8-(pyridin-2-yl)quinolin-7-ol as a platform for conjugated proton cranes: a DFT structural design

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Table S1. Frank-Condon states (vertical transitions) of the **E1K** form of **4**-**7** and **11**-**12**.

Compound	Environment	Singlet excited state					
		S_1			S_2		
		E*, kcal/mol	*f*	origin	E*, kcal/mol	*f*	origin
4	vacuum	26	0.08	mainly HOMO-LUMO	27	0.0	mainly (HOMO-2)-LUMO
	toluene	27	0.13		30	0.0	
	acetonitrile	29	0.12		34	0.0	
5	vacuum	25	0.23	HOMO-LUMO	36	0.0	mainly (HOMO-2)-LUMO
	toluene	20	0.33		32	0.0	
	acetonitrile	21	0.30		32	0.0	
6	vacuum	20	0.21	HOMO-LUMO	30	0.0	mainly (HOMO-3)-LUMO
	toluene	19	0.29		30	0.0	
	acetonitrile	21	0.26		31	0.0	
7	vacuum	22	0.28	mainly HOMO-LUMO	32	0.08	mainly HOMO-(LUMO+1)
	toluene	20	0.40		31	0.12	
	acetonitrile	22	0.39		33	0.10	
11	vacuum	33	0.17	HOMO-LUMO	38	0.0	mixed
	toluene	28	0.21	mainly HOMO-LUMO	36	0.0	
	acetonitrile	26	0.17		35	0.0	
12	vacuum	24	0.44	mainly HOMO-LUMO	30	0.0	mixed
	toluene	18	0.57		28	0.0	
	acetonitrile	16	0.54		26	0.0	

* relative energy in respect of the most stable optimized structure in S_1 (Table 1 and Figures 1-2).

Table S2. Important structural parameters of the tautomers of **4**-**7** and **11**-**12** in ground and excited S_1 (in brackets) state.

Compound	Environment	E1K	K1K	K2K	K2E
		r_{XH} (X=O, $N_{1'}$ or N_{10}), in Å			
4	vacuum	0.963 (0.965)	-	-	1.009 (1.010)
	toluene	0.964 (0.967)	-	-	1.011 (1.010)
	acetonitrile	0.965 (0.968)	-	-	1.012 (1.011)
5	vacuum	0.996 (1.047)	- (-)	1.057 (-)	1.055 (1.024)
	toluene	0.998 (1.059)	- (-)	1.056 (-)	1.052 (1.024)
	acetonitrile	0.999 (1.076)	- (1.013)	1.056 (1.029)	1.043 (1.024)
6	vacuum	1.007	-	1.052	1.064

		(1.068)	(-)	(1.054)	(1.027)
	toluene	1.009 (-)	- (1.018)	1.049 (1.039)	1.062 (1.027)
	acetonitrile	1.009 (-)	1.080 (1.023)	1.046 (1.031)	1.056 (1.027)
7	vacuum	0.993 (1.013)	- ()	1.060 ()	1.049 (1.020)
	toluene	0.995 (1.015)	- ()	1.059 ()	1.045 (1.021)
	acetonitrile	0.996 (1.017)	- (1.017)	1.058 (1.033)	1.040 (1.023)
11	vacuum	0.991 (-)	- (-)	1.061 (-)	1.044 (1.022)
	toluene	0.992 (-)	- (-)	1.062 (-)	1.041 (1.026)
	acetonitrile	0.993 (-)	- (-)	1.064 (1.030)	1.038 (1.080)
12	vacuum	0.993 (-)	- (-)	1.065 (-)	1.049 (1.022)
	toluene	0.993 (-)	- (-)	1.067 (-)	1.045 (1.026)
	acetonitrile	0.993 1.060	- (-)	1.069 1.061	1.039 (1.046)

Table S3. Natural charges in vacuum in selected atoms in 4 and 5 in ground state* and excited state (in brackets).

Comp.	E1K			K2K			K2E		
	O	**N_{quin}**	**N_{pyr}**	**O**	**N_{quin}**	**N_{pyr}**	**O**	**N_{quin}**	**N_{pyr}**
4	−0.647 (−0.584)	−0.406 (−0.437)	-	-	-	-	−0.584 (−0.532)	−0.488 (−0.454)	-
5	−0.663 (−0.597)	−0.439 (−0.431)	−0.489 (−0.499)	−0.632 (−0.48)**	−0.519 (−0.36)**	−0.486 (−0.53)**	−0.619 (−0.569)	−0.492 (−0.484)	−0.513 (−0.470)
6	−0.665 (−0.595)	−0.443 (−0.450)	−0.525 (−0.524)	−0.648 (−0.574)	−0.520 (−0.486)	−0.509 (−0.512)	−0.628 (−0.576)	−0.492 (−0.488)	−0.546 (−0.508)
7	−0.667 (−0.621)	−0.438 (−0.480)	−0.463 (−0.470)	−0.645 (-)	−0.523 (-)	−0.464 (-)	−0.626 (−0.596)	−0.494 (−0.493)	−0.487 (−0.444)
11	−0.656 (-)	−0.443 (-)	−0.470 (-)	−0.610 (-)	−0.515 (-)	−0.486 (-)	−0.605 (−0.557)	−0.489 (−0.476)	−0.497 (−0.452)
12	−0.653 (-)	−0.443 (-)	−0.483 (-)	−0.608 (-)	−0.512 (-)	−0.485 (-)	−0.607 (−0.558)	−0.485 (−0.474)	−0.509 (−0.462)

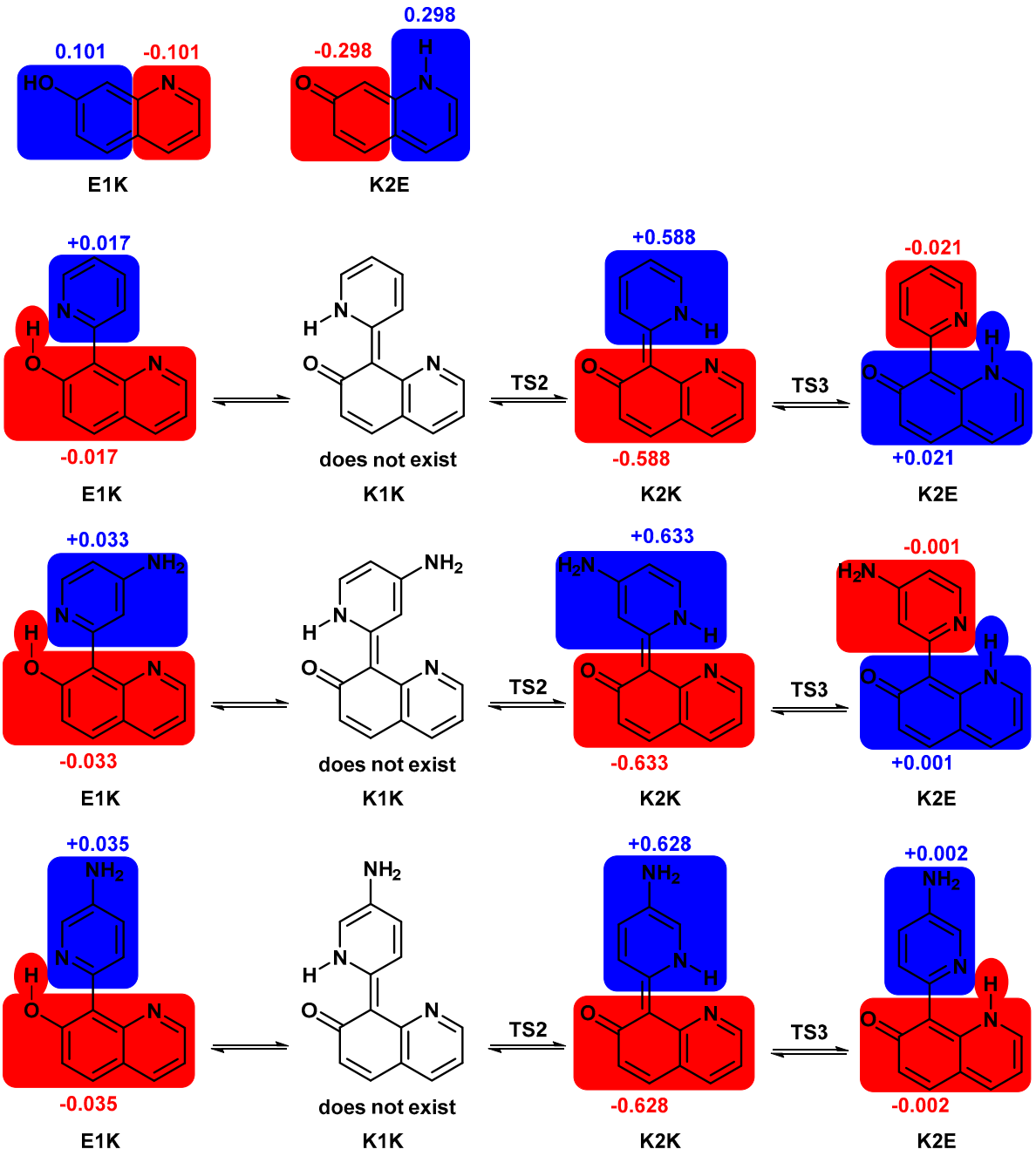
* The corresponding value for the nitrogen atom in pyridine is −0.41; ** data for **TS2**, because **K2K** spontaneously relaxes to it.

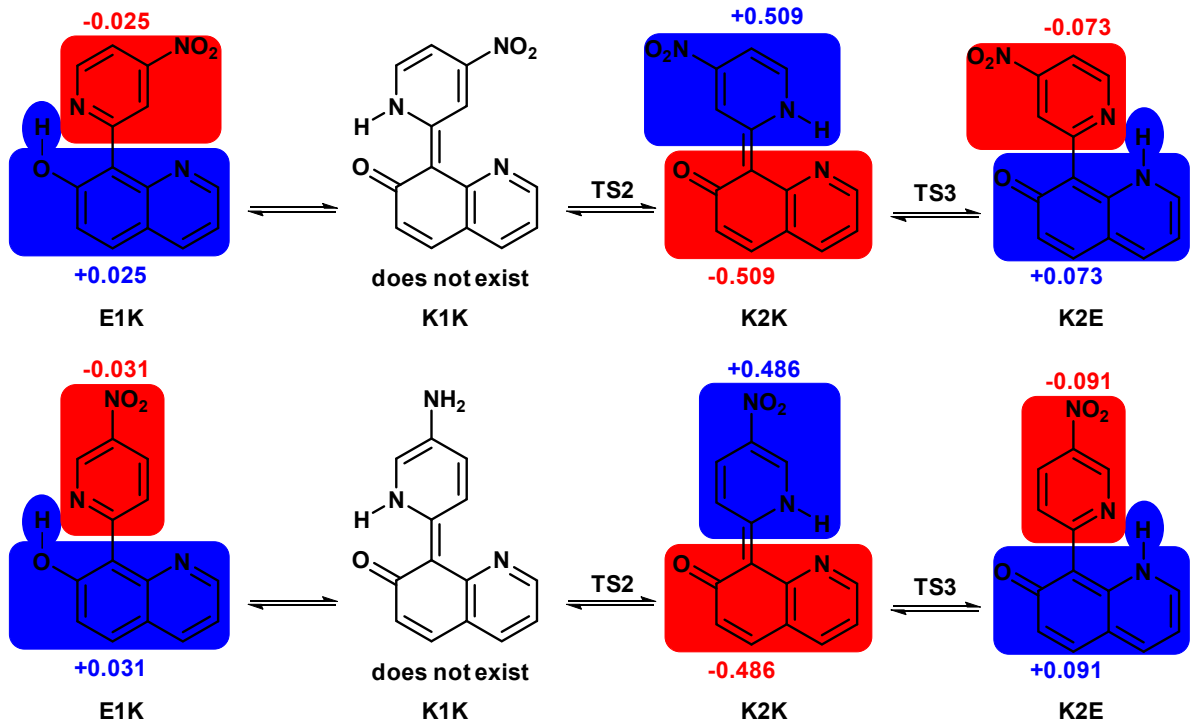
Table S4. Milliken atomic charges in vacuum in selected atoms in ground state*.

Comp.	E1K			K2K			K2E		
	O	**N_{quin}**	**N_{pyr}**	**O**	**N_{quin}**	**N_{pyr}**	**O**	**N_{quin}**	**N_{pyr}**
4	−0.33	−0.08	-	-	-	-	−0.38	−0.28	-
5	−0.33	−0.16	−0.30	−0.44	−0.33	−0.22	−0.43	−0.21	−0.34
6	−0.33	−0.17	−0.32	−0.46	−0.33	−0.23	−0.43	−0.21	−0.35
7	−0.34	−0.16	−0.29	−0.45	−0.33	−0.17	−0.43	−0.22	−0.33
11	−0.32	−0.17	−0.28	−0.42	−0.33	−0.22	−0.41	−0.21	−0.32

12	−0.32	−0.17	−0.29	−0.42	−0.32	−0.23	−0.42	−0.20	−0.34

* The corresponding value for the nitrogen atom in pyridine is −0.13.





Scheme S1. Ground state NBO charges of the different tautomers of 4-7 and of 11-12. The donor (in blue) – acceptor (in red) interactions in the molecular backbones are presented by summing the natural charges of the different parts in the molecules.

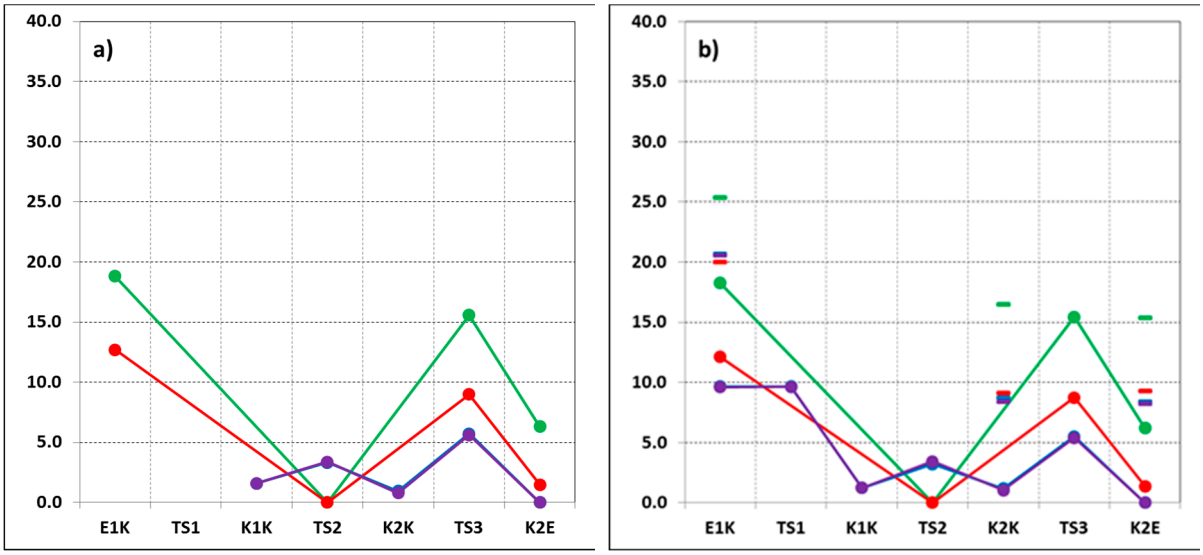


Figure S1. Comparison between the excited (S_1) state energy landscapes (in relative energies in kcal/mol units) of of **5** obtained by CAM-B3LYP/TZVP (**a**) and M06-2X/TZVP (**b**, the same as in Figure 2b) in vacuum (green), toluene (red), acetonitrile (blue) and formamide (violet). The filled circles represent optimized structures.

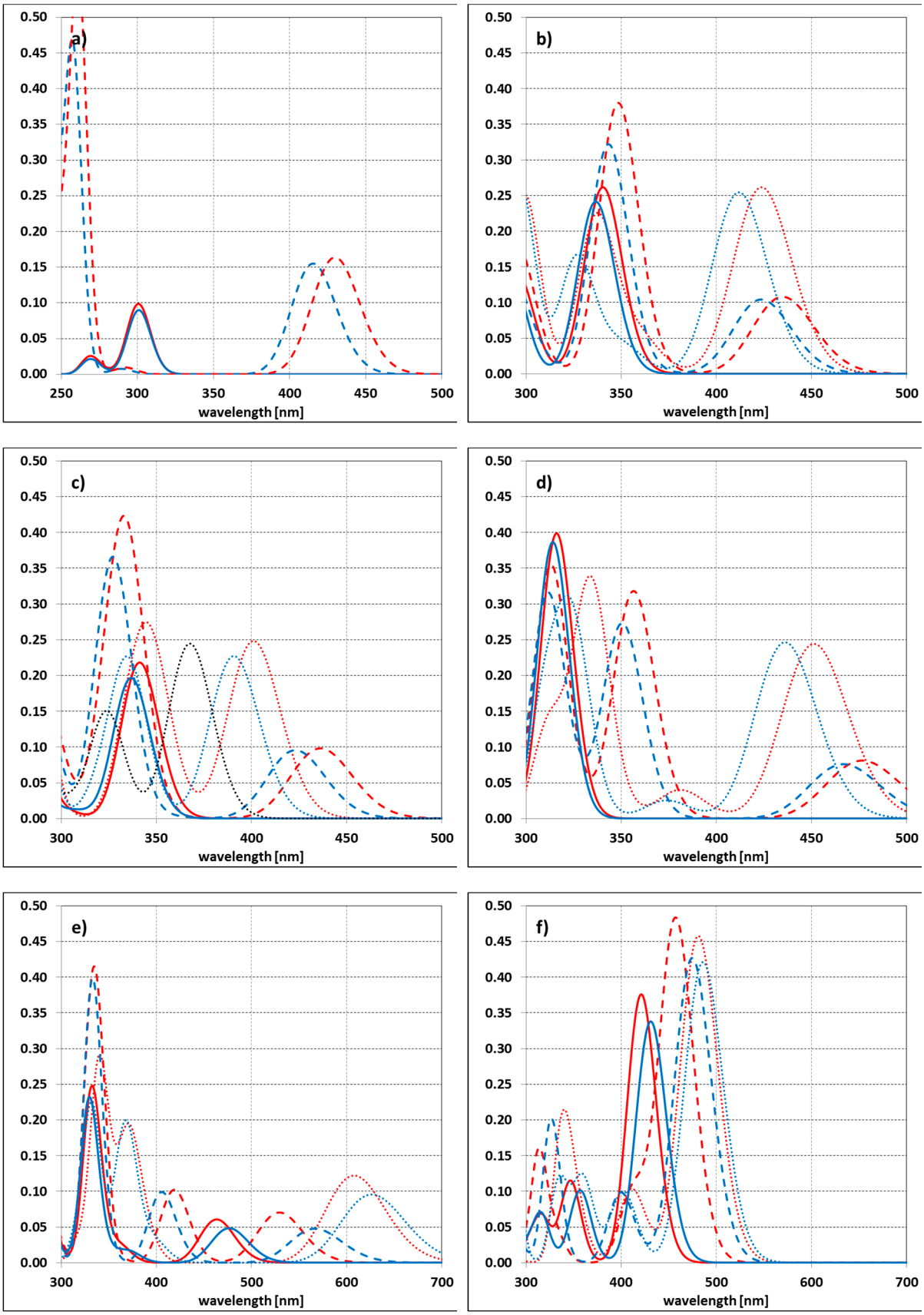


Figure S2. Predicted absorption spectra (B3LYP/TZVP//M06-2X/TZVP) in toluene (red) and in acetonitrile (blue) of the different tautomers of **4-7** (**a**–**d**) and of **11-12** (**e**–**f**): **E1K** – solid line, **K2E** – dashes, **K2K** – dots, **K1K** (only in **6** in acetonitrile) – black dots. The spectra in formamide are practically identical to those in acetonitrile.

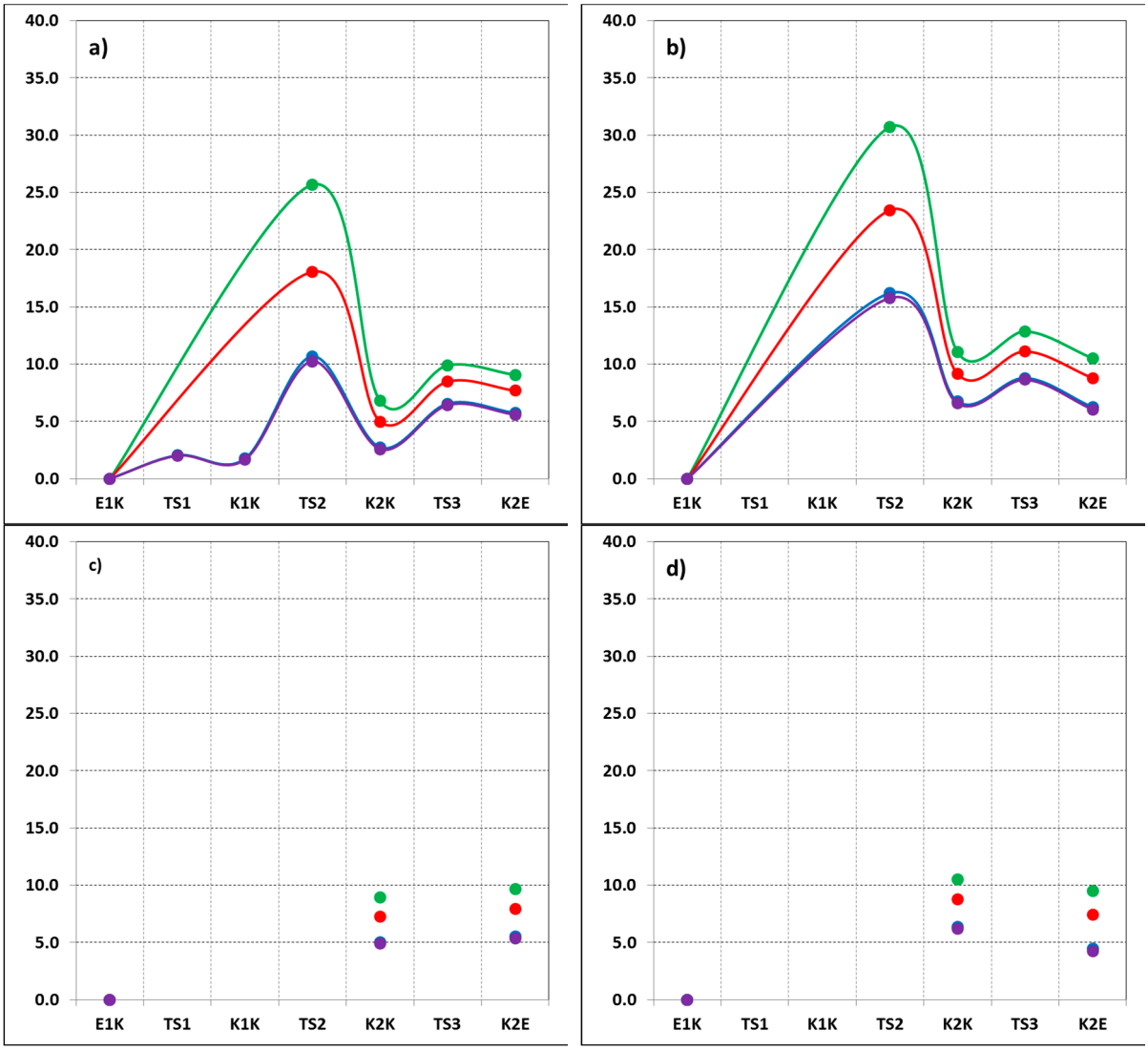


Figure S3. Ground state energy landscape (change of the relative energies in kcal/mol units) of **8**-**10** (**a**–**c**) and **13** (**d**) in vacuum (green), toluene (red), acetonitrile (blue) and formamide (violet). The filled circles represent optimized structures.