Supplemental Information: Mechanistic Examination of Aerobic Pt Oxidation: Insertion of Molecular Oxygen into Pt-H Bonds Through a Radical Chain Mechanism

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Radical Initiation with •In instead of •OOIn

The reaction was found to proceed through H• abstraction to form a five-coordinate Pt^{III} radical species **2** and the corresponding $HC(CH_3)_2CN$ (HIn, Figure S1). Population analysis of the doublet species **2** demonstrates a spin density of 0.76 electrons on the Pt and an additional 0.19 electrons located on the axial N ligand (formerly trans to H) consistent with doublet Pt^{III}. The barrier for this process was calculated to be $\Delta G^{\ddagger}$ = 17.29 kcal/mol and the overall thermodynamics correspond with ΔG = –6.50 kcal/mol. The reaction was found to be downhill an additional 12.17 kcal/mol (ΔG = –18.67 kcal/mol) through the reaction of **2** with triplet O_2, designated as •OO•, in a radical propagation step that results in the formation of Pt^{IV} superoxo **3**. Population analysis of the doublet species **3** demonstrates a spin density of 0.38 and 0.64 electrons of the α- and β-O atoms respectively and indicates that this is indeed a Pt^{IV} superoxo species.

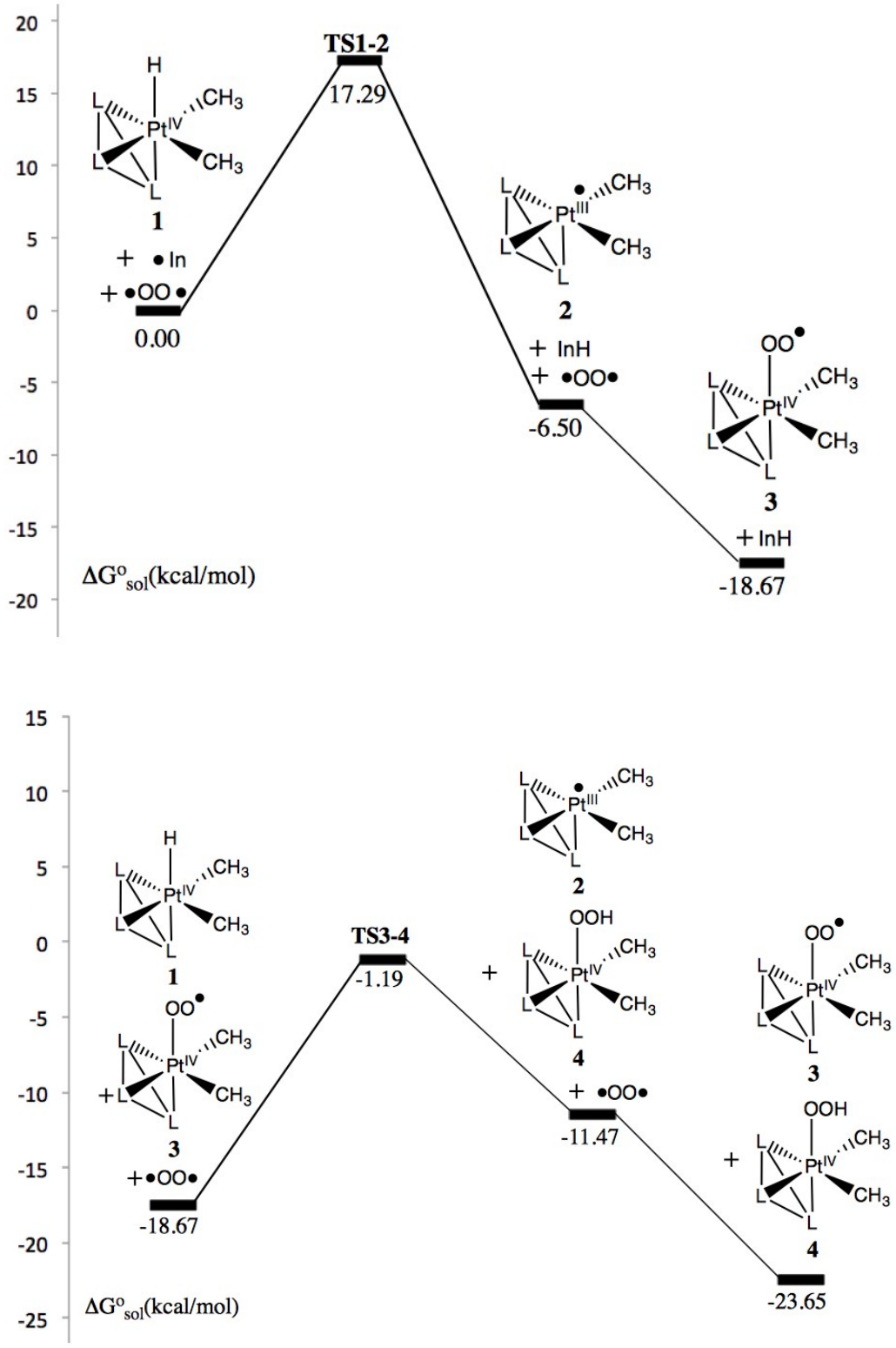

Figure S1. Potential Energy Surfaces of the reaction of **1** with the radical initiator $\bullet C(CH_3)_2CN$ (•In) and O_2 (•OO•).

The transition state for this reaction, **TS1-2**, is illustrated in Figure S2. As can be seen in this optimized transition state the Pt-H-C bond angle is deviated slightly from the ideal linear H• transfer geometry with a bond angle of 171.9° due to steric interaction between •In and the four nearby methyl groups (two on Pt and two on the Tp^{Me_2} ligand). In addition the geometry around the central C of •In has begun to shift from trigonal planar to tetrahedral with the three resulting C-C-C angles adding up to ~346.5° (with 360° corresponding to planar and 328.5°corresponding to an idealized tetrahedron). The Pt-H bond has stretched from 1.54 Å to 1.66 Å. Spin density examination shows 0.27 electrons on Pt and 0.58 electrons on the central carbon of •In (down from 0.80 electrons in free •In) demonstrating a relocation of the radical character from •In to Pt (spin density on the H atom is -0.08 electrons). Examination of the transition state's only imaginary vibrational frequency shows molecular motion involving only the H atom and the central C atom of •In in accordance with the expected molecular rearrangements.

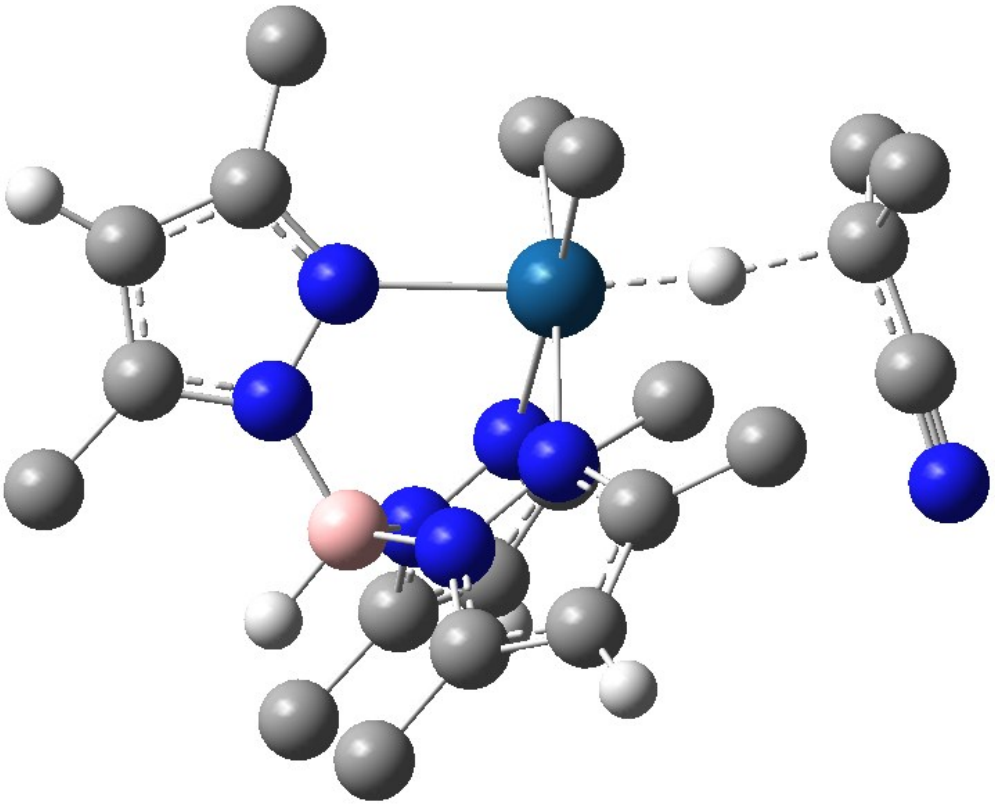

Figure S2. Optimized transition state **TS1-2** for the hydrogen atom abstraction radical propagation step between **1** and •C$(CH_3)_2$CN (•In). For ease of illustration the hydrogen atoms on the methyl groups have been hidden in this representation.

Similar to reactions between •OOIn and **1**, autoacceleration was also examined for reaction with •In only. The reaction of **4** was found to proceed through H• abstraction by •In to reform the Pt^{IV} superoxo radical species **3** and the corresponding HIn (Figure S3). The barrier for this process was calculated to be $\Delta G^{‡}$ = 14.52 kcal/mol which is 2.77 kcal/mol lower than the barrier for initiation between 1 and •In. From 3 the reaction can proceed by the previously discussed mechanism through TS3-4 to form products and propagate the radical reaction through regeneration of species **2**.

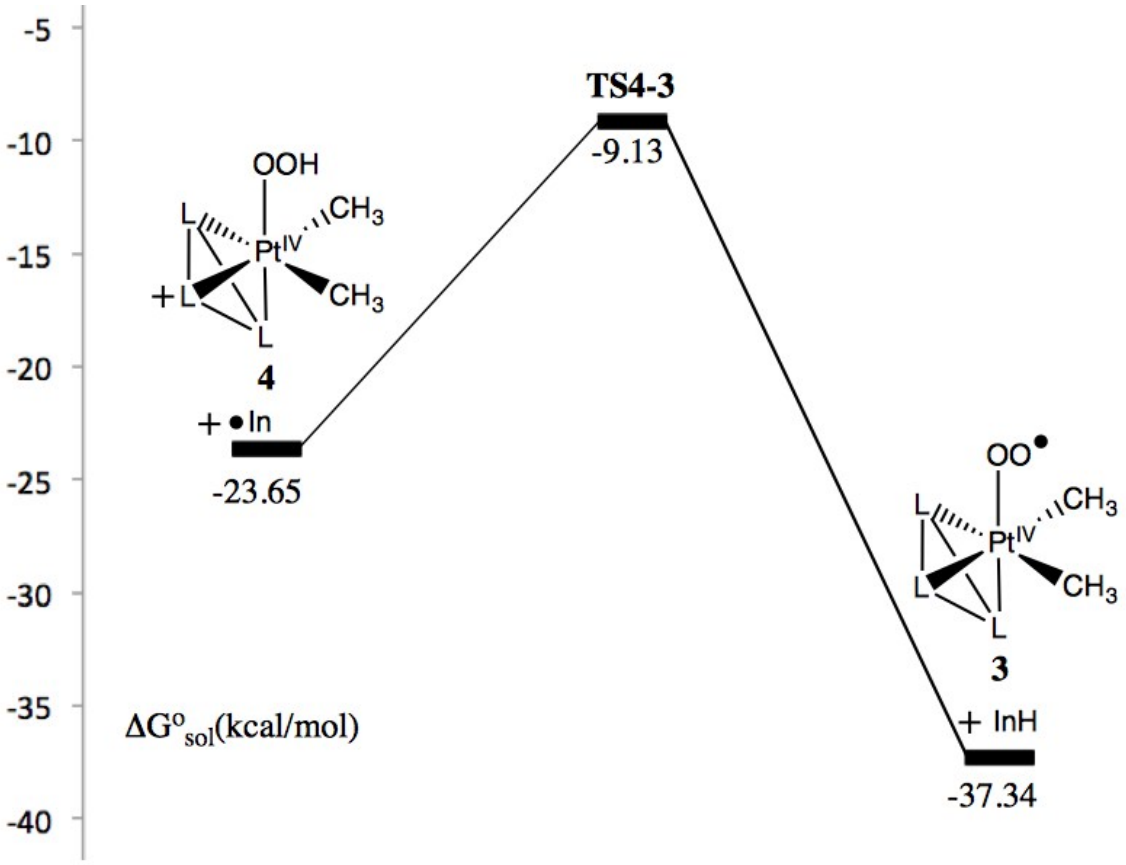

Figure S3. Potential Energy Surface of the reaction of **3** with O_2 (•OO•) and the radical initiator •C$(CH_3)_2$CN (•In).

The transition state for this step, **TS4-3**, is illustrated in Figure S4. Overall this radical H• abstraction transition state is also similar to **TS1-2** above. The O-H-C bond angle is deviated from linear with a bond angle of 164.2°. In addition the Pt-O-O-H dihedral is 85.4° (with a Pt-O-O-C dihedral angle of 93.3°). The O-H bond has stretched from 0.97 Å to 1.12 Å. Spin density examination shows 0.17 and 0.29 electrons on the α- and β-O atoms bound to Pt and a decrease in spin density on the central C atom of •In to 0.47 electrons (down from 0.80 electrons in free •In) demonstrating a relocation of the radical character from •In to PtOO• (spin density on the H atom is -0.05 electrons). In addition the geometry around the central C of

•In has begun to shift from trigonal planar to tetrahedral with the three resulting C-C-C angles adding up to ~348.2°. Examination of the transition states only imaginary vibrational frequency shows molecular motion involving only the H atom and the central C atom of •In as expected with the observed molecular rearrangement.

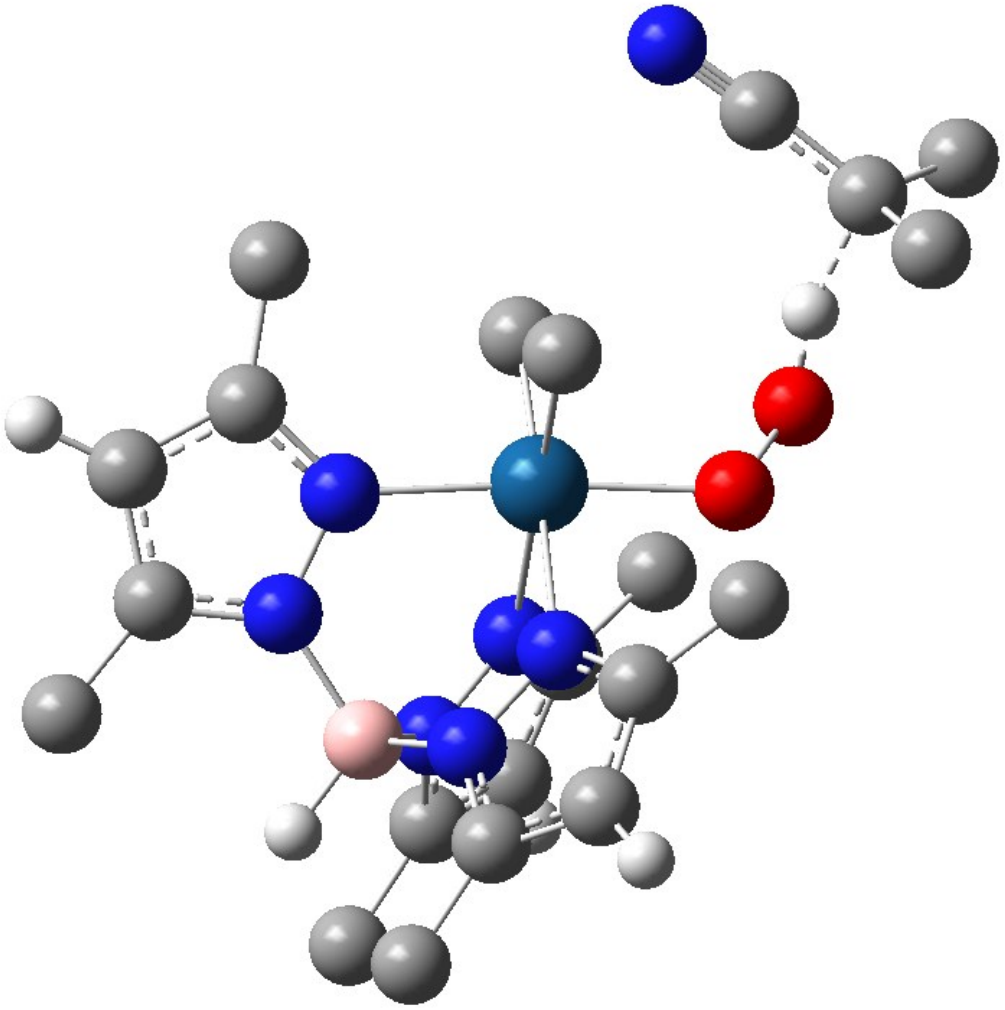

Figure S4. Optimized transition state **TS3-4** for the hydrogen atom abstraction radical propagation step between **3** and •$C(CH_3)_2CN$ (•In). For ease of illustration the hydrogen atoms on the methyl groups have been hidden in this representation.

TDDFT output for Excited States 1-5 for Species 1 (The HOMO is #98)

TD=Singlets

Excited State 1: Singlet-A 5.2591 eV 235.75 nm f=0.0055 <S**2>=0.000
96 -> 99 0.37919
96 ->101 -0.20764
97 -> 99 0.38075
97 ->101 -0.14797
98 ->100 -0.15529
98 ->102 0.25671
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1137.86328427
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 5.2960 eV 234.11 nm f=0.0324 <S**2>=0.000
96 ->100 -0.14100
98 -> 99 0.56318
98 ->101 -0.33539

Excited State 3: Singlet-A 5.3821 eV 230.37 nm f=0.0058 <S**2>=0.000
88 ->102 -0.10064
92 ->102 0.17943
96 -> 99 -0.15111
97 -> 99 -0.26542
98 ->100 -0.31507
98 ->102 0.46219
98 ->105 -0.11722

Excited State 4: Singlet-A 5.5270 eV 224.33 nm f=0.0282 <S**2>=0.000
96 -> 99 -0.47209
97 -> 99 0.47897
98 ->102 0.11689

Excited State 5: Singlet-A 5.6000 eV 221.40 nm f=0.0086 <S**2>=0.000
95 -> 99 0.10414
96 ->101 -0.11410
97 -> 99 -0.14202
98 ->100 0.57896
98 ->102 0.29654

TD=Triplets

Excited State 1: Triplet-A 4.1749 eV 296.98 nm f=0.0000 <S**2>=2.000
93 -> 99 -0.14456
95 ->100 0.12986
95 ->103 -0.26638
96 ->100 -0.21064
96 ->103 0.12542
97 ->100 -0.11097
98 -> 99 0.47268
98 ->101 0.14866
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1137.90312779
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Triplet-A 4.1894 eV 295.95 nm f=0.0000 <S**2>=2.000
93 ->103 0.10947
95 -> 99 0.38963
95 ->101 0.15463
96 -> 99 -0.28151
96 ->100 0.10789
98 ->100 0.25652
98 ->103 -0.25589

Excited State 3: Triplet-A 4.1985 eV 295.31 nm f=0.0000 <S**2>=2.000
89 ->100 -0.11257
94 ->100 0.13451
94 ->103 0.10113
95 ->100 0.39268
95 ->103 0.10606
96 ->100 0.26869
96 ->103 0.17341
97 ->100 0.32471
97 ->103 0.15916
98 -> 99 0.10488

Excited State 4: Triplet-A 4.6950 eV 264.08 nm f=0.0000 <S**2>=2.000
93 ->100 -0.17935
93 ->103 0.21234
94 -> 99 -0.20013
96 -> 99 -0.19409

97 -> 99 0.51781
97 ->101 0.14674
98 ->100 -0.10996

Excited State 5: Triplet-A 4.7389 eV 261.63 nm f=0.0000 <S**2>=2.000
93 -> 99 0.20263
94 ->100 -0.22169
94 ->103 -0.22123
96 ->100 0.41913
97 ->100 -0.36011
98 -> 99 0.12150

TDDFT Calculated Excitations

Examination of the low lying excited states for **1** does indeed show promise with respect to photolytically breaking the Pt-H bond. Excited state 2 at 234.11 nm (5.30 eV, f = 0.0324) has significant contribution from HOMO → LUMO+2 (Figure S5), a transition that corresponds exactly with the hypothetical charge transfer transition described above (i.e. a transition to a Pt-H σ* orbital). Population analysis of these orbitals does demonstrate that the HOMO has ~30% Pt character and with most of the electron density residing on the Tp^{Me2} ligand (contribution from the Me groups and the H are near 0), while the LUMO+2 has ~45% Pt character and ~20% H character and is clearly Pt-H antibonding in nature. A considerable concern here is the high energy of this transition at ~230 nm, which is higher in energy than would

be expected based on experiment by almost 2 eV. In fact, no transitions were calculated for $\lambda > 236$ nm ($E < 5.26$ eV).

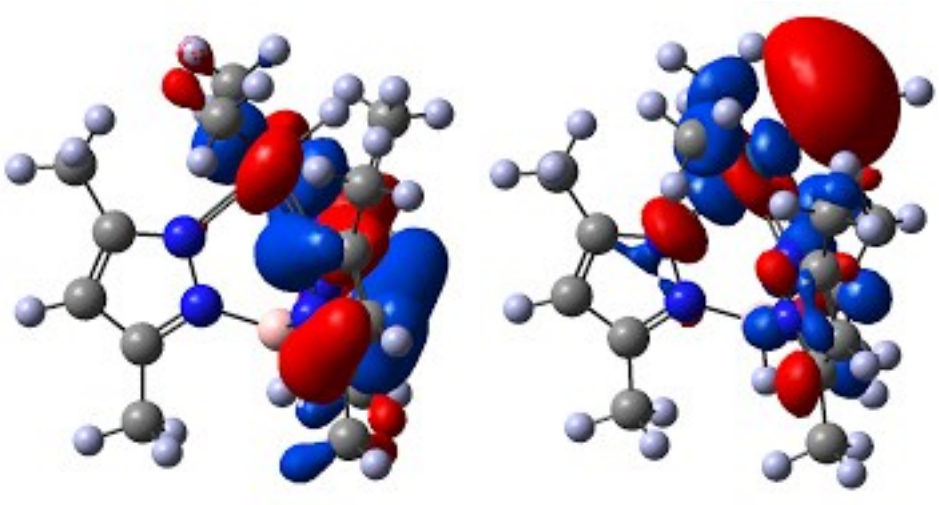

Figure S5. Kohn-Sham orbitals for the HOMO (left) and LUMO+2 (right) from the ground state electronic structure of **1**.

Structural Information:

1	Atom	cartesian coordinates			Mulliken Populations	
	Type	x	y	z	Charge	Spin Density
1	Pt	1.325811	0.258844	-0.07004	0.419515	
2	H	2.04543	1.547222	-0.527328	0.057632	
3	C	2.664152	-0.782929	-1.249383	-0.421492	
4	H	2.095066	-1.500315	-1.851682	0.113241	
5	H	3.215777	-0.121902	-1.922457	0.106308	
6	H	3.392223	-1.33108	-0.646513	0.096575	
7	C	2.651446	0.225575	1.515038	-0.421179	
8	H	3.035988	1.222727	1.740995	0.100741	
9	H	2.118762	-0.149399	2.396585	0.115048	
10	H	3.512067	-0.420868	1.31942	0.099696	
11	N	0.275338	-1.579916	0.570746	-0.348097	
12	C	0.65261	-2.801284	0.972951	0.27899	
13	C	-1.578404	-2.75851	0.948117	0.287048	
14	C	-0.492201	-3.57713	1.225014	-0.251783	
15	H	-0.521583	-4.60196	1.565111	0.080568	
16	N	-1.090724	-1.556473	0.554807	-0.300149	
17	B	-1.848522	-0.291346	0.101693	0.566756	

18	H	-3.02561	-0.48392	0.159498	-0.130383
19	C	2.0846	-3.218244	1.085277	-0.367815
20	H	2.517145	-3.409448	0.098392	0.134923
21	H	2.687049	-2.446338	1.565164	0.138126
22	H	2.160116	-4.136961	1.672523	0.106209
23	C	-3.04133	-3.059578	1.039716	-0.362181
24	H	-3.53708	-2.955629	0.068928	0.127931
25	H	-3.183785	-4.08528	1.387665	0.115676
26	H	-3.550107	-2.386806	1.737698	0.128105
27	N	-0.180239	1.34154	1.080875	-0.36028
28	C	-0.161877	2.433738	1.855111	0.283768
29	C	-2.26995	1.70788	1.754725	0.286106
30	C	-1.467088	2.696806	2.30691	-0.252397
31	H	-1.783697	3.505859	2.948796	0.080906
32	N	-0.15257	0.340213	-1.665707	-0.360645
33	C	-0.104601	0.669752	-2.962343	0.281458
34	C	-2.225869	0.191955	-2.45824	0.285454
35	C	-1.399463	0.584157	-3.50334	-0.252233
36	H	-1.694738	0.786467	-4.522489	0.080967
37	N	-1.450209	0.050272	-1.355089	-0.302824
38	N	-1.471138	0.898614	1.015809	-0.302995
39	C	-3.703044	-0.047832	-2.455265	-0.362813
40	H	-4.103432	0.114384	-3.45861	0.115991
41	H	-3.945397	-1.071137	-2.150519	0.128245
42	H	-4.221107	0.627587	-1.766427	0.128345
43	C	1.170069	1.056098	-3.641455	-0.368794
44	H	0.956239	1.626736	-4.548909	0.107997
45	H	1.791859	1.663582	-2.979248	0.147997
46	H	1.754536	0.174612	-3.923599	0.134317
47	C	1.091835	3.197119	2.138959	-0.370649
48	H	1.744553	3.209103	1.262772	0.148995
49	H	0.850314	4.227316	2.413731	0.108478
50	H	1.653469	2.750118	2.965779	0.134655
51	C	-3.745857	1.500052	1.888414	-0.362609
52	H	-3.978768	0.512393	2.299222	0.128449
53	H	-4.164106	2.256209	2.55675	0.115863
54	H	-4.255195	1.578125	0.92211	0.128239

2	Atom	cartesian coordinates			Mulliken Populations	
	Type	x	y	z	Charge	Spin Density
1	C	2.723176	-0.69549	-1.284464	-0.46392	0.015205
2	H	2.20139	-1.2784	-2.052427	0.109279	-0.000345
3	H	3.335893	0.063422	-1.788091	0.101691	0.002265

4	H	3.403218	-1.36212	-0.746419	0.096651	-0.001217
5	C	2.721024	0.131503	1.483721	-0.464599	0.01447
6	H	2.202361	-0.00221	2.440303	0.110685	-0.00007
7	H	3.450101	-0.675963	1.367588	0.09662	-0.001233
8	H	3.283468	1.073146	1.529618	0.10036	0.00255
9	N	0.183579	-1.635619	0.466577	-0.304528	0.191791
10	C	0.517956	-2.887175	0.79977	0.284251	-0.009464
11	C	-1.712145	-2.754239	0.762931	0.286158	-0.004135
12	C	-0.65991	-3.629878	0.999132	-0.254575	0.00972
13	H	-0.732252	-4.670504	1.280038	0.081636	0.002665
14	N	-1.175226	-1.550986	0.441076	-0.294238	0.001317
15	B	-1.866137	-0.223494	0.061005	0.563503	0.002224
16	H	-3.051467	-0.365637	0.095011	-0.132031	-0.000154
17	C	1.938203	-3.342721	0.901813	-0.366723	0.002286
18	H	2.414134	-3.364626	-0.082919	0.138755	-0.000619
19	H	2.522475	-2.670701	1.533598	0.14205	-0.000333
20	H	1.97986	-4.348437	1.327057	0.105442	-0.000159
21	C	-3.186754	-3.000488	0.828064	-0.362054	0.002546
22	H	-3.669635	-2.821789	-0.138291	0.12829	-0.000622
23	H	-3.373167	-4.037492	1.116691	0.116124	0.000311
24	H	-3.673733	-2.347938	1.560045	0.128298	-0.000606
25	N	-0.136307	1.264895	1.160135	-0.369802	0.001744
26	C	-0.077348	2.285969	2.024663	0.28079	0.000983
27	C	-2.212927	1.66169	1.859438	0.286162	0.000632
28	C	-1.372332	2.566371	2.494309	-0.251774	-0.000082
29	H	-1.658699	3.332791	3.19959	0.080605	0.000041
30	N	-0.121576	0.452743	-1.643625	-0.370023	0.002334
31	C	-0.049084	0.868833	-2.914402	0.280632	0.000881
32	C	-2.190987	0.435304	-2.464124	0.285964	0.000531
33	C	-1.339484	0.867693	-3.472343	-0.251733	-0.000028
34	H	-1.616067	1.151191	-4.477307	0.08064	0.00005
35	N	-1.433311	0.190897	-1.366016	-0.301167	-0.00082
36	N	-1.444749	0.884269	1.056202	-0.301809	-0.000807
37	C	-3.675887	0.251467	-2.491182	-0.36261	-0.000056
38	H	-4.057632	0.491703	-3.486155	0.115733	-0.000009
39	H	-3.959997	-0.779131	-2.254814	0.128	0.000014
40	H	-4.177276	0.900915	-1.766003	0.128269	0.000032
41	C	1.244965	1.264927	-3.551608	-0.368566	0.002308
42	H	1.058753	1.916301	-4.40951	0.108994	0.00025
43	H	1.881443	1.796698	-2.839433	0.143077	-0.00124
44	H	1.804918	0.392225	-3.902139	0.13505	-0.000082
45	C	1.208253	2.969023	2.368382	-0.368513	0.002092
46	H	1.84416	3.067895	1.484641	0.142343	-0.001149

47	H	1.009063	3.965969	2.769978	0.108695	0.000229
48	H	1.774497	2.406634	3.117449	0.135592	-0.000062
49	C	-3.696952	1.505968	1.972401	-0.362564	-0.000069
50	H	-3.973193	0.500281	2.305357	0.128122	0.000019
51	H	-4.087942	2.225416	2.695526	0.115672	-0.000009
52	H	-4.195985	1.678979	1.013146	0.128174	0.000038
53	Pt	1.348802	0.213371	-0.049956	0.54892	0.763842

3	Atom	cartesian coordinates			Mulliken Populations	
	Type	x	y	z	Charge	Spin Density
1	Pt	-1.149857	-0.154636	0.000699	0.819805	-0.007388
2	C	-2.331048	-0.976132	1.474124	-0.416989	-0.001792
3	H	-1.69469	-1.371638	2.272481	0.115491	0.000535
4	H	-2.972102	-0.183195	1.862391	0.132942	-0.001419
5	H	-2.974733	-1.77097	1.091229	0.106649	0.000087
6	C	-2.331187	-0.982859	-1.468722	-0.417027	-0.001771
7	H	-1.694883	-1.379532	-2.266539	0.11547	0.000535
8	H	-2.972778	-1.77789	-1.082756	0.106547	0.000086
9	H	-2.974209	-0.192286	-1.858571	0.133085	-0.001423
10	N	0.207727	-1.7522	0.003488	-0.381803	-0.010766
11	C	0.097997	-3.092895	0.005691	0.282546	0.001845
12	C	2.272262	-2.579743	0.004692	0.293649	0.001592
13	C	1.385428	-3.647747	0.006566	-0.247319	-0.000399
14	H	1.63401	-4.698609	0.008352	0.089301	-0.000164
15	N	1.542703	-1.440322	0.002823	-0.304389	0
16	B	2.039803	0.028435	-0.000319	0.565272	-0.000144
17	H	3.233165	0.043338	-0.000649	-0.123225	-0.000005
18	C	-1.199787	-3.833253	0.006263	-0.367633	-0.000154
19	H	-1.799248	-3.588346	0.884922	0.141611	0.000062
20	H	-1.794135	-3.598234	-0.878648	0.141622	0.000063
21	H	-1.003072	-4.907789	0.012767	0.111085	0.000006
22	C	3.76847	-2.59742	0.004631	-0.362151	-0.000267
23	H	4.177781	-2.092962	0.885463	0.133285	0.000107
24	H	4.120447	-3.631375	0.006527	0.118923	-0.000011
25	H	4.177668	-2.096237	-0.878124	0.133286	0.000107
26	N	0.159646	0.801953	-1.485367	-0.364828	0.002052
27	C	-0.039278	1.54546	-2.581806	0.286058	-0.000092
28	C	2.162448	1.441294	-2.215488	0.285312	-0.000073
29	C	1.208231	1.966637	-3.076325	-0.250516	0.000046
30	H	1.387971	2.578924	-3.947819	0.084053	0.000015
31	N	0.160359	0.808513	1.482185	-0.364811	0.002047
32	C	-0.037935	1.556601	2.575632	0.286072	-0.000093
33	C	2.16363	1.45023	2.209012	0.285306	-0.000072

34	C	1.209878	1.979385	3.068015	-0.250506	0.000046
35	H	1.390102	2.595202	3.936917	0.084047	0.000015
36	N	1.505433	0.743667	1.257469	-0.3019	-0.000002
37	N	1.504807	0.738382	-1.260858	-0.301912	-0.000002
38	C	3.653367	1.586738	2.238977	-0.363681	0.000022
39	H	3.951142	2.180245	3.1062	0.118944	0.000003
40	H	4.147576	0.611954	2.303916	0.127475	-0.000008
41	H	4.030987	2.083474	1.338967	0.12909	-0.000009
42	C	-1.39909	1.845148	3.125183	-0.382246	0.000678
43	H	-1.348479	2.688647	3.818189	0.107937	0.000178
44	H	-2.099305	2.087254	2.324045	0.168946	-0.00228
45	H	-1.796925	0.983188	3.670586	0.13126	0.000122
46	C	-1.40079	1.831144	-3.131957	-0.38222	0.000666
47	H	-2.100561	2.077108	-2.331599	0.168936	-0.002292
48	H	-1.350737	2.671182	-3.829186	0.107927	0.000176
49	H	-1.798853	0.966396	-3.672741	0.131261	0.000122
50	C	3.652124	1.578174	-2.246534	-0.363685	0.000022
51	H	4.146653	0.6033	-2.307584	0.127476	-0.000008
52	H	3.949399	2.16817	-3.11632	0.118946	0.000003
53	H	4.029861	2.078788	-1.348725	0.129095	-0.00001
54	O	-2.292484	1.506331	-0.002346	-0.281984	0.380765
55	O	-3.593175	1.377025	-0.002973	-0.189889	0.638642

4	Atom	cartesian coordinates			Mulliken Populations	
	Type	x	y	z	Charge	Spin Density
1	Pt	-1.133628	-0.163494	-0.01118	0.847252	
2	C	-2.264564	-1.163466	1.385189	-0.420635	
3	H	-1.609101	-1.766868	2.021026	0.120139	
4	H	-2.766121	-0.425926	2.01697	0.087206	
5	H	-3.020772	-1.808276	0.929859	0.107388	
6	C	-2.277919	-0.869307	-1.57019	-0.407244	
7	H	-2.757471	-0.014406	-2.043664	0.137681	
8	H	-1.631438	-1.384847	-2.287925	0.112994	
9	H	-3.064392	-1.545803	-1.225914	0.10451	
10	N	0.223073	-1.743824	-0.169302	-0.381823	
11	C	0.100405	-3.080127	-0.265074	0.27944	
12	C	2.278748	-2.583997	-0.278135	0.292127	
13	C	1.383184	-3.642688	-0.33956	-0.247192	
14	H	1.622847	-4.691968	-0.42761	0.087375	
15	N	1.558267	-1.443014	-0.174731	-0.301817	
16	B	2.056766	0.016942	-0.036649	0.565102	
17	H	3.250177	0.031781	-0.053164	-0.12548	
18	C	-1.204435	-3.809916	-0.256142	-0.36606	

19	H	-1.627028	-3.851424	0.751819	0.135928
20	H	-1.939322	-3.33216	-0.902543	0.141176
21	H	-1.049951	-4.835192	-0.601019	0.111282
22	C	3.774247	-2.608452	-0.314683	-0.361984
23	H	4.207058	-2.188031	0.598607	0.132317
24	H	4.119924	-3.639756	-0.414866	0.117801
25	H	4.166276	-2.030551	-1.157425	0.133092
26	N	0.153007	0.970483	-1.382996	-0.365321
27	C	-0.05941	1.864311	-2.357607	0.290393
28	C	2.14902	1.679373	-2.06816	0.284568
29	C	1.184096	2.331665	-2.822213	-0.250936
30	H	1.353264	3.057413	-3.604207	0.081597
31	N	0.200299	0.670017	1.541871	-0.357446
32	C	0.026956	1.326603	2.695592	0.290201
33	C	2.222141	1.208567	2.30202	0.284917
34	C	1.286536	1.680512	3.212472	-0.251404
35	H	1.486323	2.217496	4.128228	0.081658
36	N	1.54267	0.598598	1.299405	-0.304127
37	N	1.503001	0.857967	-1.20368	-0.302878
38	C	3.714439	1.31538	2.32985	-0.363637
39	H	4.030614	1.810698	3.250669	0.117464
40	H	4.191392	0.330785	2.288658	0.126685
41	H	4.093825	1.896036	1.482279	0.129072
42	C	-1.327668	1.60569	3.265668	-0.385385
43	H	-1.277305	2.456006	3.950835	0.107091
44	H	-2.02691	1.832948	2.45846	0.163076
45	H	-1.708732	0.745383	3.827312	0.123854
46	C	-1.428608	2.254351	-2.815778	-0.389145
47	H	-2.114685	2.280632	-1.967493	0.188694
48	H	-1.394954	3.240552	-3.286686	0.103102
49	H	-1.816223	1.54521	-3.555289	0.124516
50	C	3.639607	1.801682	-2.118076	-0.363335
51	H	4.118615	0.835643	-2.307561	0.126402
52	H	3.925469	2.488455	-2.917957	0.117701
53	H	4.045594	2.186697	-1.176489	0.127896
54	O	-2.301603	1.446791	0.18033	-0.432227
55	O	-3.71266	1.187001	-0.037433	-0.3271
56	H	-3.9966	0.924288	0.852248	0.323477

TS1-2	Atom	cartesian coordinates			Mulliken Populations	
	Type	x	y	z	Charge	Spin Density
1	Pt	-0.675496	-0.667879	-0.047362	0.504646	0.26962
2	C	-1.284017	-2.070344	1.336401	-0.423047	0.018802

3	H	-0.39214	-2.476081	1.822558	0.121356	-0.001447
4	H	-1.909227	-1.613431	2.105117	0.093944	-0.000289
5	H	-1.846729	-2.896501	0.889555	0.092941	-0.00037
6	C	-1.293973	-1.850286	-1.619851	-0.427248	0.017988
7	H	-1.884019	-1.272059	-2.332779	0.092268	-0.000233
8	H	-0.402634	-2.2162	-2.139106	0.125236	-0.001451
9	H	-1.897831	-2.70837	-1.30399	0.093783	-0.000318
10	N	1.362205	-1.60618	-0.095065	-0.327051	0.09479
11	C	1.814337	-2.86847	-0.133002	0.274024	-0.004414
12	C	3.585508	-1.508951	-0.082397	0.282266	-0.00155
13	C	3.221153	-2.847082	-0.130751	-0.247949	0.004271
14	H	3.884242	-3.699518	-0.160033	0.080776	0.001317
15	N	2.44274	-0.780022	-0.061756	-0.29033	0.000823
16	B	2.237997	0.741788	0.02508	0.566278	0.000918
17	H	3.302478	1.280717	0.054161	-0.132504	-0.000053
18	C	0.927061	-4.073694	-0.132707	-0.368611	0.000924
19	H	0.810622	-4.471807	0.881525	0.127937	-0.000408
20	H	-0.06556	-3.845499	-0.514529	0.141779	0.000057
21	H	1.367141	-4.863224	-0.748872	0.112524	-0.000199
22	C	4.94953	-0.894098	-0.057469	-0.362974	0.001239
23	H	5.107003	-0.297695	0.847107	0.129156	-0.000287
24	H	5.707503	-1.680283	-0.085133	0.116104	0.000164
25	H	5.110704	-0.23234	-0.914719	0.128977	-0.000286
26	N	0.14244	0.866774	-1.413393	-0.357585	-0.000351
27	C	-0.302706	1.566577	-2.467616	0.285265	0.000284
28	C	1.816536	2.163111	-2.122141	0.287967	-0.000132
29	C	0.72713	2.389924	-2.949376	-0.246686	-0.000011
30	H	0.675637	3.070712	-3.786244	0.082146	-0.000006
31	N	0.161455	0.667951	1.500026	-0.356653	-0.000025
32	C	-0.27482	1.226973	2.638087	0.285875	0.000246
33	C	1.824709	1.906044	2.326179	0.287857	-0.000165
34	C	0.748745	2.009823	3.19487	-0.246617	0.000015
35	H	0.702174	2.585095	4.107788	0.082153	-0.000004
36	N	1.45064	1.091993	1.30885	-0.302644	-0.000251
37	N	1.443178	1.241705	-1.200934	-0.301271	-0.000246
38	C	3.175365	2.543869	2.418266	-0.363191	-0.000007
39	H	3.243597	3.122089	3.342597	0.116107	-0.000007
40	H	3.976569	1.797845	2.420344	0.127004	-0.000009
41	H	3.362215	3.219849	1.577475	0.130189	-0.000004
42	C	-1.663194	1.055783	3.159895	-0.376545	-0.000361
43	H	-1.778148	1.610575	4.094093	0.110727	-0.000027
44	H	-2.390314	1.447831	2.444248	0.148417	0.000002
45	H	-1.896097	0.006708	3.356529	0.12805	-0.000024

46	C	-1.704244	1.492343	-2.977067	-0.37616	-0.000384
47	H	-2.410012	1.767433	-2.189794	0.148732	-0.000002
48	H	-1.83345	2.193863	-3.804676	0.111014	-0.00003
49	H	-1.954999	0.492294	-3.339189	0.127219	-0.000022
50	C	3.17828	2.782434	-2.164396	-0.363094	-0.000012
51	H	3.964624	2.02636	-2.255721	0.127197	-0.000008
52	H	3.247208	3.453985	-3.023266	0.116078	-0.000007
53	H	3.387746	3.362078	-1.259356	0.130123	-0.000003
54	H	-2.245593	-0.120421	-0.00605	-0.023671	-0.078291
55	C	-3.804275	0.186209	0.02122	-0.037613	0.575307
56	C	-4.325201	-0.37193	-1.287491	-0.307895	-0.034818
57	H	-5.419423	-0.275775	-1.317943	0.117507	0.02997
58	H	-3.919075	0.140911	-2.157483	0.122402	0.002856
59	H	-4.079338	-1.433713	-1.359694	0.134787	0.008289
60	C	-4.315805	-0.546152	1.244923	-0.308221	-0.034823
61	H	-4.074764	-1.608805	1.167424	0.135086	0.008186
62	H	-3.898602	-0.159479	2.173087	0.122625	0.002927
63	H	-5.409155	-0.450919	1.29934	0.117493	0.03001
64	C	-3.730779	1.606449	0.119906	0.242107	-0.104631
65	N	-3.611187	2.766089	0.201065	-0.36056	0.196959

TS3-4	Atom	cartesian coordinates			Mulliken Populations	
	Type	x	y	z	Charge	Spin Density
1	Pt	-2.60633	0.625621	-0.173964	0.860196	0.004851
2	C	-2.063299	2.528563	0.400883	-0.410286	0.000329
3	H	-2.961985	3.101744	0.650618	0.116248	0.000804
4	H	-1.420436	2.448086	1.276594	0.131656	-0.000339
5	H	-1.498882	3.043937	-0.379966	0.105731	0.000016
6	C	-1.616273	0.814683	-1.964832	-0.420378	-0.000134
7	H	-0.687654	0.252948	-1.883075	0.141232	0.000142
8	H	-2.233594	0.390958	-2.763182	0.11885	-0.000023
9	H	-1.375852	1.852309	-2.201721	0.100885	0.000002
10	N	-4.411234	1.27572	-0.97681	-0.386241	-0.002739
11	C	-4.772393	2.272887	-1.805163	0.280772	0.000654
12	C	-6.613604	1.13701	-1.247147	0.290851	0.000687
13	C	-6.160551	2.216373	-1.993175	-0.244478	0.00004
14	H	-6.755712	2.881626	-2.600939	0.088559	-0.000037
15	N	-5.541907	0.578599	-0.638809	-0.303525	-0.000097
16	B	-5.485565	-0.684109	0.262507	0.565761	-0.000023
17	H	-6.584541	-1.133005	0.386643	-0.123984	0.000002
18	C	-3.819852	3.238134	-2.433262	-0.367469	-0.000031
19	H	-3.108457	3.635443	-1.710121	0.141419	-0.000024
20	H	-3.249207	2.76045	-3.234432	0.141803	0.000072

21	H	-4.380006	4.070866	-2.865216	0.111354	0
22	C	-8.008261	0.619033	-1.088937	-0.362393	-0.000099
23	H	-8.32492	0.628133	-0.041365	0.133642	0.000041
24	H	-8.696671	1.244476	-1.661623	0.118334	-0.000005
25	H	-8.099291	-0.410833	-1.448388	0.133481	0.000045
26	N	-3.265274	-1.404309	-0.68271	-0.366044	0.000795
27	C	-2.672611	-2.488375	-1.198622	0.281464	-0.000275
28	C	-4.794975	-3.018464	-0.741414	0.282957	-0.000006
29	C	-3.612028	-3.534622	-1.2526	-0.249557	0.000146
30	H	-3.445676	-4.538852	-1.613943	0.082973	-0.000004
31	N	-3.680237	0.280638	1.726887	-0.360411	0.001592
32	C	-3.375381	0.401523	3.026035	0.28836	0.000101
33	C	-5.395631	-0.543223	2.883736	0.282563	-0.000049
34	C	-4.441552	-0.10557	3.79142	-0.248725	-0.000021
35	H	-4.50308	-0.149303	4.868991	0.081832	0.00002
36	N	-4.914671	-0.297735	1.640191	-0.300026	-0.000007
37	N	-4.563233	-1.725473	-0.404561	-0.302021	0.000008
38	C	-6.723893	-1.185713	3.132538	-0.363526	0.000027
39	H	-6.906684	-1.248577	4.207604	0.117931	0
40	H	-7.540673	-0.61558	2.678161	0.126652	-0.000007
41	H	-6.765346	-2.199174	2.71941	0.128727	-0.000006
42	C	-2.091935	0.994768	3.514656	-0.386072	-0.000296
43	H	-1.9094	0.681766	4.54603	0.104108	0.000014
44	H	-1.255774	0.675103	2.892395	0.177649	-0.001658
45	H	-2.13027	2.089267	3.499911	0.128493	0.00007
46	C	-1.242542	-2.488905	-1.629697	-0.382152	0.002813
47	H	-0.646837	-1.840346	-0.989156	0.182623	0.000455
48	H	-0.830836	-3.49957	-1.578294	0.113305	-0.000052
49	H	-1.137403	-2.13437	-2.660673	0.12826	-0.000095
50	C	-6.120272	-3.685863	-0.548746	-0.363852	-0.000006
51	H	-6.916741	-3.16966	-1.094638	0.126404	-0.000003
52	H	-6.069402	-4.715378	-0.910129	0.118485	0.000003
53	H	-6.411408	-3.708603	0.506833	0.128479	0.000002
54	O	-0.9836	-0.151364	0.709248	-0.370575	0.18323
55	O	0.152723	0.62598	0.721859	-0.284857	0.384024
56	Pt	2.604015	-0.533931	-0.439296	0.34576	0.35298
57	C	1.905142	-2.448437	-0.138567	-0.447223	0.012013
58	C	1.936319	-0.539951	-2.390093	-0.442989	0.011039
59	N	4.65995	-1.245055	-1.001698	-0.319803	0.113718
60	N	3.386531	1.495767	-0.611535	-0.362307	0.000511
61	N	3.403128	-0.432675	1.586293	-0.3611	0.000886
62	H	2.668035	-3.007723	0.415611	0.1118	-0.000702
63	H	0.984495	-2.440841	0.452054	0.112554	0.000509

64	H	1.702559	-2.97198	-1.076771	0.089171	-0.0008
65	H	1.260655	0.295596	-2.584269	0.097497	0.000679
66	H	2.805902	-0.426814	-3.048294	0.112731	-0.000739
67	H	1.410574	-1.462234	-2.658842	0.092675	-0.000167
68	C	5.149277	-2.225515	-1.769401	0.275193	-0.005388
69	N	5.711832	-0.567356	-0.463987	-0.297332	0.000892
70	C	2.886319	2.667626	-1.025875	0.282171	0.000535
71	N	4.660587	1.720482	-0.169332	-0.301646	-0.000398
72	C	2.939632	-0.752348	2.801786	0.283626	0.000521
73	N	4.662904	0.077808	1.740433	-0.304064	-0.000395
74	C	6.554997	-2.173817	-1.730879	-0.250082	0.005378
75	C	4.275561	-3.205223	-2.487386	-0.367585	0.001179
76	C	6.876885	-1.113676	-0.893267	0.280655	-0.001969
77	B	5.466096	0.596155	0.522307	0.571199	0.000993
78	C	3.862433	3.666254	-0.859257	-0.249729	-0.000088
79	C	1.492329	2.813124	-1.547084	-0.383629	-0.000507
80	C	4.969422	3.033643	-0.311564	0.283872	0.00014
81	C	3.922337	-0.44501	3.76011	-0.250623	-0.00005
82	C	1.582288	-1.341763	3.017985	-0.385476	-0.00017
83	C	4.99695	0.078673	3.054912	0.28382	0.00015
84	H	7.245234	-2.825813	-2.246503	0.076881	0.001491
85	H	3.878524	-3.954995	-1.795511	0.134677	-0.000396
86	H	3.423922	-2.711209	-2.957221	0.141133	-0.000097
87	H	4.850073	-3.7249	-3.258717	0.103375	-0.00012
88	C	8.221835	-0.598873	-0.48595	-0.361932	0.001465
89	H	6.516023	1.029873	0.891873	-0.13574	-0.00007
90	H	3.767639	4.715124	-1.099848	0.07621	0.000014
91	H	0.805905	2.16257	-1.002812	0.170798	-0.001589
92	H	1.159278	3.848385	-1.429686	0.102109	-0.000012
93	H	1.430983	2.561165	-2.611178	0.126379	0.000011
94	C	6.289781	3.613495	0.08832	-0.3622	-0.00003
95	H	3.853633	-0.582603	4.829397	0.075594	0.000018
96	H	1.269024	-1.184972	4.053905	0.098041	0.000019
97	H	0.851099	-0.879777	2.353832	0.180934	-0.001127
98	H	1.582568	-2.419579	2.825021	0.126523	-0.000027
99	C	6.311171	0.580749	3.565276	-0.362604	-0.000029
100	H	8.365061	-0.654514	0.598237	0.127407	-0.000347
101	H	9.003229	-1.193592	-0.964919	0.113452	0.00021
102	H	8.360101	0.447329	-0.777944	0.127228	-0.000347
103	H	7.121144	3.117894	-0.423333	0.126313	0
104	H	6.315669	4.675807	-0.165679	0.113117	-0.000006
105	H	6.466176	3.514751	1.164681	0.127535	0.000017
106	H	6.354783	0.457791	4.650012	0.113147	-0.000006

107	H	7.151728	0.035037	3.124201	0.12605	0.000002
108	H	6.456613	1.641513	3.335135	0.126815	0.000015
109	H	1.066646	0.053837	0.093599	0.344153	-0.064759

TS1-2O$_2$	Atom Type	cartesian coordinates			Mulliken Populations	
		x	y	z	Charge	Spin Density
1	Pt	-1.04115	-0.589857	0.028155	0.328294	0.516226
2	C	-1.94002	-1.683436	1.529754	-0.437079	0.011757
3	H	-1.243566	-1.784416	2.36987	0.115328	-0.000159
4	H	-2.840475	-1.174107	1.891203	0.107315	0.003321
5	H	-2.240701	-2.682006	1.200182	0.100641	-0.000953
6	C	-1.897044	-1.829913	-1.378543	-0.43727	0.012818
7	H	-2.834783	-1.402477	-1.751733	0.109713	0.003272
8	H	-1.208546	-1.940422	-2.223636	0.113891	-0.000313
9	H	-2.120988	-2.821693	-0.977501	0.099676	-0.001026
10	N	0.892863	-1.655298	0.089504	-0.332524	0.171551
11	C	1.260703	-2.942425	0.137916	0.282768	-0.006972
12	C	3.112703	-1.692079	0.113864	0.287609	-0.003148
13	C	2.664475	-3.006233	0.157088	-0.251828	0.008229
14	H	3.272291	-3.89828	0.197707	0.085097	0.002299
15	N	2.0209	-0.889825	0.072949	-0.30143	0.001354
16	B	1.929226	0.652942	-0.008624	0.568202	0.001356
17	H	3.029921	1.114911	-0.022242	-0.127308	-0.000076
18	C	0.282394	-4.072583	0.144037	-0.368269	0.001692
19	H	-0.21378	-4.168138	-0.826178	0.139447	-0.000484
20	H	0.799843	-5.010932	0.357528	0.109018	-0.000128
21	H	-0.492668	-3.922423	0.897453	0.141313	-0.000206
22	C	4.51388	-1.166871	0.110891	-0.362446	0.002146
23	H	4.701335	-0.512324	0.968138	0.130546	-0.000508
24	H	5.218084	-2.000704	0.156117	0.117722	0.000315
25	H	4.725665	-0.587386	-0.7935	0.130399	-0.000512
26	N	-0.112144	0.652826	-1.500816	-0.364169	0.000329
27	C	-0.523447	1.175964	-2.664393	0.283549	0.002169
28	C	1.588549	1.821102	-2.337608	0.287071	0.001559
29	C	0.527004	1.921388	-3.226528	-0.249443	-0.000487
30	H	0.510487	2.467427	-4.158287	0.083288	0.00004
31	N	-0.138616	0.803133	1.442365	-0.363915	0.000193
32	C	-0.571594	1.458771	2.528705	0.283138	0.002078
33	C	1.539061	2.082735	2.157058	0.287461	0.001478
34	C	0.463079	2.277629	3.011898	-0.249185	-0.000469
35	H	0.427139	2.931075	3.87112	0.083293	0.000034
36	N	1.153734	1.187207	1.215104	-0.303616	-0.000762
37	N	1.179984	1.049738	-1.3003	-0.303263	-0.000811

38	C	2.899592	2.705001	2.187596	-0.363001	-0.000142
39	H	2.976824	3.375944	3.046103	0.117568	-0.000005
40	H	3.688199	1.950044	2.270015	0.127742	0.000059
41	H	3.098746	3.285464	1.280677	0.129673	0.000095
42	C	-1.949007	1.291701	3.086601	-0.370023	-0.000602
43	H	-2.172268	2.111602	3.773704	0.111231	0.000178
44	H	-2.700996	1.292644	2.295965	0.139902	-0.003169
45	H	-2.04489	0.350951	3.637253	0.134214	0.000088
46	C	-1.89549	0.952607	-3.215921	-0.368977	-0.000617
47	H	-2.652547	1.017903	-2.433164	0.139839	-0.003378
48	H	-2.118409	1.707486	-3.973992	0.11163	0.000187
49	H	-1.982605	-0.033688	-3.681994	0.133041	0.000125
50	C	2.957252	2.41952	-2.422372	-0.363195	-0.000147
51	H	3.735985	1.649956	-2.408979	0.127647	0.000064
52	H	3.053109	2.986778	-3.350917	0.11766	-0.000005
53	H	3.154881	3.096877	-1.585134	0.129596	0.000099
54	O	-3.561926	1.036829	-0.056718	-0.190704	0.53494
55	O	-3.25214	2.288265	-0.168985	-0.128814	0.781779
56	H	-2.618757	0.431563	-0.024993	0.441939	-0.036747