

ORGANIC LETTERS

A Clicked Bistable [2]Rotaxane

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Supplementary Information

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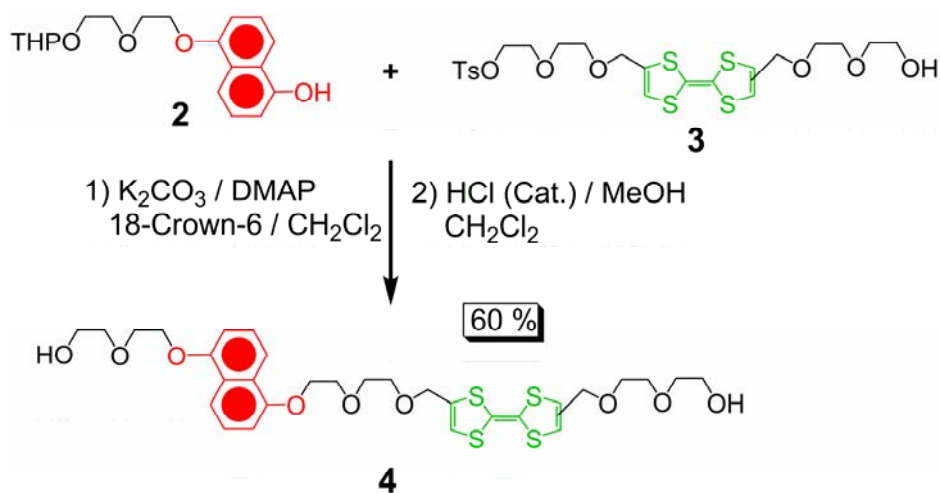
Experimental Section

General: All reagents and starting materials were purchased from Aldrich and used without further purification. Cyclobis(paraquat-*p*-phenylene) tetrakis(hexafluorophosphate)^{S1} (CBPQT·4PF₆), 5-(2-(2-(tetrahydro-2*H*-pran-2-yloxy)ethoxy)ethoxynaphthalene-1-ol)^{S2} (**2**), the monotosylated tetrathiafulvalene derivative^{S3} **3** and 4-[bis[4-(*t*-butyl)phenyl][4-(isopropyl)phenyl]methyl]phenyl propargyl ether^{S4} (**6**) were prepared according to literature procedures. Thin layer chromatography (TLC) was performed on silica gel 60 F254 (E. Merck). Column chromatography was performed on silica gel 60F (Merck 9385, 0.040–0.063 mm). Melting points were recorded on an Electrothermal 9100 instrument in open capillary tubes and are uncorrected. Deuterated solvents (Cambridge Isotope Laboratories) for NMR spectroscopic analyses were used as received. NMR spectra were recorded on Bruker Avance 500 and 600 spectrometers, with working frequencies of 500.13 and 600.13 MHz for ¹H nuclei, and 125.70 and 150.90 MHz for ¹³C nuclei, respectively. Chemical shifts are quoted in ppm relative to tetramethylsilane, using the residual solvent peak as a reference standard. High resolution fast atom bombardment (HR-FAB) mass spectra were obtained on a JEOL JMS-600H high resolution mass spectrometer equipped with a FAB probe. Electrospray ionization (ESI) mass spectra were measured on an IonSpec FT-ICR mass spectrometer. Electrochemical and spectroelectrochemical experiments were carried out at room temperature in argon-purged MeCN solutions, with a Princeton Applied Research 263A Multipurpose instrument interfaced to a PC. Cyclic voltammetry experiments were performed using a glassy carbon working electrode (0.018 cm², Cypress Systems). Its surface was polished

routinely with 0.05 μm alumina-water slurry on a felt surface immediately before use. The counter electrode was a Pt coil and the reference electrode was a standard calomel electrode (SCE). The concentration of the sample and supporting electrolyte [tetrabutylammonium hexafluorophosphate (**TBA**•**PF₆**)] were 0.5 mM and 0.1 M, respectively. The scan rate was set to 200 mVs^{-1} . In the differential pulse voltammetry (DPV) experiment, the pulse height, pulse width, step height and step time were set to 50 mV, 50 ms, 5 mV, 500 ms, respectively. The peak top potentials for the overlapped peaks were determined by using the curve-fitting operation of the IGOR Pro software (Version 5.04B, Wavematrix, Inc.). Spectroelectrochemical experiments were made in a custom-built optically-transparent thin layer electrochemical (OTTLE) cell with an optical path of 1 mm, using a Pt grid as working electrode, a Pt wire as counter electrode and a Ag wire pseudo-reference electrode. Experimental errors: potential values, ± 10 mV; absorption maxima, ± 2 nm. The scan rate was set to 0.25 mV s^{-1} and the UV-Vis spectra were recorded every two minutes.

Synthesis

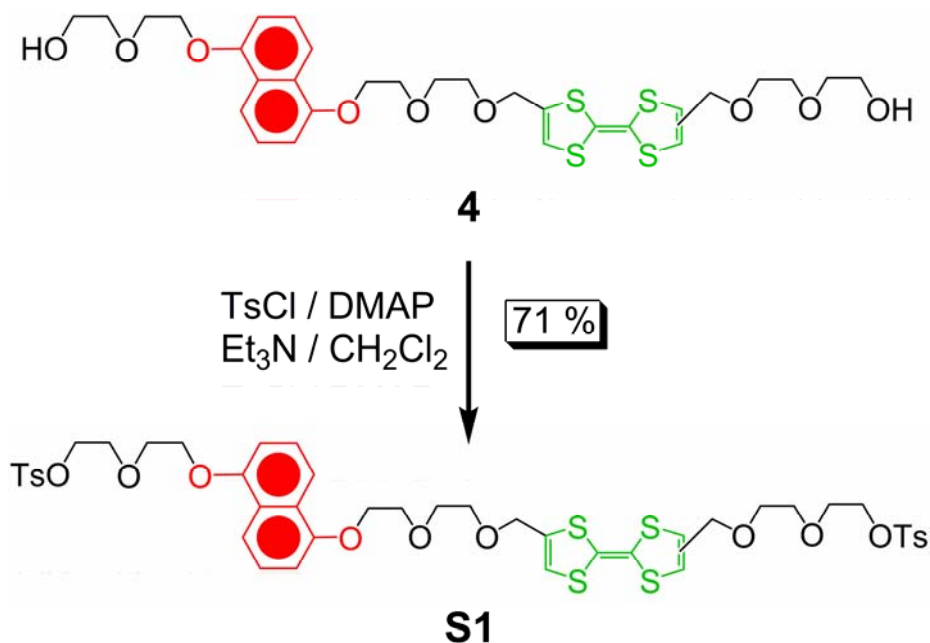
Scheme S1. Synthesis of the DNP/TTF-containing diol derivative **4**



4: A solution of 5-(2-(2-(tetrahydro-2*H*-pran-2-yloxy)ethoxy)ethoxynaphthalen-1-ol)^{S2} (**2**) (62 mg, 0.18 mmol), the TTF-monotosylate^{S3} **3** (100 mg, 0.17 mmol), K₂CO₃ (92 mg, 0.68 mmol), and [18]crown-6 (5 mg) in dry MeCN (30 mL) was heated under reflux for 16 h. After cooling down to room temperature, the reaction mixture was filtered and the residue was washed with MeCN (20 mL). The combined organic solution was evaporated in vacuo to obtain the crude THP-protected compound as a yellow oil, which was re-dissolved in MeOH / CH₂Cl₂ (1:1, 100 mL). A conc. HCl aqueous solution (0.5 mL) was added and the reaction mixture was stirred at room temperature for 1h. 1N NaOH aqueous solution (100 mL) was added to the reaction mixture and it was extracted by CH₂Cl₂ (3 x 100 mL) and dried (MgSO₄). After removal of the solvent, the residue was purified by column chromatography (SiO₂: CH₂Cl₂/EtOH 99:1) to give the diol **4** (68 mg, 60%) as a yellow oil; ¹H NMR (500 MHz, CD₂Cl₂): δ = 7.88 (dd, *J* = 7.6 Hz, 2H), 7.41 (dd, *J* = 7.6 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 2H), 6.28, 6.26, 6.24, 6.23 (4×s, 2H), 4.34–4.29 (m, 8H), 4.02–4.01 (m, 4H), 3.76–3.59 (m, H16); ¹³C NMR (125 MHz, CD₂Cl₂): δ = 154.8, 154.7, 135.1, 135.0, 134.9, 134.8, 127.1, 127.0, 125.6, 125.5, 116.9, 116.7, 116.6, 116.5, 114.9, 114.6, 106.1, 73.1, 72.9, 71.3, 70.6, 70.2, 70.1, 69.9, 69.9, 69.8, 68.5, 68.4, 68.43, 68.4, 68.3, 62.1, 62.0 (x 2);^{S5} HRMS (FAB): *m/z* calcd for C₃₀H₃₈O₉S₄: 670.1398; found: 670.1407.

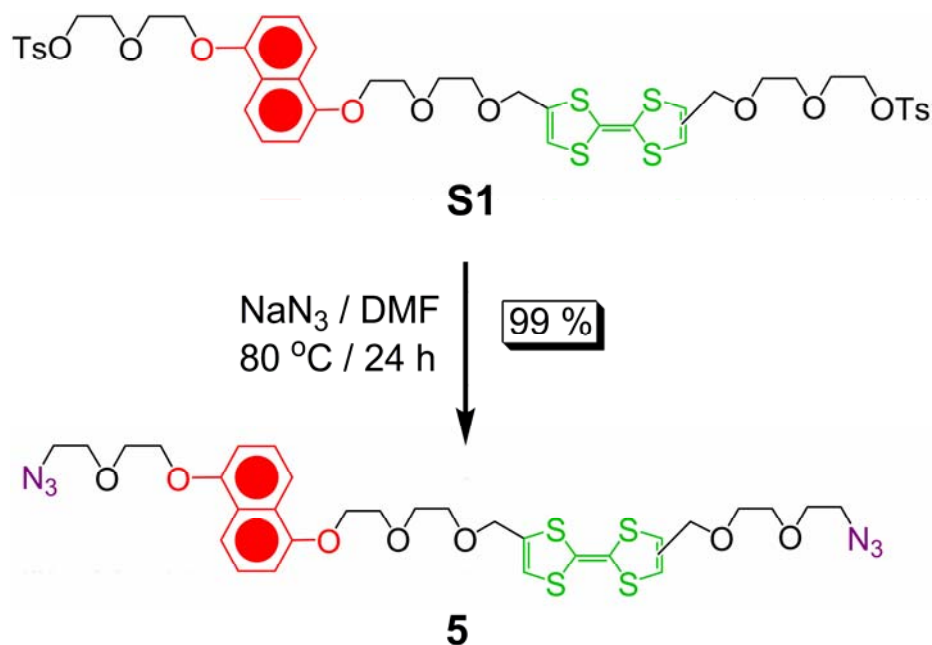
S1: A solution of TsCl (102 mg, 0.54 mmol) in CH₂Cl₂ (2 mL) was added dropwise to a solution of the diol (**4**) (90 mg, 0.13 mmol), Et₃N (0.15 mL, 1.04 mmol) and DMAP (5 mg) in CH₂Cl₂ (20 mL) at 0 °C. The reaction mixture was then stirred for 16h at room temperature.

Scheme S2. Synthesis of the DNP/TTF-containing ditosylate **S1**



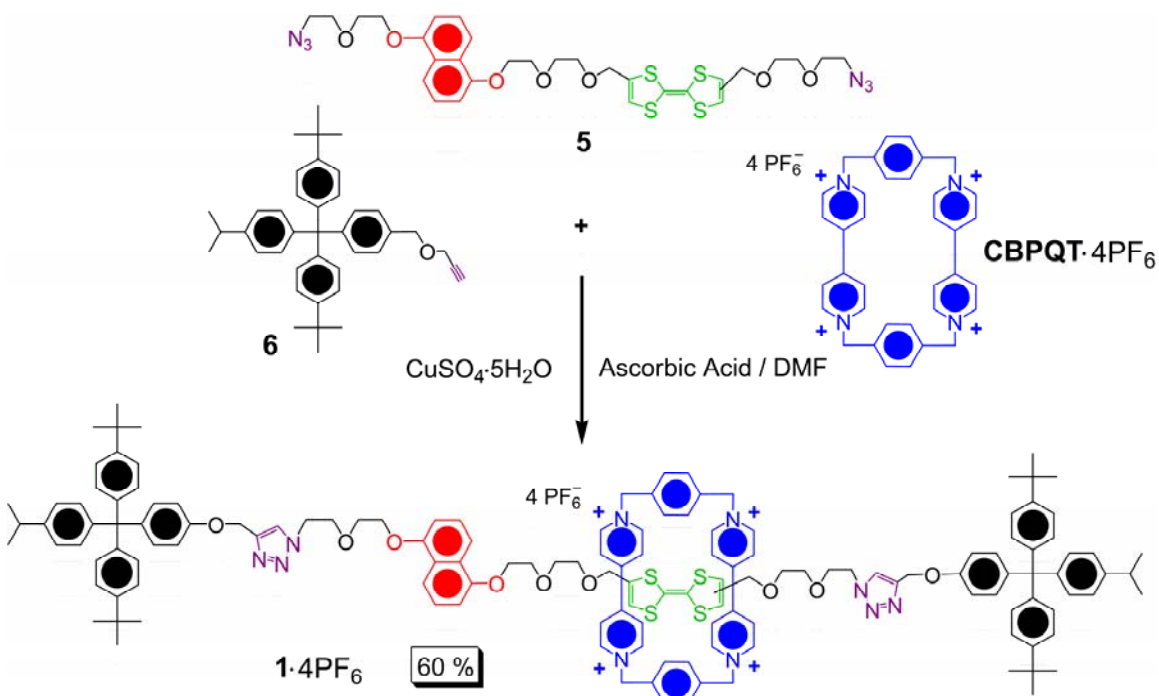
After removal of the solvent, the residue was purified by column chromatography (SiO₂ CH₂Cl₂/EtOH 99:1) to give the ditosylate **S1** (73 mg, 71%) as a yellow oil; ¹H NMR (500 MHz, CD₂Cl₂): δ = 7.84 (d, *J* = 8.1 Hz, 1H), 7.79–7.74 (m, 5H), 7.35 (s, 4H), 7.27 (d, *J* = 7.3 Hz, 2H), 6.86 (d, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 7.2 Hz, 1H), 6.20 (s, 2H), 4.28 (br, 4H), 4.20 (br, 6H), 4.11 (br, 2H), 3.96 (br, 2H), 3.89 (br, 2H), 3.79 (br, 2H), 3.76 (br, 2H), 3.64 (br, 4H), 3.52 (br, 4H), 2.43 (s, 3H), 2.36 (s, 3H); ¹³C NMR (125 MHz, CD₂Cl₂): δ = 154.8, 154.6, 145.5, 145.4, 135.1, 135.0, 134.9, 134.8, 133.2, 130.3, 130.2, 128.2, 128.2, 127.1, 127.0, 125.6, 125.6, 116.8, 116.7, 116.4, 116.6, 114.8, 114.7, 110.9, 110.7, 106.0, 106.1, 71.3, 71.0, 70.2, 70.1, 70.0, 69.9, 69.8, 69.7, 69.3, 69.0, 68.5 (x 2), 68.5, 68.4, 68.3, 21.8, 21.7;^{S5} HRMS (FAB): *m/z* calcd for C₄₄H₅₁O₁₃S₆: 978.1576; found: 978.1589.

Scheme S3. Synthesis of the DNP/TTF-containing diazide **5**



5: A solution of ditosylate **S1** (93 mg, 0.09 mmol), and NaN_3 (48 mg, 0.72 mmol) in dry DMF (10 mL) was heated at $80\text{ }^\circ\text{C}$ for 1 d. After removal of the solvent, the residue was dissolved in CH_2Cl_2 (50 mL) and then washed with a saturated aqueous solution of NH_4Cl (2 x 30 mL) followed by a saturated aqueous solution of K_2CO_3 (30 mL) followed by drying (MgSO_4). The crude product, obtained after the removal of the solvent, was purified by column chromatography (SiO_2 : $\text{CH}_2\text{Cl}_2/\text{EtOH}$ 99:1) to give the diazide **5** (68 mg, 60%) as a yellow oil; ^1H NMR (500 MHz, CD_2Cl_2): δ = 7.84 (d, J = 8.4 Hz, 2H), 7.36 (dd, J = 7.7 Hz, 2H), 6.87 (d, J = 7.5 Hz, 2H), 6.23, 6.22, 6.20 (3×s, 4H), 4.28 (m, 8H), 3.98 (m, 4H), 3.77 (m, 4H), 3.62 (m, 8H), 3.40 (m, 4H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 154.8, 154.7, 135.0, 127.1, 125.6, 116.7, 116.6, 116.5, 114.8, 114.7, 110.7, 106.1, 106.1, 71.3, 70.9, 70.7, 70.4, 70.2, 69.9, 69.89, 68.6, 68.4, 51.3, 51.2;^[SS] HRMS (FAB): m/z calcd for $\text{C}_{30}\text{H}_{36}\text{N}_6\text{O}_7\text{S}_4$: 720.1528; found: 720.1550.

Scheme S4. Synthesis of the bistable [2]rotaxane **1**·4PF₆



1·4PF₆: The TTF/DNP-containing diazide **5** (9.7 mg, 0.013 mmol), **CBPQT**·4PF₆ (15.5 mg, 0.014 mmol), and the alkyne-functionalized stopper⁴ **7** (14.9 mg, 0.028 mmol) were dissolved in DMF (0.18 mL) at room temperature to afford a deep green solution. Stock solutions of CuSO₄·5H₂O in DMF (20 μL, 0.006M) and ascorbic acid in DMF (20 μL, 0.012M) were added. The solution was stirred at room temperature for 48 h. The crude product, obtained after the removal of the solvent, was purified by column chromatography (SiO₂: Me₂CO followed by a 1% w/v NH₄PF₆ solution in Me₂CO). The green compound present in this salt solution was concentrated into a small volume and the pure product was precipitated from this concentrate following the addition of an excess of cold water. The bistable [2]rotaxane **1**·4PF₆ was isolated as a green solid (23 mg, 60% yield, mp 150 °C with decomposition); ¹H NMR (600 MHz, CD₃CN): δ =

8.86–8.79 (m 12H), 8.66 (s, 2H), 8.63 (s, 2H), 7.93 (s, 1H), 7.69 (s, 3H), 7.78 (br, 2H), 7.69–7.46 (m, 30H), 7.38–7.33 (m, 5H), 7.25 (br, 12H), 7.12 (br, 45H), 6.97–6.92 (m, 3H), 6.85–6.77 (m, 8H), 6.76 (d, $J = 7.6$ Hz, 1H), 6.68 (d, $J = 7.6$ Hz, 1H), 6.42 (d, $J = 7.2$ Hz, 2H), 6.14 (s, 1H), 6.03 (s, 2H), 5.87 (s, 1H), 5.66–5.58 (m, 6H), 5.49–5.38 (m, 12H), 5.04 (s, 2H), 5.03 (s, 2H), 5.01 (s, 2H), 4.99 (s, 2H), 4.61–4.57 (m, 8H), 4.33 (br, 4H), 4.25 (br, 4H), 4.11 (s, 2H), 4.09 (br 4H), 4.06 (br, 6H), 4.00–3.95 (m, 12H), 3.90 (br, 6H), 3.84 (br, 4H), 3.79 (br, 6H), 3.74 (br, 2H), 3.71 (br, 2H), 3.61 (br, 2H), 2.83 (hextet, $J = 6.9$ Hz, 4H), 1.25 (br, H72), 1.18–1.16 (m, 24H); MS (ESI): $m/z = 1294 [M - 2PF_6]^{2+}$, 814 $[M - 3PF_6]^{3+}$, 574 $[M - 4PF_6]^{4+}$; HRMS (FAB): m/z calcd for $C_{144}H_{156}F_{12}N_{10}O_9P_2S_4$: 1294.0130; found: 1294.0108 $[M - 2PF_6]^{2+}$.

NMR Spectra of New Compounds

Figure 1. 1H NMR spectrum of the diol derivative **4**

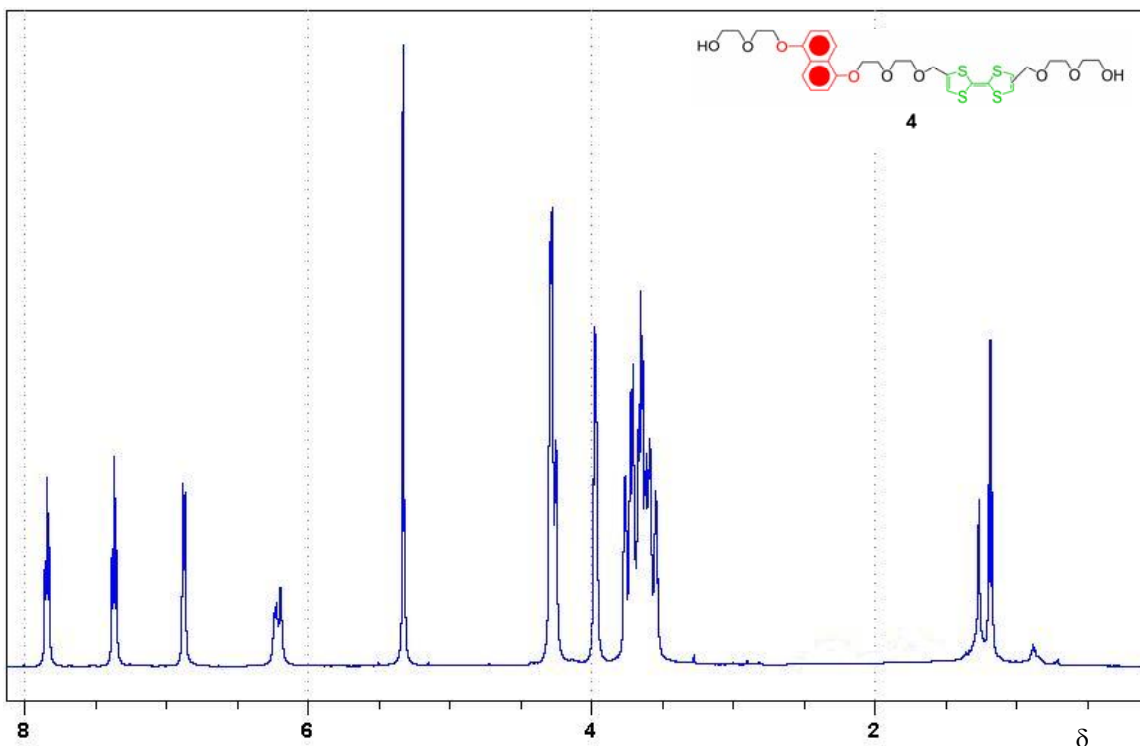


Figure 2. ^{13}C NMR spectrum of the diol derivative **4**

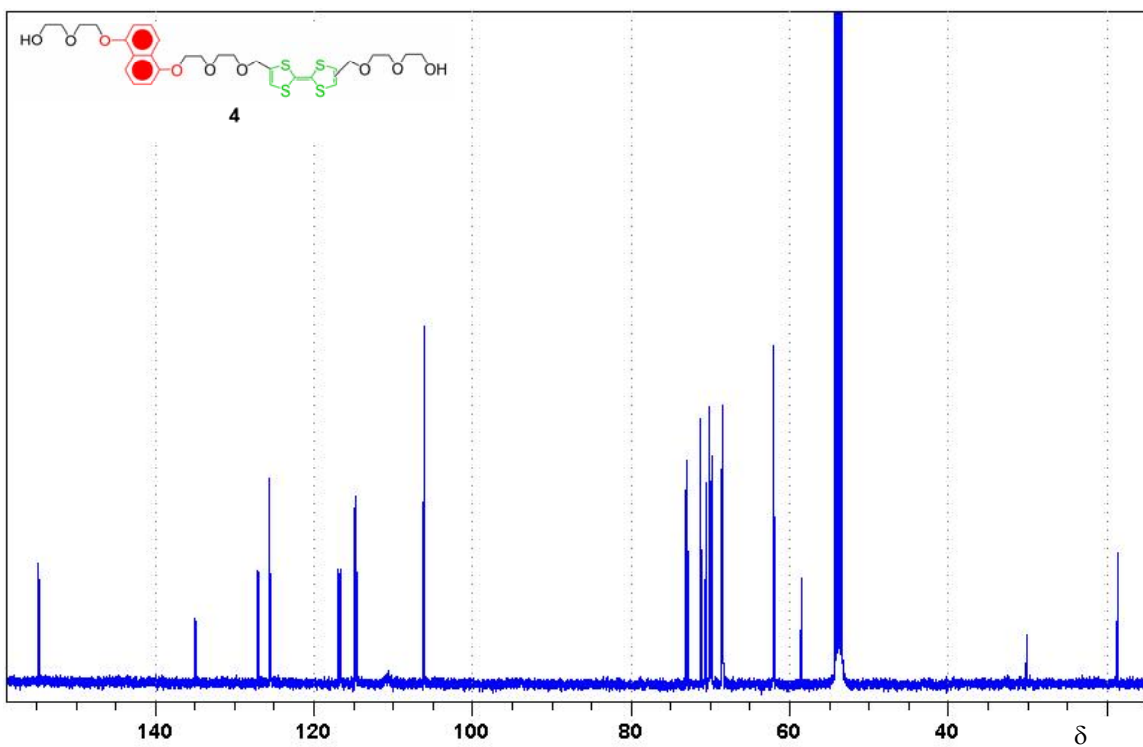


Figure 3. ^1H NMR spectrum of the ditosyl derivative **S1**

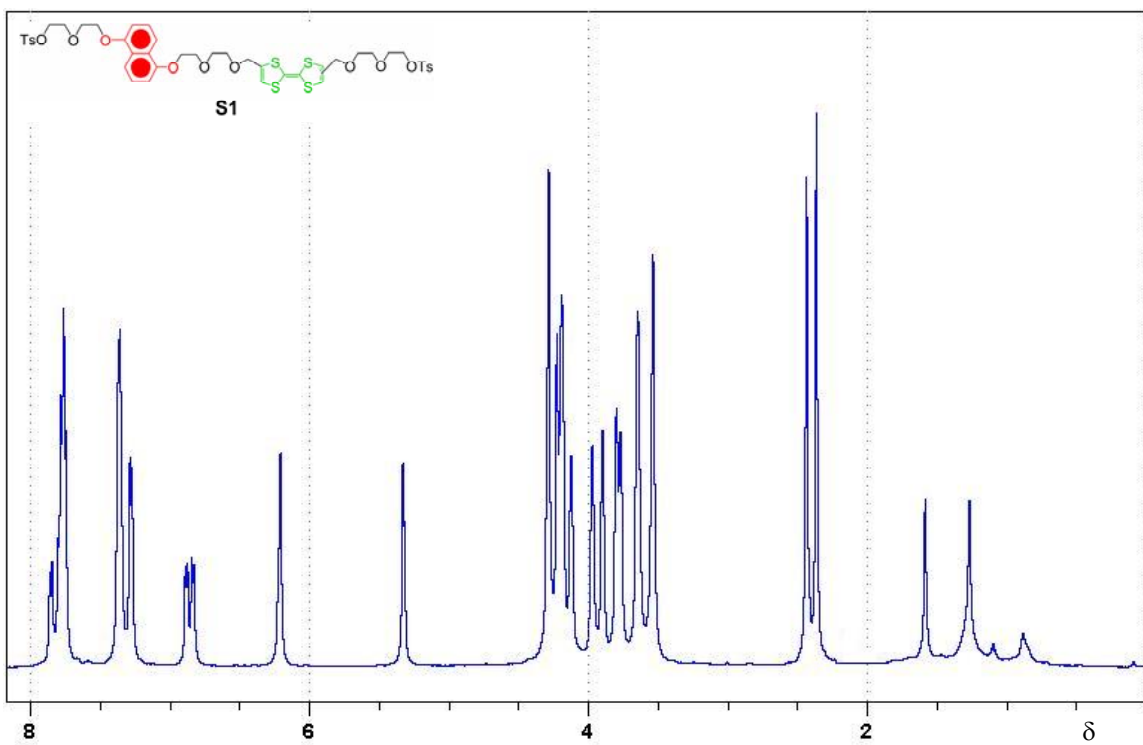


Figure 4. ^{13}C NMR spectrum of the diol derivative **S1**

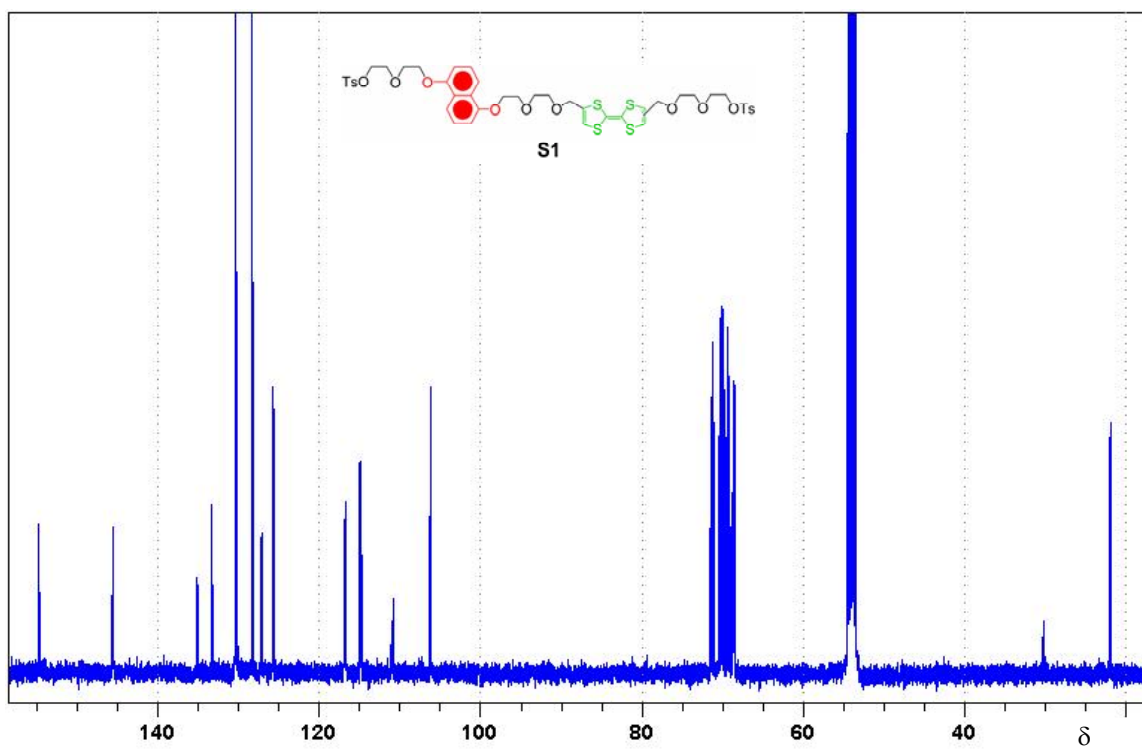


Figure 5. ^1H NMR spectrum of the ditosyl derivative **5**

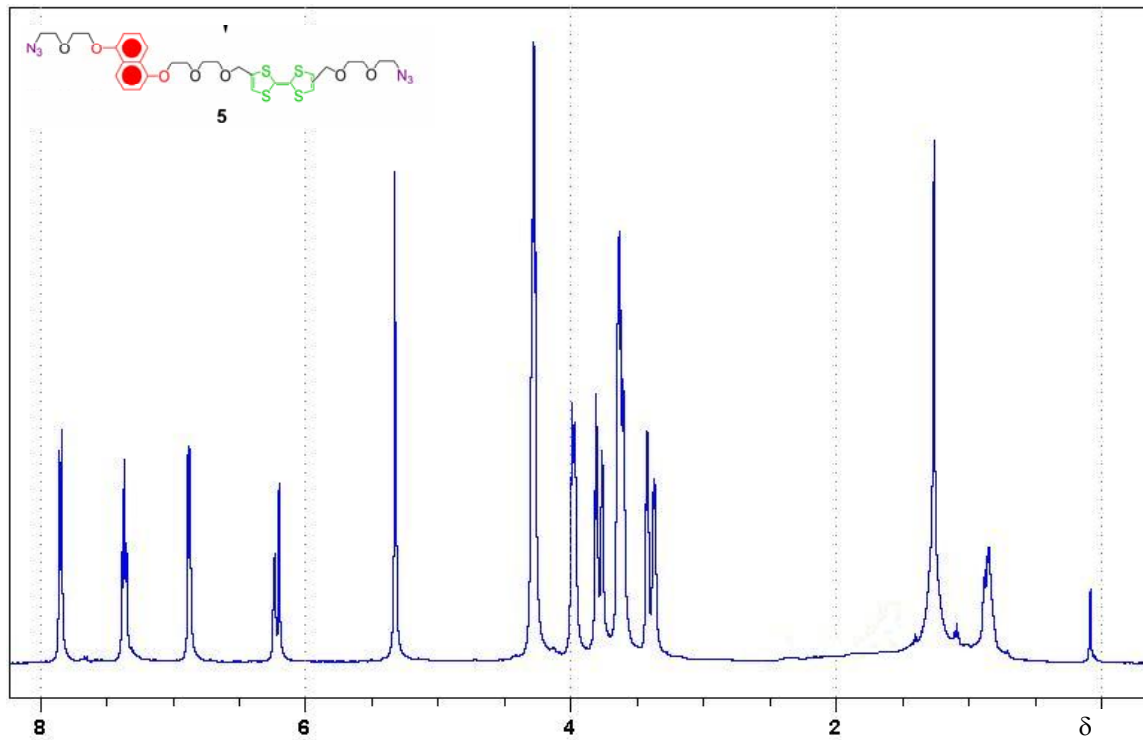


Figure 6. ^{13}C NMR spectrum of the ditosyl derivative **5**

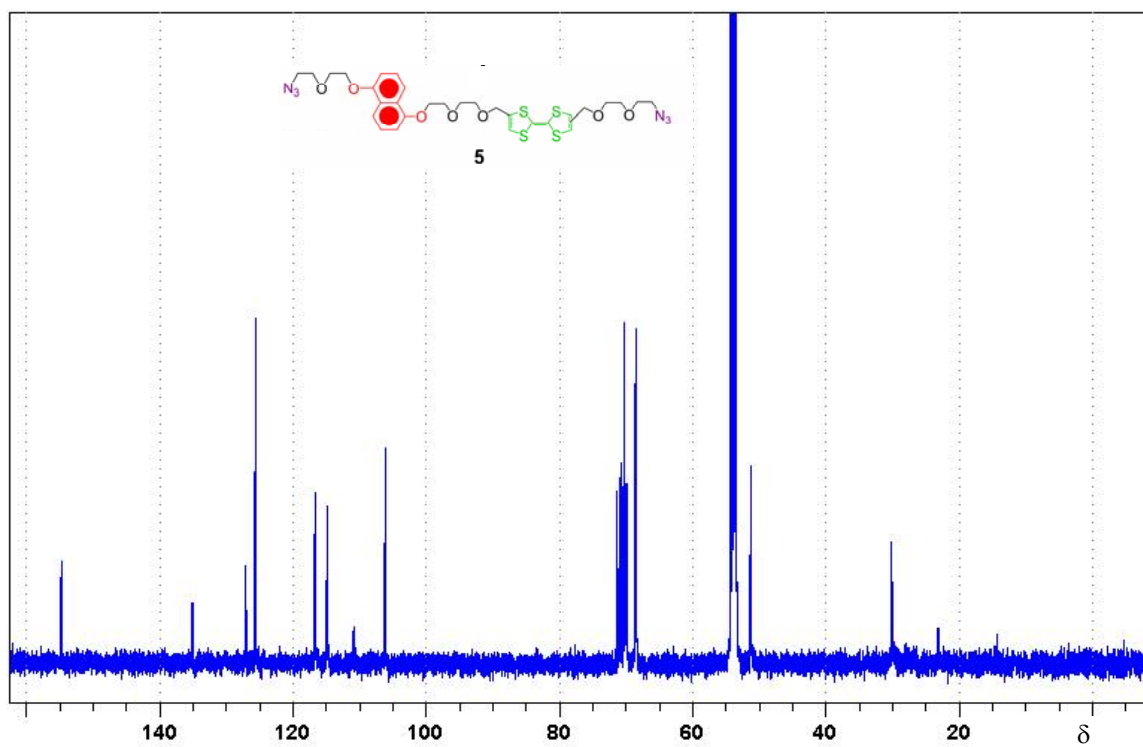


Figure 7. ^1H NMR spectrum of the rotaxane $1\cdot 4\text{PF}_6$

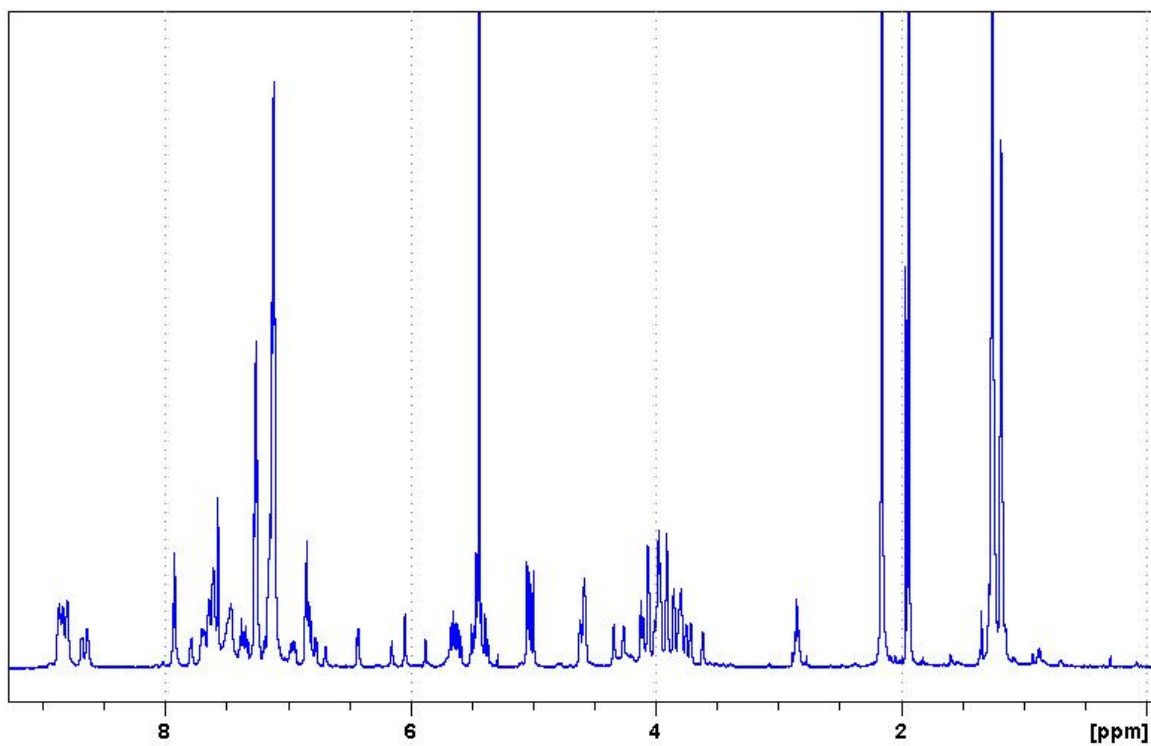


Figure 8. COSY spectrum of the rotaxane $1\cdot 4\text{PF}_6$

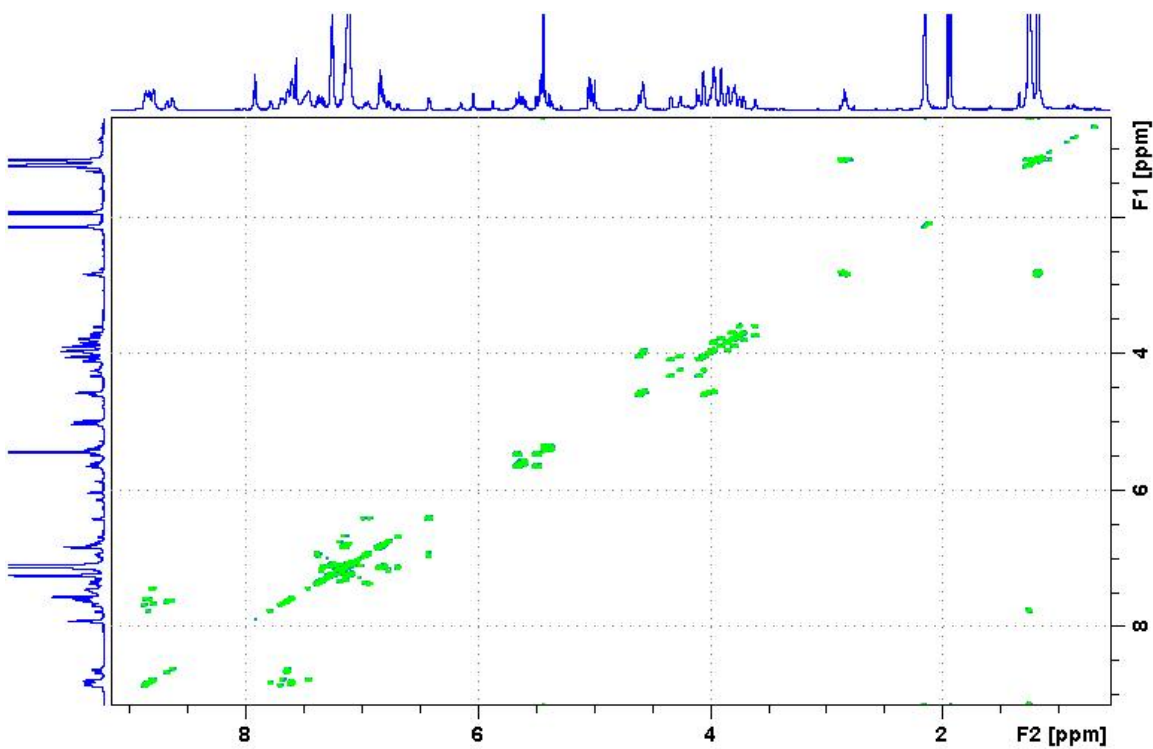
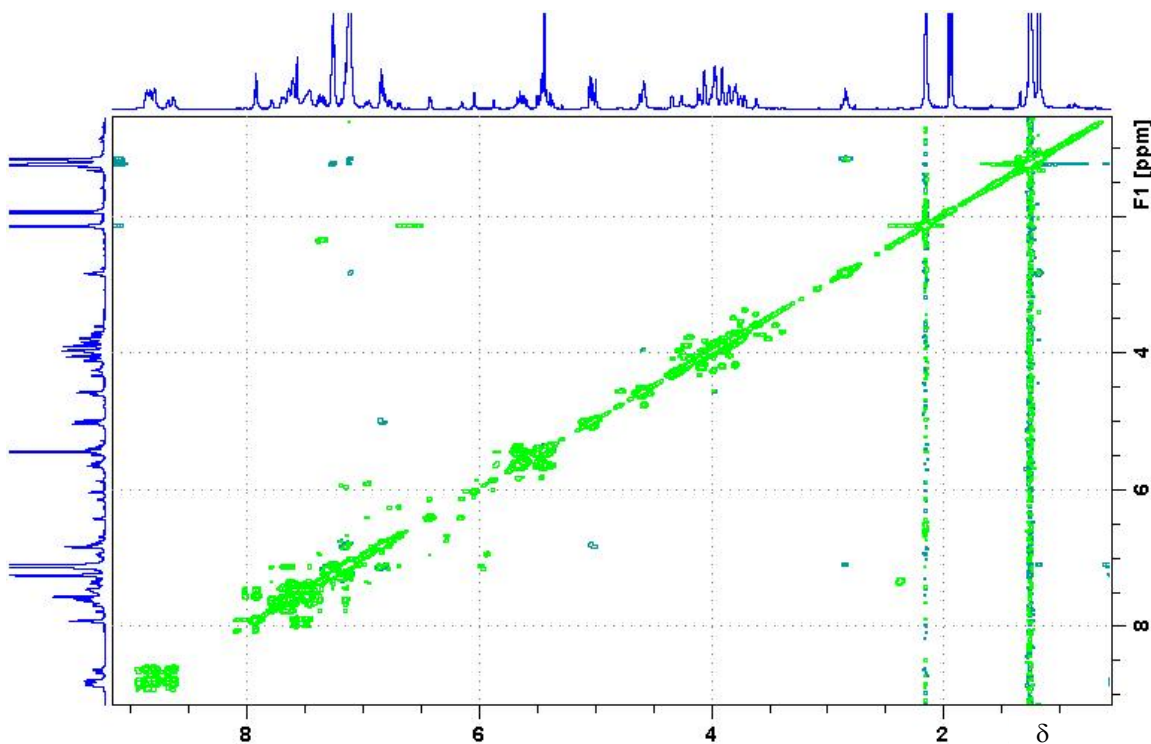


Figure 9. NOESY spectrum of the rotaxane **1**·4PF₆



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- (S4) Dichtel, W. R.; Miljanić, O. Š.; Spruell, J. M.; Heath, J. R.; Stoddart, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 10388–10390.
- (S5) Some of the signals in the ¹³C NMR spectrum are duplicated because of the *cis/trans* isomerism.