Electronic Supporting Information

Mechanism of Enhanced Triplet Decay of Thionucleobase by Glycosylation and Rate-Modulating Strategies

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S1. Cartesian coordinates of optimized structures of 2tThy

Table S1. 2tThy optimized structures using CASPT2(10,7)/ano-rcc-vdzp calculation (xyz, Angstrom).

S_0

C -3.12550356 -0.46186309 0.37553996
C -1.03943832 0.67382799 -0.40210936
C -1.77989506 1.93559207 -0.44861375
C -3.09118222 1.91826372 -0.11515271
H -3.70622335 2.81104870 -0.12087438
O 0.14757042 0.54267847 -0.68297642
C -1.03382223 3.16407101 -0.86622807
H -0.19156694 3.34632652 -0.19140520
H -0.61492577 3.03251070 -1.86883375
H -1.68695545 4.04016370 -0.86532250
S -3.91230250 -1.83351319 0.90791225
N -3.74462879 0.76230469 0.26234386
H -4.71826023 0.77961252 0.53149026
N -1.80221372 -0.43249691 0.00956356
H -1.30496327 -1.31547491 0.07293525

T_1 op-S

C -3.19942123 -0.52989058 0.09260824
C -1.04618366 0.64893405 -0.43977648
C -1.78413405 1.91323767 -0.45743157
C -3.11143518 1.89341963 -0.14197073
H -3.71446216 2.79496055 -0.11695721
O 0.15654640 0.54518555 -0.68710621
C -1.02902811 3.15969566 -0.79673049
H -0.20294872 3.31253246 -0.09453268
H -0.58440219 3.08053439 -1.79349072
H -1.68208369 4.03598013 -0.77158641
S -3.76051949 -1.59317445 1.45668716
N -3.77295784 0.74193051 0.16821982
H -4.76041882 0.76776428 0.37353857
N -1.80706536 -0.46395024 -0.09345853
H -1.30579692 -1.34410760 -0.09974378

ISC crossing point

C -3.17388889 -0.66146413 0.10628046
C -1.06239735 0.59464090 -0.47336412
C -1.81471028 1.87316856 -0.41005838
C -3.13446312 1.82364310 -0.18791552
H -3.76275811 2.71245919 -0.18173767
O 0.14650608 0.54816571 -0.69947123
C -1.04826720 3.13113194 -0.66543759
H -0.22024300 3.23139382 0.04379571
H -0.60280517 3.10543112 -1.66537436
H -1.69620126 4.00832592 -0.58847132
S -3.45643919 -0.73377483 1.93785313
N -3.81539103 0.64206885 0.00448513
H -4.82189748 0.64179535 0.09638702
N -1.83463301 -0.54595409 -0.33895467
H -1.30677742 -1.40791953 -0.37972507

Table S2. 2tThy optimized structures using X3LYP/6-311++G(d,p) calculation (xyz, Angstrom).

S_0

C	-3.122357	-0.452449	0.366808
C	-1.038942	0.671058	-0.385205
C	-1.768785	1.930579	-0.442828
C	-3.077429	1.914122	-0.104280
C	-1.039067	3.166774	-0.869931
N	-3.723964	0.763272	0.284917
N	-1.802677	-0.435565	0.025447
O	0.143186	0.519548	-0.658845
S	-3.932030	-1.845251	0.844639
H	-4.703950	0.800628	0.528678
H	-1.311022	-1.320298	0.071203
H	-3.697491	2.800715	-0.117597
H	-0.198772	3.372217	-0.201499
H	-0.627205	3.046768	-1.875447
H	-1.703807	4.030931	-0.867794

ISC crossing point

C	-3.16132052	-0.63657651	0.16541147
C	-1.06618863	0.58056225	-0.48895099
C	-1.80189405	1.86107578	-0.41387553
C	-3.13801870	1.82363169	-0.18484714
C	-1.04850136	3.13167562	-0.65852803
N	-3.81135185	0.65331992	0.05888000
N	-1.82213011	-0.55517017	-0.30869842
O	0.13114256	0.51572002	-0.76054345
S	-3.44463741	-0.73287508	1.95634635
H	-4.82240887	0.65971063	0.02134902
H	-1.32938751	-1.42940991	-0.42551949
H	-3.75602728	2.71406353	-0.19711462
H	-0.24429668	3.25489314	0.07298160
H	-0.57946234	3.12589902	-1.64610023
H	-1.70980725	3.99655006	-0.59253052

T_1 op-S

C	-3.185483	-0.533815	0.141138
C	-1.046647	0.626634	-0.452382
C	-1.777093	1.901793	-0.456600
C	-3.114724	1.884472	-0.145557
C	-1.037534	3.157938	-0.779465
N	-3.772419	0.745827	0.140600
N	-1.795578	-0.480427	-0.124112
O	0.152155	0.528822	-0.714720
S	-3.745528	-1.520695	1.509043
H	-4.764018	0.783007	0.334876
H	-1.303272	-1.363965	-0.136341
H	-3.710251	2.788451	-0.124302
H	-0.226334	3.328901	-0.064499
H	-0.574086	3.094861	-1.768619
H	-1.703501	4.021248	-0.760792

T_1 $B_{3,6}$

C	-3.184068	-0.461985	0.362860
C	-1.022683	0.749812	0.242043
C	-1.729712	1.928450	-0.134805
C	-3.215010	1.923262	-0.052511
C	-1.036467	3.140496	-0.613924
N	-3.808830	0.689175	0.015395
N	-1.838985	-0.350006	0.623710
O	0.204427	0.613248	0.271711
S	-4.014906	-1.916528	0.500571
H	-4.804837	0.608844	-0.150222
H	-1.347614	-1.208366	0.833135
H	-3.818440	2.739343	-0.416245
H	0.043741	3.009148	-0.613491
H	-1.370258	3.397640	-1.628669
H	-1.299710	4.002892	0.013821

S2. Cartesian coordinates of optimized structures of 2tThd

Table S3. 2tThd optimized structures using X3LYP/6-311++G(d,p) calculation (xyz, Angstrom).

1. anti conformers

S_0				anti-up: T_1 minimum				anti-up: ISC crossing point			
C	-5.715338	2.253814	1.112188	C	-5.781680	2.293934	1.175353	C	-5.86761904	2.26447985	1.13831607
C	-4.819395	2.587775	-0.080914	C	-4.833632	2.552340	0.004281	C	-4.85248650	2.49924309	0.01936721
O	-5.220163	3.880793	-0.509085	O	-5.198489	3.833362	-0.500196	O	-5.17465797	3.77618608	-0.52667357
C	-6.581786	4.137576	-0.097172	C	-6.569279	4.130614	-0.154570	C	-6.53574681	4.13514252	-0.19261383
C	-7.035979	2.902223	0.709406	C	-7.074438	2.942501	0.692274	C	-7.11603660	2.94275226	0.59146846
N	-3.374148	2.635558	0.227400	N	-3.397834	2.587766	0.335657	N	-3.43816326	2.50405017	0.43325999
C	-2.545539	1.616028	-0.160873	C	-2.530354	1.677043	-0.318178	C	-2.53647845	1.58000133	-0.22511953
N	-1.236903	1.791055	0.192188	N	-1.169686	2.028443	-0.201015	N	-1.22588532	2.10326139	-0.33742111
C	-0.659793	2.849512	0.904005	C	-0.618605	3.009676	0.585595	C	-0.67190109	3.08171591	0.45019872
C	-1.602202	3.883206	1.297032	C	-1.592960	3.818765	1.332228	C	-1.62366308	3.80872560	1.32112561
C	-2.894025	3.720568	0.939913	C	-2.921864	3.575040	1.140268	C	-2.94148637	3.51955508	1.23203741
S	-3.023082	0.227987	-0.988514	S	-2.991782	-0.017616	0.010714	S	-2.86419956	0.24131258	0.94537720
O	0.540568	2.841635	1.141533	O	0.597698	3.191112	0.631727	O	0.52129766	3.36892710	0.38150713
C	-1.103275	5.069969	2.063277	C	-1.091646	4.892594	2.241580	C	-1.07853742	4.86996473	2.22615482
C	-6.610762	5.445471	0.682193	C	-6.603637	5.475103	0.559529	C	-6.52510811	5.44425384	0.58660708
O	-7.981987	5.802129	0.846626	O	-7.973365	5.862011	0.657426	O	-7.88461204	5.85535833	0.72567216
O	-7.747161	1.962985	-0.100094	O	-7.769871	1.975892	-0.099270	O	-7.76926277	2.00336685	-0.26699142
H	-3.644433	4.460192	1.176475	H	-3.671725	4.199104	1.607794	H	-3.68287030	4.09682519	1.77107740
H	-0.642791	4.758325	3.004554	H	-0.488418	4.467891	3.050213	H	-0.45263331	4.42662552	3.00771998
H	-0.338922	5.605697	1.494038	H	-0.444688	5.588803	1.700424	H	-0.44566326	5.56606089	1.67117213
H	-1.917434	5.759888	2.286622	H	-1.917623	5.450385	2.683721	H	-1.88267921	5.42780060	2.70737488
H	-0.605969	1.047762	-0.083876	H	-0.511111	1.442306	-0.697825	H	-0.58702723	1.61319426	-0.94981174
H	-7.198557	4.245956	-0.993942	H	-7.151081	4.205043	-1.078128	H	-7.09020393	4.28266524	-1.12390755
H	-5.324863	2.713840	2.022674	H	-5.421972	2.787164	2.080223	H	-5.54101035	2.74528440	2.06213216
H	-8.592366	2.349296	-0.356075	H	-8.599533	2.360993	-0.403261	H	-8.55989905	2.41449117	-0.63419952
H	-7.640774	3.195531	1.570313	H	-7.707537	3.285347	1.513607	H	-7.79633463	3.27910073	1.37669885
H	-4.926873	1.862781	-0.884781	H	-4.936712	1.792446	-0.768887	H	-4.91644485	1.73099464	-0.75256270
H	-6.068042	6.207705	0.113457	H	-6.027648	6.199798	-0.025220	H	-5.94174642	6.18444801	0.02913759
H	-6.118921	5.323526	1.654888	H	-6.148111	5.393476	1.553734	H	-6.05609075	5.30295720	1.56770041
H	-8.032919	6.599862	1.382859	H	-8.027862	6.687065	1.150192	H	-7.91624750	6.64591224	1.27370965
H	-5.816788	1.182186	1.277120	H	-5.905177	1.232428	1.383446	H	-6.02725246	1.20619320	1.33493605

anti-$B_{3,6}$ T_1 minimum				anti-down: T_1 minimum				anti-down: ISC crossing point			
C	3.663461	0.214246	1.317522	C	-5.677470	2.273899	0.844254	C	-5.64517891	2.29310326	0.88619785
C	5.685176	1.557499	0.780818	C	-4.842062	2.746502	-0.351374	C	-4.86723254	2.69808081	-0.37148582
C	4.833205	2.588409	0.301635	O	-5.326200	4.040029	-0.663582	O	-5.39862184	3.95658717	-0.75589520
C	3.386458	2.496887	0.626750	C	-6.688011	4.183974	-0.198282	C	-6.72248172	4.13066528	-0.20579221
C	5.327351	3.721982	-0.505364	C	-7.044834	2.865444	0.521303	C	-7.03564589	2.83845985	0.57326219
N	2.872196	1.237966	0.868549	N	-3.397685	2.825348	-0.095970	N	-3.41651009	2.83589241	-0.19227399
N	5.002055	0.515096	1.458372	C	-2.617279	1.707754	-0.488775	C	-2.58096103	1.73978541	-0.63820621
O	6.914370	1.499090	0.671147	N	-1.326120	1.715258	0.084274	N	-1.43198652	1.60030929	0.17884347
S	3.109040	-1.313431	1.752385	C	-0.729666	2.714738	0.819452	C	-0.83002278	2.59815391	0.91001325
H	5.583110	-0.253925	1.765165	C	-1.593619	3.863277	1.099116	C	-1.63628019	3.82843853	1.07955439
H	2.694947	3.217868	0.224450								

H	6.403542	3.663446	-0.657659	C	-2.886547	3.833169	0.647224	C	-2.89513294	3.85448024	0.58213246
H	4.824359	3.746642	-1.481662	S	-2.662931	1.311065	-2.229446	S	-2.40538346	2.38099382	-2.32408480
H	5.080167	4.674654	-0.017416	O	0.432417	2.611004	1.213517	O	0.26882189	2.44014158	1.43717164
C	0.607906	1.701809	1.892241	C	-1.042441	5.007000	1.886477	C	-1.03819802	4.98448829	1.82037221
C	1.405901	1.049250	0.760483	C	-6.770982	5.425121	0.680004	C	-6.73623313	5.39350619	0.64551995
O	0.961865	1.672457	-0.433071	O	-8.156418	5.684833	0.900769	O	-8.10303244	5.70467300	0.91068089
C	-0.349624	2.247526	-0.236795	O	-7.718893	1.946982	-0.341951	O	-7.70266830	1.87223582	-0.24190543
C	-0.740431	1.951958	1.225771	H	-3.576588	4.637128	0.866233	H	-3.56840252	4.68455193	0.75695520
C	-0.287654	3.729569	-0.583758	H	-0.671898	4.668376	2.858491	H	-0.67059712	4.68254972	2.80360963
O	-1.632699	4.201961	-0.639181	H	-0.192000	5.462289	1.368924	H	-0.18183559	5.39115265	1.27189531
O	-1.509107	0.752621	1.345660	H	-1.799550	5.774770	2.048395	H	-1.76924311	5.78422796	1.94676325
H	-1.045833	1.753419	-0.920432	H	-0.739424	0.920019	-0.134219	H	-0.89763296	0.74985586	0.06797840
H	1.072835	2.644606	2.186243	H	-7.336044	4.322921	-1.068534	H	-7.42605180	4.25533047	-1.03419785
H	-2.372737	0.894246	0.941769	H	-5.283867	2.701120	1.768695	H	-5.23161726	2.78331891	1.77000504
H	-1.278821	2.793910	1.666671	H	-8.591216	2.299555	-0.551260	H	-8.56537300	2.22192270	-0.49254958
H	1.243860	-0.024831	0.716540	H	-7.643011	3.054660	1.415555	H	-7.62082008	3.04797931	1.47182809
H	0.213071	3.844490	-1.550755	H	-4.951884	2.075156	-1.205496	H	-4.99423552	1.96480485	-1.16847670
H	0.288038	4.278102	0.171585	H	-6.289306	6.259205	0.159059	H	-6.24542263	6.19924518	0.08965049
H	-1.621434	5.150192	-0.804267	H	-6.247357	5.260819	1.629239	H	-6.18392772	5.23123092	1.57863144
H	0.520686	1.061977	2.769047	H	-8.239762	6.430540	1.503555	H	-8.13851868	6.44884869	1.52009718
				H	-5.707959	1.189789	0.939374	H	-5.64818396	1.21671628	1.04870518

2. syn conformers

S_0				syn-up							
				T_1 minimum				ISC crossing point			
C	-5.559840	3.341332	1.520364	C	-5.537762	3.437925	1.505720	C	-5.48179095	3.40801369	1.42345563
C	-6.709736	4.088325	2.195520	C	-6.728012	4.150735	2.146439	C	-6.59655824	4.20557384	2.08904789
O	-7.702331	3.124619	2.482442	O	-7.607454	3.086902	2.548960	O	-7.50843941	3.17485856	2.59804848
C	-7.517072	1.963925	1.632169	C	-7.434299	1.955858	1.660263	C	-7.43269862	2.00805169	1.72622384
C	-6.328081	2.298347	0.710049	C	-6.190279	2.261461	0.789534	C	-6.21409132	2.23134548	0.79199874
N	-6.395020	4.887435	3.406593	N	-6.422763	4.971167	3.300369	N	-6.20732215	5.04729612	3.18219907
C	-5.920434	4.356780	4.581079	C	-5.804210	4.379499	4.410081	C	-5.64897571	4.39745932	4.30643984
N	-5.680218	5.280804	5.561461	N	-5.215848	5.296540	5.285332	N	-5.20981738	5.29769363	5.28491010
C	-5.852956	6.667781	5.527752	C	-5.518260	6.652874	5.370870	C	-5.56941882	6.63368528	5.40843694
C	-6.377629	7.160372	4.267673	C	-6.387214	7.156350	4.313633	C	-6.39198611	7.16023620	4.32238380
C	-6.619531	6.255393	3.296901	C	-6.745113	6.305498	3.319134	C	-6.65313093	6.35009292	3.27054659
S	-5.622179	2.732795	4.910627	S	-6.682335	3.044747	5.271867	S	-6.93146000	3.15825833	5.01157252
O	-5.574327	7.343809	6.508697	O	-5.019281	7.340199	6.260745	O	-5.15885175	7.30141746	6.35813495
C	-6.632396	8.627552	4.105552	C	-6.769662	8.608103	4.319289	C	-6.82937255	8.59602357	4.38289983
C	-7.265606	0.718740	2.487089	C	-7.323475	0.688922	2.494023	C	-7.34976176	0.72155519	2.53341996
O	-8.148228	0.647238	3.598079	O	-8.489359	0.460145	3.279335	O	-8.53447236	0.44897076	3.27255000
O	-6.742116	2.920187	-0.509381	O	-6.552474	2.696418	-0.523616	O	-6.61535045	2.61361014	-0.52516020
H	-7.015072	6.565714	2.339963	H	-7.296724	6.655410	2.454107	H	-7.19433725	6.71029785	2.40282794
H	-7.340968	8.982675	4.858393	H	-7.357047	8.861675	5.206626	H	-7.40790075	8.79300557	5.28910582
H	-5.709165	9.197672	4.238944	H	-5.884425	9.250287	4.327467	H	-5.97081005	9.27481557	4.39724241
H	-7.036320	8.846718	3.116927	H	-7.364546	8.853976	3.438125	H	-7.45152004	8.84914520	3.52305153
H	-5.328446	4.900244	6.432559	H	-4.596085	4.939710	6.002066	H	-4.62082652	4.93995483	6.02547876
H	-8.438562	1.842448	1.056819	H	-8.324344	1.894699	1.025871	H	-8.35307300	2.00126469	1.13454777
H	-4.922951	2.859505	2.259377	H	-4.861789	3.088605	2.288695	H	-4.77906688	3.06421856	2.18415535
H	-7.226507	2.277439	-1.039724	H	-6.937362	1.955818	-1.005644	H	-7.02114990	1.85714001	-0.96367464
H	-5.724933	1.411599	0.495831	H	-5.524792	1.396252	0.725453	H	-5.58465297	1.33871443	0.74283127

H	-7.118680	4.821232	1.498426
H	-6.225766	0.696213	2.828063
H	-7.445158	-0.168261	1.875766
H	-7.919440	1.392900	4.170844
H	-4.960571	3.990202	0.882748

H	-7.243249	4.791952	1.427434
H	-6.431046	0.737195	3.130050
H	-7.228301	-0.169855	1.826892
H	-8.596717	1.206063	3.881486
H	-4.986012	4.076605	0.816995

H	-7.14532581	4.81244721	1.36719458
H	-6.47411033	0.74429349	3.19013930
H	-7.23297669	-0.10545615	1.82985071
H	-8.54740022	1.00496186	4.05912863
H	-4.94359131	3.99278416	0.67862243

syn-down

T_1 minimum			
C	-1.869690	1.225514	-1.609645
C	-0.907310	1.236616	-0.425841
O	-1.524517	0.395182	0.562546
C	-2.945933	0.289752	0.312246
C	-3.228442	1.175509	-0.915981
N	0.449771	0.764478	-0.664934
C	0.702486	-0.272746	-1.581928
N	1.880688	-0.986260	-1.313455
C	2.926470	-0.595699	-0.475536
C	2.651770	0.590297	0.317319
C	1.418262	1.154742	0.220050
S	0.656654	0.049437	-3.365652
O	3.951884	-1.270948	-0.420497
C	3.701049	1.089133	1.265679
C	-3.292398	-1.179966	0.107430
O	-2.855135	-1.974079	1.206422
O	-3.575563	2.512268	-0.549205
H	1.130657	1.970694	0.873467
H	3.995883	0.308817	1.972962
H	4.605514	1.392290	0.729955
H	3.336197	1.947718	1.831316
H	2.044098	-1.828330	-1.852792
H	-3.468983	0.671753	1.193725
H	-1.742029	0.321030	-2.206517
H	-4.444045	2.507339	-0.131299
H	-4.003097	0.745983	-1.557137
H	-0.811851	2.245772	-0.018381
H	-2.850578	-1.545909	-0.827795
H	-4.376065	-1.297413	0.046060
H	-1.909155	-1.814513	1.313249
H	-1.767283	2.097877	-2.252814

ISC crossing point			
C	-1.87256455	1.21865052	-1.58450359
C	-0.93068570	1.22662811	-0.38343915
O	-1.57199543	0.38617065	0.59558870
C	-2.98565585	0.27881677	0.31288471
C	-3.24329417	1.16683804	-0.91938764
N	0.41498626	0.74881489	-0.62507527
C	0.64140957	-0.26590449	-1.59128316
N	1.84530343	-1.00391391	-1.33854517
C	2.90674394	-0.60090566	-0.50257442
C	2.65666661	0.59910658	0.27198088
C	1.41737236	1.15455299	0.21478336
S	1.17013295	0.25532924	-3.25746560
O	3.90604301	-1.30792266	-0.42792681
C	3.73046314	1.10620137	1.19352733
C	-3.31885542	-1.19269164	0.09767400
O	-2.87229553	-1.98596715	1.19412399
O	-3.59339308	2.50430668	-0.55352300
H	1.15295560	1.97476285	0.87500584
H	4.03914858	0.33715236	1.90682200
H	4.62208745	1.40667651	0.63655080
H	3.37435042	1.97098631	1.75560349
H	1.91811193	-1.94177294	-1.71691575
H	-3.53187405	0.65522967	1.18278577
H	-1.71865026	0.31641099	-2.17843949
H	-4.46110005	2.49872599	-0.13437102
H	-4.00984348	0.74087952	-1.57289042
H	-0.83878545	2.23355941	0.03099121
H	-2.86954775	-1.54716362	-0.83853246
H	-4.40085886	-1.32322526	0.03371688
H	-1.93847012	-1.77899734	1.32757531
H	-1.75859537	2.09499536	-2.22171142

S3. Cartesian coordinates of optimized structures of 2tThr

Table S4. 2tThr optimized structures using X3LYP/6-311++G(d,p) calculation (xyz, Angstrom).

1. anti conformers

S_0				anti-up: T_1 minimum				anti-up: ISC crossing point			
C	-5.647452	2.371209	1.281683	C	-5.876675	2.270730	1.097526	C	-5.91929899	2.26989889	1.11942308
C	-4.789738	2.632142	0.027926	C	-4.867679	2.573809	-0.032813	C	-4.87539912	2.50866480	0.01056314
O	-5.188088	3.918116	-0.413645	O	-5.201982	3.873103	-0.477049	O	-5.15843035	3.80034422	-0.49277437
C	-6.593295	4.105111	-0.115986	C	-6.572569	4.197199	-0.124290	C	-6.52655607	4.17360578	-0.18330353
C	-6.999150	2.967027	0.842434	C	-7.144758	2.940867	0.552493	C	-7.15234412	2.96292949	0.53256909
N	-3.341334	2.654893	0.255164	N	-3.445035	2.587051	0.368756	N	-3.47425922	2.47725835	0.46058223
C	-2.515543	1.735913	-0.345878	C	-2.596434	1.547948	-0.104133	C	-2.57574174	1.52140143	-0.15524837
N	-1.194593	1.885015	-0.031032	N	-1.228355	1.886379	-0.045349	N	-1.27221811	2.04557181	-0.31072426
C	-0.594138	2.844699	0.793070	C	-0.656623	2.926988	0.641854	C	-0.71311044	3.05503232	0.43429494
C	-1.525364	3.801058	1.368134	C	-1.618221	3.844435	1.277962	C	-1.65408783	3.78543369	1.31886923
C	-2.832759	3.655127	1.069311	C	-2.955290	3.639216	1.069700	C	-2.97318712	3.50397354	1.24603305
S	-3.001047	0.504395	-1.386535	S	-3.089216	-0.047968	0.499925	S	-2.88499399	0.23535466	1.08053004
O	0.616177	2.826127	0.967459	O	0.561879	3.082692	0.689665	O	0.46811110	3.36947577	0.31920567
C	-0.996756	4.891908	2.247864	C	-1.096692	4.989964	2.077989	C	-1.10717307	4.85505733	2.20923258
C	-6.768590	5.507713	0.445604	C	-6.576297	5.454885	0.736034	C	-6.51292661	5.46795282	0.61984475
O	-8.171926	5.753314	0.513016	O	-7.932844	5.882973	0.831829	O	-7.86739640	5.90201264	0.72109962
O	-7.693775	1.914331	0.172455	O	-7.747576	2.061352	-0.387985	O	-7.77162798	2.06995053	-0.38485792
O	-5.711310	1.024932	1.675647	O	-6.065997	0.916030	1.399733	O	-6.15309425	0.92086994	1.42720384
H	-3.575810	4.344556	1.443022	H	-3.688200	4.348670	1.428488	H	-3.70932011	4.08853397	1.78315322
H	-0.475267	4.473172	3.112628	H	-0.530237	4.630773	2.943301	H	-0.45331055	4.42347143	2.97378606
H	-0.275987	5.510883	1.706962	H	-0.405854	5.593167	1.482084	H	-0.50491418	5.56480182	1.63873662
H	-1.804732	5.530775	2.605026	H	-1.907721	5.625629	2.433481	H	-1.91185893	5.39351445	2.71097393
H	-0.566105	1.212528	-0.454767	H	-0.583730	1.222123	-0.455213	H	-0.65440108	1.56850982	-0.95255970
H	-7.167245	4.012602	-1.042526	H	-7.116857	4.403074	-1.049088	H	-7.04895599	4.35250972	-1.12654242
H	-5.248843	2.941534	2.123240	H	-5.557831	2.826002	1.989754	H	-5.61113025	2.82442920	2.01532103
H	-8.642256	2.074173	0.210260	H	-8.577482	2.452081	-0.682980	H	-8.57817190	2.48178374	-0.71356080
H	-7.584616	3.334227	1.685821	H	-7.844200	3.197265	1.351684	H	-7.85573624	3.27407629	1.30796838
H	-4.968853	1.866514	-0.726908	H	-4.944558	1.838652	-0.835305	H	-4.95443998	1.74236816	-0.76461133
H	-6.271887	6.220000	-0.221381	H	-5.953027	6.213410	0.251111	H	-5.89903635	6.20269802	0.08857934
H	-6.308651	5.583386	1.437603	H	-6.160937	5.249540	1.729719	H	-6.07803215	5.30805153	1.61323925
H	-8.316709	6.605624	0.936197	H	-7.976457	6.647750	1.414778	H	-7.90043716	6.69540229	1.26503664
H	-6.425006	0.617845	1.161583	H	-5.223195	0.445063	1.269789	H	-5.29718084	0.47592158	1.53138698
				anti-down: T_1 minimum				anti-down: ISC crossing point			
				C	-5.631879	2.323728	0.913773	C	-5.65376569	2.28820706	0.88505585
				C	-6.046709	2.741521	-0.519711	C	-6.12875789	2.69514487	-0.53253864
				O	-6.416291	4.098888	-0.404502	O	-6.55569951	4.03680420	-0.40940320
				C	-6.926171	4.358943	0.927998	C	-6.92104956	4.32989498	0.96222146
				C	-6.674248	3.084392	1.751807	C	-6.68264689	3.03560727	1.75199805
				N	-4.993619	2.618298	-1.524519	N	-5.10679735	2.63375943	-1.57855612
				C	-5.051315	1.499829	-2.396636	C	-5.08599672	1.46654537	-2.44355611
				N	-3.842426	1.291737	-3.095484	N	-3.76272768	1.15596750	-2.85445557
				C	-2.734473	2.106841	-3.136844	C	-2.70383947	2.01691555	-2.92043132
				C	-2.815854	3.291603	-2.277931	C	-2.91300026	3.33011229	-2.26189942
				C	-3.931012	3.460370	-1.504200	C	-4.06675363	3.54708354	-1.59460473

	S	-6.536409	1.394665	-3.385699	S	-6.25269951	2.16749486	-3.64327029
	O	-1.760116	1.827162	-3.835347	O	-1.63361470	1.69502533	-3.43428596
	C	-1.671684	4.251937	-2.262187	C	-1.81443509	4.34343533	-2.32786887
	C	-6.235430	5.605681	1.461826	C	-6.11059509	5.53059036	1.43520662
	O	-6.917141	5.975325	2.658519	O	-6.68295478	5.96020700	2.66871185
	O	-7.821307	2.235809	1.810131	O	-7.84072446	2.19983984	1.77500120
	H	-4.020843	4.298429	-0.825794	H	-4.25424969	4.45365327	-1.03556846
	H	-0.740927	3.743512	-1.994343	H	-0.86875106	3.91531584	-1.98929591
	H	-1.516075	4.688703	-3.253834	H	-1.65775907	4.68437519	-3.35655783
	H	-1.846579	5.060617	-1.552023	H	-2.04891130	5.21226225	-1.71215565
	H	-3.813459	0.480104	-3.699464	H	-3.62570959	0.24843230	-3.28031425
	H	-8.001668	4.543161	0.860827	H	-7.98224155	4.58893301	0.98642442
	H	-4.632038	2.710774	1.121172	H	-4.65192553	2.68196699	1.06979231
	H	-8.358112	2.465417	2.575705	H	-8.42801704	2.47581100	2.48896668
	H	-6.314348	3.312408	2.755808	H	-6.32460249	3.22514594	2.76464658
	H	-6.875062	2.120227	-0.869945	H	-6.93790630	2.03659980	-0.85983908
	H	-6.301110	6.395362	0.706250	H	-6.17533439	6.31374641	0.67258926
	H	-5.176197	5.402837	1.659562	H	-5.05601805	5.26219639	1.56661009
	H	-6.459458	6.722171	3.057572	H	-6.14867030	6.67784851	3.02408164
	O	-5.613071	0.940282	1.138735	O	-5.60730702	0.90181832	1.10131023
	H	-6.518460	0.682982	1.370315	H	-6.51002819	0.62296007	1.31351496

2. syn conformers

S_0				**syn-up**						
				T_1 minimum				**ISC crossing point**		
C	-5.563722	3.328593	1.513961	C	-5.521606	3.397690	1.530915	C	-5.47109054	3.40356171	1.42365958
C	-6.713920	4.076032	2.195415	C	-6.708356	4.132707	2.159598	C	-6.59241019	4.20570596	2.08542428
O	-7.693362	3.112257	2.491247	O	-7.583274	3.078996	2.570676	O	-7.49488063	3.18109737	2.59239944
C	-7.514490	1.951361	1.629292	C	-7.446696	1.957320	1.653650	C	-7.42565950	2.00642984	1.72199064
C	-6.359658	2.304194	0.675441	C	-6.216137	2.255229	0.764308	C	-6.22164974	2.22594470	0.77254457
N	-6.389199	4.883012	3.391673	N	-6.392457	4.966184	3.294006	N	-6.19927090	5.04777810	3.16890400
C	-5.909426	4.357862	4.567449	C	-5.743881	4.393857	4.397452	C	-5.64713304	4.39407275	4.29866742
N	-5.677363	5.284384	5.545729	N	-5.164829	5.327913	5.259403	N	-5.19771087	5.29490633	5.27433389
C	-5.859412	6.671039	5.508240	C	-5.494190	6.677782	5.341092	C	-5.56819977	6.62529212	5.40554143
C	-6.378613	7.158524	4.243784	C	-6.390868	7.157179	4.294595	C	-6.39338909	7.15334159	4.31975684
C	-6.614919	6.250633	3.274736	C	-6.745871	6.294743	3.310743	C	-6.64898595	6.34933882	3.26277581
S	-5.596204	2.735869	4.892428	S	-6.580945	3.034986	5.266474	S	-6.94064833	3.17665224	5.01335184
O	-5.590787	7.349522	6.489781	O	-4.996575	7.381652	6.218067	O	-5.16477693	7.29049166	6.35984872
C	-6.636110	8.624559	4.075463	C	-6.805029	8.600007	4.300735	C	-6.83546928	8.58787568	4.38165075
C	-7.238628	0.705933	2.476629	C	-7.353782	0.673437	2.462507	C	-7.34643642	0.72616245	2.53818864
O	-8.099702	0.630411	3.603110	O	-8.511052	0.461519	3.263890	O	-8.53003225	0.46717834	3.28318036
O	-6.808654	2.954906	-0.506843	O	-6.588111	2.732287	-0.522307	O	-6.63879985	2.60300216	-0.53154673
H	-7.007733	6.555993	2.315281	H	-7.320257	6.626833	2.453795	H	-7.18819921	6.71174402	2.39508190
H	-7.356684	8.978394	4.817452	H	-7.376521	8.845706	5.200488	H	-7.41821706	8.78618673	5.28538000
H	-5.716858	9.198109	4.220683	H	-5.934072	9.261231	4.284550	H	-5.97698628	9.26578649	4.39897550
H	-7.026918	8.840384	3.080836	H	-7.425926	8.826868	3.432545	H	-7.45183358	8.83959200	3.51677027
H	-5.325122	4.908752	6.418864	H	-4.526046	4.989075	5.968003	H	-4.60968204	4.93080416	6.01244205
H	-8.448713	1.825878	1.077317	H	-8.347569	1.930473	1.033485	H	-8.35180834	2.00093633	1.13964235
H	-4.974314	2.792489	2.258497	H	-4.923754	2.962535	2.338998	H	-4.82209762	3.00711868	2.21117301
H	-7.279178	2.313687	-1.050648	H	-6.936709	1.994429	-1.034396	H	-7.02242024	1.83079394	-0.96167655
H	-5.755733	1.426187	0.427642	H	-5.564118	1.381892	0.671551	H	-5.58597533	1.33722222	0.72262591
H	-7.100938	4.801861	1.476377	H	-7.192200	4.766373	1.411256	H	-7.11454321	4.81052950	1.34066210

H	-6.192319	0.682868	2.797305	H	-6.448537	0.682880	3.081278	H	-6.46733113	0.74002480	3.19073718
H	-7.427585	-0.179150	1.865494	H	-7.294355	-0.173202	1.776141	H	-7.23863049	-0.10296938	1.83637881
H	-7.857425	1.371073	4.177237	H	-8.583446	1.192984	3.888490	H	-8.53716160	1.02745034	4.06676456
O	-4.773599	4.250213	0.797354	O	-4.759928	4.301298	0.766681	O	-4.76160492	4.25067252	0.55069678
H	-3.916822	3.852699	0.610195	H	-3.927014	3.885668	0.518751	H	-3.94107563	3.82380582	0.28109464
				syn-down							
				T_1 minimum				**ISC crossing point**			
				C	-5.367589	3.263992	1.210521	C	-5.40741223	3.33436171	1.33021028
				C	-6.392256	4.180250	1.886846	C	-6.50435750	4.10447321	2.07211983
				O	-7.437778	3.320056	2.329274	O	-7.36181756	3.08383764	2.57849231
				C	-7.356893	2.030572	1.665120	C	-7.35221375	1.95236984	1.67324911
				C	-6.269893	2.179114	0.589998	C	-6.18682020	2.17509893	0.67929995
				N	-5.915870	4.984875	3.004776	N	-6.05595732	4.95988400	3.14600061
				C	-5.213634	4.379543	4.066479	C	-5.14742475	4.44561247	4.10533503
				N	-5.323422	5.074050	5.281323	N	-5.18071083	5.19137863	5.32871388
				C	-5.735351	6.396447	5.456296	C	-5.61359486	6.52810586	5.45778907
				C	-6.287859	7.015435	4.264272	C	-6.22404843	7.08893434	4.26704012
				C	-6.407703	6.254994	3.142753	C	-6.47337378	6.26269174	3.21803710
				S	-3.482947	3.884465	3.886849	S	-3.35159300	4.69427452	3.83908371
				O	-5.663894	6.918749	6.566266	O	-5.51080372	7.08558978	6.54488797
				C	-6.788614	8.426853	4.344617	C	-6.64126888	8.53212271	4.28776118
				C	-7.073430	0.956840	2.710019	C	-7.24311642	0.68391493	2.50269954
				O	-8.041347	0.986761	3.753539	O	-8.32923807	0.55672627	3.41616392
				O	-6.789967	2.680351	-0.634487	O	-6.63537216	2.59208756	-0.60387957
				H	-6.924917	6.638109	2.270652	H	-7.03291276	6.61438473	2.35840059
				H	-7.537047	8.535097	5.134616	H	-7.25825132	8.75654474	5.16156345
				H	-5.975718	9.120956	4.578084	H	-5.76811176	9.19015037	4.33232485
				H	-7.237002	8.734014	3.398750	H	-7.20743411	8.78360499	3.38932698
				H	-4.965277	4.613923	6.110043	H	-4.88363270	4.73331362	6.18312168
				H	-8.330569	1.842713	1.206134	H	-8.29643102	1.94728356	1.11921827
				H	-4.743422	2.776928	1.967341	H	-4.72229534	2.89699416	2.06529588
				H	-7.313285	1.987778	-1.052709	H	-6.98342036	1.82561931	-1.07168193
				H	-5.724043	1.245405	0.425408	H	-5.55733792	1.28515638	0.58621701
				H	-6.771800	4.885049	1.142883	H	-7.03880720	4.74196842	1.36102210
				H	-6.064142	1.076940	3.122023	H	-6.28526421	0.66652740	3.03695032
				H	-7.139311	-0.029287	2.246232	H	-7.28706927	-0.18587028	1.84367766
				H	-8.033426	1.878020	4.124303	H	-8.31094730	1.32248409	4.00240171
				O	-4.583041	4.020154	0.321924	O	-4.73150308	4.20814888	0.45654206
				H	-3.819001	3.500725	0.048943	H	-4.12790712	3.70209584	-0.09829488

S4. Cartesian coordinates of optimized structures of 6tGua

Table S5. Optimized structures of 6tGua using X3LYP/6-311++G(d,p) calculation (xyz, Angstrom).

S_0

C	-0.446739	0.877510	0.027716
C	-0.214864	3.271180	0.265737
C	-2.337663	2.045711	0.013874
C	0.383419	1.998290	0.184759
C	1.680378	0.308599	0.109115
N	0.400763	-0.189565	-0.018746
N	1.710622	1.608713	0.232213
N	-1.784890	0.850126	-0.065494
N	-1.602250	3.195142	0.171480
N	-3.683932	2.170011	-0.019144
S	0.532932	4.771792	0.454230
H	-2.089954	4.080711	0.239981
H	0.138702	-1.159864	-0.123233
H	-4.115650	3.062177	-0.203104
H	-4.207445	1.350335	-0.284998
H	2.539580	-0.344191	0.102312

T_1 op-S

C	-0.441147	0.882289	0.006844
C	-0.198538	3.290403	0.437203
C	-2.331769	2.095463	0.005659
C	0.405708	2.001686	0.268785
C	1.667156	0.274082	0.142693
N	0.403096	-0.193784	-0.054326
N	1.694771	1.598314	0.340864
N	-1.771825	0.868677	-0.113228
N	-1.633711	3.214968	0.250788
N	-3.665582	2.162420	-0.123887
S	0.580719	4.790852	0.102616
H	-2.130613	4.091084	0.338045
H	0.137629	-1.152836	-0.230257
H	-4.174255	3.030532	-0.078973
H	-4.167701	1.315664	-0.336839
H	2.529071	-0.373138	0.130710

ISC crossing point

C	-0.39946659	0.97420882	-0.11854301
C	-0.21095930	3.35362195	0.57790573
C	-2.31159135	2.13139204	0.00478383
C	0.41153362	2.04265216	0.37267005
C	1.66153395	0.31124900	0.29102759
N	0.43602531	-0.10985070	-0.16213709
N	1.67639722	1.58609246	0.62591395
N	-1.71286320	0.97531978	-0.34216617
N	-1.66136530	3.17372773	0.56657623
N	-3.63541507	2.21546267	-0.19309767
S	0.45712920	4.23855721	-0.81234189
H	-2.20484100	3.98896900	0.81187814
H	0.19029725	-1.04869831	-0.44485148
H	-4.16879040	3.03106070	0.06063368
H	-4.12848319	1.39332817	-0.50362742
H	2.50389882	-0.36041268	0.35205553

S5. Cartesian coordinates of optimized structures of 6tGuo

Table S6. Optimized structures of 6tGuo using X3LYP/6-311++G(d,p) calculation (xyz, Angstrom).

1. anti conformers

S_0				anti-up							
				T_1 minimum				ISC crossing point			
C	-3.926241	2.424432	0.672205	C	-3.908443	2.431667	0.669994	C	-3.89549433	2.49639215	0.59658501
C	-3.668140	4.712576	1.402386	C	-3.626719	4.725378	1.508368	C	-3.60176450	4.75433230	1.59810736
C	-5.774788	3.436745	1.382568	C	-5.757765	3.456437	1.432609	C	-5.72925787	3.45757806	1.45092000
C	-3.096140	3.532253	0.889747	C	-3.057348	3.546498	0.923228	C	-3.01987718	3.55028054	0.99158681
C	-1.838894	1.993912	0.118509	C	-1.831848	1.990757	0.106136	C	-1.78401429	1.96110061	0.27648326
N	-3.111491	1.443330	0.167648	N	-3.091677	1.454214	0.147033	N	-3.07607324	1.49194292	0.13411810
N	-1.793370	3.228687	0.535885	N	-1.788764	3.246278	0.564354	N	-1.72096826	3.17252048	0.78713109
N	-5.244406	2.330263	0.895650	N	-5.216815	2.329695	0.911094	N	-5.21475682	2.42411976	0.75482215
N	-5.036569	4.570178	1.621103	N	-5.053320	4.565625	1.704290	N	-4.97970097	4.44591889	1.97933347
N	-7.087201	3.468043	1.702172	N	-7.074205	3.427288	1.686305	N	-7.05413536	3.45915161	1.64954300
S	-2.909690	6.178065	1.753086	S	-3.014856	6.320074	1.274034	S	-3.41446500	5.90730050	0.25457987
C	-3.133365	-0.373414	-1.579106	C	-3.079844	-0.359074	-1.605599	C	-3.07022976	-0.32257314	-1.62712638
C	-3.514797	0.090210	-0.172740	C	-3.506258	0.107911	-0.213794	C	-3.50265401	0.15353504	-0.23942501
O	-2.864994	-0.820073	0.715762	O	-2.908532	-0.815135	0.696907	O	-2.92344138	-0.77548366	0.67827683
C	-2.578634	-2.058945	0.033453	C	-2.615576	-2.056621	0.022233	C	-2.62878049	-2.01920976	0.00961069
C	-3.085051	-1.887881	-1.414436	C	-3.065760	-1.874774	-1.442155	C	-3.06445736	-1.83854676	-1.45899470
C	-1.085247	-2.335976	0.146999	C	-1.131382	-2.356375	0.188785	C	-1.14847908	-2.32961555	0.19084023
O	-0.869618	-3.671769	-0.307752	O	-0.920685	-3.696005	-0.257001	O	-0.94658439	-3.67591070	-0.23892574
O	-4.417826	-2.380617	-1.579391	O	-4.400451	-2.342131	-1.656445	O	-4.39929997	-2.30217087	-1.68156121
H	-3.127351	-2.865789	0.528882	H	-3.193326	-2.856288	0.495800	H	-3.21547119	-2.81375298	0.48058248
H	-2.150136	0.009315	-1.857624	H	-2.079436	0.004853	-1.845206	H	-2.06723828	0.03816980	-1.86173239
H	-4.407905	-3.340386	-1.491631	H	-4.412029	-3.301658	-1.566337	H	-4.42101521	-3.25757159	-1.55470643
H	-2.412212	-2.369010	-2.127698	H	-2.376110	-2.367257	-2.131126	H	-2.37205397	-2.33643177	-2.14165124
H	-4.595251	0.057029	-0.020609	H	-4.591869	0.095113	-0.101704	H	-4.58949556	0.15562162	-0.13861794
H	-0.784816	-2.221036	1.193689	H	-0.866216	-2.244493	1.245296	H	-0.88966812	-2.20827071	1.24792575
H	-0.516038	-1.618632	-0.455756	H	-0.530156	-1.649290	-0.394626	H	-0.53627802	-1.63532308	-0.39641728
H	0.076080	-3.850792	-0.305704	H	0.020645	-3.892070	-0.213996	H	-0.00573247	-3.87509647	-0.19974263
H	-3.854780	-0.063972	-2.334022	H	-3.765826	-0.035055	-2.386992	H	-3.75108679	0.00089232	-2.41350597
H	-5.500632	5.387581	2.000044	H	-5.531245	5.362998	2.102134	H	-5.44843706	5.15248310	2.52775151
H	-7.564051	4.341109	1.862696	H	-7.573799	4.214819	2.066553	H	-7.52055557	4.18938957	2.16283314
H	-7.650205	2.692592	1.388971	H	-7.586626	2.590638	1.458171	H	-7.59491473	2.67592750	1.31885339
H	-0.990747	1.424068	-0.226949	H	-0.978265	1.438077	-0.250307	H	-0.92815876	1.36541028	0.00057281

2. syn conformers

S_0				syn-up							
				T_1 minimum				ISC crossing point			
C	-5.758647	0.531772	-4.267189	C	-5.739905	0.540821	-4.271809	C	-5.79349103	0.47997501	-4.31412977
C	-6.932448	1.261063	-6.254914	C	-6.893279	1.328639	-6.299281	C	-6.87781865	1.41227382	-6.35198719
C	-7.552406	1.811822	-3.939849	C	-7.559681	1.833090	-3.967320	C	-7.53590071	1.85490607	-3.99164555
C	-5.873028	0.543152	-5.665621	C	-5.836953	0.572751	-5.695238	C	-5.79746031	0.63946009	-5.73377759
C	-4.165417	-0.644167	-5.231988	C	-4.118034	-0.601048	-5.216056	C	-4.03363434	-0.45492194	-5.25038714
N	-4.646775	-0.232691	-3.997974	N	-4.611223	-0.210162	-4.001016	N	-4.64104108	-0.22837052	-4.03229624
N	-4.859845	-0.201798	-6.240915	N	-4.828994	-0.141164	-6.246993	N	-4.68264348	0.05676436	-6.27199626
N	-6.564311	1.137863	-3.382604	N	-6.543298	1.147815	-3.393085	N	-6.63881993	1.01719236	-3.43728205

N	-7.735567	1.874519	-5.298918	N	-7.745916	1.924288	-5.292641	N	-7.54905422	2.17606450	-5.30329359
N	-8.411591	2.509847	-3.164033	N	-8.410349	2.450834	-3.134543	N	-8.42890451	2.41931869	-3.16679274
S	-7.292672	1.434918	-7.893790	S	-7.580228	0.990085	-7.843126	S	-7.83372276	0.09692055	-7.07269915
C	-3.883322	0.465232	-1.679986	C	-3.872237	0.469270	-1.671347	C	-3.91232362	0.45439658	-1.70552284
C	-4.065155	-0.630664	-2.729413	C	-4.043416	-0.621003	-2.728514	C	-4.08211663	-0.64184074	-2.75717695
O	-4.909050	-1.591823	-2.104440	O	-4.899265	-1.581641	-2.122542	O	-4.93622726	-1.59917709	-2.14367084
C	-4.578247	-1.636961	-0.699810	C	-4.586769	-1.638613	-0.714139	C	-4.61327469	-1.64912251	-0.73615010
C	-3.759971	-0.348927	-0.395810	C	-3.780066	-0.348977	-0.386536	C	-3.80398311	-0.35771736	-0.41944411
C	-5.837138	-1.823665	0.122082	C	-5.855332	-1.842117	0.088154	C	-5.87074595	-1.84890621	0.08511644
O	-6.629678	-0.637726	0.076300	O	-6.650585	-0.658054	0.049723	O	-6.66824235	-0.66613700	0.05602468
O	-2.371821	-0.638931	-0.191248	O	-2.397624	-0.636675	-0.144265	O	-2.41832285	-0.64224017	-0.19186264
H	-3.933033	-2.505443	-0.522779	H	-3.937967	-2.504503	-0.537959	H	-3.96287632	-2.51399402	-0.56196778
H	-4.772383	1.092649	-1.648372	H	-4.756603	1.104157	-1.656113	H	-4.80431108	1.07899909	-1.68832344
H	-2.271285	-1.114960	0.640619	H	-2.320154	-1.115088	0.688752	H	-2.32839454	-1.10115551	0.65079101
H	-4.161684	0.182309	0.468440	H	-4.206161	0.179682	0.467488	H	-4.22121889	0.17167739	0.43820532
H	-3.101836	-1.086326	-2.981376	H	-3.079310	-1.078194	-2.974321	H	-3.11686210	-1.10028301	-2.99855706
H	-5.537684	-2.051751	1.152195	H	-5.568854	-2.084940	1.118606	H	-5.56513449	-2.08527001	1.11196749
H	-6.394597	-2.681550	-0.270405	H	-6.404595	-2.695582	-0.324857	H	-6.42670712	-2.70516247	-0.31222413
H	-7.407895	-0.769649	0.626932	H	-7.439512	-0.802791	0.581604	H	-7.46380614	-0.82164063	0.57465716
H	-3.002510	1.081435	-1.857478	H	-2.983269	1.078930	-1.829710	H	-3.03116972	1.07233984	-1.87442256
H	-8.510273	2.415354	-5.665042	H	-8.526457	2.462770	-5.643364	H	-8.23578040	2.84715839	-5.61695573
H	-9.289531	2.842683	-3.530521	H	-9.193959	2.994168	-3.459020	H	-9.13178001	3.06419052	-3.48940945
H	-8.368211	2.340215	-2.171174	H	-8.257816	2.361170	-2.142984	H	-8.35459445	2.23517781	-2.17903273
H	-3.286776	-1.268757	-5.297431	H	-3.236976	-1.218870	-5.294059	H	-3.10443725	-1.00179589	-5.31223445

S6. Cartesian coordinates of optimized structures of 6m-2tThd

Table S7. Optimized ground state minima of 6m-2tThd using X3LYP/6-311++G(d,p) calculation (xyz, Angstrom).

anti				syn			
C	-5.727670	2.084570	0.970913	C	-5.489759	3.286693	1.576295
C	-4.742967	2.734560	-0.029275	C	-6.656413	4.080871	2.169554
O	-5.182142	4.070165	-0.248440	O	-7.694779	3.146979	2.431392
C	-6.607391	4.032862	-0.147304	C	-7.502256	1.970844	1.607591
C	-6.900617	3.074734	1.025191	C	-6.245781	2.241051	0.755339
N	-3.309517	2.747949	0.335621	N	-6.407214	4.925807	3.359548
C	-2.491228	1.876588	-0.351526	C	-5.846288	4.406779	4.505222
N	-1.161716	2.009391	-0.104615	N	-5.482712	5.330727	5.438644
C	-0.532006	2.911052	0.751625	C	-5.645864	6.712319	5.399088
C	-1.442390	3.754674	1.496842	C	-6.368731	7.189363	4.236797
C	-2.787023	3.634968	1.298343	C	-6.753564	6.297479	3.281854
S	-3.003352	0.675445	-1.424821	S	-5.590510	2.780293	4.866853
O	0.691918	2.910668	0.828949	O	-5.219923	7.395931	6.323530
C	-0.835859	4.719670	2.481148	C	-6.677765	8.662991	4.180889
C	-7.144601	5.437963	0.043167	C	-7.358965	0.738639	2.501744
O	-8.559416	5.284508	0.204686	O	-8.344103	0.714039	3.527217
O	-8.144670	2.401212	0.889866	O	-6.564283	2.833362	-0.507687
H	-1.017102	4.412089	3.515738	H	-7.742762	8.860280	4.335564
H	0.241818	4.754492	2.330446	H	-6.128839	9.172407	4.971157
H	-1.233173	5.728992	2.358896	H	-6.389484	9.104071	3.225139
H	-0.555304	1.369509	-0.603582	H	-5.056117	4.954955	6.277399
H	-7.036475	3.596434	-1.060179	H	-8.387936	1.871948	0.973920
H	-5.280121	1.903438	1.946814	H	-4.886971	2.808593	2.343268
H	-8.827334	3.085104	0.852701	H	-7.040361	2.189463	-1.044021
H	-6.891316	3.638432	1.964764	H	-5.659551	1.329855	0.605835
H	-4.776357	2.190032	-0.969555	H	-6.994178	4.766487	1.402722
H	-6.912751	6.061083	-0.826067	H	-6.357267	0.707807	2.940667
H	-6.697052	5.890551	0.934416	H	-7.502986	-0.159335	1.897377
H	-8.948214	6.139976	0.412698	H	-8.187830	1.499108	4.069059
H	-6.070339	1.126945	0.577376	H	-4.856253	3.907926	0.943836
C	-3.732197	4.460053	2.124665	C	-7.595094	6.752844	2.120675
H	-3.994501	5.384357	1.606843	H	-7.017304	6.824182	1.194877
H	-4.653717	3.936543	2.356230	H	-8.436845	6.079836	1.949481
H	-3.253156	4.717927	3.066201	H	-7.998627	7.739140	2.329992

S7. Cartesian coordinates of optimized structures of 1'm-2tThd

Table S8. Optimized structures of 1'm-2tThd using X3LYP/6-311++G(d,p) calculation (xyz, Angstrom).

1. anti conformers

S_0				anti-up							
				T_1 minimum				ISC crossing point			
C	-5.948055	1.863384	0.599396	C	-5.876466	2.094547	0.996217	C	-5.96313145	2.08095135	0.98467661
C	-4.877745	2.506859	-0.313449	C	-4.854179	2.512038	-0.081779	C	-4.86386119	2.46014676	-0.02739184
O	-5.325568	3.832903	-0.540859	O	-5.223070	3.841745	-0.426293	O	-5.17901631	3.79192534	-0.42347575
C	-6.546486	4.129932	0.168720	C	-6.580268	4.143999	-0.030982	C	-6.53913519	4.14474427	-0.08387743
C	-7.171683	2.763848	0.449521	C	-7.137280	2.871676	0.631674	C	-7.17572085	2.89116784	0.54388016
N	-3.511709	2.615217	0.396308	N	-3.437647	2.590196	0.458769	N	-3.49011558	2.51544593	0.60695515
C	-2.880344	1.524516	0.934655	C	-2.618681	1.428698	0.434888	C	-2.59620710	1.38417412	0.49428279
N	-1.668283	1.794521	1.514380	N	-1.239734	1.719528	0.558677	N	-1.25375821	1.77333016	0.27916246
C	-0.974588	3.005201	1.574221	C	-0.663257	2.890770	0.977759	C	-0.69457877	2.95094394	0.70115799
C	-1.662642	4.098773	0.920596	C	-1.613627	3.989224	1.170699	C	-1.65888275	3.95814113	1.20253300
C	-2.873368	3.845098	0.374322	C	-2.934014	3.780984	0.854185	C	-2.98505746	3.71903137	1.07956836
S	-3.437166	-0.067924	0.937711	S	-3.219574	0.049203	1.377012	S	-3.09186970	0.63942719	2.05372762
O	0.114181	3.061378	2.134775	O	0.553805	2.993709	1.143556	O	0.51194955	3.17088054	0.60704671
C	-1.014645	5.449616	0.877499	C	-1.106064	5.309840	1.647180	C	-1.11384200	5.23517082	1.76404769
C	-6.254395	4.958390	1.417003	C	-6.567069	5.367534	0.876818	C	-6.52027177	5.35672613	0.83986020
O	-7.513573	5.392194	1.928984	O	-7.921749	5.793682	1.014157	O	-7.86708650	5.81409253	0.95009976
O	-7.941290	2.287201	-0.657912	O	-7.916588	2.080077	-0.269544	O	-7.92334320	2.12097763	-0.40117163
H	-3.436258	4.620006	-0.120265	C	-4.861899	1.645235	-1.337710	C	-4.81452477	1.55963764	-1.25730210
H	-0.823937	5.821812	1.887815	H	-3.637268	4.599392	0.870603	H	-3.71620974	4.47929420	1.31441527
H	-0.049169	5.402211	0.366377	H	-0.672028	5.222009	2.648617	H	-0.60430171	5.05284043	2.71627606
H	-1.647526	6.168826	0.356693	H	-0.309219	5.677968	0.994101	H	-0.37457465	5.67242322	1.08911320
H	-1.203212	0.995772	1.929473	H	-1.905034	6.050935	1.681432	H	-1.91027933	5.95984049	1.93741420
H	-7.166439	4.722108	-0.507764	H	-0.614101	0.929365	0.465613	H	-0.61934760	1.08110832	-0.09691343
H	-5.614617	1.856017	1.636074	H	-7.149588	4.381527	-0.933716	H	-7.06038484	4.41326721	-1.00677544
H	-8.739781	2.821724	-0.733152	H	-5.515150	2.406315	1.977136	H	-5.65443317	2.38282609	1.98550202
H	-7.781591	2.781048	1.355537	H	-8.742182	2.542855	-0.451896	H	-8.73241150	2.59859603	-0.61527630
H	-5.628863	5.811546	1.134545	H	-7.730535	3.120701	1.514543	H	-7.81302168	3.16260308	1.38837454
H	-5.713004	4.364961	2.163120	H	-5.953134	6.147607	0.414288	H	-5.87506391	6.12715213	0.40485787
H	-7.363638	5.890523	2.738786	H	-6.135782	5.116975	1.853475	H	-6.12009464	5.08363177	1.82371331
H	-6.172309	0.840307	0.313399	H	-7.955914	6.520611	1.644114	H	-7.89956470	6.53362853	1.58854779
C	-4.672245	1.847572	-1.670810	H	-6.049002	1.021985	1.020099	H	-6.16735375	1.01243600	0.99765222
H	-4.016306	2.469350	-2.283629	H	-4.164153	2.049969	-2.072821	H	-4.08897017	1.94284199	-1.97720201
H	-4.237364	0.855180	-1.565266	H	-4.589144	0.615683	-1.112169	H	-4.55002305	0.53641249	-0.99375272
H	-5.641794	1.763117	-2.163020	H	-5.870766	1.662314	-1.750125	H	-5.80586118	1.56307331	-1.71115629
				anti-down							
				T_1 minimum				ISC crossing point			
				C	-5.874806	1.586011	0.024049	C	-5.91886459	1.59776847	0.01746012
				C	-4.848541	2.445275	-0.752122	C	-4.87595062	2.45756496	-0.73762232
				O	-5.416840	3.749597	-0.842844	O	-5.44879982	3.76026005	-0.85067216
				C	-6.556463	3.875589	0.024848	C	-6.57993859	3.89210776	0.02417107
				C	-7.128233	2.457319	0.111647	C	-7.16503062	2.47885814	0.10199267
				N	-3.559884	2.572104	0.020849	N	-3.61247620	2.58810513	0.05643204
				C	-3.118170	1.566736	0.881817	C	-3.17584019	1.51631763	0.86614259
				N	-2.116494	1.975445	1.762909	N	-2.11159356	1.91171905	1.74616424

	C	-1.252152	3.048224	1.565662	C	-1.23432584	2.99976539	1.53659583
	C	-1.591724	3.904060	0.434550	C	-1.58810610	3.85715809	0.42487908
	C	-2.745287	3.649190	-0.234622	C	-2.77097840	3.63335368	-0.21105927
	S	-2.813537	-0.091990	0.150934	S	-2.18435947	0.16211129	0.12135027
	O	-0.323220	3.246095	2.347408	O	-0.31359675	3.18269306	2.32847065
	C	-0.715154	5.082891	0.127419	C	-0.70766890	5.03236195	0.10260206
	C	-6.153653	4.469416	1.373113	C	-6.16910283	4.47014537	1.37742984
	O	-7.360371	4.765910	2.076781	O	-7.37530042	4.76869976	2.08243484
	O	-7.963830	2.145308	-1.007026	O	-7.99726829	2.18314706	-1.02491951
	C	-4.566967	1.968667	-2.173433	C	-4.56465958	1.96767586	-2.14744450
	H	-3.111088	4.328699	-0.993096	H	-3.13090446	4.33184937	-0.95592308
	H	-0.606811	5.732781	1.000482	H	-0.59591605	5.69783198	0.96377660
	H	0.291539	4.766532	-0.161426	H	0.29672842	4.71048998	-0.18841145
	H	-1.132780	5.671438	-0.691064	H	-1.12889748	5.60808839	-0.72351369
	H	-1.895985	1.373815	2.547019	H	-2.00258115	1.41661349	2.62562978
	H	-7.253652	4.559440	-0.464467	H	-7.27280129	4.58780669	-0.45429423
	H	-5.500898	1.354242	1.020765	H	-5.55653070	1.34332289	1.01187008
	H	-8.777273	2.657644	-0.937543	H	-8.80809157	2.69935634	-0.95274319
	H	-7.674024	2.301684	1.045049	H	-7.72007367	2.32390309	1.02991232
	H	-5.568096	5.376922	1.193515	H	-5.57674924	5.37479509	1.20476424
	H	-5.534066	3.766225	1.941120	H	-5.55377380	3.75907140	1.94003885
	H	-7.134120	5.114086	2.945213	H	-7.15095280	5.09744049	2.95874637
	H	-6.091547	0.647333	-0.483223	H	-6.13673007	0.66836199	-0.50764592
	H	-3.914038	2.674446	-2.690866	H	-3.91065282	2.67735037	-2.65868445
	H	-4.083300	0.989579	-2.166664	H	-4.06593079	0.99698283	-2.11657293
	H	-5.508090	1.892733	-2.719368	H	-5.49183179	1.87037301	-2.71396673

2. syn conformers

S_0

C	-5.697096	3.694125	0.024390
C	-4.751487	2.545270	-0.410542
O	-4.492945	2.790889	-1.780995
C	-5.271693	3.886288	-2.298311
C	-6.380592	4.119888	-1.269468
N	-3.426620	2.611349	0.353275
C	-2.266258	2.038218	-0.115626
N	-1.163722	2.284078	0.666450
C	-1.090208	2.891198	1.919916
C	-2.379172	3.304802	2.437704
C	-3.453622	3.142183	1.635383
S	-2.064775	1.068989	-1.476969
O	-0.009532	3.008849	2.485640
C	-2.463970	3.885688	3.816230
C	-4.368240	5.092915	-2.533788
O	-5.138376	6.064663	-3.241330
O	-7.516264	3.280913	-1.486813
C	-5.359491	1.159323	-0.214277
H	-4.429894	3.429277	1.991352
H	-2.081906	3.180861	4.559514
H	-1.857404	4.792224	3.892523
H	-3.493990	4.135299	4.072705
H	-0.297550	1.895847	0.311784

H	-5.686994	3.565558	-3.256938
H	-5.131199	4.546246	0.400007
H	-7.976286	3.582828	-2.278078
H	-6.684732	5.168554	-1.239337
H	-3.502928	4.769041	-3.120726
H	-4.005516	5.498294	-1.581868
H	-4.587568	6.836984	-3.404446
H	-6.417445	3.392013	0.783254
H	-4.700708	0.396842	-0.627018
H	-5.518981	0.960967	0.848130
H	-6.321414	1.123901	-0.725986

S8. Parameters used in the quasi-Marcus equation

The classical limit of the Fermi's Golden rule in the harmonic approximation is the classic Marcus formula:[1-3]

$$k_{isc} = \frac{2\pi}{\hbar}|H_{SOC}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\lambda+\Delta G^0)^2}{4\lambda k_B T}\right) \quad \text{(SI-1)}$$

where the k_{isc} is the ISC rate, H_{SOC} is the spin orbit coupling, λ is the reorganization energy, k_B is the Boltzmann constant, T is the absolute temperature, and ΔG^0 is the total Gibbs free energy variation for the transfer. The term in the exponential is a quadratic approximation for the activation energy $\Delta G^{\ddagger}_{ISC}$:

$$\Delta G^{\ddagger}_{ISC} \approx \frac{(\lambda+\Delta G^0)^2}{4\lambda}. \quad \text{(SI-2)}$$

These parameters are shown in Figure S1:

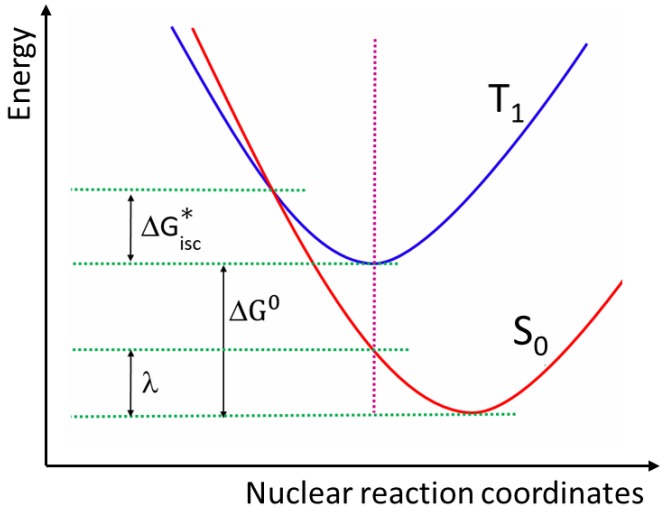

Figure S1. Marcus model in the inverted region.

In the case of small couplings, as it is for triplet/singlet crossings, the diabatic crossing point can be optimized directly because it is practically coincident with the crossing of the adiabatic states. We take advantage of this fact to obtain a more precise estimate of the activation free energy $\Delta G^{\ddagger}_{ISC}$, and writing a quasi-Marcus formula for intersystem crossing as follows:[4]

$$k_{isc} = \frac{2\pi}{\hbar}|H_{SOC}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{\Delta G^{\ddagger}_{ISC}}{k_B T}\right). \quad \text{(SI-3)}$$

In Ref.[5], we discuss the conditions under which this rate can be further simplified to

$$k_{isc} = \frac{2\pi}{\hbar}|H_{SOC}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{\Delta G^{\ddagger}_{ISC}}{k_B T}\right). \quad \text{(SI-4)}$$

where energy $\Delta G^{\ddagger}_{ISC}$ is the activation energy.

S9. Comparison between $B_{3,6}$ and op_S minima

Table S9. T_1 energy gap between $B_{3,6}$ and op_S minima of 2tThy and 2tThd at different levels. All geometries are optimized at X3LYP level. For 2tThd, the $B_{3,6}$ minimum is obtained from anti conformer, while the op-S minimum can be either anti-up or anti-down.

	$E(B_{3,6})$-E(op_S) /eV		
	2tThy	2tThd	
		anti-up	anti-down
X3LYP	-0.120	-0.072	-0.036
CC2	-0.016	0.017	0.022
CASPT2	0.010	0.013	0.039

S10. Supplementary References

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