Supporting Information for

Theoretical and Experimental Studies on Reaction Mechanism for Aerobic Alcohol Oxidation by Supported Ruthenium Hydroxide Catalysts

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Additional Experimental Section

General. The GC analyses were performed on Shimadzu GC-17A using a flame ionization detector (FID) equipped with a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30 m). The ICP-AES analyses (for elemental analyses) were performed with Shimadzu ICPS-8100. The XRD patterns were measured with Rigaku MultiFlex using Cu Kα radiation (40 kV–50 mA). The ESR measurements (X-band) were performed with JEOL JES-RE-1X at 103 K under Ar atmosphere. The XPS measurements were carried out on JEOL JPS-90 using monochromated Al Kα radiation ($h\nu$ = 1486.6 eV). The X-ray anode was run at 200 W and the voltage was kept at 10 kV. The pass energy was fixed at 10.0 eV to ensure sufficient resolution to determine peak positions accurately. The binding energies were calibrated by using the Au $4f_{7/2}$ signal at 84.0 eV. The X-ray absorption spectra were recorded at the NW10A beamline of PF at KEK, Japan (proposal No. 2007G096). A Si(311) single crystal was used to obtain the monochromated X-ray beam. Two ion chambers filled with Ar and Kr were used as I_0 and I detectors, respectively. For EXAFS analysis, the oscillation was first extracted from the EXAFS data by a spline smoothing method. The Fourier transformation of the k^3-weighted EXAFS oscillation from k space to r space was performed over the range 3.0–16.5 $Å^{-1}$ to obtain a RDF. For the curve-fitting analysis, the empirical phase shift and amplitude functions for Ru–O and Ru–Ru were extracted from the data for RuO_2 and Ru metal. The data were analyzed using REX2000 software (version 2.5, Rigaku).

Reagents. Substrates and solvents were commercially obtained from Tokyo Kasei, Aldrich, and Fluka (reagent grade), and purified before the use.[S1] (*S*)-1-Deuterio-1-phenylethanol (>99%*ee*, >99% D at α-position),[6c] (*S*)-1-deuterio-1-(*p*-tolyl)ethanol (>99%*ee*, >99% D at α-position),[6c] and α-deuterio-*p*-methylbenzyl alcohol (>99% D at α-position)[5b] were synthesized according to the literature procedures. Anatase TiO_2 (TiO_2(A), ST-01, 316 $m^2 g^{-1}$), anatase TiO_2 (TiO_2(B), JRC-TIO-1, 73 $m^2 g^{-1}$), rutile TiO_2 (TiO_2(C), SUPER-TITANIA G-2, 3.2 $m^2 g^{-1}$), and Al_2O_3 (KHS-24, BET surface area: 160 $m^2 g^{-1}$) were obtained from Ishihara Sangyo Kaisya Ltd., the Catalysis Society of Japan, Showa Denko K. K., and Sumitomo Chemical, respectively.

Preparation of Catalysts. The supported ruthenium hydroxide catalysts ($Ru(OH)_x$/support, support = TiO_2 or Al_2O_3) were prepared by the reaction of TiO_2 (or Al_2O_3) with $RuCl_3$ in aqueous medium followed by the treatment with NaOH.[5,6] The TiO_2 (or Al_2O_3) powder (2.0 g, pretreated at 550°C for 3 h) was vigorously stirred with 60 mL of an aqueous solution of $RuCl_3$ (8.3 mM, pH ca. 2.0) at room temperature. After 15 min, the pH of the solution was adjusted to 13.2 by addition of an aqueous solution of NaOH (1.0 M) and the resulting slurry was stirred for 24 h. The dark green solid was then filtered off, washed with a large amount of water, and dried in vacuo to afford the supported ruthenium hydroxide catalyst. The ruthenium contents in $Ru(OH)_x$/support catalysts were 2.2–2.1 wt%. The BET surface areas of $Ru(OH)_x$/support catalysts were very close to those of the parent supports. The XRD patterns of supported ruthenium hydroxide catalysts were the same as those of the parent supports and no signals due to Ru metal clusters and RuO_2 were observed. These facts suggest that ruthenium species is highly dispersed on the surface of supports. The ESR spectrum of $Ru(OH)_x$/support catalysts showed an intense signal with rhombic *g* tensor characteristic of low spin Ru^{3+} species (g_1 = 2.07, g_2 = 1.98, g_3 = 1.92).[S2] The more detailed characterization of $Ru(OH)_x$/support catalysts has been reported elsewhere.[5,6]

The ruthenium chloride species supported on TiO_2(B) ($RuCl_x$/support catalyst) was prepared according to the following procedure. The acetone solution of $RuCl_3$ (12.5 mM, 20 mL) containing the TiO_2(B) powder (1.0 g) was vigorously stirred at room temperature. After 1 h, acetone was removed by evaporation to afford $RuCl_x$/support as a brown powder. The content of ruthenium in $RuCl_x$/support was 2.5 wt%.

Catalytic Aerobic Oxidation. The catalytic aerobic alcohol oxidations were carried out as follows. A suspension of the $Ru(OH)_x$/support catalyst in toluene was stirred for 5 min.

Then, an alcohol was added and O_2 was passed through the suspension. The mixture was stirred (800 rpm) at 54–96°C under 1 atm of O_2 (see Equations and captions of Tables and Figures in the Supporting Information for the detailed reaction conditions). The alcohol conversions and product yields were periodically determined by GC analysis.

Additional Results and Discussion

Experimentally Proposed Reaction Mechanism. The ruthenium hydroxide catalyst supported on TiO_2 ($Ru(OH)_x/TiO_2$) showed the high catalytic activity and selectivity for various kinds of structurally diverse alcohols including benzylic, allylic, aliphatic, and heteroatom-containing ones (Table S1) and was used to investigate the reaction mechanism. It has been reported that 2,2-dimethyl-1-phenyl-1-propanol was oxidized to give the corresponding ketone with two-electron transfer oxidant and that one-electron transfer oxidant gave benzaldehyde and *tert*-butyl radical as primary products.[S3] The $Ru(OH)_x/TiO_2$-catalyzed oxidation of 2,2-dimethyl-1-phenyl-1-propanol was found to yield only the corresponding ketone (entry 3 in Table S1). Also, the oxidation of radical clock substrate of cyclopropylphenyl carbinol exclusively produced cyclopropylphenyl ketone (entry 4 in Table S1). The lack of ring-opened product(s) indicates that free-radical intermediates are not involved. Furthermore, the addition of radical scavengers such as 2,6-di-*tert*-butyl-4-methylphenol and hydroquinone (one equivalent with respect to Ru species) did not affect the reaction rates as well as the product selectivity. All these results show that radical intermediates are not involved in the present aerobic alcohol oxidation and that direct abstraction of α-hydrogen from an alcohol (radical mechanism) is not caused by $Ru(OH)_x$/support catalysts.

When the competitive oxidation of benzyl alcohol (primary alcohol) and 1-phelylethanol (secondary alcohol) was carried out with $Ru(OH)_x/TiO_2$, the oxidation of benzyl alcohol proceeded much faster than that of 1-phenylethanol (Figure S4). The faster oxidation of a primary alcohol in the presence of a secondary alcohol suggests the formation of an alcoholate species via the ligand exchange between an alcohol and the ruthenium hydroxide species.[S4] The $Ru(OH)_x/TiO_2$-catalyzed competitive oxidations of *p*-substituted benzyl alcohols gave the following reactivity order: *p*-OCH_3 (R_X/R_H = 2.4) > *p*-CH_3 (1.6) > *p*-H (1.0) > *p*-Cl (0.95) (the values in the parentheses were the relative rates and the rate of benzyl alcohol (R_H) was taken as a unity). The relative rates ($\log(R_X/R_H)$) are plotted against the

Brown-Okamoto σ^+ values (Figure S5). The slope of the linear line in Figure S5 gave the Hammett ρ^+ value of –0.47. The negative Hammett ρ^+ value can be interpreted in terms of the formation of a positively charged transition state at α-carbon atom adjacent to phenyl ring.[S5] Therefore, the formation of the ruthenium hydride species via hydride abstraction from the alcoholate species (*β*-hydride elimination) is likely included in the oxidation path, in which electron-donating substituents can stabilize a carbocation-type transition state.[S5] In addition, the formation of the ruthenium hydride species was evidenced by the fact that $Ru(OH)_x/TiO_2$ showed high catalytic activity for the hydrogen-transfer reactions such as the racemization of chiral secondary alcohols and MPV-type reduction of carbonyl compounds using 2-propanol as a hydrogen source.[6f] When the $Ru(OH)_x/TiO_2$-catalyzed racemization of (*S*)-1-deuterio-1-phenylethanol was carried out, the deuterium was almost retained at α-position of the racemic alcohol after complete racemization (Figure S6), suggesting the formation of the "*monohydride*" species (Ru–H).[S6] The monitoring the formation of water revealed that the amount of water produced was the same as that of carbonyl compound produced. It was confirmed by the measurement of O_2 uptake during the oxidation that the amount of O_2 consumed was approximately half that of carbonyl compound produced. These respective 1:1 (H_2O:product) and 1:2 (O_2:product) stoichiometries show that the simple dehydrogenation does not proceed and support the overall catalytic cycle in Figure 1.

On the basis of the above-mentioned experimental results, we here propose a possible reaction mechanism (Figure 1). First, the ruthenium alcoholate species is formed via the ligand exchange between an alcohol and the ruthenium hydroxide species on $Ru(OH)_x$/support (step 1 in Figure 1). Then, the typical *β*-hydride elimination proceeds to give the corresponding carbonyl compound and the Ru–H species (step 2 in Figure 1). Finally, the hydride species is reacted with O_2 to regenerate the hydroxide species (step 3 in Figure 1). In the step 3, the Ru–OOH species is likely formed as an intermediate by the reaction of the Ru–H with O_2.[8] The reaction rates were almost independent of the partial pressure of O_2 (> 0.5 atm, Figure S7). The k_H/k_D values (kinetic isotope effects) for the oxidation of α-deuterio-*p*-methylbenzyl alcohol with $Ru(OH)_x$/support catalysts were in the range of 4.9–5.3. These results show that the C–H bond breaking (*β*-hydride elimination, step 2 in Figure 1) is included in the rate-determining step for the $Ru(OH)_x$/support-catalyzed aerobic alcohol oxidation.

Additional References

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Cartesian coordinates of the optimized and the transition state structures (in Å)

p-OCH_3 (ruthenium alcoholate)

O	-3.475135	2.019152	0.041678
O	-4.647010	-1.029861	-0.638697
O	-2.693363	-0.232610	1.925378
Ru	-3.023602	-0.123344	0.021406
O	-2.501430	-2.201464	0.132908
H	-2.550026	2.200997	-0.148439
H	-5.478961	-0.549657	-0.640729
H	-2.905683	0.595274	2.369196
H	-2.411599	-2.300812	1.107619
H	-3.380476	-2.541525	-0.093789
H	-3.993828	2.340040	-0.753869
O	-1.334858	0.848506	-0.380429
C	-0.049999	0.327917	-0.136014
H	0.133564	0.266541	0.945056
H	0.037823	-0.690026	-0.537026
C	1.010527	1.228625	-0.791366
H	0.786557	1.293366	-1.858614
H	0.903230	2.235706	-0.381195
C	2.417398	0.721874	-0.578337
C	3.001536	-0.191157	-1.468420
C	3.170273	1.110231	0.529352
C	4.278551	-0.690545	-1.262027
H	2.446329	-0.510547	-2.342128
C	4.458177	0.619936	0.756061
H	2.751603	1.817700	1.235089
C	5.018479	-0.288316	-0.144178
H	4.727921	-1.390000	-1.953532
H	5.005504	0.954036	1.624788
O	6.266894	-0.832073	-0.028496
C	7.061321	-0.460896	1.087900
H	7.996057	-1.005523	0.984107
H	7.268610	0.613125	1.093898
H	6.583486	-0.740779	2.031132

p-OCH_3 (TS)

O	-2.886208	0.813316	1.654921
O	-4.269940	-0.065704	-0.152537
O	-2.398304	-2.033343	0.700530
Ru	-2.152211	-0.232111	-0.048841
O	-1.812361	-1.477563	-1.802048
H	-2.710553	1.743789	1.486384
H	-4.756813	-0.893271	-0.113148
H	-3.280120	-2.115916	1.081180
H	-1.929229	-2.293763	-1.265243
H	-2.614389	-1.406275	-2.341886
H	-3.776372	0.626536	1.233463
O	-1.804955	1.660722	-0.776058
C	-0.596914	1.169862	-0.731597
H	-0.566886	-0.419118	0.226367
H	-0.190901	0.731474	-1.648703
C	0.437543	1.837152	0.167041
H	0.585011	2.838914	-0.252154
H	0.011552	1.973284	1.161692
C	1.758208	1.109055	0.233559
C	2.730489	1.295435	-0.748195
C	2.036158	0.199753	1.264197
C	3.943690	0.605322	-0.721877
H	2.551562	1.999662	-1.552080
C	3.236040	-0.492801	1.308802
H	1.301933	0.032836	2.041960
C	4.200341	-0.297307	0.312575
H	4.670500	0.784368	-1.499761
H	3.451287	-1.191242	2.105395
O	5.346884	-1.023786	0.444165
C	6.361639	-0.869121	-0.538335
H	6.736618	0.157712	-0.568563
H	7.166630	-1.536436	-0.242889
H	6.003373	-1.152889	-1.531802

p-CH_3 (ruthenium alcoholate)

O	3.080669	-2.038116	-0.126575
O	4.298731	1.014221	-0.671472
O	2.385807	0.135628	1.893392
Ru	2.670747	0.109918	-0.020978
O	2.197449	2.188173	0.211260
H	2.147604	-2.194155	-0.300019
H	5.119415	0.516723	-0.713726
H	2.583283	-0.717425	2.294197
H	2.130454	2.234622	1.191747
H	3.078211	2.523164	-0.016322
H	3.572336	-2.325059	-0.951702
O	0.952079	-0.809304	-0.423344
C	-0.315186	-0.287199	-0.103369
H	-0.449104	-0.261504	0.986300
H	-0.413160	0.744213	-0.465820
C	-1.412128	-1.157267	-0.740577
H	-1.241028	-1.182650	-1.818987
H	-1.293480	-2.179074	-0.371923
C	-2.802128	-0.649193	-0.439639
C	-3.435033	0.269496	-1.282852
C	-3.483373	-1.045900	0.715693
C	-4.700355	0.768373	-0.984897
H	-2.932316	0.596053	-2.185500
C	-4.748611	-0.547447	1.013636
H	-3.018388	-1.756338	1.389002
C	-5.382276	0.367891	0.167790
H	-5.165143	1.478231	-1.658987
H	-5.251244	-0.875226	1.915982
C	-6.769380	0.881326	0.472792
H	-6.923650	1.879255	0.060723
H	-7.534839	0.228991	0.042949
H	-6.948892	0.928500	1.547561

p-CH_3 (TS)

O	2.410697	0.627915	-1.819908
O	3.939776	0.024746	-0.021156
O	2.073654	-2.080649	-0.469026
Ru	1.824921	-0.199996	0.051536
O	1.635642	-1.208942	1.971579
H	2.221891	1.569129	-1.760673
H	4.452429	-0.787399	0.011391
H	2.935721	-2.198651	-0.884138
H	1.744211	-2.084931	1.537003
H	2.466978	-1.049248	2.443949
H	3.331847	0.513997	-1.441211
O	1.469038	1.760847	0.555085
C	0.273164	1.242463	0.637535
H	0.232858	-0.457922	-0.088787
H	-0.075658	0.922440	1.624238
C	-0.818881	1.770363	-0.285654
H	-0.996419	2.803940	0.032382
H	-0.431529	1.816111	-1.304005
C	-2.108193	0.987158	-0.229697
C	-3.053283	1.229503	0.771618
C	-2.381704	-0.018064	-1.161790
C	-4.229537	0.488133	0.841249
H	-2.875878	2.014907	1.497000
C	-3.559694	-0.756400	-1.091952
H	-1.669195	-0.222672	-1.950901
C	-4.503010	-0.520654	-0.087452
H	-4.948160	0.702376	1.623108
H	-3.749106	-1.525029	-1.831284
C	-5.766147	-1.342786	0.004982
H	-6.078367	-1.704010	-0.975215
H	-5.617591	-2.217934	0.643575
H	-6.587286	-0.764917	0.430350

p-H (ruthenium alcoholate)

O	2.608239	-2.071894	-0.380083
O	3.939905	0.981820	-0.625914
O	2.084869	-0.119772	1.875890
Ru	2.292556	0.066002	-0.038204
O	1.917376	2.122260	0.438794
H	1.665311	-2.174317	-0.539567
H	4.740986	0.465607	-0.745858
H	2.272649	-1.019341	2.164081
H	1.881128	2.062932	1.420204
H	2.808022	2.436665	0.220490
H	3.066457	-2.294083	-1.243550
O	0.525961	-0.737746	-0.480367
C	-0.711712	-0.211865	-0.066273
H	-0.839060	-0.350665	1.015712
H	-0.762356	0.867028	-0.261801
C	-1.855667	-0.916412	-0.816362
H	-1.700267	-0.771310	-1.887560
H	-1.782047	-1.989017	-0.622177
C	-3.215135	-0.401290	-0.406339
C	-3.805601	0.678965	-1.071928
C	-3.900167	-0.964291	0.676425
C	-5.041691	1.180963	-0.670732
H	-3.293718	1.125400	-1.916034
C	-5.136558	-0.466559	1.081626
H	-3.462497	-1.804691	1.201742
C	-5.711943	0.609547	0.409038
H	-5.482131	2.014401	-1.202761
H	-5.651279	-0.920346	1.918757
H	-6.673609	0.995957	0.720037

p-H (TS)

O	-2.059292	-0.760179	-1.806421
O	-3.609810	-0.290036	0.015678
O	-1.967843	1.980562	-0.485331
Ru	-1.528866	0.139804	0.048806
O	-1.413359	1.179755	1.957771
H	-1.779977	-1.678220	-1.741426
H	-4.198451	0.468767	0.051363
H	-2.839014	2.007785	-0.897227
H	-1.611080	2.039350	1.521878
H	-2.219442	0.943486	2.441675
H	-2.981666	-0.732555	-1.414799
O	-0.969013	-1.772823	0.558099
C	0.168740	-1.136698	0.627395
H	0.031787	0.544368	-0.116865
H	0.490877	-0.774795	1.608667
C	1.301928	-1.563909	-0.298954
H	1.568264	-2.579472	0.014428
H	0.921180	-1.637281	-1.317895
C	2.518822	-0.672380	-0.235411
C	3.475148	-0.844270	0.771144
C	2.700238	0.360803	-1.160694
C	4.583114	-0.004076	0.854533
H	3.357763	-1.647828	1.488534
C	3.808255	1.201280	-1.081451
H	1.969906	0.507625	-1.946199
C	4.752308	1.022134	-0.072518
H	5.314989	-0.154825	1.637292
H	3.933750	1.993643	-1.807531
H	5.614414	1.673050	-0.011972

p-Cl (ruthenium alcoholate)

O	-3.502305	1.987943	-0.008508
O	-4.601001	-1.076610	-0.697093
O	-2.690822	-0.235597	1.896649
Ru	-3.007829	-0.144035	-0.010202
O	-2.445769	-2.211195	0.115587
H	-2.579594	2.193883	-0.185238
H	-5.439937	-0.608951	-0.718475
H	-2.929249	0.587627	2.336005
H	-2.370221	-2.310094	1.091554
H	-3.310804	-2.575154	-0.127323
H	-4.017955	2.295760	-0.811166
O	-1.327081	0.855935	-0.389715
C	-0.045116	0.353208	-0.107274
H	0.105169	0.285175	0.978633
H	0.073913	-0.659522	-0.513962
C	1.020419	1.278369	-0.721701
H	0.832646	1.346471	-1.795150
H	0.883050	2.279523	-0.306786
C	2.426006	0.792178	-0.463636
C	3.068514	-0.065023	-1.363158
C	3.111190	1.151670	0.701977
C	4.351093	-0.548641	-1.117587
H	2.563048	-0.356429	-2.275436
C	4.394020	0.679329	0.966648
H	2.639417	1.817095	1.414296
C	5.002784	-0.170018	0.050147
H	4.839173	-1.205721	-1.822685
H	4.915033	0.968175	1.867870
Cl	6.629599	-0.771208	0.371113

p-Cl (TS)

O	2.758534	0.561930	-1.814322
O	4.235192	-0.123643	-0.001388
O	2.267938	-2.122526	-0.472582
Ru	2.116578	-0.235001	0.052711
O	1.855707	-1.233050	1.969206
H	2.623801	1.512383	-1.754933
H	4.703836	-0.961197	0.046690
H	3.122318	-2.284599	-0.888857
H	1.918634	-2.116953	1.541706
H	2.686616	-1.120374	2.455672
H	3.670763	0.396729	-1.432940
O	1.848997	1.744345	0.547545
C	0.631921	1.278812	0.628479
H	0.511616	-0.406343	-0.097014
H	0.265579	0.979915	1.615558
C	-0.432032	1.858779	-0.298434
H	-0.556728	2.901843	0.012285
H	-0.044322	1.876855	-1.317231
C	-1.759594	1.143618	-0.237035
C	-2.691577	1.450130	0.759368
C	-2.077515	0.138576	-1.156029
C	-3.907594	0.777028	0.843980
H	-2.474177	2.232400	1.476227
C	-3.289327	-0.543367	-1.088518
H	-1.372158	-0.116630	-1.936056
C	-4.194234	-0.216667	-0.084909
H	-4.623946	1.023251	1.614042
H	-3.528208	-1.315994	-1.804458
Cl	-5.732017	-1.070540	0.007115

p-NO_2 (ruthenium alcoholate)

O	3.813528	-1.932509	-0.154175
O	4.806712	1.206992	-0.570480
O	2.904876	0.093770	1.913011
Ru	3.237984	0.169889	0.009051
O	2.609365	2.200197	0.307477
H	2.903687	-2.168494	-0.357989
H	5.661564	0.770539	-0.614478
H	3.175935	-0.750837	2.288408
H	2.525208	2.208750	1.287703
H	3.463770	2.611564	0.106167
H	4.352899	-2.159478	-0.968098
O	1.591057	-0.851147	-0.464704
C	0.300150	-0.400716	-0.147462
H	0.140579	-0.433238	0.938927
H	0.162220	0.641792	-0.462685
C	-0.745255	-1.287981	-0.851295
H	-0.545654	-1.261894	-1.924020
H	-0.599965	-2.317489	-0.517075
C	-2.155637	-0.838288	-0.567820
C	-2.803822	0.067977	-1.417624
C	-2.833252	-1.280702	0.576593
C	-4.088131	0.521005	-1.143464
H	-2.296747	0.417155	-2.307801
C	-4.117547	-0.839941	0.869188
H	-2.349352	-1.983813	1.242228
C	-4.728431	0.059110	0.001306
H	-4.598491	1.215031	-1.792966
H	-4.650007	-1.176734	1.745036
N	-6.094400	0.532425	0.300929
O	-6.633729	0.108311	1.315617
O	-6.607383	1.322169	-0.482323

p-NO_2 (TS)

O	2.994253	0.306610	-1.856387
O	4.435622	-0.220408	0.038234
O	2.401054	-2.184821	-0.222006
Ru	2.320827	-0.247784	0.086137
O	2.022870	-1.002968	2.104910
H	2.896998	1.262112	-1.907357
H	4.875142	-1.061229	0.191086
H	3.244556	-2.425759	-0.622246
H	2.048878	-1.935928	1.793603
H	2.857233	-0.863749	2.578422
H	3.900307	0.152485	-1.456117
O	2.111920	1.785401	0.345331
C	0.883416	1.365172	0.478249
H	0.707743	-0.372119	-0.053283
H	0.509179	1.196408	1.492822
C	-0.164024	1.873711	-0.510640
H	-0.263050	2.946128	-0.312079
H	0.224713	1.770744	-1.523331
C	-1.507657	1.202332	-0.377510
C	-2.420069	1.624676	0.597527
C	-1.854677	0.127010	-1.204709
C	-3.649521	0.995270	0.749748
H	-2.171613	2.461276	1.237969
C	-3.080769	-0.512745	-1.069519
H	-1.159159	-0.212066	-1.960509
C	-3.961414	-0.067435	-0.090373
H	-4.364140	1.311819	1.493300
H	-3.362879	-1.339589	-1.702303
N	-5.270739	-0.738719	0.057785
O	-6.021545	-0.329567	0.933944
O	-5.523779	-1.662368	-0.704168

1

O	-1.645987	-1.016176	0.982306
O	0.780821	-1.775642	-0.495301
O	1.398769	0.382323	1.444821
Ru	0.071231	-0.057359	0.032175
O	-1.611981	0.018271	-1.238461
O	1.809730	0.640085	-1.010790
H	-2.088753	-0.509042	1.669191
H	0.258390	-2.503333	-0.141661
H	1.404127	-0.209365	2.200908
H	-1.491960	-0.223359	-2.158596
H	2.286012	0.741879	-0.155922
H	2.125875	-0.204518	-1.366406
H	-2.114597	-0.829551	0.115998
O	-0.822682	2.038610	0.084670
H	-1.327317	2.279726	0.866791
H	-1.455302	1.681586	-0.583950

2

O	2.007382	-0.891517	0.058970
O	-0.775023	-0.719135	1.554227
O	-1.012170	-1.063895	-1.269984
Ru	0.046416	0.062347	-0.024695
O	1.388569	1.497882	-0.127556
O	-1.895770	0.996592	-0.081348
H	2.210573	-1.348112	-0.762781
H	-0.205578	-1.374400	1.969471
H	-0.891177	-2.013244	-1.179735
H	1.121334	2.419893	-0.101854
H	-2.218792	0.300400	-0.696956
H	-2.213225	0.707384	0.787753
H	2.450640	0.005415	-0.003814

3

O	-1.020253	-2.250458	-0.007391
O	-2.941356	0.121606	-0.159377
O	-0.556961	0.499998	-1.925529
Ru	-1.013477	-0.080785	-0.062468
O	-0.856054	-0.722213	1.911098
O	-1.215045	2.070854	-0.111550
H	-0.142542	-2.568760	-0.238360
H	-3.399125	-0.720689	-0.238357
H	-0.782597	-0.115898	-2.625854
H	-1.399000	-0.276327	2.563545
H	1.009196	-0.372803	1.340335
H	-1.040102	2.047097	-1.079450
H	-2.181419	2.100477	-0.040842
H	-1.021281	-2.140206	0.988977
O	1.162748	-0.323315	0.377576
C	2.199941	0.636216	0.025755
H	1.966696	0.884385	-1.010694
C	3.567396	-0.044926	0.102991
H	4.325539	0.702880	-0.146944
H	3.756096	-0.339239	1.141019
C	3.709974	-1.256029	-0.821960
H	4.702924	-1.699460	-0.736825
H	2.976795	-2.023785	-0.575025
H	3.558199	-0.973277	-1.865671
C	2.096921	1.880430	0.899295
H	2.828315	2.624935	0.581001
H	1.103437	2.320690	0.830603
H	2.301871	1.638570	1.946000

TS4

O	-0.687220	-2.238796	0.297713
O	-2.946386	0.023234	0.170483
O	-0.920208	0.005117	-2.009347
Ru	-1.006116	-0.118853	-0.055804
O	-0.411712	-0.274590	2.053490
O	-1.409229	1.955585	-0.460733
H	0.255284	-2.272661	0.109092
H	-3.405448	-0.817123	0.247618
H	-1.053796	-0.826171	-2.471965
H	-0.595870	0.487574	2.607116
H	0.613926	-0.168542	1.423784
H	-1.340091	1.838689	-1.435184
H	-2.359829	1.893458	-0.281135
H	-0.719979	-2.197920	1.298793
O	1.123046	-0.253180	0.310600
C	2.111588	0.692852	-0.110375
H	1.931959	0.879116	-1.174943
C	3.505684	0.073330	0.047278
H	4.247960	0.826831	-0.233183
H	3.668025	-0.146525	1.107561
C	3.718040	-1.191797	-0.787263
H	4.726101	-1.587934	-0.654230
H	3.011719	-1.970946	-0.500319
H	3.577065	-0.989906	-1.851563
C	1.977995	2.010840	0.654414
H	2.699595	2.743517	0.288045
H	0.978512	2.428357	0.533316
H	2.167810	1.859408	1.720619

5

O	-0.379409	-2.197592	0.386485
O	-2.942665	-0.095271	0.022072
O	-0.734076	-0.247365	-1.981988
Ru	-0.954963	-0.149556	-0.056125
O	-0.763427	0.081050	2.206304
O	-1.508513	1.843532	-0.663894
H	0.531775	-1.908802	0.493180
H	-3.393343	-0.935800	-0.084640
H	-0.522599	-1.132688	-2.292482
H	-1.107239	0.922201	2.522318
H	0.195333	0.205029	2.009255
H	-1.284825	1.728839	-1.615109
H	-2.450744	1.621832	-0.610921
H	-0.698461	-2.433503	1.307060
O	1.065360	-0.139099	0.437488
C	2.039009	0.704975	-0.156092
H	1.860370	0.731083	-1.240391
C	3.438302	0.119442	0.085203
H	4.180240	0.829592	-0.292837
H	3.595016	0.045755	1.166520
C	3.660548	-1.246229	-0.568228
H	4.673532	-1.610879	-0.388483
H	2.966369	-1.989298	-0.174483
H	3.512435	-1.193316	-1.649350
C	1.924763	2.132684	0.387212
H	2.631440	2.803485	-0.106627
H	0.918283	2.519856	0.225852
H	2.136882	2.149809	1.460335

6

O	0.525217	-2.133260	-0.808195
O	2.866059	0.221448	-0.602130
O	0.734258	-0.541268	1.798882
Ru	0.994901	-0.125348	-0.073132
O	1.399595	1.805890	0.770671
H	-0.386210	-1.858439	-0.945361
H	3.423649	-0.522201	-0.844770
H	0.544117	-1.475637	1.932947
H	1.344193	1.575830	1.725660
H	2.343316	1.813441	0.549111
H	0.898785	-2.338623	-1.715487
O	-0.942975	-0.167997	-0.527147
C	-1.922913	0.741953	-0.057148
H	-1.733797	0.938380	1.008245
C	-3.305676	0.086369	-0.181214
H	-4.067488	0.830925	0.068808
H	-3.458997	-0.181755	-1.231447
C	-3.480424	-1.147238	0.707882
H	-4.464346	-1.599889	0.571628
H	-2.727852	-1.902904	0.480517
H	-3.376677	-0.886885	1.763814
C	-1.842877	2.063394	-0.826311
H	-2.585823	2.777475	-0.463197
H	-0.855146	2.509380	-0.708116
H	-2.019247	1.890853	-1.890443

TS7

O	-0.443457	-2.152455	0.182116
O	-1.955088	-0.664968	1.420131
O	-2.042875	-0.125522	-1.459688
Ru	-0.637245	-0.033739	-0.099896
O	-1.360405	2.026342	-0.285082
H	-1.162453	-1.997770	0.863309
H	-2.887068	-0.548763	1.216849
H	-2.537485	-0.950393	-1.428864
H	-1.988018	1.737335	-0.985495
H	-1.911782	2.174413	0.498380
H	0.370722	-2.274893	0.679269
O	1.082695	-0.053855	1.187643
C	1.703220	0.635333	0.317003
H	0.529132	0.381299	-1.204166
C	2.884611	0.027343	-0.426687
H	2.996286	0.534276	-1.385727
H	3.763595	0.310249	0.167961
C	2.847891	-1.487255	-0.602889
H	3.753299	-1.831858	-1.103120
H	2.790486	-1.989885	0.363013
H	1.991606	-1.789860	-1.205590
C	1.710841	2.146956	0.413870
H	1.739812	2.614774	-0.568141
H	0.847484	2.507431	0.963241
H	2.616808	2.437576	0.955736

8a

O	-0.913009	-2.042627	-0.857175
O	-0.917536	-1.353055	1.498097
O	-2.885291	0.244643	-0.331593
Ru	-0.965208	0.007158	-0.184131
O	-1.359043	1.901962	0.858480
H	-0.918021	-2.209607	0.131258
H	-1.746475	-1.379117	1.983248
H	-3.295577	-0.318769	-0.993960
H	-2.287799	1.891082	0.533989
H	-1.416220	1.644031	1.791195
H	-0.036157	-2.270601	-1.179972
O	1.190472	-0.163476	-0.009072
C	2.112783	0.640146	-0.118189
H	-0.627267	0.836323	-1.548341
C	3.536247	0.167927	0.055396
H	4.103938	0.511741	-0.816957
H	3.952006	0.734279	0.897492
C	3.690081	-1.334568	0.272479
H	4.738670	-1.591276	0.422716
H	3.123284	-1.662921	1.142370
H	3.323488	-1.893478	-0.588491
C	1.870780	2.088650	-0.432205
H	1.643328	2.172018	-1.498559
H	0.988578	2.443404	0.098189
H	2.739300	2.705426	-0.207180

9

O	-1.948685	-0.955291	-0.086334
O	-1.358440	1.420052	-0.244776
O	1.362244	-1.412244	-0.247355
Ru	-0.001728	-0.004748	0.057589
O	1.966523	0.949311	0.115503
H	-2.357987	-0.042757	-0.154596
H	-1.148622	2.342712	-0.090015
H	1.097262	-2.332963	-0.288978
H	2.388068	0.068992	-0.008347
H	2.157992	1.450915	-0.691646
H	-2.204255	-1.292746	0.777291
H	-0.029567	0.000139	1.626086

9b

O	-1.528739	2.152662	-0.382698
O	-2.875216	-0.613832	0.069982
O	-0.370441	-0.117025	1.801164
Ru	-1.063103	0.007209	-0.201014
O	-0.706057	-2.058773	0.261894
H	-0.728273	2.606774	-0.103268
H	-1.537576	2.236758	-1.381575
H	-3.538596	0.052562	-0.131093
H	-0.906768	0.317168	2.468231
H	-0.553897	-1.745623	1.182102
H	-1.622114	-2.375367	0.242796
H	-1.131630	0.030128	-1.855666
O	1.057553	0.697900	-0.589785
H	1.286486	0.478817	-1.497726
C	2.210453	0.464436	0.295211
H	1.752636	0.067462	1.200466
C	3.174308	-0.538328	-0.335406
H	3.522343	-0.134883	-1.295848
H	4.061331	-0.582346	0.302221
C	2.607161	-1.949135	-0.523959
H	1.702249	-1.952333	-1.130943
H	3.341368	-2.594871	-1.007808
H	2.346335	-2.395719	0.435975
C	2.858028	1.811909	0.586158
H	2.129024	2.497173	1.019145
H	3.672245	1.693373	1.303241
H	3.264858	2.262999	-0.322106

9c

O	-1.969044	-1.024271	0.376022
O	1.104222	-1.699407	0.313926
O	0.392026	1.301102	1.357667
Ru	-0.005235	-0.200622	-0.190048
O	1.933298	0.656382	-0.526343
H	-2.529097	-0.247678	0.467054
H	-2.263763	-1.444627	-0.484993
H	0.605190	-2.472086	0.595674
H	0.230039	1.113345	2.284211
H	1.840281	1.113465	0.339927
H	2.483574	-0.123657	-0.357561
H	-0.374849	-0.738702	-1.676608
O	-1.223859	1.692350	-0.499017
H	-0.905293	2.227007	-1.265424
H	-0.748870	1.991043	0.281796

10

O	0.658704	1.715633	-0.468761
O	0.319590	-1.595331	-0.619200
O	-1.741461	1.674354	0.044641
Ru	-0.627182	0.031327	0.000559
O	-1.977541	-1.653587	0.277725
H	-0.116493	2.334909	-0.325682
H	1.229095	-1.535952	-0.918461
H	-2.669848	1.624421	0.279315
H	-1.284010	-2.266134	-0.056643
H	-2.066887	-1.845128	1.223814
H	1.269758	1.872446	0.257229
H	-0.178295	0.008965	1.507562
O	3.260382	0.284450	0.649192
O	3.406914	-0.622009	-0.132561

10a

O	0.716590	1.969267	0.819918
O	1.357972	-0.051515	2.065563
O	3.019247	0.481144	-0.520298
Ru	1.173917	0.069928	-0.087128
O	2.032490	-1.877722	-0.639974
H	0.918436	1.453988	1.655772
H	2.273044	-0.121412	2.350703
H	3.185909	1.419315	-0.649845
H	2.854216	-1.437452	-0.954503
H	2.268502	-2.268828	0.215065
H	-0.228588	2.146545	0.804044
O	-0.876618	-0.480361	0.356095
C	-1.680443	-1.240251	-0.177728
H	0.628448	0.269006	-1.612939
C	-3.062203	-1.395023	0.410277
H	-3.782254	-1.237481	-0.401003
H	-3.170562	-2.453592	0.675816
C	-3.353393	-0.494017	1.606931
H	-4.351160	-0.692879	1.997938
H	-2.628222	-0.656812	2.402721
H	-3.301279	0.557737	1.326430
C	-1.334778	-2.020157	-1.413757
H	-1.350789	-1.332891	-2.263961
H	-0.315396	-2.396514	-1.343581
H	-2.039881	-2.828997	-1.597147
O	-2.118310	2.656052	-0.643205
O	-2.384855	1.978150	-1.603874

10b

O	0.123858	-2.552699	-1.356083
O	2.376352	-1.458009	0.523925
O	-0.472564	-1.280906	1.696899
Ru	0.636672	-0.844100	-0.060114
O	1.098279	0.640396	1.422714
H	-0.836231	-2.530097	-1.408593
H	0.435919	-2.188874	-2.236510
H	2.720414	-2.188808	0.002316
H	-0.389646	-2.171863	2.044079
H	0.565809	0.079109	2.030525
H	2.022706	0.399676	1.587772
H	1.165324	-0.163643	-1.473232
O	-1.358718	-0.063261	-0.788732
H	-1.185725	0.623128	-1.439860
C	-2.479437	0.332948	0.082287
H	-2.162576	-0.008588	1.066892
O	2.079872	2.952649	-1.176794
O	2.900301	2.751717	-0.316735
C	-2.677304	1.846575	0.047667
H	-2.924579	2.147237	-0.979119
H	-3.568014	2.068975	0.641406
C	-1.493507	2.666000	0.571704
H	-0.581335	2.482970	0.004126
H	-1.713914	3.732990	0.516941
H	-1.274286	2.417732	1.610276
C	-3.713668	-0.440040	-0.362102
H	-3.520928	-1.512581	-0.331376
H	-4.550132	-0.232262	0.307556
H	-4.011942	-0.166704	-1.377075

10c

O	-2.259354	-0.322708	-1.436900
O	-0.340783	-2.043736	0.347363
O	-1.309851	0.765304	1.695266
Ru	-0.505621	-0.174810	-0.113458
O	1.052862	-0.034675	1.358491
H	-2.650990	0.555735	-1.436203
H	-1.817469	-0.400216	-2.333358
H	-0.973047	-2.609686	-0.106218
H	-2.147239	0.483899	2.068465
H	0.367068	0.259087	1.999895
H	1.194531	-0.977393	1.534455
H	0.349015	-0.258269	-1.491521
O	-0.815264	2.058448	-0.383356
H	0.040123	2.550972	-0.404660
H	-1.100775	2.017684	0.533881
O	3.551412	0.711291	-0.743624
O	3.744245	-0.375198	-0.258813

TS11

O	1.811360	1.049573	0.717917
O	-0.710327	-0.815262	1.661693
O	1.694420	-0.848801	-0.951917
Ru	0.166038	-0.165885	-0.004660
O	-1.357738	-1.569243	-0.606451
H	2.497135	0.608542	0.134726
H	-0.928578	-0.122950	2.292579
H	1.548532	-1.526636	-1.618197
H	-1.629445	-1.624969	0.337514
H	-2.073828	-1.110977	-1.072245
H	1.737782	1.956449	0.406143
H	-0.336823	0.945859	-1.273218
O	-1.231229	1.904174	-0.944237
O	-1.221541	1.301260	0.247714

TS11a

O	1.280048	-1.521858	1.613545
O	0.733592	-2.077654	-0.708289
O	2.826679	-0.141747	-0.524932
Ru	0.874621	-0.138678	-0.016104
O	0.961649	0.732314	-1.985828
H	1.077197	-2.188656	0.893033
H	1.609725	-2.284786	-1.055451
H	3.315320	0.481604	0.020759
H	1.936609	0.649833	-1.882635
H	0.699516	0.015738	-2.583792
H	0.572493	-1.580803	2.262338
O	-1.326792	-0.327304	0.021969
C	-2.231812	0.474776	-0.200841
H	0.218391	0.416145	1.380230
C	-3.663752	-0.001139	-0.164328
H	-4.210283	0.676129	0.502112
H	-4.082496	0.193761	-1.159161
C	-3.847663	-1.460682	0.239685
H	-4.903784	-1.729190	0.218358
H	-3.306631	-2.124357	-0.433022
H	-3.470742	-1.638005	1.246655
C	-1.968607	1.922974	-0.501678
H	-1.622322	2.408386	0.414390
H	-1.156194	2.014546	-1.222030
H	-2.859778	2.430677	-0.864400
O	0.415710	1.881655	1.784803
O	1.105448	1.797750	0.640501

TS11b

O	-0.891128	-2.238270	-0.177444
O	-2.771829	0.202924	-0.849404
O	-0.025465	0.319465	-1.961508
Ru	-0.921839	-0.064217	-0.159904
O	-1.102484	2.051295	-0.511316
H	0.025946	-2.401886	0.061816
H	-1.430484	-2.535780	0.613433
H	-3.415127	-0.052060	-0.180801
H	-0.568884	-0.027875	-2.675547
H	-0.638655	1.884442	-1.362799
H	-2.039924	1.931580	-0.727259
H	-0.355225	0.751090	1.179116
O	1.222424	-0.697155	0.456317
H	1.363729	-0.509059	1.393121
C	2.441951	-0.389424	-0.316390
H	2.039813	-0.073817	-1.278532
O	-1.638921	-0.396802	1.734352
O	-0.800577	0.334120	2.499153
C	3.228328	0.740431	0.344551
H	3.513507	0.429311	1.358045
H	4.166913	0.840719	-0.207077
C	2.512680	2.094240	0.382127
H	1.590386	2.058082	0.961696
H	3.154574	2.852627	0.831971
H	2.253793	2.424023	-0.624546
C	3.249119	-1.672476	-0.461929
H	2.648491	-2.456624	-0.924003
H	4.116811	-1.499415	-1.100554
H	3.606607	-2.031048	0.506358

TS11c

O	-0.342394	1.554842	1.503545
O	0.064934	-1.617103	1.333105
O	2.146734	0.153588	-0.111494
Ru	0.091156	-0.054206	0.102878
O	0.737626	-1.728710	-1.076300
H	-0.188738	2.338659	0.967764
H	-1.329882	1.535271	1.674980
H	-0.828105	-1.788051	1.648970
H	2.607901	0.137628	0.731270
H	1.670470	-1.433161	-0.974063
H	0.582149	-2.313418	-0.318870
H	-0.829434	-0.003013	-1.324005
O	0.640659	1.929168	-0.987827
H	0.462328	1.983078	-1.957370
H	1.529687	1.583906	-0.865660
O	-1.971859	-0.196741	0.063846
O	-2.236603	-0.052023	-1.238581

12

O	2.134305	-0.631397	-0.559467
O	0.310042	2.074699	-0.503802
O	0.715913	-1.217018	1.396721
Ru	0.233444	0.212945	0.083312
O	-1.631297	0.999567	0.809627
H	2.126049	-1.223216	0.249600
H	1.031570	2.326230	-1.087170
H	0.258631	-1.200486	2.240443
H	-1.609075	1.866497	0.344935
H	-2.249361	0.423118	0.334801
H	1.967020	-1.213081	-1.306928
H	-1.947762	-2.030117	-0.066809
O	-2.073251	-1.254335	-0.630039
O	-0.686789	-1.011332	-1.059864

13a

O	-0.637021	1.632651	1.493876
O	-1.165844	1.915616	-0.961635
O	-2.927660	0.002434	0.000419
Ru	-0.904881	0.137400	-0.033596
O	-1.524881	-1.067161	-1.726100
H	-0.826073	2.281283	0.753308
H	-2.095469	2.020358	-1.191414
H	-3.192972	-0.460826	0.800378
H	-2.414473	-0.968443	-1.317591
H	-1.521611	-0.460641	-2.482326
H	0.305065	1.693716	1.677680
O	1.247295	0.373379	-0.200408
C	2.133660	-0.441157	-0.458585
H	-0.060582	-1.949731	2.715180
C	3.578364	-0.010296	-0.395127
H	4.105393	-0.743355	0.225640
H	3.989809	-0.151435	-1.401895
C	3.809027	1.414043	0.100343
H	4.872137	1.653812	0.083532
H	3.282846	2.136234	-0.522311
H	3.451884	1.534865	1.123160
C	1.830282	-1.865395	-0.810655
H	1.579173	-2.376960	0.122975
H	0.944186	-1.923755	-1.440765
H	2.679057	-2.357875	-1.281308
O	0.335443	-1.430252	2.005721
O	-0.751285	-1.496168	1.012892

13b

O	1.375737	-1.649938	-1.469449
O	2.664004	-0.118932	0.854625
O	0.107478	-1.350451	1.685197
Ru	0.866542	-0.262905	0.145697
O	0.552574	1.096642	1.776145
H	0.555019	-2.049733	-1.772148
H	1.554086	-0.892126	-2.100969
H	3.316757	-0.533571	0.282504
H	0.515131	-2.206911	1.831011
H	0.354499	0.316692	2.342222
H	1.482062	1.309707	1.950529
H	0.957706	2.703753	-1.849549
O	-1.198495	-0.398211	-0.748065
H	-1.198741	0.334628	-1.376681
C	-2.451184	-0.460620	0.010305
H	-2.123363	-0.681589	1.025897
O	1.062396	0.845927	-1.514135
O	1.595526	2.189462	-1.340461
C	-3.189042	0.875790	-0.053323
H	-3.454433	1.078131	-1.098954
H	-4.138776	0.746918	0.472682
C	-2.429931	2.066242	0.542162
H	-1.477879	2.243358	0.040908
H	-3.025664	2.976465	0.461196
H	-2.202910	1.902881	1.595659
C	-3.274387	-1.622525	-0.529598
H	-2.697450	-2.546019	-0.487328
H	-4.176557	-1.758854	0.069318
H	-3.573826	-1.445212	-1.565090

13c

O	-0.184622	1.895510	1.167325
O	-0.339020	-1.160038	1.593338
O	2.189702	-0.398002	0.105621
Ru	0.134344	0.002027	0.119349
O	0.403279	-1.914203	-0.797746
H	0.267345	2.582728	0.668829
H	-1.144230	1.951030	0.882765
H	-0.722472	-0.678648	2.332956
H	2.659240	-0.237599	0.926597
H	1.350396	-1.889543	-0.532488
H	-0.041502	-2.454305	-0.126765
H	-2.797824	-0.267545	-1.641818
O	1.156186	1.306454	-1.465858
H	0.971263	1.012942	-2.390183
H	1.949570	0.847269	-1.175699
O	-1.652474	0.594774	-0.417996
O	-2.623416	-0.443933	-0.709130

TS14b

O	-0.736910	-0.379075	2.248849
O	-2.828709	0.636186	-0.058899
O	-1.429182	-1.982532	-0.320489
Ru	-1.017545	-0.117162	0.102759
O	-1.343056	-0.042243	-2.015216
H	0.212865	-0.504259	2.163433
H	-0.844680	0.508443	2.702285
H	-3.420331	0.405318	0.662178
H	-1.451121	-2.567297	0.442255
H	-1.473902	-1.010305	-2.132415
H	-2.241917	0.310265	-1.928369
H	-0.785955	3.068990	-0.652257
O	1.122576	-0.228863	0.466568
H	0.814537	1.015123	0.437507
C	2.140079	-0.732774	-0.409486
H	1.934735	-0.367471	-1.424459
O	-0.063612	1.770656	0.494645
O	0.086855	2.656181	-0.651576
C	3.507962	-0.197507	0.030438
H	3.691787	-0.533886	1.055749
H	4.270225	-0.670314	-0.596056
C	3.646700	1.324979	-0.057592
H	2.954033	1.833981	0.613608
H	4.655680	1.640824	0.212725
H	3.445937	1.682491	-1.069861
C	2.090358	-2.258118	-0.412026
H	1.094573	-2.603971	-0.688045
H	2.813300	-2.668059	-1.120194
H	2.327940	-2.646702	0.581485

TS14c

O	0.259175	2.004473	0.977423
O	0.530837	-1.213047	1.541391
O	2.138438	0.085707	-0.613420
Ru	0.298257	0.034287	0.039991
O	0.513842	-1.866558	-0.923447
H	-0.039417	2.469364	0.190175
H	-0.523818	2.031321	1.602808
H	0.923334	-0.827967	2.329207
H	2.639755	0.859594	-0.342230
H	1.432352	-1.701360	-1.234974
H	0.629195	-2.357413	-0.095492
H	-2.496233	-1.480337	0.664443
O	-0.665718	1.374469	-1.379107
H	-1.588153	0.819309	-0.707076
H	-0.653322	1.123885	-2.307307
O	-1.830694	0.231692	0.277567
O	-2.626755	-0.922363	-0.112799

15b

O	-0.619547	-0.135508	2.272200
O	-2.706900	-0.014632	-0.447584
O	-0.766945	-2.278098	0.000140
Ru	-0.732034	-0.337931	0.109553
O	-0.805665	-0.679807	-2.014348
H	0.338896	-0.067356	2.229970
H	-0.934038	0.787529	2.504586
H	-3.377397	-0.348016	0.152704
H	-0.715878	-2.703948	0.860883
H	-0.689655	-1.655747	-1.968725
H	-1.766689	-0.555594	-2.041890
H	-2.549292	1.571383	-0.446700
O	1.181223	-0.059031	0.544050
H	-0.164111	2.288073	-0.371089
C	2.269026	-0.355036	-0.317083
H	1.929578	-0.273946	-1.360296
O	-0.832232	1.930866	0.228894
O	-2.071107	2.456975	-0.333904
C	3.378530	0.683263	-0.097826
H	3.727183	0.598616	0.936131
H	4.226206	0.424519	-0.739295
C	2.935019	2.120965	-0.378002
H	2.133932	2.413102	0.302907
H	3.756562	2.826293	-0.243039
H	2.574031	2.229750	-1.404611
C	2.759489	-1.784313	-0.073927
H	1.939288	-2.488046	-0.214755
H	3.568063	-2.046416	-0.760434
H	3.129813	-1.886641	0.948777

15c

O	-0.480869	1.863537	-1.110133
O	0.896948	-1.296927	-1.113844
O	-2.020641	-0.768608	-0.508836
Ru	-0.306582	-0.006396	-0.021337
O	-0.314774	-1.869587	1.054321
H	-0.820526	2.303027	-0.324944
H	0.442677	2.232580	-1.235734
H	0.838864	-1.241044	-2.069962
H	-2.538560	-0.198435	-1.084378
H	-1.240342	-2.109286	0.822223
H	0.221126	-2.313043	0.379107
H	1.735638	0.839187	0.455775
O	2.805683	-0.086930	0.101979

3Cl

O	0.708415	-0.044113	-2.206502
Ru	0.755228	-0.040758	-0.070866
O	0.865064	-0.075730	2.071388
H	-0.193020	-0.211071	-2.497330
H	-1.329018	1.458823	-0.278492
H	0.747505	-1.038067	2.238981
H	1.801127	0.102794	2.249350
H	0.904692	0.912022	-2.434951
O	-1.383093	0.490325	-0.243922
C	-2.488993	0.082477	0.637078
H	-2.265339	-0.962054	0.847549
C	-3.802757	0.186977	-0.136705
H	-4.604306	-0.092606	0.552740
H	-3.979315	1.235976	-0.397903
C	-3.868074	-0.691556	-1.388054
H	-4.842615	-0.606983	-1.869779
H	-3.111770	-0.398983	-2.116542
H	-3.704415	-1.741906	-1.141767
C	-2.469402	0.907144	1.916223
H	-3.241800	0.550506	2.598927
H	-1.505016	0.833599	2.415374
H	-2.671804	1.960641	1.706195
Cl	3.030156	-0.404879	0.005004
Cl	0.102582	-2.295647	0.197621
Cl	0.927106	2.342678	-0.313989

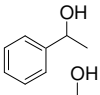
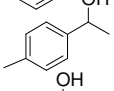
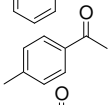
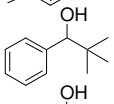
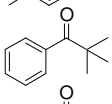
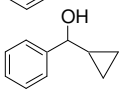
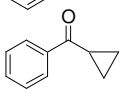
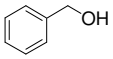
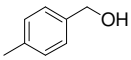
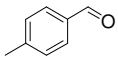
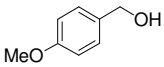
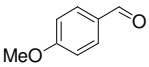
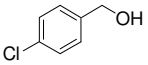
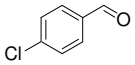
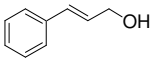
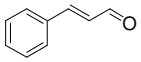
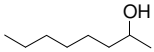
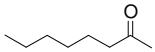
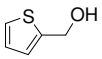
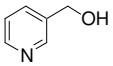
TS4Cl

O	0.382672	-0.346525	-2.197685
Ru	0.600215	-0.190199	-0.078397
O	0.707637	-0.062233	2.060440
H	-0.483064	0.060276	-2.297959
H	-0.063068	2.733901	-0.449852
H	0.403719	-0.961554	2.319005
H	1.668723	-0.083807	2.185352
H	1.040512	0.213898	-2.705699
O	-1.207655	0.513080	-0.338651
C	-2.275686	0.467322	0.605442
H	-2.128340	-0.396116	1.265876
C	-3.591543	0.273067	-0.159957
H	-4.418431	0.370388	0.549846
H	-3.691124	1.098606	-0.872181
C	-3.688874	-1.069627	-0.887446
H	-4.621590	-1.144478	-1.448817
H	-2.861951	-1.202023	-1.585066
H	-3.653358	-1.902443	-0.183041
C	-2.282661	1.743149	1.451085
H	-3.083495	1.713901	2.192436
H	-1.336293	1.858834	1.979858
H	-2.445445	2.619858	0.817906
Cl	2.973173	-0.450226	0.147233
Cl	0.011308	-2.382730	0.311420
Cl	1.205819	2.484219	-0.491933

5Cl

O	-0.361495	-0.330758	2.217522
Ru	-0.496092	-0.182897	0.080115
O	-0.510419	-0.096822	-2.071879
H	0.516983	0.044531	2.329211
H	-2.627615	1.239457	0.199007
H	-0.195948	-1.005597	-2.279812
H	-1.453051	-0.105907	-2.297970
H	-0.994348	0.304718	2.665375
O	1.252763	0.542493	0.397058
C	2.300227	0.653719	-0.568567
H	2.200592	-0.163032	-1.293754
C	3.639097	0.498217	0.163593
H	4.440234	0.706003	-0.551619
H	3.695290	1.275716	0.931477
C	3.845596	-0.883007	0.789207
H	4.799364	-0.934366	1.316679
H	3.053471	-1.117635	1.500172
H	3.841078	-1.665669	0.028370
C	2.184160	1.993637	-1.296964
H	2.975934	2.094062	-2.041833
H	1.223545	2.071035	-1.804737
H	2.269780	2.818681	-0.587761
Cl	-2.957170	-0.546687	-0.248263
Cl	0.133445	-2.373633	-0.282090
Cl	-1.692659	2.213895	0.500758

Table S1. Aerobic oxidation of various alcohols catalyzed by $Ru(OH)_x$/support[a]

Entry	Substrate	Product	Time [h]	Conv. [%]	Select. [%]
1			2	>99	>99
2			1.2	>99	>99
3			1	>99	>99
4			1	>99	>99
5			1	>99	>99
6			0.7	>99	>99
7			0.7	>99	>99
8			1	>99	>99
9			7	>99	>99
10[b]			3	84	>99
11			3	76	>99
12[c]			6	>99	>99
13[c]			4.5	>99	>99

[a] Reaction conditions: Substrate (1 mmol), $Ru(OH)_x$/support (using $Ru(OH)_x/TiO_2$(B), Ru: 1 mol%), toluene (3 mL), 80°C, under 1 atm of O_2. [b] 2 mol%. [c] 5 mol%.

Table S2. The relationship between TOFs and CNs of nearest-neighbor Ru atoms for the oxidation of 1-phenylethanol[a]

Entry	Catalyst	CN of nearest-neighbor Ru atoms	TOF for β-hydride elimination [h^{-1}]
1	$Ru(OH)_x/TiO_2$(A)	0.37 (± 0.17)	152
2	$Ru(OH)_x/TiO_2$(B)	0.76 (± 0.21)	146
3	$Ru(OH)_x/Al_2O_3$	0.94 (± 0.22)	95
4	$Ru(OH)_x/TiO_2$(C)	0.91 (± 0.20)	65
5	$Ru(OH)_x$	1.4 (± 0.2)	No reaction

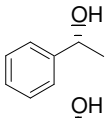
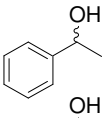
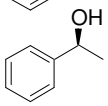
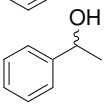
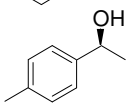
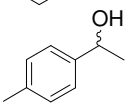
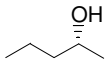
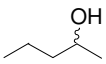
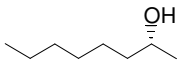
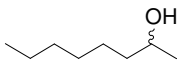
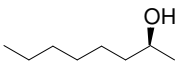
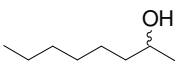
[a] Reaction conditions: 1-Phenylethanol (1 mmol), catalyst (Ru: 1 mol%), toluene (3 mL), 80°C, under 1 atm of O_2. TOF = turnover frequency.

Table S3. Curve-fitting analyses for $Ru(OH)_x$/support catalysts (for the first Ru–O shells)

Entry	Catalyst	CN	*d* [Å]	DW [Å^2]
1	$Ru(OH)_x/TiO_2$(A)	5.9 (± 0.7)	2.01 (± 0.01)	0.0108
2	$Ru(OH)_x/TiO_2$(B)	6.1 (± 0.7)	2.03 (± 0.01)	0.0117
3	$Ru(OH)_x/Al_2O_3$	5.7 (± 0.5)	2.03 (± 0.01)	0.0083
4	$Ru(OH)_x/TiO_2$(C)	6.6 (± 0.9)	2.02 (± 0.01)	00142
5	$Ru(OH)_x$	6.3 (± 0.7)	2.02 (± 0.01)	0.0117

CN = (average) coordination number. *d* = (average) interatomic distance. DW= the Debye-Waller factor.

Table S4. $Ru(OH)_x$/support-catalyzed racemization of various chiral secondary alcohols[a]

Entry	Substrate	Product	Time [h]	*ee* [%]	Select.[%]
1			3	<1	83
2			3	<1	83
3[b]			4	6	76
4			8	<1	76
5[b]			4	4	84
6[b]			4	2	85

[a] Reaction conditions: Substrate (1 mmol), $Ru(OH)_x$/support (using $Ru(OH)_x/TiO_2$(A), Ru: 1 mol%), toluene (3 mL), 90°C, in 1 atm of Ar. The main by-products were ketones. [b] Ru: 2 mol%.

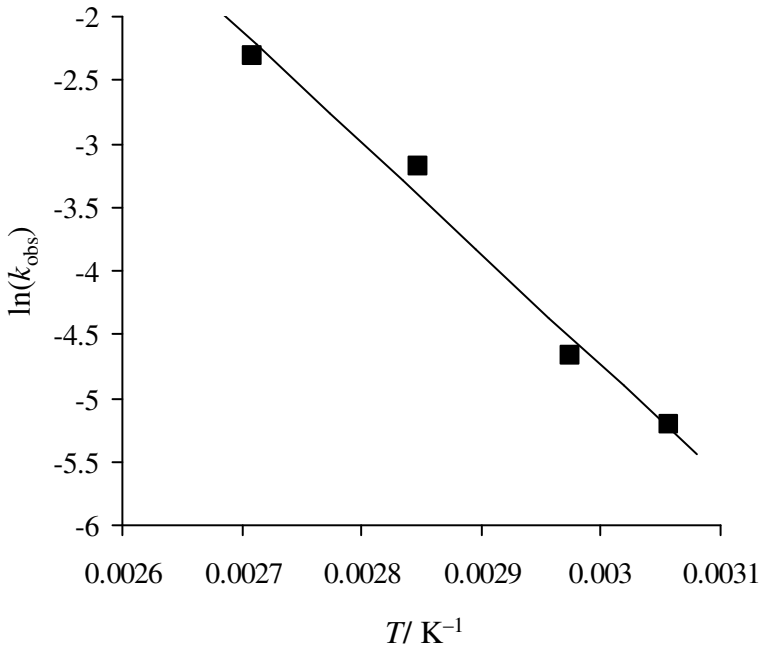
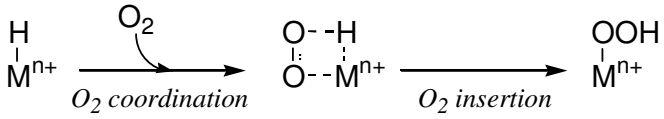
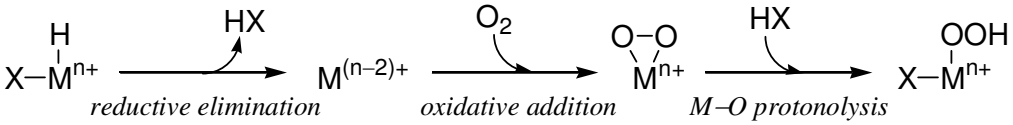


Figure S1. Arrhenius plots for the oxidation of 2-butanol. Reaction conditions: 2-Butanol (1 mmol), $Ru(OH)_x$/support (using $Ru(OH)_x/TiO_2$(B), Ru: 1 mol%, toluene (3 mL), 54–96°C.

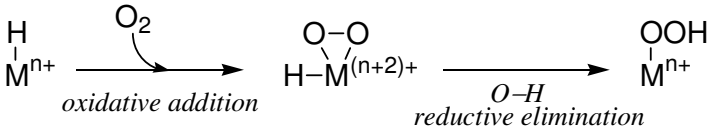
(i) direct O_2 insertion path



(ii) reductive elimination path



(iii) direct oxidative addition path



(iv) free radical path

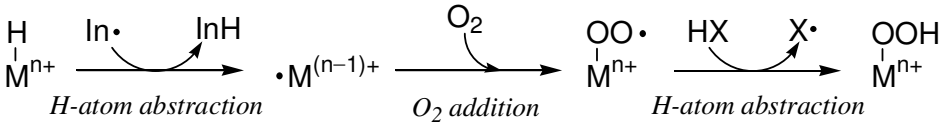


Figure S2. Possible paths for the reaction of M–H species with O_2 to produce M–OOH species.

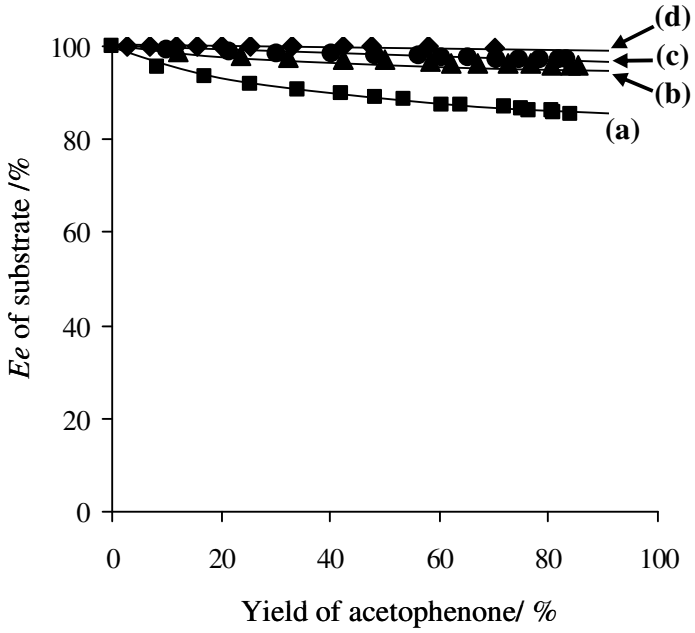


Figure S3. The *ee* of the substrate *vs* yield of acetophenone plots for the oxidation of (*R*)-1-phenylethanol with (a) $Ru(OH)_x/TiO_2$(A) and (b) $Ru(OH)_x/TiO_2$(B), (c) $Ru(OH)_x/Al_2O_3$, and (d) $Ru(OH)_x/TiO_2$(C). Reaction conditions: (*R*)-1-Phenylethanol (1 mmol), catalyst (Ru: 1 mol%), toluene (3 mL), 80°C, under 1 atm of O_2. Under the present conditions, the oxidation preferentially proceeded rather than the racemization in all cases.

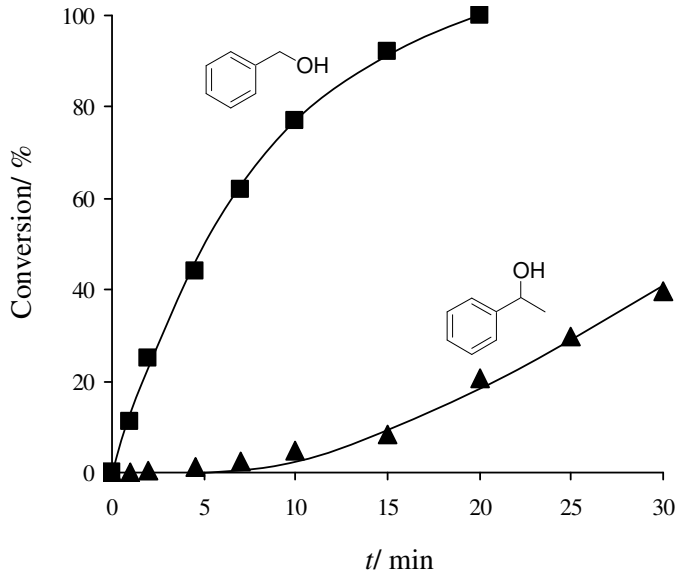


Figure S4. The reaction profiles for the competitive oxidation of benzyl alcohol and 1-phenylethanol. Reaction conditions: benzyl alcohol (0.5 mmol), 1-phenylethanol (0.5 mmol), $Ru(OH)_x$/support (using $Ru(OH)_x/TiO_2$(B), Ru: 1 mol%), toluene (3 mL), 80°C, under 1 atm of O_2.

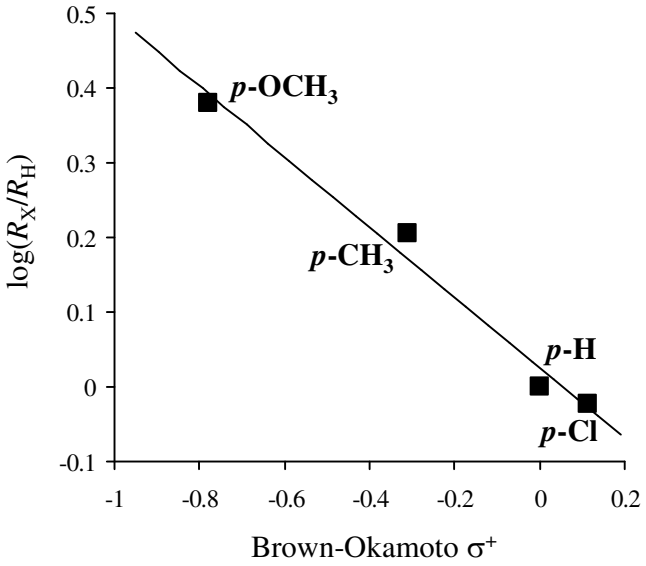


Figure S5. Hammett plots for competitive oxidation of benzyl alcohol and *p*-substituted benzyl alcohols. Reaction conditions: Benzyl alcohol (0.5 mmol), *p*-substituted benzyl alcohol (0.5 mmol), $Ru(OH)_x$/support (using $Ru(OH)_x/TiO_2$(B), Ru: 1 mol%), toluene (3 mL), 60^oC, under 1 atm of O_2.

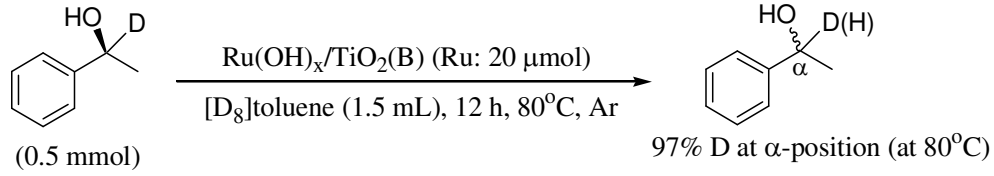


Figure S6. Racemization of (*S*)-1-deuterio-1-phenylethanol.

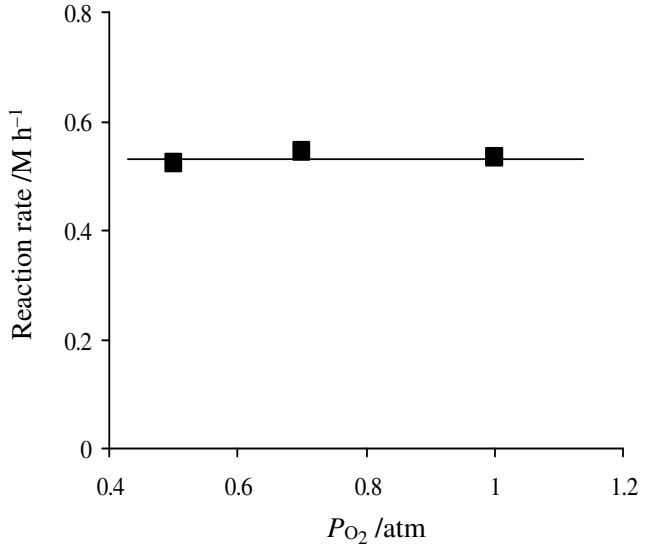


Figure S7. Reaction rate as a function of the partial pressure of O_2 (P_{O_2}). Reaction conditions: 1-Phenylethanol (1 mmol), $Ru(OH)_x$/support (using $Ru(OH)_x/TiO_2$(B), Ru: 1 mol%, toluene (3 mL), 80°C.