Supradecoration induced homogenous electrochemical sensing: Development of Ru(II)half sandwich complex as isoniazid and rifamipicin dual sensor

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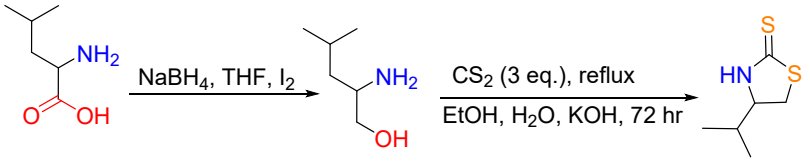
Supplementary Data:

Scheme S1: Synthesis of the ligand and the mechanism

Table S1: Comparative EIS parameters of Bare GCE, GCE/Ru(II) salt and GCE/Ru(II) half sandwich complex calculated through Z-fit analysis.

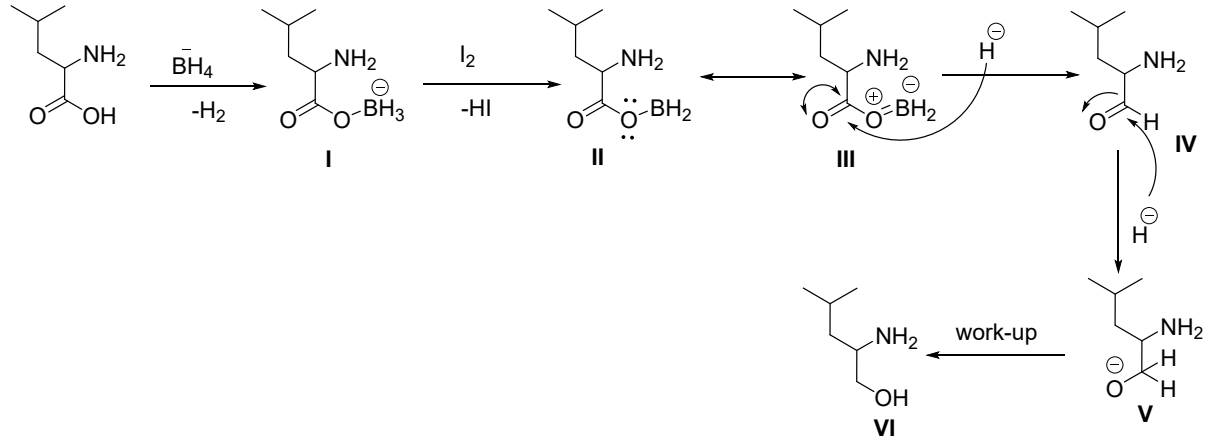
Fig. S1:DPVs measurements on GCE/Ru complex in acetonitrile solvent using NBu_4PF_6 as supporting electrolyte at scan rate of 50mV/s (A) Comparative DPVs of commercial tablet sample and laboratory test sample (B) Simultaneous determination of binary mixtures with varied concentrations of RIF and INH tablets.

Fig.S2: DPV measurements on GCE/Ru complex in acetonitrile solvent using NBu_4PF_6 as supporting electrolyte at scan rate of 50mV/s for RIF and INH in presence of naphthalene.

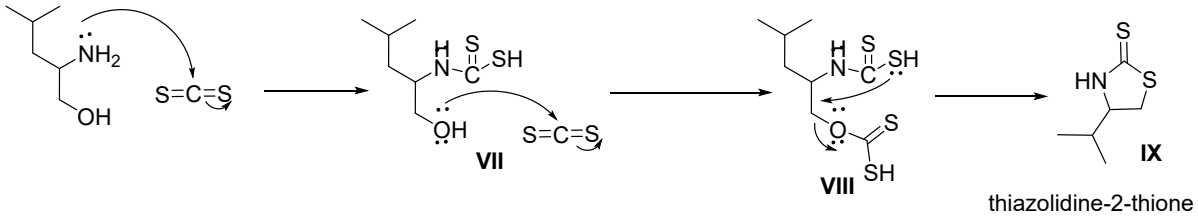


Mechanism:

Step I



Step II

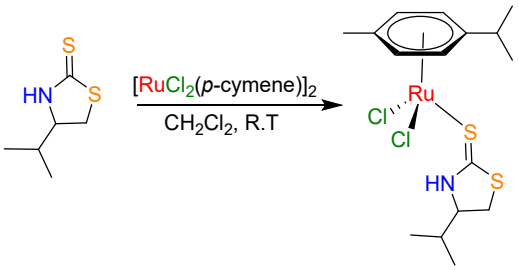


Scheme S1: Synthesis of the ligand (top) and the mechanism.

Step I: Reduction of the amino acid: The reduction of valine was carried out using sodium borohydride and iodine. Initially, the hydride ion from sodium borohydride reacts with the acidic proton of valine, converting it into a carboxylate ion. This carboxylate ion forms an adduct (I) with borane (BH_3). Subsequent reaction with iodine results in the removal of a hydride ion, leading to intermediate II. A nucleophilic substitution reaction then converts the intermediate into an amino aldehyde (IV), which undergoes further reduction by another hydride ion to form the amino alcohol (VI).

Step II: Formation of the thiazolidine-2-thione ring: The amino alcohol produced in Step I undergoes nucleophilic addition with carbon disulfide (CS_2) via the amine group, resulting in intermediate VII. This intermediate then reacts with another molecule of CS_2 through its hydroxyl group, forming intermediate VIII. The addition of CS_2 enhances the hydroxyl group's leaving ability, enabling its elimination during a nucleophilic substitution by a thiol group, ultimately forming the thiazolidine-2-thione ring (IX).

Synthesis of the complex: The synthesis of the complex was attempted under room temperature stirring in DCM solvent as shown in Scheme S2.



Scheme S2. Synthesis of the ruthenium(II) half sandwich complex.

Table S1: EIS parameters of Bare GCE, GCE/Ru(II) salt and GCE/Ru(II) half sandwich complex calculated through Z-fit analysis.

Parameters	Bare GCE	GCE/Ru(II) salt	GCE/Ru(II) half sandwich complex
R1(kΩ)	0.99	0.66	0.36
R3(kΩ)	1130	1030	727

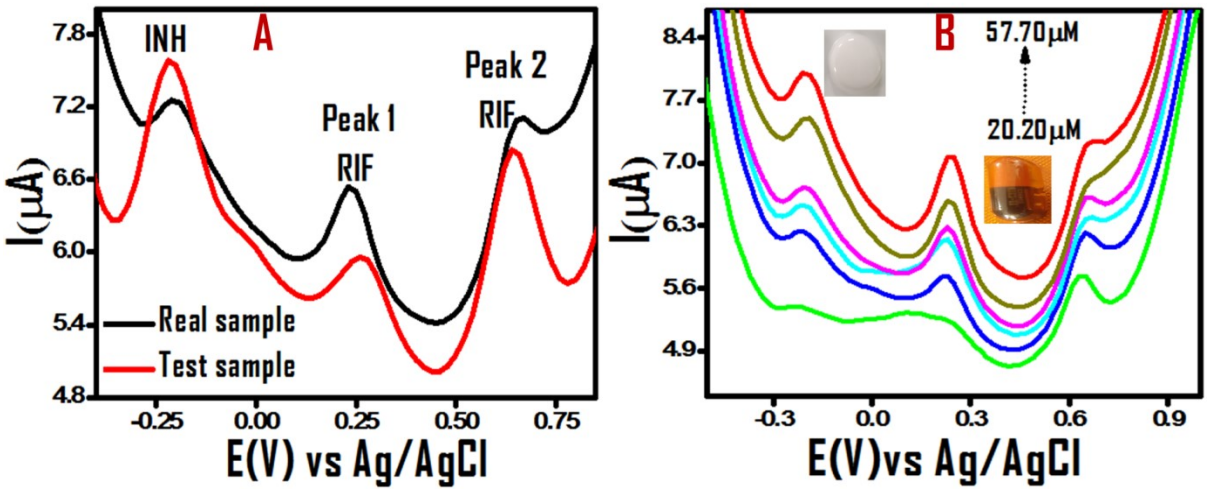


Fig.S1. DPVs measurements on GCE/Ru complex in acetonitrile solvent using NBu_4PF_6 as supporting electrolyte at scan rate of 50mV/s (A) Comparative DPVs of commercialtablet sample and laboratory test sample (B)Simultaneous determination of binary mixtures with varied concentrations of RIF and INH tablets.

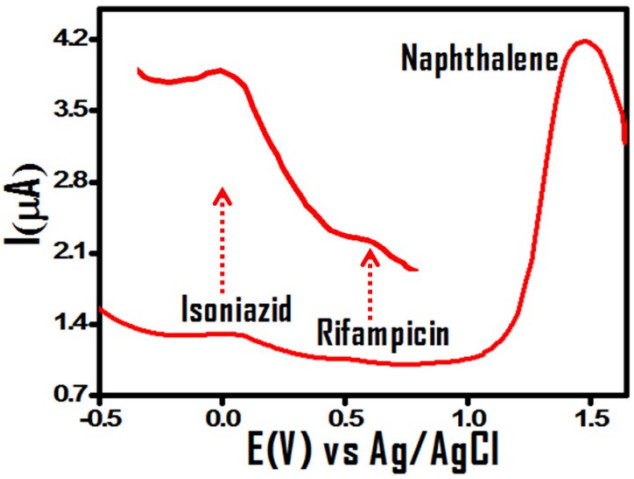


Fig.S2.DPV measurements on GCE/Ru complex in acetonitrile solvent using NBu_4PF_6 as supporting electrolyte at scan rate of 50mV/sfor RIF and INHin presence of naphthalene.