Three types of copper derivatives formed by $CuCl_2 \cdot 2H_2O$ interaction with with (*Z*)-3-aryl-2-(methylthio)-5-(pyridine-2-ylmethylene)-3,5-dihydro-4*H*-imidazol-4-ones

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Supplementary Information

The control of the reactions and confirmation of the products individuality was carried out by thin layer chromatography on a fixed layer of silica gel (Silufol).

^{1}H and ^{13}C NMR spectra were recorded on a Brucker-Avance instrument (400 MHz for ^{1}H and 101 MHz for ^{13}C). Deuterochloroform ($CDCl_3$) and dimethyl sulfoxide-d6 (DMSO-d6) were used as the solvents. Chemical shifts are reported in ppm on a δ scale relative to hexamethyldisiloxane as internal standard.

High resolution mass spectra (HRMS) were recorded on an Orbitrap Elite mass spectrometer (Thermo Scientific). For the solutions with a concentration of 0.1 - 9 μg/ml (in 1% formic acid in acetonitrile), direct injection into the ion source was used by a syringe pump (5 μL/min). Spray voltage ± 3.5 kV, capillary temperature 275ºC. Mass spectra were recorded using an Orbitrap analyzer with a resolution of 480000 (1 microscan). Maximum input time 900 ms, averaging over 9 spectra, mass range 90 - 2000 Da, in some cases 200 - 4000 Da. For internal calibration, the signals of DMSO and diisooctyl phthalate (m/z 157.03515 and 413.26623) in the positive mode and the signal of dodecyl sulfate (m/z 265.14790) in the negative mode were used.

Mass spectra of matrix-activated laser desorption/ionization (MALDI) were recorded on a Bruker Autoflex II instrument (resolution FWHM 18000) equipped with a nitrogen laser with a working wavelength of 337 nm and a time-of-flight mass analyzer operating in the reflectron mode. Accelerating voltage 20 kV. The samples were applied to a polished steel substrate. The spectra were recorded in the positive ion mode. The resulting spectrum was the sum of 50 spectra obtained at different points in the sample. 2,5-Dihydroxybenzoic acid (DHB) (Acros,

99%) and α-cyano-4-hydroxycinnamic acid (HCCA) (Acros, 99%) were used as matrices where needed to facilitate ionization.

EPR spectra were recorded on a Varian E-3 EPR Spectrometer at the boiling point of liquid nitrogen (77.4 K). DMF grade "pure" was purified by stirring over freshly calcined $CuSO_4$ for 3 days, followed by distillation in vacuum over CaH2 at $t \leq 45°C$.

Electronic absorption spectra were measured on a Hitachi U2900 instrument with an operating wavelength range of 190-1100 nm in a quartz cuvette from Agilent Technologies with an optical path of 10 mm. Before recording each spectrum, the background signal was recorded in pure solvent; the background signal was subtracted by the spectrophotometer in an automatic mode.

An IPC Pro M potentiostat was used for electrochemical studies. The working electrode was a glassy carbon disk (d = 2 mm), the reference electrode was Ag/AgCl/KCl (sat.). The auxiliary electrode was a platinum plate, and the supporting electrolyte was a 0.1 M Bu_4NClO_4 solution in DMF. In the study by the CV method, the potential sweep rate is 100 mV/s, in the study by the VDE method - 20 mV/s. All measurements were carried out in a dry argon atmosphere; samples were dissolved in a previously deaerated solvent.

1. Synthesis

1.1 3-Arylsubstituted 5-((Z)-2-pyridylmethylene)-2-hioxotetrahydro-4H-imidazol-4-ones (2a-m).

Compounds **2a-m** were synthesized analogously to previously published procedure [3, 7-10].

General procedure:

Isothiocyanate ethylacetate (1 molar equivalent) added dropwise to a vigorously stirred solution of the substituted aniline (1 molar equivalent) in 10 ml of diethyl ether. The mixture was stirred until the white solid precipitated, afterwards the ether was evaporated. 1.1 molar equivalent of potassium hydroxide in 50 ml of ethanol was added to form a clear red solution. Then 1.1 molar equivalent of 2-pyridinecarbaldehyde was added dropwise and the mixture was stirred for 3 hours. Aqueous hydrochloric acid was then added to pH = 7, the precipitate was filtered off, washed with water, cold ethanol, diethyl ether and dried on air. Final products were purified by preparative column chromatography on silica gel, eluent CH_2Cl_2: MeOH (20: 1). The products were isolated as yellow powders.

3-(4-fluorophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one (2a). From 4-fluoroaniline, 200 mg (1.45 mmol) by reaction with isothiocyanate

ethylacetate, 210 mg (1.45 mmol) followed by pyridine-2-carbaldehyde 171 mg (1.6 mmol) and solid KOH 90 mg (1.6 mmol) **2a** obtained as light yellow powder. Yield: 347 mg (80%) after column chromatography. ^{1}H NMR (400 MHZ, DMSO-d6. δ, ppm): 11.87 (brs, 1H, NH), 8.76 (d, 1H, J=4.89 Hz, Hα-Py), 7.89 (td, 1H, J_1=7.83 Hz, J_2=1.76 Hz, Hβ-Py), 7.75 (d, 1H, J=7.83 Hz, Hβ'-Py), 7.47-7.30 (m, 5H, Hγ-Py, Hα, Hα', Hβ, Hβ'-Ph), 6.79 (s, 1H, -CH=). ^{13}C NMR (101 MHz, DMSO-d6, δ) 178.2, 161.1, 153.6, 150.3, 137.9, 131.5, 127.1, 123.8, 116.3, 109.0. HRMS (*neg.*) calculated $C_{15}H_9FN_3OS$: 298.0450 (**2a**-H). Found: 298.0452 (**2a**-H).

3-(3-fluorophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one (2b). From 3-fluoroaniline, 200 mg (1.45 (1.45 mmol) by reaction with isothiocyanate ethylacetate, 210 mg (1.45 mmol) followed by pyridine-2-carbaldehyde 171 mg (1.6 mmol) and solid KOH 90 mg (1.6 mmol) **2b** was obtained as light yellow powder. Yield: 364 mg (84%) after column chromatography. ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 12.71 (brs, 1H, NH), 8.78 (d, 1H, J = 4.89 Hz, Hα-Py), 8.63 (m, 1H, Hγ-Py), 7.91 (td, 1H, J_1 = 7.82 Hz, J_2 = 1.96 Hz, Hβ-Py), 7.79 (m, 1H, Hβ'-Py), 7.57 (m, 2H, Hα, Hβ-Ph), 7.33 (m, 3H, Hβ ', Hγ-Ph, Hα'-Ph), 6.82 (s, 1H, -CH=). ^{13}C NMR (101 MHz, DMSO-d6, δ) 177.8, 163.6, 153.5, 150.4, 137.9, 130.9, 130.2, 127.2, 125.7, 123.8, 116.7, 109.2. HRMS (*neg.*) calculated $C_{15}H_9FN_3OS$: 298.0451 (**2b**-H). Found: 298.0449 (**2b**-H).

3-(2-fluorophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one (2c). From 2-fluoroaniline, 200 mg (1.45 mmol) by reaction with isothiocyanate ethylacetate, 210 mg (1.45 mmol), followed by pyridine-2-carbaldehyde 171 mg (1.6 mmol) and solid KOH 90 mg (1.6 mmol), **2c** was obtained as a yellow powder. Yield: 325 mg (75%) after column chromatography. ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 12.06 (brs, 1H, NH), 8.76 (d, 1H, J = 4.89 Hz, Hα-Py), 7.90 (td, 1H, J_1 = 7.83 Hz, J_2 = 1.76 Hz , Hβ-Py), 7.77 (m, 1H, H β'-Py), 7.53 (m, 2H, Hβ, Hβ'-Ph), 7.35 – 7.40 (m, 3H, Hγ-Py, Hα, Hγ-Ph), 6.85 (s, 1H, -CH=). ^{13}C NMR (101 MHz, DMSO-d6, δ) 177.3, 163.1, 153.3, 150.4, 145.1, 137.9, 133.4, 132.1, 127.3, 123.9, 116.9, 110.0. HRMS (*neg.*) calculated $C_{15}H_9FN_3OS$: 298.0456 (**2c**-H). Found: 298.0453 (**2c**-H).

(Z)-3-(4-bromophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one (2d). From the 4-bromoaniline, 200 mg (1.16 mmol) by reaction with isothiocyanate ethylacetate, 168 mg (1.16 mmol) followed by pyridine-2-carbaldehyde 137 mg (1.28 mmol) and solid KOH 72 mg (1.28 mmol) **2d** was obtained as a yellow powder. Yield: 330 mg (79%) after column chromatography. ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 8.76 (d, 1H, J = 4.30 Hz, Hα-Py), 7.89 (td, 1H, J_1 = 7.83 Hz, J_2 = 1.96 Hz , Hβ-Py), 7.76 (d, 1H, J = 7.83 Hz, Hβ'-Py), 7.45 (m, 2H, Hβ, Hβ'-Ph), 7.32 – 7.36 (m, 3H, Hγ-Py, Hα, Hα '-Ph), 6.78 (s, 1H, -CH=).

^{13}C NMR (101 MHz, DMSO-d6, δ) 177.9, 163.6, 153.5, 150.3, 137.9, 132.4, 131.5, 127.2, 123.8, 122.6, 109.1. HRMS (*pos.*) calculated $C_{15}H_{11}BrN_3OS^+$: 361.2358 (**2d**+H isotopic), 359.9801 (**2d**+H). Found: 361.9778, 359.9804 (**2d**+H).

3-(3-bromophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one (2e). From the 3-bromoaniline of 200 mg (1.16 mmol) by reaction with isothiocyanate ethylacetate, 168 mg (1.16 mmol), followed by pyridine-2-carbaldehyde 137 mg (1.28 mmol) and 72 mg (1.28 mmol) of solid KOH, **2e** was obtained as a yellow powder. Yield: 321 mg (77%) after column chromatography. ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 8.77 (d, 1H, J = 4.37 Hz, Hα-Py), 7.91 (td, 1H, J_1 = 7.79 Hz, J_2 = 1.78 Hz, Hβ-Py), 7.72 – 7.78 (m, 3H, Hγ-Py, Hα, Hα'-Ph), 7.41 (m, 3H, Hβ'-Py, Hβ-Ph, Hγ-Ph), 6.81 (s, 1H, -CH=).^{13}C NMR (101 MHz, DMSO-d6, δ) 169.9, 155.8, 154.9, 150.3, 137.8, 135.4, 132.0, 131.1, 128.6, 126.9, 121.4, 109.2. HRMS (*pos.*) calculated $C_{15}H_{11}BrN_3OS^+$: 361.2358 (**2e**+H isotopic) 359.9801 (**2e**+H). Found: 361.9779 (**2e**+H) 359.9804 (**2e**+H).

3-(2-bromophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one (2f). From 2-bromoaniline, 200 mg (1.16 mmol) by reaction with isothiocyanate ethylacetate, 168 mg (1.16 mmol) followed by pyridine-2-carbaldehyde 137 mg (1.28 mmol) and solid KOH 72 mg (1.28 mmol) **2f** was obtained as a yellow powder. Yield: 225 mg (54%) after column chromatography. ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 8.86 (d, 1H, J = 4.69 Hz, Hα-Py), 7.99 (td, 1H, J_1 = 8.03 Hz, J_2 = 1.66 Hz , Hβ-Py), 7.65 (m, 3H, Hβ, Hβ'-Ph, Hβ'-Py), 7.31 (m, 3H, Hγ-Py, Hα, Hγ-Ph), 6.78 (s, 1H, -CH=). ^{13}C NMR (101 MHz, DMSO-d6, δ) 177.3, 163.1, 153.3, 150.4, 137.9, 133.4, 132.4, 129.2, 127.3, 123.5, 109.8. HRMS (*pos.*) calculated $C_{15}H_{11}BrN_3OS^+$: 361.9786 (**2f**+H isotopic), 359.9806 (**2f**+H). Found: 361.9782 (**2f**+H isotopic), 359.9812 (**2f**+H).

3-(4-chlorophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one (2g). From the 4-chloroaniline, 200 mg (1.57 mmol) by the reaction with isothiocyanate ethylacetate, 228 mg (1.57 mmol) followed by pyridine-2-carbaldehyde 185 mg (1.72 mmol) and solid KOH 97 mg (1.72 mmol) **2g** was obtained as a white-yellow powder. Yield: 401 mg (81%) after column chromatography. ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 8.78 (d, 1H, J = 4.34 Hz, Hα-Py), 8.58 (m, 1H, Hβ-Py) 8.45 (m, 1H, Hβ'-Py), 7.45 – 7.34 (m, 5H, J = 7.63 Hz, Hγ-Py, Hα, Hα', Hβ, Hβ'-Ph), 6.83 (s, 1H, -CH=). ^{13}C NMR (101 MHz, DMSO-d6, δ) 177.3, 163.2, 153.3, 150.3, 137.9, 132.8, 132.1, 131.9, 128.6, 127.3, 123.9, 109.9. HRMS (*neg.*) calculated $C_{15}H_9ClN_3OS^-$: 316.0130 (**2g**-H isotopic), 314.0160 (**2g**-H). Found: 316.0125 (**2g**-H isotopic), 314.0158 (**2g**-H).

3-(3-chlorophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one (2h). From the 4-chloroaniline, 200 mg (1.57 mmol) by the reaction with isothiocyanate ethylacetate, 228 mg (1.57 mmol) followed by pyridine-2-carbaldehyde 185 mg (1.72 mmol) and solid KOH 97 mg (1.72 mmol) **2h** was obtained as a white-yellow powder. Yield: 401 mg (81%) after column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.78 (d, 1H, J=3.91 Hz, Hα-Py), 7.91 (m, 1H, Hβ-Py), 7.78 (d, 1H, J = 7.82 Hz, Hβ'-Py), 7.58 (m, 1H, Hα'-Ph), 7.55 (m, 1H, Hα, Hβ -Ph), 7.41 (m, 4H, Hγ-Py, Hγ-Ph), 6.81 (s, 1H, -CH=). ^{13}C NMR (101 MHz, DMSO-d6, δ) 177.4, 165.5, 149.9, 137.6, 134.47, 132.9, 130.5, 128.9, 127.9, 126.8, 124.9, 123.4. HRMS (*neg.*) calculated $C_{15}H_9ClN_3OS^-$: 314.0155 (**2h**–H isotopic), 316.0125 (**2h**–H isotopic). Found: 314.0160 (**2h**-H), 316.0129 (**2h**-H).

3-(2-chlorophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one (2i). From the 2-chloroaniline, 200 mg (1.57 mmol) by the reaction with isothiocyanate ethylacetate, 228 mg (1.57 mmol) followed by pyridine-2-carbaldehyde 185 mg (1.72 mmol) and solid KOH 97 mg (1.72 mmol) **2i** was obtained as a white yellow powder. Yield: 376 mg (76%) after column chromatography. ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 8.76 (d, 1H, J = 4.73 Hz, Hα-Py), 7.89 (td, 1H, J_1 = 7.91 Hz, J_2 = 1.94 Hz , Hβ-Py), 7.76 (m, 1H, Hβ'-Py), 7.47 – 7.43 (m, 2H, Hβ, Hβ'-Ph), 7.37 – 7.32 (m, 3H, Hγ-Py, Hα, Hγ-Ph), 6.78 (s, 1H, -CH=). ^{13}C NMR (101 MHz, DMSO-d6, δ) 177.4, 163.3, 153.3, 150.4, 137.9, 132.2, 129.9, 127.3, 123.9, 120.4, 116.8, 110.0. HRMS (*neg.*) calculated $C_{15}H_9ClN_3OS^-$: 316.0130 (**2i**-H isotopic), 314.0160 (**2i**-H). Found: 314.0159 (**2i**-H) 316.0126 (**2i**-H isotopic).

3-(4-methoxyphenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one (2j). From the 4-methoxyaniline 200 mg (1.63 mmol) by the reaction with isothiocyanate ethylacetate, 236 mg (1.63 mmol) followed by pyridine-2-carbaldehyde 191 mg (1.79 mmol) and solid KOH 100 mg (1.79 mmol) **2j** was obtained as a yellow powder. Yield: 466 mg (92%) after column chromatography. ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 8.46 (d, 1H, J = 3.74 Hz, Hα-Py), 7.73 (td, 1H, J_1 = 6.91 Hz, J_2 = 1.73 Hz, Hβ-Py), 7.39 (d, 1H, J = 6.81 Hz, Hβ'-Py), 7.25 (dd, 1H, J_1 = 7.52 Hz, J_2 = 2.02 Hz, Hγ-Py) , 7.17 (m, 2H, Hα, Hα'-Ph), 6.87 (m, 2H, Hβ, Hβ'-Ph), 6.83 (s, 1H, -CH=), 3.90 (s, 3H, p-OCH_3). HRMS (*neg.*) calculated $C_{16}H_{12}N_3O_2S^-$: 310.3504 (**2j**-H). Found: 310.0654 (**2j**-H).

3-(4-ethoxyphenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one (2k). From 4-ethoxyaniline, 200 mg (1.46 mmol) by the reaction with isothiocyanate ethylacetate, 212 mg (1.46 mmol) followed by pyridine-2-carbaldehyde 172 mg (1.60 mmol) and solid KOH 90 mg (1.60 mmol) **2k** was obtained as a yellow powder. Yield: 419 mg (89%) after column chromatography. ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 8.75 (d, 1H, J = 4.40 Hz, Hα-

Py), 7.89 (td, 1H, J_1 = 7.70 Hz, J_2 = 1.83 Hz, Hβ-Py), 7.75 (d, 1H, J = 7.89 Hz, Hβ'-Py), 7.38 (m, 1H, Hγ-Py), 7.26 (m, 2H, Hα, Hα'-Ph), 7.01 (m, 2H, Hβ, Hβ-Ph), 6.76 (s, 1H, -CH=), 4.05 (q, 2H, J = 6.97 Hz, OCH_2-), 1.32 (t, 3H, J = 6.97 Hz, -CH_3). ^{13}C NMR (101 MHz, DMSO-d6, δ) 178.6, 163.9, 159.1, 153.7, 150.3, 137.9, 130.4, 127.1, 125.1, 123.7, 114.9, 109.8, 63.8, 15.1. HRMS (*neg.*) calculated $C_{17}H_{14}O_2N_3S^-$ (**2k**-H): 324.0807. Found: 324.0812 (**2k**-H).

3-(3,4-dimethoxyphenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one (2l). From 3,4-dimethoxyaniline, 200 mg (1.31 mmol) by the reaction with isothiocyanate ethylacetate, 190 mg (1.31 mmol) followed by pyridine-2-carbaldehyde 154 mg (1.44 mmol) and solid KOH 80 mg (1.44 mmol) **2l** was obtained as yellow powder. Yield: 322 mg (72%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.69 (d, 1H, J = 4.04 Hz, Hα-Py), 7.77 (td, 1H, J1 = 7.70 Hz, J2 = 1.65 Hz, Hβ-Py), 7.44 (d, 1H, J = 7.89 Hz, Hβ'-Py), 7.29 (dd, 1H, J1 = 7.52 Hz, J2 = 2.02 Hz, Hγ-Py) , 6.96 (m, 2H, Hα, Hβ-Ph), 6.85 (m, 1H, Hα'-Ph), 6.60 (s, 1H, -CH=), 3.91 (s, 3H, p-OCH_3), 3.88 s, 3H, m-OCH_3). ^{13}C NMR (101 MHz, DMSO-d6, δ) 178.6, 163.93, 153.6, 150.3, 149.2, 137.9, 127.1, 123.7, 121.7, 113.0, 111.8, 108.7, 56.1. HRMS (*neg.*) calculated $C_{17}H_{14}O_3N_3S^-$: 340.0756 (**2l**-H). Found: 340.0760 (**2l**-H).

3-(4-t-butylphenyl)-5-((Z) -2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one (2m). From 4-tertbutylaniline, 200 mg (1.34 mmol) by the reaction with isothiocyanate ethylacetate, 194 mg (1.34 mmol) followed by pyridine-2-carbaldehyde 158 mg (1.48 mmol) and solid KOH 83 mg (1.48 mmol) **2m** was obtained as a yellow powder. Yield: 402 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.72 (d, 1H, J = 5.38 Hz, Hα-Py), 7.84 (m, 1H, Hβ-Py), 7.53 (m, 3H, Hβ, Hβ'-Ph, Hβ'-Py), 7.33 (m, 3H, Hγ-Py, Hα, Hα'-Ph), 6.62 (s, 1H, -CH=), 1.36 (m, 9H, $C(CH_3)_3$). HRMS (*pos.*) calculated $C_{19}H_{18}N_3OS^-$: 338.1327 (**2m**+H). Found: 338.1322 (**2m**+H).

1.2 Alkylation of compounds (2a-m) with methyl iodide. Synthesis of compounds 3a-m

General procedure:

1.2 molar equivalent of solid KOH was added to a water-ethanol (1:1) suspension of the starting 3-aryl-5-((Z) -2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one **2** (1 ml of water and 1 ml of EtOH per 100 mg of compound). After a clear red solution was formed, methyl iodide (2.3 molar equivalents) was added dropwise with stirring and the reaction mixture was stirred for 10 minutes. The mixture was then placed in a freezer, the formed precipitate was filtered off, washed with an aqueous KOH to remove the residues of the starting compound, water, small amounts of ice-cold ethanol and diethyl ether. The products were isolated as light yellow

powders after purification by preparative column chromatography on silica gel, eluent CH_2Cl_2: MeOH 10: 1.

5-(Z)-3-(4-fluorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one (3a). From 100 mg (0.33 mmol) of **3-(4-fluorophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one 1** as a result of reaction with methyl iodide, 110 mg (0.77 mmol) in the presence of 22 mg (0.39 mmol) of solid KOH, **3a** was obtained as a white-yellow powder. Yield: 39 mg (38%) after column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.92 (d, 1H, J=8.27 Hz, Hα-Py), 8.81 (d, 1H, J=5.09 Hz, Hβ'-Py), 8.04 (t, 1H, J=8.42 Hz, Hγ-Py), 7.48 (m, 1H, Hβ-Py,), 7.30 (m, 2H, Hβ, Hβ' -Ph), 7.19 (m, 2H, Hα, Hα'-Ph), 7.12 (s, 1H, -CH=), 2.76 (s, 3H, -CH3). ^{13}C NMR (101 MHz, DMSO-d6, δ) 181.6, 168.4, 165.0, 161.4, 153.5, 150.4, 140.4, 137.0, 130.6, 128.9, 126.8, 124.0, 122.6, 116.8, 13.43.HRMS (*pos.*) calculated for $C_{16}H_{13}FN_3OS^+$: 314.0758 (**3a**+H). Found: 314.0761 (**3a**+H).

5-(Z)-3-(3-fluorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one (3b). From 100 mg (0.33 mmol) of **3-(3-fluorophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one 2** as a result of reaction with methyl iodide, 110 mg (0.77 mmol) in the presence of 22 mg (0.39 mmol) of solid KOH, **3b** was obtained as a white-yellow powder. Yield: 43 mg (42%) after column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.81 (d, 1H, J=8.03 Hz, Hα-Py), 8.68 (d, 1H, J=3.91 Hz, Hβ'-Py), 7.76 (t, 1H, J=8.02 Hz, Hγ-Py), 7.44 (m, 1H, Hβ-Py), 7.24 - 7.21 (m, 2H, Hα, Hα'-Ph), 7.16 – 7.09 (m, 3H, Hβ, Hγ-Ph, -CH=), 2.72 (s, 3H, -CH_3). ^{13}C NMR (101 MHz, DMSO-d6, δ) 168.0, 167.8, 161.2, 153.1, 150.4, 140.3, 137.0, 134.2, 131.6, 126.9, 124.5, 122.8, 116.8, 115.6, 100.3, 87.9, 13.50. HRMS (*pos.*) calculated for $C_{16}H_{13}FN_3OS^+$: 314.0758 (**3b**+H). Found: 314.0761 (**3b**+H).

5-(Z)-3-(2-fluorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one (3c). From 100 mg (0.33 mmol) of **3-(2-fluorophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one 3** as a result of reaction with methyl iodide, 110 mg (0.77 mmol) in the presence of 22 mg (0.39 mmol) of solid KOH, **3c** was obtained as a white-yellow powder. Yield: 32 mg (31%) after column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.89 (d, 1H, J = 7.82 Hz, Hα-Py), 8.76 (d, 1H, J = 3.91 Hz, Hβ'-Py), 7.91 (t, 1H, J = 7.82 Hz, Hy-Py), 7.50 (m, 1H, Hα-Ph), 7.38 -7.25 (m, 5H, Hβ, Hβ ', Hγ-Ph, Hβ-Py -CH=), 2.76 (s, 3H, -CH3). ^{13}C NMR (101 MHz, DMSO-d6, δ) 171.4, 168.2, 167.8, 153.3, 150.4, 139.9, 137.0, 131.2, 127.0, 124.2, 123.3, 117.1, 13.30. HRMS (*pos.*) calculated for $C_{16}H_{13}FN_3OS^+$: 314.0758 (**3c**+H). Found: 314.0763 (**3c**+H).

5-(Z)-3-(4-bromophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one (3d). From 100 mg (0.28 mmol) of **3-(4-bromophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one 4** as a result of reaction with methyl iodide, 93 mg (0.65 mmol) in the presence of 19 mg (0.33 mmol) of solid KOH, **3d** was obtained as a white-yellow powder. Yield: 42 mg (40%) after column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.80 (d, 1H, J=8.22 Hz, Hα-Py), 8.68 (d, 1H, J=4.70 Hz, Hβ'-Py), 7.76 (dt, 1H, J_1=7.63 Hz, J_2=1.37 Hz, Hγ-Py), 7.61 (m, 2H, Hβ-Py, -CH=), 7.25 (m, 2H, Hβ, Hβ' -Ph), 7.20 (m, 2H, Hα, Hα'-Ph), 2.72 (s, 3H, -CH_3). HRMS (*pos.*) calculated: $C_{16}H_{13}BrN_3OS^+$ 373.9958 (**3d**+H). Found: 373.9963 (**3d**+H).

5-(Z)-3-(3-bromophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one (3e). From 100 mg (0.28 mmol) of **3-(3-bromophenyl)-5-((Z) -2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one 5** as a result of reaction with methyl iodide, 93 mg (0.65 mmol) in the presence of 19 mg (0.33 mmol) of solid KOH, **3e** was obtained as a white-yellow powder. Yield: 52 mg (50%) after column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$. δ, ppm): 8.80 (d, 1H, J=7.83 Hz, Hα-Py), 8.68 (d, 1H, J=5.67 Hz, Hβ'-Py), 7.76 (t, 1H, J=8.23 Hz, Hγ-Py), 7.58 (m, 1H, Hα-Ph), 7.52 (s, 1H, -CH=), 7.36 (m, 1H, Hβ-Py), 7.30 (m, 1H, Hα'-Ph), 7.29 – 7.20 (m, 2H, Hβ, Hγ-Ph), 2.72 (s, 3H, -CH_3). HRMS (*pos.*) calculated: $C_{16}H_{13}BrN_3OS^+$ 373.9958 (**3e**+H). Found: 373.9962 (**3e**+H).

5-(Z)-3-(2-bromophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one (3f). From 100 mg (0.28 mmol) of **3-(2-bromophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one 6** as a result of reaction with methyl iodide, 93 mg (0.65 mmol) in the presence of 19 mg (0.33 mmol) of solid KOH, **3f** was obtained as a white-yellow powder. Yield: 30 mg (29%) after column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.82 (d, 1H, J = 9.00 Hz, Hα-Py), 8.69 (d, 1H, J = 4.70 Hz, Hβ'-Py), 7.74 (m, 2H, Hγ-Py, Hα-Ph), 7.45 (m, 1H, Hβ-Py), 7.34 (m, 2H, Hβ, Hβ'-Ph), 7.21 (m, 2H, Hγ-Ph, -CH=), 2.71 (s, 3H, -CH_3). ^{13}C NMR (101 MHz, DMSO-d6, δ) 168.0, 153.2, 150.5, 140.1, 137.1, 133.9, 131.9, 129.6, 126.9, 124.2, 122.9, 13.3. HRMS (*pos.*) calculated: $C_{16}H_{13}BrN_3OS^+$ 373.9958 (**3f**+H). Found: 373.9967 (**3f**+H).

5-(Z)-3-(4-chlorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one (3g). From 100 mg (0.32 mmol) of **3-(4-chlorophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one 8** as a result of reaction with methyl iodide, 103 mg (0.72 mmol) in the presence of 21.5 mg (0.38 mmol) of solid KOH, **3g** was obtained as a white-yellow powder. Yield: 50 mg (47%) after column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.82 (d, 1H, J = 7.83 Hz, Hα-Py), 8.72 (d, 1H, J_1 = 4.89 Hz, Hβ'-Py), 7.80 (t, 1H, J = 6.85

Hz, Hγ-Py), 7.48 (m, 2H, Hα, Hα'-Ph), 7.42 – 7.30 (m, 3H, Hβ, Hβ '-Ph, Hβ-Py,), 7.22 (s, 1H, -CH=), 2.74 (s, 3H, -CH_3). HRMS (*pos.*) calculated: $C_{16}H_{13}ClN_3OS^+$ 330.0463 (**3g**+H). Found: 330.0464 (**3g**+H).

5-(Z)-3-(3-chlorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one (3h). From 100 mg (0.32 mmol) of **3-(4-chlorophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one 9** as a result of reaction with methyl iodide, 104 mg (0.73 mmol) in the presence of 21 mg (0.38 mmol) of solid KOH, **3h** was obtained as a white-yellow powder. Yield: 33 mg (31%) after column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.86 (d, 1H, J=7.83 Hz, Hα-Py), 8.73 (d, 1H, J=3.91 Hz, Hβ'-Py), 7.85 (t, 1H, J=7.83 Hz, Hγ-Py), 7.44 (m, 2H, Hα, Hα'-Ph), 7.38 (m, 1H, Hβ-Py), 7.28 (m, 3H, Hβ, Hγ-Ph, -CH=), 3.05 (s, 3H, -SCH_3). HRMS (*pos.*) calculated: $C_{16}H_{13}ClN_3OS^+$: 330.0468 (**3h**+H), 332.0438 (**3h**+H isotopic). Found: 330.0454 (**3h**+H), 332.0422 (**3h**+H isotopic).

5-(Z)-3-(2-chlorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one (3i). From 100 mg (0.32 mmol) of **3-(2-chlorophenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one 10** as a result of reaction with methyl iodide, 103 mg (0.72 mmol) in the presence of 21.5 mg (0.38 mmol) of solid KOH, **3i** was obtained as a white-yellow powder. Yield: 52 mg (49%) after column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.82 (d, 1H, J = 7.83 Hz, Hα-Py), 8.69 (d, 1H, J = 3.91 Hz, Hβ'-Py), 7.76 (t, 1H, J = 7.43 Hz, Hy-Py), 7.56 (m, 1H, Hα-Ph), 7.46 – 7.32 (m, 4H, Hβ-Py, Hγ, Hβ, Hβ '-Ph), 7.20 (s, 1H, -CH=), 2.71 (s, 3H, -CH_3). HRMS (*pos.*) calculated: $C_{16}H_{13}ClN_3OS^+$ 330.0463 (**3i**+H). Found: 330.0468 (**3i**+H).

5-(Z)-3-(4-methoxyphenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one (3j). From 100 mg (0.32 mmol) of **3-(4-methoxyphenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one 11** as a result of reaction with methyl iodide, 105 mg (0.74 mmol) in the presence of 21 mg (0.38 mmol) of solid KOH, **3j** was obtained as a white-yellow powder. Yield: 63 mg (61%) after column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.87 (d, 1H, J = 8.11 Hz, Hα-Py), 8.76 (d, 1H, J = 4.45 Hz, Hβ'-Py), 7.93 (t, 1H, J = 8.42 Hz, Hγ-Py), 7.27 (m, 4H, Hα, Hα', Hβ, Hβ'-Ph), 6.96 (m, 2H, Hβ-Py, -CH=), 2.72 (s, 3H, -CH_3). ^{13}C NMR (101 MHz, DMSO-d6, δ) 169.0, 165.1, 160.3, 153.6, 150.4, 140.6, 137.0, 129.6, 126.8, 125.0, 124.8, 122.4, 115.2, 56.0, 13.38. HRMS (*pos.*) calculated: $C_{17}H_{16}N_3O_2S^+$ 326.0958 (**3j**+H). Found: 326.0963 (**3j**+H).

5-(Z)-3-(4-ethoxyphenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one (3k). From 100 mg (0.31 mmol) of **3-(4-ethoxyphenyl)-5-((Z)-2-pyridylmethylidene)-2-**

thioxotetrahydro-4H-imidazol-4-one 12 as a result of reaction with methyl iodide, 101 mg (0.71 mmol) in the presence of 21 mg (0.37 mmol) of solid KOH, **3k** was obtained as a white-yellow powder. Yield: 48 mg (46%) after column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.86 (d, 1H, J = 7.83 Hz, Hα-Py), 8.77 (m, 1H, J = 4.45 Hz, Hβ-Py), 7.92 (t, 1H, J = 8.31 Hz, Hγ-Py), 7.34 (m, 2H, Hβ, Hβ '-Ph), 7.24 – 7.19 (m, 4H, Hβ'-Py, Hα, Hα'-Ph, -CH=), 4.06 (q, 2H, J = 6.99 Hz, -CH_2-), 2.72 (s, 3H, -SCH_3), 1.42 (t, 3H, J = 6.97 Hz, -CH_3). ^{13}C NMR (101 MHz, DMSO-d6, δ) 168.8, 165.2, 159.6, 153.6, 150.1, 140.5, 136.6, 129.3, 126.8, 124.8, 122.6, 115.5, 63.9, 14.9, 13.34. HRMS (*pos.*) calculated: $C_{18}H_{18}N_3O_2S^+$ 340.1115 (**3k**+H). Found: 340.1116 (**3k**+H).

5-(Z)-3-(3,4-dimethoxyphenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one (3l). From 100 mg (0.29 mmol) of **3-(3,4-dimethoxyphenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one 13** as a result of reaction with methyl iodide, 95 mg (0.67 mmol) in the presence of 19.5 mg (0.35 mmol) of solid KOH, **3l** was obtained as a white-yellow powder. Yield: 78 mg (76%) after column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.90 (m, 2H, J = 7.83 Hz, Hα, Hβ-Py), 8.08 (m, 1H, Hγ-Py), 7.51 (m, 1H, Hβ-Py), 6.97 – 6.81 (m, 4H, Hα, Hα', Hβ –Ph, -CH=), 3.93 (s, 3H, p-OCH_3), 3.90 (s, 3H, m-OCH_3), 2.78 (s, 3H, -SCH_3). HRMS (*pos.*) calculated: $C_{18}H_{18}N_3O_3S^+$ 356.1064 (**3l**+H). Found: 356.1065 (**3l**+H).

5-(Z)-3-(4-t-butylphenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one (3m). From 100 mg (0.30 mmol) of **3-(4-tert-butylphenyl)-5-((Z)-2-pyridylmethylidene)-2-thioxotetrahydro-4H-imidazol-4-one 14** as a result of reaction with methyl iodide, 98 mg (0.69 mmol) in the presence of 20 mg (0.36 mmol) of solid KOH, **3m** was obtained as a white-yellow powder. Yield: 96 mg (91%) after column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$ δ, ppm): 8.84 (m, 1H, Hα-Py), 8.69 (d, 1H, J=4.89 Hz, Hβ'-Py), 7.78 (m, 1H, Hγ-Py), 7.50 (m, 2H, Hβ, Hβ' -Ph), 7.22 – 7.21 (m, 4H, Hβ-Py, Hα, Hα'-Ph, -CH=), 2.72 (s, 3H, -SCH_3), 1.64 (s, 9H, -tBu). HRMS (*pos.*) calculated: $C_{20}H_{22}N_3OS^+$ 352.1479 (**3m**+H). Found: 352.1479 (**3m**+H).

1.3. Synthesis of copper-containing compounds.

General procedure:

0.1 ml of solvent* was carefully added to a solution of 15 mg of the corresponding ligand **3** in 1.5 ml of dichloromethane to achieve separated layers. A solution of $CuCl_2 \cdot 2H_2O$ in 1.5 ml of solvent* was then carefully added, keeping the separation in a two-phase system. Tightly closed reaction mixture was left for 4-5 days in the dark place until crystallization occurred. If a

clear solution without signs of crystallization or precipitation was formed, crystallization was activated by ether diffusion: an open vial with a reaction solution was placed in a larger vial containing a small amount of diethyl ether, tightly closed and left to stand for 24 hours in the dark.

The precipitate was separated by decanting, washed with a small amount of dichloromethane and then by diethyl ether until the washing solvent become colorless. The final products were obtained as crystalline powders after drying on air. Melting points in open capillary were >200°C (with decomposition) for all obtained compounds **4**, **5**, **6**.

** The choice of solvent is important and determines the ratio of products **4**, **5**, **6** in the final mixture. Acetone using leads to formation of only complexes **4a-m**, while cyclohexanol leads to crystallization of complexes **6a-c**. In other alcohols: methanol, ethanol, isopropanol, isobutanol, tert-butanol, the mixtures of compounds **4** and **6** were obtained in various ratios (from 1: 1 in the case of isopropanol to ~1:20 in the case of tert-butanol). N-butanol could be used to isolate salts **5** with admixtures of compounds **4**, **6** in different amounts*.

Compounds 4 obtained at $CHCl_3$/acetone solvent system:

Preparation of the coordination compound 5-(Z)-3-(4-fluorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one 30 with copper (II) chloride dihydrate (4a). Complex **4a** was obtained as a black crystalline precipitate from 5-(Z)-3-(4-fluorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one **3a** 15 mg (50 μmol) and copper(II) chloride dihydrate 8.5 mg (50 μmol). Yield: 11.2 mg (62%). MALDI: m/z = 313 (**3a**$^+$) 100%, 376 (**3a**)Cu^+ 70%, 690 (**3a**)$_2Cu^+$ 100%. HRMS: calculated: 423.0114 ($C_{16}H_{13}CuFN_3OS$*$HCOOH^+$), found: 423.0111 ($C_{16}H_{12}CuFN_3OS$*$HCOOH^+$), UV-vis (λ, nm/ε, l mol^{-1} cm^{-1}): 386/71632.

Preparation of the coordination compound 5-(Z)-3-(3-fluorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one 31 with copper (II) chloride dihydrate (4b). Complex **4b** was obtained as a black crystalline precipitate from 5-(Z)-3-(3-fluorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one **3b** 15 mg (50 μmol) and copper(II) chloride dihydrate 8.5 mg (50 μmol). Yield: 11.2 mg (61%). MALDI: m/z = 313 (**3b**$^+$) 20%, 376 (**3b**)Cu^+ 68%, 690 (**3b**)$_2Cu^+$ 100%. HRMS: calculated: 423.0114 ($C_{16}H_{13}CuFN_3OS$*$HCOOH^+$), found: 423.0074 ($C_{16}H_{12}CuFN_3OS$*$HCOOH^+$), UV-vis (λ, nm/ε, l mol^{-1} cm^{-1}): 383/20841.

Preparation of the coordination compound 5-(Z)-3-(2-fluorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one 32 with copper (II) chloride dihydrate (4c). Complex **4c** was obtained as a black crystalline precipitate from 5-(Z)-3-(2-fluorophenyl)-2-

(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one **3c** 15 mg (50 μmol) and copper(II) chloride dihydrate 8.5 mg (50 μmol). Yield: 11.3 mg (63%). MALDI: m/z = 313 (**3c**$^+$) 11%, 692 (**3c**)$_2$Cu$^+$ 100%. HRMS: calculated: 423.0114 ($C_{16}H_{13}CuFN_3OS$*HCOOH$^+$), found: 423.0109 ($C_{16}H_{12}CuFN_3OS$*HCOOH$^+$), UV-vis (λ, nm/ε, l mol^{-1} cm^{-1}): 366/28496.

Preparation of the coordination compound 5-(Z)-3-(4-bromophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one 33 with copper (II) chloride dihydrate (4d). Complex **4d** was obtained as a black crystalline precipitate from 5-(Z)-3-(4-bromophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one **3d** 15 mg (42 μmol) and copper(II) chloride dihydrate 7 mg (42 μmol). Yield: 11.6 mg (63%). MALDI: m/z = 375 (**3d**+CH_3) 100%, 478 (**3d**)CuCl$^+$ 12%, 814 (**3d**)$_2$Cu$^+$ 100%. HRMS: calculated: 482.9314 ($C_{16}H_{13}CuBrN_3OS$*HCOOH$^+$), found: 482.9303 ($C_{16}H_{13}CuBrN_3OS$*HCOOH$^+$), UV-vis (λ, nm/ε, l mol^{-1} cm^{-1}): 393/13361.

Preparation of the coordination compound 5-(Z)-3-(3-bromophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one 34 with copper (II) chloride dihydrate (4e). Complex **4e** was obtained as a black crystalline precipitate from 5-(Z)-3-(3-bromophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one **3e** 15 mg (42 μmol) and copper(II) chloride dihydrate 7 mg (42 μmol). Yield: 11.5 mg (62%). MALDI: m/z = 375 (**3e**+H$^+$) 80%, 438 (**3e**)Cu$^+$ 32%, 815 (**3e**)$_2$Cu$^+$ 100%. HRMS: calculated: 482.9314 ($C_{16}H_{13}CuBrN_3OS$*HCOOH$^+$), found: 482.9310 ($C_{16}H_{13}CuBrN_3OS$*HCOOH$^+$), UV-vis (λ, nm/ε, l mol^{-1} cm^{-1}): 366/16828.

Preparation of the coordination compound 5-(Z)-3-(2-bromophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one 35 with copper (II) chloride dihydrate (4f). Complex **4f** was obtained as a black crystalline precipitate from 5-(Z)-3-(2-bromophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one **3f** 15 mg (42 μmol) and copper(II) chloride dihydrate 7 mg (42 μmol). Yield: 11.5 mg (62%). MALDI: m/z = 375 (**3f**+H$^+$) 34%, 475 (**3f**)CuCl$^+$ 18%, 814 (**3f**)$_2$Cu$^+$ 100%. HRMS: calculated: 482.9314 ($C_{16}H_{13}CuBrN_3OS$*HCOOH$^+$), found: 482.9307 ($C_{16}H_{13}CuBrN_3OS$*HCOOH$^+$), UV-vis (λ, nm/ε, l mol^{-1} cm^{-1}): 366/41910.

Preparation of the coordination compound 5-(Z)-3-(4-chlorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one 37 with copper (II) chloride dihydrate (4g). Complex **4g** was obtained as a black crystalline precipitate from 5-(Z)-3-(4-chlorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one **3g** 15 mg (47 μmol) and copper(II) chloride dihydrate 8 mg (47 μmol). Yield: 11.6 mg (62%). MALDI: m/z = 330 (**3g**)$^+$ 100%, 392

(**3g**)Cu^+ 82%, 814 (**3g**)$_2Cu^+$ 100%. HRMS: calculated: 438.9819 ($C_{16}H_{13}CuClN_3OS$*$HCOOH^+$), found: 438.9811 ($C_{16}H_{13}CuClN_3OS$*$HCOOH^+$), UV-vis (λ, nm/ε, l mol^{-1} cm^{-1}): 382/18034.

Preparation of the coordination compound 5-(Z)-3-(2-chlorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one 39 with copper (II) chloride dihydrate (4i). Complex **4i** was obtained as a black crystalline precipitate from 5-(Z)-3-(2-chlorophenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one **3i** 15 mg (47 μmol) and copper(II) chloride dihydrate 8 mg (47 μmol). Yield: 11.2 mg (60%). MALDI: m/z = 330 (**39**$^+$) 37%, 392 (**39**)Cu^+ 100%, 814 (**39**)$_2Cu^+$ 73%. HRMS: calculated: 438.9819 ($C_{16}H_{13}CuClN_3OS$*$HCOOH^+$), found: 438.9815 ($C_{16}H_{13}CuClN_3OS$*$HCOOH^+$), UV-vis (λ, nm/ε, l mol^{-1} cm^{-1}): 382/17298.

Preparation of the coordination compound 5-(Z)-3-(4-methoxyphenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one 40 with copper (II) chloride dihydrate (4j). Complex **4j** was obtained as a black crystalline precipitate from 5-(Z)-3-(4-methoxyphenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one **3j** 15 mg (44 μmol) and copper(II) chloride dihydrate 7.5 mg (44 μmol). Yield: 11.0 mg (59%). MALDI: m/z = 326 (**3j**+H^+) 100%, 388 (**3j**)Cu^+ 47%, 423 (**3j**)$CuCl^+$, 649 (**3j**-OMe)$_2Cu^+$ 51%. HRMS: calculated: 435.0314 ($C_{17}H_{17}CuN_3O_2S$*$HCOOH^+$), found: 435.0316 ($C_{17}H_{17}CuN_3O_2S$*$HCOOH^+$), UV-vis (λ, nm/ε, l mol^{-1} cm^{-1}): 382/17298.

Preparation of the coordination compound 5-(Z)-3-(4-Ethoxyphenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one 41 with copper (II) chloride dihydrate (4k). Complex **4k** was obtained as a black crystalline precipitate from 5-(Z)-3-(4-Ethoxyphenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one **3k** 15 mg (47 μmol) and copper(II) chloride dihydrate 8.1 mg (47 μmol). Yield: 11.1 mg (65%). MALDI: m/z = 342 (**3k**+H^+) 50%, 441 (**3k**)$CuCl^+$ 32%, 747 (**3k**)$_2Cu^+$ 100%. HRMS: calculated: 449.0471 ($C_{18}H_{19}CuN_3O_2S$*$HCOOH^+$), found: 449.0471 ($C_{18}H_{19}CuN_3O_2S$*$HCOOH^+$), UV-vis (λ, nm/ε, l mol^{-1} cm^{-1}): 370/22145.

Preparation of the coordination compound 5-(Z)-3-(4-t-butylphenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one 43 with copper (II) chloride dihydrate (4m). Complex **4m** was obtained as a black crystalline precipitate from 5-(Z)-3-(4-dtretbuthylphenyl)-2-(methylthio)-5-(pyridin-2-ylmethylidene)-1H-imidazol-4-one **3m** 15 mg (44 μmol) copper(II) chloride dihydrate 7.5 mg (44 μmol). Yield: 11.7 mg (69%). MALDI: m/z = 353 (**3m**+H^+) 53%, 669 ((**3m**-tBu)-Me)Cu^+ 27%, 685 (**3m**-tBu)$_2CuCl^+$ 100%, 701 (**3m**-tBu)$_2$+Me)Cu^+ 27%. HRMS: calculated: 461.0834 ($C_{20}H_{22}CuN_3OS$*$HCOOH^+$), found: 461.0833 ($C_{20}H_{22}CuN_3OS$*$HCOOH^+$), UV-vis (λ, nm/ε, l mol^{-1} cm^{-1}): 366/13487.

2. X-Ray

Accession Codes CCDC 2002967 (**4a**), CCDC 2019537 (**4c**), 2002968 (**5c**), 2002966 (**6a**) and 20002969 (**6b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic DataCentre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +441223 336033.

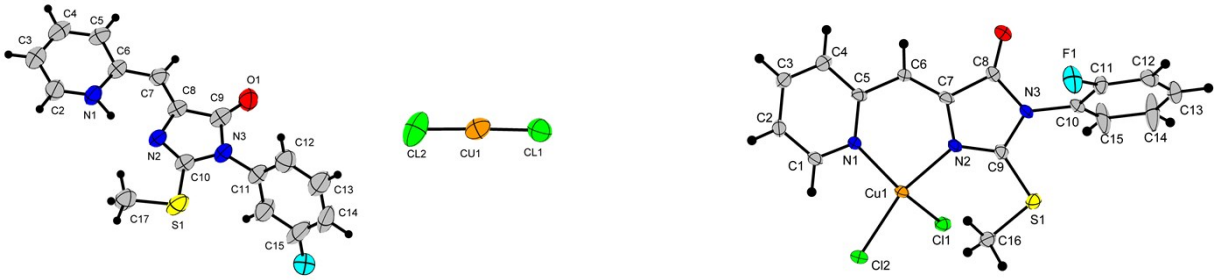

Figure S1. Molecular structure of compound **6b** (left) and **4c** (right). Thermal ellipsoids are given with 30% probability.

Tables S1. Crystal data and structure refinement for compound **4a**

Empirical formula	C16 H12 Cl2 Cu F N3 O S	
Formula weight	447.79	
Temperature	293(2) K	
Wavelength	1.54186 Å	
Crystal system	Orthorhombic	
Space group	F d d 2	
Unit cell dimensions	a = 46.8170(10) Å	α= 90°.
	b = 20.7265(5) Å	β= 90°.
	c = 7.27860(10) Å	γ = 90°.
Volume	7062.8(2) $Å^3$	
Z	16	
Density (calculated)	1.684 Mg/m^3	
Absorption coefficient	5.819 mm^{-1}	
F(000)	3600	
Theta range for data collection	3.777 to 66.904°.	
Index ranges	-37<=h<=55, -24<=k<=24, -7<=l<=8	
Reflections collected	33441	
Independent reflections	2989 [R(int) = 0.1099]	
Completeness to theta = 66.904°	99.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2989 / 1 / 227	
Goodness-of-fit on F^2	0.903	
Final R indices [I>2sigma(I)]	R1 = 0.0397, wR2 = 0.0794	
R indices (all data)	R1 = 0.0711, wR2 = 0.0877	
Absolute structure parameter	0.07(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.404 and -0.532 $e.Å^{-3}$	

Tables S2. Crystal data and structure refinement for compound **4c**

Empirical formula	$C_8H_5N_5O$
Formula weight	187.16
Temperature	120 K
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	4
a, Å	7.287(2)
b, Å	22.731(7)
c, Å	11.092(3)
α, °	90
β, °	108.638(6)
γ, °	90
V, $Å^3$	1741.1(9)
Density (calculated)	1.708 Mg/m^3
F(000)	904
Reflections collected	16266
Independent reflections	3373
Reflections with $I>2\sigma(I)$	2701
Parameters	232
R1	0.0600
wR2	0.1443
Goodness-of-fit on F^2	1.029
Largest diff. peak and hole, $e.Å^{-3}$ (d_{max}/d_{min})	2.03/ -1.30

Tables S3. Crystal data and structure refinement for compound **5b**.

Empirical formula	C16 H12 Cl Cu F N3 O S	
Formula weight	412.34	
Temperature	293(2) K	
Wavelength	1.54186 E	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 28.4118(8) E	α= 90°.
	b = 9.2731(3) E	β= 111.2410(10)°.
	c = 13.7925(5) E	γ = 90°.
Volume	3386.98(19) E^3	
Z	8	
Density (calculated)	1.617 Mg/m^3	
Absorption coefficient	4.593 mm^{-1}	
F(000)	1664	
Crystal size	.18 x .14 x .12 mm^3	
Theta range for data collection	3.338 to 68.805°.	
Index ranges	-22<=h<=34, -11<=k<=11, -16<=l<=14	
Reflections collected	17508	
Independent reflections	3095 [R(int) = 0.0844]	
Completeness to theta = 67.686°	99.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3095 / 0 / 219	
Goodness-of-fit on F^2	0.990	
Final R indices [I>2sigma(I)]	R1 = 0.0542, wR2 = 0.1193	
R indices (all data)	R1 = 0.0838, wR2 = 0.1460	
Extinction coefficient	0.00142(11)	
Largest diff. peak and hole	1.031 and -1.015 $e.E^{-3}$	

Tables S4. Crystal data and structure refinement for compound **6a**.

Empirical formula	C16 H13 Cl2 Cu F N3 O S	
Formula weight	448.79	
Temperature	293(2) K	
Wavelength	1.54186 E	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.7555(3) E	α= 90°.
	b = 11.7896(3) E	β= 108.304(2)°.
	c = 15.2935(5) E	γ = 90°.
Volume	1841.14(9) E^3	
Z	5	
Density (calculated)	1.619 Mg/m^3	
Absorption coefficient	5.581 mm^{-1}	
F(000)	904	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	4.443 to 67.868°.	
Index ranges	-12<=h<=12, -13<=k<=8, -17<=l<=18	
Reflections collected	21916	
Independent reflections	3266 [R(int) = 0.0438]	
Completeness to theta = 67.686°	98.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3266 / 0 / 232	
Goodness-of-fit on F^2	0.921	
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0979	
R indices (all data)	R1 = 0.0711, wR2 = 0.1078	
Extinction coefficient	0.00057(12)	
Largest diff. peak and hole	0.542 and -0.274 $e.E^{-3}$	

Tables S5. Crystal data and structure refinement for compound **6b**.

Identification code	shelx	
Empirical formula	C16 H13 Cl2 Cu F N3 O S	
Formula weight	448.79	
Temperature	293(2) K	
Wavelength	1.54186 E	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.5590(6) E	α= 90°.
	b = 11.5979(7) E	β= 72.947(6)°.
	c = 15.9749(12) E	γ = 90°.
Volume	1870.3(2) E^3	
Z	4	
Density (calculated)	1.594 Mg/m^3	
Absorption coefficient	5.494 mm^{-1}	
F(000)	904	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	4.380 to 71.537°.	
Index ranges	-12<=h<=10, -14<=k<=12, -19<=l<=9	
Reflections collected	19780	
Independent reflections	3580 [R(int) = 0.1023]	
Completeness to theta = 67.686°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3580 / 0 / 235	
Goodness-of-fit on F^2	0.822	
Final R indices [I>2sigma(I)]	R1 = 0.0549, wR2 = 0.1362	
R indices (all data)	R1 = 0.1280, wR2 = 0.1586	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.481 and -0.364 $e.E^{-3}$	

3. Electrochemistry

Table S6. Electrochemical potentials of the ligands **3** and complexes **4** in DMF in the presence of 0.1M Bu_4NClO_4 on GC electrodes relative to Ag/AgCl/KCl (sat.); potential scan rate is 100 mV s^{-1}.

Compound	E_{pc}, V	$E_{1/2}^{Red}$, V	E_{pa}, V	$E_{1/2}^{Ox}$, V
3a	-1.27; -1.41 м; -1.80	-1.24; -1.82	1.65	1.62
4a	0.40/0.55; -1.24; -1.54; -1.77	0.48; -1.28; -1.57	1.22; 1.66	1.20; 1.73
3b	-1.26; -1.39; -1.78	-1.24; -1.80	1.65	1.62
4b	0.42/0.56; -1.21; -1.47; -1.77	0.47; -1.19; -1.44; -1.74	1.13; 1.61	1.08 1.59
3c	-1.27; -1.73	-1.24; -1.80	1.65	1.69
4c	0.41/0.56; -1.19; -1.49; -1.75	0.43; -1.21; -1.49; -1.79	1.17	1.10
3d	-1.24; -1.37 м; -1.71	-1.22; -1.74	1.62	1.59
4d	0.32/0.56; -1.22; -1.50; -1.71	0.44; -0.48; -1.20	1.20; 1.64	1.18; 1.72
3e	-1.24; -1.40 м; -1.84	-1.21; -1.40; -1.83	1.51	1.48
4e	0.33/0.54; -0.90 м; -1.24; -141; 1.57	0.48; -0.46; -1.20; -1.41; --1.78	1.15;1.53	1.12; 1.55
3f	-1.28; -1.76	-1.25; -1.78	1.63	1.61
4f	0.42/0.53; -1.25; -1.73	0.48; -1.23; -1.85	1.12; 1.64?	1.13; 1.62?
3g	-1.25; -1.40; -1.70; -1.89	-1.20; -1.90	1.68	1.65
3g	0.36/0.58; -1.22; -1.58	0.43; -0.46; -1.21; -1.66;	1.23; 1.32; 1.70	1.26; 1.69
3i	-1.29; -1.76	-1.26; -1.81	1.69	1.65
4i	0.36/0.58; -1.23; -1.56; -1.80	0.44; -0.49; -1.24; -	1.25; 1.72?	1.17;

		1.56; -1.88		1.73
3j	-1.30; -1.45; -1.78	-1.26; -1.85	1.64	1.68
4j	0.39/0.57; -1.27; -1.57; -1.79	0.41; -1.27; -1.57; -1.92	1.25; 1.67	1.20; 1.69
3k	-1.33; -1.80	-1.28; -1.84	1.62	1.57
4k	0.42/0.55; -1.28; -1.78	0.49; -0.74; -1.27; -1.90	1.15; 1.60	1.12; 1.5
3l	-1.29; -1.44;-1.80	-1.26; -1.86	1.54	1.51
4l	0.37/0.56; -0.95 м; -1.28; -1.56; -1.88	0.43; -1.25; -1.59; -1.90	1.18; 1.54	1.14; 1.55
3m	-1.23; -1.84	-1.21; -1.84	1.52	1.48
4m	0.41/0.51; -0.44; 1.22; -1.79	0.48; -1.21; -1.55; -1.86	1.16; 1.52	1.13; 1.55

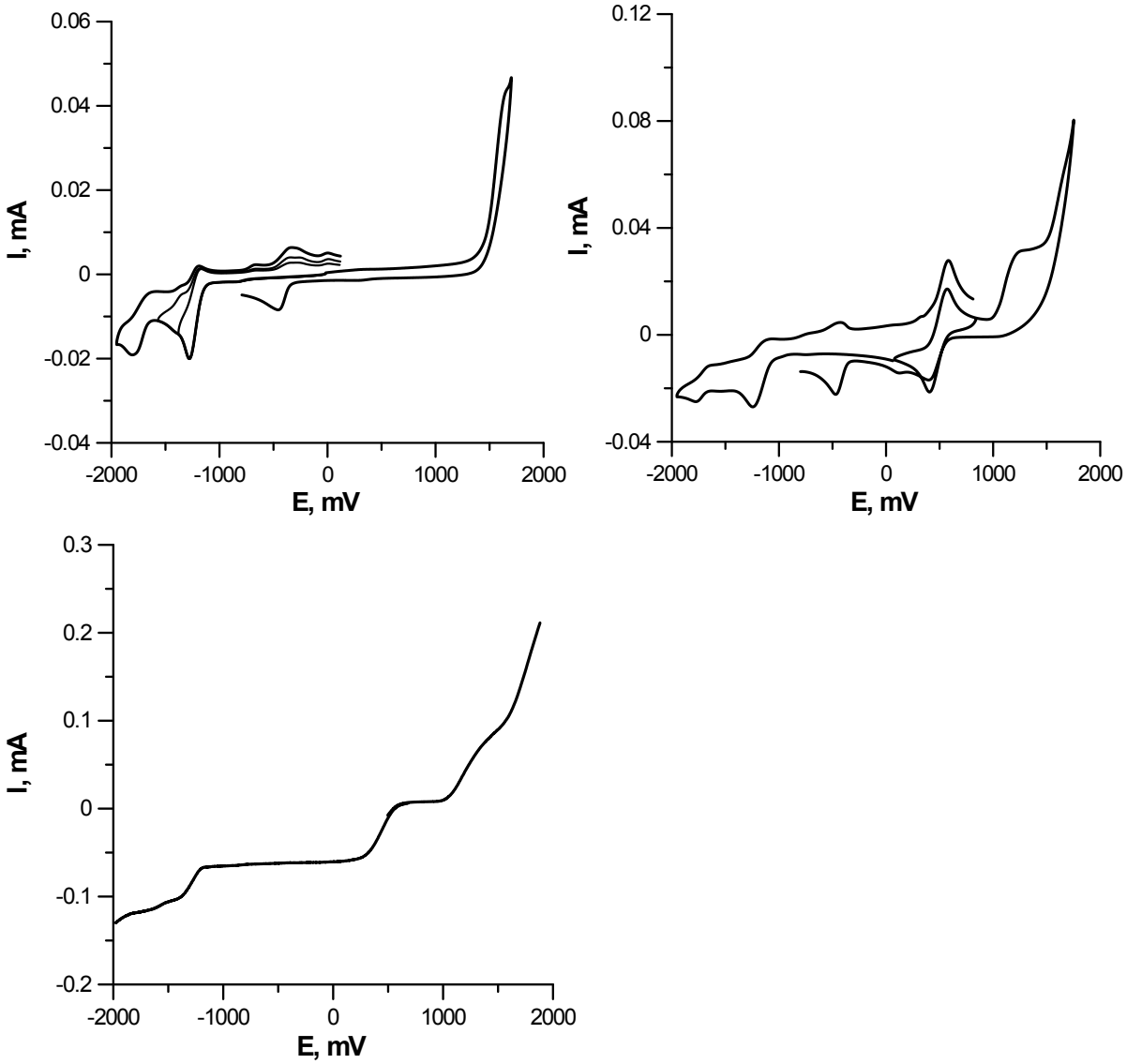

Figure S2. CV curves of ligand **3a** (top left) and its coordination compound **4a** (top right); RDE curve for complex **4a** (bottom).

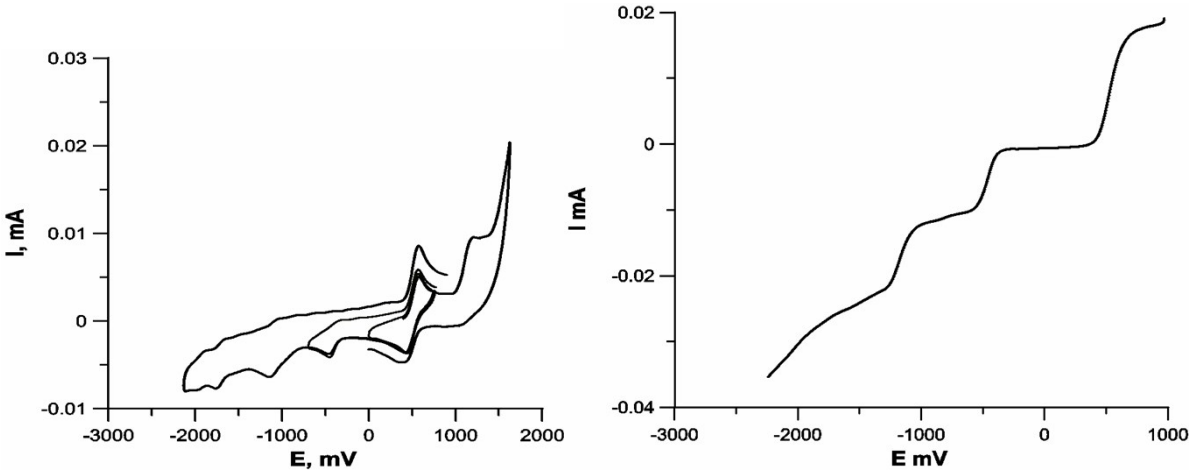

Figure S3. CV (left) and RDE (right) curves of compound **4b**.

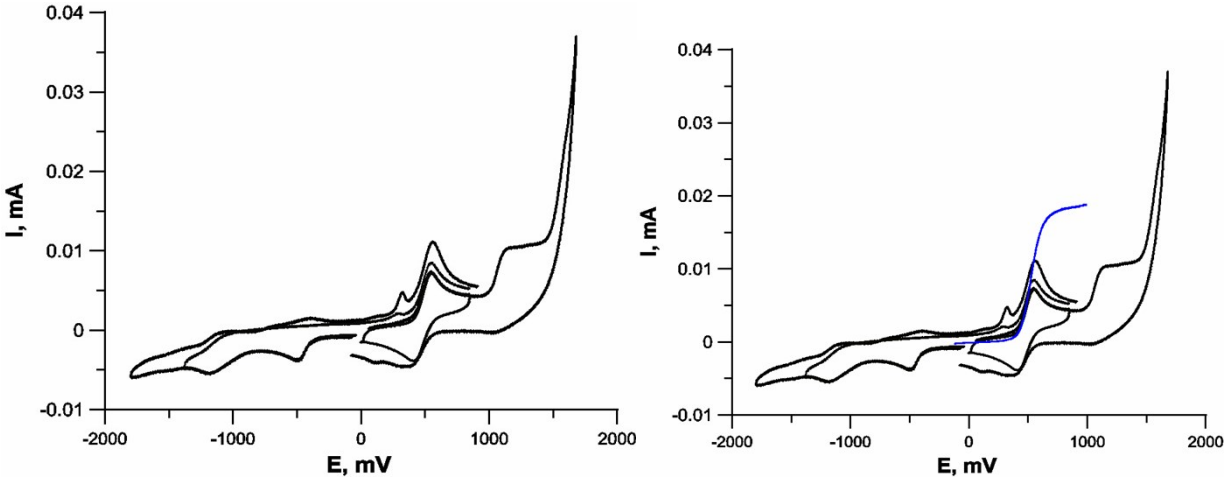

Figure S4. CV (left) and RDE (right, blue line) curves of compound **5b**.

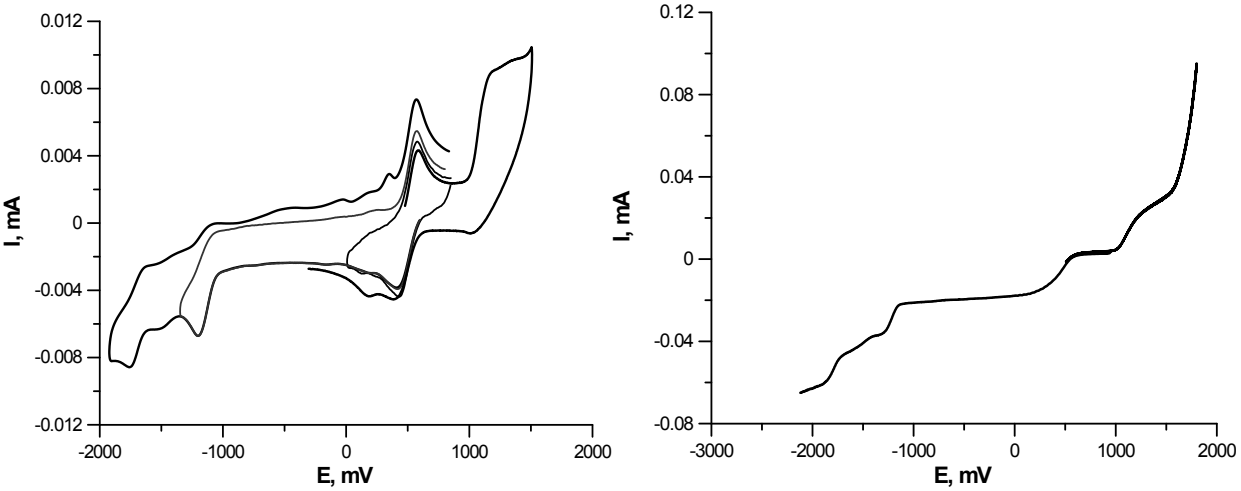

Figure S5. CV (left) and RDE (right) curves of coordination compound **4c**.

Figure S6. CV (left) and RDE (right) curves of compound **5c**.

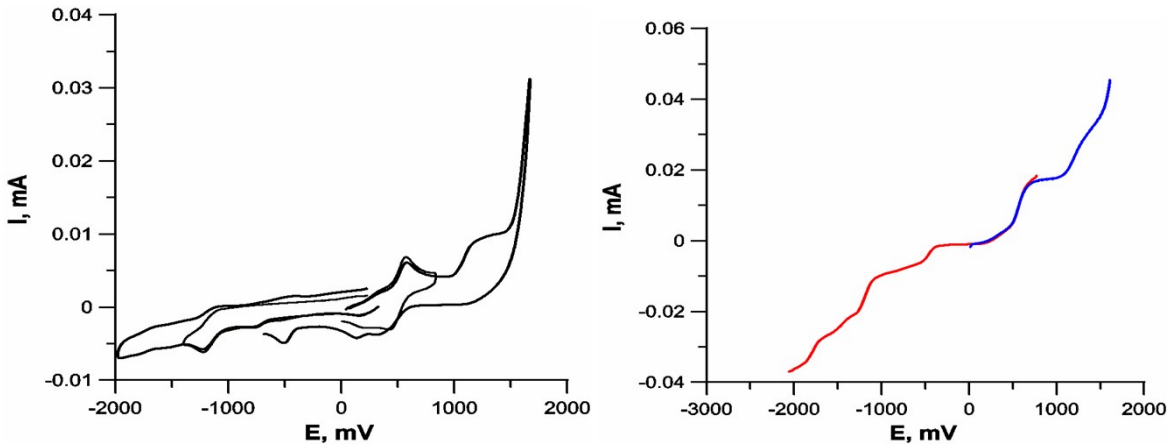

Figure S7. CV (left) and RDE (right) curves of coordination compound **6c**.

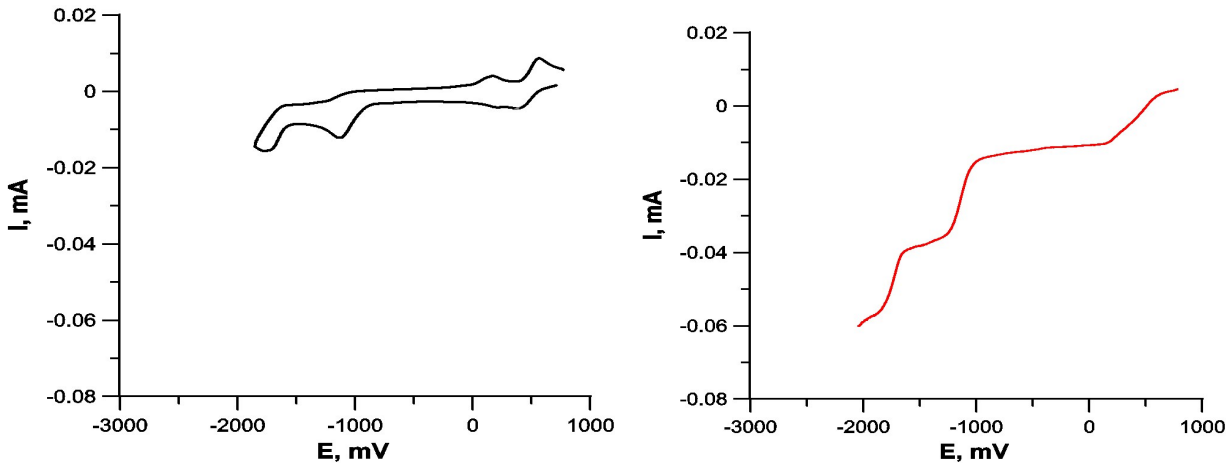

Figure S8. CV (left) and RDE (right) curves of coordination compound **4d**.

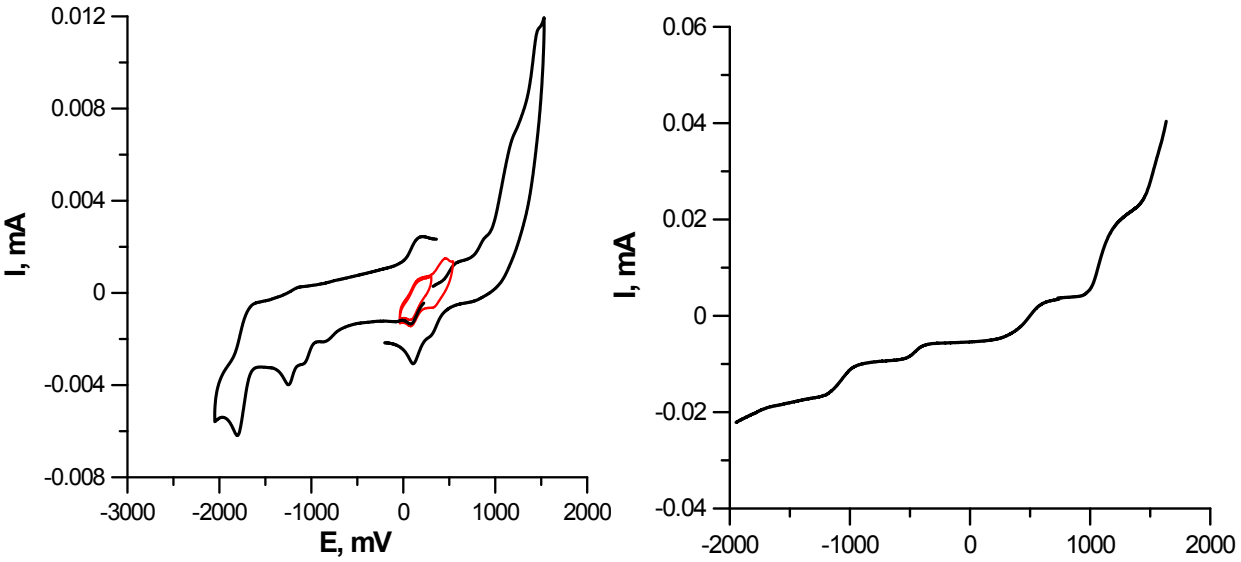

Figure S9. CV (left) and RDE (right) curves of coordination compound **4e**.

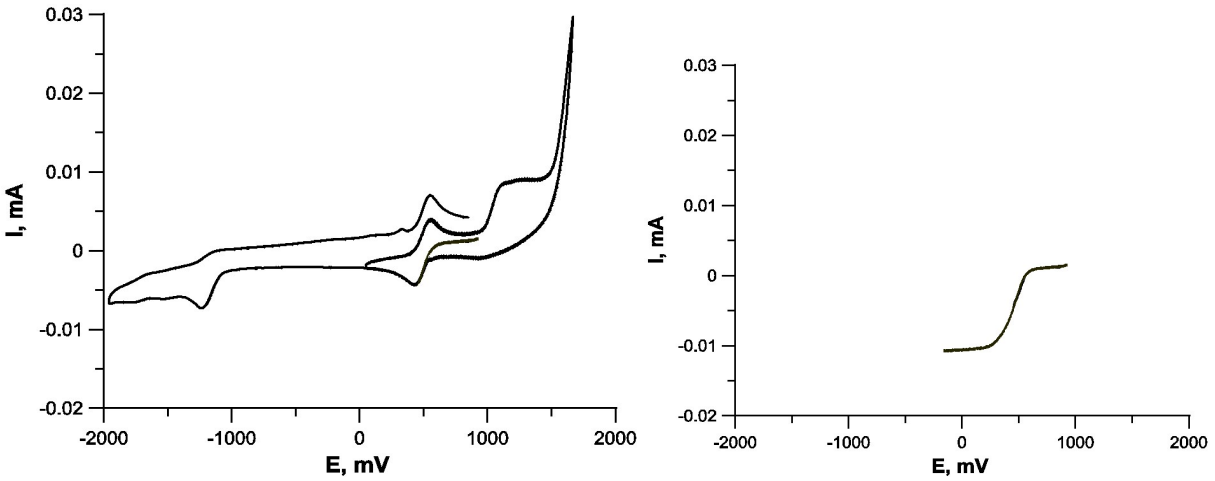

Figure S10. CV (left) and RDE (right) curves of coordination compound **4f**.

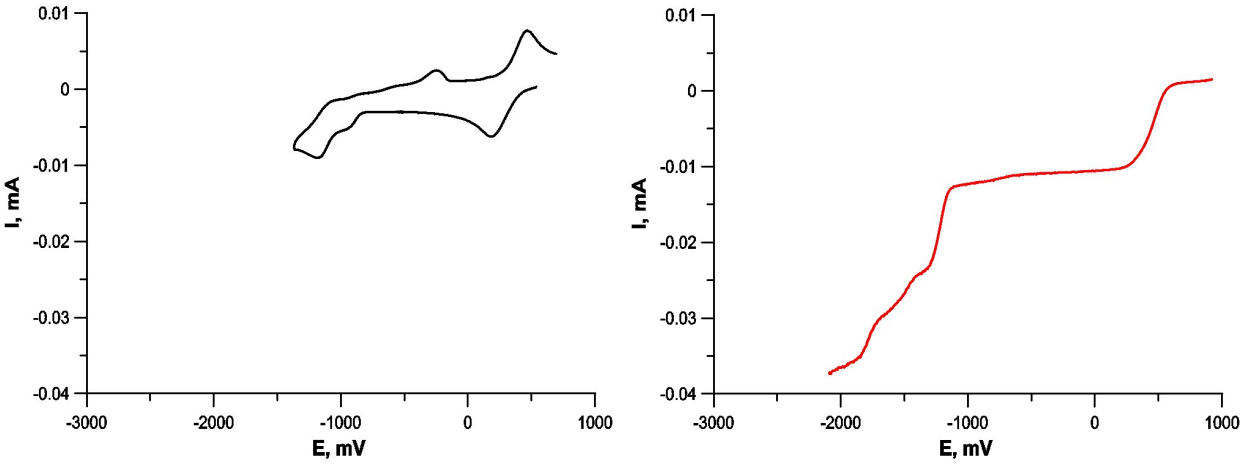

Figure S11. CV (left) and RDE (right) curves of coordination compound **4g**.

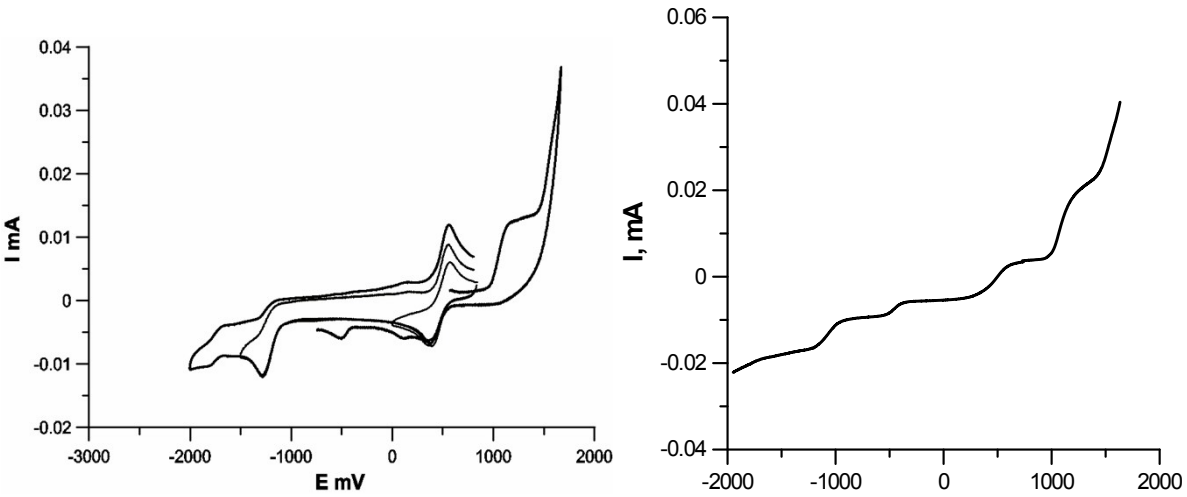

Figure S12. CV (left) and RDE (right) curves of coordination compound **4h**.

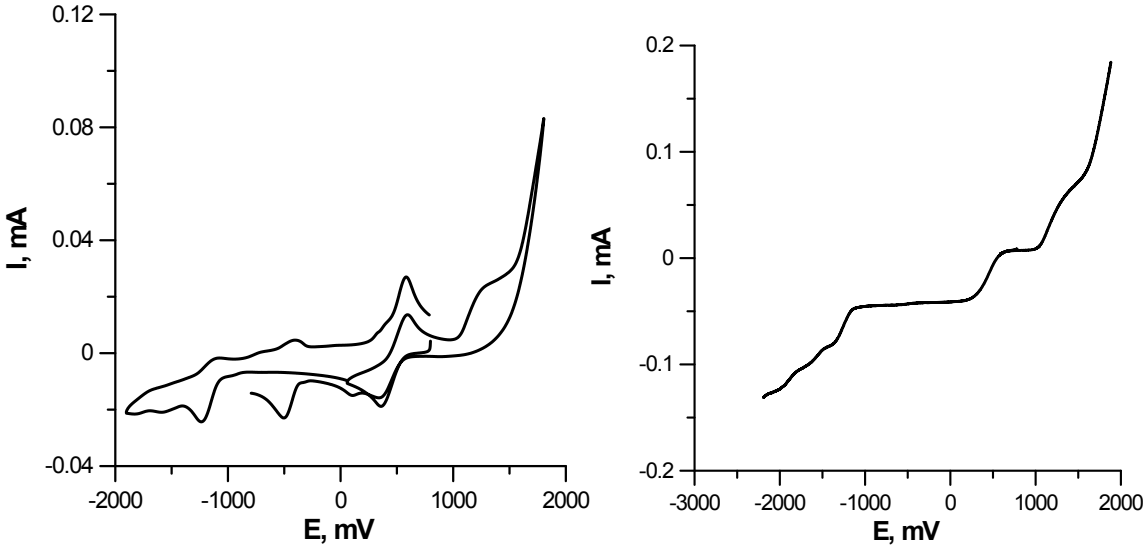

Figure S13. CV (left) and RDE (right) curves of coordination compound **4i**.

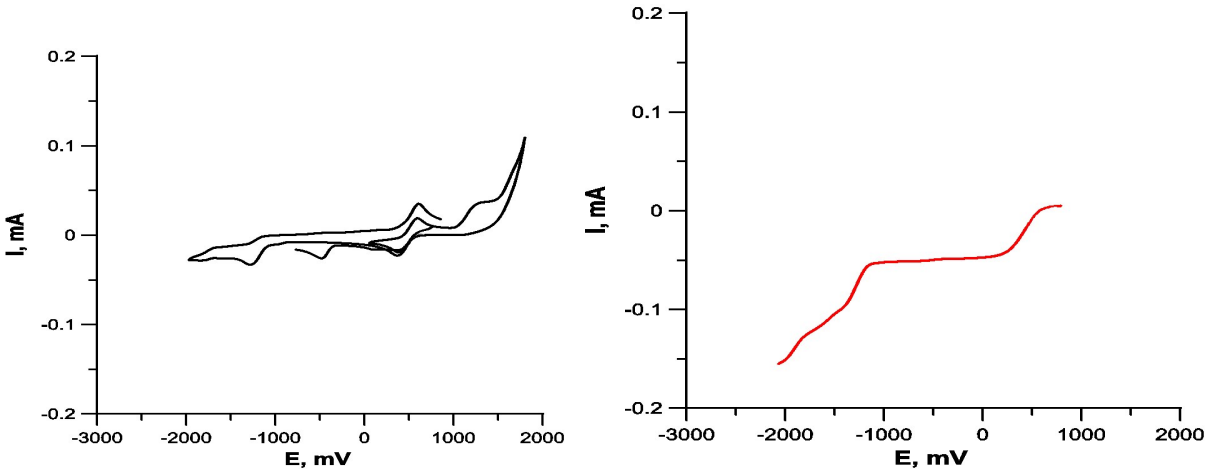

Figure S14. CV (left) and RDE (right) curves of coordination compound **4j**.

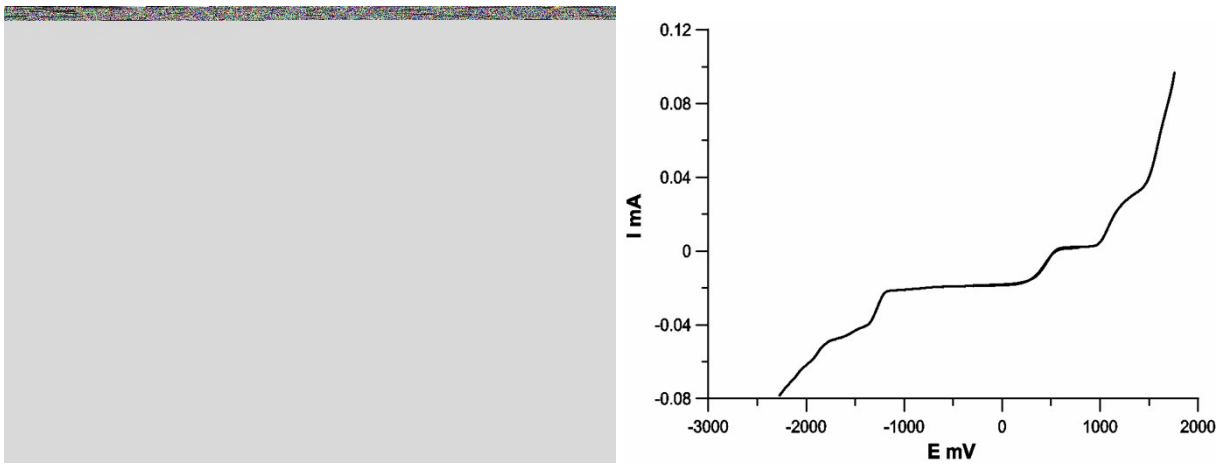

Figure S15. CV (left) and RDE (right) curves of coordination compound **4k**.

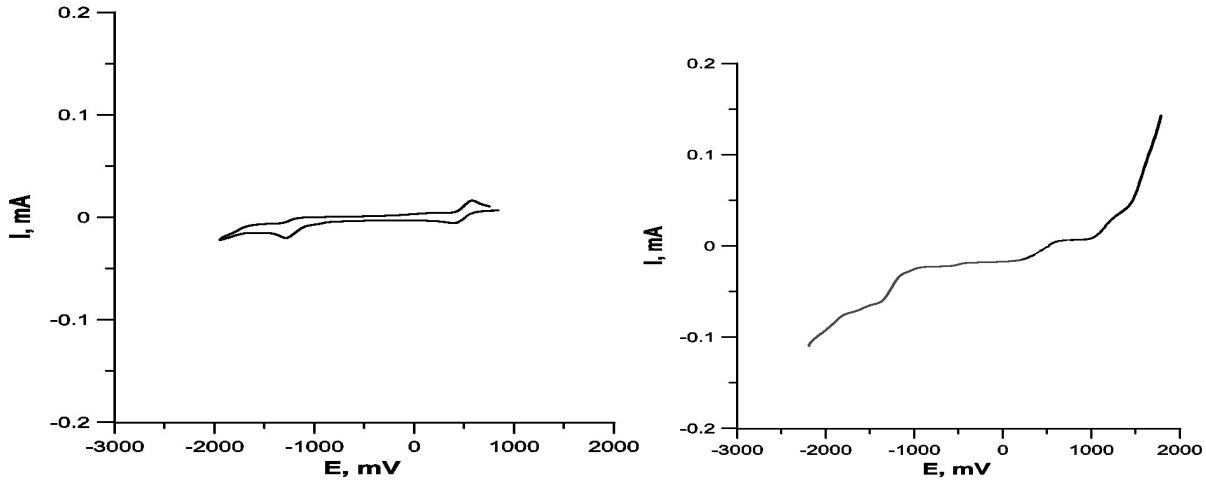

Figure S16. CV (left) and RDE (right) curves of coordination compound **4l**.

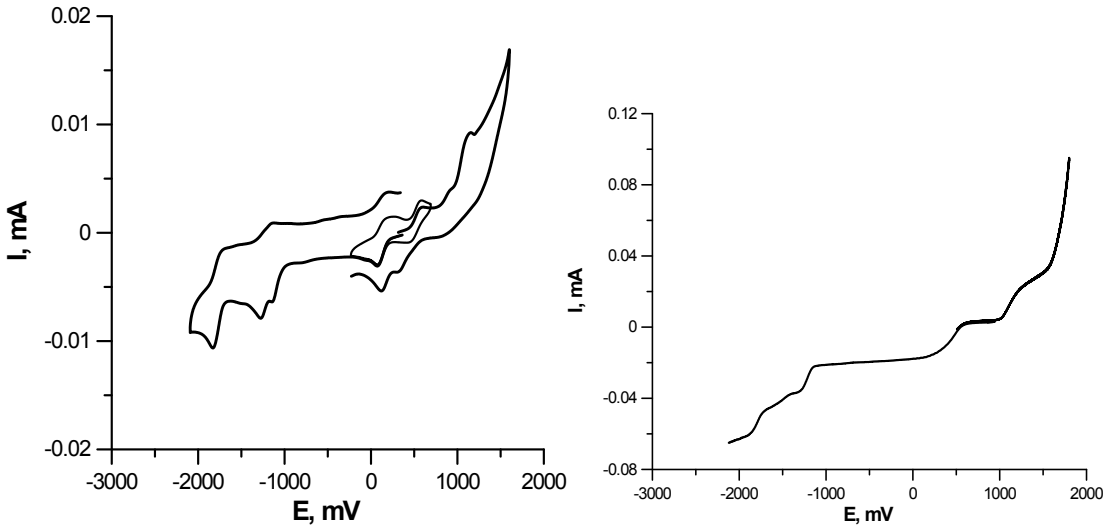

Figure S17. CV (left) and RDE (right) curves of coordination compound **4m**.

4. UV-vis

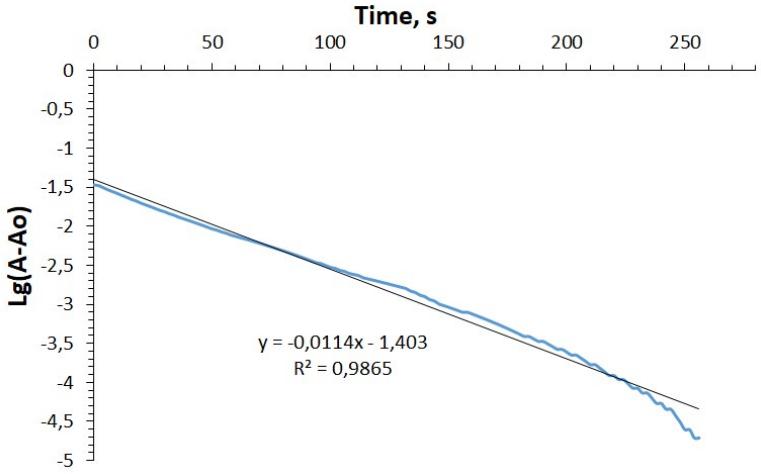

Figure S18. Linearization of the initial part of the kinetic curve of Cu^{II} disappearance based on UV-Vis spectroscopy data in coordinates Lg ($A-A_o$) / time.

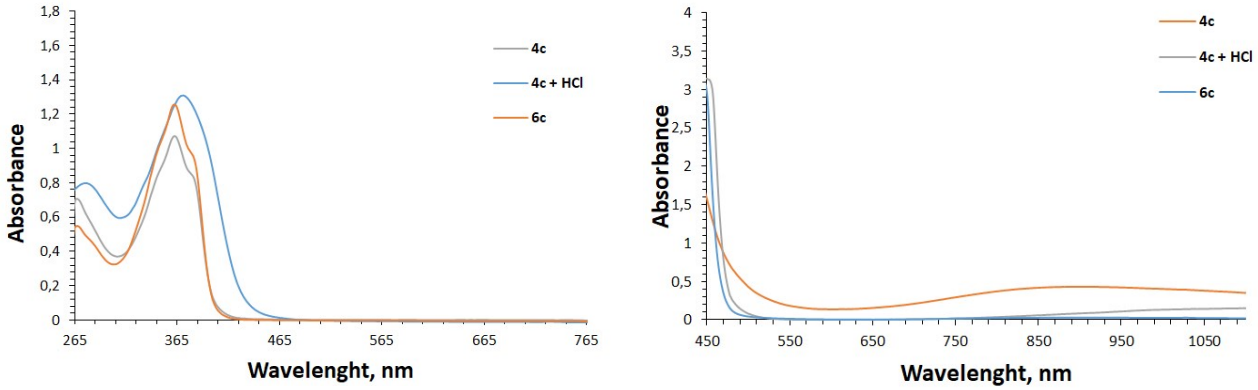

Figure S19. UV-vis spectra of the solutions of coordination compound **4c** in DMF before and after treatment with an equimolar amount of aqueous HCl, $6*10^{-5}$M (*left*), $6*10^{-3}$M (*right*).

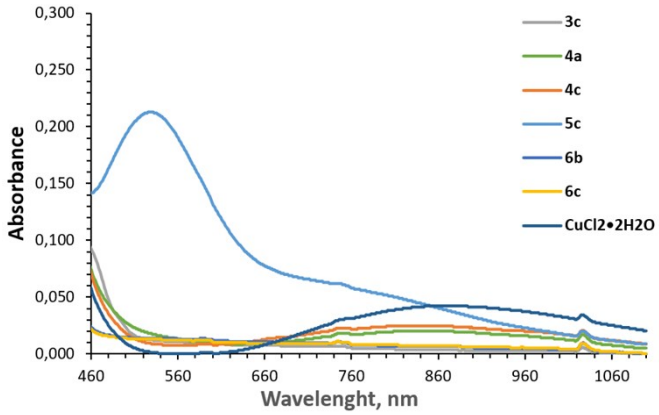

Figure S20. UV-vis spectra of the solutions of compounds **3c**, **4a**, **4c**, **5c**, **6b**, **6c** and $CuCl_2*2H_2O$ in DMF, $6*10^{-4}$M.

5. EPR

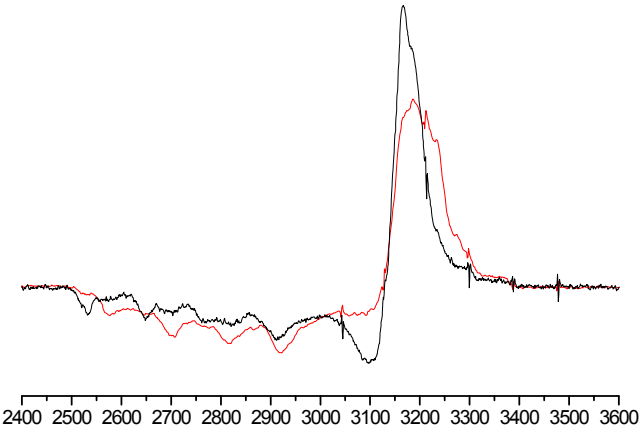

Figure S21. Comparison of EPR spectra of the solutions of $CuCl_2$ (*red*) and $CuCl_2*2H_2O$ (*black*) in DMF, $1.3*10^{-2}$M