Dear Editor,

we thank Reviewers for the efforts and their comments on the Manuscript entitled **Redox properties of alkyl-substituted 4-aryl-2,4-dioxobutanoic acids**.

Here is our response to these comments

**Response to Reviewer A:**

1. **Reviewer A**: “The authors state that enol form of aryldiketo acids is the predominant one in aqueous solution under a broad range of pH values. Beta-dicarbonyl compounds can generally exist in several enol forms such as chelated enol, rotamer Z and E tautomers (see for instance: Phys.Chem.Chem.Phys., 2016, 18, 22168 and JSCS, Serb. Chem. Soc. (2016), doi: 10.2298/JSC160531085K). Thus, additional discussion about tautomer equilibrium in the examined solution as a function of pH is necessary in order to interpret the experimental results.“

We previously studied the keto-enol tautomerism of some representatives of aryldiketo acids. Detailed study of the tautomeric equilibria of 4-phenyl-2,4-dioxobutanoic acid (compound **1**) in aqueous media by 1H and 13C NMR spectroscopy was presented at the 49th *Meeting of the Serbian Chemical Soc*iety, Kragujevac, Serbia, 2011, and published as a 5 pages report within a Proeceedings book, **Ref 26** within this Manuscript:

T. Ž. Verbić, M. F. Zloh, D. M. Stanković, M. M. Sentić, D. D. Manojlović, I. O. Juranić, *Keto-enol tautomerism of aryldiketo acids in aqueous solution: NMR spectroscopy and cyclic voltammetry* study, in *Proceedings of the* 49th *Meeting of the Serbian Chemical Soc*iety, Kragujevac, Serbia, 2011, **pp. 16-20**.

Within this report we discussed NMR spectral data within pD range 1-10, and regions where comp. **1** is present as H2A, HA- and/or A2-. The results showed that when dissolved in highly acidic media (CF3COOD), **1** is in molecular (H2A) form and the enolate **I** is predominant, diketo form was not observed and the existence of enolate **III** was confirmed, but its concentration is negligible.

No signals of enolate **III,** and diketo form **II** were observed in NMR spectra of HA– and A2– forms. The reason for rather complicated structure of 1H NMR spectrum of HA– is possible rotation around single bond within keto-enol part of the molecule and the presence of *Z* and *E* isomers of the –CH=CH(OH)– bond. In A2– form *E* isomer is predominant, due to electrostatic repulsion between –COO– and –CH=C–O–. Since *π*-electron delocalization occurs in keto-enol part of the molecule, the distinction between tautomers is not possible.

As we plan to publish these results along with other NMR findings, we would rather keep these details for further publication.

Examples of keto-enol tautomerism studies of β-diketones are numerous, still we hope that literature cited within this Manuscript might be representative enough.

2. **Reviewer A**: “The optimized geometries and energies of all structures should be given in the SI.”

Optimized geometries and energies of studied compounds **1**-**9** in their molecular (H2A) and monoanionic (HA–) form are added as **Figures S22** and **S23** in Supplementary data material.

The following sentence was added to the main Manuscript text (EXPERIMENTAL/*Calculations setup* – 2nd sentence in the paragraph): “Geometries and energies of H2A and HA– forms of **1**-**9** are given in Supplementary data, Fig. S22 and S23”.

3. **Reviewer A**: “In Figure 2, the phenyl ring substituent R is missing in the structure I.”

Figure 2 is redrawn, the phenyl ring substituent R is added to the enol form I.

**Response to Reviewer B:**

1. **Reviewer B:** “**line 16:** missing verb; it should be : The aim of this work was to…..”

Missing verb “was” is added, now the sentence is written as follows: “The aim of this work was to evaluate effects…”

2. **Reviewer B:** “**lines 75, 76 and 77** We observed strong quantitative linear correlations between reduction potentials and energies of frontier orbitals of compounds and a descriptor that accounts for steric factors.

This sentence should be deleted because it is already in the conclusion where it belongs.**”**

As suggested by the Reviewer, the whole sentence (the last from the Introduction) is deleted.

We truly hope that changes we made according to Reviewers’ comments will contribute to have this Manuscript accepted for publication in Journal of the Serbian Chemical Society.

On behalf of authors Belgrade

Respectfully, February 4, 2017

Tatjana Verbić