Supplementary file 1. Synthetic route for 1-hydroxy-5-R-pyridine-2(1*H*)-thiones 2a-c.

General Procedure

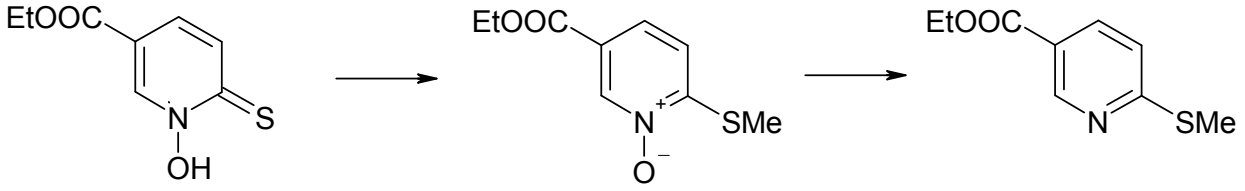
Solution of 2-{[amino(imino)methyl]thio}-1-hydroxy-5-R-pyridinium chloride (1 mmol) in 15 mL of water was treated by solution of 2 mmol sodium carbonate in 10 mL of water at room temperature. After 4 hours reaction mixture was acidified by conc water hydrochloric acid to pH~1 and formatted solid was filtered off.

Methyl 1-hydroxy-6-thioxo-1,6-dihydropyridine-3-carboxylate **2a.** Yield 58%. Mp. 76-9ºC (hexane). Mass (EI), *m/z* ($I_{relat.}$(%)): 184.2014 $[M]^+$ (72). $C_7H_7NO_3S$. ^{1}H NMR (DMSO-d_6): 3.77 (s, 3H, OCH_3), 7.57 (d, 1H, *J* = 9.8 Hz, CH), 7.69 (d, 1H, *J* = 9.8 Hz, CH), 8.74 (s, 1H, CH) ppm.

Ethyl 1-hydroxy-6-thioxo-1,6-dihydropyridine-3-carboxylate **2b.** Yield 74%. Mp. 67-9ºC (hexane). Mass (EI), *m/z* ($I_{relat.}$(%)): 198.2280 $[M]^+$ (84). $C_8H_9NO_3S$. ^{1}H NMR (DMSO-d_6): 1.28 (t, 3H, *J* = 6.9 Hz, CH_3), 4.28 (q, 2H, *J* = 7.2 Hz, CH_2), 7.59 (d, 1H, *J* = 9.8 Hz, CH), 7.68 (d, 1H, *J* = 9.8 Hz, CH), 8.74 (s, 1H, CH) ppm.

1-Hydroxy-5-(trifluoromethyl)pyridine-2(1H)-thione **2c.** Yield 67%. Mp. 83-5ºC (hexane). Mass (EI), *m/z* ($I_{relat.}$(%)): 194.1633 $[M]^+$ (62). $C_6H_4F_3NOS$. ^{1}H NMR (DMSO-d_6): 7.41 (d, 1H, *J* = 9.7 Hz, CH), 7.58 (d, 1H, *J* = 9.7 Hz, CH), 8.69 (s, 1H, CH) ppm.

Supplementary file 2. Synthesis of metabolites **3** and **4** of [2HPT-Cu^{2+}]**.**



Ethyl 6-(methylthio)nicotinate 1-oxide **3**

Solution of ethyl 1-hydroxy-6-thioxo-1,6-dihydropyridine-3-carboxylate 2b (500 mg, 2.35 mmol) in 15 mL of ethanol was treated by solution sodium hydroxide (100 mg, 2.5 mmol) in 1 mL of water at room temperature. After 1 hours reaction mixture was treated by methyl iodide (0.3 mL, 4.8 mmol) in one portion, left at this temperature for 2 hours and evaporated under vacuum. The yellow residue was recrystallised from ethylacetate. The yield of aim ethyl 6-(methylthio)nicotinate 1-oxide 3 was 88%. Mp. 119-21ºC. Mass (EI), *m/z* ($I_{relat.}$(%)): 212.2546 $[M]^+$ (37). $C_9H_{11}NO_3S$. ^1H NMR (DMSO-d_6): 1.29 (t, 3H, *J* = 6.8 Hz, CH_3), 2.56 (s, 3H, SCH_3), 4.31 (q, 2H, *J* = 7.2 Hz, CH_2), 7.61 (d, 1H, *J* = 9.7 Hz, CH), 7.72 (d, 1H, *J* = 9.7 Hz, CH), 8.67 (s, 1H, CH) ppm.

Ethyl 6-(methylthio)nicotinate **4**

Ethyl 6-(methylthio)nicotinate 1-oxide **3** (300 mg, 1.4 mmol) was solved in 15 ml of chloroform and phosphorus trichloride (0.24 mL, 2.8 mmol) was slow added by drop at 20 ^oC. The reaction mixture was left for 1 hour at room temperature, new portion of phosphorus trichloride (0.24 mL, 2.8 mmol) was added. The mixture was refluxed for 5 hours, cooled, dissolved by 50 mL of cold water and treated by saturated solution of sodium carbonate in water till pH~9. Organic phase was separated and washed 3 times by water, dried by sodium sulfate, filtered off through silica gel cushion and evaporated in vacuum. The yield of aim ethyl 6-(methylthio)nicotinate **4** **w**as 39% as yellow oil. Mass (EI), *m/z* ($I_{relat.}$(%)): 196.2552 $[M]^+$ (93). $C_9H_{11}NO_2S$. ^1H NMR (DMSO-d_6): 1.33 (t, 3H, *J* = 6.8 Hz, CH_3), 2.49 (s, 3H, SCH_3), 4.32 (q, 2H, *J* = 7.2 Hz, CH_2), 7.12 (d, 1H, *J* = 8.6 Hz, CH), 7.71 (d, 1H, *J* = 8.6 Hz, CH), 8.91 (s, 1H, CH) ppm.

Supplementary file 3. qPCR primers

	qPCR
Rv0186A_F	GGCTGTGGCTGTCGGGTTCG
Rv0186A_R	TGCAGCGGTAGGCGTCAC
Rv0846_F	GGACGGACGGCATCGGGAAGT
Rv0846_R	TGTCGGCGGCGGCGCTGTTGATGA
Rv0967_F	GGCGCTGAACCGGCTGAAGA
Rv0967_R	CGAGGACTGAACCGCTGAAT
Rv1909c_F	TGAATGCGCATCCACACG
Rv1909c_R	CGCAAGACCGGCAGAGGA
Rv1992c_F	GCTACCGCGGCCAACAACTC
Rv1992c_R	GGCGGCGGCGACTAATACCAC
Rv1994c_F	TTCTGGTGGCGTTGCTGGATG
Rv1994c_R	CACCGCGAGAACGACCTGGAC
Rv2641_F	GCCGCAATCACGTTCTACTCC
Rv2641_R	ACGTGGTGCCGATCTCCTTCT
Rv3270_F	GCGCGGCAACCAGGACACG
Rv3270_R	CGCGCACCACGACCGAACC