**Double-armed and tetra-armed cyclen-based cryptands**

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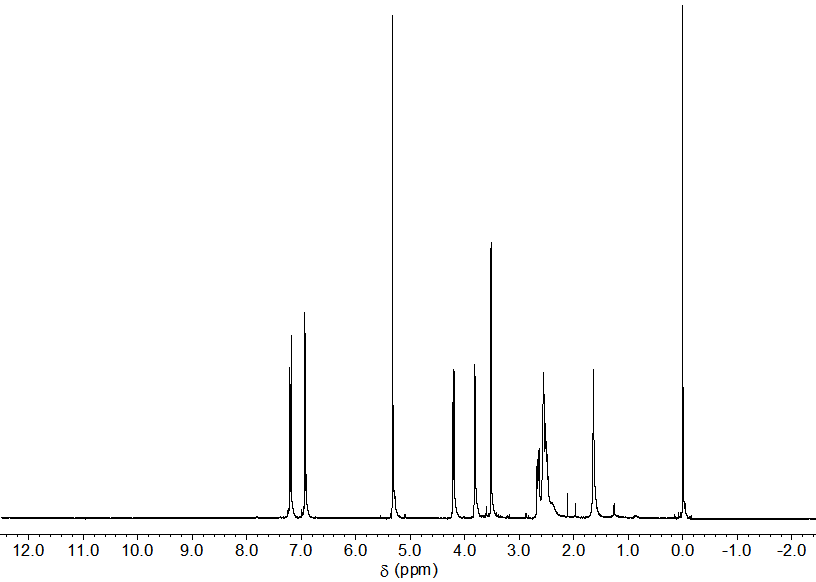
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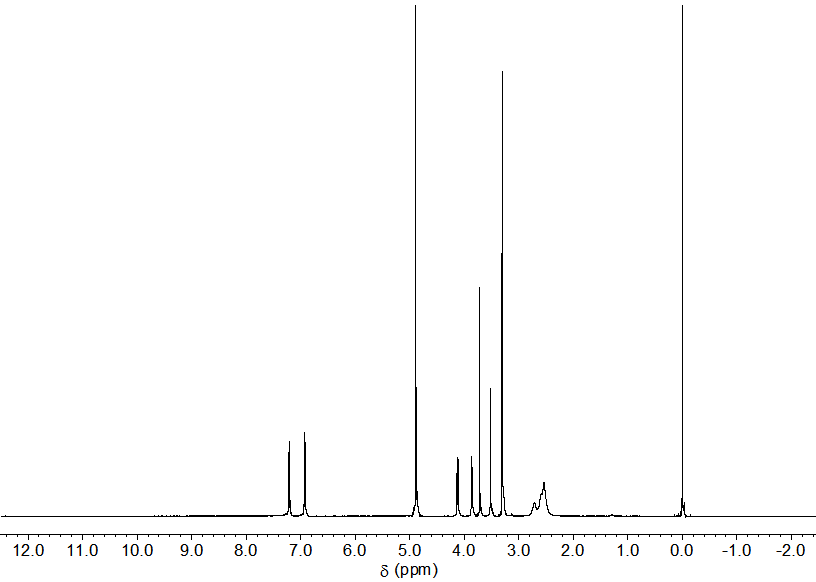
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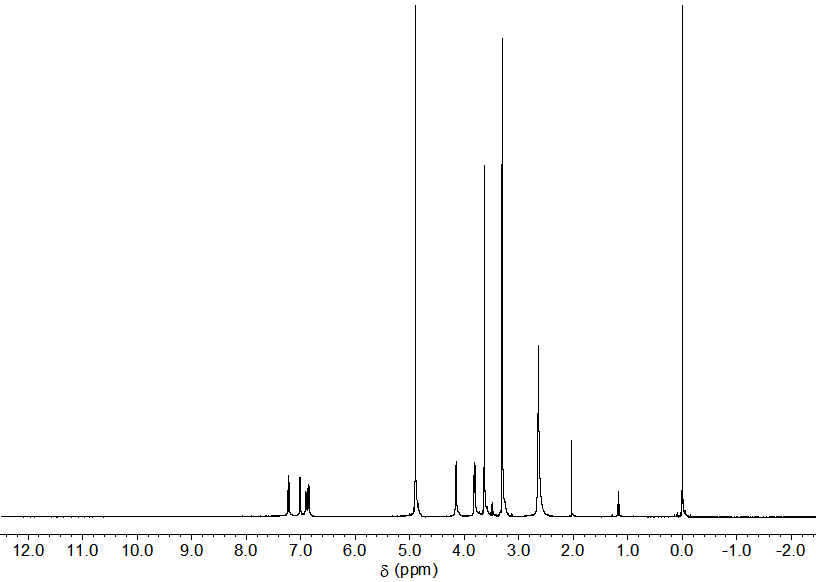
**Fig. S30.** HOMOs and LUMOs of **1a**, **1b**, and **1d**. 13



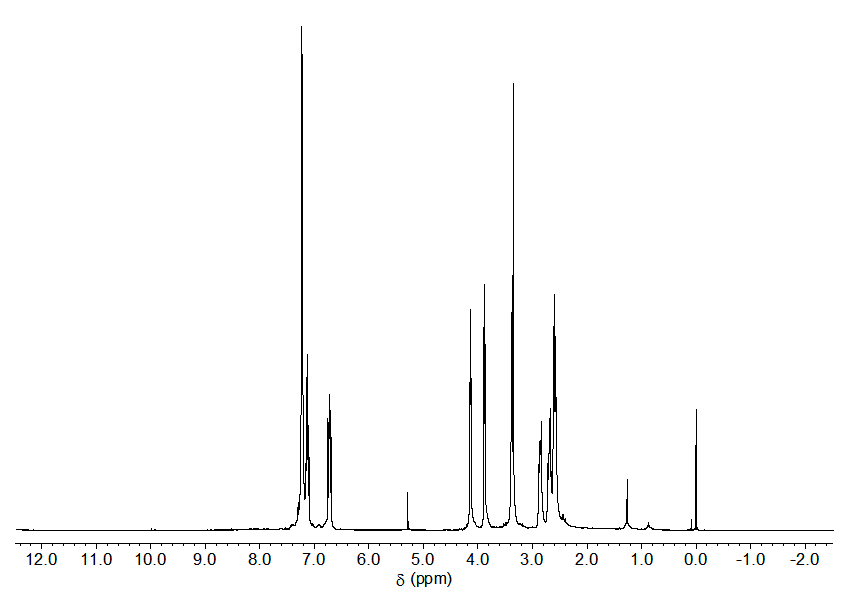
**Fig. S1.**  1H NMR of **1a** in CD2Cl2.



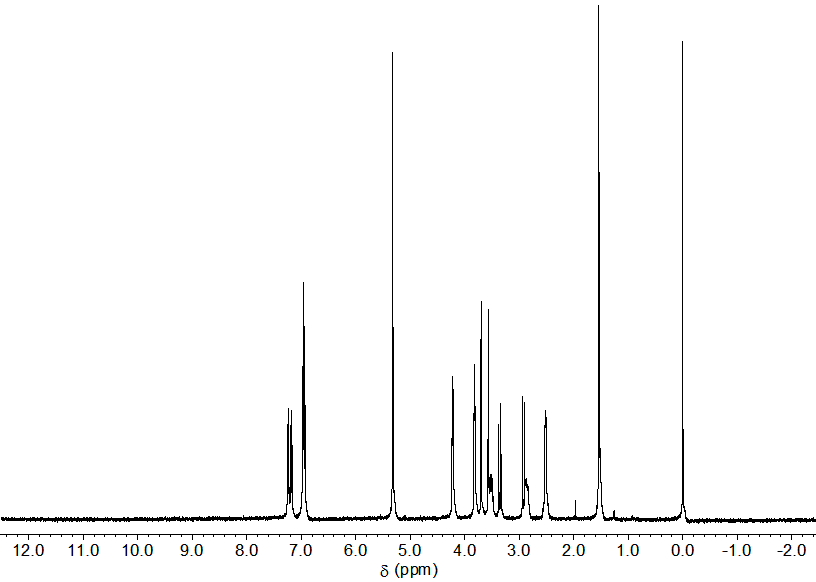
**Fig. S2.** 1H NMR of **1b** in CD2Cl2.



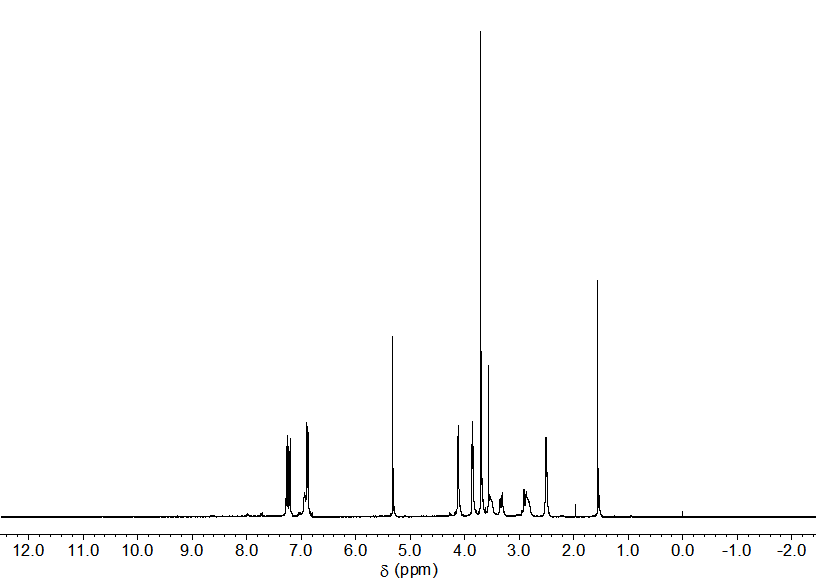
**Fig. S3.** 1H NMR of **1d** in CD2Cl2.



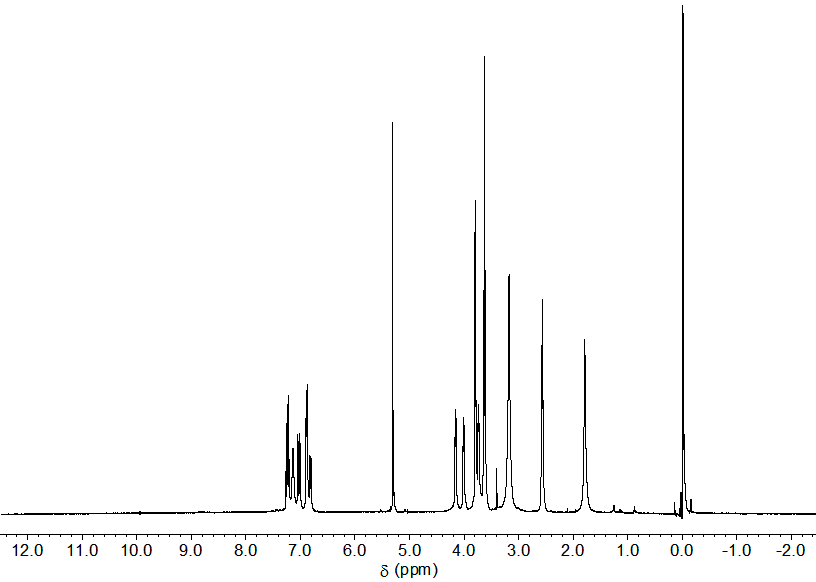
**Fig. S4.**  1H NMR of **2** in CD2Cl2.



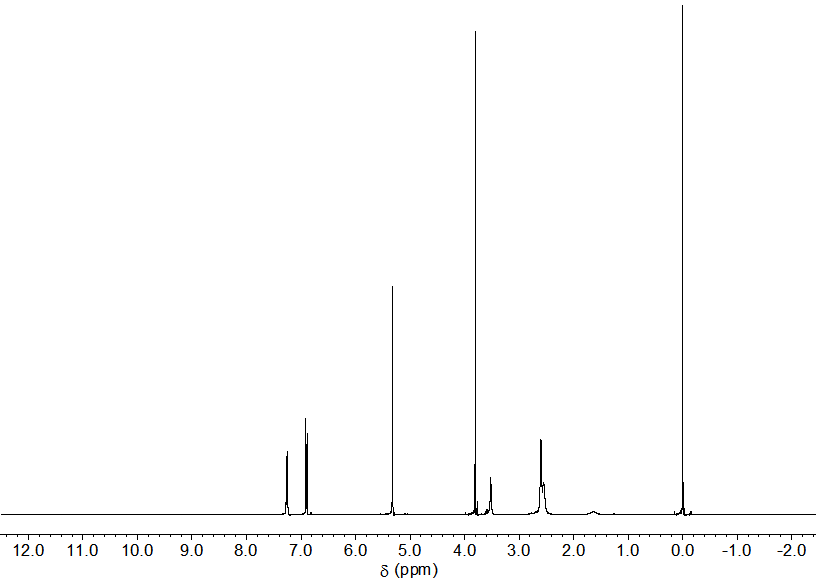
**Fig. S5.**  1H NMR of **1a-pre** in CD2Cl2.



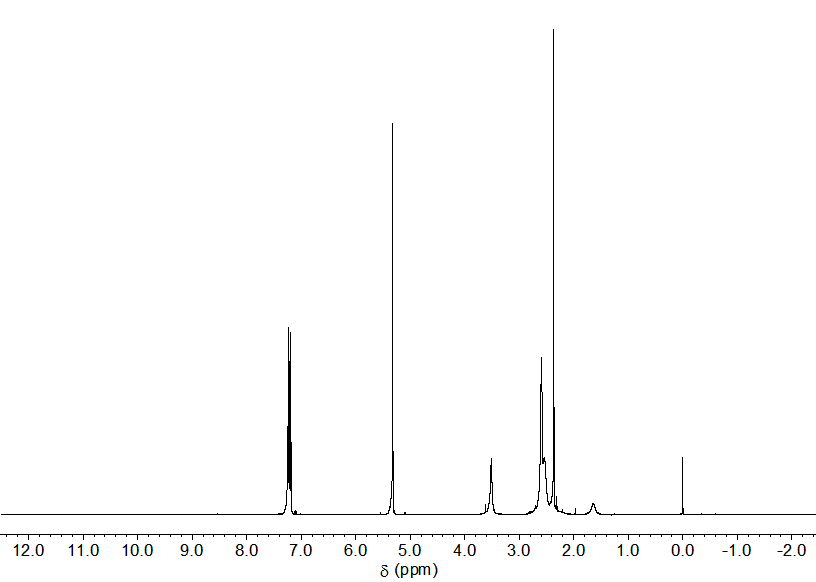
**Fig. S6.** 1H NMR of **1b-pre** in CD2Cl2.



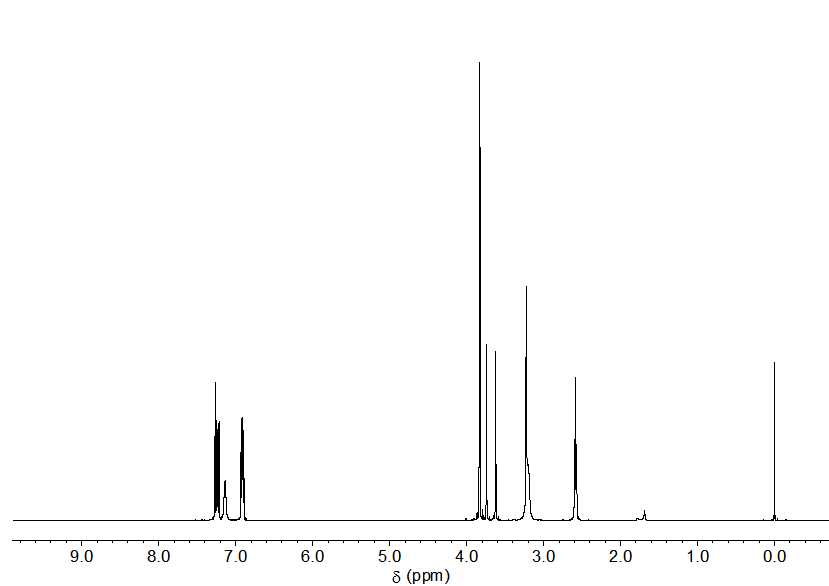
**Fig. S7.**  1H NMR of **1d-pre** in CD2Cl2.



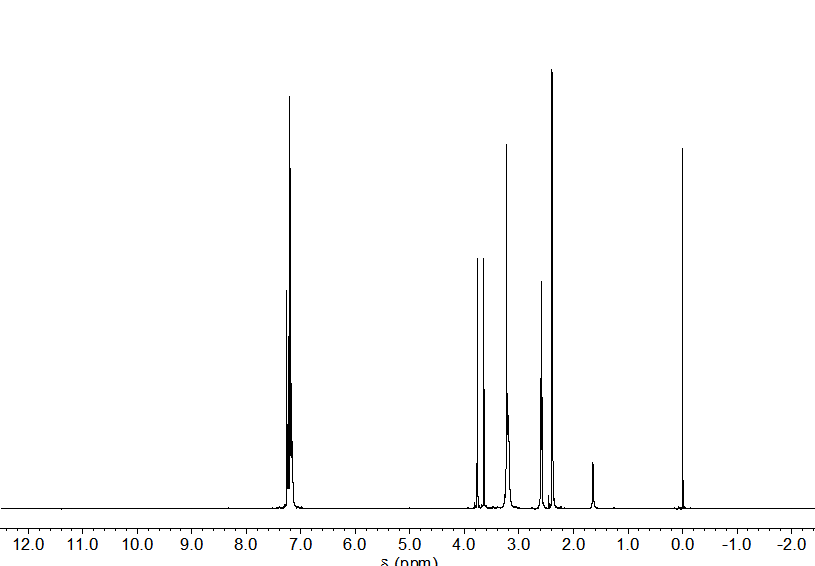
**Fig. S8.**  1H NMR of **3a** in CD2Cl2.



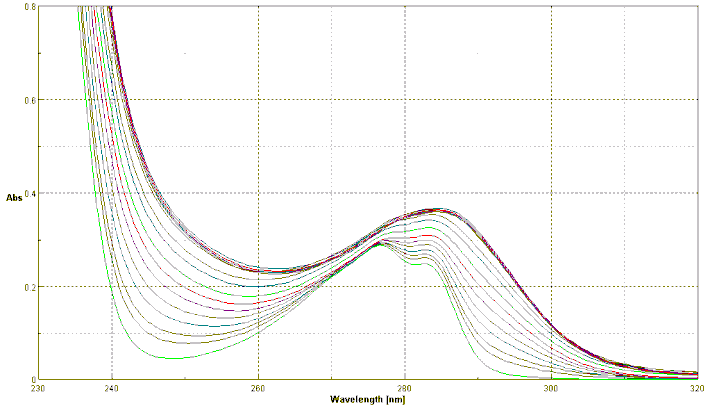
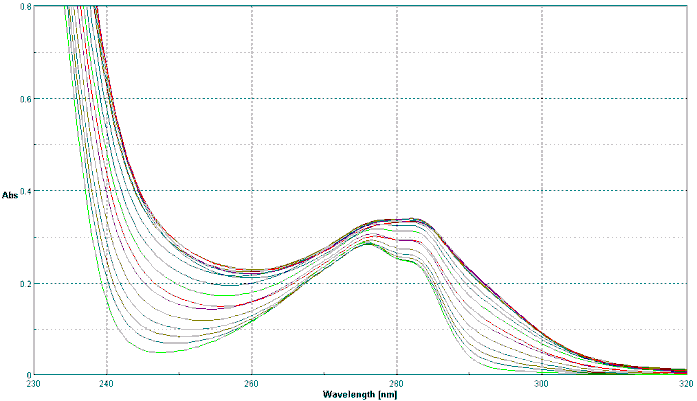
**Fig. S9.**  1H NMR of **3b** in CD2Cl2.



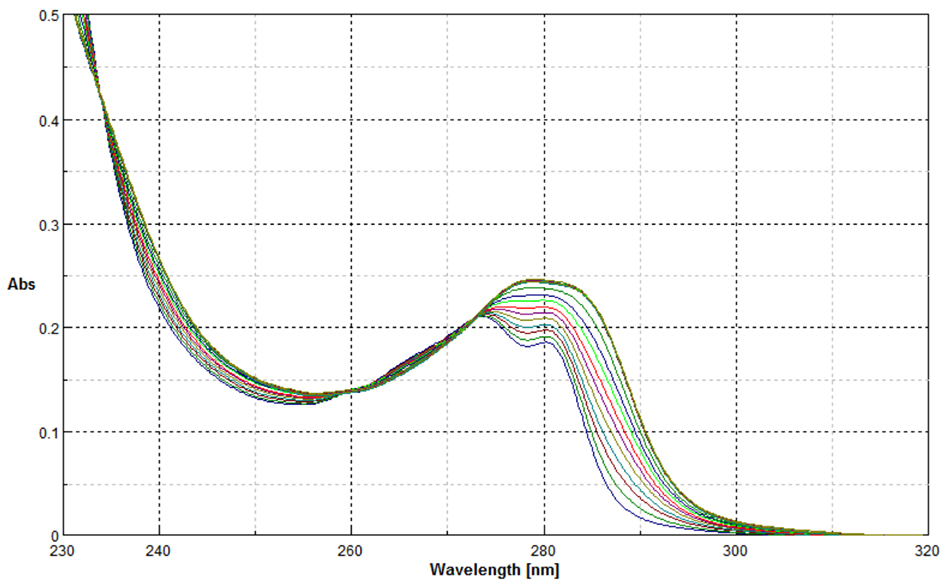
**Fig. S10.**  1H NMR of **3a-pre** in D2O in the presence of NaOD.

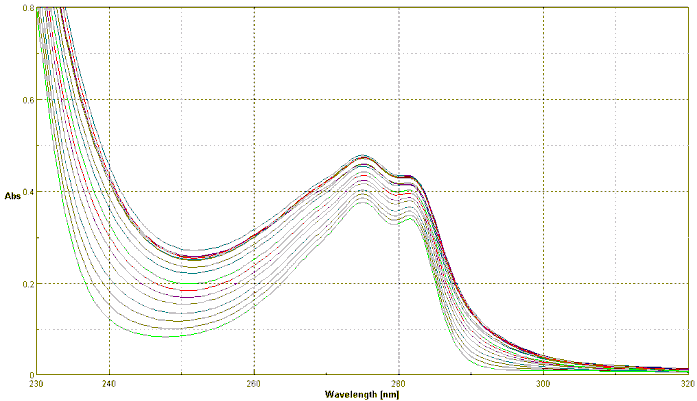


**Fig. S11.** 1H NMR of **3b-pre** in D2O in the presence of NaOD.

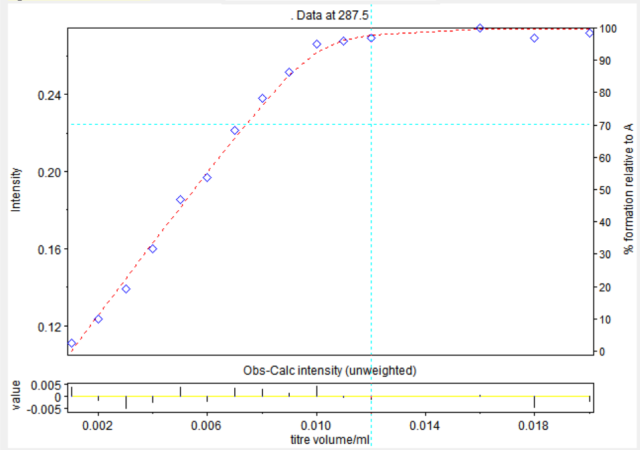


**Fig. S12.** Ag+-ion-induced UV spectral changes of **1a**. **Fig. S13.** Ag+-ion-induced UV spectral changes of **1b**.





**Fig. S14.** Ag+-ion-induced UV spectral changes of **1d**. **Fig. S15.** Ag+-ion-induced UV spectral changes of **2**.

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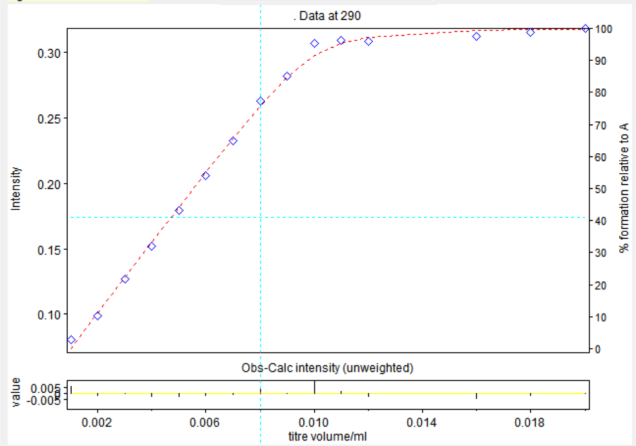
Converged in 1 iterations with sigma = 3.4080E-03

standard

Log beta value deviation

AB 6.1089 0.0121

**Fig. S16.** UV titration curve of **1a**/Ag+ system at 287.5 nm. **♢**: Observed. ----: Calculated.



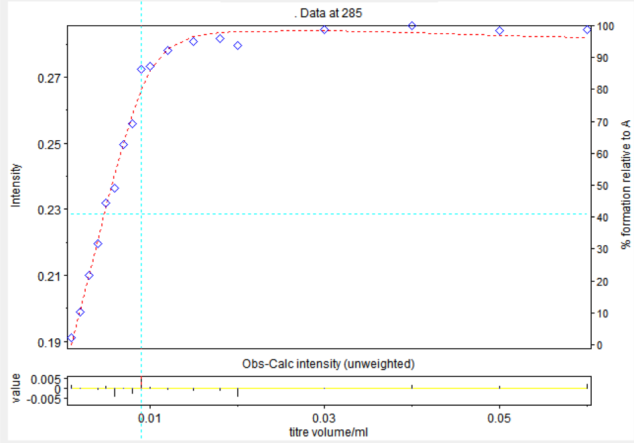
Converged in 1 iterations with sigma = 2.9043E-03

standard

Log beta value deviation

AB 6.085 0.0101

**Fig. S17.** UV titration curve of **1b**/Ag+system at 290 nm. **♢**: Observed. ----: Calculated.



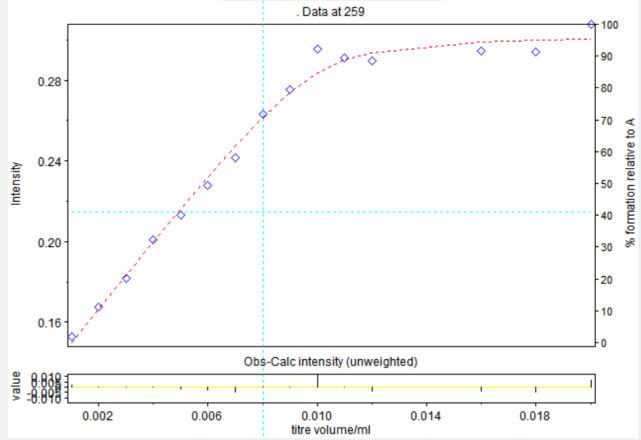
Converged in 1 iterations with sigma = 3.8735E-03

standard

Log beta value deviation

AB 5.6671 0.0324

**Fig. S18.** UV titration curve of **1c**/Ag+system at 285 nm. **♢**: Observed. ----: Calculated.



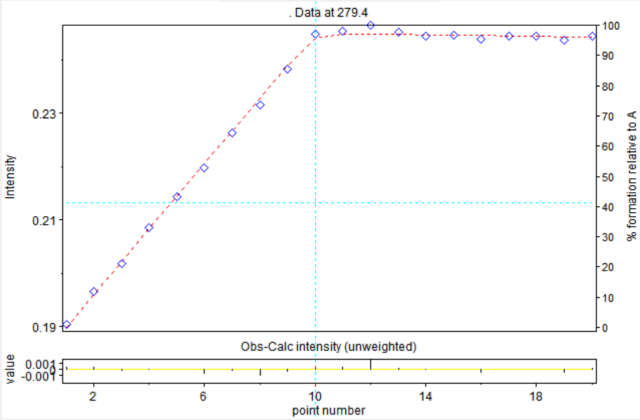
Converged in 1 iterations with sigma = 2.6978E-03

standard

Log beta value deviation

AB 5.8053 0.0093

**Fig. S19.** UV titration curve of **1d**/Ag+system at 259 nm. **♢**: Observed. ----: Calculated.



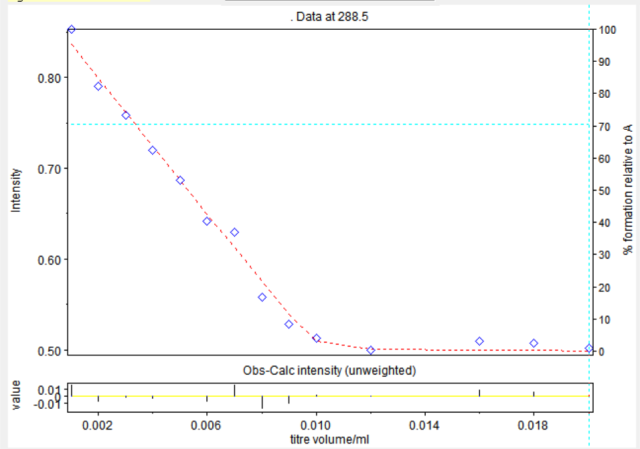
Converged in 1 iterations with sigma = 1.3159E-03

standard

Log beta value deviation

AB 7.9219 0.0313

**Fig. S20.** UV titration curve of **2**/Ag+system at 279.4 nm. **♢**: Observed. ----: Calculated.

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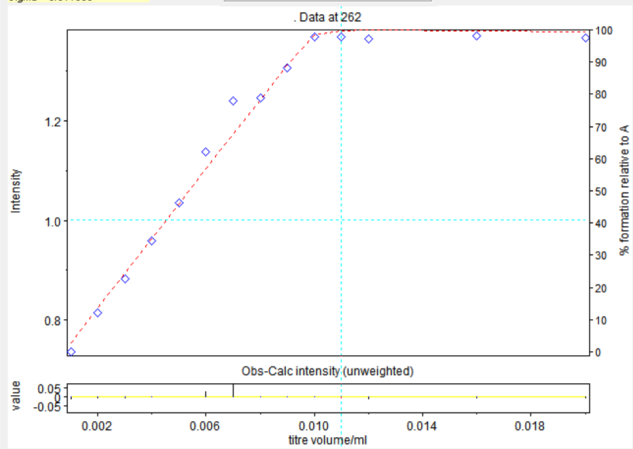
Converged in 1 iterations with sigma = 3.1942E-03

standard

Log beta value deviation

AB 7.1555 0.0721

**Fig. S21.** UV titration curve of **3a**/Ag+system at 288.5 nm. **♢**: Observed. ----: Calculated.



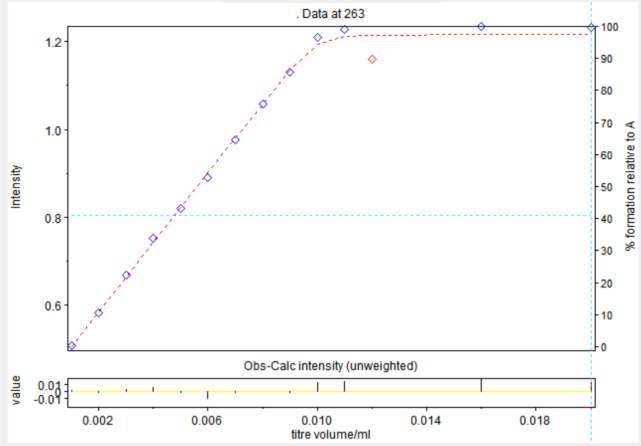
Converged in 1 iterations with sigma = 6.8238E-03

standard

Log beta value deviation

AB 7.6289 0.0606

**Fig. S22.** UV titration curve of **3b**/Ag+system at 262 nm. **♢**: Observed. ----: Calculated.



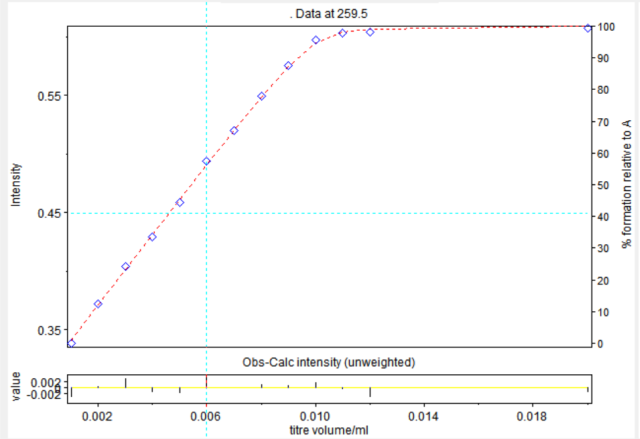
Converged in 1 iterations with sigma = 3.8410E-03

standard

Log beta value deviation

AB 7.1124 0.0298

**Fig. S23.** UV titration curve of **3c**/Ag+system at 263 nm. **♢**: Observed. ----: Calculated.



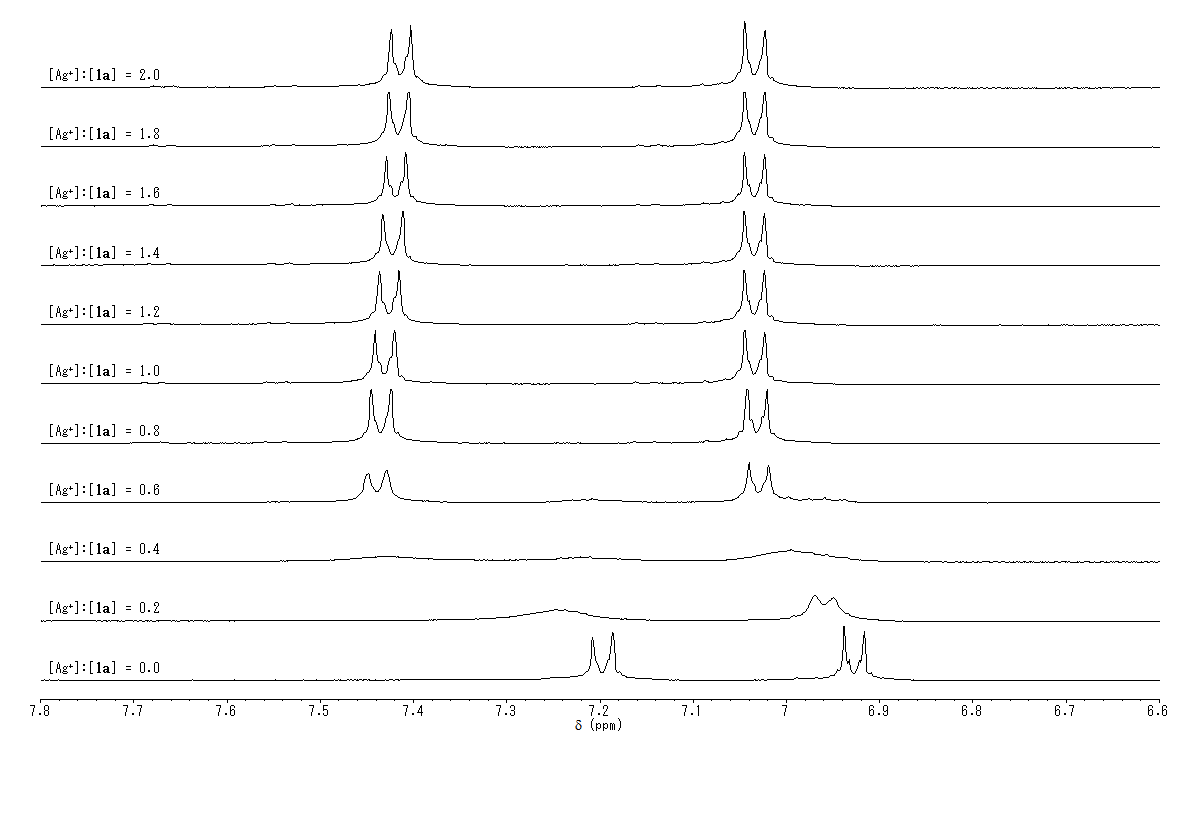
Converged in 1 iterations with sigma =2.4159E-03

standard

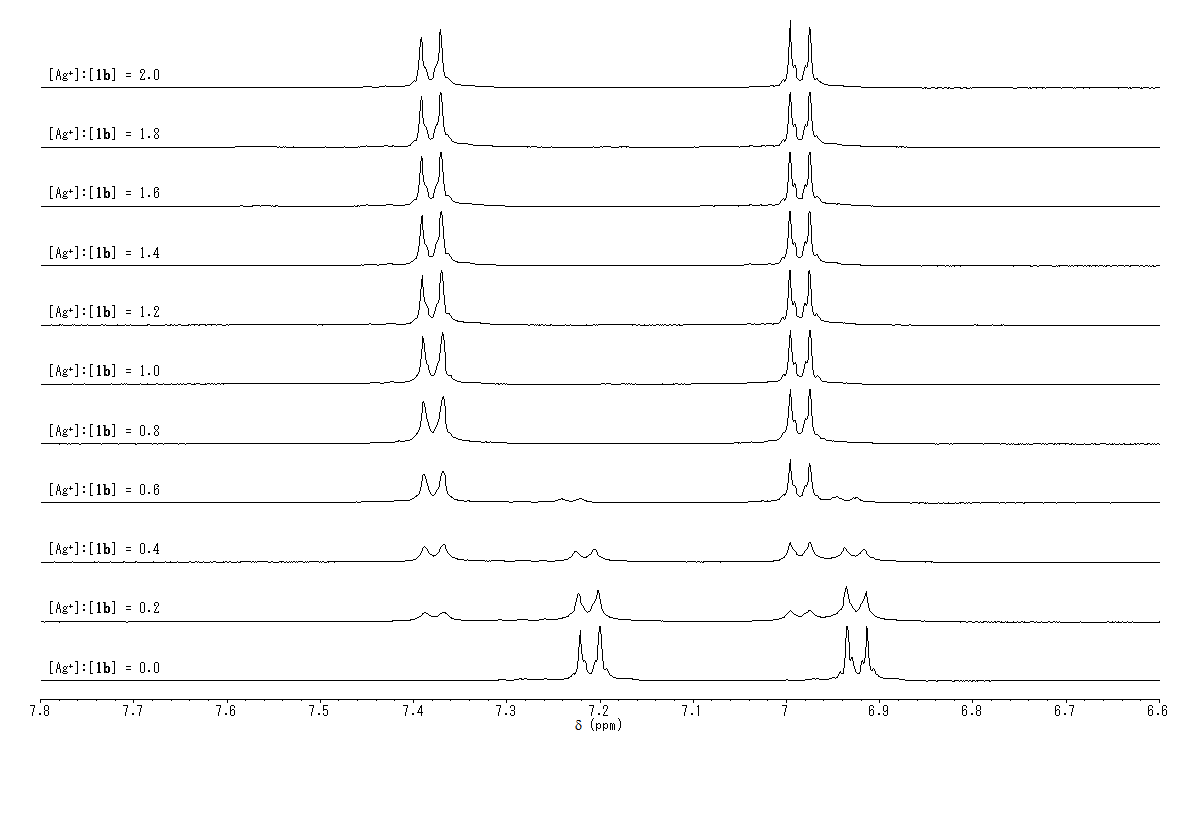
Log beta value deviation

AB 6.451 0.0227

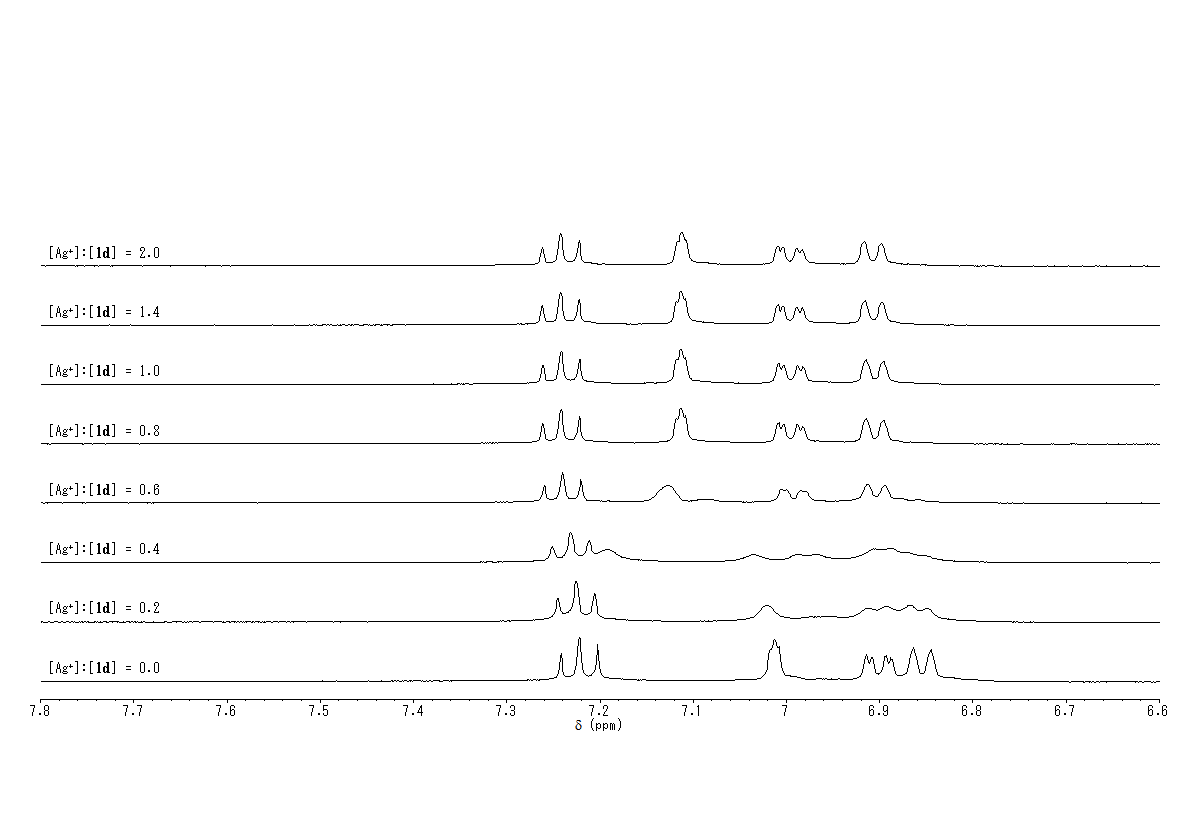
**Fig. S24.** UV titration curve of **4**/Ag+system at 259.5 nm. **♢**: Observed. ----: Calculated.



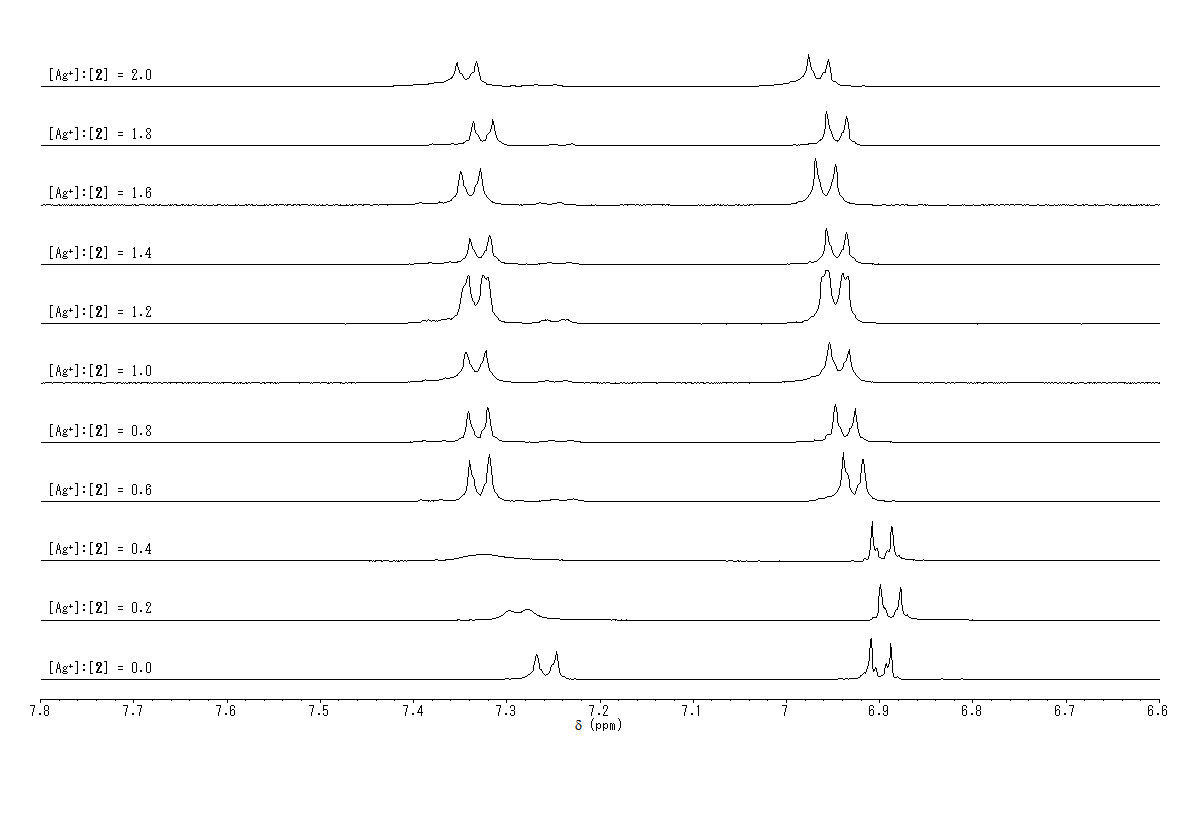
**Fig. S25**. Ag+-ion-induced-1H NMR spectral changes (aromatic regin) of **1a**.



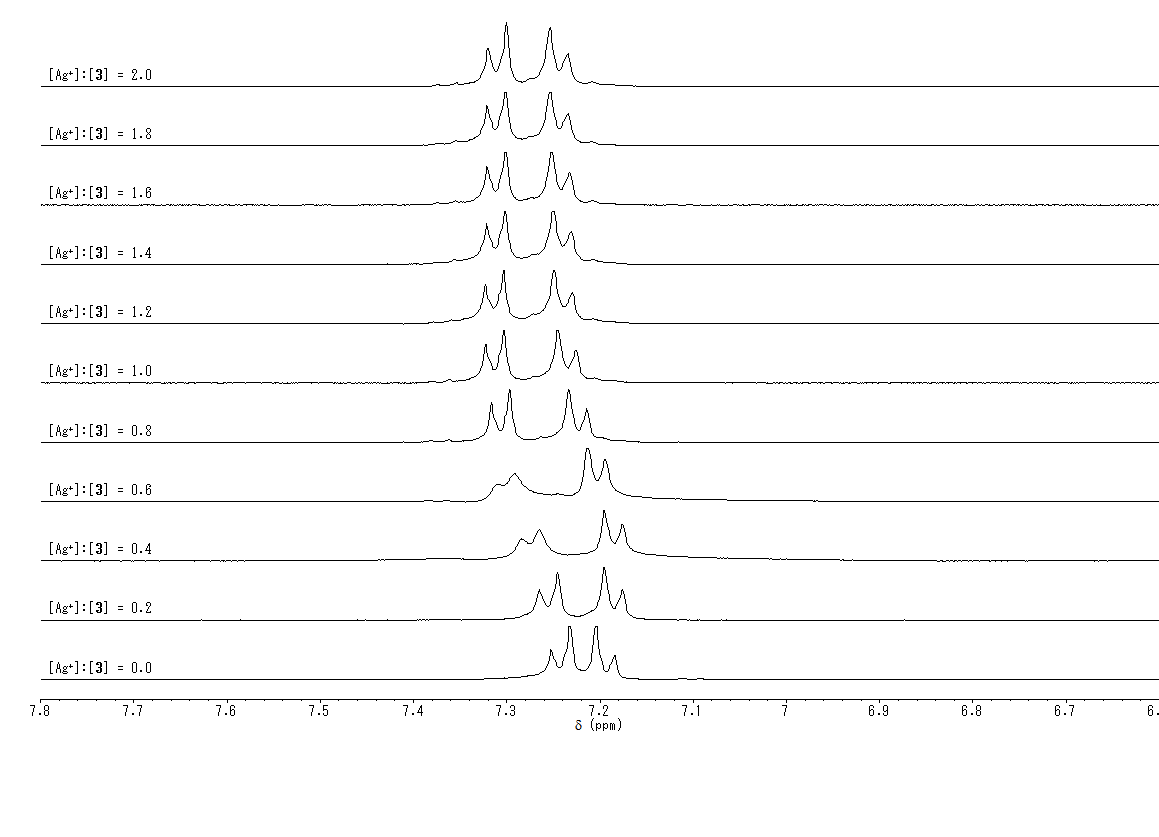
**Fig. S26**. Ag+-ion-induced-1H NMR spectral changes (aromatic regin) of **1b**.



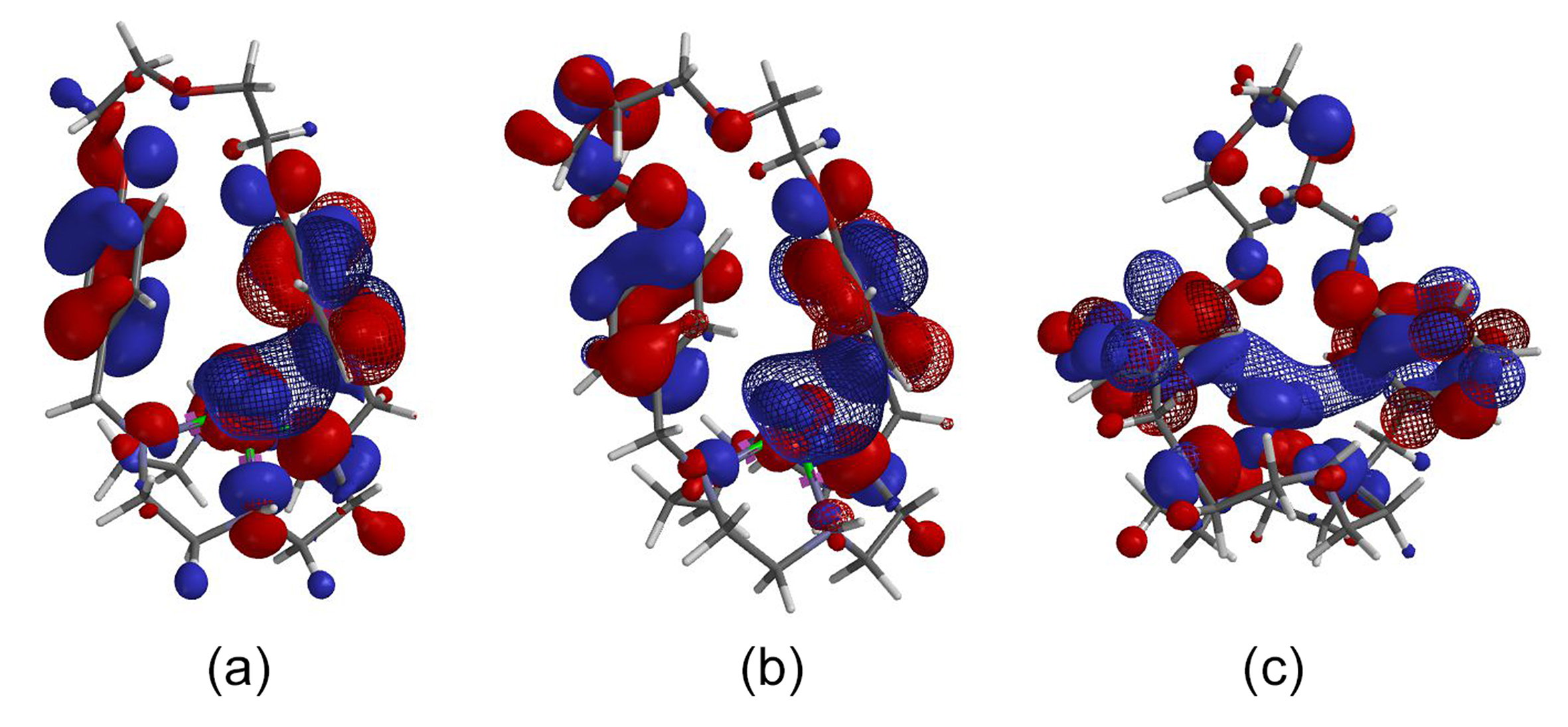
**Fig. S27**. Ag+-ion-induced-1H NMR spectral changes (aromatic regin) of **1d**.



**Fig. S28**. Ag+-ion-induced-1H NMR spectral changes (aromatic regin) of **3a**.



**Fig. S29**. Ag+-ion-induced-1H NMR spectral changes (aromatic regin) of **3b**.



**Fig. S30**. LUMO (mesh) and HOMOs (solid) of **1a**/Ag+, **1b**/Ag+, and **1d**/Ag+ complexes. These structures were optimized using the DFT (the B3LYP/3-21G\*). (a) LUMO, HOMO[–1], and HOMO[–2] of **1a**/Ag+, (b) LUMO, HOMO[–1], and HOMO[–2] of **1b**/Ag+, and (c) LUMO, HOMO[–1], and HOMO[–4] of **1d**/Ag+.