

Supporting Information

Formation of a Ruthenium(IV)-Oxo Complex
by Electron-Transfer Oxidation of a
Coordinatively Saturated Ruthenium(II)
Complex and Detection of an Oxygen-Rebound
Intermediates in C-H Bond Oxygenation

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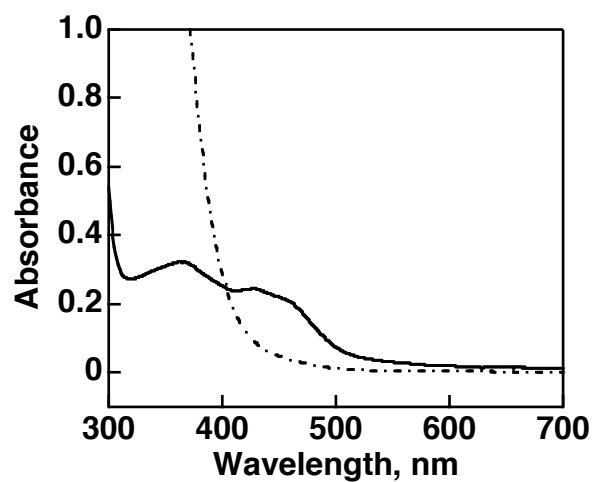


Figure S1. UV-vis spectral change upon addition of CAN (10 μmol) to an aqueous solution of **1** (0.9 μmol) in 3 mL of H_2O at pH 2.0. The solid line and dotted line are spectra before and after addition of CAN, respectively.

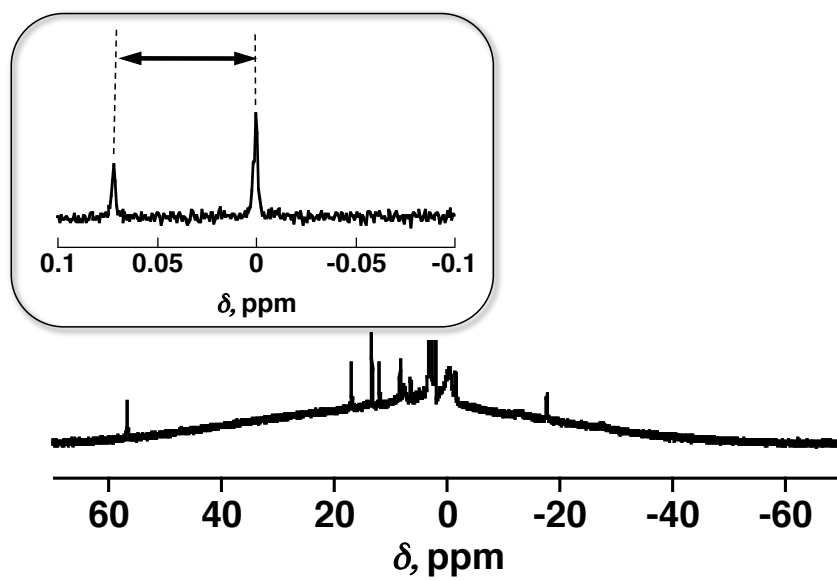


Figure S2. ^1H NMR spectrum of **2** in $(\text{CD}_3)_2\text{CO}$. Inset: Signals due to TMS for the Evans' method.

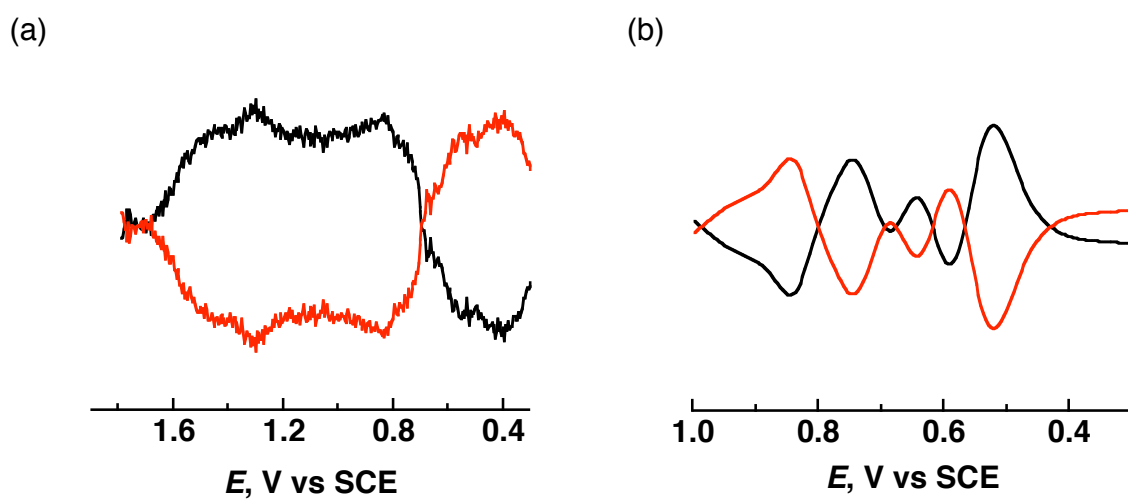


Figure S3. Second harmonic ac voltammograms of **2**: (a) in CH_3CN (b) in aqueous Na_2SO_4 (0.1 M) at pH 1 (adjusted by portions of H_2SO_4).

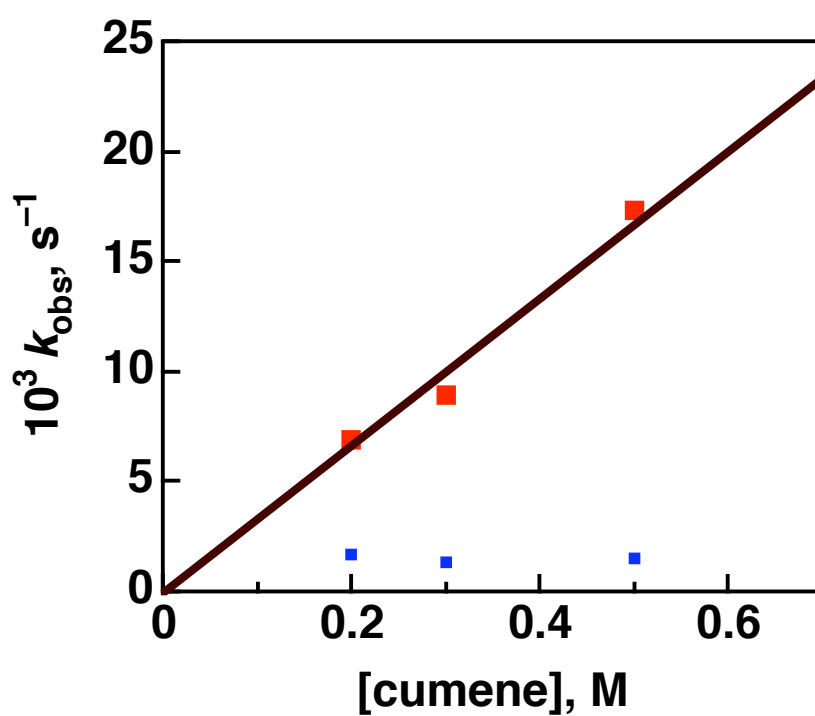


Figure S4. Plots of pseudo-first-order rate constants of reaction of **2** with cumene in CH_3CN at 298 K under O_2 atmosphere vs concentration of cumene: red, the first step; blue, the second step.

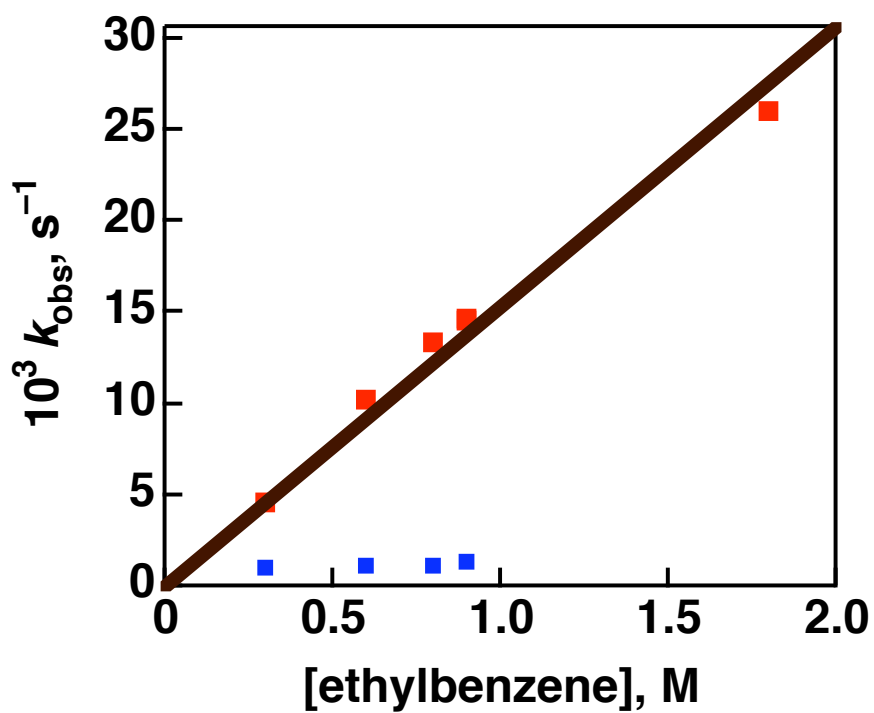


Figure S5. Plots of the observed first-order rate constant of the first step (red squares) and the second step (blue squares) in the oxidation of ethylbenzene in CH_3CN at 298 K vs concentration of ethylbenzene.

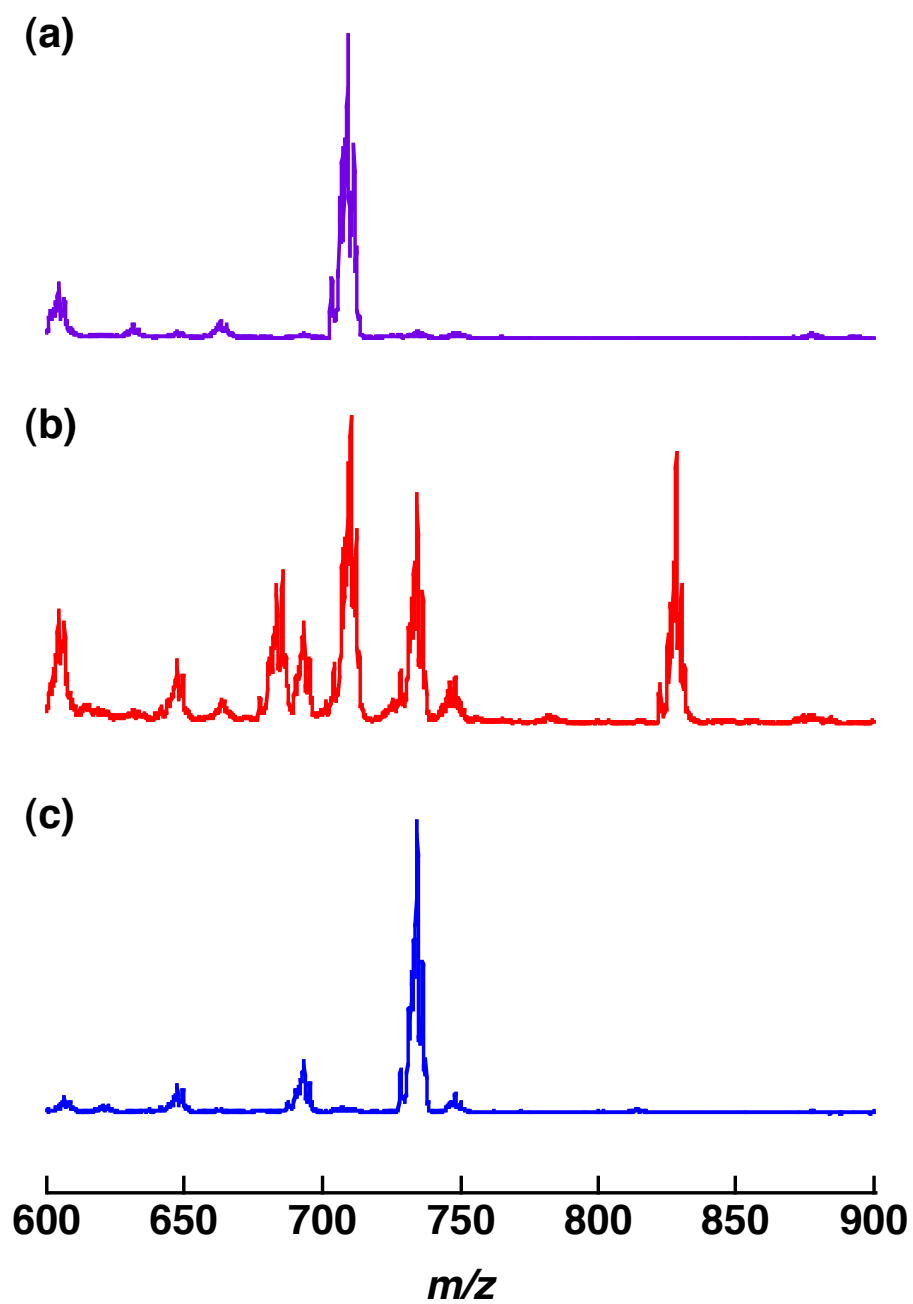


Figure S6. Time-course of ESI-MS spectra of the reaction mixture of **2** (0.10 mM) and cumene (200 mM) in CH₃CN: (a) 0 min, (b) 15 min, (c) 300 min.

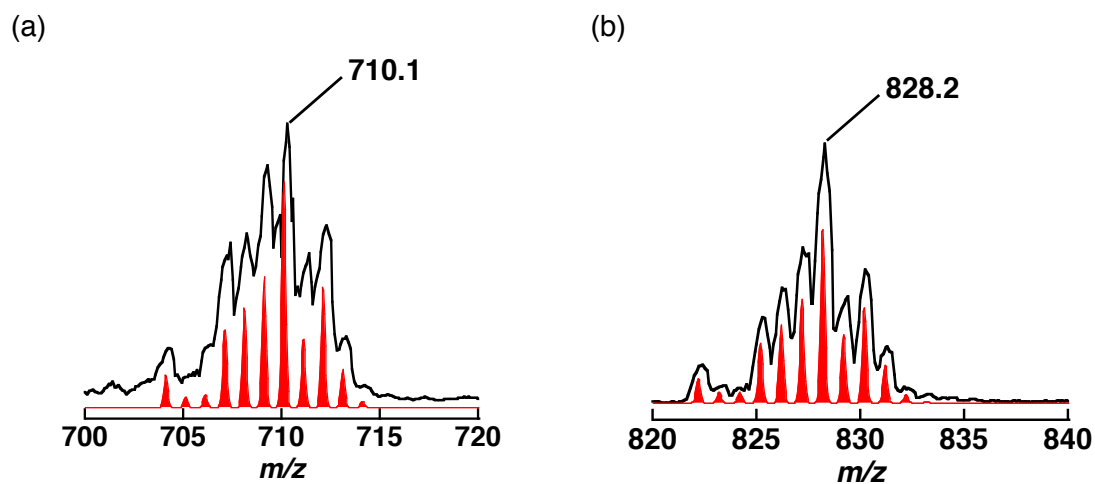


Figure S7. Positive-ion ESI-MS spectra of the mixture of cumene (200 mM) and **2** (0.10 mM) (see also Figure 12): (a) A peak cluster at $m/z = 710.1$ ascribed to $\{3(^{16}\text{O}) - \text{H}^+ - 2(\text{PF}_6^-)\}^+$; (b) a peak cluster at $m/z = 828.2$ assigned to $\{4(^{16}\text{O}) - \text{H}^+ - 2(\text{PF}_6^-)\}^+$.

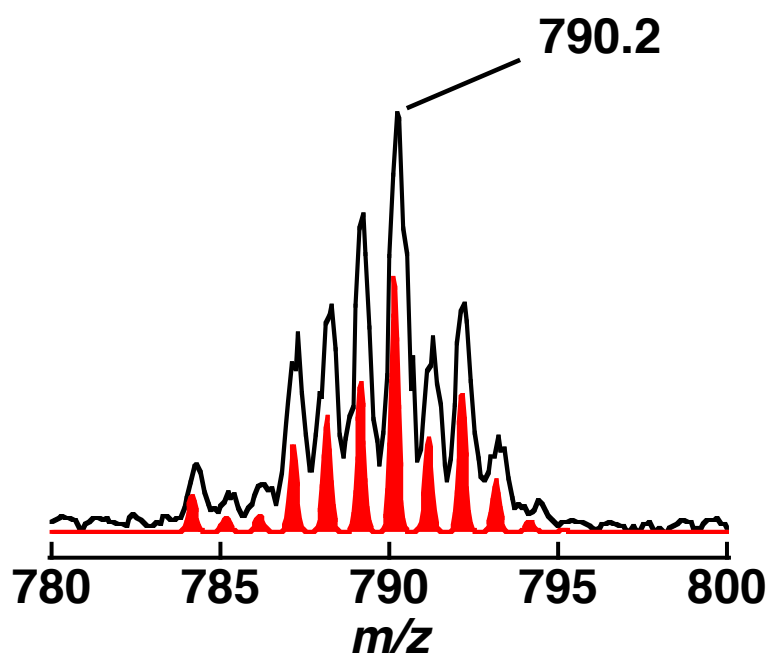


Figure S8. Positive-ion ESI-MS spectrum of the mixture of cyclohexene (120 mM) and **2** (0.10 mM) in CH_3CN : A peak cluster at $m/z = 790.2$ assigned to $\{[\text{Ru}^{\text{III}}(\text{OC}_6\text{H}_9)(\text{TPA})(\text{bpy})](\text{PF}_6^-)\}^+$.

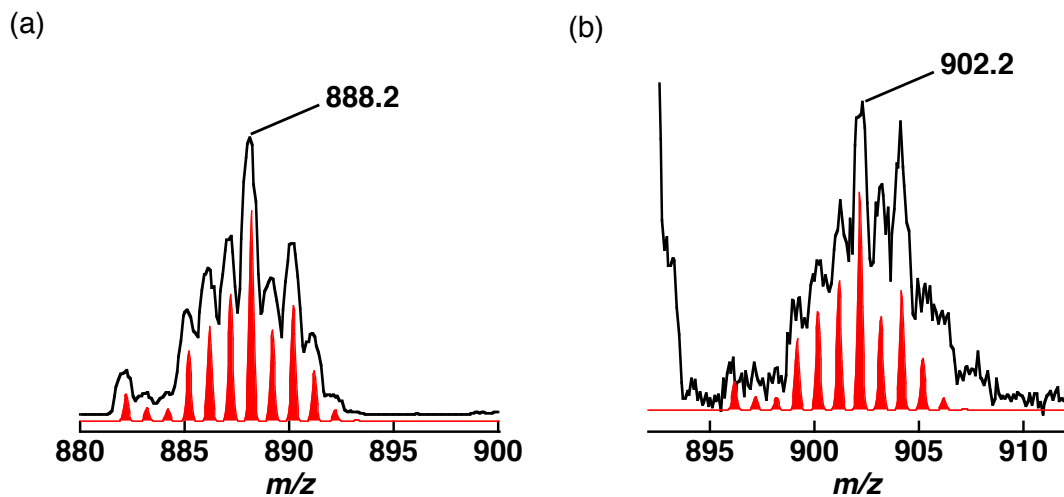


Figure S9. Positive-ion ESI-MS spectra of the mixture of DHA (50 mM) and **2** (5.0 mM) in CD_3CN : (a) A peak cluster at m/z 888.2 assigned to $\{[\text{Ru}^{\text{III}}(\text{OC}_{14}\text{H}_{11})(\text{TPA})(\text{bpy})](\text{PF}_6^-)\}^+$; (b) a peak cluster at m/z 902.2 ascribed to $\{[\text{Ru}^{\text{III}}(\text{OC}_{14}\text{H}_9\text{O})(\text{TPA})(\text{bpy})](\text{PF}_6^-)\}^+$.

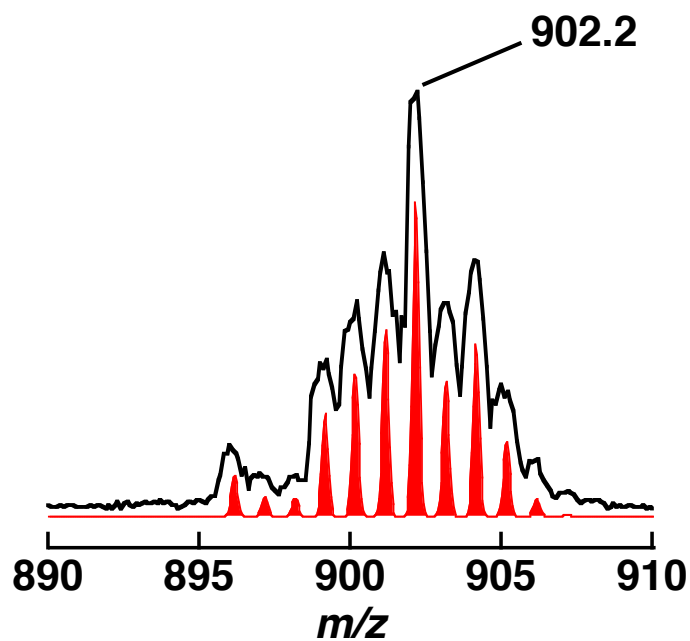


Figure S10. Positive-ion ESI-MS spectrum of the mixture of anthrone (50 mM) and **2** (5.0 mM) in CD_3CN : A peak cluster at $m/z = 902.2$ assigned to $\{[\text{Ru}^{\text{III}}(\text{OC}_{14}\text{H}_9\text{O})(\text{TPA})(\text{bpy})](\text{PF}_6^-)\}^+$.

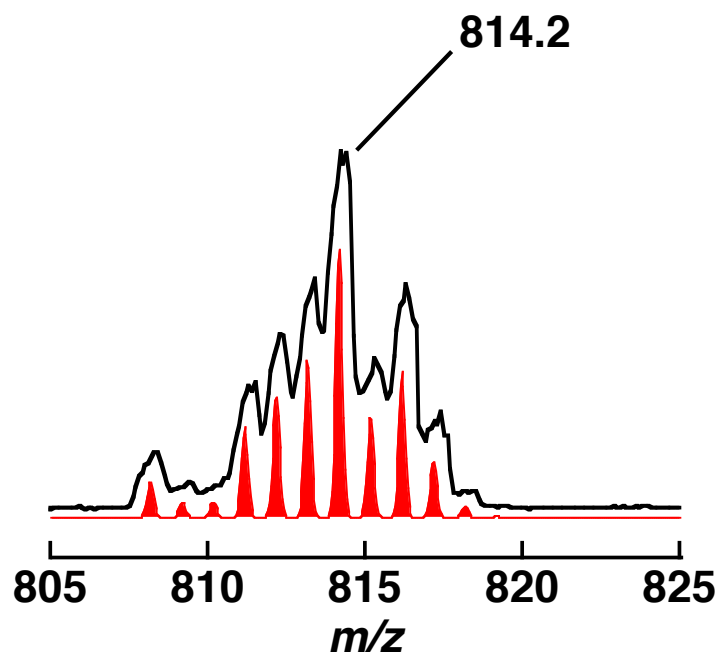


Figure S11. Positive-ion ESI-MS spectrum of the mixture of ethylbenzene (100 mM) and **2** (5.0 mM) in CD_3CN : A peak cluster at $m/z = 814.2$ assigned to $\{[\text{Ru}^{\text{III}}(\text{OCCH}(\text{CH}_3)(\text{C}_6\text{H}_5))(\text{TPA})(\text{bpy})](\text{PF}_6^-)\}^+$.

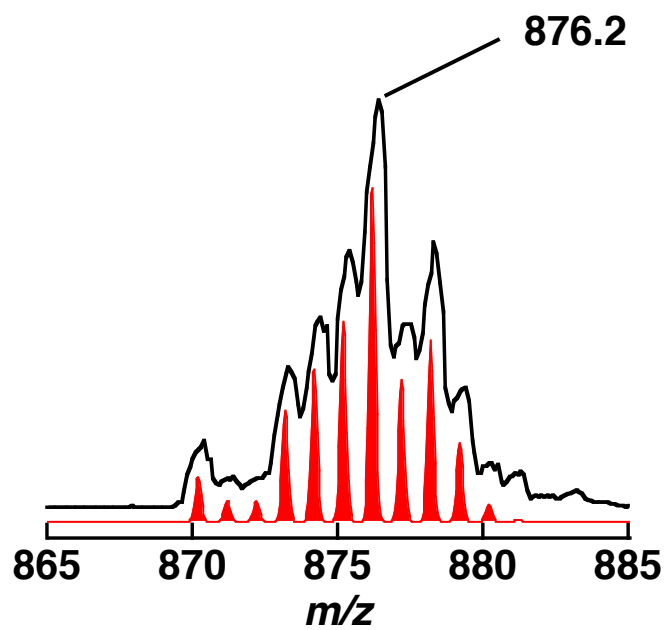


Figure S12. Positive-ion ESI-MS spectrum of the mixture of diphenylmethane (15 mM) and **2** (5.0 mM) in CD_3CN : A peak cluster at $m/z = 876.2$ ascribed to $\{[\text{Ru}^{\text{III}}(\text{OCCH}(\text{C}_6\text{H}_5)_2)(\text{TPA})(\text{bpy})](\text{PF}_6^-)\}^+$.

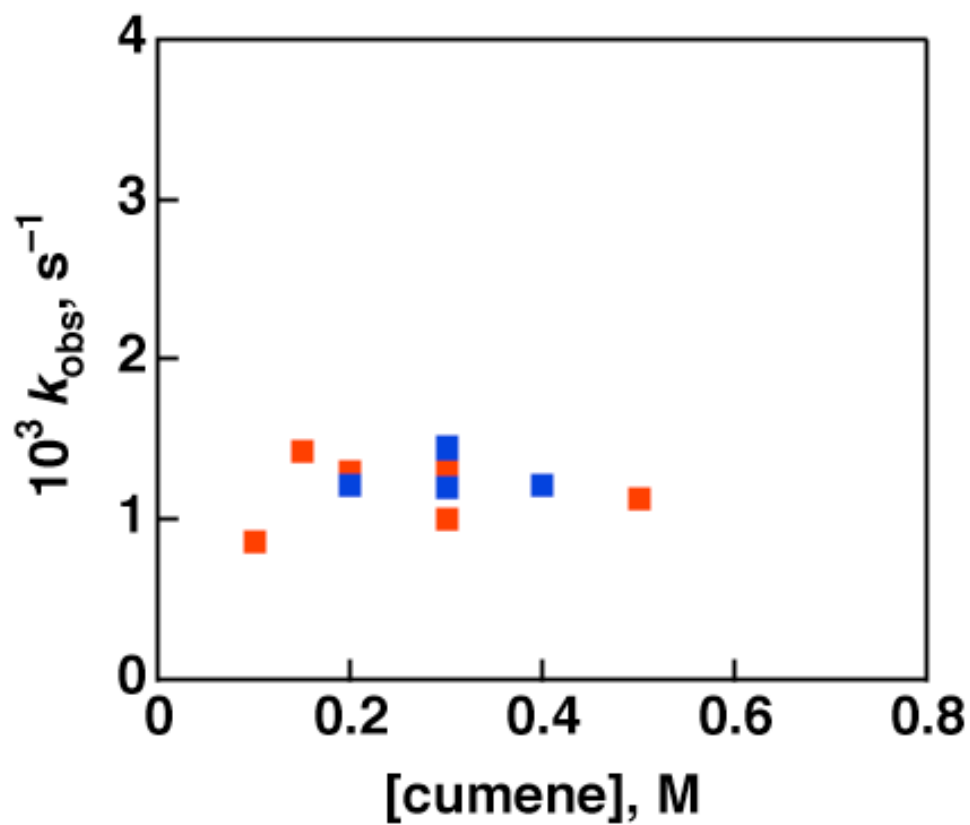


Figure S13. Concentration dependence of first-order rate constants for the second step in the cumene oxygenation by **2** in CH_3CN at 298 K (red, in the absence of D_2O ; blue, in the presence of excess amount of D_2O (2M)).