Supporting Information

Rapid Identification of Short-lived Intermediates in Alternating-Current Electrolysis by Mass Spectrometry

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1. Experimental

1.1 Chemicals

N-tosyl-2-methyl-4-methoxyaniline (**1**, 98%) was purchased from Nanjing Yanchuang Pharmaceutical Technology Corporation (Nanjing, Jiangsu, China). Ethylene glycol (EG, > 99% (GC)), Acetonitrile (ACN, ≥ 99.9%), 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO, 98%) and Tris(2,2′-bipyridine)dichlororuthenium(II) hexahydrate ($Ru(bpy)_3Cl_2 \cdot 6H_2O$, 98%) were obtained from Shanghai Aladdin Biochemical Technology Co.,Ltd. (Shanghai, China). Pure water was purchased from Wahaha Company (Hangzhou, Zhejiang, China).

1.2 Fabrication and characterization of the bare and BPE-decorated quartz micropipettes

A bare micropipette was fabricated from a quartz capillary (QF100-70-7.5, Sutter Instrument, Novato, CA) using a laser-based P-2000 pipette puller (Sutter Instrument Co., Novato, CA, USA). The parameters to fabricate micropipette with a ~1 μm opening are as follows:

Line 1: HEAT:690, FIL:2, VEL:28, DEL:128, PUL:70;

Line 2: HEAT:690, FIL:2, VEL:28, DEL:128, PUL:110.

For carbon deposit decoration, the previously reported method of butane pyrolysis was used with some minor modification. In brief, As shown in Figure S1, a butane gas (~10 mL min^{-1}) was passed through a bare micropipette from its rear and heated by butane flame under a nitrogen atmosphere (~150 mL min^{-1} through an outer quartz tube of O.D. 3.0 mm and I.D. 1.5mm). The temperature inside the tube was maintained at 700 – 800 ˚C for about for 5 min, so that the desired thickness of the carbon layer (~89 nm) could be obtained by butane pyrolysis. A combined energy dispersive X-ray spectroscopy (EDX) and elements mapping analysis system attached to the SEM (SM-7800F, JEOL Ltd., Japan) were used for characterizing the hollow structure of a bipolar electrode integrated micropipette (see Figure S2), with a thin layer of Au (about 5 nm) sputtered.

1.3 Mass spectrometry

All mass spectra were obtained using a Q-TOF mass spectrometer (6530B, Agilent Technologies, Inc., Santa Clara, U.S.A.) with a data acquisition rate of 1 Hz in positive mode. The emitter was placed in front of the MS inset with a distance about 5 mm. Instrumental parameters for acquiring MS spectra were as follows: gas temp = 300 ℃, drying gas = 1.5 V/min, nebulizer = 0 psig, Vcap = 0 kV, respectively. The AC high voltage was generated by a function/arbitrary waveform generator (Rigol, DG1022U), which was then amplified by a signal amplifier (Aigtek, ATA-7020). Tandem mass spectra (Figures S4-S11) were obtained under a collision energy of 0-5 eV, using a widow of 0.7 Da for the isolation of the parent ions. The theoretical isotopic distributions were calculated using the Isotopic Distribution Calculator (Release B633.0 Agilent).

Figures and Tables

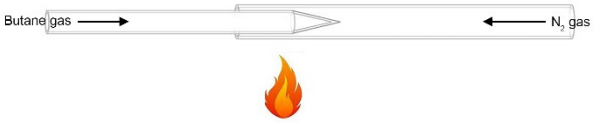


Figure S1. Schematic illustration of BPE integration by butane pyrolysis.

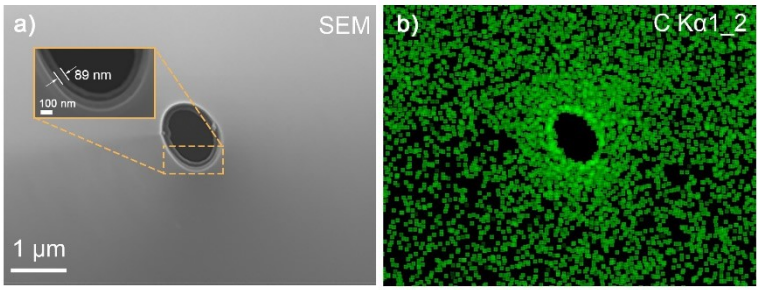


Figure S2. (a) SEM image of a carbon deposited quartz micropipette (top view) and (b) its elemental (carbon) mapping.

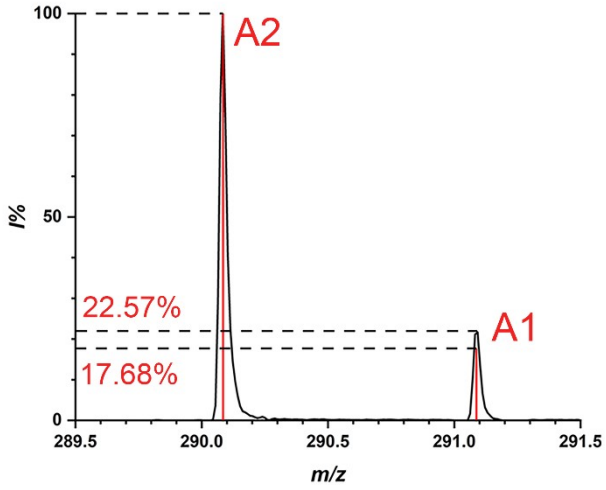


Figure S3. Detection of the electrogenerated **A1** and **A2** under AC electrolysis. The red drop line showed the theoretical isotopic distribution of **A2** ion. Given the theoretical isotopic distribution of **A2** ($[C_{15}H_{16}NO_3S]^+$, m/z 290.0845, 100%; m/z 291.0876, 17.68%; m/z 292.0835, 6.56%; m/z 293.0854, 0.94%) and **A1** ($[C_{15}H_{17}NO_3S]^+$, m/z 291.0924, 100%; m/z 292.0955, 17.69%; m/z 293.0913, 6.56%; m/z 294.0932, 0.94%) as well as their measure relative intensity, the expected mass at around m/z 291 should be 291.0886 (namely 291.0876×(17.68/22.57) + 291.0924×(1-17.68/22.57) = 291.0886).

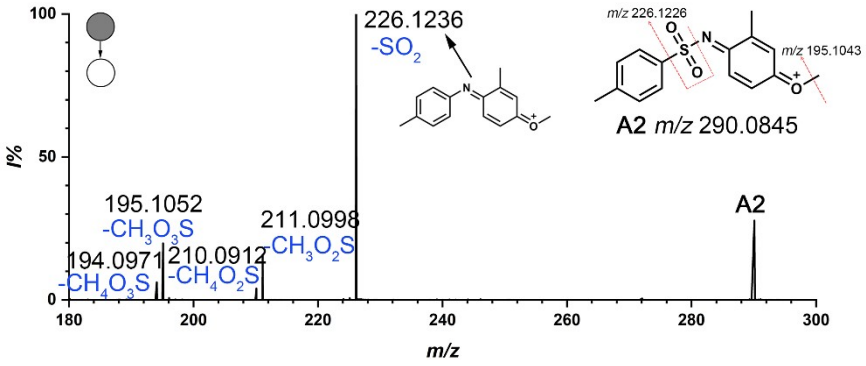


Figure S4. Tandem mass spectra of **A2**. CID energy: 1 eV.

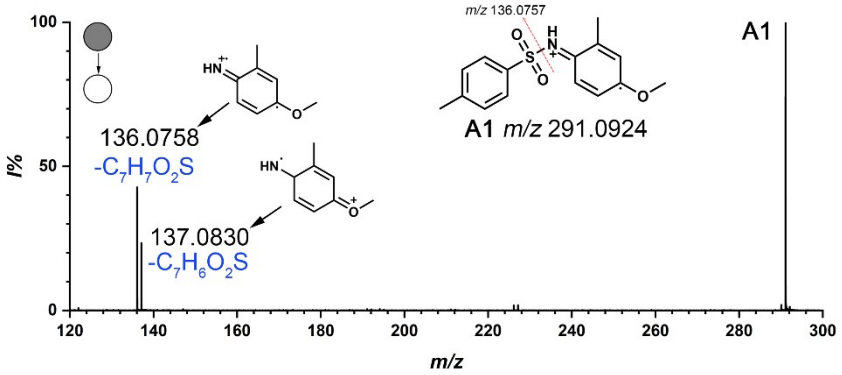


Figure S5. Tandem mass spectra of **A1**. CID energy: 5 eV.

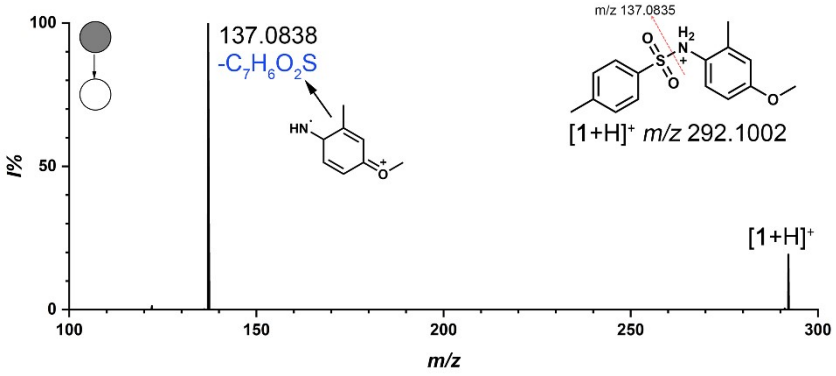


Figure S6. Tandem mass spectra of H^+ adduceted **1**. CID energy: 0 eV.

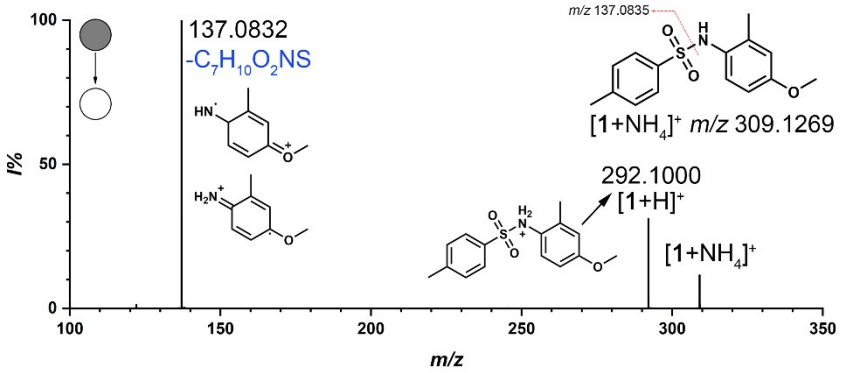
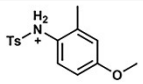
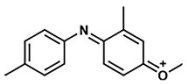
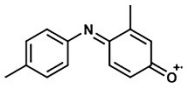
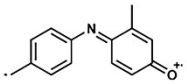
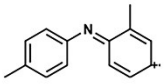
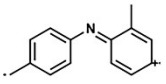
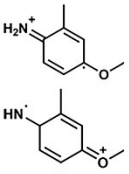
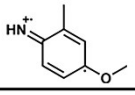


Figure S7. Tandem mass spectra of NH_4^+ adduceted **1**. CID energy: 3 eV.

Table S1. Fragmentation ions from **A2**, **A1**, H^+ adduceted **1** and NH_4^+ adduceted **1**.

NO.	Measured Mass	Calculated Mass	Δm (mDa)	Chemical Formula	Chemical Structure
1	292.1000	292.1002	-0.2	$[C_{15}H_{18}NO_3S]^+$	
2	226.1236	226.1226	1.0	$[C_{15}H_{16}NO]^+$	
3	211.0998	211.0992	0.7	$[C_{14}H_{13}NO]^+$	
4	210.0912	210.0913	-0.1	$[C_{14}H_{12}NO]^+$	
5	195.1052	195.1043	0.9	$[C_{14}H_{13}N]^+$	
6	194.0971	194.0964	0.7	$[C_{14}H_{12}N]^+$	
7	137.0830 137.0838 137.0832	137.0835	-0.5 0.3 -0.3	$[C_8H_{11}NO]^+$	
8	136.0758	136.0757	0.1	$[C_8H_{10}NO]^+$	

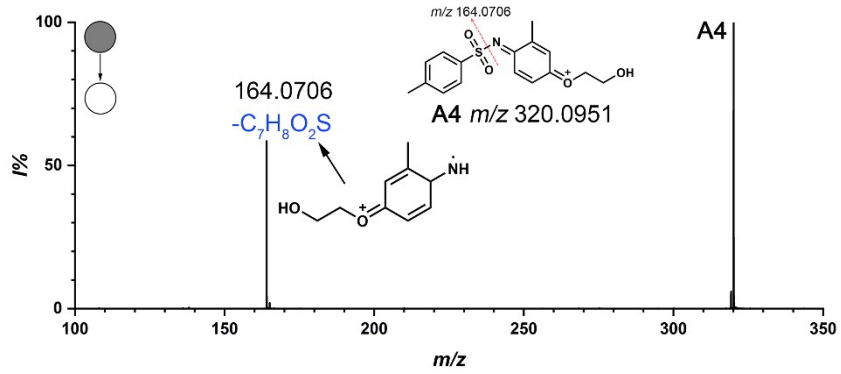


Figure S8. Tandem mass spectra of **A4**. CID energy: 0 eV.

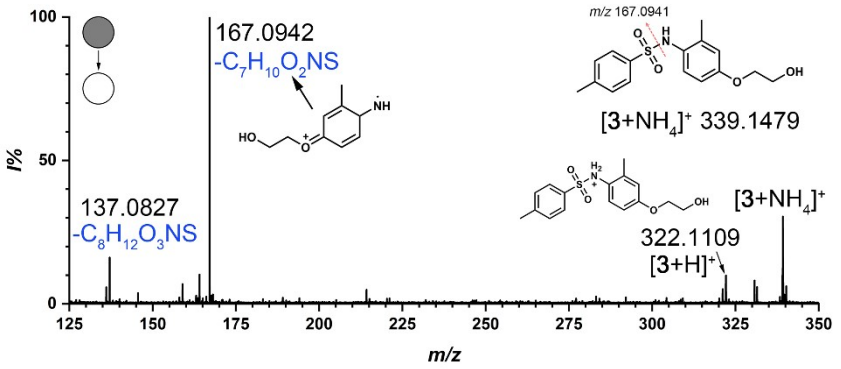
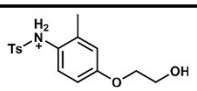
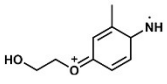
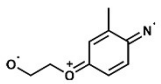
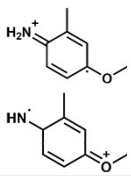


Figure S9. Tandem mass spectra of NH_4^+ adduceted **3**. CID energy: 0 eV.

Table S2. Fragmentation ions from **A4** and NH_4^+ adduceted **3**.

NO.	Measured Mass	Calculated Mass	Δm (mDa)	Chemical Formula	Chemical Structure
1	322.1109	322.1108	0.1	$[C_{16}H_{20}NO_4S]^+$	
2	167.0942	167.0941	0.1	$[C_{15}H_{18}NO_3S]^+$	
3	164.0706	164.0706	0.0	$[C_{15}H_{16}NO]^+$	
4	137.0827	137.0835	-0.8	$[C_{14}H_{13}NO]^+$	

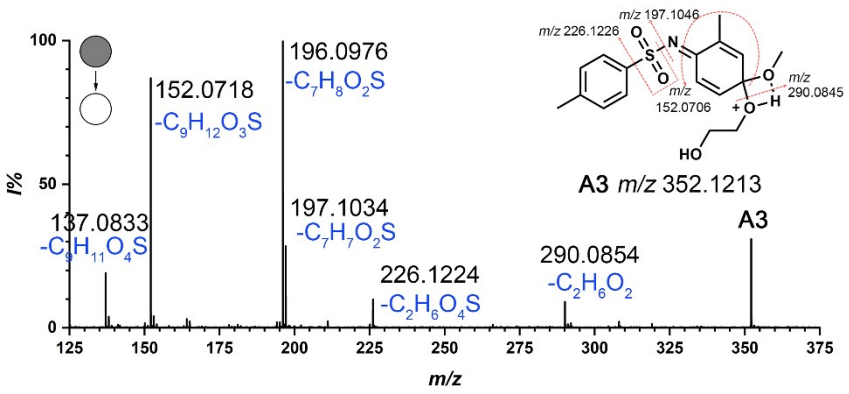


Fig. S10 Tandem mass spectra of **A3**. CID energy: 0 eV.

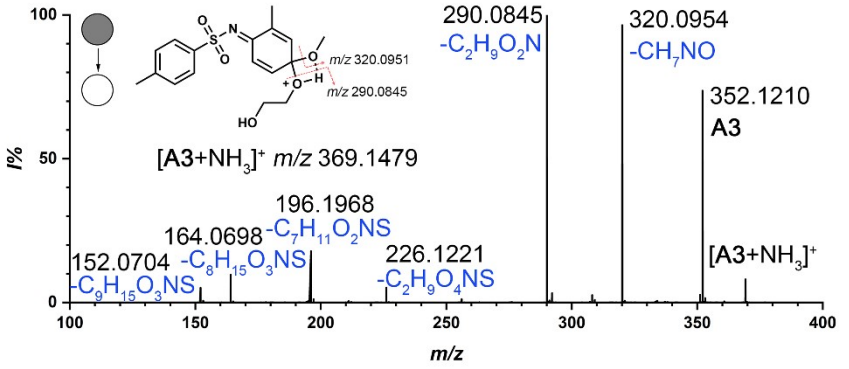
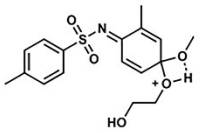
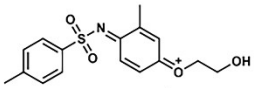
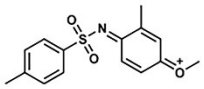
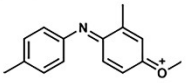
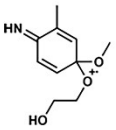
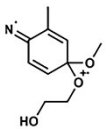
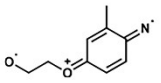
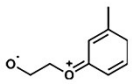


Figure S11. Tandem mass spectra of NH_4^+ adduceted **A3**. CID energy: 0 eV.

Table S3. Fragmentation ions from **A3** and NH_4^+ adduceted **A3**.

NO.	Measured Mass	Calculated Mass	Δm (mDa)	Chemical Formula	Chemical Structure
1	352.1210	352.1213	-0.3	$[C_{17}H_{22}NO_5S]^+$	
2	320.0954	320.0951	0.3	$[C_{16}H_{18}N_4O]^+$	
3	290.0854 290.0845	290.0845	0.9 0.0	$[C_{15}H_{16}NO_3S]^+$	
4	226.1224 226.1221	226.1226	-0.2 -0.5	$[C_{15}H_{16}NO]^+$	
5	197.1034	197.1046	-1.2	$[C_{10}H_{15}NO_3]^+$	
6	196.0976 196.0968	196.0968	0.8 0.0	$[C_{10}H_{14}NO_3]^+$	
7	164.0698	164.0706	-0.8	$[C_9H_{10}NO_2]^+$	
8	152.0718 152.0704	152.0706	1.2 -0.2	$[C_8H_{10}NO_2]^+$	
9	137.0822	137.0835	-1.3	$[C_{14}H_{13}NO]^+$