Supporting Information for

Phenol - Quinone Tautomerism in Arylazo Naphthols and the Analogous Schiff Bases: Benchmark Calculations

S. Tahir Ali,[a,c] Liudmil Antonov,[b] Walter M. F. Fabian[c,*]

[a]Department of Chemistry, Federal Urdu University of Arts, Science & Technology, Karachi, Sindh, Pakistan.

[b]Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

[c]Institut für Chemie, Karl-Franzens-Universität Graz, Heinrichstr. 28, A-8010 Graz, Austria

Table S1. Selected calculated [B3LYP/6-31+G(d,p), M06-2X/6-31+G(d,p), MP2/cc-pVDZ, IEFPCM(CH_3OH)-B3LYP/6-31+G(d,p)], and CAM-B3LYP/6-31+G(d,p) structural data of the investigated compounds.[a]

	B3LYP/6-31+G(d,p)									
1	**1aA**	**1aH**	**1bA**	**1bH**	**1cA**	**1cH**	**1dA**	**1dH**	**1eA**	**1eH**
C1 – O	1.369	1.236	1.367	1.235	1.365	1.234	1.362	1.233	1.361	1.232
C1 – C1a	1.426	1.485	1.426	1.485	1.426	1.485	1.426	1.485	1.427	1.485
C1 – C2	1.385	1.468	1.385	1.470	1.386	1.471	1.388	1.474	1.389	1.474
C2 – C3	1.404	1.356	1.403	1.355	1.402	1.354	1.400	1.352	1.399	1.351
C3 – C4	1.389	1.448	1.390	1.450	1.390	1.452	1.392	1.455	1.393	1.456
C4 – C4a	1.438	1.473	1.438	1.474	1.438	1.476	1.439	1.477	1.440	1.478
C1a – C4a	1.434	1.416	1.433	1.416	1.433	1.415	1.433	1.415	1.432	1.415
C4 – N	1.411	1.320	1.410	1.317	1.409	1.315	1.403	1.311	1.402	1.311
N – N	1.265	1.317	1.263	1.320	1.262	1.323	1.264	1.330	1.265	1.332
N – Cipso	1.405	1.406	1.411	1.406	1.417	1.403	1.415	1.394	1.415	1.391
Cpara – R	1.382	1.392	1.363	1.367	-	-	1.434	1.432	1.469	1.461
C1a – C1 – C2	120.9	116.5	120.9	116.6	121.0	116.6	121.1	116.7	121.1	116.7
C1 – C2 – C3	120.4	122.1	120.3	122.1	120.3	122.2	120.2	122.2	120.2	122.2
C2 – C1 – O	122.5	121.0	122.5	120.9	122.4	120.8	122.3	120.6	122.3	120.6
C2 – C3 – C4	121.2	122.5	121.2	122.4	121.1	122.4	121.1	122.3	121.1	122.2
C3 – C4 – C4a	119.5	118.1	119.6	118.1	119.7	118.1	119.7	118.1	119.8	118.1
C3 – C4 – N	124.0	125.1	123.9	125.0	123.8	125.1	123.7	125.1	123.6	125.1
C4 – N – N	115.5	121.8	115.6	121.8	115.8	121.8	116.1	121.5	116.1	121.3
N – N – Cipso	115.8	122.3	115.6	122.1	115.3	122.0	114.9	121.7	114.8	121.7
C3 – C4 – N – N	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N – N – Cipso – Cortho	0.1	-0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

	M06-2X/6-31+G(d,p)									
1	**1aA**	**1aH**	**1bA**	**1bH**	**1cA**	**1cH**	**1dA**	**1dH**	**1eA**	**1eH**
C1 – O	1.360	1.224	1.356	1.223	1.358	1.222	1.355	1.221	1.355	1.221
C1 – C1a	1.425	1.486	1.425	1.486	1.425	1.487	1.425	1.486	1.425	1.487
C1 – C2	1.378	1.475	1.378	1.476	1.379	1.477	1.380	1.479	1.381	1.480
C2 – C3	1.406	1.347	1.405	1.346	1.405	1.345	1.403	1.344	1.402	1.343
C3 – C4	1.380	1.455	1.380	1.457	1.380	1.458	1.382	1.461	1.382	1.462
C4 – C4a	1.432	1.474	1.432	1.475	1.432	1.477	1.432	1.478	1.432	1.479
C1a – C4a	1.422	1.406	1.422	1.406	1.422	1.405	1.422	1.404	1.421	1.405
C4 – N	1.418	1.305	1.418	1.303	1.417	1.301	1.412	1.298	1.411	1.297
N – N	1.248	1.313	1.247	1.316	1.246	1.319	1.247	1.327	1.247	1.329
N – Cipso	1.412	1.406	1.417	1.404	1.424	1.400	1.423	1.391	1.423	1.389
Cpara – R	1.377	1.390	1.356	1.361	-	-	1.439	1.437	1.472	1.463
C1a – C1 – C2	120.9	116.6	120.9	116.7	121.0	116.7	121.1	116.8	121.1	116.8
C1 – C2 – C3	120.2	122.0	120.2	122.0	120.1	122.1	120.1	122.1	120.0	122.1
C2 – C1 – O	122.9	121.0	122.8	120.9	122.8	120.9	122.8	120.7	122.8	120.7
C2 – C3 – C4	120.9	122.3	120.9	122.3	120.9	122.2	120.9	122.1	120.8	122.1
C3 – C4 – C4a	119.9	118.1	120.0	118.1	120.1	118.1	120.2	118.1	120.3	118.1
C3 – C4 – N	123.8	125.2	123.7	125.1	123.6	125.2	123.5	125.2	123.5	125.2
C4 – N – N	115.0	122.4	115.1	122.2	115.3	122.2	115.6	121.8	115.7	121.8
N – N – Cipso	115.3	121.2	115.1	121.1	114.7	121.0	114.3	120.7	114.1	120.7
C3 – C4 – N – N	-0.5	-0.4	-2.4	0.3	-4.7	0.3	-4.5	0.7	-5.6	0.5
N – N – Cipso – Cortho	-0.7	-1.8	-1.2	0.6	-5.4	0.8	-7.5	1.8	-11.0	1.0
	MP2/cc-pVDZ									
1	**1aA**	**1aH**	**1bA**	**1bH**	**1cA**	**1cH**	**1dA**	**1dH**	**1eA**	**1eH**
C1 – O	1.367	1.238	1.367	1.237	1.366	1.237	1.365	1.236	1.365	1.236
C1 – C1a	1.431	1.491	1.431	1.491	1.431	1.491	1.432	1.491	1.432	1.491

C1 – C2	1.395	1.475	1.395	1.476	1.395	1.477	1.396	1.478	1.395	1.478
C2 – C3	1.411	1.369	1.411	1.368	1.410	1.368	1.409	1.366	1.410	1.366
C3 – C4	1.398	1.450	1.398	1.451	1.398	1.453	1.399	1.455	1.398	1.455
C4 – C4a	1.438	1.471	1.438	1.471	1.438	1.472	1.438	1.474	1.438	1.474
C1a – C4a	1.440	1.421	1.439	1.421	1.439	1.420	1.439	1.420	1.439	1.420
C4 – N	1.416	1.337	1.416	1.336	1.416	1.334	1.413	1.331	1.414	1.331
N – N	1.286	1.318	1.284	1.319	1.282	1.322	1.283	1.327	1.282	1.327
N – Cipso	1.412	1.403	1.416	1.404	1.423	1.402	1.422	1.396	1.423	1.397
Cpara – R	1.394	1.401	1.364	1.366	-	-	1.443	1.442	1.481	1.476
C1a – C1 – C2	120.4	116.1	120.5	116.1	120.5	116.2	120.5	116.3	120.5	116.3
C1 – C2 – C3	120.7	122.3	120.6	122.3	120.6	122.3	120.6	122.3	120.6	122.2
C2 – C1 – O	123.2	121.4	123.2	121.3	123.2	121.2	123.2	121.1	123.2	121.1
C2 – C3 – C4	120.8	122.1	120.8	122.1	120.7	122.0	120.7	121.9	120.7	121.9
C3 – C4 – C4a	119.8	118.5	119.9	118.5	120.0	118.5	120.0	118.5	120.0	118.6
C3 – C4 – N	123.9	125.4	123.9	125.4	123.8	125.4	123.8	125.3	123.8	125.3
C4 – N – N	113.4	120.3	113.5	120.3	113.5	120.3	113.8	120.1	113.7	120.1
N – N – Cipso	113.6	121.4	113.4	121.3	113.2	121.2	112.9	120.8	112.9	120.8
C3 – C4 – N – N	12.7	-0.2	-7.2	0.3	-14.5	0.3	-13.5	0.4	-13.8	0.4
N – N – Cipso – Cortho	5.8	-0.6	-13.5	0.7	-12.5	0.8	-13.5	1.3	-14.0	1.0

	IEFPCM(CH3OH)-B3LYP/6-31+G(d,p)									
1	**1aA**	**1aH**	**1bA**	**1bH**	**1cA**	**1cH**	**1dA**	**1dH**	**1eA**	**1eH**
C1 – O	1.366	1.250	1.363	1.247	1.361	1.245	1.357	1.243	1.355	1.241
C1 – C1a	1.428	1.480	1.428	1.481	1.428	1.482	1.429	1.482	1.429	1.482
C1 – C2	1.386	1.456	1.387	1.460	1.388	1.462	1.390	1.465	1.392	1.467
C2 – C3	1.404	1.362	1.403	1.359	1.401	1.357	1.398	1.355	1.397	1.354
C3 – C4	1.391	1.439	1.391	1.443	1.392	1.446	1.395	1.450	1.397	1.452
C4 – C4a	1.440	1.468	1.439	1.471	1.439	1.473	1.441	1.475	1.442	1.476

C1a – C4a	1.435	1.420	1.434	1.419	1.434	1.418	1.433	1.417	1.432	1.416
C4 – N	1.410	1.330	1.409	1.324	1.407	1.320	1.400	1.315	1.395	1.313
N – N	1.270	1.306	1.265	1.310	1.264	1.314	1.266	1.323	1.269	1.327
N – Cipso	1.400	1.406	1.410	1.407	1.418	1.405	1.416	1.393	1.413	1.387
Cpara – R	1.370	1.382	1.360	1.366	-	-	1.432	1.430	1.458	1.447
C1a – C1 – C2	120.8	116.7	120.9	116.8	120.9	116.9	121.0	117.0	121.1	117.0
C1 – C2 – C3	120.3	122.2	120.2	122.2	120.2	122.2	120.1	122.2	120.1	122.2
C2 – C1 – O	122.6	121.2	122.5	121.0	122.5	120.9	122.4	120.7	122.3	120.7
C2 – C3 – C4	121.5	122.3	121.4	122.2	121.4	122.2	121.3	122.1	121.3	122.0
C3 – C4 – C4a	119.3	118.2	119.5	118.3	119.6	118.2	119.6	118.3	119.7	118.3
C3 – C4 – N	124.3	125.3	124.2	125.2	124.0	125.2	123.9	125.2	123.8	125.2
C4 – N – N	115.8	122.0	116.1	122.2	116.3	122.1	116.5	121.8	116.6	121.5
N – N – Cipso	116.1	122.5	115.6	122.0	115.3	121.9	114.8	121.5	114.6	121.4
C3 – C4 – N – N	0.0	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
N – N – Cipso – Cortho	0.0	-0.3	0.0	0.1	0.0	0.0	-0.1	0.0	0.0	0.1

	CAM-B3LYP/6-31+G(d,p)									
1	**1aA**	**1aH**	**1bA**	**1bH**	**1cA**	**1cH**	**1dA**	**1dH**	**1eA**	**1eH**
C1 – O	1.363	1.227	1.361	1.226	1.360	1.225	1.357	1.224	1.356	1.223
C1 – C1a	1.422	1.483	1.422	1.483	1.423	1.483	1.423	1.483	1.423	1.483
C1 – C2	1.375	1.470	1.376	1.471	1.376	1.472	1.378	1.474	1.378	1.475
C2 – C3	1.404	1.344	1.403	1.344	1.402	1.343	1.400	1.341	1.400	1.341
C3 – C4	1.378	1.453	1.378	1.455	1.378	1.456	1.380	1.459	1.381	1.460
C4 – C4a	1.431	1.474	1.431	1.475	1.431	1.476	1.432	1.478	1.432	1.478
C1a – C4a	1.422	1.406	1.422	1.405	1.422	1.405	1.421	1.405	1.421	1.405
C4 – N	1.415	1.303	1.415	1.301	1.414	1.299	1.409	1.296	1.407	1.296
N – N	1.250	1.315	1.248	1.318	1.247	1.321	1.249	1.329	1.249	1.331
N – Cipso	1.409	1.406	1.415	1.405	1.421	1.401	1.420	1.391	1.420	1.388
Cpara – R	1.378	1.391	1.358	1.363	-	-	1.436	1.434	1.467	1.459

C1a – C1 – C2	120.9	116.7	121.0	116.8	121.0	116.8	121.1	116.9	121.1	116.9
C1 – C2 – C3	120.2	122.0	120.2	122.0	120.1	122.0	120.1	122.1	120.0	122.1
C2 – C1 – O	122.7	120.8	122.6	120.8	122.6	120.7	122.5	120.5	122.5	120.5
C2 – C3 – C4	121.1	122.5	121.0	122.4	121.0	122.4	121.0	122.3	121.0	122.2
C3 – C4 – C4a	119.8	118.0	119.9	118.0	120.0	118.0	120.0	118.0	120.1	118.0
C3 – C4 – N	123.8	124.9	123.6	124.9	123.6	125.0	123.4	125.0	123.4	125.0
C4 – N – N	115.5	122.3	115.6	122.2	115.7	122.1	116.0	121.7	116.1	121.6
N – N – Cipso	115.7	121.7	115.6	121.5	115.2	121.5	114.8	121.2	114.7	121.2
C3 – C4 – N – N	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N – N – Cipso – Cortho	0.1	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	B3LYP/6-31+G(d,p)									
2	**2aA**	**2aH**	**2bA**	**2bH**	**2cA**	**2cH**	**2dA**	**2dH**	**2eA**	**2eH**
C2 – O	1.340	1.265	1.338	1.262	1.336	1.260	1.333	1.257	1.322	1.256
C1 – C1a	1.445	1.462	1.446	1.464	1.447	1.466	1.449	1.468	1.450	1.469
C1 – C2	1.413	1.467	1.414	1.470	1.416	1.474	1.420	1.480	1.421	1.483
C2 – C3	1.418	1.451	1.418	1.451	1.419	1.452	1.418	1.452	1.418	1.452
C3 – C4	1.372	1.360	1.372	1.359	1.372	1.358	1.372	1.358	1.372	1.358
C4 – C4a	1.429	1.443	1.426	1.444	1.427	1.445	1.427	1.446	1.428	1.447
C1a – C4a	1.430	1.423	1.430	1.422	1.429	1.421	1.428	1.420	1.428	1.420
C1 – N	1.389	1.338	1.387	1.334	1.384	1.330	1.377	1.325	1.375	1.323
N – N	1.278	1.302	1.276	1.304	1.276	1.307	1.280	1.313	1.281	1.316
N – Cipso	1.402	1.401	1.408	1.403	1.413	1.403	1.410	1.395	1.409	1.393
Cpara – R	1.379	1.387	1.362	1.365	-	-	1.433	1.432	1.469	1.464
C1a – C1 – C2	119.3	120.4	119.4	120.3	119.5	120.2	119.5	120.0	119.5	120.0
C1 – C2 – C3	120.4	117.3	120.4	117.4	120.3	117.4	120.3	117.4	120.3	117.5
C1 – C2 – O	122.0	121.6	122.0	121.5	121.9	121.5	121.9	121.3	121.8	121.2
C2 – C3 – C4	120.5	121.4	120.4	121.4	120.3	121.3	120.2	121.3	120.2	121.2
C3 – C4 – C4a	121.5	122.6	121.6	122.7	121.8	122.7	121.9	122.9	122.0	122.9

C2 – C1 – N	124.0	122.8	123.9	122.8	123.8	122.9	123.7	123.0	123.6	123.1
C1 – N – N	116.8	119.2	116.9	119.4	117.0	119.7	117.2	119.7	117.2	119.7
N – N – Cipso	116.9	122.0	116.6	121.8	116.5	121.7	116.1	121.4	116.0	121.3
C2 – C1 – N – N	0.1	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N – N – Cipso – Cortho	0.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	M06-2X/6-31+G(d,p)									
2	**2aA**	**2aH**	**2bA**	**2bH**	**2cA**	**2cH**	**2dA**	**2dH**	**2eA**	**2eH**
C2 – O	1.335	1.248	1.333	1.247	1.331	1.244	1.328	1.241	1.328	1.241
C1 – C1a	1.439	1.463	1.440	1.465	1.440	1.467	1.443	1.470	1.443	1.471
C1 – C2	1.401	1.466	1.402	1.469	1.403	1.473	1.406	1.480	1.408	1.482
C2 – C3	1.420	1.458	1.420	1.458	1.420	1.459	1.420	1.459	1.420	1.459
C3 – C4	1.366	1.351	1.365	1.350	1.365	1.349	1.365	1.349	1.365	1.349
C4 – C4a	1.425	1.449	1.426	1.449	1.426	1.451	1.427	1.452	1.428	1.453
C1a – C4a	1.420	1.412	1.420	1.412	1.419	1.411	1.418	1.410	1.418	1.410
C1 – N	1.396	1.325	1.394	1.322	1.391	1.318	1.385	1.312	1.383	1.311
N – N	1.259	1.293	1.258	1.295	1.258	1.299	1.261	1.307	1.262	1.309
N – Cipso	1.410	1.404	1.414	1.404	1.420	1.403	1.417	1.395	1.416	1.392
Cpara – R	1.374	1.384	1.355	1.359	-	-	1.439	1.437	1.471	1.466
C1a – C1 – C2	119.6	120.5	119.7	120.4	119.8	120.3	119.8	120.1	119.8	120.0
C1 – C2 – C3	120.2	117.1	120.2	117.2	120.1	117.2	120.1	117.3	120.2	117.3
C1 – C2 – O	122.7	121.8	122.7	121.8	122.6	121.7	122.6	121.5	122.5	121.5
C2 – C3 – C4	120.4	121.3	120.4	121.2	120.3	121.2	120.2	121.1	120.1	121.1
C3 – C4 – C4a	121.4	122.7	121.5	122.8	121.6	122.9	121.8	123.0	121.8	123.0
C2 – C1 – N	124.1	122.7	124.0	122.7	123.8	122.9	123.7	123.0	123.6	123.0
C1 – N – N	116.7	120.5	116.7	120.4	116.9	120.8	117.2	120.7	117.1	120.7
N – N – Cipso	116.4	121.0	116.2	121.0	115.9	120.8	115.5	120.5	115.5	120.5
C2 – C1 – N – N	-0.2	0.0	0.5	0.0	0.0	0.0	0.4	0.0	-0.2	0.2
N – N – Cipso – Cortho	-0.5	0.5	1.2	-0.3	0.0	0.0	1.3	0.0	-0.9	0.2

	MP2/cc-pVDZ									
2	**2aA**	**2aH**	**2bA**	**2bH**	**2cA**	**2cH**	**2dA**	**2dH**	**2eA**	**2eH**
C2 – O	1.341	1.269	1.341	1.267	1.340	1.263	1.339	1.261	1.340	1.260
C1 – C1a	1.447	1.460	1.447	1.462	1.448	1.463	1.449	1.465	1.448	1.465
C1 – C2	1.421	1.464	1.420	1.467	1.420	1.471	1.421	1.476	1.420	1.476
C2 – C3	1.424	1.459	1.424	1.460	1.425	1.461	1.425	1.462	1.425	1.462
C3 – C4	1.383	1.370	1.383	1.369	1.382	1.368	1.382	1.367	1.382	1.367
C4 – C4a	1.431	1.448	1.431	1.449	1.431	1.450	1.432	1.452	1.432	1.452
C1a – C4a	1.436	1.427	1.436	1.427	1.436	1.426	1.435	1.426	1.435	1.426
C1 – N	1.394	1.353	1.394	1.351	1.393	1.348	1.390	1.345	1.391	1.345
N – N	1.299	1.308	1.297	1.308	1.294	1.310	1.294	1.313	1.293	1.313
N – Cipso	1.406	1.398	1.411	1.400	1.417	1.402	1.417	1.398	1.418	1.399
Cpara – R	1.390	1.395	1.361	1.364	-	-	1.443	1.442	1.482	1.478
C1a – C1 – C2	119.7	120.9	119.7	120.9	119.8	120.8	119.8	120.7	119.8	120.7
C1 – C2 – C3	119.6	116.9	119.6	116.9	119.6	116.9	119.7	117.0	119.7	117.0
C1 – C2 – O	122.9	122.3	122.9	122.2	122.9	122.2	122.9	122.1	123.0	122.1
C2 – C3 – C4	121.1	121.7	121.0	121.7	121.0	121.6	120.9	121.5	120.9	121.5
C3 – C4 – C4a	121.1	122.1	121.2	122.1	121.2	122.2	121.3	122.3	121.3	122.4
C2 – C1 – N	124.5	122.7	124.5	122.8	124.4	122.9	124.4	122.9	124.4	123.0
C1 – N – N	115.0	116.7	115.1	116.9	115.2	117.3	115.5	117.5	115.5	117.6
N – N – Cipso	115.1	121.2	114.8	121.0	114.7	121.0	114.4	120.6	114.3	120.6
C2 – C1 – N – N	-0.2	0.1	0.0	0.0	0.8	0.0	1.5	0.0	-1.8	0.0
N – N – Cipso – Cortho	-1.2	0.5	0.0	0.0	4.3	0.0	7.6	0.1	-9.6	0.0
	IEFPCM(CH_3OH)-B3LYP/6-31+G(d,p)									
2	**2aA**	**2aH**	**2bA**	**2bH**	**2cA**	**2cH**	**2dA**	**2dH**	**2eA**	**2eH**
C2 – O	1.348	1.276	1.344	1.271	1.342	1.268	1.337	1.263	1.335	1.261
C1 – C1a	1.446	1.462	1.446	1.465	1.447	1.467	1.450	1.470	1.451	1.471
C1 – C2	1.412	1.460	1.414	1.466	1.415	1.470	1.420	1.478	1.423	1.483

C2 – C3	1.417	1.446	1.417	1.447	1.417	1.448	1.417	1.448	1.416	1.448
C3 – C4	1.374	1.363	1.374	1.362	1.373	1.361	1.373	1.360	1.373	1.360
C4 – C4a	1.426	1.440	1.427	1.442	1.427	1.443	1.428	1.445	1.429	1.446
C1a – C4a	1.432	1.424	1.431	1.423	1.431	1.422	1.429	1.421	1.429	1.421
C1 – N	1.392	1.344	1.389	1.337	1.386	1.333	1.377	1.325	1.373	1.322
N – N	1.281	1.298	1.277	1.300	1.276	1.303	1.280	1.312	1.283	1.316
N – Cipso	1.398	1.401	1.407	1.405	1.414	1.406	1.410	1.396	1.406	1.390
Cpara – R	1.370	1.378	1.362	1.365	-	-	1.432	1.430	1.455	1.449
C1a – C1 – C2	119.1	120.3	119.3	120.2	119.4	120.1	119.4	119.9	119.3	119.8
C1 – C2 – C3	120.7	117.6	120.6	117.6	120.6	117.6	120.5	117.6	120.5	117.7
C1 – C2 – O	121.6	121.4	121.6	121.3	121.6	121.3	121.5	121.1	121.4	121.0
C2 – C3 – C4	120.4	121.5	120.3	121.4	120.2	121.4	120.1	121.3	120.1	121.3
C3 – C4 – C4a	121.3	122.3	121.5	122.5	121.6	122.6	121.8	122.7	121.9	122.8
C2 – C1 – N	124.2	123.2	124.0	123.2	123.8	123.3	123.7	123.4	123.6	123.5
C1 – N – N	116.5	119.7	116.8	120.1	116.9	120.3	117.1	120.4	117.2	120.4
N – N – Cipso	117.6	122.4	117.1	122.0	116.9	121.8	116.3	121.3	116.2	121.2
C2 – C1 – N – N	0.0	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
N – N – Cipso – Cortho	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.1	0.1
	CAM-B3LYP/6-31+G(d,p)									
2	**2aA**	**2aH**	**2bA**	**2bH**	**2cA**	**2cH**	**2dA**	**2dH**	**2eA**	**2eH**
C2 – O	1.335	1.254	1.334	1.252	1.331	1.249	1.329	1.247	1.328	1.246
C1 – C1a	1.439	1.462	1.440	1.464	1.441	1.466	1.443	1.469	1.444	1.469
C1 – C2	1.400	1.460	1.401	1.464	1.402	1.468	1.405	1.475	1.407	1.477
C2 – C3	1.417	1.453	1.417	1.453	1.418	1.454	1.417	1.453	1.417	1.453
C3 – C4	1.363	1.349	1.363	1.349	1.363	1.348	1.362	1.348	1.362	1.347
C4 – C4a	1.424	1.445	1.424	1.446	1.425	1.447	1.426	1.449	1.426	1.449
C1a – C4a	1.419	1.411	1.419	1.410	1.418	1.410	1.417	1.409	1.417	1.409

C1 – N	1.392	1.326	1.390	1.323	1.387	1.319	1.380	1.312	1.378	1.311
N – N	1.261	1.293	1.260	1.296	1.261	1.300	1.264	1.308	1.265	1.310
N – Cipso	1.408	1.405	1.412	1.405	1.417	1.404	1.415	1.395	1.414	1.393
Cpara – R	1.376	1.385	1.356	1.360	-	-	1.436	1.434	1.467	1.461
C1a – C1 – C2	119.6	120.3	119.7	120.3	119.7	120.1	119.7	119.9	119.7	119.9
C1 – C2 – C3	120.3	117.4	120.3	117.4	120.2	117.4	120.2	117.5	120.2	117.5
C1 – C2 – O	122.4	121.7	123.8	121.6	122.4	121.6	122.3	121.4	122.2	121.3
C2 – C3 – C4	120.4	121.3	120.3	121.2	120.2	121.2	120.1	121.1	120.1	121.1
C3 – C4 – C4a	121.5	122.7	121.6	122.8	121.7	122.8	121.9	123.0	121.9	123.0
C2 – C1 – N	123.9	122.6	123.8	122.7	123.7	122.8	123.5	122.9	123.5	122.9
C1 – N – N	116.9	120.0	117.1	120.1	117.1	120.3	117.4	120.3	117.4	120.3
N – N – Cipso	116.8	121.6	116.5	121.4	116.3	121.3	115.9	121.0	115.8	120.9
C2 – C1 – N – N	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N – N – Cipso – Cortho	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

	B3LYP/6-31+G(d,p)									
3	**3aA**	**3aH**	**3bA**	**3bH**	**3cA**	**3cH**	**3dA**	**3dH**	**3eA**	**3eH**
C1 – O	1.340	1.262	1.338	1.260	1.336	1.257	1.333	1.254	1.332	1.253
C1 – C1a	1.431	1.469	1.431	1.470	1.431	1.471	1.431	1.470	1.431	1.470
C1 – C2	1.411	1.465	1.412	1.468	1.413	1.472	1.417	1.478	1.418	1.480
C2 – C3	1.427	1.441	1.427	1.442	1.428	1.444	1.430	1.445	1.431	1.446
C3 – C4	1.369	1.359	1.368	1.358	1.368	1.357	1.366	1.356	1.366	1.355
C4 – C4a	1.429	1.445	1.429	1.446	1.430	1.448	1.432	1.449	1.432	1.450
C1a – C4a	1.431	1.423	1.431	1.422	1.431	1.422	1.431	1.421	1.431	1.421
C2 – N	1.393	1.341	1.391	1.338	1.389	1.334	1.382	1.329	1.380	1.327
N – N	1.277	1.302	1.275	1.304	1.274	1.307	1.278	1.313	1.279	1.316
N – Cipso	1.403	1.401	1.409	1.403	1.415	1.403	1.411	1.396	1.410	1.393
Cpara – R	1.381	1.387	1.362	1.365	-	-	1.433	1.432	1.469	1.464
C1a – C1 – C2	120.2	117.1	120.1	117.1	120.1	117.1	120.1	117.1	120.1	117.2

C1 – C2 – C3	119.2	120.1	119.3	120.0	119.4	119.9	119.4	119.8	119.4	119.7
C2 – C1 – O	121.5	121.3	121.5	121.3	121.5	121.2	121.4	121.0	121.4	121.0
C2 – C3 – C4	121.5	121.6	121.4	121.5	121.4	121.5	121.3	121.4	121.2	121.4
C3 – C4 – C4a	120.3	120.9	120.4	121.0	120.4	121.1	120.5	121.3	120.5	121.4
C1 – C2 – N	124.8	123.7	124.7	123.7	124.6	123.8	124.5	123.9	124.4	124.0
C2 – N – N	116.4	118.9	116.6	119.1	116.6	119.3	116.8	119.3	116.9	119.3
N – N – Cipso	116.9	122.0	116.6	121.7	116.4	121.6	116.0	121.3	115.9	121.2
C1 – C2 – N – N	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N – N – Cipso – Cortho	-0.3	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	M06-2X/6-31+G(d,p)									
3	**3aA**	**3aH**	**3bA**	**3bH**	**3cA**	**3cH**	**3dA**	**3dH**	**3eA**	**3eH**
C1 – O	1.335	1.246	1.333	1.244	1.331	1.242	1.328	1.239	1.328	1.238
C1 – C1a	1.430	1.475	1.430	1.475	1.431	1.475	1.430	1.475	1.430	1.475
C1 – C2	1.398	1.464	1.400	1.467	1.400	1.471	1.403	1.478	1.404	1.479
C2 – C3	1.424	1.445	1.424	1.446	1.425	1.448	1.427	1.450	1.427	1.450
C3 – C4	1.364	1.350	1.363	1.349	1.363	1.348	1.361	1.347	1.361	1.347
C4 – C4a	1.427	1.450	1.428	1.451	1.429	1.453	1.430	1.455	1.430	1.455
C1a – C4a	1.420	1.413	1.420	1.412	1.420	1.412	1.420	1.411	1.420	1.411
C2 – N	1.399	1.328	1.398	1.324	1.396	1.321	1.389	1.315	1.388	1.314
N – N	1.258	1.292	1.257	1.295	1.256	1.299	1.259	1.306	1.260	1.308
N – Cipso	1.411	1.406	1.415	1.406	1.421	1.404	1.418	1.395	1.418	1.394
Cpara – R	1.375	1.384	1.355	1.359	-	-	1.439	1.437	1.472	1.467
C1a – C1 – C2	119.8	116.6	119.7	116.6	119.7	116.7	119.7	116.7	119.7	116.8
C1 – C2 – C3	119.7	120.3	119.8	120.2	119.9	120.0	119.8	119.9	119.8	119.8
C2 – C1 – O	122.4	121.8	122.4	121.7	122.4	121.7	122.3	121.5	122.3	121.5
C2 – C3 – C4	121.5	121.6	121.4	121.6	121.3	121.6	121.2	121.5	121.2	121.4
C3 – C4 – C4a	120.0	120.7	120.0	120.8	120.0	121.0	120.1	121.2	120.1	121.2
C1 – C2 – N	124.7	123.7	124.6	123.7	124.5	123.8	124.4	123.9	124.4	123.9

C2 – N – N	116.4	120.4	116.3	120.5	116.6	120.5	116.8	120.5	116.9	120.4
N – N – Cipso	116.2	120.8	116.2	120.5	115.8	120.7	115.4	120.3	115.2	120.5
C1 – C2 – N – N	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0
N – N – Cipso – Cortho	-0.3	0.2	0.0	0.2	0.0	0.0	0.0	-0.1	0.7	0.0
	MP2/cc-pVDZ									
3	**3aA**	**3aH**	**3bA**	**3bH**	**3cA**	**3cH**	**3dA**	**3dH**	**3eA**	**3eH**
C1 – O	1.342	1.265	1.341	1.263	1.340	1.260	1.340	1.258	1.340	1.258
C1 – C1a	1.436	1.477	1.436	1.477	1.436	1.479	1.436	1.479	1.436	1.479
C1 – C2	1.417	1.464	1.417	1.466	1.417	1.470	1.418	1.475	1.417	1.475
C2 – C3	1.432	1.443	1.432	1.444	1.432	1.445	1.433	1.446	1.433	1.446
C3 – C4	1.380	1.371	1.379	1.370	1.379	1.369	1.378	1.369	1.378	1.369
C4 – C4a	1.433	1.449	1.433	1.450	1.433	1.451	1.434	1.453	1.434	1.453
C1a – C4a	1.437	1.427	1.437	1.426	1.437	1.426	1.436	1.425	1.436	1.425
C2 – N	1.398	1.355	1.398	1.353	1.397	1.350	1.394	1.347	1.395	1.348
N – N	1.297	1.308	1.295	1.309	1.293	1.310	1.292	1.314	1.291	1.313
N – Cipso	1.407	1.399	1.412	1.401	1.419	1.403	1.418	1.398	1.420	1.399
Cpara – R	1.390	1.396	1.361	1.364	-	-	1.443	1.442	1.482	1.478
C1a – C1 – C2	119.5	116.7	119.4	116.7	119.4	116.7	119.5	116.7	119.5	116.7
C1 – C2 – C3	119.8	120.8	119.9	120.7	120.0	120.6	120.0	120.5	120.0	120.6
C2 – C1 – O	122.6	122.1	122.6	122.1	122.6	122.0	122.6	121.9	122.6	121.9
C2 – C3 – C4	121.4	121.2	121.3	121.2	121.2	121.2	121.1	121.1	121.1	121.1
C3 – C4 – C4a	120.1	120.8	120.1	120.8	120.1	120.9	120.2	121.1	120.2	121.1
C1 – C2 – N	125.1	123.5	125.1	123.5	125.0	123.6	125.0	123.7	125.0	123.7
C2 – N – N	114.7	116.6	114.8	116.8	114.9	117.1	115.2	117.3	115.2	117.3
N – N – Cipso	115.0	121.1	114.7	120.9	114.6	120.9	114.3	120.5	114.3	120.5
C1 – C2 – N – N	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.0	0.0
N – N – Cipso – Cortho	-0.6	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

	IEFPCM(CH_3OH)-B3LYP/6-31+G(d,p)									
3	**3aA**	**3aH**	**3bA**	**3bH**	**3cA**	**3cH**	**3dA**	**3dH**	**3eA**	**3eH**
C1 – O	1.346	1.271	1.343	1.266	1.340	1.262	1.336	1.257	1.334	1.255
C1 – C1a	1.430	1.466	1.431	1.468	1.431	1.469	1.431	1.469	1.431	1.469
C1 – C2	1.410	1.458	1.411	1.464	1.413	1.469	1.417	1.477	1.419	1.481
C2 – C3	1.428	1.440	1.428	1.443	1.429	1.444	1.431	1.447	1.432	1.447
C3 – C4	1.371	1.361	1.370	1.359	1.369	1.358	1.367	1.356	1.366	1.356
C4 – C4a	1.429	1.444	1.430	1.446	1.431	1.447	1.433	1.450	1.434	1.451
C1a – C4a	1.433	1.426	1.433	1.425	1.432	1.424	1.432	1.423	1.432	1.422
C2 – N	1.397	1.348	1.394	1.341	1.391	1.337	1.383	1.329	1.379	1.326
N – N	1.279	1.298	1.276	1.300	1.275	1.303	1.278	1.312	1.281	1.316
N – Cipso	1.397	1.401	1.407	1.405	1.414	1.406	1.411	1.397	1.408	1.391
Cpara – R	1.370	1.378	1.361	1.365	-	-	1.432	1.430	1.457	1.449
C1a – C1 – C2	120.4	117.2	120.2	117.2	120.2	117.1	120.1	117.2	120.1	117.2
C1 – C2 – C3	119.2	120.2	119.4	120.1	119.5	120.0	119.5	119.8	119.5	119.7
C2 – C1 – O	121.2	121.1	121.3	121.1	121.3	121.0	121.2	120.9	121.1	120.8
C2 – C3 – C4	121.5	121.6	121.4	121.5	121.3	121.5	121.2	121.4	121.1	121.4
C3 – C4 – C4a	120.3	120.7	120.3	120.8	120.3	121.0	120.4	121.2	120.5	121.3
C1 – C2 – N	124.9	124.0	124.7	124.0	124.5	124.1	124.4	124.2	124.3	124.3
C2 – N – N	116.2	119.4	116.5	119.8	116.6	120.1	116.8	120.2	116.9	120.2
N – N – Cipso	117.8	122.5	117.2	122.0	116.9	121.8	116.3	121.2	116.1	121.0
C1 – C2 – N – N	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.1
N – N – Cipso – Cortho	0.0	0.6	0.1	0.2	0.0	0.1	0.0	0.0	-0.1	-0.1
	CAM-B3LYP/6-31+G(d,p)									
3	**3aA**	**3aH**	**3bA**	**3bH**	**3cA**	**3cH**	**3dA**	**3dH**	**3eA**	**3eH**
C1 – O	1.335	1.252	1.334	1.250	1.332	1.248	1.329	1.245	1.328	1.244
C1 – C1a	1.429	1.469	1.429	1.469	1.429	1.470	1.429	1.470	1.429	1.470
C1 – C2	1.397	1.458	1.398	1.461	1.400	1.465	1.403	1.472	1.403	1.474

C2 – C3	1.422	1.442	1.423	1.444	1.424	1.445	1.426	1.448	1.426	1.448
C3 – C4	1.362	1.349	1.361	1.348	1.360	1.347	1.359	1.345	1.358	1.345
C4 – C4a	1.426	1.448	1.427	1.449	1.428	1.450	1.429	1.452	1.430	1.453
C1a – C4a	1.419	1.412	1.419	1.411	1.419	1.411	1.419	1.410	1.419	1.410
C2 – N	1.396	1.330	1.394	1.326	1.391	1.322	1.385	1.316	1.383	1.314
N – N	1.260	1.293	1.259	1.296	1.259	1.299	1.262	1.307	1.263	1.309
N – Cipso	1.408	1.405	1.413	1.405	1.418	1.404	1.416	1.396	1.416	1.393
Cpara – R	1.377	1.385	1.356	1.360	-	-	1.436	1.434	1.467	1.462
C1a – C1 – C2	120.0	117.0	120.0	117.0	119.9	117.0	119.9	117.1	119.9	117.1
C1 – C2 – C3	119.5	120.1	119.6	120.0	119.6	119.9	119.6	119.7	119.6	119.7
C2 – C1 – O	122.0	121.5	122.0	121.4	122.0	121.4	121.9	121.2	121.9	121.2
C2 – C3 – C4	121.5	121.6	121.4	121.5	121.3	121.5	121.2	121.4	121.2	121.4
C3 – C4 – C4a	120.1	120.8	120.2	120.9	120.2	121.0	120.3	121.3	120.3	121.3
C1 – C2 – N	124.7	123.4	124.6	123.5	124.4	123.6	124.3	123.7	124.3	123.8
C2 – N – N	116.5	119.6	116.7	119.7	116.8	119.9	117.0	120.0	117.1	120.0
N – N – Cipso	116.8	121.6	116.4	121.4	116.2	121.2	115.8	120.9	115.7	120.8
C1 – C2 – N – N	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N – N – Cipso – Cortho	-0.3	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	B3LYP/6-31+G(d,p)									
4	**4aA**	**4aH**	**4bA**	**4bH**	**4cA**	**4cH**	**4dA**	**4dH**	**4eA**	**4eH**
C2 – O	1.338	1.267	1.338	1.266	1.337	1.264	1.336	1.262	1.336	1.261
C1 – C1a	1.448	1.462	1.448	1.463	1.448	1.465	1.450	1.468	1.451	1.469
C1 – C2	1.412	1.462	1.412	1.463	1.413	1.466	1.414	1.470	1.415	1.472
C2 – C3	1.420	1.452	1.420	1.452	1.420	1.453	1.420	1.452	1.420	1.452
C3 – C4	1.370	1.358	1.369	1.358	1.369	1.357	1.369	1.357	1.369	1.356
C4 – C4a	1.426	1.441	1.426	1.442	1.426	1.443	1.427	1.444	1.427	1.444
C1a – C4a	1.434	1.427	1.433	1.426	1.433	1.426	1.432	1.425	1.432	1.424
C1 – CH	1.449	1.400	1.448	1.397	1.447	1.395	1.442	1.390	1.441	1.388

CH – N	1.299	1.333	1.299	1.335	1.299	1.338	1.302	1.344	1.303	1.346
N – Cipso	1.405	1.408	1.407	1.408	1.408	1.406	1.402	1.396	1.400	1.394
Cpara – R	1.389	1.390	1.367	1.366	-	-	1.433	1.432	1.467	1.463
C1a – C1 – C2	118.9	120.3	119.0	120.3	119.1	120.2	119.1	120.1	119.1	120.1
C1 – C2 – C3	120.9	117.5	120.9	117.5	120.8	117.6	120.9	117.6	120.9	117.6
C1 – C2 – O	122.2	122.4	122.3	122.4	122.4	122.3	122.4	122.2	122.4	122.2
C2 – C3 – C4	120.2	121.5	120.2	121.4	120.2	121.4	120.1	121.3	120.1	121.3
C3 – C4 – C4a	121.5	122.4	121.6	122.5	121.6	122.6	121.8	122.7	121.8	122.7
C2 – C1 – CH	119.4	118.5	119.3	118.5	119.3	118.6	119.4	118.7	119.4	118.7
C1 – CH – N	122.2	123.5	122.3	123.4	122.4	123.6	122.5	123.4	122.5	123.4
CH – N – Cipso	122.2	127.6	121.6	127.5	121.2	127.7	121.2	128.1	121.3	128.1
C2 – C1 – CH – N	0.9	0.4	1.9	0.8	2.1	0.7	2.1	0.0	1.9	0.0
CH – N – Cipso – Cortho	27.2	17.3	31.6	18.1	36.4	13.5	37.2	-0.2	37.2	0.0
	M06-2X/6-31+G(d,p)									
4	**4aA**	**4aH**	**4bA**	**4bH**	**4cA**	**4cH**	**4dA**	**4dH**	**4eA**	**4eH**
C2 – O	1.331	1.253	1.331	1.254	1.330	1.251	1.330	1.249	1.329	1.248
C1 – C1a	1.442	1.461	1.442	1.462	1.443	1.464	1.445	1.467	1.445	1.467
C1 – C2	1.402	1.457	1.402	1.458	1.402	1.461	1.403	1.466	1.404	1.468
C2 – C3	1.422	1.458	1.422	1.457	1.422	1.459	1.421	1.458	1.421	1.458
C3 – C4	1.363	1.350	1.363	1.350	1.362	1.349	1.362	1.348	1.362	1.348
C4 – C4a	1.426	1.446	1.426	1.446	1.426	1.447	1.427	1.448	1.427	1.449
C1a – C4a	1.424	1.417	1.423	1.416	1.423	1.416	1.422	1.415	1.422	1.414
C1 – CH	1.452	1.392	1.452	1.391	1.450	1.387	1.446	1.382	1.445	1.381
CH – N	1.289	1.329	1.289	1.330	1.289	1.334	1.292	1.340	1.293	1.342
N – Cipso	1.409	1.410	1.409	1.408	1.410	1.406	1.404	1.395	1.402	1.393
Cpara – R	1.385	1.386	1.359	1.359	-	-	1.438	1.437	1.469	1.465
C1a – C1 – C2	119.2	120.7	119.2	120.6	119.3	120.5	119.3	120.3	119.3	120.2
C1 – C2 – C3	120.8	117.2	120.8	117.3	120.8	117.3	120.8	117.5	120.8	117.5

C1 – C2 – O	122.7	122.7	122.7	122.7	122.7	122.7	122.8	122.5	122.8	122.5
C2 – C3 – C4	120.1	121.3	120.1	121.3	120.1	121.3	120.0	121.2	120.0	121.1
C3 – C4 – C4a	121.4	122.6	121.5	122.6	121.5	122.7	121.6	122.7	121.6	122.8
C2 – C1 – CH	119.2	118.3	119.2	118.3	119.2	118.4	119.2	118.6	119.2	118.6
C1 – CH – N	122.1	124.3	122.0	123.8	122.3	124.4	122.5	123.9	122.4	123.8
CH – N – Cipso	120.9	125.9	120.8	126.7	120.1	126.1	120.1	127.6	120.3	127.6
C2 – C1 – CH – N	2.2	0.5	1.6	0.1	1.6	1.1	1.7	0.0	1.4	0.0
CH – N – Cipso – Cortho	34.5	26.2	35.9	21.6	39.0	21.8	39.4	0.0	39.2	0.9
	MP2/cc-pVDZ									
4	**4aA**	**4aH**	**4bA**	**4bH**	**4cA**	**4cH**	**4dA**	**4dH**	**4eA**	**4eH**
C2 – O	1.342	1.270	1.342	1.269	1.341	1.267	1.341	1.264	1.341	1.264
C1 – C1a	1.448	1.461	1.448	1.462	1.449	1.464	1.450	1.466	1.450	1.466
C1 – C2	1.416	1.462	1.416	1.463	1.416	1.465	1.416	1.470	1.416	1.470
C2 – C3	1.425	1.459	1.425	1.460	1.426	1.461	1.425	1.461	1.426	1.461
C3 – C4	1.381	1.369	1.381	1.369	1.380	1.368	1.380	1.367	1.380	1.367
C4 – C4a	1.430	1.446	1.430	1.447	1.430	1.448	1.430	1.449	1.430	1.449
C1a – C4a	1.440	1.431	1.440	1.430	1.440	1.430	1.439	1.429	1.439	1.429
C1 – CH	1.456	1.407	1.456	1.406	1.456	1.403	1.453	1.399	1.453	1.399
CH – N	1.309	1.336	1.309	1.337	1.308	1.339	1.309	1.344	1.308	1.344
N – Cipso	1.413	1.406	1.415	1.407	1.417	1.407	1.413	1.400	1.414	1.400
Cpara – R	1.398	1.397	1.365	1.364	-	-	1.443	1.443	1.480	1.478
C1a – C1 – C2	119.5	121.1	119.5	121.1	119.6	121.0	119.6	120.9	119.6	120.9
C1 – C2 – C3	120.1	116.8	120.1	116.8	120.1	116.8	120.1	116.9	120.1	116.9
C1 – C2 – O	123.3	123.3	123.3	123.3	123.3	123.3	123.4	123.3	123.4	123.3
C2 – C3 – C4	120.9	121.9	120.9	121.8	120.8	121.8	120.8	121.7	120.8	121.7
C3 – C4 – C4a	121.8	122.0	121.0	122.0	121.1	122.1	121.2	122.2	121.2	122.2
C2 – C1 – CH	119.3	117.5	119.3	117.6	119.2	117.7	119.3	117.8	119.3	117.8
C1 – CH – N	121.6	121.8	121.6	121.8	121.7	122.1	121.9	122.2	121.9	122.2

CH – N – Cipso	119.1	126.3	118.9	126.4	118.5	126.4	118.4	126.7	118.4	126.7
C2 – C1 – CH – N	0.9	0.2	1.5	-0.1	1.0	-0.2	1.7	0.2	1.6	0.3
CH – N – Cipso – Cortho	35.7	24.4	37.0	24.1	41.4	23.8	42.3	18.9	43.0	-18.8
	IEFPCM(CH_3OH)-B3LYP/6-31+G(d,p)									
4	**4aA**	**4aH**	**4bA**	**4bH**	**4cA**	**4cH**	**4dA**	**4dH**	**4eA**	**4eH**
C2 – O	1.346	1.278	1.345	1.278	1.344	1.276	1.343	1.273	1.342	1.271
C1 – C1a	1.449	1.462	1.449	1.464	1.449	1.465	1.451	1.469	1.452	1.470
C1 – C2	1.412	1.454	1.412	1.456	1.412	1.458	1.414	1.464	1.415	1.467
C2 – C3	1.419	1.449	1.419	1.448	1.419	1.449	1.419	1.448	1.418	1.448
C3 – C4	1.372	1.361	1.372	1.361	1.371	1.361	1.371	1.360	1.371	1.359
C4 – C4a	1.426	1.438	1.426	1.439	1.427	1.440	1.427	1.441	1.427	1.442
C1a – C4a	1.435	1.429	1.435	1.428	1.434	1.427	1.433	1.426	1.433	1.426
C1 – CH	1.451	1.408	1.450	1.405	1.449	1.402	1.444	1.396	1.442	1.392
CH – N	1.301	1.328	1.301	1.331	1.300	1.333	1.303	1.341	1.305	1.344
N – Cipso	1.407	1.411	1.409	1.413	1.410	1.412	1.402	1.400	1.397	1.394
Cpara – R	1.385	1.383	1.368	1.367	-	-	1.431	1.430	1.452	1.449
C1a – C1 – C2	118.8	120.3	118.9	120.1	118.9	120.1	118.9	119.9	118.9	119.8
C1 – C2 – C3	121.2	117.7	121.2	117.8	121.2	117.8	121.2	117.9	121.2	117.9
C1 – C2 – O	121.6	122.3	121.7	122.3	121.8	122.3	122.0	122.2	119.5	122.1
C2 – C3 – C4	120.1	121.6	120.1	121.5	120.1	121.5	120.0	121.4	120.0	121.4
C3 – C4 – C4a	121.4	122.2	121.4	122.2	121.5	122.3	121.6	122.4	121.7	122.5
C2 – C1 – CH	119.5	119.1	119.4	119.2	119.4	119.2	119.5	119.3	119.5	119.4
C1 – CH – N	121.5	123.7	121.6	123.7	121.7	123.8	121.8	123.5	121.8	123.5
CH – N – Cipso	123.0	128.1	122.4	127.5	121.6	127.5	121.6	128.2	121.8	128.1
C2 – C1 – CH – N	0.5	-0.1	-0.1	0.9	1.1	1.0	1.2	0.1	1.2	0.1
CH – N – Cipso – Cortho	23.3	12.1	27.1	19.2	35.2	17.8	37.0	-0.6	36.5	0.0

	CAM-B3LYP/6-31+G(d,p)									
4	**4aA**	**4aH**	**4bA**	**4bH**	**4cA**	**4cH**	**4dA**	**4dH**	**4eA**	**4eH**
C2 – O	1.333	1.258	1.332	1.258	1.332	1.256	1.331	1.254	1.331	1.253
C1 – C1a	1.443	1.461	1.443	1.462	1.444	1.464	1.446	1.467	1.446	1.468
C1 – C2	1.400	1.452	1.400	1.454	1.401	1.457	1.402	1.462	1.402	1.463
C2 – C3	1.419	1.453	1.419	1.453	1.419	1.454	1.419	1.453	1.419	1.453
C3 – C4	1.361	1.348	1.360	1.348	1.360	1.348	1.360	1.347	1.360	1.347
C4 – C4a	1.424	1.443	1.425	1.443	1.425	1.444	1.425	1.445	1.425	1.446
C1a – C4a	1.422	1.415	1.422	1.415	1.421	1.414	1.421	1.413	1.421	1.413
C1 – CH	1.450	1.392	1.448	1.389	1.447	1.386	1.443	1.381	1.442	1.379
CH – N	1.288	1.326	1.288	1.329	1.289	1.332	1.291	1.339	1.292	1.341
N – Cipso	1.409	1.410	1.410	1.409	1.409	1.406	1.403	1.396	1.402	1.393
Cpara – R	1.387	1.387	1.361	1.360	-	-	1.435	1.434	1.464	1.461
C1a – C1 – C2	119.1	120.4	119.2	120.3	119.2	120.3	119.2	120.1	119.2	120.0
C1 – C2 – C3	120.9	117.6	120.9	117.6	120.8	117.6	120.9	117.7	120.9	117.7
C1 – C2 – O	122.5	122.5	122.5	122.5	122.6	122.5	122.6	122.3	122.7	122.3
C2 – C3 – C4	120.1	121.3	120.1	121.3	120.1	121.2	120.0	121.2	120.0	121.1
C3 – C4 – C4a	121.5	122.5	121.6	122.6	121.6	122.6	121.7	122.7	121.7	122.7
C2 – C1 – CH	119.2	118.3	119.2	118.4	119.2	118.5	119.3	118.6	119.3	118.7
C1 – CH – N	122.3	123.9	122.4	123.9	122.4	124.0	122.6	123.7	122.6	123.7
CH – N – Cipso	121.2	126.3	120.8	126.4	120.5	126.7	120.5	127.7	120.5	127.7
C2 – C1 – CH – N	1.4	0.7	1.9	0.6	1.9	0.7	1.7	0.0	1.6	0.0
CH – N – Cipso – Cortho	34.0	27.0	36.8	25.1	40.5	20.5	41.1	-0.1	41.4	0.0
	B3LYP/6-31+G(d,p)									
5	**5aA**	**5aH**	**5bA**	**5bH**	**5cA**	**5cH**	**5dA**	**5dH**	**5eA**	**5eH**
C1 – O	1.339	1.263	1.339	1.262	1.338	1.260	1.337	1.259	1.337	1.258
C1 – C1a	1.432	1.471	1.432	1.471	1.432	1.472	1.432	1.471	1.432	1.471
C1 – C2	1.408	1.459	1.408	1.461	1.409	1.463	1.410	1.468	1.411	1.469

C2 – C3	1.427	1.440	1.428	1.441	1.428	1.442	1.430	1.444	1.430	1.444
C3 – C4	1.370	1.361	1.370	1.360	1.369	1.359	1.368	1.357	1.368	1.357
C4 – C4a	1.428	1.443	1.428	1.444	1.429	1.445	1.430	1.446	1.430	1.447
C1a – C4a	1.431	1.423	1.431	1.423	1.431	1.422	1.431	1.422	1.430	1.422
C2 – CH	1.448	1.398	1.447	1.395	1.446	1.393	1.441	1.388	1.440	1.387
CH – N	1.297	1.334	1.296	1.336	1.296	1.339	1.299	1.345	1.300	1.347
N – Cipso	1.406	1.408	1.408	1.408	1.409	1.405	1.402	1.396	1.400	1.394
Cpara – R	1.390	1.391	1.367	1.366	-	-	1.433	1.432	1.467	1.463
C1a – C1 – C2	120.5	117.0	120.4	117.0	120.4	117.0	120.4	117.1	120.4	117.1
C1 – C2 – C3	119.0	120.1	119.0	120.0	119.1	120.0	119.1	119.9	119.1	119.8
C2 – C1 – O	121.5	121.8	121.6	121.8	121.6	121.8	121.7	121.6	121.7	121.6
C2 – C3 – C4	121.7	121.9	121.7	121.8	121.6	121.8	121.5	121.7	121.5	121.7
C3 – C4 – C4a	120.2	120.6	120.2	120.6	120.3	120.7	120.3	120.9	120.3	120.9
C1 – C2 – CH	121.0	120.1	120.9	120.2	120.9	120.3	121.0	120.4	121.0	120.4
C2 – CH – N	122.1	123.5	122.3	123.5	122.3	123.5	122.5	123.4	122.5	123.4
CH – N – Cipso	122.5	128.0	121.8	127.9	121.5	128.2	121.5	128.3	121.5	128.3
C1 – C2 – CH – N	0.6	0.0	0.7	0.0	0.6	0.0	0.7	0.0	0.8	0.0
CH – N – Cipso – Cortho	27.2	-15.0	32.8	15.2	35.4	8.2	35.7	0.0	35.8	0.3
	M06-2X/6-31+G(d,p)									
5	**5aA**	**5aH**	**5bA**	**5bH**	**5cA**	**5cH**	**5dA**	**5dH**	**5eA**	**5eH**
C1 – O	1.333	1.250	1.332	1.248	1.332	1.247	1.331	1.245	1.331	1.245
C1 – C1a	1.431	1.475	1.431	1.475	1.432	1.476	1.431	1.475	1.431	1.475
C1 – C2	1.398	1.455	1.398	1.457	1.398	1.459	1.399	1.464	1.400	1.465
C2 – C3	1.424	1.441	1.425	1.442	1.426	1.443	1.427	1.445	1.427	1.446
C3 – C4	1.365	1.352	1.365	1.351	1.364	1.351	1.363	1.350	1.363	1.349
C4 – C4a	1.427	1.447	1.428	1.448	1.428	1.449	1.429	1.451	1.429	1.451
C1a – C4a	1.420	1.413	1.420	1.413	1.420	1.412	1.419	1.412	1.419	1.412
C2 – CH	1.452	1.389	1.451	1.386	1.450	1.384	1.445	1.380	1.444	1.378

CH – N	1.287	1.330	1.287	1.332	1.287	1.335	1.290	1.341	1.290	1.343
N – Cipso	1.409	1.410	1.410	1.410	1.410	1.405	1.404	1.395	1.403	1.393
Cpara – R	1.386	1.386	1.360	1.359	-	-	1.439	1.437	1.469	1.465
C1a – C1 – C2	120.2	116.5	120.2	116.5	120.2	116.5	120.2	116.7	120.2	116.7
C1 – C2 – C3	119.3	120.4	119.3	120.4	119.3	120.3	119.4	120.1	119.4	120.1
C2 – C1 – O	122.1	122.3	122.2	122.3	122.3	122.3	122.3	122.1	122.3	122.1
C2 – C3 – C4	121.6	121.9	121.6	121.8	121.6	121.8	121.5	121.7	121.5	121.7
C3 – C4 – C4a	120.0	120.4	120.0	120.4	120.0	120.5	120.0	120.7	120.1	120.7
C1 – C2 – CH	120.7	120.1	120.7	120.1	120.7	120.3	120.8	120.3	120.9	120.4
C2 – CH – N	122.1	124.5	122.2	124.6	122.3	124.5	122.5	124.0	122.5	124.0
CH – N – Cipso	120.8	126.2	120.5	125.6	120.4	126.6	120.2	127.7	120.1	127.6
C1 – C2 – CH – N	0.8	0.1	0.8	0.2	0.4	0.0	0.9	0.0	0.6	0.1
CH – N – Cipso – Cortho	34.0	-25.1	38.0	27.7	38.7	18.6	40.0	0.0	39.8	1.1
	MP2/cc-pVDZ									
5	**5aA**	**5aH**	**5bA**	**5bH**	**5cA**	**5cH**	**5dA**	**5dH**	**5eA**	**5eH**
C1 – O	1.343	1.265	1.343	1.264	1.343	1.263	1.343	1.260	1.343	1.260
C1 – C1a	1.436	1.478	1.436	1.478	1.436	1.479	1.436	1.479	1.436	1.480
C1 – C2	1.412	1.460	1.412	1.461	1.412	1.464	1.412	1.468	1.412	1.468
C2 – C3	1.431	1.443	1.432	1.444	1.432	1.445	1.432	1.447	1.432	1.447
C3 – C4	1.382	1.371	1.381	1.371	1.381	1.370	1.381	1.369	1.381	1.369
C4 – C4a	1.431	1.447	1.431	1.448	1.431	1.449	1.431	1.450	1.431	1.450
C1a – C4a	1.437	1.428	1.437	1.427	1.437	1.427	1.437	1.426	1.437	1.426
C2 – CH	1.455	1.405	1.455	1.403	1.454	1.401	1.452	1.397	1.452	1.397
CH – N	1.307	1.337	1.307	1.338	1.306	1.341	1.307	1.346	1.306	1.346
N – Cipso	1.413	1.406	1.415	1.407	1.417	1.406	1.413	1.400	1.414	1.400
Cpara – R	1.398	1.398	1.365	1.365	-	-	1.443	1.442	1.481	1.478
C1a – C1 – C2	119.8	116.3	119.8	116.3	119.8	116.3	119.8	116.4	119.8	116.4
C1 – C2 – C3	119.7	121.0	119.8	121.0	119.8	120.9	119.9	120.8	119.9	120.8

C2 – C1 – O	122.6	122.9	122.6	122.8	122.7	122.8	122.7	122.7	122.7	122.7
C2 – C3 – C4	121.3	121.4	121.3	121.3	121.3	121.3	121.2	121.3	121.2	121.3
C3 – C4 – C4a	120.1	120.4	120.1	120.5	120.1	120.5	120.1	120.7	120.1	120.7
C1 – C2 – CH	120.7	119.0	120.7	119.0	120.7	119.2	120.7	119.4	120.7	119.4
C2 – CH – N	121.5	122.0	121.6	122.1	121.7	122.2	121.9	122.2	121.9	122.3
CH – N – Cipso	119.4	126.9	119.1	126.7	118.8	127.0	118.7	127.3	118.7	127.3
C1 – C2 – CH – N	0.3	0.4	0.4	-0.4	0.4	-0.4	0.5	0.3	0.4	0.2
CH – N – Cipso – Cortho	35.5	-22.8	38.6	24.4	41.3	21.5	42.2	-15.8	43.0	-15.4

IEFPCM(CH_3OH)-B3LYP/6-31+G(d,p)										
5	**5aA**	**5aH**	**5bA**	**5bH**	**5cA**	**5cH**	**5dA**	**5dH**	**5eA**	**5eH**
C1 – O	1.346	1.274	1.346	1.272	1.344	1.270	1.343	1.267	1.342	1.265
C1 – C1a	1.431	1.468	1.431	1.469	1.431	1.470	1.431	1.470	1.431	1.470
C1 – C2	1.407	1.450	1.407	1.453	1.408	1.455	1.409	1.460	1.410	1.463
C2 – C3	1.428	1.439	1.428	1.440	1.429	1.441	1.430	1.444	1.431	1.445
C3 – C4	1.372	1.363	1.371	1.362	1.371	1.361	1.370	1.360	1.369	1.359
C4 – C4a	1.428	1.441	1.429	1.442	1.429	1.443	1.430	1.445	1.431	1.446
C1a – C4a	1.433	1.427	1.433	1.426	1.433	1.426	1.432	1.425	1.432	1.424
C2 – CH	1.451	1.407	1.450	1.403	1.448	1.401	1.444	1.394	1.441	1.392
CH – N	1.299	1.328	1.298	1.330	1.298	1.333	1.301	1.340	1.303	1.344
N – Cipso	1.407	1.412	1.410	1.413	1.411	1.412	1.403	1.400	1.398	1.394
Cpara – R	1.385	1.385	1.369	1.367	-	-	1.431	1.430	1.452	1.449
C1a – C1 – C2	120.7	117.1	120.6	117.1	120.6	117.1	120.5	117.1	120.5	117.2
C1 – C2 – C3	119.0	120.3	119.1	120.3	119.2	120.2	119.2	120.1	119.2	120.0
C2 – C1 – O	121.0	121.7	121.2	121.7	121.2	121.7	121.3	121.6	121.4	121.6
C2 – C3 – C4	121.6	121.9	121.5	121.8	121.5	121.8	121.4	121.7	121.4	121.7
C3 – C4 – C4a	120.3	120.3	120.3	120.4	120.3	120.5	120.3	120.6	120.3	120.7
C1 – C2 – CH	121.1	121.0	121.2	121.0	121.0	121.1	121.1	121.2	121.1	121.2

C2 – CH – N	121.5	123.8	121.8	123.9	121.7	123.9	121.8	123.8	121.8	123.6
CH – N – Cipso	123.2	128.2	122.1	127.8	121.7	128.0	121.6	128.0	121.7	128.0
C1 – C2 – CH – N	0.3	-0.1	0.4	0.1	0.4	0.1	0.5	0.0	0.7	0.0
CH – N – Cipso – Cortho	20.5	-12.5	29.7	15.0	33.2	8.5	34.3	0.0	34.1	0.1
IEFPCM(CH_3CN)-B3LYP/6-31+G(d,p)										
5	**5aA**	**5aH**	**5bA**	**5bH**	**5cA**	**5cH**	**5dA**	**5dH**	**5eA**	**5eH**
C1 – O	1.346	1.274	1.345	1.272	1.344	1.270	1.343	1.267	1.342	1.265
C1 – C1a	1.431	1.468	1.431	1.469	1.431	1.470	1.431	1.470	1.431	1.470
C1 – C2	1.407	1.450	1.407	1.453	1.407	1.455	1.409	1.460	1.410	1.463
C2 – C3	1.428	1.439	1.428	1.440	1.429	1.441	1.430	1.444	1.431	1.445
C3 – C4	1.372	1.363	1.371	1.362	1.371	1.361	1.370	1.360	1.369	1.359
C4 – C4a	1.428	1.441	1.429	1.442	1.429	1.443	1.430	1.445	1.431	1.446
C1a – C4a	1.433	1.427	1.432	1.426	1.433	1.426	1.432	1.425	1.432	1.424
C2 – CH	1.451	1.407	1.449	1.403	1.448	1.401	1.444	1.394	1.441	1.392
CH – N	1.299	1.328	1.298	1.330	1.298	1.333	1.301	1.340	1.303	1.344
N – Cipso	1.407	1.412	1.410	1.413	1.411	1.412	1.403	1.400	1.398	1.394
Cpara – R	1.385	1.385	1.368	1.367	-	-	1.431	1.430	1.452	1.448
C1a – C1 – C2	120.7	117.1	120.6	117.1	120.6	117.1	120.5	117.1	120.5	117.2
C1 – C2 – C3	119.0	120.3	119.1	120.3	119.2	120.2	119.2	120.1	119.2	120.0
C2 – C1 – O	121.0	121.7	121.1	121.7	121.2	121.7	121.3	121.6	121.3	121.5
C2 – C3 – C4	121.6	121.9	121.5	121.8	121.5	121.8	121.4	121.7	121.4	121.7
C3 – C4 – C4a	120.3	120.3	120.3	120.4	120.3	120.5	120.3	120.6	120.3	120.7
C1 – C2 – CH	121.1	121.0	121.0	121.0	121.0	121.1	121.1	121.2	121.1	121.2
C2 – CH – N	121.4	123.7	121.7	123.9	121.7	123.9	121.8	123.8	121.8	123.6
CH – N – Cipso	123.3	128.2	122.1	127.7	121.7	128.0	121.6	128.0	121.7	128.0
C1 – C2 – CH – N	0.3	-0.1	0.5	0.1	0.4	0.1	0.5	0.0	0.6	0.0
CH – N – Cipso – Cortho	20.4	-12.0	30.2	15.7	33.3	8.7	34.3	-0.1	33.6	-0.1

	CAM-B3LYP/6-31+G(d,p)									
5	**5aA**	**5aH**	**5bA**	**5bH**	**5cA**	**5cH**	**5dA**	**5dH**	**5eA**	**5eH**
C1 – O	1.334	1.255	1.333	1.254	1.333	1.253	1.332	1.251	1.332	1.250
C1 – C1a	1.429	1.470	1.430	1.470	1.430	1.470	1.429	1.470	1.429	1.470
C1 – C2	1.396	1.450	1.396	1.452	1.397	1.454	1.398	1.459	1.398	1.460
C2 – C3	1.423	1.440	1.424	1.441	1.424	1.442	1.426	1.445	1.426	1.445
C3 – C4	1.363	1.351	1.362	1.350	1.362	1.349	1.361	1.348	1.360	1.347
C4 – C4a	1.426	1.445	1.426	1.446	1.426	1.446	1.427	1.448	1.428	1.449
C1a – C4a	1.419	1.412	1.419	1.412	1.419	1.412	1.419	1.411	1.419	1.411
C2 – CH	1.449	1.390	1.447	1.387	1.446	1.385	1.442	1.379	1.441	1.378
CH – N	1.286	1.327	1.286	1.329	1.287	1.332	1.289	1.340	1.290	1.342
N – Cipso	1.409	1.410	1.410	1.409	1.410	1.406	1.404	1.396	1.402	1.393
Cpara – R	1.387	1.387	1.361	1.360	-	-	1.435	1.434	1.464	1.461
C1a – C1 – C2	120.4	117.0	120.4	117.0	120.3	117.0	120.4	117.1	120.4	117.1
C1 – C2 – C3	119.1	120.1	119.2	120.1	119.2	120.0	119.2	119.8	119.2	119.8
C2 – C1 – O	121.8	122.0	121.8	122.0	121.9	121.9	122.0	121.8	122.0	121.8
C2 – C3 – C4	121.7	121.9	121.6	121.8	121.6	121.8	121.5	121.8	121.5	121.7
C3 – C4 – C4a	120.1	120.5	120.1	120.5	120.1	120.6	120.2	120.8	120.2	120.8
C1 – C2 – CH	120.8	119.9	120.8	120.0	120.8	120.1	120.9	120.2	120.9	120.3
C2 – CH – N	122.2	123.8	122.4	123.9	122.4	123.8	122.6	123.6	122.6	123.6
CH – N – Cipso	121.4	126.8	121.0	126.7	120.8	127.3	120.7	127.9	120.8	127.9
C1 – C2 – CH – N	0.7	0.1	0.7	0.0	0.6	0.0	0.7	0.0	0.7	0.0
CH – N – Cipso – Cortho	33.7	-24.8	37.5	25.1	39.6	16.4	40.3	0.0	40.6	0.3

[a]distances in Å; bond and dihedral angles in degrees.

Table S2. Calculated tautomerization energies ΔE (kcal mol^{-1})[a] using B3LYP/6-31+G(d,p) geometries and errors with respect to CEPA/1 def2-CBS results.

	ΔE					**ERROR with respect to CEPA/1 results**				
	1a	**1b**	**1c**	**1d**	**1e**	**1a**	**1b**	**1c**	**1d**	**1e**
B3LYP / 6-31+G(d,p)	2.12	1.37	-0.22	-0.32	-0.85	1.33	1.79	1.70	1.07	1.52
M06-2X/ 6-31+G(d,p)	5.22	4.37	2.64	2.04	1.60	-1.77	-1.21	-1.17	-1.28	-0.92
M06-2X / aug-cc-pVTZ	4.60	3.75	1.97	1.35	0.86	-1.15	-0.58	-0.50	-0.60	-0.19
PW6B95 / def2-TZVPP	2.47	1.66	-0.02	-0.22	-0.70	0.98	1.50	1.49	0.98	1.37
B2PLYP/ def2-TZVPP	2.43	1.69	0.07	-0.10	-0.50	1.02	1.47	1.40	0.86	1.18
mPW2PLYP/def2-TZVPP	2.70	1.95	0.28	0.02	-0.41	0.76	1.22	1.19	0.73	1.08
PWPB95/ def2-TZVPP	2.25	1.44	-0.23	-0.60	-0.99	1.20	1.72	1.71	1.35	1.67
MP2/6-311++G(2d,2p)	5.75	5.20	3.91	3.75	3.48	-2.29	-2.03	-2.44	-3.00	-2.81
MP2/aug-cc-pVDZ	5.68	5.40	4.05	4.00	3.78	-2.23	-2.24	-2.58	-3.24	-3.10
MP2/aug-cc-pVTZ	5.62	5.16	3.82	3.69	3.49	-2.17	-2.00	-2.35	-2.93	-2.81
SCS-MP2/6-311++G(2d,2p)	3.31	2.55	1.02	0.06	-0.36	0.14	0.62	0.45	0.69	1.03
SCS-MP2/aug-cc-pVDZ	3.14	2.63	1.05	0.18	-0.19	0.31	0.53	0.42	0.57	0.87
SCS-MP2/aug-cc-pVTZ	3.07	2.39	0.79	-0.16	-0.52	0.39	0.77	0.68	0.91	1.19
LPNO-CEPA-1/def2-TZVP	3.24	2.59	1.18	0.24	0.11	0.22	0.57	0.30	0.51	0.56
LPNO-CEPA-1/def2-TZVPP	3.65	3.26	1.59	0.66	0.60	-0.20	-0.09	-0.12	0.10	0.07
LPNO-CEPA-1/def2-QZVPP	3.52	3.18	1.51	0.70	0.62	-0.06	-0.02	-0.04	0.06	0.05
LPNO-CEPA-1/CBS (3 / 4)	3.45	3.16	1.47	0.75	0.67					
	2a	**2b**	**2c**	**2d**	**2e**	**2a**	**2b**	**2c**	**2d**	**2e**
B3LYP / 6-31+G(d,p)	0.45	-0.02	-1.13	-1.53	-1.87	2.05	1.68	1.80	0.38	1.20
M06-2X/ 6-31+G(d,p)	3.02	2.45	1.15	0.36	0.02	-0.52	-0.79	-0.49	-1.51	-0.68
M06-2X / aug-cc-pVTZ	2.68	2.09	0.75	-0.05	-0.42	-0.18	-0.43	-0.09	-1.10	-0.25

PW6B95 / def2-TZVPP	0.83	0.29	-0.92	-1.41	-1.72	1.67	1.37	1.59	0.26	1.05
B2PLYP/ def2-TZVPP	0.80	0.37	-0.77	-1.16	-1.40	1.70	1.28	1.43	0.01	0.74
mPW2PLYP/def2-TZVPP	0.98	0.54	-0.65	-1.13	-1.39	1.52	1.12	1.32	-0.02	0.73
PWPB95/ def2-TZVPP	0.89	0.38	-0.86	-1.45	-1.70	1.61	1.28	1.52	0.29	1.03
MP2/6-311++G(2d,2p)	3.44	3.17	2.21	1.80	1.67	-0.95	-1.51	-1.54	-2.95	-2.33
MP2/aug-cc-pVDZ	2.94	3.19	2.11	1.68	1.32	-0.45	-1.53	-1.44	-2.84	-1.99
MP2/aug-cc-pVTZ	3.39	3.14	2.19	1.83	1.67	-0.90	-1.48	-1.53	-2.98	-2.34
SCS-MP2/6-311++G(2d,2p)	2.42	1.86	0.35	-0.91	-1.30	0.08	-0.20	0.32	-0.24	0.63
SCS-MP2/aug-cc-pVDZ	1.87	1.80	0.18	-1.09	-1.69	0.62	-0.14	0.48	-0.07	1.03
SCS-MP2/aug-cc-pVTZ	2.29	1.74	0.24	-0.98	-1.40	0.21	-0.09	0.43	-0.18	0.73
LPNO-CEPA-1/def2-TZVP	2.25	1.94	0.66	-1.02	-0.71	0.25	-0.28	0.01	-0.13	0.05
LPNO-CEPA-1/def2-TZVPP	2.41	1.94	0.84	-0.83	-0.62	0.09	-0.28	-0.17	-0.33	-0.04
LPNO-CEPA-1/def2-QZVPP	2.47	1.71	0.74	-1.00	-0.60	0.03	-0.05	-0.07	-0.15	-0.06
LPNO-CEPA-1/CBS (3 / 4)	2.50	1.66	0.67	-1.15	-0.66					
	3a	**3b**	**3c**	**3d**	**3e**	**3a**	**3b**	**3c**	**3d**	**3e**
B3LYP / 6-31+G(d,p)	-0.40	-0.86	-1.99	-2.42	-2.80	1.95	2.22	2.03	1.29	1.52
M06-2X/ 6-31+G(d,p)	2.27	1.73	0.43	-0.32	-0.69	-0.72	-0.37	-0.38	-0.80	-0.59
M06-2X / aug-cc-pVTZ	2.00	1.45	0.12	-0.72	-1.06	-0.45	-0.10	-0.08	-0.40	-0.22
PW6B95 / def2-TZVPP	-0.05	-0.56	-1.79	-2.31	-2.63	1.60	1.92	1.84	1.19	1.35
B2PLYP/ def2-TZVPP	-0.07	-0.49	-1.66	-2.10	-2.34	1.62	1.85	1.70	0.97	1.06
mPW2PLYP/def2-TZVPP	0.14	-0.30	-1.51	-2.03	-2.29	1.41	1.66	1.55	0.90	1.01
PWPB95/ def2-TZVPP	0.05	-0.47	-1.72	-2.33	-2.60	1.50	1.83	1.76	1.21	1.32
MP2/6-311++G(2d,2p)	2.77	2.49	1.52	1.09	0.96	-1.22	-1.14	-1.48	-2.21	-2.24
MP2/aug-cc-pVDZ	2.20	2.02	1.09	0.74	0.59	-0.65	-0.66	-1.05	-1.86	-1.87
MP2/aug-cc-pVTZ	2.73	2.50	1.55	1.07	1.01	-1.18	-1.14	-1.51	-2.20	-2.29
SCS-MP2/6-311++G(2d,2p)	1.81	1.25	-0.24	-1.51	-1.88	-0.26	0.10	0.29	0.39	0.60
SCS-MP2/aug-cc-pVDZ	1.22	0.76	-0.70	-1.89	-2.28	0.33	0.60	0.74	0.76	1.00
SCS-MP2/aug-cc-pVTZ	1.70	1.20	-0.29	-1.61	-1.92	-0.15	0.16	0.34	0.49	0.64
LPNO-CEPA-1/def2-TZVP	1.76	1.39	-0.01	-1.21	-1.30	-0.21	-0.03	0.05	0.08	0.02
LPNO-CEPA-1/def2-TZVPP	1.93	1.58	0.17	-1.04	-1.12	-0.38	-0.23	-0.13	-0.08	-0.16
LPNO-CEPA-1/def2-QZVPP	1.73	1.48	0.13	-1.07	-1.17	-0.18	-0.12	-0.08	-0.05	-0.11

LPNO-CEPA-1/CBS (3 / 4)	1.55	1.36	0.04	-1.12	-1.28					
	4a	**4b**	**4c**	**4d**	**4e**	**4a**	**4b**	**4c**	**4d**	**4e**
B3LYP / 6-31+G(d,p)	0.67	0.82	0.54	0.89	0.77	2.59	2.59	2.61	2.21	2.53
M06-2X/ 6-31+G(d,p)	3.11	3.29	3.04	3.33	3.23	0.15	0.12	0.10	-0.23	0.07
M06-2X / aug-cc-pVTZ	2.75	2.97	2.67	2.94	2.85	0.51	0.44	0.47	0.16	0.45
PW6B95 / def2-TZVPP	1.21	1.38	1.06	1.41	1.30	2.06	2.02	2.08	1.69	1.99
B2PLYP/ def2-TZVPP	1.48	1.68	1.43	1.75	1.64	1.79	1.73	1.71	1.35	1.66
mPW2PLYP/def2-TZVPP	1.57	1.77	1.50	1.82	1.71	1.70	1.63	1.64	1.28	1.59
PWPB95/ def2-TZVPP	1.46	1.67	1.39	1.66	1.56	1.81	1.73	1.75	1.44	1.74
MP2/6-311++G(2d,2p)	4.57	4.82	4.72	4.99	4.85	-1.31	-1.41	-1.58	-1.89	-1.56
MP2/aug-cc-pVDZ	4.47	4.70	4.58	4.96	4.70	-1.20	-1.29	-1.44	-1.87	-1.41
MP2/aug-cc-pVTZ	4.46	4.70	4.57	4.73	4.69	-1.20	-1.29	-1.42	-1.64	-1.40
SCS-MP2/6-311++G(2d,2p)	2.91	3.16	2.92	3.03	2.81	0.35	0.24	0.22	0.07	0.49
SCS-MP2/aug-cc-pVDZ	2.81	3.05	2.79	3.01	2.67	0.45	0.36	0.35	0.08	0.63
SCS-MP2/aug-cc-pVTZ	2.74	2.97	2.71	2.74	2.61	0.53	0.43	0.43	0.36	0.69
LPNO-CEPA-1/def2-TZVP	3.28	3.53	3.17	3.28	3.43	-0.01	-0.12	-0.03	-0.18	-0.13
LPNO-CEPA-1/def2-TZVPP	3.43	3.57	3.32	3.43	3.53	-0.16	-0.17	-0.17	-0.33	-0.23
LPNO-CEPA-1/def2-QZVPP	3.32	3.47	3.20	3.22	3.40	-0.05	-0.06	-0.06	-0.12	-0.10
LPNO-CEPA-1/CBS (3 / 4)	3.27	3.41	3.14	3.10	3.30					
	5a	**5b**	**5c**	**5d**	**5e**	**5a**	**5b**	**5c**	**5d**	**5e**
B3LYP / 6-31+G(d,p)	-0.08	0.04	-0.35	-0.02	-0.18	2.72	2.61	2.84	2.40	2.68
M06-2X/ 6-31+G(d,p)	2.42	2.60	2.21	2.45	2.34	0.21	0.06	0.27	-0.07	0.16
M06-2X / aug-cc-pVTZ	2.15	2.33	1.93	2.18	2.05	0.48	0.32	0.55	0.20	0.46
PW6B95 / def2-TZVPP	0.46	0.58	0.17	0.49	0.36	2.17	2.07	2.31	1.89	2.15
B2PLYP/ def2-TZVPP	0.77	0.92	0.56	0.85	0.72	1.87	1.73	1.92	1.54	1.79
mPW2PLYP/def2-TZVPP	0.87	1.02	0.65	0.93	0.80	1.77	1.63	1.83	1.45	1.71
PWPB95/ def2-TZVPP	0.76	0.94	0.52	0.76	0.63	1.87	1.71	1.96	1.62	1.88
MP2/6-311++G(2d,2p)	4.08	4.31	4.09	4.29	4.14	-1.44	-1.65	-1.60	-1.91	-1.63
MP2/aug-cc-pVDZ	3.66	4.17	3.60	4.03	3.79	-1.03	-1.52	-1.12	-1.64	-1.28
MP2/aug-cc-pVTZ	3.98	4.27	3.98	4.13	3.98	-1.35	-1.62	-1.50	-1.75	-1.48
SCS-MP2/6-311++G(2d,2p)	2.41	2.62	2.25	2.25	2.02	0.22	0.03	0.24	0.13	0.48

SCS-MP2/aug-cc-pVDZ	2.04	2.52	1.82	2.04	1.72	0.59	0.14	0.66	0.35	0.79
SCS-MP2/aug-cc-pVTZ	2.27	2.53	2.11	2.06	1.83	0.37	0.12	0.38	0.32	0.67
LPNO-CEPA-1/def2-TZVP	2.60	2.88	2.50	2.55	2.73	0.03	-0.23	-0.02	-0.16	-0.22
LPNO-CEPA-1/def2-TZVPP	2.79	2.97	2.57	2.64	2.78	-0.16	-0.32	-0.09	-0.26	-0.28
LPNO-CEPA-1/def2-QZVPP	2.69	2.71	2.51	2.49	2.63	-0.05	-0.06	-0.03	-0.10	-0.13
LPNO-CEPA-1/CBS (3 / 4)	2.63	2.65	2.48	2.38	2.51					

[a]A negative sign indicates greater stability of the keto tautomer.

Table S3. Calculated differences in solvation energies ΔG_{solv} (kcal mol^{-1}).

	solvent	IEFPCM-B3LYP[a,b]	COSMO-B3LYP[a,b]	SM8-B3LYP[a,b]	SM8-M06-2X[a,b]	SMD-M06-2X[a,c]	PBF-M06-2X[a,d]	MC-FEP[e]	IEFPCM-B3LYP[f]	PBF-M06-2X[d,g]	SM8-M06-2X[b,g]	SM8-M06-2X[b,h]
1a	CH_3OH	-2.1	-2.9	-0.8	-0.3	-0.8	-2.9	-3.0	-2.7	-0.2	-1.1	
	CH_3CN	-2.1	-2.9	-0.4	-0.3	0.0	-2.9	-3.1	-2.6	-0.4	-1.1	
	$CHCl_3$	-1.4	-1.9	-0.5	-0.3	-0.2	-2.0	-2.0	-1.8	-0.3	-0.9	
	CCl_4	-1.1	-1.0	-0.7	-0.6	-0.4	-1.1	-1.2	-1.0	-0.6	-0.9	
1b	CH_3OH	-2.5	-3.4	-1.6	-0.8	-1.2	-3.3	-3.5	-3.2	-1.0	-1.5	
	CH_3CN	-2.5	-3.5	-1.0	-1.0	-0.5	-3.4	-3.6	-3.3	-1.3	-1.7	
	$CHCl_3$	-1.6	-2.2	-1.3	-0.8	-0.6	-2.2	-2.4	-2.1	-0.9	-1.2	
	CCl_4	-1.3	-1.2	-1.2	-0.8	-0.6	-1.2	-1.4	-1.1	-1.0	-1.1	
1c	CH_3OH	-2.3	-3.3	-1.1	-0.7	-1.1	-3.2	-3.3	-3.0	-0.6	-1.2	
	CH_3CN	-2.3	-3.4	-1.3	-1.1	-0.4	-3.2	-3.4	-3.0	-1.2	-1.5	
	$CHCl_3$	-1.5	-2.2	-1.0	-0.8	-0.5	-2.2	-2.3	-2.0	-0.8	-1.1	
	CCl_4	-1.3	-1.2	-1.0	-1.0	-0.6	-1.2	-1.3	-1.1	-0.9	-1.1	
1d	CH_3OH	-3.3	-4.4	-2.4	-1.8	-1.9	-4.4	-4.2	-4.3	-2.0	-2.5	
	CH_3CN	-3.3	-4.4	-2.5	-2.5	-1.3	-4.4	-4.2	-4.3	-2.8	-3.2	
	$CHCl_3$	-2.1	-2.8	-2.0	-1.7	-1.2	-3.0	-2.8	-2.8	-1.9	-2.2	
	CCl_4	-1.6	-1.5	-1.7	-1.5	-1.0	-1.6	-1.6	-1.6	-1.6	-1.8	
1e	CH_3OH	-3.5	-4.6	-2.2	-2.1	-2.1	-4.5	-4.4	-4.4	-2.1	-2.3	
	CH_3CN	-3.5	-4.6	-2.6	-2.5	-1.3	-4.5	-4.5	-4.4	-2.7	-2.8	
	$CHCl_3$	-2.2	-2.9	-1.8	-1.8	-1.3	-3.0	-3.0	-2.8	-1.9	-1.9	

	CCl_4	-1.6	-1.6	-1.5	-1.5	-1.0	-1.5		-1.7	-1.6	-1.6	-1.6
2a	CH_3OH	-1.6	-1.3	-1.5	-0.8	-0.4	-1.5	-2.4	-1.7	-2.0	-1.1	-1.3
	CH_3CN	-1.6	-1.3	0.0	0.4	0.0	-1.5	-1.5	-1.7	-2.1	0.3	0.0
	$CHCl_3$	-1.3	-1.0	-0.3	0.0	-0.1	-1.1	-1.0	-1.2	-1.5	-0.1	-0.3
	CCl_4	-0.7	-0.6	-0.2	0.0	-0.1	-0.7	-0.7	-0.8	-1.0	0.0	-0.2
2b	CH_3OH	-1.8	-1.6	-1.8	-1.3	-1.0	-2.0	-2.4	-2.0	-1.9	-1.4	-1.6
	CH_3CN	-1.8	-1.6	-0.5	-0.2	-0.7	-1.9	-1.9	-1.9	-1.9	-0.3	-0.4
	$CHCl_3$	-1.3	-1.2	-0.6	-0.3	-0.6	-1.3	-1.2	-1.4	-1.3	-0.4	-0.6
	CCl_4	-0.8	-0.7	-0.3	-0.2	-0.4	-0.8	-0.7	-0.9	-0.8	-0.2	-0.3
2c	CH_3OH	-1.7	-1.7	-1.4	-1.3	-0.7	-2.0	-2.4	-1.9	-1.9	-1.0	-1.3
	CH_3CN	-1.7	-1.7	-0.4	-0.2	-0.5	-1.9	-1.8	-1.9	-1.9	-0.2	-0.3
	$CHCl_3$	-1.3	-1.2	-0.5	-0.4	-0.4	-1.3	-1.2	-1.3	-1.3	-0.3	-0.4
	CCl_4	-0.8	-0.7	-0.3	-0.2	-0.3	-0.8	-0.7	-0.8	-0.8	-0.2	-0.3
2d	CH_3OH	-2.0	-1.9	-2.0	-1.5	-1.1	-2.3	-2.4	-2.1	-2.3	-1.6	-1.7
	CH_3CN	-2.0	-2.0	-1.1	-0.7	-1.0	-2.3	-2.2	-2.1	-2.2	-0.8	-0.9
	$CHCl_3$	-1.4	-1.4	-1.0	-0.7	-0.8	-1.6	-1.2	-1.5	-1.6	-0.8	-0.9
	CCl_4	-0.9	-0.8	-0.6	-0.4	-0.6	-0.9	-0.7	-0.9	-1.0	-0.5	-0.5
2e	CH_3OH	-2.1	-2.0	-2.0	-1.8	-1.2	-2.3	-2.6	-2.3	-2.2	-1.7	-1.6
	CH_3CN	-1.8	-2.0	-1.0	-0.8	-1.0	-2.2	-2.4	-2.2	-2.2	-0.8	-0.7
	$CHCl_3$	-1.6	-1.4	-0.9	-0.8	-0.7	-1.6	-1.3	-1.6	-1.6	-0.8	-0.7
	CCl_4	-0.9	-0.8	-0.5	-0.5	-0.6	-1.0	-0.7	-0.9	-1.0	-0.5	-0.4
3a	CH_3OH	-1.0	-0.8	-0.9	-0.2	-0.4	-1.3		-1.2	-1.3	-0.6	-0.8
	CH_3CN	-1.1	-0.8	0.2	0.6	-0.2	-1.2		-1.2	-1.3	0.4	0.2
	$CHCl_3$	-0.9	-0.6	-0.1	0.3	-0.2	-0.9		-0.8	-1.0	0.1	-0.1

	CCl_4	-0.5	-0.4	0.0	0.2	-0.2	-0.6		-0.5	-0.5	0.1	0.0
3b	CH_3OH	-1.2	-1.3	-1.2	-0.7	-0.5	-1.7		-1.5	-1.7	-0.9	-0.9
	CH_3CN	-1.3	-1.3	-0.3	0.1	-0.4	-1.7		-1.4	-1.6	-0.1	-0.1
	$CHCl_3$	-1.0	-0.9	-0.4	-0.1	-0.3	-1.1		-1.0	-1.1	-0.2	-0.2
	CCl_4	-0.6	-0.5	-0.2	0.0	-0.3	-0.7		-0.6	-0.7	-0.1	-0.1
3c	CH_3OH	-1.3	-1.3	-1.2	-0.6	-0.5	-1.6	-1.9	-1.4	-1.6	-0.7	-0.9
	CH_3CN	-1.4	-1.3	-0.3	0.1	-0.4	-1.6	-1.7	-1.4	-1.6	-0.1	-0.1
	$CHCl_3$	-1.0	-0.9	-0.4	-0.1	-0.3	-1.1	-1.0	-1.0	-1.2	-0.2	-0.3
	CCl_4	-0.6	-0.6	-0.2	0.0	-0.3	-0.7	-0.7	-0.6	-0.7	-0.1	-0.2
3d	CH_3OH	-1.6	-1.6	-1.4	-1.0	-0.7	-2.1		-1.8	-2.0	-1.3	-1.2
	CH_3CN	-1.6	-1.6	-0.8	-0.5	-0.7	-2.0		-1.7	-2.0	-0.7	-0.7
	$CHCl_3$	-1.2	-1.2	-0.7	-0.5	-0.5	-1.4		-1.2	-1.5	-0.7	-0.6
	CCl_4	-0.8	-0.7	-0.4	-0.3	-0.4	-0.9		-0.8	-0.9	-0.4	-0.4
3e	CH_3OH	-1.8	-1.7	-1.3	-1.2	-0.8	-2.1		-2.0	-2.1	-1.1	-1.3
	CH_3CN	-1.8	-1.8	-0.6	-0.5	-0.8	-2.1		-1.9	-2.1	-0.5	-0.7
	$CHCl_3$	-1.3	-1.2	-0.6	-0.5	-0.6	-1.5		-1.3	-1.5	-0.5	-0.6
	CCl_4	-0.8	-0.7	-0.3	-0.3	-0.5	-0.9		-0.8	-0.9	-0.3	-0.4
4a	CH_3OH	-3.0	-2.9	-2.1	-2.1	-2.3	-3.2	-4.7	-2.3	-3.3	-1.9	-2.0
	CH_3CN	-2.9	-2.9	-0.8	-0.8	-1.5	-3.2	-3.5	-3.2	-3.2	-0.7	-0.9
	$CHCl_3$	-2.1	-2.0	-0.8	-0.8	-1.3	-2.3	-1.8	-2.2	-2.3	-0.7	-0.9
	CCl_4	-1.3	-1.2	-0.5	-0.5	-0.8	-1.4	-0.8	-1.3	-1.3	-0.4	-0.6
4b	CH_3OH	-3.0	-2.9	-2.2	-2.2	-2.1	-3.2	-5.2	-3.2	-3.1	-2.0	-2.1
	CH_3CN	-2.9	-2.9	-1.0	-1.1	-1.4	-3.3	-3.0	-3.2	-3.1	-0.9	-1.1
	$CHCl_3$	-2.1	-2.0	-1.0	-1.0	-1.2	-2.3	-1.8	-2.2	-2.2	-0.9	-1.0

	CCl_4	-1.3	-1.1	-0.6	-0.6	-0.8	-1.3	-0.5	-1.3	-1.3	-0.5	-0.7
4c	CH_3OH	-2.9	-2.8	-1.8	-1.8	-2.0	-3.1	-4.7	-3.2	-3.0	-1.6	-1.8
	CH_3CN	-2.8	-2.8	-0.7	-0.7	-1.4	-3.1	-3.1	-3.1	-3.0	-0.6	-0.8
	$CHCl_3$	-1.9	-1.9	-0.7	-0.7	-1.1	-2.2	-1.8	-2.1	-2.1	-0.6	-0.8
	CCl_4	-1.2	-1.1	-0.4	-0.4	-0.7	-1.3	-0.9	-1.2	-1.2	-0.4	-0.5
4d	CH_3OH	-2.8	-2.8	-2.6	-1.8	-1.5	-3.3	-4.4	-3.0	-3.1	-2.1	-2.0
	CH_3CN	-2.7	-2.8	-1.6	-0.9	-1.1	-3.3	-2.9	-2.9	-3.2	-1.4	-1.3
	$CHCl_3$	-1.8	-1.9	-1.3	-0.8	-0.9	-2.2	-1.5	-1.9	-2.1	-1.1	-1.1
	CCl_4	-1.1	-1.1	-0.8	-0.5	-0.6	-1.2	-0.8	-1.1	-1.2	-0.7	-0.7
4e	CH_3OH	-2.8	-2.8	-2.3	-2.4	-1.4	-3.3	-4.2	-2.9	-3.1	-2.2	-1.9
	CH_3CN	-2.7	-2.8	-1.3	-1.3	-1.1	-3.3	-3.6	-2.8	-3.1	-1.2	-1.1
	$CHCl_3$	-1.8	-1.9	-1.1	-1.1	-0.9	-2.1	-1.5	-1.9	-2.0	-1.0	-1.0
	CCl_4	-1.1	-1.1	-0.7	-0.7	-0.5	-1.2	-0.8	-1.2	-1.2	-0.6	-0.6
5a	CH_3OH	-2.8	-2.7	-2.3	-2.4	-1.6	-3.2	-4.8	-3.2	-3.3	-2.4	-2.4
	CH_3CN	-2.8	-2.7	-1.2	-1.2	-1.2	-3.1	-3.4	-3.1	-3.2	-1.2	-1.3
	$CHCl_3$	-2.0	-1.9	-1.1	-1.1	-1.0	-2.2	-1.9	-2.1	-2.4	-1.1	-1.2
	CCl_4	-1.2	-1.1	-0.6	-0.6	-0.6	-1.3	-0.8	-1.2	-1.4	-0.6	-0.8
5b	CH_3OH	-2.8	-2.7	-2.4	-2.4	-1.9	-3.1	-4.7	-3.2	-3.3	-2.5	-2.4
	CH_3CN	-2.8	-2.8	-1.4	-1.4	-1.5	-3.2	-3.5	-3.1	-3.3	-1.4	-1.5
	$CHCl_3$	-1.9	-1.9	-1.2	-1.2	-1.2	-2.2	-2.0	-2.1	-2.3	-1.2	-1.3
	CCl_4	-1.2	-1.1	-0.7	-0.7	-0.8	-1.3	-0.8	-1.2	-1.3	-0.7	-0.8
5c	CH_3OH	-2.7	-2.6	-2.0	-1.9	-1.4	-3.0	-4.2	-3.0	-3.0	-1.9	-2.0
	CH_3CN	-2.6	-2.6	-1.0	-1.0	-1.1	-3.0	-3.2	-3.0	-3.0	-1.0	-1.2
	$CHCl_3$	-1.8	-1.8	-0.9	-0.8	-0.9	-2.2	-1.7	-2.0	-2.2	-0.8	-1.0

	CCl_4	-1.1	-1.0	-0.5	-0.5	-0.6	-1.2	-0.8	-1.2	-1.2	-0.5	-0.7
5d	CH_3OH	-2.7	-2.6	-2.7	-2.2	-1.8	-3.1	-3.7	-3.0	-2.9	-2.6	-2.3
	CH_3CN	-2.6	-2.6	-1.9	-1.4	-1.5	-3.1	-2.8	-2.9	-3.0	-1.8	-1.6
	$CHCl_3$	-1.8	-1.8	-1.5	-1.1	-1.2	-2.2	-1.5	-1.9	-2.1	-1.4	-1.3
	CCl_4	-1.0	-1.0	-0.9	-0.7	-0.8	-1.2	-0.8	-1.1	-1.2	-0.8	-0.8
5e	CH_3OH	-2.7	-2.6	-2.3	-2.3	-1.4	-3.0	-3.3	-2.9	-3.0	-2.1	-2.1
	CH_3CN	-2.7	-2.6	-1.5	-1.4	-1.1	-3.0	-3.1	-2.8	-2.9	-1.5	-1.4
	$CHCl_3$	-1.8	-1.8	-1.2	-1.2	-0.9	-2.1	-1.4	-1.9	-2.1	-1.1	-1.2
	CCl_4	-1.1	-1.0	-0.7	-0.7	-0.6	-1.2	-0.9	-1.1	-1.2	-0.6	-0.7

[a]B3LYP/6-31+G(d,p) gas phase geometries. [b]6-31+G(d,p) basis set for single point calculation in solvent. [c]6-31G(d) basis set for single point calculation in solvent. [d]aug-cc-pVTZ(-f) basis set for single point calculation in solvent. [e]Monte-Carlo free energy perturbation calculations using the OPLSAA force field with IEFPCM-B3LYP/6-31+G(d,p) optimized structures and CHELPG charges in the respective solvent. [f]IEFPCM-B3LYP/6-31+G(d,p)//IEFPCM-B3LYP/6-31+G(d,p). [g]M06-2X/6-31+G(d,p) gas phase geometries. [h]MP2/cc-pVDZ gas phase geometries. $\Delta G_{solv} = G_{solv}$(quinone) - G_{solv}(phenol). Hence, a negative sign indicates greater stabilization of the quinone tautomer

Table S4. LPNO-CEPA/1-CBS tautomerization energies obtained using IEFPCM-B3LYP/6-31+G(d,p) geometries.

compound	Solvent	1	2	3	4	5
a	CH_3OH	3.93	2.47	1.67	3.15	2.71
	CH_3CN	3.95	2.52	1.57	3.30	2.59
	$CHCl_3$	3.80	2.38	1.71	3.32	2.68
	CCl_4	3.62	2.33	1.61	3.23	2.63
	gas phase	3.45	2.50	1.55	3.27	2.63
b	CH_3OH	3.91	1.97	1.38	3.42	2.96
	CH_3CN	3.92	1.98	1.37	3.50	2.77
	$CHCl_3$	3.65	1.92	1.41	3.43	2.78
	CCl_4	3.55	1.90	1.32	3.39	2.75
	gas phase	3.16	1.66	1.36	3.41	2.65
c	CH_3OH	1.82	0.79	0.08	3.16	2.51
	CH_3CN	1.80	0.79	0.09	3.25	2.47
	$CHCl_3$	1.65	0.75	0.04	3.20	2.37
	CCl_4	1.54	0.72	0.06	3.05	2.45
	gas phase	1.47	0.68	0.04	3.14	2.48
d	CH_3OH	1.18	-0.59	-1.13	3.08	2.43
	CH_3CN	1.21	-0.60	-1.15	3.03	2.56
	$CHCl_3$	1.02	-0.88	-1.10	3.14	2.40
	CCl_4	0.83	-1.17	-1.13	3.13	2.39
	gas phase	0.75	-1.15	-1.12	3.10	2.38

e	CH_3OH	1.08	-0.73	-1.13	3.27	2.74
	CH_3CN	1.08	-0.72	-1.05	3.29	2.61
	$CHCl_3$	0.95	-0.34	-1.18	3.17	2.63
	CCl_4	0.72	-0.76	-1.29	3.22	2.65
	gas phase	0.67	-0.66	-1.28	3.30	2.51

Table S5. Dispersion correction (DFT-D3, kcal mol^{-1}) to density functional results [B3LYP/6-31+G(d,p) geometries].

	B3LYP	Δ*E*	M06-2X	Δ*E*	PW6B95	Δ*E*	PWPB95	Δ*E*	B2PLYP	Δ*E*	CAM-B3LYP[a]	Δ*E*
1aA	-20.62		-1.24		-9.66		-7.78		-11.06		-14.31	
1aH	-21.08	-0.46	-1.26	-0.03	-9.92	-0.26	-7.99	-0.21	-11.35	-0.29	-14.68	-0.37
1bA	-18.07		-1.07		-8.45		-6.81		-9.69		-12.53	
1bH	-18.53	-0.46	-1.10	-0.03	-8.71	-0.26	-7.02	-0.21	-9.98	-0.29	-12.89	-0.36
1cA	-15.33		-0.92		-7.12		-5.73		-8.16		-10.59	
1cH	-15.79	-0.46	-0.94	-0.03	-7.38	-0.26	-5.94	-0.21	-8.45	-0.29	-10.95	-0.36
1dA	-16.48		-0.98		-7.66		-6.17		-8.78		-11.39	
1dH	-16.93	-0.45	-1.01	-0.03	-7.92	-0.26	-6.38	-0.21	-9.07	-0.28	-11.74	-0.35
1eA	-17.67		-1.04		-8.26		-6.66		-9.47		-12.24	
1eH	-18.13	-0.45	-1.07	-0.03	-8.52	-0.26	-6.87	-0.21	-9.75	-0.28	-12.59	-0.35
2aA	-21.04		-1.27		-9.87		-7.95		-11.30		-14.62	
2aH	-21.02	0.02	-1.28	0.00	-9.88	-0.01	-7.96	-0.01	-11.30	0.00	-14.63	-0.01
2bA	-18.50		-1.10		-8.66		-6.98		-9.92		-12.83	
2bH	-18.48	0.02	-1.11	-0.01	-8.67	-0.01	-6.99	-0.01	-9.93	-0.01	-12.84	-0.01
2cA	-15.75		-0.95		-7.32		-5.90		-8.39		-10.89	
2cH	-15.74	0.00	-0.95	-0.01	-7.34	-0.02	-5.91	-0.02	-8.41	-0.02	-10.91	-0.02
2dA	-16.89		-1.02		-7.87		-6.34		-9.01		-11.68	
2dH	-16.89	0.00	-1.02	-0.01	-7.89	-0.02	-6.36	-0.02	-9.03	-0.02	-11.71	-0.03
2eA	-18.08		-1.08		-8.47		-6.82		-9.70		-12.53	
2eH	-18.09	-0.01	-1.08	-0.01	-8.49	-0.03	-6.84	-0.02	-9.72	-0.03	-12.57	-0.03
3aA	-20.77		-1.22		-9.75		-7.86		-11.17		-14.42	
3aH	-20.80	-0.03	-1.22	-0.01	-9.79	-0.04	-7.89	-0.03	-11.21	-0.04	-14.47	-0.05
3bA	-18.22		-1.05		-8.54		-6.89		-9.80		-12.63	
3bH	-18.25	-0.03	-1.05	-0.01	-8.59	-0.05	-6.92	-0.04	-9.84	-0.05	-12.68	-0.05

3cA	-15.47		-0.90		-7.20		-5.81		-8.27		-10.69	
3cH	-15.52	-0.05	-0.90	-0.01	-7.26	-0.05	-5.85	-0.04	-8.32	-0.05	-10.75	-0.06
3dA	-16.60		-0.96		-7.74		-6.24		-8.88		-11.47	
3dH	-16.66	-0.05	-0.97	-0.01	-7.80	-0.06	-6.29	-0.05	-8.94	-0.06	-11.54	-0.07
3eA	-17.80		-1.02		-8.34		-6.72		-9.57		-12.32	
3eH	-17.85	-0.06	-1.03	-0.01	-8.40	-0.06	-6.77	-0.05	-9.63	-0.06	-12.39	-0.07
4aA	-21.73		-1.33		-10.25		-8.26		-11.72		-15.13	
4aH	-21.78	-0.05	-1.33	0.00	-10.29	-0.04	-8.29	-0.03	-11.76	-0.04	-15.20	-0.06
4bA	-19.18		-1.16		-9.04		-7.29		-10.34		-13.34	
4bH	-19.22	-0.05	-1.16	0.00	-9.08	-0.04	-7.32	-0.03	-10.39	-0.04	-13.40	-0.06
4cA	-16.44		-1.01		-7.71		-6.21		-8.82		-11.41	
4cH	-16.47	-0.03	-1.00	0.01	-7.74	-0.03	-6.24	-0.02	-8.85	-0.04	-11.45	-0.04
4dA	-17.59		-1.08		-8.26		-6.66		-9.44		-12.21	
4dH	-17.59	-0.01	-1.07	0.01	-8.27	-0.01	-6.67	-0.01	-9.46	-0.02	-12.22	-0.01
4eA	-18.79		-1.14		-8.86		-7.14		-10.13		-13.06	
4eH	-18.79	-0.01	-1.13	0.01	-8.87	-0.01	-7.15	-0.01	-10.15	-0.02	-13.07	-0.01
5aA	-21.55		-1.27		-10.15		-8.18		-11.62		-14.99	
5aH	-21.64	-0.09	-1.27	0.00	-10.22	-0.07	-8.24	-0.06	-11.70	-0.08	-15.09	-0.10
5bA	-19.00		-1.10		-8.95		-7.21		-10.25		-13.20	
5bH	-19.08	-0.08	-1.10	0.00	-9.01	-0.07	-7.27	-0.06	-10.33	-0.07	-13.29	-0.09
5cA	-16.27		-0.95		-7.61		-6.14		-8.73		-11.27	
5cH	-16.32	-0.06	-0.95	0.00	-7.67	-0.06	-6.18	-0.05	-8.79	-0.06	-11.33	-0.07
5dA	-17.41		-1.02		-8.16		-6.58		-9.35		-12.06	
5dH	-17.45	-0.05	-1.01	0.00	-8.21	-0.05	-6.62	-0.04	-9.40	-0.05	-12.11	-0.05
5eA	-18.61		-1.07		-8.76		-7.06		-10.04		-12.91	
5eH	-18.65	-0.04	-1.07	0.00	-8.81	-0.05	-7.10	-0.04	-10.09	-0.05	-12.96	-0.05

[a]CAM-B3LYP/6-31+G(d,p) geometries were used.

Table S6. Comparison of calculated and experimental tautomerization Gibbs free energies (kcal mol^{-1}) using the quasi RRHO approach for calculating entropies.[a]

	solvent	ΔG_T(exp)	SM8[b]	IEFPCM[b]	COSMO[b]	PBF[c]	SMD[d]	MC-FEP[e]	IEFPCM[f]
1a[g]	CH_3OH	0.04	2.93	1.62	0.82	0.84	2.90		2.08
	CH_3CN	0.05	3.36	1.66	0.79	0.86	3.70		2.04
	$CHCl_3$	-0.25	3.18	2.34	1.84	1.73	3.50		2.91
1b[g]	CH_3OH	0.87	1.76	0.91	-0.02	0.10	2.24		1.24
	CH_3CN	1.49	2.36	0.94	-0.05	0.03	2.94		1.21
	$CHCl_3$	0.90	2.13	1.78	1.19	1.22	2.83		2.01
1c[g]	CH_3OH	0.82	0.80	-0.47	-1.50	-1.33	0.77		-0.68
	CH_3CN	0.33	0.51	-0.42	-1.53	-1.34	1.48		-0.75
	$CHCl_3$	-0.17	0.87	0.36	-0.33	-0.34	1.31		0.17
1d[g]	CH_3OH	-0.45	-1.23	-2.21	-3.25	-3.28	-0.74		-2.12
	CH_3CN	-0.53	-1.37	-2.17	-3.29	-3.28	-0.15		-2.14
	$CHCl_3$	-0.60	-0.92	-0.97	-1.70	-1.87	-0.06		-1.23
1e[g]	CH_3OH	-0.58	-1.15	-2.48	-3.53	-3.45	-1.00		-2.43
	CH_3CN	-0.31	-1.59	-2.41	-3.57	-3.49	-0.22		-2.48
2c	CH_3OH[g]	0.11	-0.44	-0.76	-0.67	-0.97	0.25	-1.44	-0.65
	CH_3CN[h]	0.25	0.60	-0.73	-0.68	-0.87	0.48	-0.86	-0.63
	$CHCl_3$[i]	-0.23	0.47	-0.27	-0.19	-0.36	0.55	-0.19	-0.14
	CCl_4[i]	0.34	0.70	0.19	0.29	0.20	0.66	0.28	0.28

3c[j]	CH_3OH	-0.42	-0.79	-0.94	-0.90	-1.19	-0.10	-1.47	-0.94
	CH_3CN	-0.47	0.12	-1.02	-0.91	-1.17	0.01	-1.34	-0.90
	$CHCl_3$	-0.55	0.01	-0.59	-0.55	-0.75	0.09	-0.60	-0.53
	CCl_4	-0.45	0.18	-0.23	-0.17	-0.34	0.12	-0.30	-0.17
4a	CH_3OH[g]	-0.05	1.22	0.28	0.38	0.05	1.01	-1.39	0.88
	CH_3CN[g]	0.71	2.51	0.34	0.36	0.05	1.80	-0.19	0.42
	$CHCl_3$[k]	0.24	2.46	1.20	1.27	1.01	2.03	1.47	1.04
	CCl_4[k]	1.13	2.82	2.01	2.13	1.93	2.50	2.52	1.32
4b	CH_3OH[g]	-0.31	1.28	0.49	0.59	0.23	1.40	-1.72	0.55
	CH_3CN[g]	0.90	2.42	0.58	0.57	0.19	2.06	0.44	0.81
	$CHCl_3$[k]	0.17	2.48	1.41	1.47	1.18	2.28	1.66	1.61
	CCl_4[k]	1.26	2.89	2.21	2.32	2.14	2.71	2.94	2.37
4c[k]	CH_3OH	0.03	1.15	0.07	0.19	-0.11	0.97	-1.70	0.42
	CH_3CN	0.34	2.22	0.17	0.17	-0.15	1.58	-0.19	0.61
	$CHCl_3$	0.38	2.22	1.01	1.04	0.74	1.81	1.15	1.45
	CCl_4	1.13	2.54	1.77	1.86	1.68	2.21	2.10	2.03
4d	CH_3OH[g]	0.32	0.40	0.12	0.16	-0.35	1.44	-1.39	0.15
	CH_3CN[g]	0.90	1.33	0.26	0.14	-0.33	1.84	0.03	0.28
	$CHCl_3$[k]	0.52	1.62	1.12	1.04	0.81	2.04	1.41	0.92
	CCl_4[k]	1.14	2.17	1.87	1.87	1.73	2.36	2.20	1.86
4e[k]	$CHCl_3$	0.52	2.03	1.38	1.26	1.07	2.28	1.63	1.32
	CCl_4	1.18	2.52	2.09	2.09	1.96	2.62	2.34	2.06
5a	CH_3OH[g]	-0.44	0.58	0.08	0.25	-0.28	1.29	-1.88	-0.09

	CH_3CN^g	0.08	1.75	0.12	0.23	-0.15	1.76	-0.51	-0.31
	$CHCl_3^g$	0.05	1.86	0.94	1.06	0.76	1.95	1.03	0.89
	CCl_4^g	1.12	2.31	1.73	1.85	1.60	2.32	2.08	1.71
5b	CH_3OH^g	-0.42	0.29	-0.12	-0.05	-0.46	0.80	-1.97	0.00
	CH_3CN^l	0.27	1.31	-0.07	-0.07	-0.50	1.19	-0.81	-0.09
	$CHCl_3^g$	0.02	1.51	0.75	0.79	0.44	1.48	0.68	0.89
	CCl_4^g	0.98	2.00	1.52	1.60	1.39	1.92	1.91	1.64
5c	CH_3OH^l	-0.09	0.45	-0.22	-0.10	-0.50	1.09	-1.74	-0.51
	CH_3CN^l	-0.13	1.43	-0.17	-0.12	-0.52	1.39	-0.77	-0.43
	$CHCl_3^g$	0.19	1.56	0.63	0.69	0.32	1.60	0.75	0.45
	CCl_4^l	0.90	1.96	1.38	1.45	1.23	1.91	1.67	1.30
5d	CH_3CN^l	0.33	0.38	-0.31	-0.33	-0.78	0.76	-0.55	-0.37
5e	CH_3CN^l	0.34	1.00	-0.20	-0.16	-0.49	1.36	-0.59	0.06
MUE			1.16	0.71	0.84	0.83	1.20	0.98	0.77
RMSE			1.38	0.90	1.14	1.11	1.42	1.08	0.99

[a]ΔG_T(calc) = ΔG(keto) - ΔG(enol) = $\Delta\Delta G_{gas}$[CEPA/1-CBS//B3LYP/6-31+G(d,p)] + $\Delta\Delta G_{therm}$ [B3LYP/6-31+G(d,p)] + $\Delta\Delta G_{solv}$.

[b]B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) single point calculations in the respective solvent using the SM8, IEFPCM, and COSMO solvation models. [c]PBF M06-2X/aug-cc-pVTZ(-f)//B3LYP/6-31+G(d,p) single point calculations. [d]SMD M06-2X/6-31G(d)//B3LYP/6-31+G(d,p) single point calculations. [e]Monte-Carlo free energy perturbation calculations using the OPLSAA force field with IEFPCM-B3LYP/6-31+G(d,p) optimized structures and CHELPG charges in the respective solvent. [f]IEFPCM-B3LYP/6-31+G(d,p) geometries optimized in the respective solvent; $\Delta\Delta G_{solv}$ calculated as *E* [IEFPCM-B3LYP/6-31G(d,p)//IEFPCM-B3LYP/6-31+G(d,p)] –

E[B3LYP/6-31G(d,p)//IEFPCM-B3LYP/6-31+G(d,p)] [g]experimental values, this work; the data for **1a** are not very reliable; for **2c** in ref. [1] $\Delta G_T(CH_3OH)$ = -0.26 kcal mol^{-1} has been quoted; for **5a** in ref. [2] $\Delta G_T(CH_3OH)$ = 0.17 kcal mol^{-1} has been quoted. [h]experimental values, ref. [3]. [i]experimental values, ref. [1]. [j]experimental values, ref. [4]. [k]experimental values, ref. [5]. [l]experimental values, ref. [2].

Table S7. Gibbs free energies of tautomerization obtained by IEFPCM-QCISD(T)/6-31G(d)//IEFPCM-B3LYP/6-31+G(d,p) + MC-FEP calculations.

	ΔG_T(calc)			
	CH_3OH	CH_3CN	$CHCl_3$	CCl_4
2c	-1.93	-1.35	-1.18	-1.17
3c	-2.95	-2.83	-2.32	-2.26
4a	0.94	-0.22	0.53	-0.23
4b	-1.06	0.75	1.52	2.09
4c	-0.50	0.96	1.24	1.38
4d	-0.58	0.16	0.47	0.96
4e			0.85	0.68
5b	-1.77	-0.04	0.35	0.62
5c	-1.57	-0.48	0.05	0.20
5d	-1.41	-0.24		
5e		-0.85		

Table S8. Comparison of experimental Gibbs free energies of tautomerization ΔG_T(exp) in hydrocarbon solvents[a] with calculated ΔG_T-values in the respective solvent and in gas phase using quasi-RRHO entropies.

		B3LYP/6-31+G(d,p) geometries		MP2/cc-pVDZ geometries	
	ΔG_T(exp)	solution	gas phase	solution	gas phase
1c	1.31	1.31	1.85	0.09	0.71
2c	0.42	0.69	0.99	1.00	1.36
3c	-0.24	0.15	0.39	0.13	0.39
4c	1.44	2.32	2.95	2.56	3.13
5a	1.31	2.36	2.92	1.89	2.76
5b	1.36	1.99	2.69	2.11	2.91
5c	0.95	1.95	2.48	1.70	2.43
5d	1.57	1.54	2.30	1.67	2.48
5e	1.66	1.57	2.47	1.95	2.59
MUE		0.48	1.03	0.64	1.13
RMSE		0.62	1.11	0.73	1.20

[a] **1c – 3c**: iso-octane(ref. [4]); **4c**: hexane (ref. [5]); **8a – 8e**: cyclohexane (ref. [2, 5]). A negative sign indicates greater stability of the keto tautomer.

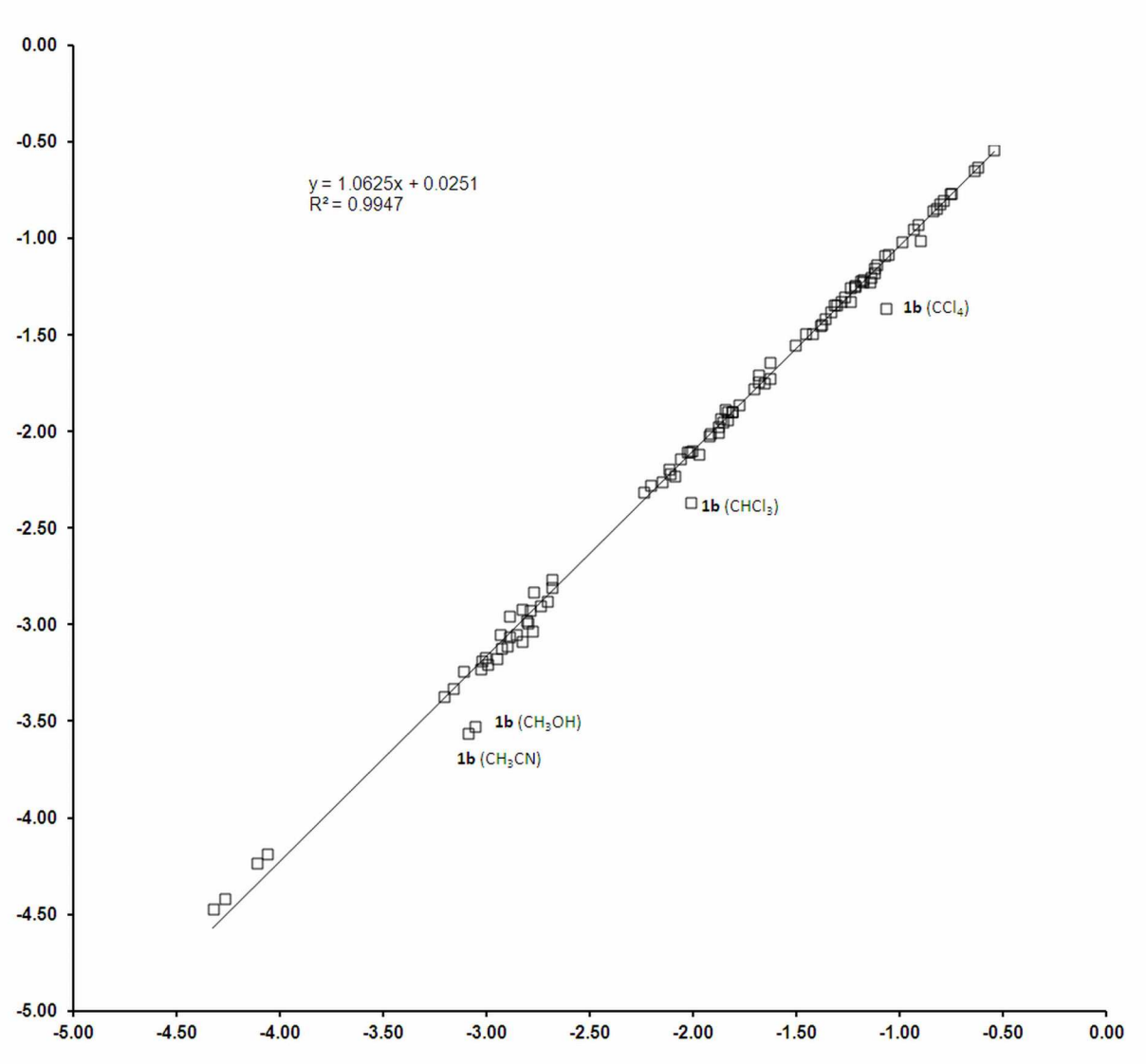

Figure S1. Plot of IEFPCM ΔG_{solv} using gas phase geometries vs those using in-solution geometries.

References

(1) Antonov, L.; Stoyanov, S.; Stoyanova, T. Tautomeric Equilibrium in 1-Phenylazo-2-Naphthol - A Quantitative Study. *Dyes Pigm.* **1995**, *27*, 133-142.

(2) Fabian, W. M. F.; Antonov, L.; Nedeltcheva, D.; Kamounah, F. S.; Taylor, P. J. Tautomerism in Hydroxynaphthaldehyde Anils and Azo Analogues: A Combined Experimental and Computational Study. *J. Phys. Chem. A* **2004**, *108*, 7603-7612.
(3) Antonov, L.; Fabian, W. M. F.; Taylor, P. J. Tautomerism in some Aromatic Schiff Bases and Related Azo Compounds: An LSER Study. *J. Phys. Org. Chem.* **2005**, *18*, 1169-1175.
(4) Antonov, L.; Stoyanov, S. Azo-Quinonehydrazone Tautomerism in 2-Phenylazo-1-Naphthol. *Dyes Pigm.* **1995**, *28*, 31-39.
(5) Antonov, L.; Fabian, W. M. F.; Nedeltcheva, D.; Kamounah, F. S. Tautomerism of 2-Hydroxynaphthaldehyde Schiff Bases. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1173-1179.