

## Supplementary material

### Assessing the potential of *para*-donor and *para*-acceptor substituted 5-benzylidenebarbituric acid derivatives as push-pull electronic systems: Experimental and Quantum Chemical Study.

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#### 2.2. Materials and methods

Acidity constants of *p*-dimethylaminoderivative (**1**) were determined by spectrophotometric titration at 25±1 °C. The 10 mmol stock solution of **1** in DMSO was diluted in 25 mmol phosphate buffer (Merck, pH 6.88) to prepare 200 mL of 5.0×10<sup>-5</sup> M working solution. The starting pH value was adjusted below 3 with the addition of conc. H<sub>3</sub>PO<sub>4</sub>. Increments of 2.5 M KOH were added dropwise in a stirring solution of **1**, pH was equilibrated, and UV/Vis absorption spectra were recorded after each 0.15-0.20 pH unit change until pH ~13 was reached. Acidity constants ( $K_{a1}$ ,  $K_{a2}$ , and  $K_{a3}$ ) were calculated according to full (equation S1) or transformed form (equations S2 and S3) of the classical spectrophotometric equation[1]:

$$\text{pH} = \text{p}K_{a2} - \log \frac{A - A_{\text{HA}^-}}{A_{\text{H}_2\text{A}} - A} \quad (\text{S1})$$

$$A = A_{\text{H}_3\text{A}^+} + \frac{A_{\text{H}_2\text{A}} - A}{[\text{H}_3\text{O}^+]} \times K_{a1} \quad (\text{S2})$$

$$A = A_{\text{A}^{2-}} + (A_{\text{HA}^-} - A) \times [\text{H}_3\text{O}^+] \times \frac{1}{K_{a3}} \quad (\text{S3})$$

The transformed forms are used when the spectrum in the acidic or basic solution (H<sub>3</sub>A<sup>+</sup> and A<sup>2-</sup> forms) cannot be acquired due to the absence of isosbestic point. Absorbances at 250-260 nm are chosen for the calculation of acidity constants as pH-dependent absorption spectra changes are the most pronounced in this wavelength range.

**Table S1**

Solvent parameters [2,3] used in Kamlet–Taft equation.

<i>Solvent<sup>a</sup></i>	$\pi^*$	$\beta$	$\alpha$
<b>2,2,2-Trifluoroethanol (TFE)</b>	0.73	0	1.51
<b>Ethylene glycol (EG)</b>	0.92	0.52	0.90
<b>Methanol (MeOH)</b>	0.60	0.66	0.98
<b>2-Chloroethanol</b>	0.46	0.53	1.28
<b>1,2-Propanediol (1,2-PDO)</b>	0.76	0.78	0.83
<b>Ethanol (EtOH)</b>	0.54	0.75	0.86
<b>2-Propanol (IPA)</b>	0.48	0.84	0.76
<b>2-Methyl-1-propanol (Isobutanol)</b>	0.40	0.84	0.79
<b>1-Butanol (BuOH)</b>	0.47	0.84	0.84
<b>Dimethyl sulfoxide (DMSO)</b>	1.00	0.76	0
<b><i>N,N</i>-Dimethylacetamide (DMA)</b>	0.88	0.76	0
<b>Acetonitrile (MeCN)</b>	0.75	0.40	0.19
<b><i>N,N</i>-Dimethylformamide (DMF)</b>	0.88	0.69	0
<b><i>N</i>-Methyl-2-pyrrolidinone (NMP)</b>	0.92	0.77	0
<b>Tetrahydrofuran (THF)</b>	0.58	0.55	0
<b>Ethyl acetate (EtOAc)</b>	0.55	0.45	0
<b>1,2-Dimethoxyethane (DME)</b>	0.53	0.41	0
<b>Anisole</b>	0.73	0.32	0
<b>Trichloromethane (TCM)</b>	0.58	0.10	0.20
<b>Diisopropyl ether (DIPE)</b>	0.27	0.49	0

<sup>a</sup>Solvent abbreviation was taken from www.chemnetbase

\*Data not found for Diethylene glycol (DEG)

LFER methodology

The Hammett Equation:

$$s = \rho\sigma + s_0 \quad (\text{S4})$$

The extended Hammett Equation:

$$s = \rho_I\sigma_I + \rho_R\sigma_R + s_0 \quad (\text{S5})$$

The Swain–Lupton Equation:

$$s = fF + rR + s_0 \quad (\text{S6})$$

The calculated value  $s$  is the measured spectral property or calculated value,  $\rho$ ,  $\rho_I$ ,  $\rho_R$ ,  $f$ , and  $r$  are proportionality constants reflecting the sensitivity of the spectral characteristics to substituent effect,  $\sigma_m/p$ ,  $\sigma_I$ ,  $\sigma_R$ ,  $F$ , and  $R$  represent the corresponding substituent constant and  $s_0$  is the intercept. The values of the corresponding substituent constants used in Eqs. (S4-S6) are given in Table S2.

**Table S2**  
Substituent constants [4] used in correlation analysis (Eqs. S4-S6).

<i>Substituent</i>	$\sigma_{p+}$	$\sigma_I$	$\sigma_{R+}$	$F$	$R+$
<b>N(CH<sub>3</sub>)<sub>2</sub></b>	-1.7	0.06	-1.22	0.15	-1.85
<b>OH</b>	-0.92	0.29	-0.64	0.33	-1.25
<b>OCH<sub>3</sub></b>	-0.78	0.27	-0.66	0.29	-1.07
<b>OCH<sub>2</sub>CH<sub>3</sub></b>	-0.81	0.28	-0.65	0.26	-1.07
<b>CH<sub>3</sub></b>	-0.31	-0.04	-0.25	0.04	-0.32
<b>CH(CH<sub>3</sub>)<sub>2</sub></b>	-0.28	0.01	-0.12	0.01	-0.32
<b>H</b>	0	0	0	0	0
<b>F</b>	-0.07	0.52	-0.37	0.45	-0.52
<b>Cl</b>	0.11	0.47	-0.21	0.42	-0.31
<b>Br</b>	0.15	0.44	-0.19	0.45	-0.3
<b>CN</b>	0.66	0.53	0.13	0.51	0.15
<b>NO<sub>2</sub></b>	0.79	0.64	0.15	0.65	0.14

### 2.3. Characterization of 5-benzylidenebarbituric acid derivatives

#### 5-(4-(Dimethylamino)benzylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (1)

Red powder; yield 89%, m.p.: 270 °C; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 11.06 (s, 1H, NH), 10.92 (s, 1H, NH), 8.43-8.39 (d, 2H, ArH), 8.14 (1H, CH), 6.80-6.75 (d, 2H, ArH), 3.11 (S, 6H, CH<sub>3</sub>N); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 165.03, 163.02, 155.80, 154.45, 150.63, 139.37, 120.26, 111.46, 109.75, 39.95, 39.86; IR (KBr, cm<sup>-1</sup>): 3178, 3033, 2863, 1724, 1654, 1607, 1495, 1359, 1192, 828. Elemental Analysis for C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub>; Calculated: % C, 60.22; %H, 5.05; %N, 16.21; Found: %C, 60.00; %H, 4.94; %N, 16.16.

**5-(4-Hydroxybenzylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (2)**

Yellow powder; yield 99%, m.p. >300 °C; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>): δ = 11.26 (s, 1H, NH), 11.12 (s, 1H, NH), 10.83 (s, 1H, OH), 8.34-8.30 (d, 2H, ArH), 8.21 (s, 1H, CH), 6.90-6.85 (d, 2H, ArH); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>): δ = 164.49, 163.36, 162.65, 155.90, 150.58, 138.65, 124.13, 115.84, 114.49; IR (KBr, cm<sup>-1</sup>): 3275, 3199, 2816, 1722, 1673, 1614, 1536, 1509, 1410, 1289, 834. Elemental Analysis for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>; Calculated: %C, 56.90; %H, 3.47; %N, 12.06; Found: %C, 56.68; %H, 3.31; %N, 12.04.

**5-(4-methoxybenzylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (3)**

Yellow powder; yield 89%, m.p.: 295-297 °C; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>): δ = 11.31 (s, 1H, NH), 11.18 (s, 1H, NH), 8.38-8.34 (d, 2H, ArH), 8.24 (s, 1H, CH), 7.07-7.03 (d, 2H, ArH), 3.87 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>): δ = 164.23, 163.75, 162.48, 155.29, 150.52, 137.79, 125.43, 115.78, 114.23, 55.95; IR (KBr, cm<sup>-1</sup>): 3203, 3066, 2840, 1730, 1671, 1600, 1549, 1508, 1438, 1270, 836. Elemental Analysis for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>; Calculated: %C, 58.54; %H, 4.09; %N, 11.38; Found: %C 58.29; %H 3.88; %N 11.41.

**5-(4-ethoxybenzylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4)**

Pale yellow powder; yield 69%, m.p.: 294-296 °C; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>): δ = 11.30 (s, 1H, NH), 11.17 (s, 1H, NH), 8.38-8.33 (d, 2H, ArH), 8.24 (s, 1H, CH), 7.06-7.01 (d, 2H, ArH), 4.17-4.14 (q, 2H, O-CH<sub>2</sub>-), 1.39-1.32 (t, 3H, -CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>): δ = 164.25, 163.12, 162.49, 155.31, 150.51, 137.87, 125.27, 115.64, 114.57, 64.02, 14.68; IR (KBr, cm<sup>-1</sup>): 3185, 3035, 2864, 1730, 1663, 1599, 1522, 1502, 1451, 1266, 843. Elemental Analysis for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>; Calculated: %C, 60.00; %H, 4.65; %N, 10.76; Found: %C, 59.65; %H, 4.44; %N, 10.71.

**5-(4-methylbenzylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (5)**

White crystalline powder; yield 56%, m.p.: 274-275 °C; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>): δ = 11.36 (s, 1H, NH), 11.21 (s, 1H, NH), 8.24 (s, 1H, CH), 8.11-8.06 (d, 2H, ArH), 7.31-7.27 (d, 2H, ArH), 2.37 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>): δ = 163.93, 162.11, 155.30, 150.53, 143.79, 134.27, 129.15, 118.12, 21.62; IR (KBr, cm<sup>-1</sup>): 3207, 3086, 2851, 1750, 1702,

1668, 1575, 1509, 1442, 1220, 801. Elemental Analysis for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>; Calculated: %C, 62.60; %H, 4.38; %N, 12.17; Found: %C, 62.35; %H, 4.28; %N, 12.25.

**5-(4-isopropylbenzylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (6)**

Pale yellow powder; yield 70%, m.p.: 222-224 °C; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>): δ = 11.38 (s, 1H, NH), 11.23 (s, 1H, NH), 8.26 (s, 1H, CH), 8.13-8.09 (d, 2H, ArH), 7.38-7.34 (d, 2H, ArH), 2.95 (m, 1H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.24-1.20 (d, 12H, -(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>): δ = 163.93, 162.09, 155.26, 154.22, 150.53, 134.41, 130.53, 126.51, 118.19, 33.91, 23.64; IR (KBr, cm<sup>-1</sup>): 3313, 3207, 3094, 2973, 2868, 1737, 1698, 1607, 1579, 1511, 1439, 1219, 792. Elemental Analysis for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>; Calculated: %C, 65.11; %H, 5.46; %N, 10.85; Found: %C, 57.10; %H, 4.96; %N, 10.52.

**5-benzylidenepyrimidine-2,4,6(1H,3H,5H)-trione (7)**

White crystalline powder; yield 47%, m.p.: 262-265 °C; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>): δ = 11.40 (s, 1H, NH), 11.24 (s, 1H, NH), 8.28 (s, 1H, CH), 8.09-8.06 (d, *J* = Hz, 2H, ArH), 7.54-7.42 (t, 3H, ArH); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>): δ = 163.72, 161.90, 155.01, 150.53, 133.38, 132.95, 132.51, 128.34, 119.38; IR (KBr, cm<sup>-1</sup>): 3215, 3058, 2850, 1742, 1679, 1584, 1564, 1449, 1201, 803. Elemental Analysis for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>; Calculated: %C, 61.11; %H, 3.73; %N, 12.96; Found: %C, 60.63; %H, 3.80; %N, 12.90.

**5-(4-fluorobenzylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (8)**

White powder; yield 82%, m.p. > 300 °C; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>): δ = 11.41 (s, 1H, NH), 11.26 (s, 1H, NH), 8.26 (s, 1H, CH), 8.23-8.22 (m, 2H, ArH), 7.35-7.26 (m, 2H, ArH); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>): δ = 167.01, 163.72, 162.06, 153.78, 150.52, 136.77, 136.59, 129.56, 129.49, 118.98, 115.74, 115.30; IR (KBr, cm<sup>-1</sup>): 3204, 3087, 2853, 1750, 1700, 1671, 1565, 1506, 1442, 1300, 811. Elemental Analysis for C<sub>11</sub>H<sub>7</sub>FN<sub>2</sub>O<sub>3</sub>; Calculated: %C, 56.42; %H, 3.01; %N, 11.96; Found: %C, 56.18; %H, 2.76; %N, 11.92.

**5-(4-chlorobenzylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (9)**

White powder; yield 82%, m.p.: 299-300 °C; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>): δ = 11.43 (s, 1H, NH), 11.27 (s, 1H, NH), 8.24 (s, 1H, CH), 8.09-8.05 (d, 2H, ArH), 7.54-7.50 (d, 2H, ArH); <sup>13</sup>C

NMR (50 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 163.55, 161.91, 153.32, 150.52, 137.04, 135.00, 131.87, 128.40, 119.97; IR (KBr, cm<sup>-1</sup>): 3211, 3084, 2849, 1754, 1703, 1675, 1574, 1443, 1289, 810. Elemental Analysis for C<sub>11</sub>H<sub>7</sub>ClN<sub>2</sub>O<sub>3</sub>; Calculated: %C, 52.71; %H, 2.82; %N, 11.18; Found: %C, 52.55; %H, 2.66; %N, 11.13.

**5-(4-bromobenzylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (10)**

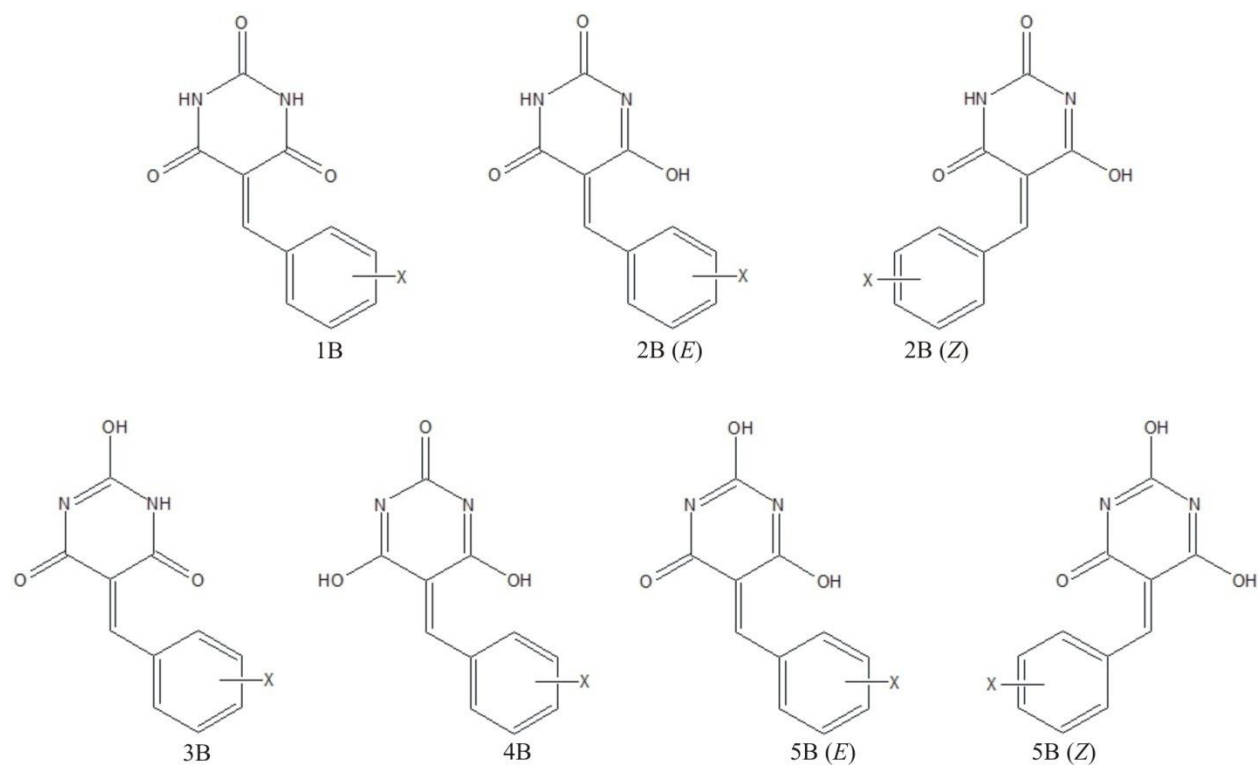
White powder; yield 74%, m.p.: 293-294 °C; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 11.43 (s, 1H, NH), 11.28 (s, 1H, NH), 8.22 (s, 1H, CH), 8.00-7.96 (d, 2H, ArH), 7.69-7.64 (d, 2H, ArH); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 163.53, 161.90, 153.39, 150.50, 135.00, 132.24, 131.34, 126.14, 120.07; IR (KBr, cm<sup>-1</sup>): 3207, 3088, 2854, 1753, 1701, 1672, 1572, 1441, 808. Elemental Analysis for C<sub>11</sub>H<sub>7</sub>BrN<sub>2</sub>O<sub>3</sub>; Calculated: %C, 44.77; %H, 2.39; %N, 9.49; Found: %C, 44.60; %H, 2.17; %N, 9.42.

**4-((2,4,6-trioxotetrahydropyrimidin-5(6*H*)-ylidene)methyl)benzonitrile (11)**

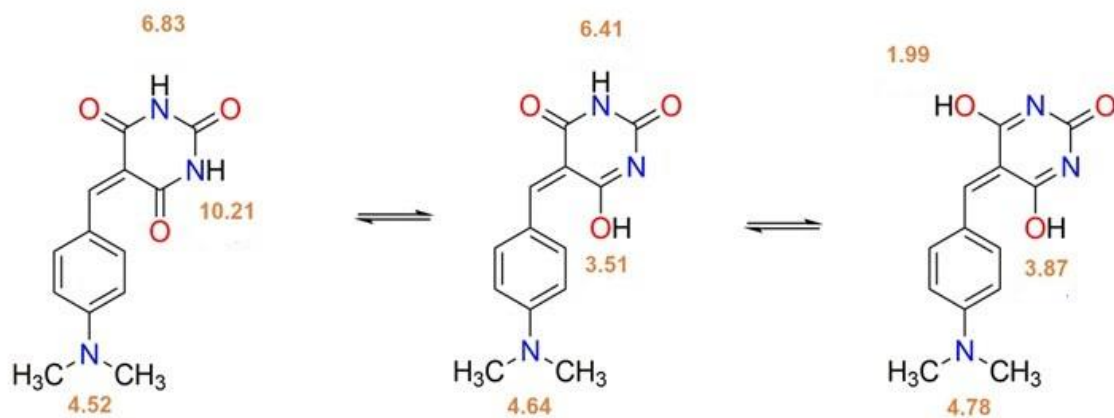
White powder; yield 35%, m.p. > 300 °C; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 11.48 (s, 1H, NH), 11.31 (s, 1H, NH), 8.29 (s, 1H, CH), 8.01-7.86 (m, 4H, ArH); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 163.09, 161.52, 152.02, 150.53, 138.22, 132.23, 131.83, 122.16, 118.83, 112.96; IR (KBr, cm<sup>-1</sup>): 3218, 3058, 2846, 2233, 1745, 1696, 1579, 1444, 1201, 802. Elemental Analysis for C<sub>12</sub>H<sub>7</sub>N<sub>3</sub>O<sub>3</sub>; Calculated: %C, 59.75; %H, 2.93; %N, 17.42; Found: %C, 58.87; %H, 2.75; %N, 17.27.

**5-(4-nitrobenzylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (12)**

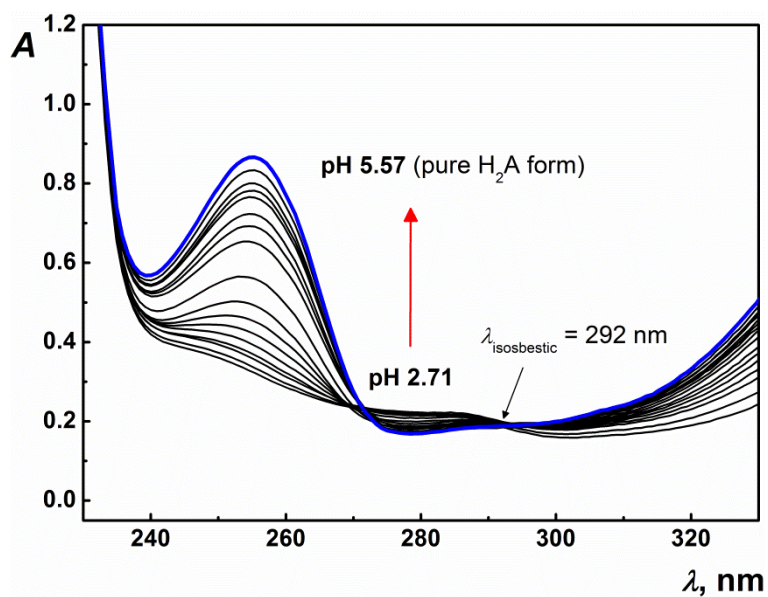
White powder; yield 59%, m.p.: 283-286 °C; <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 11.51 (s, 1H, NH), 11.33 (s, 1H, NH), 8.32 (s, 1H, CH), 8.27-7.99 (m, 4H, ArH); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 162.99, 162.66, 151.45, 150.53, 148.33, 140.34, 132.55, 122.99, 122.64; IR (KBr, cm<sup>-1</sup>): 3194, 3089, 2965, 2857, 1741, 1692, 1645, 1515, 1344, 1323, 852. Elemental Analysis for C<sub>11</sub>H<sub>7</sub>N<sub>3</sub>O<sub>5</sub>; Calculated: %C, 50.58; %H, 2.70; %N, 16.09; Found: %C, 49.47; %H, 4.36; %N, 17.14.



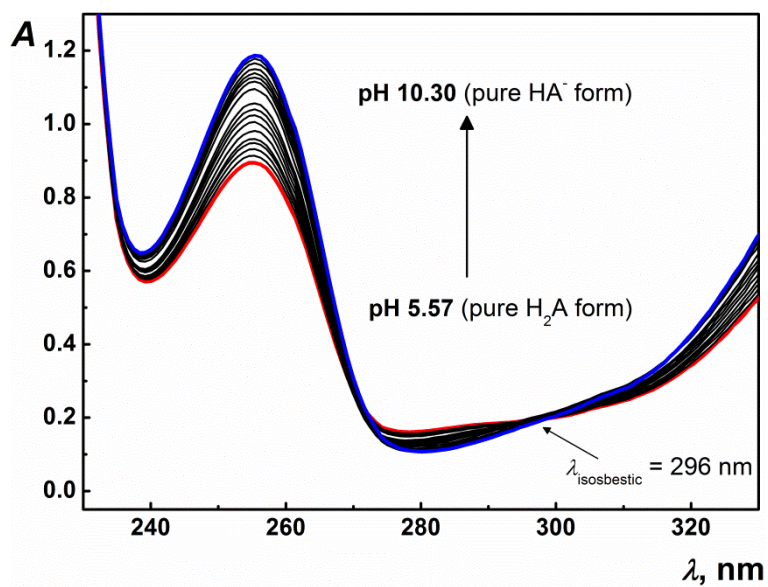
**Fig.S1.** Structures of keto and enol forms of 5-benzylidenebarbituric acid derivatives; *E* and *Z* isomers



**Fig.S2.** The tautomeric equilibria and predicted ionization constants for compound **1**. The  $pK_a$  values are predicted by MarvinSketch software.

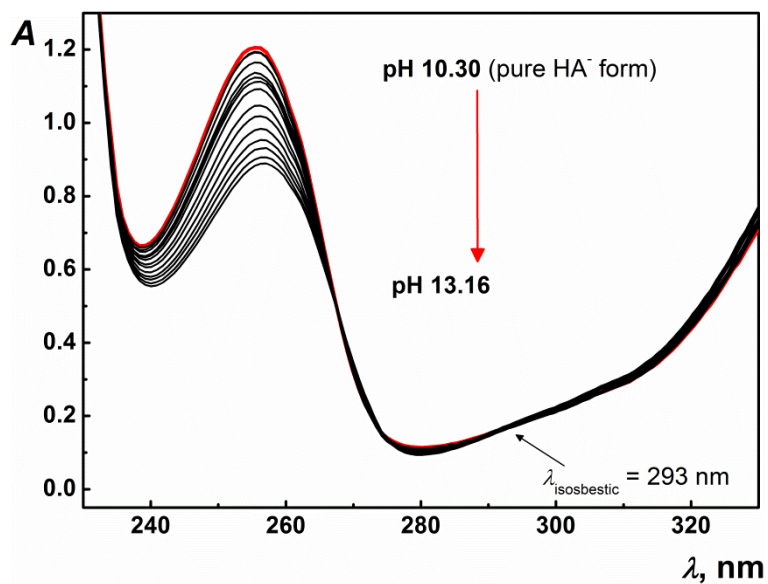


**Fig.S3.** The UV/Vis spectra of compound **1** at different pH used for  $K_{a1}$  determination. The spectrum of pure  $H_2A$  form (solid blue line) and the isosbestic point is indicated.

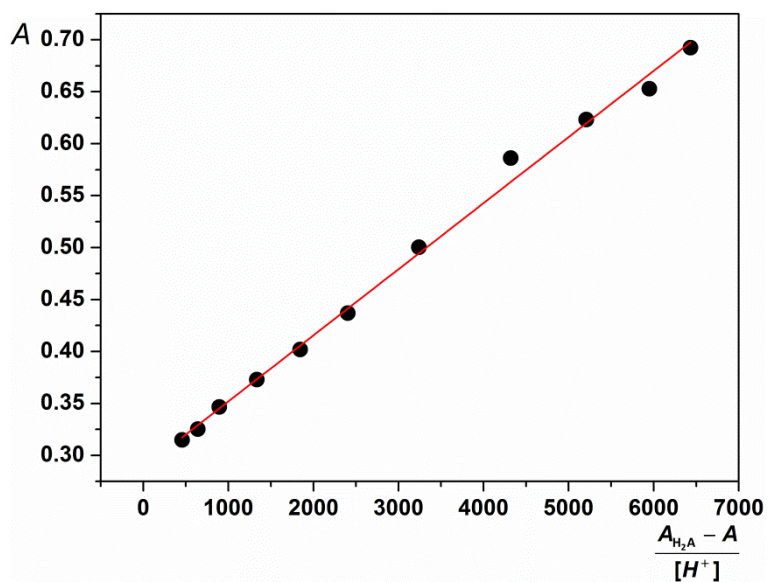


**Fig.S4.** The UV/Vis spectra of compound **1** at different pH used for  $K_{a2}$  determination. The spectra of pure  $H_2A$  and  $HA^-$  forms of the compound (solid red and blue lines, respectively) and the isosbestic point are indicated.

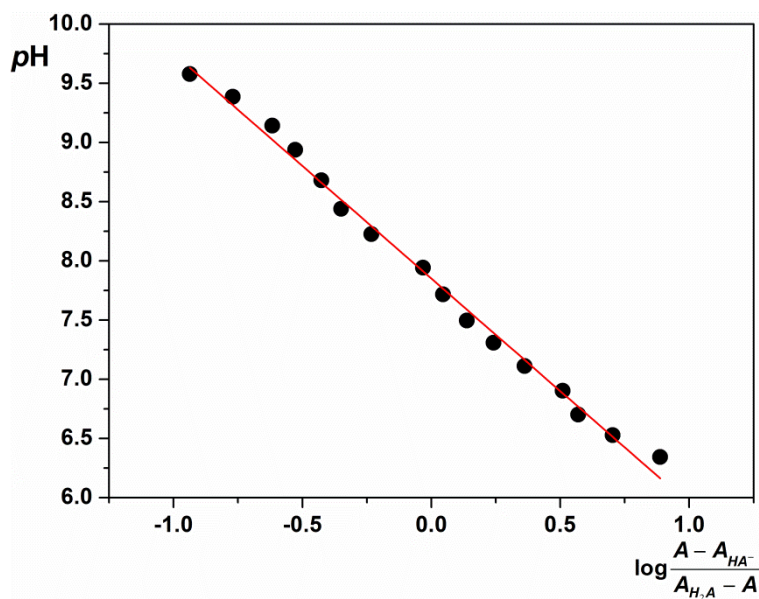




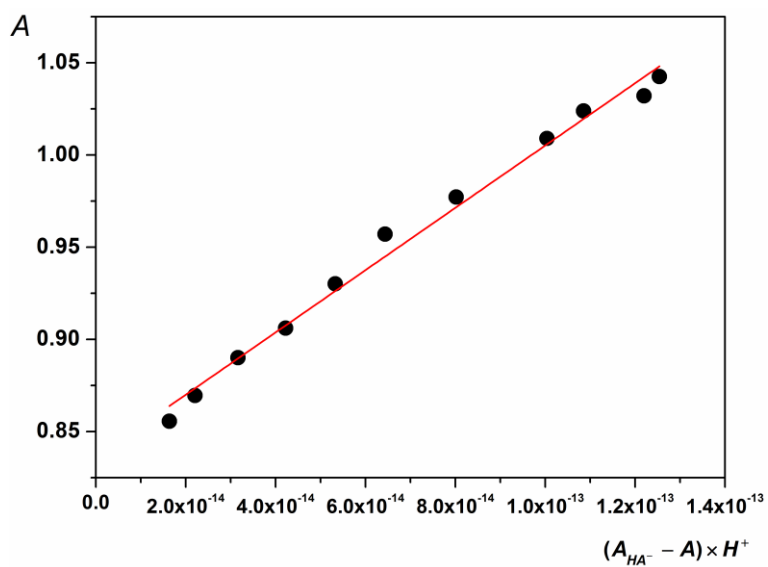
**Fig.S5.** The UV/Vis spectra of compound **1** at different pH used for  $K_{a3}$  determination. The spectrum of pure  $\text{HA}^-$  form of the compound (solid red line) and the isosbestic point is indicated.



**Fig. S6.** Linearization of spectral data for calculating the  $pK_{a1}$  of compound **1** according to the equation 2;  $\lambda_{\text{det}} = 255.4 \text{ nm}$ ; Slope =  $K_{a1} = 6.29(\pm 0.16) \times 10^{-5}$ , intercept =  $A_{\text{H}_3\text{A}^+} = 0.330 \pm 0.006$ .



**Fig. S7.** Linearization of spectral data for calculating the  $pK_{a2}$  of compound **1** according to the equation 1;  $\lambda_{det} = 255.4$  nm; Slope =  $-1$ ; intercept =  $pK_{a2} = 7.88 \pm 0.12$ .



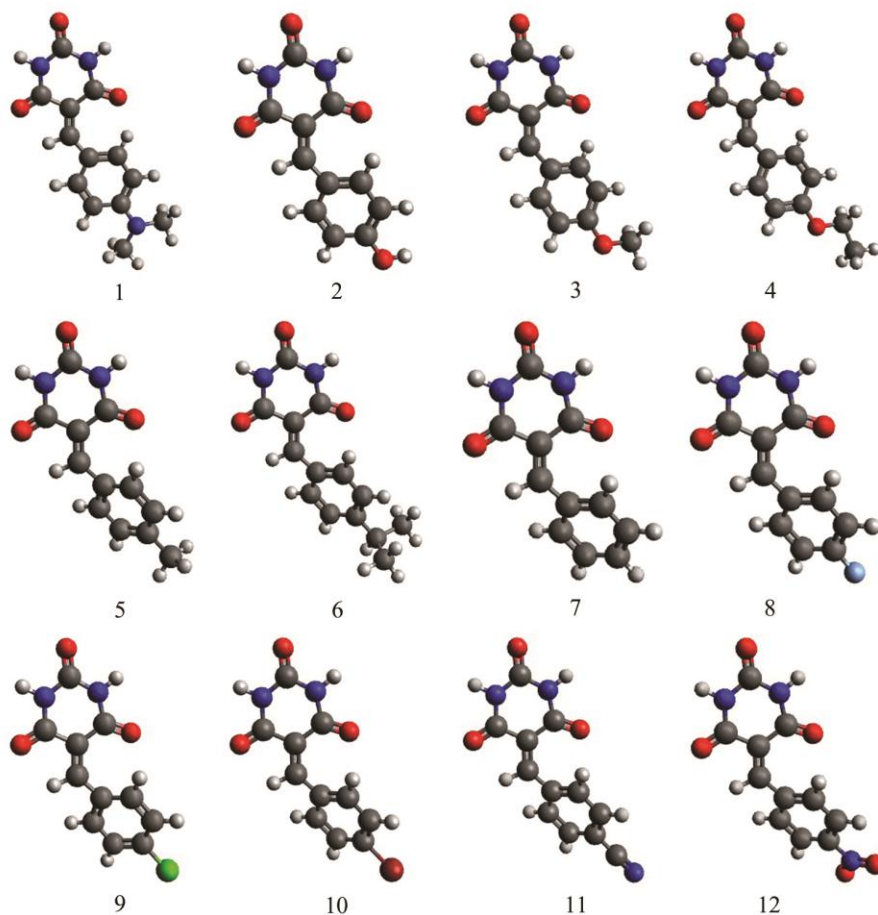
**Fig. S8.** Linearization of spectral data for calculating the  $pK_{a3}$  of compound **1** according to the equation 3;  $\lambda_{det} = 255.4$  nm; Slope =  $1/K_{a3} = 1.86(\pm 0.03) \times 10^{12}$ , intercept =  $A_{A^{2-}} = 0.851 \pm 0.002$ .

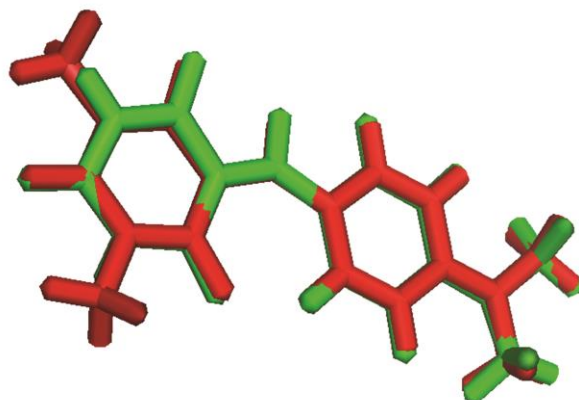
**Table S4**

Optimized energies of isomers of 5-benzylidene barbituric acid derivatives in kcal/mol.

Molecule	Energy of Isomer 1B	Energy of Isomer 3B*	Energy of Isomer 4B*	Energy of Isomer 2B*		Energy of Isomer 5B*	
				E	Z	E	Z
1	0.0	19.9	33.7	16.2	15.4	34.9	33.4
2	0.0	19.8	33.0	16.0	15.7	34.7	33.8
3	0.0	20.6	32.9	16.0	15.4	34.8	33.3
4	0.0	19.7	33.8	16.9	15.4	35.8	33.3
5	0.0	19.6	32.5	15.6	15.5	34.4	33.6
6	0.0	19.6	32.5	15.6	15.5	34.4	33.6
7	0.0	19.6	32.5	15.5	15.5	34.3	34.2
8	0.0	19.5	32.8	15.8	15.5	34.5	33.6
9	0.0	19.5	32.7	15.7	15.5	34.5	33.6
10	0.0	19.5	32.7	15.7	15.5	34.5	33.6
11	0.0	19.3	32.8	15.8	15.6	34.6	34.2
12	0.0	19.4	32.9	15.8	15.6	34.6	34.3

\*The energies of isomers are relative to the energy of isomer 1B

**Fig.S9.** Optimal geometries for compounds 1-12



**Fig.S10.** Aligned crystal structure of 5-(4-(Dimethylamino)benzylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (CSD Refcode: FOMJEX[5], red) with MP2/6-311G(d,p) optimized structure of compound **1** (green).

#### 4.2 Geometry optimization of 5-benzylidenebarbituric acid derivatives

It is well known that the geometry of the molecules with unsaturated vinyl group bound to an aromatic ring is determined by two effects acting in the opposite directions: delocalization of pi electrons (stabilizing planar conformation) and steric repulsion between *ortho* proton/substituent from benzene ring and protons/substituents from the vinyl group (stabilizing twisted conformation). In the case of styrene, the smallest molecule of the series, the gas-phase electron diffraction experiments have shown that the twisted geometry is most stable, with a dihedral angle between benzene and vinyl group planes of 28° [6]. Also, it was shown that popular DFT methods tend to overestimate pi delocalization and predict the planar structure of styrene as the most stable [7–9]. On the other hand, MP2 theory predicts twisted styrene (with very low rotation barrier to planar structure) as the global energy minimum structure [6–10]. The results of the MP2 calculations are in much better agreement with experimental results. For this reason, the MP2/6-311G(d,p) method is chosen for geometry optimization in this paper.

#### 4.2.1 Correlation between dihedral angles and Hammett and Swain-Lupton substituent constants

Correlation of the dihedral angles values for the compounds **1-12** from Table 2 with Hammett and Swain-Lupton parameters:

$$\theta = -0.02(\pm 0.30)F + 1.59(\pm 0.10)R + 0.90(\pm 0.13) \quad (\text{S7})$$

$$(r=0.98, sd=0.20, F=127.34, n=11)$$

$$\theta = -0.02(\pm 0.38)\sigma_{I+} + 2.44(\pm 0.23)\sigma_{R++} + 0.82(\pm 0.17) \quad (\text{S8})$$

$$(r=0.97, sd=0.28, F=65.34, n=11)$$

**Table S5**

NMR chemical shifts differences of the unsubstituted compound (**7**) and the corresponding derivatives **1-6** and **8-12**.

Substituent	C2	C4	C5	C6	C7	C8	C9	C10	C11
<b>NMe<sub>2</sub></b>	0.1	1.1	-7.9	1.3	0.8	-13.1	6.9	-23.2	26.1
<b>OH</b>	0.1	1.5	-3.5	0.8	0.9	-9.3	6.1	-18.5	34.3
<b>OCH<sub>3</sub></b>	0.0	1.8	-3.6	0.5	0.3	-7.9	5.3	-18.7	34.1
<b>OCH<sub>2</sub>CH<sub>3</sub></b>	0.0	1.2	-3.7	0.5	0.3	-8.1	5.4	-18.4	34.2
<b>CH(CH<sub>3</sub>)<sub>2</sub></b>	0.0	0.2	-1.2	0.2	0.3	-2.8	1.9	-6.4	25.9
<b>CH<sub>3</sub></b>	0.0	0.2	-1.3	0.2	0.3	-3.3	1.8	-3.8	15.5
<b>H</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>	<b>0.0</b>
<b>F</b>	0.0	0.2	-0.4	0.0	-1.2	-3.8	4.3	-17.7	38.7
<b>Cl</b>	0.0	0.0	0.6	-0.2	-1.7	-1.5	2.5	-4.5	8.7
<b>Br</b>	0.0	0.0	0.7	-0.2	-1.6	-1.0	2.5	-1.6	-2.2
<b>CN</b>	0.0	-0.4	2.8	-0.6	-3.0	4.8	-0.3	-1.1	-15.4
<b>NO<sub>2</sub></b>	0.0	0.8	3.3	-0.7	-3.6	7.0	0.0	-10.0	20.0

**Table S6**

Absorption frequencies of the investigated compounds in select solvents.

Solvent/compound	$\nu_{\max} \times 10^{-3} (\text{cm}^{-1})$											
	1	2	3	4	5	6	7	8	9	10	11	12
<b>2,2,2-Trifluoroethanol</b> (TFE)	20.75	24.91	23.98	24.07	28.01	27.51	27.93	28.37	27.59	26.63	30.96	29.73
<b>Ethylene glycol</b> (EG)	20.94	25.64	26.08	25.84	28.61	27.55	31.25	29.90	29.54	29.46	31.17	31.23
<b>Methanol</b> (MeOH)	21.62	26.11	26.77	26.49	29.41	29.28	30.82	30.58	30.26	29.50	32.15	28.87
<b>2-Chloroethanol</b>	20.94	25.48	25.58	25.45	28.05	27.93	30.12	29.72	29.37	29.41	31.70	31.77
<b>1,2-Propanediol</b> (1,2-PDO)	21.14	24.94	25.67	25.87	27.51	30.03	29.28	30.17	28.74	28.65	30.71	28.23
<b>Diethylene glycol</b> (DEG)	20.77	25.19	23.78	24.45	27.93	27.74	27.89	27.70	27.62	27.47	27.64	27.88
<b>Ethanol</b> (EtOH)	21.74	26.04	26.74	26.42	29.24	29.03	30.86	30.35	30.21	30.12	32.21	30.15
<b>2-Propanol</b> (IPA)	21.79	25.61	27.03	26.60	29.41	29.33	30.53	30.40	29.76	29.72	31.70	31.95
<b>2-Methyl-1-propanol</b> (Isobutanol)	21.62	25.61	26.39	26.25	28.94	28.82	30.63	30.30	29.94	29.54	31.75	31.77
<b>1-Butanol</b> (BuOH)	21.60	25.58	26.53	26.49	28.99	28.86	30.44	30.12	29.63	29.72	38.61	32.70
<b>Dimethyl sulfoxide</b> (DMSO)	21.60	26.28	26.81	26.88	29.46	29.11	30.77	30.67	30.63	30.30	32.00	31.30
<b>N,N-Dimethylacetamide</b> (DMA)	21.91	26.35	27.06	26.92	29.50	29.50	30.86	30.82	30.58	30.40	32.26	31.96
<b>Acetonitrile</b> (MeCN)	21.79	27.10	26.88	26.56	29.24	29.46	30.72	30.67	30.30	30.35	31.85	31.80
<b>N,N-Dimethylformamide</b> (DMF)	21.79	26.28	26.92	26.88	29.46	29.11	31.10	30.72	30.30	29.50	31.07	31.59
<b>N-Methyl-2-pyrrolidinone</b> (NMP)	21.76	21.37	27.06	26.88	29.33	29.33	30.91	30.86	30.49	30.40	31.95	31.99
<b>Tetrahydrofuran</b> (THF)	22.27	26.85	27.55	27.14	29.59	29.46	31.10	30.86	30.53	30.44	31.75	31.80
<b>Ethyl acetate</b> (EtOAc)	22.25	26.77	27.17	27.17	29.28	29.28	31.15	30.91	30.91	31.01	31.40	31.40
<b>1,2-Dimethoxyethane</b> (DME)	22.22	26.70	27.06	27.25	29.54	29.41	30.86	30.77	30.58	30.26	31.80	31.60
<b>Anisole</b>	21.69	26.42	26.49	26.35	28.65	28.65	30.40	29.90	29.67	29.41	31.20	32.36
<b>Trichloromethane</b> (TCM)	21.37	26.70	25.74	25.67	28.05	28.01	29.63	29.28	29.03	28.69	31.10	30.82
<b>Diisopropyl ether</b> (DIPE)	22.70	26.01	27.59	27.51	29.76	29.33	31.15	30.86	30.44	30.21	31.85	31.65

**Table S7**

Results of the correlation analysis of 5-benzylidenebarbiturates according to Kamlet–Taft equation.

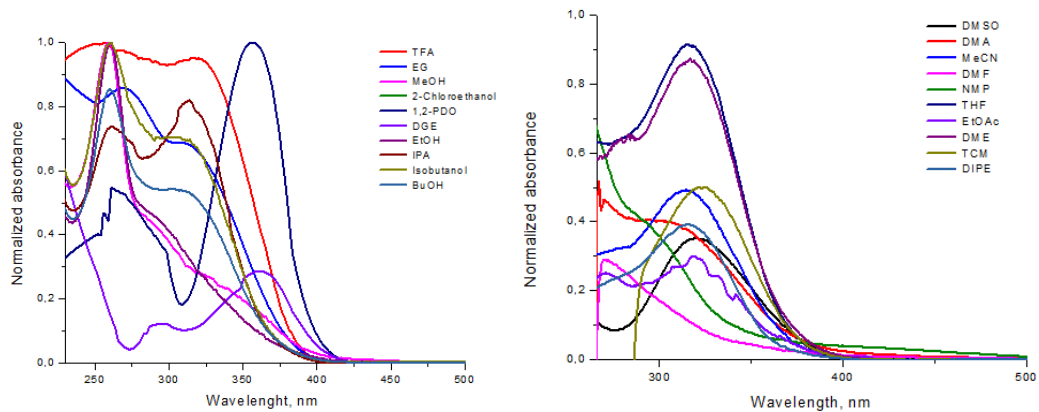
Comp.	1	2	3	4	5	6	7	8	9	10	11	12
$\nu \times 10^{-3}$ ( $\text{cm}^{-1}$ )	2.06±0.42	1.00±0.31	0.35±0.40	0.57±0.38	0.53±0.30	-0.18±0.46	-0.04±0.38	-0.39±0.47	-0.27±0.44	-0.19±0.47	-0.07±0.02	0.55±0.54
$s \times 10^{-3}$ ( $\text{cm}^{-1}$ )	-2.67±0.49	-0.25±0.35 <sup>f</sup>	-1.30±0.47	-1.41±0.44	-1.37±0.42	-1.92±0.58	-1.17±0.46	-0.60±0.55 <sup>f</sup>	-0.36±0.51 <sup>f</sup>	-0.54±0.56 <sup>f</sup>	-0.01±0.02 <sup>f</sup>	1.32±0.66 <sup>f</sup>
$b \times 10^{-3}$ ( $\text{cm}^{-1}$ )	0.78±0.39 <sup>f</sup>	-0.27±0.24 <sup>f</sup>	2.09±0.38	1.91±0.35	2.24±0.37	3.41±0.61	2.41±0.34	2.45±0.43	2.09±0.41	2.24±0.44	0.12±0.02	-1.75±0.65
$a \times 10^{-3}$ ( $\text{cm}^{-1}$ )	-1.68±0.19	-0.95±0.12	-1.55±0.19	-1.63±0.17	-1.55±0.20	-1.80±0.30	-1.51±0.17	-1.48±0.23	-1.51±0.20	-1.50±0.22	0.00±0.01 <sup>f</sup>	-1.84±0.25
$r^c$	0.93	0.91	0.93	0.94	0.92	0.90	0.94	0.91	0.92	0.91	0.91	0.92
$sd^d$	0.41	0.25	0.40	0.37	0.28	0.44	0.36	0.46	0.43	0.46	0.02	0.48
$t^s$	-5.50	-0.72	-2.75	-3.23	-3.29	-3.31	-2.55	-1.09	-0.71	-0.96	-0.62	2.01
$t^b$	1.99	-1.12	5.51	5.41	6.04	5.61	7.05	5.63	5.11	5.06	6.47	-2.68
$t^a$	-8.81	-7.71	-8.36	-9.46	-7.77	-6.05	-8.68	-6.57	-7.57	-6.89	-0.14	-7.33
$F^e$	31.69	21.23	34.01	40.37	23.49	16.20	41.47	24.97	28.59	24.28	15.37	19.23
<b>Solvent excluded from correlation</b>	-	NMP and DIPE	-	-	TFE, 1,2-PDO, and EG	2-Chloroethanol, Isobutanol, TFE, and MeCN	EG	2-Chloroethanol	-	DMF	EG, 2-Chloroethanol, IPA, Isobutanol, BuOH, and DMF	MeOH, 2-Propanol, Isobutanol, BuOH, and TCM

<sup>s,b,a</sup>  $t_{kr(\alpha=0.05, v=16)}=2.12$ ;  $t_{kr(\alpha=0.05, v=15)}=2.13$ ;  $t_{kr(\alpha=0.05, v=14)}=2.14$ ;  $t_{kr(\alpha=0.05, v=13)}=2.16$ ;  $t_{kr(\alpha=0.05, v=12)}=2.18$ ;  $t_{kr(\alpha=0.05, v=11)}=2.20$ ;  $t_{kr(\alpha=0.05, v=10)}=2.23$ ;

<sup>d</sup>  $F_{kr(\alpha=0.05, v=3, v=16)}=3.24$ ;  $F_{kr(\alpha=0.05, v=3, v=15)}=3.29$ ;  $F_{kr(\alpha=0.05, v=3, v=14)}=3.34$ ;  $F_{kr(\alpha=0.05, v=3, v=13)}=3.41$ ;  $F_{kr(\alpha=0.05, v=3, v=12)}=3.49$ ;

 $F_{kr(\alpha=0.05, v=3, v=11)}=3.59$ ;  $F_{kr(\alpha=0.05, v=3, v=10)}=3.71$ ;

<sup>s,b,a</sup>  $t$  test for individual [regression coefficients](#); <sup>c</sup> Correlation coefficient; <sup>d</sup> Standard deviation; <sup>e</sup> Fisher test of significance; <sup>f</sup> Statistically insignificant result.



**Fig. S11.** Absorption spectra of compound **12** in considered solvents



**Table S8**

Results of the correlation analysis of 5-benzylidene barbiturates according to Hammett equations.

Solvent	$\rho_I$	$\rho_R$	$r$	$sd$	$I_t$	$R_t$	$F$	$\rho R/\rho F$	Compound excluded from correlation
<b>2,2,2-Trifluoroethanol</b>	0.47±0.44	2.30±0.26	0.96	0.33	1.05	8.70	46.70	4.89	-
<b>Ethylene glycol</b>	0.58±0.44	2.27±0.26	0.96	0.32	1.32	8.73	48.29	3.91	-
<b>Methanol</b>	0.81±0.38	2.53±0.22	0.98	0.26	2.14	11.71	78.35	3.12	12
<b>2-Chloroethanol</b>	0.90±0.27	2.25±0.16	0.98	0.20	3.29	13.86	131.37	2.50	-
<b>1,2-Propanediol</b>	0.75±0.53	2.47±0.30	0.95	0.36	1.41	8.18	38.04	3.29	12
<b>Diethylene glycol</b>	-0.63±0.49	2.47±0.28	0.96	0.34	-1.29	8.95	42.24	3.92	8
<b>Ethanol</b>	0.90±0.32	2.49±0.18	0.98	0.22	2.79	13.60	107.46	2.77	12
<b>2-Propanol</b>	0.54±0.36	2.32±0.21	0.97	0.27	1.49	10.85	73.67	4.30	-
<b>2-Methyl-1-propanol</b>	0.65±0.34	2.30±0.20	0.97	0.25	1.92	11.46	84.33	3.54	-
<b>1-Butanol</b>	0.62±0.21	1.71±0.13	0.98	0.15	2.89	13.26	108.00	2.76	-
<b>Dimethyl sulfoxide</b>	0.64±0.42	2.26±0.25	0.96	0.31	1.55	9.17	54.02	3.53	-
<b><i>N,N</i>-Dimethylacetamide</b>	0.68±0.35	2.28±0.21	0.97	0.26	1.96	10.98	78.13	3.35	-
<b>Acetonitrile</b>	0.70±0.35	2.28±0.21	0.97	0.26	2.00	10.98	78.51	3.26	-
<b><i>N,N</i>-Dimethylformamide</b>	0.46±0.45	2.30±0.27	0.95	0.33	1.02	8.57	45.27	5.00	-
<b><i>N</i>-Methyl-2-pyrrolidinone</b>	0.61±0.31	1.81±0.19	0.97	0.23	1.98	9.59	61.85	2.97	-
<b>Tetrahydrofuran</b>	0.63±0.40	2.28±0.24	0.96	0.29	1.57	9.63	59.36	3.62	-
<b>Ethyl acetate</b>	0.69±0.47	2.22±0.28	0.95	0.35	1.48	7.97	41.42	3.22	-
<b>1,2-Dimethoxyethane</b>	0.63±0.39	2.28±0.23	0.97	0.29	1.62	9.82	61.75	3.62	-
<b>Anisole</b>	0.81±0.28	2.27±0.16	0.98	0.20	2.95	13.86	128.51	2.80	-
<b>Trichloromethane</b>	0.80±0.32	2.26±0.19	0.98	0.23	2.54	12.04	96.86	2.83	-
<b>Diisopropyl ether</b>	0.53±0.45	2.28±0.27	0.95	0.33	1.19	8.53	45.61	4.30	-

<sup>LR</sup> $t_{kr(\alpha=0.05, v=9)}=2.26$ ; <sup>LR</sup> $t_{kr(\alpha=0.05, v=8)}=2.31$ ;<sup>d</sup> $F_{kr(\alpha=0.05, v=2, v=9)}=4.31$ ;  $F_{kr(\alpha=0.05, v=2, v=8)}=4.46$ .

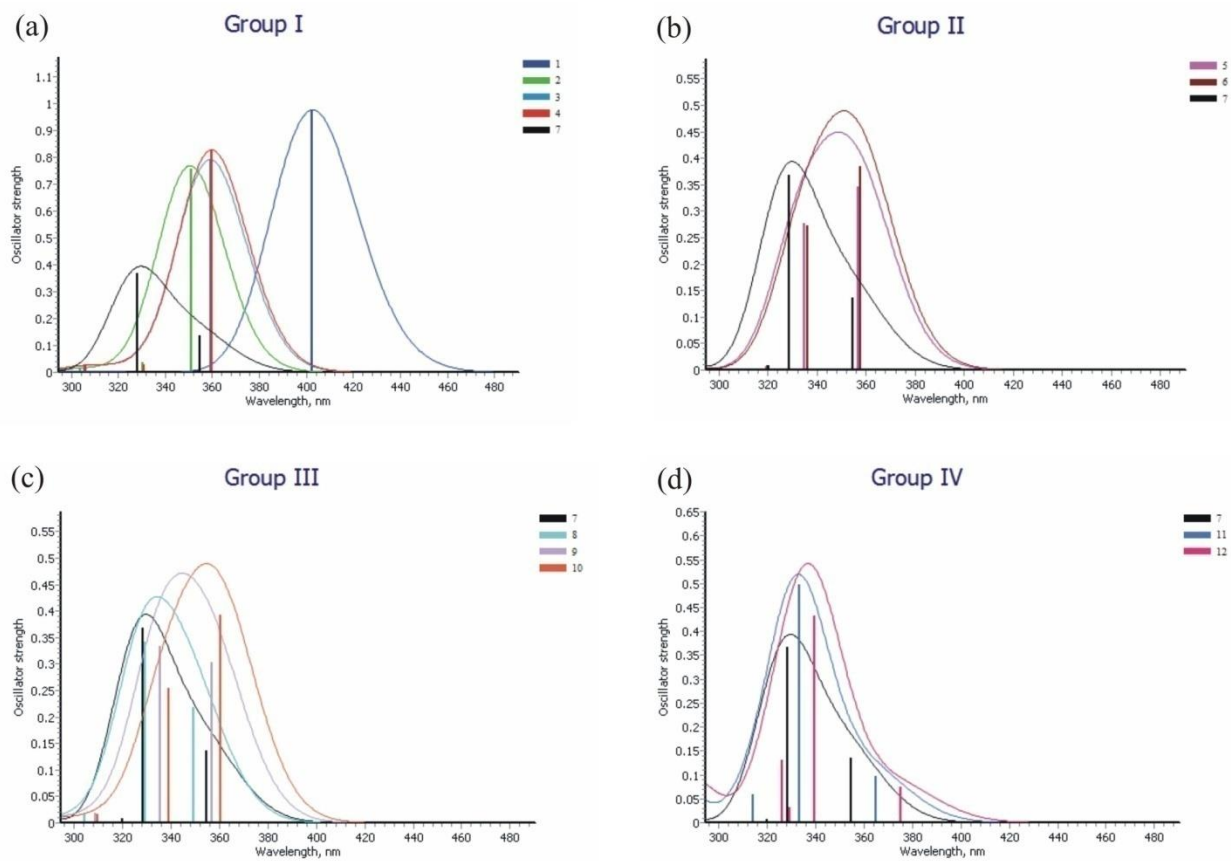
**Table S9**

Results of TDDFT calculations for transitions from ground to the first vertical excited state for compounds **1-12** in solvent acetonitrile.

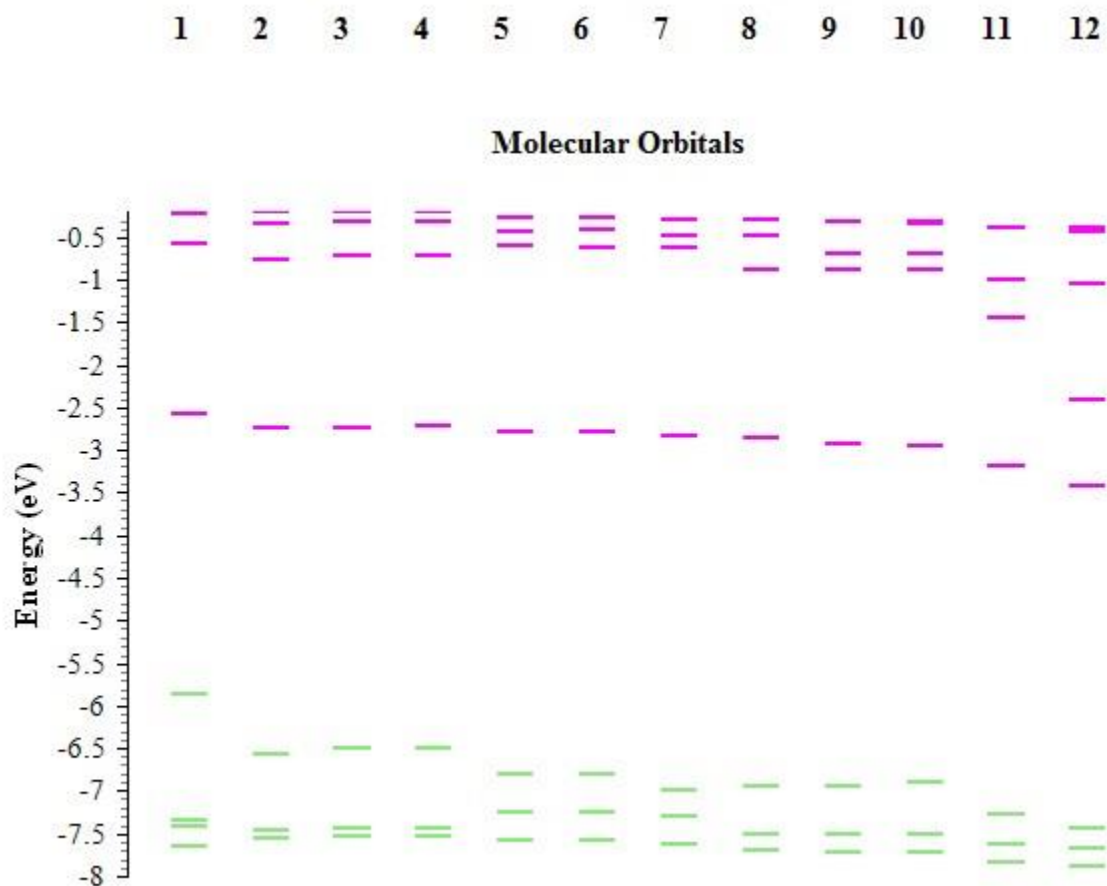
Comp. No.	Excited state	Energy (eV)	Oscillator strength	Excitation	CI expansion coefficient*	% of single particle excitation contribution	D <sub>CT</sub> (Å)	Q <sub>CT</sub> (e <sup>-</sup> )
<b>1</b>	<i>es1</i>	3.0791	0.9751	HOMO → LUMO	0.70612	99.72	4.199	0.678
<b>2</b>	<i>es1</i>	3.5332	0.7564	HOMO → LUMO	0.69412	96.36	3.048	0.620
<b>3</b>	<i>es1</i>	3.4509	0.7875	HOMO → LUMO	0.69810	97.47	3.374	0.627
<b>4</b>	<i>es1</i>	3.4454	0.8242	HOMO → LUMO	0.69882	97.67	3.392	0.626
<b>5</b>	<i>es1</i>	3.4757	0.3454	HOMO → LUMO	0.60419	73.01	1.877	0.659
				<u>HOMO-1 → LUMO</u>	-0.26593	<u>14.14</u>		
	<i>es2</i>	3.7063	0.2770	HOMO-1 → LUMO	0.49909	49.82	1.158	0.677
				HOMO → LUMO	0.34996	24.49		
				HOMO-2 → LUMO	0.34104	23.26		
<b>6</b>	<i>es1</i>	3.4667	0.3838	HOMO → LUMO	0.60900	74.18	1.957	0.658
				<u>HOMO-1 → LUMO</u>	-0.26252	<u>13.78</u>		
	<i>es2</i>	3.6896	0.2725	HOMO-1 → LUMO	0.51359	52.75	1.331	0.679
				HOMO → LUMO	0.34177	23.36		
				HOMO-2 → LUMO	0.32807	21.53		
<b>7</b>	<i>es1</i>	3.4968	0.1355	HOMO → LUMO	0.53018	56.22	1.276	0.694
				HOMO-1 → LUMO	0.33541	22.50		
				<u>HOMO-2 → LUMO</u>	-0.30327	<u>18.39</u>		
	<i>es2</i>	3.7754	0.3676	HOMO-1 → LUMO	0.45714	41.80	1.740	0.676
				HOMO → LUMO	-0.44381	39.39		
				HOMO-2 → LUMO	-0.27835	15.50		
<b>8</b>	<i>es1</i>	3.5468	0.2172	HOMO → LUMO	0.52856	55.88	1.057	0.672
				<u>HOMO-1 → LUMO</u>	-0.41001	<u>33.62</u>		
	<i>es2</i>	3.7646	0.3414	HOMO-1 → LUMO	0.45749	41.86	0.478	0.667
				HOMO → LUMO	0.45217	40.89		
				HOMO-2 → LUMO	0.26792	14.36		
<b>9</b>	<i>es1</i>	3.4743	0.3024	HOMO → LUMO	0.56739	64.39	1.437	0.662
				<u>HOMO-1 → LUMO</u>	0.36470	<u>26.60</u>		
	<i>es2</i>	3.6919	0.3334	HOMO-1 → LUMO	0.49217	48.45	0.392	0.678
				HOMO → LUMO	-0.40611	32.99		
				HOMO-2 → LUMO	0.28239	15.95		
<b>10</b>	<i>es1</i>	3.4367	0.3923	HOMO → LUMO	0.61078	74.61	2.197	0.661
				<u>HOMO-1 → LUMO</u>	0.30383	<u>18.46</u>		
	<i>es2</i>	3.6574	0.2538	HOMO-1 → LUMO	0.52985	56.15	0.271	0.704
				HOMO → LUMO	-0.34087	23.24		
				HOMO-2 → LUMO	0.30094	18.11		

<b>11</b>	<i>es1</i>	3.3952	0.0963	HOMO → LUMO	0.47831	45.76	1.294	0.706
				<u>HOMO-1 → LUMO</u>	-0.46470	<u>43.19</u>		
	<i>es2</i>	3.7208	0.4975	HOMO → LUMO	0.49512	49.03	1.077	0.620
				HOMO-1 → LUMO	0.41330	34.16		
				<u>HOMO-2 → LUMO</u>	0.24598	<u>12.10</u>		
	<i>es3</i>	3.946	0.0574	HOMO-2 → LUMO	0.61494	75.63	2.693	0.731
HOMO-1 → LUMO				-0.30924	19.13			
<b>12</b>	<i>es1</i>	3.3044	0.0734	HOMO → LUMO	0.53904	58.11	2.132	0.719
				<u>HOMO-1 → LUMO</u>	0.38845	<u>30.18</u>		
	<i>es2</i>	3.6505	0.4326	HOMO-1 → LUMO	0.44832	40.20	1.370	0.609
				HOMO → LUMO	-0.39777	31.64		
				<u>HOMO-2 → LUMO</u>	0.24639	<u>12.14</u>		
	<i>es4</i>	3.7995	0.1300	HOMO-5 → LUMO	0.41120	33.82	1.414	0.646
				HOMO-6 → LUMO	0.31880	20.33		
				HOMO-5 → LUMO+2	-0.25375	12.88		
HOMO-1 → LUMO				0.24754	12.26			

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**Fig.S12.** Calculated TDDFT UV absorption spectra of compounds **1-12** in acetonitrile



**Fig.S13.** Occupied (green) and virtual (violet) molecular orbitals for compounds **1-12**

Conceptual DFT global reactivity descriptors were estimated from HOMO and LUMO energies according to equations S9 – S13. HOMO and LUMO energies were calculated with B3LYP/6-311G(d,p) method

Electronic chemical potential

$$\mu = \frac{\varepsilon_{H^+} + \varepsilon_L}{2} \quad (\text{S9})$$

Electronegativity

$$\chi = -\mu \quad (\text{S10})$$

Chemical hardness

$$\eta = \varepsilon_L - \varepsilon_H \quad (\text{S11})$$

Global electrophilicity

$$\omega = \frac{\mu^2}{2\eta} \quad (\text{S12})$$

Nucleophilicity index

$$N = \varepsilon_H - \varepsilon_{H(\text{TCE})} \quad (\text{S13})$$

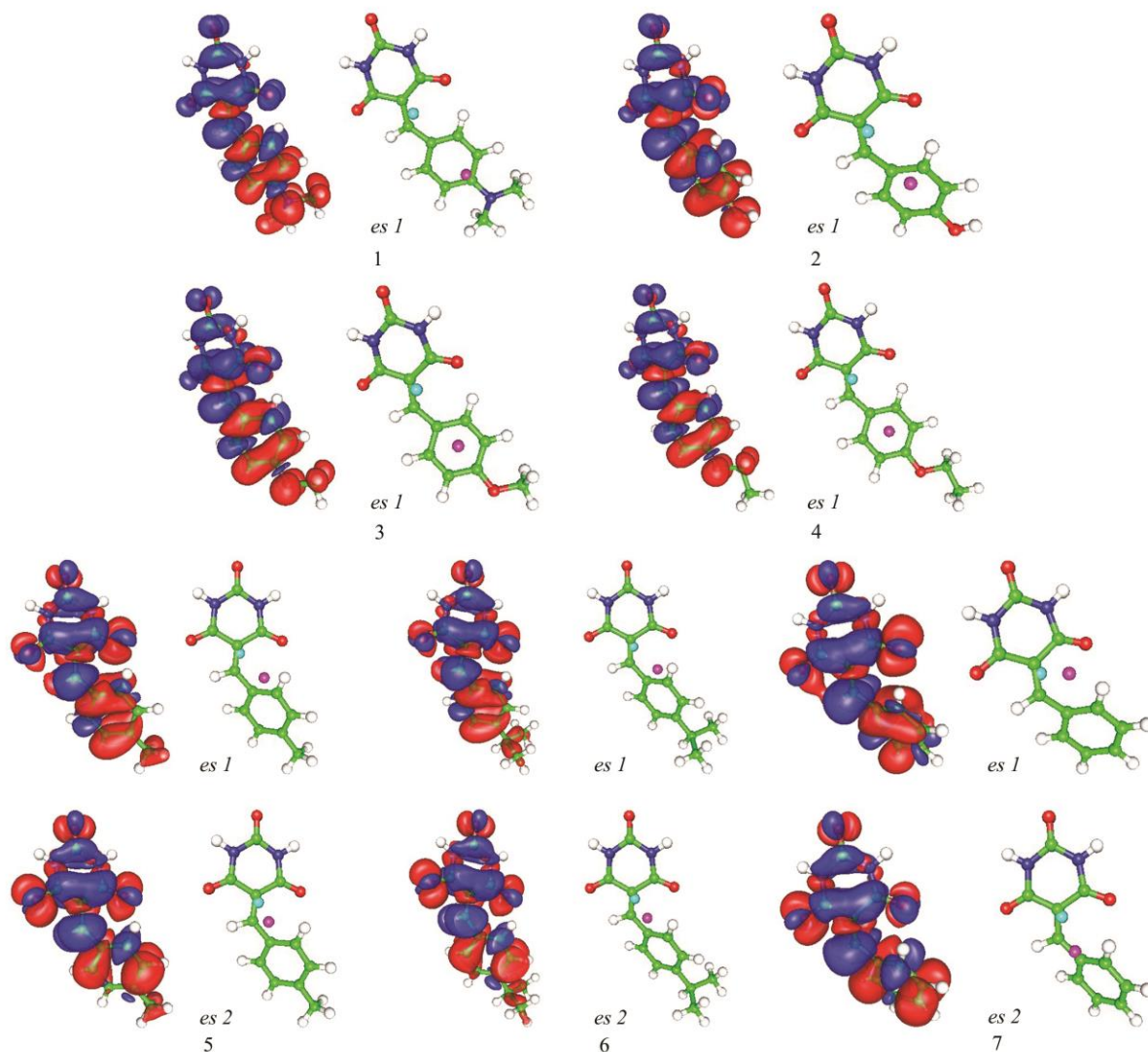
**Table S10**

Global reactivity indices<sup>a</sup> of all investigated compounds [11–18].

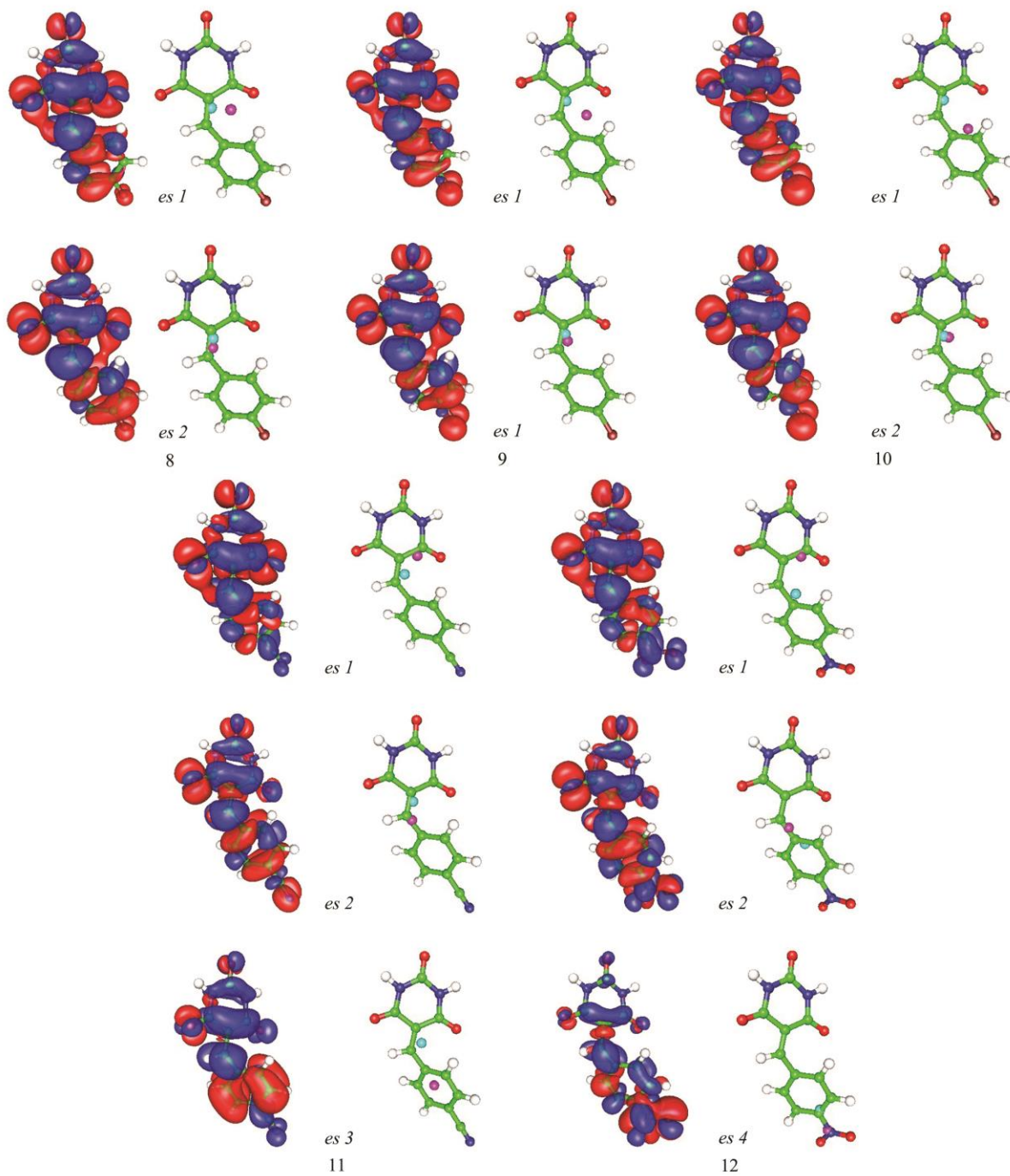
Compound	$\mu$ [eV]	$\chi$ [eV]	$\eta$ [eV]	$\omega$ [eV]	$N$ [eV] <sup>b</sup> [19]
<b>1</b>	-4.158	4.158	3.416	2.531	3.503
<b>2</b>	-4.736	4.736	3.863	2.903	2.702
<b>3</b>	-4.649	4.649	3.798	2.845	2.821
<b>4</b>	-4.621	4.621	3.790	2.817	2.853
<b>5</b>	-4.915	4.915	4.036	2.993	2.436
<b>6</b>	-4.908	4.908	4.031	2.987	2.446
<b>7</b>	-5.080	5.080	4.157	3.103	2.211
<b>8</b>	-5.103	5.103	4.092	3.182	2.220
<b>9</b>	-5.173	5.173	3.995	3.349	2.199
<b>10</b>	-5.136	5.136	3.923	3.361	2.272
<b>11</b>	-5.573	5.573	3.998	3.884	1.797
<b>12</b>	-5.778	5.778	4.037	4.134	1.573

<sup>a</sup> $\mu$  – electronic chemical potential;  $\chi$  - electronegativity;  $\eta$  - chemical hardness;  $\omega$  - global electrophilicity;  $N$  - nucleophilicity index.

<sup>b</sup> HOMO energy of tetracyanoethylene (TCE) is  $-0.34431$  au ( $-9.369$  eV) calculated with B3LYP/6-311G(d,p) method.



**Fig. S14.** ICT processes in compounds **1-7** in solvent acetonitrile; Left image - the difference between densities in the excited and ground state (blue and red density increase and decrease upon transition, respectively); Right images - position of barycentres describing charge loss (violet circle) and charge gain (cyan circle) upon transition.



**Fig. S14. continued** ICT processes in compounds **8-12** in solvent acetonitrile.





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