Table 1S: Proton chemical shifts of the α(OH)PdG•dC duplex recorded at 25°C

	H6/H8	H1'	H3'	H4'	H2''	H2'	H2/Me/H5	T(N3H)/G(N1H)[a]	C(N4H)$_{hb}$/C(N4H)[a] $_{nhb}$
C1	7.61	5.75	4.67	4.04	2.41	2.00	5.88		
G2	7.95	5.95	4.95	4.34	2.76	2.66		12.76	
T3(*R*) T3(*S*)	7.21	5.68 4.69	4.84	4.15	2.40	2.05	1.48	13.43	
A4(*R*) A4(*S*)	8.23 8.21	6.08	4.98 4.97	4.37	2.77 2.75	2.62 2.61			
C5(*R*) C5(*S*)	7.09 7.05	5.71	4.67 4.63	4.17 4.15	2.42 2.46	1.67 1.65	5.11 5.16		7.91/6.70 7.91/6.83
α(OH)PdG(*R*)[b,c] α(OH)PdG(*S*)[b,c]	7.28 7.23	5.73 5.75	4.78		2.46 2.47	2.19 2.18			8.42 8.53
C7(*R*) C7(*S*)	7.57 7.59	4.91 4.93	4.79 4.80		2.33	2.33	5.67 5.62		8.11/6.44 7.96/6.54
A8(*R*) A8(*S*)	8.26 8.25	6.21	4.98	4.35	2.90	2.67	7.63		
T9	7.05	5.70	4.81	4.08	2.30	1.90	1.42	13.56	
G10	7.82	5.88	4.93	4.32	2.65	2.56		12.70	
C11	7.41	6.14	4.45	4.03	2.15	2.15	5.39		8.13/6.58
G12	7.92	5.95	4.80	4.20	2.75	2.59		12.92	
C13	7.46	5.65	4.86	4.19	2.46	2.14	5.40		8.37/6.53
A14	8.32	6.25	5.02	4.41	2.92	2.69	7.67		
T15(*R*) T15(*S*)	7.04 7.05	5.64 5.62	4.81	4.08	2.25 2.26	1.84 1.86	1.41 1.42	13.32/13.30[d]	
G16(*R*) G16(*S*)	7.86 7.89	5.80 5.86	4.94 4.95	4.34 4.36	2.64 2.71	2.64 2.65		12.46/12.37[d]	
C17(*R*) C17(*S*)	7.45 7.41	5.74 5.70	4.78	4.10 4.07	2.30 2.28	1.61	5.66 5.57		9.78/8.77 9.78/8.82
G18(*R*) G18(*S*)	8.02 8.00	5.92 5.90	4.96 4.95	4.32 4.31	2.79 2.76	2.69 2.68		12.76 12.63	
T19(*R*) T19(*S*)	7.19 7.20	5.66	4.83		2.39	2.04	1.44 1.46	13.43 13.48	
A20(*R*) A20(*S*)	8.25	6.17	4.98	4.37	2.82	2.66	7.41 7.40		
C21	7.24	5.62	4.74	4.10	2.24	1.82	5.32		
G22	7.85	6.10	4.62	4.12	2.32	2.54			

Chemical shifts referenced TSP. [a]Determined at 5°C. [b]H2'/H2'' were not specifically assigned. [c]The chemical shift of exocyclic protons is Hα: 5.26 and 5.18 ppm; Hββ': 2.15/1.74 and 2.10/1.82 ppm; Hγγ': 4.04/3.38 and 4.30/3.15 ppm. [d]Enantiomer specific signals not assigned.

Table 2S. Empirical Structural Restraints	
G•C Watson-Crick HB Distances (Å)	
G(H1)-C(N3)	1.940 ±0.10
G(O6)-C(H4)	1.900 ±0.10
G(H2)-C(O2)	1.840 ±0.10
A•T Watson-Crick HB Distances (Å)	
T(H3)-A(N1)	1.810 ±0.10
T(O4)-A(N6)	1.840 ±0.10
Backbone Dihedral Angles (°)	
α (O3'-P-O5'-C5')	290 ±18
β (P-O5'-C5'-C4')	182 ±20
γ (O5'-C5'-C4'-C3')	52 ±11
δ (C5'-C4'-C3'-O3')	103 ±24
ε (C4'-C3'-O3'-P)	188 ±9
ζ (C3'-O3'-P-O5')	288 ±30

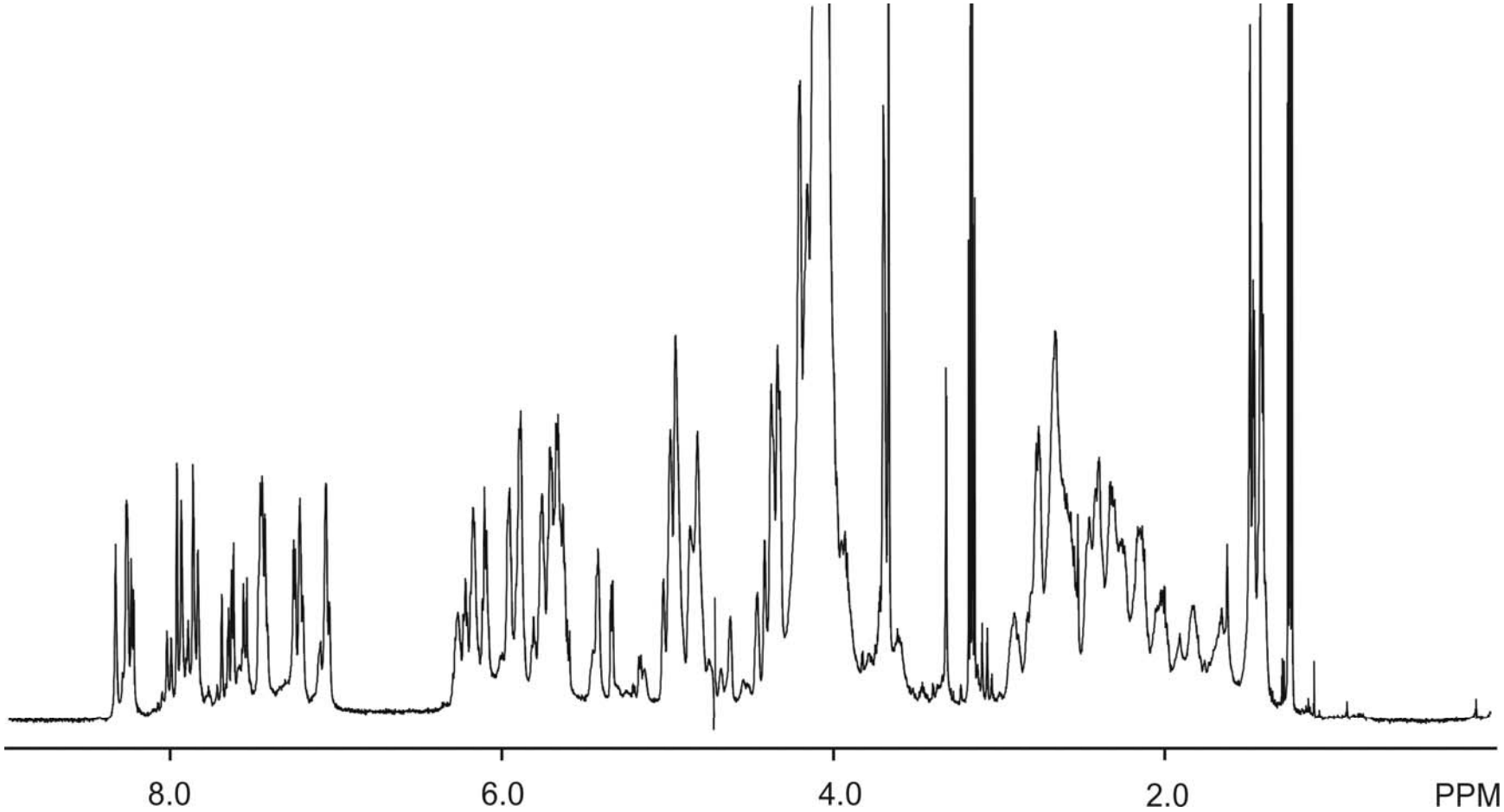

Figure 1S: 500 MHz proton spectrum of the α-(OH)-PdG•dC duplex recorded at 25°C with the sample dissolved in 100% D_2O buffer (25 mM phosphate containing 50 mM NaCl and 1 mM EDTA), pH 5.9.

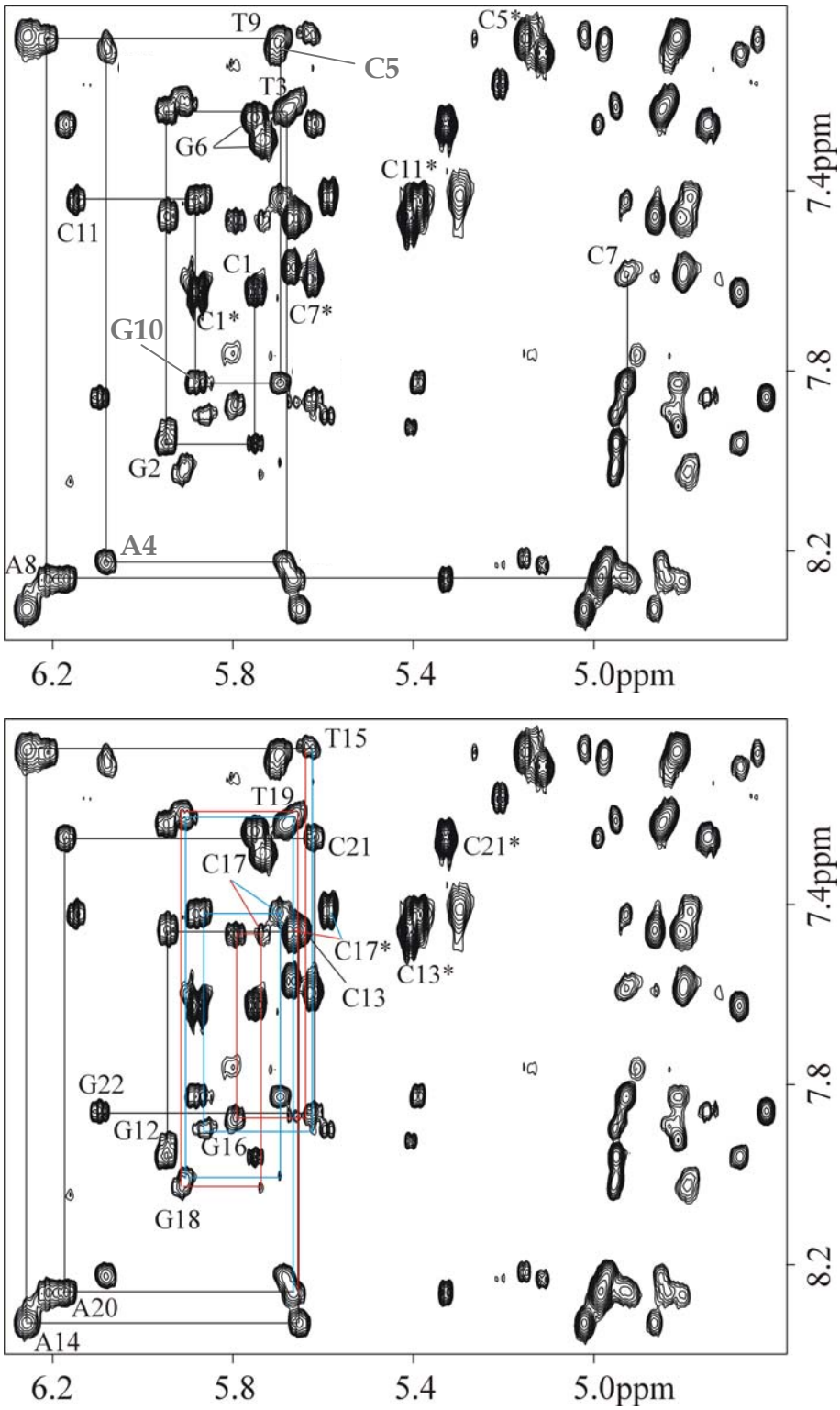

Figure 2S: Finger print region of a 500 MHz NOESY (300 ms mixing time) spectrum recorded with the sample dissolved in 100% D_2O buffer, pH 5.9, at 25°C. The figure shows the NOESY 'walk' on the α-OH-PdG•dC duplex, from C1 to C5 and C7 to C11 in the lesion-containing strand (top panel) and from G12 to G22 in the unmodified strand (bottom panel).

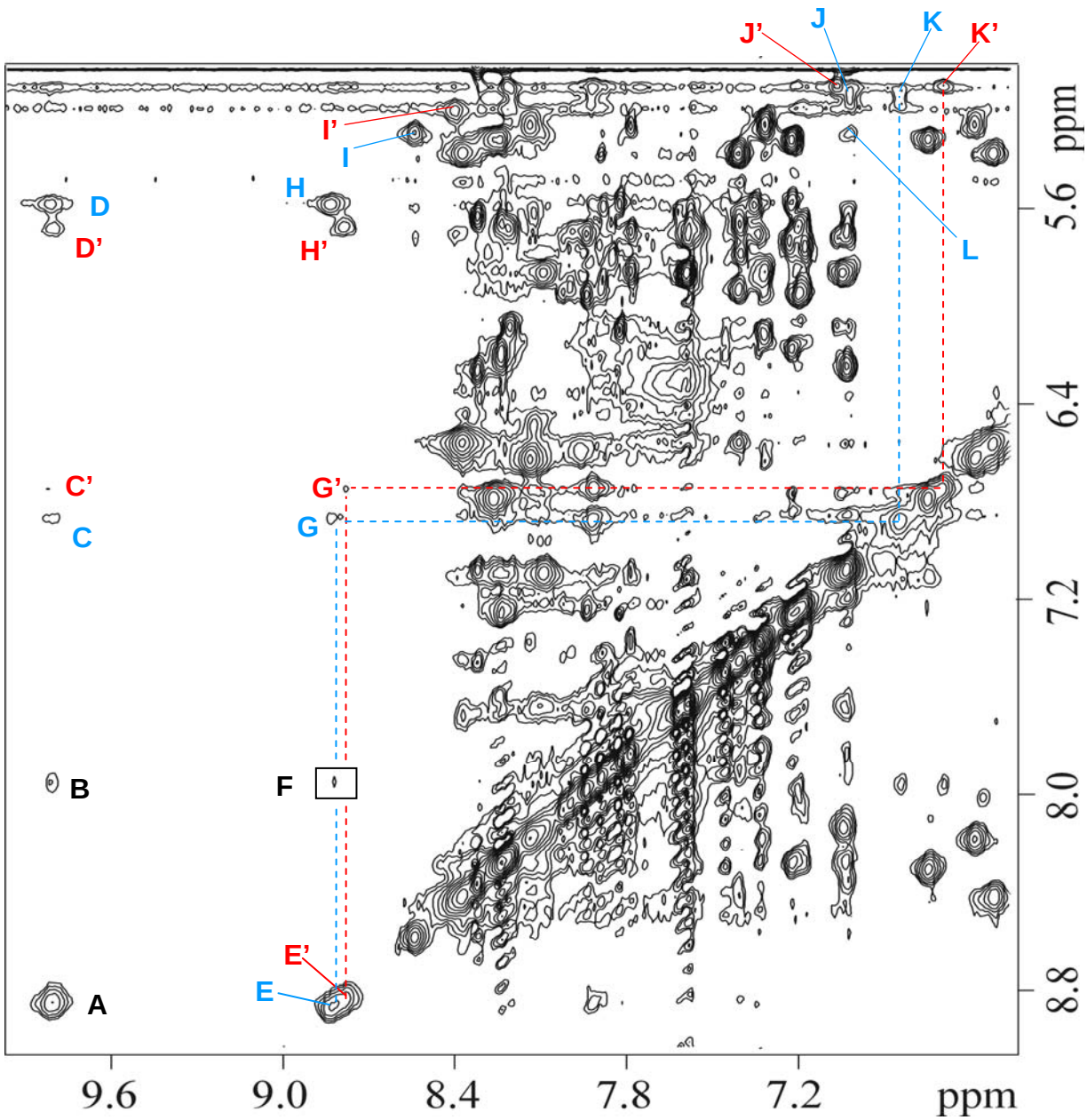

Figure 3S: Expanded region of a 220 ms mixing time NOESY recorded at 5°C with the sample disolved in 10% D_2O phosphate buffer, pH 5.9, depicting NOE interactions used for enantiomer specific assigment on the unmodified strand. Non-primed (blue) and primed (red) labels differenciate NOE interactions on the *S* and *R* isomers, respectively. Peaks are assigned as follow: A, C17(N4H)$_{hb}$-C17(N4H)$_{nhb}$; B, C17(N4H)$_{hb}$-C5(N4H)$_{hb}$; C, C17(N4H)$_{hb}$-C5(N4H)$_{nhb}$; D, C17(N4H)$_{hb}$-C17(H5); E, C17(N4H)$_{nhb}$; F, C17(N4H)$_{nhb}$-C5(N4H)$_{hb}$; G, C17(N4H)$_{nhb}$-C5(N4H)$_{nhb}$; H, C17(N4H)$_{nhb}$-C17(H5); I, G6(N2H)-X6(Hα); J, C5(H6)-C5(H5); K, C5(N4H)$_{nhb}$-C5(H5); L, C5(H6)-G6(Hα).

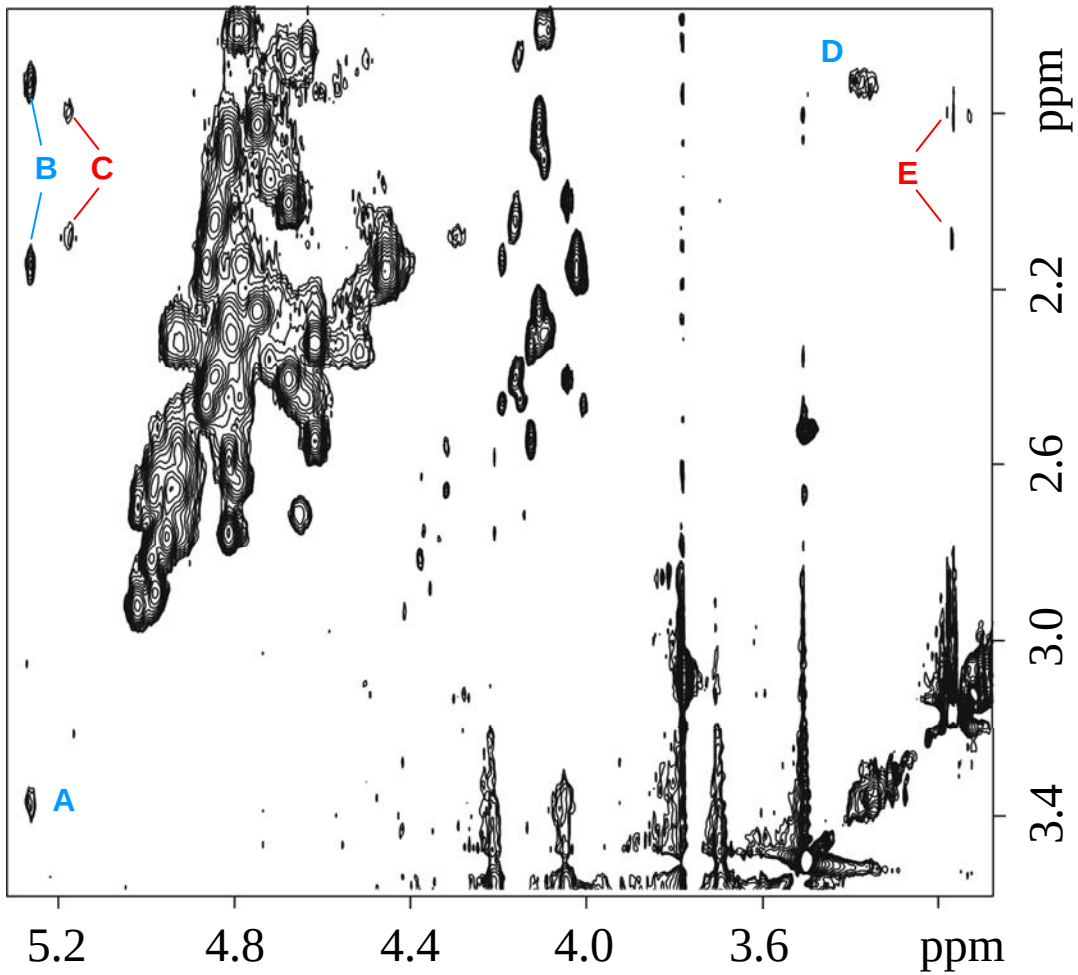

Figure 4S: Expanded region of a 120 ms isotropic mixing time TOCSY strum recorded at 25°C with the sample disolved in 100% D_2O phosphate buffer, pH 5.9. The figure displays interactions among protons of the exocyclic propano ring with blue and red colors indicating the S and R isomers, respectively. Labeles are assigned as follow: A, α-OH-PdG(Hα)-α-OH-PdG(Hγ); B, α-OH-PdG(Hα)-α-OH-PdG(Hβ/β'); C, α-OH-PdG(Hα)-α-OH-PdG(Hβ/β'); D, α-OH-PdG(Hγ)-α-OH-PdG(Hβ); E, α-OH-PdG(Hγ)-α-OH-PdG(Hβ/β').

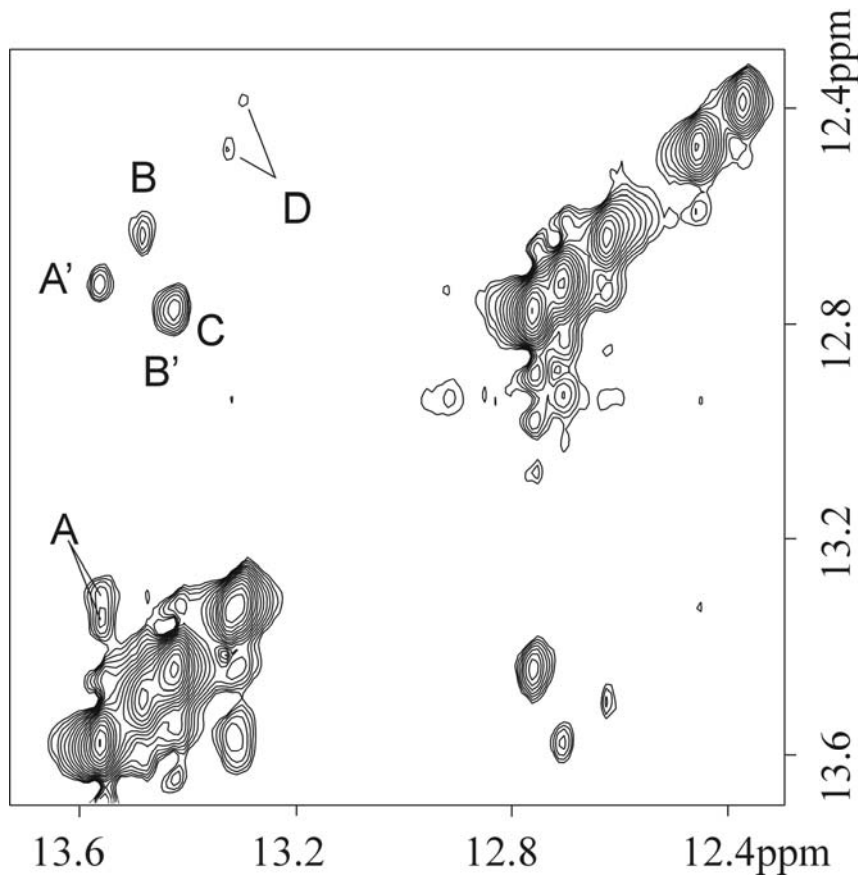

Figure 5S: Expanded region of a NOESY (220 ms mixing time) spectrum recorded at 5ºC with the sample dissolved in 10% D2O phosphate buffer pH 5.9 (10 mM phosphate, 50 mM NaCl and 1 mM EDTA). Labeled peaks are assigned as follows: A, T9(N3H)-T15(N3H); A', T9(N3H)-G10(N1H); B, (*S*) T19(N3H)-G18(N1H); B', (*R*) T19r(N3H)-G18r(N1H); C, T3(N3H)-G2(N1H); D, T15(N3H)-G16(N1H).

α-OH-PdG•dC⁺ Duplexes

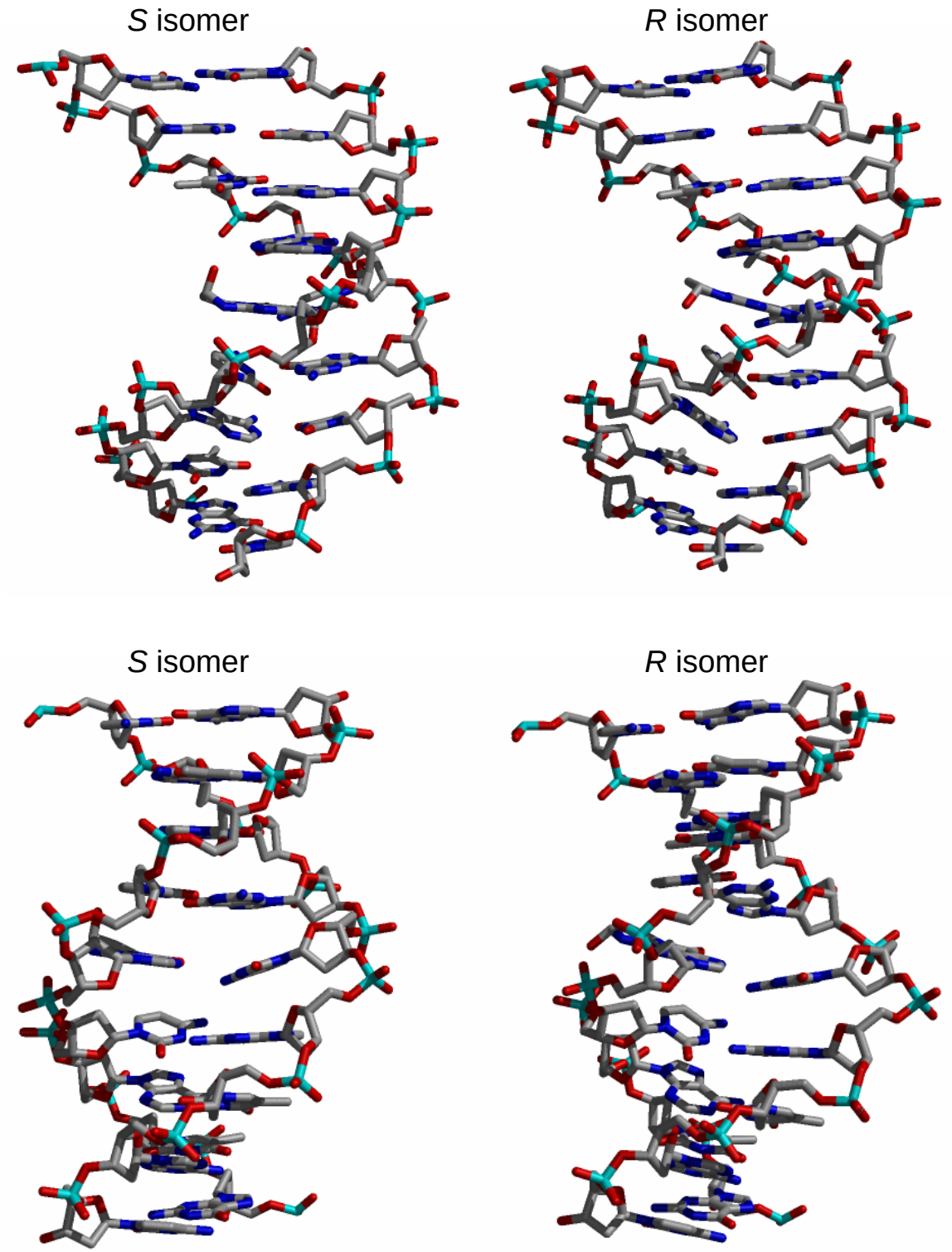

Figure 6S: Three-dimensional structure of α-OH-PdG•dC⁺ duplexes seen with the sugar-phosphate backbone (top) or the minor groove (bottom) prominent.