*Supplementary data for*

**Redox properties of alkyl-substituted 4-aryl-2,4-dioxobutanoic acids**

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Fig. S1. Chromatogram for the assessment of compound 1 purity, with the tables showing the detector response at three wavelengths

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Fig. S2. Chromatogram for the assessment of compound 2 purity, with the tables showing the detector response at three wavelengths.

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Fig. S3. Chromatogram for the assessment of compound 3 purity, with the tables showing the detector response at three wavelengths.

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Fig. S4. Chromatogram for the assessment of compound 4 purity, with the tables showing the detector response at three wavelengths.

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Fig. S5. Chromatogram for the assessment of compound 5 purity, with the tables showing the detector response at three wavelengths.

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Fig. S6. Chromatogram for the assessment of compound 6 purity, with the tables showing the detector response at three wavelengths.

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Fig. S7. Chromatogram for the assessment of compound 7 purity, with the tables showing the detector response at three wavelengths.

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Fig. S8. Chromatogram for the assessment of compound 8 purity, with the tables showing the detector response at three wavelengths.

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Fig. S9. Chromatogram for the assessment of compound 9 purity, with the tables showing the detector response at three wavelengths.

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| u boji Jelena.tif | 2 K1 LG.tif |

Fig. S10. Absorption spectra of compound 2 used for *K*a1 determination in solutions of different acidity, pH values are indicated; b) Spectrophotometric determination of *K*a1 according to Equation 1; *c*2=5.023×10-5 M; λ=302.9 nm; *t* = 25 °C, *I* = 0.1 M (NaCl); scan speed 500 nm/min.

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| u boji Jelena.tif | u boji Jelena2.tif |

Fig. S11.Absorption spectra of compound 2 used for *K*a2 determination in solutions of different acidity, pH values are indicated; b) Spectrophotometric determination of *K*a2 according to Equation 2; *c*2=5.023×10-5 M; λ=299.5 nm; *t* = 25 °C, *I* = 0.1 M (NaCl); scan speed 500 nm/min.

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| u boji Jelena.tif | 3 K1 LG.tif |

Fig. S12. Absorption spectra of compound 3 used for *K*a1 determination in solutions of different acidity, pH values are indicated; b) Spectrophotometric determination of *K*a1 according to Equation 1; *c*3=4.908×10-5 M; λ=305.4 nm; *t* = 25 °C, *I* = 0.1 M (NaCl); scan speed 500 nm/min.

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| u boji Jelena1.tif | u boji Jelena.tif |

Fig. S13. Absorption spectra of compound 3 used for *K*a2 determination in solutions of different acidity, pH values are indicated; b) Spectrophotometric determination of *K*a2 according to Equation 2; *c*3=4.908×10-5 M; λ=250.0 nm; *t* = 25 °C, *I* = 0.1 M (NaCl); scan speed 500 nm/min.

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| u boji Jelena.tif | 5 K1 LG.tif |

Fig. S14. Absorption spectra of compound 5 used for *K*a1 determination in solutions of different acidity, pH values are indicated; b) Spectrophotometric determination of *K*a1 according to Equation 1; *c*5=6.021×10-5 M; λ=312.3 nm; *t* = 25 °C, *I* = 0.1 M (NaCl); scan speed 500 nm/min.

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| u boji Jelena1.tif | u boji Jelena2.tif |

Fig. S15. Absorption spectra of compound 5 used for *K*a2 determination in solutions of different acidity, pH values are indicated; b) Spectrophotometric determination of *K*a2 according to Equation 2; *c*5=6.021×10-5 M; λ=305.9 nm; *t* = 25 °C, *I* = 0.1 M (NaCl); scan speed 500 nm/min.

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| u boji Jelena.tif | u boji Jelena1.tif |

Fig. S16. Absorption spectra of compound 6 used for *K*a1 determination in solutions of different acidity, pH values are indicated; b) Spectrophotometric determination of *K*a1 according to Equation 1; *c*6=9.014×10-5 M; λ=306.3 nm; *t* = 25 °C, *I* = 0.1 M (NaCl); scan speed 500 nm/min.

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| u boji Jelena2.tif | u boji Jelena4.tif |

Fig. S17. Absorption spectra of compound 6 used for *K*a2 determination in solutions of different acidity, pH values are indicated; b) Spectrophotometric determination of *K*a2 according to Equation 2; *c*6=9.014×10-5 M; λ=303.7 nm; *t* = 25 °C, *I* = 0.1 M (NaCl); scan speed 500 nm/min.

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| 8 K1.tif | 8 K1 LG.tif |

Fig. S18. Absorption spectra of compound 8 used for *K*a1 determination in solutions of different acidity, pH values are indicated; b) Spectrophotometric determination of *K*a1 according to Equation 1; *c*8=5.904×10-5 М; λ=308.8 nm; *t* = 25 °C, *I* = 0.1 M (NaCl); scan speed 500 nm/min.

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| 8 K2.tif | 8 K2 LG.tif |

Fig. S19. Absorption spectra of compound 8 used for *K*a2 determination in solutions of different acidity, pH values are indicated; b) Spectrophotometric determination of *K*a2 according to Equation 2; *c*8=5.904×10-5 М; λ=308.0 nm; *t* = 25 °C, *I* = 0.1 M (NaCl); scan speed 500 nm/min.

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| 9 K1.tif | 9 K1 LG.tif |

Fig. S20. Absorption spectra of compound 9 used for *K*a1 determination in solutions of different acidity, pH values are indicated; b) Spectrophotometric determination of *K*a1 according to Equation 1; *c*9=6.066×10-5 M; λ=293.0 nm; *t* = 25 °C, *I* = 0.1 M (NaCl); scan speed 500 nm/min.

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| 9 K2.tif | 9 K2 LG.tif |

Fig. S21. Absorption spectra of compound 9 used for *K*a2 determination in solutions of different acidity, pH values are indicated; b) Spectrophotometric determination of *K*a2 according to Equation 2; *c*9=6.066×10-5 M; λ=296.0 nm; *t* = 25 °C, *I* = 0.1 M (NaCl); scan speed 500 nm/min.

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| 1.tif  *E*MP2 (**1**) = – 684.84726595 a.u. | 2.tif  *E*MP2 (**2**) = –724.03224506 a.u. | 3.tif  *E*MP2 (**3**) = –724.03498687 a.u. |
| 4.tif  *E*MP2 (**4**) = –724.03499614 a.u. | 5.tif  *E*MP2 (**5**) = – 763.21997190 a.u. | 6.tif  *E*MP2 (**6**) = –763.21991834 a.u. |
| *7.tif*  *E*MP2 (**7**) = –763.22322889 a.u. | *8.tifE*MP2 (**8**) = –802.40826292 a.u. | *9.tifE*MP2 (**9**) = –841.58953327 a.u. |

Fig. S22. Optimized geometries and energies of 1-9 in their molecular (H2A) form; MP2/6-31g (d,p) with PCM water solvation.

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| 1.tif  *E*MP2 (**1**) = –684.37315611a.u. | *2an.tifE*MP2 (**2**) = –723.55802347 a.u. | 3.tif  *E*MP2 (**3**) = –723.56071545 a.u. |
| 4.tif  *E*MP2 (**4**) = –723.56057061 a.u. | 5.tif  *E*MP2 (**5**) = –762.74543555 a.u. | 6.tif  *E*MP2 (**6**) = –762.74547392 a.u. |
| *7.tif*  *E*MP2 (**7**) = –762.74862068 a.u. | *8.tifE*MP2 (**8**) = –801.93348802 a.u. | *9.tifE*MP2 (**9**) = -841.11570354 a.u. |

Fig. S23. Optimized geometries and energies of **1**-**9** in their monoanionic (HA–) form; MP2/6-31g (d,p) with PCM water solvation.

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| 1 CV.tif | 2 CV.tif |
| 3 CV.tif | 5 CV.tif |
| 6 CV.tif | 7 CV.tif |
| 8 CV.tif | 9 CV.tif |

Fig. S24. Cyclic voltammograms of compounds 1-3 and 5-9 in Britton-Robinson buffer at pH 1, pH 5, and pH 10. a) 1, *c*1= 5.46×10-5 M; b) 2, *c*2 = 4.61×10-5 M; c) 3, *c*3 = 6.54×10-5 M; d) 5, *c*5 = 6.58×10-5 M; e) 6, *c*6 = 4.09×10-5 M; f) 7, *c*7 = 5.22×10-5 M; g) 8, *c*8 = 4.06×10-5 M; h) 9, *c*9 = 4.43×10-5 M; scan rate 100 mV/s, *t*=25±1 ºC.

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| 2DPP.tif | 3 DPP.tif |
| 4 DPP.tif | 5 DPP.tif |
| 6 DPP.tif | 7 DPP.tif |
| 8 DPP.tif | 9 DPP.tif |

Fig. S25. Differential pulse polarograms of comp. 2-9 in Britton-Robinson buffer at pH 1, pH 5, and pH 10; a) 2, *c*2 = 4.61×10-5 M; b) 3, *c*3 = 6.54×10-5 M; c) 4, *c*4 = 4.77×10-5 M d) 5, *c*5 = 6.58×10-5 M; e) 6, *c*6 = 4.09×10-5 M; f) 7, *c*7 = 5.22×10-5 M; g) 8, *c*8 = 4.06×10-5 M; h) 9, *c*9 = 4.43×10-5 M; scan rate 13 mV/s, *t*=25±1 ºC.

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| 4Me_homo | 25diMe_homo | 2356tetraMe_homo |
| Compound **4** | Compound **6** | Compound **9** |

Fig. S26. HOMO orbitals of H2A form of compounds 4, 6 and 9 plotted on isocontour level 0.03.

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| 4Me_lumo | 25diMe_lumo | 2356tetraMe_lumo |
| Compound **4** | Compound **6** | Compound **9** |

Fig. S7. LUMO orbitals of H2A form of compounds **4**, **6** and **9** plotted on isocontour level 0.03.

Table SI. Energies of FMOs (given in Hartree), and dipoles (given in Debye) for molecular and monoanionic form of compounds 1-9.

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|  | **Neutral (H2A)** | | | | **Anion (HA–)** | | | |
| Compound | HOMO | LUMO | HOMO-LUMO gap | Dipole | HOMO | LUMO | HOMO-LUMO gap | Dipole |
| **1** | -0.3470 | 0.0367 | 0.3837 | 2.7040 | -0.3321 | 0.0625 | 0.3946 | 20.1289 |
| **2** | -0.3359 | 0.0406 | 0.3764 | 2.3366 | -0.3274 | 0.0670 | 0.3944 | 20.7147 |
| **3** | -0.3363 | 0.0377 | 0.3740 | 2.8168 | -0.3266 | 0.0625 | 0.3891 | 22.3967 |
| **4** | -0.3360 | 0.0394 | 0.3754 | 3.2365 | -0.3244 | 0.0641 | 0.3885 | 22.8528 |
| **5** | -0.3299 | 0.0417 | 0.3716 | 2.8786 | -0.3213 | 0.0683 | 0.3896 | 23.1538 |
| **6** | -0.3236 | 0.0401 | 0.3638 | 2.6851 | -0.3172 | 0.0670 | 0.3842 | 21.9031 |
| **7** | -0.3300 | 0.0403 | 0.3703 | 3.3452 | -0.3199 | 0.0641 | 0.3840 | 24.8252 |
| **8** | -0.3196 | 0.0425 | 0.3621 | 3.1584 | -0.3129 | 0.0687 | 0.3816 | 24.0766 |
| **9** | -0.3100 | 0.0448 | 0.3548 | 2.4134 | -0.3063 | 0.0778 | 0.3840 | 22.9021 |

Table SII. Energies of FMOs (given in Hartree), and dipole moments (given in Debye) for radical anion and radical cation derived from molecular form (H2A) or monoanionic form (HA–) of compounds 1-9. Energies of αSOMO and αLUMO are shown.

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|  | **Radical anion from H2A** | | | | **Radical cation from H2A** | | | |
| Compound | SOMO | LUMO | SOMO-LUMO gap | Dipole | SOMO | LUMO | SOMO-LUMO gap | Dipole |
| **1** | 0.0757 | 0.2471 | 0.1713 | 5.1253 | -0.3009 | -0.1600 | 0.1409 | 2.2888 |
| **2** | 0.0767 | 0.2475 | 0.1708 | 5.6837 | -0.2996 | -0.1579 | 0.1417 | 3.0584 |
| **3** | 0.0756 | 0.2459 | 0.1703 | 6.6132 | -0.2989 | -0.1576 | 0.1413 | 3.3480 |
| **4** | 0.0765 | 0.2458 | 0.1693 | 7.3901 | -0.2970 | -0.1551 | 0.1419 | 2.9073 |
| **5** | 0.0774 | 0.2465 | 0.1691 | 7.7582 | -0.2761 | -0.1313 | 0.1449 | 2.9050 |
| **6** | 0.0766 | 0.2443 | 0.1677 | 7.0045 | -0.2975 | -0.1555 | 0.1421 | 3.4272 |
| **7** | 0.0763 | 0.2452 | 0.1690 | 8.6434 | -0.2749 | -0.1306 | 0.1443 | 3.1645 |
| **8** | 0.0772 | 0.2461 | 0.1689 | 8.8467 | -0.2751 | -0.1316 | 0.1435 | 1.9357 |
| **9** | 0.0784 | 0.2537 | 0.1754 | 8.6062 | -0.2532 | -0.0821 | 0.1711 | 10.3233 |
|  | **Radical dianion from HA-** | | | |  |  |  |  |
| Compound | SOMO | LUMO | SOMO-LUMO gap | Dipole |  |  |  |  |
| **1** | 0.1658 | 0.3866 | 0.2208 | 12.3478 |  |  |  |  |
| **2** | 0.1685 | 0.3824 | 0.2138 | 14.5640 |  |  |  |  |
| **3** | 0.1641 | 0.3836 | 0.2195 | 15.5722 |  |  |  |  |
| **4** | 0.1645 | 0.3812 | 0.2167 | 15.8690 |  |  |  |  |
| **5** | 0.1669 | 0.3779 | 0.2109 | 17.5080 |  |  |  |  |
| **6** | 0.1664 | 0.3836 | 0.2172 | 16.0213 |  |  |  |  |
| **7** | 0.1631 | 0.3817 | 0.2186 | 18.6586 |  |  |  |  |
| **8** | 0.1665 | 0.3795 | 0.2130 | 19.1801 |  |  |  |  |
| **9** | 0.1875 | 0.3529 | 0.1654 | 23.1287 |  |  |  |  |

Table SIII. Intercorrelation matrix (*r* values) between oxidation/reduction potentials at pH 1 and at pH 5 and descriptors extracted from QM calculations. Indicator variable (*I*) is also included. ‘Molecular’ refer to neutral form of compounds; ‘anion’ refer to anionic form of compounds (deprotonated carboxyl group); ‘RA’ refer to radical anion/dianion (derived from neutral/anionic form); ‘RC’ refer to radical cation derived from neutral form.

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| ***E*ox-pH\_1** | | ***E*red-pH\_1** | |
| HOMO molecular | -0.6797 | HOMO molecular | 0.3250 |
| LUMO molecular | -0.5739 | LUMO molecular | 0.2916 |
| HOMO-LUMO gap/molecular | 0.6876 | HOMO-LUMO gap/molecular | -0.3233 |
| Dipole molecular | 0.3642 | Dipole molecular | -0.6104 |
| SOMO (RC) | -0.6565 | SOMO (RA) | 0.3298 |
| LUMO (RC) | -0.7924 | LUMO (RA) | 0.8713 |
| SOMO-LUMO gap/RC | -0.9352 | SOMO-LUMO gap/RA | 0.9361 |
| Dipole RC | -0.9519 | Dipole RA | -0.0503 |
| *I* | -0.7908 | *I* | 0.5906 |
| ***E*ox-pH\_5** | | ***E*red-pH\_5** | |
| HOMO molecular | -0.4092 | HOMO anion | 0.8213 |
| LUMO molecular | -0.3958 | LUMO anion | 0.7433 |
| HOMO-LUMO gap/molecular | 0.3999 | HOMO-LUMO gap/anion | -0.6495 |
| Dipole molecular | 0.4117 | Dipole molecular | -0.3518 |
| SOMO (RC) | -0.4353 | SOMO dianion (RA) | 0.6858 |
| LUMO (RC) | -0.6048 | LUMO dianion (RA) | -0.6739 |
| SOMO-LUMO gap/cation (RC) | -0.8283 | SOMO-LUMO gap/dianion (RA) | -0.6869 |
| Dipole (RC) | -0.9067 | Dipole dianion (RA) | 0.7311 |
| *I* | -0.5295 | *I* | 0.9533 |

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2. &*We regret to inform that Branko Drakulić has passed away since completion of this work.* [↑](#footnote-ref-2)