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SUPPLEMENTARY MATERIAL TO

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

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*2,4-Dioxo-4-phenylbutanoic acid (**1**)*. Yield: 7.90 g, 80 %; pale yellow powder; m.p.: 142–143 °C, dcc** (from AcOEt/benzene); $C_{10}H_8O_4$, FW: 192.17; IR (ATR, cm^{-1}): 2997 *br* (COO–H st), 1720 (C=O st), 1626 (C=O st***), 1275 (C–O st); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 13.55 (1H, *s*, COOH), 8.00 (2H, *d*, *J* = 8.4 Hz, *o*-H), 7.65 (1H, *t*, *J* = 7.3 Hz, *p*-H), 7.51 (2H, *t*, *J* = 7.3 Hz, *m*-H), 7.32 (1H, *s*, probably from CH of the less abundant enol form), 7.08 (1H, *s*, CH of the enol form), 4.57 (1H, *bs*, CH_2 of the diketo from); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 190.88, 170.60, 163.56, 134.97, 134.33, 129.43, 129.22, 128.83, 128.68, 128.20, 98.21, 49.60. Two tautomeric forms were visible in DMSO solution, and the signal at 49.60 ppm corresponds to the methylene group of the diketo tautomer.

*4-(2-Methylphenyl)-2,4-dioxobutanoic acid (**2**)*. Yield: 1.25 g, 76 %; white solid; m.p.: 106–108 °C, dcc (from EtOH); $C_{11}H_{10}O_4$, FW: 206.19; IR (ATR, cm^{-1}): 2991 *br* (COO–H st), 1710 (C=O st), 1635 (C=O st), 1279 (C–O st); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 7.68 (1H, *d*, *J* = 8.4 Hz, *o*-H), 7.48 (1H, *t*, *J* = 7.3 Hz, *m*-H), 7.35 (1H, *t*, *p*-H), overlapped with 7.31 (1H, *d*, *J* = Hz, *m*-H), 6.71 (1H, *s*, CH of enol form), 4.48 (*bs*, CH_2 of diketo form), 2.45 (3H, *s*, CH_3); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 194.66, 168.48, 163.35, 137.50,

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Decomposition; * stretching

135.86, 132.13, 131.83, 129.04, 126.32, 101.69, 51.78, 20.62; ESI-HR/MS: Calcd. for $C_{11}H_9O_4$ (M–H): 205.0501. Found: 205.0509.

*4-(3-Methylphenyl)-2,4-dioxobutanoic acid (**3**)*. Yield: 0.82 g, 73 %; white solid; m.p.: 98–99 °C (from EtOH), $C_{11}H_{10}O_4$, FW: 206.19; IR (ATR, cm^{-1}): 3501 *br* (COO–H st), 1683 (C=O st), 1628 (C=O st), 1257 (C–O st); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 7.84 (1H, *s*, *o*-H), 7.80 (1H, *d*, *J* = 8.0 Hz, *o*-H), 7.45 (1H, *d*, *J* = 8.0 Hz, *p*-H) , 7.41 (1H, *t*, *J* = 8.0 Hz, *m*-H), 7.06 (1H, *s*, CH of enol form), 4.53 (*bs*, CH_2 of diketo form), 2.36 (3H, *s*, CH_3); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 190.70, 170.30, 163.30, 138.72, 134.78, 134.70, 129.08, 128.30, 125.15, 97.95, 53.13, 20.84; ESI-HR/MS: Calcd. for $C_{11}H_9O_4$ (M–H): 205.0501. Found: 205.0508.

*4-(4-Methylphenyl)-2,4-dioxobutanoic acid (**4**)*. Yield: 6.30 g, 61 %; light yellow crystals; m.p.: 140–141 °C (from AcOEt/PhMe); $C_{11}H_{10}O_4$, FW: 206.19; IR (ATR, cm^{-1}): 3520 *br* (COO–H st), 1603 (C=O st), 1248 (C–O st); ^{1}H-NMR (500 MHz, CD_3OD, δ / ppm): 7.93 (2H, *d*, *J* = 8.2 Hz, 2× *o*-H), 7.85 (less abundant tautomer, *d*, *J* = 8.2 Hz), 7.35 (2H, *d*, *J* = 8.0 Hz, 2× *m*-H), 7.30 (less abundant tautomer, *d*, *J* = 8.0 Hz), 7.09 (1H, *s*, CH of enol form), 2.41 (3H, *s*, CH_3); ^{13}C-NMR (125 MHz, CD_3OD, δ / ppm): 191.98, 171.05, 165.15, 146.49, 133.91, 130.68, 129.20, 98.77, 21.84.

*4-(2,4-Dimethylphenyl)-2,4-dioxobutanoic acid (**5**)*. Yield: 5.21 g, 78 %; pale yellow solid; m.p.: 123–124 °C (from AcOEt/PhMe); $C_{12}H_{12}O_4$, FW: 220.22; IR (ATR, cm^{-1}): 2969 *br* (COO–H st), 1710 (C=O st), 1633 (C=O st), 1271 (C–O st); ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 7.60 (1H, *d*, *J* = 8.4 Hz, *o*-H), 7.11–7.15 (2H, *m*, overlapped *d* and *s* from 2× *m*-H), 6.96 (1H, *s*, CH of enol form), 2.55 (3H, *s*, CH_3), 2.38 (3H, *s*, CH_3); ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 194.32, 168.65, 164.85, 143.78, 139.32, 133.24, 131.90, 129.81, 127.02, 100.92, 21.59; ESI-HR/MS: Calcd. for $C_{12}H_{11}O_4$ (M–H): 219.0657. Found: 219.0663.

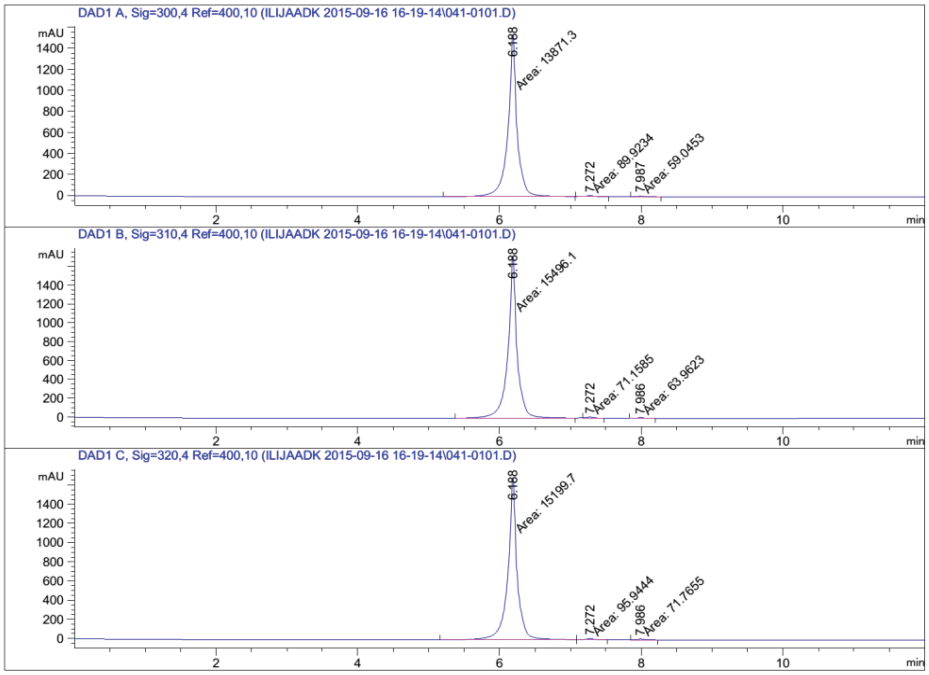
*4-(2,5-Dimethylphenyl)-2,4-dioxobutanoic acid (**6**)*. Yield: 7.93 g, 72 %; white powder; m.p.: 150–152 °C (from AcOEt/PhMe); $C_{12}H_{12}O_4$, FW: 220.22; IR (ATR, cm^{-1}): 2969 *br* (COO–H st), 1701 (C=O st), 1619 (C=O st), 1292 (C–O st); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 7.76 (1H, *s*, *o*-H), 7.71 (1H, *d*, *J* = 8.1 Hz, *p*-H), 7.28 (1H, *d*, *J* = 7.9 Hz, *m*-H), 6.65 (1H, *bs*, CH of enol form), 4.40 (*bs*, CH_2 of diketo form), 2.29 (6H, *s*, 2× CH_3); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 164.36, 137.00, 133.28, 130.00, 128.36, 125.10, 97.88, 19.61, 19.37.

*4-(3,4-Dimethylphenyl)-2,4-dioxobutanoic acid (**7**)*. Yield: 6.30 g, 57 %; white powder; m.p.: 175–177 °C, dcc (from AcOEt/PhMe); $C_{12}H_{12}O_4$, FW: 220.22; IR (ATR, cm^{-1}): 3474 *br* (COO–H st), 1705 (C=O st), 1612 (C=O st), 1261 (C–O st); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 7.78 (1H, *s*, *o*-H), 7.73 (1H, *d*, *J* = 8.1 Hz, *o*-H), 7.29 (1H, *d*, *J* = 7.9 Hz, *m*-H), 6.77 (1H, *bs*, CH of enol

form), 4.43 (*bs*, CH_2 of diketo from), 2.29 (6H, *s*, 2× CH_3); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 164.23, 142.62, 137.15, 133.09, 130.11, 128.49, 125.27, 97.73, 19.65, 19.36.

*2,4-Dioxo-4-(2,4,5-trimethylphenylbutanoic acid (**8**)*. Yield: 4.58 g, 68 %; pale yellow solid; m.p.: 139–141 °C (from AcOEt/PhMe); $C_{13}H_{14}O_4$, FW: 234.25; IR (ATR, cm^{-1}): 2925 *br* (COO–H st), 1709 (C=O st), 1619 (C=O st), 1275 (C–O st); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 7.52 (1H, *s*, *o*-H), 7.10 (1H, *s*, *m*-H), 6.80 (1H, *s*, CH of enol form), 4.47 (*bs*, CH_2 of diketo form), 2.43 (3H, *s*, CH3), 2.24 (6H, *s*, 2× CH_3); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 195.23, 167.80, 163.43, 141.66, 135.50, 134.29, 133.27, 132.81, 130.31, 101.23, 51.46, 20.52, 19.35, 18.65. Two tautomeric forms are visible in DMSO solution, and the signal at 51.46 ppm corresponds to the methylene group of the diketo tautomer; ESI-HR/MS: Calcd. for $C_{13}H_{13}O_4$ (M–H): 233.0819. Found: 233.0821.

*2,4-Dioxo-4-(2,3,5,6-tetramethylphenylbutanoic acid (**9**)*. Yield: 5.20 g, 78 %; white solid; m.p.: 156–158 °C dcc, (from AcOEt/PhMe); $C_{14}H_{16}O_4$, FW: 248.27; IR (ATR, cm^{-1}): 2962 *br* (COO–H st), 1743 (C=O st), 1599 (C=O st), 1261 (C–O st); ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 6.96 (1H, *s*, *p*-H), 6.21 (1H, *s*, CH of enol form), 2.13 (6H, *s*, 2× CH_3), 2.04 (6H, *s*, 2× CH_3); ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 196.89, 169.17, 163.77, 138.70, 133.87, 132.00, 129.19, 103.77, 19.29, 15.98; ESI-HR/MS: Calcd. for $C_{14}H_{15}O_4$ (M–H): 247.0976. Found: 247.0976.



Signal 1: DAD1 A, Sig=300,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.188	MM	0.1499	1.38713e4	1542.77527	98.9375
2	7.272	MM	0.1237	89.92340	12.11744	0.6414
3	7.987	MM	0.1303	59.04533	7.55190	0.4211
Totals :				1.40203e4	1562.44460	

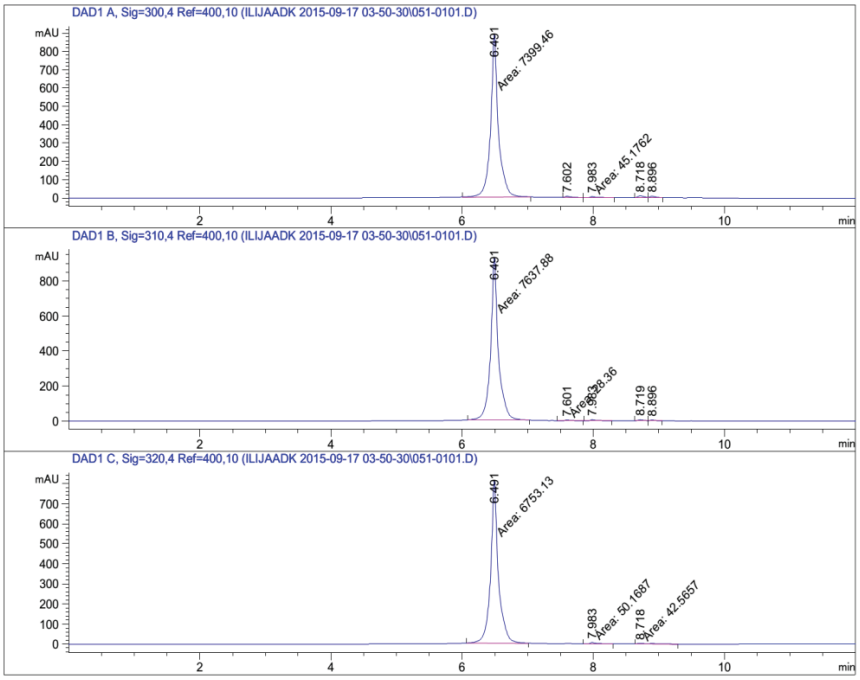
Signal 2: DAD1 B, Sig=310,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.188	MM	0.1498	1.54961e4	1723.59949	99.1356
2	7.272	MM	0.0992	71.15846	11.95799	0.4552
3	7.986	MM	0.1170	63.96226	9.10771	0.4092
Totals :				1.56312e4	1744.66518	

Signal 3: DAD1 C, Sig=320,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.188	MM	0.1498	1.51997e4	1690.71960	98.9087
2	7.272	MM	0.1266	95.94437	12.63321	0.6243
3	7.986	MM	0.1167	71.76546	10.25321	0.4670
Totals :				1.53674e4	1713.60602	

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



Signal 1: DAD1 A, Sig=300,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.491	MM	0.1384	7399.45605	891.22644	97.3957
2	7.602	BB	0.0747	43.75071	8.13640	0.5759
3	7.983	MM	0.1336	45.17621	5.63593	0.5946
4	8.718	BV	0.0936	63.11792	10.00004	0.8308
5	8.896	VB	0.0746	45.81448	8.81991	0.6030
Totals :				7597.31538	923.81872	

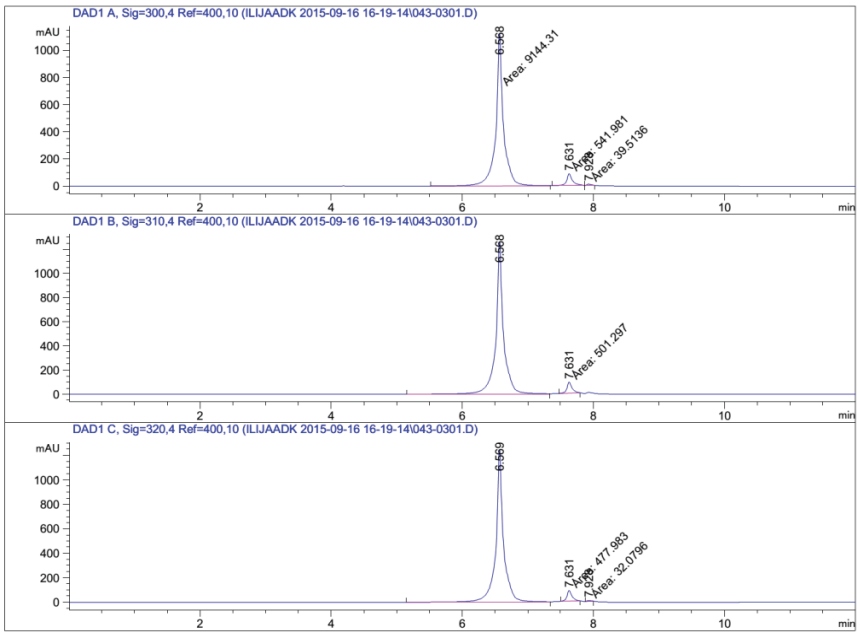
Signal 2: DAD1 B, Sig=310,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.491	MM	0.1368	7637.88330	930.65759	98.2398
2	7.601	MM	0.1015	28.35998	4.65668	0.3648
3	7.983	BB	0.0900	44.02977	6.75667	0.5663
4	8.719	VV	0.0939	37.49060	5.91716	0.4822
5	8.896	VB	0.0739	26.97103	5.25505	0.3469
Totals :				7774.73468	953.24315	

Signal 3: DAD1 C, Sig=320,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.188	MM	0.1498	1.51997e4	1690.71960	98.9087
2	7.272	MM	0.1266	95.94437	12.63321	0.6243
3	7.986	MM	0.1167	71.76546	10.25321	0.4670
Totals :				1.53674e4	1713.60602	

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



Signal 1: DAD1 A, Sig=300,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.568	MM	0.1354	9144.30762	1125.57922	94.0211
2	7.631	MM	0.1035	541.98132	87.25426	5.5726
3	7.928	MM	0.0752	39.51355	8.76017	0.4063
Totals :				9725.80249	1221.59366	

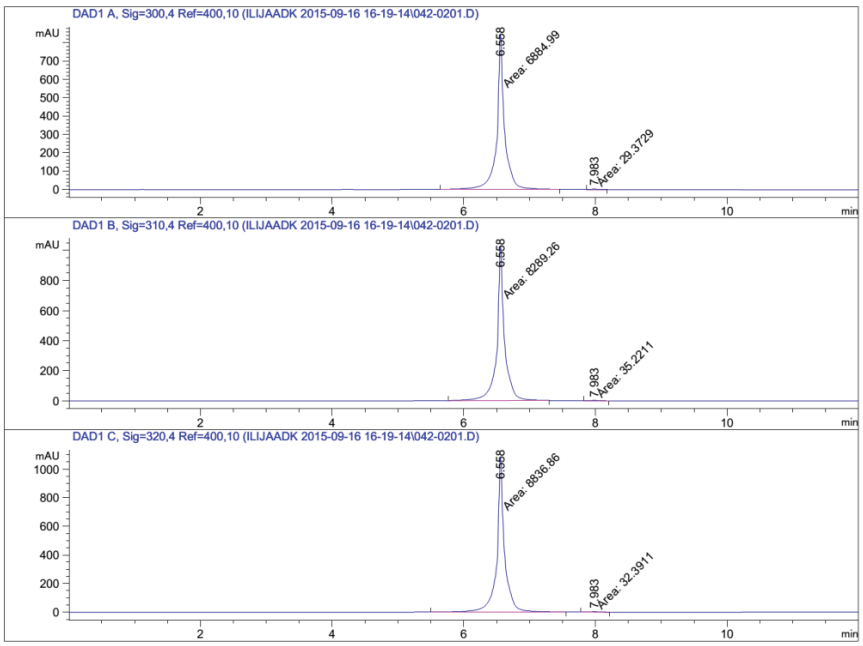
Signal 2: DAD1 B, Sig=310,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.568	BV	0.1105	1.04653e4	1265.41760	95.4289
2	7.631	MM	0.0912	501.29694	91.58324	4.5711
Totals :				1.09666e4	1357.00084	

Signal 3: DAD1 C, Sig=320,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.569	BV	0.1125	1.03210e4	1247.92981	95.2907
2	7.631	MM	0.0909	477.98343	87.68449	4.4131
3	7.928	MM	0.0651	32.07959	8.20785	0.2962
Totals :				1.08310e4	1343.82214	

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



Signal 1: DAD1 A, Sig=300,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.558	MM	0.1359	6884.98584	844.67102	99.5752
2	7.983	MM	0.1335	29.37285	3.66623	0.4248
Totals :				6914.35869	848.33725	

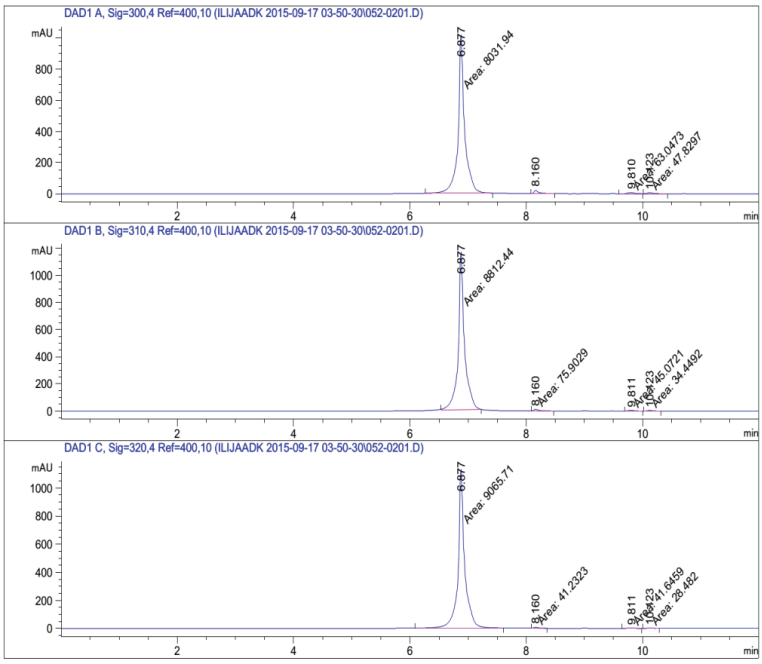
Signal 2: DAD1 B, Sig=310,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.558	MM	0.1343	8289.25977	1029.00488	99.5769
2	7.983	MM	0.1359	35.22105	4.31915	0.4231
Totals :				8324.48082	1033.32404	

Signal 3: DAD1 C, Sig=320,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.558	MM	0.1359	8836.85742	1083.69934	99.6348
2	7.983	MM	0.1194	32.39113	4.52258	0.3652
Totals :				8869.24855	1088.22192	

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



Signal 1: DAD1 A, Sig=300,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.877	MM	0.1312	8031.94043	1020.67456	97.2473
2	8.160	BV	0.0785	116.47652	21.05224	1.4102
3	9.810	MM	0.1373	63.04733	7.65068	0.7634
4	10.123	MM	0.1081	47.82969	7.37333	0.5791
Totals :				8259.29396	1056.75080	

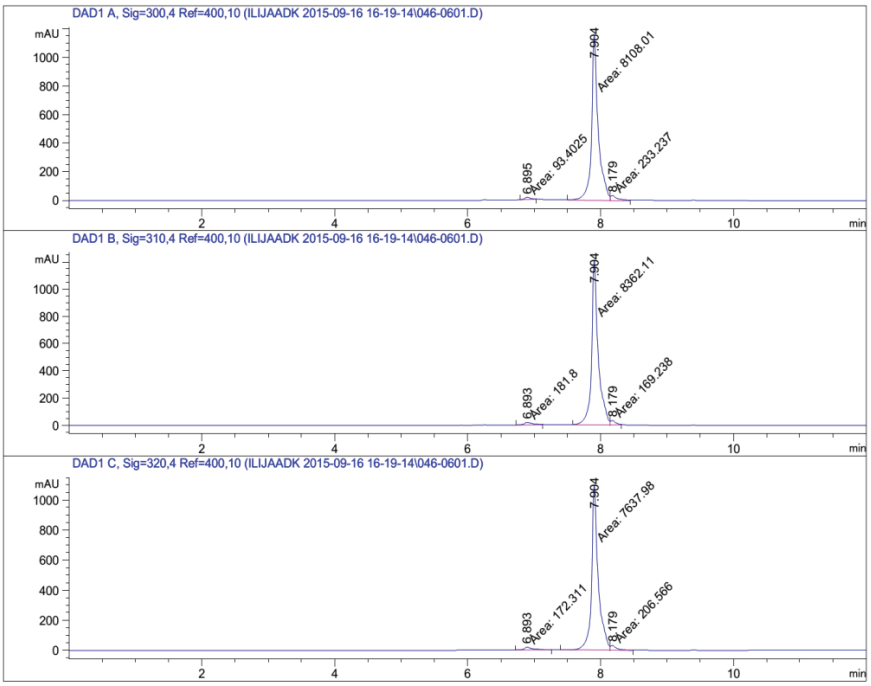
Signal 2: DAD1 B, Sig=310,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.877	MM	0.1261	8812.43652	1164.66846	98.2669
2	8.160	MM	0.0959	75.90292	13.19241	0.8464
3	9.811	MM	0.1394	45.07211	5.38910	0.5026
4	10.123	MM	0.1095	34.44922	5.24225	0.3841
Totals :				8967.86077	1188.49222	

Signal 3: DAD1 C, Sig=320,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.877	MM	0.1330	9065.71289	1136.19385	98.7865
2	8.160	MM	0.0936	41.23225	7.34139	0.4493
3	9.811	MM	0.1716	41.64587	4.04555	0.4538
4	10.123	MM	0.1264	28.48196	3.75556	0.3104
Totals :				9177.07297	1151.33635	

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



Signal 1: DAD1 A, Sig=300,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.895	MM	0.1019	93.40249	15.26987	1.1074
2	7.904	MM	0.1164	8108.01123	1161.14124	96.1274
3	8.179	MM	0.1122	233.23743	34.65784	2.7652
Totals :				8434.65115	1211.06895	

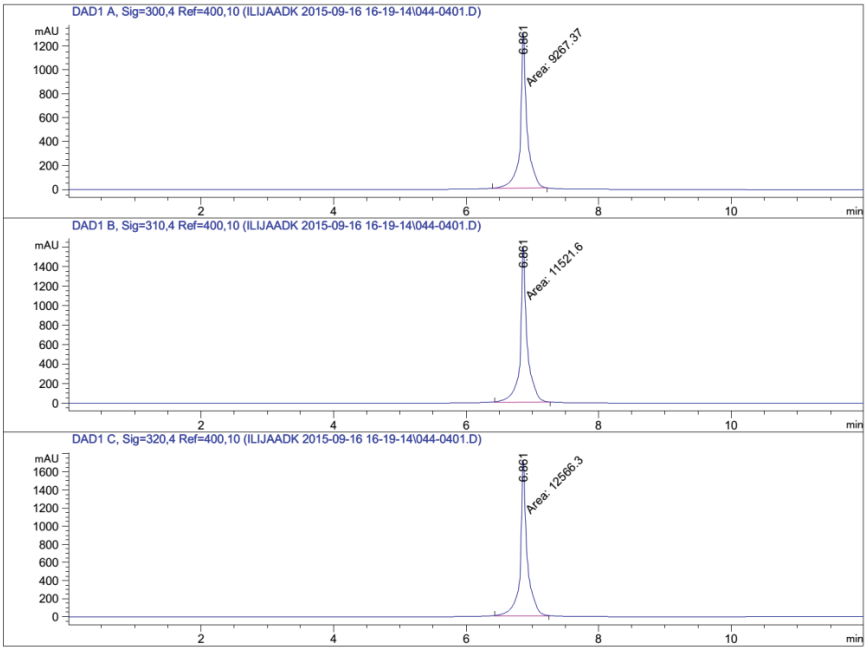
Signal 2: DAD1 B, Sig=310,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.893	MM	0.1523	181.80042	19.89683	2.0865
2	7.904	MF	0.1147	8362.10840	1214.82483	95.9712
3	8.179	FM	0.0895	169.23830	31.51430	1.9423
Totals :				8713.14711	1266.23596	

Signal 3: DAD1 C, Sig=320,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.893	MM	0.1620	172.31148	17.72326	2.1494
2	7.904	MF	0.1155	7637.97559	1101.79370	95.2740
3	8.179	FM	0.1095	206.56557	31.44277	2.5766
Totals :				8016.85263	1150.95973	

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



Signal 1: DAD1 A, Sig=300,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.861	MM	0.1185	9267.36816	1303.51819	100.0000
Totals :				9267.36816	1303.51819	

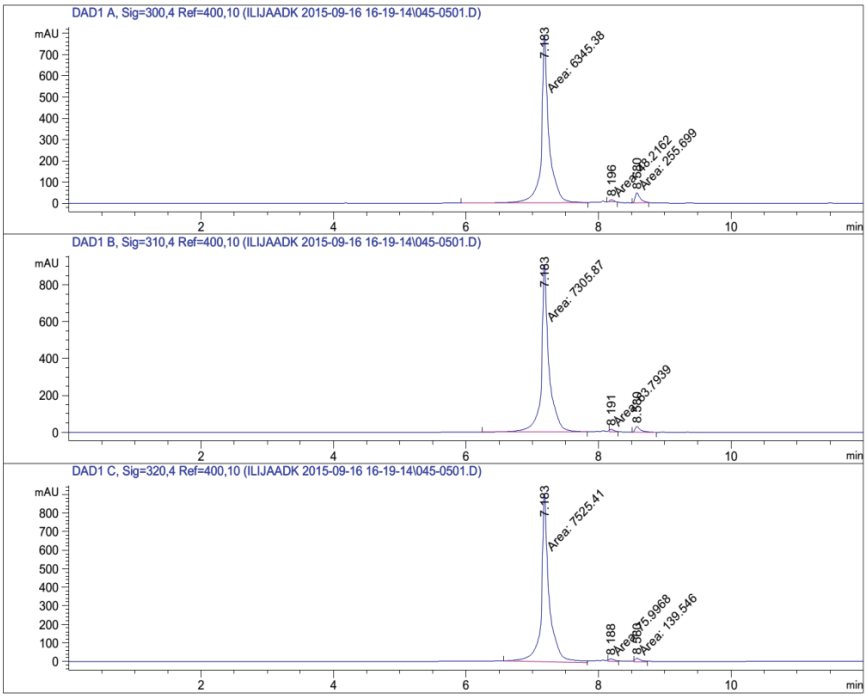
Signal 2: DAD1 B, Sig=310,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.861	MM	0.1199	1.15216e4	1601.59851	100.0000
Totals :				1.15216e4	1601.59851	

Signal 3: DAD1 C, Sig=320,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.861	MM	0.1211	1.25663e4	1729.70715	100.0000
Totals :				1.25663e4	1729.70715	

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



Signal 1: DAD1 A, Sig=300,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.183	MM	0.1338	6345.37500	790.56934	95.4294
2	8.196	MM	0.0748	48.21621	10.74792	0.7251
3	8.580	MM	0.0883	255.69875	48.24373	3.8455
Totals :				6649.28996	849.56099	

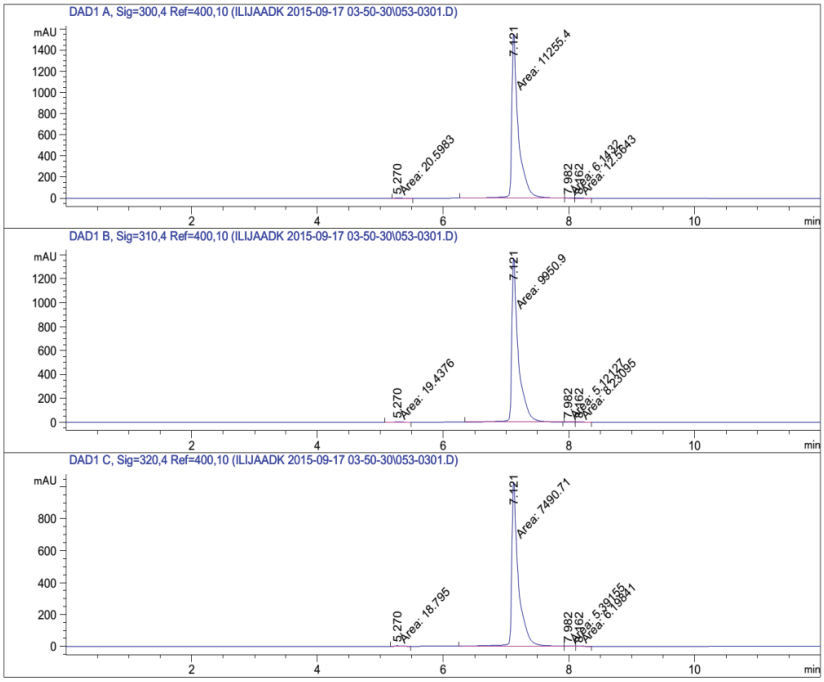
Signal 2: DAD1 B, Sig=310,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.183	MM	0.1336	7305.87354	911.51147	96.7396
2	8.191	MM	0.0764	63.79385	13.90957	0.8447
3	8.580	BB	0.0839	182.43127	31.36720	2.4156
Totals :				7552.09866	956.78825	

Signal 3: DAD1 C, Sig=320,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.183	MM	0.1379	7525.41113	909.51855	97.2156
2	8.188	MM	0.0982	75.99679	12.90106	0.9817
3	8.580	MM	0.1109	139.54582	20.97921	1.8027
Totals :				7740.95374	943.39883	

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



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.270	MM	0.1076	20.59832	3.18970	0.1824
2	7.121	MM	0.1205	1.12554e4	1556.25171	99.6520
3	7.982	MM	0.0917	6.14320	1.11701	0.0544
4	8.162	MM	0.1114	12.56429	1.87958	0.1112

Totals : 1.12947e4 1562.43800

Signal 2: DAD1 B, Sig=310,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.270	MM	0.0926	19.43761	3.49813	0.1947
2	7.121	MM	0.1205	9950.90234	1375.92627	99.6716
3	7.982	MM	0.0745	5.12127	1.14633	0.0513
4	8.162	MM	0.0911	8.23095	1.50506	0.0824

Totals : 9983.69218 1382.07579

Signal 3: DAD1 C, Sig=320,4 Ref=400,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.270	MM	0.0944	18.79499	3.31737	0.2499
2	7.121	MM	0.1210	7490.70850	1032.15369	99.5960
3	7.982	MM	0.0718	5.39155	1.25197	0.0717
4	8.162	MM	0.0935	6.19841	1.10505	0.0824

Totals : 7521.09344 1037.82807

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

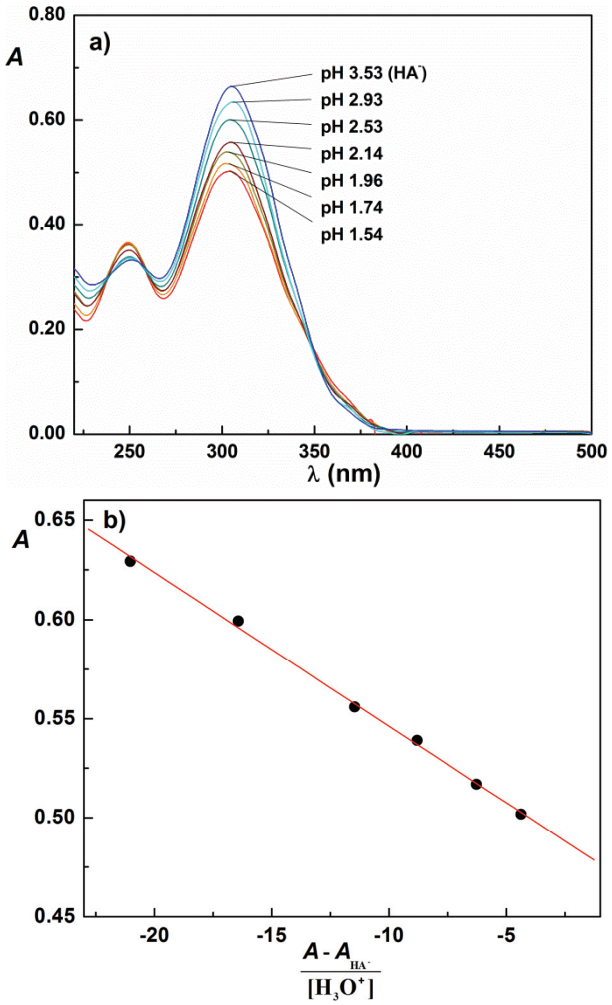


Fig. S-10. Absorption spectra of compound **2** used for K_{a1} determination in solutions of different acidity, the pH values are indicated; b) Spectrophotometric determination of K_{a1} according to Eq. (1); $c_2 = 5.023\times10^{-5}$ M; $\lambda = 302.9$ nm; $t = 25$ °C, $I = 0.1$ M (NaCl); scan speed 500 nm min^{-1}.

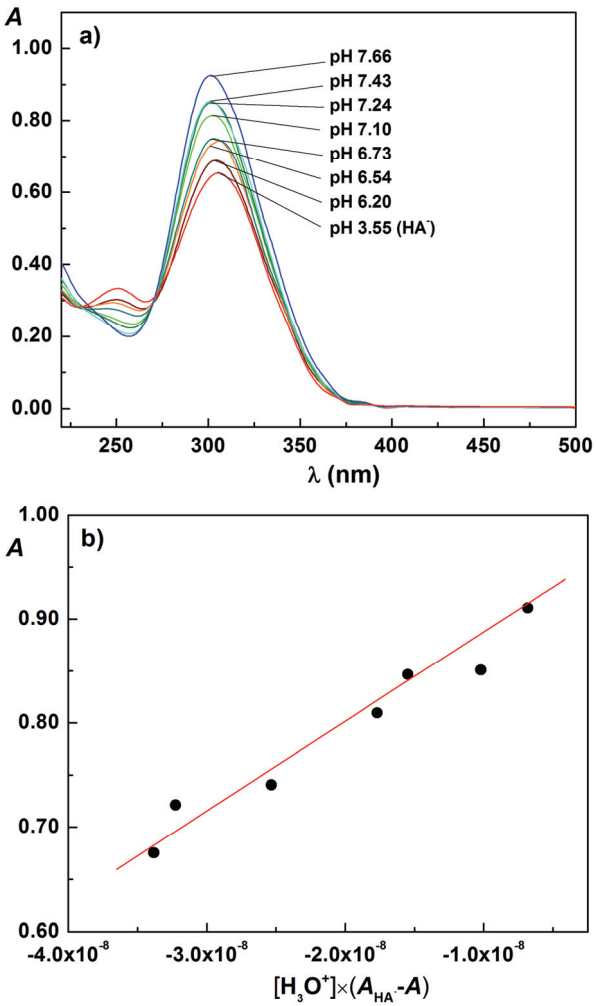


Fig. S-11.Absorption spectra of compound **2** used for K_{a2} determination in solutions of different acidity, the pH values are indicated; b) Spectrophotometric determination of K_{a2} according to Eq. (2); $c_2 = 5.023\times10^{-5}$ M; $\lambda = 299.5$ nm; $t = 25$ °C, $I = 0.1$ M (NaCl); scan speed 500 nm min^{-1}.

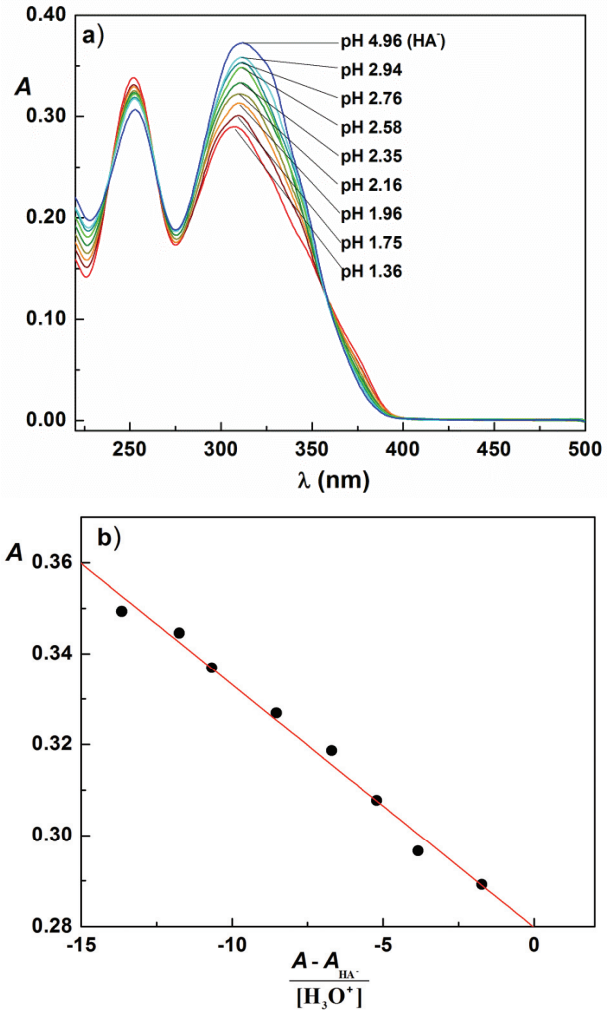


Fig. S-12. Absorption spectra of compound **3** used for K_{a1} determination in solutions of different acidity, the pH values are indicated; b) Spectrophotometric determination of K_{a1} according to Eq. (1); $c_3 = 4.908\times10^{-5}$ M; $\lambda = 305.4$ nm; $t = 25$ °C, $I = 0.1$ M (NaCl); scan speed 500 nm min^{-1}.

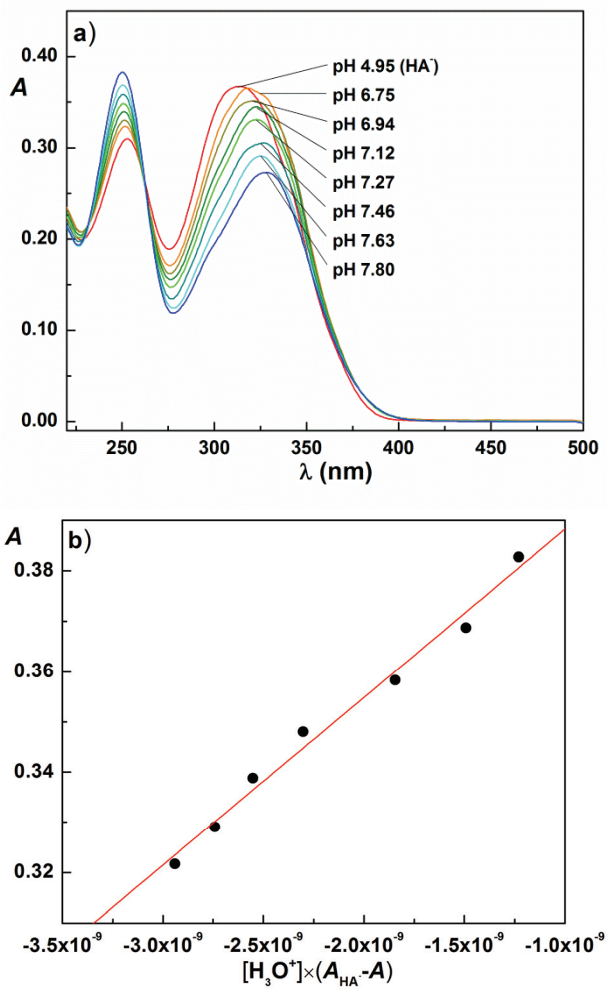


Fig. S-13. Absorption spectra of compound **3** used for K_{a2} determination in solutions of different acidity, the pH values are indicated; b) Spectrophotometric determination of K_{a2} according to Eq. (2); $c_3 = 4.908\times10^{-5}$ M; $\lambda = 250.0$ nm; $t = 25$ °C, $I = 0.1$ M (NaCl); scan speed 500 nm min^{-1}.

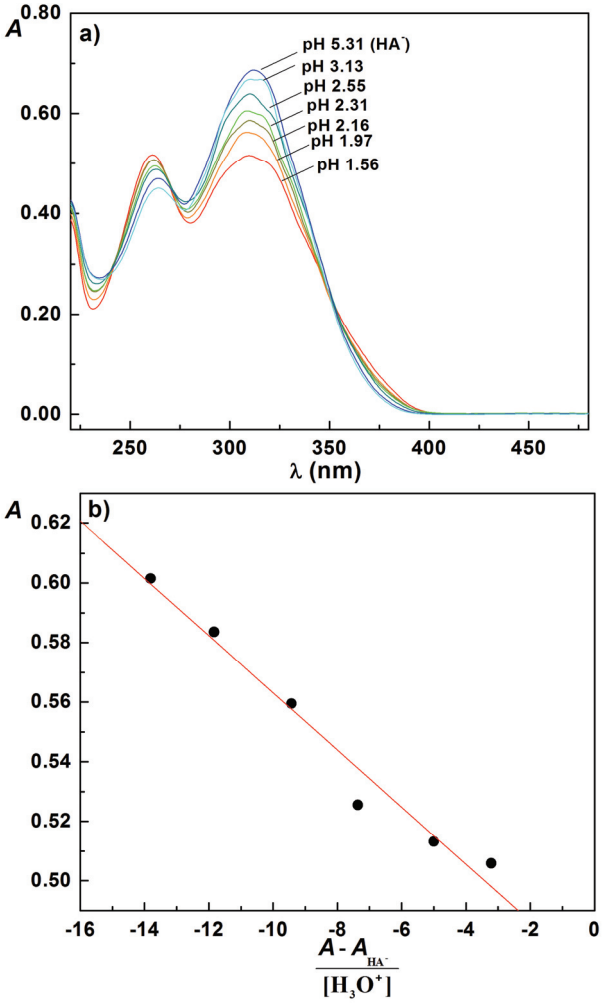


Fig. S-14. Absorption spectra of compound **5** used for K_{a1} determination in solutions of different acidity, the pH values are indicated; b) Spectrophotometric determination of K_{a1} according to Eq (1); $c_5 = 6.021\times10^{-5}$ M; $\lambda = 312.3$ nm; $t = 25$ °C, $I = 0.1$ M (NaCl); scan speed 500 nm min^{-1}.

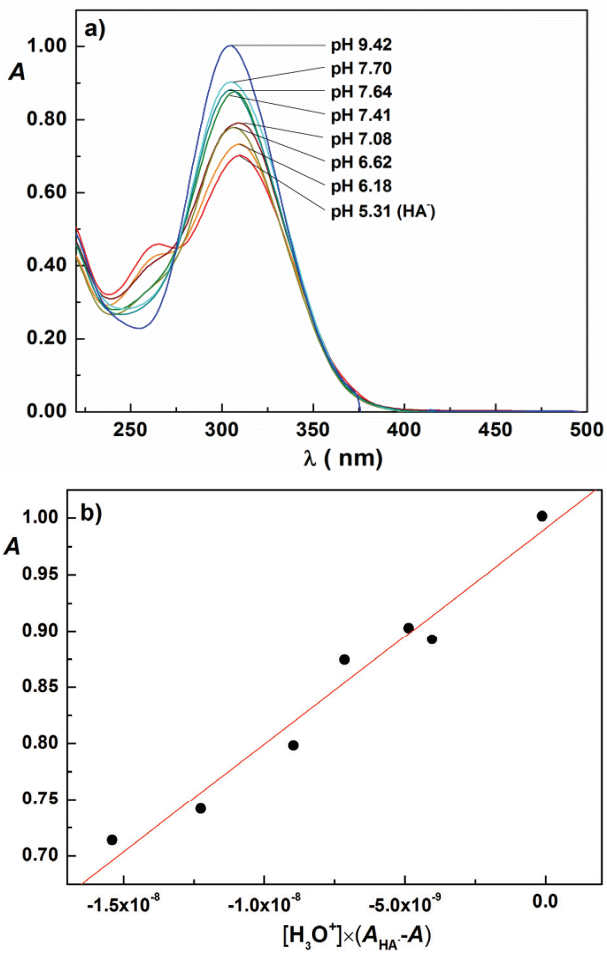


Fig. S-15. Absorption spectra of compound **5** used for K_{a2} determination in solutions of different acidity, the pH values are indicated; b) Spectrophotometric determination of K_{a2} according to Eq. (2); $c_5 = 6.021\times10^{-5}$ M; $\lambda = 305.9$ nm; $t = 25$ °C, $I = 0.1$ M (NaCl); scan speed 500 nm min^{-1}.

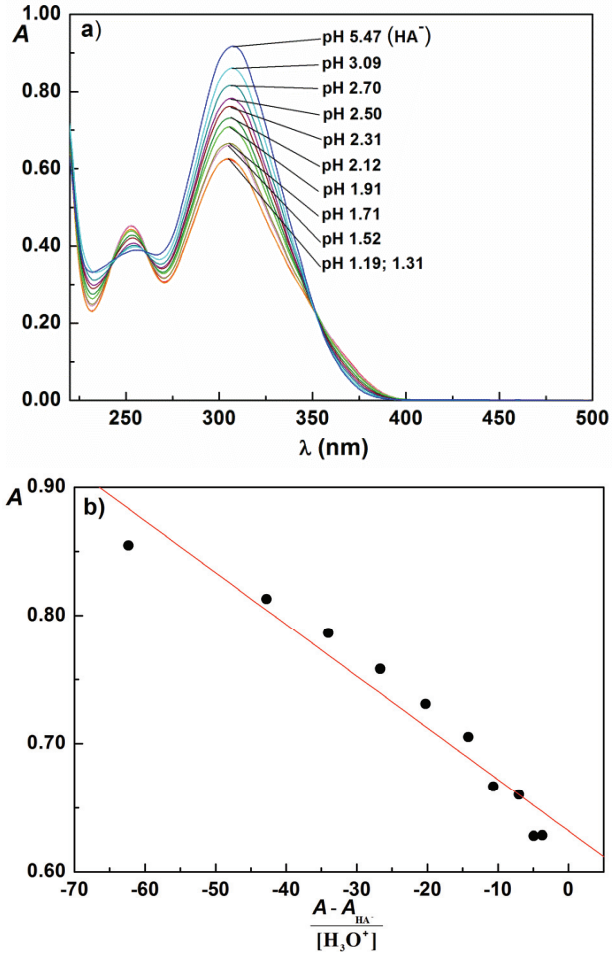


Fig. S-16. Absorption spectra of compound **6** used for K_{a1} determination in solutions of different acidity, the pH values are indicated; b) Spectrophotometric determination of K_{a1} according to Eq (1); $c_6 = 9.014\times10^{-5}$ M; $\lambda = 306.3$ nm; $t = 25$ °C, $I = 0.1$ M (NaCl); scan speed 500 nm min^{-1}.

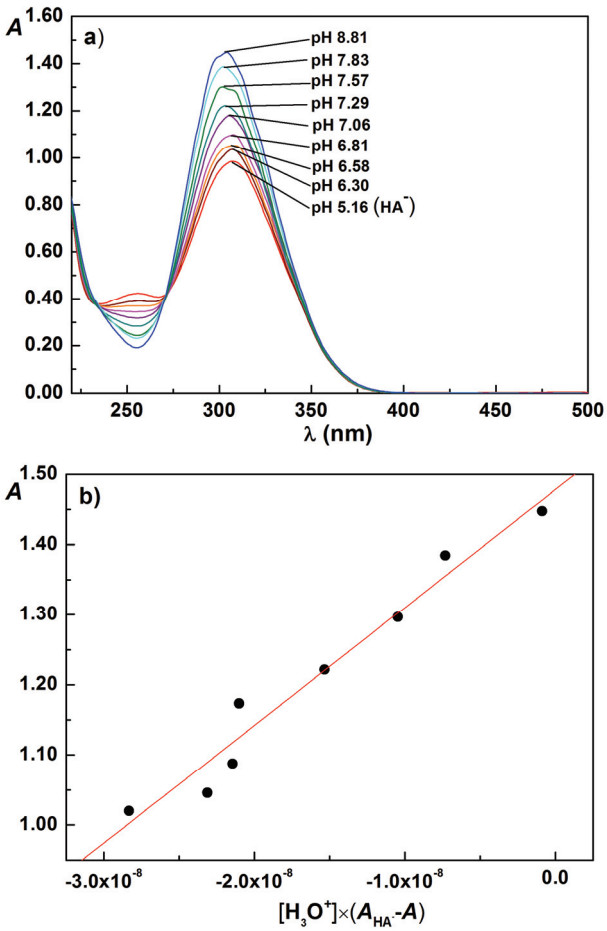


Fig. S-17. Absorption spectra of compound **6** used for K_{a2} determination in solutions of different acidity, the pH values are indicated; b) Spectrophotometric determination of K_{a2} according to Eq, (2); $c_6 = 9.014\times10^{-5}$ M; $\lambda = 303.7$ nm; $t = 25$ °C, $I = 0.1$ M (NaCl); scan speed 500 nm min^{-1}.

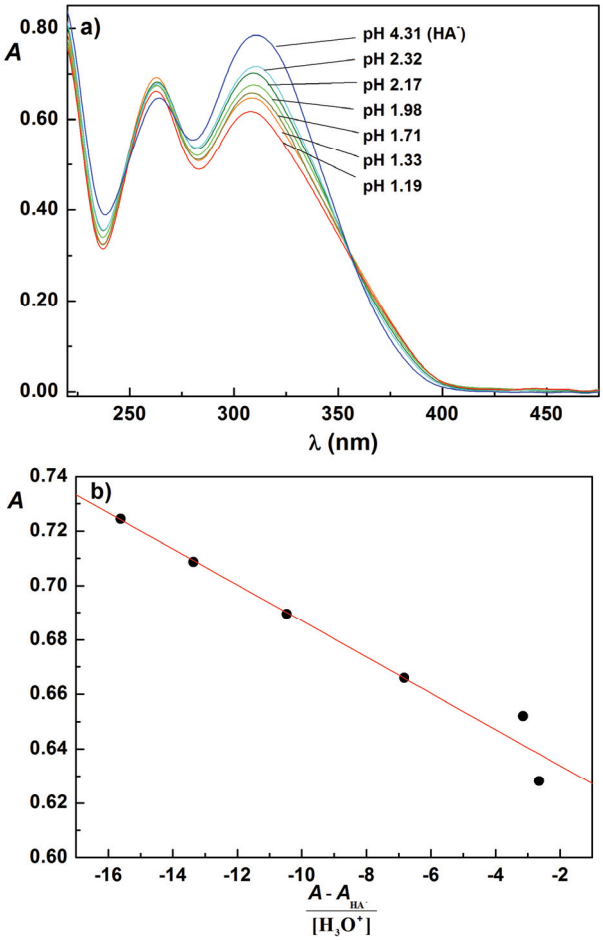


Fig. S-18. Absorption spectra of compound **8** used for K_{a1} determination in solutions of different acidity, the pH values are indicated; b) Spectrophotometric determination of K_{a1} according to Eq. (1); $c_8 = 5.904\times10^{-5}$ M; $\lambda = 308.8$ nm; $t = 25$ °C, $I = 0.1$ M (NaCl); scan speed 500 nm min^{-1}.

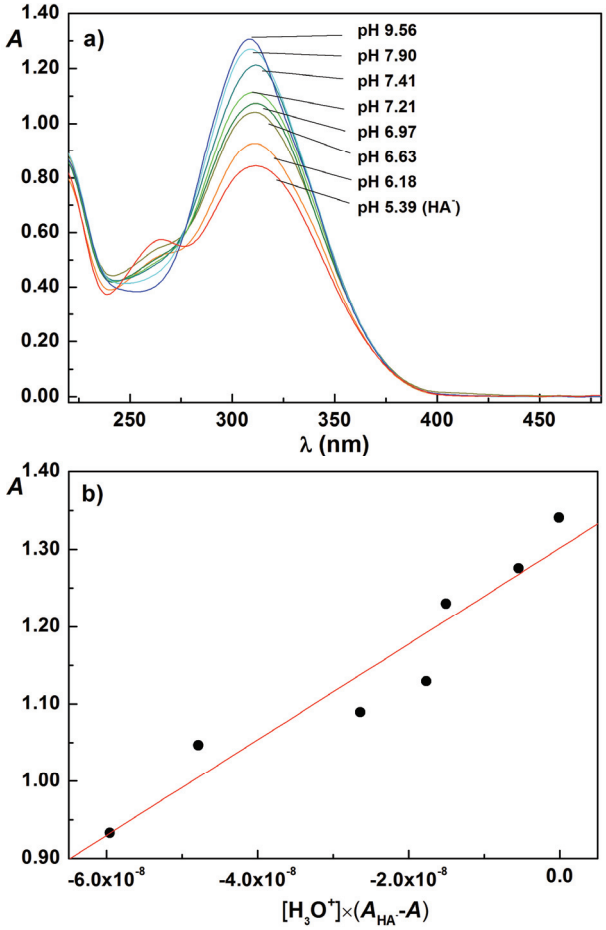


Fig. S-19. Absorption spectra of compound **8** used for K_{a2} determination in solutions of different acidity, the pH values are indicated; b) Spectrophotometric determination of K_{a2} according to Eq. (2); $c_8 = 5.904\times10^{-5}$ M; $\lambda = 308.0$ nm; $t = 25$ °C, $I = 0.1$ M (NaCl); scan speed 500 nm min^{-1}.

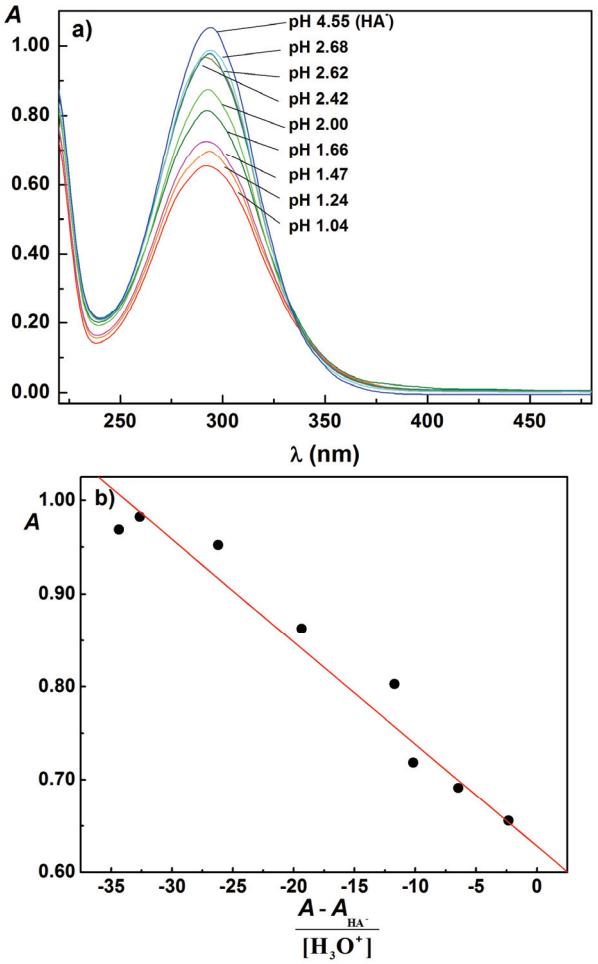


Fig. S-20. Absorption spectra of compound **9** used for K_{a1} determination in solutions of different acidity, the pH values are indicated; b) Spectrophotometric determination of K_{a1} according to Eq. (1); $c_9 = 6.066\times10^{-5}$ M; $\lambda = 293.0$ nm; $t = 25$ °C, $I = 0.1$ M (NaCl); scan speed 500 nm min^{-1}.

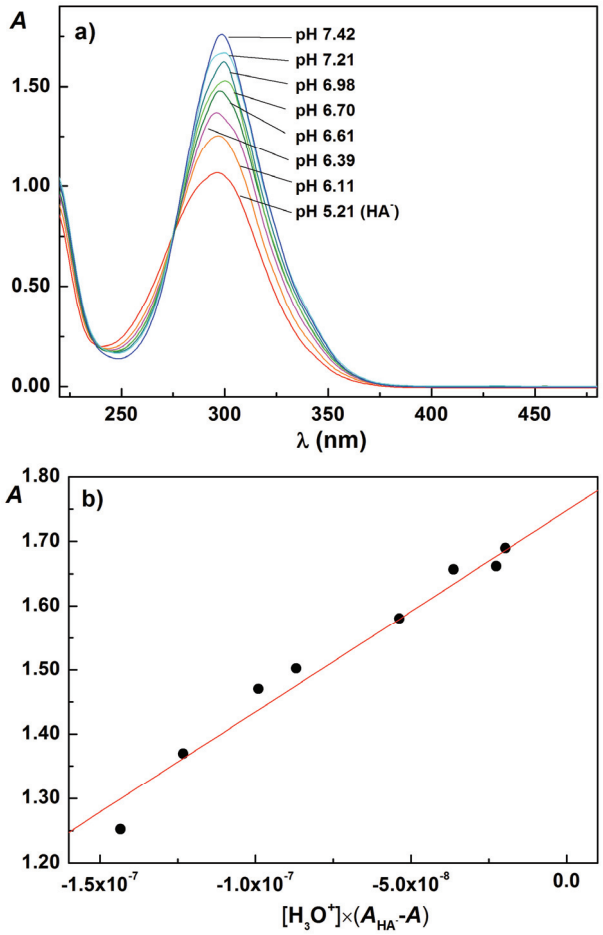
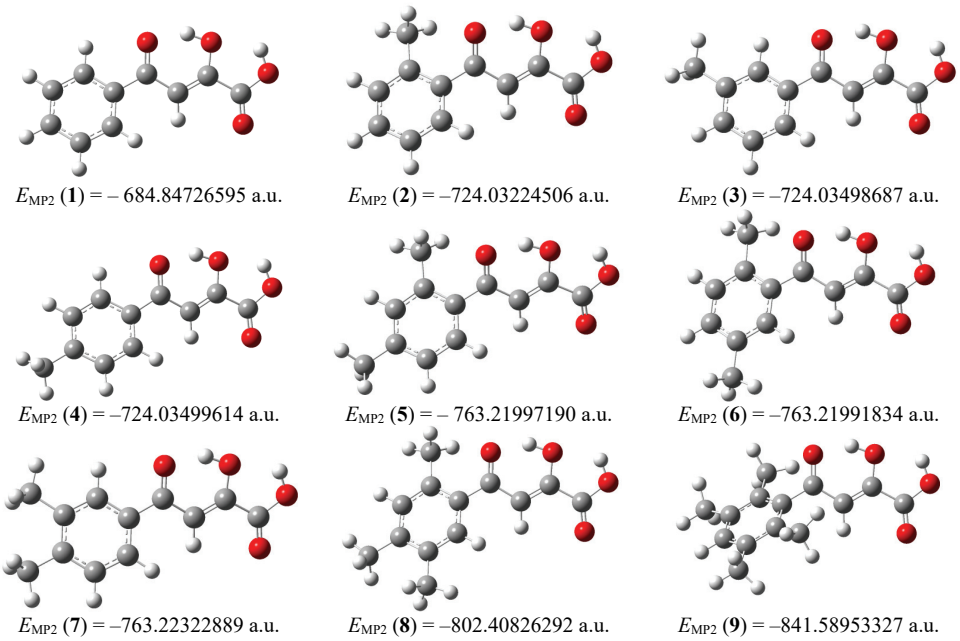


Fig. S-21. Absorption spectra of compound **9** used for K_{a2} determination in solutions of different acidity, the pH values are indicated; b) Spectrophotometric determination of K_{a2} according to Eq. (2); $c_9 = 6.066\times10^{-5}$ M; $\lambda = 296.0$ nm; $t = 25$ °C, $I = 0.1$ M (NaCl); scan speed 500 nm min^{-1}.

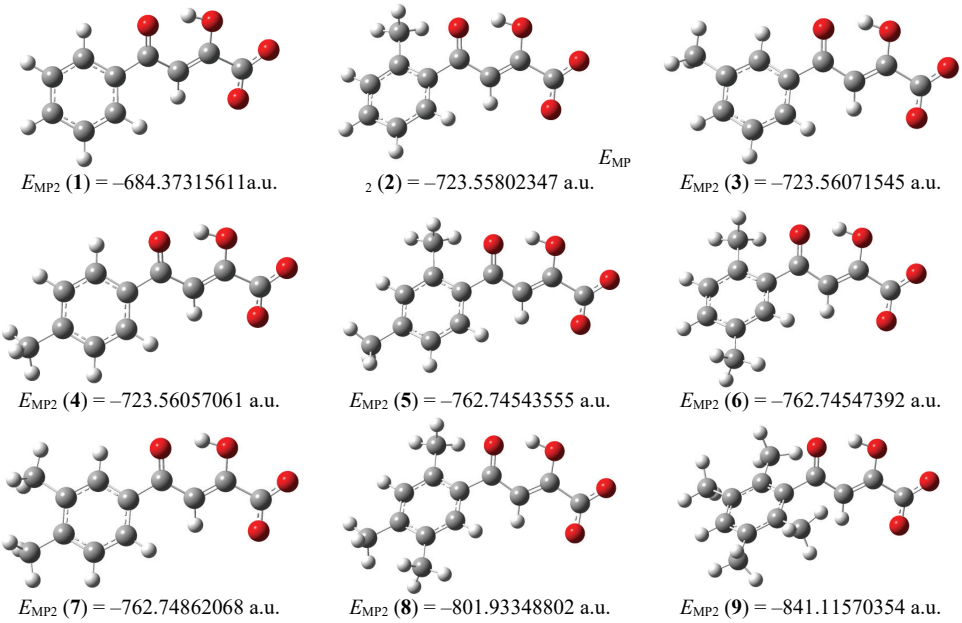


E_{MP2} (**1**) = – 684.84726595 a.u. E_{MP2} (**2**) = –724.03224506 a.u. E_{MP2} (**3**) = –724.03498687 a.u.

E_{MP2} (**4**) = –724.03499614 a.u. E_{MP2} (**5**) = – 763.21997190 a.u. E_{MP2} (**6**) = –763.21991834 a.u.

E_{MP2} (**7**) = –763.22322889 a.u. E_{MP2} (**8**) = –802.40826292 a.u. E_{MP2} (**9**) = –841.58953327 a.u.

Fig. S-22. Optimized geometries and energies of **1**–**9** in their molecular (H_2A) form; MP2/6-31g (d,p) with PCM water solvation.



E_{MP2} (**1**) = –684.37315611a.u. E_{MP2} (**2**) = –723.55802347 a.u. E_{MP2} (**3**) = –723.56071545 a.u.

E_{MP2} (**4**) = –723.56057061 a.u. E_{MP2} (**5**) = –762.74543555 a.u. E_{MP2} (**6**) = –762.74547392 a.u.

E_{MP2} (**7**) = –762.74862068 a.u. E_{MP2} (**8**) = –801.93348802 a.u. E_{MP2} (**9**) = –841.11570354 a.u.

Fig. S-23. Optimized geometries and energies of **1**–**9** in their monoanionic (HA^-) form; MP2/6-31g (d,p) with PCM water solvation.

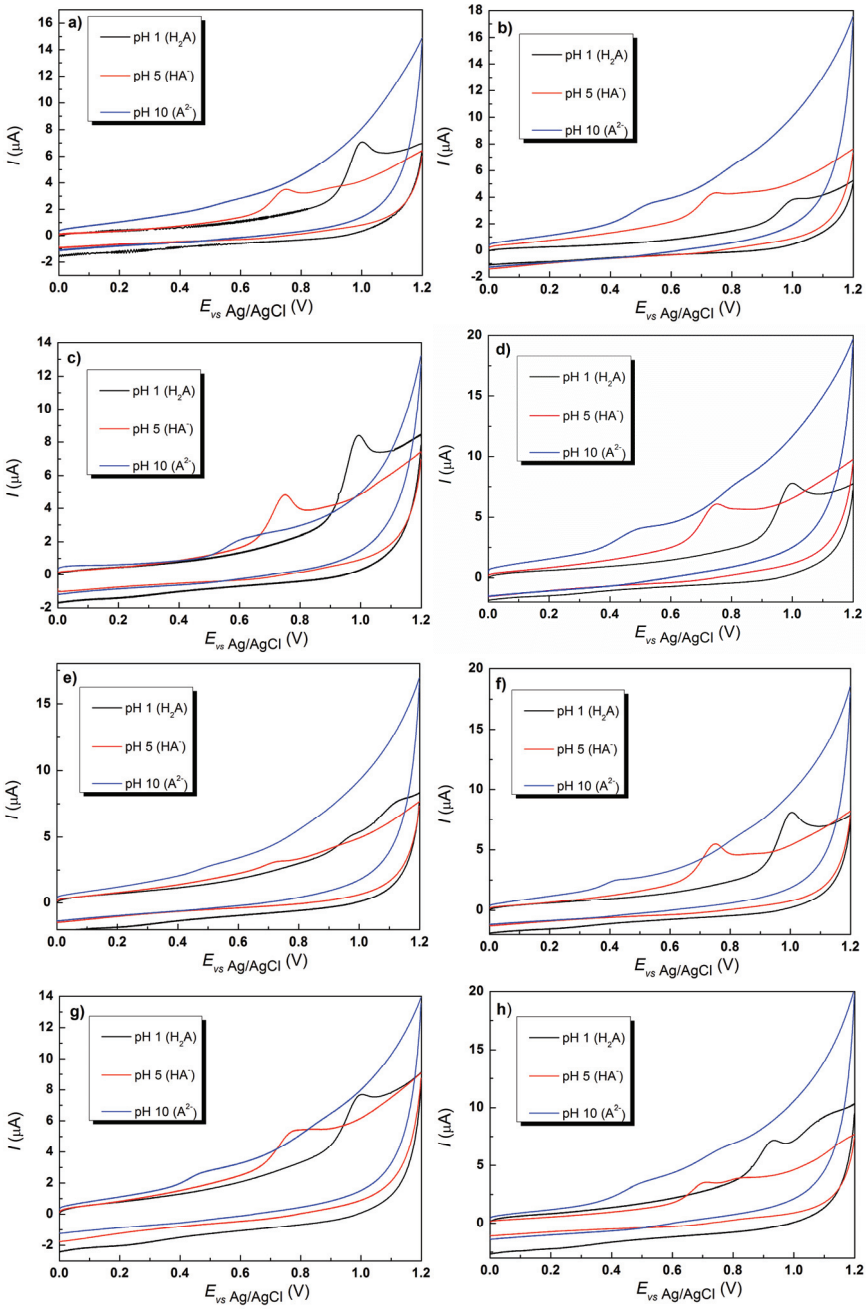


Fig. S-24. Cyclic voltammograms of compounds **1**–**3** and **5**–**9** in Britton–Robinson buffer at pH 1, pH 5, and pH 10. a) **1**, $c_1 = 5.46\times10^{-5}$ M; b) **2**, $c_2 = 4.61\times10^{-5}$ M; c) **3**, $c_3 = 6.54\times10^{-5}$ M; d) **5**, $c_5 = 6.58\times10^{-5}$ M; e) **6**, $c_6 = 4.09\times10^{-5}$ M; f) **7**, $c_7 = 5.22\times10^{-5}$ M; g) **8**, $c_8 = 4.06\times10^{-5}$ M; h) **9**, $c_9 = 4.43\times10^{-5}$ M; scan rate 100 mV s^{-1}, t=25±1 °C.

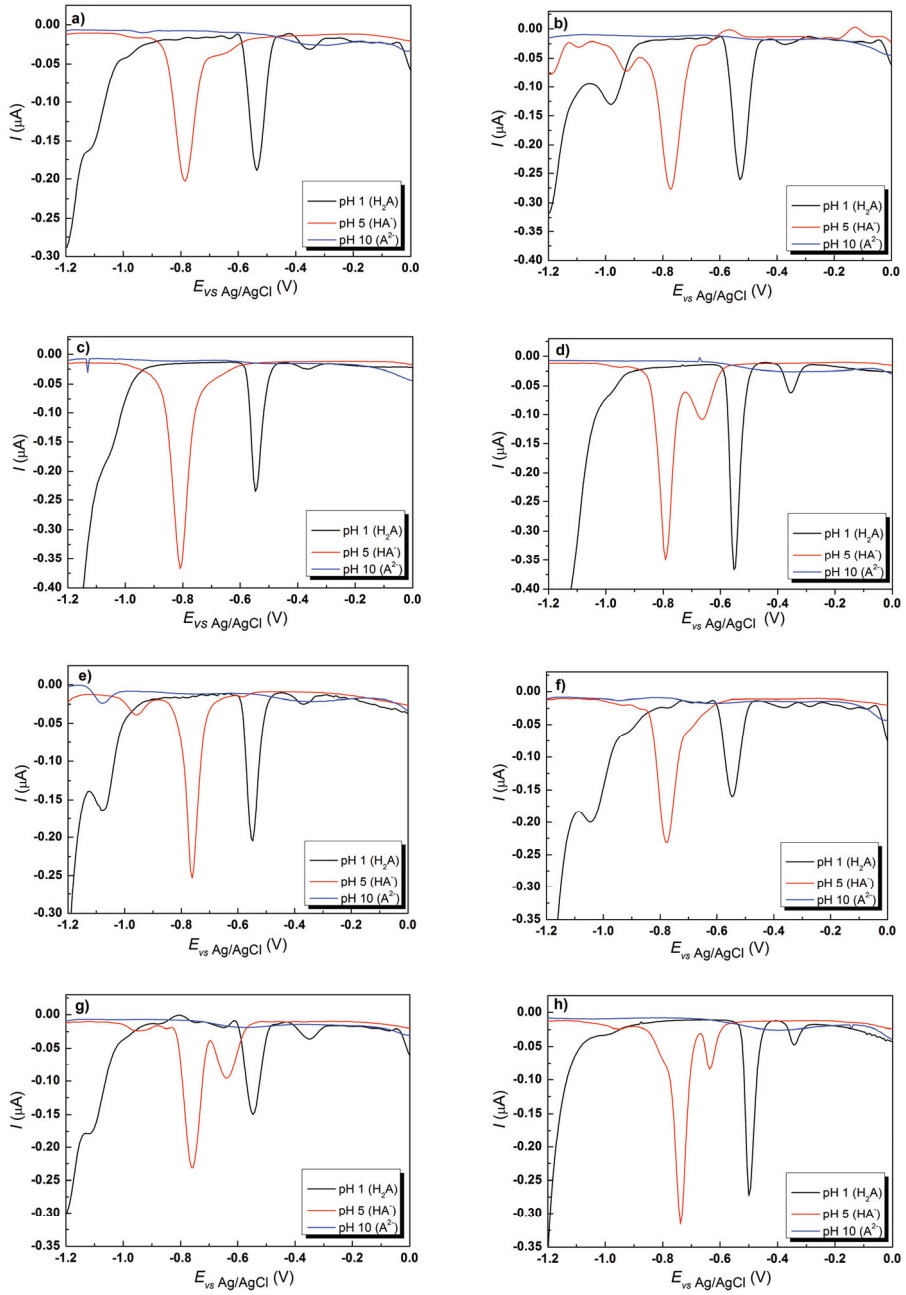
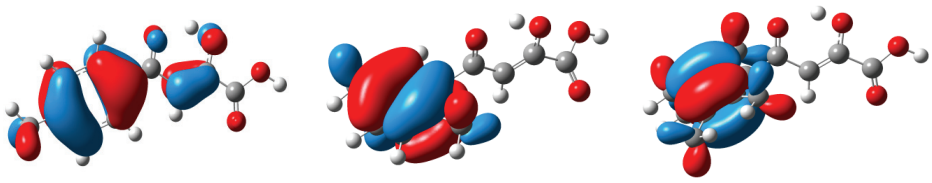


Fig. S-25. Differential pulse polarograms of compound **2**–**9** in Britton–Robinson buffer at pH 1, pH 5, and pH 10; a) **2**, $c_2 = 4.61\times10^{-5}$ M; b) **3**, $c_3 = 6.54\times10^{-5}$ M; c) **4**, $c_4 = 4.77\times10^{-5}$ M; d) **5**, $c_5 = 6.58\times10^{-5}$ M; e) **6**, $c_6 = 4.09\times10^{-5}$ M; f) **7**, $c_7 = 5.22\times10^{-5}$ M; g) **8**, $c_8 = 4.06\times10^{-5}$ M; h) **9**, $c_9 = 4.43\times10^{-5}$ M; scan rate 13 mV s^{-1}, t =25±1 °C.



Compound **4** Compound **6** Compound **9**

Fig. S-26. HOMO orbitals of the H_2A form of compounds **4**, **6** and **9** plotted on the isocontour level 0.03.

Compound **4** Compound **6** Compound **9**

Fig. S-27. LUMO orbitals of the H_2A form of compounds **4**, **6** and **9** plotted on the isocontour level 0.03.

TABLE S-I. Energies of the FMOs (given in Hartree), and dipoles (given in Debye) for the molecular and monoanionic forms of compounds **1**–**9**

Compound	Neutral (H_2A)				Anion (HA^-)			
	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 S-II. Energies of the FMOs (given in Hartree), and dipole moments (given in Debye) for the radical anions and radical cations derived from molecular form (H_2A) or monoanionic form (HA^-) of compounds **1**–**9**. Energies of αSOMO and αLUMO are shown.

Compound	Radical anion from H_2A				Radical cation from H_2A			
	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

Compound	Radical dianion from HA^-			
	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 S-III. Intercorrelation matrix (r values) between oxidation/reduction potentials at pH 1 and at pH 5 and the descriptors extracted from QM calculations. The indicator variable (I) is also included. 'molecular' refers to the neutral form of the compounds; 'anion' refers to the anionic form of the compounds (deprotonated carboxyl group); 'RA' refers to the radical anion/dianion (derived from the neutral/anionic form); 'RC' refers to the radical cation derived from the neutral form

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

Table S-III. Continued

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 (RC)	–0.8283	SOMO/LUMO gap dianion (RA)	–0.6869
Dipole (RC)	–0.9067	Dipole of dianion (RA)	0.7311
I	–0.5295	*I*	0.9533