Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Unravelling the solvent polarity effect on the excited state intramolecular proton *trans*fer mechanism of the 1- and 2-salicylideneanthrylamine. A TD-DFT case study.

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Electronic Supplementary Material

List of contents:

Fig. S13 Optimized structures of the *trans*-enol (**(1')S_1**, **(4')S_1**), twisted-enol (**(1')$S_{1\text{-Tw}}$**, **(4')$S_{1\text{-Tw}}$**), *cis*-keto (**(2')S_1**, **(5')S_1**), twisted-keto (**(2')$S_{1\text{-Tw}}$**, **(5')$S_{1\text{-Tw}}$)** and *trans*-keto (**(3')S_1**, **(6')S_1**) forms of 2-AntSA in the S_1 state in cyclohexane. The energies are relative to the more stable forms **(1')$S_{1\text{-Tw}}$** and **(4')$S_{1\text{-Tw}}$**, respectively.

Table S1. Selected parameters of the optimized *trans*-enol (**(1)S_1**, **(1')S_1**), *cis*-keto (**(2)S_1**, **(2')S_1**) and *trans*-keto (**(2)$S_{1\text{-Tw}}$**, **(2')$S_{1\text{-Tw}}$**) forms in the S_0 and S_1 states.

Table S2 Excitation energies (eV), oscillator strengths *f* and largest excitation coefficients for the *trans*-enol, *cis-keto* and *trans*-keto forms of 1-AntSA and 2-AntSA in **A** methanol and **B** cyclohexane computed at the PCM/TD/CAM-B3LYP/6-311+G(d,p) level of theory.

Table S3. TD-DFT first excited states relative energies (RE, kcal/mol), intramolecular hydrogen bond (IMHB, Å) and torsional angles (ϕ_i, degrees) of the *trans*-enol (**(1)S_1**, **(1')S_1**), twisted-enol (**(1)$S_{1\text{-Tw}}$**, **(1')$S_{1\text{-Tw}}$**), *cis*-keto (**(2)S_1**, **(2')S_1**), twisted-keto (**(2)$S_{1\text{-Tw}}$**, **(2')$S_{1\text{-Tw}}$**) and *trans*-keto (**(3)S_1**, **(3')S_1**) forms.

Fig. S1 Ground state optimized structures of the rotamers and tautomers of 1-AntSA in acetonitrile calculated at the PCM/B3LYP/6-311+G(d,p) level of theory. Ground state relative energies are referred to **1**.

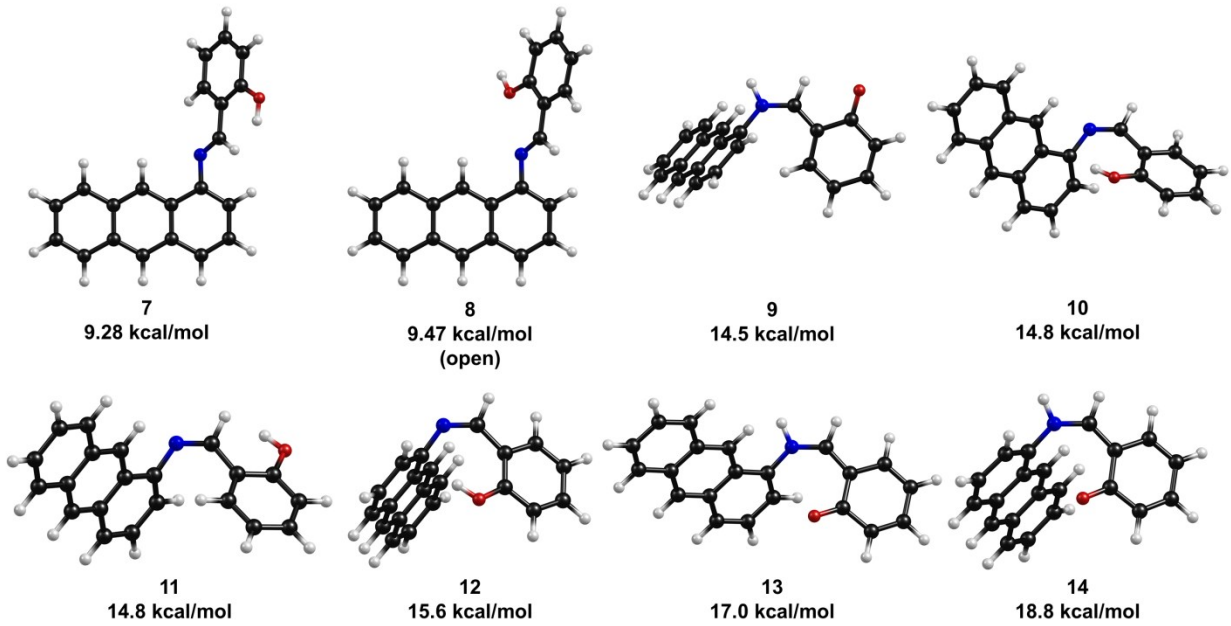


Fig. S2 Ground state optimized structures of the rotamers and tautomers of 1-AntSA in acetonitrile calculated at the PCM/B3LYP/6-311+G(d,p) level of theory. Ground state relative energies are referred to **1'**.

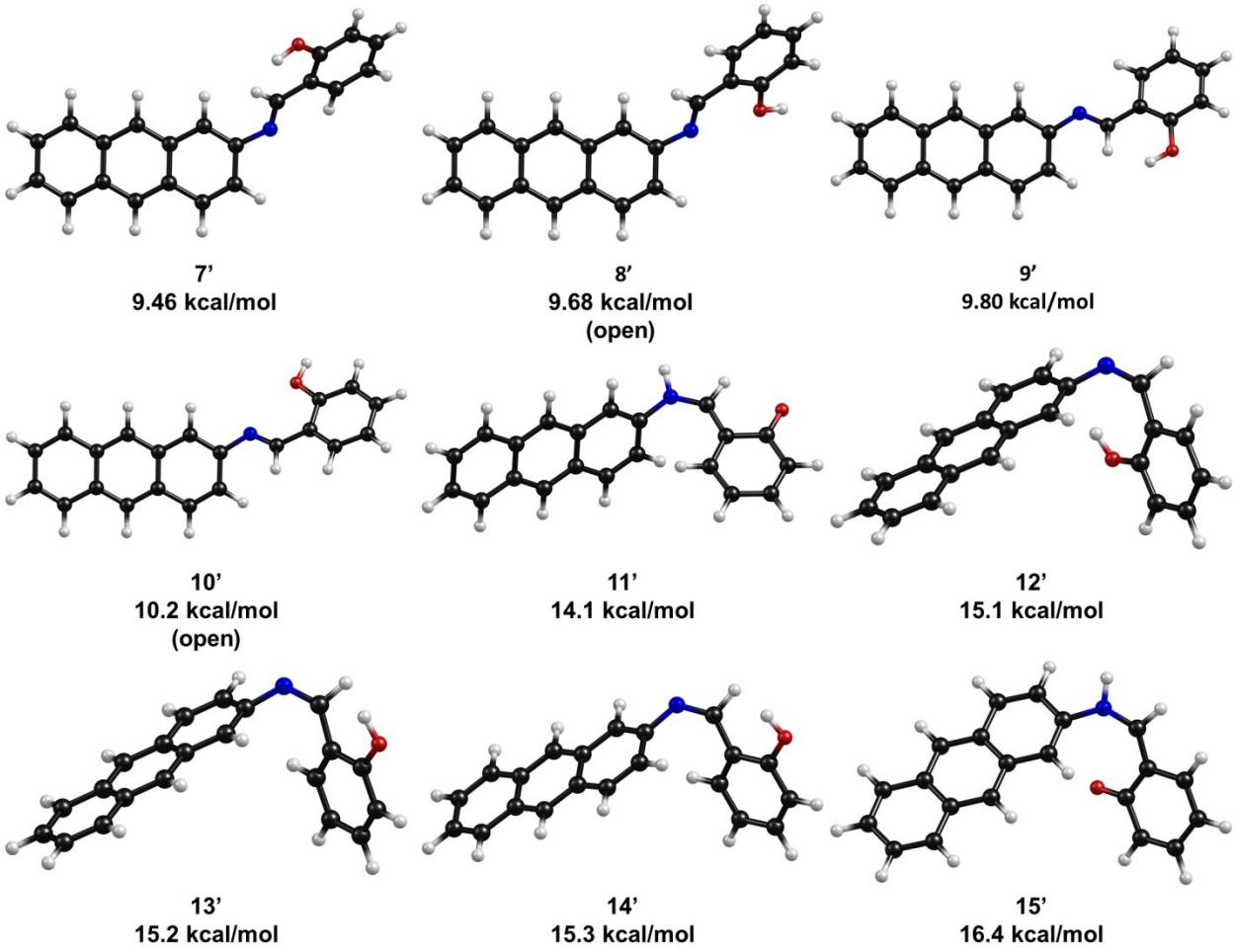


Fig. S3 Ground state optimized structures of the different rotamers and tautomers of 1-AntSA in methanol calculated at the PCM/B3LYP/6-311+G(d,p) level of theory. Ground state relative energies are referred to **1**. Intramolecular hydrogen bond distance in Å and torsional angles in degrees (ϕ_1, ϕ_2, ϕ_3).

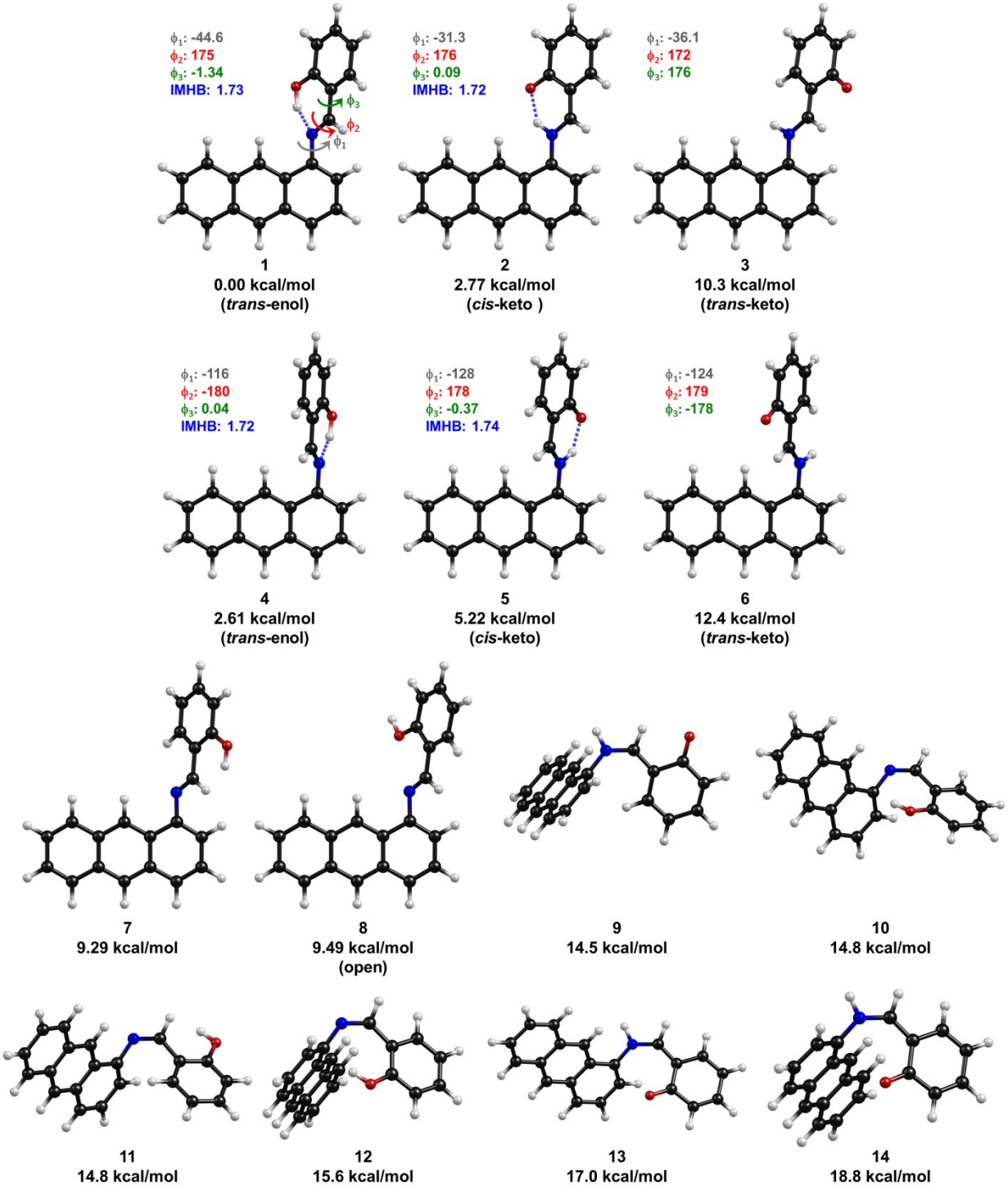


Fig. S4 Ground state optimized structures of the different rotamers and tautomers of 2-AntSA in methanol calculated at the PCM/B3LYP/6-311+G(d,p) level of theory. Ground state relative energies are referred to **1'**. Intramolecular hydrogen bond distance in Å and torsional angles in degrees (ϕ_1, ϕ_2, ϕ_3).

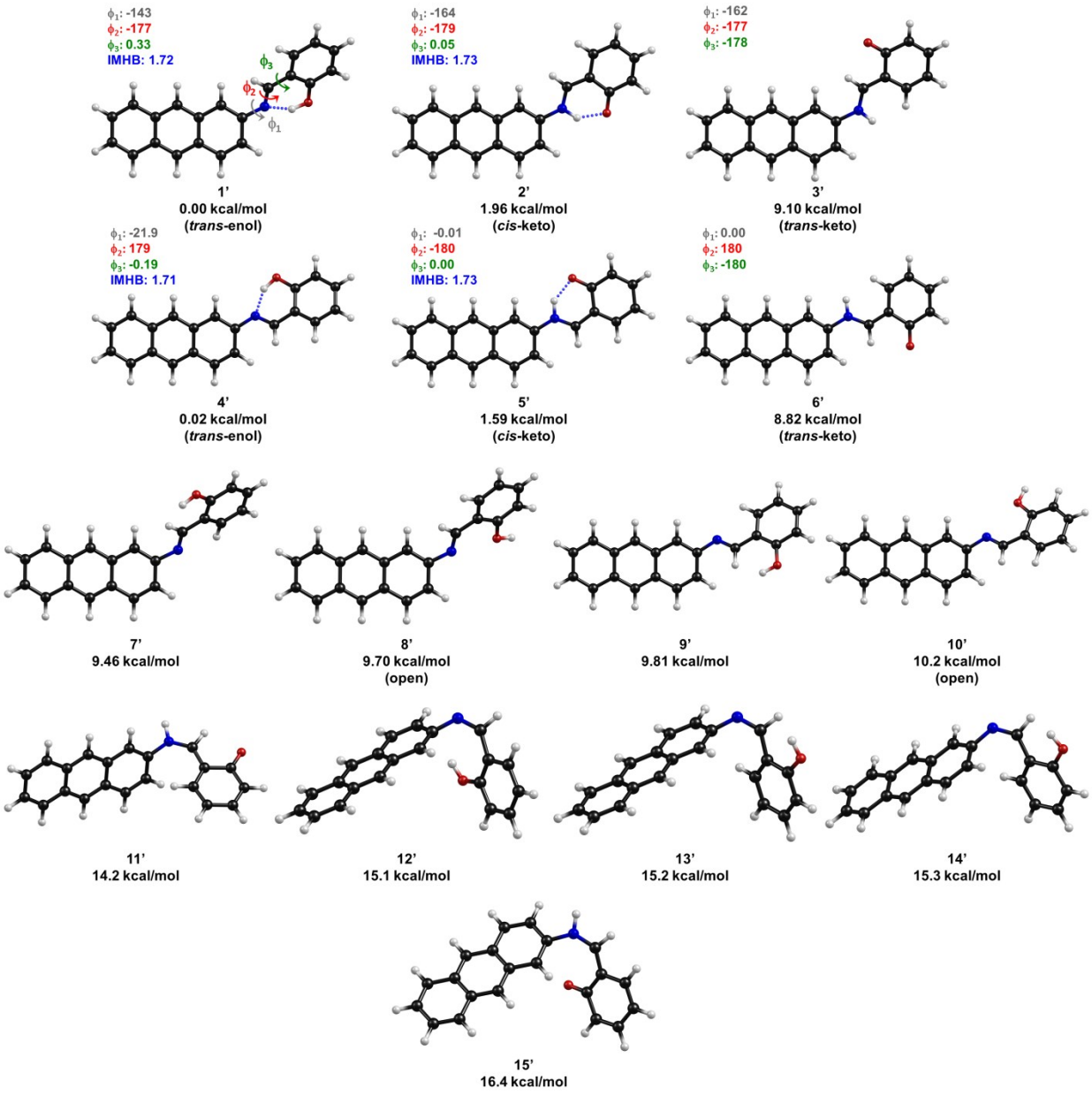


Fig. S5 Ground state optimized structures of the different rotamers and tautomers of 1-AntSA in cyclohexane calculated at the PCM/B3LYP/6-311+G(d,p) level of theory. Ground state relative energies are referred to **1**. Intramolecular hydrogen bond distance in Å and torsional angles in degrees (ϕ_1, ϕ_2, ϕ_3).

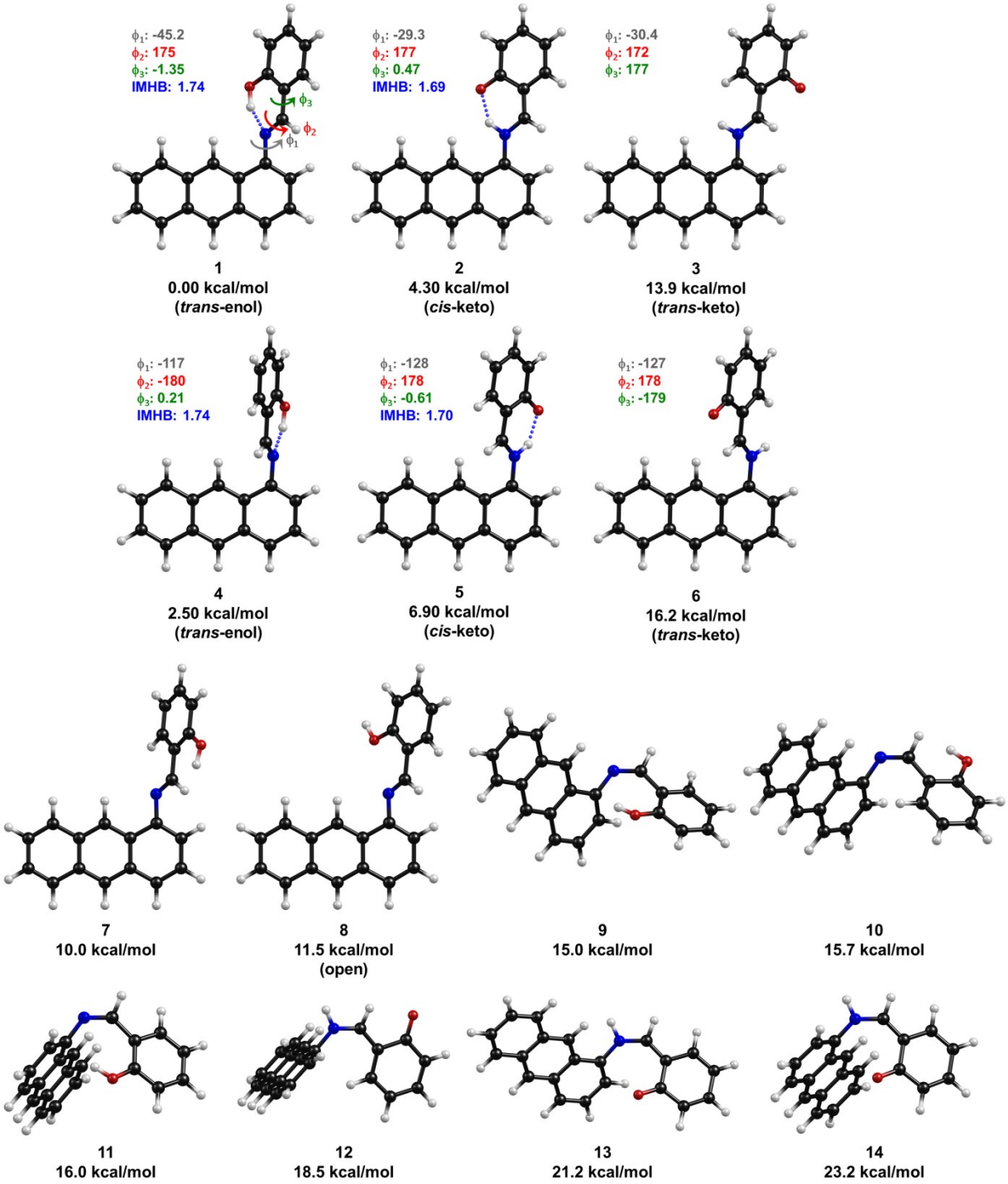


Fig. S6 Ground state optimized structures of the different rotamers and tautomers of 2-AntSA in cyclohexane calculated at the PCM/B3LYP/6-311+G(d,p) level of theory. Ground state relative energies are referred to **1'**. Intramolecular hydrogen bond distance in Å and torsional angles in degrees (ϕ_1, ϕ_2, ϕ_3).

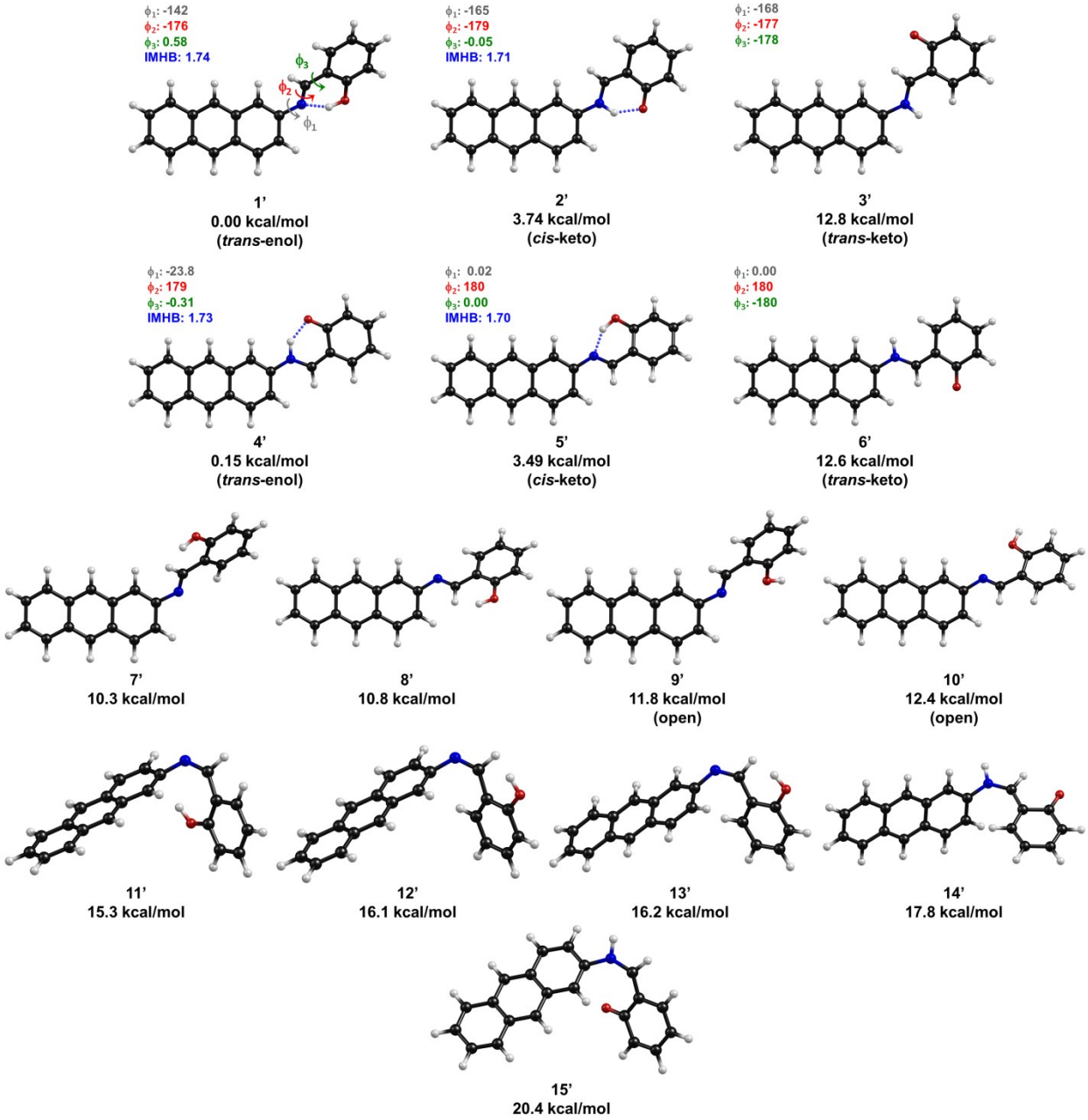


Fig. S7 Isosurfaces of the frontier Kohn-Sham orbitals of (B) *trans*-enol **4** and *cis*-keto **5**, and (C) *trans*-enol **1'** and *cis*-keto **2'** in acetonitrile calculated at the PCM/TD/CAM-B3LYP/6-311+G(d,p) level of theory.

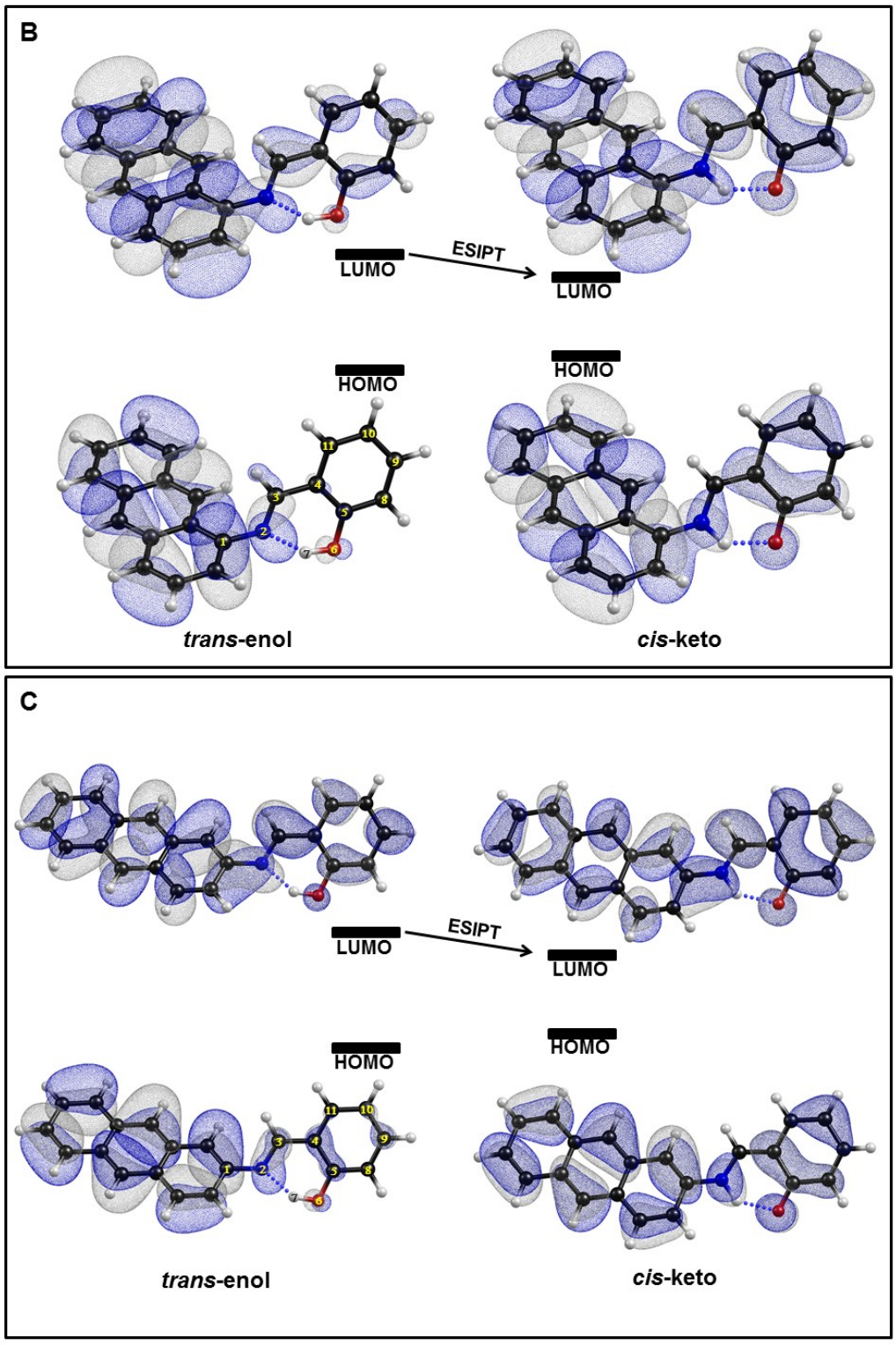


Fig. S8 Isosurfaces of the frontier Kohn-Sham orbitals of (A) *trans*-enol **1** and *cis*-keto **2**, (B) *trans*-enol **4** and *cis*-keto **5**, (C) *trans*-enol **1'** and *cis*-keto **2'** and (D) *trans*-enol **4'** and *cis*-keto **5'** in methanol calculated at the PCM/TD/CAM-B3LYP/6-311+G(d,p) level of theory.

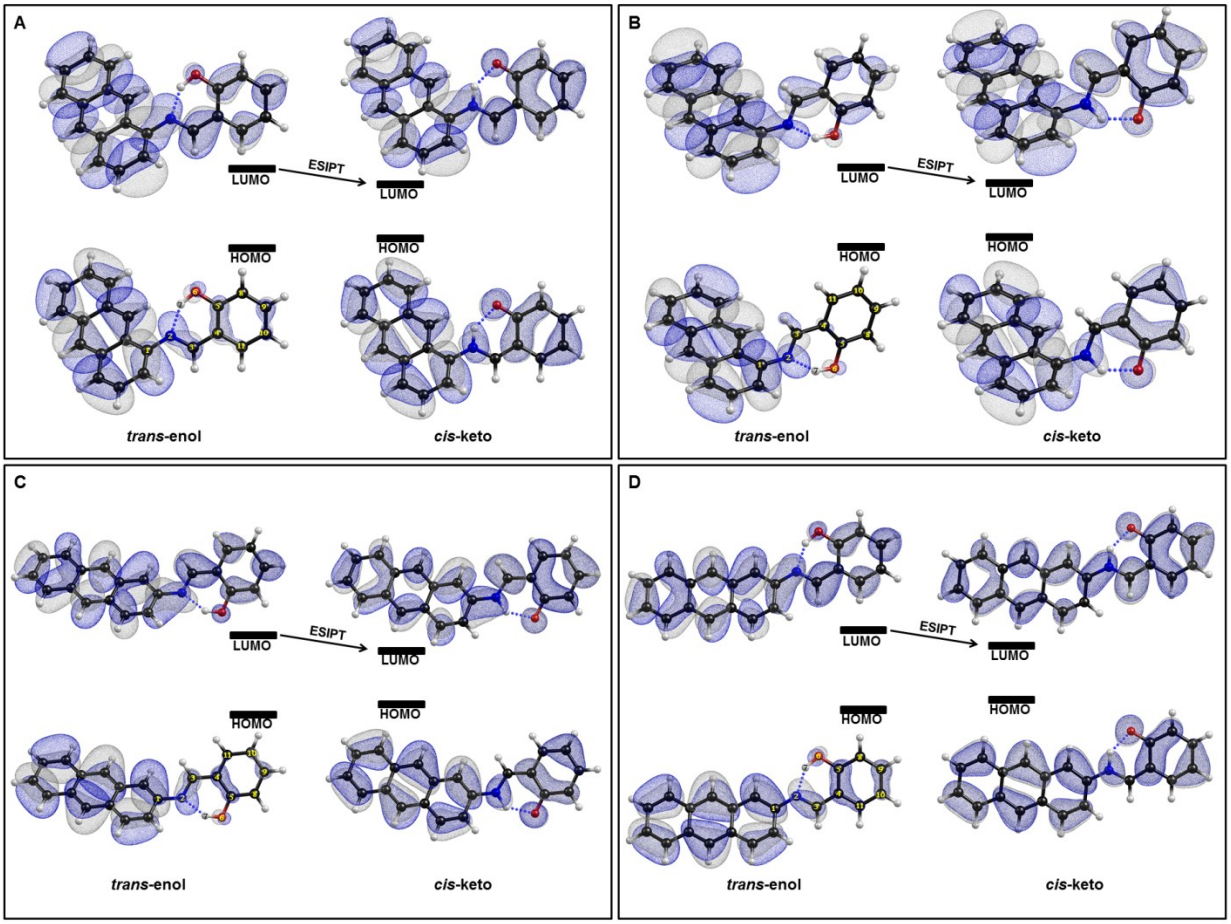


Fig. S9 Isosurfaces of the frontier Kohn-Sham orbitals of (A) *trans*-enol **1** and *cis*-keto **2**, (B) *trans*-enol **4** and *cis*-keto **5**, (C) *trans*-enol **1'** and *cis*-keto **2'** and (D) *trans*-enol **4'** and *cis*-keto **5'** in cyclohexane calculated at the PCM/TD/CAM-B3LYP/6-311+G(d,p) level of theory.

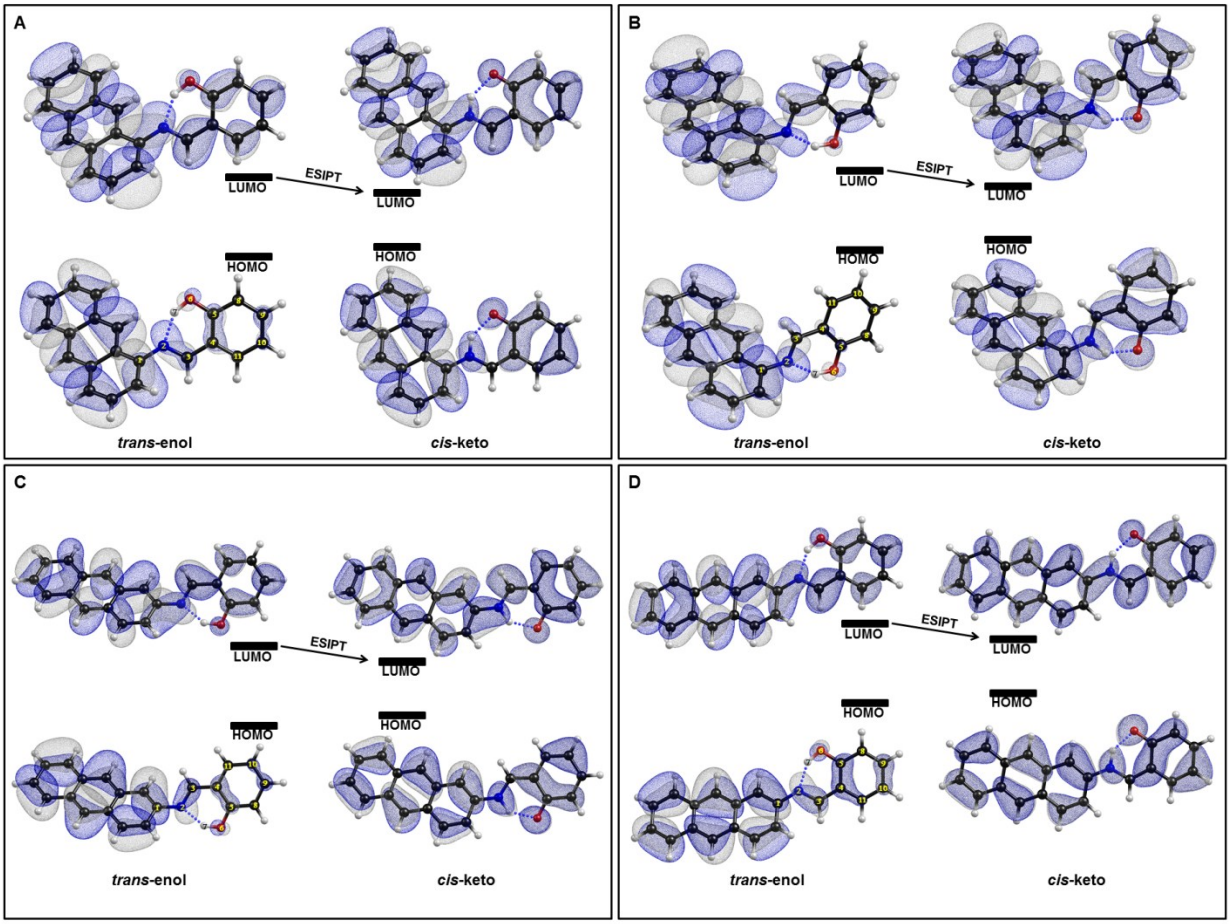


Fig. S10 Optimized structures of the *trans*-enol (**(1)S_1**, **(4)S_1**), twisted-enol (**(1)$S_{1\text{-Tw}}$**, **(4)$S_{1\text{-Tw}}$**), *cis*-keto (**(2)S_1**, **(5)S_1**), twisted-keto (**(2)$S_{1\text{-Tw}}$**, **(5)$S_{1\text{-Tw}}$**) and *trans*-keto (**(3)S_1**, **(6)S_1**) forms of 1-AntSA in the S_1 state in methanol. The energies are relative to the more stable forms **(1)$S_{1\text{-Tw}}$** and **(4)S_1**, respectively.

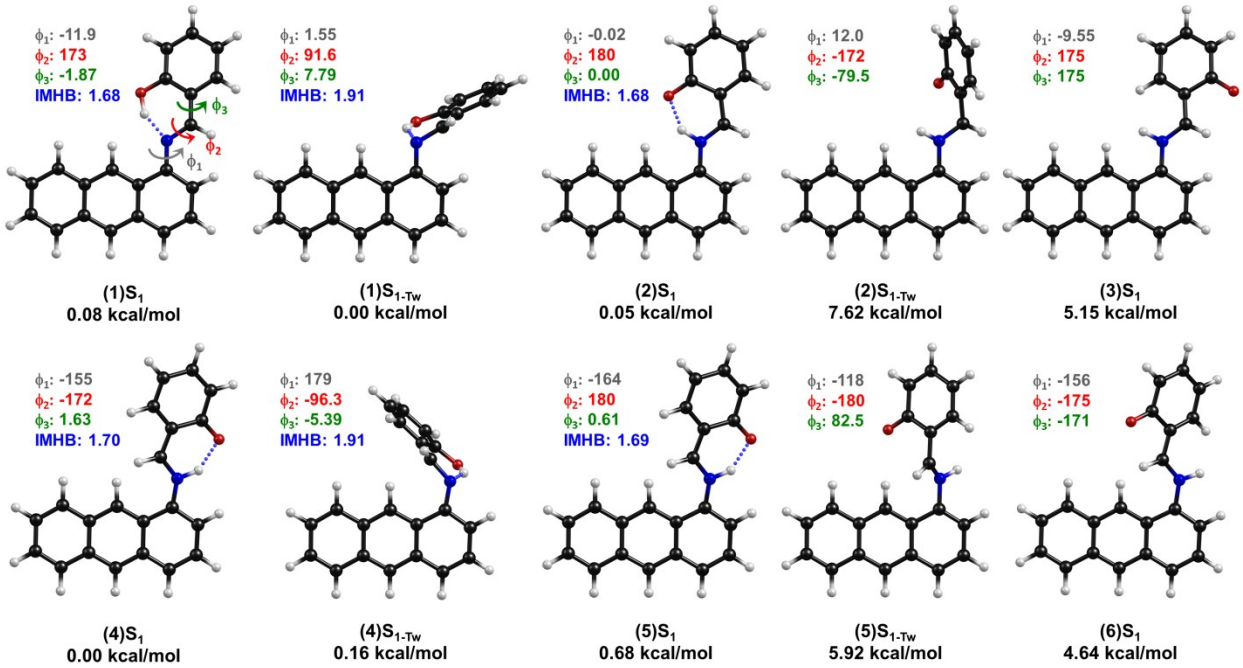


Fig. S11 Optimized structures of the *trans*-enol (**(1')S_1**, **(4')S_1**), twisted-enol (**(1')$S_{1\text{-Tw}}$**, **(4')$S_{1\text{-Tw}}$**), *cis*-keto (**(2')S_1**, **(5')S_1**), twisted-keto (**(2')$S_{1\text{-Tw}}$**, **(5')$S_{1\text{-Tw}}$)** and *trans*-keto (**(3')S_1**, **(6')S_1**) forms of 2-AntSA in the S_1 state in methanol. The energies are relative to the more stable forms **(2')S_1** and **(5')S_1**, respectively.

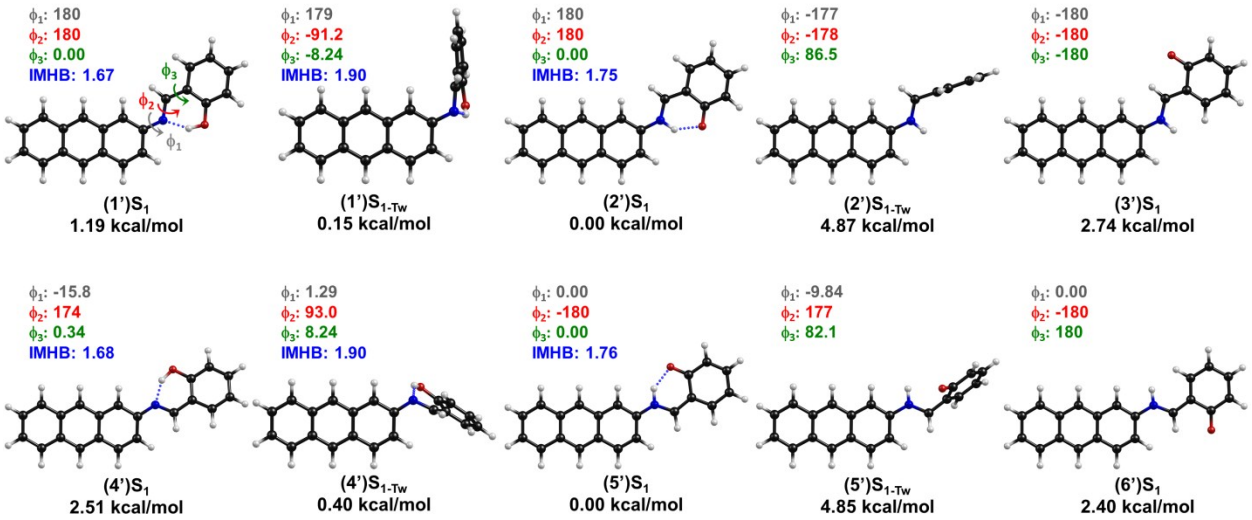


Fig. S12 Optimized structures of the *trans*-enol (**(1)S_1**, **(4)S_1**), twisted-enol (**(1)$S_{1\text{-Tw}}$**, **(4)$S_{1\text{-Tw}}$**), *cis*-keto (**(2)S_1**, **(5)S_1**), twisted-keto (**(2)$S_{1\text{-Tw}}$**, **(5)$S_{1\text{-Tw}}$**) and *trans*-keto (**(3)S_1**, **(6)S_1**) forms of 1-AntSA in the S_1 state in cyclohexane. The energies are relative to the more stable forms **(1)$S_{1\text{-Tw}}$** and **(4)$S_{1\text{-Tw}}$**, respectively.

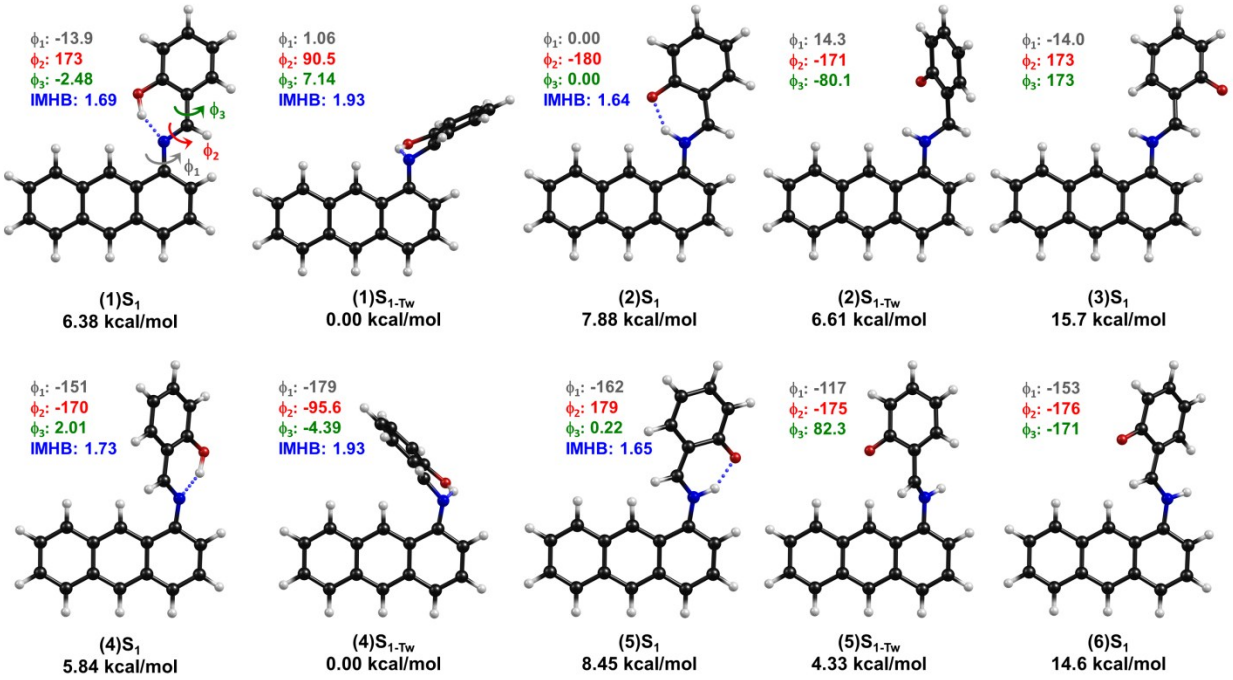


Fig. S13 Optimized structures of the *trans*-enol (**(1')S_1**, **(4')S_1**), twisted-enol (**(1')$S_{1\text{-Tw}}$**, **(4')$S_{1\text{-Tw}}$**), *cis*-keto (**(2')S_1**, **(5')S_1**), twisted-keto (**(2')$S_{1\text{-Tw}}$**, **(5')$S_{1\text{-Tw}}$**) and *trans*-keto (**(3')S_1**, **(6')S_1**) forms of 2-AntSA in the S_1 state in cyclohexane. The energies are relative to the more stable forms **(1')$S_{1\text{-Tw}}$** and **(4')$S_{1\text{-Tw}}$**, respectively.

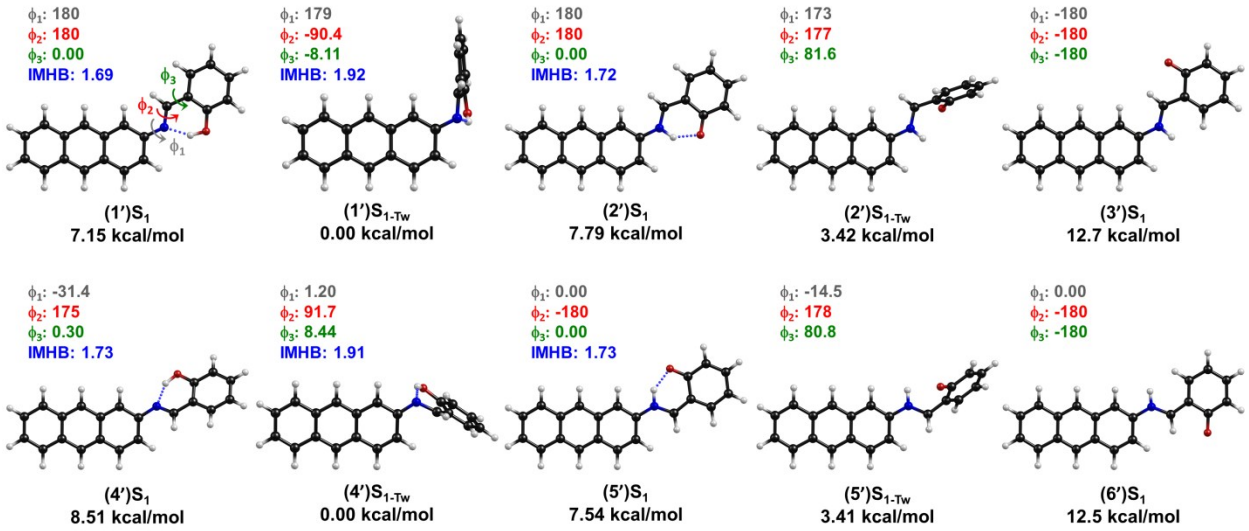
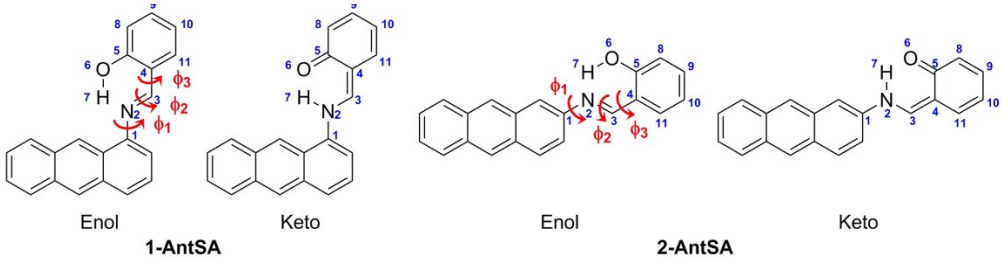


Table S1. Selected parameters of the optimized *trans*-enol (**(1)S_1**, **(1')S_1**), *cis*-keto (**(2)S_1**, **(2')S_1**) and *trans*-keto (**(2)$S_{1\text{-}Tw}$**, **(2')$S_{1\text{-}Tw}$**) forms in the S_0 and S_1 states.



1-AntSA												
Acetonitrile												
	trans-enol		*cis*-keto		*trans*-keto		*trans*-enol		*cis*-keto		*trans*-keto	
Structural parameters	**1**	**(1)S_1**	**2**	**(2)S_1**	**3**	**(3)S_1**	**4**	**(4)S_1**	**5**	**(5)S_1**	**6**	**(6)S_1**
C_1–N_2	1.406	1.343	1.412	1.348	1.418	1.370	1.415	1.345	1.424	1.355	1.4302	1.374
N_2–C_3	1.290	1.330	1.325	1.353	1.334	1.348	1.286	1.321	1.323	1.351	1.333	1.351
C_3–C_4	1.451	1.422	1.404	1.406	1.391	1.414	1.453	1.426	1.404	1.408	1.392	1.413
C_4–C_5	1.419	1.426	1.461	1.468	1.477	1.476	1.419	1.423	1.460	1.467	1.476	1.475
C_5–C_8	1.399	1.391	1.437	1.427	1.452	1.426	1.399	1.390	1.437	1.427	1.453	1.426
C_8–C_9	1.389	1.385	1.373	1.371	1.364	1.382	1.389	1.385	1.373	1.372	1.365	1.382
C_9–C_{10}	1.401	1.401	1.422	1.414	1.430	1.400	1.401	1.399	1.422	1.413	1.430	1.401
C_{10}–C_{11}	1.386	1.375	1.370	1.373	1.364	1.394	1.386	1.377	1.370	1.374	1.364	1.394
C_{11}–C_4	1.408	1.414	1.426	1.414	1.432	1.397	1.407	1.412	1.426	1.414	1.432	1.398
C_5–O_6	1.348	1.341	1.274	1.272	1.253	1.258	1.348	1.344	1.273	1.271	1.253	1.258
O_6–H_7	0.996	1.000	1.720	1.678	----	----	0.996	0.996	1.737	1.687	----	----
N_2–H_7	1.728	1.676	1.040	1.041	1.013	1.011	1.724	1.704	1.039	1.043	1.012	1.015
ϕ_1	-44.64	-11.91	-31.31	-0.015	-36.13	-9.553	-115.9	-155.2	-127.7	-163.8	-124.0	-156.1
ϕ_2	175.2	173.1	176.2	180.0	172.2	174.6	-179.8	-171.6	178.2	180.0	179.2	-175.3
ϕ_3	-1.318	-1.866	0.087	0.003	175.9	175.4	0.038	1.614	-0.368	0.618	-177.9	-170.7
Methanol												
	trans-enol		*cis*-keto		*trans*-keto		*trans*-enol		*cis*-keto		*trans*-keto	
Structural parameters	**1**	**(1)S_1**	**2**	**(2)S_1**	**3**	**(3)S_1**	**4**	**(4)S_1**	**5**	**(5)S_1**	**6**	**(6)S_1**
C_1–N_2	1.406	1.343	1.412	1.348	1.418	1.370	1.415	1.345	1.424	1.355	1.430	1.374
N_2–C_3	1.290	1.330	1.325	1.353	1.335	1.348	1.286	1.321	1.323	1.351	1.338	1.351
C_3–C_4	1.451	1.422	1.404	1.406	1.391	1.414	1.453	1.426	1.404	1.408	1.392	1.413
C_4–C_5	1.419	1.426	1.461	1.468	1.477	1.476	1.419	1.423	1.460	1.467	1.476	1.475
C_5–C_8	1.399	1.391	1.437	1.427	1.453	1.426	1.399	1.390	1.437	1.427	1.453	1.426
C_8–C_9	1.389	1.385	1.373	1.371	1.365	1.382	1.389	1.385	1.373	1.372	1.365	1.382
C_9–C_{10}	1.401	1.401	1.422	1.414	1.431	1.400	1.401	1.399	1.422	1.413	1.430	1.401
C_{10}–C_{11}	1.386	1.375	1.370	1.373	1.364	1.394	1.386	1.377	1.370	1.374	1.364	1.394
C_{11}–C_4	1.408	1.414	1.426	1.414	1.433	1.397	1.407	1.412	1.426	1.414	1.432	1.398
C_5–O_6	1.348	1.341	1.274	1.272	1.253	1.258	1.348	1.344	1.273	1.270	1.253	1.258
O_6–H_7	0.996	1.000	1.720	1.678	----	----	0.996	0.996	1.737	1.686	----	----
N_2–H_7	1.728	1.676	1.040	1.041	1.013	1.011	1.724	1.705	1.039	1.043	1.013	1.015

ϕ_1	-44.63	-11.91	-31.30	-0.02	-36.08	-9.553	-115.9	-155.2	-127.7	-163.8	-124.0	-156.1
ϕ_2	175.2	173.1	176.2	180.0	172.2	174.6	-179.8	-171.6	178.2	180.0	179.2	-175.3
ϕ_3	-1.341	-1.866	0.091	0.003	175.9	175.4	0.038	1.628	-0.368	0.614	-177.9	-170.7
Cyclohexane												
	trans-enol		*cis*-keto		*trans*-keto		*trans*-enol		*cis*-keto		*trans*-keto	
Structural parameters	**1**	**(1)S_1**	**2**	**(2)S_1**	**3**	**(3)S_1**	**4**	**(4)S_1**	**5**	**(5)S_1**	**6**	**(6)S_1**
C_1–N_2	1.405	1.348	1.409	1.350	1.414	1.382	1.414	1.349	1.421	1.361	1.427	1.386
N_2–C_3	1.289	1.325	1.328	1.352	1.343	1.342	1.286	1.317	1.327	1.346	1.343	1.344
C_3–C_4	1.450	1.425	1.399	1.405	1.383	1.416	1.452	1.427	1.400	1.409	1.384	1.417
C_4–C_5	1.420	1.424	1.465	1.469	1.485	1.473	1.420	1.422	1.464	1.469	1.484	1.473
C_5–C_8	1.399	1.391	1.439	1.428	1.459	1.424	1.400	1.391	1.440	1.430	1.459	1.424
C_8–C_9	1.388	1.383	1.370	1.370	1.360	1.387	1.388	1.384	1.369	1.370	1.360	1.387
C_9–C_{10}	1.401	1.400	1.425	1.414	1.436	1.394	1.401	1.399	1.425	1.413	1.435	1.394
C_{10}–C_{11}	1.385	1.375	1.368	1.373	1.361	1.403	1.385	1.376	1.368	1.375	1.361	1.403
C_{11}–C_4	1.408	1.412	1.427	1.413	1.435	1.390	1.407	1.411	1.427	1.410	1.435	1.391
C_5–O_6	1.345	1.339	1.267	1.268	1.242	1.254	1.344	1.341	1.266	1.264	1.242	1.254
O_6–H_7	0.993	0.997	1.689	1.639	----	----	0.994	0.991	1.703	1.654	----	----
N_2–H_7	1.743	1.689	1.043	1.047	1.011		1.740	1.732	1.043	1.048	1.011	1.014
ϕ_1	-45.21	-13.90	-29.27	0.001	-30.38	-14.00	-116.7	-151.1	-128.1	-162.1	-127.0	-152.6
ϕ_2	175.3	172.8	176.9	-180.0	171.9	173.4	-179.6	-170.8	177.8	178.8	178.0	-176.2
ϕ_3	-1.345	-2.480	0.476	0.002	176.8	172.9	0.209	2.009	-0.610	0.222	-179.1	-171.3
2-AntSA												
Acetonitrile												
	trans-enol		*cis*-keto		*trans*-keto		*trans*-enol		*cis*-keto		*trans*-keto	
Structural parameters	**1'**	**(1')S_1**	**2'**	**(2')S_1**	**3'**	**(3')S_1**	**4'**	**(4')S_1**	**5'**	**(5')S_1**	**6'**	**(6')S_1**
C_1–N_2	1.407	1.350	1.408	1.355	1.414	1.377	1.406	1.355	1.408	1.358	1.412	1.379
N_2–C_3	1.289	1.327	1.325	1.352	1.334	1.345	1.291	1.318	1.325	1.351	1.333	1.346
C_3–C_4	1.451	1.425	1.405	1.411	1.390	1.417	1.451	1.427	1.405	1.414	1.392	1.418
C_4–C_5	1.420	1.426	1.461	1.473	1.478	1.476	1.420	1.425	1.461	1.477	1.477	1.477
C_5–C_8	1.399	1.392	1.437	1.428	1.453	1.424	1.399	1.392	1.437	1.426	1.452	1.422
C_8–C_9	1.389	1.384	1.373	1.374	1.364	1.385	1.389	1.384	1.373	1.378	1.365	1.389
C_9–C_{10}	1.401	1.401	1.422	1.410	1.431	1.397	1.401	1.400	1.422	1.406	1.430	1.395
C_{10}–C_{11}	1.386	1.376	1.370	1.381	1.364	1.399	1.386	1.376	1.370	1.387	1.365	1.403
C_{11}–C_4	1.408	1.413	1.426	1.407	1.433	1.393	1.408	1.412	1.426	1.402	1.432	1.392
C_5–O_6	1.348	1.340	1.273	1.267	1.252	1.258	1.348	1.341	1.273	1.267	1.254	1.259
O_6–H_7	0.997	1.003	1.731	1.748	----	----	0.999	1.001	1.731	1.756	----	----
N_2–H_7	1.722	1.667	1.039	1.037	1.012	1.013	1.711	1.678	1.039	1.035	1.013	1.013
ϕ_1	-143.1	180.0	-163.6	180.0	-161.9	-179.8	-21.87	-15.86	-0.008	0.000	0.001	0.000
ϕ_2	-176.5	180.0	-178.5	180.0	-177.0	-179.8	178.9	174.1	180.0	-180.0	180.0	180.0
ϕ_3	0.331	-0.001	0.050	0.001	-177.6	-179.9	-0.191	0.344	-0.003	0.000	-180.0	-180.0
Methanol												
	trans-enol		*cis*-keto		*trans*-keto		*trans*-enol		*cis*-keto		*trans*-keto	
Structural	**1'**	**(1')S_1**	**2'**	**(2')S_1**	**3'**	**(3')S_1**	**4'**	**(4')S_1**	**5'**	**(5')S_1**	**6'**	**(6')S_1**

parameters												
C_1–N_2	1.407	1.350	1.410	1.355	1.414	1.377	1.406	1.355	1.408	1.358	1.412	1.379
N_2–C_3	1.290	1.327	1.325	1.352	1.334	1.345	1.291	1.318	1.325	1.351	1.333	1.346
C_3–C_4	1.451	1.425	1.402	1.411	1.390	1.417	1.451	1.427	1.404	1.414	1.392	1.418
C_4–C_5	1.420	1.426	1.462	1.473	1.478	1.476	1.420	1.425	1.461	1.477	1.477	1.477
C_5–C_8	1.399	1.392	1.438	1.428	1.453	1.424	1.399	1.392	1.437	1.426	1.452	1.422
C_8–C_9	1.389	1.384	1.372	1.374	1.364	1.385	1.389	1.384	1.373	1.378	1.365	1.389
C_9–C_{10}	1.401	1.401	1.423	1.410	1.431	1.397	1.401	1.400	1.422	1.406	1.430	1.395
C_{10}–C_{11}	1.386	1.376	1.369	1.381	1.364	1.399	1.386	1.376	1.370	1.387	1.365	1.403
C_{11}–C_4	1.408	1.413	1.427	1.407	1.433	1.393	1.408	1.412	1.426	1.402	1.432	1.391
C_5–O_6	1.348	1.340	1.272	1.267	1.252	1.258	1.348	1.341	1.273	1.267	1.253	1.259
O_6–H_7	0.997	1.003	1.739	1.748	----	----	0.999	1.001	1.731	1.756	----	----
N_2–H_7	1.722	1.667	1.038	1.037	1.013	1.013	1.711	1.678	1.039	1.035	1.013	1.013
ϕ_1	-143.1	180.0	-163.6	180.0	-161.8	-179.8	-21.87	-15.86	-0.012	0.000	0.001	0.001
ϕ_2	-176.5	180.0	-178.6	180.0	-177.0	-179.8	178.9	174.1	-180.0	-180.0	180.0	-180.0
ϕ_3	0.331	0.000	0.054	0.001	-177.5	-179.9	-0.191	0.344	0.001	0.000	-180.0	180.0
Cyclohexane												
	trans-enol		*cis*-keto		*trans*-keto		*trans*-enol		*cis*-keto		*trans*-keto	
Structural parameters	**1'**	**(1')S_1**	**2'**	**(2')S_1**	**3'**	**(3')S_1**	**4'**	**(4')S_1**	**5'**	**(5')S_1**	**6'**	**(6')S_1**
C_1–N_2	1.407	1.357	1.407	1.362	1.411	1.386	1.406	1.378	1.405	1.366	1.40948	1.38814
N_2–C_3	1.289	1.319	1.329	1.346	1.342	1.339	1.291	1.295	1.328	1.344	1.34130	1.33999
C_3–C_4	1.450	1.429	1.398	1.416	1.382	1.420	1.450	1.440	1.400	1.421	1.38340	1.42156
C_4–C_5	1.420	1.423	1.467	1.473	1.486	1.472	1.421	1.416	1.466	1.474	1.48514	1.47176
C_5–C_8	1.400	1.393	1.441	1.430	1.459	1.422	1.400	1.394	1.440	1.426	1.45816	1.41856
C_8–C_9	1.388	1.383	1.369	1.376	1.360	1.390	1.388	1.382	1.369	1.383	1.36038	1.39498
C_9–C_{10}	1.401	1.400	1.426	1.405	1.436	1.391	1.401	1.397	1.425	1.398	1.43508	1.38723
C_{10}–C_{11}	1.385	1.376	1.367	1.388	1.361	1.406	1.385	1.378	1.368	1.398	1.36153	1.41121
C_{11}–C_4	1.408	1.410	1.428	1.399	1.435	1.387	1.408	1.405	1.427	1.392	1.43457	1.38465
C_5–O_6	1.344	1.337	1.265	1.263	1.242	1.255	1.344	1.339	1.266	1.264	1.24248	1.25746
O_6–H_7	0.994	0.999	1.708	1.718	----	----	0.996	0.992	1.697	1.726	----	----
N_2–H_7	1.740	1.689	1.041	1.042	1.011	1.012	1.729	1.725	1.044	1.040	1.01192	1.01242
ϕ_1	-141.8	180.0	-165.2	180.0	-167.8	-179.8	-23.84	-31.41	0.017	0.001	0.000	0.005
ϕ_2	-176.4	180.0	-178.5	180.0	-177.1	-179.9	178.7	174.5	180.0	-180.0	180.0	-179.999
ϕ_3	0.576	-0.004	-0.051	-0.003	-178.1	-179.9	-0.305	0.285	0.000	0.002	-180.0	-179.989

Table S2 Excitation energies (eV), oscillator strengths *f* and largest excitation coefficients for the *trans*-enol, *cis-keto* and *trans*-keto forms of 1-AntSA and 2-AntSA in **A** methanol and **B** cyclohexane computed at the PCM/TD/CAM-B3LYP/6-311+G(d,p) level of theory.

	1-AntSA					2-AntSA				
A. Methanol										
Compound	**State**	**Transition**	**Coefficient**	**Energy**	***f***	**State**	**Transition**	**Coefficient**	**Energy**	***f***
1 (**1'**)[a] (*trans*-enol)	S_1	78 → 79	0.68	3.28	0.3832	S_1	78 → 79	0.67	3.35	0.1892
	S_2	78 → 80	0.59	3.88	0.1329	S_2	78 → 80	0.49	3.83	0.0987
	S_3	78 → 81	0.47	3.99	0.0070	S_3	77 → 79	0.56	3.93	1.0273
2 (**2'**) (*cis*-keto)	S_1	78 → 79	0.64	3.05	0.5349	S_1	78 → 79	0.61	3.03	0.6728
	S_2	77 → 79	0.53	3.45	0.0181	S_2	77 → 79	0.54	3.41	0.1128
	S_3	74 → 79	0.47	3.88	0.0077	S_3	78 → 80	0.47	3.77	0.0162
3 (**3'**) (*trans*-keto)	S_1	78 → 79	0.62	2.93	0.6470	S_1	78 → 79	0.60	2.87	0.6288
	S_2	77 → 79	0.48	3.42	0.0390	S_2	77 → 79	0.49	3.39	0.1608
	S_3	75 → 79	0.59	3.63	0.0008	S_3	75 → 79	0.63	3.59	0.0014
4 (**4'**) (*trans*-enol)	S_1	78 → 79	0.69	3.36	0.2280	S_1	78 → 79	0.67	3.34	0.3284
	S_2	78 → 80	0.63	3.78	0.0203	S_2	78 → 80	0.59	3.71	0.3260
	S_3	78 → 81	0.52	3.99	0.0122	S_3	77 → 79	0.61	3.92	0.8862
5 (**5'**) (*cis*-keto)	S_1	78 → 79	0.61	3.22	0.4963	S_1	78 → 79	0.61	3.06	0.6930
	S_2	77 → 79	0.47	3.48	0.0231	S_2	78 → 80	0.53	3.47	0.2035
	S_3	78 → 80	0.39	3.83	0.0047	S_3	77 → 79	0.42	3.70	0.0430
6 (**6'**) (*trans*-keto)	S_1	78 → 79	0.55	3.06	0.4641	S_1	78 → 79	0.60	2.90	0.9012
	S_2	78 → 80	0.49	3.43	0.0586	S_2	78 → 80	0.56	3.42	0.0684
	S_3	75 → 79	0.59	3.67	0.0001	S_3	75 → 79	0.64	3.62	0.0001
A. Cyclohexane										
1 (**1'**) (*trans*-enol)	S_1	78 → 79	0.68	3.26	0.4054	S_1	78 → 79	0.67	3.34	0.2039
	S_2	78 → 80	0.58	3.85	0.1233	S_2	78 → 80	0.52	3.83	0.1621
	S_3	78 → 81	0.48	3.98	0.0048	S_3	77 → 79	0.57	3.89	0.9548
2 (**2'**) (*cis*-keto)	S_1	78 → 79	0.64	2.99	0.5558	S_1	78 → 79	0.63	2.98	0.7245
	S_2	77 → 79	0.55	3.41	0.0215	S_2	77 → 79	0.56	3.40	0.0960
	S_3	74 → 79	0.51	3.75	0.0011	S_3	75 → 79	0.59	3.71	0.0061
3 (**3'**) (*trans*-keto)	S_1	78 → 79	0.63	2.88	0.6742	S_1	78 → 79	0.62	2.84	0.6483
	S_2	77 → 79	0.43	3.40	0.0295	S_2	77 → 79	0.45	3.38	0.1459
	S_3	76 → 79	0.49	3.42	0.0074	S_3	75 → 79	0.56	3.39	0.0379
4 (**4'**) (*trans*-enol)	S_1	78 → 79	0.69	3.35	0.2482	S_1	78 → 79	0.67	3.32	0.3549
	S_2	78 → 80	0.63	3.75	0.0218	S_2	78 → 80	0.60	3.70	0.4262
	S_3	78 → 81	0.52	3.98	0.0101	S_3	77 → 79	0.60	3.89	0.7539
5 (**5'**) (*cis*-keto)	S_1	78 → 79	0.60	3.18	0.5275	S_1	78 → 79	0.62	3.00	0.7227
	S_2	77 → 79	0.49	3.46	0.0211	S_2	78 → 80	0.54	3.44	0.1973
	S_3	75 → 80	0.38	3.75	0.0014	S_3	77 → 79	0.46	3.70	0.0465
6 (**6'**) (*trans*-keto)	S_1	78 → 79	0.58	3.01	0.5053	S_1	78 → 79	0.61	2.90	0.9040
	S_2	78 → 80	0.45	3.41	0.0537	S_2	78 → 80	0.56	3.39	0.0750
	S_3	76 → 79	0.53	3.46	0.0002	S_3	75 → 79	0.62	3.43	0.0001

[a] The number in parenthesis corresponds to the conformers of 2-AntSA (right columns).

Table S3. TD-DFT first excited states relative energies (RE, kcal/mol), intramolecular hydrogen bond (IMHB, Å) and torsional angles (ϕ_i, degrees) of the *trans*-enol (**(1)S_1**, **(1')S_1**), twisted-enol (**(1)$S_{1\text{-Tw}}$**, **(1')$S_{1\text{-Tw}}$**), *cis*-keto (**(2)S_1**, **(2')S_1**), twisted-keto (**(2)$S_{1\text{-Tw}}$**, **(2')$S_{1\text{-Tw}}$**) and *trans*-keto (**(3)S_1**, **(3')S_1**) forms.

	1-AntSA [a]		
Structure	**Acetonitrile**	**Methanol**	**Cyclohexane**
(1)S_1	RE: 0.04, IMHB: 1.68 ϕ_1: -11.9, ϕ_2: 173, ϕ_3: -1.87	RE: 0.08, IMHB: 1.68 ϕ_1: -11.9, ϕ_2: 173, ϕ_3: -1.87	RE: 6.38, IMHB: 1.69 ϕ_1: -13.9, ϕ_2: 173, ϕ_3: -2.48
(1)$S_{1\text{-Tw}}$	RE: 0.00, IMHB: 1.90 ϕ_1: 1.55, ϕ_2: 91.6, ϕ_3: 7.79	RE: 0.00, IMHB: 1.91 ϕ_1: 1.54, ϕ_2: 91.6, ϕ_3: 7.78	RE: 0.00, IMHB: 1.93 ϕ_1: 1.06, ϕ_2: 90.5, ϕ_3: 7.14
(2)S_1	RE: 0.00, IMHB: 1.68 ϕ_1: -0.02, ϕ_2: 180, ϕ_3: 0.00	RE: 0.05, IMHB: 1.68 ϕ_1: -0.02, ϕ_2: 180, ϕ_3: 0.00	RE: 7.88, IMHB: 1.64 ϕ_1: 0.00, ϕ_2: -180, ϕ_3: 0.00
(2)$S_{1\text{-Tw}}$	RE: 7.63 ϕ_1: 12.0, ϕ_2: -172, ϕ_3: -79.5	RE: 7.62 ϕ_1: 12.0, ϕ_2: -172, ϕ_3: -79.5	RE: 6.61 ϕ_1: 14.3, ϕ_2: -171ϕ_3: -80.1
(3)S_1	RE: 5.08 ϕ_1: -9.55, ϕ_2: 175, ϕ_3: 175	RE: 5.15 ϕ_1: -9.55, ϕ_2: 175, ϕ_3: 175	RE: 15.7 ϕ_1: -14.0, ϕ_2: 173, ϕ_3: 173
(4)S_1	RE: 0.00, IMHB: 1.70 ϕ_1: -155, ϕ_2: -171, ϕ_3: 1.61	RE: 0.00, IMHB: 1.70 ϕ_1: -155, ϕ_2: -172, ϕ_3: 1.63	RE: 5.84, IMHB: 1.73 ϕ_1: -151, ϕ_2: -170, ϕ_3: 2.01
(4)$S_{1\text{-Tw}}$	RE: 0.21, IMHB: 1.91 ϕ_1: 179, ϕ_2: -96.3, ϕ_3: -5.38	RE: 0.16, IMHB: 1.91 ϕ_1: 179, ϕ_2: -96.3, ϕ_3: -5.39	RE: 0.00, IMHB: 1.93 ϕ_1: -179, ϕ_2: -95.6, ϕ_3: -4.39
(5)S_1	RE: 0.67, IMHB: 1.69 ϕ_1: -164, ϕ_2: 180, ϕ_3: 0.62	RE: 0.68, IMHB: 1.69 ϕ_1: -164, ϕ_2: 180, ϕ_3: 0.61	RE: 8.45, IMHB: 1.65 ϕ_1: -162, ϕ_2: 179, ϕ_3: 0.22
(5)$S_{1\text{-Tw}}$	RE: 5.98 ϕ_1: -118, ϕ_2: -180, ϕ_3: 82.5	RE: 5.92 ϕ_1: -118, ϕ_2: -180, ϕ_3: 82.6	RE: 4.33 ϕ_1: -117, ϕ_2: -175, ϕ_3: 82.3
(6)S_1	RE: 4.61 ϕ_1: -156, ϕ_2: -175, ϕ_3: -171	RE: 4.64 ϕ_1: -156, ϕ_2: -175, ϕ_3: -171	RE: 14.6 ϕ_1: -153, ϕ_2: -176, ϕ_3: -171
	2-AntSA [a]		
Structure	**Acetonitrile**	**Methanol**	**Cyclohexane**
(1')S_1	RE: 1.21, IMHB: 1.67 ϕ_1: 180, ϕ_2: 180, ϕ_3: 0.00	RE: 1.19, IMHB: 1.67 ϕ_1: 180, ϕ_2: 180, ϕ_3: 0.00	RE: 7.15, IMHB: 1.69 ϕ_1: 180, ϕ_2: 180, ϕ_3: 0.00
(1')$S_{1\text{-Tw}}$	RE: 0.21, IMHB: 1.90 ϕ_1: 178, ϕ_2: -91.2, ϕ_3: -8.28	RE: 0.15, IMHB: 1.90 ϕ_1: 179, ϕ_2: -91.2, ϕ_3: -8.24	RE: 0.00, IMHB: 1.92 ϕ_1: 179, ϕ_2: -90.4, ϕ_3: -8.11
(2')S_1	RE: 0.00, IMHB: 1.75 ϕ_1: 180, ϕ_2: 180, ϕ_3: 0.00	RE: 0.00, IMHB: 1.75 ϕ_1: 180, ϕ_2: 180, ϕ_3: 0.00	RE: 7.79, IMHB: 1.72 ϕ_1: 180, ϕ_2: 180, ϕ_3: 0.00
(2')$S_{1\text{-Tw}}$	RE: 4.93 ϕ_1: -177, ϕ_2: -178, ϕ_3: 86.5	RE: 4.87 ϕ_1: -177, ϕ_2: -178, ϕ_3: 86.5	RE: 3.42 ϕ_1: 173, ϕ_2: 177, ϕ_3: 81.6
(3')S_1	RE: 2.72 ϕ_1: -180, ϕ_2: -180, ϕ_3: -180	RE: 2.74 ϕ_1: -180, ϕ_2: -180, ϕ_3: -180	RE: 12.7 ϕ_1: -180, ϕ_2: -180, ϕ_3: -180
(4')S_1	RE: 2.52, IMHB: 1.68 ϕ_1: -15.9, ϕ_2: 174, ϕ_3: 0.34	RE: 2.51, IMHB: 1.68 ϕ_1: -15.8, ϕ_2: 174, ϕ_3: 0.34	RE: 8.51, IMHB: 1.73 ϕ_1: -31.4, ϕ_2: 175, ϕ_3: 0.30

(4')$S_{1\text{-}Tw}$	RE: 0.46, IMHB: 1.90 ϕ_1: 1.30, ϕ_2: 93.0, ϕ_3: 8.25	RE: 0.40, IMHB: 1.90 ϕ_1: 1.29, ϕ_2: 93.0, ϕ_3: 8.24	RE: 0.00, IMHB: 1.91 ϕ_1: 1.20, ϕ_2: 91.7, ϕ_3: 8.44
(5')S_1	RE: 0.00, IMHB: 1.76 ϕ_1: 0.00, ϕ_2: -180, ϕ_3: 0.00	RE: 0.00, IMHB: 1.76 ϕ_1: 0.00, ϕ_2: -180, ϕ_3: 0.00	RE: 7.54, IMHB: 1.73 ϕ_1: 0.00, ϕ_2: -180, ϕ_3: 0.00
(5')$S_{1\text{-}Tw}$	RE: 4.91 ϕ_1: -9.82, ϕ_2: 177, ϕ_3: 82.0	RE: 4.85 ϕ_1: -9.84, ϕ_2: 177, ϕ_3: 82.1	RE: 3.41 ϕ_1: -14.5, ϕ_2: 178, ϕ_3: 80.8
(6')S_1	RE: 2.37 ϕ_1: 0.00, ϕ_2: 180, ϕ_3: -180	RE: 2.40 ϕ_1: 0.00, ϕ_2: -180, ϕ_3: 180	RE: 12.5 ϕ_1: 0.00, ϕ_2: -180, ϕ_3: -180

[a] Relative energies were calculated independently for conformers **1**, **4**, **1´** and **4´,** and their corresponding products using the most stable conformers as reference.