How is the vitamin B1 oxidized to thiochrome? – Elementary processes revealed by a DFT study

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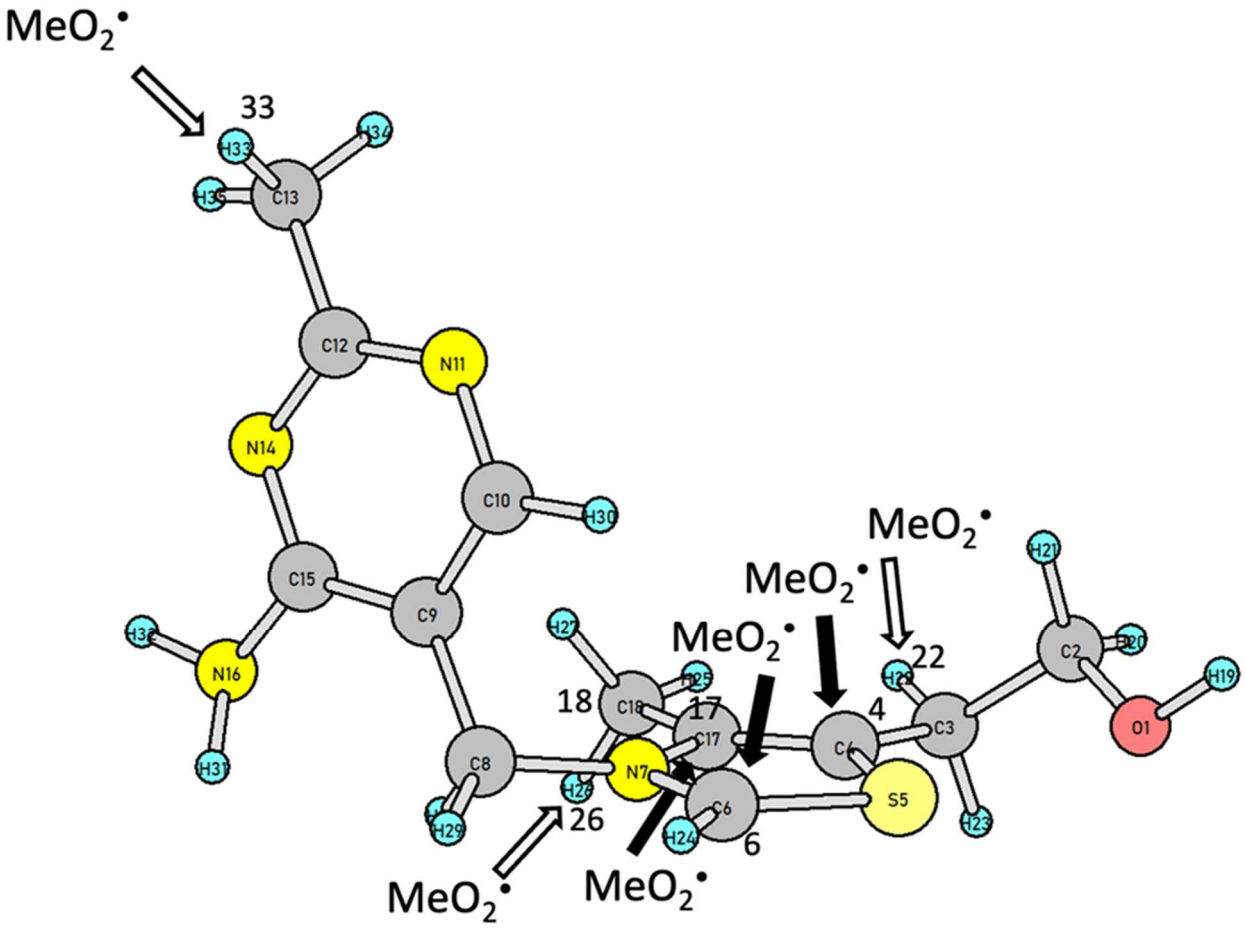
⇨ : C-H cleavage by $MeO_2^{\bullet}$

	Figure	$\nu^{\ddagger}$ (cm^{-1})	$\Delta(E_T+ZPE)$ (kcal/mol)
C(3)-H(22)	S6-1	2179.3899*i*	+18.54
C(18)-H(26)	S6-2	2167.2841*i*	+19.54
C(13)-H(33)	S6-3	2124.1337*i*	+19.62

➡ : Addition of $MeO_2^{\bullet}$

to C(4)	S6-4	649.6888*i*	+14.58
to C(17)	S6-5	647.9570*i*	+14.12
to C(6)	S6-6	775.2271*i*	**+12.49**



Scheme S1. Reactions between thiamine and methyl peroxy radical. Three empty arrows show the C-H bond scission ones, and their transition states are exhibited in Figures S6-1to S6-3. Three black ones do addition reactions, and their transition states are exhibited in Figures S6-4 to S6-6.

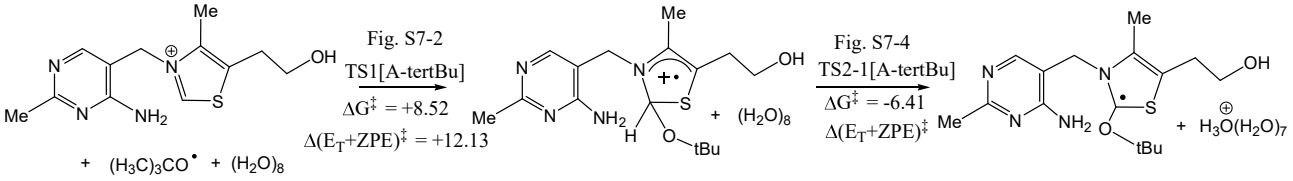


Fig. S7-1 Precursor[A-tertBu]
$\Delta G° = 0$ kcal/mol
$\Delta(E_T+ZPE) = 0$ kcal/mol

Fig. S7-2
TS1[A-tertBu]
$\Delta G^{‡} = +8.52$
$\Delta(E_T+ZPE)^{‡} = +12.13$

Fig. S7-3 Int1-1[A-tertBu]
$\Delta G° = -25.05$
$\Delta(E_T+ZPE) = -28.16$

Fig. S7-4
TS2-1[A-tertBu]
$\Delta G^{‡} = -6.41$
$\Delta(E_T+ZPE)^{‡}$

Fig. S7-5 Int1-2[A-tertBu]
$\Delta G° = -8.97$
$\Delta(E_T+ZPE) = -13.84$

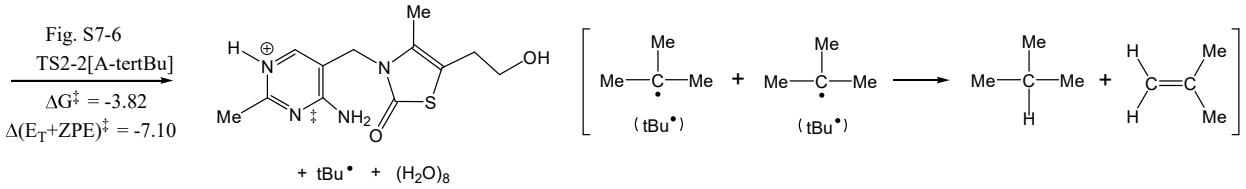
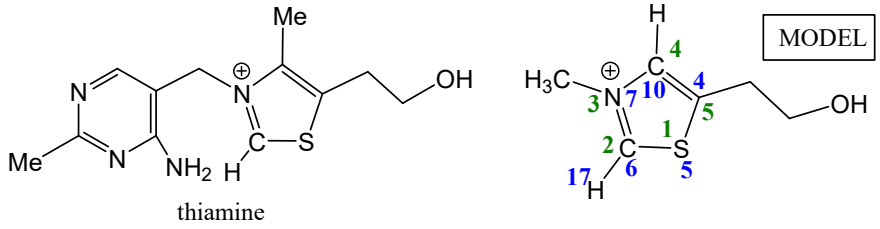


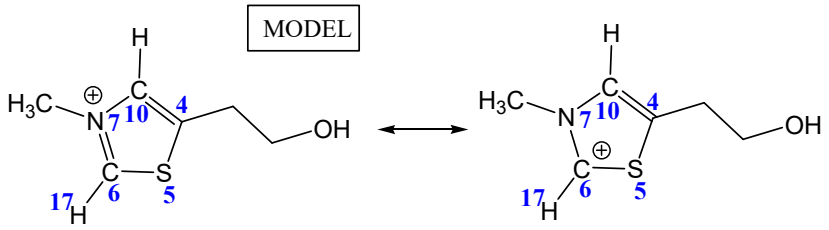
Fig. S7-6
TS2-2[A-tertBu]
$\Delta G^{‡} = -3.82$
$\Delta(E_T+ZPE)^{‡} = -7.10$

Fig. S7-7 Int2[A-tertBu]
$\Delta G° = -35.83$
$\Delta(E_T+ZPE) = -36.60$

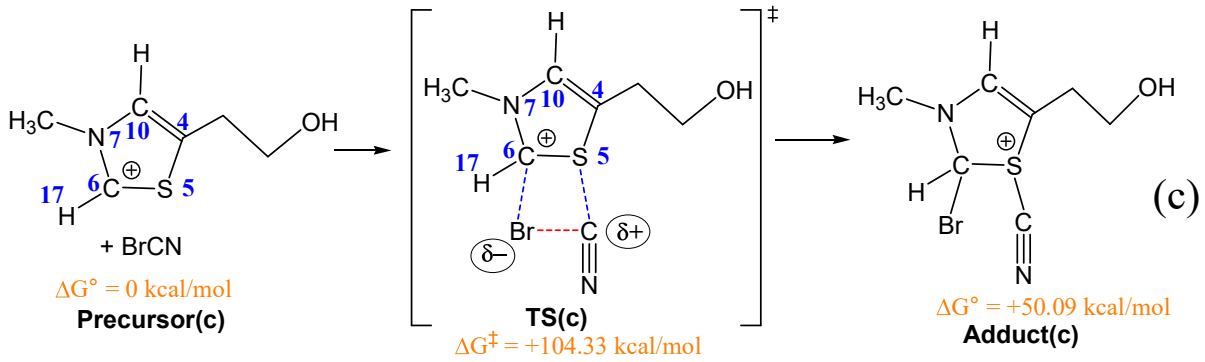
Scheme S2. A reaction of thiamine, *tert*-butoxy radical and $(H_2O)_8$ leading to the N-protonated thiazolone intermediate. Each geometry is shown in Figure S7. In the square bracket, the disproportionation of the *tert*-butyl radical formed at Int2[A-*tert*Bu] is shown. Practically, from the N-protonated thiazolone intermediate, Int2[A-*tert*Bu], the deprotonation needs to occur for the thiochrome-ring formation, because the pyrimidne ring should be nucleophilic toward C(6) of the newly formed carbonyl bond. Energy changes are in kcal/mol.



(a)



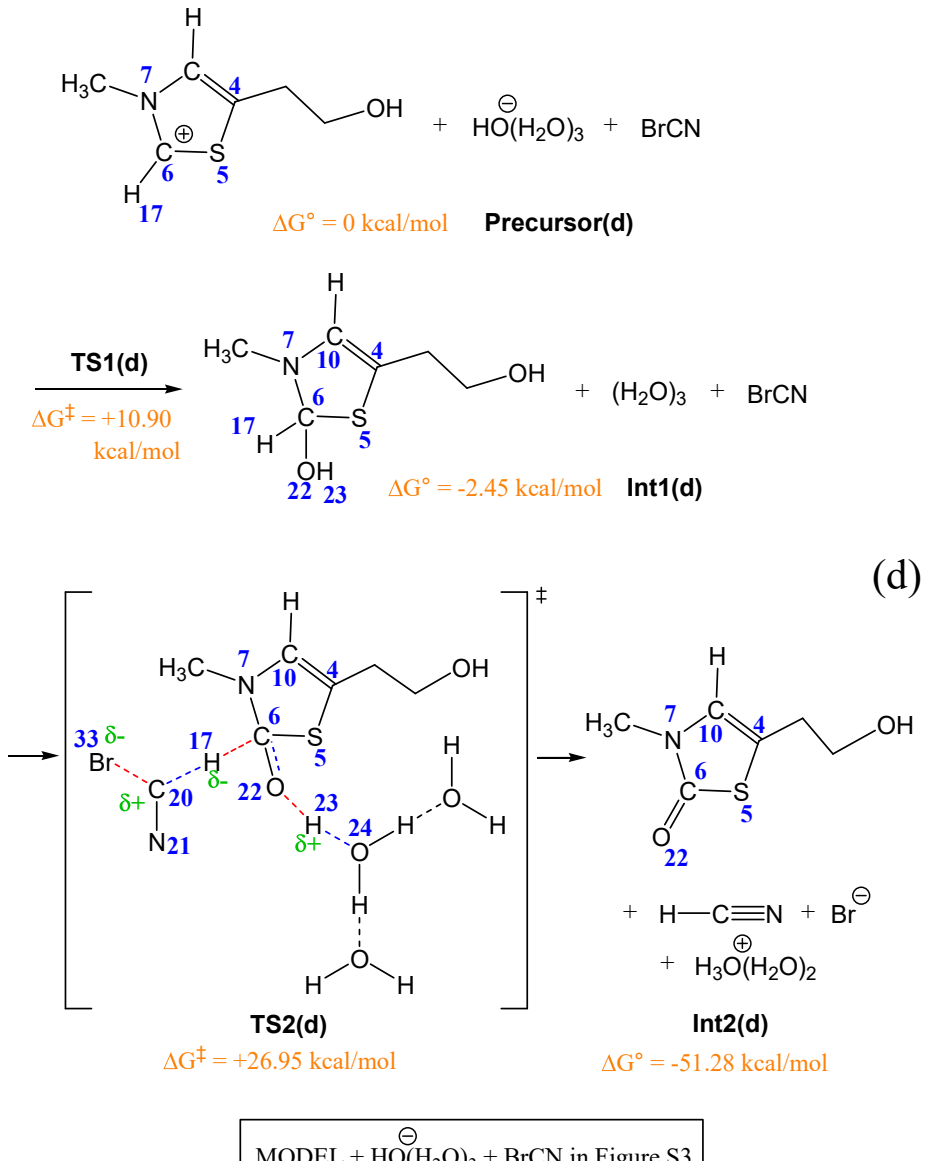
(b)



(c)

MODEL + BrCN in Figure S2

(Scheme S3 continues)



MODEL + $HO^{\ominus}(H_2O)_3$ + BrCN in Figure S3

Scheme S3. Preliminary examination of the role of BrCN by the use of a model substrate, "MODEL". Blue-color atom numbers are for the present calculations. (a) Structural formulae of thiamine and MODEL. (b) Canonical resonance structures of MODEL. (c) A reaction between MODEL and $Br^{-}CN^{+}$. (d) A reaction affording the C=O bond moiety.

In analogy with the protein-cleavage reaction, ^{+}CN would add to S(5) and Br^{-} to the cationic methine carbon C(6), which is shown in Scheme S3(c). However, the reaction giving Adduct (c) was calculated to have an extremely large activation free energy, $\Delta G^{\ddagger} = +104.33$ kcal/mol (TS(c) in Figure S2) and is ruled out.

Many other attempts to seek the direct (MODEL.....BrCN) interaction were made. However, the energetically favorable interaction could not be found. Then, a reaction of MODEL + BrCN + $OH^{-}(H_2O)_3$ was scrutinized, which follows the experimental condition (alkaline aqueous solution with BrCN). Scheme S3(d) and Figure S3 exhibit the obtained reaction path starting from

"Precursor(d)".

The first step is the HO^- addition to the cationic methine carbon C(6) at TS1(d). Indeed, the HO adduct was detected by the potentiometric titrations for thiamine.[58] From the adduct, Int1(d), TS2(d) was obtained which involves removal of both the proton H(23)[+0.269] and the hydride ion H(17)[-0.028]. Here, values in square brackets denote natural electronic net charges. BrCN undergoes heterolytic cleavage by accepting the hydride H(17), leading to the oxidation of MODEL. After TS2(d), the thiazolone intermediate Int2(d) was afforded. $\Delta G^{\ddagger}$(TS1(d)) = +10.90 kcal/mol, $\Delta G^{\ddagger}$(TS2(d)) = +26.95 kcal/mol and $\Delta G°$(Int2(d)) = -51.28 kcal/mol. These energies indicate the reaction of Scheme S3(d) is likely.

Precursor[A]

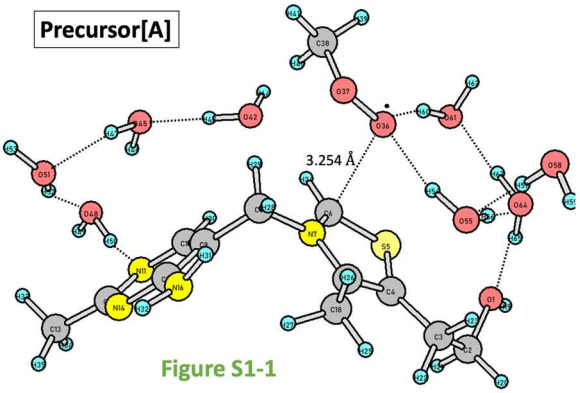


Figure S1-1

$\Delta (E_T+ZPE) = 0$ kcal/mol

$\Delta G° = 0$ kcal/mol

⇩

TS1[A]

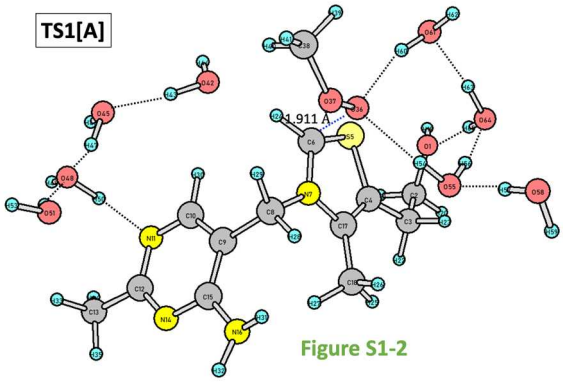


Figure S1-2

$\Delta (E_T+ZPE)^{\ddagger} = +16.74$ kcal/mol

$\Delta G^{\ddagger} = +19.69$ kcal/mol

$\nu^{\ddagger} = 750.0254i$ cm^{-1}

⇩

Int1[A]

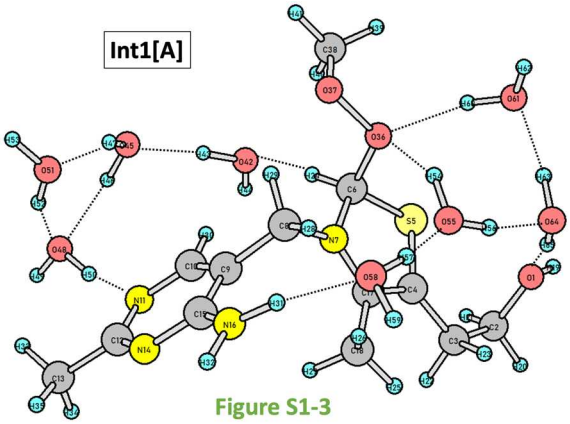


Figure S1-3

$\Delta (E_T+ZPE) = -3.77$ kcal/mol

$\Delta G° = -1.11$ kcal/mol

⇩

TS2[A]

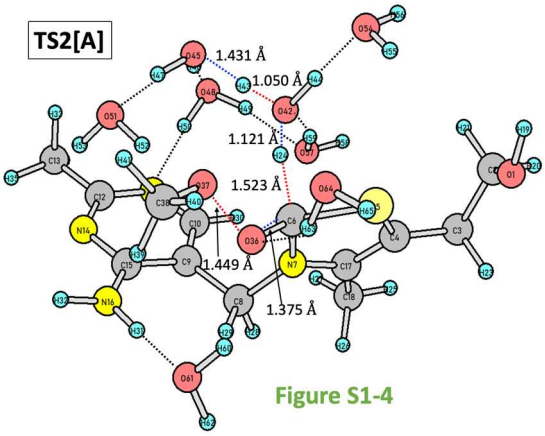


Figure S1-4

$\Delta (E_T+ZPE)^{\ddagger} = +15.32$ kcal/mol

$\Delta G^{\ddagger} = +21.36$ kcal/mol

$\nu^{\ddagger} = 882.5910i$ cm^{-1}

⇩

Int2[A]

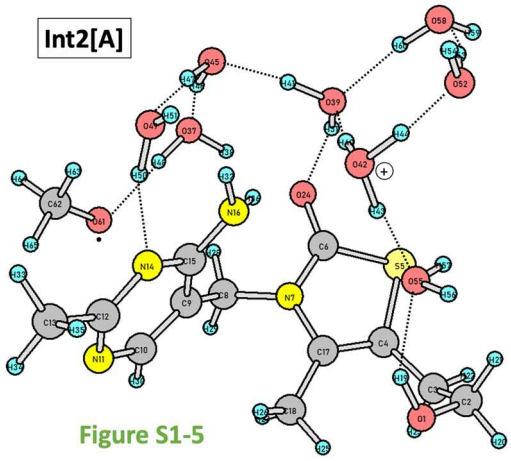


Figure S1-5

$\Delta (E_T+ZPE) = -59.37$ kcal/mol

$\Delta G° = -53.27$ kcal/mol

⇩

TS3[A]

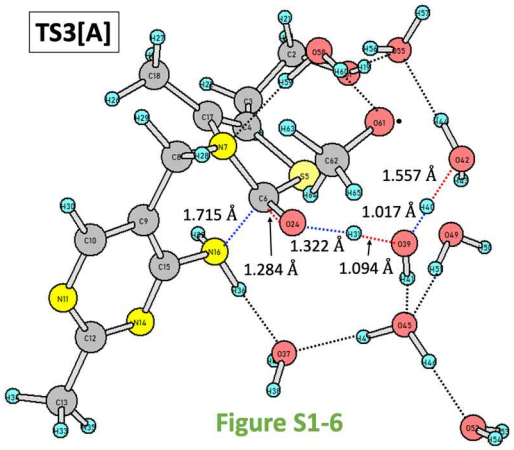


Figure S1-6

$\Delta (E_T+ZPE)^{\ddagger} = -29.11$ kcal/mol

$\Delta G^{\ddagger} = -24.14$ kcal/mol

$\nu^{\ddagger} = 179.5905i$ cm^{-1}

⇩

Int3[A]

(Figure S1 continues)

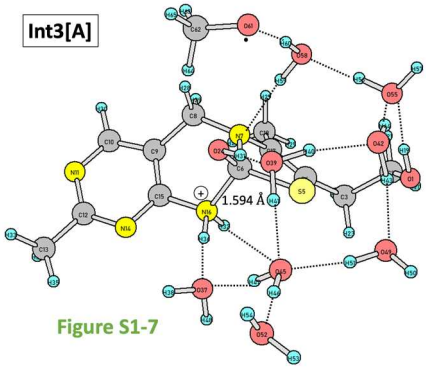


Figure S1-7

$\Delta(E_T+ZPE)$ = -29.89 kcal/mol

$\Delta G°$= -26.83 kcal/mol

⇩

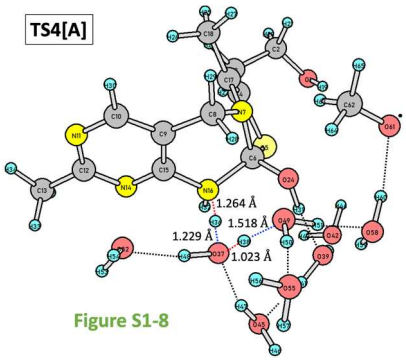


Figure S1-8

$\Delta(E_T+ZPE)^{\ddagger}$ = -25.23 kcal/mol

$\Delta G^{\ddagger}$ = -24.23 kcal/mol

$\nu^{\ddagger}$ = 963.7055*i* cm^{-1}

⇩

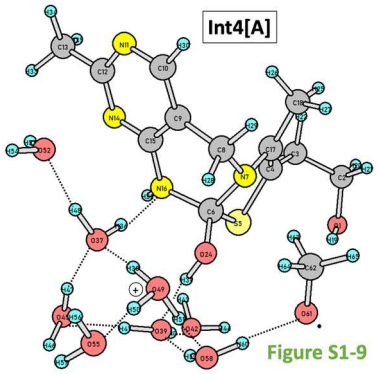


Figure S1-9

$\Delta(E_T+ZPE)$ = -31.50 kcal/mol

$\Delta G°$= -29.03 kcal/mol

⇩

TS5[A]

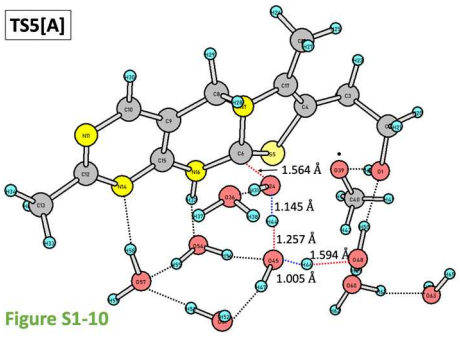


Figure S1-10

$\Delta(E_T+ZPE)^{\ddagger}$ = -29.99 kcal/mol

$\Delta G^{\ddagger}$ = -26.01 kcal/mol

$\nu^{\ddagger}$ = 576.7727*i* cm^{-1}

⇩

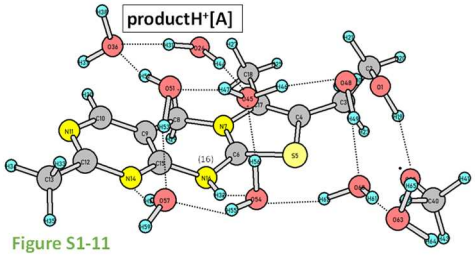


Figure S1-11

$\Delta(E_T+ZPE)$ = -61.24 kcal/mol

$\Delta G°$= -56.79 kcal/mol

⇩

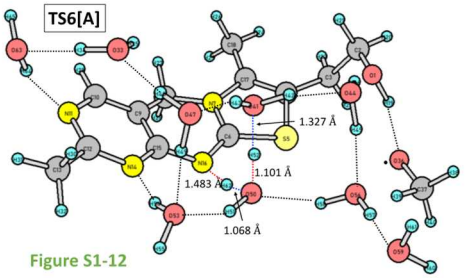


Figure S1-12

$\Delta(E_T+ZPE)^{\ddagger}$ = -53.54 kcal/mol

$\Delta G^{\ddagger}$ = -48.84 kcal/mol

$\nu^{\ddagger}$ = 272.1149*i* cm^{-1}

⇩

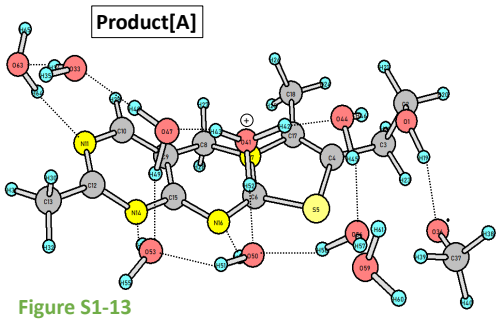


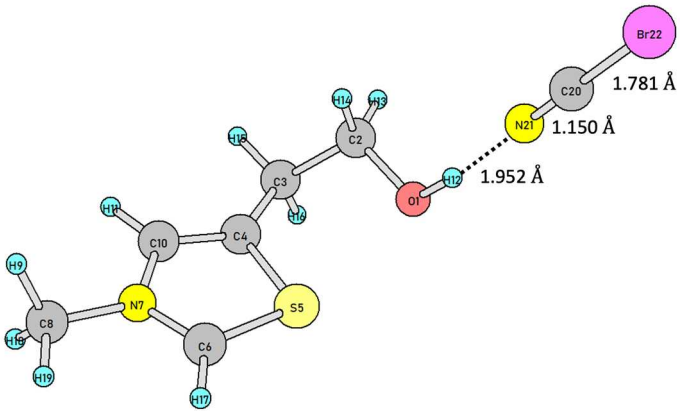
Figure S1-13

$\Delta(E_T+ZPE)$ = -55.69 kcal/mol

$\Delta G°$= -51.37 kcal/mol

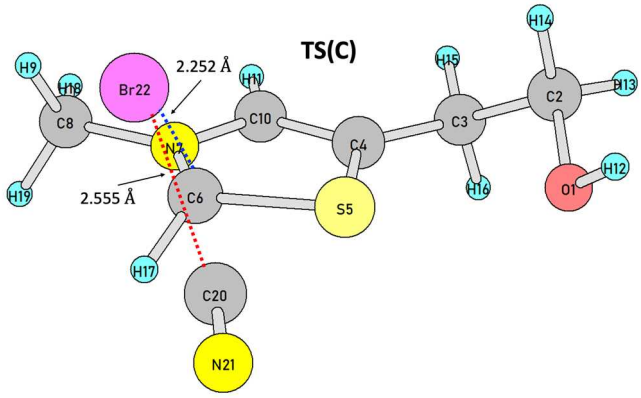
Figure S1. Geometries, $\Delta(E_T+ZPE)$s and ΔGs of species in Scheme 2. They were obtained by

UwB97X-D/6-311+G(d,p) SCRF=(PCM, solvent=water) calculations. Red and blue broken lines in TS1[A] to TS6[A] stand for covalent bonds cleaved and formed, respectively.



ΔG°= 0 kcal/mol

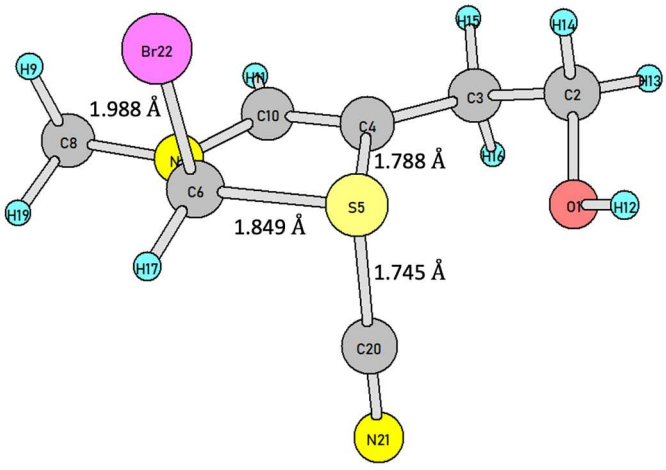
⇩



ΔG‡ = +104.33 kcal/mol

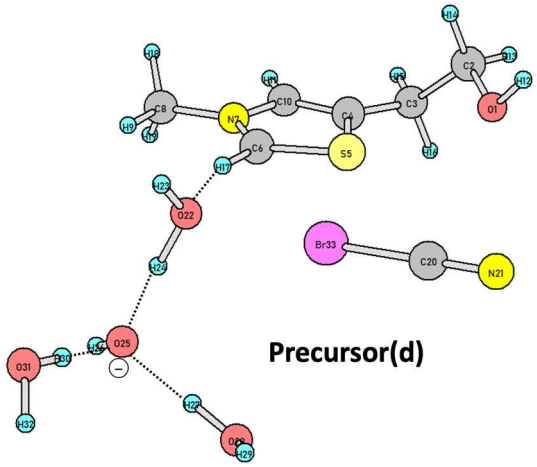
$\nu^{\ddagger}$ = 717.2904*i* cm^{-1}

⇩



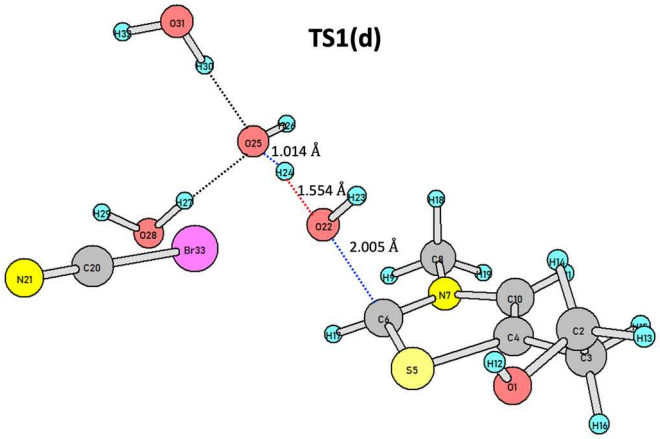
ΔG°= +50.09 kcal/mol

Figure S2. A model addition reaction between 3-methyl-5-(2-hydroxyethyl)thiazolium ion (MODEL) and BrCN. The numbering is for the present calculations and is shown by blue color in Scheme S3(c).



ΔG°= 0 kcal/mol

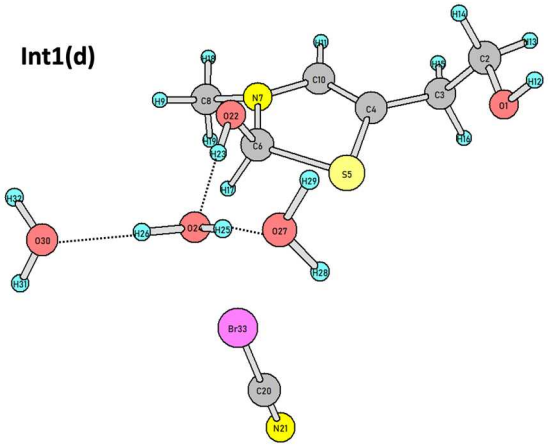
⇩



$\Delta G^{\ddagger}$ = +10.90 kcal/mol

$\nu^{\ddagger}$ = 342.1927*i* cm^{-1}

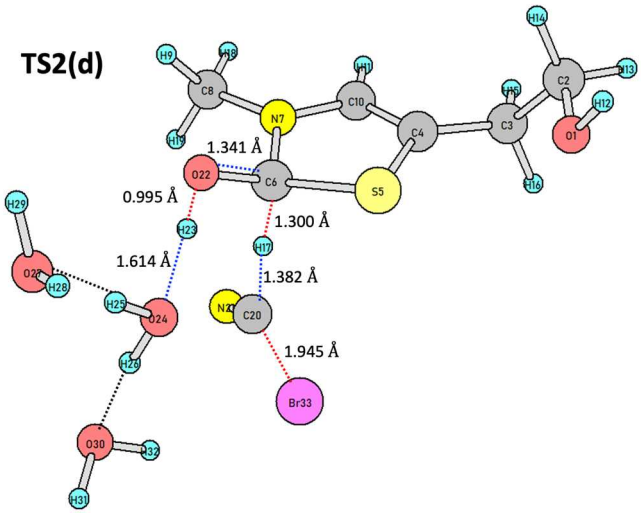
⇩



ΔG°= -2.45 kcal/mol

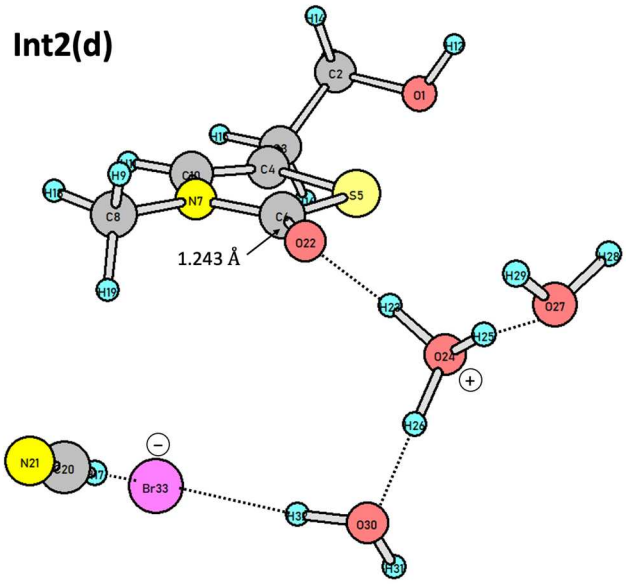
⇩

TS2(d)



$\Delta G^{\ddagger}$ = +26.95 kcal/mol

$\nu^{\ddagger}$ = 792.7629*i* cm^{-1}



$\Delta G°$= -51.28 kcal/mol

Figure S3. A model addition reaction of 3-methyl-5-(2-hydroxyethyl)thiazolium ion (MODEL), BrCN and $HO^{-}(H_2O)_3$, which is shown in Scheme S3(d).

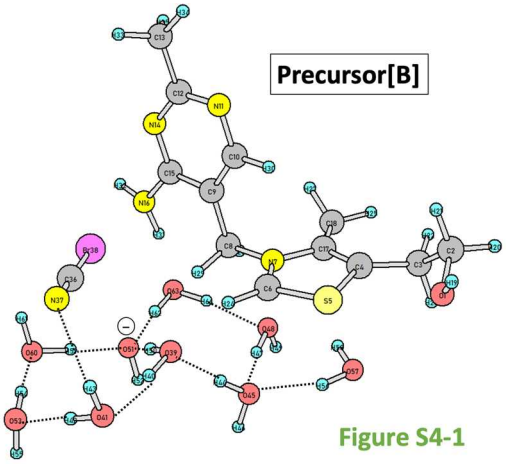


Figure S4-1

$\Delta (E_T+ZPE) = 0$ kcal/mol

$\Delta G° = 0$ kcal/mol

⇩

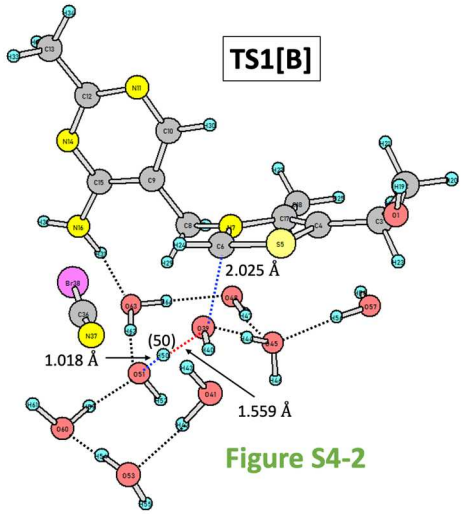


Figure S4-2

$\Delta (E_T+ZPE)^{\ddagger} = +11.46$ kcal/mol

$\Delta G^{\ddagger} = +12.69$ kcal/mol

$\nu^{\ddagger} = 339.5929i$ cm^{-1}

⇩

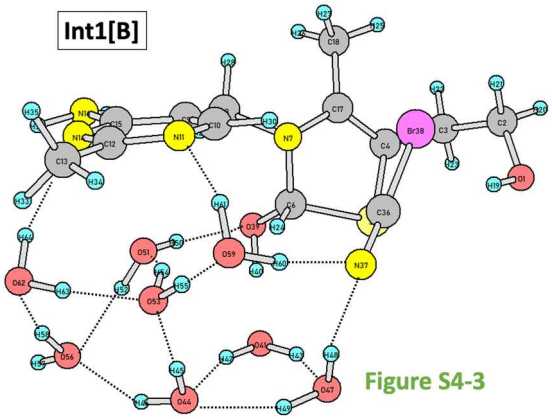


Figure S4-3

$\Delta (E_T+ZPE) = +1.01$ kcal/mol

$\Delta G° = +0.58$ kcal/mol

⇩

TS2[B]

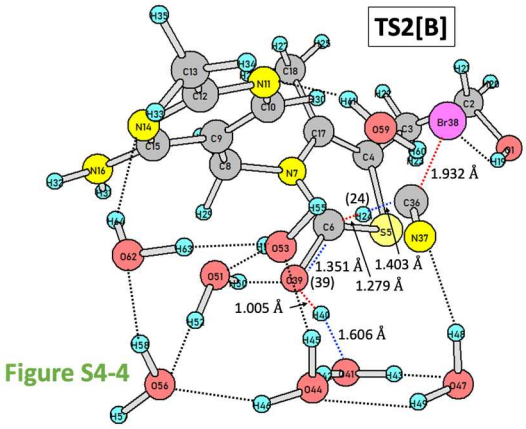


Figure S4-4

$\Delta (E_T+ZPE)^{\ddagger} = +26.76$ kcal/mol

$\Delta G^{\ddagger} = +31.35$ kcal/mol

$\nu^{\ddagger} = 1030.5620i$ cm^{-1}

⇩

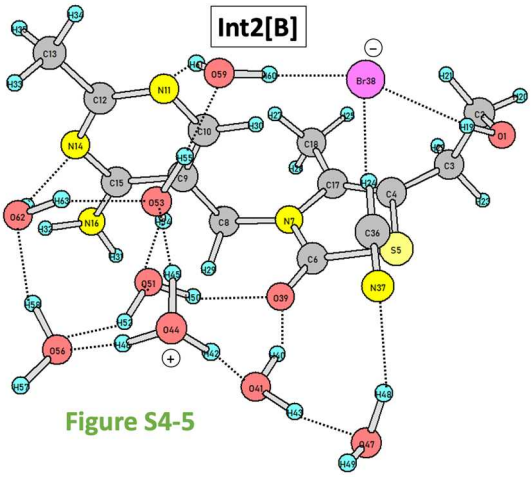


Figure S4-5

$\Delta (E_T+ZPE) = -54.41$ kcal/mol

$\Delta G° = -52.04$ kcal/mol

⇩

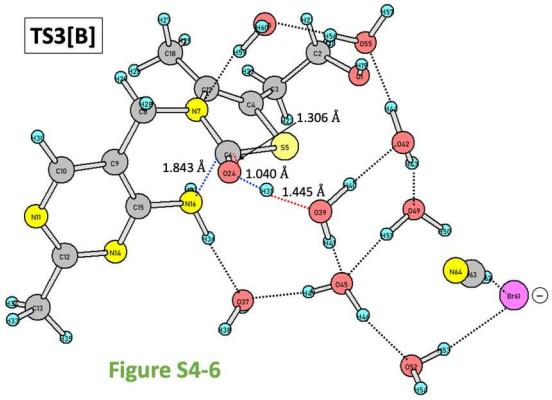


Figure S4-6

$\Delta (E_T+ZPE)^{\ddagger} = -18.75$ kcal/mol

$\Delta G^{\ddagger} = -18.78$ kcal/mol

$\nu^{\ddagger} = 294.4008i$ cm^{-1}

⇩

Int3[B]

(Figure S4 continues)

Int3[B]

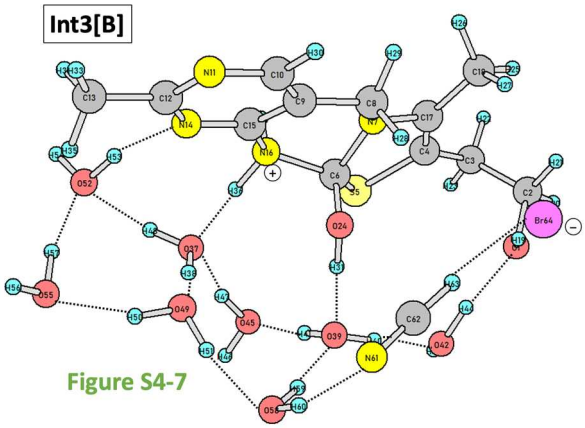


Figure S4-7

Δ (E_T+ZPE) = -21.83 kcal/mol

ΔG°= -19.29 kcal/mol

⇩

TS4[B]

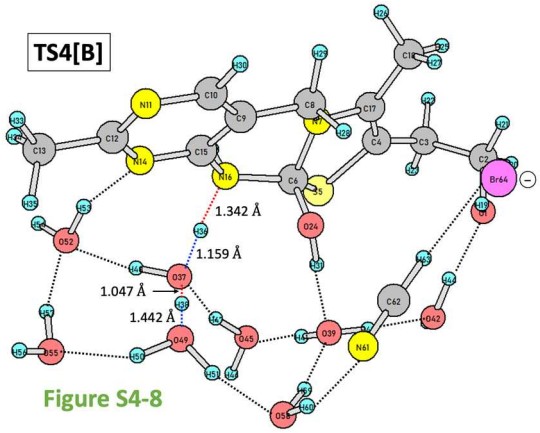


Figure S4-8

Δ (E_T+ZPE)‡ = -21.06 kcal/mol

ΔG‡ = -16.73 kcal/mol

$\nu^‡$ = 735.8292*i* cm^{-1}

⇩

Int4[B]

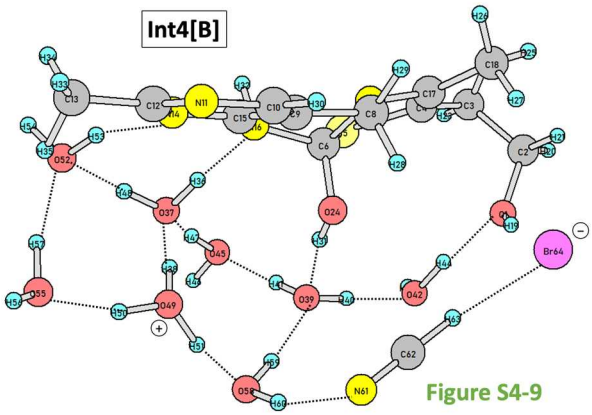


Figure S4-9

Δ (E_T+ZPE) = -23.52 kcal/mol

ΔG°= -19.52 kcal/mol

⇩

TS5[B]

TS5[B]

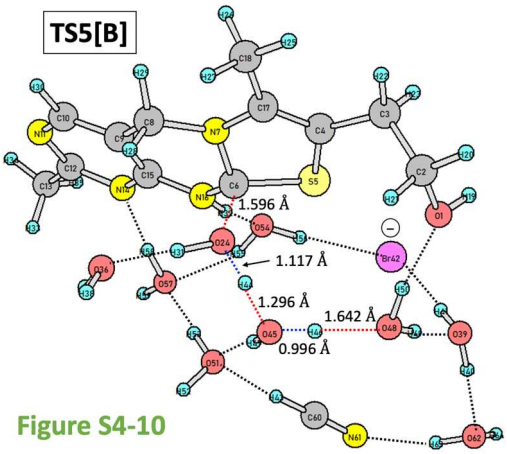


Figure S4-10

Δ (E_T+ZPE)‡ = -22.72 kcal/mol

ΔG‡ = -22.39 kcal/mol

$\nu^‡$ = 428.8141*i* cm^{-1}

⇩

ProductH$^+$[B]

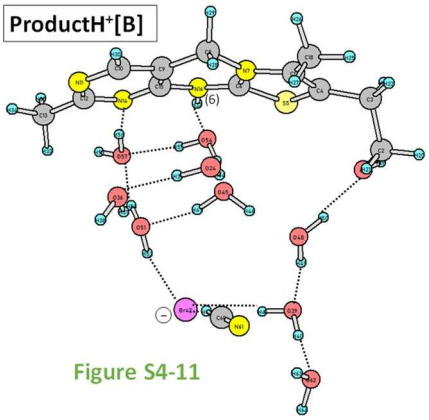
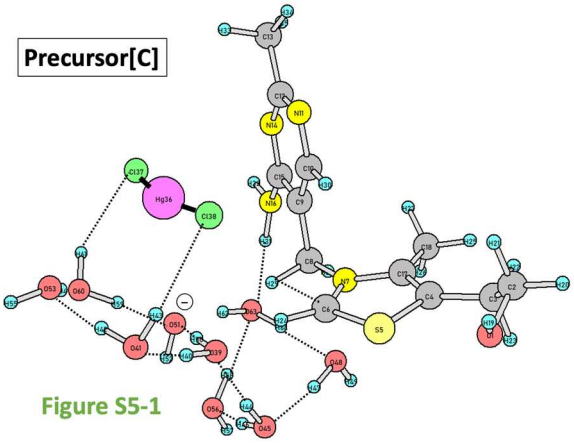


Figure S4-11

Δ (E_T+ZPE) = -48.93 kcal/mol

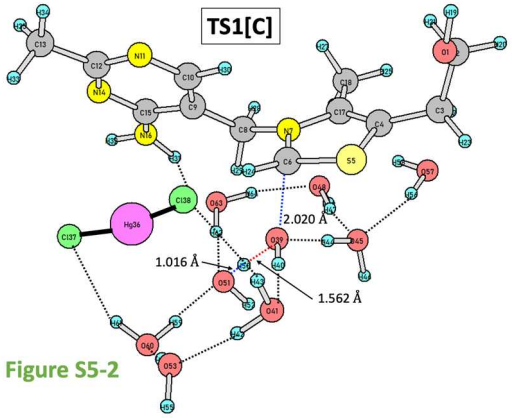
ΔG°= -50.31 kcal/mol

Figure S4. Geometries, Δ(E_T+ZPE)s and ΔGs of species in Scheme 3. They were obtained by RwB97X-D/6-311+G(d,p) SCRF=(PCM, solvent=water) calculations.



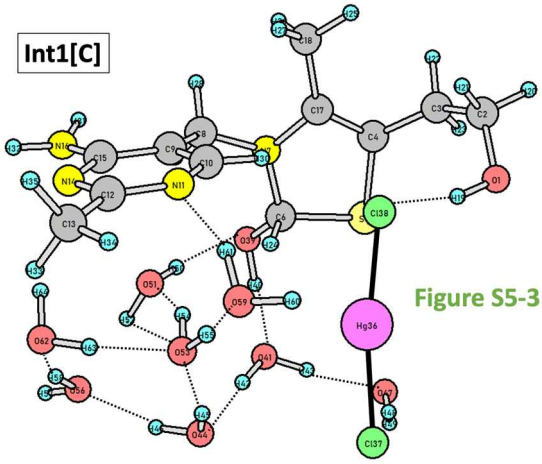
$\Delta(E_T+ZPE)$ = 0 kcal/mol
$\Delta G°$= 0 kcal/mol

⇩



$\Delta(E_T+ZPE)^{‡}$ = +7.21 kcal/mol
$\Delta G^{‡}$ = +10.31 kcal/mol
$\nu^{‡}$ = 345.0405*i* cm^{-1}

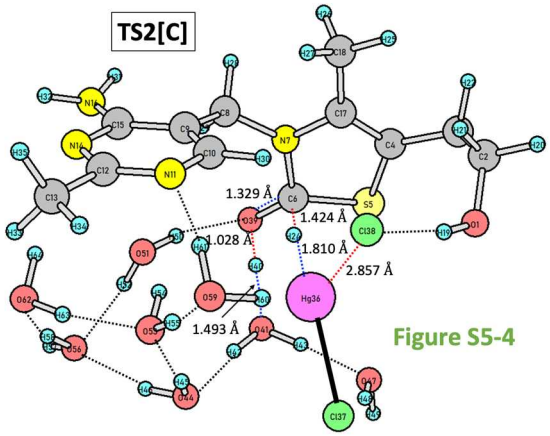
⇩



$\Delta(E_T+ZPE)$ = -4.24 kcal/mol
$\Delta G°$= +1.38 kcal/mol

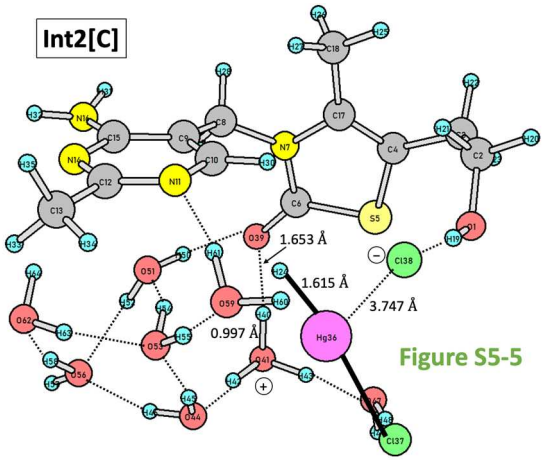
⇩

TS2[C]



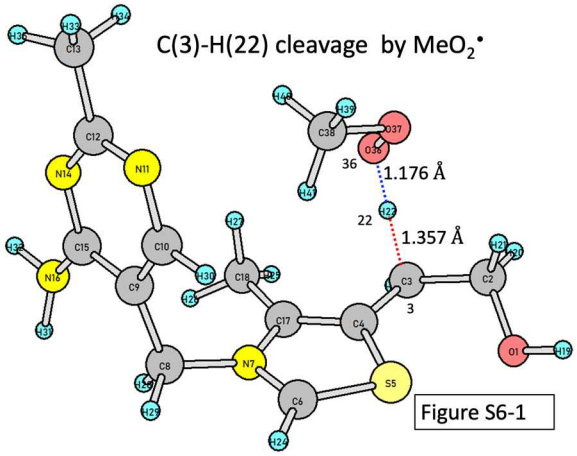
$\Delta(E_T+ZPE)^{‡}$ = +15.51 kcal/mol
$\Delta G^{‡}$ = +23.79 kcal/mol
$\nu^{‡}$ = 870.0093*i* cm^{-1}

⇩



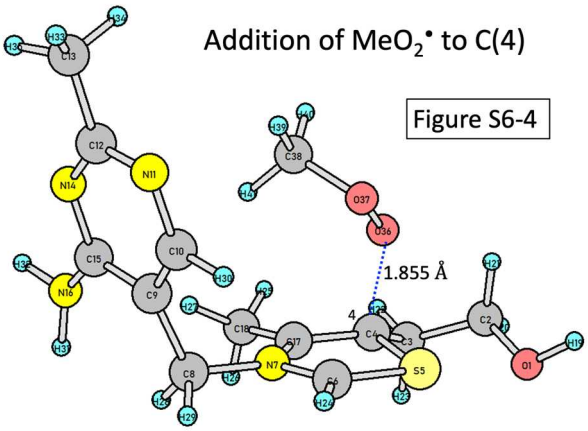
$\Delta(E_T+ZPE)$ = -16.09 kcal/mol
$\Delta G°$= -9.05kcal/mol

Figure S5. Geometries, $\Delta(E_T+ZPE)$s and ΔGs of species in Scheme 4. They were obtained by RwB97X-D/6-311(+)G(d,p)&SDD SCRF=(PCM, solvent=water) calculations.



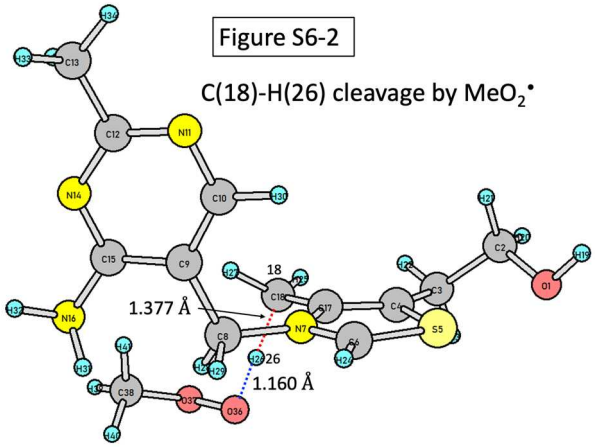
$\Delta (E_T+ZPE)^‡ = +18.54$ kcal/mol

$\nu^‡ = 2179.3899i$ cm^{-1}



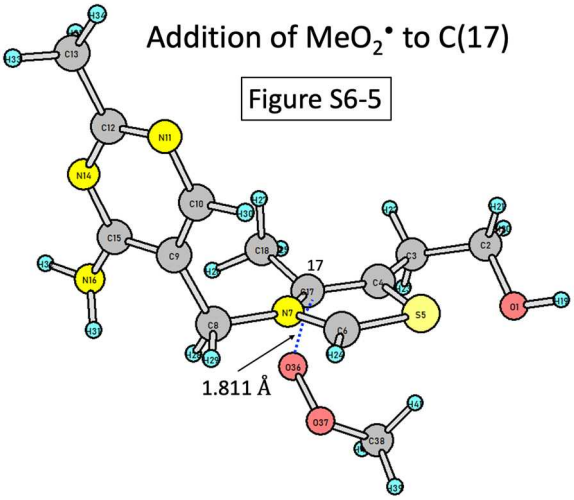
$\Delta (E_T+ZPE)^‡ = +14.58$ kcal/mol

$\nu^‡ = 649.6888i$ cm^{-1}



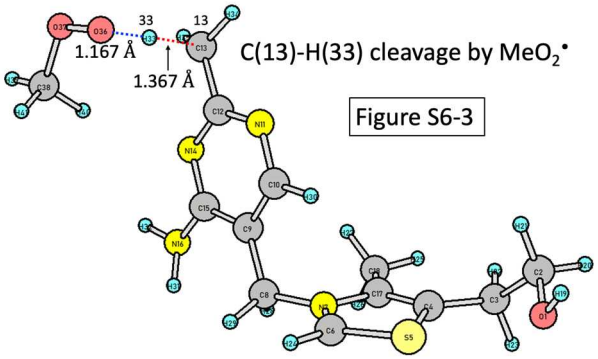
$\Delta (E_T+ZPE)^‡ = +19.54$ kcal/mol

$\nu^‡ = 2167.2841i$ cm^{-1}



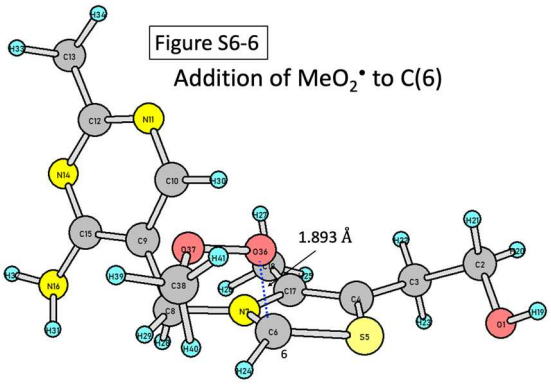
$\Delta (E_T+ZPE)^‡ = +14.12$ kcal/mol

$\nu^‡ = 647.9570i$ cm^{-1}



$\Delta (E_T+ZPE)^‡ = +19.62$ kcal/mol

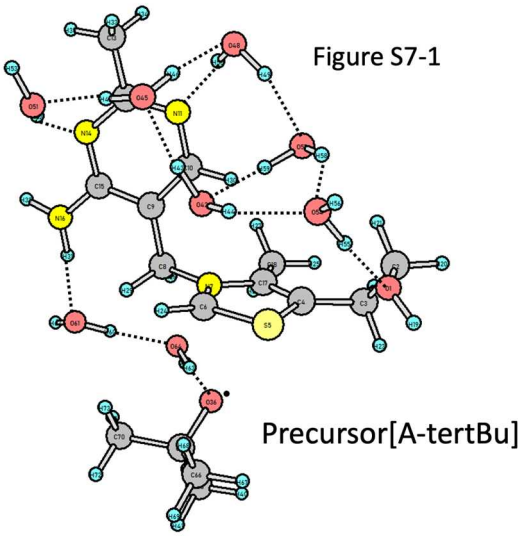
$\nu^‡ = 2124.1337i$ cm^{-1}



$\Delta (E_T+ZPE)^‡ = +12.49$ kcal/mol

$\nu^‡ = 775.2271i$ cm^{-1}

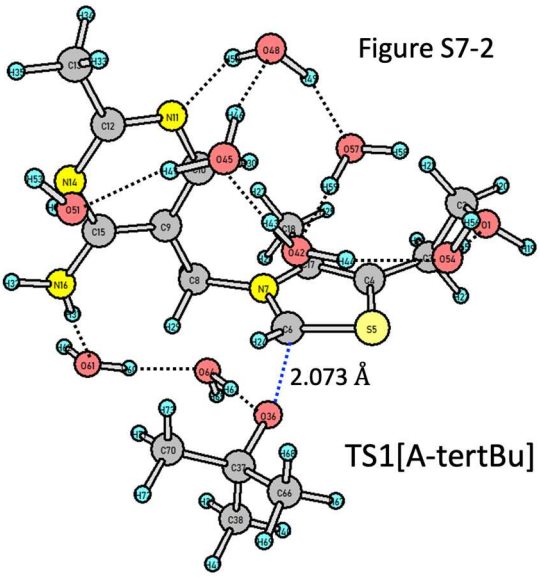
Figure S6. Transition states (TSs) of reactions between thiamine and methyl peroxy radical calculated by uwB97XD/6-31G* with SCRF=(PCM, solvent=water). Figures S6-1 to S6-3 show TSs of the C-H cleavage by the $H_3C\text{-}O_2\cdot$ radical. Figures S6-4 to S6-6 do TSs of the radical addition. Each reaction mode is explained in Scheme S1.



$\Delta (E_T+ZPE) = 0$ kcal/mol

$\Delta G° = 0$ kcal/mol

⇩



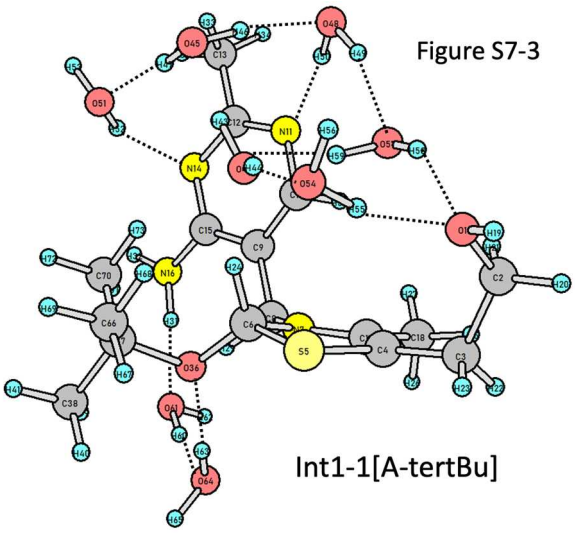
$\Delta (E_T+ZPE)^{‡} = +8.52$ kcal/mol

$\Delta G^{‡} = +12.13$ kcal/mol

$\nu^{‡} = 503.4486i$ cm^{-1}

⇩

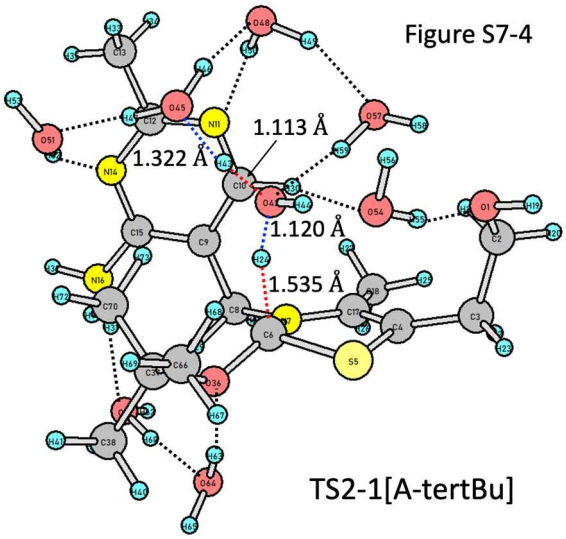
Int1-1[A-tertBu]



$\Delta (E_T+ZPE) = -28.16$ kcal/mol

$\Delta G° = -25.05$ kcal/mol

⇩



$\Delta (E_T+ZPE)^{‡} = -11.69$ kcal/mol

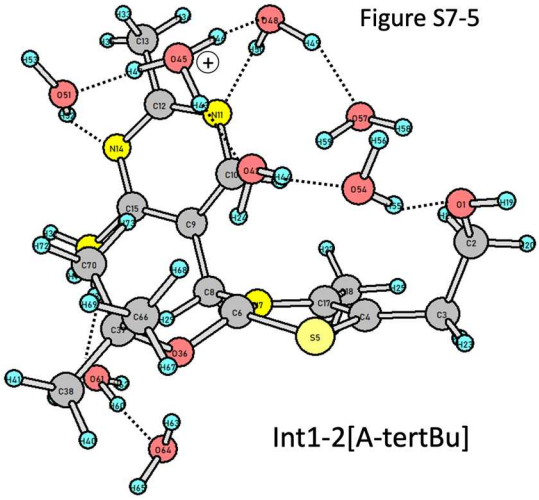
$\Delta G^{‡} = -6.41$ kcal/mol

$\nu^{‡} = 1003.8421i$ cm^{-1}

⇩

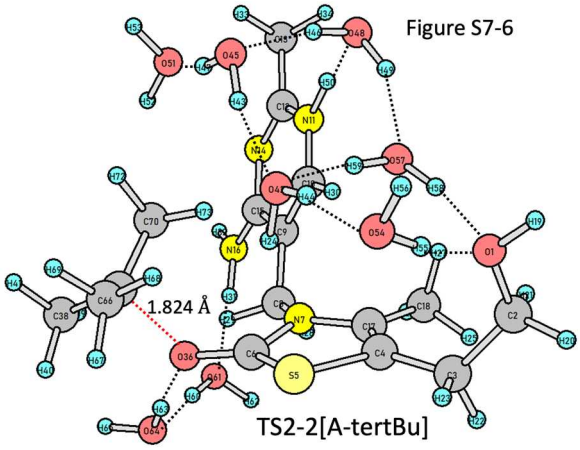
Int1-2[A-tertBu]

(Figure S7 continues)



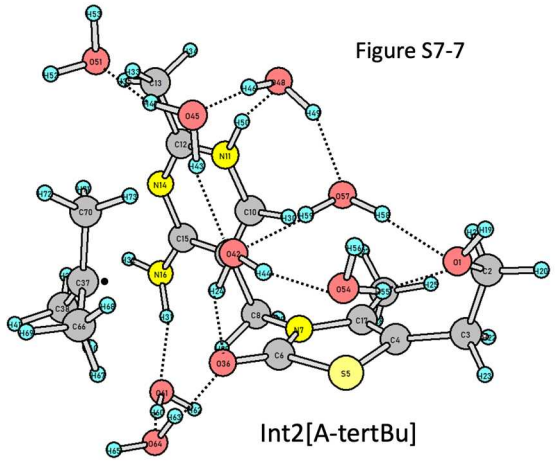
$\Delta (E_T+ZPE)$ = -13.84 kcal/mol
$\Delta G°$= -8.97 kcal/mol

⇩



$\Delta (E_T+ZPE)^{‡}$ = -7.10 kcal/mol
$\Delta G^{‡}$ = -3.82 kcal/mol
$\nu^{‡}$ = 682.1451*i* cm^{-1}

⇩



$\Delta (E_T+ZPE)$ = -36.60 kcal/mol
$\Delta G°$= -35.83 kcal/mol

Figure S7. Geometries optimized with uwB97XD/6-31G* with SCRF=(PCM, solvent=water) in the reaction of thiamine, *tert*-butoxy radical and $(H_2O)_8$ shown in Scheme S2.

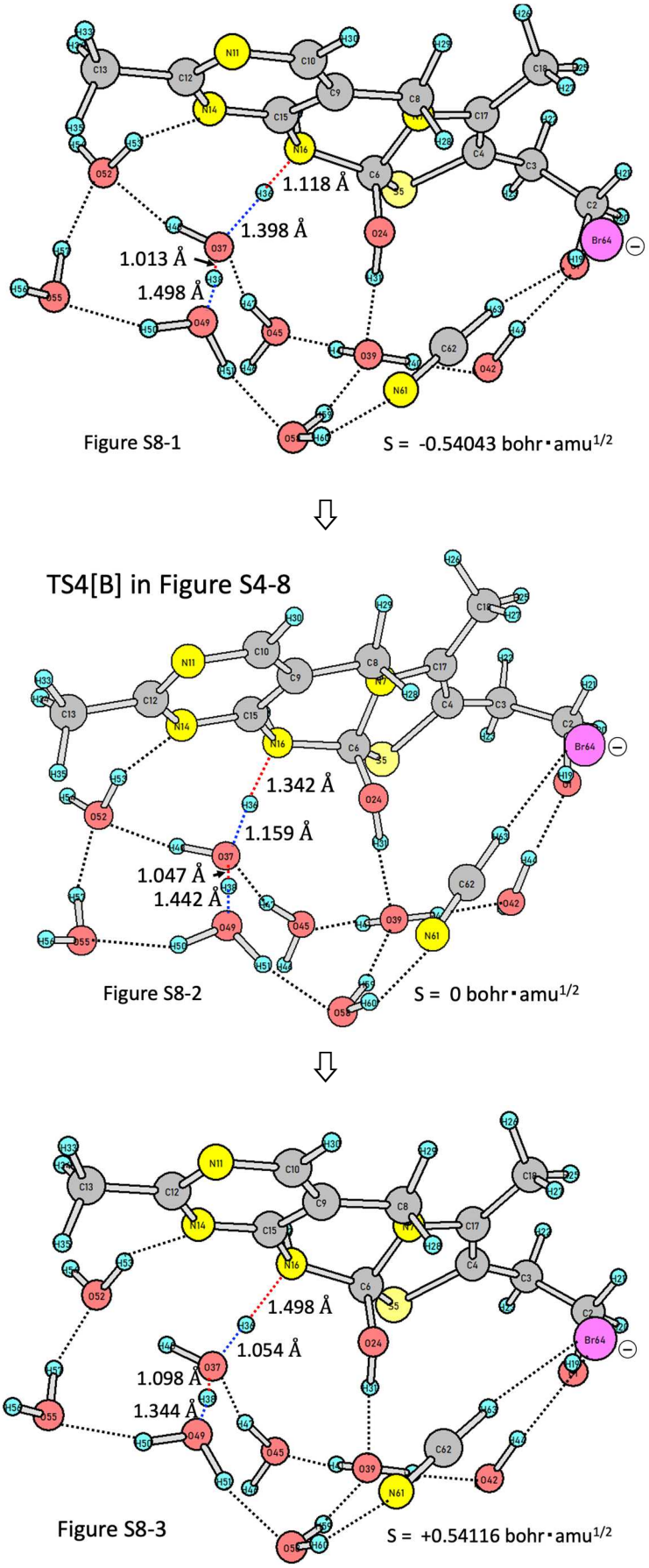


Figure S8. Geometric changes along the intrinsic reaction coordinate (IRC) starting from TS4[B] in Figure S4-8.

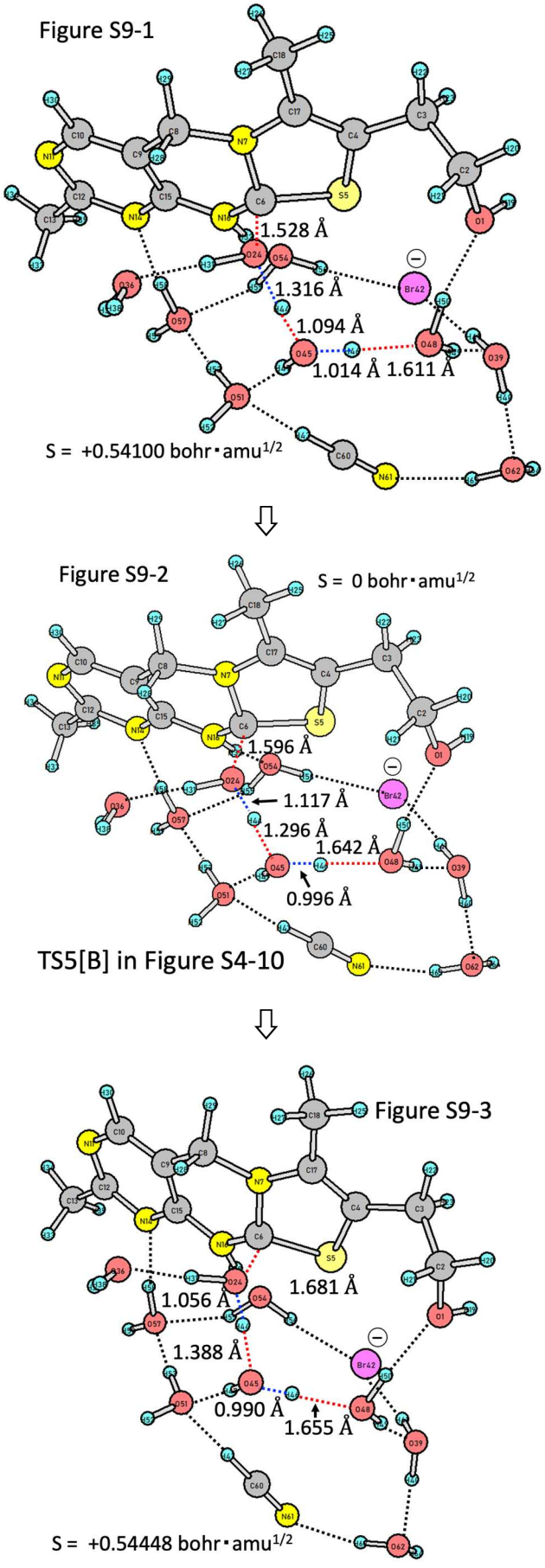
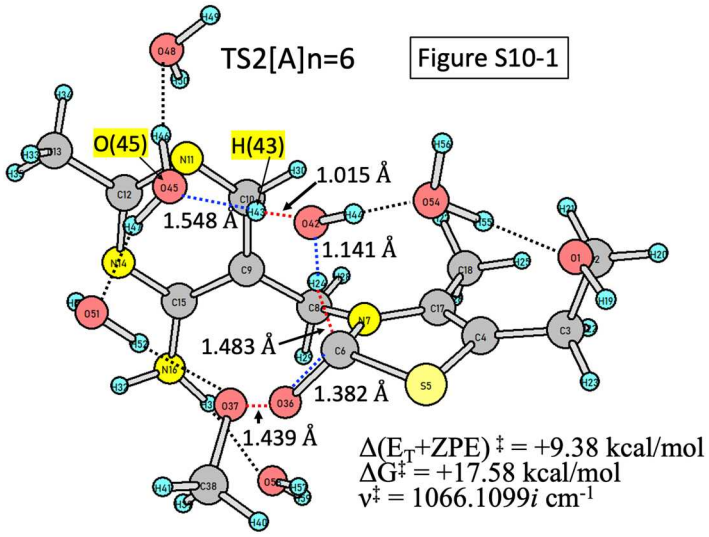
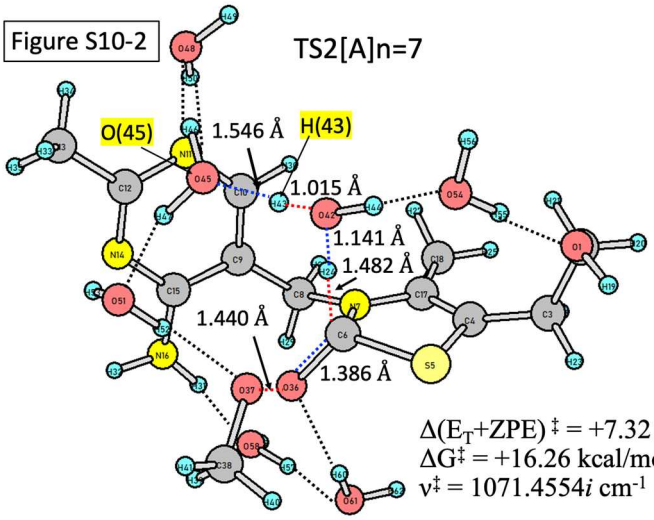
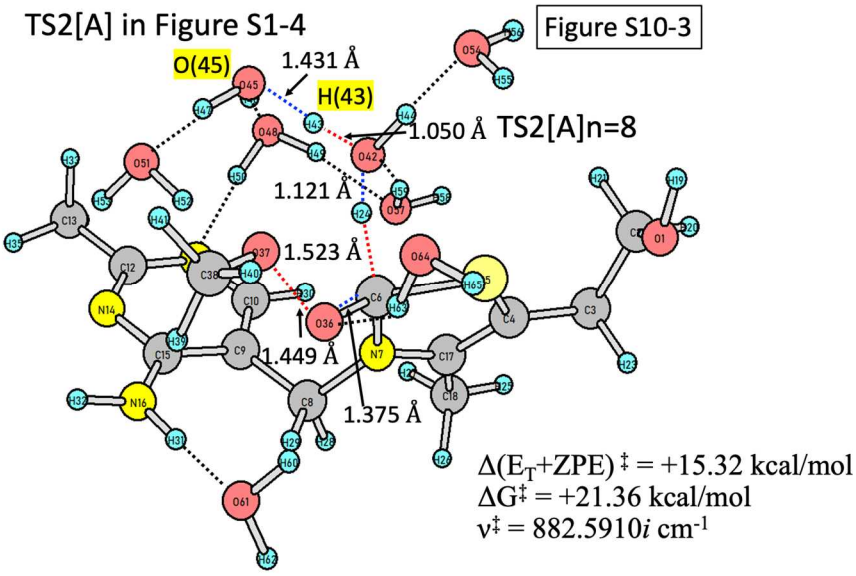


Figure S9. Geometric changes along the intrinsic reaction coordinate (IRC) starting from TS5[B] in Figure S4-10.







(Figure S10 continues)

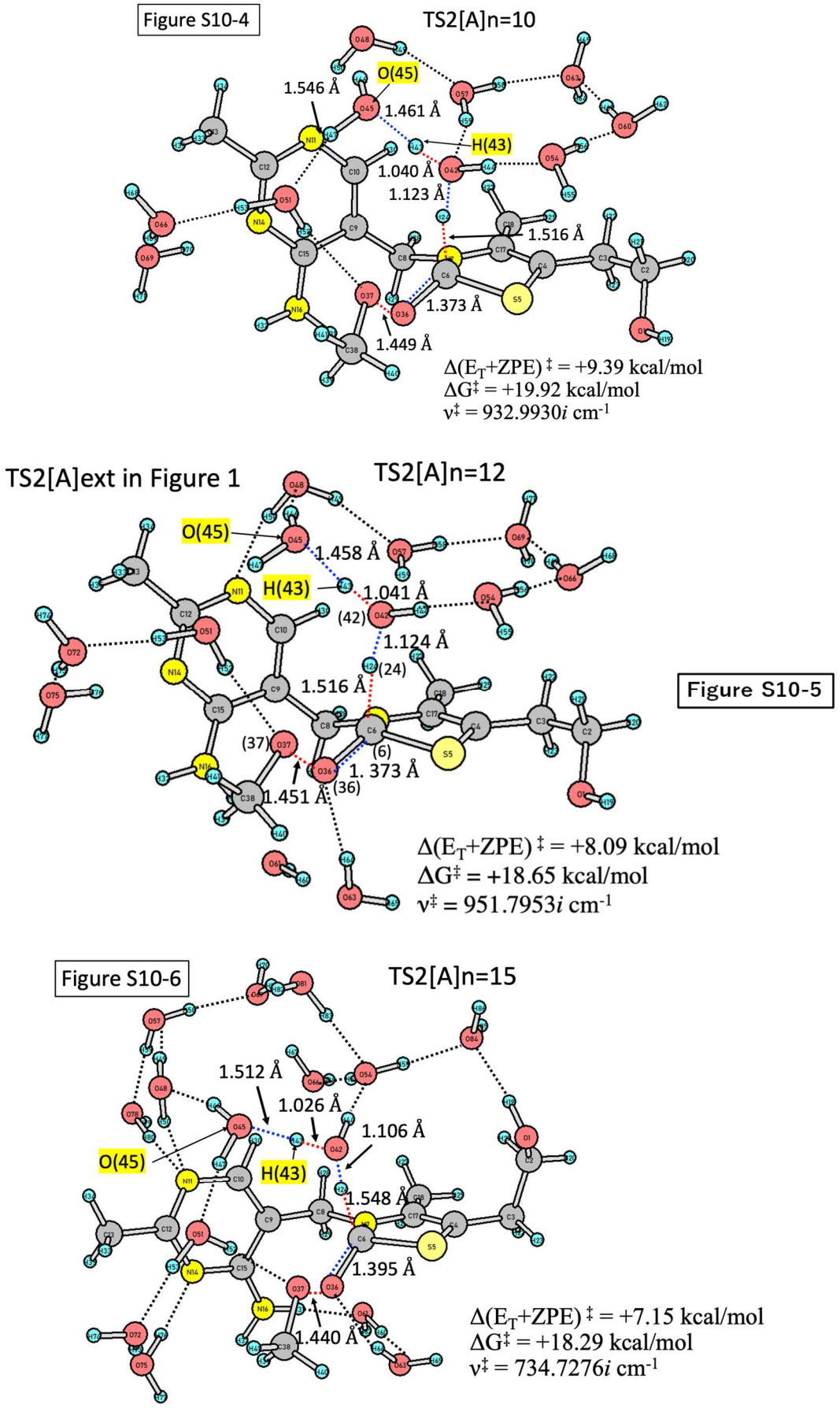


Figure S10. Geometries of TS2[A] in the reaction of thiamine + MeO_2·+ $(H_2O)_n$, n=6, 7, 8, 10, 12 and 15. The n=8 geometry is also shown in Figure S1-4, and the n=12 one is in Figure 1.

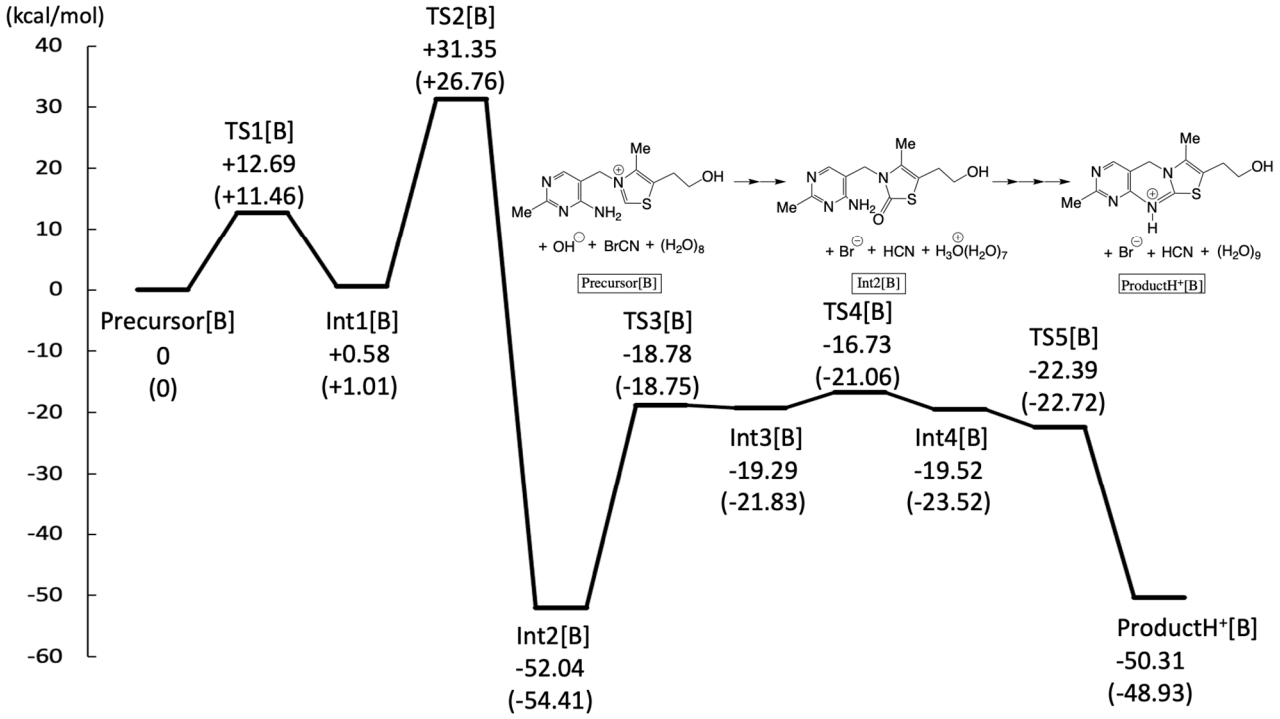


Figure S11. Changes of ΔG and Δ(E_T+ZPE) (in the parenthesis) in reaction [B] which is shown in Scheme 3.

Cartesian coordinates and energies of calculated species

========== Figure 1 ==========

---------Precursor[A]ext----------
thiamine + H3C-O2(.) + (H2O)12 obtained by uwB97x-D/6-311+G(d,p) SCRF=(PCM, solvent=water) calculations.

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Stoichiometry C13H44N4O15S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.063931	-1.245126	2.558676
2	6	0	-3.403848	-2.501789	2.549417
3	6	0	-2.733074	-2.688120	1.200448
4	6	0	-1.691408	-1.659769	0.864643
5	16	0	-1.514978	-0.166827	1.729712
6	6	0	-0.239973	0.292578	0.744155
7	7	0	0.034685	-0.605415	-0.183379
8	6	0	1.141379	-0.366982	-1.143782
9	6	0	2.488591	-0.714255	-0.569050
10	6	0	3.127683	0.193825	0.243934
11	7	0	4.301483	-0.032301	0.845914
12	6	0	4.861197	-1.222541	0.623463
13	6	0	6.137162	-1.540206	1.337529
14	7	0	4.360803	-2.152773	-0.181439
15	6	0	3.193633	-1.919026	-0.809211
16	7	0	2.760405	-2.886383	-1.640118
17	6	0	-0.780022	-1.732378	-0.142425
18	6	0	-0.636230	-2.839582	-1.128463
19	1	0	-4.363378	-1.037245	3.463664
20	1	0	-4.118527	-3.316013	2.702903
21	1	0	-2.661664	-2.543942	3.355247
22	1	0	-2.266480	-3.676148	1.186780
23	1	0	-3.489851	-2.678175	0.409501
24	1	0	0.285568	1.241729	0.795221
25	1	0	-1.448292	-3.551672	-0.998357
26	1	0	-0.694199	-2.467282	-2.154139
27	1	0	0.308637	-3.369411	-0.992076
28	1	0	0.905722	-0.901443	-2.060489
29	1	0	1.113068	0.698103	-1.370844
30	1	0	2.679291	1.167924	0.422474
31	1	0	2.054799	-2.698434	-2.330131
32	1	0	3.388125	-3.662227	-1.821326
33	1	0	6.770622	-2.182613	0.726466
34	1	0	6.671269	-0.626291	1.595197
35	1	0	5.906025	-2.074488	2.263783
36	8	0	-1.847051	0.831725	-2.184103
37	8	0	-1.029312	1.156827	-3.135191
38	6	0	-0.644007	2.553457	-3.080758
39	1	0	-1.543781	3.162444	-3.162959
40	1	0	-0.114327	2.733118	-2.142432
41	1	0	0.007233	2.694057	-3.939984
42	8	0	0.983480	2.908675	-0.136531
43	1	0	1.801876	3.354844	0.152959
44	1	0	0.242076	3.389910	0.273810
45	8	0	3.360488	4.010058	0.744092
46	1	0	3.809075	3.465409	1.409988
47	1	0	4.060129	4.128835	0.083924
48	8	0	5.273705	2.291354	1.922147
49	1	0	5.686940	2.220404	2.784440
50	1	0	4.999801	1.380086	1.650656
51	8	0	5.922990	3.638255	-0.424388
52	1	0	5.974735	3.158428	0.420407
53	1	0	6.634636	4.280720	-0.405399
54	1	0	-3.000535	-0.826693	-2.143002
55	8	0	-3.733992	-1.383055	-1.856635
56	1	0	-4.149664	-0.887392	-1.120849
57	1	0	-4.780294	-2.086158	-3.115163
58	8	0	-5.350042	-2.477706	-3.804475
59	1	0	-5.268270	-3.424984	-3.684251

60	1	0	-2.764128	2.028652	-0.976756
61	8	0	-3.294274	2.426199	-0.270622
62	1	0	-3.910806	3.040998	-0.717006
63	1	0	-4.318940	0.913765	0.201882
64	8	0	-4.804103	0.071308	0.220901
65	1	0	-4.605506	-0.342237	1.078784
66	8	0	-4.818827	-0.742293	5.140398
67	1	0	-4.475947	0.055599	5.550263
68	1	0	-5.754945	-0.759327	5.353815
69	8	0	-1.328384	3.869889	1.067249
70	1	0	-1.564524	4.799456	1.054801
71	1	0	-2.073485	3.401990	0.642920
72	8	0	-5.021108	4.151143	-1.530608
73	1	0	-5.950633	3.910157	-1.535994
74	1	0	-4.996730	5.075099	-1.270317
75	1	0	5.143452	-3.809270	-0.734355
76	8	0	5.221925	-4.601526	-1.299177
77	1	0	5.210847	-5.350032	-0.699564

SCF Done: E(UwB97XD) = -2267.42146141 A.U. after 2 cycles

Zero-point correction= 0.637427 (a.u.)
Thermal correction to Energy= 0.696462
Thermal correction to Enthalpy= 0.697406
Thermal correction to Gibbs Free Energy= 0.529422
Sum of electronic and zero-point Energies= -2266.784035
Sum of electronic and thermal Energies= -2266.724999
Sum of electronic and thermal Enthalpies= -2266.724055
Sum of electronic and thermal Free Energies= -2266.892040

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	437.036	195.853	353.553

Item	Value	Threshold	Converged?
Maximum Force	0.000010	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.008900	0.001800	NO
RMS Displacement	0.001284	0.001200	NO

----------TS2[A]ext----------

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Stoichiometry C13H44N4O15S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-5.210978	2.298185	1.177653
2	6	0	-5.375116	0.953070	0.745058
3	6	0	-4.592279	0.764838	-0.539312
4	6	0	-3.104160	0.938263	-0.414135
5	16	0	-2.339067	1.511570	1.039509
6	6	0	-0.713943	1.061286	0.370931
7	7	0	-0.893084	0.882038	-1.025043
8	6	0	0.230784	1.042837	-1.952849
9	6	0	1.424738	0.196176	-1.597003
10	6	0	1.326807	-1.170513	-1.625684
11	7	0	2.336994	-2.007481	-1.339770
12	6	0	3.495430	-1.438683	-1.019066
13	6	0	4.637105	-2.333977	-0.649864
14	7	0	3.715840	-0.124601	-0.986322
15	6	0	2.702613	0.717872	-1.268049
16	7	0	2.973305	2.028725	-1.215942
17	6	0	-2.188964	0.683630	-1.403298
18	6	0	-2.523620	0.215157	-2.781957
19	1	0	-5.587866	2.387677	2.054908
20	1	0	-6.429977	0.735354	0.548282
21	1	0	-5.022357	0.251684	1.507622
22	1	0	-4.803002	-0.243118	-0.906810
23	1	0	-4.971444	1.467097	-1.289978
24	1	0	-0.612955	-0.350010	0.914789
25	1	0	-3.581431	-0.030518	-2.849286
26	1	0	-2.314959	0.989052	-3.524767
27	1	0	-1.949188	-0.678641	-3.037048

28	1	0	-0.128381	0.767302	-2.942210
29	1	0	0.482079	2.103816	-1.990045
30	1	0	0.379436	-1.641733	-1.879171
31	1	0	2.313199	2.757672	-1.476064
32	1	0	3.917347	2.309722	-1.011541
33	1	0	4.840785	-2.235068	0.419768
34	1	0	4.393469	-3.371785	-0.870424
35	1	0	5.541754	-2.045057	-1.187253
36	8	0	0.291775	1.956113	0.643518
37	8	0	1.187132	1.376151	1.626842
38	6	0	1.904014	2.471783	2.172414
39	1	0	2.465001	2.989656	1.391085
40	1	0	1.229361	3.154117	2.694523
41	1	0	2.592864	2.013770	2.883250
42	8	0	-0.812991	-1.428416	1.161849
43	1	0	-0.006162	-2.000889	1.486405
44	1	0	-1.597437	-1.520947	1.789343
45	8	0	1.071498	-2.914267	1.845482
46	1	0	1.174912	-3.515997	1.077035
47	1	0	1.876652	-2.358217	1.913686
48	8	0	1.066840	-4.347835	-0.500703
49	1	0	0.175166	-4.102000	-0.800222
50	1	0	1.645233	-3.680631	-0.926707
51	8	0	2.853133	-0.954378	2.138588
52	1	0	2.456768	-0.207566	1.675880
53	1	0	3.812939	-0.779862	2.202608
54	8	0	-2.893280	-1.790875	2.629822
55	1	0	-3.179632	-1.063000	3.186208
56	1	0	-3.645178	-2.004541	2.033920
57	8	0	-1.337365	-3.003248	-1.189087
58	1	0	-2.264399	-3.213510	-1.381185
59	1	0	-1.357093	-2.427505	-0.412584
60	1	0	0.672948	4.573144	-1.236626
61	8	0	1.331858	4.297625	-1.901011
62	1	0	0.985692	4.561694	-2.755291
63	8	0	-0.346943	4.752463	0.237299
64	1	0	-0.241673	3.875784	0.628708
65	1	0	-1.293972	4.876581	0.138627
66	8	0	-4.873867	-2.362527	0.880409
67	1	0	-4.627261	-2.768663	0.031383
68	1	0	-5.650989	-2.835793	1.184598
69	8	0	-4.106192	-3.453073	-1.596835
70	1	0	-4.467950	-2.978028	-2.350646
71	1	0	-4.362943	-4.371266	-1.722724
72	8	0	5.533427	-0.435135	2.412482
73	1	0	5.917175	-0.083292	1.582668
74	1	0	6.099352	-1.161308	2.681691
75	8	0	6.286553	0.487969	-0.033440
76	1	0	5.406915	0.376479	-0.459647
77	1	0	6.545650	1.402009	-0.165426

SCF Done: E(UwB97XD) = -2267.40686894 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-951.7953	19.7083	24.7631

Zero-point correction= 0.635731 (a.u.)
Thermal correction to Energy= 0.689958
Thermal correction to Enthalpy= 0.690902
Thermal correction to Gibbs Free Energy= 0.544550
Sum of electronic and zero-point Energies= -2266.771138
Sum of electronic and thermal Energies= -2266.716911
Sum of electronic and thermal Enthalpies= -2266.715967
Sum of electronic and thermal Free Energies= -2266.862319

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	432.955	189.159	308.024

Item	Value	Threshold	Converged?
Maximum Force	0.000024	0.000450	YES
RMS Force	0.000003	0.000300	YES
Maximum Displacement	0.001015	0.001800	YES
RMS Displacement	0.000213	0.001200	YES

----------Precursor [B]ext ----------

thiamine + Br-CN + HO(-) + (H2O)12 obtained by rwB97x-D/
6-311+G(d,p) SCRF=(PCM, solvent=water) calculations.

vita-b1brcng3x.for.high.log

Stoichiometry C13H42BrN5O14S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-6.927806	0.689484	1.663831
2	6	0	-6.900973	0.050832	0.394435
3	6	0	-5.899982	0.796393	-0.475255
4	6	0	-4.487310	0.683021	0.008373
5	16	0	-4.038199	1.187310	1.608946
6	6	0	-2.428153	0.818645	1.312568
7	7	0	-2.241941	0.329068	0.102252
8	6	0	-0.931644	-0.178387	-0.343046
9	6	0	-0.844018	-1.677166	-0.190463
10	6	0	-1.143516	-2.280145	1.013201
11	7	0	-1.098808	-3.596512	1.233726
12	6	0	-0.721246	-4.339833	0.189632
13	6	0	-0.622397	-5.820854	0.403022
14	7	0	-0.394586	-3.878649	-1.012435
15	6	0	-0.440540	-2.551452	-1.228329
16	7	0	-0.110936	-2.134962	-2.466556
17	6	0	-3.395622	0.241639	-0.671127
18	6	0	-3.302255	-0.260081	-2.072179
19	1	0	-7.374450	0.120727	2.293393
20	1	0	-7.887092	0.091285	-0.079334
21	1	0	-6.604336	-0.998837	0.494163
22	1	0	-5.960958	0.406533	-1.491826
23	1	0	-6.187308	1.851251	-0.521504
24	1	0	-1.611650	0.914442	2.024265
25	1	0	-4.288666	-0.309066	-2.527255
26	1	0	-2.678870	0.409867	-2.670158
27	1	0	-2.865510	-1.260680	-2.102089
28	1	0	-0.785499	0.147553	-1.369901
29	1	0	-0.181896	0.320884	0.269011
30	1	0	-1.446750	-1.670044	1.860818
31	1	0	0.134780	-1.168226	-2.693587
32	1	0	0.232340	-2.848483	-3.089788
33	1	0	0.368744	-6.060947	0.800410
34	1	0	-1.363806	-6.153750	1.129347
35	1	0	-0.750277	-6.356942	-0.536872
36	6	0	2.532083	-2.405876	1.065972
37	7	0	2.460650	-3.350520	1.722272
38	35	0	2.642847	-0.928274	0.055747
39	8	0	1.589704	2.411014	0.646672
40	1	0	2.423101	2.565626	1.122675
41	8	0	4.092742	1.968129	1.862192
42	1	0	4.760554	1.847146	1.156901
43	1	0	3.796733	1.080281	2.111796
44	1	0	0.494344	3.515960	-0.075727
45	8	0	-0.181984	3.987627	-0.613451
46	1	0	0.171801	4.862438	-0.787956
47	1	0	-0.738148	3.034483	-2.068644
48	8	0	-1.202331	2.473204	-2.719783
49	1	0	-1.425788	3.054912	-3.450255
50	1	0	1.895997	1.920014	-0.178896
51	8	0	2.496661	1.326994	-1.532556
52	1	0	2.715645	2.197500	-1.876978
53	8	0	5.948047	1.561337	-0.152189
54	1	0	5.613343	1.175186	-0.985990
55	1	0	6.504069	2.299564	-0.408733
56	1	0	-2.067830	3.848174	-0.355948
57	8	0	-3.001197	3.651846	-0.527072
58	1	0	-2.962650	3.108526	-1.319826
59	1	0	3.859509	0.679070	-2.046476
60	8	0	4.763821	0.419785	-2.409636
61	1	0	4.831459	-0.535377	-2.342276
62	1	0	1.393586	0.805442	-2.531657
63	8	0	0.737154	0.478799	-3.225358
64	1	0	0.050005	1.164598	-3.246437
65	1	0	3.110375	-0.851965	3.902566
66	8	0	2.846933	0.012676	3.581032
67	1	0	3.218343	0.669125	4.200058
68	1	0	1.085182	0.447906	3.023603

69	8	0	0.335306	0.892546	2.599045
70	1	0	0.754588	1.457904	1.923442
71	1	0	2.216428	0.516183	-4.431665
72	8	0	3.070921	0.531474	-4.893647
73	1	0	3.726952	0.540781	-4.183835
74	1	0	4.251675	2.453819	3.685397
75	8	0	4.095247	2.242978	4.621963
76	1	0	3.590499	2.977247	4.977512

SCF Done: E(RwB97XD) = -4820.18216636 A.U. after 1 cycles

Zero-point correction= 0.616817 (a.u.)
Thermal correction to Energy= 0.674211
Thermal correction to Enthalpy= 0.675155
Thermal correction to Gibbs Free Energy= 0.516435
Sum of electronic and zero-point Energies= -4819.565349
Sum of electronic and thermal Energies= -4819.507955
Sum of electronic and thermal Enthalpies= -4819.507011
Sum of electronic and thermal Free Energies= -4819.665731

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	423.074	196.285	334.055

Item	Value	Threshold	Converged?
Maximum Force	0.000049	0.000450	YES
RMS Force	0.000005	0.000300	YES
Maximum Displacement	0.003140	0.001800	NO
RMS Displacement	0.000392	0.001200	YES

----------TS2[B]ext----------

vita-b1brcnfx.high.log

Stoichiometry C13H42BrN5O14S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-5.283170	1.027512	-1.641000
2	6	0	-5.275192	-0.297170	-1.133735
3	6	0	-4.394422	-1.194247	-2.002554
4	6	0	-2.925995	-0.929649	-1.867327
5	16	0	-2.336366	0.740903	-1.828311
6	6	0	-0.671947	0.162971	-1.440071
7	7	0	-0.641438	-1.213285	-1.684911
8	6	0	0.612069	-1.887385	-1.984027
9	6	0	1.469095	-2.189500	-0.779476
10	6	0	1.015319	-2.131367	0.509290
11	7	0	1.799025	-2.298351	1.591039
12	6	0	3.088559	-2.531934	1.351817
13	6	0	4.000458	-2.708987	2.528641
14	7	0	3.639082	-2.642377	0.144025
15	6	0	2.847539	-2.490736	-0.923648
16	7	0	3.421556	-2.660809	-2.131105
17	6	0	-1.906247	-1.808160	-1.805412
18	6	0	-1.991591	-3.299168	-1.874033
19	1	0	-4.988891	1.644267	-0.951621
20	1	0	-6.296151	-0.692115	-1.146462
21	1	0	-4.925142	-0.312471	-0.095555
22	1	0	-4.596406	-2.236343	-1.745110
23	1	0	-4.702996	-1.057374	-3.045446
24	1	0	-0.583445	0.356449	-0.184574
25	1	0	-3.019000	-3.630271	-1.736498
26	1	0	-1.651329	-3.669439	-2.845064
27	1	0	-1.377929	-3.764290	-1.097937
28	1	0	0.382755	-2.799588	-2.536419
29	1	0	1.170219	-1.242616	-2.669854
30	1	0	-0.032542	-1.928401	0.707744
31	1	0	2.941156	-2.441818	-2.985869
32	1	0	4.424130	-2.744558	-2.170055
33	1	0	4.976996	-2.270618	2.321175
34	1	0	3.575873	-2.257024	3.424057
35	1	0	4.145337	-3.776833	2.717221
36	6	0	-0.501849	0.733439	1.174902
37	7	0	0.364847	1.399764	1.604853
38	35	0	-2.122916	-0.116435	1.783182

39	8	0	0.380660	0.852009	-1.935613
40	1	0	0.354240	1.821327	-1.629194
41	8	0	0.423196	3.271766	-1.108681
42	1	0	1.200722	3.305367	-0.510463
43	1	0	-0.360307	3.455463	-0.553010
44	8	0	2.619997	3.367266	0.580378
45	1	0	2.464744	2.645695	1.204942
46	1	0	3.464967	3.130913	0.160533
47	8	0	-1.758423	3.743137	0.535704
48	1	0	-1.482861	3.403061	1.390692
49	1	0	-2.659179	3.395223	0.400387
50	1	0	2.118538	0.586697	-1.227159
51	8	0	2.971874	0.425284	-0.804746
52	1	0	3.548477	1.171993	-1.032771
53	8	0	3.424072	0.738381	1.898590
54	1	0	3.011898	0.524528	1.039913
55	1	0	2.858755	0.342961	2.583399
56	8	0	4.966685	2.314071	-0.642532
57	1	0	5.566677	2.723637	-1.290748
58	1	0	5.444423	1.575637	-0.223831
59	8	0	1.572343	-0.458350	3.715785
60	1	0	0.900169	0.174475	3.440859
61	1	0	1.482117	-1.205732	3.088127
62	8	0	5.739367	-0.063756	0.701366
63	1	0	5.022507	0.151432	1.329815
64	1	0	5.373964	-0.796997	0.193026
65	8	0	-4.441711	2.862035	0.333636
66	1	0	-4.683963	2.481549	1.203645
67	1	0	-4.984798	3.649459	0.240596
68	8	0	6.652984	3.489858	-2.510274
69	1	0	6.280616	3.651790	-3.380406
70	1	0	7.077856	4.312972	-2.257418
71	1	0	-3.361769	-2.333450	0.479284
72	8	0	-4.002353	-2.952683	0.842521
73	1	0	-3.467151	-3.638835	1.247789
74	1	0	-4.449897	1.678376	3.384929
75	8	0	-5.160837	1.788565	2.748379
76	1	0	-5.593268	0.932258	2.697317

SCF Done: E(RwB97XD) = -4820.13378960 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-1001.2203	-43.4572	-16.8293

Zero-point correction= 0.612636 (a.u.)
Thermal correction to Energy= 0.667933
Thermal correction to Enthalpy= 0.668878
Thermal correction to Gibbs Free Energy= 0.520096
Sum of electronic and zero-point Energies= -4819.521153
Sum of electronic and thermal Energies= -4819.465856
Sum of electronic and thermal Enthalpies= -4819.464912
Sum of electronic and thermal Free Energies= -4819.613694

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	419.135	190.903	313.138

Item	Value	Threshold	Converged?
Maximum Force	0.000240	0.000450	YES
RMS Force	0.000030	0.000300	YES
Maximum Displacement	0.012297	0.001800	NO
RMS Displacement	0.001928	0.001200	NO

---------Precursor[C]ext---------------------------------
thiamine + HgCl2 + HO(-) + (H2O)12 obtained by
rwB97x-D/6-311(+)G(d,p)&SDD SCRF=(PCM, solvent=water) calculations.

vita-b1hgcl2g3.revx.pcmhigh.log

Stoichiometry C12H42Cl2HgN4O14S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	8	0	6.105248	-0.370310	-2.556889
2	6	0	6.467714	-0.498423	-1.193492
3	6	0	5.895354	0.707033	-0.459776
4	6	0	4.398040	0.718435	-0.424779
5	16	0	3.461483	0.787691	-1.889121
6	6	0	2.030938	0.791582	-1.011078
7	7	0	2.239952	0.725763	0.286638
8	6	0	1.140907	0.610580	1.256074
9	6	0	1.037731	-0.789810	1.804050
10	6	0	1.458186	-1.901801	1.102777
11	7	0	1.378270	-3.151612	1.561927
12	6	0	0.880713	-3.280262	2.792830
13	6	0	0.735507	-4.670533	3.333196
14	7	0	0.473629	-2.287975	3.577849
15	6	0	0.512087	-1.044716	3.091971
16	7	0	0.079763	-0.055484	3.915262
17	6	0	3.581616	0.696156	0.660071
18	6	0	3.944392	0.707515	2.105441
19	1	0	6.230962	-1.205434	-3.007594
20	1	0	7.558100	-0.507167	-1.080046
21	1	0	6.063133	-1.421939	-0.761973
22	1	0	6.275468	0.714940	0.563009
23	1	0	6.265683	1.615963	-0.943343
24	1	0	1.030062	0.841551	-1.442112
25	1	0	5.018828	0.591187	2.232980
26	1	0	3.640755	1.666406	2.533032
27	1	0	3.446478	-0.102169	2.642558
28	1	0	1.336589	1.341741	2.042117
29	1	0	0.228061	0.920322	0.741553
30	1	0	1.883033	-1.797764	0.106941
31	1	0	-0.349234	0.782858	3.529316
32	1	0	-0.359174	-0.406093	4.752520
33	1	0	-0.286694	-5.014190	3.147756
34	1	0	1.423310	-5.348056	2.828945
35	1	0	0.901102	-4.680472	4.410651
36	80	0	-1.453792	-1.941545	-0.820928
37	17	0	-2.443349	-2.105053	1.333993
38	17	0	0.359819	-2.032227	-2.373481
39	8	0	-0.768742	1.427153	-1.819073
40	1	0	-1.167008	1.043175	-2.638131
41	8	0	-1.917104	0.155055	-3.879538
42	1	0	-2.526583	-0.394217	-3.322491
43	1	0	-1.255592	-0.470214	-4.185600
44	1	0	-0.651577	3.118810	-1.534630
45	8	0	-0.626288	4.036605	-1.180858
46	1	0	-1.559026	4.290703	-1.104235
47	1	0	-0.284214	4.210711	0.565307
48	8	0	-0.169205	4.319061	1.531589
49	1	0	-0.885692	4.895428	1.820995
50	1	0	-1.405415	1.264871	-1.097156
51	8	0	-2.402844	1.422945	0.347669
52	1	0	-2.699269	2.334689	0.144255
53	8	0	-3.274595	-1.294643	-2.115251
54	1	0	-4.163859	-0.510534	-1.134623
55	1	0	-3.728862	-2.051712	-2.490192
56	8	0	-2.897048	4.509389	2.568290
57	1	0	-3.452245	4.852801	3.268676
58	1	0	-2.559687	3.641804	2.866141
59	1	0	-3.195529	0.859527	0.209170
60	8	0	-4.615635	0.050015	-0.413120
61	1	0	-4.897489	-0.570219	0.262641
62	1	0	-1.808313	1.723304	2.003422
63	8	0	-1.397239	2.182062	2.763185
64	1	0	-0.786662	2.819394	2.346513
65	1	0	-5.284293	1.657918	-0.782955
66	8	0	-5.472041	2.602034	-0.956073
67	1	0	-5.884693	2.635265	-1.819113
68	1	0	1.185341	4.339079	-1.349791
69	8	0	2.140023	4.179496	-1.265436
70	1	0	2.570036	4.878956	-1.757379
71	1	0	1.742851	3.960479	1.787779
72	8	0	2.546739	3.521176	1.483675
73	1	0	2.577323	3.759274	0.544896
74	1	0	-3.365770	4.326295	0.733333
75	8	0	-3.257437	3.993241	-0.171615
76	1	0	-4.131642	3.691439	-0.489540

SCF Done: E(RwB97XD) = -3227.28068629 A.U. after 16 cycles
NFock= 16 Conv=0.16D-08 -V/T= 2.0362

Zero-point correction= 0.620171 (a.u.)
Thermal correction to Energy= 0.675782
Thermal correction to Enthalpy= 0.676726
Thermal correction to Gibbs Free Energy= 0.524116
Sum of electronic and zero-point Energies= -3226.660515
Sum of electronic and thermal Energies= -3226.604904
Sum of electronic and thermal Enthalpies= -3226.603960
Sum of electronic and thermal Free Energies= -3226.756570

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	424.060	192.548	321.196

Item	Value	Threshold	Converged?
Maximum Force	0.000020	0.000450	YES
RMS Force	0.000004	0.000300	YES
Maximum Displacement	0.012062	0.001800	NO
RMS Displacement	0.001996	0.001200	NO

----------TS2[C]ext----------

vita-b1hgcl2fx.pcmhigh.log

Stoichiometry C12H42Cl2HgN4O14S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.850732	-0.977727	0.915200
2	6	0	-4.803357	-2.304453	0.430225
3	6	0	-4.508358	-2.358840	-1.073046
4	6	0	-3.140299	-1.867147	-1.436747
5	16	0	-2.900307	-0.204622	-1.956921
6	6	0	-1.124946	-0.414921	-1.876173
7	7	0	-0.871075	-1.769813	-1.793621
8	6	0	0.482830	-2.287466	-1.914119
9	6	0	1.259254	-2.363943	-0.616145
10	6	0	0.669145	-2.342349	0.626140
11	7	0	1.339362	-2.501931	1.776983
12	6	0	2.645596	-2.705196	1.675261
13	6	0	3.430939	-2.845162	2.942421
14	7	0	3.327915	-2.735635	0.527734
15	6	0	2.663513	-2.550249	-0.619973
16	7	0	3.381602	-2.580755	-1.775063
17	6	0	-1.979513	-2.546085	-1.426318
18	6	0	-1.799137	-3.998620	-1.126647
19	1	0	-4.005800	-0.764414	1.351616
20	1	0	-5.779491	-2.761627	0.616533
21	1	0	-4.048648	-2.871578	0.984359
22	1	0	-4.629188	-3.391232	-1.415916
23	1	0	-5.264815	-1.768517	-1.598235
24	1	0	-0.795168	0.093598	-0.594580
25	1	0	-2.733224	-4.424430	-0.764829
26	1	0	-1.505334	-4.550383	-2.024777
27	1	0	-1.038878	-4.167261	-0.361170
28	1	0	0.426257	-3.282710	-2.362727
29	1	0	0.996402	-1.657704	-2.636920
30	1	0	-0.398152	-2.171470	0.738800
31	1	0	3.084509	-1.901687	-2.466463
32	1	0	4.384361	-2.572756	-1.633148
33	1	0	3.778311	-1.855361	3.253910
34	1	0	2.797799	-3.243393	3.734110
35	1	0	4.298017	-3.489122	2.793527
36	80	0	-0.737301	1.018166	0.948558
37	17	0	0.025365	2.898007	2.247573
38	17	0	-2.075612	-0.743107	2.274282
39	8	0	-0.340828	0.303995	-2.666639
40	1	0	-0.381185	1.328420	-2.440807
41	8	0	-0.294640	2.707836	-2.098127
42	1	0	0.578049	2.941413	-1.693330
43	1	0	-0.988360	2.992470	-1.473405
44	8	0	2.079724	3.151990	-0.961105
45	1	0	2.185367	2.614270	-0.162760
46	1	0	2.881783	2.957586	-1.472587
47	8	0	-2.242607	2.999047	-0.200439

```
    48        1          0      -2.132224    3.654098    0.494430
    49        1          0      -3.184685    3.024113   -0.488473
    50        1          0       1.611579    0.406819   -2.574947
    51        8          0       2.485687    0.110604   -2.298205
    52        1          0       3.115134    0.812327   -2.538152
    53        8          0       2.772410    0.819399    0.560567
    54        1          0       2.481355    0.312797   -0.211277
    55        1          0       2.346177    0.472094    1.367623
    56        8          0       4.385064    2.059475   -2.227228
    57        1          0       5.106979    2.605278   -2.555759
    58        1          0       4.801910    1.574163   -1.485486
    59        8          0       1.615668    0.017714    2.939093
    60        1          0       1.114663    0.692301    3.406518
    61        1          0       1.124636   -0.815413    2.985432
    62        8          0       5.456692    0.823705   -0.019558
    63        1          0       4.591645    0.842500    0.430104
    64        1          0       5.715844   -0.113857   -0.053758
    65        8          0      -4.766515    3.062363   -1.072305
    66        1          0      -4.904318    3.262629   -1.998200
    67        1          0      -5.312678    2.271992   -0.875343
    68        8          0       7.005555    2.828002   -1.278391
    69        1          0       7.310377    3.586714   -0.781428
    70        1          0       6.659292    2.203725   -0.623149
    71        1          0       5.104919   -2.341891    0.357053
    72        8          0       5.907773   -1.945119   -0.048192
    73        1          0       6.670301   -2.369554    0.345271
    74        1          0      -5.715083    0.214522    0.047290
    75        8          0      -6.222559    0.847478   -0.504967
    76        1          0      -7.049437    0.991347   -0.043543
 ---------------------------------------------------------------------

SCF Done:  E(RwB97XD) =  -3227.24413940    A.U. after   16 cycles

 Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering
                     1                  2                  3
                    A                  A                  A
 Frequencies --   -577.6023            20.8879            25.6580

 Zero-point correction=                          0.615056 (a.u.)
 Thermal correction to Energy=                    0.669986
 Thermal correction to Enthalpy=                  0.670931
 Thermal correction to Gibbs Free Energy=         0.522619
 Sum of electronic and zero-point Energies=         -3226.629083
 Sum of electronic and thermal Energies=            -3226.574153
 Sum of electronic and thermal Enthalpies=          -3226.573208
 Sum of electronic and thermal Free Energies=       -3226.721520

                  E (Thermal)             CV              S
                   KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total               420.423           191.644           312.149

        Item             Value     Threshold  Converged?
 Maximum Force           0.000020    0.000450     YES
 RMS     Force           0.000004    0.000300     YES
 Maximum Displacement    0.014557    0.001800     NO
 RMS     Displacement    0.001184    0.001200     YES
 Predicted change in Energy=-2.963298D-07


 ==================Figure S1 and scheme 2=======================

 obtained by uwB97x-D/6-311+G(d,p) SCRF=(PCM, solvent=water)
  calculations

 -----Figure S1-1, precursor[A], thiamine + H3C-O2(.) + (H2O)8-----
  vita-b106e.rev.high.log

 Stoichiometry   C13H36N4O11S(1+,2)

                    Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic           Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
     1          8           0        3.823011    1.191305    1.139043
     2          6           0        3.564200    2.580573    1.241592
     3          6           0        2.959521    3.157312   -0.041185
     4          6           0        1.613269    2.594312   -0.371799
     5         16           0        1.475402    0.953578   -0.970703
     6          6           0       -0.219487    1.114181   -1.060269
```

7	7	0	-0.632419	2.309512	-0.670257
8	6	0	-2.050819	2.693540	-0.693556
9	6	0	-2.913292	1.465644	-0.709343
10	6	0	-4.229251	1.454340	-0.308141
11	7	0	-4.992284	0.353989	-0.343981
12	6	0	-4.425052	-0.761897	-0.793709
13	6	0	-5.253253	-2.006926	-0.850710
14	7	0	-3.140757	-0.867774	-1.166172
15	6	0	-2.405279	0.233050	-1.113074
16	7	0	-1.063964	0.129790	-1.440170
17	6	0	0.397137	3.169226	-0.263305
18	6	0	0.052635	4.533906	0.226240
19	1	0	4.501742	1.026891	0.461409
20	1	0	4.484698	3.124921	1.475314
21	1	0	2.870154	2.708002	2.074212
22	1	0	2.873545	4.239710	0.071241
23	1	0	3.649390	2.987035	-0.873438
24	8	0	-1.439613	1.177596	2.024638
25	1	0	0.957711	5.110768	0.402536
26	1	0	-0.558156	5.073248	-0.500901
27	1	0	-0.498234	4.478121	1.168499
28	1	0	-2.258184	3.282426	0.197712
29	1	0	-2.222744	3.311722	-1.578474
30	1	0	-4.698365	2.357589	0.069789
31	1	0	-2.277864	0.725418	2.191879
32	1	0	-0.653401	-0.809386	-1.545492
33	1	0	-4.941889	-2.694660	-0.058985
34	1	0	-6.305547	-1.767321	-0.712913
35	1	0	-5.111627	-2.513948	-1.806611
36	8	0	-3.842013	-0.441841	2.482075
37	1	0	-4.607729	-0.252639	1.928383
38	1	0	-4.166600	-0.415269	3.386392
39	8	0	5.479570	0.368586	-0.944114
40	6	0	5.770602	-0.946845	-0.783803
41	1	0	6.117478	-1.175570	0.234652
42	1	0	4.790977	-1.480890	-0.862954
43	1	0	6.438768	-1.343457	-1.556190
44	1	0	-0.815404	0.453320	1.850078
45	8	0	0.093733	-1.117903	1.474158
46	1	0	0.997835	-1.205497	1.847214
47	1	0	-0.520559	-1.745545	1.903219
48	8	0	2.752246	-1.259234	1.958954
49	1	0	2.957864	-1.785352	1.162401
50	1	0	3.089162	-0.368767	1.759893
51	8	0	-2.073830	-2.671475	2.065527
52	1	0	-2.765515	-1.996712	2.152161
53	1	0	-2.184010	-3.054870	1.180188
54	8	0	0.353050	-2.230881	-0.981358
55	1	0	-0.309298	-2.940950	-1.015100
56	1	0	0.283149	-1.886691	-0.061089
57	8	0	-2.107669	-3.463828	-0.681196
58	1	0	-2.521624	-2.655330	-1.044434
59	1	0	-2.564274	-4.212526	-1.071341
60	8	0	3.078457	-2.658361	-0.435371
61	1	0	3.335892	-3.595998	-0.388965
62	1	0	2.174931	-2.636091	-0.793845
63	8	0	3.861639	-5.331509	-0.280494
64	1	0	4.614310	-5.589425	-0.817940
65	1	0	4.048737	-5.670280	0.598274

```
---------------------------------------------------------------------
Standard basis: 6-311+G(d,p) (6D, 7F)
  891 basis functions
  123 alpha electrons     122 beta electrons
     nuclear repulsion energy     3633.0807142581 Hartrees.
NAtoms=   65 NActive=   65

Force inversion solution in PCM.
-----------------------------------------------------
Polarizable Continuum Model (PCM)
=================================
Model              : PCM.
Solvent : Water, Eps=  78.355300 Eps(inf)=   1.777849
-----------------------------------------------------

SCF Done:  E(UwB97XD) =  -1961.71516090 A.U. after 2 cycles

Zero-point correction=                        0.538896 (a.u.)
Thermal correction to Energy=                  0.583534
Thermal correction to Enthalpy=                0.584478
Thermal correction to Gibbs Free Energy=       0.457258
```

Sum of electronic and zero-point Energies= -1961.176265
Sum of electronic and thermal Energies= -1961.131627
Sum of electronic and thermal Enthalpies= -1961.130683
Sum of electronic and thermal Free Energies= -1961.257902

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	366.173	155.827	267.757

Item	Value	Threshold	Converged?
Maximum Force	0.000005	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.002582	0.001800	NO
RMS Displacement	0.000318	0.001200	YES

-------Figure S1-2, TS1[A], Me-O2(.) addition to C(6) of thiamine---
vita-b10h.high.log

Stoichiometry C13H36N4O11S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.018936	-1.020996	1.443587
2	6	0	-3.833741	-2.424330	1.526985
3	6	0	-3.354168	-3.039123	0.208466
4	6	0	-1.994769	-2.574792	-0.209783
5	16	0	-1.790007	-0.977506	-0.907187
6	6	0	-0.087247	-1.208508	-1.025295
7	7	0	0.256970	-2.423154	-0.577679
8	6	0	1.633503	-2.902784	-0.736837
9	6	0	2.554144	-1.716931	-0.764601
10	6	0	3.878299	-1.778825	-0.409401
11	7	0	4.706068	-0.728653	-0.508602
12	6	0	4.184263	0.408088	-0.963631
13	6	0	5.087737	1.597080	-1.081200
14	7	0	2.899449	0.584609	-1.288709
15	6	0	2.073775	-0.463393	-1.182318
16	7	0	0.741943	-0.254379	-1.439076
17	6	0	-0.808893	-3.207903	-0.111974
18	6	0	-0.526364	-4.571101	0.422127
19	1	0	-4.712782	-0.822737	0.791232
20	1	0	-4.767356	-2.912573	1.825734
21	1	0	-3.093317	-2.594578	2.310584
22	1	0	-3.343856	-4.125385	0.320237
23	1	0	-4.083024	-2.818262	-0.577725
24	1	0	-1.454471	-5.074850	0.683258
25	1	0	-0.003027	-5.183749	-0.315591
26	1	0	0.089884	-4.516946	1.323165
27	1	0	1.880327	-3.564678	0.091897
28	1	0	1.697109	-3.476117	-1.667349
29	1	0	4.308268	-2.700205	-0.028188
30	1	0	4.879995	2.298038	-0.267454
31	1	0	6.130680	1.292392	-1.019398
32	1	0	4.914542	2.116200	-2.025080
33	8	0	3.755993	0.758005	2.542281
34	1	0	4.677027	0.534046	2.307029
35	1	0	3.271526	-0.067923	2.480787
36	8	0	-5.731390	-0.221409	-0.615688
37	6	0	-5.942439	1.118692	-0.570614
38	1	0	-6.220456	1.461791	0.436725
39	1	0	-4.942077	1.582966	-0.749432
40	1	0	-6.630396	1.478423	-1.343494
41	8	0	-0.175093	1.407350	1.412752
42	1	0	-1.058548	1.460990	1.849611
43	1	0	0.515953	1.959710	1.840021
44	8	0	-2.762885	1.418736	2.010850
45	1	0	-2.999447	1.887476	1.187968
46	1	0	-3.119276	0.520163	1.895313
47	8	0	2.057815	2.830078	1.870793
48	1	0	2.745936	2.161857	2.052850
49	1	0	2.195252	3.108832	0.952880
50	8	0	-0.247664	2.017797	-0.931879
51	1	0	0.450399	2.705255	-1.069859
52	1	0	-0.254771	1.799156	0.147009
53	8	0	2.073190	3.230095	-1.001910
54	1	0	2.456825	2.364023	-1.274327
55	1	0	2.456846	3.910823	-1.559341

56	8	0	-3.107604	2.660945	-0.462346
57	1	0	-3.285957	3.619880	-0.469365
58	1	0	-2.255542	2.543350	-0.898837
59	8	0	-3.641504	5.378345	-0.456326
60	1	0	-4.483181	5.657607	-0.824640
61	1	0	-3.575075	5.821802	0.392765
62	1	0	0.177240	1.110575	-1.303372
63	8	0	6.291670	-0.013186	1.695660
64	1	0	5.978957	-0.415852	0.861904
65	1	0	6.731566	-0.713475	2.182209

SCF Done: E(UwB97XD) = -1961.69703564 A.U. after 2 cycles
Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

1	2	3
A	A	A
Frequencies -- -272.1149	14.2035	16.9723

Zero-point correction= 0.533049 (a.u.)
Thermal correction to Energy= 0.576632
Thermal correction to Enthalpy= 0.577576
Thermal correction to Gibbs Free Energy= 0.451805
Sum of electronic and zero-point Energies= -1961.163986
Sum of electronic and thermal Energies= -1961.120403
Sum of electronic and thermal Enthalpies= -1961.119459
Sum of electronic and thermal Free Energies= -1961.245230

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	361.842	151.770	264.707

Item	Value	Threshold	Converged?
Maximum Force	0.000030	0.000450	YES
RMS Force	0.000003	0.000300	YES
Maximum Displacement	0.005109	0.001800	NO
RMS Displacement	0.001087	0.001200	YES

-------Figure S1-3, Int1[A], MeO2 adduct---------
vita-b105a.for.high.log

Stoichiometry C13H36N4O11S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	5.104494	-0.084721	-2.155907
2	6	0	4.131719	-0.167949	-3.189800
3	6	0	2.960379	-0.982987	-2.673983
4	6	0	2.175526	-0.356605	-1.567347
5	16	0	2.203008	1.329701	-1.245140
6	6	0	1.025754	1.151645	0.128076
7	7	0	0.639488	-0.249400	0.133285
8	6	0	-0.353436	-0.703438	1.123085
9	6	0	-1.642912	-1.177010	0.502678
10	6	0	-2.426522	-0.308923	-0.224596
11	7	0	-3.593817	-0.649956	-0.780038
12	6	0	-3.994889	-1.914303	-0.590789
13	6	0	-5.306600	-2.303071	-1.202424
14	7	0	-3.332635	-2.830228	0.096792
15	6	0	-2.157700	-2.487582	0.663026
16	7	0	-1.540835	-3.449598	1.365692
17	6	0	1.274178	-1.038279	-0.730796
18	6	0	0.994952	-2.493643	-0.796494
19	1	0	5.808239	0.510983	-2.421827
20	1	0	4.547272	-0.674107	-4.065028
21	1	0	3.811976	0.833144	-3.500367
22	1	0	2.277307	-1.180713	-3.508638
23	1	0	3.332752	-1.955206	-2.339368
24	1	0	0.154656	1.798736	-0.028076
25	1	0	1.683777	-2.997367	-1.468523
26	1	0	1.076348	-2.942494	0.195964
27	1	0	-0.022275	-2.653805	-1.163821
28	1	0	0.118562	-1.469339	1.735270
29	1	0	-0.539581	0.145363	1.779352
30	1	0	-2.106468	0.720426	-0.377263
31	1	0	-0.632346	-3.349269	1.808725
32	1	0	-1.984229	-4.353027	1.394927
33	1	0	-6.112081	-1.720698	-0.747149
34	1	0	-5.303404	-2.079065	-2.271355

35	1	0	-5.502758	-3.362769	-1.051713
36	8	0	1.698357	1.518604	1.314337
37	8	0	0.746777	2.016627	2.258367
38	6	0	0.736062	3.439725	2.170895
39	1	0	1.725882	3.845064	2.387829
40	1	0	0.372097	3.766403	1.193769
41	1	0	0.030543	3.739832	2.946390
42	8	0	-1.229189	3.045598	-0.718501
43	1	0	-2.180582	3.254453	-0.611496
44	1	0	-0.998513	3.357344	-1.595899
45	8	0	-3.906189	3.567698	-0.563285
46	1	0	-4.336032	2.917997	-1.144996
47	1	0	-4.361946	3.409833	0.276488
48	8	0	-5.317815	1.348861	-1.481970
49	1	0	-5.881398	1.138257	-2.228468
50	1	0	-4.705418	0.579673	-1.345999
51	8	0	-5.757729	2.217052	1.136029
52	1	0	-5.873253	1.809077	0.260976
53	1	0	-6.621883	2.549335	1.385814
54	1	0	2.547276	-0.453663	2.392954
55	8	0	2.850721	-1.327578	2.134051
56	1	0	3.597445	-1.164957	1.519615
57	1	0	1.853425	-2.731974	2.467024
58	8	0	1.126225	-3.374566	2.582895
59	1	0	1.535176	-4.230305	2.723944
60	1	0	3.654076	2.107232	1.563753
61	8	0	4.617596	2.070094	1.547198
62	1	0	4.897785	2.288733	2.439095
63	1	0	4.979176	0.382053	0.932175
64	8	0	4.969349	-0.539264	0.616742
65	1	0	4.985023	-0.468823	-0.350787

SCF Done: E(UwB97XD) = -1961.62300431 A.U. after 2 cycles

Zero-point correction= 0.538330 (a.u.)
Thermal correction to Energy= 0.584036
Thermal correction to Enthalpy= 0.584980
Thermal correction to Gibbs Free Energy= 0.453836
Sum of electronic and zero-point Energies= -1961.084675
Sum of electronic and thermal Energies= -1961.038969
Sum of electronic and thermal Enthalpies= -1961.038025
Sum of electronic and thermal Free Energies= -1961.169169

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	366.488	157.399	276.016

Item	Value	Threshold	Converged?
Maximum Force	0.000041	0.000450	YES
RMS Force	0.000005	0.000300	YES
Maximum Displacement	0.009047	0.001800	NO
RMS Displacement	0.001732	0.001200	NO

----Figure S1-4, TS2[A], MeO and methine-proton dissociation------
vita-b103a.high.log

Stoichiometry C13H36N4O11S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	5.442566	0.663798	0.691858
2	6	0	4.976031	1.556845	-0.310993
3	6	0	4.272941	0.738572	-1.381610
4	6	0	2.960887	0.147480	-0.958708
5	16	0	2.717030	-0.463680	0.655850
6	6	0	0.945240	-0.643524	0.324060
7	7	0	0.785666	-0.577491	-1.079465
8	6	0	-0.391209	-1.162813	-1.730446
9	6	0	-1.697756	-0.550795	-1.294045
10	6	0	-1.966726	0.771536	-1.552270
11	7	0	-3.121234	1.380489	-1.246661
12	6	0	-4.039573	0.624514	-0.642794
13	6	0	-5.320799	1.291339	-0.243422
14	7	0	-3.890634	-0.657542	-0.327710
15	6	0	-2.733904	-1.273563	-0.651233
16	7	0	-2.635426	-2.563810	-0.298954

17	6	0	1.847660	-0.024369	-1.740710
18	6	0	1.730537	0.329203	-3.188157
19	1	0	5.734521	1.172727	1.450447
20	1	0	5.815082	2.092101	-0.767252
21	1	0	4.286423	2.294491	0.115312
22	1	0	4.112523	1.383118	-2.247237
23	1	0	4.949618	-0.061437	-1.703525
24	1	0	0.502504	0.716015	0.849574
25	1	0	2.590600	0.909846	-3.512238
26	1	0	1.688465	-0.569431	-3.808577
27	1	0	0.833335	0.922702	-3.375166
28	1	0	-0.265133	-1.025837	-2.801859
29	1	0	-0.370462	-2.237602	-1.548569
30	1	0	-1.211137	1.400780	-2.017747
31	1	0	-1.873917	-3.175038	-0.584227
32	1	0	-3.456183	-2.991434	0.098349
33	1	0	-5.181780	1.801326	0.715201
34	1	0	-5.604030	2.042928	-0.980480
35	1	0	-6.118490	0.558905	-0.129006
36	8	0	0.349422	-1.764766	0.850574
37	8	0	-0.375111	-1.392145	2.049302
38	6	0	-0.538804	-2.600419	2.777765
39	1	0	-1.102312	-3.327976	2.189286
40	1	0	0.430926	-3.000351	3.080837
41	1	0	-1.113035	-2.308008	3.657307
42	8	0	0.398597	1.805019	1.092984
43	1	0	-0.542482	2.076545	1.471890
44	1	0	1.114120	2.064103	1.737889
45	8	0	-1.826486	2.528423	1.914037
46	1	0	-2.200157	3.060173	1.175611
47	1	0	-2.381153	1.733754	2.050341
48	8	0	-2.469692	3.934098	-0.343153
49	1	0	-1.575480	3.969908	-0.721707
50	1	0	-2.873691	3.171389	-0.806492
51	8	0	-2.854800	0.036935	2.382563
52	1	0	-2.058779	-0.458995	2.138141
53	1	0	-3.542309	-0.318687	1.806283
54	8	0	2.300533	2.465901	2.785878
55	1	0	3.000521	1.809883	2.849568
56	1	0	2.741606	3.306329	2.635039
57	8	0	0.131166	3.345359	-1.325813
58	1	0	0.848115	3.903897	-1.633113
59	1	0	0.474653	2.869207	-0.557070
60	1	0	0.217886	-4.552489	-0.666103
61	8	0	-0.665581	-4.527631	-1.078217
62	1	0	-0.560043	-4.870796	-1.967408
63	1	0	1.478640	-3.439068	0.729894
64	8	0	1.690284	-4.297622	0.343072
65	1	0	2.535618	-4.178609	-0.096581

SCF Done: E(UwB97XD) = -1961.58827203 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-882.5910	14.7040	22.9021

Zero-point correction= 0.534015 (a.u.)
Thermal correction to Energy= 0.577804
Thermal correction to Enthalpy= 0.578748
Thermal correction to Gibbs Free Energy= 0.454902
Sum of electronic and zero-point Energies= -1961.054257
Sum of electronic and thermal Energies= -1961.010468
Sum of electronic and thermal Enthalpies= -1961.009524
Sum of electronic and thermal Free Energies= -1961.133370

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	362.577	153.550	260.655

Item	Value	Threshold	Converged?
Maximum Force	0.000014	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.008986	0.001800	NO
RMS Displacement	0.001096	0.001200	YES

--------Figure S1-5, Int2[A], ketone intermediate----------
vita-b104c3.rev.high.log

Stoichiometry C13H36N4O11S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-3.492047	2.499313	2.125251
2	6	0	-4.444480	2.600397	1.083351
3	6	0	-3.848548	3.152643	-0.217616
4	6	0	-2.684578	2.362991	-0.726920
5	16	0	-2.935820	0.789113	-1.483858
6	6	0	-1.203779	0.549006	-1.662554
7	7	0	-0.551947	1.645150	-1.203485
8	6	0	0.895960	1.789544	-1.393481
9	6	0	1.746074	1.600615	-0.165068
10	6	0	2.627644	2.578928	0.237812
11	7	0	3.485917	2.452728	1.259225
12	6	0	3.467112	1.283081	1.893159
13	6	0	4.451497	1.057973	2.999114
14	7	0	2.652079	0.265346	1.604422
15	6	0	1.777430	0.410102	0.598768
16	7	0	0.939774	-0.623199	0.373354
17	6	0	-1.373107	2.651408	-0.659157
18	6	0	-0.736919	3.870415	-0.079984
19	1	0	-3.033919	1.656473	2.036864
20	1	0	-5.223459	3.284413	1.425322
21	1	0	-4.923389	1.631016	0.900830
22	1	0	-4.639853	3.187453	-0.973086
23	1	0	-3.529962	4.183143	-0.052041
24	8	0	-0.675933	-0.471783	-2.120314
25	1	0	-1.495231	4.533512	0.329073
26	1	0	-0.051932	3.603871	0.727767
27	1	0	-0.175838	4.424775	-0.836440
28	1	0	1.174765	1.072469	-2.164506
29	1	0	1.084152	2.777657	-1.812906
30	1	0	2.658815	3.524914	-0.297118
31	1	0	-0.968066	-2.302201	-1.402202
32	1	0	1.148779	-1.483764	0.857191
33	1	0	5.205546	0.335292	2.673738
34	1	0	4.948165	1.989507	3.264287
35	1	0	3.951785	0.640693	3.874853
36	1	0	0.482136	-0.714661	-0.522405
37	8	0	1.963847	-1.542346	-2.905796
38	1	0	1.093545	-1.123542	-2.877051
39	8	0	-0.813392	-3.028499	-0.777335
40	1	0	-1.231311	-2.685008	0.673173
41	1	0	0.154066	-3.254373	-0.832319
42	8	0	-1.542529	-2.568316	1.634871
43	1	0	-2.119025	-1.752064	1.690929
44	1	0	-2.091985	-3.411083	1.872105
45	8	0	1.804722	-3.454490	-0.923785
46	1	0	2.026515	-2.814829	-1.628384
47	1	0	2.316872	-3.185988	-0.141276
48	1	0	2.599903	-0.843886	-2.680234
49	8	0	3.149001	-2.526733	1.396881
50	1	0	3.114901	-1.597983	1.699872
51	1	0	3.250047	-3.066978	2.183103
52	8	0	-2.877387	-4.667435	1.967609
53	1	0	-2.834052	-5.056608	1.064414
54	1	0	-2.554153	-5.331574	2.581394
55	8	0	-3.110275	-0.461937	1.628738
56	1	0	-3.943546	-0.664878	2.067273
57	1	0	-3.325448	-0.354293	0.691542
58	8	0	-2.479170	-5.291004	-0.615757
59	1	0	-3.201764	-5.325920	-1.246179
60	1	0	-1.920573	-4.541564	-0.884323
61	8	0	3.816984	0.427699	-2.013633
62	6	0	4.717815	-0.054567	-1.109455
63	1	0	4.359913	-0.935298	-0.563129
64	1	0	5.593298	-0.370525	-1.712098
65	1	0	5.089376	0.734875	-0.442571

SCF Done: E(UwB97XD) = -1961.71278730 A.U. after 2 cycles

Zero-point correction= 0.539505 (a.u.)
Thermal correction to Energy= 0.582902
Thermal correction to Enthalpy= 0.583846
Thermal correction to Gibbs Free Energy= 0.460486
Sum of electronic and zero-point Energies= -1961.173282

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Sum of electronic and thermal Energies=           -1961.129886
Sum of electronic and thermal Enthalpies=         -1961.128941
Sum of electronic and thermal Free Energies=      -1961.252301

                 E (Thermal)           CV             S
                  KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total               365.776          152.616          259.633

       Item             Value    Threshold  Converged?
Maximum Force          0.000005    0.000450    YES
RMS     Force          0.000001    0.000300    YES
Maximum Displacement    0.001061    0.001800    YES
RMS     Displacement    0.000159    0.001200    YES

 -----Figure S1-6, TS3[A], ring closure ---------
  vita-b10xx.high.log

                     Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic           Coordinates (Angstroms)
Number     Number      Type             X           Y           Z
---------------------------------------------------------------------
    1          8          0      -3.780956   -2.068697   -1.833464
    2          6          0      -2.904512   -3.125219   -2.178910
    3          6          0      -1.518140   -2.626131   -2.599628
    4          6          0      -0.750478   -1.977868   -1.490246
    5         16          0      -1.207988   -0.340571   -0.960542
    6          6          0       0.299628   -0.263146    0.067567
    7          7          0       0.647537   -1.630915    0.323255
    8          6          0       1.919329   -1.797569    1.017542
    9          6          0       3.035378   -0.971348    0.428780
   10          6          0       4.355076   -1.081562    0.858896
   11          7          0       5.332180   -0.306098    0.408530
   12          6          0       5.007156    0.635788   -0.485651
   13          6          0       6.102619    1.527787   -0.978510
   14          7          0       3.776584    0.825577   -0.963670
   15          6          0       2.832055    0.019859   -0.511224
   16          7          0       1.507041    0.218808   -1.050429
   17          6          0       0.237226   -2.486705   -0.735987
   18          6          0       0.842160   -3.847583   -0.835995
   19          1          0      -3.764797   -1.941740   -0.870582
   20          1          0      -3.349704   -3.661796   -3.021559
   21          1          0      -2.803504   -3.831815   -1.346650
   22          1          0      -0.949600   -3.474247   -2.989054
   23          1          0      -1.637272   -1.920527   -3.427845
   24          8          0       0.369850    0.556351    1.053924
   25          1          0       0.377922   -4.415900   -1.639023
   26          1          0       1.916483   -3.796250   -1.033007
   27          1          0       0.694078   -4.403038    0.094801
   28          1          0       1.780309   -1.489709    2.056357
   29          1          0       2.185455   -2.852499    1.034250
   30          1          0       4.626061   -1.830554    1.597988
   31          1          0      -0.650022    1.362999    1.294400
   32          1          0       1.381022   -0.338083   -1.898566
   33          1          0       6.570476    2.042286   -0.136370
   34          1          0       6.874805    0.929828   -1.468047
   35          1          0       5.713936    2.261512   -1.682230
   36          1          0       1.354811    1.211238   -1.298209
   37          8          0       0.957893    2.960039   -1.822323
   38          1          0       1.675551    3.544802   -1.559028
   39          8          0      -1.467500    2.060295    1.501359
   40          1          0      -2.371212    1.599992    1.429244
   41          1          0      -1.446159    2.758700    0.786193
   42          8          0      -3.799594    1.054591    1.135976
   43          1          0      -3.983787    1.433388    0.254109
   44          1          0      -3.847354    0.083337    1.043429
   45          8          0      -1.437822    3.673097   -0.556913
   46          1          0      -1.474111    4.644059   -0.429776
   47          1          0      -0.624440    3.479095   -1.057893
   48          1          0       0.921681    3.016128   -2.782374
   49          8          0      -3.848472    2.421277   -1.258457
   50          1          0      -4.534459    3.065257   -1.445904
   51          1          0      -3.026684    2.932806   -1.149893
   52          8          0      -1.551896    6.373799   -0.208334
   53          1          0      -2.294409    6.832603   -0.608905
   54          1          0      -1.499496    6.704784    0.691673
   55          8          0      -3.828132   -1.720930    0.942618
   56          1          0      -3.002647   -1.983531    1.413128
   57          1          0      -4.546963   -2.186333    1.377040
   58          8          0      -1.531991   -2.308845    2.237486
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59	1	0	-0.793970	-2.130996	1.632926
60	1	0	-1.417879	-1.663818	2.956226
61	8	0	-1.063928	-0.275953	4.152832
62	6	0	0.268366	-0.034063	4.280842
63	1	0	0.831410	-0.964264	4.451985
64	1	0	0.596939	0.308439	3.274361
65	1	0	0.507148	0.737746	5.019196

SCF Done: E(UwB97XD) = -1961.66065119 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-179.5905	17.3394	19.3059

Zero-point correction= 0.535588 (a.u.)
Thermal correction to Energy= 0.578670
Thermal correction to Enthalpy= 0.579614
Thermal correction to Gibbs Free Energy= 0.454769
Sum of electronic and zero-point Energies= -1961.125063
Sum of electronic and thermal Energies= -1961.081981
Sum of electronic and thermal Enthalpies= -1961.081037
Sum of electronic and thermal Free Energies= -1961.205882

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	363.121	150.689	262.759

Item	Value	Threshold	Converged?
Maximum Force	0.000012	0.000450	YES
RMS Force	0.000003	0.000300	YES
Maximum Displacement	0.006484	0.001800	NO
RMS Displacement	0.000851	0.001200	YES

------Figure S1-7, Int3[A], the ring formed intermediate------
vita-b10xx.revrev.high.log

Stoichiometry C13H36N4O11S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-3.752666	-1.832411	-1.856622
2	6	0	-2.918605	-2.863510	-2.352047
3	6	0	-1.536896	-2.341681	-2.755208
4	6	0	-0.737085	-1.813070	-1.606467
5	16	0	-1.188145	-0.238327	-0.888976
6	6	0	0.383563	-0.246888	0.019453
7	7	0	0.724641	-1.628786	0.178782
8	6	0	2.012186	-1.860435	0.828681
9	6	0	3.095513	-0.946128	0.319976
10	6	0	4.434284	-1.058769	0.691082
11	7	0	5.368280	-0.208216	0.290177
12	6	0	4.986694	0.809693	-0.491988
13	6	0	6.039064	1.772667	-0.939748
14	7	0	3.732629	1.010244	-0.901641
15	6	0	2.837531	0.133575	-0.495192
16	7	0	1.477279	0.355240	-0.971592
17	6	0	0.277886	-2.386881	-0.943355
18	6	0	0.884621	-3.725929	-1.194541
19	1	0	-3.756420	-1.872823	-0.885858
20	1	0	-3.399324	-3.292666	-3.235968
21	1	0	-2.808509	-3.661202	-1.608436
22	1	0	-0.985337	-3.151888	-3.238046
23	1	0	-1.664119	-1.556109	-3.506568
24	8	0	0.475250	0.459912	1.150592
25	1	0	0.391298	-4.219119	-2.029116
26	1	0	1.949897	-3.646836	-1.427282
27	1	0	0.774731	-4.367234	-0.315401
28	1	0	1.889857	-1.690600	1.900916
29	1	0	2.293906	-2.903834	0.704505
30	1	0	4.755096	-1.872336	1.335425
31	1	0	-0.348142	1.036686	1.341502
32	1	0	1.353144	-0.102173	-1.880505
33	1	0	6.616990	2.120386	-0.081809
34	1	0	6.730191	1.269088	-1.620601
35	1	0	5.590571	2.621953	-1.451768

36	1	0	1.308161	1.374617	-1.118147
37	8	0	0.960897	3.085939	-1.486503
38	1	0	1.600847	3.659370	-1.052428
39	8	0	-1.517163	1.909155	1.667534
40	1	0	-2.387341	1.449992	1.625575
41	1	0	-1.572721	2.619999	0.997408
42	8	0	-3.969994	0.810064	1.277654
43	1	0	-4.088844	1.212608	0.397612
44	1	0	-3.946606	-0.152340	1.136712
45	8	0	-1.625892	3.636655	-0.456651
46	1	0	-1.725892	4.599937	-0.326596
47	1	0	-0.771251	3.498910	-0.897017
48	1	0	1.058351	3.259045	-2.428412
49	8	0	-3.932002	2.228705	-1.117693
50	1	0	-4.635278	2.849675	-1.317556
51	1	0	-3.129852	2.769649	-0.992371
52	8	0	-1.929875	6.343084	-0.081515
53	1	0	-2.704936	6.750198	-0.476117
54	1	0	-1.908232	6.658704	0.825179
55	8	0	-3.764209	-1.972838	0.918675
56	1	0	-2.909712	-2.207626	1.348245
57	1	0	-4.430500	-2.544387	1.307062
58	8	0	-1.390504	-2.510402	2.101540
59	1	0	-0.677663	-2.264836	1.492213
60	1	0	-1.267237	-1.926003	2.868807
61	8	0	-0.904623	-0.680392	4.209937
62	6	0	0.424044	-0.450850	4.399843
63	1	0	0.987765	-1.394628	4.452851
64	1	0	0.777483	0.031094	3.464608
65	1	0	0.639594	0.208049	5.246395

SCF Done: E(UwB97XD) = -1961.66428897 A.U. after 2 cycles
NFock= 2 Conv=0.73D-09 -V/T= 2.0039

Zero-point correction= 0.537977 (a.u.)
Thermal correction to Energy= 0.582295
Thermal correction to Enthalpy= 0.583239
Thermal correction to Gibbs Free Energy= 0.454128
Sum of electronic and zero-point Energies= -1961.126312
Sum of electronic and thermal Energies= -1961.081994
Sum of electronic and thermal Enthalpies= -1961.081050
Sum of electronic and thermal Free Energies= -1961.210161

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	365.396	153.801	271.738

Item	Value	Threshold	Converged?
Maximum Force	0.000003	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.004085	0.001800	NO
RMS Displacement	0.000514	0.001200	YES

------Figure S1-8, TS4[A], deprotonation from N(16)-----
vita-b104c2.high.log

Stoichiometry C13H36N4O11S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-5.167010	-1.726893	0.302024
2	6	0	-5.425261	-0.403890	-0.144019
3	6	0	-4.481705	0.632372	0.471815
4	6	0	-3.040325	0.407444	0.121666
5	16	0	-2.038416	-0.622112	1.173376
6	6	0	-0.560720	-0.278254	0.137631
7	7	0	-1.055020	0.280973	-1.087192
8	6	0	-0.048984	1.070276	-1.806800
9	6	0	0.264074	2.281732	-0.977545
10	6	0	0.377281	3.596568	-1.387431
11	7	0	0.583396	4.598388	-0.530139
12	6	0	0.649872	4.295344	0.767010
13	6	0	0.900657	5.404268	1.740055
14	7	0	0.530006	3.058492	1.270480
15	6	0	0.351899	2.093903	0.393257
16	7	0	0.346835	0.750115	0.881358

17	6	0	-2.374850	0.786216	-0.974762
18	6	0	-2.916155	1.597050	-2.104706
19	1	0	-4.329455	-2.017358	-0.067232
20	1	0	-6.451256	-0.178635	0.152598
21	1	0	-5.368586	-0.351666	-1.237721
22	1	0	-4.789439	1.624047	0.128434
23	1	0	-4.603515	0.628181	1.558593
24	8	0	0.211124	-1.362006	-0.134332
25	1	0	-3.969661	1.819038	-1.945585
26	1	0	-2.385272	2.547708	-2.210271
27	1	0	-2.823387	1.050955	-3.047637
28	1	0	0.831856	0.438189	-1.946738
29	1	0	-0.418981	1.331362	-2.796177
30	1	0	0.303727	3.857448	-2.439338
31	1	0	0.446855	-1.895789	0.668910
32	1	0	0.132178	0.752785	1.877997
33	1	0	1.963485	5.424110	1.999574
34	1	0	0.635294	6.365026	1.301943
35	1	0	0.336691	5.241323	2.658725
36	1	0	1.548372	0.378710	0.752152
37	8	0	2.743264	0.119581	0.624652
38	1	0	2.912614	-0.508760	-0.164881
39	8	0	1.029350	-2.969944	1.760402
40	1	0	0.374401	-3.364177	2.368996
41	1	0	1.744759	-2.567681	2.293432
42	8	0	-0.894866	-4.025794	3.406450
43	1	0	-1.781819	-3.699745	3.234511
44	1	0	-0.975844	-4.982019	3.442140
45	8	0	3.048853	-1.536912	2.908600
46	1	0	3.913995	-1.932683	3.034248
47	1	0	3.153660	-0.886257	2.196956
48	1	0	3.222226	0.971850	0.473634
49	8	0	3.137728	-1.468255	-1.319836
50	1	0	4.073408	-1.665222	-1.510200
51	1	0	2.689458	-2.328992	-1.170602
52	8	0	3.742730	2.553393	0.229308
53	1	0	3.889931	3.097719	1.006994
54	1	0	4.489037	2.717891	-0.352460
55	8	0	5.801693	-1.996417	-1.866380
56	1	0	6.210995	-1.510333	-2.586165
57	1	0	6.423467	-1.944828	-1.136588
58	8	0	1.869628	-3.848546	-0.802046
59	1	0	1.608513	-3.748872	0.127839
60	1	0	1.035535	-3.818396	-1.299956
61	8	0	-0.565059	-3.629922	-2.291517
62	6	0	-0.664591	-2.504314	-3.042555
63	1	0	-0.960037	-1.704236	-2.324009
64	1	0	0.300410	-2.178235	-3.454463
65	1	0	-1.452094	-2.563016	-3.803508

SCF Done: E(UwB97XD) = -1961.65013165 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-963.7055	11.2897	15.3351

Zero-point correction= 0.531250 (a.u.)
Thermal correction to Energy= 0.576525
Thermal correction to Enthalpy= 0.577469
Thermal correction to Gibbs Free Energy= 0.444110
Sum of electronic and zero-point Energies= -1961.118881
Sum of electronic and thermal Energies= -1961.073607
Sum of electronic and thermal Enthalpies= -1961.072662
Sum of electronic and thermal Free Energies= -1961.206021

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	361.775	154.074	280.678

Item	Value	Threshold	Converged?
Maximum Force	0.000005	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.002820	0.001800	NO
RMS Displacement	0.000279	0.001200	YES

------Figure S1-9, Int4[A]-----------
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Stoichiometry C13H36N4O11S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-5.247893	-1.785447	0.225907
2	6	0	-5.521381	-0.429025	-0.093700
3	6	0	-4.576364	0.552962	0.602821
4	6	0	-3.137151	0.358773	0.223808
5	16	0	-2.110858	-0.726124	1.195211
6	6	0	-0.633590	-0.212887	0.210299
7	7	0	-1.175212	0.302970	-1.026303
8	6	0	-0.197281	1.100319	-1.773013
9	6	0	0.187595	2.292964	-0.949941
10	6	0	0.405778	3.578055	-1.386256
11	7	0	0.724177	4.584870	-0.560808
12	6	0	0.798364	4.291446	0.736993
13	6	0	1.125008	5.403948	1.687633
14	7	0	0.578392	3.086301	1.275545
15	6	0	0.280003	2.102149	0.434481
16	7	0	0.115147	0.834547	0.954986
17	6	0	-2.492181	0.801087	-0.862616
18	6	0	-3.060100	1.669837	-1.935675
19	1	0	-4.393467	-2.019753	-0.145358
20	1	0	-6.546003	-0.241555	0.232736
21	1	0	-5.477289	-0.277432	-1.178918
22	1	0	-4.889366	1.569742	0.348255
23	1	0	-4.690393	0.454631	1.685929
24	8	0	0.204415	-1.259553	-0.090151
25	1	0	-4.103041	1.902679	-1.728360
26	1	0	-2.513420	2.613623	-2.019731
27	1	0	-3.012491	1.164783	-2.904816
28	1	0	0.664845	0.457255	-1.968331
29	1	0	-0.613130	1.381904	-2.739076
30	1	0	0.330018	3.820163	-2.443129
31	1	0	0.512982	-1.743134	0.710557
32	1	0	-0.024853	0.822686	1.958056
33	1	0	1.772490	5.045903	2.488970
34	1	0	1.603509	6.228675	1.161371
35	1	0	0.203459	5.774869	2.146182
36	1	0	2.006861	0.269752	0.701600
37	8	0	2.941738	0.088458	0.498981
38	1	0	3.013670	-0.913688	-0.721730
39	8	0	1.242448	-2.905684	1.719434
40	1	0	0.657163	-3.312918	2.387437
41	1	0	2.040664	-2.561910	2.170811
42	8	0	-0.496994	-3.977308	3.549762
43	1	0	-1.330495	-3.504119	3.611421
44	1	0	-0.734827	-4.902578	3.452457
45	8	0	3.489427	-1.649380	2.609612
46	1	0	4.332480	-2.103121	2.546448
47	1	0	3.494600	-0.972515	1.910215
48	1	0	3.358952	0.969895	0.377984
49	8	0	3.057749	-1.586166	-1.472392
50	1	0	4.012332	-1.794109	-1.690645
51	1	0	2.530164	-2.458007	-1.220380
52	8	0	3.882961	2.604831	0.177274
53	1	0	3.784874	3.168700	0.948640
54	1	0	4.761383	2.785617	-0.166377
55	8	0	5.513306	-2.158764	-2.101722
56	1	0	5.982675	-1.536085	-2.663186
57	1	0	6.123043	-2.396133	-1.398074
58	8	0	1.810779	-3.653863	-0.864474
59	1	0	1.613804	-3.597008	0.091906
60	1	0	0.941707	-3.648718	-1.313917
61	8	0	-0.670840	-3.537574	-2.129253
62	6	0	-0.891238	-2.448760	-2.903979
63	1	0	-1.128067	-1.623889	-2.185147
64	1	0	0.009139	-2.110005	-3.435280
65	1	0	-1.759319	-2.558646	-3.564772

SCF Done: E(UwB97XD) = -1961.66455969 A.U. after 2 cycles

Zero-point correction= 0.535697 (a.u.)
Thermal correction to Energy= 0.580519
Thermal correction to Enthalpy= 0.581463
Thermal correction to Gibbs Free Energy= 0.450886

```
Sum of electronic and zero-point Energies=         -1961.128863
Sum of electronic and thermal Energies=           -1961.084041
Sum of electronic and thermal Enthalpies=         -1961.083097
Sum of electronic and thermal Free Energies=      -1961.213673

                 E (Thermal)           CV              S
                  KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total               364.281          154.132          274.822

       Item             Value    Threshold  Converged?
Maximum Force          0.000001    0.000450    YES
RMS     Force          0.000000    0.000300    YES
Maximum Displacement    0.000185    0.001800    YES
RMS     Displacement    0.000031    0.001200    YES
Predicted change in Energy=-6.049230D-11
```

-----Figure S1-10, TS5[A], H2O elimination-------
vita-b106e.high.log

Stoichiometry C13H36N4O11S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	3.577650	1.530735	0.457607
2	6	0	3.139508	2.861631	0.683248
3	6	0	2.144052	3.363290	-0.368569
4	6	0	0.826384	2.655996	-0.355872
5	16	0	0.673718	1.067995	-1.158240
6	6	0	-0.869148	0.809310	-0.269066
7	7	0	-1.377521	2.083697	0.011644
8	6	0	-2.662145	2.173005	0.698524
9	6	0	-3.590229	1.110294	0.171148
10	6	0	-4.946756	1.105932	0.397813
11	7	0	-5.763846	0.121065	-0.002681
12	6	0	-5.195467	-0.904284	-0.628146
13	6	0	-6.057116	-2.066042	-1.017721
14	7	0	-3.891015	-1.000863	-0.917321
15	6	0	-3.102111	0.009504	-0.548337
16	7	0	-1.783543	-0.056560	-0.891629
17	6	0	-0.339924	3.026043	0.192266
18	6	0	-0.649446	4.298259	0.907637
19	1	0	4.045818	1.483227	-0.393209
20	1	0	4.001174	3.538728	0.707071
21	1	0	2.672531	2.871001	1.670006
22	1	0	1.982927	4.430241	-0.194079
23	1	0	2.604664	3.286304	-1.360076
24	8	0	-0.431264	0.151345	1.080048
25	1	0	0.240291	4.919326	0.990817
26	1	0	-1.413333	4.869621	0.372601
27	1	0	-1.021071	4.102862	1.916949
28	1	0	-2.543177	2.048186	1.782913
29	1	0	-3.084970	3.161551	0.519293
30	1	0	-5.412325	1.930729	0.930574
31	1	0	-1.207657	-0.068520	1.663379
32	1	0	-1.406374	-0.893257	-1.349336
33	1	0	-5.935074	-2.870974	-0.286352
34	1	0	-7.105584	-1.773426	-1.034654
35	1	0	-5.762268	-2.454063	-1.993442
36	8	0	-2.430615	-0.455349	2.706985
37	1	0	-2.984682	-1.213416	2.503003
38	1	0	-2.172941	-0.555703	3.627325
39	8	0	4.996565	1.069821	-1.915348
40	6	0	6.160846	0.453813	-1.589749
41	1	0	6.651383	0.917930	-0.721789
42	1	0	5.860537	-0.561442	-1.230017
43	1	0	6.839688	0.325121	-2.440142
44	1	0	0.167990	-0.805408	0.889746
45	8	0	0.827371	-1.845300	0.638645
46	1	0	1.779919	-1.696644	0.920272
47	1	0	0.394048	-2.625439	1.059297
48	8	0	3.224567	-1.116412	1.262791
49	1	0	3.941933	-1.546524	0.757696
50	1	0	3.278319	-0.166402	1.047184
51	8	0	-0.824084	-3.795767	1.354162
52	1	0	-1.262097	-3.795313	2.207696
53	1	0	-1.530513	-3.732753	0.683806
54	8	0	-0.347612	-2.288804	-1.961052

55	1	0	-0.997071	-2.964303	-1.707597
56	1	0	0.310495	-2.297158	-1.252888
57	8	0	-2.574431	-3.517947	-0.801213
58	1	0	-3.121746	-2.709752	-0.911962
59	1	0	-3.110901	-4.257360	-1.096122
60	8	0	5.216599	-2.328980	-0.211284
61	1	0	5.972410	-2.698197	0.285995
62	1	0	4.924257	-3.023519	-0.805596
63	8	0	7.355762	-3.327747	1.203715
64	1	0	8.202855	-2.900169	1.056274
65	1	0	7.257777	-3.379636	2.157588

SCF Done: E(UwB97XD) = -1961.6592254 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-576.7727	10.6749	12.8207

Zero-point correction= 0.532764 (a.u.)
Thermal correction to Energy= 0.576881
Thermal correction to Enthalpy= 0.577826
Thermal correction to Gibbs Free Energy= 0.450372
Sum of electronic and zero-point Energies= -1961.126462
Sum of electronic and thermal Energies= -1961.082344
Sum of electronic and thermal Enthalpies= -1961.081400
Sum of electronic and thermal Free Energies= -1961.208853

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	361.999	153.391	268.248

Item	Value	Threshold	Converged?
Maximum Force	0.000024	0.000450	YES
RMS Force	0.000004	0.000300	YES
Maximum Displacement	0.007903	0.001800	NO
RMS Displacement	0.001406	0.001200	NO

------Figure S1-11, ProductH+[A], the N-protonated thiochrome----
vita-b106e.rev.high.log

Stoichiometry C13H36N4O11S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	3.823011	1.191305	1.139043
2	6	0	3.564200	2.580573	1.241592
3	6	0	2.959521	3.157312	-0.041185
4	6	0	1.613269	2.594312	-0.371799
5	16	0	1.475402	0.953578	-0.970703
6	6	0	-0.219487	1.114181	-1.060269
7	7	0	-0.632419	2.309512	-0.670257
8	6	0	-2.050819	2.693540	-0.693556
9	6	0	-2.913292	1.465644	-0.709343
10	6	0	-4.229251	1.454340	-0.308141
11	7	0	-4.992284	0.353989	-0.343981
12	6	0	-4.425052	-0.761897	-0.793709
13	6	0	-5.253253	-2.006926	-0.850710
14	7	0	-3.140757	-0.867774	-1.166172
15	6	0	-2.405279	0.233050	-1.113074
16	7	0	-1.063964	0.129790	-1.440170
17	6	0	0.397137	3.169226	-0.263305
18	6	0	0.052635	4.533906	0.226240
19	1	0	4.501742	1.026891	0.461409
20	1	0	4.484698	3.124921	1.475314
21	1	0	2.870154	2.708002	2.074212
22	1	0	2.873545	4.239710	0.071241
23	1	0	3.649390	2.987035	-0.873438
24	8	0	-1.439613	1.177596	2.024638
25	1	0	0.957711	5.110768	0.402536
26	1	0	-0.558156	5.073248	-0.500901
27	1	0	-0.498234	4.478121	1.168499
28	1	0	-2.258184	3.282426	0.197712
29	1	0	-2.222744	3.311722	-1.578474
30	1	0	-4.698365	2.357589	0.069789
31	1	0	-2.277864	0.725418	2.191879

32	1	0	-0.653401	-0.809386	-1.545492
33	1	0	-4.941889	-2.694660	-0.058985
34	1	0	-6.305547	-1.767321	-0.712913
35	1	0	-5.111627	-2.513948	-1.806611
36	8	0	-3.842013	-0.441841	2.482075
37	1	0	-4.607729	-0.252639	1.928383
38	1	0	-4.166600	-0.415269	3.386392
39	8	0	5.479570	0.368586	-0.944114
40	6	0	5.770602	-0.946845	-0.783803
41	1	0	6.117478	-1.175570	0.234652
42	1	0	4.790977	-1.480890	-0.862954
43	1	0	6.438768	-1.343457	-1.556190
44	1	0	-0.815404	0.453320	1.850078
45	8	0	0.093733	-1.117903	1.474158
46	1	0	0.997835	-1.205497	1.847214
47	1	0	-0.520559	-1.745545	1.903219
48	8	0	2.752246	-1.259234	1.958954
49	1	0	2.957864	-1.785352	1.162401
50	1	0	3.089162	-0.368767	1.759893
51	8	0	-2.073830	-2.671475	2.065527
52	1	0	-2.765515	-1.996712	2.152161
53	1	0	-2.184010	-3.054870	1.180188
54	8	0	0.353050	-2.230881	-0.981358
55	1	0	-0.309298	-2.940950	-1.015100
56	1	0	0.283149	-1.886691	-0.061089
57	8	0	-2.107669	-3.463828	-0.681196
58	1	0	-2.521624	-2.655330	-1.044434
59	1	0	-2.564274	-4.212526	-1.071341
60	8	0	3.078457	-2.658361	-0.435371
61	1	0	3.335892	-3.595998	-0.388965
62	1	0	2.174931	-2.636091	-0.793845
63	8	0	3.861639	-5.331509	-0.280494
64	1	0	4.614310	-5.589425	-0.817940
65	1	0	4.048737	-5.670280	0.598274

SCF Done: E(UwB97XD) = -1961.71516090 A.U. after 2 cycles

Zero-point correction= 0.538896 (a.u.)
Thermal correction to Energy= 0.583534
Thermal correction to Enthalpy= 0.584478
Thermal correction to Gibbs Free Energy= 0.457258
Sum of electronic and zero-point Energies= -1961.176265
Sum of electronic and thermal Energies= -1961.131627
Sum of electronic and thermal Enthalpies= -1961.130683
Sum of electronic and thermal Free Energies= -1961.257902

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	366.173	155.827	267.757

Item	Value	Threshold	Converged?
Maximum Force	0.000005	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.002582	0.001800	NO
RMS Displacement	0.000318	0.001200	YES

-----Figure S1-12, TS6[A], deprotonation-------
vita-b10h.high.log

Stoichiometry C13H36N4O11S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.018936	-1.020996	1.443587
2	6	0	-3.833741	-2.424330	1.526985
3	6	0	-3.354168	-3.039123	0.208466
4	6	0	-1.994769	-2.574792	-0.209783
5	16	0	-1.790007	-0.977506	-0.907187
6	6	0	-0.087247	-1.208508	-1.025295
7	7	0	0.256970	-2.423154	-0.577679
8	6	0	1.633503	-2.902784	-0.736837
9	6	0	2.554144	-1.716931	-0.764601
10	6	0	3.878299	-1.778825	-0.409401
11	7	0	4.706068	-0.728653	-0.508602
12	6	0	4.184263	0.408088	-0.963631
13	6	0	5.087737	1.597080	-1.081200

14	7	0	2.899449	0.584609	-1.288709
15	6	0	2.073775	-0.463393	-1.182318
16	7	0	0.741943	-0.254379	-1.439076
17	6	0	-0.808893	-3.207903	-0.111974
18	6	0	-0.526364	-4.571101	0.422127
19	1	0	-4.712782	-0.822737	0.791232
20	1	0	-4.767356	-2.912573	1.825734
21	1	0	-3.093317	-2.594578	2.310584
22	1	0	-3.343856	-4.125385	0.320237
23	1	0	-4.083024	-2.818262	-0.577725
24	1	0	-1.454471	-5.074850	0.683258
25	1	0	-0.003027	-5.183749	-0.315591
26	1	0	0.089884	-4.516946	1.323165
27	1	0	1.880327	-3.564678	0.091897
28	1	0	1.697109	-3.476117	-1.667349
29	1	0	4.308268	-2.700205	-0.028188
30	1	0	4.879995	2.298038	-0.267454
31	1	0	6.130680	1.292392	-1.019398
32	1	0	4.914542	2.116200	-2.025080
33	8	0	3.755993	0.758005	2.542281
34	1	0	4.677027	0.534046	2.307029
35	1	0	3.271526	-0.067923	2.480787
36	8	0	-5.731390	-0.221409	-0.615688
37	6	0	-5.942439	1.118692	-0.570614
38	1	0	-6.220456	1.461791	0.436725
39	1	0	-4.942077	1.582966	-0.749432
40	1	0	-6.630396	1.478423	-1.343494
41	8	0	-0.175093	1.407350	1.412752
42	1	0	-1.058548	1.460990	1.849611
43	1	0	0.515953	1.959710	1.840021
44	8	0	-2.762885	1.418736	2.010850
45	1	0	-2.999447	1.887476	1.187968
46	1	0	-3.119276	0.520163	1.895313
47	8	0	2.057815	2.830078	1.870793
48	1	0	2.745936	2.161857	2.052850
49	1	0	2.195252	3.108832	0.952880
50	8	0	-0.247664	2.017797	-0.931879
51	1	0	0.450399	2.705255	-1.069859
52	1	0	-0.254771	1.799156	0.147009
53	8	0	2.073190	3.230095	-1.001910
54	1	0	2.456825	2.364023	-1.274327
55	1	0	2.456846	3.910823	-1.559341
56	8	0	-3.107604	2.660945	-0.462346
57	1	0	-3.285957	3.619880	-0.469365
58	1	0	-2.255542	2.543350	-0.898837
59	8	0	-3.641504	5.378345	-0.456326
60	1	0	-4.483181	5.657607	-0.824640
61	1	0	-3.575075	5.821802	0.392765
62	1	0	0.177240	1.110575	-1.303372
63	8	0	6.291670	-0.013186	1.695660
64	1	0	5.978957	-0.415852	0.861904
65	1	0	6.731566	-0.713475	2.182209

SCF Done: E(UwB97XD) = -1961.69703564 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-272.1149	14.2035	16.9723

Zero-point correction= 0.533049 (a.u.)
Thermal correction to Energy= 0.576632
Thermal correction to Enthalpy= 0.577576
Thermal correction to Gibbs Free Energy= 0.451805
Sum of electronic and zero-point Energies= -1961.163986
Sum of electronic and thermal Energies= -1961.120403
Sum of electronic and thermal Enthalpies= -1961.119459
Sum of electronic and thermal Free Energies= -1961.245230

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	361.842	151.770	264.707

Item	Value	Threshold	Converged?
Maximum Force	0.000030	0.000450	YES
RMS Force	0.000003	0.000300	YES
Maximum Displacement	0.005109	0.001800	NO
RMS Displacement	0.001087	0.001200	YES

---Figure S1-13, product[A], thiochrome + H3C-O(.) + H3O(+)(H2O)8----
vita-b1product.high.log

Stoichiometry C13H36N4O11S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.024335	-0.679625	1.566271
2	6	0	-4.077681	-2.097231	1.570834
3	6	0	-3.726385	-2.711102	0.212631
4	6	0	-2.323256	-2.419837	-0.222128
5	16	0	-1.964412	-1.022463	-1.221492
6	6	0	-0.269156	-1.365347	-1.164421
7	7	0	-0.049127	-2.478556	-0.441920
8	6	0	1.293256	-3.061037	-0.403845
9	6	0	2.289461	-1.952114	-0.574518
10	6	0	3.564959	-1.999323	-0.074412
11	7	0	4.467970	-1.035126	-0.303692
12	6	0	4.067533	0.001169	-1.038099
13	6	0	5.066312	1.088069	-1.299252
14	7	0	2.832499	0.170867	-1.518420
15	6	0	1.924993	-0.791253	-1.285847
16	7	0	0.640129	-0.569148	-1.701771
17	6	0	-1.193992	-3.081422	0.094362
18	6	0	-1.055772	-4.311448	0.926004
19	1	0	-4.656493	-0.338814	0.909158
20	1	0	-5.076646	-2.434908	1.866862
21	1	0	-3.366825	-2.431413	2.328795
22	1	0	-3.869965	-3.792908	0.277667
23	1	0	-4.434931	-2.353624	-0.539971
24	1	0	-2.037897	-4.686116	1.208668
25	1	0	-0.534533	-5.102132	0.381013
26	1	0	-0.499302	-4.102895	1.843542
27	1	0	1.438484	-3.570634	0.547732
28	1	0	1.379019	-3.800630	-1.207312
29	1	0	3.894089	-2.837129	0.533431
30	1	0	4.962206	1.870238	-0.540821
31	1	0	6.080003	0.694099	-1.243714
32	1	0	4.900231	1.538605	-2.277887
33	8	0	4.400883	1.601474	2.696369
34	1	0	5.050746	0.945529	2.368754
35	1	0	4.918793	2.332141	3.040022
36	8	0	-5.580073	0.365696	-0.501672
37	6	0	-5.735607	1.711481	-0.442639
38	1	0	-6.044719	2.052234	0.556454
39	1	0	-4.704473	2.128382	-0.564566
40	1	0	-6.368099	2.114156	-1.241316
41	8	0	0.087557	1.041754	1.044307
42	1	0	-0.811865	1.144612	1.559100
43	1	0	0.894149	1.578252	1.384925
44	8	0	-2.206690	1.332925	1.966553
45	1	0	-2.534269	1.940501	1.267474
46	1	0	-2.761562	0.529891	1.887832
47	8	0	2.125988	2.450636	1.484866
48	1	0	2.954715	2.096091	1.873827
49	1	0	2.333819	2.748300	0.581541
50	8	0	-0.304371	1.986704	-1.370014
51	1	0	0.440160	2.607501	-1.470607
52	1	0	-0.087263	1.392196	0.118722
53	8	0	2.253992	2.902057	-1.289036
54	1	0	2.503914	1.997594	-1.583415
55	1	0	2.772262	3.524689	-1.803529
56	8	0	-2.752108	2.849519	-0.232236
57	1	0	-2.760444	3.822254	-0.165481
58	1	0	-2.000410	2.620279	-0.801030
59	8	0	-2.788467	5.613492	-0.032135
60	1	0	-3.542218	6.068587	-0.415207
61	1	0	-2.682022	5.989471	0.845000
62	1	0	0.010312	1.156885	-1.797281
63	8	0	6.201614	-0.234609	1.728167
64	1	0	5.726446	-0.649676	0.975918
65	1	0	6.444969	-0.952277	2.316648

SCF Done: E(UwB97XD) = -1961.70365175 A.U. after 2 cycles

Zero-point correction= 0.536227 (a.u.)

```
Thermal correction to Energy=                 0.579989
Thermal correction to Enthalpy=               0.580933
Thermal correction to Gibbs Free Energy=       0.454375
Sum of electronic and zero-point Energies=         -1961.167424
Sum of electronic and thermal Energies=            -1961.123663
Sum of electronic and thermal Enthalpies=          -1961.122719
Sum of electronic and thermal Free Energies=       -1961.249277

                 E (Thermal)           CV             S
                  KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total               363.948          152.399          266.364

       Item             Value    Threshold  Converged?
Maximum Force          0.000009    0.000450    YES
RMS     Force          0.000002    0.000300    YES
Maximum Displacement    0.004091    0.001800    NO
RMS     Displacement    0.000668    0.001200    YES

==================Figure S2 and scheme S3(c)=======================

 obtained by RwB97x-D/6-311+G(d,p) SCRF=(PCM, solvent=water)
  calculations

   -------Figure S2-1, MODEL......NCBr----------------
  vita-b1model24.for.high.log

 Stoichiometry   C7H10BrN2OS(1+)

                     Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic           Coordinates (Angstroms)
Number     Number      Type             X         Y         Z
---------------------------------------------------------------------
    1         8          0       0.290978    1.801026    0.755971
    2         6          0       0.729470    2.080364   -0.561752
    3         6          0       2.251231    2.096016   -0.550961
    4         6          0       2.848225    0.769227   -0.203883
    5        16          0       2.366455   -0.151451    1.190197
    6         6          0       3.487526   -1.355339    0.816186
    7         7          0       4.167840   -1.093681   -0.279129
    8         6          0       5.196941   -1.975237   -0.841896
    9         1          0       4.887028   -2.286452   -1.837893
   10         6          0       3.820468    0.104838   -0.869057
   11         1          0       4.323627    0.414748   -1.772034
   12         1          0      -0.603468    1.435704    0.711663
   13         1          0       0.365836    3.057549   -0.896975
   14         1          0       0.365564    1.319501   -1.261671
   15         1          0       2.624181    2.393400   -1.532953
   16         1          0       2.591748    2.845920    0.169379
   17         1          0       3.629427   -2.254981    1.395621
   18         1          0       6.136524   -1.428453   -0.892712
   19         1          0       5.307537   -2.843309   -0.198072
   20         6          0      -3.356549    0.121348    0.147571
   21         7          0      -2.341228    0.611058    0.376827
   22        35          0      -4.927693   -0.637359   -0.207897
---------------------------------------------------------------------

SCF Done:  E(RwB97XD) =  -3429.64287233  A.U. after  1 cycles

Zero-point correction=                         0.168849 (a.u.)
Thermal correction to Energy=                  0.183128
Thermal correction to Enthalpy=                0.184072
Thermal correction to Gibbs Free Energy=       0.120206
Sum of electronic and zero-point Energies=         -3429.474023
Sum of electronic and thermal Energies=            -3429.459744
Sum of electronic and thermal Enthalpies=          -3429.458800
Sum of electronic and thermal Free Energies=       -3429.522666

                 E (Thermal)           CV             S
                  KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total               114.915           47.619          134.417

       Item             Value    Threshold  Converged?
Maximum Force          0.000002    0.000450    YES
RMS     Force          0.000000    0.000300    YES
Maximum Displacement    0.014652    0.001800    NO
RMS     Displacement    0.002844    0.001200    NO

   -------Figure S2-2, TS between MODEL and BrCN--------
vita-b1model24.high.log
```

Stoichiometry C7H10BrN2OS(1+)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-3.135377	-1.808412	0.142143
2	6	0	-3.503036	-0.847531	-0.835690
3	6	0	-3.187141	0.515017	-0.244475
4	6	0	-1.764720	0.680181	0.160809
5	16	0	-0.740311	-0.566210	0.639962
6	6	0	0.607074	0.549266	0.801200
7	7	0	0.162534	1.839281	0.604887
8	6	0	1.095961	2.962508	0.665844
9	1	0	1.748985	2.901074	-0.209586
10	6	0	-1.088947	1.917463	0.186009
11	1	0	-1.518482	2.866407	-0.104026
12	1	0	-3.135475	-2.683811	-0.251296
13	1	0	-4.571057	-0.898212	-1.061705
14	1	0	-2.939726	-0.997794	-1.762431
15	1	0	-3.442642	1.307221	-0.951180
16	1	0	-3.799906	0.678898	0.651182
17	1	0	1.348876	0.388207	1.568000
18	1	0	0.533637	3.891215	0.657485
19	1	0	1.686169	2.880531	1.575741
20	6	0	2.047630	-1.940226	0.791804
21	7	0	2.553557	-2.938067	1.111533
22	35	0	1.907544	-0.061019	-0.933047

SCF Done: E(RwB97XD) = -3429.47848024 A.U. after 1 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-717.2904	30.0495	40.8430

Zero-point correction= 0.165911 (a.u.)
Thermal correction to Energy= 0.180143
Thermal correction to Enthalpy= 0.181087
Thermal correction to Gibbs Free Energy= 0.122071
Sum of electronic and zero-point Energies= -3429.312569
Sum of electronic and thermal Energies= -3429.298337
Sum of electronic and thermal Enthalpies= -3429.297393
Sum of electronic and thermal Free Energies= -3429.356410

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	113.042	47.627	124.212

Item	Value	Threshold	Converged?
Maximum Force	0.000004	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.000657	0.001800	YES
RMS Displacement	0.000156	0.001200	YES

-----Figure S2-3, the Br and CN adduct to MODEL-------
vita-b1model24.rev.high.log

Stoichiometry C7H10BrN2OS(1+)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-3.169468	-0.856202	0.478689
2	6	0	-2.983123	-1.382175	-0.835958
3	6	0	-2.312515	-0.279550	-1.633002
4	6	0	-1.019627	0.167679	-1.017824
5	16	0	-0.670830	-0.118257	0.712853
6	6	0	1.046730	0.529953	0.491662
7	7	0	0.985622	1.309167	-0.673027
8	6	0	2.174292	2.024081	-1.130191
9	1	0	2.913003	1.332312	-1.542262
10	6	0	-0.030170	0.935550	-1.509297
11	1	0	-0.015973	1.294140	-2.530381
12	1	0	-3.441207	-1.558136	1.075414

13	1	0	-3.943681	-1.637056	-1.288168
14	1	0	-2.357534	-2.280384	-0.803016
15	1	0	-2.114466	-0.630625	-2.647389
16	1	0	-2.996393	0.571870	-1.698037
17	1	0	1.392377	1.046642	1.382334
18	1	0	1.872590	2.740234	-1.891331
19	1	0	2.605069	2.564750	-0.288937
20	6	0	-1.397750	1.278637	1.465018
21	7	0	-1.881029	2.178769	1.989649
22	35	0	2.159316	-1.107504	0.308509

SCF Done: E(RwB97XD) = -3429.57057024 A.U. after 1 cycles

Zero-point correction= 0.168974 (a.u.)
Thermal correction to Energy= 0.182512
Thermal correction to Enthalpy= 0.183456
Thermal correction to Gibbs Free Energy= 0.127720
Sum of electronic and zero-point Energies= -3429.401596
Sum of electronic and thermal Energies= -3429.388058
Sum of electronic and thermal Enthalpies= -3429.387114
Sum of electronic and thermal Free Energies= -3429.442850

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	114.528	47.905	117.307

Item	Value	Threshold	Converged?
Maximum Force	0.000060	0.000450	YES
RMS Force	0.000007	0.000300	YES
Maximum Displacement	0.000647	0.001800	YES
RMS Displacement	0.000137	0.001200	YES

==========Figure S3 and scheme S3(d)==========
obtained by rwB97x-D/6-311+G(d,p) SCRF=(PCM, solvent=water) calculations

-----Figure S3-1, precursor(MODEL), MODEL + BrCN + HO(-)(H2O)3-----
vita-b1model55.for.high.log

Stoichiometry C7H17BrN2O5S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.405493	2.212381	-0.247746
2	6	0	5.193968	1.075895	0.078709
3	6	0	4.374824	0.208191	1.021237
4	6	0	3.146906	-0.366221	0.387597
5	16	0	1.940693	0.601071	-0.410794
6	6	0	1.006914	-0.767923	-0.734178
7	7	0	1.567387	-1.869586	-0.288677
8	6	0	0.958417	-3.195033	-0.426247
9	1	0	-0.082436	-3.067355	-0.716074
10	6	0	2.773348	-1.664617	0.349328
11	1	0	3.305567	-2.509121	0.759548
12	1	0	4.798562	2.663949	-0.996708
13	1	0	6.118813	1.376743	0.581114
14	1	0	5.454485	0.512003	-0.823476
15	1	0	4.991598	-0.618928	1.378164
16	1	0	4.092142	0.803675	1.894417
17	1	0	0.047687	-0.762079	-1.254084
18	1	0	1.508156	-3.764701	-1.174392
19	1	0	1.001112	-3.694101	0.539429
20	6	0	-2.641617	2.828310	0.537842
21	7	0	-2.821849	3.787411	1.151600
22	8	0	-1.831594	-0.939970	-1.752826
23	1	0	-2.273151	-1.104630	-2.587331
24	1	0	-2.117095	-1.681738	-1.094586
25	8	0	-2.432485	-2.594610	0.039413
26	1	0	-2.449401	-3.531056	-0.162812
27	1	0	-1.356515	-2.067289	1.174282
28	8	0	-0.713673	-1.688886	1.835790
29	1	0	-0.972944	-0.771977	1.937407
30	1	0	-3.835248	-2.020043	0.663610
31	8	0	-4.666214	-1.626283	1.053396
32	1	0	-4.898831	-0.906018	0.465912

```
   33       35         0      -2.359176    1.328231   -0.421775
---------------------------------------------------------------------

SCF Done:  E(RwB97XD) =  -3734.96720235    A.U. after   1 cycles

Zero-point correction=                          0.253434 (a.u.)
Thermal correction to Energy=                    0.279141
Thermal correction to Enthalpy=                  0.280086
Thermal correction to Gibbs Free Energy=         0.189657
Sum of electronic and zero-point Energies=         -3734.713769
Sum of electronic and thermal Energies=            -3734.688061
Sum of electronic and thermal Enthalpies=          -3734.687117
Sum of electronic and thermal Free Energies=       -3734.777545

                 E (Thermal)             CV                S
                  KCal/Mol       Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total               175.164           83.527           190.322

       Item             Value     Threshold  Converged?
Maximum Force           0.000033    0.000450     YES
RMS     Force           0.000008    0.000300     YES
Maximum Displacement    0.369592    0.001800     NO
RMS     Displacement    0.054192    0.001200     NO

  -------Figure S3-2, TS1(MODEL), HO(-) addition TS-------
 vita-b1model55.high.log

Stoichiometry   C7H17BrN2O5S

                     Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic           Coordinates (Angstroms)
Number     Number      Type             X         Y         Z
---------------------------------------------------------------------
    1         8          0       3.582223    2.671521   -0.088636
    2         6          0       4.251462    1.757541   -0.948362
    3         6          0       4.450999    0.457886   -0.184517
    4         6          0       3.188612   -0.302815    0.073776
    5        16          0       1.799864    0.394829    0.906040
    6         6          0       0.887586   -1.053641    0.650567
    7         7          0       1.680825   -2.029361    0.197443
    8         6          0       1.182543   -3.370277   -0.076644
    9         1          0       0.354171   -3.580986    0.597158
   10         6          0       2.931000   -1.585362   -0.224093
   11         1          0       3.594516   -2.280556   -0.716807
   12         1          0       3.268102    3.413974   -0.607450
   13         1          0       5.228409    2.155302   -1.244047
   14         1          0       3.662441    1.574969   -1.854166
   15         1          0       5.122237   -0.189424   -0.754035
   16         1          0       4.951649    0.686549    0.762310
   17         1          0       0.012832   -1.290237    1.242723
   18         1          0       0.838342   -3.437408   -1.110449
   19         1          0       1.980632   -4.091403    0.093967
   20         6          0      -3.021624    2.634990    0.412635
   21         7          0      -3.730293    3.476601    0.759152
   22         8          0      -0.383600   -0.637647   -0.842722
   23         1          0       0.159690   -0.439219   -1.610880
   24         1          0      -1.461399   -1.748586   -0.980790
   25         8          0      -2.216544   -2.415712   -0.868754
   26         1          0      -2.016020   -3.174025   -1.420521
   27         1          0      -1.999809   -2.590575    0.916831
   28         8          0      -1.682917   -2.561018    1.839329
   29         1          0      -2.407457   -2.193998    2.348866
   30         1          0      -3.858151   -1.688004   -1.065962
   31         8          0      -4.749888   -1.302075   -1.149410
   32         1          0      -4.807477   -0.659265   -0.440679
   33        35          0      -1.905483    1.308985   -0.133928
---------------------------------------------------------------------

SCF Done:  E(RwB97XD) =  -3734.95374386  A.U. after 1 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman
                 1                  2                  3
                 A                  A                  A
Frequencies --   -342.1927            14.1645             18.8033

Zero-point correction=                          0.254254 (a.u.)
Thermal correction to Energy=                    0.279429
Thermal correction to Enthalpy=                  0.280374
Thermal correction to Gibbs Free Energy=         0.193565
```

Sum of electronic and zero-point Energies= -3734.699490
Sum of electronic and thermal Energies= -3734.674315
Sum of electronic and thermal Enthalpies= -3734.673370
Sum of electronic and thermal Free Energies= -3734.760178

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	175.345	82.765	182.703

Item	Value	Threshold	Converged?
Maximum Force	0.000007	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.000775	0.001800	YES
RMS Displacement	0.000177	0.001200	YES

-------Figure S3-3, Int1(MODEL), HO-adduct---------
vita-b1model54.rev.high.log

Stoichiometry C7H17BrN2O5S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.568297	-2.218472	-1.771478
2	6	0	3.768750	-1.684246	-1.218317
3	6	0	3.830991	-0.157276	-1.256342
4	6	0	2.883442	0.546302	-0.338306
5	16	0	1.123377	0.516932	-0.597248
6	6	0	0.881791	1.223665	1.110121
7	7	0	2.137906	1.814019	1.486574
8	6	0	2.163307	3.262712	1.663681
9	1	0	1.396146	3.559194	2.380154
10	6	0	3.197403	1.268798	0.740683
11	1	0	4.209740	1.471184	1.069903
12	1	0	2.494814	-1.954309	-2.691544
13	1	0	4.631814	-2.094149	-1.752881
14	1	0	3.803796	-2.040485	-0.187457
15	1	0	4.849447	0.140161	-0.987981
16	1	0	3.670456	0.175200	-2.289591
17	1	0	0.095617	1.981427	1.054100
18	1	0	3.135140	3.550440	2.068170
19	1	0	2.005677	3.804729	0.721318
20	6	0	-3.712136	1.546601	-1.471655
21	7	0	-4.297253	2.330592	-2.081475
22	8	0	0.560071	0.223051	2.027838
23	1	0	-0.171490	-0.324123	1.673568
24	8	0	-1.350109	-1.438006	0.953935
25	1	0	-0.785253	-2.059916	0.451575
26	1	0	-1.864104	-1.972384	1.586069
27	8	0	0.363057	-3.133343	-0.358249
28	1	0	0.051183	-3.855503	-0.906834
29	1	0	1.109770	-2.735843	-0.843687
30	8	0	-2.868133	-2.866902	2.796300
31	1	0	-2.402091	-3.236433	3.550101
32	1	0	-3.420944	-3.578751	2.465219
33	35	0	-2.798145	0.323326	-0.520168

SCF Done: E(RwB97XD) = -3734.97811403 A.U. after 1 cycles

Zero-point correction= 0.257917 (a.u.)
Thermal correction to Energy= 0.282860
Thermal correction to Enthalpy= 0.283804
Thermal correction to Gibbs Free Energy= 0.196665
Sum of electronic and zero-point Energies= -3734.720197
Sum of electronic and thermal Energies= -3734.695254
Sum of electronic and thermal Enthalpies= -3734.694310
Sum of electronic and thermal Free Energies= -3734.781449

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	177.497	82.263	183.399

Item	Value	Threshold	Converged?
Maximum Force	0.000016	0.000450	YES
RMS Force	0.000003	0.000300	YES
Maximum Displacement	0.074276	0.001800	NO
RMS Displacement	0.010903	0.001200	NO

-----Figure S3-4, TS2(MODEL) ----------
vita-b1model54.high.log

Stoichiometry C7H17BrN2O5S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-3.774811	1.348280	-2.174945
2	6	0	-4.549361	0.740812	-1.154323
3	6	0	-3.729161	-0.396742	-0.562942
4	6	0	-2.526987	0.055821	0.201589
5	16	0	-1.206072	0.966007	-0.545047
6	6	0	-0.197131	0.666282	0.936257
7	7	0	-1.062611	0.309690	1.963732
8	6	0	-0.627802	0.241220	3.347444
9	1	0	-0.850118	1.174556	3.872981
10	6	0	-2.270086	-0.166700	1.500747
11	1	0	-2.909286	-0.708781	2.183938
12	1	0	-4.149351	2.200596	-2.395370
13	1	0	-5.484412	0.340561	-1.567634
14	1	0	-4.797733	1.463381	-0.366647
15	1	0	-4.365367	-0.976489	0.112845
16	1	0	-3.430774	-1.064759	-1.378076
17	1	0	0.390276	-0.459979	0.661688
18	1	0	-1.129303	-0.593417	3.836237
19	1	0	0.444484	0.058821	3.381315
20	6	0	0.591552	-1.823279	0.765047
21	7	0	0.266946	-2.406504	1.732502
22	8	0	0.756336	1.542124	1.286868
23	1	0	1.484018	1.572619	0.608414
24	8	0	2.657517	1.666288	-0.495214
25	1	0	3.122187	2.515514	-0.528620
26	1	0	3.328133	0.963008	-0.467877
27	8	0	3.783213	4.252443	-0.528022
28	1	0	3.387607	4.842224	-1.171835
29	1	0	3.733938	4.709124	0.313417
30	8	0	4.297080	-0.574814	-0.315782
31	1	0	4.980477	-0.816918	-0.942023
32	1	0	3.627827	-1.266478	-0.382511
33	35	0	1.302382	-2.186030	-1.008837

SCF Done: E(RwB97XD) = -3734.92524607 A.U. after 17 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-792.7629	9.1958	13.6837

Zero-point correction= 0.253036 (a.u.)
Thermal correction to Energy= 0.278337
Thermal correction to Enthalpy= 0.279282
Thermal correction to Gibbs Free Energy= 0.190645
Sum of electronic and zero-point Energies= -3734.672210
Sum of electronic and thermal Energies= -3734.646909
Sum of electronic and thermal Enthalpies= -3734.645964
Sum of electronic and thermal Free Energies= -3734.734601

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	174.659	81.772	186.552

------Figure S3-5, Int2(MODEL), thio-lactone type intermediate----
vita-b1model54.for.high.log

Stoichiometry C7H17BrN2O5S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.427903	1.715594	-1.072728
2	6	0	-4.933315	0.733064	-0.177091
3	6	0	-3.975298	-0.447806	-0.189195

4	6	0	-2.637970	-0.159150	0.415682
5	16	0	-1.581012	1.120797	-0.164952
6	6	0	-0.336138	0.672780	0.993363
7	7	0	-0.778693	-0.341449	1.761531
8	6	0	0.065674	-0.983531	2.759055
9	1	0	0.850433	-0.289000	3.050234
10	6	0	-2.043286	-0.810132	1.425228
11	1	0	-2.447730	-1.646744	1.975709
12	1	0	-4.910490	2.533533	-0.941830
13	1	0	-5.925191	0.395998	-0.497681
14	1	0	-5.015714	1.139704	0.837090
15	1	0	-4.424338	-1.273299	0.368921
16	1	0	-3.853412	-0.786826	-1.223323
17	1	0	2.592005	-1.260104	0.515930
18	1	0	-0.537402	-1.237540	3.629428
19	1	0	0.511835	-1.886899	2.338293
20	6	0	3.390181	-0.640035	0.920125
21	7	0	4.233207	0.041863	1.293794
22	8	0	0.771177	1.224088	1.111314
23	1	0	1.492490	1.908316	0.005303
24	8	0	2.030598	2.276146	-0.787495
25	1	0	2.987346	2.433435	-0.504406
26	1	0	1.976222	1.581005	-1.530046
27	8	0	4.465656	2.608406	-0.010450
28	1	0	4.677076	3.420103	0.457908
29	1	0	4.678752	1.877366	0.589165
30	8	0	1.801956	0.443556	-2.543182
31	1	0	1.177077	0.613163	-3.253108
32	1	0	1.510885	-0.390741	-2.116627
33	35	0	0.898965	-2.265731	-0.940333

SCF Done: E(RwB97XD) = -3735.05643114 A.U. after 1 cycles

Zero-point correction= 0.256111 (a.u.)
Thermal correction to Energy= 0.280690
Thermal correction to Enthalpy= 0.281634
Thermal correction to Gibbs Free Energy= 0.197172
Sum of electronic and zero-point Energies= -3734.800320
Sum of electronic and thermal Energies= -3734.775742
Sum of electronic and thermal Enthalpies= -3734.774797
Sum of electronic and thermal Free Energies= -3734.859259

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	176.135	80.704	177.764

Item	Value	Threshold	Converged?
Maximum Force	0.000033	0.000450	YES
RMS Force	0.000007	0.000300	YES
Maximum Displacement	0.002331	0.001800	NO
RMS Displacement	0.000509	0.001200	YES

==========Figure S4 and scheme 3==========
obtained by rwB97x-D/6-311+G(d,p) SCRF=(PCM, solvent=water)
calculations

-----Figure S4-1, precursor[B], thiamine + BrCN + HO(-) + (H2O)8-----
vita-b1brcng3.for.high.log

Stoichiometry C13H34BrN5O10S

Standard orientation:

1	8	0	-5.140237	2.417878	-2.238497
2	6	0	-5.077529	2.929423	-0.913707
3	6	0	-4.844900	1.753169	0.021595
4	6	0	-3.518653	1.086427	-0.170932
5	16	0	-3.028195	0.491213	-1.729764
6	6	0	-1.600523	-0.110964	-1.085579
7	7	0	-1.488568	0.126204	0.205305
8	6	0	-0.289696	-0.245812	0.962518
9	6	0	0.648593	0.914633	1.159931
10	6	0	0.496261	2.146448	0.569139
11	7	0	1.336313	3.176303	0.752132
12	6	0	2.365484	2.949117	1.565304

13	6	0	3.344303	4.063571	1.785994
14	7	0	2.618997	1.798756	2.190986
15	6	0	1.782506	0.774387	1.996294
16	7	0	2.097838	-0.404338	2.589173
17	6	0	-2.572030	0.804936	0.762688
18	6	0	-2.585629	1.092555	2.225419
19	1	0	-5.066266	3.143473	-2.860912
20	1	0	-6.017844	3.420730	-0.644094
21	1	0	-4.263799	3.656204	-0.816704
22	1	0	-4.921145	2.104384	1.051292
23	1	0	-5.639081	1.015122	-0.126062
24	1	0	-0.830259	-0.616102	-1.646844
25	1	0	-3.464085	1.675749	2.491054
26	1	0	-2.605937	0.153805	2.784507
27	1	0	-1.699527	1.658377	2.521557
28	1	0	-0.628630	-0.649563	1.916818
29	1	0	0.181857	-1.069935	0.420535
30	1	0	-0.343700	2.340204	-0.092607
31	1	0	1.402710	-1.146341	2.743391
32	1	0	2.833723	-0.348776	3.277879
33	1	0	4.271474	3.848159	1.246644
34	1	0	2.940595	5.007347	1.422615
35	1	0	3.592446	4.149347	2.845062
36	6	0	2.313332	0.602318	-1.993139
37	7	0	1.315355	0.286698	-2.473760
38	35	0	3.856106	1.106807	-1.261666
39	8	0	-0.318952	-2.929717	-0.857514
40	1	0	0.109807	-2.936345	-1.730204
41	8	0	1.086731	-2.648552	-3.283279
42	1	0	1.997703	-2.618094	-2.923211
43	1	0	0.899682	-1.728385	-3.492194
44	1	0	-1.877667	-3.147826	-0.427998
45	8	0	-2.770556	-3.251238	-0.002039
46	1	0	-2.998684	-4.179963	-0.084646
47	1	0	-2.526128	-2.696519	1.687710
48	8	0	-2.330543	-2.281405	2.550566
49	1	0	-3.003423	-2.600691	3.155048
50	1	0	0.306771	-3.388376	-0.201777
51	8	0	1.233947	-3.936454	0.907631
52	1	0	1.368448	-4.884628	0.927881
53	8	0	3.571379	-2.388486	-2.160610
54	1	0	3.493882	-2.353678	-1.177637
55	1	0	4.285286	-3.000082	-2.348926
56	1	0	-4.299959	-2.211280	0.059772
57	8	0	-5.133471	-1.741651	0.227714
58	1	0	-5.009630	-1.330263	1.085128
59	1	0	2.503395	-3.050718	0.675511
60	8	0	3.267506	-2.409406	0.502905
61	1	0	3.076005	-1.639233	1.050543
62	1	0	0.725045	-3.233659	2.271036
63	8	0	0.444890	-2.677896	3.056369
64	1	0	-0.519893	-2.611272	2.988411

SCF Done: E(RwB97XD) = -4514.37663484 A.U. after 2 cycles

Zero-point correction= 0.514370 (a.u.)
Thermal correction to Energy= 0.560554
Thermal correction to Enthalpy= 0.561499
Thermal correction to Gibbs Free Energy= 0.429115
Sum of electronic and zero-point Energies= -4513.862265
Sum of electronic and thermal Energies= -4513.816080
Sum of electronic and thermal Enthalpies= -4513.815136
Sum of electronic and thermal Free Energies= -4513.947520

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	351.753	159.028	278.624

Item	Value	Threshold	Converged?
Maximum Force	0.000226	0.000450	YES
RMS Force	0.000023	0.000300	YES
Maximum Displacement	0.006062	0.001800	NO
RMS Displacement	0.001431	0.001200	NO

-----Figure S4-2, TS1[B], addition of HO(-) to thiamine----
vita-b1brcng3.high.log

Stoichiometry C13H34BrN5O10S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.477764	-1.658599	-3.350210
2	6	0	4.479979	-2.647903	-2.327954
3	6	0	4.387616	-1.936861	-0.986749
4	6	0	3.076411	-1.254283	-0.749654
5	16	0	2.467654	-0.048664	-1.884738
6	6	0	1.148144	0.305202	-0.841329
7	7	0	1.090877	-0.574820	0.161430
8	6	0	-0.017425	-0.555810	1.104292
9	6	0	-1.099738	-1.548769	0.777227
10	6	0	-1.069885	-2.391048	-0.305704
11	7	0	-2.038572	-3.276155	-0.598493
12	6	0	-3.070059	-3.302737	0.242313
13	6	0	-4.193093	-4.251074	-0.060871
14	7	0	-3.212311	-2.538823	1.326349
15	6	0	-2.245020	-1.654729	1.608428
16	7	0	-2.412586	-0.882137	2.696377
17	6	0	2.214961	-1.409472	0.275114
18	6	0	2.312693	-2.325703	1.448729
19	1	0	4.330154	-2.084389	-4.196433
20	1	0	5.405712	-3.232474	-2.363399
21	1	0	3.632300	-3.331396	-2.450101
22	1	0	4.550603	-2.674725	-0.199037
23	1	0	5.203854	-1.211748	-0.910534
24	1	0	0.251919	0.765966	-1.223836
25	1	0	3.182132	-2.974199	1.360306
26	1	0	2.389951	-1.755955	2.379217
27	1	0	1.427571	-2.964502	1.515244
28	1	0	0.383163	-0.726892	2.105653
29	1	0	-0.413303	0.462092	1.108992
30	1	0	-0.225785	-2.368273	-0.989791
31	1	0	-1.754000	-0.165297	3.006909
32	1	0	-3.256833	-1.013680	3.229032
33	1	0	-5.027317	-3.699059	-0.504582
34	1	0	-3.870910	-5.015383	-0.766833
35	1	0	-4.557027	-4.719840	0.854387
36	6	0	-2.673030	1.060484	-1.621863
37	7	0	-1.768095	1.731703	-1.860974
38	35	0	-4.072785	0.029328	-1.241311
39	8	0	1.519646	2.059009	0.100828
40	1	0	1.526646	2.669236	-0.650701
41	8	0	0.699949	3.523240	-2.300180
42	1	0	0.375530	4.400641	-2.026325
43	1	0	-0.093260	2.974090	-2.303276
44	1	0	2.696896	1.874137	1.092602
45	8	0	3.349612	1.680709	1.843669
46	1	0	3.672598	2.532009	2.147191
47	1	0	2.472375	0.797808	3.094693
48	8	0	1.935217	0.266575	3.720129
49	1	0	2.474586	0.155011	4.505224
50	1	0	0.505857	2.691747	1.101427
51	8	0	-0.139036	3.115971	1.764390
52	1	0	0.368707	3.794166	2.217125
53	8	0	-0.508713	5.874716	-1.401408
54	1	0	-1.099418	5.448168	-0.746924
55	1	0	-0.011122	6.534802	-0.915113
56	1	0	4.680180	0.468360	1.703538
57	8	0	5.438679	-0.143695	1.726510
58	1	0	5.055307	-1.008767	1.878247
59	1	0	-1.422924	3.913345	0.864153
60	8	0	-2.066679	4.439967	0.343849
61	1	0	-2.601275	3.799929	-0.130680
62	1	0	-0.594803	1.913279	3.073454
63	8	0	-0.697649	1.202444	3.732159
64	1	0	0.212096	0.879092	3.859270

SCF Done: E(RwB97XD) = -4514.35795948 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-339.5929	-52.4371	-14.6818

Zero-point correction= 0.513953 (a.u.)
Thermal correction to Energy= 0.558533

```
Thermal correction to Enthalpy=               0.559477
Thermal correction to Gibbs Free Energy=      0.430663
Sum of electronic and zero-point Energies=        -4513.844006
Sum of electronic and thermal Energies=           -4513.799426
Sum of electronic and thermal Enthalpies=         -4513.798482
Sum of electronic and thermal Free Energies=      -4513.927297

                E (Thermal)           CV              S
                 KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              350.485          154.768          271.113

       Item             Value    Threshold  Converged?
Maximum Force          0.000224    0.000450    YES
RMS    Force           0.000031    0.000300    YES
Maximum Displacement    0.040288    0.001800    NO
RMS    Displacement     0.004576    0.001200    NO

 ----Figure S4-3, Int1[B]. the HO adduct------
 vita-b1brcng3.rev.high.log

 Stoichiometry   C13H34BrN5O10S

                    Standard orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic           Coordinates (Angstroms)
Number     Number      Type             X         Y         Z
---------------------------------------------------------------------
    1         8          0       4.975763   -0.843418   -2.703294
    2         6          0       5.405360   -0.744635   -1.350756
    3         6          0       4.769421    0.485749   -0.719485
    4         6          0       3.277771    0.414957   -0.589477
    5        16          0       2.222346    0.977800   -1.913499
    6         6          0       0.748972    0.872764   -0.839417
    7         7          0       1.163491    0.121698    0.295831
    8         6          0       0.190617   -0.650710    1.031312
    9         6          0      -0.038078   -2.049710    0.515795
   10         6          0       0.623121   -2.585561   -0.559602
   11         7          0       0.427394   -3.836478   -1.017562
   12         6          0      -0.470093   -4.560470   -0.355130
   13         6          0      -0.727926   -5.962601   -0.826075
   14         7          0      -1.178057   -4.151049    0.700719
   15         6          0      -0.977503   -2.904488    1.145859
   16         7          0      -1.700321   -2.502518    2.211952
   17         6          0       2.548859   -0.025280    0.445538
   18         6          0       3.059658   -0.628841    1.712438
   19         1          0       5.320783   -1.657563   -3.073710
   20         1          0       6.497323   -0.651237   -1.303605
   21         1          0       5.111217   -1.639725   -0.789356
   22         1          0       5.210584    0.624760    0.271299
   23         1          0       5.053143    1.367757   -1.302375
   24         1          0      -0.057372    0.384967   -1.391356
   25         1          0       4.148789   -0.621386    1.730783
   26         1          0       2.679278   -0.090294    2.585550
   27         1          0       2.737050   -1.670997    1.803260
   28         1          0       0.486438   -0.683700    2.083446
   29         1          0      -0.751589   -0.096933    1.022932
   30         1          0       1.358045   -1.989236   -1.094881
   31         1          0      -1.700376   -1.549559    2.573521
   32         1          0      -2.380943   -3.147345    2.578910
   33         1          0      -1.768147   -6.064652   -1.145722
   34         1          0      -0.072039   -6.213851   -1.658282
   35         1          0      -0.565821   -6.670396   -0.009867
   36         6          0      -2.929815    0.102006   -1.767429
   37         7          0      -2.490999    0.751783   -2.610880
   38        35          0      -3.583354   -0.896962   -0.445709
   39         8          0       0.275702    2.150856   -0.402601
   40         1          0      -0.093909    2.639431   -1.182687
   41         8          0      -0.861859    3.238309   -2.567304
   42         1          0      -1.536072    3.910132   -2.332774
   43         1          0      -1.375228    2.486216   -2.889491
   44         1          0       1.201320    2.739687    1.022962
   45         8          0       1.579091    2.952534    1.898395
   46         1          0       1.379406    3.878983    2.055772
   47         1          0       1.004594    1.782979    3.179667
   48         8          0       0.727056    1.114236    3.832913
   49         1          0       1.009770    1.450749    4.685583
   50         1          0      -1.142674    2.223412    0.770426
   51         8          0      -1.875602    2.344508    1.404395
   52         1          0      -1.573288    3.031644    2.005313
   53         8          0      -2.895299    4.929171   -1.865500
```

54	1	0	-3.372530	4.442301	-1.162524
55	1	0	-2.716226	5.801554	-1.509422
56	1	0	3.410666	2.660046	2.115688
57	8	0	4.358198	2.599451	2.320184
58	1	0	4.466453	1.744267	2.739209
59	1	0	-3.353989	2.960981	0.560077
60	8	0	-4.073128	3.431069	0.097789
61	1	0	-4.713146	2.762831	-0.154859
62	1	0	-2.107722	0.854495	2.675819
63	8	0	-1.881476	0.206971	3.359350
64	1	0	-0.994225	0.495906	3.640011

SCF Done: E(RwB97XD) = -4514.37849900 A.U. after 1 cycles

Zero-point correction= 0.517850 (a.u.)
Thermal correction to Energy= 0.564462
Thermal correction to Enthalpy= 0.565406
Thermal correction to Gibbs Free Energy= 0.431898
Sum of electronic and zero-point Energies= -4513.860649
Sum of electronic and thermal Energies= -4513.814037
Sum of electronic and thermal Enthalpies= -4513.813093
Sum of electronic and thermal Free Energies= -4513.946601

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	354.205	160.550	280.991

Item	Value	Threshold	Converged?
Maximum Force	0.000005	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.003569	0.001800	NO
RMS Displacement	0.000582	0.001200	YES

----Figure S4-4, TS2[B], the hydride H(24) removal---
vita-b1brcnf.high.log

Stoichiometry C13H34BrN5O10S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-5.610442	1.021237	0.359651
2	6	0	-5.685925	-0.390994	0.243532
3	6	0	-5.111677	-0.924991	-1.072656
4	6	0	-3.629692	-0.764744	-1.214191
5	16	0	-2.956741	0.797470	-1.705235
6	6	0	-1.282618	0.219591	-1.329750
7	7	0	-1.358544	-1.167633	-1.173948
8	6	0	-0.210156	-2.023938	-1.439255
9	6	0	0.788598	-2.119950	-0.313811
10	6	0	0.554827	-1.661944	0.952568
11	7	0	1.476947	-1.654627	1.933951
12	6	0	2.680080	-2.124262	1.611559
13	6	0	3.740765	-2.112189	2.670703
14	7	0	3.017822	-2.623301	0.421782
15	6	0	2.083292	-2.655095	-0.536585
16	7	0	2.428051	-3.236907	-1.701109
17	6	0	-2.656778	-1.664512	-0.986159
18	6	0	-2.829184	-3.081767	-0.544398
19	1	0	-4.691129	1.273427	0.482784
20	1	0	-6.747599	-0.639665	0.290811
21	1	0	-5.185506	-0.876582	1.089751
22	1	0	-5.365193	-1.985062	-1.149824
23	1	0	-5.617236	-0.423848	-1.904058
24	1	0	-1.036424	0.748956	-0.191683
25	1	0	-3.845526	-3.250728	-0.194440
26	1	0	-2.635352	-3.783924	-1.359829
27	1	0	-2.147093	-3.315986	0.276627
28	1	0	-0.588010	-3.012530	-1.703852
29	1	0	0.288062	-1.637519	-2.333211
30	1	0	-0.420619	-1.265684	1.214055
31	1	0	1.851558	-3.164189	-2.521066
32	1	0	3.395571	-3.479697	-1.839310
33	1	0	4.727395	-1.986664	2.225158
34	1	0	3.557731	-1.319207	3.395173
35	1	0	3.730123	-3.068256	3.202463
36	6	0	-0.810469	1.426519	1.015560

37	7	0	0.072938	2.184657	1.172266
38	35	0	-2.300482	0.708682	2.013207
39	8	0	-0.263725	0.641216	-2.109605
40	1	0	-0.038989	1.614882	-2.005509
41	8	0	0.708755	3.035779	-2.041008
42	1	0	1.643968	2.951079	-1.764655
43	1	0	0.380653	3.711116	-1.431304
44	8	0	3.293365	3.126963	-0.939547
45	1	0	3.314212	2.526647	-0.169681
46	1	0	3.958668	2.739413	-1.528811
47	8	0	1.142877	4.726046	0.264181
48	1	0	0.893253	3.914671	0.733094
49	1	0	2.037451	4.551330	-0.052238
50	1	0	1.603339	0.240797	-1.878425
51	8	0	2.474510	0.045654	-1.515256
52	1	0	3.136014	0.482107	-2.073058
53	8	0	3.356694	1.030660	0.871897
54	1	0	2.798361	0.599399	0.196121
55	1	0	2.872927	1.004262	1.719929
56	8	0	4.903893	1.168375	-2.252747
57	1	0	5.476576	1.121145	-3.020443
58	1	0	5.239657	0.516243	-1.604116
59	8	0	1.850663	0.838399	3.219716
60	1	0	1.135089	1.420209	2.938639
61	1	0	1.553278	-0.062630	2.980979
62	8	0	5.352913	-0.578378	-0.145422
63	1	0	4.794887	-0.011668	0.419124
64	1	0	4.831732	-1.388526	-0.225881

SCF Done: E(RwB97XD) = -4514.33519643 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-1030.5620	20.5583	27.7726

Zero-point correction= 0.515575 (a.u.)
Thermal correction to Energy= 0.559506
Thermal correction to Enthalpy= 0.560451
Thermal correction to Gibbs Free Energy= 0.437632
Sum of electronic and zero-point Energies= -4513.819622
Sum of electronic and thermal Energies= -4513.775690
Sum of electronic and thermal Enthalpies= -4513.774746
Sum of electronic and thermal Free Energies= -4513.897564

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	351.096	156.321	258.493

Item	Value	Threshold	Converged?
Maximum Force	0.000017	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.005314	0.001800	NO
RMS Displacement	0.000607	0.001200	YES

----Figure S4-5, Int2[B], the thio-lactone type intermediate----
vita-b1brcnf.for.high.log

Stoichiometry C13H34BrN5O10S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.982683	0.138203	0.651208
2	6	0	-5.128673	-1.064170	-0.081415
3	6	0	-4.633210	-0.929928	-1.522712
4	6	0	-3.164126	-0.661933	-1.653080
5	16	0	-2.545483	0.983715	-1.603187
6	6	0	-0.905780	0.430328	-1.868278
7	7	0	-0.903773	-0.925355	-1.967335
8	6	0	0.332373	-1.640230	-2.253106
9	6	0	1.124063	-2.007371	-1.023677
10	6	0	0.642748	-1.903094	0.254024
11	7	0	1.378992	-2.168396	1.349360
12	6	0	2.648258	-2.511828	1.145592
13	6	0	3.490057	-2.778823	2.357388
14	7	0	3.228888	-2.631900	-0.047439

15	6	0	2.476528	-2.416110	-1.136402
16	7	0	3.071503	-2.612530	-2.327487
17	6	0	-2.163053	-1.540116	-1.841157
18	6	0	-2.261398	-3.026698	-1.933564
19	1	0	-4.177058	0.064645	1.185303
20	1	0	-6.192663	-1.316417	-0.103560
21	1	0	-4.598397	-1.882296	0.418893
22	1	0	-4.877777	-1.849393	-2.061492
23	1	0	-5.193661	-0.128294	-2.012426
24	1	0	-2.083550	1.789466	1.903082
25	1	0	-3.268102	-3.352384	-1.679275
26	1	0	-2.034554	-3.381544	-2.942669
27	1	0	-1.569634	-3.509089	-1.238009
28	1	0	0.087317	-2.525408	-2.842784
29	1	0	0.931053	-0.988423	-2.895081
30	1	0	-0.374015	-1.566909	0.445067
31	1	0	2.638868	-2.342833	-3.193327
32	1	0	4.063503	-2.784874	-2.338610
33	1	0	4.544035	-2.837675	2.090893
34	1	0	3.342282	-1.997499	3.105253
35	1	0	3.188589	-3.728247	2.808069
36	6	0	-1.954612	2.819084	1.573010
37	7	0	-1.816606	3.900772	1.220943
38	35	0	-2.336729	-0.542287	2.540759
39	8	0	0.087144	1.159525	-1.961298
40	1	0	0.661938	2.836754	-1.453356
41	8	0	1.195987	3.619014	-1.228846
42	1	0	2.243415	3.433490	-0.261068
43	1	0	0.578664	4.364816	-1.059896
44	8	0	3.026567	3.278262	0.420509
45	1	0	2.791757	2.467145	0.982928
46	1	0	3.842482	2.994078	-0.084631
47	8	0	-0.559283	5.611656	-0.698109
48	1	0	-1.081430	5.244712	0.033151
49	1	0	-0.209578	6.448210	-0.383533
50	1	0	1.824701	0.782257	-1.669741
51	8	0	2.661530	0.539404	-1.241930
52	1	0	3.348621	1.127561	-1.576496
53	8	0	2.624271	0.976591	1.438402
54	1	0	2.401725	0.620312	0.554808
55	1	0	1.954447	0.664683	2.090862
56	8	0	4.983812	2.103114	-0.856406
57	1	0	5.785806	2.495610	-1.207657
58	1	0	5.234873	1.297298	-0.351943
59	8	0	0.934161	-0.159084	3.213441
60	1	0	-0.017753	0.013492	3.159768
61	1	0	1.022782	-1.022209	2.754897
62	8	0	5.127407	-0.136839	0.688055
63	1	0	4.367369	0.143983	1.223455
64	1	0	4.813815	-0.925995	0.227317

SCF Done: E(RwB97XD) = -4514.46674610 A.U. after 1 cycles

Zero-point correction= 0.517781 (a.u.)
Thermal correction to Energy= 0.562475
Thermal correction to Enthalpy= 0.563419
Thermal correction to Gibbs Free Energy= 0.436290
Sum of electronic and zero-point Energies= -4513.948965
Sum of electronic and thermal Energies= -4513.904271
Sum of electronic and thermal Enthalpies= -4513.903327
Sum of electronic and thermal Free Energies= -4514.030456

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	352.959	155.757	267.567

Item	Value	Threshold	Converged?
Maximum Force	0.000008	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.003984	0.001800	NO
RMS Displacement	0.000976	0.001200	YES

----Figure S4-6, TS3[B], ring closure------
vita-b1brcnxx.high.log

Stoichiometry C13H34BrN5O10S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.883319	-3.873724	-1.326682
2	6	0	0.365643	-4.310183	-1.830536
3	6	0	1.224269	-3.141626	-2.324023
4	6	0	1.647571	-2.211128	-1.232023
5	16	0	0.426648	-1.157765	-0.479552
6	6	0	1.729348	-0.313168	0.398647
7	7	0	2.840566	-1.158854	0.442299
8	6	0	4.053337	-0.583148	1.019945
9	6	0	4.380780	0.792311	0.490549
10	6	0	5.529215	1.467999	0.891923
11	7	0	5.805006	2.713792	0.528931
12	6	0	4.904057	3.340548	-0.237121
13	6	0	5.198330	4.751510	-0.639427
14	7	0	3.774494	2.785987	-0.677990
15	6	0	3.542909	1.531144	-0.327646
16	7	0	2.330429	0.938406	-0.813676
17	6	0	2.847890	-2.075055	-0.645990
18	6	0	4.104152	-2.818547	-0.951779
19	1	0	-0.849308	-3.868662	-0.356007
20	1	0	0.175410	-4.980140	-2.673837
21	1	0	0.914278	-4.875337	-1.068581
22	1	0	2.109698	-3.543624	-2.821477
23	1	0	0.660461	-2.588360	-3.081486
24	8	0	1.493513	0.383641	1.477795
25	1	0	3.938695	-3.529250	-1.758228
26	1	0	4.906657	-2.141338	-1.255747
27	1	0	4.443145	-3.379813	-0.076675
28	1	0	3.909181	-0.509267	2.100581
29	1	0	4.879320	-1.271674	0.855953
30	1	0	6.252412	0.976449	1.537310
31	1	0	0.482047	0.564140	1.637610
32	1	0	2.500986	0.411752	-1.671361
33	1	0	5.558066	5.321482	0.218213
34	1	0	5.987724	4.758321	-1.396294
35	1	0	4.310747	5.225492	-1.055118
36	1	0	1.620055	1.656829	-1.021885
37	8	0	0.283713	2.868960	-1.592533
38	1	0	0.504052	3.761861	-1.310439
39	8	0	-0.925821	0.746152	1.905768
40	1	0	-1.418266	-0.105891	1.970336
41	1	0	-1.365741	1.245302	1.184970
42	8	0	-2.373990	-1.545067	1.804113
43	1	0	-2.767447	-1.349929	0.931117
44	1	0	-1.840921	-2.349555	1.685571
45	8	0	-2.004421	1.878955	-0.306599
46	1	0	-2.762717	2.496479	-0.349358
47	1	0	-1.279570	2.262566	-0.828334
48	1	0	0.246584	2.905967	-2.553033
49	8	0	-3.258946	-0.607720	-0.640139
50	1	0	-4.187256	-0.342898	-0.735940
51	1	0	-2.765919	0.231913	-0.656183
52	8	0	-4.300793	3.332362	-0.527932
53	1	0	-4.992716	2.657730	-0.651594
54	1	0	-4.613220	3.899824	0.180392
55	8	0	-0.762064	-3.847442	1.460832
56	1	0	0.130115	-3.646414	1.813930
57	1	0	-1.046904	-4.655612	1.894107
58	8	0	1.728222	-3.213556	2.413507
59	1	0	2.144562	-2.539707	1.858520
60	1	0	1.719486	-2.839703	3.298315
61	35	0	-6.365095	0.735516	-0.821278
62	1	0	-5.241174	0.980946	1.408952
63	6	0	-4.773865	1.205357	2.362107
64	7	0	-4.293515	1.455629	3.373359

SCF Done: E(RwB97XD) = -4514.40877705 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-294.4008	14.0721	15.0584

Zero-point correction= 0.516632 (a.u.)
Thermal correction to Energy= 0.561743
Thermal correction to Enthalpy= 0.562687
Thermal correction to Gibbs Free Energy= 0.431336

Sum of electronic and zero-point Energies= -4513.892145
Sum of electronic and thermal Energies= -4513.847035
Sum of electronic and thermal Enthalpies= -4513.846090
Sum of electronic and thermal Free Energies= -4513.977441

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	352.499	155.600	276.450

Item	Value	Threshold	Converged?
Maximum Force	0.000004	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.004447	0.001800	NO
RMS Displacement	0.000493	0.001200	YES

-----Figure S4-7, Int3[B] with -NH2(+)-C(OH)- moiety-------
vita-b1brcn04c2.for.high.log

Stoichiometry C13H34BrN5O10S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.348592	-1.131035	0.455071
2	6	0	-4.803902	-0.368292	1.563079
3	6	0	-3.741874	-0.197923	2.657683
4	6	0	-2.423952	0.283236	2.127369
5	16	0	-1.019146	-0.818562	2.187543
6	6	0	-0.133582	0.247874	1.004310
7	7	0	-0.779099	1.520999	1.082898
8	6	0	-0.360274	2.461699	0.058075
9	6	0	1.141749	2.471447	-0.002217
10	6	0	1.861040	3.400041	-0.746820
11	7	0	3.187183	3.414422	-0.807207
12	6	0	3.846800	2.485416	-0.114718
13	6	0	5.341172	2.479903	-0.167716
14	7	0	3.251120	1.541188	0.626256
15	6	0	1.932765	1.554486	0.661333
16	7	0	1.308505	0.499586	1.467435
17	6	0	-2.112543	1.438384	1.533223
18	6	0	-2.988984	2.636008	1.387966
19	1	0	-4.048719	-0.516415	-0.238843
20	1	0	-5.672167	-0.879926	1.985378
21	1	0	-5.135579	0.611063	1.205842
22	1	0	-4.136445	0.493767	3.409806
23	1	0	-3.599366	-1.154715	3.166746
24	8	0	-0.041525	-0.239601	-0.268876
25	1	0	-3.937250	2.475452	1.898788
26	1	0	-2.511757	3.512791	1.835562
27	1	0	-3.195913	2.846087	0.335537
28	1	0	-0.773679	2.207242	-0.925946
29	1	0	-0.713047	3.457712	0.326255
30	1	0	1.336774	4.163883	-1.313640
31	1	0	-0.128554	-1.230848	-0.304657
32	1	0	1.294028	0.781658	2.450025
33	1	0	5.698904	3.319395	-0.759653
34	1	0	5.756324	2.543720	0.840423
35	1	0	5.694686	1.548034	-0.615167
36	1	0	1.882085	-0.397473	1.390187
37	8	0	2.726917	-1.772044	1.208992
38	1	0	2.910461	-1.777440	0.228624
39	8	0	-0.280143	-2.871662	-0.488186
40	1	0	-1.234168	-3.078660	-0.378449
41	1	0	0.172731	-3.332250	0.250320
42	8	0	-2.919256	-3.411072	-0.038727
43	1	0	-3.051543	-4.072219	0.643749
44	1	0	-3.422337	-2.623481	0.251714
45	8	0	1.135469	-3.962115	1.581133
46	1	0	1.593097	-4.790770	1.424683
47	1	0	1.824544	-3.270906	1.587271
48	1	0	3.592132	-1.591604	1.614410
49	8	0	3.276075	-1.619606	-1.353550
50	1	0	4.231920	-1.783214	-1.417489
51	1	0	2.789271	-2.258878	-1.908665
52	8	0	5.092505	-0.452201	1.626970
53	1	0	4.536103	0.320505	1.410310
54	1	0	5.636687	-0.205577	2.378217
55	8	0	5.966729	-1.718249	-0.722470

56	1	0	6.666770	-1.249247	-1.180366
57	1	0	5.824685	-1.239135	0.112491
58	8	0	1.442880	-3.191703	-2.672839
59	1	0	0.770904	-3.174205	-1.966257
60	1	0	1.095583	-2.580125	-3.334572
61	7	0	0.009997	-0.948358	-3.961276
62	6	0	-0.851446	-0.396224	-3.443049
63	1	0	-1.684839	0.109136	-2.955055
64	35	0	-3.692863	1.019907	-1.972465

SCF Done: E(RwB97XD) = -4514.41676301 A.U. after 2 cycles

Zero-point correction= 0.519705 (a.u.)
Thermal correction to Energy= 0.564068
Thermal correction to Enthalpy= 0.565012
Thermal correction to Gibbs Free Energy= 0.438496
Sum of electronic and zero-point Energies= -4513.897058
Sum of electronic and thermal Energies= -4513.852695
Sum of electronic and thermal Enthalpies= -4513.851751
Sum of electronic and thermal Free Energies= -4513.978267

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	353.958	154.807	266.275

Item	Value	Threshold	Converged?
Maximum Force	0.000003	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.000769	0.001800	YES
RMS Displacement	0.000110	0.001200	YES

--------Figure S4-8, TS4[B], the deprotonation--------
vita-b1brcn04c2.high.log

Stoichiometry C13H34BrN5O10S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.328702	-1.068657	0.493546
2	6	0	-4.760781	-0.277034	1.591007
3	6	0	-3.687325	-0.104117	2.673565
4	6	0	-2.366351	0.359064	2.133465
5	16	0	-0.945631	-0.716142	2.270154
6	6	0	-0.068428	0.294702	1.026655
7	7	0	-0.713900	1.578910	1.079110
8	6	0	-0.304586	2.464307	0.002282
9	6	0	1.197792	2.457525	-0.068618
10	6	0	1.915051	3.383646	-0.812257
11	7	0	3.243492	3.414712	-0.856065
12	6	0	3.897591	2.503185	-0.137890
13	6	0	5.393962	2.516906	-0.165991
14	7	0	3.302562	1.554521	0.597136
15	6	0	1.976900	1.538049	0.617117
16	7	0	1.369721	0.481131	1.395957
17	6	0	-2.053687	1.496253	1.503426
18	6	0	-2.936256	2.683709	1.310590
19	1	0	-4.030134	-0.474829	-0.218316
20	1	0	-5.633006	-0.767168	2.030619
21	1	0	-5.081686	0.699567	1.217457
22	1	0	-4.073313	0.597122	3.421950
23	1	0	-3.550734	-1.057889	3.190070
24	8	0	-0.092466	-0.237358	-0.248094
25	1	0	-3.883253	2.543519	1.829804
26	1	0	-2.459621	3.578844	1.721115
27	1	0	-3.145352	2.851858	0.251012
28	1	0	-0.733360	2.163613	-0.962451
29	1	0	-0.646318	3.475893	0.223495
30	1	0	1.390343	4.139886	-1.389451
31	1	0	-0.169231	-1.222136	-0.236569
32	1	0	1.433492	0.719614	2.385971
33	1	0	5.752240	3.427325	-0.642021
34	1	0	5.798509	2.450525	0.845509
35	1	0	5.761469	1.656246	-0.731096
36	1	0	2.059454	-0.657312	1.228816
37	8	0	2.680465	-1.623100	1.073765
38	1	0	2.841374	-1.724003	0.044510

39	8	0	-0.326962	-2.928255	-0.369104
40	1	0	-1.280488	-3.115990	-0.228001
41	1	0	0.135719	-3.358793	0.377838
42	8	0	-2.963537	-3.407627	0.161918
43	1	0	-3.082321	-3.987270	0.917161
44	1	0	-3.448221	-2.584947	0.379791
45	8	0	1.162833	-3.934053	1.714899
46	1	0	1.625590	-4.764885	1.585309
47	1	0	1.842950	-3.245675	1.682799
48	1	0	3.570664	-1.430626	1.454930
49	8	0	3.155403	-1.748078	-1.362206
50	1	0	4.113921	-1.906807	-1.444255
51	1	0	2.638594	-2.410769	-1.871969
52	8	0	5.018229	-0.496382	1.558033
53	1	0	4.547086	0.340782	1.360338
54	1	0	5.524787	-0.363556	2.362845
55	8	0	5.837615	-1.790982	-0.826706
56	1	0	6.488085	-1.316055	-1.347897
57	1	0	5.752618	-1.298114	0.006378
58	8	0	1.337176	-3.345096	-2.555163
59	1	0	0.669685	-3.299627	-1.843441
60	1	0	0.976670	-2.773294	-3.245544
61	7	0	-0.093430	-1.162388	-3.918790
62	6	0	-0.925317	-0.553524	-3.416127
63	1	0	-1.733443	0.005300	-2.944077
64	35	0	-3.717532	1.016012	-2.013914

SCF Done: E(RwB97XD) = -4514.41120992 A.U. after 1 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-735.8292	18.0098	25.2088

Zero-point correction= 0.515387 (a.u.)
Thermal correction to Energy= 0.558559
Thermal correction to Enthalpy= 0.559503
Thermal correction to Gibbs Free Energy= 0.437034
Sum of electronic and zero-point Energies= -4513.895823
Sum of electronic and thermal Energies= -4513.852651
Sum of electronic and thermal Enthalpies= -4513.851707
Sum of electronic and thermal Free Energies= -4513.974176

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	350.501	152.262	257.757

Item	Value	Threshold	Converged?
Maximum Force	0.000014	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.001114	0.001800	YES
RMS Displacement	0.000162	0.001200	YES

------Figure S4-9, Int4[B]----------

vita-b1brcn04c2.rev.high.log

Stoichiometry C13H34BrN5O10S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.272253	-1.055800	0.649500
2	6	0	-4.702445	-0.170817	1.674494
3	6	0	-3.623765	0.104427	2.729167
4	6	0	-2.305295	0.528115	2.151042
5	16	0	-0.875650	-0.518609	2.387857
6	6	0	-0.004211	0.392320	1.062244
7	7	0	-0.648732	1.684198	1.032356
8	6	0	-0.228583	2.477921	-0.110185
9	6	0	1.276579	2.446734	-0.174734
10	6	0	2.000751	3.338905	-0.944531
11	7	0	3.332594	3.383125	-0.961642
12	6	0	3.971281	2.513126	-0.182997
13	6	0	5.468836	2.557695	-0.156835
14	7	0	3.370444	1.584355	0.572850
15	6	0	2.039392	1.548058	0.571720
16	7	0	1.425126	0.546992	1.367583

17	6	0	-1.994657	1.616897	1.436851
18	6	0	-2.889200	2.773006	1.135222
19	1	0	-4.068822	-0.527273	-0.142439
20	1	0	-5.570839	-0.619327	2.164523
21	1	0	-5.027969	0.766513	1.214547
22	1	0	-4.014482	0.865560	3.414441
23	1	0	-3.478923	-0.798877	3.327892
24	8	0	-0.122076	-0.216480	-0.182622
25	1	0	-3.840543	2.667219	1.654942
26	1	0	-2.426625	3.706397	1.469608
27	1	0	-3.091432	2.848401	0.063333
28	1	0	-0.657362	2.107241	-1.050647
29	1	0	-0.558816	3.508035	0.028768
30	1	0	1.483493	4.067422	-1.563303
31	1	0	-0.094336	-1.194842	-0.106833
32	1	0	1.570450	0.744280	2.354456
33	1	0	5.827398	3.429542	-0.700251
34	1	0	5.831450	2.595986	0.872356
35	1	0	5.880364	1.657954	-0.621242
36	1	0	2.306088	-1.028054	1.300676
37	8	0	2.838949	-1.847559	1.164523
38	1	0	2.954176	-1.848267	-0.383114
39	8	0	-0.213343	-2.969694	-0.191548
40	1	0	-1.172113	-3.135760	-0.060975
41	1	0	0.234649	-3.394050	0.569286
42	8	0	-2.866047	-3.372859	0.314152
43	1	0	-3.033435	-3.991034	1.028382
44	1	0	-3.355620	-2.557593	0.546015
45	8	0	1.249397	-3.969105	1.900244
46	1	0	1.656417	-4.831609	1.794942
47	1	0	1.963827	-3.318150	1.784007
48	1	0	3.737063	-1.604902	1.459604
49	8	0	3.102756	-1.781944	-1.383564
50	1	0	4.091175	-1.861786	-1.527967
51	1	0	2.468331	-2.445973	-1.875442
52	8	0	5.175160	-0.487077	1.260819
53	1	0	4.605956	0.307788	1.150038
54	1	0	5.815161	-0.285748	1.947379
55	8	0	5.669970	-1.721931	-1.184530
56	1	0	6.225026	-1.239479	-1.801479
57	1	0	5.702698	-1.235327	-0.338367
58	8	0	1.365163	-3.255255	-2.383727
59	1	0	0.715598	-3.280679	-1.644347
60	1	0	0.912542	-2.748565	-3.076900
61	7	0	-0.331794	-1.392895	-3.757441
62	6	0	-1.191545	-0.764534	-3.332563
63	1	0	-2.023410	-0.186450	-2.927941
64	35	0	-3.997555	0.850550	-2.033284

SCF Done: E(RwB97XD) = -4514.41903559 A.U. after 2 cycles

Zero-point correction= 0.519294 (a.u.)
Thermal correction to Energy= 0.562404
Thermal correction to Enthalpy= 0.563348
Thermal correction to Gibbs Free Energy= 0.440401
Sum of electronic and zero-point Energies= -4513.899741
Sum of electronic and thermal Energies= -4513.856632
Sum of electronic and thermal Enthalpies= -4513.855688
Sum of electronic and thermal Free Energies= -4513.978634

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	352.914	152.271	258.763

Item	Value	Threshold	Converged?
Maximum Force	0.000006	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.001528	0.001800	YES
RMS Displacement	0.000209	0.001200	YES

------Figure S4-10, TS5[B], H2O elimination------
vita-b1brcn06e.high.log

Stoichiometry C13H34BrN5O10S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	8	0	2.054372	3.914693	0.137872
2	6	0	0.950868	4.815858	0.178483
3	6	0	-0.116215	4.505006	-0.872248
4	6	0	-0.890346	3.250811	-0.621407
5	16	0	-0.040868	1.680837	-0.646738
6	6	0	-1.501160	0.907514	0.049927
7	7	0	-2.583018	1.728688	-0.269648
8	6	0	-3.911159	1.290621	0.141713
9	6	0	-4.053081	-0.174667	-0.170741
10	6	0	-5.260410	-0.816919	-0.308489
11	7	0	-5.379017	-2.129264	-0.559155
12	6	0	-4.247501	-2.816243	-0.671075
13	6	0	-4.330879	-4.293415	-0.906716
14	7	0	-3.018043	-2.294742	-0.568341
15	6	0	-2.919268	-0.985414	-0.332100
16	7	0	-1.667005	-0.453444	-0.243907
17	6	0	-2.204238	3.080342	-0.410872
18	6	0	-3.271826	4.122042	-0.369782
19	1	0	2.541383	4.044065	-0.679357
20	1	0	1.306547	5.841836	0.042141
21	1	0	0.531035	4.728965	1.181881
22	1	0	-0.808964	5.348822	-0.905809
23	1	0	0.362173	4.465283	-1.858673
24	8	0	-1.289573	1.012697	1.628176
25	1	0	-2.844624	5.118426	-0.460846
26	1	0	-3.981616	3.984059	-1.190284
27	1	0	-3.829159	4.076429	0.569484
28	1	0	-4.075760	1.468453	1.212435
29	1	0	-4.656101	1.861108	-0.411637
30	1	0	-6.187909	-0.257954	-0.218284
31	1	0	-1.997808	0.511627	2.113462
32	1	0	-0.861257	-0.977565	-0.612869
33	1	0	-4.077632	-4.827113	0.014145
34	1	0	-5.339148	-4.574357	-1.205307
35	1	0	-3.618370	-4.599358	-1.674502
36	8	0	-3.167441	-0.322273	2.952772
37	1	0	-3.098724	-1.280122	2.985065
38	1	0	-3.322933	-0.037738	3.857266
39	8	0	4.924944	0.864801	0.142306
40	1	0	5.653236	0.346981	0.530830
41	1	0	4.569319	0.308857	-0.571620
42	35	0	3.560977	-1.063514	-2.226062
43	1	0	2.628525	-2.860610	1.828091
44	1	0	-0.307399	0.584333	1.944530
45	8	0	0.809608	0.082246	2.368220
46	1	0	1.609239	0.582567	2.047222
47	1	0	0.880045	-0.872728	2.166731
48	8	0	2.798194	1.646751	1.661978
49	1	0	3.577992	1.327773	1.160459
50	1	0	2.465216	2.407622	1.156954
51	8	0	0.750382	-2.646975	2.059817
52	1	0	0.444386	-3.004082	2.897720
53	1	0	0.186607	-3.060919	1.371746
54	8	0	0.405818	-1.838373	-1.497386
55	1	0	0.378048	-2.723590	-1.108603
56	1	0	1.340685	-1.611440	-1.641368
57	8	0	-0.732905	-3.791697	0.070556
58	1	0	-1.584665	-3.365931	-0.184718
59	1	0	-0.876990	-4.740249	0.070956
60	6	0	3.714847	-2.807450	1.768989
61	7	0	4.857220	-2.730649	1.718080
62	8	0	6.915577	-0.750147	1.265855
63	1	0	6.406943	-1.556702	1.440182
64	1	0	7.626804	-1.013593	0.677952

```
SCF Done:  E(RwB97XD) =  -4514.41110303 A.U. after 2 cycles
         NFock=  2  Conv=0.77D-09    -V/T= 2.0023

Harmonic frequencies (cm**-1), IR intensities (KM/Mole)
                 1                 2                 3
                 A                 A                 A
Frequencies --   -428.8141              9.5466             12.8645

Zero-point correction=                          0.512633 (a.u.)
Thermal correction to Energy=                    0.557943
Thermal correction to Enthalpy=                  0.558887
Thermal correction to Gibbs Free Energy=         0.427909
Sum of electronic and zero-point Energies=          -4513.898470
```

Sum of electronic and thermal Energies= -4513.853160
Sum of electronic and thermal Enthalpies= -4513.852216
Sum of electronic and thermal Free Energies= -4513.983194

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	350.115	156.633	275.666

Item	Value	Threshold	Converged?
Maximum Force	0.000035	0.000450	YES
RMS Force	0.000004	0.000300	YES
Maximum Displacement	0.002941	0.001800	NO
RMS Displacement	0.000397	0.001200	YES

-----Figure S4-11, ProductH+[B] the N-protonated thiochrome------
vita-b1brcn06e.rev.high.log

Stoichiometry C13H34BrN5O10S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.539079	4.251047	-1.111022
2	6	0	-0.334434	4.899874	-0.192313
3	6	0	-1.806671	4.699052	-0.556911
4	6	0	-2.242748	3.269546	-0.479139
5	16	0	-1.642723	2.112694	-1.650677
6	6	0	-2.503988	0.860400	-0.875740
7	7	0	-3.191745	1.295611	0.169514
8	6	0	-4.040773	0.404431	0.973062
9	6	0	-3.637021	-1.026494	0.758144
10	6	0	-3.989330	-2.050835	1.608282
11	7	0	-3.642202	-3.324730	1.398753
12	6	0	-2.897819	-3.577084	0.328709
13	6	0	-2.447728	-4.983146	0.086708
14	7	0	-2.495077	-2.655177	-0.559955
15	6	0	-2.870479	-1.403985	-0.340837
16	7	0	-2.453760	-0.435447	-1.239830
17	6	0	-3.047946	2.667666	0.421084
18	6	0	-3.746958	3.267279	1.592918
19	1	0	0.609453	4.771130	-1.914551
20	1	0	-0.113279	5.969334	-0.145015
21	1	0	-0.126549	4.461138	0.784913
22	1	0	-2.414940	5.294683	0.126444
23	1	0	-1.988104	5.094571	-1.560929
24	8	0	-0.928914	0.168819	1.858161
25	1	0	-3.625018	4.348070	1.592261
26	1	0	-4.816343	3.046568	1.570782
27	1	0	-3.333757	2.883292	2.529041
28	1	0	-3.918607	0.673019	2.020981
29	1	0	-5.081784	0.572668	0.684341
30	1	0	-4.580024	-1.848159	2.496989
31	1	0	-0.827907	-0.774310	2.067177
32	1	0	-1.769909	-0.682784	-1.978540
33	1	0	-1.360068	-5.038834	0.184620
34	1	0	-2.903741	-5.657066	0.808958
35	1	0	-2.709925	-5.299533	-0.925124
36	8	0	-0.349168	-2.596138	2.063483
37	1	0	0.351200	-2.686251	1.392681
38	1	0	0.007304	-2.983262	2.865139
39	8	0	4.794402	1.654682	-0.566347
40	1	0	5.269361	1.840010	0.263102
41	1	0	4.810503	0.690225	-0.665592
42	35	0	4.575220	-1.769265	-0.653369
43	1	0	3.711831	-0.662119	1.409309
44	1	0	-0.415380	0.255885	1.039021
45	8	0	0.647369	0.015188	-0.512763
46	1	0	1.283219	0.751170	-0.365284
47	1	0	1.069835	-0.825270	-0.262163
48	8	0	2.140343	2.196596	-0.066784
49	1	0	3.082524	2.132973	-0.314619
50	1	0	1.747755	2.956260	-0.524196
51	8	0	1.416258	-2.627144	-0.073698
52	1	0	2.373024	-2.601903	-0.243394
53	1	0	0.986556	-3.020757	-0.855507
54	8	0	-0.312712	-0.721787	-2.969159
55	1	0	-0.142293	-1.677224	-2.970227
56	1	0	0.220196	-0.384149	-2.222036

57	8	0	-0.259359	-3.382037	-2.140139
58	1	0	-1.114053	-3.226647	-1.682455
59	1	0	-0.323281	-4.231849	-2.581298
60	6	0	3.538557	-0.060439	2.296633
61	7	0	3.397190	0.591948	3.230044
62	8	0	5.929212	2.284736	1.915207
63	1	0	5.331438	1.982469	2.606021
64	1	0	6.792733	1.943118	2.159105

SCF Done: E(RwB97XD) = -4514.45707758 A.U. after 2 cycles

Zero-point correction= 0.516838 (a.u.)
Thermal correction to Energy= 0.563727
Thermal correction to Enthalpy= 0.564671
Thermal correction to Gibbs Free Energy= 0.429385
Sum of electronic and zero-point Energies= -4513.940240
Sum of electronic and thermal Energies= -4513.893351
Sum of electronic and thermal Enthalpies= -4513.892407
Sum of electronic and thermal Free Energies= -4514.027692

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	353.744	160.178	284.732

Item	Value	Threshold	Converged?
Maximum Force	0.000004	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.005733	0.001800	NO
RMS Displacement	0.000516	0.001200	YES

==========Figure S5 and scheme 4==========

obtained by rwB97x-D/6-311(+)G(d,p)&SDD SCRF=(PCM, solvent=water) calculations

-----Figure S5-1, precursor[C], thiamine + HgCl2 + HO(-)(H2O)8-----
vita-b1hgcl2g3.reva.high.log

Stoichiometry C12H34Cl2HgN4O10S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-6.523807	0.532420	-1.815692
2	6	0	-6.769207	0.043840	-0.506943
3	6	0	-5.954353	-1.229479	-0.321005
4	6	0	-4.477497	-0.988934	-0.400910
5	16	0	-3.608064	-1.146187	-1.890251
6	6	0	-2.168222	-0.727846	-1.138915
7	7	0	-2.332195	-0.474073	0.143941
8	6	0	-1.216946	-0.071753	1.004981
9	6	0	-1.039330	1.419690	1.058583
10	6	0	-1.633702	2.306996	0.195976
11	7	0	-1.417294	3.631493	0.213361
12	6	0	-0.561997	4.061495	1.137650
13	6	0	-0.254694	5.530611	1.166846
14	7	0	0.067124	3.304170	2.036743
15	6	0	-0.160263	1.983929	2.018271
16	7	0	0.452522	1.233403	2.954030
17	6	0	-3.639370	-0.604246	0.596831
18	6	0	-3.968919	-0.338285	2.025417
19	1	0	-6.984170	1.366110	-1.925763
20	1	0	-7.829927	-0.191192	-0.368978
21	1	0	-6.478245	0.786285	0.245196
22	1	0	-6.191474	-1.664320	0.652250
23	1	0	-6.255272	-1.961524	-1.073656
24	1	0	-1.203337	-0.670927	-1.620231
25	1	0	-5.042869	-0.415246	2.182990
26	1	0	-3.464156	-1.062128	2.670439
27	1	0	-3.654501	0.668169	2.312342
28	1	0	-1.408416	-0.488704	1.993647
29	1	0	-0.327824	-0.573734	0.615330
30	1	0	-2.328375	1.957549	-0.563165
31	1	0	0.580495	0.221220	2.855216
32	1	0	1.163966	1.712023	3.483586
33	1	0	0.756190	5.703025	0.786292
34	1	0	-0.960705	6.079029	0.544958

35	1	0	-0.289123	5.907962	2.190167
36	80	0	2.110207	0.975442	-0.594822
37	17	0	3.540497	0.990294	1.368287
38	17	0	0.929724	1.365283	-2.683583
39	8	0	0.423621	-2.288122	-0.661839
40	1	0	0.799113	-2.244954	-1.557964
41	8	0	1.519068	-1.870456	-3.219725
42	1	0	2.486095	-1.864061	-3.063395
43	1	0	1.289065	-0.939939	-3.328306
44	1	0	-0.929533	-3.165884	-0.225171
45	8	0	-1.744406	-3.564910	0.170421
46	1	0	-1.718281	-4.498810	-0.044876
47	1	0	-1.756007	-3.144381	1.867719
48	8	0	-1.690600	-2.763149	2.769418
49	1	0	-1.963212	-3.456084	3.373439
50	1	0	1.182303	-2.519985	-0.018066
51	8	0	2.260413	-2.802359	1.031028
52	1	0	2.326808	-3.741239	1.238692
53	8	0	4.186796	-1.750587	-2.630962
54	1	0	4.307812	-1.825910	-1.651393
55	1	0	4.797608	-2.375755	-3.024901
56	8	0	2.532605	-5.737822	1.738128
57	1	0	3.445397	-6.025464	1.664362
58	1	0	2.299839	-5.895140	2.655903
59	1	0	3.576130	-2.303106	0.437302
60	8	0	4.433335	-1.924396	0.022768
61	1	0	4.518428	-1.051314	0.419861
62	1	0	1.441782	-2.047736	2.239489
63	8	0	0.897876	-1.596687	2.948203
64	1	0	0.049810	-2.067563	2.955276

SCF Done: E(RwB97XD) = -2921.46869045 A.U. after 1 cycles

Zero-point correction= 0.507075 (a.u.)
Thermal correction to Energy= 0.555179
Thermal correction to Enthalpy= 0.556123
Thermal correction to Gibbs Free Energy= 0.418119
Sum of electronic and zero-point Energies= -2920.961615
Sum of electronic and thermal Energies= -2920.913512
Sum of electronic and thermal Enthalpies= -2920.912567
Sum of electronic and thermal Free Energies= -2921.050572

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	348.380	162.397	290.455

Item	Value	Threshold	Converged?
Maximum Force	0.000027	0.000450	YES
RMS Force	0.000003	0.000300	YES
Maximum Displacement	0.002270	0.001800	NO
RMS Displacement	0.000492	0.001200	YES

------Figure S5-2, TS1[C] HO(-), addition to thiamine-----
vita-b1hgcl2g3.high.log

Stoichiometry C12H34Cl2HgN4O10S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.863158	2.250957	-2.923228
2	6	0	-5.581505	2.026312	-1.717569
3	6	0	-5.306427	0.605608	-1.247481
4	6	0	-3.871929	0.364459	-0.887256
5	16	0	-2.748966	-0.331492	-2.045232
6	6	0	-1.503334	-0.369809	-0.864076
7	7	0	-1.882885	0.287465	0.236665
8	6	0	-0.953526	0.457002	1.342669
9	6	0	-0.047206	1.647262	1.192950
10	6	0	-0.050096	2.492670	0.112367
11	7	0	0.786275	3.534994	-0.029499
12	6	0	1.643382	3.723004	0.971003
13	6	0	2.625657	4.851190	0.841830
14	7	0	1.729021	2.988178	2.079993
15	6	0	0.898381	1.945736	2.207240
16	7	0	0.988791	1.216729	3.334991
17	6	0	-3.240003	0.643836	0.268130

18	6	0	-3.810086	1.279788	1.489785
19	1	0	-4.987130	3.163908	-3.188109
20	1	0	-6.658341	2.146931	-1.882128
21	1	0	-5.268927	2.740470	-0.946491
22	1	0	-5.926682	0.383602	-0.375675
23	1	0	-5.615269	-0.093216	-2.029576
24	1	0	-0.470510	-0.398335	-1.168064
25	1	0	-4.861184	1.514475	1.330776
26	1	0	-3.727446	0.612766	2.352242
27	1	0	-3.285663	2.210926	1.722427
28	1	0	-1.529316	0.518123	2.267289
29	1	0	-0.369810	-0.463788	1.410690
30	1	0	-0.754705	2.335541	-0.699775
31	1	0	0.516839	0.323151	3.476092
32	1	0	1.740578	1.451351	3.961944
33	1	0	3.618374	4.449306	0.618473
34	1	0	2.332365	5.523266	0.036697
35	1	0	2.698656	5.403434	1.780051
36	80	0	2.532852	-0.031747	-0.788706
37	17	0	3.947540	-0.066301	1.186134
38	17	0	1.410904	0.342161	-2.915083
39	8	0	-1.273549	-2.270041	-0.220119
40	1	0	-0.926341	-2.674054	-1.028587
41	8	0	0.275744	-2.874594	-2.646283
42	1	0	1.134724	-3.201819	-2.314856
43	1	0	0.479262	-1.993105	-2.977869
44	1	0	-2.635954	-2.629439	0.471586
45	8	0	-3.443376	-2.771506	1.061685
46	1	0	-3.567563	-3.720698	1.127067
47	1	0	-3.114316	-1.970982	2.613878
48	8	0	-2.955632	-1.428563	3.414247
49	1	0	-3.540719	-1.779364	4.088761
50	1	0	-0.346672	-2.750310	0.941662
51	8	0	0.231802	-3.069445	1.713776
52	1	0	-0.099128	-3.941140	1.943119
53	8	0	2.753006	-3.621694	-1.688813
54	1	0	2.842605	-3.506060	-0.718728
55	1	0	3.121108	-4.483988	-1.889878
56	1	0	-5.043543	-1.853494	1.148304
57	8	0	-5.900654	-1.445185	1.360686
58	1	0	-5.752434	-0.989710	2.191200
59	1	0	1.941109	-3.142539	1.296254
60	8	0	2.873471	-3.207105	1.002490
61	1	0	3.274206	-2.355859	1.218971
62	1	0	0.049679	-2.001113	3.193497
63	8	0	-0.198109	-1.375015	3.897443
64	1	0	-1.170759	-1.370598	3.853459

SCF Done: E(RwB97XD) = -2921.45966961 A.U. after 1 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-345.0405	20.1306	23.1873

Zero-point correction= 0.509539 (a.u.)
Thermal correction to Energy= 0.556229
Thermal correction to Enthalpy= 0.557173
Thermal correction to Gibbs Free Energy= 0.425521
Sum of electronic and zero-point Energies= -2920.950130
Sum of electronic and thermal Energies= -2920.903441
Sum of electronic and thermal Enthalpies= -2920.902497
Sum of electronic and thermal Free Energies= -2921.034149

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	349.039	161.039	277.084

Item	Value	Threshold	Converged?
Maximum Force	0.000008	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.003125	0.001800	NO
RMS Displacement	0.000403	0.001200	YES

-------Figure S5-3, Int1[C], HO adduct of thiamine----
vita-b1hgcl2f.for.high.log

Stoichiometry C12H34Cl2HgN4O10S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.322491	2.045262	-0.847926
2	6	0	-4.056414	3.373215	-0.426562
3	6	0	-3.515526	3.457768	1.003409
4	6	0	-2.194787	2.775204	1.194639
5	16	0	-2.148725	1.058007	1.665637
6	6	0	-0.305665	1.043963	1.707095
7	7	0	0.080274	2.349347	1.239675
8	6	0	1.485670	2.692795	1.242465
9	6	0	2.249333	2.178387	0.044038
10	6	0	1.638703	1.780693	-1.112763
11	7	0	2.301464	1.285498	-2.178150
12	6	0	3.616510	1.150688	-2.045678
13	6	0	4.366847	0.517178	-3.179416
14	7	0	4.320084	1.491197	-0.964998
15	6	0	3.660492	2.038984	0.065922
16	7	0	4.408097	2.461465	1.103109
17	6	0	-0.957730	3.260734	1.022950
18	6	0	-0.617818	4.655051	0.604190
19	1	0	-3.486794	1.621366	-1.077830
20	1	0	-5.005378	3.911891	-0.485437
21	1	0	-3.350978	3.856391	-1.113892
22	1	0	-3.431322	4.515648	1.271367
23	1	0	-4.255845	3.027605	1.685496
24	1	0	0.045471	0.252455	1.033075
25	1	0	-1.521187	5.208488	0.354229
26	1	0	-0.098001	5.198541	1.398741
27	1	0	0.028231	4.650540	-0.278561
28	1	0	1.591474	3.776756	1.312774
29	1	0	1.933745	2.292096	2.156308
30	1	0	0.557328	1.828819	-1.202305
31	1	0	3.986637	2.695223	1.984842
32	1	0	5.380059	2.199053	1.113345
33	1	0	4.400476	-0.567058	-3.034992
34	1	0	3.866188	0.716878	-4.126458
35	1	0	5.391862	0.884691	-3.212871
36	80	0	-1.688714	-1.385055	-0.949478
37	17	0	-1.882673	-3.685172	-0.139371
38	17	0	-1.693912	0.619809	-2.341027
39	8	0	0.214613	0.796875	2.987370
40	1	0	0.109373	-0.169365	3.162499
41	8	0	0.079749	-1.860540	3.280770
42	1	0	0.672070	-2.396757	2.717372
43	1	0	-0.802361	-2.269168	3.218377
44	8	0	1.783331	-3.393311	1.674277
45	1	0	1.768384	-2.966874	0.801168
46	1	0	2.692407	-3.235901	1.974987
47	8	0	-2.456190	-2.952579	2.948653
48	1	0	-2.437669	-3.257875	2.029277
49	1	0	-2.703191	-3.720414	3.469031
50	1	0	2.026636	0.057003	2.466852
51	8	0	2.658242	-0.240248	1.801337
52	1	0	3.216490	-0.915655	2.216849
53	8	0	2.159671	-1.672765	-0.516689
54	1	0	2.093334	-0.942456	0.123587
55	1	0	1.689719	-1.441532	-1.340305
56	8	0	4.391192	-2.372491	2.193119
57	1	0	5.103352	-2.580570	2.800323
58	1	0	4.797545	-2.107267	1.341423
59	8	0	1.200777	-1.061823	-3.083610
60	1	0	0.265832	-0.976407	-3.288576
61	1	0	1.515925	-0.135207	-2.991185
62	8	0	4.938569	-1.481859	-0.331468
63	1	0	4.001684	-1.609839	-0.573156
64	1	0	5.070360	-0.526326	-0.397345

SCF Done: E(RwB97XD) = -2921.48323285 A.U. after 1 cycles

Zero-point correction= 0.514854 (a.u.)
Thermal correction to Energy= 0.560484
Thermal correction to Enthalpy= 0.561429
Thermal correction to Gibbs Free Energy= 0.434853
Sum of electronic and zero-point Energies= -2920.968379
Sum of electronic and thermal Energies= -2920.922748
Sum of electronic and thermal Enthalpies= -2920.921804

Sum of electronic and thermal Free Energies= -2921.048380

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	351.709	160.574	266.401

Item	Value	Threshold	Converged?
Maximum Force	0.000101	0.000450	YES
RMS Force	0.000012	0.000300	YES
Maximum Displacement	0.015087	0.001800	NO
RMS Displacement	0.001568	0.001200	NO

------Figure S5-4, TS2[C], elimination of H(24) and H(40)------
vita-b1hgcl2f.high.log

Stoichiometry C12H34Cl2HgN4O10S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.511112	0.432616	1.043626
2	6	0	4.663790	1.831530	0.902970
3	6	0	4.433443	2.298864	-0.538458
4	6	0	3.046917	2.034455	-1.040025
5	16	0	2.720851	0.650984	-2.078421
6	6	0	0.969922	0.892297	-1.834165
7	7	0	0.786351	2.186257	-1.407999
8	6	0	-0.514997	2.835548	-1.468899
9	6	0	-1.430805	2.539761	-0.307075
10	6	0	-1.011505	2.016156	0.887569
11	7	0	-1.846592	1.701044	1.892410
12	6	0	-3.145888	1.884290	1.667764
13	6	0	-4.088947	1.473557	2.759228
14	7	0	-3.671376	2.377610	0.550291
15	6	0	-2.829615	2.737824	-0.430866
16	7	0	-3.385378	3.275533	-1.528414
17	6	0	1.925050	2.746699	-0.814263
18	6	0	1.812793	4.030143	-0.060756
19	1	0	3.672952	0.266646	1.500612
20	1	0	5.684863	2.098194	1.191869
21	1	0	3.977219	2.357133	1.575650
22	1	0	4.645451	3.370689	-0.594211
23	1	0	5.159547	1.804831	-1.189212
24	1	0	0.700796	0.122127	-0.666776
25	1	0	2.758893	4.264805	0.423063
26	1	0	1.567169	4.856745	-0.733001
27	1	0	1.041493	3.979704	0.710913
28	1	0	-0.343261	3.908690	-1.574675
29	1	0	-0.983274	2.502985	-2.398451
30	1	0	0.038958	1.808451	1.073039
31	1	0	-2.846438	3.643887	-2.290724
32	1	0	-4.384601	3.388620	-1.553858
33	1	0	-4.083355	0.384928	2.862749
34	1	0	-3.764674	1.895597	3.711998
35	1	0	-5.102199	1.802617	2.536382
36	80	0	0.798028	-1.241264	0.519987
37	17	0	0.810203	-3.730093	0.974920
38	17	0	1.835908	0.200024	2.758036
39	8	0	0.095369	0.411633	-2.712360
40	1	0	0.103669	-0.615953	-2.740349
41	8	0	-0.079904	-2.097618	-2.759216
42	1	0	-0.836345	-2.458615	-2.245157
43	1	0	0.695176	-2.652651	-2.537627
44	8	0	-2.205979	-3.162999	-1.364604
45	1	0	-2.225301	-2.770378	-0.476185
46	1	0	-3.037726	-2.852090	-1.757347
47	8	0	2.033937	-3.666914	-1.984572
48	1	0	1.796403	-3.872043	-1.066463
49	1	0	2.152182	-4.514545	-2.419308
50	1	0	-1.724726	0.209600	-2.073915
51	8	0	-2.495404	0.030928	-1.524626
52	1	0	-3.094204	-0.521714	-2.049491
53	8	0	-2.621229	-1.389109	0.817582
54	1	0	-2.308905	-0.754844	0.145583
55	1	0	-2.129291	-1.220419	1.643827
56	8	0	-4.524888	-1.739231	-2.181595
57	1	0	-5.181301	-1.845495	-2.872255
58	1	0	-4.966841	-1.314456	-1.417364

59	8	0	-1.341960	-0.659400	3.227383
60	1	0	-0.383098	-0.750814	3.291842
61	1	0	-1.456023	0.275601	2.944499
62	8	0	-5.162421	-0.446800	0.152823
63	1	0	-4.364131	-0.811538	0.578740
64	1	0	-4.969837	0.495559	0.063488

SCF Done: E(RwB97XD) = -2921.44795240 A.U. after 1 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

1	2	3
A	A	A
Frequencies -- -870.0093	28.1350	40.9326

Zero-point correction= 0.511059 (a.u.)
Thermal correction to Energy= 0.555359
Thermal correction to Enthalpy= 0.556303
Thermal correction to Gibbs Free Energy= 0.435293
Sum of electronic and zero-point Energies= -2920.936894
Sum of electronic and thermal Energies= -2920.892593
Sum of electronic and thermal Enthalpies= -2920.891649
Sum of electronic and thermal Free Energies= -2921.012660

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	348.493	157.525	254.688

Item	Value	Threshold	Converged?
Maximum Force	0.000103	0.000450	YES
RMS Force	0.000012	0.000300	YES
Maximum Displacement	0.005135	0.001800	NO
RMS Displacement	0.001408	0.001200	NO

-----Figure S5-5, Int2[C], the thio-lactone type intermediate----
vita-b1hgcl2f.rev.high.log

Stoichiometry C12H34Cl2HgN4O10S

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	3.627771	1.801431	0.876192
2	6	0	3.363811	3.190880	0.848169
3	6	0	3.100586	3.645939	-0.587887
4	6	0	1.870551	3.014944	-1.166129
5	16	0	1.979621	1.542241	-2.110663
6	6	0	0.243999	1.409100	-2.194191
7	7	0	-0.320528	2.479725	-1.585187
8	6	0	-1.769537	2.633046	-1.530376
9	6	0	-2.396222	2.080672	-0.273607
10	6	0	-1.694237	1.756829	0.857859
11	7	0	-2.249029	1.189983	1.941170
12	6	0	-3.546128	0.899896	1.861767
13	6	0	-4.157639	0.200109	3.038893
14	7	0	-4.329816	1.161400	0.819640
15	6	0	-3.780360	1.778902	-0.237351
16	7	0	-4.602140	2.057991	-1.264168
17	6	0	0.587048	3.380623	-0.999094
18	6	0	0.073317	4.599083	-0.306174
19	1	0	3.203219	1.422272	1.664066
20	1	0	4.220586	3.749976	1.243835
21	1	0	2.492344	3.426344	1.469939
22	1	0	3.000768	4.734355	-0.600929
23	1	0	3.970988	3.407160	-1.204590
24	1	0	0.196784	-0.153724	0.067317
25	1	0	0.894685	5.133635	0.167039
26	1	0	-0.406663	5.278351	-1.015852
27	1	0	-0.654797	4.348951	0.468884
28	1	0	-2.004171	3.691659	-1.662328
29	1	0	-2.170284	2.106021	-2.399691
30	1	0	-0.623155	1.926269	0.915938
31	1	0	-4.326929	2.643812	-2.031851
32	1	0	-5.581886	1.856072	-1.155355
33	1	0	-5.234501	0.104015	2.913864
34	1	0	-3.718581	-0.795520	3.145918
35	1	0	-3.941455	0.752644	3.955205
36	80	0	1.368414	-1.231447	0.341616

37	17	0	3.106331	-2.945727	0.660631
38	17	0	2.147089	0.692552	3.461325
39	8	0	-0.379628	0.468615	-2.718284
40	1	0	0.103443	-1.111712	-2.755737
41	8	0	0.260961	-2.095578	-2.792925
42	1	0	-0.295341	-2.617542	-2.069872
43	1	0	1.243573	-2.310832	-2.698848
44	8	0	-1.047960	-3.440662	-1.151726
45	1	0	-1.151394	-3.020980	-0.273488
46	1	0	-1.969613	-3.536149	-1.462298
47	8	0	2.753960	-2.703732	-2.548900
48	1	0	3.014103	-2.909054	-1.635648
49	1	0	3.064959	-3.431980	-3.092895
50	1	0	-1.891532	-0.255035	-1.909287
51	8	0	-2.545620	-0.682940	-1.338798
52	1	0	-2.934402	-1.411560	-1.842133
53	8	0	-1.972518	-1.990372	1.015135
54	1	0	-1.995098	-1.296833	0.328502
55	1	0	-1.454216	-1.638854	1.766734
56	8	0	-3.731213	-3.165605	-1.787772
57	1	0	-4.317791	-3.636685	-2.382279
58	1	0	-4.255134	-2.900773	-1.002630
59	8	0	-0.762385	-0.772789	3.228193
60	1	0	0.167424	-0.498048	3.277733
61	1	0	-1.234500	0.043076	2.956006
62	8	0	-4.706757	-2.098410	0.545331
63	1	0	-3.814382	-2.121009	0.937800
64	1	0	-4.885725	-1.157927	0.421963

SCF Done: E(RwB97XD) = -2921.49867652 A.U. after 1 cycles

Zero-point correction= 0.511421 (a.u.)
Thermal correction to Energy= 0.555870
Thermal correction to Enthalpy= 0.556814
Thermal correction to Gibbs Free Energy= 0.433686
Sum of electronic and zero-point Energies= -2920.987255
Sum of electronic and thermal Energies= -2920.942807
Sum of electronic and thermal Enthalpies= -2920.941863
Sum of electronic and thermal Free Energies= -2921.064990

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	348.813	157.588	259.143

Item	Value	Threshold	Converged?
Maximum Force	0.000054	0.000450	YES
RMS Force	0.000010	0.000300	YES
Maximum Displacement	0.010850	0.001800	NO
RMS Displacement	0.001287	0.001200	NO

==========Figure S6 and scheme S1==========

The MeO2(.) attack to thiamine in C-H abstractions and additions

-------- Figure S6-1, C(3)-H(22) cleavage by MeO2(.)----------
vita-b1.eli22.log

Stoichiometry C13H20N4O3S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.896572	-0.086678	-0.065959
2	6	0	-4.107927	1.006289	0.380830
3	6	0	-2.882792	0.454262	1.070398
4	6	0	-2.091701	-0.544204	0.358976
5	16	0	-2.578252	-1.274253	-1.144611
6	6	0	-1.097565	-2.066521	-1.258112
7	7	0	-0.297093	-1.822590	-0.232103
8	6	0	1.088925	-2.339947	-0.169424
9	6	0	2.071182	-1.203874	-0.297995
10	6	0	2.009173	-0.336533	-1.375529
11	7	0	2.762956	0.757491	-1.506511
12	6	0	3.615963	0.991206	-0.499397
13	6	0	4.411506	2.262556	-0.559566
14	7	0	3.806819	0.204924	0.558600

15	6	0	3.059925	-0.904616	0.665018
16	7	0	3.274799	-1.669999	1.770316
17	6	0	-0.836128	-0.966599	0.717279
18	6	0	-0.075965	-0.518822	1.919931
19	1	0	-5.508812	0.239128	-0.738269
20	1	0	-4.661541	1.641863	1.080537
21	1	0	-3.789672	1.629134	-0.467402
22	1	0	-2.089605	1.552730	1.140453
23	1	0	-2.982655	0.260919	2.141068
24	1	0	-0.819816	-2.724164	-2.070104
25	1	0	-0.767995	-0.334193	2.744134
26	1	0	0.653522	-1.259646	2.252190
27	1	0	0.453952	0.416823	1.711410
28	1	0	1.184616	-2.883884	0.770221
29	1	0	1.188386	-3.066903	-0.976630
30	1	0	1.295242	-0.520001	-2.178565
31	1	0	3.099709	-2.662830	1.734986
32	1	0	4.086863	-1.411189	2.314316
33	1	0	4.628438	2.529536	-1.595871
34	1	0	3.826685	3.078599	-0.118876
35	1	0	5.339392	2.166157	0.006899
36	8	0	-1.447392	2.537454	1.158755
37	8	0	-1.344570	2.921446	-0.162924
38	6	0	-0.120906	2.423757	-0.696372
39	1	0	-0.064465	2.827483	-1.708620
40	1	0	0.727592	2.769234	-0.099814
41	1	0	-0.134051	1.330980	-0.735611

Standard basis: 6-31G(d) (6D, 7F)

SCF Done: E(UwB97XD) = -1349.66332320 A.U. after 1 cycles
NFock= 1 Conv=0.15D-08 -V/T= 2.0073
<Sx>= 0.0000 <Sy>= 0.0000 <Sz>= 0.5000
<S**2>= 0.7655 S= 0.5077
<L.S>= 0.000000000000E+00
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7655, after 0.7502

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-2179.3899	-15.7015	25.3576

Zero-point correction= 0.332565 (a.u.)
Thermal correction to Energy= 0.354167
Thermal correction to Enthalpy= 0.355112
Thermal correction to Gibbs Free Energy= 0.280524
Sum of electronic and zero-point Energies= -1349.330758
Sum of electronic and thermal Energies= -1349.309156
Sum of electronic and thermal Enthalpies= -1349.308212
Sum of electronic and thermal Free Energies= -1349.382800

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	222.243	80.098	156.984

Item	Value	Threshold	Converged?
Maximum Force	0.000002	0.000450	YES
RMS Force	0.000000	0.000300	YES
Maximum Displacement	0.013579	0.001800	NO
RMS Displacement	0.002024	0.001200	NO

------Figure S6-2, C(18)-H(26) clevage by MeO2(.)------

vita-b1.eli26.log

Stoichiometry C13H20N4O3S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-5.224369	-1.235879	-0.375320
2	6	0	-4.461941	-1.026961	-1.552970
3	6	0	-3.550610	0.163694	-1.285965
4	6	0	-2.574657	-0.080018	-0.175740
5	16	0	-3.026629	-0.916992	1.276844
6	6	0	-1.476902	-0.707299	1.909506
7	7	0	-0.667237	-0.061899	1.093893

8	6	0	0.725588	0.259792	1.437517
9	6	0	1.716418	-0.599961	0.694929
10	6	0	1.407026	-1.823525	0.136991
11	7	0	2.279308	-2.578848	-0.544242
12	6	0	3.509305	-2.074086	-0.668412
13	6	0	4.517396	-2.873486	-1.443199
14	7	0	3.933928	-0.914255	-0.159523
15	6	0	3.057316	-0.176632	0.529970
16	7	0	3.505626	1.013327	1.013721
17	6	0	-1.258769	0.312564	-0.119142
18	6	0	-0.514929	1.086614	-1.090482
19	1	0	-5.582615	-2.131914	-0.392330
20	1	0	-5.109820	-0.797422	-2.407223
21	1	0	-3.862611	-1.911745	-1.800857
22	1	0	-3.004470	0.405931	-2.200836
23	1	0	-4.168231	1.034481	-1.035515
24	1	0	-1.161275	-1.066764	2.879348
25	1	0	-1.022846	1.259710	-2.035341
26	1	0	-0.433814	2.357282	-0.566460
27	1	0	0.540281	0.842281	-1.204956
28	1	0	0.861843	1.320678	1.203008
29	1	0	0.820602	0.152574	2.520891
30	1	0	0.401102	-2.230351	0.223230
31	1	0	3.060166	1.442413	1.810517
32	1	0	4.504205	1.158649	0.956870
33	1	0	5.384068	-3.100102	-0.814549
34	1	0	4.074489	-3.804985	-1.798055
35	1	0	4.878015	-2.295174	-2.299792
36	8	0	-0.275893	3.361051	-0.006574
37	8	0	0.534287	4.115830	-0.831480
38	6	0	1.890720	3.915891	-0.451303
39	1	0	2.465427	4.593885	-1.085210
40	1	0	2.034612	4.165785	0.603607
41	1	0	2.197604	2.880842	-0.636001

SCF Done: E(UwB97XD) = -1349.66148205 A.U. after 1 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-2167.2841	19.6772	25.9698

Zero-point correction= 0.332314 (a.u.)
Thermal correction to Energy= 0.354815
Thermal correction to Enthalpy= 0.355759
Thermal correction to Gibbs Free Energy= 0.276944
Sum of electronic and zero-point Energies= -1349.329168
Sum of electronic and thermal Energies= -1349.306667
Sum of electronic and thermal Enthalpies= -1349.305723
Sum of electronic and thermal Free Energies= -1349.384538

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	222.650	81.947	165.880

Item	Value	Threshold	Converged?
Maximum Force	0.000009	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.001975	0.001800	NO
RMS Displacement	0.000471	0.001200	YES

-------- Figure S6-3, C(13)-H(33) cleavage by MeO2(.)-------
vita-b1.eli33.log

Stoichiometry C13H20N4O3S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	5.756209	-1.671464	-0.421321
2	6	0	5.151554	-1.718012	0.861298
3	6	0	4.653510	-0.312904	1.171466
4	6	0	3.576632	0.149705	0.234819
5	16	0	3.700265	-0.105178	-1.481771
6	6	0	2.235874	0.683790	-1.731505
7	7	0	1.685144	1.105378	-0.606477
8	6	0	0.374704	1.767073	-0.569571

9	6	0	-0.723850	0.836455	-0.121836
10	6	0	-0.619772	-0.541503	-0.128620
11	7	0	-1.586903	-1.367442	0.285717
12	6	0	-2.700558	-0.773207	0.736732
13	6	0	-3.788481	-1.641953	1.183793
14	7	0	-2.928475	0.546699	0.772311
15	6	0	-1.959895	1.357992	0.338309
16	7	0	-2.201828	2.691483	0.403724
17	6	0	2.429670	0.820529	0.539108
18	6	0	1.943613	1.278708	1.875302
19	1	0	5.809558	-2.569315	-0.770940
20	1	0	5.876484	-2.019376	1.627149
21	1	0	4.314201	-2.426784	0.880246
22	1	0	4.274605	-0.289500	2.195766
23	1	0	5.500433	0.381186	1.123459
24	1	0	1.768833	0.819497	-2.696974
25	1	0	2.580634	0.885116	2.666562
26	1	0	1.963926	2.371052	1.943120
27	1	0	0.921588	0.938269	2.063976
28	1	0	0.463145	2.621218	0.107695
29	1	0	0.186430	2.166702	-1.569741
30	1	0	0.291454	-1.024951	-0.475219
31	1	0	-1.696331	3.335723	-0.184308
32	1	0	-3.152874	2.958876	0.616105
33	1	0	-4.604391	-1.776880	0.095520
34	1	0	-3.513681	-2.673697	1.392536
35	1	0	-4.508372	-1.191841	1.866527
36	8	0	-5.353841	-1.833728	-0.796646
37	8	0	-6.439447	-1.080341	-0.393472
38	6	0	-6.191590	0.285457	-0.710554
39	1	0	-7.102677	0.813494	-0.421340
40	1	0	-5.336147	0.659946	-0.136910
41	1	0	-6.008482	0.402757	-1.782737

SCF Done: E(UwB97XD) = -1349.66131965 A.U. after 1 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-2124.1337	11.5283	27.2087

Zero-point correction= 0.332275 (a.u.)
Thermal correction to Energy= 0.354676
Thermal correction to Enthalpy= 0.355621
Thermal correction to Gibbs Free Energy= 0.276779
Sum of electronic and zero-point Energies= -1349.329045
Sum of electronic and thermal Energies= -1349.306643
Sum of electronic and thermal Enthalpies= -1349.305699
Sum of electronic and thermal Free Energies= -1349.384540

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	222.563	81.980	165.935

Item	Value	Threshold	Converged?
Maximum Force	0.000009	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.001554	0.001800	YES
RMS Displacement	0.000332	0.001200	YES

---------Figure S6-4, addition of MeO2(.) to C(4)------------

vita-b1.add04.log

Stoichiometry C13H20N4O3S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.998735	0.540806	-0.269214
2	6	0	-4.492982	0.622525	1.054225
3	6	0	-3.405240	-0.431429	1.197021
4	6	0	-2.243929	-0.264241	0.243459
5	16	0	-2.560958	0.033072	-1.472934
6	6	0	-1.054998	-0.617194	-1.877581
7	7	0	-0.402956	-1.146330	-0.847733
8	6	0	0.911737	-1.814902	-1.031391

9	6	0	2.057320	-0.902895	-0.679723
10	6	0	2.307141	0.227691	-1.442336
11	7	0	3.240497	1.136863	-1.159991
12	6	0	3.957719	0.900013	-0.051548
13	6	0	4.950301	1.950082	0.353240
14	7	0	3.855361	-0.175855	0.725246
15	6	0	2.931716	-1.098541	0.412045
16	7	0	2.867767	-2.178738	1.239907
17	6	0	-1.056741	-1.031597	0.357818
18	6	0	-0.546153	-1.640255	1.615682
19	1	0	-5.453701	1.366272	-0.475632
20	1	0	-5.280114	0.411766	1.788865
21	1	0	-4.084451	1.616377	1.259353
22	1	0	-3.020735	-0.405662	2.220297
23	1	0	-3.834214	-1.426039	1.033862
24	1	0	-0.660017	-0.646174	-2.883386
25	1	0	-0.900741	-1.063993	2.471860
26	1	0	-0.913733	-2.668374	1.719208
27	1	0	0.545042	-1.664069	1.661349
28	1	0	0.882831	-2.728211	-0.438709
29	1	0	0.952267	-2.120936	-2.077720
30	1	0	1.708359	0.425406	-2.330892
31	1	0	2.536772	-3.064302	0.886816
32	1	0	3.633645	-2.254512	1.896008
33	1	0	5.449981	2.362087	-0.526541
34	1	0	4.426004	2.773385	0.852194
35	1	0	5.687063	1.540338	1.045713
36	8	0	-1.688051	1.376261	0.907071
37	8	0	-0.695609	1.927812	0.143805
38	6	0	0.513679	1.931521	0.899194
39	1	0	1.249631	2.417137	0.256336
40	1	0	0.378742	2.496383	1.824448
41	1	0	0.829749	0.908679	1.127586

SCF Done: E(UwB97XD) = -1349.67476263 A.U. after 1 cycles
NFock= 1 Conv=0.44D-08 -V/T= 2.0073

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-649.6888	33.1644	40.1336

Zero-point correction= 0.337689 (a.u.)
Thermal correction to Energy= 0.359758
Thermal correction to Enthalpy= 0.360702
Thermal correction to Gibbs Free Energy= 0.285371
Sum of electronic and zero-point Energies= -1349.337074
Sum of electronic and thermal Energies= -1349.315005
Sum of electronic and thermal Enthalpies= -1349.314061
Sum of electronic and thermal Free Energies= -1349.389392

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	225.751	81.480	158.548

Item	Value	Threshold	Converged?
Maximum Force	0.000014	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.002304	0.001800	NO
RMS Displacement	0.000396	0.001200	YES

----------Figure S6-5, addition of MeO2(.) to C(17)----------

vita-b1.add17.log

Stoichiometry C13H20N4O3S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.618015	-1.549060	-0.202622
2	6	0	-3.754555	-2.213835	-1.110145
3	6	0	-2.670643	-1.223302	-1.502119
4	6	0	-1.909481	-0.662956	-0.344187
5	16	0	-2.350545	-0.886786	1.312946
6	6	0	-0.970011	-0.040931	1.810321
7	7	0	-0.225138	0.402279	0.824849

8	6	0	0.983715	1.221175	1.031317
9	6	0	2.233973	0.474215	0.641888
10	6	0	2.516358	-0.766258	1.183111
11	7	0	3.577949	-1.509833	0.854112
12	6	0	4.388452	-0.976928	-0.066873
13	6	0	5.583926	-1.780138	-0.492316
14	7	0	4.237295	0.216031	-0.644121
15	6	0	3.176898	0.956219	-0.294838
16	7	0	3.041267	2.149676	-0.938614
17	6	0	-0.792256	0.203612	-0.460487
18	6	0	0.092480	0.191069	-1.674195
19	1	0	-5.222764	-2.196767	0.180392
20	1	0	-4.290393	-2.532310	-2.011818
21	1	0	-3.304297	-3.102439	-0.648016
22	1	0	-1.969349	-1.715842	-2.185553
23	1	0	-3.120526	-0.388368	-2.056174
24	1	0	-0.718972	0.127898	2.849225
25	1	0	-0.532993	0.218758	-2.568018
26	1	0	0.750555	1.061790	-1.696934
27	1	0	0.696491	-0.719812	-1.691022
28	1	0	0.826204	2.129272	0.447487
29	1	0	0.995898	1.511167	2.083665
30	1	0	1.842914	-1.202306	1.919992
31	1	0	2.553630	2.911969	-0.493632
32	1	0	3.845729	2.432038	-1.482018
33	1	0	6.504647	-1.228731	-0.277318
34	1	0	5.606658	-2.737367	0.030137
35	1	0	5.554014	-1.956299	-1.572105
36	8	0	-1.495326	1.845878	-0.755311
37	8	0	-2.212827	2.267435	0.338146
38	6	0	-3.606195	2.218653	0.031724
39	1	0	-4.100561	2.638023	0.909608
40	1	0	-3.817022	2.825725	-0.851727
41	1	0	-3.937369	1.187523	-0.127813

SCF Done: E(UwB97XD) = -1349.67566253 A.U. after 1 cycles
NFock= 1 Conv=0.47D-08 -V/T= 2.0073

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-647.9570	15.4472	23.2688

Zero-point correction= 0.337856 (a.u.)
Thermal correction to Energy= 0.359920
Thermal correction to Enthalpy= 0.360865
Thermal correction to Gibbs Free Energy= 0.283927
Sum of electronic and zero-point Energies= -1349.337807
Sum of electronic and thermal Energies= -1349.315742
Sum of electronic and thermal Enthalpies= -1349.314798
Sum of electronic and thermal Free Energies= -1349.391736

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	225.853	81.271	161.930

Item	Value	Threshold	Converged?
Maximum Force	0.000003	0.000450	YES
RMS Force	0.000000	0.000300	YES
Maximum Displacement	0.001119	0.001800	YES
RMS Displacement	0.000152	0.001200	YES

----------Figure S6-6, addition of MeO2(.) to C(6)----------

vita-b1.add06.log

Stoichiometry C13H20N4O3S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-5.183349	-0.794002	0.462459
2	6	0	-4.339451	-1.712644	1.137594
3	6	0	-3.231920	-2.095485	0.167885
4	6	0	-2.382752	-0.936866	-0.260447
5	16	0	-2.965053	0.687107	-0.312502
6	6	0	-1.390201	1.260979	-0.733342

7	7	0	-0.552966	0.220384	-0.987577
8	6	0	0.805266	0.442785	-1.501804
9	6	0	1.889528	0.019570	-0.543114
10	6	0	1.722044	-0.059047	0.824681
11	7	0	2.672744	-0.476851	1.672457
12	6	0	3.833273	-0.829581	1.114019
13	6	0	4.921211	-1.330884	2.020692
14	7	0	4.123506	-0.773219	-0.188299
15	6	0	3.170497	-0.340900	-1.022062
16	7	0	3.483880	-0.318934	-2.347766
17	6	0	-1.069745	-1.011235	-0.679486
18	6	0	-0.267697	-2.262615	-0.814881
19	1	0	-5.730931	-0.340541	1.115473
20	1	0	-4.889045	-2.615785	1.428020
21	1	0	-3.908650	-1.265421	2.042570
22	1	0	-2.595538	-2.852574	0.634973
23	1	0	-3.680931	-2.552387	-0.723404
24	1	0	-1.274263	2.180698	-1.291252
25	1	0	-0.929982	-3.110910	-0.991839
26	1	0	0.432183	-2.201417	-1.651174
27	1	0	0.309126	-2.456115	0.095213
28	1	0	0.885180	-0.111557	-2.442641
29	1	0	0.878312	1.505754	-1.744627
30	1	0	0.770196	0.216546	1.273054
31	1	0	3.016149	0.326357	-2.966249
32	1	0	4.461462	-0.465582	-2.559045
33	1	0	5.811981	-0.701906	1.926901
34	1	0	4.584829	-1.327732	3.058383
35	1	0	5.209128	-2.348234	1.737180
36	8	0	-0.789169	1.998126	0.903478
37	8	0	0.312444	2.746885	0.673369
38	6	0	-0.052528	4.121424	0.507954
39	1	0	0.894927	4.654657	0.427267
40	1	0	-0.637865	4.251251	-0.407257
41	1	0	-0.620126	4.460449	1.376209

SCF Done: E(UwB97XD) = -1349.67819276 A.U. after 1 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-775.2271	24.5751	30.4596

Zero-point correction= 0.337785 (a.u.)
Thermal correction to Energy= 0.360172
Thermal correction to Enthalpy= 0.361116
Thermal correction to Gibbs Free Energy= 0.283728
Sum of electronic and zero-point Energies= -1349.340408
Sum of electronic and thermal Energies= -1349.318021
Sum of electronic and thermal Enthalpies= -1349.317076
Sum of electronic and thermal Free Energies= -1349.394465

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	226.012	81.363	162.879

Item	Value	Threshold	Converged?
Maximum Force	0.000043	0.000450	YES
RMS Force	0.000007	0.000300	YES
Maximum Displacement	0.007434	0.001800	NO
RMS Displacement	0.001317	0.001200	NO

==========Figure S7 and Scheme S2==========

thiamine + tert-butoxyl radical t-BuO(.) + (H2O)8

-------Figure S7-1, Precursor[A-tertBu]----------

vita-b103c.tbu.revrev.log

Stoichiometry C16H42N4O10S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.927484	4.769752	-0.036334
2	6	0	0.825753	4.340092	-1.389544

3	6	0	1.810921	3.206807	-1.697152
4	6	0	1.504053	1.975918	-0.901586
5	16	0	1.495405	2.033632	0.833819
6	6	0	1.009073	0.430749	0.915594
7	7	0	0.866500	-0.118708	-0.275405
8	6	0	0.396445	-1.500716	-0.435342
9	6	0	-1.098011	-1.599796	-0.590324
10	6	0	-1.907521	-0.569007	-1.003519
11	7	0	-3.240944	-0.671443	-1.129346
12	6	0	-3.778850	-1.836961	-0.770036
13	6	0	-5.276851	-1.931680	-0.811592
14	7	0	-3.103342	-2.904000	-0.343453
15	6	0	-1.756987	-2.822253	-0.290732
16	7	0	-1.092636	-3.922906	0.091845
17	6	0	1.157756	0.733949	-1.341241
18	6	0	1.108716	0.212321	-2.740364
19	1	0	1.722144	5.307054	0.076097
20	1	0	0.997734	5.176694	-2.073889
21	1	0	-0.199979	3.983205	-1.509813
22	1	0	1.753773	2.972892	-2.763182
23	1	0	2.834870	3.543896	-1.499426
24	1	0	0.789786	-0.095147	1.832454
25	1	0	1.320959	1.009821	-3.451679
26	1	0	1.855516	-0.577515	-2.873911
27	1	0	0.125036	-0.201514	-2.982231
28	1	0	0.927215	-1.932026	-1.287070
29	1	0	0.726574	-2.051370	0.448998
30	1	0	-1.492148	0.407095	-1.240350
31	1	0	-0.078647	-4.038473	-0.007574
32	1	0	-1.642754	-4.755840	0.244876
33	1	0	-5.708798	-1.274077	-0.049729
34	1	0	-5.649075	-1.598180	-1.784027
35	1	0	-5.606417	-2.954677	-0.625267
36	8	0	3.791721	-0.540295	-0.011341
37	6	0	4.616535	-0.951926	1.013409
38	6	0	5.978982	-1.193038	0.290627
39	1	0	5.886596	-1.985233	-0.455682
40	1	0	6.327834	-0.275229	-0.187774
41	1	0	6.701160	-1.498673	1.053025
42	8	0	-1.597757	1.361954	1.553565
43	1	0	-2.514901	1.078862	1.802169
44	1	0	-1.494690	2.264584	1.905360
45	8	0	-4.164977	0.639557	1.991494
46	1	0	-4.493529	0.942815	1.113927
47	1	0	-4.214899	-0.337385	1.990817
48	8	0	-4.773239	1.621508	-0.530125
49	1	0	-4.022454	2.253482	-0.572586
50	1	0	-4.377875	0.835043	-0.963462
51	8	0	-4.272655	-2.173786	2.304081
52	1	0	-3.918089	-2.717151	1.580141
53	1	0	-5.190338	-2.459521	2.394394
54	8	0	-1.291732	4.218977	1.536923
55	1	0	-0.455729	4.512255	1.123026
56	1	0	-1.597749	4.965143	2.066092
57	8	0	-2.290667	2.848885	-0.651308
58	1	0	-2.173678	3.636013	-0.086865
59	1	0	-1.987907	2.155337	-0.021135
60	1	0	2.238051	-3.804852	-0.765882
61	8	0	1.747528	-4.349318	-0.112815
62	1	0	1.869517	-5.260605	-0.406136
63	1	0	3.381888	-1.861836	-1.220466
64	8	0	3.003062	-2.555165	-1.798798
65	1	0	3.717520	-2.830332	-2.386884
66	6	0	4.761126	0.135287	2.079991
67	1	0	5.098352	1.071344	1.625026
68	1	0	3.800311	0.312525	2.573536
69	1	0	5.484916	-0.166331	2.843033
70	6	0	4.107329	-2.279341	1.600627
71	1	0	3.968824	-3.030181	0.818869
72	1	0	4.826752	-2.655209	2.334010
73	1	0	3.149844	-2.124394	2.106953

Standard basis: 6-31G(d) (6D, 7F)

SCF Done: E(UwB97XD) = -2003.79300089 A.U. after 1 cycles

Zero-point correction= 0.626263 (a.u.)
Thermal correction to Energy= 0.672583
Thermal correction to Enthalpy= 0.673527

Thermal correction to Gibbs Free Energy= 0.544140
Sum of electronic and zero-point Energies= -2003.166738
Sum of electronic and thermal Energies= -2003.120418
Sum of electronic and thermal Enthalpies= -2003.119474
Sum of electronic and thermal Free Energies= -2003.248861

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	422.052	166.297	272.318

Item	Value	Threshold	Converged?
Maximum Force	0.000020	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.031403	0.001800	NO
RMS Displacement	0.004846	0.001200	NO

----------Figure S7-2, TS1[A-tert-Bu]----------

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Stoichiometry C16H42N4O10S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.357233	4.593930	0.025716
2	6	0	1.555352	4.332005	-1.359082
3	6	0	2.569033	3.199773	-1.598145
4	6	0	2.069229	1.910183	-1.033692
5	16	0	2.050553	1.658560	0.664067
6	6	0	1.327224	0.128590	0.469329
7	7	0	1.016813	-0.096269	-0.818893
8	6	0	0.325782	-1.334065	-1.201662
9	6	0	-1.170541	-1.234918	-1.100893
10	6	0	-1.878238	-0.084944	-1.358457
11	7	0	-3.215017	0.001098	-1.267172
12	6	0	-3.848611	-1.092782	-0.842949
13	6	0	-5.332719	-0.981320	-0.645421
14	7	0	-3.270810	-2.256186	-0.542542
15	6	0	-1.936261	-2.364018	-0.708176
16	7	0	-1.378724	-3.557780	-0.440946
17	6	0	1.476775	0.854016	-1.695511
18	6	0	1.329766	0.656639	-3.165880
19	1	0	2.089507	5.137250	0.346265
20	1	0	1.895353	5.235824	-1.872822
21	1	0	0.582140	4.043207	-1.759040
22	1	0	2.735441	3.097292	-2.673369
23	1	0	3.532341	3.464894	-1.150727
24	1	0	0.773611	-0.343498	1.267802
25	1	0	1.649081	1.545407	-3.708407
26	1	0	1.947770	-0.188678	-3.486883
27	1	0	0.290511	0.451391	-3.438686
28	1	0	0.666233	-1.613125	-2.199178
29	1	0	0.700972	-2.101450	-0.525923
30	1	0	-1.370021	0.839697	-1.624297
31	1	0	-0.447260	-3.819384	-0.777008
32	1	0	-2.014728	-4.312204	-0.224737
33	1	0	-5.540812	-0.382177	0.247703
34	1	0	-5.789430	-0.473406	-1.498391
35	1	0	-5.783557	-1.966593	-0.518506
36	8	0	2.966375	-1.131766	0.620252
37	6	0	3.002785	-1.957367	1.755364
38	6	0	4.355443	-2.691389	1.564544
39	1	0	4.349218	-3.272383	0.638224
40	1	0	5.180630	-1.975796	1.538225
41	1	0	4.498558	-3.374015	2.407683
42	8	0	-0.979657	1.242345	1.725632
43	1	0	-1.929562	1.119195	1.985495
44	1	0	-0.661215	2.024990	2.220448
45	8	0	-3.617872	0.998405	2.199036
46	1	0	-3.891031	1.453727	1.369822
47	1	0	-3.827459	0.047427	2.099849
48	8	0	-4.049242	2.432727	-0.140944
49	1	0	-3.146082	2.808746	-0.199271
50	1	0	-3.965666	1.662716	-0.742044
51	8	0	-4.066612	-1.784510	2.240648
52	1	0	-3.857454	-2.253475	1.413258
53	1	0	-4.991657	-1.997864	2.415424

54	8	0	0.094353	3.704567	2.465628
55	1	0	0.520148	4.004357	1.643176
56	1	0	-0.551730	4.389907	2.676535
57	8	0	-1.290911	2.882839	-0.413637
58	1	0	-0.955757	3.714490	-0.054056
59	1	0	-1.144219	2.228068	0.316151
60	1	0	1.919803	-3.734740	-1.658810
61	8	0	1.219354	-4.384696	-1.430294
62	1	0	1.044665	-4.861464	-2.250898
63	1	0	3.116772	-1.899193	-1.036253
64	8	0	3.020690	-2.340909	-1.903617
65	1	0	3.919450	-2.541031	-2.193236
66	6	0	3.039626	-1.121051	3.037243
67	1	0	3.831597	-0.368996	2.976270
68	1	0	2.083641	-0.611809	3.204211
69	1	0	3.227291	-1.760691	3.904650
70	6	0	1.862740	-2.979758	1.770902
71	1	0	1.860210	-3.578290	0.854277
72	1	0	1.977883	-3.659040	2.620995
73	1	0	0.886117	-2.493274	1.875438

SCF Done: E(UwB97XD) = -2003.77853187 A.U. after 1 cycles
NFock= 1 Conv=0.61D-09 -V/T= 2.0078

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-503.4486	-49.9861	-16.7085

Zero-point correction= 0.625377 (a.u.)
Thermal correction to Energy= 0.669185
Thermal correction to Enthalpy= 0.670129
Thermal correction to Gibbs Free Energy= 0.549003
Sum of electronic and zero-point Energies= -2003.153155
Sum of electronic and thermal Energies= -2003.109347
Sum of electronic and thermal Enthalpies= -2003.108402
Sum of electronic and thermal Free Energies= -2003.229529

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	419.920	160.659	254.931

Item	Value	Threshold	Converged?
Maximum Force	0.000194	0.000450	YES
RMS Force	0.000026	0.000300	YES
Maximum Displacement	0.011941	0.001800	NO
RMS Displacement	0.002186	0.001200	NO

---------Figure S7-3, Int1-1[A-tertBu]-----------

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Stoichiometry C16H42N4O10S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.298561	-1.933939	-0.080791
2	6	0	-4.411744	-1.336772	-1.370089
3	6	0	-4.334501	0.198994	-1.310949
4	6	0	-2.986340	0.668303	-0.871848
5	16	0	-2.667804	1.051726	0.763076
6	6	0	-0.846996	1.184731	0.442752
7	7	0	-0.737437	1.113364	-1.015085
8	6	0	0.587311	1.308663	-1.598296
9	6	0	1.484739	0.107360	-1.421613
10	6	0	1.010422	-1.183873	-1.458605
11	7	0	1.786841	-2.270781	-1.328059
12	6	0	3.081587	-2.045178	-1.099084
13	6	0	3.948898	-3.250806	-0.879214
14	7	0	3.654327	-0.846107	-1.012125
15	6	0	2.883411	0.246345	-1.210646
16	7	0	3.507797	1.431176	-1.167725
17	6	0	-1.842018	0.768842	-1.681852
18	6	0	-1.816849	0.553942	-3.158215
19	1	0	-5.185171	-2.124833	0.250758
20	1	0	-5.354257	-1.627122	-1.840618

21	1	0	-3.589029	-1.731497	-1.971105
22	1	0	-4.564333	0.597141	-2.304409
23	1	0	-5.104216	0.573303	-0.630288
24	1	0	-0.411182	0.275512	0.880877
25	1	0	-2.744415	0.101221	-3.504850
26	1	0	-1.695815	1.513950	-3.671620
27	1	0	-0.989343	-0.098275	-3.449215
28	1	0	0.462573	1.574397	-2.649945
29	1	0	1.011972	2.184836	-1.108675
30	1	0	-0.052137	-1.389753	-1.573639
31	1	0	3.061006	2.339940	-1.324824
32	1	0	4.501549	1.418846	-0.990058
33	1	0	3.629868	-3.776930	0.026359
34	1	0	3.845300	-3.945346	-1.717682
35	1	0	4.995044	-2.961234	-0.772999
36	8	0	-0.283455	2.341261	0.904584
37	6	0	0.491843	2.276467	2.159908
38	6	0	0.888238	3.728136	2.389009
39	1	0	1.486146	4.099976	1.551313
40	1	0	0.000309	4.357977	2.501364
41	1	0	1.485392	3.807047	3.301138
42	8	0	-0.532342	-1.513515	1.618201
43	1	0	0.173646	-2.148318	1.910927
44	1	0	-1.326863	-1.660356	2.175967
45	8	0	1.422587	-3.275100	2.078568
46	1	0	1.208182	-3.786805	1.263530
47	1	0	2.214175	-2.734411	1.882776
48	8	0	0.544816	-4.534660	-0.227760
49	1	0	-0.360070	-4.161767	-0.272331
50	1	0	1.032779	-3.905430	-0.803361
51	8	0	3.656659	-1.554583	1.919200
52	1	0	3.917006	-1.144663	1.078111
53	1	0	4.444970	-2.028110	2.213441
54	8	0	-3.077805	-1.826204	2.565416
55	1	0	-3.470530	-1.689519	1.685086
56	1	0	-3.271844	-2.749304	2.773495
57	8	0	-1.623476	-2.809882	-0.521638
58	1	0	-2.556905	-2.903975	-0.273466
59	1	0	-1.227480	-2.293687	0.220484
60	1	0	1.567796	4.331348	-1.266115
61	8	0	2.443729	4.048408	-1.613505
62	1	0	2.354214	4.128716	-2.571544
63	1	0	-0.337167	3.946818	-0.099084
64	8	0	-0.097477	4.638680	-0.740158
65	1	0	-0.160038	5.466974	-0.247925
66	6	0	-0.406167	1.756669	3.278600
67	1	0	-1.317781	2.357775	3.356746
68	1	0	-0.671920	0.705029	3.124862
69	1	0	0.128329	1.822435	4.230678
70	6	0	1.720708	1.394957	1.965206
71	1	0	2.337084	1.763362	1.139951
72	1	0	2.324634	1.421178	2.876953
73	1	0	1.460030	0.348001	1.783342

SCF Done: E(UwB97XD) = -2003.8419230 A.U. after 1 cycles

Zero-point correction= 0.630305 (a.u.)
Thermal correction to Energy= 0.675190
Thermal correction to Enthalpy= 0.676134
Thermal correction to Gibbs Free Energy= 0.553149
Sum of electronic and zero-point Energies= -2003.211618
Sum of electronic and thermal Energies= -2003.166733
Sum of electronic and thermal Enthalpies= -2003.165789
Sum of electronic and thermal Free Energies= -2003.288774

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	423.688	163.580	258.845

Item	Value	Threshold	Converged?
Maximum Force	0.000032	0.000450	YES
RMS Force	0.000005	0.000300	YES
Maximum Displacement	0.002640	0.001800	NO
RMS Displacement	0.000539	0.001200	YES

----------Figure S7-4, TS2-1[A-tertBu]----------

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Stoichiometry C16H42N4O10S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.400069	-1.686983	0.098558
2	6	0	-4.493090	-1.146800	-1.225629
3	6	0	-4.334649	0.376572	-1.260784
4	6	0	-2.949283	0.828925	-0.900687
5	16	0	-2.590674	1.477588	0.672285
6	6	0	-0.805978	1.319266	0.370333
7	7	0	-0.679610	1.117744	-1.032757
8	6	0	0.643502	1.153238	-1.640347
9	6	0	1.442455	-0.113917	-1.434568
10	6	0	0.871360	-1.364423	-1.410108
11	7	0	1.558005	-2.506787	-1.234969
12	6	0	2.868941	-2.374942	-1.028053
13	6	0	3.641100	-3.630065	-0.740645
14	7	0	3.536189	-1.222306	-1.005969
15	6	0	2.852709	-0.081781	-1.250381
16	7	0	3.572494	1.047535	-1.274906
17	6	0	-1.828462	0.744852	-1.681751
18	6	0	-1.790963	0.346143	-3.124769
19	1	0	-5.293587	-1.849198	0.426592
20	1	0	-5.452512	-1.427369	-1.668143
21	1	0	-3.695788	-1.620416	-1.804278
22	1	0	-4.582729	0.716738	-2.272592
23	1	0	-5.070348	0.832934	-0.591555
24	1	0	-0.617831	-0.079932	0.973806
25	1	0	-2.759466	-0.039956	-3.442281
26	1	0	-1.556811	1.212827	-3.752246
27	1	0	-1.041645	-0.425155	-3.322898
28	1	0	0.525838	1.379067	-2.702793
29	1	0	1.165596	2.003046	-1.202615
30	1	0	-0.203852	-1.486020	-1.517058
31	1	0	3.198791	1.983748	-1.461199
32	1	0	4.564552	0.961796	-1.108045
33	1	0	3.389667	-3.998369	0.260059
34	1	0	3.373034	-4.411543	-1.456162
35	1	0	4.714645	-3.442288	-0.784540
36	8	0	-0.033276	2.365951	0.813003
37	6	0	0.721826	2.235102	2.061307
38	6	0	1.291974	3.633203	2.270903
39	1	0	1.911093	3.925543	1.417143
40	1	0	0.487193	4.364757	2.393975
41	1	0	1.914410	3.649387	3.169570
42	8	0	-0.735490	-1.145515	1.296624
43	1	0	0.133114	-1.706877	1.706863
44	1	0	-1.536402	-1.200883	1.911534
45	8	0	1.047325	-2.567907	2.120973
46	1	0	0.887677	-3.361611	1.535483
47	1	0	1.980131	-2.260608	1.997447
48	8	0	0.336019	-4.458805	0.359888
49	1	0	-0.607504	-4.231977	0.227291
50	1	0	0.762627	-3.988121	-0.391349
51	8	0	3.594932	-1.621686	1.929788
52	1	0	3.881990	-1.356130	1.038462
53	1	0	4.264657	-2.247144	2.234787
54	8	0	-3.013254	-1.301082	2.532280
55	1	0	-3.557857	-1.270062	1.719512
56	1	0	-3.171248	-2.178468	2.906860
57	8	0	-1.947622	-3.065525	-0.386660
58	1	0	-2.882595	-2.996341	-0.130075
59	1	0	-1.534352	-2.317978	0.080859
60	1	0	1.918731	4.104367	-1.430889
61	8	0	2.746675	3.729732	-1.809746
62	1	0	2.607621	3.772153	-2.764254
63	1	0	0.056447	3.915284	-0.199579
64	8	0	0.326412	4.597734	-0.842340
65	1	0	0.389259	5.412276	-0.327842
66	6	0	-0.218529	1.855596	3.201457
67	1	0	-1.046669	2.568123	3.271874
68	1	0	-0.626434	0.848016	3.079371
69	1	0	0.330568	1.874798	4.147345
70	6	0	1.844258	1.221280	1.877218
71	1	0	2.526967	1.540815	1.084486
72	1	0	2.415305	1.125999	2.804928
73	1	0	1.462716	0.229262	1.625873

SCF Done: E(UwB97XD) = -2003.80833691 A.U. after 1 cycles
NFock= 1 Conv=0.37D-08 -V/T= 2.0078

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-1003.8421	31.2495	34.5070

Zero-point correction= 0.622974 (a.u.)
Thermal correction to Energy= 0.666291
Thermal correction to Enthalpy= 0.667235
Thermal correction to Gibbs Free Energy= 0.549258
Sum of electronic and zero-point Energies= -2003.185363
Sum of electronic and thermal Energies= -2003.142046
Sum of electronic and thermal Enthalpies= -2003.141102
Sum of electronic and thermal Free Energies= -2003.259079

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	418.104	160.342	248.303

Item	Value	Threshold	Converged?
Maximum Force	0.000108	0.000450	YES
RMS Force	0.000011	0.000300	YES
Maximum Displacement	0.003961	0.001800	NO
RMS Displacement	0.000696	0.001200	YES

----------Figure S7-5, Int1-2[A-tertBu]----------

vita-b103a.tbu.for.log

Stoichiometry C16H42N4O10S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.403358	-1.682556	-0.174920
2	6	0	-4.398337	-1.136672	-1.501822
3	6	0	-4.217767	0.382360	-1.515656
4	6	0	-2.859066	0.827046	-1.054059
5	16	0	-2.622241	1.488678	0.557384
6	6	0	-0.839110	1.438120	0.357103
7	7	0	-0.590237	1.179789	-1.006492
8	6	0	0.775823	1.190067	-1.494158
9	6	0	1.524026	-0.110979	-1.308289
10	6	0	0.914226	-1.339495	-1.255667
11	7	0	1.579920	-2.506123	-1.133837
12	6	0	2.904411	-2.421538	-1.009267
13	6	0	3.660076	-3.704927	-0.814910
14	7	0	3.605252	-1.287767	-0.984660
15	6	0	2.941676	-0.125208	-1.172480
16	7	0	3.683814	0.989678	-1.187460
17	6	0	-1.691445	0.764613	-1.739969
18	6	0	-1.522282	0.360434	-3.172276
19	1	0	-5.312522	-1.900936	0.064468
20	1	0	-5.328846	-1.404452	-2.009994
21	1	0	-3.568406	-1.614351	-2.029642
22	1	0	-4.390980	0.727644	-2.541748
23	1	0	-4.998607	0.842773	-0.901656
24	1	0	-0.712078	-0.328311	1.223813
25	1	0	-2.461236	-0.017505	-3.577918
26	1	0	-1.218474	1.219631	-3.780330
27	1	0	-0.766109	-0.420693	-3.296334
28	1	0	0.771528	1.485439	-2.547428
29	1	0	1.289132	1.988436	-0.958348
30	1	0	-0.168493	-1.429632	-1.301551
31	1	0	3.329382	1.931487	-1.386843
32	1	0	4.681637	0.876082	-1.082828
33	1	0	3.651113	-3.982447	0.245366
34	1	0	3.189243	-4.514489	-1.376745
35	1	0	4.699071	-3.590323	-1.127380
36	8	0	-0.124975	2.503095	0.850508
37	6	0	0.605356	2.357082	2.110978
38	6	0	1.191684	3.745521	2.337988
39	1	0	1.841499	4.027054	1.503306
40	1	0	0.394823	4.489884	2.433586

41	1	0	1.786224	3.754205	3.255565
42	8	0	-0.871493	-1.237167	1.579453
43	1	0	0.287050	-2.178080	2.103688
44	1	0	-1.741918	-1.198201	2.062648
45	8	0	0.951456	-2.933973	2.216599
46	1	0	0.698955	-3.631410	1.440883
47	1	0	1.877707	-2.555116	2.090285
48	8	0	0.265922	-4.409281	0.326591
49	1	0	-0.670520	-4.144576	0.156443
50	1	0	0.749495	-3.923009	-0.393314
51	8	0	3.316901	-1.797752	2.037725
52	1	0	3.660861	-1.511724	1.174373
53	1	0	4.034852	-2.294496	2.452046
54	8	0	-3.384149	-1.247624	2.441248
55	1	0	-3.763247	-1.192922	1.542053
56	1	0	-3.621236	-2.131707	2.751377
57	8	0	-1.894778	-2.947458	-0.340488
58	1	0	-2.859987	-2.901953	-0.228996
59	1	0	-1.563366	-2.251754	0.263556
60	1	0	2.095928	4.054389	-1.445215
61	8	0	2.940325	3.677872	-1.783217
62	1	0	2.841709	3.703029	-2.743132
63	1	0	0.163726	3.950938	-0.257112
64	8	0	0.496451	4.593605	-0.912617
65	1	0	0.566843	5.426171	-0.428906
66	6	0	-0.366542	1.983428	3.226204
67	1	0	-1.192938	2.699896	3.271856
68	1	0	-0.774839	0.978440	3.084846
69	1	0	0.154841	1.996794	4.188011
70	6	0	1.713489	1.321439	1.953117
71	1	0	2.420599	1.619760	1.172606
72	1	0	2.264488	1.224112	2.893065
73	1	0	1.311967	0.336197	1.702523

SCF Done: E(UwB97XD) = -2003.81772555 A.U. after 1 cycles

Zero-point correction= 0.628938 (a.u.)
Thermal correction to Energy= 0.672504
Thermal correction to Enthalpy= 0.673448
Thermal correction to Gibbs Free Energy= 0.554572
Sum of electronic and zero-point Energies= -2003.188788
Sum of electronic and thermal Energies= -2003.145222
Sum of electronic and thermal Enthalpies= -2003.144278
Sum of electronic and thermal Free Energies= -2003.263154

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	422.002	160.831	250.196

Item	Value	Threshold	Converged?
Maximum Force	0.000009	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.002573	0.001800	NO
RMS Displacement	0.000349	0.001200	YES

--------Figure S7-6, TS2-2[A-tertBu]------------

vita-b103b.tbu.log

Stoichiometry C16H42N4O10S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.391265	-1.264550	-1.167425
2	6	0	-4.328722	-0.375417	-2.290263
3	6	0	-3.898599	1.014692	-1.840630
4	6	0	-2.533116	1.162832	-1.217462
5	16	0	-2.385809	2.026775	0.327255
6	6	0	-0.625950	2.092290	0.139696
7	7	0	-0.245992	1.232135	-0.908220
8	6	0	1.148589	1.171007	-1.293398
9	6	0	1.754636	-0.205021	-1.171101
10	6	0	1.028922	-1.306797	-0.846665
11	7	0	1.626113	-2.513906	-0.703323
12	6	0	2.956216	-2.647735	-0.860817
13	6	0	3.550937	-3.992843	-0.604580

14	7	0	3.722825	-1.634059	-1.188888
15	6	0	3.160227	-0.409096	-1.350668
16	7	0	3.980769	0.584374	-1.667716
17	6	0	-1.320117	0.849495	-1.720415
18	6	0	-1.070397	0.146130	-3.020176
19	1	0	-4.930224	-2.028548	-1.415161
20	1	0	-5.319904	-0.295910	-2.747496
21	1	0	-3.642444	-0.790198	-3.034498
22	1	0	-3.966763	1.664140	-2.723738
23	1	0	-4.653133	1.385249	-1.138841
24	1	0	-2.002105	-0.058835	1.603068
25	1	0	-1.851469	0.400140	-3.740208
26	1	0	-0.114539	0.430801	-3.465399
27	1	0	-1.070566	-0.940721	-2.884071
28	1	0	1.291274	1.563874	-2.306831
29	1	0	1.683283	1.854041	-0.629016
30	1	0	-0.046565	-1.302616	-0.690881
31	1	0	3.698082	1.566550	-1.803370
32	1	0	4.962074	0.360372	-1.759992
33	1	0	3.632935	-4.127564	0.479016
34	1	0	2.915092	-4.787814	-1.001757
35	1	0	4.543472	-4.051676	-1.050505
36	8	0	0.180623	2.625078	0.978558
37	6	0	0.701750	1.843543	2.542422
38	6	0	1.829282	2.772463	2.890969
39	1	0	2.622247	2.729889	2.137281
40	1	0	1.471485	3.803791	2.979160
41	1	0	2.268649	2.487943	3.855732
42	8	0	-2.134330	-0.960843	1.936812
43	1	0	-0.785206	-2.184044	2.480703
44	1	0	-3.123140	-1.030393	1.977880
45	8	0	-0.192728	-2.946089	2.614218
46	1	0	-0.226092	-3.939674	1.149130
47	1	0	0.720539	-2.607606	2.536703
48	8	0	-0.211285	-4.276626	0.220659
49	1	0	-0.964508	-3.791834	-0.179701
50	1	0	1.020633	-3.313226	-0.386473
51	8	0	2.552745	-2.538333	2.263005
52	1	0	3.006383	-1.693732	2.149679
53	1	0	2.985573	-2.941733	3.026786
54	8	0	-4.795271	-0.882500	1.585440
55	1	0	-4.767535	-0.905882	0.608183
56	1	0	-5.283450	-1.677579	1.834562
57	8	0	-1.879384	-2.259881	-0.490604
58	1	0	-2.736698	-2.009209	-0.882405
59	1	0	-1.924444	-1.856078	0.402430
60	1	0	2.936375	3.761209	-1.327646
61	8	0	3.464485	3.319476	-2.032093
62	1	0	3.006032	3.532290	-2.853847
63	1	0	1.311223	3.914483	0.346243
64	8	0	1.965809	4.510920	-0.067565
65	1	0	2.537587	4.792724	0.657154
66	6	0	-0.509681	1.963916	3.424961
67	1	0	-0.915550	2.979982	3.394950
68	1	0	-1.294905	1.256715	3.144555
69	1	0	-0.233415	1.742593	4.465188
70	6	0	1.108105	0.446168	2.184850
71	1	0	2.001339	0.444149	1.552683
72	1	0	1.329334	-0.126867	3.095600
73	1	0	0.308297	-0.084379	1.657717

SCF Done: E(UwB97XD) = -2003.80396814 A.U. after 1 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-682.1451	29.9004	36.1665

Zero-point correction= 0.625912 (a.u.)
Thermal correction to Energy= 0.671432
Thermal correction to Enthalpy= 0.672376
Thermal correction to Gibbs Free Energy= 0.549024
Sum of electronic and zero-point Energies= -2003.178056
Sum of electronic and thermal Energies= -2003.132536
Sum of electronic and thermal Enthalpies= -2003.131592
Sum of electronic and thermal Free Energies= -2003.254944

E (Thermal)	CV	S
KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin

Total 421.330 165.248 259.616

Item	Value	Threshold	Converged?
Maximum Force	0.000027	0.000450	YES
RMS Force	0.000003	0.000300	YES
Maximum Displacement	0.001429	0.001800	YES
RMS Displacement	0.000292	0.001200	YES

------Figure S7-7, Int2[A-tertBu]----------

vita-b103b.tbu.for.log

Stoichiometry C16H42N4O10S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.552053	-1.626467	-0.035022
2	6	0	-4.946479	-0.852599	-1.178093
3	6	0	-4.826249	0.635424	-0.864010
4	6	0	-3.442829	1.054209	-0.461271
5	16	0	-2.978210	0.980720	1.228962
6	6	0	-1.326345	1.423047	0.845453
7	7	0	-1.232197	1.671153	-0.491105
8	6	0	0.041760	2.111254	-1.038287
9	6	0	0.970143	0.972637	-1.379347
10	6	0	0.557415	-0.321107	-1.406905
11	7	0	1.412600	-1.316789	-1.742323
12	6	0	2.687781	-1.043224	-2.079451
13	6	0	3.571964	-2.196267	-2.419836
14	7	0	3.157155	0.183547	-2.083205
15	6	0	2.339845	1.204715	-1.723067
16	7	0	2.873744	2.421080	-1.720496
17	6	0	-2.406556	1.441039	-1.232325
18	6	0	-2.384022	1.622733	-2.714826
19	1	0	-4.970708	-2.495158	-0.100691
20	1	0	-5.984037	-1.082751	-1.436686
21	1	0	-4.306459	-1.110423	-2.030216
22	1	0	-5.138731	1.189762	-1.754454
23	1	0	-5.537087	0.892238	-0.071902
24	1	0	-0.283940	-0.576442	1.988941
25	1	0	-3.334644	1.309431	-3.147877
26	1	0	-2.219854	2.671133	-2.985943
27	1	0	-1.592485	1.023071	-3.176614
28	1	0	-0.148060	2.725654	-1.922436
29	1	0	0.506455	2.765100	-0.299539
30	1	0	-0.455893	-0.639359	-1.172582
31	1	0	2.439651	3.240936	-1.273793
32	1	0	3.859981	2.483942	-1.934725
33	1	0	3.685605	-2.840326	-1.538634
34	1	0	3.126930	-2.794687	-3.220435
35	1	0	4.547354	-1.828574	-2.736770
36	8	0	-0.394336	1.472219	1.655008
37	6	0	2.816862	0.336258	2.027919
38	6	0	3.558377	1.566726	1.617012
39	1	0	4.042215	1.450090	0.642468
40	1	0	2.887820	2.434838	1.559488
41	1	0	4.345155	1.832773	2.344406
42	8	0	-0.531160	-1.510101	1.874096
43	1	0	0.517048	-3.049184	1.592529
44	1	0	-1.392738	-1.635215	2.335892
45	8	0	0.822681	-3.913096	1.257262
46	1	0	0.412638	-3.875799	-0.441235
47	1	0	1.794580	-3.853352	1.167819
48	8	0	0.150957	-3.676206	-1.374211
49	1	0	-0.729291	-3.261098	-1.253339
50	1	0	1.043988	-2.303169	-1.686752
51	8	0	3.474380	-3.992909	0.435783
52	1	0	4.224659	-3.706483	0.971700
53	1	0	3.666923	-4.913732	0.215883
54	8	0	-3.123407	-2.051058	2.581467
55	1	0	-3.663371	-1.731568	1.839229
56	1	0	-3.226292	-3.011400	2.563024
57	8	0	-1.823402	-1.989328	-0.543806
58	1	0	-2.781688	-1.949319	-0.361822
59	1	0	-1.387656	-1.845147	0.322308
60	1	0	1.636028	4.470943	0.603369
61	8	0	1.979801	4.684806	-0.293376

62	1	0	1.290986	5.225843	-0.698935
63	1	0	0.481054	3.045093	2.041044
64	8	0	0.890185	3.929279	2.118970
65	1	0	1.521652	3.855794	2.845373
66	6	0	2.117916	0.347066	3.349758
67	1	0	1.571614	1.282587	3.514988
68	1	0	1.407099	-0.482074	3.441561
69	1	0	2.836410	0.244780	4.182115
70	6	0	3.123165	-0.987937	1.408607
71	1	0	3.719735	-0.887277	0.496495
72	1	0	3.686021	-1.636773	2.101727
73	1	0	2.207907	-1.540105	1.154196

SCF Done: E(UwB97XD) = -2003.85049656 A.U. after 1 cycles

Zero-point correction= 0.625433 (a.u.)
Thermal correction to Energy= 0.672550
Thermal correction to Enthalpy= 0.673494
Thermal correction to Gibbs Free Energy= 0.544548
Sum of electronic and zero-point Energies= -2003.225064
Sum of electronic and thermal Energies= -2003.177947
Sum of electronic and thermal Enthalpies= -2003.177003
Sum of electronic and thermal Free Energies= -2003.305948

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	422.031	167.384	271.389

Item	Value	Threshold	Converged?
Maximum Force	0.000192	0.000450	YES
RMS Force	0.000023	0.000300	YES
Maximum Displacement	0.007784	0.001800	NO
RMS Displacement	0.001145	0.001200	YES

==========Figure S10, TS2[A] with (H2O)n========

It was examined how the reaction center of TS2[A] is affected by the number (n) of water molecules

----------Precursor of TS2[A]n=6----------

vita-b1.prea.n6.log

Stoichiometry C13H32N4O9S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.269092	-2.807901	-1.124217
2	6	0	3.667029	-3.274807	0.083657
3	6	0	3.337496	-2.063587	0.936117
4	6	0	2.313977	-1.138506	0.346396
5	16	0	2.155511	-0.876412	-1.365589
6	6	0	0.908288	0.221007	-1.117258
7	7	0	0.633449	0.386822	0.161581
8	6	0	-0.459241	1.270347	0.612103
9	6	0	-1.680325	0.481816	1.012122
10	6	0	-2.249573	-0.406135	0.127858
11	7	0	-3.332614	-1.138924	0.398616
12	6	0	-3.873001	-0.973656	1.611478
13	6	0	-5.102458	-1.768738	1.925096
14	7	0	-3.421131	-0.139326	2.536820
15	6	0	-2.341593	0.608884	2.255470
16	7	0	-1.928910	1.440963	3.234393
17	6	0	1.421068	-0.369535	1.024420
18	6	0	1.252209	-0.239310	2.499322
19	1	0	4.376373	-3.536700	-1.739362
20	1	0	4.360038	-3.920637	0.628816
21	1	0	2.761825	-3.844646	-0.147508
22	1	0	2.967965	-2.424042	1.897706
23	1	0	4.250119	-1.494626	1.138434
24	1	0	0.345388	0.734678	-1.892865
25	1	0	1.902559	-0.939930	3.017780
26	1	0	1.521132	0.767529	2.828993
27	1	0	0.223486	-0.440953	2.803460
28	1	0	-0.061530	1.883170	1.418070
29	1	0	-0.694544	1.922722	-0.229297

30	1	0	-1.816694	-0.548421	-0.858938
31	1	0	-1.287558	2.194253	3.060541
32	1	0	-2.521740	1.527451	4.044147
33	1	0	-5.973723	-1.270043	1.489786
34	1	0	-5.035672	-2.765219	1.487603
35	1	0	-5.249182	-1.840996	3.001498
36	8	0	2.988848	2.632006	-0.473894
37	8	0	2.053293	3.201818	0.224717
38	6	0	1.422999	4.285971	-0.496417
39	1	0	2.165053	5.063118	-0.674112
40	1	0	1.024592	3.897382	-1.433025
41	1	0	0.629889	4.639323	0.158404
42	8	0	-1.320146	1.777162	-2.455109
43	1	0	-2.129355	1.298453	-2.729387
44	1	0	-1.220182	2.500516	-3.076608
45	8	0	-3.564364	0.386045	-3.188617
46	1	0	-3.628088	-0.553140	-2.958082
47	1	0	-4.413338	0.727676	-2.865987
48	8	0	-4.553659	-1.943455	-1.903632
49	1	0	-4.684384	-2.881238	-2.053773
50	1	0	-4.128539	-1.839629	-1.016527
51	8	0	-6.105780	0.358456	-1.948375
52	1	0	-5.834834	-0.574966	-1.906695
53	1	0	-6.940080	0.369934	-2.421209
54	1	0	4.219536	1.479659	0.598809
55	8	0	4.939892	1.001342	1.026752
56	1	0	5.331757	0.460417	0.320392
57	1	0	6.142891	-0.265860	-1.820646
58	8	0	6.049941	-0.667565	-0.954315
59	1	0	5.494914	-1.455179	-1.089528

Standard basis: 6-311+G(d,p) (6D, 7F)

SCF Done: E(UwB97XD) = -1808.71015893 A.U. after 2 cycles

Zero-point correction= 0.485708 (a.u.)
Thermal correction to Energy= 0.527321
Thermal correction to Enthalpy= 0.528265
Thermal correction to Gibbs Free Energy= 0.402212
Sum of electronic and zero-point Energies= -1808.224451
Sum of electronic and thermal Energies= -1808.182838
Sum of electronic and thermal Enthalpies= -1808.181894
Sum of electronic and thermal Free Energies= -1808.307947

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	330.899	141.083	265.300

Item	Value	Threshold	Converged?
Maximum Force	0.000110	0.000450	YES
RMS Force	0.000017	0.000300	YES
Maximum Displacement	0.125923	0.001800	NO
RMS Displacement	0.019037	0.001200	NO

-------Figure S10-1, TS2[A]n=6 ---------

vita-b1.ts2a.n6.log

Stoichiometry C13H32N4O9S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.712968	-2.024624	0.515245
2	6	0	-4.965911	-1.379096	-0.728167
3	6	0	-4.689145	0.126113	-0.685875
4	6	0	-3.248210	0.472727	-0.474105
5	16	0	-2.611112	0.656652	1.129506
6	6	0	-0.922074	0.745789	0.474567
7	7	0	-1.042254	0.908954	-0.925695
8	6	0	0.100884	1.362187	-1.731432
9	6	0	1.393548	0.652092	-1.423464
10	6	0	1.563093	-0.672131	-1.751224
11	7	0	2.706291	-1.351873	-1.579489
12	6	0	3.725372	-0.659877	-1.065183
13	6	0	5.020202	-1.383977	-0.849370
14	7	0	3.676404	0.613025	-0.689080

15	6	0	2.523011	1.292069	-0.852744
16	7	0	2.532413	2.572144	-0.455109
17	6	0	-2.285206	0.654749	-1.433113
18	6	0	-2.508511	0.587515	-2.909353
19	1	0	-5.343861	-1.720211	1.172341
20	1	0	-6.003948	-1.546539	-1.028917
21	1	0	-4.314544	-1.866813	-1.454710
22	1	0	-5.037458	0.561241	-1.625680
23	1	0	-5.297961	0.580361	0.101460
24	1	0	-0.445187	-0.646954	0.652649
25	1	0	-3.535525	0.303167	-3.125740
26	1	0	-2.321860	1.555911	-3.379327
27	1	0	-1.853689	-0.153641	-3.373068
28	1	0	-0.158426	1.193747	-2.774051
29	1	0	0.197329	2.440949	-1.600594
30	1	0	0.735463	-1.234199	-2.174806
31	1	0	1.702463	3.153510	-0.403156
32	1	0	3.378724	2.917440	-0.032678
33	1	0	5.051698	-1.786558	0.167850
34	1	0	5.115259	-2.217549	-1.544174
35	1	0	5.860950	-0.700939	-0.965929
36	8	0	-0.123095	1.741950	1.002582
37	8	0	0.566884	1.209547	2.147156
38	6	0	0.614395	2.267360	3.097356
39	1	0	1.167882	3.119072	2.695834
40	1	0	-0.393991	2.559104	3.395283
41	1	0	1.151094	1.841668	3.945614
42	8	0	-0.239236	-1.768489	0.622577
43	1	0	0.607543	-2.050980	1.105349
44	1	0	-1.031950	-2.276938	0.959796
45	8	0	1.935289	-2.550644	1.723827
46	1	0	2.348867	-3.089697	1.020280
47	1	0	2.504423	-1.771138	1.874074
48	8	0	2.802616	-3.927365	-0.515234
49	1	0	2.153487	-4.552875	-0.843765
50	1	0	2.738305	-3.137964	-1.095450
51	8	0	3.115077	-0.082289	2.158608
52	1	0	2.287844	0.412081	2.050270
53	1	0	3.681283	0.250166	1.450799
54	8	0	-2.361241	-3.046528	1.434044
55	1	0	-3.197373	-2.669637	1.092005
56	1	0	-2.391115	-3.985548	1.237539
57	1	0	-0.377889	3.935061	0.479100
58	8	0	0.265566	4.382710	-0.077550
59	1	0	-0.229832	5.015278	-0.602061

SCF Done: E(UwB97XD) = -1808.69405787 A.U. after 2 cycles
NFock= 2 Conv=0.63D-09 -V/T= 2.0039

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-1066.1099	22.3531	26.6414

Zero-point correction= 0.484556 (a.u.)
Thermal correction to Energy= 0.522183
Thermal correction to Enthalpy= 0.523127
Thermal correction to Gibbs Free Energy= 0.414131
Sum of electronic and zero-point Energies= -1808.209502
Sum of electronic and thermal Energies= -1808.171875
Sum of electronic and thermal Enthalpies= -1808.170931
Sum of electronic and thermal Free Energies= -1808.279927

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	327.675	134.361	229.402

Item	Value	Threshold	Converged?
Maximum Force	0.000004	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.001574	0.001800	YES
RMS Displacement	0.000204	0.001200	YES

---------Precursor of TS2[A]n=7 ----------

vita-b1.prea.n7a.log

Stoichiometry C13H34N4O10S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	3.566516	2.704227	0.048106
2	6	0	2.583616	3.018911	-0.926904
3	6	0	2.009330	1.717089	-1.454610
4	6	0	1.328328	0.868327	-0.420364
5	16	0	1.593615	1.053025	1.286017
6	6	0	0.492153	-0.167518	1.621692
7	7	0	-0.027064	-0.696121	0.529693
8	6	0	-1.037906	-1.757838	0.571117
9	6	0	-2.419885	-1.243262	0.264780
10	6	0	-2.778704	0.079988	0.350844
11	7	0	-4.005939	0.533190	0.066496
12	6	0	-4.904846	-0.375275	-0.322555
13	6	0	-6.267765	0.123825	-0.693213
14	7	0	-4.674927	-1.679401	-0.422861
15	6	0	-3.449905	-2.132510	-0.124490
16	7	0	-3.252447	-3.461261	-0.239790
17	6	0	0.435980	-0.131179	-0.655293
18	6	0	-0.029182	-0.643677	-1.974424
19	1	0	3.854800	3.519213	0.501224
20	1	0	3.025206	3.574482	-1.759596
21	1	0	1.794439	3.636573	-0.483002
22	1	0	1.287797	1.947523	-2.241478
23	1	0	2.806461	1.129916	-1.918284
24	1	0	0.232589	-0.500489	2.615209
25	1	0	0.524164	-0.161910	-2.778803
26	1	0	0.153377	-1.718140	-2.055208
27	1	0	-1.097903	-0.466321	-2.115194
28	1	0	-0.734106	-2.518704	-0.150552
29	1	0	-0.990959	-2.212307	1.562324
30	1	0	-2.058003	0.835226	0.650979
31	1	0	-2.442769	-3.921217	0.138175
32	1	0	-4.052936	-4.036736	-0.445920
33	1	0	-6.583999	0.917042	-0.014380
34	1	0	-6.236565	0.543463	-1.703169
35	1	0	-6.990722	-0.690066	-0.679417
36	8	0	2.519496	-2.529198	0.534561
37	8	0	1.706845	-3.531846	0.653175
38	6	0	1.813856	-4.179593	1.943793
39	1	0	2.810709	-4.609779	2.031293
40	1	0	1.628430	-3.439919	2.721667
41	1	0	1.047859	-4.950772	1.935095
42	8	0	4.277825	5.044177	1.272103
43	1	0	4.032545	5.147705	2.194742
44	1	0	5.194307	5.325514	1.216728
45	8	0	-4.661067	3.222916	0.310576
46	1	0	-4.409089	3.664026	-0.502976
47	1	0	-4.402606	2.277501	0.195201
48	8	0	-7.333163	3.333214	1.038894
49	1	0	-6.400173	3.325373	0.752656
50	1	0	-7.842168	3.306757	0.227152
51	1	0	3.074168	-1.819752	-1.284444
52	8	0	3.635553	-1.346114	-1.909368
53	1	0	4.150960	-0.725638	-1.352909
54	1	0	2.881510	-0.757856	-3.432249
55	8	0	2.443153	-0.448246	-4.247239
56	1	0	3.051954	0.183184	-4.633920
57	1	0	3.868638	-1.796132	1.803344
58	8	0	4.540770	-1.172667	2.109294
59	1	0	5.251804	-1.713030	2.461110
60	1	0	4.920562	-0.123369	0.647483
61	8	0	5.008525	0.328881	-0.210036
62	1	0	4.588481	1.198885	-0.096663

SCF Done: E(UwB97XD) = -1885.15843332 A.U. after 1 cycles

Zero-point correction= 0.510404 (a.u.)
Thermal correction to Energy= 0.555551
Thermal correction to Enthalpy= 0.556495
Thermal correction to Gibbs Free Energy= 0.422718
Sum of electronic and zero-point Energies= -1884.648029
Sum of electronic and thermal Energies= -1884.602882
Sum of electronic and thermal Enthalpies= -1884.601938
Sum of electronic and thermal Free Energies= -1884.735715

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	348.614	150.746	281.557

Item	Value	Threshold	Converged?
Maximum Force	0.000008	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.002316	0.001800	NO
RMS Displacement	0.000390	0.001200	YES

--------Figure S10-2, TS2[A]n=7 -----------

vita-b1.ts2a.n7.log

Stoichiometry C13H34N4O10S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.497504	-2.547349	0.442492
2	6	0	-4.789152	-1.901776	-0.792206
3	6	0	-4.612828	-0.382218	-0.724587
4	6	0	-3.199527	0.053960	-0.495815
5	16	0	-2.583093	0.231060	1.115234
6	6	0	-0.901789	0.476920	0.478073
7	7	0	-1.026921	0.652547	-0.921902
8	6	0	0.087533	1.203294	-1.709095
9	6	0	1.426887	0.588273	-1.395162
10	6	0	1.695283	-0.717095	-1.731591
11	7	0	2.881253	-1.316398	-1.549721
12	6	0	3.840208	-0.559787	-1.010974
13	6	0	5.178353	-1.194115	-0.776585
14	7	0	3.697337	0.703691	-0.628870
15	6	0	2.502958	1.304903	-0.810187
16	7	0	2.416530	2.575667	-0.397788
17	6	0	-2.244160	0.326721	-1.443675
18	6	0	-2.455913	0.281176	-2.922280
19	1	0	-5.151070	-2.297333	1.100482
20	1	0	-5.813084	-2.132115	-1.099425
21	1	0	-4.105284	-2.334034	-1.523870
22	1	0	-4.983639	0.045661	-1.659024
23	1	0	-5.254156	0.017299	0.066544
24	1	0	-0.310989	-0.872576	0.643986
25	1	0	-3.458707	-0.070789	-3.152037
26	1	0	-2.335998	1.272050	-3.366246
27	1	0	-1.748019	-0.399928	-3.399619
28	1	0	-0.147568	1.029103	-2.756488
29	1	0	0.097952	2.284463	-1.561581
30	1	0	0.915472	-1.332258	-2.171473
31	1	0	1.597885	3.164605	-0.526693
32	1	0	3.255401	3.000645	-0.037981
33	1	0	5.224734	-1.589941	0.242788
34	1	0	5.338733	-2.021387	-1.466826
35	1	0	5.972260	-0.455907	-0.885484
36	8	0	-0.217277	1.550111	1.025773
37	8	0	0.552707	1.075320	2.146333
38	6	0	0.610286	2.163565	3.059544
39	1	0	1.075300	3.032638	2.589023
40	1	0	-0.386832	2.402086	3.435091
41	1	0	1.238737	1.799392	3.872582
42	8	0	-0.035816	-1.978703	0.598655
43	1	0	0.822377	-2.221910	1.083031
44	1	0	-0.798240	-2.542684	0.915762
45	8	0	2.169909	-2.655754	1.704644
46	1	0	2.622812	-3.149682	0.992010
47	1	0	2.682654	-1.841851	1.873014
48	8	0	3.148258	-3.906122	-0.560581
49	1	0	2.547651	-4.563408	-0.918076
50	1	0	3.035054	-3.102940	-1.114789
51	8	0	3.151162	-0.112278	2.187340
52	1	0	2.295276	0.322087	2.051095
53	1	0	3.719456	0.281146	1.513628
54	8	0	-2.079006	-3.411969	1.361008
55	1	0	-2.938240	-3.091421	1.019516
56	1	0	-2.040442	-4.347766	1.151063
57	1	0	-0.567684	4.411367	-0.299121
58	8	0	0.275213	4.479175	-0.783978
59	1	0	0.090392	4.964569	-1.589886

60	1	0	-1.538659	3.139015	1.186122
61	8	0	-1.902471	3.959464	0.832146
62	1	0	-2.751665	3.718214	0.453694

SCF Done: E(UwB97XD) = -1885.14621865 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-1071.4554	26.1400	29.5950

Zero-point correction= 0.509852 (a.u.)
Thermal correction to Energy= 0.550166
Thermal correction to Enthalpy= 0.551110
Thermal correction to Gibbs Free Energy= 0.436417
Sum of electronic and zero-point Energies= -1884.636366
Sum of electronic and thermal Energies= -1884.596053
Sum of electronic and thermal Enthalpies= -1884.595109
Sum of electronic and thermal Free Energies= -1884.709802

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	345.234	143.709	241.391

Item	Value	Threshold	Converged?
Maximum Force	0.000015	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.002034	0.001800	NO
RMS Displacement	0.000463	0.001200	YES

-------Precursor of TS2[A]n=8 ---------
This is the same as Precursor[A] in Figure S1-1

vita-b105a.rev.high.log

Stoichiometry C13H36N4O11S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.022672	-0.052178	-3.129162
2	6	0	3.342182	-1.304918	-3.191268
3	6	0	2.902680	-1.664528	-1.785380
4	6	0	1.916532	-0.716858	-1.164945
5	16	0	1.683198	0.914332	-1.714941
6	6	0	0.495202	1.172731	-0.557258
7	7	0	0.295433	0.112083	0.201669
8	6	0	-0.725434	0.110227	1.269557
9	6	0	-1.938330	-0.693047	0.879480
10	6	0	-2.671812	-0.319922	-0.224168
11	7	0	-3.761206	-0.962461	-0.650754
12	6	0	-4.137967	-2.029034	0.065219
13	6	0	-5.369275	-2.751824	-0.385995
14	7	0	-3.522580	-2.469228	1.152809
15	6	0	-2.434106	-1.811282	1.588437
16	7	0	-1.857335	-2.303722	2.702669
17	6	0	1.092568	-0.982313	-0.116471
18	6	0	0.997485	-2.247835	0.662900
19	1	0	4.238425	0.247974	-4.014593
20	1	0	4.010179	-2.084058	-3.567210
21	1	0	2.480038	-1.230494	-3.862273
22	1	0	2.454489	-2.659992	-1.814304
23	1	0	3.781010	-1.733906	-1.137667
24	1	0	-0.079628	2.086038	-0.427399
25	1	0	1.801611	-2.924638	0.378799
26	1	0	1.104784	-2.054500	1.732881
27	1	0	0.038207	-2.743374	0.497440
28	1	0	-0.243015	-0.243291	2.177907
29	1	0	-1.005304	1.152945	1.421613
30	1	0	-2.372187	0.546888	-0.807784
31	1	0	-1.164249	-1.795176	3.221634
32	1	0	-2.336741	-3.047271	3.183683
33	1	0	-6.253333	-2.198148	-0.055882
34	1	0	-5.400633	-2.809216	-1.474579
35	1	0	-5.407182	-3.751822	0.042676
36	8	0	2.535817	1.333063	1.960910
37	8	0	1.759807	1.466225	2.990466

38	6	0	1.447051	2.851913	3.270827
39	1	0	2.372203	3.372029	3.516190
40	1	0	0.964688	3.284873	2.395202
41	1	0	0.771770	2.820233	4.121952
42	8	0	-1.731863	3.038392	0.312848
43	1	0	-2.578471	3.045910	-0.179151
44	1	0	-1.644087	3.911135	0.700144
45	8	0	-4.084549	2.984111	-1.096571
46	1	0	-4.208440	2.290402	-1.762386
47	1	0	-4.895706	2.899753	-0.570884
48	8	0	-5.178305	0.668110	-2.317617
49	1	0	-5.388749	0.341856	-3.194213
50	1	0	-4.706918	-0.056530	-1.835857
51	8	0	-6.574012	1.923419	-0.273233
52	1	0	-6.355121	1.391917	-1.058382
53	1	0	-7.423118	2.329095	-0.457968
54	1	0	3.631084	-0.359342	1.657989
55	8	0	4.372452	-0.875593	1.320773
56	1	0	4.726912	-0.343677	0.578744
57	1	0	4.171808	-2.645312	1.095533
58	8	0	4.043305	-3.605003	0.973644
59	1	0	4.812585	-3.899500	0.483399
60	1	0	3.446483	2.716927	0.857574
61	8	0	4.021605	3.061253	0.161133
62	1	0	4.553780	3.741313	0.580309
63	1	0	4.900358	1.595726	-0.503948
64	8	0	5.282509	0.728022	-0.726588
65	1	0	4.934943	0.500788	-1.603333

SCF Done: E(UwB97XD) = -1961.61507041 A.U. after 2 cycles

Zero-point correction= 0.536399 (a.u.)
Thermal correction to Energy= 0.583589
Thermal correction to Enthalpy= 0.584534
Thermal correction to Gibbs Free Energy= 0.447664
Sum of electronic and zero-point Energies= -1961.078672
Sum of electronic and thermal Energies= -1961.031481
Sum of electronic and thermal Enthalpies= -1961.030537
Sum of electronic and thermal Free Energies= -1961.167406

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	366.208	159.589	288.065

Item	Value	Threshold	Converged?
Maximum Force	0.000028	0.000450	YES
RMS Force	0.000005	0.000300	YES
Maximum Displacement	0.009716	0.001800	NO
RMS Displacement	0.002831	0.001200	NO

---------Figure S1-3, TS2[A]n=8 ---------
This is the same as TS2[A] in Figure S1-4

vita-b103a.high.log

Stoichiometry C13H36N4O11S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	5.442566	0.663798	0.691858
2	6	0	4.976031	1.556845	-0.310993
3	6	0	4.272941	0.738572	-1.381610
4	6	0	2.960887	0.147480	-0.958708
5	16	0	2.717030	-0.463680	0.655850
6	6	0	0.945240	-0.643524	0.324060
7	7	0	0.785666	-0.577491	-1.079465
8	6	0	-0.391209	-1.162813	-1.730446
9	6	0	-1.697756	-0.550795	-1.294045
10	6	0	-1.966726	0.771536	-1.552270
11	7	0	-3.121234	1.380489	-1.246661
12	6	0	-4.039573	0.624514	-0.642794
13	6	0	-5.320799	1.291339	-0.243422
14	7	0	-3.890634	-0.657542	-0.327710
15	6	0	-2.733904	-1.273563	-0.651233
16	7	0	-2.635426	-2.563810	-0.298954
17	6	0	1.847660	-0.024369	-1.740710

18	6	0	1.730537	0.329203	-3.188157
19	1	0	5.734521	1.172727	1.450447
20	1	0	5.815082	2.092101	-0.767252
21	1	0	4.286423	2.294491	0.115312
22	1	0	4.112523	1.383118	-2.247237
23	1	0	4.949618	-0.061437	-1.703525
24	1	0	0.502504	0.716015	0.849574
25	1	0	2.590600	0.909846	-3.512238
26	1	0	1.688465	-0.569431	-3.808577
27	1	0	0.833335	0.922702	-3.375166
28	1	0	-0.265133	-1.025837	-2.801859
29	1	0	-0.370462	-2.237602	-1.548569
30	1	0	-1.211137	1.400780	-2.017747
31	1	0	-1.873917	-3.175038	-0.584227
32	1	0	-3.456183	-2.991434	0.098349
33	1	0	-5.181780	1.801326	0.715201
34	1	0	-5.604030	2.042928	-0.980480
35	1	0	-6.118490	0.558905	-0.129006
36	8	0	0.349422	-1.764766	0.850574
37	8	0	-0.375111	-1.392145	2.049302
38	6	0	-0.538804	-2.600419	2.777765
39	1	0	-1.102312	-3.327976	2.189286
40	1	0	0.430926	-3.000351	3.080837
41	1	0	-1.113035	-2.308008	3.657307
42	8	0	0.398597	1.805019	1.092984
43	1	0	-0.542482	2.076545	1.471890
44	1	0	1.114120	2.064103	1.737889
45	8	0	-1.826486	2.528423	1.914037
46	1	0	-2.200157	3.060173	1.175611
47	1	0	-2.381153	1.733754	2.050341
48	8	0	-2.469692	3.934098	-0.343153
49	1	0	-1.575480	3.969908	-0.721707
50	1	0	-2.873691	3.171389	-0.806492
51	8	0	-2.854800	0.036935	2.382563
52	1	0	-2.058779	-0.458995	2.138141
53	1	0	-3.542309	-0.318687	1.806283
54	8	0	2.300533	2.465901	2.785878
55	1	0	3.000521	1.809883	2.849568
56	1	0	2.741606	3.306329	2.635039
57	8	0	0.131166	3.345359	-1.325813
58	1	0	0.848115	3.903897	-1.633113
59	1	0	0.474653	2.869207	-0.557070
60	1	0	0.217886	-4.552489	-0.666103
61	8	0	-0.665581	-4.527631	-1.078217
62	1	0	-0.560043	-4.870796	-1.967408
63	1	0	1.478640	-3.439068	0.729894
64	8	0	1.690284	-4.297622	0.343072
65	1	0	2.535618	-4.178609	-0.096581

SCF Done: E(UwB97XD) = -1961.58827203 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-882.5910	14.7040	22.9021

Zero-point correction= 0.534015 (a.u.)
Thermal correction to Energy= 0.577804
Thermal correction to Enthalpy= 0.578748
Thermal correction to Gibbs Free Energy= 0.454902
Sum of electronic and zero-point Energies= -1961.054257
Sum of electronic and thermal Energies= -1961.010468
Sum of electronic and thermal Enthalpies= -1961.009524
Sum of electronic and thermal Free Energies= -1961.133370

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	362.577	153.550	260.655

Item	Value	Threshold	Converged?
Maximum Force	0.000014	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.008986	0.001800	NO
RMS Displacement	0.001096	0.001200	YES

--------- Precursor of TS2[A] n=10 --------

vita-b1.prea.n10.log

Stoichiometry C13H40N4O13S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.264019	-1.858055	1.682442
2	6	0	-3.678004	-3.085742	1.276849
3	6	0	-2.954112	-2.866040	-0.039152
4	6	0	-1.840287	-1.859911	0.013093
5	16	0	-1.627706	-0.742923	1.323660
6	6	0	-0.276782	-0.081324	0.584483
7	7	0	-0.002202	-0.649577	-0.574504
8	6	0	1.166562	-0.197395	-1.369674
9	6	0	2.450735	-0.842397	-0.922092
10	6	0	3.100064	-0.346533	0.187228
11	7	0	4.218776	-0.870747	0.695055
12	6	0	4.709860	-1.943863	0.065330
13	6	0	5.917919	-2.597292	0.660724
14	7	0	4.200616	-2.473973	-1.038536
15	6	0	3.092490	-1.927628	-1.562592
16	7	0	2.639710	-2.491006	-2.705450
17	6	0	-0.878659	-1.669400	-0.929766
18	6	0	-0.734812	-2.406451	-2.216064
19	1	0	-4.592184	-1.937568	2.597624
20	1	0	-4.445131	-3.852727	1.133193
21	1	0	-2.979921	-3.441989	2.043519
22	1	0	-2.544359	-3.825085	-0.365534
23	1	0	-3.669102	-2.543694	-0.803037
24	1	0	0.298783	0.759911	0.957372
25	1	0	-1.570707	-3.091213	-2.341642
26	1	0	-0.745578	-1.721080	-3.067248
27	1	0	0.190482	-2.985495	-2.238931
28	1	0	0.935720	-0.362835	-2.418873
29	1	0	1.232429	0.878883	-1.211454
30	1	0	2.708397	0.530408	0.696529
31	1	0	2.022223	-1.987351	-3.318553
32	1	0	3.251505	-3.158843	-3.148037
33	1	0	6.489308	-3.119625	-0.105128
34	1	0	6.546305	-1.859514	1.159911
35	1	0	5.598041	-3.329232	1.408502
36	8	0	-1.686348	1.311805	-2.183048
37	8	0	-0.816689	1.881093	-2.957517
38	6	0	-0.379408	3.166576	-2.450052
39	1	0	-1.248602	3.818274	-2.366349
40	1	0	0.110303	3.015729	-1.485598
41	1	0	0.319264	3.535969	-3.196680
42	8	0	1.189462	2.567176	0.523494
43	1	0	2.014136	2.797496	0.991462
44	1	0	0.458322	2.967315	1.027960
45	8	0	3.567734	3.040741	1.857324
46	1	0	3.916630	2.273298	2.337257
47	1	0	4.330815	3.298288	1.317951
48	8	0	5.256334	0.868241	2.530873
49	1	0	5.587925	0.487823	3.346137
50	1	0	4.952281	0.119830	1.958388
51	8	0	6.195581	2.832670	0.800686
52	1	0	6.139997	2.104771	1.444073
53	1	0	6.938021	3.372294	1.078473
54	1	0	-3.044509	-0.180876	-2.690198
55	8	0	-3.863339	-0.680208	-2.609079
56	1	0	-4.231638	-0.394126	-1.752155
57	1	0	-2.558295	2.165151	-0.688076
58	8	0	-3.087034	2.417300	0.083292
59	1	0	-3.624761	3.182328	-0.204877
60	1	0	-4.270334	0.937172	0.099331
61	8	0	-4.838066	0.183250	-0.131798
62	1	0	-4.692640	-0.491379	0.553065
63	8	0	-5.101999	-2.185076	4.268639
64	1	0	-4.791747	-1.550437	4.919136
65	1	0	-6.043505	-2.280862	4.431605
66	8	0	-1.133516	3.299458	1.853255
67	1	0	-1.330403	4.204181	2.103648
68	1	0	-1.871391	3.017191	1.278434
69	8	0	-4.585190	4.572918	-0.725990
70	1	0	-5.538411	4.460751	-0.757350
71	1	0	-4.439346	5.404671	-0.268821

SCF Done: E(UwB97XD) = -2114.51927551 A.U. after 2 cycles

Zero-point correction=   0.587764 (a.u.)
Thermal correction to Energy=   0.640476
Thermal correction to Enthalpy=   0.641420
Thermal correction to Gibbs Free Energy=   0.489407
Sum of electronic and zero-point Energies=   -2113.931512
Sum of electronic and thermal Energies=   -2113.878800
Sum of electronic and thermal Enthalpies=   -2113.877856
Sum of electronic and thermal Free Energies=   -2114.029869

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	401.905	177.016	319.939

Item	Value	Threshold	Converged?
Maximum Force	0.000007	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.011622	0.001800	NO
RMS Displacement	0.002558	0.001200	NO

----------Figure S10-4, TS2[A]n=10 ----------

vita-b1.ts2a.n10.log

Stoichiometry   C13H40N4O13S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	5.235596	-2.697403	0.571228
2	6	0	5.374733	-1.287509	0.442189
3	6	0	4.631254	-0.845989	-0.803052
4	6	0	3.141913	-1.051584	-0.765598
5	16	0	2.351776	-2.009438	0.455489
6	6	0	0.739731	-1.399860	-0.099803
7	7	0	0.941433	-0.837853	-1.383970
8	6	0	-0.164274	-0.693167	-2.333961
9	6	0	-1.399042	-0.052972	-1.754965
10	6	0	-1.410845	1.292035	-1.479782
11	7	0	-2.481265	1.955995	-1.019711
12	6	0	-3.593870	1.244537	-0.864473
13	6	0	-4.810504	1.943670	-0.345109
14	7	0	-3.703049	-0.061143	-1.117714
15	6	0	-2.619206	-0.734059	-1.532513
16	7	0	-2.769448	-2.058440	-1.762360
17	6	0	2.246123	-0.541489	-1.667226
18	6	0	2.603697	0.281427	-2.861777
19	1	0	5.568369	-2.962978	1.430501
20	1	0	6.429276	-1.011240	0.339123
21	1	0	4.974729	-0.772139	1.320828
22	1	0	4.838885	0.217337	-0.948611
23	1	0	5.046371	-1.376558	-1.667436
24	1	0	0.591532	-0.189155	0.800200
25	1	0	3.671069	0.491733	-2.868148
26	1	0	2.364777	-0.244073	-3.789531
27	1	0	2.068791	1.234374	-2.853135
28	1	0	0.196501	-0.075406	-3.153353
29	1	0	-0.384438	-1.673245	-2.761810
30	1	0	-0.508757	1.883831	-1.618428
31	1	0	-1.952186	-2.646537	-1.724346
32	1	0	-3.616863	-2.483824	-1.421454
33	1	0	-5.048824	1.561639	0.651059
34	1	0	-4.636937	3.016468	-0.285399
35	1	0	-5.669291	1.744714	-0.988729
36	8	0	-0.275472	-2.323646	-0.089185
37	8	0	-1.148795	-2.034176	1.030208
38	6	0	-1.508484	-3.290473	1.582949
39	1	0	-2.036451	-3.902252	0.847688
40	1	0	-0.627890	-3.811885	1.963206
41	1	0	-2.181079	-3.038212	2.403919
42	8	0	0.728031	0.789370	1.335015
43	1	0	-0.116037	1.192779	1.789776
44	1	0	1.503345	0.737935	1.978648
45	8	0	-1.255961	1.907587	2.359347
46	1	0	-1.389353	2.700220	1.796707
47	1	0	-2.040128	1.325297	2.266350
48	8	0	-1.314731	3.978464	0.544107

49	1	0	-0.412096	3.868659	0.198952
50	1	0	-1.867368	3.475598	-0.086922
51	8	0	-3.006627	-0.092156	2.108969
52	1	0	-2.591648	-0.688117	1.475189
53	1	0	-3.966500	-0.275334	2.090713
54	8	0	2.789741	0.785113	2.873337
55	1	0	3.090502	-0.068520	3.193334
56	1	0	3.533999	1.174684	2.362532
57	8	0	1.150491	3.007959	-0.453628
58	1	0	2.072525	3.279410	-0.582054
59	1	0	1.188514	2.224540	0.111855
60	8	0	4.739682	1.876178	1.355630
61	1	0	4.468225	2.475424	0.638646
62	1	0	5.492160	2.294300	1.779061
63	8	0	3.917923	3.552425	-0.746721
64	1	0	4.261837	3.269512	-1.598961
65	1	0	4.189481	4.469982	-0.650769
66	8	0	-5.688424	-0.689751	2.131293
67	1	0	-6.020256	-0.855332	1.225156
68	1	0	-6.298831	-0.067081	2.530907
69	8	0	-6.277429	-1.040401	-0.504165
70	1	0	-5.390093	-0.781817	-0.836061
71	1	0	-6.477529	-1.897540	-0.885506

SCF Done: E(UwB97XD) = -2114.50340693 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

	1	2	3
	A	A	A
Frequencies --	-932.9930	25.5539	29.1728

Zero-point correction= 0.586855 (a.u.)
Thermal correction to Energy= 0.634453
Thermal correction to Enthalpy= 0.635398
Thermal correction to Gibbs Free Energy= 0.505288
Sum of electronic and zero-point Energies= -2113.916552
Sum of electronic and thermal Energies= -2113.868954
Sum of electronic and thermal Enthalpies= -2113.868009
Sum of electronic and thermal Free Energies= -2113.998119

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	398.125	169.263	273.838

Item	Value	Threshold	Converged?
Maximum Force	0.000012	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.001796	0.001800	YES
RMS Displacement	0.000269	0.001200	YES

--------Precursor of TS2[A]n=12 ------
This is the same as Precursor for TS2[A]ext in Figure 1

vita-b105ax.rev.high.log

Stoichiometry C13H44N4O15S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.063931	-1.245126	2.558676
2	6	0	-3.403848	-2.501789	2.549417
3	6	0	-2.733074	-2.688120	1.200448
4	6	0	-1.691408	-1.659769	0.864643
5	16	0	-1.514978	-0.166827	1.729712
6	6	0	-0.239973	0.292578	0.744155
7	7	0	0.034685	-0.605415	-0.183379
8	6	0	1.141379	-0.366982	-1.143782
9	6	0	2.488591	-0.714255	-0.569050
10	6	0	3.127683	0.193825	0.243934
11	7	0	4.301483	-0.032301	0.845914
12	6	0	4.861197	-1.222541	0.623463
13	6	0	6.137162	-1.540206	1.337529
14	7	0	4.360803	-2.152773	-0.181439
15	6	0	3.193633	-1.919026	-0.809211
16	7	0	2.760405	-2.886383	-1.640118
17	6	0	-0.780022	-1.732378	-0.142425

18	6	0	-0.636230	-2.839582	-1.128463
19	1	0	-4.363378	-1.037245	3.463664
20	1	0	-4.118527	-3.316013	2.702903
21	1	0	-2.661664	-2.543942	3.355247
22	1	0	-2.266480	-3.676148	1.186780
23	1	0	-3.489851	-2.678175	0.409501
24	1	0	0.285568	1.241729	0.795221
25	1	0	-1.448292	-3.551672	-0.998357
26	1	0	-0.694199	-2.467282	-2.154139
27	1	0	0.308637	-3.369411	-0.992076
28	1	0	0.905722	-0.901443	-2.060489
29	1	0	1.113068	0.698103	-1.370844
30	1	0	2.679291	1.167924	0.422474
31	1	0	2.054799	-2.698434	-2.330131
32	1	0	3.388125	-3.662227	-1.821326
33	1	0	6.770622	-2.182613	0.726466
34	1	0	6.671269	-0.626291	1.595197
35	1	0	5.906025	-2.074488	2.263783
36	8	0	-1.847051	0.831725	-2.184103
37	8	0	-1.029312	1.156827	-3.135191
38	6	0	-0.644007	2.553457	-3.080758
39	1	0	-1.543781	3.162444	-3.162959
40	1	0	-0.114327	2.733118	-2.142432
41	1	0	0.007233	2.694057	-3.939984
42	8	0	0.983480	2.908675	-0.136531
43	1	0	1.801876	3.354844	0.152959
44	1	0	0.242076	3.389910	0.273810
45	8	0	3.360488	4.010058	0.744092
46	1	0	3.809075	3.465409	1.409988
47	1	0	4.060129	4.128835	0.083924
48	8	0	5.273705	2.291354	1.922147
49	1	0	5.686940	2.220404	2.784440
50	1	0	4.999801	1.380086	1.650656
51	8	0	5.922990	3.638255	-0.424388
52	1	0	5.974735	3.158428	0.420407
53	1	0	6.634636	4.280720	-0.405399
54	1	0	-3.000535	-0.826693	-2.143002
55	8	0	-3.733992	-1.383055	-1.856635
56	1	0	-4.149664	-0.887392	-1.120849
57	1	0	-4.780294	-2.086158	-3.115163
58	8	0	-5.350042	-2.477706	-3.804475
59	1	0	-5.268270	-3.424984	-3.684251
60	1	0	-2.764128	2.028652	-0.976756
61	8	0	-3.294274	2.426199	-0.270622
62	1	0	-3.910806	3.040998	-0.717006
63	1	0	-4.318940	0.913765	0.201882
64	8	0	-4.804103	0.071308	0.220901
65	1	0	-4.605506	-0.342237	1.078784
66	8	0	-4.818827	-0.742293	5.140398
67	1	0	-4.475947	0.055599	5.550263
68	1	0	-5.754945	-0.759327	5.353815
69	8	0	-1.328384	3.869889	1.067249
70	1	0	-1.564524	4.799456	1.054801
71	1	0	-2.073485	3.401990	0.642920
72	8	0	-5.021108	4.151143	-1.530608
73	1	0	-5.950633	3.910157	-1.535994
74	1	0	-4.996730	5.075099	-1.270317
75	1	0	5.143452	-3.809270	-0.734355
76	8	0	5.221925	-4.601526	-1.299177
77	1	0	5.210847	-5.350032	-0.699564

SCF Done: E(UwB97XD) = -2267.42146141 A.U. after 2 cycles

Zero-point correction= 0.637427 (a.u.)
Thermal correction to Energy= 0.696462
Thermal correction to Enthalpy= 0.697406
Thermal correction to Gibbs Free Energy= 0.529422
Sum of electronic and zero-point Energies= -2266.784035
Sum of electronic and thermal Energies= -2266.724999
Sum of electronic and thermal Enthalpies= -2266.724055
Sum of electronic and thermal Free Energies= -2266.892040

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	437.036	195.853	353.553

Item	Value	Threshold	Converged?
Maximum Force	0.000010	0.000450	YES
RMS Force	0.000002	0.000300	YES

Maximum Displacement 0.008900 0.001800 NO
RMS Displacement 0.001284 0.001200 NO

-------Figure S1-5, TS2[A]n=8 ---------
This is the sama as TS2[A] in Figure 1.

vita-b103ax.high.log

Stoichiometry C13H44N4O15S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-5.210978	2.298185	1.177653
2	6	0	-5.375116	0.953070	0.745058
3	6	0	-4.592279	0.764838	-0.539312
4	6	0	-3.104160	0.938263	-0.414135
5	16	0	-2.339067	1.511570	1.039509
6	6	0	-0.713943	1.061286	0.370931
7	7	0	-0.893084	0.882038	-1.025043
8	6	0	0.230784	1.042837	-1.952849
9	6	0	1.424738	0.196176	-1.597003
10	6	0	1.326807	-1.170513	-1.625684
11	7	0	2.336994	-2.007481	-1.339770
12	6	0	3.495430	-1.438683	-1.019066
13	6	0	4.637105	-2.333977	-0.649864
14	7	0	3.715840	-0.124601	-0.986322
15	6	0	2.702613	0.717872	-1.268049
16	7	0	2.973305	2.028725	-1.215942
17	6	0	-2.188964	0.683630	-1.403298
18	6	0	-2.523620	0.215157	-2.781957
19	1	0	-5.587866	2.387677	2.054908
20	1	0	-6.429977	0.735354	0.548282
21	1	0	-5.022357	0.251684	1.507622
22	1	0	-4.803002	-0.243118	-0.906810
23	1	0	-4.971444	1.467097	-1.289978
24	1	0	-0.612955	-0.350010	0.914789
25	1	0	-3.581431	-0.030518	-2.849286
26	1	0	-2.314959	0.989052	-3.524767
27	1	0	-1.949188	-0.678641	-3.037048
28	1	0	-0.128381	0.767302	-2.942210
29	1	0	0.482079	2.103816	-1.990045
30	1	0	0.379436	-1.641733	-1.879171
31	1	0	2.313199	2.757672	-1.476064
32	1	0	3.917347	2.309722	-1.011541
33	1	0	4.840785	-2.235068	0.419768
34	1	0	4.393469	-3.371785	-0.870424
35	1	0	5.541754	-2.045057	-1.187253
36	8	0	0.291775	1.956113	0.643518
37	8	0	1.187132	1.376151	1.626842
38	6	0	1.904014	2.471783	2.172414
39	1	0	2.465001	2.989656	1.391085
40	1	0	1.229361	3.154117	2.694523
41	1	0	2.592864	2.013770	2.883250
42	8	0	-0.812991	-1.428416	1.161849
43	1	0	-0.006162	-2.000889	1.486405
44	1	0	-1.597437	-1.520947	1.789343
45	8	0	1.071498	-2.914267	1.845482
46	1	0	1.174912	-3.515997	1.077035
47	1	0	1.876652	-2.358217	1.913686
48	8	0	1.066840	-4.347835	-0.500703
49	1	0	0.175166	-4.102000	-0.800222
50	1	0	1.645233	-3.680631	-0.926707
51	8	0	2.853133	-0.954378	2.138588
52	1	0	2.456768	-0.207566	1.675880
53	1	0	3.812939	-0.779862	2.202608
54	8	0	-2.893280	-1.790875	2.629822
55	1	0	-3.179632	-1.063000	3.186208
56	1	0	-3.645178	-2.004541	2.033920
57	8	0	-1.337365	-3.003248	-1.189087
58	1	0	-2.264399	-3.213510	-1.381185
59	1	0	-1.357093	-2.427505	-0.412584
60	1	0	0.672948	4.573144	-1.236626
61	8	0	1.331858	4.297625	-1.901011
62	1	0	0.985692	4.561694	-2.755291
63	8	0	-0.346943	4.752463	0.237299
64	1	0	-0.241673	3.875784	0.628708
65	1	0	-1.293972	4.876581	0.138627

66	8	0	-4.873867	-2.362527	0.880409
67	1	0	-4.627261	-2.768663	0.031383
68	1	0	-5.650989	-2.835793	1.184598
69	8	0	-4.106192	-3.453073	-1.596835
70	1	0	-4.467950	-2.978028	-2.350646
71	1	0	-4.362943	-4.371266	-1.722724
72	8	0	5.533427	-0.435135	2.412482
73	1	0	5.917175	-0.083292	1.582668
74	1	0	6.099352	-1.161308	2.681691
75	8	0	6.286553	0.487969	-0.033440
76	1	0	5.406915	0.376479	-0.459647
77	1	0	6.545650	1.402009	-0.165426

SCF Done: E(UwB97XD) = -2267.40686894 A.U. after 2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman

1	2	3
A	A	A
Frequencies -- -951.7953	19.7083	24.7631

Zero-point correction= 0.635731 (a.u.)
Thermal correction to Energy= 0.689958
Thermal correction to Enthalpy= 0.690902
Thermal correction to Gibbs Free Energy= 0.544550
Sum of electronic and zero-point Energies= -2266.771138
Sum of electronic and thermal Energies= -2266.716911
Sum of electronic and thermal Enthalpies= -2266.715967
Sum of electronic and thermal Free Energies= -2266.862319

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	432.955	189.159	308.024

Item	Value	Threshold	Converged?
Maximum Force	0.000024	0.000450	YES
RMS Force	0.000003	0.000300	YES
Maximum Displacement	0.001015	0.001800	YES
RMS Displacement	0.000213	0.001200	YES

----------Precursor of TS2[A]n=15 ------------

vita-b1.prea.n15.log

Stoichiometry C13H50N4O18S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-3.639923	-2.399718	1.447280
2	6	0	-2.896610	-3.518475	0.990841
3	6	0	-2.120551	-3.117832	-0.251215
4	6	0	-1.122789	-2.012836	-0.048993
5	16	0	-1.081543	-1.012313	1.368516
6	6	0	0.211596	-0.138667	0.756978
7	7	0	0.591050	-0.563177	-0.433890
8	6	0	1.740322	0.071555	-1.123421
9	6	0	3.055172	-0.548315	-0.729353
10	6	0	3.598949	-0.241161	0.496906
11	7	0	4.739162	-0.759700	0.966179
12	6	0	5.366749	-1.626102	0.168343
13	6	0	6.608827	-2.279217	0.687464
14	7	0	4.960489	-1.959258	-1.050737
15	6	0	3.824521	-1.422114	-1.535393
16	7	0	3.488584	-1.776591	-2.789457
17	6	0	-0.151211	-1.633531	-0.921579
18	6	0	0.127812	-2.225093	-2.259546
19	1	0	-4.060932	-2.609264	2.307884
20	1	0	-3.562732	-4.348184	0.735424
21	1	0	-2.211758	-3.861898	1.775297
22	1	0	-1.594014	-4.000512	-0.622481
23	1	0	-2.822524	-2.811123	-1.033625
24	1	0	0.681358	0.719975	1.232847
25	1	0	-0.592971	-3.011917	-2.471443
26	1	0	0.033726	-1.475941	-3.049656
27	1	0	1.128718	-2.659121	-2.300470
28	1	0	1.544480	0.041742	-2.192324
29	1	0	1.730499	1.116543	-0.814056

30	1	0	3.098207	0.472206	1.146412
31	1	0	2.792976	-1.271599	-3.308915
32	1	0	4.153237	-2.332439	-3.316383
33	1	0	7.297176	-2.501487	-0.127315
34	1	0	7.096756	-1.643200	1.425395
35	1	0	6.341518	-3.222286	1.173314
36	8	0	-1.108848	1.517464	-1.908108
37	8	0	-0.339059	2.317966	-2.575298
38	6	0	0.011469	3.504881	-1.820270
39	1	0	-0.899245	4.039818	-1.552842
40	1	0	0.568172	3.201162	-0.932031
41	1	0	0.630607	4.089784	-2.495964
42	8	0	1.568225	2.506839	1.137551
43	1	0	2.305729	2.695352	1.747271
44	1	0	0.792537	3.012192	1.450807
45	8	0	3.725152	2.824042	2.848919
46	1	0	4.074611	1.981111	3.177951
47	1	0	4.520888	3.234175	2.477698
48	8	0	5.478915	0.624516	3.209996
49	1	0	5.748790	0.098621	3.965002
50	1	0	5.288777	-0.002094	2.468351
51	8	0	6.463608	2.974736	2.095173
52	1	0	6.381987	2.112448	2.538669
53	1	0	7.135015	3.456648	2.581574
54	1	0	-2.259801	0.039239	-2.655172
55	8	0	-3.017427	-0.558447	-2.660394
56	1	0	-3.374816	-0.508977	-1.752128
57	1	0	-4.356142	0.120019	-3.626704
58	8	0	-5.155059	0.574660	-3.963928
59	1	0	-5.627914	-0.076225	-4.486096
60	1	0	-2.091992	1.993165	-0.325154
61	8	0	-2.683892	2.100818	0.433626
62	1	0	-3.398981	2.695940	0.115414
63	1	0	-3.622752	0.499181	0.257756
64	8	0	-4.139612	-0.228021	-0.135796
65	1	0	-4.067063	-0.994060	0.465321
66	8	0	-4.766379	-3.068594	3.801627
67	1	0	-4.563676	-2.522418	4.563712
68	1	0	-5.737433	-3.168846	3.790818
69	8	0	-0.814998	3.734924	1.798476
70	1	0	-0.932959	4.543353	1.271473
71	1	0	-1.498411	3.130033	1.461846
72	8	0	-4.764833	3.515778	-0.598981
73	1	0	-5.333971	2.786243	-0.931144
74	1	0	-5.320705	4.053520	-0.031744
75	1	0	5.847828	-3.036561	-2.361739
76	8	0	5.993093	-3.384770	-3.262003
77	1	0	5.985943	-4.339950	-3.175870
78	8	0	-1.212996	5.945725	0.105795
79	1	0	-2.024797	6.445738	0.219481
80	1	0	-0.519355	6.603587	0.015841
81	8	0	-7.508357	-3.360726	3.726862
82	1	0	-7.960908	-2.951881	2.985148
83	1	0	-7.855785	-4.254467	3.777642
84	8	0	-6.090726	1.290807	-1.434918
85	1	0	-5.888286	1.086568	-2.366852
86	1	0	-5.570500	0.641622	-0.930761

SCF Done: E(UwB97XD) = -2496.78600090 A.U. after 2 cycles

Zero-point correction= 0.715761 (a.u.)
Thermal correction to Energy= 0.781722
Thermal correction to Enthalpy= 0.782666
Thermal correction to Gibbs Free Energy= 0.599783
Sum of electronic and zero-point Energies= -2496.070240
Sum of electronic and thermal Energies= -2496.004279
Sum of electronic and thermal Enthalpies= -2496.003335
Sum of electronic and thermal Free Energies= -2496.186218

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	490.538	220.738	384.909

Item	Value	Threshold	Converged?
Maximum Force	0.000008	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.007366	0.001800	NO
RMS Displacement	0.000810	0.001200	YES

-------Figure S10-6, TS2[A]n=15 ---------

vita-b1.ts2a.n15.log

Stoichiometry C13H50N4O18S(1+,2)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-5.482854	0.494028	-1.495804
2	6	0	-5.810119	0.027339	-0.201138
3	6	0	-5.181171	-1.345407	0.039577
4	6	0	-3.683972	-1.320523	0.045574
5	16	0	-2.768063	-1.805975	-1.336412
6	6	0	-1.201806	-1.341350	-0.548353
7	7	0	-1.537675	-0.933853	0.770856
8	6	0	-0.553848	-0.400022	1.736935
9	6	0	0.885609	-0.426742	1.319947
10	6	0	1.503571	0.730361	0.924321
11	7	0	2.818817	0.829491	0.652625
12	6	0	3.523128	-0.300705	0.727281
13	6	0	4.964526	-0.251980	0.330024
14	7	0	3.038096	-1.472664	1.127789
15	6	0	1.742748	-1.549949	1.494499
16	7	0	1.329139	-2.696822	2.033660
17	6	0	-2.867407	-0.885770	1.060344
18	6	0	-3.332362	-0.379329	2.384542
19	1	0	-5.224488	1.422698	-1.425688
20	1	0	-6.897398	-0.066191	-0.097538
21	1	0	-5.462455	0.732882	0.561435
22	1	0	-5.542966	-1.735350	0.995802
23	1	0	-5.535272	-2.034863	-0.730723
24	1	0	-0.790945	-0.098994	-1.375641
25	1	0	-4.413047	-0.470351	2.469063
26	1	0	-2.873183	-0.955865	3.190419
27	1	0	-3.069771	0.673137	2.518079
28	1	0	-0.823573	0.641138	1.928198
29	1	0	-0.689881	-0.959589	2.664557
30	1	0	0.928584	1.649315	0.848552
31	1	0	0.368322	-2.858817	2.332790
32	1	0	2.001801	-3.432018	2.176798
33	1	0	5.070669	-0.689514	-0.666473
34	1	0	5.318022	0.777529	0.294444
35	1	0	5.575558	-0.832516	1.021703
36	8	0	-0.297982	-2.400641	-0.470690
37	8	0	0.630944	-2.312911	-1.568157
38	6	0	1.184690	-3.615051	-1.695723
39	1	0	1.667404	-3.917508	-0.763475
40	1	0	0.416703	-4.333277	-1.990872
41	1	0	1.932877	-3.519041	-2.483423
42	8	0	-0.746784	0.842873	-1.954659
43	1	0	0.185567	1.151304	-2.250124
44	1	0	-1.209136	1.561364	-1.435429
45	8	0	1.515804	1.599688	-2.812855
46	1	0	2.000436	2.255292	-2.266181
47	1	0	2.095454	0.811357	-2.803534
48	8	0	3.162563	2.995031	-1.192788
49	1	0	3.073089	3.805424	-0.655253
50	1	0	3.191159	2.269998	-0.540448
51	8	0	2.816370	-0.694384	-2.321803
52	1	0	2.109445	-1.140450	-1.837762
53	1	0	3.502371	-1.372045	-2.471664
54	8	0	-1.939469	2.721201	-0.606560
55	1	0	-2.904573	2.832814	-0.689969
56	1	0	-1.704463	2.787549	0.344247
57	8	0	3.041524	5.049427	0.673640
58	1	0	2.112749	5.236042	0.891410
59	1	0	3.361034	4.455098	1.374836
60	1	0	-1.705342	-3.804902	2.165786
61	8	0	-1.394918	-3.242344	2.899985
62	1	0	-1.486917	-3.766423	3.697977
63	8	0	-1.838499	-4.631916	0.571615
64	1	0	-1.259258	-4.095918	0.013463
65	1	0	-2.690388	-4.626110	0.127942
66	8	0	-0.913715	3.086303	1.875860
67	1	0	-0.463879	3.944231	1.741501
68	1	0	-1.447068	3.188349	2.667234
69	8	0	0.290530	5.437941	1.056142

```
   70        1          0      -0.012601    6.271761    1.423136
   71        1          0      -0.022050    5.409241    0.123728
   72        8          0       4.591127   -2.781361   -2.504576
   73        1          0       4.657262   -3.136647   -1.593944
   74        1          0       5.492203   -2.662851   -2.811166
   75        8          0       4.618253   -3.584813    0.105518
   76        1          0       4.057749   -2.933277    0.578686
   77        1          0       4.284346   -4.452818    0.340602
   78        8          0       3.969863    2.979248    2.287293
   79        1          0       3.671779    2.819221    3.185334
   80        1          0       3.624592    2.236313    1.763273
   81        8          0      -0.599424    5.005763   -1.459096
   82        1          0       0.071159    4.795435   -2.112796
   83        1          0      -1.096451    4.180234   -1.307889
   84        8          0      -4.653050    3.164715   -1.019987
   85        1          0      -5.126615    3.571793   -0.288640
   86        1          0      -4.772029    3.760344   -1.765876
---------------------------------------------------------------------

SCF Done:  E(UwB97XD) =  -2496.77422246  A.U. after  2 cycles

Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman
                 1                  2                  3
                 A                  A                  A
Frequencies --   -734.7276            24.6861             24.9055

Zero-point correction=                          0.715378 (a.u.)
Thermal correction to Energy=                    0.776250
Thermal correction to Enthalpy=                  0.777194
Thermal correction to Gibbs Free Energy=         0.617152
Sum of electronic and zero-point Energies=         -2496.058845
Sum of electronic and thermal Energies=            -2495.997972
Sum of electronic and thermal Enthalpies=          -2495.997028
Sum of electronic and thermal Free Energies=       -2496.157070

                E (Thermal)           CV              S
                 KCal/Mol       Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total               487.104          214.022          336.837

       Item             Value     Threshold  Converged?
Maximum Force           0.000004    0.000450     YES
RMS     Force           0.000001    0.000300     YES
Maximum Displacement    0.001450    0.001800     YES
RMS     Displacement    0.000314    0.001200     YES
```