Electronic Supplementary Information (ESI) for: Excited-state hydrogen atom abstraction initiates the photochemistry of β-2′-deoxycytidine

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Experimental section

General Experimental. All reagents were purchased from commercial sources and used without further purification. ^{1}H and ^{13}C-NMR spectra were acquired using a Bruker AMX 500 spectrometer with autosampler, operating at ambient probe temperature, using an internal deuterium lock. Deuterium oxide was purchased from Sigma-Aldrich.

Synthesis of [6-D]-β-dC. The deuterated β-dC was prepared by a modification of the reported procedure [1] giving rise to selective deuteration of the C(6) and C(5) positions at levels of 97% and 85%, respectively. Since the H-C(5) proton is readily exchanged under irradiation conditions anyway, its deuteration did not present any problems. β-dC (587 mg, 2.58 mmol) was dissolved in D_2O and lyophilized three times, then dissolved in D_6-DMSO (4 mL). A solution of MeONa (2.5 M in MeOD, 2.4 mL) was added under nitrogen and stirred at 60 °C for 17 h. ^{1}H NMR spectroscopic analysis of the crude showed a replacement of 97% of H-C(6) by D and 86% of H-C(5) by D. The mixture was diluted with water and rapidly neutralized with diluted aq. HCl to pH 7. The solution was concentrated under vacuum and three times co-evaporated from toluene. Purification by reverse phase column chromatography (Eluent: H_2O) gave [6-^{2}H]-dC (553 mg, 94%) as a white solid. ^{1}H NMR (400 MHz, D_2O): δ=2.21 (1 H, m, H–C(2′a)), 2.34 (1 H, m, H–C(2′b)), 3.67 (1 H, m, H–C(5′a)), 3.75 (1 H, m, H–C(5′b)), 3.97 (1 H, m, H–C(4′)), 4.35 (1 H, m, H–C(3′)), 6.18 (1 H, t, J=6.8 Hz, H–C(1′)); ESI-MS (neg., $CDCl_3$) 228.0 (100) $[M]^-$, (pos., $CDCl_3$) 252.2 (20) $[M+Na]^+$, calcd. for $C_{19}H_{11}D_2N_3O_4$: 229.1032.

General Procedure for Photochemical Reactions. β-dC (30 mg, 0.13 mmol) was dissolved in D_2O (5 mL) and the pH adjusted to 6.5 using degassed 1M HCl and a Russel RL150 pH meter. The solution was purged with N_2 for 10 min and then, with a continuous stream of N_2 bubbling through the solution to agitate it, irradiated with an unfiltered Hg lamp (254 nm, cooled to 15 °C by a quartz water jacket). After 44 h of irradiation, the solution was heated at 90 °C for 40 h, lyophilized, and the residue re-dissolved in D_2O (0.75 mL). ^{1}H NMR spectra were then acquired before and after spiking the sample with authentic standards of β-dC, β-dU, α-dC and α-dU.

Computational methods

All the stationary points on the ground-state PE surface were located using the Kohn–Sham formulation of Density Functional Theory (KS-DFT). We have selected the M06-2X functional due to reasonable performance in computing thermodynamic properties. [2,3] These ground-state calculations were carried out using the 6-311++G(2d,2p) basis set. The equilibrium geometries and transition states were optimized in gas phase. The character of all the located stationary points was confirmed by analytical calculation of the Hessian. Thermodynamic properties were computed assuming the rigid rotor and harmonic oscillator approximations. The solvent screening effects exerted by bulk water on the computed energies were estimated based on single-point calculations for the equilibrium gas-phase geometries using the conductor-like polarizable continuum model (C-PCM) including electrostatic, exchange-repulsion, dispersion and cavitation contributions as implemented in the GAUSSIAN 09 code. [4–6]

Vertical excitation energies of β-dC were calculated at the CC2/cc-pVTZ level. The relaxed scans for the hydrogen atom abstraction mechanisms were performed by fixing the C=O···H–C1′ distances and optimizing all the remaining coordinates at the SA4-CASSCF(10,8)/cc-pVDZ level (SA4 denotes averaging over 4 singlet states in the CASSCF procedure). The active space that consisted of five occupied molecular orbitals (one n and four π), and three unoccupied molecular orbitals (of π* character) was the most stable choice for the entire reaction path. The final six structures before the optimized conical intersection, that correspond to the energies on the right hand side of the graph in Fig. 5, where obtained by LIIC (linear interpolation in internal coordinates). Single-point CASPT2 energy correction was computed at every point of the potential energy profile in order to account for dynamic electron correlation. The minima on the S_1 hyper-

surface were optimized at the SA4-CASSCF/cc-pVDZ level assuming the same active space as described above. The minimum-energy conical intersections were optimized at the SA2-CASSCF(2,2)/cc-pVDZ level.

The CC2 vertical excitation energy calculations were performed using the TURBOMOLE 6.3 package,[7,8] whereas the constrained CASSCF optimizations, the CASPT2 excitation energies MOLCAS 7.8 package.[9,10] The optimizations of conical intersection at the CASSCF level were performed with the COLUMBUS 7.0 program package.[11,12] All the KS-DFT calculations reported in this study were performed using the GAUSSIAN 09 quantum chemistry package.[13]

Electronic structure of the ground-state H–C1′ hydrogen atom abstraction intermediate

The process of H–C1′ hydrogen atom abstraction after photoexcitation occurs on the electronically excited state hypersurface having biradical character. It leads to the subsequent non-adiabatic transition to the electronic ground state resulting in the redistribution of the electronic structure. Fig. S1 illustrates shapes of the natural orbitals comprising the active space in the CASSCF(6,6) calculations on the ground-state H–C1′ hydrogen atom abstraction intermediate. The results of CASSCF calculations indicate that indeed only one closed-shell configuration predominantly contributes to the ground-state wavefunction. The natural orbitals in the top row are nearly doubly occupied (with occupation numbers equal to 1.91, 1.95 and 1.70 respectively for a, b and c), while the bottom row presents 3 orbitals with small occupation numbers (0,30, 0.09 and 0.05 respectively for d, e and f). The analysis of the CASSCF wavefunction in terms of the spin-coupled valence bond structures using the CASVB approach[14] reveals that it can be represented by two dominant resonance structures shown in brackets in Fig. S2. This is schematically represented by the zwitterionic-like closed-shell structure on the right of Fig. S2 that is also shown in top right corner of Fig. 3 in the article. The Mulliken electron population analysis indicates that about 0.8 electron is transferred from the nucleobase to the sugar moiety (mostly to lone *p* orbital of C1′).

References

1 J. A. Rabi and J. J. Fox, *J. Am. Chem. Soc.*, 1973, **95**, 1628–1632.

2 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.

3 L. Goerigk and S. Grimme, *Phys. Chem. Chem. Phys.*, 2011, **13**, 6670–6688.

4 V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995–2001.

5 G. Scalmani and M. J. Frisch, *J. Chem. Phys.*, 2010, **132**, 114110–114110–15.

6 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3094.

7 C. Hättig and F. Weigend, *J. Chem. Phys.*, 2000, **113**, 5154–5161.

8 *TURBOMOLE v6.3 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007*, 2011, http://www.turbomole.com.

9 G. Karlström, R. Lindh, P.-A. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady and L. Seijo, *Comput. Mater. Sci.*, 2003, **28**, 222–239.

10 F. Aquilante, L. De Vico, N. Ferre, G. Ghigo, P.-A. Malmqvist, P. Neogrady, T. B. Pedersen, M. Pitonak, M. Reiher, B. O. Roos, L. Serrano-Andres, M. Urban, V. Veryazov and R. Lindh, *J. Comput. Chem.*, 2010, **31**, 224–247.

11 H. Lischka, T. Müller, P. G. Szalay, I. Shavitt, R. M. Pitzer and R. Shepard, *Wiley Interdiscip. Rev. Comput. Mol. Sci*, 2011, **1**, 191–199.

12 H. Lischka, R. Shepard, I. Shavitt, R. M. Pitzer, M. Dallos, T. Müller, P. G. Szalay, F. B. Brown, R. Ahlrichs, H. J. Böhm, A. Chang, D. C. Comeau, R. Gdanitz, H. Dachsel, C. Ehrhardt, M. Ernzerhof, P. Höchtl, S. Irle, G. Kedziora, T. Kovar, V. Parasuk, M. J. M. Pepper, P. Scharf, H. Schiffer, M. Schindler, M. Schüler, M. Seth, E. A. Stahlberg, J.-G. Zhao, S. Yabushita, Z. Zhang, M. Barbatti, S. Matsika, M. Schuurmann, D. R. Yarkony, S. R. Brozell, E. V. Beck, J.-P. Blaudeau, M. Ruckenbauer, B. Sellner, F. Plasser and J. J. Szymczak, *COLUMBUS, relase 7.0 2012, an ab initio electronic structure program*, 2012, http://www.univie.ac.at/columbus.

13 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, revision C.01*, 2009, Gaussian Inc. Wallingford CT.

14 T. Thorsteinsson, D. L. Cooper, J. Gerratt, P. B. Karadakov and M. Raimondi, *Theoret. Chim. Acta*, 1996, **93**, 343–366.

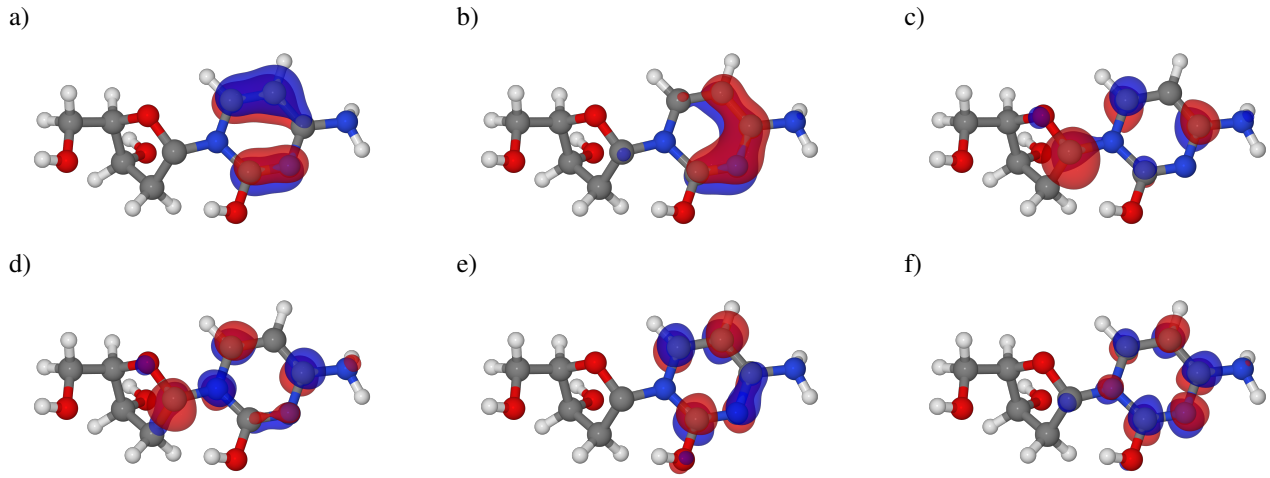

Fig. S1 Natural orbitals comprising the active space in CASSCF(6,6) calculations on the ground-state of H–C1′ hydrogen atom abstraction intermediate.

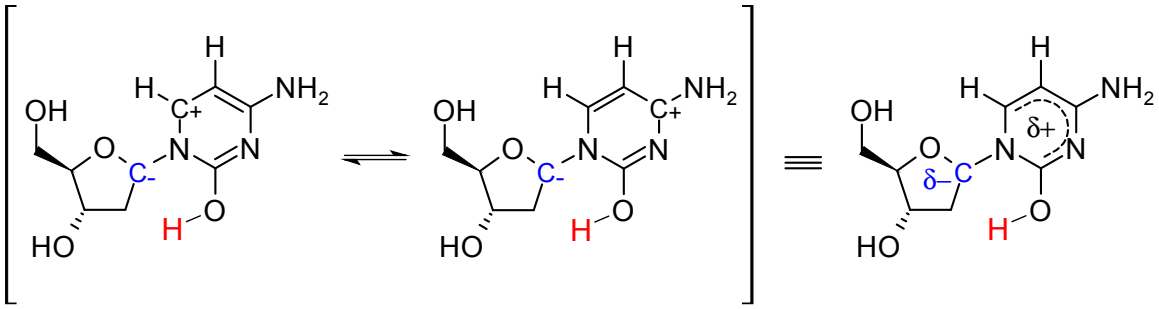

Fig. S2 Schematic representation of the resonance structures that predominantly contribute to the wavefunction of the H–C1′ hydrogen atom abstraction intermediate. This intermediate was introduced in Fig. 3 in the main manuscript and discussed later in the text.

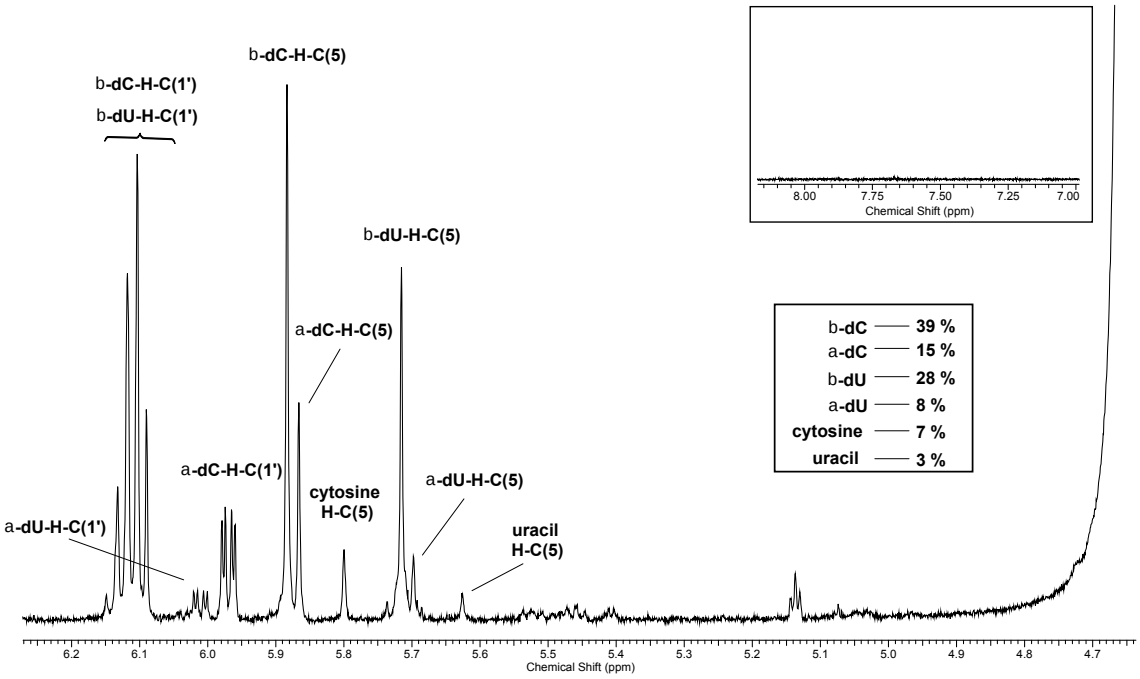

Fig. S3 ^{1}H-NMR analysis of the photoproducts of the 44h UV-irradiation of [6-D]-β-dC. Absence of peaks that could correspond to protons in the C(6) position of the nucleobase indicate that the deuterium remained in place. Consequently, the [1,3]-hydrogen shift mechanism can be ruled out. More detailed analysis of this experiment is described in the main article.

Cartesian coordinates of the stationary points considered in the article

Ground-state geometries of both considered conformers of β-dC optimized at the M06-2x/6-311++G(2d,2p) level

The S (South) Conformer

N	3.428124	0.273164	-0.860370
N	1.081721	0.296725	-0.482465
N	4.873813	0.024346	0.884701
C	3.593449	0.113476	0.426375
C	2.513231	-0.007446	1.357303
C	1.269475	0.100473	0.841737
C	2.170849	0.317828	-1.396499
C	-0.268060	0.392554	-1.025298
C	-2.379616	0.634230	-0.056283
C	-2.435885	-0.557996	-1.029682
C	-0.976297	-0.952144	-1.152368
C	-2.711510	0.283748	1.378206
O	1.937710	0.375054	-2.585121
O	-1.057744	1.154460	-0.126218
O	-1.889159	-0.801506	1.780452
O	-2.873073	-0.158216	-2.317311
H	0.368174	0.042198	1.436474
H	2.676641	-0.166786	2.410154
H	5.054921	0.189774	1.857889
H	5.592036	0.285524	0.229936
H	-0.176832	0.895437	-1.983801
H	-3.076444	1.409968	-0.387735
H	-2.116692	-1.055810	2.676207
H	-2.531593	1.161137	2.004624
H	-3.770970	0.015384	1.441055
H	-3.785179	0.135331	-2.270122
H	-3.056637	-1.366097	-0.637010
H	-0.694134	-1.591742	-0.317785
H	-0.760323	-1.443067	-2.097042

The N (North) Conformer

N	1.669181	1.817803	-2.375888
N	0.420288	1.060169	-0.498650
N	3.685395	0.875537	-2.870612
C	0.526974	1.903741	-1.635529
C	1.378610	0.163291	-0.186432
C	2.493667	0.055653	-0.946229
C	2.592653	0.944531	-2.059500
C	-0.813675	1.216517	0.294960
C	-2.000476	0.504400	-0.350389
C	-1.964305	-0.853183	0.332486
C	-1.545590	-0.448617	1.746587
C	-0.917948	-1.530687	2.587762
O	-0.400484	2.651050	-1.880046
O	-0.625216	0.624066	1.561899
O	0.144039	-2.129987	1.861287
O	-3.224638	-1.485608	0.296011
H	-2.929982	1.006260	-0.079199
H	-0.554954	-1.090820	3.519601
H	-1.692104	-2.267156	2.827715
H	0.615131	-2.735275	2.435682
H	3.262986	-0.662263	-0.715111
H	1.194047	-0.444855	0.687536
H	3.793688	1.631251	-3.526123
H	4.521390	0.440779	-2.525334
H	-0.971112	2.285634	0.399048
H	-1.192519	-1.488047	-0.109826
H	-2.437838	-0.086606	2.270069
H	-1.921906	0.475877	-1.432230
H	-3.105301	-2.433457	0.370454

Stationary points on the S_1 hypersurface optimized at the SA-CASSCF/cc-pVDZ level

S1 minimum optimized at the
SA4-CASSCF(10,8)/cc-pVDZ level

N	3.05530789	0.79691493	-0.60126492
C	3.38080630	0.04162573	0.53320005
C	2.38783544	-0.46382667	1.34461180
C	1.04371883	-0.38068358	0.93836276
N	0.79103023	0.16356299	-0.34478812
C	1.83460860	0.82983422	-0.93640788
N	4.75929845	-0.10342074	0.74379292
O	1.47996798	1.57788468	-1.99479756
C	-0.54640493	0.18129065	-0.87181661
O	-1.36094107	1.01003704	-0.07447862
C	-2.68120313	0.52469572	-0.00382932
C	-2.71481656	-0.75040578	-0.86818228
C	-1.25674893	-1.17087965	-0.88730483
C	-3.08209686	0.32623466	1.44413472
O	-2.37659972	-0.75882006	1.98498132
O	-3.08267023	-0.45920496	-2.19408404
H	0.19864830	-0.48450425	1.59544131
H	2.62274191	-0.91976853	2.29671129
H	4.98676861	-0.26284571	1.70745704
H	5.25343190	0.70511519	0.41238847
H	-0.50054091	0.58434038	-1.87843653
H	-3.35205483	1.27534276	-0.43148881
H	-2.56189628	-0.83093554	2.90870625
H	-2.86557357	1.24835141	1.98971851
H	-4.16277421	0.14654328	1.48958531
H	-3.97754270	-0.15568164	-2.22096045
H	-3.36782194	-1.51528501	-0.44437395
H	-1.01895600	-1.74317851	0.00412801
H	-1.01478660	-1.75416899	-1.77323582

Conical intersection responsible for the H--C1’
hydrogen atom abstraction optimized at the
SA2-CASSCF(2,2) level

C	-1.298081	-1.269275	-0.836036
C	-0.549909	0.035529	-0.707390
C	-2.685894	0.484498	0.018070
C	-2.744261	-0.798700	-0.834093
C	1.066505	-0.399065	1.066638
C	2.405770	-0.447810	1.456456
C	3.357582	-0.007518	0.573731
C	1.804735	0.515696	-0.995941
C	-3.106862	0.306773	1.463138
O	-1.349141	0.931443	-0.032160
O	1.486043	0.995417	-2.174017
O	-2.418607	-0.781423	2.019088
O	-3.108005	-0.518940	-2.161553
N	0.780657	0.055515	-0.225338
N	3.039465	0.502382	-0.658265
N	4.712043	-0.067455	0.815864
H	0.219210	-0.619214	1.688773
H	2.673745	-0.823996	2.433058
H	4.975550	-0.062477	1.780457
H	5.233044	0.585525	0.264287
H	0.539393	0.918283	-2.283833
H	-3.320727	1.255138	-0.425117
H	-2.607497	-0.839878	2.943044
H	-2.886286	1.230689	2.003880
H	-4.190092	0.139700	1.496696
H	-4.009498	-0.236221	-2.192285
H	-3.419179	-1.537876	-0.398642
H	-1.109396	-1.921694	0.020196
H	-1.060627	-1.809243	-1.750666

The branching space coordinates responsible for the degeneracy lifting at the intersection point obtained at the SA2-CASSCF(2,2) level. The atom ordering corresponds to the atom ordering of the MECI structure listed above

The energy difference gradient vector (g)

0.721	-0.166	1.423
0.428	-0.534	-5.969
0.912	0.153	-0.057
0.197	0.068	0.019
2.620	1.971	-3.242
-3.037	-1.386	1.594
1.812	1.664	-3.771
-2.804	1.005	-1.872
-0.162	0.085	-0.219
-1.662	1.625	2.255
2.208	-0.036	1.320
0.211	-0.107	0.262
-0.189	-0.069	-0.099
0.637	-1.360	4.638
2.222	-1.167	2.686
-1.514	0.337	0.300
-0.237	-0.202	-0.011
0.056	-0.061	-0.003
0.056	-0.162	0.069
0.048	-0.130	-0.195
-1.618	-0.745	0.720
-0.110	0.018	-0.029
-0.078	0.009	-0.036
0.010	0.008	0.018
-0.035	-0.047	0.088
0.033	0.003	0.055
-0.081	-0.036	-0.011
-0.580	-0.714	0.084
-0.064	-0.023	-0.017

The nonadiabatic coupling vector (h)

-0.558	-0.649	0.833
-0.320	-1.375	2.330
-0.546	-0.073	-0.232
-0.085	-0.126	0.057
-1.567	-0.482	0.990
1.495	-0.466	-0.861
-0.810	-0.319	1.705
0.446	0.803	1.412
0.173	-0.012	0.128
1.346	-0.218	-1.650
-0.933	0.407	-0.285
-0.109	0.042	-0.115
0.077	0.063	0.029
0.868	1.728	-1.901
-0.581	-0.027	-1.372
0.454	-0.061	-0.166
0.058	0.371	0.049
0.043	-0.220	-0.077
-0.027	0.037	0.001
-0.025	0.029	0.064
0.688	0.099	-0.376
0.031	-0.020	0.011
0.034	0.003	0.017
-0.003	-0.008	-0.002
0.032	0.032	-0.069
-0.015	-0.002	-0.029
0.008	0.053	-0.001
-0.263	0.214	-0.432
0.090	0.177	-0.059

Intermediates after the H–C1′ hydrogen atom abstraction optimized at the M06-2X/6-311++G(2d,2p) level

alpha-configured C1′-endo

C	1.184027	1.814440	-0.981385
C	0.091604	1.015590	-1.698930
O	-0.424847	1.853695	-2.722686
C	0.682597	2.601575	-3.205492
C	1.475985	2.970343	-1.945390
N	-0.990163	0.564973	-0.932674
C	-2.296717	0.759936	-1.293221
C	-3.325030	0.171531	-0.594888
C	-3.019374	-0.599880	0.518174
N	-1.737698	-0.765107	0.882405
C	-0.798821	-0.204871	0.183211
O	0.480710	-0.408720	0.495497
N	-3.974345	-1.180984	1.329156
C	1.491447	1.794826	-4.211137
O	2.180653	0.712021	-3.626317
O	0.985327	4.163258	-1.346927
H	-2.440794	1.372939	-2.163681
H	-4.343792	0.331853	-0.911692
H	-4.855945	-1.386470	0.889551
H	-3.622683	-1.934599	1.898328
H	0.277284	3.488485	-3.695471
H	1.546699	0.246283	-3.054331
H	0.814944	1.453010	-5.001378
H	2.243313	2.443899	-4.664995
H	1.167604	4.901519	-1.931999
H	2.541849	3.060689	-2.161757
H	2.071646	1.218315	-0.792754
H	0.843504	2.240751	-0.034099
H	0.490747	-0.983198	1.269797

alpha-configured S conformer

C	-0.464206	-0.023834	-2.969773
N	0.000548	0.177838	-1.707789
C	1.318453	-0.108026	-1.525703
N	2.137776	-0.535764	-2.447641
C	1.684926	-0.710229	-3.693600
C	0.349311	-0.447692	-3.989099
C	-0.780782	0.840910	-0.675222
O	-2.082340	1.037107	-1.186238
C	-2.992299	0.002515	-0.749862
C	-2.175134	-0.909073	0.168936
C	-0.986669	-0.025666	0.554378
O	-1.647312	-2.026950	-0.543445
C	-4.160407	0.707592	-0.084083
O	-3.727737	1.517791	0.985879
O	1.783634	0.108889	-0.298244
N	2.604570	-1.090214	-4.643481
H	-1.503332	0.217481	-3.107970
H	-0.048229	-0.567301	-4.984728
H	2.242735	-1.565348	-5.452924
H	3.449468	-1.490577	-4.268867
H	2.729455	-0.076818	-0.325173
H	-3.353322	-0.562577	-1.616880
H	-3.033358	2.085585	0.632813
H	-4.688624	1.303620	-0.834949
H	-4.858881	-0.022199	0.325928
H	-2.371855	-2.595581	-0.811877
H	-2.758452	-1.241176	1.030381
H	-1.266407	0.600778	1.399002
H	-0.128881	-0.627453	0.832610

beta-configured S conformer

C	1.565930	-0.868397	-0.733392
N	0.622953	0.069967	-0.354702
C	1.058063	0.944358	0.622392
C	2.339674	0.880834	1.124830
C	3.199695	-0.101213	0.669191
N	2.769163	-0.960747	-0.269507
C	-0.590667	0.171971	-0.978280
C	-1.436322	-1.054608	-1.238958
C	-2.849434	-0.580417	-0.899371
C	-2.614088	0.628876	0.012504
O	-1.375642	1.181749	-0.416363
C	-2.568853	0.279964	1.488128
O	-1.612636	-0.748485	1.677964
O	-3.482923	-0.207034	-2.112223
N	4.491246	-0.302666	1.166847
O	1.165360	-1.669191	-1.732458
H	0.345080	1.694635	0.906527
H	2.643936	1.595803	1.874447
H	4.947896	0.545861	1.463913
H	5.067372	-0.815722	0.515784
H	1.918714	-2.230566	-1.946409
H	-3.382388	1.389497	-0.141012
H	-1.349730	-0.777837	2.598210
H	-2.296907	1.177903	2.048185
H	-3.563104	-0.048503	1.812416
H	-4.360892	0.127477	-1.918852
H	-3.424771	-1.356805	-0.389468
H	-1.152388	-1.877623	-0.581428
H	-1.409995	-1.401466	-2.268754

alpha-configured N conformer

O	0.060046	1.149602	-2.758619
C	0.316705	0.788423	-1.413011
C	1.154257	1.876787	-0.775344
C	1.761827	2.546317	-1.999383
C	0.632565	2.429904	-3.019593
N	-0.865800	0.391357	-0.805991
C	-0.921768	0.046377	0.526112
N	-1.951526	-0.449301	1.136739
C	-3.092189	-0.661639	0.462630
C	-3.150832	-0.345652	-0.885426
C	-2.039969	0.190455	-1.495023
O	0.234963	0.195711	1.179407
N	-4.173119	-1.139403	1.191906
O	2.118209	3.885158	-1.723584
C	1.060430	2.451535	-4.470900
O	1.960495	1.404460	-4.758251
H	-2.001586	0.445377	-2.537317
H	-4.048071	-0.497775	-1.465470
H	-4.842455	-1.670201	0.658343
H	-3.898597	-1.608789	2.041213
H	-0.092638	3.228833	-2.826358
H	1.579426	0.603180	-4.383271
H	0.176394	2.395884	-5.113499
H	1.571765	3.391124	-4.685379
H	2.789599	4.164660	-2.347733
H	2.623082	1.974918	-2.352357
H	1.909920	1.510030	-0.088999
H	0.545281	2.623088	-0.246329
H	0.081080	-0.108990	2.080940

beta-configured N conformer

C	2.829723	-1.127434	-2.457087
N	2.156448	-0.405433	-1.486024
C	2.284868	-0.913272	-0.204445
N	2.950244	-1.968818	0.123076
C	3.584259	-2.690349	-0.820615
C	3.516863	-2.279671	-2.137890
C	1.359853	0.658585	-1.768823
O	1.424066	0.980986	-3.130566
C	0.821966	2.256767	-3.250535
C	1.336201	3.013008	-2.023971
C	1.332921	1.927940	-0.942711
O	0.513632	4.102638	-1.658718
C	1.152681	2.868969	-4.587552
O	2.519804	3.241122	-4.616615
O	1.576466	-0.240698	0.715250
N	4.210057	-3.867640	-0.399647
H	2.737917	-0.743159	-3.454984
H	3.995481	-2.838180	-2.928025
H	5.034992	-4.101861	-0.930544
H	4.405147	-3.854791	0.590421
H	-0.267737	2.164167	-3.164686
H	2.774937	3.425756	-5.520940
H	0.923011	2.141754	-5.370070
H	0.509075	3.743588	-4.729300
H	0.806413	4.883325	-2.131467
H	2.355898	3.343796	-2.222279
H	0.433223	2.026753	-0.336125
H	2.193726	2.023539	-0.280293
H	1.683569	-0.721042	1.543793

H–C1′ atom abstraction intermediates after the deprotonation from the photochemically formed O–H group optimized at the M06-2X/6-311++G(2d,2p) level.

alpha-configured C1′-endo conformer

C	1.086203	2.062167	-0.699161
N	0.127999	1.298488	-1.443294
C	-0.480150	1.840888	-2.502817
C	-0.254489	3.145919	-2.885759
C	0.660057	3.865498	-2.111273
N	1.294457	3.356237	-1.078490
C	-0.214184	-0.013052	-0.944714
C	0.951824	-0.997273	-0.959312
C	0.209999	-2.329482	-0.966153
C	-1.185230	-1.956122	-1.527236
O	-1.080154	-0.615414	-1.964845
C	-2.288833	-2.076908	-0.482258
O	-2.034324	-1.293996	0.653502
O	0.905505	-3.281892	-1.775674
N	0.977597	5.190332	-2.438885
O	1.658529	1.534137	0.236553
H	-1.171250	1.195907	-3.019202
H	-0.751239	3.568753	-3.744232
H	0.202742	5.709899	-2.820106
H	1.403209	5.659042	-1.652502
H	-1.425483	-2.577601	-2.394321
H	-1.385869	-0.574676	0.350475
H	-3.237555	-1.786310	-0.953823
H	-2.377537	-3.131437	-0.183687
H	0.451513	-4.122038	-1.692564
H	0.106036	-2.723183	0.047833
H	1.620723	-0.876552	-0.115105
H	1.526577	-0.928540	-1.895892

alpha-configured S conformer conformer

C	-0.540125	0.178716	-3.349662
C	-0.304244	0.642152	-1.916883
O	1.132072	0.661278	-1.850188
C	1.724344	-0.309156	-2.737873
C	0.585918	-0.828254	-3.628808
N	-0.753141	-0.397315	-0.951563
C	0.070204	-0.902733	-0.025503
C	-0.369035	-1.690445	1.018195
C	-1.739230	-1.958666	1.049079
N	-2.583358	-1.494047	0.153881
C	-2.160351	-0.689018	-0.864311
O	-2.914437	-0.227990	-1.702567
N	-2.293673	-2.718951	2.087954
C	2.830908	0.428634	-3.472463
O	2.332415	1.598724	-4.089744
O	0.224749	-2.168199	-3.298980
H	1.103483	-0.611550	-0.126299
H	0.314318	-2.052813	1.769578
H	-1.691989	-3.460034	2.412009
H	-3.209911	-3.055902	1.830545
H	2.152315	-1.148363	-2.178202
H	1.721139	1.974965	-3.442136
H	3.624537	0.683406	-2.760385
H	3.258559	-0.201606	-4.253388
H	-0.300425	-2.133167	-2.494253
H	0.891766	-0.855844	-4.674848
H	-0.413602	1.034378	-4.014894
H	-1.524717	-0.246216	-3.513590

beta-configured S conformer

O	1.583149	-1.304018	-0.155408
C	0.638859	-0.212874	-0.368031
C	1.127283	0.839650	0.626099
C	2.641593	0.622224	0.665166
C	2.838763	-0.680634	-0.136328
N	-0.647598	-0.748980	-0.066590
C	-1.752119	0.178021	0.007634
N	-3.000528	-0.336213	0.150979
C	-3.196333	-1.639321	0.231959
C	-2.164341	-2.569971	0.188913
C	-0.882492	-2.061887	0.054437
O	-1.511183	1.369774	-0.079631
N	-4.530225	-2.048890	0.411821
O	3.336288	1.725202	0.082945
C	3.825428	-1.659900	0.466573
O	3.389796	-2.116995	1.733066
H	-0.017589	-2.699896	-0.006033
H	-2.332198	-3.631582	0.278691
H	-4.741511	-2.921052	-0.048105
H	-5.159105	-1.313894	0.121126
H	3.145680	-0.401654	-1.153167
H	2.428310	-2.177685	1.658605
H	3.963808	-2.505479	-0.215781
H	4.794849	-1.174211	0.606229
H	4.276689	1.544507	0.138587
H	2.992417	0.484507	1.691160
H	0.710662	0.673168	1.632616
H	0.882822	1.852500	0.326008