

Supporting Information

**Nickel(III)-Mediated Oxidative Cascade from a Thiol-Bearing
Nickel(II) Precursor to the Nickel(IV) Product**

Hao-Ching Chang, Sheng-Hsiang Lin, Yu-Chen Hsu, Shao-Wei Jen and Way-Zen Lee*

Department of Chemistry, National Taiwan Normal University, Taipei 11677, Taiwan

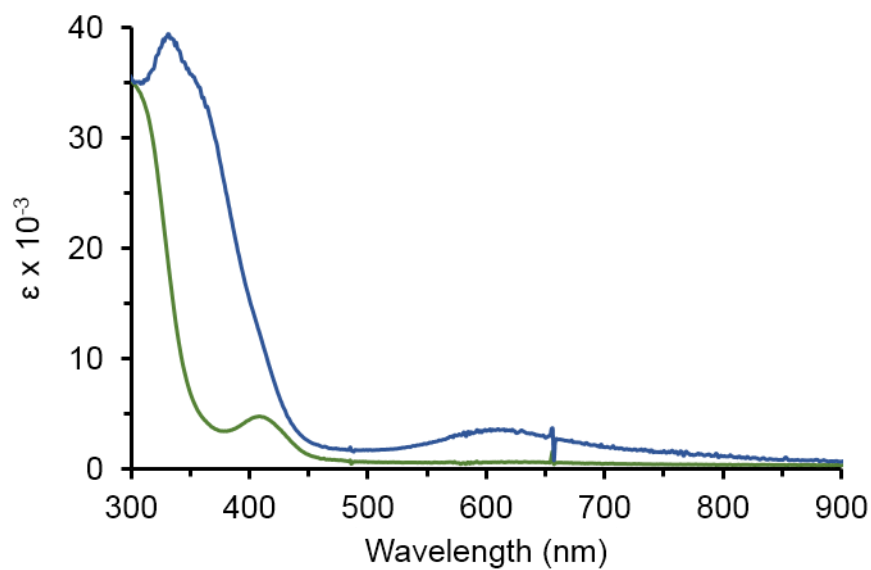


Fig. S1 UV-vis spectra of **1** (green) and **2** (blue) at room temperature.

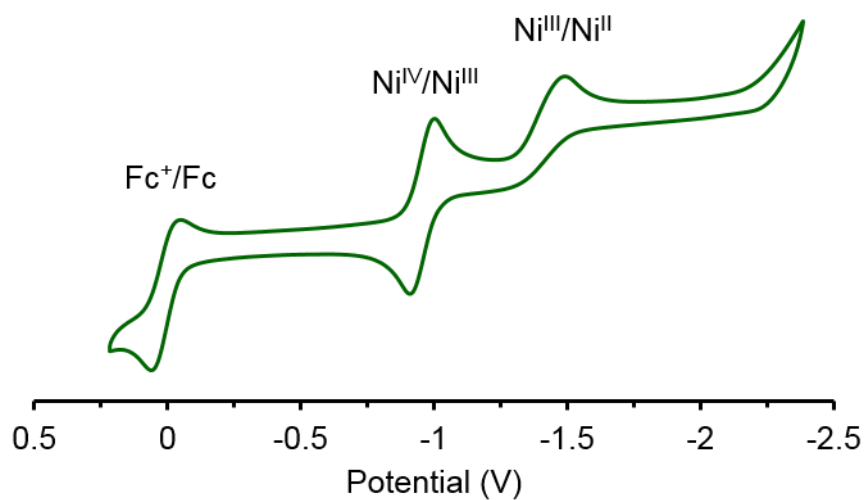


Fig. S2 Cyclic voltammetry of **2** in CH₂Cl₂, with 1 mM tetra-*n*-butylammonium tetrafluoroborate as supporting electrolyte. Potential is adjusted by internal reference of additive ferrocene.

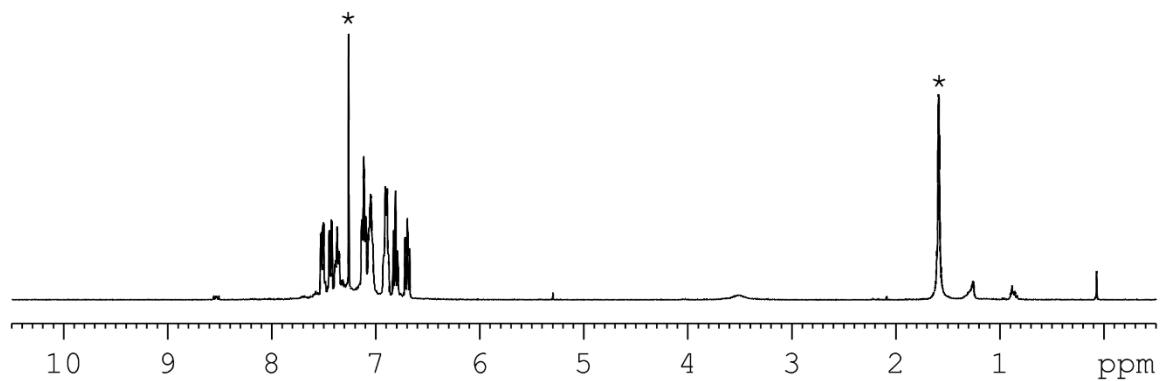


Fig. S3 ^1H NMR spectrum of **2** in CDCl_3 . Asterisks (*) label solvent residue of CHCl_3 and H_2O .

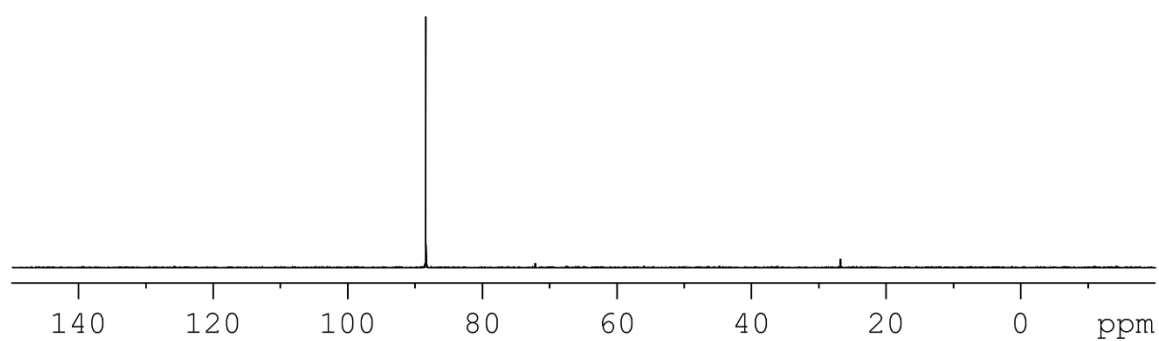


Fig. S4 ^{31}P NMR spectrum of **2** in CDCl_3 .

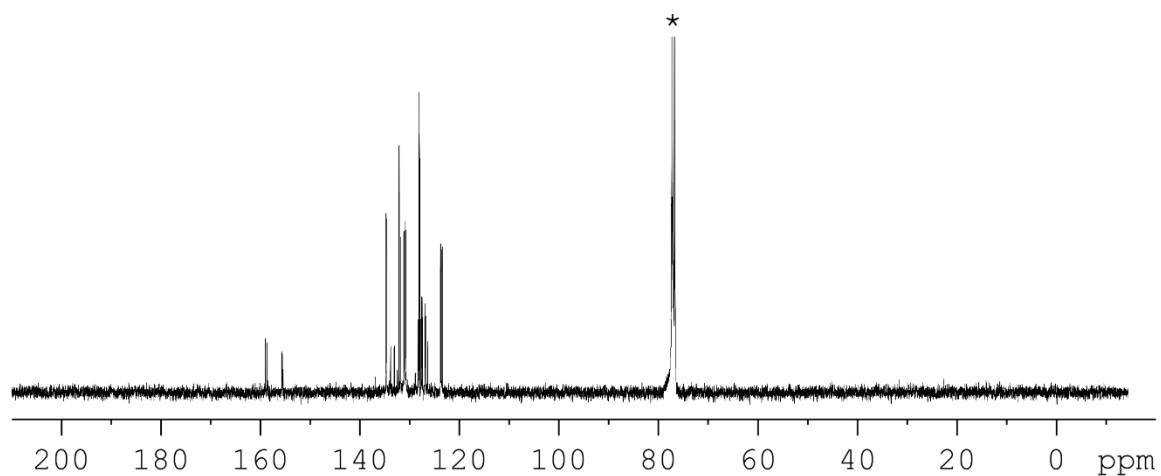


Fig. S5 ^{13}C NMR spectrum of **2** in CDCl_3 . Asterisk (*) labels solvent residue of CHCl_3 .

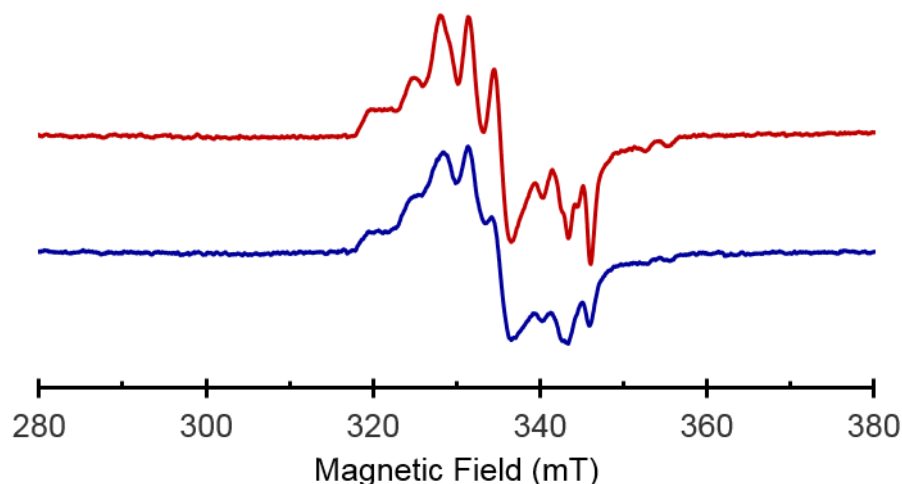


Fig. S6 77 K EPR spectra of oxygenated solution of **1'** in CH_2Cl_2 , either with additive excess DMPO (red trace) or without it (blue trace).

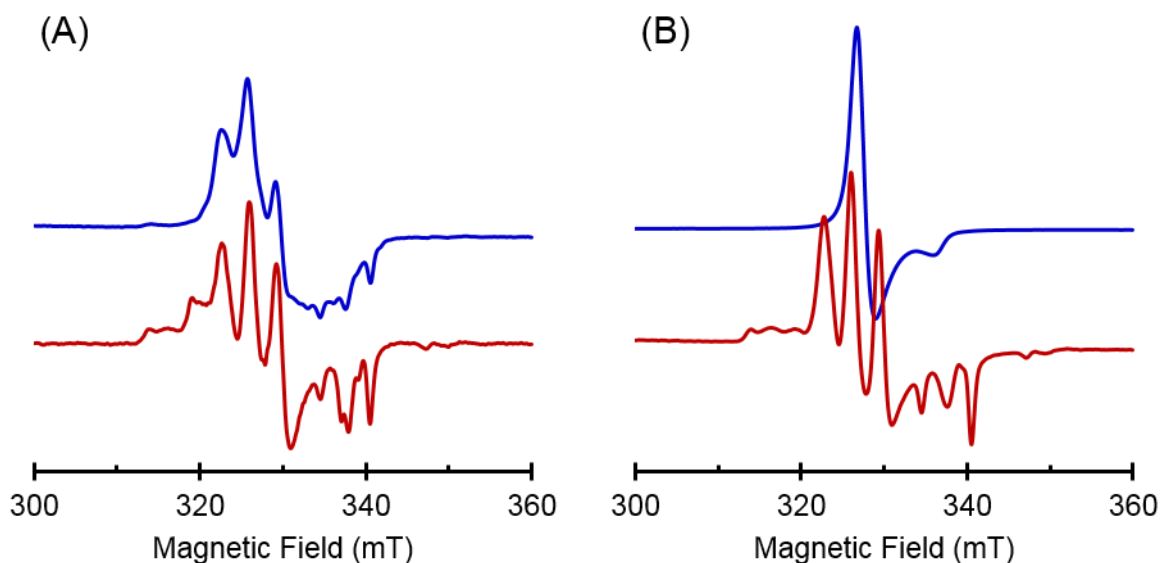


Fig. S7 77 K EPR spectra of oxygenated solution of **1'** (A) and CoCp_2 -reduced **2** (B). Samples were prepared in MeTHF (blue traces) or *n*-PrCN (red traces). Oxygenated intermediates in both solvent and reduced nickel(III) species in MeTHF are similar to that in CH_2Cl_2 (discussed in content as mixture of **3** and **4**), but reduction of **2** in *n*-PrCN showed an EPR pattern more close to intermediate **4**, probably due to protonation.

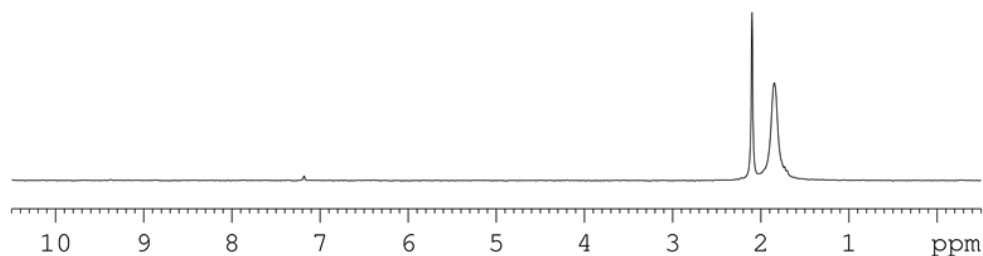


Fig. S8 ^2D NMR spectrum of oxygenation reaction solution by using deuterated **1** as starting material. Broaden peak at 1.84 ppm represents produced D_2O ; sharp peak at 2.10 ppm is CD_3CN as internal reference.

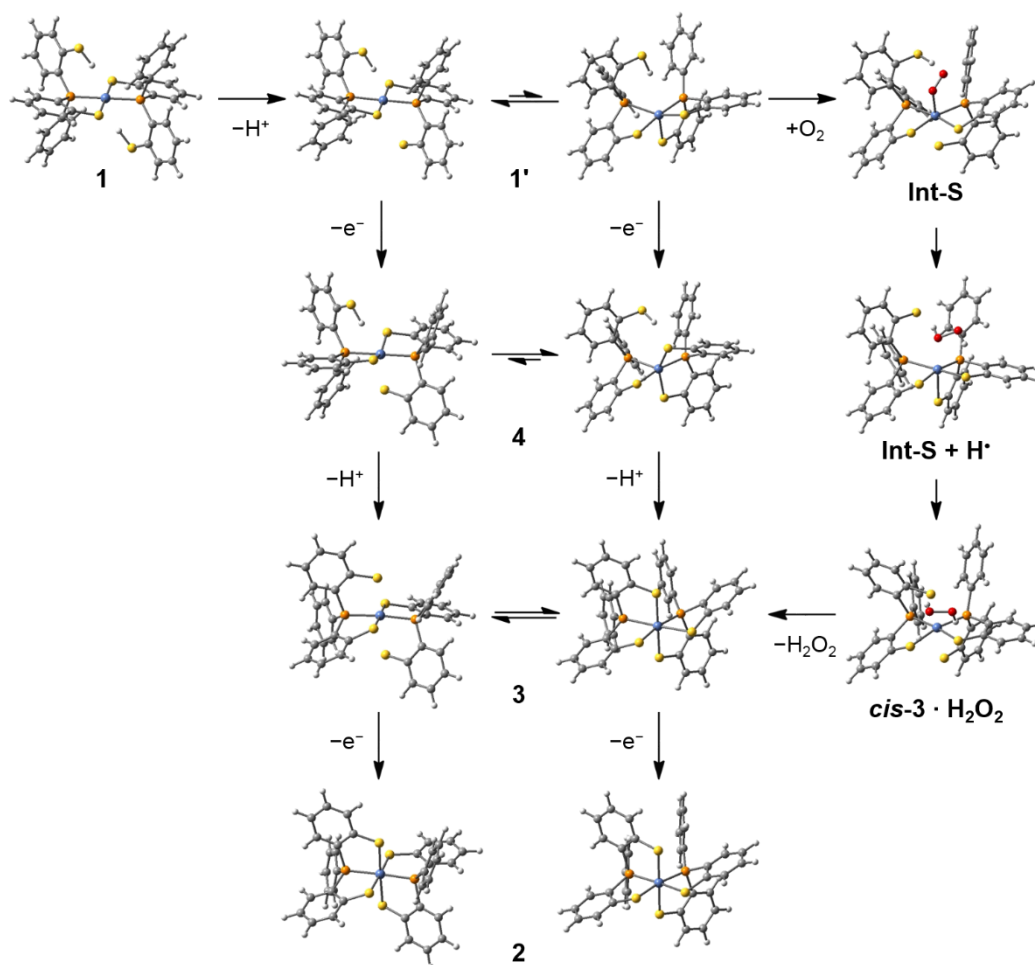


Fig. S9 Optimized species involving proposed reaction pathways. Atoms of nickel, phosphorous, sulfur, oxygen represent in blue, orange, yellow and red, respectively.

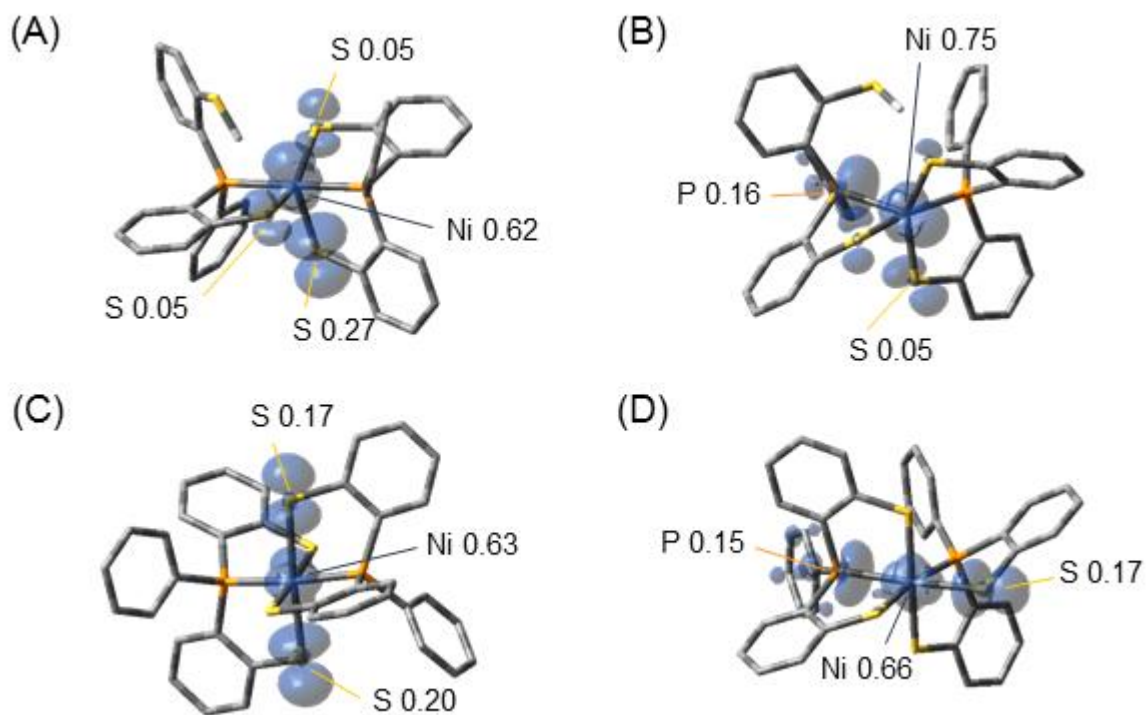


Fig. S10 Spin population of nickel(III) intermediates: *trans*-4 (A), *cis*-4 (B), *trans*-3 (C) and *cis*-3 (D). Surfaces are plotted with 0.002 e Bohr⁻³ isodensity.

Table S1 Coordinates of singlet **1**.

Ni	0.00000	0.00002	-0.00001
P	-2.22668	0.17250	0.03890
C	-2.75653	1.86592	-0.42143
C	-2.30669	2.42360	-1.63382
H	-1.65735	1.84209	-2.29371
C	-2.68006	3.71978	-1.99808
H	-2.32562	4.13806	-2.94503
C	-3.49516	4.48229	-1.15291
H	-3.78150	5.49968	-1.43645
C	-3.93660	3.93997	0.05765
H	-4.56946	4.53017	0.72730
C	-3.57154	2.63938	0.42292
H	-3.92342	2.23350	1.37333
C	-2.74312	-0.06451	1.75789
C	-4.05899	-0.32659	2.16991
H	-4.84863	-0.45599	1.42385
C	-4.36113	-0.42625	3.52964
H	-5.38452	-0.63759	3.85217
C	-3.33872	-0.25514	4.47541
H	-3.56628	-0.33105	5.54354
C	-2.02655	-0.00184	4.07228
H	-1.23585	0.11429	4.81909
C	-1.70743	0.08529	2.70296
S	-0.03968	0.36345	2.18765
C	-3.24858	-0.97051	-0.95996
C	-4.24507	-0.47085	-1.81931
H	-4.39321	0.60758	-1.89961
C	-5.06227	-1.32257	-2.56520
H	-5.83352	-0.90344	-3.21743
C	-4.88520	-2.70569	-2.46936
H	-5.51458	-3.38741	-3.04917
C	-3.88834	-3.22388	-1.64203
H	-3.73622	-4.30559	-1.58528
C	-3.06405	-2.37619	-0.88247
S	-1.89536	-3.19413	0.17350
P	2.22668	-0.17249	-0.03891
C	2.75649	-1.86592	0.42142
C	3.57150	-2.63939	-0.42292
H	3.92340	-2.23352	-1.37332

C	3.93654	-3.93999	-0.05765
H	4.56939	-4.53020	-0.72729
C	3.49508	-4.48230	1.15291
H	3.78140	-5.49970	1.43645
C	2.67998	-3.71979	1.99807
H	2.32553	-4.13806	2.94502
C	2.30663	-2.42359	1.63381
H	1.65729	-1.84208	2.29370
C	2.74313	0.06451	-1.75788
C	4.05900	0.32656	-2.16991
H	4.84865	0.45595	-1.42384
C	4.36116	0.42622	-3.52963
H	5.38455	0.63755	-3.85216
C	3.33875	0.25513	-4.47540
H	3.56631	0.33104	-5.54354
C	2.02657	0.00185	-4.07228
H	1.23587	-0.11426	-4.81910
C	1.70744	-0.08527	-2.70297
S	0.03969	-0.36339	-2.18766
C	3.24859	0.97049	0.95997
C	4.24506	0.47082	1.81933
H	4.39317	-0.60761	1.89964
C	5.06225	1.32253	2.56524
H	5.83349	0.90338	3.21748
C	4.88521	2.70565	2.46939
H	5.51460	3.38736	3.04921
C	3.88838	3.22386	1.64204
H	3.73628	4.30558	1.58528
C	3.06409	2.37618	0.88247
S	1.89543	3.19415	-0.17352
H	0.97525	2.18783	-0.25127
H	-0.97516	-2.18782	0.25118

Table S2 Coordinates of singlet *cis*-2.

Ni	0.00000	-1.27278	0.00000
P	1.78385	0.11408	-0.06945
C	1.79485	1.75035	0.72390
C	1.94316	1.84889	2.12292
H	2.03486	0.94468	2.72713
C	1.98121	3.09974	2.74153
H	2.10075	3.16211	3.82713
C	1.87714	4.26804	1.97585
H	1.91733	5.24750	2.46202
C	1.72144	4.17879	0.58963
H	1.63349	5.08604	-0.01485
C	1.67015	2.92834	-0.03411
H	1.53810	2.87627	-1.11624
C	2.15022	0.36192	-1.82694
C	3.27301	1.09078	-2.26513
H	3.94765	1.54471	-1.53406
C	3.53615	1.23523	-3.62478
H	4.41189	1.79815	-3.95898
C	2.66738	0.64591	-4.55883
H	2.86301	0.75418	-5.63032
C	1.56003	-0.08485	-4.13842
H	0.89868	-0.54837	-4.87585
C	1.28468	-0.24623	-2.76100
S	-0.09245	-1.22172	-2.28396
C	3.17374	-0.80159	0.64614
C	4.36118	-0.19725	1.08997
H	4.45216	0.89192	1.10171
C	5.43126	-0.98417	1.52052
H	6.35420	-0.51171	1.86779
C	5.30735	-2.38100	1.50791
H	6.13853	-3.00594	1.84952
C	4.12791	-2.98971	1.07729
H	4.03860	-4.07955	1.08574
C	3.04137	-2.20683	0.63769
S	1.57202	-2.97518	0.06012
P	-1.78385	0.11408	0.06945
C	-1.79485	1.75035	-0.72389
C	-1.94316	1.84890	-2.12292
H	-2.03486	0.94469	-2.72713

C	-1.98122	3.09974	-2.74152
H	-2.10075	3.16212	-3.82712
C	-1.87714	4.26804	-1.97584
H	-1.91734	5.24751	-2.46201
C	-1.72144	4.17880	-0.58962
H	-1.63349	5.08604	0.01486
C	-1.67015	2.92834	0.03412
H	-1.53810	2.87627	1.11625
C	-3.17374	-0.80159	-0.64614
C	-4.36118	-0.19725	-1.08997
H	-4.45216	0.89192	-1.10170
C	-5.43126	-0.98417	-1.52052
H	-6.35420	-0.51171	-1.86778
C	-5.30735	-2.38099	-1.50792
H	-6.13853	-3.00593	-1.84953
C	-4.12791	-2.98971	-1.07730
H	-4.03860	-4.07954	-1.08575
C	-3.04137	-2.20683	-0.63770
S	-1.57202	-2.97518	-0.06013
C	-2.15022	0.36191	1.82695
C	-3.27301	1.09077	2.26513
H	-3.94765	1.54471	1.53407
C	-3.53615	1.23522	3.62478
H	-4.41189	1.79814	3.95898
C	-2.66738	0.64590	4.55884
H	-2.86301	0.75416	5.63032
C	-1.56003	-0.08486	4.13842
H	-0.89867	-0.54839	4.87585
C	-1.28468	-0.24624	2.76100
S	0.09245	-1.22173	2.28396

Table S3 Coordinates of singlet *trans*-2.

Ni	-0.00002	-0.04654	0.00004
P	2.23772	-0.00609	0.09999
C	3.17576	-0.23114	-1.43700
C	3.41701	0.86579	-2.28660
H	3.08968	1.86648	-1.99559
C	4.07409	0.68160	-3.50498
H	4.25727	1.54218	-4.15536
C	4.49220	-0.59588	-3.89316
H	5.00755	-0.73762	-4.84825
C	4.24587	-1.69200	-3.06038
H	4.56467	-2.69449	-3.36147
C	3.58773	-1.51469	-1.84081
H	3.39391	-2.37827	-1.20080
C	2.71452	-1.32077	1.24189
C	4.06049	-1.61434	1.53335
H	4.85761	-1.05725	1.03195
C	4.38667	-2.60774	2.45106
H	5.43352	-2.83206	2.67407
C	3.35220	-3.31736	3.08606
H	3.59461	-4.10403	3.80806
C	2.01942	-3.03561	2.81002
H	1.22489	-3.59526	3.31138
C	1.66880	-2.02406	1.88344
S	-0.02215	-1.69222	1.60873
C	2.70899	1.59205	0.80030
C	4.00982	2.11986	0.75732
H	4.79371	1.59534	0.20338
C	4.30664	3.31575	1.41097
H	5.31886	3.72806	1.37253
C	3.29066	3.98386	2.11130
H	3.51049	4.92726	2.62177
C	1.99621	3.47029	2.15732
H	1.21079	4.00699	2.69653
C	1.68160	2.25956	1.50405
S	0.06646	1.59729	1.63127
P	-2.23774	-0.00614	-0.09998
C	-3.17578	-0.23089	1.43707
C	-3.41681	0.86619	2.28653
H	-3.08934	1.86679	1.99537

C	-4.07385	0.68226	3.50498
H	-4.25684	1.54294	4.15527
C	-4.49213	-0.59512	3.89334
H	-5.00745	-0.73666	4.84848
C	-4.24603	-1.69138	3.06068
H	-4.56498	-2.69378	3.36191
C	-3.58793	-1.51432	1.84105
H	-3.39427	-2.37801	1.20114
C	-2.70899	1.59187	-0.80061
C	-4.00974	2.11984	-0.75754
H	-4.79360	1.59558	-0.20332
C	-4.30653	3.31559	-1.41147
H	-5.31869	3.72804	-1.37298
C	-3.29059	3.98338	-2.11217
H	-3.51040	4.92666	-2.62287
C	-1.99621	3.46964	-2.15826
H	-1.21082	4.00610	-2.69774
C	-1.68163	2.25907	-1.50470
S	-0.06660	1.59652	-1.63200
C	-2.71453	-1.32100	-1.24166
C	-4.06049	-1.61447	-1.53326
H	-4.85762	-1.05717	-1.03212
C	-4.38665	-2.60803	-2.45080
H	-5.43350	-2.83227	-2.67393
C	-3.35218	-3.31792	-3.08549
H	-3.59457	-4.10471	-3.80736
C	-2.01941	-3.03628	-2.80930
H	-1.22487	-3.59614	-3.31041
C	-1.66880	-2.02458	-1.88288
S	0.02215	-1.69295	-1.60793

Table S4 Coordinates of triplet *cis-1'*.

Ni	-0.09249	-1.16444	-0.77901
P	-2.05320	0.02478	0.00466
C	-2.31698	1.83515	0.14160
C	-2.86560	2.57019	-0.92706
H	-3.22833	2.05068	-1.81721
C	-2.95772	3.96478	-0.86362
H	-3.39167	4.51531	-1.70424
C	-2.50337	4.65202	0.26721
H	-2.57945	5.74259	0.31763
C	-1.94682	3.93343	1.33188
H	-1.58220	4.45926	2.21980
C	-1.84844	2.54074	1.26769
H	-1.40265	1.99826	2.10516
C	-2.44643	-0.64210	1.65574
C	-3.43151	-0.08515	2.49309
H	-3.96397	0.81603	2.17602
C	-3.73745	-0.65219	3.73040
H	-4.50541	-0.20464	4.36829
C	-3.04487	-1.80220	4.14028
H	-3.26989	-2.26259	5.10836
C	-2.06388	-2.36302	3.32662
H	-1.52519	-3.25516	3.65982
C	-1.73549	-1.80270	2.06751
S	-0.48410	-2.56238	1.09540
C	-3.39735	-0.53648	-1.10186
C	-4.74522	-0.23143	-0.83862
H	-5.00371	0.34086	0.05688
C	-5.76319	-0.63963	-1.69986
H	-6.80628	-0.39552	-1.47769
C	-5.42658	-1.36614	-2.85251
H	-6.21079	-1.69408	-3.54321
C	-4.09774	-1.68226	-3.12372
H	-3.84701	-2.25776	-4.01956
C	-3.05115	-1.28515	-2.25655
S	-1.40003	-1.75794	-2.64084
P	1.93353	0.05900	0.03912
C	1.97501	1.13023	1.53040
C	2.67126	2.34821	1.60239
H	3.24737	2.70218	0.74410

C	2.63740	3.11882	2.77093
H	3.18429	4.06625	2.80967
C	1.91453	2.67942	3.88465
H	1.89252	3.28095	4.79880
C	1.21892	1.46498	3.82370
H	0.65044	1.11227	4.68987
C	1.24187	0.70087	2.65383
H	0.69016	-0.24319	2.60885
C	3.02617	-1.33612	0.45872
C	3.96526	-1.30563	1.50159
H	4.05882	-0.40867	2.11992
C	4.78664	-2.40685	1.75843
H	5.51299	-2.37344	2.57607
C	4.66540	-3.55061	0.95659
H	5.30084	-4.42241	1.14612
C	3.73152	-3.59439	-0.07918
H	3.63515	-4.49661	-0.69032
C	2.88791	-2.49481	-0.35220
S	1.71389	-2.56016	-1.65806
C	2.90357	1.00636	-1.22074
C	4.23888	0.64973	-1.49124
H	4.68893	-0.17660	-0.93803
C	5.00881	1.32239	-2.44207
H	6.04368	1.01584	-2.62020
C	4.44646	2.38183	-3.16016
H	5.03237	2.91892	-3.91236
C	3.12240	2.74846	-2.92404
H	2.67404	3.56679	-3.49579
C	2.34380	2.07478	-1.96540
S	0.69966	2.70687	-1.76146
H	0.18283	1.65680	-1.07822

Table S5 Coordinates of singlet *trans-1'*.

Ni	-0.01970	0.07793	-0.00332
P	-2.24932	-0.06384	-0.02694
C	-2.80015	-1.73460	0.53383
C	-2.44481	-2.17202	1.82534
H	-1.86934	-1.51297	2.48102
C	-2.81091	-3.44292	2.27655
H	-2.52742	-3.76140	3.28474
C	-3.53004	-4.30759	1.44208
H	-3.81255	-5.30490	1.79384
C	-3.88001	-3.88890	0.15528
H	-4.43842	-4.55720	-0.50791
C	-3.51913	-2.61300	-0.29509
H	-3.80232	-2.30549	-1.30362
C	-2.76344	0.01176	-1.76703
C	-4.07967	0.23011	-2.19719
H	-4.86296	0.43087	-1.45991
C	-4.39205	0.19986	-3.55923
H	-5.41811	0.38032	-3.89349
C	-3.37647	-0.06121	-4.49112
H	-3.60964	-0.08818	-5.56081
C	-2.06248	-0.27596	-4.06998
H	-1.27484	-0.46523	-4.80564
C	-1.73605	-0.23328	-2.69976
S	-0.07146	-0.47312	-2.16413
C	-3.25886	1.11416	0.90917
C	-4.28993	0.71184	1.77905
H	-4.51046	-0.35118	1.90326
C	-5.04190	1.65027	2.48634
H	-5.84332	1.32409	3.15614
C	-4.75182	3.01538	2.32276
H	-5.32979	3.76656	2.87294
C	-3.73546	3.42707	1.46603
H	-3.52188	4.49359	1.34641
C	-2.95533	2.50009	0.72303
S	-1.70644	3.01866	-0.37006
P	2.20335	0.17709	0.02817
C	2.84062	1.80080	-0.54023
C	3.89348	2.46523	0.11264
H	4.36405	2.02248	0.99290

C	4.34479	3.70554	-0.35087
H	5.16276	4.21192	0.17089
C	3.75104	4.29726	-1.47071
H	4.10307	5.26926	-1.83017
C	2.69816	3.64573	-2.12259
H	2.22020	4.10610	-2.99256
C	2.24047	2.40912	-1.65802
H	1.40767	1.91218	-2.16285
C	2.72804	0.00481	1.75513
C	4.03575	-0.28648	2.17458
H	4.81351	-0.48683	1.43141
C	4.34753	-0.32927	3.53511
H	5.36553	-0.56129	3.86111
C	3.33860	-0.07212	4.47707
H	3.57184	-0.09939	5.54667
C	2.03332	0.20195	4.06904
H	1.25224	0.38077	4.81394
C	1.70035	0.22953	2.69771
S	0.04036	0.51880	2.18363
C	3.16842	-1.07756	-0.89774
C	4.17336	-0.68911	-1.80251
H	4.37026	0.37328	-1.95965
C	4.93787	-1.63001	-2.49633
H	5.71805	-1.29601	-3.18635
C	4.69707	-2.99289	-2.30029
H	5.28535	-3.74339	-2.83703
C	3.68686	-3.40228	-1.42884
H	3.48150	-4.46854	-1.29611
C	2.91457	-2.46361	-0.72331
S	1.70582	-3.13727	0.38856
H	0.84318	-2.06942	0.38799

Table S6 Coordinates of doublet *cis-3*.

Ni	0.15080	-1.24248	-0.13111
P	1.87852	0.19810	-0.04909
C	1.64379	1.87282	0.64365
C	1.56587	2.05706	2.03864
H	1.66869	1.19896	2.70609
C	1.36293	3.33103	2.57560
H	1.31225	3.45768	3.66146
C	1.22990	4.43991	1.73102
H	1.07676	5.43781	2.15377
C	1.28917	4.26467	0.34505
H	1.17816	5.12338	-0.32384
C	1.48992	2.99059	-0.19579
H	1.53136	2.86995	-1.28024
C	2.44970	0.44075	-1.75881
C	3.62420	1.14605	-2.07630
H	4.23812	1.56602	-1.27374
C	4.01544	1.31403	-3.40377
H	4.93146	1.86100	-3.64505
C	3.22000	0.76667	-4.42510
H	3.51541	0.89011	-5.47237
C	2.06147	0.05642	-4.12173
H	1.45961	-0.37739	-4.92582
C	1.65375	-0.12548	-2.77857
S	0.21657	-1.06400	-2.42166
C	3.26781	-0.54026	0.85294
C	4.26340	0.20920	1.50143
H	4.19363	1.29991	1.52875
C	5.34737	-0.42417	2.11327
H	6.11945	0.16678	2.61470
C	5.42865	-1.82459	2.07586
H	6.27043	-2.33595	2.55519
C	4.44422	-2.57791	1.43828
H	4.51696	-3.66925	1.42188
C	3.34063	-1.95951	0.80432
S	2.12332	-2.89978	-0.03037
P	-1.89767	0.05706	0.04021
C	-2.21803	1.77052	-0.51284
C	-2.25813	2.03507	-1.89813
H	-2.16183	1.21179	-2.61117

C	-2.42452	3.33823	-2.37265
H	-2.45996	3.52016	-3.45145
C	-2.54596	4.40628	-1.47451
H	-2.68033	5.42682	-1.84654
C	-2.49038	4.15826	-0.09957
H	-2.57720	4.98537	0.61210
C	-2.32280	2.85358	0.37817
H	-2.27430	2.68220	1.45558
C	-3.16071	-0.94997	-0.80609
C	-4.39484	-0.44930	-1.25301
H	-4.62153	0.61379	-1.13320
C	-5.33944	-1.28716	-1.85045
H	-6.29714	-0.88277	-2.19164
C	-5.04156	-2.64838	-2.00795
H	-5.76831	-3.31857	-2.47927
C	-3.81733	-3.15883	-1.57790
H	-3.59022	-4.22006	-1.71633
C	-2.85345	-2.32679	-0.96463
S	-1.34754	-3.02750	-0.38872
C	-2.33953	-0.01266	1.80601
C	-3.56802	0.46580	2.30059
H	-4.29628	0.89258	1.60418
C	-3.87446	0.40699	3.65864
H	-4.83357	0.78287	4.02699
C	-2.93363	-0.14477	4.54420
H	-3.15418	-0.19747	5.61565
C	-1.72228	-0.63950	4.07104
H	-1.00583	-1.08264	4.76915
C	-1.39958	-0.59747	2.69179
S	0.12089	-1.31397	2.18281

Table S7 Coordinates of doublet *trans*-3.

Ni	-0.00402	-0.13064	0.10040	C	-3.67337	3.26748	1.95021
P	2.22428	-0.00132	0.05573	H	-3.61601	4.35237	1.81504
C	3.15548	-1.53770	-0.29757	C	-4.34396	2.72955	3.05513
C	3.13634	-2.07047	-1.60111	H	-4.82039	3.39199	3.78576
H	2.61826	-1.53416	-2.40074	C	-4.39166	1.34335	3.22738
C	3.76563	-3.28492	-1.88142	H	-4.90306	0.91369	4.09515
H	3.73865	-3.68454	-2.90036	C	-3.78176	0.49594	2.29629
C	4.41528	-3.99388	-0.86427	H	-3.81795	-0.58599	2.44258
H	4.90404	-4.94895	-1.08450	C	-2.67000	0.56687	-1.66187
C	4.42545	-3.48177	0.43602	C	-3.89025	1.15510	-2.01767
H	4.92051	-4.03432	1.24150	H	-4.63573	1.36943	-1.24574
C	3.79766	-2.26409	0.71910	C	-4.15884	1.47812	-3.35130
H	3.80363	-1.87790	1.74082	H	-5.10980	1.94539	-3.62577
C	2.75707	0.56634	1.69278	C	-3.19145	1.19944	-4.32779
C	4.08712	0.91661	1.97983	H	-3.38654	1.45221	-5.37629
H	4.83894	0.86808	1.18547	C	-1.97119	0.61963	-3.98166
C	4.45566	1.32999	3.25878	H	-1.21651	0.42361	-4.74887
H	5.49242	1.60540	3.47602	C	-1.68202	0.29587	-2.63825
C	3.47080	1.39587	4.26076	S	-0.17095	-0.46801	-2.19973
H	3.74286	1.72082	5.27167	C	-2.90437	-1.71085	0.15060
C	2.14870	1.06613	3.98502	C	-4.28588	-1.94890	0.01444
H	1.38888	1.13632	4.76905	H	-4.95770	-1.10786	-0.18621
C	1.75425	0.64679	2.68884	C	-4.81387	-3.23123	0.12789
S	0.08664	0.26194	2.37405	H	-5.88921	-3.40265	0.01772
C	2.78925	1.22702	-1.14852	C	-3.93330	-4.30063	0.38065
C	3.99759	1.16122	-1.85766	H	-4.32629	-5.31999	0.47401
H	4.65125	0.29234	-1.73757	C	-2.56871	-4.08485	0.50609
C	4.37391	2.19643	-2.71698	H	-1.89520	-4.92623	0.69319
H	5.31738	2.14075	-3.26935	C	-1.99617	-2.78504	0.39005
C	3.52158	3.30249	-2.86281	S	-0.28152	-2.59194	0.53965
H	3.80055	4.11924	-3.53903				
C	2.31794	3.37536	-2.16555				
H	1.65763	4.23798	-2.29371				
C	1.91678	2.34448	-1.28152				
S	0.44868	2.43829	-0.35501				
P	-2.22824	-0.03954	-0.00748				
C	-3.12208	1.02668	1.17535				
C	-3.06259	2.42492	1.01938				
H	-2.52441	2.85492	0.16994				

Table S8 Coordinates of doublet *cis-4*.

Ni	-0.17134	-0.48390	-1.19816
P	-2.05690	-0.09657	-0.02678
C	-2.16391	1.13501	1.30976
C	-2.65474	2.43045	1.06527
H	-2.99582	2.71225	0.06676
C	-2.71900	3.36637	2.10182
H	-3.10676	4.36928	1.90059
C	-2.29417	3.02092	3.38929
H	-2.34676	3.75463	4.19929
C	-1.80263	1.73425	3.63893
H	-1.46774	1.45744	4.64282
C	-1.73587	0.79595	2.60668
H	-1.35067	-0.20423	2.81609
C	-2.63780	-1.65436	0.67703
C	-3.73969	-1.76771	1.54340
H	-4.27399	-0.87183	1.87135
C	-4.15129	-3.02251	1.99371
H	-5.01127	-3.11080	2.66320
C	-3.44996	-4.16620	1.58123
H	-3.76389	-5.15411	1.93280
C	-2.34464	-4.06101	0.73725
H	-1.79740	-4.95866	0.43608
C	-1.91495	-2.79892	0.27726
S	-0.50462	-2.68068	-0.77376
C	-3.19421	0.48831	-1.31399
C	-4.58884	0.34963	-1.26269
H	-5.05531	-0.20902	-0.44684
C	-5.38604	0.91754	-2.25938
H	-6.47241	0.79727	-2.22805
C	-4.77991	1.63732	-3.29867
H	-5.39710	2.08719	-4.08275
C	-3.39133	1.77689	-3.35768
H	-2.92974	2.32658	-4.18267
C	-2.57562	1.19412	-2.36948
S	-0.81175	1.33533	-2.46252
P	1.81336	-0.02480	0.09112
C	1.86946	-0.18275	1.91334
C	2.51302	0.74334	2.75023
H	3.01054	1.61809	2.32635

C	2.53249	0.55036	4.13615
H	3.03861	1.28043	4.77503
C	1.91489	-0.56984	4.70156
H	1.93446	-0.72004	5.78529
C	1.27473	-1.50050	3.87383
H	0.79226	-2.38215	4.30649
C	1.24652	-1.30606	2.49055
H	0.74173	-2.03812	1.85287
C	2.84098	-1.41530	-0.49841
C	3.82224	-2.06092	0.26664
H	3.98824	-1.76435	1.30553
C	4.59891	-3.08044	-0.29414
H	5.36190	-3.58133	0.30860
C	4.39213	-3.45260	-1.62838
H	4.99408	-4.25103	-2.07372
C	3.40676	-2.82543	-2.39608
H	3.23626	-3.13557	-3.43077
C	2.61503	-1.80552	-1.83902
S	1.37880	-0.98073	-2.79167
C	2.82815	1.46255	-0.32288
C	4.12459	1.29518	-0.84396
H	4.51728	0.29093	-1.00766
C	4.93767	2.39084	-1.14664
H	5.94377	2.22352	-1.54190
C	4.46380	3.68736	-0.93903
H	5.09086	4.55336	-1.17092
C	3.17038	3.87627	-0.44627
H	2.78154	4.88713	-0.30017
C	2.34466	2.78255	-0.14445
S	0.73490	3.13935	0.53914
H	-0.00025	2.58953	-0.47611

Table S9 Coordinates of doublet *trans*-4.

Ni	-0.13134	0.04696	-0.00254
P	-2.35086	-0.02633	-0.05808
C	-3.14825	-1.55400	0.52296
C	-3.39787	-1.75508	1.89403
H	-3.17184	-0.96552	2.61414
C	-3.93661	-2.96392	2.34161
H	-4.13040	-3.10646	3.40907
C	-4.22224	-3.98750	1.43201
H	-4.64271	-4.93411	1.78563
C	-3.96634	-3.79930	0.06951
H	-4.18451	-4.59737	-0.64669
C	-3.43147	-2.59139	-0.38443
H	-3.23400	-2.45486	-1.45044
C	-2.82790	0.17621	-1.79499
C	-4.14036	0.44373	-2.21216
H	-4.93422	0.57107	-1.47016
C	-4.43419	0.55809	-3.57146
H	-5.45570	0.77408	-3.89730
C	-3.40560	0.40182	-4.51276
H	-3.62664	0.49258	-5.58128
C	-2.09761	0.14290	-4.10474
H	-1.30006	0.03441	-4.84497
C	-1.78752	0.02829	-2.73423
S	-0.13503	-0.30558	-2.22502
C	-3.00147	1.35775	0.89120
C	-4.31299	1.43645	1.38979
H	-4.99182	0.58596	1.27818
C	-4.75207	2.59361	2.03250
H	-5.77158	2.65399	2.42388
C	-3.86803	3.67548	2.17229
H	-4.20089	4.58711	2.67966
C	-2.56541	3.60461	1.68417
H	-1.88389	4.45054	1.80935
C	-2.09980	2.44178	1.03092
S	-0.47296	2.37239	0.39024
P	2.14513	0.12530	0.05075
C	2.73439	1.82286	-0.27558
C	3.43133	2.57073	0.68699
H	3.66316	2.13716	1.66120

C	3.82240	3.88554	0.41226
H	4.36210	4.45691	1.17373
C	3.51920	4.46815	-0.82066
H	3.82405	5.49787	-1.03201
C	2.81027	3.73464	-1.77876
H	2.55132	4.18891	-2.73987
C	2.41141	2.42499	-1.50736
H	1.83284	1.87203	-2.25270
C	2.64566	-0.32909	1.72908
C	3.98881	-0.41412	2.13659
H	4.78866	-0.21492	1.41701
C	4.30665	-0.75173	3.45084
H	5.35200	-0.81205	3.76686
C	3.27082	-1.01126	4.36250
H	3.50946	-1.27148	5.39888
C	1.93832	-0.95519	3.96198
H	1.13912	-1.17847	4.67401
C	1.60207	-0.63091	2.63001
S	-0.07961	-0.71748	2.12423
C	3.10391	-0.96894	-1.06634
C	4.08346	-0.41897	-1.91772
H	4.25737	0.65778	-1.90811
C	4.84967	-1.21153	-2.77104
H	5.60378	-0.74861	-3.41385
C	4.64023	-2.59335	-2.79478
H	5.22558	-3.23345	-3.46213
C	3.67443	-3.16127	-1.96880
H	3.50534	-4.24204	-1.99451
C	2.89887	-2.37524	-1.09441
S	1.79062	-3.31484	-0.08737
H	1.01150	-2.32154	0.42389

Table S10 Coordinates of triplet **Int-S**.

Ni	-0.12581	-1.10009	-0.63070
P	-1.98998	0.12148	0.00568
C	-2.07059	1.93900	0.22270
C	-2.30687	2.78939	-0.87536
H	-2.46102	2.36455	-1.86832
C	-2.34037	4.17644	-0.70758
H	-2.53270	4.81960	-1.57181
C	-2.12664	4.74092	0.55561
H	-2.15034	5.82745	0.68439
C	-1.88113	3.90696	1.65070
H	-1.70980	4.33610	2.64264
C	-1.85606	2.51834	1.48652
H	-1.67503	1.88356	2.35549
C	-2.56836	-0.56203	1.59500
C	-3.78704	-0.11188	2.14303
H	-4.36074	0.65900	1.62022
C	-4.28223	-0.63005	3.33609
H	-5.23215	-0.27184	3.74361
C	-3.54199	-1.62313	4.00145
H	-3.91313	-2.04528	4.94164
C	-2.34032	-2.08008	3.47388
H	-1.77618	-2.85640	3.99889
C	-1.81421	-1.57134	2.25526
S	-0.30080	-2.19692	1.65073
C	-3.31920	-0.28987	-1.17524
C	-4.49900	0.44552	-1.36454
H	-4.64279	1.39572	-0.84408
C	-5.49970	-0.02379	-2.22092
H	-6.41275	0.56015	-2.36921
C	-5.31810	-1.24329	-2.88752
H	-6.09184	-1.61759	-3.56593
C	-4.15024	-1.98490	-2.70348
H	-4.01307	-2.93221	-3.23325
C	-3.13498	-1.52017	-1.84224
S	-1.69913	-2.49414	-1.56291
P	1.85516	-0.03505	0.07332
C	2.00721	1.10534	1.50974
C	3.02257	2.07740	1.57791
H	3.71144	2.21588	0.74198

C	3.16678	2.87809	2.71482
H	3.96194	3.62943	2.74803
C	2.30254	2.71906	3.80394
H	2.41669	3.34643	4.69350
C	1.29519	1.75097	3.74802
H	0.61644	1.61295	4.59537
C	1.14688	0.95134	2.60946
H	0.37382	0.18011	2.58318
C	2.88480	-1.46240	0.57782
C	3.89599	-1.40655	1.54647
H	4.07407	-0.47903	2.09629
C	4.68311	-2.53110	1.81576
H	5.46469	-2.48319	2.57966
C	4.45644	-3.71595	1.10333
H	5.06434	-4.60334	1.30821
C	3.44426	-3.78446	0.14293
H	3.26049	-4.71903	-0.39488
C	2.63849	-2.66119	-0.12901
S	1.37713	-2.72161	-1.35257
C	2.87416	0.76495	-1.25227
C	4.01332	0.09670	-1.73762
H	4.27699	-0.88240	-1.33656
C	4.83629	0.66412	-2.71454
H	5.71655	0.11641	-3.06386
C	4.53327	1.92481	-3.23125
H	5.17124	2.38349	-3.99283
C	3.39371	2.59522	-2.78018
H	3.13441	3.57360	-3.19271
C	2.55258	2.02775	-1.81020
S	1.14030	2.98837	-1.29051
H	0.18397	2.13433	-1.78700
O	0.01535	-0.24182	-2.59021
O	-0.64707	0.85750	-2.83288

Table S11 Coordinates of doublet **Int-S+H[•]**,
hydrogen abstraction product of **Int-S**.

Ni	-0.16282	-0.93612	-0.88983
P	-1.93995	0.14434	0.08006
C	-2.15421	1.95341	0.06363
C	-2.91782	2.58031	-0.93706
H	-3.40345	1.98035	-1.70891
C	-3.05245	3.97027	-0.95770
H	-3.64778	4.44336	-1.74516
C	-2.42108	4.75288	0.01463
H	-2.52321	5.84293	-0.00555
C	-1.63955	4.14001	0.99813
H	-1.11625	4.74507	1.74447
C	-1.49548	2.75077	1.01742
H	-0.86418	2.28744	1.77865
C	-2.09852	-0.37470	1.81355
C	-2.84477	0.32279	2.77788
H	-3.27561	1.29664	2.52989
C	-3.04336	-0.21158	4.05151
H	-3.62381	0.34030	4.79722
C	-2.49273	-1.46701	4.35599
H	-2.64442	-1.90324	5.35004
C	-1.74686	-2.16528	3.41079
H	-1.31251	-3.13773	3.66077
C	-1.52023	-1.63573	2.11570
S	-0.54105	-2.50229	0.96353
C	-3.44827	-0.52306	-0.70489
C	-4.73409	-0.16467	-0.26497
H	-4.84443	0.55095	0.55482
C	-5.87081	-0.71186	-0.85734
H	-6.86749	-0.42682	-0.50661
C	-5.71741	-1.63911	-1.90064
H	-6.60100	-2.08204	-2.37362
C	-4.44964	-2.00965	-2.33791
H	-4.33638	-2.73958	-3.14464
C	-3.28736	-1.45590	-1.75064
S	-1.70946	-1.94854	-2.33107
P	1.87150	0.00230	0.05340
C	1.92231	0.79664	1.71550

C	2.54982	2.03358	1.94268
H	3.00596	2.57404	1.11343
C	2.59046	2.58214	3.22816
H	3.08441	3.54702	3.38418
C	2.00138	1.91048	4.30535
H	2.02913	2.34703	5.30972
C	1.38154	0.67612	4.08979
H	0.91852	0.13414	4.92042
C	1.34661	0.12176	2.80572
H	0.88055	-0.85324	2.65131
C	2.80184	-1.55376	0.34189
C	3.77637	-1.72939	1.33089
H	3.96418	-0.93126	2.05399
C	4.51635	-2.91546	1.39979
H	5.26864	-3.04889	2.18371
C	4.28022	-3.92650	0.46051
H	4.84925	-4.86185	0.50651
C	3.30664	-3.76388	-0.52733
H	3.10918	-4.56480	-1.24565
C	2.55066	-2.57724	-0.59800
S	1.35001	-2.35847	-1.85867
C	3.02612	0.95720	-1.00738
C	4.26259	0.40914	-1.40160
H	4.53408	-0.60015	-1.08925
C	5.15893	1.13585	-2.18365
H	6.11523	0.69062	-2.47606
C	4.81899	2.43672	-2.58486
H	5.51453	3.02223	-3.19770
C	3.59482	2.98498	-2.22052
H	3.31941	3.99204	-2.54631
C	2.65242	2.26244	-1.44380
S	1.10679	2.95380	-1.04207
H	-1.47639	-0.03575	-3.40599
O	0.12018	0.60786	-2.67771
O	-1.07887	0.87659	-3.45319
H	0.27798	1.49915	-2.20793

Table S12 Coordinates of doublet **3·H₂O₂** adduct, transformed form **Int-S+H⁺** species.

Ni	-0.03072	0.85257	-0.69620
P	-1.78187	-0.43262	0.03985
C	-2.05775	-0.72416	1.82156
C	-2.81838	0.18835	2.57615
H	-3.29060	1.04308	2.08702
C	-2.98014	0.01288	3.95295
H	-3.57793	0.73102	4.52243
C	-2.37863	-1.07236	4.60031
H	-2.50673	-1.20974	5.67847
C	-1.61089	-1.97899	3.86180
H	-1.13331	-2.82946	4.35805
C	-1.44815	-1.80508	2.48381
H	-0.84486	-2.52242	1.92505
C	-1.80403	-2.05567	-0.77261
C	-2.52126	-3.16169	-0.28034
H	-3.04347	-3.09067	0.67722
C	-2.58376	-4.35360	-1.00237
H	-3.14752	-5.20552	-0.61125
C	-1.91911	-4.43933	-2.23621
H	-1.95937	-5.36784	-2.81578
C	-1.20365	-3.35285	-2.73329
H	-0.68633	-3.43315	-3.69376
C	-1.12634	-2.13188	-2.01960
S	-0.22745	-0.77676	-2.66467
C	-3.29870	0.40454	-0.53289
C	-4.57495	-0.14854	-0.32208
H	-4.67372	-1.10153	0.20565
C	-5.71891	0.50487	-0.77681
H	-6.70725	0.06784	-0.60783
C	-5.58538	1.72748	-1.45530
H	-6.47523	2.25194	-1.81842
C	-4.32713	2.28083	-1.67737
H	-4.23335	3.22931	-2.21407
C	-3.15955	1.62739	-1.22017
S	-1.58622	2.33592	-1.54457
P	1.82741	-0.20764	0.05355
C	1.84754	-1.94711	0.61000

C	1.94864	-2.27970	1.97314
H	2.02601	-1.49210	2.72513
C	1.95520	-3.61851	2.37871
H	2.04096	-3.85982	3.44268
C	1.85474	-4.64197	1.43070
H	1.86188	-5.68909	1.74885
C	1.74545	-4.32055	0.07219
H	1.66328	-5.11439	-0.67621
C	1.73932	-2.98464	-0.33640
H	1.65235	-2.74372	-1.39795
C	3.07231	-0.09432	-1.26582
C	4.17077	-0.94844	-1.43358
H	4.27884	-1.83351	-0.80091
C	5.13173	-0.67498	-2.41234
H	5.98438	-1.34672	-2.54749
C	4.98929	0.46465	-3.21599
H	5.73515	0.68622	-3.98641
C	3.89552	1.31877	-3.05703
H	3.78784	2.19723	-3.69989
C	2.91555	1.04737	-2.08184
S	1.53855	2.11584	-1.85511
C	2.52736	0.75922	1.42941
C	3.83011	0.49450	1.89459
H	4.41760	-0.30517	1.43386
C	4.38917	1.23993	2.93009
H	5.40340	1.02615	3.27963
C	3.63295	2.27212	3.51007
H	4.05700	2.87103	4.32303
C	2.34729	2.54863	3.05545
H	1.77152	3.36065	3.50867
C	1.75913	1.80325	2.00336
S	0.13976	2.18278	1.45674
H	-1.71265	4.25426	-0.30872
O	-0.17080	5.16218	0.37848
O	-1.61197	5.00831	0.33855
H	0.10476	4.30733	0.82766