BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

Tautomerism and switching in 7-hydroxy-8-(azophenyl)quinoline and similar compounds

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Additional figures and tables

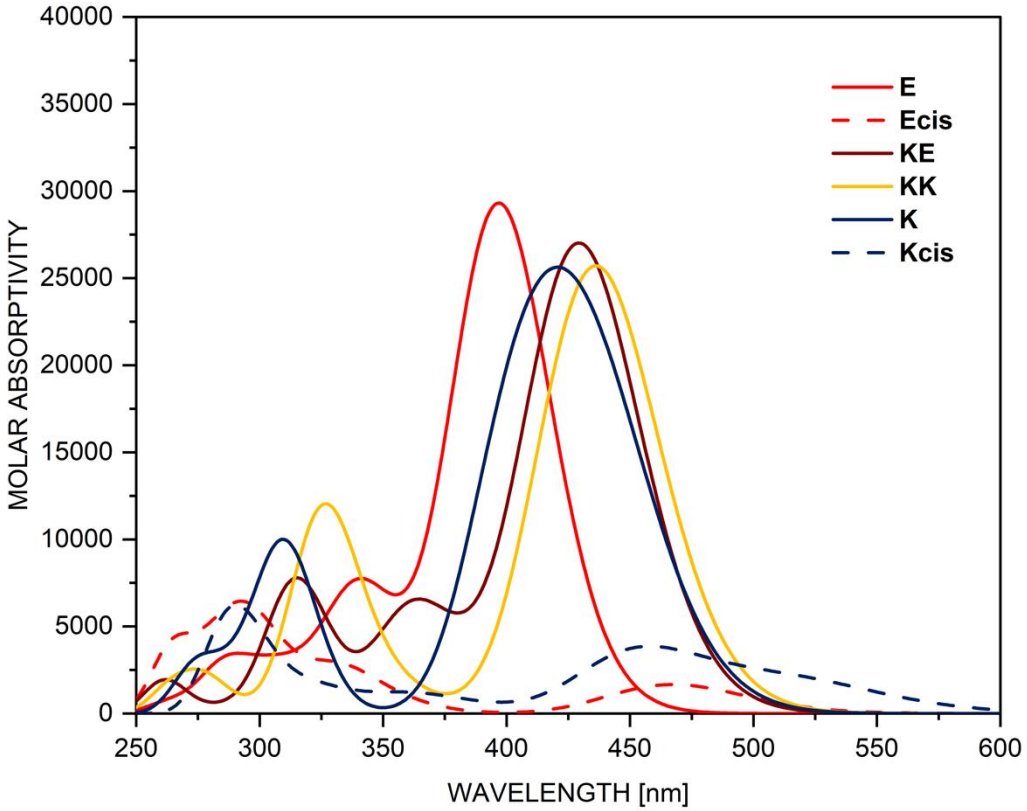


Figure S1. Simulated absorption spectra of the tautomers and isomers of **1** in acetonitrile.

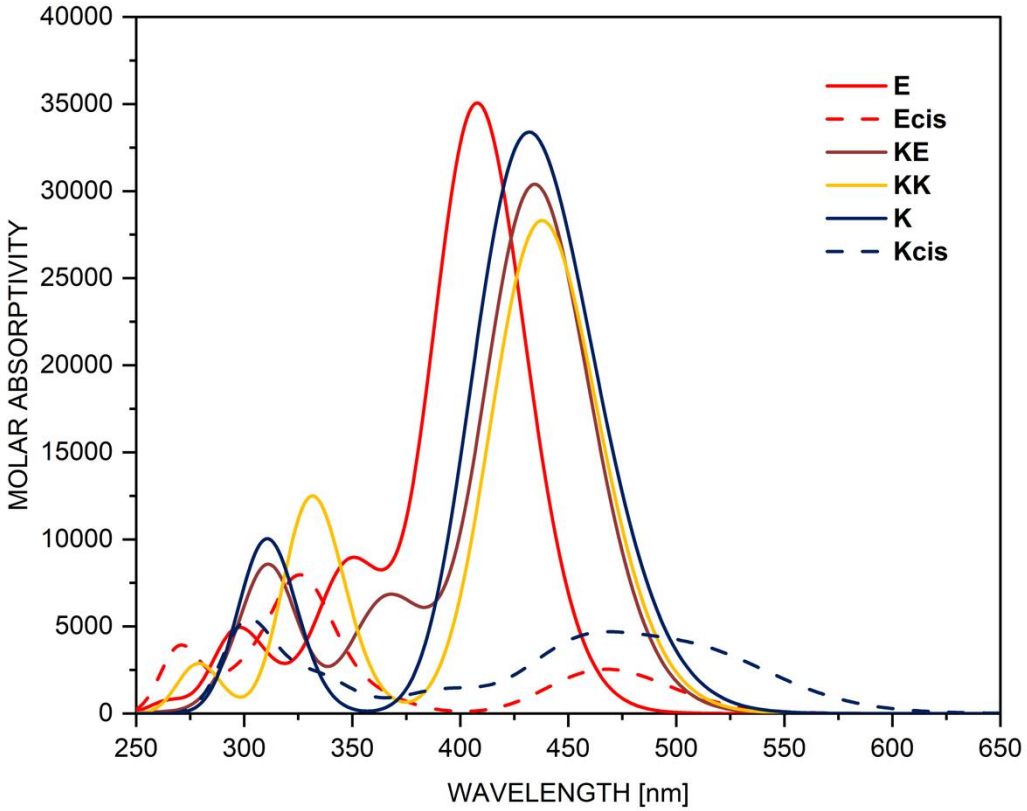


Figure S2. Simulated absorption spectra of the tautomers and isomers of **2** in toluene.

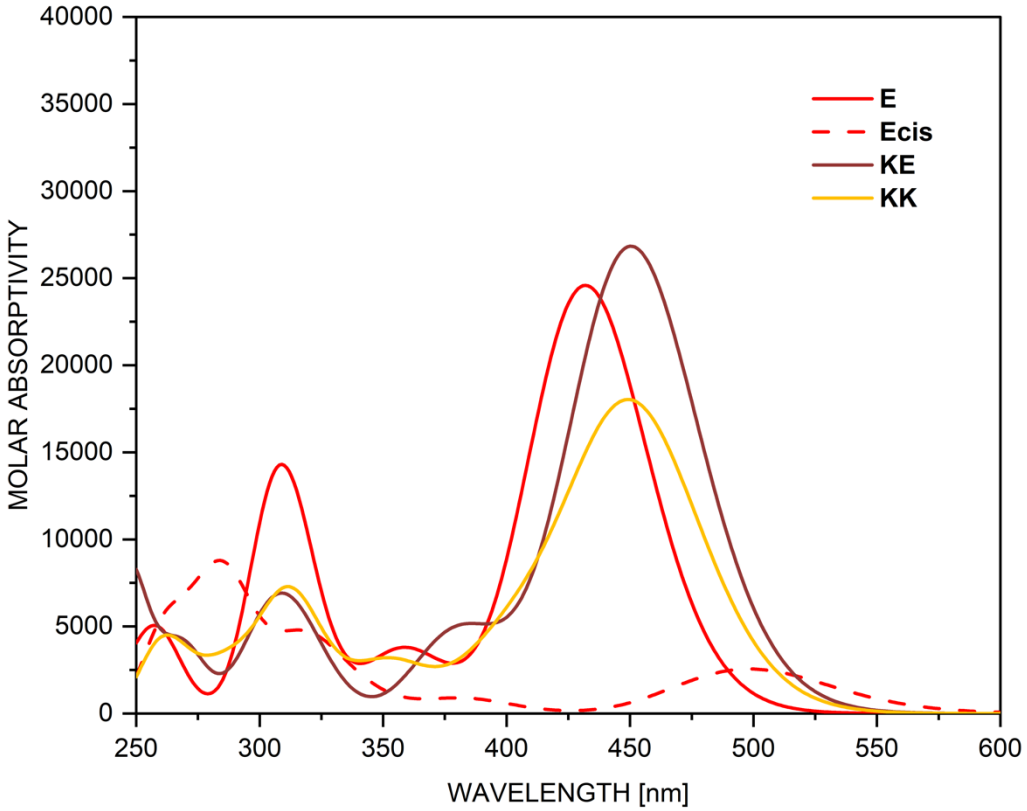


Figure S3. Simulated absorption spectra of the tautomers of **3** in toluene.

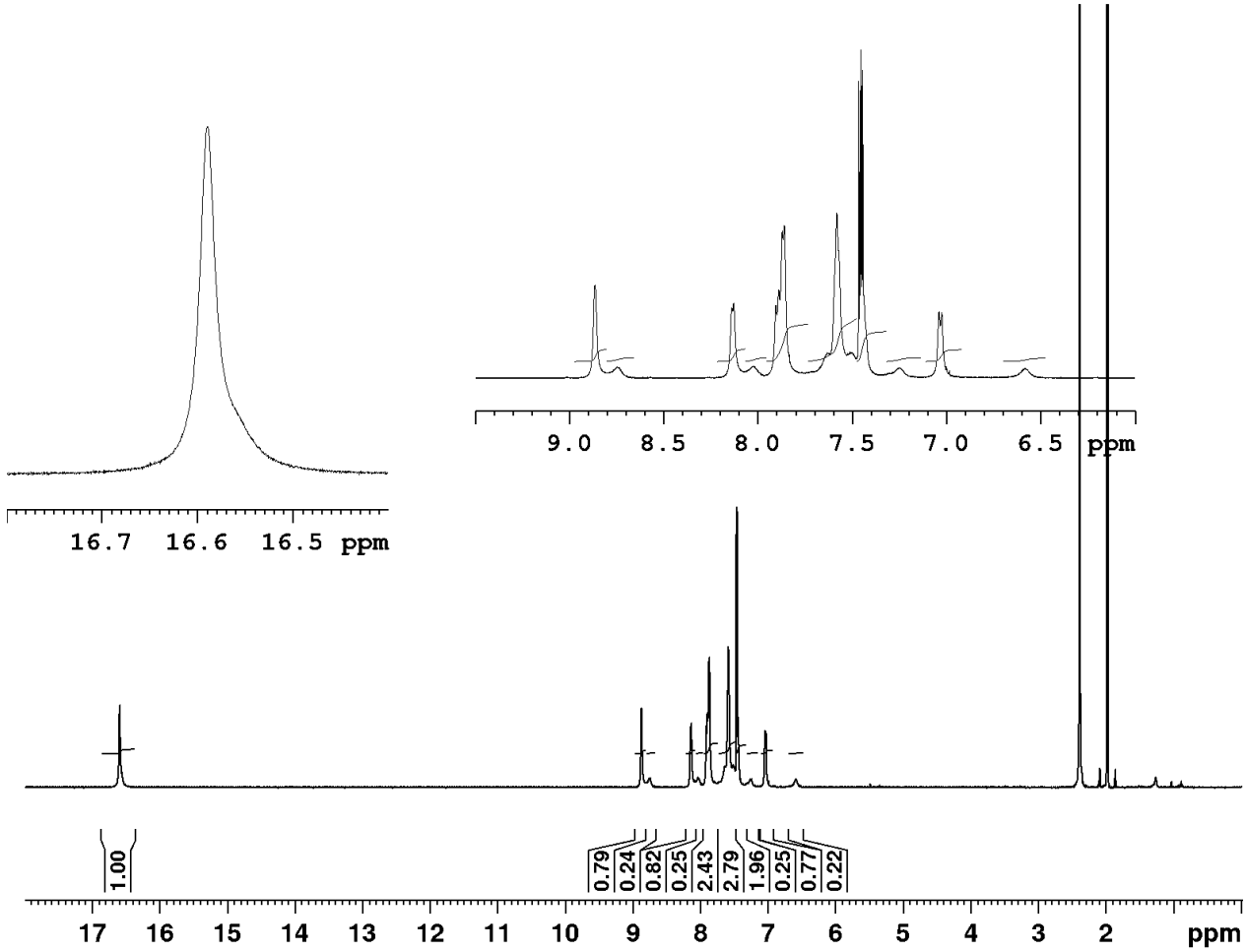
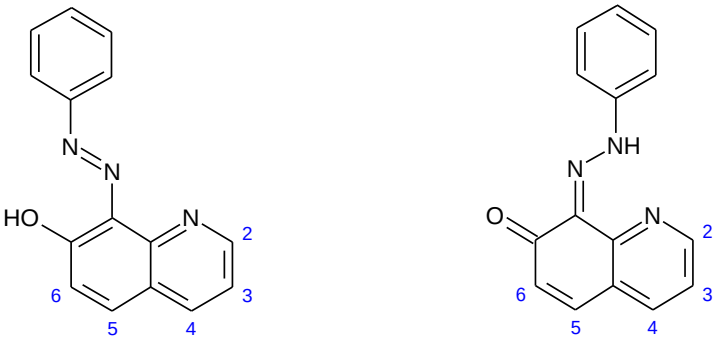


Figure S4. ^{1}H NMR spectrum of **1** in acetonitrile-d_3 at 243 K.

^{1}H NMR (CD_3CN, 243 K): Signals of major tautomeric form: δ = 7.03 (bd, *J*=8.8 Hz, 1H, H-6), 7.44 (s, 1H, p-Ph), 7.46 (dd, J=4.5, 7.9 Hz, 1H, H-3), 7.58 (bs, 2H, m-Ph), 7.87 (bd, J=6.9 Hz, 2H, o-Ph), 7.90 (bd, J=9.5 Hz, 1H, H-5), 8.14 (d, J=6.7 Hz, 1H, H-4), 8.87 (s, 1H, H-2), 16.59 (bs, 1H, OH); Resolved signals of minor tautomeric form: 6.58 (bs, 1H, H-6), 7.25 (bs, 1H, p-Ph), 7.50 (bs, 1H, m-Ph), 7.63 (bs, 1H, o-Ph), 8.02 (bs, 1H, H-4), 8.75 (bs, 1H, H-2).



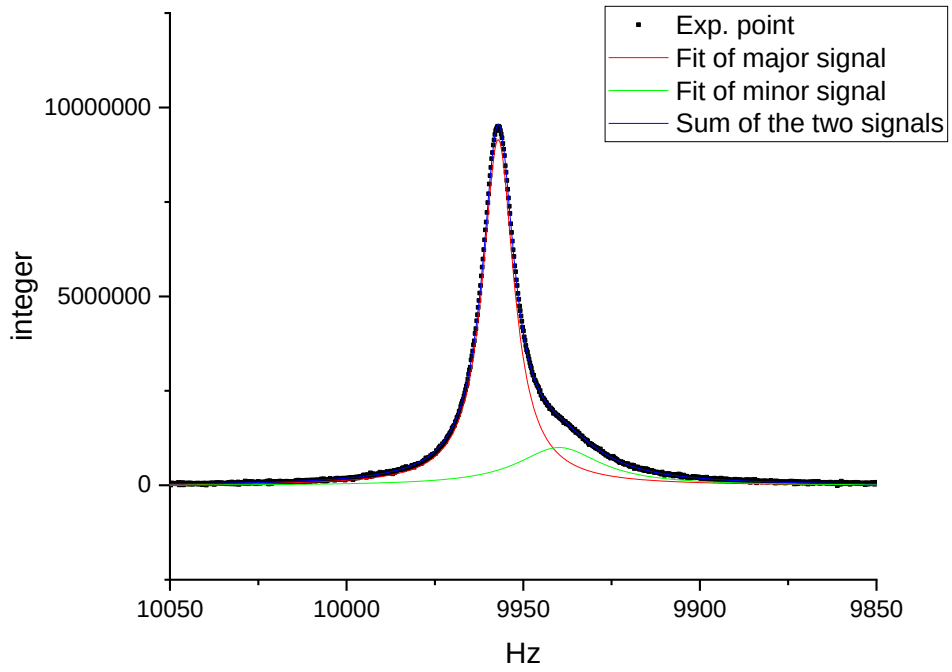


Figure S5. Deconvolution of two overlapped signals at 16.59 ppm in ^{1}H NMR spectrum of **1** in acetonitrile-d_3 at 243 K. The integrals of fitted signals are in relation: 78:22.

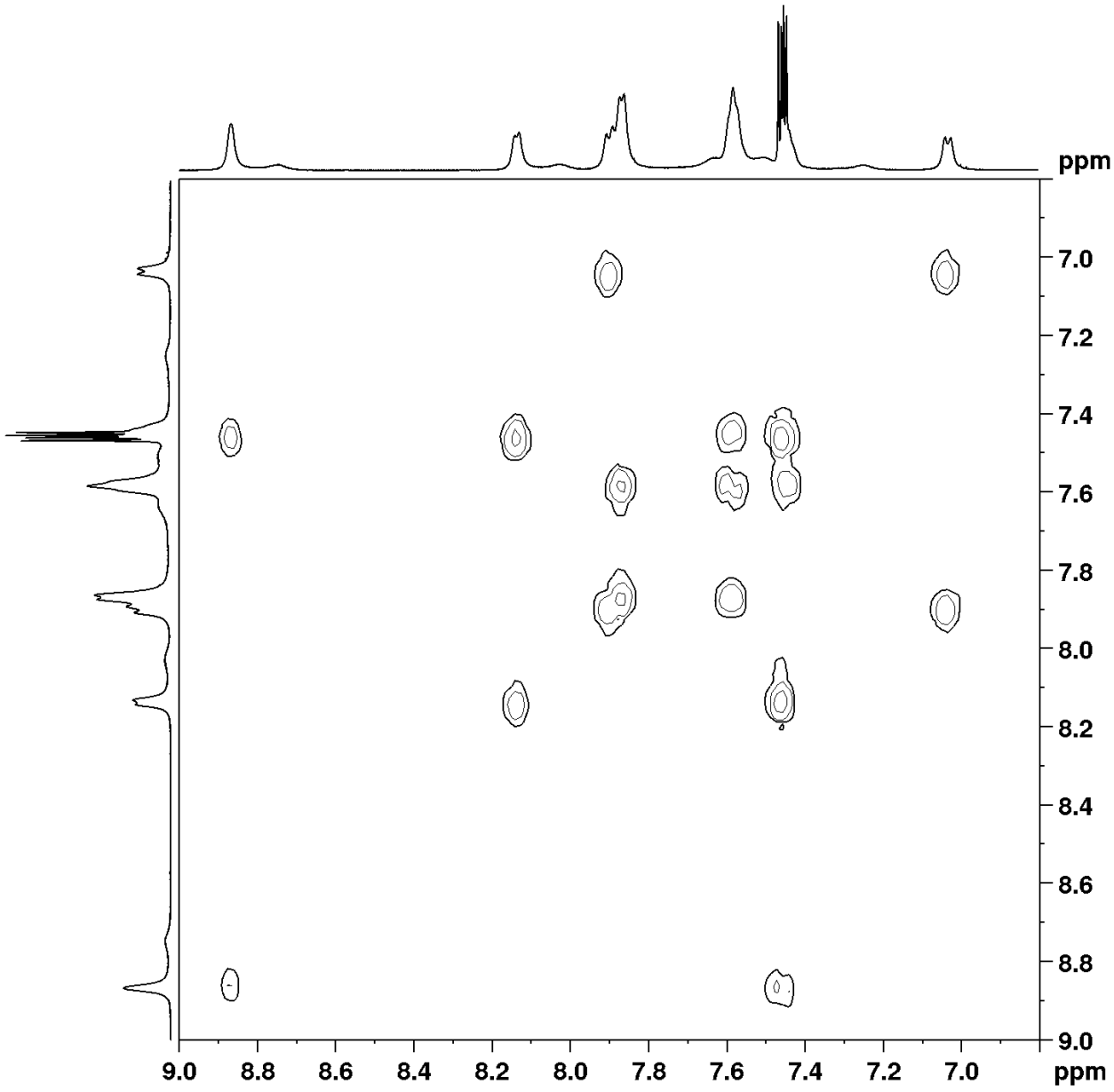


Figure S6. COSY spectrum of **1** in acetonitrile-d_3 at temperature 243 K.

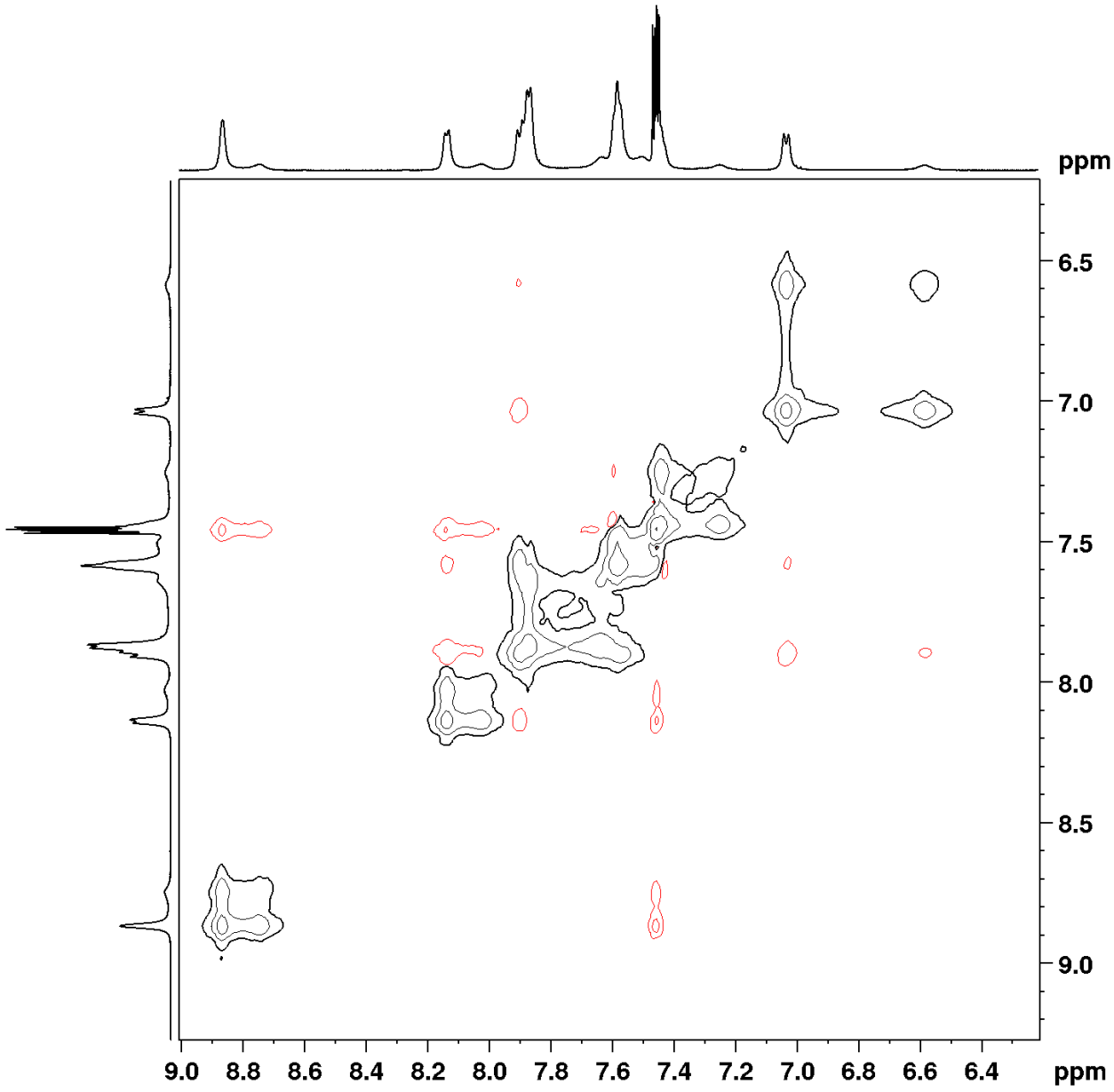


Figure S7. NOESY spectrum of **1** in acetonitrile-d_3 at temperature 243 K.

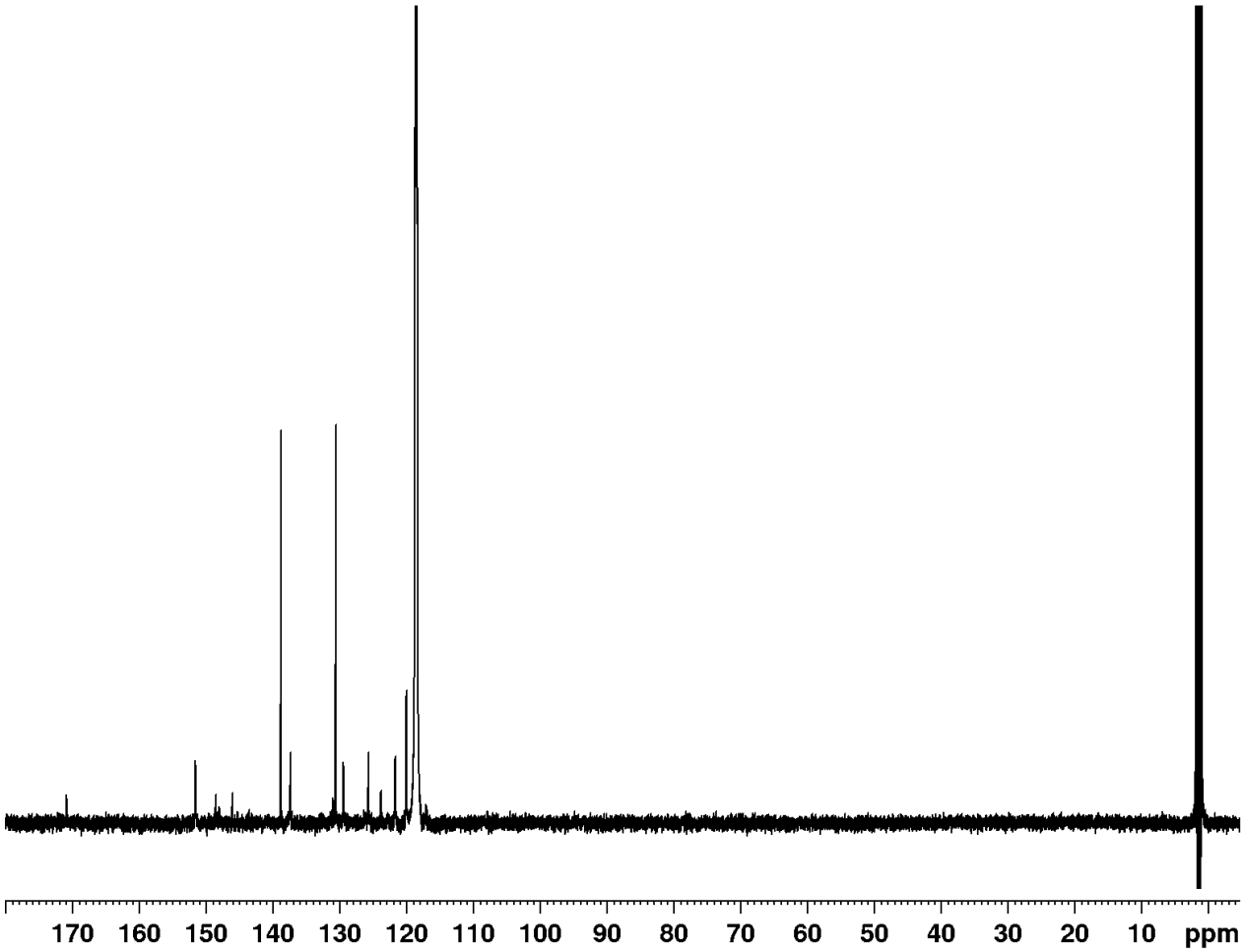


Figure S8. ^{13}C NMR spectrum of **1** in acetonitrile-d_3 at temperature 243 K.

^{13}C NMR (CD_3CN, 243 K): Signals of major component: δ = 120.03 (o-Ph), 121.69 (C-3), 125.71 (C-6), 129.46 (p-Ph), 130.61 (m-Ph), 137.37 (C-4), 138.82 (C-5), 151.62 (C-2).

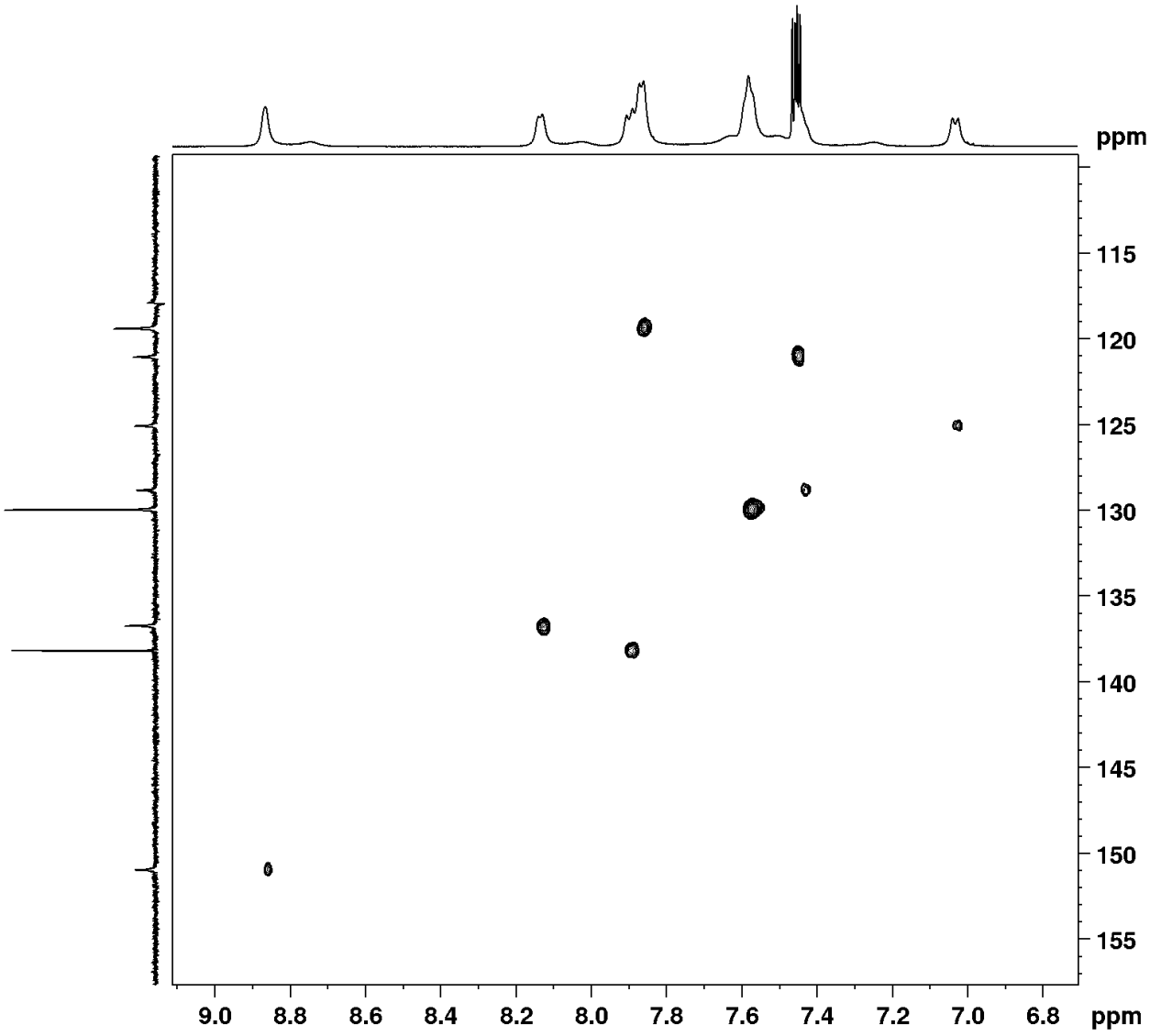


Figure S9. HSQC spectrum of **1** in acetonitrile-d_3 at temperature 243 K.

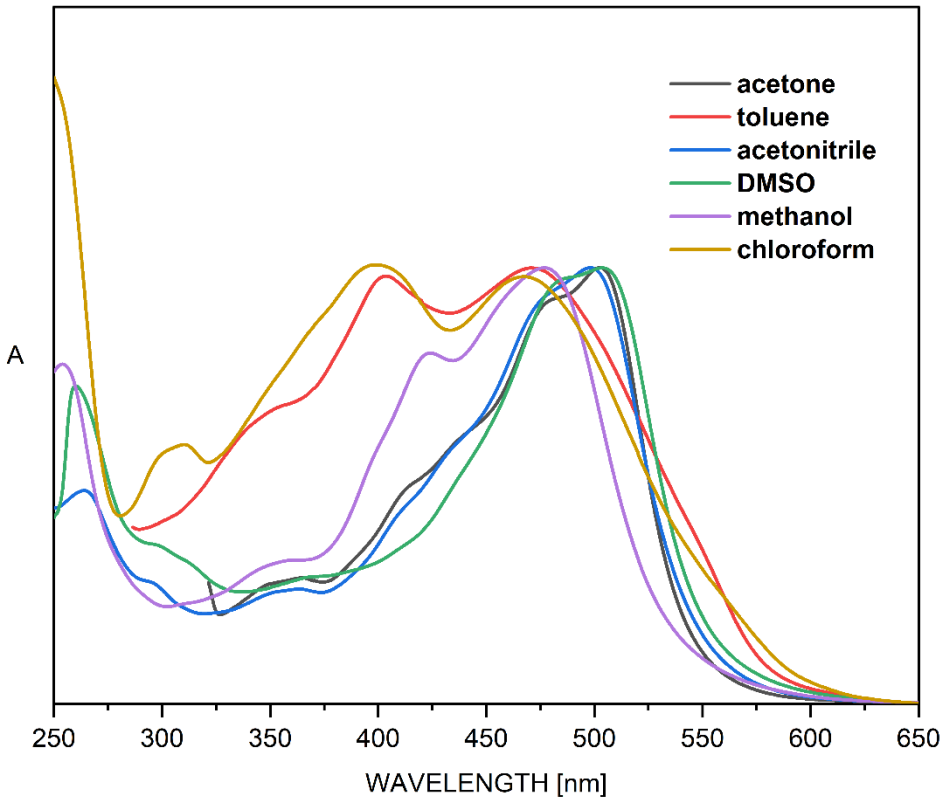


Figure S10. Normalized absorption spectra of **2**.

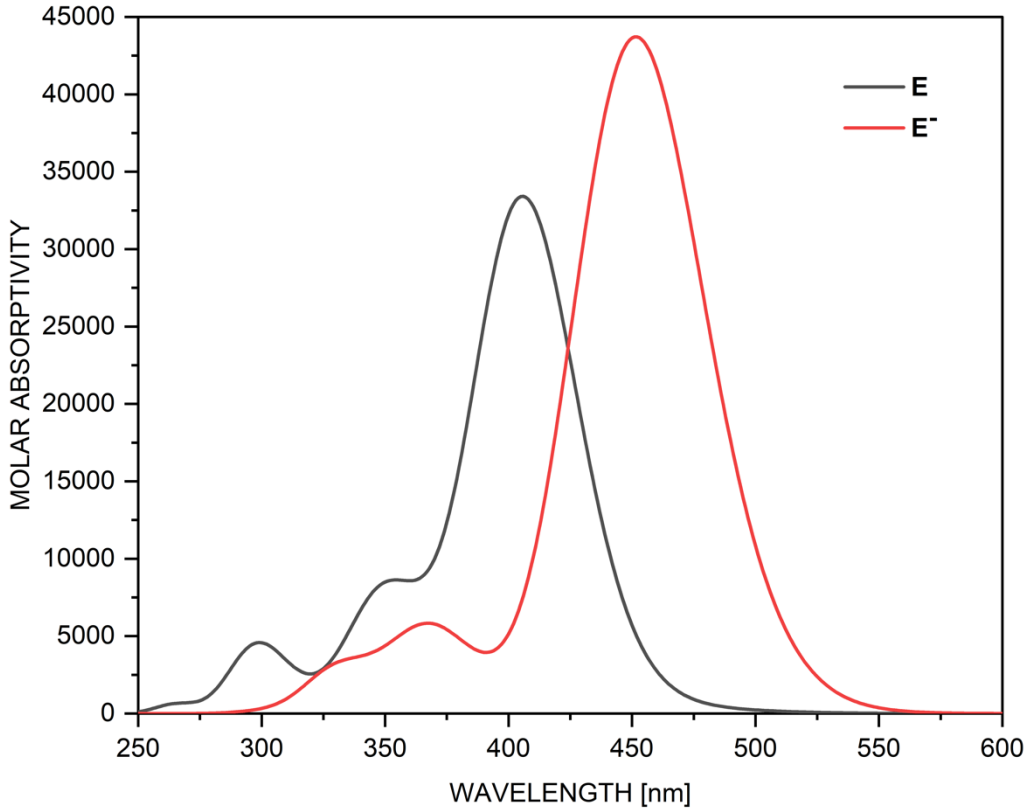


Figure S11. Comparison between the simulated spectra of **2E** and **2E**$^{-}$ in acetonitrile.

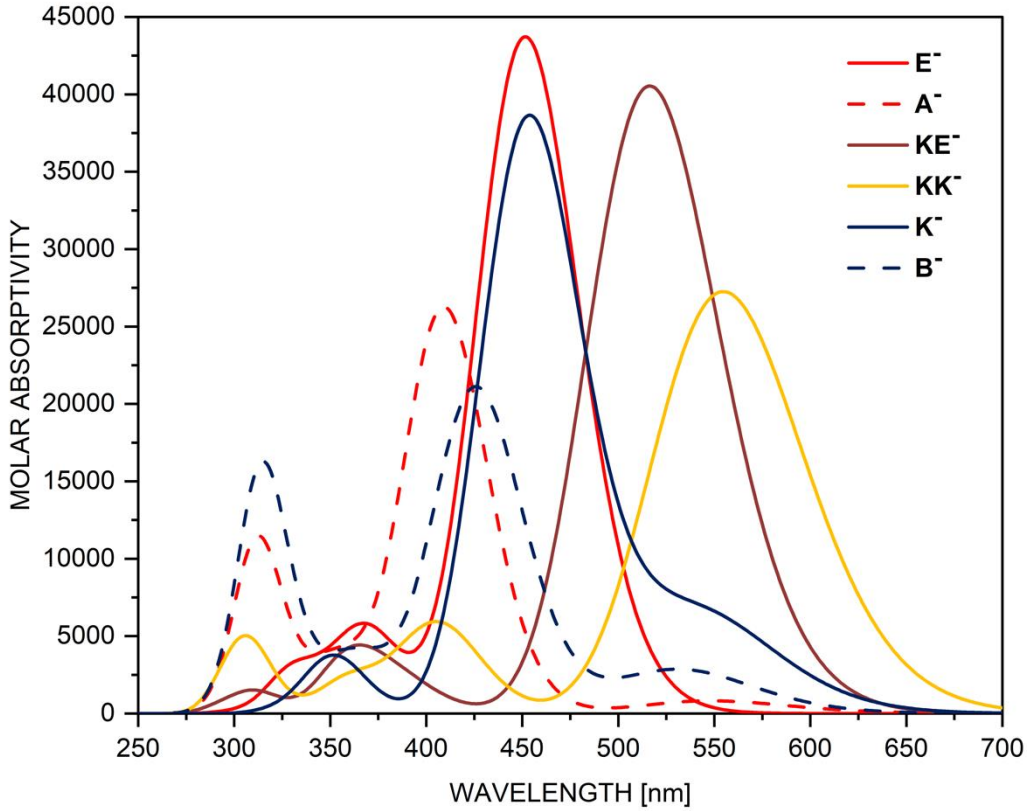


Figure S12. Simulated spectra of $\mathbf{2}^-$ in acetonitrile. The abbreviations are given in Table S2.

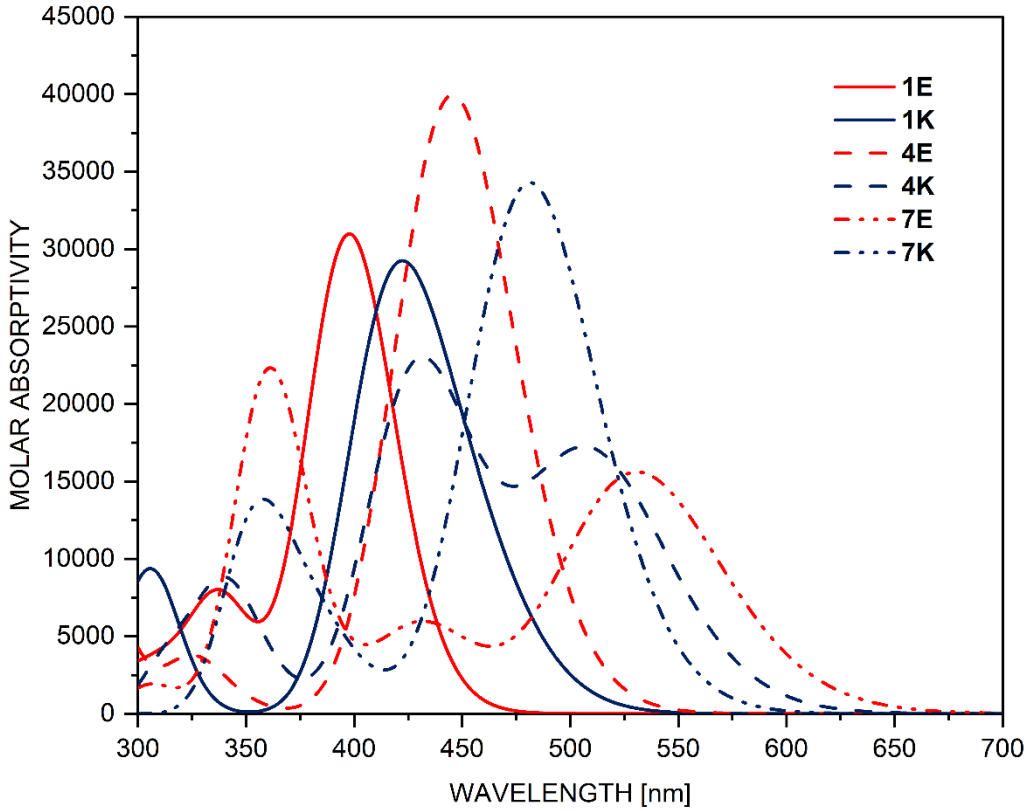


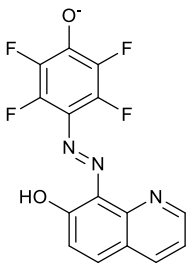
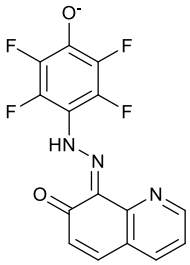
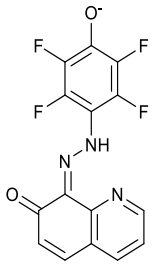
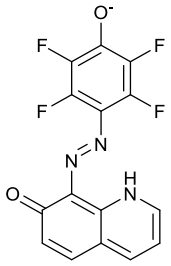
Figure S13. Simulated spectra of the end tautomeric forms of **1**, **4** and **7**$^{-}$ in toluene.

Table S1. Comparison of the relative energies (ΔE) of the tautomers and of the transition states (in kcal/mol units) of **1** in the ground state in toluene and in acetonitrile (in brackets), obtained by a variety of methods.

Structure	M06-2X/ TZVP	MP2/ TZVP*	MP3/ TZVP*	full MP4/ TZVP*	CCSD/ TZVP*	CCSD(T)/ TZVP*
E_{cis}	17 (16)	10 (9.2)	12 (11)	10 (9.1)	11 (10)	11 (9.7)
TS(E-E_{cis})	49 (49)	52 (52)	53 (53)	51 (51)	52 (52)	52 (51)
E	0.0 (0.28)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
TS(E-KE)	3.9 (3.9)	3.8 (3.6)	7.5 (7.3)	3.4 (3.3)	6.4 (6.2)	4.8 (4.6)
KE	0.11 (0.0)	2.15 (1.8)	2.8 (2.4)	0.37 (0.07)	1.4 (1.2)	1.3 (1.0)
TS(KE-KK)	41 (35)	41 (36)	41 (35)	38 (33)	39 (33)	39 (33)
KK	1.3 (0.16)	3.1 (1.8)	3.2 (2.0)	1.3 (0.11)	1.9 (0.70)	2.2 (0.95)
TS(K-KK)	9.8 (7.1)	11 (7.8)	14 (11)	9.6 (7.0)	13 (10)	11 (8.6)
K	7.5 (3.8)	9.5 (5.9)	9.9 (6.1)	7.6 (4.2)	8.7 (5.0)	8.3 (4.9)
TS(K-K_{cis})	54 (-)	59 (-)	61 (-)	56 (-)	59 (-)	57 (-)
K_{cis}	27 (22)	23 (18)	25 (20)	20 (16)	23 (18)	22 (17)

* single point calculations using M06-2X/TZVP geometries with TZVP basis set in the corresponding solvent environment.

Table S2. Relative stability (M06-2X/TZVP) and spectral characteristics of the ground-state tautomers and isomers of the deprotonated **2** in acetonitrile.

Structure	ΔE [kcal/mol]	ΔG^0 [kcal/mol]
E$^-$ 	0.0	0.0
KE$^-$ 	4.7	4.2
KK$^-$ 	5.5	5.8
K$^-$ 	5.4	4.9

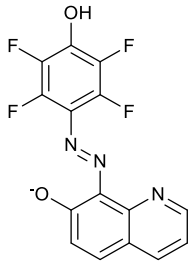
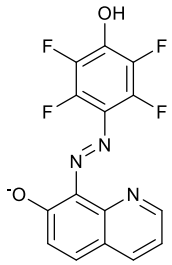
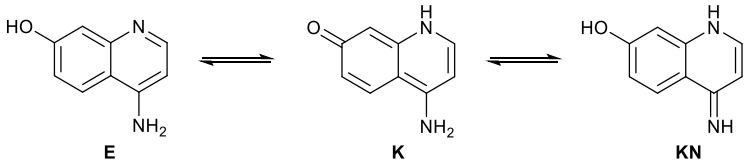
A^{-} 	15	14
B^{-} 	16	16

Table S3. Relative stabilization of **E** and **K** tautomers of **7OHQ** in toluene as a function of the substituents.

Subst.	ΔE [kcal/mol]		ΔG^0 [kcal/mol]	
	E	**K**	**E**	**K**
H	0.0	11	0.0	12
2-CN	0.0	16	0.0	17
3-CN	0.0	12	0.0	13
4-CN	0.0	13	0.0	13
5-CN	0.0	11	0.0	11
6-CN	0.0	9.3	0.0	9.5
8-CN	0.0	6.8	0.0	6.8
2-NH_2 *	0.0	15 (9.4)	0.0	15 (9.6)
3-NH_2	0.0	15	0.0	16
4-NH_2 *	0.0	8.5 (10)	0.0	7.6 (10)
5-NH_2 *	0.0	11 (25)	0.0	12 (25)
6-NH_2	0.0	5.9	0.0	6.4
8-NH_2	0.0	11	0.0	11
2-NMe_2	0.0	13	0.0	13
3-NMe_2	0.0	14	0.0	14
4-NMe_2	0.0	9.9	0.0	10
5-NMe_2	0.0	11	0.0	11
6-NMe_2	0.0	7.8	0.0	8.4
8-NMe_2	0.0	11	0.0	10
2-F	0.0	19	0.0	20
3-F	0.0	15	0.0	16
4-F	0.0	12	0.0	12
5-F	0.0	11	0.0	11
6-F	0.0	8.8	0.0	10
8-F	0.0	11	0.0	13
2-Cl	0.0	17	0.0	18
3-Cl	0.0	14	0.0	15
4-Cl	0.0	12	0.0	12
5-Cl	0.0	11	0.0	9.9
6-Cl	0.0	8.9	0.0	9.3
8-Cl	0.0	9.5	0.0	9.7
2-CF_3	0.0	17	0.0	17
3-CF_3	0.0	12	0.0	13
4-CF_3	0.0	14	0.0	14
5-CF_3	0.0	11	0.0	11

6-CF_3	0.0	9.4	0.0	9.8
8-CF_3	0.0	8.2	0.0	7.7
2-CH_3	0.0	11	0.0	11
3-CH_3	0.0	12	0.0	12
4-CH_3	0.0	11	0.0	11
5-CH_3	0.0	11	0.0	12
6-CH_3	0.0	10	0.0	9.8
8-CH_3	0.0	11	0.0	11

* NH_2 group on positions 2, 4 and 5 opens possibility for additional tautomer, **KN** (see the scheme below in the case of 4-substituted compound as an example). The relative energies are given in brackets below the values for **K** in the table.

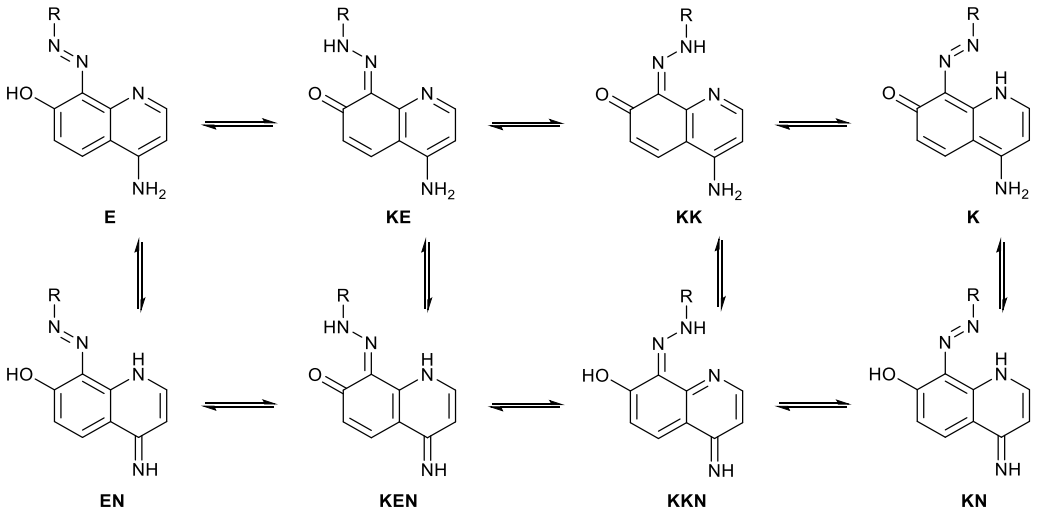


E **K** **KN**

Table S4. Relative stabilization of the tautomers of **1** in toluene as a function of the substituents in 7-hydroxyquinoline part.

Subst.	ΔE [kcal/mol]				ΔG^0 [kcal/mol]			
	E	**KE**	**KK**	**K**	**E**	**KE**	**KK**	**K**
H	0.0	0.11	1.3	7.6	0.0	1.7	2.4	8.4
2-CN	0.0	0.04	2.2	13	0.43	0.0	3.3	14
3-CN	0.0	0.19	2.6	10	0.0	0.81	3.0	11
4-CN	0.0	0.36	2.7	10	0.0	1.8	3.8	11
5-CN	0.0	0.89	2.0	7.7	0.0	1.8	3.4	7.9
6-CN	0.85	0.0	1.4	7.2	0.0	0.0	1.2	6.8
2-NH_2 *	0.0 (6.0)	0.68 (9.8)	3.0 (23)	11 (7.8)	0.0 (6.4)	0.59 (10)	3.5 (23)	10 (8.4)
3-NH_2	0.0	0.04	0.72	9.4	0.0	0.24	1.4	9.8
4-NH_2 *	0.0 (5.3)	0.44 (8.8)	0.99 (20)	4.7 (6.8)	0.0 (5.6)	1.1 (9.7)	1.1 (20)	3.2 (7.1)
5-NH_2 *	1.5 (17)	0.0 (21)	2.3 (5.3)	10 (15)	0.99 (17)	0.0 (22)	2.2 (5.3)	10 (15)
6-NH_2	2.4	0.67	0.0	4.4	1.9	0.45	0.0	4.2
2-NMe_2	0.0	0.51	1.7	8.1	0.0	1.4	2.9	9.2
3-NMe_2	0.14	0.0	0.42	8.9	0.0	0.69	0.53	9.0
4-NMe_2	0.0	0.40	1.3	5.8	0.0	0.65	1.2	6.0
5-NMe_2	1.4	0.0	1.7	9.1	0.66	0.0	1.9	8.2
6-NMe_2	1.7	0.17	0.0	5.4	0.49	0.0	0.02	5.1
2-F	0.0	0.67	3.3	16	0.0	0.17	3.4	15
3-F	0.0	0.24	1.9	11	0.79	0.0	2.5	12
4-F	0.0	0.30	2.0	8.5	0.0	0.96	2.2	8.7
5-F	0.85	0.0	1.5	8.5	0.70	0.0	0.50	8.6
6-F	0.82	0.0	0.40	5.9	0.51	0.06	0.0	6.4
2-CH_3	0.0	0.24	1.3	6.7	0.0	0.81	2.4	6.9
3-CH_3	0.0	0.24	1.2	7.6	0.0	0.83	2.5	9.0
4-CH_3	0.0	0.43	1.6	7.4	0.0	1.4	2.1	6.9
5-CH_3	0.35	0.0	1.3	7.8	0.0	0.05	1.5	7.9
6-CH_3	0.45	0.0	0.84	6.8	0.0	0.40	1.5	6.9

* NH_2 group on positions 2, 4 and 5 opens possibility for additional tautomers **EN**, **KEN**, **KKN** and **KN** (see the scheme below in the case of 4-substituted compound as an example). The relative energies are given in brackets below the values of the corresponding major tautomers in the table.


E
KE
KK
K
EN
KEN
KKN
KN