Supplementary Information

A Family of Ethyl *N*-salicylideneglycinate Dyes Stabilized by Intramolecular Hydrogen Bonding: Photophysical Properties and Computational Study

Larisa E. Alkhimova [1], Maria G. Babashkina [2] and Damir A. Safin [1,3,4,*]

[1] University of Tyumen, Volodarskogo Str. 6, 625003 Tyumen, Russia
[2] Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium; maria.babashkina@gmail.com
[3] Kurgan State University, Sovetskaya Str. 63/4, Kurgan 640020, Russia
[4] Innovation Center for Chemical and Pharmaceutical Technologies, Ural Federal University named after the First President of Russia B.N. Eltsin, Mira Str. 19, Ekaterinburg 620002, Russian Federation
* Correspondence: l.e.alkhim@gmail.com (L.E.A.); damir.a.safin@gmail.com (D.A.S.)

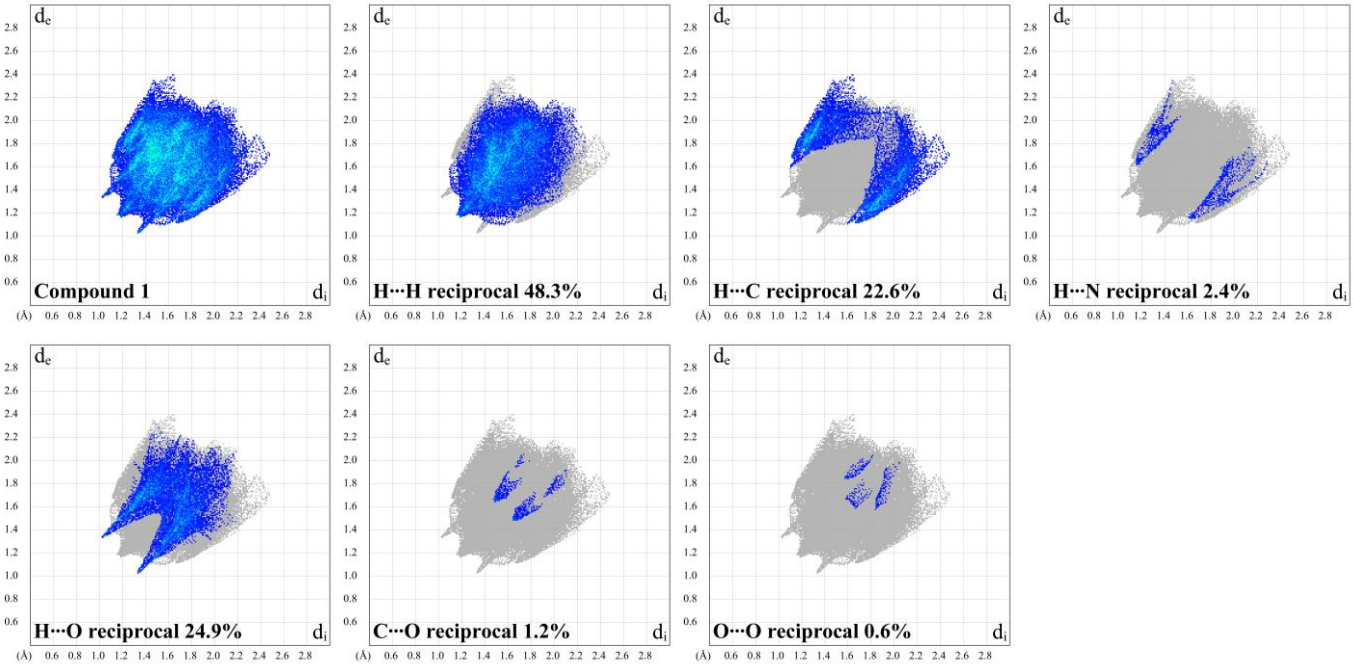

Figure S1. 2D and decomposed 2D fingerprint plots of observed contacts for the crystal structure of **1**.

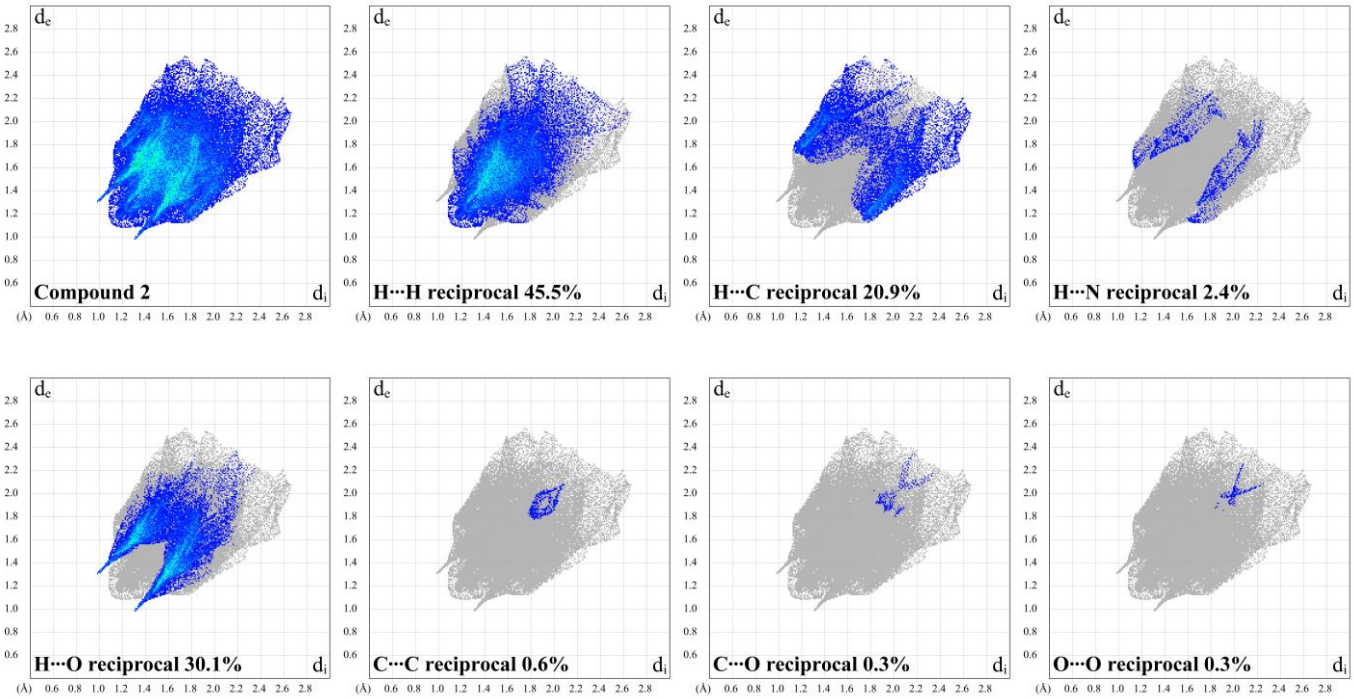

Figure S2. 2D and decomposed 2D fingerprint plots of observed contacts for the crystal structure of **2**.

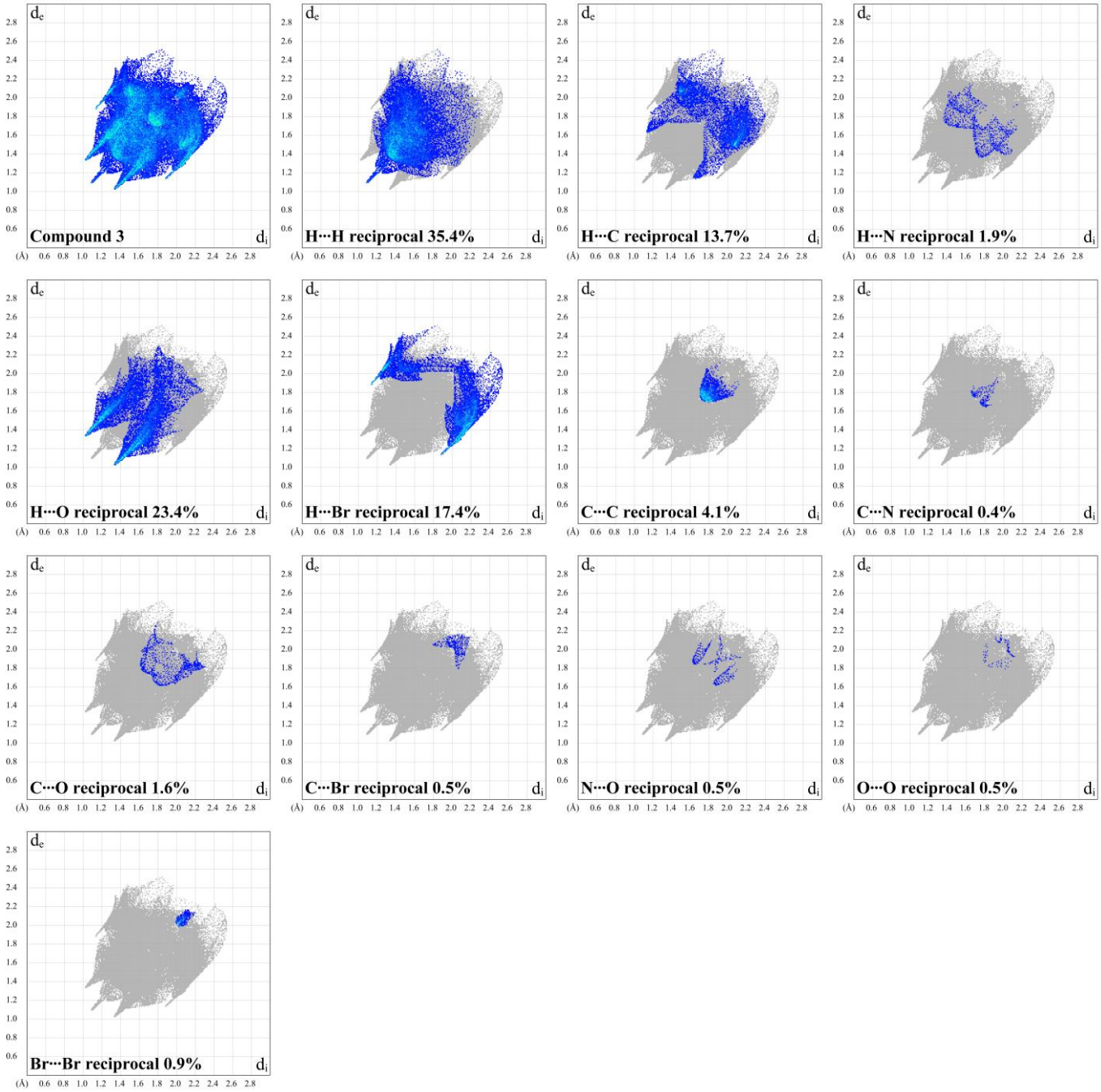

Figure S3. 2D and decomposed 2D fingerprint plots of observed contacts for the crystal structure of **3**.

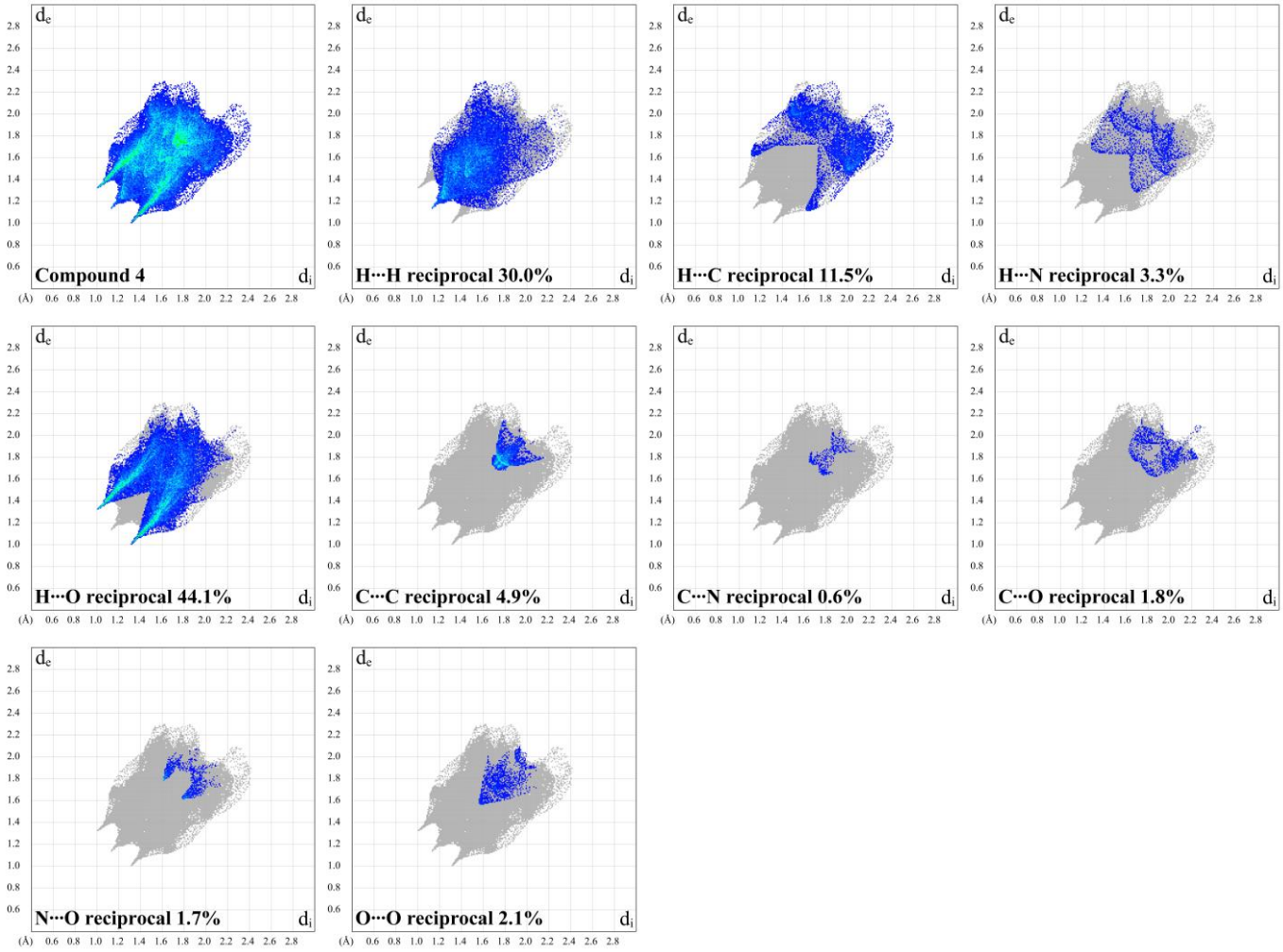

Figure S4. 2D and decomposed 2D fingerprint plots of observed contacts for the crystal structure of **4**.

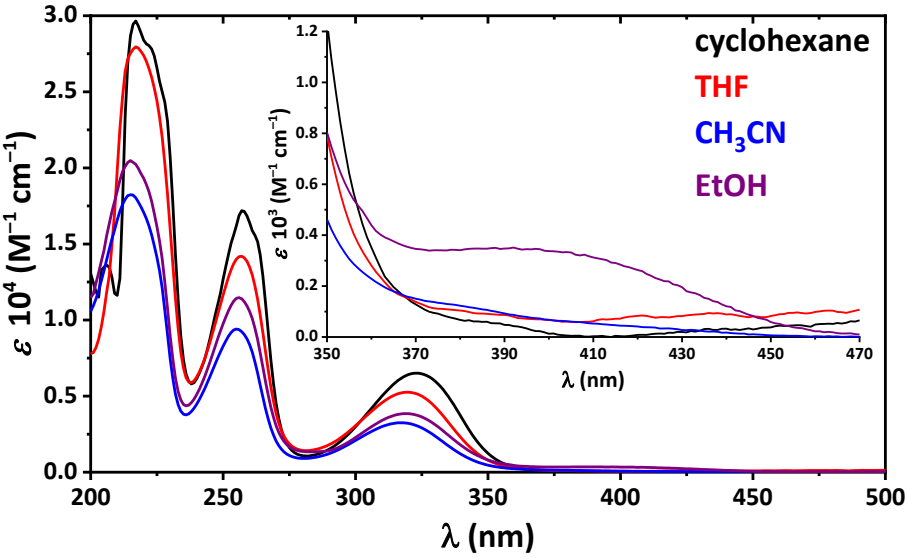

Figure S5. UV-vis spectra of **1** in the applied solvents.

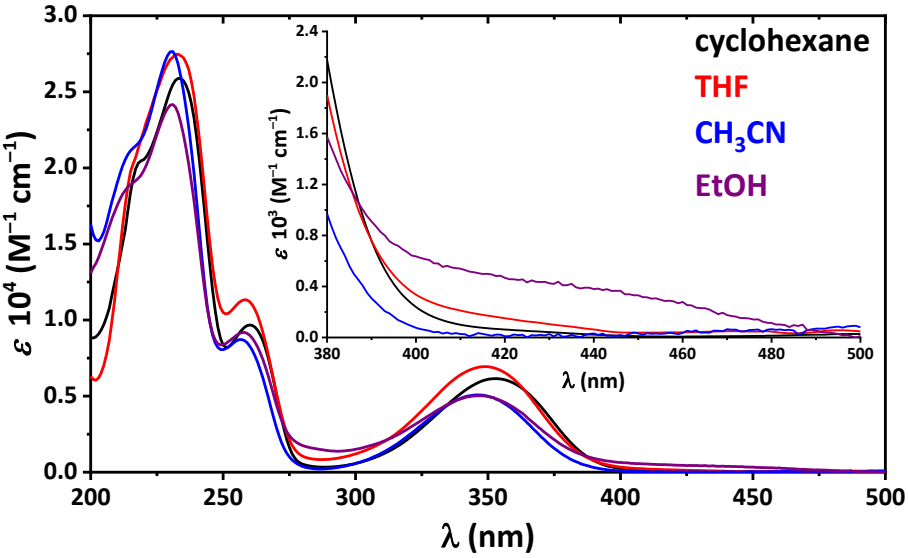

Figure S6. UV-vis spectra of **2** in the applied solvents.

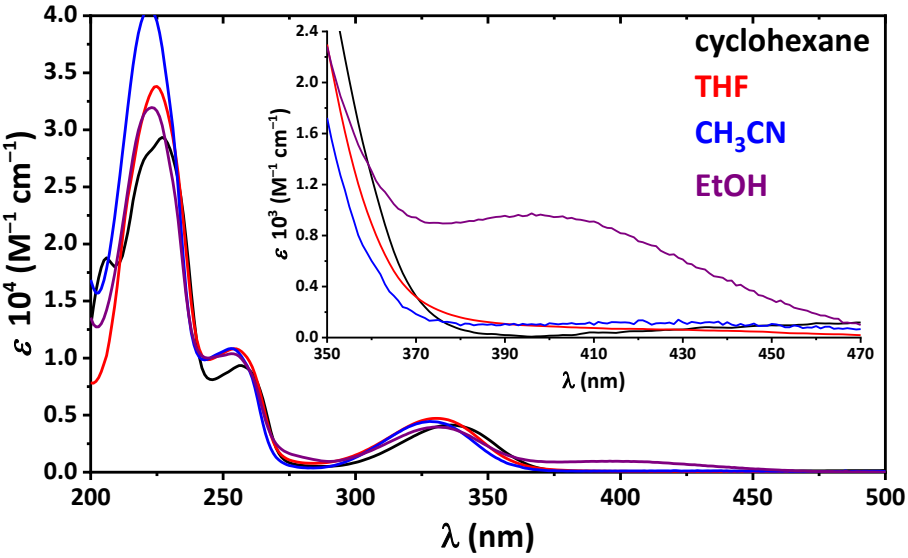

Figure S7. UV-vis spectra of **3** in the applied solvents.

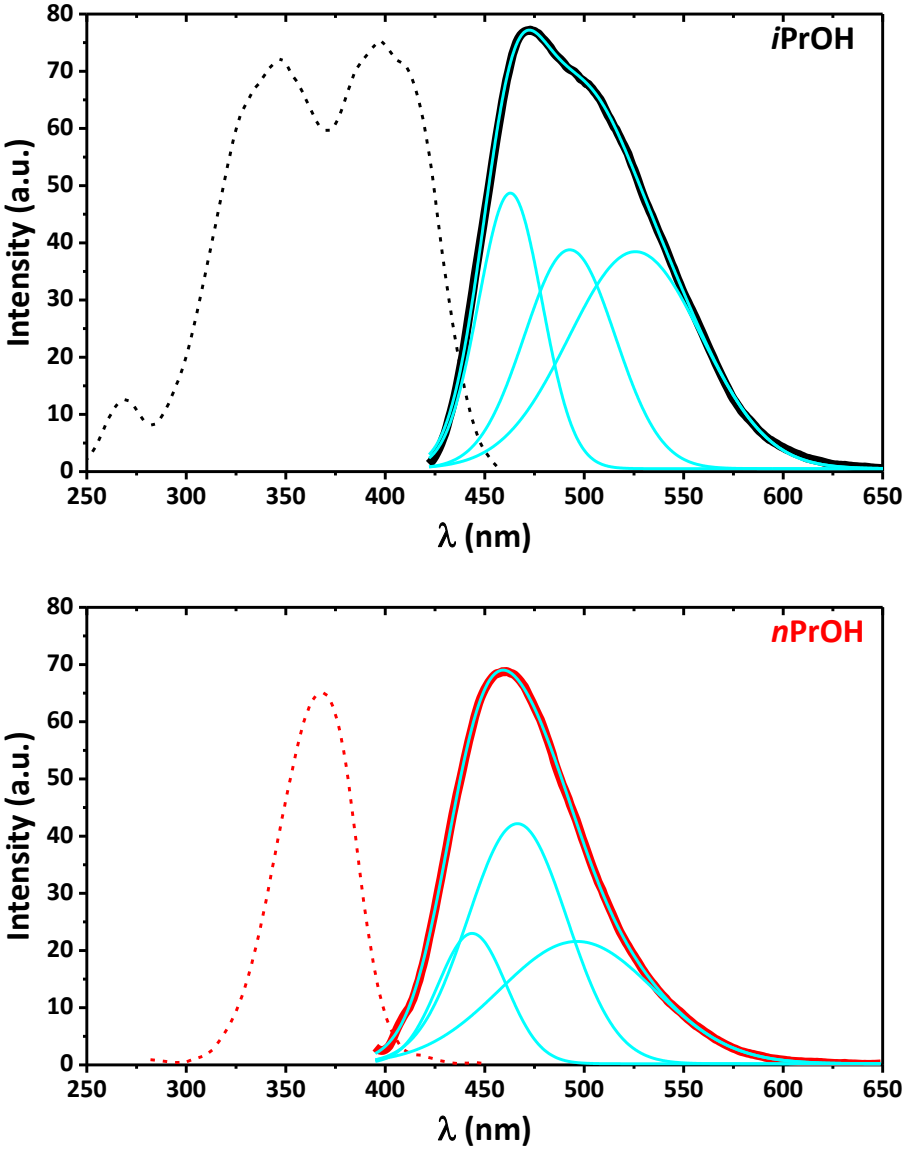

Figure S8. Emission (solid line) and excitation (dashed line) spectra of **4** in *n*PrOH (λ_{exc} = 360 nm, λ_{em} = 460 nm) and *i*PrOH (λ_{exc} = 400 nm, λ_{em} = 475 nm).

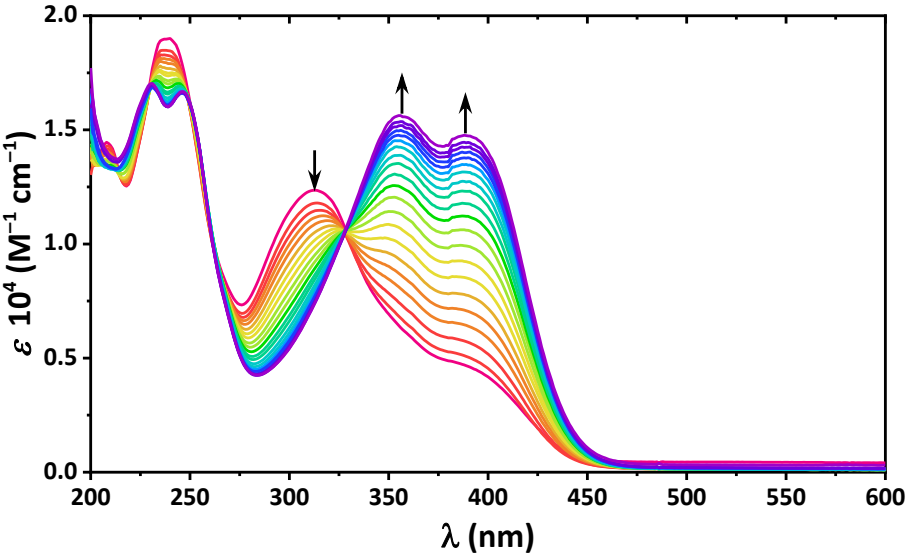

Figure S9. UV-vis spectra of **4** in EtOH upon gradual addition of NEt_3 up to 2 eqv. with a step of 0.1 eqv.

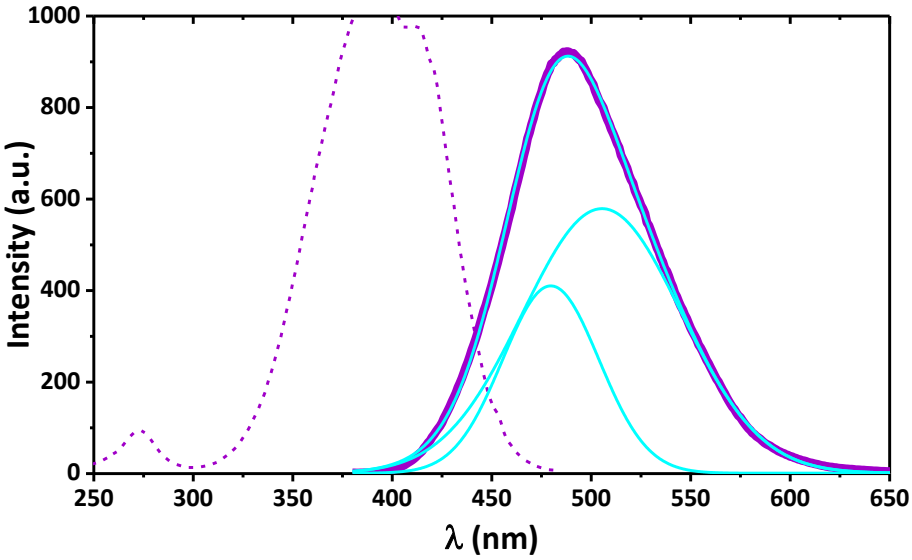

Figure S10. Emission (solid line) and excitation (dashed line) spectra of **3** in EtOH after addition of 5 eqv. of NaOH (λ_{exc} = 375 nm, λ_{em} = 490 nm).

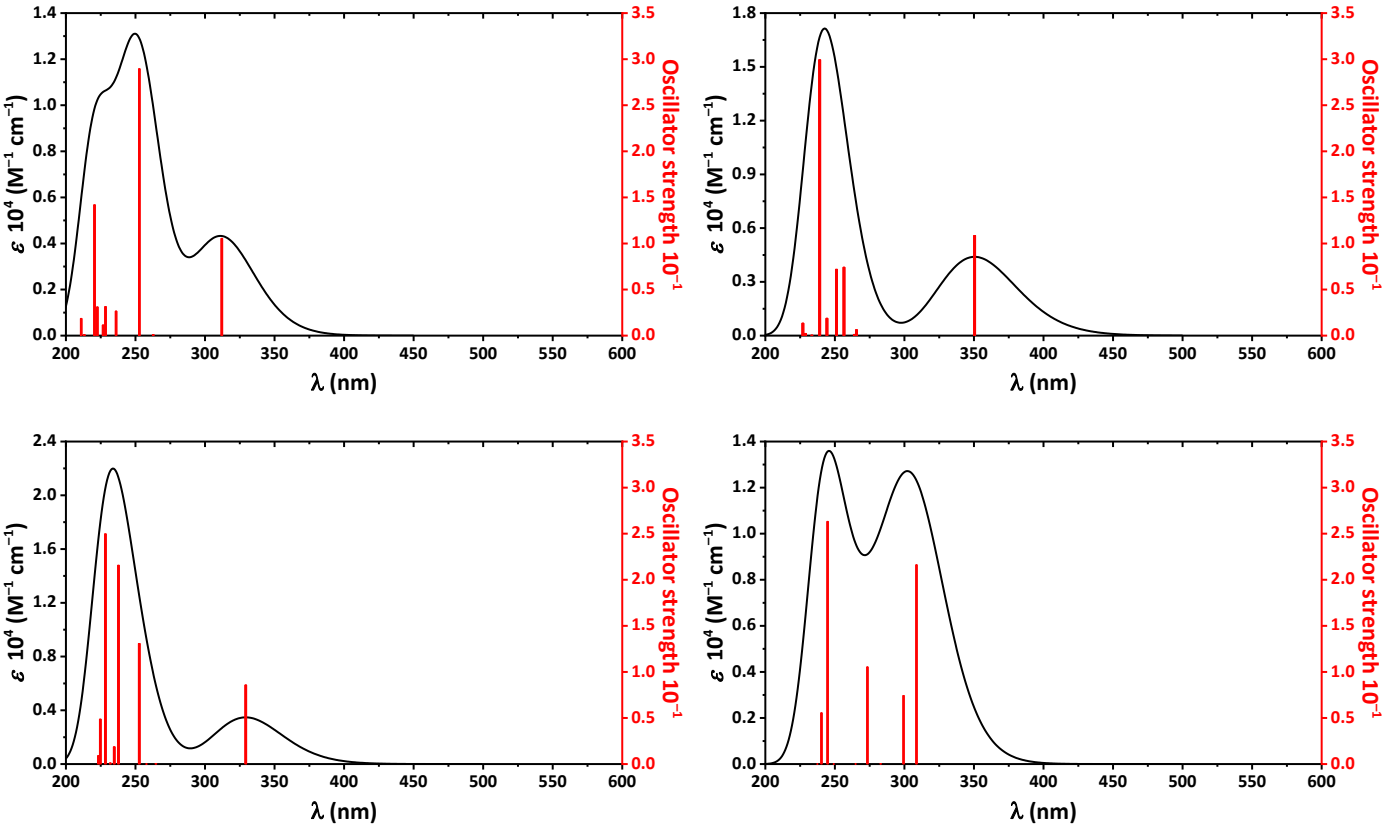

Figure S11. The calculated UV-vis spectra of the ground states of the enol-imine tautomers of **1** (top left), **2** (top right), **3** (bottom left) and **4** (bottom right), obtained by using the TD-DFT/B3LYP/6-311++G(d,p) method.

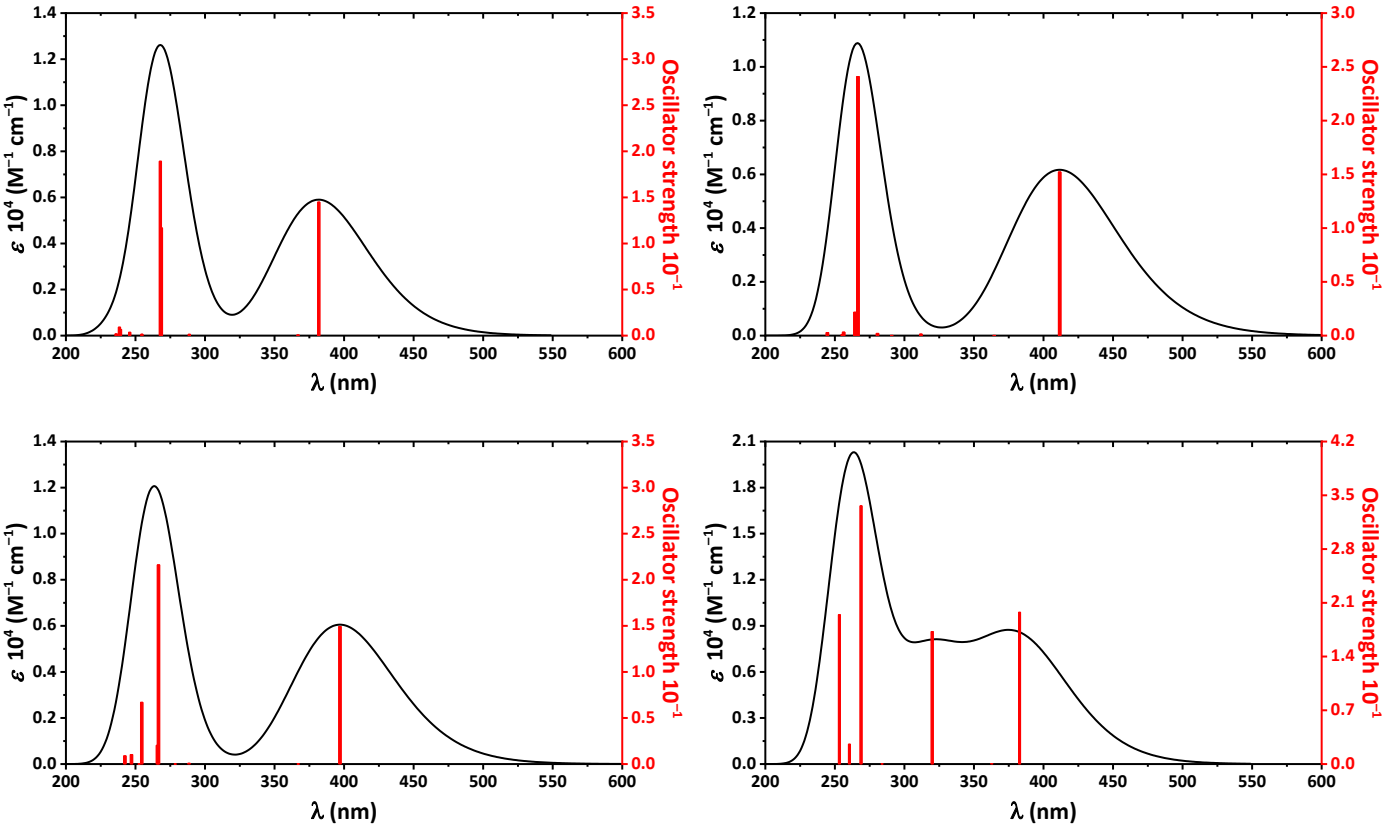

Figure S12. The calculated UV-vis spectra of the ground states of the *cis*-keto-enamine tautomers of **1** (top left), **2** (top right), **3** (bottom left) and **4** (bottom right), obtained by using the TD-DFT/B3LYP/6-311++G(d,p) method.

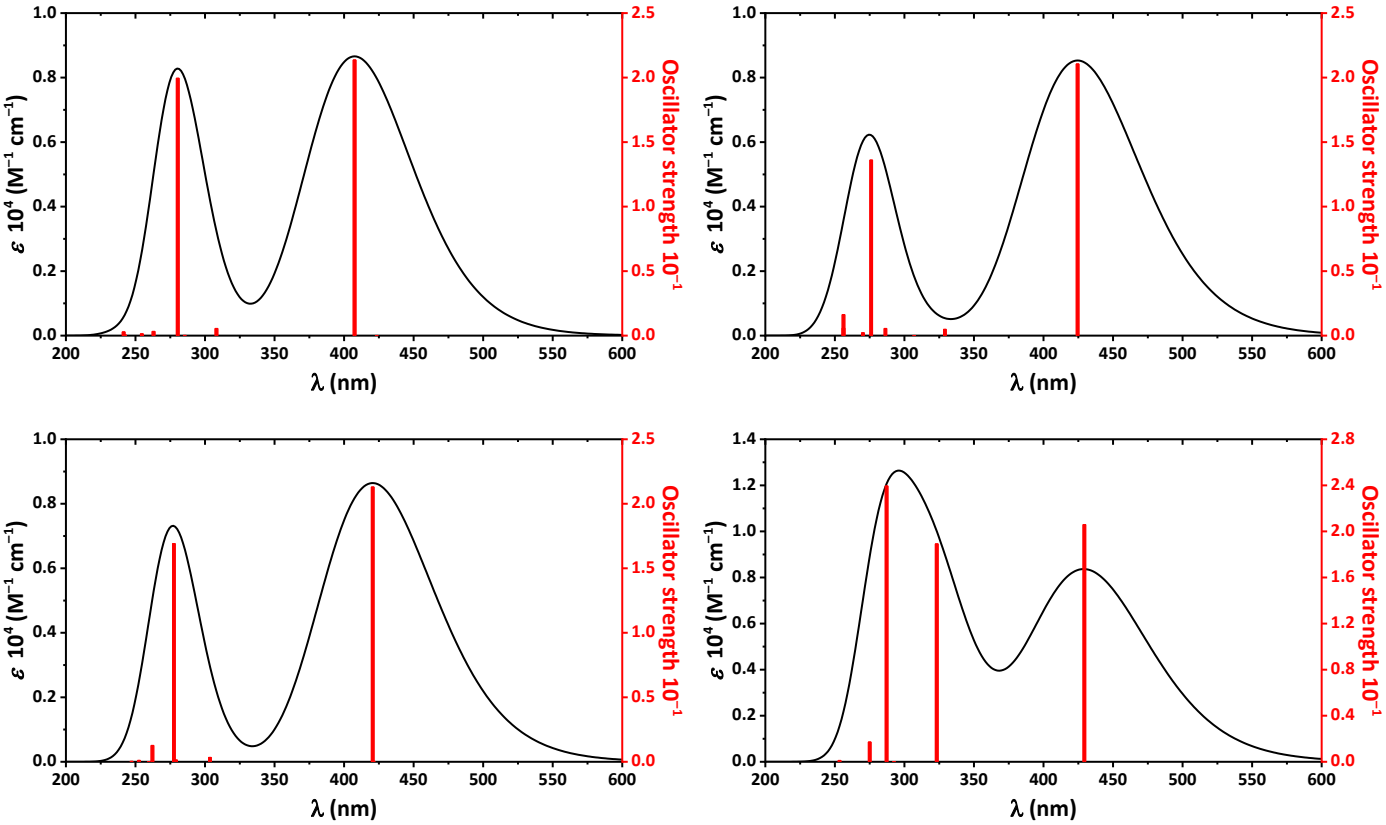

Figure S13. The calculated UV-vis spectra of the ground states of the *trans*-keto-enamine tautomers of **1** (top left), **2** (top right), **3** (bottom left) and **4** (bottom right), obtained by using the TD-DFT/B3LYP/6-311++G(d,p) method.

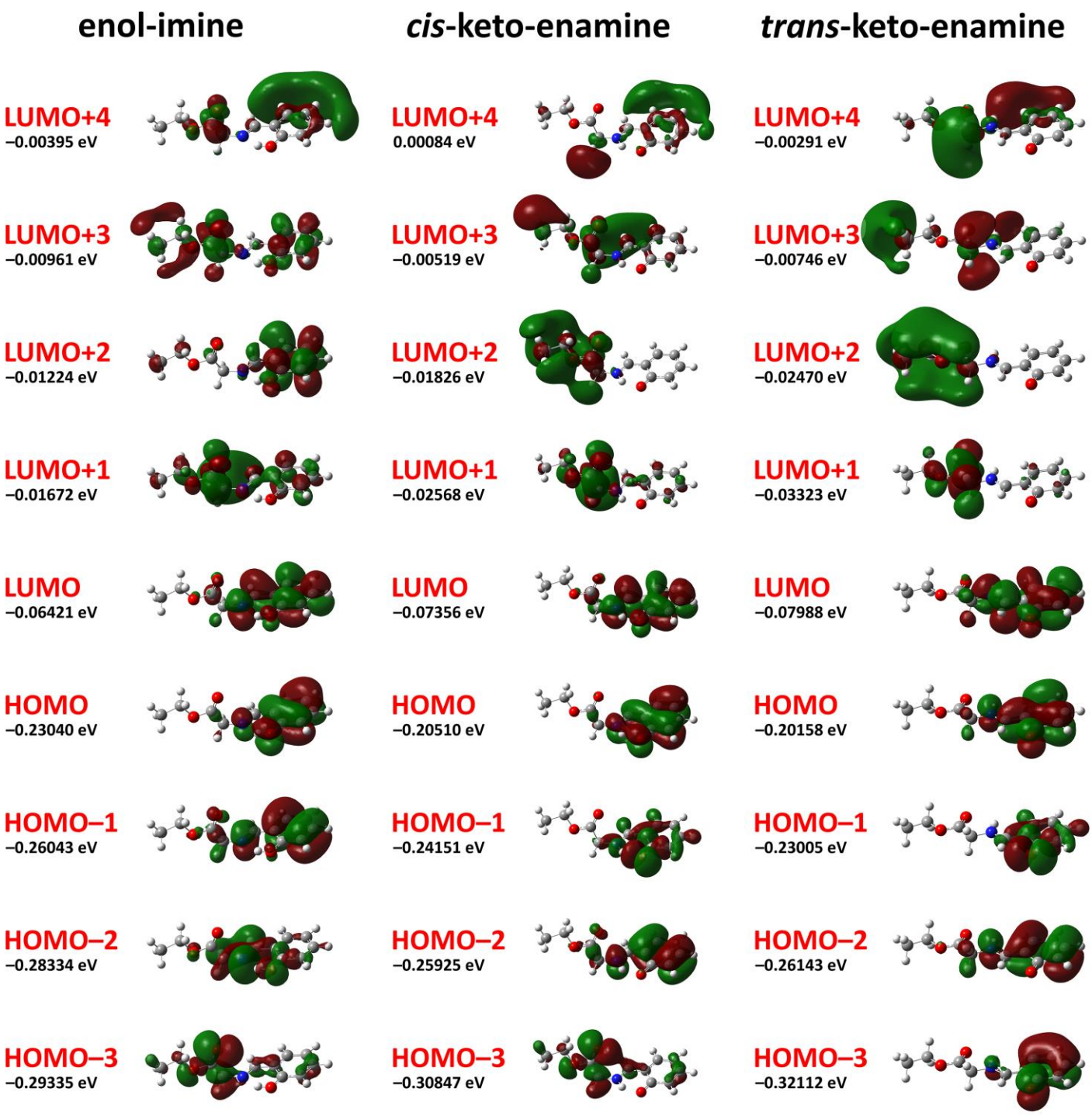

Figure S14. Energy levels and views on the electronic isosurfaces of the selected molecular orbitals of the ground state of **1**, obtained by using the B3LYP/6-311++G(d,p) method.

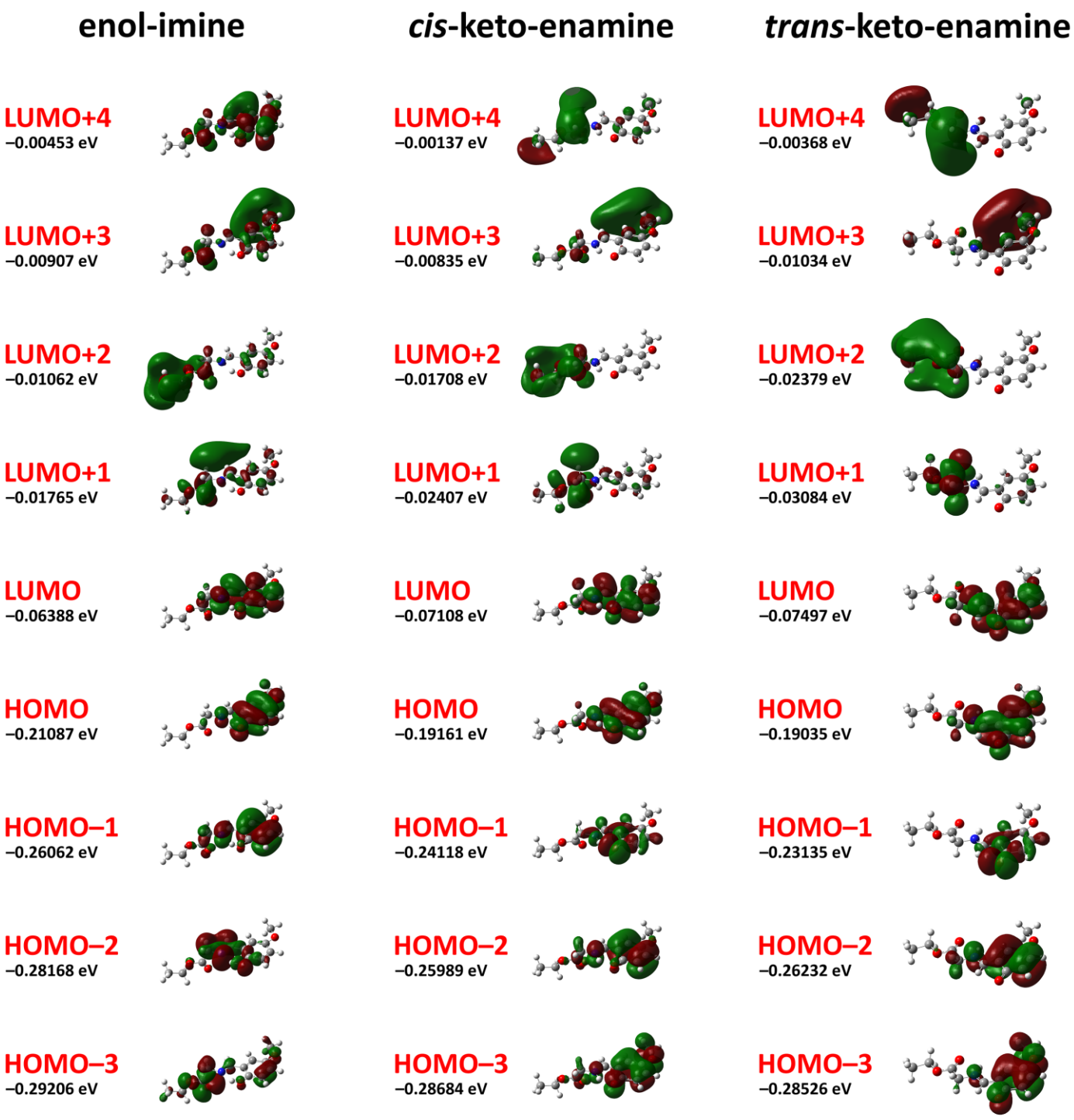

Figure S15. Energy levels and views on the electronic isosurfaces of the selected molecular orbitals of the ground state of **2**, obtained by using the B3LYP/6-311++G(d,p) method.

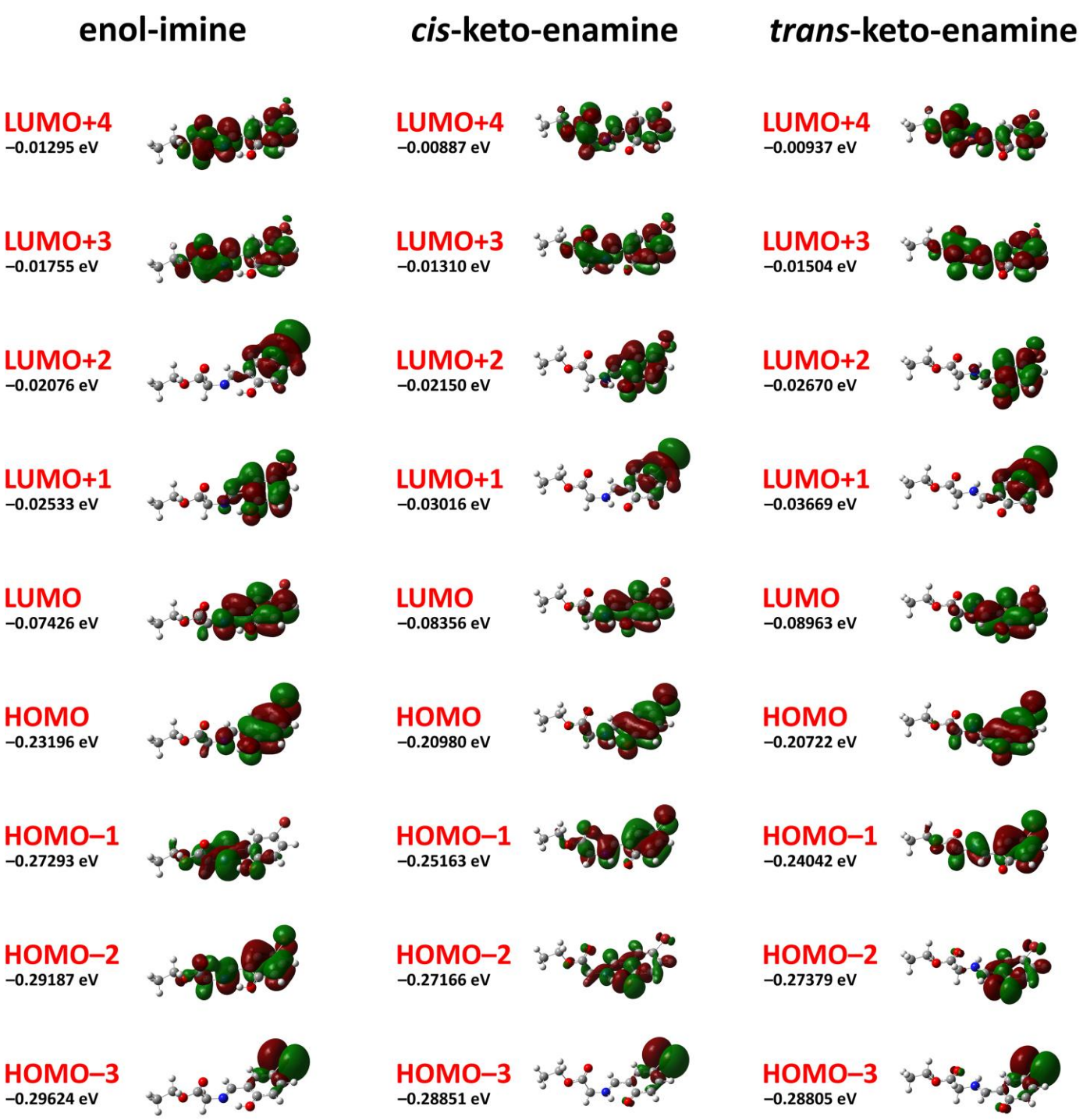

Figure S16. Energy levels and views on the electronic isosurfaces of the selected molecular orbitals of the ground state of **3**, obtained by using the B3LYP/6-311++G(d,p) method.

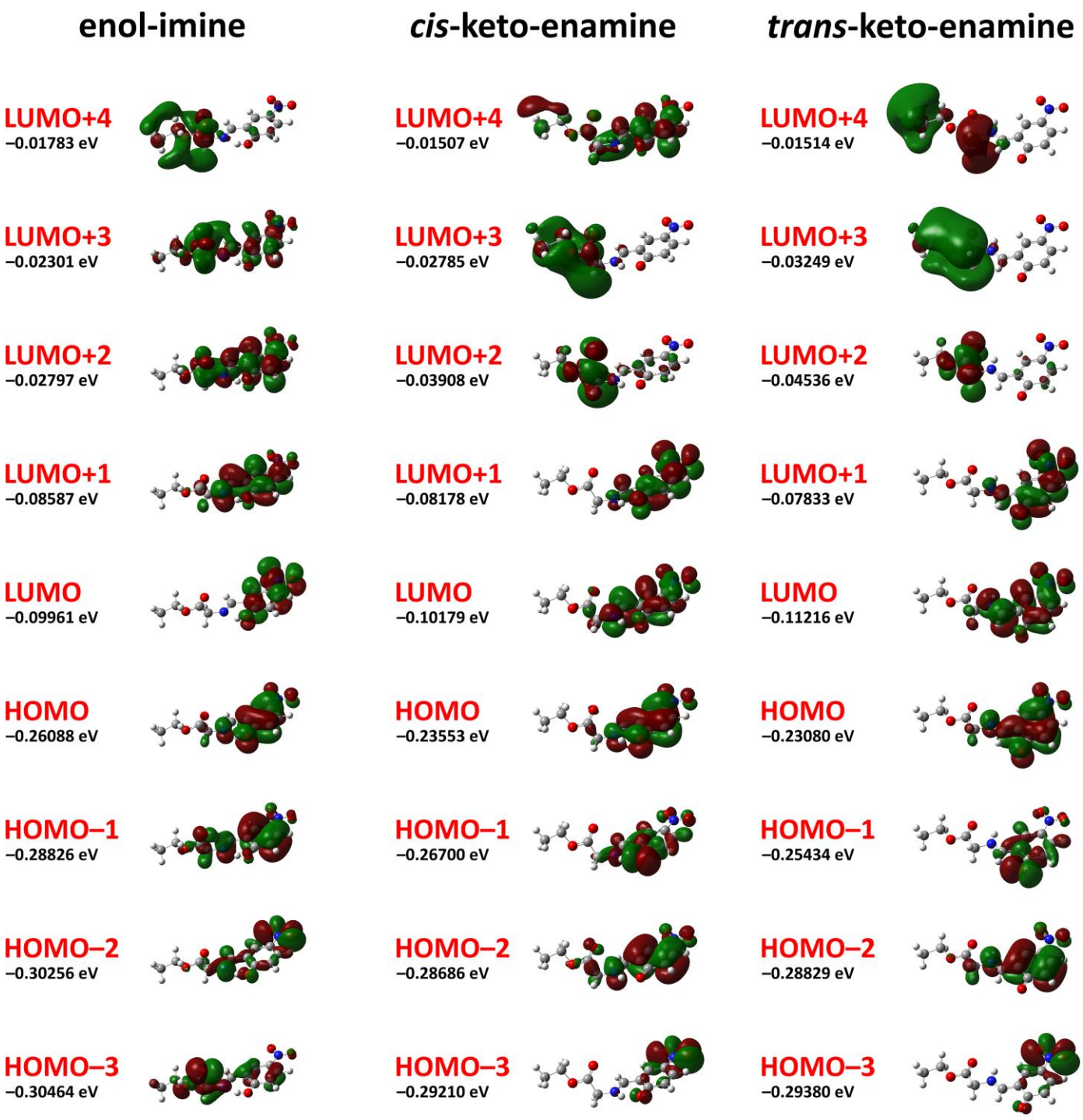

Figure S17. Energy levels and views on the electronic isosurfaces of the selected molecular orbitals of the ground state of **4**, obtained by using the B3LYP/6-311++G(d,p) method.

Table S1. Values for the main maxima in the experimental UV-vis spectra of **1–4** in different solvents, and in the calculated UV-vis spectra of the ground state for different tautomers of **1–4**, obtained by using the TD-DFT/B3LYP/6-311++G(d,p) method.

	Experimental λ_{max} (nm)				**Calculated λ_{max} (nm)**		
	cyclohexane	THF	CH_3CN	EtOH	enol-imine	*cis*-keto-enamine	*trans*-keto-enaimne
1	217, 257, 323	217, 257, 320	215, 256, 319	215, 255, 317, 392	225, 250, 311	268, 382	280, 407
2	233, 260, 353	233, 258, 349	231, 257, 346	231, 258, 347, 418	243, 351	266, 412	274, 424
3	227, 257, 336	225, 254, 331	222, 253, 328	223, 253, 330, 396	234, 329	263, 397	277, 420
4	217, 236, 255, 307, 351	217, 237, 316, 397	217, 238, 318, 404	209, 240, 313, 389	245, 302	264, 323, 375	295, 428

Table S2. Values for the calculated UV-vis spectra of the ground state for the *cis*-keto-enamine tautomers of **1–4**, obtained by using the TD-DFT/B3LYP/6-311++G(d,p) method.

1			**2**		
λ_{max} (nm)	Oscillator strength	Transitions	λ_{max} (nm)	Oscillator strength	Transitions
238.5	0.0092	HOMO → LUMO+3 (2.9%) HOMO → LUMO+5 (35.8%) HOMO → LUMO+6 (46.4%) HOMO → LUMO+8 (8.8%)	244.6	0.0028	HOMO → LUMO+5 (13.7%) HOMO → LUMO+7 (3.2%) HOMO → LUMO+8 (68.8%) HOMO → LUMO+9 (12.6%)
239.2	0.0068	HOMO → LUMO+4 (5.5%) HOMO → LUMO+5 (47.2%) HOMO → LUMO+6 (35.5%) HOMO → LUMO+8 (3.4%)	256.3	0.0033	HOMO–3 → LUMO (4.8%) HOMO → LUMO+4 (9.6%) HOMO → LUMO+6 (76.9%)
267.9	0.1893	HOMO–2 → LUMO (55.6%) HOMO → LUMO+2 (32.9%) HOMO → LUMO+3 (4.1%)	264.4	0.0218	HOMO–2 → LUMO (9.5%) HOMO → LUMO+2 (3.7%) HOMO → LUMO+3 (3.0%) HOMO → LUMO+4 (72.0%) HOMO → LUMO+6 (7.6%)
268.6	0.1169	HOMO–2 → LUMO (35.3%) HOMO → LUMO+2 (52.5%) HOMO → LUMO+3 (7.5%)	266.6	0.2410	HOMO–2 → LUMO (79.4%) HOMO → LUMO+4 (6.0%) HOMO → LUMO+6 (3.2%) HOMO → LUMO+14 (4.5%)
381.8	0.1450	HOMO → LUMO (97.6%)	411.6	0.1523	HOMO → LUMO (98.8%)
3			**4**		
λ_{max} (nm)	Oscillator strength	Transitions	λ_{max} (nm)	Oscillator strength	Transitions
247.1	0.0103	HOMO–3 → LUMO (38.1%) HOMO → LUMO+2 (4.2%) HOMO → LUMO+3 (2.2%) HOMO → LUMO+4 (46.5%) HOMO → LUMO+6 (2.1%)	253.2	0.1945	HOMO–3 → LUMO (7.2%) HOMO–3 → LUMO+1 (83.5%)
254.5	0.0670	HOMO–3 → LUMO (46.7%) HOMO → LUMO+4 (34.2%) HOMO → LUMO+5 (13.5%)	260.4	0.0259	HOMO–2 → LUMO (2.7%) HOMO → LUMO+2 (94.5%)
265.8	0.0204	HOMO–2 → LUMO (6.6%) HOMO → LUMO+2 (81.5%) HOMO → LUMO+4 (6.0%) HOMO → LUMO+5 (2.8%)	268.8	0.3364	HOMO–2 → LUMO (80.4%) HOMO–2 → LUMO+1 (8.8%) HOMO → LUMO+1 (2.6%) HOMO → LUMO+2 (2.1%)
266.6	0.2162	HOMO–2 → LUMO (81.6%) HOMO → LUMO+2 (6.2%) HOMO → LUMO+4 (2.3%) HOMO → LUMO+10 (5.6%)	320.0	0.1726	HOMO–2 → LUMO (2.7%) HOMO → LUMO+1 (95.3%)
397.1	0.1493	HOMO → LUMO (98.6%)	382.8	0.1977	HOMO → LUMO (97.7%)

Table S3. Values for the calculated UV-vis spectra of the ground state for the *trans*-keto-enamine tautomers of **1–4**, obtained by using the TD-DFT/B3LYP/6-311++G(d,p) method.

1			**2**		
λ_{max} (nm)	Oscillator strength	Transitions	λ_{max} (nm)	Oscillator strength	Transitions
241.5	0.0029	HOMO–3 → LUMO (2.2%) HOMO → LUMO+5 (80.3%) HOMO → LUMO+7 (14.7%)	256.2	0.0058	HOMO → LUMO+5 (54.9%) HOMO → LUMO+6 (19.5%) HOMO → LUMO+7 (16.4%) HOMO → LUMO+8 (3.1%)
263.0	0.0033	HOMO → LUMO+2 (6.1%) HOMO → LUMO+3 (40.8%) HOMO → LUMO+4 (45.3%) HOMO → LUMO+6(6.2%)	256.2	0.0163	HOMO–3 → LUMO (2.8%) HOMO–2 → LUMO (2.7%) HOMO → LUMO+5 (18.2%) HOMO → LUMO+6 (58.8%) HOMO → LUMO+7 (5.6%) HOMO → LUMO+8 (9.1%)
280.4	0.1995	HOMO–2 → LUMO (92.7%) HOMO → LUMO+10 (3.3%)	276.1	0.1361	HOMO–3 → LUMO (2.3%) HOMO–2 → LUMO (87.3%) HOMO → LUMO+8 (3.4%)
308.2	0.0056	HOMO → LUMO+1 (99.2%)	329.1	0.0049	HOMO → LUMO+1 (99.4%)
407.5	0.2137	HOMO → LUMO (98.9%)	424.5	0.2106	HOMO → LUMO (99.6%) HOMO ← LUMO (2.1%)
3			**4**		
λ_{max} (nm)	Oscillator strength	Transitions	λ_{max} (nm)	Oscillator strength	Transitions
262.2	0.0127	HOMO–3 → LUMO (85.3%) HOMO → LUMO+6 (8.4%) HOMO → LUMO+7 (4.1%)	253.4	0.0012	HOMO → LUMO+3 (91.0%) HOMO → LUMO+4 (7.5%)
277.6	0.1691	HOMO–2 → LUMO (90.9%) HOMO → LUMO+10 (5.4%)	275.0	0.0172	HOMO → LUMO+2 (97.1%)
279.2	0.0014	HOMO → LUMO+2 (85.9%) HOMO → LUMO+3 (3.8%) HOMO → LUMO+4 (9.0%)	287.2	0.2395	HOMO–2 → LUMO (89.4%) HOMO → LUMO+1 (2.3%) HOMO → LUMO+2 (2.1%)
303.5	0.0034	HOMO → LUMO+1 (99.2%)	323.2	0.1892	HOMO–2 → LUMO (2.4%) HOMO → LUMO+1 (95.4%)
420.6	0.2130	HOMO → LUMO (99.3%)	429.4	0.2059	HOMO → LUMO (98.6%)

Table S4. Cartesian atomic coordinates for the optimized structures of **1**, obtained by using the DFT/B3LYP/6–311++G(d,p) method.

enol-imine tautomer				*cis*-keto-enamine tautomer				*trans*-keto-enamine tautomer			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C1	3.909396	1.198362	–0.284570	C1	3.981774	0.949362	–0.623489	C1	4.682733	0.410773	0.000266
C2	2.582566	0.911321	0.060196	C2	2.605675	0.945330	–0.192517	C2	3.363638	1.039599	–0.000075
C3	2.176368	–0.441352	0.200683	C3	2.094958	–0.335779	0.304993	C3	2.215010	0.094719	–0.000054
C4	3.119888	–1.461892	–0.012678	C4	2.940319	–1.484665	0.345542	C4	2.444855	–1.322040	–0.000006
C5	4.429927	–1.171073	–0.354208	C5	4.238918	–1.419191	–0.074729	C5	3.706285	–1.831199	–0.000074
C6	4.816417	0.168955	–0.488022	C6	4.750267	–0.180559	–0.562312	C6	4.833370	–0.939677	0.000001
H7	4.200241	2.236738	–0.387751	H7	4.377526	1.886799	–0.996346	H7	5.535531	1.079739	0.000811
H8	2.801043	–2.494282	0.093019	H8	2.528469	–2.419478	0.715723	H8	1.599624	–2.005122	0.000226
H9	5.145456	–1.967546	–0.517088	H9	4.877421	–2.293362	–0.044172	H9	3.870874	–2.901892	0.000190
H10	5.839513	0.409438	–0.755743	H10	5.782879	–0.138163	–0.895403	H10	5.831587	–1.367363	0.000614
O11	1.732175	1.930610	0.250156	O11	1.882005	1.979527	–0.236728	O11	3.220815	2.269251	–0.000319
H12	0.845257	1.544671	0.473692	C12	0.767894	–0.430547	0.731637	C12	0.962383	0.673786	0.000037
C13	0.809711	–0.783498	0.554377	H13	0.381052	–1.382302	1.088863	N13	–0.227733	0.059690	–0.000236
H14	0.581679	–1.855079	0.636066	N14	–0.062441	0.602075	0.732853	C14	–1.492461	0.764786	0.000199
N15	–0.093198	0.100551	0.768076	C15	–1.454562	0.534380	1.100500	H15	–1.599284	1.405861	0.882381
C16	–1.433182	–0.330052	1.093510	H16	–1.831444	1.542630	1.269667	H16	–1.599211	1.407088	–0.880989
H17	–1.827595	0.271687	1.914389	H17	–1.582745	–0.015324	2.040688	C17	–2.629847	–0.241886	–0.000122
H18	–1.472028	–1.38535	1.407309	C18	–2.326870	–0.164612	0.052879	O18	–2.469530	–1.439254	–0.000720
C19	–2.374614	–0.201486	–0.103166	O19	–1.923543	–0.947817	–0.766806	O19	–3.811366	0.376711	0.000518
O20	–2.043943	–0.284450	–1.257249	O20	–3.610270	0.189646	0.214440	C20	–4.999183	–0.469649	0.000922
O21	–3.642034	–0.029178	0.316622	C21	–4.579747	–0.448561	–0.665476	H21	–4.961828	–1.107926	0.885771
C22	–4.664091	0.024755	–0.714557	H22	–4.295960	–0.234882	–1.697709	H22	–4.961027	–1.109977	–0.882382
H23	–4.423553	0.843958	–1.395213	H23	–4.519661	–1.528587	–0.515133	C23	–6.207350	0.441426	–0.000646
H24	–4.629527	–0.906423	–1.284724	C24	–5.945504	0.104286	–0.319392	H24	–7.117871	–0.163250	–0.000434
C25	–5.998477	0.225049	–0.027416	H25	–5.980847	1.185453	–0.469186	H25	–6.219996	1.079523	0.885420
H26	–6.011165	1.158004	0.540278	H26	–6.698718	–0.355478	–0.964554	H26	–6.219133	1.077559	–0.888144
H27	–6.793032	0.269195	–0.777015	H27	–6.206520	–0.111639	0.718936	H27	–0.301080	–0.950557	–0.000676
H28	–6.216967	–0.599250	0.655122	H28	0.381363	1.462296	0.345584	H28	0.939993	1.761002	0.000346

Table S5. Cartesian atomic coordinates for the optimized structures of **2**, obtained by using the DFT/B3LYP/6–311++G(d,p) method.

Enol-imine tautomer				*Cis*-keto-enamine tautomer				*Trans*-keto-enamine tautomer			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C1	–2.989397	1.990841	–0.370350	C1	–3.110512	1.896766	–0.575500	C1	–3.415254	0.902318	0.000118
C2	–1.704654	1.563907	–0.003463	C2	–1.749093	1.661443	–0.148794	C2	–2.094066	0.574314	0.000040
C3	–1.496217	0.197373	0.285550	C3	–1.446651	0.297305	0.280940	C3	–1.687681	–0.810127	–0.000035
C4	–2.576175	–0.709830	0.198120	C4	–2.459542	–0.720852	0.269516	C4	–2.697840	–1.895336	0.000167
C5	–3.838165	–0.271998	–0.168258	C5	–3.726691	–0.426054	–0.145919	C5	–4.091451	–1.443757	0.000146
C6	–4.034434	1.090855	–0.451231	C6	–4.041611	0.902802	–0.570203	C6	–4.419917	–0.131086	0.000093
H7	–3.140552	3.040624	–0.590444	H7	–3.358985	2.900106	–0.900417	H7	–1.339556	1.351584	0.000204
H8	–2.387017	–1.752357	0.421321	H8	–2.186736	–1.718378	0.592390	H8	–4.850482	–2.217173	0.000166
H9	–5.027065	1.419084	–0.736265	H9	–5.060025	1.092230	–0.892730	H9	–5.456339	0.190163	0.000025
O10	–0.717079	2.474326	0.062081	O10	–0.883028	2.579386	–0.147276	C10	–0.373448	–1.218242	–0.000371
H11	0.111574	1.996114	0.321422	C11	–0.154918	–0.017064	0.698704	H11	–0.203096	–2.291346	–0.000259
C12	–0.186200	–0.296125	0.671371	H12	0.081734	–1.032240	1.008667	C12	2.072913	–0.970822	–0.000621
H13	–0.111757	–1.372460	0.879566	N13	0.831434	0.873763	0.751375	H13	2.268187	–1.592349	–0.882254
N14	0.839546	0.465894	0.776354	C14	2.191399	0.564612	1.109726	H14	2.267463	–1.593128	0.880608
C15	2.109277	–0.116399	1.144559	H15	2.226786	–0.046919	2.019700	C15	3.065693	0.178170	0.000220
H16	1.998917	–1.112543	1.602313	H16	2.724283	1.488918	1.332184	O16	4.320069	–0.277090	0.000797
H17	2.616023	0.524207	1.868340	C17	2.952158	–0.206453	0.026153	C17	5.383349	0.720141	0.000447
C18	3.019766	–0.301404	–0.068831	O18	2.440491	–0.854083	–0.849467	H18	5.261550	1.348761	0.884661
O19	2.642272	–0.526069	–1.189358	O19	4.274605	–0.090202	0.224683	H19	5.260579	1.349141	–0.883381
O20	4.312330	–0.226994	0.299523	C20	5.139244	–0.825877	–0.686283	C20	6.702972	–0.020612	–0.000370
C21	5.297268	–0.468213	–0.740909	H21	4.882433	–1.885525	–0.623354	H21	7.524193	0.700738	–0.000508
H22	5.127567	–1.465430	–1.153348	H22	4.930540	–0.487871	–1.703183	H22	6.800906	–0.650590	0.886190
H23	5.137527	0.257338	–1.541118	C23	6.571187	–0.557513	–0.275234	H23	6.800131	–0.650096	–0.887360
C24	6.668866	–0.334701	–0.113333	H24	6.756685	–0.894436	0.746986	O24	2.749701	1.344434	0.000271
H25	6.806062	–1.061816	0.690141	H25	7.249213	–1.096561	–0.942073	O25	–3.934513	2.167663	0.000256
H26	7.436874	–0.511879	–0.870937	H26	6.804698	0.507477	–0.337898	C26	–3.026041	3.256838	–0.000310
H27	6.816803	0.666825	0.296425	O27	–4.781265	–1.301312	–0.207789	H27	–2.391779	3.244804	–0.894362
O28	–4.947591	–1.067850	–0.283774	C28	–4.548058	–2.642391	0.186372	H28	–3.635555	4.159039	–0.000640
C29	–4.805358	–2.455041	–0.024231	H29	–5.495200	–3.164554	0.058973	H29	–2.391728	3.245628	0.893725
H30	–5.791378	–2.891346	–0.176127	H30	–3.784519	–3.116208	–0.441952	N30	0.726270	–0.443811	–0.000914
H31	–4.093336	–2.921287	–0.715150	H31	–4.239223	–2.702369	1.236944	H31	0.661108	0.565906	–0.000735
H32	–4.483995	–2.639225	1.007632	H32	0.540391	1.809335	0.408055	O32	–2.407114	–3.098156	0.000324

Table S6. Cartesian atomic coordinates for the optimized structures of **3**, obtained by using the DFT/B3LYP/6–311++G(d,p) method.

Enol-imine tautomer				*Cis*-keto-enamine tautomer				*Trans*-keto-enamine tautomer			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C1	2.163472	2.237242	–0.288396	C1	2.299267	2.224618	–0.614265	C1	3.277298	2.202277	0.000075
C2	0.903433	1.719169	0.037718	C2	0.947509	1.930585	–0.201754	C2	1.840245	2.473959	0.000141
C3	0.776869	0.335775	0.322864	C3	0.713650	0.572264	0.291909	C3	0.973320	1.268394	–0.000040
C4	1.916201	–0.486263	0.270501	C4	1.777098	–0.377551	0.347911	C4	1.550814	–0.045706	–0.000079
C5	3.148061	0.049159	–0.053641	C5	3.028667	–0.023467	–0.058734	C5	2.899316	–0.196681	0.000001
C6	3.277031	1.412718	–0.334505	C6	3.292687	1.288773	–0.543992	C6	3.775924	0.939732	0.000113
H7	2.246735	3.295099	–0.505330	H7	2.497190	3.223575	–0.984153	H7	3.933767	3.064489	–0.000181
H8	1.817369	–1.543614	0.486440	H8	1.574513	–1.378219	0.712906	H8	0.915142	–0.924349	–0.000315
H9	4.245295	1.824978	–0.588747	H9	4.298565	1.538883	–0.860446	H9	4.846585	0.771943	–0.000183
O10	–0.144810	2.551601	0.071621	O10	0.025593	2.789077	–0.259640	O10	1.392033	3.626332	0.000342
H11	–0.947659	2.015724	0.305762	C11	–0.568524	0.196653	0.706315	C11	–0.387619	1.506322	–0.000224
C12	–0.510615	–0.248419	0.665555	H12	–0.747312	–0.814332	1.063710	N12	–1.380192	0.610193	0.000277
H13	–0.520603	–1.329070	0.862114	N13	–1.598287	1.028521	0.693140	C13	–2.784426	0.968748	–0.000531
N14	–1.581903	0.448005	0.741463	C14	–2.947763	0.667757	1.053541	H14	–3.050734	1.562297	0.880777
C15	–2.825084	–0.206781	1.076248	H15	–3.545001	1.573320	1.154800	H15	–3.050380	1.560011	–0.883520
H16	–3.323979	0.336984	1.881614	H16	–2.971219	0.161568	2.025888	C16	–3.623669	–0.297882	0.000783
H17	–2.678245	–1.242858	1.419529	C17	–3.615101	–0.270879	0.043118	O17	–3.156977	–1.412039	0.002146
C18	–3.769299	–0.269539	–0.122710	O18	–3.025878	–0.962856	–0.745639	O18	–4.923986	–0.006187	0.000082
O19	–3.430706	–0.236219	–1.276638	O19	–4.945182	–0.240157	0.201007	C19	–5.852556	–1.132345	0.000692
O20	–5.039621	–0.412282	0.297817	C20	–5.725480	–1.137738	–0.641259	H20	–5.650632	–1.737979	0.886113
C21	–6.050840	–0.566969	–0.734693	H21	–5.517131	–0.892674	–1.684402	H21	–5.648436	–1.740871	–0.882230
H22	–6.015326	0.309552	–1.384836	H22	–5.385793	–2.159376	–0.458954	C22	–7.255437	–0.565627	–0.001920
H23	–5.798202	–1.442503	–1.336981	C23	–7.184008	–0.945402	–0.286058	H23	–7.977731	–1.385942	–0.001489
C24	–7.390895	–0.713946	–0.045330	H24	–7.500578	0.083667	–0.468666	H24	–7.433644	0.047672	0.883799
H25	–7.621661	0.168269	0.555759	H25	–7.798713	–1.607060	–0.901858	H25	–7.431485	0.044852	–0.890013
H26	–8.177042	–0.832399	–0.795694	H26	–7.368396	–1.185412	0.763290	H26	–1.195972	–0.386342	0.001514
H27	–7.404178	–1.590679	0.605943	Br27	4.470142	–1.289974	0.009429	H27	–0.685178	2.552198	–0.000784
Br28	4.695483	–1.082949	–0.119996	H28	–1.347352	1.963309	0.309682	Br28	3.689206	–1.945466	–0.000287

Table S7. Cartesian atomic coordinates for the optimized structures of **4**, obtained by using the DFT/B3LYP/6–311++G(d,p) method.

Enol-imine tautomer				*Cis*-keto-enamine tautomer				*Trans*-keto-enamine tautomer			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C1	2.679264	2.027798	–0.185635	C1	2.838151	1.962604	–0.570747	C1	3.771804	1.738400	–0.000047
C2	1.401628	1.525894	0.114928	C2	1.469966	1.740071	–0.160324	C2	2.359491	2.118085	0.000006
C3	1.225730	0.127124	0.316921	C3	1.150003	0.383116	0.304141	C3	1.398028	0.980399	0.000024
C4	2.330295	–0.721228	0.209922	C4	2.141908	–0.621229	0.338975	C4	1.864052	–0.359168	0.000069
C5	3.578379	–0.198263	–0.086921	C5	3.420232	–0.331319	–0.063368	C5	3.205268	–0.615574	0.000010
C6	3.760725	1.175265	–0.286431	C6	3.771246	0.970112	–0.523220	C6	4.172360	0.443210	–0.000044
H7	2.790236	3.094080	–0.336593	H7	3.091577	2.956558	–0.918432	H7	4.489788	2.549528	–0.000106
H8	2.222961	–1.788620	0.356224	H8	1.905173	–1.622318	0.678988	H8	1.184536	–1.203739	0.000128
H9	4.748963	1.548627	–0.517825	H9	4.793589	1.145429	–0.831544	H9	5.220750	0.175329	–0.000104
O10	0.385848	2.379436	0.203975	O10	0.601401	2.647497	–0.193428	O10	1.990182	3.295336	0.000025
H11	–0.437072	1.853489	0.411751	C11	–0.158046	0.072540	0.712690	C11	0.052089	1.327661	0.000049
C12	–0.085428	–0.427188	0.626501	H12	–0.394746	–0.935630	1.042476	N12	–1.001167	0.518840	–0.000093
H13	–0.141576	–1.516703	0.747734	N13	–1.129171	0.963045	0.723311	C13	–2.378738	0.980236	–0.000090
N14	–1.120789	0.312563	0.752847	C14	–2.502992	0.677845	1.069897	H14	–2.596956	1.589028	0.882891
C15	–2.397550	–0.297162	1.046030	H15	–2.562112	0.163106	2.035423	H15	–2.597031	1.588888	–0.883185
H16	–2.309383	–1.366745	1.289900	H16	–3.045927	1.616163	1.175283	C16	–3.301633	–0.228741	–0.000114
H17	–2.852761	0.198374	1.906718	C17	–3.206167	–0.210410	0.037444	O17	–2.903655	–1.368959	–0.000450
C18	–3.354919	–0.185019	–0.139231	O18	–2.638511	–0.918206	–0.753190	O18	–4.577176	0.148143	0.000195
O19	–3.024936	–0.013237	–1.283320	O19	–4.531762	–0.113333	0.180757	C19	–5.580310	–0.915370	–0.000007
O20	–4.622206	–0.346201	0.278274	C20	–5.349421	–0.957891	–0.684258	H20	–5.416532	–1.533786	0.884242
C21	–5.651318	–0.339205	–0.749853	H21	–5.116989	–0.706442	–1.720632	H21	–5.416648	–1.533356	–0.884577
H22	–5.597927	0.612640	–1.282062	H22	–5.062619	–1.997514	–0.514150	C22	–6.942063	–0.256909	0.000239
H23	–5.431054	–1.136553	–1.462975	C23	–6.799310	–0.696734	–0.339453	H23	–7.716159	–1.028462	0.000197
C24	–6.985994	–0.537239	–0.063370	H24	–7.006732	–0.944050	0.703803	H24	–7.079029	0.364654	0.887471
H25	–7.016919	–1.490111	0.469487	H25	–7.061756	0.349670	–0.508655	H25	–7.079216	0.364935	–0.886768
H26	–7.183912	0.266082	0.649554	H26	–7.439852	–1.316628	–0.972015	H26	–0.896726	–0.491412	–0.000285
H27	–7.784085	–0.536441	–0.810376	O27	4.111252	–2.489000	0.387087	H27	–0.156936	2.395343	0.000200
O28	4.533950	–2.300796	–0.011787	O28	5.571617	–1.083152	–0.394478	N28	3.665606	–1.999794	0.000065
O29	5.819657	–0.608716	–0.456720	N29	4.437347	–1.374811	–0.020476	O29	2.822272	–2.896191	0.000082
N30	4.727812	–1.102087	–0.193143	H30	–0.822244	1.891342	0.364960	O30	4.879252	–2.196286	0.000088