Supplementary Information

Theoretical Study of The Role of The Non-innocent Phenolate Ligand of a Nickel Complex in Water Oxidation

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Table S1. The comparison of redox potentials calculated at different functionals. The potentials here were versus NHE at pH = 7.

	L_1Ni^{II}-$2H_2O$ → $(L_1•)Ni^{II}$-$2H_2O$	$(L_1•)Ni^{II}$-$2H_2O$ → $(L_1•)(H_2O)Ni^{III}$-OH	Experiment	
			$E_{p,a}$	E_{cat}
B3lyp	1.04	2.11	0.99	1.42
M06	1.11	2.07		
M06-d3	1.14	2.07		
M06L	1.00	1.56		

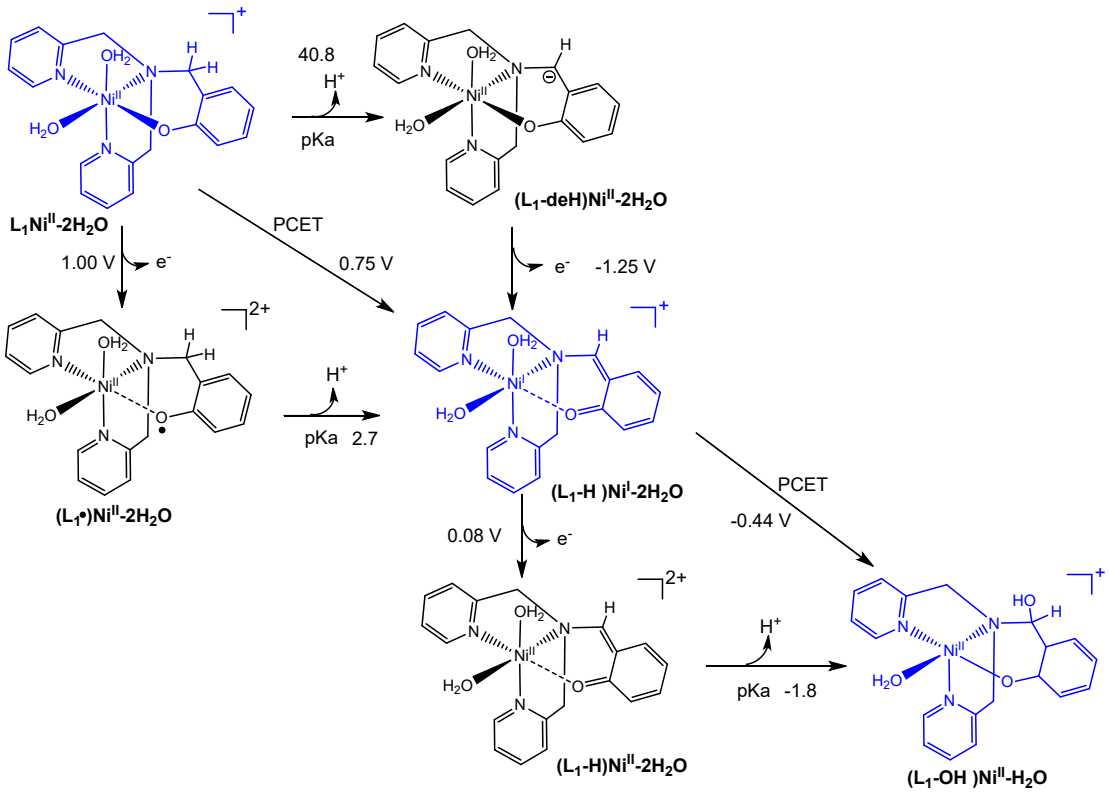

Fig. S1. Calculated electrochemical properties of L_1Ni^{II}-$2H_2O$ with oxidation of ligand at pH = 7. The potentials here were versus NHE. The blue path represents the energetically favorable one during oxidation.

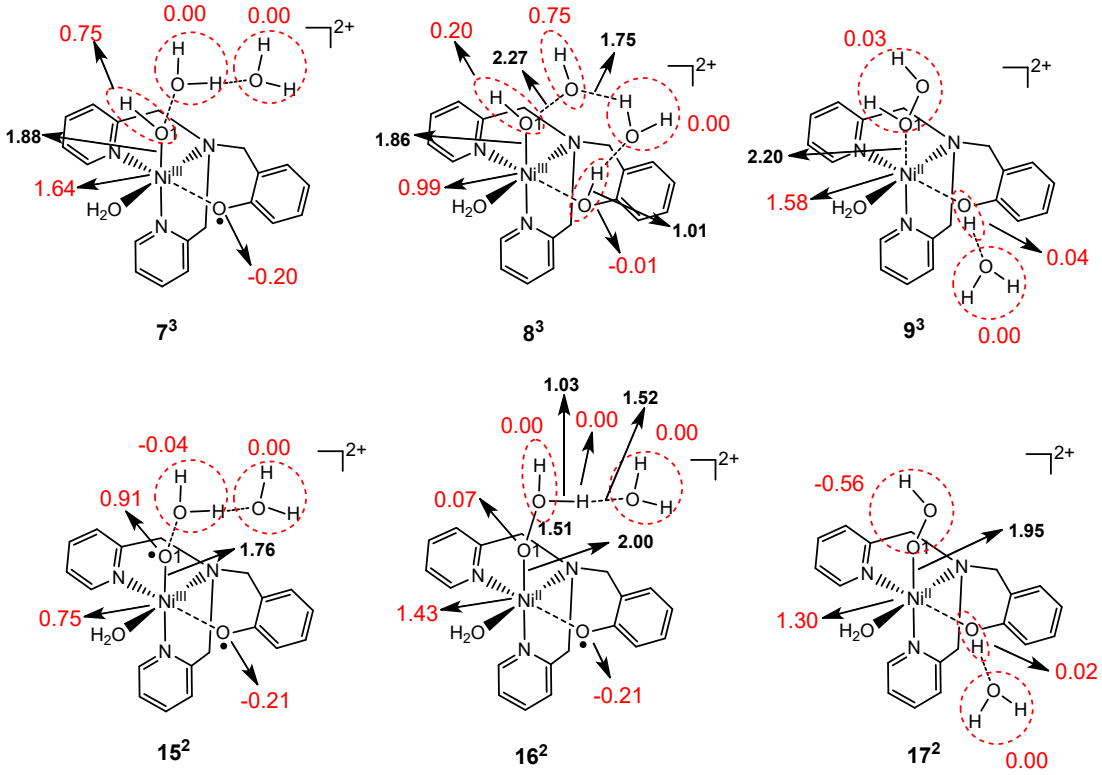

Fig. S2. Selected bond length (Å) and Mulliken spin density of **7**^{3}, **8**^{3}, **9**^{3}, **15**^{2}, **16**^{2}, and

17². The bond lengths are in black. The Mulliken spin density is in red.

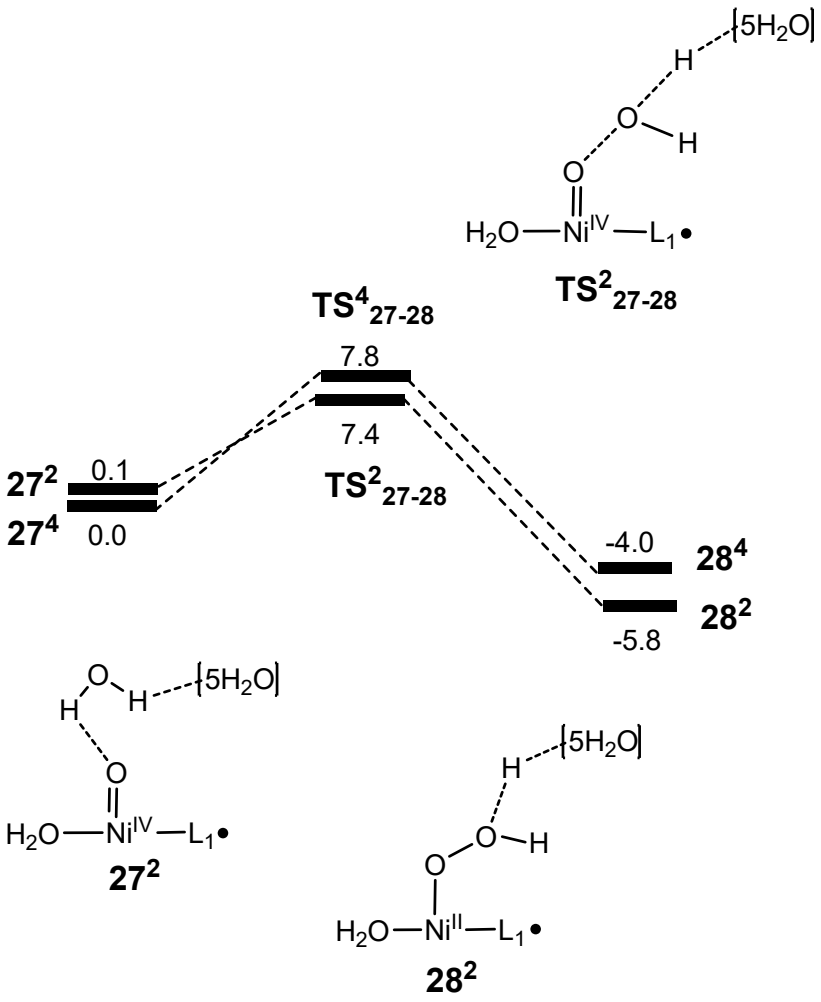

Fig. S3. Free energy diagram (kcal/mol) for O-O bond formation from $(L_1\bullet)(H_2O)Ni^{IV}=O_a$ with six explicit water molecules via normal water nucleophilic pathway. The exponent in the label represents the spin state of the species. The barriers agree well with those in Fig 4(b)

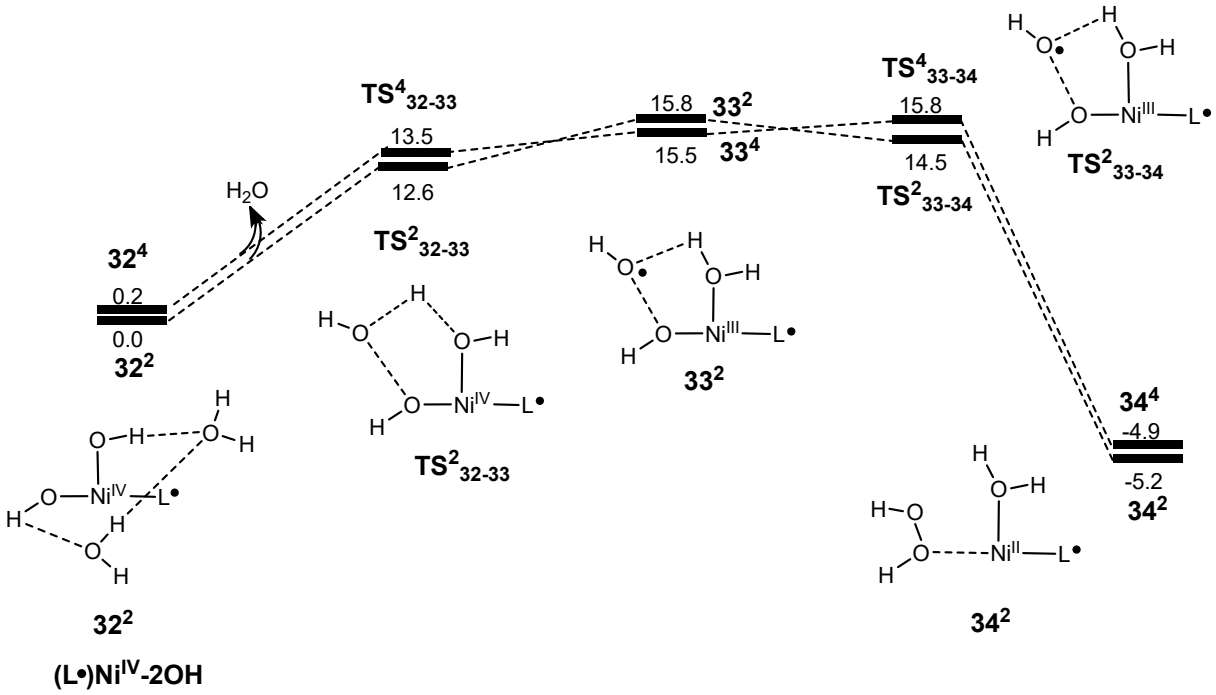

Fig. S4. Free energy diagram (kcal/mol) for O-O bond formation from (L•)Ni^{IV}-2OH via OH-involved water nucleophilic pathway. The exponent in the label represents the spin state of the species.

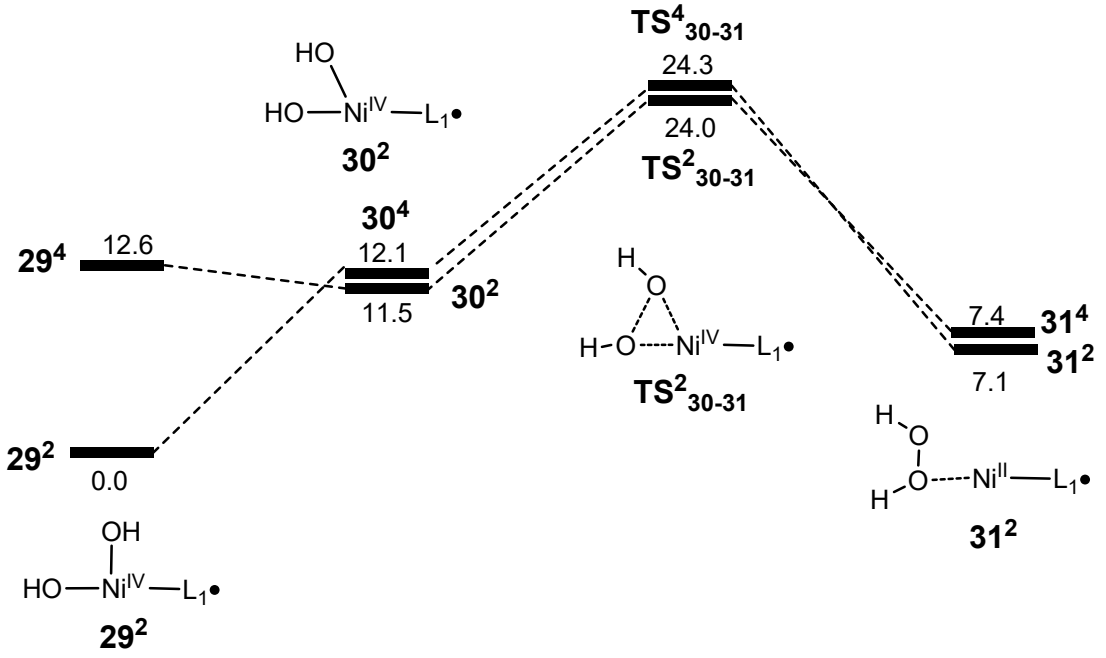

Fig. S5. Free energy diagram (kcal/mol) for O-O bond formation from (L_1•)Ni^{IV}-2OH via HO-OH coupling pathway. The exponent in the label represents the spin state of the species.

Table S2. The calculated spin populations for species in Fig. 8.

	Ni	L_1	OH_e/H_2O_e	OH_a/H_2O_a	H_2O/OH	HOOH	total
$\mathbf{3^2}$	0.02	1.00	-0.01	-0.01	0.00		1
$\mathbf{21^2}$	0.78	-0.73	-0.09	0.67	0.37		1
$\mathbf{21^4}$	0.83	1.22	-0.10	0.68	0.37		3
$\mathbf{TS^2_{21\text{-}22}}$	0.75	-0.72	0.01	0.35	0.61		1
$\mathbf{TS^4_{21\text{-}22}}$	0.81	1.22	0.02	0.38	0.57		3
$\mathbf{22^2}$	0.82	-0.81	0.06	0.15	0.79		1
$\mathbf{22^4}$	0.81	1.20	0.05	0.15	0.79		3
$\mathbf{TS^2_{22\text{-}23}}$	1.10	-0.79	0.06	0.05	0.57		1
$\mathbf{TS^4_{22\text{-}23}}$	1.10	1.22	0.05	0.06	0.57		3
$\mathbf{23^2}$	1.52	-0.58	0.04			0.03	1
$\mathbf{23^4}$	1.58	1.35	0.04			0.03	3

24^2	0.82	-0.80	0.74	-0.09	0.33		1
24^4	0.83	1.20	0.74	-0.10	0.33		3
$TS^2_{24\text{-}25}$	0.83	1.24	-0.45	0.01	-0.63		1
$TS^4_{24\text{-}25}$	0.80	1.22	0.32	0.02	0.64		3
25^2	0.87	1.18	-0.30	0.07	-0.83		1
25^4	0.84	1.17	0.11	0.05	0.83		3
$TS^2_{25\text{-}26}$	0.99	-0.72	0.08	0.04	0.61		1
$TS^4_{25\text{-}26}$	1.05	1.20	0.08	0.05	0.62		3
26^2	1.49	-0.53		0.04		0.03	
26^4	1.58	1.38		0.04		0.03	

Table S3. The calculated energies at M06L level, solvation energies and the single-point energies at higher basis set. The most stable species were labelled in yellow.

species	Gas phase E a.u.	Gas phase G a.u.	Solvation E a.u.	E 6-311++G** a.u.
L_1Ni^{II}-$2H_2OM3$	-1449.251383	-1448.866345	-1449.314344	-1449.557936
$(L_1\bullet)Ni^{II}$-$2H_2OM2$	-1448.918414	-1448.537357	-1449.120639	-1449.220712
$(L_1\bullet)Ni^{II}$-$2H_2OM4$	-1448.913785	-1448.535701	-1449.114859	-1449.216311
$L_1(H_2O)Ni^{II}$-OH_eM3	-1448.799479	-1448.43102	-1448.823744	-1449.115957
$L_1(H_2O)Ni^{II}$-OH_eM5	-1448.699406	-1448.334583	-1448.71582	-1449.013379
$L_1(H_2O)Ni^{II}$-OH_aM3	-1448.801539	-1448.431902	-1448.823849	-1449.116567
$L_1(H_2O)Ni^{II}$-OH_aM5	-1448.69836	-1448.333992	-1448.714776	-1449.012889
$(L_1\bullet)(H_2O)Ni^{II}$-$OH_eM2$	-1448.592451	-1448.218261	-1448.655661	-1448.898941
$(L_1\bullet)(H_2O)Ni^{II}$-$OH_eM4$	-1448.578095	-1448.209026	-1448.639436	-1448.885034
$(L_1\bullet)(H_2O)Ni^{II}$-$OH_aM2$	-1448.591982	-1448.218839	-1448.654786	-1448.897153
$(L_1\bullet)(H_2O)Ni^{II}$-$OH_aM4$	-1448.590431	-1448.219181	-1448.652456	-1448.896359
$(L_1\bullet)Ni^{III}$-$2H_2OM1$	-1448.417936	-1448.033084	-1448.871924	-1448.713676
$(L_1\bullet)Ni^{III}$-$2H_2OM3$	-1448.436227	-1448.054585	-1448.883781	-1448.733386
$(L_1\bullet)Ni^{III}$-$2H_2OM5$	-1448.40935	-1448.032275	-1448.794384	-1448.640442

$(L_1•)(H_2O)Ni^{III}$-OH_eM3	-1448.240716	-1447.872192	-1448.445689	-1448.542526
$(L_1•)(H_2O)Ni^{III}$-OH_eM5	-1448.2369	-1447.867154	-1448.438982	-1448.536728
$(L_1•)(H_2O)Ni^{III}$-OH_aM3	-1448.24407	-1447.872413	-1448.451177	-1448.545944
$(L_1•)(H_2O)Ni^{III}$-OH_aM5	-1448.235237	-1447.866428	-1448.436421	-1448.535829
$(L_1•)(H_2O)Ni^{III}=O_a$M3	-1447.906602	-1447.547839	-1447.969729	-1448.211412
$(L_1•)(H_2O)Ni^{III}=O_a$M5	-1447.913097	-1447.555532	-1447.9755	-1448.220621
$(L_1•)(H_2O)Ni^{III}=O_e$M1	-1447.890462	-1447.528488	-1447.957428	-1448.195591
$(L_1•)(H_2O)Ni^{III}=O_e$M3	-1447.911304	-1447.550754	-1447.976522	-1448.215564
$(L_1•)(H_2O)Ni^{III}=O_e$M5	-1447.906528	-1447.54964	-1447.969962	-1448.21097
$(L_1•)Ni^{III}$-2OHM3	-1447.928163	-1447.567438	-1447.997488	-1448.23267
$(L_1•)Ni^{III}$-2OHM5	-1447.911231	-1447.554087	-1447.973648	-1448.216189
$(L_1•)(H_2O)Ni^{IV}=O_e$M2	-1447.559026	-1447.196549	-1447.769367	-1447.855454
$(L_1•)(H_2O)Ni^{IV}=O_e$M4	-1447.561309	-1447.20333	-1447.767961	-1447.858931
$(L_1•)(H_2O)Ni^{IV}=O_a$M2	-1447.568762	-1447.210382	-1447.772435	-1447.867662
$(L_1•)(H_2O)Ni^{IV}=O_a$M4	-1447.569271	-1447.210427	-1447.773043	-1447.867631
$(L_1•)Ni^{IV}$-2OHM2	-1447.576008	-1447.215333	-1447.779896	-1447.877718
$(L_1•)Ni^{IV}$-2OHM4	-1447.556421	-1447.201269	-1447.758857	-1447.855945
$(L_1•)(H_2O)Ni^{IV}$-OH_eM2	-1447.760351	-1447.387813	-1448.212919	-1448.055408
$(L_1•)(H_2O)Ni^{IV}$-OH_eM4	-1447.741276	-1447.374805	-1448.193146	-1448.036656
$(L_1•)(H_2O)Ni^{IV}$-OH_aM2	-1447.76139	-1447.389725	-1448.213474	-1448.057438
$(L_1•)(H_2O)Ni^{IV}$-OH_aM4	-1447.744628	-1447.377013	-1448.19187	-1448.039179
$(L_1$-H$)Ni^{I}$-$2H_2$OM2	-1448.609747	-1448.23847	-1448.669744	-1448.916487
$(L_1$-H$)Ni^{I}$-$2H_2$OM4	-1448.594486	-1448.225205	-1448.658486	-1448.90129
$(L_1$-deH$)Ni^{II}$-$2H_2$OM3	-1448.749564	-1448.381597	-1448.769972	-1449.063994
$(L_1$-H$)Ni^{II}$-$2H_2$OM3	-1448.308401	-1447.936959	-1448.514664	-1448.61008
$(L_1$-OH$)Ni^{III}$-H_2OM3	-1448.01486	-1447.652521	-1448.075592	-1448.319614
$\mathbf{1^3}$	-1753.980913	-1753.522068	-1754.175159	-1754.387735
$\mathbf{TS^3_{1\text{-}2}}$	-1753.941069	-1753.478272	-1754.144978	-1754.342269

2^3	-1753.95161	-1753.484945	-1754.159015	-1754.351771
4^2	-1447.552739	-1447.19652	-1447.758099	-1447.852988
4^4	-1447.55386	-1447.198691	-1447.759116	-1447.854128
$TS^2_{4\text{-}5}$	-1447.546297	-1447.188758	-1447.752642	-1447.844352
$TS^4_{4\text{-}5}$	-1447.54441	-1447.188539	-1447.74993	-1447.842582
5^2	-1447.551898	-1447.192983	-1447.762097	-1447.849541
5^4	-1447.549847	-1447.192177	-1447.758755	-1447.847889
7^3	-1448.235439	-1447.866024	-1448.436764	-1448.535479
7^5	-1448.2356	-1447.867599	-1448.436729	-1448.535939
$TS^3_{7\text{-}8}$	-1448.188226	-1447.819427	-1448.398174	-1448.487434
8^3	-1448.190378	-1447.816433	-1448.400561	-1448.490345
8^5	-1448.173176	-1447.80454	-1448.381226	-1448.474558
$TS^3_{8\text{-}9}$	-1448.187085	-1447.81427	-1448.399099	-1448.486952
9^3	-1448.214547	-1447.841079	-1448.430373	-1448.513771
10^3	-1371.783934	-1371.438678	-1371.995418	-1372.058105
$TS^3_{10\text{-}11}$	-1371.746164	-1371.397257	-1371.961856	-1372.019561
11^3	-1371.766276	-1371.415966	-1371.986432	-1372.04023
12^2	-1371.108876	-1370.772091	-1371.323049	-1371.381625
12^4	-1371.095199	-1370.761808	-1371.306501	-1371.368385
$TS^2_{12\text{-}13}$	-1371.074531	-1370.73508	-1371.291299	-1371.347071
13^2	-1371.092837	-1370.751625	-1371.314782	-1371.364869
13^4	-1371.081784	-1370.745777	-1371.300131	-1371.354721
15^2	-1447.570066	-1447.209206	-1447.774904	-1447.86803
15^4	-1447.562232	-1447.20575	-1447.765257	-1447.860704
$TS^2_{15\text{-}16}$	-1447.550031	-1447.189106	-1447.7565	-1447.847028
16^2	-1447.555579	-1447.19319	-1447.765108	-1447.852861
$TS^2_{16\text{-}17}$	-1447.554329	-1447.194566	-1447.765087	-1447.850814
17^2	-1447.577364	-1447.213404	-1447.791157	-1447.875254
$TS^4_{15\text{-}17}$	-1447.518827	-1447.160867	-1447.727907	-1447.816227
17^4	-1447.578166	-1447.216096	-1447.792037	-1447.876142
19^2	-1371.114497	-1370.779267	-1371.328768	-1371.386725
19^4	-1371.115606	-1370.781096	-1371.327896	-1371.388055
$TS^2_{19\text{-}20}$	-1371.103826	-1370.766483	-1371.317515	-1371.375008
$TS^4_{19\text{-}20}$	-1371.078909	-1370.742813	-1371.29316	-1371.350789
20^2	-1371.132473	-1370.792027	-1371.351418	-1371.404649
20^4	-1371.131053	-1370.793515	-1371.348302	-1371.403033
21^2	-1371.11599	-1370.777789	-1371.330003	-1371.387706

21^4	-1371.114909	-1370.778724	-1371.327857	-1371.386933
TS^2_{21-22}	-1371.110714	-1370.77632	-1371.324847	-1371.381666
TS^4_{21-22}	-1371.110913	-1370.777864	-1371.322567	-1371.381712
22^2	-1371.114765	-1370.778214	-1371.325041	-1371.387352
22^4	-1371.115502	-1370.779628	-1371.325852	-1371.388013
TS^2_{22-23}	-1371.109046	-1370.773555	-1371.321003	-1371.38177
TS^4_{22-23}	-1371.109841	-1370.774724	-1371.321744	-1371.382512
23^2	-1371.140901	-1370.80313	-1371.353448	-1371.413056
23^4	-1371.139231	-1370.802734	-1371.351173	-1371.411615
24^2	-1371.11246	-1370.776241	-1371.323838	-1371.384976
24^4	-1371.113076	-1370.777561	-1371.324369	-1371.385703
TS^2_{24-25}	-1371.109107	-1370.775479	-1371.323096	-1371.381556
TS^4_{24-25}	-1371.10892	-1370.775969	-1371.323023	-1371.381395
25^2	-1371.112964	-1370.776057	-1371.326268	-1371.387412
25^4	-1371.11247	-1370.776239	-1371.325806	-1371.386861
TS^2_{25-26}	-1371.111347	-1370.773793	-1371.326281	-1371.384116
TS^4_{25-26}	-1371.110046	-1370.773921	-1371.324488	-1371.383195
26^2	-1371.144832	-1370.807117	-1371.355842	-1371.416549
26^4	-1371.143009	-1370.806661	-1371.353658	-1371.414999
27^2	-1753.308953	-1752.860758	-1753.502394	-1753.713506
28^2	-1753.324307	-1752.871112	-1753.522302	-1753.723294
27^4	-1753.308936	-1752.861317	-1753.501895	-1753.713565
28^4	-1753.321973	-1752.869324	-1753.518825	-1753.721076
TS^4_{27-28}	-1753.302407	-1752.852439	-1753.494814	-1753.70409
TS^2_{27-28}	-1753.303944	-1752.852784	-1753.496471	-1753.705753
29^2	-1294.702508	-1294.385798	-1294.915762	-1294.950667
29^4	-1294.674246	-1294.362074	-1294.890736	-1294.922804
30^2	-1294.675863	-1294.361963	-1294.894683	-1294.92402
30^4	-1294.673313	-1294.361576	-1294.89088	-1294.922148
TS^2_{30-31}	-1294.65766	-1294.34468	-1294.874972	-1294.904639
TS^4_{30-31}	-1294.65545	-1294.344655	-1294.871937	-1294.902805
31^2	-1294.687176	-1294.373277	-1294.903203	-1294.933825
31^4	-1294.68574	-1294.373347	-1294.901149	-1294.93239
32^2	-1796.489994	-1795.975869	-1796.677506	-1796.948353
32^4	-1796.488644	-1795.976346	-1796.675038	-1796.947304
TS^2_{32-33}	-1720.014299	-1719.52756	-1720.213257	-1720.445312
TS^4_{32-33}	-1720.012032	-1719.52684	-1720.209596	-1720.4437
33^2	-1720.011703	-1719.5209	-1720.211585	-1720.443315
33^4	-1720.011431	-1719.521572	-1720.211119	-1720.443067

$TS^{2}_{33\text{-}34}$	-1720.013053	-1719.52429	-1720.211001	-1720.445255
$TS^{4}_{33\text{-}34}$	-1720.010738	-1719.521806	-1720.208437	-1720.44362
34^{2}	-1720.052604	-1719.558445	-1720.25183	-1720.480858
34^{4}	-1720.05063	-1719.557772	-1720.249614	-1720.47921