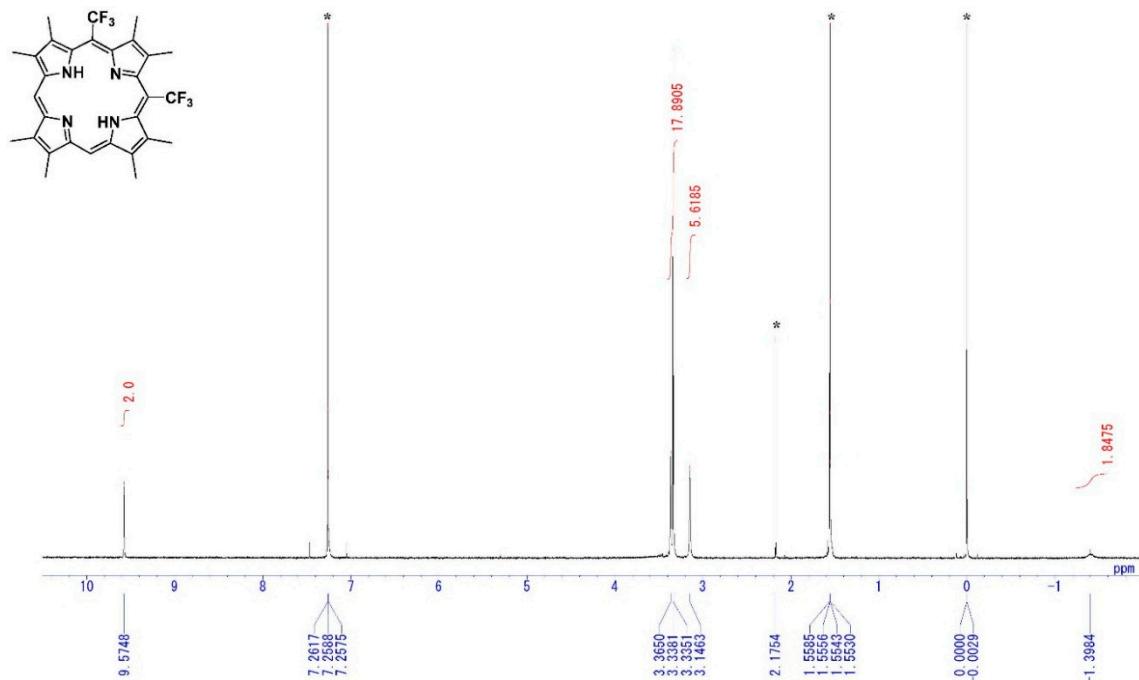
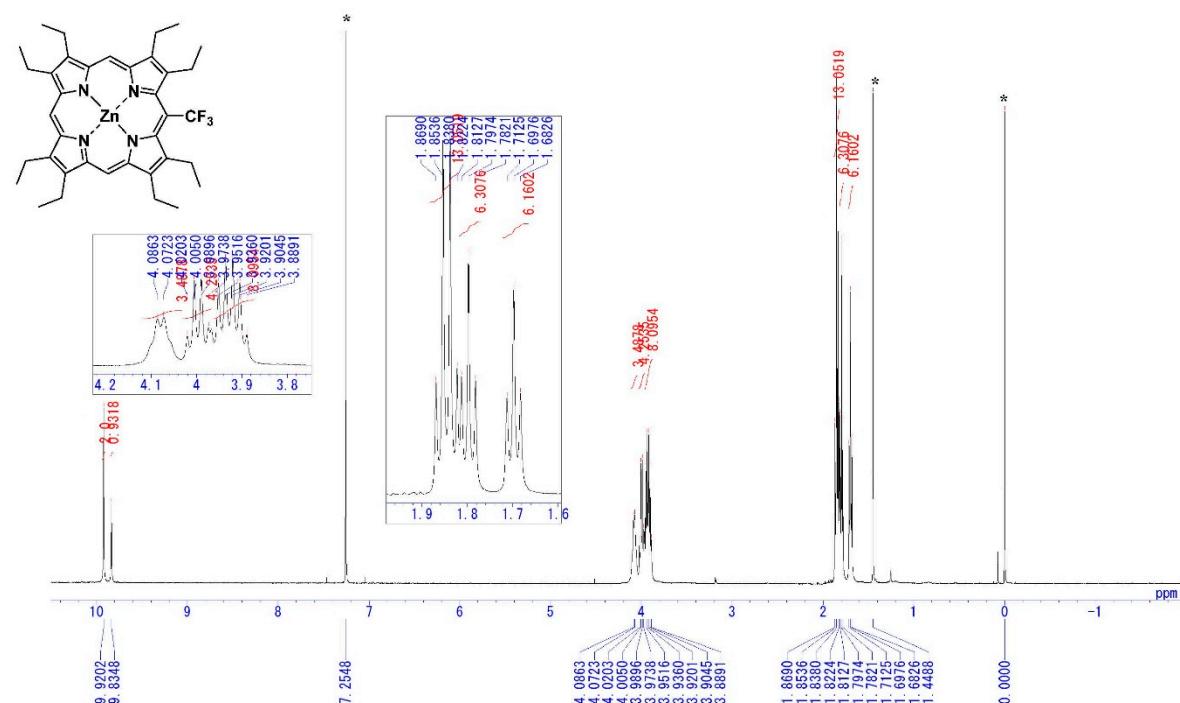


# Supplementary Materials: Synthesis of 5,10-bis(Trifluoromethyl) Substituted $\beta$ -Octamethylporphyrins and Central-Metal-Dependent Solvolysis of their *meso*-trifluoromethyl Groups

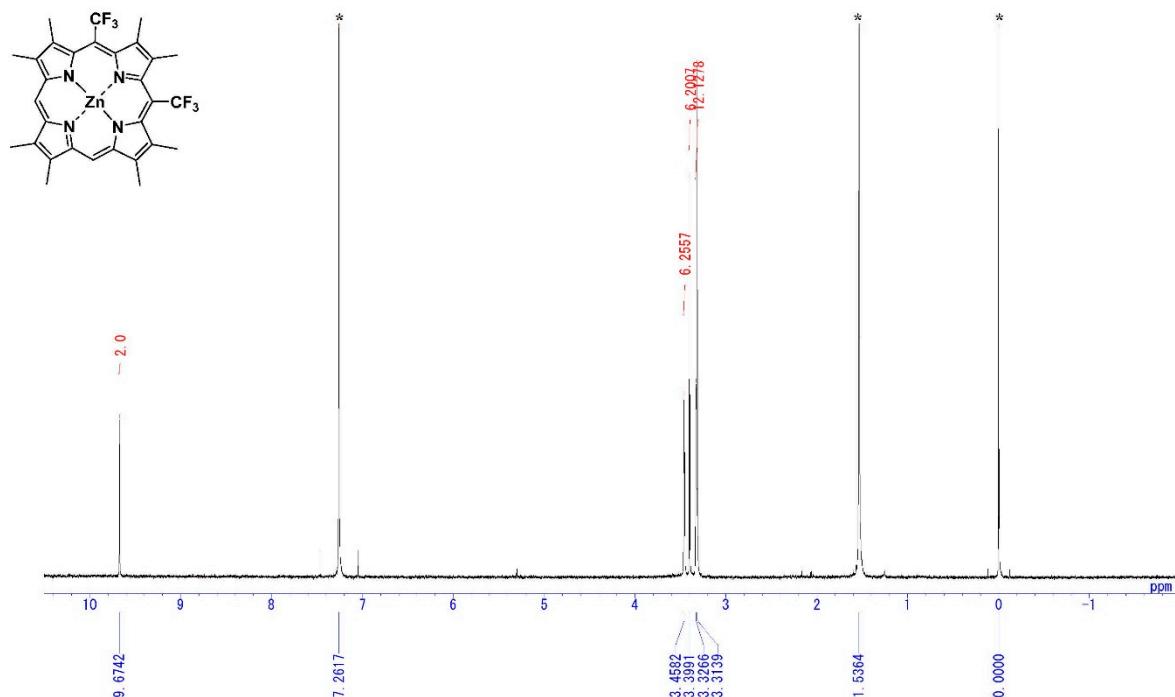
Masaaki Suzuki <sup>1,2,\*</sup>, Saburo Neya <sup>2</sup> and Yutaka Nishigaichi <sup>1</sup>



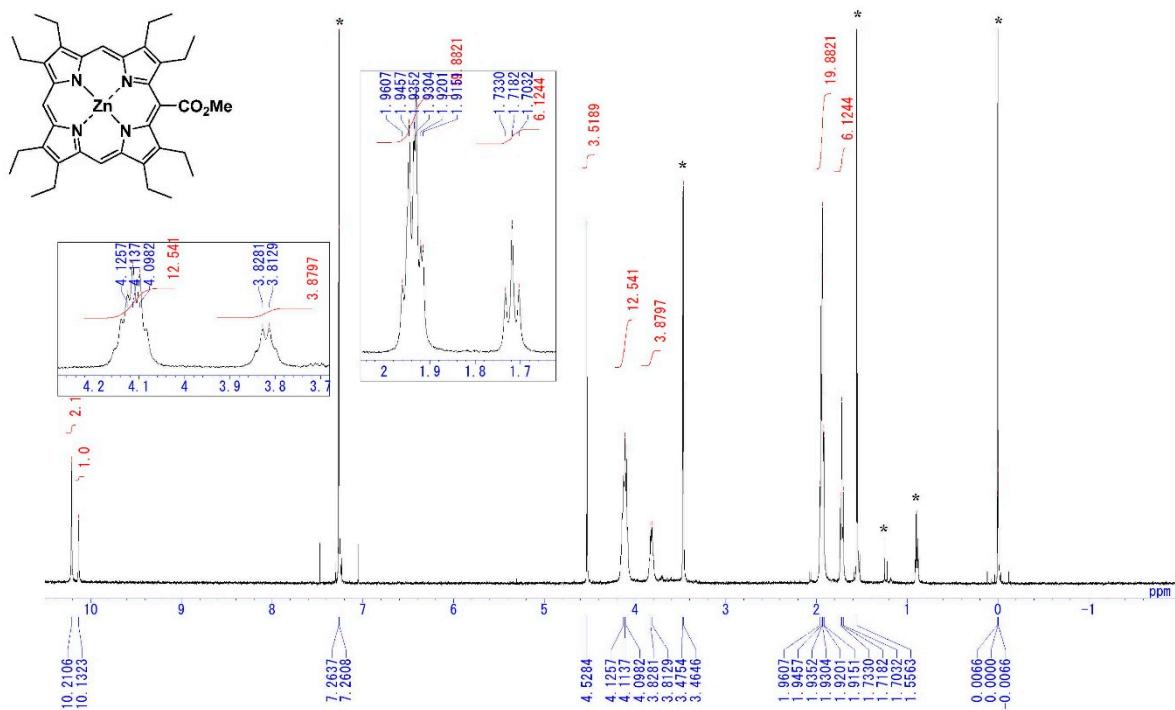
**Figure S1.**  $^1\text{H}$  NMR spectrum of **9** in  $\text{CDCl}_3$ . \*: solvent and impurity.



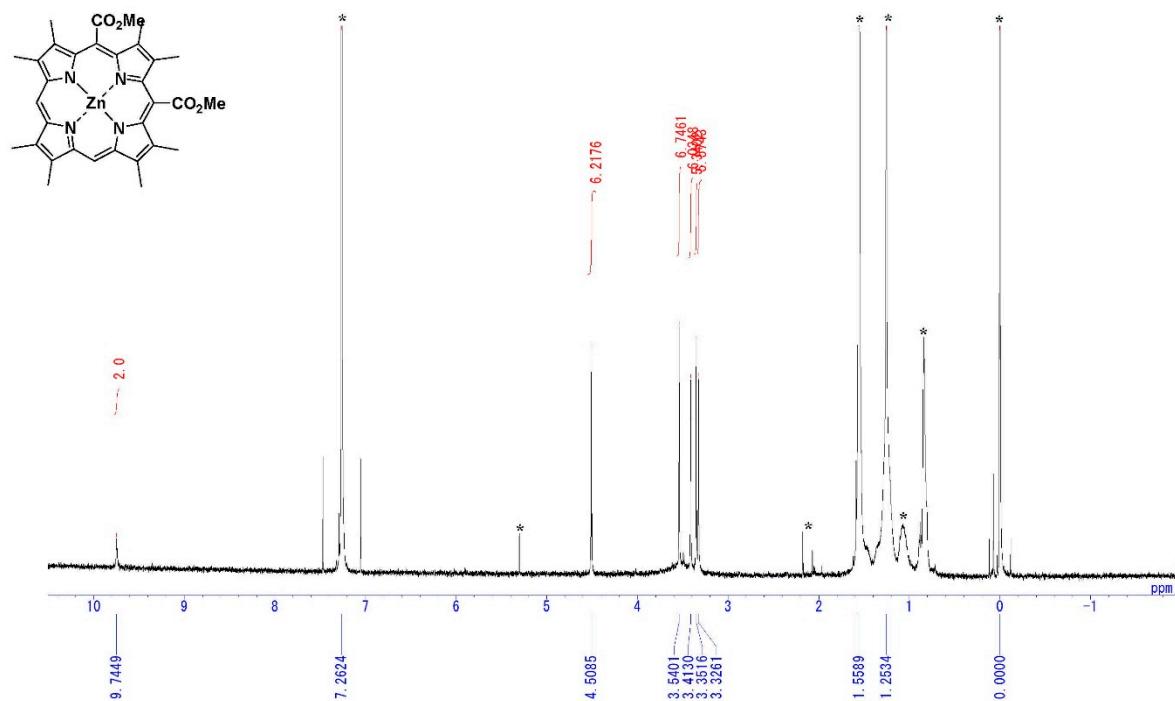
**Figure S2.**  $^1\text{H}$  NMR spectrum of **7Zn** in  $\text{CDCl}_3$ . \*: solvent and impurity.



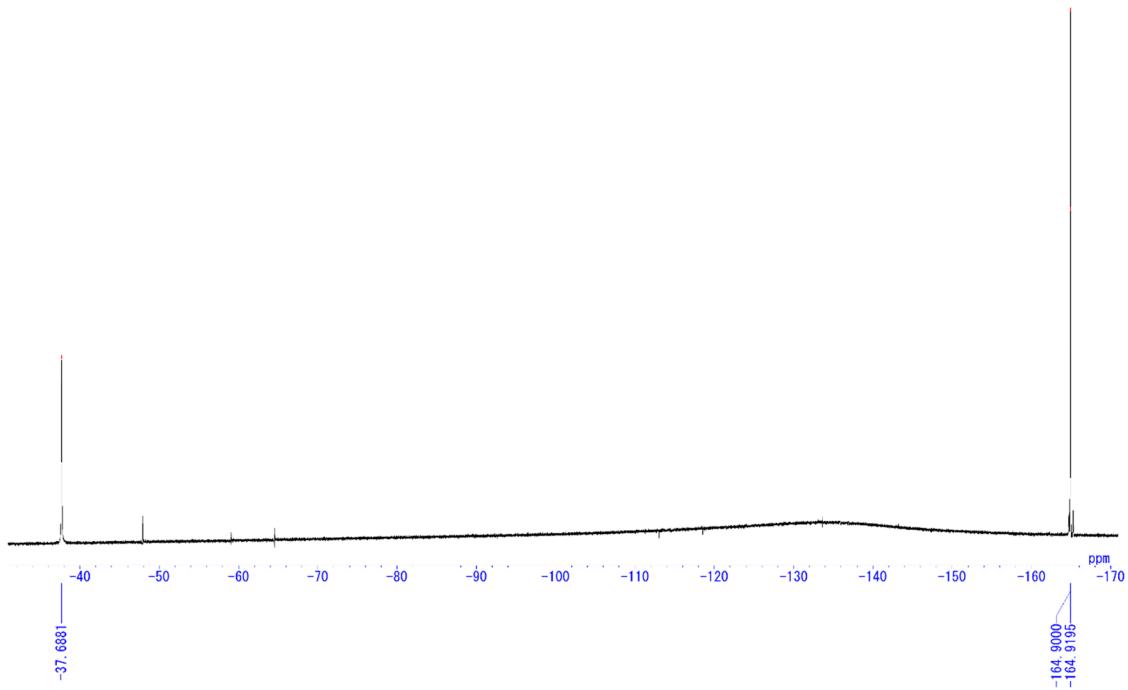
**Figure S3.**  $^1\text{H}$  NMR spectrum of **9Zn** in  $\text{CDCl}_3$ . \*: solvent and impurity.



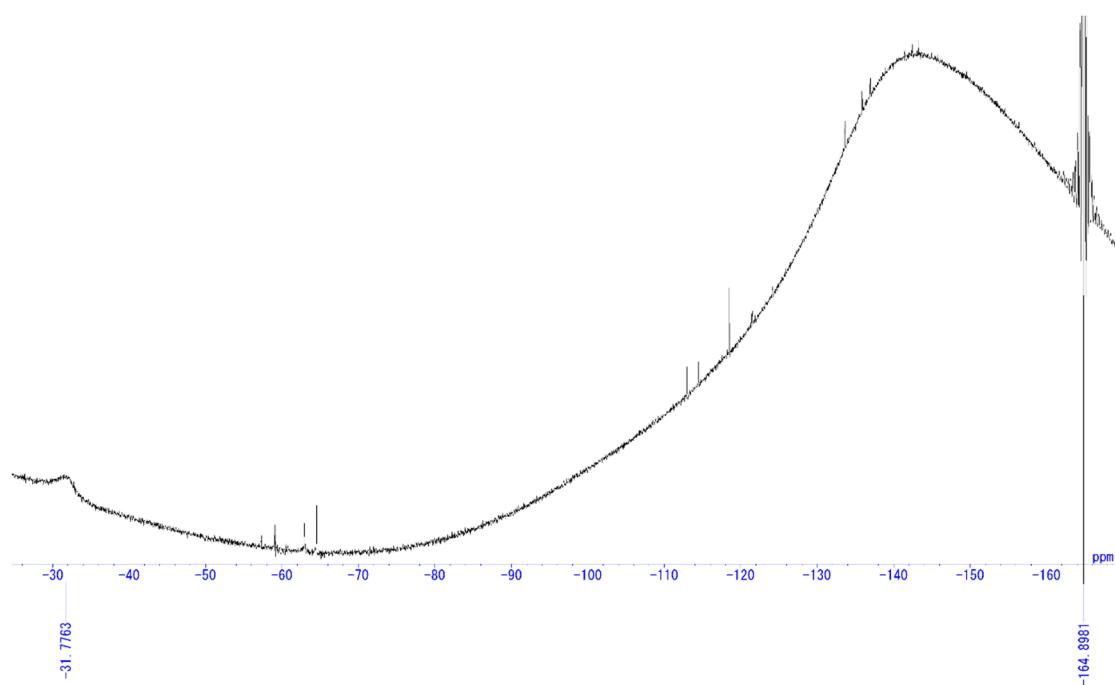
**Figure S4.**  $^1\text{H}$  NMR spectrum of **11Zn** in  $\text{CDCl}_3$ . \*: solvent and impurity.



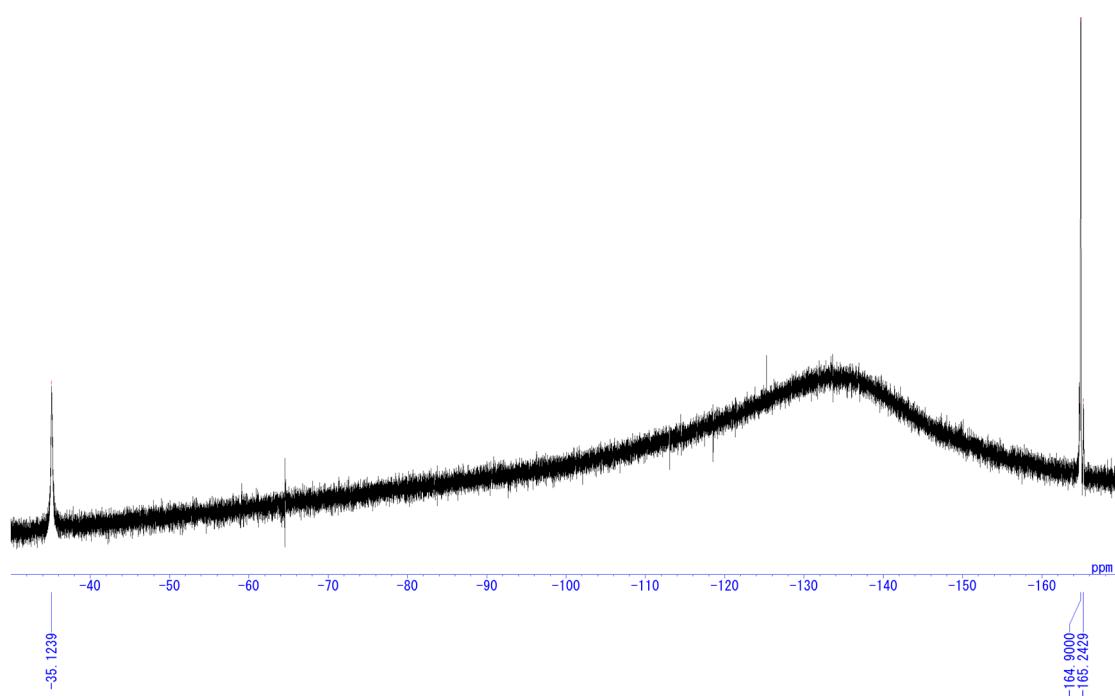
**Figure S5.** <sup>1</sup>H NMR spectrum of **12Zn** in CDCl<sub>3</sub>. \*: solvent and impurity.



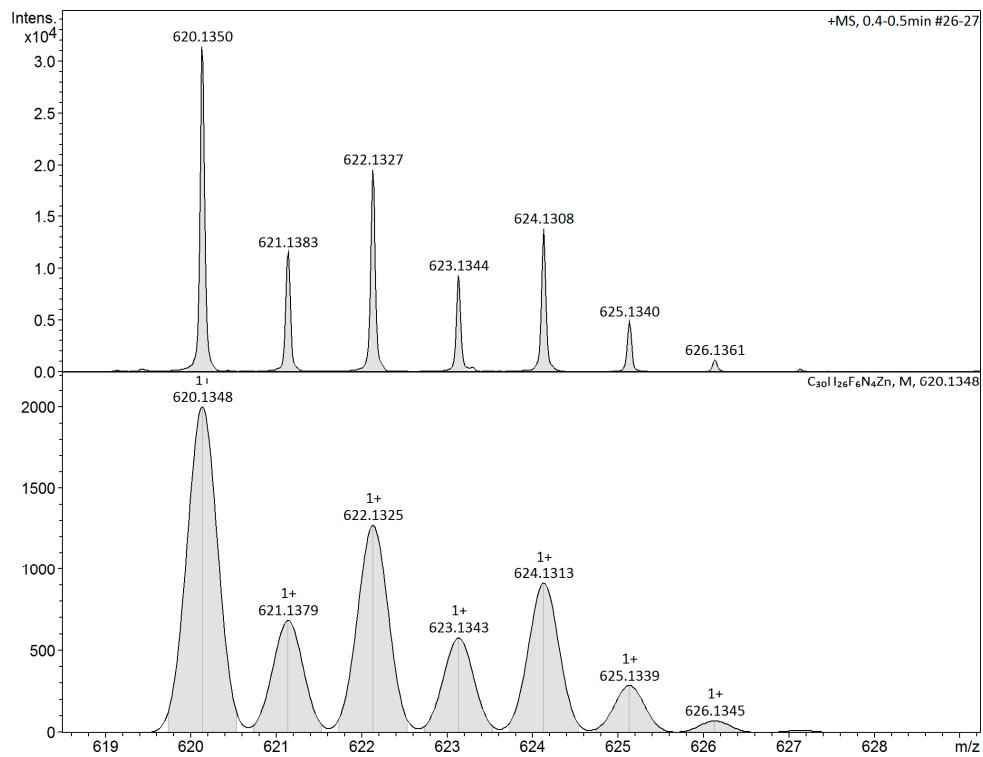
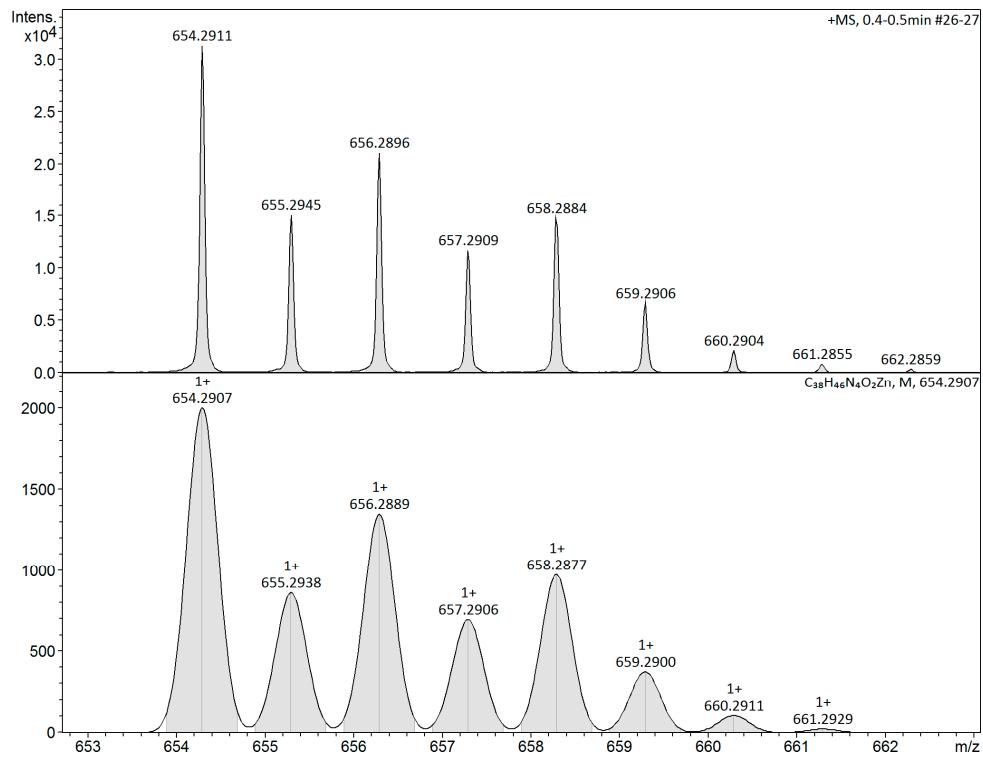
**Figure S6.** <sup>19</sup>F NMR spectrum of **9** in CDCl<sub>3</sub>.

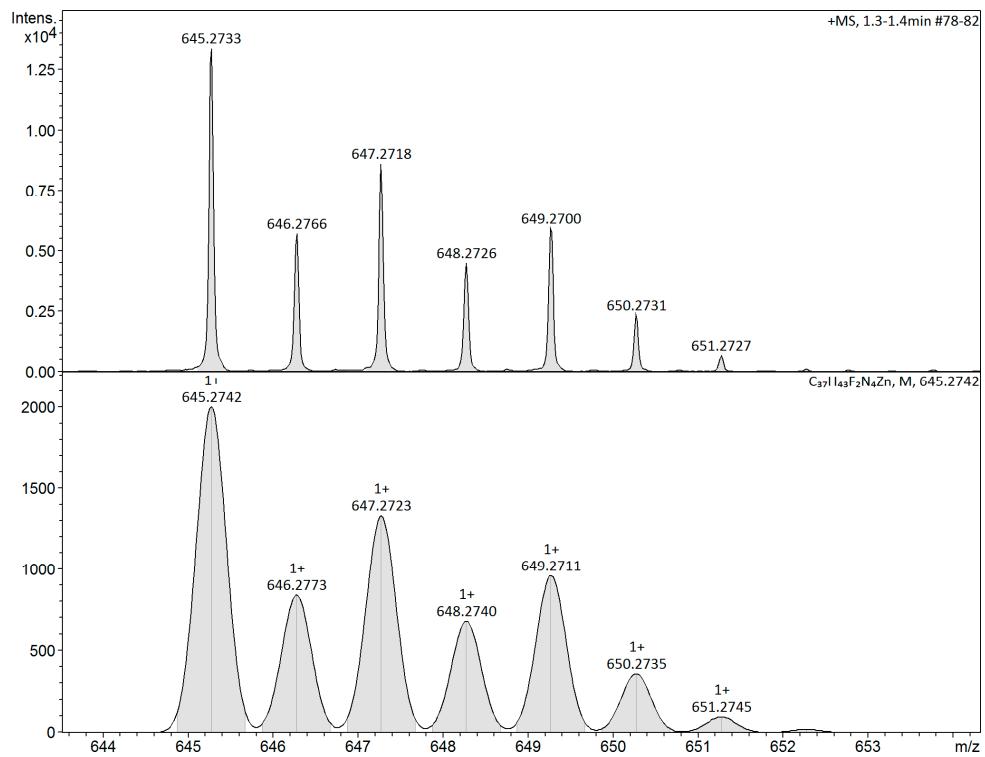
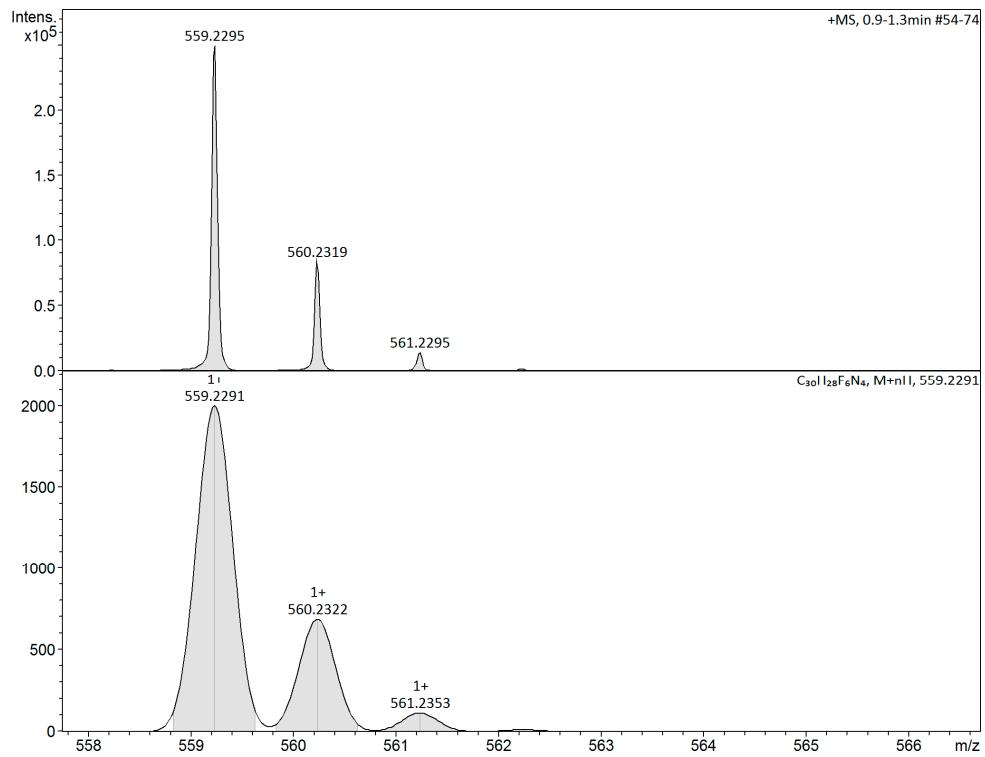


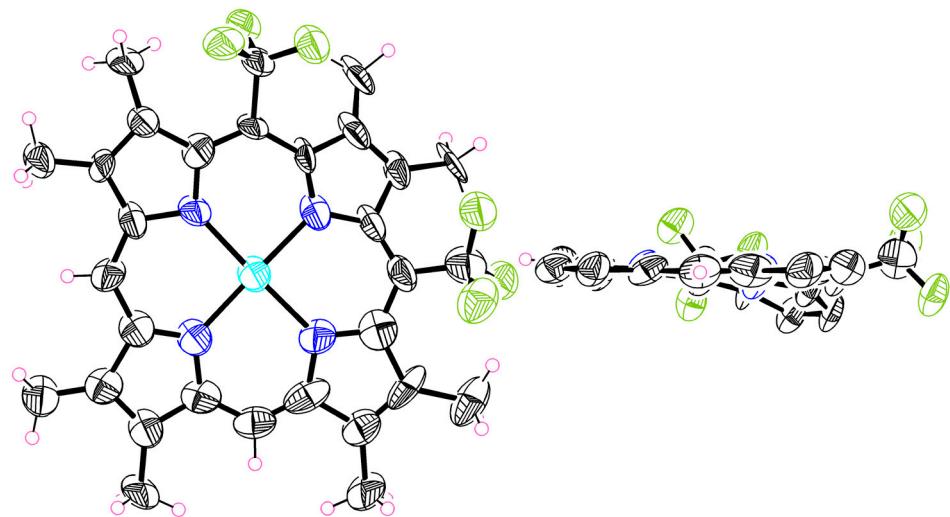
**Figure S7.** <sup>19</sup>F NMR spectrum of **7Zn** in  $\text{CDCl}_3$ .



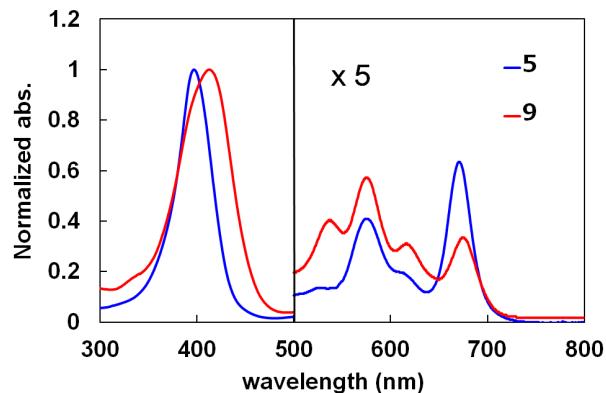
**Figure S8.** <sup>19</sup>F NMR spectrum of **9Zn** in  $\text{CDCl}_3$ .

**Figure S9.** HR-ESI mass spectrum of **9**. Upper: found, lower: calcd.**Figure S10.** HR-ESI mass spectrum of **7Zn**. Upper: found, lower: calcd.

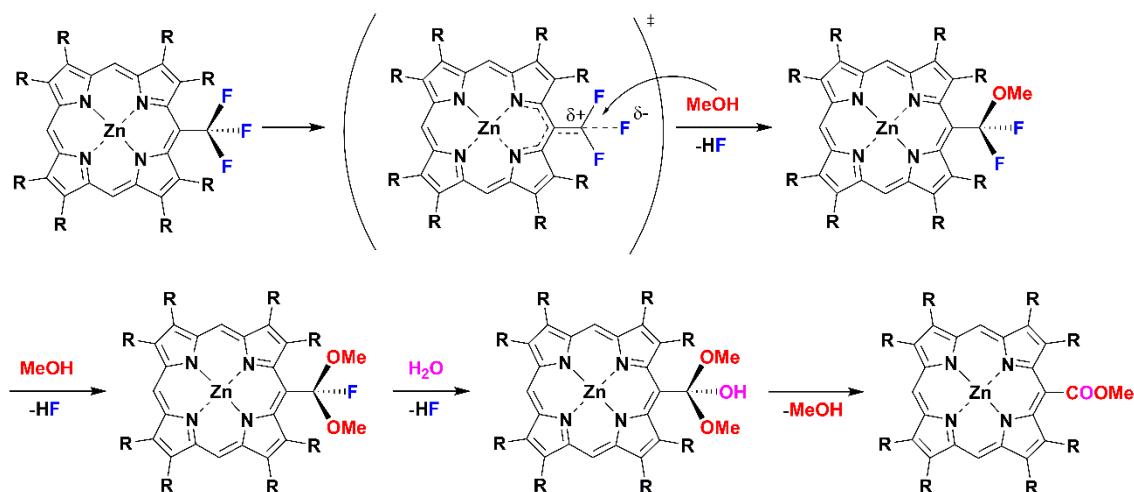
**Figure S11.** HR-ESI mass spectrum of **9Zn**. Upper: found, lower: calcd.**Figure S12.** HR-ESI mass spectrum of **11Zn**. Upper: found, lower: calcd.



**Figure S13.** Preliminary crystal structure of **9Zn**. Left: top view; right: side view. The  $\beta$ -methyl substituents are omitted for clarity in the side view. Thermal ellipsoids are set at the 50% probability level.



**Figure S14.** Comparison between UV-vis spectrum of **5** and that of **9** in  $\text{CH}_2\text{Cl}_2$ .



**Scheme S1.** A proposed mechanism of solvolysis.