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## 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** 

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Fig. S11 Optimized structures of the *trans*-enol  $((1')S_1, (4')S_1)$ , twisted-enol  $((1')S_{1-Tw}, (4')S_{1-Tw})$ , *cis*-keto  $((2')S_1$ , (5')S\_1), twisted-keto  $((2')S_{1-Tw}, (5')S_{1-Tw})$  and *trans*-keto  $((3')S_1, (6')S_1)$  forms of 2-AntSA in the S<sub>1</sub> 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<sub>1</sub>, (4)S<sub>1</sub>), twisted-enol ((1)S<sub>1-Tw</sub>, (4)S<sub>1-Tw</sub>), *cis*-keto ((2)S<sub>1</sub>, (5)S<sub>1</sub>), twisted-keto ((2)S<sub>1-Tw</sub>, (5)S<sub>1-Tw</sub>) and *trans*-keto ((3)S<sub>1</sub>, (6)S<sub>1</sub>) forms of 1-AntSA in the S<sub>1</sub> state in cyclohexane. The energies are relative to the more stable forms (1)S<sub>1-Tw</sub> and (4)S<sub>1-Tw</sub>, respectively.

Fig. S13 Optimized structures of the *trans*-enol  $((1')S_1, (4')S_1)$ , twisted-enol  $((1')S_{1-Tw}, (4')S_{1-Tw})$ , *cis*-keto  $((2')S_1$ , (5')S\_1), twisted-keto  $((2')S_{1-Tw}, (5')S_{1-Tw})$  and *trans*-keto  $((3')S_1, (6')S_1)$  forms of 2-AntSA in the S<sub>1</sub> state in cyclohexane. The energies are relative to the more stable forms  $(1')S_{1-Tw}$  and  $(4')S_{1-Tw}$ , 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) $S_{1-Tw}$ , (2') $S_{1-Tw}$ ) forms in the  $S_0$  and  $S_1$  states.

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**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  $\mathbf{1}$ .



**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 ( $\phi_1$ ,  $\phi_2$ ,  $\phi_3$ ).



**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 ( $\phi_1$ ,  $\phi_2$ ,  $\phi_3$ ).



15' 16.4 kcal/mol **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 ( $\phi_1$ ,  $\phi_2$ ,  $\phi_3$ ).



16.0 kcal/mol

12 18.5 kcal/mol 13 21.2 kcal/mol **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 ( $\phi_1$ ,  $\phi_2$ ,  $\phi_3$ ).



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



Fig. S13 Optimized structures of the *trans*-enol  $((1')S_1, (4')S_1)$ , twisted-enol  $((1')S_{1-Tw}, (4')S_{1-Tw})$ , *cis*-keto  $((2')S_1$ , (5')S<sub>1</sub>), twisted-keto  $((2')S_{1-Tw}, (5')S_{1-Tw})$  and *trans*-keto  $((3')S_1, (6')S_1)$  forms of 2-AntSA in the S<sub>1</sub> state in cyclohexane. The energies are relative to the more stable forms  $(1')S_{1-Tw}$  and  $(4')S_{1-Tw}$ , 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) $S_{1-Tw}$ , (2') $S_{1-Tw}$ ) forms in the  $S_0$  and  $S_1$  states.



	1-AntSA											
	Acetonitrile											
	trans	-enol	cis-	keto	trans-keto		trans-enol		<i>cis</i> -keto		trans-keto	
Structural parameters	1	(1)S <sub>1</sub>	2	(2)S <sub>1</sub>	3	(3)S <sub>1</sub>	4	(4)S <sub>1</sub>	5	(5)S <sub>1</sub>	6	(6)S <sub>1</sub>
C <sub>1</sub> -N <sub>2</sub>	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 <sub>2</sub> -C <sub>3</sub>	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 <sub>3</sub> -C <sub>4</sub>	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 <sub>4</sub> -C <sub>5</sub>	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 <sub>5</sub> -C <sub>8</sub>	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 <sub>8</sub> –C <sub>9</sub>	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 <sub>9</sub> -C <sub>10</sub>	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 <sub>10</sub> -C <sub>11</sub>	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 <sub>11</sub> -C <sub>4</sub>	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 <sub>5</sub> -O <sub>6</sub>	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 <sub>6</sub> -H <sub>7</sub>	0.996	1.000	1.720	1.678			0.996	0.996	1.737	1.687		
N <sub>2</sub> -H <sub>7</sub>	1.728	1.676	1.040	1.041	1.013	1.011	1.724	1.704	1.039	1.043	1.012	1.015
$\phi_1$	-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 <sub>2</sub>	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 <sub>3</sub>	-1.318	-1.866	0.087	0.003	175.9	175.4	0.038	1.614	-0.368	0.618	-177.9	-170.7
					1	Methanol						
	trans	-enol	cis-l	keto	trans	-keto	trans	-enol	cis-	keto	trans	s-keto
Structural parameters	1	(1)S <sub>1</sub>	2	(2)S <sub>1</sub>	3	(3)S <sub>1</sub>	4	(4)S <sub>1</sub>	5	(5)S1	6	(6)S <sub>1</sub>
C <sub>1</sub> -N <sub>2</sub>	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 <sub>2</sub> -C <sub>3</sub>	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 <sub>3</sub> C <sub>4</sub>	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 <sub>4</sub> -C <sub>5</sub>	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 <sub>5</sub> C <sub>8</sub>	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 <sub>8</sub> –C <sub>9</sub>	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 <sub>9</sub> -C <sub>10</sub>	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 <sub>10</sub> -C <sub>11</sub>	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 <sub>11</sub> -C <sub>4</sub>	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 <sub>5</sub> -O <sub>6</sub>	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 <sub>6</sub> -H <sub>7</sub>	0.996	1.000	1.720	1.678			0.996	0.996	1.737	1.686		
N <sub>2</sub> -H <sub>7</sub>	1.728	1.676	1.040	1.041	1.013	1.011	1.724	1.705	1.039	1.043	1.013	1.015

$\phi_1$	-44.63	-11.91	-31.30	-0.02	-36.08	-9.553	-115.9	-155.2	-127.7	-163.8	-124.0	-156.1
φ2	175.2	173.1	176.2	180.0	172.2	174.6	-179.8	-171.6	178.2	180.0	179.2	-175.3
фз	-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-k	keto	trans	-keto	trans	-enol	cis-	keto	trans	-keto
Structural	1	(1)S <sub>1</sub>	2	(2)S <sub>1</sub>	3	(3)S <sub>1</sub>	4	(4)S <sub>1</sub>	5	(5)S1	6	(6)S <sub>1</sub>
C <sub>1</sub> -N <sub>2</sub>	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 <sub>2</sub> -C <sub>3</sub>	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 <sub>3</sub> -C <sub>4</sub>	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 <sub>4</sub> –C <sub>5</sub>	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 <sub>5</sub> –C <sub>8</sub>	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 <sub>8</sub> –C <sub>9</sub>	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 <sub>9</sub> -C <sub>10</sub>	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 <sub>10</sub> -C <sub>11</sub>	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 <sub>11</sub> -C <sub>4</sub>	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 <sub>5</sub> -O <sub>6</sub>	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 <sub>6</sub> -H <sub>7</sub>	0.993	0.997	1.689	1.639			0.994	0.991	1.703	1.654		
N <sub>2</sub> -H <sub>7</sub>	1.743	1.689	1.043	1.047	1.011		1.740	1.732	1.043	1.048	1.011	1.014
φ <sub>1</sub>	-45.21	-13.90	-29.27	0.001	-30.38	-14.00	-116.7	-151.1	-128.1	-162.1	-127.0	-152.6
ф <sub>2</sub>	175.3	172.8	176.9	-180.0	171.9	173.4	-179.6	-170.8	177.8	178.8	178.0	-176.2
$\phi_3$	-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						
					Ac	etonitril	2					
Churchtung	trans	-enol	CIS-k	ceto	trans	-keto	trans	-enol	CIS-	keto I	trans	s-keto
parameters	1′	(1′)S <sub>1</sub>	2'	(2′)S <sub>1</sub>	3′	(3′)S <sub>1</sub>	4'	(4′)S <sub>1</sub>	5′	(5′)S <sub>1</sub>	6'	(6′)S <sub>1</sub>
C <sub>1</sub> -N <sub>2</sub>	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 <sub>2</sub> -C <sub>3</sub>	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 <sub>3</sub> –C <sub>4</sub>	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 <sub>4</sub> –C <sub>5</sub>	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 <sub>5</sub> –C <sub>8</sub>	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 <sub>8</sub> –C <sub>9</sub>	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 <sub>9</sub> -C <sub>10</sub>	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 <sub>10</sub> -C <sub>11</sub>	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 <sub>11</sub> -C <sub>4</sub>	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 <sub>5</sub> -O <sub>6</sub>	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 <sub>6</sub> -H <sub>7</sub>	0.997	1.003	1.731	1.748			0.999	1.001	1.731	1.756		
N <sub>2</sub> -H <sub>7</sub>	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 <sub>1</sub>	-143.1	180.0	-163.6	180.0	-161.9	-179.8	-21.87	-15.86	-0.008	0.000	0.001	0.000
φ2	-176.5	180.0	-178.5	180.0	-177.0	-179.8	178.9	174.1	180.0	-180.0	180.0	180.0
ф <sub>3</sub>	0.331	-0.001	0.050	0.001	-177.6	-179.9	-0.191	0.344	-0.003	0.000	-180.0	-180.0
					-	1 a 4 l						
	Methanol											
		anal	ata I	(ata	<b>*</b>	kote	+	anal	-t- 1	(ata	<b>1</b>	kata
Chanachanal	trans	-enol	cis-k	keto	trans	-keto	trans	-enol	cis-l	keto	trans	-keto

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 <sub>2</sub> -C <sub>3</sub>	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 <sub>3</sub> –C <sub>4</sub>	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 <sub>4</sub> -C <sub>5</sub>	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 <sub>5</sub> -C <sub>8</sub>	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 <sub>8</sub> –C <sub>9</sub>	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 <sub>9</sub> -C <sub>10</sub>	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 <sub>10</sub> -C <sub>11</sub>	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 <sub>11</sub> -C <sub>4</sub>	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 <sub>5</sub> -O <sub>6</sub>	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 <sub>6</sub> -H <sub>7</sub>	0.997	1.003	1.739	1.748			0.999	1.001	1.731	1.756		
N <sub>2</sub> -H <sub>7</sub>	1.722	1.667	1.038	1.037	1.013	1.013	1.711	1.678	1.039	1.035	1.013	1.013
$\phi_1$	-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 <sub>2</sub>	-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 <sub>3</sub>	0.331	0.000	0.054	0.001	-177.5	-179.9	-0.191	0.344	0.001	0.000	-180.0	180.0
					Cv	clohexan	<u>م</u>					
					-,	elenexan						
	trans	-enol	cis-l	keto	trans	-keto	trans	-enol	cis-l	keto	trans	s-keto
Structural parameters	trans 1'	-enol (1')S <sub>1</sub>	cis-I <b>2'</b>	(2')S <sub>1</sub>	trans 3'	-keto (3')S <sub>1</sub>	trans 4'	-enol (4')S <sub>1</sub>	cis-  <b>5'</b>	keto (5')S <sub>1</sub>	trans 6'	5-keto (6')S <sub>1</sub>
Structural parameters C <sub>1</sub> -N <sub>2</sub>	trans <b>1'</b> 1.407	-enol (1')S <sub>1</sub> 1.357	<i>cis-</i>   <b>2'</b> 1.407	(2')S <sub>1</sub>	trans 3'	-keto (3')S <sub>1</sub> 1.386	trans 4' 1.406	-enol (4')S <sub>1</sub> 1.378	<i>cis-</i>   <b>5'</b> 1.405	<pre>keto (5')S1 1.366</pre>	trans 6' 1.40948	-keto (6')S <sub>1</sub> 1.38814
Structural parameters C <sub>1</sub> -N <sub>2</sub> N <sub>2</sub> -C <sub>3</sub>	trans 1' 1.407 1.289	-enol (1')S <sub>1</sub> 1.357 1.319	<i>cis</i> -l <b>2'</b> 1.407 1.329	<pre>(eto     (2')S1     1.362     1.346</pre>	trans 3' 1.411 1.342	-keto (3')S <sub>1</sub> 1.386 1.339	<i>trans</i> <i>4'</i> 1.406 1.291	-enol (4')S <sub>1</sub> 1.378 1.295	<i>cis</i> -l <b>5'</b> 1.405 1.328	<pre>(eto (5')S1 1.366 1.344</pre>	trans 6' 1.40948 1.34130	-keto (6')S <sub>1</sub> 1.38814 1.33999
$\begin{tabular}{ c c c c } \hline Structural \\ parameters \\ \hline C_1 - N_2 \\ \hline N_2 - C_3 \\ \hline C_3 - C_4 \end{tabular}$	trans 1' 1.407 1.289 1.450	-enol (1')S <sub>1</sub> 1.357 1.319 1.429	<i>cis</i> -l <b>2'</b> 1.407 1.329 1.398	<b>(2')S</b> <sub>1</sub> 1.362 1.346 1.416	trans 3' 1.411 1.342 1.382	-keto (3')S <sub>1</sub> 1.386 1.339 1.420	trans 4' 1.406 1.291 1.450	-enol (4')\$ <sub>1</sub> 1.378 1.295 1.440	<i>cis</i> -1 <b>5'</b> 1.405 1.328 1.400	<pre>(eto) (5')S1 1.366 1.344 1.421</pre>	trans 6' 1.40948 1.34130 1.38340	-keto (6')S <sub>1</sub> 1.38814 1.33999 1.42156
$\begin{tabular}{ c c c c } \hline Structural \\ parameters \\ \hline C_1 - N_2 \\ \hline N_2 - C_3 \\ \hline C_3 - C_4 \\ \hline C_4 - C_5 \end{tabular}$	trans 1' 1.407 1.289 1.450 1.420	-enol (1')S <sub>1</sub> 1.357 1.319 1.429 1.423	<i>cis</i> -1 <b>2'</b> 1.407 1.329 1.398 1.467	<b>(2')S</b> 1 1.362 1.346 1.416 1.473	trans 3' 1.411 1.342 1.382 1.486	-keto (3')S <sub>1</sub> 1.386 1.339 1.420 1.472	trans 4' 1.406 1.291 1.450 1.421	-enol (4')S <sub>1</sub> 1.378 1.295 1.440 1.416	<i>cis</i> -1 <b>5'</b> 1.405 1.328 1.400 1.466	<pre>(5')\$1 1.366 1.344 1.421 1.474</pre>	trans 6' 1.40948 1.34130 1.38340 1.48514	-keto (6')S <sub>1</sub> 1.38814 1.33999 1.42156 1.47176
$\begin{tabular}{ c c c c } \hline Structural \\ parameters \\ \hline C_1 - N_2 \\ \hline N_2 - C_3 \\ \hline C_3 - C_4 \\ \hline C_4 - C_5 \\ \hline C_5 - C_8 \\ \hline \end{tabular}$	trans 1' 1.407 1.289 1.450 1.420 1.400	-enol (1')S <sub>1</sub> 1.357 1.319 1.429 1.423 1.393	<i>cis</i> -l <b>2'</b> 1.407 1.329 1.398 1.467 1.441	<b>(2')S</b> <sub>1</sub> 1.362 1.346 1.416 1.473 1.430	trans 3' 1.411 1.342 1.382 1.486 1.459	-keto (3')S <sub>1</sub> 1.386 1.339 1.420 1.472 1.422	trans 4' 1.406 1.291 1.450 1.421 1.400	-enol (4')S <sub>1</sub> 1.378 1.295 1.440 1.416 1.394	<i>cis</i> -l <b>5'</b> 1.405 1.328 1.400 1.466 1.440	<pre>(5')\$1 1.366 1.344 1.421 1.474 1.426</pre>	trans 6' 1.40948 1.34130 1.38340 1.48514 1.45816	-keto (6')S <sub>1</sub> 1.38814 1.33999 1.42156 1.47176 1.41856
$\begin{tabular}{ c c c c } \hline Structural \\ parameters \\ \hline C_1 - N_2 \\ \hline N_2 - C_3 \\ \hline C_3 - C_4 \\ \hline C_3 - C_4 \\ \hline C_4 - C_5 \\ \hline C_5 - C_8 \\ \hline C_8 - C_9 \end{tabular}$	trans 1' 1.407 1.289 1.450 1.420 1.400 1.388	-enol (1')S <sub>1</sub> 1.357 1.319 1.429 1.423 1.393 1.383	<i>cis</i> -l <b>2'</b> 1.407 1.329 1.398 1.467 1.441 1.369	<b>(2')S</b> <sub>1</sub> 1.362 1.346 1.416 1.473 1.430 1.376	trans 3' 1.411 1.342 1.382 1.486 1.459 1.360	-keto (3')S <sub>1</sub> 1.386 1.339 1.420 1.472 1.422 1.390	trans 4' 1.406 1.291 1.450 1.421 1.400 1.388	-enol (4')S <sub>1</sub> 1.378 1.295 1.440 1.416 1.394 1.382	<i>cis</i> -l <b>5'</b> 1.405 1.328 1.400 1.466 1.440 1.369	<pre>(5')S1 1.366 1.344 1.421 1.474 1.426 1.383</pre>	trans 6' 1.40948 1.34130 1.38340 1.48514 1.45816 1.36038	-keto (6')S <sub>1</sub> 1.38814 1.33999 1.42156 1.47176 1.41856 1.39498
$\begin{tabular}{ c c c c } \hline Structural \\ parameters \\ \hline C_1 - N_2 \\ \hline N_2 - C_3 \\ \hline C_3 - C_4 \\ \hline C_3 - C_4 \\ \hline C_4 - C_5 \\ \hline C_5 - C_8 \\ \hline C_5 - C_8 \\ \hline C_8 - C_9 \\ \hline C_9 - C_{10} \\ \hline \end{tabular}$	trans 1' 1.407 1.289 1.450 1.420 1.400 1.388 1.401	-enol (1')S <sub>1</sub> 1.357 1.319 1.429 1.423 1.393 1.383 1.400	<i>cis</i> -l <b>2'</b> 1.407 1.329 1.398 1.467 1.441 1.369 1.426	<b>(2')S</b> 1 1.362 1.346 1.416 1.473 1.430 1.376 1.405	trans 3' 1.411 1.342 1.382 1.486 1.459 1.360 1.436	-keto (3')S <sub>1</sub> 1.386 1.339 1.420 1.472 1.422 1.390 1.391	trans 4' 1.406 1.291 1.450 1.421 1.400 1.388 1.401	-enol (4')S <sub>1</sub> 1.378 1.295 1.440 1.416 1.394 1.382 1.397	<i>cis</i> -l <b>5'</b> 1.405 1.328 1.400 1.466 1.440 1.369 1.425	<pre>(5')\$1 1.366 1.344 1.421 1.474 1.426 1.383 1.398</pre>	trans 6' 1.40948 1.34130 1.38340 1.48514 1.45816 1.36038 1.43508	-keto (6')S <sub>1</sub> 1.38814 1.33999 1.42156 1.47176 1.41856 1.39498 1.38723
$\begin{tabular}{ c c c c } \hline Structural \\ parameters \\ \hline C_1 - N_2 \\ \hline N_2 - C_3 \\ \hline C_3 - C_4 \\ \hline C_4 - C_5 \\ \hline C_5 - C_8 \\ \hline C_5 - C_8 \\ \hline C_8 - C_9 \\ \hline C_9 - C_{10} \\ \hline C_{10} - C_{11} \\ \hline \end{tabular}$	trans 1' 1.407 1.289 1.450 1.420 1.420 1.388 1.401 1.385	-enol (1')S <sub>1</sub> 1.357 1.319 1.429 1.423 1.393 1.383 1.400 1.376	<i>cis</i> -l 2' 1.407 1.329 1.398 1.467 1.441 1.369 1.426 1.367	<b>(2')S</b> <sub>1</sub> 1.362 1.346 1.416 1.473 1.430 1.376 1.405 1.388	trans 3' 1.411 1.342 1.382 1.486 1.459 1.360 1.436 1.361	-keto (3')S <sub>1</sub> 1.386 1.339 1.420 1.472 1.422 1.390 1.391 1.406	trans 4' 1.406 1.291 1.450 1.421 1.400 1.388 1.401 1.385	-enol (4')S <sub>1</sub> 1.378 1.295 1.440 1.416 1.394 1.382 1.397 1.378	<i>cis</i> -l 5' 1.405 1.328 1.400 1.466 1.440 1.369 1.425 1.368	<pre>(cto) (5')S1 1.366 1.344 1.421 1.474 1.426 1.383 1.398 1.398</pre>	trans 6' 1.40948 1.34130 1.38340 1.48514 1.45816 1.36038 1.43508 1.36153	-keto (6')S <sub>1</sub> 1.38814 1.33999 1.42156 1.47176 1.41856 1.39498 1.38723 1.41121
$\begin{tabular}{ c c c c } \hline Structural \\ parameters \\ \hline C_1 - N_2 \\ \hline C_2 - C_3 \\ \hline C_3 - C_4 \\ \hline C_4 - C_5 \\ \hline C_5 - C_8 \\ \hline C_5 - C_8 \\ \hline C_8 - C_9 \\ \hline C_9 - C_{10} \\ \hline C_{10} - C_{11} \\ \hline C_{11} - C_4 \\ \hline \end{tabular}$	trans 1' 1.407 1.289 1.450 1.420 1.400 1.388 1.401 1.385 1.408	-enol (1')S <sub>1</sub> 1.357 1.319 1.429 1.423 1.393 1.383 1.383 1.400 1.376 1.410	<i>cis</i> -l 2' 1.407 1.329 1.398 1.467 1.441 1.369 1.426 1.367 1.428	<b>(2')S</b> <sub>1</sub> 1.362 1.346 1.416 1.473 1.430 1.376 1.405 1.388 1.399	trans 3' 1.411 1.342 1.382 1.486 1.459 1.360 1.436 1.361 1.435	-keto (3')S <sub>1</sub> 1.386 1.339 1.420 1.472 1.422 1.390 1.391 1.406 1.387	trans 4' 1.406 1.291 1.450 1.421 1.400 1.388 1.401 1.385 1.408	-enol (4')S <sub>1</sub> 1.378 1.295 1.440 1.416 1.394 1.382 1.397 1.378 1.405	<i>cis</i> -l 5' 1.405 1.328 1.400 1.466 1.440 1.369 1.425 1.368 1.427	<pre>     (5')S1     1.366     1.344     1.421     1.474     1.426     1.383     1.398     1.398     1.392 </pre>	trans 6' 1.40948 1.34130 1.38340 1.48514 1.45816 1.36038 1.43508 1.43508 1.36153 1.43457	-keto (6')S <sub>1</sub> 1.38814 1.33999 1.42156 1.47176 1.47856 1.39498 1.38723 1.41121 1.38465
$\begin{tabular}{ c c c c } \hline Structural \\ parameters \\ \hline C_1 - N_2 \\ \hline N_2 - C_3 \\ \hline C_3 - C_4 \\ \hline C_4 - C_5 \\ \hline C_5 - C_8 \\ \hline C_8 - C_9 \\ \hline C_9 - C_{10} \\ \hline C_{10} - C_{11} \\ \hline C_{11} - C_4 \\ \hline C_5 - O_6 \\ \hline \end{tabular}$	trans 1' 1.407 1.289 1.450 1.420 1.400 1.388 1.401 1.385 1.408 1.344	-enol (1')S <sub>1</sub> 1.357 1.319 1.429 1.423 1.393 1.383 1.400 1.376 1.410 1.337	<i>cis</i> -l 2' 1.407 1.329 1.398 1.467 1.441 1.369 1.426 1.367 1.428 1.265	ceto (2')S <sub>1</sub> 1.362 1.346 1.416 1.473 1.430 1.376 1.405 1.388 1.399 1.263	trans 3' 1.411 1.342 1.382 1.486 1.459 1.360 1.436 1.436 1.435 1.242	-keto (3')S <sub>1</sub> 1.386 1.339 1.420 1.472 1.422 1.390 1.391 1.406 1.387 1.255	trans 4' 1.406 1.291 1.450 1.421 1.400 1.388 1.401 1.385 1.408 1.344	-enol (4')S <sub>1</sub> 1.378 1.295 1.440 1.416 1.394 1.382 1.397 1.378 1.405 1.339	<i>cis</i> -l 5' 1.405 1.328 1.400 1.466 1.440 1.369 1.425 1.368 1.427 1.266	<pre>     (5')\$<sub>1</sub>     1.366     1.344     1.421     1.474     1.426     1.383     1.398     1.398     1.392     1.264 </pre>	trans 6' 1.40948 1.34130 1.38340 1.48514 1.45816 1.36038 1.43508 1.43508 1.43457 1.24248	-keto (6')S <sub>1</sub> 1.38814 1.33999 1.42156 1.47176 1.41856 1.39498 1.38723 1.41121 1.38465 1.25746
$\begin{tabular}{ c c c c } \hline Structural \\ parameters \\ \hline C_1 - N_2 \\ \hline N_2 - C_3 \\ \hline C_3 - C_4 \\ \hline C_4 - C_5 \\ \hline C_5 - C_8 \\ \hline C_9 - C_1 \\ \hline C_9 - C_{10} \\ \hline C_{10} - C_{11} \\ \hline C_{11} - C_4 \\ \hline C_5 - O_6 \\ \hline O_6 - H_7 \\ \hline \end{tabular}$	trans 1' 1.407 1.289 1.450 1.420 1.420 1.388 1.400 1.388 1.401 1.385 1.408 1.344 0.994	-enol (1')S <sub>1</sub> 1.357 1.319 1.429 1.423 1.393 1.383 1.383 1.400 1.376 1.410 1.337 0.999	<i>cis</i> -l 2' 1.407 1.329 1.398 1.467 1.441 1.369 1.426 1.367 1.428 1.265 1.708	ceto (2')S <sub>1</sub> 1.362 1.346 1.416 1.473 1.430 1.376 1.405 1.388 1.399 1.263 1.718	trans         3'         1.411         1.342         1.382         1.486         1.459         1.360         1.436         1.361         1.435         1.242	-keto (3')S <sub>1</sub> 1.386 1.339 1.420 1.472 1.422 1.390 1.391 1.406 1.387 1.255 	trans 4' 1.406 1.291 1.450 1.421 1.400 1.388 1.401 1.385 1.408 1.344 0.996	-enol (4')S <sub>1</sub> 1.378 1.295 1.440 1.416 1.394 1.382 1.397 1.378 1.405 1.339 0.992	<i>cis</i> -l <b>5'</b> 1.405 1.328 1.400 1.466 1.440 1.369 1.425 1.368 1.427 1.266 1.697	<pre>(ceto) (5')S1 1.366 1.344 1.421 1.474 1.426 1.383 1.398 1.398 1.398 1.392 1.264 1.726</pre>	trans 6' 1.40948 1.34130 1.38340 1.48514 1.45816 1.36038 1.43508 1.43508 1.43457 1.24248 	-keto (6')S <sub>1</sub> 1.38814 1.33999 1.42156 1.47176 1.41856 1.39498 1.38723 1.41121 1.38465 1.25746 
$\begin{tabular}{ c c c c } \hline Structural \\ parameters \\ \hline C_1 - N_2 \\ \hline N_2 - C_3 \\ \hline C_3 - C_4 \\ \hline C_4 - C_5 \\ \hline C_5 - C_8 \\ \hline C_5 - C_8 \\ \hline C_9 - C_{10} \\ \hline C_{10} - C_{11} \\ \hline C_{10} - C_{11} \\ \hline C_{11} - C_4 \\ \hline C_5 - O_6 \\ \hline O_6 - H_7 \\ \hline N_2 - H_7 \end{tabular}$	trans 1' 1.407 1.289 1.450 1.420 1.420 1.388 1.400 1.388 1.401 1.385 1.408 1.344 0.994 1.740	-enol (1')S <sub>1</sub> 1.357 1.319 1.429 1.423 1.393 1.383 1.400 1.376 1.410 1.337 0.999 1.689	<i>cis</i> -l 2' 1.407 1.329 1.398 1.467 1.441 1.369 1.426 1.367 1.428 1.265 1.708 1.041	(2')S1         1.362         1.346         1.416         1.473         1.430         1.376         1.388         1.399         1.263         1.718         1.042	trans         3'         1.411         1.342         1.382         1.486         1.459         1.360         1.436         1.361         1.435         1.242            1.011	-keto (3')S <sub>1</sub> 1.386 1.339 1.420 1.472 1.472 1.390 1.391 1.406 1.387 1.255  1.012	trans 4' 1.406 1.291 1.450 1.421 1.400 1.388 1.401 1.385 1.408 1.344 0.996 1.729	-enol (4')S <sub>1</sub> 1.378 1.295 1.440 1.416 1.394 1.382 1.397 1.378 1.405 1.339 0.992 1.725	<i>cis</i> -l <b>5'</b> 1.405 1.328 1.400 1.466 1.440 1.369 1.425 1.368 1.427 1.266 1.697 1.044	<pre>     (5')S1     1.366     1.344     1.421     1.474     1.426     1.383     1.398     1.398     1.398     1.392     1.264     1.726     1.040 </pre>	trans 6' 1.40948 1.34130 1.38340 1.48514 1.45816 1.36038 1.43508 1.43508 1.43508 1.43457 1.24248  1.01192	-keto (6')S <sub>1</sub> 1.38814 1.33999 1.42156 1.47176 1.47856 1.39498 1.38723 1.41121 1.38465 1.25746  1.01242
$\begin{tabular}{ c c c c } \hline Structural \\ parameters \\ \hline C_1 - N_2 \\ \hline N_2 - C_3 \\ \hline C_3 - C_4 \\ \hline C_4 - C_5 \\ \hline C_5 - C_8 \\ \hline C_8 - C_9 \\ \hline C_9 - C_{10} \\ \hline C_{10} - C_{11} \\ \hline C_{10} - C_{11} \\ \hline C_{11} - C_4 \\ \hline C_5 - O_6 \\ \hline O_6 - H_7 \\ \hline N_2 - H_7 \\ \hline \varphi_1 \end{tabular}$	trans 1' 1.407 1.289 1.450 1.420 1.400 1.388 1.401 1.385 1.408 1.344 0.994 1.740 -141.8	-enol (1')S <sub>1</sub> 1.357 1.319 1.429 1.423 1.393 1.383 1.400 1.376 1.410 1.337 0.999 1.689 180.0	<i>cis</i> -l 2' 1.407 1.329 1.398 1.467 1.441 1.369 1.426 1.367 1.428 1.265 1.708 1.041 -165.2	(2')S1         1.362         1.346         1.416         1.473         1.430         1.376         1.388         1.399         1.263         1.718         1.042         180.0	trans         3'         1.411         1.342         1.382         1.486         1.459         1.360         1.436         1.361         1.435         1.242            1.011         -167.8	-keto (3')S <sub>1</sub> 1.386 1.339 1.420 1.472 1.422 1.390 1.391 1.406 1.387 1.255  1.012 -179.8	trans 4' 1.406 1.291 1.450 1.421 1.400 1.388 1.401 1.385 1.408 1.344 0.996 1.729 -23.84	-enol (4')S <sub>1</sub> 1.378 1.295 1.440 1.416 1.394 1.382 1.397 1.378 1.405 1.339 0.992 1.725 -31.41	cis-l         5'         1.405         1.328         1.400         1.466         1.440         1.369         1.425         1.368         1.427         1.266         1.697         1.044         0.017	<pre>     (5')S<sub>1</sub>     1.366     1.344     1.421     1.474     1.426     1.383     1.398     1.398     1.392     1.264     1.726     1.040     0.001 </pre>	trans 6' 1.40948 1.34130 1.38340 1.48514 1.45816 1.36038 1.43508 1.36153 1.43457 1.24248  1.01192 0.000	-keto (6')S <sub>1</sub> 1.38814 1.33999 1.42156 1.47176 1.41856 1.39498 1.38723 1.41121 1.38465 1.25746  1.01242 0.005
$\begin{tabular}{ c c c c } \hline Structural \\ parameters \\ \hline C_1 - N_2 \\ \hline N_2 - C_3 \\ \hline C_3 - C_4 \\ \hline C_4 - C_5 \\ \hline C_5 - C_8 \\ \hline C_8 - C_9 \\ \hline C_9 - C_{10} \\ \hline C_{10} - C_{11} \\ \hline C_{10} - C_{11} \\ \hline C_{11} - C_4 \\ \hline C_5 - O_6 \\ \hline O_6 - H_7 \\ \hline N_2 - H_7 \\ \hline \varphi_1 \\ \hline \varphi_2 \end{tabular}$	trans 1' 1.407 1.289 1.450 1.420 1.400 1.388 1.401 1.385 1.408 1.344 0.994 1.740 -141.8 -176.4	-enol (1')S <sub>1</sub> 1.357 1.319 1.429 1.423 1.393 1.383 1.383 1.400 1.376 1.410 1.337 0.999 1.689 180.0 180.0	<i>cis</i> -l 2' 1.407 1.329 1.398 1.467 1.441 1.369 1.426 1.367 1.428 1.265 1.708 1.041 -165.2 -178.5	(2')S1         1.362         1.346         1.416         1.473         1.430         1.376         1.405         1.388         1.399         1.263         1.718         1.042         180.0         180.0	trans         trans         3'         1.411         1.342         1.382         1.486         1.459         1.360         1.436         1.361         1.435         1.242            1.011         -167.8         -177.1	-keto (3')S <sub>1</sub> 1.386 1.339 1.420 1.472 1.422 1.390 1.391 1.406 1.387 1.255  1.012 -179.8 -179.9	trans 4' 1.406 1.291 1.450 1.421 1.400 1.388 1.401 1.385 1.408 1.344 0.996 1.729 -23.84 178.7	-enol (4')S <sub>1</sub> 1.378 1.295 1.440 1.416 1.394 1.382 1.397 1.378 1.405 1.339 0.992 1.725 -31.41 174.5	<i>cis</i> -l <b>5'</b> 1.405 1.328 1.400 1.466 1.440 1.369 1.425 1.368 1.427 1.266 1.697 1.044 0.017 180.0	<pre>     (5')\$<sub>1</sub>     1.366     1.344     1.421     1.474     1.426     1.383     1.398     1.398     1.392     1.264     1.726     1.040     0.001     -180.0 </pre>	trans 6' 1.40948 1.34130 1.38340 1.48514 1.45816 1.36038 1.43508 1.43508 1.43457 1.24248  1.01192 0.000 180.0	-keto (6')S <sub>1</sub> 1.38814 1.33999 1.42156 1.47176 1.41856 1.39498 1.38723 1.41121 1.38465 1.25746  1.01242 0.005 -179.999

**Table S2** Excitation energies (eV), oscillator strengths *f* and largest excitation coefficients for the *trans*-enol, *cisketo* 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
4 (4/)a	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.68	3.28	0.3832	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.67	3.35	0.1892
(trans-enol)	S <sub>2</sub>	$78 \rightarrow 80$	0.59	3.88	0.1329	S <sub>2</sub>	$78 \rightarrow 80$	0.49	3.83	0.0987
	S <sub>3</sub>	$78 \rightarrow 81$	0.47	3.99	0.0070	S <sub>3</sub>	$77 \rightarrow 79$	0.56	3.93	1.0273
2 (21)	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.64	3.05	0.5349	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.61	3.03	0.6728
(cis-keto)	S <sub>2</sub>	$77 \rightarrow 79$	0.53	3.45	0.0181	S <sub>2</sub>	$77 \rightarrow 79$	0.54	3.41	0.1128
	<b>S</b> <sub>3</sub>	$74 \rightarrow 79$	0.47	3.88	0.0077	S <sub>3</sub>	$78 \rightarrow 80$	0.47	3.77	0.0162
2 (21)	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.62	2.93	0.6470	S <sub>1</sub>	$78 \rightarrow 79$	0.60	2.87	0.6288
<b>3 (3')</b>	S <sub>2</sub>	$77 \rightarrow 79$	0.48	3.42	0.0390	S <sub>2</sub>	$77 \rightarrow 79$	0.49	3.39	0.1608
	S <sub>3</sub>	$75 \rightarrow 79$	0.59	3.63	0.0008	S <sub>3</sub>	$75 \rightarrow 79$	0.63	3.59	0.0014
A (A')	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.69	3.36	0.2280	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.67	3.34	0.3284
(trans-enol)	S <sub>2</sub>	$78 \rightarrow 80$	0.63	3.78	0.0203	S <sub>2</sub>	$78 \rightarrow 80$	0.59	3.71	0.3260
	S <sub>3</sub>	$78 \rightarrow 81$	0.52	3.99	0.0122	S <sub>3</sub>	$77 \rightarrow 79$	0.61	3.92	0.8862
F (F/)	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.61	3.22	0.4963	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.61	3.06	0.6930
(cis-keto)	S <sub>2</sub>	$77 \rightarrow 79$	0.47	3.48	0.0231	S <sub>2</sub>	$78 \rightarrow 80$	0.53	3.47	0.2035
(03-Ket0)	S <sub>3</sub>	$78 \rightarrow 80$	0.39	3.83	0.0047	S <sub>3</sub>	$77 \rightarrow 79$	0.42	3.70	0.0430
C (CI)	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.55	3.06	0.4641	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.60	2.90	0.9012
	S <sub>2</sub>	$78 \rightarrow 80$	0.49	3.43	0.0586	S <sub>2</sub>	$78 \rightarrow 80$	0.56	3.42	0.0684
(trans-keto)	S <sub>3</sub>	75  ightarrow 79	0.59	3.67	0.0001	S <sub>3</sub>	$75 \rightarrow 79$	0.64	3.62	0.0001
				Α.	Cyclohex	ane				
1 (1')	S <sub>1</sub>	$78 \rightarrow 79$	0.68	3.26	0.4054	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.67	3.34	0.2039
(trans-enol)	S <sub>2</sub>	$78 \rightarrow 80$	0.58	3.85	0.1233	S <sub>2</sub>	$78 \rightarrow 80$	0.52	3.83	0.1621
	S <sub>3</sub>	$78 \rightarrow 81$	0.48	3.98	0.0048	S <sub>3</sub>	$77 \rightarrow 79$	0.57	3.89	0.9548
2 (2')	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.64	2.99	0.5558	S <sub>1</sub>	$78 \rightarrow 79$	0.63	2.98	0.7245
( <i>cis</i> -keto)	S <sub>2</sub>	$77 \rightarrow 79$	0.55	3.41	0.0215	S <sub>2</sub>	$77 \rightarrow 79$	0.56	3.40	0.0960
	S <sub>3</sub>	$74 \rightarrow 79$	0.51	3.75	0.0011	S <sub>3</sub>	$75 \rightarrow 79$	0.59	3.71	0.0061
3 (3')	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.63	2.88	0.6742	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.62	2.84	0.6483
( <i>trans</i> -keto)	S <sub>2</sub>	$77 \rightarrow 79$	0.43	3.40	0.0295	S <sub>2</sub>	$77 \rightarrow 79$	0.45	3.38	0.1459
(,	S <sub>3</sub>	$76 \rightarrow 79$	0.49	3.42	0.0074	<b>S</b> <sub>3</sub>	$75 \rightarrow 79$	0.56	3.39	0.0379
<b>4</b> ( <b>4</b> ')	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.69	3.35	0.2482	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.67	3.32	0.3549
(trans-enol)	S <sub>2</sub>	$78 \rightarrow 80$	0.63	3.75	0.0218	S <sub>2</sub>	$78 \rightarrow 80$	0.60	3.70	0.4262
(	S <sub>3</sub>	$78 \rightarrow 81$	0.52	3.98	0.0101	S <sub>3</sub>	$77 \rightarrow 79$	0.60	3.89	0.7539
5 (5')	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.60	3.18	0.5275	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.62	3.00	0.7227
(cis-keto)	S <sub>2</sub>	$77 \rightarrow 79$	0.49	3.46	0.0211	S <sub>2</sub>	$78 \rightarrow 80$	0.54	3.44	0.1973
(0.0 /(0.0)	S <sub>3</sub>	$75 \rightarrow 80$	0.38	3.75	0.0014	S <sub>3</sub>	$77 \rightarrow 79$	0.46	3.70	0.0465
6 (5')	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.58	3.01	0.5053	<b>S</b> <sub>1</sub>	$78 \rightarrow 79$	0.61	2.90	0.9040
(trans-keto)	S <sub>2</sub>	$78 \rightarrow 80$	0.45	3.41	0.0537	S <sub>2</sub>	$78 \rightarrow 80$	0.56	3.39	0.0750
	S <sub>3</sub>	$76 \rightarrow 79$	0.53	3.46	0.0002	S <sub>3</sub>	$75 \rightarrow 79$	0.62	3.43	0.0001

<sup>a</sup> 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 ( $\phi_i$ , degrees) of the *trans*-enol ((1)S<sub>1</sub>, (1')S<sub>1</sub>), twisted-enol ((1)S<sub>1-Tw</sub>, (1')S<sub>1-Tw</sub>), *cis*-keto ((2)S<sub>1</sub>, (2')S<sub>1</sub>), twisted-keto ((2)S<sub>1-Tw</sub>, (2')S<sub>1-Tw</sub>) and *trans*-keto ((3)S<sub>1</sub>, (3')S<sub>1</sub>) forms.

		1-AntSA <sup>a</sup>	
Structure	Acetonitrile	Methanol	Cyclohexane
(1)6	RE: 0.04, IMHB: 1.68	RE: 0.08, IMHB: 1.68	RE: 6.38, IMHB: 1.69
(1)51	φ <sub>1</sub> : -11.9, φ <sub>2</sub> : 173, φ <sub>3</sub> : -1.87	$\phi_1$ : -11.9, $\phi_2$ : 173, $\phi_3$ : -1.87	φ <sub>1</sub> : -13.9, φ <sub>2</sub> : 173, φ <sub>3</sub> : -2.48
(4)0	RE: 0.00, IMHB: 1.90	RE: 0.00, IMHB: 1.91	RE: 0.00, IMHB: 1.93
(1)S <sub>1-Tw</sub>	φ <sub>1</sub> : 1.55, φ <sub>2</sub> : 91.6, φ <sub>3</sub> : 7.79	φ <sub>1</sub> : 1.54, φ <sub>2</sub> : 91.6, φ <sub>3</sub> : 7.78	φ <sub>1</sub> : 1.06, φ <sub>2</sub> : 90.5, φ <sub>3</sub> : 7.14
(2) (	RE: 0.00, IMHB: 1.68	RE: 0.05, IMHB: 1.68	RE: 7.88, IMHB: 1.64
(2)S <sub>1</sub>	φ <sub>1</sub> : -0.02, φ <sub>2</sub> : 180, φ <sub>3</sub> : 0.00	φ <sub>1</sub> : -0.02, φ <sub>2</sub> : 180, φ <sub>3</sub> : 0.00	φ <sub>1</sub> : 0.00, φ <sub>2</sub> : -180, φ <sub>3</sub> : 0.00
(2)0	RE: 7.63	RE: 7.62	RE: 6.61
(2)S <sub>1-Tw</sub>	φ <sub>1</sub> : 12.0, φ <sub>2</sub> : -172, φ <sub>3</sub> : -79.5	φ <sub>1</sub> : 12.0, φ <sub>2</sub> : -172, φ <sub>3</sub> : -79.5	φ <sub>1</sub> : 14.3, φ <sub>2</sub> : -171φ <sub>3</sub> : -80.1
(2) (	RE: 5.08	RE: 5.15	RE: 15.7
(3)51	φ <sub>1</sub> : -9.55, φ <sub>2</sub> : 175, φ <sub>3</sub> : 175	φ <sub>1</sub> : -9.55, φ <sub>2</sub> : 175, φ <sub>3</sub> : 175	$\phi_1$ : -14.0, $\phi_2$ : 173, $\phi_3$ : 173
(4)0	RE: 0.00, IMHB: 1.70	RE: 0.00, IMHB: 1.70	RE: 5.84, IMHB: 1.73
(4)51	φ <sub>1</sub> : -155, φ <sub>2</sub> : -171, φ <sub>3</sub> : 1.61	φ <sub>1</sub> : -155, φ <sub>2</sub> : -172, φ <sub>3</sub> : 1.63	φ <sub>1</sub> : -151, φ <sub>2</sub> : -170, φ <sub>3</sub> : 2.01
(4)6	RE: 0.21, IMHB: 1.91	RE: 0.16, IMHB: 1.91	RE: 0.00, IMHB: 1.93
(4)S <sub>1-Tw</sub>	φ <sub>1</sub> : 179, φ <sub>2</sub> : -96.3, φ <sub>3</sub> : -5.38	$\phi_1$ : 179, $\phi_2$ : -96.3, $\phi_3$ : -5.39	φ <sub>1</sub> : -179, φ <sub>2</sub> : -95.6, φ <sub>3</sub> : -4.39
(5)6	RE: 0.67, IMHB: 1.69	RE: 0.68, IMHB: 1.69	RE: 8.45, IMHB: 1.65
(5)51	$\phi_1$ : -164, $\phi_2$ : 180, $\phi_3$ : 0.62	$\phi_1$ : -164, $\phi_2$ : 180, $\phi_3$ : 0.61	$\phi_1$ : -162, $\phi_2$ : 179, $\phi_3$ : 0.22
(5)6	RE: 5.98	RE: 5.92	RE: 4.33
(5)5 <sub>1-Tw</sub>	$\phi_1$ : -118, $\phi_2$ : -180, $\phi_3$ : 82.5	$\phi_1$ : -118, $\phi_2$ : -180, $\phi_3$ : 82.6	$\phi_1$ : -117, $\phi_2$ : -175, $\phi_3$ : 82.3
(6)5	RE: 4.61	RE: 4.64	RE: 14.6
(0)31	φ <sub>1</sub> : -156, φ <sub>2</sub> : -175, φ <sub>3</sub> : -171	φ <sub>1</sub> : -156, φ <sub>2</sub> : -175, φ <sub>3</sub> : -171	φ <sub>1</sub> : -153, φ <sub>2</sub> : -176, φ <sub>3</sub> : -171
		2-AntSA <sup>a</sup>	
Structure	Acetonitrile	Methanol	Cyclohexane
(1')5,	RE: 1.21, IMHB: 1.67	RE: 1.19, IMHB: 1.67	RE: 7.15, IMHB: 1.69
(1)01	φ <sub>1</sub> : 180, φ <sub>2</sub> : 180, φ <sub>3</sub> : 0.00	φ <sub>1</sub> : 180, φ <sub>2</sub> : 180, φ <sub>3</sub> : 0.00	φ <sub>1</sub> : 180, φ <sub>2</sub> : 180, φ <sub>3</sub> : 0.00
(1')5	RE: 0.21, IMHB: 1.90	RE: 0.15, IMHB: 1.90	RE: 0.00, IMHB: 1.92
(1)91-1W	φ <sub>1</sub> : 178, φ <sub>2</sub> : -91.2, φ <sub>3</sub> : -8.28	φ <sub>1</sub> : 179, φ <sub>2</sub> : -91.2, φ <sub>3</sub> : -8.24	φ <sub>1</sub> : 179, φ <sub>2</sub> : -90.4, φ <sub>3</sub> : -8.11
(2')5.	RE: 0.00, IMHB: 1.75	RE: 0.00, IMHB: 1.75	RE: 7.79, IMHB: 1.72
(2)51	φ <sub>1</sub> : 180, φ <sub>2</sub> : 180, φ <sub>3</sub> : 0.00	φ <sub>1</sub> : 180, φ <sub>2</sub> : 180, φ <sub>3</sub> : 0.00	φ <sub>1</sub> : 180, φ <sub>2</sub> : 180, φ <sub>3</sub> : 0.00
(2')5	RE: 4.93	RE: 4.87	RE: 3.42
(2 )3 <sub>1-Tw</sub>	$\phi_1$ : -177, $\phi_2$ : -178, $\phi_3$ : 86.5	$\phi_1$ : -177, $\phi_2$ : -178, $\phi_3$ : 86.5	φ <sub>1</sub> : 173, φ <sub>2</sub> : 177, φ <sub>3</sub> : 81.6
(2')6	RE: 2.72	RE: 2.74	RE: 12.7
(5) 31	φ <sub>1</sub> : -180, φ <sub>2</sub> : -180, φ <sub>3</sub> : -180	φ <sub>1</sub> : -180, φ <sub>2</sub> : -180, φ <sub>3</sub> : -180	φ <sub>1</sub> : -180, φ <sub>2</sub> : -180, φ <sub>3</sub> : -180
(1)6	RE: 2.52, IMHB: 1.68	RE: 2.51, IMHB: 1.68	RE: 8.51, IMHB: 1.73
(4)31	$\phi_1$ : -15.9, $\phi_2$ : 174, $\phi_3$ : 0.34	$\phi_1$ : -15.8, $\phi_2$ : 174, $\phi_3$ : 0.34	$\phi_1$ : -31.4, $\phi_2$ : 175, $\phi_3$ : 0.30

(4′)S <sub>1-Tw</sub>	RE: 0.46, IMHB: 1.90	RE: 0.40, IMHB: 1.90	RE: 0.00, IMHB: 1.91
	φ <sub>1</sub> : 1.30, φ <sub>2</sub> : 93.0, φ <sub>3</sub> : 8.25	φ <sub>1</sub> : 1.29, φ <sub>2</sub> : 93.0, φ <sub>3</sub> : 8.24	φ <sub>1</sub> : 1.20, φ <sub>2</sub> : 91.7, φ <sub>3</sub> : 8.44
(5′)S1	RE: 0.00, IMHB: 1.76	RE: 0.00, IMHB: 1.76	RE: 7.54, IMHB: 1.73
	\$\overline{4}_1\$: 0.00, \$\overline{4}_2\$: -180, \$\overline{4}_3\$: 0.00	\$\overline{4}_1\$: 0.00, \$\overline{4}_2\$: -180, \$\overline{4}_3\$: 0.00	φ <sub>1</sub> : 0.00, φ <sub>2</sub> : -180, φ <sub>3</sub> : 0.00
(5′)S <sub>1-Tw</sub>	RE: 4.91	RE: 4.85	RE: 3.41
	φ <sub>1</sub> : -9.82, φ <sub>2</sub> : 177, φ <sub>3</sub> : 82.0	φ <sub>1</sub> : -9.84, φ <sub>2</sub> : 177, φ <sub>3</sub> : 82.1	φ <sub>1</sub> : -14.5, φ <sub>2</sub> : 178, φ <sub>3</sub> : 80.8
(6′)S1	RE: 2.37	RE: 2.40	RE: 12.5
	φ <sub>1</sub> : 0.00, φ <sub>2</sub> : 180, φ <sub>3</sub> : -180	φ <sub>1</sub> : 0.00, φ <sub>2</sub> : -180, φ <sub>3</sub> : 180	φ <sub>1</sub> : 0.00, φ <sub>2</sub> : -180, φ <sub>3</sub> : -180

<sup>a</sup> Relative energies were calculated independently for conformers **1**, **4**, **1**' and **4**', and their corresponding products using the most stable conformers as reference.