Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Spectroscopic and Theoretical Studies on Hydrogen Bonding Clusters, Triplet Species and Relaxation Mechanism of Light ($^1\pi\pi^*$) State of 4-Methyl-1, 2, 4-Triazole-3-Thione

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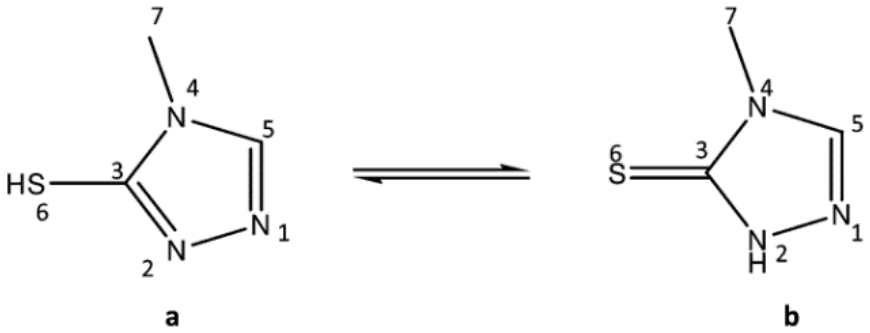
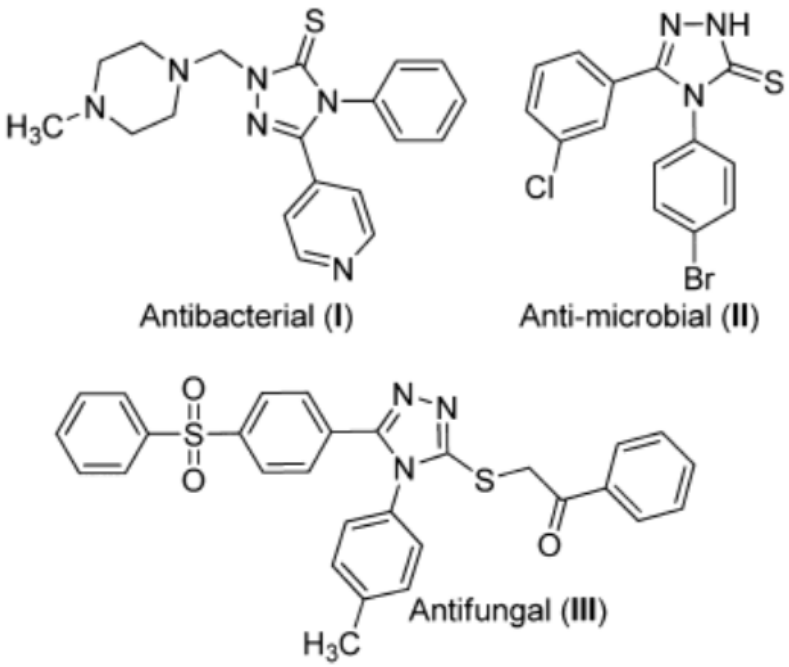


Scheme S1. 4-MTT in (a) thiol and (b) thione forms.



Scheme S2. Some biologically active 1,2,4-triazole-3-thione derivatives.

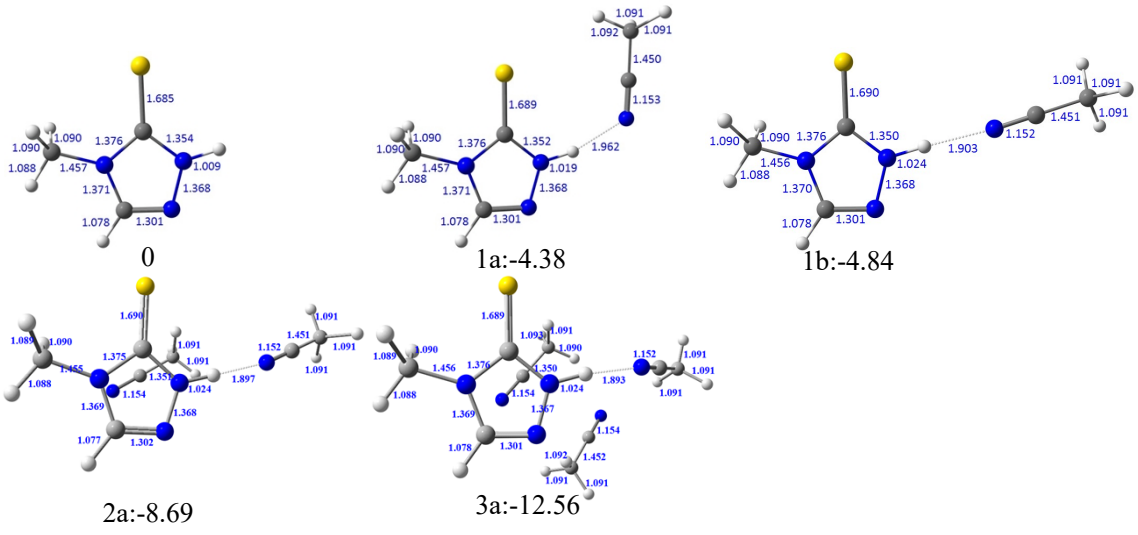


Figure S1. Optimized bond lengths (in Å) and relative energies (ΔE, in kcal/mol) of 4MTT and 4MTT$(CH_3CN)_n$ (n=1~3) clusters at B3LYP-D3(BJ)/6-311++G(d, p) level with PCM solvent model.

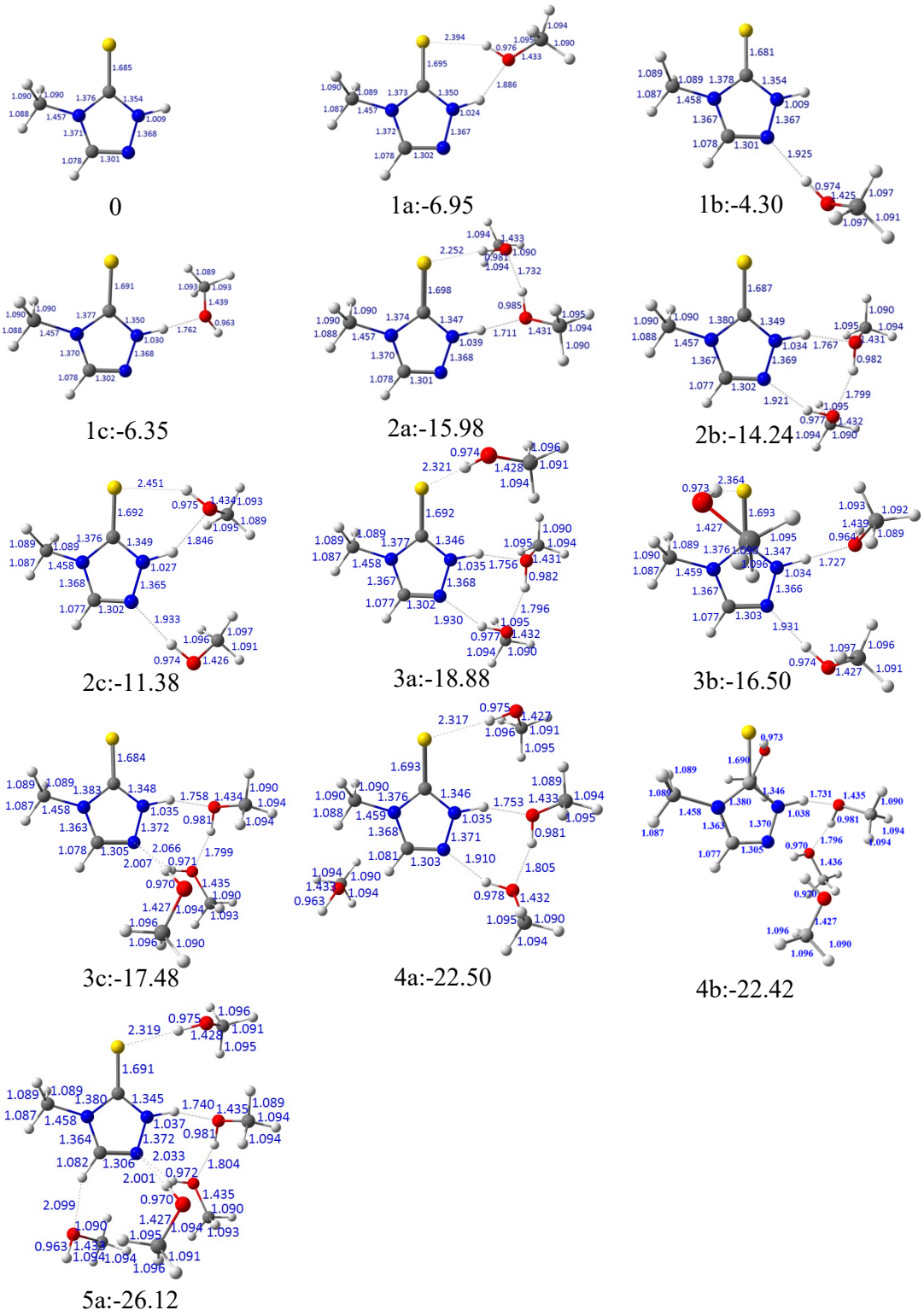


Figure S2. Optimized bond lengths (in Å) and relative energies (ΔE, in kcal/mol) of 4MTT and 4MTT$(CH_3OH)_n$ (n=1~5) clusters at B3LYP-D3(BJ)/6-311++G(d,p) level with PCM solvent model.

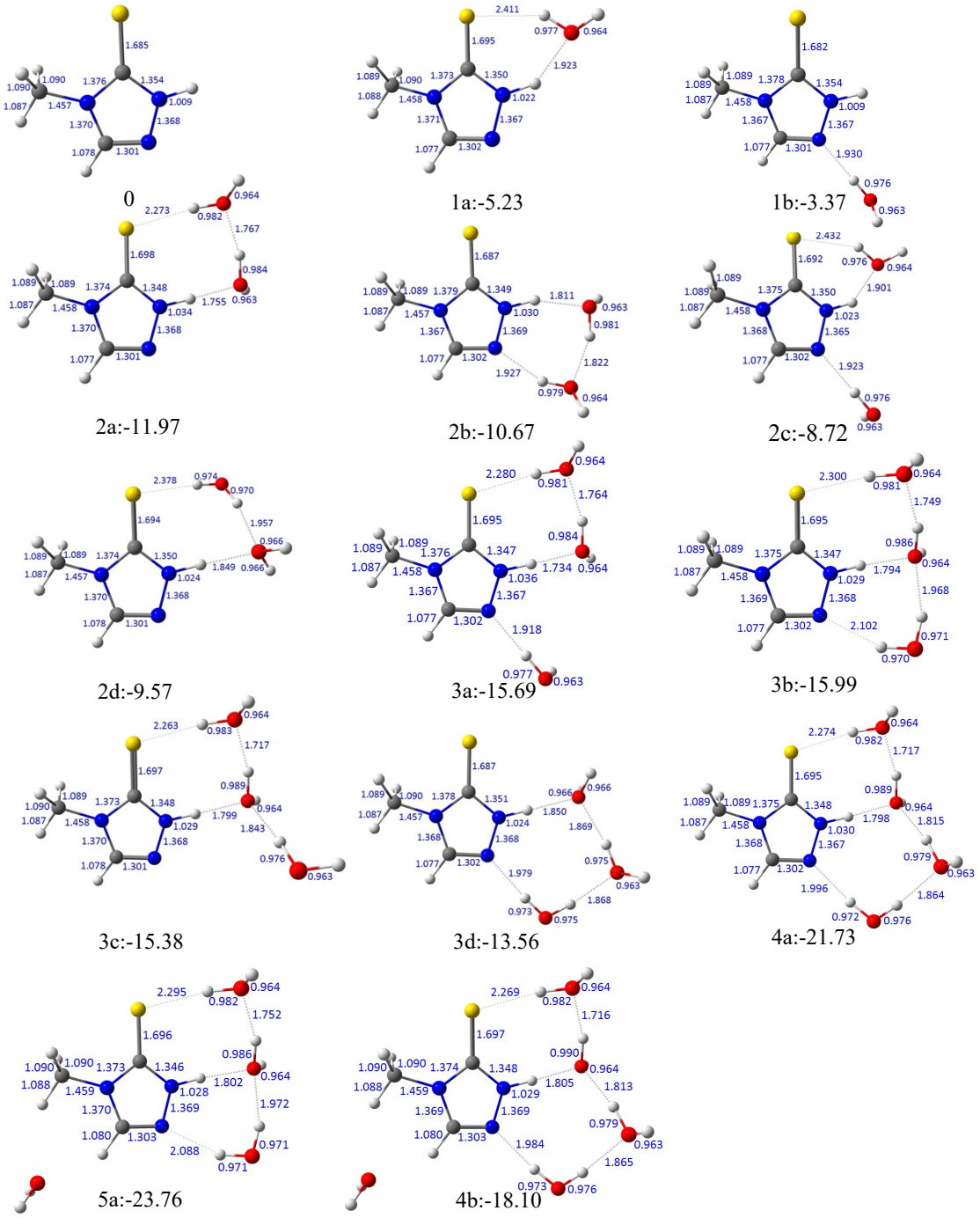


Figure S3. Optimized bond lengths (in Å) and relative energies (ΔE, in kcal/mol) of 4MTT and 4MTT$(H_2O)_n$ (n=1~5) clusters at B3LYP-D3(BJ)/6-311++G(d, p) level with PCM solvent model.

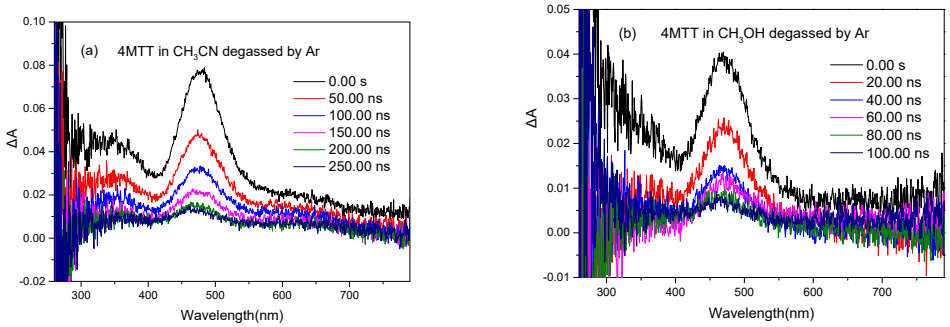


Figure S4. Nanosecond transient absorption spectra(λ_{ex}=266 nm) in (a) CH_3CN and(b) CH_3OH in degassed by Ar.

Figure S5. Calculated potential decay energy profile of the excited singlet and triplet electronic states from vertical excited $S_2(\pi\pi^*)$ state at (TD)B3LYP-D3(BJ) /6-311G(d, p) level with PCM Water model. The red dotted line indicated one most possible decay path direct to the triplet state observed experimentally.

The ground planar 4MTT was stimulated to the S_2 state in the Frank-condo district (S_2-FC) with ~120 kcal/mol^{-1}using 266 nm laser, which was corresponding to the first observed band at ~250 nm. Two relaxation pathways that connect the S_2-FC point were shown in Figure 9. One directs to the pyramidal minimum structure S_{2min} ($\pi\pi^*$) with ~95 kcal/mol, the other along with the relaxation of S_1 ($n\pi^*$) state with ~107 kcal/mol via a very fast internal conversion(IC) point. And then along ($^1n\pi^*$) state to the intersystem crossing points (S_1/T_1) was seamlessly reached to the ($^3\pi\pi^*$) state. However, excited state intramolecular proton transfer (ESIPT) from S_1/T_1 point could pass a barrier of ~16 kcal/mol^{-1} to tautomeric triplet. Furthermore, the photophysical pathways were calculated either direct to S_{1min} or to normal triplet species via conical intersection point S_0/T_1). Thus four possible decay pathways were proposed. According to our experiments, one of the most possible relaxation pathways direct to the triplet state species was observed. The mechanism was proposed as $S_2(\pi\pi^*) \rightarrow S_1(n\pi^*) \rightarrow S_1(n\pi^*)/T_1(\pi\pi^*) \rightarrow S_0/T_1(\pi\pi^*) \rightarrow {}^3(\pi\pi^*)_{min}$ or nonradiative to ground state from $T_1(\pi\pi^*)$ via the $S_0/T_1(\pi\pi^*)$.

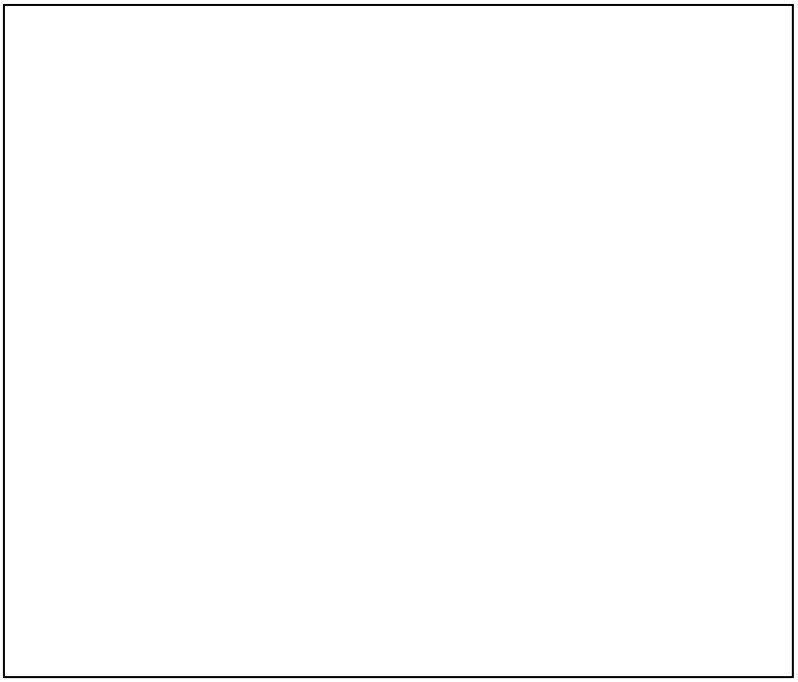


Figure S6. Calculated potential decay energy profile of the excited singlet and triplet electronic states from vertical excited $S_2(\pi\pi^*)$ state at (TD)B3LYP-D3(BJ) /6-311G(d,p) level with PCM acetonitrile model. The red dotted line indicated one most possible decay path direct to the triplet state observed experimentally.

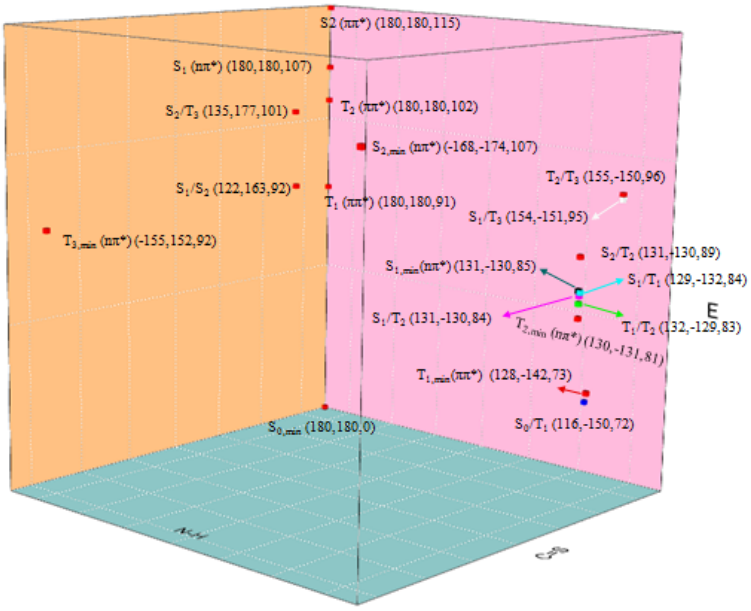
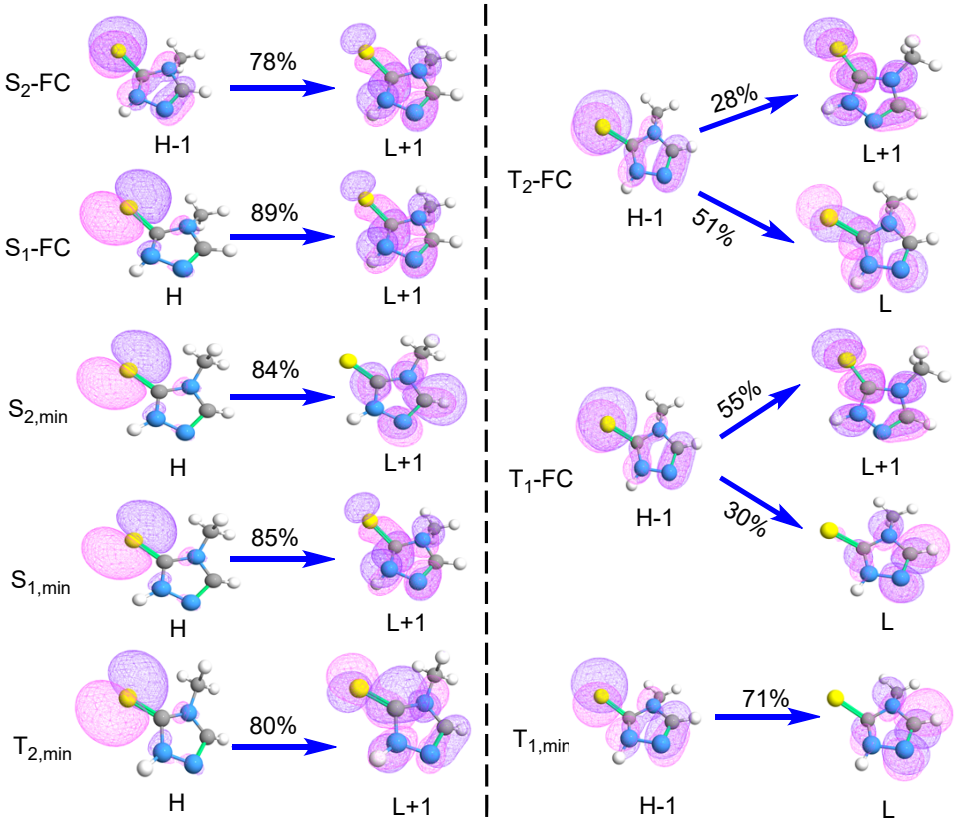


Figure S7. The Optimized all the minima at CASSCF(12e,9o)/cc-pVDZ level (the data in parentheses are indicated (Φ_1=$D_{N4\text{-}C1\text{-}C5\text{-}S7}$,$\Phi_2$=$D_{C1\text{-}N5\text{-}N4\text{-}H9}$, energy relative to S_0).



nπ* **ππ***

Figure S8. Frontier molecular orbitals of 4MTT in excited states calculated at CASSCF(12e,9o)/cc-pVDZ level.

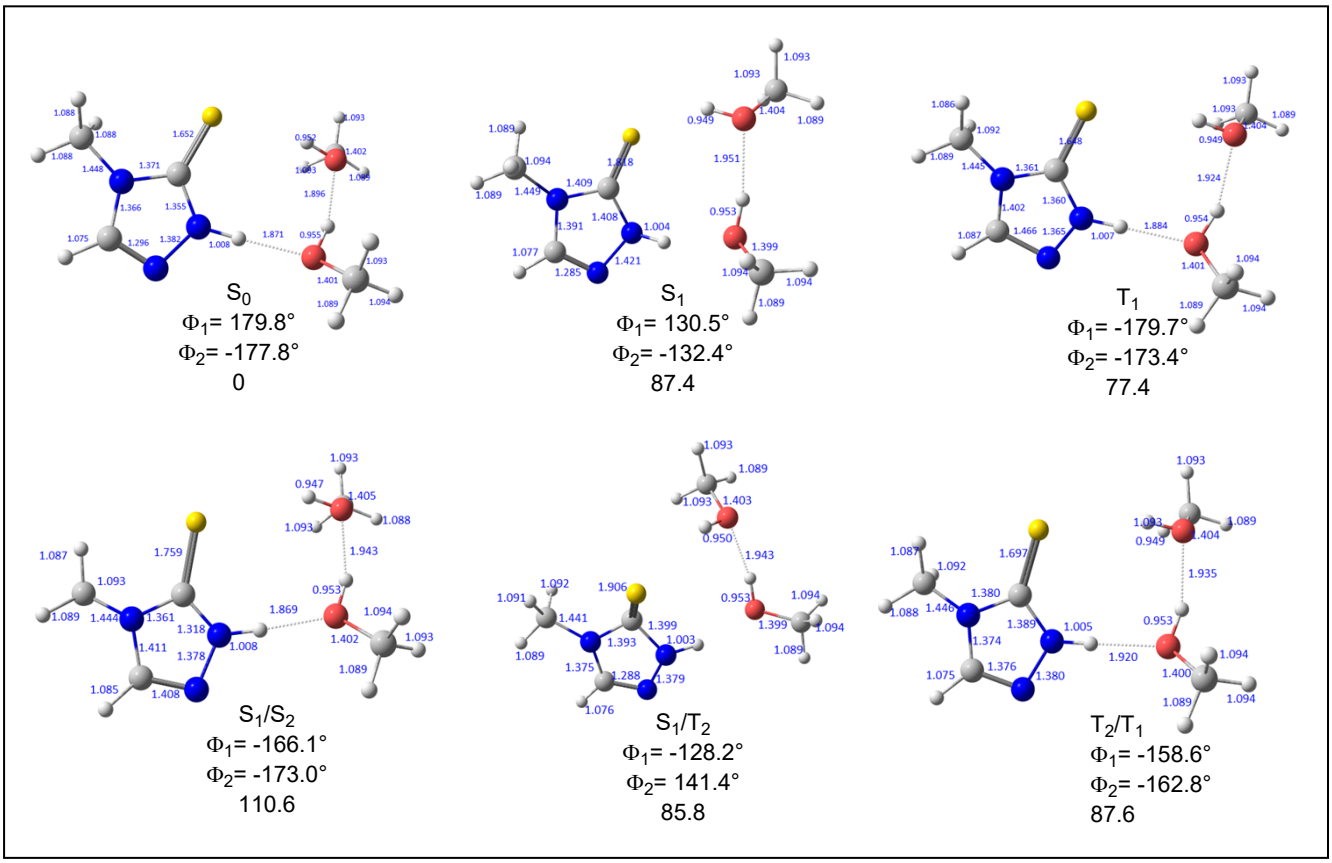


Figure S9. Optimized bond lengths and angles for different minimum structures (S_{2min}, S_{1min}, and T_{1min}), and CI points(S_2/S_1, S_2/T_2, S_1/T_2, and T_1/T_2) at CASSCF(12e/9o)/cc-pVDZ level (the arrow in dotted points to the plane and the solid points out of the plane,$\Phi_1=D_{N4\text{-}C1\text{-}C5\text{-}S7}$,$\Phi_2=D_{C1\text{-}N5\text{-}N4\text{-}H9}$).

Table S1. Experimental and calculated vibrational frequencies at B3LYP-D3/6-311++G(d, p) level and assignments of 4MTTdimer.

Mode (C_s)	Calc. (Raman activity/ IR intensity)	Exp. FT-Raman	Exp. FT-IR	Descriptions (PED%)
ν_1	3263.3(0.001/1959.6)			N_2H_6+$N_{14}H_{18}$ stretch
ν_2	3260.4(333.6/0.04)			N_2H_6+$N_{14}H_{18}$+C_5H_9+$C_{17}H_{21}$ stretch
ν_3	3258.5(0.005/1172.5)		3120	C_5H_9+$C_{17}H_{21}$ stretch
ν_4	3214.1(1389.7/0.007)	3128		N_2H_6+$N_{14}H_{18}$+C_5H_9+$C_{17}H_{21}$ stretch
ν_5	3142.1(88.7/3.6)			C_8H_{11}+$C_{20}H_{23}$ stretch
ν_6	3142.1(21.3/14.8)			C_8H_{11}+$C_{20}H_{23}$ stretch
ν_7	3119.7(19.4/9.7)			C_8H_{10}+C_8H_{12}+$C_{20}H_{22}$+$C_{20}H_{24}$ stretch
ν_8	3119.7(72.5/2.6)	3085		C_8H_{10}+C_8H_{12}+$C_{20}H_{22}$+$C_{20}H_{24}$ stretch
ν_9	3050.6(349.3/0.003)	2943		C_8H_{10}+C_8H_{11}+C_8H_{12}+$C_{20}H_{22}$+$C_{20}H_{23}$+$C_{20}H_{24}$ stretch
ν_{10}	3050.5(0.02/56.7)		2943	C_8H_{10}+C_8H_{11}+C_8H_{12}+$C_{20}H_{22}$+$C_{20}H_{23}$+$C_{20}H_{24}$ stretch
ν_{11}	1604.1(28.5/0.0004)	1552		N_1C_5 stretch+$N_{13}C_{17}$ stretch+$H_{18}N_{14}N_{13}$ bend+$C_3N_2H_6$ bend+$N_1N_2H_6$ bend
ν_{12}	1599.3(0.0001/132.2)		1552	N_1C_5 stretch+$N_{13}C_{17}$ stretch+$C_3N_2H_6$ bend+$N_1N_2H_6$ bend
ν_{13}	1540.5(0.0004/297.6)		1489	N_2C_3 stretch+$N_{14}C_{15}$ stretch+$H_{18}N_{14}N_{13}$ bend+$C_3N_2H_6$ bend+$N_2H_6S_{19}C_{15}$ tors+$N_1N_2H_6S_{19}$ tors
ν_{14}	1532.3(44.5/0.002)	1493		N_2C_3 stretch+$N_{14}C_{15}$ stretch+$H_{18}N_{14}N_{13}$ bend+$C_3N_2H_6$ bend+$N_2H_6S_{19}C_{15}$ tors+$N_1N_2H_6S_{19}$ tors
ν_{15}	1508.3(0.002/24.6)	**1423/ 1431**		$H_{10}C_8H_{12}$ bend+$H_{22}C_{20}H_{24}$ bend+$H_{10}C_8N_4C_3$ tors+$H_{12}C_8N_4C_3$ tors+$H_{22}C_{20}N_{16}C_{15}$ tors+$H_{24}C_{20}N_{16}C_{15}$ tors
ν_{16}	1507.6(20.9/0.003)		**1425**	$H_{10}C_8H_{12}$ bend+$H_{22}C_{20}H_{24}$ bend+$H_{10}C_8N_4C_3$ tors+$H_{12}C_8N_4C_3$ tors+$H_{22}C_{20}N_{16}C_{15}$ tors+$H_{24}C_{20}N_{16}C_{15}$ tors

ν_{17}	1473.9(10.8/11.2)	**1425**	$H_{11}C_8H_{10}$+$H_{23}C_{20}H_{22}$ bend
ν_{18}	1473.9(6.9/17.5)	**1394**	$H_{11}C_8H_{10}$+$H_{23}C_{20}H_{22}$ bend
ν_{19}	1469.0(0.001/16.5)	**1394**	$H_{11}C_8H_{10}$ bend+$H_{12}C_8H_{11}$ bend+$H_{23}C_{20}H_{22}$ bend+$H_{24}C_{20}H_{23}$ bend+$H_{11}C_8N_4C_3$ tors+ $H_{23}C_{20}N_{16}C_{15}$ tors
ν_{20}	1468.4(15.1/0.001)	**1390**	$H_{11}C_8H_{10}$ bend+$H_{12}C_8H_{11}$ bend+$H_{23}C_{20}H_{22}$ bend+$H_{24}C_{20}H_{23}$ bend+$H_{11}C_8N_4C_3$ tors+ $H_{23}C_{20}N_{16}C_{15}$ tors
ν_{21}	1411.0(53.9/0.0)	1361	N_1C_5 stretch+$N_{13}C_{17}$ stretch+$C_3N_2H_6$ bend
ν_{22}	1405.5(0.0/61.6)	**1361**	N_1C_5 stretch+$N_{13}C_{17}$ stretch+N_4C_8 stretch+$N_{16}C_{20}$ stretch+$C_3N_2H_6$ bend
ν_{23}	1357.6(0.005/261.0)	1323	$N_{16}C_{17}$ stretch+$N_4C_5N_1$ bend+$N_{16}C_{17}N_{13}$ bend+$H_{18}N_{14}N_{13}$ bend+$C_3N_2H_6$ bend+$N_1N_2H_6$ bend
ν_{24}	1353.9(37.5/0.03)	1325	$N_4C_5N_1$ bend+$N_{16}C_{17}N_{13}$ bend+$C_3N_2H_6$ bend+$N_1N_2H_6$ bend+$N_2H_6S_{19}C_{15}$ tors+$N_1N_2H_6S_{19}$ tors
ν_{25}	1293.1(32.6/0.008)	**1275**	N_2C_3 stretch+$N_{14}C_{15}$ stretch+$C_3N_2H_6$ bend+$N_2H_6S_{19}C_{15}$ tors+$N_1N_2H_6S_{19}$ tors
ν_{26}	1287.6(0.004/82.5)	**1267**	N_2C_3 stretch+$N_{14}C_{15}$ stretch+$C_3N_2H_6$ bend
ν_{27}	1251.1(0.0001/42.2)	**1219**	$H_9C_5N_1$+$H_{21}C_{17}N_{13}$ bend
ν_{28}	1250.4(18.1/0.0002)	**1216**	$H_9C_5N_1$+$H_{21}C_{17}N_{13}$ bend
ν_{29}	1179.2(0.0001/30.1)	1151	$C_{15}N_{14}N_{13}$+$N_1N_2H_6$ bend
ν_{30}	1167.4(32.3/0.0001)	1149	$C_{15}N_{14}N_{13}$+$N_1N_2H_6$ bend
ν_{31}	1150.6(0.1/0.1)		$H_{10}C_8N_4C_3$+$H_{11}C_8N_4C_3$+$H_{12}C_8N_4C_3$+$H_{22}C_{20}N_{16}C_{15}$+$H_{23}C_{20}N_{16}C_{15}$+$H_{24}C_{20}N_{16}C_{15}$ tors
ν_{32}	1150.6(1.6/0.004)		$H_{10}C_8N_4C_3$+$H_{11}C_8N_4C_3$+$H_{12}C_8N_4C_3$+$H_{22}C_{20}N_{16}C_{15}$+$H_{23}C_{20}N_{16}C_{15}$+$H_{24}C_{20}N_{16}C_{15}$ tors
ν_{33}	1106.5(6.2/0.0008)	1082	N_1N_2+$N_{14}N_{13}$ stretch
ν_{34}	1105.2(0.0005/8.5)	1078	N_1N_2+$N_{14}N_{13}$ stretch
ν_{35}	1062.0(9.2/0.0009)	1043	$N_4C_5N_1$ bend+$N_{16}C_{17}N_{13}$

ν_{36}	1061.3(0.0001/63.5)		bend+$H_{10}C_8N_4C_3$+$H_{12}C_8N_4C_3$+$H_{22}C_{20}N_{16}C_{15}$+$H_{24}C_{20}N_{16}C_{15}$ tors
		1041	$N_4C_5N_1$ bend+$N_{16}C_{17}N_{13}$
			bend+$H_{10}C_8N_4C_3$+$H_{12}C_8N_4C_3$+$H_{22}C_{20}N_{16}C_{15}$+$H_{24}C_{20}N_{16}C_{15}$ tors
ν_{37}	957.6(0.0001/72.6)	950	$N_4C_5N_1$+$N_{16}C_{17}N_{13}$+$C_5N_1N_2$+$N_{14}N_{13}C_{17}$ bend
ν_{38}	952.2(29.5/0.0002)	941	$N_4C_5N_1$+$N_{16}C_{17}N_{13}$+$C_5N_1N_2$+$N_{14}N_{13}C_{17}$ bend
ν_{39}	832.6(0.0/86.4)	**881**	$N_2H_6S_{19}C_{15}$+$H_9C_5N_1N_2$+$H_{21}C_{17}N_{13}N_{14}$+$N_1N_2H_6S_{19}$ tors
ν_{40}	827.7(0.4/0.002)		$N_2H_6S_{19}C_{15}$+$H_9C_5N_1N_2$+$H_{21}C_{17}N_{13}N_{14}$+$N_1N_2H_6S_{19}$ tors
ν_{41}	810.9(0.0/13.5)	852	$N_2H_6S_{19}C_{15}$+$H_{18}N_{14}N_{13}C_{17}$+$C_5N_1N_2H_6$+$H_6N_2C_3N_4$+$N_1N_2H_6S_{19}$ tors
ν_{42}	793.6(5.3/0.0)	852	$N_2H_6S_{19}C_{15}$+$H_{18}N_{14}N_{13}C_{17}$+$C_5N_1N_2H_6$+$H_6N_2C_3N_4$+$N_1N_2H_6S_{19}$ tors
ν_{43}	705.0(0.0/8.4)	690	N_4C_8 stretch+$N_{16}C_{20}$ stretch+$N_4C_5N_1$ bend+$N_{16}C_{17}N_{13}$ bend
ν_{44}	701.8(31.4/0.0)	698	N_4C_8 stretch+$N_{16}C_{20}$ stretch+$N_4C_5N_1$ bend+$N_{16}C_{17}N_{13}$ bend
ν_{45}	674.3(3.5/0.0)		$N_2H_6S_{19}C_{15}$ tors+$C_5N_1N_2H_6$ tors+$C_{15}N_{14}N_{13}C_{17}$ tors+$N_1N_2H_6S_{19}$ tors+$S_7N_2N_4C_3$ out+ $S_{19}N_{14}N_{16}C_{15}$ out
ν_{46}	673.2(0.0/8.6)	673	$N_2H_6S_{19}C_{15}$ tors+$C_5N_1N_2H_6$ tors+$C_{15}N_{14}N_{13}C_{17}$ tors+$N_1N_2H_6S_{19}$ tors+$S_7N_2N_4C_3$ out+ $S_{19}N_{14}N_{16}C_{15}$ out
ν_{47}	638.8(0.6/0.0)		$N_2H_6S_{19}C_{15}$+$N_4C_5N_1N_2$+$N_{16}C_{17}N_{13}N_{14}$+$N_1N_2H_6S_{19}$ tors
ν_{48}	638.7(0.0/5.8)		$N_2H_6S_{19}C_{15}$+$N_4C_5N_1N_2$+$N_{16}C_{17}N_{13}N_{14}$+$N_1N_2H_6S_{19}$ tors
ν_{49}	542.0(0.0001/28.8)	542	S_7C_3 stretch+$S_{19}C_{15}$ stretch+$C_{15}N_{14}N_{13}$ bend
ν_{50}	539.6(17.4/0.0001)	544	S_7C_3 stretch+$S_{19}C_{15}$ stretch+$C_{15}N_{14}N_{13}$ bend
ν_{51}	431.1(0.0/1.2)		$S_7C_3N_4$ bend+$C_8N_4C_5$ bend+$C_{20}N_{16}C_{17}$ bend+$S_{19}C_{15}N_{16}$ bend+$N_2H_6S_{19}C_{15}$ tors+ $N_1N_2H_6S_{19}$ tors
ν_{52}	418.1(2.2/0.0)	422	$S_7C_3N_4$ bend+$C_8N_4C_5$ bend+$S_{19}C_{15}N_{16}$ bend +$C_{20}N_{16}C_{17}$ bend
ν_{53}	262.2(0.0/26.7)		$S_7C_3N_4$ bend+$C_8N_4C_5$ bend+$C_{20}N_{16}C_{17}$ bend+$S_{19}C_{15}N_{16}$ bend+$N_2H_6S_{19}C_{15}$ tors
ν_{54}	248.7(6.3/0.0)	251	$S_7C_3N_4$ bend+$C_8N_4C_5$ bend+$C_{20}N_{16}C_{17}$ bend+$S_{19}C_{15}N_{16}$ bend+$N_2H_6S_{19}C_{15}$ tors
ν_{55}	231.5(0.2/0.0)		$N_2H_6S_{19}C_{15}$ tors+$C_5N_1N_2H_6$ tors+$C_{15}N_{14}N_{13}C_{17}$ tors+$N_1N_2H_6S_{19}$

		tors+$S_7N_2N_4C_3$ out+ $S_{19}N_{14}N_{16}C_{15}$ out
ν_{56}	230.4(0.0/0.03)	$C_5N_1N_2H_6$ tors+$H_6N_2C_3N_4$ tors+$C_{15}N_{14}N_{13}C_{17}$ tors+$S_7N_2N_4C_3$ out+ $S_{19}N_{14}N_{16}C_{15}$ out
ν_{57}	199.3(1.1/0.0)	$N_2H_6S_{19}C_{15}$ tors+$C_5N_1N_2H_6$ tors+$H_6N_2C_3N_4$ tors+$N_1N_2H_6S_{19}$ tors+$C_{20}C_{15}C_{17}N_{16}$ out+ $C_8C_3C_5N_4$ out
ν_{58}	198.2(0.0/1.2)	$N_2H_6S_{19}C_{15}$ tors+$C_5N_1N_2H_6$ tors+$H_6N_2C_3N_4$ tors+$N_1N_2H_6S_{19}$ tors+$C_{20}C_{15}C_{17}N_{16}$ out+ $C_8C_3C_5N_4$ out
ν_{59}	113.3(0.9/0.0)	$H_{10}C_8N_4C_3$+$H_{11}C_8N_4C_3$+$H_{12}C_8N_4C_3$+$H_{22}C_{20}N_{16}C_{15}$+$H_{23}C_{20}N_{16}C_{15}$+$H_{24}C_{20}N_{16}C_{15}$ tors
ν_{60}	104.7(0.0002/0.1)	$H_{10}C_8N_4C_3$+$H_{11}C_8N_4C_3$+$H_{12}C_8N_4C_3$+$H_{22}C_{20}N_{16}C_{15}$+$H_{23}C_{20}N_{16}C_{15}$+$H_{24}C_{20}N_{16}C_{15}$ tors
ν_{61}	104.3(0.9/0.0)	$S_{19}H_6$ stretch+$N_2H_6S_{19}$ bend+$H_6S_{19}C_{15}$ bend+$N_2H_6S_{19}C_{15}$ tors+$N_1N_2H_6S_{19}$ tors
ν_{62}	83.2(0.0/12.0)	$N_2H_6S_{19}$ bend+$H_6S_{19}C_{15}$ bend+$N_2H_6S_{19}C_{15}$ tors+$N_1N_2H_6S_{19}$ tors
ν_{63}	78.3(1.7/0.0)	$S_{19}H_6$ stretch+$N_2H_6S_{19}$ bend+$H_6S_{19}C_{15}$ bend+$N_2H_6S_{19}C_{15}$ tors+$N_1N_2H_6S_{19}$ tors
ν_{64}	45.9(2.6/0.0)	$N_2H_6S_{19}$ bend+$N_2H_6S_{19}C_{15}$ tors+$H_6S_{19}C_{15}N_{14}$ tors+$C_5N_1N_2H_6$ tors+$H_6N_2C_3N_4$ tors+ $N_1N_2H_6S_{19}$ tors
ν_{65}	34.5(0.0/4.2)	$N_2H_6S_{19}C_{15}$ tors+$C_5N_1N_2H_6$ tors+$H_6N_2C_3N_4$ tors+ $N_1N_2H_6S_{19}$ tors
ν_{66}	7.8(0.0/6.2)	$N_2H_6S_{19}C_{15}$ tors+$H_6S_{19}C_{15}N_{14}$ tors+$C_5N_1N_2H_6$ tors+$H_6N_2C_3N_4$ tors+ $N_1N_2H_6S_{19}$ tors

PED=potential energy distribution, only contributions larger than 10% were given.

Table S2. The assignments of 488 nm Raman in different solvents and calculated spectra at B3LYP-D3(BJ)/6-311++G(d, p)level for 4MTT(H_2O)$_2$.

Mode	Exp.			Cal.	Descriptions (PED%)
	In CH_3CN	In CH_3OH	In H_2O	(Raman activity/IR intensity)	
ν_1				3274(220.9/1.0)	C_5H_9(99)stretch
ν_2				3172(424.9/1534.0)	N_2H_6(93)stretch
ν_3				3165(122.4/10.3)	C_8H_{10}(11)+C_8H_{11}(79)+C_8H_{12}(11)stretch
ν_4				3137(97.5/11.1)	C_8H_{10}(50)+C_8H_{12}(50)stretch
ν_5				3066(342.1/29.0)	C_8H_{10}(39)+C_8H_{11}(21)+C_8H_{12}(39)stretch
ν_6	1556(m)	1559(w)	1561(w)	1544(125.6/267.9)	N_1C_5(14)stretch+N_2C_3(17)stretch+N_4C_5(12)stretch+ $H_6N_2N_1$(16)bend
ν_7	1480(w)	1498(m)	1500(vs)	1503(21.4/35.6)	$H_{10}C_8H_{12}$(52)bend+$H_{11}C_8H_{10}$(12)bend+$H_{10}C_8N_4C_3$(11)tors+ $H_{12}C_8N_4C_3$(10)tors
ν_8				1470(17.6/21.0)	$H_{11}C_8H_{10}$(47)bend+$H_{12}C_8H_{11}$(27)bend+$H_{11}C_8N_4C_3$(18)tors
ν_9	1427(vw)	1425(w)	1428(s)	1466(41.5/18.4)	N_1C_5(20)stretch+$H_{10}C_8H_{12}$(14)bend+$H_{11}C_8H_{10}$(14)bend+ $H_{12}C_8H_{11}$(40)bend
ν_{10}	1362(m)	1365(m)	1365(m)	1411(38.4/24.2)	N_1C_5(26)+N_4C_5(21)+N_4C_8(15)stretch
ν_{11}	1326(w)	1334(s)	1339(vs)	1362(156.9/276.5)	$N_4C_5N_1$(14)+$C_3N_2N_1$(14)bend
ν_{12}	1255(w)	1274(m)	1284(m)	1301(51.7/36.5)	N_2C_3(49)+N_4C_5(15)stretch
ν_{13}	1224(vw)	1225(vw)	1227 (vw)	1254(14.8/56.9)	N_4C_8(12)stretch+$H_9C_5N_1$(67)bend
ν_{14}	1154(vw)	1154(w)	1157(w)	1176(25.7/71.7)	N_4C_8(11)stretch+S_7C_3(17)stretch+$C_3N_2N_1$(39)bend
ν_{15}				1150(1.4/0.1)	$H_{11}C_8H_{10}$(18)bend+$H_{12}C_8H_{11}$(16)bend+$H_{10}C_8N_4C_3$(17)tors $H_{11}C_8N_4C_3$(31)tors+$H_{12}C_8N_4C_3$(17)tors
ν_{16}	1071(vvw)	1074(vw)	1078(vvw)	1107(7.4/15.7)	N_2N_1(65)stretch
ν_{17}	1036(vw)	1049(vvw)	1047(vvw)	1067(14.1/87.1)	N_4C_5(17)stretch+N_2N_1(14)stretch+$N_4C_5N_1$(15)bend+$H_{10}C_8N_4C_3$(1

					2)tors+$H_{12}C_8N_4C_3$(12)tors
ν_{18}	935(s)	935(s)	946(s)	961(27.7/55.7)	$N_4C_5N_1$(13)+$N_2N_1C_5$(61)bend
ν_{19}				854(2.1/13.8)	$H_9C_5N_1N_2$(80)tors
ν_{20}	689(vvs)	689(vvs)	688(vvs)	701(32.2/5.2)	N_4C_8(46)stretch+$N_4C_5N_1$(22)bend
ν_{21}				682(3.6/9.7)	$C_3N_2N_1C_5$(38)tors+$S_7N_2N_4C_3$(46)out
ν_{22}				646(1.0/5.7)	$H_9C_5N_1N_2$(12)+$N_4C_5N_1N_2$(75)tors
ν_{23}	535(vs)	535(vs)	530(m)	535(13.7/29.1)	S_7C_3(55)stretch+$C_3N_2N_1$(14)bend+$C_8N_4C_5$(11)bend
ν_{24}	402(m)	402(w)	404(w)	420(4.1/8.7)	$S_7C_3N_4$(21)+$C_8N_4C_5$(41)bend
ν_{25}	238(s)	240(m)	243(m)	207(2.2/4.4)	$H_{11}C_8N_4C_3$(10)tors+$C_3N_2N_1C_5$(30)tors+ $C_8C_3C_5N_4$(35)out+$S_7N_2N_4C_3$(10)out
ν_{26}				105(0.8/0.2)	$H_{10}C_8N_4C_3$(25)tors+$H_{11}C_8N_4C_3$(27)tors+$H_{12}C_8N_4C_3$(25)tors+C_8C_3 C_5N_4(20)out
ν_1'				3858(114.2/99.6)	$O_{13}H_{15}$(99)stretch
ν_2'				3849(95.0/132.5)	$O_{16}H_{17}$(98)stretch
ν_3'				3477(512.9/1326.0)	$O_{13}H_{14}$(28)+$O_{16}H_{18}$(71)stretch
ν_4'				3418(359.0/1095.1)	$O_{13}H_{14}$(66)+$O_{16}H_{18}$(27)stretch
ν_5'				1640(2.7/17.6)	$H_{15}O_{13}H_6N_2$(38)+$H_{14}O_{13}H_6N_2$(13)tors
ν_6'				1610(8.7/108.4)	$H_{17}O_{16}H_{18}$(38)bend+$H_6N_2N_1$(15)bend+$H_{15}O_{13}H_6N_2$(10)tors
ν_7'				1606(17.4/156.5)	$H_{17}O_{16}H_{18}$(47)bend+$H_{15}O_{13}H_6N_2$(19)tors
ν_8'				910(1.2/161.7)	$O_{13}H_6N_2$(31)bend+$H_{15}O_{13}H_6$(19)bend+$H_6N_2N_1C_5$(29)tors
ν_9'				860(1.7/218.0)	$O_{16}H_{14}O_{13}$(32)bend+$H_{17}O_{16}H_{18}S_7$(10)tors+ $H_{18}O_{16}H_{14}O_{13}$(12)tors+$O_{16}H_{14}O_{13}N_2$(12)tors
ν_{10}'				644(6.7/201.7)	$H_{18}O_{16}H_{14}$(38)bend+$O_{16}H_{14}O_{13}$(20)bend+ $H_{17}O_{16}H_{18}S_7$(11)tors+$H_{18}O_{16}H_{14}O_{13}$(10)tors
ν_{11}'				462(1.8/99.6)	$H_{15}O_{13}H_6$(14)bend+$O_{16}H_{14}O_{13}$(11)bend+ $H_{18}O_{16}H_{14}O_{13}$(21)tors+ $O_{16}H_{14}O_{13}N_2$(18)tors
ν_{12}'				348(1.9/40.4)	$H_{17}O_{16}H_{18}S_7$(28)+$H_{18}O_{16}H_{14}O_{13}$(13)+$O_{16}H_{14}O_{13}N_2$(22)tors
ν_{13}'				296(0.4/174.7)	$H_{15}O_{13}H_6$(40)bend+$H_{17}O_{16}H_{18}S_7$(15)tors

ν_{14}'	255(2.6/30.2)	$O_{16}H_{14}$(16)stretch+$S_7C_3N_4$(22)bend+$C_8N_4C_5$(12)bend
ν_{15}'	250(1.3/117.1)	$S_7C_3N_4$(11)bend+$H_{17}O_{16}H_{18}S_7$(16)tors+$H_{18}O_{16}H_{14}O_{13}$(17)tors+$O_{16}H_{14}O_{13}N_2$(15)tors
ν_{16}'	245(0.9/57.5)	$O_{16}H_{14}$(42)stretch+$C_8C_3C_5N_4$(10)out
ν_{17}'	244(0.1/70.3)	$O_{16}H_{14}$(16)stretch+$C_8C_3C_5N_4$(15)out+$S_7N_2N_4C_3$(24)out
ν_{18}'	185(0.4/23.5)	$O_{13}H_6$(84)stretch
ν_{19}'	147(0.7/17.2)	$S_7C_3N_4$(11)bend+$H_{14}O_{13}H_6$(36)bend+$O_{13}H_6N_2C_3$(11)tors
ν_{20}'	87(2.5/0.8)	$H_{14}O_{13}H_6$(20)bend+$H_6N_2N_1$(27)bend+$O_{13}H_6N_2C_3$(15)tors
ν_{21}'	60(1.4/8.1)	$O_{13}H_6N_2$(25)bend+$H_6N_2N_1C_5$(33)tors+$C_8C_3C_5N_4$(11)out

m=middle, s= strong, vs= very strong, w=weak, vw=very weak; PED=potential energy distribution, only contributions larger than 10% were given.

Table S3. Calculated and experimental electronic transition energy (△E, in kcal/mol) and oscillator intensity (f) for 4MMT(CH_3CN), 4MMT$(CH_3OH)_2$ and 4MMT$(H_2O)_2$ clusters in singlet states at TD-B3LYP-D3(BJ)/6-311++G(d,p), PCM level.

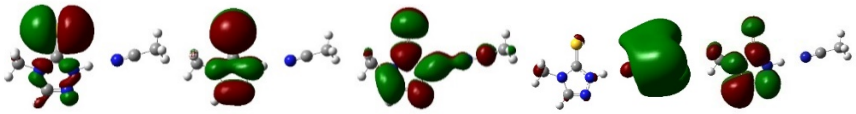
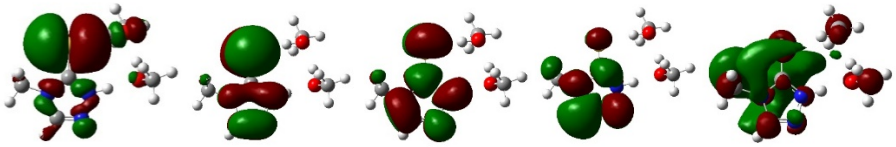
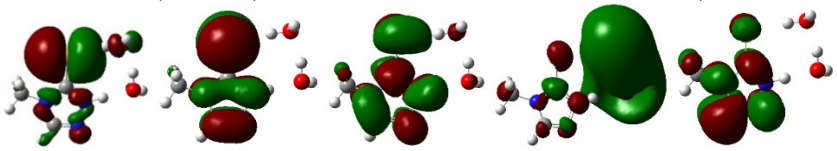
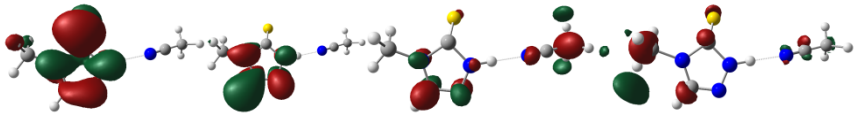
	Orbitals(coefficient)	Electronic transition	Transition Energy(nm)		Oscillator strength(f)	
			Calc.(a)	Expt.	Calc.	Expt.
In CH_3CN						
S_1	40→42(0.66302)	n→π*	268.3(269[a])		0.0004	
S_2	**41→42(0.68625)**	**π→π***	245.6(263[a])	**255**	**0.1964**	**0.1324**
S_3	41→43(0.58499)	π→Ryd_1	239.8(232[a])		0.0559	
S_4	41→44(0.68646)	π→π*	237.4(216[a])	222	0.1383	
						
	40n	41π	42π*	43Ryd_1	44π*	
In CH_3OH						
S_1	47→49(0.67053)	n→π*	253.9		0.0021	
S_2	**48→49(0.68233)**	**π→π***	**240.0**	**251**	**0.2319**	**0.1431**
S_3	48→51(0.65948)	π→Ryd_1	236.0		0.0546	
S_4	48→50(0.66678)	π→π*	233.1		0.1078	
						
	47 n	48 π	49 π*	50 π*	51 Ryd_1	
In H_2O						
S_1	39→41(0.66857)	n→π*	253.2(242[a])		0.0012	
S_2	40→42(0.51193)	π→Ryd_1	241.5(253[a])		0.1068	
S_3	**40→41(0.50007)**	**π→π***	**238.4**(218[a])	**245**	**0.1843**	**0.1032**
S_4	40→43(0.69426)	π→π*	232.5(144[a])		0.1162	
						
	39n	40 π	41 π*	42 Ryd_1	43π*	

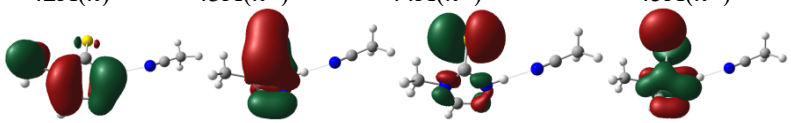
Table S4. Calculated and experimental electronic transition energy (△E, in kcal/mol) and oscillator intensity (f) for 4MMT(CH_3CN), 4MMT$(CH_3OH)_2$ and 4MMT$(H_2O)_2$ clusters in triplet states at TD- B3LYP -D3(BJ)/6-311++G(d, p), PCM level.

	Orbitals(coefficient)	Electronic transition	Transition Energy(nm)		Oscillator strength(f)	
			Calc.(a)	Expt.	Calc.	Expt.
In CH_3CN						
T_2	42A→43A(0.66264) 39B→41B(0.74234)	π→π* π→π*	496.6		0.0559	
T_3	**42A→43A(0.60196)** **39B→41B(0.63109)**	**π→π*** **π→π***	**457.7**	**470**	**0.0482**	
T_4	38B→41B(0.93748)	π→π*	384.1		0.0266	
T_5	**42A→44A(0.72983)**	**π→π***	**368.0**	**350**	**0.0266**	

42A →45A(0.60226 **π→π***



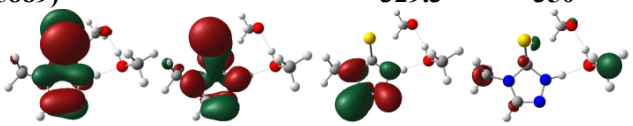
42A(π) 43A(π*) 44A(π*) 45A(π*)



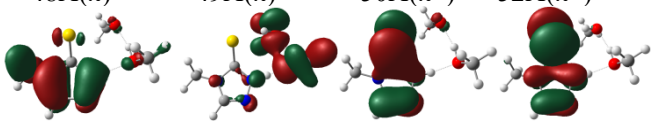
38B(π) 39B(π) 40B(n) 41B(π*)

In CH_3OH

T_2	49A→50A(0.51168)	π→π*	501.19		0.0653
	46B→48B(0.81893)	π→π*			
T_3	**49A→50A(0.73861)**	**π→π***	**459.5**	**470**	**0.0314**
	46B→48B(0.65542)	**π→π***			
T_6	43B→48B(0.65542)	π→π*	389.34		0.0130
	44B→48B(0.65542)	Ryd_1→π*			
T_9	**49A→52A(0.65889)**		**329.3**	**350**	**0.0396**



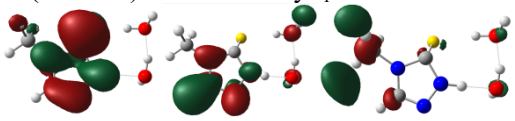
48A(π) 49A(π) 50A(π*) 52A(π*)



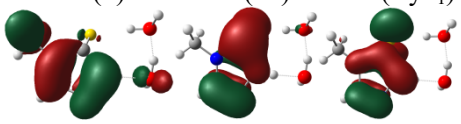
43B(π) 44B(Ryd_1) 46B(π) 48B(π)

In H_2O

T_2	41A→42A(0.60086)	π→π*	500.4		0.0703
	38B→40B(0.82498)	π→π*			
T_3	38B→40B(0.51149)	π→π*	457.9		0.0337
T_4	37B→40B(0.91099)	π→π*	397.8		0.0221
T_7	41A→44A(0.95501)	π→Ryd_1	335.0		0.0206



41A(π) 42A(π*) 44A(Ryd_1)

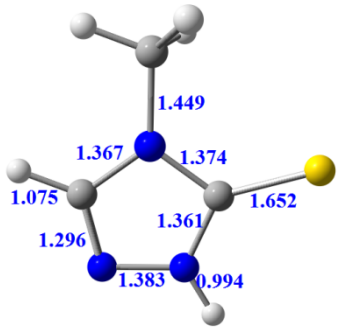
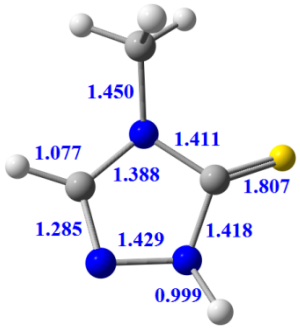


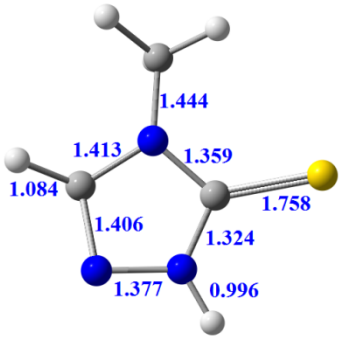
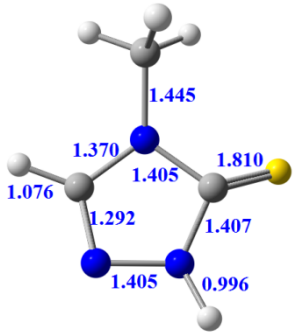
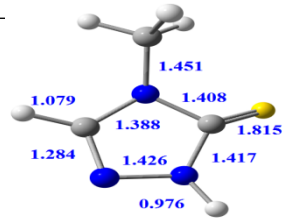
37B(π) 38B(π) 40B(π*)

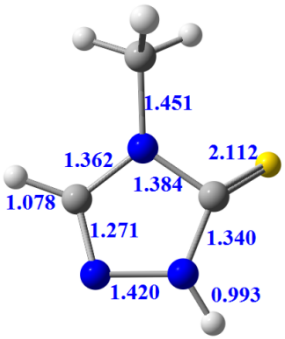
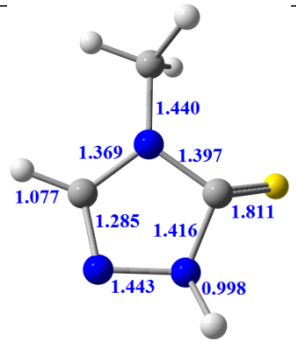
Table S5. Optimized bond lengths and angles for different minimum structures (S_{2min}, S_{1min}, and T_{2min}), and ISC points(S_1/T_1 and S_0/T_1) (TD-)B3LYP-D3(BJ)/6-311G(d, p) levels with PCM (solvent=acetonitrile) model. (Atom number referred to Figure S1)

	$d(S_7–C_3–N_2–N_1)$	$C_3=S_7$	$N_1–N_2$	$N_2–H_6$	$N_2–C_3$	$C_3–N_4$	$N_4–C_5$	$N_4–H_8$	$N_1–C_5$	$C_5–H_9$
S_0	180.0	1.688	1.367	1.008	1.353	1.374	1.371	1.457	1.300	1.077
S_{2min}	125.0	1.875	1.370	1.007	1.400	1.411	1.358	1.449	1.306	1.078
S_{1min}	125.0	1.874	1.370	1.007	1.400	1.411	1.358	1.449	1.306	1.078
T_{1min}	119.4	1.759	1.357	1.010	1.443	1.446	1.340	1.449	1.319	1.079
S_1/T_1	105.8	1.844	1.438	1.028	1.473	1.421	1.412	1.465	1.280	1.081
S_0/T_1	165.1	1.648	1.365	1.013	1.404	1.373	1.429	1.456	1.468	1.101

Table S6. Optimized Cartesian coordinates and Hartree-Fock energies (a.u.) at CASSCF(12e/9o)/cc-pVDZ level.

State	HF energy	Structure	Cartesian coordinates		
$S_{0,min}$	−678.46027		C 0.45490073	1.31869935	0.03582096
			C −0.2345193	−0.7924653	0.0042314
			C −2.0227182	0.98389392	−0.0094002
			N −0.6544216	0.50878365	0.0088384
			N 1.47793492	0.42052945	0.04563403
			N 1.05745911	−0.897038	0.02625257
			S 0.53120189	2.96874506	0.05217782
			H −0.9062152	−1.6311936	−0.0157399
			H 2.44719002	0.63772897	0.06625092
			H −2.2208185	1.58480666	0.87527623
			H −2.194984	1.59353923	−0.8935499
			H −2.6874096	0.12298192	−0.0233414
$S_{1,min}$	−678.33025		C 0.43662423	1.36550339	0.06934993
			C −0.2218552	−0.7469508	−0.104321
			C −2.0128661	0.94391418	0.10582193
			N −0.6673314	0.55645472	−0.2721521
			N 1.5409475	0.47783534	0.02479787
			N 1.04390338	−0.8608563	0.085128
			S 0.66315487	2.91920734	−0.8246342
			H −0.885243	−1.5916753	−0.1819305
			H 2.26130915	0.61374561	0.70325371
			H −2.1285983	1.03430148	1.18938889
			H −2.2628298	1.89848109	−0.3538083
			H −2.714508	0.19994029	−0.2681463

$S_{2,min}$	-678.30277		C	0.44911543	1.26841398	0.10381955
			C	-0.2763262	-0.7965428	-0.2710408
			C	-2.0261407	0.97934322	-0.0409605
			N	-0.6728872	0.50234122	0.12072973
			N	1.4709932	0.43614435	-0.0207996
			N	1.11959661	-0.8906101	-0.1297813
			S	0.57730982	2.97129558	0.52177361
			H	-0.8890154	-1.6242801	0.06602354
			H	2.43336676	0.68363335	0.04458994
			H	-2.1455796	1.93487329	0.46391402
			H	-2.2844743	1.08867498	-1.0966267
			H	-2.703251	0.25661413	0.41110651
$T_{1,min}$	-678.34883		C	0.43498552	1.36565477	0.17526186
			C	-0.2246557	-0.7506409	-0.0670139
			C	-2.0346869	0.95676349	0.0954269
			N	-0.6662595	0.54484496	-0.1199996
			N	1.51140897	0.46902312	0.0497773
			N	1.0575688	-0.8608862	0.04749891
			S	0.660073	2.87409471	-0.79876
			H	-0.884069	-1.5957789	-0.1647695
			H	2.36824395	0.61799224	0.53535443
			H	-2.2505443	1.09553107	1.15720857
			H	-2.2154949	1.893478	-0.4273543
			H	-2.7038626	0.19982455	-0.3098826
$T_{2,min}$	-678.33552		C	0.44156691	1.36698283	0.07095964
			C	-0.2199391	-0.7476218	-0.1051957
			C	-2.0088144	0.94689677	0.10827326
			N	-0.6614051	0.55825329	-0.2648092
			N	1.54110024	0.47298294	0.03794874
			N	1.04414752	-0.8621262	0.09120168

			S	0.62615232	2.91635315	-0.8558438
			H	-0.884069	-1.5957789	-0.1647695
			H	2.36824395	0.61799224	0.53535443
			H	-2.2505443	1.09553107	1.15720857
			H	-2.2154949	1.893478	-0.4273543
			H	-2.7038626	0.19982455	-0.3098826
S_1/S_2	-678.31869		C	0.45168082	1.3292891	0.32321865
			C	-0.2030692	-0.7449139	-0.1141762
			C	-2.0301862	0.95525847	0.09706694
			N	-0.6431788	0.53700411	0.02478555
			N	1.44496342	0.43464966	0.42001008
			N	1.04568202	-0.8835734	0.0756995
			S	0.59224607	2.92033234	-1.0588398
			H	-0.861399	-1.5614708	-0.3608926
			H	2.41696307	0.63481342	0.44300777
			H	-2.3909901	0.94538573	1.1262346
			H	-2.1308944	1.96130019	-0.2998493
			H	-2.6391104	0.28182609	-0.5035173
S_2/T_2	-678.32362		C	0.43722014	1.34810603	0.30676611
			C	-0.1958307	-0.7411021	-0.1348184
			C	-2.0369535	0.95662896	0.10717846
			N	-0.669823	0.50814568	0.1627594
			N	1.54171128	0.52526558	-0.0219544
			N	1.08408887	-0.8301099	-0.213114
			S	0.61357386	2.88020536	-0.643013
			H	-0.8515648	-1.5857819	-0.2653749
			H	2.3243388	0.54875855	0.59711229
			H	-2.3159988	1.46078795	1.03285272
			H	-2.1876151	1.64248139	-0.730317
	-678.3299					

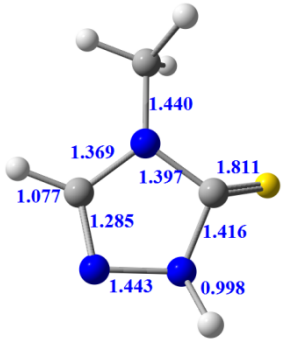
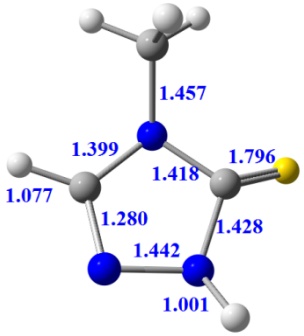
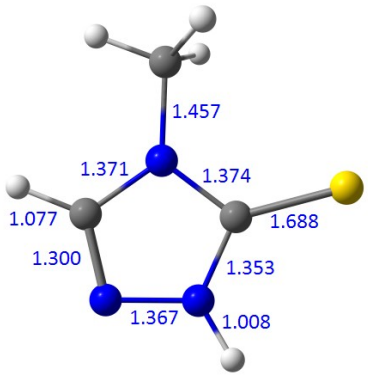
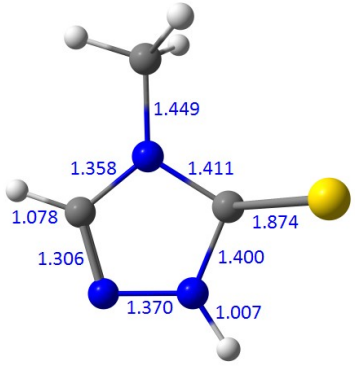
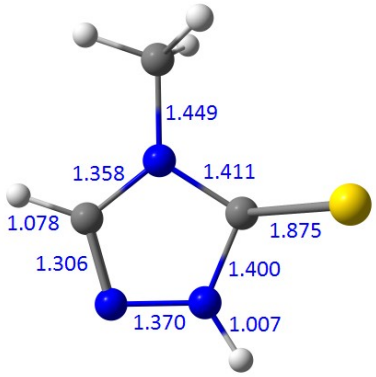
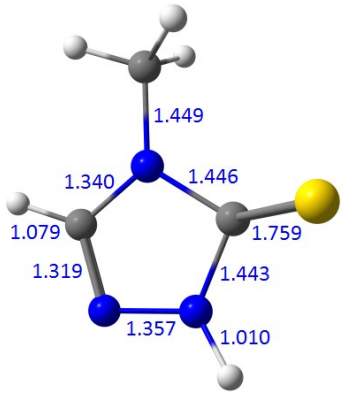
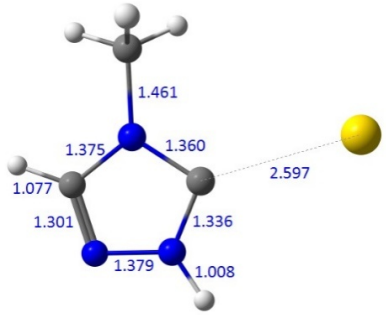
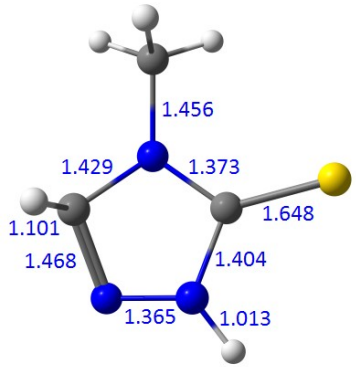
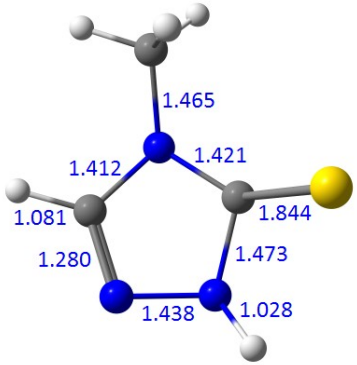
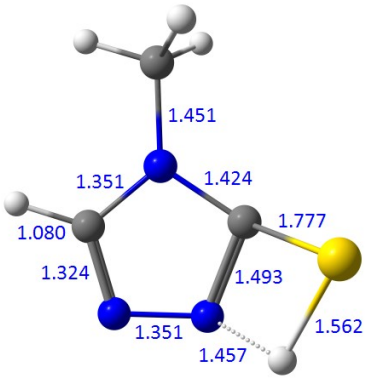
			H	-2.6904397	0.09651539	-0.0253294
S_1/T_2	-678.3299 -678.32209		C	0.43722014	1.34810603	0.30676611
			C	-0.1958307	-0.7411021	-0.1348184
			C	-2.0369535	0.95662896	0.10717846
			N	-0.669823	0.50814568	0.1627594
			N	1.54171128	0.52526558	-0.0219544
			N	1.08408887	-0.8301099	-0.213114
			S	0.61357386	2.88020536	-0.643013
			H	-0.8515648	-1.5857819	-0.2653749
			H	2.3243388	0.54875855	0.59711229
			H	-2.3159988	1.46078795	1.03285272
			H	-2.1876151	1.64248139	-0.730317
			H	-2.6904397	0.09651539	-0.0253294
T_1/T_2	-678.33409 -678.33473		C	0.43777585	1.38569347	-0.0329063
			C	-0.2184649	-0.7313767	-0.1715402
			C	-1.9858701	0.93346052	0.14918433
			N	-0.6746504	0.57545964	-0.3758382
			N	1.54996351	0.49754473	0.08132909
			N	1.02603108	-0.8458376	0.10392862
			S	0.69117747	2.8691731	-1.0135847
			H	-0.8751793	-1.5782408	-0.281495
			H	2.10561209	0.62543782	0.90367172
			H	-2.0041938	0.96523266	1.24227163
			H	-2.2832535	1.90850943	-0.2320972
			H	-2.7162408	0.20484464	-0.2001759

Table S7. Optimized Cartesian coordinates and Hartree-Fock energies (a.u.) at (TD-)B3LYP-(D3)BJ/6-311G(d, p) level with PCM acetonitrile model.

State	H-F energy	Structure	Cartesian coordinates		
S_0	-679.89932840	 d(S-C-N-N): 180.0	N	-1.77609500	-1.15252300	0.00000400
			N	-0.43844100	-1.43621800	0.00001300
			C	0.35302500	-0.33916000	-0.00000200
			N	-0.55435900	0.69313500	-0.00002800
			C	-1.81204000	0.14707500	-0.00004400
			H	-0.11801800	-2.39236900	0.00004100
			S	2.03857200	-0.24692200	0.00003200
			C	-0.21071600	2.10863200	-0.00001400
			H	-2.71271700	0.73817400	-0.00006700
			H	0.37379200	2.34491500	-0.88861000
			H	-1.13277700	2.68493000	-0.00036400
			H	0.37321500	2.34506700	0.88892500
S_{1min}	-679.76005806	 d(S-C-N-N): 125.0	N	1.38008500	-1.46201600	-0.23532500
			N	0.13128300	-1.44340300	0.32745600
			C	-0.35113800	-0.15927600	0.60767900
			N	0.70904400	0.62582900	0.10736000
			C	1.68857500	-0.19805900	-0.34696100
			H	-0.30141500	-2.30942300	0.60322300
			S	-2.01254900	0.03012800	-0.23869100
			C	0.70336200	2.07448200	0.11308000
			H	2.62112300	0.16006700	-0.75291000

			H	0.70082400	2.45047300	1.13765800
			H	1.58590600	2.43895000	-0.40827600
			H	-0.19332400	2.43212600	-0.39987100
S_{2min}	-679.74743943	 d(S-C-N-N): 125.0	N	1.37925000	-1.46257700	-0.23545800
			N	0.13054400	-1.44342200	0.32774400
			C	-0.35095900	-0.15898200	0.60808200
			N	0.70949400	0.62564000	0.10750300
			C	1.68828300	-0.19878500	-0.34745800
			H	-0.30202000	-2.30920100	0.60449100
			S	-2.01254700	0.03077900	-0.23887400
			C	0.70434700	2.07431900	0.11319500
			H	2.62088300	0.15884600	-0.75374700
			H	0.70180100	2.45029300	1.13776800
			H	1.58711700	2.43846700	-0.40800900
			H	-0.19206500	2.43232700	-0.39995100
T_{1min}	-679.78442281	 d(S-C-N-N): 119.4	N	1.37554600	-1.46018400	-0.22836400
			N	0.17296500	-1.47869000	0.40064800
			C	-0.41800800	-0.17041800	0.55020900
			N	0.68694000	0.63366000	0.07885300
			C	1.66166100	-0.17863800	-0.35341700
			H	-0.37547800	-2.32598200	0.35958700
			S	-1.97813800	0.03477200	-0.23687800
			C	0.70310000	2.08112000	0.13654900
			H	2.58737100	0.17949500	-0.77639500
			H	0.72363300	2.41339200	1.17681000

			H	1.58303000	2.45115100	-0.38555500
			H	-0.19700800	2.46970900	-0.34241400
T_{2min}	-679.7828686	 d(S-C-N-N): 137.1	N	2.00967700	-1.08547300	-0.23717000
			N	0.75883900	-1.42224100	0.23563600
			C	-0.05638200	-0.38831700	0.46279600
			N	0.71882100	0.67240000	0.11091500
			C	1.94666600	0.21201200	-0.30386500
			H	0.54130800	-2.39577600	0.38210500
			S	-2.57484500	-0.26016100	-0.15778300
			C	0.27536800	2.06409400	0.11579900
			H	2.74877600	0.85212600	-0.63163400
			H	-0.30121900	2.25029500	1.01897900
			H	1.14671900	2.71574200	0.10124200
			H	-0.34334600	2.26065900	-0.76021900
S_0/T_1	-679.76186289	 d(S-C-N-N): 165.1	N	-1.81202200	-1.16914000	-0.33201100
			N	-0.54312100	-1.42461400	0.10054500
			C	0.27219100	-0.29600100	-0.08177600
			N	-0.60106100	0.74082200	-0.30029300
			C	-1.88752000	0.24095700	0.06919800
			H	-0.16014900	-2.35356300	-0.02999400
			S	1.91916600	-0.28378700	-0.01935400
			C	-0.23202500	2.14153100	-0.15440000
			H	-2.15247800	0.41982100	1.12318100
			H	0.74561100	2.30027300	-0.60418700
			H	-0.97230100	2.74804600	-0.67234000

			H	-0.19528900	2.42948000	0.90131800
S_1/T_1	-679.74785189	 d(S-C-N-N): 105.8	N	1.24163900	-1.41817300	-0.38780200
			N	0.21441100	-1.55081400	0.61034900
			C	-0.19558800	-0.14243900	0.74667500
			N	0.95708400	0.65832100	0.52658600
			C	1.62722400	-0.19816100	-0.37441600
			H	-0.53535100	-2.12747400	0.20821400
			S	-1.82799200	0.00082300	-0.09878900
			C	0.71715000	2.04822500	0.13038000
			H	2.47405800	0.16300600	-0.94164500
			H	0.40772900	2.62935900	0.99859000
			H	1.64472000	2.46861700	-0.25589600
			H	-0.06364400	2.10993300	-0.64564000
T_1-TS	-679.72096069	 d(S-C-N-N): 117.4	N	0.47224200	-1.83557800	-0.20322000
			N	-0.55804400	-1.32448800	0.50625100
			C	-0.33908800	0.14759000	0.62969900
			N	0.97968200	0.32423700	0.12185400
			C	1.35786400	-0.86852600	-0.38695600
			S	-1.78860000	0.67634700	-0.25134200
			C	1.69128600	1.58718000	0.06632400
			H	2.29788800	-1.01082500	-0.90005100
			H	1.72754000	2.03010800	1.06267100
			H	2.70501600	1.40882300	-0.28737300
			H	1.18910900	2.27837300	-0.61497100
			H	-1.81948200	-0.87469700	-0.06740600

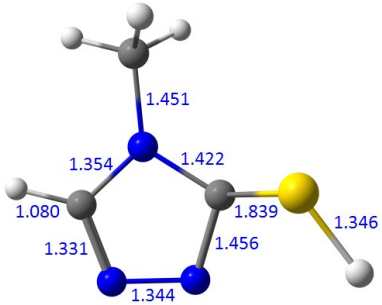
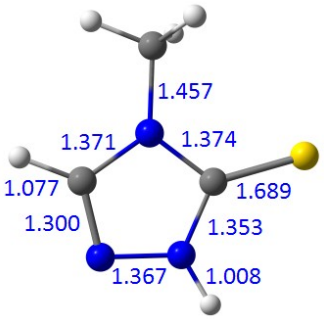
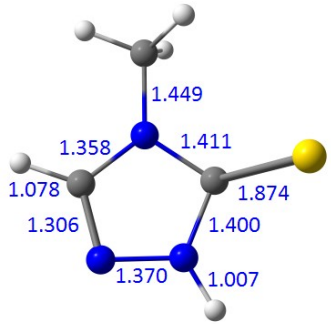
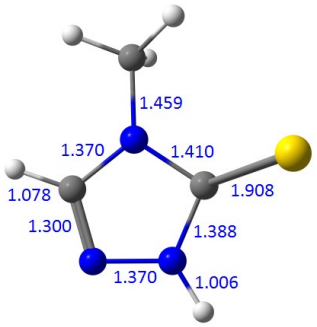
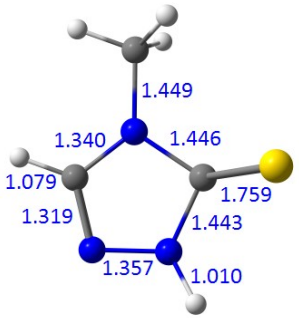
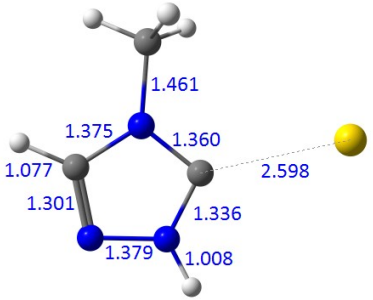
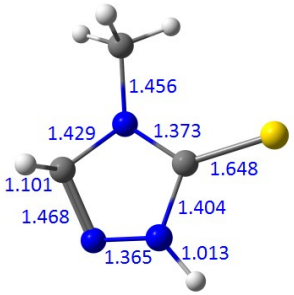
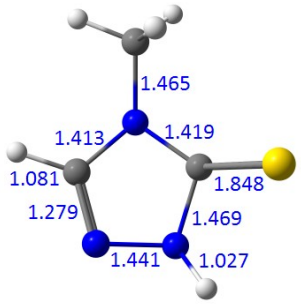
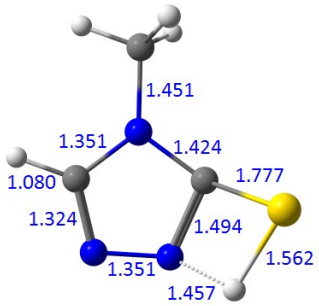
T_{1min}'	-679.74663123	 d(S-C-N-N): 113.5	N	1.19105300	-1.59144900	-0.25326500
			N	0.05887700	-1.57368500	0.47143000
			C	-0.32438400	-0.17689500	0.61536800
			N	0.80087500	0.56694600	0.16631500
			C	1.61719200	-0.34109100	-0.41822800
			S	-1.89391000	0.18844400	-0.27146600
			C	0.89917900	2.01432200	0.13089600
			H	2.51826300	-0.07092000	-0.94827600
			H	0.67681200	2.41853400	1.11871600
			H	1.91215200	2.29455100	-0.15213400
			H	0.19743800	2.43664900	-0.59442300
			H	-2.50965300	-0.88462200	0.25999500

Table S8. Optimized Cartesian coordinates and Hartree-Fock energies (a.u.) at (TD-)B3LYP-(D3)BJ/6-311G(d, p) level with PCM (solvent=water)model.

State	H-F energy	Structure	Cartesian coordinates		
S_0	-679.8997099	 d(S-C-N-N): 180.0	N	-1.77570100	-1.15293300	0.00000600
			N	-0.43805400	-1.43632300	0.00001400
			C	0.35270900	-0.33907600	-0.00000300
			N	-0.55457300	0.69299900	-0.00002800
			C	-1.81209900	0.14668700	-0.00004600
			H	-0.11743200	-2.39244600	0.00004300
			S	2.03886400	-0.24652000	0.00003100
			C	-0.21140800	2.10869500	-0.00001300
			H	-2.71287500	0.73757800	-0.00007000
			H	0.37286100	2.34515000	-0.88871200
			H	-1.13357600	2.68471300	-0.00036100
			H	0.37228800	2.34530000	0.88902600
S_{1min}	-679.760175520	 d(S-C-N-N): 125.0	N	1.38050200	-1.46161900	-0.23543900
			N	0.13198200	-1.44389500	0.32798400
			C	-0.35130800	-0.15967400	0.60718200
			N	0.70872800	0.62598800	0.10725500
			C	1.68839600	-0.19746000	-0.34749300
			H	-0.30003200	-2.31006400	0.60445000
			S	-2.01259800	0.02987500	-0.23878800
			C	0.70296300	2.07469300	0.11359100
			H	2.62059900	0.16111400	-0.75382500

			H	0.70044300	2.45019700	1.13833500
			H	1.58550000	2.43943400	-0.40753000
			H	-0.19373500	2.43263600	-0.39911400
S_{2min}	-679.75441601	 d(S-C-N-N): 121.1	N	1.67728900	-1.19508300	-0.21745100
			N	0.46127900	-1.44338000	0.36285800
			C	-0.30728300	-0.30855300	0.57997800
			N	0.51997500	0.68644000	0.02001500
			C	1.67574400	0.08994700	-0.41126500
			H	0.21818800	-2.38600500	0.61638100
			S	-2.02617700	-0.21656900	-0.24238500
			C	0.33554300	2.12252500	0.20296300
			H	2.48993800	0.63832100	-0.85643100
			H	0.54412700	2.40151400	1.23853800
			H	1.01796600	2.64937700	-0.46125700
			H	-0.68522000	2.40254900	-0.04707600
T_{1min}	-679.7846827	 d(S-C-N-N): 119.4	N	1.37501600	-1.46054500	-0.22842900
			N	0.17264900	-1.47893400	0.40081100
			C	-0.41812800	-0.17036000	0.55003300
			N	0.68709100	0.63349500	0.07875300
			C	1.66150100	-0.17886800	-0.35349400
			H	-0.37596800	-2.32614800	0.35962800
			S	-1.97810500	0.03527600	-0.23686600
			C	0.70377700	2.08102800	0.13667200
			H	2.58729000	0.17907900	-0.77643200
			H	0.72385300	2.41296100	1.17702400

			H	1.58417900	2.45072500	-0.38477500
			H	-0.19585300	2.47005600	-0.34280200
T_{2min}	-679.7831993	 d(S-C-N-N): 136.8	N	2.00686300	-1.08762700	-0.23893400
			N	0.75729200	-1.42222700	0.23835500
			C	-0.05598000	-0.38704500	0.46668300
			N	0.71943300	0.67233400	0.11077500
			C	1.94525800	0.21001300	-0.30709500
			H	0.53905000	-2.39530200	0.38706400
			S	-2.57443500	-0.25919600	-0.15908300
			C	0.27840000	2.06481800	0.11720100
			H	2.74705400	0.84873900	-0.63829400
			H	-0.27532900	2.25917800	1.03293800
			H	1.15035900	2.71438800	0.07623500
			H	-0.36134200	2.25605500	-0.74471700
S_0/T_1	-679.762029508	 d(S-C-N-N): 165.2	N	-1.81047700	-1.16991800	-0.33511600
			N	-0.54409900	-1.42427300	0.10520800
			C	0.27225000	-0.29626500	-0.07559600
			N	-0.59929700	0.74003200	-0.30247600
			C	-1.88790000	0.24134600	0.06183800
			H	-0.16055400	-2.35382100	-0.01949500
			S	1.91901100	-0.28413500	-0.00321800
			C	-0.23087100	2.14114400	-0.15798400
			H	-2.15793700	0.42297500	1.11396800
			H	0.74836700	2.29915800	-0.60450700
			H	-0.96927300	2.74642200	-0.67997900

			H	-0.19821700	2.43115900	0.89724400
S_1/T_1	-679.749000534	 d(S-C-N-N): 106.4	N	1.24433900	-1.42038000	-0.38624300
			N	0.20955800	-1.54758100	0.60796300
			C	-0.19472800	-0.14225400	0.74992300
			N	0.95527500	0.65689400	0.52349600
			C	1.63028500	-0.20139500	-0.37312200
			H	-0.53938700	-2.12316100	0.20394700
			S	-1.83377300	0.00821000	-0.08935700
			C	0.71772500	2.04699300	0.12757900
			H	2.48027700	0.15925200	-0.93601900
			H	0.40891900	2.62876600	0.99566600
			H	1.64580400	2.46616000	-0.25868400
			H	-0.06285300	2.10972000	-0.64854200
T_1-TS	-679.7212113	 d(S-C-N-N): 117.3	N	0.47180200	-1.83570000	-0.20310200
			N	-0.55828000	-1.32446400	0.50678700
			C	-0.33892200	0.14794700	0.62965800
			N	0.97958300	0.32405600	0.12130100
			C	1.35744400	-0.86862300	-0.38742500
			S	-1.78865700	0.67672400	-0.25145100
			C	1.69223200	1.58662400	0.06672100
			H	2.29721800	-1.01094700	-0.90093600
			H	1.73057300	2.02773800	1.06377100
			H	2.70509400	1.40794400	-0.28916400
			H	1.18925500	2.27918100	-0.61251700
			H	-1.81987900	-0.87442400	-0.06656900

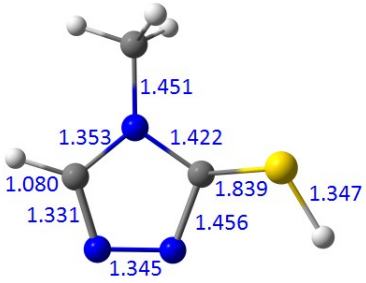
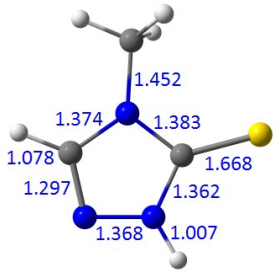
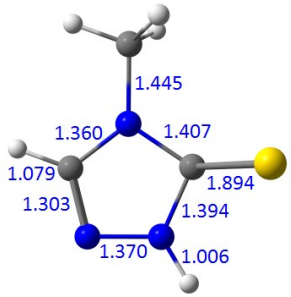
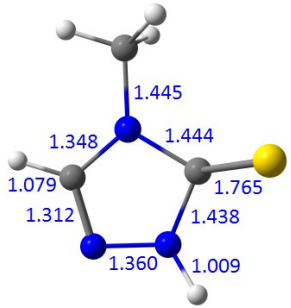
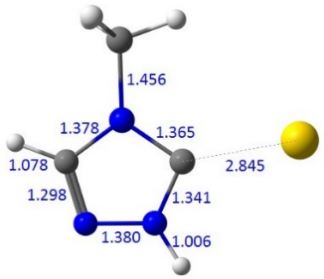
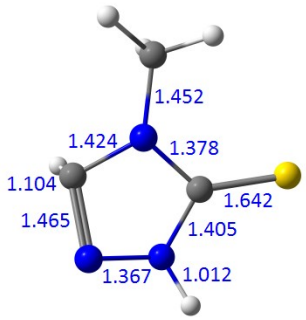
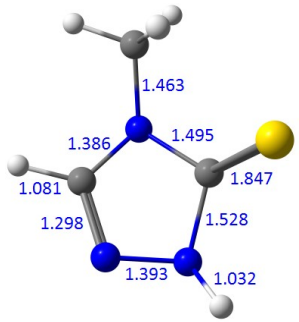
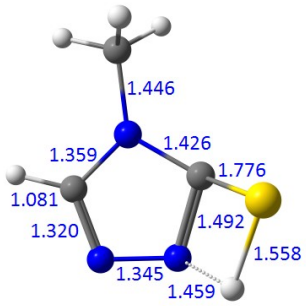
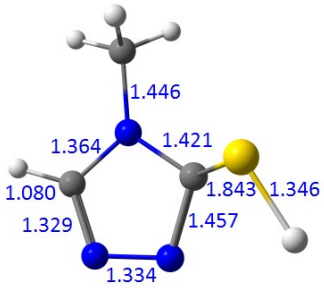
T_{1min}'	-679.7469643	 d(S-C-N-N): 113.5	N	1.19128700	-1.59143300	-0.25326800
			N	0.05889900	-1.57377200	0.47161900
			C	-0.32453900	-0.17701800	0.61513600
			N	0.80063800	0.56683800	0.16578500
			C	1.61718800	-0.34090700	-0.41819800
			S	-1.89389300	0.18840400	-0.27159600
			C	0.89934300	2.01433600	0.13123600
			H	2.51840200	-0.07056900	-0.94790100
			H	0.67794100	2.41787300	1.11952900
			H	1.91212900	2.29428800	-0.15259100
			H	0.19703900	2.43705200	-0.59322900
			H	-2.51094800	-0.88299700	0.26172800

Table S9. Optimized Cartesian coordinates and Hartree-Fock energies (a.u.) at (TD-)B3LYP-(D3)BJ/6-311G(d, p) level in vacuum.

State	H-F energy	Structure	Cartesian coordinates			
S_0	-679.8850049	 d(S-C-N-N): 180.0	N	-1.79733600	-1.12646000	-0.00005100
			N	-0.46296700	-1.42952500	0.00000200
			C	0.35907600	-0.34391000	0.00001700
			N	-0.54516700	0.70313100	-0.00003500
			C	-1.81140700	0.17094600	-0.00002200
			H	-0.15326600	-2.38725300	0.00001800
			S	2.02524100	-0.27276100	0.00005900
			C	-0.16477300	2.10468800	-0.00003200
			H	-2.70714200	0.77039800	-0.00004500
			H	0.43367900	2.32467000	-0.88477900
			H	-1.06935000	2.71115300	-0.00037000
			H	0.43313200	2.32484300	0.88504400
S_{1min}	-679.753590536	 d(S-C-N-N): 125.5	N	1.33693000	-1.49133900	-0.23963700
			N	0.08843500	-1.42618000	0.32021900
			C	-0.34161100	-0.13750900	0.63284200
			N	0.73392300	0.61373700	0.12400700
			C	1.68459100	-0.24008300	-0.34291300
			H	-0.36999600	-2.27762600	0.59638600
			S	-2.01053900	0.05960100	-0.24047300
			C	0.74853300	2.05879600	0.09572600
			H	2.63022000	0.08692500	-0.74555700
			H	0.71874000	2.45973300	1.11111500
			H	1.65259600	2.40205700	-0.40537700

			H	-0.12702100	2.41454100	-0.45505000
T_{1min}	-679.7745007	 d(S-C-N-N): 119.8	N	1.40462800	-1.43841100	-0.22591200
			N	0.19564800	-1.46986500	0.39520700
			C	-0.41228500	-0.17601400	0.55483900
			N	0.67834000	0.64370400	0.08230900
			C	1.67044100	-0.15945600	-0.34946600
			H	-0.34392200	-2.32096500	0.34866400
			S	-1.97897500	0.00550900	-0.23669300
			C	0.66075500	2.08760900	0.13190900
			H	2.59168100	0.21046200	-0.77279400
			H	0.70333800	2.43329300	1.16848200
			H	1.51371400	2.47999500	-0.42111800
			H	-0.26499600	2.44822700	-0.32106500
T_{2min}	-679.75777507	 d(S-C-N-N): 117.7	N	1.97853500	-1.06722400	-0.37662900
			N	0.86276900	-1.39493200	0.36648900
			C	0.06946600	-0.37158000	0.71347000
			N	0.73372800	0.68005100	0.15077900
			C	1.86237200	0.22022800	-0.49327400
			H	0.70725000	-2.36316800	0.59252100
			S	-2.61700700	-0.29041600	-0.22068200
			C	0.26203700	2.05735300	0.17835200
			H	2.56129600	0.85120800	-1.01755900
			H	1.08337900	2.73182400	0.42377600
			H	-0.16248900	2.33543300	-0.78822200

			H	-0.50580700	2.13009900	0.94463800
S_0/T_1	-679.755321997	 d(S-C-N-N): 164.3	N	-1.82574000	-1.14201500	0.31946900
			N	-0.55800200	-1.41645900	-0.11094200
			C	0.28083900	-0.30640300	0.08106900
			N	-0.58487300	0.74606100	0.28654200
			C	-1.87931000	0.27029600	-0.06709600
			H	-0.18946300	-2.34759000	0.03720600
			S	1.92233600	-0.32208600	0.04413400
			C	-0.19050700	2.13689100	0.15230200
			H	-2.16488000	0.46917300	-1.11471400
			H	-0.19480800	2.44919800	-0.89870000
			H	-0.88921400	2.75290100	0.71645600
			H	0.81334200	2.25995500	0.55408000
S_1/T_1	-679.71160035	 d(S-C-N-N): 93.2	N	1.18414600	-1.40464400	-0.35945700
			N	0.26389400	-1.61959400	0.66390100
			C	-0.20446600	-0.16708900	0.73152000
			N	1.03052200	0.66458300	0.59294000
			C	1.60582800	-0.17677400	-0.34567200
			H	-0.50439300	-2.15949400	0.23531900
			S	-1.68596600	0.23891900	-0.29401200
			C	0.71449800	2.02380400	0.15511600
			H	2.41353100	0.14864800	-0.98659800
			H	0.44847100	2.64270400	1.01116900
			H	1.57006000	2.45946900	-0.36296800

			H	-0.17468300	1.99069200	-0.52465200
T_1-TS	-679.7116299	 d(S-C-N-N): 117.1	N	0.46930800	-1.83291600	-0.20680300
			N	-0.55610000	-1.32300500	0.49885600
			C	-0.33895100	0.14651500	0.63728600
			N	0.98605000	0.32381700	0.14157700
			C	1.35736300	-0.87328500	-0.38464600
			S	-1.78251100	0.67427400	-0.25301000
			C	1.67825100	1.59009000	0.05675700
			H	2.29363100	-1.01880100	-0.90438200
			H	1.64521700	2.08945600	1.02702200
			H	2.71861000	1.41536600	-0.21818600
			H	1.21553500	2.24152100	-0.69140800
			H	-1.82760300	-0.87112200	-0.05667500
T_{1min}'	-679.7343833	 d(S-C-N-N): 113.7	N	1.18589500	-1.58832700	-0.25500000
			N	0.06018000	-1.57120200	0.46110200
			C	-0.31927800	-0.17373800	0.62439100
			N	0.81030900	0.57286400	0.19265600
			C	1.61882700	-0.34181500	-0.41684000
			S	-1.89185200	0.18533400	-0.26656900
			C	0.88259600	2.01494400	0.11494100
			H	2.51590100	-0.07610500	-0.95619900
			H	0.57929000	2.44644800	1.06989600
			H	1.90932300	2.31396300	-0.09672800
			H	0.22999600	2.40932900	-0.67285600

			H	-2.45244500	-0.94867400	0.19473400