Supporting Information

Dissociative electron attachment to the halogenated nucleotides: A quest for better radiosensitizer

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1. **Electron affinities of the 5X-3′-dCMPH (X = H, F, Cl, Br, I) moieties calculated at the B3LYP/ aug-cc-pVDZ level of theory in the gas phase and aqueous phase.**

Table S1: Vertical electron affinity (VEA), adiabatic electron affinity (AEA), and vertical detachment energy (VDE) calculated at the B3LYP/aug-cc-pVDZ level of theory in the gas phase. (All the energies are in eV).

System	VEA	AEA	VDE
3′-dCMPH	0.18	0.49	1.04
5F-3′-dCMPH	0.05	0.72	1.44
5Cl-3′-dCMPH	0.08	0.80	1.51
5Br-3′-dCMPH	0.08	0.83	1.59
5I-3′-dCMPH	0.09	0.88	1.74

Table S2: Vertical electron affinity (VEA), adiabatic electron affinity (AEA), and vertical detachment energy (VDE) calculated at the B3LYP/aug-cc-pVDZ level of theory in the aqueous phase. (All the energies are in eV).

System	VEA	AEA	VDE
3′-dCMPH	1.47	2.08	2.45
5F-3′-dCMPH	1.68	2.30	2.78
5Cl-3′-dCMPH	1.75	2.34	2.82
5Br-3′-dCMPH	1.75	2.36	2.91
5I-3′-dCMPH	1.73	2.38	2.90

2. **Bond length of dissociative C_5—X bonds of the 5X-3′-dCMPH (X = H, F, Cl, Br, I) moieties before and after electron attachment calculated at the B3LYP/ aug-cc-pVDZ level of theory in the gas phase and aqueous phase.**

Table S3: C_5—X bond length of neutral and anionic 5X-3′-dCMPH at equilibrium geometries calculated at the B3LYP/aug-cc-pVDZ level of theory.

System	Gas Phase		Aqueous Phase	
	Neutral	Anion	Neutral	Anion
3′-dCMPH	1.087	1.090	1.086	1.090
5F-3′-dCMPH	1.367	1.391	1.363	1.387
5Cl-3′-dCMPH	1.761	1.788	1.757	1.782
5Br-3′-dCMPH	1.943	1.986	1.938	1.986
5I-3′-dCMPH	2.119	2.170	2.116	2.170

3. **Natural population analysis (NPA) charge distributions along the $C_{3'}$—$O_{3'}$ and C-N bond cleavage pathways calculated at the M06-2X/ aug-cc-pVDZ level of theory in the aqueous phase.**

Table S4: Natural Population Analysis (NPA) charge distributions on the base fragment (B), sugar fragment (S), and phosphate group (P) of reactants, transition states, and products along the $C_{3'}$—$O_{3'}$ bond-cleavage pathway calculated at the M06-2X/aug-cc-pVDZ level of theory in the aqueous phase.

System	Reactant			Transition State			Product		
	B	S	P	B	S	P	B	S	P
3′-dCMPH	-1.19	0.56	-0.37	-0.30	0.38	-1.08	-0.33	0.31	-0.98
5F-3′-dCMPH	-1.20	0.57	-0.36	-0.31	0.39	-1.08	-0.34	0.32	-0.98
5Cl-3′-dCMPH	-1.21	0.57	-0.36	-0.32	0.40	-1.08	-0.34	0.32	-0.98
5Br-3′-dCMPH	-1.21	0.57	-0.36	-0.32	0.40	-1.08	-0.35	0.33	-0.98
5I-3′-dCMPH	-1.21	0.57	-0.36	-0.32	0.40	-1.08	-0.35	0.33	-0.98

Table S5: Natural Population Analysis (NPA) charge distributions on the base fragment (B), sugar fragment (S), and phosphate group (P) of reactants, transition states, and products along the C-N bond-cleavage pathway calculated at the M06-2X/aug-cc-pVDZ level of theory in the aqueous phase.

System	Reactant			Transition State			Product		
	B	S	P	B	S	P	B	S	P
3′-dCMPH	-1.19	0.56	-0.37	-1.03	0.40	-0.37	-0.98	0.34	-0.36
5F-3′-dCMPH	-1.20	0.57	-0.36	-1.06	0.42	-0.36	-0.98	0.34	-0.36
5Cl-3′-dCMPH	-1.21	0.57	-0.36	-1.08	0.44	-0.36	-0.98	0.34	-0.36
5Br-3′-dCMPH	-1.21	0.57	-0.36	-1.08	0.44	-0.36	-0.98	0.34	-0.36
5I-3′-dCMPH	-1.21	0.57	-0.36	-1.07	0.44	-0.36	-0.98	0.34	-0.36

4. **Molecular orbital pictures of neutral and anionic structures in ground state, transition states, and products of different DEA processes calculated at the M06-2X/ aug-cc-pVDZ level of theory in the aqueous phase.**

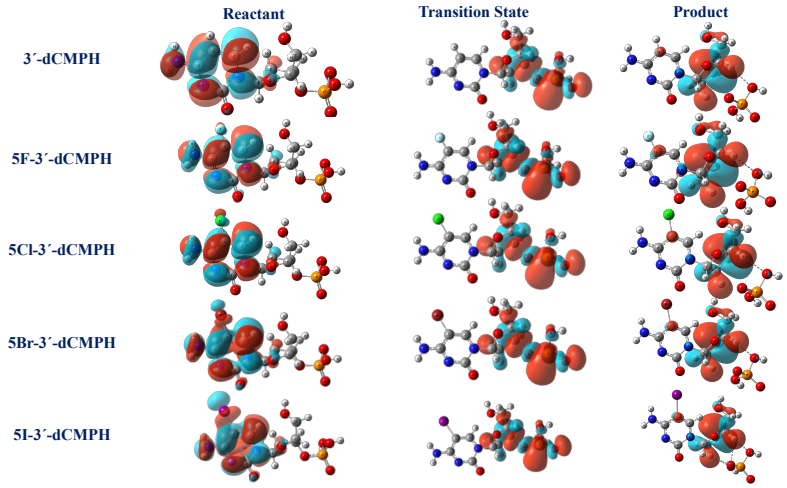

Fig. S1: The singly occupied molecular orbitals (SOMOs) of reactants, transition states, and products for anionic 5X-3′-dCMPH (X = F, Cl, Br, I) along the $C_{3'}$–$O_{3'}$ bond cleavage calculated at the M06-2X/aug-cc- pVDZ level of theory in the aqueous phase.

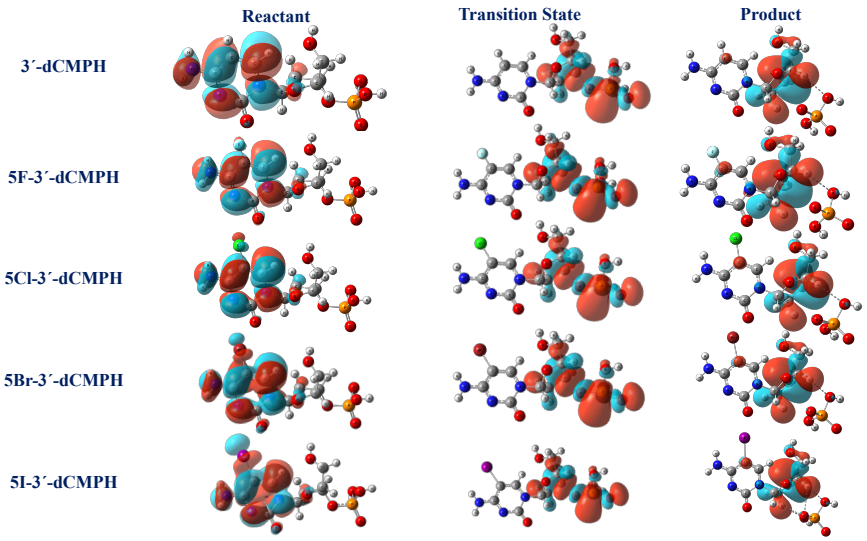

Fig. S2: The singly occupied molecular orbitals (SOMOs) of reactants, transition states, and products for anionic 5X-3′-dCMPH (X = F, Cl, Br, I) along the $C_{3'}$–$O_{3'}$ bond cleavage calculated at the M06-2X/aug-cc- pVDZ level of theory in the aqueous phase.

5. **Activation energies, reaction energies and rate constants for C_5–X, $C_{3'}$–$O_{3'}$, and C-N bond cleavage pathways calculated at the B3LYP/ aug-cc-pVDZ level of theory in the aqueous phase.**

Table S6: Activation energies ($E^{\ddagger}$) and activation free energies ($G^{\ddagger}$) for dehalogenation, single-strand break, and base release calculated at the B3LYP/aug-cc-pVDZ level of theory in the aqueous phase. (All the energies are in kcal/mol.)

	C_5–X bond cleavage		$C_{3'}$–$O_{3'}$ bond cleavage		C–N bond cleavage	
System	$E^{\ddagger}$	$G^{\ddagger}$	$E^{\ddagger}$	$G^{\ddagger}$	$E^{\ddagger}$	$G^{\ddagger}$
3′-dCMPH	--	--	14.56	12.80	22.96	22.84
5F-3′-dCMPH	11.79	12.11	16.32	13.99	24.28	23.78
5Cl-3′-dCMPH	3.51	3.89	16.57	14.18	24.09	23.91
5Br-3′-dCMPH	0.06	0.37	16.82	14.31	23.84	23.78
5I-3′-dCMPH	0.0	--	17.44	14.06	24.59	23.53

Table S7: The reaction energies (E_r) and the reaction free energies (G_r) for dehalogenation, single-strand break, and base release calculated at the B3LYP/aug-cc-pVDZ level of theory in the aqueous phase. (All the energies are in kcal/mol.)

	C_5–X bond cleavage		$C_{3'}$–$O_{3'}$ bond cleavage		C–N bond cleavage	
System	E_r	G_r	E_r	G_r	E_r	G_r
3′-dCMPH	--	--	–21.52	–26.42	2.1	5.14
5F-3′-dCMPH	–3.57	–4.89	–16.44	–21.46	5.21	6.15
5Cl-3′-dCMPH	–14.12	–15.75	–15.49	–19.89	–0.75	5.27
5Br-3′-dCMPH	–17.51	–18.57	–14.99	–20.02	4.95	5.33
5I-3′-dCMPH	--	--	–14.74	–21.33	5.71	5.02

Table S8: Rate Constants, k_{TST} (in s^{-1}) calculated with Eyring's equation from B3LYP/aug-cc-pVDZ optimized structures for dehalogenation, strand break, base release.

System	C_5–X bond cleavage		$C_{3'}$–$O_{3'}$ bond cleavage		C–N bond cleavage	
	k_{TST}	k_{SC}	k_{TST}	k_{SC}	k_{TST}	k_{SC}
3′-dCMPH	—	—	$3.13\times10^{+03}$	$2.59\times10^{+04}$	1.12×10^{-04}	3.47×10^{-03}
5F-3′-dCMPH	$8.24\times10^{+03}$	$2.37\times10^{+04}$	$4.47\times10^{+02}$	$2.96\times10^{+03}$	2.29×10^{-05}	6.46×10^{-02}
5Cl-3′-dCMPH	$8.74\times10^{+09}$	$1.06\times10^{+10}$	$3.03\times10^{+02}$	$1.93\times10^{+03}$	1.86×10^{-05}	3.66×10^{-05}
5Br-3′-dCMPH	$3.29\times10^{+12}$	$3.05\times10^{+12}$	$2.05\times10^{+02}$	$1.30\times10^{+03}$	2.29×10^{-05}	8.88×10^{-02}
5I-3′-dCMPH	$6.21\times10^{+12}$	—	$3.03\times10^{+02}$	$2.02\times10^{+03}$	3.50×10^{-05}	8.88×10^{-02}

6. **Potential energy curves (PECs) for different DEA processes calculated at the B3LYP/ aug-cc-pVDZ level of theory in the aqueous phase.**

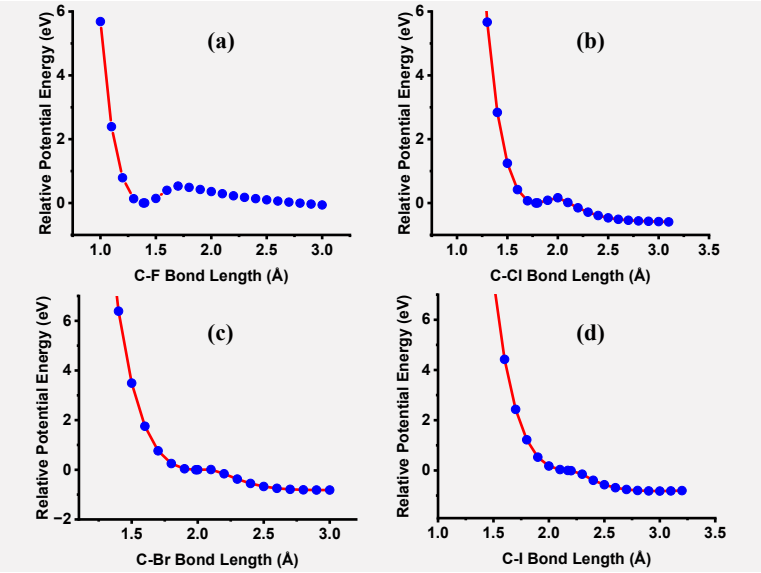

Fig. S3: The relaxed potential energy curves (PECs) for the anionic (a) 5F-3′-dCMPH, (b) 5Cl-3′-dCMPH, (c) 5Br-3′-dCMPH, and (d) 5I-3′-dCMPH along the C_5-X bond calculated at the B3LYP/aug-cc-pVDZ level of theory in the aqueous phase.

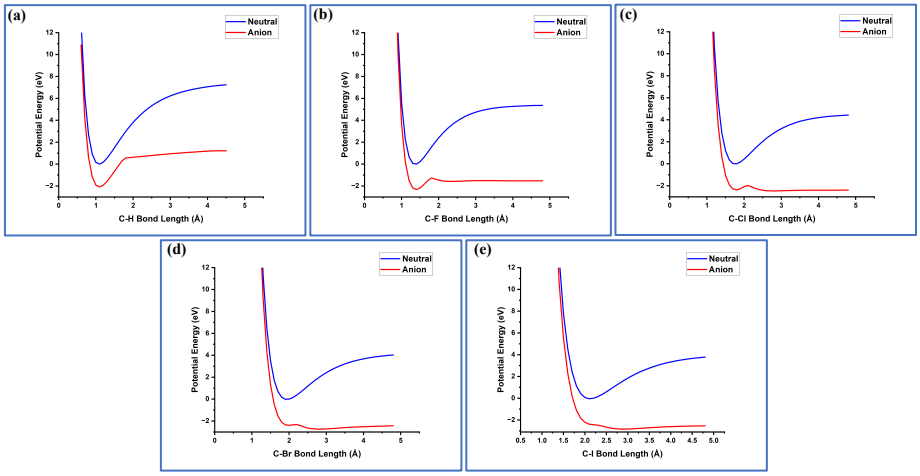

Fig. S4: The rigid potential energy curves (PECs) for the C_5-X bond cleavage in both neutral and anionic forms of (a) 3′-dCMPH, (b) 5F-3′-dCMPH, (c) 5Cl-3′-dCMPH, (d) 5Br-3′-dCMPH, and (e) 5I-3′-dCMPH calculated at the B3LYP/aug-cc-pVDZ level of theory in the aqueous phase.

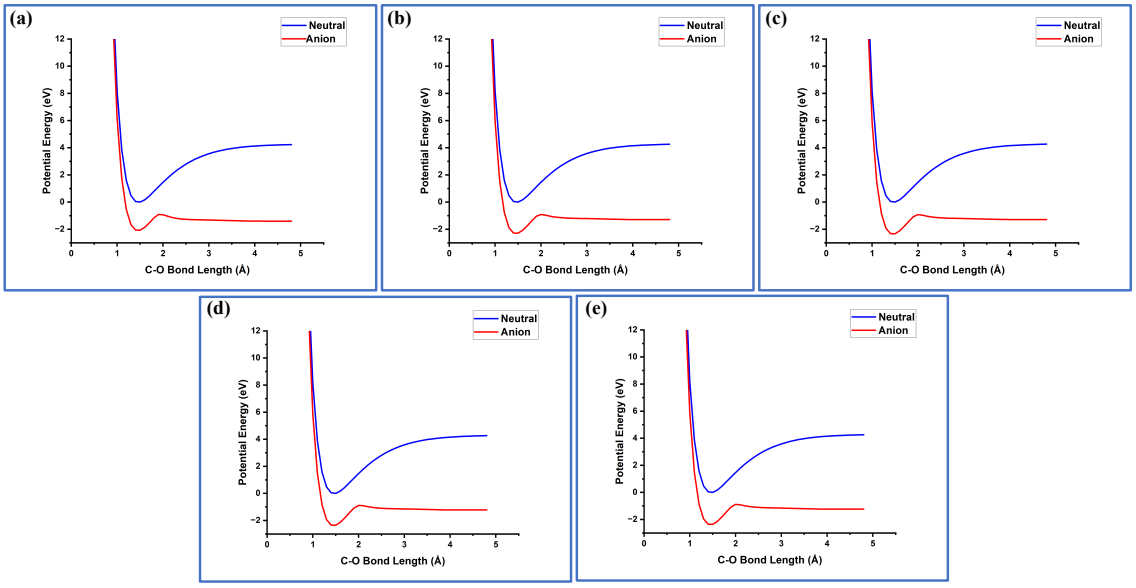

Fig. S5: The rigid potential energy curves (PECs) for the $C_{3'}$–$O_{3'}$ bond cleavage in both neutral and anionic forms of (a) 3′-dCMPH, (b) 5F-3′-dCMPH, (c) 5Cl-3′-dCMPH, (d) 5Br-3′-dCMPH, and (e) 5I-3′-dCMPH calculated at the B3LYP/aug-cc-pVDZ level of theory in the aqueous phase.

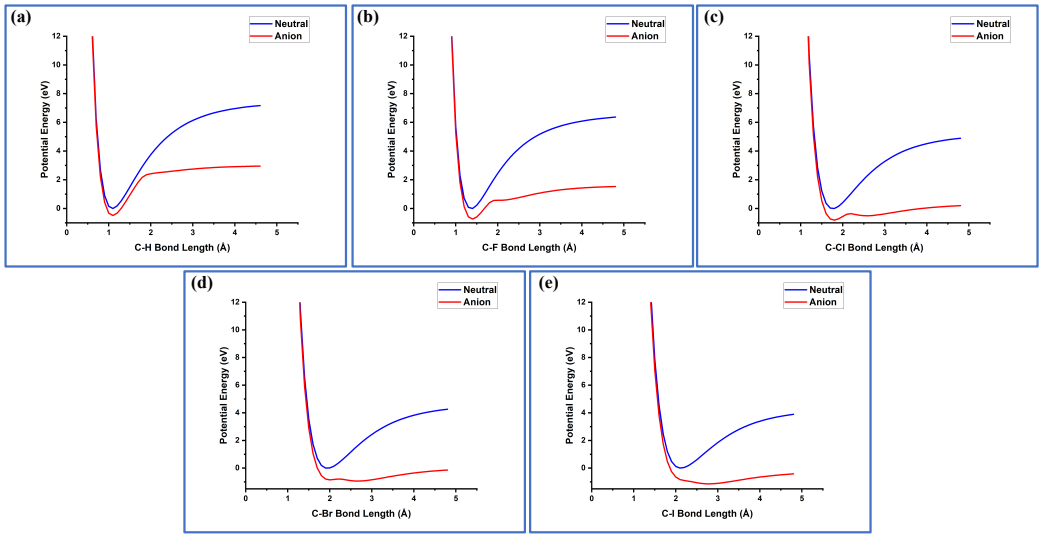

Fig. S6: The rigid potential energy curves (PECs) for the C-N bond cleavage in both neutral and anionic forms of (a) 3′-dCMPH, (b) 5F-3′-dCMPH, (c) 5Cl-3′-dCMPH, (d) 5Br-3′-dCMPH, and (e) 5I-3′-dCMPH calculated at the B3LYP/aug-cc-pVDZ level of theory in the aqueous phase.

7. Intrinsic reaction coordinates (IRCs) for different DEA processes calculated at the M06-2X/ aug-cc-pVDZ level of theory in the aqueous phase.

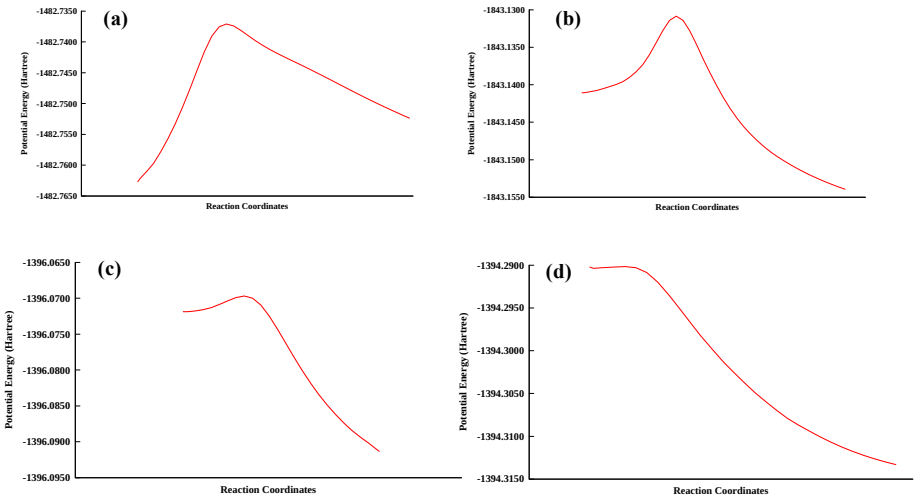

Fig. S7: The intrinsic reaction coordinate (IRC) profiles for the C_5-X bond cleavage of anionic (a) 5F-3′-dCMPH, (b) 5Cl-3′-dCMPH, (c) 5Br-3′-dCMPH and (d) 5I-3′-dCMPH calculated at the B3LYP/aug-cc-pVDZ level of theory in the aqueous phase.

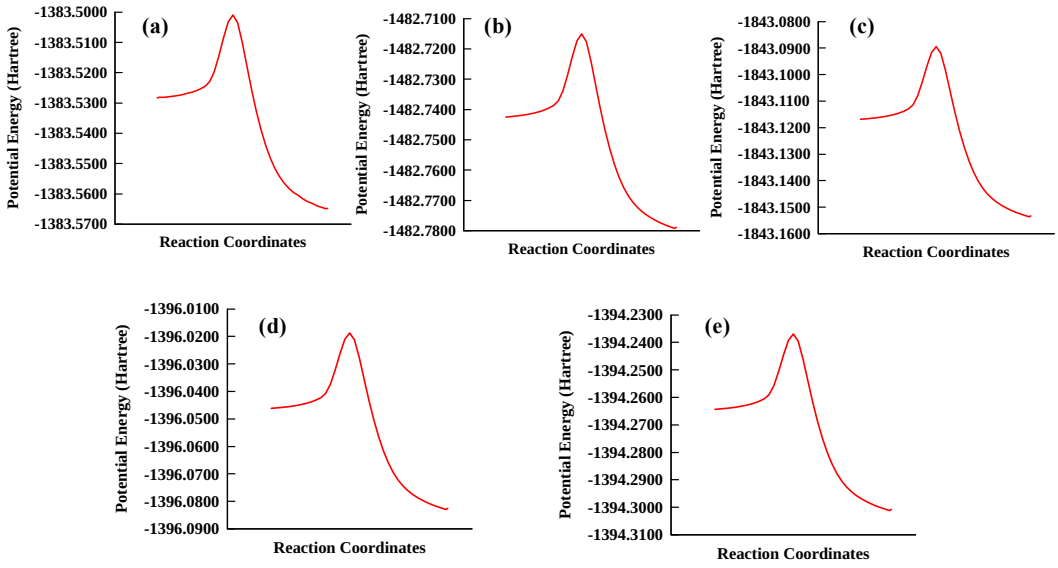

Fig. S8: The intrinsic reaction coordinate (IRC) profiles for the $C_{3'}$–$O_{3'}$ bond cleavage of anionic (a) 3′-dCMPH, (b) 5F-3′-dCMPH, (c) 5Cl-3′-dCMPH, (d) 5Br-3′-dCMPH, and (e) 5I-3′-dCMPH calculated at the B3LYP/aug-cc-pVDZ level of theory in the aqueous phase.

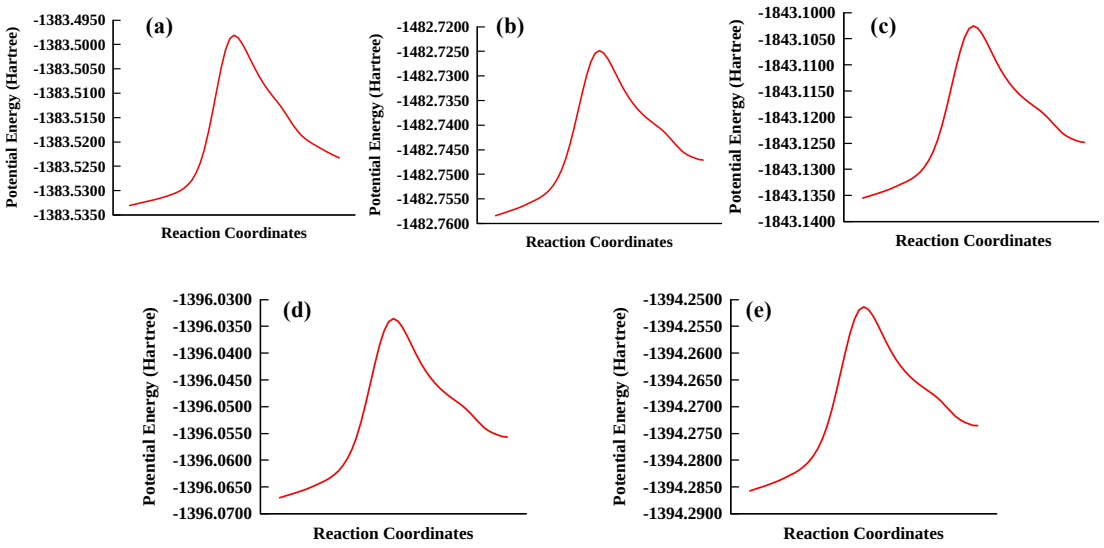

Fig. S9: The intrinsic reaction coordinate (IRC) profiles for the C-N bond cleavage of anionic (a) 3′-dCMPH, (b) 5F-3′-dCMPH, (c) 5Cl-3′-dCMPH, (d) 5Br-3′-dCMPH, and (e) 5I-3′-dCMPH calculated at the B3LYP/aug-cc-pVDZ level of theory in the aqueous phase.

8. **Time evolution of the C_5−X, $C_{3'}$−$O_{3'}$, and the C-N bonds, along with singly occupied molecular orbitals, at regular intervals during ab initio molecular dynamics simulations calculated at the B3LYP/def2-SVP level of theory in the aqueous phase.**

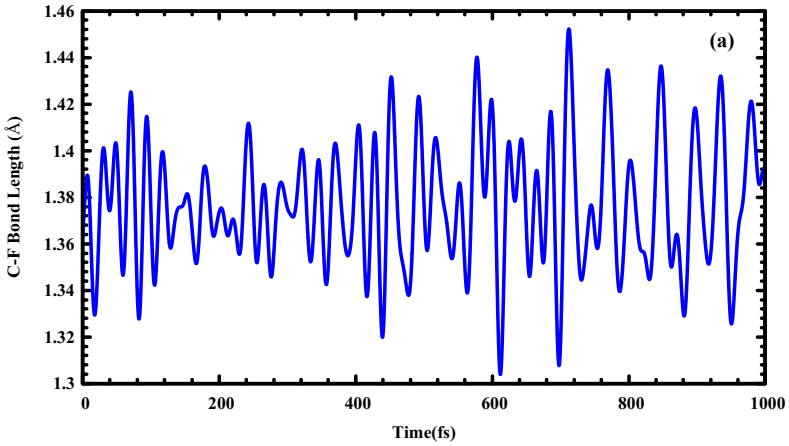

Fig. S10: The time evolution of the C_5−F bond, after the electron attachment to the neutral geometry of 5F−3′−dCMPH, during ab initio molecular dynamics simulation calculated at the B3LYP/def2-SVP level of theory in the aqueous phase.

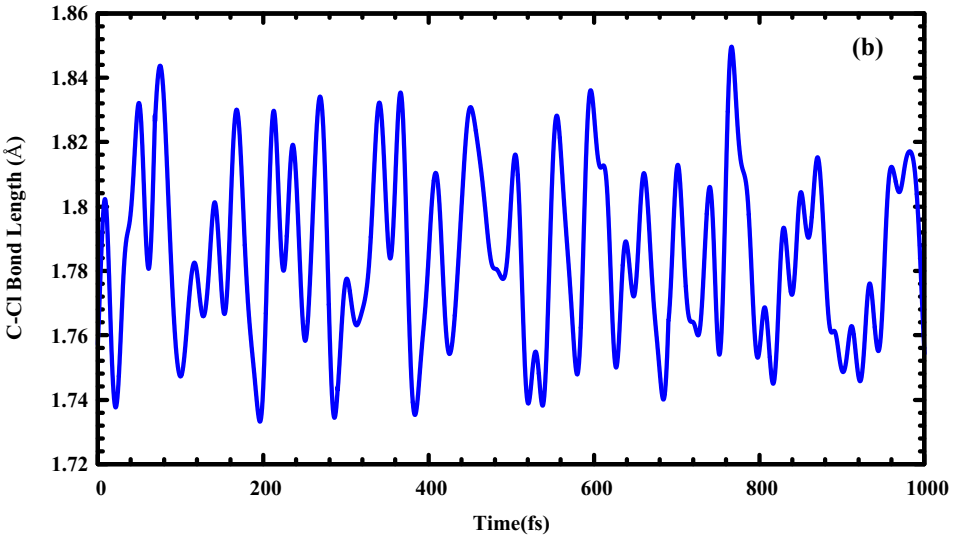

Fig. S11: The time evolution of the C_5−Cl bond, after the electron attachment to the neutral geometry of 5Cl−3′−dCMPH, during ab initio molecular dynamics simulation calculated at the B3LYP/def2-SVP level of theory in the aqueous phase.

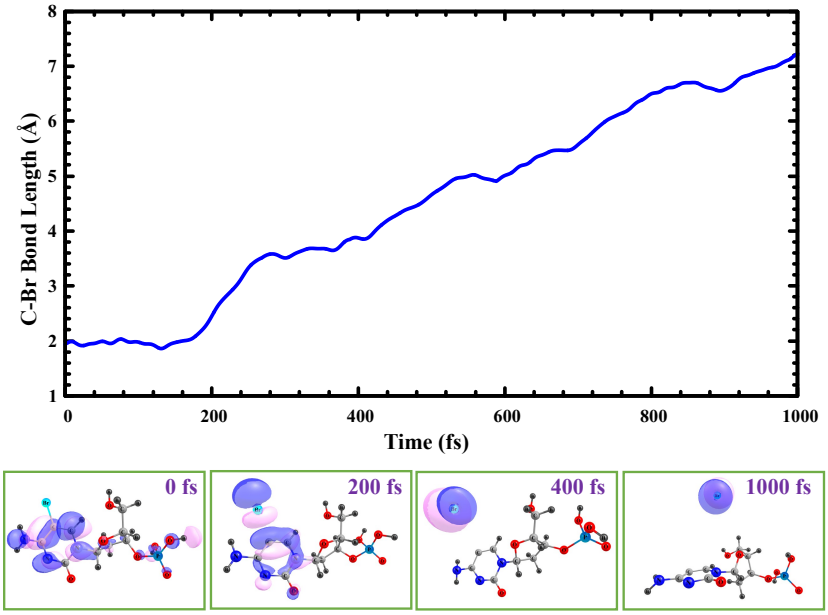

Fig. S12: The time evolution of the C_5−Br bond length, along with singly occupied molecular orbitals (SOMOs) at time = 0 fs, 200 fs, 400 fs, and 1000 fs during ab initio molecular dynamics simulation calculated at the B3LYP/def2-SVP level of theory in the aqueous phase.

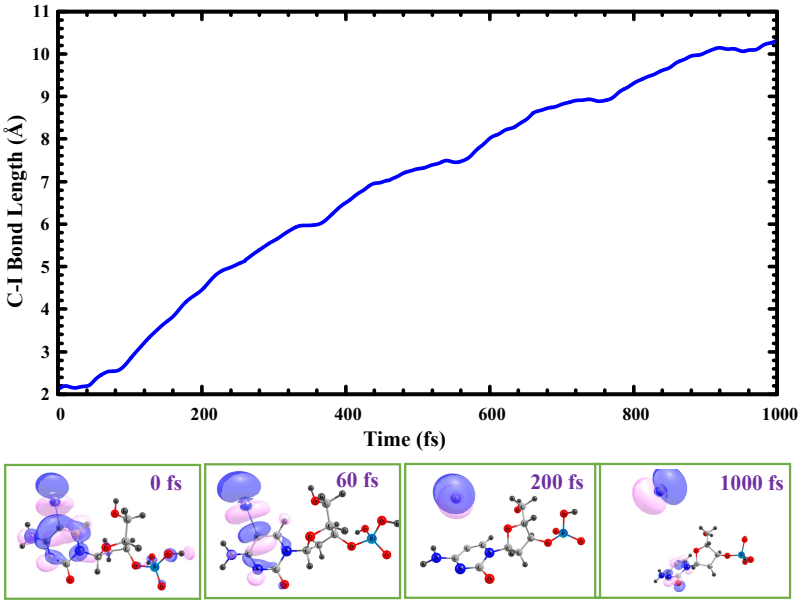

Fig. S13: The time evolution of the C_5–I bond length, along with singly occupied molecular orbitals (SOMOs) at time = 0 fs, 60 fs, 200 fs, and 1000 fs during ab initio molecular dynamics simulation calculated at the B3LYP/def2-SVP level of theory in the aqueous phase.

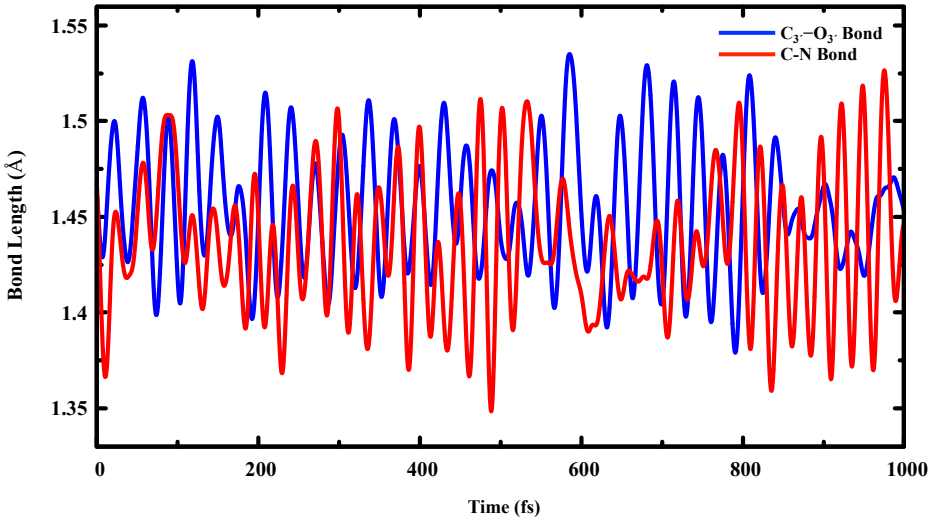

Fig. S14: The time evolution of the $C_{3'}$–$O_{3'}$ bond (blue line) and the C-N bond (red line), after the electron attachment to the neutral geometry of 5F–3′–dCMPH.

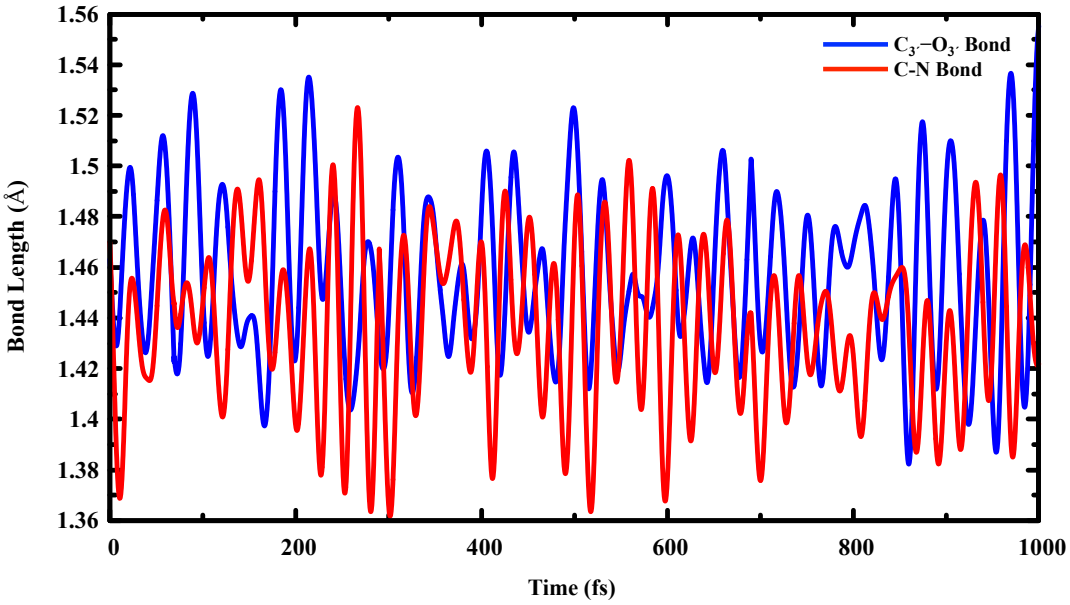

Fig. S12: The time evolution of the $C_{3'}$–$O_{3'}$ bond (blue line) and the C-N bond (red line), after the electron attachment to the neutral geometry of 5Cl–3′–dCMPH.

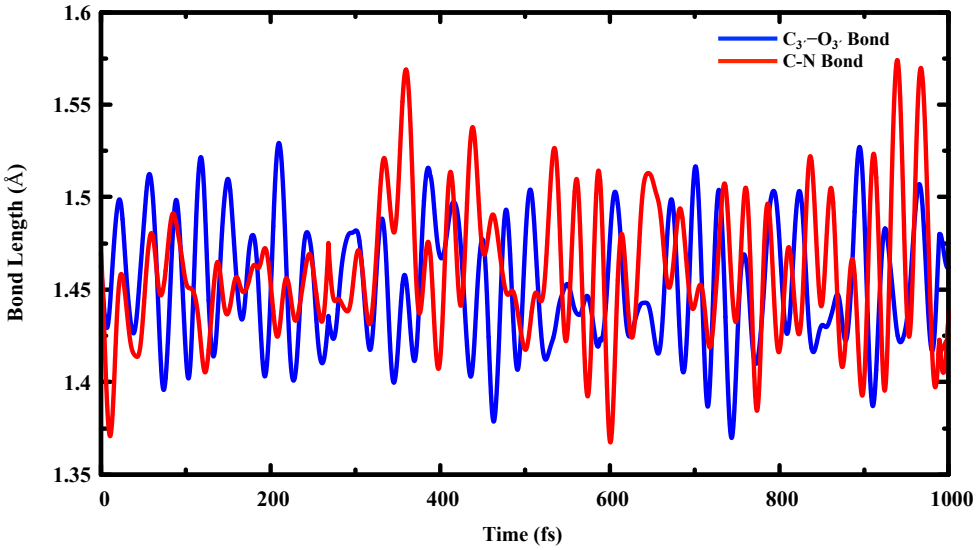

Fig. S13: The time evolution of the $C_{3'}$–$O_{3'}$ bond (blue line) and the C-N bond (red line), after the electron attachment to the neutral geometry of 5Br–3′–dCMPH.

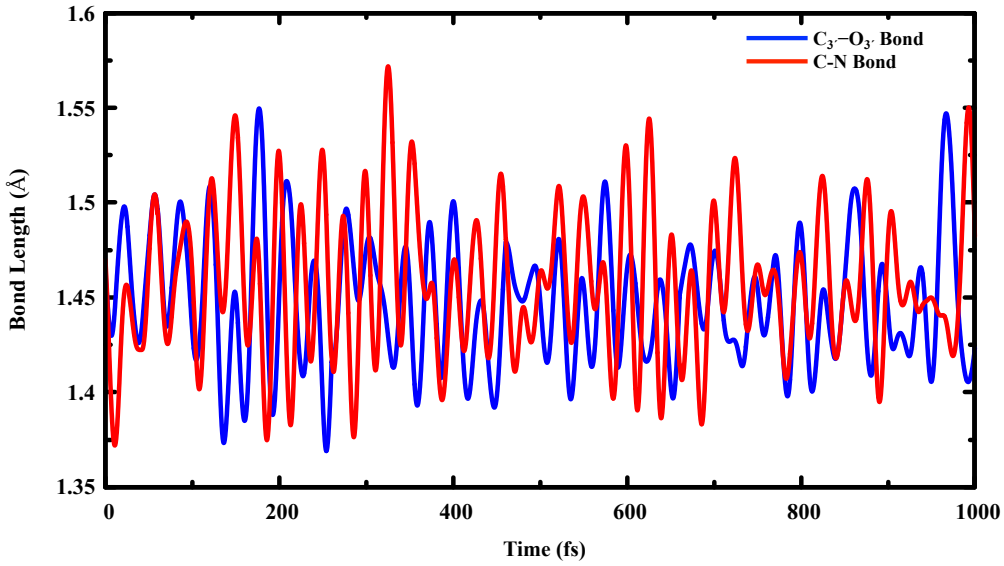

Fig. S14: The time evolution of the $C_{3'}$–$O_{3'}$ bond (blue line) and the C-N bond (red line), after the electron attachment to the neutral geometry of 5I–3′–dCMPH.

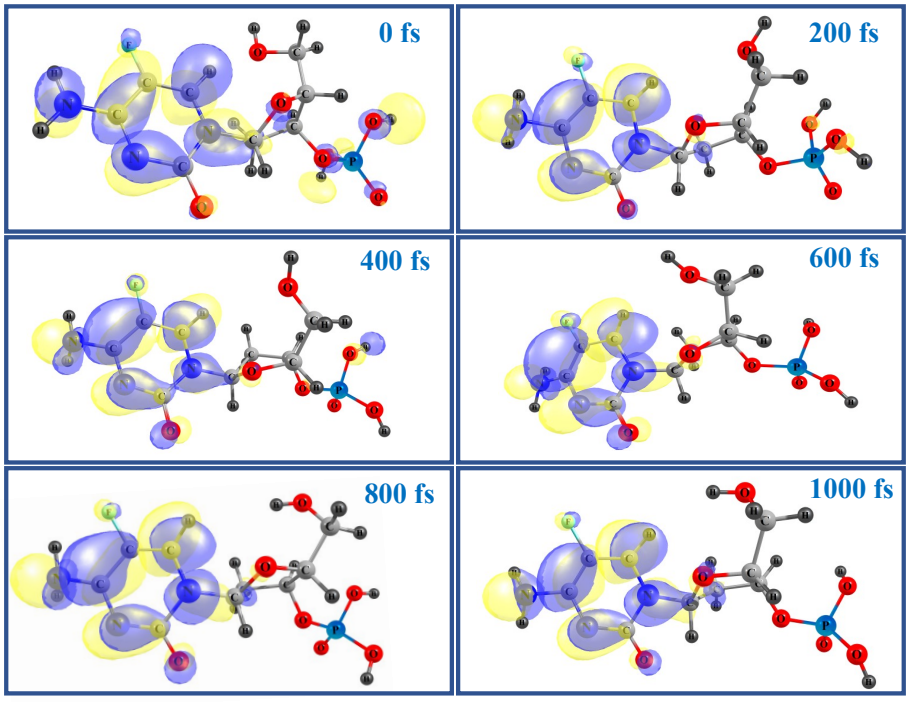

Fig. S15: Singly occupied molecular orbitals (SOMOs) of 5F-3′-dCMPH at various time intervals during *ab initio* molecular dynamics simulation conducted after the electron attachment.

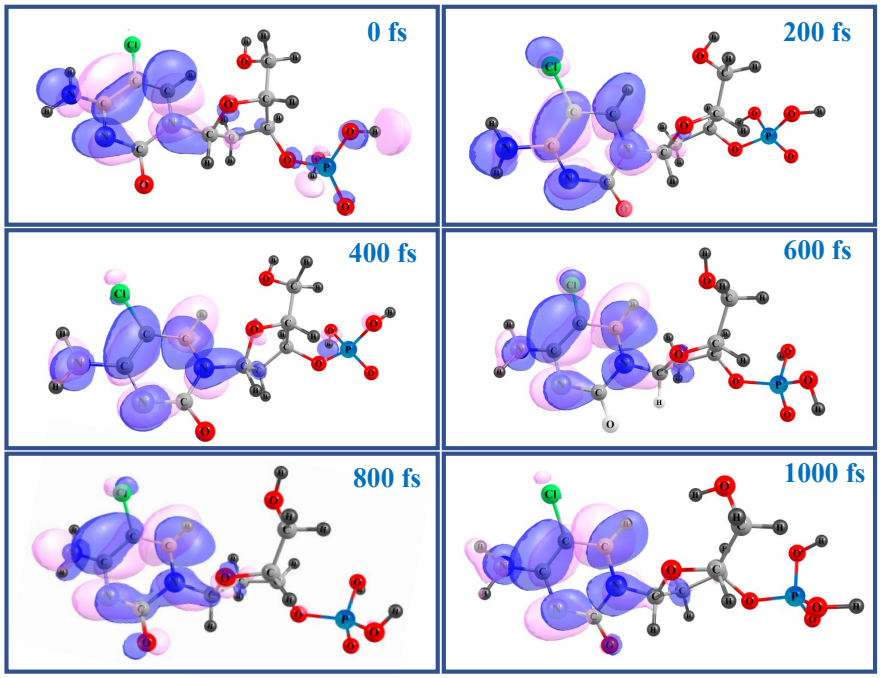

Fig. S16: Singly occupied molecular orbitals (SOMOs) of 5Cl-3′-dCMPH at various time intervals during *ab initio* molecular dynamics simulation conducted after the electron attachment.

9. Cartesian coordinates of neutral 5X-3′-dCMPH moieties optimized at the M06-2X/ aug-cc-pVDZ level of theory in the aqueous phase.

(i) 3′-dCMPH

C	0.30330000	-0.24027300	0.16010600
O	0.08259600	-0.63237000	1.53706600
H	0.44067600	-0.28765500	-3.56411500
O	0.70736300	-0.21355000	-2.64158500
C	0.61745900	-1.49712600	-2.03402700
H	1.28081700	-2.21614600	-2.53345000
H	-0.41349200	-1.87846500	-2.06498300
C	1.03723500	-1.36607800	-0.58516400
H	0.86346500	-2.32200100	-0.07859400
O	2.43355600	-1.05164600	-0.50401000

C	2.64281900	0.16573300	0.19677600
H	2.97696900	-0.02933700	1.21818100
N	3.73238400	0.88520500	-0.45719400
C	3.69439400	1.04519700	-1.80962900
H	2.82775500	0.61344300	-2.31020000
C	4.68817900	1.69066800	-2.46425200
C	5.76810300	2.18080500	-1.65549100
N	6.79817200	2.81437100	-2.24441900
H	7.55718500	3.16084500	-1.67673600
H	6.82585700	2.95523300	-3.24190300
N	5.80521200	2.03996500	-0.33677000
C	4.79057100	1.40701900	0.31477400
O	4.76359300	1.27979200	1.54126900
H	-0.64939500	0.02326900	-0.30883000
C	1.30320000	0.90105000	0.15510500
H	1.20987300	1.45167200	-0.78623500
H	1.16675000	1.58087300	0.99938100
P	-1.34310400	-1.24476600	1.95761300
O	-1.38742700	-1.63832400	3.39404400
O	-1.52788600	-2.38575500	0.83152200
O	-2.46568400	-0.17688200	1.49151200
H	-2.69386000	0.44223200	2.20034400
H	-2.37013400	-2.85893500	0.90015500
H	4.67214000	1.81921000	-3.54147900

(ii) 5F-3′-dCMPH

C	0.30340900	-0.24006300	0.16498700
O	0.07429800	-0.63868100	1.53824000
H	0.48092700	-0.26471600	-3.56039300
O	0.74507900	-0.19943100	-2.63638000

C	0.63325500	-1.48461800	-2.03513200
H	1.29366100	-2.20897800	-2.53055600
H	-0.40158600	-1.85351700	-2.07898500
C	1.03888200	-1.36375400	-0.58146500
H	0.85800300	-2.32227100	-0.08267300
O	2.43610400	-1.05505700	-0.48506300
C	2.64434000	0.16213400	0.21370300
H	2.98367900	-0.02926300	1.23414000
N	3.73358000	0.88064800	-0.44451200
C	3.68873600	1.01918200	-1.80308900
H	2.83473900	0.58233300	-2.32141600
C	4.68956400	1.66570100	-2.42644100
C	5.77771700	2.18264100	-1.65076700
N	6.78247300	2.80644100	-2.28134800
H	7.55439700	3.17266300	-1.74390000
H	6.77857900	2.91345600	-3.28424400
N	5.80106600	2.05175800	-0.33596300
C	4.78410000	1.41919300	0.32163400
O	4.75748700	1.31057600	1.54890200
H	-0.64580300	0.02832900	-0.30830500
C	1.30562300	0.89942500	0.17175100
H	1.21709200	1.45721500	-0.76586300
H	1.16719900	1.57372100	1.02003100
P	-1.35525400	-1.25023100	1.94798800
O	-1.40778300	-1.65086800	3.38209200
O	-1.53584000	-2.38488400	0.81494000
O	-2.47256600	-0.17745800	1.48088900
H	-2.70300300	0.43925100	2.19110700
H	-2.37958500	-2.85648100	0.87590000
F	4.71637500	1.83286800	-3.76593400

(iii) 5Cl-3′-dCMPH

C	0.30606800	-0.24324500	0.16766900
O	0.08032100	-0.64589300	1.54005300
H	0.48130300	-0.25586200	-3.55942200
O	0.74412400	-0.19359500	-2.63480600
C	0.63133500	-1.48054500	-2.03766000
H	1.29008800	-2.20427800	-2.53615900
H	-0.40400700	-1.84806100	-2.08111800
C	1.03915800	-1.36469200	-0.58425400
H	0.85937200	-2.32481700	-0.08833100
O	2.43718700	-1.05702000	-0.48900600
C	2.64693000	0.15847400	0.20981800
H	2.99264500	-0.03337500	1.22811100
N	3.73364500	0.88048300	-0.45376700
C	3.69736400	1.00861500	-1.80613700
H	2.84312800	0.56001400	-2.31432600
C	4.69130400	1.65597200	-2.45657300
C	5.77371200	2.18546100	-1.66866000
N	6.79566100	2.81346200	-2.26583300
H	7.54553500	3.17653500	-1.69596000
H	6.83186400	2.92718200	-3.26721700
N	5.78742300	2.06775300	-0.34976500
C	4.77656300	1.43994200	0.31330100
O	4.73977100	1.34733800	1.54042900
H	-0.64408200	0.02720700	-0.30255200
C	1.30842200	0.89630000	0.17514600
H	1.21722000	1.45683600	-0.76057200
H	1.17280400	1.56793500	1.02596300

P	-1.34842800	-1.25889000	1.95112000
O	-1.39785700	-1.66312100	3.38427800
O	-1.53058200	-2.39055800	0.81538400
O	-2.46673700	-0.18519800	1.48873900
H	-2.69619500	0.42972600	2.20082800
H	-2.37445300	-2.86200500	0.87584300
Cl	4.67782100	1.82915800	-4.18635900

(iv) 5Br-3′-dCMPH

C	0.30561100	-0.24312300	0.16594200
O	0.07419800	-0.64048600	1.53883000
H	0.50251200	-0.26975300	-3.56088500
O	0.75962800	-0.20373600	-2.63490200
C	0.64387100	-1.48834500	-2.03323800
H	1.30571700	-2.21379100	-2.52510600
H	-0.39108100	-1.85637000	-2.08119900
C	1.04319100	-1.36687000	-0.57789200
H	0.86110200	-2.32536000	-0.07971800
O	2.44067800	-1.05851600	-0.47492700
C	2.64609700	0.16171600	0.21611800
H	2.99031200	-0.02258200	1.23636800
N	3.73291700	0.88208600	-0.45002200
C	3.70357700	0.99598700	-1.80309000
H	2.85362000	0.53516400	-2.30761400
C	4.69507700	1.64427000	-2.45643500
C	5.77193500	2.18795300	-1.67182700
N	6.79912600	2.81577100	-2.26011300
H	7.53925700	3.18423400	-1.68083600
H	6.85214800	2.92202300	-3.26149700
N	5.77696300	2.08435400	-0.35064500

C	4.76730800	1.45930000	0.31562300
O	4.72366400	1.38286600	1.54345800
H	-0.64261300	0.02450200	-0.30979400
C	1.30669800	0.89753700	0.17310400
H	1.21911500	1.45408100	-0.76532900
H	1.16673500	1.57260300	1.02047900
P	-1.35613500	-1.25252700	1.94600100
O	-1.41120400	-1.65259800	3.38010400
O	-1.53350900	-2.38745700	0.81277800
O	-2.47258000	-0.18025200	1.47599800
H	-2.70465700	0.43688800	2.18531700
H	-2.37725100	-2.85934900	0.87153000
Br	4.66815900	1.79701500	-4.36678300

(v) 5I-3′-dCMPH

C	0.31025200	-0.24384500	0.16796000
O	0.07697700	-0.64524100	1.53941400
H	0.50254100	-0.26136200	-3.55981400
O	0.75618000	-0.19704400	-2.63274600
C	0.64298900	-1.48375200	-2.03498500
H	1.30479900	-2.20686400	-2.53031700
H	-0.39169100	-1.85265900	-2.08256000
C	1.04445800	-1.36723000	-0.57970300
H	0.86008800	-2.32669800	-0.08420200
O	2.44277400	-1.06311700	-0.47675000
C	2.65263700	0.15523000	0.21693300
H	2.99850500	-0.03284100	1.23593900
N	3.73918000	0.87550100	-0.44964600
C	3.70280000	1.00045300	-1.80125900

H	2.84504400	0.54271300	-2.29516800
C	4.68804800	1.64984000	-2.46957700
C	5.76889600	2.18436300	-1.67819800
N	6.79929900	2.81899300	-2.25617800
H	7.53783300	3.17732300	-1.66847400
H	6.85962100	2.94057800	-3.25549100
N	5.78424000	2.07072400	-0.35679800
C	4.78019200	1.44275700	0.31315700
O	4.74661100	1.35568700	1.54095000
H	-0.63703200	0.02824900	-0.30708900
C	1.31452500	0.89397900	0.17884600
H	1.22678000	1.45504500	-0.75688300
H	1.17716700	1.56569400	1.02931500
P	-1.35603200	-1.25293600	1.94356200
O	-1.41375300	-1.65751200	3.37630800
O	-1.53711700	-2.38343100	0.80647400
O	-2.46810400	-0.17487100	1.47628900
H	-2.69850700	0.44081800	2.18741200
H	-2.38363000	-2.85074600	0.86184200
I	4.61117600	1.81942600	-4.55674700

10. Cartesian coordinates of anionic 5X-3′-dCMPH moieties optimized at the M06-2X/ aug-cc-pVDZ level of theory in the aqueous phase.

(i) 3′-dCMPH

C	0.29804200	-0.24393800	0.11267900
O	0.08681200	-0.55884400	1.51664200
H	0.32373300	-0.55330400	-3.59596400

O	0.59906400	-0.39949000	-2.68609400
C	0.58466700	-1.64154700	-1.99225400
H	1.26275400	-2.36426300	-2.46706800
H	-0.43040600	-2.06585200	-1.96727600
C	1.04164300	-1.40662400	-0.56632300
H	0.87754100	-2.32895700	0.00538800
O	2.42612700	-1.07244900	-0.53432200
C	2.63975000	0.19253100	0.13045200
H	2.92274000	0.01243600	1.16973800
N	3.73310200	0.87631800	-0.48678700
C	3.62768800	1.21052200	-1.85753500
H	2.77109900	0.81119700	-2.38881900
C	4.71161000	1.87202400	-2.44591800
C	5.81606400	2.15534600	-1.66581000
N	6.97496900	2.77174400	-2.18746700
H	7.44114300	3.32873000	-1.47761700
H	6.78369100	3.34023200	-3.00538100
N	5.92650600	1.79823300	-0.33907600
C	4.90768400	1.15391000	0.25246000
O	4.94582300	0.79482500	1.45282700
H	-0.66401200	-0.02538300	-0.36057700
C	1.28526400	0.90182500	0.03469700
H	1.18818300	1.39262900	-0.93796900
H	1.13857800	1.62943100	0.83739700
P	-1.33193200	-1.14488100	1.98174900
O	-1.36551100	-1.46835500	3.43691400
O	-1.53905700	-2.34205100	0.91849400

O	-2.46234800	-0.09918200	1.48067900
H	-2.68099500	0.54945900	2.16551500
H	-2.38329300	-2.80418400	1.02491400
H	4.68191800	2.14518400	-3.49950800

(ii) 5F-3′-dCMPH

C	0.28995000	-0.24484900	0.11863400
O	0.06675500	-0.56365600	1.51929500
H	0.39295200	-0.54665600	-3.59290600
O	0.64992500	-0.39121600	-2.67791100
C	0.63305000	-1.63363500	-1.98459600
H	1.32594900	-2.35036700	-2.44680200
H	-0.37852900	-2.06665200	-1.97806700
C	1.06207100	-1.39399300	-0.55089300
H	0.90506400	-2.31993100	0.01673200
O	2.44081400	-1.03674200	-0.49658900
C	2.62283100	0.23514200	0.16233000
H	2.90827200	0.06702900	1.20293300
N	3.70483500	0.93942900	-0.45424200
C	3.57817000	1.27225800	-1.82264300
H	2.78303600	0.80010300	-2.39027000
C	4.65827800	1.94423000	-2.37451400
C	5.77443900	2.25690300	-1.63540200
N	6.80883200	3.06718200	-2.13874500
H	7.69926700	2.81412200	-1.72129000
H	6.87285600	3.03656200	-3.15088800
N	5.90478700	1.85346600	-0.32562200
C	4.90267600	1.18493800	0.26616300
O	4.96839700	0.77797300	1.44908900

H	-0.66938800	-0.04257700	-0.36723200
C	1.25717500	0.91880200	0.05304200
H	1.16156200	1.40876200	-0.92032400
H	1.08820400	1.64309700	0.85417500
P	-1.34890600	-1.17172400	1.96639200
O	-1.39512500	-1.49703000	3.42069800
O	-1.52373100	-2.37039400	0.89915200
O	-2.48835000	-0.14277300	1.45186500
H	-2.72274700	0.50412100	2.13316600
H	-2.36141500	-2.84665400	0.99461300
F	4.60698900	2.31199500	-3.69546900

(iii) 5Cl-3′-dCMPH

C	0.29156600	-0.24741100	0.11783900
O	0.06678100	-0.55744000	1.52006600
H	0.39909900	-0.57370400	-3.59169900
O	0.65146600	-0.41137000	-2.67661500
C	0.63888900	-1.64961800	-1.97592800
H	1.33488300	-2.36651900	-2.43314700
H	-0.37101700	-2.08648300	-1.96747900
C	1.06579300	-1.39985800	-0.54334700
H	0.90989800	-2.32222200	0.03025300
O	2.44430500	-1.04030900	-0.48960000
C	2.62333400	0.23576300	0.15962800
H	2.90966800	0.07571300	1.20135800
N	3.70447900	0.93871900	-0.46322900
C	3.57877100	1.26112700	-1.83155400
H	2.78720800	0.77440100	-2.39153200

C	4.65579500	1.94426200	-2.40251700
C	5.77180100	2.25710600	-1.65582100
N	6.81428500	3.06506300	-2.12782800
H	7.68435600	2.85297400	-1.65177500
H	6.92868100	3.04415900	-3.13488700
N	5.90822000	1.84100000	-0.35260100
C	4.90664000	1.17433300	0.24721900
O	4.98441700	0.76587300	1.42627200
H	-0.66719600	-0.04923800	-0.37078100
C	1.25726000	0.91733000	0.04578400
H	1.16163400	1.40138700	-0.93050200
H	1.08691100	1.64601000	0.84259100
P	-1.34896600	-1.16464400	1.96854600
O	-1.39709700	-1.48100100	3.42472800
O	-1.52015800	-2.36990400	0.90820400
O	-2.48876600	-0.14036800	1.44571400
H	-2.72526600	0.51030800	2.12267600
H	-2.35813800	-2.84564200	1.00366800
Cl	4.54888700	2.41744000	-4.09550000

(iv) 5Br-3′-dCMPH

C	0.29295800	-0.24260300	0.10743600
O	0.05403600	-0.51794900	1.51443700
H	0.43557600	-0.65357700	-3.59231700
O	0.67889900	-0.47169000	-2.67846500
C	0.65354300	-1.69379000	-1.95023100
H	1.35047400	-2.42400400	-2.38431800

H	-0.35849500	-2.12572800	-1.94179000
C	1.06813500	-1.41334600	-0.51969200
H	0.90305200	-2.32161400	0.07347000
O	2.44756600	-1.05792600	-0.46188500
C	2.62537500	0.23281600	0.15914100
H	2.90229900	0.09272000	1.20650300
N	3.71195100	0.92190200	-0.46829400
C	3.60123000	1.21622500	-1.84318900
H	2.81778800	0.71853100	-2.40584100
C	4.64837800	1.95178900	-2.39377200
C	5.76853900	2.25709500	-1.65017900
N	6.77229500	3.13924900	-2.06599800
H	7.65281000	2.92961100	-1.60832900
H	6.88037900	3.20059500	-3.07213300
N	5.95223400	1.72800300	-0.39396100
C	4.95163400	1.06263700	0.20768500
O	5.05599500	0.58250200	1.35620600
H	-0.66031500	-0.05174100	-0.39460500
C	1.26411000	0.91651000	0.01707300
H	1.17915900	1.37783600	-0.97115300
H	1.08939000	1.66436100	0.79487700
P	-1.36772200	-1.10992600	1.96444000
O	-1.43227300	-1.38418400	3.42848900
O	-1.52929700	-2.34467000	0.93707500
O	-2.49992200	-0.09948000	1.39996500
H	-2.74436200	0.56908100	2.05633800
H	-2.37112600	-2.81334400	1.03356700

Br	4.46589400	2.58134400	-4.23075200

(v) 5I-3′-dCMPH

C	0.30070000	-0.23919500	0.10156300
O	0.05105500	-0.49207300	1.51075600
H	0.46105600	-0.70204000	-3.59074100
O	0.69755200	-0.50933200	-2.67731600
C	0.66123600	-1.72173800	-1.93345000
H	1.35632200	-2.46151400	-2.35400300
H	-0.35331700	-2.14772200	-1.92504200
C	1.06961000	-1.42504400	-0.50433800
H	0.89358500	-2.32358400	0.10028500
O	2.45179600	-1.08031500	-0.44272600
C	2.63676000	0.21851900	0.15809300
H	2.90967400	0.09154300	1.20839800
N	3.72804600	0.89355500	-0.47746900
C	3.63405300	1.15573000	-1.85742500
H	2.84813400	0.65255500	-2.41311900
C	4.64384100	1.93679800	-2.40693100
C	5.75543600	2.25587400	-1.64657000
N	6.71730400	3.20150500	-2.01185200
H	7.60969900	3.00936800	-1.57000900
H	6.81176200	3.34341300	-3.01140800
N	5.98206100	1.65075400	-0.43383100
C	4.98710500	0.98113000	0.17360500
O	5.11079100	0.45803200	1.30029200
H	-0.64775300	-0.04727200	-0.40907400

C	1.28209300	0.91060400	0.00033400
H	1.20614500	1.35840500	-0.99494200
H	1.10933300	1.67090600	0.76635300
P	-1.37757300	-1.06796800	1.96026200
O	-1.45348300	-1.31913700	3.42788800
O	-1.54019800	-2.31740600	0.95098600
O	-2.49932500	-0.05921400	1.37252400
H	-2.74531100	0.61980900	2.01746900
H	-2.38646800	-2.77800300	1.04759400
I	4.37602500	2.70028100	-4.39434100

11. Cartesian coordinates transition states for C_5-X bond cleavage calculated at the M06-2X/ aug-cc-pVDZ level of theory in the aqueous phase.

(i) 5F-3′-dCMPH

C	0.31721400	-0.21433300	-0.01547900
O	0.06883000	-0.47711800	1.39033100
H	0.44238200	-0.63434100	-3.71336600
O	0.68654000	-0.46242700	-2.79779000
C	0.61781300	-1.68331700	-2.07102300
H	1.28714000	-2.43841300	-2.50546500
H	-0.40897600	-2.07839500	-2.06004800
C	1.04380900	-1.41593400	-0.64202900
H	0.85027700	-2.31520000	-0.04466400
O	2.43899300	-1.11205400	-0.59010200
C	2.66211700	0.15934300	0.03177600
H	2.93870000	0.01526500	1.07891000
N	3.78343500	0.80726300	-0.60645500

C	3.71624700	1.06158800	-1.98708400
H	2.84676100	0.63364300	-2.48281100
C	4.73885800	1.71200300	-2.61642500
C	5.81115800	2.13154200	-1.75950000
N	6.74050900	2.97880500	-2.25786900
H	7.39726700	3.40466300	-1.62045300
H	6.50119300	3.45544400	-3.11582000
N	5.97935000	1.68924700	-0.51669000
C	4.95935900	1.01909600	0.10482200
O	5.06106700	0.64038400	1.28581000
H	-0.62605900	0.01633300	-0.51936400
C	1.33534000	0.90528000	-0.10855300
H	1.26600500	1.36836900	-1.09718100
H	1.19398900	1.66090600	0.66814900
P	-1.37803700	-1.00649000	1.84227200
O	-1.45210700	-1.27673700	3.30630500
O	-1.59220600	-2.23305700	0.81521400
O	-2.46301500	0.05316400	1.27650300
H	-2.67329600	0.73700100	1.92907700
H	-2.44895100	-2.67253300	0.91828700
F	4.38657000	3.06867500	-3.61603100

(ii) 5Cl-3′-dCMPH

C	0.32285900	-0.21432400	-0.01628500
O	0.07151200	-0.45746400	1.39330600
H	0.44036800	-0.68801000	-3.70842400
O	0.69042200	-0.50452800	-2.79669800

C	0.61132900	-1.71354700	-2.05128700
H	1.27355200	-2.48103300	-2.47498700
H	-0.41898100	-2.09933000	-2.03412700
C	1.04115400	-1.42928900	-0.62640300
H	0.83964100	-2.31899600	-0.01693100
O	2.43718600	-1.13495600	-0.57932800
C	2.67255900	0.14856200	0.02391300
H	2.95106400	0.01217600	1.07169800
N	3.78777100	0.78280600	-0.62549200
C	3.70354900	1.05623600	-2.00152600
H	2.89995900	0.56020000	-2.54218900
C	4.70794700	1.80851300	-2.56331600
C	5.79529000	2.17332400	-1.75467200
N	6.71576500	3.10517000	-2.14304900
H	7.32360400	3.46471700	-1.42152300
H	6.46742700	3.72855800	-2.89774700
N	6.03925400	1.54831000	-0.58274600
C	5.02236500	0.88712300	0.03552700
O	5.14985500	0.40858400	1.17716900
H	-0.61914100	0.01557500	-0.52297100
C	1.34804800	0.89666900	-0.12372100
H	1.28335700	1.34633300	-1.11908100
H	1.21083300	1.66375300	0.64254300
P	-1.38191900	-0.96122400	1.85170600
O	-1.46037000	-1.21084100	3.31931400
O	-1.61353200	-2.19892900	0.84176700
O	-2.45328300	0.10484400	1.27156300

H	-2.65204200	0.80200300	1.91355200
H	-2.47621100	-2.62491200	0.95184200
Cl	4.28104100	3.08337800	-4.03367000

(iii) 5Br-3′-dCMPH

C	0.31675800	-0.20754800	-0.01457500
O	0.07122300	-0.45472200	1.39560200
H	0.44026600	-0.67089100	-3.70917600
O	0.69015000	-0.48827300	-2.79722100
C	0.61479400	-1.69906600	-2.05410600
H	1.28061000	-2.46301000	-2.47865700
H	-0.41404300	-2.08893300	-2.03930600
C	1.04201300	-1.41667900	-0.62793700
H	0.84404100	-2.30951400	-0.02176200
O	2.43585400	-1.11498700	-0.57826300
C	2.66429300	0.17203400	0.02501800
H	2.94340300	0.03494800	1.07255300
N	3.77280100	0.81462400	-0.62220300
C	3.68181400	1.09056700	-1.99650500
H	2.89723900	0.58325200	-2.55437300
C	4.68761300	1.85797400	-2.53136700
C	5.79165700	2.19031500	-1.75792800
N	6.74269200	3.11623700	-2.13721000
H	7.29341800	3.47947300	-1.37051400
H	6.44850400	3.80830800	-2.81344900
N	6.04628600	1.52314700	-0.59753600
C	5.03351700	0.86876600	0.01757500

O	5.16231100	0.34233100	1.13890100
H	-0.62840900	0.01650000	-0.51806000
C	1.33425100	0.91020900	-0.12233900
H	1.26649400	1.35927600	-1.11780400
H	1.19192100	1.67639900	0.64394000
P	-1.37671500	-0.96974900	1.85822300
O	-1.44808700	-1.22290900	3.32562400
O	-1.60363100	-2.20708700	0.84673500
O	-2.45793200	0.08992800	1.28453400
H	-2.65998400	0.78338400	1.92948300
H	-2.46313700	-2.63885000	0.95899300
Br	4.32932200	2.95160900	-4.29528800

(iv) 5I-3′-dCMPH

C	0.30837600	-0.23938800	0.10399400
O	0.04799000	-0.48195900	1.51255800
H	0.48727600	-0.72108600	-3.58465200
O	0.72029900	-0.52742900	-2.67051600
C	0.66524200	-1.73595400	-1.92163600
H	1.35466200	-2.48552200	-2.33398600
H	-0.35404400	-2.15042900	-1.91783300
C	1.06728700	-1.43678100	-0.49134800
H	0.87852500	-2.33024500	0.11671700
O	2.45350800	-1.10680400	-0.42252300
C	2.64852000	0.19231000	0.16950500
H	2.91984800	0.07098900	1.22101400
N	3.74777200	0.85332700	-0.47224300
C	3.66820300	1.09548100	-1.85249400

H	2.89298700	0.57260200	-2.40824400
C	4.65753000	1.88459500	-2.39805300
C	5.75275400	2.23743600	-1.62139100
N	6.65823600	3.23688800	-1.95796100
H	7.56135400	3.10149500	-1.51830400
H	6.72463200	3.44155400	-2.94840400
N	6.00715900	1.59509700	-0.43985500
C	5.00963500	0.92735500	0.17386900
O	5.13826600	0.39877700	1.29545800
H	-0.63446900	-0.03896000	-0.41365600
C	1.30329700	0.89898700	0.00201000
H	1.23784900	1.34129500	-0.99666600
H	1.13507700	1.66608300	0.76213600
P	-1.39029100	-1.03878500	1.95636100
O	-1.47692100	-1.28425000	3.42428400
O	-1.56246000	-2.28919200	0.94998200
O	-2.49561500	-0.01773200	1.35911900
H	-2.73573100	0.66723000	2.00001200
H	-2.41349500	-2.74126300	1.04515200
I	4.34140800	2.75625600	-4.40662900

12. Cartesian coordinates transition states for $C_{3'}$−$O_{3'}$ bond cleavage calculated at the M06-2X/ aug-cc-pVDZ level of theory in the aqueous phase.

(i) 3′-dCMPH

C	0.24566500	-0.14265100	0.13254800
O	0.02012400	-0.60178300	1.81442800
H	0.69970900	-0.41442100	-3.61644900
O	0.85167300	-0.26645600	-2.67702700

C	0.65566400	-1.49830000	-1.98878800
H	1.31695200	-2.27807300	-2.39391000
H	-0.38774700	-1.83605000	-2.07709100
C	0.96908600	-1.29870900	-0.51677200
H	0.74492200	-2.23800000	0.00546800
O	2.37248600	-1.01288900	-0.36099000
C	2.55687200	0.22069500	0.31531300
H	2.82520800	0.05135300	1.35979300
N	3.70151000	0.90296900	-0.29411400
C	3.74679600	1.01475100	-1.64928800
H	2.90931000	0.56529400	-2.18311700
C	4.78147900	1.63564600	-2.26648400
C	5.80983400	2.15443000	-1.41214200
N	6.87783200	2.76601600	-1.95842100
H	7.59911200	3.13510500	-1.35703000
H	6.96688400	2.87226600	-2.95644100
N	5.76449000	2.06286800	-0.08931100
C	4.70759600	1.45554700	0.52056600
O	4.60498200	1.37978200	1.74833300
H	-0.76322700	0.06729900	-0.21796600
C	1.23740800	0.98253600	0.17881000
H	1.24089700	1.55576500	-0.76138300
H	1.07912900	1.67111900	1.01493500
P	-1.33879300	-1.26039100	2.40259700
O	-2.00557500	-1.92391100	3.63576500
O	-1.54966300	-2.38777300	1.17704900
O	-2.40266000	-0.05154400	1.93668800

H	-3.24179200	-0.20658900	2.38900200
H	-2.22528900	-3.01360000	1.46682700
H	4.83172900	1.72477400	-3.34671400

(ii) 5F-3′-dCMPH

C	0.24463700	-0.14123700	0.14016600
O	0.01015300	-0.60670900	1.81777200
H	0.74277500	-0.39258200	-3.60598500
O	0.89063100	-0.25242000	-2.66462100
C	0.67613100	-1.48622000	-1.98457600
H	1.33665700	-2.26884700	-2.38516300
H	-0.36858400	-1.81501000	-2.08777500
C	0.97268500	-1.29463800	-0.50807000
H	0.74281000	-2.23639800	0.00684200
O	2.37503800	-1.01116600	-0.33520000
C	2.55516500	0.22506300	0.33534200
H	2.82920600	0.06291500	1.37950700
N	3.69818400	0.90686500	-0.27991900
C	3.72629500	1.00950600	-1.64049300
H	2.89440700	0.56575300	-2.18927500
C	4.76648100	1.62861800	-2.22860400
C	5.81743900	2.15521800	-1.41236800
N	6.86262800	2.75211600	-2.00502000
H	7.60840900	3.12533100	-1.43665800
H	6.91317000	2.83214800	-3.00901500
N	5.76992700	2.06040600	-0.09499600
C	4.71105600	1.45611300	0.52437600
O	4.62147700	1.38454500	1.75242800

H	-0.76209100	0.06942300	-0.21606200
C	1.23469100	0.98504400	0.19626800
H	1.24102000	1.56407300	-0.74036700
H	1.07186800	1.66904900	1.03518900
P	-1.35224800	-1.26961300	2.39420300
O	-2.02638700	-1.94020000	3.61932300
O	-1.55349000	-2.39078500	1.16143600
O	-2.41349400	-0.05911300	1.92715400
H	-3.25602000	-0.21739000	2.37200000
H	-2.23014600	-3.01906500	1.44340000
F	4.86439400	1.75804500	-3.57030700

(iii) 5Cl-3′-dCMPH

C	0.24438800	-0.14178100	0.14024900
O	0.01306300	-0.60719400	1.81751200
H	0.74488300	-0.39198000	-3.60757200
O	0.88870600	-0.25160200	-2.66560400
C	0.67366700	-1.48565400	-1.98623000
H	1.33352200	-2.26853900	-2.38734600
H	-0.37128200	-1.81378400	-2.08907600
C	0.97097200	-1.29502300	-0.50978500
H	0.74163900	-2.23697500	0.00490800
O	2.37397800	-1.01215000	-0.33773200
C	2.55471700	0.22341400	0.33188600
H	2.83232300	0.06227700	1.37532600
N	3.69730000	0.90664400	-0.28715500
C	3.72838500	1.00813900	-1.64028700

H	2.89179000	0.55992800	-2.17845200
C	4.76354200	1.62677000	-2.25592800
C	5.81466600	2.15500000	-1.42890800
N	6.87494400	2.75674900	-1.98788300
H	7.60215900	3.11901100	-1.38909300
H	6.96101300	2.85007500	-2.98816800
N	5.76375900	2.06272500	-0.10882000
C	4.71107600	1.46303700	0.51672000
O	4.61888600	1.39608100	1.74348200
H	-0.76277500	0.06957900	-0.21425600
C	1.23465300	0.98440200	0.19506800
H	1.23998500	1.56330300	-0.74168500
H	1.07307900	1.66847100	1.03413200
P	-1.34893700	-1.26938500	2.39629400
O	-2.02180900	-1.93813400	3.62301900
O	-1.55163300	-2.39166500	1.16489300
O	-2.41002800	-0.05893000	1.92904500
H	-3.25223400	-0.21623200	2.37484100
H	-2.22813700	-3.01960500	1.44798600
Cl	4.83359900	1.76554200	-3.98862400

(iv) 5Br-3′-dCMPH

C	0.24531500	-0.13985600	0.14337000
O	0.01305000	-0.61033600	1.81889400
H	0.75127300	-0.37870100	-3.60580500
O	0.89346300	-0.24176500	-2.66305200
C	0.67316700	-1.47726200	-1.98789500

H	1.33082300	-2.26112400	-2.39069700
H	-0.37277700	-1.80137100	-2.09327700
C	0.96898900	-1.29275100	-0.51032000
H	0.73644500	-2.23596100	0.00050000
O	2.37275900	-1.01493800	-0.33475800
C	2.55686600	0.21923000	0.33550600
H	2.83713100	0.05680700	1.37811800
N	3.69914600	0.90181800	-0.28605800
C	3.73344500	0.99439600	-1.63891800
H	2.89944300	0.53599800	-2.17253900
C	4.76469700	1.61657300	-2.25767900
C	5.81211900	2.15706400	-1.43514000
N	6.87499200	2.76257400	-1.98511800
H	7.59257900	3.12984500	-1.37763500
H	6.97426100	2.85482000	-2.98424000
N	5.75614200	2.07340700	-0.11360200
C	4.70665300	1.47303800	0.51539500
O	4.61114200	1.41687300	1.74226600
H	-0.76123300	0.07536500	-0.21058800
C	1.23842100	0.98366000	0.20177800
H	1.24561800	1.56536100	-0.73324400
H	1.07871900	1.66563100	1.04290200
P	-1.34958500	-1.27344900	2.39539500
O	-2.02308000	-1.94581200	3.61977800
O	-1.55289700	-2.39155200	1.16029100
O	-2.40972300	-0.06072000	1.93193700
H	-3.25200600	-0.21870900	2.37735000

H	-2.22997000	-3.01985300	1.44121300
Br	4.82542100	1.73653500	-4.17070300

(v) 5I-3′-dCMPH

C	0.24663200	-0.14024300	0.14169700
O	0.01360600	-0.60915700	1.81769100
H	0.75696000	-0.38483400	-3.60821700
O	0.89182800	-0.24468100	-2.66485300
C	0.67559000	-1.48001600	-1.98804500
H	1.33559700	-2.26234100	-2.38996400
H	-0.36938400	-1.80748900	-2.09299300
C	0.97100400	-1.29353300	-0.51052600
H	0.73823200	-2.23630100	0.00109400
O	2.37451000	-1.01537000	-0.33429700
C	2.55821800	0.21983500	0.33482000
H	2.83742700	0.05810300	1.37783300
N	3.70062100	0.90233400	-0.28626200
C	3.73319500	1.00039800	-1.63849500
H	2.89359900	0.54245000	-2.16354600
C	4.76111200	1.62192600	-2.27070300
C	5.80899300	2.15616500	-1.43895800
N	6.87727800	2.76493400	-1.97745400
H	7.59230300	3.12228700	-1.36103700
H	6.99006200	2.86142900	-2.97479200
N	5.75732600	2.06904500	-0.11642800
C	4.71013100	1.46919400	0.51463900
O	4.61806000	1.40957200	1.74193300
H	-0.75982300	0.07437100	-0.21290600

C	1.23940400	0.98357300	0.19977100
H	1.24663200	1.56479800	-0.73553500
H	1.07892500	1.66596800	1.04041100
P	-1.34951700	-1.27076100	2.39461500
O	-2.02383200	-1.94102900	3.61972900
O	-1.55315200	-2.39041900	1.16097000
O	-2.40889300	-0.05806400	1.92925500
H	-3.25133400	-0.21496200	2.37474900
H	-2.23061500	-3.01797400	1.44262100
I	4.78891300	1.75123700	-4.36254600

13. Cartesian coordinates of transition states for C-N bond cleavage calculated at the M06-2X/ aug-cc-pVDZ level of theory in the aqueous phase.

(i) 3′-dCMPH

C	0.77961400	-0.15652200	0.11398200
O	0.24412000	-0.46018600	1.43113800
H	0.97606000	-0.24953200	-3.60229200
O	1.14186600	-0.21474300	-2.65455400
C	0.76347300	-1.45926800	-2.08301900
H	1.27821100	-2.29554800	-2.57650300
H	-0.32326000	-1.61243800	-2.16369700
C	1.13277900	-1.46350800	-0.61464200
H	0.61950500	-2.30398400	-0.13082000
O	2.54869000	-1.64586100	-0.43621900
C	3.08114600	-0.63893100	0.35579200
H	3.52260800	-0.97040800	1.29415200
N	4.73818000	-0.14041500	-0.63927600

C	4.45350700	0.15702700	-1.92469100
H	4.10801900	-0.67436100	-2.53999900
C	4.54786500	1.44801700	-2.45696700
C	5.04193000	2.42976900	-1.60073400
N	5.26710800	3.73826200	-2.03747600
H	5.26034600	4.41041800	-1.27922400
H	4.68197900	4.02877100	-2.81107600
N	5.39827000	2.16993400	-0.32909700
C	5.25026500	0.90857100	0.15452400
O	5.54744700	0.64040000	1.34545700
H	0.05812100	0.45200700	-0.43881000
C	2.13430800	0.51989900	0.30057700
H	2.34690200	1.10965500	-0.60663400
H	2.15728900	1.16786500	1.18020300
P	-1.34544900	-0.50841700	1.63553100
O	-1.72976200	-0.87354900	3.02956600
O	-1.78857100	-1.48971900	0.43197600
O	-1.93648100	0.90321100	1.10493100
H	-2.00196800	1.55561900	1.81744100
H	-2.74624600	-1.62499200	0.38461500
H	4.29021000	1.66123900	-3.49190500

(i) 5F-3′-dCMPH

C	0.79013400	-0.12700200	0.36148800
O	0.17618300	-0.84205300	1.46644200
H	2.51374700	0.73581300	-2.18238200
O	1.54820100	0.80994800	-2.22076900

C	0.99890700	-0.49506000	-2.14517600
H	1.46550100	-1.16793600	-2.87901500
H	-0.06770800	-0.40473100	-2.38487100
C	1.12628800	-1.11115400	-0.76232900
H	0.48607000	-1.99901000	-0.70578500
O	2.47677400	-1.54164400	-0.49866200
C	3.06862500	-0.77113200	0.47992700
H	3.56214900	-1.34885800	1.25756500
N	4.76325200	-0.12153700	-0.44854000
C	4.68959800	-0.24981600	-1.79206500
H	4.68409800	-1.25425200	-2.21563800
C	4.62737100	0.86356500	-2.61898600
C	4.71272500	2.13395800	-2.05971000
N	4.72517000	3.27356300	-2.85334400
H	4.42813900	4.10500800	-2.35664700
H	4.27616800	3.17011500	-3.75510000
N	4.84998900	2.28337700	-0.73209700
C	4.90307400	1.18064600	0.06751600
O	5.04095000	1.29598900	1.30851600
H	0.12645900	0.67724200	0.02995800
C	2.15648600	0.37111700	0.82613700
H	2.41817100	1.27709300	0.25683900
H	2.16111000	0.62077700	1.88976600
P	-1.42235200	-0.84635100	1.60330500
O	-1.89017500	-1.64699300	2.77103900
O	-1.86366700	-1.31204900	0.12172500
O	-1.90328600	0.69965800	1.58737800

H	-1.97094000	1.06515200	2.48144600
H	-2.82436200	-1.34527000	0.00415000
F	4.53788200	0.72649300	-3.97860000

(ii) 5Cl-3′-dCMPH

C	0.79139900	-0.12449800	0.36939900
O	0.17436900	-0.85408800	1.46283200
H	2.51655100	0.81309600	-2.19718100
O	1.54888100	0.86268900	-2.18025500
C	1.03416000	-0.45774600	-2.13833600
H	1.53718200	-1.10587000	-2.87044900
H	-0.02848900	-0.39257900	-2.40358900
C	1.13797200	-1.09543600	-0.76196200
H	0.49076000	-1.97921400	-0.72939200
O	2.47784200	-1.54347600	-0.47518200
C	3.06976500	-0.76800700	0.49738800
H	3.56929500	-1.34245800	1.27359600
N	4.75402100	-0.12315100	-0.44361100
C	4.67848800	-0.27045100	-1.77959800
H	4.67067200	-1.28415900	-2.18000900
C	4.60358400	0.82918100	-2.64239400
C	4.69761600	2.10921200	-2.09053000
N	4.69933200	3.25273600	-2.87038700
H	4.44756400	4.08840200	-2.35760000
H	4.24886500	3.17445600	-3.77320900
N	4.84835600	2.27537400	-0.76543200
C	4.89997000	1.18726700	0.05274500

O	5.04498400	1.32187800	1.28788000
H	0.12783000	0.68177900	0.04301300
C	2.15435200	0.37189200	0.84650600
H	2.41720700	1.28248500	0.28622800
H	2.15144700	0.61188400	1.91251100
P	-1.42472300	-0.86212200	1.59361600
O	-1.89592000	-1.68256400	2.74612400
O	-1.85960200	-1.30339600	0.10272200
O	-1.90681300	0.68355900	1.60219800
H	-1.98386600	1.03155200	2.50248900
H	-2.81972000	-1.33127400	-0.02072900
Cl	4.46547100	0.59314100	-4.37694100

(iii) 5Br-3′-dCMPH

C	0.79715500	-0.12275600	0.36614600
O	0.17678100	-0.84932900	1.45961000
H	2.50924700	0.83331300	-2.22187300
O	1.54158000	0.86862400	-2.17721600
C	1.04724400	-0.45953500	-2.14004500
H	1.56745800	-1.09927900	-2.86773600
H	-0.01393200	-0.41164300	-2.41513400
C	1.14631700	-1.09624100	-0.76219800
H	0.49765200	-1.97895100	-0.73070800
O	2.48359800	-1.54747800	-0.46737300
C	3.07327500	-0.77033700	0.50433700
H	3.57145100	-1.34231700	1.28321000
N	4.76076900	-0.13046800	-0.43998600

C	4.67513200	-0.27772700	-1.77434000
H	4.66715300	-1.29148200	-2.17382500
C	4.58113400	0.82418900	-2.63291700
C	4.68664800	2.10543600	-2.08667100
N	4.67477100	3.25468100	-2.85615800
H	4.43814400	4.08648500	-2.33010000
H	4.20972500	3.18835700	-3.75240100
N	4.85868700	2.26813900	-0.76303000
C	4.91205500	1.18000300	0.05516500
O	5.06508300	1.31497000	1.28869700
H	0.13552500	0.68357000	0.03627700
C	2.15958100	0.37324500	0.84559400
H	2.42593400	1.28006200	0.28105400
H	2.15353800	0.61819600	1.91048300
P	-1.42267300	-0.85464100	1.58643200
O	-1.89805700	-1.67092800	2.74016300
O	-1.85430400	-1.29968900	0.09572900
O	-1.90240300	0.69179700	1.58915100
H	-1.98082400	1.04278300	2.48815700
H	-2.81413200	-1.32744800	-0.02993000
Br	4.39738100	0.54578600	-4.53825100

(iv) 5I-3′-dCMPH

C	0.79322000	-0.12160500	0.37101300
O	0.17462800	-0.85848300	1.45872200
H	2.51665100	0.85547200	-2.21968700
O	1.54979900	0.89191900	-2.15774800

C	1.05381600	-0.43591500	-2.13632400
H	1.57749800	-1.06886400	-2.86769500
H	-0.00600400	-0.38500200	-2.41642700
C	1.14518300	-1.08596500	-0.76405500
H	0.49430800	-1.96734900	-0.74394300
O	2.47926300	-1.54317700	-0.46556600
C	3.07015100	-0.76685400	0.50653000
H	3.56934700	-1.34114300	1.28313700
N	4.75323400	-0.12400200	-0.43896700
C	4.67691900	-0.28122400	-1.77207300
H	4.66998800	-1.30154300	-2.15524500
C	4.59129600	0.80996400	-2.65224400
C	4.68950900	2.09493600	-2.10432500
N	4.67808500	3.24705100	-2.87163300
H	4.44938100	4.07755700	-2.33993600
H	4.20457500	3.18954500	-3.76414100
N	4.85614300	2.26911400	-0.78112300
C	4.90482800	1.18884200	0.04693200
O	5.05414700	1.33434700	1.27956300
H	0.12957300	0.68557800	0.04729000
C	2.15456000	0.37357700	0.85435900
H	2.41962500	1.28427100	0.29585900
H	2.14739700	0.61126600	1.92093600
P	-1.42463400	-0.86845500	1.58640900
O	-1.89764800	-1.69885600	2.73103700
O	-1.85654600	-1.29731900	0.09103200
O	-1.90754000	0.67689400	1.60736300

H	-1.98794900	1.01650400	2.51056400
H	-2.81640800	-1.32455900	-0.03444500
I	4.40535400	0.46732800	-4.72253900

14. Cartesian coordinates of products for the C_5-X bond cleavage calculated at the M06-2X/ aug-cc-pVDZ level of theory in the aqueous phase.

(i) 5F-3′-dCMPH

C	-1.73207900	-0.50238400	0.43295900
O	-1.92804200	-0.88891900	1.81622200
H	-1.63731700	-0.57113300	-3.29390700
O	-1.37035600	-0.48466100	-2.37255400
C	-1.42686600	-1.76647700	-1.75700500
H	-0.75673200	-2.47511900	-2.26222000
H	-2.45090900	-2.16729700	-1.77251300
C	-0.98954200	-1.62139200	-0.31418500
H	-1.14543300	-2.57714500	0.19905300
O	0.40117300	-1.28652800	-0.25188200
C	0.60290300	-0.05735400	0.43993600
H	0.94596600	-0.24329100	1.46042800
N	1.67414500	0.66789300	-0.22074500
C	1.59438300	0.87322500	-1.58128500
H	0.71319200	0.46239000	-2.07631900
C	2.58434700	1.52884100	-2.19298100
C	3.73245800	2.00733300	-1.47323600
N	4.70486400	2.64044800	-2.10350800
H	5.46993000	2.93371900	-1.50732100
H	4.67021100	2.83105600	-3.24899500

N	3.77928200	1.78714700	-0.14564800
C	2.78597700	1.13726800	0.51280700
O	2.81501100	0.94460300	1.73658400
H	-2.69589400	-0.25874300	-0.02390600
C	-0.75060600	0.65391300	0.40733600
H	-0.86575300	1.19729800	-0.53568700
H	-0.88818000	1.33720600	1.24873900
P	-3.33740700	-1.52018200	2.26076600
O	-3.35661700	-1.90311500	3.70082200
O	-3.52060400	-2.67349500	1.14685600
O	-4.48400200	-0.47432700	1.80250200
H	-4.71119600	0.14683200	2.50981100
H	-4.35449100	-3.15862800	1.23161700
F	4.60007700	3.02078300	-4.49654900

(ii) 5Cl-3′-dCMPH

C	-1.80537400	-0.61431400	0.65388300
O	-2.01312300	-1.04027200	2.02302500
H	-1.70256000	-0.56543100	-3.07563900
O	-1.43493600	-0.51808800	-2.15158400
C	-1.53845700	-1.81602100	-1.57741600
H	-0.89236700	-2.53152600	-2.10367700
H	-2.57576500	-2.17990500	-1.60692800
C	-1.10016700	-1.73167300	-0.13042400
H	-1.28586900	-2.69805100	0.35161400
O	0.30195400	-1.44443300	-0.05628700
C	0.54172500	-0.24526600	0.66808200

H	0.88929700	-0.46837200	1.67954400
N	1.63161400	0.46910500	0.01462700
C	1.56498800	0.67713500	-1.34195300
H	0.67991100	0.28356800	-1.84435700
C	2.57113000	1.32061200	-1.94659700
C	3.70253800	1.76931600	-1.20007100
N	4.71419000	2.39138900	-1.81013100
H	5.50555800	2.69353800	-1.26109400
H	4.67891500	2.53696300	-2.82184500
N	3.74661500	1.56532800	0.11494500
C	2.72941700	0.93208200	0.76759000
O	2.73898900	0.75632800	1.98962900
H	-2.76021900	-0.32366000	0.20581200
C	-0.78729600	0.51061400	0.66451600
H	-0.88579000	1.08828100	-0.25991100
H	-0.90094300	1.16953100	1.52851400
P	-3.44543700	-1.63331200	2.44838100
O	-3.47457900	-2.07534400	3.87109600
O	-3.67719800	-2.72999400	1.28760600
O	-4.54982600	-0.52338700	2.04003700
H	-4.74509000	0.08040600	2.77173700
H	-4.52771200	-3.18797100	1.35685000
Cl	4.11159000	2.57136400	-4.97277300

(iii) 5Br-3′-dCMPH

C	-2.05350300	-0.87803300	1.08457500
O	-2.28446900	-1.27732600	2.45817400

H	-1.90330900	-0.89508800	-2.64058900
O	-1.64881400	-0.83208200	-1.71380500
C	-1.75851000	-2.12040400	-1.11962800
H	-1.10497100	-2.84388300	-1.62541800
H	-2.79507800	-2.48584400	-1.15650600
C	-1.33907800	-2.01112200	0.33134100
H	-1.53337800	-2.96811000	0.82854400
O	0.06208800	-1.72451000	0.41820400
C	0.29387600	-0.51531200	1.12974300
H	0.62076000	-0.72535500	2.15079900
N	1.39743500	0.18559300	0.48739000
C	1.34192000	0.39917500	-0.87027100
H	0.45535000	0.01405000	-1.37654700
C	2.35605200	1.03235800	-1.47367700
C	3.48350600	1.46378100	-0.71004600
N	4.50686900	2.08273500	-1.30786700
H	5.29638100	2.38284800	-0.75550200
H	4.46176600	2.24654000	-2.31130400
N	3.52505700	1.25135500	0.60351700
C	2.49892200	0.62377800	1.24736900
O	2.50532200	0.43471200	2.46816200
H	-3.00041400	-0.59325800	0.61635300
C	-1.03250800	0.24423600	1.09102500
H	-1.11535700	0.80592200	0.15537600
H	-1.15794000	0.91849300	1.94147300
P	-3.72258100	-1.86463700	2.87104500
O	-3.77893900	-2.26582600	4.30502900

O	-3.92626000	-2.99548900	1.73798600
O	-4.82374200	-0.77304200	2.40821100
H	-5.04183800	-0.15312900	3.11951500
H	-4.77834500	-3.45154400	1.80058900
Br	3.32655900	2.10688200	-4.48443500

(iv) 5I-3′-dCMPH

C	-2.25521900	-1.09809100	1.51289900
O	-2.51042400	-1.49793600	2.88282500
H	-2.04886900	-1.12621700	-2.20788500
O	-1.82063100	-1.05436200	-1.27498400
C	-1.91075000	-2.34390900	-0.68090600
H	-1.23471800	-3.05387500	-1.17637100
H	-2.93879300	-2.73156400	-0.73230700
C	-1.51526500	-2.22601500	0.77638300
H	-1.71022100	-3.18344600	1.27303000
O	-0.11967500	-1.92534900	0.88681000
C	0.08714800	-0.71573000	1.60972500
H	0.38217300	-0.93108500	2.63939300
N	1.20271100	-0.00560900	1.00494600
C	1.17948200	0.23282900	-0.35587000
H	0.29955500	-0.15188400	-0.87435700
C	2.19469800	0.87607800	-0.95764200
C	3.28808000	1.28496800	-0.12701700
N	4.33186900	1.92397900	-0.68352100
H	5.11185000	2.21226200	-0.11228200
H	4.32709300	2.09602700	-1.67970000

N	3.31762300	1.05885900	1.18541000
C	2.28073900	0.41726900	1.79631600
O	2.26459700	0.20652800	3.01697400
H	-3.19545100	-0.82332600	1.02566500
C	-1.24428300	0.03263100	1.53805400
H	-1.31020700	0.58946200	0.59825700
H	-1.39476000	0.70875000	2.38307900
P	-3.95171200	-2.09472500	3.26791000
O	-4.03293800	-2.49774100	4.70034400
O	-4.12817400	-3.22629000	2.13081300
O	-5.05172600	-1.01011800	2.78580400
H	-5.28476000	-0.39105300	3.49305100
H	-4.97892700	-3.68665000	2.17804000
I	2.41683900	1.46343300	-3.77766200

15. Cartesian coordinates of products for the $C_{3'}$–$O_{3'}$ bond cleavage calculated at the M06-2X/ aug-cc-pVDZ level of theory in the aqueous phase.

(i) 3′-dCMPH

C	-1.53173100	0.16864700	-0.89298400
O	-1.21408200	-1.45580500	2.04079400
H	-0.42355600	-1.12115500	-4.31147400
O	-0.45086800	-0.74670100	-3.42460200
C	-1.03596800	-1.70377700	-2.54951000
H	-0.49866500	-2.66091400	-2.60575400
H	-2.09196400	-1.87754000	-2.80495300
C	-0.97742400	-1.19336100	-1.12234300
H	-1.48731800	-1.93319100	-0.48287300

O	0.39221000	-1.10690400	-0.69227700
C	0.62101400	0.04955100	0.07696000
H	0.91666800	-0.22623900	1.08918400
N	1.77384200	0.76850600	-0.51278600
C	2.01720600	0.71681300	-1.84580900
H	1.33669700	0.09730200	-2.42783900
C	3.05729400	1.40059700	-2.39131200
C	3.86652800	2.15819900	-1.48605800
N	4.94198500	2.82491100	-1.95125300
H	5.50674000	3.36266000	-1.31121500
H	5.18985600	2.80298600	-2.92753700
N	3.60765700	2.24399500	-0.18629500
C	2.53368600	1.58979600	0.33591600
O	2.20072700	1.68875300	1.52262500
H	-2.53534200	0.46286300	-1.18123800
C	-0.66323800	0.90187200	0.06599100
H	-0.44942600	1.93558100	-0.23576000
H	-1.10273700	0.92105500	1.07209300
P	-2.70161800	-1.41031300	2.32245800
O	-3.33827900	-1.98520700	3.58044300
O	-3.45156600	-2.09744800	1.00868600
O	-3.15600800	0.18217800	2.19756600
H	-3.98384600	0.31355000	2.67677400
H	-4.33124200	-2.39833400	1.26932500
H	3.26876000	1.35924600	-3.45475900

(ii) 5F-3′-dCMPH

C	-1.65031100	0.07629200	-0.63742300
O	-1.46735500	-1.67298500	2.23978000
H	-0.55200400	-1.19345500	-4.07389300
O	-0.58253800	-0.82487500	-3.18459200
C	-1.17736600	-1.78406800	-2.31797500
H	-0.65030900	-2.74609400	-2.38376600
H	-2.23507300	-1.94383600	-2.57486600
C	-1.11411600	-1.28920200	-0.88638600
H	-1.63201400	-2.02954400	-0.25503200
O	0.25773600	-1.22468700	-0.45013900
C	0.49851900	-0.07806400	0.32698900
H	0.83368300	-0.36193200	1.32506200
N	1.62776600	0.66225800	-0.28690500
C	1.82811100	0.61682300	-1.63115000
H	1.15509700	-0.00519700	-2.22099300
C	2.84170200	1.33117200	-2.16253600
C	3.67973700	2.10511400	-1.30410100
N	4.71277100	2.78110800	-1.83339300
H	5.30809200	3.32858600	-1.23012900
H	4.90223000	2.74675800	-2.82310300
N	3.45010500	2.16467000	-0.00234200
C	2.39936000	1.48532400	0.54516600
O	2.10442700	1.56796800	1.74235100
H	-2.64316400	0.39457900	-0.93641500
C	-0.79098400	0.76389800	0.36300800
H	-0.58572100	1.81489600	0.12376500

H	-1.23207700	0.71801000	1.36783900
P	-2.95800600	-1.54926800	2.47931500
O	-3.67843500	-2.19495000	3.65474700
O	-3.70511300	-2.05126300	1.08262600
O	-3.29472100	0.07695900	2.49664800
H	-4.13446800	0.22298800	2.95029800
H	-4.60846000	-2.32263100	1.28894800
F	3.10755100	1.32168100	-3.48946200

(iii) 5Cl-3′-dCMPH

C	-1.71725300	0.02275100	-0.34709600
O	-1.69232200	-1.80394900	2.49976800
H	-0.71409400	-1.22998600	-3.82385600
O	-0.72421500	-0.86892600	-2.93093800
C	-1.31984600	-1.82629500	-2.06296400
H	-0.81340300	-2.79758300	-2.14992200
H	-2.38534700	-1.96274300	-2.30052200
C	-1.22202600	-1.35177100	-0.62692300
H	-1.74972000	-2.08741400	0.00145200
O	0.15802100	-1.33088300	-0.20163900
C	0.43956000	-0.19436100	0.57300900
H	0.83150800	-0.49100100	1.54722300
N	1.53387200	0.56529100	-0.08720800
C	1.72415400	0.49032200	-1.42303900
H	1.06041800	-0.17036600	-1.97890300
C	2.70565200	1.22101800	-2.01182200
C	3.52100000	2.05209900	-1.17499400

N	4.52878000	2.76681600	-1.70092700
H	5.08458200	3.34785700	-1.09128600
H	4.73233300	2.74287200	-2.68805600
N	3.30228000	2.13712900	0.13033300
C	2.29126100	1.43691200	0.71414500
O	2.00999300	1.53268700	1.91220900
H	-2.70263900	0.37489200	-0.63229000
C	-0.84436300	0.64712800	0.68302600
H	-0.64036100	1.71081100	0.51279100
H	-1.27227700	0.53023700	1.68811500
P	-3.18952200	-1.64104400	2.66408200
O	-3.98287400	-2.25156700	3.81085800
O	-3.87630200	-2.14677900	1.23819700
O	-3.48773400	-0.00752300	2.64341200
H	-4.34078700	0.16437600	3.06178800
H	-4.79749800	-2.38697300	1.39923500
Cl	2.98109200	1.13433700	-3.72885700

(iv) 5Br-3′-dCMPH

C	-2.03679300	-0.13753900	0.11374000
O	-2.01033400	-1.98347200	2.94740200
H	-1.01415000	-1.35524400	-3.36876200
O	-1.03129000	-1.00375900	-2.47211500
C	-1.63571900	-1.96918500	-1.61909100
H	-1.13180300	-2.94104000	-1.71393200
H	-2.70008200	-2.09926500	-1.86508300
C	-1.54511100	-1.51107100	-0.17707500

H	-2.07893200	-2.25176400	0.44023500
O	-0.16752700	-1.49994600	0.25611300
C	0.11531700	-0.37111800	1.04099100
H	0.50066500	-0.67703200	2.01503200
N	1.21667500	0.38811000	0.39172100
C	1.41329500	0.32219900	-0.94296300
H	0.74889700	-0.33407900	-1.50324200
C	2.39760300	1.05547400	-1.52388500
C	3.21542700	1.87615200	-0.68031000
N	4.23176900	2.59328900	-1.18585900
H	4.78500200	3.15936100	-0.55982300
H	4.45447400	2.57582200	-2.16890900
N	2.98915400	1.95174900	0.62535700
C	1.97333200	1.25311600	1.20140300
O	1.68697800	1.34338700	2.39840300
H	-3.01992800	0.22050300	-0.17202100
C	-1.16451700	0.47661600	1.15048200
H	-0.95426000	1.54004700	0.98603500
H	-1.59665900	0.35740800	2.15340800
P	-3.50716700	-1.82363700	3.11773700
O	-4.29578200	-2.44272900	4.26319100
O	-4.19819100	-2.32084400	1.69090800
O	-3.80745300	-0.19035700	3.10853000
H	-4.65977800	-0.02213500	3.52988200
H	-5.11858700	-2.56311100	1.85338600
Br	2.69032700	0.95349300	-3.41787100

(v) 5I-3′-dCMPH

C	-2.03074100	-0.13827900	0.11415300
O	-2.01558000	-1.98432300	2.94986400
H	-1.01019600	-1.36290400	-3.36757200
O	-1.03174100	-1.00799600	-2.47236900
C	-1.63376700	-1.97273500	-1.61689000
H	-1.12915500	-2.94428500	-1.71108800
H	-2.69841000	-2.10420200	-1.86106600
C	-1.54160000	-1.51296900	-0.17542700
H	-2.07697800	-2.25182900	0.44276600
O	-0.16409200	-1.50411600	0.25813100
C	0.12080600	-0.37474600	1.04198400
H	0.50647400	-0.68089100	2.01579300
N	1.22175100	0.38429200	0.39215900
C	1.41411700	0.32480900	-0.94322600
H	0.74349000	-0.33162500	-1.49565900
C	2.39569400	1.05725800	-1.53785800
C	3.21220600	1.87518200	-0.68479300
N	4.22932200	2.60059600	-1.17978100
H	4.77601100	3.16370200	-0.54532000
H	4.45638100	2.59902000	-2.16204000
N	2.99187400	1.94703800	0.62311300
C	1.98016300	1.24679500	1.20196400
O	1.69848000	1.33355800	2.40064000
H	-3.01278200	0.22174900	-0.17281400
C	-1.15855000	0.47374600	1.15222600
H	-0.94750200	1.53727300	0.98955100

H	-1.59149000	0.35316500	2.15465300
P	-3.51242300	-1.81973600	3.11554100
O	-4.30645000	-2.43521200	4.25921200
O	-4.20065400	-2.31630600	1.68713800
O	-3.80770700	-0.18555800	3.10392900
H	-4.66073300	-0.01435900	3.52264900
H	-5.12218000	-2.55588800	1.84718900
I	2.67839300	0.93956600	-3.61217700

16. Cartesian coordinates of products for the C-N bond cleavage calculated at the M06-2X/ aug-cc-pVDZ level of theory in the aqueous phase.

(i) 3′-dCMPH

C	-1.02408900	-0.41300900	0.12241300
O	-1.64933500	-0.22041400	1.41895100
H	-0.30536700	-1.63972800	-3.33231200
O	-0.23750400	-1.40314300	-2.40139900
C	-1.11831900	-2.23224400	-1.65619000
H	-0.89432000	-3.29542900	-1.81957000
H	-2.16793200	-2.04244000	-1.92720100
C	-0.94371400	-1.91407300	-0.18612600
H	-1.69555200	-2.46504900	0.38968300
O	0.35796100	-2.33514300	0.25627400
C	1.09265400	-1.24972400	0.67275800
H	2.16697300	-1.41349700	0.70886100
N	3.52522400	-0.09313700	-1.53533300
C	2.90050500	0.60160800	-2.48343800
H	2.76891700	0.09177400	-3.44257800

C	2.41531700	1.89252900	-2.32999700
C	2.62593400	2.45757300	-1.05530500
N	2.22136200	3.75205400	-0.78613400
H	2.13988000	3.96973200	0.19863800
H	1.47204200	4.11694500	-1.35826600
N	3.24606300	1.80935000	-0.07727200
C	3.70076300	0.52883100	-0.31379300
O	4.28452000	-0.08958900	0.61399100
H	-1.58224500	0.13998100	-0.63879600
C	0.43346300	0.01849700	0.23066200
H	0.79029300	0.33782800	-0.76098400
H	0.55826800	0.85220800	0.92856100
P	-3.21093600	0.13961800	1.48897000
O	-3.70465300	0.26022900	2.89070200
O	-3.83979100	-1.00923500	0.54468200
O	-3.43657100	1.44711200	0.56076300
H	-3.36709100	2.26728700	1.07082100
H	-4.80078600	-0.93834100	0.44793400
H	1.91026200	2.42684000	-3.12950900

(ii) 5F-3′-dCMPH

C	-1.21202300	-0.28981100	0.78234200
O	-2.00453800	-0.85757300	1.85742000
H	0.74378100	0.03456800	-1.72585900
O	-0.17673500	0.29892100	-1.86814800
C	-0.99608700	-0.84552900	-1.69674500
H	-0.70973600	-1.64652500	-2.39270000

H	-2.02656000	-0.54244300	-1.91450500
C	-0.92405300	-1.36844300	-0.27495000
H	-1.60554600	-2.21787400	-0.15124700
O	0.42046800	-1.82218000	-0.02747200
C	0.93866200	-1.17939200	1.07238400
H	2.01551700	-1.27432000	1.17624500
N	3.72716500	-0.19530000	-0.47561600
C	3.49813400	-0.16125600	-1.78793300
H	3.82843700	-1.01366700	-2.38755500
C	2.86914400	0.89549300	-2.40587100
C	2.45666300	1.97798100	-1.61151400
N	1.87023400	3.07800500	-2.19024000
H	1.35045300	3.66422200	-1.55016600
H	1.42868700	2.93155200	-3.08823000
N	2.66064200	1.96640100	-0.30201900
C	3.30275200	0.88516000	0.27446800
O	3.49309400	0.88495800	1.51615800
H	-1.73888800	0.57061300	0.35888200
C	0.16137400	0.06982500	1.33951700
H	0.57503900	0.92644500	0.78149300
H	0.10641500	0.34231000	2.39782700
P	-3.60030500	-0.68790500	1.81981900
O	-4.27237200	-1.37413900	2.96003000
O	-3.92759900	-1.18090800	0.31731000
O	-3.90472000	0.89661500	1.68821400
H	-4.03070400	1.31288300	2.55334400
H	-4.86835500	-1.12656700	0.09408600

F	2.64296300	0.92149200	-3.75297000

(iii) 5Cl-3′-dCMPH

C	-1.31798800	-0.29528900	0.98866200
O	-2.09694100	-0.87650400	2.06641500
H	0.59200500	0.07322000	-1.58229100
O	-0.33764700	0.32872100	-1.67235900
C	-1.13535100	-0.83002400	-1.49775500
H	-0.84777700	-1.62073700	-2.20479800
H	-2.17401000	-0.54203200	-1.69670600
C	-1.03532900	-1.36298500	-0.08145400
H	-1.70732700	-2.21947100	0.04632300
O	0.31641100	-1.80701100	0.14373700
C	0.83883300	-1.17681100	1.24827900
H	1.91566900	-1.27581300	1.34788200
N	3.66228300	-0.18218100	-0.20081300
C	3.42271800	-0.19944300	-1.50328400
H	3.77329900	-1.06797200	-2.06765800
C	2.75999700	0.81788700	-2.17588400
C	2.34693700	1.92877500	-1.40874300
N	1.74849700	3.01470800	-1.99371500
H	1.26098800	3.62638600	-1.35282100
H	1.29733900	2.87037300	-2.88673000
N	2.55946100	1.96548800	-0.09899400
C	3.20997000	0.91572200	0.51606200
O	3.38975300	0.95092400	1.75538600
H	-1.85310200	0.56642100	0.57846800

C	0.05904600	0.06611500	1.53585500
H	0.46234500	0.93014200	0.98165400
H	0.01341000	0.32791600	2.59724900
P	-3.69381600	-0.71466700	2.04612000
O	-4.35089800	-1.41417000	3.18698900
O	-4.03326900	-1.19643400	0.54264900
O	-4.00765500	0.86930500	1.93114400
H	-4.12832500	1.27745600	2.80087800
H	-4.97602600	-1.14218700	0.32804700
Cl	2.49252900	0.74875300	-3.90555100

(iv) 5Br-3′-dCMPH

C	-1.65781500	-0.27116800	1.31333800
O	-2.29854600	-0.88177700	2.46227000
H	0.18708100	0.05639900	-1.28850800
O	-0.73570900	0.33675100	-1.37981200
C	-1.55143300	-0.80495800	-1.17544300
H	-1.30391700	-1.60192700	-1.89070900
H	-2.59047800	-0.49662400	-1.33825300
C	-1.40304200	-1.33725800	0.23793300
H	-2.05677700	-2.20355800	0.38683900
O	-0.03765000	-1.76200900	0.41753100
C	0.55896500	-1.02289200	1.41067600
H	1.64215700	-1.09466500	1.43603200
N	3.77075800	-0.14644400	0.42862900
C	3.40186300	-0.27356400	-0.83528500
H	3.79009600	-1.13435800	-1.38624300

C	2.55850700	0.62084800	-1.48205300
C	2.13580200	1.75067300	-0.74888200
N	1.38709700	2.74736300	-1.32144900
H	0.92821800	3.35657100	-0.65677900
H	0.83285900	2.50177000	-2.13122900
N	2.48528500	1.89783300	0.52379000
C	3.27595700	0.94575100	1.12951100
O	3.55441700	1.06473800	2.34470100
H	-2.27917300	0.54930200	0.94168000
C	-0.26284700	0.18376600	1.73107800
H	0.03418700	1.05724500	1.12921200
H	-0.23470400	0.46969100	2.78731300
P	-3.89616500	-0.79671000	2.59895500
O	-4.40194500	-1.51478600	3.80329500
O	-4.35821900	-1.30932100	1.13935000
O	-4.29502200	0.76936800	2.50611800
H	-4.34343500	1.18224600	3.38066300
H	-5.31893300	-1.29913900	1.01785400
Br	2.17073100	0.41621200	-3.36347400

(v) 5I-3′-dCMPH

C	-1.83262900	-0.33282500	1.84811700
O	-2.55586700	-0.94189900	2.94868900
H	0.04813500	0.06831400	-0.74286000
O	-0.88211300	0.33031100	-0.81097300
C	-1.67946000	-0.82980000	-0.64625000
H	-1.40046600	-1.60964300	-1.36898700
H	-2.72005800	-0.53795200	-0.82934700

C	-1.56268800	-1.38489000	0.76074600
H	-2.23050900	-2.24515500	0.88324700
O	-0.20698800	-1.82892700	0.96417000
C	0.34630200	-1.17185800	2.03737500
H	1.42555300	-1.26653700	2.11073300
N	3.31569000	-0.18370000	0.81990300
C	3.03731000	-0.27279100	-0.46928400
H	3.42026000	-1.15099000	-0.99666900
C	2.29862100	0.67536500	-1.17543700
C	1.88277000	1.81441800	-0.44596400
N	1.23826200	2.86786200	-1.04473500
H	0.76731800	3.48813400	-0.39915900
H	0.73641600	2.68089400	-1.90261600
N	2.13301500	1.92154200	0.85475000
C	2.82067400	0.91909500	1.50275700
O	3.00120400	1.00043100	2.73889100
H	-2.40280000	0.51869300	1.46475000
C	-0.44566100	0.05739500	2.34833600
H	-0.08110500	0.92926400	1.78076000
H	-0.46125600	0.31834800	3.41090500
P	-4.15441100	-0.80499400	2.99999100
O	-4.74920400	-1.52658500	4.16099800
O	-4.55164100	-1.27628600	1.50754500
O	-4.49716200	0.77492500	2.91617500
H	-4.58462200	1.17282700	3.79459300
H	-5.50237000	-1.22477700	1.33089600
I	1.99096400	0.46137200	-3.24435800