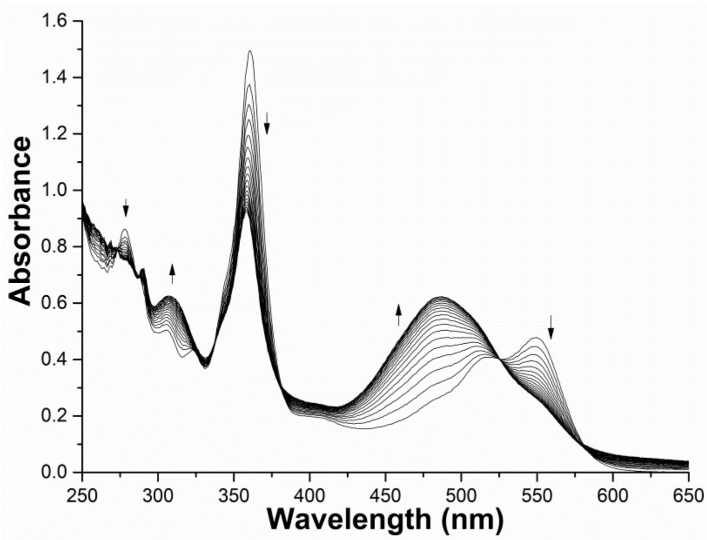

Figure S1. UV-Vis spectral changes recorded during reaction between CNCbl and KOH in ^{i}PrOH (*first step*): [CNCbl] = 6 x 10^{-5} M; [KOH] = 1 мM; 15 ^{0}C; anaerobic conditions.

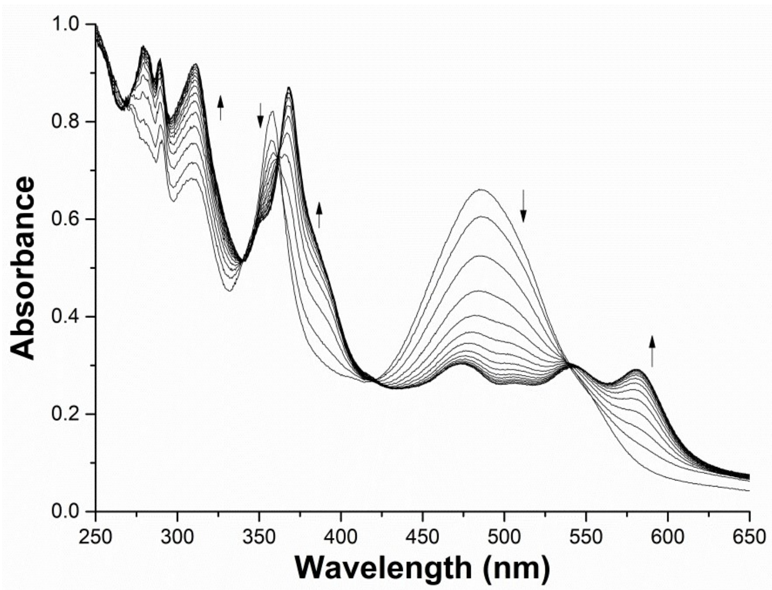

Figure S2. UV-Vis spectral changes recorded during reaction between CNCbl and KOH in ^{i}PrOH (*second step*): [CNCbl] = 6 x 10^{-5} M; [KOH] = 1 мM; 15 ^{0}C; anaerobic conditions.

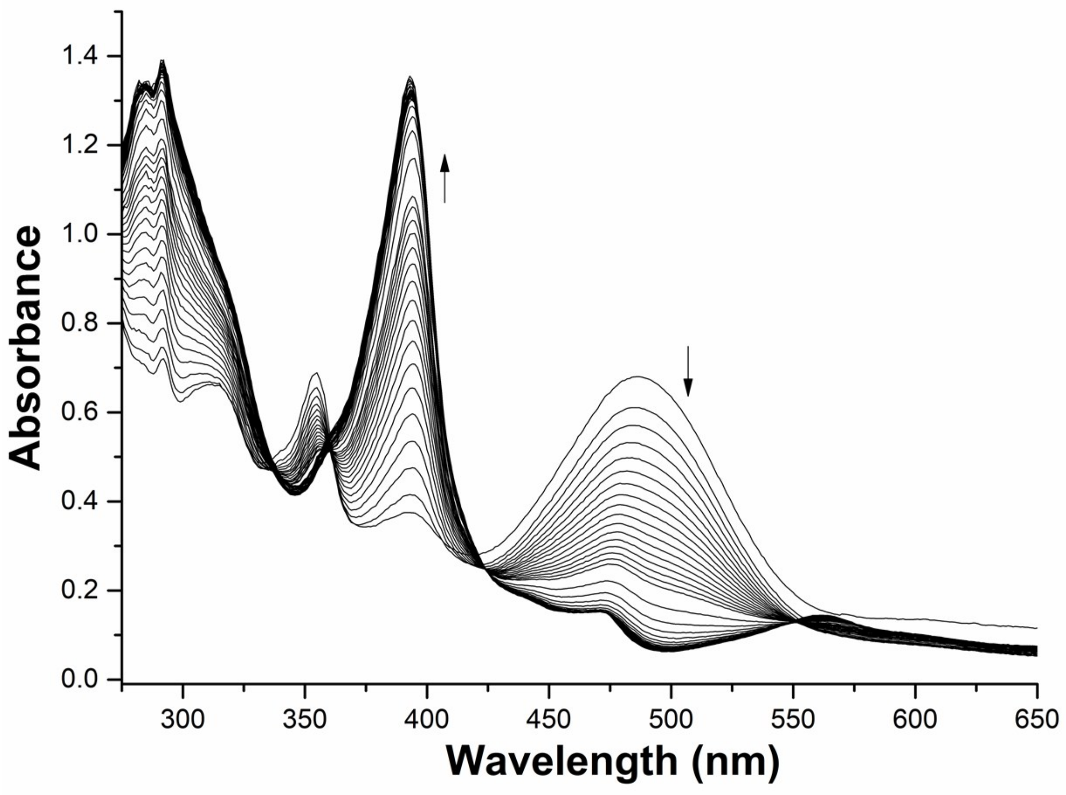

Figure S3. UV-Vis spectral changes recorded during reaction between CNCbl and KOH in DMSO (*second step*): [CNCbl] = 6 x 10^{-5} M; [KOH] = 1 мM; 15 ^{0}C; anaerobic conditions.

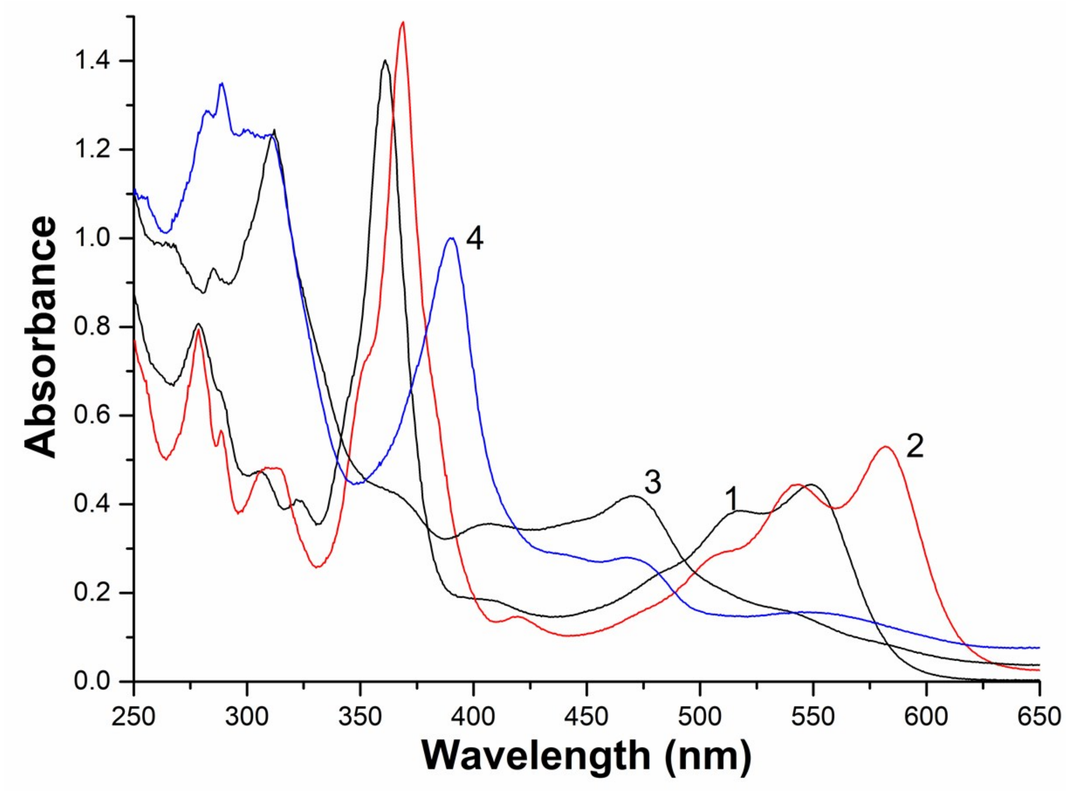

Figure S4. UV-vis spectra of different cobalamins in ^{i}PrOH: 1 - cyanocobalamin, 2 – dicyanocobalamin, 3 – reduced cobalamin Co^{2+}, 4 – super reduced cobalamin Co^{1+}: [Cbl] = 6.0 × 10^{-5} M, 25 ^{0}C.

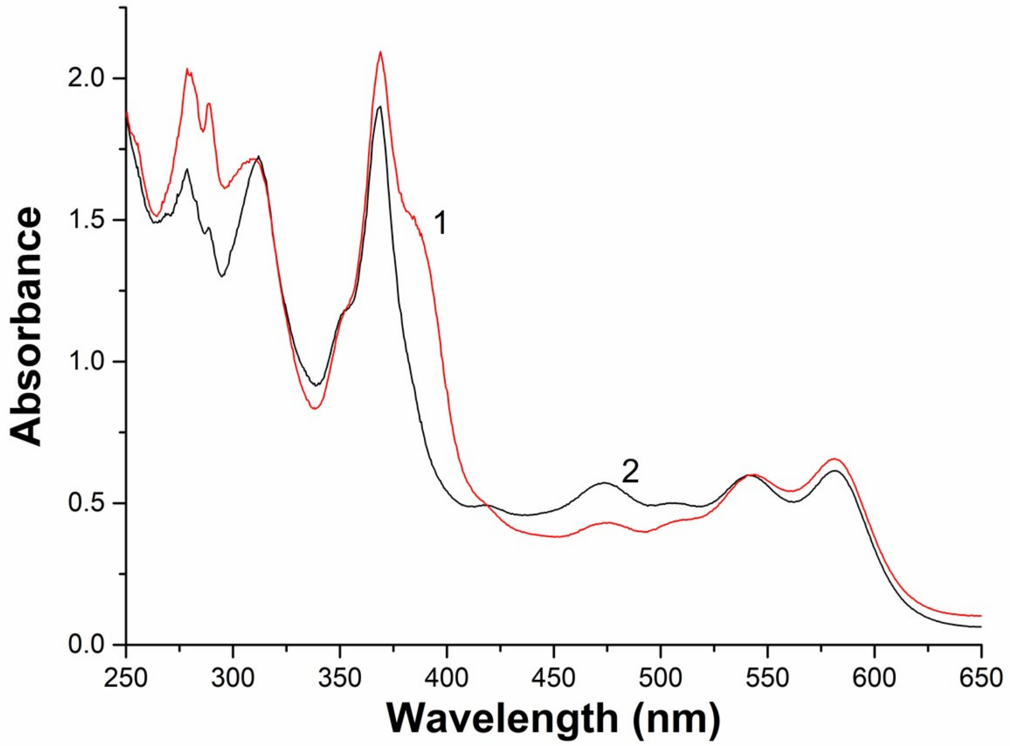

Figure S5. UV-vis spectra of mixtures: 1 – dicyanocobalamin and super reduced cobalamin Co^{1+} 1:1 ratio, 2 - dicyanocobalamin and reduced cobalamin Co^{2+} 1:1 ratio: [Cbl] = 6.0 × 10^{-5} M

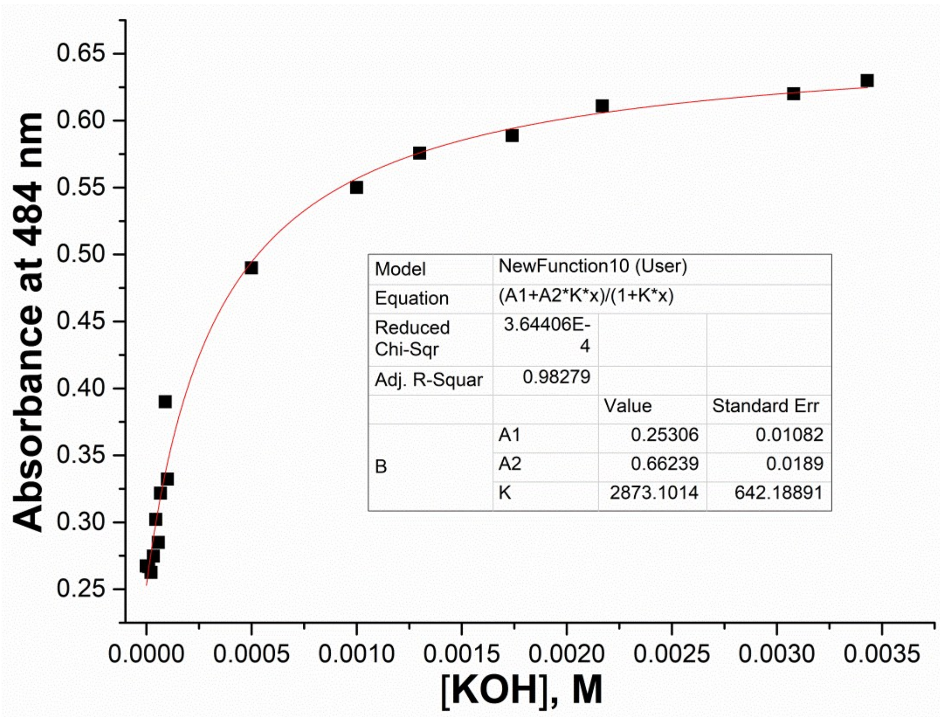

Figure S6. Dependence of the absorbance of the intermediate formed during the reaction of cyanocobalamin with potassium hydroxide at 484 nm versus [KOH] in ^{i}PrOH: [CNCbl] = 6.0 × 10^{-5} M, 25 ^{0}C, anaerobic conditions.

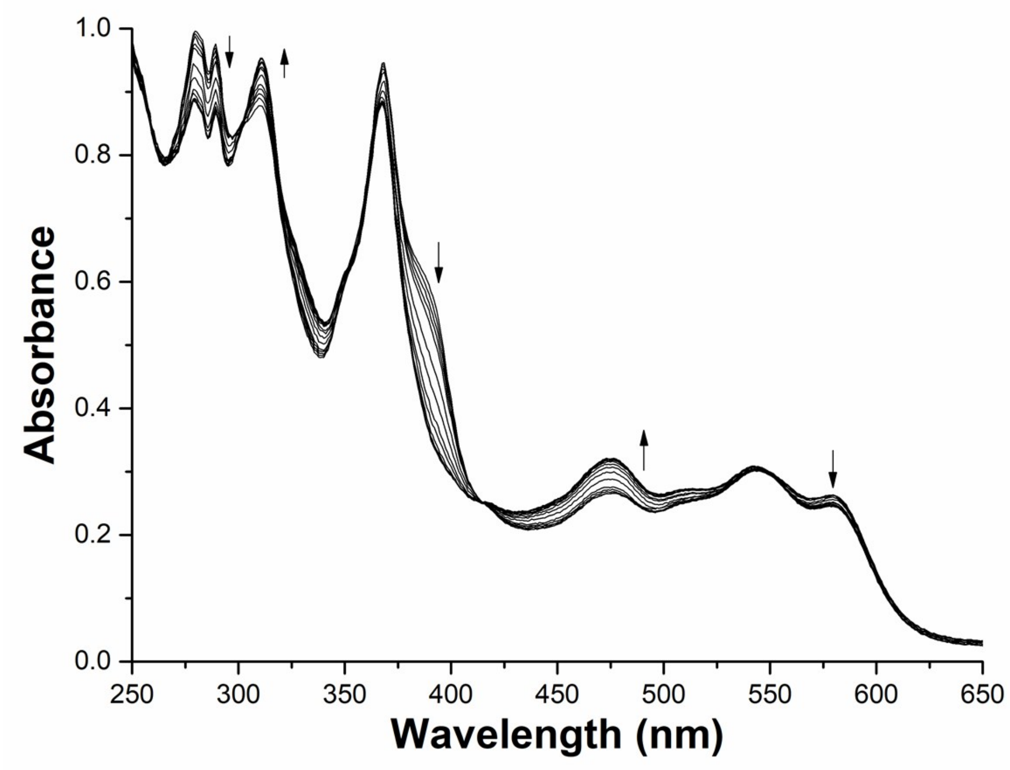

Figure S7. UV-vis spectral changes registered during storage solution of the product of reaction between cyanocobalamin and potassium hydroxide in iPrOH: [CNCbl] = 6 x 10^{-5} M; [KOH] = 1 мM; 15 ^{0}C; anaerobic conditions.

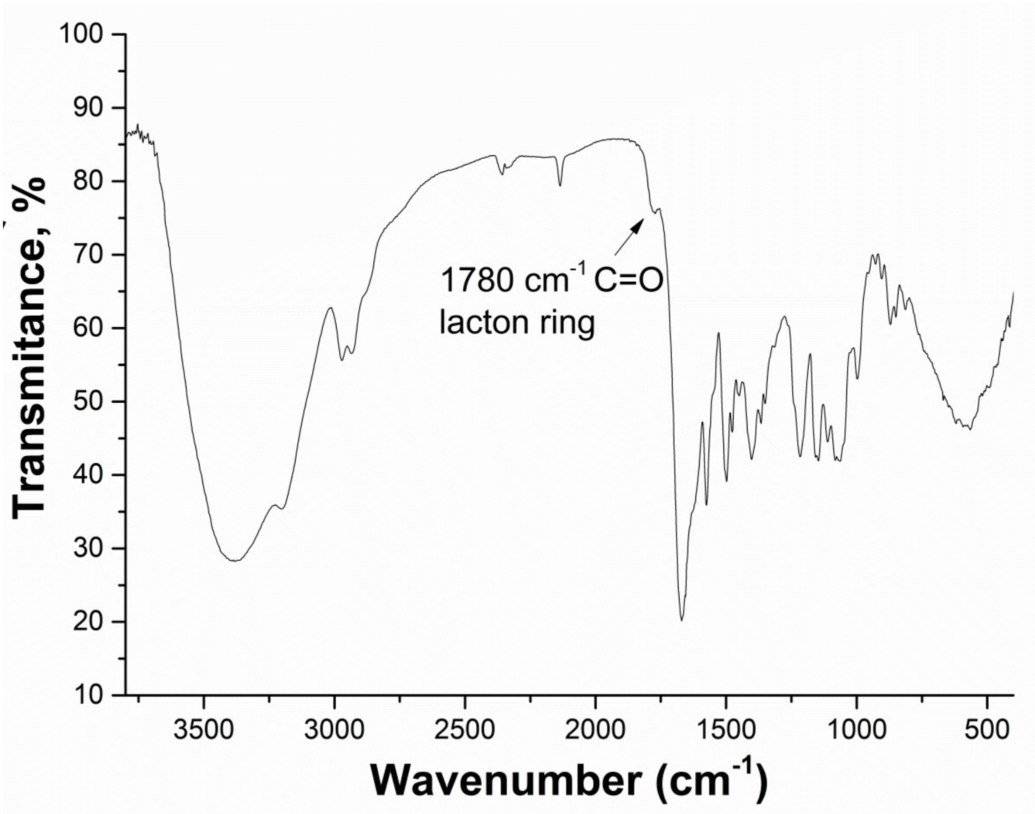

Figure S8. IR-spectrum of red product 1 (dehydrovitamin B_{12}, containing lactone ring at C8) in KBr.

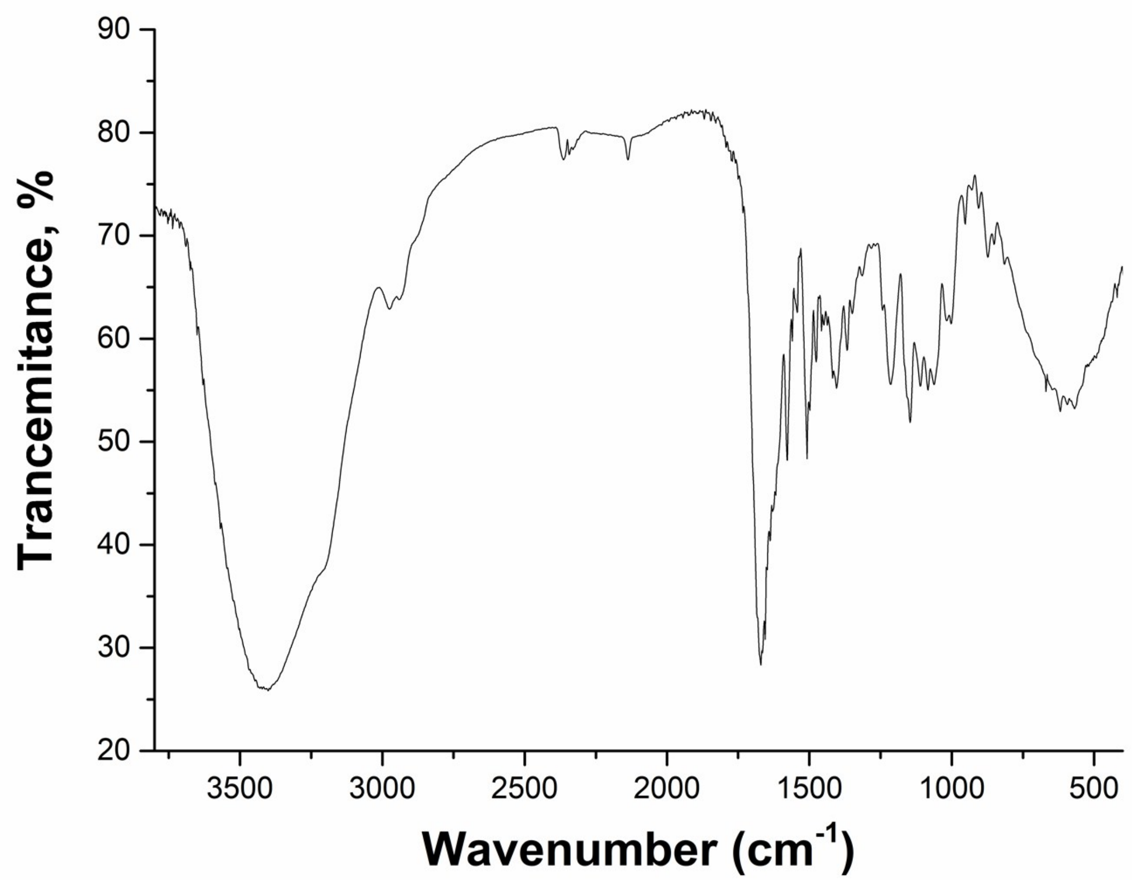

Figure S9. IR-spectrum of red product 2 (dehydrovitamin B_{12}, containing unsaturated amide side chain) in KBr.

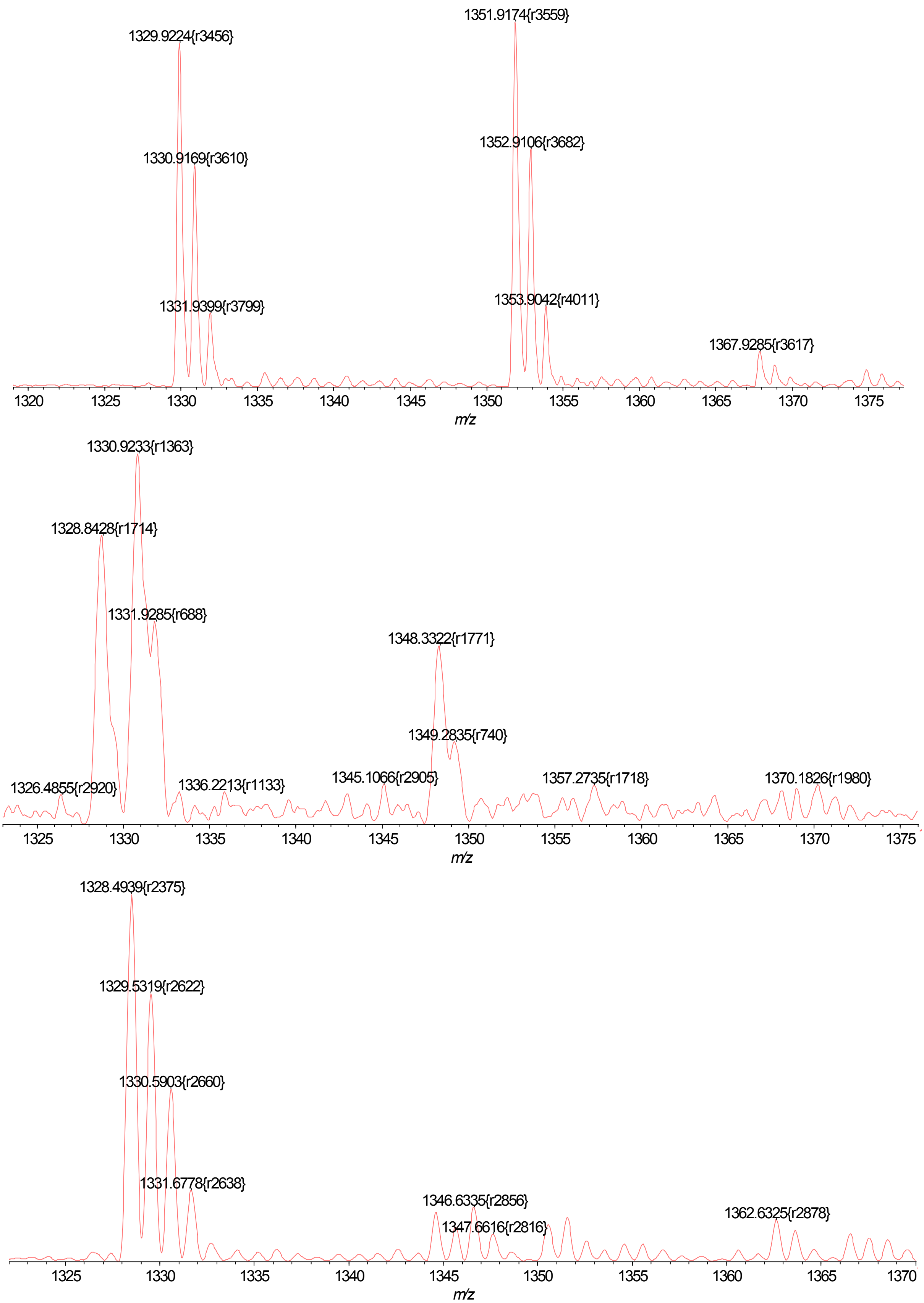

Figure S10. MALDI TOF mass spectra: top – cyanocobalamin, middle - red product 1, bottom – red product 2

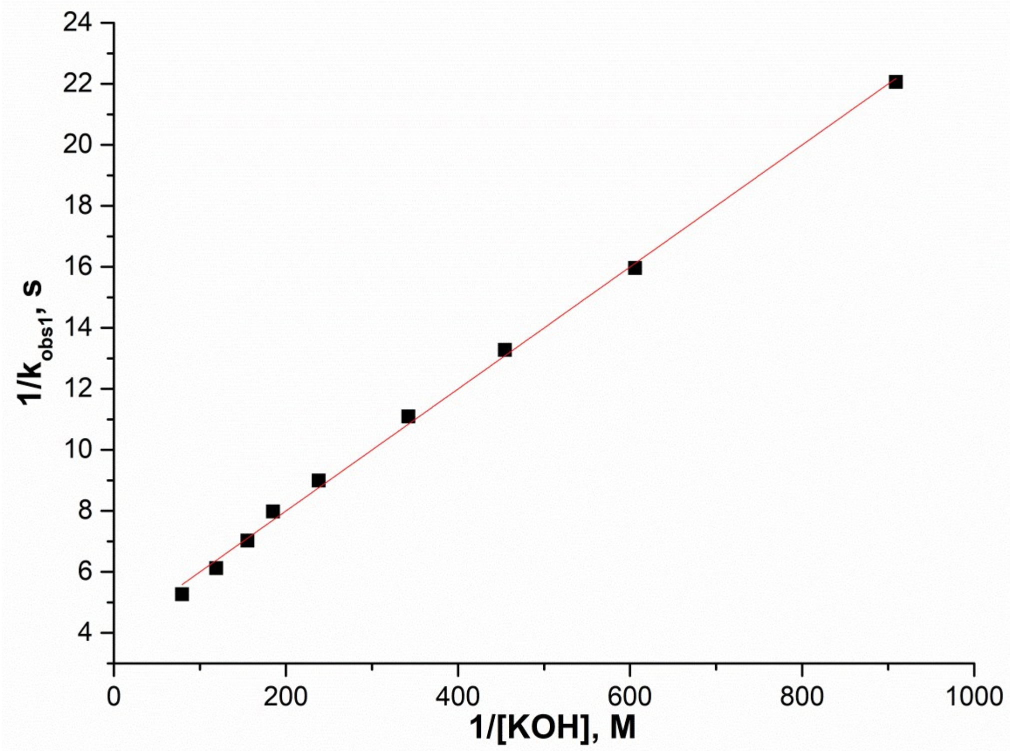

Figure S11. Plot 1/k_{obs1} vs 1/[KOH] for the reaction of cyanocobalamin with potassium hydroxide in ^{i}PrOH (first step): [CNCbl] = 6 × 10^{-5} M; 15 ^{0}C.

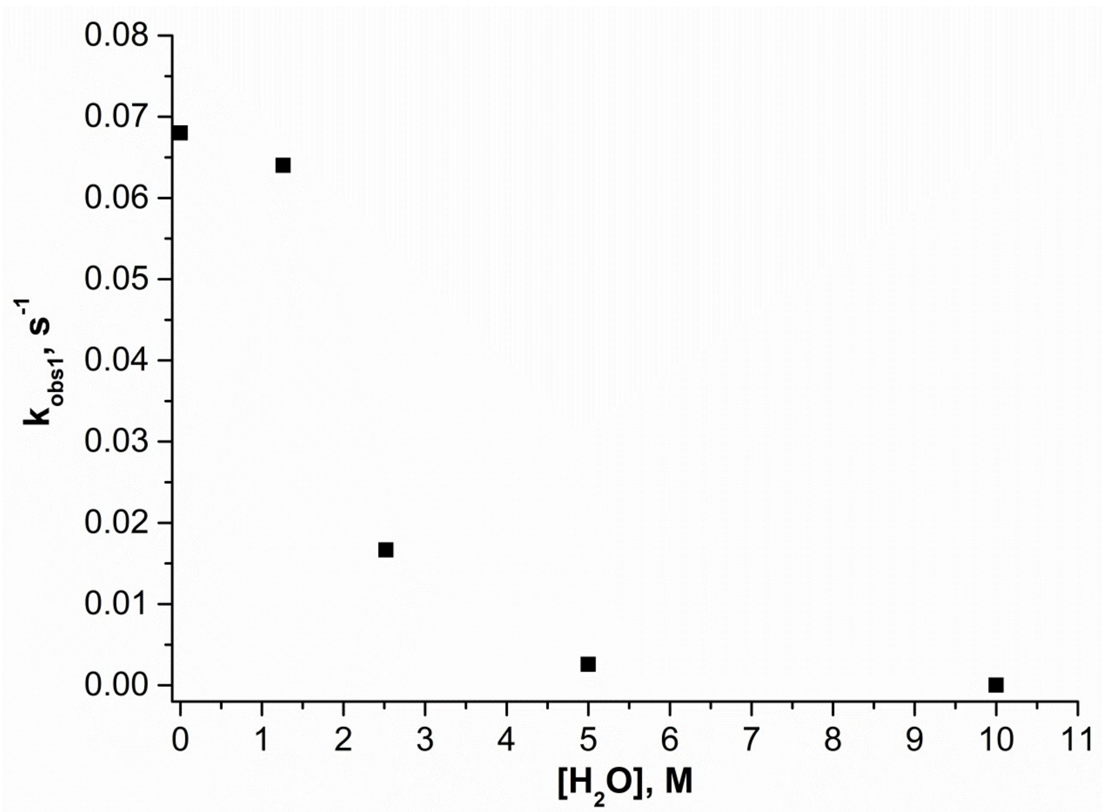

Figure S12. The dependence of k_{obs1} vs water concentration in ^{i}PrOH: [CNCbl] = 6 × 10^{-5} M; [KOH] = 1.4 мM; anaerobic conditions.

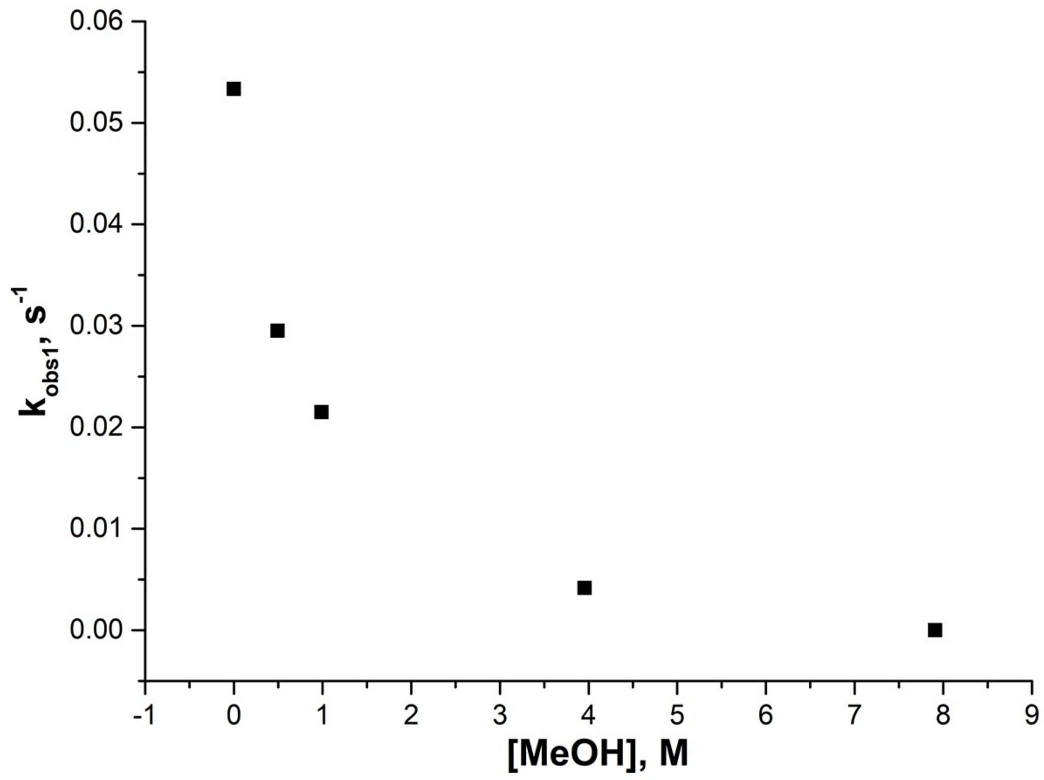

Figure S13. The dependence of k_{obs1} vs methanol concentration in ^{i}PrOH: [CNCbl] = 6 × 10^{-5} M; [KOH] = 1.4 мM; anaerobic conditions.

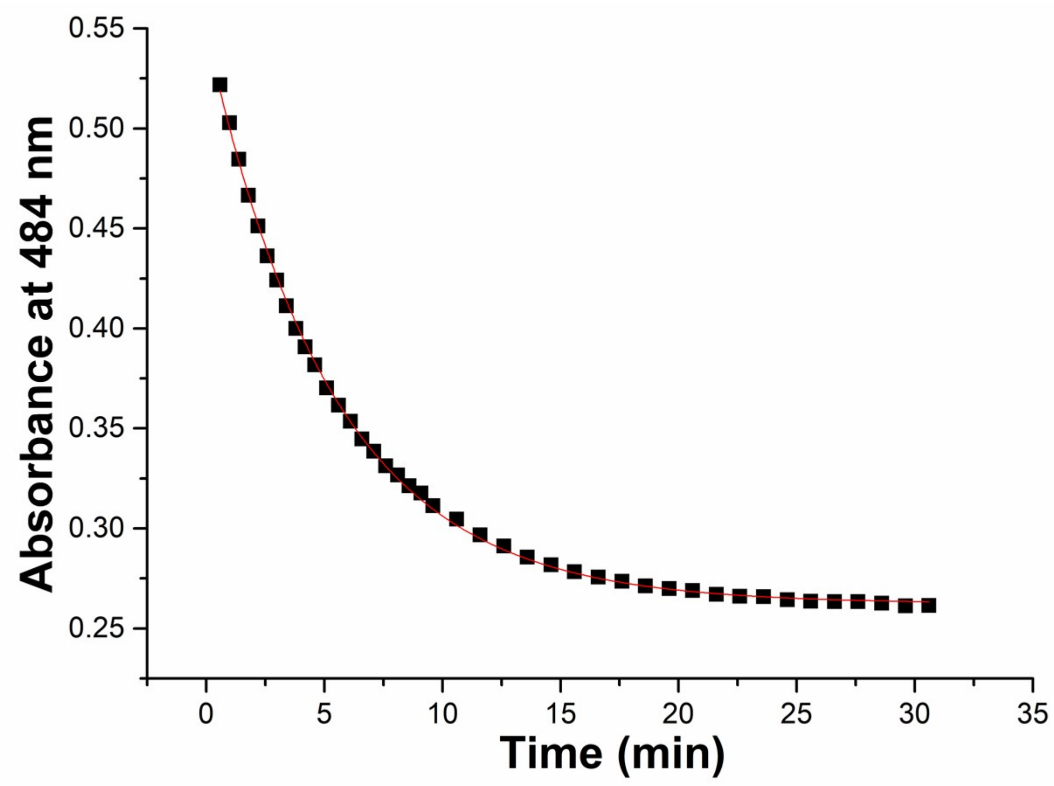

Figure S14. Typical kinetic trace recorded for decomposition of intermediate generated by mixing cyanocobalamin with potassium hydroxide at [CNCbl]:[KOH] = 1:1 ratio in DMSO: [CNCbl] = [KOH] = 6.0 × 10^{-5} M, 20 ^{0}C, anaerobic conditions

Table S1. Kinetic and thermodynamic parameters for decomposition of intermediate generated by mixing cyanocobalamin and potassium hydroxide in iPrOH or DMSO

T, °C	k_{11} 10^3, s^{-1}
35	12.9 ± 0.2
30	8.3 ± 0.3
25	3.8 ± 0.2
20	2.7 ± 0.05
15	1.2 ± 0.1
10	0.67 ± 0.02
$\Delta H^{\neq}$(k), [кДж моль$^{-1}$]	+ 84 ± 12
$\Delta S^{\neq}$(k), [кДж моль$^{-1}$]	- 7 ± 2

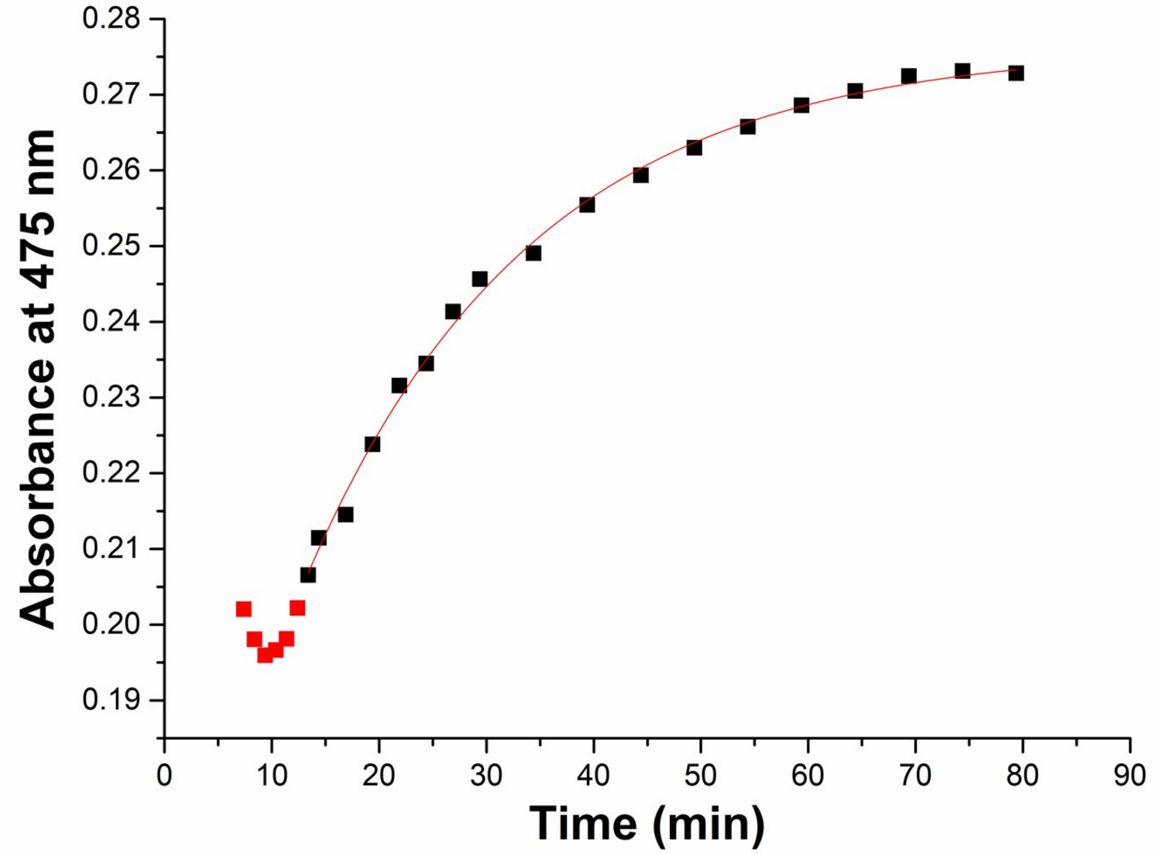

Figure S15. Typical kinetic trace recorded for decomposition of super reduced Co^{1+} generated by mixing cyanocobalamin and potassium hydroxide in iPrOH: [CNCbl] = 6 x 10^{-5} M; [KOH] = 1 мM; 15 ^{0}C; anaerobic conditions.

Table S2. Kinetic and thermodynamic parameters for decomposition of super reduced Co^{1+} generated by mixing cyanocobalamin and potassium hydroxide in iPrOH

T, °C	k_5, s^{-1}
35	0.008
30	0.004
25	0.0026
20	0.0012
15	0.00078
$\Delta H^{\neq}$(k), [кДж моль$^{-1}$]	+ 78 ± 4
$\Delta S^{\neq}$(k), [Дж K^{-1} моль$^{-1}$]	- 34 ± 3

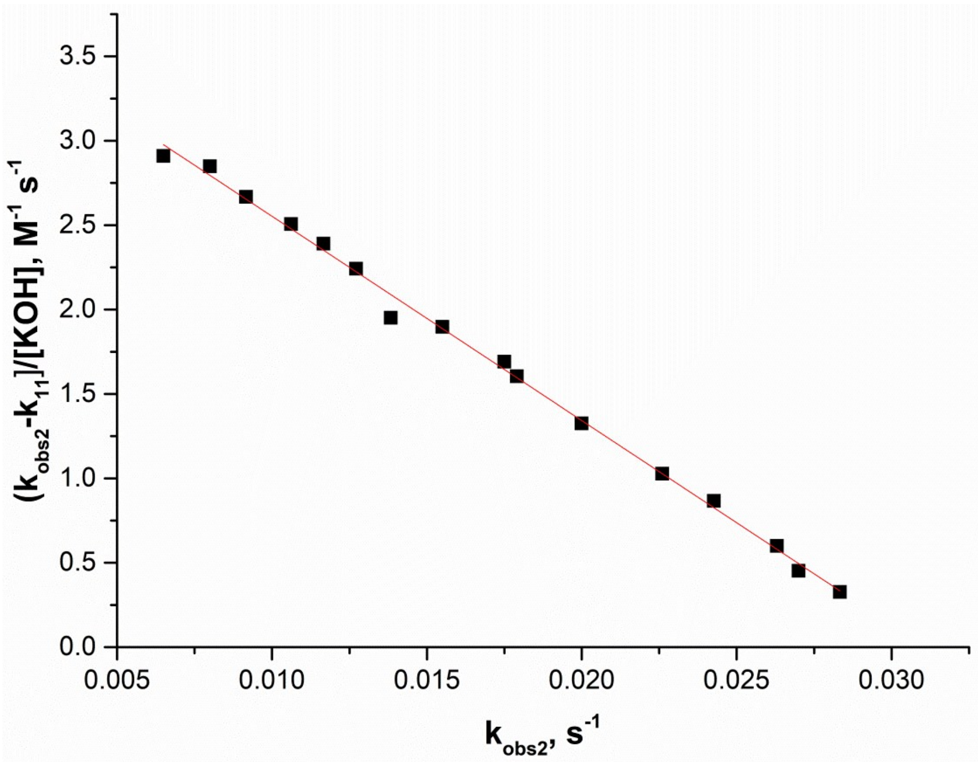

Figure S16. Plot ($k_{obs2} - k_{11}$)/[KOH] vs k_{obs2} for the reaction of cyanocobalamin with potassium hydroxide in ^{i}PrOH (*second step*): [CNCbl] = 6×10^{-5} M; 15 ^{0}C; anaerobic conditions