Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

SUPPORTING INFORMATION

Photochemistry of 6-amino-2-azido, 2-amino-6-azido and 2,6-diazido analogues of purine ribonucleosides in aqueous solutions

Krzysztof Komodziński,[a] Jolanta Lepczyńska,[a] Zofia Gdaniec,[b] Libero Bartolotti,[c] Bernard Delley,[d] Stefan Franzen[e] and Bohdan Skalski[*a]

[a] Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland

[b] Institute of Bioorganic Chemistry, Polish Academy of Science, Z. Noskowskiego 12/14, 61-704 Poznań, Poland

[c] Department of Chemistry, East Carolina University, Greenville, NC 27858, United States

[d] Paul-Scherer Institute WHGA, CH-5232, Villigen, Switzerland

[e] Department of Chemistry, North Carolina State University, Raleigh, NC 27695, United States

Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Table of Contents

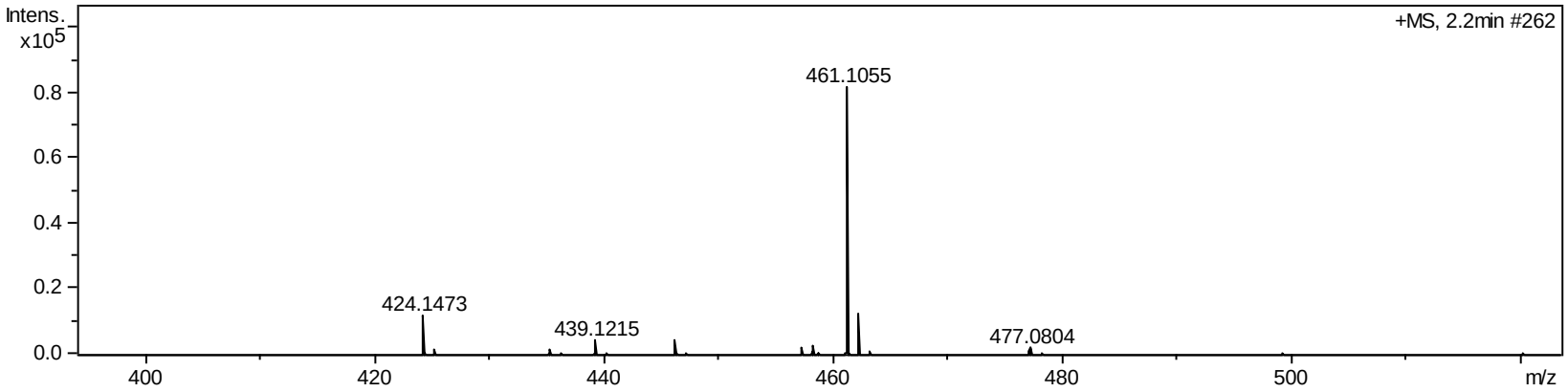

Figure S1. The HR ESI MS spectrum of photoproduct **5**.

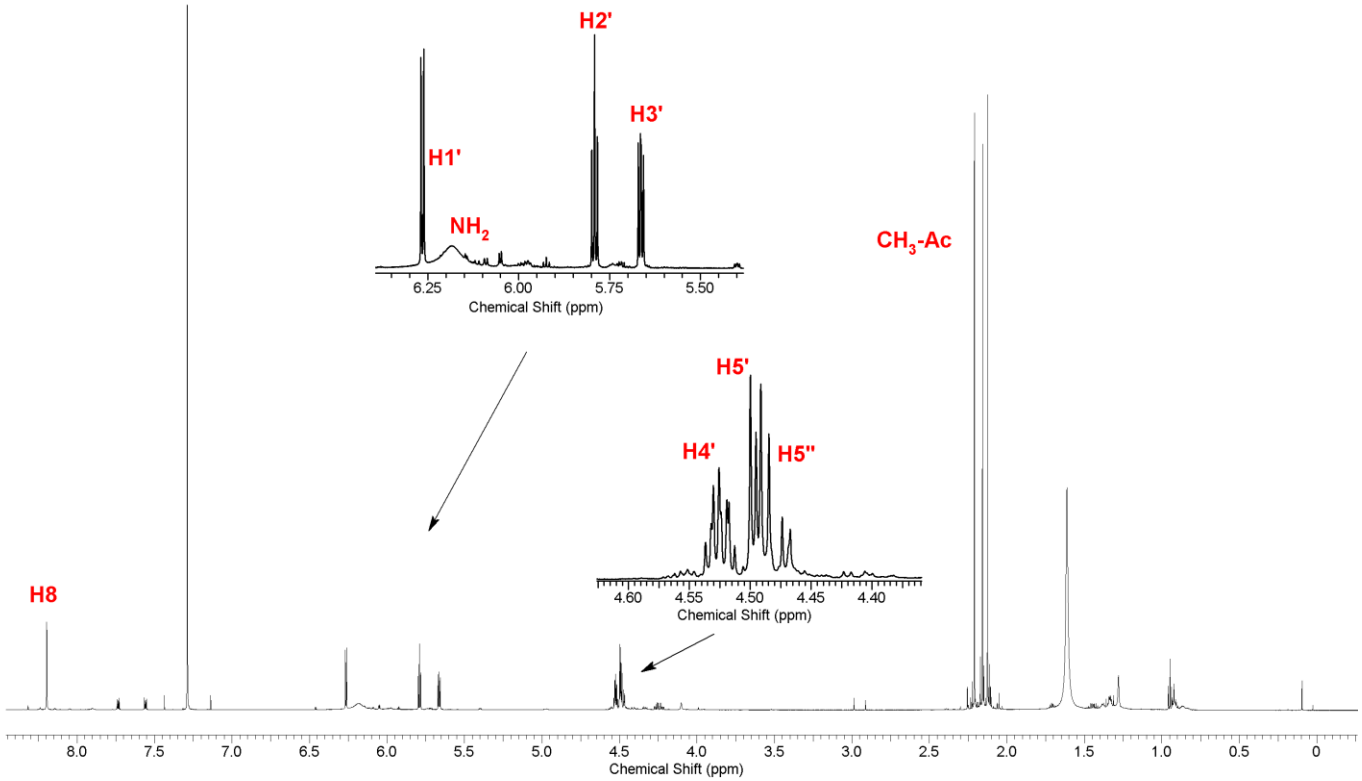

Figure S2. The ^{1}H NMR spectrum of photoproduct **5**.

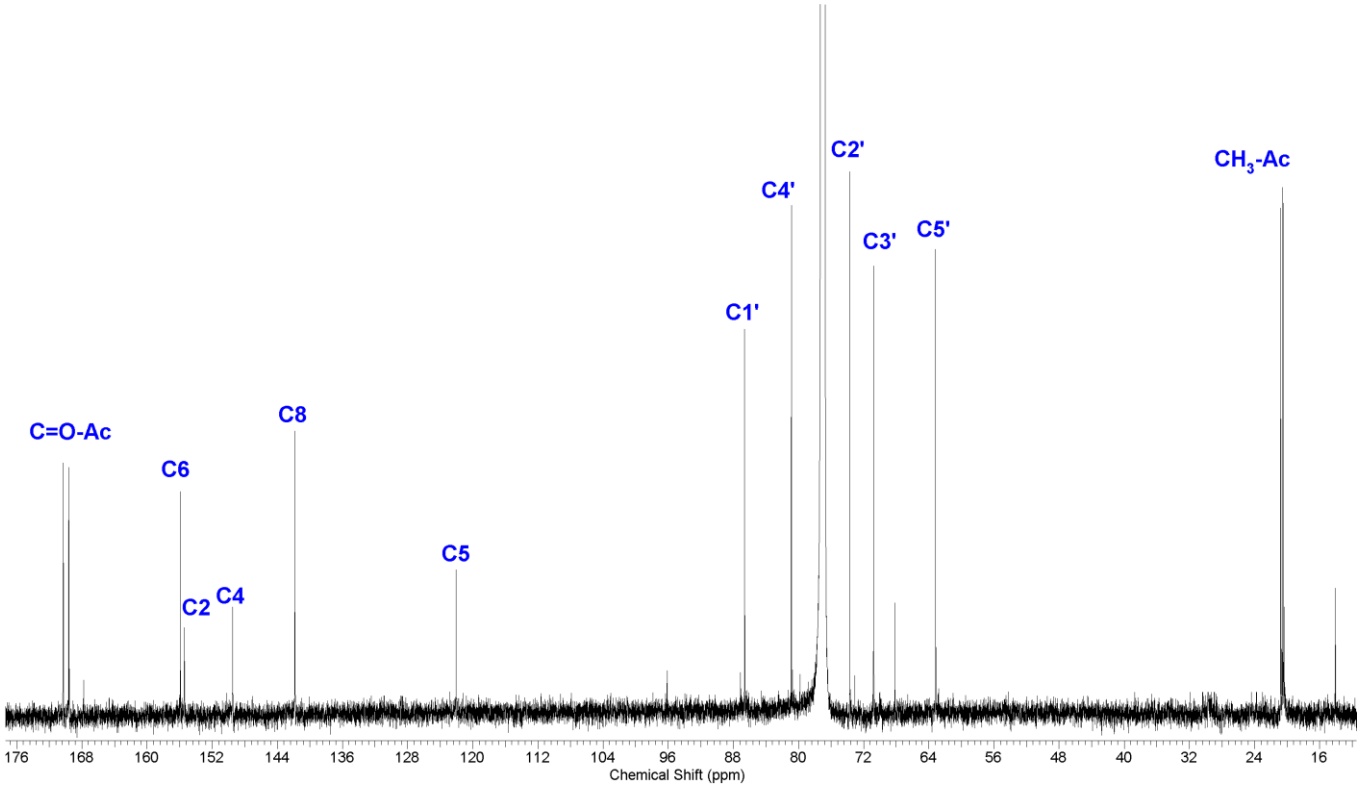

Figure S3. The ^{13}C NMR spectrum of photoproduct **5**.

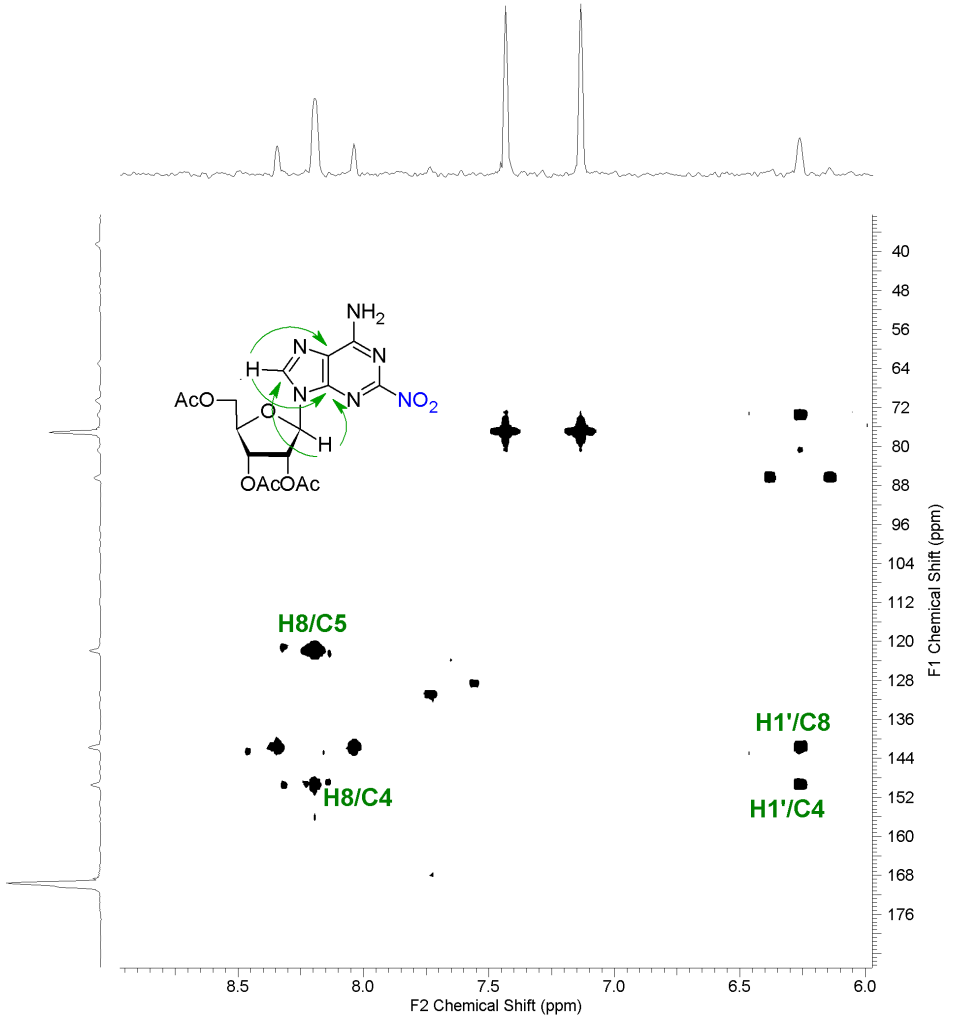

Figure S4. The ^{1}H-^{13}C HMBC spectrum of photoproduct **5**.

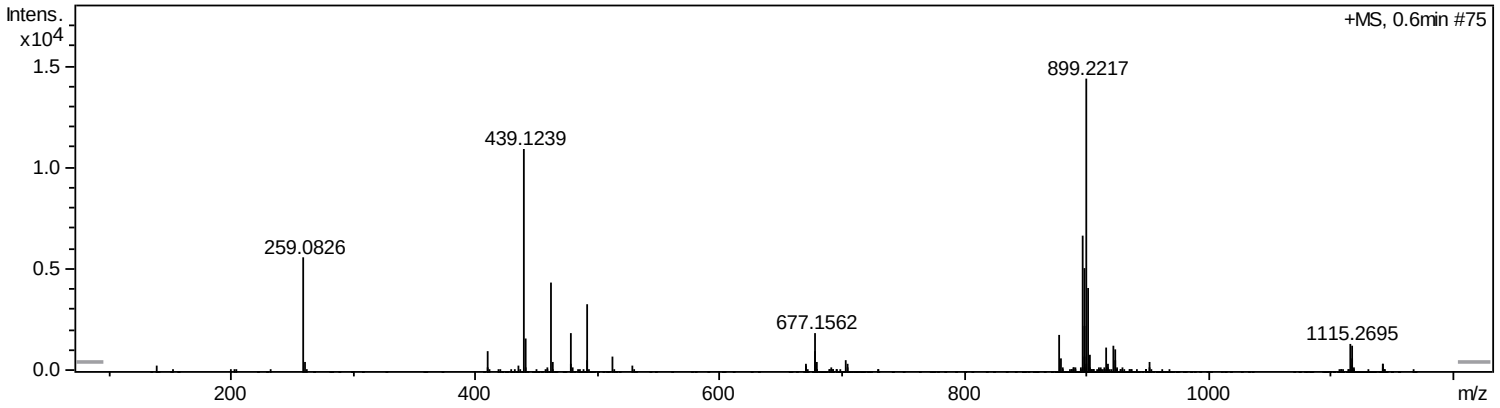

Figure S5. The HR ESI MS spectrum of photoproduct **7**.

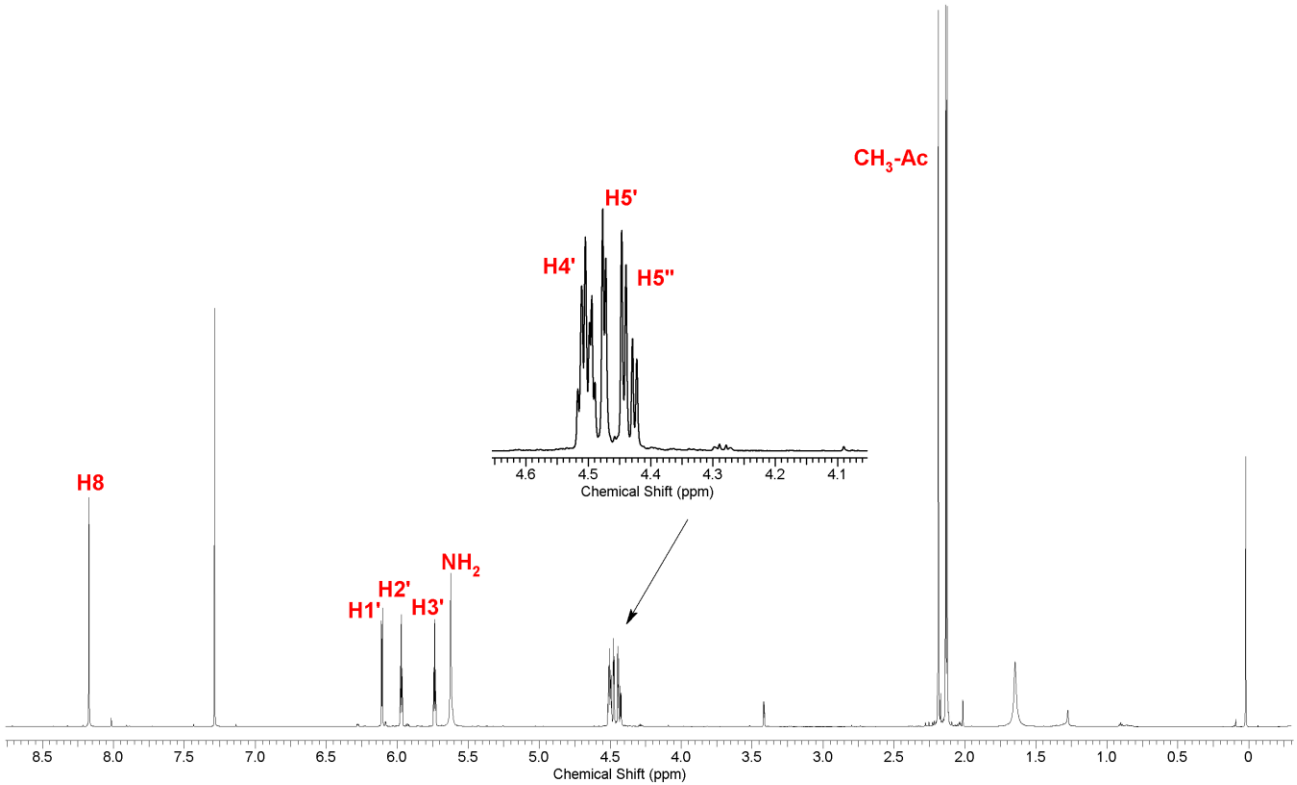

Figure S6. The ^{1}H NMR spectrum of photoproduct **7**.

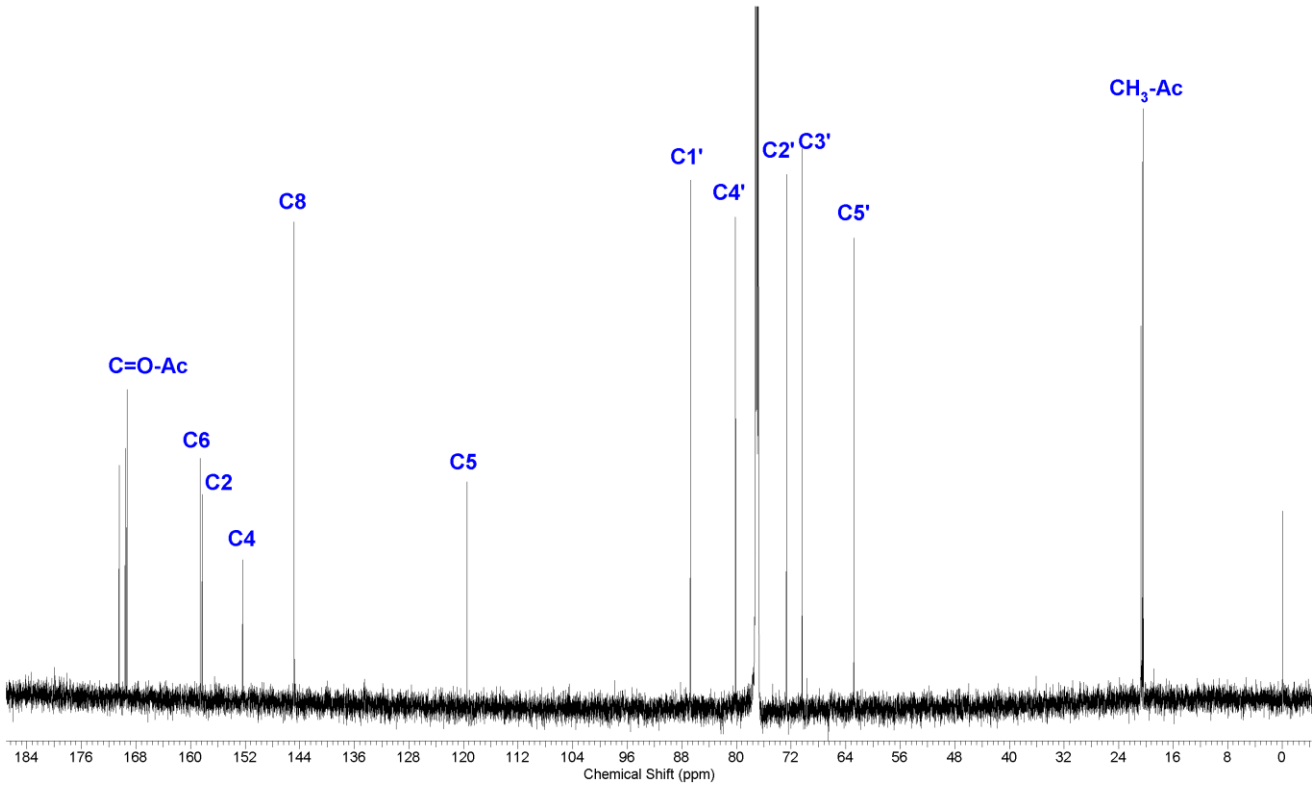

Figure S7. The ^{13}C NMR spectrum of photoproduct **7**.

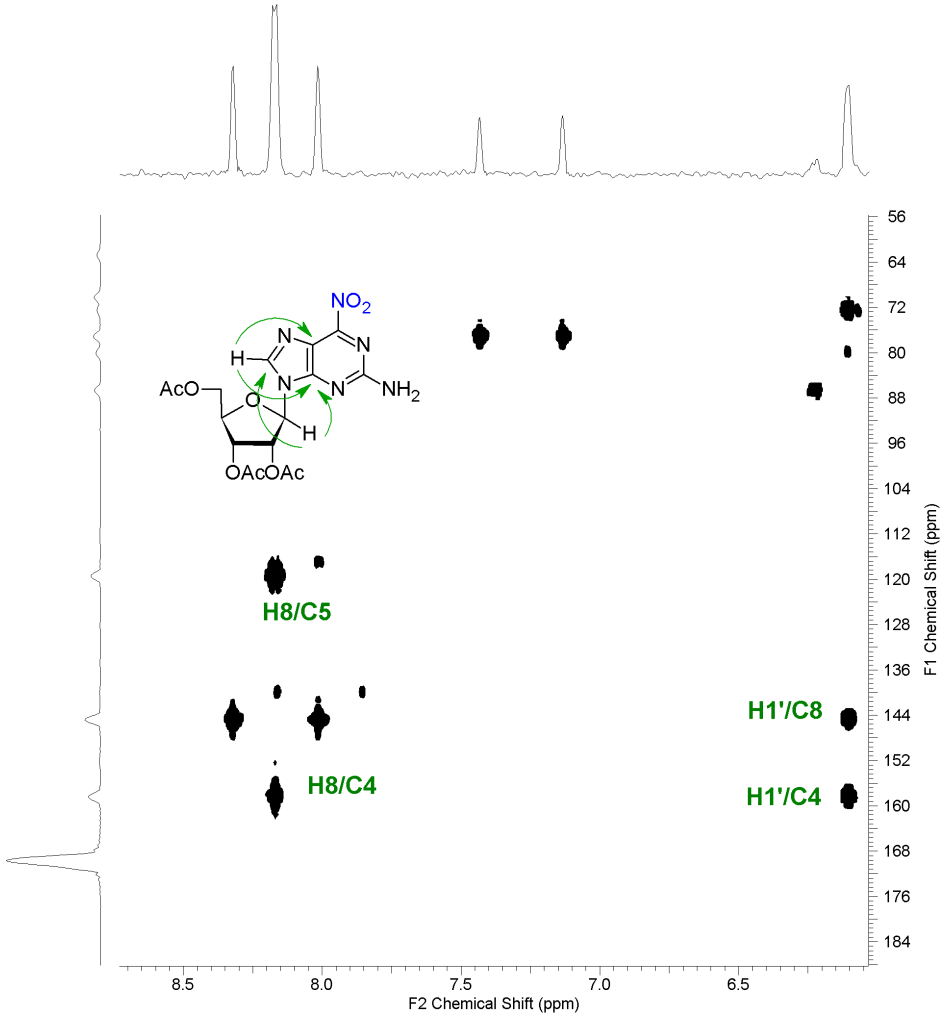

Figure S8. The ^{1}H-^{13}C HMBC spectrum of photoproduct **7**.

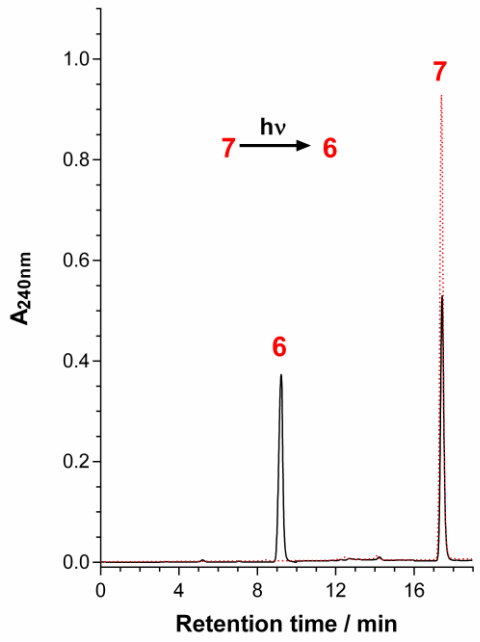

Figure S19. HPLC analysis of the solution of **7** before (dotted red line) and after 40 min photoirradiation at $\lambda > 300$ nm (solid black line).

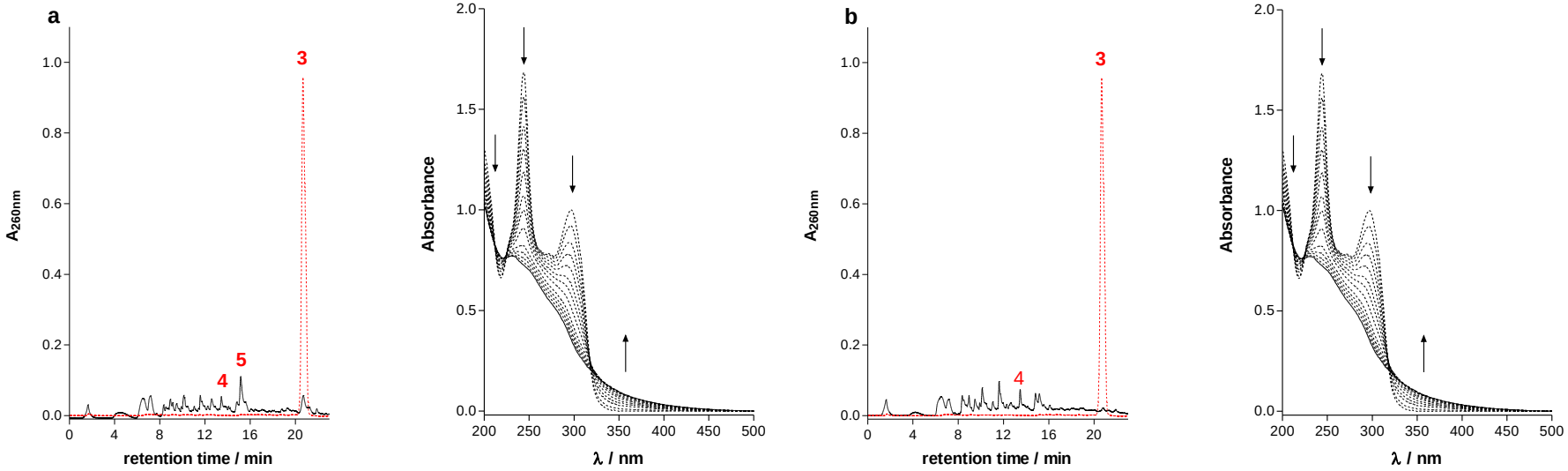

Figure S10. HPLC analysis of the solution of **3** before (dotted red line) and after 3 min irradiation (solid black line) at λ > 300 nm under aerobic (a) and anaerobic (b) conditions. Changes in the absorption spectrum of the solution of **3** during irradiation at 300 nm under aerobic (a) and anaerobic (b) conditions. The spectra were taken with 10 s time increments.

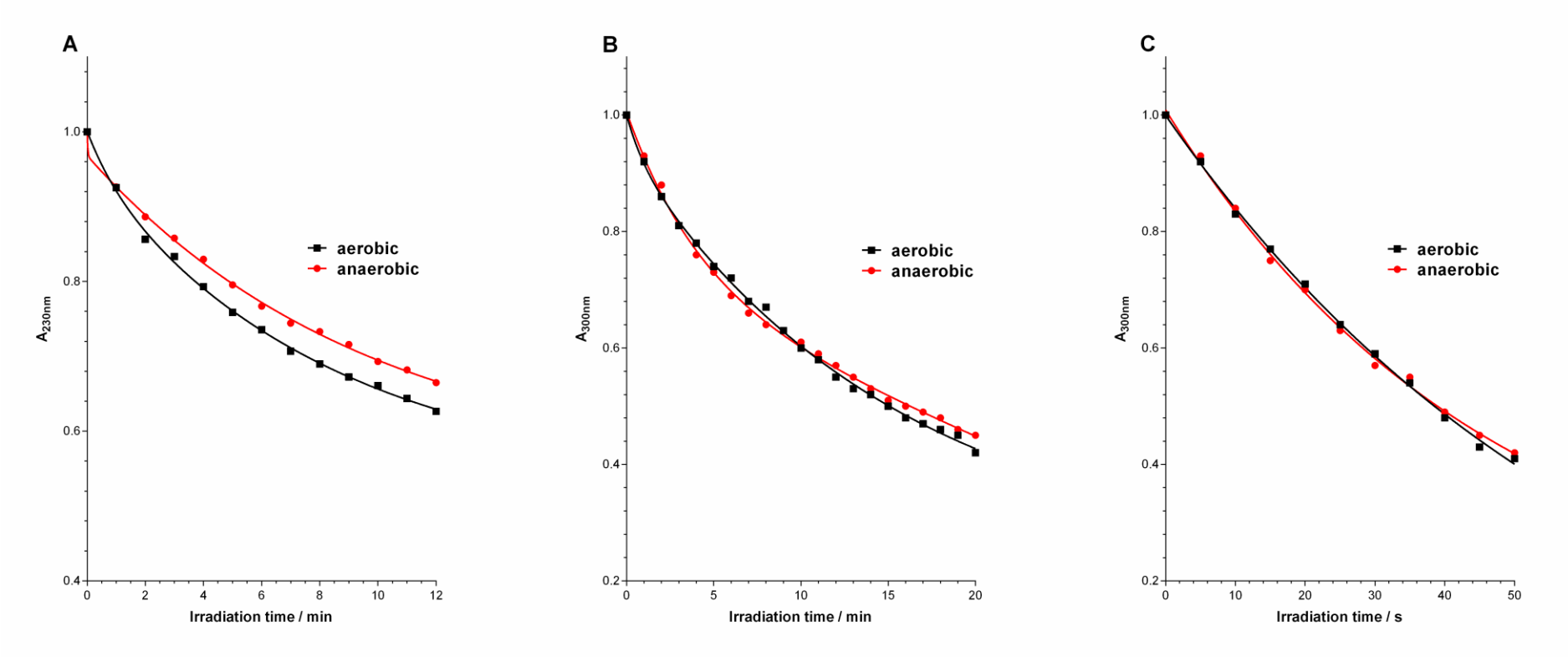

Figure S11. Comparison of the rates of disappearance of azidonucleosides **1**,**2**,**3** under aerobic and anaerobic irradiations ($\lambda > 300$ nm).

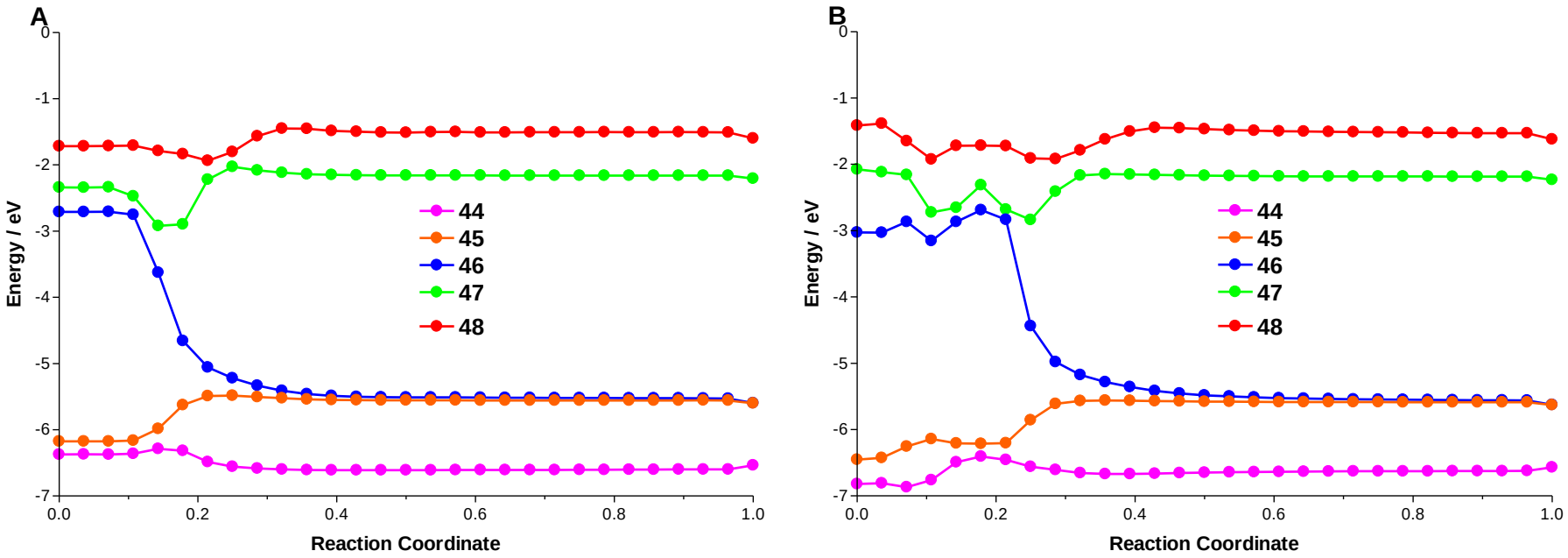

Figure S12. Energies of 5 MOs including the HOMO and LUMO in **6AzP** (A) and **TP** (B) for the structures along the bond cleavage pathway that releases N_2.

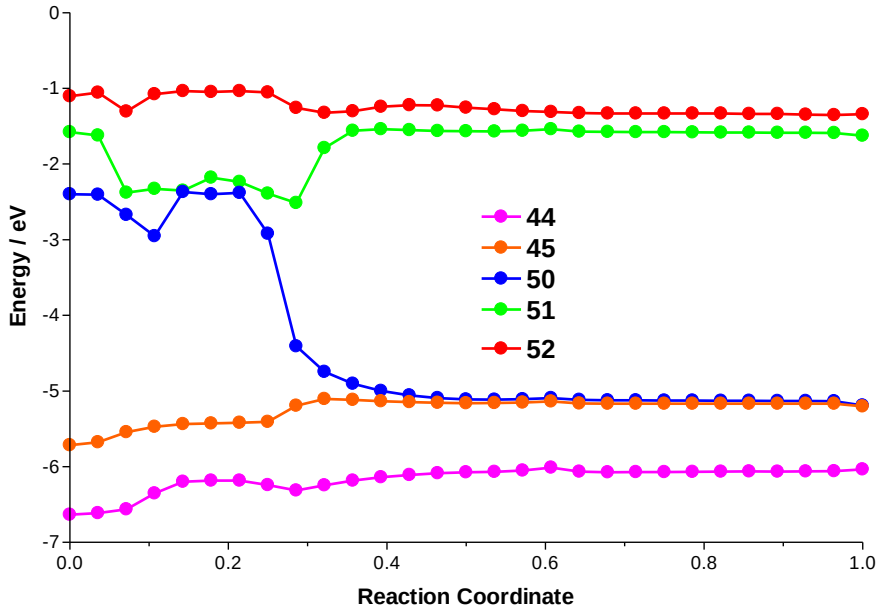

Figure S13. Energies of 5 MOs including the HOMO and LUMO in **2ATP** for the structures along the bond cleavage pathway that releases N_2.

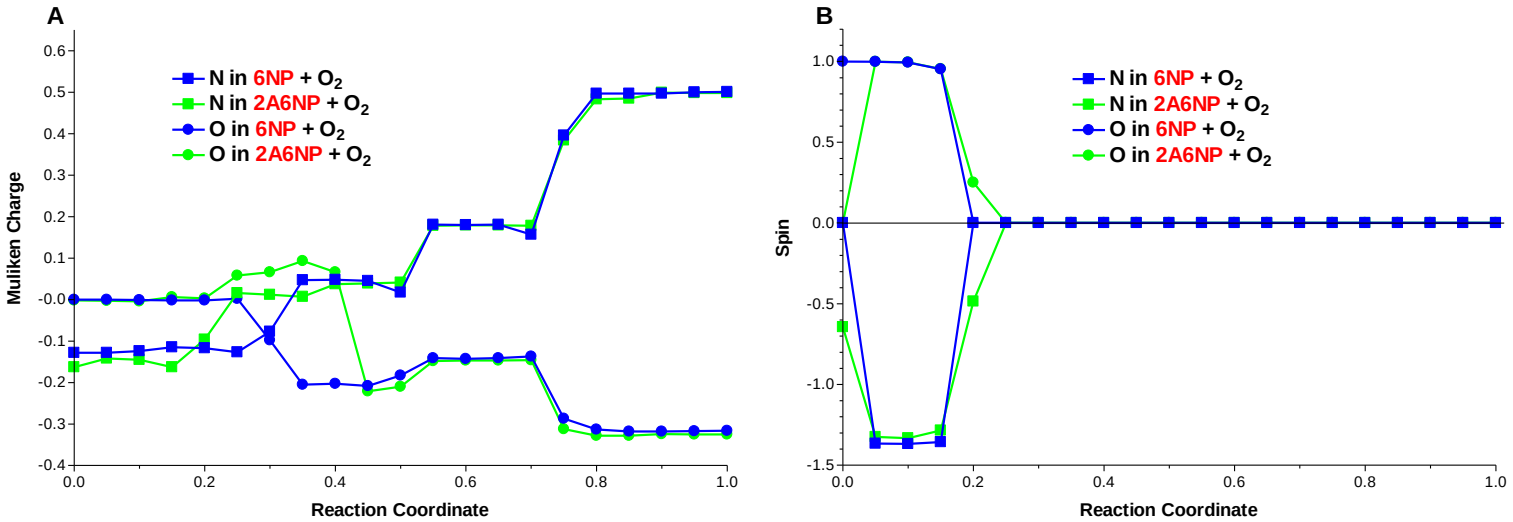

Figure S14. Mulliken charge (A) and spin (B) on the nitrene N and one of the O_2 O atoms for each of 20 structures in the NEB calculation. (The calculations address the difference in reactivity between **6NP** + O_2 and **2A6NP** + O_2. The comparisons thus far show no significant difference in the reactivity of the ring opening reaction, but there is a significant difference in the energy and detailed trajectory of the barrier for formation of the oxidation intermediates **6IP/2A6IP**. In order to examine the system in more detail, we have conducted MO and Mulliken charge calculations using unrestricted electron occupation. In this calculation the spin and charge can vary for each orbital. The result for 20 structures in the NEB calculation is shown in Figure S14. The details for the saddle point structures are provided in Tables S1 and S2. The coupling of spin on the nitrene N with the ground state triplet of the O_2 molecule is an important step in the bonding of the O_2 atom to the nitrene. Once the first contact is made between the N and O atoms the system switches to a singlet state and the differences in reactivity are then related to the occupation of the p orbitals on the nitrene N atom. These differences lead to the difference in addition of O_2 and to the formation of lower barrier for the 2-NH_2 purine relative to the 2-purine).

Table S1. Mulliken charges for the saddle points along the reaction path for 6-nitrenopurine.

		A	B	C	C
Atom	Number	Charge	Charge	Charge	Spin
N	1	-0.258	-0.266	-0.237	-0.011
C	2	0.101	0.099	0.112	0.162
N	3	-0.232	-0.242	-0.23	-0.003
C	4	0.293	0.296	0.294	0.013
C	5	0.04	0.062	0.054	0.199
N	6	-0.343	-0.351	-0.342	0.225
C	7	0.301	0.302	0.305	-0.021
N	8	-0.287	-0.297	-0.301	0.045
C	9	0.15	0.151	0.185	-0.078
H	10	0.095	0.093	0.101	-0.01
C	11	-0.185	-0.197	-0.194	0
N	12	-0.331	-0.328	-0.319	0.018
H	13	0.203	0.204	0.205	-0.001
H	14	0.211	0.211	0.214	-0.001
N	15	0.018	0.012	-0.013	0.34

O	16	-0.219	-0.222	-0.045	-0.315
O	17	0.05	0.073	-0.196	-0.561
H	18	0.135	0.127	0.132	0
H	19	0.135	0.147	0.146	-0.001
H	20	0.124	0.126	0.129	0

Table S2. Mulliken charges for the saddle points along the reaction path for 2-amino-6-nitrenopurine.

		A	B	B	C	C
Atom	Number	Charge	Charge	Spin	Charge	Spin
N	1	-0.264	-0.241	0.013	-0.26	-0.009
C	2	0.111	0.119	-0.132	0.109	-0.007
N	3	-0.232	-0.225	0.01	-0.232	-0.001
C	4	0.297	0.297	-0.02	0.294	0
C	5	0.089	0.105	-0.176	0.082	-0.011
N	6	-0.284	-0.289	-0.179	-0.289	-0.017
C	7	0.069	0.072	0.028	0.068	0.001
N	8	-0.237	-0.25	-0.112	-0.245	-0.026
C	9	0.155	0.202	0.091	0.221	0.001
H	10	0.099	0.105	0.008	0.099	0
C	11	-0.201	-0.197	0	-0.198	0
H	12	0.105	0.108	0	0.105	0
N	13	0.014	-0.012	-0.446	0.248	-0.104
O	14	-0.214	-0.178	0.584	-0.217	0.222

O	15	0.074	-0.036	0.33	-0.202	-0.05
H	16	0.132	0.135	0	0.133	0
H	17	0.155	0.155	0	0.154	0
H	18	0.131	0.132	0	0.13	0

Table S3. Mulliken charge to the reactant, transition state and product of the reaction of 6-nitrenopurine to form an expanded ring.

		Reactant		Transition state	Product
Atom	Number	Charge	Spin	Charge	Charge
N	1	-0.247	0.013	-0.216	-0.255
C	2	0.119	-0.158	0.104	0.089
N	3	-0.224	0.009	-0.222	-0.198
C	4	0.295	-0.011	0.293	0.216
C	5	0.082	-0.159	0.066	0.164
N	6	-0.298	-0.234	-0.318	-0.243
C	7	0.074	0.043	0.085	0.083
N	8	-0.149	0.54	-0.161	-0.234
N	9	-0.25	-0.096	-0.256	-0.267
C	10	0.168	0.036	0.195	0.233
H	11	0.102	0.009	0.101	0.089
C	12	-0.196	0.001	-0.193	-0.189
H	13	0.105	0.005	0.109	0.112
H	14	0.134	0	0.133	0.129
H	15	0.154	0	0.153	0.144
H	16	0.13	0	0.127	0.127

Table S4. Mulliken charge to the reactant, transition state and product of the reaction of 2-amino-6-nitrenopurine to form an expanded ring.

		Reactant		Transition state		Product
Atom	Number	Charge	Spin	Charge	Spin	Charge
N	1	-0.305	-0.034	-0.223	-0.038	-0.326
C	2	0.234	0.161	0.105	0.163	0.198
N	3	-0.395	-0.008	-0.233	-0.024	-0.371
C	4	0.369	0.015	0.289	0.029	0.274
C	5	0.025	0.275	0.054	0.153	0.174
N	6	-0.43	0.223	-0.36	0.177	-0.415
C	7	0.388	-0.031	0.312	-0.006	0.394
N	8	-0.172	1.315	-0.183	-0.455	-0.298
N	9	-0.417	0.124	-0.34	0.004	-0.39
C	10	0.231	-0.136	0.179	-0.004	0.302
H	11	0.103	-0.01	0.096	-0.01	0.087
C	12	-0.102	0.001	-0.192	-0.001	-0.096
N	13	-0.369	-0.001	-0.318	0.016	-0.359
H	14	0.12	0	0.13	-0.001	0.114

H	15	0.141	-0.001	0.144	-0.001	0.13
H	16	0.118	0	0.124	0	0.114
H	17	0.229	0.001	0.205	-0.001	0.23
H	18	0.234	-0.001	0.21	-0.001	0.238