

Supporting Information

Confined Surface-Enhanced Indole Cation-Radical Cyclization by Mass Spectrometry

Jianghui Sun, Hongwei Tan, Yixuan Gao, Jingjing Li, Juanjuan Wei, Shengxi Zhang, Jin Ouyang, Na Na*

Key Laboratory of Radiopharmaceuticals, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, China.

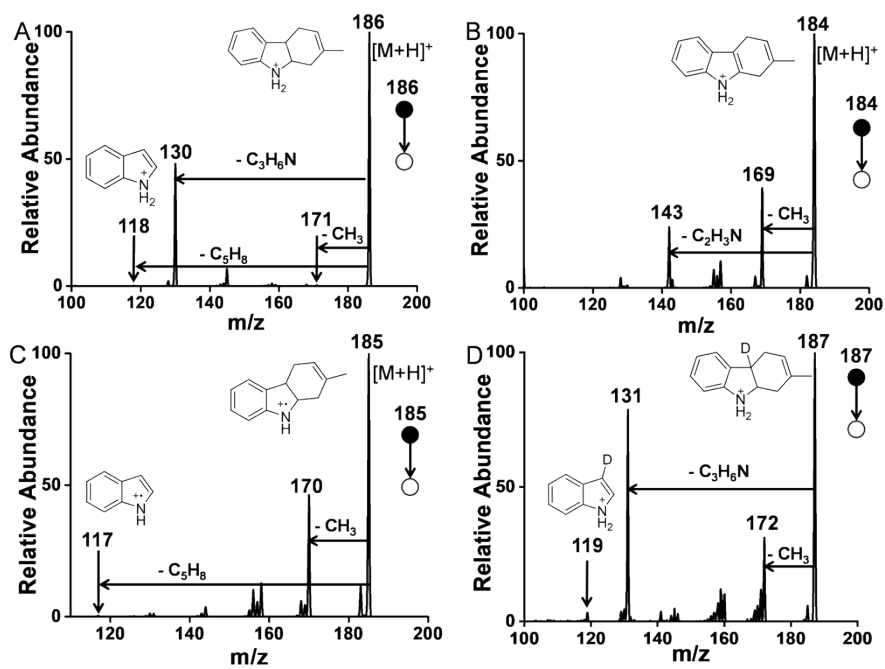


Figure S1. CID experiments to examine intermediates and product. (A) MS² CID of intermediate ion [3+H]⁺ at m/z 186. (B) MS² CID of product ion [4+H]⁺ at m/z 184. (C) MS² CID of intermediate ion 3⁺ ions at m/z 185. (D) MS² CID of [3-d₁+H]⁺ at m/z 187.

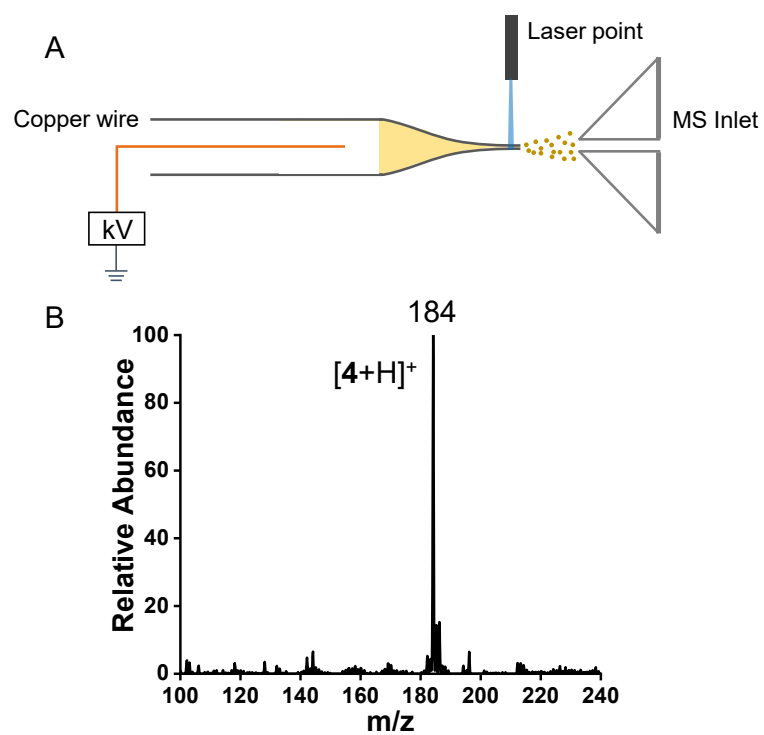


Figure S2. (A) Schematic diagram of inductive nESI. (B) Mass spectrometric analysis of Ru-catalyzed indole cation-radical cyclization in confined nanopipette using inductive nESI after reacting for 20 s.

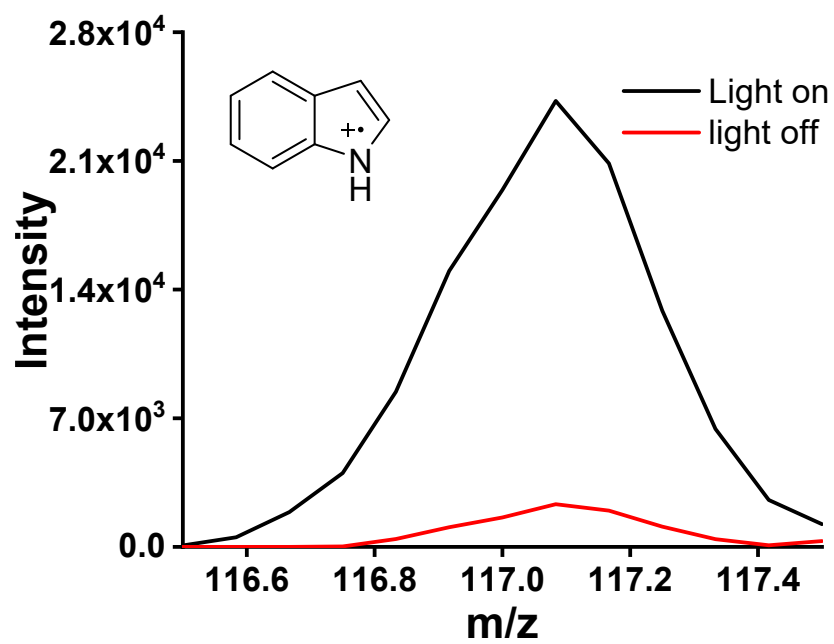


Figure S3. The formation of the cationic radical $1^{\bullet+}$.

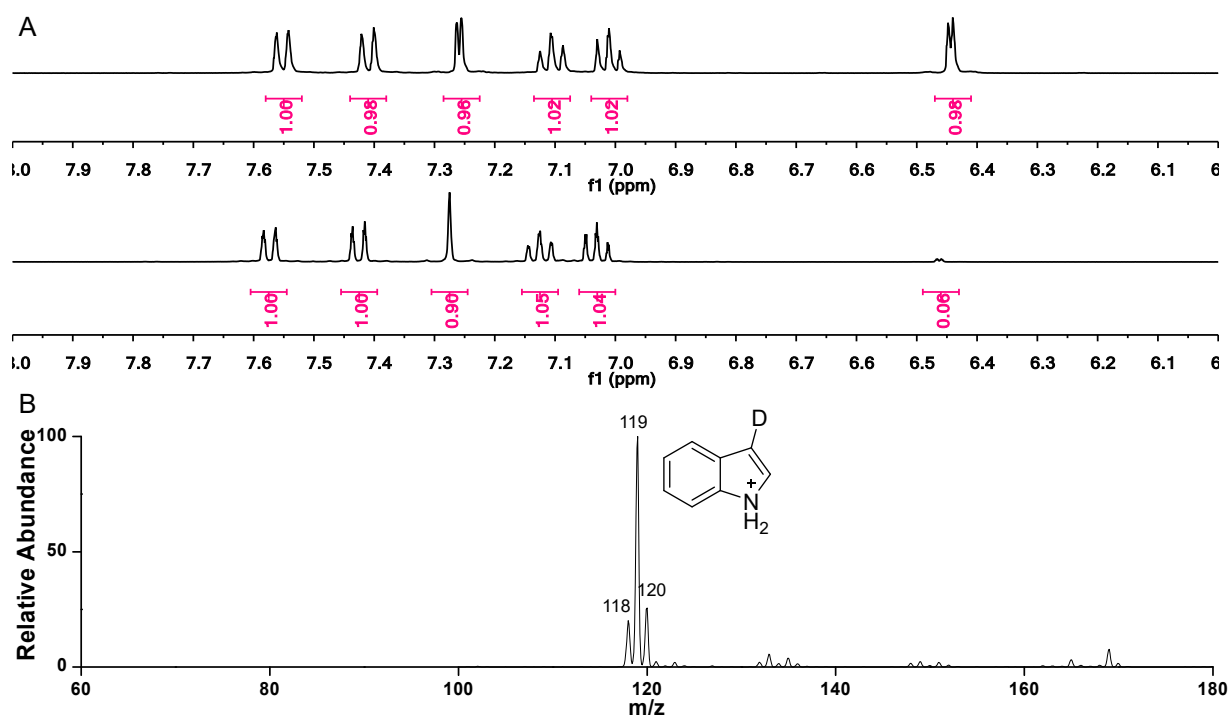


Figure S4. (A) ¹H NMR chart of indole (a) and indole-*d*₁ (b). (50% D₂O/CD₃OD, 400 MHz). (B) The mass spectra of indole-*d*₁.

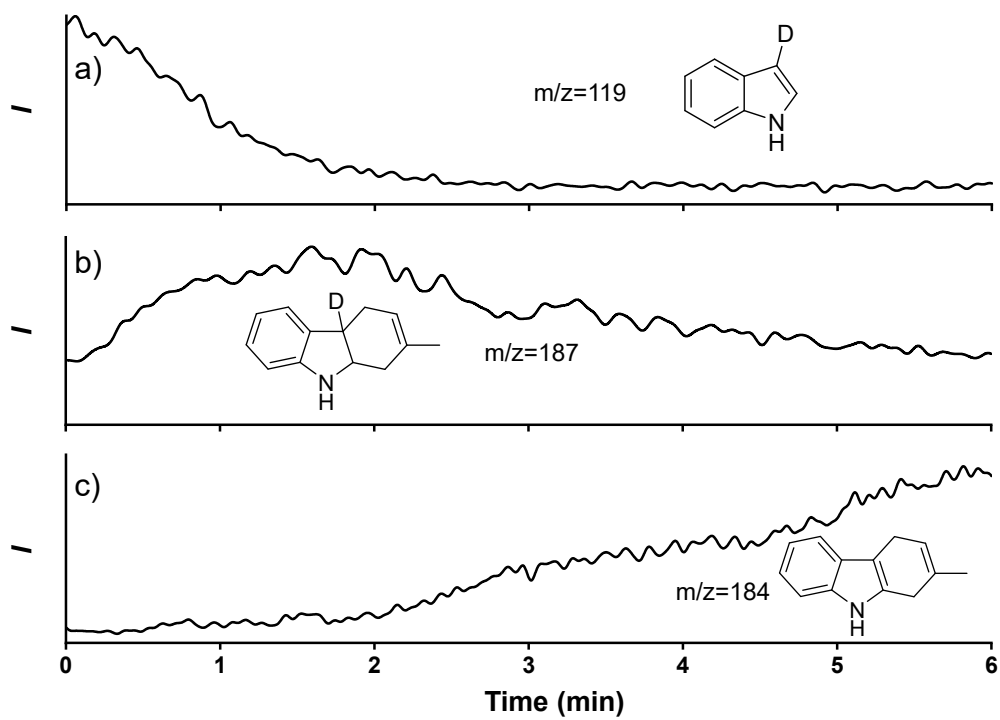


Figure S5. EICs of $[1-d_1+H]^+$ at m/z 118 (a), $[3-d_1+H]^+$ at m/z 187 (b), and $[4+H]^+$ at m/z 184 (c). I=Intensity

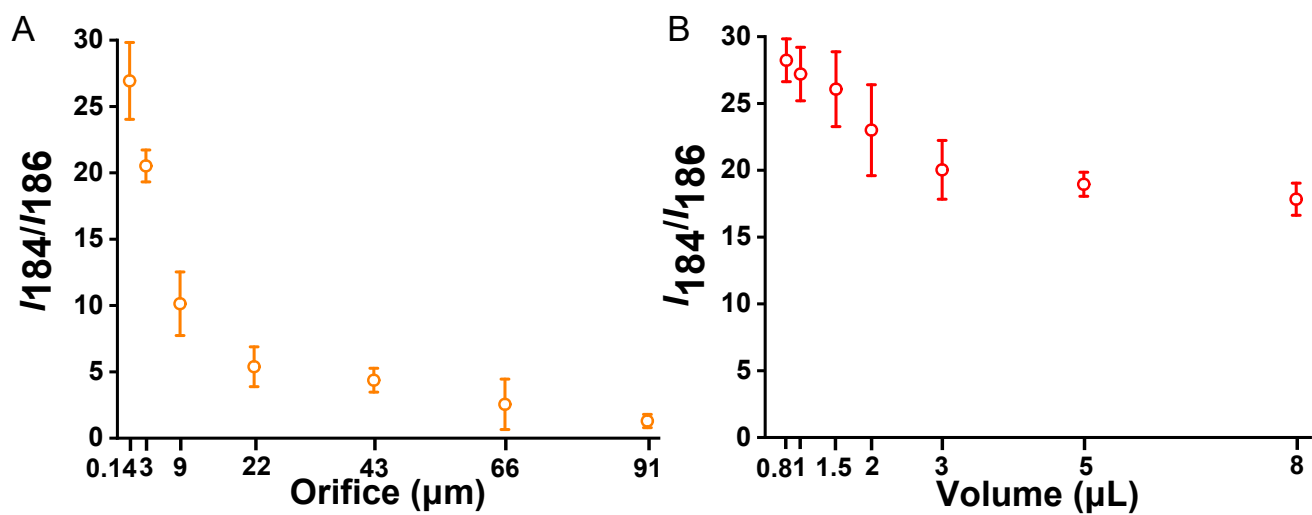


Figure S6. Optimization of the orifice size of the confined nanopipette (A) and the volume of the reaction system (B).

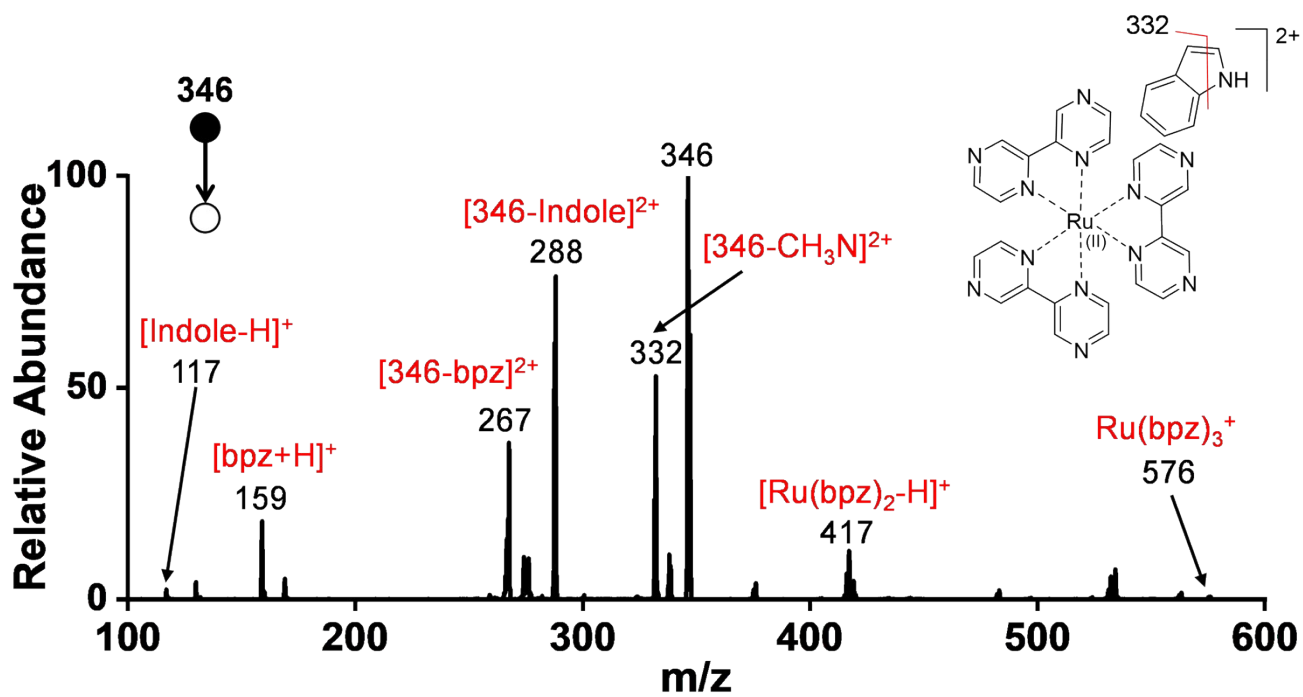


Figure S7. CID experiment to examine complex $[Ru(bpz)_3+1]^{2+}$ at m/z 346.

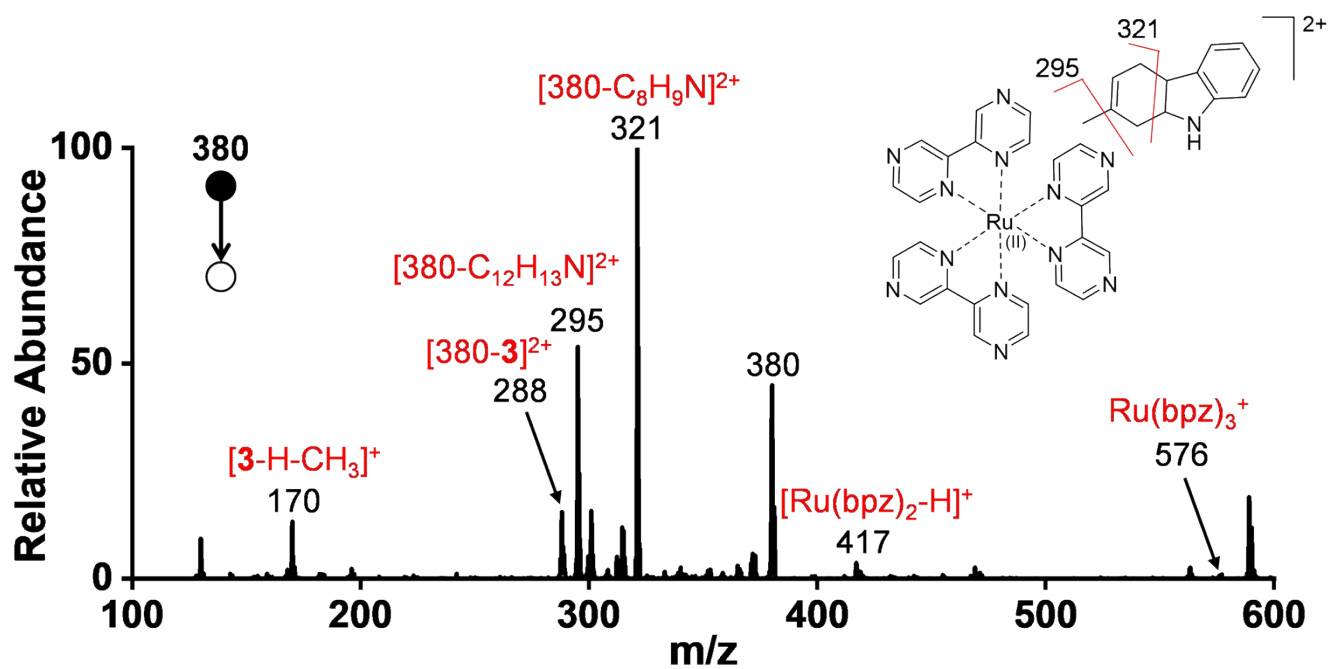


Figure S8. CID experiment to examine complex $[\text{Ru}(\text{bpz})_3+3]^{2+}$ at m/z 380.

Table S1. The possible transformations of the electronic states of ruthenium, indole and intermediate **3**

	[Ru(bpz) ₃] ²⁺	[Ru(bpz) ₃] ⁺	Reactant 1	Cationic radical 1 ^{•+}	Intermediate 3	Cationic radical 3 ^{•+}
Energy (Ha)	-1675.75613	-1676.13348	-363.82202	-363.54316	-557.59426	-557.33829

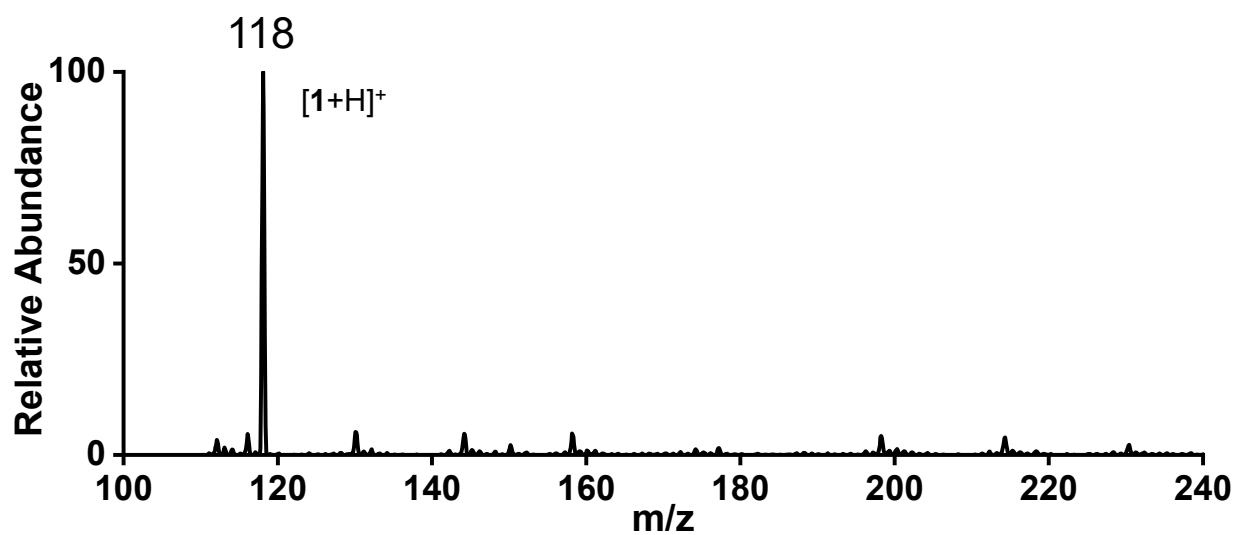


Figure S9. Mass spectrometric analysis of Ru-catalyzed indole cation-radical cyclization in silanized nanopipette after 20 s.

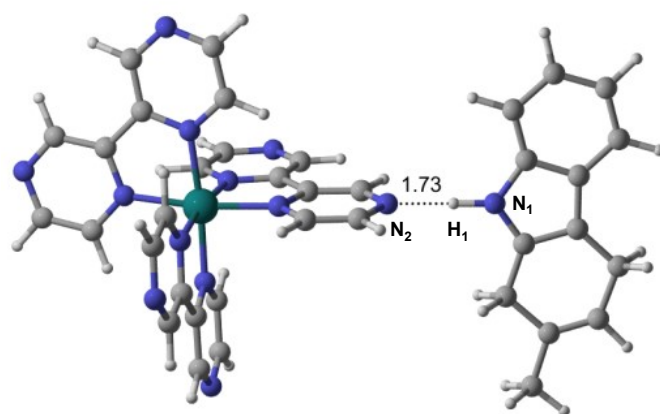


Figure S10. Calculated structure of complex $[\text{Ru}(\text{bpz})_3+3]^{2+}$.