

## Electronic Supplementary Information

### Formation and Characterization of a Reactive Chromium(V)-Oxo Complex: A Mechanistic Insight into Hydrogen-Atom Transfer Reactions

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Shiota,<sup>c</sup> Kazunari Yoshizawa<sup>c,d</sup> and Takahiko Kojima\*<sup>a</sup>

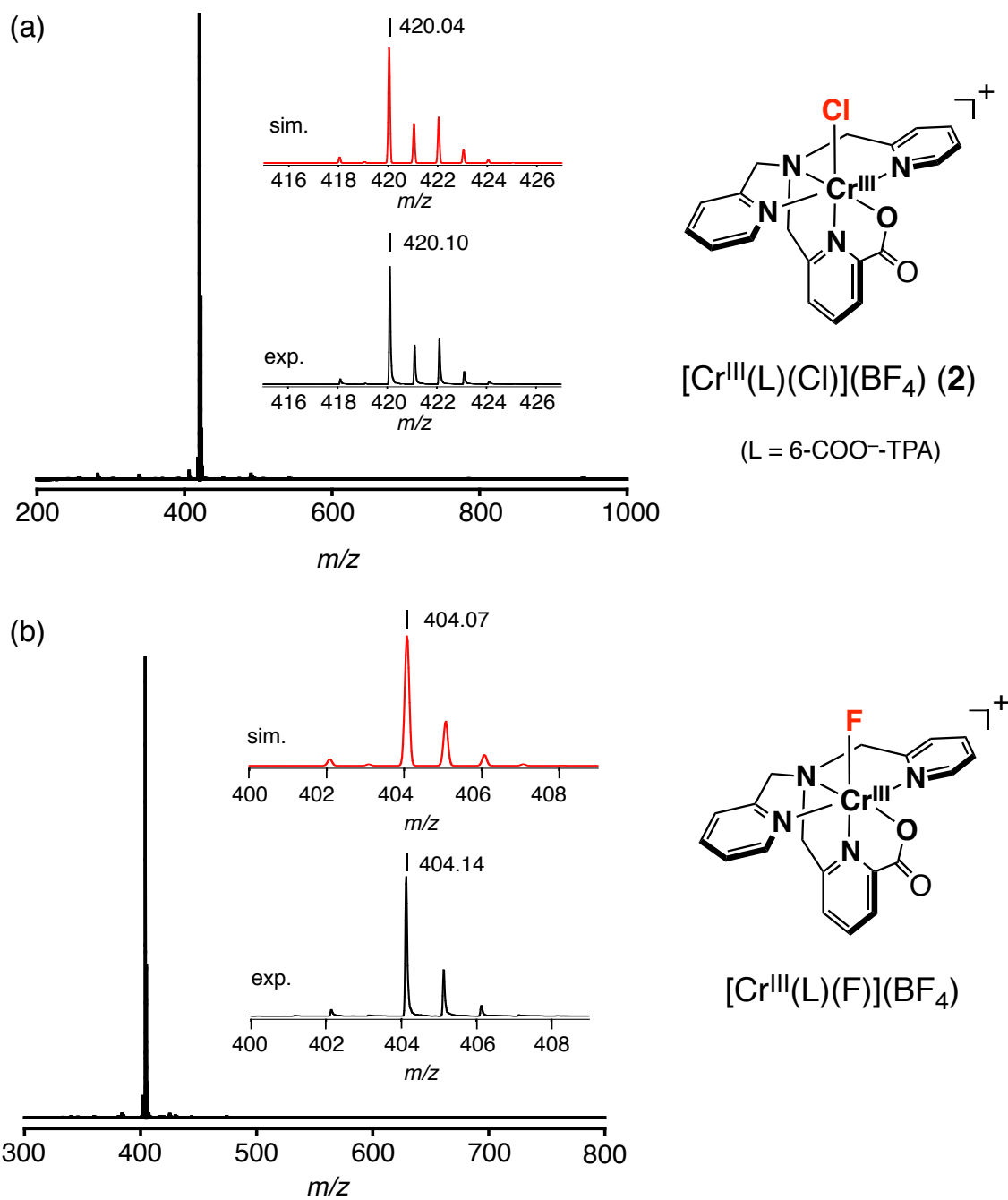
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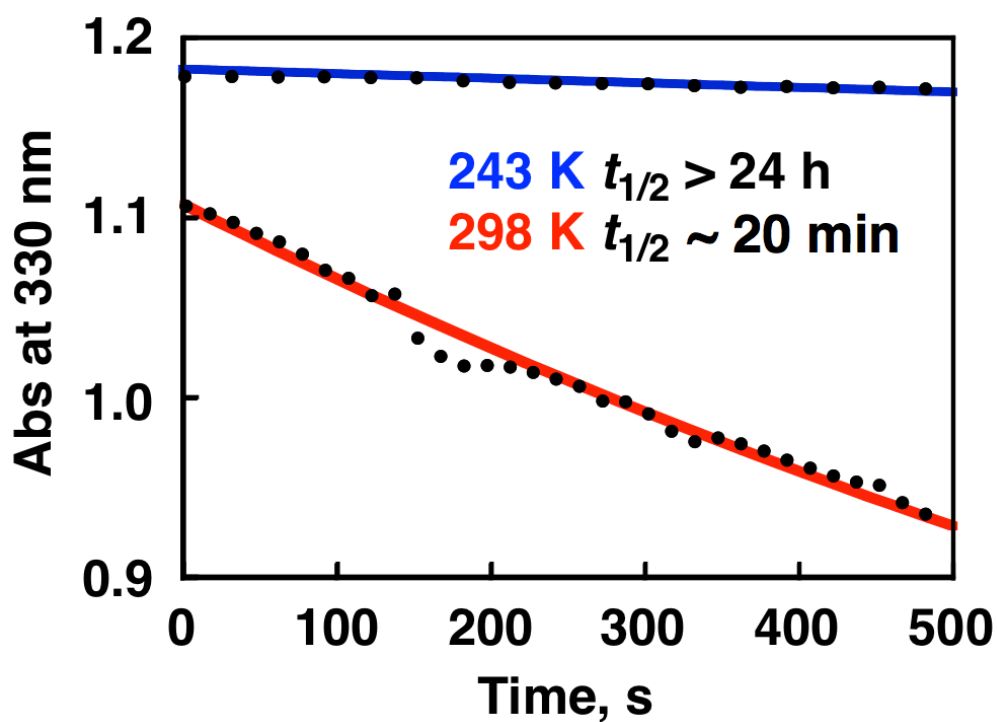
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**Table S1.** X-ray Crystallographic Data for  $[\text{Cr}^{\text{III}}(6\text{-COO}^-\text{tpa})(\text{Cl})](\text{BF}_4)$  (**2**) and  $[\text{Cr}^{\text{III}}(6\text{-COO}^-\text{tpa})(\text{BF}_4)](\text{BF}_4)$  (**3**)

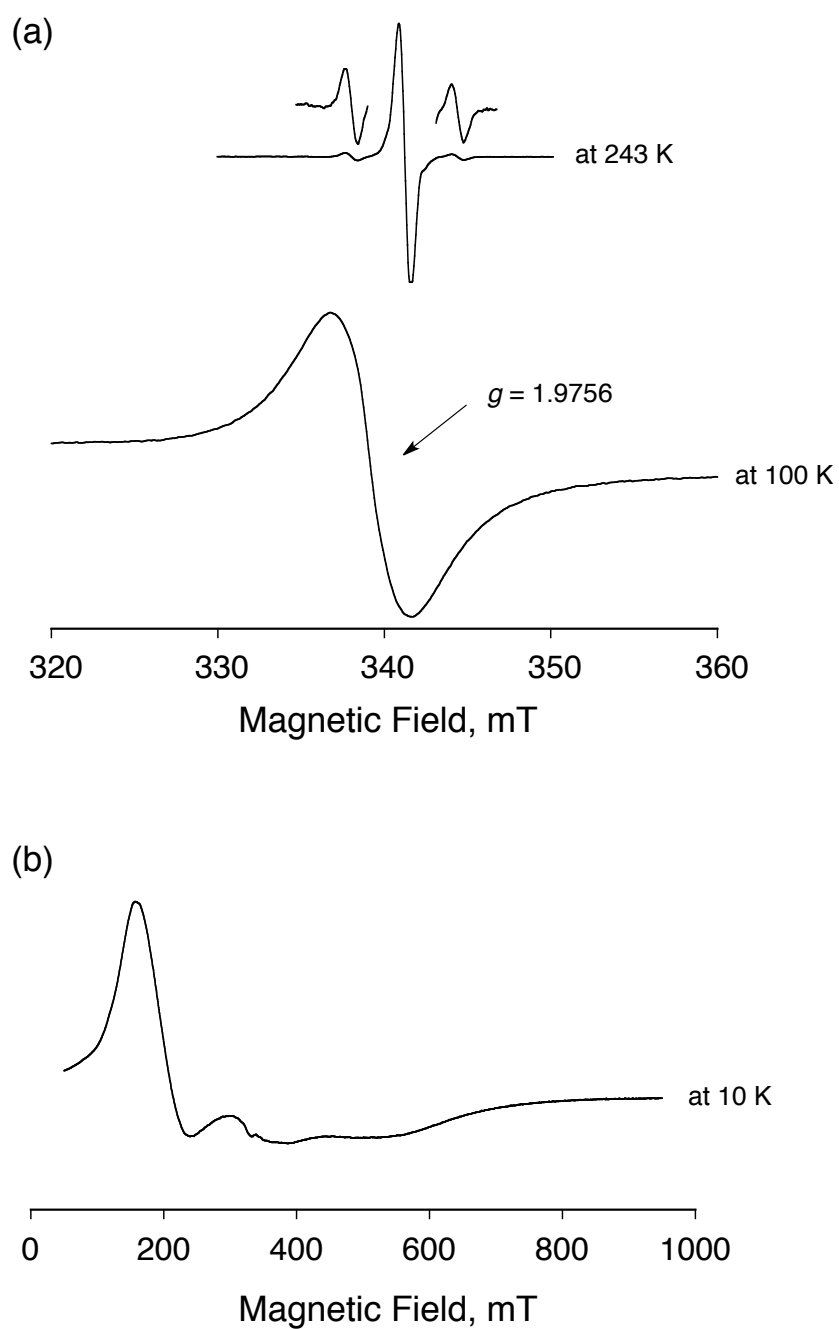
	<b>2</b>	<b>3</b>
formula	$\text{C}_{19}\text{H}_{17}\text{N}_4\text{O}_2\text{ClCrBF}_4$	$\text{C}_{19}\text{H}_{17}\text{N}_4\text{O}_2\text{CrB}_2\text{F}_8$
formula wt	507.62	558.97
cryst syst	orthorhombic	monoclinic
space group	<i>Pbcn</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> (Å)	14.5572 (8)	9.683(4)
<i>b</i> (Å)	13.9044 (8)	22.830(8)
<i>c</i> (Å)	24.0822 (14)	11.317(4)
$\alpha$ (deg)	90	90
$\beta$ (deg)	90	104.712(4)
$\gamma$ (deg)	90	90
<i>V</i> (Å <sup>3</sup> )	4874.46(5)	2419.7(15)
<i>Z</i>	8	4
<i>R</i> <sub>1</sub> (%)	5.02	5.27
<i>wR</i> <sub>2</sub> (%)	13.57	12.33
GOF	1.039	1.112



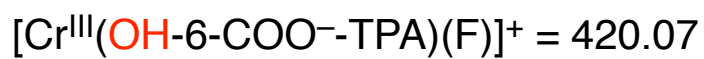
**Fig. S1** ESI-TOF-MS spectra of (a) **2** and (b) **3** at 298 K. Inset: simulated (upper) and observed (lower) isotope distribution patterns.



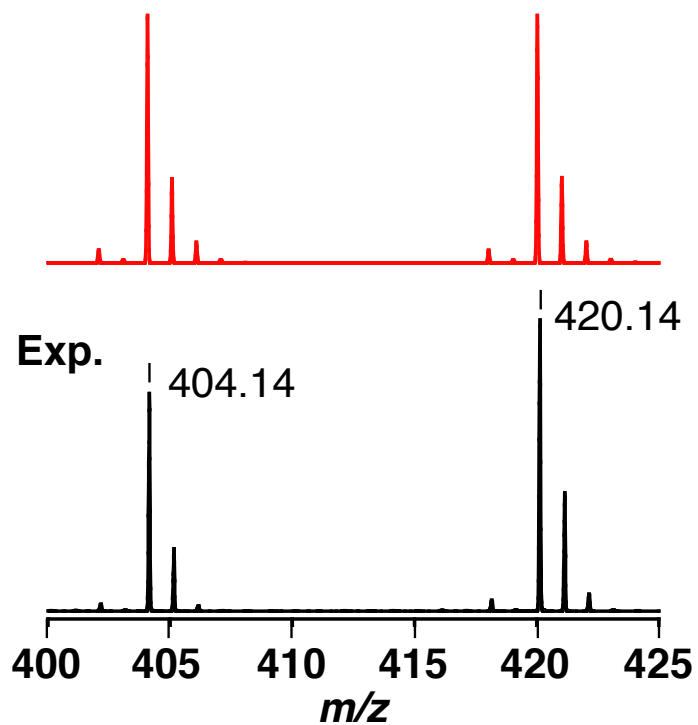
**Fig. S2** Time profile of decay of the absorption at 330 nm due to **1** in CH<sub>3</sub>CN at 243 K (blue line) and 298 K (red line).



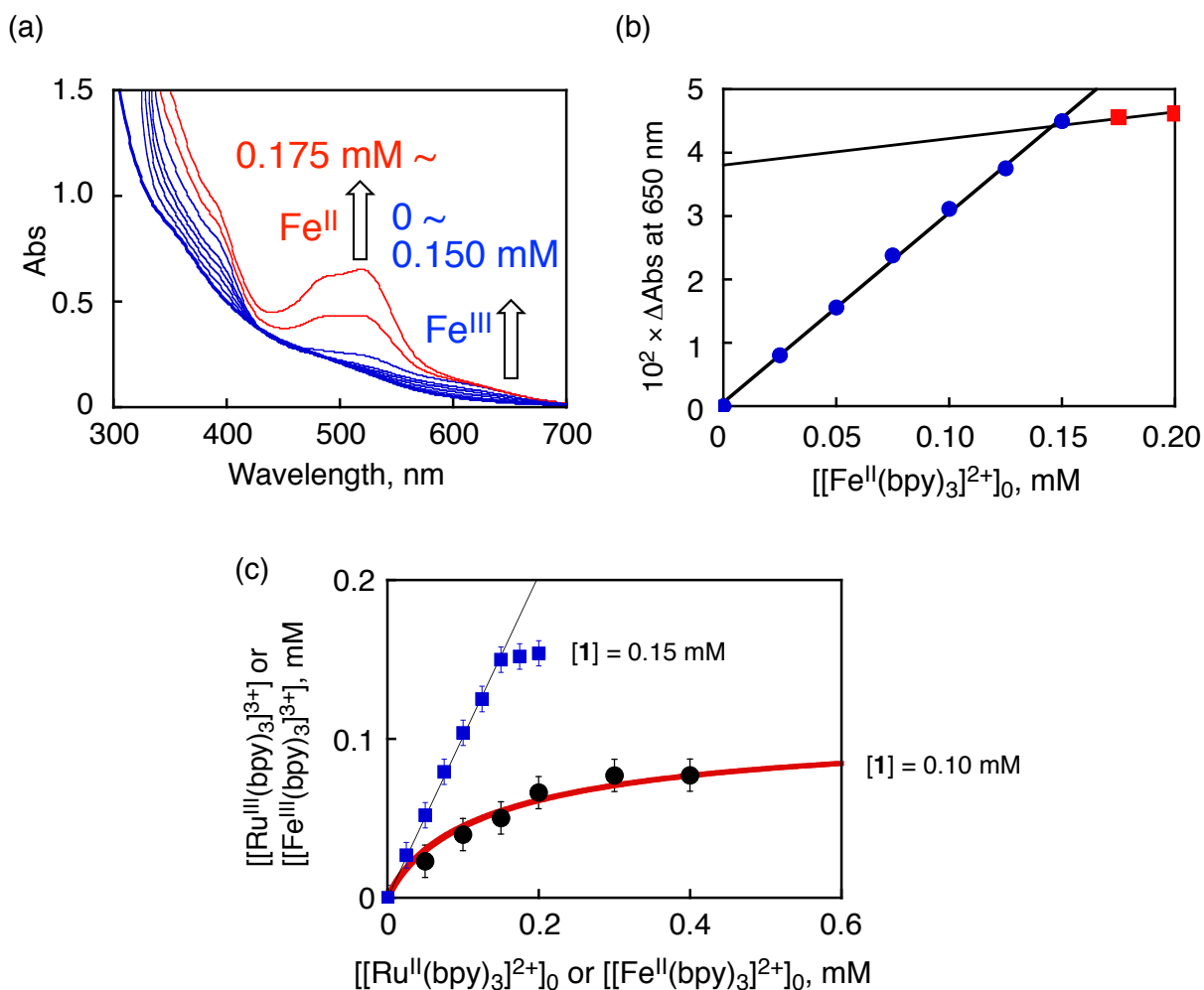
**Fig. S3** (a) X-band ESR spectrum of **1** (0.1 mM) in CH<sub>3</sub>CN at 243 K and 100 K. (b) X-band ESR spectrum of **3** (5.0 mM) in CH<sub>3</sub>CN at 10 K.



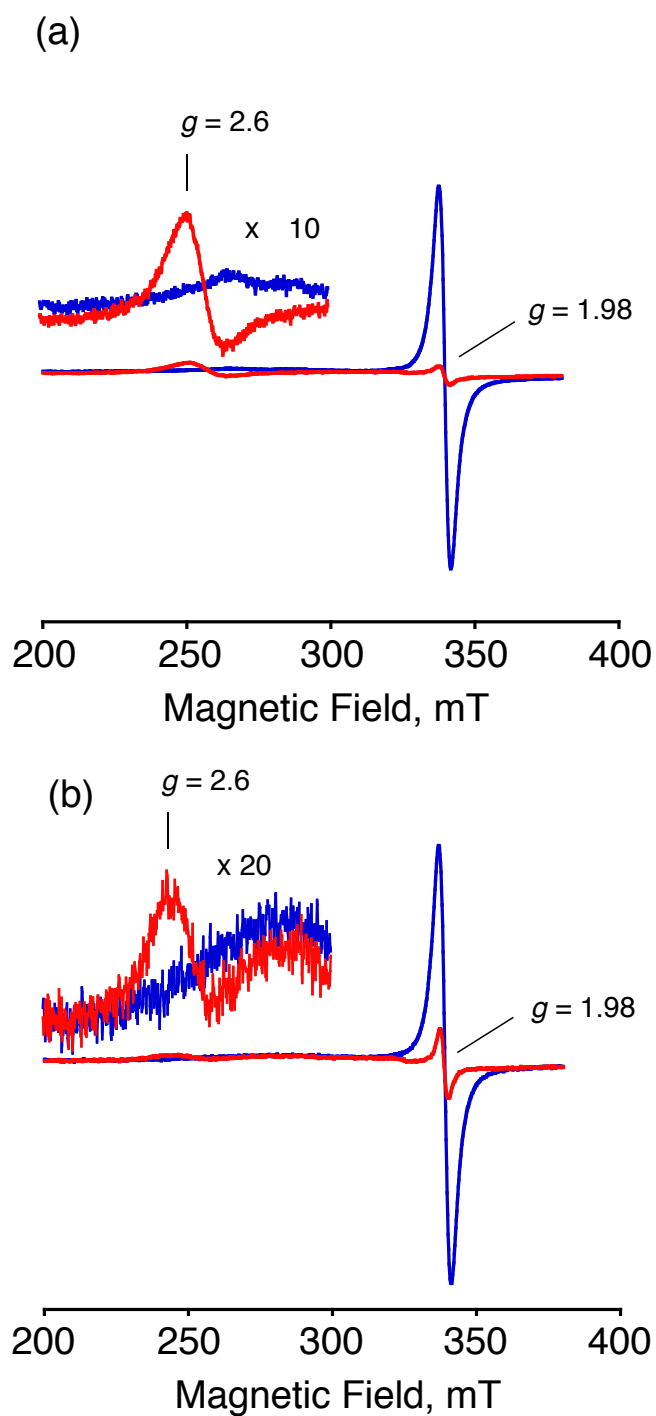
**Sim.**



**Fig. S4** ESI-TOF-MS spectra of ligand-oxidized products in  $\text{CH}_3\text{CN}$  at 298 K.

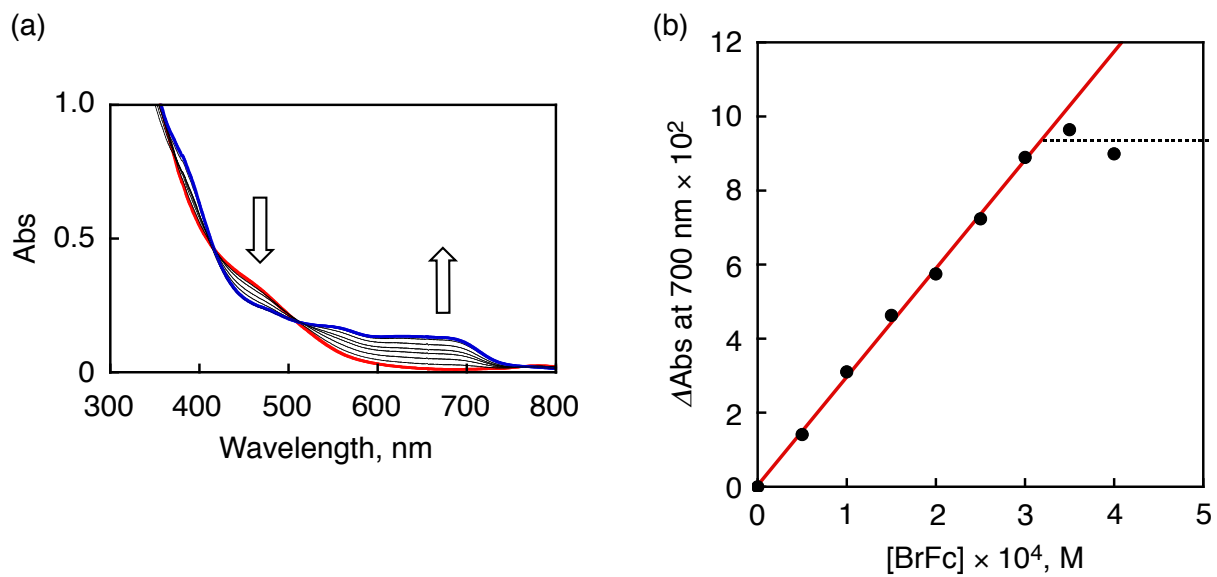


**Fig. S5** (a) UV-vis spectral changes observed upon addition of  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  to **1** (0.15 mM) in  $\text{CH}_3\text{CN}$  at 298 K. (b) A plot of  $\Delta\text{Abs}$  at 650 nm due to  $[\text{Fe}^{\text{III}}(\text{bpy})_3]^{3+}$  vs. initial concentration of  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ ,  $[[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}]_0$ . (c) Overlaid titration curves for  $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$  vs  $[[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}]_0$  (black circles) at  $[\mathbf{1}] = 0.10$  mM and 243 K (Fig 4b) and for  $[\text{Fe}^{\text{III}}(\text{bpy})_3]^{3+}$  vs  $[[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}]_0$  (blue squares) at  $[\mathbf{1}] = 0.15$  mM and 298 K.

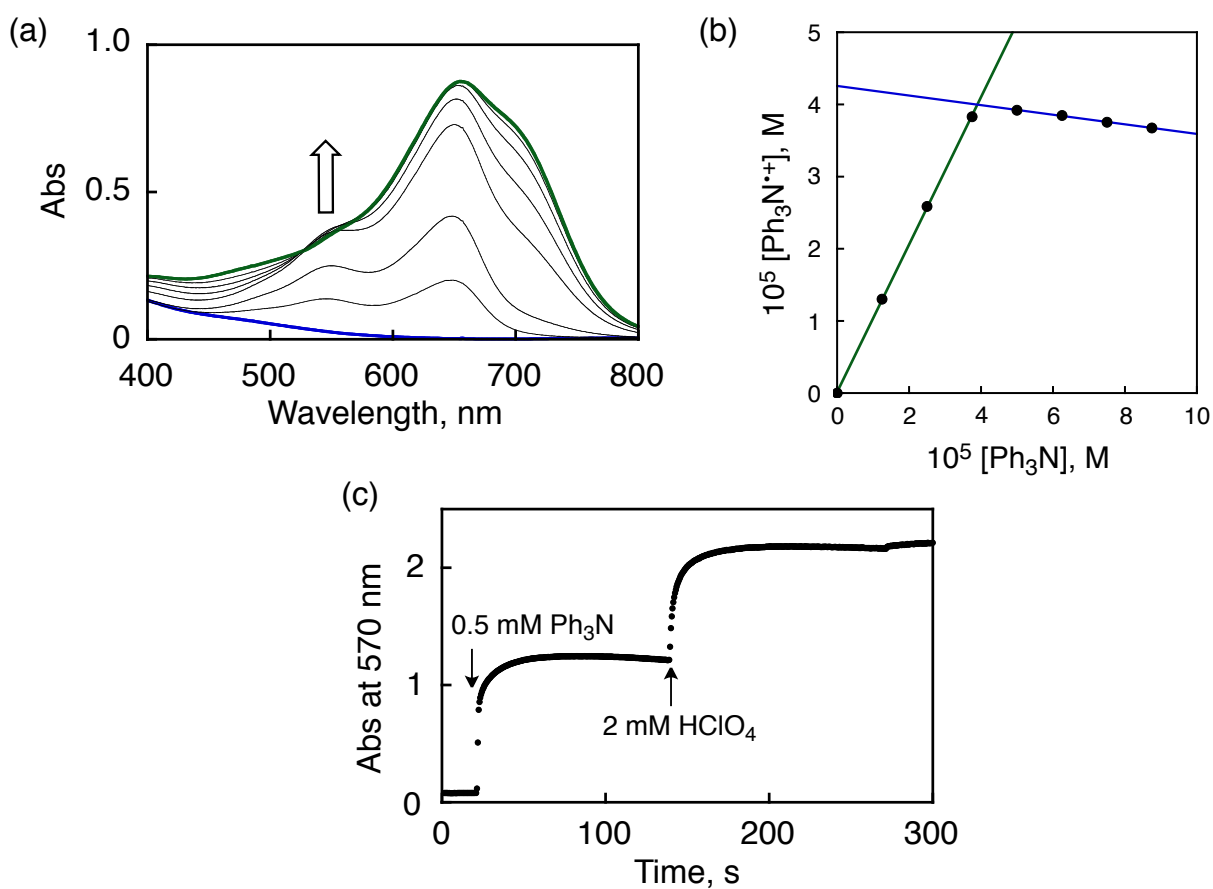


**Fig. S6** ESR spectral changes observed in an  $\text{CH}_3\text{CN}$  solution containing **1** (0.15 mM) upon addition of (a)  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  (0.4 mM) and (b)  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$  (1.7 mM), measured at 100 K.

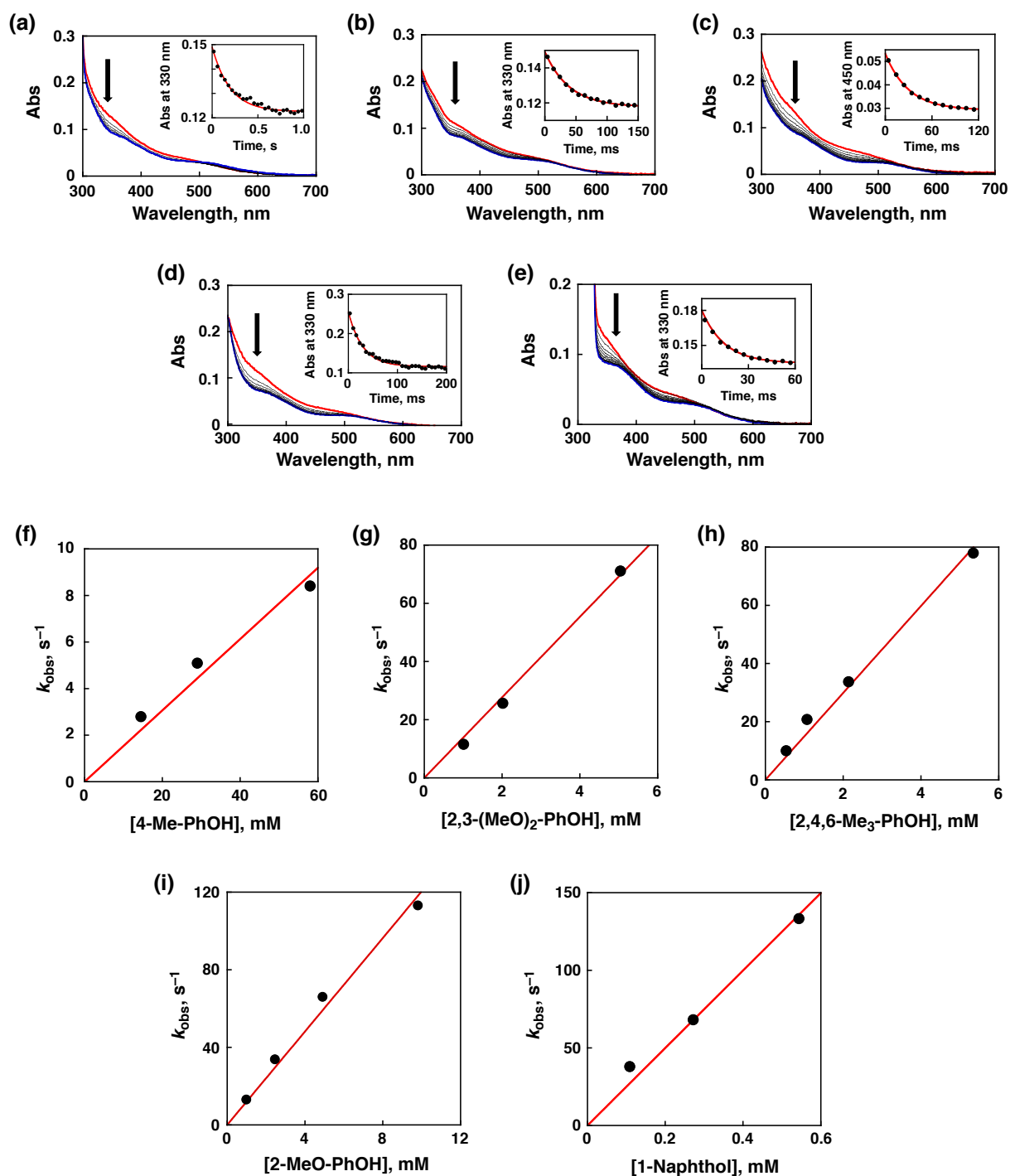




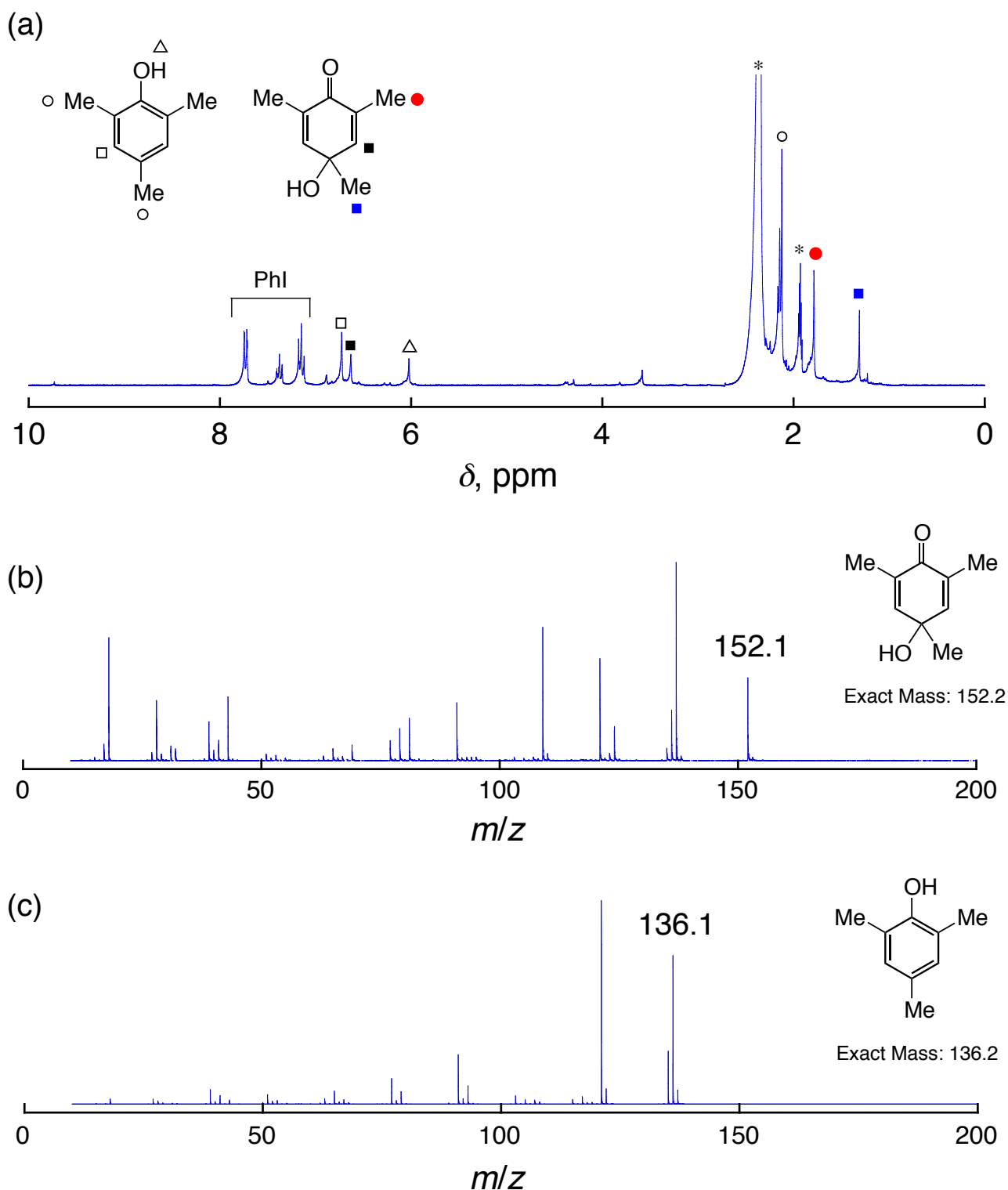
**Fig. S7** (a) UV-vis spectral changes observed upon addition of BrFc to **1** (0.17 mM) in CH<sub>3</sub>CN at 243 K. (b) A plot of  $\Delta\text{Abs}$  at 700 nm due to BrFc<sup>+</sup> vs. [BrFc].



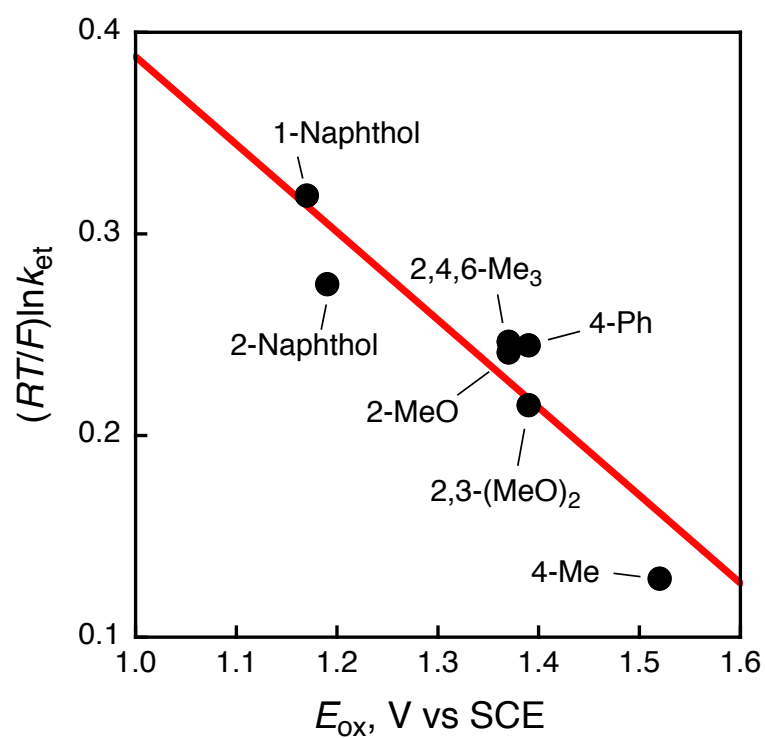
**Fig. S8** (a) UV-vis spectral changes observed upon addition of  $\text{Ph}_3\text{N}$  to **1** (0.04 mM) in  $\text{CH}_3\text{CN}$  at 243 K. (b) Plot of concentration of  $[\text{Ph}_3\text{N}^{+}]$  vs.  $[\text{Ph}_3\text{N}]$ . (c) Time profile of the absorption at 570 nm due to  $[\text{Ph}_3\text{N}^{+}]$ . 2 mM of  $\text{HClO}_4$  was added after completion of one-electron reduction of **1** (0.1 mM) at the timing indicated by an arrow.



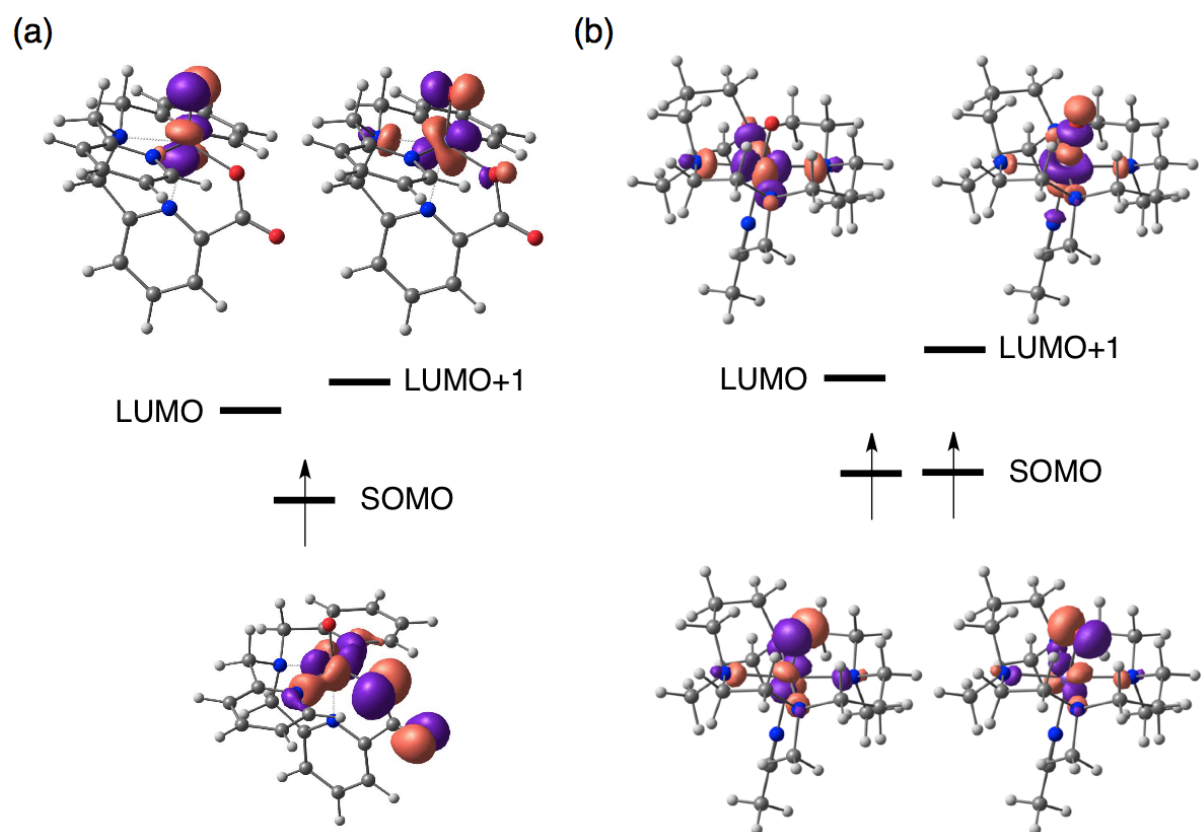
**Fig. S9** UV-vis spectral change upon addition of phenol derivatives (a, 4-Me (29 mM); b, 2,3-(MeO)<sub>2</sub> (2.0 mM); c, 2,4,6-Me<sub>3</sub> (2.0 mM); d, 2-MeO (2.5 mM); e, 1-naphthol (0.27 mM)) to **1** (0.02 mM) in CH<sub>3</sub>CN at 233 K. Plots of  $k_{\text{obs}}$  vs. [phenol derivatives]. (f, 4-Me; g, 2,3-(MeO)<sub>2</sub>; h, 2,4,6-Me<sub>3</sub>; i, 2-MeO; j, 1-naphthol).



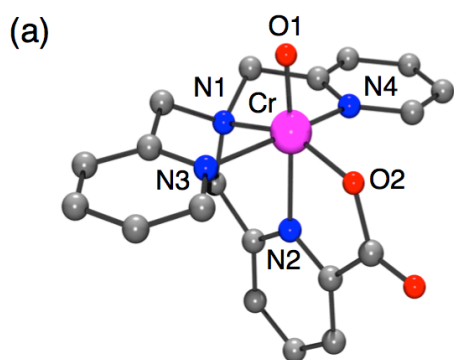
**Fig. S10** (a)  $^1\text{H}$  NMR spectra of the reaction mixture of **1** and 2,4,6- $\text{Me}_3\text{PhOH}$  in  $\text{CD}_3\text{CN}$  at 298 K. Iodobenzene (PhI) is derived from PhIO as the oxidant to generate **1**. Asterisks (\*) denote solvents peaks. (b) GC-MS spectrum of the reaction mixture of **1** and 2,4,6- $\text{Me}_3\text{PhOH}$  in  $\text{CD}_3\text{CN}$ . (c) GC-MS spectrum of the authentic sample of 2,4,6- $\text{Me}_3\text{PhOH}$  in  $\text{CD}_3\text{CN}$ .



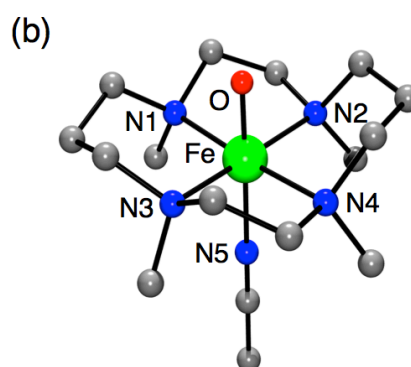
**Fig. S11** A plot of  $(RT/F)\ln(k_{et})$  against the oxidation potentials ( $E_{ox}$ ) of phenol derivatives in ET reaction from phenol derivatives to **1** at 233 K.



**Fig. S12** Relative energy levels of frontier molecular orbitals and their shapes of (a) **1** and (b)  $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{CH}_3\text{CN})]^{2+}$ .

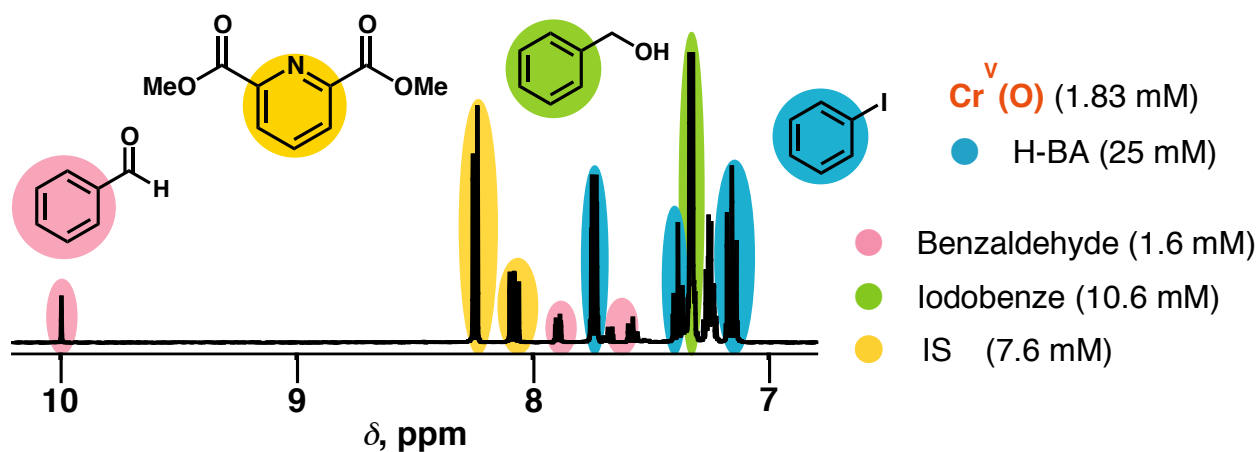


bonds	bond lengths of Cr <sup>V</sup> , Å	bond lengths of Cr <sup>IV</sup> , Å
Cr-O1 (Oxo)	1.55	1.63
Cr-O2 (COO)	1.82	1.91
Cr-N1	2.12	2.15
Cr-N2	2.14	2.13
Cr-N3	2.06	2.10
Cr-N4	2.06	2.10
average of $\Delta(\text{Cr}^{\text{IV}} - \text{Cr}^{\text{V}})$	0.044	

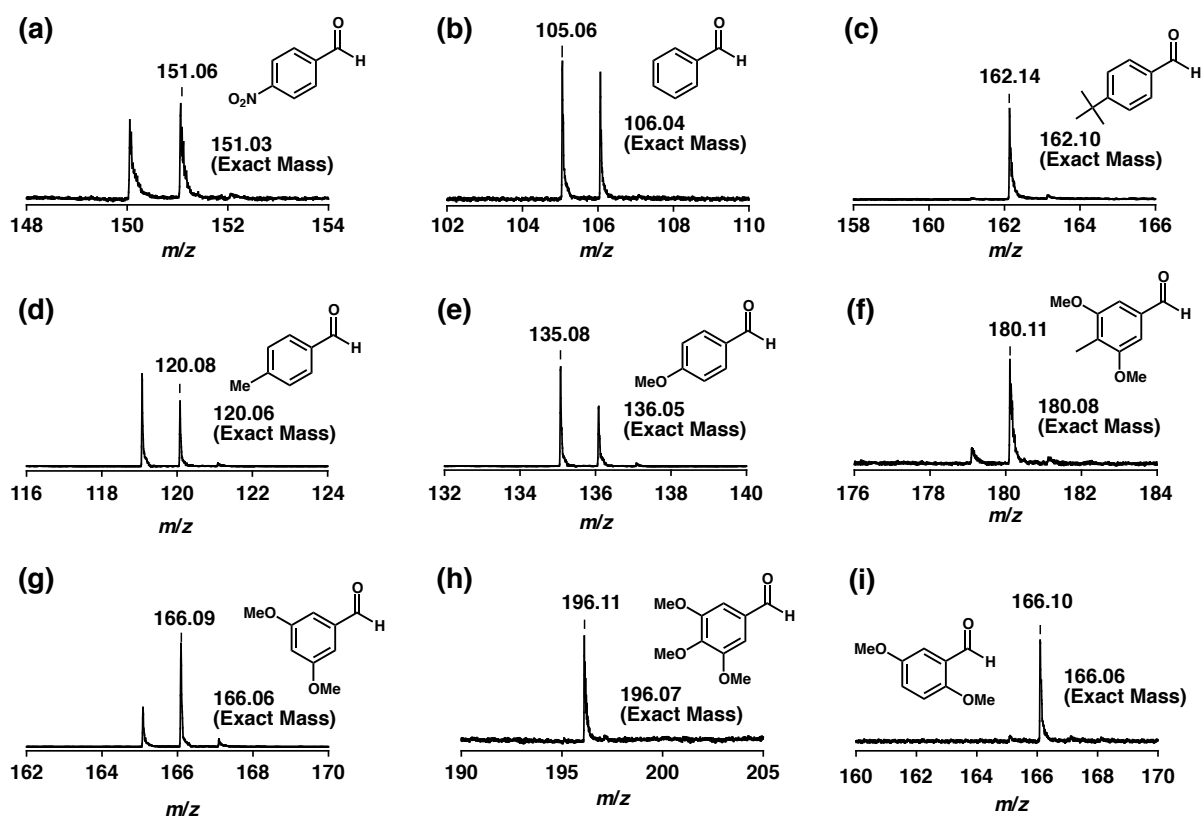


bonds	bond lengths of Fe <sup>IV</sup> , Å	bond lengths of Fe <sup>III</sup> , Å
Fe-O (Oxo)	1.62	1.63
Fe-N5	2.12	2.13
Fe-N1	2.12	2.29
Fe-N2	2.12	2.29
Fe-N3	2.15	2.24
Fe-N4	2.15	2.24
average of $\Delta(\text{Fe}^{\text{III}} - \text{Fe}^{\text{IV}})$	0.090	

**Fig. S13** DFT optimized structures of (a) **1** and (b)  $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{CH}_3\text{CN})]^{2+}$  and the difference of representative coordination bond lengths (a) between complex **1** and the corresponding  $\text{Cr}^{\text{IV}}(\text{O})$  complex and (b) between the  $\text{Fe}^{\text{IV}}$ -oxo complex and the corresponding  $\text{Fe}^{\text{III}}$ -oxo complex.

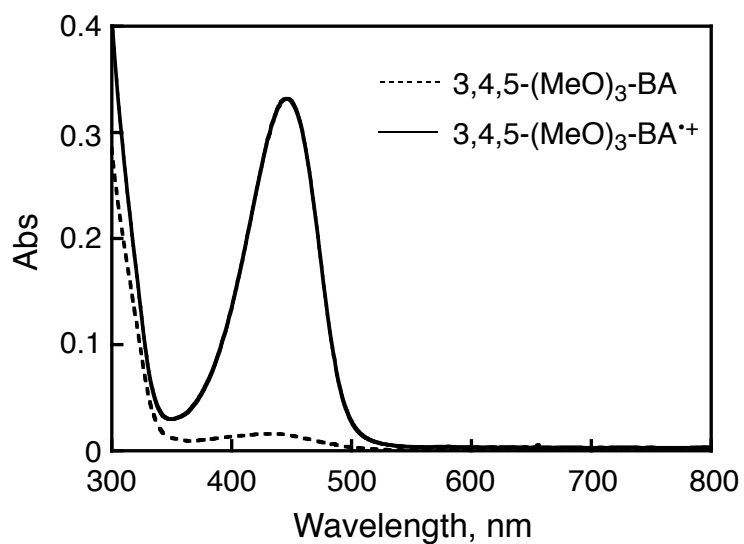


**Fig. S14**  $^1\text{H}$  NMR spectrum of the reaction mixture of **1** and H-BA in  $\text{CD}_3\text{CN}$  at 298 K.



**Fig. S15** GC-MS spectra of the reaction mixtures of **1** and R-BA ((a) 4-NO<sub>2</sub>-BA, (b) H-BA, (c) 4-*t*-Bu-BA, (d) 4-Me-BA, (e) 4-MeO-BA, (f) 3,5-(MeO)<sub>2</sub>-4-Me-BA, (g) 3,5-(MeO)<sub>2</sub>-BA, (h) 3,4,5-(MeO)<sub>3</sub>-BA, (i) 2,5-MeO<sub>2</sub>-BA).





**Fig. S16** UV-vis spectrum of 3,4,5-(MeO)<sub>3</sub>-BA radical cation (solid line) produced by addition of CAN to 3,4,5-(MeO)<sub>3</sub>-BA (0.05 mM) in CH<sub>3</sub>CN containing HClO<sub>4</sub> (0.1 M) at 233 K. The spectrum of 3,4,5-(MeO)<sub>3</sub>-BA is depicted in the dotted line.

Table S2. Cartesian coordinates of [Fe(IV)(O)(TMC)]<sup>2+</sup> in the triplet state.

Atom	Coordinates (Angstroms)		
	x	y	z
C	-1.928949	2.133867	0.936994
N	-1.417658	1.590076	-0.354738
C	-2.598590	1.268616	-1.229901
C	-3.355361	-0.000010	-0.862447
C	-2.598634	-1.268707	-1.229740
N	-1.417698	-1.590092	-0.354552
C	-1.928975	-2.133689	0.937268
Fe	-0.020837	-0.000035	-0.204834
N	-0.105407	0.000148	1.916401
C	-0.149872	0.000229	3.067170
C	-0.206675	0.000354	4.516208
O	0.007996	-0.000121	-1.822266
N	1.459785	1.561277	-0.166402
C	2.282296	1.777578	1.061970
N	1.459703	-1.561341	-0.166210
C	2.390664	-1.312609	-1.329726
C	3.176140	-0.000130	-1.275430
C	2.390701	1.312362	-1.329900
C	0.715130	2.855420	-0.389451
C	-0.617793	2.642569	-1.068096
C	0.715032	-2.855507	-0.389107
C	-0.617877	-2.642697	-1.067790
C	2.282181	-1.777494	1.062217
H	0.575196	3.329168	0.581668
H	1.332646	3.536060	-0.982380
H	-3.271894	-2.131683	-1.198677
H	-2.226364	-1.175844	-2.249364
H	-1.178708	3.583228	-1.088873
H	-0.482990	2.305993	-2.093570
H	-1.178831	-3.583334	-1.088459
H	-0.483053	-2.306241	-2.093301

H	-3.687219	0.000061	0.178897
H	-4.276068	-0.000033	-1.453604
H	3.106175	2.141646	-1.355248
H	1.793028	1.352857	-2.237877
H	1.332540	-3.536221	-0.981956
H	0.575077	-3.329138	0.582065
H	-2.226310	1.175604	-2.249506
H	-3.271824	2.131616	-1.198959
H	3.816908	-0.000198	-2.163062
H	3.874842	-0.000084	-0.435886
H	1.793010	-1.353220	-2.237711
H	3.106114	-2.141916	-1.354932
H	-2.520237	1.380057	1.451351
H	-2.561640	3.004831	0.743565
H	-1.109672	2.434660	1.583724
H	1.635934	-1.957076	1.917349
H	2.918678	-0.926269	1.271533
H	2.923401	-2.652775	0.919607
H	-1.109686	-2.434416	1.584011
H	-2.561696	-3.004661	0.743977
H	-2.520221	-1.379787	1.451540
H	2.918836	0.926395	1.271335
H	1.636074	1.957220	1.917110
H	2.923481	2.652867	0.919245
H	-0.728892	-0.892644	4.869124
H	0.805025	0.007613	4.929696
H	-0.741442	0.886157	4.868469

Table S3. Cartesian coordinates of [Fe(III)(O)(TMC)]<sup>+</sup> in the quartet state.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.998132	2.335767	-0.847416

N	1.458575	1.724230	0.382626
C	2.585659	1.300196	1.264601
C	3.292841	-0.001156	0.855180
C	2.585733	-1.303425	1.261795
N	1.458535	-1.725506	0.379054
C	1.997848	-2.334365	-0.852398
Fe	0.036783	-0.000383	0.195393
N	0.175883	0.002263	-1.932025
C	0.257505	0.004147	-3.079457
C	0.360771	0.006993	-4.527688
O	-0.012076	-0.002089	1.827234
N	-1.531137	1.668899	0.129852
C	-2.328796	1.905412	-1.092155
N	-1.531165	-1.669345	0.126427
C	-2.440889	-1.333801	1.266370
C	-3.204364	-0.001229	1.155249
C	-2.440875	1.331100	1.269102
C	-0.756505	2.915405	0.415458
C	0.587623	2.689668	1.110069
C	-0.756666	-2.916509	0.409535
C	0.587535	-2.692364	1.104528
C	-2.328829	-1.903374	-1.096068
H	-0.593742	3.424180	-0.536399
H	-1.354896	3.601300	1.029053
H	3.322927	-2.117862	1.302344
H	2.175445	-1.174615	2.262290
H	1.090587	3.662409	1.210984
H	0.425241	2.279953	2.103966
H	1.090393	-3.665374	1.203381
H	0.425278	-2.284711	2.099299
H	3.543343	-0.000015	-0.210312
H	4.258372	-0.001693	1.371766
H	-3.185378	2.136404	1.364110
H	-1.831953	1.313852	2.170100
H	-1.355137	-3.603532	1.021782
H	-0.593997	-3.423420	-0.543333

H	2.175181	1.169140	2.264724
H	3.322811	2.114572	1.307082
H	-3.902642	-0.002103	1.999543
H	-3.849534	-0.000328	0.272385
H	-1.831933	-1.318386	2.167375
H	-3.185407	-2.139278	1.359760
H	2.633975	1.622862	-1.372183
H	2.596383	3.227290	-0.615193
H	1.192512	2.627307	-1.520174
H	-1.668349	-2.130855	-1.932800
H	-2.912370	-1.023089	-1.354251
H	-3.023010	-2.744829	-0.963714
H	1.192066	-2.624207	-1.525707
H	2.595930	-3.226538	-0.622253
H	2.633712	-1.620416	-1.375679
H	-2.912262	1.025609	-1.352189
H	-1.668251	2.134756	-1.928337
H	-3.023040	2.746545	-0.958068
H	0.811157	-0.926700	-4.871461
H	-0.631664	0.107516	-4.972344
H	0.983329	0.842354	-4.855417

Table S4. Cartesian coordinates of  $[\text{Cr}(\text{V})(\text{O})(6\text{-COO}^-\text{-tpa})]^{2+}$  in the doublet state.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-2.967030	0.297236	-1.142442
N	-2.029832	-0.484847	-0.575537
C	-2.390987	-1.501335	0.246175
C	-3.723641	-1.738964	0.544363
C	-4.701048	-0.928330	-0.035624
C	-4.317942	0.098195	-0.893856
Cr	-0.000649	-0.384141	-0.926737

N	0.000209	1.055622	0.650265
C	0.000668	0.706976	1.930500
C	0.002395	1.683864	2.927012
C	0.003533	3.025045	2.541759
C	0.003064	3.372565	1.185255
C	0.001475	2.338623	0.265190
C	-0.001246	-0.785164	2.151754
N	-0.000886	-1.560196	0.839079
C	-1.256338	-2.384076	0.707677
C	0.001150	2.456819	-1.232280
O	0.001004	3.466090	-1.861697
O	-0.001051	-1.545811	-1.955735
O	0.001247	1.211183	-1.810371
N	2.028794	-0.486171	-0.575716
C	2.389343	-1.502628	0.246207
C	3.721900	-1.741377	0.544086
C	4.699837	-0.931944	-0.036617
C	4.317342	0.094498	-0.895251
C	2.966541	0.294716	-1.143398
C	1.254233	-2.384508	0.708205
H	1.071586	-3.150392	-0.050215
H	1.484073	-2.891374	1.647949
H	3.994940	-2.554162	1.206164
H	5.747605	-1.106740	0.177770
H	5.048153	0.734022	-1.373494
H	2.615831	1.071761	-1.810728
H	-0.879599	-1.078832	2.729863
H	0.875016	-1.081074	2.731875
H	0.002768	1.410298	3.975393
H	0.004855	3.800983	3.298326
H	0.003951	4.403153	0.852088
H	-1.486432	-2.891276	1.647176
H	-1.073911	-3.149611	-0.051122
H	-3.997257	-2.551796	1.206148
H	-5.748891	-1.102298	0.179072
H	-5.048326	0.738688	-1.371456

H    -2.615867    1.074237    -1.809606

Table S5. Cartesian coordinates of [Cr(IV)(O)(6-COO<sup>-</sup>-tpa)]<sup>+</sup> in the triplet state.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-3.034482	0.217695	-1.179366
N	-2.071021	-0.516899	-0.605641
C	-2.400398	-1.506805	0.249695
C	-3.724227	-1.769670	0.577932
C	-4.728942	-1.006905	-0.015531
C	-4.380350	-0.002407	-0.912075
Cr	-0.000167	-0.350376	-0.922758
N	0.000149	1.093803	0.646412
C	0.000525	0.751900	1.928247
C	0.001769	1.732253	2.919657
C	0.002386	3.071162	2.524377
C	0.001928	3.407792	1.168259
C	0.000990	2.370072	0.247982

C	-0.000964	-0.743850	2.162951
N	-0.000719	-1.532001	0.870716
C	-1.245919	-2.356061	0.734187
C	0.001125	2.496312	-1.265125
O	0.000432	3.567590	-1.818574
O	-0.001470	-1.632780	-1.924431
O	0.002500	1.312826	-1.864416
N	2.070166	-0.518570	-0.606327
C	2.399066	-1.508089	0.249694
C	3.722745	-1.771281	0.578205
C	4.727829	-1.009287	-0.015643
C	4.379723	-0.005244	-0.912872
C	3.033974	0.215258	-1.180454
C	1.244190	-2.356563	0.734519
H	1.047074	-3.112744	-0.028315
H	1.485868	-2.864436	1.672755
H	3.964409	-2.565399	1.274196
H	5.767982	-1.201373	0.219013
H	5.131170	0.601301	-1.401310
H	2.703902	0.981637	-1.871354
H	-0.878439	-1.025808	2.749750
H	0.874747	-1.027675	2.751486
H	0.002215	1.464562	3.969535
H	0.003265	3.851695	3.276098
H	0.002436	4.434069	0.824104
H	-1.487852	-2.864168	1.672240
H	-1.049148	-3.112054	-0.028920
H	-3.966282	-2.564112	1.273416
H	-5.769197	-1.198739	0.218880
H	-5.131513	0.604751	-1.400187
H	-2.704159	0.984418	-1.869774