Supplementary material

Solvatochromism of isatin based Schiff bases: LSER and LFER study

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General method for preparation of isatin derivatives

Isatine derivatives was synthesized according to literature method.[1] Isatin (5 mmol) was dissolved in methanol (40 mL), and corresponding reactants (substituted anilines or aryl amines (5 mmol) and glacial acetic acid (10 mL) were added. Reaction mixture was refluxed at 70 °C for 6 h by using magnetic stirrer. Subsequently, the mixture was left overnight without stirring at room temperature. The obtained crystals were filtered off, dried and recrystallized from methanol or appropriate solvent mixture (Table SII). The average yield was about 70–79 %.

Materials and methods

All commercially available chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA). All NMR spectral measurements were performed on a Varian 2000 (200 MHz for ^{1}H and 50 MHz for ^{13}C NMR spectra). The spectra were recorded at room temperature in deuterated dimethyl sulfoxide (DMSO-d_6). The chemical shifts were expressed in ppm values referenced to δ_H = 2.5 and δ_C = 39.5 ppm in ^{1}H and ^{13}C NMR spectra, respectively. Numeration of the atom of interest for characterization is given in Table SII. UV data were obtained using Shimadzu 1700 UV-Vis spectrophotometer in ethanol as solvent at $5x10^{-5}$ mol dm^{-3}. Fourier-transform infrared (FTIR) spectra were obtained using FTIR BOMEM MB 100 in the form of KBr pellets. FTIR spectra were recorded in the transmission mode between 400 i 4000 cm^{-1} with a resolution of 4 cm^{-1}.

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TABLE SI. Solvent parameters used in Kamlet–Taft equation[2]

	π^*	β	α
Ethanol	0.54	0.77	0.83
Methanol	0.6	0.62	0.93
2-Propanol	0.48	0.95	0.76
2-Butanol	0.4	0.8	0.69
Cyclohexanol	0.45	0.84	0.66
Benzyl alcohol (BzOH)	0.98	0.52	0.6
2-Methoxyethanol	0.71	0	0
2-Chloroethanol	0.46	0.53	1.28
1,2-dimethoxyethane (DME)	0.53	0.41	0
Toluene	0.54	0.11	0
Dichloromethane (DCM)	0.82	0.1	0.13
Tetrahydrofuran (THF)	0.58	0.55	0
Acetonitrile (AcN)	0.75	0.31	0.19
Formamide (F)	0.97	0.48	0.71
Dimethylacetamide (DMAc)	0.88	0.76	0
Dimethylformamide (DMF)	0.88	0.69	0
1-Methyl-2-pyrrolidinone (NMP)	0.92	0.77	0
Ethyl acetate (EtAc)	0.55	0.45	0
2-Pyrrolidone	0.85	0.77	0.36
Dimethylsulfoxide (DMSO)	1	0.76	0
Acetone	0.71	0.48	0.08
Cyclohexanone (ChO)	0.76	0.53	0

^{1}H and ^{13}C NMR, FTIR spectra and elemental analysis of studied compounds are given in Table SII, and general formula with labeling of atom is given on Fig S1:

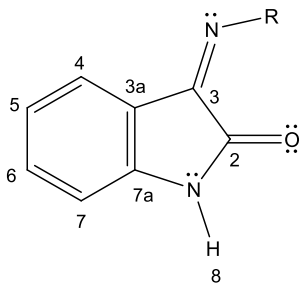
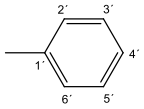
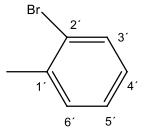
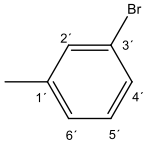
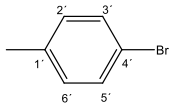
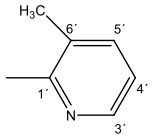
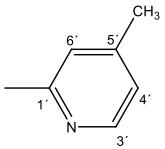


Fig. S1 General formula of 1,3-dihydro-3-(arylimino)-2*H*-indol-2-one with labeling of the atom

TABLE SII. Yield, melting point, FTIR, ^{1}H and ^{13}C NMR data of synthesized compounds

No	R	Yield and m.p.	IR (cm^{-1})	^{1}H NMR (200 MHz, DMSO-d_6)(ppm)	^{13}C NMR (50 MHz, DMSO-d_6)(ppm)
1		Yield: 76%; Exp: 221-222 °C (methanol) Lit: 209.7-211.4 °C[3]	3344, 1741, 1661, 1254.	6,65 (d, 1H, **4**), 6,74 (t, 1H, **5**), 6.95 (d, 1H, **4´**), 7,04 (d, 2H, **2´6´**), 7,26 (t, 1H, **6**), 7,30 (t, 1H, **7**), 7,44 (t, 2 H**, 3´,5)** 10.76 (s, 1H, **8**).	112.1 (C-**7**), 116.4 (C-**3a**), 118.1 (C-**2´6'**), 123.0 (C-**5**), 125.70 (C-**4**), 126.6 (C-**4'**), 129.7 (C-**3´5'**), 134.6 (C-**6**), 146.0 (C-**7a**), 151.88 (C-**1'**), 156.20 (C-**3**), 164.21 (C-**2**).
2		Yield: 69%; Exp: 223-224 ºC (methanol) Lit: 219.8-220.6 ºC[3]	3342, 1746, 1659, 1252.	6,41 (d, 1H, **4**), 6,38 (td, 1H, **5**), 6.78 (d, 1H, **6´**), 6,94 (d, 1H, **6**), 7.34 (d, 1H, **4´**), 7,36-7.43 (m, 2H, **7, 5´**), 7,62 (d, 1H, **3´**), 10.66 (s, 1H, **8**).	89.1 (C-**2'**), 111.6 (C-**7**), 116.74 (C-**3a**), 119.58 (C-**6'**), 122.21 (C-**5**), 123.4 C-**4'**), 125.82 (C-**4**), 127.13 (C-**5'**); 133.02 (C-**3'**), 135.11 (C-**6**), 147.62 (C-**1'**), 148.04 (C-**7a**), 152.1 (C-**3**), 164.1 (C-**2**).
3		Yield: 66%; Exp: 235-236 ºC (methanol) Lit: 219.1-220.2 ºC[3]	3340, 1744, 1658, 1250.	6,38 (d, 1H, **4**), 6,39 (td, 1H, **5**), 6.88 (d, 1H, **6´**), 6,91 (d, 1H, **6**), 7.28 (d, 1H, **5´**), 7,37 (dd, 1H, **7**), 7,54-7,68 (m, 2H, **2´, 4´**), 10.84 (s, 1H, **8**).	88.56 (C-**3'**), 111.8 (C-**7**), 116.70 (C-**3a**), 119.69 (C-**6'**), 122.24 (C-**5**), 123.4 C-**2'**), 125.77 (C-**4**), 126.23 (C-**4'**); 135.06 (C-**6**), 136.02 (C-**5'**), 147.61 (C-**1'**), 148.2 (C-**7a**), 152.03 (C-**3**), 164.03 (C-**2**).
4		Yield: 80%; Exp: 244-241 ºC (methanol) Lit: 220,9-223 ºC[3]	3342, 1745, 1648, 1251	6,40 (d, 1H, **4**), 6,71 (td, 1H, **5**), 6.83 (d, 2H, **2´,6´**), 6,91 (d, 1H, **6**), 7,35 (dd, 1H, **7**), 7,76 (td, 2H, **3´, 5´**), 10.81 (s, 1H, **8**).	89.55 (C-**4'**), 111.91 (C-**7**), 115.87 (C-**3a**), 119.69 (C-**2'**, C-**6'**), 122.18 (C-**5**), 125.72 (C-**4**), 135.0 (C-**6**), 138.58 (C-**3'**,C-**5'**), 147.39 (C-**7a**), 147.63 (C-**1'**), 152.09 (C-**3**), 164.11 (C-**2**).
5		Yield: 64%; Exp:239-240 ºC (DMF/methanol)	3445, 3191, 1751, 1729, 1625, 1251.	2.31 (s, 3H, CH_3), 6,41 (d, 1H, **4**), 6,72 (td, 1H, **5**), 6,96 (d, 1H, **6**), 7.06 (d, 1H, **4´**), 7,38 (dd, 1H, **7**), 7,66 (dd, 1 H**, 5´**),8,36 (dd, 1 H**, 3´**), 11.05 (s, 1H, **8**).	19,7 (CH_3); 111.88 (C-**7**), 115.98 (C-**3a**), 118.73 (C-**4'**), 122.19 (C-**5**), 125.82 (C-**4**), 131.24 (C-**3'**), 135.12 (C-**6**), 138.22 (C-**5'**), 147.44 (C-**7a**), 151.64 (C-**3'**), 152.16 (C-**3**), 158.3 (C-**1'**), 163.4 (C-**2**).
6		Yiled: 72%; Exp: 204-205 ºC (DMF/methanol) Lit: 204-206 ºC[1]	3444, 3191, 1752, 1731, 1627, 1254.	2.34 (s, 3H, CH_3), 6,41 (d, 1H, **4**), 6,68 (td, 1H, **5**), 6,93 (d, 1H, **6**), 7.11 (d, 1H, **6´**), 7,38 (dd, 1H, **7**), 7,45 (dd, 1 H**, 4´**),8,42 (dd, 1 H**, 3´**), 11.04 (s, 1H, **8**).	19,8 (CH_3); 111.91 (C-**7**), 115.99 (C-**3a**), 117.90 (C-**6'**), 122.19 (C-**5**), 125.68 (C-**4**), 127.3 (C-**4'**), 135.13 (C-**6**), 147.38 (C-**7a**), 148.58 (C-**5'**), 151.44 (C-**3'**), 152.32 (C-**3**), 155.32 (C-**1'**), 163.4 (C-**2**);

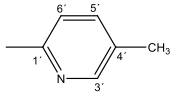
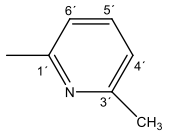
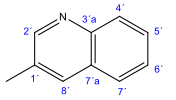
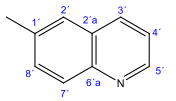
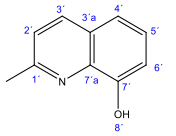
7		Yield: 60%; Exp: 203-204 ºC (DMF/methanol)	3447, 3193, 1753, 1733, 1626, 1253.	2.33 (s, 3H, CH_3), 6,43 (d, 1H, **4**), 6,72 (td, 1H, **5**), 6.88 (d, 1H, **6´**), 6,95 (d, 1H, **6**), 7,37 (dd, 1H, **7**), 7,63 (dd, 1 H**, 5´**),8,33 (dd, 1 H**, 3´**), 11.07 (s, 1H, **8**).	19,5 (CH_3); 111.88 (C-**7**), 116.01 (C-**3a**), 117.73 (C-**6'**), 122.22 (C-**5**), 125.74 (C-**4**), 132.3 (C-**4'**), 135.1 (C-**6**), 138.58 (C-**5'**), 147.41 (C-**7a**), 151.74 (C-**3'**), 152.2 (C-**3**), 154.4 (C-**1'**), 163.6 (C-**2**);
8		Yield: 71%; Exp: 185-187 ºC (DMF/methanol)	3447, 3191, 1753, 1731, 1626, 1253.	2.30 (s, 3H, CH_3), 6,43 (d, 1H, **4**), 6,74 (td, 1H, **5**), 6,88 (d, 1H, **6**), 6.94 (d, 1H, **6´**), 7,40 (dd, 1H, **7**), 7,68 (dd, 1 H**, 5´**),7,72 (dd, 1 H**, 4´**), 11.03 (s, 1H, **8**).	19,4 (CH_3); 111.92 (C-**7**), 116.01 (C-**3a**), 114.73 (C-**6'**), 122.26 (C-**5**), 123.42 (C-**4'**), 125.91 (C-**4**), 135.22 (C-**6**), 137.50 (C-**5'**), 147.51 (C-**7a**), 151.62 (C-**3'**), 152.18 (C-**3**), 156.42 (C-**1'**), 163.5 (C-**2**
9		Yield: 59%; Exp: 300-301 ºC (DMF/methanol) Lit: 303-304 ºC[4]	3048,1742, 1614, 1311, 1254.	6,33 (d, 1H, **4**), 6,69 (td, 1H, **5**), 6,92 (d, 1H, **6**), 7,11 (t, 1H, **6´**), 7,35 (dd, 1H, **7**), 7,44-7,82 (dtdd, 2H, **4´, 5´**), 7,87 – 8,15 (m, 2H, **7´, 8´**), 8.68 (dd, 1H, **2´**),11.03 (s, 1H, **8**).	111.34 (C-7), 116.20 (C-**3a**), 122.33 (C-**5**), 125.52 (C-**4**), 127,79 (C-**6'**), 128,11 (C-**4'**), 128,30 (C-**5'**), 128,50 (C-**8'**), 129,20 (C-**7'a**), 135,11 (C-**7'**),135.34 (C-**6**), 143,11 (C-**2'**), 144,51 (C-**1'**) , 146,53 (C-**3'a**), 147.70 (C-**7a**), 154.25 (C-**3**), 163.52 (C-**2**).
10		Yiled: 64%; Exp: 290-291 ºC (DMF/methanol)	3061,1742, 1618, 1302, 1254.	6,35 (d, 1H, **4**), 6,72 (td, 1H, **5**), 6,94 (d, 1H, **6**), 7,30 (t, 1H, **7´**), 7,37 (dd, 1H, **7**), 7,52 -7,85 (m, 2H, **4´, 8´**), 8,09 – 8,40 (m, 2H, **2´, 3´**), 8.79 (dd, 1H, **5´**),11.06 (s, 1H, **8**).	111.28 (C-**7**), 115.9 (C-**3a**), 122.29 (C-**5**), 125.47 (C-**4**), 126,76 (C-**2'**), 127,66 (C-**4'**), 128,10 (C-**8'**), 129,80 (C-**2'a**), 133,10 (C-**7'**), 135,11 (C-**3'**),136.56 (C-**6**), 146,98 (C-**6' a**), 147.54 (C-**7a**), 149,11 (C-**5'**), 151,11 (C-**1'**) , 154.31 (C-**3**), 163.8 (C-**2**).
11		Yiled: 70%; Exp: 283-285 ºC (DMSO/methanol)	3451, 3056, 1740,1626, 1302.	6,33 (d, 1H, **4**), 6,67 (t, 1H, **5**), 6,92 (d, 1H, **6**), 7,35 (t, 1H, **5´**), 7,45 – 7,61 (m, 3H, **7**,**4´**,**6´**), 8,14 (d, 1H, **3´**), 8,35 (d, 1H, **2´**), 9,80 (d, 1H, **8´**), 11,06 (s, 1H, **8**).	111.24 (C-**7**), 112,00 (C**6´**); 116.13 (C-**3a**), 117,71 (C**4´**); 118,65 (C**2´**); 122.41 (C-**5**), 125.58 (C-**4**), 127,97 (C**5´**); 128,71 (C**3a´**); 135.41 (C-**6**), 136,03 (C**3´**); 138,10 (C**7a´**); 147.70 (C-**7a**), 153,36 (C**1´**); 159.25 (C-**3**), 163.52 (C-**2**); 175,72 (C**7´**).

TABLE SIII. Absorption frequencies of isatin compounds in selected solvents (lower wavelength peak)

Solvent/ Compound	$\nu_{max}\times10^{-3}$ (cm^{-1})										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Methanol	34.31	33.39	33.5	33.44	33.39	33.73	33.61	33.73	32.63	33.9	34.01
Ethanol	33.17	33.28	33.44	33.17	33.22	33.39	33.33	33.39	31.5	34.07	33.22
2-Propanol	33.50	33.67	33.67	33.61	33.28	33.61	33.61	33.67	33.11	/	33.96
2-Butanol	/	/	/	/	/	/	/	/	31.35	/	
Cyclohexanol	/	/	/	/	/	/	/	/	/	/	
Benzyl alcohol (BzOH)	/	/	/	/	31.7	/	/	/	/	31.06	
2-Methoxyethanol (2-ME)	/	33.44	33.44	33.5	33.5	33.06	33.56	33.78	32.79	34.01	33.78
2-Chloroethanol (2-CE)	/	33.11	33.06	33.28	32.89	33.06	33.06	33.28	32.73	/	32.73
DME	/	34.01	33.78	33.96	34.19	34.25	34.07	34.07	31.3	34.19	34.36
Toluene	/	33.73	33.61	33.78	/	/	/	/	31.15	31.4	33.33
DCM	/	33.67	33.73	33.61	/	33.73	33.61	33.78	32.95	34.19	33.9
Acetone	/	/	/	/	/	/	/	/	/	/	
ChO	/	/	/	/	/	/	/	/	/	/	
EtAc	35.03	34.01	33.9	34.07	/	34.13	34.13	34.19	31.4	34.42	34.48
Fe	/	33.22	33.17	33.11	33.17	33.22	33.22	33.22	32.36	33.84	33.84
DMF	/	33.56	33.44	33.56	34.13	33.67	33.73	33.73	31.4	34.19	34.25
DMAc	36.30	33.67	33.67	33.67	33.73	33.73	33.61	33.78	31.3	34.25	34.25
NMP	/	33.61	33.39	33.56	/	33.78	33.56	33.61	31.2	34.19	34.07
AcN	35.97	33.84	33.96	34.01	/	33.9	33.9	33.90	32.84	34.54	34.36
DMSO	/	33.5	33.56	33.73	33.73	33.61	33.61	33.67	31.25	34.13	34.01
THF	36.83	33.84	33.73	33.67	34.25	34.13	34.07	34.13	31.3	34.25	34.25
2-Pyrrolidone	/	33.67	33.67	33.67	33.5	33.73	33.61	33.61	31.45	34.42	34.01

TABLE SIV. The results of the correlation analysis for the isatin derivatives (lower wavelength peak) according to Kamlet–Taft equation

Comp.*	$v_0\times10^{-3}$ (cm^{-1})	$s\times10^{-3}$ (cm^{-1})	$b\times10^{-3}$ (cm^{-1})	$a\times10^{-3}$ (cm^{-1})	R^a	Sd^b	F^c	P_π[d]	P_β	P_α	Solvent excluded from correlation
2	34.50 ±0.16	-0.86 ±0.18	-0.13 ±0.15	-0.62 ±0.08	0.94	0.11	24.99	53.42	8.07	38.51	2-Butanol, Cyclohexanol, BzOH, Acetone, ChO, 2-Methoxyethanol, Toluene, 2-Pyrrolidone
3	33.89 ±0.11	-0.66 ±0.15	0.55 ±0.12	-0.57 ±0.07	0.95	0.09	23.96	37.08	30.90	32.02	2-Butanol, Cyclohexanol, BzOH, Acetone, ChO, AcN, DCM, NMP, DMF, Methanol
4	34.37 ±0.13	-0.93 ±0.17	0.18 ±0.14	-0.57 ±0.08	0.94	0.10	21.35	55.36	10.71	33.93	2-Butanol, Cyclohexanol, BzOH, Acetone, ChO, AcN, Ethanol, THF, 2-Methoxyethanol, 2-Pyrrolidone
5	35.04 ±0.16	-1.21 ±0.20	-0.33 ±0.16	-0.31 ±0.11	0.94	0.10	18.86	65.41	17.84	17.76	2-Butanol, Cyclohexanol, BzOH, Toluene, Acetone, ChO, F, 2-Methoxyethanol, 2-ClEthanol, Ethanol
6	34.72 ±0.15	-0.99 ±0.17	-0.05 ±0.14	-0.83 ±0.08	0.96	0.11	40.38	52.94	2.67	44.39	2-Butanol, Cyclohexanol, BzOH, Toluene, Acetone, ChO, 2-Methoxyethanol, Methanol
7	34.63 ±0.16	-0.97 ±0.18	-0.06 ±0.16	-0.77 ±0.08	0.95	0.11	30.14	53.89	3.33	42.78	2-Butanol, Cyclohexanol, BzOH, Toluene, Acetone, ChO, Methanol, 2-Methoxyethanol
8	34.63 ±0.12	-1.00 ±0.15	0.02 ±0.10	-0.71 ±0.07	0.96	0.09	39.98	57.80	1.16	41.04	2-Butanol, Cyclohexanol, BzOH, Toluene, Acetone, ChO, Methanol
9	31.66 ±0.21	1.57 ±0.28	-2.45 ±0.18	1.42 ±0.13	0.98	0.15	80.32	28.86	45.04	26.10	Cyclohexanol, BzOH, Acetone, ChO, 2-Propanol, AcN, F, Ethanol, Toluene
10	/	/	/	/	/	/	/	/	/	/	/
11	34.62 ±0.27	-1.00 ±0.36	0.67 ±0.22	-1.32 ±0.16	0.94	0.18	24.79	33.44	22.41	44.15	2-Butanol, Cyclohexanol, BzOH, Acetone, ChO, Methanol, Toluene, F, AcN

* No statistically valuable correlations were obtained for comps. **1** and **10**; [a] Correlation coefficient; [b] Standard deviation; [c] Fisher test of significance; [d] The percentage contribution of solvatochromic parameters obtianed by the use of Kamlet-Taft equation (%);

TABLE SV. Substituent constants[5]

No.	X	σ
1	H	0
2	2-Br	0.58
3	3-Br	0.39
4	4-Br	0.23
5	3-Me-2-Pyridyl	0.63*
6	4-Me-2-Pyridyl	0.68*
7	5-Me-2-Pyridyl	0.58*
8	6-Me-2-Pyridyl	0.68*
9	Compound 38 (3-quinolinyl)	0.5
10	Compound 13 (6-quinolinyl)	0.6
11	Compound 12 (8-OH-2-quinolinyl)	0.47*

* σ constant was calculated as additive value; 4-NO_2 (0.78) and 4-CN (0.66) were taken from literature[1]

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