Supplementary Information

Five-State Molecular Switching of a [3]Rotaxane in Response to Weak and Strong Acid and Base Stimuli

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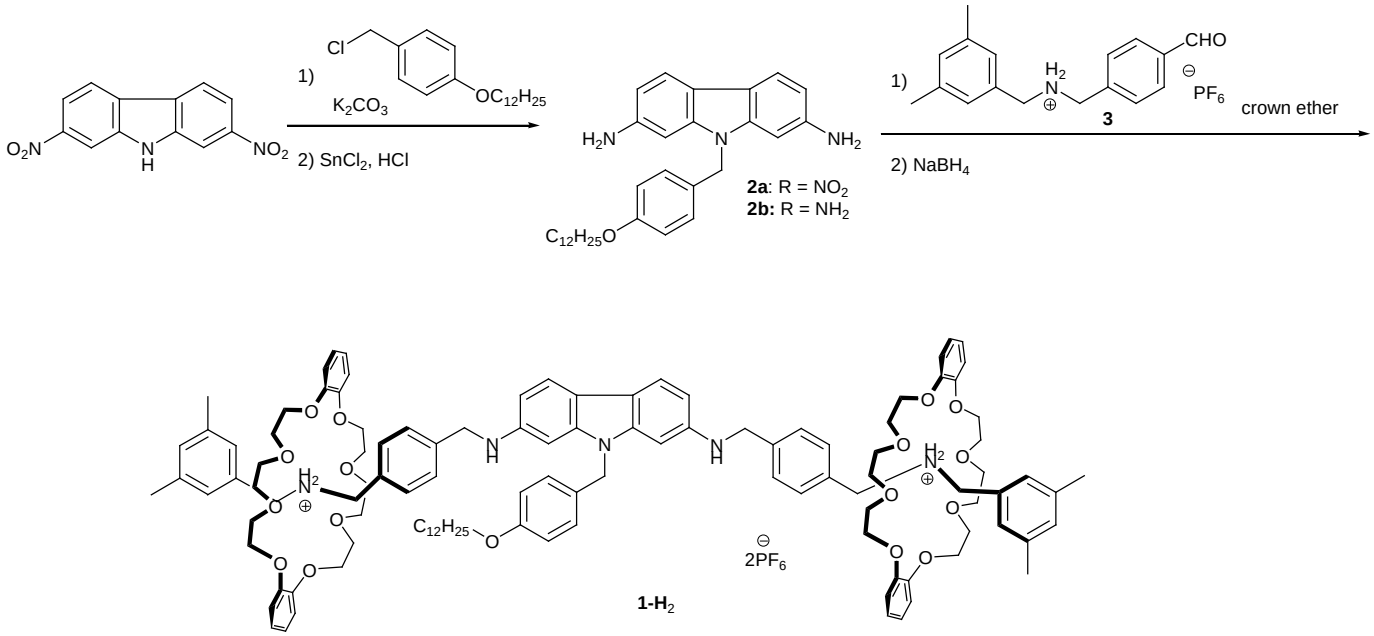


Experimental

General methods

Infrared spectra were recorded using a Shimadzu FTIR-8600PC instrument. ^{1}H NMR spectra were recorded using JEOL LA-500 spectrometers, with TMS as the internal standard. Mass spectra were recorded using a JMS-700T instrument. UV spectra were recorded using a HITACHI U-3900H spectrometer. All reactions were performed under a positive atmosphere of dry N_2. All extracts were dried over $MgSO_4$; solvents were removed through rotary evaporation under reduced pressure. Silica gel column chromatography was performed using Kanto Chemical silica gel 60N. Thin-layer chromatography was performed using Merck Kieselgel 60PF_{254}.

9-(4-Dodecanoxybenzyl)-2,7-dinitrocarbazole (2a). A suspension of the dinitrocarbazole [1] (275 mg, 1.00 mmol), 4-dodecanoxybenzyl chloride (342 mg, 1.10 mmol), and K_2CO_3 (276 mg, 2.00 mmol) in DMF (2.5 mL) was stirred at 70 °C for 24 h. Water (20 mL) was added to the reaction mixture and then the solid was filtered off and washed with H_2O and MeOH to afford **2a** as a yellow solid (493 mg, 93%). IR (KBr) ν_{max} (cm^{-1}) 2916, 2848, 1611, 1519, 1469, 1339, 1253, 1175, 1037, 822. ^{1}H NMR (500 MHz, DMSO-d_6, 90 °C) δ 8.61 (d, J = 2.1 Hz, 2H), 8.55 (d, J = 8.6 Hz, 2H), 8.13 (dd, J = 8.6, 2.1 Hz, 2H), 7.18–7.13 (m, 2H), 6.81–6.86 (m, 2H), 5.86 (s, 2H), 3.89 (t, J = 6.8 Hz, 3H), 1.64 (quint, J = 6.8 Hz, 2H), 1.39–1.13 (m, 18H), 0.84 (t, J = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6, 90 °C) δ 158.0, 146.8, 141.1, 127.9, 127.6, 125.4, 122.2, 114.6, 114.4, 105.9, 67.3, 45.6, 30.7, 28.36, 28.35, 28.31, 28.14, 28.10, 28.0, 24.9, 21.4, 13.2 HR-MS (FAB): calcd for $[M]^+$ $C_{31}H_{37}N_3O_5$, m/z 531.2733; found, m/z 531.2753.

2,7-Diamino-9-(4-dodecanoxybenzyl)carbazole (2b). A solution of the dinitrocarbazole **2a** (566 mg, 1.06 mmol) and $SnCl_2 \cdot H_2O$ (2.40 g, 10.6 mmol) in EtOH (20 mL) was heated under reflux for 24 h. After evaporation of the organic solvent, 10% NaOH (aq) was added to the residue and the mixture extracted with CH_2Cl_2. The combined extracts were washed with sat. NaCl, dried, and evaporated to give a residue, which was chromatographed (toluene:Et_2O, 3:1) to give a crude product, washing of which with MeOH afforded the **2b** (329 mg, 66%). IR (KBr) ν_{max} (cm^{-1}) 3454, 3372, 2913, 2847, 1617, 1510, 1489, 1274, 1242, 1176, 1136, 1045, 812. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.08–7.03 (m, 2H), 6.81–6.75 (m, 2H), 6.59–6.53 (m, 4H), 5.23 (s, 2H), 3.88 (t, *J* = 6.8 Hz, 2H), 3.71 (br s, 4H), 1.73 (quint, *J* = 6.8 Hz, 2H), 1.45–1.20 (m, 18H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 35 °C) δ 158.5, 144.1, 142.2, 129.1, 127.5, 119.9, 116.4, 114.8, 108.5, 94.9, 68.1, 45.9, 31.9, 29.64, 29.61, 29.58, 29.56, 29.4, 29.3, 26.0, 22.7, 14.1. HR-MS (FAB): calcd for $[M]^+$ $C_{31}H_{41}N_3O$, *m*/*z* 471.3250; found, *m*/*z* 471.3247.

[3]Rotaxane 1-H_2. A suspension of the ammonium salt **3** [2] (212 mg, 0.53 mmol), DB24C8 (285 mg, 0.64 mmol), and the carbazole **2b** (100 mg, 0.21 mmol) in CH_2ClCH_2Cl (3 mL) was heated at 70 °C for 24 h. After cooling to room temperature, $NaBH_4$ (80 mg, 2.10 mmol) and EtOH (3 mL) were added and then the mixture was stirred at room temperature for 24 h. The excess $NaBH_4$ was quenched with dil. HCl (aq.) and then the organic solvent was evaporated off. The resulting mixture was treated with dil. $NaHCO_3$ (aq.) and extracted with CH_2Cl_2. The combined extracts were washed with water, dried, and evaporated to give a residue, which was chromatographed (CH_2Cl_2: THF, 10:1) to afford the crude product. A suspension of the crude product in acetone (8 mL) and H_2O (8 mL) was treated with NH_4PF_6 (680 mg, 4.17 mmol), and stirred for 2 h. After the organic solvent had been evaporated, the resulting solid was washed with H_2O, ^{i}PrOH, and Et_2O to give a solid (258 mg, 57%). IR (KBr) ν_{max} (cm^{-1}) 3153, 3065, 2925, 1612, 1505, 1455, 1252, 1211, 1056, 954, 842, 743, 557. ^{1}H NMR (500 MHz, CD_3CN) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.32–7.24 (m, 4H), 7.23–7.15 (m, 4H), 6.99–6.93 (m, 2H), 6.86–6.70 (m, 24H), 6.50 (d, *J* = 1.8 Hz, 2H), 6.42 (dd, *J* = 8.2 and 1.8 Hz, 2H), 5.09 (s, 2H), 4.93–4.84 (m, 2H), 4.62–4.48 (m, 4H), 4.23 (d, *J* = 4.6 Hz, 2H), 4.03–3.91 (m, 16H), 3.84 (t, *J* = 7.2 Hz, 2H), 3.72–3.60 (m, 16H), 3.48–3.40 (m, 16H), 2.05 (s, 12H), 1.64 (quint, *J* = 7.2 Hz, 2H), 1.40–1.18 (m, 18H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, CD_3CN, 30 °C) δ 159.4, 148.5, 142.9, 142.7, 139.2, 133.0, 131.5, 131.1, 130.9, 130.7, 129.1, 128.7, 127.8, 126.4, 122.2, 120.3, 118.3, 115.9, 115.5, 113.5, 108.1, 71.6, 71.1, 69.0, 68.9, 53.4, 53.2, 48.3, 46.2, 32.6, 30.7, 30.35, 30.30, 30.13, 30.07, 29.97, 26.7, 23.4, 21.2, 14.4. HR-MS (FAB): calcd for $[\mathbf{3\text{-}H_2\text{-}PF_6}]^+$ $C_{113}H_{145}F_6N_5O_{17}P$, *m*/*z* 1989.0272; found, *m*/*z* 1989.0314.

References

1. P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, 1951, **73**, 2435–2437.
2. Y. Tokunaga, M. Kawabata, Y. Yamauchi and N. Harada, *Heterocycles*, 2010, **81**, 67–72.

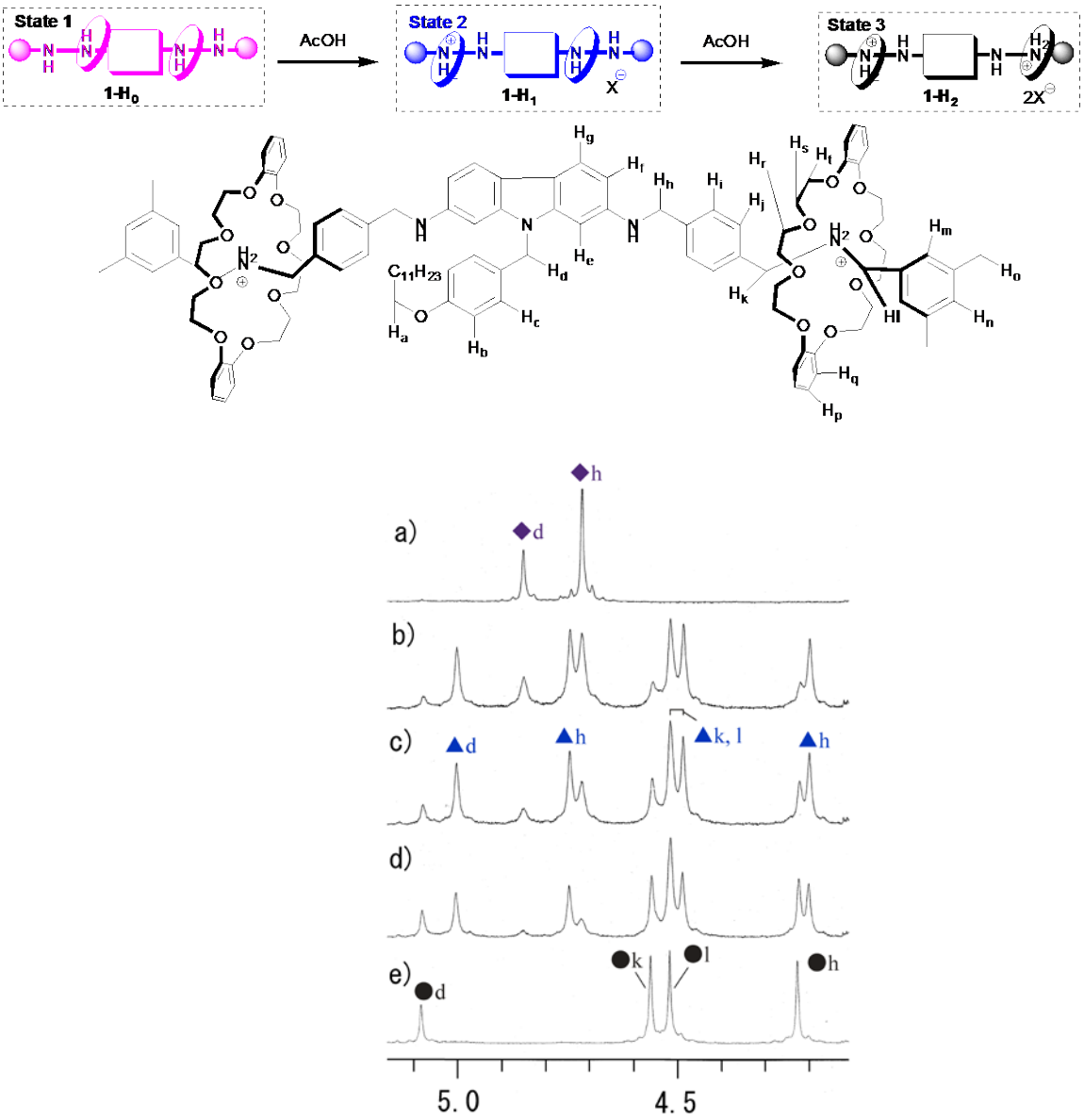


Fig. S1. Detailed view of the conversion of **1-H$_0$** to **1-H$_2$** through the addition of various amounts of AcOH (from state 1 to state 3, as defined in Scheme 2). Partial ^{1}H NMR spectra (500 MHz; CD_3CN/CD_3OD, 10:1) of (a) the [3]rotaxane **1-H$_2$** and ^{t}BuOK (2.5 eq) and (b–e) the sample in (a) after the addition of (b) 1.1, (c) 1.5, (d) 1.7, and (e) 2.6 eq of AcOH. ◆: **1-H$_0$**; ▲: **1-H$_1$**; ●: **1-H$_2$**. For atom labels, see Fig. 2.

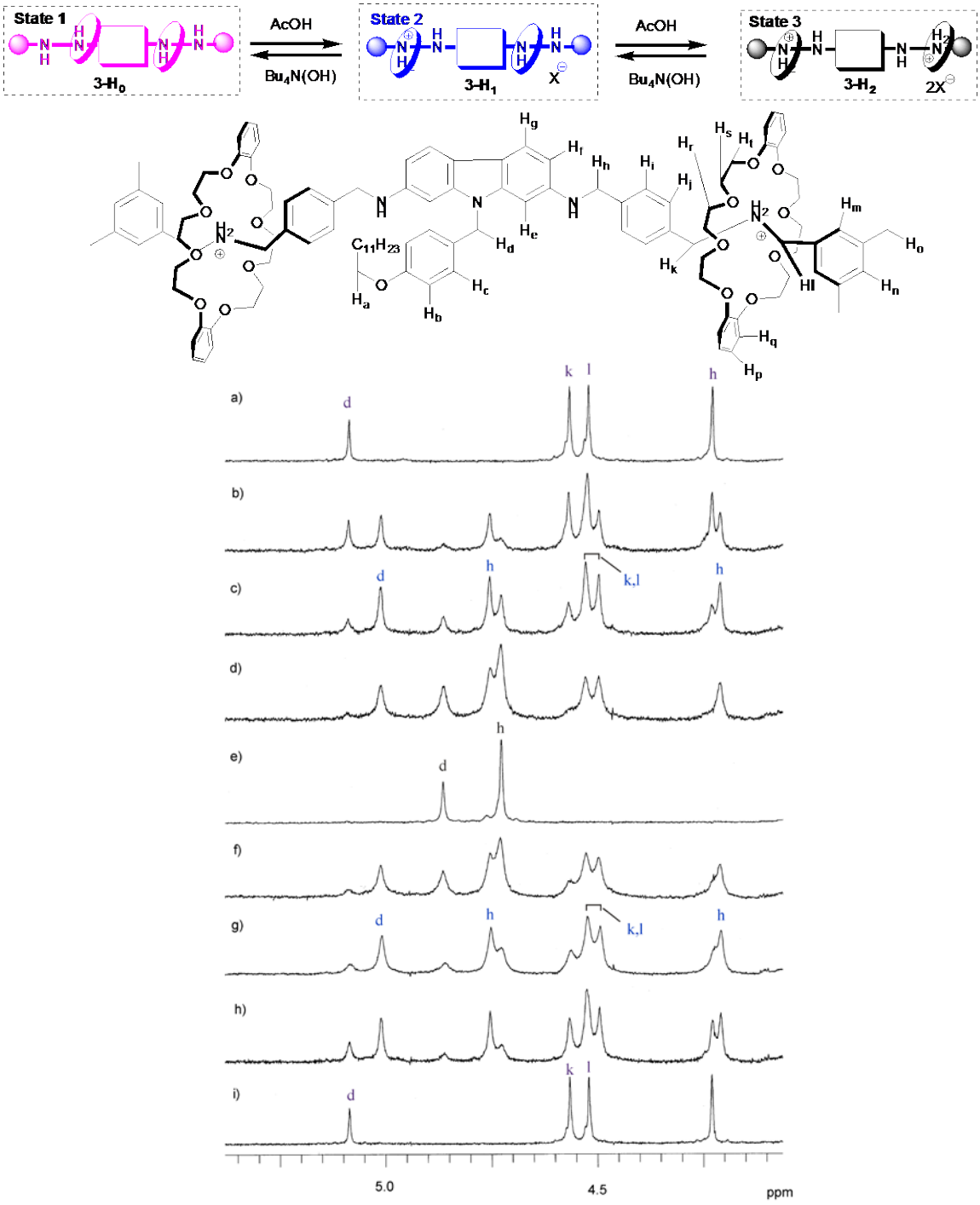


Fig. S2. Partial ^{1}H NMR spectra (500 MHz; CD_3CN/CD_3OD, 10:1) of the [3]rotaxane **1-H$_2$** after sequential additions of Bu_4NOH as a base and acetic acid as an acid. (a) [3]rotaxane **1-H$_2$**; (b–e) the sample in (a) after the addition of (b) 0.5, (c) 1.0, (d) 1.5, and (e) 2.1 eq of Bu_4NOH in MeOH; (f–i) the sample in (e) after the addition of (f) 0.6, (g) 1.1, (h) 1.6, and (i) 2.2 eq of AcOH.

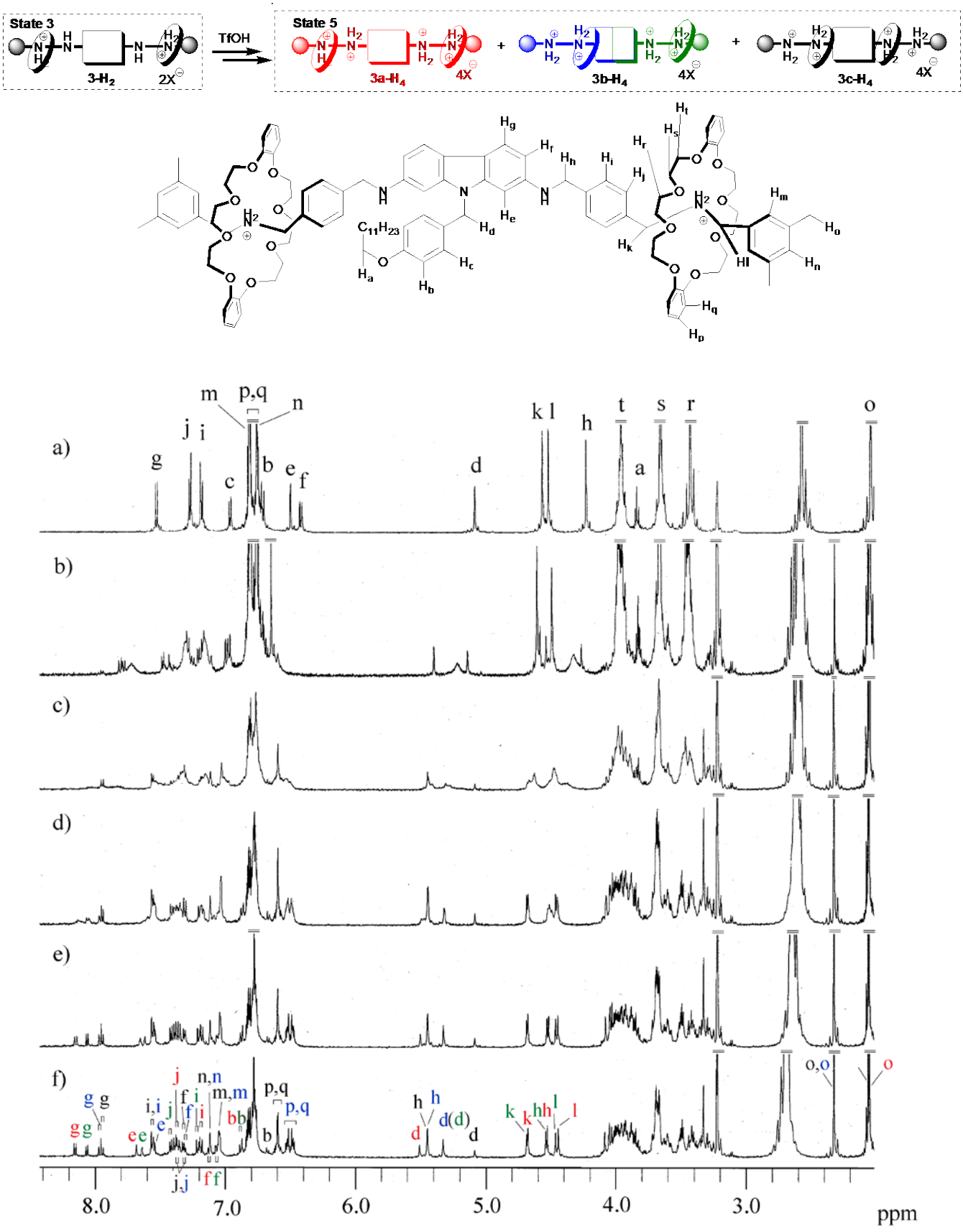


Fig. S3. ^{1}H NMR spectra (500 MHz; CD_3CN/CD_3OD, 10:1) of the [3]rotaxane **1-H$_2$** (1.5 mM) in the presence of (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, and (f) 6 eq of TfOH.

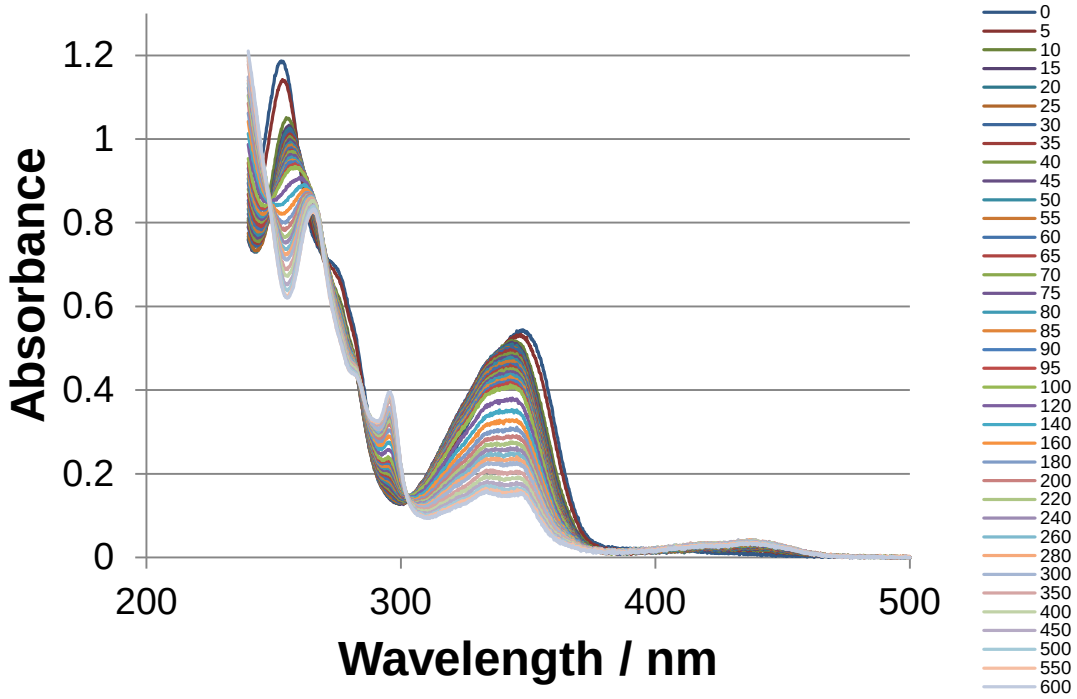


Fig. S4. UV spectra of the [3]rotaxane **1-H$_2$** [20 μM in CH_3CN/CH_3OH (1:1)] in the presence of TfOH (0–600 eq).

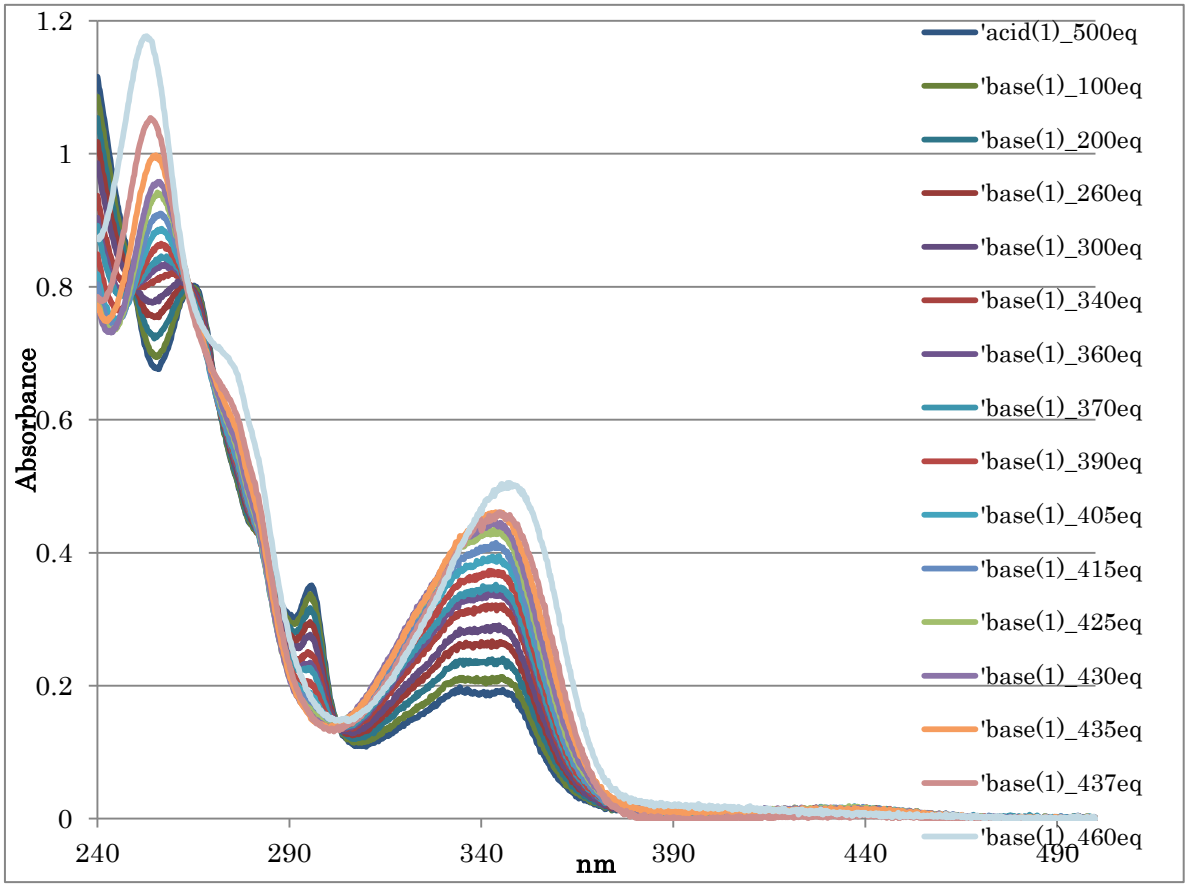


Fig. S5. UV spectra of the [3]rotaxane **1-H$_2$** in the presence of Et_3N (0–460 eq) after the addition of TfOH (500 eq).

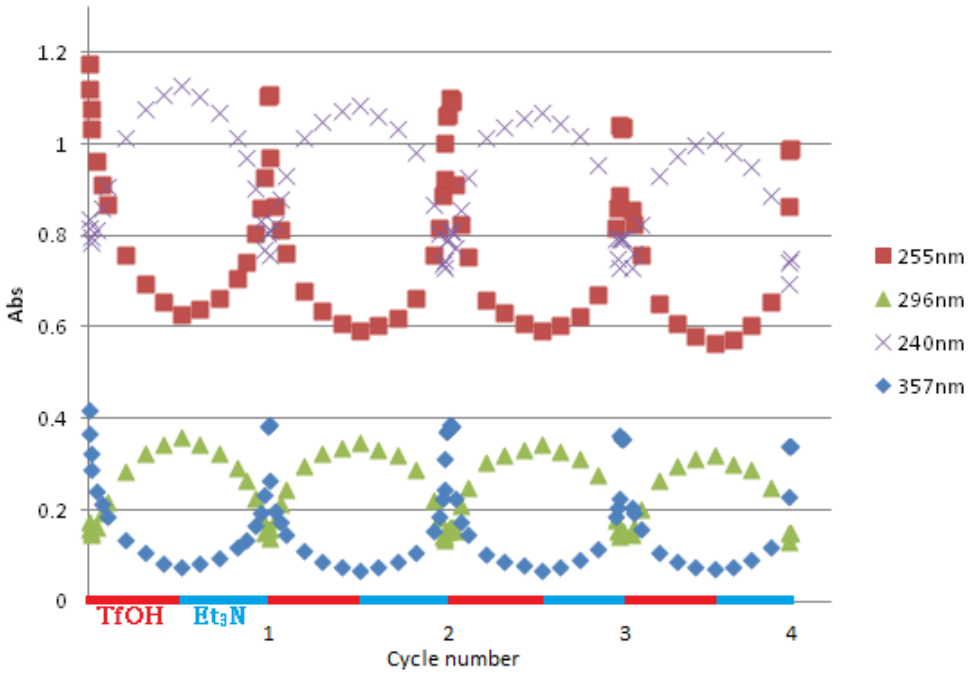


Fig. S6. Plots of the UV spectral data of the [3]rotaxane **1-H$_2$** after sequential additions of acid (TfOH) and base (Et_3N).

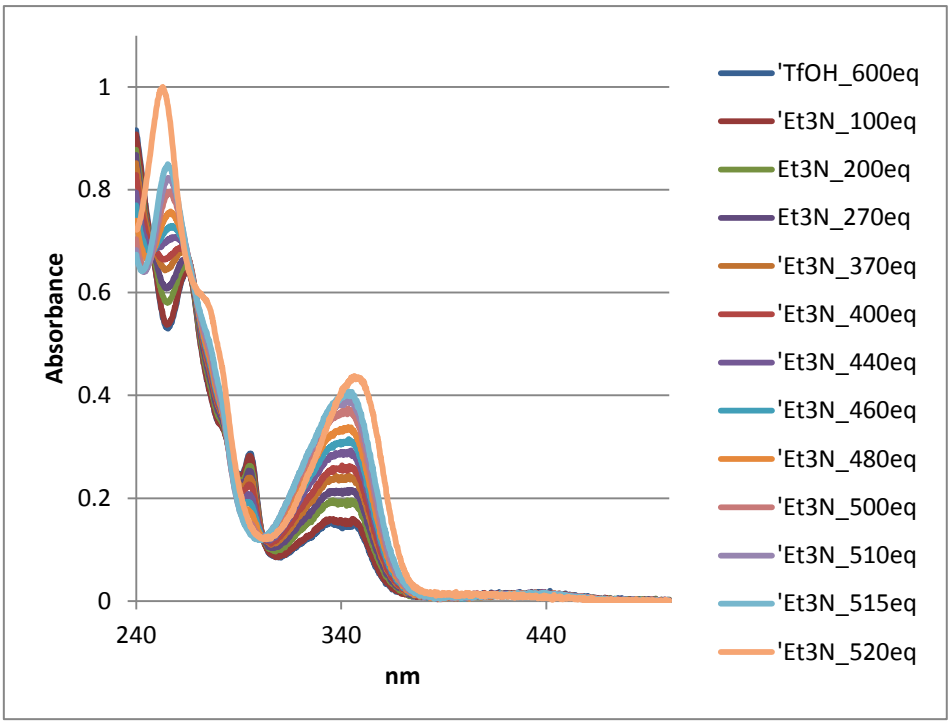


Fig. S7. UV spectra of the [3]rotaxane **1-H$_2$** in the presence of Et_3N and TfOH after sequential additions of Bu_4NOH and AcOH (NMR experiments).

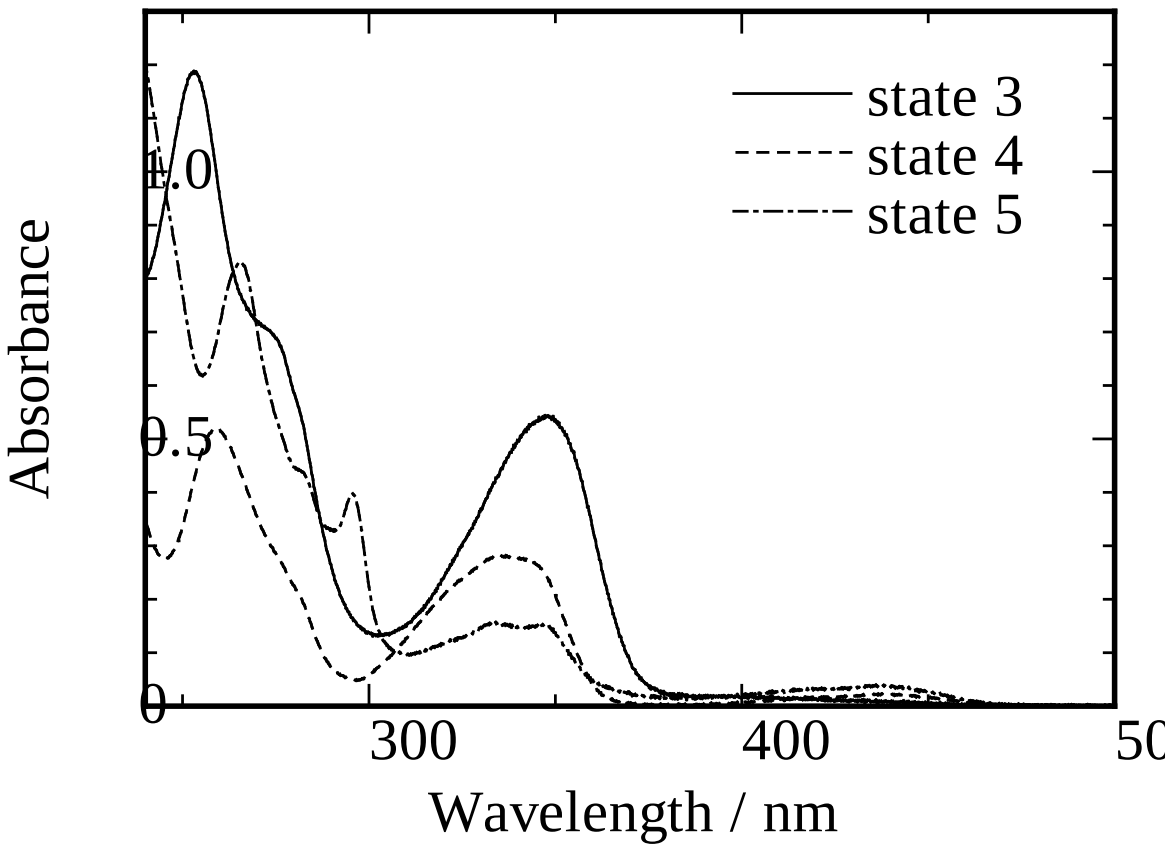


Fig. S8a. UV spectra of **states 3**, **4**, and **5** determined through target factor analysis.

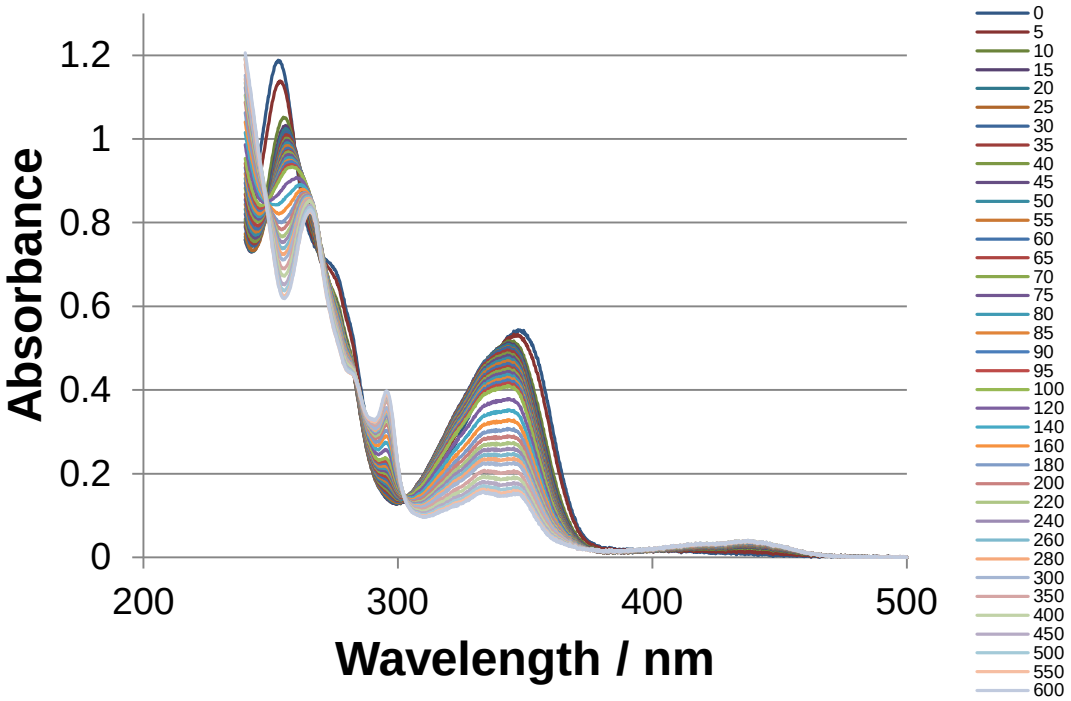


Fig. S8b. UV spectra of the [3]rotaxane **1-H$_2$** in the presence of TfOH (0–600 eq), calculated using target factor analysis.

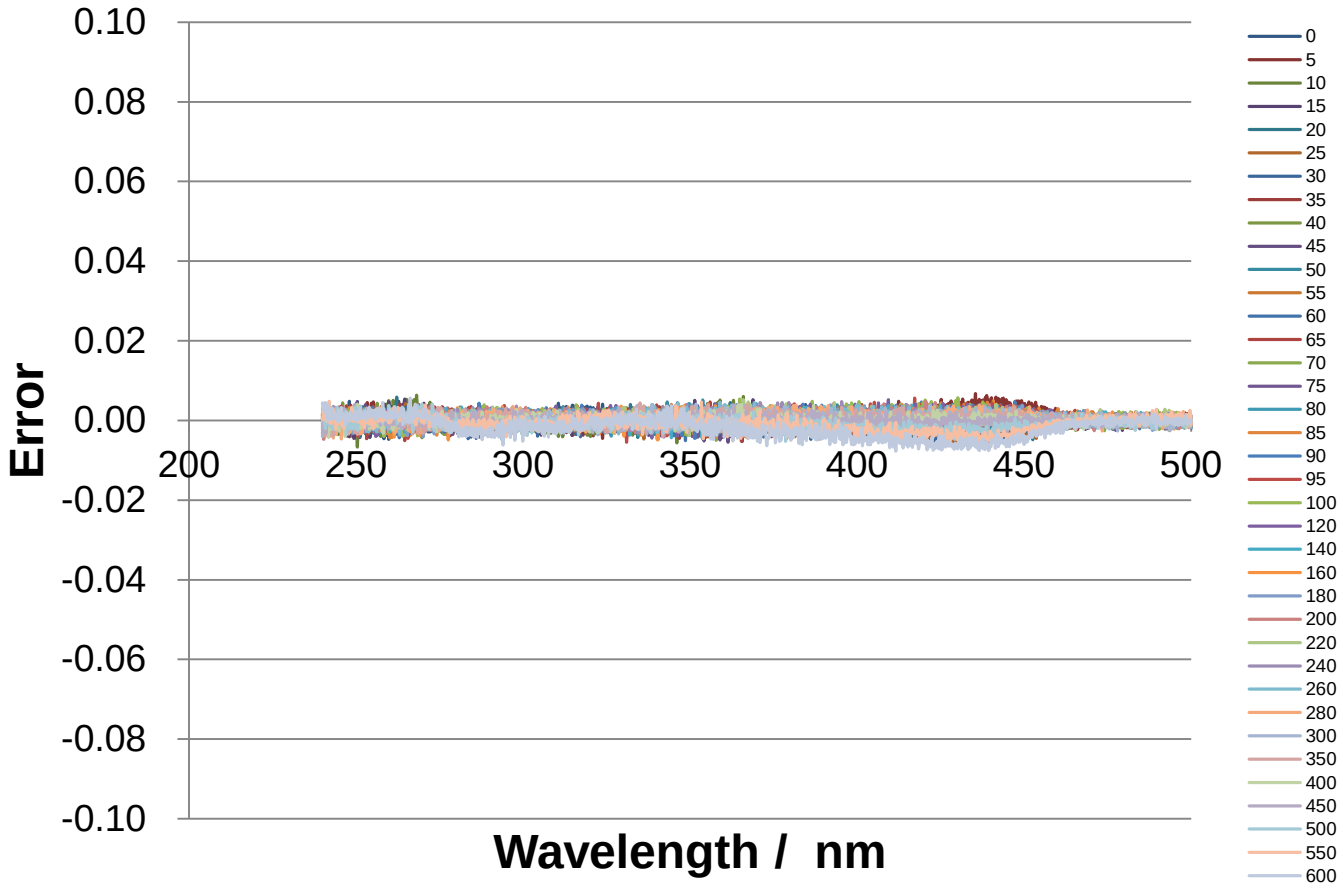


Fig. S8c. Errors between experimental and calculated UV data (differences between Fig. S4 and S8b).

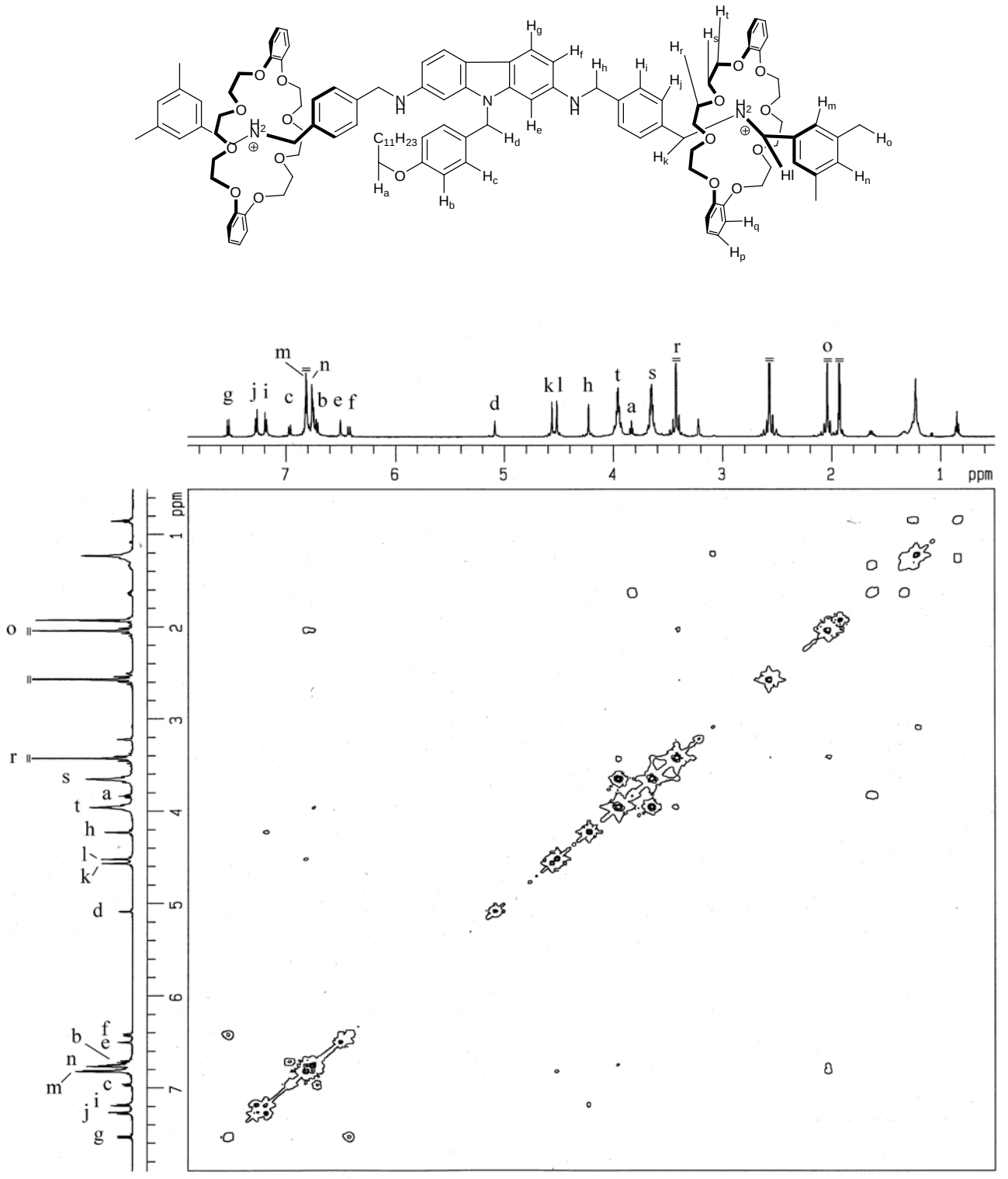


Fig. S9a. COSY spectrum (500 MHz; CD_3CN/CD_3OD, 10:1; 4.2 mM) of the [3]rotaxane **1-H$_2$**.

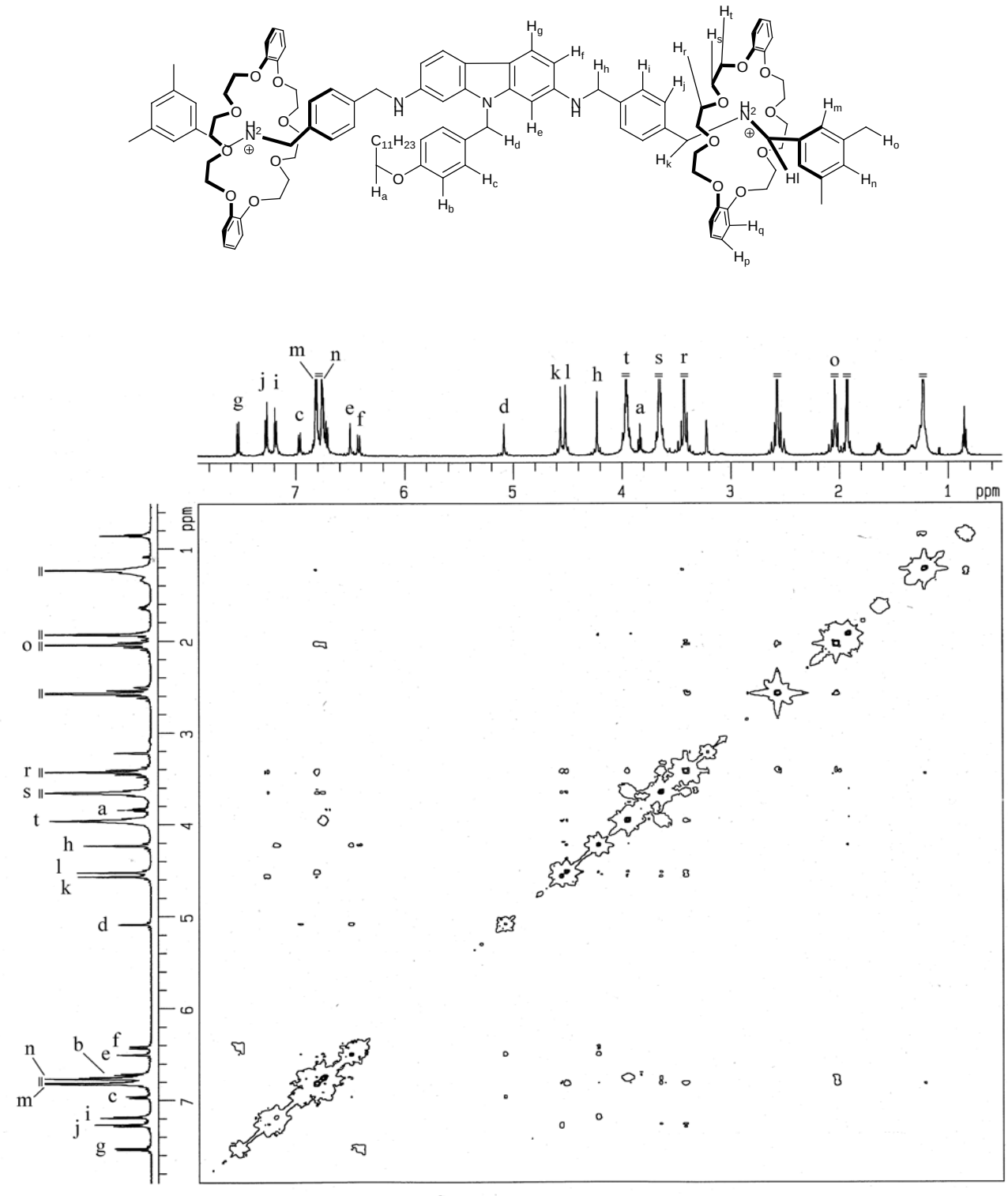
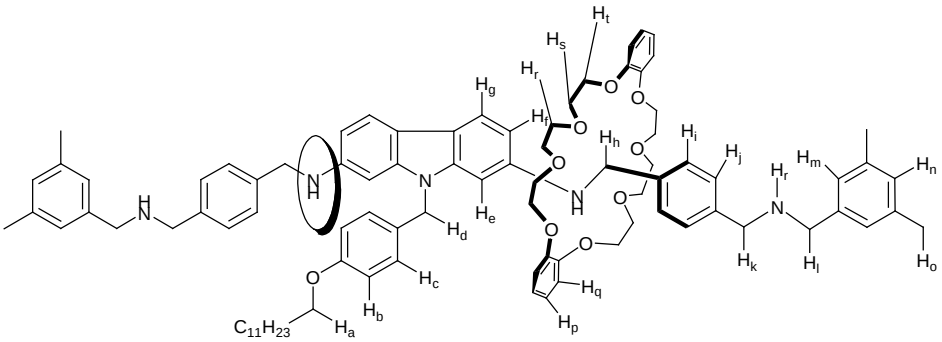


Fig. S9b. NOESY spectrum (500 MHz; CD_3CN/CD_3OD, 10:1; 4.2 mM) of the [3]rotaxane **1-H$_2$**.



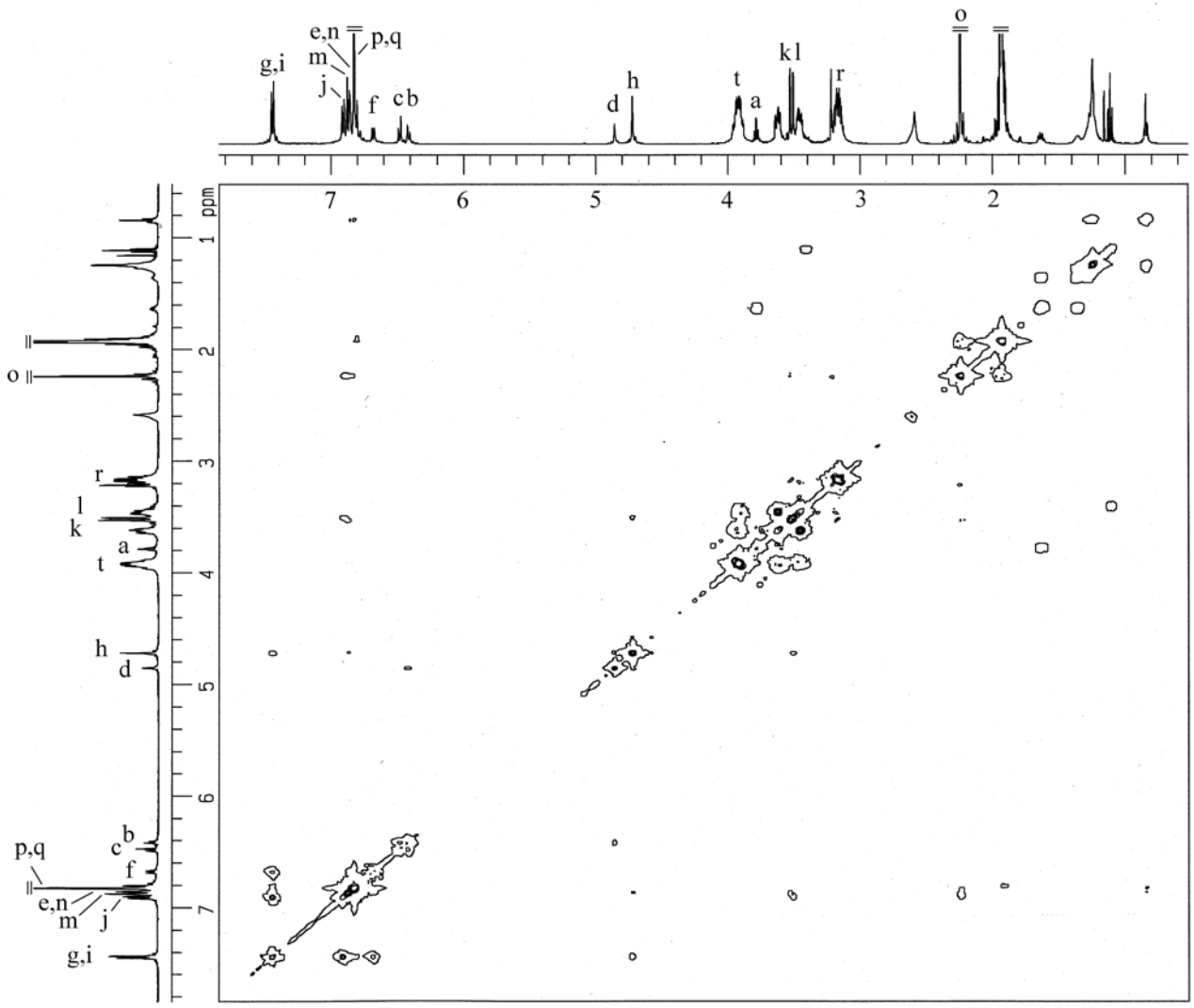


Fig. S10a. COSY spectrum (500 MHz; CD_3CN-CD_3OD, 10:1; 4.2 mM) of the [3]rotaxane **1-H$_2$** in the presence of ^{t}BuOK (2.1 eq).

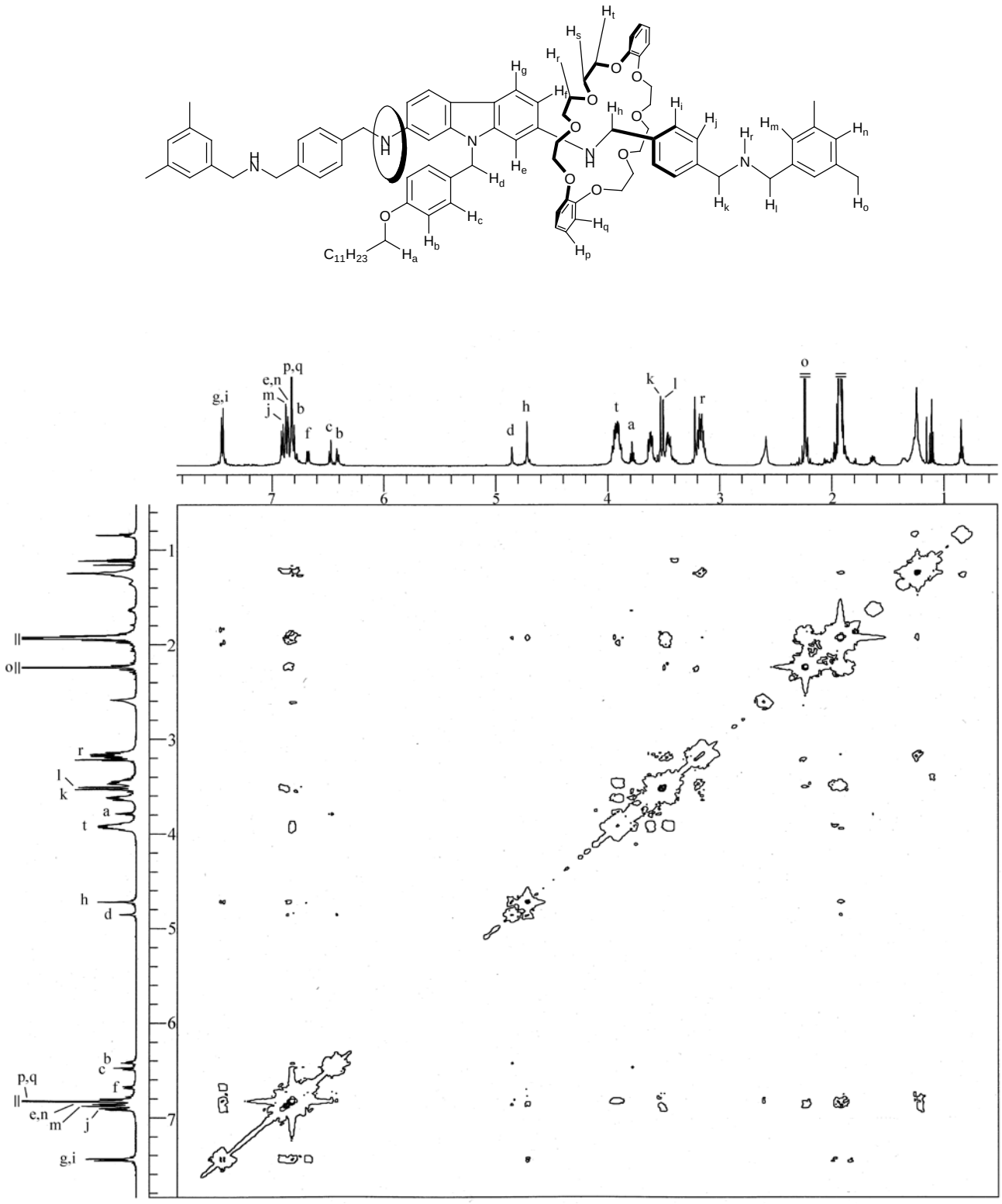


Fig. S10b. NOESY spectrum (500 MHz; CD_3CN/CD_3OD, 10:1; 4.2 mM) of the [3]rotaxane **1-H$_2$** in the presence of ^{t}BuOK (2.1 eq).

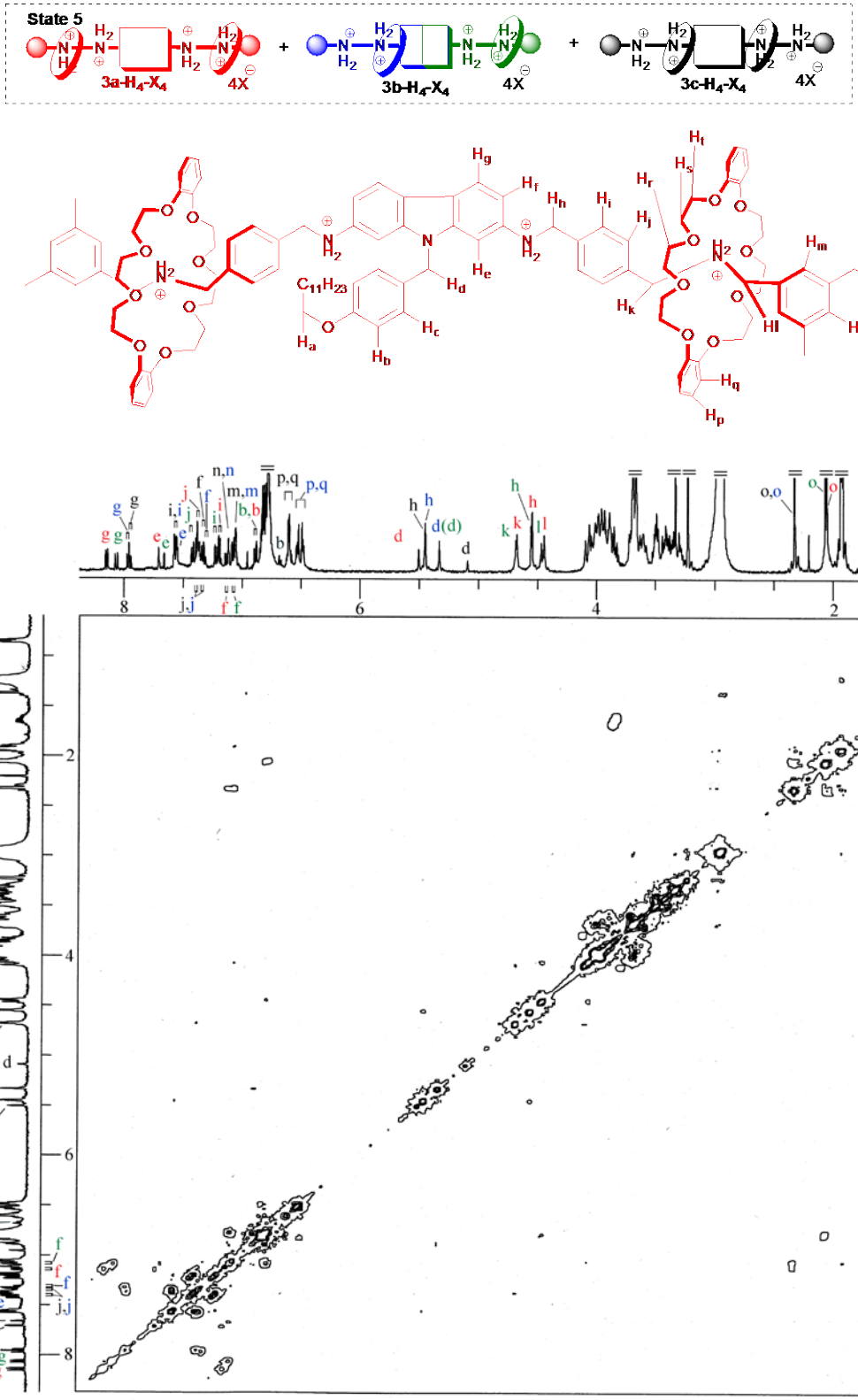


Fig. S11a. COSY spectrum (500 MHz; CD_3CN-CD_3OD, 10:1; 6.1 mM) of the [3]rotaxane **1-H$_2$** in the presence of TfOH (5 eq).

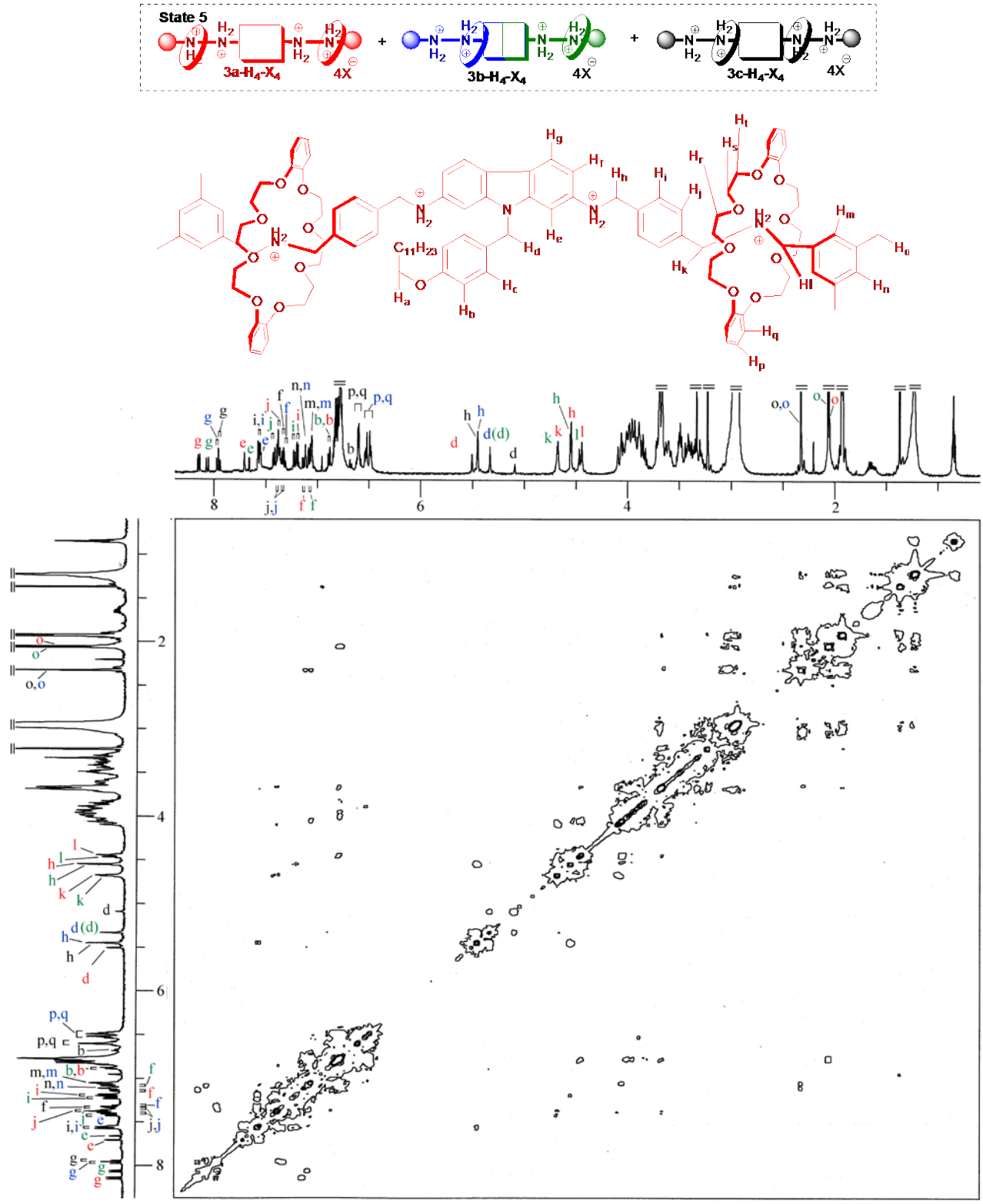
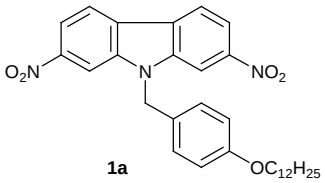


Fig. S11b. NOESY spectrum (500 MHz; CD_3CN/CD_3OD, 10:1; 6.1 mM) of the [3]rotaxanes **1-H$_2$** in the presence of TfOH (5 eq).



1a

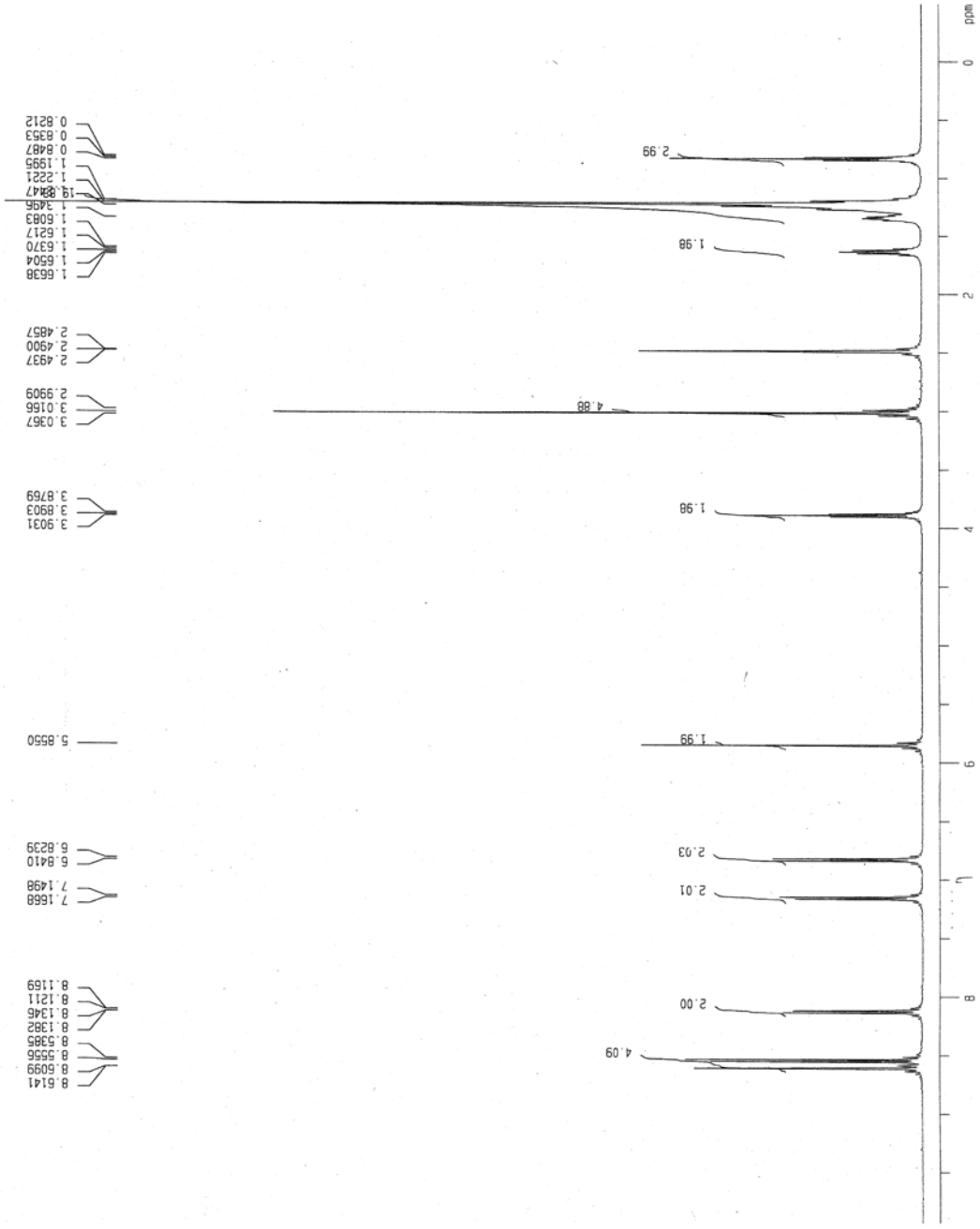


Fig. S12a. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the carbazole **2a**.

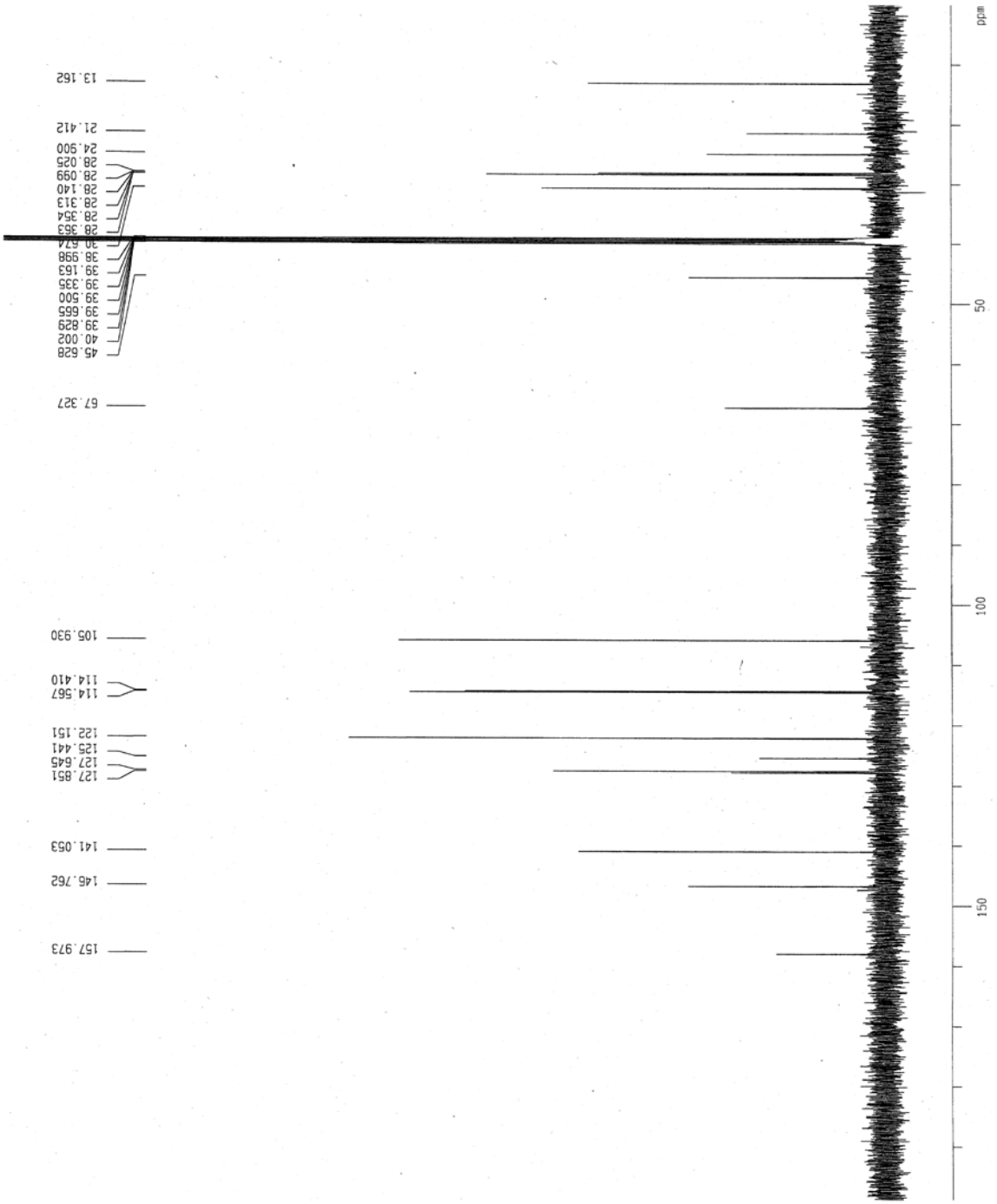
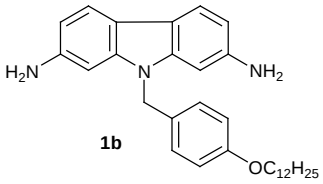


Fig. S12b. ^{13}C NMR spectrum (500 MHz, DMSO-d_6) of the carbazole **2a**.



1b

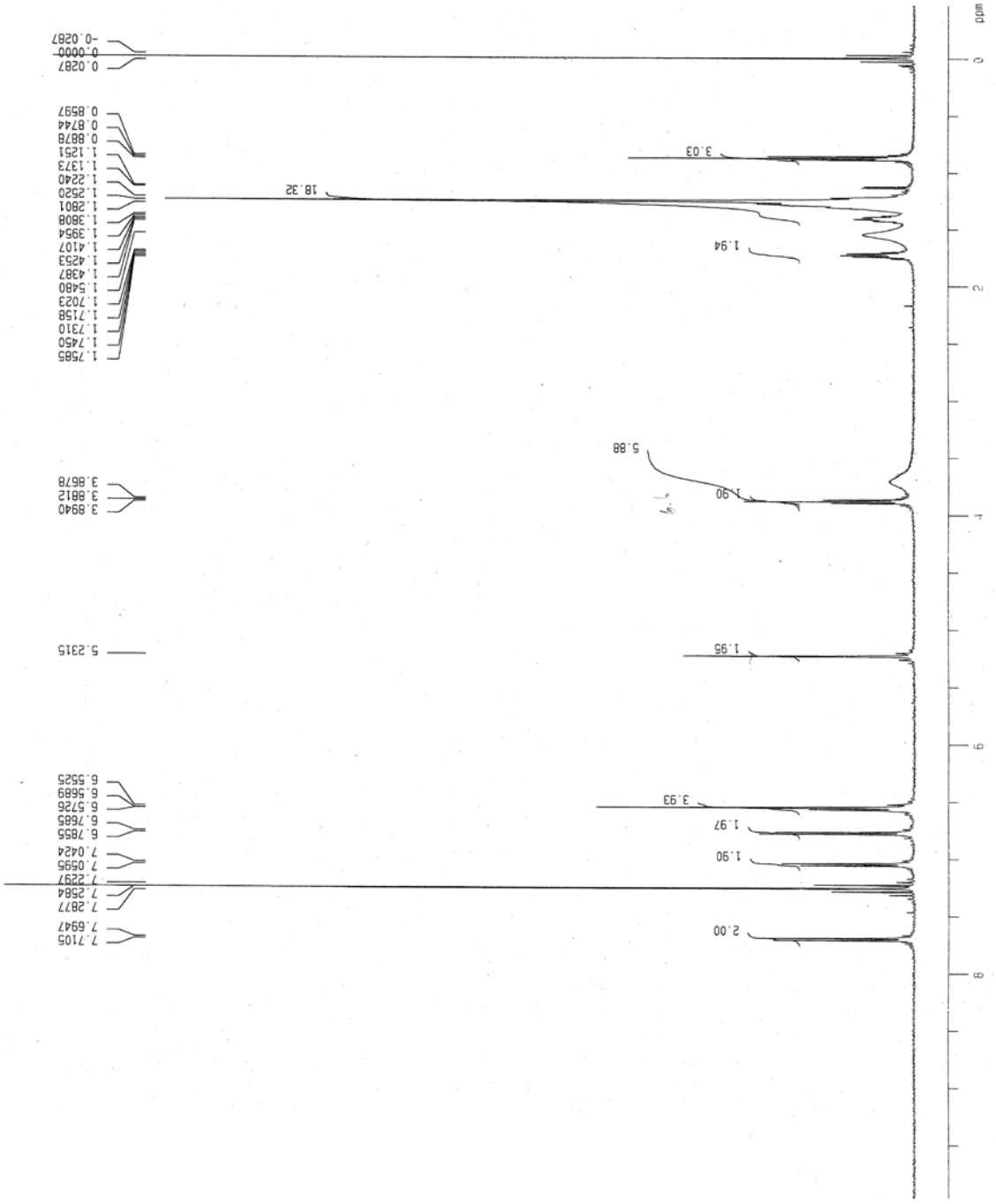


Fig. S13a. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the carbazole **2b**.

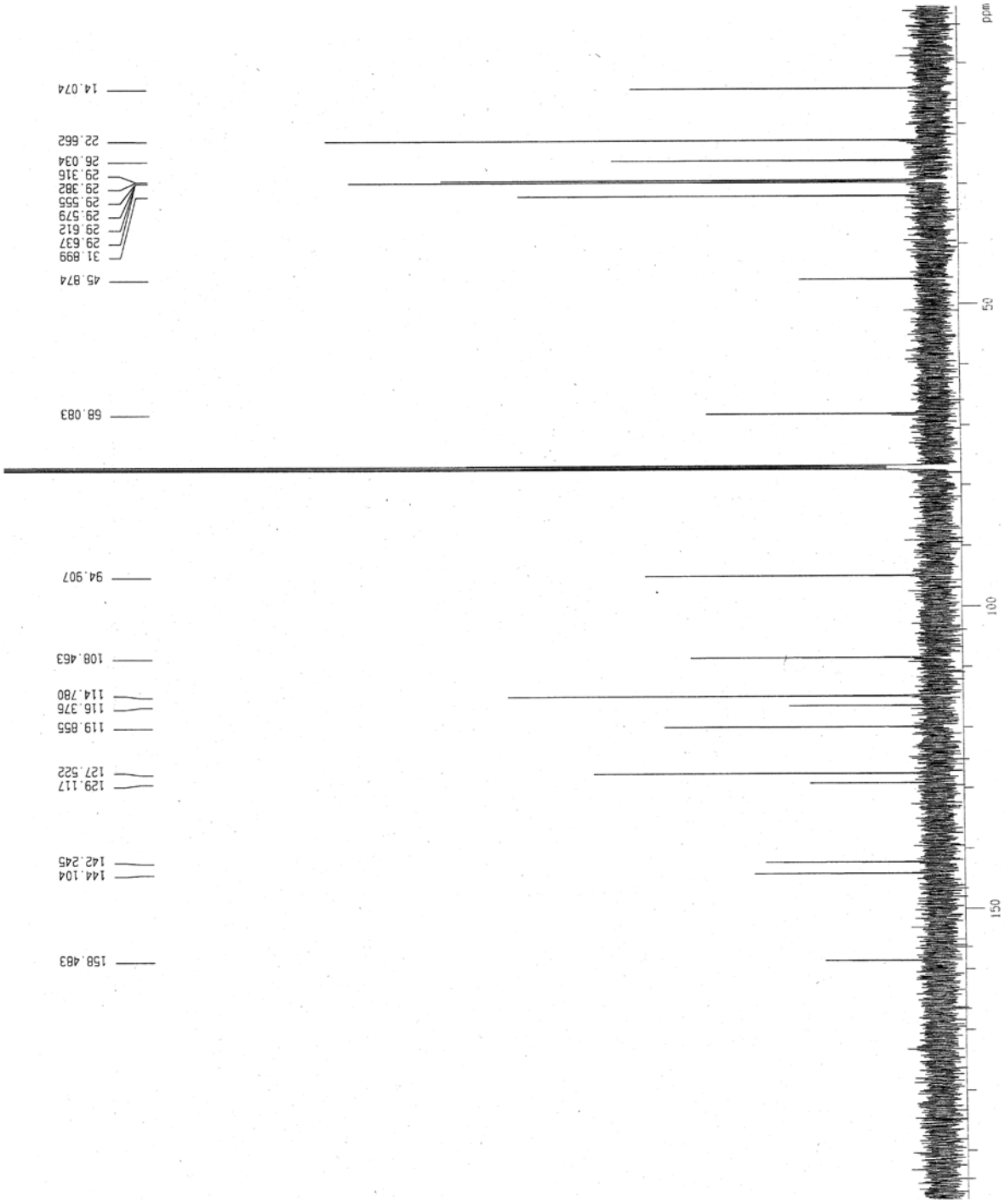


Fig. S13b. ^{13}C NMR spectrum (500 MHz, $CDCl_3$) of the carbazole **2b**.