Supplementary material to:

Me_2-NHC based robust Ir catalyst for efficient water oxidation

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General procedures: All reactions were carried out under argon or nitrogen atmosphere. Every solution addition or transfer was performed via syringes. Nuclear Magnetic Resonance experiments were performed on a Varian Inova spectrometer (^{1}H: 500 MHz), a Varian Mercury (^{1}H: 300 MHz) or a Bruker ARX-400 (^{1}H: 400 MHz). Chemical shifts are referenced to the solvent signal. Complex **1** was prepared via literature procedures.[1] ESI mass spectrometry was recorded on a Shimadzu LCMS-2010A wherein the sample was directly injected into the mass spectrometer; High resolution mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; electrochemistry was recorded on an autolab PGSTAT10; Elemental analysis were sent to Mikroanalytisches Labor Kolbe.

Synthesis of 2: Complex **1** (97 mg) was added to a mixture of Ag_2O (50 mg, excess) in water and stirred vigorously. After a couple of minutes the complex becomes soluble. The mixture was stirred for 4 hours and filtrated through Celite. The mixture was dissolved in dichloromethane, again filtered trough Celite and evaporated. Then the mixture was redissolved in dichloromethane and again evaporated to remove some more water. Pentane was added to suspend the product, which was subsequently obtained in a 40 mg yield of **2** (45% isolated yield).

^{1}H NMR (CD_2Cl_2): 6.84 (s, 2H, NHC), 3.61 (s, 6H, Me), 1.59 (s, 15H, Cp*).

MS(FAB$^+$): m/z calculated for $C_{15}H_{24}ON_2{}^{193}Ir$ ($[M-OH]^+$): 441.1518, observed: 441.1519.

Kinetics: rate = k[**2**][Ce^{IV}]; k = 4.5 $M^{-1}s^{-1}$

Elemental analysis of **2** · 4.25 H_2O: found (calculated) C: 34.08 (33.73), H: 6.73 (6.32), N: 4.91 (5.24).

Catalytic experiments: In a typical catalytic run, 548 mg of cerium ammonium nitrate (1 mmol) was dissolved in 2 mL of demineralized water and placed with a stir bar in a roundbottom Schlenk flask equipped with a septum. The Schlenk flask was connected to needle which through which overpressure can escape into a burette, from where very precisely the amount of gas production can be determined. The appropriate amount of catalyst, between 1.2 x 10^{-4} mmol to 1.2 x 10^{-2} mmol, was dissolved in 1 mL demineralized water and carefully added through the septum into the reaction flask via a syringe (see Figure S1). The mixture was vigorously stirred throughout the whole time. After a couple of seconds, when the pressure buildup as a result of the addition of catalyst solution has stopped, the volume of produced oxygen was followed and recorded in time. The system was carefully calibrated, by adding known amounts of gas with a syringe through the septum of the setup. Moreover it is important to note that in all cases exactly 5.6 mL of gas was obtained (0.25 mmol), which corresponds to full conversion 1 mmol Ce^{IV}. Since several milliliters of gas are formed, quantification with this setup is very accurate (The error in the burette is 1% of the full scale (10 mL)). The headspace of the setup was led over a Clarck electrode, showing that the headspace was significantly enriched with dioxygen. Control experiments that were carried out under standard conditions without any catalyst did not produce more than 0.1 mL of gas, even after hours.

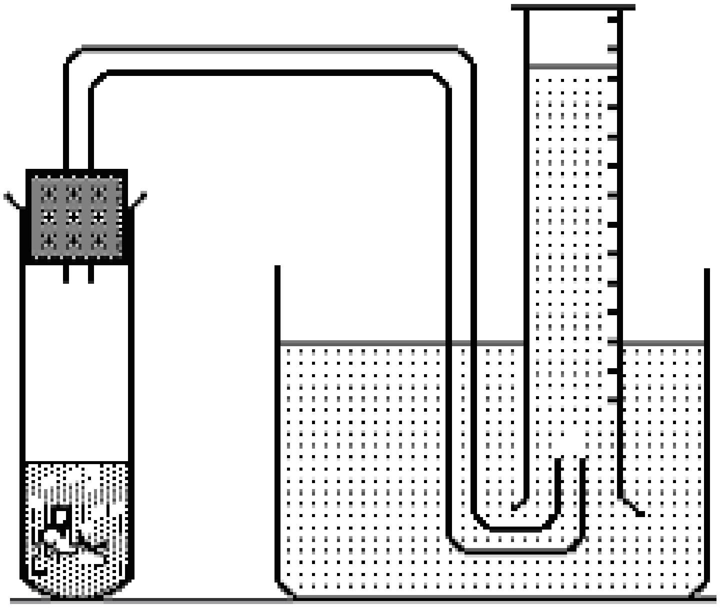

Figure S1. Schematic representation of the setup to measure the gas evolution. A 10 mL volumetric cylinder is place up side down in demineralized water, while filled with water. A very thin needle is bend and placed inside the cylinder. The needles is connected to the reaction flask. All changes in volume are recorded by reading the numbers on the volumetric cylinder. It is important that significant amount of gas is produced, compared to the full scale of the cylinder for accuracy. Since we chose to use standard a 1 mmol concentration of Ce^{IV}, a total amount of 5.6 mL of gas was produced in every single run of **1** or **2** that was carried out. Although the setup is very low-tech, results reproduced well.

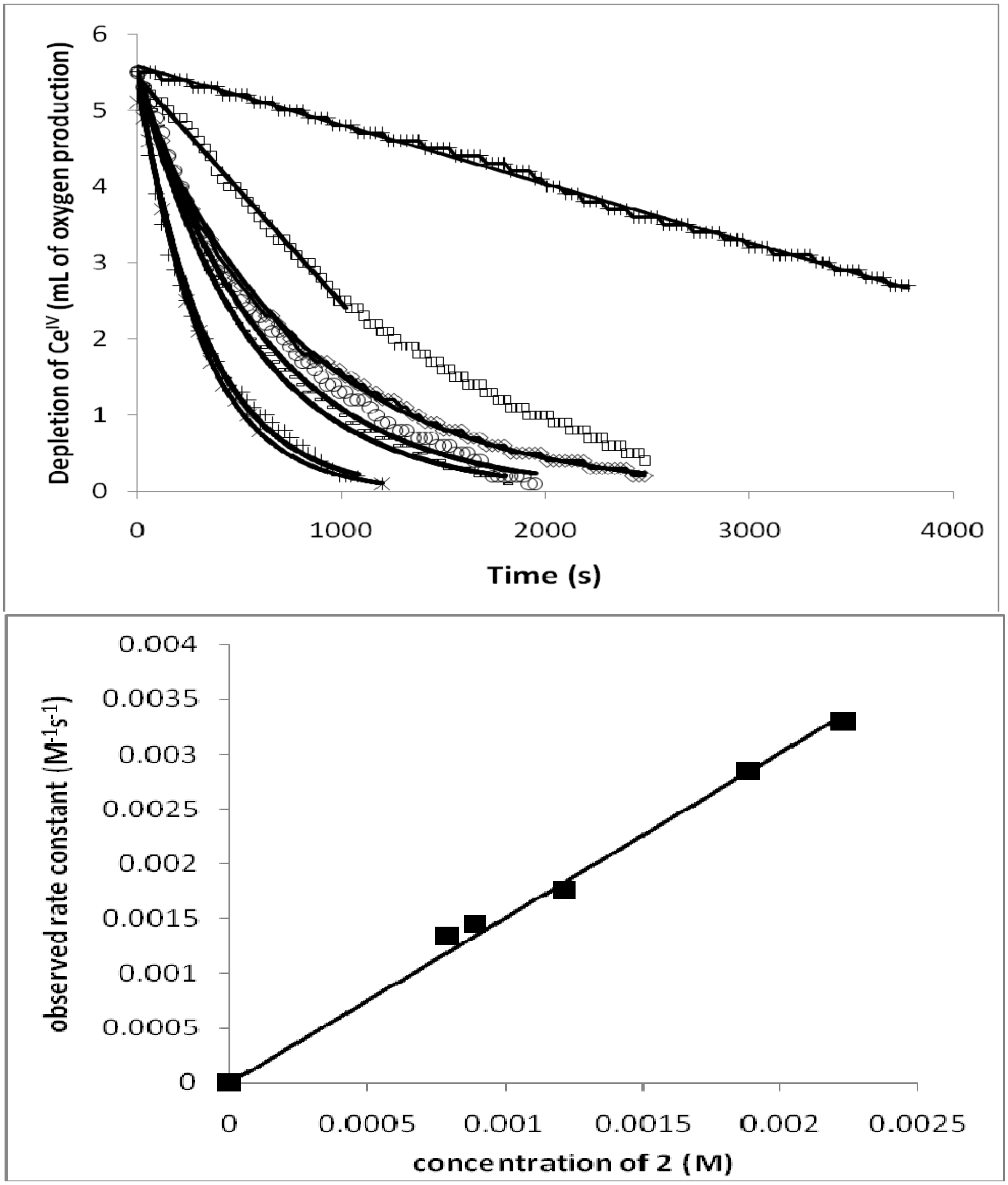

Figure S2. Kinetic diagram of [Ce^{IV}] versus time at [**2**] of 4.0 x 10^{-5}, 1.15 x 10^{-4}, 2.63 x 10^{-4}, 2.97 x 10^{-4}, 4.0 x 10^{-4}, 6.3 x 10^{-4}, 7.4 x 10^{-4} and 7.4 x 10^{-4} Mconcentrations (top). At high concentrations of [**2**] (> 4 x 10^{-4}) a rate order of v = k[Ce^{IV}][**2**] is obtained with k = 4.5 s^{-1}. At lower catalysts loadings the rate becomes pseudo first order in [Ce^{IV}]. The bottom figure shows the linear relationship between the amount of **1** used and k_{obs}. In all cases a 0.33 M concentration of Ce^{IV} was used. This represents 8000 to 450 equivalents, depending on the amount of catalyst used..

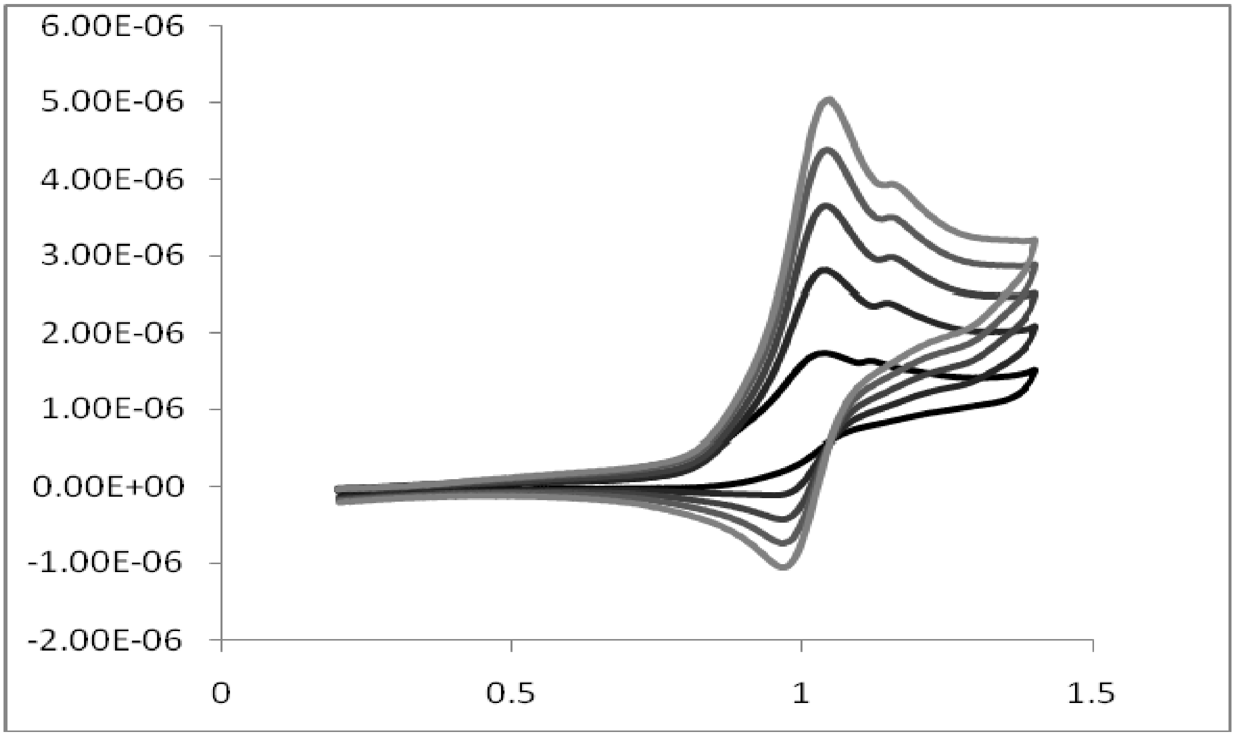

Figure S3. Cyclic voltammetry diagram in MeCN of **2** at scanrates varying from 200 mV/s (black) to 1000 mV/s (grey). The voltammogram was recorded with a 1 M concentration of tetrabutylammonium hexafluorophosphate as an electrolyte and referenced against ferrocene.

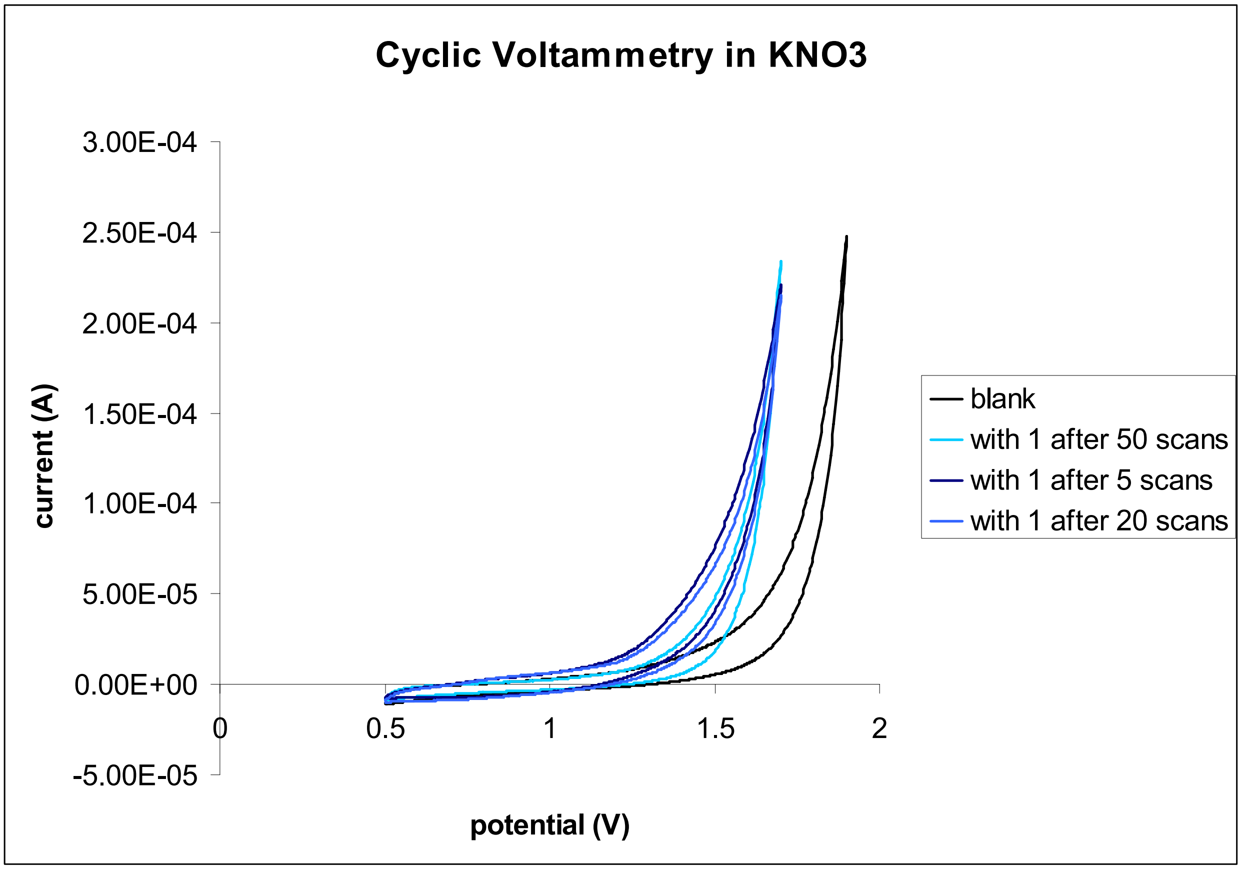

Figure S4. Cyclic voltammogram of 1 mM of catalyst **1** in a 0.1 M KNO_3 solution Upon successive scanning (up to 50 scans at 100 mV/s), no increase in water oxidation waves is observed, suggesting that catalysis does not occur by deposited iridium oxide at the carbon electrode as in reference 14 in the main article. The small decrease in the oxidation wave is most likely the result of local acidification of the solution. Rinsing the electrode with demineralized water and subsequent scanning in a blank 0.1 M KNO_3 solution does not reveal any remains of catalytic activity (black line).

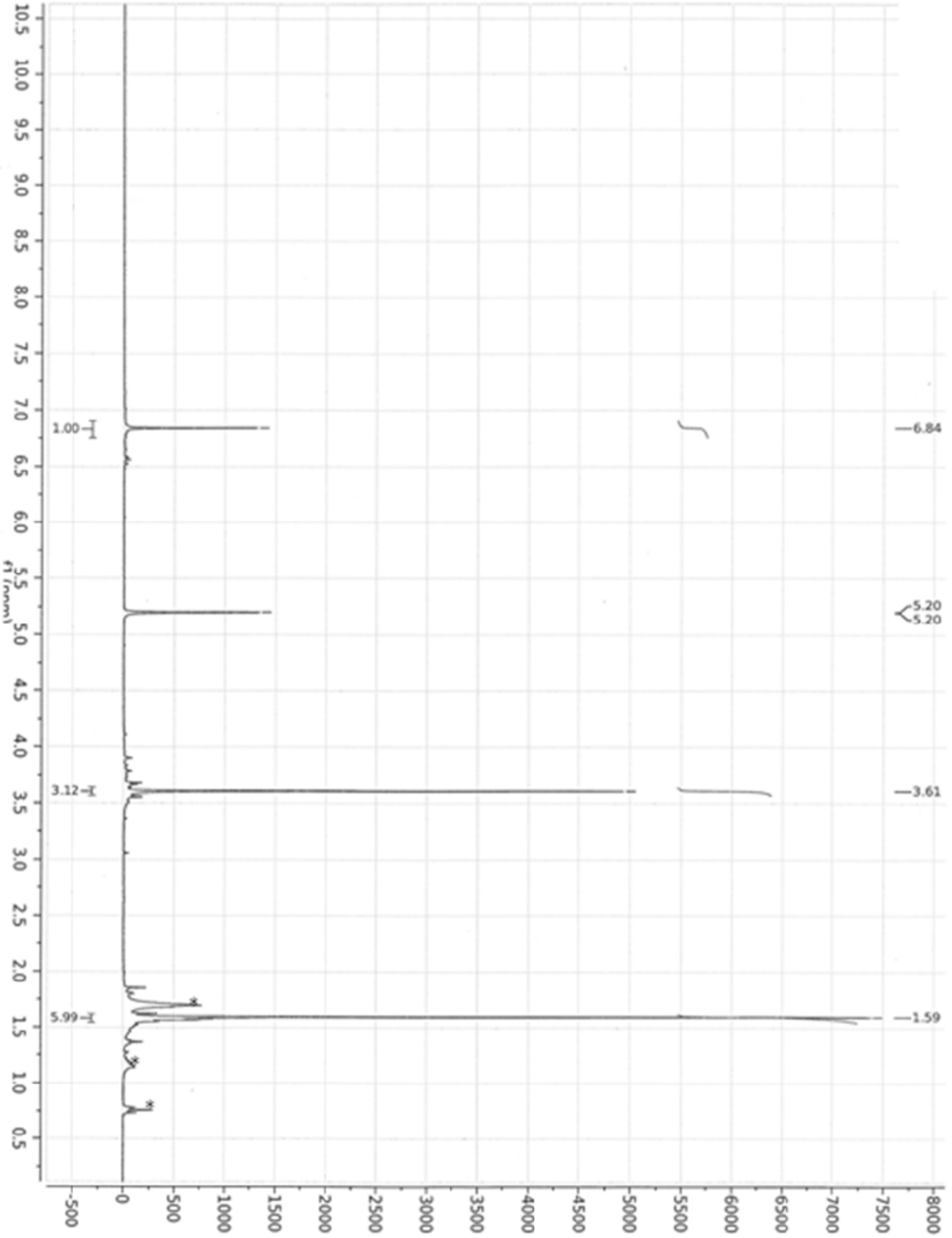

Figure S5. ^{1}H NMR spectrum of 2 in dichloromethane (CD_2Cl_2 signal at 5.20 ppm). The marked signals (*) are due to small traces of water and pentane that remained in the sample, even after several hours in vacuo.

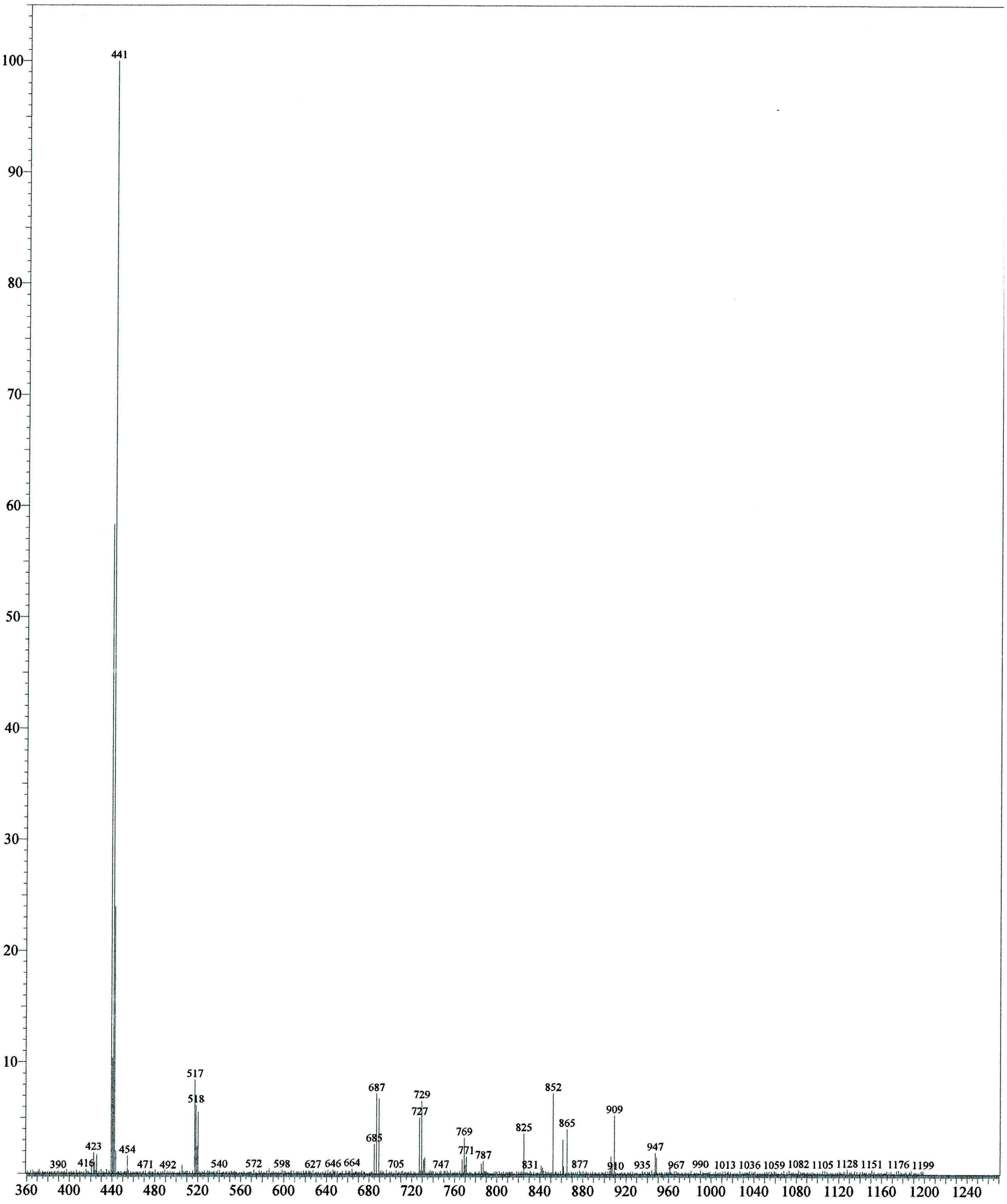

Figure S6. ESI-MS spectrum of **2** in water. The main peak at 441 cooresponds to $[M - OH]^+$.

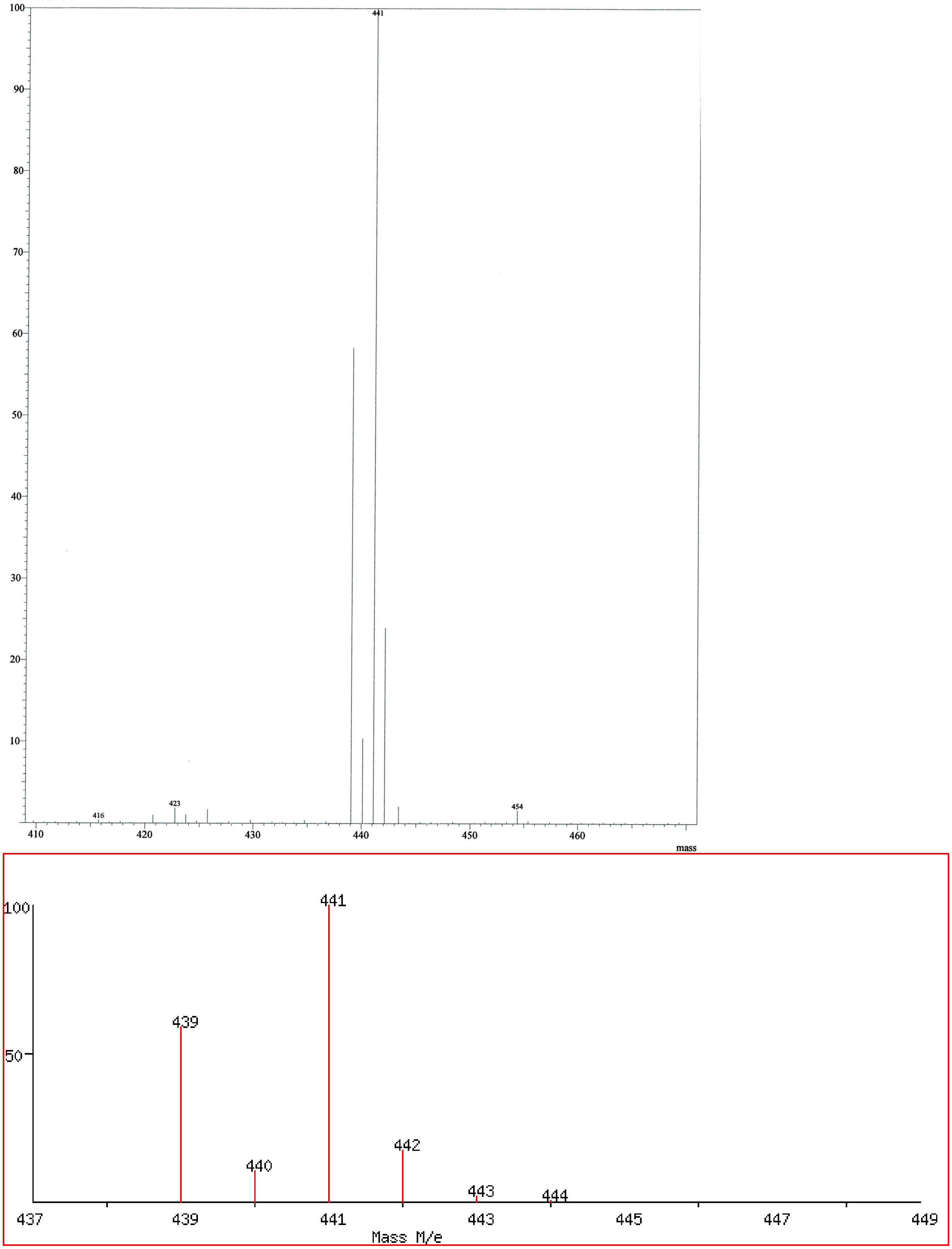

Figure S7. Isotopic Pattern of the ESI-MS signal at 441 measured (top) and calculated (bottom).

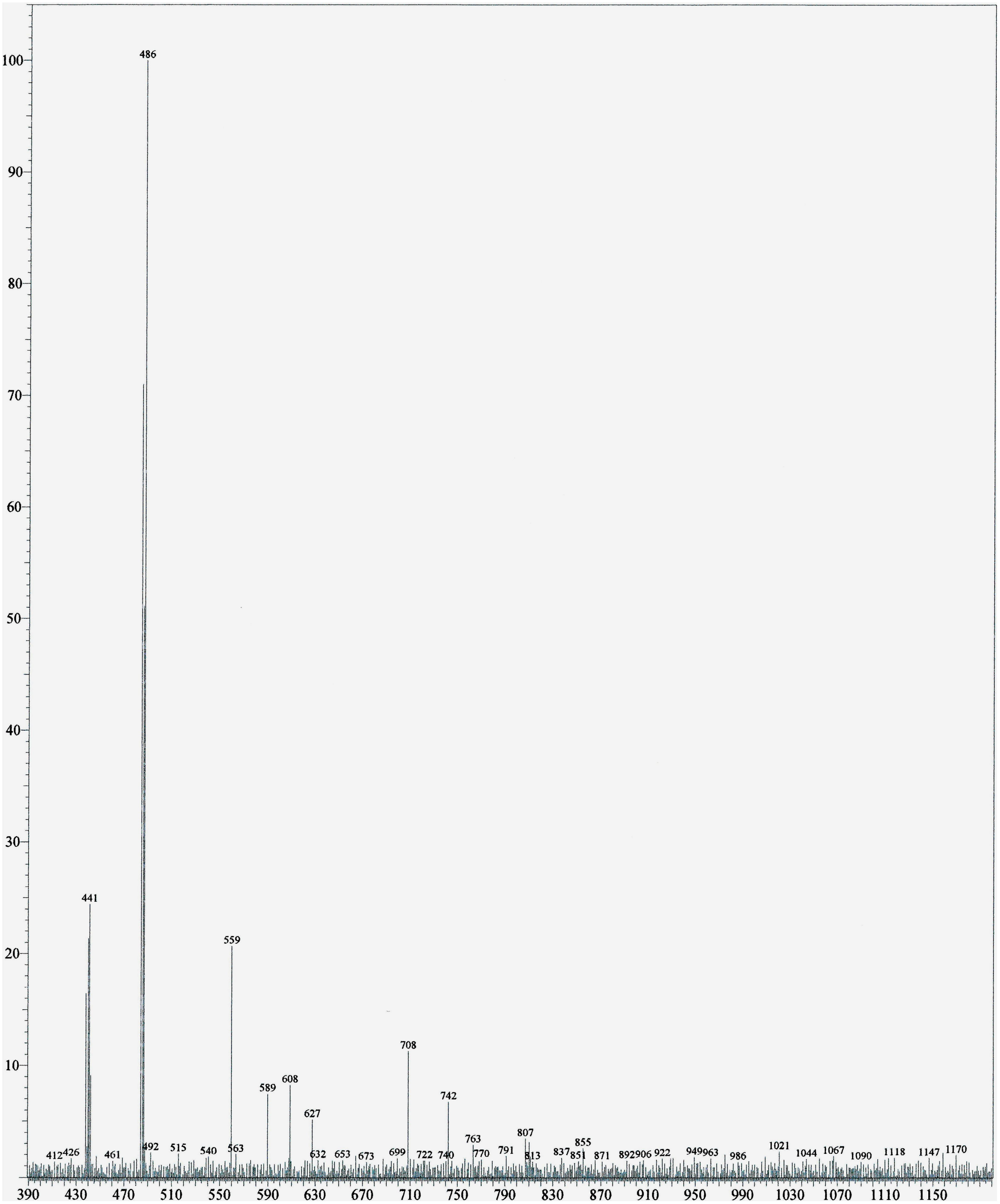

Figure S8. ESI-MS spectrum of **2** after treatment with 10 equivalents of Ce^{IV}.

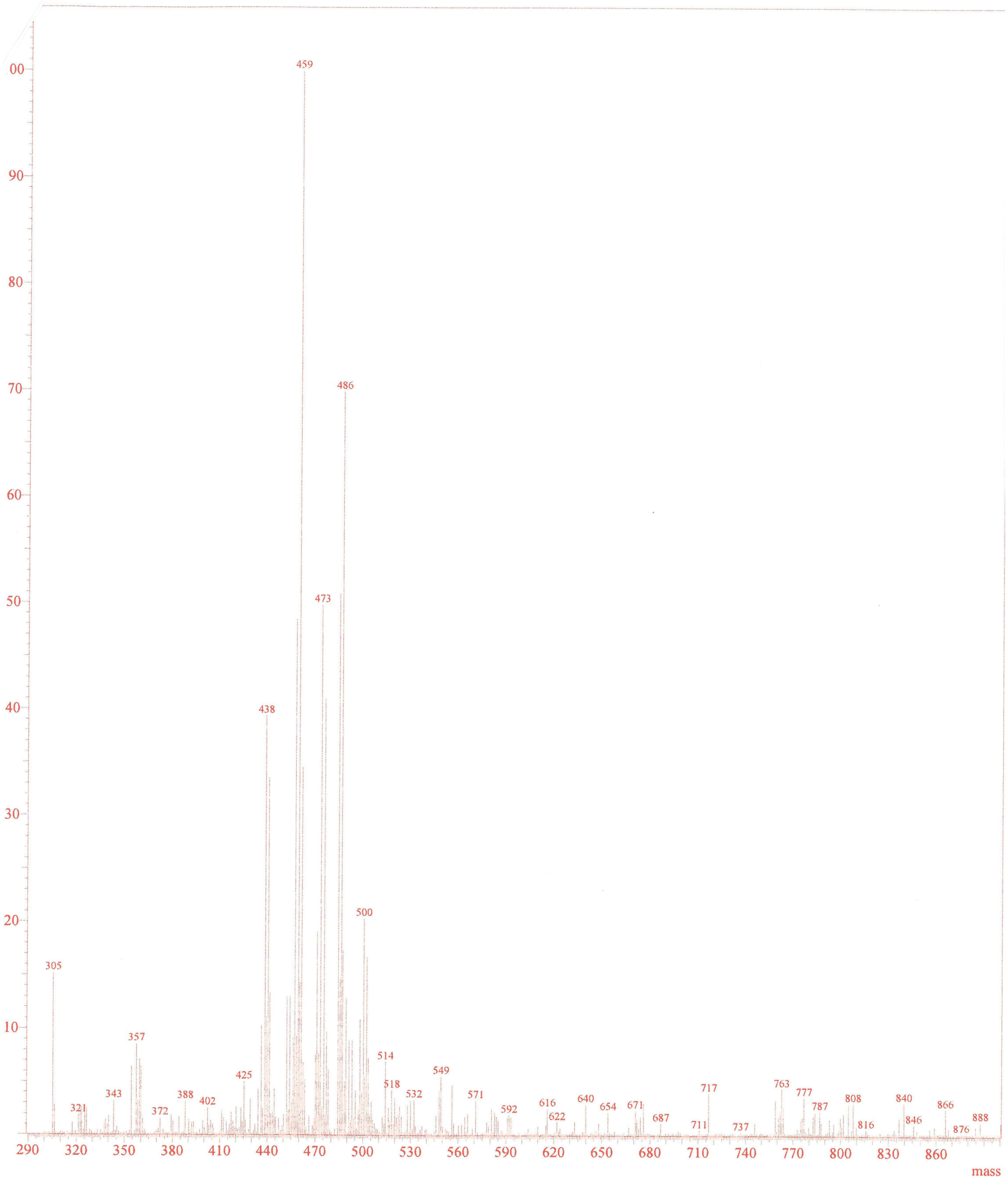

Figure S9. Mass spectrum of **1** after treatment with 5 equivalents of Ce^{IV}. Peaks at 440 {(IrCp*=O}$^+$, 475 {IrCp* (OH)$_3$}$^+$, 486 {IrCp*=O • 2Na}$^+$ and 502 m/z {IrCp*(O$_2$) • 2Na}$^+$ are observed, suggesting that in case of **1**, the same (active) species as in case of **2** are formed, albeit in lower concentrations.

References:

[1] X.-Q. Xiao, G.-X. Jin, *J. Organomet. Chem*. 2008, **693**, 3363.