Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences

SUPPORTING INFORMATION

for

"Temperature influence on deactivation paths and tautomeric equilibrium of some photochromic Schiff bases studied by time-resolved and stationary spectroscopy."

by

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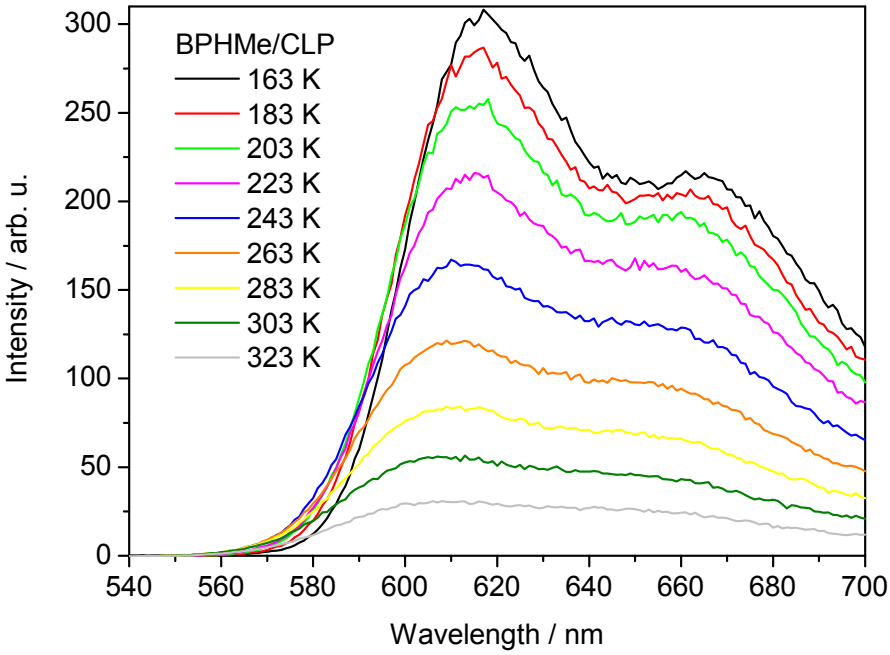


Fig. S1.
Stationary emission spectra of BPHMe in ClP.

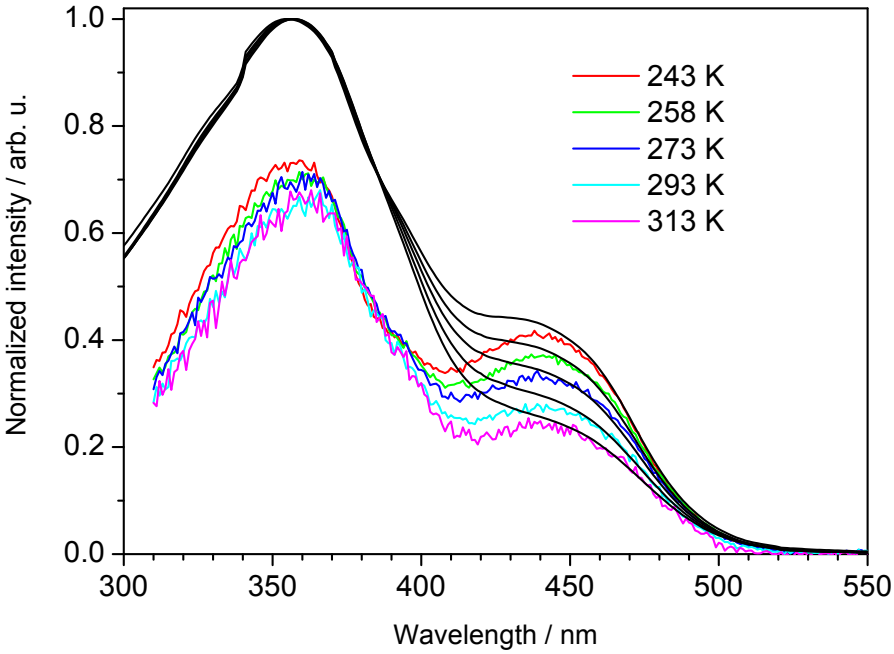


Fig. S2.

Normalized fluorescence excitation spectra at different temperatures (colors) measured at the keto fluorescence band (600 nm) for BSP in TFE compared with the stationary absorption spectra ($1\text{-}10^{-A}$, where A is absorbance), normalized to 1, for corresponding temperatures (black lines). The normalization has been performed at the keto absorption band (maximum around 440 nm) and the decrease in excitation spectra at the enol band (around 360 nm) indicates that significant portion (30-35%) of excited enol tautomer is not transferred to the keto tautomer (see J. Chem. Phys. 124 (2006) 124518) and this ratio is rather not sensitive to temperature. Small increase (5%) in the intensity of fluorescence excitation spectra with lowering temperature is probably due to the contribution of the higher states of keto tautomer of absorption maximum close to 360 nm enol band.

Table S1.

Two-exponential analysis of the fluorescence decay measured at the emission band of the keto form for different systems at different temperatures T. The errors of lifetimes are about 5 ps for τ_1 and 20 ps for τ_2. The amplitudes are normalized to 1.

BSP in ClP (emission wavelength 570 nm):

T / K	τ_1 / ps	A_1	τ_2 / ps	A_2
313	15	1.00	-	-
293	24	0.97	110	0.03
283	34	0.99	210	0.01
263	46	0.99	350	0.01
243	96	0.95	590	0.05
223	110	0.93	690	0.05
203	160	0.94	800	0.06
183	230	0.96	760	0.04
163	470	0.96	2050	0.04

BSP in MeOH (emission wavelength 570 nm):

T / K	τ_1 / ps	A_1	τ_2 / ps	A_2
323	5	1.00	-	-
303	10	1.00	-	-
293	13	1.00	-	-
283	15	1.00	-	-
263	24	1.00	-	-
243	38	1.00	-	-
223	58	1.00	-	-
203	90	0.93	190	0.07
183	155	0.94	340	0.06

Table S1. (continued)

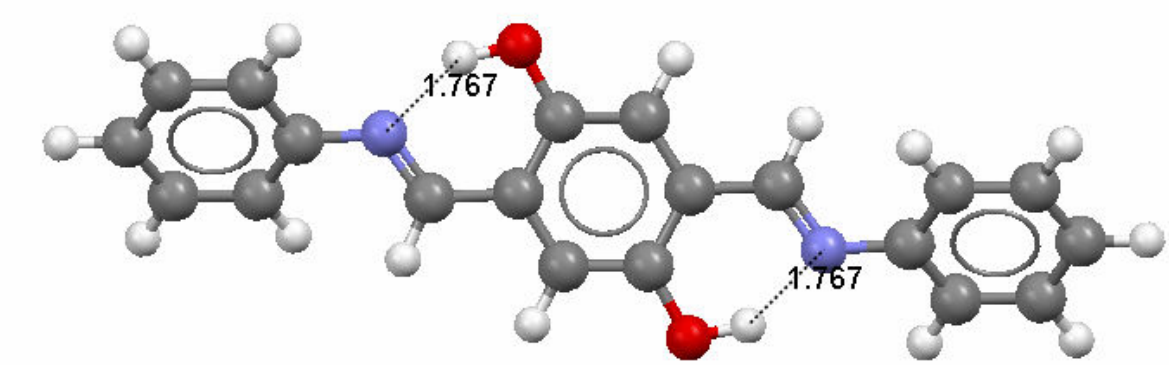
BPHMe in ClP (emission wavelength 620 nm):

T / K	τ_1 / ps	A_1	τ_2 / ps	A_2
313	340	0.53	40	0.47
293	480	0.59	39	0.41
283	590	0.70	48	0.30
263	820	0.55	47	0.45
243	1090	0.85	520	0.15
223	1330	0.79	700	0.21
203	1540	0.78	870	0.22
183	1870	0.73	1040	0.27
163	1900	0.72	1190	0.28

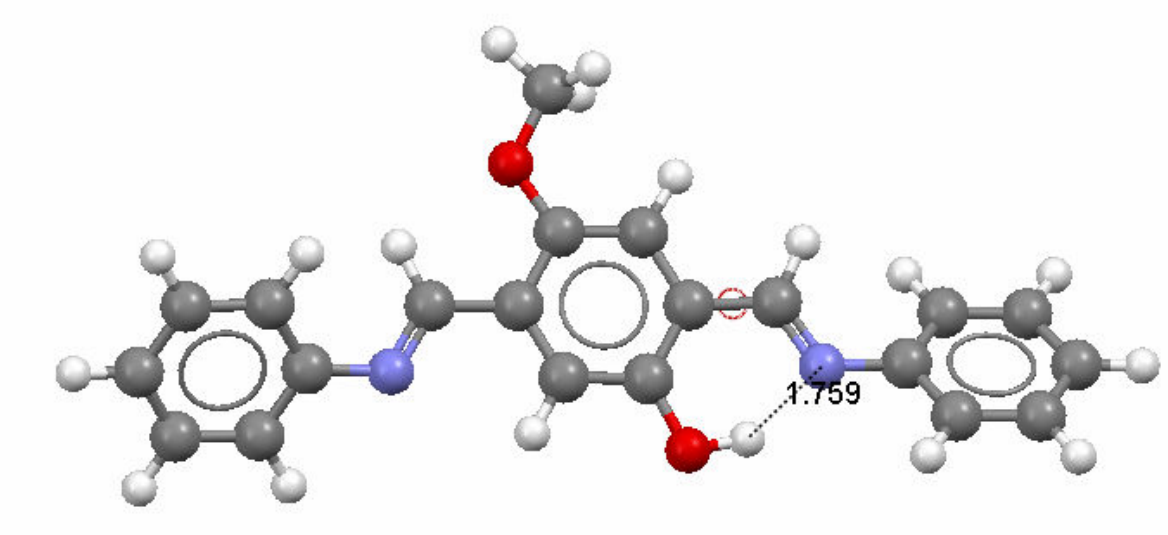
BPHMe in MeOH (emission wavelength 620 nm):

T / K	τ_1 / ps	A_1	τ_2 / ps	A_2
323	220	0.67	52	0.33
303	310	0.50	46	0.50
293	360	0.63	60	0.37
283	440	0.62	60	0.38
263	600	0.60	60	0.40
243	790	0.79	135	0.21
223	1020	0.82	320	0.18
203	1210	0.81	520	0.19
183	1360	0.87	530	0.13

BPH:



BPHMe:



BSP:

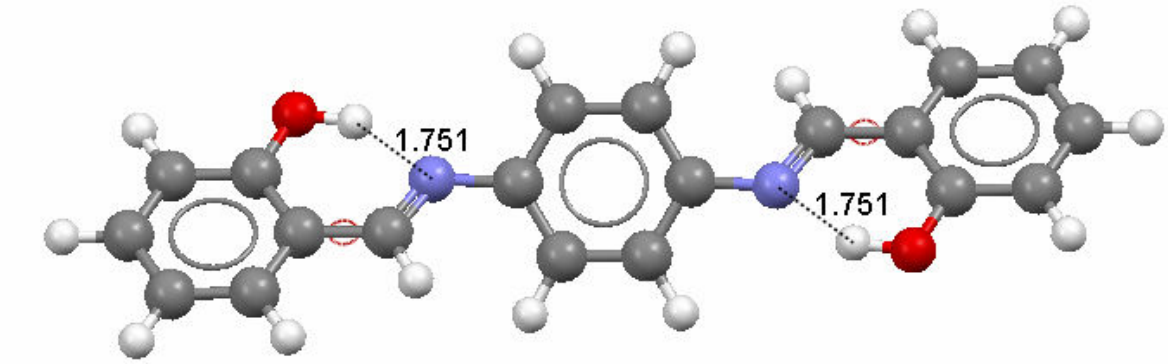
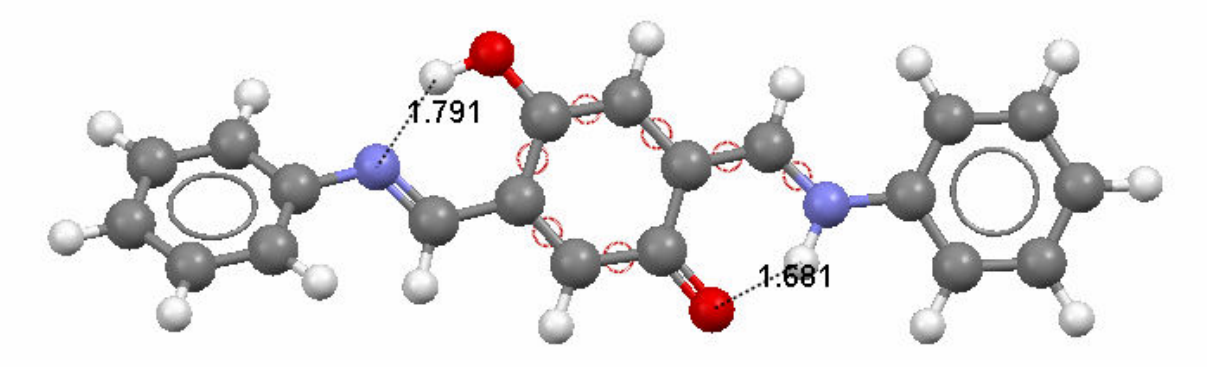
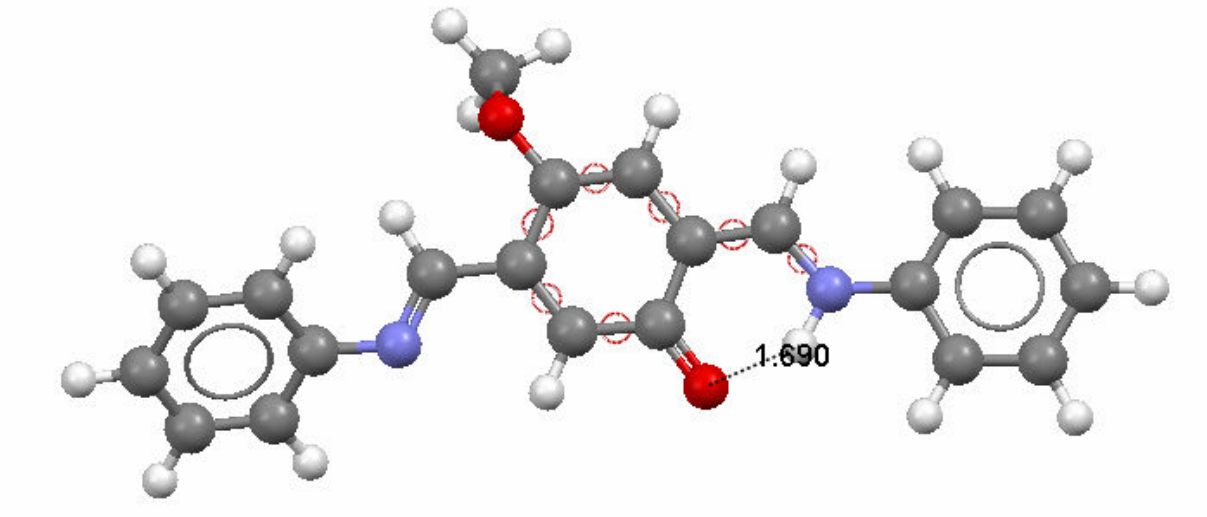


Fig. S3. Optimized structures of isolated enol tautomers with the length of hydrogen bonds. For all enol tautomers the enolic phenyl ring is twisted by around 30 degrees with respect to the imine phenyl ring. The visualization was done with the help of Mercury 1.4.2 program.

BPH:



BPHMe:



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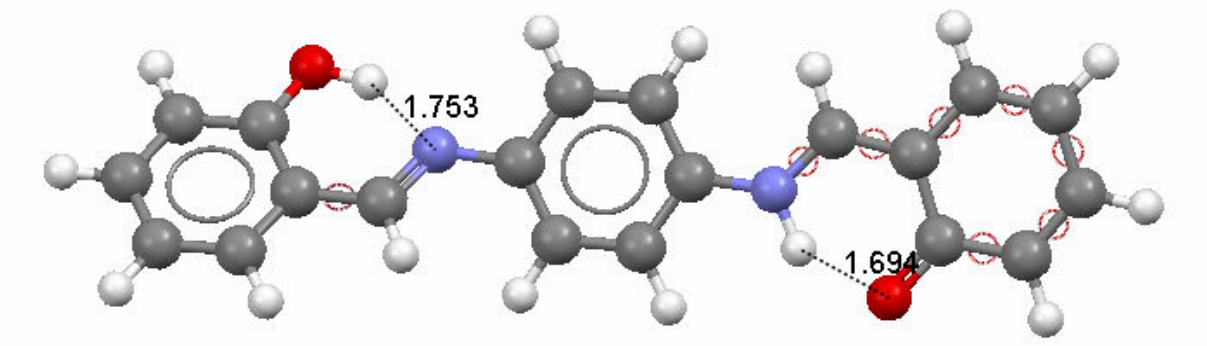
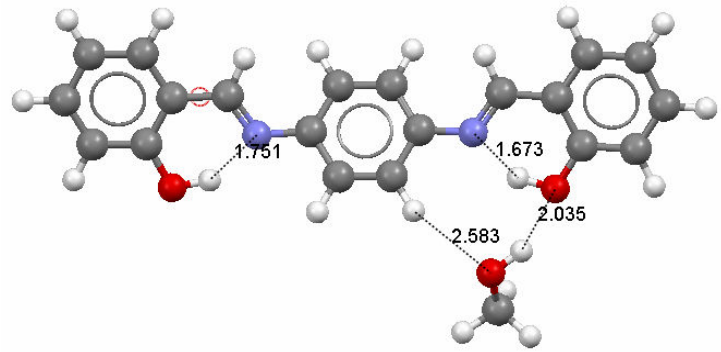
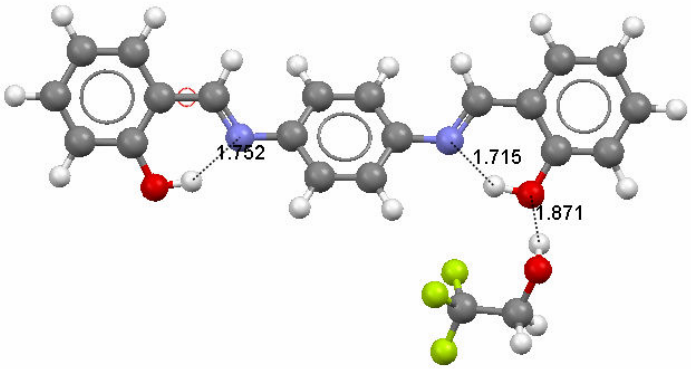


Fig. S4. Optimized structures of isolated keto tautomers with the length of hydrogen bonds. The keto and amine phenyl rings lie in the same plane.

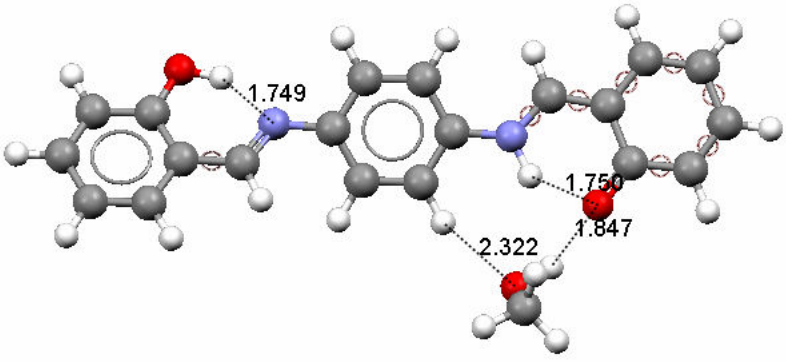
BSP enol + MeOH:



BSP enol + TFE:



BSP keto + MeOH:



BSP keto + TFE:

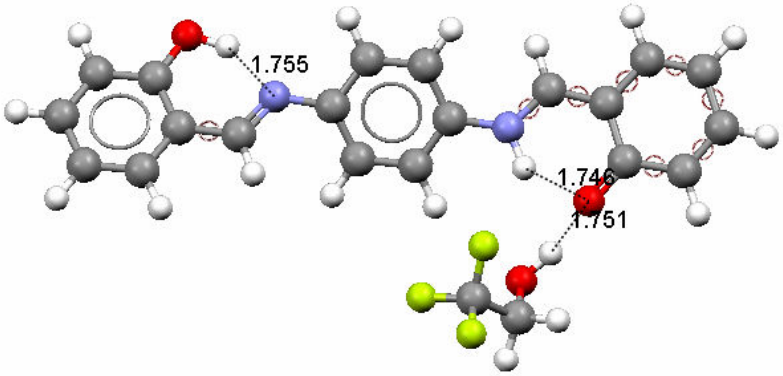


Fig. S5. Optimized structures of BSP complexes with MeOH and TFE with the length of hydrogen bonds. It can be noted that MeOH forms both types of intermolecular hydrogen bonds while TFE has only proton donation ability, but this type of hydrogen bonds is stronger than for MeOH and even comparable to the intramolecular hydrogen bonds.

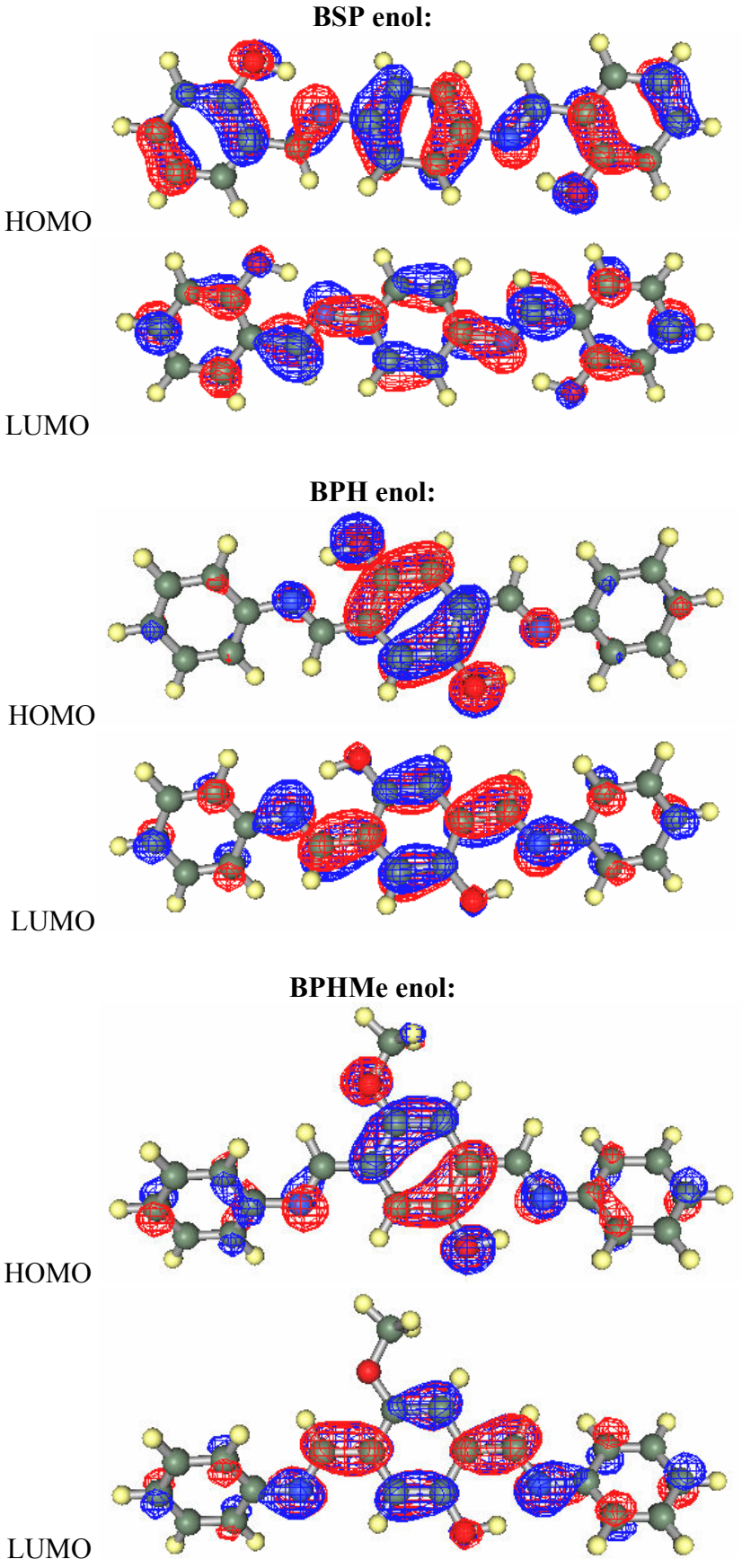
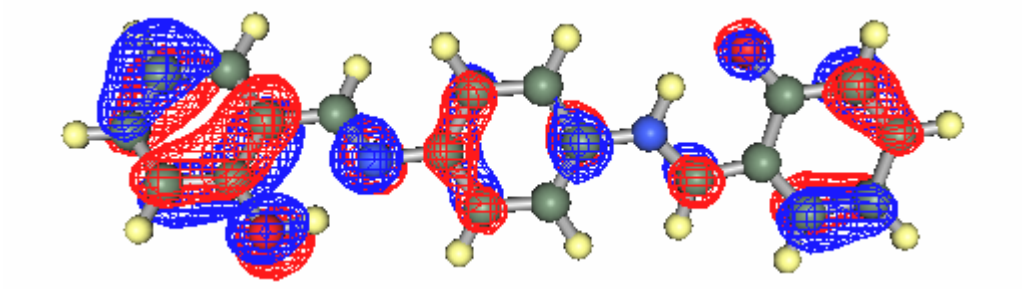


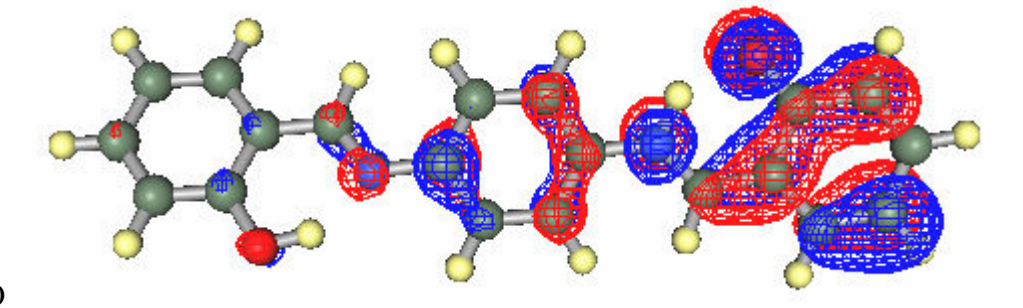
Fig. S6. Molecular orbitals of isolated BSP, BPH and BPHMe enol tautomers.

BSP keto:

HOMO-1



HOMO



LUMO

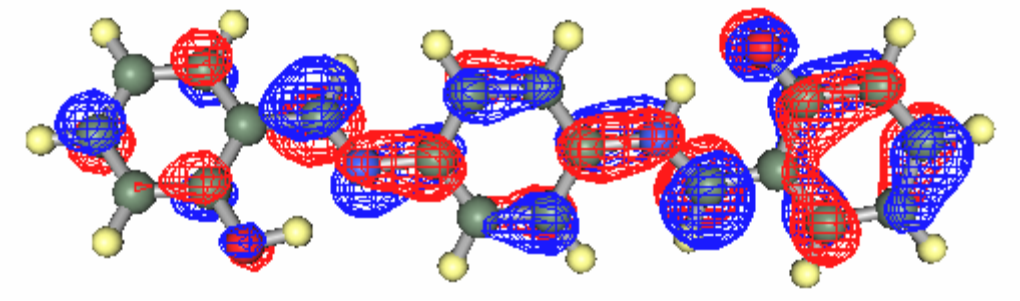


Fig. S7. Molecular orbitals of isolated BSP keto tautomer. The visualization was done with the help of Winmostar V3.75i program.

Table S2.

Calculated Mulliken charge on the atoms taking part in ESIPT process and dipole moment (μ) for two singlet states of the compounds studied.

Compound and tautomer	state	O atom	N atom	H atom	μ, D
BSP enol	S_0	-0.65	-0.59	0.44	0.0
	S_1	-0.60	-0.60	0.44	0.0
BSP keto	S_0	-0.61	-0.70	0.41	2.3
	S_1	-0.49	-0.65	0.41	13.4
BPH enol	S_0	-0.66	-0.58	0.44	0.0
	S_1	-0.52	-0.67	0.44	0.0
BPH keto	S_0	-0.63	-0.70	0.41	0.9
	S_1	-0.54	-0.70	0.41	6.0
BPHMe enol	S_0	-0.66	-0.58	0.44	4.9
	S_1	-0.54	-0.66	0.44	5.8
BPHMe keto	S_0	-0.62	-0.70	0.41	5.2
	S_1	-0.51	-0.69	0.41	8.4