

Supporting Information

Title: Time-Resolved Resonance Raman Investigation of the 2-Fluorenylnitrenium Ion Reactions With C8 Guanosine Derivatives

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Description: Description of the preparation and characterization of the 2-fluorenyl azide precursor and the C8-methylguanosine sample used in the TR³ experiments are given. Figures 1S to 3S present an overview TR³ spectra with more time delays from 10 ns to 50 μ s time scale, and are obtained by 368.9 nm probe after 309.1 nm photolysis of 0.3 mM 2-fluorenyl azide in the presence of 0.9 mM guanosine (Figure 1S), C8-methylguanosine (Figure 2S), and C8-bromoguanosine (Figure 3S) in a water:acetonitrile (50:50) mixed solvent with a 0.002 M Na₂HPO₄:0.002 M NaH₂PO₄ buffer. Figure 4S compares the 10 ns spectra shown in Figures 1-3 of the paper to the TR³ spectrum of the 2-fluorenylnitrenium ion reported in reference 36(a). Figure 5S displays a comparison of the 15 μ s spectrum of Figure 1 with the 8 μ s spectrum obtained in reference 38 for the **C8 intermediate** species. Figure 6S presents schematic diagrams for the structures of guanosine, C8-methylguanosine, C8-bromoguanosine and the 2-fluorenylnitrenium ion determined from BPW91/cc-PVDZ calculations. Table 1S lists selected structural parameters for the BPW91/cc-PVDZ optimized geometries for the **C8 intermediate**, the **C8-methyl intermediate** and the **C8-bromo intermediate** species. Tables 2S, 3S and 4S compare the experimental Raman band vibrational frequencies from the ns-TR³ spectra of Figure 7 to the BPW91/cc-PVDZ calculated normal Raman vibrational frequencies for the **C8 intermediate**, the **C8-methyl intermediate** and the **C8-bromo intermediate** species. Table 5S presents selected structural parameters determined for guanosine, C8-methylguanosine and C8-bromoguanosine from BPW91/cc-PVDZ calculations. Cartesian coordinates, total energies, and vibrational zero-point energies for the optimized geometry from the BPW91/cc-PVDZ calculations for the **C8 intermediate**, the **C8-methyl intermediate**, the **C8-bromo intermediate**, guanosine, C8-methylguanosine, C8-bromoguanosine and the 2-fluorenylnitrenium ion.

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Description of the preparation and characterization of the C8-methylguanosine sample used in the TR³ experiments. S4

Figure 1S displays an overview TR³ spectra with more time delays from 10 ns to 15 μ s time scale, which is obtained by 368.9 nm probe after 309.1 nm photolysis of 0.3 mM 2-fluorenyl azide in the presence of 0.9 mM guanosine in a water:acetonitrile (50:50) mixed solvent with a 0.002 M Na₂HPO₄:0.002 M NaH₂PO₄ buffer. S5

Figure 2S displays an overview TR³ spectra with more time delays from 10 ns to 50 μ s time scale, which is obtained by 368.9 nm probe after 309.1 nm photolysis of 0.3 mM 2-fluorenyl azide in the presence of 0.9 mM C8-methylguanosine in a water:acetonitrile (50:50) mixed solvent with a 0.002 M Na₂HPO₄:0.002 M NaH₂PO₄ buffer. S6

Figure 3S shows an overview TR³ spectra with more time delays from 10 ns to 50 μ s time scale, which is obtained by 368.9 nm probe after 309.1 nm photolysis of 0.3 mM 2-fluorenyl azide in the presence of 0.9 mM C8-bromoguanosine in a water:acetonitrile (50:50) mixed solvent with a 0.002 M Na₂HPO₄:0.002 M NaH₂PO₄ buffer. S7

Figure 4S compares the 10 ns spectra shown in Figures 1-3 of the paper to the TR³ spectrum of the 2-fluorenylnitrenium ion reported in reference 38. This comparison confirms the first species observed in the ns-TR³ spectra of Figures 1-3 is the 2-fluorenylnitrenium ion.

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Figure 5S displays a comparison of the 15 μs spectrum of Figure 1 with the 8 μs spectrum obtained in reference 38 for the **C8 intermediate** species and these spectra are almost identical and obviously due to the same species.

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Figure 6S presents schematic diagrams for the structures of guanosine, C8-methylguanosine, C8-bromoguanosine and the 2-fluorenylnitrenium ion determined from BPW91/cc-PVDZ calculations.

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Table 1S lists selected structural parameters for the BPW91/cc-PVDZ optimized geometries for the **C8 intermediate**, the **C8-methyl intermediate** and the **C8-bromo intermediate** species.

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Table 2S compares the BPW91/cc-PVDZ calculated Raman vibrational frequencies for the **C8 intermediate** to those observed for the 15 μs TR³ experimental spectrum of Figure 1.

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Table 3S compares the BPW91/cc-PVDZ calculated Raman vibrational frequencies for the **C8-methyl intermediate** to those observed for the 50 μs TR³ experimental spectrum of Figure 2.

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Table 5S presents selected structural parameters determined for guanosine, C8-methylguanosine and C8-bromoguanosine from BPW91/cc-PVDZ calculations.

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Cartesian coordinates, total energies, and vibrational zero-point energies for the optimized geometry from the BPW91/cc-PVDZ calculations for the **C8 intermediate**, the **C8-methyl intermediate**, the **C8-bromo intermediate**, guanosine, C8-methylguanosine, C8-bromoguanosine and the 2-fluorenylnitrenium ion.

S21-S30

Description of the preparation and characterization of the 2-fluorenyl azide precursor used to generate the 2-fluorenylnitrenium ion in the TR³ experiments.

2-Fluorenyl azide was prepared based on a literature procedure given in reference White, W. E. Jr.; Yielding, L. W. In *Methods in Enzymology Vol. XLVI Affinity Labeling*, W. B. Jakoby and M. Wilchek, Eds.; Academic Press, Inc.: Orlando, Florida, U.S.A., 1977; pp. 646-647.

2-Fluorenyl azide:

To 2-aminofluorene (12.96 g) in 300 mL of THF and 200 mL of water was added 28 mL of concentrated hydrochloric acid. The solution was cooled to 0-5°C. A solution of 5.4 g sodium nitrite in 50 mL of water was added drop-wise at 0-5°C. The reaction was stirred for 30 min at 0-5°C. A solution of 5.1 g sodium azide in 50 mL of water was added drop-wise at 0-5°C and stirred for 1 hr. The product was extracted with ether. The combined organic layers were dried over anhydrous MgSO₄ and concentrated in vacuo. Flash chromatography on silica gel (1:99 EtOAc/hexane) afforded 13.99 g of 2-fluorenyl azide as a bright yellow solid. ¹H NMR (500 MHz, CDCl₃), δ: 7.73 (d, *J*=8.0 Hz, 2H), 7.52 (d, *J*=7.4 Hz, 1H), 7.38 (t, *J*=7.4 Hz, 1H), 7.29 (m, 1H), 7.21 (s, 1H), 7.02 (m, 1H), 3.89 (s, 2H). IR (KBr disc), ν: 2113, 1604, 1581, 1454, 1401, 1307, 1292, 1281, 838, 766, 732 cm⁻¹. MS (EI): 179 (C₁₃H₉N⁺, 100), 152 (24), 111 (27), 97 (45), 85 (53), 77 (73), 71 (58). Purity: >95% estimated according to NMR data.

Description of the preparation and characterization of the C8-methylguanosine sample used in the TR³ experiments

C8-methylguanosine was synthesized according to methods of Kennedy, S. A.; Novak, M.; Kolb, B. A. *J. Am. Chem. Soc.* **1997**, *119*, 7654-7664 and Maeda, M.; Nushi, K.; Kawazoe, Y. *Tetrahedron*, **1974**, *30*, 2677-2682.

To a solution of guanosine (4.0 g, 14.0 mmol) in 1M H₂SO₄ (800 mL), was added FeSO₄·H₂O (16.0 g, 57.0 mmol). At room temperature, *t*-butylhydroperoxide (6.7 mL, 49.0 mmol) in water (100 mL) was then added dropwise. After the addition was complete, the mixture was stirred for 1 h more. The mixture was then neutralized with aqueous KOH and centrifuged to separate the resulting emulsion. The aqueous layer was poured off and the precipitate was washed twice with hot water. The washings were combined with the previously collected aqueous layer and this mixture was concentrated on at reduced pressure on a rotary evaporator until a white precipitate formed. After standing overnight, the precipitate was filtered off and dried. This crude product was repeatedly recrystallized from hot water to afford pure 8-methylguanosine (1.0 g, 24%) as white solid. ¹H-NMR (DMSO, 400 MHz): 2.39 (3H, s), 3.54 (1H, m), 3.63 (1H, m), 3.84 (1H, m), 4.07 (1H, m), 4.68 (1H, q, *J* = 6.1 Hz), 5.11 (2H, m), 5.34 (1H, d, *J* = 6.5 Hz), 5.66 (1H, d, *J* = 6.9 Hz), 6.30 (2H, s), 10.60 (1H, s). Purity: >95% estimated according to NMR data.

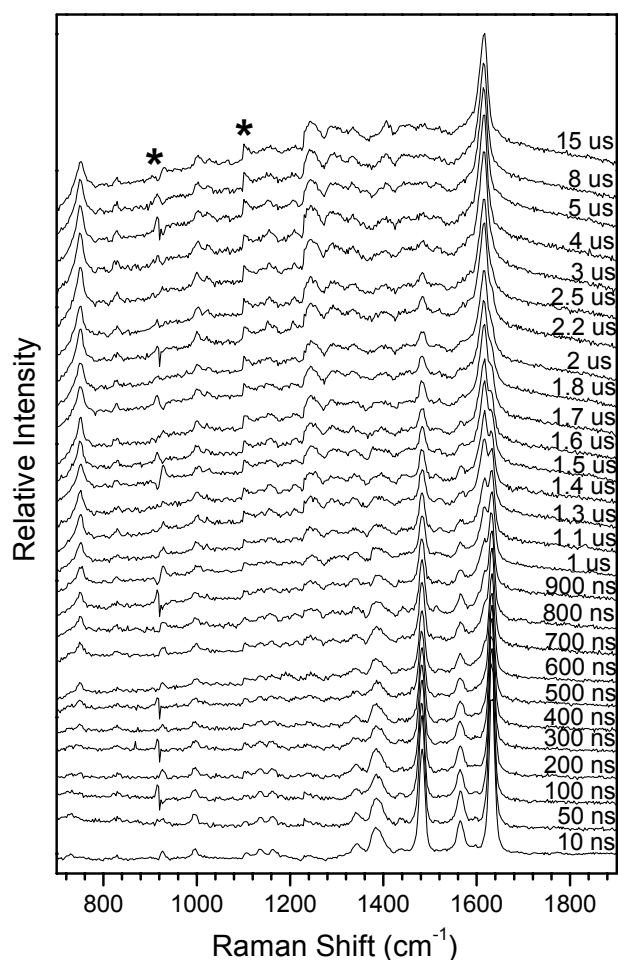


FIGURE 1S. Selected TR³ spectra obtained by 368.9 nm probe after 309.1 nm photolysis of 0.3 mM 2-fluorenyl azide in the presence of 0.9 mM guanosine in a water:acetonitrile (50:50) mixed solvent with a 0.002 M Na₂HPO₄:0.002 M NaH₂PO₄ buffer. The time delays between the pump (309.1 nm) and probe (368.9 nm) laser beams are shown to the right of each spectrum. Star symbols mark solvent-subtraction artifacts, stray-light and ambient-light artifacts. See text for more details.

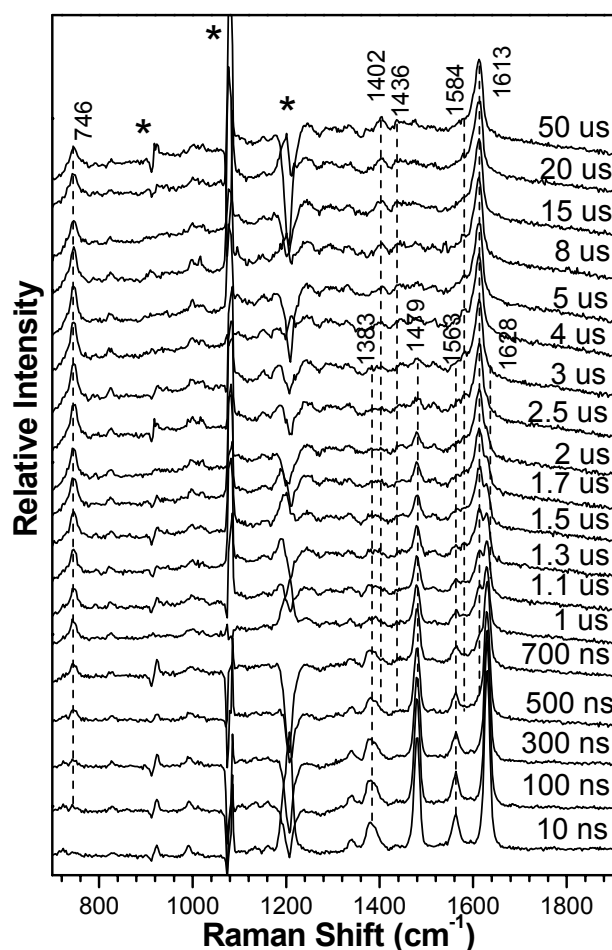


FIGURE 2S. Selected TR³ spectra obtained by 368.9 nm probe after 309.1 nm photolysis of 0.3 mM 2-fluorenyl azide in the presence of 0.9 mM C8-methylguanosine in a water:acetonitrile (50:50) mixed solvent with a 0.002 M Na₂HPO₄:0.002 M NaH₂PO₄ buffer. The time delays between the pump (309.1 nm) and probe (368.9 nm) laser beams are shown to the right of each spectrum and the Raman shifts of selected bands are presented at the top of the 3 μ s and 50 μ s spectra. Star symbols mark solvent-subtraction artifacts, stray-light and ambient-light artifacts. See text for more details.

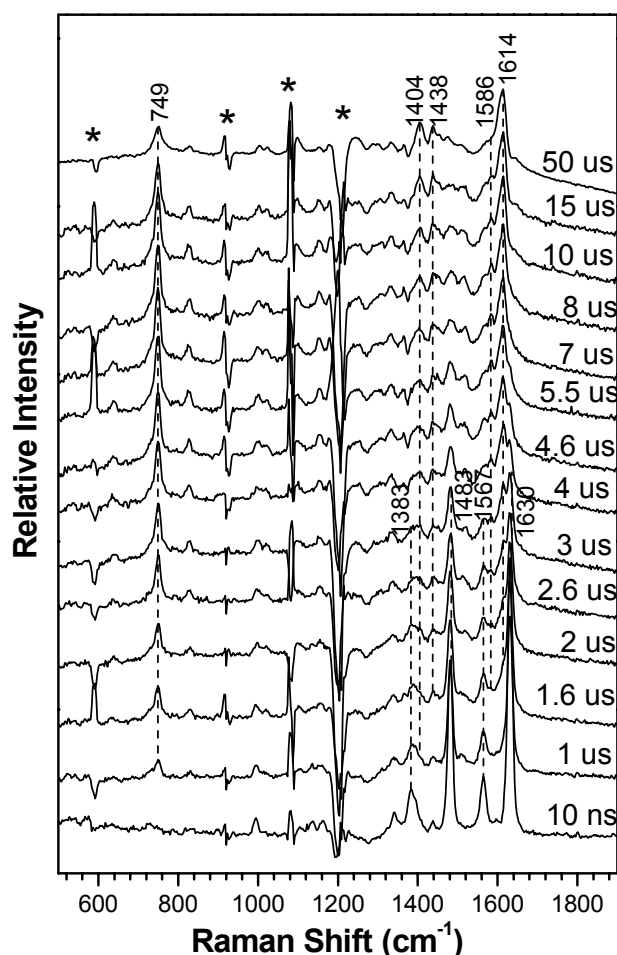


FIGURE 3S. Selected TR³ spectra obtained by 368.9 nm probe after 309.1 nm photolysis of 0.3 mM 2-fluorenyl azide in the presence of 0.9 mM C8-bromoguanosine in a water:acetonitrile (50:50) mixed solvent with a 0.002 M Na₂HPO₄:0.002 M NaH₂PO₄ buffer. The time delays between the pump (309.1 nm) and probe (368.9 nm) laser beams are shown to the right of each spectrum and the Raman shifts of selected bands are presented at the top of the 3 μ s and 50 μ s spectra. Star symbols mark solvent-subtraction artifacts, stray-light and ambient-light artifacts. See text for more details.

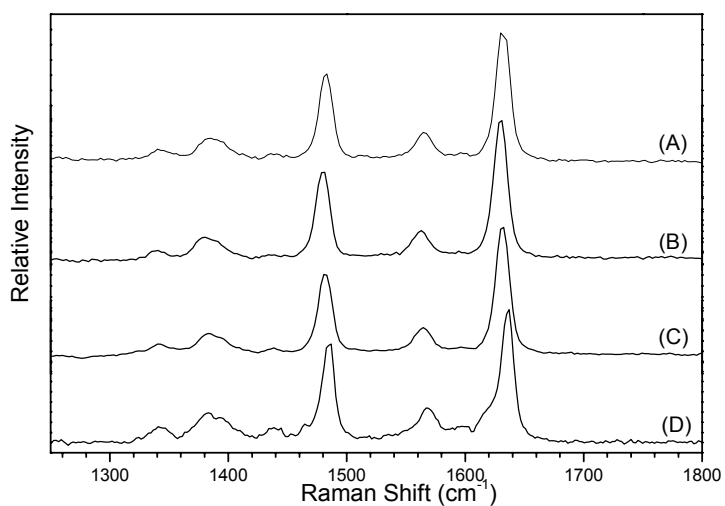


FIGURE 4S. Comparison of the 10 ns 368.9 nm probe TR³ spectrum (A) from Figure 1 of paper (guanosine present) and (B) from Figure 2 of the paper (with C8-methylguanosine present) and (C) from Figure 3 of the paper (with C8-bromoguanosine) to (D) a 10 ns 416.0 nm probe TR³ spectrum previously reported for the 2-fluorenylnitrenium ion in reference Zhu, P.; Ong, S. Y.; Chan, P. Y.; Leung, K. H.; Phillips, D. L. *J. Am. Chem. Soc.* **2001**, *123*, 2645-2649 that was obtained after 266 nm photolysis of 2-fluorenylazide in a water:acetonitrile (75:25) solution.

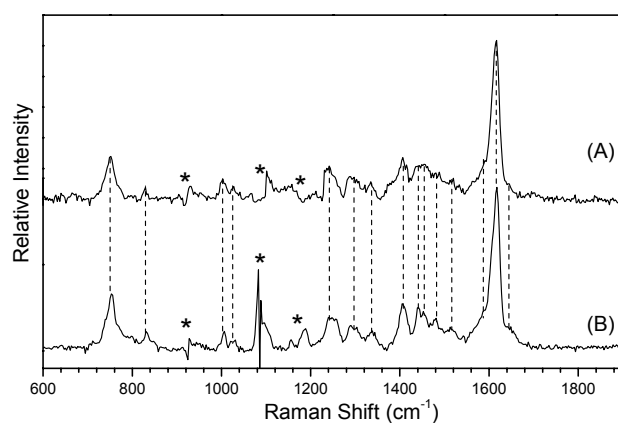
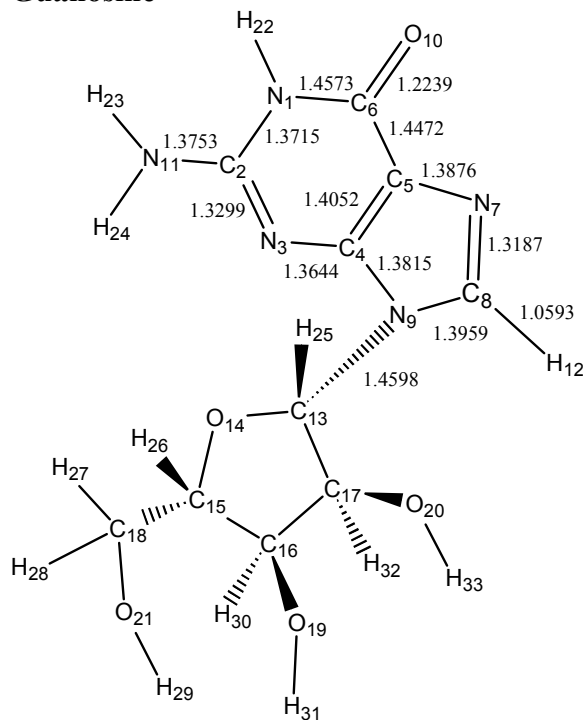


FIGURE 2S. A comparison of (A) the 15 μs spectrum of Figure 1 with (B) the 8 μs spectrum obtained in reference Chan, P. Y.; Kwok, W. M.; Lam, S. K.; Chiu, P.; Phillips, D. L. *J. Am. Chem. Soc.* **2005**, *127*, 8246-8247 for the **C8 intermediate** species is shown. Star symbols mark solvent-subtraction artifacts, stray-light and ambient-light artifacts. See text for more details.

FIGURE 3S. Simple schematic diagrams of guanosine, C8-bromoguanosine, C8-methylguanosine and 2-fluorenylnitrenium ion with selected bond lengths shown from the BPW91/cc-PVDZ calculated optimized geometry.

Guanosine



C8-bromoguanosine

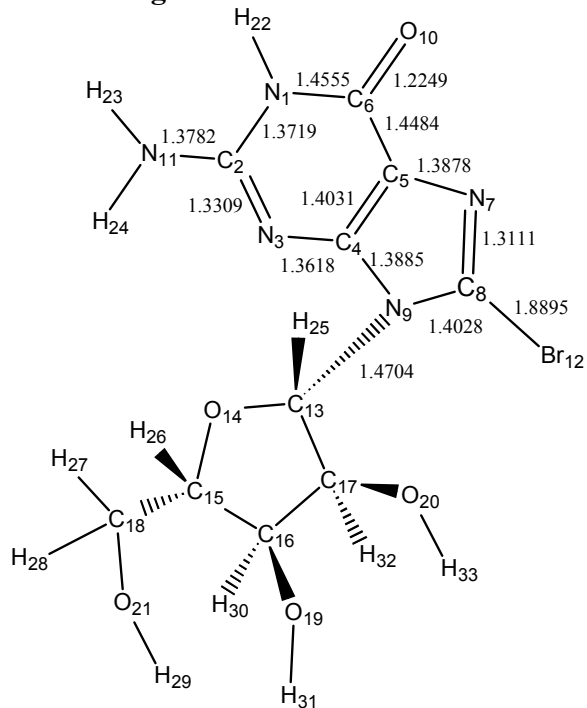


Table 1S. Selected structural parameters for the BPW91/cc-PVDZ optimized geometries for the **C8 intermediate** (indicated by C8 below), the **C8-methyl intermediate** (indicated by MeC8 below) and the **C8-bromo intermediate** (indicated by BrC8 below) species are listed.

	Bond Length (Å)		
	BrC8	C8	MeC8
N1-C2	1.3732	1.3742	1.3747
N1-C6	1.4429	1.4409	1.4411
C2-N3	1.3511	1.3494	1.3486
C2-N11	1.3437	1.3440	1.3436
N3-C4	1.3336	1.3369	1.3364
C4-C5	1.4515	1.4666	1.4636
C4-N9	1.3528	1.3406	1.3396
C5-C6	1.4757	1.4789	1.4796
C5-N7	1.3162	1.3112	1.3089
C6-O10	1.2151	1.2159	1.2152
N7-C8	1.4226	1.4558	1.4624
C8-N9	1.4594	1.4989	1.5131
C8-R12 (R=Br,Me)	2.2222	1.1075	1.5288
N9-C13	1.4754	1.4625	1.4679
C8-N34	1.3913	1.4553	1.4870
N34-H35	1.0214	1.0269	1.0280
N34-C37	1.3969	1.4159	1.4252
C36-C37	1.4207	1.4186	1.4188
C36-C41	1.3943	1.3963	1.3975
C37-C38	1.4231	1.4165	1.4170
C38-C39	1.3873	1.3926	1.3925
C39-C40	1.4286	1.4241	1.4261
C39-C42	1.5145	1.5143	1.5144
C40-C41	1.4124	1.4116	1.4096
C42-C43	1.5152	1.5153	1.5153
C43-C44	1.4269	1.4148	1.4239
C43-C45	1.3970	1.3975	1.3979
C44-C48	1.4116	1.4096	1.4094
C45-C46	1.4082	1.4076	1.4074
C46-C47	1.4122	1.4107	1.4106
C47-C48	1.3995	1.4008	1.4008
	Bond Angle (degree)		
	BrC8	C8	MeC8
C4-C5-N7	112.6	113.3	113.0
C4-N9-C8	106.5	107.8	108.1
C5-C4-N9	106.6	106.3	106.7
C5-N7-C8	105.5	106.1	107.1
N7-C8-N9	108.7	106.3	105.1
N7-C8-R12(R=Br,H,Me)	100.0	109.1	109.8
C8-N34-C37	128.8	120.7	121.4
C8-N34-H35	114.0	110.7	107.6
N9-C8-N34	112.9	111.8	107.2
R12-C8-N34(R=Br,H,Me)	111.9	108.6	114.1
N34-C37-C36	122.7	120.6	119.4
N34-C37-C38	116.7	119.2	120.2
C36-C37-C38	120.6	120.1	119.9
C37-C38-C39	119.1	119.3	119.4
C38-C39-C40	120.5	120.7	120.6

C39-C40-C41	120.0	119.8	120.0
C40-C41-C36	120.0	119.6	119.3
C41-C36-C37	119.8	120.5	120.8
Dihedral (degree)			
	BrC8	C8	MeC8
C4-C5-N7-C8	-2.8	2.6	1.8
C5-N7-C8-N9	3.9	0.4	-0.1
C5-N7-C8-R12(R=Br,H,Me)	-107.4	-116.4	-119.4
C5-N7-C8-N34	132.3	123.1	114.6
N7-C8-N34-H35	-138.2	-40.2	-48.5
N7-C8-N34-C37	52.3	93.6	79.6
C8-N34-C37-C36	-3.9	49.1	78.9
C8-N34-C37-C38	176.2	-134.9	-106.0
N34-C37-C36-C41	179.0	175.5	175.7
N34-C37-C38-C39	-179.0	-174.7	-174.7
H35-N34-C37-C38	6.8	-1.7	20.9
C37-C38-C39-C40	-0.5	-1.5	-1.0

Table 2S. Comparison of the BPW91/cc-PVDZ calculated Raman vibrational frequencies for the **C8 intermediate** to those observed for the 15 μs TR³ experimental spectrum of Figure 1. ^[a]

	Vibrational mode possible description	Calc.		Expt. Raman Shift (cm ⁻¹)
		Raman Activity	BPW91/cc-PVDZ Frequencies calc.(cm ⁻¹)	
v ₆₀	CCC bend (F)	109	732	
v₆₁	CCC bend	219	763	753
v ₆₂	C-H bend (F, out of plane)	2	770	
v ₆₃	C-H bend (F, out of plane)	80	771	
v ₆₄	(CH ₂)OH bend (G)	53	802	
v ₆₅	C-H bend + CCC bend (F)	34	813	
v ₆₆	C-H bend + CCC bend (F)	233	817	
v ₆₇	Ring deformation	147	822	
v₆₈	O-H bend & CNC bend (G) + C-H bend (F)	240	825	831
v ₆₉	C-H bend (F, out of plane)	74	839	
v ₇₀	Ring deformation	68	849	
v ₈₃	CCC bend (F) + C-N stretch (G)	39	991	
v₈₄	C-C stretch + C-O stretch (G)	309	1011	1007
v₈₅	C-C stretch (F)	630	1022	1026
v ₈₆	NH ₂ rock + C-O stretch (G)	55	1031	
v ₈₇	NH ₂ rock + C-C stretch + C-O stretch + C-N stretch (G)	46	1033	
v ₈₈	NH ₂ rock + C-O stretch + C-N stretch (G)	102	1051	
v ₉₈	C-N stretch + C-C stretch (G) + C-H bend (All)	133	1144	
v₉₉	C-H bend (F, in the plane)	434	1147	
v₁₀₀	C8-H bend + O-H bend + C-H bend (G)	282	1155	1156
v ₁₀₁	C-H bend (in the plane) + C-CH ₂ stretch + CH ₂ wag (F)	232	1171	
v ₁₀₂	C8-H bend (G)	98	1174	
v ₁₀₃	C-CH ₂ stretch + C-H bend (in the plane) + CH ₂ wag (F)	660	1188	
v ₁₀₄	C-H bend + O-H bend (G)	45	1199	
v ₁₀₅	C-H bend (All)	25	1204	
v ₁₀₆	C-H bend + O-H bend (G)	85	1205	
v ₁₀₇	C-H bend + O-H bend (G)	54	1225	
v₁₀₈	C-H bend + O-H bend (G)	28	1244	
v₁₀₉	C8-H bend (G) + N-H bend + C-C stretch + C-H bend (F)	812	1250	1248
v ₁₁₀	C-C stretch + C-N stretch + C-H bend + O-H bend (G)	869	1264	
v ₁₁₁	C-H bend + O-H bend + C-C stretch + C-N stretch (G)	147	1269	
v ₁₁₂	C8-H bend (G) + CH ₂ wag + C-H bend (F)	176	1272	
v ₁₁₃	C-H bend + C-N stretch C-CH ₂ stretch (F)	70	1282	
v₁₁₄	C-H bend (G)	318	1287	
v₁₁₅	C-C stretch + C-H bend (F) + C8-H bend (G)	1549	1296	1290
v₁₁₆	C-H bend + O-H bend (G)	385	1311	1304
v ₁₁₇	N-H bend (G, in the plane)	37	1325	
v₁₁₈	C-H bend (G)	1525	1338	1336
v₁₁₉	C-H bend + O-H bend (G)	547	1342	
v ₁₂₀	C-C stretch + N-H bend (F) + C-H bend (G)	606	1346	
v ₁₂₁	CH ₂ bend (scissor) (F)	52	1366	
v ₁₂₂	C-H bend + O-H bend (G)	233	1370	
v ₁₂₃	CH ₂ bend (scissor) + C-C stretch (F)	111	1377	
v ₁₂₄	C-H bend + O-H bend (G)	351	1392	
v₁₂₅	C-C stretch + C-H bend + O-H bend (G)	2367	1411	1405
v ₁₂₆	C-H bend + O-H bend + C-C stretch (G)	596	1419	
v ₁₂₇	N-H bend + C-C stretch (F) + C8-H bend (G)	22	1425	
v ₁₂₈	(OH)CH ₂ (scissor) (G)	15	1429	
v₁₂₉	C-C stretch + C-N stretch +N-H bend (F)	566	1442	1442
v₁₃₀	C-C stretch +N-H bend (F)	647	1447	1452
v ₁₃₁	C-C stretch +N-H bend (F)	187	1475	

v₁₃₂	C-C stretch + C-N stretch +N-H bend (F) + C-N stretch (G)	247	1483	1482
v ₁₃₃	C-N stretch (G) + N-H bend (F)	196	1496	
v₁₃₄	NH2 scissor + N-H bend & C-N stretch (G) + N-H bend (F)	595	1522	1513
v ₁₃₅	NH2 scissor + N-H bend + C-C stretch & C-N stretch (G) + N-H bend (F)	150	1541	
v ₁₃₆	C-C stretch (F ring 1stronger) and N-H bend (F)	142	1569	
v₁₃₇	C-C stretch (F ring 2 stronger) and N-H bend (F)	1476	1576	1576
v₁₃₈	C-C stretch (F, ring 2 stronger)	9317	1606	1618
v₁₃₉	C-C stretch (F, ring 1 stronger)	116	1613	
v ₁₄₀	C-N stretch & NH2 scissor (G)	310	1625	
v₁₄₁	C-N stretch & NH2 scissor ()	2555	1640	1641
v ₁₄₂	C=O stretch (G)	2242	1766	

[a] Possible vibrational band assignments are also shown based on comparison with calculated vibrational frequencies from BPW91/cc-PVDZ computations in the 700-1800 cm⁻¹ fingerprint region for the ground singlet state of **C8 intermediate** (see text). F=2-fluorenylnitrenium ion, G=guanosine.

Table 3S. Comparison of the BPW91/cc-PVDZ calculated Raman vibrational frequencies for the **C8-methyl intermediate** to those observed for the 50 μs TR³ experimental spectrum of Figure 2. ^[a]

Calc.			Expt.
		Raman	Raman
		Activity	Shift
Vibrational mode possible description		BPW91/cc-PVDZ	Shift
		Frequencies	(cm ⁻¹)
		calc.(cm ⁻¹)	(cm ⁻¹)
v ₆₂	CCC bend & C-H bend (F, out of the plane)	178	728
v ₆₃	CCC bend & C-H bend (F, out of the plane)	121	732
v₆₄	CCC bend & N-H bend (F) + CNC bend & O-H bend (G)	459	746
v ₆₅	CCC bend & N-H bend (F)	13	770
v ₆₆	CC bend & CN bend (G, out of the plane) + N-H bend (F)	5	772
v ₆₇	CCC bend & N-H bend (F) + CH ₃ bend (G)	8	782
v ₆₈	CCC bend (F) + O-H bend & CNC bend (G)	2	815
v₆₉	CCC bend & N-H bend (F) + O-H bend (G)	251	818
v₇₀	C-H bend (F) + O-H bend (G)	8	824
v ₇₁	O-H bend (G)	62	833
v ₇₂	CCC bend (F) + CNC bend & COC bend (G)	28	838
v ₈₆	CCC bend (F) + CH ₃ wag & NH ₂ wag (G)	63	986
v₈₇	CCC bend (F) + CH₃ wag & NH₂ wag (G)	553	998
v₈₈	C-C stretch (G) & NH₂ wag & O-H bend (G)	374	1019
v₈₉	CCC bend (F)	581	1019
v ₉₀	C-N stretch & C-O stretch & CH ₃ wag (G)	50	1024
v ₁₀₁	CH ₂ wag (F)	4	1116
v ₁₀₂	C-C stretch (F) & C-N stretch & C-H bend (F)	253	1129
v ₁₀₃	C-N stretch & C-CH ₃ stretch (G)	399	1130
v₁₀₄	C-C stretch (F) & C-N stretch & C-H bend (F)	494	1150
v ₁₀₅	C-N stretch (G) & NH ₂ wag & O-H bend (G) + C-H bend (all)	73	1153
v ₁₀₆	C-N stretch (G) & NH ₂ wag & O-H bend (G) + C-H bend (all)	103	1165
v ₁₀₇	C-C stretch & C-H bend (F)	445	1169
v ₁₀₈	C-C stretch & C-H bend (F)	813	1188
v ₁₀₉	C-H bend & O-H bend & C-C stretch (G)	218	1202
v ₁₁₀	C-C stretch (F) + C-H bend (all)	32	1204
v ₁₁₁	C-C stretch (F) + C-H bend (all)	21	1205
v ₁₁₂	C-H bend & O-H bend (G)	69	1223
v₁₁₃	C-H bend & O-H bend (G)	28	1243
v₁₁₄	C-C stretch (all) + C-N stretch (F)	1369	1244
v ₁₁₅	C-C stretch & C-N stretch (all)	122	1257
v ₁₁₆	C-H bend & O-H bend (G)	71	1267
v ₁₁₇	C-CH ₃ stretch (G) + C-C stretch (F)	17	1271
v₁₁₈	C-H bend & O-H bend (G)	203	1285
v₁₁₉	C-C stretch (F) & C-H bend (F)	1230	1295
v ₁₂₀	C-H bend & O-H bend (G)	396	1310
v ₁₂₁	C-N stretch & N-H bend (G)	106	1325
v₁₂₂	C-C stretch (all) + C-H bend (all) & O-H bend (G) + CH₃ scissor	3130	1332
v ₁₂₃	C-C stretch (all) + C-H bend (all) & O-H bend (G) + CH ₃ scissor	163	1340
v ₁₂₄	C-C stretch (all) + C-H bend (G) & O-H bend (G)	456	1341
v ₁₂₅	CH ₃ scissor (F) & C-C stretch (F)	4	1350
v ₁₂₆	C-C stretch (F, ring 2 stronger) & CH ₂ scissor (F)	49	1366
v ₁₂₇	CH ₂ scissor & O-H bend (G)	261	1368
v ₁₂₈	C-C stretch (F, ring 2 stronger) & N-H bend & CH ₂ scissor (F)	51	1376
v₁₂₉	CH₃ wag & O-H bend (G) + C-C stretch (all)	282	1401
v₁₃₀	CH₃ wag & O-H bend (G)	389	1401
v ₁₃₁	C-C stretch (G) + N-H bend + CH ₃ scissor + O-H bend	1536	1413
v ₁₃₂	C-C stretch (F, ring 1 stronger, G) & N-H bend (F) + CH ₃ scissor	2788	1420
v ₁₃₃	C-C stretch (F, ring 1 stronger, G) & N-H bend (F) + CH ₂ scissor + CH ₃ scissor	126	1428
v ₁₃₄	C-C stretch (F, ring 1 stronger, G) & N-H bend (F) + CH ₂ scissor + CH ₃ scissor	321	1428

v₁₃₅	CH2 scissor (G) & O-H bend (G)	110	1432	
v₁₃₆	C-C stretch (F, both ring 1 and 2 symmetry) & N-H bend (F) + C-C stretch (G)	278	1440	1436
v₁₃₇	C-C stretch (F, both ring 1 and 2 symmetry) & N-H bend (F) + C-C stretch (G)	642	1444	1452
v₁₃₈	C-C stretch (F, both ring 1 and 2 symmetry) & N-H bend (F) + C-N stretch (G)	86	1471	
v₁₃₉	C-C stretch (F, both ring 1 and 2 symmetry) & N-H bend (F)	657	1476	1476
v₁₄₀	C-N stretch (G) + N-H bend (F)	244	1496	
v₁₄₁	C-N stretch & N-H bend & NH2 scissor (G) + C-C stretch (F)	1581	1522	1510
v₁₄₂	C-N stretch & N-H bend & NH2 scissor (G)	83	1544	
v₁₄₃	C-C stretch (ring 1 stronger) & N-H bend (F)	604	1567	
v₁₄₄	C-C stretch (ring 2 stronger) & N-H bend (F)	1315	1578	1576
v₁₄₅	C-C stretch (F, both ring 1 and 2 symmetry) + C-N stretch (all)	8442	1607	1613
v₁₄₆	C-C stretch (F, both ring 1 and 2 symmetry) & C-N stretch (F)	1269	1610	
v₁₄₇	C-N stretch & NH2 scissor (G)	107	1626	
v₁₄₈	C-N stretch & NH2 scissor (G)	2191	1640	1639
v₁₄₉	C=O stretch & N-H bend (G)	2669	1768	

[a] Possible vibrational band assignments are also shown based on comparison with calculated vibrational frequencies from BPW91/cc-PVDZ computations in the 700-1800 cm⁻¹ fingerprint region for the ground singlet state of **C8-methyl intermediate** (see text). F=2-fluorenylnitrenium ion, G=C8-methylguanosine.

Table 4S. Comparison of the BPW91/cc-PVDZ calculated Raman vibrational frequencies for the **C8-bromo intermediate** to those observed for the 50 μ s TR³ experimental spectrum of Figure 2. ^[a]

Calc.			BPW91/cc-PVDZ	Expt.
	Vibrational mode possible description	Raman Activity	Frequencies calc.(cm ⁻¹)	Raman shift (cm ⁻¹)
v ₆₀	NCN bend & O-H bend (G)	11	705	
v ₆₁	CCC bend (F) + COC bend & CNC bend (G)	49	722	
v ₆₂	C-H bend (out of the plane) & CH ₂ rock & CCC bend (F)	2	728	
v₆₃	CCC bend + CNC bend & C-Br bend (G)	55	731	749
v ₆₄	CCC bend	34	767	
v ₆₅	CCC bend	41	768	
v₇₁	CCC bend + CNC bend (G)	81	824	827
v ₇₂	C-H bend (out of the plane) (F)	1	834	
v ₇₃	CNC bend & C-C stretch (G)	147	853	
v ₇₄	C-H bend (out of the plane) (F) + CNC bend & C-C stretch (G)	139	857	
v ₇₅	C-H bend (out of the plane) (F) + CNC bend & C-C stretch (G)	187	857	
v ₈₄	CCC bend (F) + C-N stretch & NH ₂ rock (G)	400	989	
v ₈₅	CCC bend (F) + C-N stretch & C-C stretch & NH ₂ rock (G)	72	993	
v₈₆	C-H bend (F, in the plane) + CNC bend & C-C stretch & NH2 rock (G)	240	1014	1003
v ₈₇	C-N stretch & C-C stretch (G) + C-Br bend	67	1017	
v₈₈	C-C stretch (F)	537	1021	1022
v ₈₉	C-N stretch & C-O stretch & NH ₂ rock (G) + C-Br bend	42	1028	
v ₉₀	C-N stretch & C-O stretch (G) + C-Br bend	613	1041	
v₁₀₁	C-H bend (in the plane) & C-C stretch (F)	226	1149	1152
v ₁₀₂	(CH)OH bend (G)	85	1158	
v ₁₀₃	C-H bend (in the plane) & C-C stretch (F)	400	1172	
v ₁₀₄	C-H bend (in the plane) & C-C stretch (F)	396	1188	
v ₁₀₅	N-H bend (F) + C-H bend & O-H bend (G)	199	1204	
v ₁₀₆	N-H bend (F) + C-H bend + O-H bend (G)	86	1207	
v ₁₀₇	C-H bend + C-C stretch (F) + O-H bend (G)	109	1210	
v ₁₀₈	C-H bend & O-H bend (G)	75	1222	
v₁₀₉	C-C stretch (F) + C-C stretch & C-H bend & O-H bend (G)	29	1242	1247
v ₁₁₀	C-C stretch & N-H bend (F) + C-C stretch & C-N stretch & O-H bend (G)	85	1254	
v ₁₁₁	C-C stretch & C-N stretch (F) + C-C stretch & C-N stretch & O-H bend (G)	87	1263	
v ₁₁₂	C-C stretch + C-N stretch	94	1264	
v₁₁₃	C8-N34 stretch + C-H bend + C-Br bend	907	1285	1287
v₁₁₄	C-C stretch & C-N stretch & N-H bend (F)	59	1292	
v₁₁₅	C-C stretch (F) + C8-N34 stretch + C-H bend	540	1295	1303
v₁₁₆	C-C stretch (F) + C8-N34 stretch + C-H bend + C-Br bend	55	1302	
v ₁₁₇	C8-N34 stretch + C-H bend & N-H bend (G)	30	1315	
v₁₁₈	C-N stretch & N-H bend (in the plane) (G)	609	1326	
v₁₁₉	C-C stretch (F) + C-C stretch & C-H bend & O-H bend (G)	1015	1336	1332
v ₁₂₀	C-C stretch & C-H bend & O-H bend (G)	1582	1343	
v ₁₂₁	C-C stretch & N-H bend (F) + C-C stretch & C-H bend (G)	888	1357	
v ₁₂₂	C-C stretch & CH ₂ scissor (F)	43	1367	
v ₁₂₃	C-C stretch (F) + O-H bend & C-H bend (G)	422	1369	
v ₁₂₄	C-C stretch & CH ₂ scissor (F)	94	1378	
v₁₂₅	(CH)OH bend (G)	177	1400	
v₁₂₆	C-C stretch & N-H bend (F) + C-C stretch & C-N stretch & O-H bend (G)	1969	1415	1404
v ₁₂₇	CH ₂ scissor (G)	56	1424	
v ₁₂₈	C-C stretch & N-H bend (F)	47	1427	
v₁₂₉	C-C stretch (F) + O-H bend (G)	198	1434	1438
v ₁₃₀	C-C stretch (both ring 1 and 2) & N-H bend (F) + C-C stretch & C-N stretch(G)	305	1445	
v₁₃₁	C-C stretch (F, both ring 1 and 2) + C-C stretch (G)	425	1451	1454
v₁₃₂	C-C stretch (both ring 1 and 2) & N-H bend (F)	130	1478	1475
v ₁₃₃	C-N stretch (G) + C-C stretch & N-H bend (F)	344	1484	

ν_{134}	C-N stretch & C-C stretch & NH₂ scissor (G) + C-C stretch & N-H bend (F)	60	1504	1510
ν_{135}	C-N stretch & NH ₂ scissor (G) + C-C stretch & N-H bend (F)	209	1523	
ν_{136}	C-N stretch & NH ₂ scissor (G)	259	1542	
ν_{137}	C-C stretch (both ring 1 and 2) & N-H bend (F)	450	1556	
ν_{138}	C-C stretch (F, both ring 1 and 2) & N-H bend (F)	496	1571	1575
ν_{139}	C-C stretch (F, ring 2 stronger) + C-N stretch (G)	5860	1604	
ν_{140}	C-C stretch (F, ring 1 stronger) + C-N stretch & NH₂ scissor & O-H bend (G)	619	1615	1614
ν_{141}	C-C stretch (F, ring 1 stronger) + C-N stretch (G)	267	1621	
ν_{142}	C-N stretch & NH₂ scissor (G)	908	1635	1646
ν_{143}	C=O stretch (G)	1309	1771	

[a] Possible vibrational band assignments are also shown based on comparison with calculated vibrational frequencies from BPW91/cc-PVDZ computations in the 700-1800 cm⁻¹ fingerprint region for the ground singlet state of **C8-bromo intermediate** (see text). F=2-fluorenylnitrenium ion, G=C8-bromoguanosine.

Table 5S. Selected bond lengths determined from the BPW91/cc-PVDZ calculated optimized geometries for guanosine, C8-bromoguanosine and C8-methylguanosine.

	Bond Length (Å)		
	C8-bromoguanosine	guanosine	C8-methylguanosine
N1-C2	1.3719	1.3715	1.3708
N1-C6	1.4555	1.4573	1.4569
C2-N3	1.3309	1.3299	1.3287
C2-N11	1.3782	1.3753	1.3816
N3-C4	1.3618	1.3644	1.3653
C4-C5	1.4031	1.4052	1.4031
C4-N9	1.3885	1.3815	1.3846
C5-C6	1.4484	1.4472	1.4469
C5-N7	1.3878	1.3876	1.3858
C6-O10	1.2249	1.2239	1.2263
N7-C8	1.3111	1.3187	1.3239
C8-N9	1.4028	1.3959	1.4074
C8-R12 (R=Br,Me)	1.8895	1.0593	1.4945
N9-C13	1.4704	1.4598	1.4597

Cartesian coordinates, total energies, and vibrational zero-point energies for the optimized geometry from the BPW91/cc-PVDZ calculations for the **C8 intermediate**, the **C8-methyl intermediate**, the **C8-bromo intermediate**, guanosine, C8-methylguanosine, C8-bromoguanosine and the 2-fluorenylnitrenium ion.

C8 intermediate

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	4.228425	3.340579	-0.339871
2	6	0	4.816122	2.119964	-0.109538
3	7	0	4.119019	0.974982	0.044748
4	6	0	2.793297	1.088953	-0.084931
5	6	0	2.057971	2.318590	-0.398458
6	6	0	2.816203	3.585154	-0.487817
7	7	0	0.776480	2.120738	-0.593056
8	6	0	0.545685	0.703032	-0.355909
9	7	0	1.875185	0.116990	0.012621
10	8	0	2.398578	4.712089	-0.672163
11	7	0	6.154013	2.028430	-0.019883
12	1	0	0.201136	0.230113	-1.296197
13	6	0	2.047411	-1.302300	0.320397
14	8	0	3.007118	-1.445746	1.340824
15	6	0	3.787417	-2.673482	1.121308
16	6	0	3.235484	-3.315725	-0.172519
17	6	0	2.539350	-2.143579	-0.900219
18	6	0	5.268542	-2.283697	1.098597
19	8	0	2.180495	-4.256221	0.089605
20	8	0	1.505709	-2.528899	-1.768443
21	8	0	5.591922	-1.425427	0.010038
22	1	0	4.802595	4.185917	-0.424543
23	1	0	6.778331	2.819537	-0.164588
24	1	0	6.552746	1.094159	0.112669
25	1	0	1.037908	-1.649584	0.637839
26	1	0	3.587942	-3.350098	1.978576
27	1	0	5.518382	-1.827427	2.084527
28	1	0	5.886033	-3.199331	0.997233
29	1	0	4.995050	-0.637175	0.100071
30	1	0	4.037989	-3.760465	-0.793077
31	1	0	2.564380	-5.151181	0.142450
32	1	0	3.291861	-1.558259	-1.462774
33	1	0	1.194715	-3.386623	-1.389486
34	7	0	-0.453823	0.466933	0.675115
35	1	0	-0.340189	1.132029	1.449167
36	6	0	-2.180736	-0.644679	-0.683763
37	6	0	-1.814024	0.275427	0.331723
38	6	0	-2.814496	0.950581	1.073066
39	6	0	-4.155362	0.680398	0.811430
40	6	0	-4.525917	-0.240196	-0.209892
41	6	0	-3.526126	-0.899938	-0.956695

42	6	0	-5.396065	1.255402	1.461845
43	6	0	-6.519643	0.575951	0.705568
44	6	0	-5.984833	-0.304012	-0.279165
45	6	0	-7.902436	0.710369	0.856674
46	6	0	-8.751924	-0.037377	0.019606
47	6	0	-8.224550	-0.908114	-0.957018
48	6	0	-6.840020	-1.049364	-1.115869
49	1	0	-1.405638	-1.187224	-1.242657
50	1	0	-2.526337	1.677950	1.846266
51	1	0	-3.791875	-1.617804	-1.743323
52	1	0	-5.431063	1.033475	2.548866
53	1	0	-5.438370	2.360541	1.368117
54	1	0	-8.325298	1.385894	1.612738
55	1	0	-9.840618	0.058232	0.127649
56	1	0	-8.908182	-1.479866	-1.598352
57	1	0	-6.435126	-1.728073	-1.878328

SCF Done: E(RB-PW91) = -1594.67504895 A.U. after 8 cycles
Zero-point correction= 0.438854 (Hartree/Particle)

C8-methyl intermediate

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-3.470434	3.633900	0.205231
2	6	0	-4.280998	2.554813	-0.055965
3	7	0	-3.843989	1.279057	-0.042362
4	6	0	-2.550786	1.112061	0.250415
5	6	0	-1.597830	2.175315	0.572035
6	6	0	-2.063694	3.578380	0.513279
7	7	0	-0.409512	1.721332	0.880190
8	6	0	-0.457726	0.266027	0.744205
9	7	0	-1.873674	-0.042309	0.308862
10	8	0	-1.429267	4.600035	0.692539
11	7	0	-5.579118	2.740776	-0.348357
12	1	0	-0.146090	-0.390277	2.089285
13	6	0	-2.328485	-1.367115	-0.130095
14	8	0	-3.038886	-1.212727	-1.342863
15	6	0	-4.142053	-2.181342	-1.413011
16	6	0	-4.093630	-2.990124	-0.098350
17	6	0	-3.286853	-2.091166	0.869891
18	6	0	-5.441069	-1.411156	-1.670811
19	8	0	-3.309717	-4.189058	-0.225312
20	8	0	-2.626501	-2.803657	1.882471
21	8	0	-5.823511	-0.590871	-0.570452
22	1	0	-3.845590	4.587334	0.166108
23	1	0	-6.021936	3.657138	-0.371865
24	1	0	-6.138433	1.902631	-0.545161
25	1	0	-1.395048	-1.957027	-0.266293
26	1	0	-3.932316	-2.858465	-2.267487
27	1	0	-5.312154	-0.825255	-2.610465
28	1	0	-6.262274	-2.135271	-1.848038
29	1	0	-5.036662	-0.011806	-0.383534
30	1	0	-5.105666	-3.201633	0.298328
31	1	0	-3.909658	-4.935978	-0.407405
32	1	0	-3.960750	-1.343774	1.330940
33	1	0	-2.493590	-3.698041	1.484097
34	7	0	0.442773	-0.156201	-0.361278
35	1	0	0.236863	0.438442	-1.174126
36	6	0	2.393939	-1.396152	0.479062
37	6	0	1.851912	-0.259370	-0.174281
38	6	0	2.717519	0.715296	-0.729705
39	6	0	4.095511	0.540631	-0.632009
40	6	0	4.637826	-0.595388	0.038065
41	6	0	3.776658	-1.562861	0.594296
42	6	0	5.216433	1.423106	-1.140146
43	6	0	6.459688	0.677604	-0.698791
44	6	0	6.097522	-0.511808	-0.004722
45	6	0	7.806106	1.004232	-0.885125

46	6	0	8.790801	0.137115	-0.376074
47	6	0	8.433948	-1.041394	0.312052
48	6	0	7.087424	-1.375978	0.504761
49	1	0	1.717106	-2.171635	0.856316
50	1	0	2.293913	1.603399	-1.220217
51	1	0	4.177302	-2.455568	1.091682
52	1	0	5.174361	1.548816	-2.242162
53	1	0	5.166521	2.444304	-0.708076
54	1	0	8.097031	1.919134	-1.419061
55	1	0	9.852410	0.380818	-0.516396
56	1	0	9.220895	-1.701523	0.699946
57	1	0	6.815081	-2.294396	1.041699
58	1	0	-0.817920	0.027869	2.860454
59	1	0	0.896373	-0.167406	2.373025
60	1	0	-0.311555	-1.480455	2.041075

SCF Done: E(RB-PW91) = -1633.98458435 A.U. after 13 cycles
Zero-point correction= 0.465660 (Hartree/Particle)

C8-bromo intermediate

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-3.604197	3.444872	-0.906247
2	6	0	-4.332755	2.284824	-1.002278
3	7	0	-3.824655	1.068881	-0.704152
4	6	0	-2.544630	1.060533	-0.330110
5	6	0	-1.668150	2.212448	-0.221556
6	6	0	-2.215622	3.548165	-0.527979
7	7	0	-0.440958	1.882817	0.121499
8	6	0	-0.467020	0.474640	0.321640
9	7	0	-1.795586	-0.022719	-0.021030
10	8	0	-1.661038	4.628859	-0.496079
11	7	0	-5.611609	2.319245	-1.413083
12	35	0	-0.321134	0.398493	2.537794
13	6	0	-2.235309	-1.430739	0.006901
14	8	0	-2.683668	-1.753528	-1.295130
15	6	0	-3.817661	-2.693560	-1.224728
16	6	0	-4.033572	-2.984518	0.272518
17	6	0	-3.406518	-1.765747	0.997852
18	6	0	-5.019829	-2.079125	-1.949179
19	8	0	-3.263059	-4.112311	0.721403
20	8	0	-3.012040	-2.036929	2.307090
21	8	0	-5.600898	-0.992629	-1.233160
22	1	0	-4.033446	4.347324	-1.135682
23	1	0	-6.086053	3.178335	-1.684228
24	1	0	-6.099095	1.421850	-1.514816
25	1	0	-1.341503	-2.017805	0.316852
26	1	0	-3.500150	-3.619458	-1.747533
27	1	0	-5.803680	-2.855493	-2.062341
28	1	0	-4.695710	-1.787480	-2.975172
29	1	0	-4.862864	-0.350307	-1.061571
30	1	0	-5.106377	-3.088331	0.525592
31	1	0	-3.833196	-4.903297	0.710863
32	1	0	-4.126706	-0.927268	1.003990
33	1	0	-2.787633	-2.997339	2.296073
34	7	0	0.554619	-0.246243	-0.288580
35	1	0	0.261973	-1.121139	-0.726906
36	6	0	2.512054	1.048671	0.488795
37	6	0	1.934662	-0.043605	-0.212621
38	6	0	2.757623	-0.993405	-0.880247
39	6	0	4.136382	-0.852020	-0.820312
40	6	0	4.723895	0.237344	-0.106950
41	6	0	3.898895	1.181365	0.543473
42	6	0	5.221530	-1.717867	-1.425657
43	6	0	6.491729	-1.010763	-0.998476
44	6	0	6.174091	0.140824	-0.218150
45	6	0	7.823735	-1.336773	-1.265217
46	6	0	8.839690	-0.509373	-0.749301

47	6	0	8.528331	0.630368	0.024145
48	6	0	7.197237	0.965859	0.296801
49	1	0	1.867253	1.785537	0.975949
50	1	0	2.299426	-1.830765	-1.427205
51	1	0	4.334647	2.025904	1.092335
52	1	0	5.131924	-1.784790	-2.529810
53	1	0	5.178217	-2.759565	-1.044956
54	1	0	8.081270	-2.220364	-1.864849
55	1	0	9.891306	-0.754095	-0.950670
56	1	0	9.340475	1.257601	0.414543
57	1	0	6.959227	1.852836	0.898721

SCF Done: E(RB-PW91) = -4168.38109677 A.U. after 12 cycles
Zero-point correction= 0.427936 (Hartree/Particle)

Guanosine

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	3.314429	0.989936	0.280856
2	6	0	2.087712	1.603165	0.277115
3	7	0	0.956164	0.930909	0.086362
4	6	0	1.137251	-0.403368	-0.133991
5	6	0	2.341164	-1.127730	-0.157845
6	6	0	3.587046	-0.424401	0.059724
7	7	0	2.107321	-2.471929	-0.410584
8	6	0	0.797571	-2.550000	-0.542588
9	7	0	0.141315	-1.328844	-0.379058
10	8	0	4.747796	-0.811373	0.088930
11	7	0	2.025031	2.971078	0.405231
12	1	0	0.231579	-3.465001	-0.747579
13	6	0	-1.298725	-1.098839	-0.445869
14	8	0	-1.562693	-0.068215	-1.387954
15	6	0	-2.660801	0.774489	-0.923403
16	6	0	-3.157601	0.159910	0.399651
17	6	0	-1.946609	-0.657668	0.900304
18	6	0	-2.167015	2.222358	-0.799183
19	8	0	-4.210719	-0.807689	0.197005
20	8	0	-2.293346	-1.724514	1.750528
21	8	0	-1.294334	2.418181	0.302000
22	1	0	4.166243	1.546903	0.387753
23	1	0	2.737168	3.428583	0.973948
24	1	0	1.073687	3.320687	0.554830
25	1	0	-1.745813	-2.068298	-0.759419
26	1	0	-3.468803	0.722763	-1.685719
27	1	0	-1.699974	2.505520	-1.772129
28	1	0	-3.048064	2.885463	-0.656402
29	1	0	-0.503416	1.810904	0.151385
30	1	0	-3.456756	0.936269	1.131268
31	1	0	-5.063860	-0.342653	0.255939
32	1	0	-1.248147	0.014522	1.432240
33	1	0	-3.197270	-1.972347	1.446665

SCF Done: E(RB-PW91) = -1038.76169032 A.U. after 8 cycles
Zero-point correction= 0.248297 (Hartree/Particle)

C8-methylguanosine

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	3.316598	1.197446	0.289670
2	6	0	2.090159	1.809723	0.281044
3	7	0	0.958934	1.138322	0.093925
4	6	0	1.138839	-0.199239	-0.112308
5	6	0	2.339978	-0.924456	-0.111718
6	6	0	3.586883	-0.221512	0.099654
7	7	0	2.104174	-2.271740	-0.334623
8	6	0	0.791360	-2.370411	-0.474496
9	7	0	0.140573	-1.128758	-0.349912
10	8	0	4.749047	-0.611515	0.132488
11	7	0	2.032183	3.184843	0.401971
12	6	0	0.057617	-3.651848	-0.704877
13	6	0	-1.294441	-0.872231	-0.424828
14	8	0	-1.532893	0.203296	-1.325613
15	6	0	-2.645593	1.019575	-0.851776
16	6	0	-3.159001	0.354526	0.442803
17	6	0	-1.954132	-0.479360	0.928015
18	6	0	-2.163743	2.466566	-0.677341
19	8	0	-4.201444	-0.612234	0.187333
20	8	0	-2.312699	-1.581747	1.731216
21	8	0	-1.290288	2.631641	0.427775
22	1	0	4.166926	1.759904	0.378285
23	1	0	2.707937	3.619500	1.032981
24	1	0	1.073177	3.525464	0.533872
25	1	0	-1.760825	-1.812922	-0.787837
26	1	0	-3.443117	0.985944	-1.626862
27	1	0	-1.701521	2.787302	-1.641278
28	1	0	-3.048438	3.117679	-0.507179
29	1	0	-0.506350	2.019051	0.259306
30	1	0	-3.475070	1.099857	1.199266
31	1	0	-5.058217	-0.151907	0.244311
32	1	0	-1.262157	0.169182	1.496755
33	1	0	-3.217017	-1.808340	1.412435
34	1	0	-0.489858	-3.654802	-1.669524
35	1	0	-0.674394	-3.853030	0.101979
36	1	0	0.800379	-4.467193	-0.724339

SCF Done: E(RB-PW91) = -1078.07801661 A.U. after 7 cycles

Zero-point correction= 0.274938 (Hartree/Particle)

C8-bromoguanosine

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-3.041517	1.975056	-0.6986
2	6	0	-1.755511	2.444168	-0.6081
3	7	0	-0.726100	1.658336	-0.3013
4	6	0	-1.074779	0.358193	-0.0950
5	6	0	-2.352505	-0.219909	-0.1390
6	6	0	-3.492399	0.610319	-0.4693
7	7	0	-2.298052	-1.575132	0.1546
8	6	0	-1.023731	-1.797052	0.3685
9	7	0	-0.200039	-0.669950	0.2302
10	8	0	-4.683797	0.349575	-0.5831
11	7	0	-1.507752	3.768229	-0.8995
12	35	0	-0.318200	-3.488133	0.8296
13	6	0	1.262958	-0.597248	0.3578
14	8	0	1.597079	0.490212	1.2193
15	6	0	2.664816	1.280542	0.6432
16	6	0	2.567813	1.048728	-0.8738
17	6	0	2.036722	-0.407028	-0.9763
18	6	0	2.472599	2.732852	1.0828
19	8	0	3.876163	1.174322	-1.4544
20	8	0	3.130430	-1.310221	-0.9993
21	8	0	1.304845	3.325092	0.5312
22	1	0	-3.797885	2.604528	-0.9805
23	1	0	-2.242128	4.438393	-0.6661
24	1	0	-0.569032	4.070746	-0.6139
25	1	0	1.574747	-1.565193	0.7973
26	1	0	3.652172	0.908351	1.0015
27	1	0	2.461930	2.759155	2.1978
28	1	0	3.353451	3.318070	0.7448
29	1	0	0.621408	2.599575	0.4648
30	1	0	1.855609	1.775114	-1.3088
31	1	0	3.755557	1.436411	-2.3874
32	1	0	1.364300	-0.563918	-1.8493
33	1	0	3.887411	-0.745571	-1.2886
34	1	0	-0.508992	-3.643236	-1.7421
35	1	0	-0.645135	-3.950257	0.0042
36	1	0	0.736157	-4.600350	-0.9078

SCF Done: E(RB-PW91) = -3612.46797551 A.U. after 9 cycles

Zero-point correction= 0.237802 (Hartree/Particle)

2-Fluorenylnitrenium ion

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.019556	1.516727	-0.000033
2	6	0	1.082220	0.445714	-0.000130
3	6	0	1.519530	-0.926292	-0.000118
4	6	0	2.882604	-1.222265	-0.000109
5	6	0	3.799082	-0.153137	0.000072
6	6	0	3.374234	1.202245	0.000009
7	6	0	-0.347130	0.467413	0.000168
8	6	0	-0.839134	-0.896236	0.000079
9	6	0	0.330818	-1.854409	-0.000085
10	6	0	-1.244604	1.590101	0.000226
11	6	0	-2.594431	1.354403	0.000033
12	6	0	-3.130011	-0.017970	-0.000327
13	6	0	-2.185368	-1.143529	0.000051
14	7	0	-4.401711	-0.322289	-0.000082
15	1	0	-4.984066	0.539566	0.000340
16	1	0	4.875882	-0.371180	0.000078
17	1	0	4.126124	2.001376	0.000005
18	1	0	-3.312427	2.186897	0.000126
19	1	0	3.241196	-2.259548	0.000350
20	1	0	1.686402	2.562258	-0.000319
21	1	0	-0.851520	2.614567	-0.000282
22	1	0	-2.616652	-2.153469	0.000754
23	1	0	0.321306	-2.520919	-0.887346
24	1	0	0.321532	-2.520113	0.887857

SCF Done: E(RB-PW91) = -555.858627663 A.U. after 10 cycles

Zero-point correction = 0.187915 (Hartree/Particle)