

Supporting Information

Ambient catalyst-free oxidation reactions of aromatic amines by water radical cations

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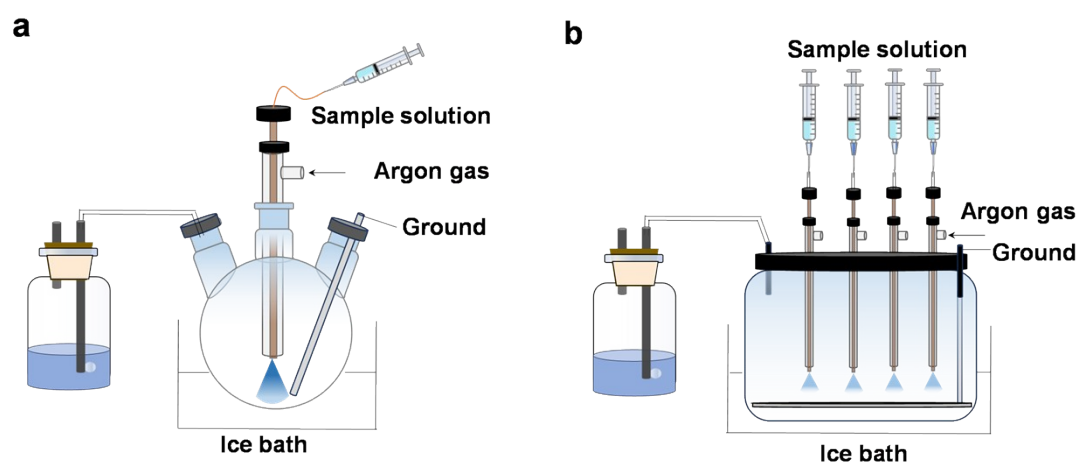


Figure S1. Scale-up experimental setup for the N-hydroxylation reaction of N,N-dimethylaniline. (a) Single-channel spray device. (b) Multi-channel spray device.

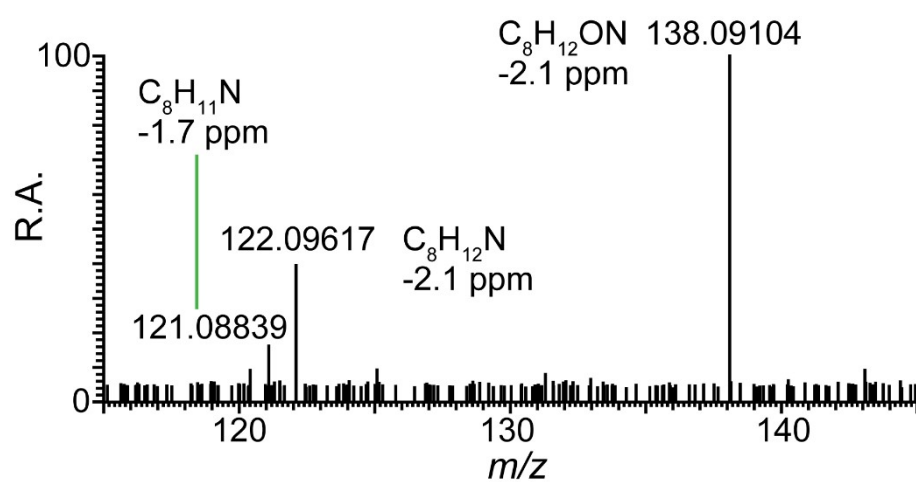


Figure S2. High resolution mass spectrum of ionic products when spraying N,N-dimethylaniline water solution. Relative abundance (R.A.).

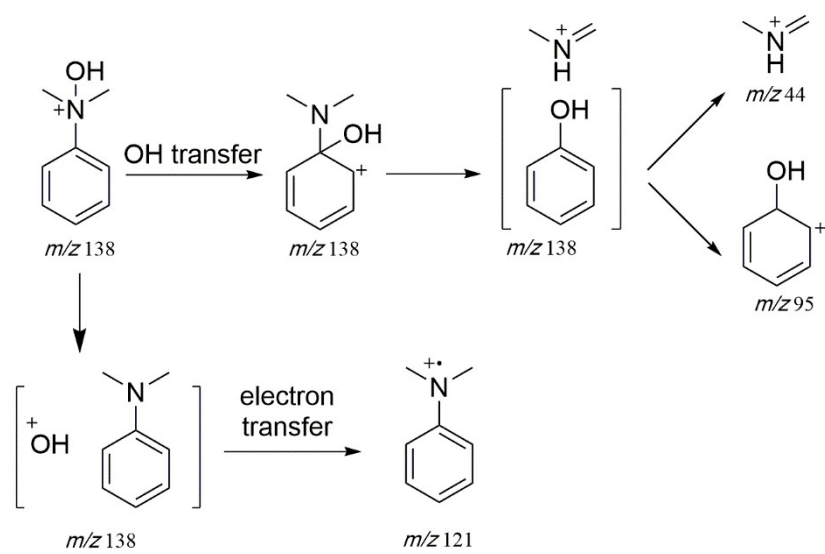


Figure S3. The fragmentation process of m/z 44, 95 and 121 in the dissociation of m/z 138.

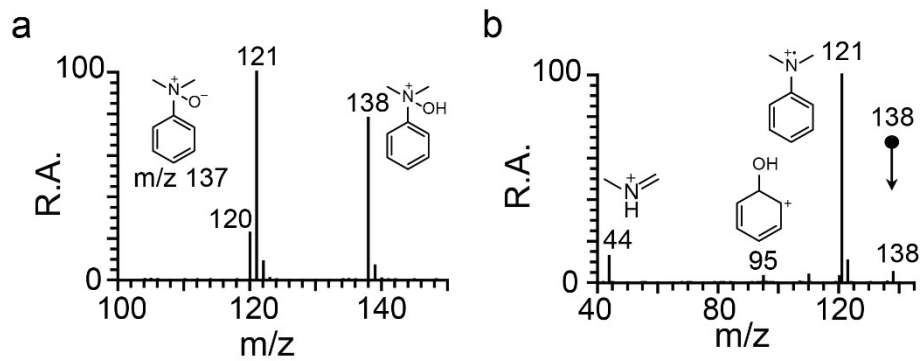


Figure S4. Mass spectra data for N,N-dimethylaniline N-oxide standard. (a) Mass spectrum of standard. (b) Tandem mass spectrum of m/z 138. Relative abundance (R.A.).

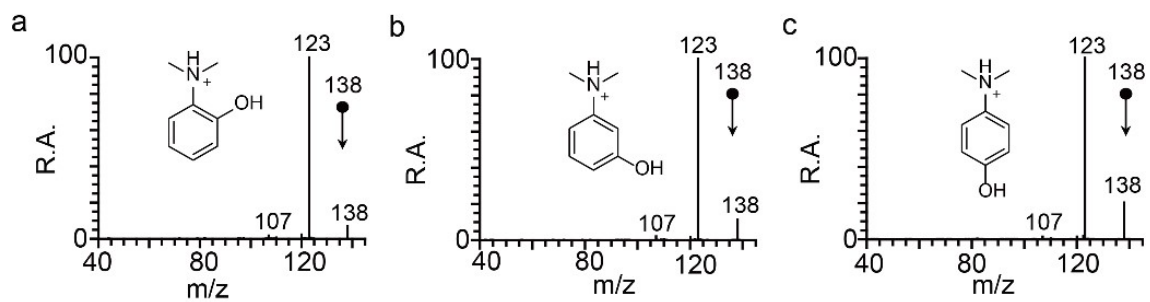


Figure S5. Tandem mass spectra of hydroxy-substituted N,N-dimethylaniline standards in benzene ring. (a) 2-hydroxy-N,N-dimethylaniline. (b) 3-hydroxy-N,N-dimethylaniline. (c) 4-hydroxy-N,N-dimethylaniline. Relative abundance (R.A.).

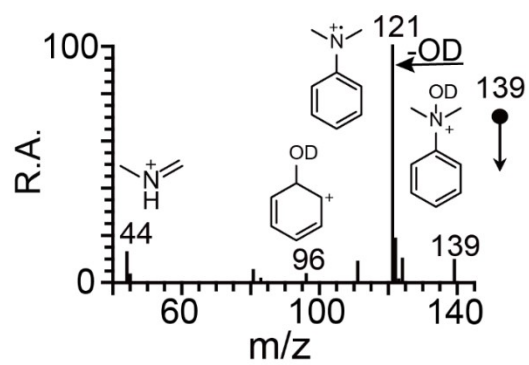


Figure S6. Tandem mass spectrum of product ion at m/z 139. Relative abundance (R.A.).

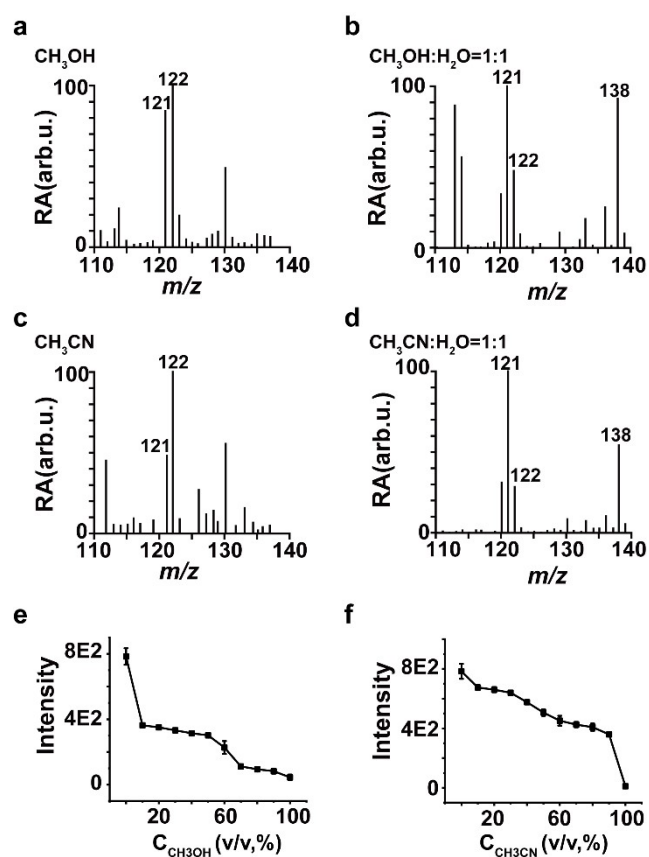


Figure S7. Effect of different solvents on the intensity of DMA-OH at m/z 138. (a) Mass spectrum of DMA with CH_3OH . (b) Mass spectrum of DMA with $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (1:1). (c) Mass spectrum of DMA with CH_3CN . (d) Mass spectrum of DMA with $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1). (e) Intensity of m/z 138 as a function of the concentration of CH_3OH . (f) Intensity of m/z 138 as a function of the concentration of CH_3CN . C: concentration.

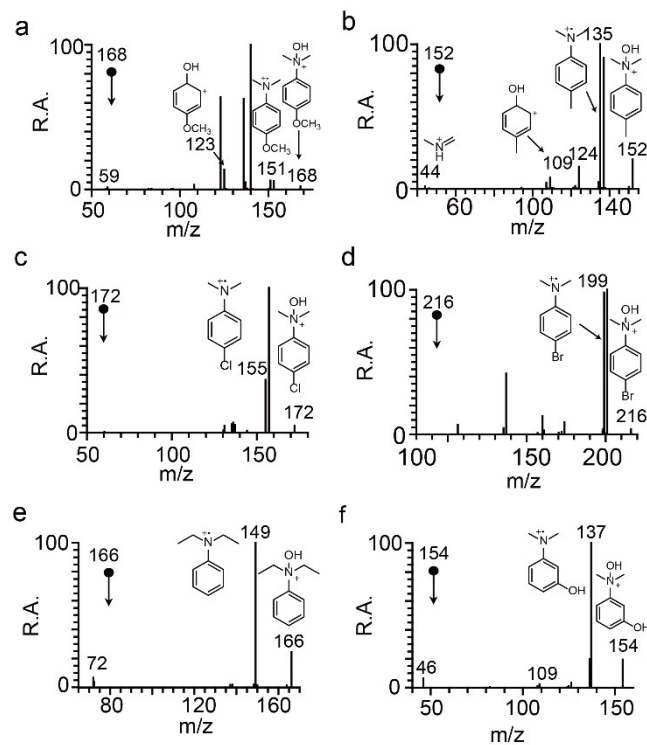


Figure S8. Tandem mass spectra of *N*-hydroxylation of DMA derivatives. (a) *N*-hydroxylation of 4-OMe-DMA (mass=151) at m/z 168. (b) *N*-hydroxylation of 4-Me-DMA (mass=135) at m/z 152. (c) *N*-hydroxylation of 4-Cl-DMA (mass=155) at m/z 172. (d) *N*-hydroxylation of 4-Br-DMA (mass=199) at m/z 216. (e) *N*-hydroxylation of DEA (mass=149) at m/z 166. (f) *N*-hydroxylation of 3-OH-DMA (mass=137) at m/z 154. DEA: N,N-diethylaniline. DMA: N,N-dimethylaniline. Relative abundance (R.A.).

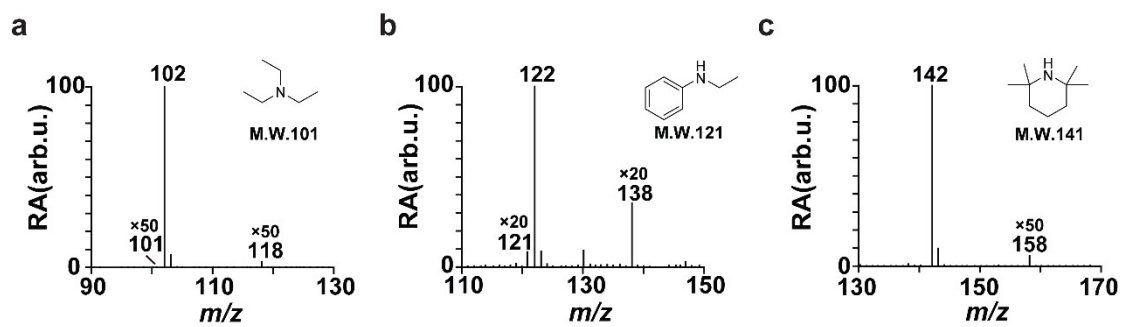


Figure S9. Reaction scope of the N-hydroxylation reaction of other amines in water microdroplets. (a) Triethylamine. (b) N-Ethylaniline. (c) 2,2,6,6-tetramethylpiperidine.

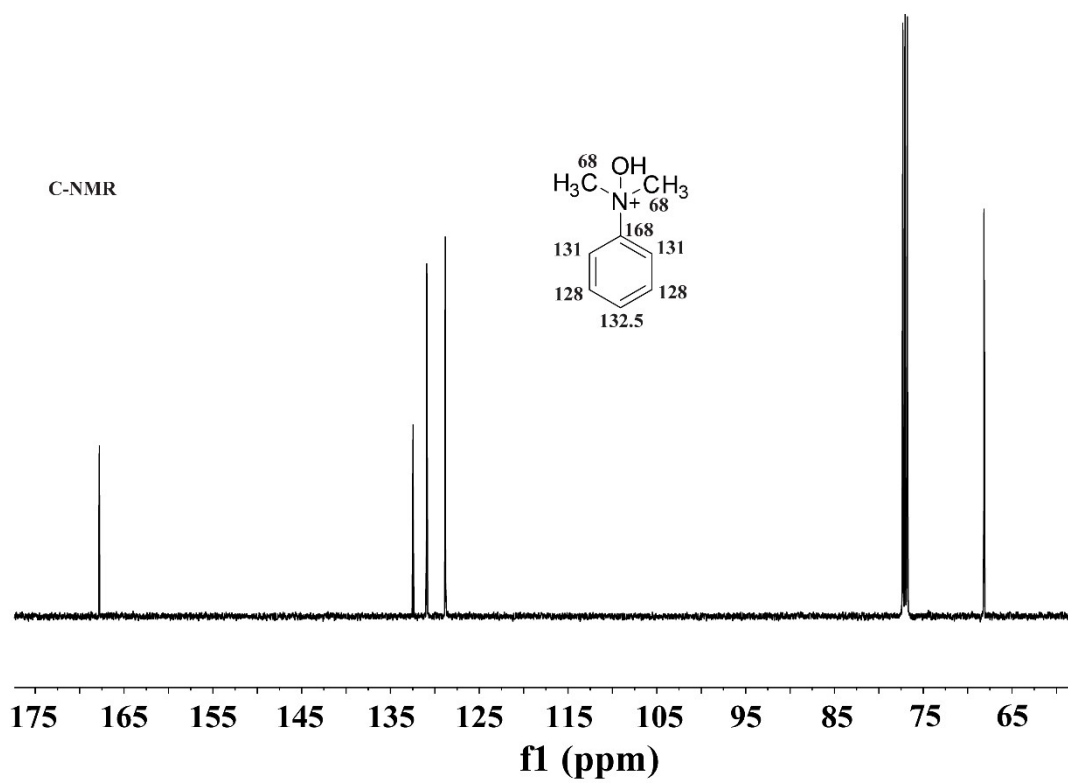


Figure S10. ¹³C-nuclear magnetic resonance (NMR) spectroscopy of N-hydroxyl-N,N-dimethylanilinium.

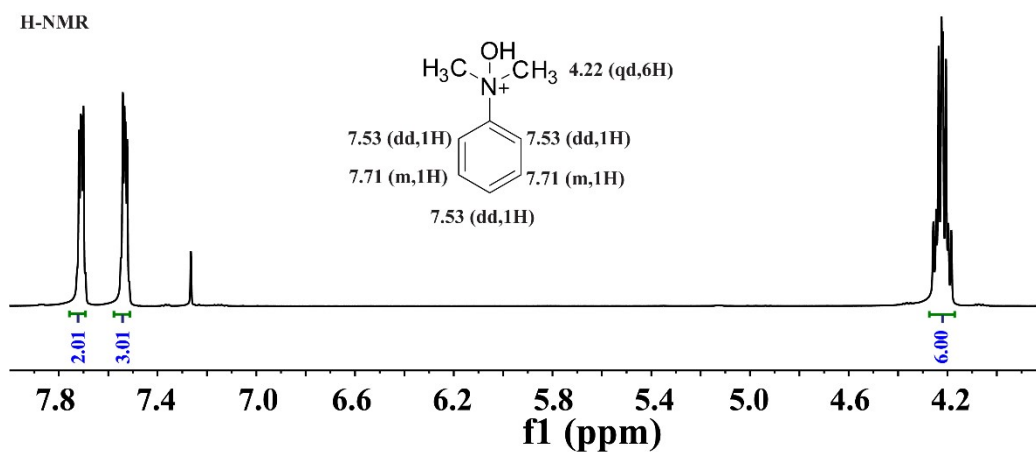


Figure S11. ^1H -nuclear magnetic resonance (NMR) spectroscopy of N-hydroxyl-N,N-dimethylanilinium.

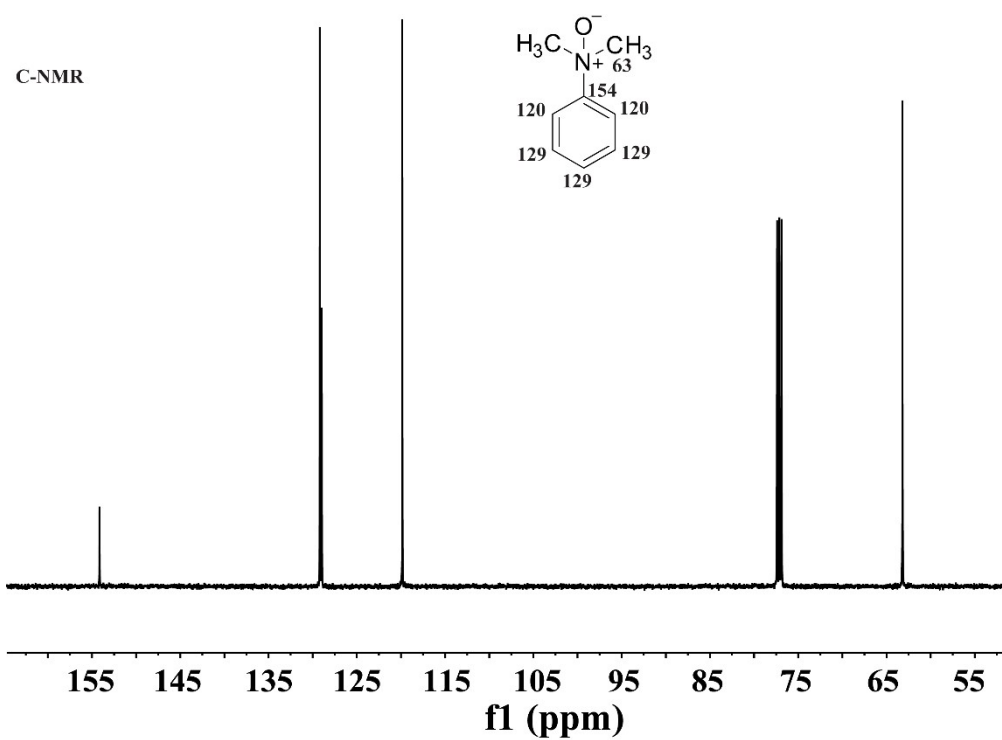


Figure S12. ^{13}C -nuclear magnetic resonance (NMR) spectroscopy of *N,N*-dimethylaniline *N*-oxide standard.

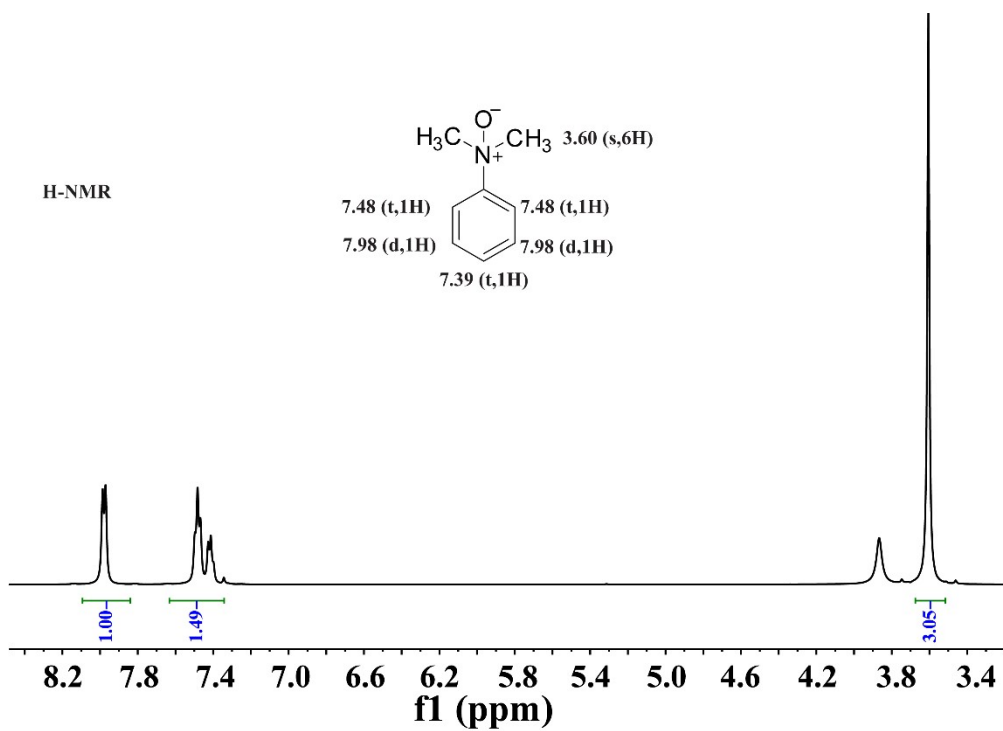


Figure S13. ^1H -nuclear magnetic resonance (NMR) spectroscopy of N,N-dimethylaniline N-oxide standard.

H-NMR

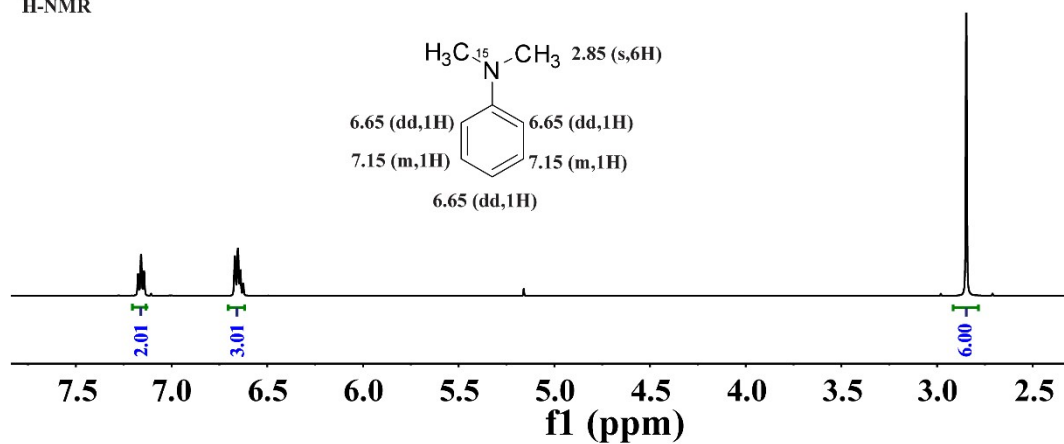


Figure S14. ¹H-nuclear magnetic resonance (NMR) spectroscopy of ¹⁵N-DMA. DMA: N,N-dimethylaniline.

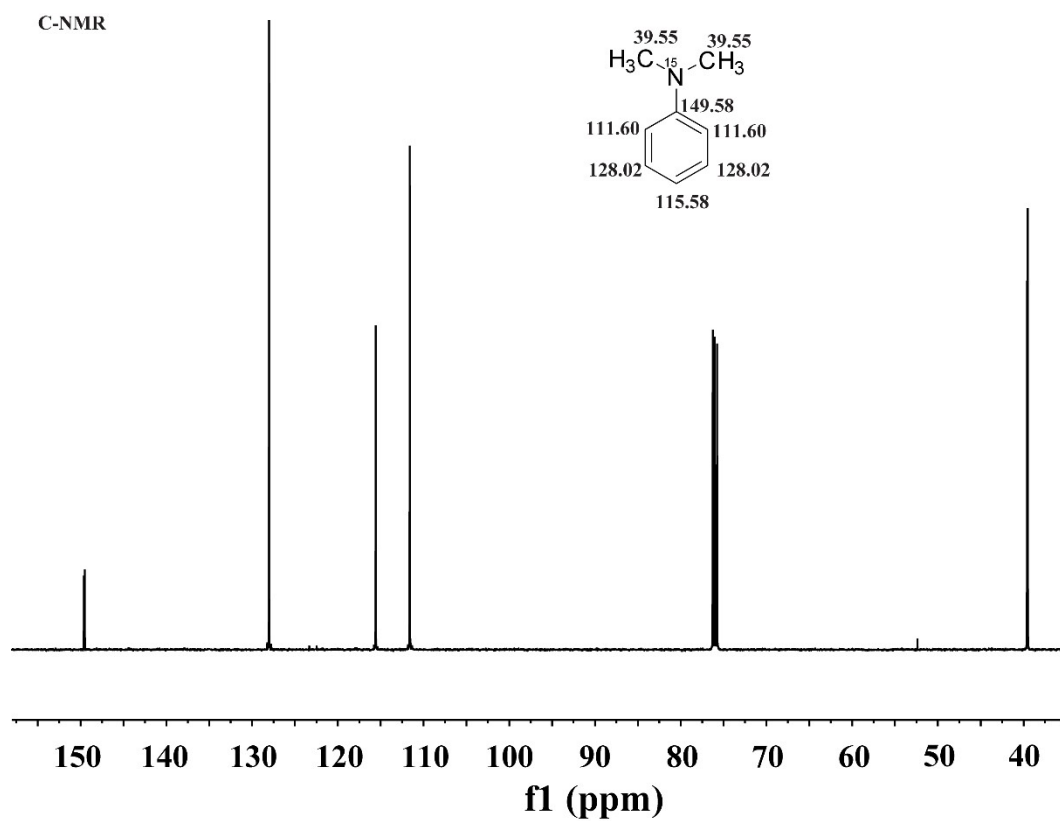


Figure S15. ¹³C-nuclear magnetic resonance (NMR) spectroscopy of ¹⁵N-DMA. DMA: N,N-dimethylaniline.

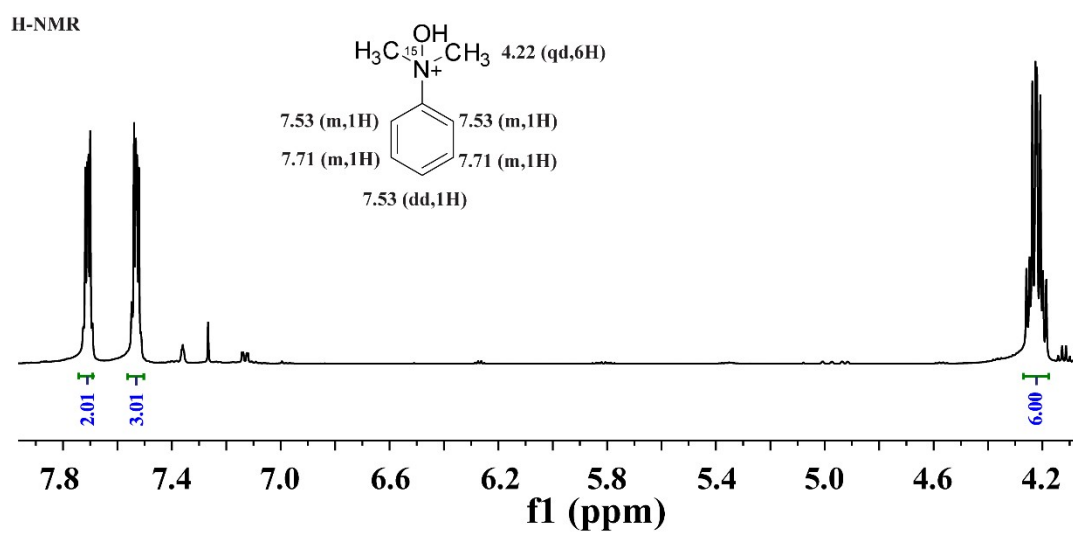


Figure S16. ¹H-nuclear magnetic resonance (NMR) spectroscopy of ¹⁵N-DMA-OH⁺. DMA: N,N-dimethylaniline.

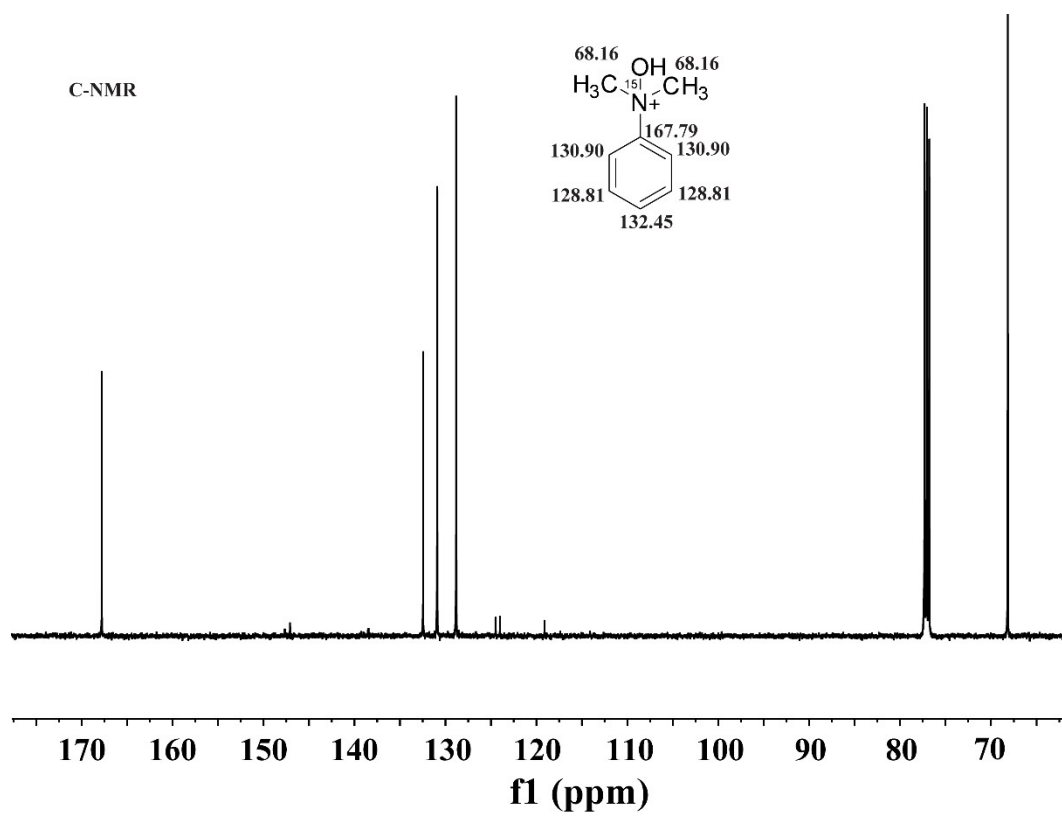


Figure S17. ¹³C-nuclear magnetic resonance (NMR) spectroscopy of ¹⁵N-DMA-OH⁺. DMA: N,N-dimethylaniline.

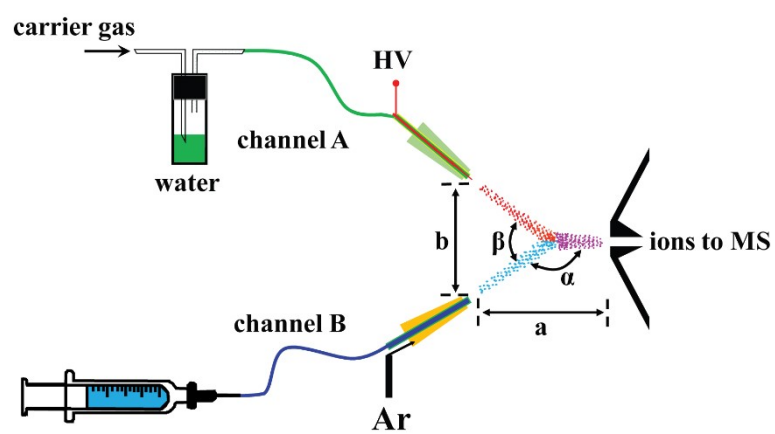


Figure S18. Schematic setup of low energy corona discharge ionization mass spectrometry. Ar: argon. MS: mass spectrometry. HV: high voltage.

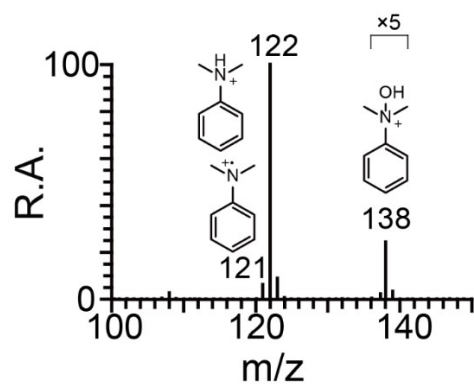


Figure S19. Mass spectrum of spraying N,N-dimethylaniline solution by low energy corona discharge ionization mass spectrometry. Relative abundance (R.A.).

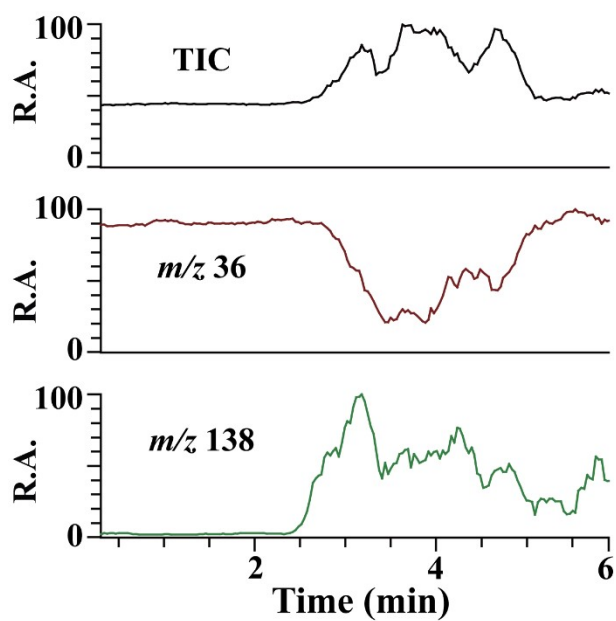


Figure S20. Typical total ion chromatogram (TIC) and extracted ion chromatogram showing reactant at m/z 36 and products m/z 138 before and after spraying N,N-dimethylaniline solution by low energy corona discharge ionization mass spectrometry (in Figure S13). Relative abundance (R.A.). Mass-to-charge (m/z).