

## Supplementary Material

### Ruthenium-Cyclopentadienyl-Cycloparaphenylene Complexes: Sizable Multicharged Cations Exhibiting High DNA-Binding Affinity and Remarkable Cytotoxicity

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**FIGURE S1.** <sup>1</sup>H NMR spectrum of complex  $[(\eta^6\text{-[11]CPP})[\text{Ru}(\eta^5\text{-Cp})]_{11}](\text{PF}_6)_{11}$  (**3**) in acetone- $\text{d}_6$ .

**FIGURE S2.** HR-ESI-MS spectrum of complex  $[(\eta^6\text{-[11]CPP})[\text{Ru}(\eta^5\text{-Cp})]_{11}](\text{PF}_6)_{11}$  (**3**).

**FIGURE S3.** Stern–Volmer plots for the interaction of  $[(\eta^6\text{-[12]CPP})[\text{Ru}(\eta^5\text{-Cp})]_{12}]\text{Cl}_{12}$  with d(5'-CGCGAATTCGCG-3')<sub>2</sub>-EtBr at 298 K.

**FIGURE S4.** The double-log plots of  $[(\eta^6\text{-[12]CPP})[\text{Ru}(\eta^5\text{-Cp})]_{12}]\text{Cl}_{12}$  fluorescence quenching effect, on d(5'-CGCGAATTCGCG-3')<sub>2</sub>-EtBr at 298 K.

**FIGURE S5.** <sup>1</sup>H NMR spectrum of **3p** in  $\text{CD}_2\text{Cl}_2$ .

**FIGURE S6.** HR-ESI-MS spectrum of **3p**.

**FIGURE S7.** <sup>1</sup>H NMR spectrum of [11]CPP in acetone- $\text{d}_6$ .

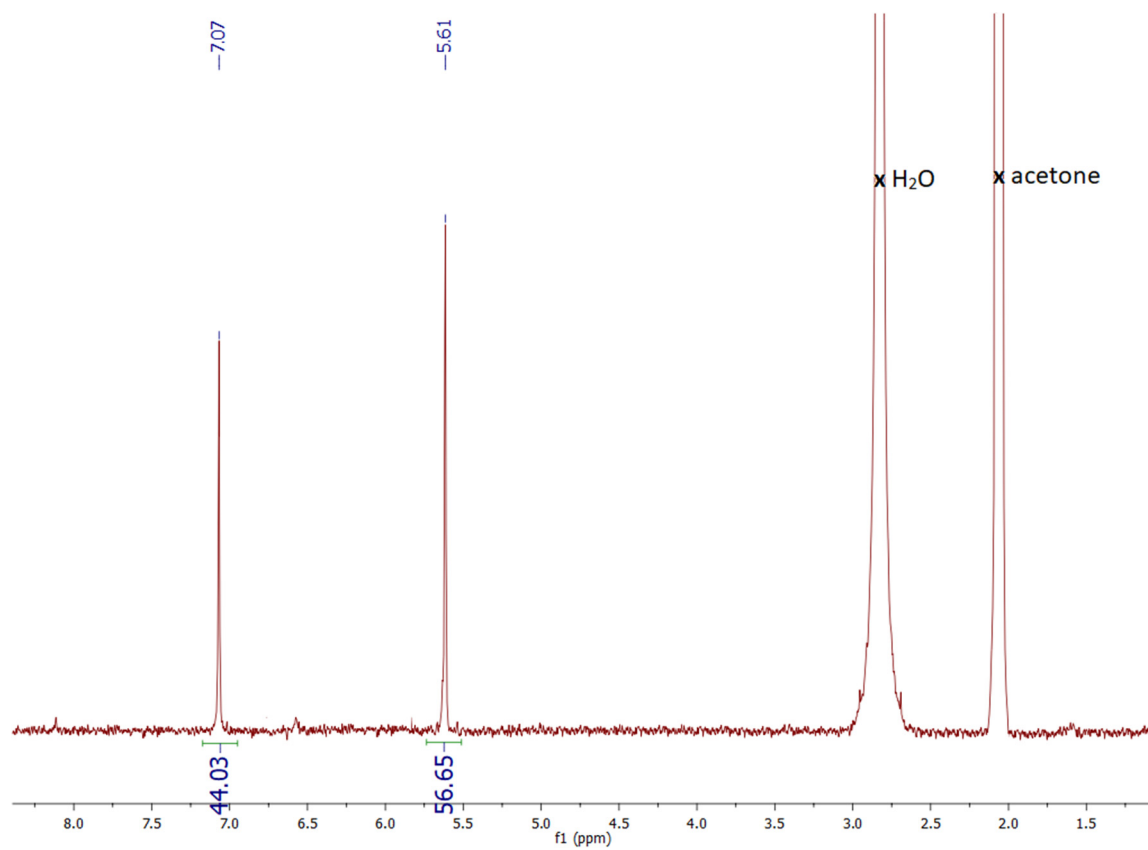
**FIGURE S7.** <sup>1</sup>H NMR spectrum of [11]CPP in acetone- $\text{d}_6$ .

**FIGURE S8.** <sup>1</sup>H NMR spectrum of (**2**) in  $\text{D}_2\text{O}$  after 48h and 72h.

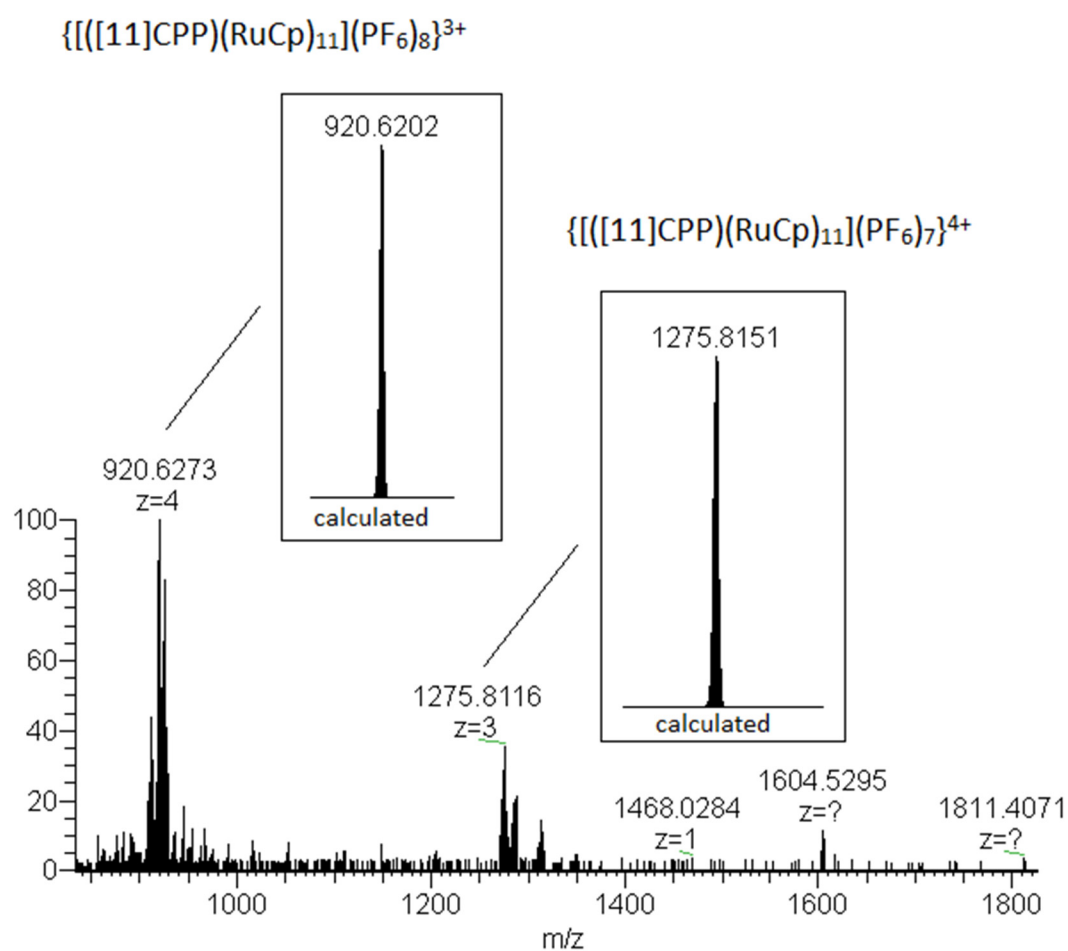
**FIGURE S9.** <sup>1</sup>H NMR spectrum of (**4**) in  $\text{D}_2\text{O}$  after 48h and 72h.

**FIGURE S10.** HR-ESI-MS spectrum of (**2**).

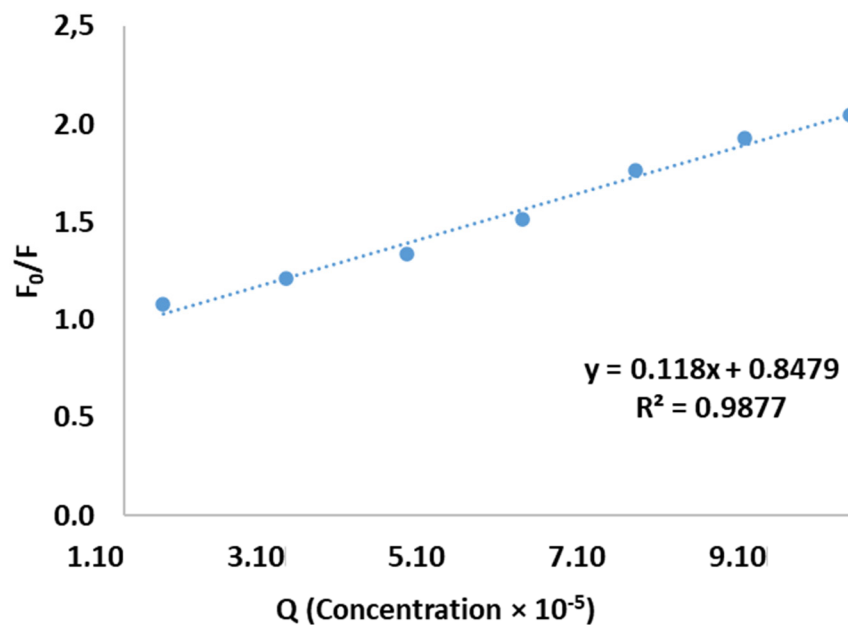
**FIGURE S11.** HR-ESI-MS spectrum of (**4**).



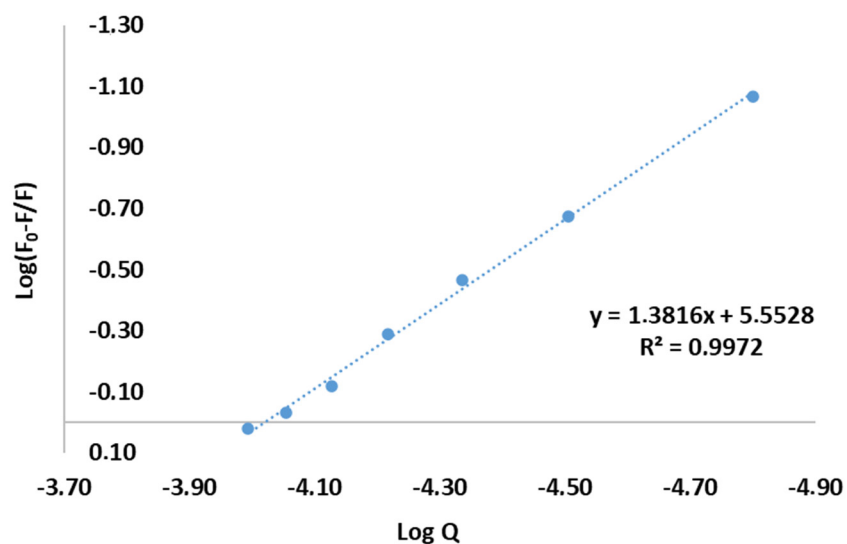
**FIGURE S1.**  $^1\text{H}$  NMR spectrum of complex  $[(\eta^6\text{-[11]CPP})[\text{Ru}(\eta^5\text{-Cp})]_{11}](\text{PF}_6)_{11}$  (**3**) in acetone- $\text{d}_6$ .



**FIGURE S2.** HR-ESI-MS spectrum of complex  $[(\eta^6\text{-}[11]CPP)[Ru(\eta^5\text{-Cp})]_{11}](PF_6)_{11}$  (**3**)



**FIGURE S3.** Stern–Volmer plots for the interaction of  $[(\eta^6\text{-[12]CPP})[\text{Ru}(\eta^5\text{-Cp})]_{12}]\text{Cl}_{12}$  with d(5'-CGCGAATTCGCG-3')<sub>2</sub>-EtBr at 298 K



**FIGURE S4.** The double-log plots of  $[(\eta^6\text{-[12]CPP})[\text{Ru}(\eta^5\text{-Cp})]_{12}]\text{Cl}_{12}$  fluorescence quenching effect, on d(5'-CGCGAATTCGCG-3')<sub>2</sub>-EtBr at 298 K.

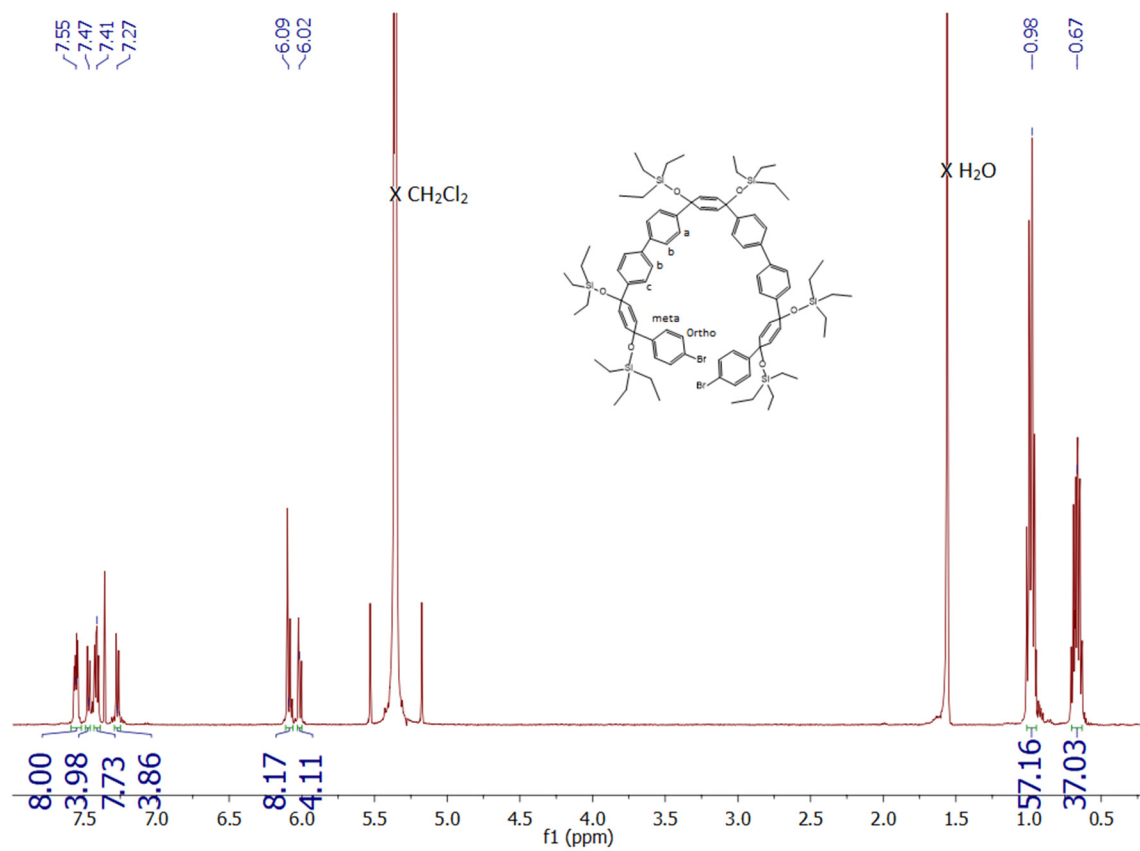
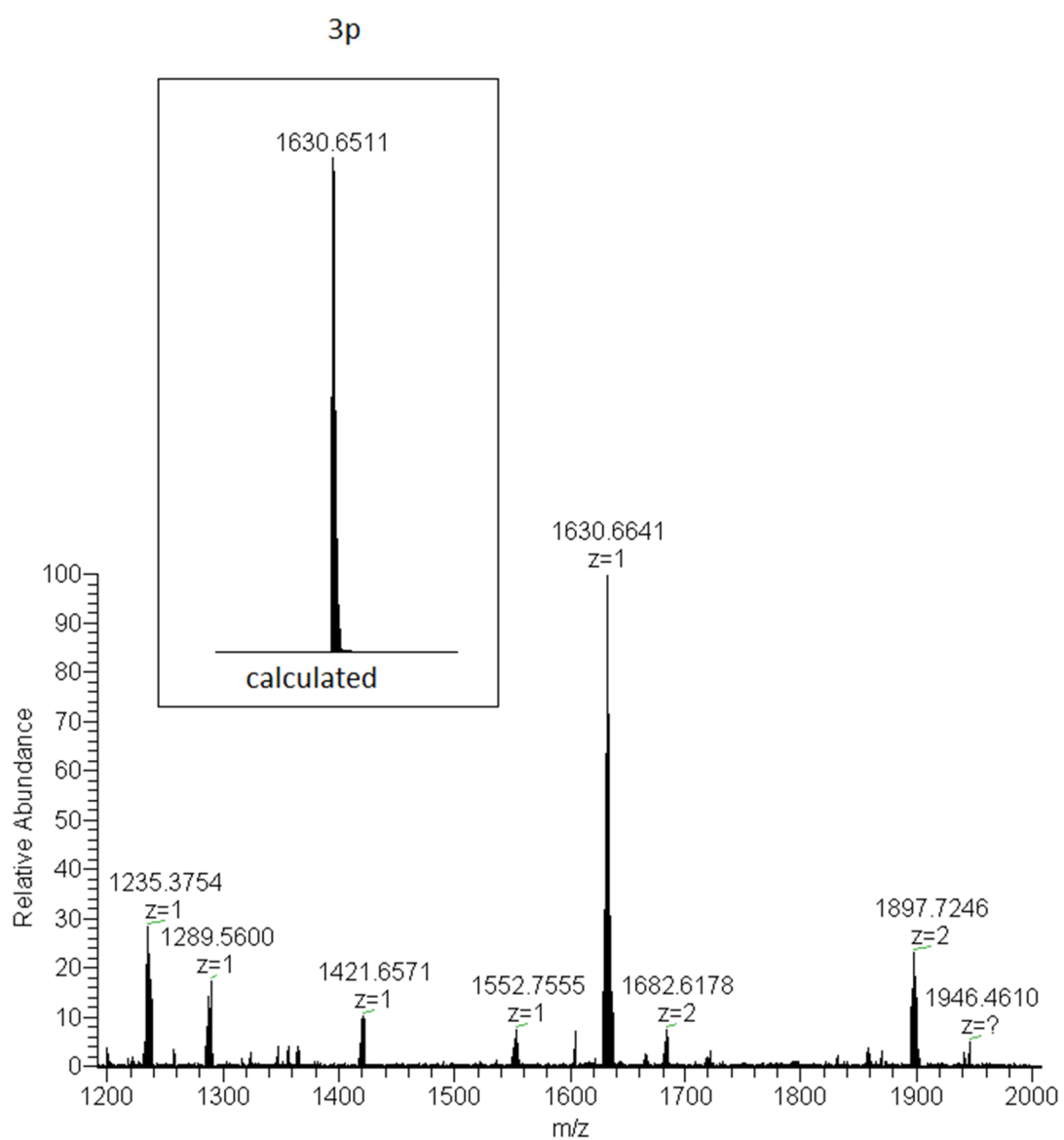
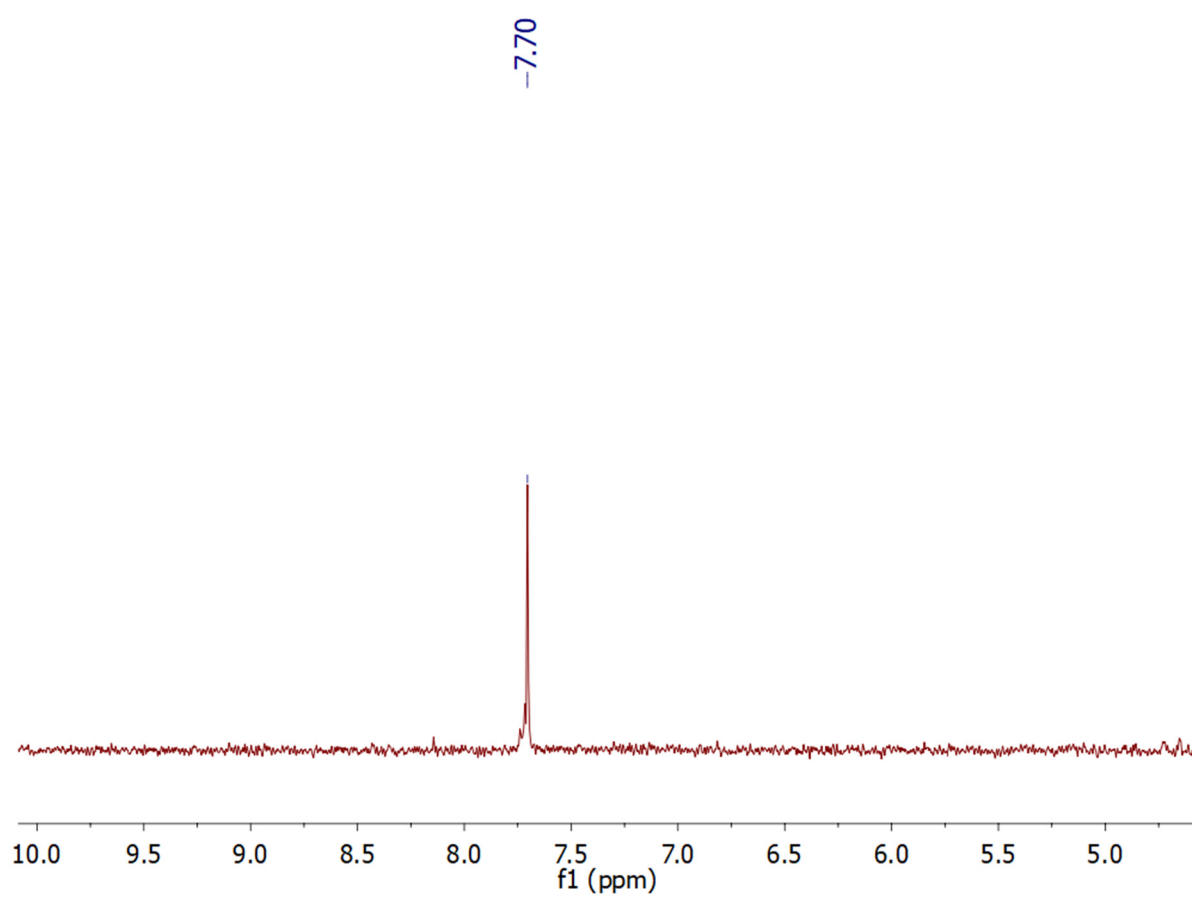


FIGURE S5. <sup>1</sup>H NMR spectrum of **3p** in CD<sub>2</sub>Cl<sub>2</sub>.

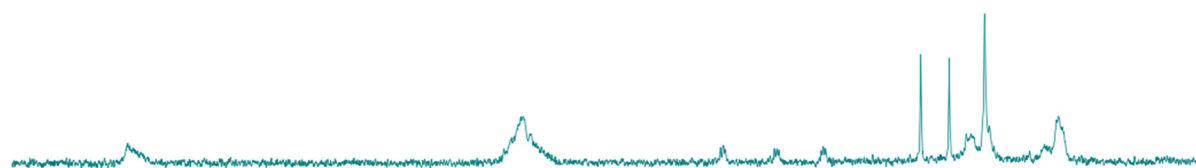


**FIGURE S6.** HR-ESI-MS spectrum of **3p**.

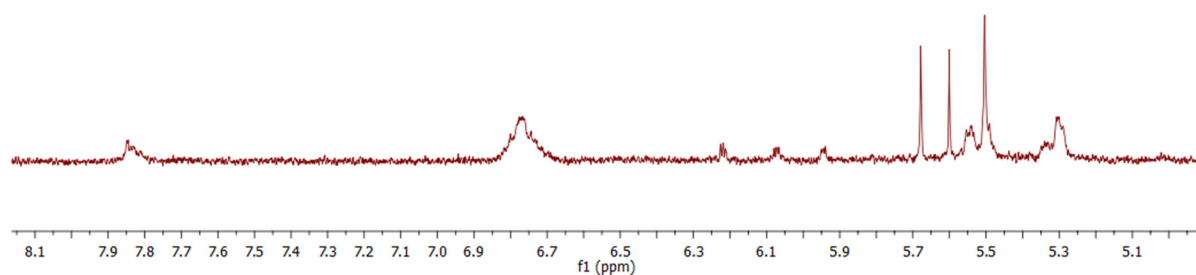


**FIGURE S7.**  $^1\text{H}$  NMR spectrum of [11]CPP in acetone- $\text{d}_6$ .

(a) 48 h



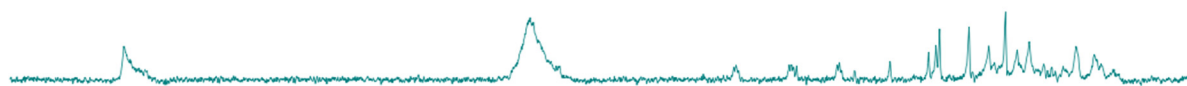
(b) 72 h



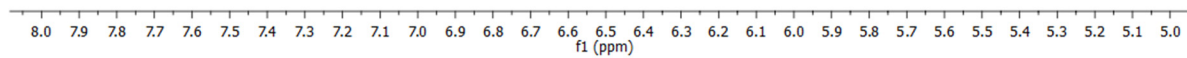
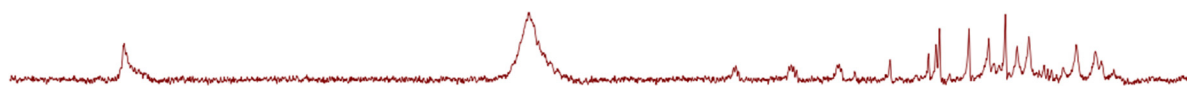
**FIGURE S8.**  $^1\text{H}$  NMR spectrum of (**2**) in  $\text{D}_2\text{O}$  after 48h and 72h.



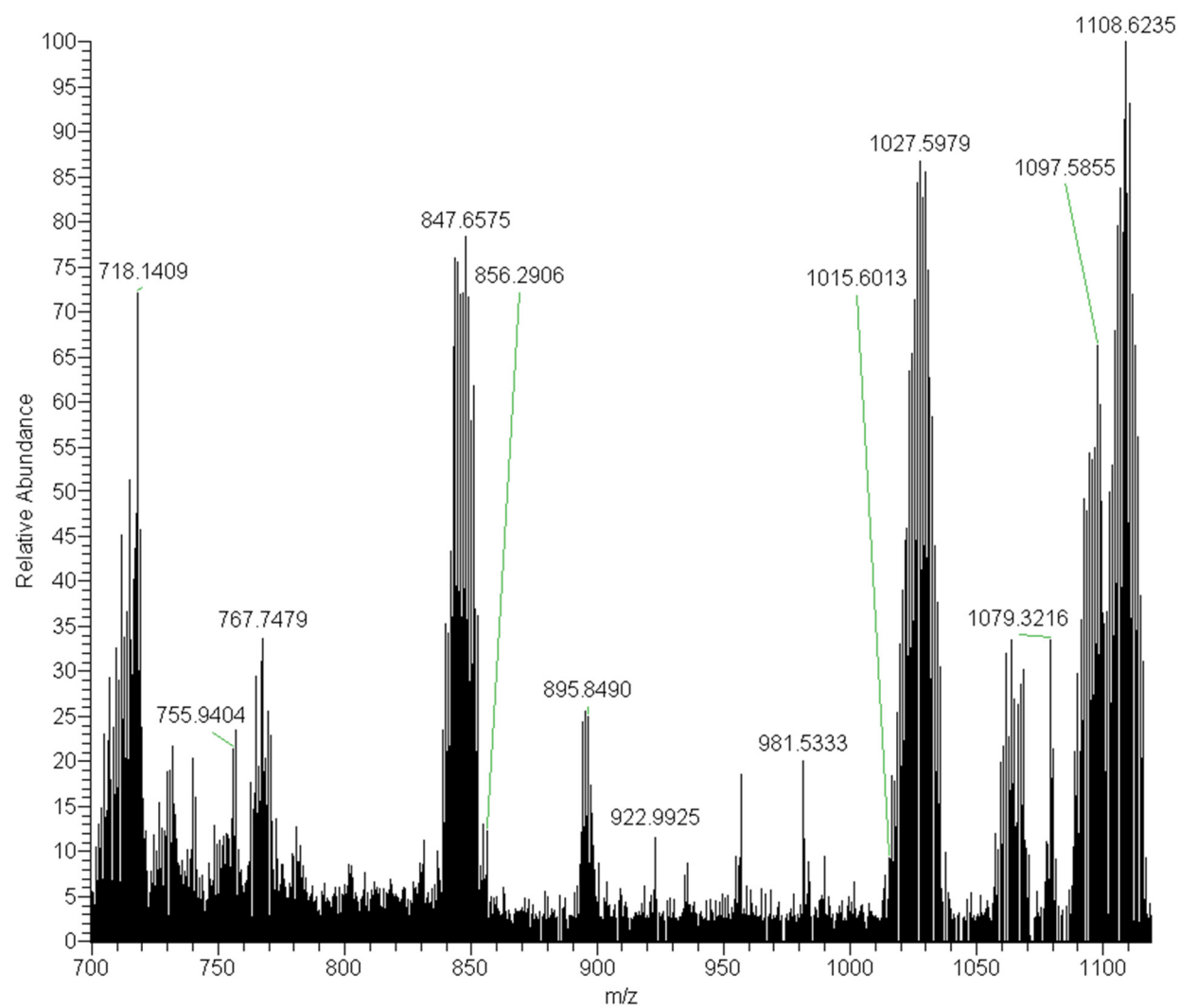
(a) 48 h



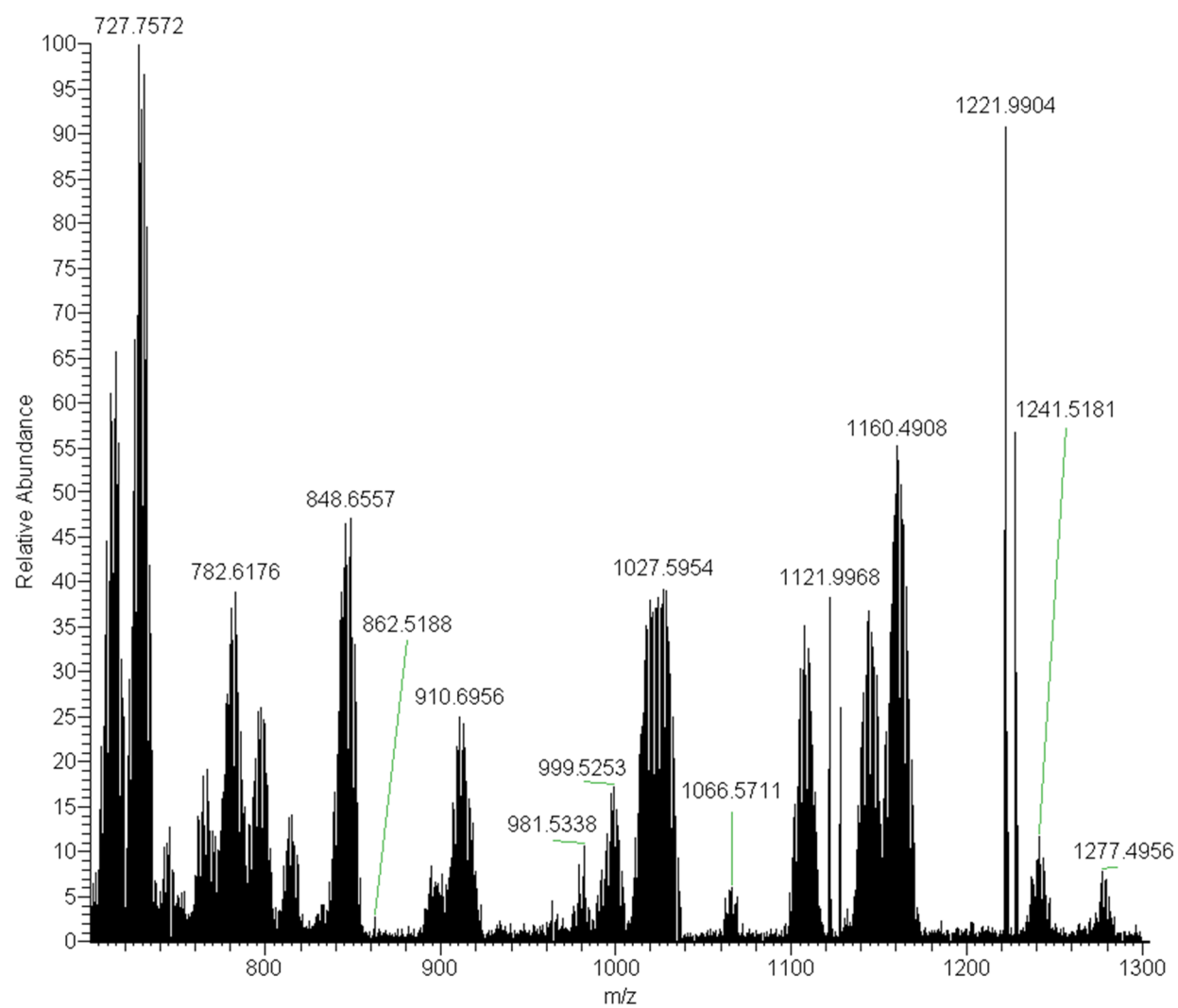
(b) 72 h



**FIGURE S9.**  $^1\text{H}$  NMR spectrum of (**4**) in  $\text{D}_2\text{O}$  after 48h and 72h.



**FIGURE S10.** HR-ESI-MS spectrum of (2).



**FIGURE S11.** HR-ESI-MS spectrum of (4).