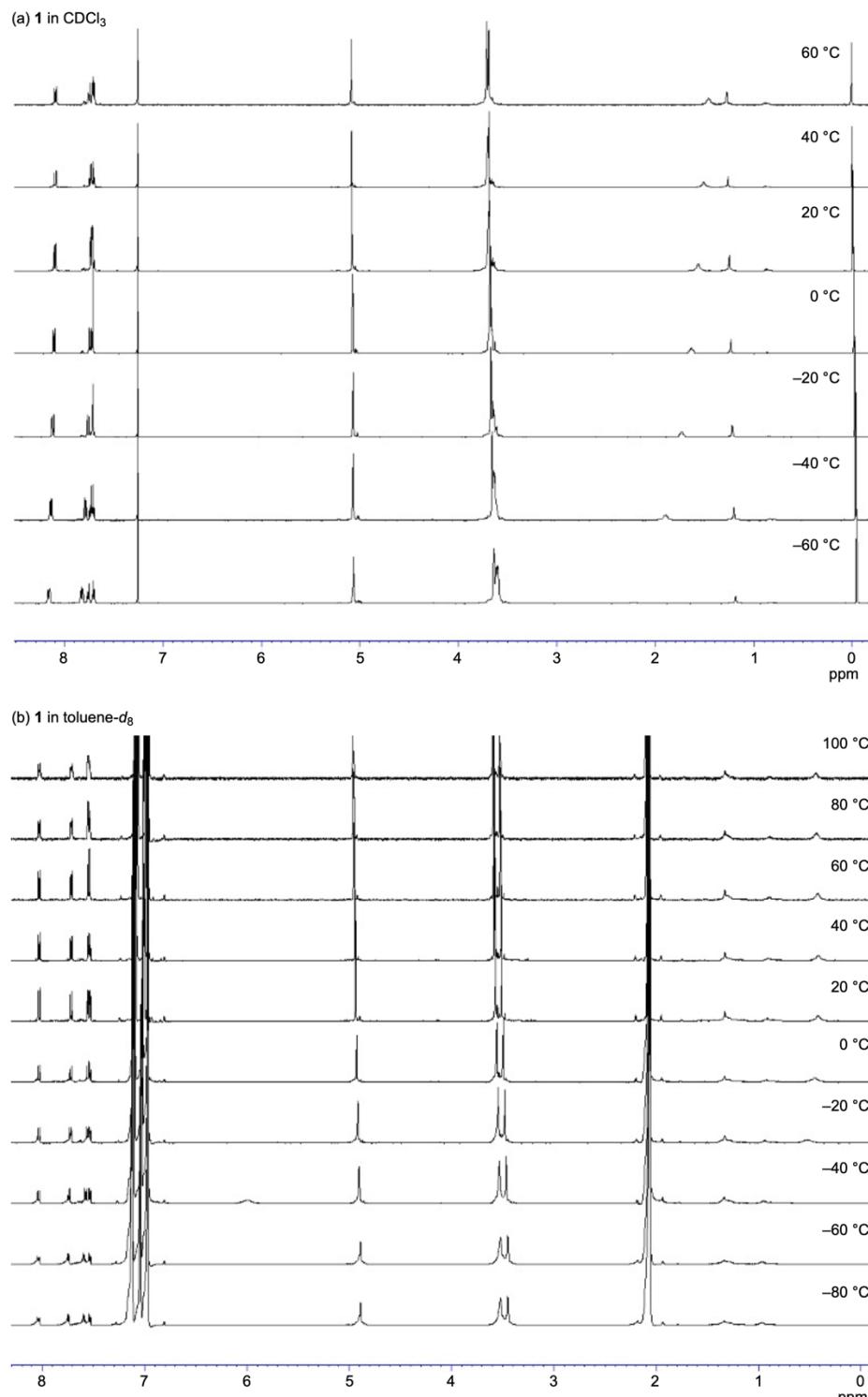


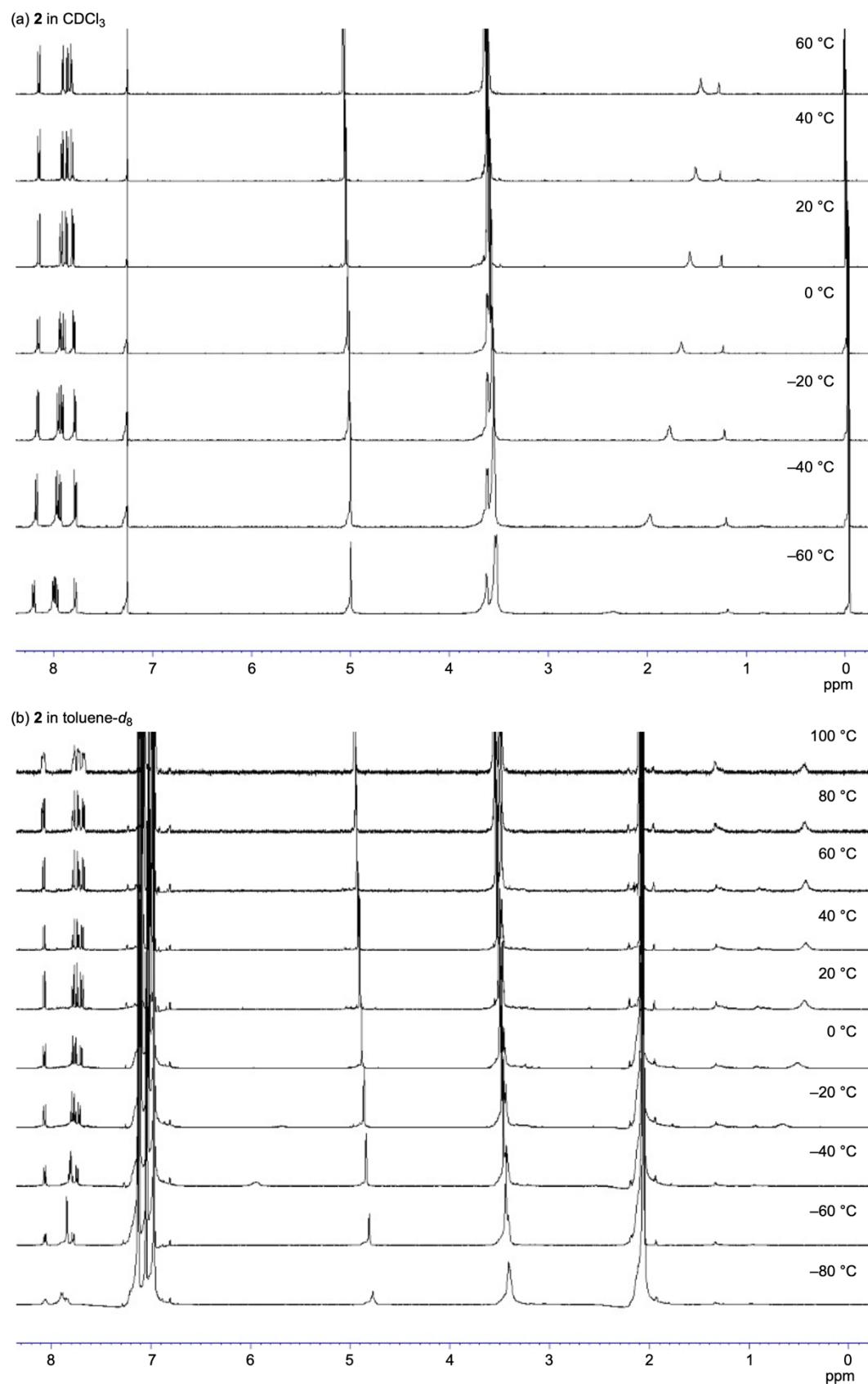
Supporting Information for

**(1,6)Pyrenophanes containing crown ether moieties as fluorescence sensors for metal and ammonium ions. Formation of sandwich, dumbbell, and pseudorotaxane complexes**

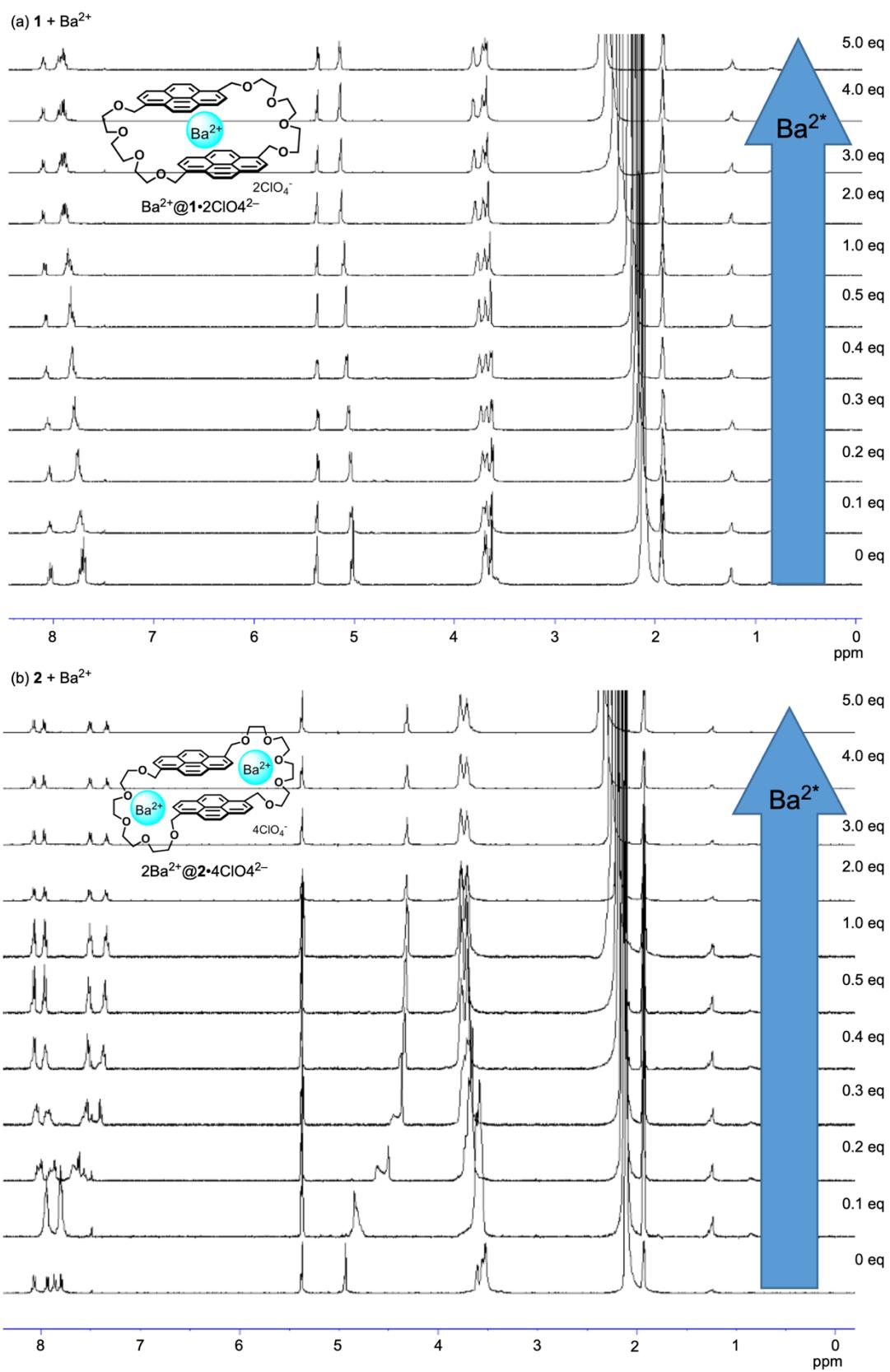
Hajime Maeda,\* Genki Saito, Taniyuki Furuyama and Masahito Segi



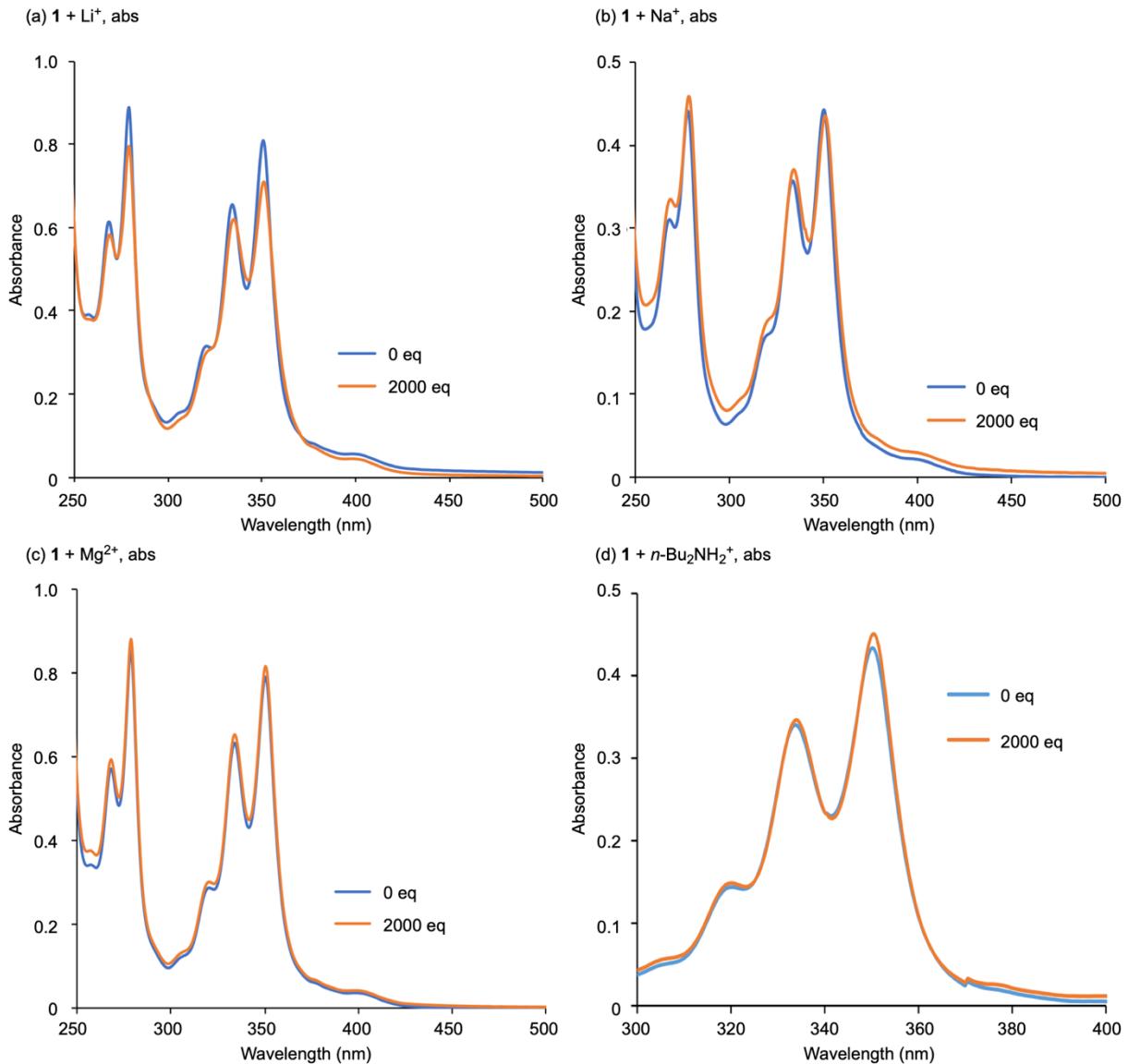
**Fig. S1** Variable-temperature 500 MHz  $^1\text{H}$  NMR spectra of **1** in (a)  $\text{CDCl}_3$  and (b)  $\text{toluene-}d_8$ .



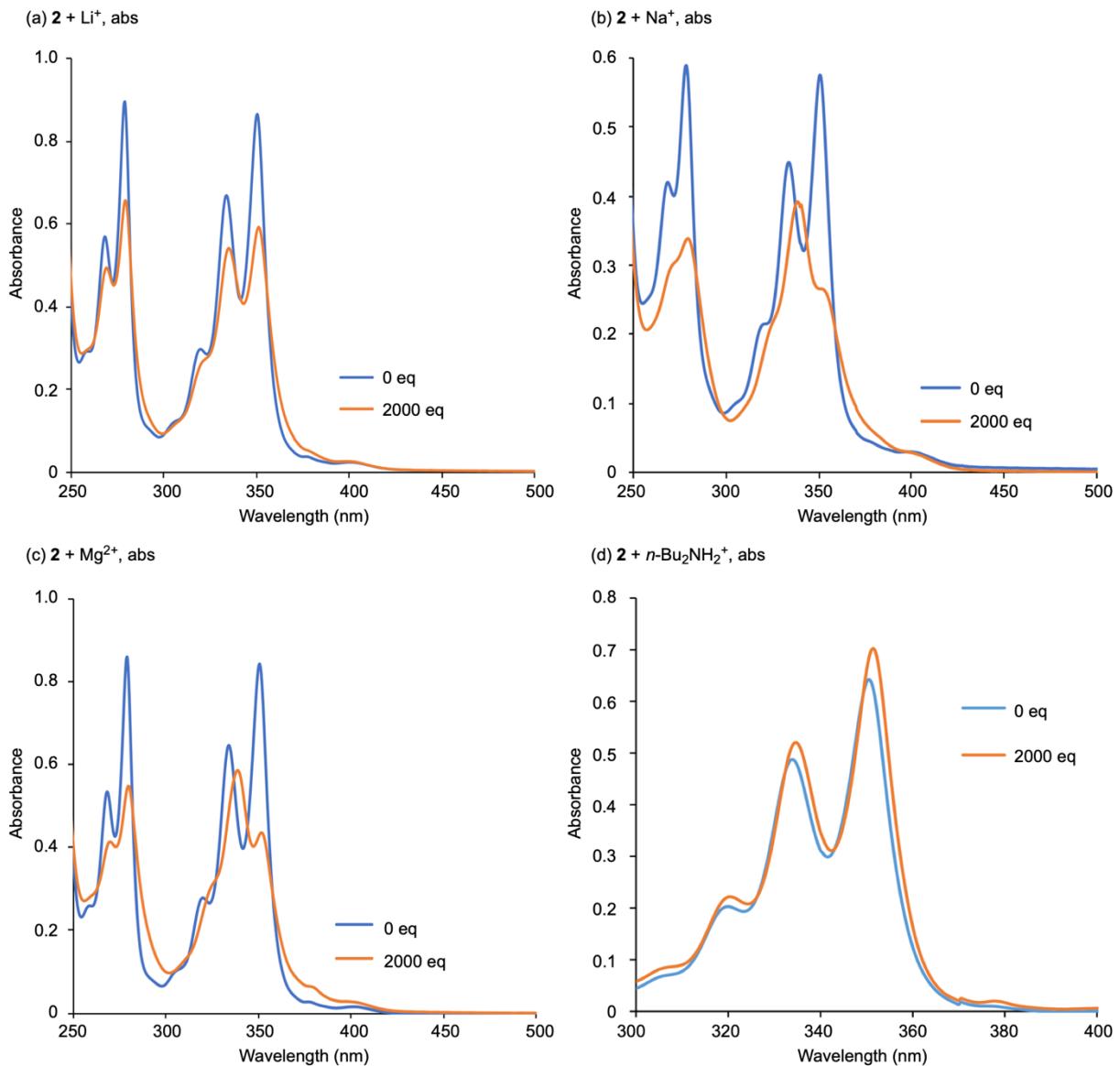
**Fig. S2** Variable-temperature 500 MHz  $^1\text{H}$  NMR spectra of **2** in (a)  $\text{CDCl}_3$  and (b)  $\text{toluene}-d_8$ .



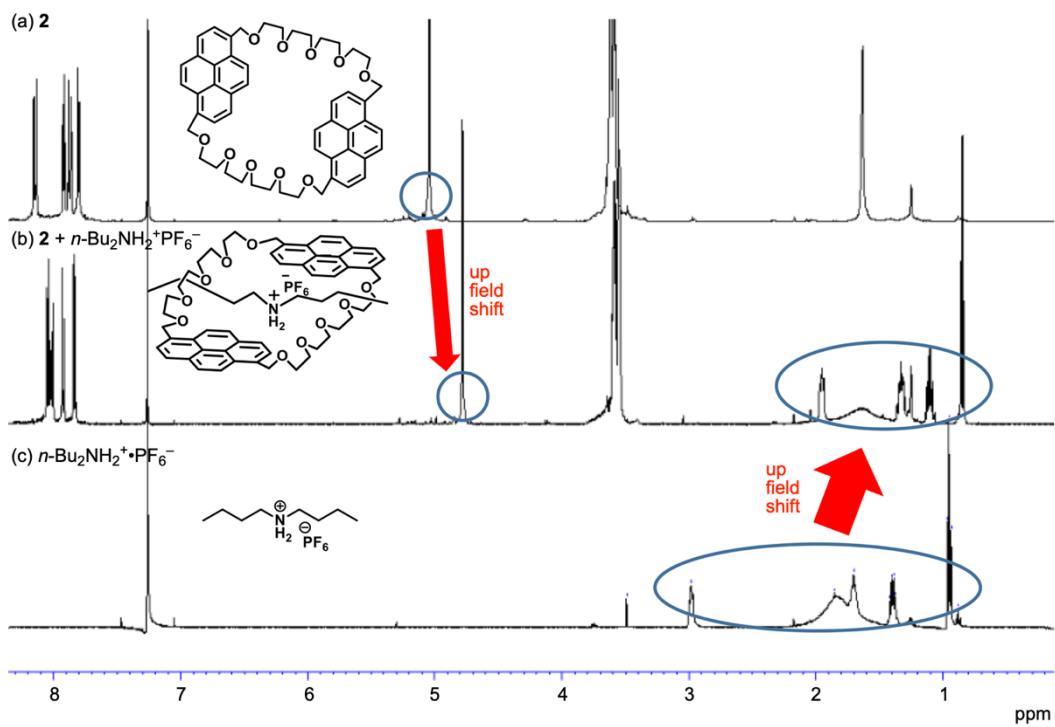
**Fig. S3** 500 MHz  $^1\text{H}$  NMR spectra of (a) **1** and (b) **2** upon addition of  $\text{Ba}(\text{ClO}_4)_2$ .



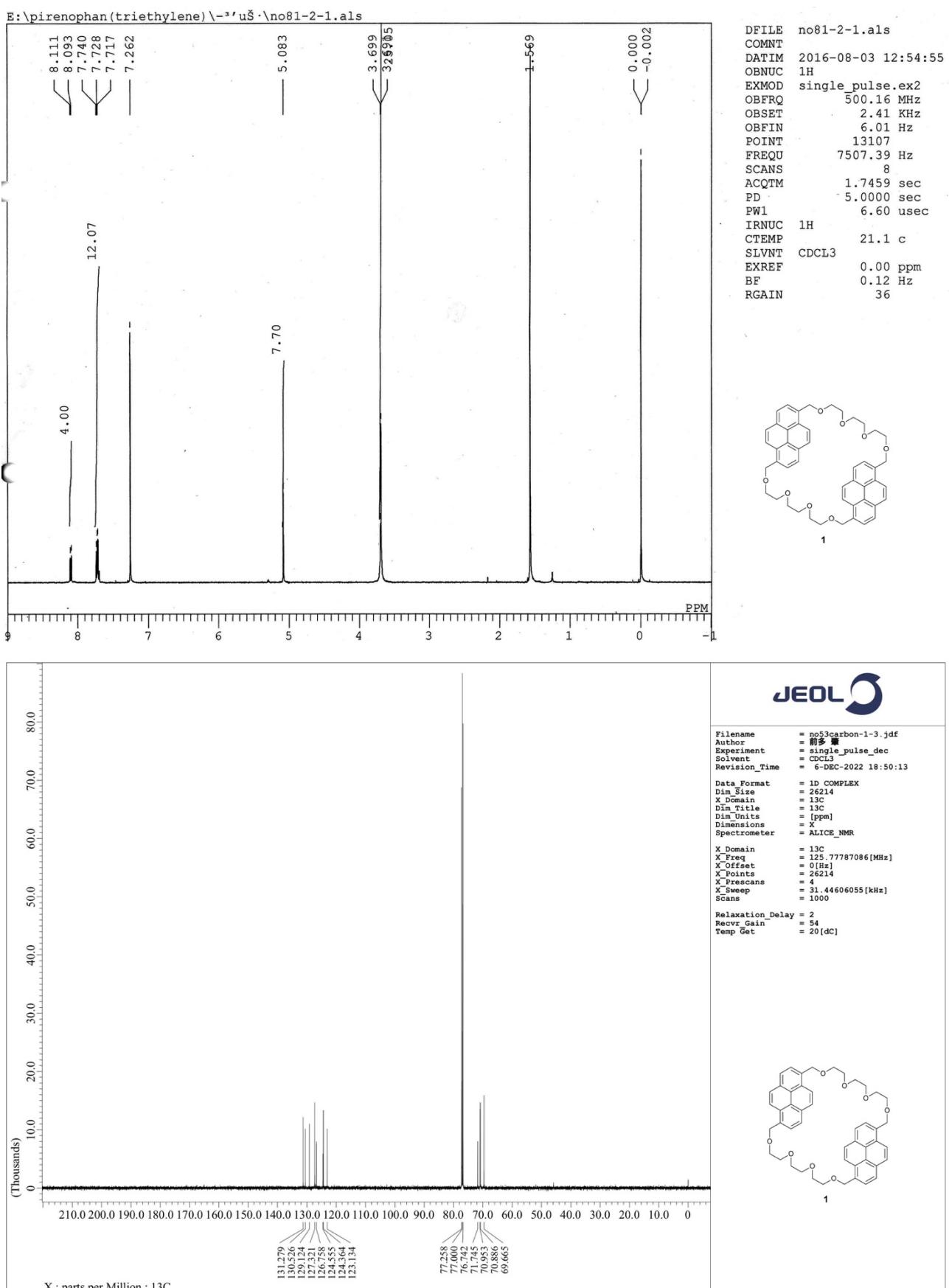
**Fig. S4** Absorption spectra of **1** (1.0 × 10<sup>-5</sup> M in CH<sub>2</sub>Cl<sub>2</sub> : CH<sub>3</sub>CN = 1 : 1) upon addition of (a) LiClO<sub>4</sub> (0-2000 equiv), (b) NaClO<sub>4</sub> (0-2000 equiv), (c) Mg(ClO<sub>4</sub>)<sub>2</sub> (0-2000 equiv), and (d) *n*-Bu<sub>2</sub>NH<sub>2</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup> (0-2000 equiv).

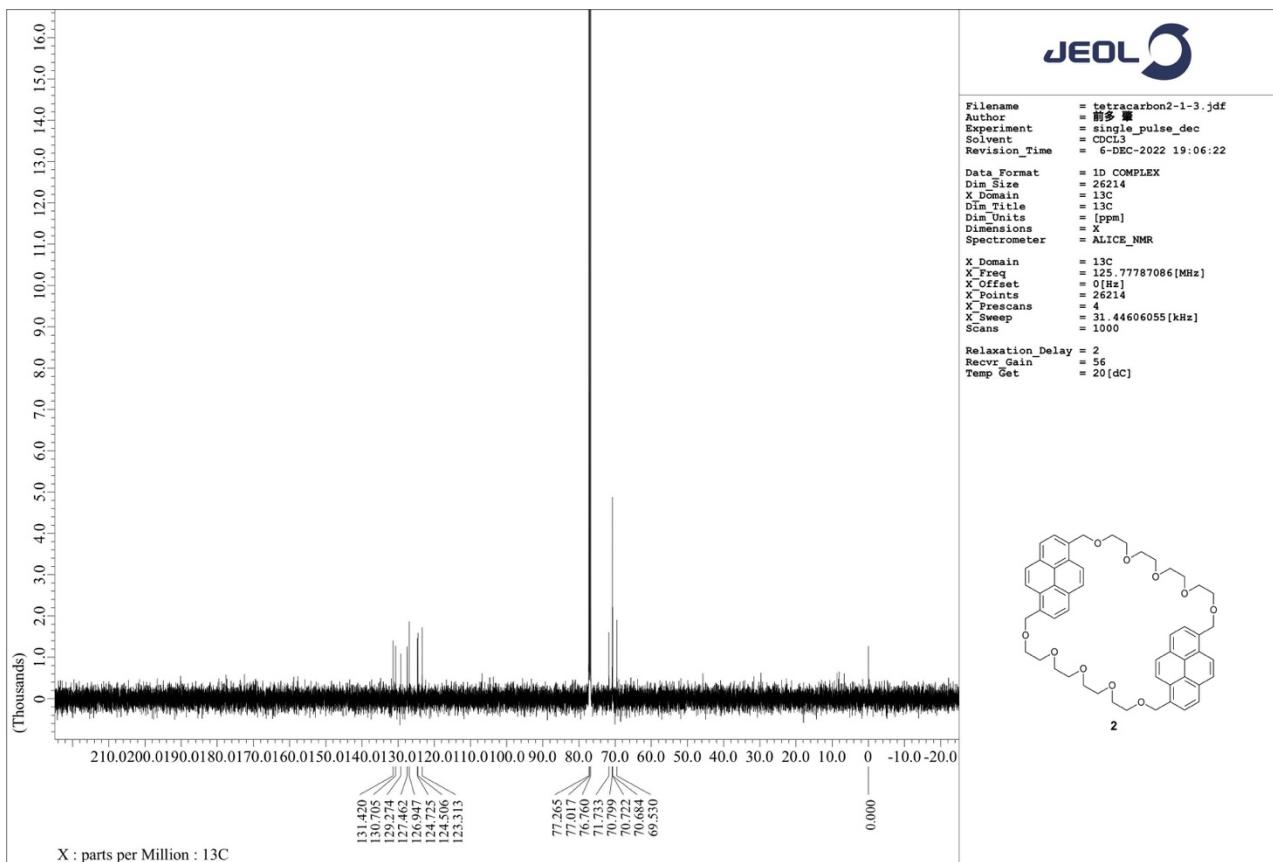
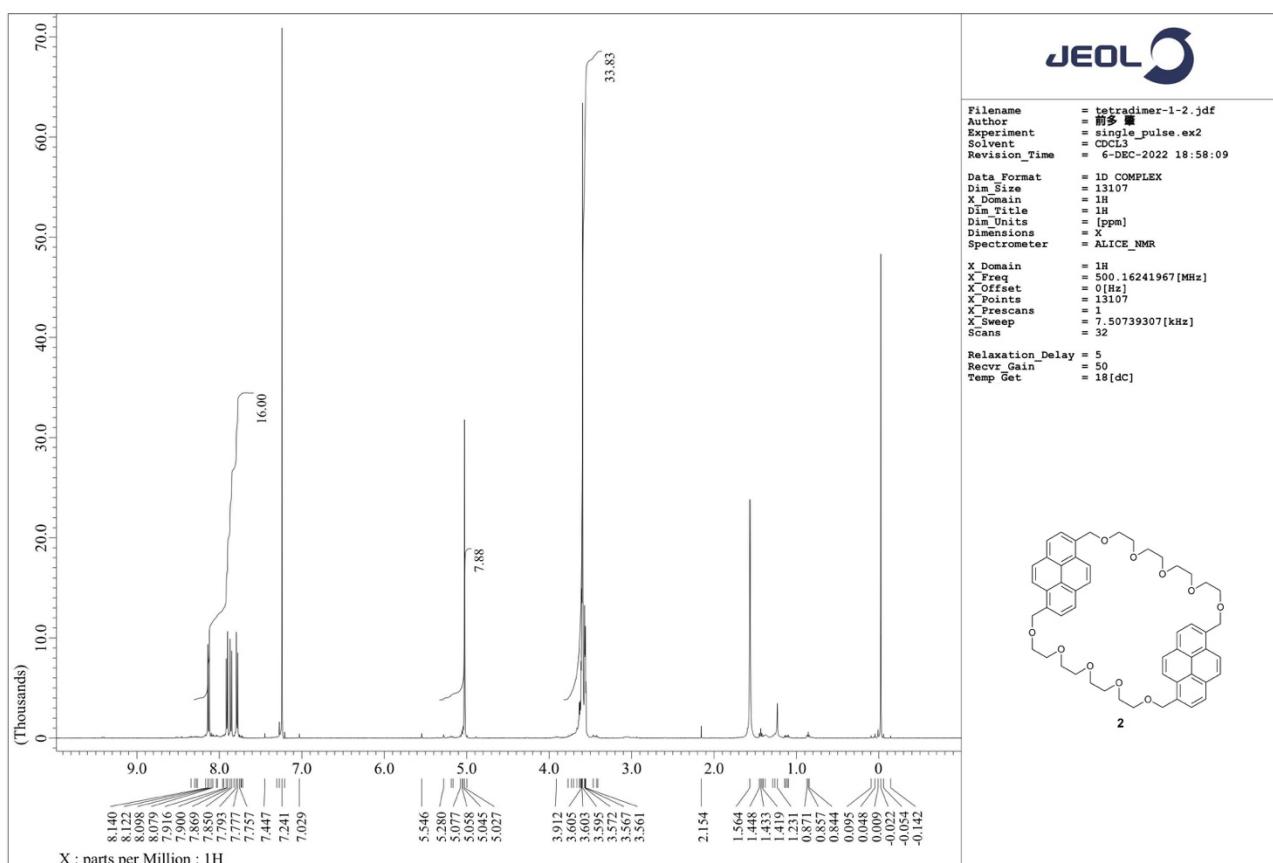


**Fig. S5** Absorption spectra of **2** (1.0 × 10<sup>-5</sup> M in CH<sub>2</sub>Cl<sub>2</sub> : CH<sub>3</sub>CN = 1 : 1) upon addition of (a) LiClO<sub>4</sub> (0-2000 equiv), (b) NaClO<sub>4</sub> (0-2000 equiv), (c) Mg(ClO<sub>4</sub>)<sub>2</sub> (0-2000 equiv), and (d) *n*-Bu<sub>2</sub>NH<sub>2</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup> (0-2000 equiv).

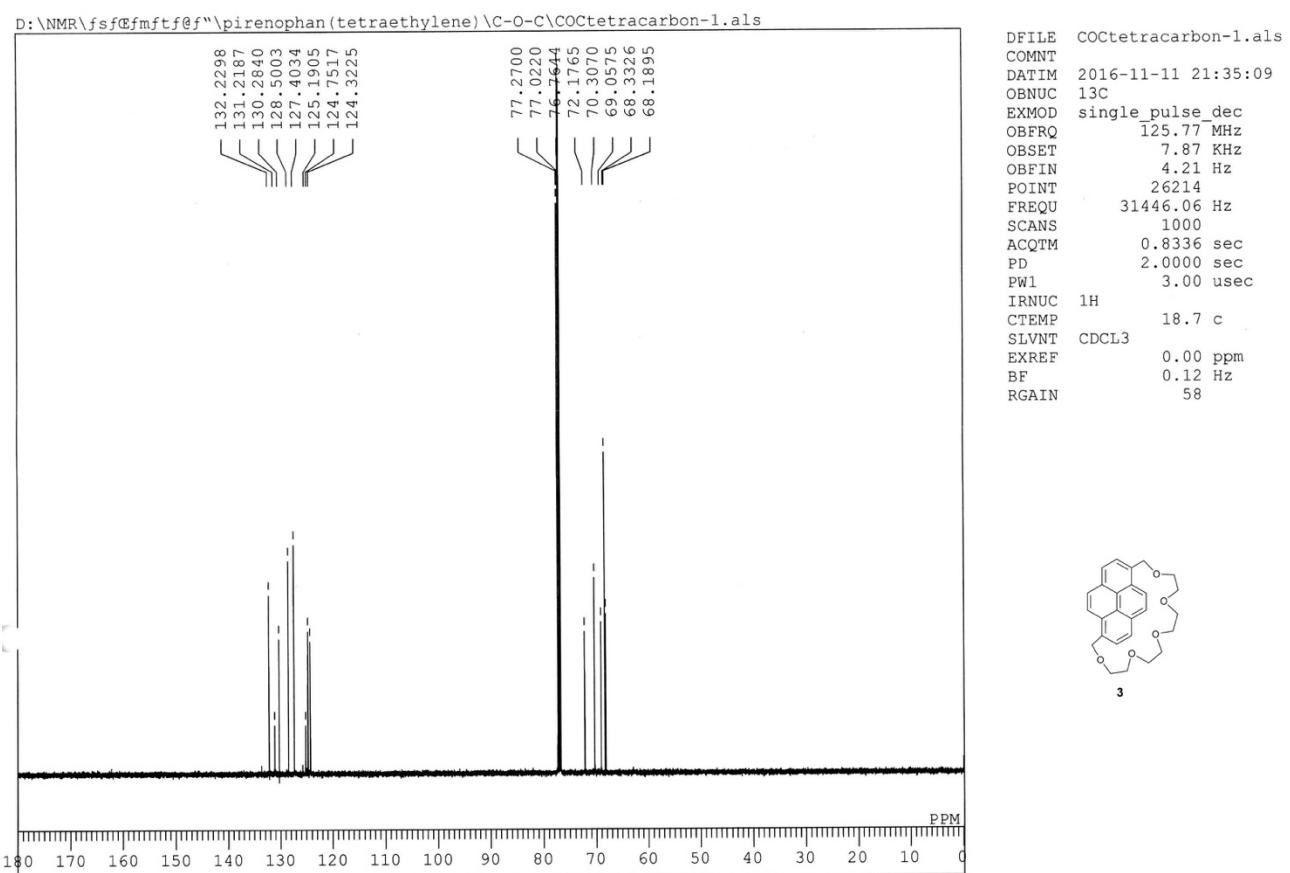
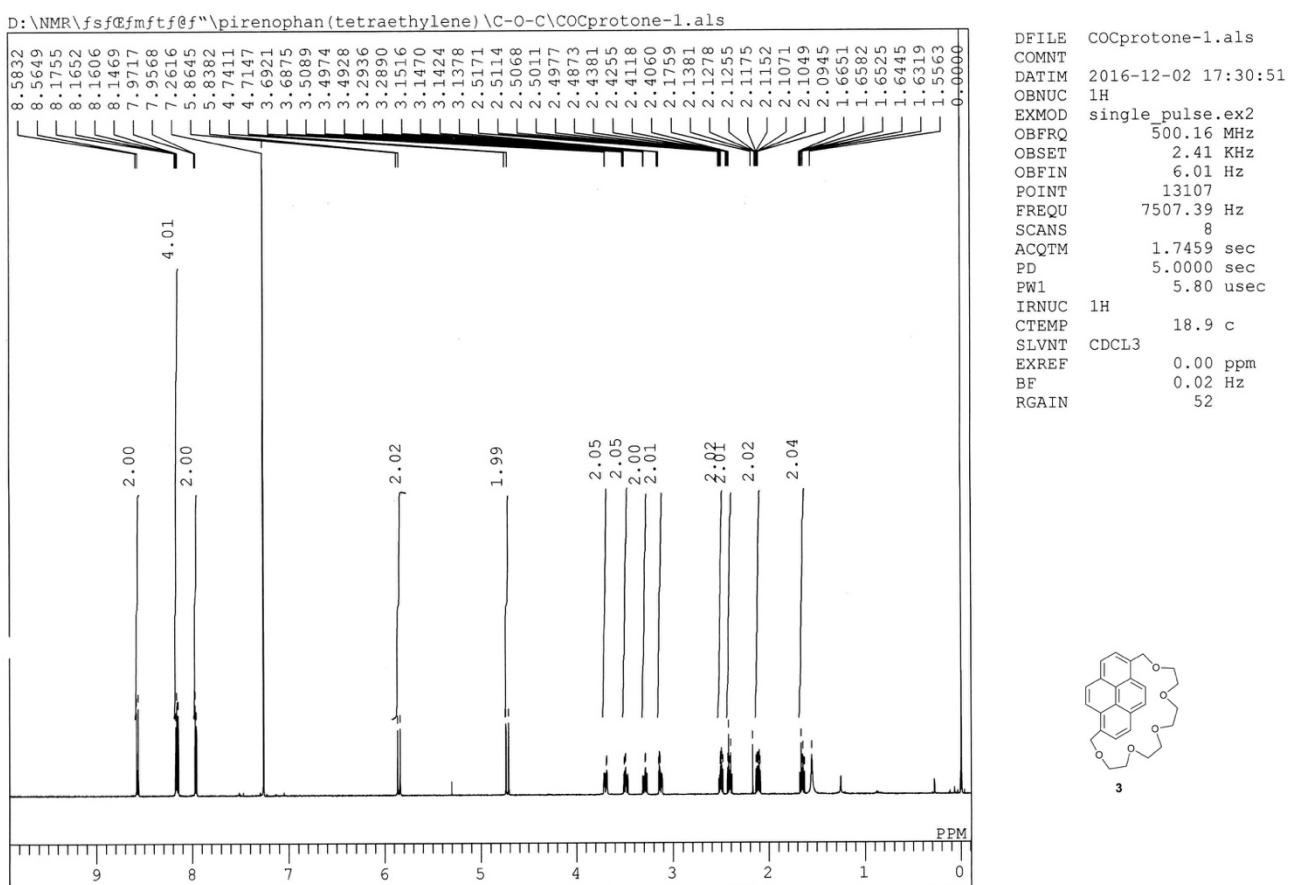


**Fig. S6** 500 MHz  $^1\text{H}$  NMR spectra of (a) **2**, (b) a mixture of **2** with  $n\text{-Bu}_2\text{NH}_2^+\text{PF}_6^-$ , and (c)  $n\text{-Bu}_2\text{NH}_2^+\text{PF}_6^-$  in  $\text{CDCl}_3$ .

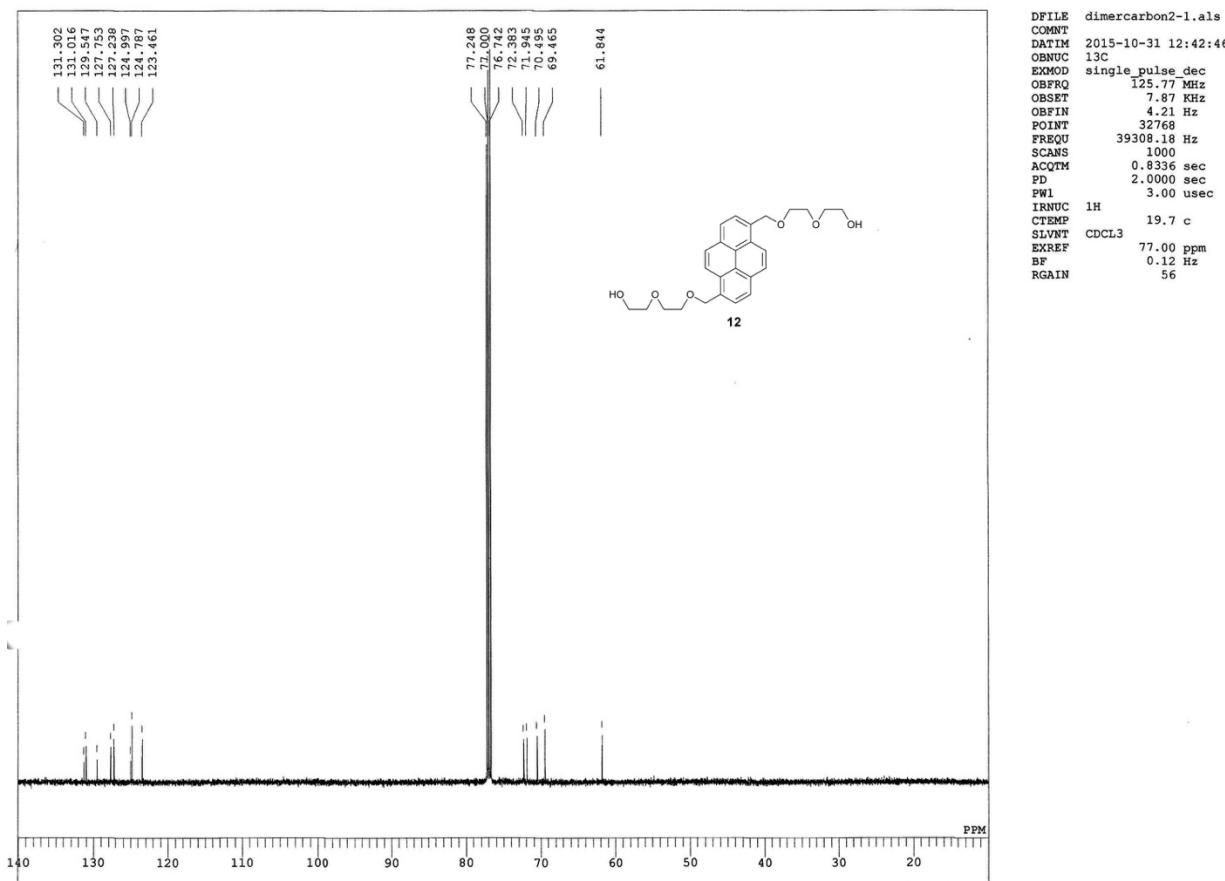
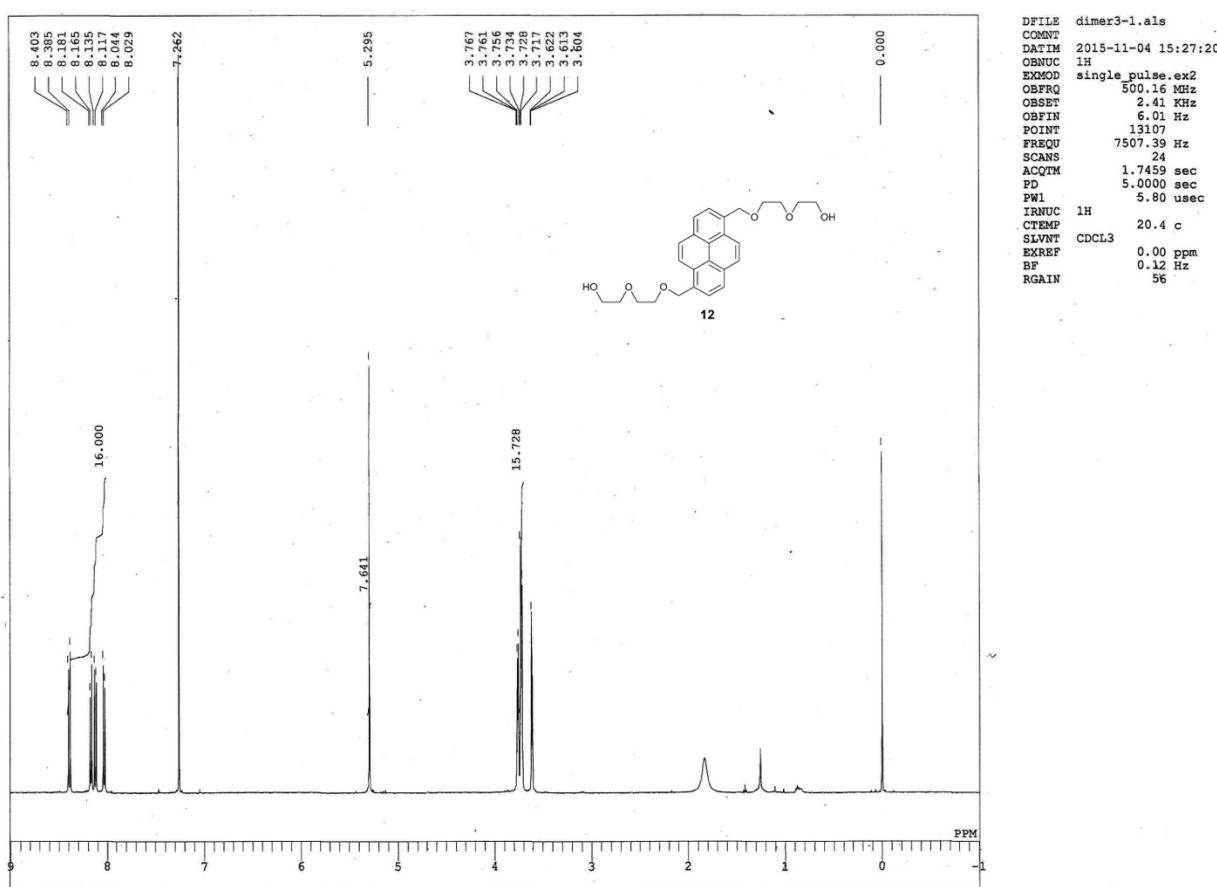




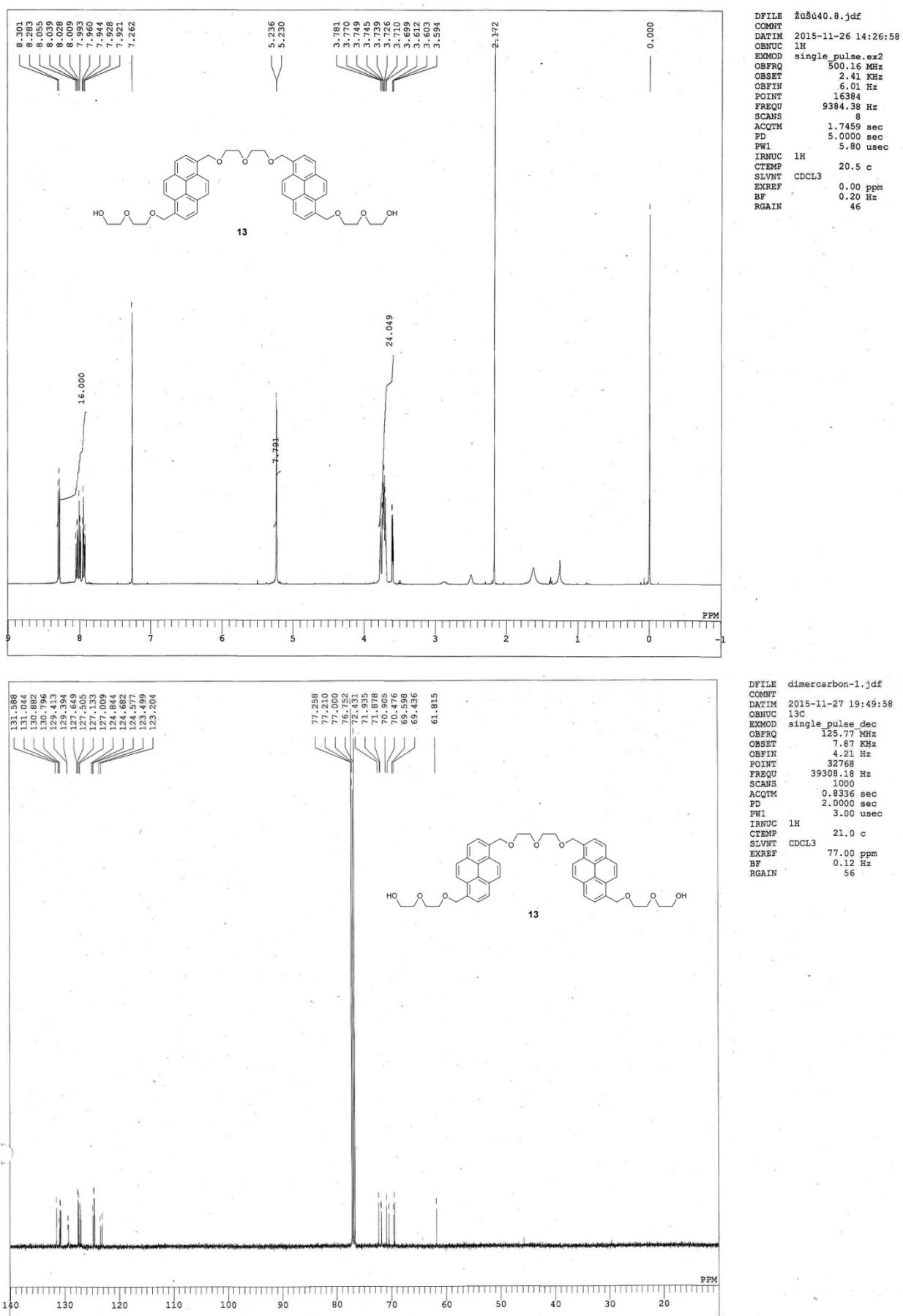
**Fig. S8** 500 MHz <sup>1</sup>H and 125 MHz <sup>13</sup>C NMR spectra of **2** in CDCl<sub>3</sub>.



**Fig. S9** 500 MHz <sup>1</sup>H and 125 MHz <sup>13</sup>C NMR spectra of **3** in CDCl<sub>3</sub>.



**Fig. S10** 500 MHz  $^1\text{H}$  and 125 MHz  $^{13}\text{C}$  NMR spectra of **12** in  $\text{CDCl}_3$ .



**Fig. S11** 500 MHz <sup>1</sup>H and 125 MHz <sup>13</sup>C NMR spectra of **13** in CDCl<sub>3</sub>.