Electronic Supplementary Information
for
Fundamental electron-transfer and proton-coupled electron-transfer properties of Ru(IV)-oxo complexes

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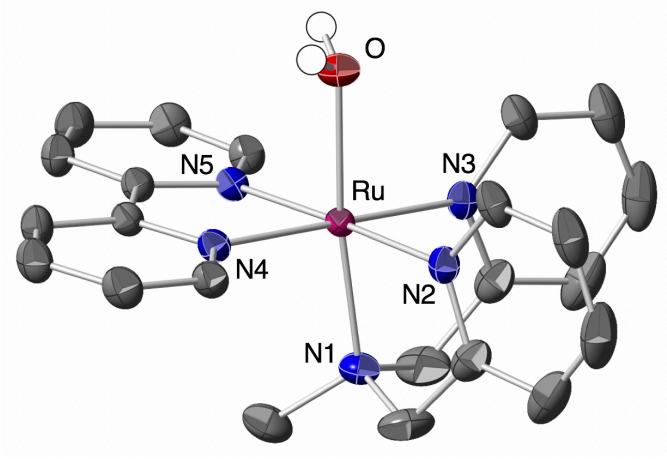


Fig. S1 An ORTEP drawing of $[Ru^{II}(Mebpa)(bpy)(OH_2)]^{2+}$ (**3**) with 50% probability thermal ellipsoids. Hydrogen atoms and PF_6^- ions were omitted for clarity except for protons of the H_2O ligand.

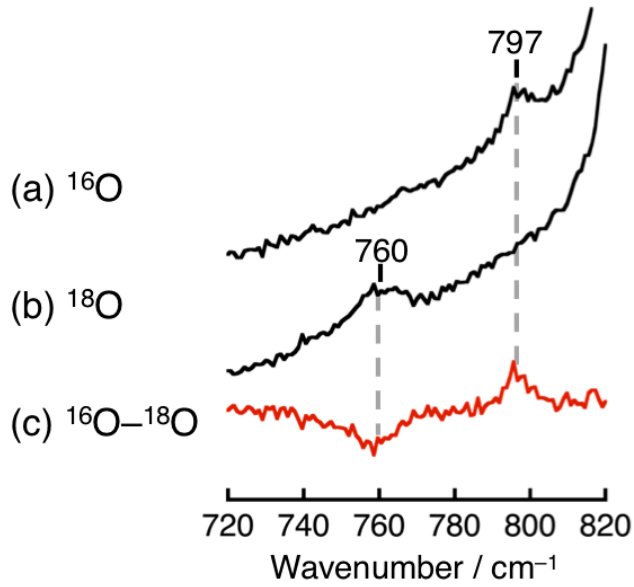


Fig. S2 Resonance Raman spectra of (a) **1**-^{16}O, (b) **1**-^{18}O, and (c) the differential spectrum, measured at 243 K in CD_3CN with 441.6 nm excitation.

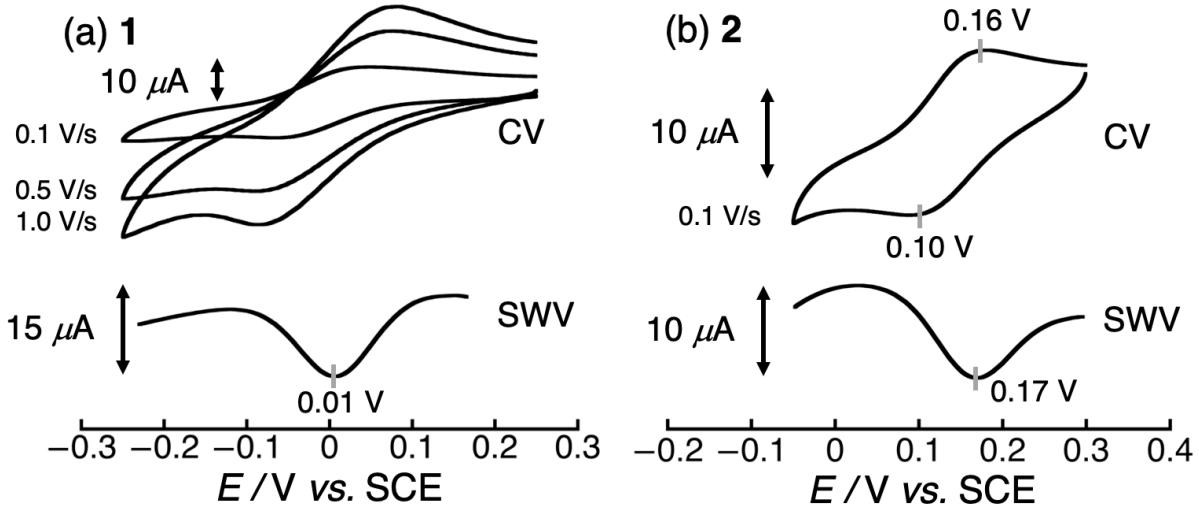


Fig. S3 CV and SWV traces for (a) **1** (1.0 mM) and (b) **2** (1.0 mM) in CH_3CN containing 0.1 M $TBAPF_6$ as an electrolyte at 298 K.

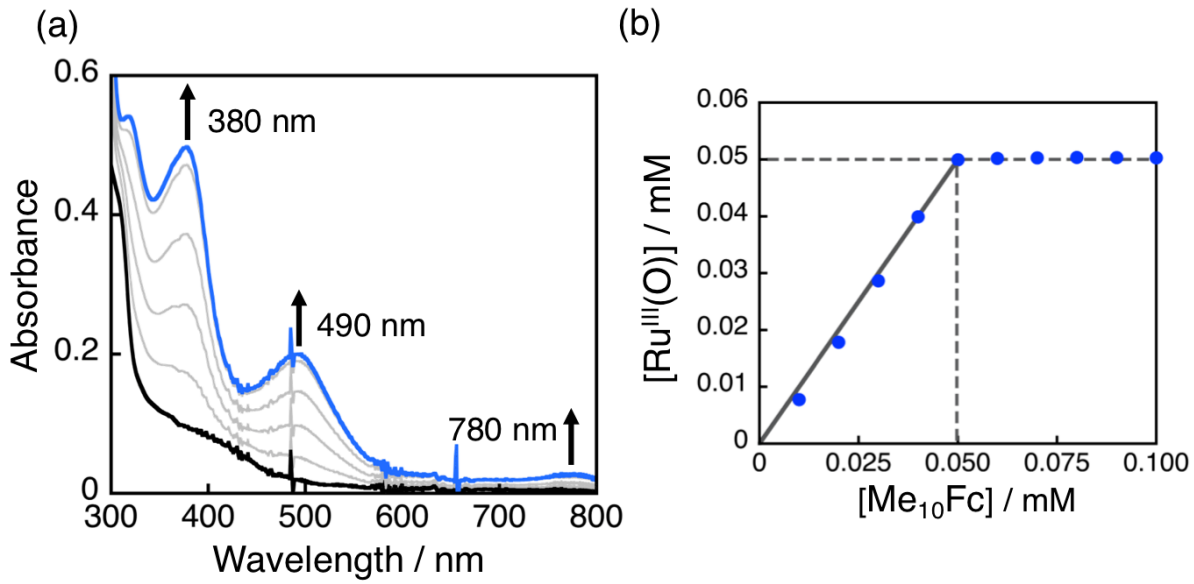


Fig. S4 (a) UV-vis spectral changes in an ET reaction from $Me_{10}Fc$ (0 to 0.05 mM) to **1** (0.05 mM) in CH_3CN at 298 K. (b) A plot of concentration of the formed $Ru^{III}(O)$ complex ($[Ru^{III}(O)]$) relative to $[Me_{10}Fc]$.

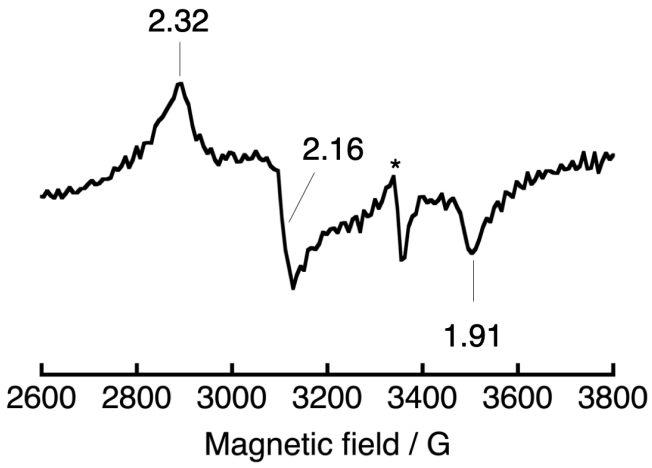


Fig. S5 An ESR spectrum of the Ru^{III} species formed by the reaction of **1** (1.0 mM) with Me_8Fc (1.0 mM) in CH_3CN. The spectrum was measured at 20 K. The peak marked with an asterisk is ascribed to the impurity in the ESR cavity.

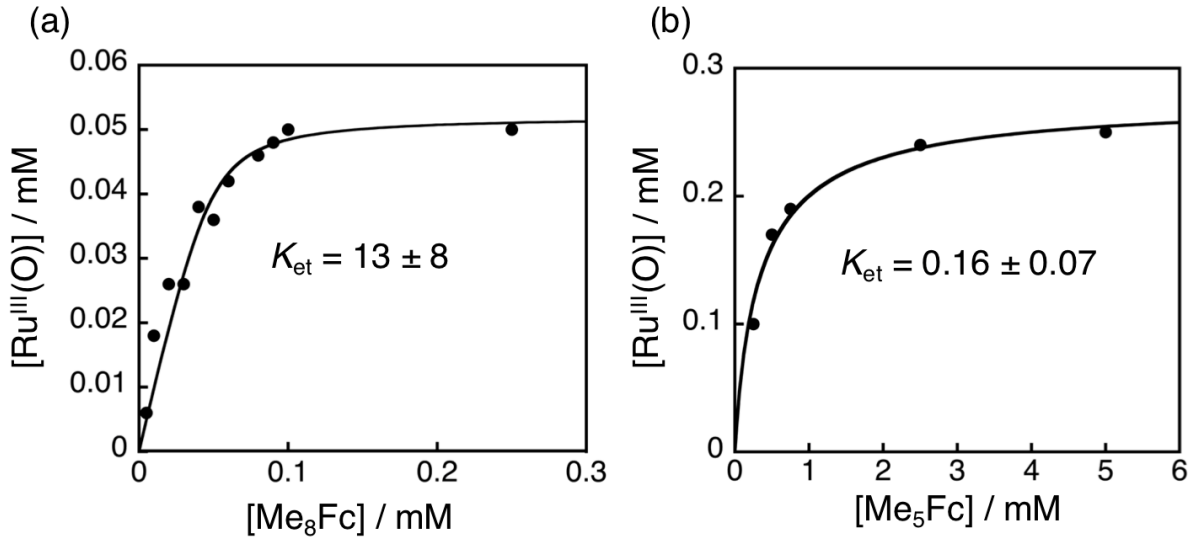


Fig. S6 Plots of $[Ru^{III}(O)]$ produced in an ET reaction from Me_8Fc to (a) **1** (0.05 mM) and (b) **2** (0.25 mM) with Me_5Fc in CH_3CN at 243 K.

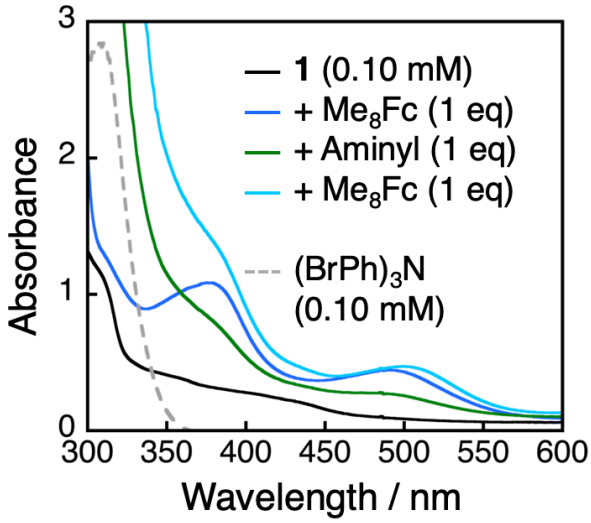


Fig. S7 UV-vis spectral change observed in redox reactions by addition of 1 equivalent of Me_8Fc (blue trace) and 1 equivalent of tris(4-bromophenyl)ammoniumyl hexachloroantimonate (Aminyl) as a $1e^-$-oxidant (green trace) and Me_8Fc again (light blue trace) alternately to a CH_3CN solution of **1** (0.10 mM) at 298 K. The dotted line denotes UV-vis spectrum of authentic tris(4-bromophenyl)amine ($(BrPh)_3N$) (0.1 mM), which is the product of 1e-reduction of Aminyl, in CH_3CN.

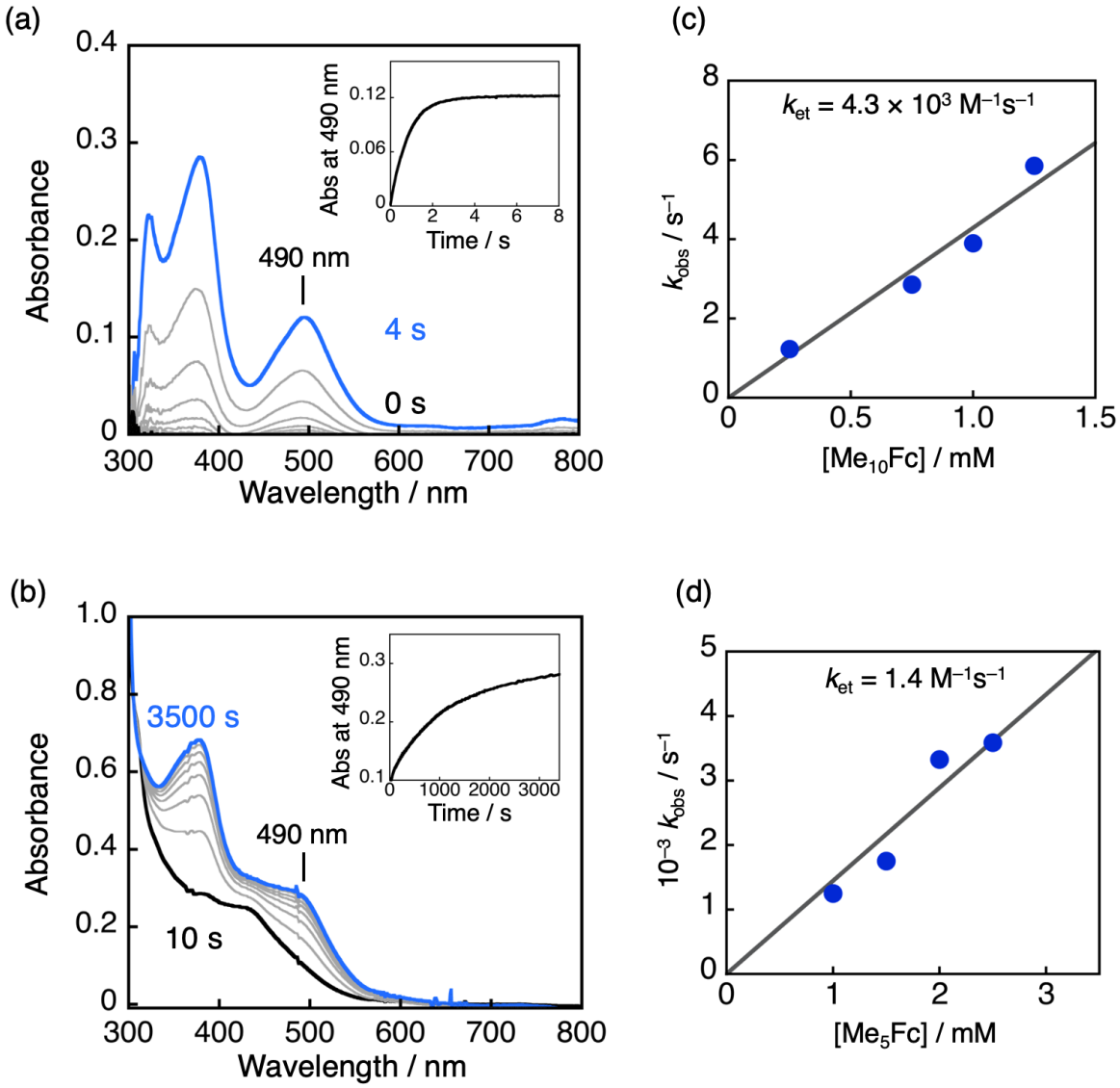


Fig. S8 (a) UV-vis spectral changes (interval: 0.5 s) in the course of an ET reaction from $Me_{10}Fc$ (0.25 mM) to **1** (0.025 mM) at 243 K. (b) UV-vis spectral changes (interval: 500 s) in the course of an ET reaction from Me_5Fc (1.00 mM) to **1** (0.05 mM). Inset: The time profile of the absorbance at λ = 490 nm. Plots of k_{obs} *vs.* (c) [$Me_{10}Fc$] and (d) [Me_5Fc].

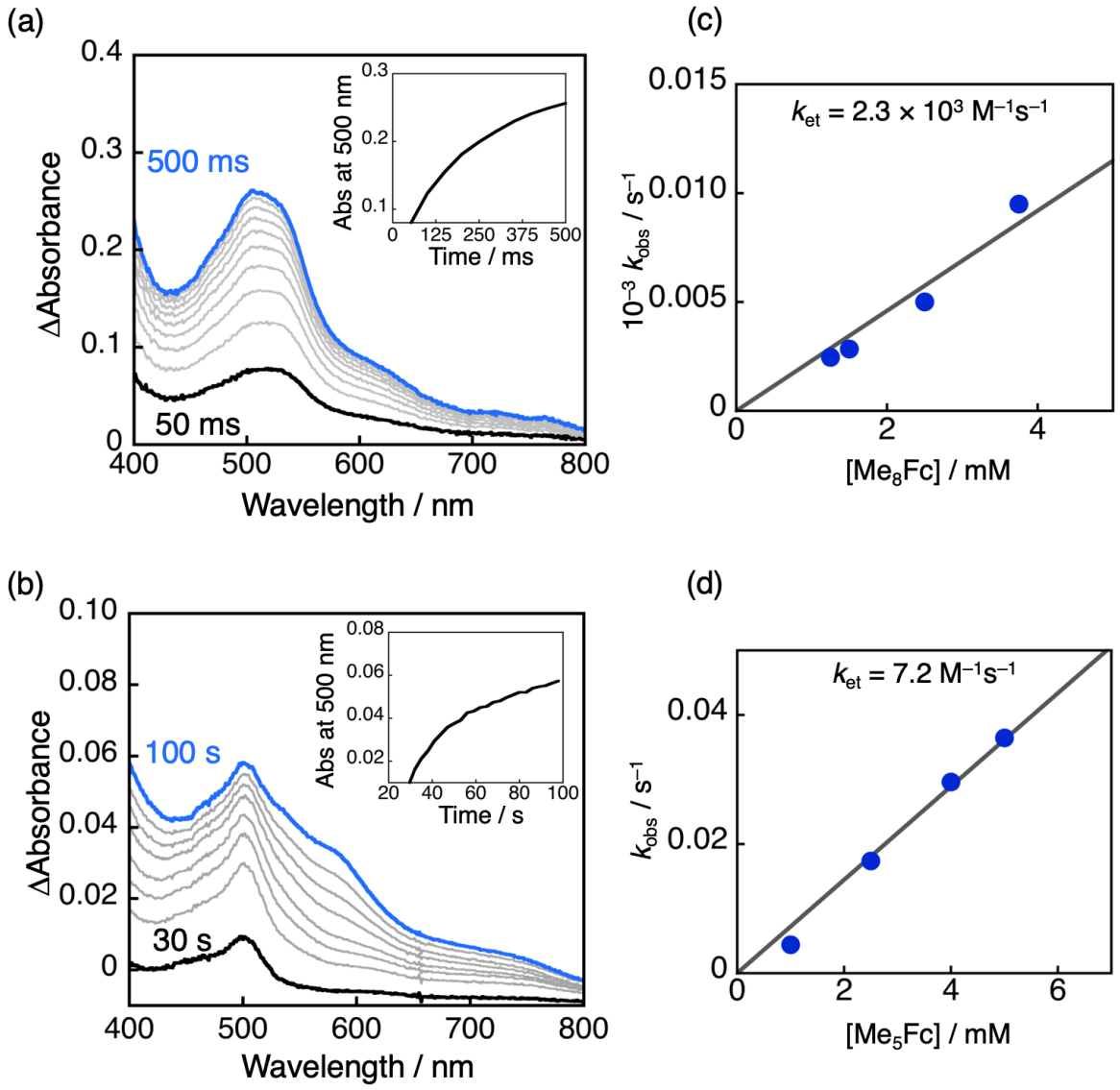


Fig. S9 (a) UV-vis spectral changes (interval: 50 ms) in the course of an ET reaction from Me_8Fc (2.5 mM) to **2** (0.10 mM) at 243 K. (b) UV-vis spectral changes (interval: 10 s) in the course of an ET reaction from Me_5Fc (1.0 mM) to **2** (0.10 mM). Inset: The time profile of the absorbance at λ = 530 nm. Plots of k_{obs} *vs.* (c) [Me_8Fc] and (d) [Me_5Fc]. The spectra shown in (a) and (b) are differential spectra obtained by subtracting the absorption spectra of excess amounts of ferrocene derivatives from the observed spectra on the basis of the fact that the absorption changes of the ferrocene derivatives are negligible under the pseudo-first-order reaction conditions.

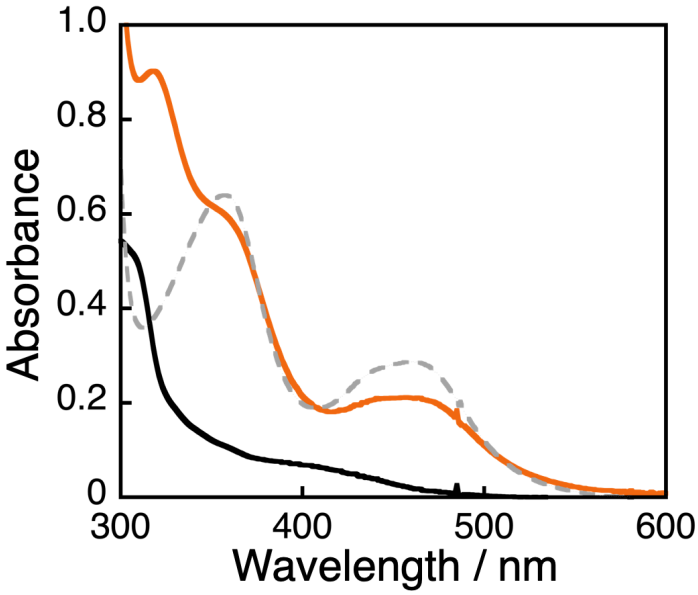


Fig. S10 UV-vis spectral changes in the course of an ET reaction from Fc (0.10 mM) to **1** (0.05 mM) before (black line) and after (orange line) addition of TFA (2.5 mM) at 298 K. The grey dotted line denotes the UV-vis spectrum of $[Ru^{II}(Mebpa)(bpy)(OH_2)]^{2+}$ (**3**) (0.05 mM).

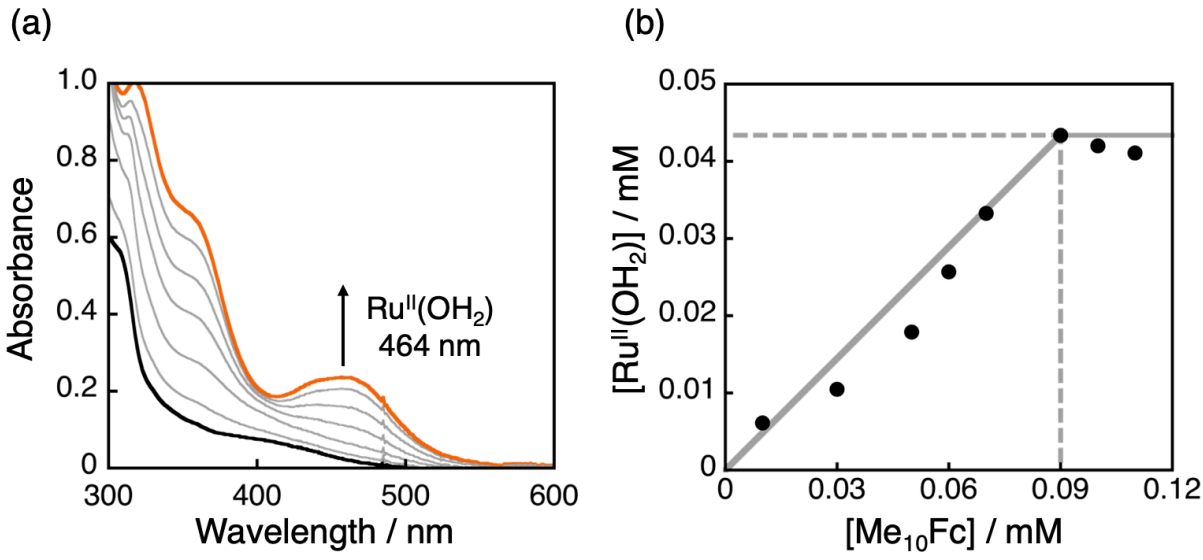


Fig. S11 (a) UV-vis spectral changes in the course of a PCET reaction from $Me_{10}Fc$ (0 to 0.09 mM) to **1** (0.05 mM) in the presence of TFA (2.5 mM) in CH_3CN at 298 K. (b) A plot of $[Ru^{II}(OH_2)]$ *vs*. $[Me_{10}Fc]$.

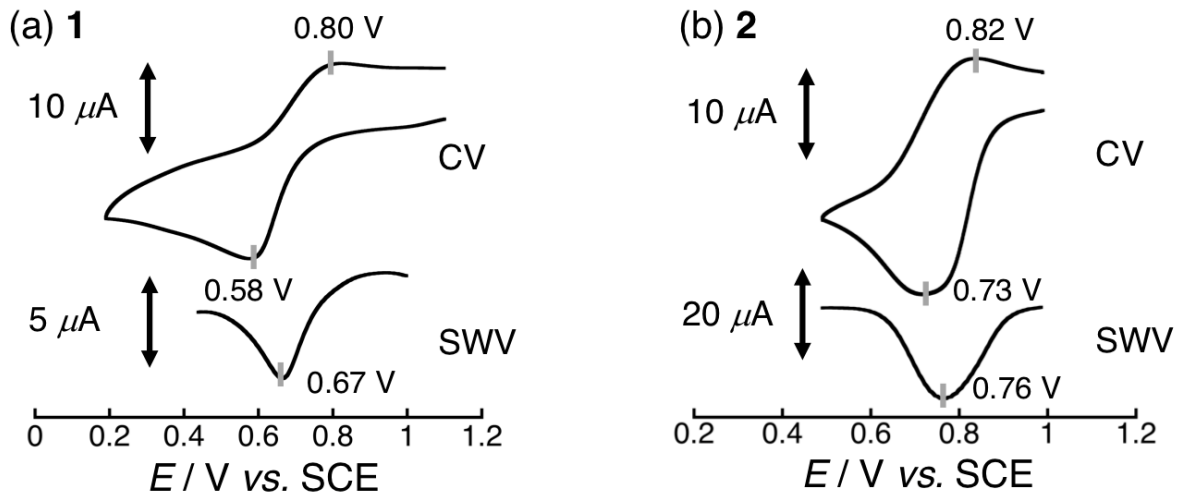


Fig. S12 CV and SWV traces for (a) **1** (1.0 mM) and (b) **2** (1.0 mM) in the presence of TFA (2.5 mM) in CH_3CN containing 0.1 M $TBAPF_6$ as an electrolyte at 298 K.

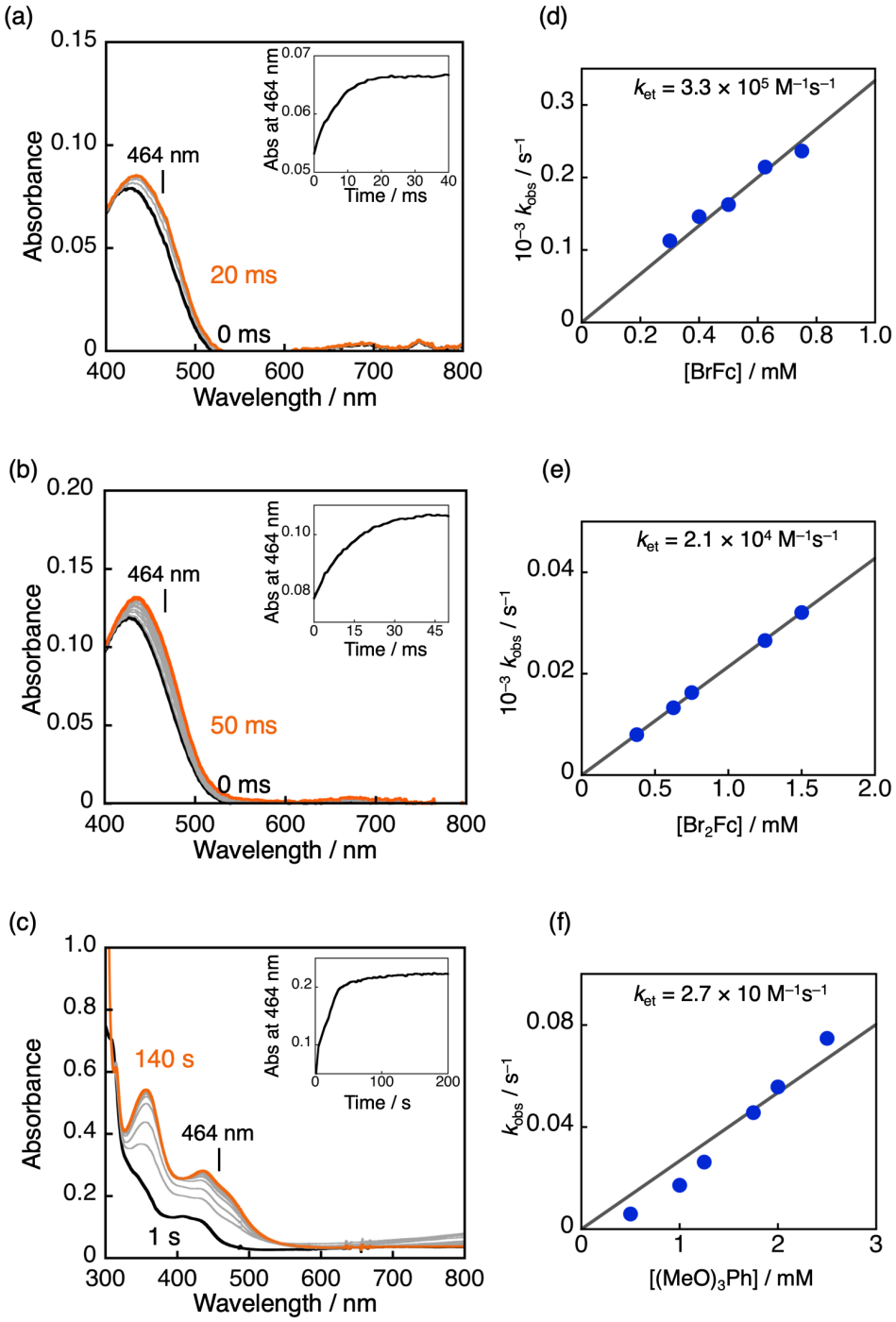


Fig. S13 UV-vis spectral changes (interval: (a), (b) 5 ms and (c) 10 s) in the presence of TFA (2.5 mM) at 243 K in CH_3CN in the course of PCET reactions (a) from BrFc (0.50 mM) to **1** (0.025 mM), (b) from Br_2Fc (0.75 mM) to **1** (0.025 mM), and (c) from $(MeO)_3Ph$ (1.75 mM) to **1** (0.05 mM). Inset: The time profile of the absorbance at λ = 464 nm. Plots of k_{obs} *vs.* (d) [BrFc], (e) [Br_2Fc], and (f) [$(MeO)_3Ph$].

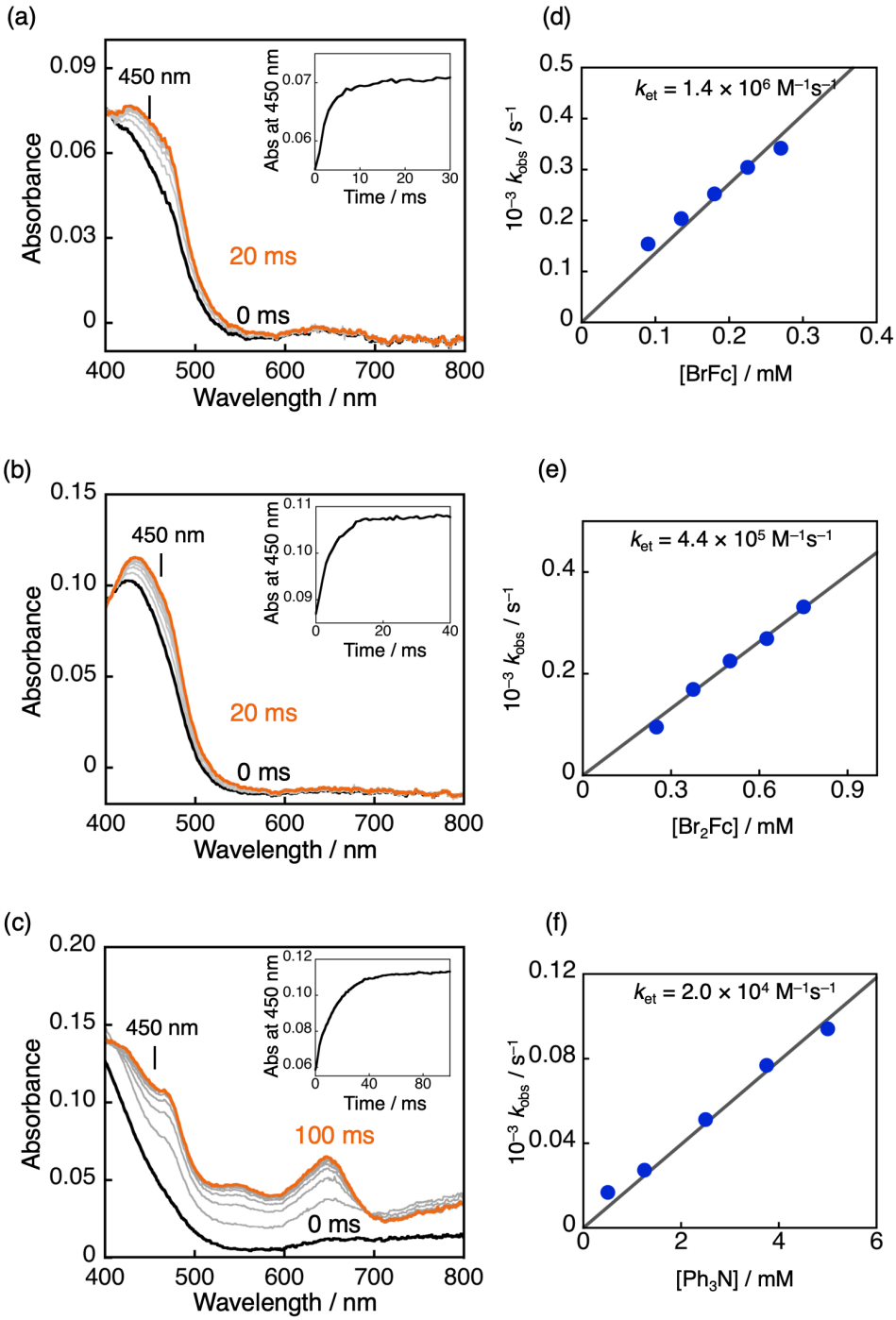
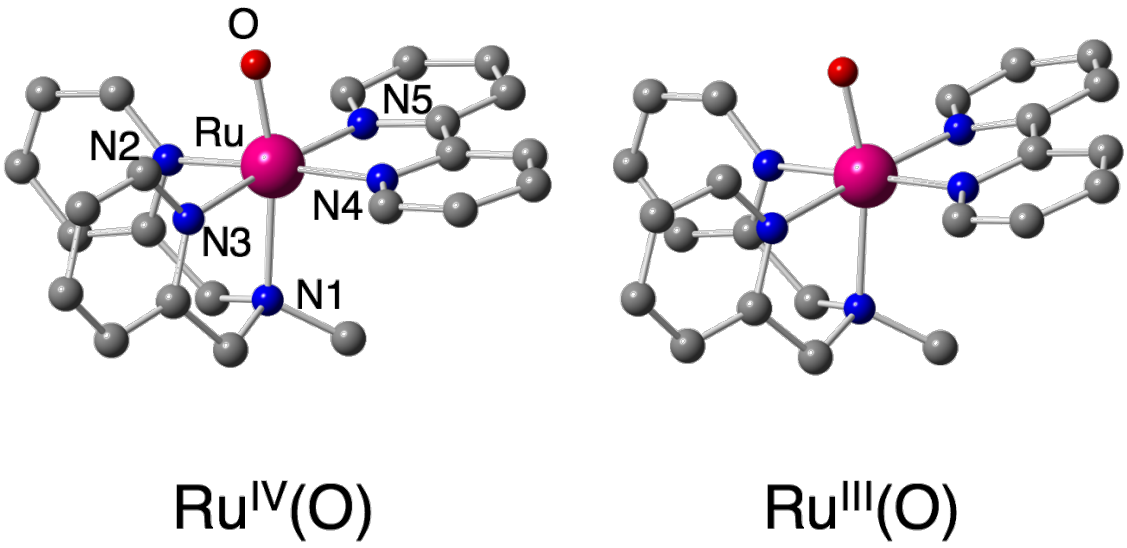
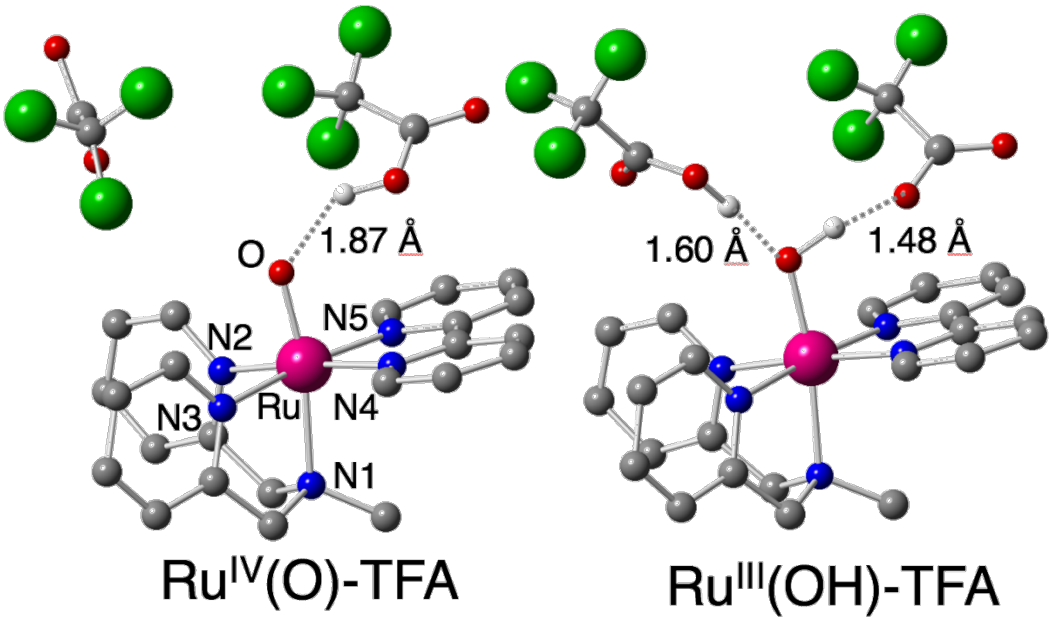


Fig. S14 UV-vis spectral changes (interval: (a), (b) 2 ms and (c) 10 ms) in the presence of TFA (2.5 mM) at 243 K in CH_3CN in the course of PCET reactios (a) from BrFc (0.30 mM) to **2** (0.01 mM), (b) from Br_2Fc (0.50 mM) to **2** (0.025 mM), and (c) from Ph_3N (3.75mM) to **2** (0.01 mM). Inset: The time profile of the absorbance at λ = 450 nm. Plots of k_{obs} *vs.* (d) [BrFc], (e) [Br_2Fc], and (f) [Ph_3N].



selected bonds	bond lengths of Ru^{IV} (Å)	bond lengths of Ru^{III} (Å)
Ru-O (Oxo)	1.77	1.86
Ru-N1	2.29	2.15
Ru-N2	2.12	2.12
Ru-N3	2.12	2.12
Ru-N4	2.11	2.05
Ru-N5	2.11	2.05
average of $\Delta\lvert Ru^{III} - Ru^{IV}\rvert$	0.058	

Fig. S15 DFT optimized structures of **1** and $Ru^{III}(O)$ and the difference of representative coordination bond lengths between complex **1** and $Ru^{III}(O)$.



selected bonds	**bond lengths of Ru^{IV} (Å)**	**bond lengths of Ru^{III} (Å)**
Ru-O (Oxo)	1.78	1.93
Ru-N1	2.28	2.23
Ru-N2	2.11	2.12
Ru-N3	2.12	2.12
Ru-N4	2.10	2.08
Ru-N5	2.11	2.08
average of $\Delta\lvert Ru^{III} - Ru^{IV}\rvert$	0.043	

Fig. S16 DFT optimized structures of **1** and the one-electron-reduced species in the presence of two TFA molecules and the difference of representative coordination bond lengths between complex **1** and the one-electron-reduced species.

Table S1. Cartesian coordinates of **1** at the B3LYP level.
Units are in angstrom.

Atom	X	Y	Z
Ru	-0.064786	-0.000000	-0.370679
O	-0.159444	0.000009	-2.138547
N	0.509726	-0.000025	1.848336
C	1.323176	1.240598	2.064881
H	2.016956	1.109064	2.904622
H	0.625748	2.034883	2.356777
N	1.506702	1.419215	-0.365736
N	1.506698	-1.419227	-0.365752
N	-1.685675	1.333218	-0.196272
N	-1.685691	-1.333207	-0.196311
C	2.062081	1.717316	0.833712
C	3.200812	2.521852	0.929092
H	3.628542	2.741580	1.904023
C	3.769817	3.044288	-0.238971
H	4.653988	3.675062	-0.186094
C	3.181414	2.738843	-1.473601
H	3.585602	3.120550	-2.406811
C	2.057667	1.913721	-1.498130
H	1.572370	1.627567	-2.427073
C	1.322876	-1.240851	2.064830
H	0.625205	-2.035052	2.356379
H	2.016476	-1.109636	2.904770
C	2.061965	-1.717436	0.833727
C	3.200707	-2.521946	0.929142
H	3.628345	-2.741760	1.904094
C	3.769841	-3.044253	-0.238919
H	4.654024	-3.675008	-0.186017
C	3.181552	-2.738706	-1.473575

H	3.585839	-3.120316	-2.406782
C	2.057784	-1.913607	-1.498137
H	1.572569	-1.627382	-2.427100
C	-0.617540	0.000082	2.829786
H	-0.243043	0.000030	3.861927
H	-1.234895	-0.888449	2.679791
H	-1.234709	0.888744	2.679808
C	-1.598767	2.676990	-0.244281
H	-0.601568	3.094407	-0.340295
C	-2.721605	3.503668	-0.192756
H	-2.600562	4.581988	-0.239714
C	-3.985286	2.909359	-0.091719
H	-4.884696	3.518985	-0.052335
C	-4.077987	1.514275	-0.052178
H	-5.052017	1.041963	0.013219
C	-2.911644	0.740794	-0.111182
C	-2.911653	-0.740773	-0.111210
C	-4.078006	-1.514242	-0.052248
H	-5.052031	-1.041922	0.013156
C	-3.985320	-2.909326	-0.091846
H	-4.884737	-3.518943	-0.052494
C	-2.721646	-3.503645	-0.192898
H	-2.600615	-4.581965	-0.239902
C	-1.598798	-2.676978	-0.244379
H	-0.601603	-3.094403	-0.340412

Table S2. Cartesian coordinates of one-electron reduced **1** at the B3LYP level. Units are in angstrom.

Atom	X	Y	Z
Ru	-0.106095	-0.000136	-0.283736
O	-0.250212	-0.000010	-2.133958
N	0.619505	-0.000332	1.912971
C	1.438941	1.236980	2.066434
H	2.181778	1.124657	2.869066
H	0.753307	2.033375	2.380677
N	1.475248	1.404347	-0.367338
N	1.475216	-1.404715	-0.367537
N	-1.683503	1.305453	-0.130697
N	-1.683724	-1.305412	-0.130934
C	2.109189	1.702586	0.789917
C	3.265362	2.488846	0.811202
H	3.756477	2.705240	1.756668
C	3.768207	2.994582	-0.393935
H	4.663199	3.612143	-0.401283
C	3.100716	2.685248	-1.586570
H	3.454564	3.050681	-2.546424
C	1.964831	1.875920	-1.533986
H	1.411081	1.560138	-2.416254
C	1.437790	-1.238432	2.066130
H	0.751078	-2.034569	2.378679
H	2.179794	-1.127569	2.869731
C	2.108977	-1.703156	0.789813
C	3.265582	-2.488720	0.811079
H	3.756577	-2.705233	1.756578
C	3.769041	-2.993673	-0.394162
H	4.664409	-3.610690	-0.401516
C	3.101685	-2.684265	-1.586828
H	3.455958	-3.049152	-2.546731
C	1.965337	-1.875534	-1.534219
H	1.411717	-1.559684	-2.416535
C	-0.451501	-0.000015	2.943741
H	-0.037668	-0.000291	3.963865

H	-1.078750	-0.885048	2.813460
H	-1.078062	0.885530	2.813651
C	-1.596976	2.656887	-0.117453
H	-0.593323	3.069985	-0.131035
C	-2.709563	3.489062	-0.109972
H	-2.574035	4.566708	-0.104904
C	-3.991157	2.908129	-0.129461
H	-4.884349	3.527224	-0.131636
C	-4.092034	1.520249	-0.156239
H	-5.068426	1.047944	-0.181055
C	-2.927471	0.731587	-0.163322
C	-2.927600	-0.731345	-0.163422
C	-4.092288	-1.519821	-0.156334
H	-5.068613	-1.047373	-0.181064
C	-3.991626	-2.907720	-0.129703
H	-4.884919	-3.526670	-0.131813
C	-2.710125	-3.488865	-0.110438
H	-2.574788	-4.566536	-0.105537
C	-1.597406	-2.656874	-0.117937
H	-0.593808	-3.070100	-0.131794

Table S3. Cartesian coordinates of one-electron reduced **1** with two H_2O molecules at the B3LYP level. Units are in angstrom.

Atom	X	Y	Z
C	1.482341	-2.677580	-0.059541
N	1.596808	-1.332505	-0.088499
C	2.835421	-0.778959	-0.242373
C	3.974948	-1.581104	-0.400854
C	3.847968	-2.970687	-0.384074
C	2.574548	-3.530274	-0.203977
Ru	0.029686	0.009583	0.109058
N	1.648371	1.290801	-0.063735
C	1.587767	2.638457	-0.005490
C	2.713789	3.449612	-0.127547
C	3.964908	2.843897	-0.314846
C	4.036427	1.451130	-0.362088
C	2.864605	0.692282	-0.226415
O	0.188714	0.009820	1.996596
N	-0.524761	0.038953	-2.087862
C	0.598070	0.068710	-3.067570
N	-1.521002	1.443869	0.132343
C	-2.087463	1.739074	-1.060814
C	-3.225472	2.547407	-1.151520
C	-3.779377	3.081389	0.016551
C	-3.175666	2.785050	1.246491
C	-2.055506	1.955276	1.261428
C	-1.366124	1.258934	-2.299209
N	-1.583015	-1.373296	0.098982
C	-2.104394	-1.663161	-1.117583
C	-3.262335	-2.433503	-1.259171
C	-3.891379	-2.937017	-0.115492
C	-3.339706	-2.643972	1.138245
C	-2.192833	-1.851650	1.204807

C	-1.309730	-1.212251	-2.319299
H	-2.075082	1.105060	-3.121399
H	-0.693405	2.066398	-2.609511
H	-3.659782	2.756333	-2.125168
H	-4.662037	3.713923	-0.031792
H	-3.565716	3.176751	2.181192
H	-1.549912	1.673836	2.179365
H	-0.589019	-2.005708	-2.548600
H	-1.960174	-1.109823	-3.196273
H	-3.654336	-2.636345	-2.251809
H	-4.791154	-3.540850	-0.201432
H	-3.789448	-3.009274	2.056807
H	-1.742509	-1.580628	2.154432
H	0.220908	0.074075	-4.099364
H	1.227819	-0.811773	-2.925051
H	1.200679	0.964218	-2.904421
H	0.603743	3.069469	0.144526
H	2.604886	4.528453	-0.072792
H	4.865341	3.443648	-0.415488
H	4.995210	0.962672	-0.495069
H	4.951265	-1.128176	-0.530538
H	4.723419	-3.603188	-0.502953
H	2.422872	-4.604841	-0.172026
H	0.483032	-3.072522	0.088823
H	1.671005	0.071852	2.617975
O	2.591701	0.114223	3.033420
H	2.440143	0.024078	3.984219
H	-0.741672	-0.226261	3.339694
O	-1.236143	-0.454165	4.179257
H	-2.056099	0.056861	4.147349

Table S4. Cartesian coordinates of **1** with TFA at the B3LYP level.
Units are in angstrom.

Atom	X	Y	Z
C	-2.521575	-0.033939	2.668588
N	-2.301759	-0.478456	1.415135
C	-2.791412	-1.693234	1.034540
C	-3.536210	-2.475113	1.925478
C	-3.771587	-2.009123	3.222579
C	-3.253257	-0.765176	3.603931
Ru	-1.111866	0.489888	-0.028675
N	-1.699239	-1.242866	-1.066727
C	-1.320681	-1.565756	-2.319508
C	-1.688899	-2.766896	-2.925659
C	-2.471481	-3.671114	-2.197842
C	-2.857657	-3.340869	-0.894613
C	-2.458995	-2.117372	-0.344402
O	0.375177	-0.258417	0.588517
N	-2.786247	1.800172	-0.853914
C	-4.132502	1.162887	-0.987725
N	-0.100630	1.462289	-1.609721
C	-0.834605	2.302548	-2.380146
C	-0.236018	3.104599	-3.353775
C	1.149987	3.026789	-3.547459
C	1.897248	2.151024	-2.750629
C	1.239032	1.393080	-1.782348
C	-2.337049	2.238533	-2.217559
N	-0.749257	2.295122	1.017363
C	-1.623794	3.308512	0.806457
C	-1.393961	4.586769	1.320817
C	-0.241913	4.820689	2.082399
C	0.652449	3.764374	2.298917
C	0.371883	2.517847	1.740204

C	-2.909528	2.958742	0.091383
H	-2.797198	3.197360	-2.486361
H	-2.715888	1.497844	-2.931744
H	-0.847148	3.772277	-3.955829
H	1.633384	3.640999	-4.303520
H	2.973263	2.048136	-2.848612
H	1.786517	0.724160	-1.127039
H	-3.643683	2.672879	0.854106
H	-3.317363	3.837132	-0.423820
H	-2.110189	5.382793	1.133696
H	-0.046032	5.807760	2.494426
H	1.561323	3.896711	2.878727
H	1.043072	1.672423	1.854343
H	-4.864618	1.874230	-1.391573
H	-4.476374	0.821197	-0.009123
H	-4.067685	0.304825	-1.660028
H	-0.692031	-0.847908	-2.836127
H	-1.352710	-2.986761	-3.934643
H	-2.766389	-4.624333	-2.629515
H	-3.445796	-4.042858	-0.314483
H	-3.915789	-3.445247	1.624823
H	-4.341201	-2.612352	3.925271
H	-3.399804	-0.368569	4.604334
H	-2.085331	0.926026	2.925768
H	6.492457	-0.335301	-1.189219
H	0.628617	-2.023487	1.150584
O	6.244182	-0.148518	-0.264038
C	5.022712	0.366340	-0.224053
O	4.288409	0.593578	-1.161581
C	4.609285	0.647829	1.250157
F	5.534760	1.360689	1.894150
F	3.449955	1.346457	1.263927
F	4.404567	-0.505786	1.903861

O	0.166219	-2.881827	1.276360
C	0.682860	-3.880675	0.543491
O	0.178402	-4.968454	0.454400
C	1.973411	-3.507223	-0.250383
F	2.750379	-2.651238	0.450885
F	2.679759	-4.577130	-0.571135
F	1.605365	-2.865675	-1.395467

Table S5. Cartesian coordinates of one-electron reduced **1** with TFA at the B3LYP level. Units are in angstrom.

Atom	X	Y	Z
C	-1.669557	0.787061	2.886934
N	-1.884417	0.486465	1.589830
C	-2.954650	-0.286951	1.254691
C	-3.855613	-0.736261	2.229227
C	-3.640007	-0.407129	3.566378
C	-2.521014	0.367275	3.905337
Ru	-0.608542	0.966218	0.013997
N	-2.087723	-0.108681	-0.974527
C	-2.092922	-0.393641	-2.291656
C	-3.086888	-1.169290	-2.886120
C	-4.107139	-1.685232	-2.078899
C	-4.095235	-1.408112	-0.710320
C	-3.073971	-0.612687	-0.177438
O	0.422222	-0.634548	0.320879
N	-1.510115	2.969305	-0.392467
C	-2.995943	3.070131	-0.299788
N	0.535199	1.533428	-1.672720
C	0.212602	2.726888	-2.227419
C	0.985176	3.297940	-3.240077
C	2.111540	2.607332	-3.709208
C	2.423885	1.365365	-3.145764
C	1.615875	0.862046	-2.123338
C	-1.099860	3.336473	-1.788257
N	0.769912	2.196868	1.062809
C	0.480769	3.520508	1.062110
C	1.376171	4.470360	1.559036
C	2.597845	4.042046	2.093874
C	2.879973	2.671158	2.113127
C	1.945070	1.781262	1.580823

C	-0.913470	3.901225	0.618255
H	-1.086430	4.427023	-1.912183
H	-1.878711	2.950384	-2.456466
H	0.703338	4.259976	-3.660559
H	2.727540	3.032026	-4.498275
H	3.282244	0.783687	-3.468740
H	1.840327	-0.089428	-1.652144
H	-1.558942	3.860987	1.503878
H	-0.937978	4.935902	0.252547
H	1.115249	5.525328	1.535706
H	3.310120	4.762771	2.488123
H	3.809091	2.284499	2.521753
H	2.126261	0.712319	1.567272
H	-3.335919	4.092632	-0.514693
H	-3.317441	2.790323	0.705312
H	-3.452118	2.384180	-1.016069
H	-1.262134	-0.007935	-2.873074
H	-3.037165	-1.383032	-3.949546
H	-4.883258	-2.318960	-2.499634
H	-4.849818	-1.837786	-0.063848
H	-4.688257	-1.371485	1.951741
H	-4.319724	-0.766089	4.334990
H	-2.298785	0.628865	4.935577
H	-0.778687	1.367157	3.106120
H	1.883716	-1.217732	0.620962
H	-0.187860	-1.440002	0.561550
O	2.776183	-1.528936	0.991056
C	3.687792	-1.628220	0.040290
O	3.558846	-1.356484	-1.137692
C	5.045654	-2.104957	0.630443
F	4.905224	-3.241410	1.326742
F	5.942907	-2.297790	-0.338739
F	5.522507	-1.150685	1.467087

O	-1.224470	-2.389902	1.009840
C	-1.729649	-3.423669	0.450356
O	-2.877016	-3.864349	0.551821
C	-0.758326	-4.138251	-0.548189
F	0.509065	-4.197633	-0.083355
F	-1.140924	-5.378198	-0.868550
F	-0.712510	-3.412412	-1.714332