Supporting Information

Controlled Oxidation of Organic Sulfides to Sulfoxides Under Ambient Conditions by a Series of Titanium Isopropoxide Complexes Using Environmentally Benign H_2O_2 as an Oxidant

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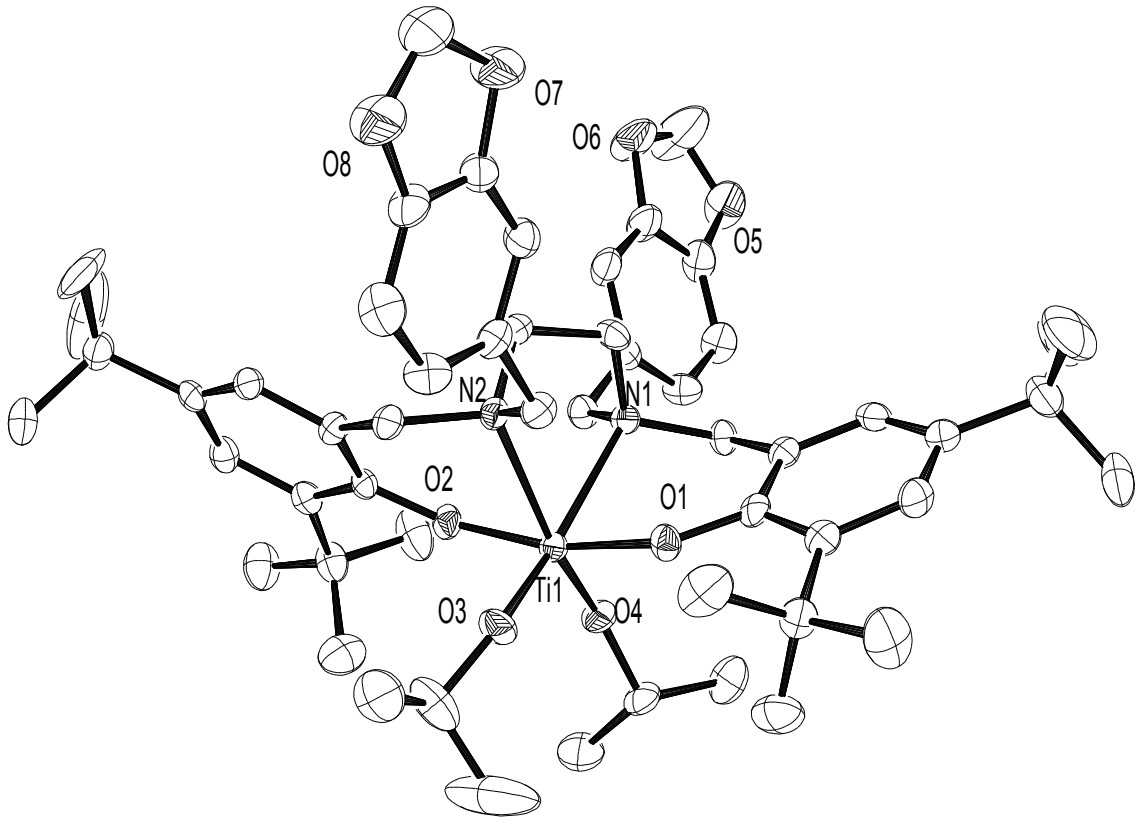


Figure S1. ORTEP of **2b.** Hydrogen atoms on carbon are omitted for clarity. Selected bond lengths (Å) and angles (°) are given: Ti1–O1 1.911(2), Ti1–O2 1.908(2), Ti1–O3 1.800(2), Ti1–O4 1.810(2), Ti1–N1 2.381(3), Ti1–N2 2.390(3), O1–Ti1–O3 90.96(9), O2–Ti1–O3 96.37(10), O2–Ti1–O4 91.76(9), O3–Ti1–O4 106.58(10), O1–Ti1–N1 80.45(9), O2–Ti1–N1 89.65(9), O3–Ti1–N1 163.21(9), O4–Ti1–N1 88.82(9).

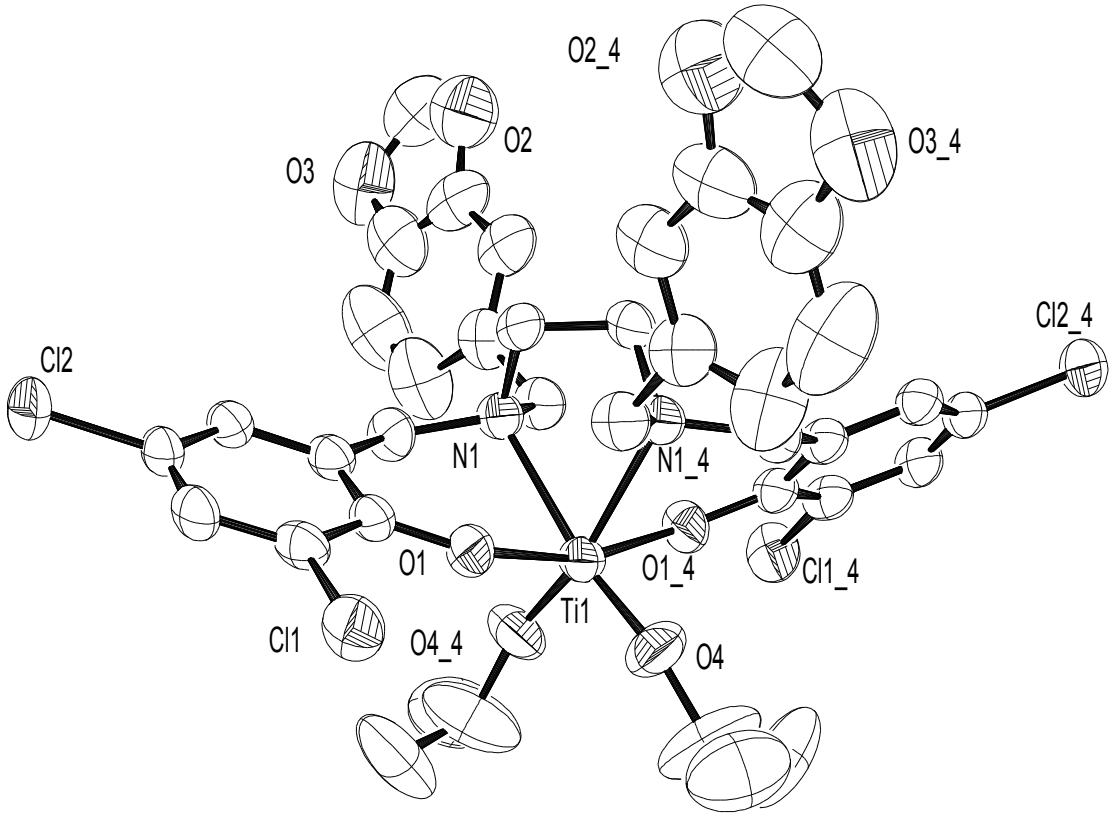


Figure S2. ORTEP of **3b.** Hydrogen atoms on carbon are omitted for clarity. Selected bond lengths (Å) and angles (°) are given: Ti1–O1 1.913(3),), Ti1–O4 1.776(4), Ti1–O1_4 1.913(3), Ti1–O4_4 1.775(4), Ti1–N1 2.354(4), Ti1–N1_4 2.353(4), O1–Ti1–O4_4 96.32(16), O4–Ti1–O1_4 96.32(16), O4–Ti1–O4_4 106.2(3), O1_4–Ti1–O4_4 93.60(15), O1–Ti1–N1_4 86.13(14), O1_4–Ti1–N1_4 80.84(13), O4_4–Ti1–N4_4 164.45(18), O4–Ti1–N1_4 88.96(19).

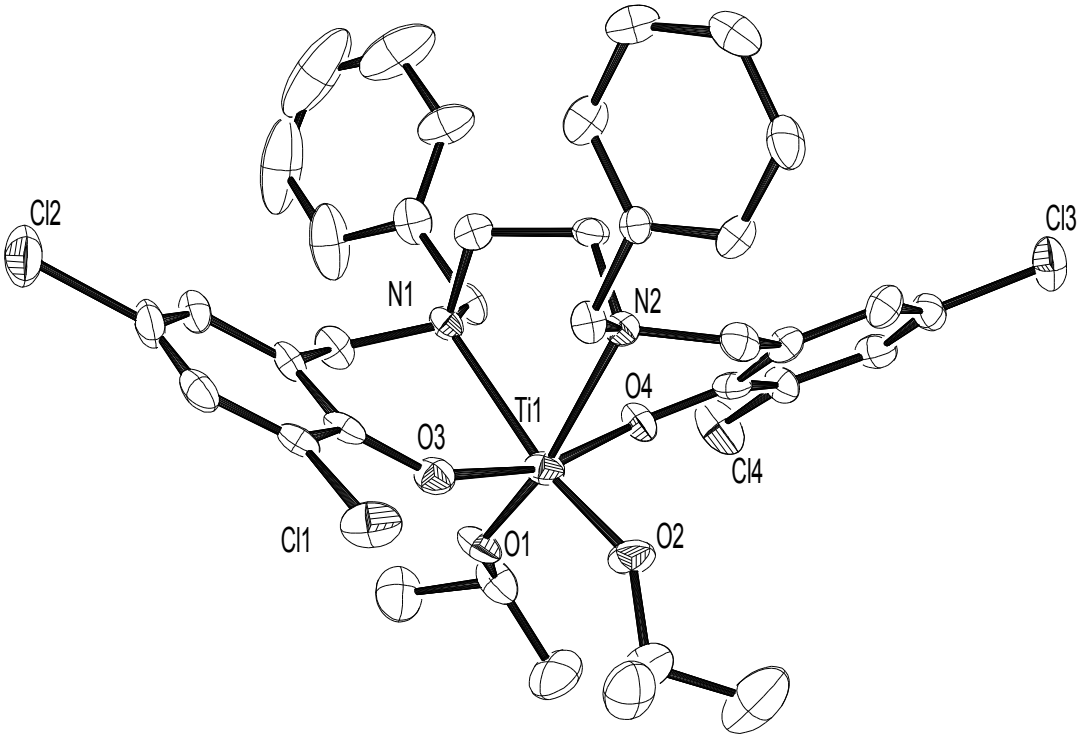


Figure S3. ORTEP of **4b.** Hydrogen atoms on carbon are omitted for clarity. Selected bond lengths (Å) and angles (°) are given: Ti1-O1 1.798(3), Ti1-O2 1.782(3), Ti1-O3 1.919(3), Ti1-O4 1.916(3), Ti1-N1 2.376(3), Ti1-N2 2.331(3), O1-Ti1-O2 105.25(14), O2-Ti1-O4 96.68(13), O1-Ti1-N1 90.10(13), O1-Ti1-N2 165.21(13), O2-Ti1-N1 164.46(13), O2-Ti1-N2 88.24(13).

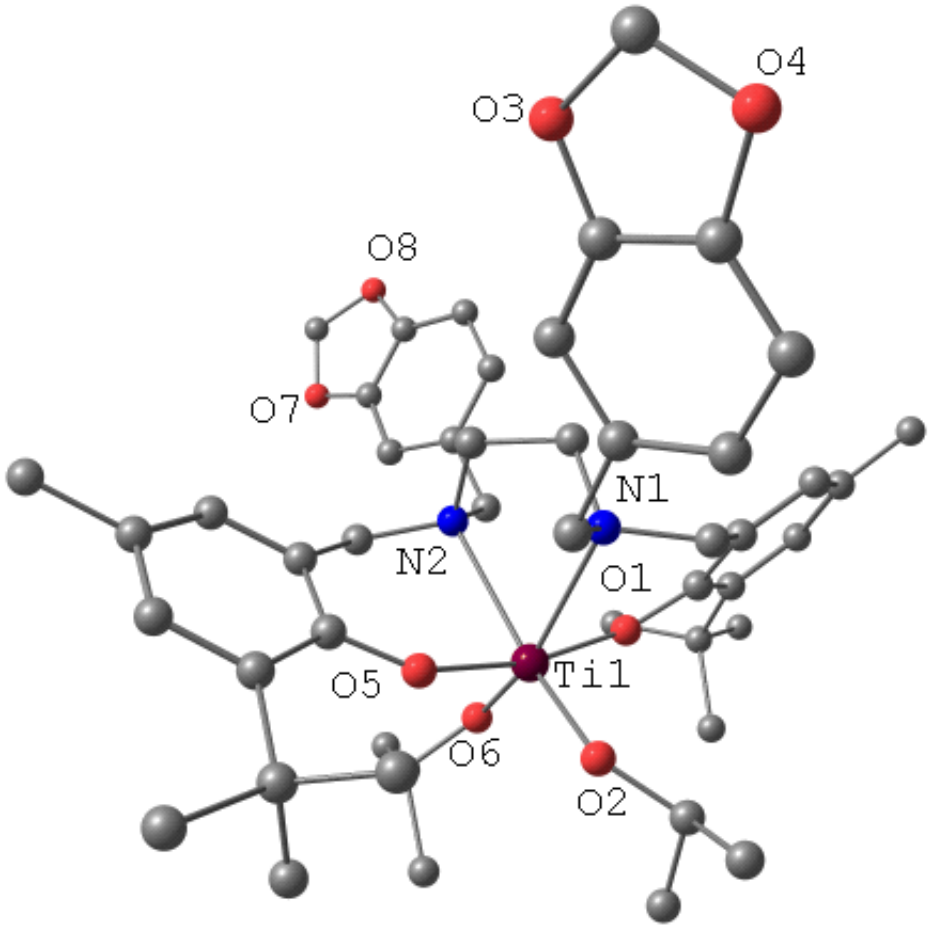


Figure S4. Geometry optimized structure of **1b'.** Selected bond lengths (Å) and angles (°): Ti1-O1 1.898, Ti1-O2 1.826, Ti1-O5 1.896, Ti1-O6 1.826, O1-Ti1-O5 167.9, O2-Ti1-O6 107.7, N1-Ti1-N2 72.0.

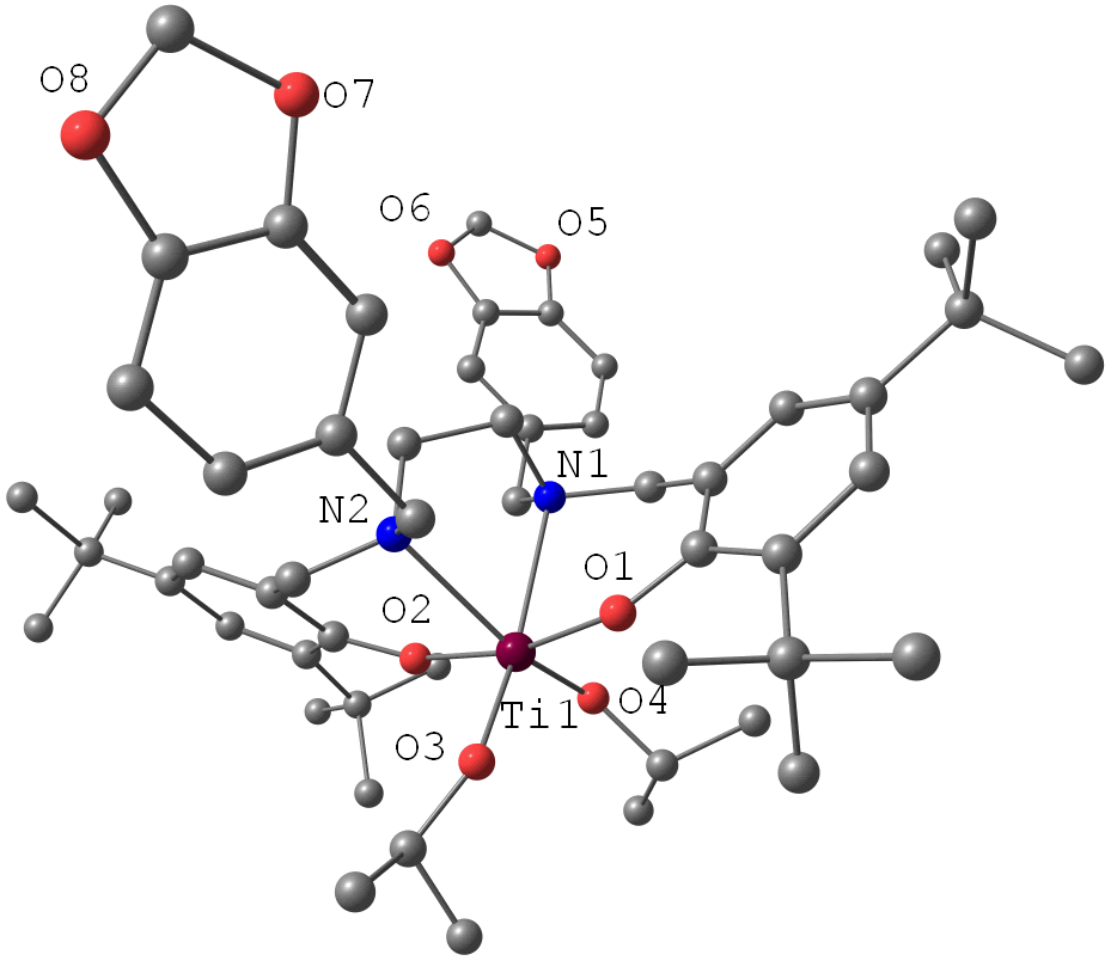


Figure S5. Geometry optimized structure of **2b'.** Selected bond lengths (Å) and angles (°): Ti1-O1 1.901, Ti1-O2 1.906, Ti1-O3 1.819, Ti1-O4 1.820, O1-Ti1-O2 166.4, Ti1-N1 2.462, Ti1-N2 2.509.

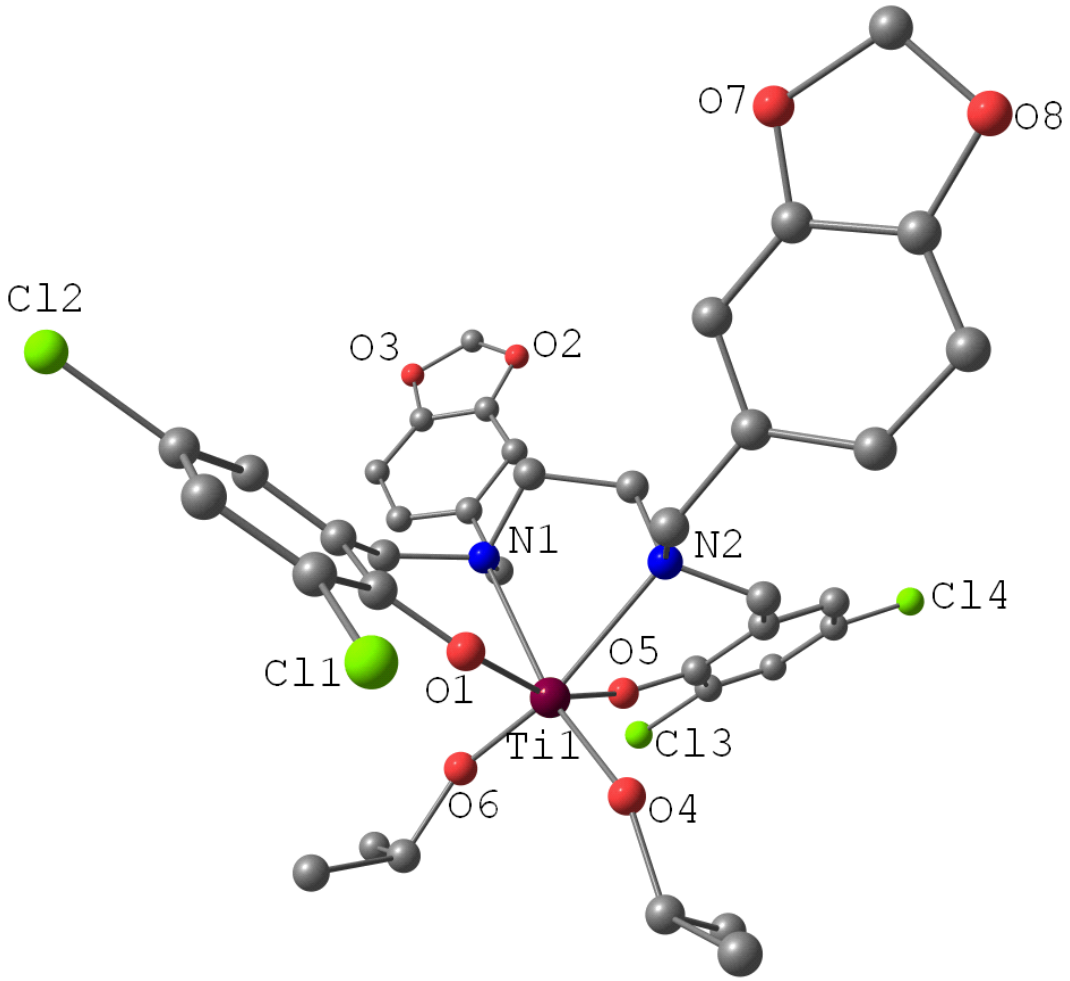


Figure S6. Geometry optimized structure of **3b'.** Selected bond lengths (Å) and angles (°): Ti1-O1 1.921, Ti1-O4 1.794, Ti1-O5 1.921, Ti1-O6 1.794, Ti1-N1 2.454, T1-N2 2.454.

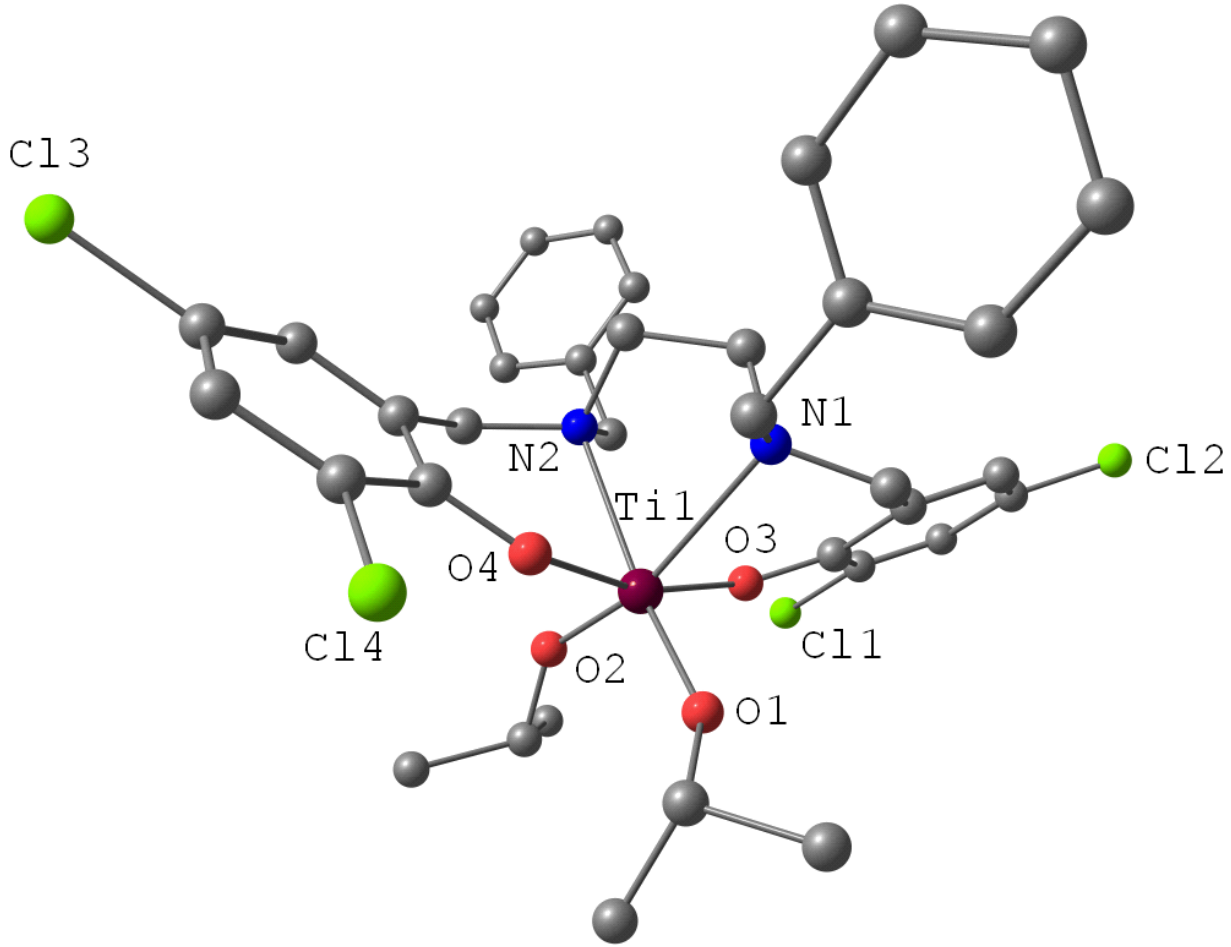


Figure S7. Geometry optimized structure of **4b'.** Selected bond lengths (Å) and angles (°): Ti1-O1 1.804, Ti1-O2 1.806, Ti1-O3 1.913, Ti1-O4 1.928, O3-Ti1-O4 162.9, O1-Ti1-O2 105.3, N1-Ti1-N2 74.7.

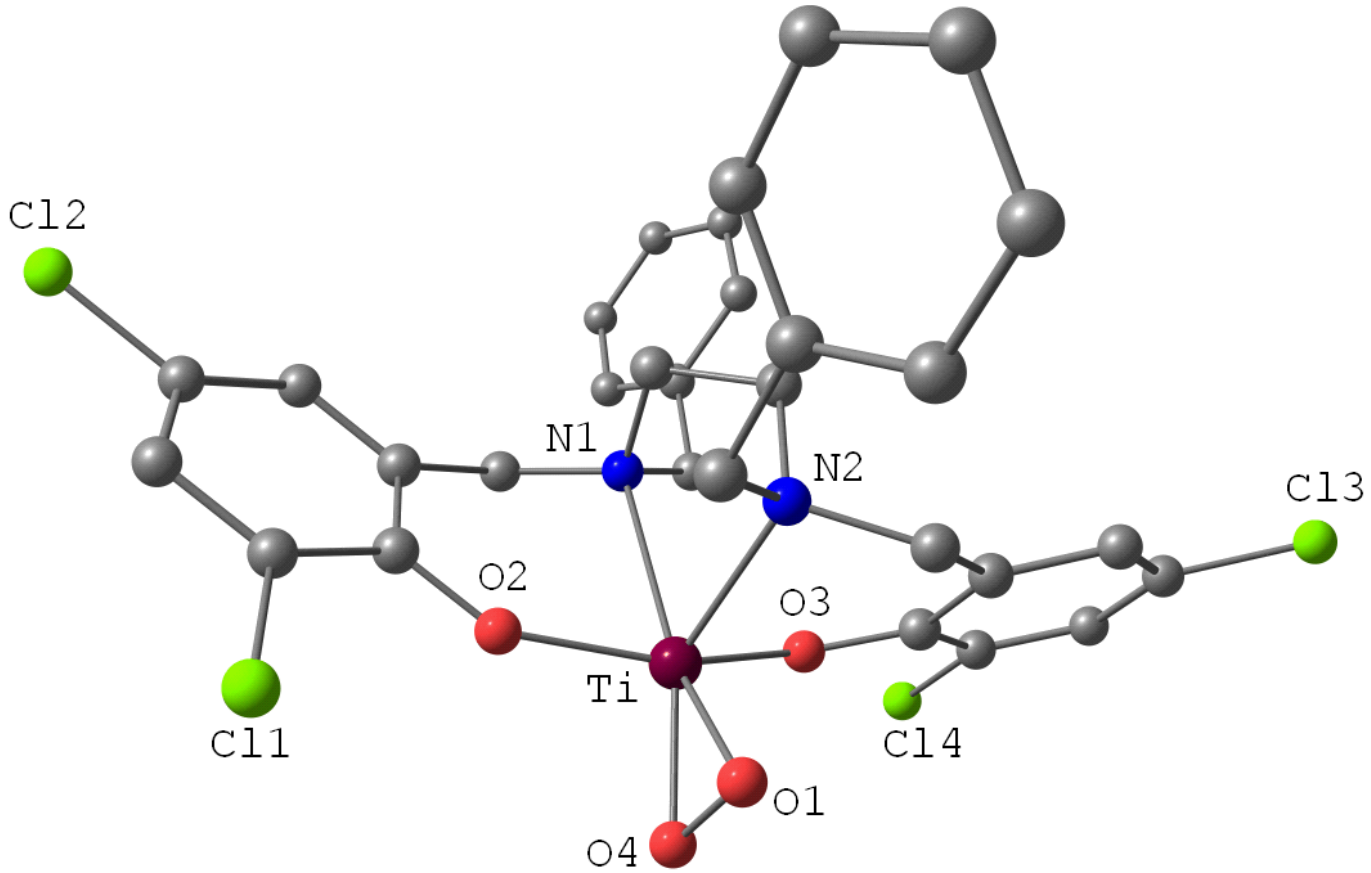


Figure S8. Geometry optimized structure of intermediate **4c'.** Selected bond lengths (Å) and angles (°): Ti1-O1 1.836, Ti1-O2 1.887, Ti1-O3 1.866, Ti1-O4 1.833, O1-O4 1.444, O1-Ti1-O4 46.3, O2-Ti1-O3 151.9.

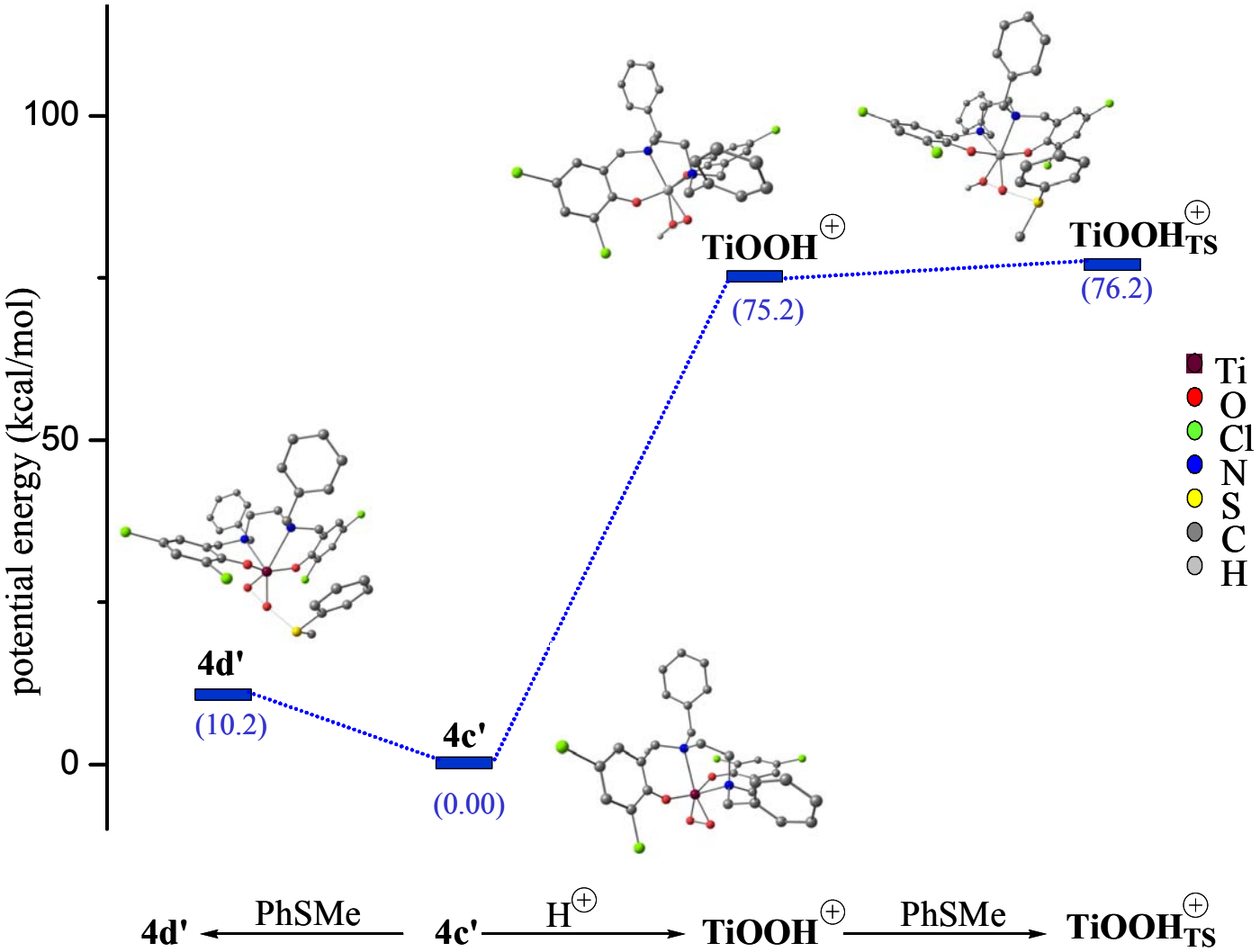


Figure S9. Comparison of the energy profiles between the peroxo and hydroperoxo pathways for the **4b** precatalyst.

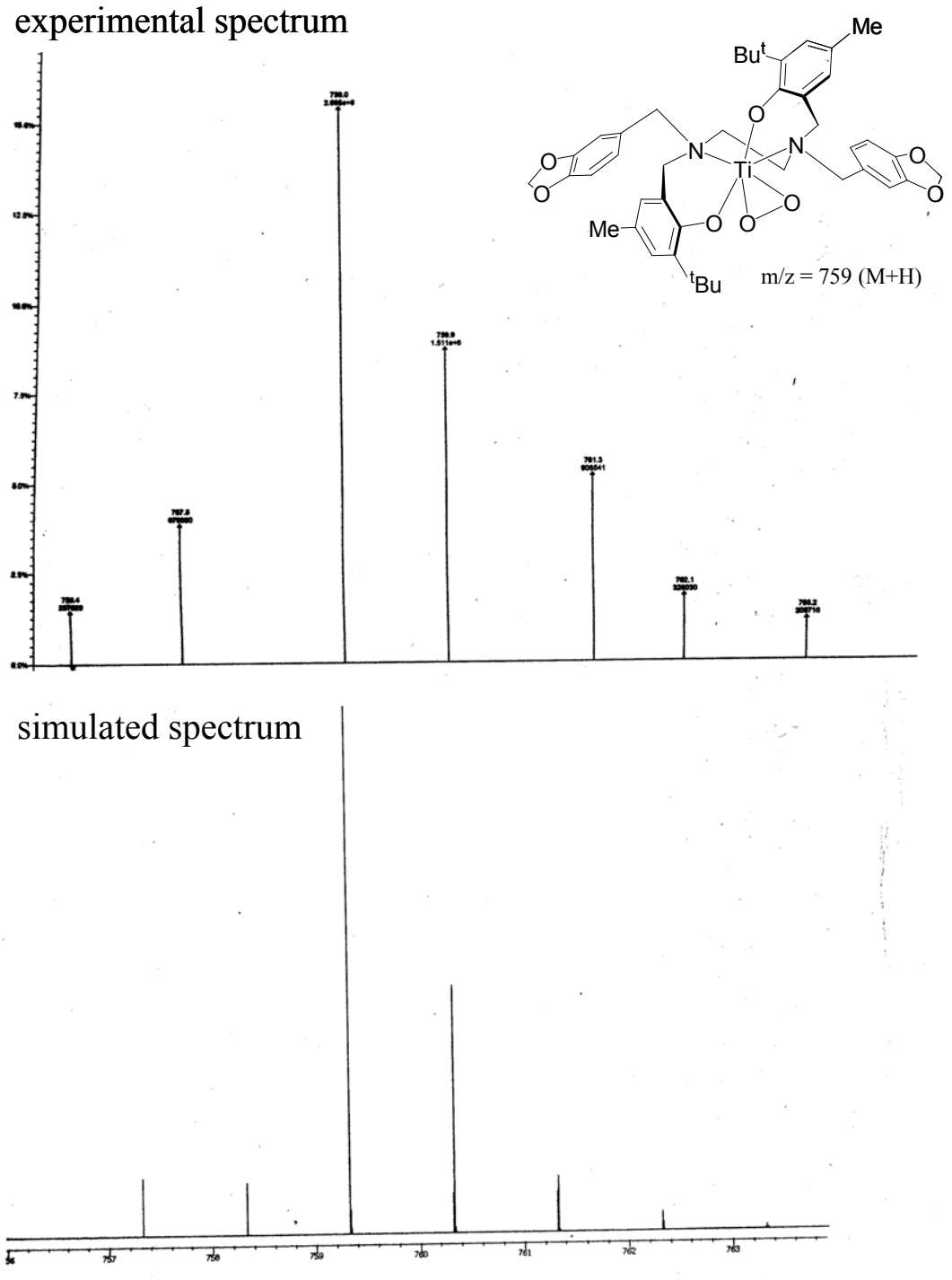


Figure S10. Overlay of experimental and simulated LCMS−APCI mass spectrum (in positive mode) of **1b** with H_2O_2 in $CH_3CN/CHCl_3$ showing the isotopic distribution of peroxo species of **1b**.

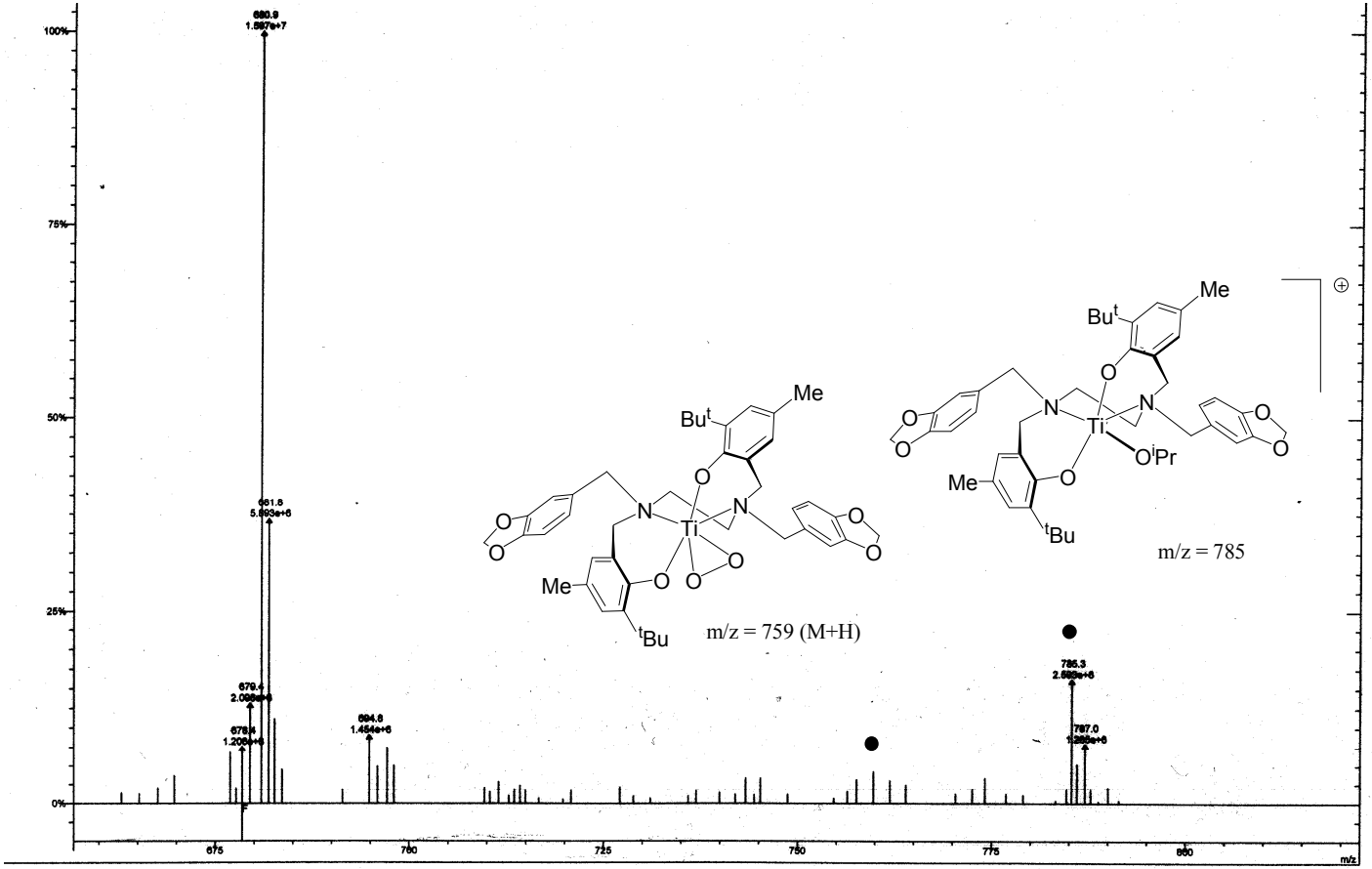


Figure S11. An expanded LCMS–APCI mass spectrum (in positive ion mode) of **1b** with H_2O_2 in $CH_3CN/CHCl_3$ showing the formation of peroxo species.

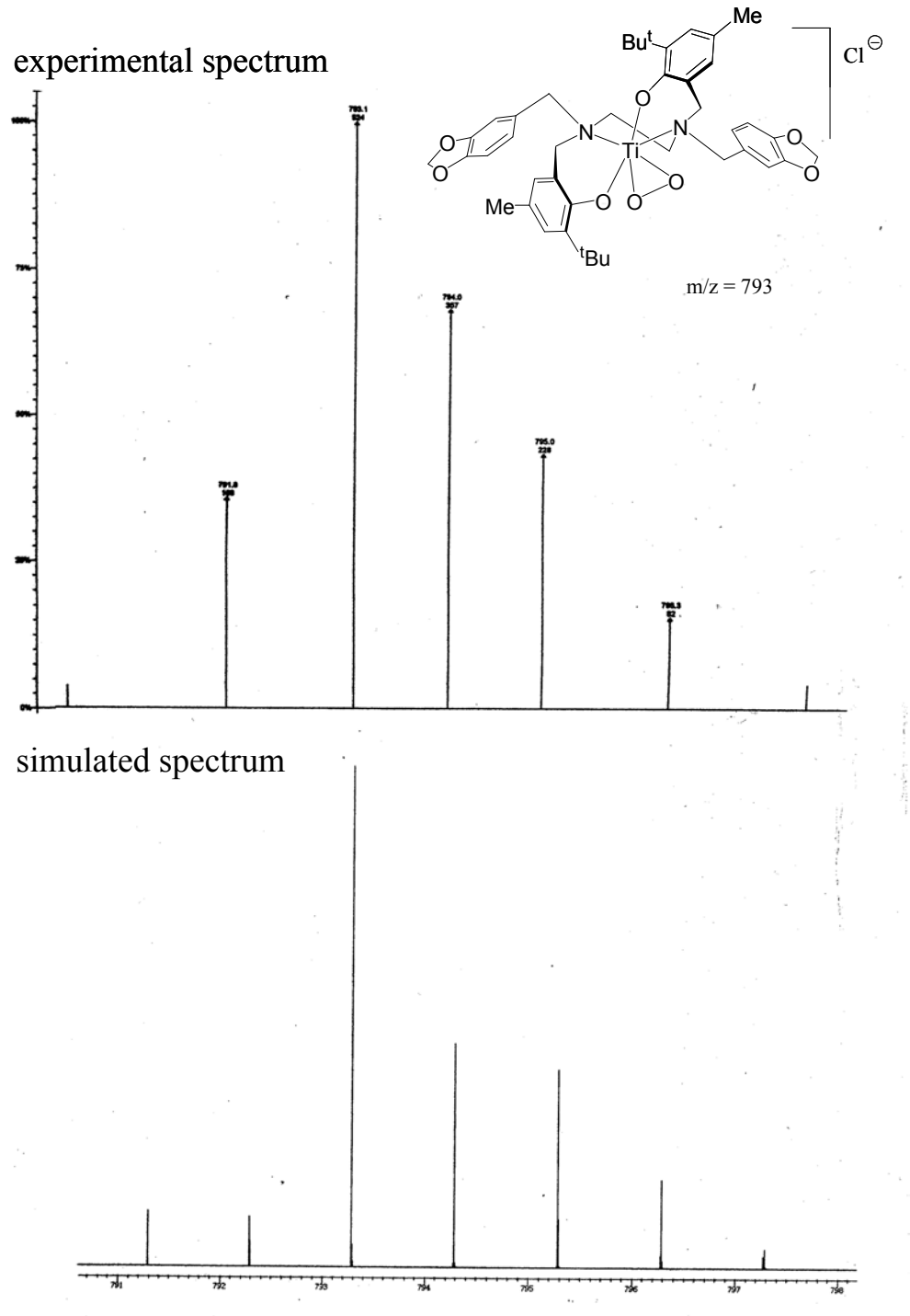


Figure S12. Overlay of experimental and simulated LCMS–APCI mass spectrum (in negative mode) of **1b** with H_2O_2 in $CH_3CN/CHCl_3$ showing the isotopic distribution of the chloride adduct of peroxo species of **1b**.

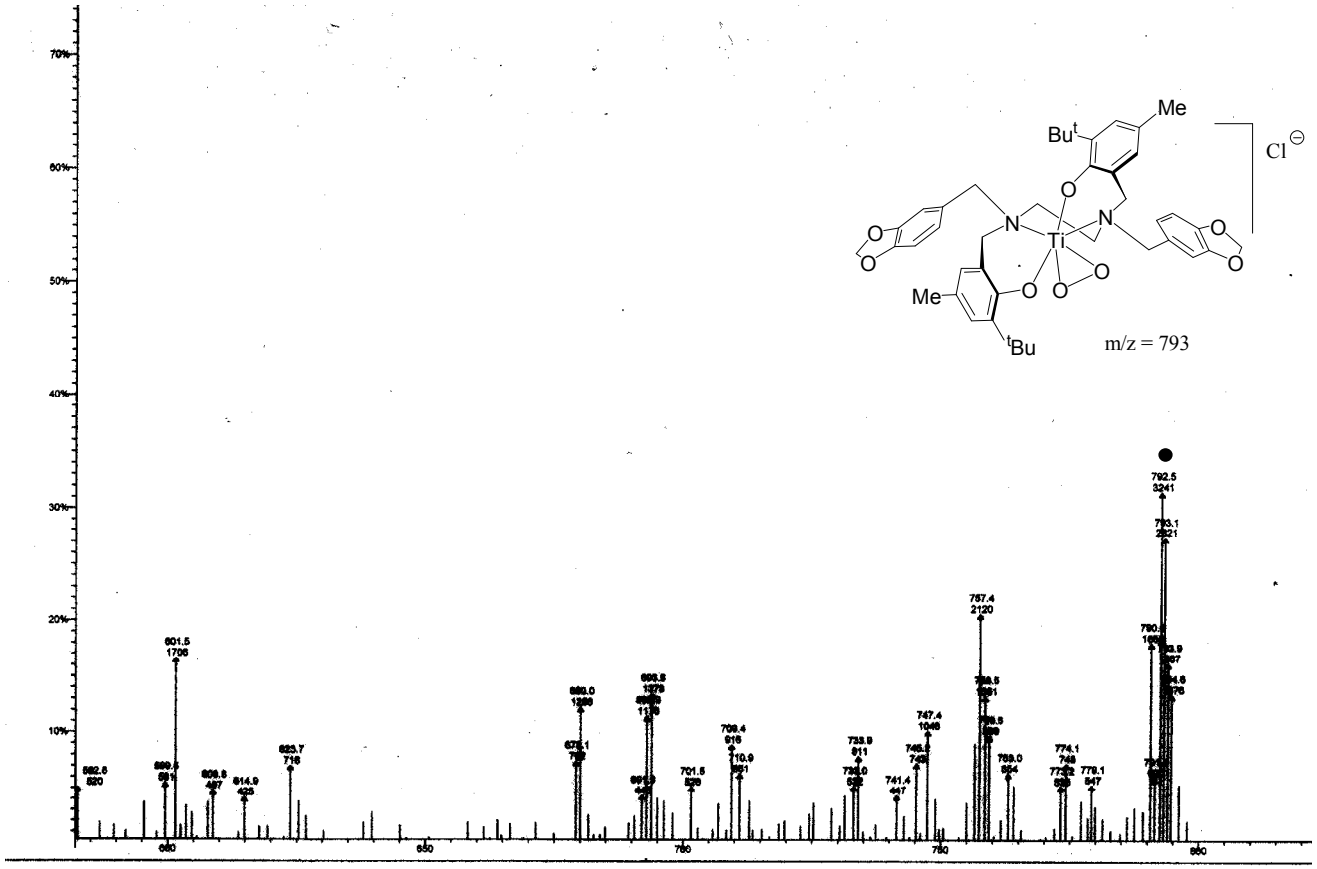


Figure S13. An expanded LCMS−APCI mass spectrum (in negative ion mode) of **1b** with H_2O_2 in $CH_3CN/CHCl_3$ showing the formation of peroxo species and its Cl^- adduct.

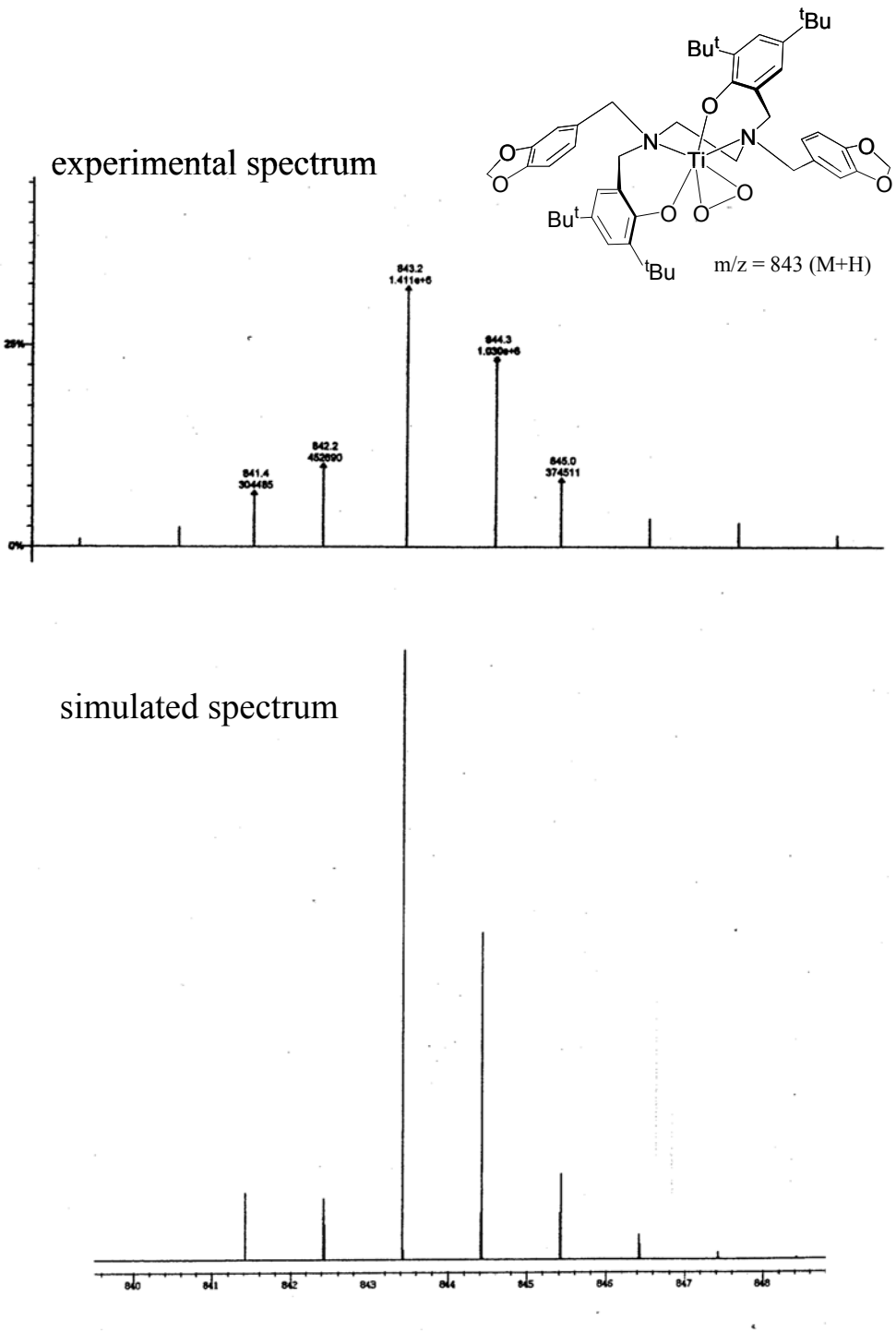


Figure S14. Overlay of experimental and simulated LCMS–APCI mass spectrum (in positive mode) of **2b** with H_2O_2 in $CH_3CN/CHCl_3$ showing the isotopic distribution of peroxo species of **2b**.

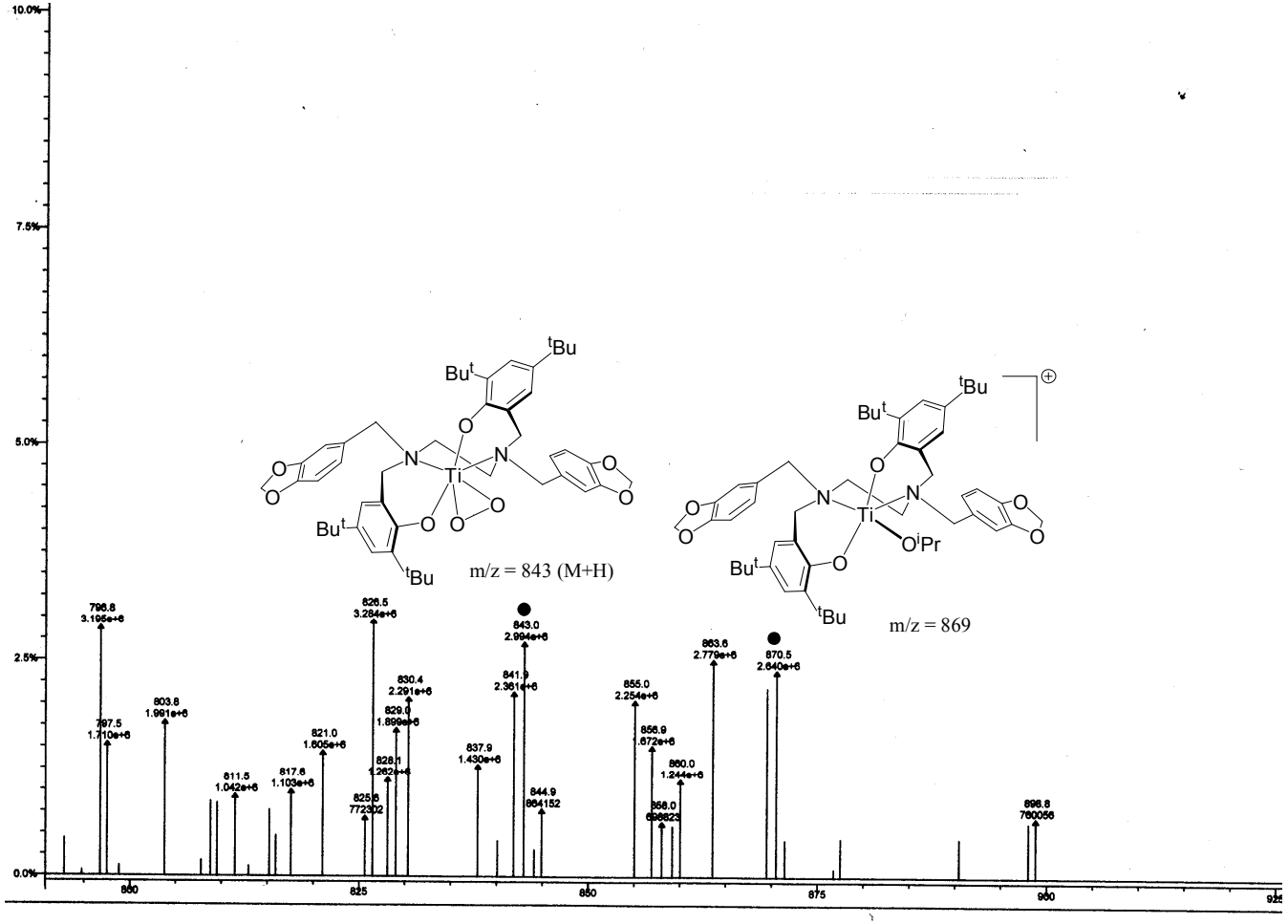


Figure S15. An expanded LCMS–APCI mass spectrum (in positive ion mode) of **2b** with H_2O_2 in $CH_3CN/CHCl_3$ showing the formation of peroxo species.

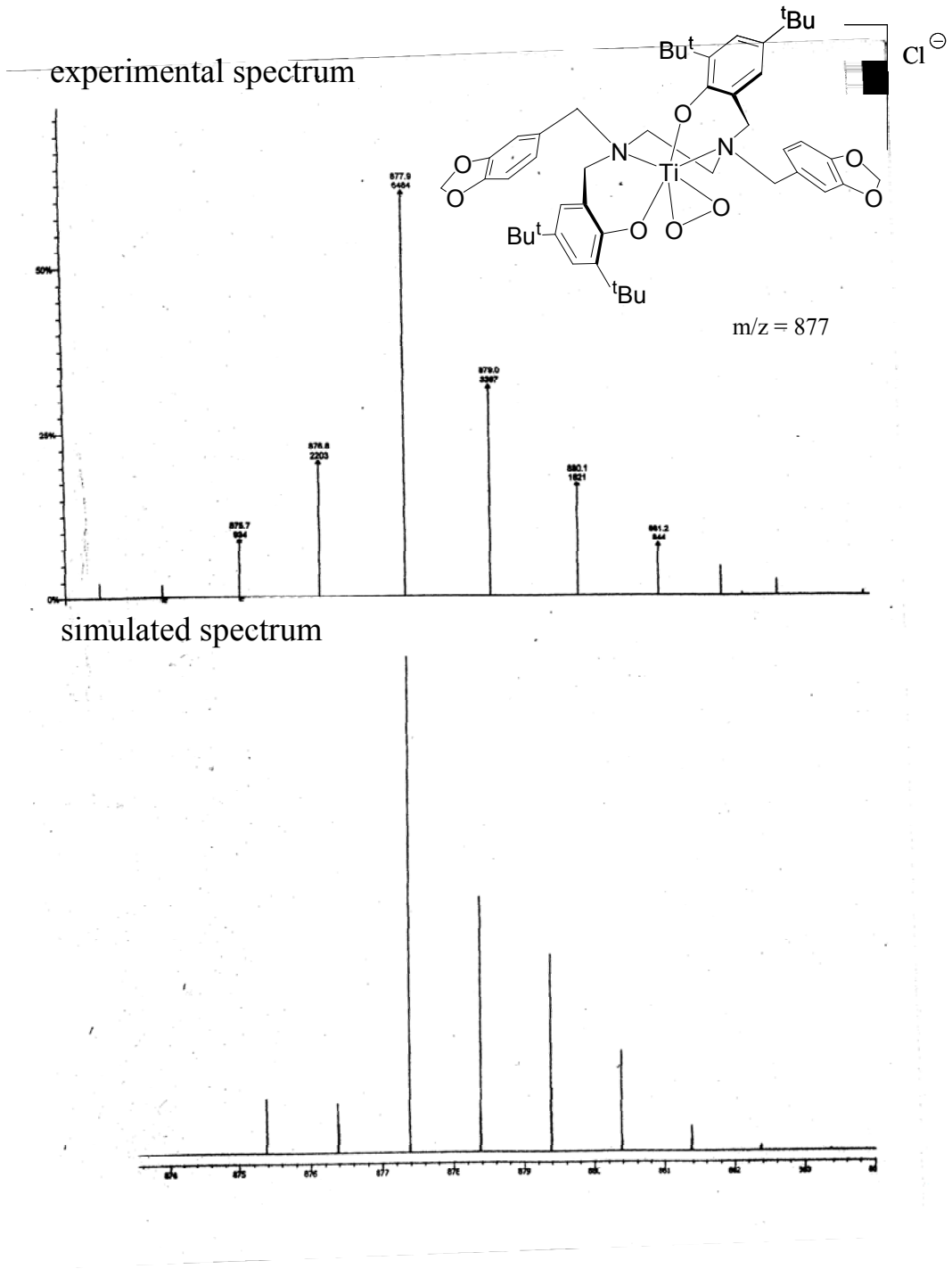


Figure S16. Overlay of experimental and simulated LCMS–APCI mass spectrum (in negative mode) of **2b** with H_2O_2 in $CH_3CN/CHCl_3$ showing the isotopic distribution of the chloride adduct of peroxo species of **2b**.

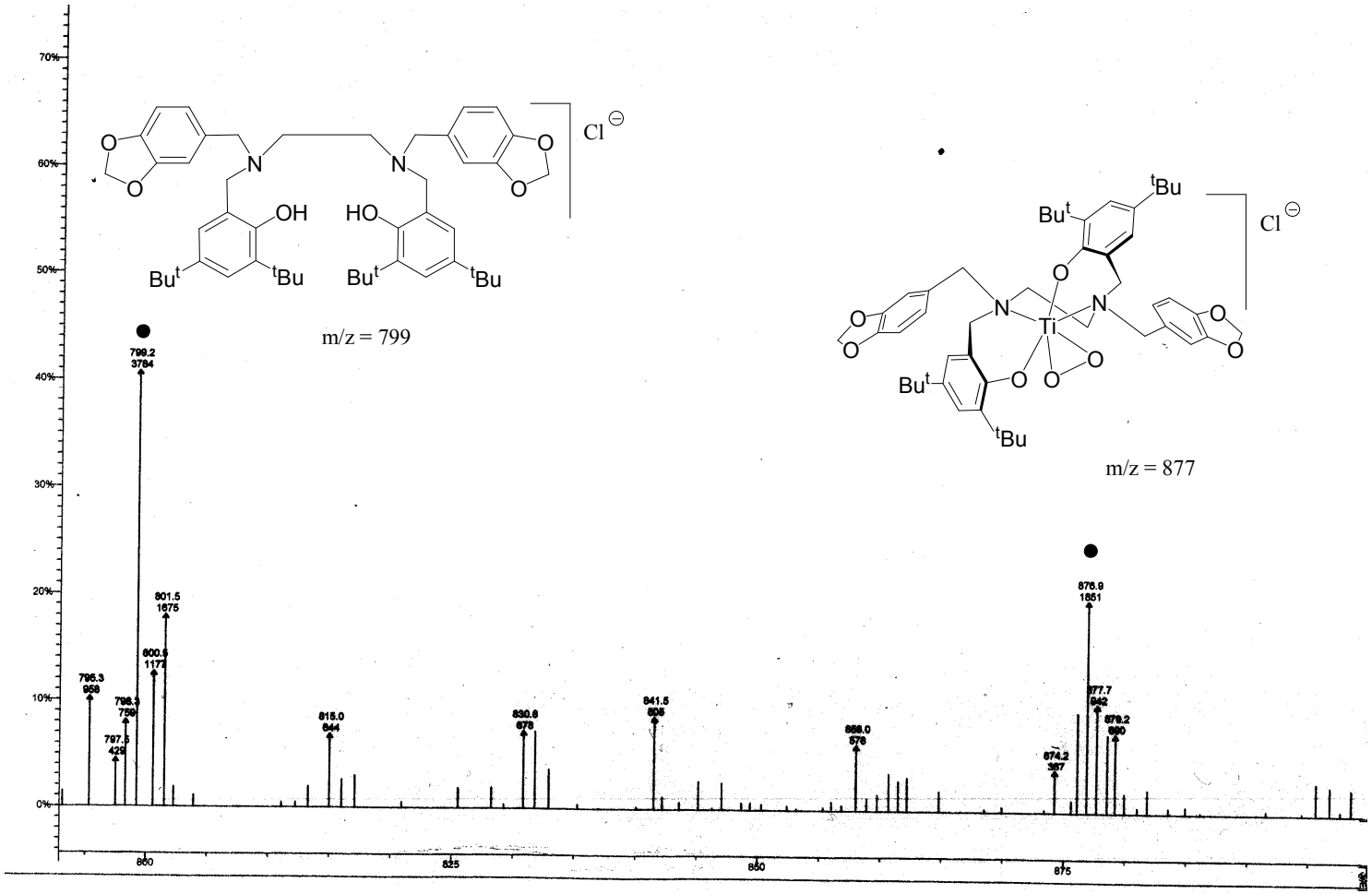
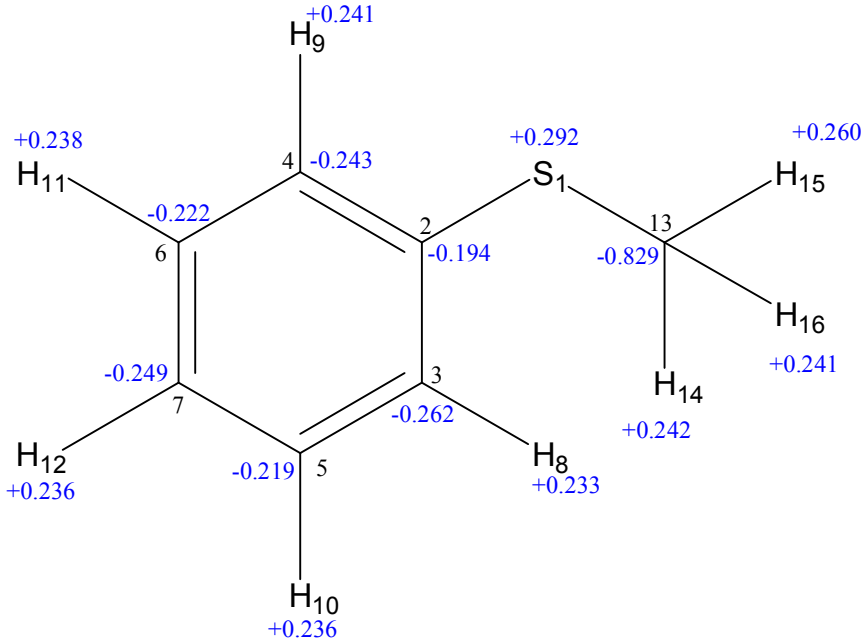


Figure S17. An expanded LCMS–APCI mass spectrum (in negative ion mode) of **2b** with H_2O_2 in $CH_3CN/CHCl_3$ showing the formation of peroxo species and its Cl^- adduct.

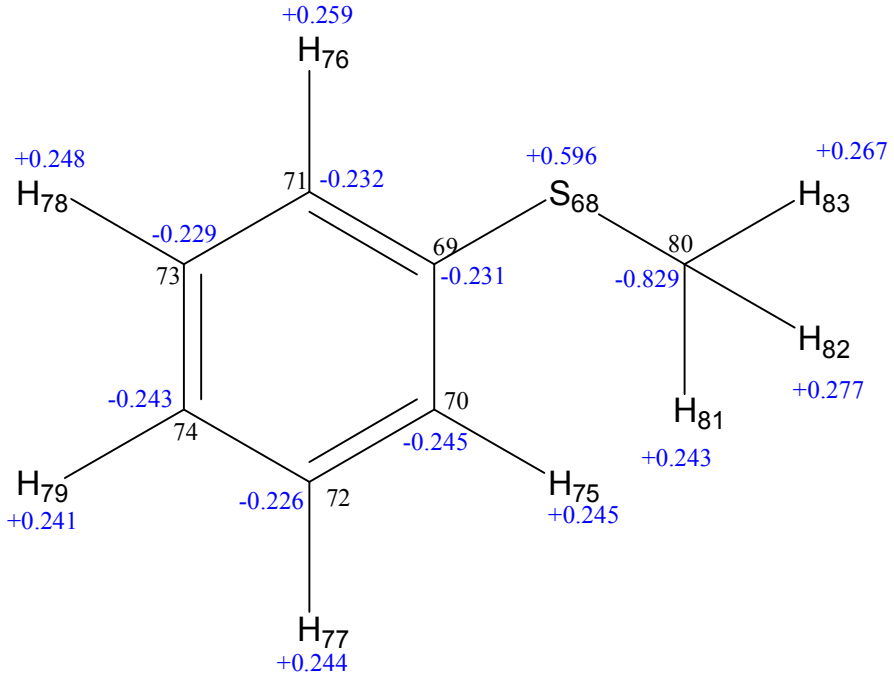


natural charges in free thioanisole

total +ve charge = 2.219
total -ve charge = 2.218

overall charge = +0.001

Figure S18



natural charge of thioanisole moiety in **4d'**

total +ve charge = 2.620
total -ve charge = 2.235

overall +ve charge = 0.385

Figure S19.

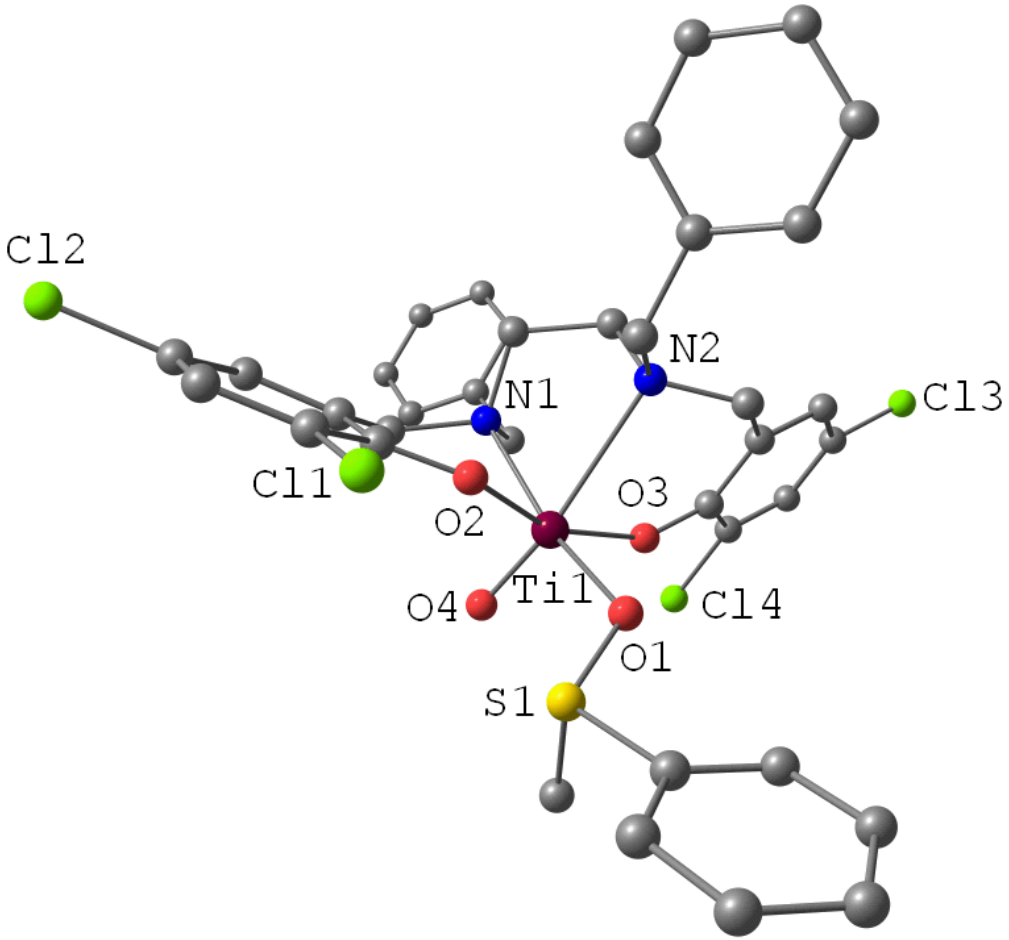


Figure S20. Geometry optimized structure of intermediate **4e'.** Selected bond lengths (Å) and angles (°): Ti1-O1 2.079, Ti1-O2 1.947, Ti1-O3 1.924, Ti1-O4 1.646, O1-O4 2.876, O1-S1 1.564, O1-Ti1-O4 100.5, O2-Ti1-O3 157.5, Ti1-O1-S1 117.8.

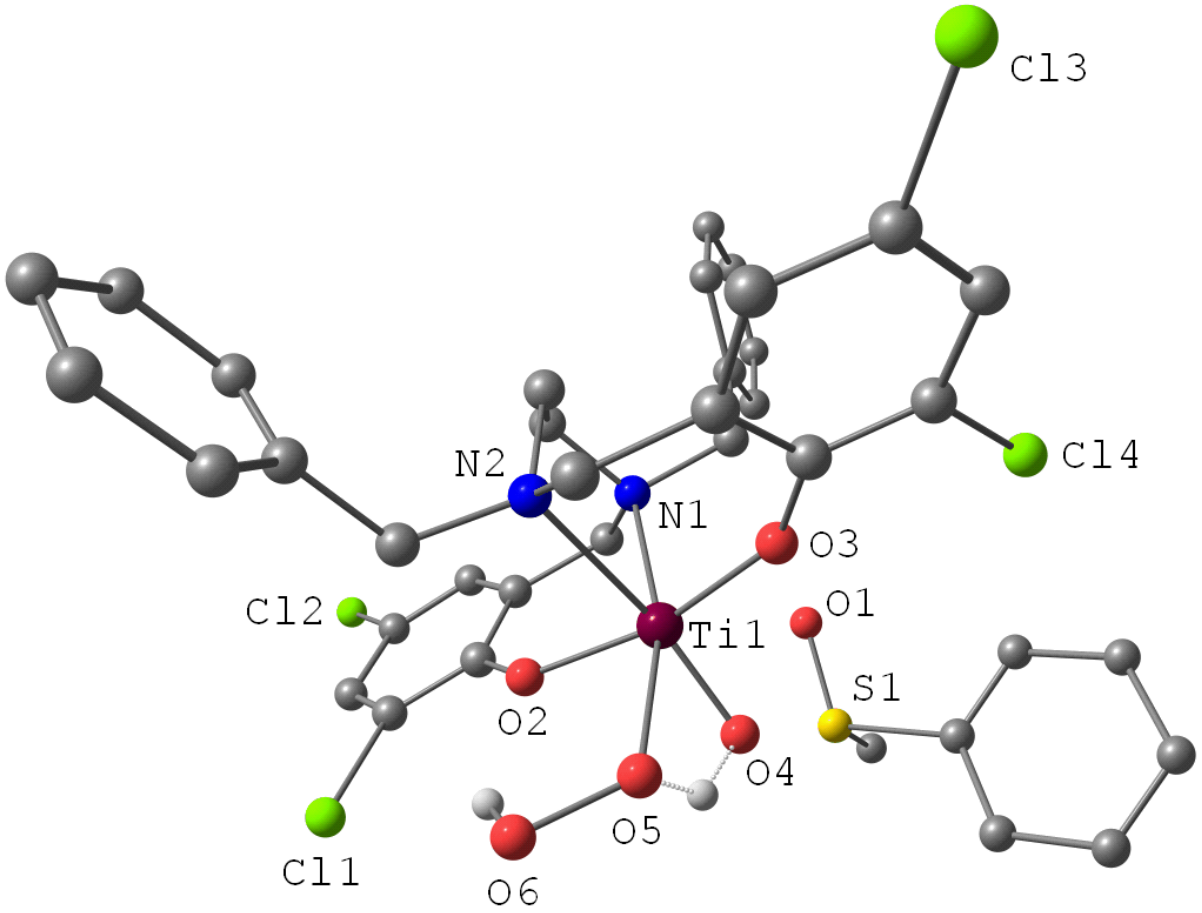


Figure S21. Fully optimized transition state **4f'.** Selected bond lengths (Å) and angles (°): Ti-O1 4.069, Ti1-O2 1.952, Ti1-O3 1.879, Ti1-O4 1.729, Ti1-O5 2.112, O4-S1 3.129, O2-Ti1-O3 164.3, O4-Ti1-O5 72.7, O5-H36-O4 135.0, H35-O6-O5 101.4.

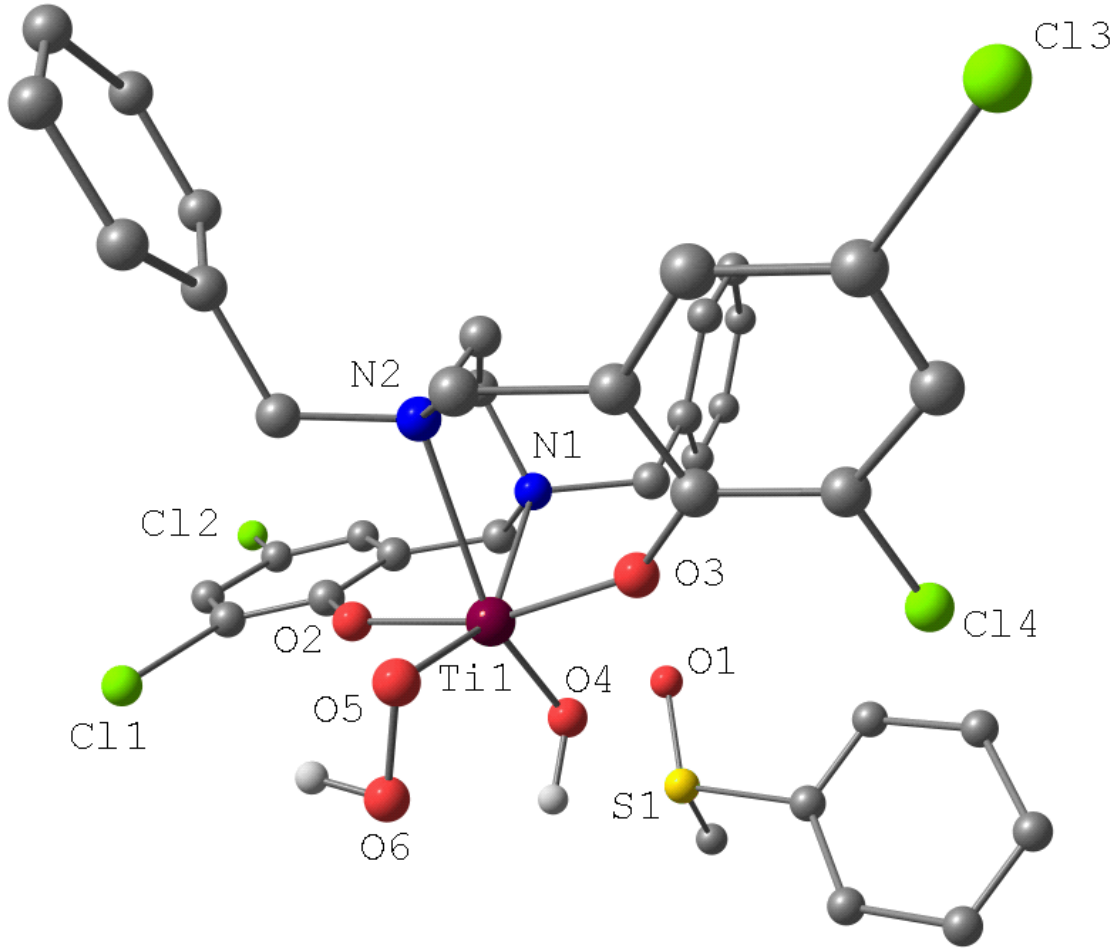


Figure S22. Geometry optimized structure of intermediate **4g'.** Selected bond lengths (Å) and angles (°): Ti1-O1 4.967, Ti1-O2 1.932, Ti1-O3 1.894, Ti1-O4 1.843, Ti1-O5 1.896, O1-O4 3.480, O1-S1 1.519, O2-Ti1-O3 164.8, O4-Ti1-O5 122.4.

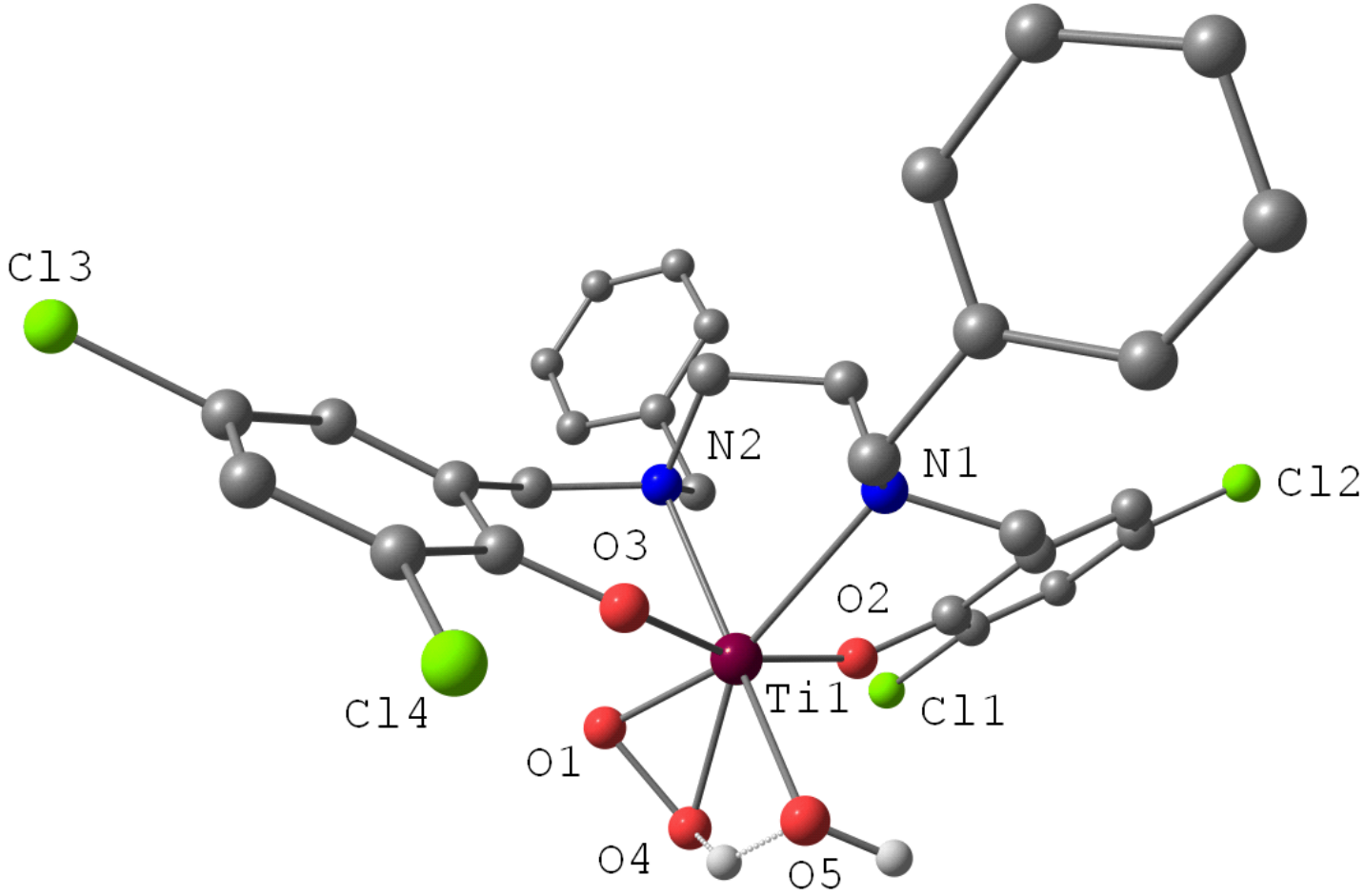


Figure S23. Fully optimized transition state **4h'.** Selected bond lengths (Å) and angles (°): Ti1-O1 1.852, Ti1-O2 1.886, Ti1-O3 1.904, Ti1-O4 2.062, Ti1-O5 2.061, O1−O4 1.447, O1-Ti1-O4 42.9, O2-Ti1-O3 160.7.

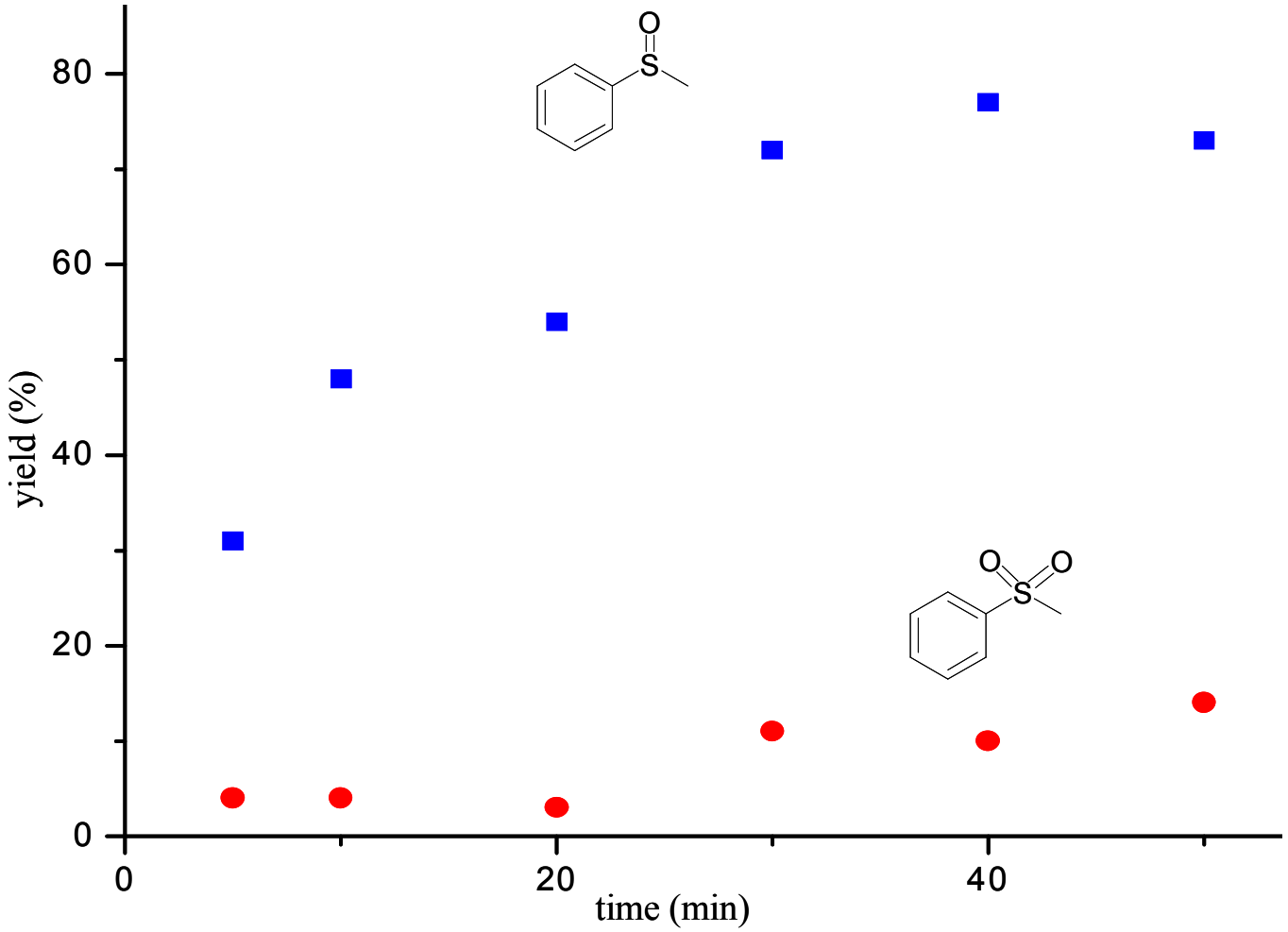


Figure S24. A time dependent profile of the oxidation of thioanisole by aqueous H_2O_2 by **1b**.

Table S1. Molecular orbital Ti–O π–interaction in **1b'**–**4b'**.

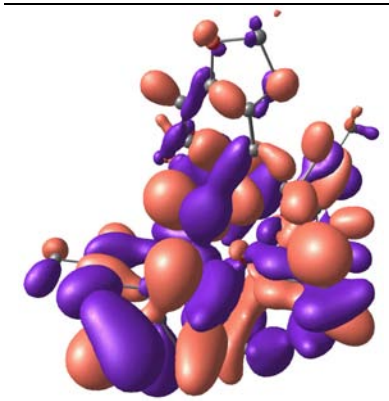
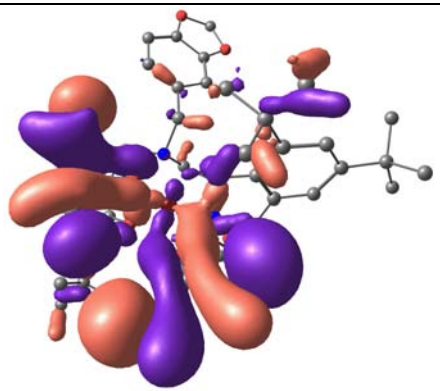
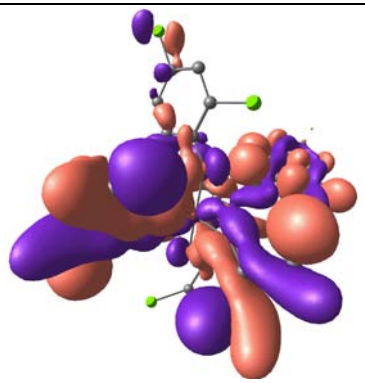
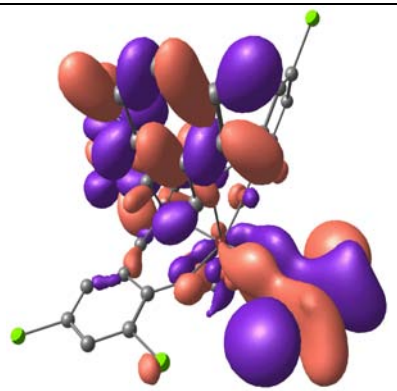
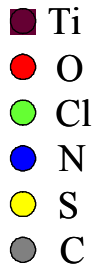
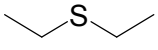
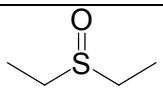
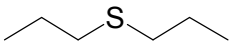
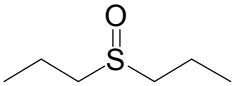
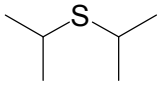
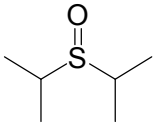
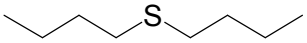
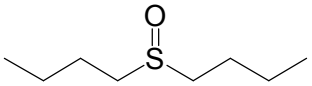
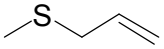
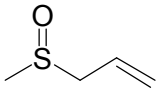
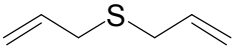
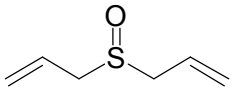
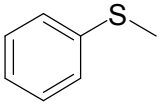
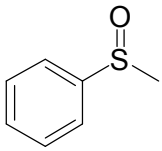
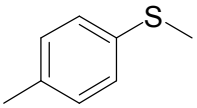
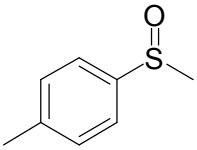
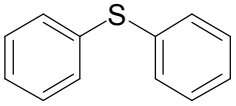
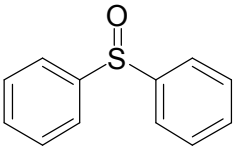
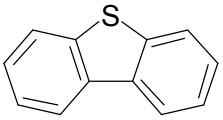
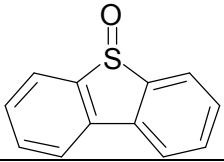
1b'	**2b'**	**3b'**	**4b'**	**atom legend**
				
MO 189	MO 212	MO 184	MO 165	

Table S2. Blank and control study of the oxidation of thioether by aqueous H_2O_2.

entry	substrate	product	conversion[a] % (SO:SO_2)[b] blank	conversion[a] % (SO:SO_2)[b] $Ti(O^iPr)_4$
1.			21 (>99:1)	29 (1:2)
2.			29 (>99:1)	57 (1.5:1)
3.			23 (>99:1)	86 (7:1)
4.			69 (>99:1)	47 (1:2)
5.			12 (>99:1)	23 (2:1)
6.			6 (>99:1)	46 (7:1)
7.			no product	57 (1:1)
8.			24 (>99:1)	61 (1:1)
9.			no product	77 (6:1)
10.			no product	20 (>99:1)

[a]Reaction conditions: 2.00 mmol of substituted thioether, 2.00 mmol of H_2O_2, 2.00 mmol of internal standard (1,2-dichlorobenzene) and 1.00×10^{-2} mmol $Ti(O^iPr)_4$ catalyst, in CH_3OH (5 mL) at room temperature (30 minute). Products were quantified by GC analysis with respect to internal standard and identified by GCMS analysis.
[b]Ratio of sulfoxide to sulfone (SO:SO_2) is given in parenthesis under yield.

Table S3. Selected results of oxidation of thianisole by different oxidants catalyzed by **1b**.

entry	oxidant	sufoxide conversion[a] (%)	product ratio (SO/SO_2)[b]
1	H_2O_2	91	10:1
2	TBHP[c]	no product	-
3	*m*-CPBA[d]	52	>99:1
4	molecular O_2	no product	-
5	air	no product	-

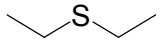
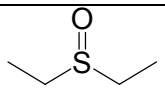
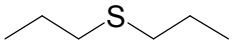
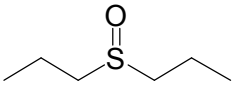
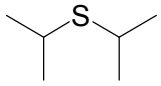
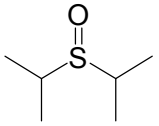
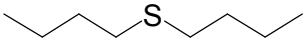
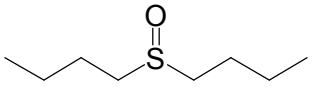
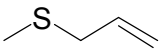
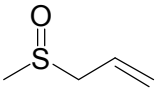
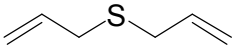
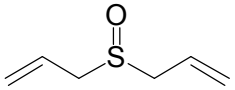
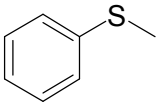
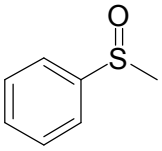
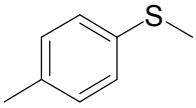
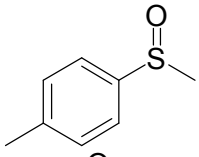
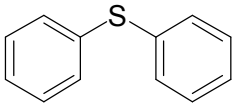
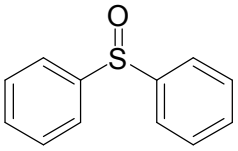
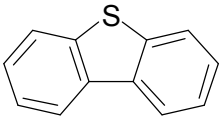
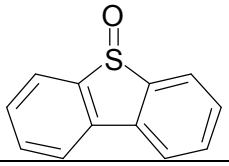
[a]Reaction conditions: 2.00 mmol of substituted thioether, 2.00 mmol of oxidant, 2.00 mmol of internal standard (1,2-dichlorobenzene) and 1.00×10^{-2} mmol Ti catalyst, in CH_3OH (5 mL) at room temperature (30 minute). Products were quantified by GC analysis and identified by GCMS analysis.
[b]Ratio of sulfoxide to sulfone.
[c]*t*-Butyl hydroperoxide.
[d]*m*-Chloroperbenzoic acid.

Table S4. Selected results of oxidation of thianisole by aqueous H_2O_2 catalyzed by **1b** at different catalyst loading.

entry	catalyst loading (mol %)	time (min)	sufoxide conversion[a] (%)	product ratio (SO/SO_2)[b]
1	0.05	30	26	>99:1
2	0.10	30	38	13:1
3	0.30	30	59	9:1
		60	69	14:1
4	0.50	30	90	10:1
5	1.00	30	73	5:1

[a]Reaction conditions: 2.00 mmol of substituted thioether, 2.00 mmol of H_2O_2, 2.00 mmol of internal standard (1,2-dichlorobenzene) and (0.05–1.00) × 10^{-2} mmol Ti catalyst, in CH_3OH (5 mL) at room temperature (30–60 minutes). Products were quantified by GC analysis with respect to internal standard and identified by GCMS analysis.
[b]Ratio of sulfoxide to sulfone.

Table S5. Isolated yield of oxidation of thioethers by aqueous H_2O_2 catalyzed by **2b**.

entry	substrate	product	isolated yield (%)[a]
1.			85
2.			80
3.			78
4.			87
5.			90
6.			92
7.			82
8.			84
9.			20
10.			10

[a]Reaction conditions: 2.00 mmol of substituted thioether, 2.00 mmol of H_2O_2 and 1.00 × 10^{-2} mmol Ti catalyst, in CH_3OH (5 mL) at room temperature (30 minute). Products were identified by GCMS and ^1H NMR after isolation.

Table S6. Selected results of oxidation of thianisole by aqueous H_2O_2 catalyzed by **1b** in different solvents.

entry	catalyst loading (mol %)	time (min)	sufoxide conversion[a] (%)	product ratio (SO/SO_2)[b]
1	methanol	30	90	10:1
2	dichloromethane	30	48	9:1
		60	71	6:1
		90	84	8:1
3	acetonitrile	30	30	7:1
4	tetrahydofuran	30	16	5:1
5	benzene	30	31	1:1

[a]Reaction conditions: 2.00 mmol of substituted thioether, 2.00 mmol of H_2O_2, 2.00 mmol of internal standard (1,2-dichlorobenzene) and 1.00×10^{-2} mmol Ti catalyst, in different solvents (5 mL) at room temperature (30–90 minutes). Products were quantified by GC analysis with respect to internal standard and identified by GCMS analysis.
[b]Ratio of sulfoxide to sulfone.

Table S7. Geometry optimized coordinates of **1b'** at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -2637.1957473 Hartree/particle

Ti	9.486912	8.140676	4.946834
O	10.93205	9.360747	5.110948
O	8.536955	8.841393	6.340052
O	5.25217	11.6206	-0.9151
O	4.470144	13.56542	0.075712
O	8.035812	7.048081	4.403635
O	10.48531	6.757156	5.597472
O	14.02038	4.714574	-0.6691
O	14.36986	6.403057	-2.22079
N	8.715194	9.984776	3.454136
N	10.16722	7.576211	2.610352
C	11.40505	10.59031	4.865938
C	12.75109	10.9421	5.184504
C	13.17754	12.22378	4.816848
H	14.19908	12.51859	5.031295
C	12.35667	13.16813	4.185622
C	11.03082	12.81332	3.947081
H	10.35322	13.53328	3.4903
C	10.54193	11.55011	4.29165
C	13.67881	9.995614	5.979125
C	13.0587	9.745111	7.375805
H	12.95724	10.68548	7.931181
H	13.70191	9.075018	7.960767
H	12.07296	9.283416	7.290262
C	13.86962	8.640418	5.259685
H	12.93285	8.085314	5.20735
H	14.5988	8.030774	5.808815
H	14.25661	8.785624	4.243325
C	15.08104	10.60259	6.194344
H	15.59939	10.78949	5.246219
H	15.69199	9.898013	6.769838
H	15.0466	11.54164	6.758212
C	12.89962	14.51982	3.78163
H	13.54727	14.44956	2.896833
H	13.50031	14.96971	4.581418
H	12.09123	15.21793	3.538908
C	8.739905	9.66363	7.477795
H	9.524848	10.39805	7.239223
C	7.437455	10.40504	7.794582
H	7.116856	11.02025	6.946474
H	7.566458	11.0619	8.663103

H	6.638422	9.687999	8.014693
C	9.209892	8.819481	8.664294
H	8.449002	8.075286	8.926414
H	9.391497	9.454618	9.539918
H	10.13648	8.293157	8.418616
C	9.066139	11.26722	4.130329
H	8.584531	11.22551	5.113485
H	8.61583	12.10691	3.584323
C	7.221401	9.862669	3.349107
H	6.852772	9.884197	4.376466
H	7.004758	8.865486	2.965192
C	6.488613	10.89886	2.512684
C	6.260679	10.66105	1.135931
H	6.594693	9.746467	0.656335
C	5.574084	11.62113	0.421242
C	5.102554	12.78926	1.015869
C	5.292179	13.04406	2.35929
H	4.909932	13.94682	2.823195
C	5.992461	12.07185	3.096757
H	6.13673	12.23287	4.161446
C	4.426486	12.77315	-1.11688
H	3.392256	12.45473	-1.30734
H	4.81575	13.35736	-1.95609
C	9.393463	9.888161	2.141946
H	10.40031	10.2915	2.2692
H	8.897798	10.51719	1.388787
C	9.461598	8.452393	1.647787
H	8.455714	8.047309	1.51764
H	9.94255	8.424391	0.659586
C	11.6593	7.74314	2.558658
H	12.05312	7.108584	3.355333
H	11.87527	8.771056	2.849315
C	12.36012	7.426792	1.247991
C	12.8238	6.115174	0.987346
H	12.69367	5.315756	1.709496
C	13.47073	5.887122	-0.20948
C	13.68315	6.901023	-1.14124
C	13.26198	8.194937	-0.90982
H	13.4475	8.987006	-1.62709
C	12.59732	8.437409	0.306714
H	12.27606	9.451841	0.527363
C	14.49606	4.994531	-1.99036
H	15.54933	4.706354	-2.06716
H	13.88706	4.447986	-2.72299
C	9.809548	6.148802	2.37259
H	10.33215	5.576472	3.147357

H	10.2122	5.823373	1.403767
C	8.334184	5.821364	2.398293
C	7.798861	5.028551	1.379492
H	8.437499	4.74118	0.545464
C	6.476117	4.592737	1.417726
C	5.707681	4.948797	2.534187
H	4.689731	4.577157	2.575517
C	6.18213	5.74192	3.585946
C	7.521001	6.223882	3.481477
C	5.882661	3.766655	0.299421
H	5.259026	2.952209	0.686948
H	6.664063	3.320577	-0.32541
H	5.244934	4.372235	-0.35943
C	5.315084	5.997496	4.839467
C	3.910306	5.372319	4.711439
H	3.342605	5.799442	3.876102
H	3.344892	5.570522	5.629013
H	3.949526	4.284989	4.580402
C	5.12637	7.508209	5.109479
H	6.073973	7.984573	5.362142
H	4.437123	7.649109	5.952236
H	4.692842	8.013645	4.237456
C	6.005876	5.348783	6.064198
H	6.11251	4.266324	5.923378
H	5.406199	5.514629	6.968539
H	6.996208	5.77876	6.227253
C	10.33501	5.402141	5.987776
H	9.542102	4.950002	5.371586
C	11.65232	4.662305	5.734725
H	11.93994	4.717186	4.678904
H	11.56226	3.604591	6.009474
H	12.45722	5.109935	6.328784
C	9.916278	5.314224	7.456962
H	10.68769	5.753316	8.100186
H	9.772235	4.267823	7.752703
H	8.979732	5.853296	7.623867

Table S8. Geometry optimized coordinates of **2b'** at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -2873.0655316 Hartree/particle

Ti	0.014379	1.188352	11.75125
O	-1.7347	0.787137	12.37973

O	1.831901	1.148051	11.17801
O	0.33388	2.27316	13.17719
O	-0.50793	2.298215	10.40619
O	0.063957	-4.96052	5.419045
O	1.44493	-5.26991	7.256396
O	-0.51248	-5.76465	15.74922
O	0.918676	-5.45934	17.54871
N	-0.5249	-0.771	10.36093
N	0.858046	-0.83986	12.96486
C	-2.8975	0.187473	12.09832
C	-4.02433	0.326672	12.96311
C	-5.16909	-0.41027	12.64372
H	-6.02729	-0.32833	13.29899
C	-5.28402	-1.25066	11.52367
C	-4.18389	-1.30887	10.66905
H	-4.21907	-1.91415	9.768455
C	-3.01014	-0.59156	10.92642
C	-4.0184	1.30482	14.15995
C	-2.91699	0.942457	15.18279
H	-3.0302	-0.09079	15.53412
H	-2.98923	1.602113	16.05727
H	-1.92536	1.061741	14.74686
C	-3.77202	2.742941	13.64015
H	-2.80576	2.818955	13.13706
H	-3.77946	3.452619	14.47768
H	-4.55937	3.043062	12.93796
C	-5.36404	1.309522	14.91536
H	-6.2006	1.604595	14.27163
H	-5.31118	2.033819	15.73605
H	-5.59572	0.331998	15.3549
C	-6.58555	-2.03709	11.28269
C	-7.76892	-1.05228	11.1252
H	-7.90226	-0.43069	12.01694
H	-8.70534	-1.59919	10.9569
H	-7.60782	-0.38226	10.27278
C	-6.85756	-2.9716	12.48591
H	-6.04084	-3.69157	12.61431
H	-7.78703	-3.53489	12.33362
H	-6.9571	-2.41151	13.42176
C	-6.51628	-2.90552	10.01178
H	-6.36515	-2.29913	9.111169
H	-7.4569	-3.45418	9.885751
H	-5.70773	-3.64378	10.06623
C	-1.92361	-0.59203	9.873667
H	-2.15808	-1.37796	9.14356
H	-1.92732	0.363037	9.337356

C	-0.41461	-2.00128	11.178
H	-0.42693	-2.90023	10.54542
H	-1.30657	-2.04805	11.80637
C	0.836939	-1.9974	12.04237
H	0.910116	-2.94728	12.5908
H	1.730326	-1.93113	11.41745
C	0.414604	-0.75791	9.187906
H	1.429496	-0.76047	9.585666
H	0.270867	0.214434	8.712338
C	0.26842	-1.86366	8.15548
C	1.001806	-3.06582	8.29938
H	1.675037	-3.22165	9.136229
C	0.854828	-4.03041	7.323771
C	1.057336	-5.81914	5.991866
H	1.931108	-5.86229	5.327399
H	0.632744	-6.81646	6.142812
C	0.026525	-3.84512	6.21928
C	-0.68885	-2.67817	6.039775
H	-1.3211	-2.53029	5.171065
C	-0.548	-1.68904	7.030375
H	-1.0811	-0.75061	6.906471
C	-0.03307	-1.03327	14.15831
H	-1.05334	-1.12172	13.78562
H	0.011425	-0.09352	14.71315
C	0.275631	-2.1955	15.08799
C	1.123297	-2.02655	16.19077
H	1.560737	-1.04941	16.3754
C	1.416823	-3.07312	17.08391
H	2.067539	-2.92821	17.93941
C	0.824451	-4.29375	16.82903
C	0.176291	-6.43667	16.80983
H	0.867473	-7.1781	16.38632
H	-0.55221	-6.91626	17.47098
C	-0.03359	-4.47644	15.74709
C	-0.33332	-3.45457	14.86948
H	-1.03108	-3.61167	14.05307
C	2.247114	-0.54863	13.41936
H	2.601073	-1.35867	14.07132
H	2.173024	0.353058	14.03905
C	3.273738	-0.33857	12.33123
C	3.042727	0.589324	11.29387
C	4.102683	0.922816	10.39886
C	5.304268	0.221493	10.5445
H	6.112375	0.450998	9.861076
C	5.537501	-0.75974	11.52297
C	4.499598	-1.00663	12.42144

H	4.625122	-1.72571	13.2255
C	3.971687	2.067928	9.369954
C	2.811271	1.818951	8.378754
H	2.938673	0.862279	7.856937
H	2.796155	2.612402	7.620479
H	1.848673	1.818555	8.89048
C	3.713527	3.39263	10.12976
H	2.792844	3.334038	10.7143
H	3.619587	4.224592	9.419836
H	4.544475	3.620522	10.80849
C	5.256319	2.25363	8.535566
H	6.12572	2.495327	9.157676
H	5.112723	3.085873	7.837077
H	5.494831	1.36369	7.940925
C	6.893071	-1.48725	11.57704
C	8.027312	-0.46233	11.81713
H	7.884675	0.061609	12.76935
H	8.067822	0.292305	11.02456
H	9.001458	-0.96667	11.84809
C	7.143026	-2.21873	10.23633
H	8.108872	-2.73934	10.25584
H	7.156486	-1.52335	9.390407
H	6.359941	-2.96159	10.04456
C	6.948072	-2.53289	12.70762
H	7.922361	-3.03523	12.70137
H	6.177717	-3.30344	12.58739
H	6.820736	-2.07359	13.69469
C	1.323338	3.145317	13.69516
H	2.305271	2.815897	13.32177
C	1.312125	3.065893	15.22452
H	0.333145	3.368998	15.61269
H	2.077299	3.72456	15.65233
H	1.511563	2.044491	15.56688
C	1.065503	4.571921	13.20262
H	1.085173	4.610434	12.10956
H	1.830932	5.257634	13.58576
H	0.083682	4.919647	13.54454
C	-1.26125	3.485445	10.20815
H	-1.40275	3.967919	11.18689
C	-0.46805	4.429105	9.300363
H	0.513445	4.649387	9.73154
H	-1.00644	5.374115	9.15858
H	-0.31166	3.967651	8.318251
C	-2.63738	3.156584	9.623143
H	-2.53244	2.696801	8.632579
H	-3.23304	4.070832	9.511497

H	-3.18339	2.467223	10.27316

Table S9. Geometry optimized coordinates of **3b'** at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = - 4082.4341217 Hartree/particle

Ti	10.31225	-0.00014	7.60748
Cl	10.14129	-0.27972	2.910712
Cl	13.06727	-4.84094	2.534428
O	10.62464	-0.58888	5.806061
O	17.00072	-2.76974	11.02789
O	16.62148	-5.05433	11.15417
O	9.203099	1.33196	7.143691
N	12.25747	-1.4581	7.942383
C	11.16314	-1.56162	5.098125
C	11.043	-1.56733	3.687066
C	11.60921	-2.56241	2.896553
H	11.49261	-2.53669	1.819578
C	12.33043	-3.58008	3.516321
C	12.48215	-3.60411	4.900191
H	13.05348	-4.40237	5.364337
C	11.89874	-2.61395	5.695522
C	12.01189	-2.72854	7.199771
H	11.07857	-3.13117	7.610226
H	12.80692	-3.44996	7.427
C	13.44715	-0.74004	7.419123
H	13.44428	-0.85015	6.332674
H	14.37694	-1.2037	7.776631
C	12.36174	-1.7688	9.414551
H	11.3907	-2.18267	9.697617
H	12.44859	-0.81787	9.936745
C	13.47807	-2.69944	9.855314
C	13.26301	-4.08025	9.955397
H	12.28312	-4.4806	9.710405
C	14.26392	-4.97051	10.38544
H	14.08421	-6.03719	10.46346
C	15.48568	-4.42018	10.71759
C	15.71308	-3.04778	10.63998
C	14.73721	-2.16622	10.22231
H	14.92889	-1.09809	10.20285
C	17.5527	-4.01367	11.47564
H	18.49875	-4.19948	10.95796
H	17.70105	-3.97852	12.56321

C	7.93	1.954365	7.192277
H	7.17696	1.171585	7.015886
C	7.836623	2.981804	6.063165
H	6.835404	3.427178	6.029516
H	8.04084	2.507454	5.098231
H	8.565227	3.787247	6.215905
C	7.694163	2.566182	8.574993
H	7.786683	1.804737	9.355441
H	6.692046	3.007793	8.632226
H	8.429783	3.353141	8.778003
O	10.62492	0.588578	9.408847
O	9.203252	-1.33226	8.071414
N	12.25707	1.458263	7.272238
C	13.44701	0.740492	7.795308
Cl	10.14213	0.279338	12.30427
Cl	13.0667	4.841493	12.68
O	16.99941	2.771042	4.185732
O	16.61961	5.055547	4.059597
C	11.16323	1.561519	10.11667
C	11.0433	1.56722	11.52775
C	11.60931	2.562493	12.31815
H	11.49289	2.536757	13.39514
C	12.33012	3.580376	11.69825
C	12.48163	3.604423	10.31436
H	13.05263	4.402851	9.850101
C	11.89841	2.614055	9.519137
C	12.0113	2.728655	8.014869
H	11.07781	3.131042	7.60456
H	12.80612	3.450259	7.787508
H	13.44429	0.850615	8.881758
H	14.37663	1.204376	7.437642
C	12.36101	1.768968	5.800047
H	11.38982	2.1826	5.517153
H	12.448	0.818054	5.27785
C	13.47703	2.699873	5.359072
C	13.26162	4.080642	5.259064
H	12.28169	4.48075	5.504277
C	14.26223	4.971147	4.828823
H	14.08224	6.037779	4.750871
C	15.48405	4.421115	4.496402
C	15.71179	3.048767	4.573927
C	14.73621	2.166967	4.991785
H	14.92815	1.09888	5.011171
C	17.55096	4.015105	3.737819
H	18.49714	4.20113	4.255205
H	17.69898	3.979999	2.650205

C	7.930691	-1.95575	8.022824
H	7.177024	-1.1736	8.19931
C	7.838189	-2.98334	9.151871
H	6.837293	-3.42944	9.185597
H	8.042169	-2.50891	10.11682
H	8.567346	-3.78826	8.999002
C	7.695278	-2.56766	6.640075
H	7.787113	-1.80608	5.859674
H	6.693521	-3.01009	6.58288
H	8.431528	-3.354	6.436947

Table S10. Geometry optimized coordinates of **4b'** at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -3705.384965 Hartree/particle

Ti	8.285817	4.953504	15.96595
Cl	3.871488	6.496422	16.43537
Cl	2.678578	3.5248	20.81915
Cl	12.2772	0.89504	11.0544
Cl	12.86374	3.70392	15.65912
O	9.14333	5.886491	17.24953
O	8.08294	6.10969	14.59293
O	6.528394	5.197454	16.68088
O	9.942386	4.160326	15.37899
N	8.062886	2.925711	17.39203
N	7.403076	3.241166	14.50809
C	10.45092	6.267494	17.66119
H	11.1545	5.536476	17.24054
C	10.52282	6.235837	19.1895
H	9.799469	6.936742	19.62157
H	11.52603	6.514114	19.53279
H	10.30058	5.233913	19.57335
C	10.78163	7.653022	17.10294
H	10.74872	7.644949	16.00946
H	11.78784	7.95955	17.41276
H	10.06327	8.395181	17.47015
C	8.090577	7.496212	14.27663
H	8.340834	8.049368	15.19319
C	9.166302	7.762104	13.22143
H	10.14863	7.433705	13.57638
H	9.22056	8.831933	12.98724
H	8.937649	7.21832	12.29706
C	6.695543	7.916615	13.81168

H	6.424149	7.388368	12.88933
H	6.667149	8.994199	13.60997
H	5.952068	7.683418	14.57896
C	5.682953	4.824303	17.62188
C	4.364807	5.338362	17.65461
C	3.444389	4.957471	18.62692
H	2.444634	5.375384	18.6251
C	3.831157	4.028431	19.58933
C	5.115127	3.488873	19.583
H	5.396941	2.761243	20.33794
C	6.043304	3.884919	18.61722
C	7.45442	3.348463	18.68873
H	8.119412	4.122391	19.0889
H	7.462082	2.509041	19.39534
C	9.434274	2.363987	17.65624
H	10.01404	3.178712	18.09721
H	9.890047	2.155169	16.68989
C	9.522688	1.129128	18.53761
C	9.697983	1.239243	19.9257
H	9.772387	2.225341	20.37857
C	9.798084	0.104355	20.73184
H	9.936565	0.214377	21.80404
C	9.731799	-1.16794	20.16048
H	9.812562	-2.05276	20.78586
C	9.578934	-1.29613	18.7789
H	9.547255	-2.28176	18.32238
C	9.481575	-0.15726	17.97755
H	9.395232	-0.27057	16.89909
C	7.192129	1.97712	16.65523
H	6.159916	2.307952	16.78798
H	7.252487	0.966553	17.08265
C	7.537616	1.918251	15.16935
H	8.570346	1.589408	15.03635
H	6.904871	1.167346	14.67704
C	5.965975	3.603773	14.22293
H	5.445948	3.628678	15.17965
H	5.989338	4.632854	13.85754
C	5.207374	2.715193	13.25267
C	4.472914	1.611231	13.7128
H	4.441167	1.395159	14.77849
C	3.758427	0.801455	12.82824
H	3.194347	-0.04635	13.20763
C	3.757074	1.089712	11.46244
H	3.197823	0.463801	10.77248
C	4.464037	2.197442	10.99028
H	4.452963	2.440782	9.931239

C	5.177793	3.002416	11.87917
H	5.708158	3.87508	11.50525
C	8.179689	3.297661	13.2333
H	8.072515	4.325967	12.87219
H	7.720376	2.632706	12.49151
C	9.647092	2.943815	13.33512
C	10.21666	2.159973	12.32848
H	9.592745	1.773121	11.52846
C	11.57991	1.876887	12.33685
C	12.39732	2.354179	13.35745
H	13.45768	2.13193	13.37385
C	11.82646	3.119739	14.36995
C	10.44813	3.444333	14.39158

Table S11. Geometry optimized coordinates of **4c'** at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -3468.1832782 Hartree/particle

Ti	1.002368	-0.21611	-0.84636
Cl	-0.34502	-4.55122	-1.15495
Cl	-5.70865	-3.70568	-1.31019
Cl	4.161501	5.079715	3.222707
Cl	2.287502	4.227271	-1.80276
O	2.54609	-1.10615	-0.40489
O	-0.21994	-1.57946	-1.30082
O	1.502811	1.598734	-0.72596
N	-1.32859	0.889796	-0.5756
N	0.763436	-0.10061	1.392402
C	-1.45339	-2.06073	-1.31096
C	-1.69807	-3.45014	-1.24593
C	-2.99447	-3.95997	-1.25054
H	-3.15806	-5.03012	-1.20234
C	-4.06837	-3.07412	-1.31299
C	-3.85984	-1.69757	-1.36965
H	-4.70933	-1.02303	-1.41425
C	-2.55967	-1.18814	-1.37543
C	-2.32348	0.294878	-1.51674
H	-1.94492	0.511346	-2.52601
H	-3.28934	0.806889	-1.42101
C	-1.26756	2.3741	-0.81281
H	-0.9228	2.504452	-1.84272
H	-0.47732	2.773519	-0.18008
C	-2.54477	3.167117	-0.58988

C	-3.43855	3.414387	-1.64334
H	-3.21252	3.034278	-2.63706
C	-4.60172	4.158648	-1.44122
H	-5.27709	4.340779	-2.27275
C	-4.88959	4.677815	-0.17746
H	-5.7927	5.260633	-0.01902
C	-4.00111	4.459255	0.876835
H	-4.20593	4.877506	1.85862
C	-2.83802	3.716171	0.66815
H	-2.13697	3.582397	1.489174
C	-1.61943	0.545127	0.835252
H	-1.93153	-0.50156	0.861933
H	-2.46305	1.130665	1.228802
C	-0.41055	0.757396	1.742948
H	-0.07616	1.794822	1.688161
H	-0.70068	0.574949	2.784846
C	0.604108	-1.52682	1.888548
H	-0.2738	-1.93614	1.384183
H	1.468631	-2.07129	1.502717
C	0.47631	-1.72342	3.386655
C	-0.78473	-1.76407	4.001296
H	-1.68183	-1.65873	3.394878
C	-0.90724	-1.96544	5.377093
H	-1.89314	-1.99751	5.832653
C	0.234142	-2.13955	6.161684
H	0.141088	-2.30107	7.23202
C	1.495101	-2.12274	5.561826
H	2.38709	-2.27725	6.162598
C	1.612974	-1.9209	4.186099
H	2.597378	-1.93335	3.724491
C	2.021562	0.495976	1.952694
H	2.831064	-0.1795	1.660448
H	1.957775	0.49171	3.046913
C	2.354107	1.906453	1.498932
C	2.968199	2.759042	2.421848
H	3.130635	2.423621	3.44151
C	3.385722	4.031987	2.043746
C	3.186792	4.49074	0.74412
H	3.505424	5.482611	0.446474
C	2.559252	3.652217	-0.17203
C	2.13427	2.349307	0.170991
O	2.423645	-0.84433	-1.81929

Table S12. Geometry optimized transition state coordinates of **4d'** at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -4137.9077853 Hartree/particle

Calculated frequency along the bond O4•••O1•••S1 is i462.

Ti	-0.16786	-0.09229	-1.45375
Cl	-3.32838	-3.44167	-0.44586
Cl	-7.38659	0.125016	0.084783
Cl	6.296609	2.252966	1.817145
Cl	3.473138	2.129691	-2.82329
O	-0.09127	-0.91244	-3.13442
O	-1.65606	-1.02263	-0.72923
O	1.688702	0.313077	-1.30226
N	-1.12635	1.697909	-0.29997
N	0.522633	-0.36531	1.220279
C	-2.94513	-0.73826	-0.59235
C	-3.88591	-1.77794	-0.41616
C	-5.24113	-1.53316	-0.21868
H	-5.93289	-2.35738	-0.09219
C	-5.68039	-0.21293	-0.1789
C	-4.78352	0.840101	-0.33432
H	-5.14723	1.862345	-0.29445
C	-3.42396	0.596129	-0.55086
C	-2.52826	1.795786	-0.81231
H	-2.44258	1.951	-1.89253
H	-3.00933	2.682514	-0.38102
C	-0.34035	2.919538	-0.71858
H	-0.33776	2.906989	-1.81123
H	0.691326	2.754046	-0.39964
C	-0.82593	4.263381	-0.20717
C	-1.75249	5.01975	-0.9415
H	-2.12254	4.63799	-1.89007
C	-2.19057	6.262165	-0.48106
H	-2.90595	6.83295	-1.06687
C	-1.70145	6.775271	0.722022
H	-2.03854	7.74431	1.079707
C	-0.76423	6.0445	1.45423
H	-0.36376	6.444635	2.381795
C	-0.32885	4.802375	0.989386
H	0.422243	4.254605	1.554295
C	-1.13622	1.501296	1.177099
H	-1.94644	0.805168	1.401587
H	-1.38791	2.446679	1.67619

C	0.179554	0.971185	1.742
H	0.997732	1.647322	1.481323
H	0.113958	0.978232	2.841372
C	-0.28642	-1.46447	1.834291
H	-1.3339	-1.25804	1.618933
H	-0.03718	-2.37386	1.27952
C	-0.10801	-1.70383	3.325685
C	-0.9298	-1.05656	4.261242
H	-1.71557	-0.38957	3.912931
C	-0.77441	-1.2748	5.631467
H	-1.42475	-0.76451	6.336979
C	0.204686	-2.15663	6.092257
H	0.325129	-2.33152	7.157908
C	1.017381	-2.8249	5.174198
H	1.770139	-3.52696	5.523266
C	0.858163	-2.60171	3.805667
H	1.480611	-3.14308	3.096756
C	1.967661	-0.67038	1.36538
H	2.122254	-1.64823	0.890338
H	2.237874	-0.78344	2.425388
C	2.910119	0.334312	0.746104
C	4.003175	0.807194	1.475916
H	4.13992	0.496657	2.507229
C	4.923233	1.670383	0.88449
C	4.769372	2.082733	-0.43687
H	5.482638	2.755615	-0.89805
C	3.673969	1.618218	-1.16085
C	2.720829	0.740015	-0.595
O	-0.74114	0.744502	-2.85523
S	0.899132	-2.86525	-3.46437
C	1.544311	-3.5848	-1.96734
C	2.880509	-3.48788	-1.55268
C	0.623616	-4.30707	-1.18713
C	3.290856	-4.12793	-0.38069
C	1.044468	-4.93802	-0.01833
C	2.380673	-4.85655	0.387617
H	3.603919	-2.92827	-2.13453
H	-0.41677	-4.36684	-1.49459
H	4.330912	-4.05724	-0.07377
H	0.325925	-5.4982	0.573431
H	2.709344	-5.3615	1.291635
C	2.317843	-1.98764	-4.18261
H	3.115909	-2.6829	-4.45554
H	1.923817	-1.50616	-5.07948
H	2.668779	-1.21264	-3.49824

Table S13. Geometry optimized coordinates of **4e'** at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -4137.9990636 Hartree/particle

Ti	0.61616	0.009415	-1.19265
Cl	-0.56441	-4.60482	-0.88359
Cl	-5.82402	-3.63111	-1.83711
Cl	3.67656	5.287395	3.35207
Cl	2.341278	4.248003	-1.81084
O	2.355141	-1.12648	-1.27366
O	-0.34654	-1.65529	-0.88544
O	1.637595	1.580115	-0.75328
N	-1.40248	0.924044	-0.56604
N	0.638022	0.003807	1.464051
C	-1.5682	-2.07332	-1.14744
C	-1.86816	-3.45769	-1.15841
C	-3.15125	-3.94772	-1.37536
H	-3.33694	-5.0153	-1.37787
C	-4.18611	-3.03787	-1.57611
C	-3.94029	-1.66804	-1.56191
H	-4.76236	-0.97507	-1.71515
C	-2.64664	-1.1769	-1.36286
C	-2.43715	0.321805	-1.46653
H	-2.11837	0.573026	-2.48335
H	-3.40103	0.812109	-1.28275
C	-1.31223	2.407182	-0.84992
H	-0.97095	2.489482	-1.88461
H	-0.51187	2.803727	-0.22571
C	-2.57187	3.22937	-0.64193
C	-3.46924	3.455016	-1.69709
H	-3.25994	3.029691	-2.67573
C	-4.61475	4.230561	-1.5135
H	-5.29426	4.394593	-2.34555
C	-4.88029	4.803344	-0.26799
H	-5.76978	5.410707	-0.12435
C	-3.98788	4.604975	0.786961
H	-4.17601	5.062588	1.75452
C	-2.84285	3.829435	0.59738
H	-2.1397	3.706513	1.418155
C	-1.7055	0.629267	0.863099
H	-2.02439	-0.41366	0.912577
H	-2.55597	1.236265	1.201675
C	-0.51688	0.859049	1.799481
H	-0.18709	1.898882	1.736997

H	-0.85593	0.706547	2.835526
C	0.491745	-1.4074	1.938492
H	-0.38508	-1.82657	1.446387
H	1.350187	-1.95287	1.533859
C	0.397946	-1.62574	3.44026
C	-0.84963	-1.65578	4.082848
H	-1.757	-1.5393	3.494083
C	-0.94772	-1.85952	5.460432
H	-1.92518	-1.88172	5.935091
C	0.206108	-2.04844	6.223185
H	0.132389	-2.21145	7.295014
C	1.454369	-2.04284	5.597493
H	2.356968	-2.20733	6.180229
C	1.54575	-1.83701	4.219919
H	2.521206	-1.85681	3.739116
C	1.931956	0.558905	1.935276
H	2.704977	-0.1041	1.522414
H	2.00765	0.497271	3.030512
C	2.231907	1.984414	1.529145
C	2.707603	2.881269	2.489287
H	2.797713	2.566354	3.524492
C	3.0749	4.174837	2.12678
C	2.968034	4.603138	0.805941
H	3.250318	5.609807	0.52097
C	2.483266	3.71339	-0.14843
C	2.102415	2.387262	0.175821
O	0.323103	0.22154	-2.79861
S	2.474268	-2.20072	-2.4042
C	4.028509	-3.03263	-2.03208
C	5.064615	-2.34354	-1.39683
C	4.147633	-4.37965	-2.37889
C	6.252224	-3.02086	-1.12355
C	5.346386	-5.04354	-2.10796
C	6.394423	-4.36521	-1.483
H	4.927103	-1.30574	-1.10938
H	3.317152	-4.90494	-2.84311
H	7.066858	-2.50048	-0.628
H	5.453916	-6.0911	-2.37341
H	7.322293	-4.88684	-1.26614
C	2.974098	-1.2275	-3.86276
H	3.14694	-1.91653	-4.6944
H	2.132476	-0.5588	-4.06554
H	3.875852	-0.65915	-3.62385

Table S14. Geometry optimized transition state coordinates of **4f'** at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -4289.5007516 Hartree/particle

Calculated frequency along the bond O4•••H36•••O5 is i1462.

Ti	-0.07156	-0.03671	-1.07775
Cl	3.585688	-2.5642	-2.91159
Cl	3.871668	-5.92747	1.343165
Cl	-0.95786	7.171985	0.899954
Cl	-3.70486	2.530163	0.254449
O	-2.84165	-2.63146	0.38757
O	1.372137	-1.31962	-1.36025
O	-1.07213	1.493123	-0.64332
N	0.179096	-0.65333	1.074701
N	1.716198	1.497134	-0.3982
C	1.914768	-2.36651	-0.75577
C	2.990377	-3.07197	-1.34094
C	3.58973	-4.16234	-0.71766
H	4.409485	-4.68304	-1.19823
C	3.119953	-4.56043	0.531137
C	2.070147	-3.88294	1.145902
H	1.720088	-4.20491	2.121808
C	1.457881	-2.79915	0.510788
C	0.258925	-2.15406	1.166881
H	-0.67669	-2.52932	0.732904
H	0.255307	-2.43665	2.225304
C	-1.06605	-0.18562	1.816773
H	-1.91308	-0.57036	1.244153
H	-1.08217	0.901089	1.744593
C	-1.20053	-0.6099	3.266541
C	-1.91833	-1.77051	3.599369
H	-2.36865	-2.35992	2.804304
C	-2.07221	-2.15187	4.933034
H	-2.63248	-3.05135	5.174374
C	-1.51971	-1.37696	5.955462
H	-1.643	-1.67375	6.993547
C	-0.82393	-0.20887	5.638991
H	-0.40997	0.411673	6.429247
C	-0.67191	0.172546	4.304553
H	-0.15859	1.102917	4.070796
C	1.431724	-0.01417	1.584701
H	2.265056	-0.64378	1.267357
H	1.431889	-0.02096	2.68171

C	1.63365	1.417715	1.084497
H	0.801434	2.046975	1.405811
H	2.535289	1.832907	1.555472
C	3.056886	1.058733	-0.93241
H	3.209185	0.03111	-0.60383
H	2.943854	1.025168	-2.01901
C	4.262007	1.897416	-0.54559
C	5.001627	1.608802	0.612137
H	4.714918	0.765247	1.236694
C	6.120126	2.367648	0.961416
H	6.678981	2.123745	1.860976
C	6.527439	3.426778	0.14849
H	7.400299	4.016178	0.415645
C	5.817797	3.71233	-1.01968
H	6.140229	4.52125	-1.66973
C	4.699663	2.951087	-1.3634
H	4.168085	3.165137	-2.28762
C	1.410155	2.865919	-0.91944
H	1.323624	2.751318	-2.00687
H	2.251733	3.539375	-0.7188
C	0.156908	3.511755	-0.37557
C	0.173822	4.856749	-0.00204
H	1.098105	5.423545	-0.05531
C	-0.99518	5.477199	0.435179
C	-2.19351	4.772354	0.518802
H	-3.10123	5.25453	0.861692
C	-2.20822	3.427864	0.155286
C	-1.04389	2.772291	-0.29999
O	-1.25522	-0.84653	-2.0443
S	-3.30708	-2.97904	-1.02636
C	-4.59438	-1.78132	-1.48069
C	-5.26326	-1.08311	-0.47622
C	-4.87155	-1.56137	-2.83
C	-6.25263	-0.16588	-0.83279
C	-5.86619	-0.64472	-3.17664
C	-6.55631	0.049567	-2.18014
H	-4.99024	-1.25097	0.561474
H	-4.31047	-2.08452	-3.60008
H	-6.78327	0.384502	-0.06051
H	-6.09052	-0.46264	-4.22391
H	-7.32308	0.768897	-2.45406
C	-4.43148	-4.41522	-0.80482
H	-4.91862	-4.64712	-1.75633
H	-3.81587	-5.25932	-0.48236
H	-5.1736	-4.17482	-0.03907
O	0.261266	0.529561	-3.08483

O	1.509716	0.11515	-3.69884
H	1.744526	-0.66813	-3.15164
H	-0.64771	-0.35746	-2.97055

Table S15. Geometry optimized coordinates of **4g'** at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -4289.5495653 Hartree/particle

Ti	1.866291	-0.90233	-1.27576
Cl	0.219359	-5.2909	-0.65362
Cl	-4.75235	-4.19534	-2.56515
Cl	4.597852	4.651734	3.022037
Cl	4.01316	3.141455	-2.16261
O	-0.18735	0.542963	-5.56124
O	0.694939	-2.43567	-1.17337
O	2.743638	0.749962	-0.98285
N	-0.19753	0.229785	-1.43599
N	1.205029	-0.43532	1.071676
C	-0.52585	-2.81051	-1.51861
C	-0.93835	-4.14655	-1.31589
C	-2.21818	-4.58754	-1.63629
H	-2.50091	-5.62038	-1.4712
C	-3.12179	-3.66908	-2.16478
C	-2.75279	-2.34235	-2.37573
H	-3.47246	-1.6446	-2.79265
C	-1.46063	-1.90518	-2.07105
C	-1.07118	-0.48541	-2.42315
H	-0.5371	-0.46435	-3.37751
H	-1.99265	0.093461	-2.55736
C	0.105024	1.611443	-1.9881
H	0.637134	1.437281	-2.92424
H	0.809521	2.078757	-1.30241
C	-1.07721	2.538602	-2.20947
C	-1.74797	2.575408	-3.44348
H	-1.41774	1.925777	-4.24995
C	-2.81503	3.453438	-3.6452
H	-3.32155	3.46963	-4.60684
C	-3.22565	4.313957	-2.62487
H	-4.05502	4.997638	-2.78596
C	-2.55366	4.30267	-1.40129
H	-2.8517	4.982257	-0.60718
C	-1.48625	3.425533	-1.20105
H	-0.94974	3.44647	-0.25439

C	-0.8574	0.284078	-0.1039
H	-1.33303	-0.68506	0.062177
H	-1.65888	1.033727	-0.10319
C	0.130801	0.583673	1.016289
H	0.603487	1.554788	0.85338
H	-0.40624	0.653309	1.972528
C	0.749313	-1.72621	1.701136
H	-0.06804	-2.11016	1.092503
H	1.580747	-2.42345	1.577918
C	0.316451	-1.67187	3.156124
C	-1.02451	-1.43776	3.498305
H	-1.76243	-1.30041	2.710864
C	-1.43349	-1.4065	4.832673
H	-2.47778	-1.22639	5.073433
C	-0.5053	-1.62067	5.853075
H	-0.82164	-1.60166	6.892412
C	0.8287	-1.87694	5.529662
H	1.554344	-2.06428	6.316623
C	1.232017	-1.90577	4.193911
H	2.268449	-2.12901	3.951613
C	2.406858	0.061101	1.804963
H	3.157017	-0.73471	1.723373
H	2.168848	0.177445	2.869809
C	2.995253	1.364023	1.313245
C	3.429564	2.307106	2.248337
H	3.287489	2.122676	3.308763
C	4.0525	3.479819	1.828955
C	4.241521	3.743812	0.474451
H	4.721204	4.658122	0.145908
C	3.793999	2.81281	-0.4583
C	3.168841	1.604687	-0.0693
O	1.918509	-0.75362	-3.11245
S	1.072472	-0.00183	-6.21321
C	2.293319	1.348236	-6.2657
C	1.893758	2.632358	-5.90246
C	3.617019	1.069357	-6.61232
C	2.836395	3.663008	-5.90756
C	4.55063	2.106432	-6.61976
C	4.160621	3.40182	-6.26767
H	0.862455	2.80615	-5.61059
H	3.922152	0.056528	-6.86661
H	2.537431	4.668332	-5.62408
H	5.583238	1.901357	-6.88803
H	4.892249	4.204905	-6.26495
C	0.720616	-0.03196	-8.0167
H	1.633239	-0.2813	-8.56548

H	-0.04051	-0.79901	-8.18277
H	0.341308	0.947388	-8.31965
O	3.175886	-1.86085	-0.29632
O	3.275258	-2.65497	-1.5079
H	2.609742	-3.35865	-1.33543
H	2.507632	-1.36668	-3.57916

Table S16. Geometry optimized transition state coordinates of **4h'** at the

B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -3544.5903857 Hartree/particle

Calculated frequency along the bond O4•••H28•••O5 is i1236.

Ti	0.130259	-0.05715	-1.76455
Cl	-3.74741	-2.56961	-2.17683
Cl	-6.91834	0.677709	0.805643
Cl	6.963364	-1.15505	0.941828
Cl	4.070023	2.526129	-1.80822
O	0.973427	-1.45965	-2.63159
O	-1.71543	-0.44209	-1.70781
O	1.829274	0.670153	-1.30626
N	-0.61945	1.452872	0.030352
N	0.538488	-1.29255	0.148257
C	-2.88816	-0.19256	-1.14344
C	-3.96635	-1.09637	-1.26443
C	-5.20172	-0.83527	-0.67551
H	-6.01608	-1.54187	-0.7835
C	-5.36743	0.341449	0.052117
C	-4.31981	1.249437	0.196866
H	-4.4675	2.158274	0.77199
C	-3.08498	0.991336	-0.40118
C	-1.96776	2.002334	-0.30751
H	-1.84485	2.514601	-1.27104
H	-2.25542	2.765562	0.425336
C	0.355712	2.601486	0.139534
H	0.40229	3.048012	-0.85734
H	1.337032	2.168199	0.317885
C	0.060833	3.660486	1.186333
C	-0.68967	4.804454	0.872286
H	-1.06786	4.934727	-0.13911
C	-0.93826	5.788283	1.830328
H	-1.51853	6.66738	1.56332
C	-0.43109	5.64969	3.123914

H	-0.6202	6.41669	3.86985
C	0.336629	4.529743	3.44758
H	0.75476	4.424315	4.444993
C	0.583357	3.549673	2.484581
H	1.212591	2.699246	2.738081
C	-0.65911	0.614743	1.257243
H	-1.60784	0.07393	1.257642
H	-0.65526	1.236024	2.162885
C	0.504476	-0.37083	1.319983
H	1.454341	0.166316	1.335961
H	0.448413	-0.94437	2.254251
C	-0.5074	-2.38516	0.234138
H	-1.47742	-1.8944	0.302929
H	-0.48047	-2.89528	-0.73182
C	-0.36847	-3.38701	1.365864
C	-0.98836	-3.16187	2.604683
H	-1.57902	-2.26069	2.754697
C	-0.88422	-4.09154	3.640759
H	-1.37477	-3.89854	4.590928
C	-0.16447	-5.27226	3.450107
H	-0.08613	-5.99968	4.253298
C	0.439948	-5.5213	2.216106
H	0.986209	-6.44622	2.052831
C	0.334184	-4.58816	1.18408
H	0.790968	-4.79972	0.220231
C	1.888188	-1.93327	0.018333
H	1.825818	-2.58289	-0.86185
H	2.059915	-2.57673	0.888879
C	3.070788	-0.99851	-0.11977
C	4.293892	-1.40391	0.423969
H	4.358737	-2.33776	0.974094
C	5.433003	-0.62294	0.257552
C	5.374761	0.585669	-0.43349
H	6.25831	1.200256	-0.5584
C	4.154588	0.999559	-0.95697
C	2.979062	0.222986	-0.8259
O	0.126074	-0.88395	-3.65297
O	0.126252	1.408471	-3.21384
H	-0.75197	1.664156	-3.54439
H	0.355132	0.303653	-3.79304

Table S17. Geometry optimized coordinates of $\mathbf{TiOOH}^{\oplus}$ at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -3468.5632795 Hartree/particle

Ti	0.821714	-0.1943	-0.72934
Cl	-0.30279	-4.50096	-1.80376
Cl	-5.67459	-3.6965	-1.77127
Cl	3.927512	5.300016	2.992145
Cl	2.329901	4.028781	-2.03222
O	2.341633	-1.23328	-0.30501
O	-0.22054	-1.55479	-1.41241
O	1.540336	1.47145	-0.7791
N	-1.29539	0.827827	-0.46862
N	0.720118	-0.08539	1.457238
C	-1.46324	-2.05081	-1.5377
C	-1.67563	-3.42887	-1.70196
C	-2.96887	-3.94128	-1.77817
H	-3.12757	-5.00617	-1.90171
C	-4.05059	-3.06354	-1.68867
C	-3.85441	-1.68915	-1.5355
H	-4.71118	-1.02498	-1.48411
C	-2.55802	-1.17625	-1.46845
C	-2.31072	0.310837	-1.45206
H	-1.94811	0.624175	-2.44042
H	-3.26037	0.828188	-1.28362
C	-1.20415	2.339204	-0.66984
H	-0.8298	2.480359	-1.68686
H	-0.42861	2.706527	-0.00099
C	-2.47468	3.138279	-0.45969
C	-3.32459	3.439099	-1.53587
H	-3.07371	3.09102	-2.53529
C	-4.47639	4.203278	-1.34617
H	-5.11782	4.431204	-2.19237
C	-4.79424	4.686164	-0.07495
H	-5.68792	5.28517	0.072534
C	-3.9477	4.414342	1.001447
H	-4.17596	4.807282	1.987869
C	-2.79482	3.652363	0.807211
H	-2.12421	3.48211	1.64706
C	-1.66261	0.474725	0.930045
H	-1.95656	-0.57901	0.939421
H	-2.53095	1.054111	1.266979
C	-0.4838	0.718084	1.861553
H	-0.19282	1.769489	1.849553
H	-0.75222	0.471008	2.893244
C	0.633899	-1.5207	2.002142
H	-0.23607	-1.97472	1.519953
H	1.517796	-2.03572	1.623531

C	0.536283	-1.66883	3.504032
C	-0.71425	-1.77556	4.133444
H	-1.62423	-1.75604	3.536918
C	-0.80617	-1.94028	5.51612
H	-1.78119	-2.0273	5.986342
C	0.354482	-2.01023	6.289015
H	0.284814	-2.14425	7.364369
C	1.605602	-1.92955	5.673423
H	2.511583	-2.0083	6.266934
C	1.695284	-1.76528	4.290861
H	2.674339	-1.73532	3.81862
C	1.983956	0.57574	1.962242
H	2.803724	-0.09773	1.697647
H	1.927182	0.614872	3.054274
C	2.284964	1.970274	1.439921
C	2.82987	2.904473	2.325004
H	2.954093	2.653686	3.373462
C	3.239369	4.15838	1.867763
C	3.10074	4.514048	0.526839
H	3.416712	5.488575	0.173945
C	2.536161	3.598468	-0.35798
C	2.127743	2.327258	0.082283
O	2.395673	-1.12603	-1.74638
H	2.071914	-2.00724	-2.044

Table S18. Geometry optimized coordinates of $\mathbf{TiOOH^{\oplus}_{TS}}$ at the B3LYP/LANL2DZ, 6-31G(d) level of theory.

E = -4128.3029438 Hartree/particle

Calculated frequency along the bond H27O4•••O1•••S1 is i338.

Ti	-0.06622	0.104876	-1.28978
Cl	-2.96359	-3.55857	-0.60605
Cl	-7.22422	-0.44028	0.619907
Cl	6.403585	2.235143	1.831229
Cl	3.147039	3.215862	-2.3994
O	0.184606	-0.469	-3.04287
O	-1.5748	-0.94555	-0.97104
O	1.557049	0.968654	-1.2295
N	-1.22569	1.720411	-0.28791
N	0.590163	-0.35023	0.925269
C	-2.85927	-0.82902	-0.6064

C	-3.65813	-1.96926	-0.39176
C	-4.99645	-1.86102	-0.02327
H	-5.59268	-2.7526	0.130684
C	-5.54988	-0.5929	0.147082
C	-4.77939	0.55257	-0.04825
H	-5.22861	1.530496	0.093259
C	-3.44013	0.446739	-0.43319
C	-2.66431	1.715827	-0.72042
H	-2.65591	1.931316	-1.79471
H	-3.174	2.554447	-0.23549
C	-0.59593	3.064229	-0.65865
H	-0.60489	3.096081	-1.75112
H	0.447446	3.009201	-0.34959
C	-1.24385	4.303019	-0.07864
C	-2.2523	4.985006	-0.77774
H	-2.57553	4.620826	-1.75032
C	-2.82815	6.142437	-0.25291
H	-3.60274	6.660477	-0.81073
C	-2.39758	6.6418	0.978254
H	-2.84158	7.545729	1.384643
C	-1.37938	5.98787	1.674345
H	-1.02268	6.385056	2.620185
C	-0.80454	4.831123	1.145892
H	0.01386	4.35208	1.679538
C	-1.14426	1.438489	1.185778
H	-1.92181	0.709479	1.419176
H	-1.3864	2.350787	1.74227
C	0.218848	0.918349	1.623341
H	0.9939	1.655687	1.408183
H	0.21689	0.770832	2.709961
C	-0.13897	-1.5568	1.499079
H	-1.2039	-1.36989	1.374138
H	0.111984	-2.39508	0.843514
C	0.148565	-1.91476	2.943768
C	-0.62384	-1.37218	3.983072
H	-1.44231	-0.69382	3.751055
C	-0.38044	-1.71708	5.313373
H	-0.99146	-1.28965	6.103079
C	0.6347	-2.62338	5.624823
H	0.821834	-2.89777	6.658806
C	1.394379	-3.19184	4.600147
H	2.17	-3.91523	4.834752
C	1.149661	-2.84318	3.271255
H	1.726659	-3.3131	2.477898
C	2.071011	-0.60384	1.020528
H	2.266956	-1.47941	0.386454

H	2.317783	-0.89377	2.046728
C	2.965656	0.542744	0.615648
C	4.114583	0.845531	1.346975
H	4.353948	0.291035	2.248783
C	4.964116	1.865096	0.913036
C	4.678979	2.600649	-0.23776
H	5.340316	3.393677	-0.56642
C	3.526922	2.305205	-0.96403
C	2.665457	1.274375	-0.54731
O	-0.86259	0.861904	-3.01391
H	-1.67458	0.382026	-3.26458
S	1.859261	-2.11384	-3.04083
C	1.854773	-3.48011	-1.8776
C	3.080045	-3.8295	-1.29025
C	0.68022	-4.15749	-1.51918
C	3.127776	-4.86562	-0.35424
C	0.741531	-5.19682	-0.59011
C	1.961998	-5.55211	-0.0066
H	3.98901	-3.31106	-1.58142
H	-0.27362	-3.87424	-1.95271
H	4.079961	-5.14622	0.086582
H	-0.16647	-5.72771	-0.31935
H	2.00352	-6.36622	0.710956
C	1.008863	-2.81952	-4.49572
H	-0.00681	-3.12791	-4.24309
H	0.972398	-2.02132	-5.23934
H	1.587189	-3.66378	-4.87724

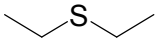
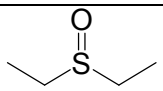
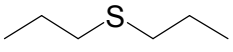
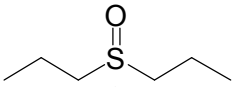
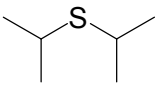
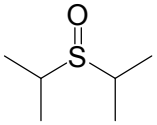
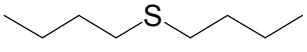
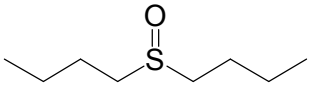
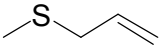
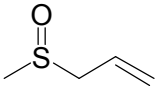
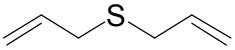
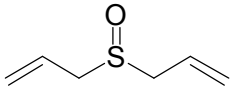
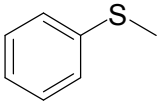
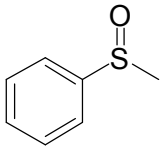
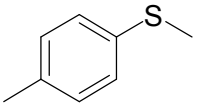
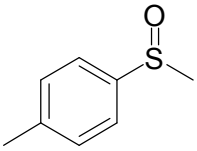
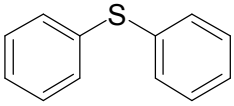
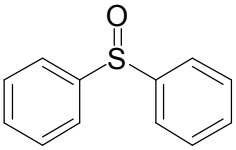
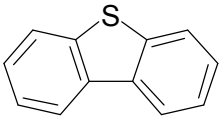
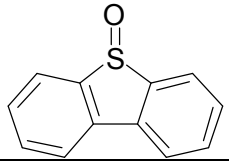
Table S19. Natural charge analysis of **4b'**–**4h'**.

		natural charge						
moiety/compound	center	**4b'**	**4c'**	**4d'**	**4e'**	**4f'**	**4g'**	**4h'**
metal	Ti1	1.536	1.573	1.554	1.428	1.528	1.469	1.447
peroxo	O1		-0.408	-0.503	-0.907	-0.995	-0.978	-0.376
	O4		-0.365	-0.516	-0.706	-0.797	-0.877	-0.454
sulfide	S1			0.596	1.317	1.307	1.291	

Table S20. Natural charge analysis of thioanisole and H_2O_2.

moiety/compound	center	natural charge	
		thioanisole	H_2O_2
sulfide	S1	0.292	
peroxo	O1		-0.480
	O2		-0.480

Table S21. Selectivity of sulfoxide formation based on the oxidant (H_2O_2) consumed.

entry	substrate	product	conversion %			
			1b	**2b**	**3b**	**4b**
1.			59	67	82	69
2.			83	69	96	89
3.			81	94	>99	89
4.			69	81	83	65
5.			79	92	91	87
6.			78	93	>99	94
7.			83	75	91	86
8.			>99	>99	79	90
9.			>99	>99	>99	>99
10.			>99	>99	>99	>99

[a]Reaction conditions: 2.00 mmol of substituted thioether, 2.00 mmol of H_2O_2, 2.00 mmol of internal standard (1,2-dichlorobenzene) and 1.00×10^{-2} mmol Ti catalyst, in CH_3OH (5 mL) at room temperature (30 minute). Products were quantified by GC analysis with respect to internal standard and identified by GCMS analysis.