Supporting Information for

Triplet Decay Dynamics in Sulfur Substituted Thymine: How Position of Substitution Matters

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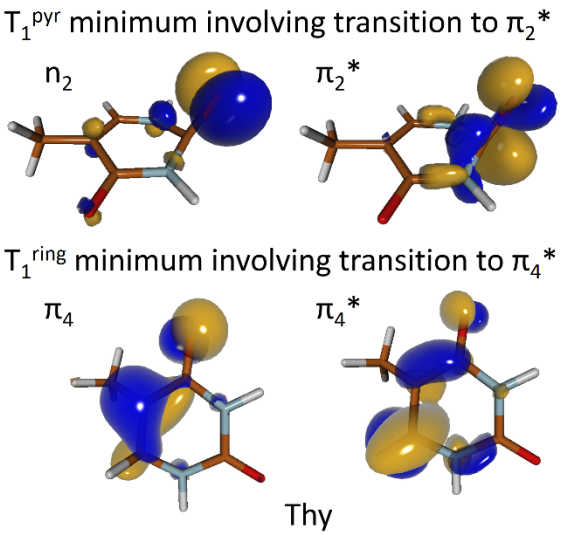

Figure S1. The two minima on the T_1 state of Thymine (Thy), shown along with the orbitals involved in the T_1 transition. The minimum with strong pyramidalization at C^2=O is characterized by a transition to the π_2^* orbital (T_1^{pyr}), while the nearly planar structure is characterized by a transition to the π_4^* orbital (T_1^{ring}).

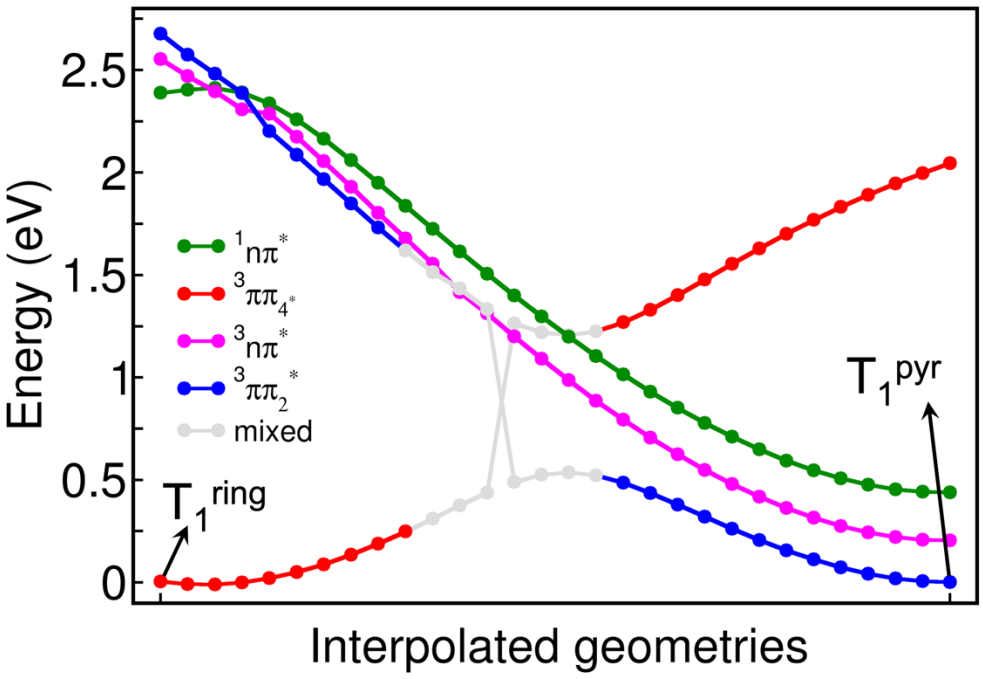

Figure S2. LIIC scan between the T_1^{ring} and T_1^{pyr} minima in 2tThy at the MS-CASPT2 level of theory, showing the diabatic natures of states. The state natures have been identified by examining the orbitals and cross-referencing them with the CI vector coefficients.

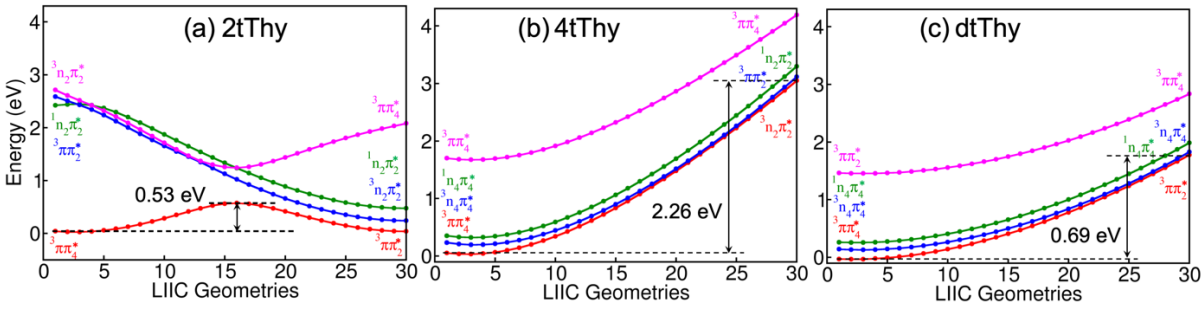

Figure S3. LIIC scans connecting the two minima on the T_1 PES of the thiothymines – 2tThy, 4tThy and dtThy. The difference between the two minima is not labelled in 2tThy, since the two minima are almost isoenergetic with a meagre difference of 0.002 eV, which is not discernable in the figure.

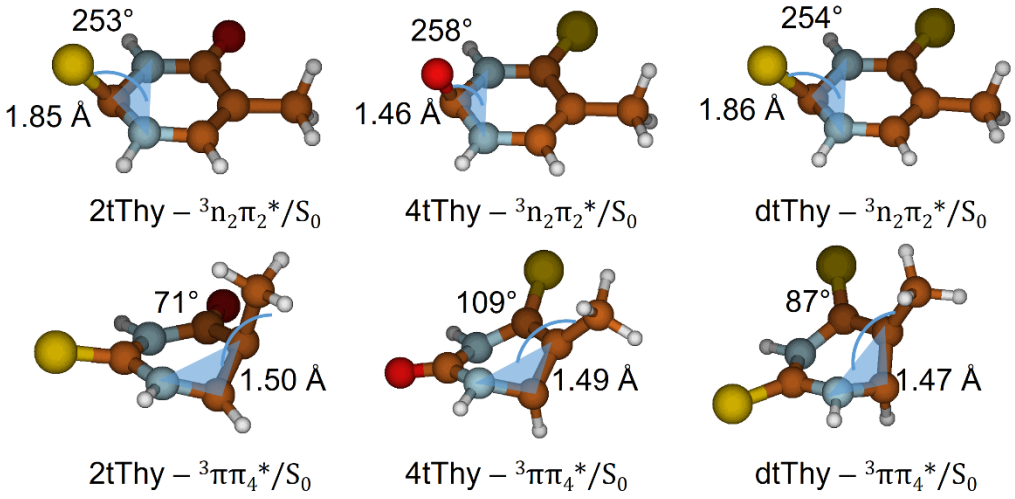

Figure S4. Two types of MECPs in the thiothymines: the MECP which is close to the T_1^{pyr} minimum (top) and the MECP which is close to the T_1^{ring} minimum (bottom).

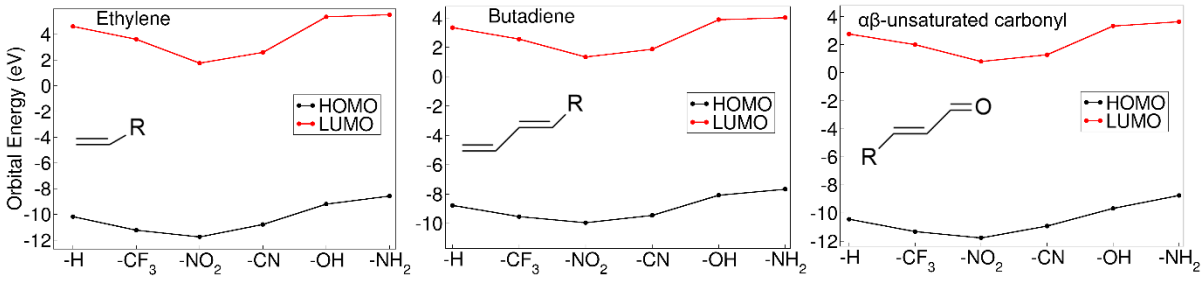

Figure S5. Orbital energies of model π systems substituted with electron withdrawing (−NO_2, −CF_3, −CN) and electron donating (−OH, −NH_2) groups.

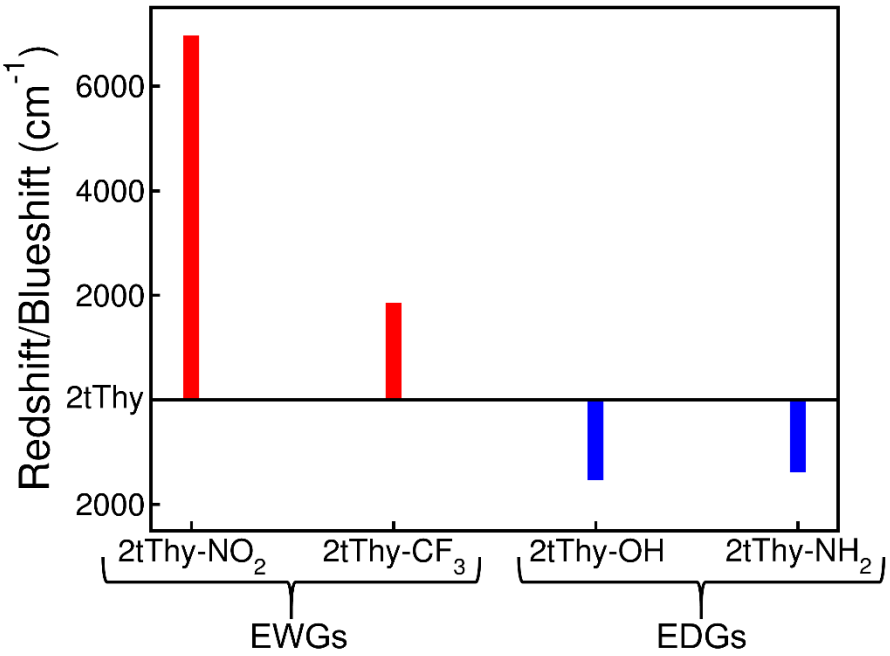

Figure S6. Redshifts/Blueshifts seen in 2tThy analogues with respect to 2tThy, by calculating the vertical excitation energy of their first bright state at CASPT2 (SA-CASSCF wave function composed of first six singlet states, 6-31G** basis set, (14,10) active space and a level shift of 0.2 a.u.) level of theory on MP2/cc-pVDZ optimized ground state geometries. The 2tThy analogues are generating by substituting EWGs ($-NO_2$, $-CF_3$) and EDGs ($-OH$, $-NH_2$) at C^6 of 2tThy.

Table S1. Some geometrical parameters for the thiothymines at their Franck-Condon structure and T_1 minima.

Molecule	Geometry	C^2=X (Å)	δ($N^1C^2N^3X$)	C^5=C^6 (Å)
2tThy	Franck-Condon[a]	1.64	180°	1.35
	T_1^{ring} minimum	1.64	180°	1.49[b]
	T_1^{pyr} minimum	1.82	230°	1.35
4tThy	Franck-Condon	1.20	180°	1.35
	T_1^{ring} minimum	1.20	180°	1.43
	T_1^{pyr} minimum	1.39	230°	1.33
dtThy	Franck-Condon	1.66	180°	1.33
	T_1^{ring} minimum	1.68	180°	1.43
	T_1^{pyr} minimum	1.81	229°	1.34
Thy	Franck-Condon	1.20	180°	1.36
	T_1^{ring} minimum	1.20	179°	1.49
	T_1^{pyr} minimum	1.39	231°	1.35

[a]Franck-Condon geometries have been optimized at the SA-CASSCF level so that the geometrical parameters can be better compared with the values of the excited minima. [b]Highlighted values are those that change significantly with respect to the Franck-Condon geometry.

Table S2. Energetic and topological parameters for Thymine.

	Thy
T_1^{pyr} – T_1^{ring} energy (eV)[a]	1.79
Relevant T_1 minimum	T_1^{ring}
$\pi_2^* - \pi_4^*$ orbital energy (eV)[b]	2.02
SOC of MECP near T_1^{pyr} (cm^{-1})	30.7
SOC of MECP near T_1^{ring} (cm^{-1})	0.5

Barrier associated with MECP near T_1^{pyr}, $\Delta E^{\ddagger}$ (eV)[a]	0.07
Barrier associated with MECP near T_1^{ring}, $\Delta E^{\ddagger}$ (eV)[a]	0.15

[a]Calculated at the MS-CASPT2 level on SA-CASSCF optimized structures with a 10,7 active space and 6-31G** basis set. [b]Orbital energies calculated at the Hartree-Fock/cc-pVDZ level on MP2/cc-pVDZ optimized ground state minima.

Table S3. Energetic and topological parameter for 2-thiothymine and 2-thiouracil.

	2- thiothymine	2-thiouracil
$T_1^{pyr} - T_1^{ring}$ energy (eV)[a]	-0.002	-0.13
Relevant T_1 minimum	Both	Both
$\pi_2^* - \pi_4^*$ orbital energy (eV)[b]	0.71	0.84
SOC of MECP near T_1^{pyr} (cm^{-1})	**105.3[c]**	**83.8**
SOC of MECP near T_1^{ring} (cm^{-1})	0.9	0.8
Barrier associated with MECP near T_1^{pyr}, $\Delta E^{\ddagger}$ (eV)[a]	**0.25**	**0.26**
Barrier associated with MECP near T_1^{ring}, $\Delta E^{\ddagger}$ (eV)[a]	0.23	0.16

[a]Calculated at the MS-CASPT2 level on SA-CASSCF optimized structures with a 10,7 active space and 6-31G** basis set. [b]Orbital energies calculated at the Hartree-Fock/cc-pVDZ level on MP2/cc-pVDZ optimized ground state minima. [c]SOCs and barriers in bold indicate the MECP involved in the feasible T_1 decay pathway and its associated barrier, respectively.

Table S4. Energies of the π_4* and π_2* orbitals and their comparison with the energy difference between the two minima optimized on the T_1 of 2-thiothymine analogues.

Molecule	2tThy	6-NO_2-2tThy	6-CF_3-2tThy	6-OH- 2tThy	6-NH_2-2tThy
π_4* energy (eV)[a]	2.4	-0.2	1.6	3.3	3.3
π_2* energy (eV)	3.1	2.3	2.7	2.7	2.8
π_2* - π_4* energy (eV)	0.7	2.5	1.1	-0.6	-0.5
$T_1^{pyr} - T_1^{ring}$ energy (eV)[b]	-0.002	1.01	0.27	–[c]	–[c]

[a]Orbital energies calculated at the Hartree-Fock/cc-pVDZ level of theory on MP2/cc-pVDZ optimized ground state structures. [b]Calculated at the MS-CASPT2/10,7/6-31G** level of theory. [c]Only the T_1^{pyr} minimum could be optimized for these molecules.

Table S5. Spin-orbit coupling values of the MECPs of the 2-thiothymine analogues.

Molecule, nature	SOC (cm^{-1})
SOC of MECP near T_1^{ring}	0.28
SOC of MECP near T_1^{pyr}	41.16
SOC of MECP near T_1^{ring}	0.40
SOC of MECP near T_1^{pyr}	102.69
SOC of MECP near T_1^{pyr}	99.17
SOC of MECP near T_1^{pyr}	106.68

Cartesian coordinates of excited minima, minimum energy crossing points, and ground state minima studied in this work.

T_1 minima of thymine and the thiothymines

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2tThy T_1^{pyr} CASSCF/10,7/6-31G** ENERGY=-774.12776846

N	0.0021467502	-0.0310763333	-0.0066461411
C	0.0051495801	0.0093671702	1.3811941979
N	1.2981020092	-0.0209475593	1.9240145904
C	2.4819151556	0.1585322322	1.2562905437
C	2.3690951756	0.2632252010	-0.2130920367
C	1.1373041717	0.1675077458	-0.7586837567
C	3.6309612166	0.4482011077	-1.0066653026
O	3.5240573278	0.2117604739	1.8462211547
S	-1.1838691852	-1.1798479281	2.0798555673
H	4.3115660674	-0.3804869762	-0.8469290292
H	4.1482306622	1.3507674645	-0.7017110380
H	3.4132393845	0.5164485785	-2.0668078910
H	1.3805190231	-0.0681397607	2.9148938179
H	-0.8827781665	0.0636556967	-0.4468706181
H	0.9746418276	0.2275458873	-1.8183460583

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2tThy T_1^{ring} CASSCF/10,7/6-31G** ENERGY=-774.09076028

C	2.6757203591	-0.5557175170	1.2920056859
C	1.4245463712	-0.4443770805	2.0960909251
N	0.4956294239	0.4132051064	1.4948871259
C	0.3067997230	0.4605889261	0.1478196677
N	1.2531237670	-0.2180142066	-0.5888899926
C	2.5072160694	-0.6262144333	-0.1594445852
S	-0.9472680271	1.2519808212	-0.5506771173
O	3.3485587273	-0.9509789857	-0.9446515894
C	4.0168113915	-0.2819185994	1.8919299170
H	-0.2357809594	0.8155698671	2.0361510817
H	1.1333870320	-0.1861594453	-1.5779770924
H	1.0334355510	-1.2977605047	2.6310245657
H	4.2079622220	-0.9503414428	2.7262514030
H	4.7942994807	-0.4147980982	1.1523474245
H	4.0622998680	0.7352505924	2.2764165802

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4tThy T_1^{pyr} CASSCF/10,7/6-31G** ENERGY=-774.08855400

C	0.3818024937	-0.1569524071	0.5976179583
C	-1.0752335424	0.0403229779	0.5462750835
C	-1.6844128592	-0.1081343951	-0.6310046734
N	-1.0229951806	-0.4020988171	-1.8018288372
C	0.3616466244	-0.2668028168	-1.8540020145
N	0.9779945524	-0.4207258012	-0.6144539996
C	-1.8431074800	0.3474527541	1.8034272360
O	0.7608276584	0.8736263506	-2.5299153730
S	1.2792928650	-0.1330154469	1.9752911702
H	-1.5000133795	1.2700662081	2.2580405149
H	-1.7228216724	-0.4380087122	2.5408879448
H	-2.8997091277	0.4502251246	1.5808435574
H	1.9634691745	-0.5556032380	-0.6028336713
H	-1.5218518251	-0.3589553631	-2.6587815949
H	-2.7523793014	-0.0328664178	-0.7221283012

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4tThy T_1^{ring} CASSCF/10,7/6-31G** ENERGY=-774.16542313

C	-0.7754055732	1.1438121838	0.0003407508
N	-0.0174248438	0.0210601882	-0.1684569799
C	1.3730940494	0.0079047084	-0.2284047467
C	2.0903915801	1.2267401022	-0.0326492478
C	1.3530576566	2.3717099190	0.1520044404
N	-0.0524224440	2.2905316401	0.1493330090
S	2.0051390869	3.9902141879	0.3798201996
O	-1.9743231742	1.1217197964	0.0173626854
H	-0.5894206676	3.1162553383	0.2785828344
H	-0.5378070154	-0.8158079143	-0.2938762173
C	3.5962920042	1.1614027569	-0.0554496930
H	1.8463305054	-0.9486130158	-0.2935660611
H	4.0459804778	2.1287825448	0.1080703208
H	3.9544421027	0.4850018496	0.7145242988
H	3.9416382553	0.7826697145	-1.0124145934

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dtThy T_1^{pyr} CASSCF/10,7/6-31G** ENERGY=-1096.75386389

N	0.0063402989	-0.0024235869	-0.0061304536
C	-0.0020980185	-0.0185786406	1.3871001340
N	1.2862522459	0.0084022390	1.9376706549
C	2.4381822003	0.3641358370	1.3085804561
C	2.3242450492	0.5560192433	-0.1468185589
C	1.1301014280	0.3616932448	-0.7067258231
C	3.5324457194	0.9280727025	-0.9606119689
S	3.8440844564	0.5274837482	2.1618193346
S	-1.1193420019	-1.2859956730	2.0336111072
H	4.3090722425	0.1763556760	-0.8762256177
H	3.9574316589	1.8661285843	-0.6222259105
H	3.2635844783	1.0294310656	-2.0064962531
H	1.3540972358	-0.1266792115	2.9215715554
H	-0.8773578420	0.1063582034	-0.4469408872
H	0.9817168486	0.4655455680	-1.7655507689

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dtThy T_1^{ring} CASSCF/10,7/6-31G** ENERGY=-1096.79704724

N	0.0037266882	-0.0534323522	0.0060026216
C	0.0138976497	-0.0001975306	1.3480009016
N	1.2327933597	0.0407741197	1.9085543933
C	2.4554358981	0.0420918055	1.2001696487
C	2.4264426020	-0.0163881853	-0.1715524903
C	1.1459351224	-0.0830491418	-0.7938335739
C	3.6417840809	-0.0300096436	-1.0621242699
S	3.8969971356	0.1040291330	2.2088384618
S	-1.3963394167	0.0138651784	2.2547083727
H	3.6944032885	-0.9654975771	-1.6100705767
H	4.5557420812	0.0862323016	-0.5003265823
H	3.5817573676	0.7745609035	-1.7879094057
H	1.2542326820	0.0805884470	2.9017542270
H	-0.8976777431	-0.0881267102	-0.4115461073
H	0.9948042040	-0.0736607479	-1.8516016204

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Thy T_1^{pyr} CASSCF/10,7/6-31G** ENERGY=-451.46736636

N	-0.0784777091	0.2621829367	0.0847809984
C	0.0466998571	-0.1862059373	1.3950997009
N	1.2578462962	0.1645955122	1.9947859987
C	2.4253368391	0.4367928978	1.3219937573
C	2.2934470386	0.5526580812	-0.1495567816

C	1.0596074489	0.4728814506	-0.6860808542
C	3.5406436999	0.8220170393	-0.9437927861
O	3.4552232763	0.6024540780	1.9086842843
O	-0.2800410498	-1.5291906447	1.4899185145
H	4.2581754087	0.0187516614	-0.8196884195
H	4.0195129445	1.7350548642	-0.6094479787
H	3.3112505613	0.9172140115	-1.9992871861
H	1.3407320261	0.0899354259	2.9840470075
H	-0.9228219678	0.0283462139	-0.3828534462
H	0.8808193302	0.6148804091	-1.7353108092

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Thy T_1^{ring} CASSCF/10,7/6-31G** ENERGY=-451.48692014

N	0.0077225782	-0.0200106179	-0.0106019808
C	0.0031251437	-0.0254020438	1.3617514550
N	1.2478376798	-0.0040546381	1.9466576480
C	2.4620274984	-0.2756654757	1.3050822528
C	2.4067014234	-0.2550096565	-0.1404765387
C	1.1561491112	0.2852387057	-0.7535039214
C	3.4787992476	-0.8619141929	-0.9849853341
O	3.4528898080	-0.5437390859	1.9491664225
O	-1.0042738238	-0.0322635090	2.0050615634
H	3.0822631261	-1.6984818124	-1.5557623093
H	4.2994976101	-1.2091156029	-0.3733437525
H	3.8609120359	-0.1383316553	-1.7005300305
H	1.2420453128	-0.0655664426	2.9408587863
H	-0.8918429597	0.1437976987	-0.4040220146
H	1.1822162081	1.2507373288	-1.2415232460

MECPs of thymine and the thiothymines

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2tThy T_1^{pyr}-MECP CASSCF/10,7/6-31G** ENERGY=-774.06393340

N	-0.0276846229	0.0141184169	0.0492999565
C	-0.0100333692	0.0709983226	1.4554678729
N	1.2971512871	0.0842445487	1.9685959852
C	2.4738497660	0.1988158682	1.2805926827
C	2.3473292418	0.2562608065	-0.1947234625
C	1.1120081039	0.1819981366	-0.7255167312
C	3.6057644719	0.3859874574	-1.0041908138
O	3.5272628225	0.2572799971	1.8485214192
S	-0.9423849375	-1.5159408294	1.6680855676
H	4.2618738657	-0.4591687630	-0.8301435264
H	4.1513660215	1.2791271585	-0.7228716693
H	3.3798166297	0.4359918456	-2.0634690151
H	1.3991647687	0.0794633260	2.9586345214
H	-0.9002020929	0.2500187612	-0.3676185778
H	0.9349990441	0.2173179471	-1.7839462093

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2tThy T_1^{ring}-MECP CASSCF/10,7/6-31G** ENERGY=-774.06027238

N	0.1460425370	2.2735188976	0.0521334503
C	-0.3913733186	1.0120967986	0.2613191876
N	0.2750419336	0.0060928590	-0.3752690789
C	1.2795964497	0.3193550686	-1.2839929435
C	2.2079358196	1.3249795979	-0.6629010284
C	1.4416879956	2.5681594802	-0.3546536342
S	-1.7230542399	0.7657508317	1.1820143714
C	3.1244002229	0.8864904962	0.4604938285
O	1.8500423414	3.6852725879	-0.3666128940

H	-0.3769379722	3.0368423256	0.4229550401
H	-0.1223987751	-0.9022303109	-0.2898444575
H	1.5908631269	-0.4387257413	-1.9733086825
H	3.8196225784	1.6886270628	0.6830511316
H	2.5827870367	0.6530609281	1.3740828345
H	3.6912082644	0.0099111181	0.1687758748

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4tThy T_1^{pyr}-MECP CASSCF/10,7/6-31G** ENERGY=-774.00062154

N	-0.9429578936	-0.2730274431	-1.7779235263
C	0.4194583087	-0.3550230121	-1.8175905720
N	1.0032274263	-0.3656697094	-0.5428050819
C	0.3861738790	-0.1359622014	0.6445746135
C	-1.0734799962	0.0425919749	0.5731680127
C	-1.6594740763	-0.0475312314	-0.6177606317
C	-1.8677660319	0.3091997733	1.8214676990
S	1.2441224566	-0.1116069787	2.0557207905
O	0.4671636832	0.9032118777	-2.5494064234
H	-1.5378543854	1.2234235441	2.3001202637
H	-1.7427365119	-0.4929120651	2.5387478567
H	-2.9212018989	0.4035699604	1.5834961574
H	1.9837048642	-0.5302340303	-0.4977050932
H	-1.4251878487	-0.3613967712	-2.6424667628
H	-2.7201219747	0.0500653123	-0.7478063020

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4tThy T_1^{ring}-MECP CASSCF/10,7/6-31G** ENERGY=-774.08143243

N	0.1381866031	-0.6307281152	0.6632398257
C	-0.8372416325	0.1959771019	0.1255498526
N	-0.3350174869	1.3486220452	-0.4451644434
C	0.9469480055	1.7055525306	0.0437631110
C	1.9084288458	0.6070142679	-0.2655933971
C	1.4694875407	-0.6313042670	0.1994792713
O	-2.0005851346	-0.0629530800	0.1898297995
C	2.9604586279	0.8294053467	-1.3096736885
S	2.3121017690	-2.0868859876	0.0752185775
H	-0.2268972802	-1.4952770182	0.9967156097
H	-1.0326740575	2.0503456932	-0.5665621469
H	0.9655992549	2.1059314476	1.0520982627
H	3.4924436518	-0.0807345513	-1.5460436700
H	2.4921717488	1.2084128414	-2.2153571696
H	3.6746765442	1.5764687447	-0.9786757944

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dtThy T_1^{pyr}-MECP CASSCF/10,7/6-31G** ENERGY=-1096.68593078

N	-1.4615690249	-0.2447895179	-1.1230554019
C	-0.1608751619	-0.6652985316	-1.4290035045
N	0.7345620125	-0.4258635764	-0.3740432938
C	0.4344786243	-0.1543480983	0.9235080906
C	-0.9920344629	0.1110311074	1.1959271043
C	-1.8436206302	0.0522809023	0.1791601916
C	-1.4413878948	0.4639805164	2.5859373386
S	1.6203371506	-0.1155210589	2.0715158063
S	0.0142842545	0.4853790868	-2.8782050972
H	-0.9506742508	1.3650323484	2.9352841168
H	-1.1944468048	-0.3266004795	3.2847446109
H	-2.5137433303	0.6231442329	2.6057532496
H	1.6951302976	-0.6093189211	-0.5592868108
H	-2.1683185736	-0.6066830091	-1.7243022865
H	-2.8923792052	0.2482539990	0.2999588859

15
dtThy T_1^{ring}-MECP CASSCF/10,7/6-31G** ENERGY=-1096.69575047

C	-0.7272028767	0.2210574812	-0.0212595518
N	-0.1984853916	1.4062719138	-0.4321602932
C	1.0134599727	1.6874009211	0.2473155621
C	1.9863720116	0.6589146889	-0.1321801148
C	1.5594782214	-0.6160556345	0.3531309140
N	0.1651614359	-0.6293529969	0.5844761178
S	2.4440008170	-2.0151361365	0.4265181960
S	-2.3347959296	-0.1636312658	-0.1767464579
H	-0.2356182092	-1.4947149700	0.8745872637
H	-0.8693047156	2.1077612919	-0.6569758075
C	2.8193424241	0.8362229634	-1.3698675303
H	0.8939735547	1.8869555402	1.3040506174
H	3.2607356373	-0.0958147475	-1.6940993685
H	2.2000812711	1.2296617128	-2.1730714548
H	3.6160167770	1.5508712383	-1.1926900920

15
Thy T_1^{pyr}-MECP CASSCF/10,7/6-31G** ENERGY=-451.38184944

N	-0.0479369995	0.1606455022	0.1175784421
C	0.0249785424	-0.1151285901	1.4654593797
N	1.2767496761	0.1762583700	2.0180337997
C	2.4336172888	0.4371590752	1.3377301537
C	2.2911999068	0.5515358006	-0.1380195770
C	1.0609157267	0.4293225853	-0.6691519288
C	3.5299820023	0.8265846954	-0.9409151545
O	3.4767636508	0.6039885589	1.9015710526
O	-0.2844645448	-1.4922084039	1.1995763944
H	4.2512116290	0.0275422569	-0.8138441034
H	4.0035678939	1.7427066592	-0.6084070298
H	3.2956054059	0.9168768430	-1.9955285740
H	1.3689122845	0.1395573378	3.0083255461
H	-0.9430288604	0.0851438030	-0.3070254309
H	0.8698813973	0.5123835063	-1.7220909699

15
Thy T_1^{ring}-MECP CASSCF/10,7/6-31G** ENERGY=-451.44732391

N	0.2207553744	-0.3779344632	-0.2055650565
C	0.1686095983	-0.3572818878	1.1701354864
N	1.2447742837	0.2585962882	1.7820342217
C	2.4867240821	0.5226283124	1.1901172734
C	2.4599149845	0.4204037154	-0.2844150164
C	1.0965206910	0.5267960395	-0.8462221612
C	3.5172625807	-0.3955873099	-0.9693389315
O	3.4654728919	0.7411069339	1.8522670884
O	-0.7390319414	-0.8142994258	1.7967136438
H	3.2223102703	-1.4424325815	-1.0188767010
H	4.4528552247	-0.3274238115	-0.4293678849
H	3.6716581959	-0.0479273899	-1.9843447941
H	1.2212872136	0.2308506704	2.7782107269
H	-0.6570320172	-0.6006018198	-0.6210683402
H	0.6967945680	1.5037017294	-1.0852855547

Ground state structures of 2tThy and its analogues

15
2tThy MP2/VDZ ENERGY=-775.47788398

N	1.1651870969	-1.0964575127	0.0948925214

C	2.4187804796	-1.6718250358	0.0395382222
C	3.5326918199	-1.0335716322	0.5029757483
C	3.3748582213	0.3090702413	1.0759831467
N	2.0441695675	0.7805484062	1.0741421176
C	0.9085338262	0.1536446624	0.6117297996
C	4.9142513288	-1.6181202576	0.4642548249
S	-0.6115835112	0.8175247341	0.6640160319
H	5.3316599833	-1.6836703822	1.4824615840
H	5.5896173260	-0.9679664331	-0.1157485663
H	4.9097640202	-2.6228383877	0.0136567028
H	1.9035991945	1.7120615850	1.4662340040
H	0.3503900954	-1.5915174174	-0.2565841247
H	2.4548568990	-2.6728071073	-0.4007436237
O	4.2825426527	0.9972345373	1.5274536111

17

2tThy-NO_2 MP2/VDZ ENERGY=-979.49567904

C	0.9057331511	0.1437540112	0.6224119957
N	1.1797816923	-1.0879425945	0.0645828763
C	2.4303556454	-1.6466756640	0.0209938122
C	3.5592959852	-1.0528077282	0.5233409188
C	3.3606436739	0.2783113717	1.1440416027
N	2.0354648555	0.7501548731	1.1290352693
C	4.9597135801	-1.6011076297	0.5121381196
O	4.2523518407	0.9531381877	1.6439001746
S	-0.6099496097	0.8002563585	0.6669377954
H	5.6138024529	-0.8601405132	0.9916666687
H	5.3075557018	-1.7931918327	-0.5142074197
H	5.0210395674	-2.5557404038	1.0567312331
H	1.8912996828	1.6658801759	1.5559325047
H	0.4065763770	-1.6169790563	-0.3386734858
N	2.4181392775	-2.9737000798	-0.6373002276
O	3.4885064715	-3.5736883415	-0.7306407297
O	1.3217706545	-3.3737411344	-1.0429461086

18

2tThy-CF_3 MP2/VDZ ENERGY=-1111.78284608

C	0.8980898645	0.1112181916	0.7608400926
N	1.1507974511	-1.1315209119	0.2197555239
C	2.4105432692	-1.6713446031	0.0591910235
C	3.5457595942	-0.9986679177	0.4239911249
C	3.3841220704	0.3395053929	1.0181070425
N	2.0491099475	0.7731380610	1.1271122411
C	4.9555188366	-1.5009175402	0.2949854571
O	4.3082460256	1.0484187828	1.3970604776
S	-0.6302390395	0.7217695534	0.9408527767
H	5.3874501031	-1.6602651553	1.2975614091
H	5.5692835037	-0.7282510278	-0.1952981672
H	5.0248202025	-2.4343535243	-0.2769358185
H	1.9156631070	1.6989987759	1.5352432067
H	0.3308276587	-1.6649163704	-0.0585737720
C	2.4389869481	-3.0592255280	-0.5524132280
F	3.0546712638	-3.9350456075	0.2557362883
F	1.1873301442	-3.5143402873	-0.7713182665
F	3.0821690495	-3.0610142840	-1.7305624120

16

2tThy-OH MP2/VDZ ENERGY=-850.53226401

C	0.8971861972	0.1661803070	0.6215407794
N	1.1715028847	-1.0167776901	-0.0344292979

C	2.4232739999	-1.5788014291	-0.1162502140
C	3.5241392601	-1.0105939568	0.4684692115
C	3.3436437781	0.2416685228	1.1940895640
N	2.0101514645	0.7215274141	1.2007855004
C	4.8954141819	-1.6273958433	0.3848293134
O	4.2228143237	0.8726784673	1.7708848137
S	-0.6254512054	0.8197412021	0.6889451728
H	5.5660656094	-1.0697845643	1.0548193550
H	5.3202021775	-1.5727531124	-0.6338474281
H	4.8976106522	-2.6838611205	0.7097931519
H	1.8595185760	1.5976783108	1.7003226630
H	0.3877447567	-1.4789392673	-0.4900110725
O	2.4024967812	-2.7281631382	-0.8258621198
H	3.3119735622	-3.0636831019	-0.8574383927

17

2tThy-NH_2 MP2/VDZ ENERGY=-830.68886298

C	0.9460662269	0.1482292076	0.5480968178
N	1.2242195977	-1.1234187757	0.0916090392
C	2.4841642985	-1.6967226431	0.0792652745
C	3.5860297491	-1.0000784633	0.5141964230
C	3.4031794926	0.3580779012	1.0107285408
N	2.0640931885	0.8229929420	0.9585627233
C	4.9706282488	-1.5900067319	0.5034135471
O	4.2840594942	1.0993999656	1.4348922111
S	-0.5964602097	0.7630393027	0.5829776743
H	5.0723120989	-2.4246054635	1.2199912576
H	5.6868552373	-0.8066166009	0.7904603823
H	5.2527700300	-1.9615202821	-0.4989811923
H	1.9121671223	1.7694418684	1.3060797504
H	0.4050243993	-1.6867174728	-0.1234206216
N	2.5046025111	-3.0253568225	-0.3354668034
H	1.9033559729	-3.2053482421	-1.1399198233
H	3.4487975414	-3.3521666895	-0.5300662007

T_1 minima of 2tThy analogues

17

2tThy-NO_2 T_1^{pyr} CASSCF/10,7/6-31G** ENERGY=-977.59514565

N	2.1111457650	0.8238267806	1.0457809518
C	0.9473367551	0.1248456188	0.7372945671
N	1.1976585557	-1.0317566383	0.0007960991
C	2.4348583365	-1.6243734534	0.0368755620
C	3.5351900370	-1.0791283586	0.5459239008
C	3.3867052706	0.3129135087	1.0510194341
S	-0.2041358021	0.0326442065	2.1451493432
N	2.4169800109	-2.9430791637	-0.5904617623
O	1.3657503608	-3.5390150184	-0.5775663912
C	4.9170766395	-1.6767163320	0.6261071142
O	4.3102428986	0.9754299617	1.4200938657
O	3.4311842276	-3.3547013030	-1.0898063821
H	5.4566410435	-1.1825267590	1.4204121965
H	5.4623888497	-1.5223328647	-0.2977571346
H	4.8869813856	-2.7385779999	0.8225670609
H	2.0316859910	1.7648294444	1.3633142479
H	0.4311256750	-1.6338286296	-0.1947006730

17

2tThy-NO_2 T_1^{ring} CASSCF/10,7/6-31G** ENERGY=-977.57979984

C	0.9772719499	-0.0196584208	0.7999161723

N	1.2113637873	-1.2951698469	0.3725618241
C	2.4214844581	-1.7493411323	-0.0131311423
C	3.6279666467	-1.0233754428	0.4664336558
C	3.4165911749	0.3944102532	0.7831945169
N	2.0877727875	0.7904957097	0.8291029163
C	4.8422657928	-1.7337276949	0.9705994853
O	4.2893943409	1.1685271819	1.0272328801
S	-0.5255410774	0.4941243297	1.2129996486
H	5.5654140056	-1.0108370729	1.3196436710
H	5.2787498569	-2.3408194303	0.1891517834
H	4.5753864240	-2.3946628365	1.7933911406
H	1.9403561542	1.7340089074	1.1159899187
H	0.4180113129	-1.8788867485	0.1994573905
N	2.4381649613	-2.7454093798	-0.9841033770
O	3.5054611491	-3.0605652194	-1.4368529884
O	1.3797372752	-3.2495031573	-1.2774624963

18

2tThy-CF_3 T_1^{pyr} CASSCF/10,7/6-31G** ENERGY=-1109.73602178

N	2.1237300403	0.7640522561	1.2514411658
C	0.9541522207	0.1414926739	0.7963778004
N	1.1683347488	-1.1584664550	0.3604083147
C	2.4216323570	-1.6686096658	0.1122483512
C	3.5577676495	-0.9995046963	0.4272656795
C	3.4079510227	0.3364854521	1.0563234494
S	-0.4899086823	0.2538896016	1.8967509371
C	2.4276650747	-3.0443952878	-0.5168756186
F	3.0721854356	-3.0518679322	-1.6668758685
C	4.9703689745	-1.4826659823	0.2338119010
O	4.3438013439	1.0033766661	1.3909438098
F	2.9970151355	-3.9373680222	0.2673540886
F	1.1928312778	-3.4622826087	-0.7577282455
H	5.4781477581	-1.5213509752	1.1901328674
H	5.5152904576	-0.7837883579	-0.3893144036
H	5.0163854804	-2.4597075248	-0.2217040138
H	2.0396125730	1.6732170236	1.6484580690
H	0.3802961320	-1.6357221653	-0.0101512838

18

2tThy-CF_3 T_1^{ring} CASSCF/10,7/6-31G** ENERGY=-1109.71394606

C	1.0447079970	-0.0745659516	0.9046045694
N	1.2923337955	-1.4139431194	0.7835792136
C	2.4597833553	-1.9464932262	0.2648218557
C	3.6551680014	-1.0641779640	0.4263348161
C	3.4165365793	0.3839200305	0.3788912291
N	2.0897928275	0.7433897815	0.5294163772
C	4.9422345890	-1.5989614267	0.9673977609
O	4.2701442235	1.2108444401	0.2698163717
S	-0.3865083591	0.5127192938	1.4392219798
H	4.8007175451	-1.9734705642	1.9796367051
H	5.6900017749	-0.8185969422	0.9829742201
H	5.3004175239	-2.4235558026	0.3619217604
H	1.9189180051	1.7240720618	0.5802915010
H	0.5101181714	-2.0107363832	0.9383524595
C	2.3042162954	-2.7784189510	-0.9706074706
F	3.3794622387	-3.5128002759	-1.1857400965
F	1.2653963066	-3.5895873126	-0.8549157695
F	2.1097091296	-2.0364516878	-2.0506624833

16

2tThy-OH T_1^{pyr} CASSCF/10,7/6-31G** ENERGY=-848.98986109

C	0.8548991550	0.0099105096	0.8768802964
N	1.1484369268	-1.0673077203	0.0459046755
C	2.4064214073	-1.5888551214	-0.0683684114
C	3.5001778394	-1.0204721469	0.4849614234
C	3.3005632481	0.2180234888	1.2523168162
N	2.0050276966	0.6656796345	1.3305744171
C	4.8935731453	-1.5751987810	0.3309634875
O	4.1890099888	0.8283012188	1.7801171067
S	-0.4365269206	1.0646072341	0.1461819443
H	5.5712849331	-0.9909533117	0.9360420223
H	5.2431034396	-1.5244376299	-0.6973549860
H	4.9608166413	-2.6080149811	0.6648940547
H	1.8828496636	1.4892961235	1.8757149487
H	0.3934645690	-1.6400975891	-0.2558303211
O	2.3938605412	-2.7119193805	-0.7999978125
H	3.2646047254	-3.0588905473	-0.9046286617

17

2tThy-NH_2 T_1^{pyr} CASSCF/10,7/6-31G** ENERGY=-829.16444825

C	0.9891652288	0.2529808245	0.2837977212
N	1.2309547799	-1.0783576327	-0.0362916671
C	2.4713921144	-1.6667468337	0.0224878683
C	3.5577328349	-1.0037563753	0.4914612056
C	3.3638710635	0.3640858726	0.9967530801
N	2.0901907644	0.8669457053	0.8888466781
C	4.9450093784	-1.5907517436	0.5439890037
O	4.2413602404	1.0361621078	1.4658979308
S	-0.5882654671	0.5004157796	1.1678622661
H	5.0676660856	-2.2741031478	1.3801327909
H	5.6641232338	-0.7939522923	0.6672424230
H	5.1891696095	-2.1261440064	-0.3690180476
H	1.9906065797	1.8145102385	1.1767429691
H	0.4469613598	-1.6644019277	-0.2029369822
N	2.4565129379	-2.9928805922	-0.4109442384
H	2.1021929461	-3.1013219954	-1.3387361270
H	3.3332213101	-3.4540609812	-0.3148678746

MECPs of the 2tThy analogues

17

2tThy-NO_2 T_1^{pyr}-MECP CASSCF/10,8/6-31G** ENERGY=-977.59514565

N	2.0546350183	0.8184183137	1.0689177237
C	0.9030026168	0.1795441233	0.5949181384
N	1.1948211206	-0.9772418515	-0.1178648265
C	2.4127365018	-1.6164603934	0.0003727219
C	3.5078834007	-1.0748151687	0.5677566259
C	3.3470776107	0.3205641659	1.0584773065
S	0.1329517693	0.0070737787	2.3026745669
N	2.3964434843	-2.9411739531	-0.6030112964
O	1.3188490406	-3.4662303995	-0.7472801047
C	4.8744804153	-1.6946581880	0.7271580183
O	4.2546961890	0.9975246152	1.4290600169
O	3.4449160062	-3.4331105112	-0.9318959961
H	5.4298647579	-1.1184092285	1.4521089221
H	5.4198007121	-1.6840108182	-0.2086936518
H	4.8087119981	-2.7203189538	1.0627127301
H	1.9828411175	1.7817577857	1.3210146083
H	0.4287042410	-1.5510503166	-0.3842735035

17

2tThy-NO_2 T_1^{ring}-MECP CASSCF/10,8/6-31G** ENERGY=-977.59514565

C	1.0753421760	-0.1982154994	0.9212569140
N	1.3410556880	-1.5463842830	0.7038880708
C	2.4914987192	-1.9276632693	0.0796876921
C	3.6869517158	-1.1464635564	0.4452472198
C	3.4641430133	0.3149803437	0.4774527721
N	2.1282737050	0.6505858079	0.6064794627
C	4.7602320141	-1.7517810857	1.2990881079
O	4.3192329411	1.1428195049	0.4597776479
S	-0.3680483980	0.3309386399	1.4593614605
H	5.5351701332	-1.0196718822	1.4806714310
H	5.1959855537	-2.6091067147	0.7994981816
H	4.3603655727	-2.0848658583	2.2546474863
H	1.9471178111	1.6240381749	0.7249858082
H	0.5422121596	-2.1410937522	0.6622116139
N	2.3510099811	-2.3908120390	-1.3428878466
O	3.3443682429	-2.3871012375	-1.9932258744
O	1.2749399710	-2.7805932940	-1.6700151486

18

2tThy-CF_3 T_1^{pyr}-MECP CASSCF/10,7/6-31G** ENERGY=-1109.67177470

N	2.1248797327	0.8457934973	1.1513303377
C	0.9304586008	0.2048116397	0.7982149610
N	1.1434045556	-1.0996361198	0.3221950682
C	2.4040837782	-1.6300008964	0.0854983373
C	3.5387156068	-0.9852117817	0.4353625244
C	3.3995744975	0.3784668093	1.0183245113
S	-0.1623265840	-0.3423083856	2.1949586434
C	2.3935154827	-3.0135565032	-0.5272866912
F	3.1586044787	-3.0757642600	-1.5983169185
C	4.9459026884	-1.5008016593	0.2935250890
O	4.3469437484	1.0351358900	1.3380394987
F	2.8157908320	-3.9272870684	0.3225210364
F	1.1686191335	-3.3553113753	-0.9002809418
H	5.4619764593	-1.3964648072	1.2392502348
H	5.4871830652	-0.9080805943	-0.4346930887
H	4.9795983224	-2.5361564666	-0.0083070285
H	2.0599820041	1.7690219375	1.5179819771
H	0.3803525976	-1.4958658561	-0.1794505506

18

2tThy-CF_3 T_1^{ring}-MECP CASSCF/10,7/6-31G** ENERGY=-1109.68073459

C	1.1810747625	-0.2103149021	0.9763086689
N	1.4945177950	-1.5549933026	0.9568202076
C	2.5535386518	-2.0179093946	0.1760330900
C	3.7488164322	-1.1514543039	0.2965626562
C	3.4576355496	0.2933207243	0.1320274862
N	2.1434536401	0.6137470469	0.4201156961
C	4.8654918191	-1.5382213566	1.2245312386
O	4.2557499398	1.1303476440	-0.1511497874
S	-0.2186979000	0.3610579024	1.5916848727
H	4.5249110840	-1.5625792263	2.2578268083
H	5.6703054038	-0.8192238314	1.1444249837
H	5.2436596548	-2.5216970459	0.9726339027
H	1.9237404054	1.5860586480	0.3996984468
H	0.7456224805	-2.1672351854	1.1926849859
C	2.2033758605	-2.6316658713	-1.1482437457
F	3.2279117132	-3.2957322474	-1.6434669456
F	1.1885422157	-3.4683216928	-1.0183436813

F	1.8535004921	-1.7119976052	-2.0348138840

16

2tThy-OH T_1^{pyr}-MECP CASSCF/10,7/6-31G** ENERGY=-848.92650349

N	2.0935264878	0.7956169346	1.2438510499
C	0.9343467054	0.2844800651	0.6454676043
N	1.1442195372	-0.9939280071	0.0916981445
C	2.4029294215	-1.5486234121	-0.0411680562
C	3.5130544554	-1.0003166660	0.4874353455
C	3.3647131423	0.2848456560	1.1948745819
S	-0.3881279393	-0.2897209036	1.8121113833
O	2.3377008646	-2.6925915781	-0.7378645226
C	4.8790851127	-1.6307764712	0.3885995828
O	4.2813861118	0.8710524282	1.6995412218
H	5.5739225245	-1.0581122830	0.9850657989
H	5.2510957350	-1.6397655360	-0.6329397147
H	4.8821934185	-2.6510980907	0.7638690197
H	2.0269399198	1.6806883966	1.6936147426
H	0.4703223486	-1.2993675874	-0.5766483537
H	3.1934631542	-3.0746079452	-0.8450178279

17

2tThy-NH_2 T_1^{pyr}-MECP CASSCF/10,7/6-31G** ENERGY=-829.09722724

N	2.1399287464	0.8763692462	1.0291311336
C	0.9822401484	0.2742360100	0.5120264571
N	1.1976559707	-1.0852803456	0.2280393103
C	2.4588772557	-1.6629103576	0.1276136219
C	3.5711995724	-0.9964155527	0.5132472207
C	3.4120485499	0.3720488572	1.0450413999
S	-0.3352316577	-0.0526855273	1.7823663950
N	2.4083779112	-2.9831043579	-0.3279695116
C	4.9612848983	-1.5758761941	0.4600683576
O	4.3288935929	1.0329094594	1.4495418109
H	5.1555272750	-2.2378675168	1.2995562079
H	5.6839892874	-0.7742185935	0.5038558468
H	5.1278530864	-2.1328781537	-0.4569092736
H	2.0697584382	1.8183975242	1.3412088441
H	0.4519181761	-1.5572497148	-0.2322904735
H	2.0453409283	-3.0704341727	-1.2554379543
H	3.2804138204	-3.4579466102	-0.2565183928

Below is the complete information of Reference 34 from the main paper

(34) Werner, H. J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; Celani, F.; Korona, T.; Lindh, R.; Mitrushenkov, A.; Rauhut, G.; R. Shamasundar, K. R.; B. Adler, T. B.; D. Amos, R. D.; Bernhardsson, A.; Berning, A.; L. Cooper, D. L.; J. O. Deegan, M. J. O.; J. Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hesselmann, A.; Hetzer, G.; Hrenar, T.; Jansen, G.; Koppl, C.; Liu, Y.; W. Lloyd, A. W.; A. Mata, R. A.; J. May, A. J.; J. McNicholas, S. J.; Meyer, W.; E. Mura, M. E.; Nicklass, A.; P. O'Neill, D. P.; Palmieri, P.; Peng, D.; Pflüger, K.; Pitzer, R.; Reiher, M.; Shiozaki, T.; Stoll, H.; J. Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M., MOLPRO, version 2012.1, a package of ab initio programs. 2012.