Supporting Information

# Rotational isomerism of the amide units in rotaxanes based on a cyclic tetraamide and secondary ammonium ions

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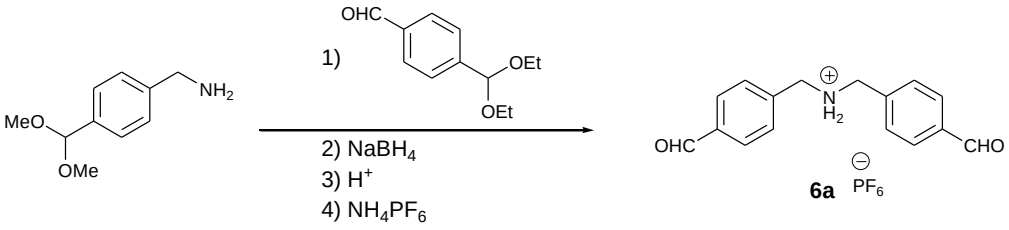
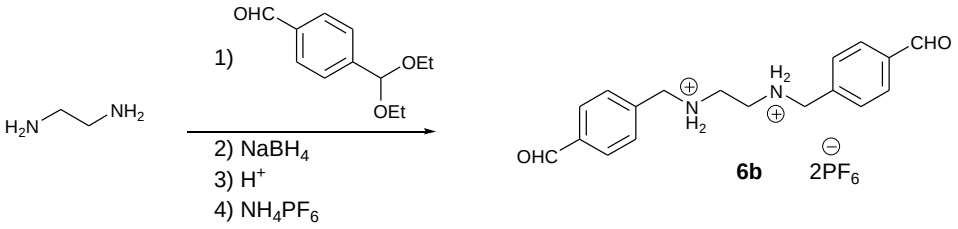
## Contents

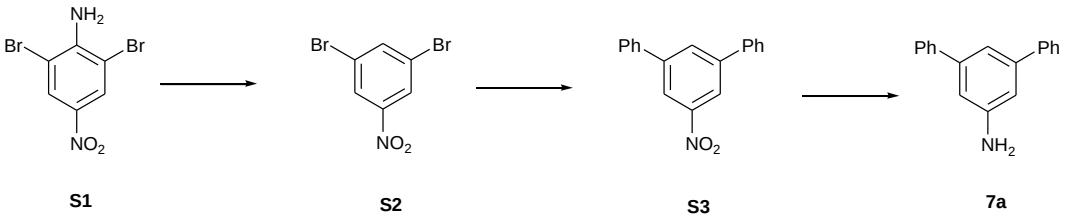
## Experimental

### Synthesis of the ammonium salts 6a and 6b.

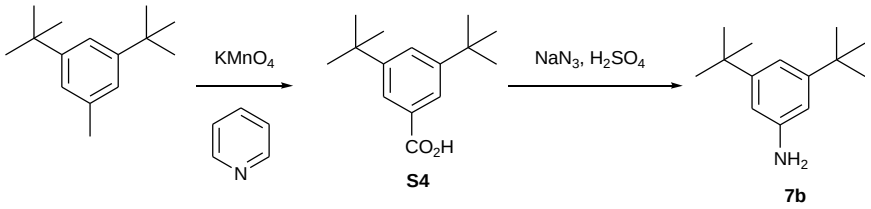


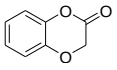

### Synthesis of the bulky aniline derivative 7a.




### Synthesis of the bulky aniline derivative 7b.



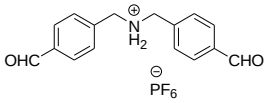

### 1,4-Benzodioxan-2-one (4)



1,4-Benzodioxan-2-one was prepared according to a literature procedure.[1] Chloroacetyl chloride (8.73 mL, 110 mmol) was added to a solution of catechol (11.0 g, 100 mmol) and $Et_3N$ (27.7 mL, 200 mmol) in $CH_2Cl_2$ (100 mL) at 0 °C and then the

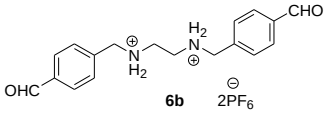
mixture was heated under reflux for 1 day. The reaction mixture was diluted with AcOEt (300 mL). The organic phase was washed sequentially with $H_2O$, 10% $NaHCO_3$, and sat. NaCl, dried ($MgSO_4$), and concentrated. The residue was purified through gel column chromatography ($SiO_2$; hexane/AcOEt, 10:1) to give colorless crystals (9.04 g, 60%). $^1$H NMR (500 MHz, $CDCl_3$) δ: 4.67 (s, 2H), 7.01–7.12 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 64.8, 117.3, 117.5, 123.4, 125.4, 141.0, 142.4, 163.2.
The $^1$H and $^{13}$C NMR spectra of **6a** were identical to those reported previously.[1]

**Mono-ammonium salt (6a)**[2]



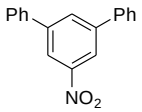

$Et_3N$ (3 drops) was added to a solution of 4-(dimethoxymethyl)benzylamine (1.20 g, 6.62 mmol) and terephthalaldehyde mono(diethyl acetal) (2.07 g, 9.93 mmol) in $CH_2Cl_2$ (23 mL) at room temperature and then the mixture was stirred for 18 h at the same temperature. After addition of $Na_2SO_4$ and filtration of the reaction mixture, the filtrate was concentrated. The residue was dissolved in EtOH (43 mol). $NaBH_4$ (0.345 g, 17.1 mmol) was added to the solution at room temperature. After stirring overnight, 1 N NaOH was added to the mixture and then the EtOH was evaporated. The residue was diluted with water. The aqueous phase was extracted with $CH_2Cl_2$. The combined extracts were dried ($Na_2SO_4$) and concentrated. The residue was purified chromatographically ($SiO_2$; AcOEt) to give a crude product (2.14 g), which was used without further purification.
A solution of the crude amine in THF (40 mL) and 10% HCl (10 mL) was stirred for 22 h. The acidic solution was neutralized with sat. $Na_2CO_3$ and then the THF was evaporated. $CH_2Cl_2$ was added. The organic phase was separated, washed with sat. NaCl, dried ($Na_2SO_4$), and concentrated. The residue was dissolved in $Et_2O$ (40 mL). A solution of HCl in dioxane (4.2 M, 2.03 mL, 8.59 mmol) was added and then the precipitate was collected through filtration and washed with $iPr_2O$. The solid was suspended in acetone (35 mL) and $H_2O$ (35 mL). $NH_4PF_6$ (4.67 g, 28.6 mmol) was added and then the mixture was stirred for 3.5 h. After evaporation of the acetone, the precipitate was filtered off and washed with water to give a white powder (1.83 g, 47%). $^1$H NMR (500 MHz, DMSO-$d_6$, 30 °C) δ: 4.33 (s, 4H), 7.69–7.74 (m, 2H), 7.69–8.01 (m, 4H), 9.38 (br s, 2H), 10.04 (s, 2H). $^{13}$C NMR (125 MHz, DMSO-$d_6$, 30 °C) δ: 50.0, 129.7, 130.6, 136.4, 138.1, 192.8.
The $^1$H and $^{13}$C NMR spectra of **6a** were identical to those reported previously.[2]

**Bis-ammnonium salt (6b)**



Compound **6b** (white powder, 4.79 g, 40%) was synthesized from ethylenediamine (0.860 mL, 12.8 mol) and 4-(dimethoxymethyl)benzylamine (5.60 g, 26.9 mmol), using the procedure described above. IR (KBr, $\nu_{max}$, $cm^{-1}$): 3617, 3549, 3381, 2918, 2763, 1694, 1612, 1445, 1216, 1179, 1021, 836, 562. $^1$H NMR (500 MHz, DMSO-$d_6$) δ: 3.25 (br s, 4H), 4.34 (br s, 4H), 7.69 (d, $J$ = 7.0 Hz, 4H), 8.01 (d, $J$ = 7.0 Hz, 4H), 8.96 (br s, 4H), 10.05 (s, 2H). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ: 42.5, 49.9, 129.9, 130.4, 192.8. HRMS (FAB) calcd. for $C_{18}H_{21}N_2O_2^+$ $[M - HCl - Cl]^+$ $m/z$ 297.1598, found 297.1623.

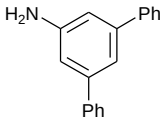
**3,5-Diphenylnitrobenzene (S3)**[3]




Tetrakis(triphenylphosphine) palladium (46.2 mg, 0.040 mmol) was added to a two-phase solution of 3,5-dibromonitrobenzene (**S2**, 1.12 g, 4.00 mmol), phenylboronic acid (1.22 g, 10.0 mmol), and triphenylphosphine (0.105 g, 0.40 mmol) in toluene (15 mL), EtOH (7.5 mL), and 2 M aqueous $Na_2CO_3$ (10 mL, 20.0 mmol) and then the mixture was heated under reflux for 40 h. After evaporation of the organic solvent, water was added to the residue. The aqueous phase was extracted with AcOEt. The combined organic phases were washed with sat. $Na_2CO_3$ and sat. NaCl, dried ($MgSO_4$), filtered, and concentrated. The residue was washed with MeOH to afford a white solid (0.562 g, 55%). $^1$H NMR (500 MHz, $CDCl_3$) δ: 7.43–7.49 (m, 2H), 7.50–7.55 (m, 4H), 7.67–7.71 (m, 4H), 8.12 (t, $J$ = 1.5 Hz, 1H), 8.43 (t, $J$ = 1.5 Hz, 4H).

The $^1$H NMR spectrum of **S3** was identical to that reported previously.[3]

**3,5-Diphenylaniline (7a)**[3]




Raney Ni (W-2, catalytic amount) was added to a solution of the nitrobenzene **S3** (0.652 g, 11.2 mmol) and hydrazine monohydrate (0.95 mL, 19.5 mmol) in THF (10 mL) and EtOH (10 mL) and then the mixture was heated under reflux overnight. The reaction mixture was filtered through Celite and the filtrate was concentrated. The residue was washed with AcOEt and hexane to afford a white solid (0.480 g, 83%). $^1$H NMR (500 MHz, $CDCl_3$) δ: 3.83 (br s, 2H), 6.90 (d, $J$ = 1.5 Hz, 2H), 7.21 (t, $J$ = 1.5 Hz, 2H), 7.32–7.38 (m, 2H), 7.41–7.47 (m, 4H), 7.59–7.64 (m, 4H).

The $^1$H NMR spectrum of **S3** was identical to that reported previously.[3]

References

1. C. A. Gandolfi, R. D. Domenico, S. Spinelli, L. Gallico, L. Fiocchi, A. Lotto, E. Menta, A. Borghi, C. D. Rosa and S. Tognella, *J. Med. Chem.*, 1995, **38**, 508–525.
2. S. J. Cantrill, S. J. Rowan and J. F. Stoddart, *Org. Lett.*, 1999, **1**, 1363–1366.
3. G. E. Greco and R. R. Schrock, *Inorg. Chem.*, 2001, **40**, 3850–3860.

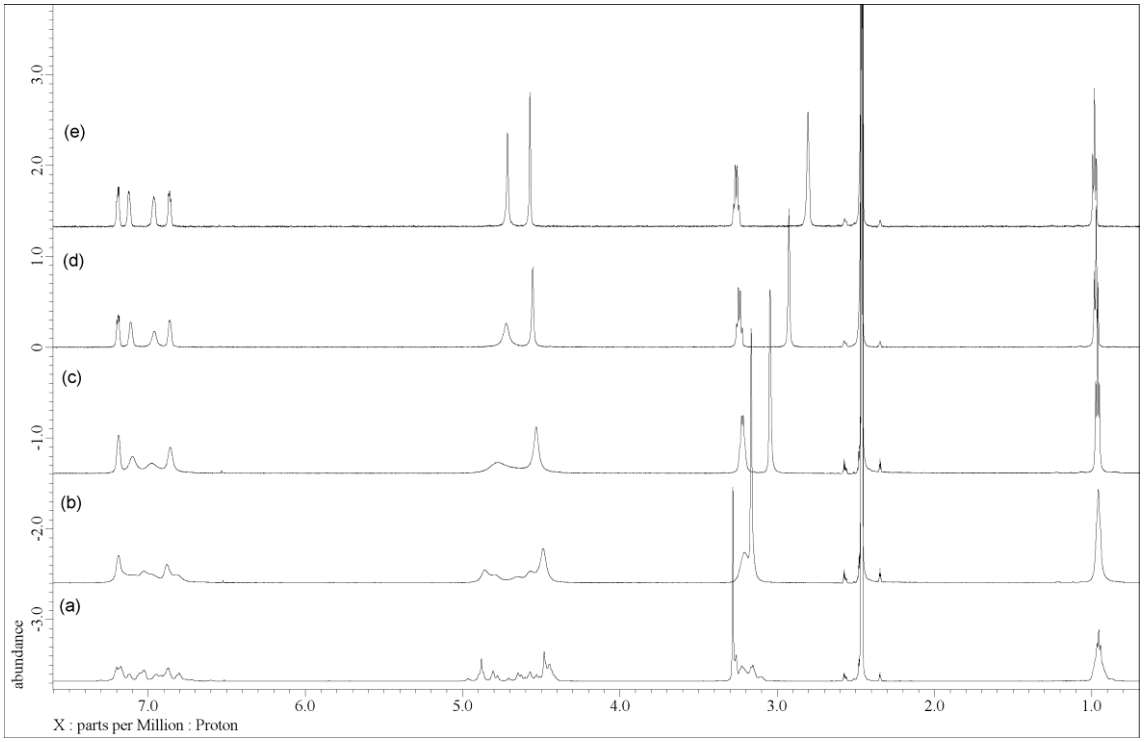



**Figure S1.** VT $^{1}$H NMR spectra (600 MHz, DMSO-$d_6$) of the cyclic tetraamide **1**, recorded at (a) 25, (b) 50, (c) 75, (d) 100, and (e) 125 °C.

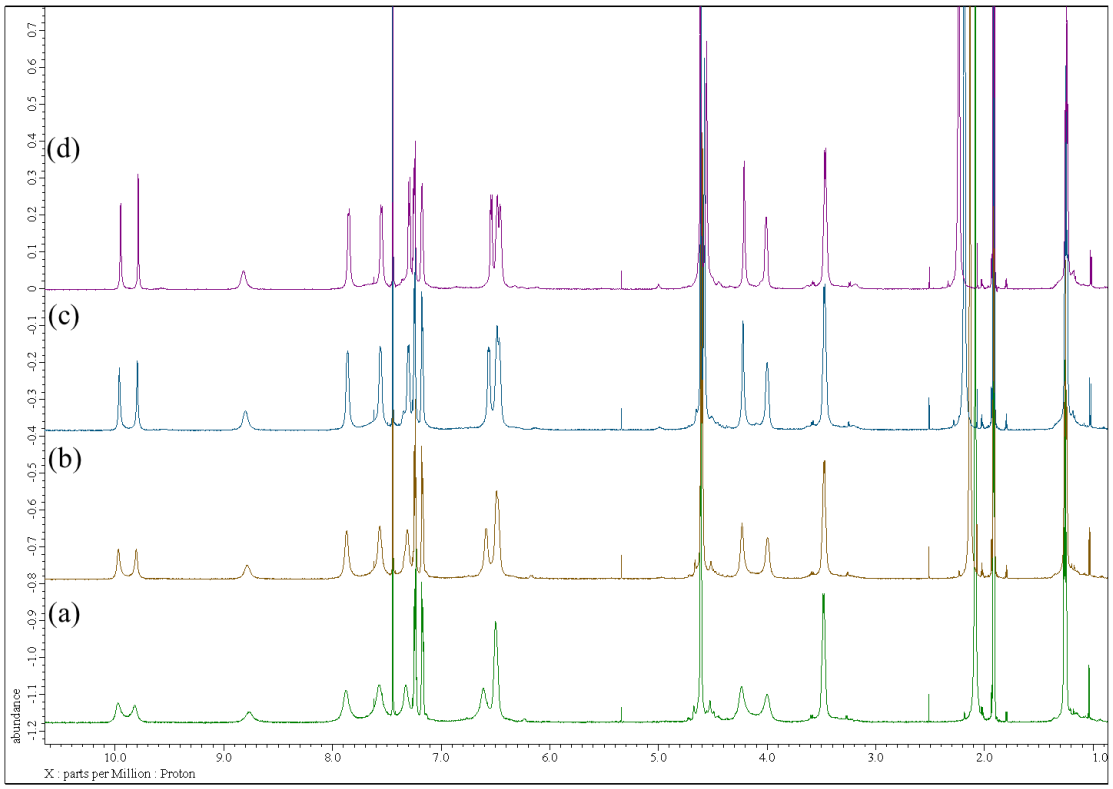
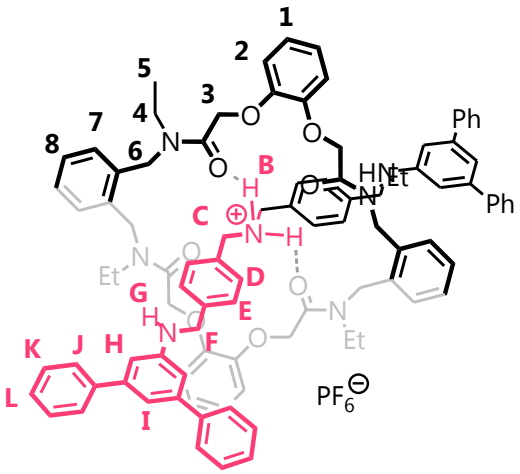



**Figure S2.** VT $^{1}$H NMR spectra [600 MHz, $CDCl_3/CD_3CN$ (1:1)] of a mixture of the cyclic tetraamide **1** (2.0 mM) and the mono-ammonium salt **6a** (1.4 eq), recorded at (a) 20, (b) 10, (c) 0, and (d) –10 °C.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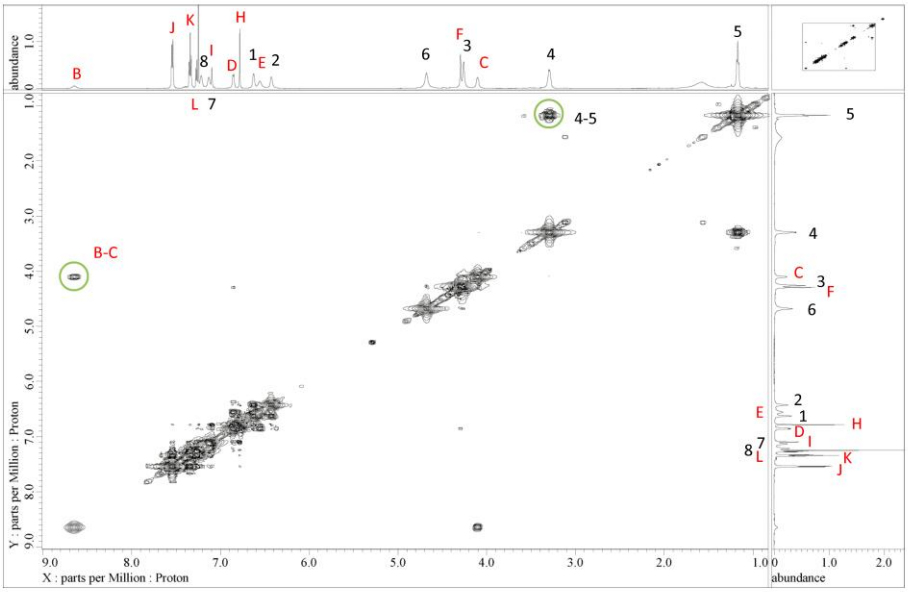
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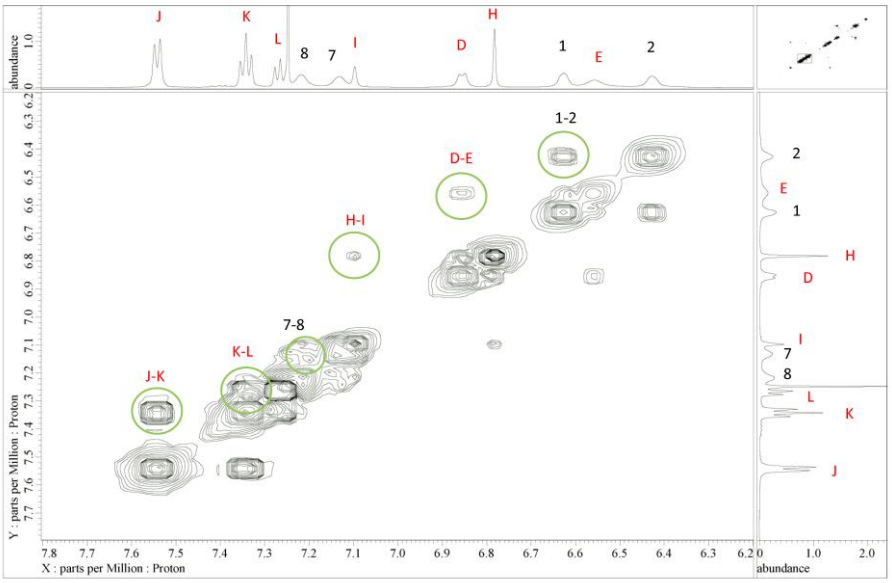
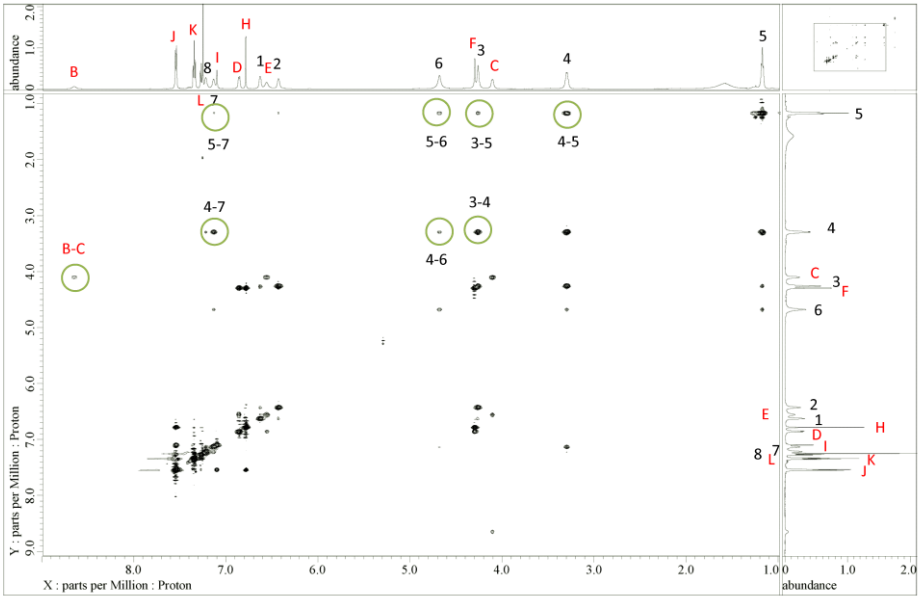



**Figure S3a.** COSY spectrum (600 MHz, $CDCl_3$, 25 °C) of the [2]rotaxane **8a**.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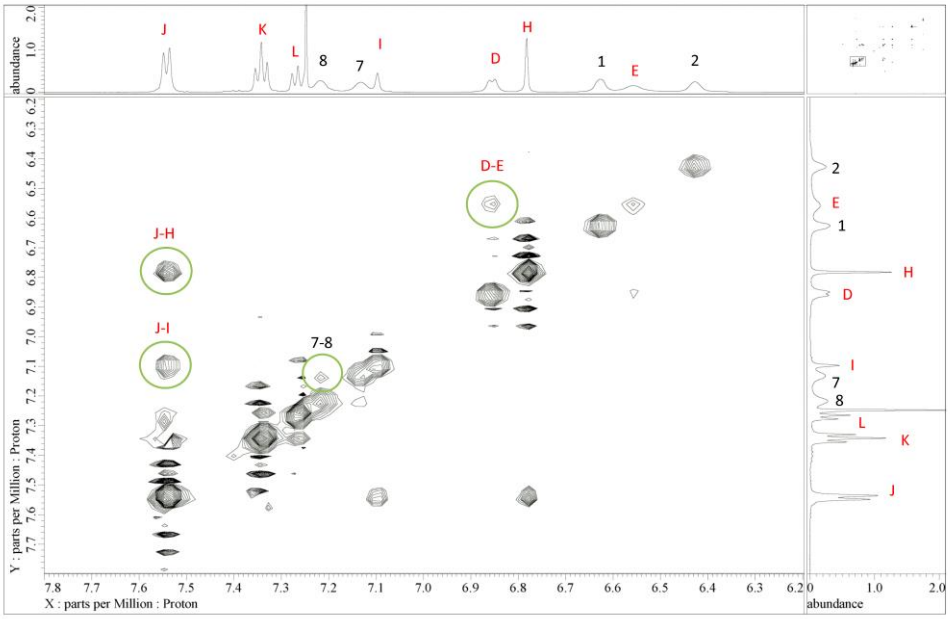
X : parts per Million : Proton
abundance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X : parts per Million : Proton
abundance

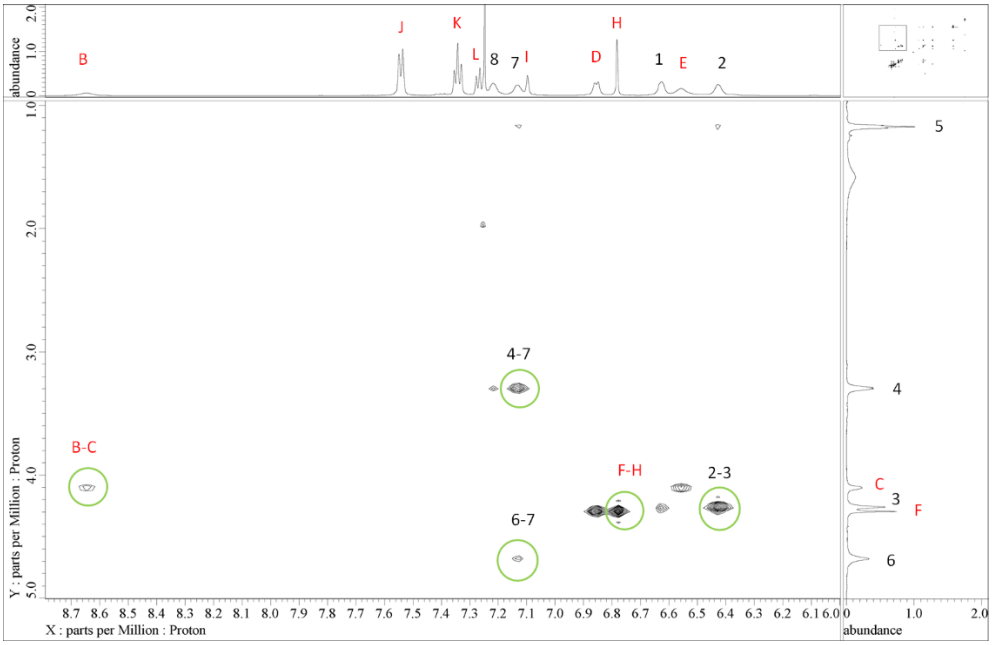
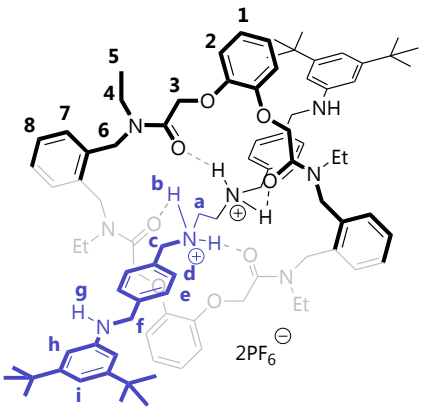



**Figure S3b.** ROESY spectrum (600 MHz, $CDCl_3$, 25 °C) of the [2]rotaxane **8a**.



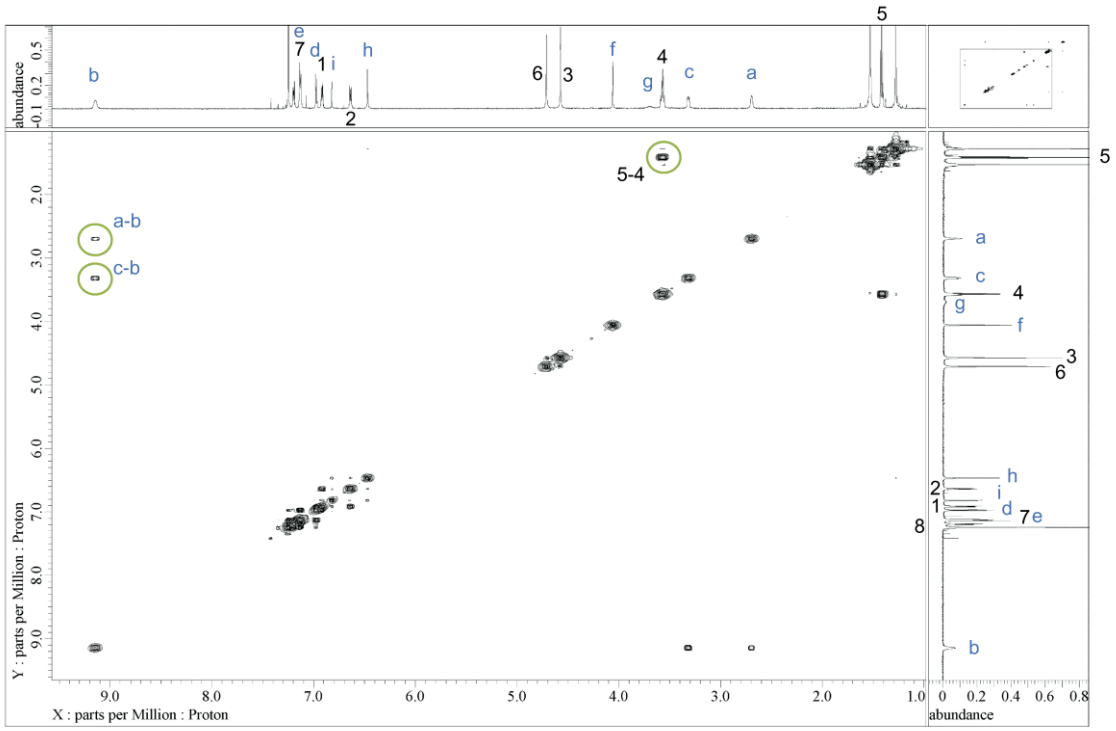
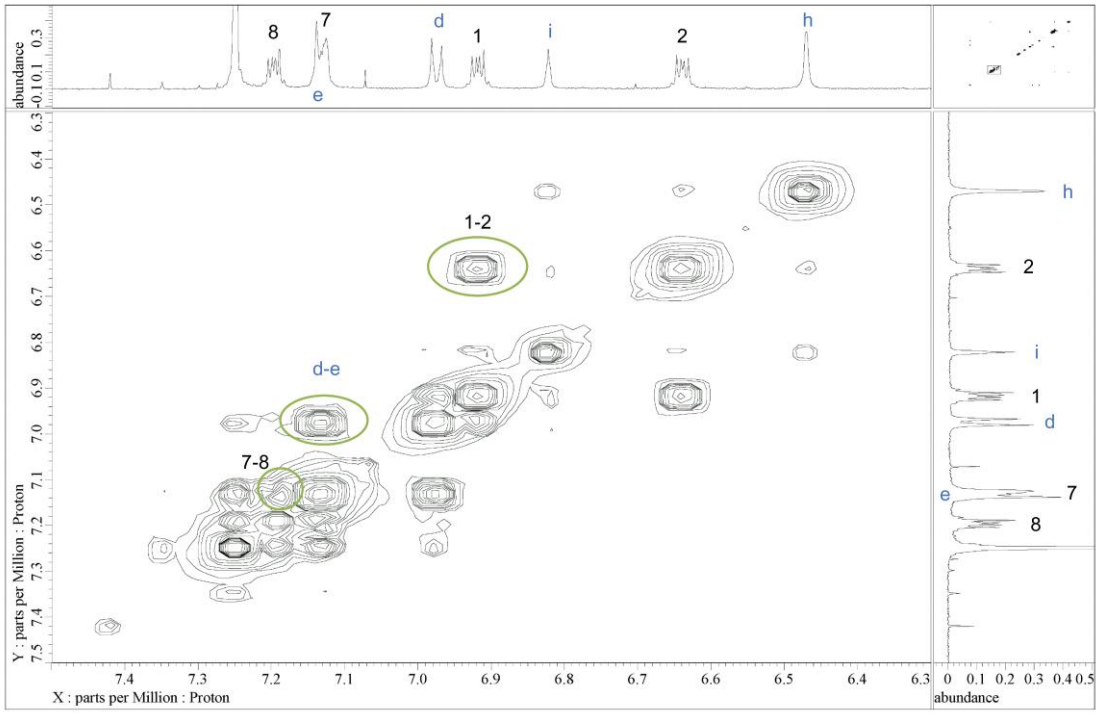




**Figure S4a.** COSY spectrum (600 MHz, $CDCl_3$, 25 °C) of the [2]rotaxane **8b**.



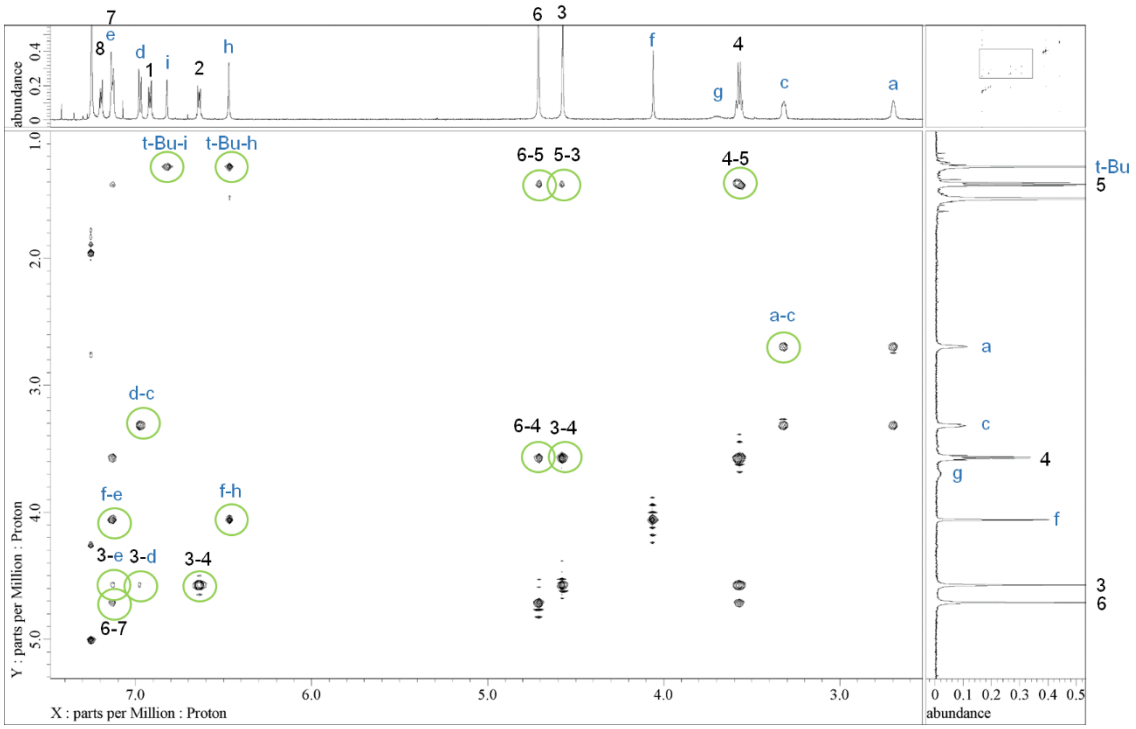




**Figure S4b.** ROESY spectrum (600 MHz, $CDCl_3$, 25 °C) of the [2]rotaxane **8b**.

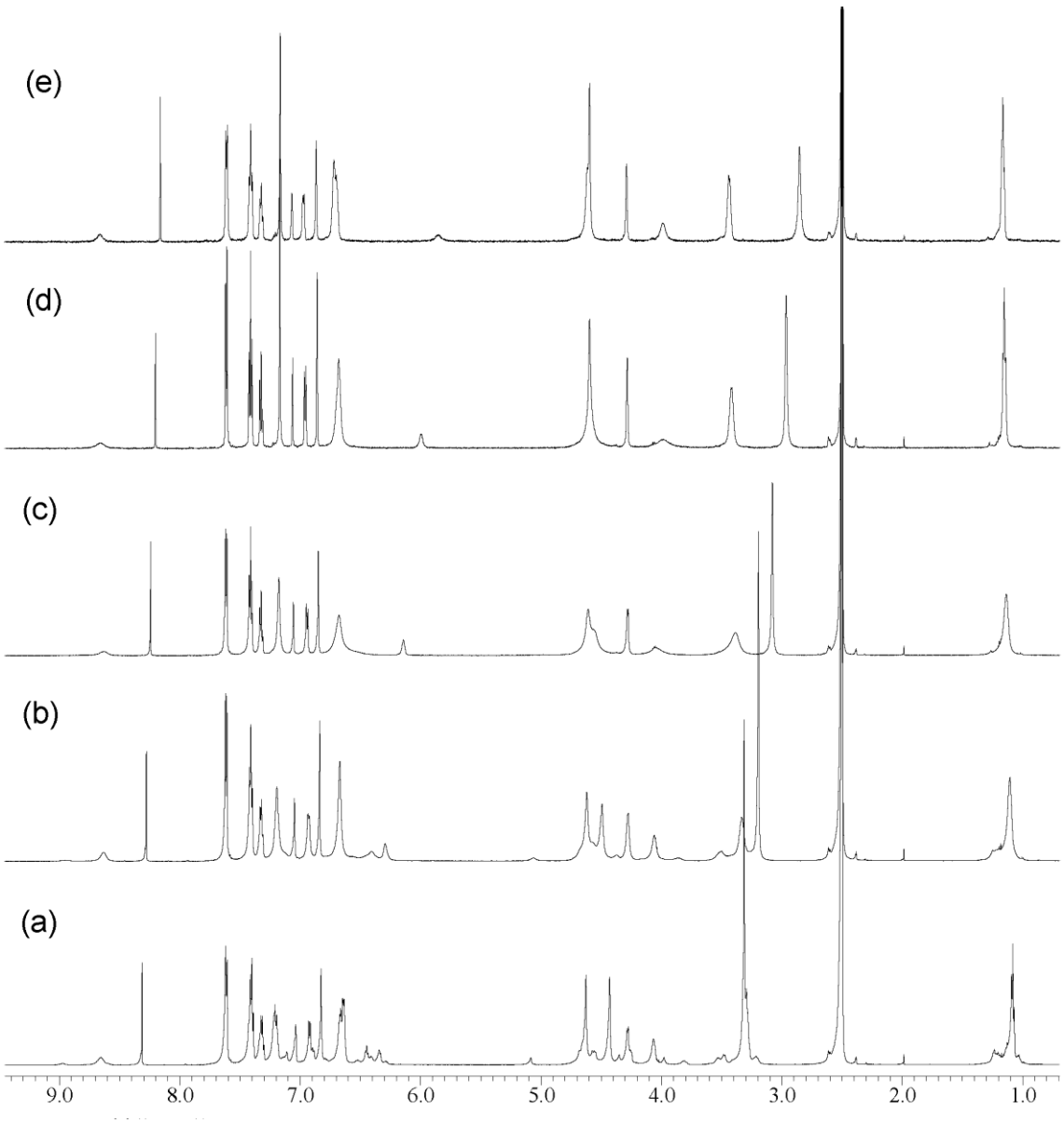



**Figure S5.** VT $^{1}$H NMR spectra (600 MHz, DMSO-$d_6$) of the [2]rotaxane **8a**, recorded at (a) 25, (b) 50, (c) 75, (d) 100, and (e) 125 °C.

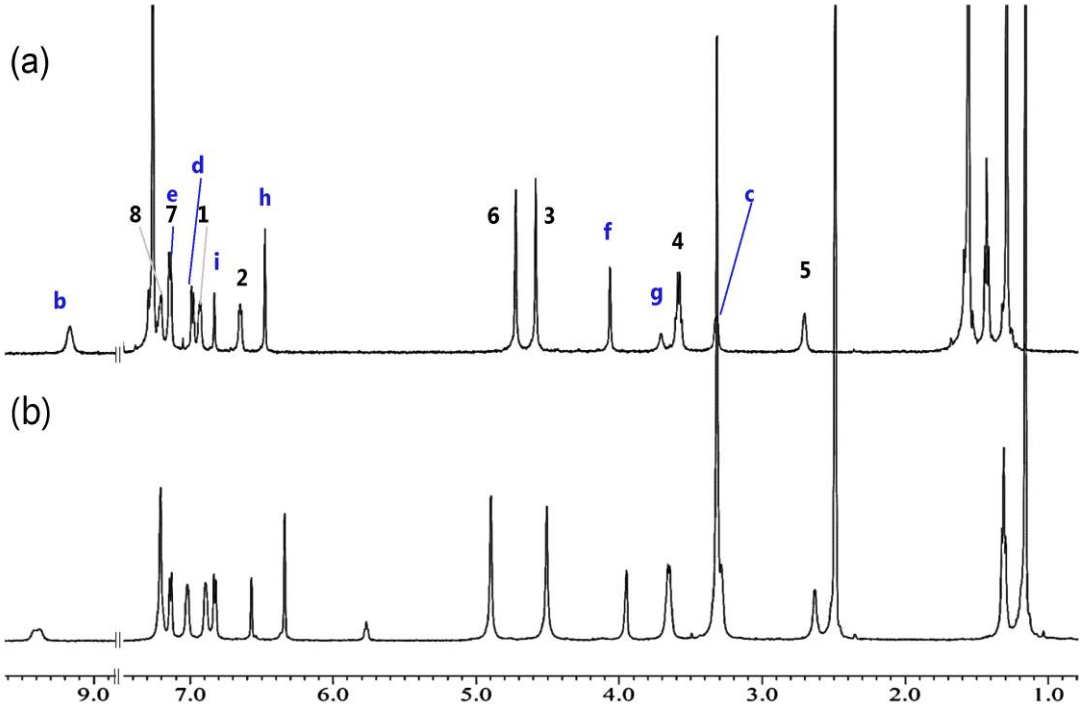
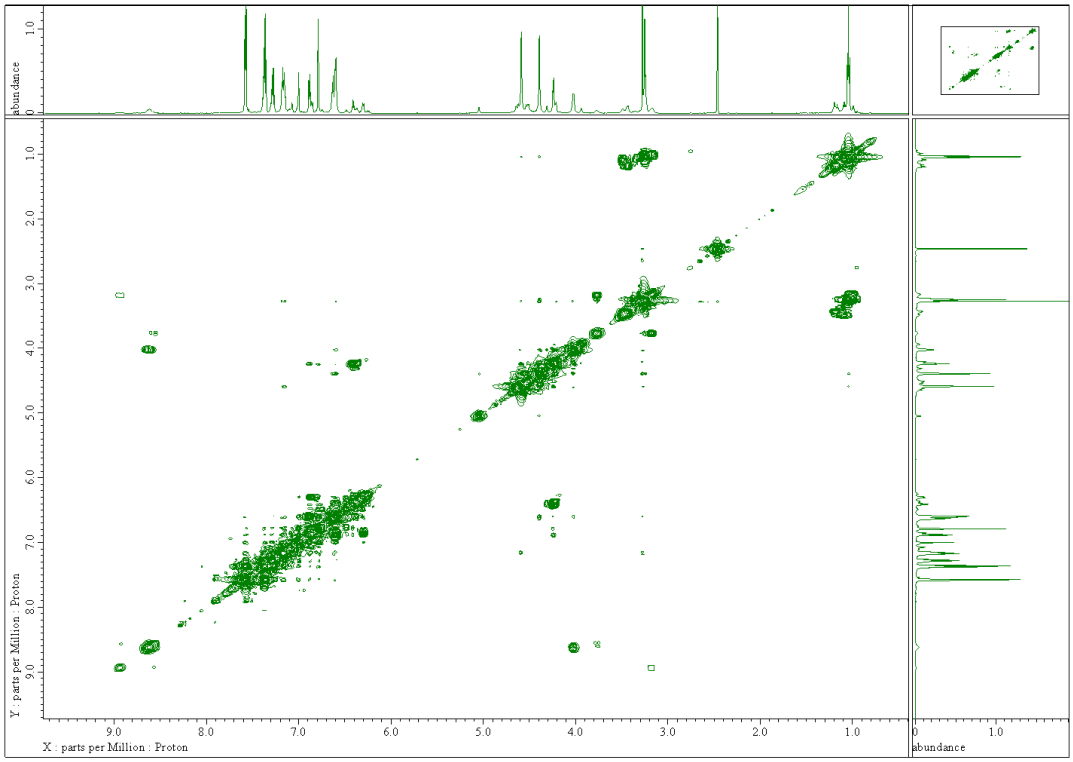



**Figure S6.** $^{1}$H NMR spectra (600 MHz) of the [2]rotaxane **8b** in (a) $CDCl_3$ and (b) DMSO-$d_6$.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X : parts per Million : Proton
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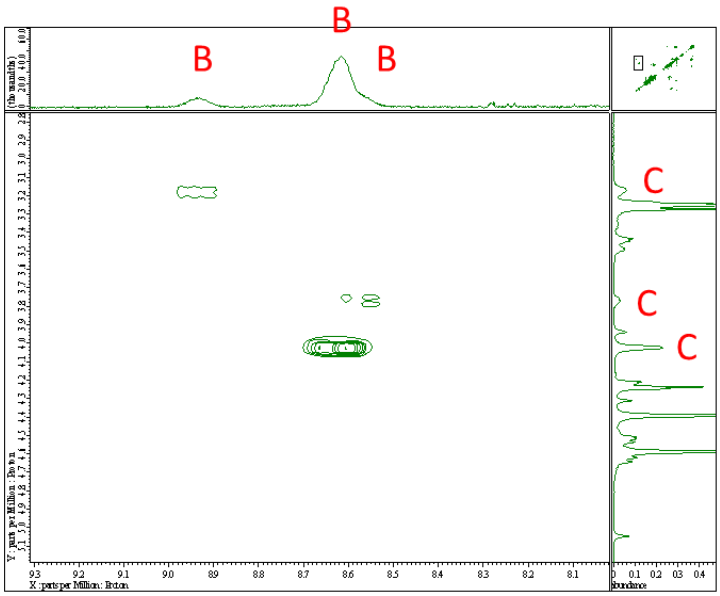
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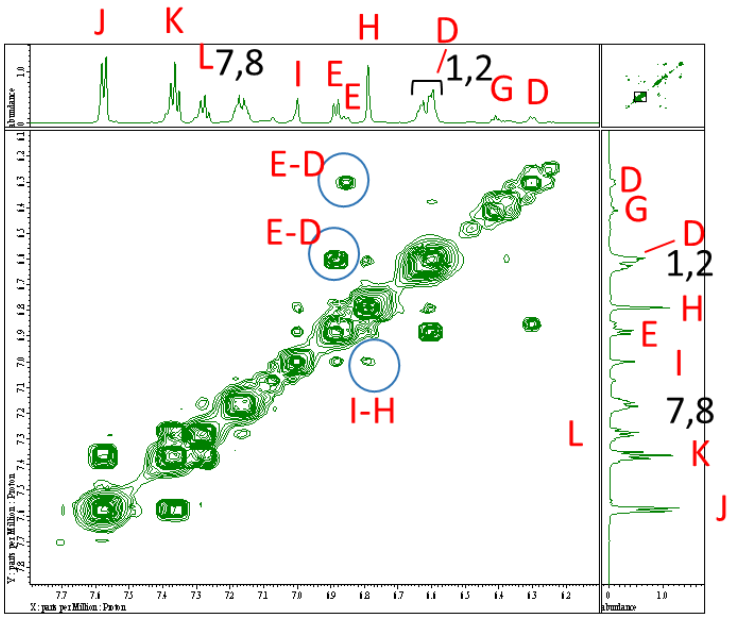


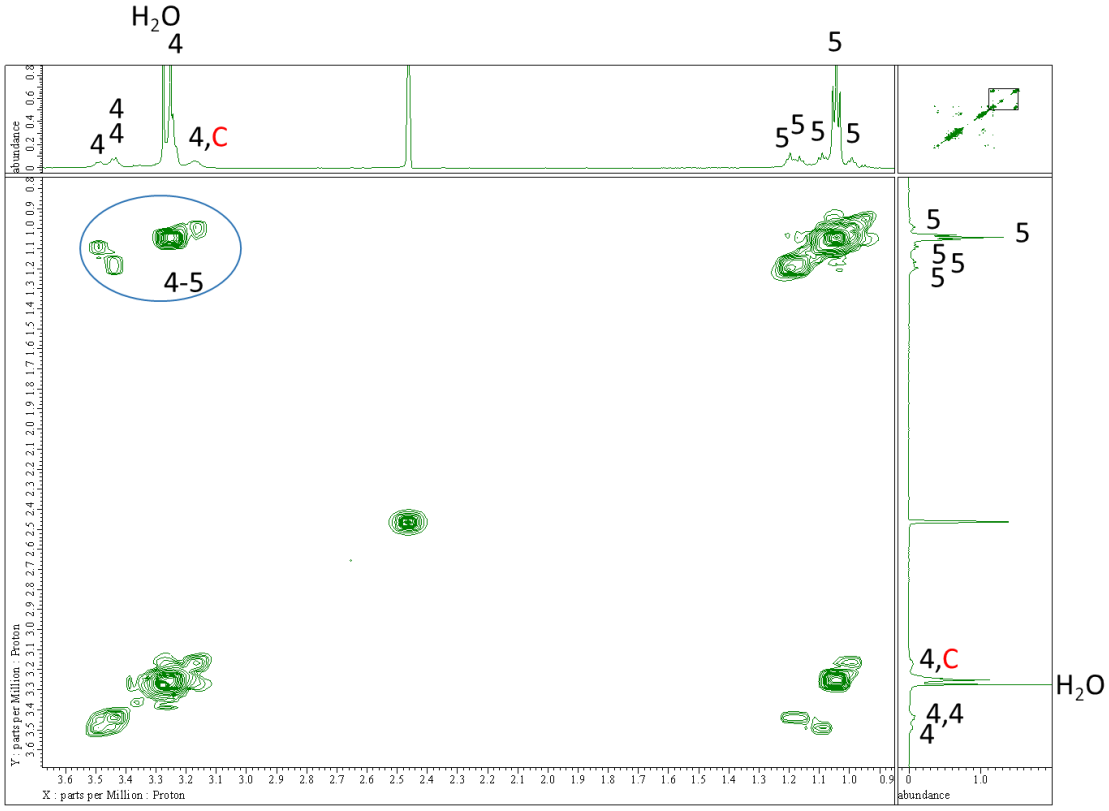
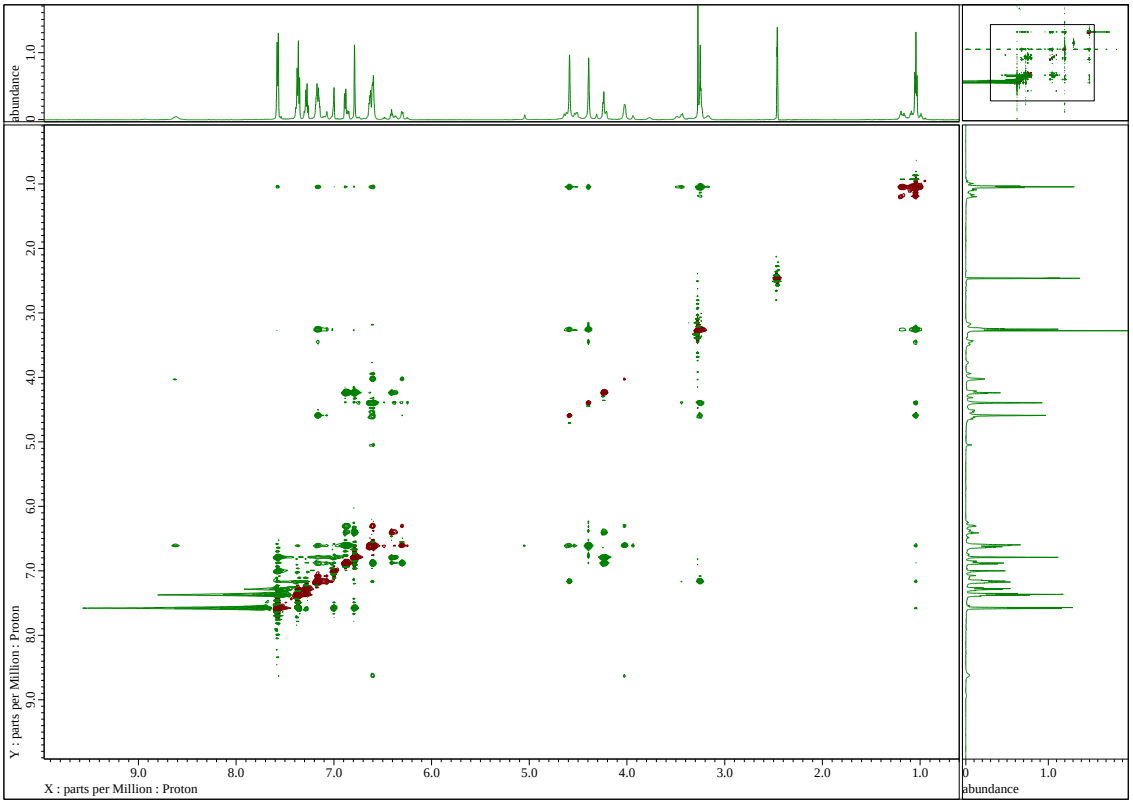




**Figure S7a.** COSY spectrum (600 MHz, DMSO-$d_6$, 25 °C) of the [2]rotaxane **8a**.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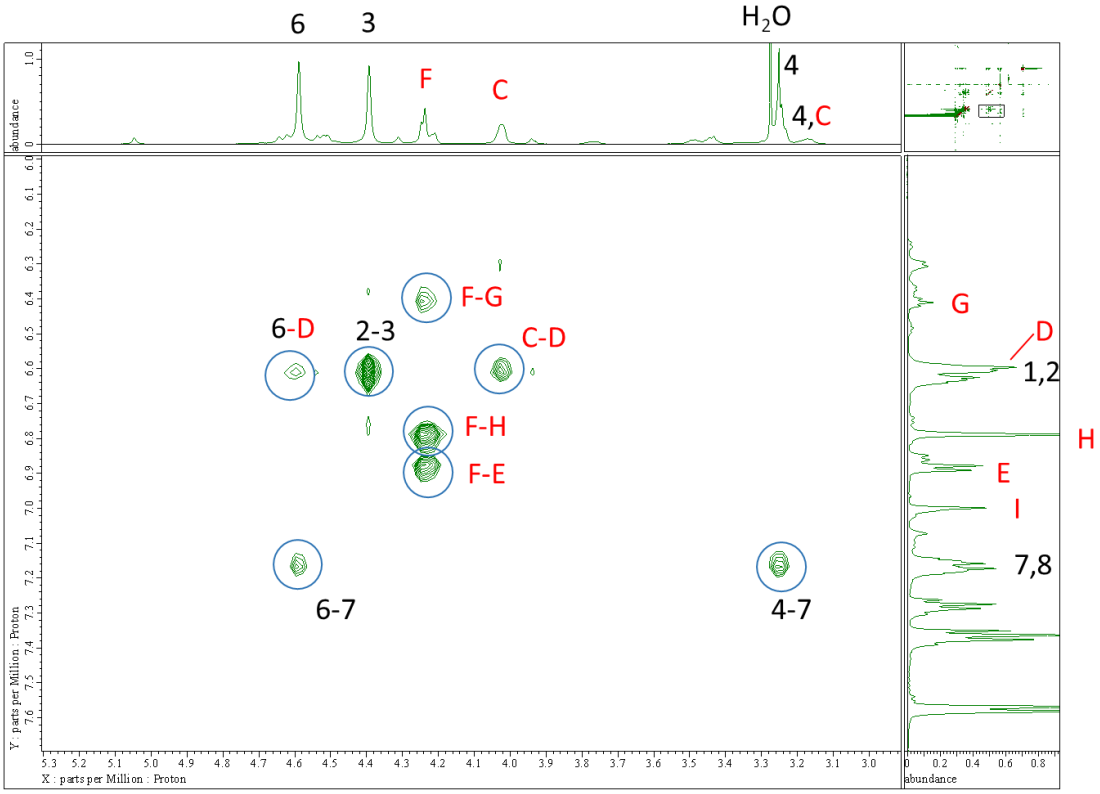
Y : parts per Million : Proton
X : parts per Million : Proton
abundance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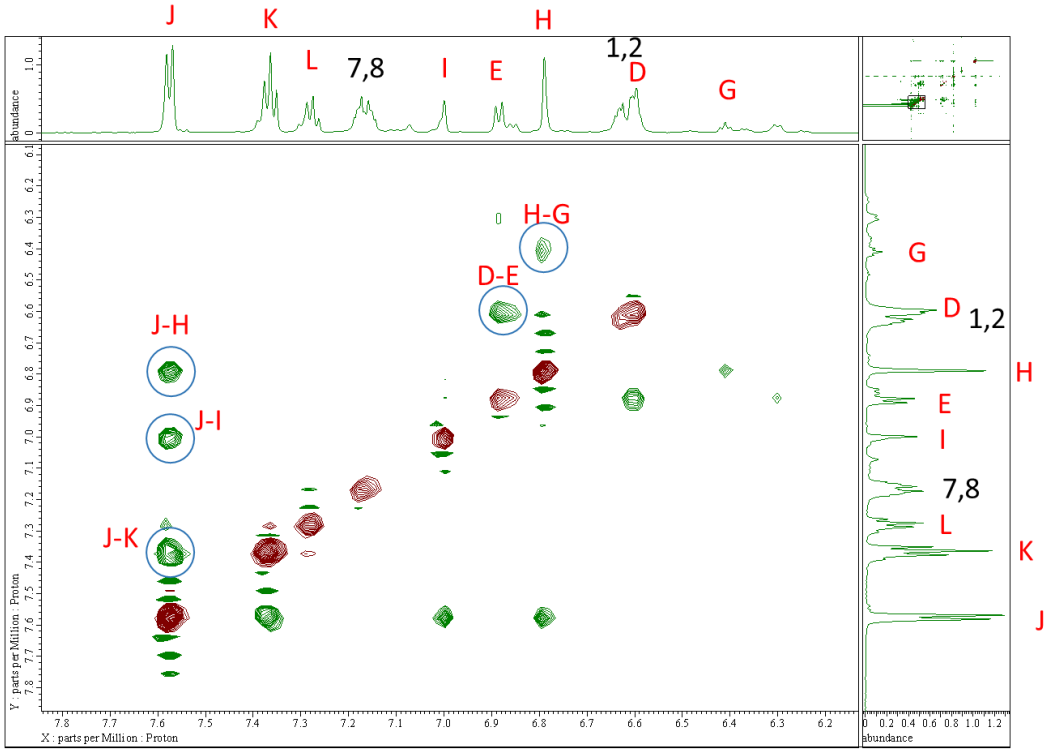



**Figure S7b.** ROESY spectrum (600 MHz, DMSO-$d_6$, 25 °C) of the [2]rotaxane **8a**.

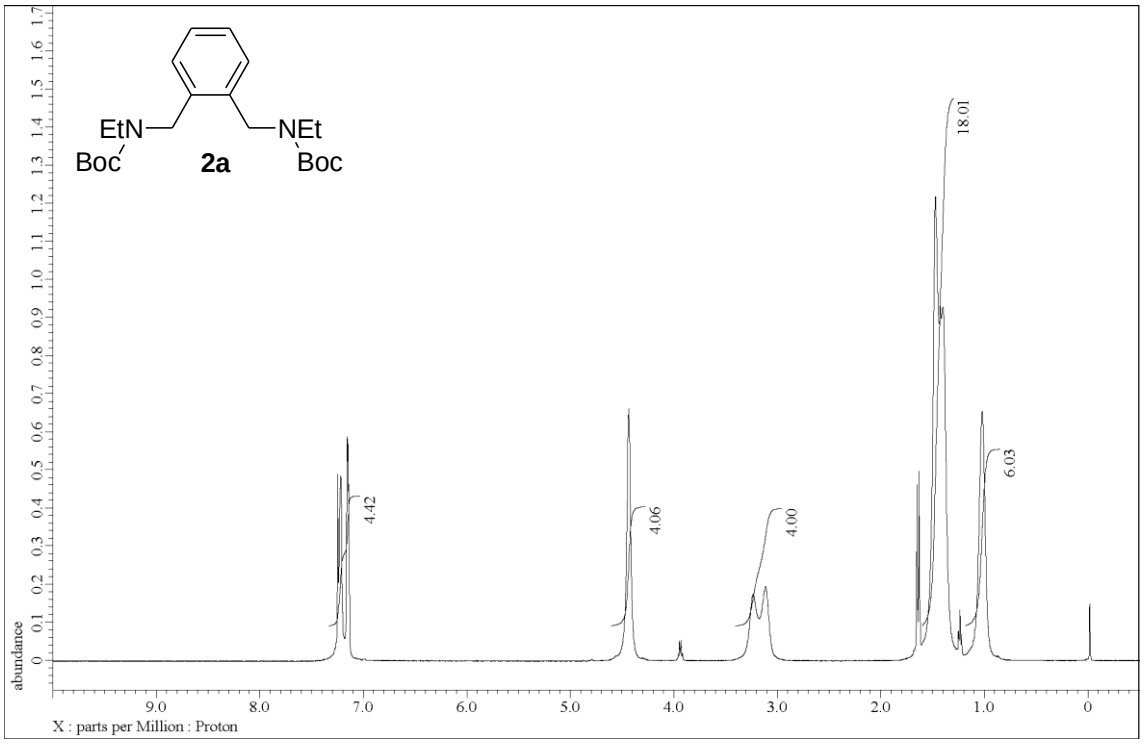



**Figure S8a**. $^{1}$H NMR spectrum (500 MHz, $CDCl_3$, 50 °C) of **2a**.

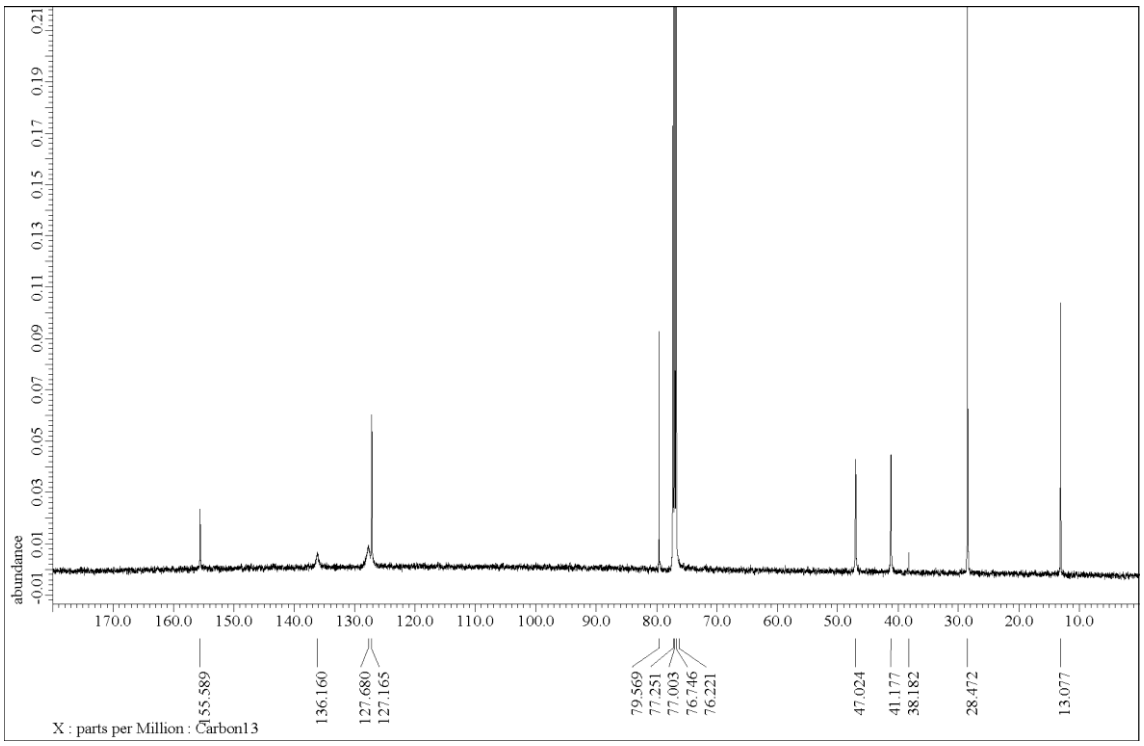



**Figure S8b**. $^{13}$C NMR spectrum (125 MHz, $CDCl_3$) of **2a**.

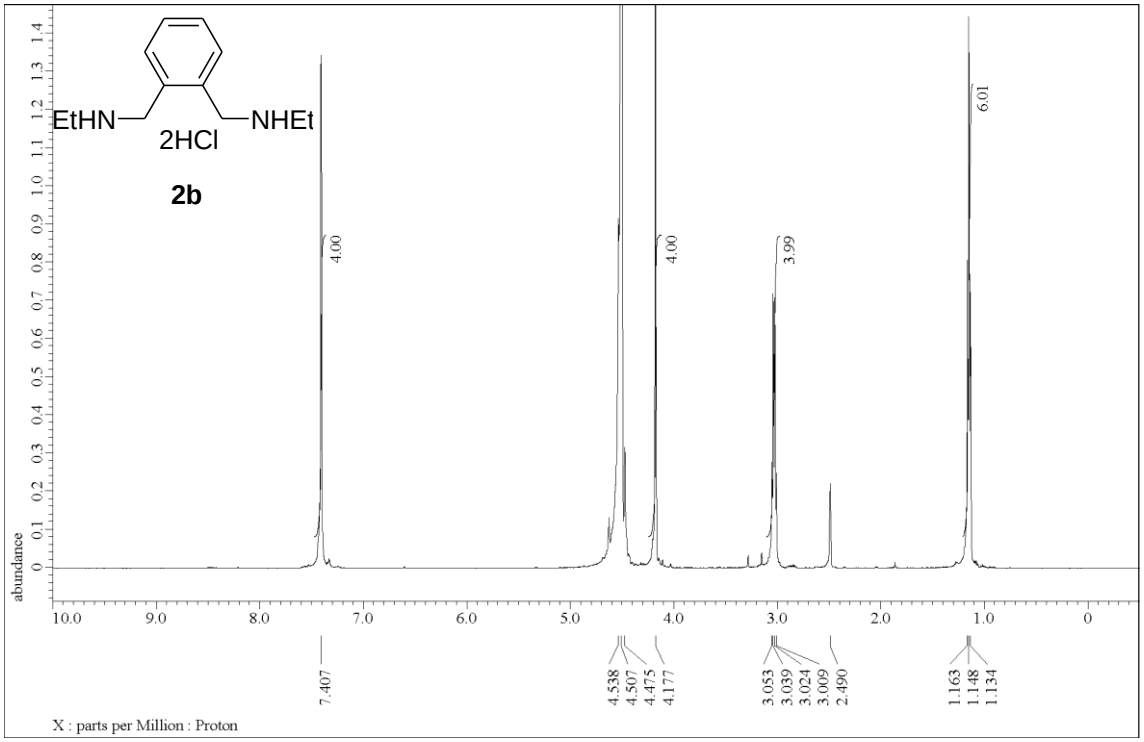



**Figure S9a.** $^{1}$H NMR spectrum (500 MHz, $D_2O$/DMSO-$d_6$, 5:1, 30 °C) of **2b**.

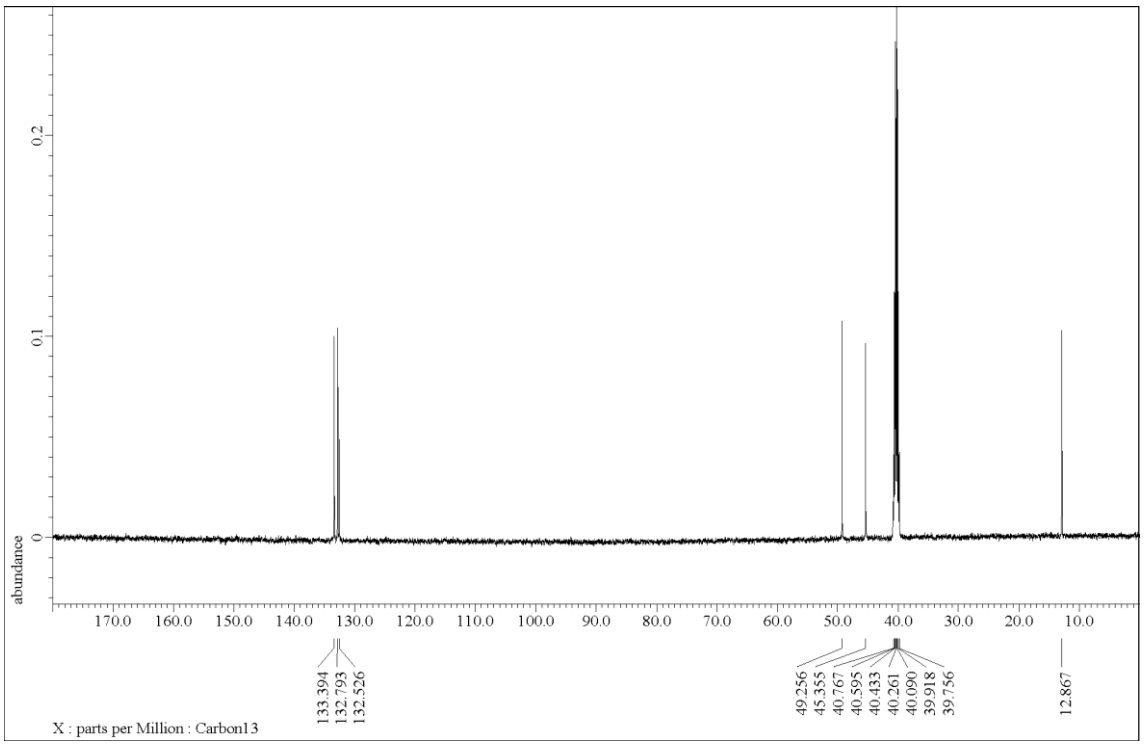



**Figure S9b.** $^{13}$C NMR spectrum (125 MHz, $D_2O$/DMSO-$d_6$, 5:1, 30 °C) of **2b**.

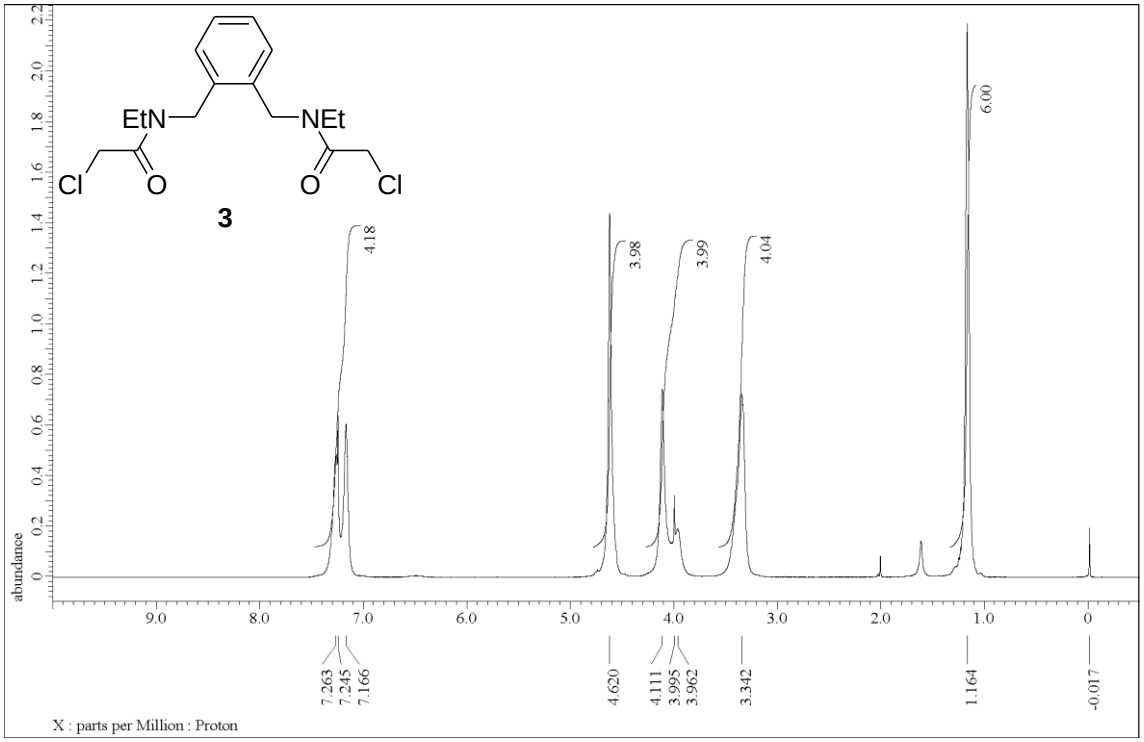



**Figure S10a**. $^{1}$H NMR spectrum (500 MHz, $CDCl_3$, 55 °C) of **3**.

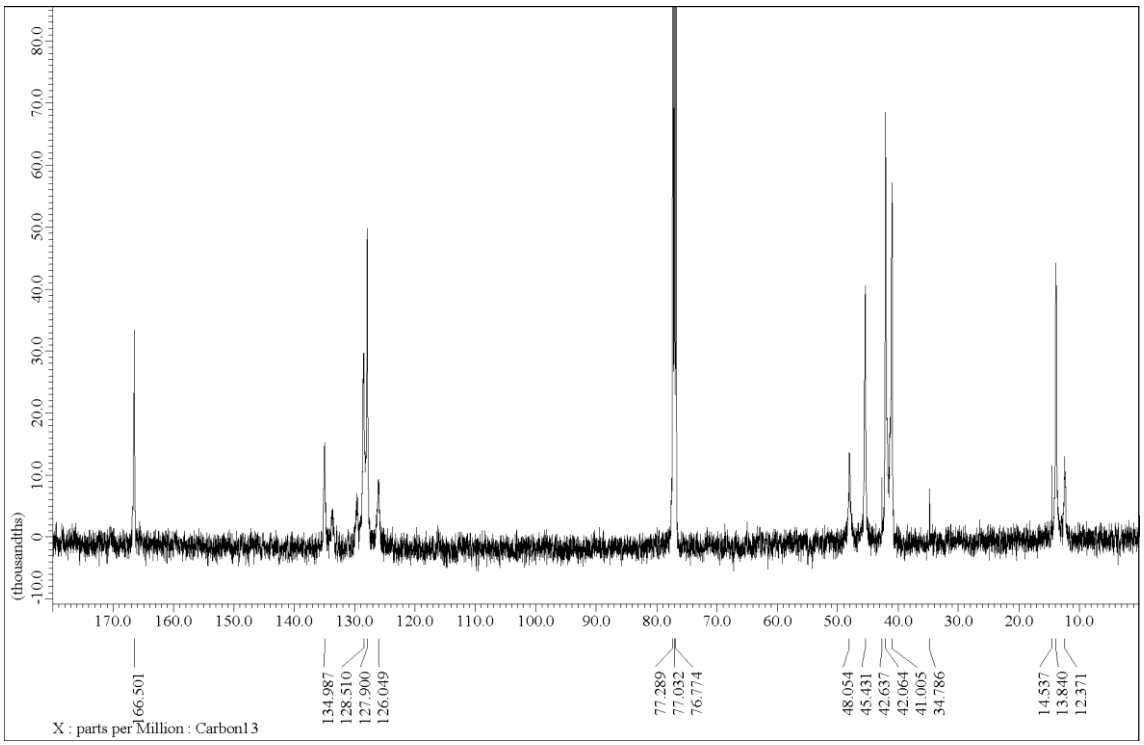



**Figure S10b.** $^{13}$C NMR spectrum (125 MHz, $CDCl_3$, 55 °C) of **3**.

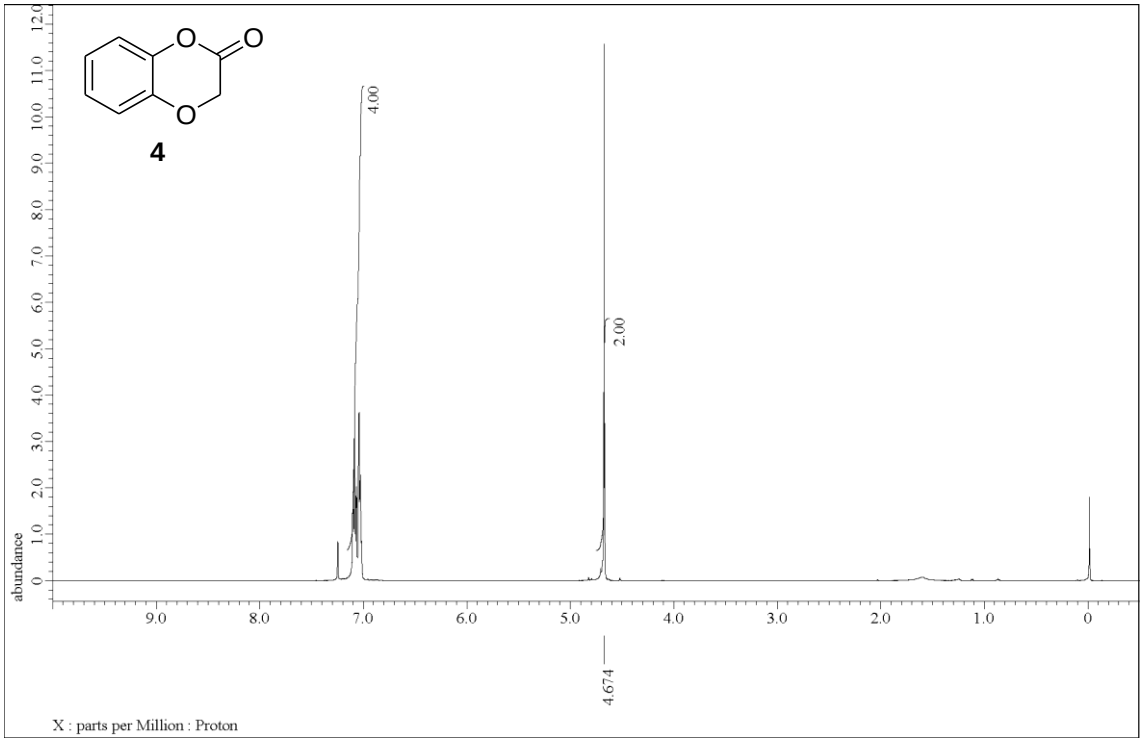



**Figure S11a.** $^{1}$H NMR spectrum (500 MHz, $CDCl_3$) of **4**.

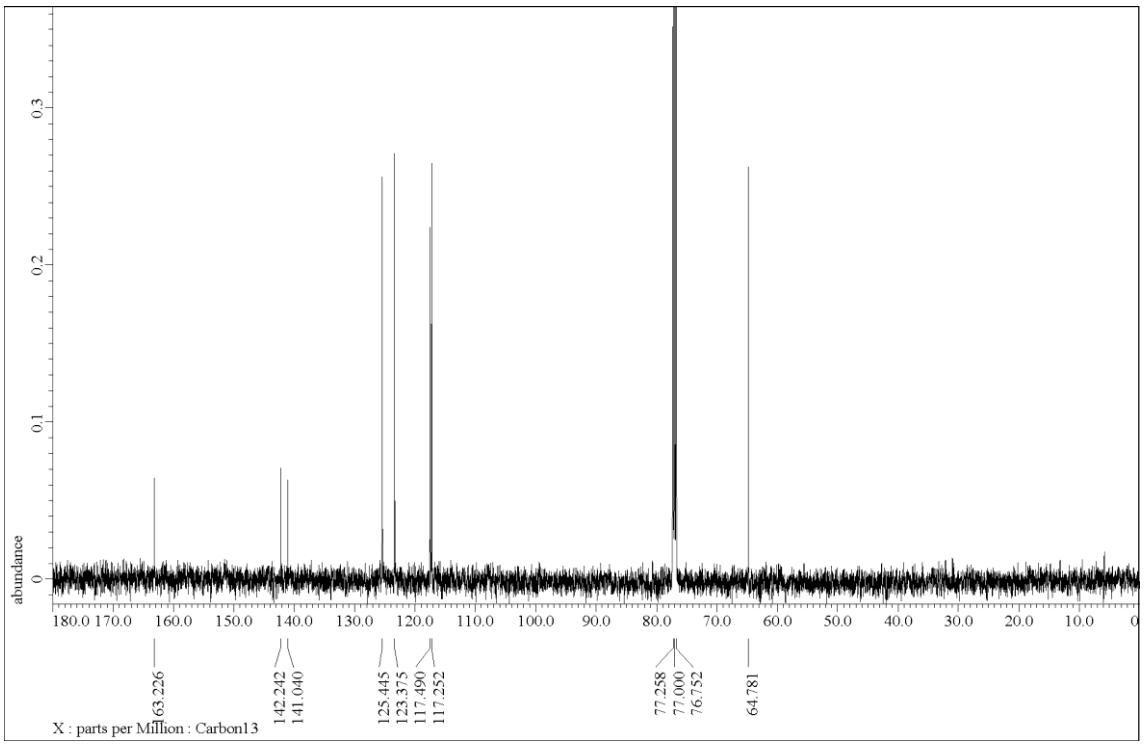



**Figure S11b.** $^{13}$C NMR spectrum (125 MHz, $CDCl_3$) of **4**.

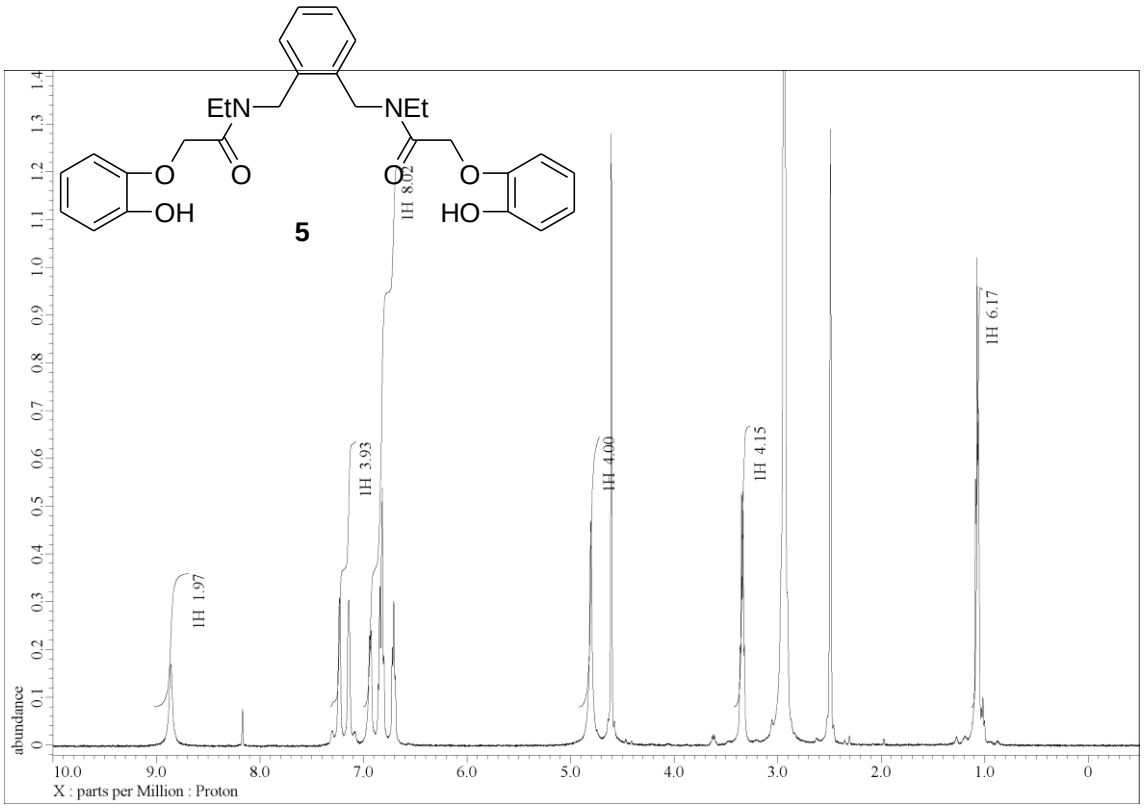



**Figure S12a.** $^{1}$H NMR spectrum (500 MHz, DMSO-$d_6$, 110 °C) of **5**.

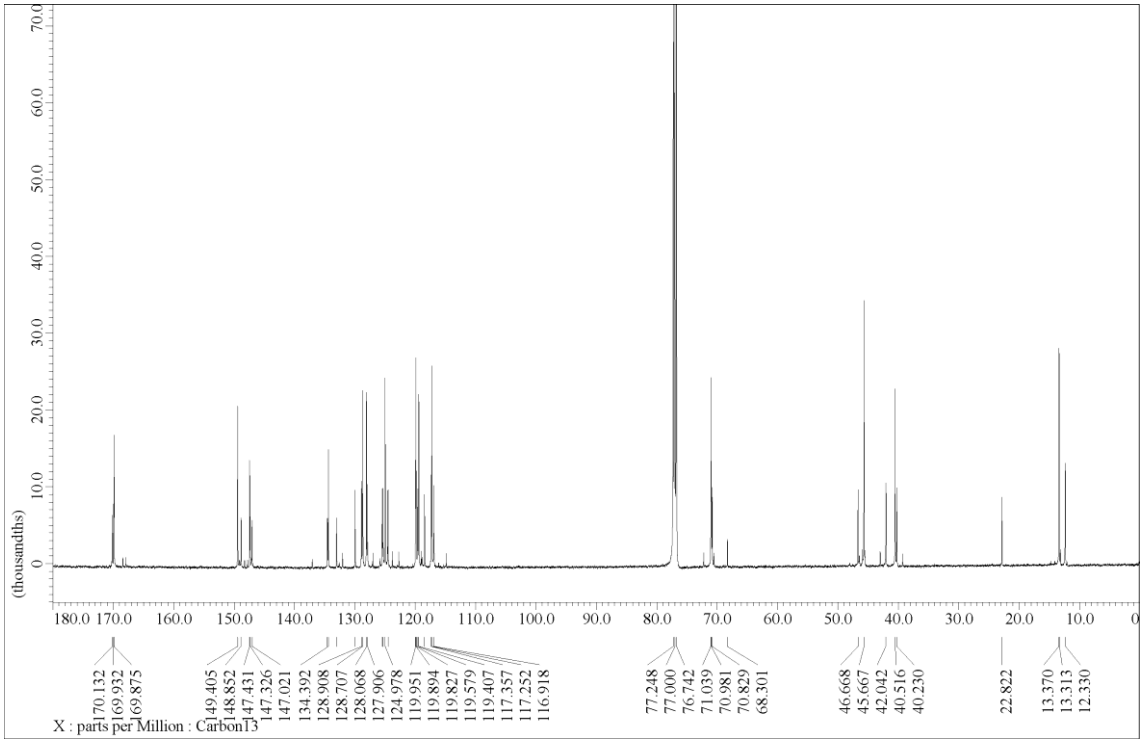



**Figure S12b.** $^{13}$C NMR spectrum (150 MHz, $CDCl_3$) of **5**.

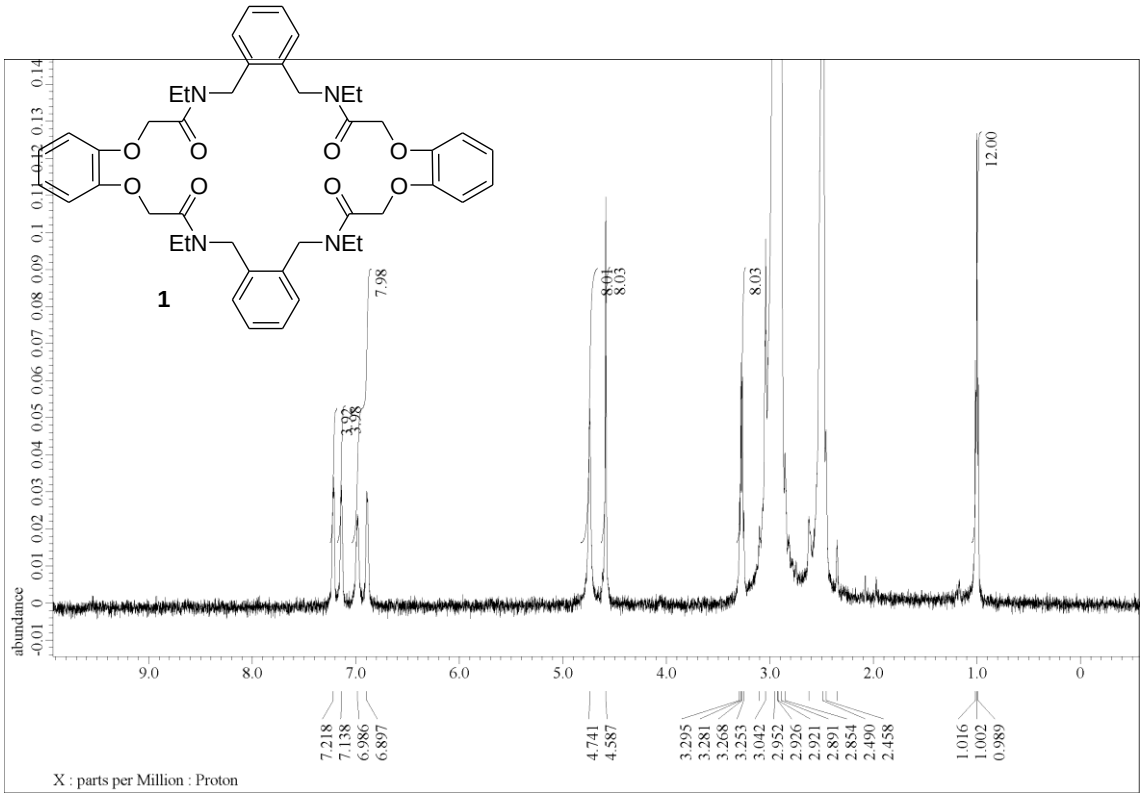



**Figure S13a.** $^{1}$H NMR spectrum (500 MHz, DMSO-$d_6$, 110 °C) of **1**.

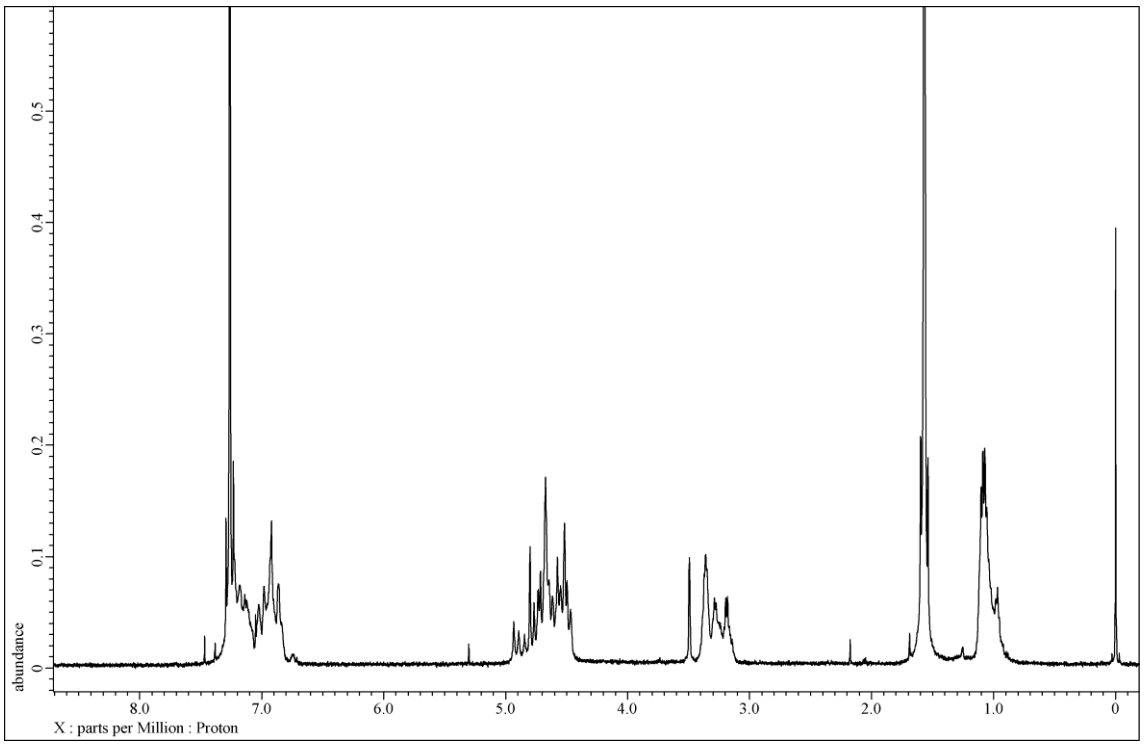



**Figure S13b.** $^{1}$H NMR spectrum (500 MHz, $CDCl_3$) of **1**.

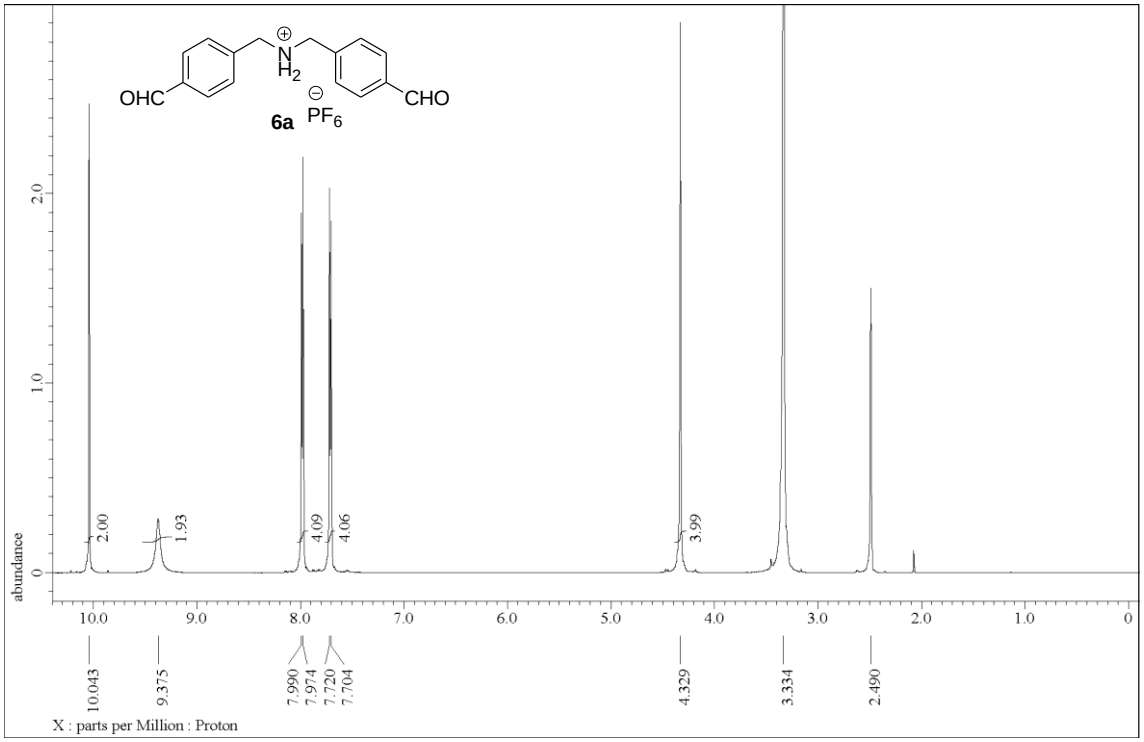



**Figure S14a.** $^{1}$H NMR spectrum (500 MHz, DMSO-$d_6$, 30 °C) of **6a**.

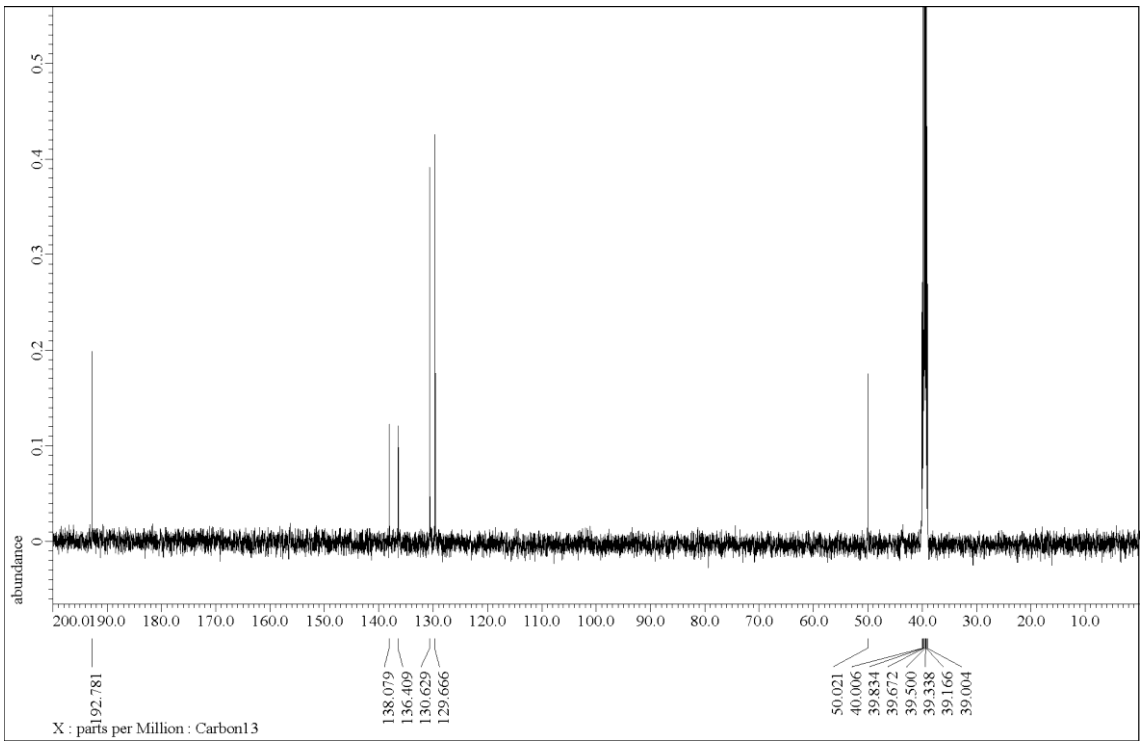



**Figure S14b.** $^{13}$C NMR spectrum (125 MHz, DMSO-$d_6$, 30 °C) of **6a**.

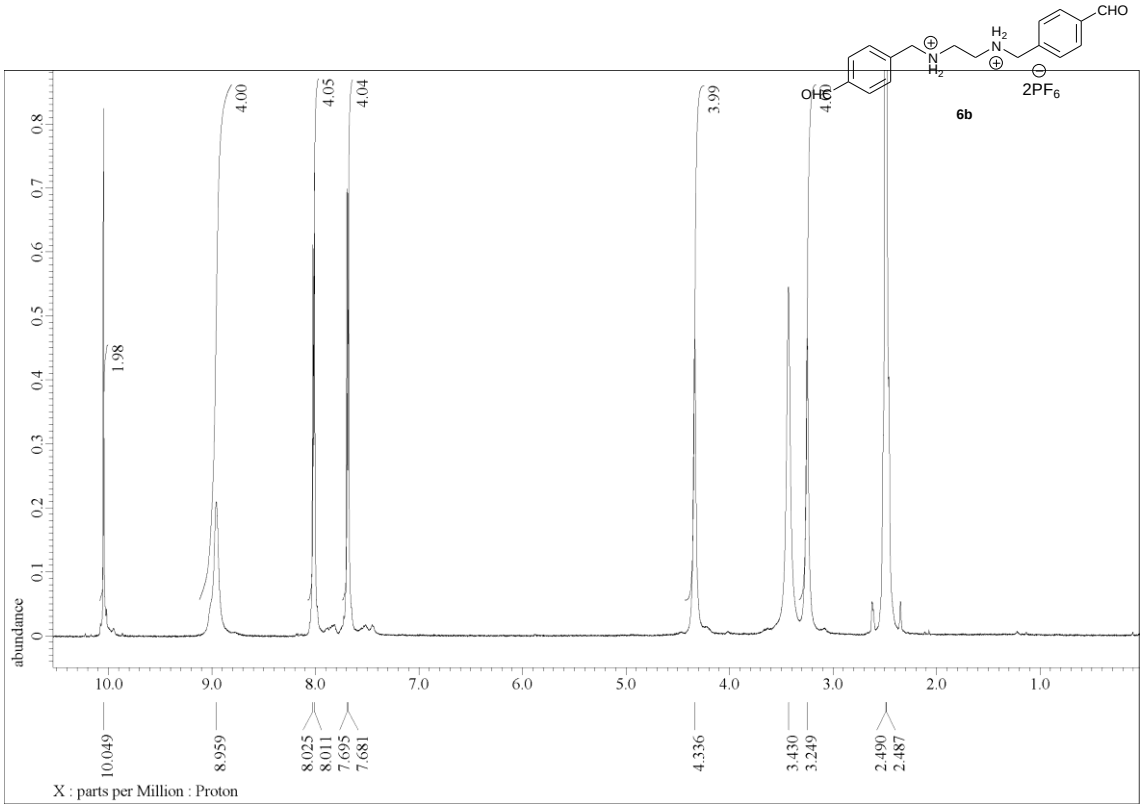



**Figure S15a.** $^{1}$H NMR spectrum (500 MHz, DMSO-$d_6$) of **6b**.

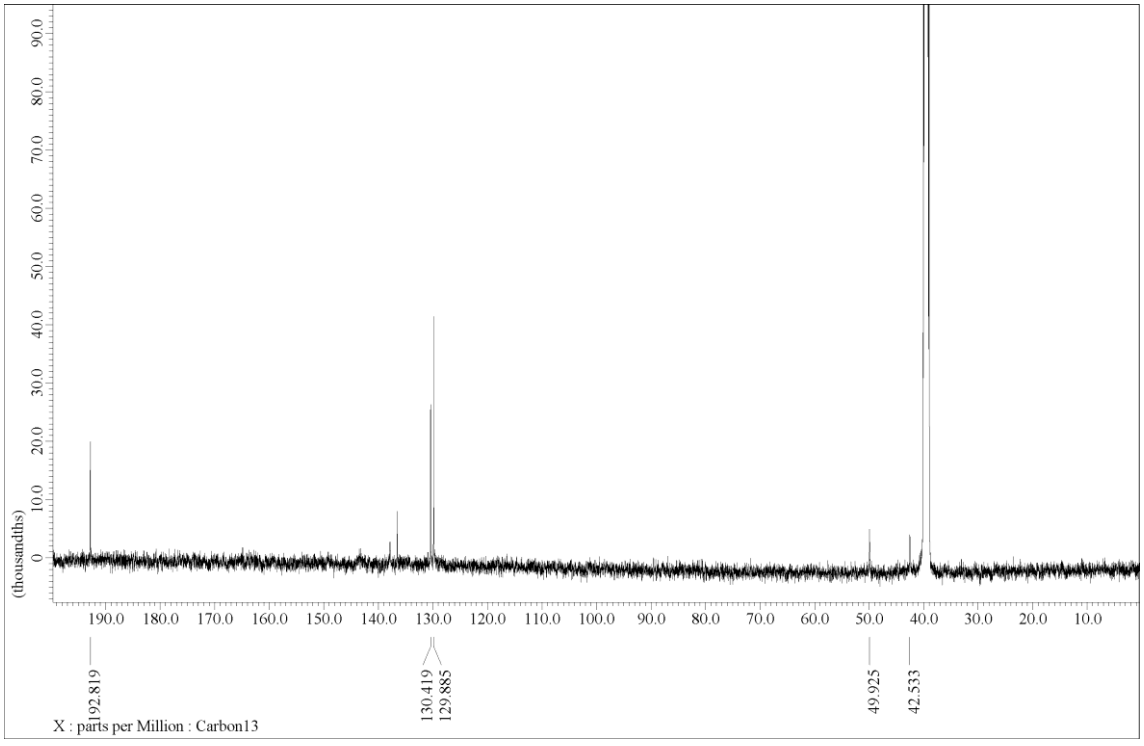



**Figure S15b.** $^{13}$C NMR spectrum (125 MHz, DMSO-$d_6$) of **6b**.

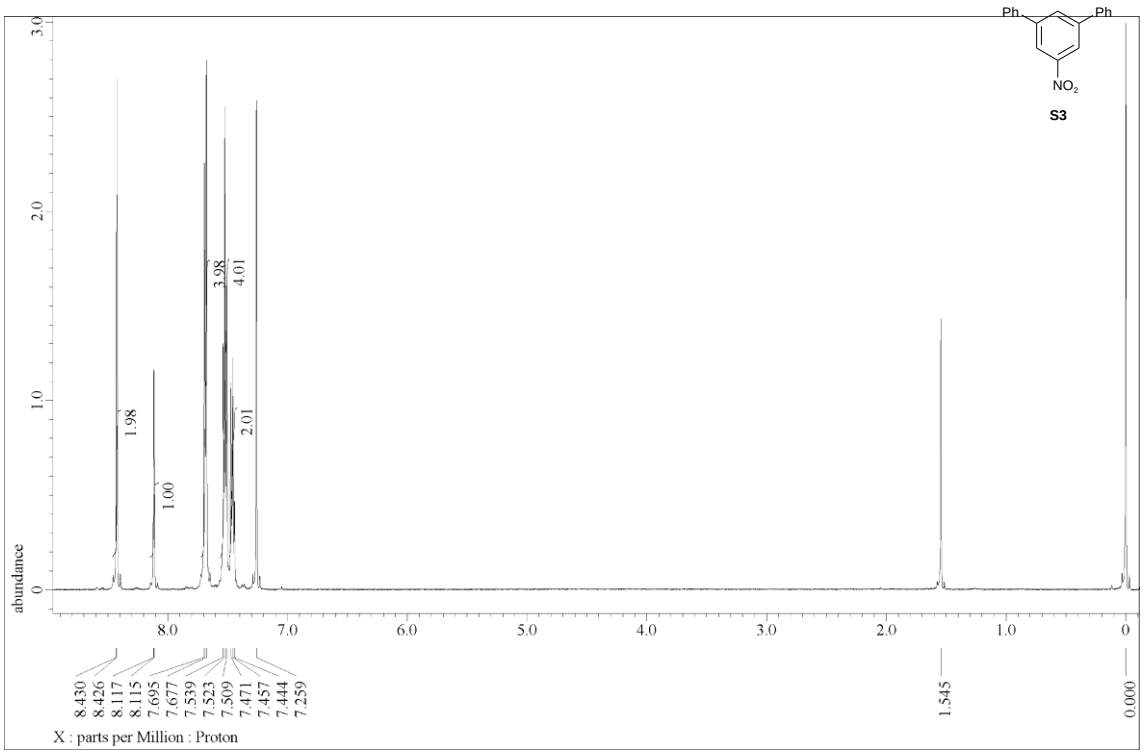



**Figure S16.** $^{1}$H NMR spectrum (500 MHz, $CDCl_3$) of **S3**.

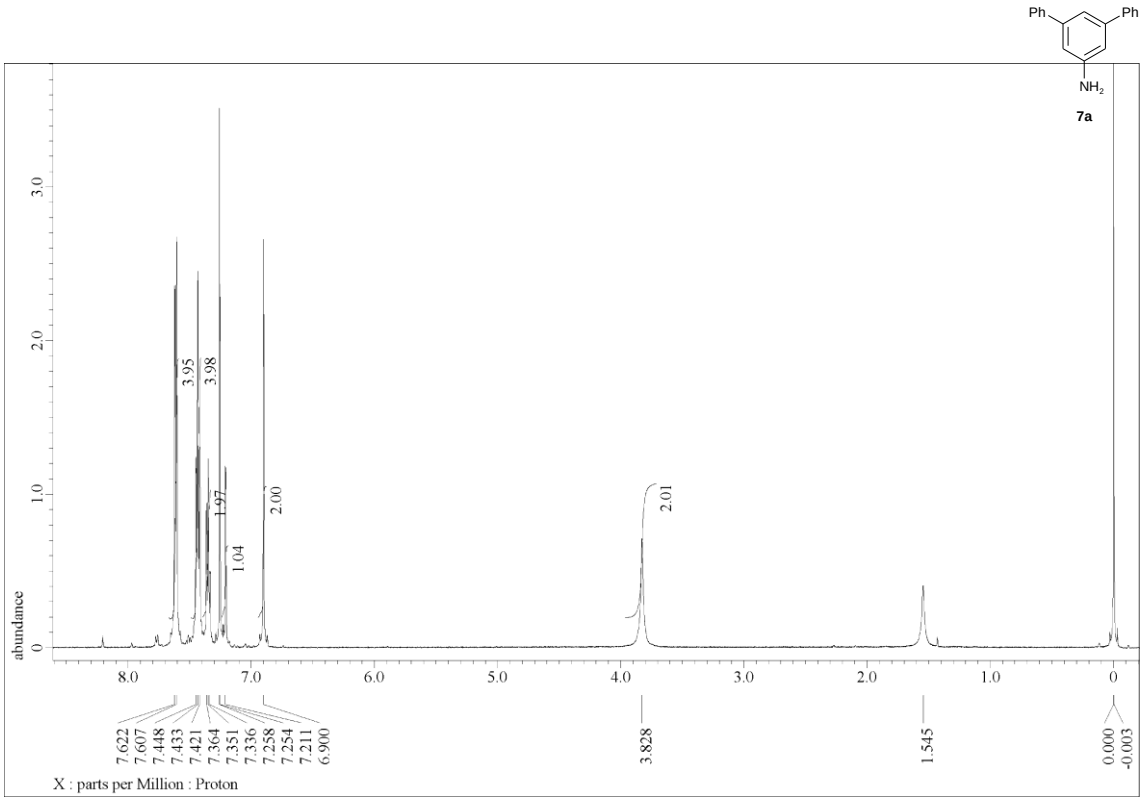
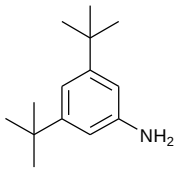



**Figure S17.** $^{1}$H NMR spectrum (500 MHz, $CDCl_3$) of **7a**.




**7b**

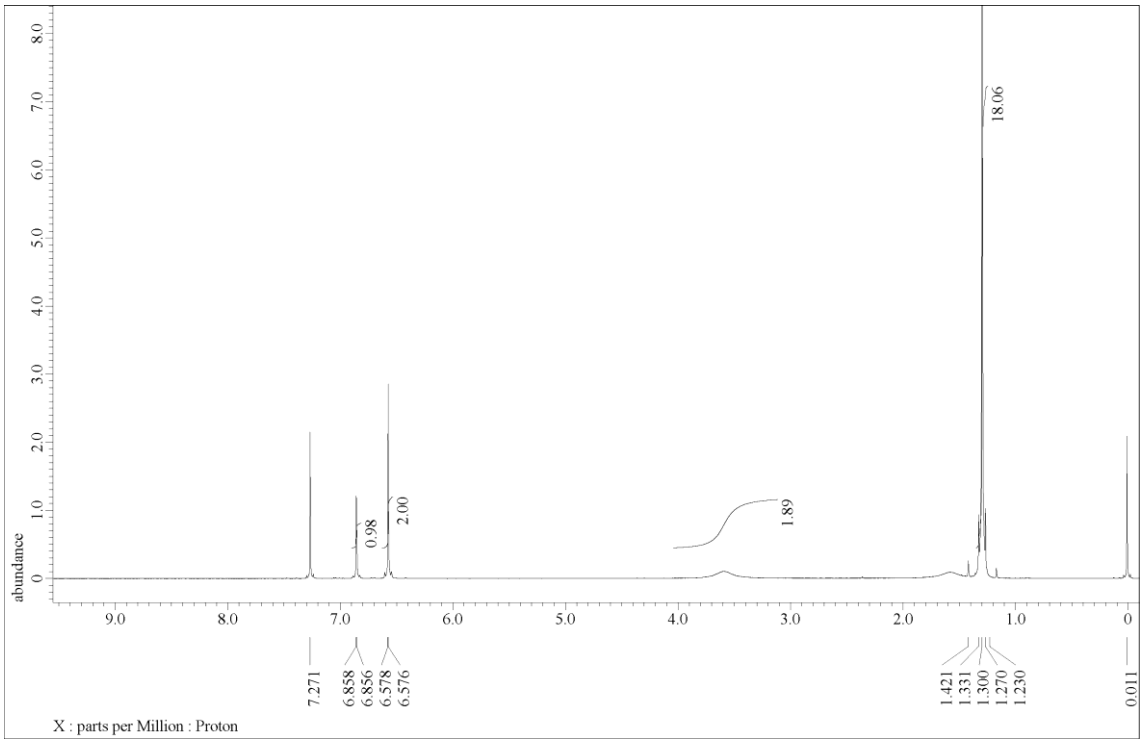



**Figure S18.** $^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of **7b**.

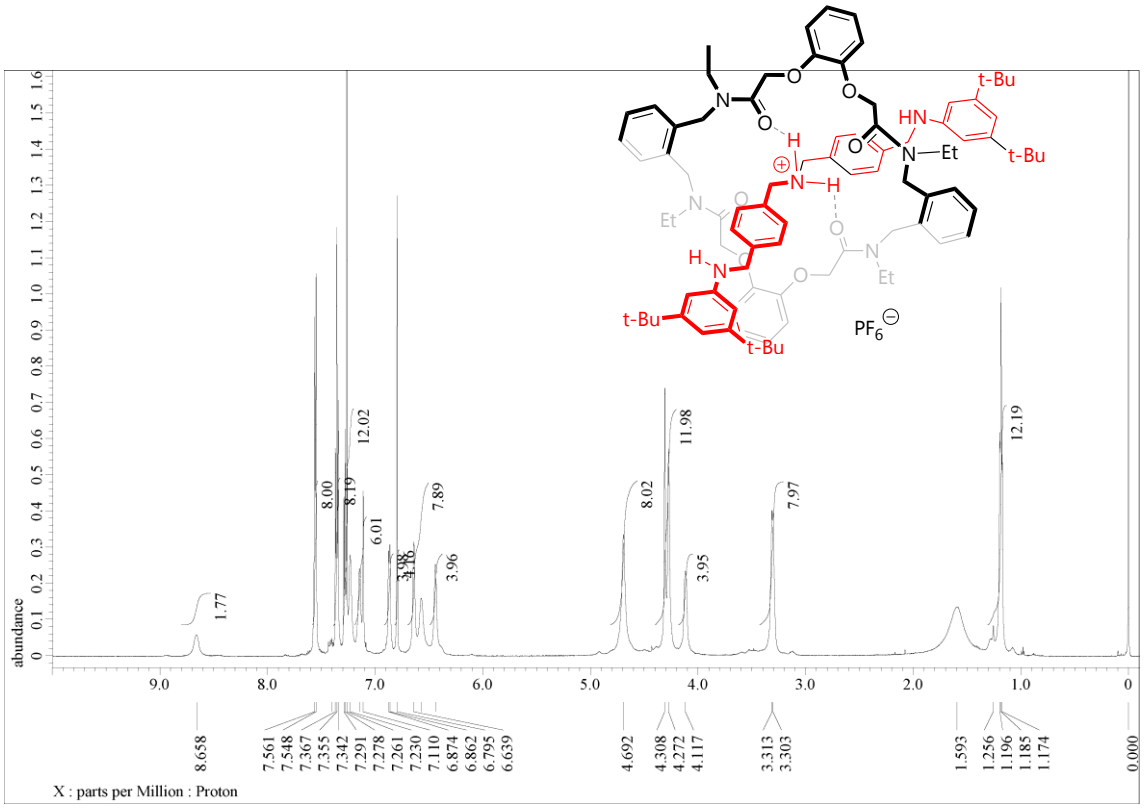



**Figure S19a.** $^{1}$H NMR spectrum (600 MHz, $CDCl_3$) of the [2]rotaxane **8a**.

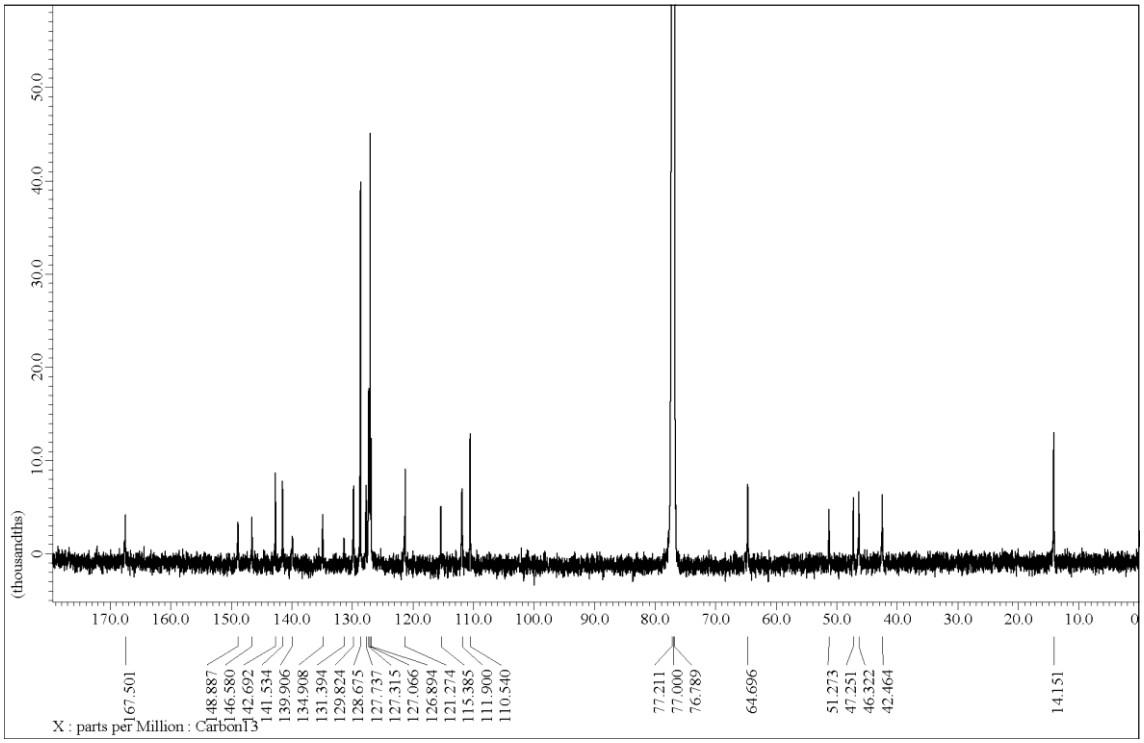



**Figure S19b.** $^{13}$C NMR spectrum (150 MHz, $CDCl_3$, 40 °C) of the [2]rotaxane **8a**.

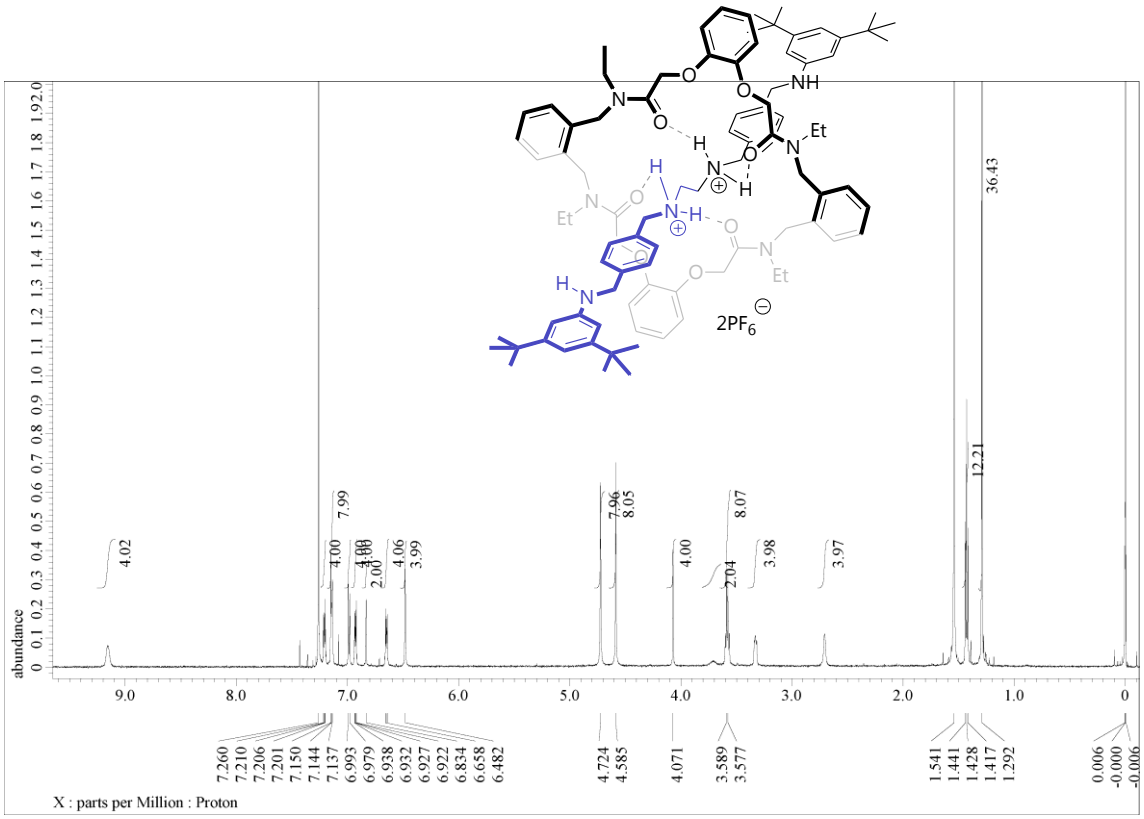



**Figure S20a.** $^{1}$H NMR spectrum (600 MHz, $CDCl_3$) of the [2]rotaxane **8b**.

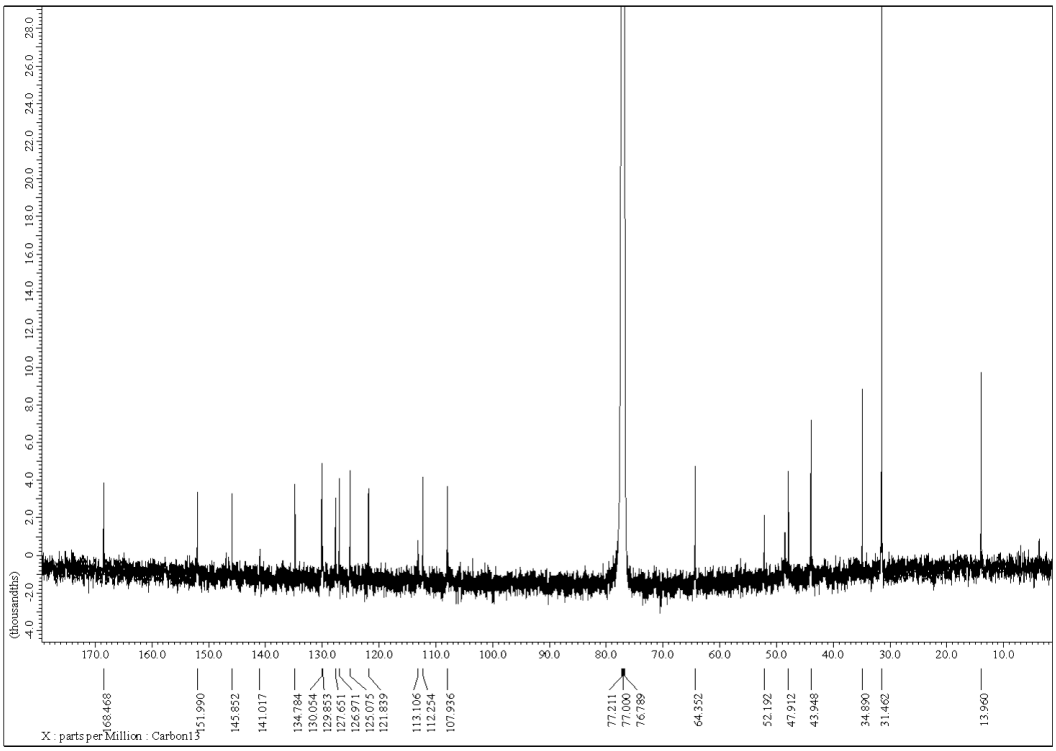



**Figure S20b.** $^{13}$C NMR spectrum (150 MHz, $CDCl_3$) of the [2]rotaxane **8b**.