Electronic Supporting Information

Supplementary Results:

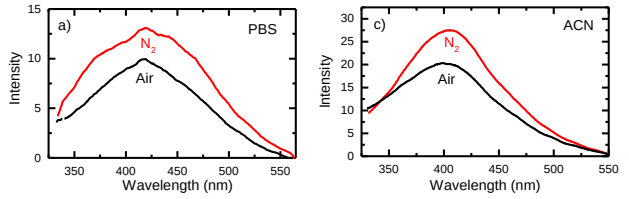


Figure S1. Emission spectra of 6MeTIno following 290 nm excitation in (a) PBS pH 7.4 and (b) acetonitrile under air- and N_2-saturated conditions.

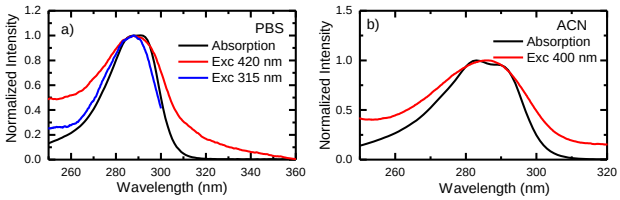


Figure S2. Excitation spectra of 6MeTIno at emission wavelengths of 420 and 315 nm in (a) PBS pH 7.4 and (b) at 400 nm in acetonitrile, plotted with the ground-state absorption spectrum. The excitation spectrum of6MeTIno at an emission wavelength of the fluorescence band could not be obtained because the low fluorescence intensity of this band in acetonitrile.

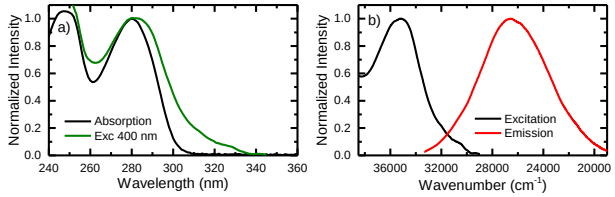


Figure S3. (a) Excitation spectra of 6MeGuo in acetonitrile at an emission wavelength of 400 nm, plotted with the ground-state absorption spectra. (b) Overlap of emission and excitation spectra in acetonitrile.

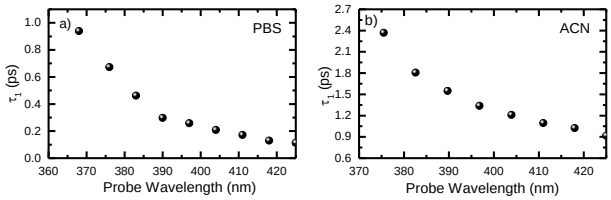


Figure S4. Value of τ_1 as a function of probe wavelength for 6MeTI in (a) PBS pH 7.4 and (b) acetonitrile following excitation at 290 nm.

Table S1. Optimized geometries of 6MeTIno conformations in vacuum.

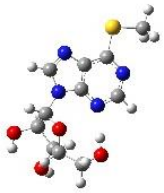
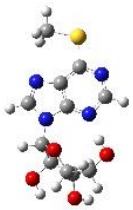
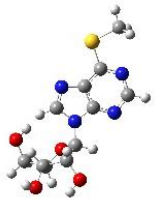
***syn*-6MeTIno**	***syn*-6MeTIno**	***anti*-6MeTIno**	***anti*-6MeTIno**
			
0.0 kcal/mol	2.2 kcal/mol	3.0 kcal/mol	5.3 kcal/mol

Table S2. Optimized geometries of 6MeTIno conformations in water.

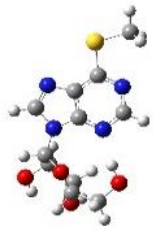
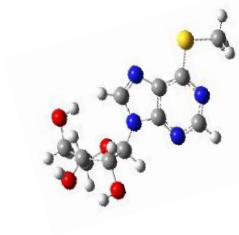
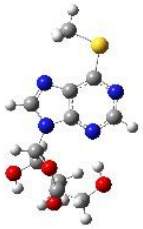
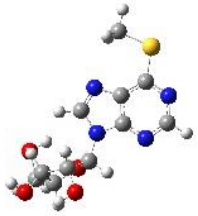
***syn*-6MeTIno**	***anti*-6MeTIno**	***syn*-6MeTIno**	***anti*-6MeTIno**
			
0.0 kcal/mol	2.2 kcal/mol	2.4 kcal/mol	4.5 kcal/mol

Table S3. Optimized geometries of 6MeTIno conformations in acetonitrile.

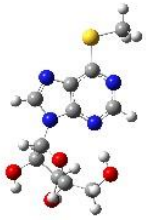
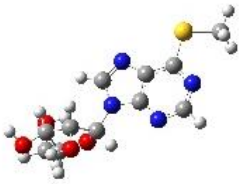
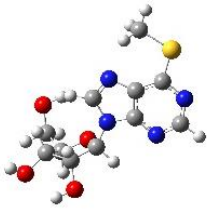
***syn*-6MeTIno**	***anti*-6MeTIno**	***anti*-6MeTIno**	***syn*-6MeTIno**
			
0.0 kcal/mol	2.2 kcal/mol	4.5 kcal/mol	14.1 kcal/mol

Table S4. Optimized geometries of 6TIno conformations in vacuum.

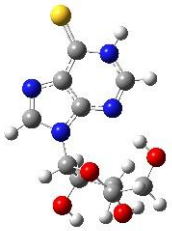
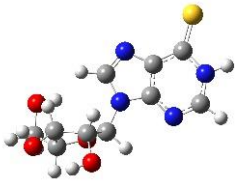
***syn*-6TIno**	***anti*-6TIno**
	
0.0 kcal/mol	1.8 kcal/mol

Table S5. Optimized geometries of 6TIno conformations in acetonitrile.

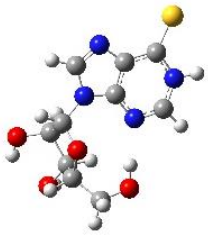
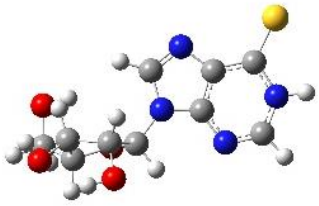
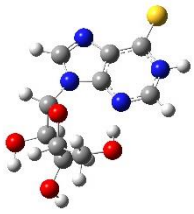
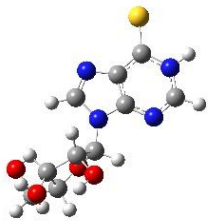
***syn*-6TIno**	***anti*-6TIno**
	
0.0 kcal/mol	1.5 kcal/mol

Table S6. Optimized geometries of 6TIno conformations in water.

***syn*-6TIno**	***anti*-6TIno**
	
0.0 kcal/mol	1.4 kcal/mol

Vertical Excitation Energies and Kohn-Sham orbitals for the primary single-electron transitions

Table S7. Vertical energies for the relevant singlet and triplet transitions of *syn*-6MeTIno with the S^6-methyl group oriented toward the N1 position in water.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	100.0	$\pi\pi*$	4.51 (0.437)
S_2	H-3→L+0	3.4	$n\pi*$	4.69 (0.003)
	H-2→L+0	30.1		
	H-1→L+0	66.5		
S_3	H-4→L+0	7.1	$\pi\pi*$	5.07 (0.016)
	H-3→L+0	17.5		
	H-0→L+1	75.4		
T_1	H-4→L+0	4.0	$\pi\pi*$	3.21
	H-→>L+0	96.0		
T_2	H-4→L+0	7.2	$\pi\pi*$	4.36
	H-3→L+1	10.6		
	H-0→L+0	2.6		
	H-0→L+1	79.6		
T_3	H-4→L+3	2.6	$n\pi*$	4.38
	H-3→L+3	2.7		
	H-2→L+0	32.1		
	H-1→L+2	62.6		

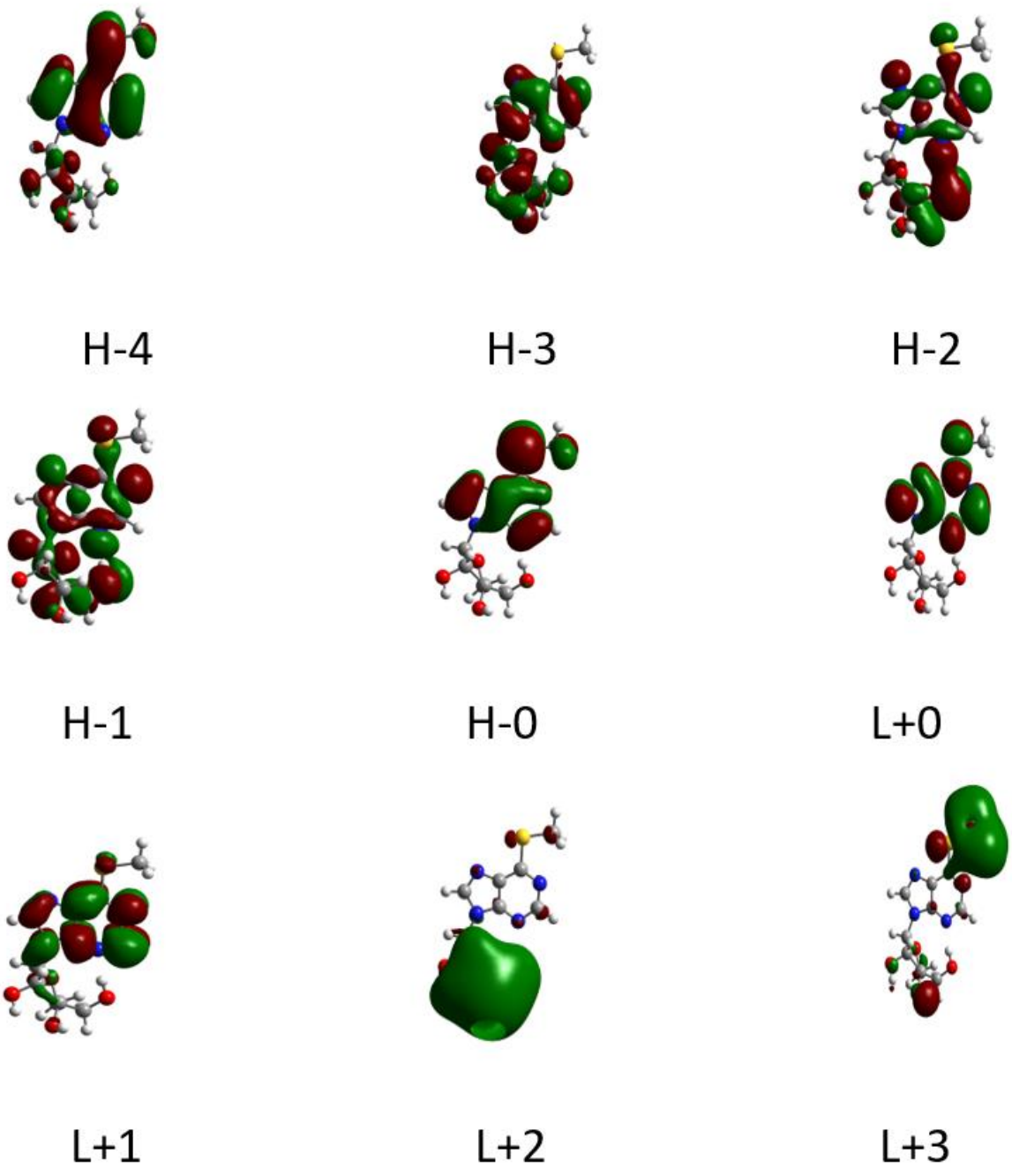


Figure S5. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6MeTIno with the S^6-methyl group oriented toward the N1 position in water.

Table S8. Vertical energies for the relevant singlet and triplet transitions of *syn*-6MeTIno with the S^6-methyl group oriented toward the N7 position in water.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	100.0	$\pi\pi*$	4.49 (0.437)
S_2	H-4→L+0	2.3	$n\pi*$	4.69 (0.005)
	H-2→L+0	27.0		
	H-1→L+0	70.6		
S_3	H-3→L+0	20.9	$CT, \pi\pi*$	4.99 (0.004)
	H-0→L+1	79.1		
T_1	H-0→L+0	100.0	$\pi\pi*$	3.18
T_2	H-4→L+0	3.7	$n\pi*$	4.37
	H-2→L+0	28.5		
	H-1→L+0	67.8		
T_3	H-4→L+0	7.8	$\pi\pi*$	4.37
	H-4→L+1	4.4		
	H-3→L+0	6.8		
	H-3→L+1	6.1		
	H-0→L+0	2.5		
	H-0→L+1	72.4		

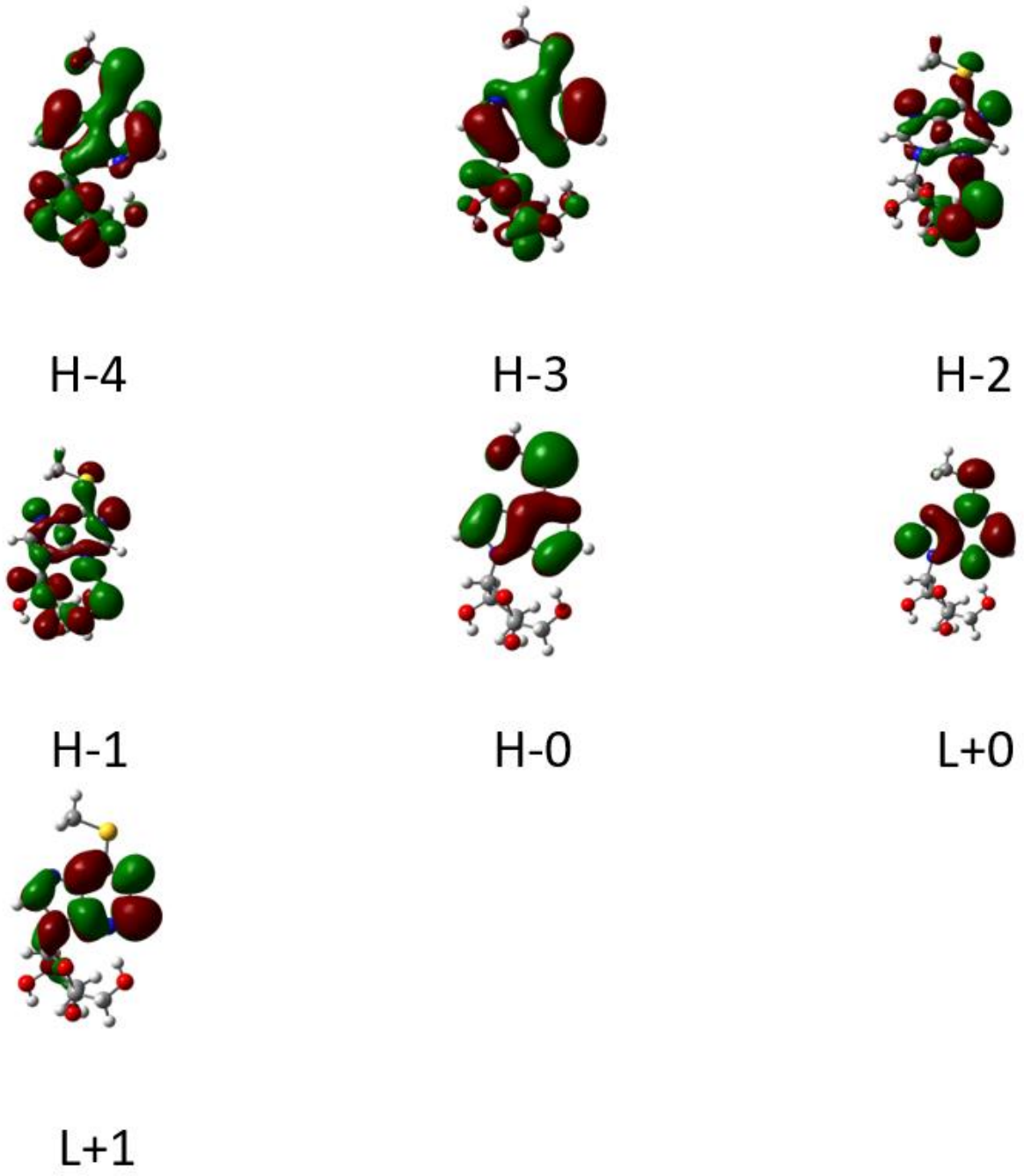


Figure S6. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6MeTIno with the S^6-methyl group oriented toward the N7 position in water.

Table S9. Vertical energies for the relevant singlet and triplet transitions of *anti*-6MeTIno with the S^6-methyl group oriented toward the N1 position in water.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	100.0	$\pi\pi*$	4.54 (0.436)
S_2	H-2→L+0	3.5	$n\pi*$	4.71 (0.002)
	H-1→L+0	96.5		
S_3	H-5→L+0	2.4	$CT, \pi\pi*$	5.11 (0.018)
	H-2→L+0	25.0		
	H-0→L+1	72.6		
T_1	H-3→L+0	4.9	$\pi\pi*$	3.24
	H-0→L+0	95.1		
T_2	H-2→L+0	2.9	$\pi\pi*$	4.37
	H-1→L+0	97.1		
T_3	H-3→L+0	10.7	$\pi\pi*$	4.41
	H-3→L+1	6.1		
	H-2→L+0	2.4		
	H-2→L+1	3.2		
	H-0→L+0	2.8		
	H-0→L+1	74.9		

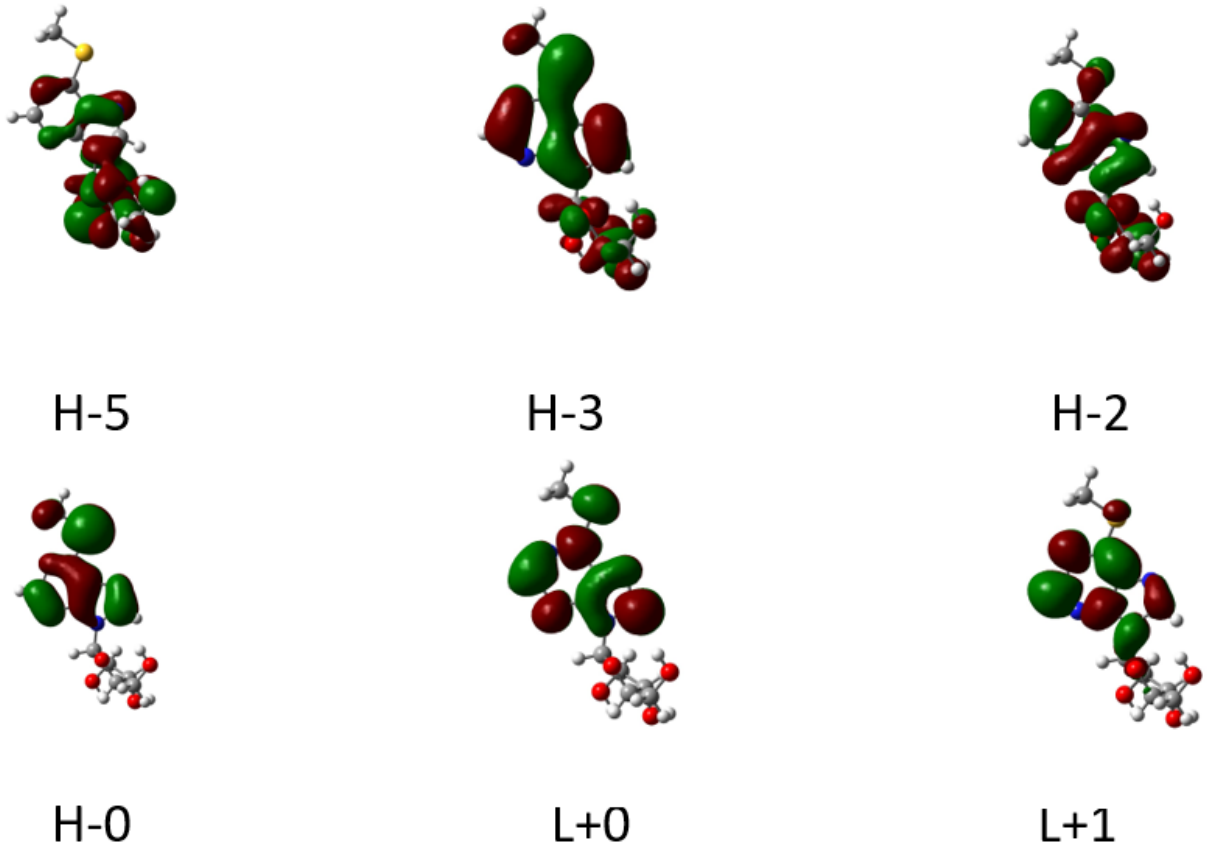


Figure S7. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *anti*-6MeTIno with the S^6-methyl group oriented toward the N1 position in water.

Table S10. Vertical energies for the relevant singlet and triplet transitions of *anti*-6MeTIno with the S^6-methyl group oriented toward the N7 position in water.

State	Transitions	% Composition	Primary Character	eV
S_1 (L_a)	H-0→L+0	100.0	$\pi\pi*$	4.53 (0.433)
S_2	H-2→L+0 H-1→L+0	3.2 96.8	$n\pi*$	4.71 (0.002)
S_3	H-2→L+0 H-0→L+1	22.1 77.9	$CT, \pi\pi*$	5.03 (0.006)
T_1	H-3→L+0 H-0→L+0	3.0 97.0	$\pi\pi*$	3.21
T_2	H-1→L+0	100.0	$n\pi*$	4.36
T_3	H-3→L+0 H-3→L+1 H-2→L+0 H-2→L+1 H-0→L+0 H-0→L+1	16.1 2.3 23.2 2.4 3.1 52.9	$\pi\pi*$	4.41

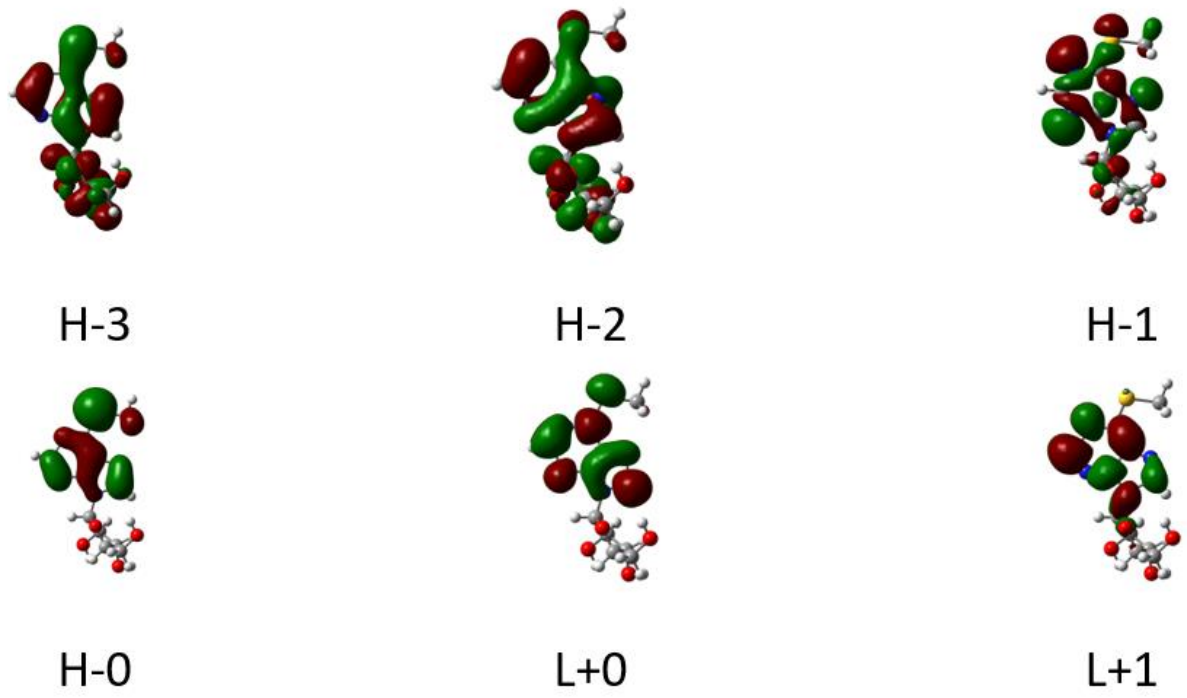


Figure S8. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *anti*-6MeTIno with the S^6-methyl group oriented toward the N7 position in water.

Table S11. Vertical energies for the relevant singlet and triplet transitions of *syn*-6TIno in water.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-1→L+0	100.0	$n\pi*$	3.45 (0.000)
S_2	H-0→L+0 H-→L+1	83.7 16.3	$\pi\pi*$	4.19 (0.483)
S_3	H-→L+0 H-→L+1	16.7 83.3	$\pi\pi*$	4.30 (0.124)
T_1	H-0→L+0	100.0	$\pi\pi*$	2.76
T_2	H-1→L+0	100.0	$n\pi*$	3.18
T_3	H-6→L+1 H-0→L+1	3.7 96.3	$\pi\pi*$	3.44

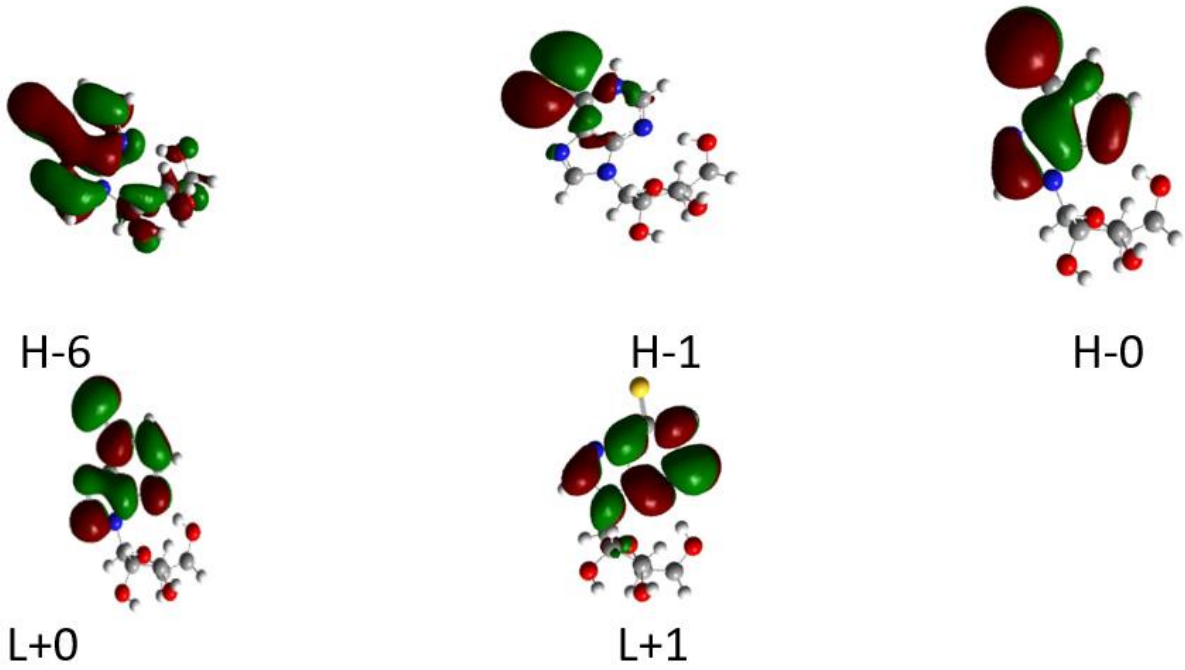


Figure S9. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6TIno in water.

Table S12. Vertical energies for the relevant singlet and triplet transitions of *anti*-TIno in water.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-1→L+0	100.0	$n\pi^*$	3.50 (0.000)
S_2	H-0→L+0 H-0→L+1	90.6 9.4	$\pi\pi^*$	4.21 (0.508)
S_3	H-0→L+0 H-0→L+1	9.7 90.3	$\pi\pi^*$	4.33 (0.092)
T_1	H-0→L+0	100.0	$\pi\pi^*$	2.8
T_2	H-1→L+0	100.0	$n\pi^*$	3.24
T_3	H-6→L+1 H-4→L+1 H-0→L+1	3.1 2.4 94.4	$\pi\pi^*$	3.47

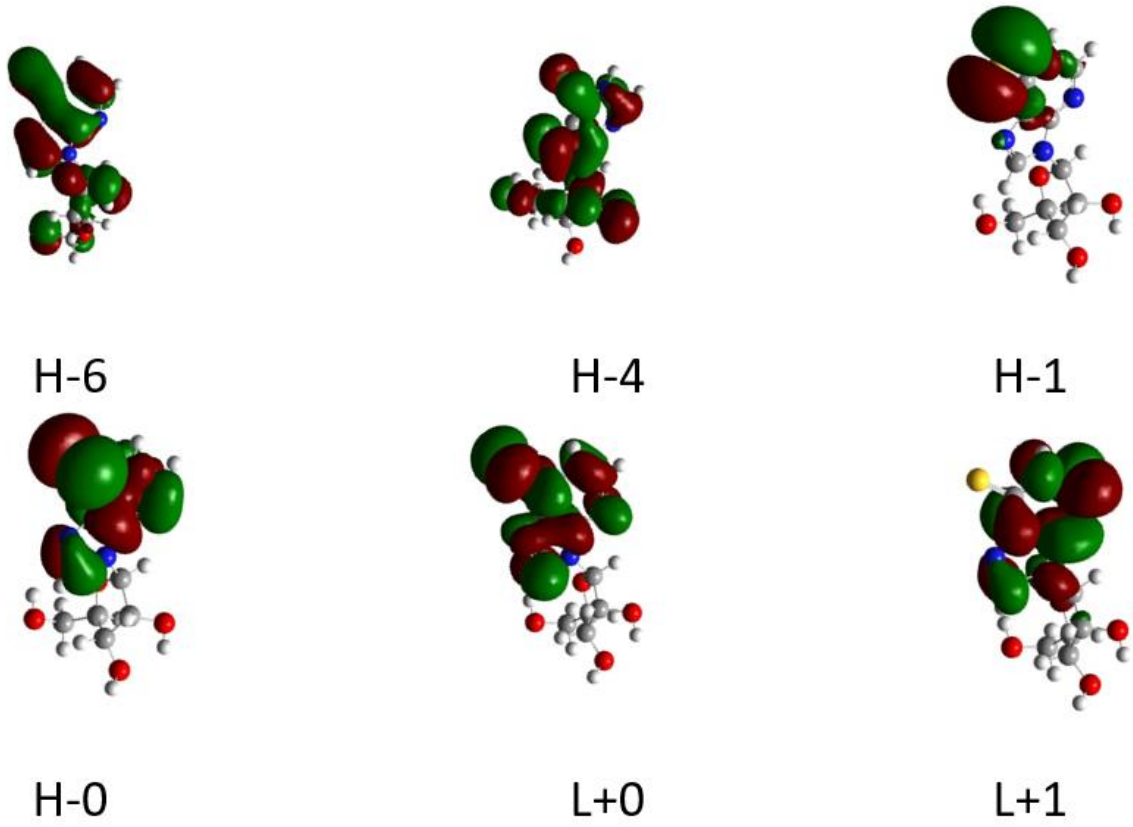


Figure S10. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *anti*-6TIno in water.

Table S13. Vertical energies for the relevant singlet and triplet transitions of *syn*-6MeTIno with the S^6-methyl group oriented toward the N1 position in acetonitrile.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	100.0	$\pi\pi*$	4.50 (0.439)
S_2	H-3→L+0 H-2→L+0 H-1→L+0	3.3 30.4 66.4	$n\pi*$	4.69 (0.003)
S_3	H-4→L+0 H-3→L+0 H-0→L+1	6.9 17.6 75.5	$CT, \pi\pi*$	5.07 (0.017)
T_1	H-4→L+0 H-0→L+0	4.0 96.0	$\pi\pi*$	3.21
T_2	H-4→L+0 H-4→L+1 H-1→L+0 H-0→L+0 H-0→L+1	7.3 10.2 2.2 2.6 77.7	$\pi\pi*$	4.36
T_3	H-4→L+0 H-3→L+0 H-2→L+0 H-1→L+0	2.6 2.6 32.4 62.4	$n\pi*$	4.38

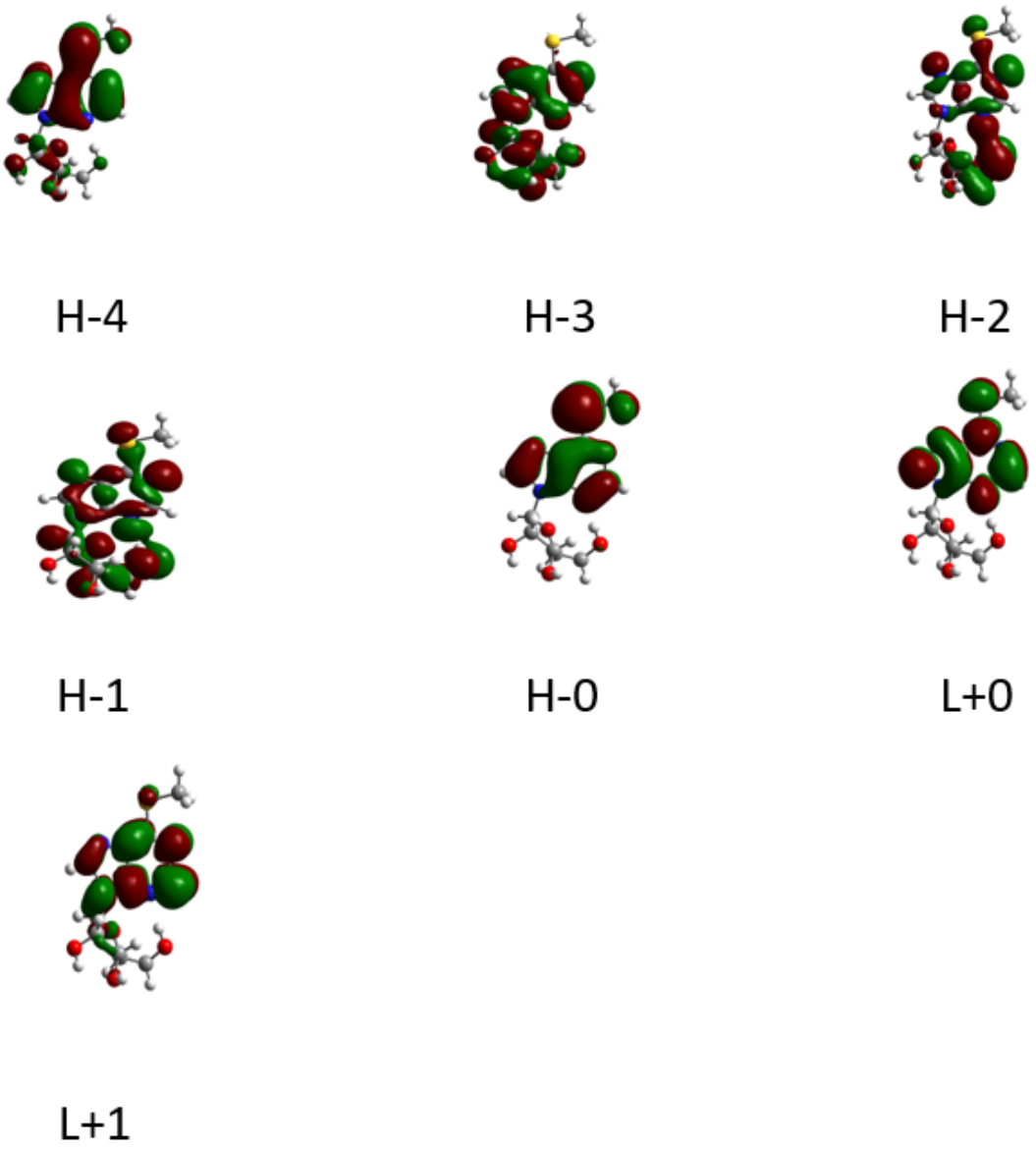


Figure S11. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6MeTIno with the S^6-methyl group oriented toward the N1 position in acetonitrile.

Table S14. Vertical energies for the relevant singlet and triplet transitions of *anti*-6MeTIno with the S^6-methyl group oriented toward the N1 position in acetonitrile.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	100.0	$\pi\pi*$	4.54 (0.438)
S_2	H-2→L+0	3.2	$n\pi*$	4.71 (0.002)
	H-1→L+0	96.8		
S_3	H-5→L+0	2.4	$CT, \pi\pi*$	5.11 (0.018)
	H-2→L+0	25.1		
	H-0→L+1	72.5		
T_1	H-3→L+0	4.9	$\pi\pi*$	3.24
	H-0→L+0	95.1		
T_2	H-2→L+0	2.6	$n\pi*$	4.37
	H-1→L+0	97.4		
T_3	H-3→L+0	10.9	$\pi\pi*$	4.41
	H-3→L+1	5.9		
	H-2→L+0	2.7		
	H-2→L+1	3.2		
	H-0→L+0	2.8		
	H-0→L+1	74.5		

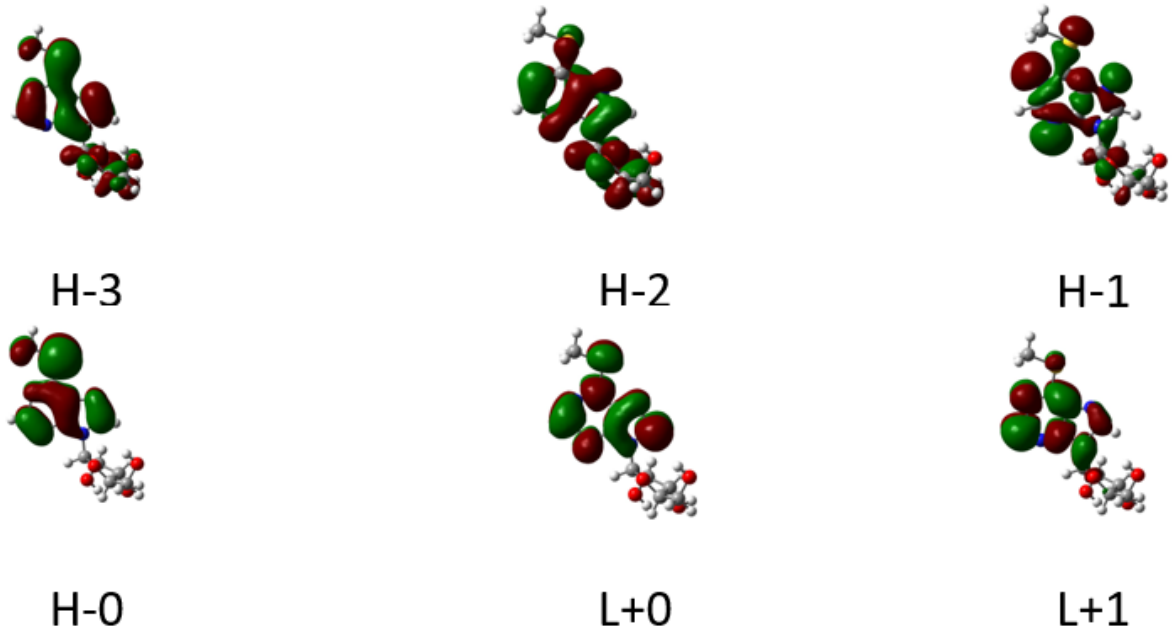


Figure S12. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *anti*-6MeTIno with the S^6-methyl group oriented toward the N1 position in acetonitrile.

Table S15. Vertical energies for the relevant singlet and triplet transitions of *anti*-6MeTIno with the S^6-methyl group oriented toward the N7 position in acetonitrile.

State	Transitions	%Composition	Primary Character	eV
S_1 (L_a)	H-0→L+0	100.0	$\pi\pi*$	4.53 (0.435)
S_2	H-2→L+0 H-1→L+0	2.9 97.1	$n\pi*$	4.71 (0.002)
S_3	H-2→L+0 H-0→L+1	22.2 77.8	$CT, \pi\pi*$	5.03 (0.006)
T_1	H-3→L+0 H-0→L+0	3.0 97.0	$\pi\pi*$	3.21
T_2	H-1→L+0	100.0	$n\pi*$	4.36
T_3	H-3→L+0 H-3→L+1 H-2→L+0 H-2→L+1 H-0→L+0 H-0→L+1	16.3 2.1 24.8 2.3 3.1 51.4	$\pi\pi*$	4.41

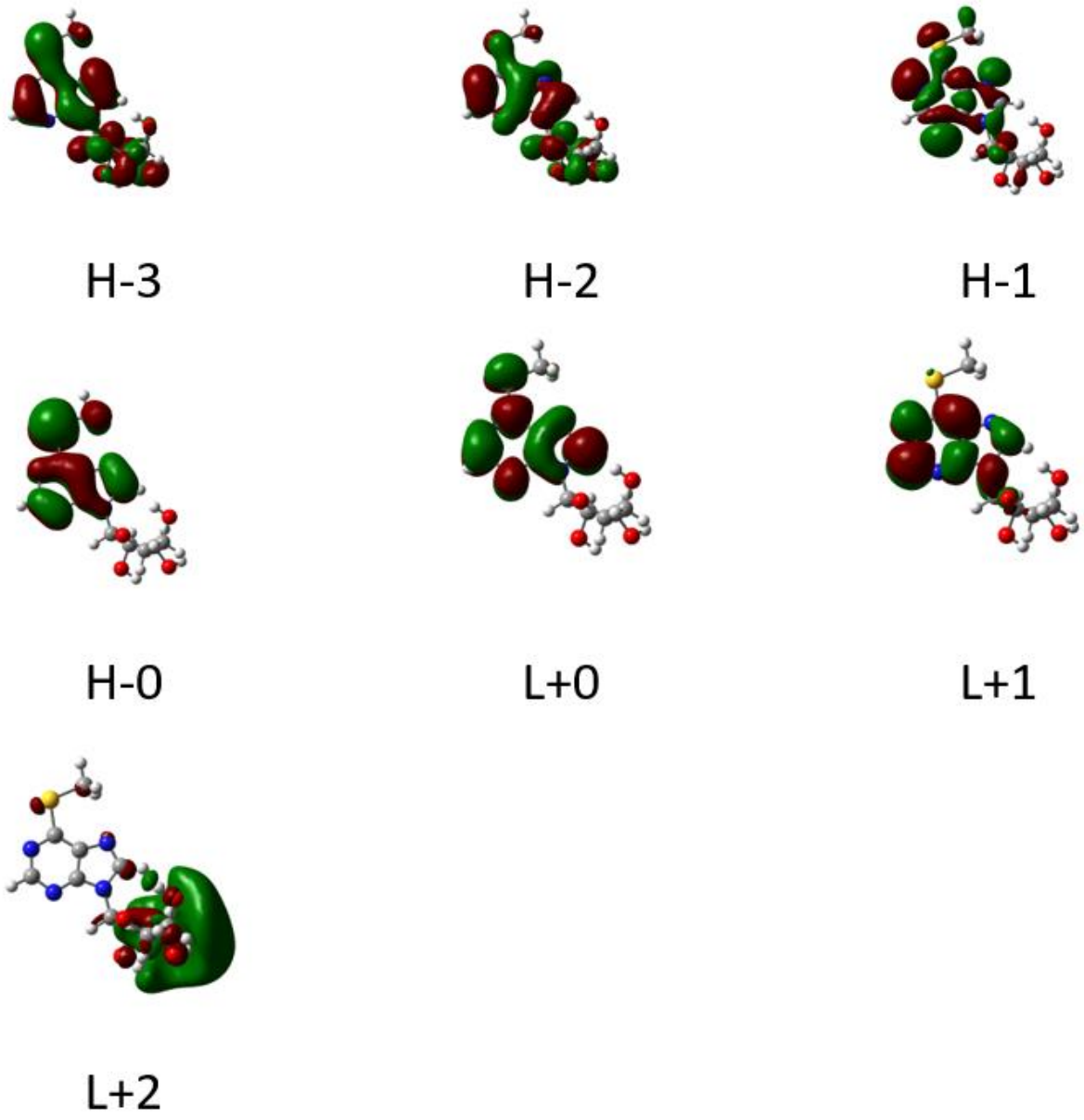


Figure S13. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *anti*-6MeTIno with the S^6-methyl group oriented toward the N7 position in acetonitrile.

Table S16. Vertical energies for the relevant singlet and triplet transitions of *syn*-6MeTIno with the S^6-methyl group oriented toward the N7 position in acetonitrile.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-1→L+0	2.2	$\pi\pi*$	4.52 (0.355)
	H-0→L+0	97.8		
S_2	H-2→L+0	29.8	$n\pi*$	4.57 (0.015)
	H-1→L+0	67.2		
	H-0→L+0	3.0		
S_3	H-3→L+0	19.0	$CT, \pi\pi*$	4.97 (0.008)
	H-0→L+1	73.1		
	H-0→L+2	7.8		
T_1	H-3→L+0	2.5	$\pi\pi*$	3.15
	H-0→L+0	97.5		
T_2	H-2→L+0	32.8	$n\pi*$	4.27
	H-1→L+0	67.2		
T_3	H-4→L+0	5.0	$\pi\pi*$	4.35
	H-3→L+0	36.3		
	H-3→L+1	4.6		
	H-0→L+0	2.8		
	H-0→L+1	44.6		
	H-0→L+2	6.6		

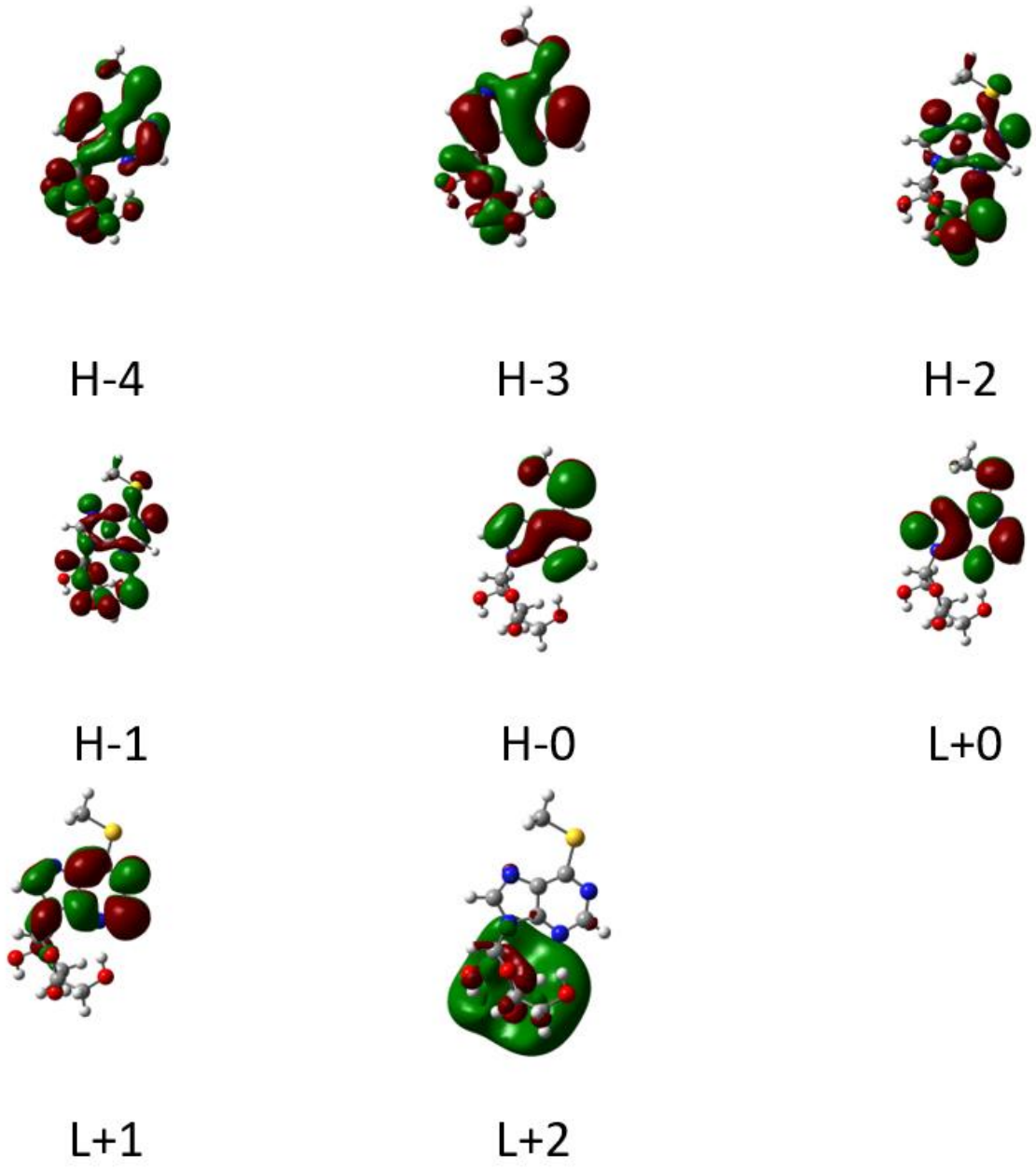


Figure S14. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6MeTIno with the S^6-methyl group oriented toward the N7 position in acetonitrile.

Table S17. Vertical energies for the relevant singlet and triplet transitions of *syn*-6TIno in acetonitrile.

State	Transitions	% Contribution	Primary Character	eV
S_1	H-1→L+0	100.0	$n\pi*$	3.44 (0.000)
S_2 (L_a)	H-0→L+0 H-0→L+1	81.8 18.2	$\pi\pi*$	4.19 (0.477)
S_3	H-0→L+0 H-0→L+1	18.5 81.5	$\pi\pi*$	4.29 (0.133)
T_1	H-0→L+0	100.0	$\pi\pi*$	2.75
T_2	H-1→L+0	100.0	$n\pi*$	3.17
T_3	H-6→L+1 H-0→L+1	3.6 96.4	$\pi\pi*$	3.43

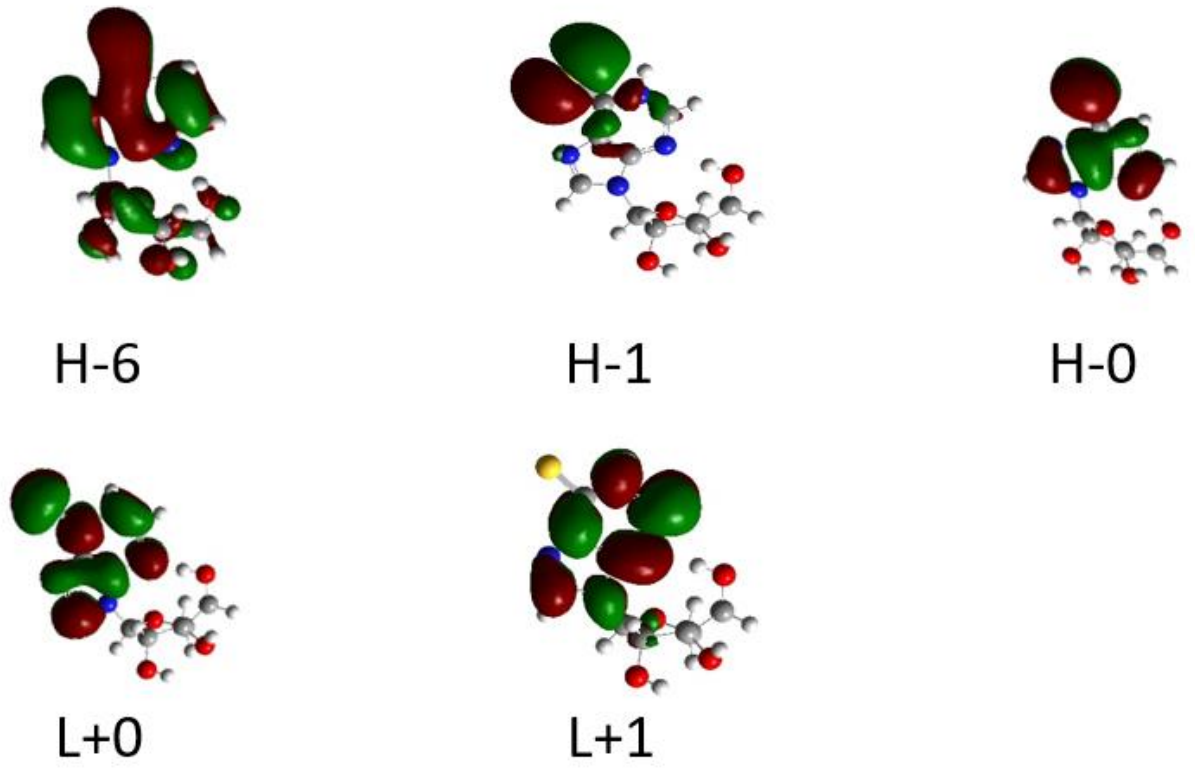


Figure S15. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6TIno in acetonitrile.

Table S18. Vertical energies for the relevant singlet and triplet transitions of *anti*-6TIno in acetonitrile.

State	Transitions	% Contribution	Primary Character	eV
S_1	H-1→L+0	100.0	$n\pi*$	3.49 (0.000)
S_2 (L_a)	H-0→L+0 H-0→L+1	89.9 10.1	$\pi\pi*$	4.21 (0.508)
S_3	H-0→L+0 H-0→L+1	10.5 89.5	$\pi\pi*$	4.32 (0.096)
T_1	H-0→L+0	100.0	$\pi\pi*$	2.8
T_2	H-1→L+0	100.0	$n\pi*$	3.23
T_3	H-6→L+1 H-4→L+1 H-0→L+1	2.9 2.6 94.5	$\pi\pi*$	3.46

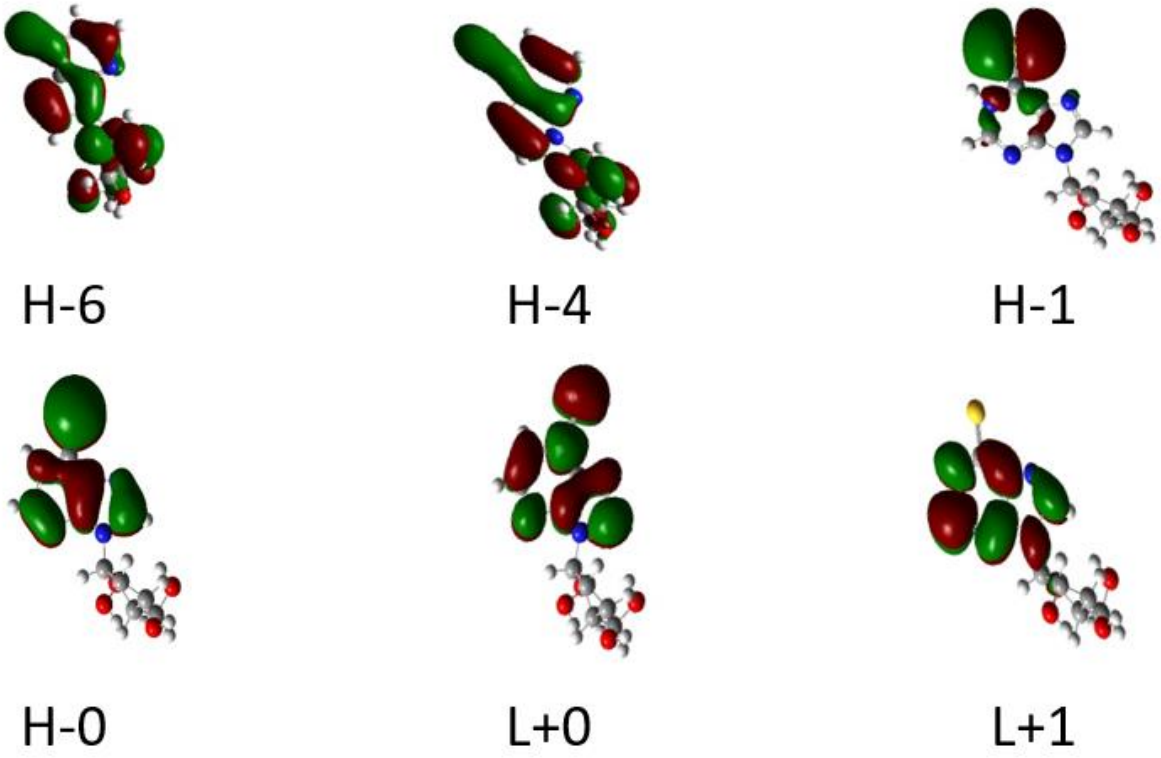


Figure S16. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *anti*-6TIno in acetonitrile.

Table S19. Vertical energies for the relevant singlet and triplet transitions of *syn*-6MeTIno with the S^6-methyl group oriented toward the N1 position in vacuum.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	100.0	$\pi\pi*$	4.54 (0.358)
S_2	H-2→L+0 H-1→L+0	38.5 61.5	$n\pi*$	4.63 (0.004)
S_3	H-3→L+0 H-0→L+1 H-0→L+2	22.0 68.0 10.0	$CT, \pi\pi*$	5.04 (0.026)
T_1	H-4→L+0 H-0→L+0	3.7 96.3	$\pi\pi*$	3.18
T_2	H-4→L+0 H-4→L+1 H-3→L+0 H-3→L+1 H-2→L+0 H-1→L+0 H-0→+0 H-0→L+1 H-0→L+2	7.5 3.1 5.8 3.3 4.8 10.8 2.4 52.4 10.0	$\pi\pi*$	4.32
T_3	H-4→L+0 H-2→L+0 H-1→L+0 H-0→L+1	5.6 36.6 48.4 9.4	$n\pi*$	4.33

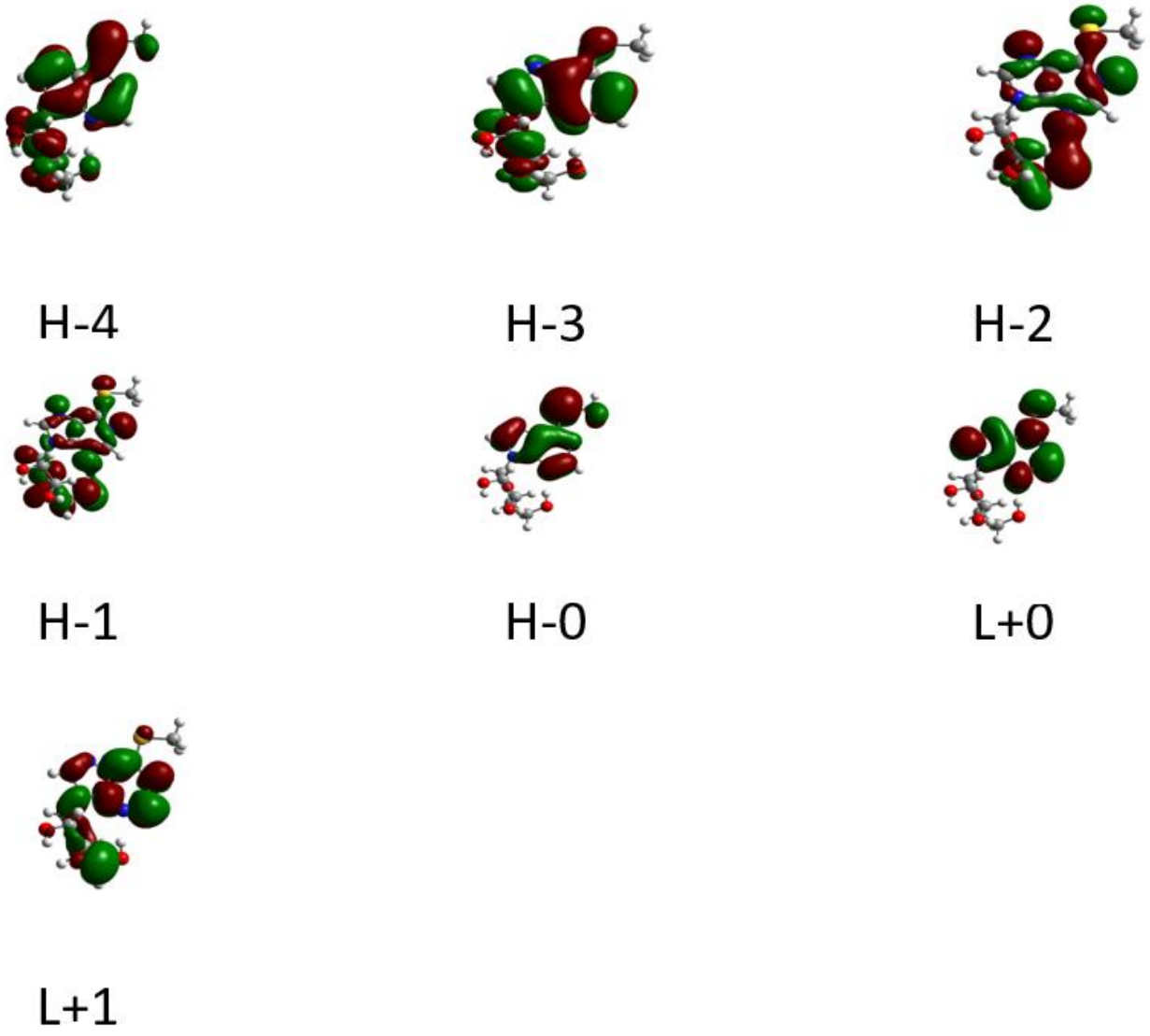


Figure S17. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6MeTIno with the S^6-methyl group oriented toward the N1 position in vacuum.

Table S20. Vertical energies for the relevant singlet and triplet transitions of *anti*-6MeTIno with the S^6-methyl group oriented toward the N1 position in vacuum.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	100.0	$\pi\pi*$	4.56 (0.357)
S_2	H-1→L+0	100.0	$n\pi*$	4.63 (0.002)
S_3	H-2→L+0 H-0→L+2	25.1 74.9	$CT, \pi\pi*$	5.10 (0.028)
T_1	H-3→L+0 H-2→L+0 H-2→L+2 H-0→L+0	3.6 2.5 2.3 91.6	$\pi\pi*$	3.21
T_2	H-1→L+0	100.0	$n\pi*$	4.28
T_3	H-3→L+0 H-2→L+0 H-2→L+2 H-0→L+0 H-0→L+2	8.1 20.7 4.4 3.0 63.7	$\pi\pi*$	4.38

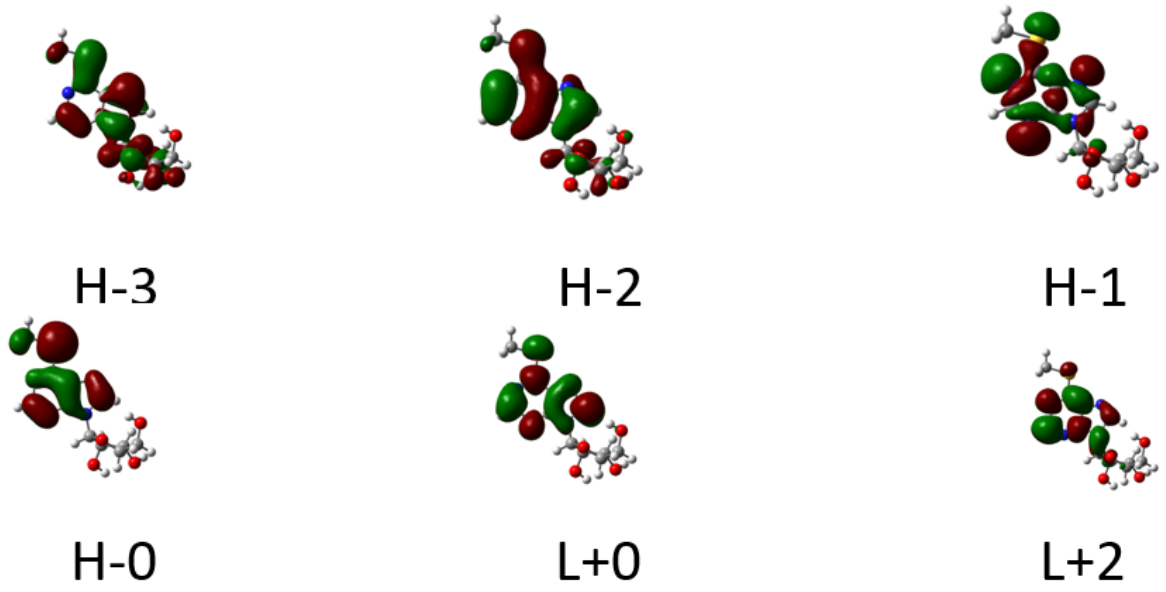


Figure S18. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *anti*-6MeTIno with the S[6]-methyl group oriented toward the N1 position in vacuum.

Table S21. Vertical energies for the relevant singlet and triplet transitions of *anti*-6MeTIno with the S[6]-methyl group oriented toward the N7 position in vacuum.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	100.0	$\pi\pi*$	4.54 (0.351)
S_2	H-1→L+0	100.0	$n\pi*$	4.57 (0.002)
S_3	H-2→L+0 H-0→L+2	22.6 77.4	$CT, \pi\pi*$	5.03 (0.014)
T_1	H-3→L+0 H-2→L+0 H-2→L+2 H-0>L+0	2.3 2.9 2.4 92.4	$\pi\pi*$	3.18
T_2	H-1→L+0 H-1>L+2	96.8 3.2	$n\pi*$	4.23
T_3	H-3→L+0 H-2→L+0 H-0→L+0 H-0→L+2	6.2 54.7 2.8 36.3	$\pi\pi*$	4.37

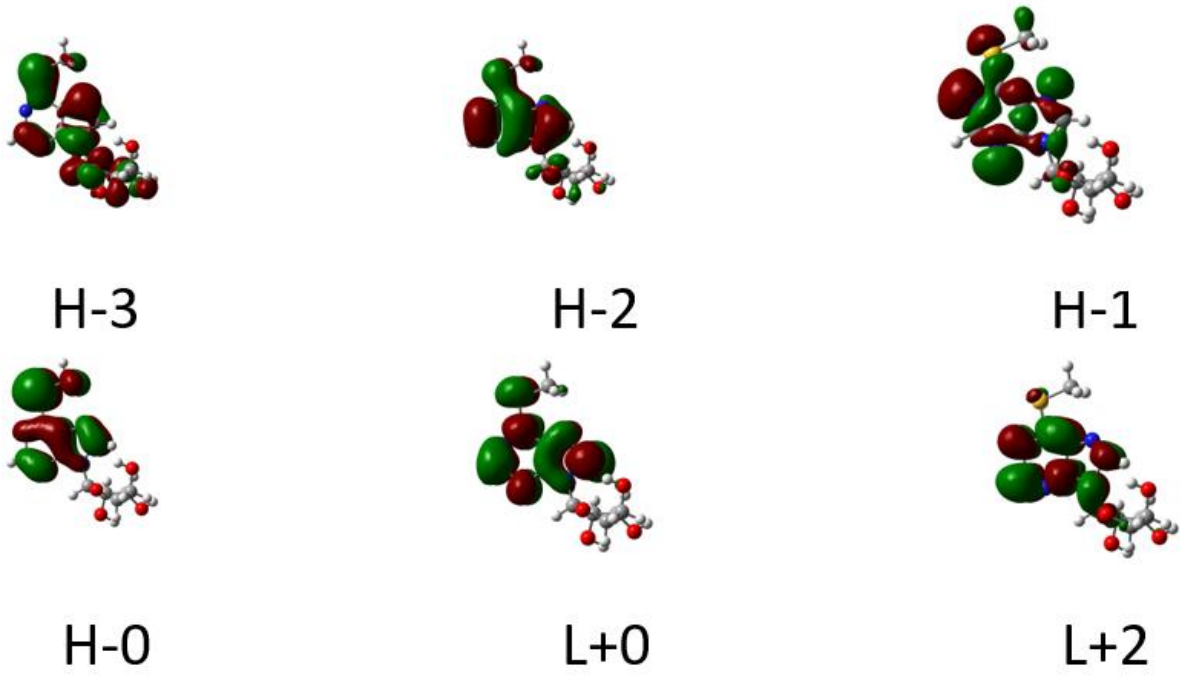


Figure S19. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *anti*-6MeTIno with the S^6-methyl group oriented toward the N7 position in vacuum.

Table S22. Vertical energies for the relevant singlet and triplet transitions of *syn*-6MeTIno with the S^6-methyl group oriented toward the N7 position in vacuum.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-1→L+0	2.2	$\pi\pi*$	4.52 (0.355)
	H-0→L+0	97.8		
S_2	H-2→L+0	29.8	$n\pi*$	4.57 (0.015)
	H-1→L+0	67.2		
	H-0→L+0	3.0		
S_3	H-3→L+0	19.1	$CT, \pi\pi*$	4.97 (0.008)
	H-0→L+1	73.1		
	H-0→L+2	7.8		
T_1	H-3→L+0	2.5	$\pi\pi*$	3.15
	H-0→L+0	97.5		
T_2	H-2→L+0	32.8	$n\pi*$	4.27
	H-1→L+0	67.2		
T_3	H-4→L+0	5.0	$\pi\pi*$	4.35
	H-3→L+0	36.3		
	H-3→L+1	4.6		
	H-0→L+0	2.8		
	H-0→L+1	44.6		
	H-0→L+2	6.6		

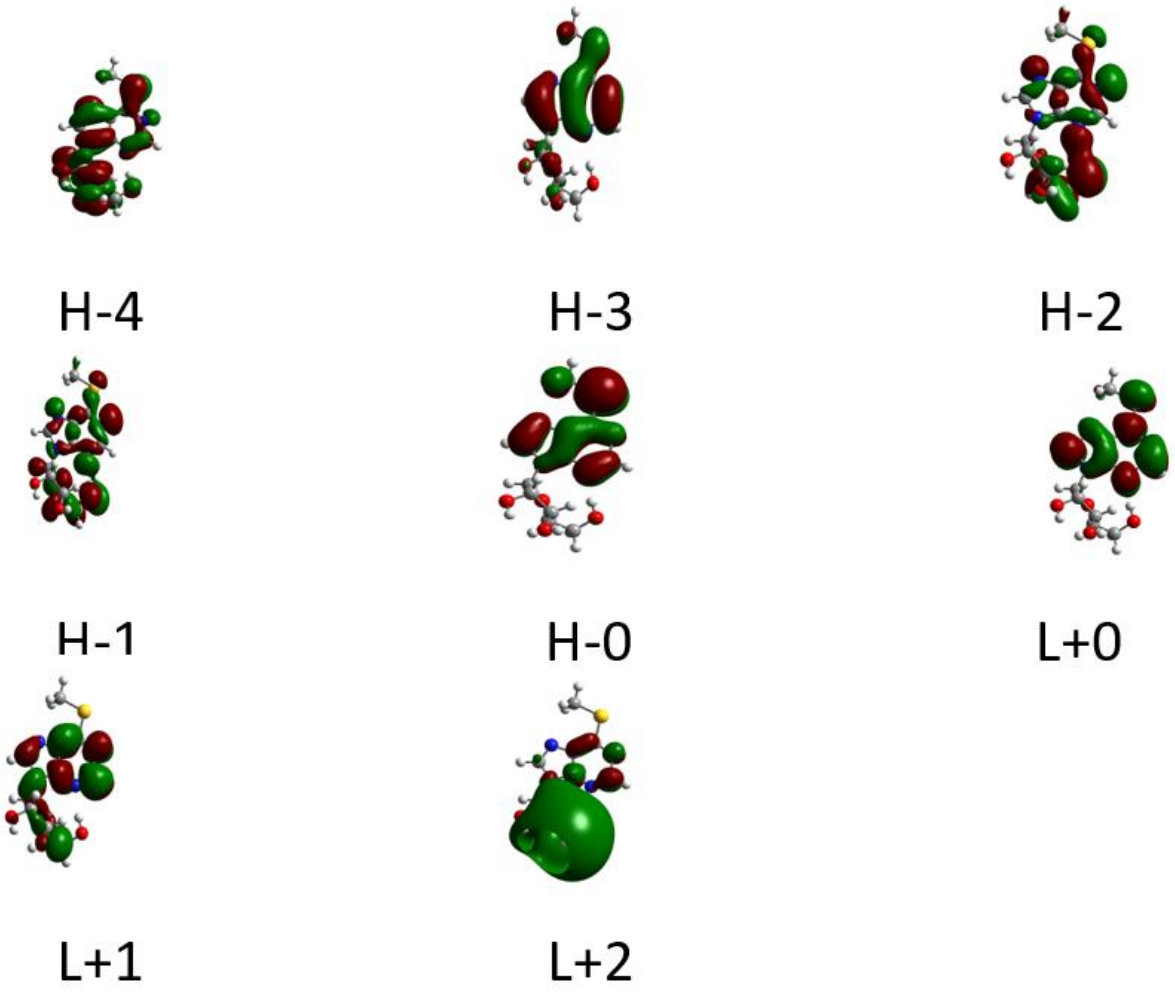


Figure S20. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6MeTIno with the S^6-methyl group oriented toward the N7 position in vacuum.

Table S23. Vertical energies for the relevant singlet and triplet transitions of *syn*-6TIno in vacuum.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0 H-0→L+1	90.2 9.8	$n\pi*$	3.17 (0.000)
S_2	H-0→L+0 H-0→L+1	9.8 90.2	$n\pi*$	3.85 (0.000)
S_3	H-1→L+0 H-1→L+1	4.9 95.1	$CT, \pi\pi*$	3.96 (0.027)
T_1	H-1→L+0 H-1→L+1	94.7 5.3	$\pi\pi*$	2.59
T_2	H-0→L+0 H-0→L+1	89.3 10.7	$n\pi*$	2.82
T_3	H-1→L+0 H-1→L+1	4.9 95.1	$\pi\pi*$	3.13

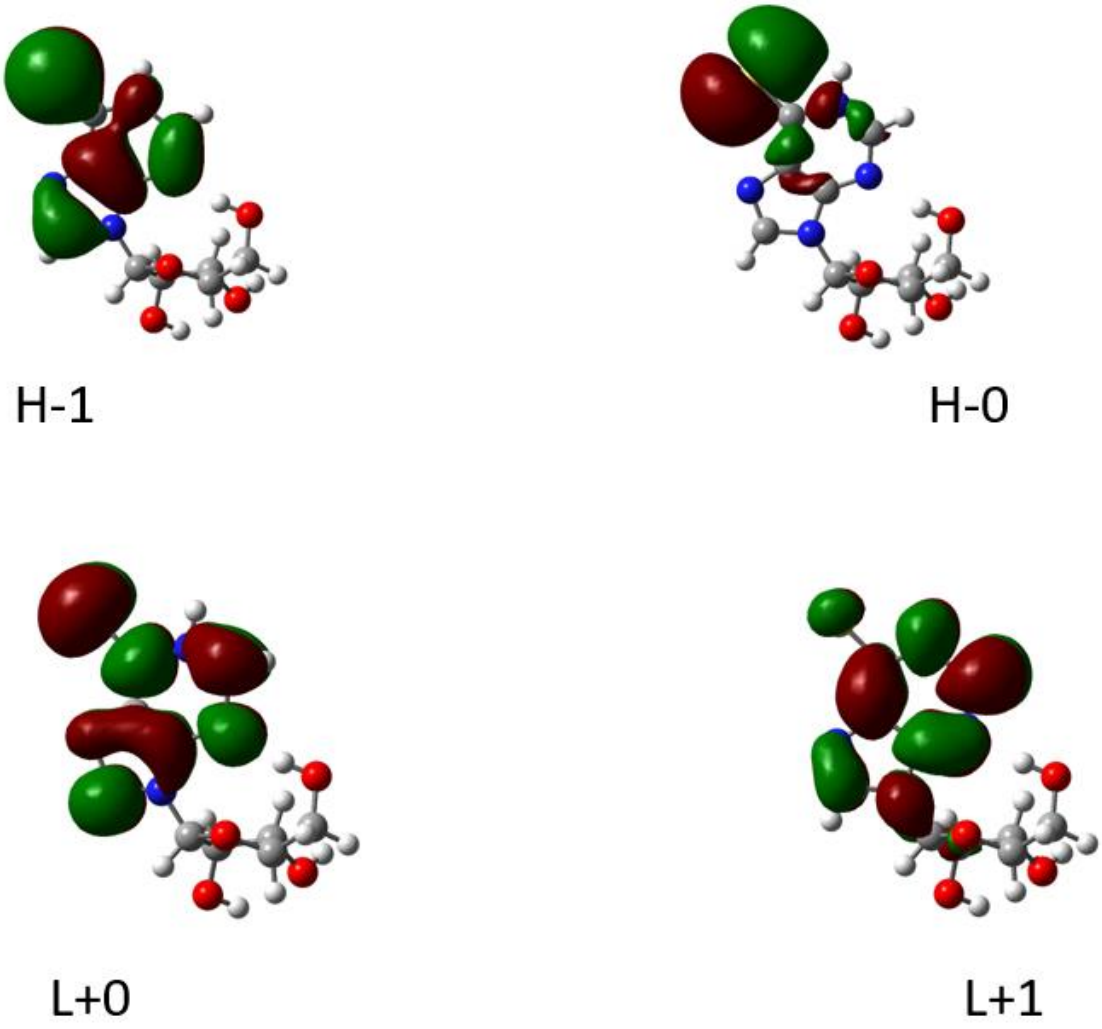


Figure S21. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6TIno in vacuum.

Table S24. Vertical energies for the relevant singlet and triplet transitions of *anti*-6TIno in vacuum.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0 H-0→L+1	89.4 10.6	$n\pi*$	3.21 (0.000)
S_2	H-0→L+0 H-0→L+1	10.4 89.6	$n\pi*$	3.91 (0.000)
S_3	H-1→L+0 H-1→L+1	6.7 73.3	$CT, \pi\pi*$	4.01 (0.032)
T_1	H-1→L+0 H-1→L+1	94.6 5.4	$\pi\pi*$	2.62
T_2	H-0→L+0 H-0→L+1	88.3 11.7	$n\pi*$	2.88
T_3	H-1→L+0 H-1→L+1	4.7 95.3	$\pi\pi*$	3.17

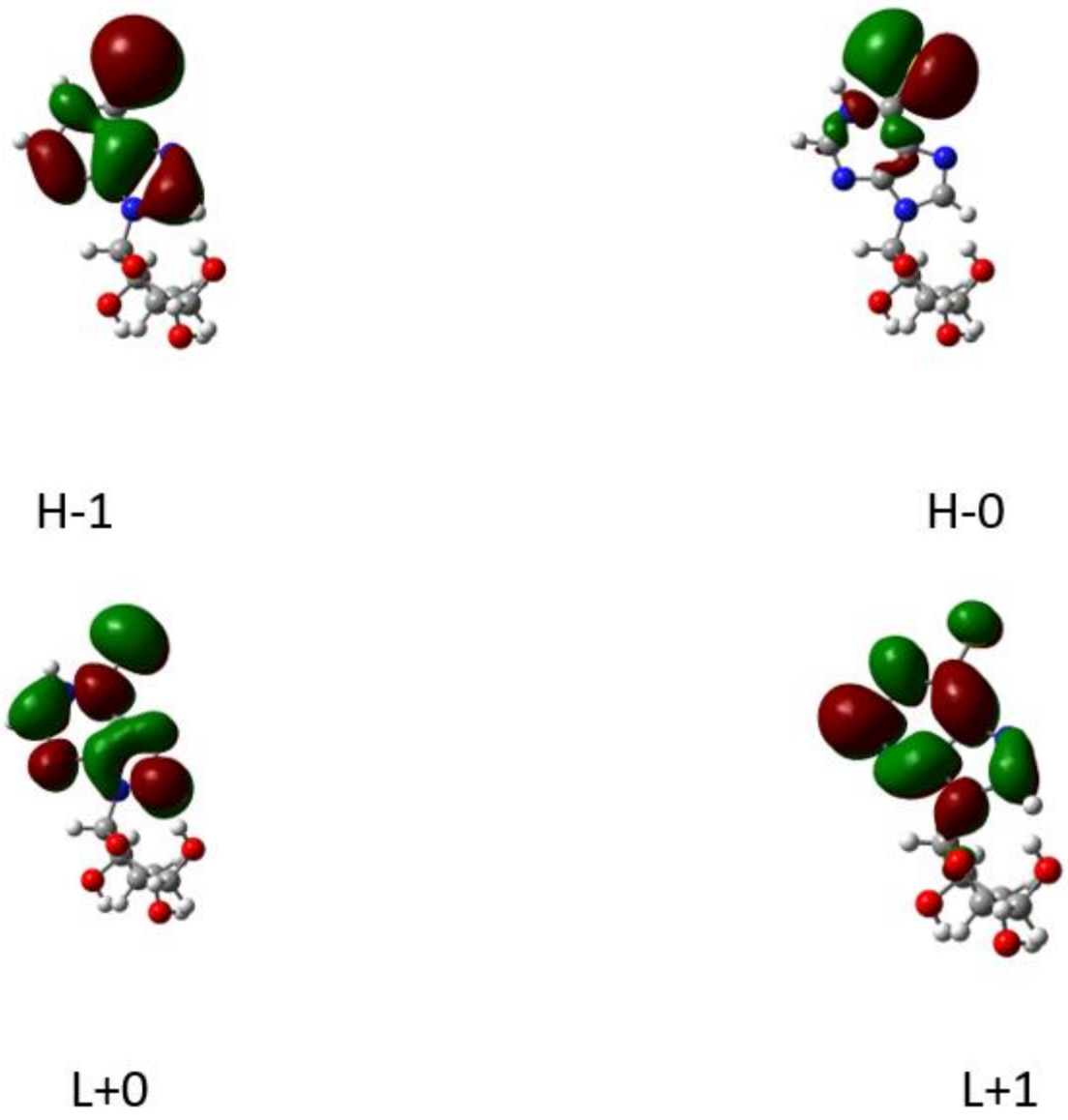


Figure S22. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6TIno in vacuum.

Table S25. Optimized geometries of 6MeGuo conformations in vacuum.

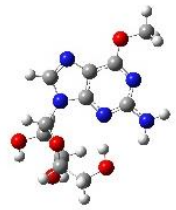
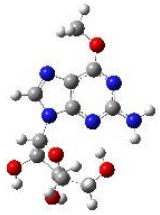
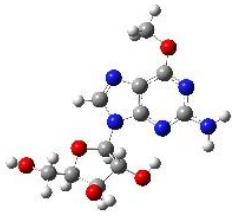
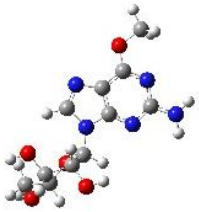
***syn*-6MeGuo**	***syn*-6MeGuo**	***anti*-6MeGuo**	***anti*-6MeGuo**
			
0.0 kcal/mol	2.5 kcal/mol	8.3 kcal/mol	10.3 kcal/mol

Table S26. Optimized geometries of 6MeGuo conformations in acetonitrile.

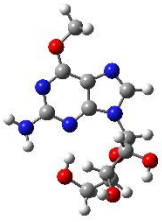
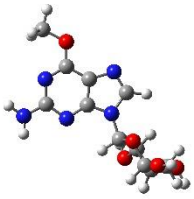
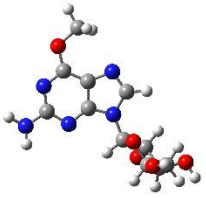
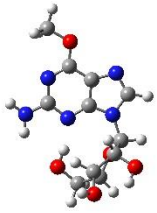
***syn*-6MeGuo**	***anti*-6MeGuo**	***anti*-6MeGuo**	***syn*-6MeGuo**
			
0.0 kcal/mol	3.8 kcal/mol	6.8 kcal/mol	9.6 kcal/mol

Table S27. Optimized geometries of 6EnolGuo conformations in vacuum.

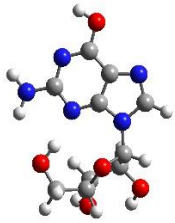
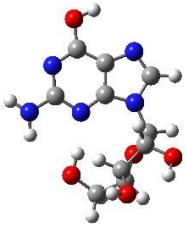
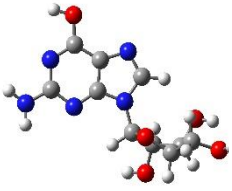
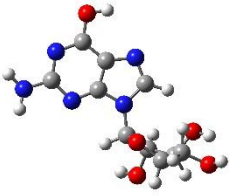
***syn*-6EnolGuo**	***syn*-6EnolGuo**	***anti*-6EnolGuo**	***anti*-6EnolGuo-**
			
0.0 kcal/mol	0.4 kcal/mol	6.3 kcal/mol	7.1 kcal/mol

Table S28. Vertical energies for the relevant singlet and triplet transitions of *syn*-6MeGuo with the O^6-methyl group oriented toward the N7 position in acetonitrile.

State	Transition	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	97.6	$\pi\pi*$	4.68 (0.173)
	H-0→L+2	2.4		
S_2	H-4→L+0	3.4	$n\pi*$	5.30 (0.005)
	H-3→L+0	15.3		
	H-2→L+0	21.8		
	H-1→L+0	55.9		
	H-0→L+2	3.4		
S_3	H-0→L+0	25.9	$\pi\pi*$	5.39 (0.127)
	H-0→L+0	3.7		
	H-0→L+1	21.2		
	H-0→L+2	49.1		
T_1	H-0→L+0	100.0	$\pi\pi*$	3.45
T_2	H-2→L+0	3.4	$\pi\pi*$	4.30
	H-0→L+0	3.4		
	H-0→L+1	14.4		
	H-0→L+2	78.6		
T_3	H-9→L+0	8.7	$\pi\pi*$	4.77
	H-4→L+0	5.3		
	H-2→L+0	19.4		
	H-2→L+2	2.5		
	H-1→L+0	16.8		
	H-0→L+2	6.8		
	H-0→L+6	30.4		
	H-0→L+7	9.8		

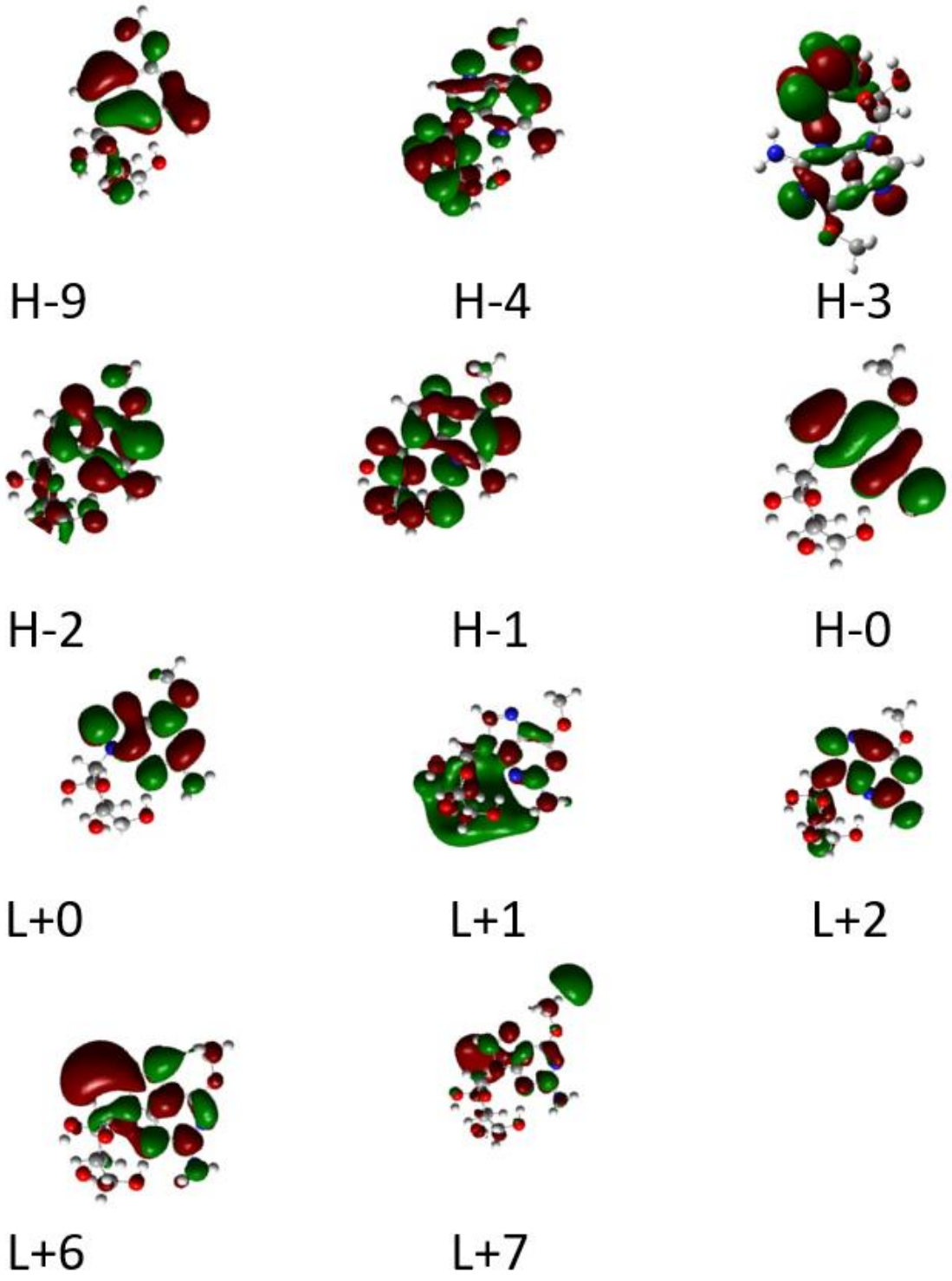


Figure S23. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of syn-6MeGuo with the O^6-methyl group oriented toward the N7 position in acetonitrile.

Table S29. Vertical energies for the relevant singlet and triplet transitions of *syn*-6MeGuo with the O^6-methyl group oriented toward the N1 position in acetonitrile.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	96.0	$\pi\pi*$	4.79 (0.198)
	H-0→L+3	4.0		
S_2	H-0→L+1	90.1	$n\pi*$	5.20 (0.003)
	H-0→L+2	6.6		
	H-0→L+3	3.2		
S_3	H-3→L+0	8.2	$n\pi*$	5.35 (0.032)
	H-2→L+0	11.7		
	H-1→L+0	57.9		
	H-0→L+3	22.2		
S_4	H-2→L+0	30.8	$n\pi*$	5.39 (0.095)
	H-1→L+0	8.3		
	H-0→L+0	3.8		
	H-0→L+2	5.6		
	H-0→L+3	51.5		
T_1	H-0→L+0	100.0	$\pi\pi*$	3.45
T_2	H-0→L+0	2.9	$n\pi*$	4.28
	H-0→L+3	97.1		
T_3	H-9→L+0	12.8	$\pi\pi*$	4.82
	H-0→L+7	43.9		
	H-0→L+8	10.1		
	H-0→L+9	15.8		
	H-0→L+11	4.3		
	H-0→L+13	9.7		
	H-0→L+14	3.3		

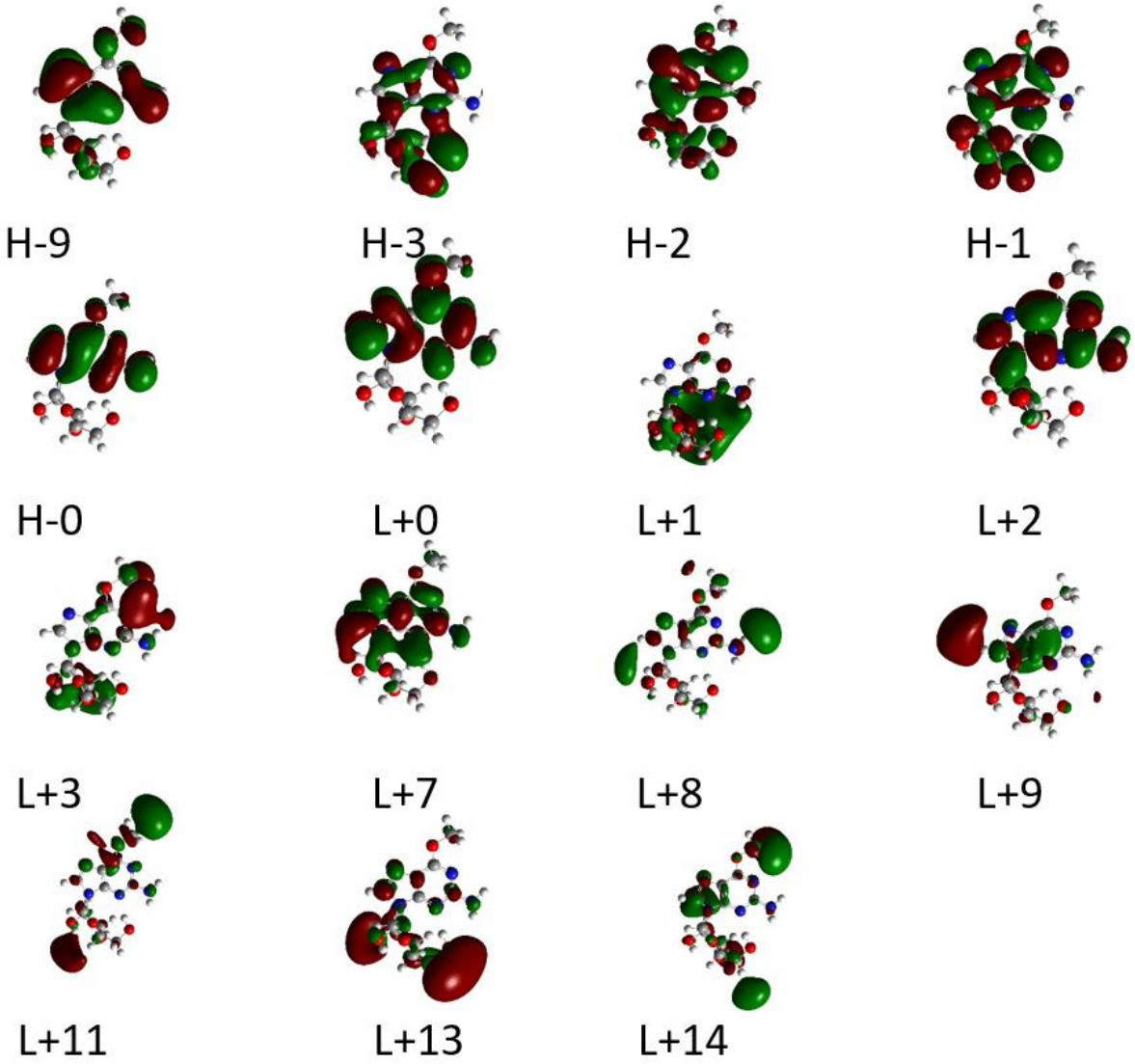


Figure S24. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6MeGuo with the O^6-methyl group oriented toward the N1 position in acetonitrile.

Table S30. Vertical energies for the relevant singlet and triplet transitions of *anti*-6MeGuo with the O^6-methyl group oriented toward the N7 position in acetonitrile.

State	Transitions	% Composition	Primary Character	eV
S_1 (L_a)	H-0→L+0 H-0→L+1	96.6 3.4	$\pi\pi*$	4.73 (0.195)
S_2	H-3→L+0 H-2→L+0 H-1→L+0	3.0 92.6 4.4	$n\pi*$	5.34 (0.002)
S_3	H-3→L+0 H-2→L+0 H-1→L+0 H-0→L+0 H-0→L+1 H-0→L+2 H-0→L+3	4.5 2.7 12.5 4.8 70.8 2.2 2.5	$\pi\pi*$	5.36 (0.169)
S_4	H-0→L+2 H-0→L+3 H-0→L+4	50.9 45.9 3.2	$n\pi*$	5.50 (0.002)
T_1	H-0→L+0	100.0	$\pi\pi*$	3.46
T_2	H-1→L+0 H-0→L+0 H-0→L+1 H-0→L+2 H-0→L+3 H-0→L+7	2.4 3.5 85.6 3.0 2.6 2.9	$\pi\pi*$	4.33
T_3	H-9→L+0 H-3→L+0 H-3→L+1 H-1→L+0 H-0→L+1 H-0→L+4 H-0→L+7 H-0→L+8 H-0→L+9	9.5 8.5 3.7 7.6 9.0 2.9 24.9 26.2 7.9	$\pi\pi*$	4.70

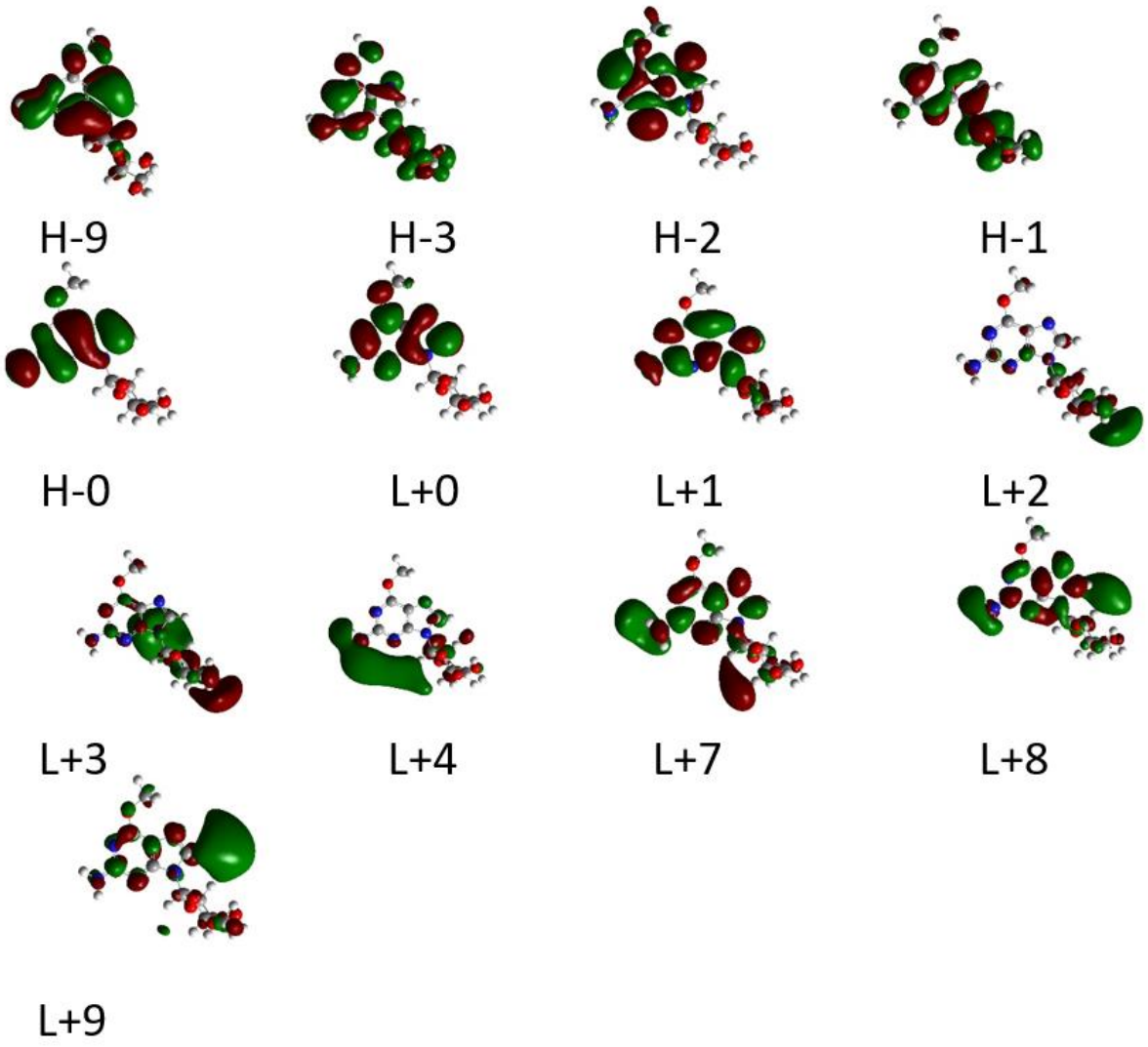


Figure S25. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *anti*-6MeGuo with the O^6-methyl group oriented toward the N7 position in acetonitrile.

Table S31. Vertical energies for the relevant singlet and triplet transitions of *anti*-6MeGuo with the O^6-methyl group oriented toward the N1 position in acetonitrile.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0 H-0→L+2	97.9 2.1	$\pi\pi*$	4.76 (0.291)
S_2	H-3→L+0 H-1→L+0 H-0→L+0 H-0→L+2 H-0→L+3	7.2 6.7 3.8 59.8 22.5	$\pi\pi*$	5.35 (0.185)
S_3	H-2→L+0 H-0→L+1 H-0→L+2 H-0→L+3	42.4 35.6 3.1 19.0	$n\pi*$	5.41 (0.001)
S_4	H-2→L+0 H-0→L+1 H-→L+2 H-→L+3	56.3 27.2 2.3 14.2	$n\pi*$	5.43 (0.003)
T_1	H-→L+0	100.0	$\pi\pi*$	3.44
T_2	H-0→L+2 H-0→L+3 H-0→L+7	67.6 29.7 2.7	$\pi\pi*$	4.31
T_3	H-9→L+0 H-0→L+2 H-0→L+4 H-0→L+6 H-0→L+7 H-0→L+9 H-0→L+14	11.3 3.7 2.9 4.5 65.9 8.3 3.3	$\pi\pi*$	4.71

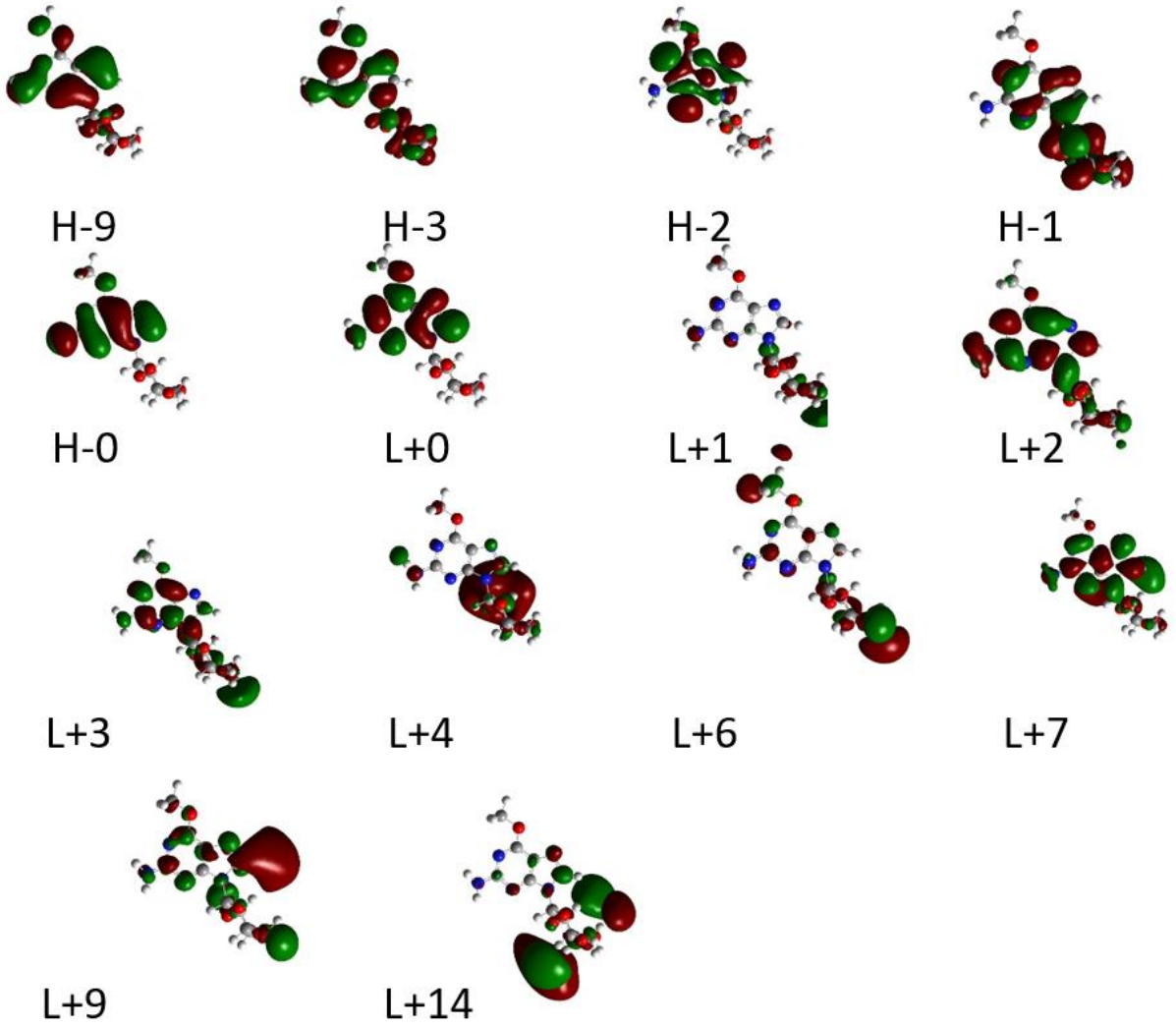


Figure S26. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *anti*-6MeGuo with the O^6-methyl group oriented toward the N1 position in acetonitrile.

Table S32. Vertical energies for the relevant singlet and triplet transitions of *syn*-6MeGuo with the O^6-methyl group oriented toward the N1 position in vacuum.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	96.0	$\pi\pi*$	4.79 (0.198)
	H-0→L+3	4.0		
S_2	H-0→L+1	90.1	$n\pi*$	5.20 (0.003)
	H-0→L+2	6.6		
	H-0→L+3	3.2		
S_3	H-3→L+0	8.2	$\pi\pi*$	5.35 (0.032)
	H-2→L+0	11.7		
	H-1→L+0	58.0		
	H-0→+3	22.2		
S_4	H-2→L+0	30.8	$CT, \pi\pi*$	5.39 (0.095)
	H-1→L+0	8.3		
	H-0→L+0	3.8		
	H-0→L+2	5.6		
	H-0→L+3	51.5		
T_1	H-0→L+0	100.0	$\pi\pi*$	3.45
T_2	H-0→L+0	2.9	$\pi\pi*$	4.28
	H-0→L+3	97.1		
T_3	H-9→L+0	12.8	$\pi\pi*$	4.82
	H-0→L+7	43.9		
	H-0→L+8	10.1		
	H-0→L+9	15.8		
	H-0→L+11	4.3		
	H-0→L+13	9.7		
	H-0→L+14	3.3		

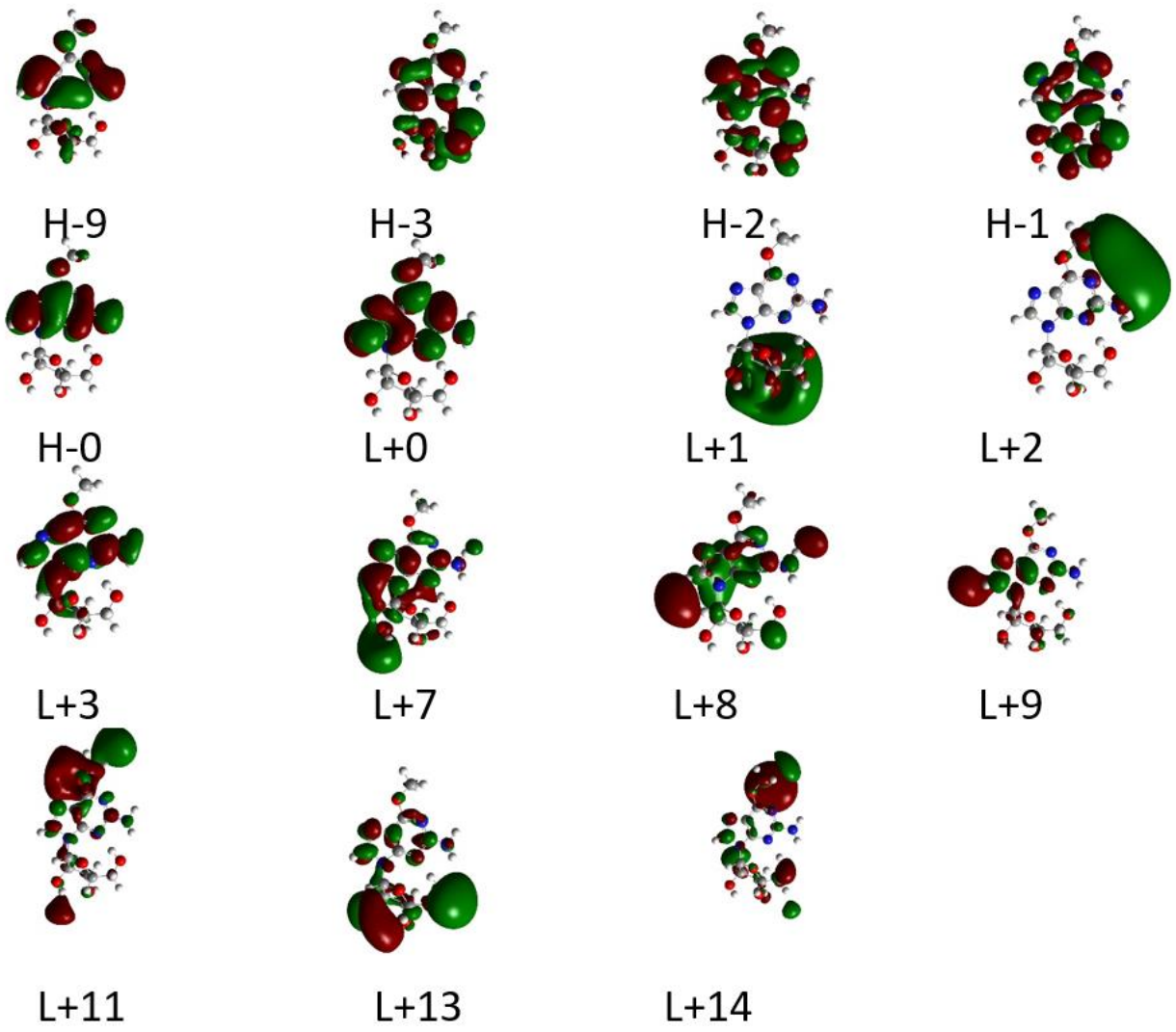


Figure S27. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6MeGuo with the O^6-methyl group oriented toward the N1 position in vacuum.

Table S33. Vertical energies for the relevant singlet and triplet transitions of *syn*-6MeGuo with the O^6-methyl group oriented toward the N7 position in vacuum.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	96.0	$\pi\pi*$	4.74 (0.140)
	H-0→L+2	4.0		
S_2	H-3→L+0	14.1	$n\pi*$	5.22 (0.001)
	H-2→L+0	19.7		
	H-1→L+0	66.2		
S_3	H-0→L+1	92.6	$n\pi*$	5.26 (0.002)
	H-0→L+2	5.2		
	H-0→L+4	2.2		
S_4	H-2→L+0	22.1	$CT, \pi\pi*$	5.40 (0.101)
	H-1→L+0	2.6		
	H-0→L+0	5.3		
	H-0→L+1	5.4		
	H-0→L+2	64.6		
T_1	H-0→L+0	100.0	$\pi\pi*$	3.48
T_2	H-2→L+0	4.0	$\pi\pi*$	4.32
	H-0→L+0	4.0		
	H-0→L+2	89.5		
	H-0→L+3	2.5		
T_3	H-9→L+0	7.0	$\pi\pi*$	4.73
	H-4→L+0	3.2		
	H-3→L+0	4.0		
	H-2→L+0	25.7		
	H-2→L+2	5.3		
	H-1→L+0	13.8		
	H-0→L+2	8.5		
	H-0→L+7	22.9		
	H-0→L+9	7.3		
	H-0→L+11	2.4		

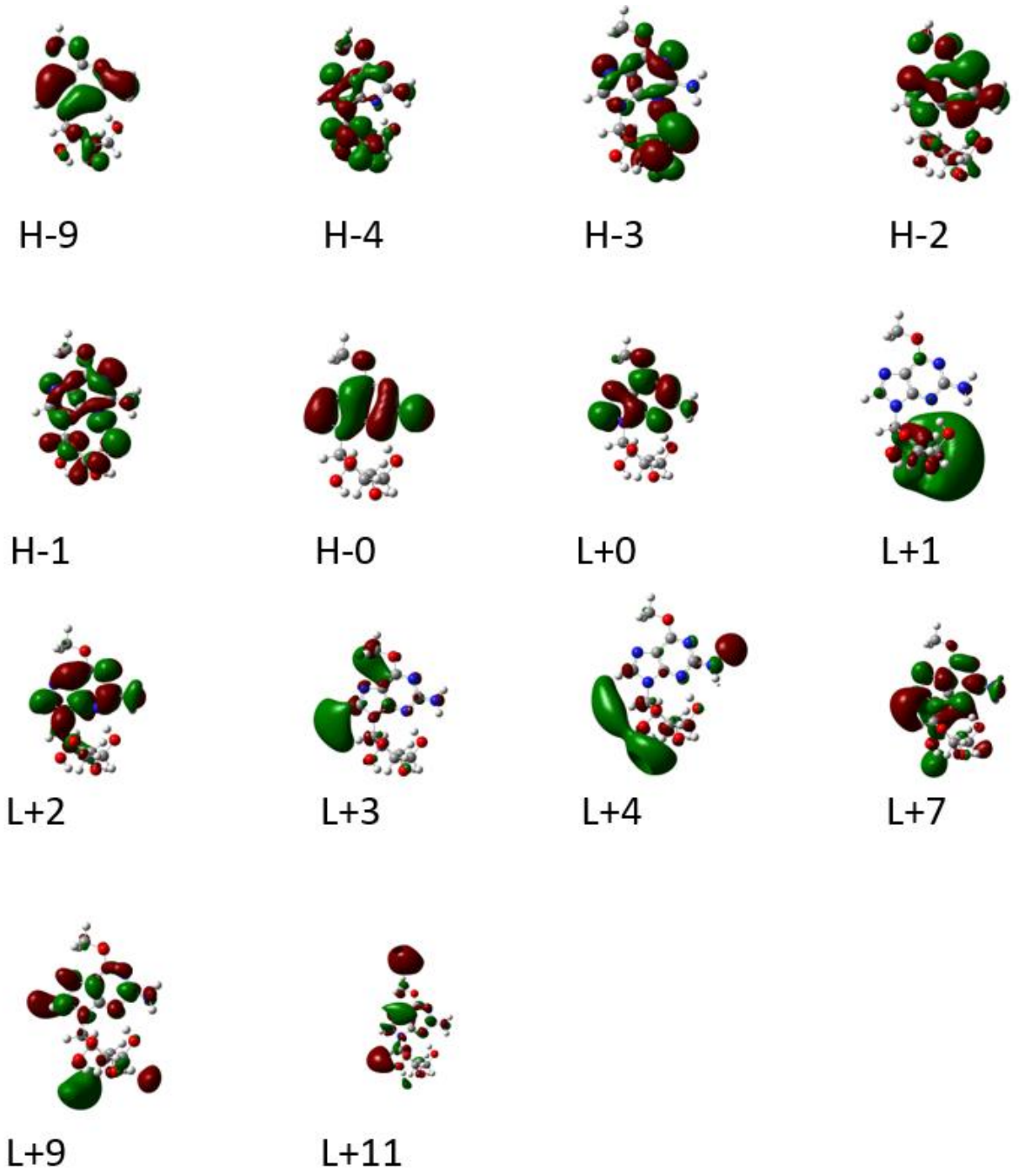


Figure S28. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6MeGuo with the O^6-methyl group oriented toward the N7 position in vacuum.

Table S34. Vertical energies for the relevant singlet and triplet transitions of *anti*-6MeGuo with the methyl group oriented toward the N1 position in vacuum.

State	Transitions	% Contribution	Primary Character	eV
S_1	H-0→L+0	7.7	$\pi\pi^*$	4.86 (0.242)
	H-0→L+1	89.3		
	H-0→L+5	3.0		
S_2 (L_a)	H-0→L+0	69.9	$n\pi^*$	5.01 (0.004)
	H-0→L+1	4.6		
	H-0→L+2	25.5		
S_3	H-0→L+0	22.8	$n\pi^*$	5.07 (0.002)
	H-0→L+1	3.1		
	H-0→L+2	66.6		
	H-0→L+4	7.5		
S_4	H-2→L+1	5.2	$n\pi^*$	5.31 (0.058)
	H-0→L+2	5.4		
	H-0→L+4	68.3		
	H-0→L+5	18.8		
	H-0→L+7	2.3		
T_1	H-0→L+0	8.5	$\pi\pi^*$	3.45
	H-0→L+1	91.5		
T_2	H-0→L+1	2.5	$\pi\pi^*$	4.32
	H-0→L+4	8.1		
	H-0→L+5	65.8		
	H-0→L+6	7.8		
	H-0→L+7	12.3		
	H-0→L+8	3.6		
T_3	H-9→L+1	4.0	$\pi\pi^*$	4.73
	H-8→L+1	5.6		
	H-0→L+0	8.6		
	H-0→L+4	3.4		
	H-0→L+6	8.2		
	H-0→L+8	20.6		
	H-0→L+9	9.7		
	H-0→L+10	3.9		
	H-0→L+11	20.0		
	H-0→L+14	7.2		
	H-0→L+15	8.8		

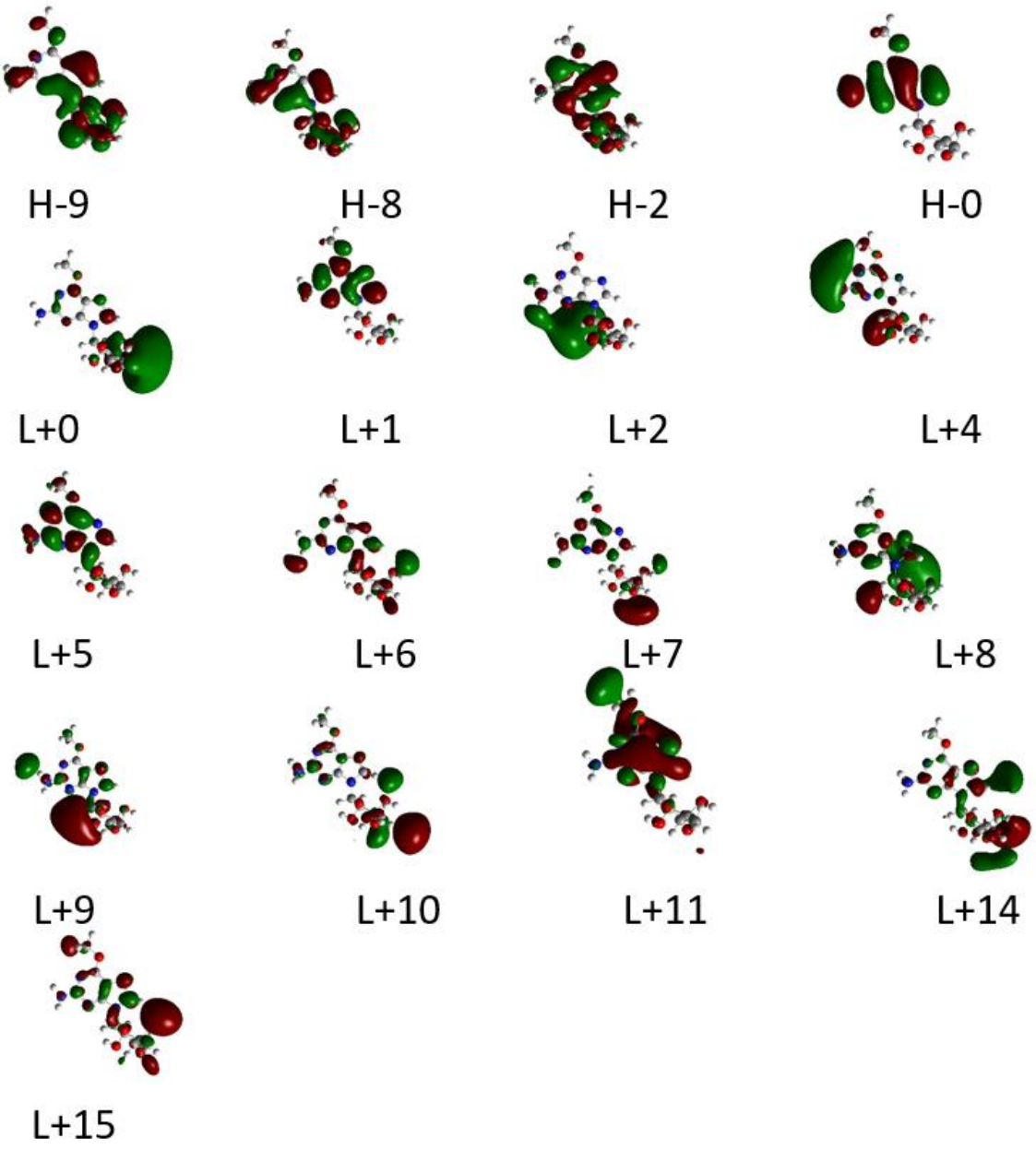


Figure S29. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *anti*-6MeGuo with the methyl group oriented toward the N1 position in vacuum.

Table S35. Vertical energies for the relevant singlet and triplet transitions of *anti*-6MeGuo with the methyl group oriented toward the N7 position in vacuum.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	100.0	$\pi\pi*$	4.82 (0.158)
S_2	H-3→L+0	14.7	$n\pi*$	5.29 (0.010)
	H-2→L+0	23.0		
	H-1→L+0	50.5		
	H-0→L+1	4.6		
	H-0→L+2	3.5		
	H-0→L+3	3.5		
S_3	H-2→L+0	25.3	$n\pi*$	5.34 (0.055)
	H-0→L+0	3.4		
	H-0→L+1	42.1		
	H-0→L+2	23.6		
	H-0→L+3	2.5		
	H-0→L+4	2.9		
S_4	H-2→L+0	13.1	$CT, \pi\pi*$	5.49 (0.027)
	H-1→L+0	3.2		
	H-0→L+1	14.6		
	H-0→L+3	50.2		
	H-0→L+4	15.5		
	H-0→L+6	3.5		
T_1	H-0→L+0	100.0	$\pi\pi*$	3.49
T_2	H-0→L+0	2.6	$\pi\pi*$	4.36
	H-0→L+1	17.8		
	H-0→L+2	20.7		
	H-0→L+3	34.1		
	H-0→L+5	6.4		
	H-0→L+6	18.3		
T_3	H-9→L+0	8.8	$\pi\pi*$	4.79
	H-3→L+0	11.9		
	H-2→L+0	20.2		
	H-1→L+0	20.0		
	H-0→L+1	2.7		
	H-0→L+3	8.3		
	H-0→L+7	5.6		
	H-0→L+8	19.9		
	H-0→L+9	2.7		

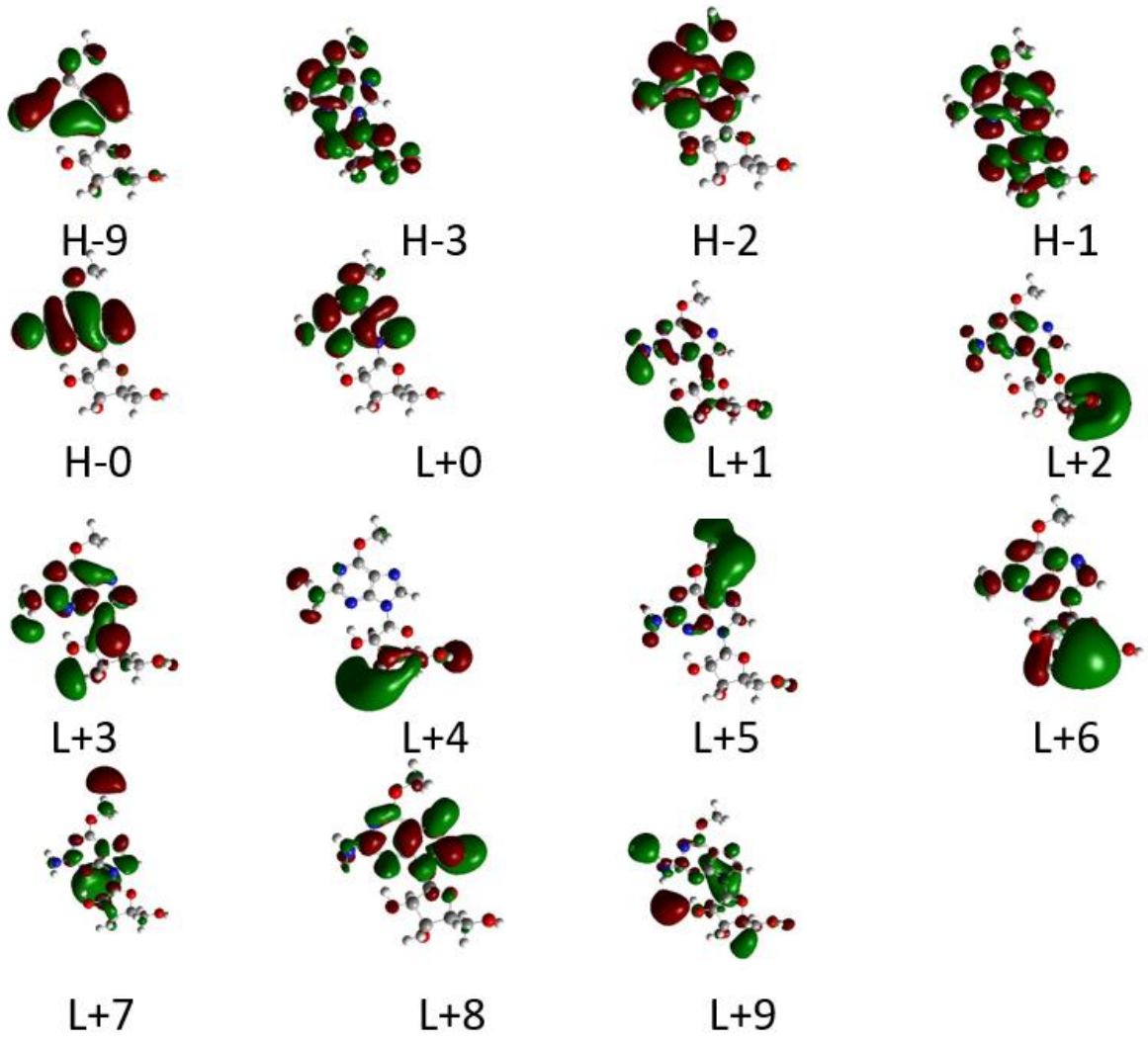


Figure S30. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *anti*-6MeGuo with the methyl group oriented toward the N7 position in vacuum.

Table S36. Vertical energies for the relevant singlet and triplet transitions of *syn*-6EnolGuo with the O^6-hydrogen oriented toward the N1 position in vacuum.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	95.4	$\pi\pi^*$	4.79 (0.145)
	H-0→L+2	4.6		
S_2	H-0→L+1	86.9	$n\pi^*$	5.29 (0.003)
	H-0→L+2	4.0		
	H-0→L+3	9.1		
S_3	H-3→L+0	11.3	$n\pi^*$	5.37 (0.018)
	H-2→L+0	19.1		
	H-1→L+0	54.3		
	H-0→L+1	3.1		
	H-0→L+2	12.1		
S_4	H-2→L+0	31.1	$\pi\pi^*$	5.42 (0.108)
	H-1→L+0	2.1		
	H-0→L+0	4.5		
	H-0→L+1	2.3		
	H-0→L+2	60.0		
T_1	H-0→L+0	100.0	$\pi\pi^*$	3.46
T_2	H-0→L+0	3.4	$\pi\pi^*$	4.28
	H-0→L+2	96.6		
T_3	H-9→L+0	15.2	$\pi\pi^*$	4.86
	H-0→L+7	52.3		
	H-0→L+8	3.1		
	H-0→L+9	17.9		
	H-0→L+11	11.5		

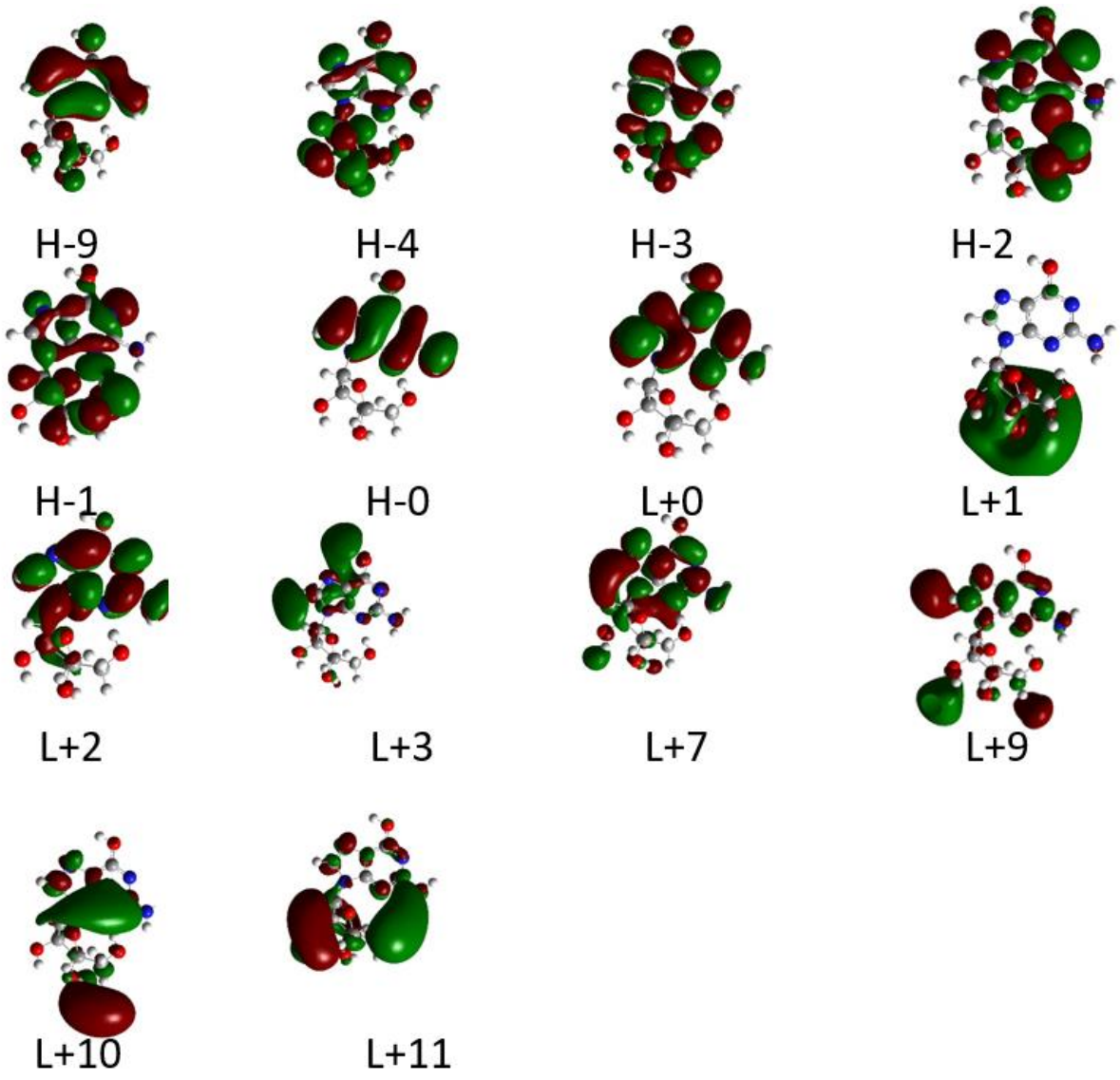


Figure S31. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6EnolGuo with the O^6-hydrogen oriented toward the N1 position in vacuum.

Table S37. Vertical energies for the relevant singlet and triplet transitions of *syn*-6EnolGuo with the O^6-hydrogen oriented toward the N7 position in vacuum.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	95.9	$\pi\pi*$	4.77 (0.156)
	H-0→L+2	4.1		
S_2	H-4→L+0	2.3	$n\pi*$	5.28 (0.001)
	H-2→L+0	33.0		
	H-1→L+0	62.1		
	H-0→L+2	2.6		
S_3	H-0→L+1	90.3	$n\pi*$	5.31 (0.002)
	H-0→L+2	6.1		
	H-0→L+3	3.6		
S_4	H-3→L+0	11.8	$\pi\pi*$	5.41 (0.120)
	H-2→L+0	7.3		
	H-0→L+0	4.9		
	H-0→L+1	6.8		
	H-0→L+2	69.1		
T_1	H-0→L+0	100.0	$\pi\pi*$	3.46
T_2	H-0→L+0	3.1	$\pi\pi*$	4.31
	H-0→L+2	96.9		
T_3	H-9→L+0	11.9	$\pi\pi*$	4.79
	H-3→L+0	3.4		
	H-3→L+2	3.4		
	H-0→L+2	4.0		
	H-0→L+7	55.2		
	H-0→L+9	12.7		
	H-0→L+10	4.3		
	H-0→L+11	5.2		

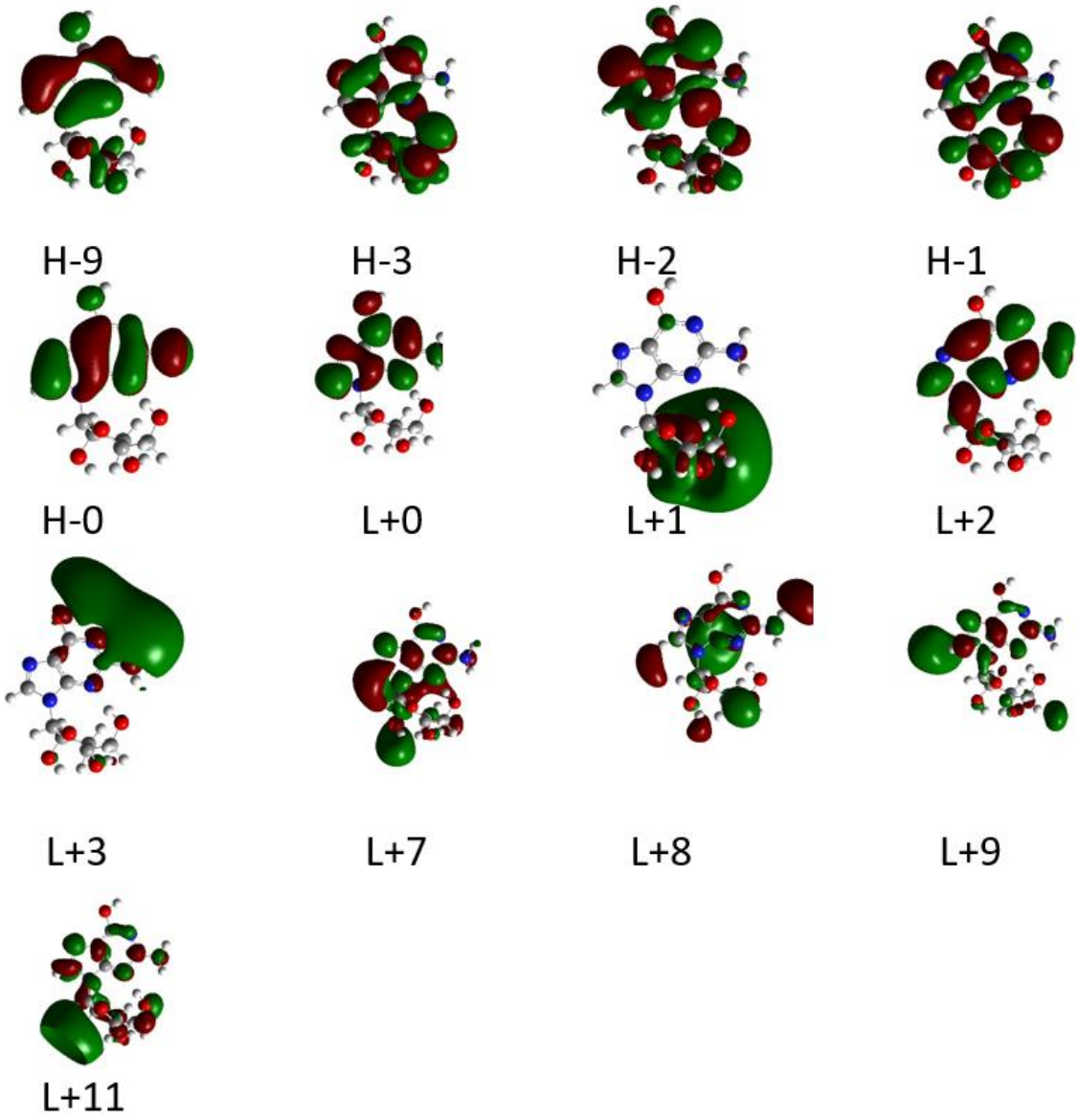


Figure S32. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6EnolGuo with the O^6-hydrogen oriented toward the N7 position in vacuum.

Table S38. Vertical energies for the relevant singlet and triplet transitions of *anti*-6EnolGuo with the O^6-hydrogen oriented toward the N1 position in vacuum.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0 H-0→L+1 H-0→L+4	81.3 14.3 4.4	$\pi\pi*$	4.87 (0.174)
S_2	H-0→L+1 H-0→L+2 H-0→L+3	3.4 86.7 9.9	$n\pi*$	5.15(0.003)
S_3	H-0→L+0 H-0→L+1 H-0→L+3	18.7 77.3 4.0	$n\pi*$	5.18 (0.010)
S_4	H-2→L+0 H-0→L+1 H-0→L+2 H-0→L+3 H-0→L+4	8.0 7.7 6.8 53.4 24.0	$n\pi*$	5.39 (0.097)
T_1	H-0→L+0 H-0→L+1	84.0 16.0	$\pi\pi*$	3.46
T_2	H-0→L+1 H-0→L+3 H-0→L+4 H-0→L+7	2.7 15.5 77.4 4.5	$\pi\pi*$	4.30
T_3	H-9→L+0 H-0→L+4 H-0→L+5 H-0→L+7 H-0→L+9 H-0→L+10 H-0→L+11 H-0→L+15	10.0 8.0 3.4 7.1 23.0 29.2 15.8 3.5	$\pi\pi*$	4.77

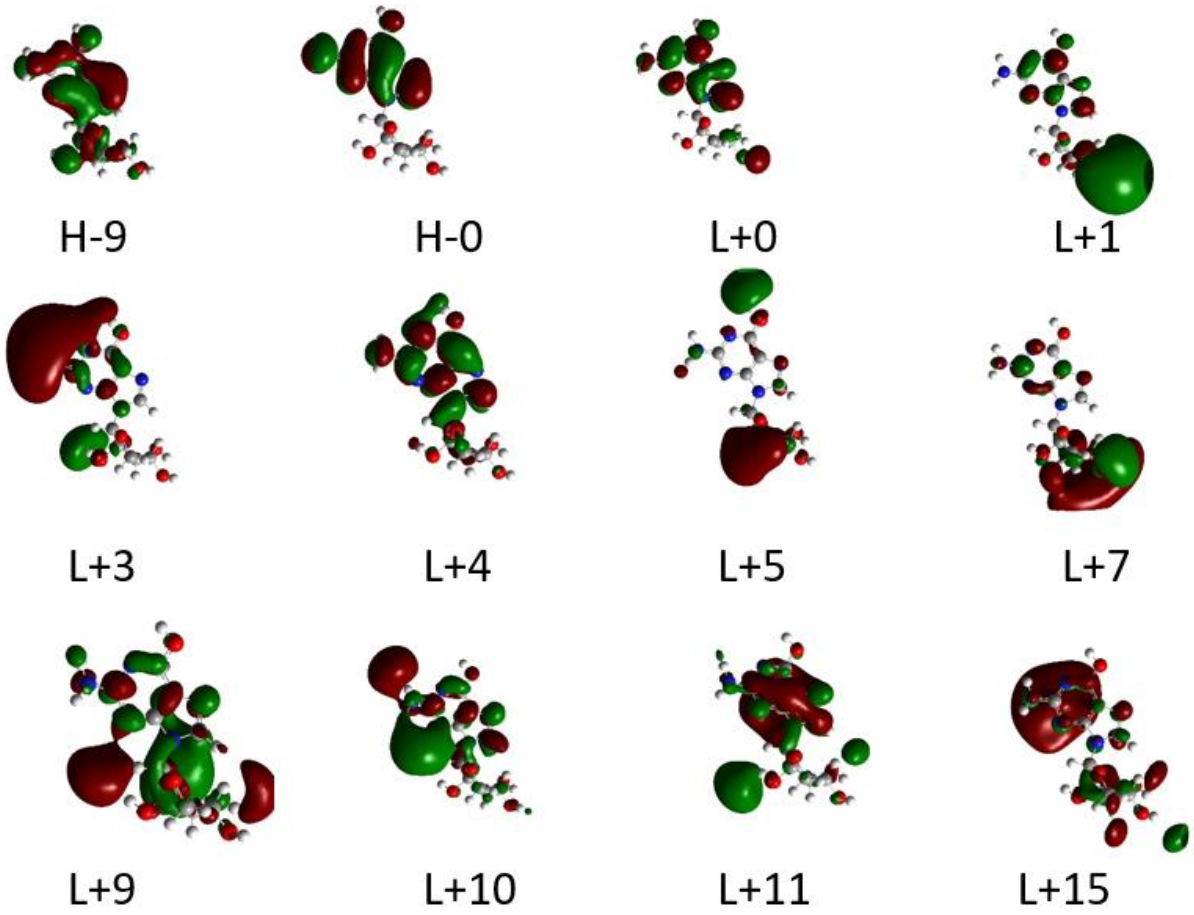


Figure S33. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *anti*-6EnolGuo with the O^6-hydrogen oriented toward the N1 position in vacuum.

Table S39. Vertical energies for the relevant singlet and triplet transitions of *anti*-6EnolGuo with the O^6-hydrogen oriented toward the N7 position in vacuum.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0 H-0→L+1 H-0→L+4	54.6 42.7 2.7	$\pi\pi*$	4.84 (0.199)
S_2	H-0→L+0 H-0→L+1 H-0→L+2	45.1 49.4 5.5	$CT, \pi\pi*$	5.09 (0.003)
S_3	H-0→L+0 H-0→L+2 H-0→L+3	2.9 88.9 8.2	$CT, \pi\pi*$	5.16 (0.002)
S_4	H-1→L+0 H-1→L+1	46.4 53.6	$CT, \pi\pi*$	5.28 (0.001)
T_1	H-0→L+0 H-0→L+1	47.9 52.1	$\pi\pi*$	3.46
T_2	H-0→L+1 H-0→L+3 H-0→L+4 H-0→L+6 H-0→L+7 H-0→L+9	3.2 27.0 53.8 2.9 9.5 3.6	$\pi\pi*$	4.34
T_3	H-9→L+0 H-9→L+1 H-2→L+1 H-2→L+4 H-0→L+4 H-0→L+7 H-0→L+9 H-0→L+10 H-0→L+11 H-0→+12 H-0→L+15	4.2 4.4 3.8 3.1 16.2 3.0 27.9 25.9 5.3 3.6 2.5	$\pi\pi*$	4.72

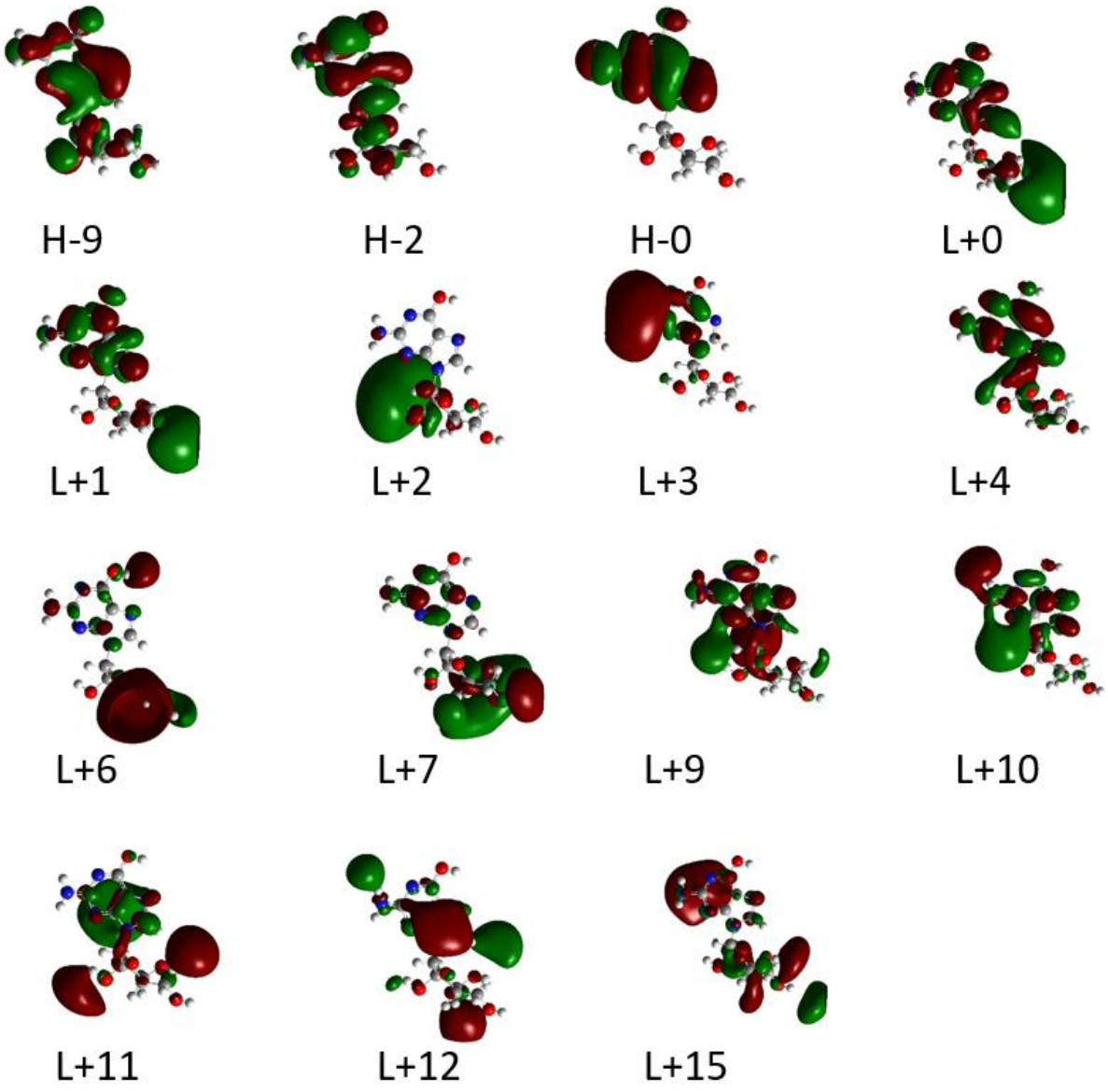


Figure S34. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *anti*-6EnolGuo with the O^6-hydrogen oriented toward the N7 position in vacuum.

Table S40. Vertical energies for the relevant singlet and triplet transitions of *syn*-6MeTGuo with the S^6-methyl oriented toward the N1 position in water.

State	Transitions	% Contribution	Primary Character	eV
S_1 (L_a)	H-0→L+0	100.0	$\pi\pi*$	4.30 (0.333)
S_2	H-3→L+0 H-2→L+0	16.7 83.3	$n\pi*$	4.85 (0.002)
S_3	H-1→L+0 H-0→L+1 H-0→L+2	75.6 9.9 14.5	$\pi\pi*$	5.05 (0.121)
T_1	H-0→L+0	100.0	$\pi\pi*$	3.11
T_2	H-4→L+0 H-1→L+0 H-1→L+1 H-1→L+2 H-0→L+1 H-0→L+2 H-0→L+7	2.6 41.1 3.0 4.9 15.9 30.0 2.5	$\pi\pi*$	4.20
T_3	H-9→L+0 H-9→L+1 H-2→L+1 H-2→L+4 H-0→L+4 H-0→L+7 H-0→L+9 H-0→L+10 H-0→L+11 H-0→L+12 H-0→L+15	4.2 4.4 3.8 3.1 16.2 3.0 27.9 25.9 5.3 3.6 2.5	$\pi\pi*$	4.28

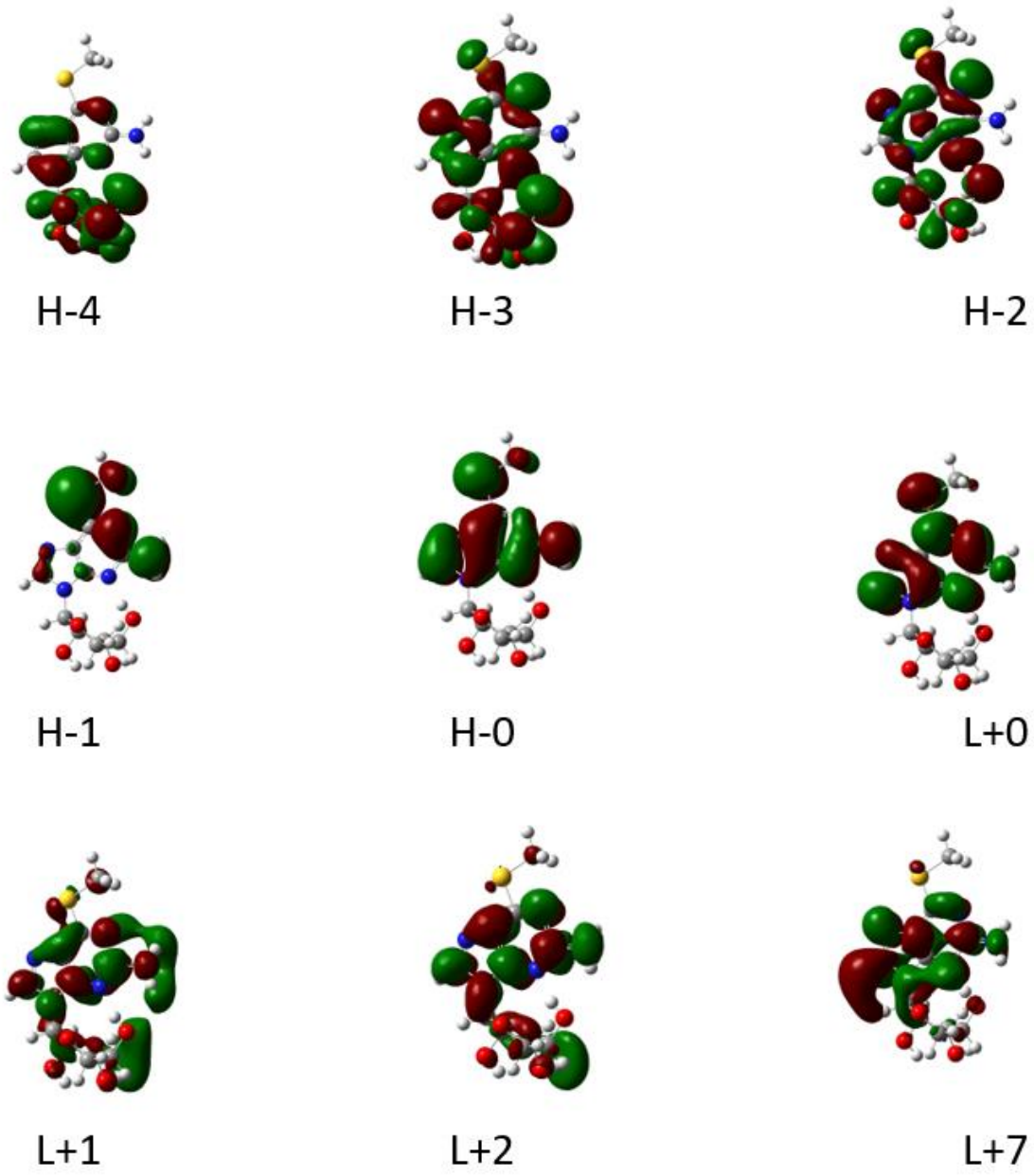


Figure S35. Kohn-Sham orbitals that contribute to the relevant singlet and triplet vertical transitions of *syn*-6MeTGuo with the O^6-methyl oriented toward the N1 position in water.