

## Supporting Information

### Alkene *cis*-Dihydroxylation by *cis*-[(Me<sub>3</sub>tacn)(CF<sub>3</sub>CO<sub>2</sub>)Ru<sup>VI</sup>O<sub>2</sub>]ClO<sub>4</sub> (Me<sub>3</sub>tacn = 1,4,7-Trimethyl-1,4,7-triazacyclononane) — Structural Characterization of [3 + 2] Cycloadducts and Kinetic Studies

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## Experimental Section

**Materials.** All solvents and substrates were purified by the standard procedures.  $[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru}^{\text{VI}}\text{O}_2]\text{ClO}_4$  (**1**),<sup>1</sup>  $[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)_2\text{Ru}^{\text{III}}(\text{OH}_2)]\text{CF}_3\text{CO}_2$ <sup>-1</sup> and *cis*- $[(\text{Tet}-\text{Me}_6)\text{Ru}^{\text{VI}}\text{O}_2](\text{ClO}_4)_2$  (**2**)<sup>2</sup> were prepared according to the published procedures. Silver trifluoromethanesulfonate (99+, Acros) was used as received. Trifluoroacetic acid and hydrocarbon substrates were purified by vacuum distillation and stored under an inert atmosphere prior to use. Acetonitrile for the stoichiometric reactions was distilled first over  $\text{KMnO}_4$  and then over  $\text{P}_2\text{O}_5$  before use.

**Instrumentation.** Mass spectra were recorded on a Finnigan MAT 95 mass spectrometer, and electrospray-ionization mass spectra were obtained on a Finnigan MAT LCQ mass spectrometer. Elemental analyses were performed by the Institute of Chemistry of the Chinese Academy of Sciences.

All the X-ray diffraction data were collected on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 253 K. The images were interpreted and intensities integrated using the program DENZO.<sup>3</sup> The structures were solved by the direct methods employing the SIR-97 program<sup>4</sup> on a PC. Structure refinements were performed by the full-matrix least-squares using the program SHELXL-97<sup>5</sup> on a PC.

**Kinetic Studies.** UV-visible kinetic measurements for rapid reaction were performed on a Hi-Tech Scientific SF-61 stopped-flow spectrophotometer. The concentrations of alkenes ( $1 \times 10^{-3}$  to 0.5 M) were at least in 10-fold excess as that of the Ru<sup>VI</sup> complex ( $2 \times 10^{-5}$  to  $5 \times 10^{-5}$  M). The progress of reaction was monitored by change in absorbance at 420 nm. Pseudo-first-order rate constants,  $k_{obs}$ , were obtained from the nonlinear least-square fits of  $A_t$  to time  $t$  according to the equation,  $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{obs}t)$ , where  $A_0$  and  $A_\infty$  are the initial and final absorbances and  $A_t$  is the absorbance at time  $t$ . Product analyses were performed by gas chromatographic analyses using a Hewlett-Packard model HP 5890 Series II Chromatograph equipped with a flame ionization detector. Quantification of gas chromatographic components was performed on a Hewlett-Packard

HP 3393 Series II integrator. A capillary column model HP 17 (cross-linked 50% phenyl methyl silicone, 0.2  $\mu\text{m}$  film thickness) was used to analyze the oxidation products.

**Structural Characterization of  $[(\text{Me}_3\text{tacn})_2\text{Ru}^{\text{III}}_2(\mu\text{-O})(\mu\text{-CF}_3\text{CO}_2)_2](\text{ClO}_4)_2$  (3).** The UV-vis spectrum of **3** exhibits two intense absorption peaks at  $\lambda_{\text{max}} = 261$  and 545 nm with  $\epsilon_{\text{max}} = 11600$  and 7300  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ , respectively (see Figure S2). A similar spectral pattern has been reported by Wieghardt and co-workers for  $[(\text{Me}_3\text{tacn})_2\text{Ru}^{\text{III}}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2](\text{PF}_6)_2$  [ $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{max}}/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ): 290 (9800), 552 (7400)].<sup>6</sup> The FAB-MS spectrum of **3** features two distinctive cluster peaks at  $m/z$  787 ( $M^+$ ) and 887 ( $[M + \text{ClO}_4]^+$ ). The molecular composition of the parent ion ( $M^+$ ) is formulated as  $[(\text{Me}_3\text{tacn})_2\text{Ru}_2(\mu\text{-O})(\mu\text{-CF}_3\text{CO}_2)_2]^+$  based on the agreement between experimental and calculated isotopic distribution patterns.

The structure of **3** has been established by X-ray crystallography, and the crystallographic data and bond distances and angles are given in Tables S1 and S2. Both Ru atoms are bridged by one  $\mu$ -oxo and two  $\mu$ -trifluoroacetate ligands. The Ru(1)–O(5) distance is 1.888(5) Å, which is comparable to the related Ru–O distances in  $[(\text{Me}_3\text{tacn})_2\text{Ru}^{\text{III}}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2](\text{PF}_6)_2$  [1.884(2) Å],<sup>6</sup>  $[(\text{Me}_3\text{tacn})_2(\text{acac})_2\text{Ru}^{\text{III}}_2(\mu\text{-O})](\text{PF}_6)_2$  [1.913(1) Å],<sup>7</sup> and  $[(\text{bpy})_2(\text{OH}_2)\text{Ru}^{\text{II}}(\mu\text{-O})\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})_2](\text{ClO}_4)_2$  [1.869(1) Å; bpy = 2,2'-bipyridine].<sup>8</sup> The Ru(1)–O(5)–Ru(2) angle of 121.7(3) $^\circ$  is similar to the corresponding angles found in  $[(\text{Me}_3\text{tacn})_2\text{Ru}^{\text{III}}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2](\text{PF}_6)_2$  [119.7(2) $^\circ$ ],<sup>6</sup> and  $[(\text{CH}_3\text{CO}_2)_2(\text{bbtp})_2\text{Ru}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2]$  [119.2(3) $^\circ$ ; bbtp = *tert*-butyl-bis(2-thienyl)phosphine].<sup>9</sup> The Ru(1)–O(2) and Ru(1)–O(4) distances are 2.092(6) and 2.108(6) Å, which are comparable to the reported values found in  $[(\text{Me}_3\text{tacn})_2\text{Ru}^{\text{III}}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2](\text{PF}_6)_2$  [2.072(3) and 2.091(3) Å].<sup>6</sup>

### Spectral characterization data of complexes 4a–i

$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\overline{\text{Ru}^{\text{III}}\text{O}(\text{H})\text{CH}(\text{CH}_2)_6\text{HCO}}]\text{ClO}_4$  (**4a**): UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{max}}/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ): 390 (1390). FAB-MS:  $m/z$  529 ( $M^+$ ). Anal. Calcd for  $\text{C}_{19}\text{H}_{36}\text{N}_3\text{O}_8\text{F}_3\text{ClRu}$  (%): C, 36.34; H, 5.78; N, 6.69. Found: C, 36.07; H, 5.92; N, 6.58.  $\mu_{\text{eff}}$ : 1.94  $\mu_{\text{B}}$ .

$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru}^{\text{III}}\overset{\text{O(H)}}{\underset{\text{PhCHCH(CH}_3\text{)O}}{\text{O}}}\text{ClO}_4$  (**4b**): UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}/\text{nm}$  ( $\varepsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 396 (1550). FAB-MS: *m/z* 537 (M<sup>+</sup>). Anal. Calcd for C<sub>20</sub>H<sub>32</sub>N<sub>3</sub>O<sub>8</sub>F<sub>3</sub>ClRu (%): C, 37.77; H, 5.07; N, 6.61. Found: C, 37.44; H, 5.17; N, 6.66.  $\mu_{\text{eff}}$ : 1.99  $\mu_{\text{B}}$ .

$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru}^{\text{III}}\overset{\text{O(H)}}{\underset{\text{CH(CH}_2)_3\text{HCO}}{\text{O}}}\text{ClO}_4$  (**4c**): UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}/\text{nm}$  ( $\varepsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 383 (1280). FAB-MS: *m/z* 487 (M<sup>+</sup>). Anal. Calcd for C<sub>16</sub>H<sub>30</sub>N<sub>3</sub>O<sub>8</sub>F<sub>3</sub>ClRu (%): C, 32.80; H, 5.16; N, 7.17. Found: C, 32.98; H, 5.34; N, 7.22.  $\mu_{\text{eff}}$ : 1.98  $\mu_{\text{B}}$ .

$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru}^{\text{III}}\overset{\text{O(H)}}{\underset{\text{CH(CH}_2)_4\text{HCO}}{\text{O}}}\text{ClO}_4$  (**4d**): UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}/\text{nm}$  ( $\varepsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 396 (1270). FAB-MS: *m/z* 501 (M<sup>+</sup>). Anal. Calcd for C<sub>17</sub>H<sub>32</sub>N<sub>3</sub>O<sub>8</sub>F<sub>3</sub>ClRu (%): C, 34.03; H, 5.38; N, 7.00. Found: C, 34.84; H, 5.68; N, 7.11.  $\mu_{\text{eff}}$ : 1.97  $\mu_{\text{B}}$ .

$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru}^{\text{III}}\overset{\text{O(H)}}{\underset{\text{CH(CH}_2)_5\text{HCO}}{\text{O}}}\text{ClO}_4$  (**4e**): UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}/\text{nm}$  ( $\varepsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 388 (1500). FAB-MS: *m/z* 515 (M<sup>+</sup>). Anal. Calcd for C<sub>18</sub>H<sub>34</sub>N<sub>3</sub>O<sub>8</sub>F<sub>3</sub>ClRu (%): C, 35.21; H, 5.58; N, 6.84. Found: C, 34.84; H, 5.83; N, 6.76.  $\mu_{\text{eff}}$ : 1.96  $\mu_{\text{B}}$ .

$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru}^{\text{III}}\overset{\text{O(H)}}{\underset{\text{PhCHCHO}}{\text{O}}}\text{ClO}_4$  (**4f**): UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}/\text{nm}$  ( $\varepsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 396 (1350). FAB-MS: *m/z* 523 (M<sup>+</sup>). Anal. Calcd for C<sub>19</sub>H<sub>30</sub>N<sub>3</sub>O<sub>8</sub>F<sub>3</sub>ClRu (%): C, 36.69; H, 4.86; N, 6.76. Found: C, 36.13; H, 5.02; N, 6.68.  $\mu_{\text{eff}}$ : 1.93  $\mu_{\text{B}}$ .

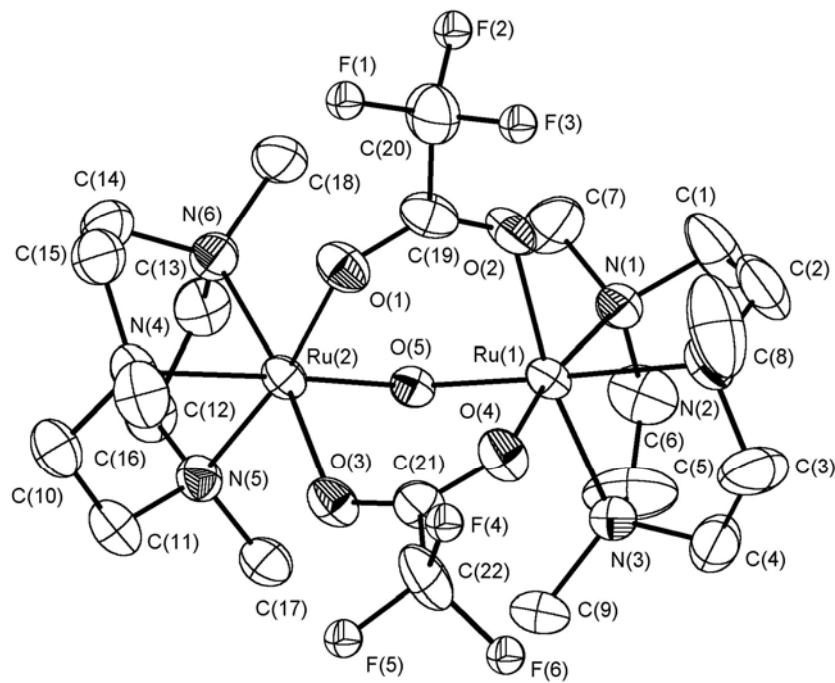
$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru}^{\text{III}}\overset{\text{O(H)}}{\underset{\text{PhCHCH(CO}_2\text{Et)O}}{\text{O}}}\text{ClO}_4$  (**4g**): UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}/\text{nm}$  ( $\varepsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 383 (1310). FAB-MS: *m/z* 595 (M<sup>+</sup>). Anal. Calcd for C<sub>22</sub>H<sub>34</sub>N<sub>3</sub>O<sub>10</sub>F<sub>3</sub>ClRu (%): C, 38.07; H, 4.94; N, 6.05. Found: C, 38.47; H, 5.11; N, 6.17.  $\mu_{\text{eff}}$ : 1.97  $\mu_{\text{B}}$ .

$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru}^{\text{III}}\overset{\text{O(H)}}{\underset{\text{AcOCHCH(OAc)O}}{\text{O}}}\text{ClO}_4$  (**4h**): UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}/\text{nm}$  ( $\varepsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 371 (1430). FAB-MS: *m/z* 591 (M<sup>+</sup>). Anal. Calcd for C<sub>19</sub>H<sub>35</sub>N<sub>3</sub>O<sub>12</sub>F<sub>3</sub>ClRu (%): C, 33.03; H, 5.11; N, 6.08. Found: C, 33.38; H, 4.93; N, 6.17.  $\mu_{\text{eff}}$ : 1.97  $\mu_{\text{B}}$ .

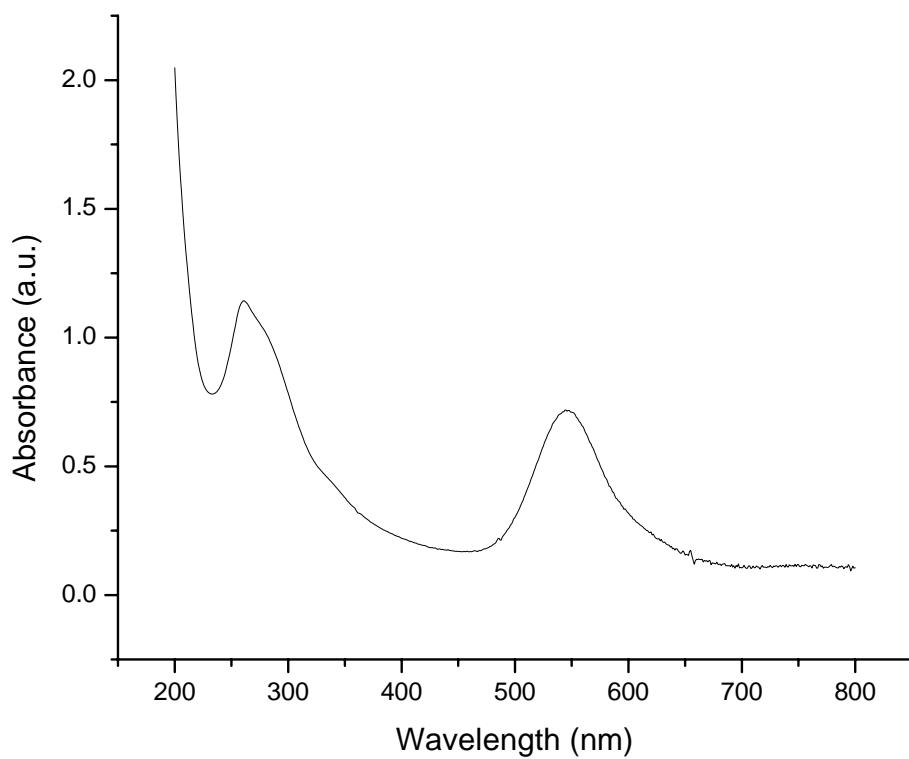
$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru}^{\text{III}}\overset{\text{O(H)}}{\underset{\text{PhCHCH(SiMe}_3\text{)O}}{\text{O}}}\text{ClO}_4$  (**4i**): UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}/\text{nm}$  ( $\varepsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 370 (1330). FAB-MS: *m/z* 595 (M<sup>+</sup>). Anal. Calcd for C<sub>22</sub>H<sub>39</sub>N<sub>3</sub>O<sub>8</sub>F<sub>3</sub>ClRuSi (%): C, 38.01; H, 5.65; N, 6.04. Found: C, 37.77; H, 5.73; N, 5.93.  $\mu_{\text{eff}}$ : 1.95  $\mu_{\text{B}}$ .

## References

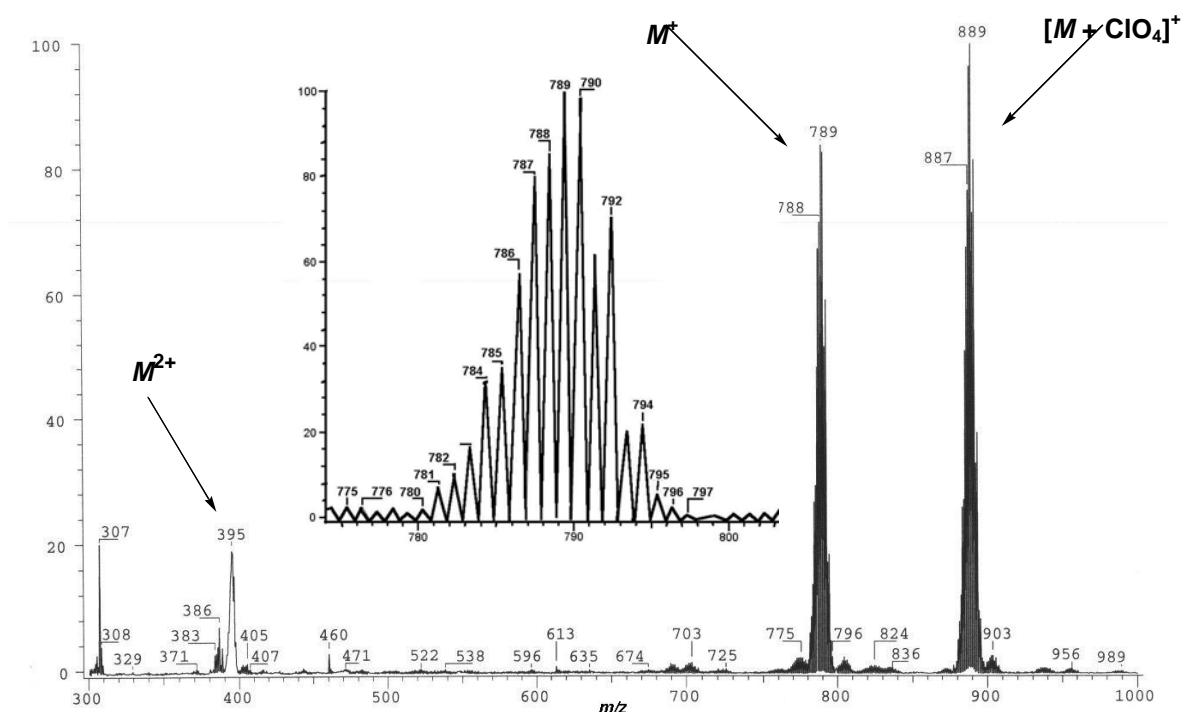
1. Che, C.-M.; Yu, W.-Y.; Chan, P.-M.; Cheng, W.-C.; Peng, S.-M.; Lau, K.-C.; Li, W.-K. *J. Am. Chem. Soc.* **2000**, *122*, 11380.
2. Li, C.-K.; Che, C.-M.; Tong, W.-F.; Tang, W.-T.; Wong, K.-Y.; Lai, T.-F. *J. Chem. Soc., Dalton Trans.* **1992**, 2109.
3. Otwinowski, Z.; Minor, W., “Processing of X-ray Diffraction Data Collected in Oscillation Mode”, Methods in Enzymology, Volume 276: Macromolecular Crystallography, part A, p. 307-326, 1997. Carter C. W., Sweet Jr. & R. M., Eds., Academic Press.
4. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna , R. *Sir97: a New Tool for Crystal Structure Determination and Refinement, J. Appl. Cryst.* **1998**, *32*, 115–119.
5. Sheldrick, G. M. *SHELX97. Programs for Crystal Structure Analysis (Release 97-2)*, University of Goetingen, Germany, 1997.
6. Neubold, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 933.
7. Schneider, R.; Weyhermüller, T.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1993**, *32*, 4925.
8. Gilbert, J. A.; Eggleston, D. S.; Murphy, Jr., W. R.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3855.
9. Barral, M. C.; Jiménez-Aparicio, R.; Kramolowsky, R.; Wagner, I. *Polyhedron* **1993**, *12*, 903.



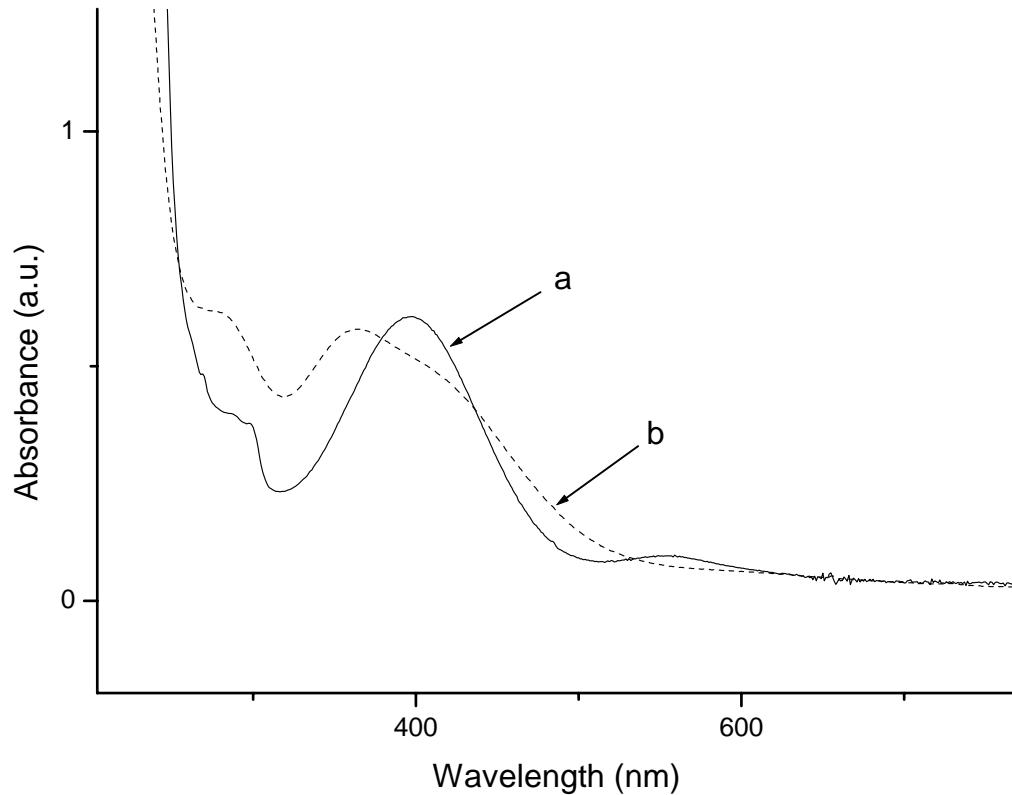
**Figure S1.** Perspective view of the cation of  $[(\text{Me}_3\text{tacn})_2\text{Ru}_2^{\text{III}}(\mu\text{-O})(\mu\text{-CF}_3\text{CO}_2)_2](\text{ClO}_4)_2$  (**3**).



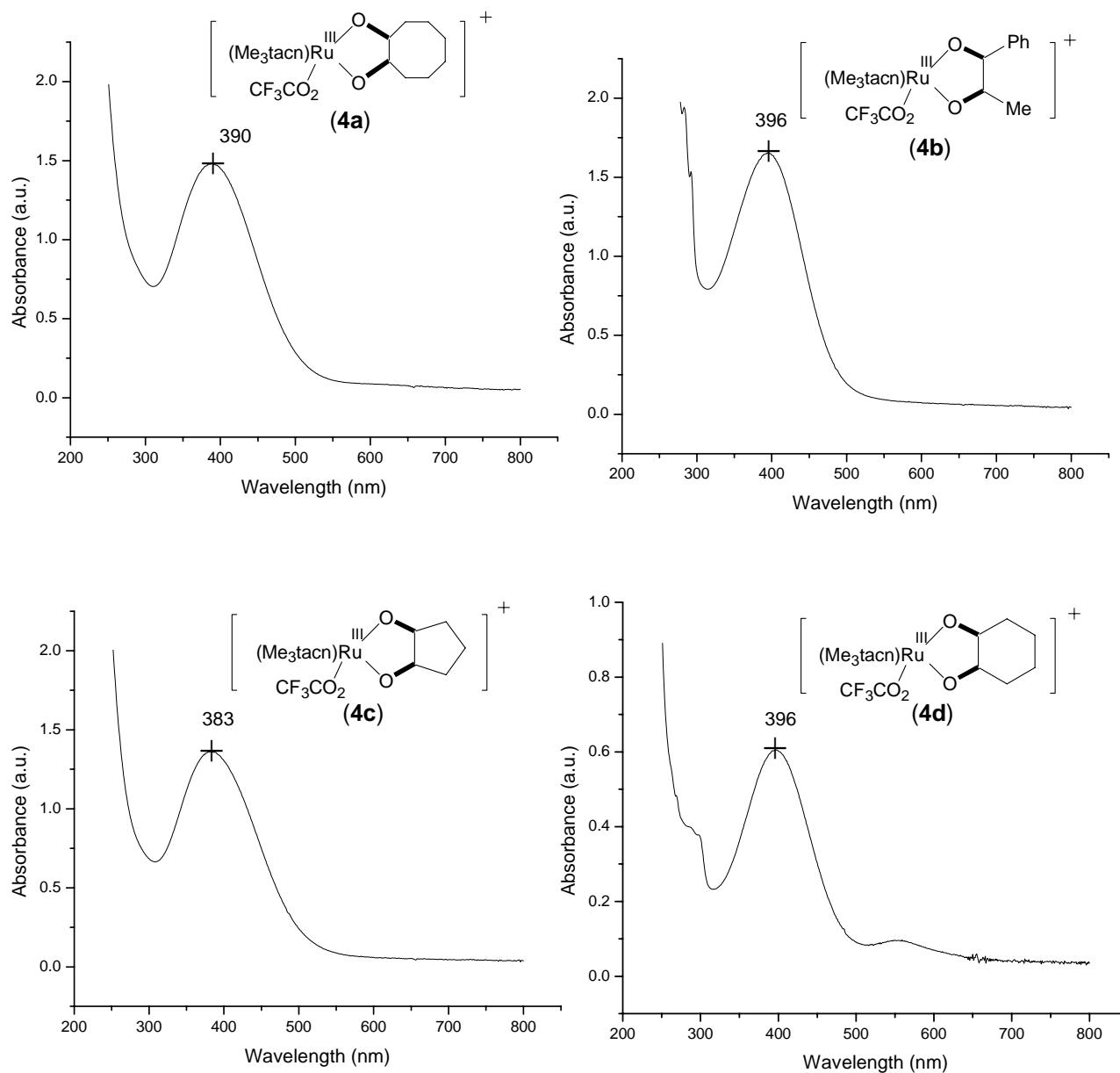
**Figure S2.** UV-vis spectrum of  $[(\text{Me}_3\text{tacn})_2\text{Ru}^{\text{III}}_2(\mu\text{-O})(\mu\text{-CF}_3\text{CO}_2)_2](\text{ClO}_4)_2$  (**3**) in distilled water.



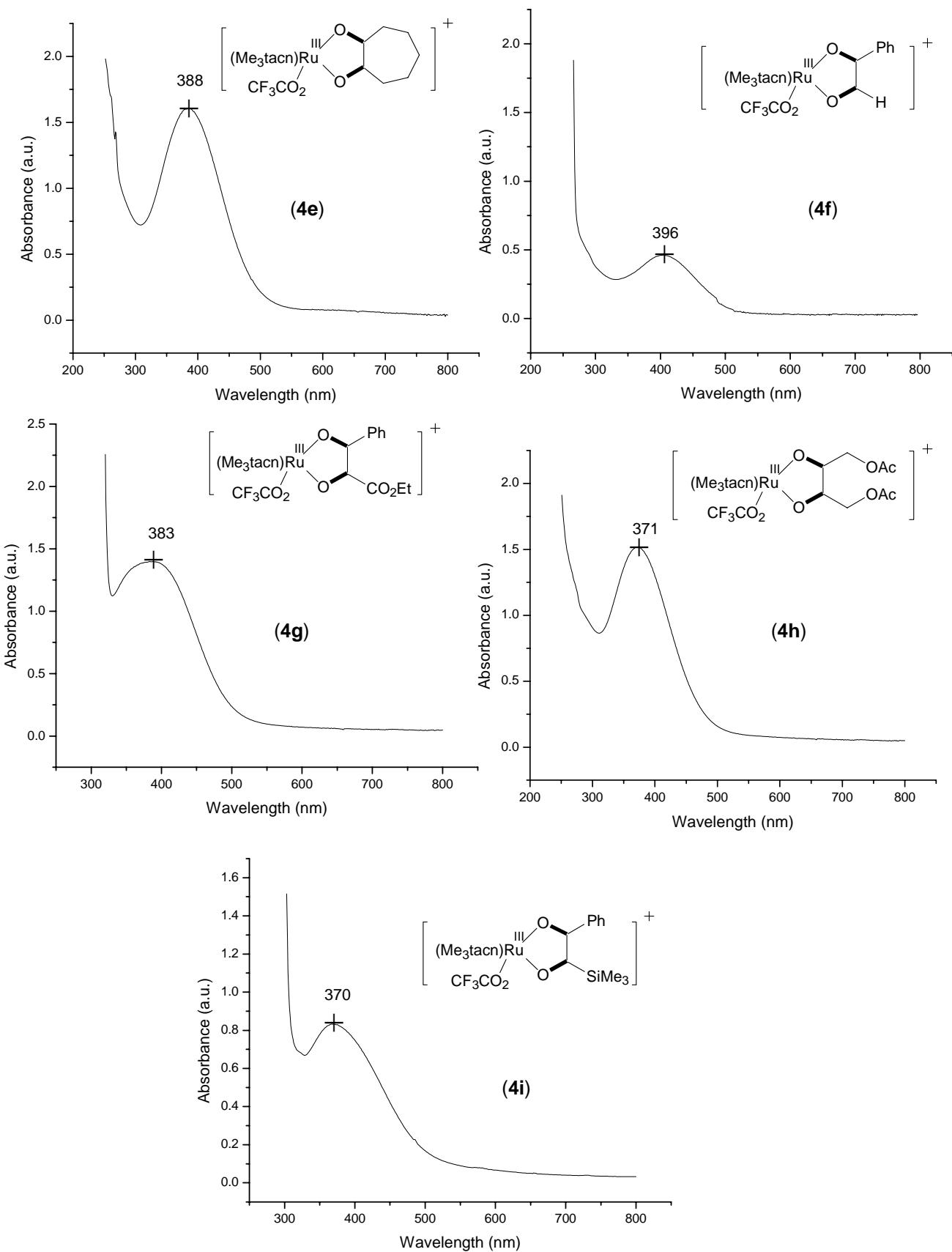
**Figure S3.** FAB-MS spectrum of  $[(\text{Me}_3\text{tacn})_2\text{Ru}^{\text{III}}_2(\mu-\text{O}^{18})(\mu-\text{CF}_3\text{CO}_2)_2](\text{ClO}_4)_2$ .



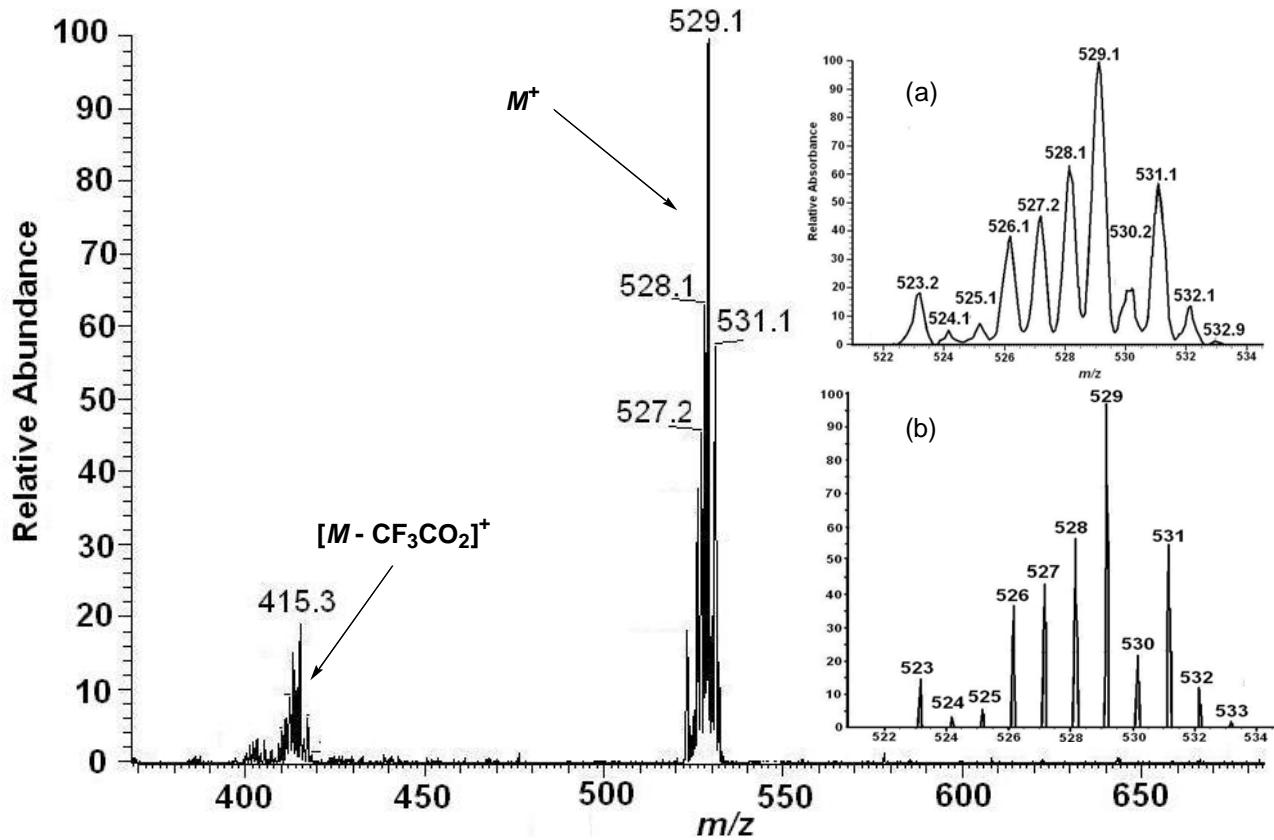
**Figure S4.** UV-vis spectra of 0.48 mM solution of reaction of **1** with cyclohexene generated (a) in aqueous *tert*-butanol ( $\text{CH}_2\text{Cl}_2$  extract) and (b) in acetonitrile solution.



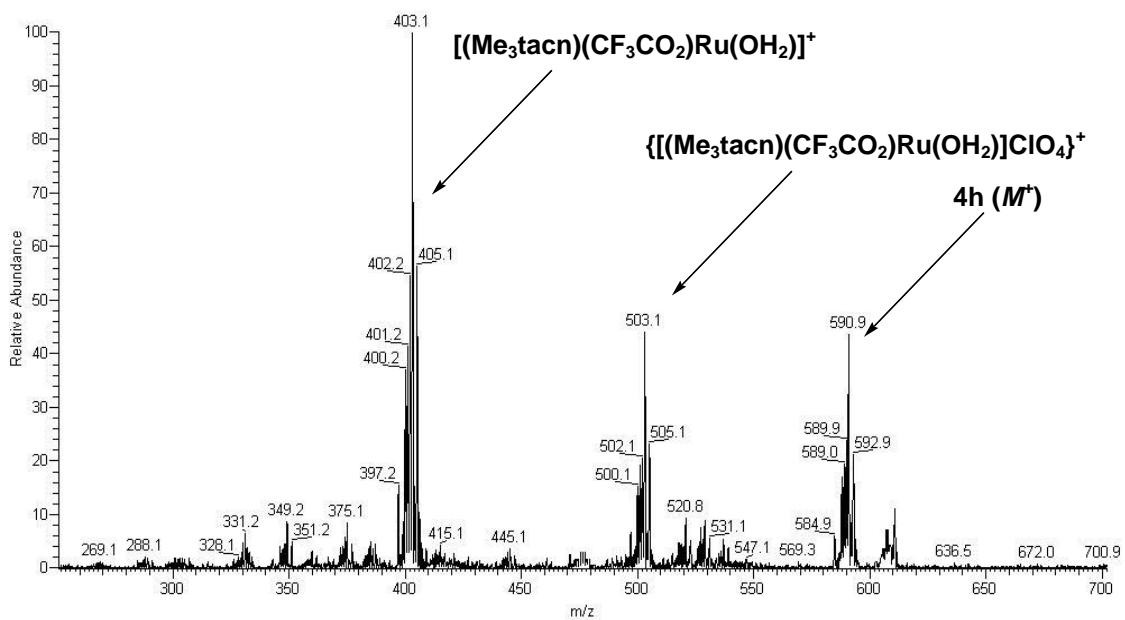
**Figure S5.** UV-vis spectra of Ru(III) cycloadducts **4a–d** in  $\text{CH}_2\text{Cl}_2$ .



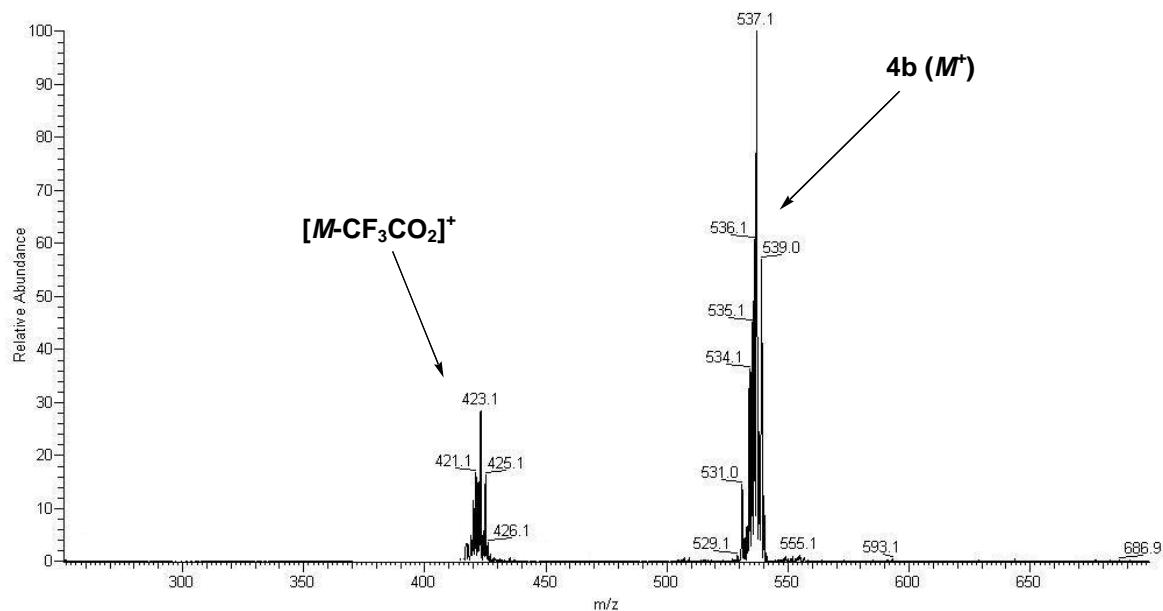
**Figure S6.** UV-vis spectra of Ru(III) cycloadducts **4e–i** in  $\text{CH}_2\text{Cl}_2$ .



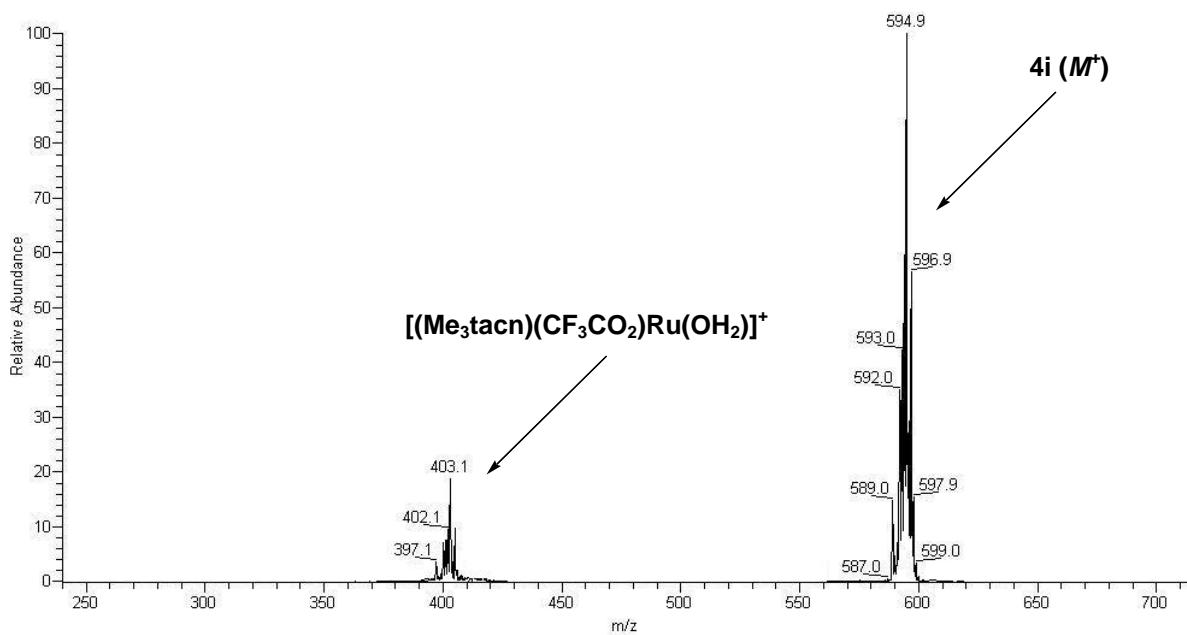
**Figure S7.** ESI-MS spectrum ( $\text{CH}_2\text{Cl}_2$  extract) of *cis*-dihydroxylation of cyclooctene by **1**. Insets: (a) Experimental and (b) calculated isotopic distribution patterns for the  $[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru}^{\text{III}}\text{O}(\text{H})\text{CH}(\text{CH}_2)_6\text{HCO}]^+$  (**4a**) complex.



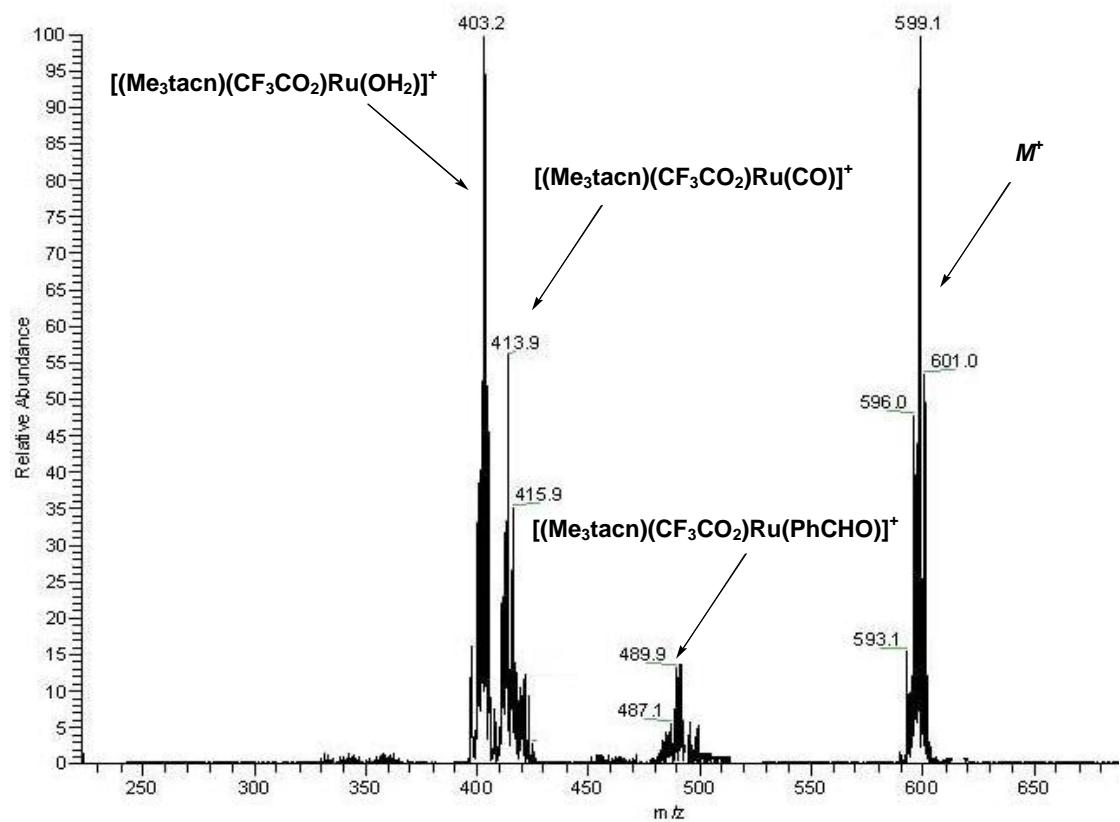
**Figure S8.** ESI-MS spectrum ( $\text{CH}_2\text{Cl}_2$  extract) for *syn*-dihydroxylation of *cis*-2-butene-1,4-diacetate by **1**.



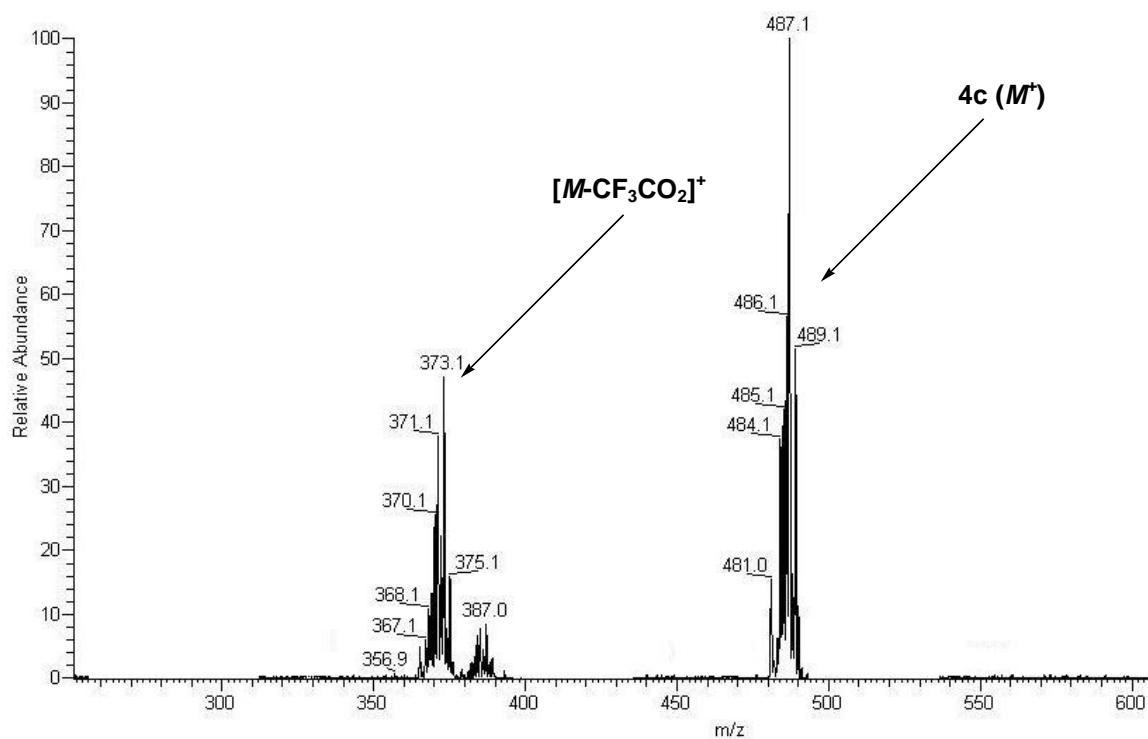
**Figure S9.** ESI-MS spectrum ( $\text{CH}_2\text{Cl}_2$  extract) for *syn*-dihydroxylation of *trans*- $\beta$ -methylstyrene by **1**.



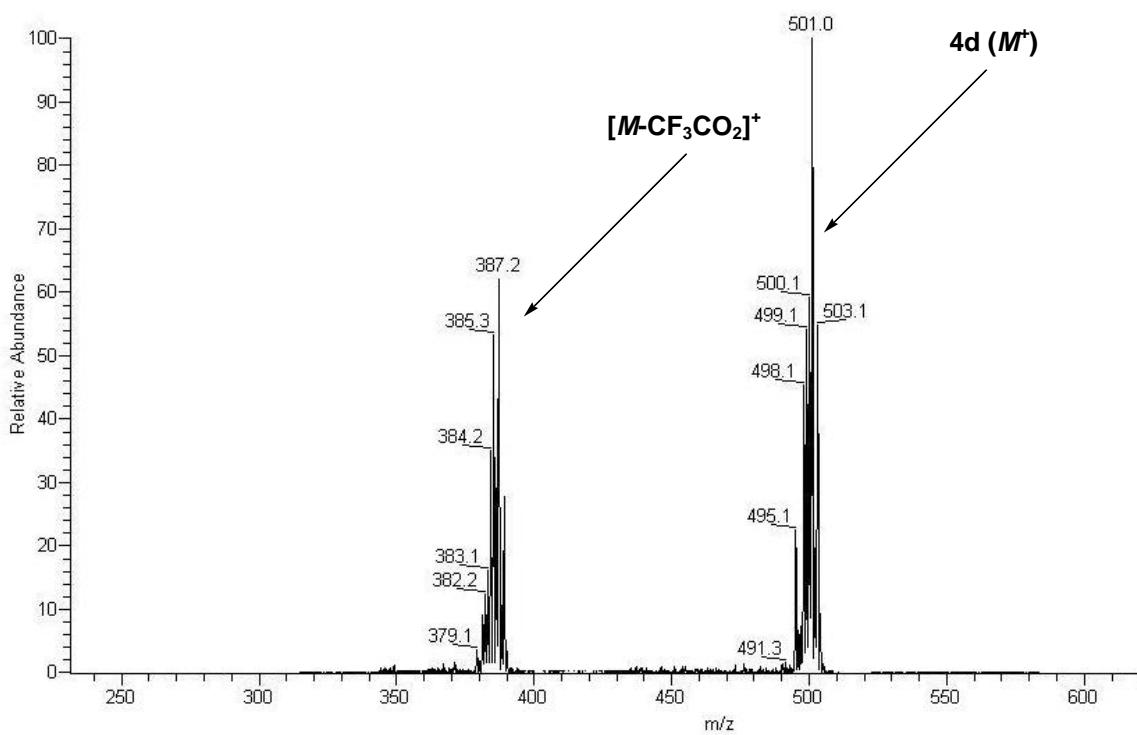
**Figure S10.** ESI-MS spectrum (CH<sub>2</sub>Cl<sub>2</sub> extract) for *syn*-dihydroxylation of *trans*- $\beta$ -(trimethylsilyl)styrene by **1**.



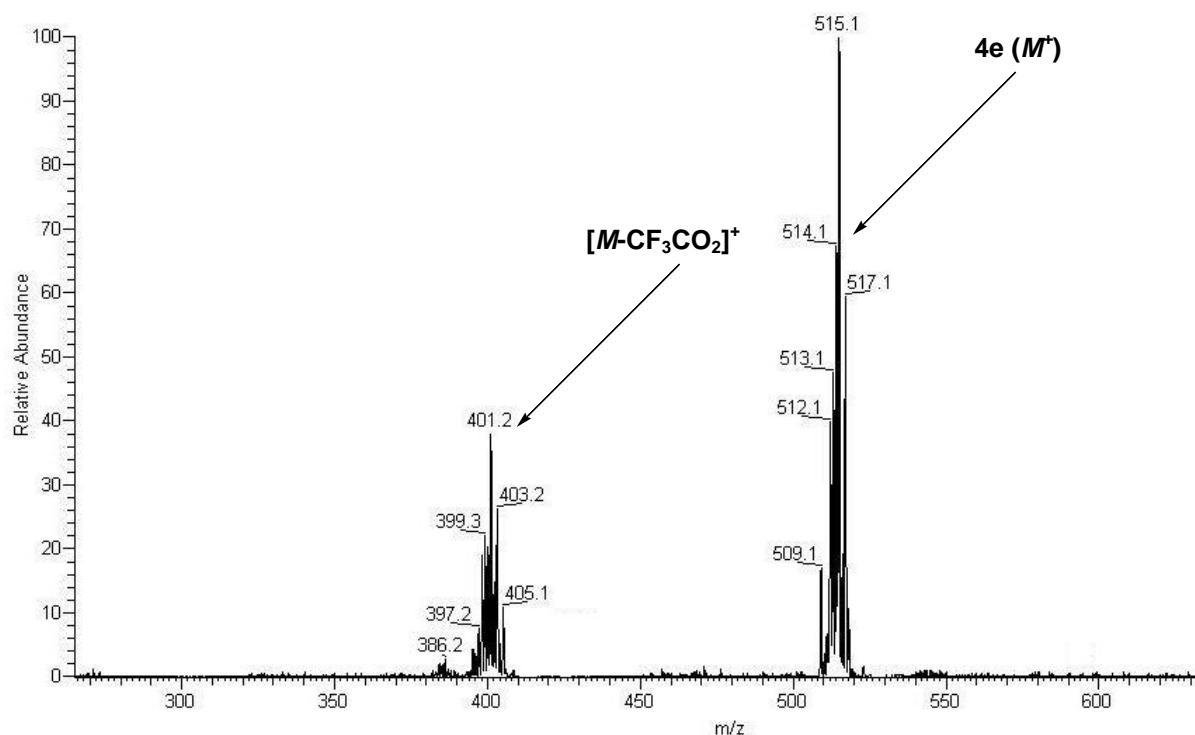
**Figure S11.** ESI-MS spectrum ( $\text{CH}_2\text{Cl}_2$  extract) of oxidation of *cis*-stilbene by **1**.



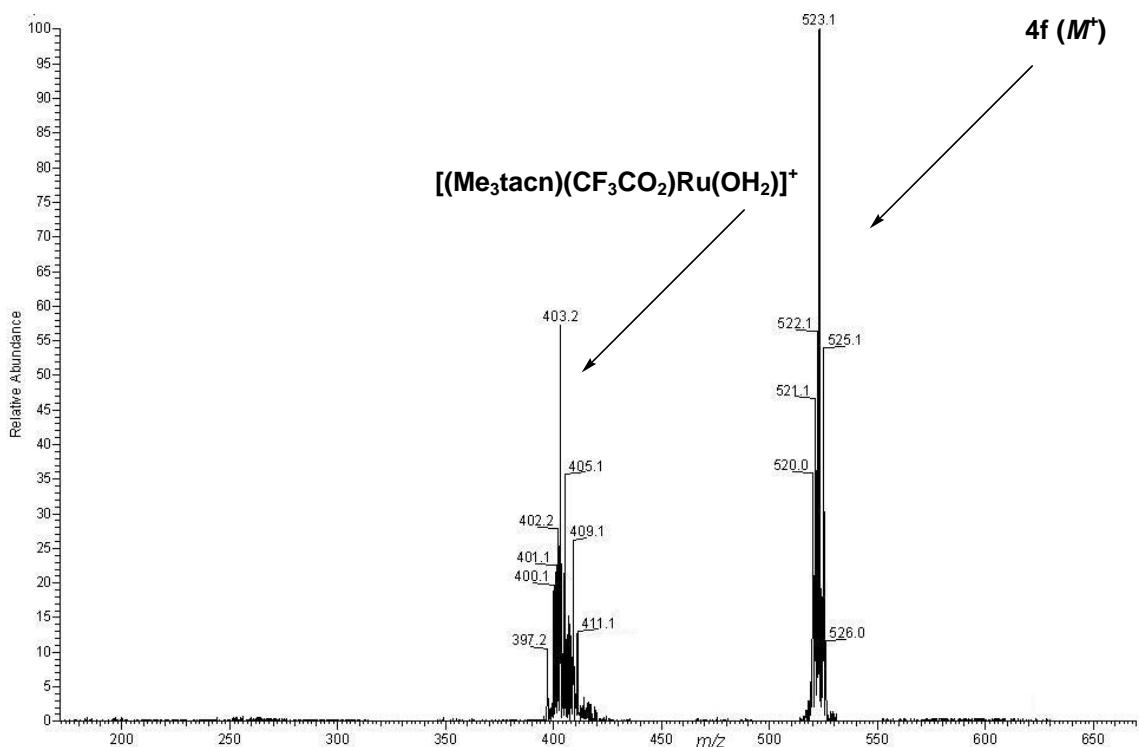
**Figure S12.** ESI-MS spectrum ( $\text{CH}_2\text{Cl}_2$  extract) for *cis*-dihydroxylation of cyclopentene by **1**.



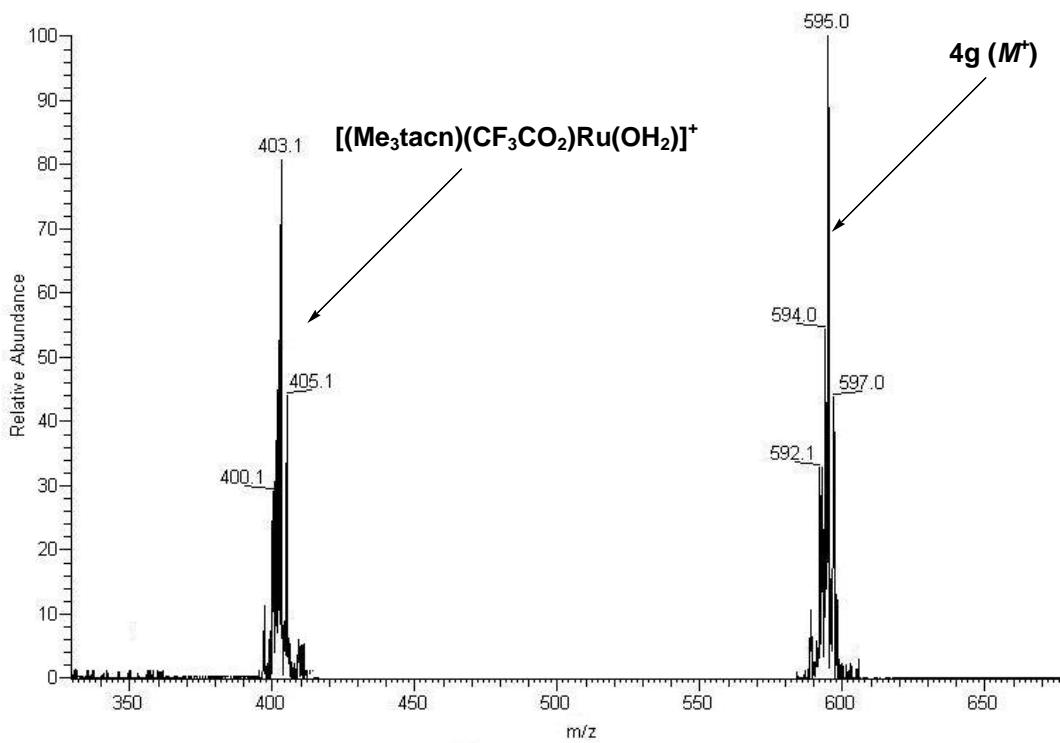
**Figure S13.** ESI-MS spectrum ( $CH_2Cl_2$  extract) for *cis*-dihydroxylation of cyclohexene by **1**.



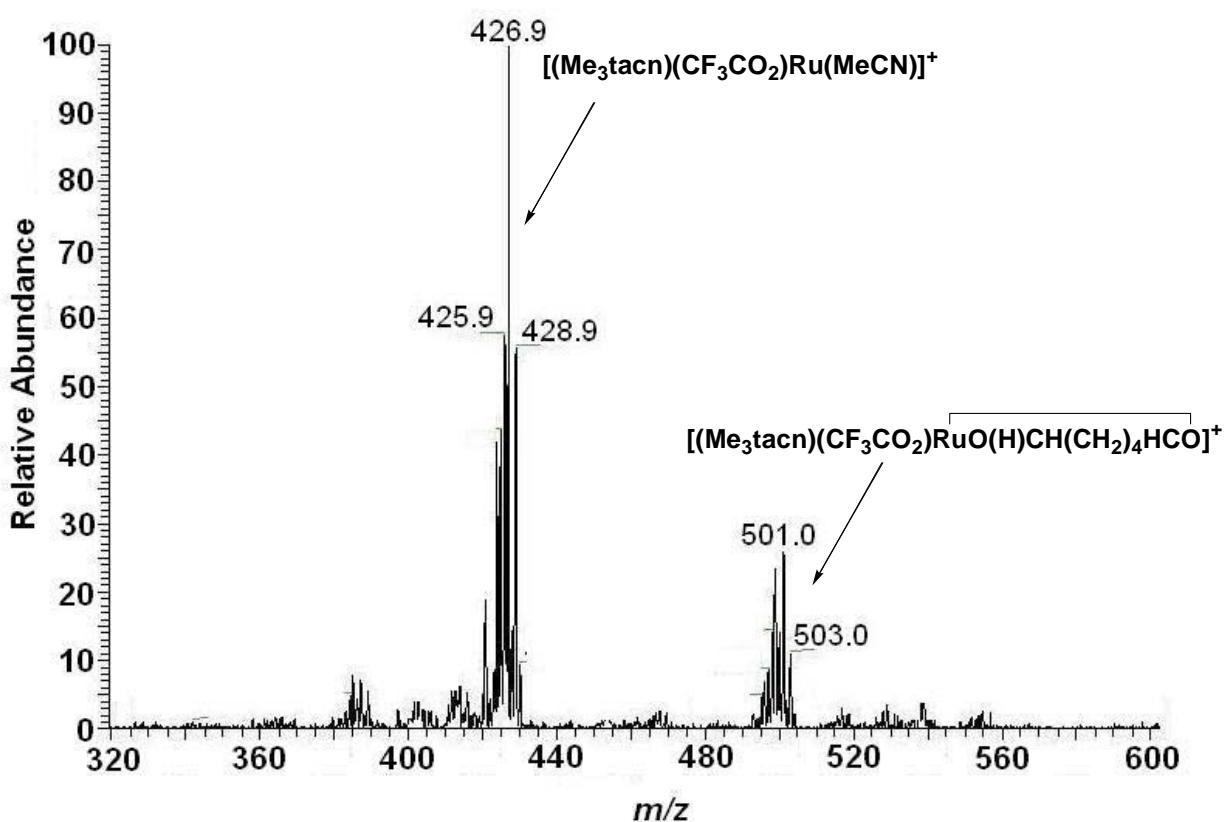
**Figure S14.** ESI-MS spectrum ( $\text{CH}_2\text{Cl}_2$  extract) for *cis*-dihydroxylation of cycloheptene by **1**.



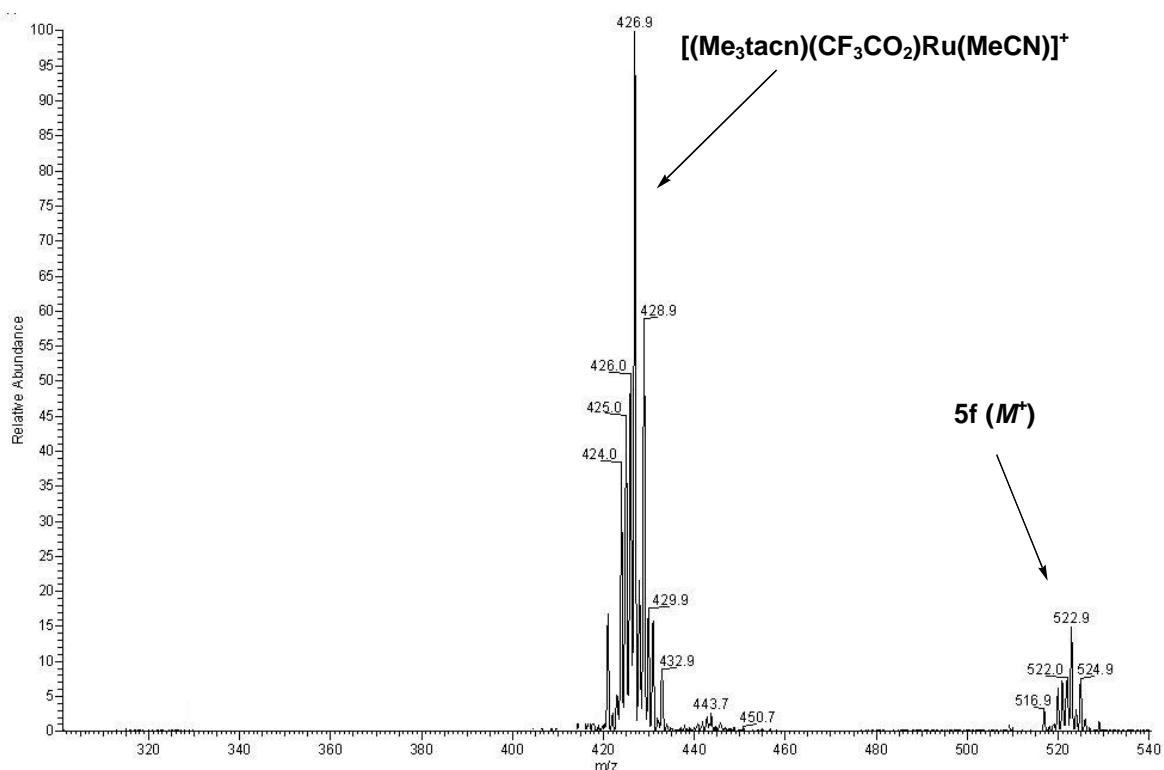
**Figure S15.** ESI-MS spectrum (CH<sub>2</sub>Cl<sub>2</sub> extract) for *syn*-dihydroxylation of styrene by **1**.



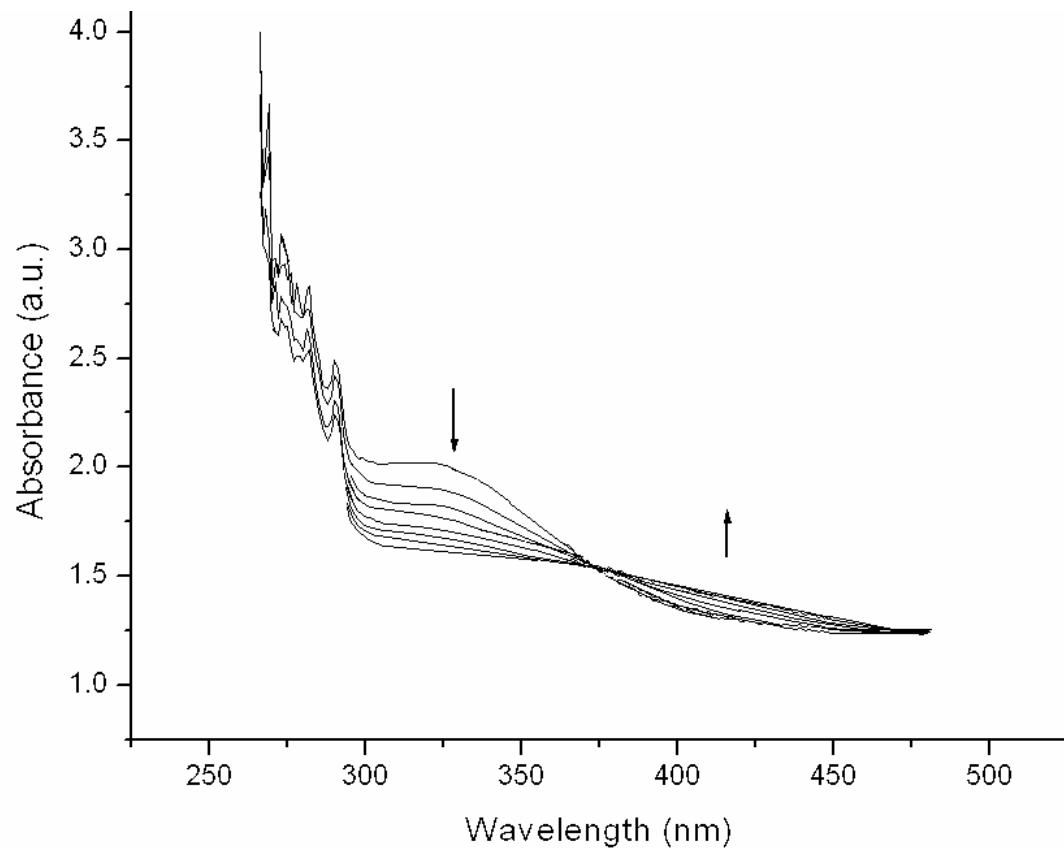
**Figure S16.** ESI-MS spectrum ( $\text{CH}_2\text{Cl}_2$  extract) of *syn*-dihydroxylation of *trans*-ethylcinnamate by **1**.



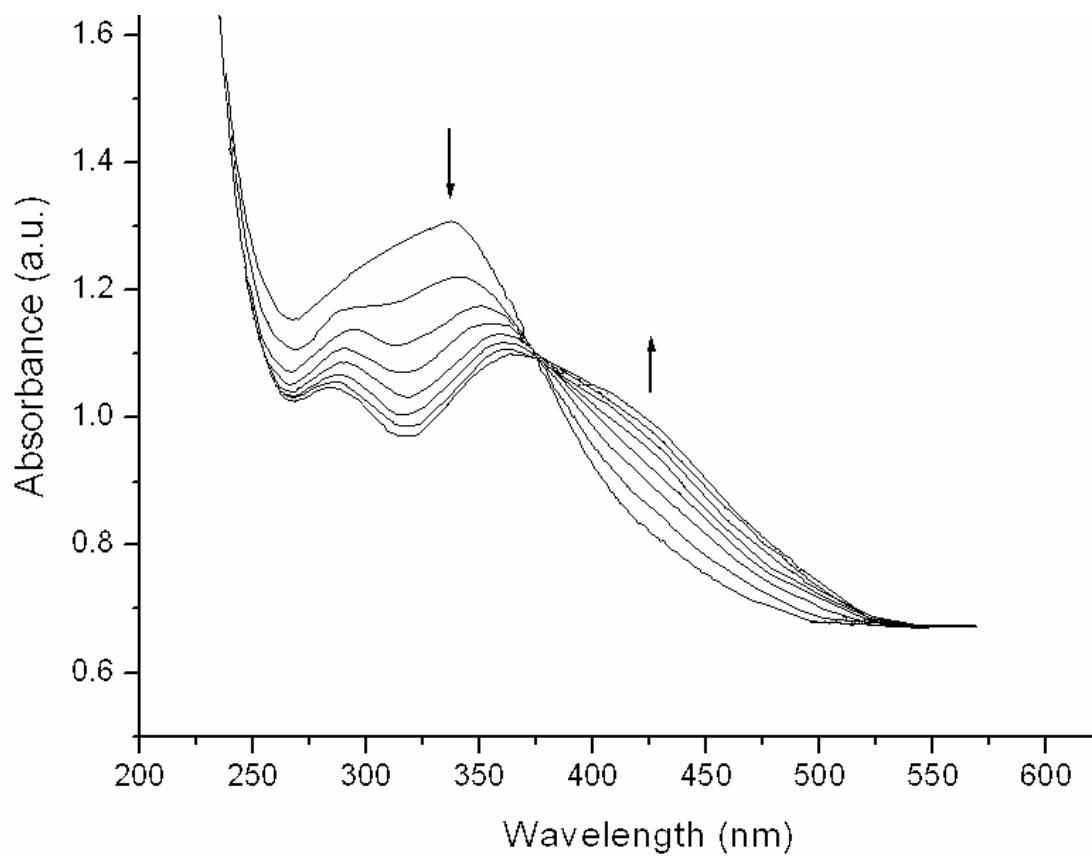
**Figure S17.** ESI-MS spectrum (MeCN) for the oxidative C=C bond cleavage of cyclohexene by **1**.



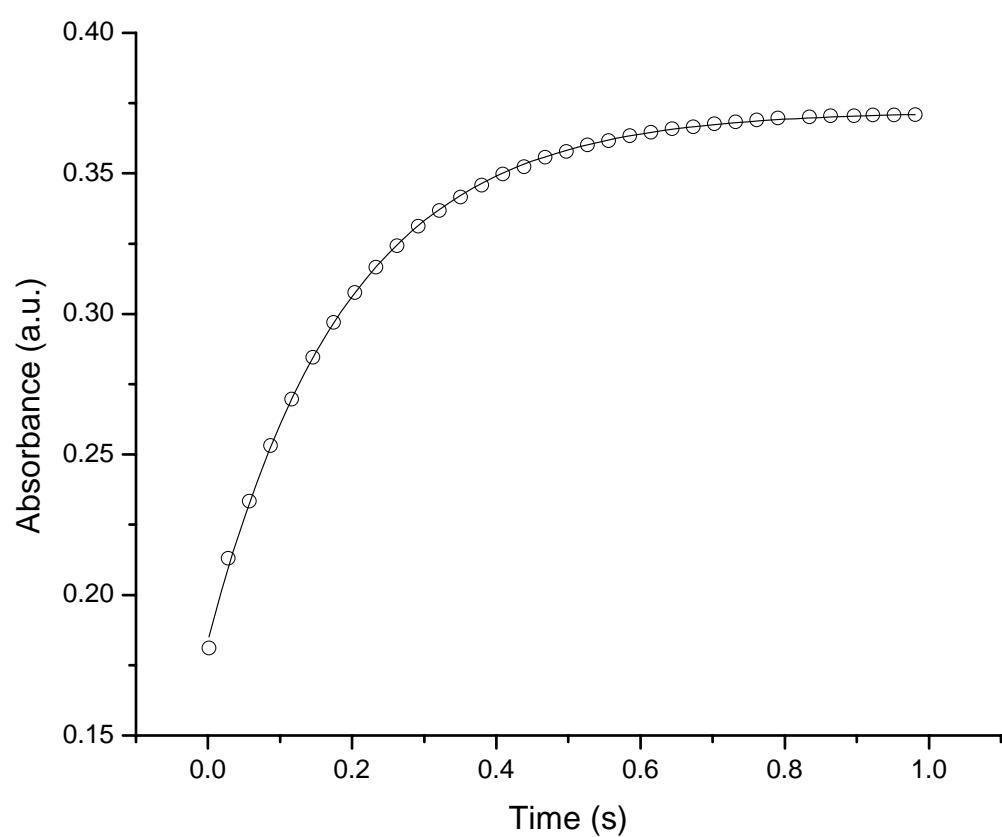
**Figure S18.** ESI-MS spectrum (MeCN) for the oxidative C=C bond cleavage of styrene by **1**.



**Figure S19.** UV-vis spectral changes for the reaction of styrene (0.2 M) with **1** in MeCN at 278 K.  
Interval = 3 s.



**Figure S20.** UV-vis spectral changes for the reaction of cyclohexene (0.2 M) with **1** in MeCN at 278 K. Interval = 2 s.

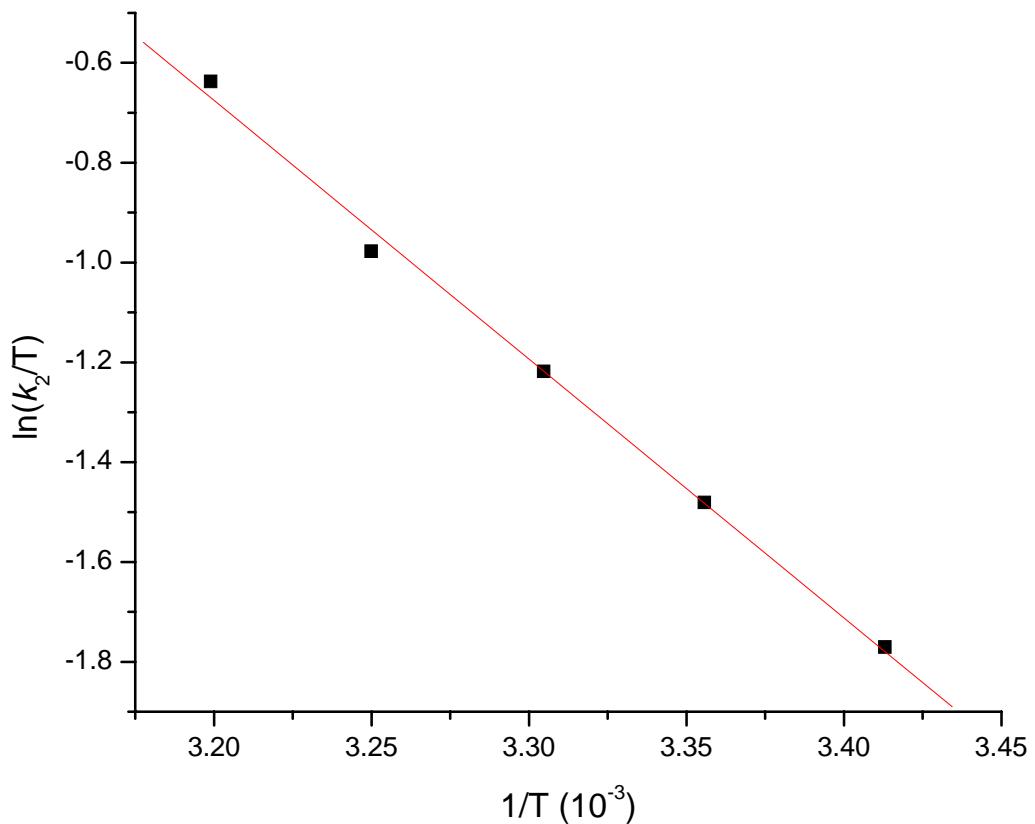


**Figure S21.** Experimental ( $\circ \circ \circ \circ$ ) and calculated (—) absorbance-time curves for the reaction of styrene with **1**.

Linear Regression:

$$Y = A + B * X$$

Parameter	Value	Error	
A	15.91504	0.62227	
B	-5.18443	0.18826	
R	SD	N	P
-0.99803	0.03178	5	1.05099E-4

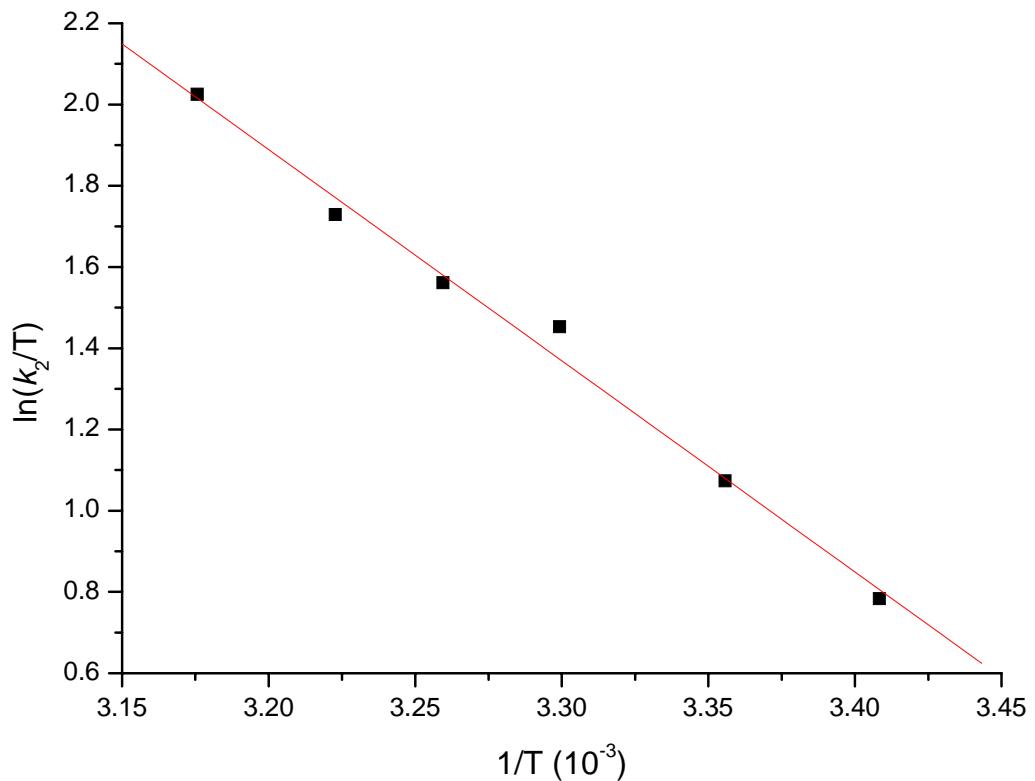


**Figure S22.** Plot of  $\ln(k_2/T)$  vs  $1/T$  for reaction of **1** with styrene.

Linear Regression:

$$Y = A + B * X$$

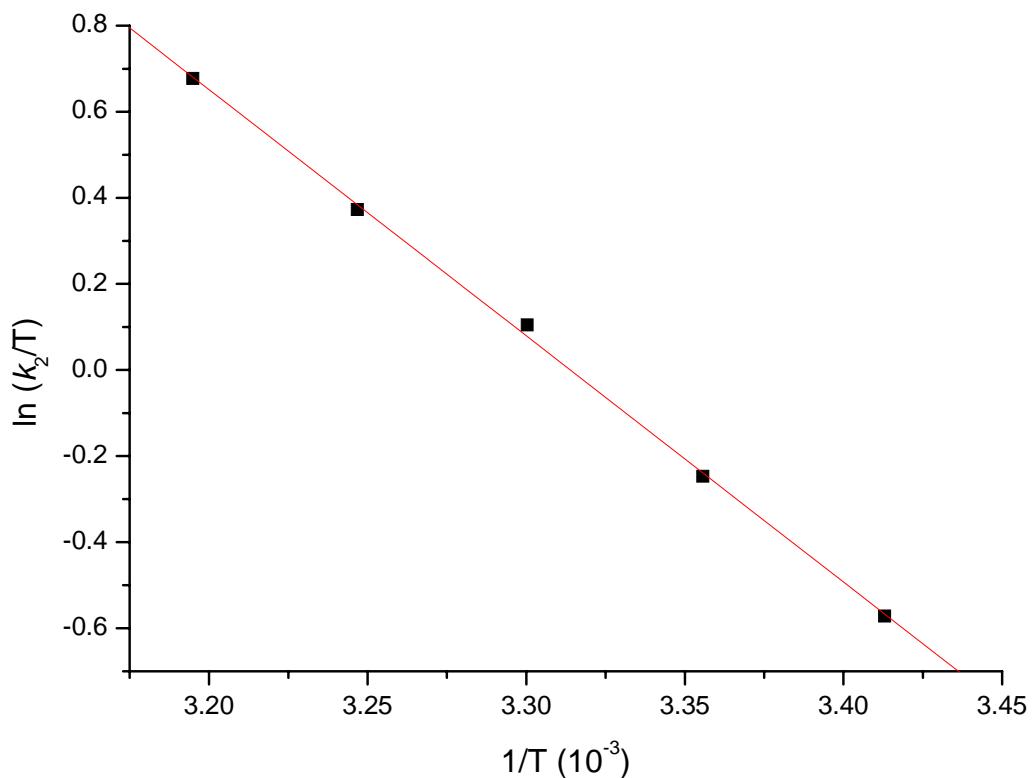
parameter	value	error	
A	18.52433	0.81609	
B	-5.19858	0.24822	
R	SD	N	P
-0.99547	0.04767	6	<0.0001



**Figure S23.** Plot of  $\ln(k_2/T)$  vs  $1/T$  for reaction of **1** with cyclooctene.

Linear Regression:  
 $Y = A + B * X$

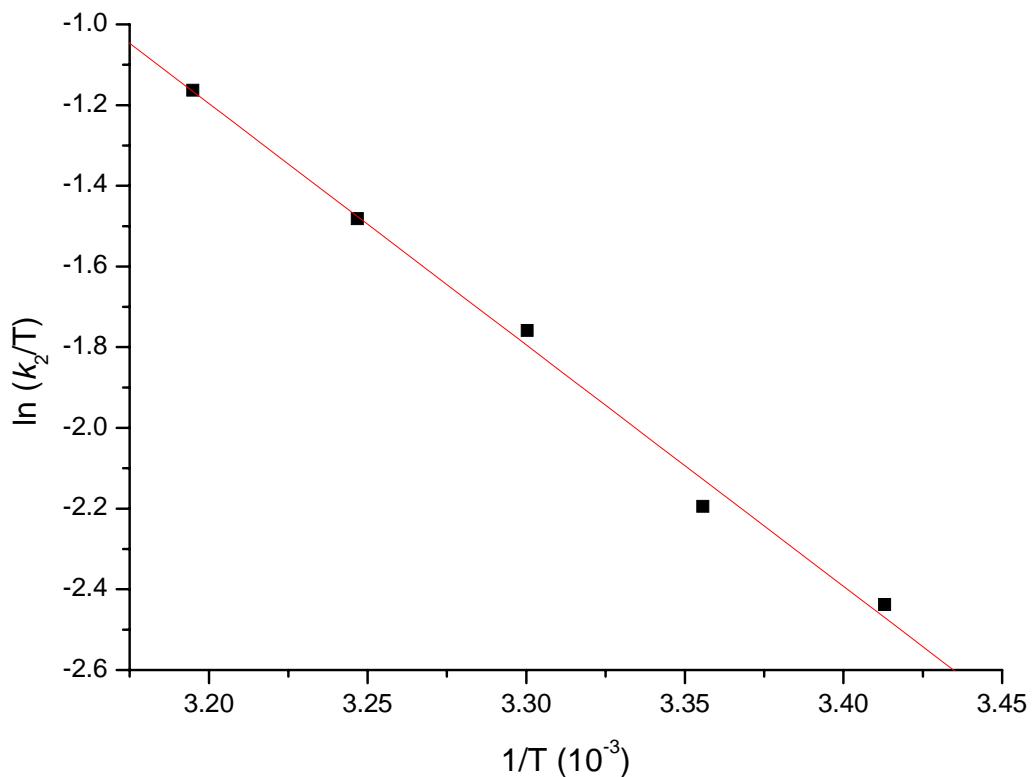
Parameter	Value	Error	
A	18.96144	0.34368	
B	-5.72181	0.10405	
R	SD	N	P
-0.9995	0.01794	5	<0.0001



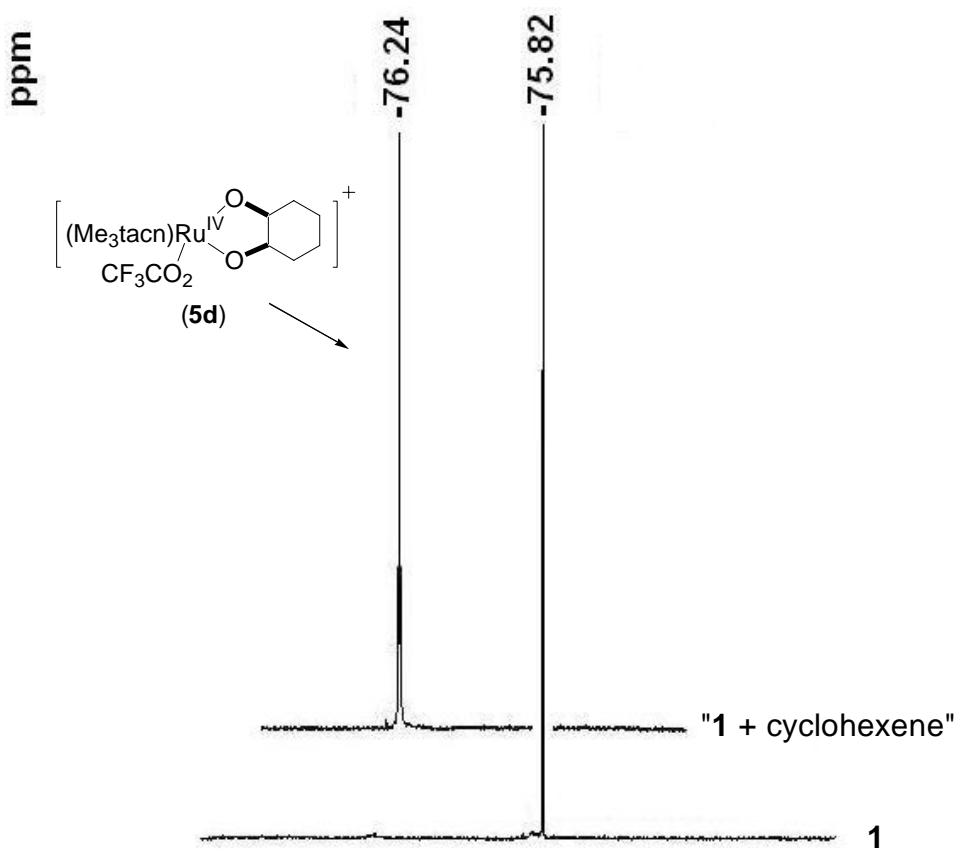
**Figure S24.** Plot of  $\ln(k_2/T)$  vs  $1/T$  for reaction of **1** with cyclohexene.

Linear Regression:  
 $Y = A + B * X$

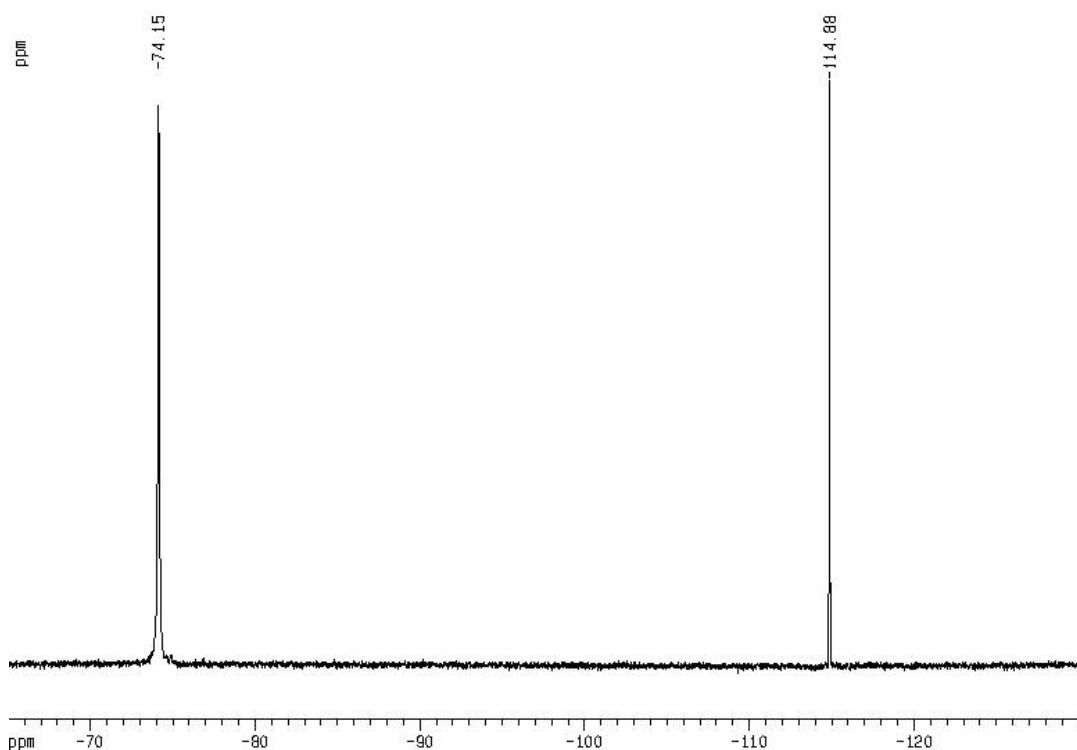
Parameter	Value	Error	
A	17.94326	0.92555	
B	-5.98111	0.28021	
R	SD	N	P
-0.99672	0.04831	5	2.24994E-4



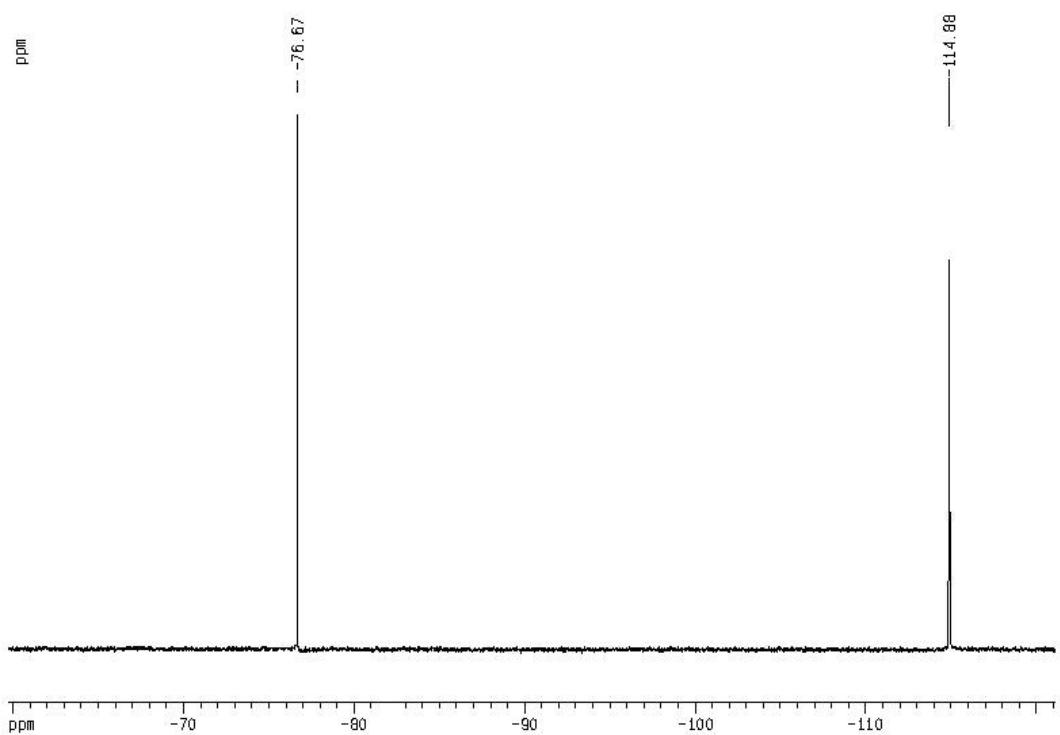
**Figure S25.** Plot of  $\ln(k_2/T)$  vs  $1/T$  for reaction of **1** with *trans*- $\beta$ -(trimethylsilyl)styrene.



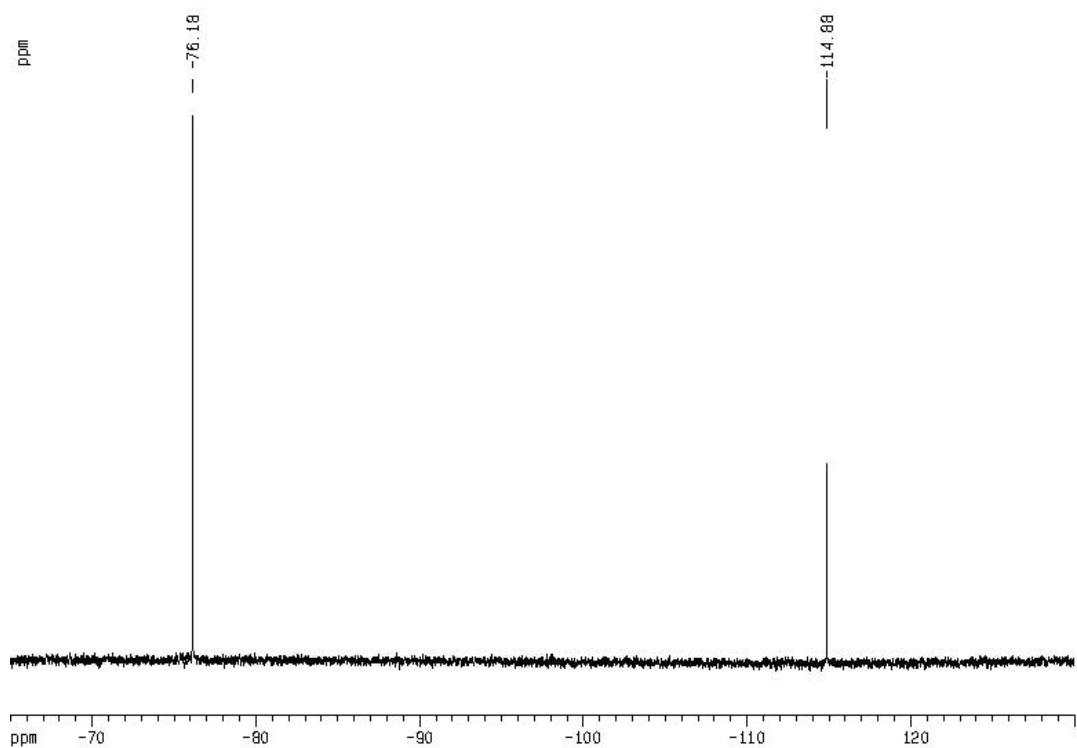
**Figure S26.**  $^{19}\text{F}$  NMR studies ( $d_3$ -MeCN) for the oxidative C=C bond cleavage of cyclohexene by **1**, showing the formation of a new absorption at  $\delta_{\text{F}} = -76.24$  ppm that we assigned to a Ru(IV) cycloadduct **5d**.



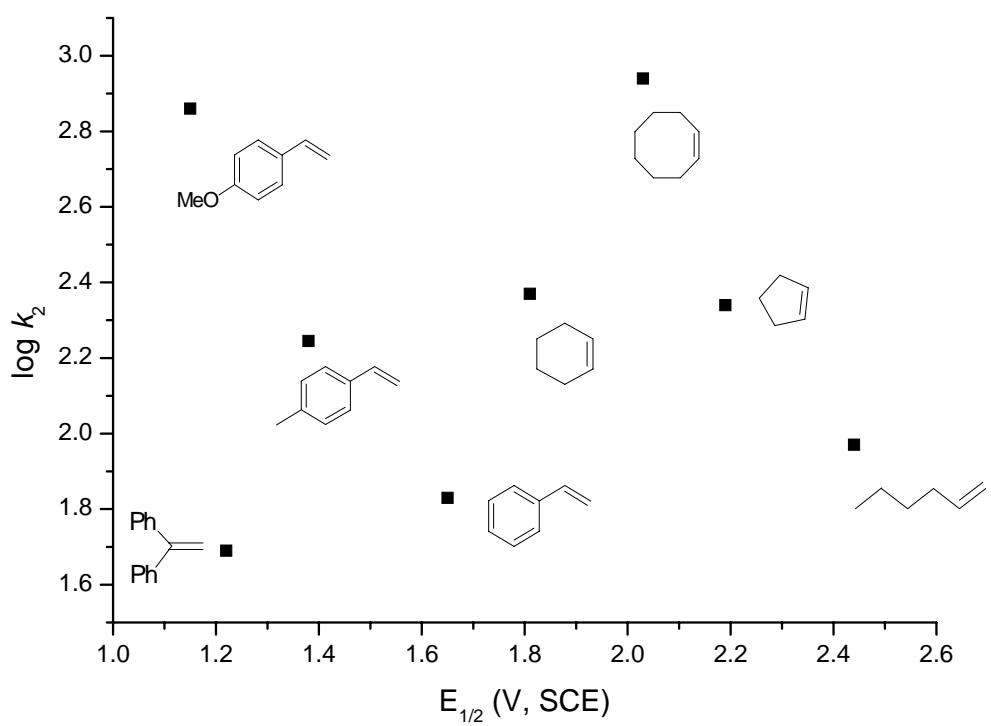
**Figure S27.** <sup>19</sup>F NMR spectrum of  $[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru}^{\text{III}}\text{O}(\text{H})\text{CH}(\text{CH}_2)_4\text{HCO}]\text{ClO}_4$  (**4d**) in  $d_3$ -MeCN with fluorobenzene ( $\delta_{\text{F}} = -114.88$  ppm) as internal standard.



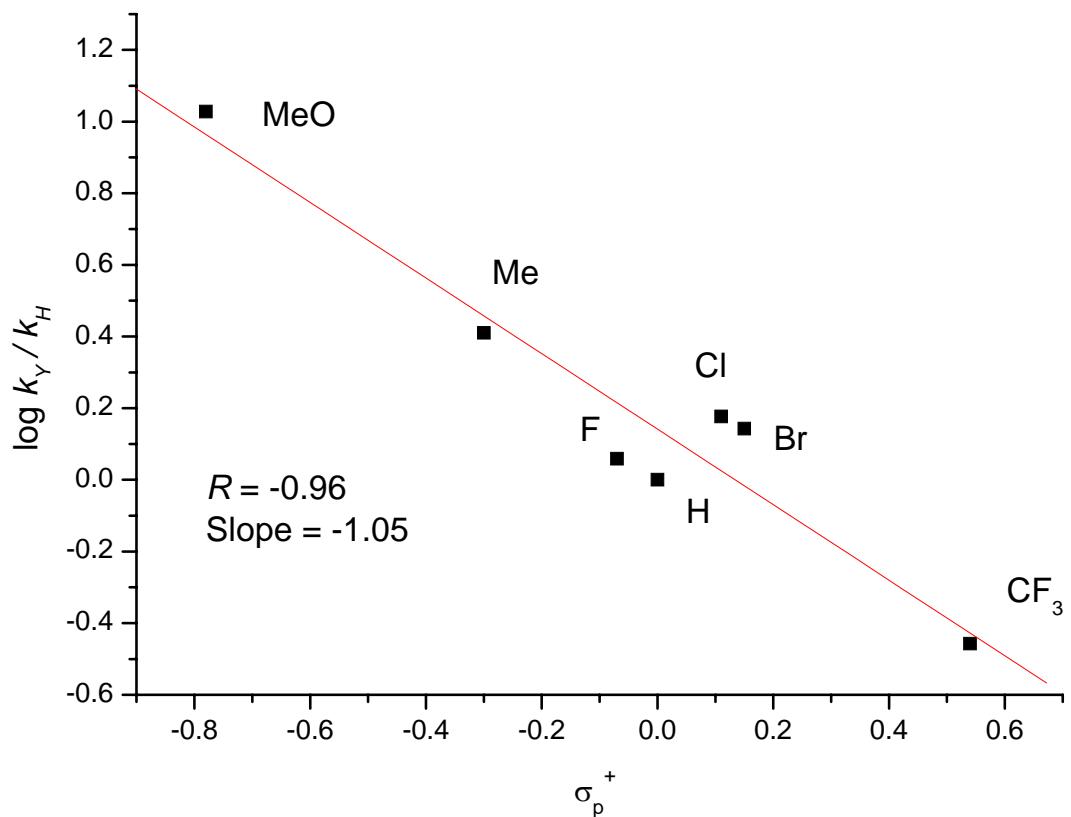
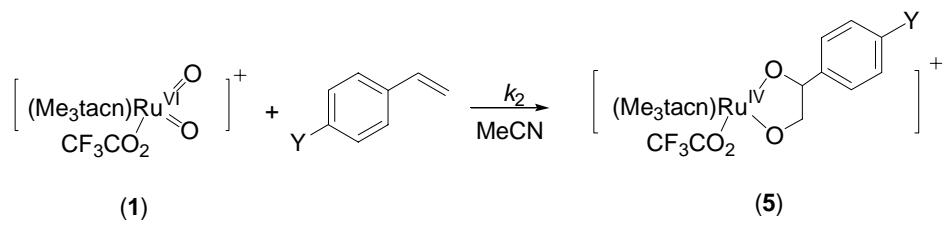
**Figure S28.** <sup>19</sup>F NMR spectra of  $[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru}^{\text{IV}}\text{OC}_2(\text{SiMe}_3)_2\text{O}]\text{ClO}_4$  in  $d_3$ -MeCN with fluorobenzene ( $\delta_{\text{F}} = -114.88$  ppm) as internal standard.



**Figure S29.** <sup>19</sup>F NMR spectra of  $[\text{Ru}^{\text{II}}(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)(\text{MeCN})_2]\text{ClO}_4$  in  $d_3\text{-MeCN}$  with fluorobenzene ( $\delta_{\text{F}} = -114.88$  ppm) as internal standard.

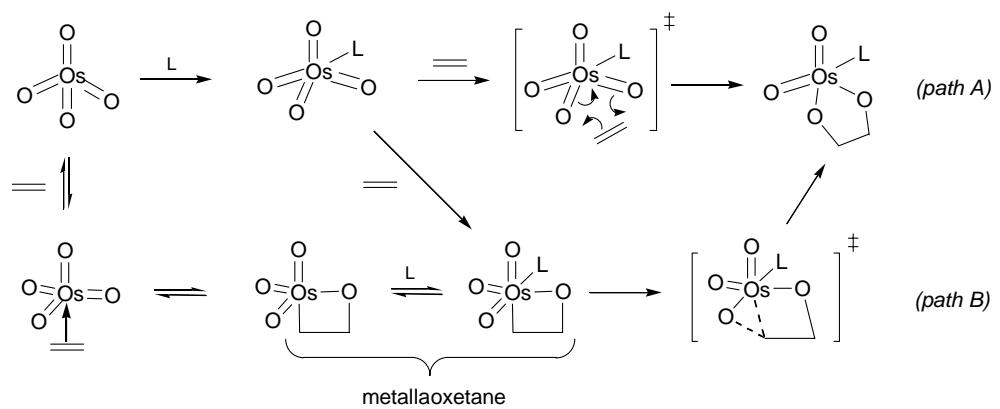


**Figure S30.** Plot of  $\log k_2$  against  $E_{1/2}$  of various alkenes.



**Figure S31.** Hammett plot for the oxidation of *para*-substituted styrenes by **1** at 298 K.

**Scheme S1.** Proposed mechanism for OsO<sub>4</sub>-mediated alkene *cis*-dihydroxylation.



**Table S1.** Crystallographic Data for Complex **3**

Formula	C <sub>23.5</sub> H <sub>45</sub> Cl <sub>2</sub> F <sub>6</sub> NO <sub>13.5</sub> Ru <sub>2</sub>
<i>M</i>	1014.70
Crystal symmetry	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	28.367(6)
<i>b</i> /Å	14.059(3)
<i>c</i> /Å	20.140(4)
$\alpha^{\circ}$	90
$\beta^{\circ}$	94.21(3)
$\gamma^{\circ}$	90
<i>V</i> /Å <sup>3</sup>	8010(3)
<i>Z</i>	8
Diffractometer	MAR
<i>D<sub>c</sub></i> /gcm <sup>-3</sup>	1.683
No. collected data	22994
No. data used	6623
No. parameters	466
$\mu$ (M <sub>o</sub> -K <sub>α</sub> ) mm <sup>-1</sup>	0.979
<i>F</i> (000)	4096
<i>R</i> <sub>1</sub>	0.098
w <i>R</i> <sub>2</sub>	0.22
Goodness-of-fit	0.99

**Table S2.** Selected Bond Distances and Angles for Complex 3

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bond distances (Å)	
Ru(1)–O(5)	1.888(5)
Ru(1)–O(2)	2.092(6)
Ru(1)–O(4)	2.108(6)
Ru(1)–N(1)	2.092(7)
Ru(1)–N(2)	2.171(8)
Ru(1)–N(3)	2.115(7)
Ru(2)–O(5)	1.901(5)
Ru(2)–O(1)	2.114(6)
Ru(2)–O(3)	2.106(5)
O(1)–C(19)	1.26(1)
O(2)–C(19)	1.24(1)
O(3)–C(21)	1.23(1)
O(4)–C(21)	1.25(1)
bond angles (°)	
Ru(1)–O(5)–Ru(2)	121.7(3)
C(19)–O(1)–Ru(2)	126.8(6)
C(19)–O(2)–Ru(1)	123.8(6)
C(21)–O(3)–Ru(2)	124.2(5)
C(21)–O(4)–Ru(1)	129.2(6)
O(3)–C(21)–O(4)	128.2(8)
O(2)–C(19)–O(1)	130.6(9)
O(5)–Ru(2)–N(4)	176.6(3)
O(5)–Ru(1)–N(2)	176.1(2)
N(5)–Ru(2)–O(1)	169.9(3)
N(6)–Ru(2)–O(3)	172.1(2)
N(1)–Ru(1)–O(4)	170.5(3)
O(2)–Ru(1)–N(3)	170.4(3)

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**Table S3.** Stoichiometric Alkene Oxidations by *cis*-[(Tet-Me<sub>6</sub>)Ru<sup>VII</sup>O<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**2**)

entry	alkenes	product(s)	yield (%) <sup>a</sup>
1			22
2			65 21 <sup>b</sup>
3		no conversion	—
4		no conversion	—
5		no conversion	—

Reaction conditions: To a degassed *tert*-butanol (10 mL) - water (2 mL) mixture containing alkene (30 mmol) was added **2** (300  $\mu$ mol) under an argon atmosphere. The reaction mixture was stirred at room temperature for 14 h. <sup>a</sup> Yields are based on the amount of **2** used. <sup>b</sup> Yield of 2-cyclohexen-1-ol was determined by GC.

**Table S4.** UV-vis Spectral Data and ESI-MS Characterization of the Ru(III) Cycloadducts

entry	alkenes	Ru(III) cycloadducts <sup>a</sup>	$\lambda/\text{nm}^b$ ( $\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	ESI-MS <sup>c</sup> $m/z$ and relative abundance
1		$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{RuO}(\text{H})\text{CH}(\text{CH}_2)_6\text{HCO}]^+ \text{ (4a)}$	390 (1390)	529.1 ( $M^+$ ) (100%), 415.3 ( $M - \text{CF}_3\text{CO}_2$ ) <sup>+</sup> (18%)
2		$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{RuO}(\text{H})\text{PhCHCH(CH}_3\text{)}\text{O}]^+ \text{ (4b)}$	396 (1550)	537.1 ( $M^+$ ) (100%), 423.1 ( $M - \text{CF}_3\text{CO}_2$ ) <sup>+</sup> (30%)
3		$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{RuO}(\text{H})\text{CH}(\text{CH}_2)_3\text{HCO}]^+ \text{ (4c)}$	383 (1280)	487.1 ( $M^+$ ) (100%), 373.1 ( $M - \text{CF}_3\text{CO}_2$ ) <sup>+</sup> (50%)
4		$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{RuO}(\text{H})\text{CH}(\text{CH}_2)_4\text{HCO}]^+ \text{ (4d)}$	396 (1270)	501.0 ( $M^+$ ) (100%), 387.2 ( $M - \text{CF}_3\text{CO}_2$ ) <sup>+</sup> (60%)
5		$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{RuO}(\text{H})\text{CH}(\text{CH}_2)_5\text{HCO}]^+ \text{ (4e)}$	388 (1500)	515.1 ( $M^+$ ) (100%), 401.2 ( $M - \text{CF}_3\text{CO}_2$ ) <sup>+</sup> (40%)
6		$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{RuO}(\text{H})\text{PhCHCHO}]^+ \text{ (4f)}$	396 (1350)	523.1 ( $M^+$ ) (100%), 403.2 [( $\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru(OH}_2)]^+ (60%)$
7		$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{RuO}(\text{H})\text{PhCHCH(CO}_2\text{Et)}\text{O}]^+ \text{ (4g)}$	383 (1310)	595.0 ( $M^+$ ) (100%), 403.1 [( $\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru(OH}_2)]^+ (80%)$
8		$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{RuO}(\text{H})\text{AcOCHCH(OAc)}\text{O}]^+ \text{ (4h)}$	371 (1430)	590.9 ( $M^+$ ) (45%), 503.1 {[( $\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru(OH}_2)]\text{ClO}_4}^+ (40%), 403.1 [(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru(OH}_2)]^+ (100%)$
9		$[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{RuO}(\text{H})\text{PhCHCH(SiMe}_3\text{)}\text{O}]^+ \text{ (4i)}$	370 (1330)	594.9 ( $M^+$ ) (100%), 403.1 [( $\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru(OH}_2)]^+ (20%)$

<sup>a</sup> All the cycloadduct complexes were isolated and recrystallized with chloroform-hexane as solvent. <sup>b</sup> UV-vis spectra taken from recrystallized samples in  $\text{CH}_2\text{Cl}_2$ . Identical spectra were obtained with MeCN as solvent. <sup>c</sup> Reaction conditions: A mixture containing alkene (0.2 mmol), *tert*-butanol (5 mL), water (1 mL) and **1** (2  $\mu\text{mol}$ ) was stirred for 10 min under an argon atmosphere.  $\text{CH}_2\text{Cl}_2$  (20 mL) was added for extraction of **4** from the aqueous *tert*-butanol medium. After removal of the residual moisture using anhydrous  $\text{MgSO}_4$ , the yellow  $\text{CH}_2\text{Cl}_2$  solution was subjected to analysis using ESI-MS.

**Table S5.** Crystallographic Data for Ru(III) Cycloadducts **4a** and **4b**

Formula	C <sub>19</sub> H <sub>37</sub> ClF <sub>3</sub> N <sub>3</sub> O <sub>9</sub> Ru ( <b>4a</b> )	C <sub>20</sub> H <sub>32</sub> ClF <sub>3</sub> N <sub>3</sub> O <sub>8</sub> Ru ( <b>4b</b> )
<i>M</i>	645.04	636.01
Crystal symmetry	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	17.884(4)	31.671(6)
<i>b</i> /Å	10.427(2)	7.705(2)
<i>c</i> /Å	14.204(3)	20.991(4)
$\alpha^{\circ}$	90	90
$\beta^{\circ}$	103.60(3)	95.95(3)
$\gamma^{\circ}$	90	90
<i>V</i> /Å <sup>3</sup>	2574.4(9)	5094.8(19)
<i>Z</i>	4	8
Diffractometer	MAR	MAR
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.664	1.658
No. collected data	11071	4793
No. data used	3690	2089
No. parameters	325	185
$\mu$ (Mo-K $\alpha$ ) mm <sup>-1</sup>	0.787	0.792
<i>F</i> (000)	1328	2600
<i>R</i> <sub>1</sub>	0.049	0.069
w <i>R</i> <sub>2</sub>	0.116	0.174
Goodness-of-fit	0.94	0.91

**Table S6.** Selected Bond Distances and Angles for **4a**

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bond distances (Å)	
Ru–O(1)	2.136(4)
Ru–O(2)	1.932(4)
Ru–N(1)	2.129(5)
Ru–N(2)	2.093(5)
Ru–N(3)	2.075(5)
O(1)–C(1)	1.477(7)
O(2)–C(2)	1.433(7)
C(1)–C(2)	1.524(9)
C(1)–C(8)	1.531(8)
C(2)–C(3)	1.535(9)
C(5)–C(6)	1.532(9)
bond angles (°)	
O(2)–Ru–N(2)	89.0(2)
N(3)–Ru–N(2)	83.8(2)
N(2)–Ru–N(1)	84.2(2)
O(2)–Ru–O(1)	80.6(2)
O(2)–Ru–O(4)	94.6(2)
O(4)–Ru–N(1)	92.3(2)
O(4)–Ru–O(1)	88.9(2)
N(2)–Ru–O(4)	171.7(2)
O(2)–Ru–N(1)	173.1(2)
N(3)–Ru–O(1)	176.0(2)
C(1)–O(1)–Ru	110.6(3)
C(2)–O(2)–Ru	117.5(4)
O(1)–C(1)–C(2)	109.6(5)
O(1)–C(1)–C(8)	107.1(5)
C(1)–C(2)–C(3)	116.7(5)
C(2)–C(1)–C(8)	117.5(6)
O(2)–C(2)–C(1)	108.6(5)
O(2)–C(2)–C(3)	110.2(5)

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**Table S7.** Selected Bond Distances and Angles for **4b**

bond distance (Å)	
Ru–O(1)	2.15(1)
Ru–O(2)	1.95(1)
Ru–N(1)	2.12(1)
Ru–N(2)	2.14(1)
Ru–N(3)	2.07(1)
O(1)–C(2)	1.50(2)
O(2)–C(3)	1.49(2)
C(1)–C(2)	1.50(2)
C(2)–C(3)	1.55(2)
C(3)–C(4)	1.49(2)
C(4)–C(5)	1.37(2)
C(7)–C(8)	1.36(2)
bond angles (°)	
O(2)–Ru–N(1)	90.0(5)
N(3)–Ru–N(1)	83.9(5)
N(1)–Ru–N(2)	84.1(5)
O(3)–Ru–N(1)	172.7(5)
N(1)–Ru–O(1)	97.6(5)
O(1)–Ru–O(2)	81.5(4)
O(1)–C(2)–C(1)	109.8(1)
O(1)–C(2)–C(3)	107.2(2)
C(1)–C(2)–C(3)	115.4(2)
C(4)–C(3)–O(2)	109.0(1)
C(4)–C(3)–C(2)	112.8(2)
O(2)–C(3)–C(2)	108.4(1)

**Table S8.** Characteristic UV-vis Profiles for the Oxidative C=C Cleavage Reaction of Selected Alkenes - Formation of Ru(IV) Cycloadducts

<b>1</b>	+		$\xrightarrow[\text{r.t.}]{\text{CH}_3\text{CN}}$	
entry	alkenes	$\lambda_{\max} / \text{nm}$		
1		383		
2		290, 360, 420(sh)		
3		340, 420(sh)		
4		355, 415(sh)		
5		347, 415(sh)		
6		351, 445(sh)		
7		358, 420(sh)		
8		365, 417(sh)		
9		357, 415(sh)		
10		353, 410(sh)		

**Table S9.** Temperature Dependence of  $k_2$  Values for Reactions of **1** with Styrene, Cyclooctene, Cyclohexene, and *trans*- $\beta$ -(Trimethylsilyl)styrene

temperature (K)	$k_2$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
	styrene
293.0	49.9±0.6
298.0	67.8±0.6
302.6	89.5±2.7
307.7	115.8±4.9
312.6	165.3±4.4
	cyclooctene
293.4	642.2±15.3
298.0	872.0±10.0
303.1	1295.5±76.3
306.8	1461.5±131.4
310.3	1748.4±70.4
314.9	2386.2±100.2
	cyclohexene
293.0	165.4±6.9
298.0	232.8±5.0
303.0	336.5±12.0
308.0	447.2±17.3
313.0	616.2±20.2
	<i>trans</i> - $\beta$ -(trimethylsilyl)styrene
293.0	25.6±1.1
298.0	33.2±1.8
303.0	52.2±2.4
308.0	70.0±3.3
313.0	97.8±3.9

**Table S10.** Activation Parameters for Oxidation of Various Alkenes with Selected *cis*-Dioxometal Complexes

entry	oxidants	alkenes	$\Delta H^\ddagger/\text{kcal mol}^{-1}$	$\Delta S^\ddagger/\text{cal mol}^{-1} \text{K}^{-1}$	ref
1	<b>1</b>	styrene	$10.3 \pm 0.4$	$-15.6 \pm 1.2$	this work
2	<b>1</b>	cyclooctene	$10.3 \pm 0.5$	$-10.4 \pm 1.6$	this work
3	<b>1</b>	cyclohexene	$11.4 \pm 0.2$	$-9.5 \pm 0.7$	this work
4	<b>1</b>	<i>trans</i> - $\beta$ -(trimethylsilyl)styrene	$11.9 \pm 0.6$	$-11.6 \pm 1.8$	this work
5	<b>1</b>	bis(trimethylsilyl)acetylene	$9.3 \pm 0.9$	$-18 \pm 1.7$	1 <sup>a</sup>
6	<b>1</b>	1-trimethylsilyl-1-hexyne	$10.9 \pm 1.2$	$-17 \pm 1.9$	1 <sup>a</sup>
7	<b>1</b>	1-(4-chlorophenyl)-2-trimethylsilylacetylene	$11.9 \pm 1.4$	$-15 \pm 1.4$	1 <sup>a</sup>
8	$\text{MnO}_4^-$	<i>endo</i> -dicyclopentadiene	$3.8 \pm 0.5$	$-39.3 \pm 1.5$	2
9	$\text{MnO}_4^-$	cinnamic acid	$4.2 \pm 0.5$	$-30 \pm 2$	2
10	$\text{MnO}_4^-$	allyl alcohol	$7.5 \pm 0.7$	$-24 \pm 2$	3
11	$\text{MnO}_4^-$	vinylacetate	$6.4 \pm 0.7$	$-28 \pm 2$	3
12	$\text{CrO}_2\text{Cl}_2$	1-hexene	6.2	-40.7	4
13	$\text{CrO}_2\text{Cl}_2$	2-methyl-2-butene	7.2	-27.4	4
14	$\text{Cp}^*\text{ReO}_3$	norbornene	$18.2 \pm 0.6$	$-30 \pm 1.8$	5
15	$\text{Cp}^*\text{ReO}_3$	cyclooctene	$11.7 \pm 0.7$	$-38.4 \pm 2.1$	5

<sup>a</sup> There is inconsistency between the error limits for  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  in this reference. The correct values for such error limits will be published in the ADDITIONS AND CORRECTIONS in the journal.

## References

- (1) Che, C.-M.; Yu, W.-Y.; Chan, P.-M.; Cheng, W.-C.; Peng, S.-M.; Lau, K.-C.; Li, W.-K. *J. Am. Chem. Soc.* **2000**, 122, 11380.
- (2) Ogino, T.; Hasegawa, K.; Hoshino, E. *J. Org. Chem.* **1990**, 55, 2653.
- (3) Wiberg, K. B.; Geer, R. D. *J. Am. Chem. Soc.* **1966**, 88, 5827.
- (4) Freeman, F.; McCart, P. D.; Yamachika, N. J. *J. Am. Chem. Soc.* **1970**, 92, 4621.
- (5) Gable, K. P.; Juliette, J. J. *J. Am. Chem. Soc.* **1995**, 117, 955.