Ring size affects the kinetic and thermodynamic formation of [2]rotaxanes featuring an unsymmetric bis-crown ether component

Masaya Naito,[a] Takaaki Fujino,[a] Shinya Tajima,[a] Shinobu Miyagawa,[a] Kazuyuki Yoshida,[b] Hajime Inoue,[b] Hiroaki Takagawa,[b] Tsuneomi Kawasaki [c] and Yuji Tokunaga*[a]

[a.] *Department of Materials Science and Engineering, Faculty of Engineering, University of Fukui, Bunkyo, Fukui 910-8507, Japan.*

[b.] *Forensic Science Laboratory, Fukui Prefectural Police H.Q., Ohte, Fukui 910-8515, Japan.*

[c.] *Department of Applied Chemistry, Tokyo University of Science, Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan.*

Supporting Information

Table of Contents

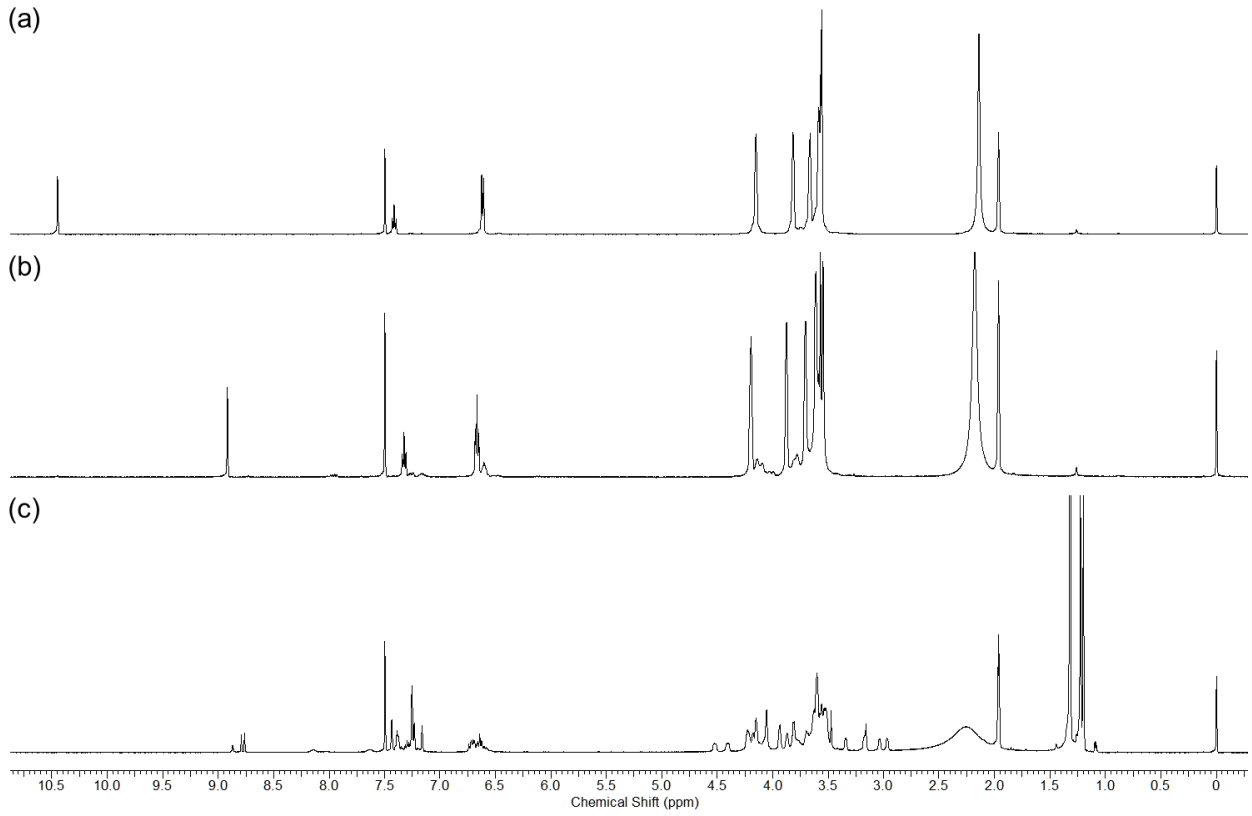
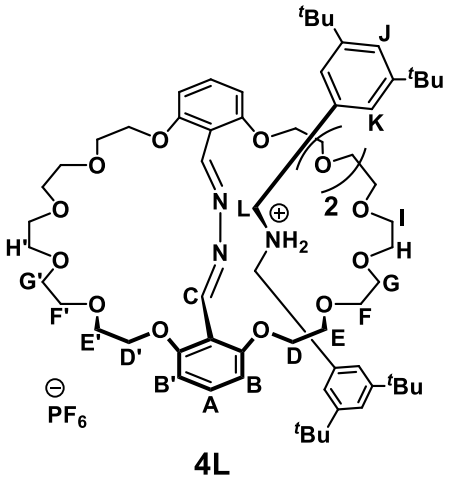


Fig. S1 ^{1}H NMR spectra [500 MHz; $CDCl_3/CD_3CN$, 1:1 (v/v); 295 K] of (a) the mono-crown ether **1** (5.0 mM), (b) a mixture of **1** (5.0 mM) and hydrazine (1.0 eq), and (c) a mixture of **1** (5.0 mM), hydrazine (1.3 eq), and the dibenzylammonium salt **3** (1.0 eq).



4L

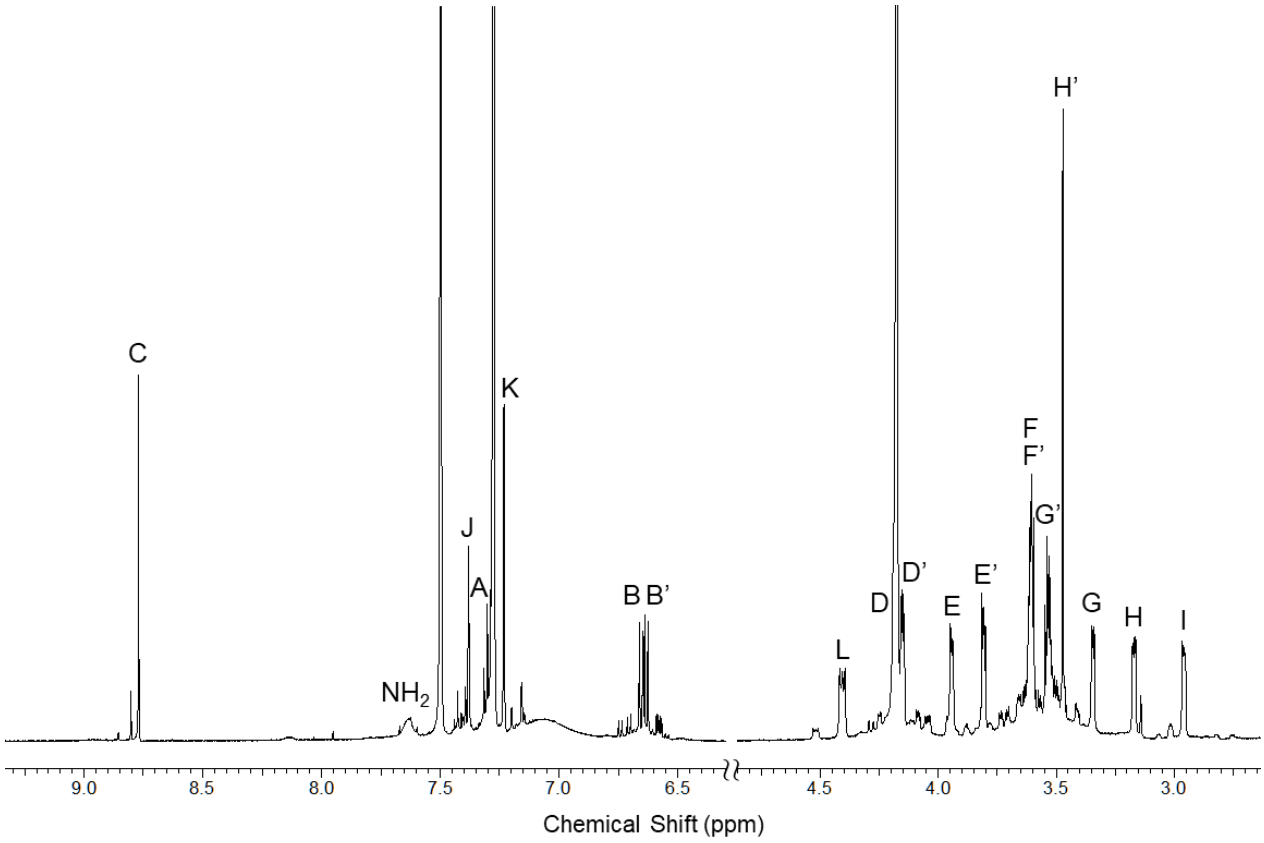


Fig. S2 ^{1}H NMR spectrum [600 MHz; $CDCl_3/CD_3CN$, 1:1 (v/v), 295 K] of a mixture of the mono-crown ether **1** in CD_3CN (1.0×10^{-2} M, 3.0×10^{-1} mL, 3.0×10^{-3} mmol) and the dibenzylammonium salt **3** in $CDCl_3$ (5.0×10^{-2} M, 3.0×10^{-1} mL, 1.5×10^{-2} mmol), recorded 10 min after adding hydrazine monohydrate in CD_3CN (3.0×10^{-1} M, 9.0×10^{-3} mL, 2.7×10^{-3} mmol).

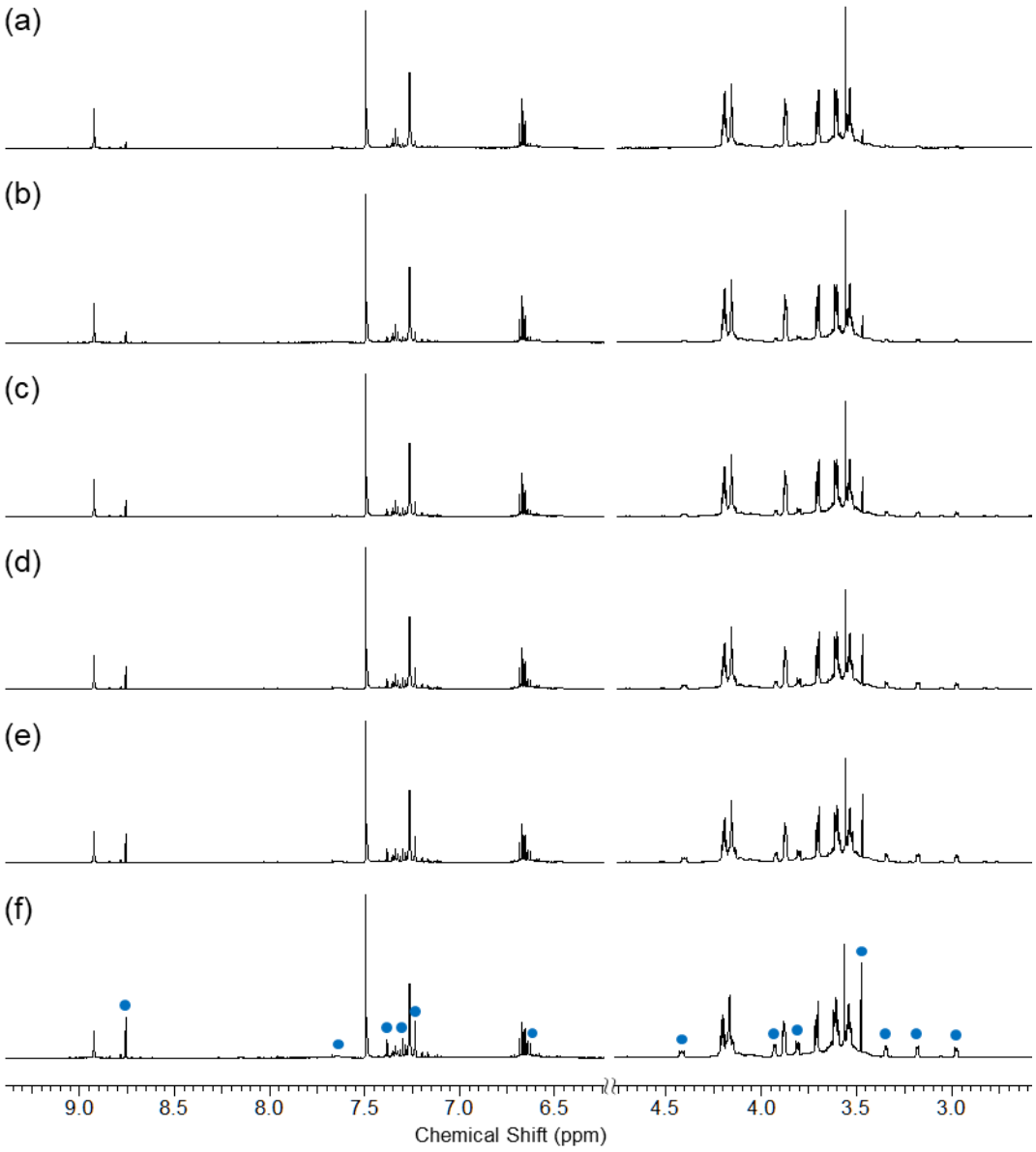


Fig. S3 Time-dependent ^{1}H NMR spectra [600 MHz; $CDCl_3/CD_3CN$, 1:1 (v/v); 295 K] of a mixture of the bis-crown ether **2** (5.0 mM, prepared *in situ* from the mono-crown ether **1** and an equimolar amount of hydrazine) and the dibenzylammonium salt **3** (1.0 eq), recorded after mixing them for (a) 15, (b) 25, (c) 40, (d) 60, (e) 80, and (f) 120 min. Blue dots denote the characteristic signals of **4L**.

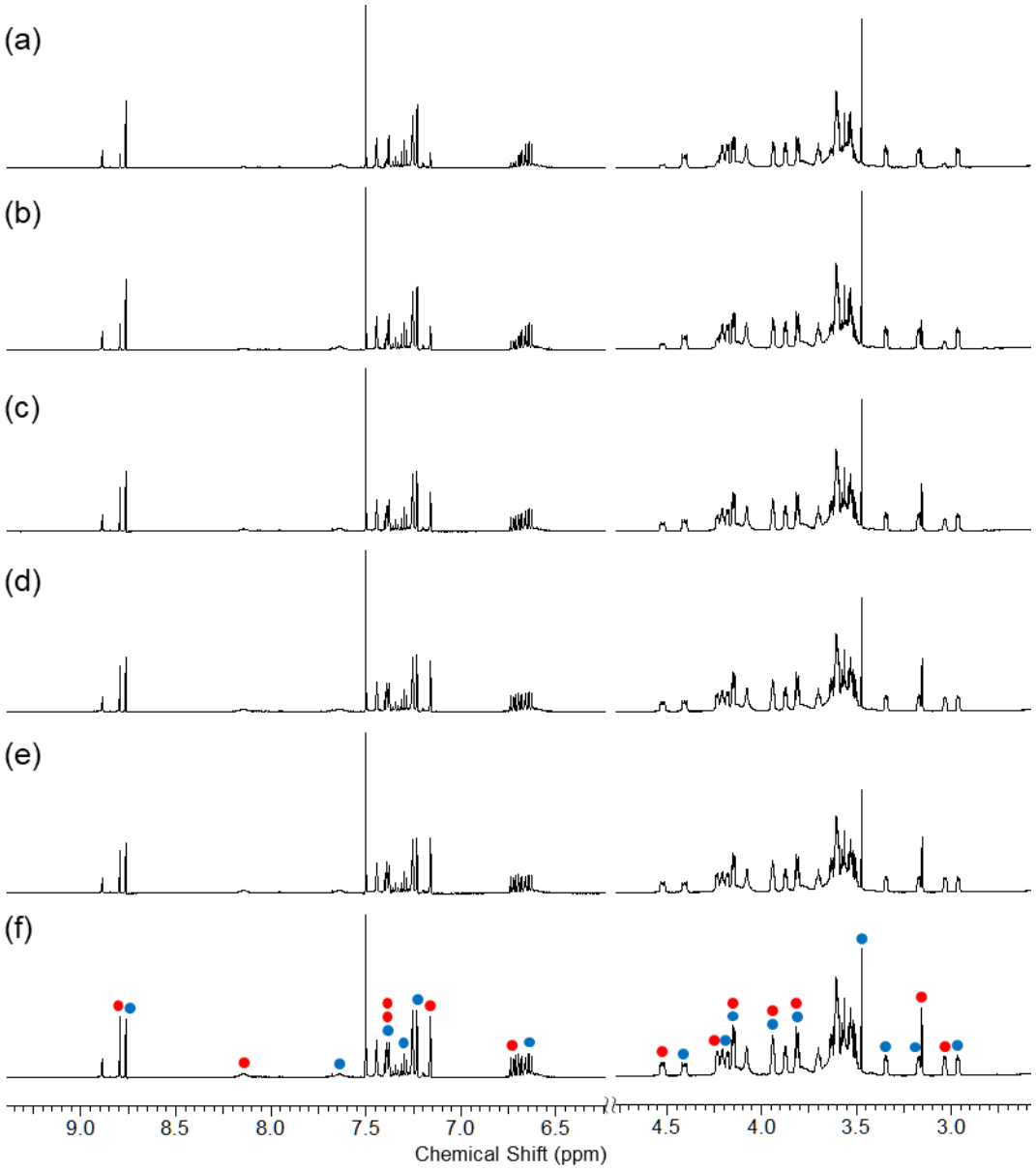


Fig. S4 Time-dependent ^{1}H NMR spectra [600 MHz; $CDCl_3/CD_3CN$, 1:1 (v/v); 295 K] of a mixture of the bis-crown ether **2** (5.0 mM, prepared *in situ* from the mono-crown ether **1** and 1.2 eq of hydrazine) and the dibenzylammonium salt **3** (1.0 eq), recorded after mixing them for (a) 0.25, (b) 0.5, (c) 1, (d) 2, (e) 4, and (f) 16 h. Blue and red dots denote the characteristic signals of **4L** and **4S**, respectively.

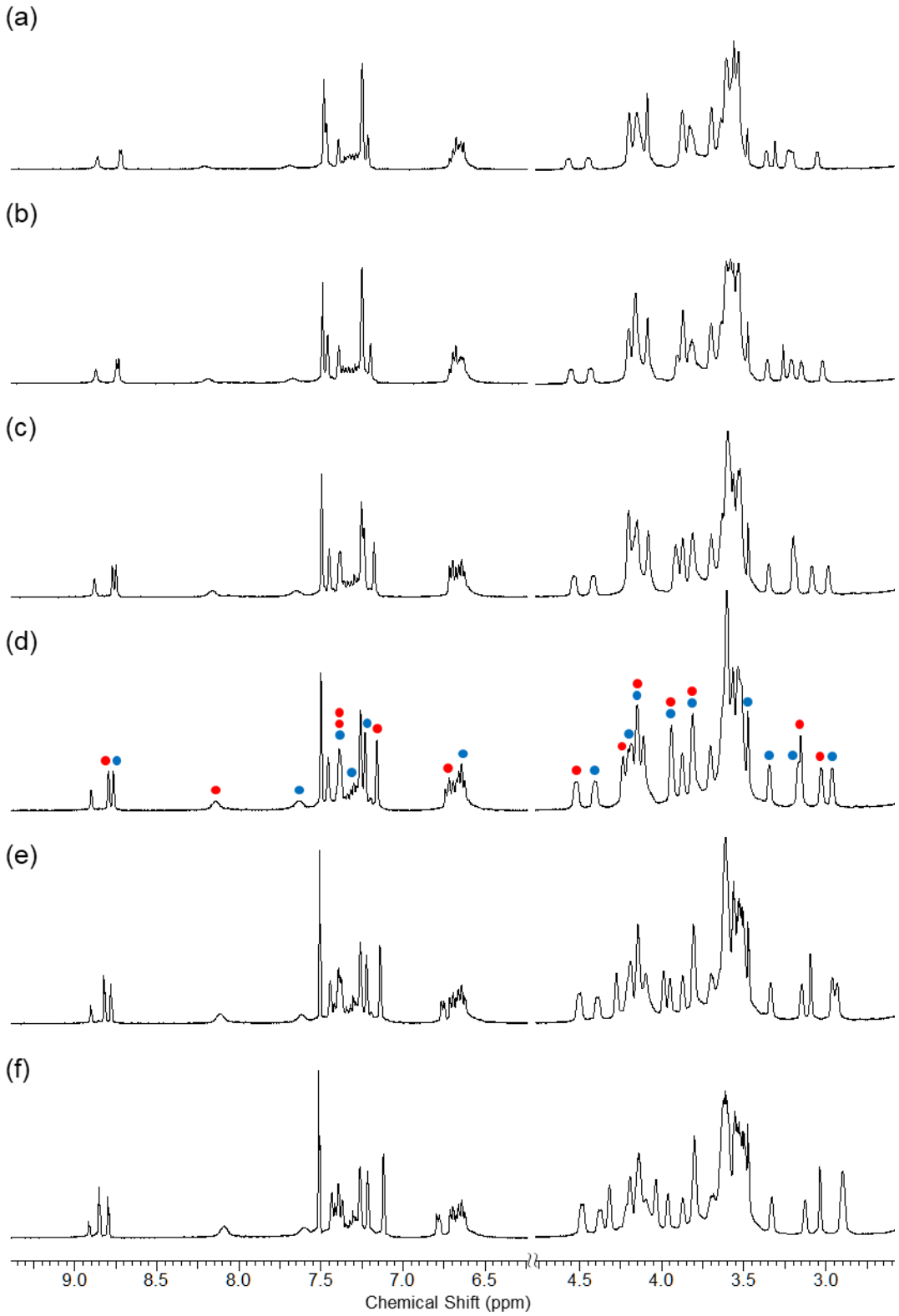


Fig. S5 Variable-temperature ^{1}H NMR spectra [500 MHz; $CDCl_3/CD_3CN$, 1:1 (v/v)] of a mixture of the bis-crown ether **2** (5.0 mM, prepared *in situ* from the mono-crown ether **1** and 1.2 eq of hydrazine) and the dibenzylammonium salt **3** (1.0 eq), recorded after reaching equilibrium at (a) 323, (b) 313, (c) 303, (d) 295, (e) 286, and (f) 277 K. Blue and red dots denote the characteristic signals of **4L** and **4S**, respectively.

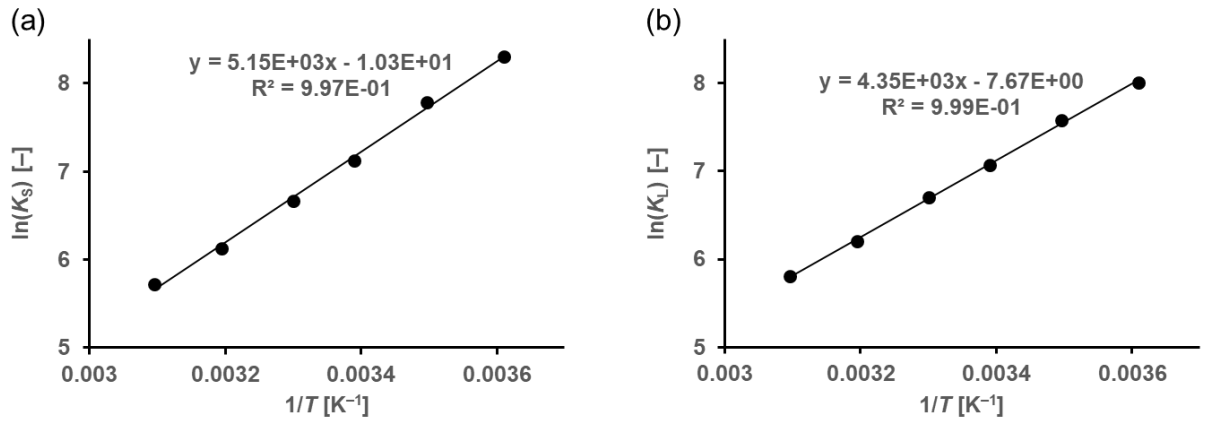


Fig. S6 Van't Hoff plots for the formation of the [2]rotaxanes (a) **4S** and (b) **4L** in $CD_3CN/CDCl_3$ (1:1, v/v).

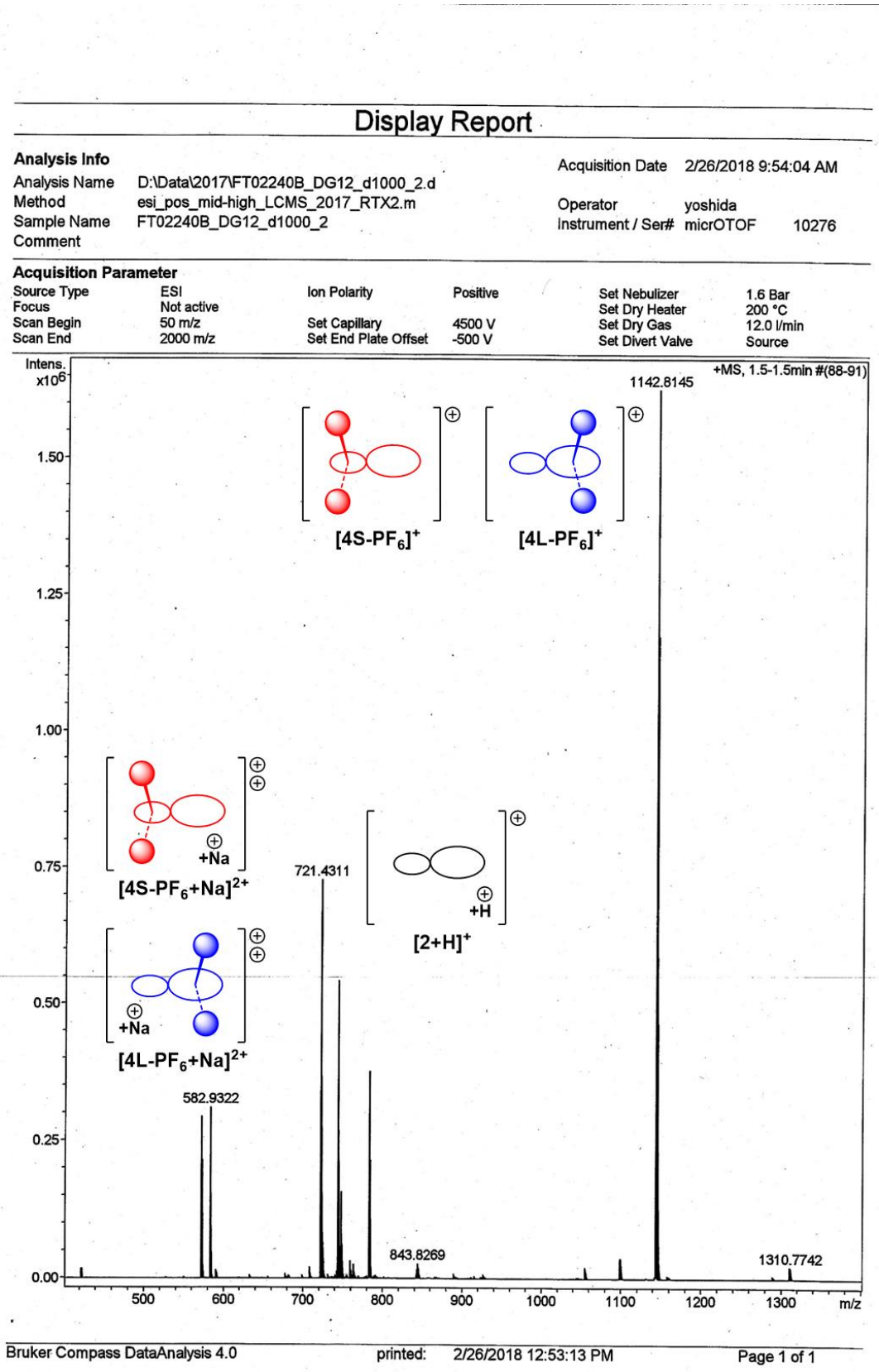


Fig. S7 ESI mass spectrum of a mixture of the mono-crown ether **1** and the dibenzylammonium salt **3** (5.0 eq) in the presence of hydrazine (0.9 eq).

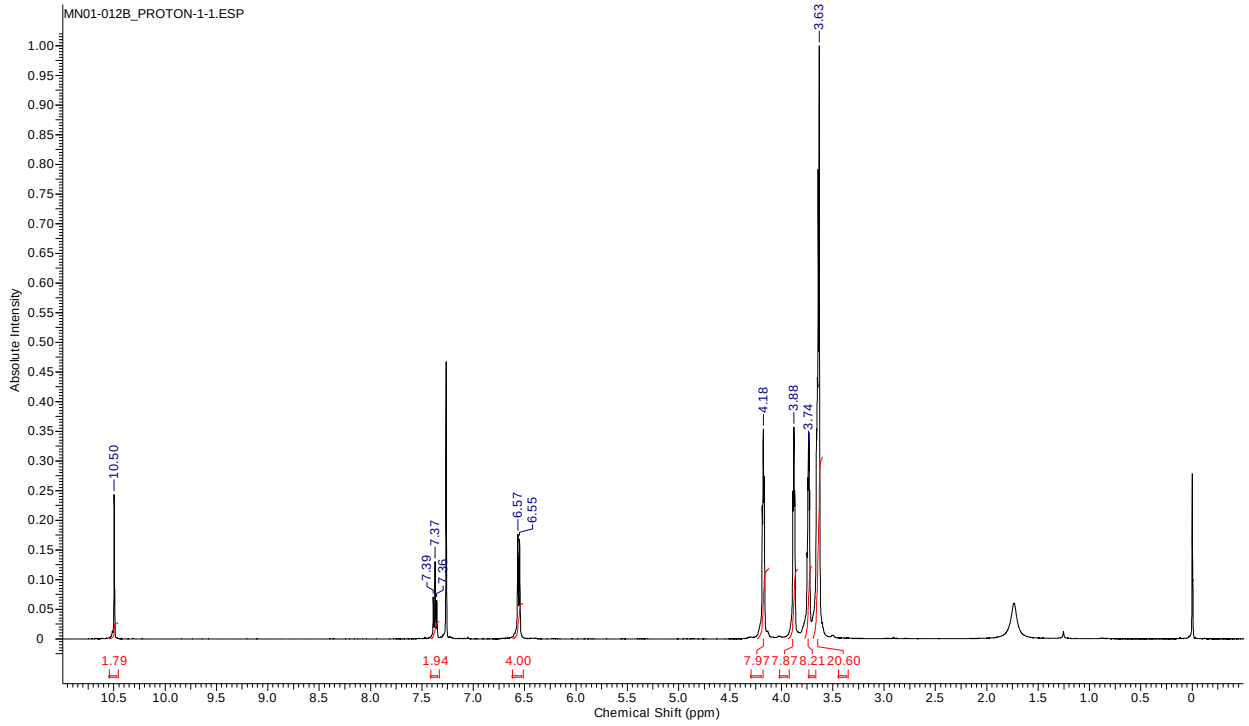


Fig. S8 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 295 K) of the mono-crown ether **1**.

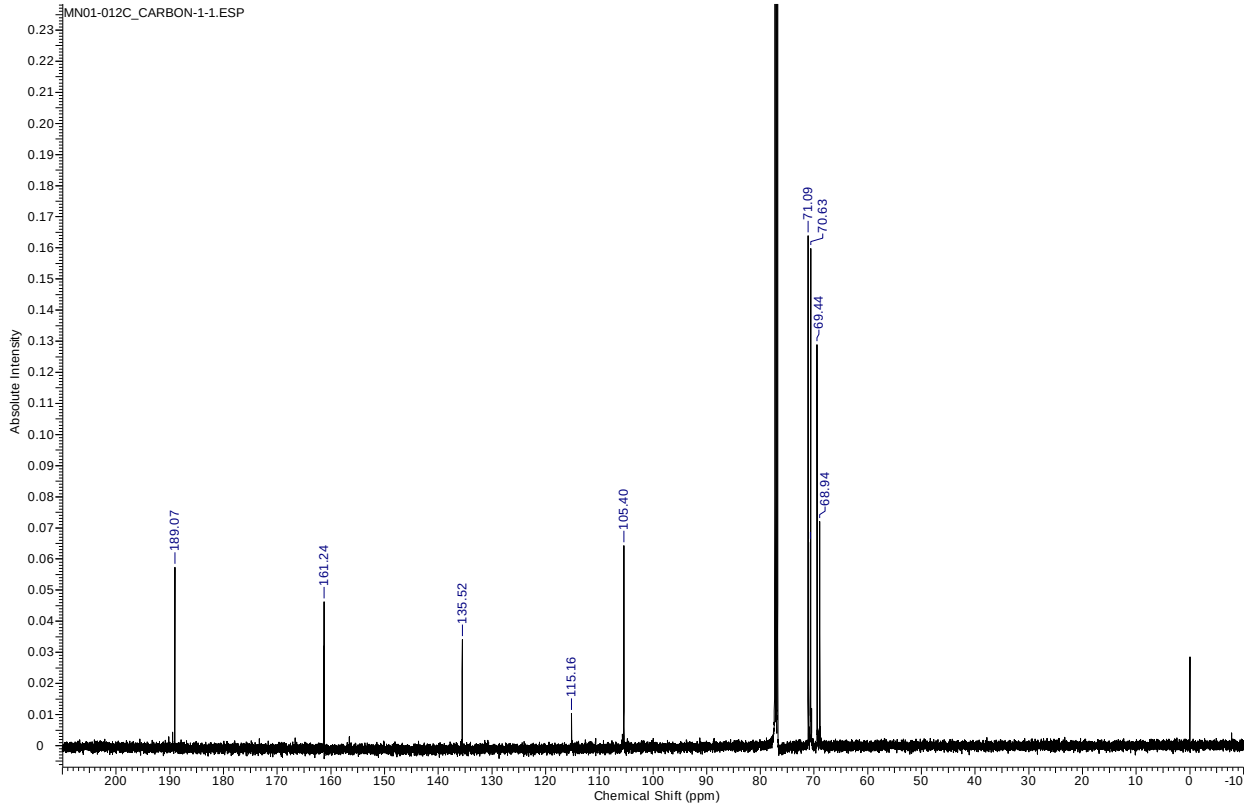


Fig. S9 ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 295 K) of the mono-crown ether **1**.

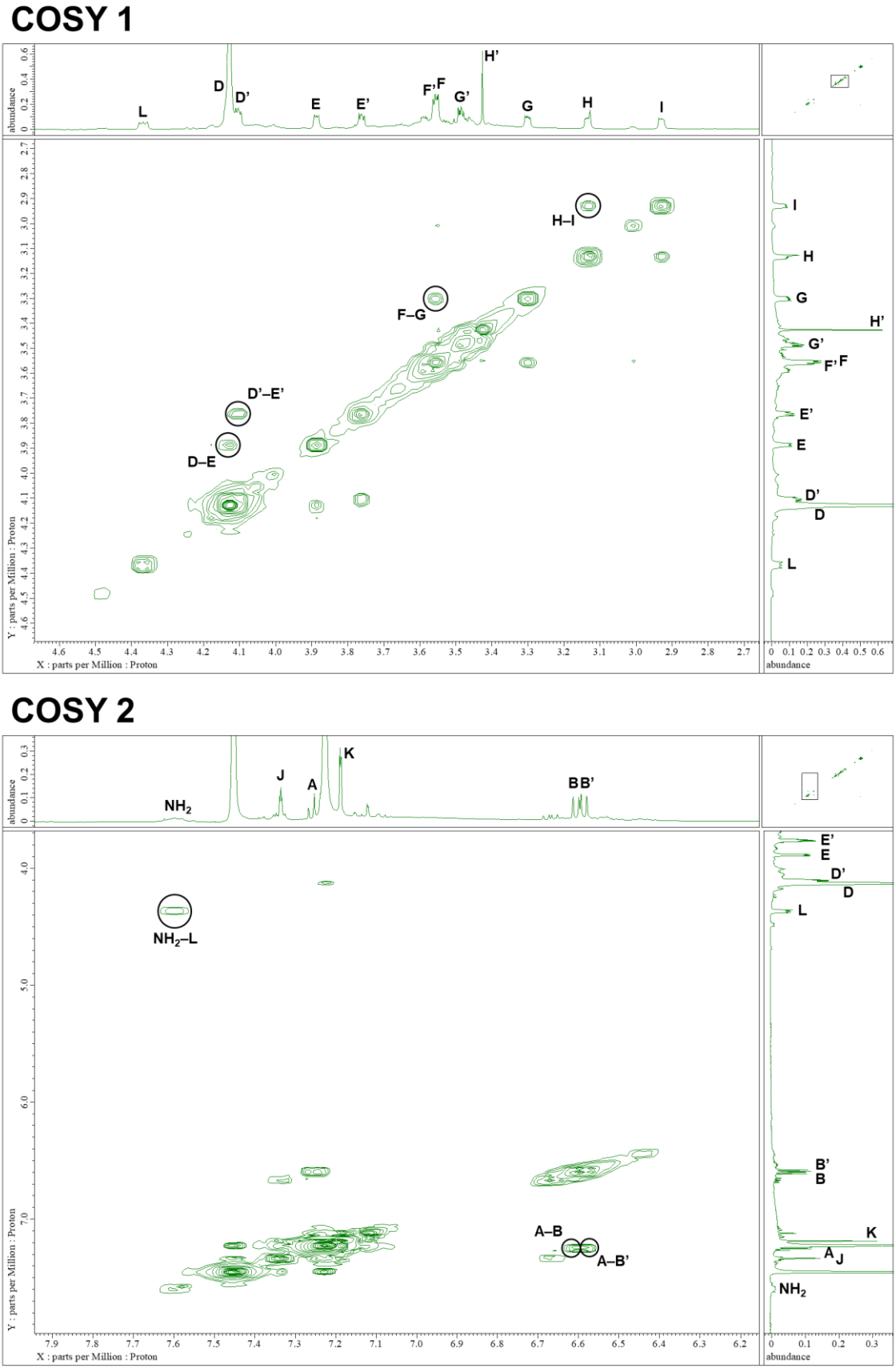


Fig. S10 COSY spectrum [600 MHz; $CDCl_3/CD_3CN$, 1:1 (v/v); 295 K] of a mixture of the mono-crown ether **1** (5.0 mM) and the dibenzylammonium salt **3** (5.0 eq) after adding hydrazine (0.9 eq).

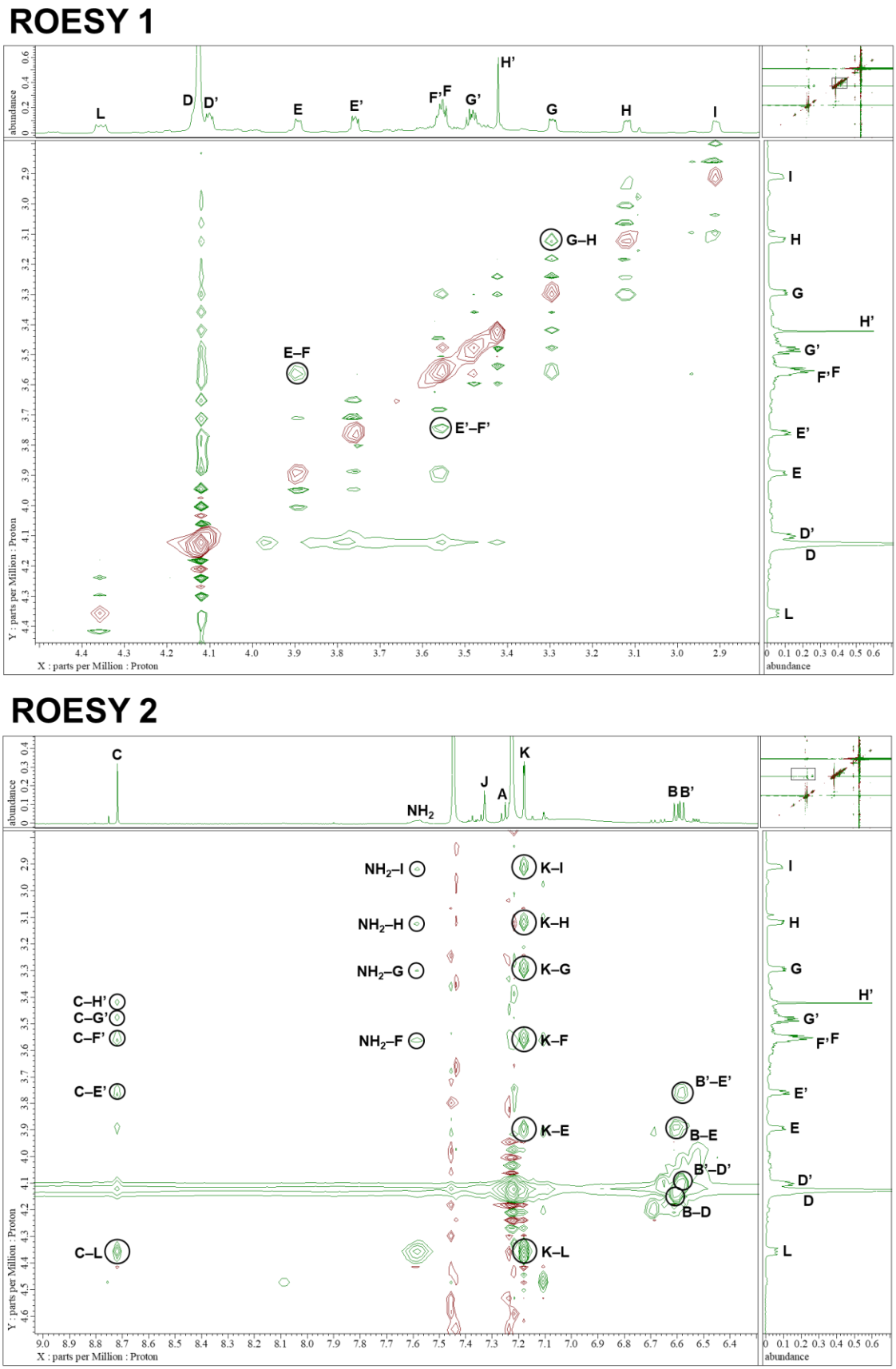


Fig. S11 ROESY spectrum [600 MHz; $CDCl_3/CD_3CN$, 1:1 (v/v); 295 K; mixing time, 0.25 s] of a mixture of the mono-crown ether **1** (5.0 mM) and the dibenzylammonium salt **3** (5.0 eq) after adding hydrazine (0.9 eq).

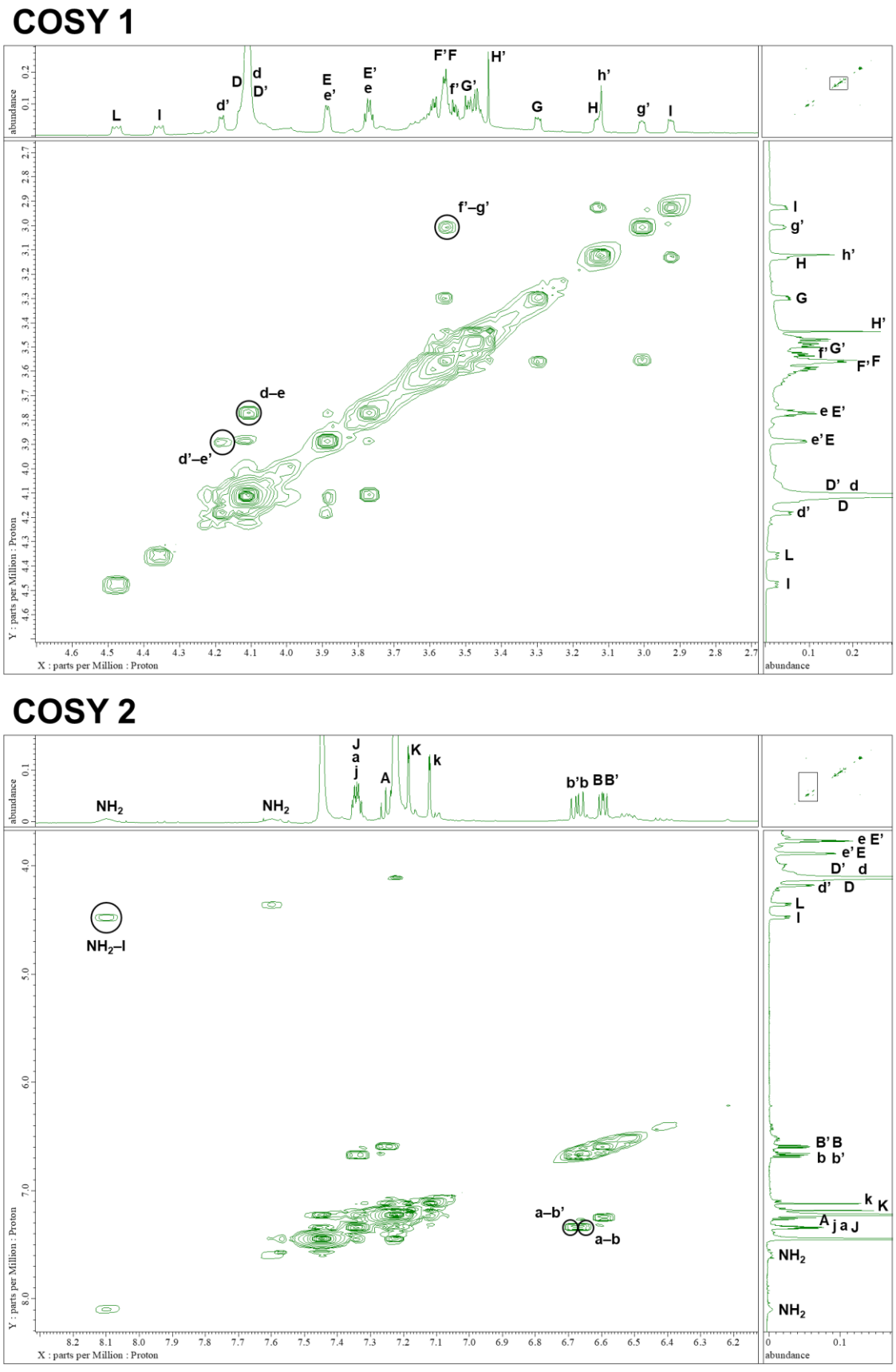


Fig. S12 COSY spectrum [600 MHz; $CDCl_3/CD_3CN$, 1:1 (v/v); 295 K] of a mixture of the mono-crown ether **1** (5.0 mM) and the dibenzylammonium salt **3** (5.0 eq) after adding hydrazine (1.2 eq).

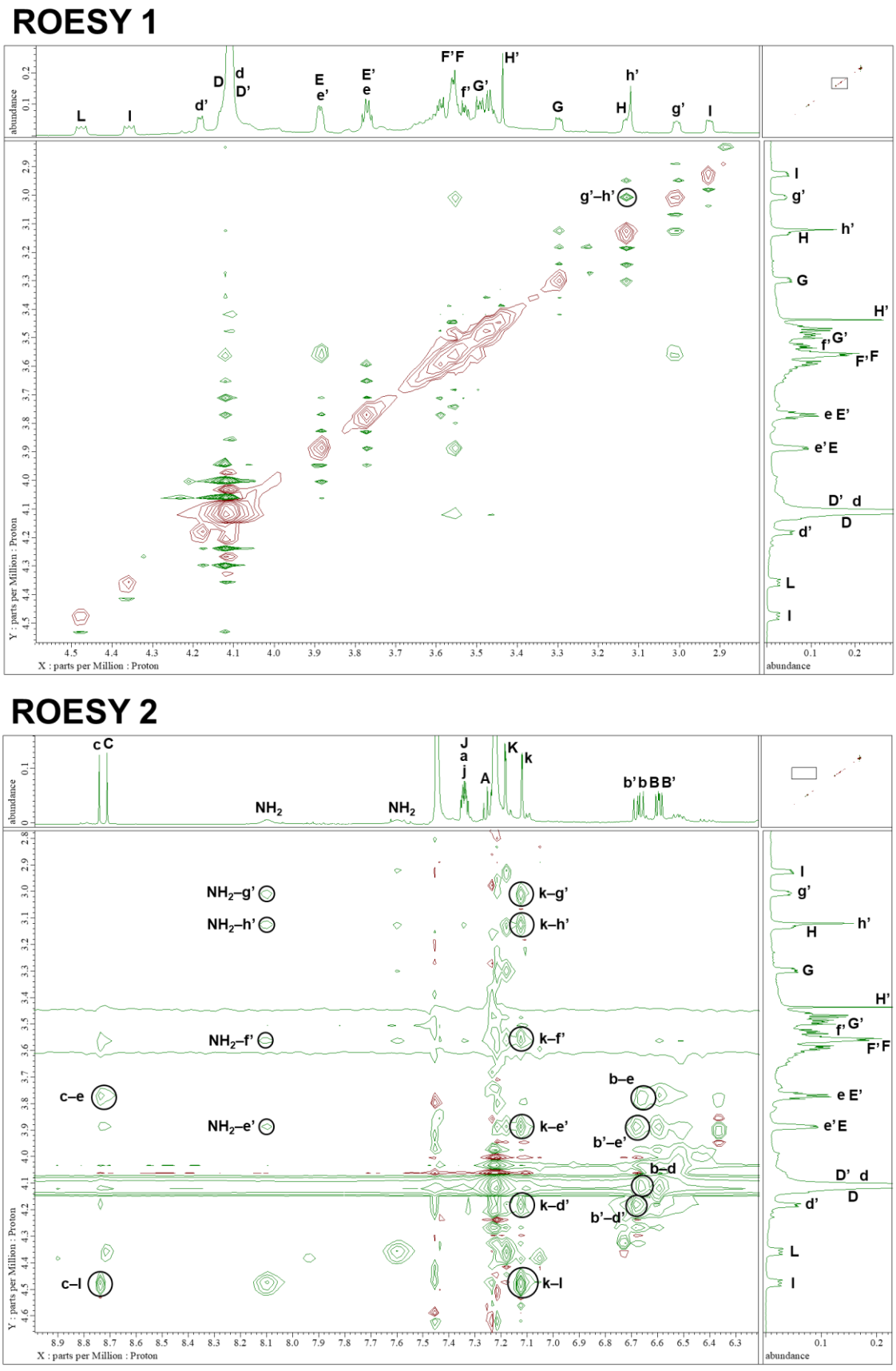


Fig. S13 ROESY spectrum [600 MHz; $CDCl_3/CD_3CN$, 1:1 (v/v); 295 K; mixing time, 0.25 s] of a mixture of the mono-crown ether **1** (5.0 mM) and the dibenzylammonium salt **3** (5.0 eq) after adding hydrazine (1.2 eq).

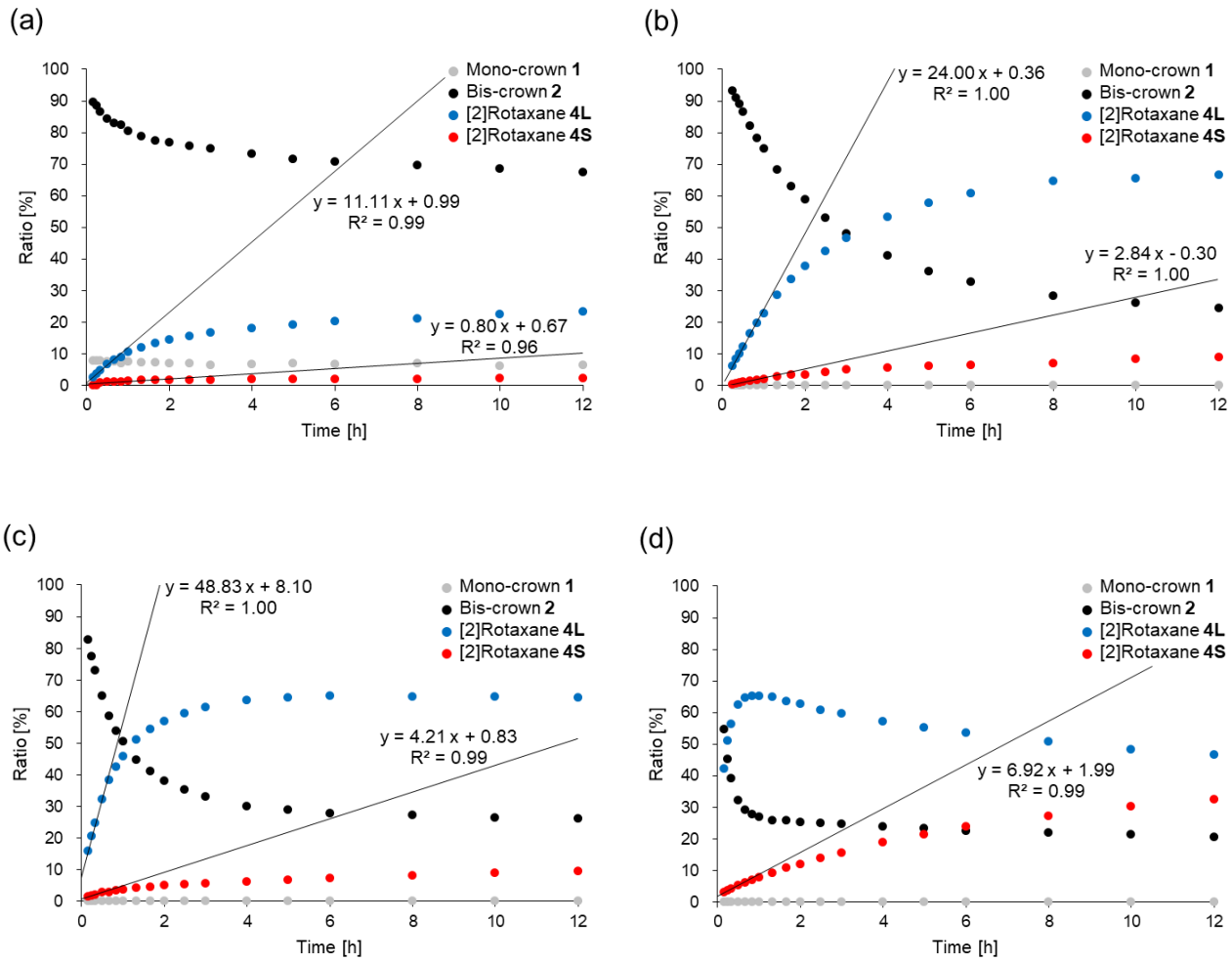


Fig. S14 Distributions of the mono-crown ether **1** (gray dots), bis-crown ether **2** (black dots), and the [2]rotaxanes **4L** (blue dots) and **4S** (red dots) after mixing of the bis-crown ether **2** and the dibenzylammonium salt **3** (5.0 mM), as determined using ^{1}H NMR spectroscopy [600 MHz; $CDCl_3/CD_3CN$, 1:1 (v/v); 295 K]. The bis-crown ether **2** was prepared *in situ* from the mono-crown ether **1** (5.0 mM) and (a) 0.95, (b) 1.00, (c) 1.05, and (d) 1.10 eq of hydrazine.