Quantum Mechanical Study of the β- and δ-Lyase Reactions during the Base Excision Repair Process: Application to FPG

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Supporting Information (20 pages)

Table S1 Relative energies (ΔE) and Gibbs energies (ΔG) for stationary points characterized along the proton abstraction and phosphate elimination reactions in the β-lyase step for the O-base pathway (kJ/mol).[a]

Reaction Step	Stationary Point	*syn*			*anti*		
		ΔE[b]	**ΔE[c]**	**ΔG[d]**	**ΔE[b]**	**ΔE[c]**	**ΔG[d]**
C2′–H Abstraction	**RC1**	0.0	0.0	0.0	0.0	0.0	0.0
	TS1	32.5	31.9	22.0	60.1	58.9	62.4
	IC1	25.3	24.9	–0.6	41.0	40.2	31.1
3′-PO_4 Elimination	**TS2**	48.4	47.4	19.3	-	-	-
	IC2	–7.6	–7.4	–18.7	-	-	-

[a]Energies reported relative to the corresponding (O-base or N-base) reactant complex. [b]Unscaled relative energies obtained with IEF-PCM-B3LYP/6-31G(d). [c]IEF-PCM-B3LYP-D3/6-311+G(2df,2p) relative energies including scaled (0.9806) zero-point vibrational energy correction. [d]SMD-M06-2X/6-311+G(2df,2p)//IEF-PCM-B3LYP/6-31G(d) relative energies including unscaled thermal corrections.

Table S2 Relative energies (ΔE) and Gibbs energies (ΔG) for stationary points characterized along the proton abstraction reaction in the β-lyase step for the N-base pathway (kJ/mol).[a]

Reaction Step	Stationary Point	*syn*			*anti*		
		ΔE[b]	**ΔE[c]**	**ΔG[d]**	**ΔE[b]**	**ΔE[c]**	**ΔG[d]**
C2′–H Abstraction	**RC1**	0.0	0.0	0.0	0.0	0.0	0.0
	TS1	54.5	53.5	51.5	89.7	88.1	83.4
	IC1	–8.0	–7.9	–2.6	17.4	17.1	7.4

[a]Energies reported relative to the corresponding (O-base or N-base) reactant complex. [b]Unscaled relative energies obtained with IEF-PCM-B3LYP/6-31G(d). [c]IEF-PCM-B3LYP-D3/6-311+G(2df,2p) relative energies including scaled (0.9806) zero-point vibrational energy correction. [d]SMD-M06-2X/6-311+G(2df,2p)//IEF-PCM-B3LYP/6-31G(d) relative energies including unscaled thermal correction.

Table S3 Relative energies (ΔE) and Gibbs energies (ΔG) for stationary points characterized along the proton abstraction reaction in the δ-lyase step for the O-base and N-base pathways (kJ/mol).[a]

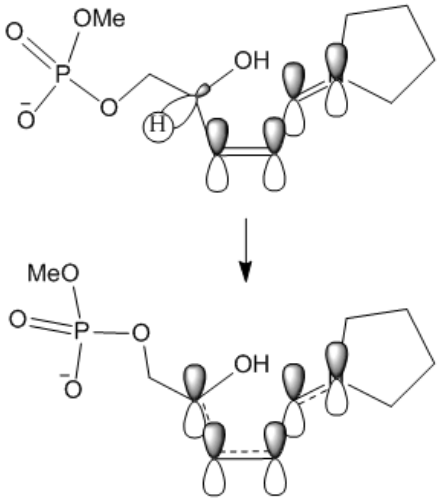
Reaction Step	Stationary Point	*O-base*			*N-base*		
		ΔE[b]	**ΔE[c]**	**ΔG[d]**	**ΔE[b]**	**ΔE[c]**	**ΔG[d]**
C4′–H Abstraction	**RC2**	0.0	0.0	0.0	0.0	0.0	0.0
	TS3	38.4	37.7	34.7	44.4	43.6	48.0
	IC3	–34.9	–34.2	–53.8	–104.6	–102.6	–102.8

[a]Energies reported relative to the corresponding (O-base or N-base) reactant complex. [b]Unscaled relative energies obtained with IEF-PCM-B3LYP/6-31G(d). [c]IEF-PCM-B3LYP-D3/6-311+G(2df,2p) relative energies including scaled (0.9806) zero-point vibrational energy correction. [d]SMD-M06-2X/6-311+G(2df,2p)//IEF-PCM-B3LYP/6-31G(d) relative energies including unscaled thermal corrections.

Table S4 Relative energies (ΔE) and Gibbs energies (ΔG) for stationary points characterized along the phosphate elimination reaction and the enol-keto rearrangement in the δ-lyase step (kJ/mol).[a]

Reaction Step	Stationary Point	*Direct*			*Assisted (N-base)*		
		ΔE[b]	**ΔE[c]**	**ΔG[d]**	**ΔE[b]**	**ΔE[c]**	**ΔG[d]**
5′-PO_4 Elimination	RC3/RC3′	0.0	0.0	0.0	0.0	0.0	0.0
	TS4′				26.7	26.2	21.9
	TS4/IC4′	160.3	157.2	188.6	7.6	7.4	18.8
	TS4″				164.3	161.1	185.3
	IC4/IC4″	81.5	79.9	78.9	74.0	72.5	92.0
Enol-Keto Rearrangement	TS5	173.2	169.8	200.6		-	
	P	151.9	148.9	176.8		-	

[a]Energies reported relative to the corresponding (O-base and N-base) reactant complex. [b]Unscaled relative energies obtained with IEF-PCM-B3LYP/6-31G(d). [c]IEF-PCM-B3LYP-D3/6-311+G(2df,2p) relative energies including scaled (0.9806) zero-point vibrational energy correction. [d]SMD-M06-2X/6-311+G(2df,2p)//IEF-PCM-B3LYP/6-31G(d) relative energies including unscaled thermal corrections.



Scheme S1 Molecular orbital interpretation of the δ-elimination reaction, which depicts bending of the phosphate group to allow the p-orbital of C4′ to contribute to the conjugated π-system and result in a more stable intermediate.

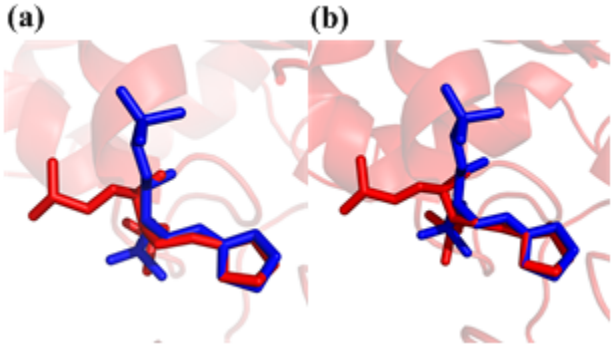


Fig. S1 Overlay of the initial 1-[4-hydroxy-3,5-diyl dimethyl bis(phosphate)pentylidene] pyrrolidinium model (blue) and the crystal structure (red) of (a) the borohydride-trapped abasic site (PDB ID: 1K82) or (b) the Schiff base intermediate (PDB ID: 1L1Z).

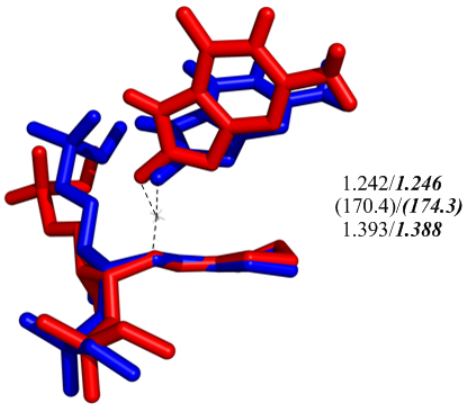


Fig. S2 Overlay of the optimized transition structures for the *syn* (red) and *anti* (blue) orientation of OG^- in the C2′–H abstraction step along the O-base pathway. Important distances (Å) and angles (deg, in parentheses) obtained with IEF-PCM-B3LYP/6-31G(d) level of theory are provided. Italicized bold values correspond to the *anti* OG complex.

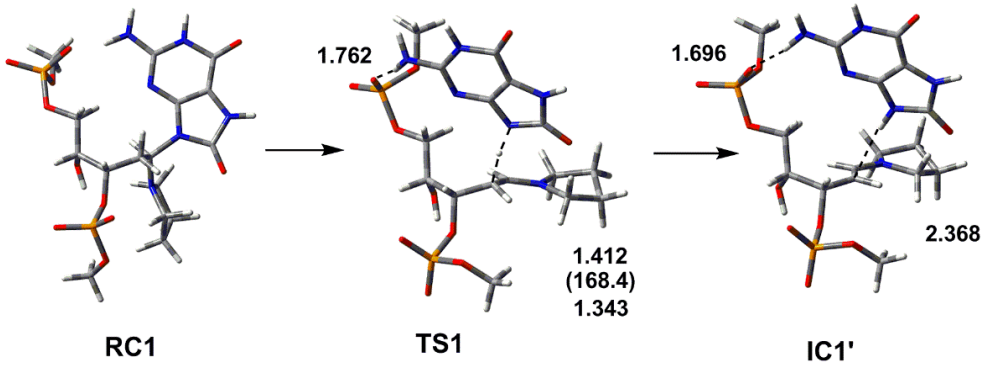


Fig. S3 Optimized structures along the C2′–H abstraction step for the *syn* N-base pathway. Important distances (Å) and angles (deg, in parentheses) obtained with IEF-PCM-B3LYP/6-31G(d) level of theory are provided.

IEF-PCM-B3LYP/6-31G(d) Coordinates and Energies (a.u.) for Transition States

C2'–H abstraction (*anti* N-base) (Figure 2, TS1) (-2464.44529)

N	-1.36710	-0.54829	-1.04782
C	-1.76274	0.02182	-2.25541
N	-2.98184	-0.56462	-2.60077
C	-3.33406	-1.49604	-1.62951
C	-4.44389	-2.35518	-1.50037
O	-5.43728	-2.50795	-2.22476
N	-4.31369	-3.13189	-0.30549
C	-3.26453	-3.06905	0.57133
N	-3.35679	-3.86765	1.69980
N	-2.23639	-2.26689	0.42205
C	-2.30004	-1.46957	-0.68858
O	-1.16631	0.87730	-2.91558
H	-3.52139	-0.30249	-3.41140
H	-5.10765	-3.72922	-0.10489
H	-3.76978	-4.78344	1.56279
H	-2.47658	-3.91666	2.19873
H	3.18902	2.02584	0.61172
C	1.00032	-3.11360	3.58383
C	1.34166	-1.65053	3.28146
N	1.36250	-1.60036	1.80258
C	1.39969	-2.95293	1.20576
C	1.64571	-3.87253	2.41053
H	0.61215	-0.93750	3.67253
H	2.19102	-2.99234	0.45246
H	0.43486	-3.15274	0.72672
H	1.22275	-4.86933	2.25837
H	-0.08718	-3.25075	3.57541
H	1.37385	-3.42951	4.56177
O	-0.01097	3.86106	0.44903
C	0.08558	2.52588	-0.04671
C	1.54828	2.23153	-0.34506
O	2.30491	2.34850	0.86694
C	1.81709	0.85567	-0.99845
O	3.26799	0.81538	-1.06582
C	1.24404	-0.37715	-0.29692
C	1.35780	-0.47957	1.10977
P	4.11603	-0.46242	-1.72498

O	5.46301	0.09454	-2.08521
O	3.24488	-1.22806	-2.67741
O	4.27867	-1.44848	-0.38210
C	5.12771	-0.99640	0.66428
H	-0.50480	2.40179	-0.96266
H	-0.30075	1.82957	0.70753
H	1.90277	2.99112	-1.05897
H	1.41930	0.86761	-2.01746
H	-0.06504	-0.40251	-0.55422
H	1.51965	-1.28134	-0.84354
H	1.39145	0.43036	1.70407
H	6.13258	-0.76791	0.29214
H	4.72212	-0.09640	1.14765
H	5.19118	-1.79692	1.40958
H	2.33245	-1.38446	3.67021
H	2.72205	-3.98792	2.58288
P	-1.50570	4.45970	0.84993
O	-2.44548	4.36622	-0.32260
O	-1.23705	5.74778	1.57288
O	-1.96982	3.32630	1.99145
C	-3.07330	2.47816	1.69855
H	-3.25451	1.86839	2.59144
H	-3.97916	3.05014	1.46685
H	-2.86849	1.81163	0.85198

C2'–H abstraction (*syn* N-base) (-2464.46263)

N	-0.31141	-2.12780	-0.29548
C	0.04601	-3.46673	-0.34499
N	-1.02190	-4.16399	-0.90260
C	-2.03189	-3.25964	-1.23275
C	-3.30819	-3.42578	-1.80584
O	-3.88337	-4.45277	-2.20160
N	-3.96171	-2.16219	-1.90574
C	-3.44261	-0.95173	-1.49853
N	-4.19859	0.16212	-1.70335
N	-2.24044	-0.83969	-0.96534
C	-1.55812	-2.00488	-0.84225
O	1.10711	-3.98905	0.03774
H	-1.00520	-5.15178	-1.10432
H	-4.87752	-2.19810	-2.33811
H	-5.19549	0.03266	-1.81449

H	-3.92846	1.00239	-1.15859
H	2.26764	2.76568	0.99906
C	2.98054	-2.61890	4.12486
C	2.57980	-1.17735	3.79890
N	2.52444	-1.16808	2.32096
C	3.28078	-2.30471	1.74027
C	3.91952	-2.98635	2.96157
H	1.61462	-0.87731	4.21267
H	4.02038	-1.92357	1.02780
H	2.58212	-2.95465	1.20246
H	4.01525	-4.06578	2.81727
H	2.09421	-3.26325	4.11835
H	3.45649	-2.70168	5.10597
O	-1.46149	2.93671	1.04953
C	-0.76098	1.76292	0.61131
C	0.64303	2.16057	0.19254
O	1.35899	2.64822	1.33461
C	1.46559	1.04923	-0.50489
O	2.78790	1.62181	-0.67825
C	1.65455	-0.28822	0.21779
C	1.86471	-0.26960	1.62233
P	3.28269	2.18815	-2.17584
O	4.50484	3.01431	-1.89100
O	2.09902	2.68522	-2.95144
O	3.72330	0.75605	-2.90061
C	4.88263	0.09403	-2.41306
H	-1.27800	1.29385	-0.23052
H	-0.73858	1.03862	1.43496
H	0.55624	2.96460	-0.55244
H	1.02107	0.86313	-1.48707
H	0.60582	-1.10770	0.03944
H	2.37947	-0.90172	-0.32671
H	1.40623	0.52139	2.20906
H	5.76240	0.74662	-2.45492
H	4.74642	-0.23925	-1.37468
H	5.05052	-0.78446	-3.04498
H	3.34342	-0.46650	4.13939
H	4.92143	-2.58142	3.14594
P	-3.10139	2.93611	1.10784
O	-3.70098	2.46516	-0.20261
O	-3.52352	4.24920	1.69836
O	-3.27499	1.71214	2.22568
C	-4.58143	1.17955	2.39121

H	-4.52175	0.38654	3.14379
H	-5.28563	1.94673	2.74378
H	-4.96337	0.75826	1.45342

C2'–H abstraction (O-base) (Figure 2, TS1) (-2464.45936)

N	-1.92603	-1.71618	-1.51013
C	-1.36323	-0.49207	-1.65102
N	-2.22865	0.51905	-1.31505
C	-3.41084	-0.09072	-0.92803
C	-4.65271	0.42819	-0.48671
O	-5.03193	1.59241	-0.31104
N	-5.54939	-0.64759	-0.20969
C	-5.26411	-1.98294	-0.35367
N	-6.26326	-2.86636	0.03703
N	-4.11363	-2.44174	-0.77220
C	-3.18359	-1.47047	-1.05486
O	-0.14653	-0.26587	-2.04889
H	-1.98181	1.52952	-1.24011
H	-6.44365	-0.35880	0.17003
H	-7.20912	-2.58230	-0.19516
H	-6.06649	-3.80631	-0.28832
H	3.11715	0.86680	1.96042
C	-1.27015	-3.84880	2.02161
C	-0.33674	-2.69401	2.40276
N	0.43901	-2.45979	1.16539
C	0.30508	-3.58555	0.21771
C	-0.41967	-4.66559	1.03243
H	-0.85829	-1.78031	2.69822
H	1.29131	-3.89655	-0.14197
H	-0.30143	-3.24064	-0.62967
H	-1.01914	-5.31962	0.39375
H	-2.16108	-3.46068	1.51568
H	-1.59056	-4.42362	2.89517
O	0.72376	3.32228	0.25292
C	0.92167	1.95179	-0.11297
C	2.28671	1.47627	0.34888
O	2.28436	1.34051	1.77504
C	2.72119	0.14231	-0.31161
O	3.89550	-0.30358	0.41226
C	1.69981	-0.99223	-0.32175
C	1.06004	-1.32639	0.89374

P	5.42270	-0.05804	-0.23290
O	6.36900	-0.49930	0.84683
O	5.48774	1.28083	-0.90633
O	5.39987	-1.17383	-1.46751
C	5.46233	-2.55119	-1.12187
H	0.83742	1.84257	-1.19804
H	0.14227	1.33168	0.34200
H	3.04048	2.22064	0.05632
H	2.99535	0.35994	-1.34864
H	2.04831	-1.84890	-0.90694
H	1.01786	-0.57447	1.67955
H	6.36852	-2.77886	-0.54892
H	4.58921	-2.85580	-0.52887
H	5.47018	-3.12351	-2.05547
H	0.34504	-2.98396	3.21250
H	0.30289	-5.28802	1.57410
H	0.68116	-0.61459	-1.18502
P	-0.81120	3.90448	0.11663
O	-1.38818	3.29214	1.55025
O	-1.53286	3.20627	-1.02427
O	-0.74132	5.40172	0.17098
C	-2.78786	3.43728	1.78441
H	-3.00817	2.95667	2.74357
H	-3.06916	4.49707	1.85052
H	-3.37981	2.95984	0.99578

C2'–H abstraction (*syn* O-base) (-2464.44695)

N	-2.72755	-0.00101	0.07389
C	-1.93326	0.80990	-0.65689
N	-2.66992	1.62410	-1.48562
C	-4.00903	1.31783	-1.27651
C	-5.20160	1.83518	-1.82992
O	-5.38268	2.72376	-2.67091
N	-6.31946	1.15732	-1.25716
C	-6.24833	0.15950	-0.31607
N	-7.46017	-0.32360	0.15386
N	-5.12762	-0.29909	0.18152
C	-3.99977	0.30627	-0.30810
O	-0.64600	0.88468	-0.63620
H	-2.28366	2.30330	-2.12515
H	-7.22244	1.50436	-1.55999

H	-8.20033	-0.40335	-0.53480
H	-7.33824	-1.18134	0.68002
H	3.82744	-1.45761	0.90725
C	-1.37614	-1.06942	4.60832
C	0.05556	-0.93541	4.07960
N	-0.07193	-1.31761	2.65830
C	-1.32316	-2.06646	2.40207
C	-1.93309	-2.25547	3.80019
H	0.46700	0.07331	4.16276
H	-1.08973	-3.01471	1.90525
H	-1.95795	-1.47254	1.73479
H	-3.02566	-2.27227	3.76649
H	-1.94275	-0.15813	4.38650
H	-1.40268	-1.23355	5.68932
O	3.72733	2.09035	-0.28725
C	2.56836	1.25431	-0.27719
C	3.02060	-0.19770	-0.28411
O	3.67736	-0.49507	0.95419
C	1.89989	-1.22861	-0.54714
O	2.52956	-2.52578	-0.37785
C	0.65723	-1.17682	0.33732
C	0.80053	-0.97890	1.72602
P	2.70852	-3.53368	-1.70310
O	3.55027	-4.67758	-1.21420
O	3.02966	-2.72027	-2.92258
O	1.13329	-4.03532	-1.90668
C	0.60169	-4.95032	-0.95809
H	1.94783	1.45525	-1.15807
H	1.96396	1.47022	0.61159
H	3.73644	-0.31987	-1.11024
H	1.58807	-1.12134	-1.59003
H	-0.06680	-1.94301	0.04772
H	1.67931	-0.45017	2.08817
H	1.20776	-5.86163	-0.90050
H	0.54931	-4.50381	0.04464
H	-0.41263	-5.20676	-1.28212
H	0.73354	-1.63171	4.59037
H	-1.59498	-3.20125	4.23994
P	3.51438	3.72842	-0.28193
O	2.91984	3.84027	1.28117
O	2.42256	4.13498	-1.23727
O	4.88715	4.33749	-0.34246
C	2.27252	5.05792	1.61740

H	1.90738	4.96762	2.64657
H	2.96657	5.90995	1.56773
H	1.42684	5.25848	0.94886
H	-0.06925	-0.06236	-0.07644

3'–PO_4 protonation/elimination (O-base) (Figure 3, TS2) (-2464.45330)

N	-2.64419	0.39426	-0.52323
C	-1.97644	0.37022	-1.69548
N	-2.58802	-0.46762	-2.60327
C	-3.70631	-1.00628	-1.97996
C	-4.69930	-1.90931	-2.41890
O	-4.84972	-2.48026	-3.50672
N	-5.63638	-2.12844	-1.36490
C	-5.57363	-1.56286	-0.11491
N	-6.61560	-1.86903	0.74783
N	-4.63823	-0.73041	0.26647
C	-3.70273	-0.44584	-0.69551
O	-0.90538	1.01153	-2.00976
H	-2.25945	-0.64905	-3.54004
H	-6.41675	-2.72569	-1.61323
H	-6.95847	-2.82251	0.70564
H	-6.40329	-1.58405	1.69706
H	-0.25181	1.79562	-1.10881
H	0.60965	-0.00520	-1.81368
C	-1.45720	-2.52093	3.85213
C	-1.16168	-2.16510	2.39154
N	-0.34615	-0.95522	2.51220
C	-0.58132	-0.25697	3.77630
C	-1.61396	-1.13703	4.50937
H	-0.61130	-2.94835	1.85866
H	-0.95795	0.76000	3.59952
H	0.35936	-0.16321	4.33867
H	-1.45430	-1.15363	5.59178
H	-0.60377	-3.05542	4.28634
H	-2.34509	-3.15153	3.96065
O	4.25687	-0.60322	-1.24739
C	3.42258	-0.11170	-0.20063
C	2.19898	0.56360	-0.81739
O	1.37074	-0.44645	-1.37931
C	1.50781	1.45719	0.23242
O	0.51687	2.33626	-0.53209

C	0.87414	0.83760	1.42608
C	0.26369	-0.37507	1.44023
P	0.21426	4.01374	-0.06697
O	-0.64840	4.50954	-1.18057
O	1.55493	4.54473	0.31737
O	-0.63236	3.79666	1.31236
C	-2.02193	3.43800	1.24349
H	3.97721	0.60824	0.41349
H	3.10003	-0.93729	0.44417
H	2.55928	1.23620	-1.61116
H	2.23431	2.21040	0.54053
H	0.83921	1.46874	2.30890
H	0.27299	-0.98739	0.54403
H	-2.57296	4.15128	0.62299
H	-2.15418	2.42721	0.84264
H	-2.40052	3.47658	2.26913
H	-2.09479	-1.96721	1.84096
H	-2.62374	-0.75260	4.32606
P	5.72238	-1.25298	-0.84237
O	5.13364	-2.66489	-0.16131
O	6.38047	-0.44418	0.24586
O	6.41970	-1.56469	-2.13672
C	6.03560	-3.39825	0.65385
H	5.47957	-4.23339	1.09440
H	6.87028	-3.80795	0.06700
H	6.44894	-2.77433	1.45582

C4'–H abstraction (N-base) (Figure 4, TS3) (-1781.47255)

O	1.92179	-1.75971	-0.08896
C	0.85847	-2.13450	0.77919
C	-0.41119	-1.38004	0.39114
O	-0.89669	-1.71103	-0.88642
C	-1.38128	-1.22429	1.41833
C	-2.76131	-1.02592	1.34190
C	-3.48616	-1.08540	0.14912
H	1.12906	-1.91942	1.82005
H	0.67223	-3.21432	0.68659
H	-0.07328	-0.13746	0.26092
H	-0.95467	-1.14905	2.41782
H	-3.28431	-0.79790	2.26617
H	-2.94596	-1.31603	-0.76349

N	-4.79020	-0.87072	0.03009
H	-0.39555	-1.16518	-1.55382
C	-5.68931	-0.50847	1.14200
H	-5.61637	-1.24686	1.94705
H	-5.38675	0.46562	1.54635
C	-7.08288	-0.45942	0.49404
H	-7.73082	0.27706	0.97618
H	-7.56860	-1.43838	0.57498
C	-5.50844	-0.92547	-1.25930
C	-6.78969	-0.13348	-0.98132
H	-5.73312	-1.96981	-1.51234
H	-4.88751	-0.50313	-2.05308
H	-7.60405	-0.41722	-1.65300
H	-6.60163	0.93888	-1.10636
P	3.40362	-2.45153	0.18774
O	3.00926	-3.97816	-0.37346
O	3.66645	-2.54285	1.66939
O	4.36737	-1.79471	-0.75681
C	3.86818	-5.03797	0.01986
H	3.45362	-5.96788	-0.38443
H	4.88308	-4.90643	-0.38257
H	3.93423	-5.11425	1.11180
N	0.23646	1.12460	-0.41603
C	0.51473	1.05544	-1.76705
N	1.15579	2.22889	-2.13543
C	1.35866	2.99879	-0.99085
C	1.96084	4.25987	-0.79441
O	2.50634	5.02582	-1.59909
N	1.88466	4.61563	0.58774
C	1.29334	3.86401	1.56995
N	1.37943	4.35584	2.85861
N	0.71128	2.70783	1.35309
C	0.77458	2.28373	0.05691
O	0.23036	0.12112	-2.54466
H	1.60084	2.36304	-3.03120
H	2.36897	5.47291	0.82851
H	1.32022	5.36185	2.96483
H	0.77375	3.85741	3.49948

C4'–H abstraction (O-base) (Figure 4, TS3) (-1781.47149)

O	0.09259	2.63856	-0.36064
C	-0.33956	1.56275	-1.19607
C	-1.10887	0.51080	-0.38786
O	-2.23591	1.00581	0.27640
C	-1.22087	-0.77546	-0.96300
C	-2.21855	-1.75034	-0.82780
C	-3.43130	-1.54364	-0.17568
H	0.55203	1.09529	-1.62363
H	-0.96913	1.95961	-2.00044
H	-0.32015	-1.08146	-1.49033
H	-2.01644	-2.72545	-1.26183
H	-3.62031	-0.57847	0.28090
N	-4.40123	-2.44798	-0.04657
H	-2.05127	1.93281	0.56161
C	-4.34347	-3.82023	-0.57891
H	-4.11657	-3.80485	-1.65021
H	-3.54246	-4.37412	-0.07221
C	-5.73320	-4.39857	-0.26635
H	-5.69803	-5.47734	-0.09347
H	-6.41288	-4.21444	-1.10605
C	-5.65644	-2.19375	0.68495
C	-6.18956	-3.60190	0.96883
H	-6.35069	-1.62669	0.05031
H	-5.45624	-1.60732	1.58562
H	-7.27355	-3.61283	1.11019
H	-5.72297	-4.00345	1.87560
P	-0.67807	4.10147	-0.39876
O	-1.86438	3.69126	0.74158
O	-1.36541	4.31626	-1.71953
O	0.25229	5.10533	0.20977
C	-3.03779	4.50243	0.76377
H	-3.70025	4.09986	1.53581
H	-2.78731	5.53986	1.01839
H	-3.54549	4.48655	-0.20674
H	-0.21225	0.14778	0.50538
N	2.07218	-0.85555	-0.23552
C	1.81488	-0.43352	1.02753
N	2.95437	-0.47108	1.80569
C	3.99551	-0.90986	0.99471
C	5.36422	-1.13865	1.24755
O	6.03146	-0.99363	2.28109

N	5.99397	-1.60405	0.05347
C	5.36104	-1.81626	-1.14663
N	6.16976	-2.21502	-2.20034
N	4.08344	-1.61331	-1.34740
C	3.40365	-1.13798	-0.25546
O	0.68919	-0.05363	1.50920
H	3.02031	-0.12394	2.75065
H	6.99816	-1.72160	0.12416
H	6.91201	-2.86537	-1.96712
H	5.62053	-2.53209	-2.99095

Proton transfer from O4' to OG (Figure 5, TS4') (-1780.98290)

O	0.80285	-2.32302	0.91572
C	0.03984	-2.45588	-0.30454
C	-1.19913	-1.57654	-0.25381
O	-1.03019	-0.27870	-0.31961
C	-2.42784	-2.19114	-0.17358
C	-3.73449	-1.55292	-0.17200
C	-4.00931	-0.22589	-0.27422
H	-0.23175	-3.50779	-0.44219
H	0.66715	-2.14345	-1.15158
H	-2.43174	-3.27682	-0.10138
H	-4.58003	-2.23984	-0.10325
H	-3.19197	0.48276	-0.35811
N	-5.28871	0.34389	-0.35946
H	0.20470	0.25303	-0.58477
C	-6.47235	-0.45242	-0.05581
H	-6.68205	-1.14800	-0.88036
H	-6.32133	-1.07217	0.84675
C	-7.60831	0.57978	0.16508
H	-7.92186	0.57026	1.21523
H	-8.49566	0.36111	-0.43799
C	-5.49133	1.70986	0.10861
C	-6.97534	1.94370	-0.18653
H	-4.82556	2.39868	-0.42487
H	-5.28746	1.82557	1.19170
H	-7.10868	2.16704	-1.25124
H	-7.40026	2.77194	0.39050
P	2.17072	-3.23475	1.07225
O	3.16242	-2.43647	-0.01477
O	1.93975	-4.63734	0.56335

O	2.69320	-2.96995	2.45681
C	3.77660	-3.16728	-1.06409
H	4.09302	-2.44662	-1.82686
H	4.66401	-3.71489	-0.71117
H	3.08776	-3.88981	-1.51227
N	1.16447	0.84344	-0.85037
C	1.94227	0.61188	-1.98120
N	2.95265	1.57306	-1.96046
C	2.82540	2.35668	-0.81590
C	3.56904	3.45300	-0.33157
O	4.57851	4.00593	-0.79123
N	2.99229	3.92468	0.88718
C	1.86992	3.41125	1.48452
N	1.50155	3.96891	2.69496
N	1.18138	2.40698	0.99674
C	1.69394	1.88494	-0.15057
O	1.78311	-0.25204	-2.84498
H	3.72950	1.57211	-2.60296
H	3.51630	4.66336	1.34224
H	1.61511	4.97245	2.78059
H	0.58414	3.65415	2.98939

Assisted 5'–PO_4 protonation/elimination (by OG) (Figure 5, TS4") (-1780.93049)

O	0.80285	-2.32302	0.91572
C	0.03984	-2.45588	-0.30454
C	-1.19913	-1.57654	-0.25381
O	-1.03019	-0.27870	-0.31961
C	-2.42784	-2.19114	-0.17358
C	-3.73449	-1.55292	-0.17200
C	-4.00931	-0.22589	-0.27422
H	-0.23175	-3.50779	-0.44219
H	0.66715	-2.14345	-1.15158
H	-2.43174	-3.27682	-0.10138
H	-4.58003	-2.23984	-0.10325
H	-3.19197	0.48276	-0.35811
N	-5.28871	0.34389	-0.35946
H	0.20470	0.25303	-0.58477
C	-6.47235	-0.45242	-0.05581
H	-6.68205	-1.14800	-0.88036
H	-6.32133	-1.07217	0.84675
C	-7.60831	0.57978	0.16508

H	-7.92186	0.57026	1.21523
H	-8.49566	0.36111	-0.43799
C	-5.49133	1.70986	0.10861
C	-6.97534	1.94370	-0.18653
H	-4.82556	2.39868	-0.42487
H	-5.28746	1.82557	1.19170
H	-7.10868	2.16704	-1.25124
H	-7.40026	2.77194	0.39050
P	2.17072	-3.23475	1.07225
O	3.16242	-2.43647	-0.01477
O	1.93975	-4.63734	0.56335
O	2.69320	-2.96995	2.45681
C	3.77660	-3.16728	-1.06409
H	4.09302	-2.44662	-1.82686
H	4.66401	-3.71489	-0.71117
H	3.08776	-3.88981	-1.51227
N	1.16447	0.84344	-0.85037
C	1.94227	0.61188	-1.98120
N	2.95265	1.57306	-1.96046
C	2.82540	2.35668	-0.81590
C	3.56904	3.45300	-0.33157
O	4.57851	4.00593	-0.79123
N	2.99229	3.92468	0.88718
C	1.86992	3.41125	1.48452
N	1.50155	3.96891	2.69496
N	1.18138	2.40698	0.99674
C	1.69394	1.88494	-0.15057
O	1.78311	-0.25204	-2.84498
H	3.72950	1.57211	-2.60296
H	3.51630	4.66336	1.34224
H	1.61511	4.97245	2.78059
H	0.58414	3.65415	2.98939

Direct 5'–PO_4 protonation/elimination (Figure 5, TS4) (-1163.63675)

O	2.30701	0.00153	-0.94531
C	1.54084	1.78103	0.31256
C	0.28067	1.19876	0.26812
O	0.21888	-0.14169	0.49571
C	-0.85826	1.95217	-0.03839
C	-2.20605	1.55019	-0.07030
C	-2.64119	0.24985	0.16194

H	1.69033	2.78302	-0.07981
H	2.33851	1.34306	0.89571
H	-0.66641	3.00444	-0.23388
H	-2.94065	2.31508	-0.30562
H	-1.90569	-0.51202	0.39757
N	-3.91063	-0.16280	0.11084
H	1.09191	-0.43297	0.05020
C	-5.05690	0.69781	-0.21969
H	-5.06973	1.58375	0.42485
H	-4.97032	1.03943	-1.25982
C	-6.27712	-0.21322	-0.01106
H	-7.10310	0.04929	-0.67730
H	-6.63669	-0.12670	1.02064
C	-4.31928	-1.55897	0.35164
C	-5.72217	-1.62643	-0.26181
H	-4.34696	-1.76012	1.43131
H	-3.60380	-2.24702	-0.10677
H	-6.33275	-2.41356	0.18854
H	-5.65104	-1.82310	-1.33757
P	3.80724	-0.40565	-0.62751
O	3.67988	-0.43719	1.07782
O	4.81211	0.68336	-0.95741
O	4.09854	-1.82751	-1.08017
C	4.89201	-0.64656	1.77294
H	4.68850	-0.59298	2.85037
H	5.31736	-1.63569	1.54673
H	5.63969	0.11465	1.51073

Enol-keto rearrangement (Figure 6, TS5) (-1163.63183)

O	-2.89911	-0.42118	0.98680
H	-1.89137	-0.83654	-0.06107
P	-4.32918	-0.19576	0.37565
O	-4.29368	1.49669	0.16672
O	-5.43222	-0.47626	1.38900
O	-4.48408	-0.79710	-1.01552
C	-5.51664	2.08131	-0.22476
H	-5.34723	3.15114	-0.40956
H	-5.90959	1.62775	-1.14803
H	-6.28424	1.97602	0.55600
C	-1.22732	-1.24015	-0.97559
C	0.19579	-1.13217	-0.66863

O	0.89008	-2.06025	-0.21048
C	0.76904	0.23002	-0.88250
C	2.06381	0.62757	-0.68388
C	3.06536	-0.25542	-0.19234
H	-1.56919	-0.60521	-1.79786
H	-1.54909	-2.27538	-1.10691
H	0.07205	0.97928	-1.24862
H	2.33148	1.65806	-0.90052
H	2.76055	-1.27672	0.02204
N	4.31533	0.07323	0.02722
C	4.90972	1.41401	-0.19502
H	4.66518	1.76860	-1.19938
H	4.48310	2.11112	0.53476
C	6.41207	1.19251	0.02876
H	6.90259	2.09572	0.39902
H	6.89331	0.90761	-0.91325
C	5.32055	-0.88194	0.55799
C	6.46213	0.02388	1.02797
H	5.63920	-1.54306	-0.25637
H	4.87054	-1.48848	1.34652
H	7.42174	-0.49848	1.02814
H	6.26650	0.37946	2.04554