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

Supplementary Information for

Revealing the Excited-state Dynamics of Cytidine and the Role of Excited-state Proton Transfer Process

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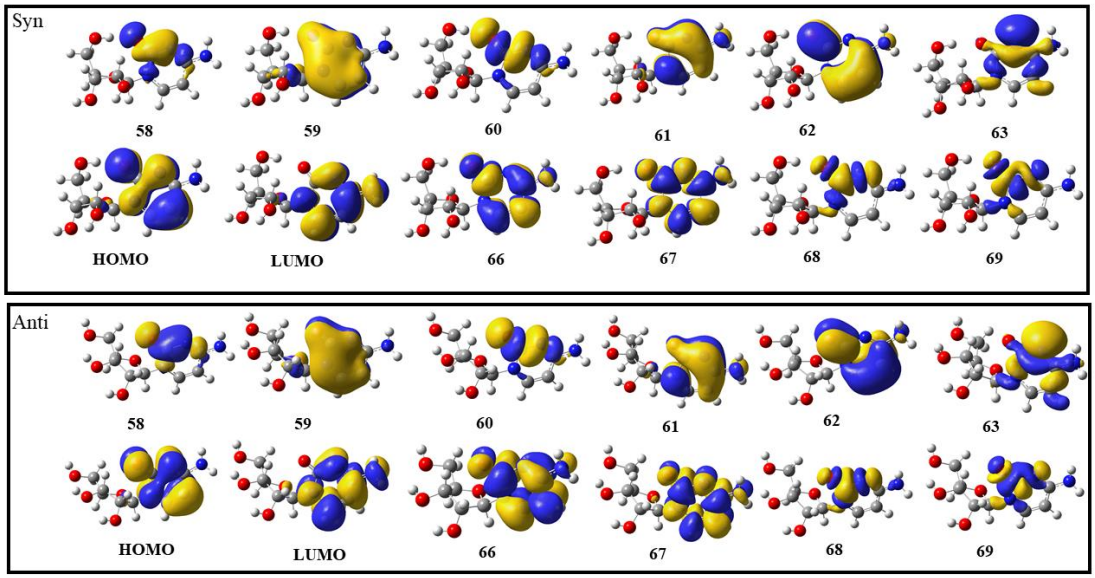

Figure S1 The active spaces included in SA3-CASSCF(14,12) calculation level for the most stable ground-state conformation of cytidine system.

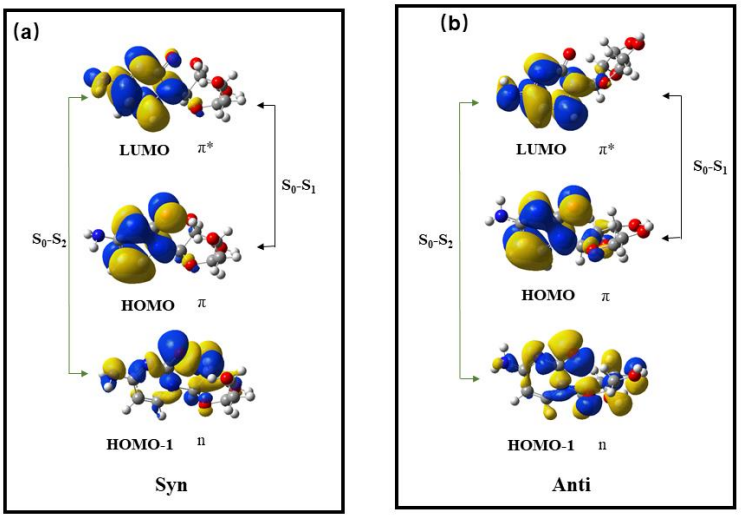

Figure S2 Orbitals and orbital promotions involved in forming the first two excited singlet states of cytidine system calculated at the SA3-CASSCF(14,12)// 6-31G* level of theory.

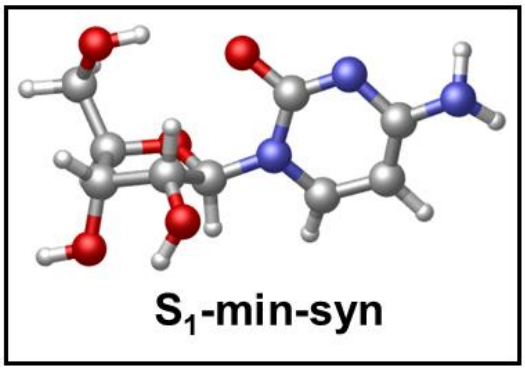

Figure S3 The stable structure of syn-Cyd in the S_1 state calculated at the SA3-CASSCF(14,12)// 6-31G* level of theory.

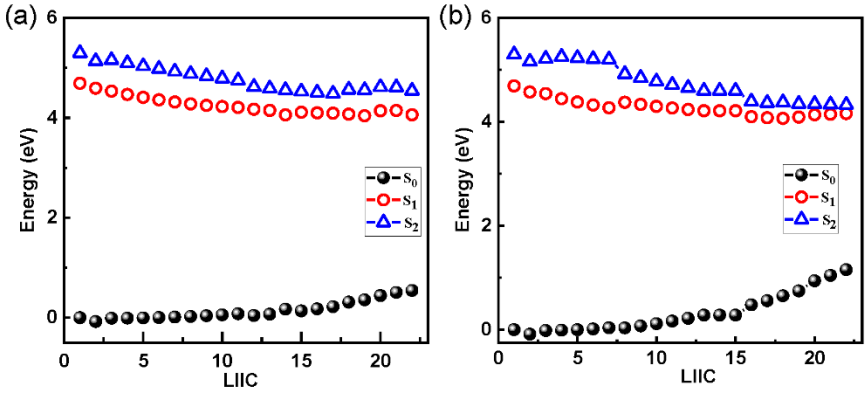

Figure S4 The energy profiles constructed by LIIC method connecting the FC point and Syn-$CI_{S2/S1}$ (a), Syn-$CI_{S2/S1}$-B (b) at CASPT2 level.

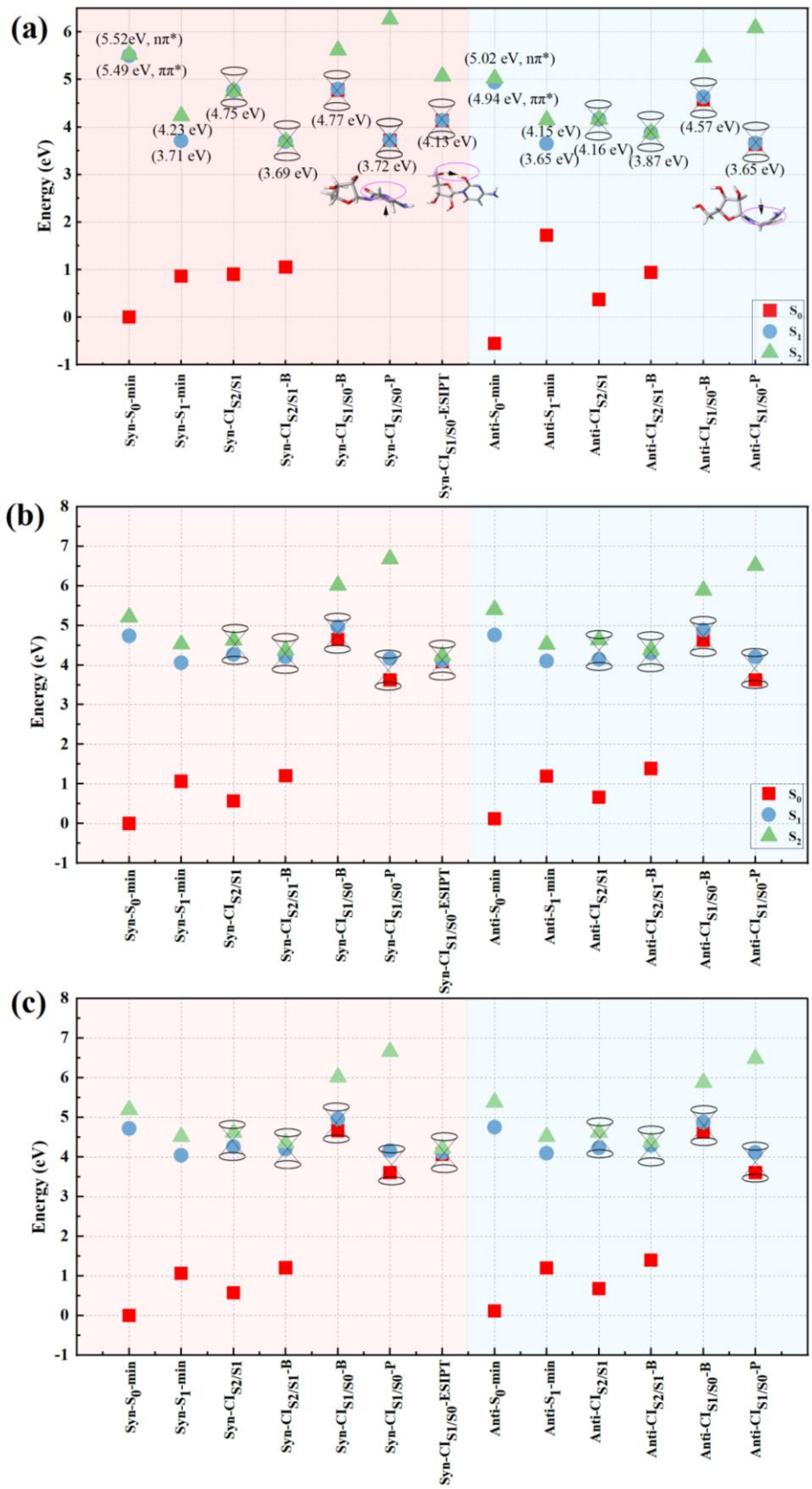

Figure S5 The energy information of critical points calculated at (a) SA3-CASSCF(14,12)/6-31G*, (b) CASPT2/SA3-CASSCF(14,12)/6-31G* level, and (c) CASPT2/SA3-CASSCF(14,12)/6-31G** level.

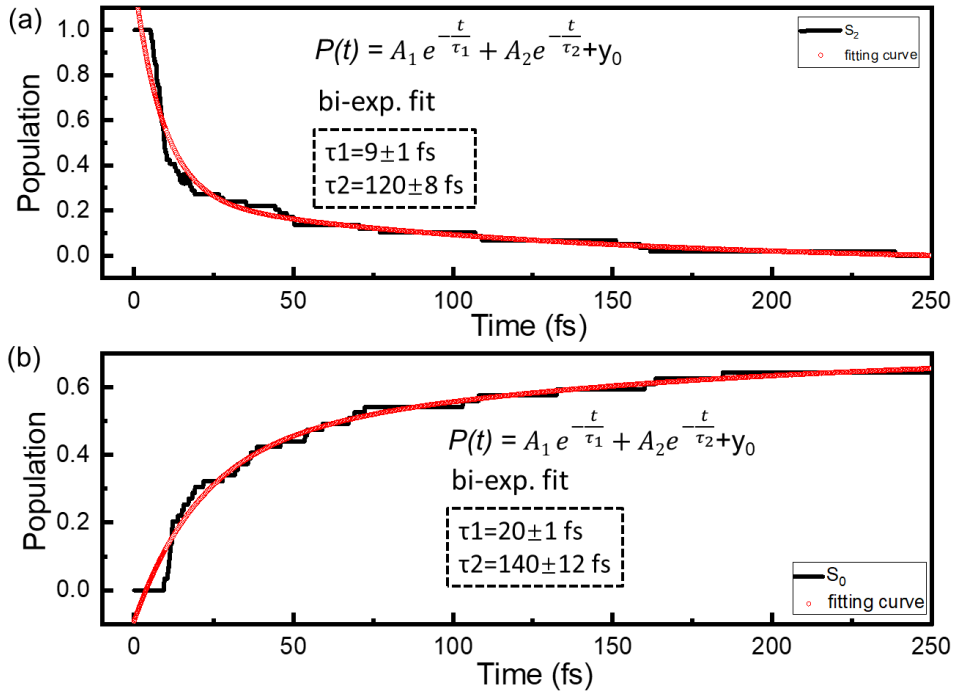

Figure S6 The time-dependent population of the S_2 (a) and S_0 (b) together with bi-exponential fitting curves.

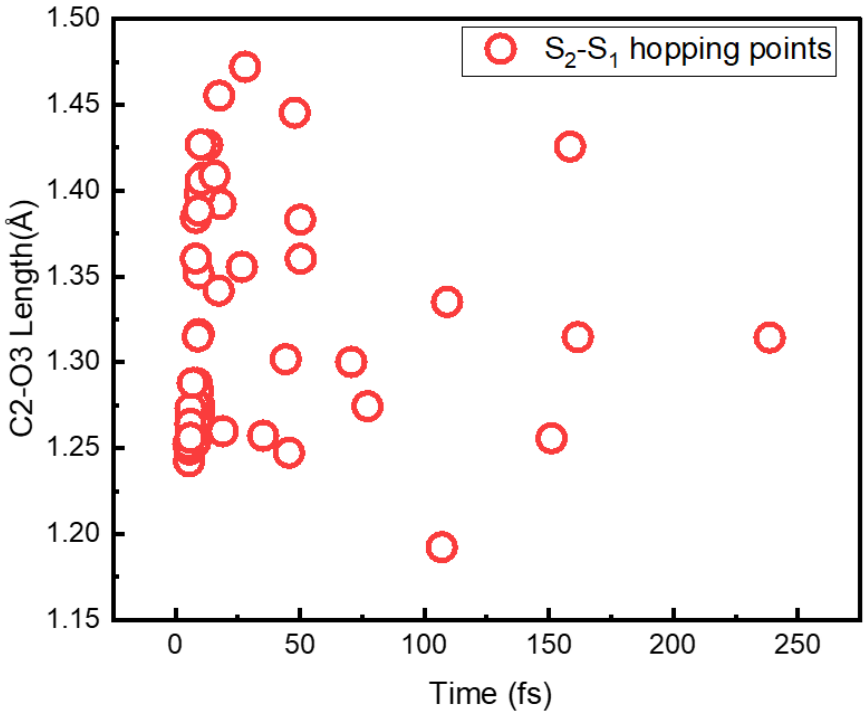

Figure S7 The C2-O3 bond lengths (ordinate) and the decay times for all S_2-S_1 hopping points (abscissa).

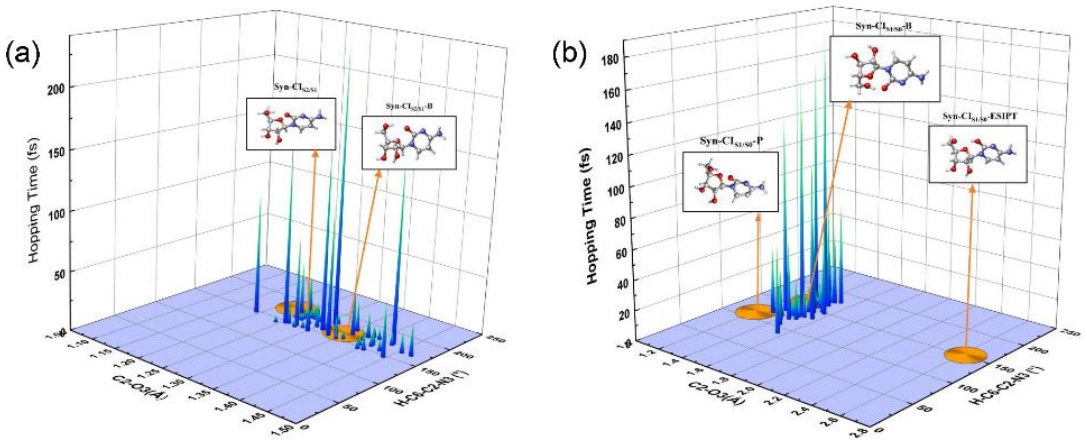

Figure S8 Geometric distribution at the $S_2 \rightarrow S_1$ (a) and $S_1 \rightarrow S_0$ hopping events (b) as functions of bond length of C2-O3 and dihedral angles of H-C6-C2-N3. Bars: hopping events; The height of each bar represents hopping time of each trajectory.

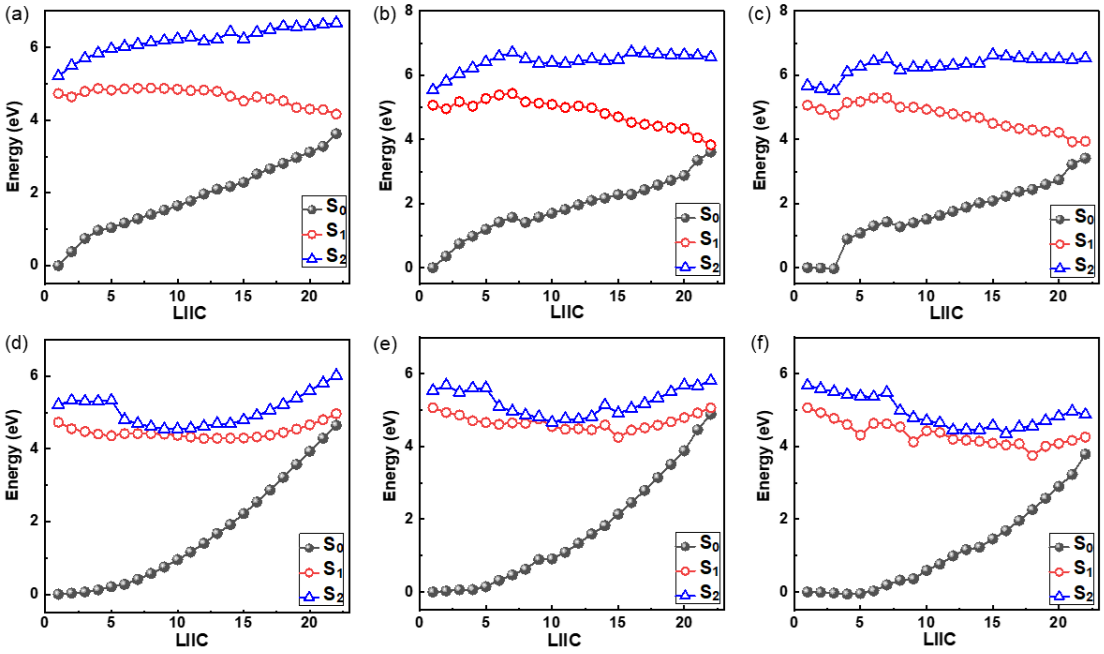

Figure S9 The energy profiles constructed by LIIC method connecting the FC point and Syn-$CI_{S1/S0}$-P (a) gas phase, (b) PCM model and (c) an explicit water molecule model; and Syn-$CI_{S1/S0}$-B (d) gas phase, (e) PCM model and (f) an explicit water molecule model at CASPT2 level.

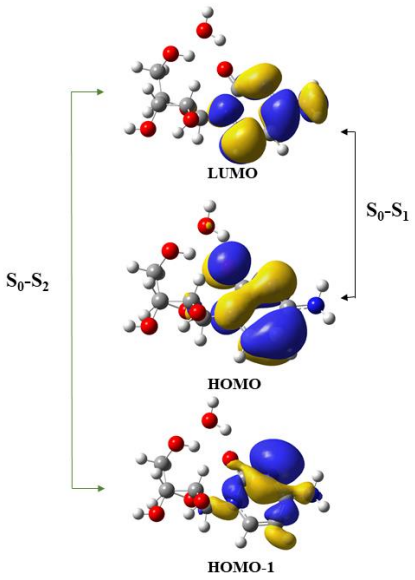

Figure S10 Orbitals and orbital promotions involved in forming the first two excited singlet states of Cyd-H_2O cluster system calculated at the SA3-CASSCF(14,12)/ 6-31G* level of theory.

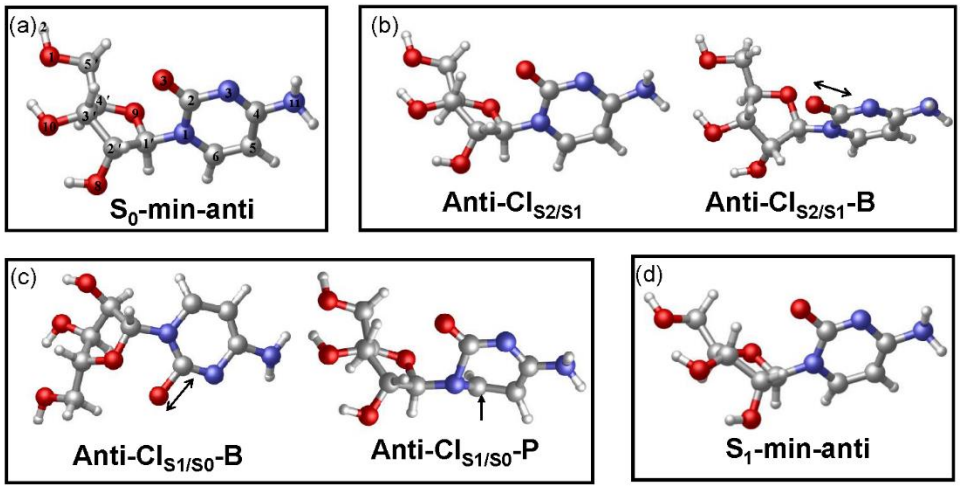

Figure S11 Optimized structures: (a) ground state structure of Anti-Cyd with atom numbering, (b) two MECIs located between S_2 and S_1, (c) two MECIs located between S_1 and S_0 states, and (d) stable structure in the S_1 state obtained at the SA3-CASSCF(14,12)/6-31G* level. Red for O atom, blue for N atom, grey for C atom, and white for H atom.

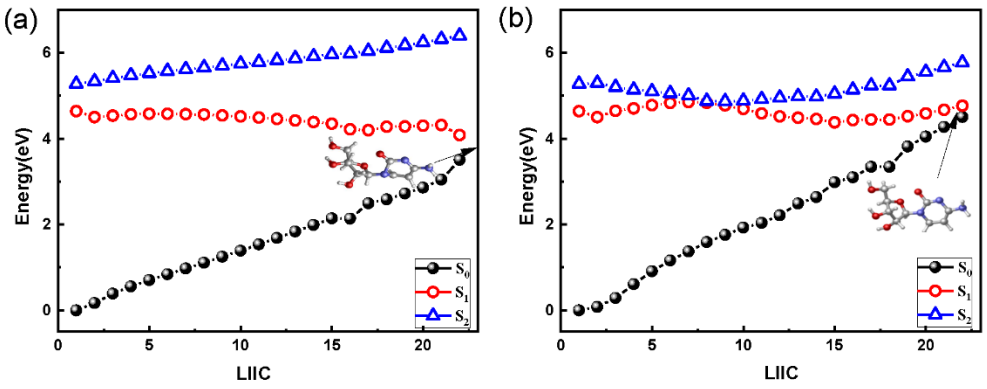

Figure S12 The energy profiles constructed by LIIC method connecting the FC point and Anti-$CI_{S1/S0}$-P (a); $CI_{S1/S0}$-B (b) at CASPT2 level.

Table S1 The absolute ground state energy (in hartree) of syn-, anti-, north-, and south-Cyd conformer optimized at the SA3-CASSCF(14,12)/6-31G* level.

Conformer	Energy
syn	-886.197104348686
anti	-886.154693719031
north	-886.150859721237
south	-886.147484992092

Table S2 The vertical excitation energies (in eV) of anti-Cyd to the two lowest singlet excited states calculated at the CASPT2 level.

Geo.	State	CASPT2/gas
anti	**$S_1(\pi\pi^*)$**	4.64
	$S_2(n\pi^*)$	5.27

Table S3 Cartesian coordinates of S_0-min of syn (left) and anti (right) conformer of cytidine system optimized at SA3-CASSCF(14,12)/6-31G* level.

SA3-CASSCF(14,12)/6-31G*			SA3-CASSCF(14,12)/6-31G*		
X	Y	Z	X	Y	Z

C	0.4530500396	-1.8617032003	-2.2101179713	C	0.4856045960	2.1362429903	-1.1238627321
C	0.6390579298	-2.7705292681	-0.9857243300	C	-0.7011271631	1.9495856719	-0.1792309838
C	0.6166776396	-1.7862929118	0.1835654404	C	-1.2390462039	0.5803899018	-0.5996259319
C	1.2530493487	-0.5563089734	-0.4696496883	C	-0.0090405265	-0.1105848922	-1.2223761787
O	0.8212755308	-0.5550277888	-1.7889780039	O	1.0051090611	0.8451576556	-1.3198323188
O	1.9198728779	-3.3660863287	-0.9663608389	O	-1.6946581276	2.9214581559	-0.3328522049
O	1.3021864982	-2.2125823701	1.3129759729	O	-2.1868358624	0.7039503322	-1.6221061959
C	-0.9640327855	-1.8398749121	-2.7584868185	C	1.5745223123	3.0240076135	-0.5636169707
O	-1.9309465393	-1.7227361477	-1.7648041537	O	0.9621598254	4.2663140290	-0.2985371544
H	-1.8628720175	-0.8681108080	-1.3487518898	H	1.5772178235	4.8493820902	0.1237596134
H	1.9555366322	-4.0977008295	-1.5669811798	H	-1.2994628489	3.7746405062	-0.1956090672
H	-0.1330217869	-3.5238340434	-0.9061784541	H	-0.3586279046	1.9054649557	0.8433811398
H	-0.4013116208	-1.5787355687	0.4637481940	H	-1.6472189081	0.0221086113	0.2316663911
H	2.3287644271	-0.6752078408	-0.4292238657	H	-0.2987568543	-0.4358605569	-2.2100199471
H	1.1353071774	-2.1634555516	-2.9988198902	H	0.1252527243	2.5456202697	-2.0639535116
H	2.0012589851	-2.7928731124	1.0340161742	H	-2.6779540884	1.5040981435	-1.4725585788
H	-1.0384872728	-1.0395648766	-3.4901480680	H	1.9673816409	2.5761993229	0.3431292640
H	-1.1538458064	-2.7763551224	-3.2719218523	H	2.3845086586	3.1322713620	-1.2782586545
C	2.0257436812	1.4713027762	0.6271932384	C	0.7486610755	-2.4222794517	-1.2760768725
C	-0.3265653728	1.2209052179	0.2306362109	C	0.8701924489	-1.2228151733	0.7957864657
C	1.8372835106	2.6779831070	1.1976595672	C	1.3023503263	-3.5140834758	-0.7119140627
H	2.9969422941	1.0358276984	0.5119970492	H	0.4756627677	-2.3834859432	-2.3110548671
C	0.4773974643	3.1441074869	1.2800272445	C	1.6298350055	-3.4245134535	0.6920017941
H	2.6593701549	3.2698130280	1.5465582250	H	1.5111329450	-4.3968081322	-1.2824038229
N	0.9752018413	0.7268491633	0.1566015561	N	0.4986662415	-1.2906215400	-0.5449875870
O	-1.2651776661	0.5963619581	-0.1912583088	O	0.6906725932	-0.1973287344	1.4399308233
N	-0.5292395218	2.4771556261	0.8401888568	N	1.4259172061	-2.3681651771	1.4013020405
N	0.2474863527	4.4260050439	1.8177628786	N	2.2294374952	-4.5101940934	1.2911504061
H	-0.7211951056	4.5812624057	2.0056526249	H	2.2611818472	-4.4550174510	2.2864511507
H	0.8200227098	4.6465440430	2.6052291799	H	1.9625411637	-5.4074131069	0.9505552939

Table S4 Cartesian coordinates of S_1-min of syn (left) and anti (right) of cytidine system optimized at SA3-CASSCF(14,12)/6-31G* level.

SA3-CASSCF(14,12)/6-31G*				SA3-CASSCF(14,12)/6-31G*			
	X	Y	Z		X	Y	Z
C	0.4704641050	-1.9163806925	-2.2025778687	C	0.5111243160	2.1454400739	-1.0852128279
C	0.6004316228	-2.7604880549	-0.9220058209	C	-0.7055402534	1.9842253370	-0.1757680506
C	0.5276339147	-1.7178248862	0.1949267667	C	-1.2334477370	0.6071679714	-0.5905375945
C	1.1762138191	-0.5173233823	-0.5028370543	C	0.0193690589	-0.0913247178	-1.1672766657
O	0.7085151145	-0.5702938967	-1.8172639776	O	1.0518288124	0.8518490849	-1.1799887987
O	1.8742532552	-3.3587733806	-0.8174969793	O	-1.6914253219	2.9528416933	-0.3710597610
O	1.1600217147	-2.0858926523	1.3697749947	O	-2.1506184365	0.7170656582	-1.6389651735

C	-0.8917121292	-1.9960349196	-2.8665487527	C	1.5674005132	3.0830506207	-0.5437528463
O	-1.9363432537	-1.7940722744	-1.9641428682	O	0.9223282070	4.3213323449	-0.3519944082
H	-1.9162659170	-0.8979793092	-1.6521245009	H	1.5261201045	4.9525923573	0.0138342730
H	1.9206568188	-4.1420628282	-1.3480570527	H	-1.2937141792	3.8100893869	-0.2688879283
H	-0.1782416843	-3.5066986321	-0.8367677608	H	-0.3900239126	1.9602284070	0.8582340981
H	-0.5035156295	-1.5038594972	0.4199509898	H	-1.6662480965	0.0584838719	0.2346821119
H	2.2488783902	-0.6593204082	-0.4832477873	H	-0.2242914750	-0.3789248046	-2.1774951654
H	1.2358934061	-2.2151651162	-2.9123688148	H	0.1776807520	2.4921677348	-2.0598193995
H	1.8905741867	-2.6533812934	1.1521728529	H	-2.6457379427	1.5195805493	-1.5172793624
H	-0.9273010426	-1.2806265191	-3.6835053029	H	1.9509052373	2.6903277460	0.3925985517
H	-1.0287211048	-2.9862719925	-3.2852299363	H	2.3911308621	3.1738376244	-1.2443314120
C	2.0637363387	1.5789072066	0.3701435975	C	0.6456551066	-2.4468058974	-1.2875859079
C	-0.2872129690	1.3623701905	0.2980638055	C	0.8911148042	-1.3686743982	0.7930001680
C	1.8734519329	2.7270968551	1.2005115750	C	1.2529846649	-3.6008129341	-0.6889788680
H	2.9781906280	1.3588107871	-0.1389484029	H	0.3388025935	-2.4037596698	-2.3086442575
C	0.6066511903	3.0823695874	1.5437687579	C	1.6524583462	-3.5419562954	0.6045699733
H	2.7334220008	3.2647262156	1.5540751384	H	1.4059154001	-4.4757098818	-1.2919356389
N	0.9607569292	0.7881067923	0.0847871495	N	0.4744602066	-1.3116336295	-0.5192832104
O	-1.2733880988	0.7104444032	-0.3064597338	O	0.6368392295	-0.2349532487	1.4628982761
N	-0.4999873302	2.4443014822	0.9503061552	N	1.4387454609	-2.3854917677	1.3920682897
N	0.2485048251	4.0749509482	2.4530849181	N	2.3417377163	-4.5344747515	1.2926584168
H	-0.6388120849	4.4763211791	2.2318151821	H	2.1762736616	-4.4913150571	2.2763322876
H	0.9420406509	4.7811819885	2.5826078306	H	2.2034515712	-5.4567229780	0.9381575705

Table S5 Cartesian coordinates of Syn-$CI_{S2/S1}$ (left) and Syn-$CI_{S2/S1}$-B (right) of cytidine optimized at SA3-CASSCF(14,12)/6-31G* level.

SA3-CASSCF(14,12)/6-31G*				SA3-CASSCF(14,12)/6-31G*			
	X	Y	Z		X	Y	Z
H	13.0158775981	17.2403903167	12.2649516255	C	0.3959708110	-1.8721424410	-2.1513259738
O	13.0688543663	18.0280733842	12.7961726862	C	0.5930921667	-2.7846120576	-0.9265337390
C	12.0505086811	18.0239174570	13.7465004571	C	0.5444125702	-1.8067466725	0.2486330468
H	11.0698978961	17.9485070906	13.2835684718	C	1.1335779221	-0.5540783743	-0.4063074200
H	12.1002957332	18.9760878324	14.2629758976	O	0.6101364570	-0.5435055909	-1.6966569225
C	12.1967938278	16.9023475984	14.7582731878	O	1.8808323935	-3.3605563445	-0.9032602463
H	11.4955647689	17.0508710544	15.5736290701	O	1.2373486274	-2.2196296171	1.3744118429
O	11.9037909048	15.6645529954	14.1310825781	C	-0.9844499581	-1.9552708005	-2.7756262060
C	12.9216065237	14.7393360504	14.3432743853	O	-2.0040333964	-1.8444545808	-1.8298097991
H	12.7291488695	14.1730457314	15.2459649892	H	-2.0151395474	-0.9626547037	-1.4790693875
N	12.9520027507	13.7579732171	13.2786696564	H	1.9254869023	-4.1056447430	-1.4864957335
C	12.6986095791	12.4237663748	13.5655585263	H	-0.1675579065	-3.5504428618	-0.8546061676
H	12.5643467920	12.1743739287	14.5947308340	H	-0.4814341931	-1.6307831970	0.5282008794
C	12.6526916031	11.4480873072	12.5348508307	H	2.2089634993	-0.6653572745	-0.4421904406

H	12.4893703107	10.4205434419	12.7994370541	H	1.1456707468	-2.1061294592	-2.9009594837
C	12.8211899812	11.8238922250	11.2349403594	H	1.9538443203	-2.7787183799	1.0961668531
N	12.9145962395	11.0081859989	10.1081891734	H	-1.0694642143	-1.1926006603	-3.5445758671
H	12.4628973030	11.4087921738	9.3105926768	H	-1.1034434684	-2.9218228407	-3.2512950069
H	12.5711728446	10.0847104030	10.2703487424	C	2.0160294481	1.4249991397	0.7166929375
N	13.0360517340	13.1859292598	10.9946901830	C	-0.3183002353	1.3136106075	0.3946787841
C	13.1009127324	14.1474125526	11.8999090837	C	1.8001457846	2.6784371639	1.3666148818
O	13.2855094798	15.3319600209	11.6333920642	H	2.9454346075	0.9008226560	0.7473162397
C	13.6445041818	16.7537083553	15.3394418616	C	0.5426105714	3.1818282130	1.4391609104
H	14.2358247941	17.6492487481	15.2047503396	H	2.6470170093	3.2131826603	1.7534044638
C	14.1966199433	15.5605486941	14.5618018519	N	0.9073311912	0.7160941145	0.2609231012
H	14.5901438679	15.8936169001	13.6169684326	O	-1.3418406721	0.5743515370	-0.0793080493
O	15.1910161243	14.8541685647	15.2221407793	N	-0.5675682266	2.4744137548	0.9296814129
H	15.0422967716	14.9337304130	16.1573115678	N	0.1946831179	4.4315814092	1.9429047012
O	13.6208898821	16.3658544952	16.6952360412	H	-0.7466593415	4.4504412154	2.2752340876
H	13.4439597553	17.1108155251	17.2527119528	H	0.8287795929	4.7931335079	2.6231495004

Table S6 Cartesian coordinates of syn-$CI_{S1/S0}$-B (left) and syn-$CI_{S1/S0}$-P (right) of cytidine optimized at SA3-CASSCF(14,12)/6-31G* level.

SA3-CASSCF(14,12)/6-31G*				SA3-CASSCF(14,12)/6-31G*			
	X	Y	Z		X	Y	Z
C	0.2986235243	-1.8428308529	-2.0913500815	C	-0.0105932303	-0.0685174514	-0.0025606098
C	0.8571099078	-2.6754712445	-0.9286633314	C	0.0190656562	0.0019645624	1.5617531476
C	1.1517846125	-1.6286063034	0.1452536349	C	1.5157840420	-0.0073358315	1.8693033768
C	1.5246188324	-0.4033063652	-0.7004575566	C	2.0281119064	-0.8855530024	0.7252707149
O	0.6960892306	-0.4986792912	-1.8255750993	O	1.2615199681	-0.5744372739	-0.3851134931
O	2.0941307838	-3.2629377136	-1.2587420116	O	-0.5051708631	-1.1707585927	2.1412981210
O	2.1176851572	-2.0124777871	1.0599355606	O	1.8527544251	-0.5109179015	3.1178621271
C	-1.2099665680	-1.8997952180	-2.2473570789	C	-0.2485537704	1.2715196887	-0.6751170027
O	-1.8774693314	-1.6076337423	-1.0552015413	O	0.5174798935	2.2952577625	-0.1227397867
H	-1.9382394207	-0.6671004670	-0.9529295197	H	1.4347535664	2.1576323586	-0.3336184466
H	1.9683601717	-4.0690163795	-1.7402992809	H	-1.4522585923	-1.1567588432	2.1326120625
H	0.1565066225	-3.4250016152	-0.5839500914	H	-0.4803197060	0.8813313376	1.9438518101
H	0.2449952356	-1.4065571032	0.6895775210	H	1.9070257361	0.9926590649	1.7910153814
H	2.5689963615	-0.4435913325	-0.9870149730	H	1.8870159662	-1.9229514045	1.0041264998
H	0.7674100183	-2.1466508761	-3.0200438848	H	-0.7677979242	-0.7781060926	-0.3196373143
H	2.7637940948	-2.5446587451	0.6092317221	H	1.1885813240	-1.1416238911	3.3729068692
H	-1.5123420940	-1.2284826315	-3.0450289331	H	-0.0651741337	1.1631761484	-1.7405667786
H	-1.4937416020	-2.9047898928	-2.5368916407	H	-1.2879249880	1.5510548228	-0.5443042652
C	2.1931946008	1.3882553144	0.8885360442	C	4.2988747577	-1.7293735114	0.7542937942
C	0.1902986540	1.6250555637	-0.3684260254	C	4.0643559365	0.5136500869	0.0793451349
C	1.6445884732	2.5746645605	1.6112332931	C	5.5866645634	-1.7536466276	0.0938545016
H	2.6222607518	0.6032933340	1.4864627549	H	3.9969836776	-2.3645604868	1.5656225793

C	0.5166904728	3.1617578655	1.2412340953	C	6.1684201986	-0.4095977447	0.0674424202
H	2.2206226771	2.9615511557	2.4323633142	H	5.3748401251	-1.9461177278	-0.9594835963
N	1.2674262308	0.8733397050	-0.0930766453	N	3.4508715246	-0.7834881501	0.3864406820
O	-0.5955100574	1.1474207941	-1.5232570942	O	3.3141731382	1.4424645865	-0.1720856042
N	-0.2623203005	2.6530702061	0.1217232081	N	5.4215753489	0.6522402232	0.1776316901
N	-0.0404847809	4.3459949703	1.7382658939	N	7.4803655949	-0.2550530868	-0.2050553325
H	-1.0389521147	4.2981094706	1.7557550276	H	7.8486884030	0.6707280476	-0.2098312462
H	0.3118169306	4.5908005804	2.6406016766	H	8.0879455550	-0.9949176697	0.0598472632

Table S7 Cartesian coordinates of syn-$CI_{S1/S0}$-ESIPT (left) and transition state (TS) structure (right) of cytidine optimized at SA3-CASSCF(14,12)/6-31G* level.

SA3-CASSCF(14,12)/6-31G*				SA3-CASSCF(14,12)/6-31G*			
X		Y	Z	X		Y	Z
H	12.2091789060	15.9898510732	12.1567433119	C	0.000000000000	0.000000000000	0.000000000000
O	13.0273160365	18.3484479971	12.9619097623	C	0.000000000000	0.000000000000	1.540177232885
C	12.1316355337	18.4041158598	14.0398726551	C	1.491349325263	0.000000000000	1.883379484915
H	11.1017235802	18.4855280341	13.7126257473	C	2.061264711150	-0.785952318472	0.696902505421
H	12.3893284500	19.2375169129	14.6905004971	O	1.310116097764	-0.334774850864	-0.403181461019
C	12.2977642044	17.1131724999	14.8535174168	O	-0.526226479400	-1.203763181937	2.050555109799
H	11.6771992280	17.2100359580	15.7370260266	O	1.795115470974	-0.549330783020	3.115984571090
O	11.8404965659	16.0205154286	14.0857785054	C	-0.401742660358	1.328329700798	-0.643376297065
C	12.6974517167	14.9105437368	14.2772371940	O	0.524716782218	2.299988918112	-0.109820230686
H	12.4458354967	14.4201711503	15.2079798609	H	2.061229508691	1.741996593631	-0.425414050428
N	12.5030334707	13.9373052203	13.2440776391	H	-1.468481122010	-1.159944675708	2.114975219770
C	12.4494227382	12.5703167073	13.6437587787	H	-0.520537878478	0.852019629158	1.956653795496
H	11.9508179801	12.3722378398	14.5703628101	H	1.870128482838	1.010512452356	1.863691981422
C	12.7298851384	11.5975689285	12.6845791221	H	1.871921882527	-1.839468377960	0.859222330017
H	12.6972656723	10.5601420509	12.9623633670	H	-0.681900702953	-0.762963715223	-0.360605654533
C	13.0613276664	11.9879494367	11.4091237316	H	1.172917177620	-1.241532287316	3.298906498443
N	13.5098060369	11.1283262771	10.4007675897	H	-0.248651437743	1.259125190308	-1.715384159181
H	13.3294097280	11.5120472537	9.4962763838	H	-1.456686120441	1.494071225704	-0.437790566463
H	13.1411909187	10.2026531094	10.4700741637	C	4.282909847732	-1.781773869519	0.683379303563
N	13.0048043190	13.3270879771	11.0292175546	C	4.075913943901	0.557979856007	0.177543226387
C	12.7569886360	14.1949841747	11.9060339733	C	5.651030154393	-1.616391944367	0.729672610386
O	12.7167777494	15.4707514697	11.5423010203	H	3.784109572085	-2.624897096711	0.250766838083
C	13.7429256549	16.7817782030	15.2777763995	C	6.172853733557	-0.335813950718	0.529373180052
H	14.4255564303	17.6046215536	15.1151624119	H	6.288284650695	-2.459290771830	0.919433238735
C	14.0797571935	15.5609459759	14.4172987748	N	3.465264423825	-0.664692700736	0.431281865162
H	14.4219649378	15.8824330209	13.4441639560	O	3.325190702767	1.561820535801	-0.111692616959
O	15.0463261190	14.7338201838	14.9554204739	N	5.377191113110	0.719953708751	0.216819332790
H	14.9524334075	14.7326552104	15.9007966734	N	7.528524337911	-0.049795007619	0.646310397582
O	13.7897657972	16.3548060841	16.6189460335	H	7.754336972430	0.853659928873	0.288088343649
H	13.9041306878	17.0897906724	17.2051481655	H	8.325921858561	-0.647772697946	0.677425402274

Table S8 Cartesian coordinates of anti-$CI_{S2/S1}$ (left) and anti-$CI_{S2/S}$-B (right) of cytidine optimized at SA3-CASSCF(14,12)/6-31G* level

SA3-CASSCF(14,12)/6-31G*				SA3-CASSCF(14,12)/6-31G*			
	X	Y	Z		X	Y	Z
C	0.4814836933	2.1432802267	-1.1167363014	C	0.8627616388	2.0661635405	-1.0460770917
C	-0.7055126546	1.9738659890	-0.1698893463	C	-0.0947201364	2.1812433731	0.1375171812
C	-1.2557407699	0.6086186329	-0.5872179268	C	-1.0688030413	1.0312393587	-0.1365353169
C	-0.0269613717	-0.1015410544	-1.1945151472	C	-0.2314075828	0.0510066543	-0.9956777272
O	0.9997528752	0.8483667671	-1.2807884216	O	1.0057408593	0.6818849936	-1.2240245886
O	-1.6898028552	2.9546880867	-0.3216446347	O	-0.7831828255	3.3898942244	0.2154217130
O	-2.1913942454	0.7421919443	-1.6192788917	O	-2.1397683217	1.4576325855	-0.9236647580
C	1.5705196399	3.0432535814	-0.5761601686	C	2.2248673355	2.6786101611	-0.8073871284
O	0.9567711270	4.2874512341	-0.3238253935	O	1.9909848424	4.0295619369	-0.4804478696
H	1.5798107677	4.8868018630	0.0625018856	H	2.8104498143	4.4735662618	-0.3130214536
H	-1.2823215387	3.8054667346	-0.2065856923	H	-0.1503874259	4.0987856164	0.1832101306
H	-0.3601938869	1.9299181757	0.8526749882	H	0.4497649664	1.9925674384	1.0569409652
H	-1.6799772190	0.0580494285	0.2407964345	H	-1.4302234394	0.5648942391	0.7723657794
H	-0.3094645260	-0.4196781841	-2.1857121301	H	-0.7572820413	-0.0736361225	-1.9290650786
H	0.1212559416	2.5325776802	-2.0654399136	H	0.4016923758	2.5220760570	-1.9185018854
H	-2.6742788489	1.5484582564	-1.4761192448	H	-2.3668301147	2.3429372187	-0.6621634192
H	1.9719694158	2.6104214244	0.3343950848	H	2.7164633724	2.1566791275	0.0074592811
H	2.3753882533	3.1434365339	-1.2975003627	H	2.8413790769	2.5904693153	-1.6957574316
C	0.7504121063	-2.4195758784	-1.2910055037	C	-0.2989570027	-2.4003465721	-1.3022555343
C	0.8590638644	-1.2535167055	0.8015892055	C	0.7510680492	-1.5287904861	0.6282973795
C	1.3363962503	-3.5697156314	-0.6955322924	C	0.1624202318	-3.6470382068	-0.8983944386
H	0.4795649224	-2.3822267478	-2.3228374011	H	-1.0362958581	-2.2525557664	-2.0608022865
C	1.6700578402	-3.5475678026	0.6239751362	C	0.9225085392	-3.7678464247	0.2483025919
H	1.5131549329	-4.4393456957	-1.2993248564	H	-0.0700807014	-4.5085361104	-1.4971343607
N	0.4562750183	-1.2923462092	-0.5269924463	N	-0.0287967775	-1.2723159821	-0.4706249131
O	0.6455969629	-0.2126914150	1.4789326257	O	1.0521289857	-0.4575885936	1.4144750292
N	1.4490530296	-2.3447981999	1.3088253434	N	1.2013687497	-2.6451437054	1.0230807575
N	2.3077336604	-4.5351940385	1.3683673988	N	1.5513121377	-4.9442482796	0.6801982123
H	1.9925493169	-4.5581618055	2.3194190395	H	1.7137621445	-4.9227203663	1.6658493603
H	2.2341175682	-5.4427667609	0.9558656728	H	1.0430025994	-5.7702847364	0.4388774911

Table S9 Cartesian coordinates of anti-$CI_{S1/S0}$-P (left) and anti-$CI_{S1/S0}$-B (right) of cytidine optimized at SA3-CASSCF(14,12)/6-31G* level

SA3-CASSCF(14,12)/6-31G*			SA3-CASSCF(14,12)/6-31G*		
X	Y	Z	X	Y	Z

C	2.4532242064	-1.2589279355	-0.3694665591	C	0.8890895285	2.1064699114	-0.9447253863
C	2.5589364089	-0.0785150130	0.5944411809	C	-0.2447126279	1.8676336648	0.0448979366
C	1.8621566834	1.0428398575	-0.1849591239	C	-1.0926503167	0.8597703264	-0.7273837829
C	0.9444503263	0.2788428775	-1.1596992310	C	-0.0326135498	0.0433444696	-1.4856515169
O	1.2043210873	-1.0937944992	-0.9884452515	O	1.1434489409	0.8179058151	-1.4696838655
O	3.8723480300	0.2897895165	0.8965897840	O	-0.9971292264	2.9971692648	0.3492986348
O	2.7779647676	1.7617064528	-0.9603970566	O	-1.8816646671	1.5112549032	-1.6750329211
C	2.4938253115	-2.6112510406	0.3070269325	C	2.1529596258	2.6843850675	-0.3440108908
O	3.7131600558	-2.6589636803	1.0128658027	O	1.7630397319	3.9088365266	0.2333945261
H	3.7798175520	-3.4705489757	1.4961422907	H	2.5096702133	4.3414536950	0.6241832344
H	4.3248287877	-0.4724965592	1.2388177834	H	-0.4063508835	3.6975058661	0.6035898027
H	2.0034282803	-0.2932808581	1.4965449583	H	0.1501105931	1.4027498115	0.9455202308
H	1.3087444506	1.7110318900	0.4599677673	H	-1.6938146519	0.2349642687	-0.0790582294
H	1.2306184286	0.5768758180	-2.1579810220	H	-0.3552576487	-0.1179031446	-2.5042603509
H	3.2552401299	-1.1892994286	-1.1003692860	H	0.5382499966	2.7540581465	-1.7386768250
H	3.5962815403	1.8112116979	-0.4796534703	H	-2.2460974641	2.2922331737	-1.2739533721
H	1.6466345155	-2.6994238155	0.9797246123	H	2.5551412391	2.0117512725	0.4050999902
H	2.4368718183	-3.4073264535	-0.4288645736	H	2.9020255810	2.8326578207	-1.1145748823
C	-1.2883196313	-0.0910279596	-1.9418784347	C	-0.6551627440	-2.3085716425	-1.0554610772
C	-1.1773781668	0.2641154904	0.3989575305	C	1.4717368194	-1.5484229352	-0.3578756965
C	-2.6347452349	0.5048048341	-1.9376895664	C	-0.2932576051	-3.5057988549	-0.2476053065
H	-1.0855052578	-1.1060316183	-2.2432321994	H	-1.6761329964	-1.9727218495	-1.0066454334
C	-3.2192339027	0.6282919219	-0.6721020054	C	0.9052065020	-3.6268856662	0.3000692811
H	-2.9010120168	1.2163078190	-2.6996724197	H	-1.0135142196	-4.2999751338	-0.1809604930
N	-0.4729568913	0.5599503433	-1.0773591090	N	0.2734412526	-1.2243863288	-0.8713175647
O	-0.4339175791	-0.0662656126	1.2690100729	O	2.4809467299	-0.5066579676	-0.4726615120
N	-2.5066335567	0.3947388802	0.4276895720	N	1.8892342059	-2.5673795566	0.1860603326
N	-4.5064333905	1.0846327991	-0.4825495530	N	1.4361671856	-4.7364338465	0.9647022418
H	-4.6468125084	1.6113722171	0.3521531004	H	2.0360096832	-4.4620263801	1.7137949047
H	-4.9596936343	1.4659002843	-1.2830752161	H	0.7368212254	-5.3688199479	1.2893885828

Table S10 Cartesian coordinates of the north conformer (left) and south conformer (right) of cytidine optimized at SA3-CASSCF(14,12)/6-31G* level.

SA3-CASSCF(14,12)/6-31G*				SA3-CASSCF(14,12)/6-31G*			
	X	Y	Z		X	Y	Z
N	1.6742852651	1.7656489137	-2.4467725640	N	3.4519472775	0.4121906595	-0.8638591672
N	0.4048038835	1.0062200041	-0.5453124815	N	1.0946013664	0.1899739144	-0.4720779934
N	3.7382660819	0.8818245241	-2.9030302773	N	4.9685359365	0.0450533792	0.8184911160
C	0.4949632592	1.8105779421	-1.6778439304	C	3.6625718845	0.1278676341	0.3735863868
C	1.4248633337	0.1662523792	-0.1926897783	C	2.6022882600	-0.1472086465	1.3156090294
C	2.5441535522	0.0968128666	-0.9462947935	C	1.3404517028	-0.0953023398	0.8420587832
C	2.6167089274	0.9558273636	-2.1013776650	C	2.1669957851	0.4462370316	-1.3726064333
C	-0.8109272643	1.1588386424	0.2650569948	C	-0.2636528992	0.2419917001	-0.9665771480

C	-2.0268223680	0.4510147326	-0.3383567574	C	-2.3780425497	0.6025582635	-0.0776978808
C	-2.0020853803	-0.8889611938	0.3960943583	C	-2.4457504349	-0.6526068373	-0.9637142219
C	-1.5353312761	-0.4528170426	1.7787038841	C	-0.9893069126	-1.1058713848	-1.0020952714
C	-0.9037598955	-1.5231157654	2.6378817092	C	-2.8141684471	0.3919486575	1.3580121958
O	-0.4423402542	2.5399794453	-1.9836334187	O	1.9445536020	0.6958437573	-2.5503655652
O	-0.6060506919	0.5783648738	1.5186125842	O	-1.0325848490	1.0303015299	-0.0991865470
O	0.1280056041	-2.1563254703	1.9273275183	O	-2.1244861940	-0.7065339072	1.8932106528
O	-3.2627652139	-1.4984758442	0.4797188372	O	-2.7883656001	-0.3309272295	-2.2903021490
H	-0.5227271147	-1.0626317610	3.5444872197	H	0.4762127197	-0.2608891136	1.4511572705
H	-1.6777519029	-2.2348125578	2.9127892280	H	2.8088462247	-0.3851943384	2.3400870051
H	0.5482618611	-2.8008284202	2.4796354228	H	5.1264209318	0.3320243193	1.7597668173
H	3.3427841562	-0.5731864223	-0.6969484946	H	5.6285050618	0.4286623934	0.1761242417
H	1.2731122068	-0.4188653500	0.6870908852	H	-0.2199506604	0.6777826859	-1.9496135818
H	3.8096196466	1.6327578737	-3.5559211109	H	-2.9982806973	1.3843318770	-0.5054161766
H	4.5959857808	0.6871264872	-2.4347104085	H	-2.3625759175	-0.8284092765	2.8019396763
H	-1.0068520090	2.2119798040	0.3674685350	H	-2.6021528680	1.2958201340	1.9207845789
H	-1.2743094304	-1.5579156478	-0.0460558382	H	-3.8887582446	0.2196432588	1.3800091878
H	-2.3833570928	-0.0465976669	2.3190988238	H	-3.7142938728	-0.1464979469	-2.3656162586
H	-1.9576703367	0.3668272757	-1.4152359313	H	-3.1095789928	-1.4121515578	-0.5692668637
H	-3.3778660533	-2.1086492502	-0.2355003746	H	-0.7687072609	-1.6594435018	-0.1015730634
O	-3.1593242187	1.1736252219	0.0388837954	O	-0.6552385883	-1.9121209865	-2.0740806744
H	-3.8967334556	0.5762599427	0.077620928	H	-1.0356549635	-1.5452351291	-2.8635796456

Table S11 Cartesian coordinates of the most stable structure of Syn-Cyd (left) employing the PCM model and Syn-Cyd-H_2O cluster (right) in the ground state optimized at DFT/B3LPY/6-31G** level.

DFT/B3LPY/6-31G**				DFT/B3LPY/6-31G**			
	X	Y	Z		X	Y	Z
C	0.466893000000	-1.857091000000	-2.241032000000	C	0.000000000000	0.000000000000	0.000000000000
C	0.647605000000	-2.780456000000	-1.021679000000	C	0.000000000000	0.000000000000	1.536170000000
C	0.621376000000	-1.812103000000	0.176215000000	C	1.488850300000	0.000000000000	1.883247200000
C	1.266205000000	-0.555942000000	-0.452620000000	C	2.050858900000	-0.810667900000	0.712382200000
O	0.853822000000	-0.525179000000	-1.804175000000	O	1.282317100000	-0.470591500000	-0.393026900000
O	1.948171000000	-3.380386000000	-0.993909000000	O	-0.521155400000	-1.203696400000	2.058098000000
O	1.312516000000	-2.292292000000	1.304918000000	O	1.794462600000	-0.553360900000	3.117974000000
C	-0.957526000000	-1.796435000000	-2.783529000000	C	-0.252328100000	1.362825700000	-0.621486700000
O	-1.928178000000	-1.593001000000	-1.773243000000	O	0.482169900000	2.378429500000	-0.019826100000
H	-1.687303000000	-0.772078000000	-1.288253000000	H	1.407344800000	2.246606900000	-0.181787900000
H	1.914970000000	-4.222565000000	-1.472836000000	H	-1.463071200000	-1.199758200000	2.031840100000
H	-0.135701000000	-3.540419000000	-0.955438000000	H	-0.519928900000	0.855006300000	1.949333600000
H	-0.407431000000	-1.595993000000	0.460503000000	H	1.867195600000	1.008075300000	1.856438100000
H	2.355971000000	-0.666249000000	-0.384820000000	H	1.926366100000	-1.862232000000	0.946685700000
H	1.152925000000	-2.163407000000	-3.040788000000	H	-0.744683500000	-0.701718900000	-0.366472000000
H	2.007498000000	-2.874842000000	0.941677000000	H	1.139435600000	-1.203929300000	3.322431500000

H	-0.998478000000	-1.010962000000	-3.555464000000
H	-1.190770000000	-2.751769000000	-3.268577000000
C	1.999419000000	1.485405000000	0.659114000000
C	-0.377453000000	1.195653000000	0.326612000000
C	1.796932000000	2.674601000000	1.278066000000
H	2.992310000000	1.078310000000	0.503816000000
C	0.435435000000	3.100043000000	1.412954000000
H	2.626512000000	3.266281000000	1.642812000000
N	0.960152000000	0.723997000000	0.194838000000
O	-1.318882000000	0.516921000000	-0.113115000000
N	-0.586172000000	2.382733000000	0.948454000000
N	0.147589000000	4.264877000000	2.023931000000
H	-0.817203000000	4.552843000000	2.105466000000
H	0.866308000000	4.865325000000	2.398606000000

H	-0.053074800000	1.295396500000	-1.688815600000
H	-1.301720900000	1.613101100000	-0.497029400000
C	4.285989200000	-1.734269100000	0.477900200000
C	3.978162600000	0.600229500000	0.045989500000
C	5.602690800000	-1.644794700000	0.206527500000
H	3.802315000000	-2.671418000000	0.665960100000
C	6.101582700000	-0.342313900000	-0.163081800000
H	6.242149700000	-2.504149400000	0.243657300000
N	3.464700600000	-0.638086900000	0.421494800000
O	3.262857300000	1.594014600000	-0.025805200000
N	5.352237200000	0.703865900000	-0.239366200000
N	7.431355100000	-0.218149100000	-0.483948700000
H	7.750784100000	0.722097000000	-0.553109400000
H	8.063896100000	-0.836005800000	-0.029855200000
O	2.201956700000	3.563761500000	-0.208160300000
H	3.022106400000	3.089162000000	-0.054180300000
H	2.375469100000	4.507872900000	-0.220289600000