## **Supporting Information**

## Perry et al. 10.1073/pnas.1207600109



Fig. S1. Zoomed-in experimental (background is subtracted; black) and calculated (red) mass spectra showing (A) [2+Na]<sup>+</sup>, (B) [4+Na]<sup>+</sup>, and (C) [7+Na]<sup>+</sup>.



Fig. S2. Comparison of the experimental (black) and calculated (red) isotope distributions for [1•3]<sup>+</sup>.



Fig. S3. Experimental (background is subtracted; black) and calculated (red) mass spectra showing the coordination complex [[Rh<sub>2</sub>(esp)<sub>2</sub>]•PhI(O<sub>2</sub>CC(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>]<sup>+</sup> formed between catalyst and PhI(O<sub>2</sub>CC(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub> oxidant.



**Fig. S4.** Representative high-resolution tandem MS (MS/MS) data. (*A*) Product ions formed by isolating and dissociating  $[5]^+$  or  $[1 \bullet 3]^+$  in single-stage mass spectra (Fig. 3). (*B*) Product ions formed by isolating and dissociating  $[1 \bullet H_2O]^+$  at *m/z* 776.0936 in *A*. (*C*) Product ions formed by isolating and then dissociating  $[1]^+$  at *m/z* 758.0831 in *A*,  $[1+H]^+$  at *m/z* 759.0853 in *B*, or  $[1]^+$  at *m/z* 758.0808 from the single-stage spectrum shown in Fig. 3. MS/MS parameters: accumulation time = 500 ms; normalized collision energy = 30%; ion activation time = 100 ms; collision gas = He. (*D*) MS<sup>2</sup> spectra for  $[9]^+$  at *m/z* 1,617.7317 in single-stage mass spectra (Fig. 3).



**Fig. 55.** Desorption electrospray ionization (DESI) MS spectra showing the overlapping isotope distributions of  $[6]^*$  and  $[8]^*$  for ROSO<sub>2</sub><sup>14</sup>N (*A*) and ROSO<sub>2</sub><sup>15</sup>N (*B*). This figure shows the complete spectrum before background subtraction (after background subtraction shown in Fig. 4 *G* and *H*).



Fig. S6. DESI-MS spectra (background is subtracted) showing a comparison of the experimental (black) and calculated (red) isotopic distribution composed of [6+Na]<sup>+</sup> and [8+Na]<sup>+</sup> (3:1) for Cl<sub>3</sub>CCH<sub>2</sub>OSO<sub>2</sub><sup>14</sup>NH<sub>2</sub> (*A*) and Cl<sub>3</sub>CCH<sub>2</sub>OSO<sub>2</sub><sup>15</sup>NH<sub>2</sub> (*B*).

DN A C



**Fig. 57.** Mass spectra showing the absolute intensities of  $[7+Na]^+$  and  $[6+Na]^+/[8+Na]^+$  for admantane concentrations of  $10^{-2}$  M (A and B) and  $10^{-1}$  M (C and D). In the experiment, the DESI spray was a mixture containing  $10^{-5}$  M 2 and  $10^{-5}$  M 3 in anhydrous CH<sub>2</sub>Cl<sub>2</sub>. A mixture containing  $10^{-2}$  M 1 and  $10^{-2}$  M adamantane (or  $10^{-1}$  M adamantane) was deposited on a glass slide.



**Fig. S8.** Spectra showing the signal intensities for the sulfonamide product of adamantace carboxylic acid (*Upper*) and  $[6+Na]^+/[8+Na]^+$  (*Lower*). In the experiment, the DESI spray was a mixture containing  $10^{-5}$  M **2** and  $10^{-5}$  M **3** in anhydrous CH<sub>2</sub>Cl<sub>2</sub>. A mixture containing  $10^{-2}$  M **1** and  $0.5 \times 10^{-2}$  M,  $10^{-2}$  M, or  $10^{-1}$  M adamantane carboxylic acid was deposited on a glass slide.



Fig. S9. Negative-mode DESI-MS spectra showing Rh<sup>2+</sup>/Rh<sup>3+</sup> species [Rh<sub>2</sub>(esp)<sub>2</sub>Cl]<sup>-</sup> at *m/z* 793.0493 and [Rh<sub>2</sub>(esp)<sub>2</sub>Cl<sub>2</sub>]<sup>-</sup> at *m/z* 828.0225.



Fig. S10. Mass spectra of a bulk solution containing 1, 2, and 3 in  $CH_2CI_2$  after several hours of reaction time. The spectra show experimental (black) and calculated (red) isotopic distributions for  $[8+Na]^+$  using  $CI_3CCH_2OSO_2^{14}NH_2$  (A) and  $CI_3CCH_2OSO_2^{15}NH_2$  (B).

AS PNAS