Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Direct experimental evidence for an enamine radical cation in SOMO catalysis

*Rita Beel, Stefanie Kobialka, Martin L. Schmidt, and Marianne Engeser**

Experimental Procedures

ESI spectra were recorded on a Bruker Apex IV FT-ICR and a micrOTOF-Q mass spectrometer equipped with Apollo ESI sources (70° off-axis stainless steel needle, 10 µm ID). Standard HPLC PEEK microreactors and connecting capillaries (0.13 mm ID) were used. Acetonitrile solutions (HPLC-MS grade) were introduced into the microreactors and ESI source, respectively, at flow rates of 3-5 µL/min using syringe pumps.

A 25 W CO_2 laser was used for IRMPD. All signal assignments were confirmed by exact mass measurements.

Simple ESI spectra were measured with 10^{-5} M acetonitrile solutions of **1**·TFA, **3**, TEMPO and styrene, respectively. Enamine solutions were prepared in situ by mixing equal volumes of acetonitrile solutions of **1**·TFA (10^{-4} M) and the respective aldehyde (10^{-3} M). After approximately 1 h, this mixture was used for the microreactor experiments; the concentration of **3** was typically $5 \cdot 10^{-4}$ M. 250 µl gastight syringes and a double syringe pump were used to ensure equal flow rates with both solutions (100 µl/h). For the reactions with TEMPO and styrene, respectively, 10^{-4} M acetonitrile solutions were introduced in the second microreactor via an additional syringe pump (flow rate 200 µl/h).

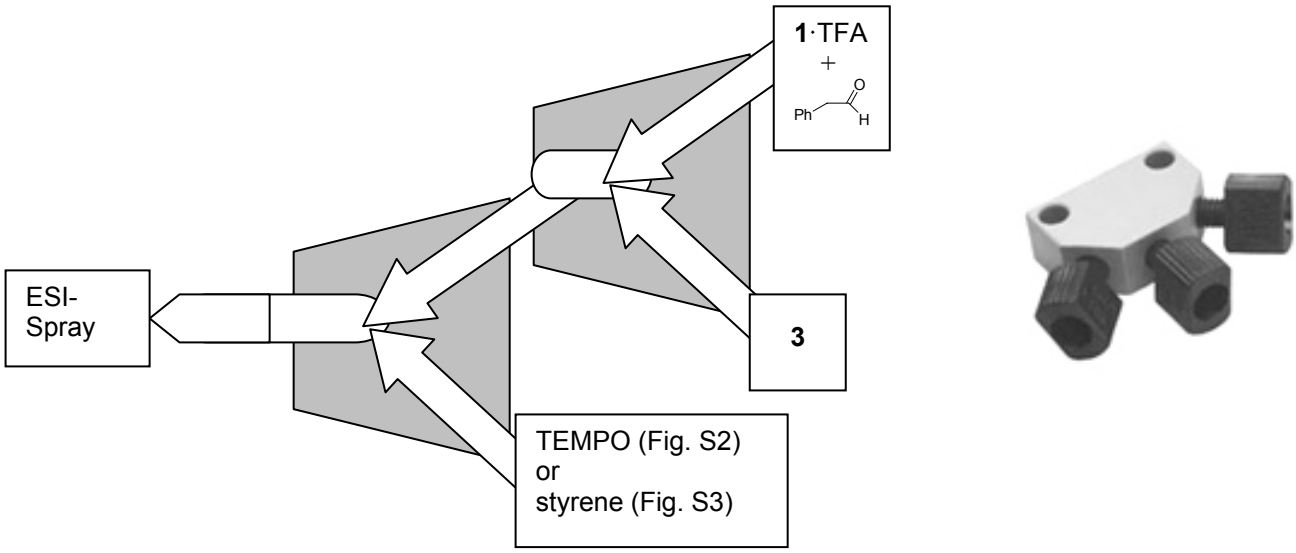

Fig. S1 Left: Scheme of the experimental setup with two microreactors coupled directly to the ESI needle used for the spectra depicted in Fig. S2 and Fig. S3. All reagents have been dissolved in acetonitrile. Right: Picture of a typical microreactor with HPLC fittings (www.vici-jour.de/mixtee.html).

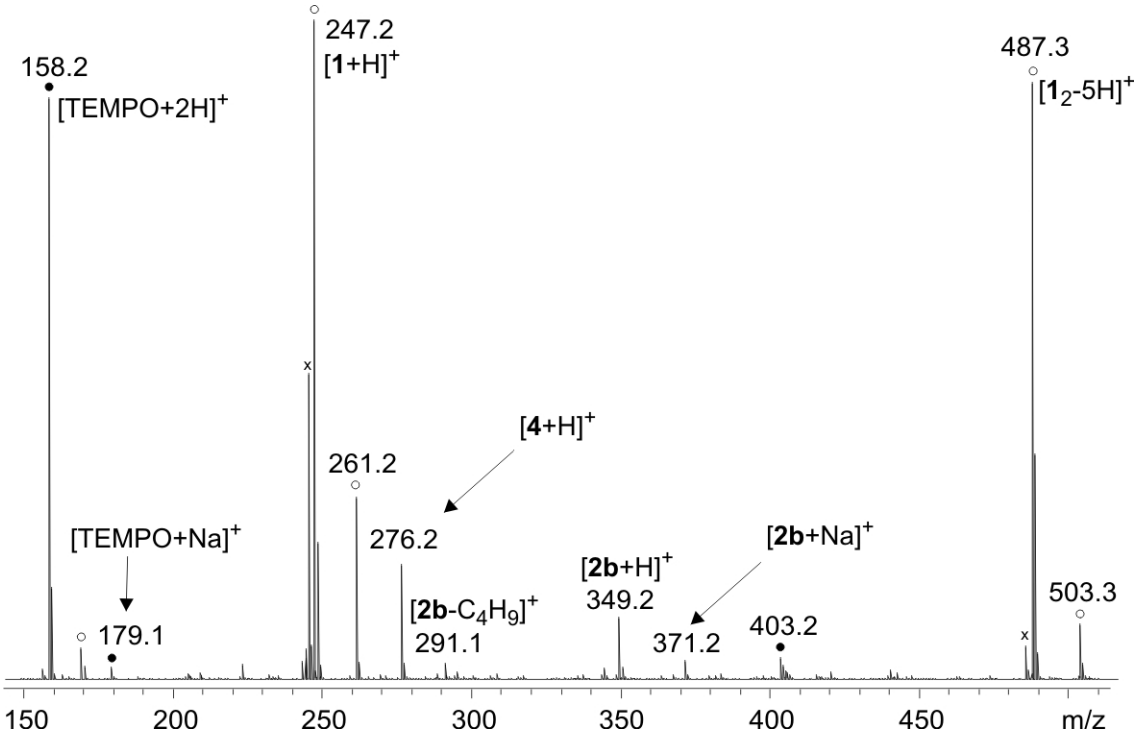

Fig. S2 Typical Q-TOF ESI mass spectrum of the reaction of enamine radical cation $[\mathbf{2b}]^{\bullet+}$ (generated by mixing acetonitrile solutions of **2b** and **3** in a first microreactor) with a TEMPO solution in acetonitrile in a second microreactor coupled directly to the ESI source. Signals marked with x correspond to loss of H_2 in the ESI source. Signals marked with a filled circle have been observed in simple ESI spectra of TEMPO solutions as well; similarly, signals marked with an open circle have been observed in ESI spectra of **1**·TFA under these conditions.

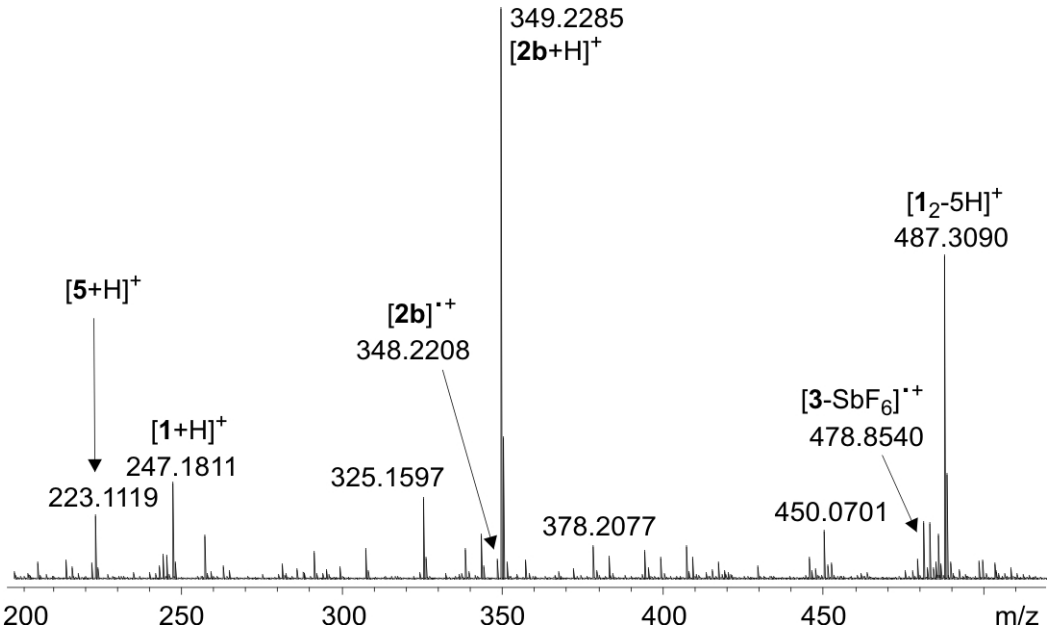

Fig. S3 Typical FT-ICR ESI mass spectrum of the reaction of the enamine radical cation $[\mathbf{2b}]^{\bullet+}$ (generated by mixing acetonitrile solutions of **2b** and **3** in a first microreactor) with a styrene solution in acetonitrile in a second microreactor coupled directly to the ESI source.