Supporting Information

Mechanical Insulation of Aza-Pechmann Dyes within [2]Rotaxanes

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1. General information

HPLC grade solvents (Scharlab) were nitrogen saturated, dried and deoxygenated by using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System. Column chromatography was carried out by using silica gel (60 Å, 70-200 μm, SDS) as stationary phase, and TLC was performed on precoated silica gel on aluminum cards (0.25 mm thick, with fluorescent indicator 254 nm) and observed under UV light. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected.

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 or 600 MHz instruments. ^{1}H NMR chemical shifts are reported relative to Me_4Si and were referenced via residual proton resonances of the corresponding deuterated solvent whereas ^{13}C NMR spectra are reported relative to Me_4Si by using the carbon signals of the deuterated solvent. Signals in the ^{1}H and ^{13}C NMR spectra of the synthesized compounds were assigned with the aid of DEPT-135, COSY, NOESY, HSQC or HMBC experiments whenever was necessary. Abbreviations of coupling patterns are as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet.

NMR diffusion measurements were performed on a 600 MHz Bruker AVANCE spectrometer. The values reported are the average of three different measurements (Δ = 50, 150 and 400 ms), which yielded *D*-values within max. ± 2.0% of the reported one. All the measurements were carried out using the ^{1}H resonances. The gradient length was set in the range of 1.3 and 3.7 ms. For all the experiments the number of scans was 32 and the experimental time was ca. 90 min. All the observed data leading to the reported *D*-values afforded lines whose correlation coefficients were above 0.9999.

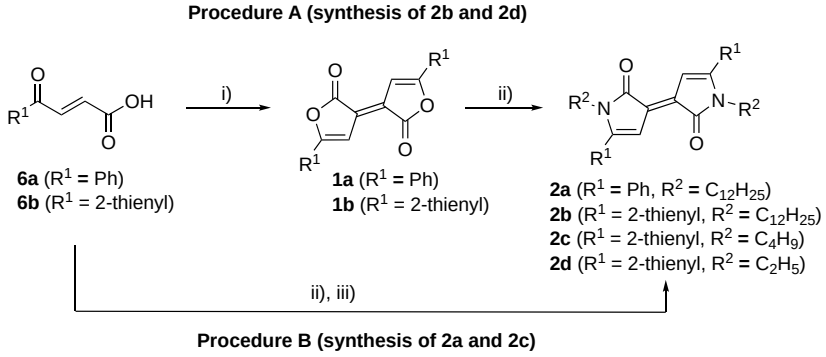
The hydrodynamic radius (r_H) was calculated from the *D* value by using the Stokes–Einstein equation. The Stokes–Einstein equation: $D = (k_B T)/(6\pi\eta r_H)$, where *D* = diffusion coefficient, k_B= Boltzman constant, *T*= temperature in degrees Kelvin, η = viscosity of $CDCl_3$ at 273 K,[1] and r_H = hydrodynamic radius (the radius of a hypothetical sphere that diffuses with the same speed as the particle under examination).[2]

NMR line shape analysis was performed with the iNMR 6.3.3 software.

High-resolution mass spectra (HRMS) were obtained using a time-of-flight (TOF) instrument equipped with electrospray ionization (ESI). IR spectra were recorded on a Jasco FT/IR-4700 or Perkin Elmer Spectrum 65 FT-IR spectrometers with an ATR unit. UV-Vis spectra were recorded on a Perkin Elmer Lambda 35 UV/Vis spectrophotometer.

2. Synthesis and experimental data of aza-Pechmann dyes 2a-d

The synthesis of aza-Pechmann derived lactams **2** was carried out from the previously described carboxylic acids **6**[3, 4] following two alternative procedures. **Procedure A** (synthesis of **2b** and **2d**) consists of two steps. First, carboxylic acid **6b** was reacted with copper(I) chloride and ammonium chloride in acetic anhydride under reflux to give Pechmann dye **1b**. After purification by column chromatography, dilactone **1b** was treated with dodecylamine or ethylamine in acetic acid under reflux to give dilactams **2b** or **2d**. Alternatively, dilactams **2a** and **2c** were obtained by **Procedure B**. In this case, dilactones **1a** or **1b** were used without further purification in the next step, and further reacted with dodecylamine or butylamine.



i) CuCl, NH_4Cl, Ac_2O, reflux, 2 h; ii) R^2NH_2, AcOH, reflux, 2 h.

ii)

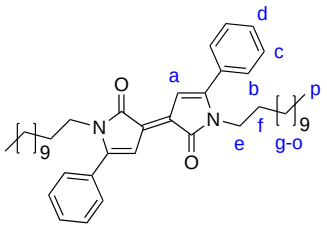
Scheme S1. Threads **2a-d** were prepared from the corresponding carboxylic acids **6a,b** following **procedures A** or **B**.

Synthesis of 6a,b

The synthesis of (*E*)-4-oxo-4-phenylbut-2-enoic and (*E*)-4-oxo-4-(thiophen-2-yl)but-2-enoic acids **6a,b** is very well-documented by the Friedel-Crafts acylation of benzene and thiophene with maleic anhydride.[3, 4]

Synthesis of aza-Pechman dyes 2a-d

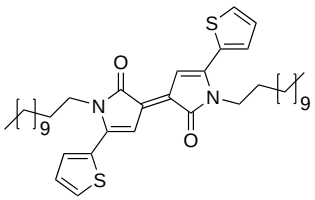
Aza-Pechmann dye 2a



To a mixture of carboxylic acid **6a** (10.0 g, 56.8 mmol), CuCl (2.0 g, 20.2 mmol) and NH_4Cl (2.2 g, 41.1 mmol), under a nitrogen-gas atmosphere, acetic anhydride was added (50 mL). The reaction was stirred for 2 hours under reflux. After cooling, the reaction mixture was filtered, washed with water (200 mL), ethanol (50 mL), and ether (50 mL) to obtain 6.2 g of crude product. The crude product was used without further purification in the next step.

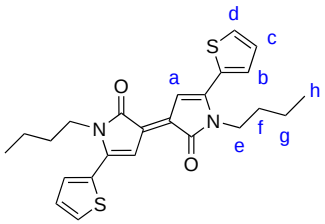
Acetic acid (19 mL) was added to a mixture of dodecylamine (2.3 g, 12.4 mmol) and 1.0 g of crude product (obtained in the previous step) and stirred under reflux for 2 h. After removal of the solvent under reduced pressure, CH_2Cl_2 (200 mL) was added and the resulting suspension was filtered through a Celite pad and subsequently washed with water (200 mL), a saturated aqueous solution of $NaHCO_3$ (200 mL) and brine (200 mL). It was then dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude product purified by silica-gel column chromatography eluting with 2:1 $CHCl_3$/hexane as eluent, to give **2a** (0.70 g; 23%); m.p. 107-109 ºC (violet prisms); IR (solid, ATR, cm^{-1}) ν = 2913 (s), 2849 (s), 1677 (vs, CO), 1471 (m), 1253 (m), 1141 (m), 760 (s), 747 (s), 701 (s); ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.52 – 7.44 (m, 10H, H_{Ar}), 6.89 (s, 2H, H_a), 3.69-3.65 (m, 4H, H_e), 1.47 – 1.40 (m, 4H, H_f), 1.31 – 1.15 (m, 36H, $H_{g\text{-}o}$), 0.87 (t, *J* = 6.9 Hz, 6H, H_p); ^{13}C RMN (100 MHz, $CDCl_3$, 298 K) 171.5 (CO), 152.9 (C), 131.6 (C), 129.9 (CH), 129.2 (C), 128.9 (CH), 127.7 (CH), 103.3 (CH), 41.1 (CH_2), 32.1 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.53 (CH_2), 29.48 (CH_2), 29.2 (CH_2), 26.7 (CH_2), 22.8 (CH_2), 14.3 (CH_3); HRMS (ESI) calcd for $C_{44}H_{63}N_2O_2$ $[M + H]^+$ 651.4884, found 651.4894.

Aza-Pechmann dye 2b



Compound **2b** was synthesized according to **procedure A**. A solution of dilactone **1b**[5] (1.09 g, 3.32 mmol) and *n*-dodecylamine (2.46 g, 13.27 mmol) in AcOH (20 mL) was stirred under reflux for 2 h. Subsequently, the excess of acetic acid was removed under reduced pressure. The resulting residue was redissolved in 200 mL of CH_2Cl_2 and sequentially washed with H_2O (200 mL), a saturated aqueous solution of $NaHCO_3$ (200 mL) and brine (200 mL). Finally, the crude product was purified by silica-gel column chromatography eluting with 3:1 $CHCl_3$/hexane, yielding the violet-coloured product **2b** (1.87 g; 85%). The product exhibited identical spectroscopic data to those reported.[5]

Aza-Pechmann dye 2c

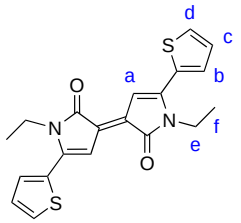


To a mixture of carboxylic acid **6b** (16.7 g, 91.7 mmol), CuCl (3.3 g, 33.3 mmol) and NH_4Cl (3.6 g, 67.3 mmol) under a nitrogen-gas atmosphere, acetic anhydride was added (85 mL). The reaction was stirred for 2 hours under reflux. After cooling, the reaction mixture was filtered, washed with water (200 mL), ethanol (50 mL), and ether (50 mL) to obtain 12.91 g of crude product. The crude product was used without further purification in the next step.

Acetic acid (220 mL) was added to a mixture of butylamine (9.7 g, 132.9 mmol, 13.1 mL) and 10.91 g of crude product (obtained from the previous step) and stirred under reflux for 2 h. After removal of the solvent under reduced pressure, CH_2Cl_2 (500 mL) was added and the resulting suspension was filtered through a Celite pad and subsequently washed with water (400 mL), a saturated aqueous solution of $NaHCO_3$ (400 mL), and brine (400 mL). It was then dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude product purified by silica-gel column chromatography eluting with 10:1 $CHCl_3$/hexane, to give **2c** (1.16 g; 7%) m.p. 162-165 ºC (violet prisms); IR (solid, ATR, cm^{-1}) ν = 2927 (w), 1667 (s, CO), 1489 (m), 1444 (m), 1270 (m), 1135 (m),

791 (s), 703 (s), 693 (s); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.47 (dd, *J* = 5.1, 1.0 Hz, 2H, H_d), 7.43 (dd, *J* = 3.8, 1.0 Hz, 2H, H_b), 7.14 (dd, *J* = 5.1, 3.8 Hz, 2H, H_c), 7.09 (s, 2H, H_a), 3.89-3.85 (m, 4H, H_e), 1.63 – 1.56 (m, 4H, H_f), 1.39-1.30 (m, 4H, H_g), 0.91 (t, *J* = 7.4 Hz, 6H, H_h); ^{13}C RMN (100 MHz, $CDCl_3$, 298 K) δ 170.9 (CO), 145.1 (C), 133.3 (C), 128.6 (CH), 128.4 (CH), 128.0 (C), 127.9 (CH), 103.1 (CH), 41.0 (CH_2), 31.9 (CH_2), 20.2 (CH_2), 13.9 (CH_3); HRMS (ESI) calcd for $C_{24}H_{27}N_2O_2S_2$ $[M + H]^+$ 439.1509, found 439.1513.

Aza-Pechmann dye 2d

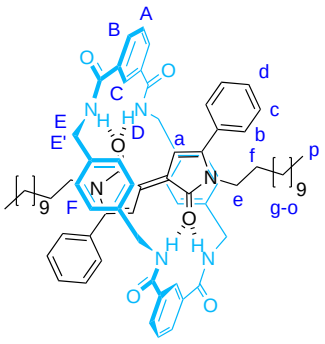


Compound **2d** was synthesized following the described **procedure A**. A solution of dilactone **1b**[5] (0.20 g, 0.61 mmol) and ethylamine (70% in water, 2.44 mmol, 0.20 mL) in AcOH (4 mL) was stirred under reflux during 2 h. Subsequently, the excess of acetic acid was removed under reduced pressure. The resulting residue was redissolved in 100 mL of CH_2Cl_2 and sequentially washed successively with H_2O (100 mL), a saturated aqueous solution of $NaHCO_3$ (100 mL) and brine (100 mL). Finally, the crude product was purified by silica-gel column chromatography by eluting with 1:1 $CHCl_3$/hexane to 100:1 $CHCl_3$/Acetone to give **2d** (0.1917 g; 82%). m.p. 235-237 ºC (violet prisms); IR (solid, ATR, cm^{-1}) ν = 1670 (s, CO), 1486 (m), 1282 (m), 1142 (m), 952 (m), 841 (m), 757 (s), 719 (s), 674 (m); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.48 (dd, *J* = 5.1, 1.0 Hz, 2H, H_d), 7.44 (dd, *J* = 3.8, 1.0 Hz, 2H, H_b), 7.15 (dd, *J* = 5.1, 3.8 Hz, 2H, H_c), 7.09 (s, 2H, H_a), 3.93 (q, *J* = 7.1 Hz, 4H, H_e), 1.25 (t, *J* = 7.1 Hz, 3H, H_f); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 170.7 (CO), 144.9 (C), 133.2 (C), 128.6 (CH), 128.5 (CH), 128.1 (C), 127.9 (CH), 103.1 (CH), 36.1 (CH_2), 15.06 (CH_3); HRMS (ESI) calcd for $C_{20}H_{19}N_2O_2S_2$ $[M + H]^+$ 383.0883, found 383.0891.

3. Synthesis and experimental data of [2]rotaxanes 3a-i

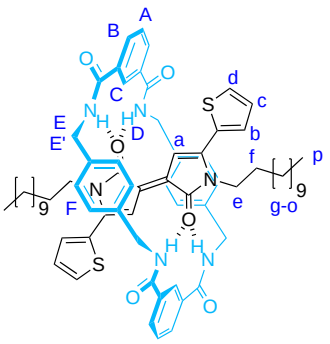
A solution of the corresponding dye **2** (1 eq) and Et_3N (12 eq) in $CHCl_3$ (300 mL/mmol of thread) was stirred vigorously whilst two solutions of i) *p*-xylylene diamine (8 eq) and Et_3N (12 eq) in $CHCl_3$ (20 mL) and ii) the corresponding isophtaloyl chloride (8 eq) in $CHCl_3$ (20 mL) were simultaneously added over a period of 4 h using a motor-driven syringe pump. After 4 h of stirring at room temperature, the resulting suspension was filtered through a Celite pad, and subsequently washed with water (400 mL), an aqueous solution of 1 M HCl (2 x 300 mL), a saturated aqueous solution of $NaHCO_3$ (2 x 300 mL) and brine (200 mL). The organic phase was dried over $MgSO_4$, and the solvent removed under reduced pressure. The resulting solid was purified by silica-gel column chromatography to yield unconsumed dye **2** and the corresponding [2]rotaxane.

Rotaxane 3a



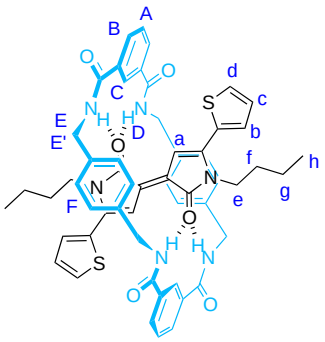
Rotaxane **3a** was obtained from **2a** (0.60 g, 0.92 mmol) by using the general procedure described above. The crude product was purified by silica-gel column chromatography eluting with 19:1 to 9:1 $CHCl_3$/acetone to give the title compound as a blue solid (192 mg; 18%); m.p. 240-242 ºC; IR (solid, ATR, cm^{-1}) ν = 3371 (w, NH), 2921 (m), 2851 (w), 1660 (s, CO), 1645 (s, CO), 1529 (s), 1265 (m), 1076 (m), 759 (m), 724 (m), 696 (m); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.07 (s, 2H, H_C), 8.24 (dd, *J* = 7.8, 1.3 Hz, 4H, H_B), 7.61 (t, *J* = 7.8 Hz, 2H, H_A), 7.54 (d, *J* = 9.0 Hz, 4H, H_D), 7.35 (t, *J* = 7.5 Hz, 2H, H_d), 7.20 (t, *J* = 7.8 Hz, 4H, H_c), 6.86 – 6.84 (m, 12H, H_{F+b}), 6.01 (s, 2H, H_a), 5.15 (dd, *J* = 14.2, 9.0 Hz, 4H, H_E), 3.78 (d, *J* = 14.2 Hz, 4H, $H_{E'}$), 3.67 – 3.63 (m, 4H, H_e), 1.58 – 1.51 (m, 4H, H_f), 1.29 – 1.19 (m, 36H, H_{g-o}), 0.86 (t, *J* = 6.9 Hz, 6H, H_p); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 172.7 (CO), 165.3 (CO), 152.4 (C), 137.2 (C), 133.7 (C), 132.0 (CH), 130.6 (CH), 129.9 (CH), 129.40 (CH), 129.36 (C), 129.1 (CH), 127.5 (C), 126.5 (CH), 123.3 (CH), 102.4 (CH), 43.9 (CH_2), 41.4 (CH_2), 32.0 (CH_2), 29.72 (CH_2), 29.70 (CH_2), 29.65 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 26.8 (CH_2), 22.8 (CH_2), 14.3 (CH_3). HRMS (ESI) calcd for $C_{76}H_{91}N_6O_6$ $[M + H]^+$ 1183.6995, found 1183.7005.

Rotaxane 3b



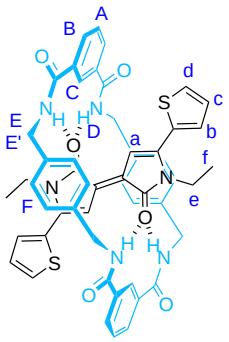
Rotaxane **3b** was obtained from **2b** (1.0 g, 1.51 mmol) by using the general procedure described above. The crude product was purified by silica-gel column chromatography eluting with 19:1 to 9:1 $CHCl_3$/acetone to give the title compound as a blue solid (213 mg; 12%); m.p. 232-234 ºC; IR (solid, ATR, cm^{-1}) ν = 3353 (w, NH), 3326 (w, NH), 2919 (w), 2851 (w), 1655 (s, CO), 1643 (s, CO), 1284 (m), 1254 (m), 1143 (m), 822 (m), 724 (s), 695 (m); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.20 (s, 2H, H_C), 8.34 (d, *J* = 7.8 Hz, 4H, H_B), 7.71 (t, *J* = 7.8 Hz, 2H, H_A), 7.60 (d, *J* = 8.6 Hz, 4H, H_D), 7.35 (d, *J* = 5.1 Hz, 2H, H_d), 6.92 – 6.90 (m, 2H, H_c), 6.82 (s, 8H, H_F), 6.66 (d, *J* = 3.7 Hz, 2H, H_b), 6.26 (s, 2H, H_a), 5.06 (dd, *J* = 14.1, 8.6 Hz, 4H, H_E), 3.86 – 3.79 (m, 8H, $H_{E'+e}$), 1.74 – 1.64 (m, 4H, H_f), 1.44 – 1.22 (m, 36H, H_{g-o}), 0.86 (t, *J* = 6.5 Hz, 6H, H_p); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 172.1 (CO), 165.5 (CO), 144.5 (C), 136.9 (C), 134.1 (C), 132.2 (CH), 131.3 (C), 130.2 (CH), 129.8 (CH), 129.2 (CH), 129.0 (CH), 128.4 (CH), 126.2 (C), 123.7 (CH), 101.7 (CH), 44.1 (CH_2), 41.5 (CH_2), 32.0 (CH_2), 30.1 (CH_2), 29.72 (CH_2), 29.67 (CH_2), 29.63 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 26.9 (CH_2), 22.8 (CH_2), 14.2 (CH_3). HRMS (ESI) calcd for $C_{72}H_{87}N_6O_6S_2$ $[M + H]^+$ 1195.6123, found 1195.6138.

Rotaxane 3c



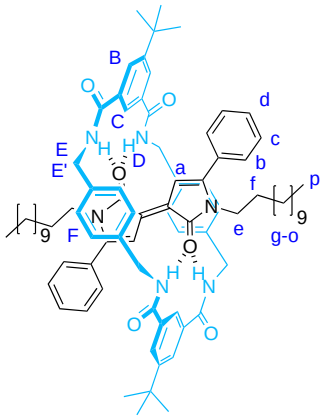
Rotaxane **3c** was obtained from **2c** (0.8 g, 1.82 mmol) by using the general procedure described above. The crude product was purified by silica-gel column chromatography eluting with 20:1 to 5:1 $CHCl_3$/acetone to give the title compound as a blue solid (258 mg; 15%); m.p. > 300 ºC; IR (solid, ATR, cm^{-1}) ν = 3386 (w, NH), 3357 (w, NH), 1657 (s, CO), 1646 (s, CO), 1528 (s), 1285 (m), 1142 (m), 851 (m), 765 (m), 725 (s), 697 (s); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.20 (s, 2H, H_C), 8.34 (dd, *J* = 7.8, 1.5 Hz, 4H, H_B), 7.71 (t, *J* = 7.8 Hz, 2H, H_A), 7.59 (d, *J* = 8.3 Hz, 4H, H_D), 7.36 (dd, *J* = 5.1, 0.9 Hz, 2H, H_d), 6.91 (dd, *J* = 5.1, 3.8 Hz, 2H, H_c), 6.82 (s, 8H, H_F), 6.67 (dd, *J* = 3.8, 0.9 Hz, 2H, H_b), 6.27 (s, 2H, H_a), 5.06 (dd, *J* = 14.1, 8.3 Hz, 4H, H_E), 3.88 – 3.80 (m, 8H, $H_{E'+e}$), 1.71 – 1.63 (m, 4H, H_f), 1.48 – 1.39 (m, 4H, H_g), 1.00 (t, *J* = 7.4 Hz, 6H, H_h); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 172.1 (CO), 165.6 (CO), 144.5 (C), 136.9 (C), 134.1 (C), 132.2 (CH), 131.3 (C), 130.2 (CH), 129.8 (CH), 129.2 (CH), 129.0 (CH), 128.4 (CH), 126.2 (C), 123.7 (CH), 101.8 (CH), 44.1 (CH_2), 41.3 (CH_2), 32.2 (CH_2), 20.2 (CH_2), 13.9 (CH_3). HRMS (ESI) calcd for $C_{56}H_{55}N_6O_6S_2$ $[M + H]^+$ 971.3619, found 971.3627.

Rotaxane 3d



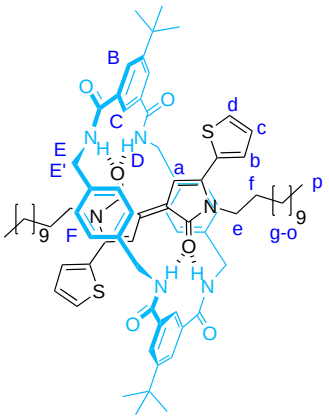
Rotaxane **3d** was obtained from **2d** (552 mg, 1.39 mmol) by using the general procedure described above. The crude product was purified by column chromatography on silica gel eluting with 49:1 to 9:1 $CHCl_3$/acetone to give a mixture (44 mg) of the dye **2d** and the title product (33 mg; 3%) as a blue solid, in a ratio of 25:75 respectively. The sample was contaminated with other unknown impurities. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.20 (s, 2H, H_C), 8.34 (dd, *J* = 7.8, 1.5 Hz, 4H, H_B), 7.71 (t, *J* = 7.8 Hz, 2H, H_A), 7.61 (d, *J* = 8.4 Hz, 4H, H_D), 7.35 (dd, *J* = 5.1, 0.9 Hz, 2H, H_d), 6.94 (dd, *J* = 5.1, 3.8 Hz, 2H, H_c), 6.83 (s, 8H, H_F), 6.74 (dd, *J* = 3.8, 0.9 Hz, 2H, H_b), 6.27 (s, 2H, H_a), 5.06 (dd, *J* = 14.1, 8.4 Hz, 4H, H_E), 3.96 (q, *J* = 6.8 Hz, 4H, H_e), 3.82 (d, *J* = 14.1 Hz, 4H, $H_{E'}$), 1.36 (t, *J* = 6.8 Hz, 6H, H_f); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): 172.0 (CO), 165.6 (CO), 144.3 (C), 136.9 (C), 134.1 (C), 132.2 (CH), 131.3 (C), 130.3 (CH), 129.8 (CH), 129.2 (CH), 129.1 (CH), 128.3 (CH), 126.3 (C), 123.7 (CH), 101.8 (CH), 44.1 (CH_2), 36.4 (CH_2), 15.4 (CH_3).

Rotaxane 3e



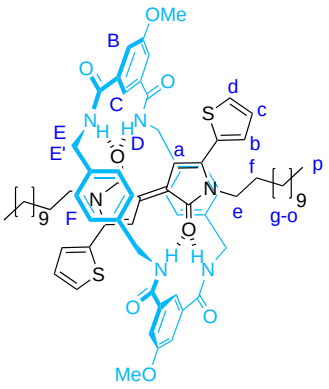
Rotaxane **3e** was obtained from **2a** (0.6 g, 0.92 mmol) by using the general procedure described above. The crude product was purified by column chromatography on silica gel eluting with 49:1 to 19:1 $CHCl_3$/acetone to give the title product as a blue solid (106 mg; 9%); m.p. 215-217 ºC; IR (solid, ATR, cm^{-1}) ν = 3382 (w, NH), 2922 (m), 2851 (m), 1645 (s, CO), 1527 (s), 1248 (s), 1137 (w), 754 (m), 696 (s); ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ 8.95 (s, 2H, H_C), 8.31 (d, *J* = 1.1 Hz, 4H, H_B), 7.50 (d, *J* = 8.7 Hz, 4H, H_D), 7.30 (t, *J* = 7.5 Hz, 2H, H_d), 7.18 (t, *J* = 7.8 Hz, 4H, H_c), 6.93 (d, *J* = 7.2 Hz, 4H, H_b), 6.88 (s, 8H, H_F), 6.13 (s, 2H, H_a), 5.12 (dd, *J* = 14.2, 8.7 Hz, 4H, H_E), 3.81 (d, *J* = 14.2 Hz, 4H, $H_{E'}$), 3.65 – 3.63 (m, 4H, H_e), 1.56 – 1.51 (m, 4H, H_f), 1.42 (s, 18H, ^{t}Bu), 1.27 – 1.18 (m, 36H, $H_{g\text{-}o}$), 0.85 (t, *J* = 7.1 Hz, 6H, H_p); ^{13}C NMR (150 MHz, $CDCl_3$, 298 K) δ 172.5 (CO), 165.7 (CO), 153.2 (C), 152.4 (C), 137.2 (C), 133.2 (C), 130.5 (CH), 129.4 (C), 129.3 (CH), 129.2 (CH), 129.1 (CH), 127.5 (C), 126.7 (CH), 120.7 (CH), 102.4 (CH), 44.0 (CH_2), 41.4 (CH_2), 35.4 (C), 32.0 (CH_2), 31.5 (CH_3), 29.69 (CH_2), 29.67 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.42 (CH_2), 29.40 (CH_2), 29.1 (CH_2), 26.8 (CH_2), 22.8 (CH_2), 14.2 (CH_3). HRMS (ESI) calcd for $C_{84}H_{107}N_6O_6$ $[M + H]^+$ 1295.8247, found 1295.8257.

Rotaxane 3f



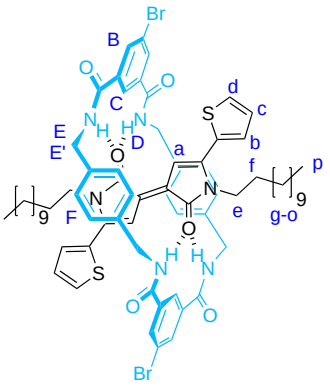
Rotaxane **3f** was obtained from **2b** (1 g, 1.51 mmol) by using the general procedure described above. The crude product was purified by column chromatography on silica gel eluting with 49:1 to 19:1 $CHCl_3$/acetone to give the title product as a blue solid (233 mg; 12%); m.p. 258-260 ºC; IR (solid, ATR, cm^{-1}) ν = 3385 (w, NH), 2923 (m), 2851 (w), 1661 (s, CO), 1645 (s, CO), 1529 (s), 1247 (m), 1141 (m), 697 (m); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.07 (s, 2H, H_C), 8.40 (s, 4H, H_B), 7.57 (d, *J* = 8.6 Hz, 4H, H_D), 7.31 (d, *J* = 5.1 Hz, 2H, H_d), 6.93 – 6.90 (m, 2H, H_c), 6.82 (s, 8H, H_F), 6.79 (d, *J* = 3.7 Hz, 2H, H_b), 6.30 (s, 2H, H_a), 5.06 (dd, *J* = 14.1, 8.6 Hz, 4H, H_E), 3.86 – 3.80 (m, 8H, $H_{E'}$ + H_e), 1.71 – 1.66 (m, 4H, H_f), 1.47 (s, 18H, ^{t}Bu), 1.42-1.22 (m, 36H, $H_{g\text{-}o}$), 0.86 (t, *J* = 6.9 Hz, 6H, H_p); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 172.0 (CO), 166.0 (CO), 153.4 (C), 144.5 (C), 137.0 (C), 133.8 (C), 131.5 (C), 130.1 (CH), 129.3 (CH), 129.2 (CH), 128.9 (CH), 128.2 (CH), 126.3 (C), 121.1 (CH), 101.8 (CH), 44.2 (CH_2), 41.5 (CH_2), 35.5 (C), 32.0 (CH_2), 31.6 (CH_3), 30.1 (CH_2), 29.73 (CH_2), 29.68 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 26.9 (CH_2), 22.8 (CH_2), 14.3 (CH_3). HRMS (ESI) calcd for $C_{80}H_{103}N_6O_6S_2$ $[M + H]^+$ 1307.7375, found 1307.7362.

Rotaxane 3g



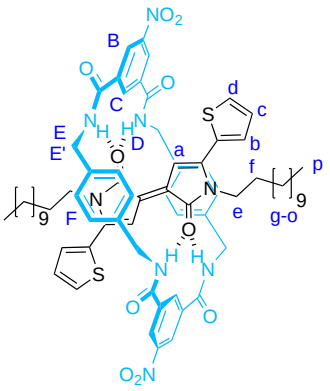
Rotaxane **3g** was obtained from **2b** (0.8 g, 1.21 mmol) by using the general procedure described above. The crude product was purified by column chromatography on silica gel eluting with 49:1 to 9:1 $CHCl_3$/acetone to give the title product as a blue solid (233 mg; 15%); m.p. 233-235 ºC; IR (solid, ATR, cm^{-1}) ν = 3381 (s, NH), 2923 (m), 2850 (w), 1666 (s, CO), 1646 (m, CO), 1524 (s), 1306 (m), 1134 (m), 722 (m); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.77 (s, 2H, H_C), 7.86 (s, 4H, H_B), 7.58 (d, *J* = 8.7 Hz, 4H, H_D), 7.38 (d, *J* = 5.0 Hz, 2H, H_d), 6.91 (dd, *J* = 5.0, 3.9 Hz, 2H, H_c), 6.80 (s, 8H, H_F), 6.57 (d, *J* = 3.9 Hz, 2H, H_b), 6.23 (s, 2H, H_a), 5.08 (dd, *J* = 14.0, 8.7 Hz, 4H, H_E), 3.98 (s, 6H, OMe), 3.86 – 3.82 (m, 4H, H_e), 3.77 (d, *J* = 14.0 Hz, 4H, $H_{E'}$), 1.71 – 1.63 (m, 4H, H_f), 1.45 – 1.23 (m, 36H, $H_{g\text{-}o}$), 0.86 (t, *J* = 6.8 Hz, 6H, H_p); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 172.0 (CO), 165.3 (CO), 161.2 (C), 144.5 (C), 137.0 (C), 135.8 (C), 131.2 (C), 130.1 (CH), 129.2 (CH), 128.8 (CH), 128.6 (CH), 126.2 (C), 117.6 (CH), 116.0 (CH), 101.8 (CH), 56.0 (CH_3), 44.1 (CH_2), 41.5 (CH_2), 32.0 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 29.70 (CH_2), 29.65 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 26.9 (CH_2), 22.8 (CH_2), 14.3 (CH_3). HRMS (ESI) calcd for $C_{74}H_{91}N_6O_8S_2$ $[M + H]^+$ 1255.6334, found 1255.6319.

Rotaxane 3h



Rotaxane **3h** was obtained from **2b** (841 mg, 1.27 mmol) by using the general procedure described above. The crude product was purified by column chromatography on silica gel eluting with 49:1 to 19:1 $CHCl_3$/acetone to give the title product as a blue solid (402 mg; 23%); m.p. 226-228 ºC; IR (solid, ATR, cm^{-1}) ν = 3393 (w, NH), 3367 (w, NH), 2922 (m), 2848 (m), 1667 (s, CO), 1644 (s, CO), 1525 (s), 1282 (m), 1134 (m), 723 (s), 670 (s); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.09 (s, 2H, H_C), 8.46 (d, *J* = 1.1 Hz, 4H, H_B), 7.54 (d, *J* = 8.6 Hz, 4H, H_D), 7.45 (dd, *J* = 5.1, 0.9 Hz, 2H, H_d), 7.04 (dd, *J* = 5.1, 3.8 Hz, 2H, H_c), 6.80 (s, 8H, H_F), 6.68 (dd, *J* = 3.8, 0.9 Hz, 2H, H_b), 6.11 (s, 2H, H_a), 5.07 (dd, *J* = 13.7, 8.6 Hz, 4H, H_E), 3.86 – 3.82 (m, 4H, H_e), 3.78 (d, *J* = 13.7 Hz, 4H, $H_{E'}$), 1.71 – 1.62 (m, 4H, H_f), 1.44 – 1.23 (m, 36H, $H_{g\text{-}o}$), 0.86 (t, *J* = 6.9 Hz, 6H, H_p); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 172.1 (CO), 164.1 (CO), 144.7 (C), 136.9 (C), 136.0 (C), 135.2 (CH), 131.1 (C), 130.5 (CH), 129.2 (CH), 129.1 (CH), 128.4 (CH), 126.2 (C), 124.5 (C), 122.2 (CH), 101.6 (CH), 44.1 (CH_2), 41.6 (CH_2), 32.0 (CH_2), 30.1 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 26.9 (CH_2), 22.8 (CH_2), 14.3 (CH_3). HRMS (ESI) calcd for $C_{72}H_{85}Br_2N_6O_6S_2$ $[M + H]^+$ 1351.4333, found 1351.4340.

Rotaxane 3i



Rotaxane **3i** was obtained from thread **2b** (584 mg, 0.88 mmol) by using the general procedure described above. The crude product was purified by column chromatography on silica gel eluting with 49:1 to 19:1 $CHCl_3$/acetone to give the title product as a blue solid (114 mg; 10%); m.p. 250-252 ºC; IR (solid, ATR, cm^{-1}) ν = 3398 (w, NH), 3351 (w, NH), 2915 (w), 2850 (w), 1671 (m, CO), 1656 (m, CO), 1632 (m), 1519 (s), 1288 (m), 721 (s); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.44 (s, 2H, H_C), 9.12 (d, *J* = 1.3 Hz, 4H, H_B), 7.60 (d, *J* = 9.2 Hz, 4H, H_D), 7.39 (dd, *J* = 5.1, 0.9 Hz, 2H, H_d), 7.00 (dd, *J* = 5.1, 3.8 Hz, 2H, H_c), 6.89 (dd, *J* = 3.8, 0.9 Hz, 2H, H_b), 6.85 (s, 8H, H_F), 6.10 (s, 2H, H_a), 5.07 (dd, *J* = 13.7, 9.2 Hz, 4H, H_E), 3.88 (d, *J* = 13.7 Hz, 4H, $H_{E'}$), 3.84-3.80 (m, 4H, H_e), 1.70 – 1.62 (m, 4H, H_f), 1.42 – 1.22 (m, 36H, $H_{g\text{-}o}$), 0.86 (t, *J* = 6.9 Hz, 6H, H_p); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 172.2 (CO), 163.3 (CO), 149.9 (C), 144.8 (C), 136.7 (C), 136.1 (C), 131.1 (C), 130.7 (CH), 129.4 (CH), 129.3 (CH), 128.5 (CH), 128.3 (CH), 126.9 (CH), 126.4 (C), 101.7 (CH), 44.4 (CH_2), 41.6 (CH_2), 32.0 (CH_2), 30.0 (CH_2), 29.73 (CH_2), 29.68 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 26.9 (CH_2), 22.8 (CH_2), 14.3 (CH_3). HRMS (ESI) calcd for $C_{72}H_{83}N_8O_{10}S_2$ $[M - H]^-$ 1283.5674, found 1283.5693.

4. ESI-HRMS of compounds 2a-d, 3a-c,e-i, 4 and 5

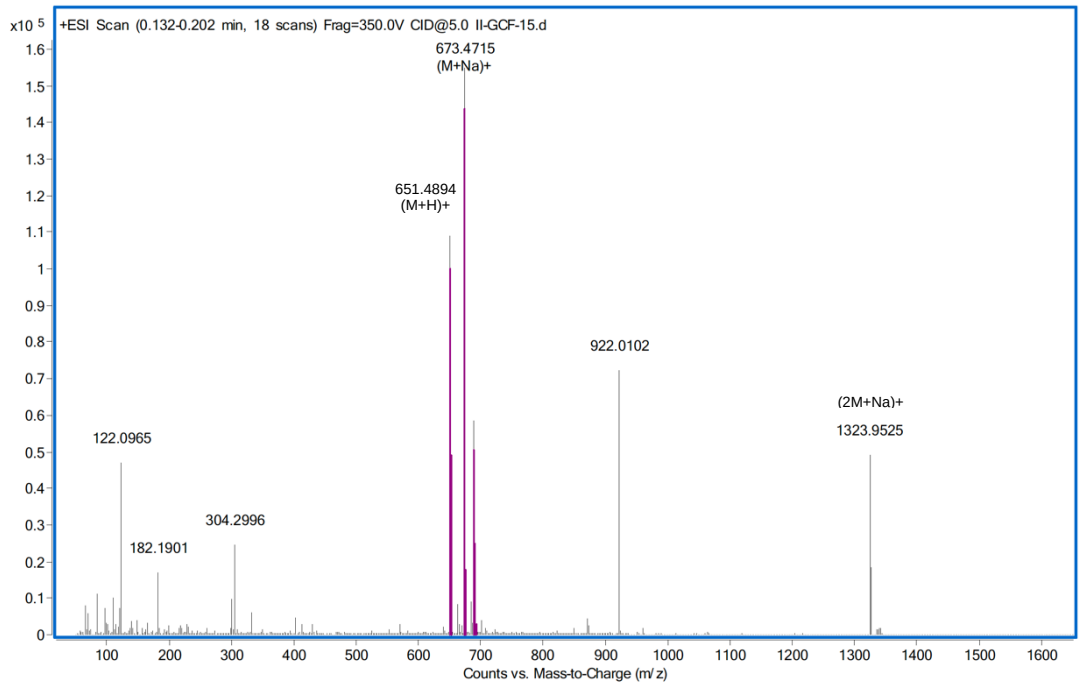


Figure S1. ESI-HRMS of **2a**.

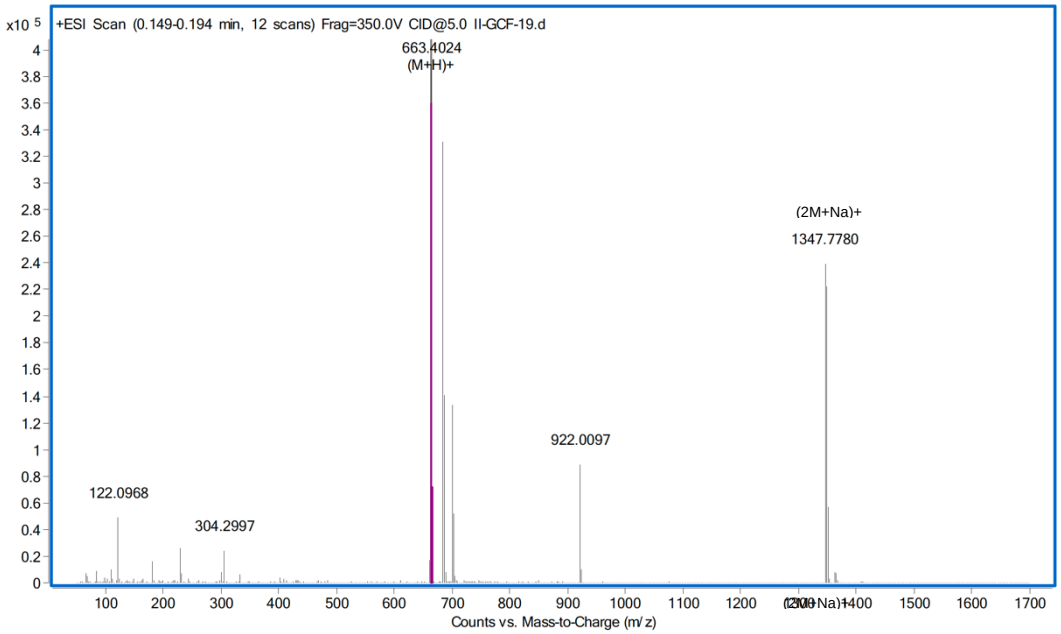


Figure S2. ESI-HRMS of **2b**.

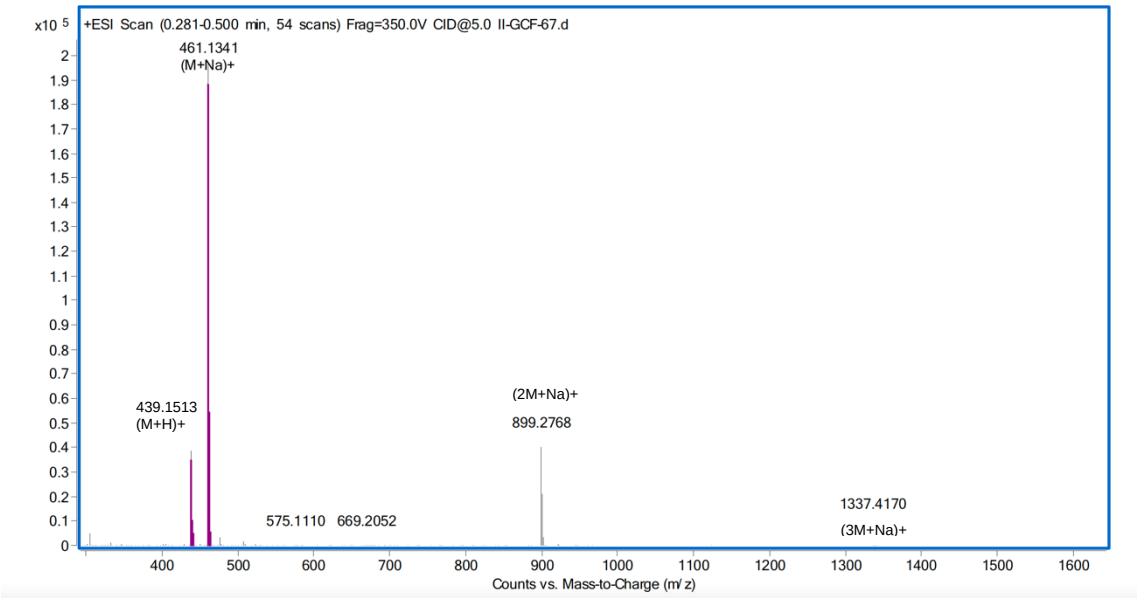


Figure S3. ESI-HRMS of **2c**.

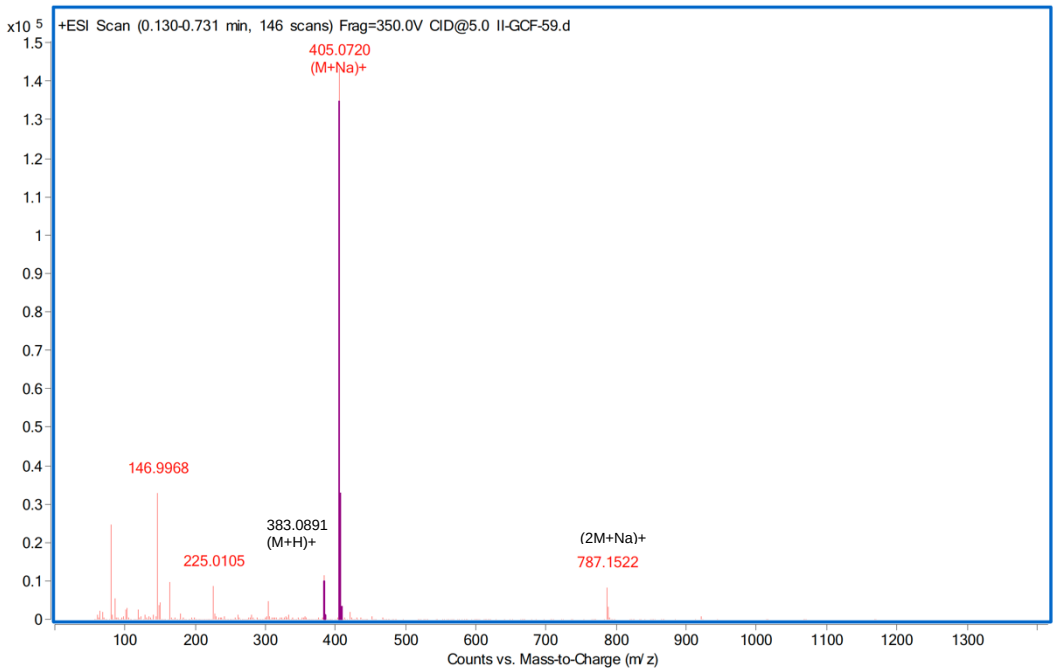


Figure S4. ESI-HRMS of **2d**.

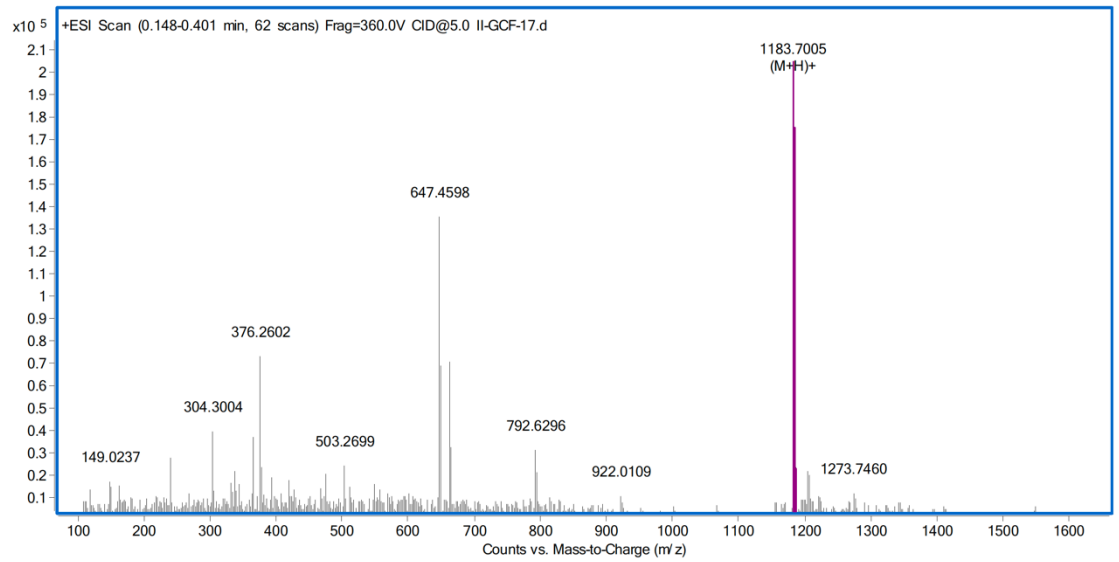


Figure S5. ESI-HRMS of **3a**.

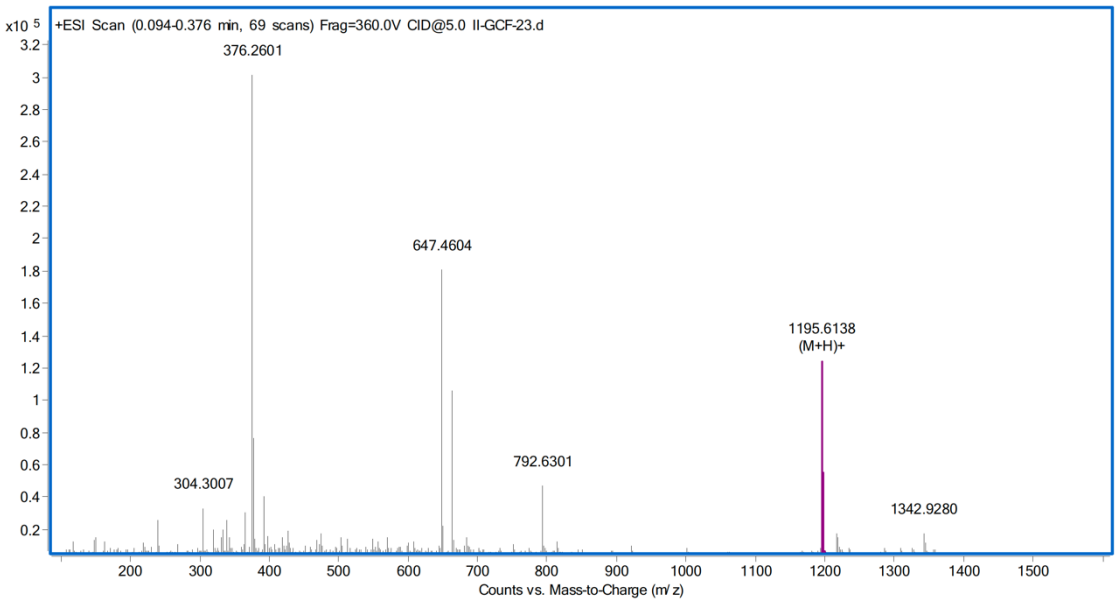


Figure S6. ESI-HRMS of **3b**.

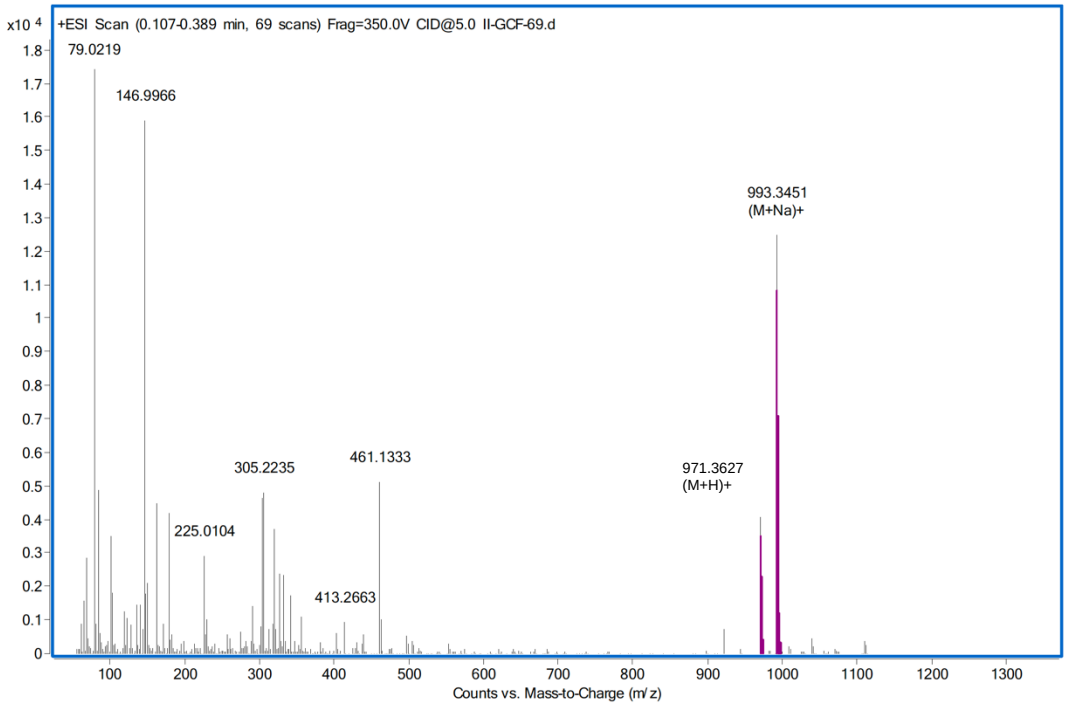


Figure S7. ESI-HRMS of **3c**.

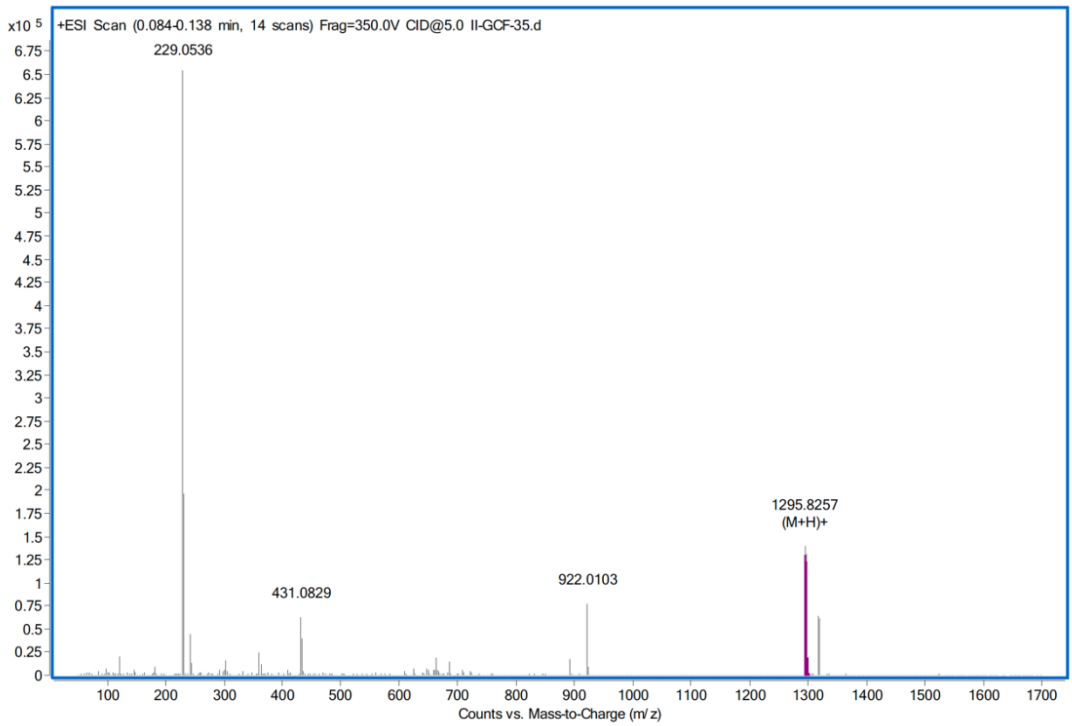


Figure S8. ESI-HRMS of **3e**.

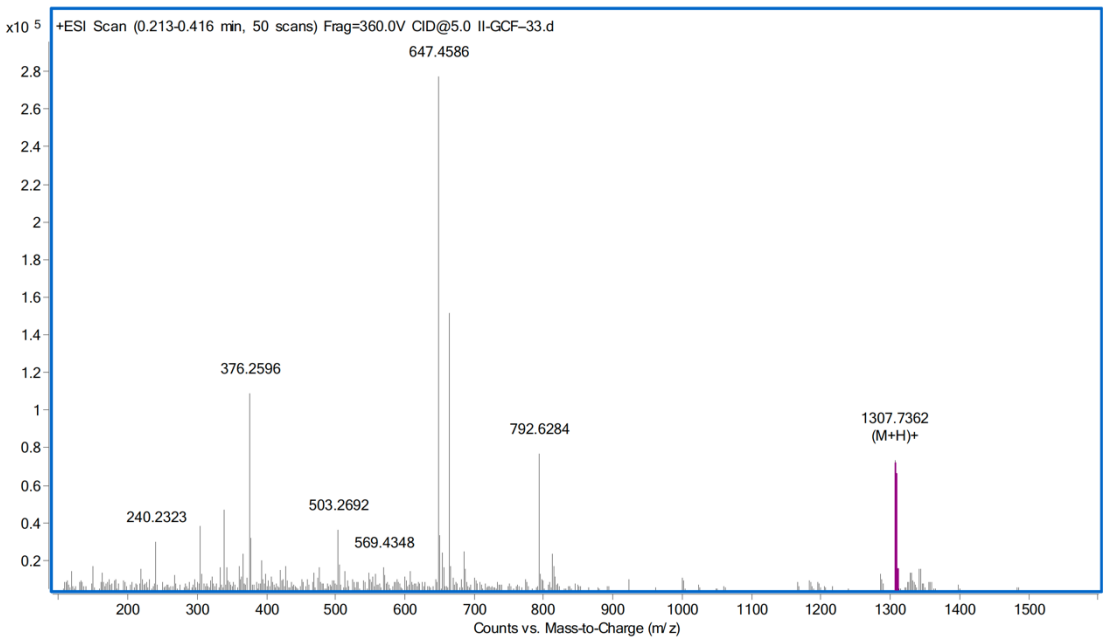


Figure S9. ESI-HRMS of **3f**.

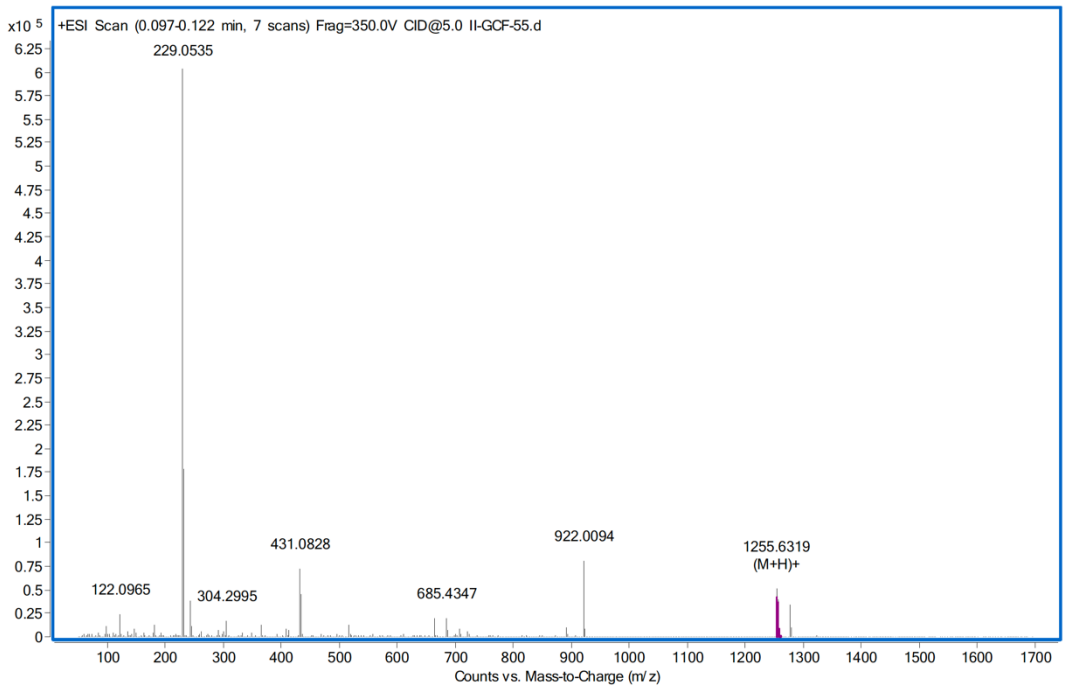


Figure S10. ESI-HRMS of **3g**.

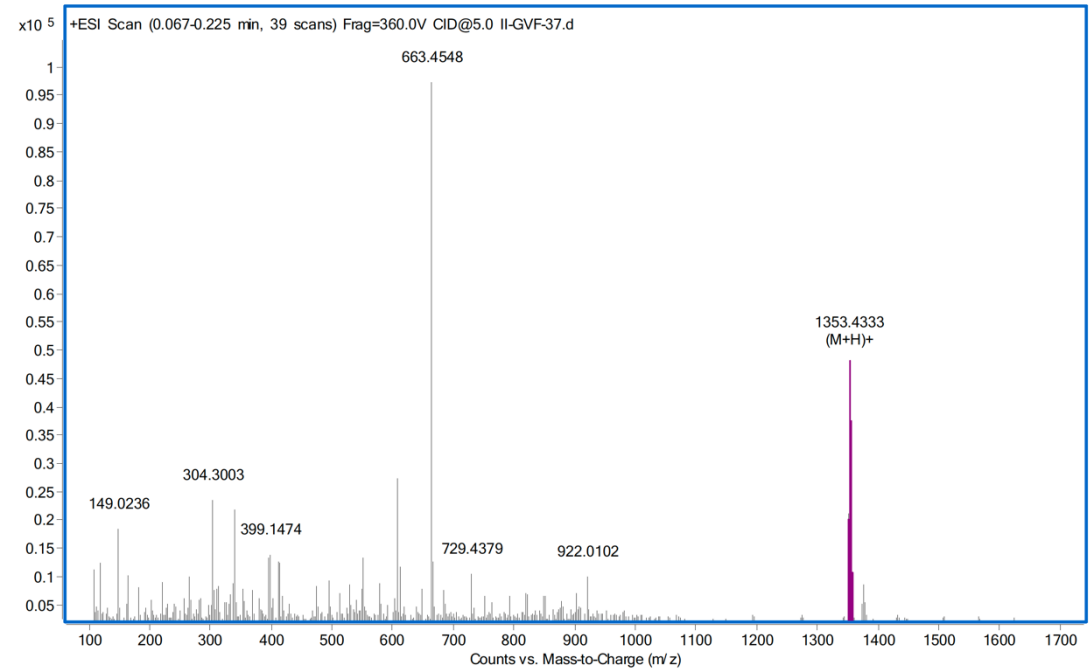


Figure S11. ESI-HRMS of **3h**.

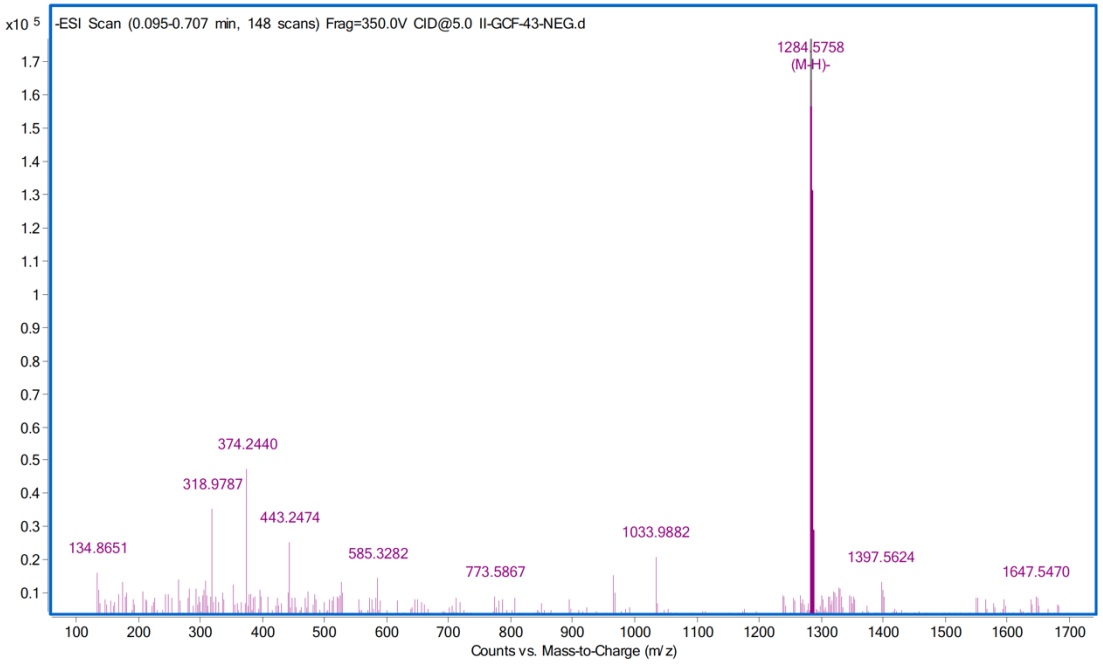


Figure S12. ESI-HRMS of **3i**.

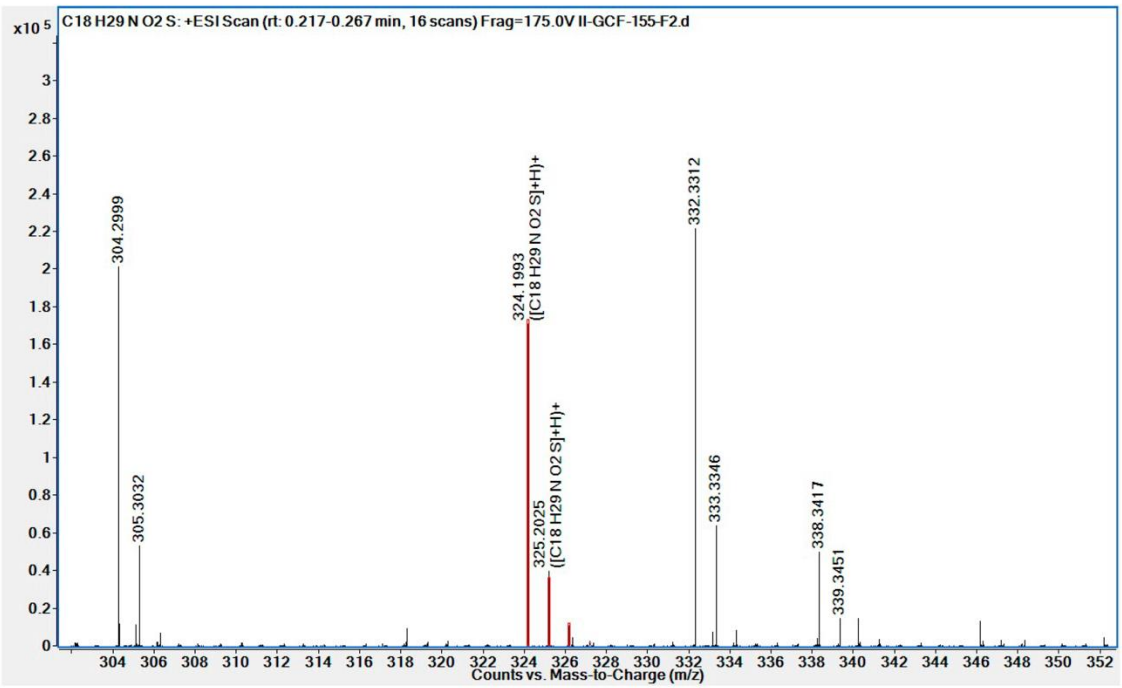


Figure S13. ESI-HRMS of **4**.

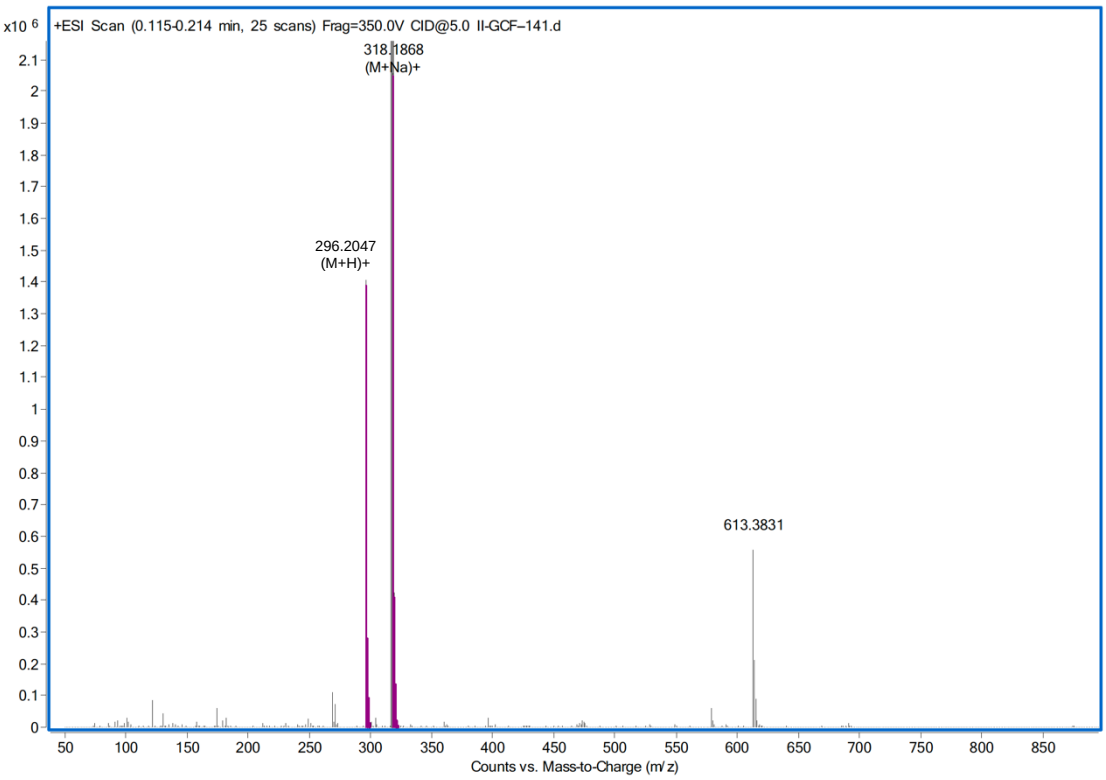


Figure S14. ESI-HRMS of **5**.

5. Crystal data and structure refinement for rotaxanes 3b and 3c

Rotaxane 3b

Single crystals of $C_{72}H_{86}N_6O_6S_2$ [II_GCF_23_0msp] were obtained by slow diffusion of pentane in a solution of $CHCl_3$. Intensities were registered at low temperature (100.0 K) on a Bruker D8 QUEST system equipped with a multilayer monochromator and a Mo K/α Incoatec microfocus sealed tube (λ = 0.71073 Å). Absorption corrections were based on multi-scans (program SADABS). Using Olex2,[6] the structure was solved with the SHELXT[7] structure solution program using Intrinsic Phasing and refined with the SHELXL[8, 9] refinement package using Least Squares minimization. Hydrogen atoms were included using a riding model. The structure was deposited with CSD (deposition number CCDC 2335405).

Table S1. Crystal data and structure refinement for **3b**.

Empirical formula	$C_{76}H_{86}N_6O_6S_2$
Formula weight	1195.58
T [K]	100(2)
Wavelength [Å]	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	14.549(5)
b (Å)	14.378(5)
c (Å)	30.473(10)
α (°)	90
β (°)	99.854(14)
γ (°)	90
V [Å^3]	6281(4)
Z	4
ρ [g·cm^{-3}]	1.264
μ [mm^{-1}]	0.144
F_{000}	2560.0
Crystal size [mm^3]	0.37 x 0.11 x 0.02
2Θ range (º)	3.578 to 56.664
h	-19 to 19
k	-19 to 19
l	-40 to 40
Reflections collected	242329
Independent reflections	15617
R(int)	0.0764
Refinement method	Full-matrix least-squares on F2

Parameters	793
Restraints	215
Goodness-of-fit on F^2	1.177
$R1$ [I > 2σ (I)]	0.0666
$wR2$ [I > 2σ (I)]	0.1650
$R1$ (all data)	0.1174
$wR2$ (all data)	0.2205
Δρ [e·Å^{-3}]	0.69/-0.81

Table S2. Hydrogen bonds for rotaxane **3b** [Å and (°)].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(03)...O(1)	0.88(3)	2.05(3)	2.917(3)	168(3)
N(4)-H(04)...O(1)	0.82(3)	2.41(4)	3.230(3)	174(3)
N(5)-H(05)...O(2)	0.79(3)	2.15(3)	2.935(3)	172(3)
N(6)-H(06)...O(2)	0.88(3)	2.31(3)	3.193(3)	178(3)

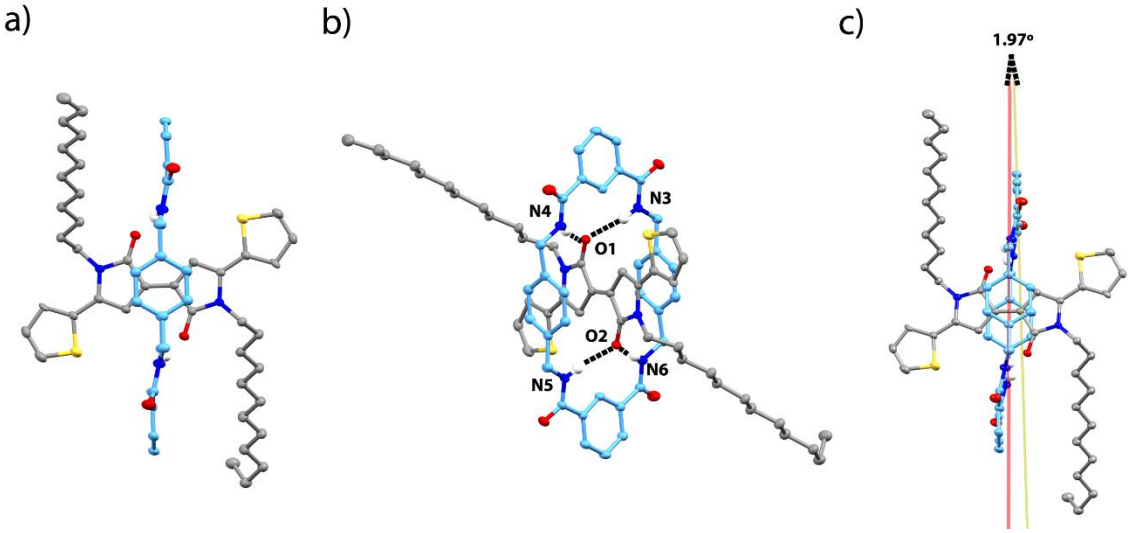


Figure S15. Molecular structure of **3b** with thermal ellipsoids drawn at 50% probability: a) lateral view; b) tilted view; c) lateral view, with intersection (angle) between two calculated planes at the macrocycle (in red: plane between carbons C50, C53, C66 and C69 of the *p*-xylylenediamine walls; in yellow: plane between carbons C42-C47 of the isophthalamide moiety). For clarity, selected hydrogens atoms have been deleted.

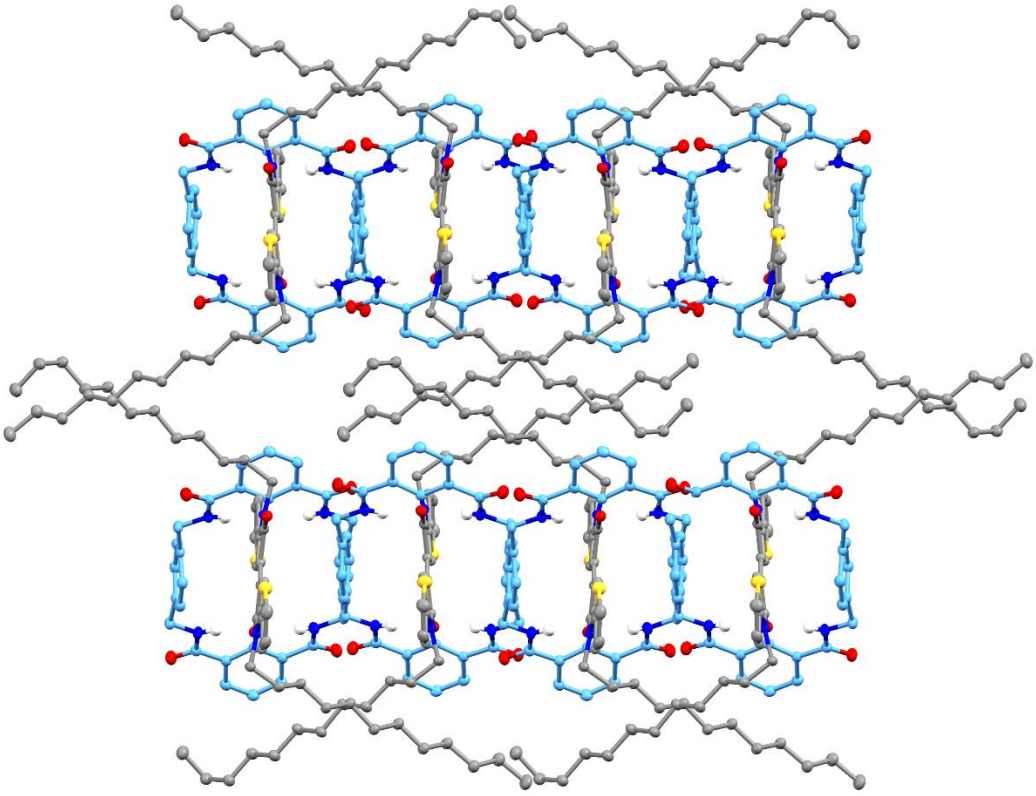


Figure S16. Packing of rotaxane **3b** view along the a-axis. For clarity, selected hydrogens atoms have been deleted.

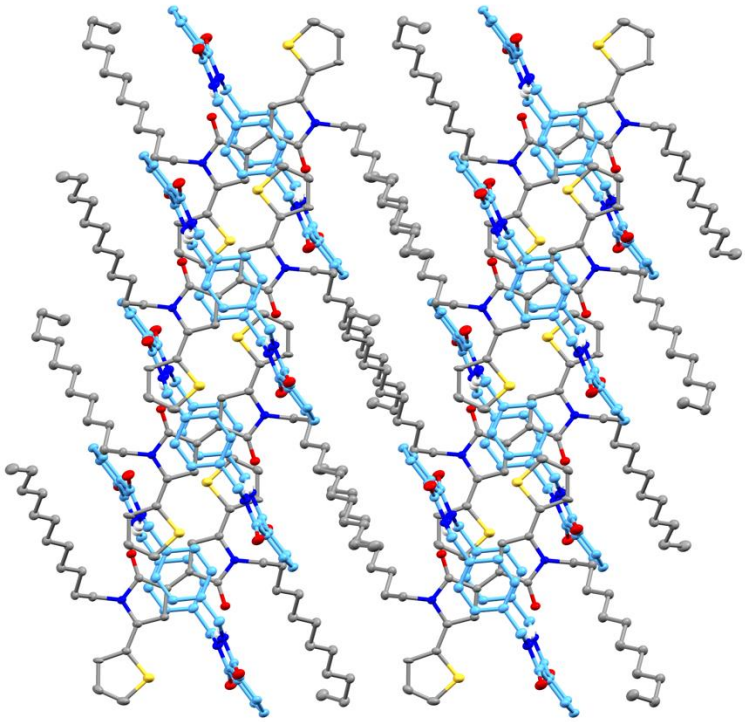


Figure S17. Packing of rotaxane **3b** view along the b-axis. For clarity, selected hydrogens atoms have been deleted.

Rotaxane 3c

Single crystals of $C_{58}H_{56}Cl_6N_6O_6S_2$ [II_GCF_69_pentano_0msp] were obtained by slow diffusion of *n*-pentane in a solution of $CHCl_3$. Intensities were registered at low temperature (100.0 K) on a Bruker D8 QUEST system equipped with a multilayer monochromator and a Mo K/α Incoatec microfocus sealed tube (λ = 0.71073 Å). Absorption corrections were based on multi-scans (program SADABS). Using Olex2,[6] the structure was solved with the SHELXT[7] structure solution program using Intrinsic Phasing and refined with the SHELXL[8, 9] refinement package using Least Squares minimization. Hydrogen atoms were included using a riding model. One molecule of chloroform is included in the unit cell. The structure was deposited with CSD (deposition number CCDC 2335404).

Table S3. Crystal data and structure refinement for **3c**.

Empirical formula	$C_{58}H_{56}Cl_6N_6O_6S_2$
Formula weight	1209.90
T [K]	100(2)
Wavelength [Å]	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.1581(8)
b (Å)	15.8205(13)
c (Å)	18.1159(15)
α (°)	90
β (°)	90.355(3)
γ (°)	90
V [Å^3]	2911.3(4)
Z	2
ρ [g·cm^{-3}]	1.380
μ [mm^{-1}]	0.422
F_{000}	1256.0
Crystal size [mm^3]	0.08 x 0.07 x 0.05
2Θ range (º)	3.418 to 52.74
h	-12 to 12
k	-19 to 19
l	-22 to 22
Reflections collected	51878
Independent reflections	5950
R(int)	0.0617
Refinement method	Full-matrix least-squares on F2

Parameters	361
Restraints	0
Goodness-of-fit on F^2	1.080
$R1$ [I > 2σ (I)]	0.0519
$wR2$ [I > 2σ (I)]	0.1296
$R1$ (all data)	0.0774
$wR2$ (all data)	0.1547
Δρ [e·Å^{-3}]	1.07/-0.52

Table S4. Hydrogen bonds for rotaxane **3c** [Å and (°)].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(02)...O(1)[1]	0.85(4)	2.10(4)	2.918(3)	164(3)
N(3)-H(03)...O(1)[1]	0.88(4)	2.16(4)	3.039(3)	171(3)
C1S-H1S…O(3)[2]	1.00	2.12	3.027(4)	150.4

[1] 1-X,1-Y,1-Z; [2] 1-X,-1/2+Y,1/2-Z

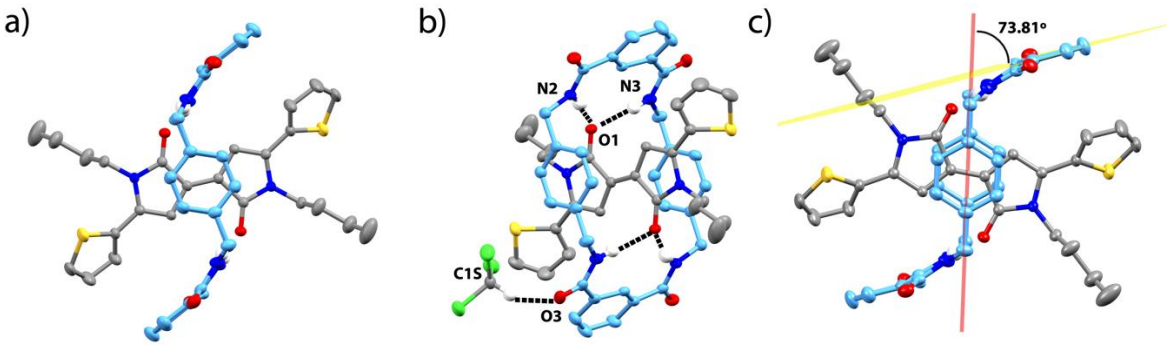


Figure S18. Molecular structure of **3c** with thermal ellipsoids drawn at 50% probability: a) lateral view; b) tilted view; c) lateral view, with intersection (angle) between two calculated planes at the macrocycle (in red: plane between carbons C15 and C18 of the *p*-xylylenediamine walls; in yellow: plane between carbons C21-C26 of the isophthalamide moiety). For clarity, selected hydrogens atoms have been deleted.

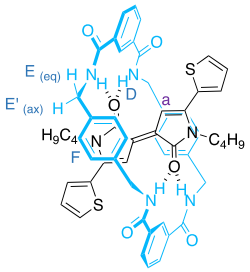
6. Determination of ΔG‡ for the pirouetting of the macrocycle in 3a and 3c

6a. VT-NMR study of rotaxane 3c

From the coalescence temperature value, the rate constant (k_c) was determined using Equation 1,[10-12] as well as the activation free energy ($\Delta G^{\ddagger}$) by using the Eyring equation (Equation 2).

$$k_C = \frac{\pi \cdot \sqrt{\Delta\upsilon^2 + J_{AB}^2}}{\sqrt{2}} \qquad (1)$$

$$\Delta G^{\ddagger} = -R \cdot T_C \cdot \ln \frac{k_C \cdot h}{k_b \cdot T_C} \qquad (2)$$



T_c = 402 K (129 ºC)

k_c = 1107 s^{-1}

ΔG‡ = 75.1 KJ/mol (18.0 Kcal/mol)

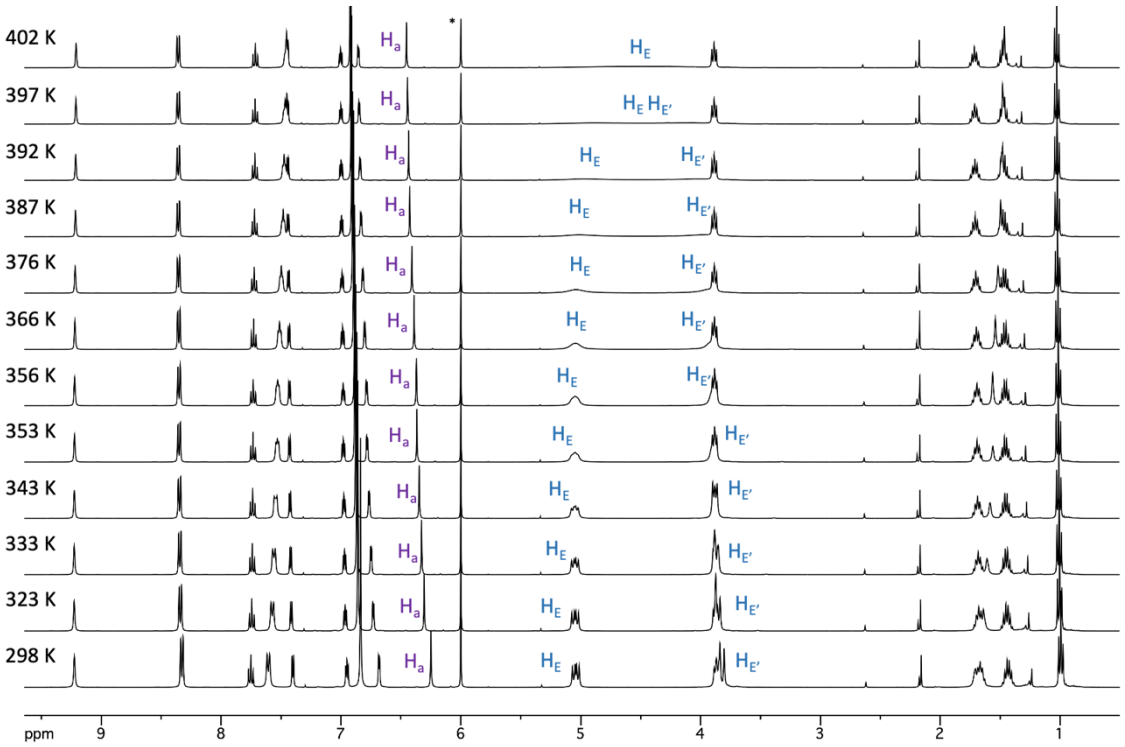


Figure S19. ^{1}H-NMR ($C_2D_2Cl_4$, 400 MHz) spectra of rotaxane **3c** measured at different temperatures; the asterisk corresponds to the solvent residual peak.

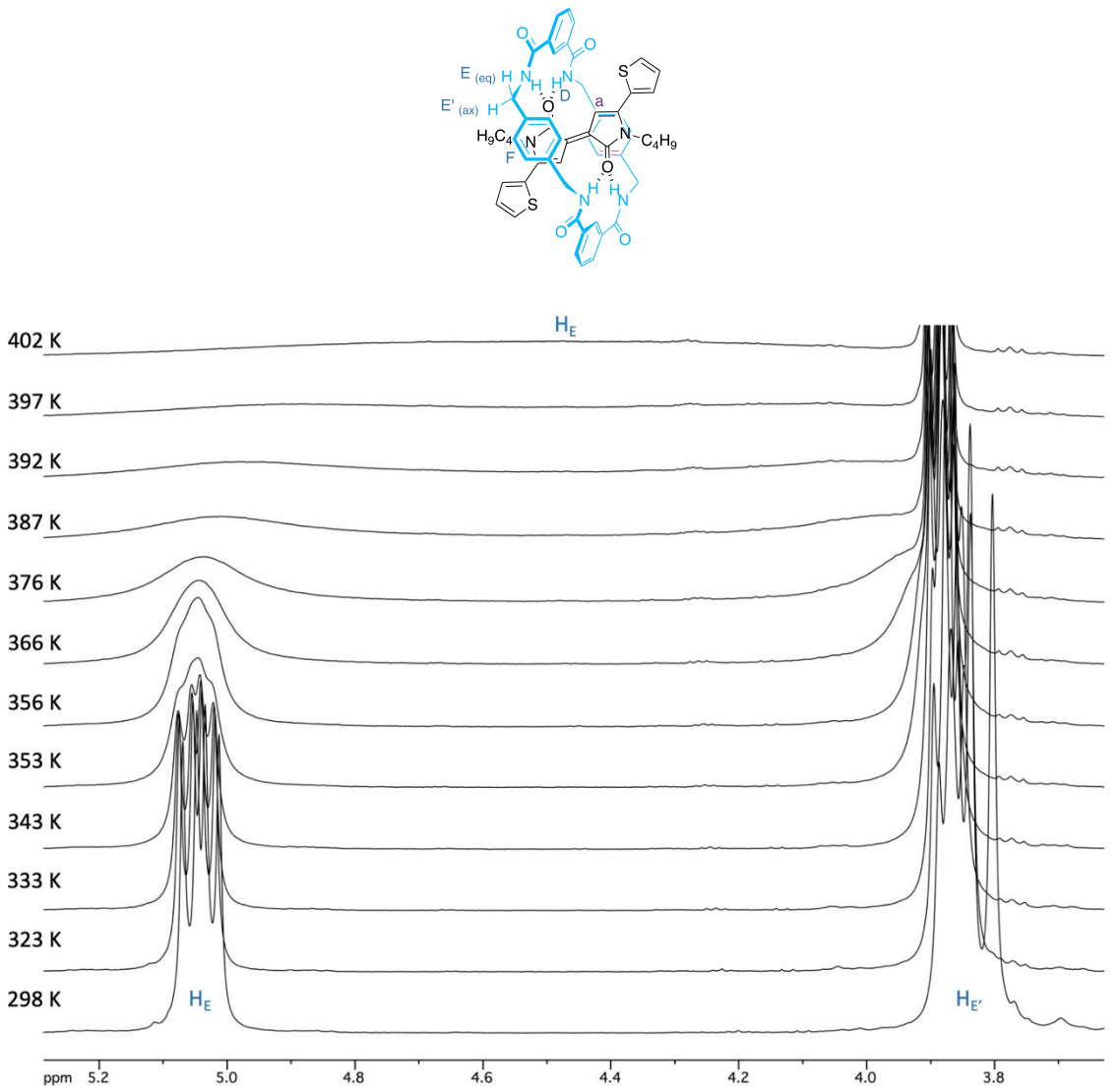


Figure S20. Expanded view of the resonance peaks for protons H_E and $H_{E'}$ in the ^{1}H-NMR ($C_2D_2Cl_4$, 400 MHz) spectra of rotaxane **3c** measured at different temperatures.

6b. VT-NMR study of rotaxane 3a

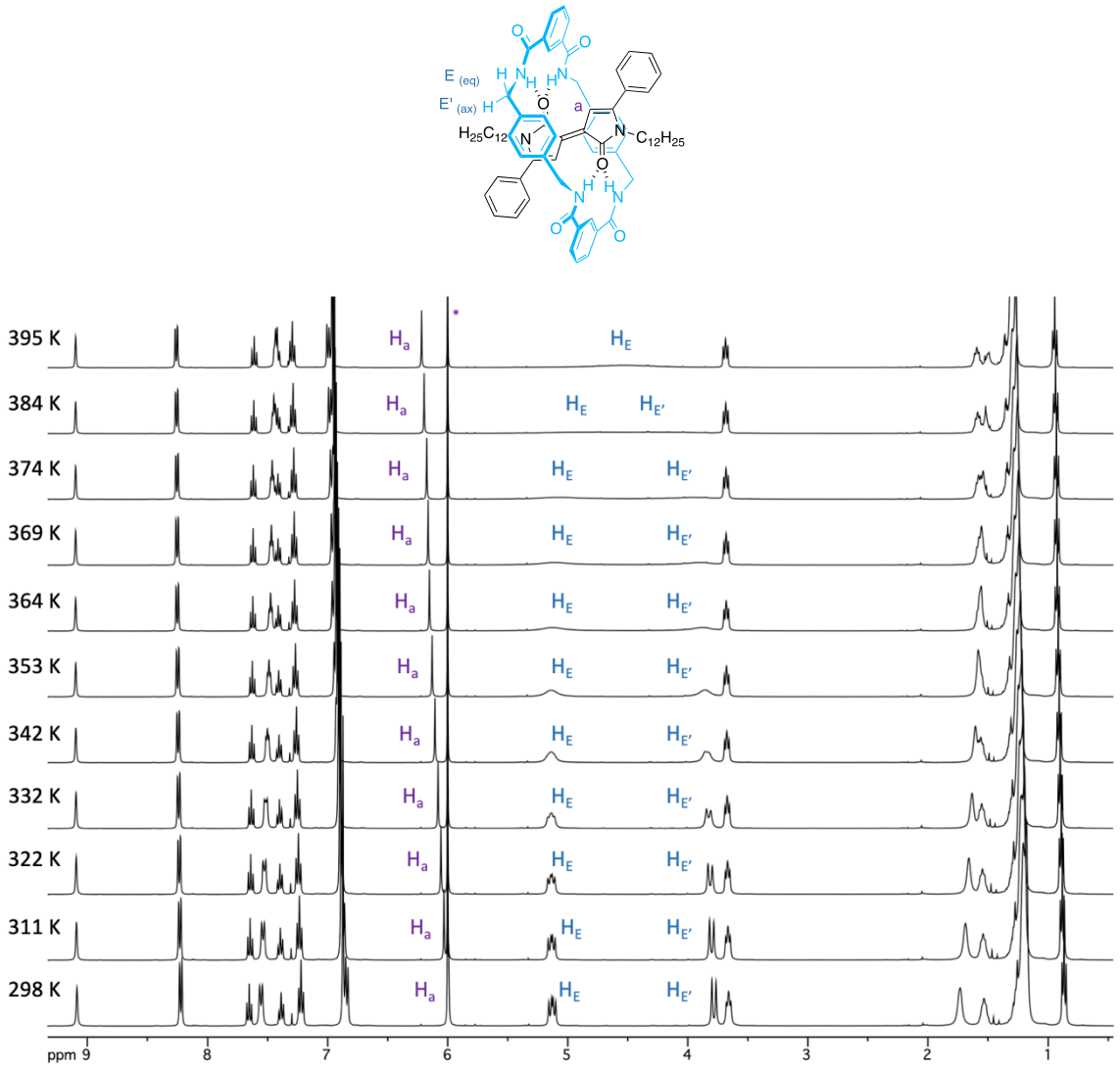


Figure S21. ^{1}H-NMR ($C_2D_2Cl_4$, 400 MHz) spectra of rotaxane **3a** measured at different temperatures; the asterisk corresponds to the solvent residual peak**.**

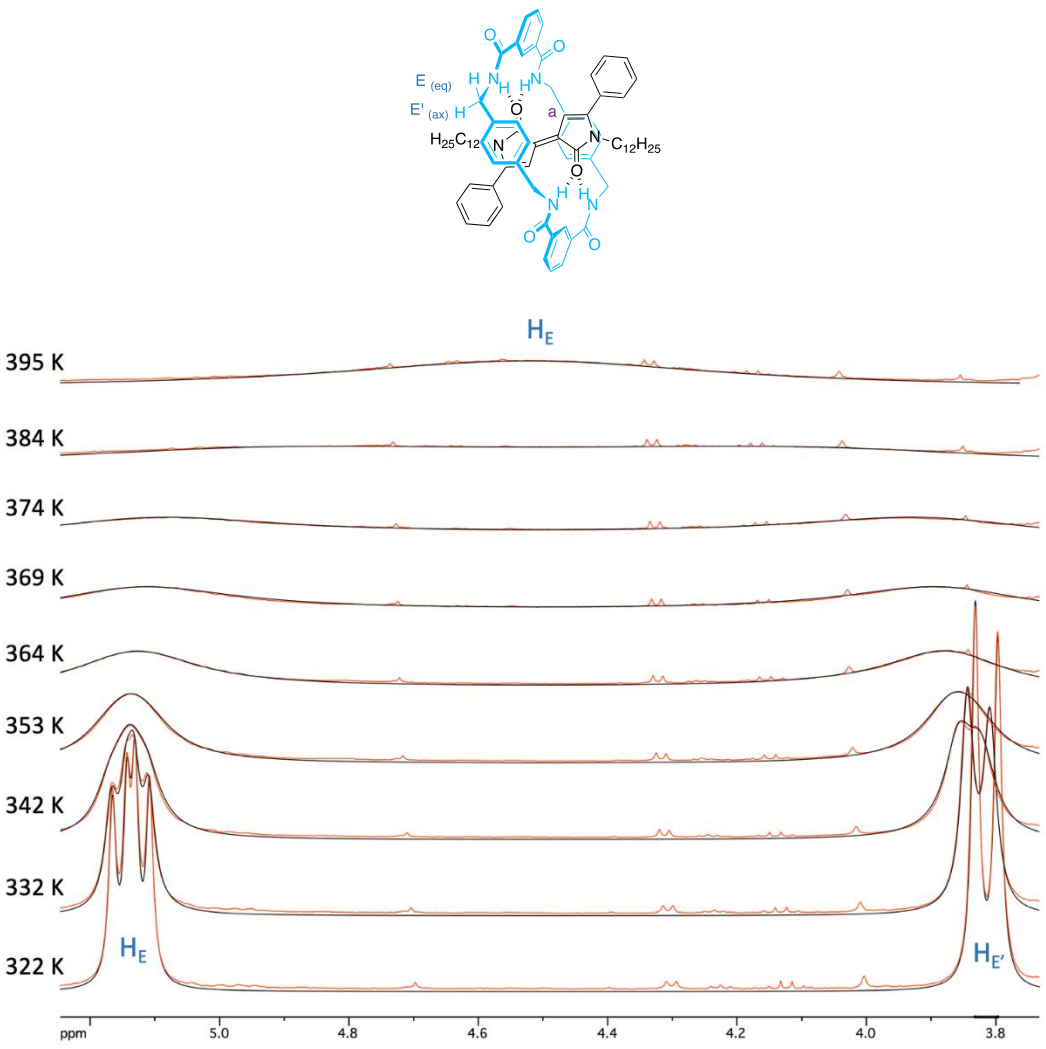


Figure S22. Simulated (black) and experimental (red) ^{1}H-NMR ($C_2D_2Cl_4$, 400 MHz) spectra of rotaxane **3a** used for the determination of the activation parameters.

Table S5. Rate constants determined by line shape analysis at different temperatures for the circumrotation of the macrocycle in **3a**.

Entry	*T* (K)	*k* (s^{-1})	1/*T*	ln(*k*/*T*)
1	322	13.5	0.00311090	-3.1701523
2	332	26.2	0.00301532	-2.5382906
3	342	63.5	0.00292543	-1.6832736
4	353	128.8	0.00282957	-1.0093680
5	364	265.8	0.00274922	-0.3136576
6	369	417.3	0.00271076	0.12327978
7	374	541.5	0.00267330	0.36990012
8	384	988.0	0.00260146	0.94399902
9	395	1886.3	0.00253331	1.56414520

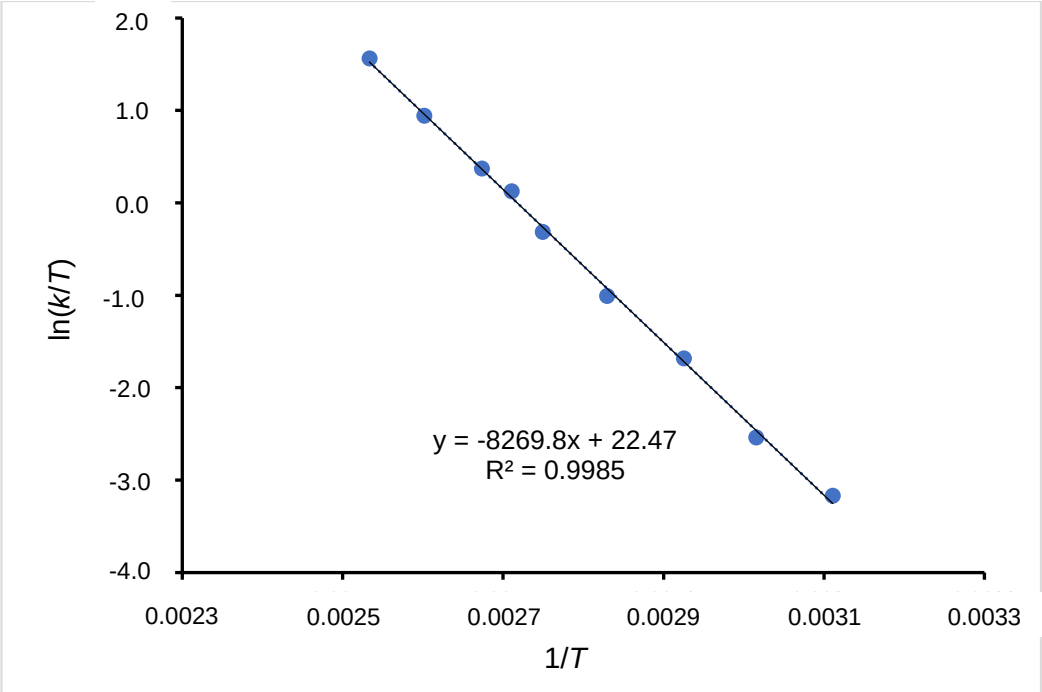


Figure S23. Eyring plot for the pirouetting of the macrocycle in **3a**.

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated from the slope and intercept using equation (5).[13]

$$\Delta G^{\ddagger} = -RTln\frac{kh}{k_b T} = -RT(ln\frac{h}{k_b} + ln\frac{k}{T}) = RT(ln\frac{k_b}{h} - ln\frac{k}{T}) \quad (3)$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\,\Delta S^{\ddagger} \quad (4)$$

$$ln\frac{k}{T} = 23.76 - \frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} \quad (5)$$

h, k_b and R are the Planck, Boltzmann and gas constants, respectively.

Table S6. Activation parameters for the pirouetting of the macrocycle around **3a.**

Entry	$\Delta H^{\ddagger}$	Standard deviation	$\Delta S^{\ddagger}$	Standard deviation
1	68.8 KJ mol^{-1}	1.0 KJ mol^{-1}	-10.7 J mol^{-1} K^{-1}	2.8 J mol^{-1} K^{-1}
2	16.5 Kcal mol^{-1}	0.24 Kcal mol^{-1}	-2.6 e.u.	0.7 e. u.

7. Thermolysis of aza-Pechmann dyes 2b-c and rotaxanes 3b-c in solution

Thermolysis of 2b

A solution of thread **2b** (5.1 mg, 0.0076 mmol) and durene (1.1 mg, 0.0082 mmol) as internal standard in $C_2D_2Cl_4$ (0.5 mL) was heated at 120 ºC (oil bath). The amount of **2b** respect to the internal standard was quantified by ^{1}H-NMR spectroscopy. Unfortunately, due to the presence of a complex mixture of products from the third day of monitoring, the amount of free dye could not be accurately quantified.

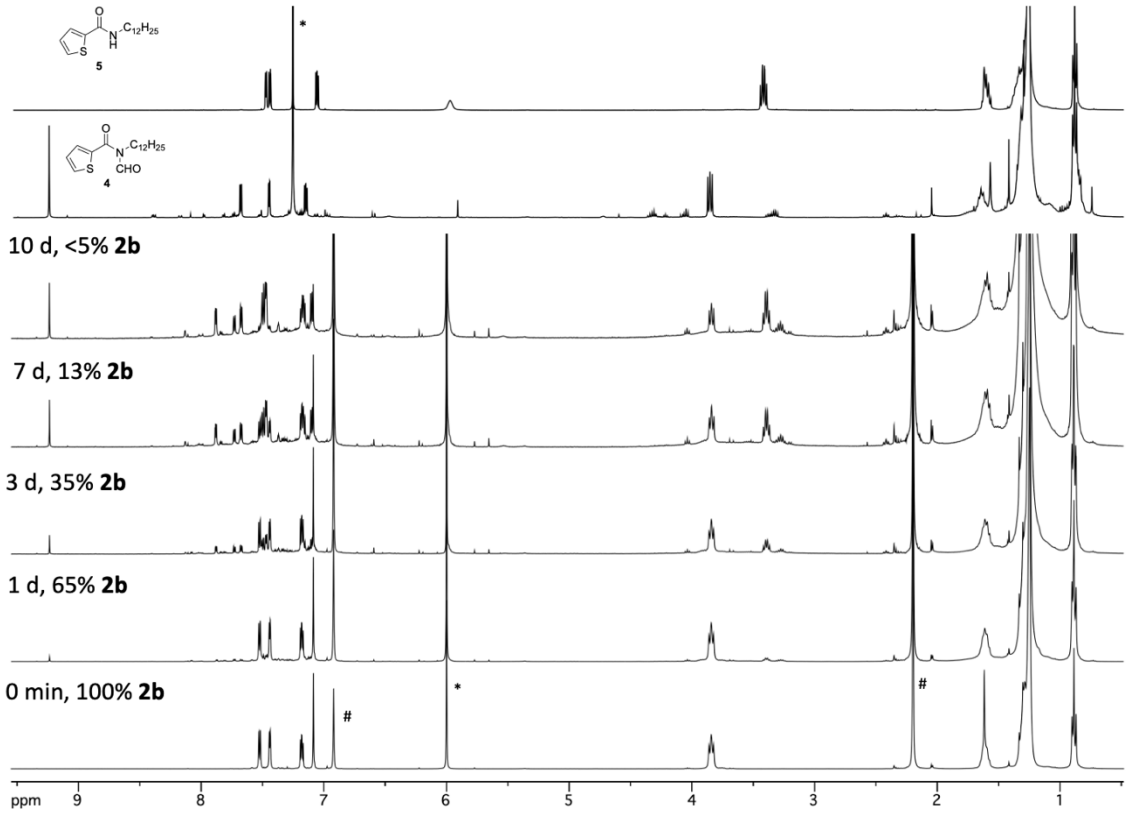


Figure S24. ^{1}H-NMR (400 MHz) spectra of the free dye **2b** after heating at 120 ºC ($C_2D_2Cl_4$) at different times, and ^{1}H-NMR (400 MHz) spectra of **4** and **5** ($CDCl_3$); asterisks (*) represent residual solvent peaks and hash signs (#) indicate the two resonances of durene (internal standard).

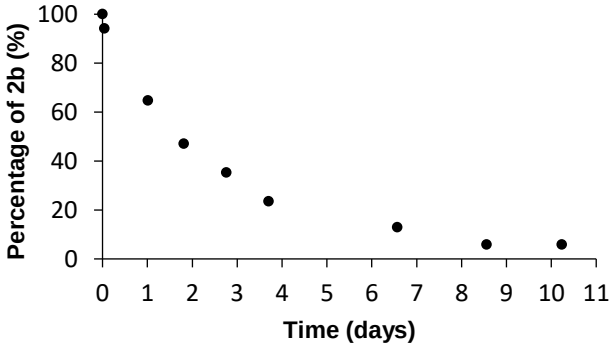
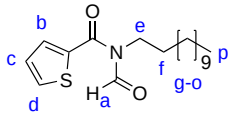


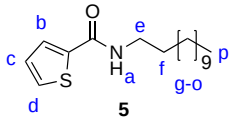
Figure S25. Percentage of the amount of **2b** respect to the internal standard over time.

Thermolysis of **2b** was reproduced on a larger scale with the aim of isolating any product resulting from its decomposition. For this purpose, a solution of **2b** (75 mg, 0.113 mmol) in $C_2H_2Cl_4$ (7.6 mL) was kept at 120 °C. After 8 days (no dye was detected by TLC) the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel eluting with 50:1 to 20:1 $CHCl_3$/acetone to give *N*-dodecyl-*N*-formylthiophene-2-carboxamide (**4**) and *N*-dodecylthiophene-2-carboxamide (**5**).[14]



4

N-Dodecyl-*N*-formylthiophene-2-carboxamide (**4**) (R_f = 0.49 in 20:1 $CHCl_3$/acetone): 9.1 mg (13%); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.25 (s, 1H, H_a), 7.69 (dd, *J* = 5.0, 1.1 Hz, 1H, H_d), 7.45 (dd, *J* = 3.8, 1.1 Hz, 1H, H_b), 7.16 (dd, *J* = 5.0, 3.8 Hz, 1H, H_c), 3.87-3.84 (m, 2H, H_e), 1.68 – 1.61 (m, 2H, H_f), 1.34 – 1.25 (m, 18H, H_{g-o}), 0.88 (t, *J* = 6.9 Hz, 3H, H_p) ; ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ 165.5 (CO), 163.9 (CHO), 136.6 (C), 133.3 (CH), 133.1 (CH), 127.8 (CH), 41.7 (CH_2) , 32.1 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.71 (CH_2), 29.65 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 28.2 (CH_2), 27.1 (CH_2), 22.8 (CH_2), 14.3 (CH_3); HRMS (ESI) calcd for $C_{18}H_{30}NO_2S$ $[M + H]^+$ 324.1992, found 324.1993.



5

N-Dodecylthiophene-2-carboxamide (**5**) (R_f = 0.37 in 20:1 $CHCl_3$/acetone): 13.7 mg (20%); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.48 (d, *J* = 3.7 Hz, 1H, H_b), 7.45 (dd, *J* = 5.0, 1.1 Hz, 1H, H_d), 7.06 (dd, *J* = 5.0, 3.7 Hz, 1H, H_c), 5.98 (s, 1H, H_a), 3.44-3.39 (m, 2H, H_e), 1.63 – 1.56 (m, 2H, H_f), 1.37 – 1.25 (m, 18H, H_{g-o}), 0.88 (t, *J* = 6.8 Hz, 3H, H_p) ; ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ 162.0 (CO), 139.3 (C), 129.7 (CH), 127.9 (CH), 127.7 (CH), 40.2 (CH_2), 32.1 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.73 (CH_2), 29.69 (CH_2), 29.49 (CH_2), 29.47 (CH_2), 27.1 (CH_2), 22.8 (CH_2), 14.3 (CH_3); HRMS (ESI) calcd for $C_{17}H_{30}NOS$ $[M + H]^+$ 296.2043, found 296.2047.

Thermolysis of 2c

A solution of thread **2c** (3.3 mg, 0.0075 mmol) and durene (1.0 mg, 0.0075 mmol) as internal standard in $C_2D_2Cl_4$ (0.5 mL) was heated at 120 ºC (oil bath). The amount of **2c** respect to the internal standard was quantified by ^{1}H-NMR spectroscopy. Unfortunately, due to the presence of a complex mixture of products from the third day of monitoring, the amount of free dye could not be accurately quantified.

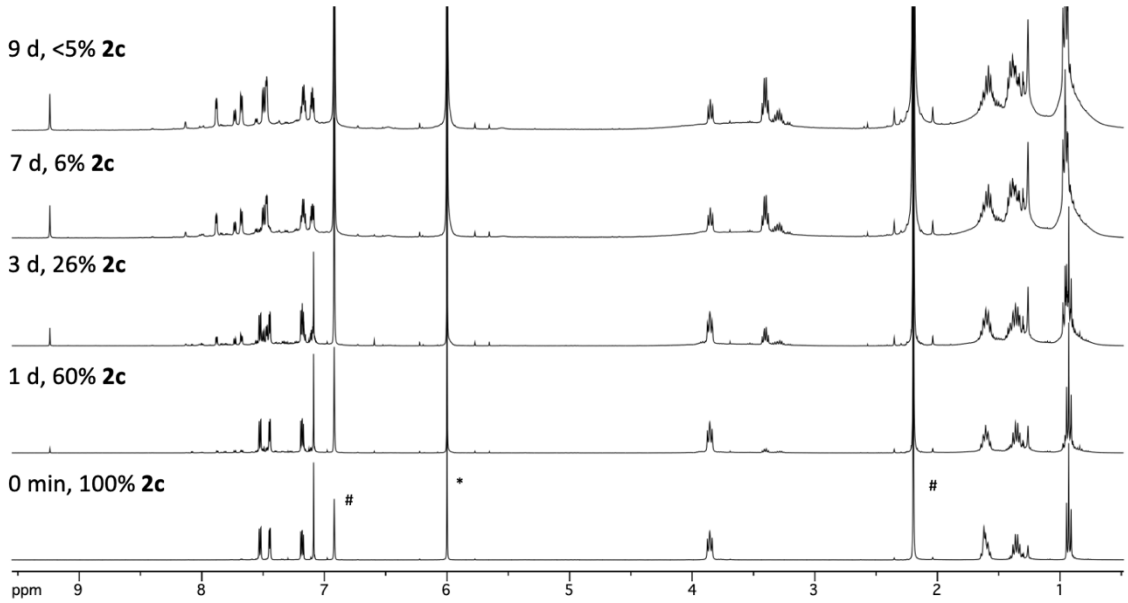


Figure S26. ^{1}H-NMR (400 MHz) spectra of the free dye **2c** after heating at 120 ºC ($C_2D_2Cl_4$) at different times; the asterisk (*) represents the residual solvent peak and hash signs (#) indicate the two resonances of durene (internal standard).

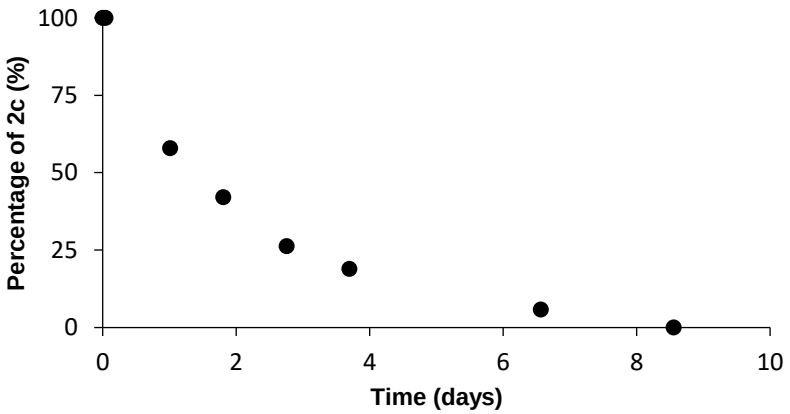


Figure S27. Percentage of the amount of **2c** respect to the internal standard over time.

Thermolysis of 3b

A solution of rotaxane **3b** (9 mg, 0.0075 mmol) and durene (1 mg, 0.0075 mmol) in $C_2D_2Cl_4$ (0.5 mL) was heated at 120 ºC (oil bath). The amount of **3b** respect to the internal standard was quantified by ^{1}H-NMR spectroscopy.

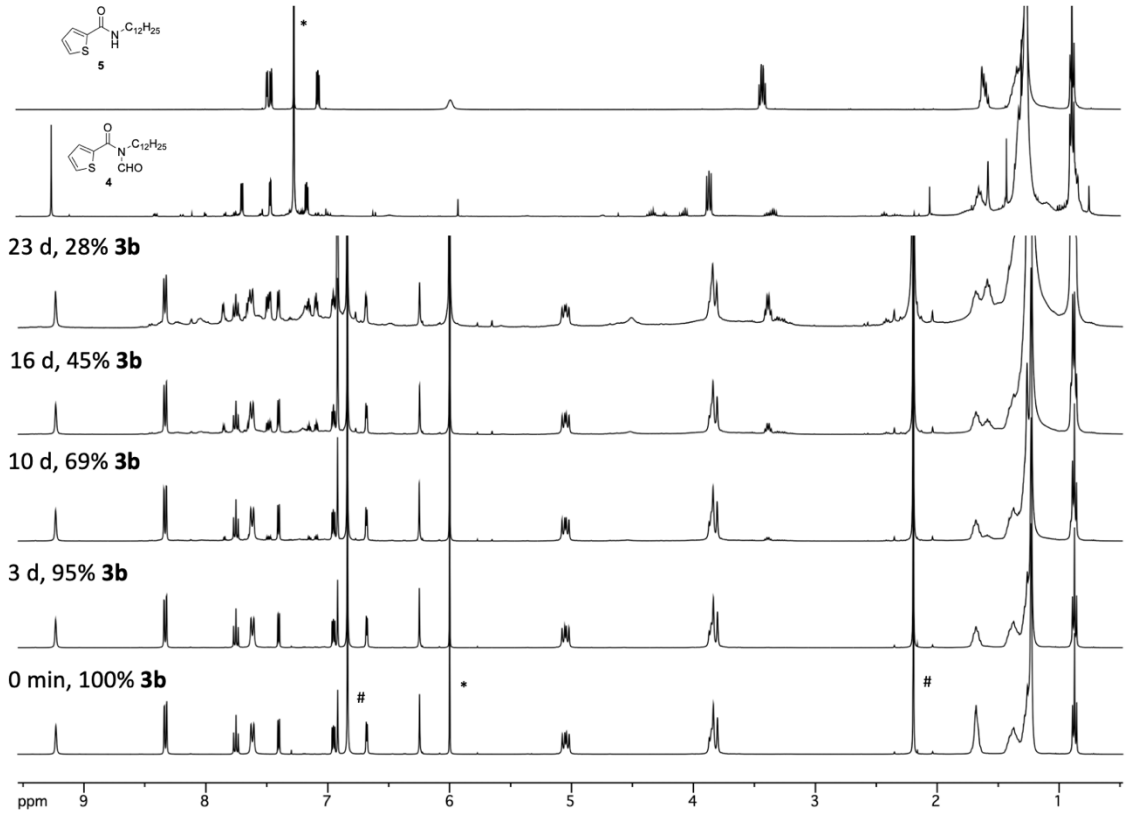


Figure S28. ^{1}H-NMR (400 MHz) spectra of rotaxane **3b** after heating at 120 ºC ($C_2D_2Cl_4$) at different times, and ^{1}H-NMR (400 MHz) spectra of **4** and **5** ($CDCl_3$); asterisks (*) represent residual solvent peaks and hash signs (#) indicate the two resonances of durene (internal standard).

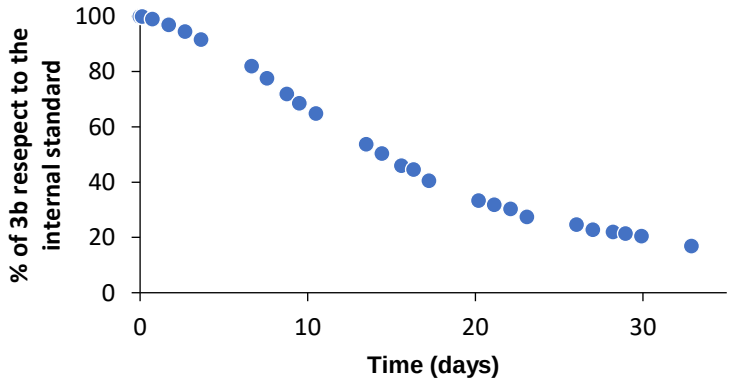


Figure S29. Percentage of the amount of **3b** respect to the internal standard over time.

Thermolysis of 3c

A solution of rotaxane **3c** (7.5 mg, 0.0077 mmol) and durene (1 mg, 0.0075 mmol) in $C_2D_2Cl_4$ (0.5 mL) was heated at 120 ºC (oil bath). The amount of **3c** respect to the internal standard was quantified by ^{1}H-NMR spectroscopy.

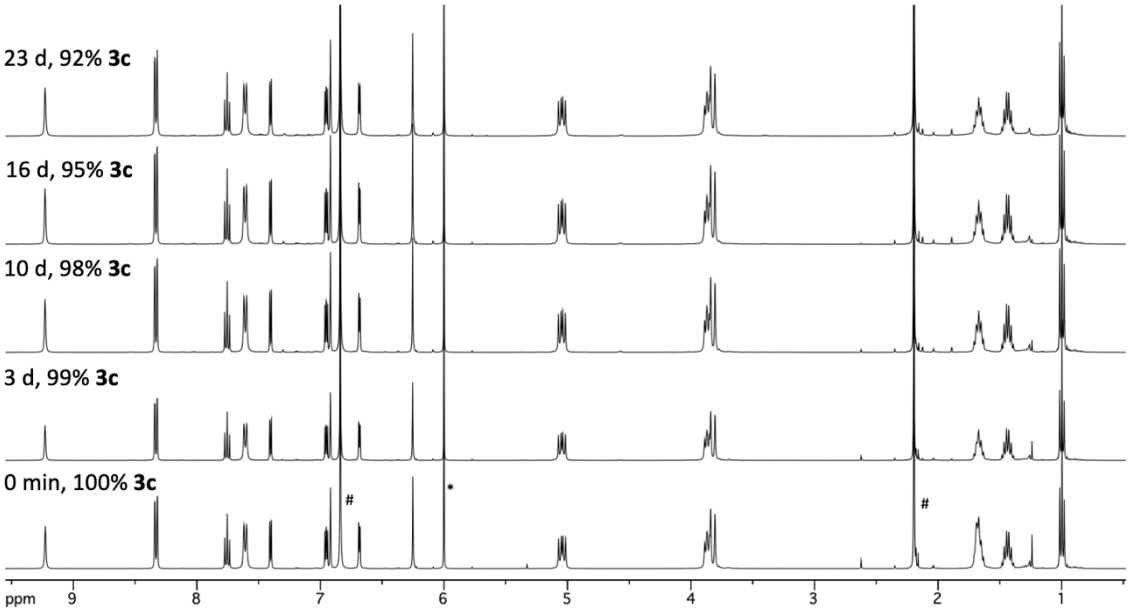


Figure S30. ^{1}H-NMR (400 MHz) spectra of rotaxane **3c** after heating at 120 ºC ($C_2D_2Cl_4$) at different times; the asterisk (*) represents the residual solvent peak and hash signs (#) indicate the two resonances of durene (internal standard).

8. TGA experiments of Pechmann lactams 2b-c and rotaxanes 3b-c

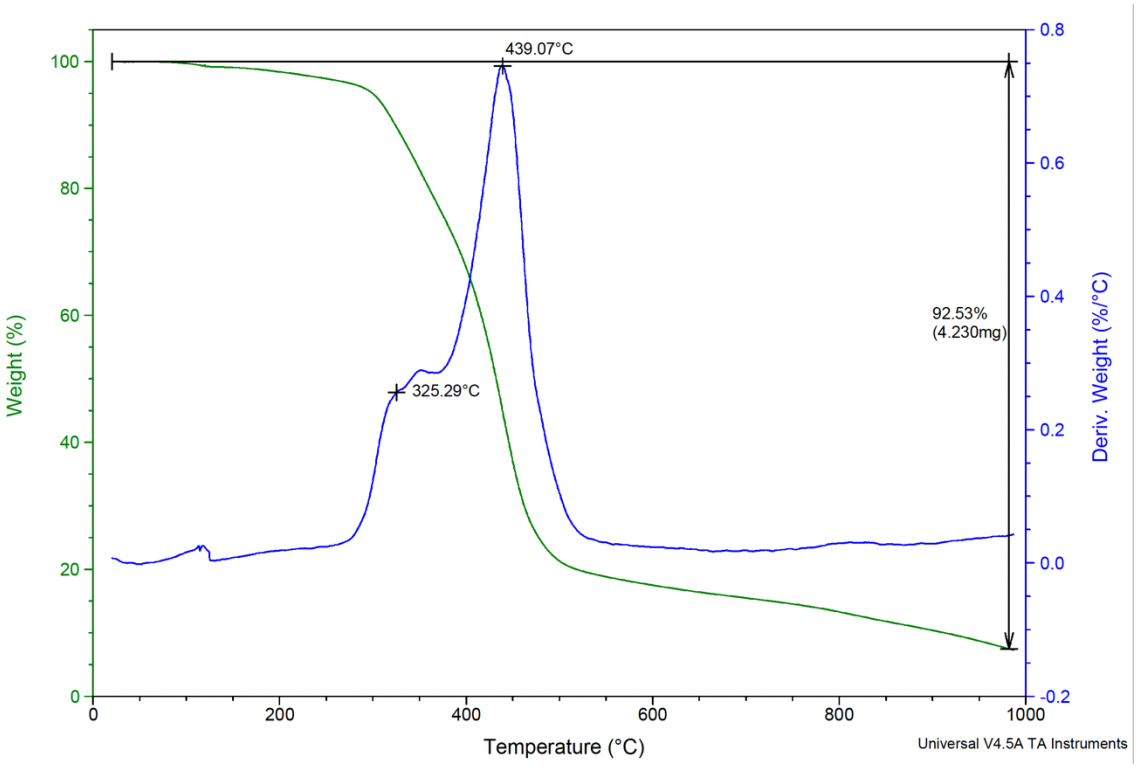


Figure S31. TGA experiment of Pechmann lactam **2b**.

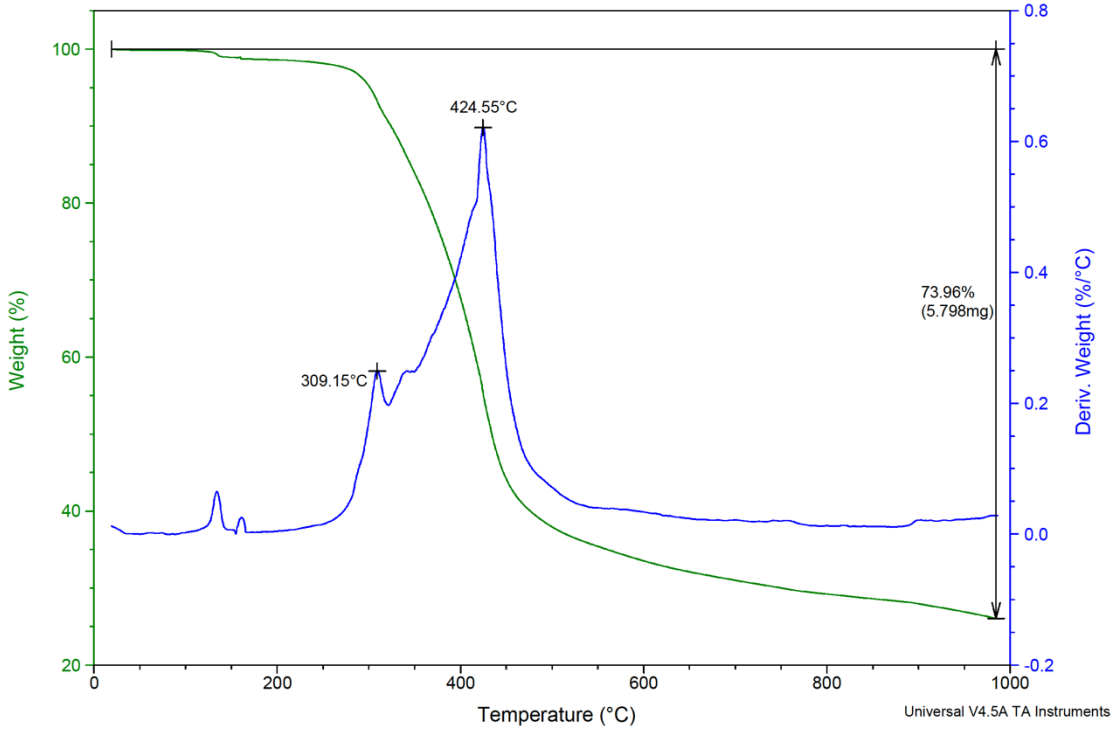


Figure S32. TGA experiment of Pechmann lactam **2c**.

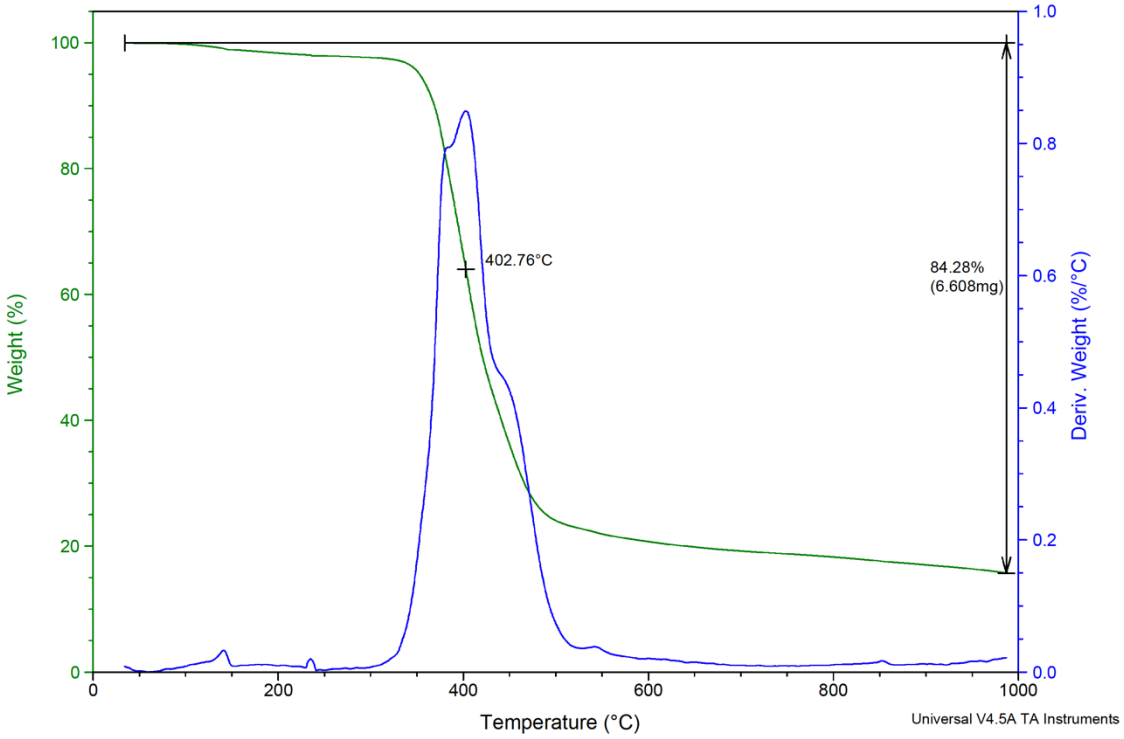


Figure S33. TGA experiment of rotaxane **3b**.

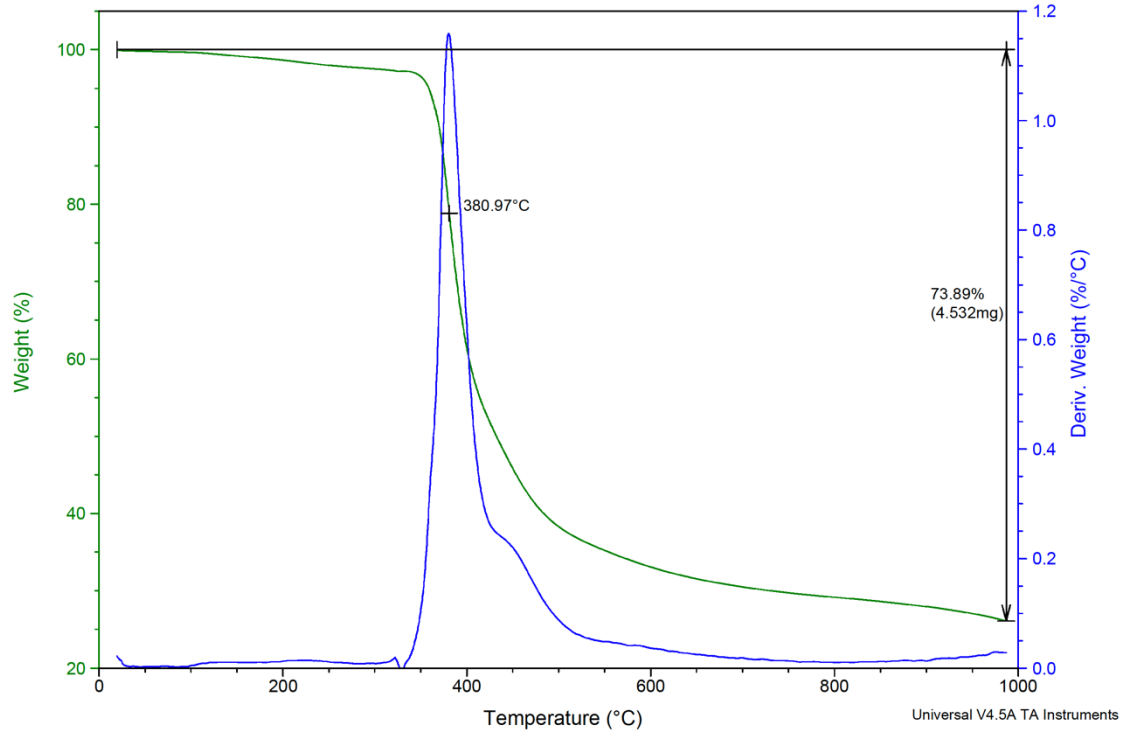


Figure S34. TGA experiment of rotaxane **3c**.

9. Ultraviolet-visible spectra of aza-Pechmann dyes 2 and rotaxanes 3

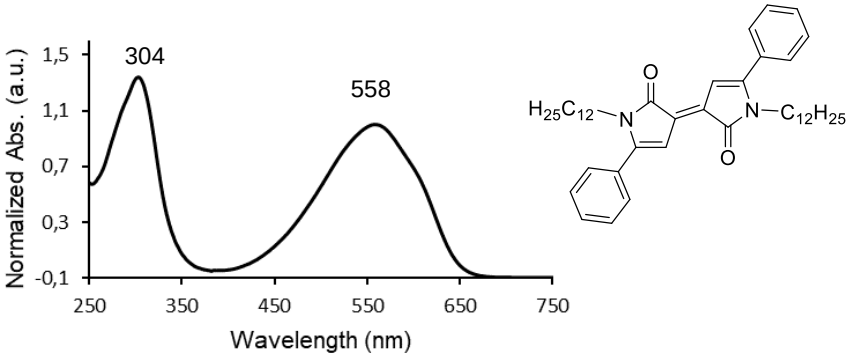


Figure S35. Absorption spectra of thread **2a** in chloroform ($c \approx 1 \times 10^{-5}$ M).

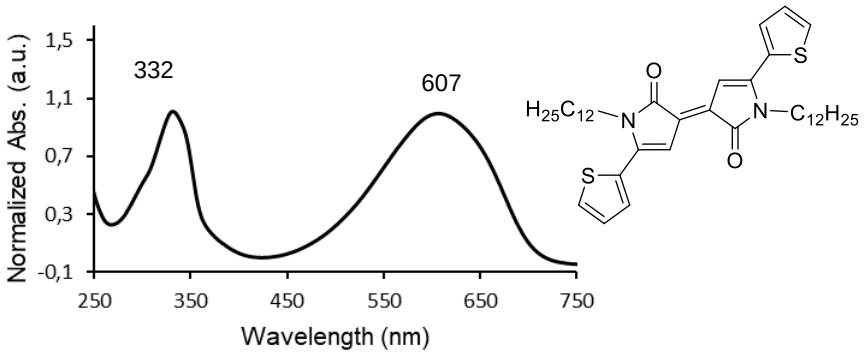


Figure S36. Absorption spectra of thread **2b** in chloroform ($c \approx 1 \times 10^{-5}$ M).

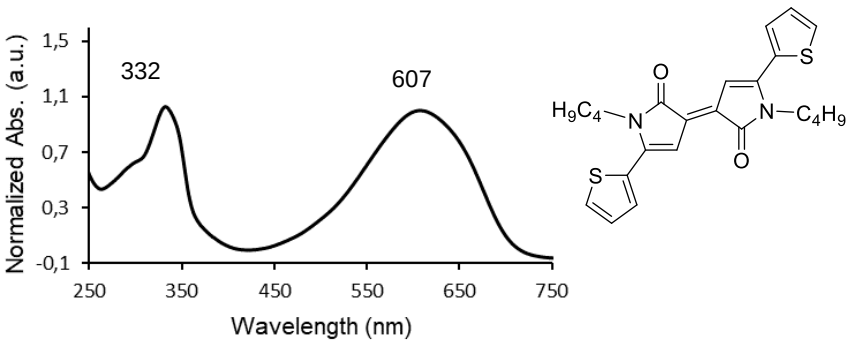


Figure S37. Absorption spectra of thread **2c** in chloroform ($c \approx 1 \times 10^{-5}$ M).

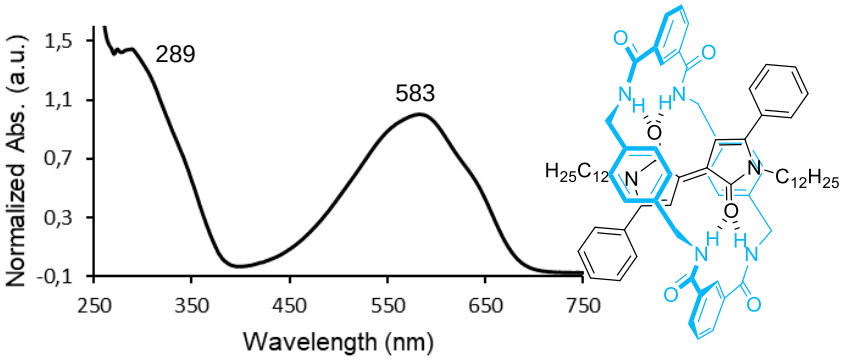


Figure S38. Absorption spectra of rotaxane **3a** in chloroform ($c \approx 1 \times 10^{-5}$ M).

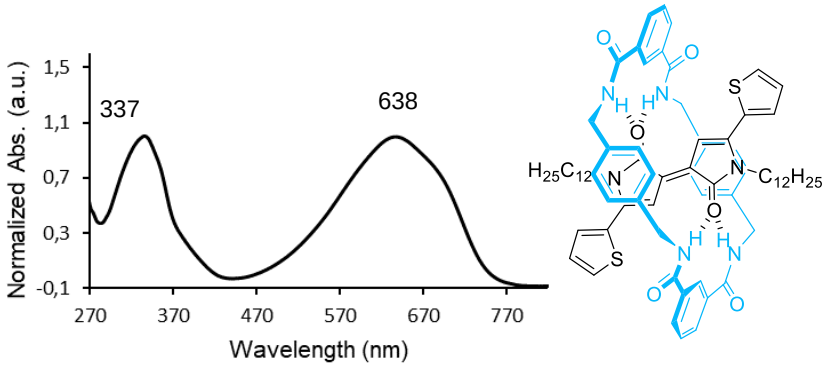


Figure S39. Absorption spectra of rotaxane **3b** in chloroform ($c \approx 1 \times 10^{-5}$ M).

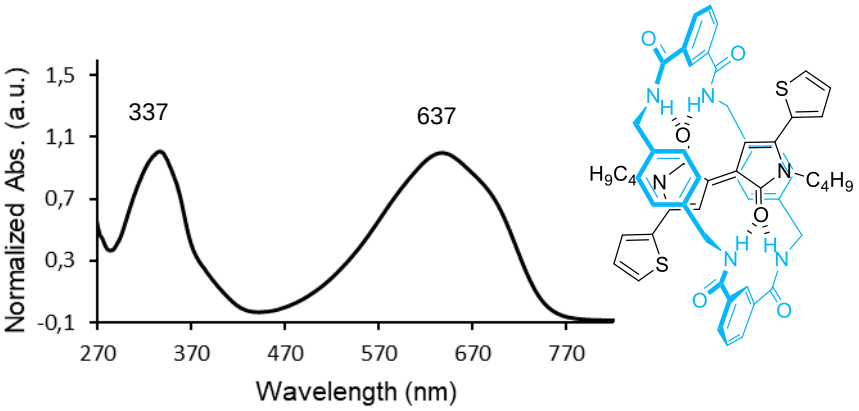


Figure S40. Absorption spectra of rotaxane **3c** in chloroform ($c \approx 1 \times 10^{-5}$ M).

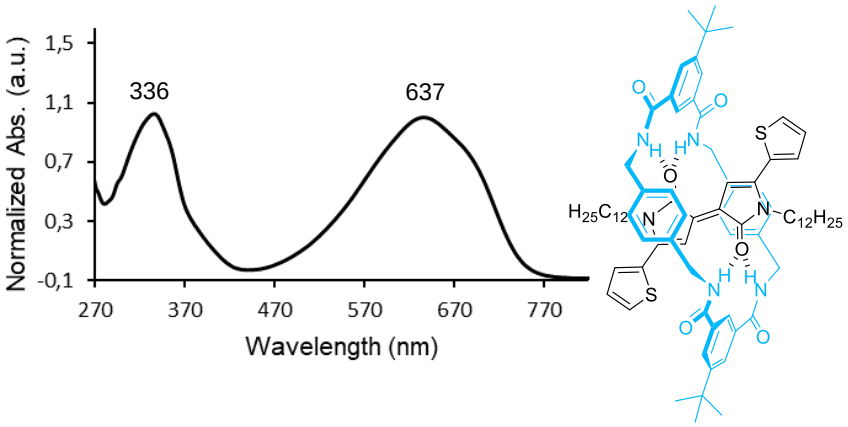


Figure S41. Absorption spectra of rotaxane **3f** in chloroform ($c \approx 1 \times 10^{-5}$ M).

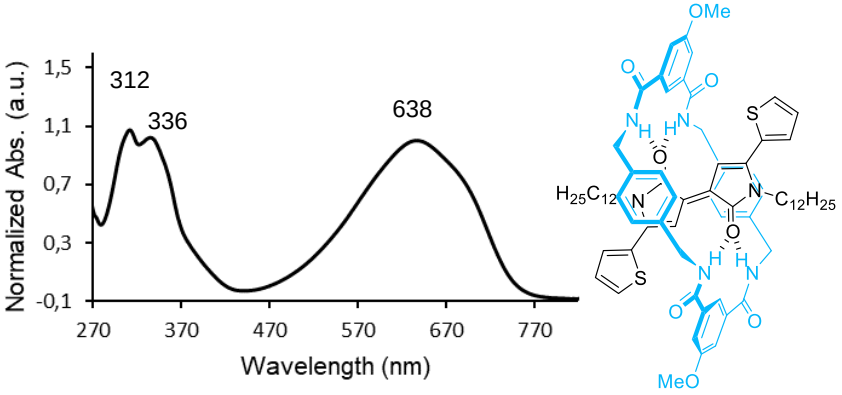


Figure S42. Absorption spectra of rotaxane **3g** in chloroform ($c \approx 1 \times 10^{-5}$ M).

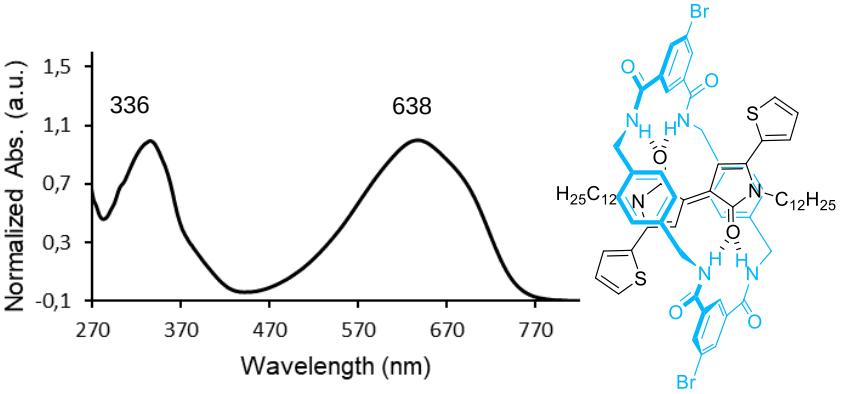


Figure S43. Absorption spectra of rotaxane **3h** in chloroform ($c \approx 1 \times 10^{-5}$ M).

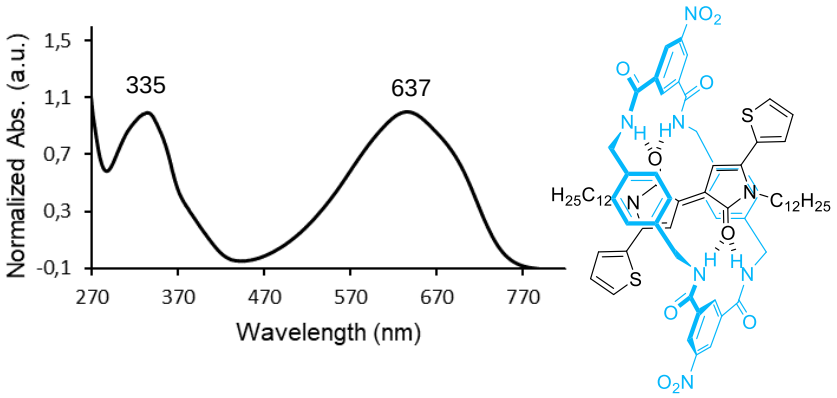


Figure S44. Absorption spectra of rotaxane **3i** in chloroform ($c \approx 1 \times 10^{-5}$ M).

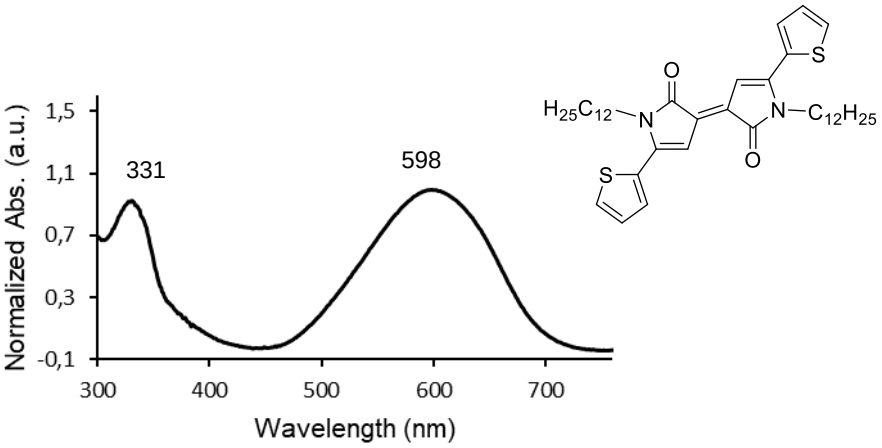


Figure S45. Absorption spectra of thread **2b** in methanol ($c \approx 1 \times 10^{-5}$ M).

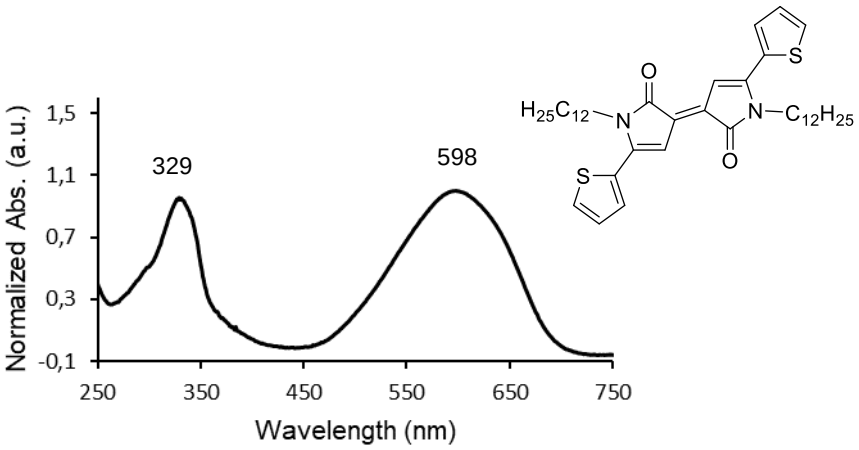


Figure S46. Absorption spectra of thread **2b** in acetonitrile ($c \approx 1 \times 10^{-5}$ M).

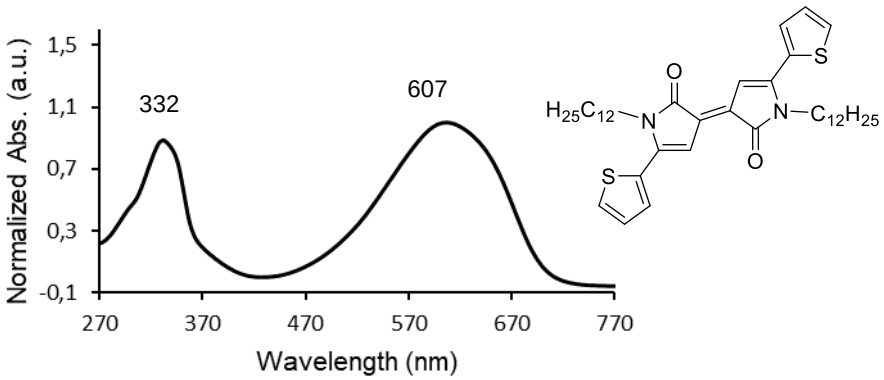


Figure S47. Absorption spectra of thread **2b** in DMF ($c \approx 1 \times 10^{-5}$ M).

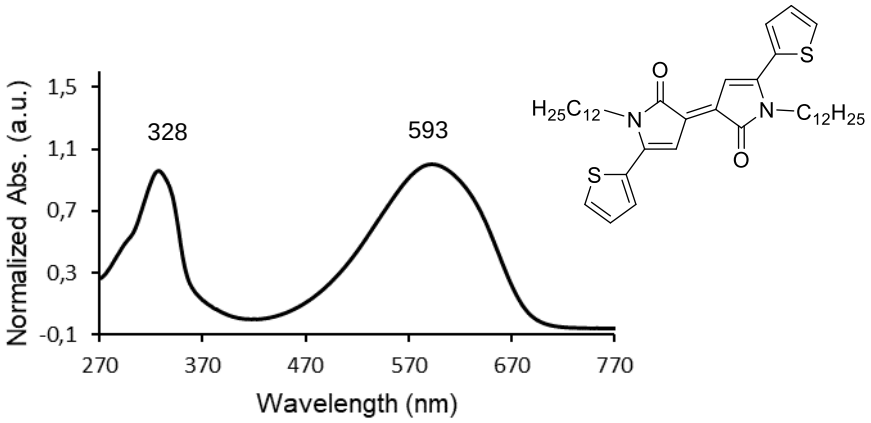


Figure S48. Absorption spectra of thread **2b** in ethyl acetate ($c \approx 1 \times 10^{-5}$ M).

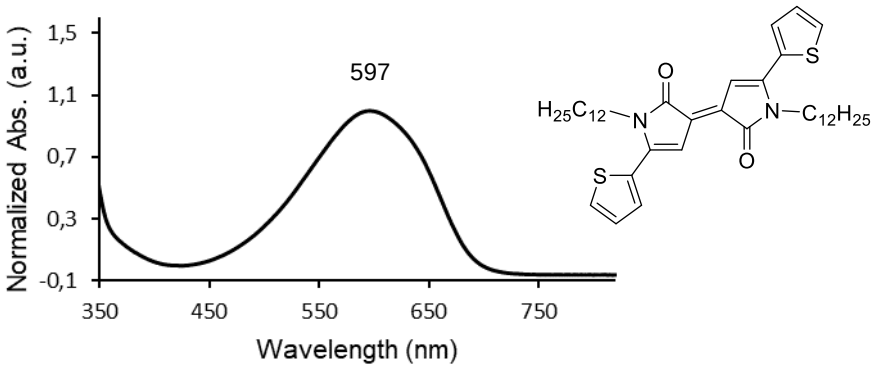


Figure S49. Absorption spectra of thread **2b** in acetone ($c \approx 1 \times 10^{-5}$ M).

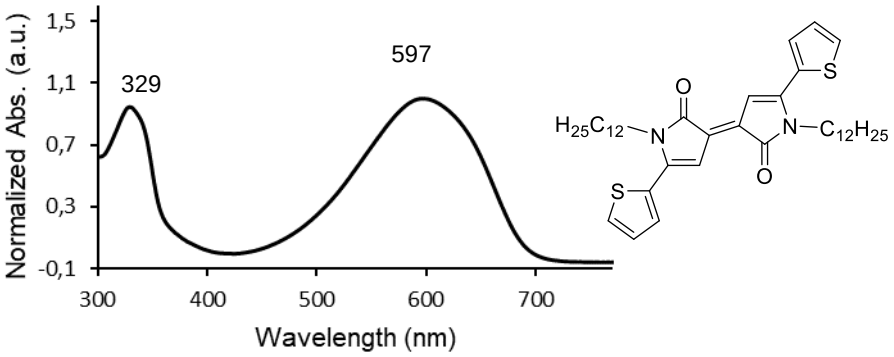


Figure S50. Absorption spectra of thread **2b** in tetrahydrofuran ($c \approx 1 \times 10^{-5}$ M).

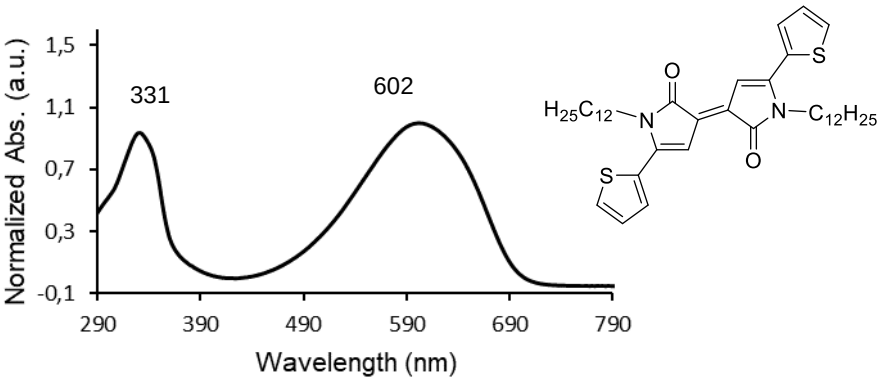


Figure S51. Absorption spectra of thread **2b** in toluene ($c \approx 1 \times 10^{-5}$ M).

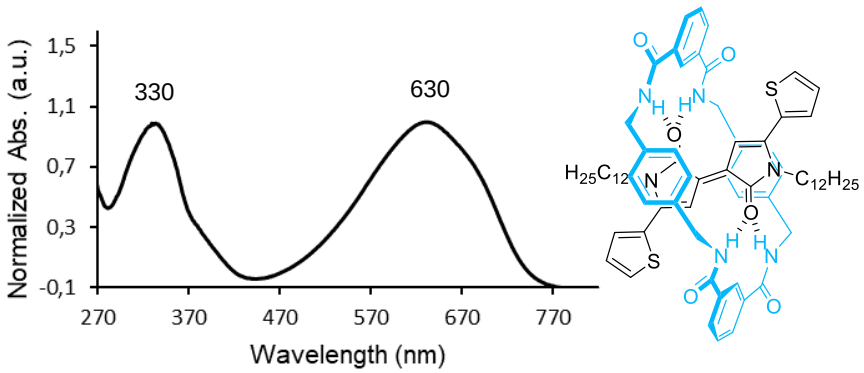


Figure S52. Absorption spectra of rotaxane **3b** in methanol ($c \approx 1 \times 10^{-5}$ M).

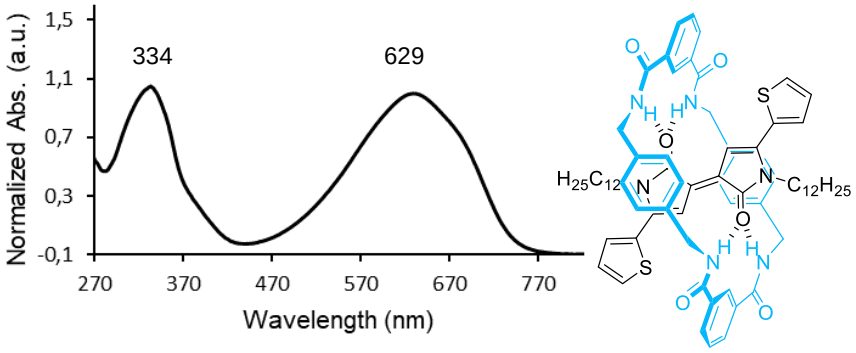


Figure S53. Absorption spectra of rotaxane **3b** in acetonitrile ($c \approx 1 \times 10^{-5}$ M).

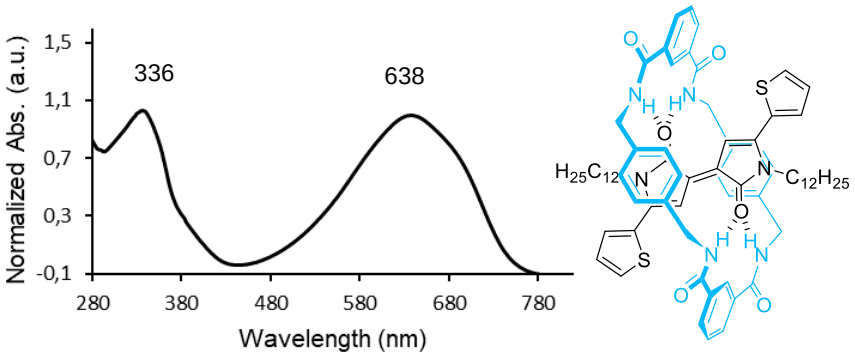


Figure S54. Absorption spectra of rotaxane **3b** in DMF ($c \approx 1 \times 10^{-5}$ M).

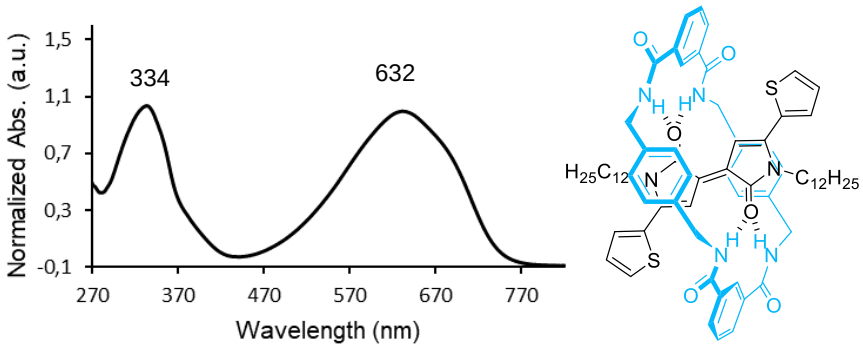


Figure S55. Absorption spectra of rotaxane **3b** in ethyl acetate ($c \approx 1 \times 10^{-5}$ M).

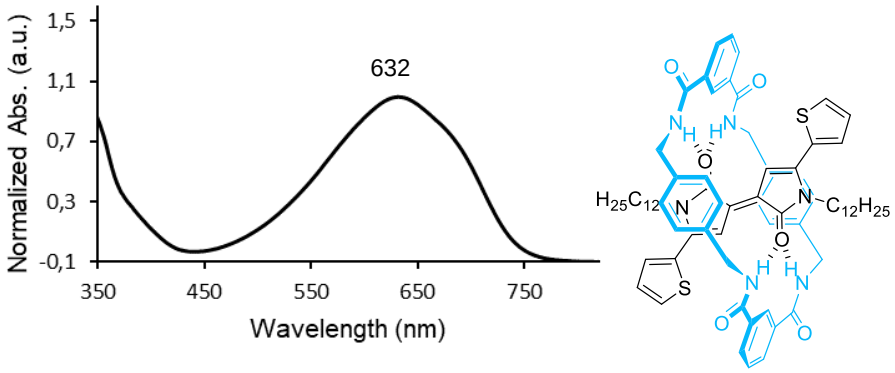


Figure S56. Absorption spectra of rotaxane **3b** in acetone ($c \approx 1 \times 10^{-5}$ M).

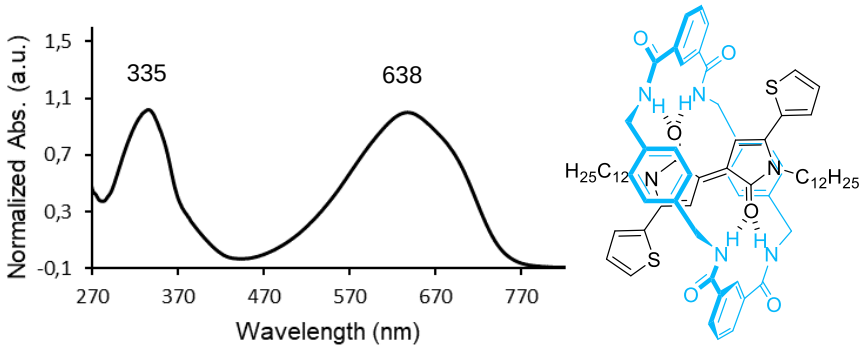


Figure S57. Absorption spectra of rotaxane **3b** in tetrahydrofuran ($c \approx 1 \times 10^{-5}$ M).

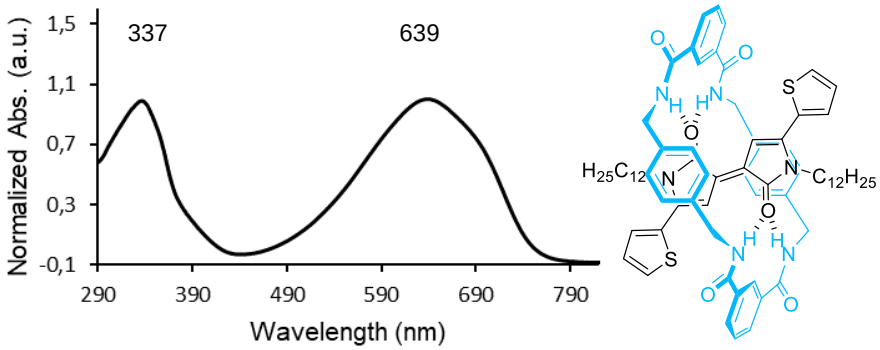


Figure S58. Absorption spectra of rotaxane **3b** in toluene ($c \approx 1 \times 10^{-5}$ M).

Table S7. Comparison of the UV-vis spectra of **2b** measured in different solvents.

Entry	Solvent	λ_1 (nm)	λ_2 (nm)
1	MeOH	331	598
2	AcCN	329	598
3	DMF	332	607
4	AcOEt	328	593
5	Acetone	-	597
6	THF	329	597
7	$CHCl_3$	332	607
8	Toluene	331	602

Table S8. Comparison of the UV-vis spectra of **3b** measured in different solvents.

Entry	Solvent	λ_1 (nm)	λ_2 (nm)
1	MeOH	330	630
2	AcCN	334	629
3	DMF	336	638
4	AcOEt	334	632
5	Acetone	-	632
6	THF	335	638
7	$CHCl_3$	337	638
8	Toluene	337	639

10. Computational study

Computational methods

The geometries of the molecules were optimized by using the M06[15] hybrid-functional with the DGDZVP basis sets.[16] This theoretical method has been used in related studies of thiophene-containing Pechmann dyes.[5] The nature of minimum nature of all compounds was confirmed by frequency analysis at the same level of theory. The stability of the resulting wave functions was checked for all the optimized structures.[17] Solvent effects were calculated with the SMD solvation model with chloroform parameters.[18] Frontiers Molecular Orbitals of all compounds were simulated at the same level of theory. Time-dependent DFT calculations (SMD($CHCl_3$)/M062-2x/DGDZVP) were carried out to compute the UV-vis absorption maxima on all the optimized structures. The pondered average of l_{max} of all the compounds was computed based on the Boltzmann distribution of all the computed conformers and their corresponding l_{max}. The ultrafine grid implemented in Gaussian 16 C. 01 was used.[19]

Frontier Molecular Orbitals

The frontier molecular orbitals of the optimized thread **2j** and [2]rotaxanes **3j-n** were computed. Figure S60 shows the electron density distribution of FMOs of compounds **3k-n** and Table S9 listed the HOMO and LUMO energies of **2j** and **3j-n**.

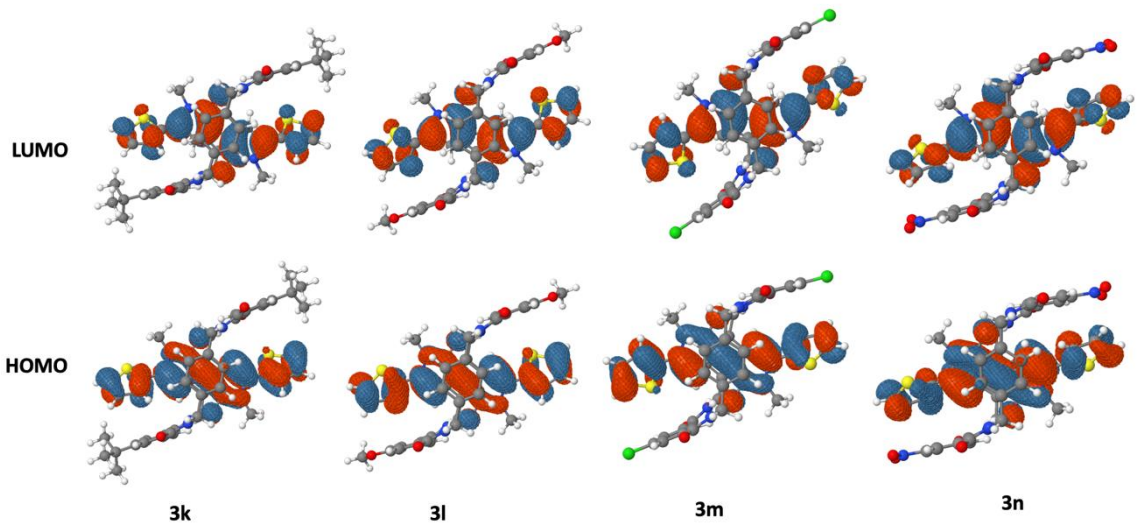


Figure S59. Frontier Molecular Orbital, HOMO and LUMO, of interlocked dyes **3k-n**.

Table S9. HOMO and LUMO energies (eV).

Entry	Compound	HOMO	LUMO	HOMO-LUMO Gap
1	**2j**	-5.33	-2.91	2.42
2	**3j**	-5.71	-3.32	2.39
3	**3k**	-5.66	-3.29	2.37
4	**3l**	-5.69	-3.29	2.39
5	**3m**	-5.82	-3.37	2.45
6	**3n**	-5.90	-3.43	2.48

UV-vis absorption analysis

Several theoretical methods were tested to calculate the pondered-average absorption maxima (l_{max}) of the optimized structures of the thread **2j** and the rotaxanes **3j-n**. Taking into account the results obtained for thread **2j**, the M062-2x functional provides the more confident results (Table S10). The functionals B3LYP and PBE0 predict l_{max} much higher than that experimentally observed.

Table S10. Pondered-average of l_{max} (nm) at SMD(CHCl3)/TD-DFT "Functional"/DGDZVP//SMD(CHCl3)/M06/DGDZVP computational level.

Entry		2j	3j	3k	3l	3m	3n
1	**Experimental**	*607*	*638*	*638*	*638*	*638*	*638*
2	**M06-2x**	610.8	630.8	636.9	624.8	615.5	614.2
3	**CAM-B3LYP**	605.2	623.8	628.1	617.7	608.0	604.3
4	**B3LYP**	661.8	786.1	692.5	682.0	674.1	673.0
5	**PBE0**	643.1	666.9	671.9	661.9	654.5	653.8

Computational Data

Table S11. Electronic ($E_{SCF,298,sol}$), Gibbs free ($G_{298,sol}$), and enthalpy ($H_{298,sol}$) energies for conformers of the systems **2j** and **3j-n** (in Hartree) computed at SMD(CHCl3)/M06/DGDZVP level. UV-vis absorption maxima lmax (nm) was calculated at the SMD(CHCl3)/TD-DFT M06-2x/DGDZVP//SMD(CHCl3)/M06/DGDZVP computational level. Pondered-average of λmax (nm) is shown in red.

Compound	$E_{SCF,298,sol}$	$G_{298,sol}$	$H_{298,sol}$	λmax (nm)
2j				
eje_tph_a_TD	-1750.0033417	-1749.7745080	-1749.6998730	615.2
eje_tph_b_TD	-1750.0033333	-1749.7747660	-1749.6999000	615.9
eje_tph_c_TD	-1750.0041923	-1749.7747640	-1749.7003590	610.9
eje_tph_d_TD	-1750.0042189	-1749.7742640	-1749.7002570	611.01
eje_tph_e_TD	-1750.0050544	-1749.7749010	-1749.7009460	606.0
eje_tph_f_TD	-1750.0050878	-1749.7748360	-1749.7009700	608.0
				610.8
3j				
rtx_tph_01_TD	-3505.3414044	-3504.6055480	-3504.4548390	628.0
rtx_tph_03_TD	-3505.3417006	-3504.6078900	-3504.4553820	631.5
rtx_tph_04_TD	-3505.3418461	-3504.6055950	-3504.4549310	628.4
rtx_tph_05_TD	-3505.3416508	-3504.6067090	-3504.4553290	629.0
rtx_tph_06_TD	-3505.3418311	-3504.6086480	-3504.4552030	630.9
				630.8
3k				
rtx_tph_tBu_01_TD	-3819.6383486	-3818.6923950	-3818.5166850	639.6
rtx_tph_tBu_03_TD	-3819.6400126	-3818.6888140	-3818.5177140	661.3
rtx_tph_tBu_06_TD	-3819.6405893	-3818.6927650	-3818.5191200	634.3
				636.9
3l				
rtx_tph_OMe_a_01_TD	-3734.3048643	-3733.5077950	-3733.3484600	598.5
rtx_tph_OMe_a_03_TD	-3734.3033993	-3733.5055540	-3733.3460480	613.6
rtx_tph_OMe_a_04_TD	-3734.3025954	-3733.5051220	-3733.3451540	616.4
rtx_tph_OMe_a_05_TD	-3734.3033997	-3733.5055290	-3733.3460490	613.6
rtx_tph_OMe_a_06_TD	-3734.3026855	-3733.5040660	-3733.3452290	609.5
rtx_tph_OMe_b_01_TD	-3734.3048645	-3733.5078170	-3733.3484640	598.6
rtx_tph_OMe_b_03_TD	-3734.3022900	-3733.5094330	-3733.3458790	636.0
rtx_tph_OMe_b_04_TD	-3734.3034214	-3733.5063490	-3733.3465240	608.9
rtx_tph_OMe_b_05_TD	-3734.3022897	-3733.5057340	-3733.3468300	636.0
rtx_tph_OMe_b_06_TD	-3734.3026098	-3733.5060270	-3733.3453300	620.2

rtx_tph_OMe_c_01_TD	-3734.3023844	-3733.5042530	-3733.3449150	615.6
rtx_tph_OMe_c_03_TD	-3734.3033975	-3733.5054540	-3733.3460360	613.6
rtx_tph_OMe_c_04_TD	-3734.3025553	-3733.5041960	-3733.3449240	625.7
rtx_tph_OMe_c_05_TD	-3734.3033977	-3733.5055910	-3733.3460440	613.6
rtx_tph_OMe_c_06_TD	-3734.3033862	-3733.5063290	-3733.3464450	610.2
				624.8
3m				
rtx_tph_Cl_01_TD	-4424.4035423	-4423.6902600	-4423.5341790	616.9
rtx_tph_Cl_03_TD	-4424.4030557	-4423.6919780	-4423.5334090	614.87
rtx_tph_Cl_04_TD	-4424.4039559	-4423.6911190	-4423.5345470	617.15
rtx_tph_Cl_05_TD	-4424.4030565	-4423.6918790	-4423.5334040	614.92
rtx_tph_Cl_06_TD	-4424.4039558	-4423.6909820	-4423.5345420	617.2
				615.6
3n				
rtx_tph_NO2_01_TD	-3914.2308488	-3913.4948960	-3913.3346930	620.86
rtx_tph_NO2_03_TD	-3914.2285225	-3913.4933410	-3913.3317360	600.77
rtx_tph_NO2_04_TD	-3914.2309817	-3913.4919470	-3913.3333120	596.67
rtx_tph_NO2_05_TD	-3914.2285231	-3913.4933620	-3913.3317590	600.82
rtx_tph_NO2_06_TD	-3914.2309820	-3913.4918720	-3913.3333000	596.63
				614.2

Cartesian Coordinates

Just the conformer of lowest energy is shown.

2j

C	-0.652036	-0.214271	0.016593
C	0.652036	0.214314	-0.016594
C	1.866092	-0.524121	0.039953
C	2.910169	0.369398	0.009073
N	2.421711	1.681090	-0.069506
C	1.033562	1.651830	-0.108041
O	0.315569	2.637375	-0.215701
C	3.165194	2.898148	-0.314488
H	3.948531	2.729873	-1.057814
H	3.610075	3.297794	0.601986
H	2.464615	3.639728	-0.704022
C	4.316901	0.059727	0.063253
C	5.382022	0.818116	0.503031
C	6.616562	0.124556	0.456285
C	6.487149	-1.150284	-0.023177
S	4.857941	-1.526016	-0.425263
H	7.263396	-1.891515	-0.172287
H	7.564206	0.550288	0.768636
H	5.280030	1.829352	0.882468
H	1.953780	-1.597352	0.152811
C	-1.866104	0.524155	-0.039921
C	-2.910167	-0.369377	-0.009094
N	-2.421696	-1.681079	0.069403
C	-1.033546	-1.651793	0.107954
O	-0.315548	-2.637327	0.215677
C	-3.165126	-2.898113	0.314709
H	-3.609933	-3.298056	-0.601674
H	-3.948513	-2.729672	1.057938
H	-2.464531	-3.639543	0.704502
C	-4.316905	-0.059712	-0.063310
C	-5.381923	-0.817965	-0.503572
C	-6.616499	-0.124475	-0.456720
C	-6.487209	1.150171	0.023292
S	-4.858047	1.525847	0.425633
H	-7.263511	1.891300	0.172621
H	-7.564088	-0.550116	-0.769366
H	-5.279811	-1.829048	-0.883392
H	-1.953830	1.597385	-0.152765

3j

S	-4.706415	-0.323250	-1.963335
O	1.366613	0.550966	-2.342385
N	-0.886970	0.639192	-2.823525
C	-0.362346	0.173883	-0.636253
C	0.187202	0.475883	-1.983499

C	-2.073923	0.437595	-2.098463
C	-1.777042	0.153700	-0.788287
H	-2.513407	0.004600	-0.009265
C	-3.379217	0.537999	-2.694409
C	-3.816272	1.283442	-3.771075
H	-3.167444	1.924265	-4.359426
C	-5.209807	1.169570	-3.992095
H	-5.744051	1.687129	-4.781692
C	-5.819529	0.335377	-3.093011
H	-6.866724	0.060837	-3.037694
C	-0.731161	0.757406	-4.259566
H	0.289703	0.462598	-4.510963
H	-0.887560	1.784910	-4.601275
S	3.841049	-1.691164	3.718008
O	-1.317381	-0.404327	2.161454
N	0.931801	-0.559909	2.649153
C	0.426744	-0.025285	0.472927
C	-0.134772	-0.349322	1.810129
C	2.123957	-0.354614	1.934859
C	1.841740	-0.028594	0.633197
H	2.597601	0.113138	-0.127437
C	3.436438	-0.495772	2.511733
C	4.560977	0.203305	2.127829
H	4.526988	1.006830	1.393887
C	5.733297	-0.211246	2.803795
H	6.712551	0.230495	2.650691
C	5.497616	-1.228429	3.688201
H	6.205684	-1.732462	4.335422
C	0.771408	-0.717896	4.081173
H	-0.261041	-0.464856	4.330860
H	0.957815	-1.747878	4.400965
O	-5.128465	-3.730147	1.005622
O	-4.900663	3.325174	2.401907
N	-3.119799	-2.693545	1.283779
H	-2.617335	-1.821702	1.433806
N	-2.958451	2.152842	2.194508
H	-2.512521	1.263996	1.977868
C	-1.416625	-3.376649	-1.184728
H	-2.450614	-3.347771	-1.530162
C	-0.373798	-3.187019	-2.088656
H	-0.595938	-3.011590	-3.141656
C	0.958424	-3.248503	-1.669097
C	1.221976	-3.465042	-0.313672
H	2.256310	-3.503912	0.031100
C	0.178104	-3.647686	0.591234
H	0.399607	-3.836622	1.642143
C	-1.153501	-3.625066	0.164660
C	-2.287253	-3.873699	1.127986
H	-2.935061	-4.679875	0.768053
H	-1.888089	-4.183628	2.102902
C	-4.476936	-2.705934	1.217202
C	-5.145665	-1.368186	1.356269
C	-6.465050	-1.233918	0.917742
H	-6.991112	-2.115211	0.558271
C	-7.080508	0.015114	0.925976
H	-8.107520	0.113528	0.584286
C	-6.379024	1.143793	1.343251
H	-6.839524	2.128413	1.322196
C	-5.061407	1.023190	1.790872
C	-4.474052	-0.241728	1.830010
H	-3.486785	-0.354960	2.265093
C	-4.312283	2.268084	2.169807
C	-2.061849	3.238233	2.546306
H	-1.663001	3.084449	3.558190
H	-2.661414	4.154654	2.569657
O	5.155182	3.795137	-0.839316
O	4.909749	-3.246836	-2.321217
N	3.168277	2.825564	-1.382801
H	2.661832	1.971118	-1.604048
N	2.986277	-2.026932	-2.315963
H	2.542488	-1.130027	-2.131668
C	1.455641	3.489292	1.097883
H	2.487127	3.448336	1.450686
C	0.405465	3.296678	1.992908
H	0.619403	3.109304	3.045424
C	-0.923772	3.370796	1.565287
C	-1.176127	3.600611	0.210112
H	-2.207247	3.646737	-0.141430
C	-0.125179	3.787513	-0.685472
H	-0.338000	3.985445	-1.736151
C	1.203092	3.754284	-0.250483
C	2.343282	4.008250	-1.205401
H	2.997089	4.801822	-0.829541
H	1.950814	4.336520	-2.176412
C	4.510155	2.798795	-1.171082
C	5.167637	1.453385	-1.299552
C	6.456014	1.294705	-0.781982
H	6.970638	2.164411	-0.380390
C	7.054276	0.037595	-0.767576
H	8.057435	-0.078794	-0.366072
C	6.360307	-1.077388	-1.229875
H	6.800836	-2.070176	-1.183462
C	5.074385	-0.934065	-1.756158
C	4.511592	0.340694	-1.826966
H	3.553314	0.470830	-2.318489
C	4.329038	-2.171241	-2.168501
C	2.088557	-3.113463	-2.659351
H	1.681546	-2.957129	-3.667304
H	2.689956	-4.028363	-2.688449
H	1.439886	-0.039662	4.617668
H	-1.427958	0.090114	-4.772370

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S	4.566218	-1.873213	1.334676
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C	-0.182226	-0.660477	1.968039
C	2.066722	-0.929815	1.973233
C	1.770696	-0.425123	0.732015
H	2.505864	-0.192555	-0.027334
C	3.355128	-1.335419	2.469255
C	3.847687	-1.366634	3.757863
H	3.276701	-1.047617	4.623830
C	5.189090	-1.812196	3.826673
H	5.754474	-1.899446	4.748330
C	5.703868	-2.125421	2.596674
H	6.690069	-2.510131	2.364245
C	0.721952	-1.716463	4.010458
H	-0.331460	-1.983998	4.112905

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C	0.119197	0.710773	-1.666925
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H	-2.576126	0.213293	0.311374
C	-3.440788	1.306478	-2.162986
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H	-4.311110	2.109518	-0.348196
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H	-6.314473	1.693975	-4.192343
C	-0.802687	1.744259	-3.716965
H	0.258388	1.963982	-3.850599
H	-1.129787	1.114512	-4.549788
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C	1.568709	-3.531136	-0.952522
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C	0.548472	-3.849579	-0.059505
H	0.793422	-4.305356	0.900531
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C	-1.080385	-3.017588	-1.618012
H	-2.119060	-2.819555	-1.885210
C	-0.057785	-2.688980	-2.505786
H	-0.300894	-2.236116	-3.467439
C	1.278588	-2.953401	-2.190447
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H	3.075737	-3.453532	-3.275541
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C	4.529981	-1.549553	-2.450241
C	5.152833	-0.334648	-1.820882
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C	7.089627	0.620302	-0.679261
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H	1.577611	4.471412	-1.209367
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H	-6.617179	-2.519163	-0.292196
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H	-1.466819	-4.364821	1.504062
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C	-8.448908	-0.494533	-0.076758
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C	-9.277023	-1.599558	0.590287
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H	-9.440639	-0.690931	-1.993938
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H	-10.304292	-1.585321	0.204707
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C	8.540296	0.470176	-0.229275
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C	8.641554	-0.689743	0.766811
C	9.426588	0.176059	-1.444413
H	9.032598	2.601652	-0.212417
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H	8.313921	-1.638999	0.325371
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H	8.025438	-0.493401	1.654734
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C	1.761048	-0.351272	0.722576
H	2.494997	0.029492	0.024637
C	3.364018	-1.040832	2.533436
C	3.777405	-1.034830	3.850435
H	3.101395	-0.915869	4.691081
C	5.182505	-1.142739	3.987159
H	5.702475	-1.142862	4.939165
C	5.823889	-1.239127	2.780710
H	6.887448	-1.341440	2.596164
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H	-0.268413	-2.366160	3.901864
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C	-5.769862	1.266506	-2.404168
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H	-6.183379	3.177174	-3.435642
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O	5.092646	-2.453069	-3.056127
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N	3.089977	-1.468011	-2.597051
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H	-0.435645	-2.249461	-3.617606
C	1.118013	-2.886494	-2.269113
C	2.250667	-2.496286	-3.186237
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C	6.356815	1.620003	-0.374123
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H	3.484574	1.007497	-2.062534
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H	-2.469199	3.458134	0.828344
C	-0.392283	3.728627	0.310129
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C	0.941636	3.579708	0.703169
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H	2.245948	2.837989	2.247538
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C	-4.519122	-0.922537	1.647649
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H	-1.724865	-4.680424	1.181627
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H	6.688145	-0.136639	-2.775464
C	5.602195	-1.980537	-3.088123
H	6.352554	-2.649733	-3.492564
C	0.870334	-1.713066	-3.726991
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H	1.554583	-1.213904	-4.417851
O	-5.072590	2.617490	-2.934384
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H	2.347690	3.170220	-2.155608
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C	-1.063220	3.055846	-2.099353
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H	-6.936191	1.530853	-1.618566
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C	-6.329024	-1.671733	-0.587653
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H	-1.537482	-4.493686	-1.388552
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N	2.944878	-1.338155	2.779756
H	2.511980	-0.509200	2.378235
N	3.145859	3.136840	0.745963
H	2.647850	2.367742	1.190898
C	1.355203	-3.239482	1.076190
H	2.413579	-3.306652	0.819932
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H	0.700544	-4.065700	-0.801156
C	-0.969861	-3.596228	0.477378
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H	-2.404430	-2.993601	1.966207
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H	-0.690389	-2.240591	3.591596
C	0.979982	-2.736416	2.324886
C	2.026898	-2.319220	3.328316
H	2.627452	-3.178547	3.644392
H	1.542576	-1.908401	4.223239
C	4.270170	-1.568727	2.591922
C	5.015390	-0.479594	1.872304
C	6.252730	-0.794687	1.310398
H	6.676415	-1.785044	1.458053
C	6.913958	0.170089	0.560682
C	6.355706	1.416766	0.308295
H	6.858322	2.142298	-0.327482
C	5.113644	1.728255	0.863764
C	4.483479	0.795766	1.686245
H	3.567103	1.066691	2.199211
C	4.464860	3.021964	0.449279
C	2.314057	4.256262	0.334957
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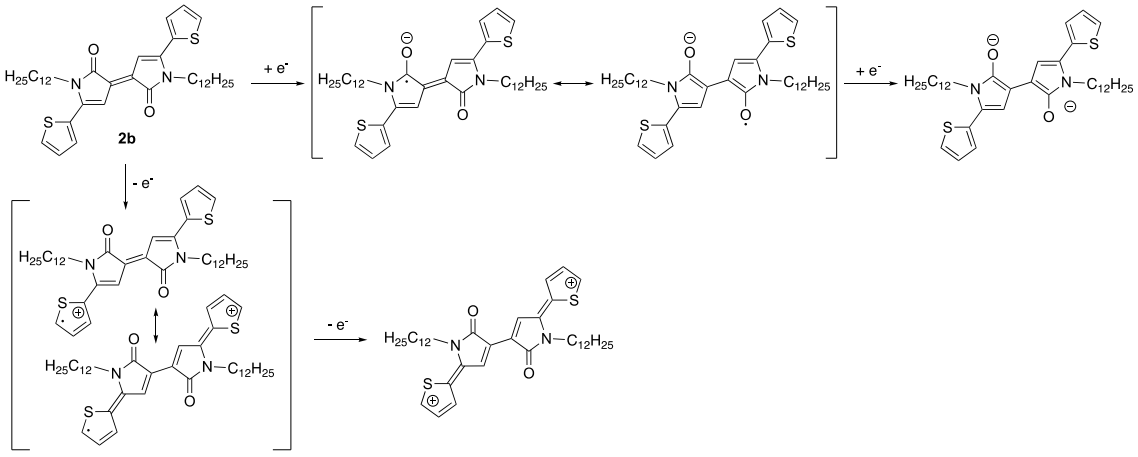
H	-4.260247	1.783154	1.466709
C	-5.906887	0.612165	2.391015
H	-6.719870	1.328267	2.322271
C	-6.047718	-0.631785	2.943195
H	-6.938842	-1.080429	3.367132
C	-1.397022	-1.206650	3.900101
H	-0.381285	-1.224603	4.299506
H	-1.829936	-2.205656	4.008904
S	4.587905	1.452865	-2.957043
O	-0.978506	0.924598	-2.301836
N	1.320999	0.808391	-2.496918
C	0.462147	0.092757	-0.491636
C	0.130806	0.665869	-1.825855

C	2.356393	0.264966	-1.714889
C	1.860653	-0.171056	-0.516715
H	2.461277	-0.596908	0.273347
C	3.726619	0.164197	-2.155365
C	4.562132	-0.905375	-1.917988
H	4.215165	-1.819716	-1.440286
C	5.881259	-0.697938	-2.392620
H	6.679052	-1.430445	-2.319792
C	6.044540	0.534506	-2.964194
H	6.941864	0.958125	-3.400749
C	1.397531	1.211858	-3.887125
H	0.379485	1.256558	-4.278496
H	1.852964	2.201171	-3.993307
O	-5.142119	3.637398	-1.086905
O	-4.161666	-3.332852	-2.547150
N	-3.094633	2.945771	-1.809590
H	-2.493695	2.153258	-2.029719
N	-2.344539	-1.957319	-2.489152
H	-1.985687	-1.037210	-2.240818
C	-1.833843	3.764088	0.928186
H	-2.896597	3.877552	1.144087
C	-0.943634	3.447810	1.950867
H	-1.314714	3.308990	2.966257
C	0.423200	3.310568	1.692834
C	0.878429	3.500036	0.384739
H	1.943409	3.410681	0.166300
C	-0.016061	3.802230	-0.640532
H	0.352411	3.939812	-1.657761
C	-1.383665	3.934902	-0.382816
C	-2.375398	4.175919	-1.494545
H	-3.119680	4.925187	-1.210750
H	-1.863134	4.531367	-2.395731
C	-4.398097	2.745200	-1.493242
C	-4.890800	1.323746	-1.587760
C	-6.113639	1.038660	-0.985398
H	-6.716063	1.845149	-0.576352
C	-6.518751	-0.285549	-0.883807
C	-5.744962	-1.341540	-1.345012
H	-6.066822	-2.371714	-1.221106
C	-4.530355	-1.055657	-1.962758
C	-4.134543	0.274162	-2.114185
H	-3.213248	0.488150	-2.649330
C	-3.672178	-2.218619	-2.372848
C	-1.365751	-2.977792	-2.819366
H	-0.798807	-2.662290	-3.703960
H	-1.929096	-3.874597	-3.097988
O	5.139911	-3.630238	1.115032
O	4.173388	3.352496	2.524066
N	3.092330	-2.928177	1.827250
H	2.493886	-2.132682	2.043452
N	2.353812	1.979660	2.490087
H	1.991265	1.058129	2.252386
C	1.842515	-3.717349	-0.909938
H	2.909298	-3.809464	-1.117562
C	0.956955	-3.400381	-1.936352
H	1.334988	-3.242733	-2.946539
C	-0.413702	-3.284321	-1.688591
C	-0.877403	-3.493857	-0.386521
H	-1.945100	-3.418955	-0.175794
C	0.012207	-3.797419	0.642621
H	-0.362959	-3.951697	1.654933
C	1.383349	-3.910824	0.394787
C	2.368885	-4.155341	1.511383
H	3.110884	-4.908577	1.231968
H	1.850752	-4.507446	2.410506
C	4.397229	-2.733381	1.513307
C	4.891797	-1.311958	1.596758
C	6.110623	-1.032338	0.983903
H	6.709882	-1.842606	0.577758
C	6.514979	0.290817	0.867650
C	5.745092	1.350701	1.326398
H	6.066143	2.379756	1.191641
C	4.535042	1.070330	1.955669
C	4.139300	-0.258045	2.119934
H	3.221090	-0.467597	2.662177
C	3.681088	2.237559	2.362450
C	1.380238	3.005222	2.819831
H	0.816642	2.695979	3.708688
H	1.948176	3.901289	3.091466
H	1.969118	0.483059	-4.467993
H	-1.990937	-0.488755	4.471873
N	7.774050	0.583992	0.172175
O	8.482582	-0.360245	-0.156318
O	8.045681	1.757524	-0.051443
N	-7.784062	-0.585291	-0.202566
O	-8.060519	-1.761084	0.002311
O	-8.493003	0.356079	0.133402

11. Electrochemical analysis of aza-Pechmann dyes 2b-c and rotaxanes 3b-c,f-i

The electrochemical properties of free dyes **2b-c** and rotaxanes **3b-c,f-i** (conc. aprox. 0.1 mM) at 25 ºC have been studied by cyclic voltammetry (CV) in dichloromethane (DCM)/Bu_4NPF_6 ($TBAPF_6$) (0.1 M). The peak potentials (summarized in Table 1 in the main text) are quoted with respect to the *Ag/Ag$^+$(sat)* reference electrode, when a Pt wire was used as the working and as the auxiliary electrode. The band gaps are determined from the difference between the energy of the LUMO levels (electron affinity) estimated from the first onset reduction potential (E^{red1}_{onset}) and the HOMO levels energy (ionization potential) estimated from the onset potential value (E^{ox}_{onset}) of the first anodic peak in the cyclic voltammograms (that is not reversible under these experimental conditions), applying the following equations[20]: LUMO= -(*Epc$_1$* + 4.41) eV, HOMO= -(*E^{ox}onset* + 4.41) eV.



Scheme S2. Mechanism of electroreduction and electrooxidation of **2b** to give the corresponding dianions or dications.

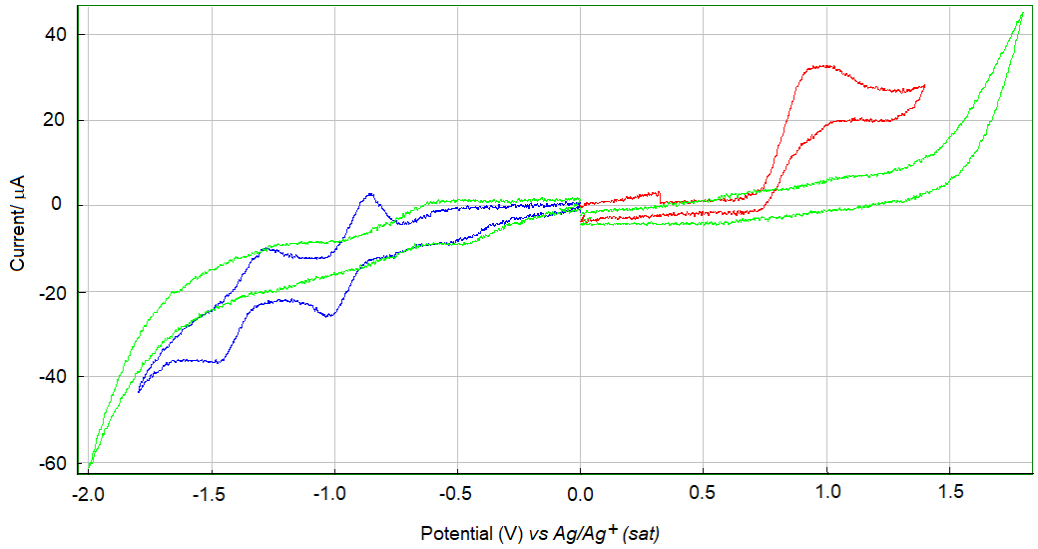


Figure S60. Cyclic voltammetry (cathodic-blue and anodic-red scans) of **2b** in DCM-$TBAPF_6$ as SSE (green curves). Scan rate: 50mV/s.

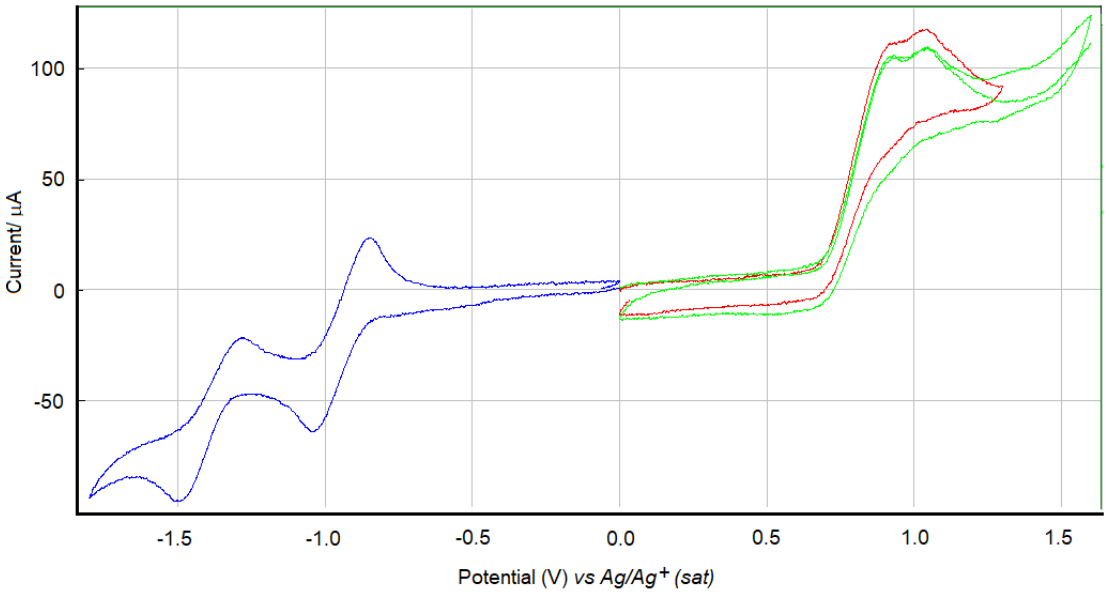


Figure S61. Cyclic voltammetry of **2c** in DCM-$TBAPF_6$-50mV/s.

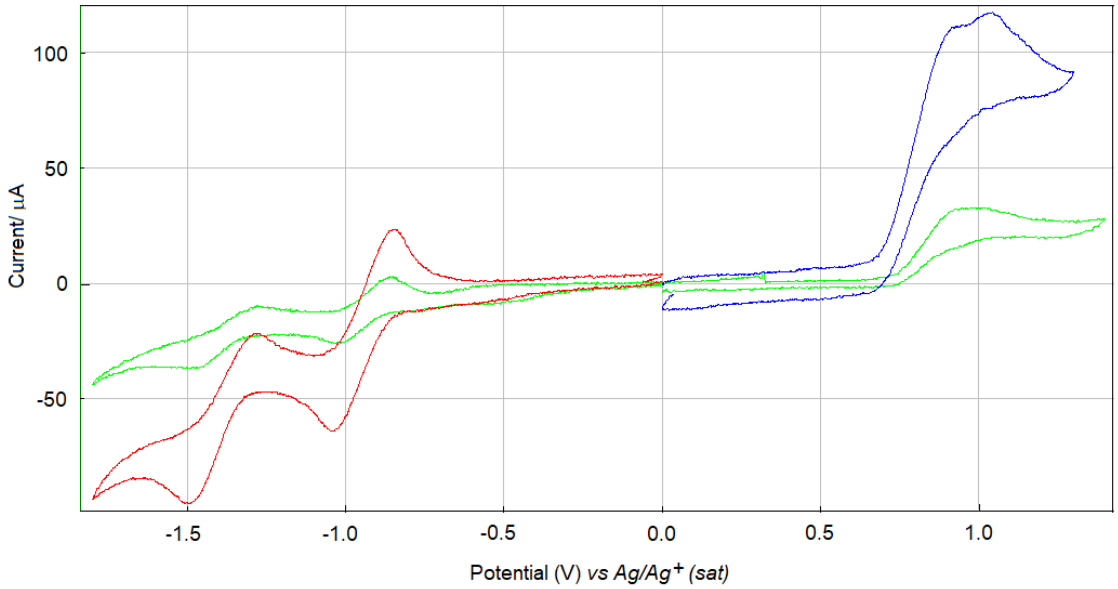


Figure S62. Cyclic voltammetry of **2b** (green) and **2c** (red and blue).

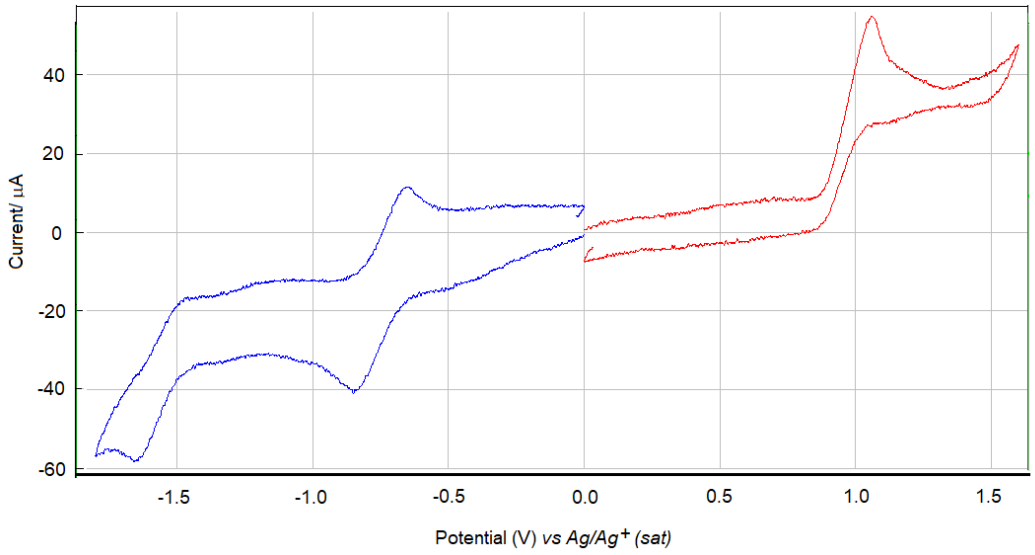


Figure S63. Cyclic voltammetry of **3c** in DCM-TBAPF$_6$-50mV/s/s-0+1600.

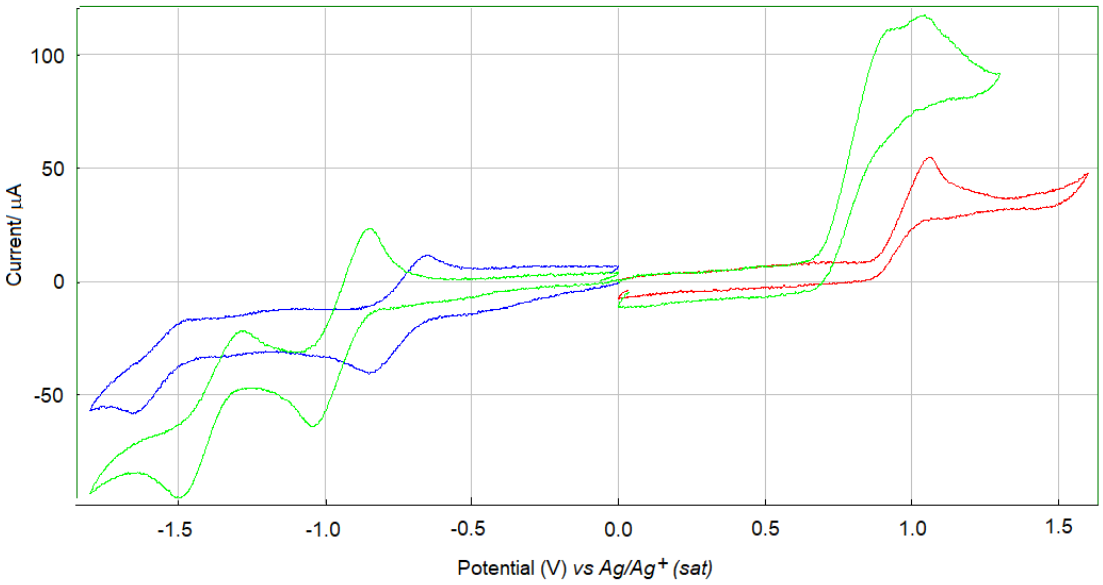


Figure S64. Cyclic voltammetry of **2c** (green) and **3c** (blue and red).

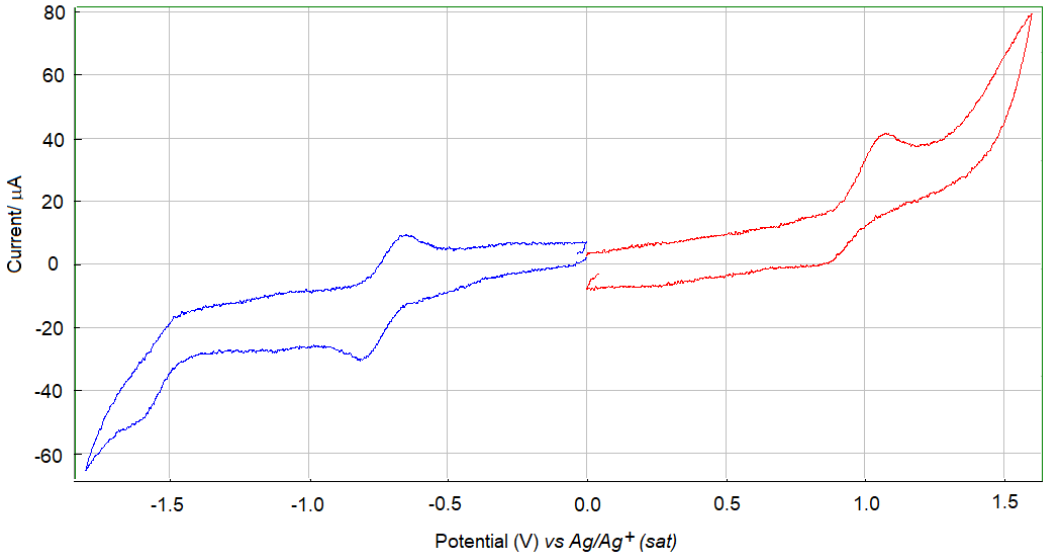


Figure S65. Cyclic voltammetry of **3b** in DCM-TBAPF$_6$-50mV/s/s-0+1600.

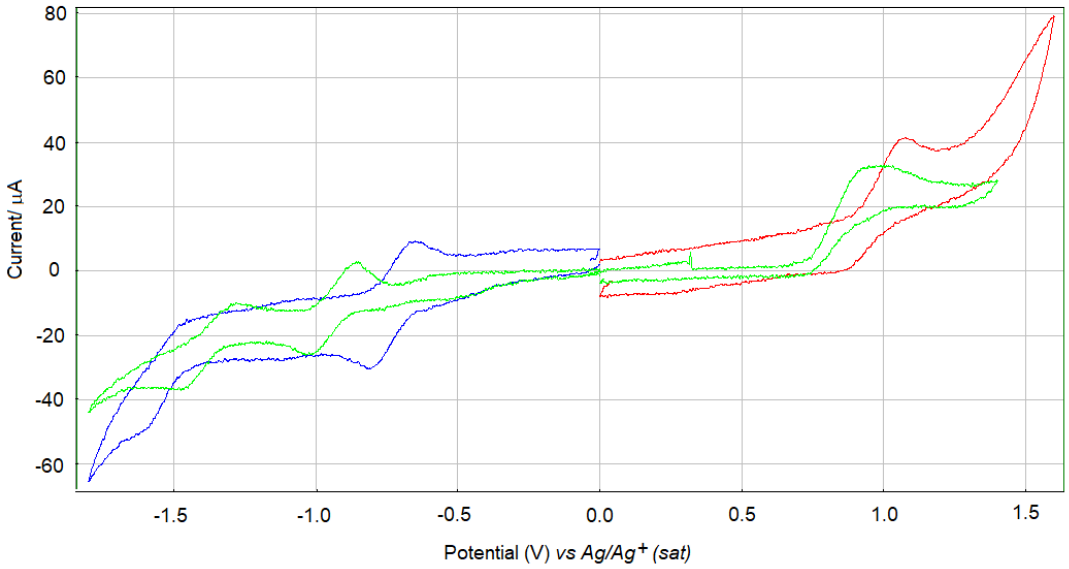


Figure S66. Cyclic voltammetry of **2b** (green) and **3b** (blue and red).

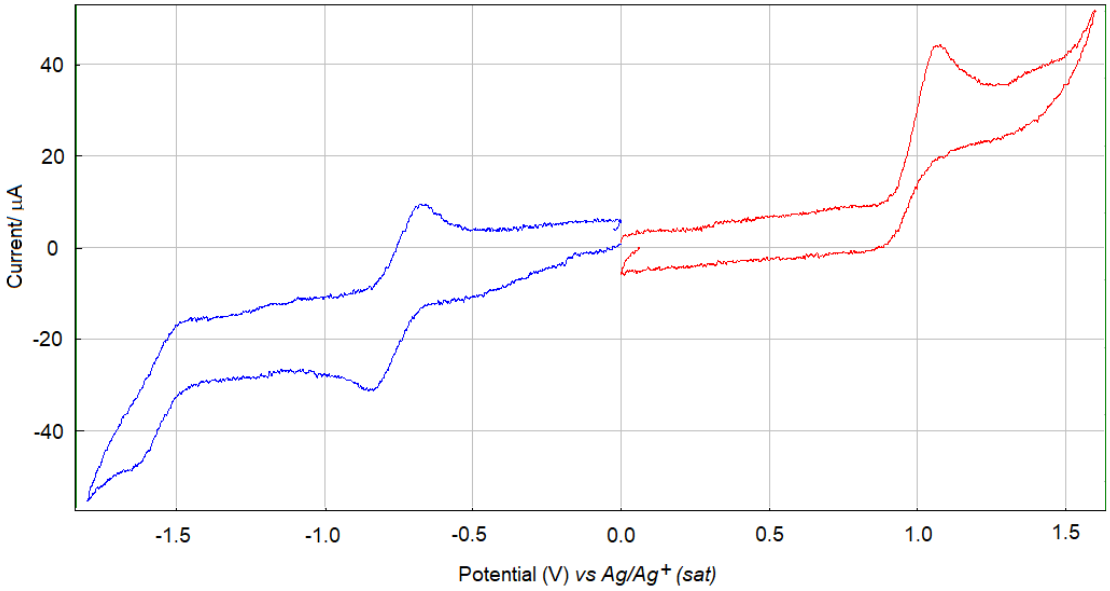


Figure S67. Cyclic voltammetry of **3f** in DCM-TBAPF$_6$-50mV/s/s-0+1600.

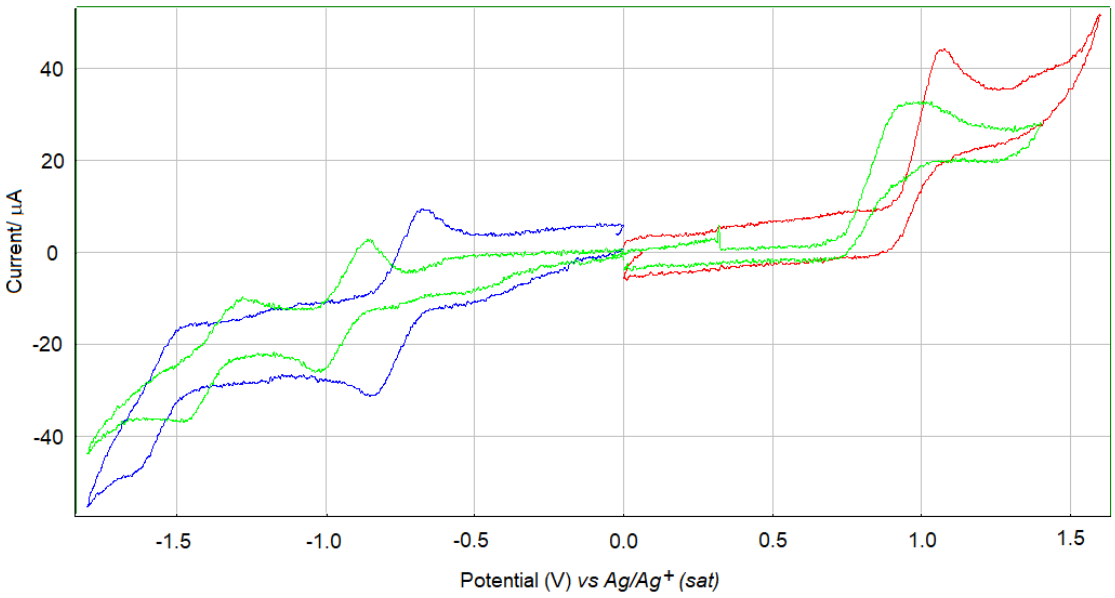


Figure S68. Cyclic voltammetry of **2b** (green) and **3f** (blue and red).

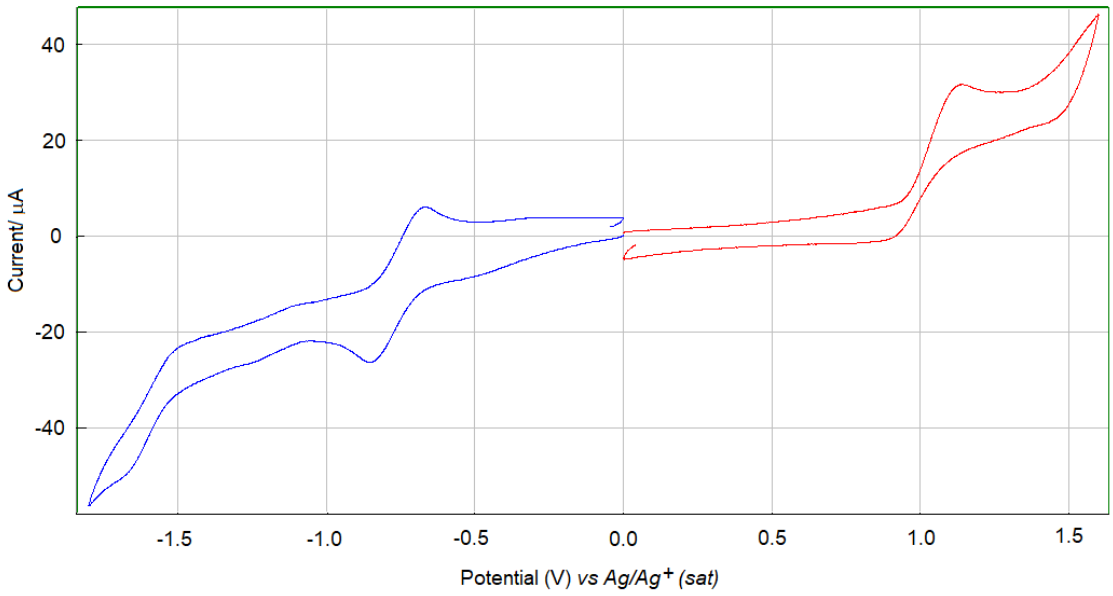


Figure S69. Cyclic voltammetry of **3g** in DCM-TBAPF$_6$-50mV/s/s-0+1600.

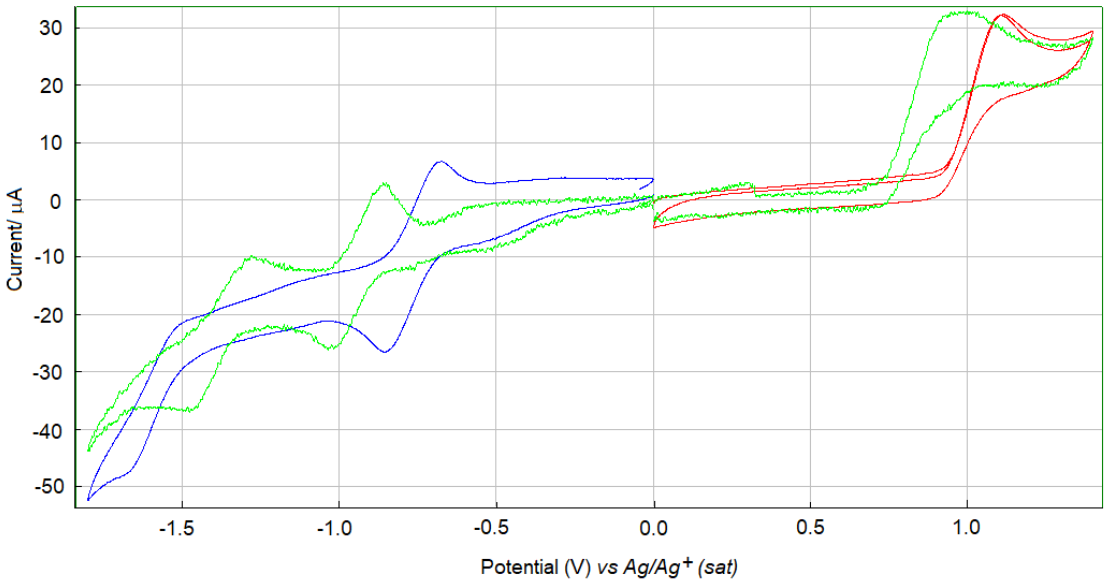


Figure S70. Cyclic voltammetry of **2b** (green) and **3g** (blue and red).

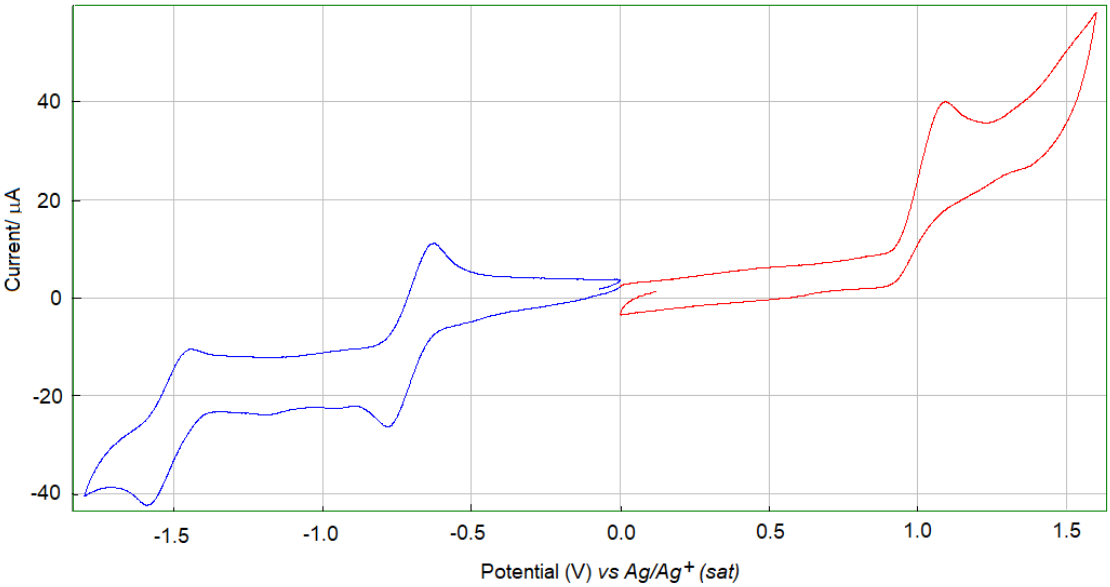


Figure S71. Cyclic voltammetry of **3h** in DCM-TBAPF$_6$-50mV/s/s-0+1400.

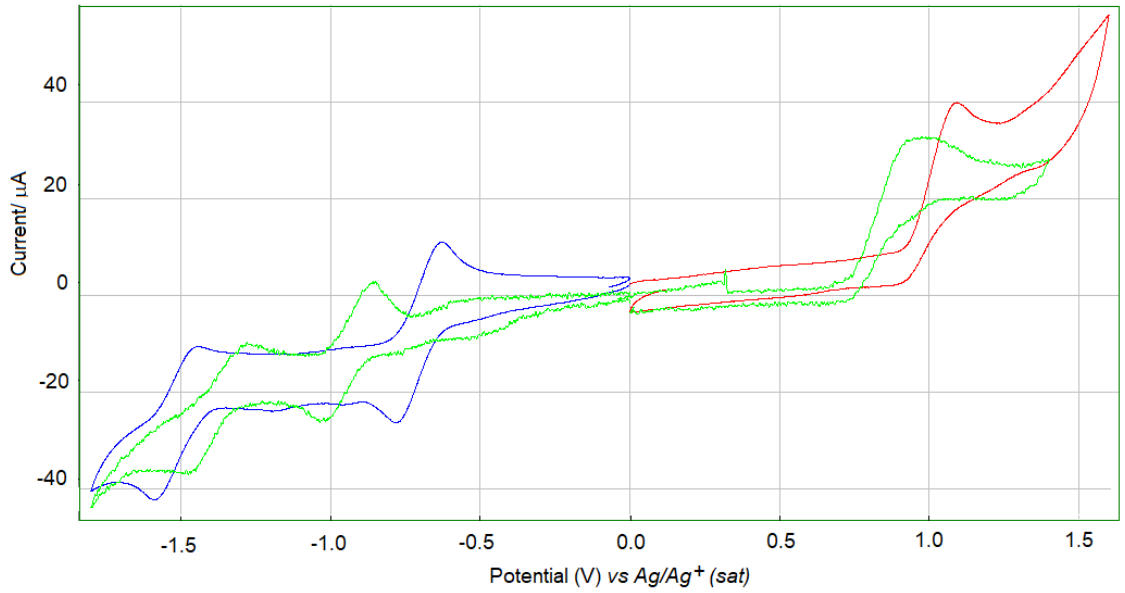


Figure S72. Cyclic voltammetry of **2b** (green) and **3h** (blue and red).

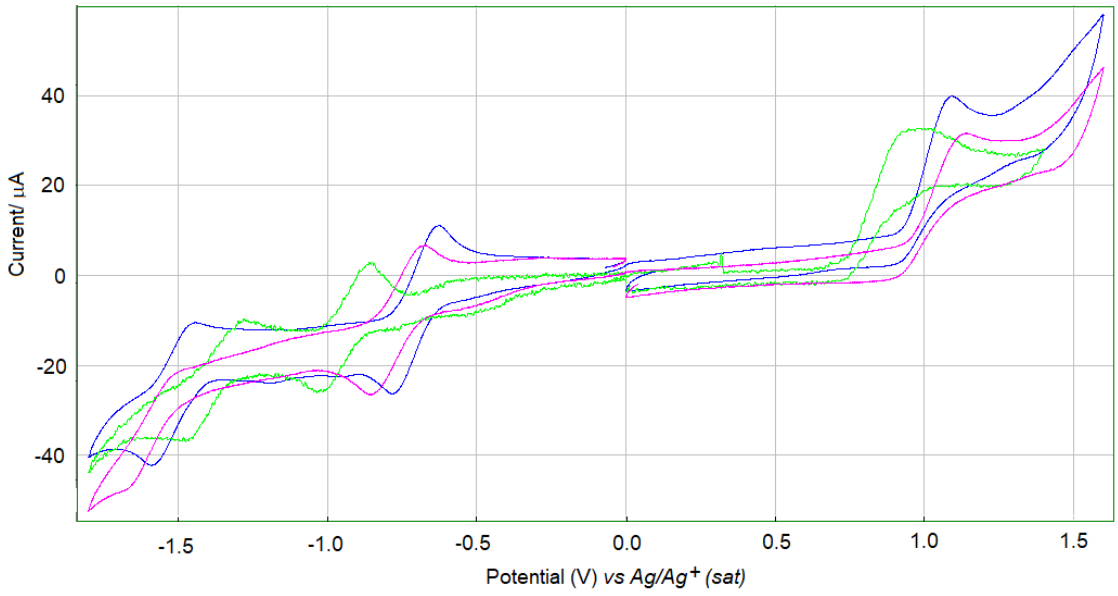


Figure S73. Cyclic voltammetry of **2b** (green), **3g** (pink) and **3h** (blue).

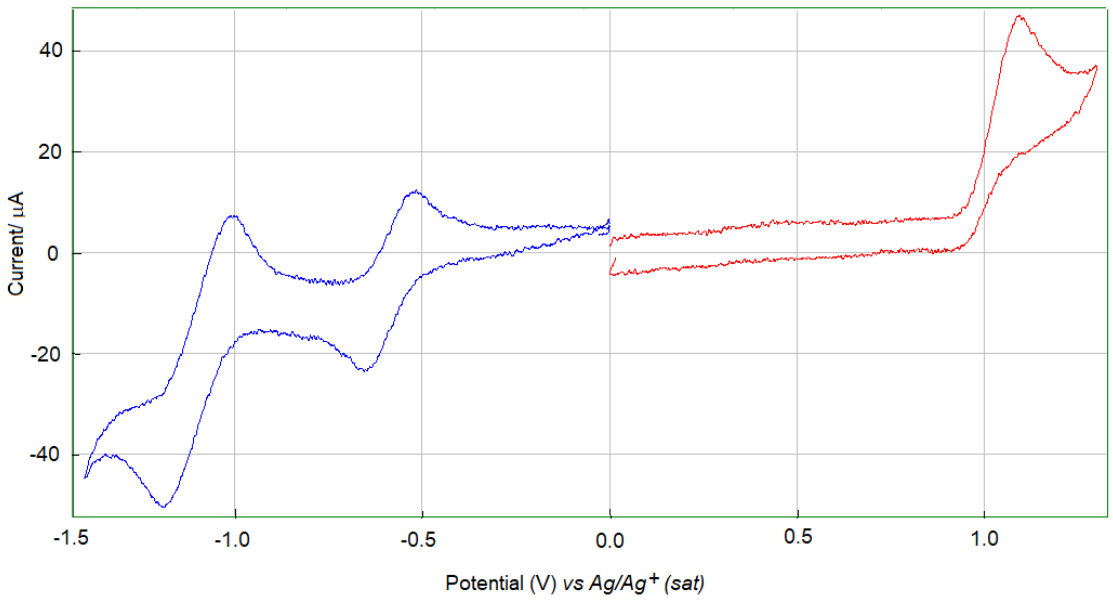


Figure S74. Cyclic voltammetry of **3i** in DCM-TBAPF$_6$-50mV/s(Pt/Pt).

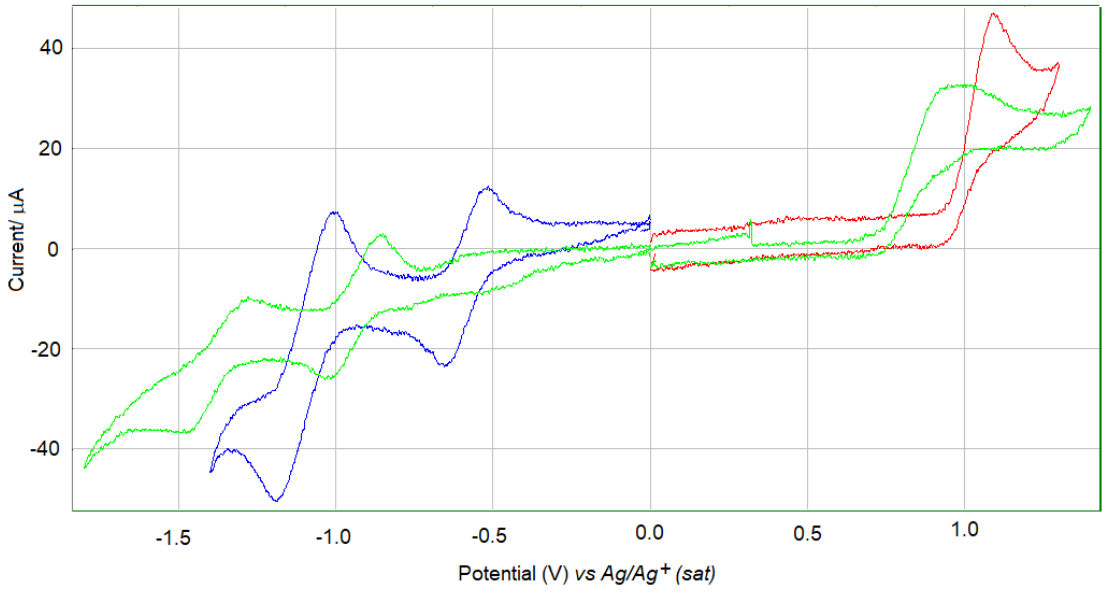


Figure S75. Cyclic voltammetry of **2b** (green) and **3i** (blue and red).

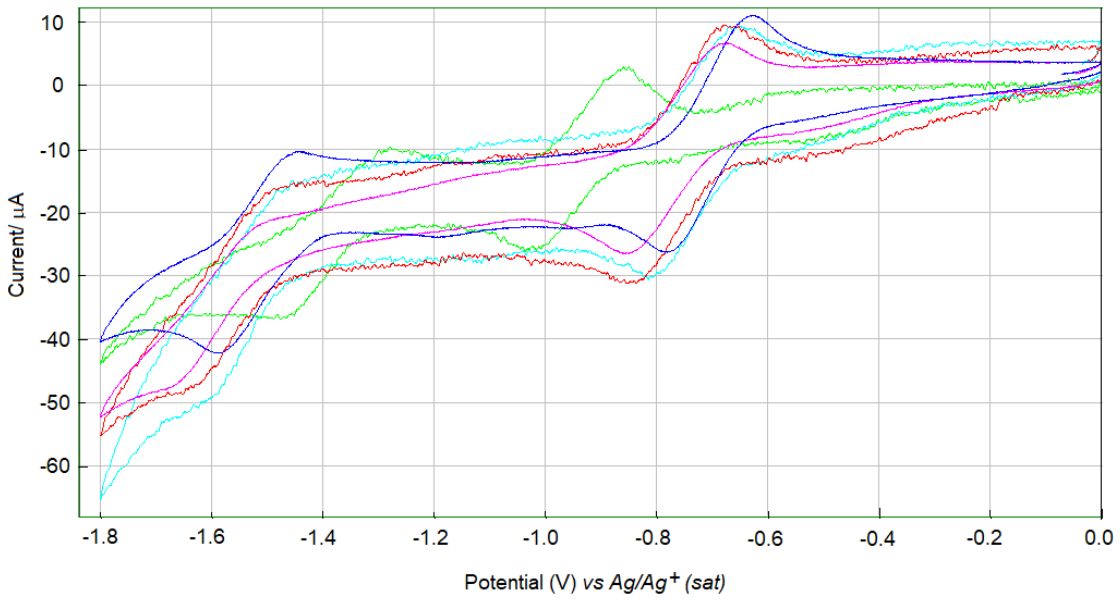


Figure S76. Cyclic voltammetry (catodic) of **3b** (light blue), **3f** (red), **3g** (pink), **3h** (dark blue), and **3i** (green).

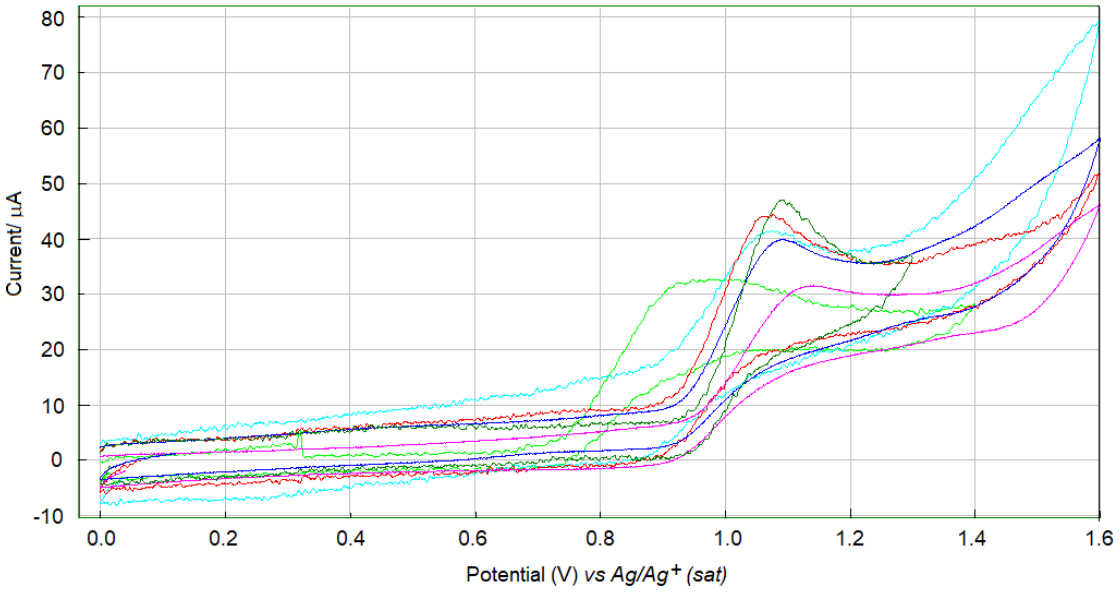
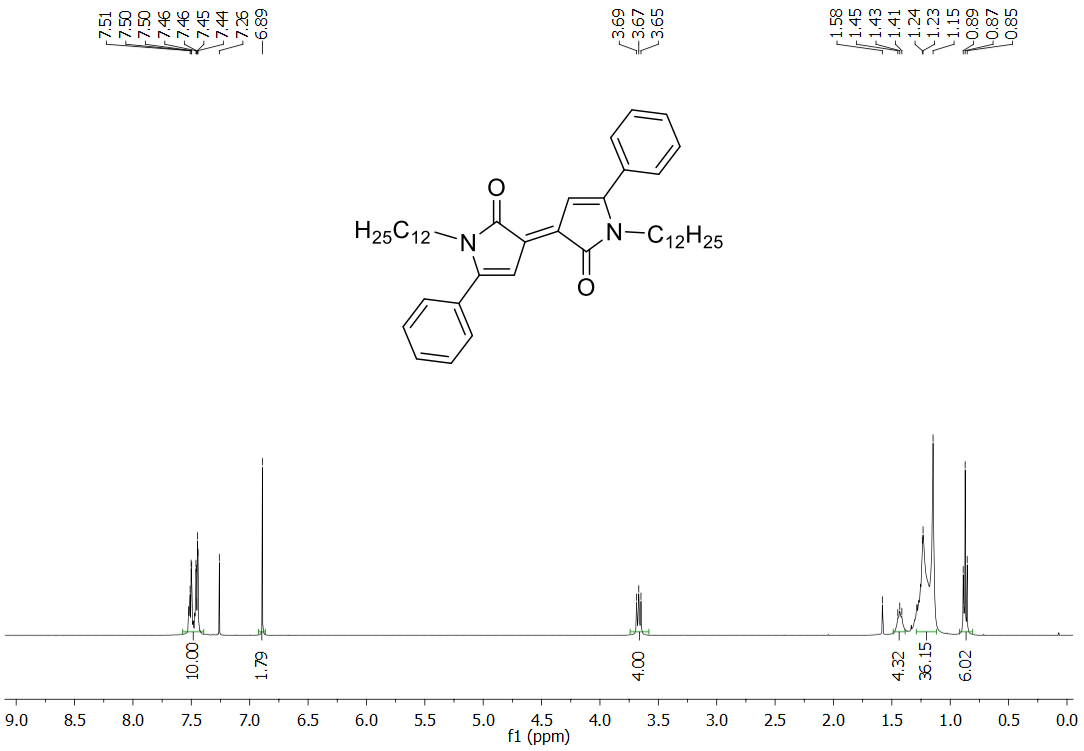


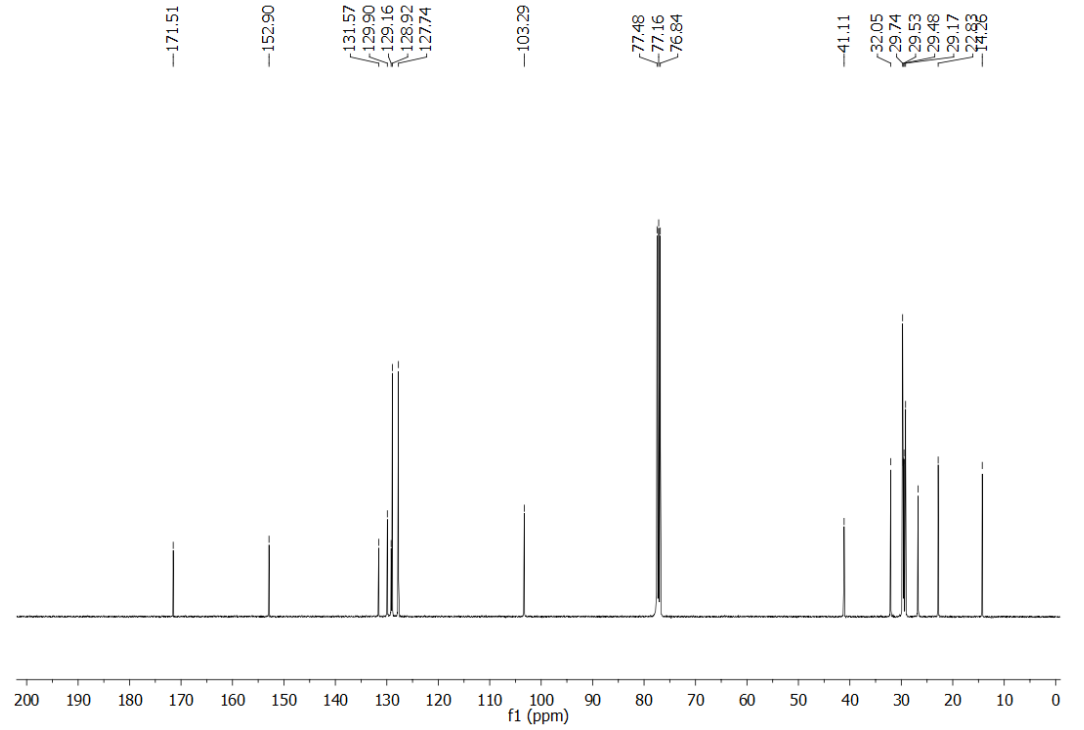
Figure S77. Cyclic voltammetry (anodic) of **3b** (light blue), **3f** (red), **3g** (pink), **3h** (dark blue), and **3i** (green).

12. ^{1}H and ^{13}C NMR spectra of all new synthesized compounds (HMBC, HSQC, COSY, NOESY and DOSY of selected compounds are also included)

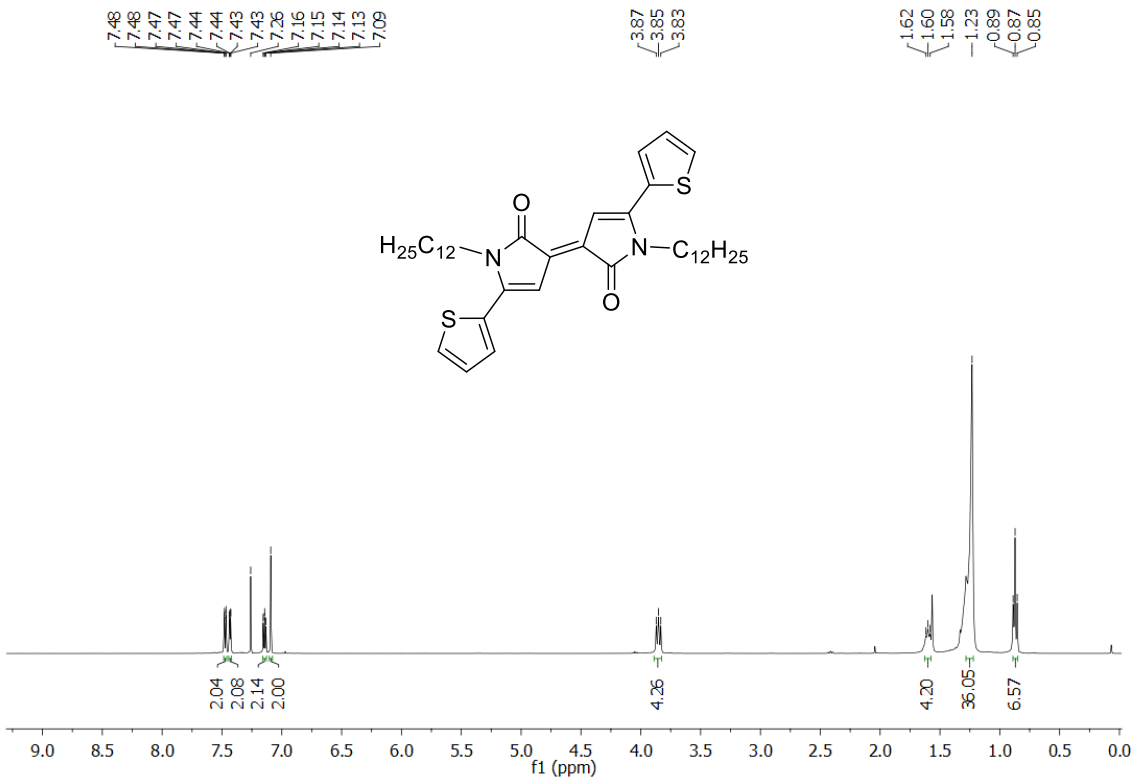
Thread **2a** (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



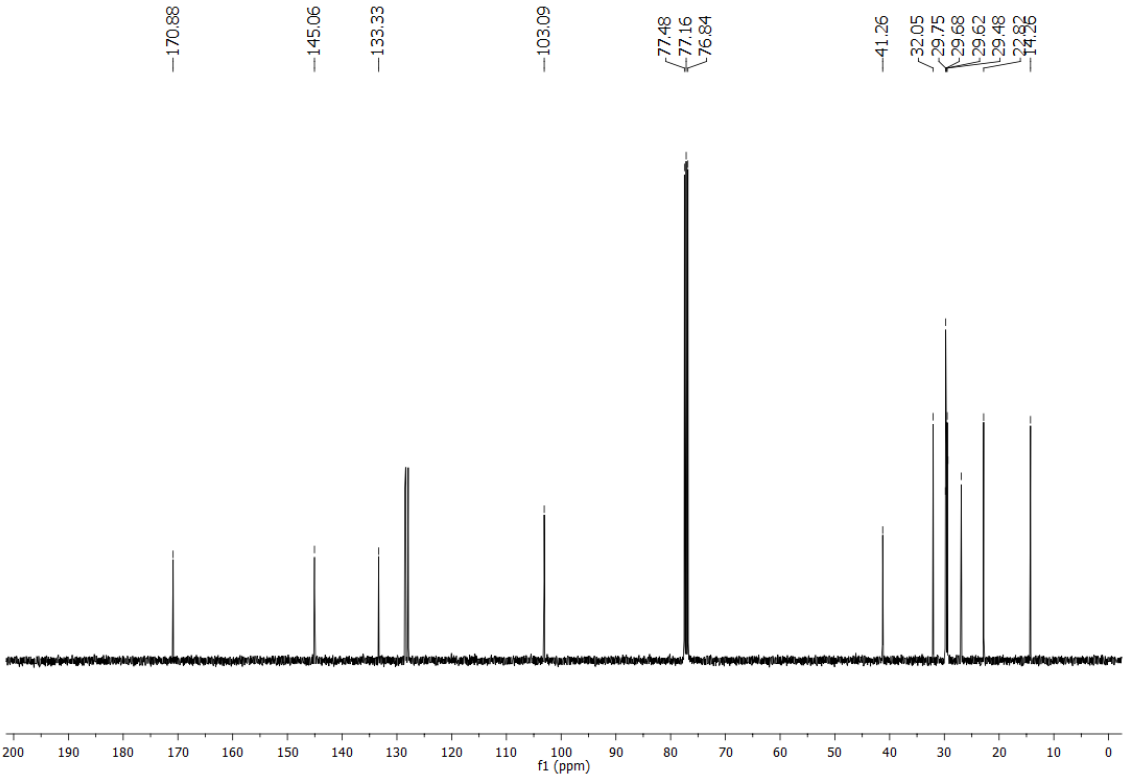
Thread **2a** (^{13}C RMN, 100 MHz, $CDCl_3$, 298 K)



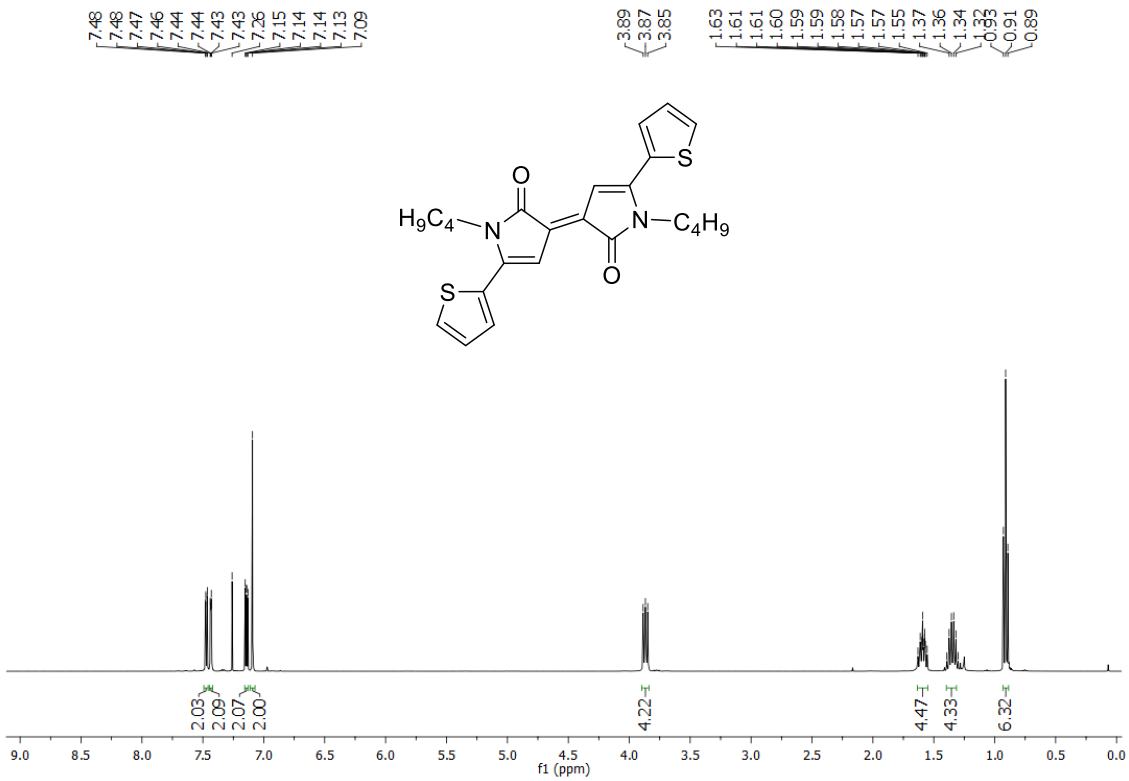
Thread **2b** (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



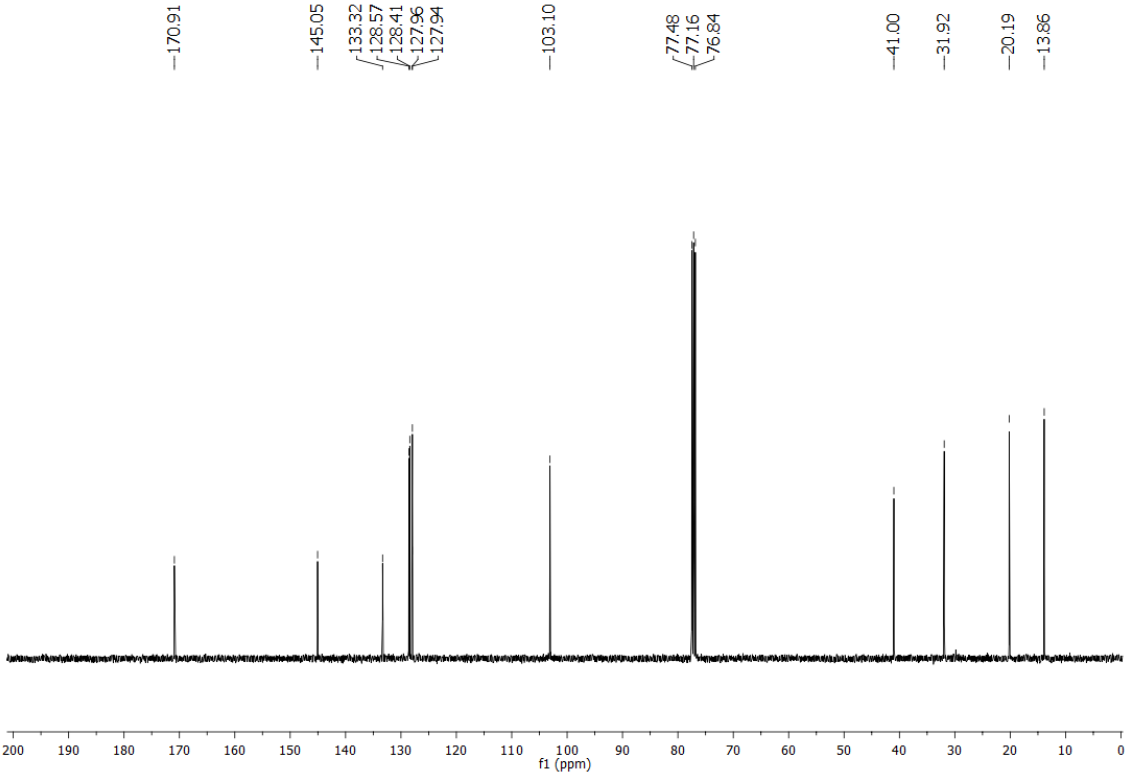
Thread **2b** (^{13}C RMN, 100 MHz, $CDCl_3$, 298 K)



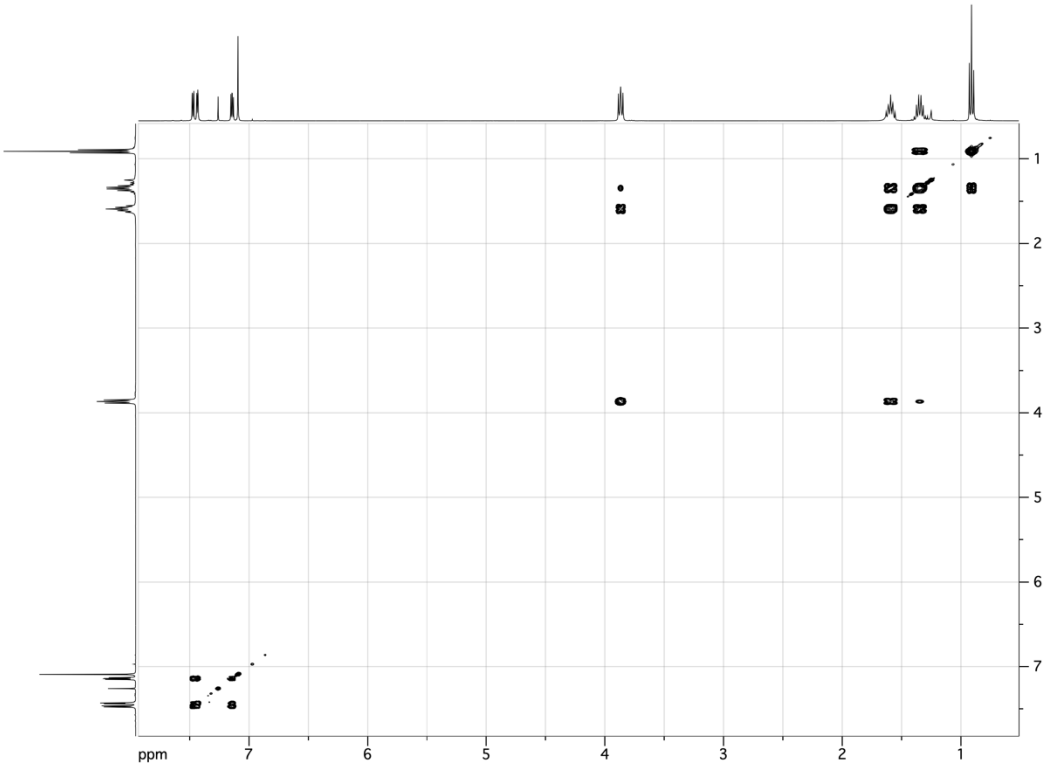
Thread **2c** (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



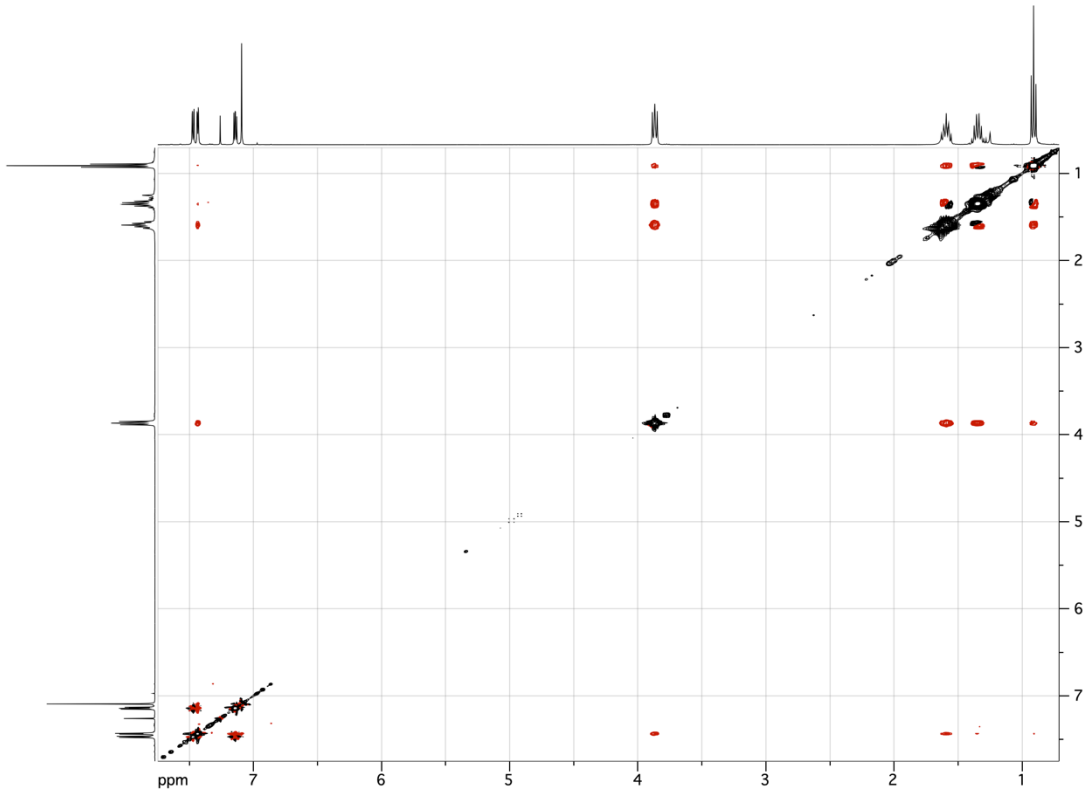
Thread **2c** (^{13}C RMN, 100 MHz, $CDCl_3$, 298 K)



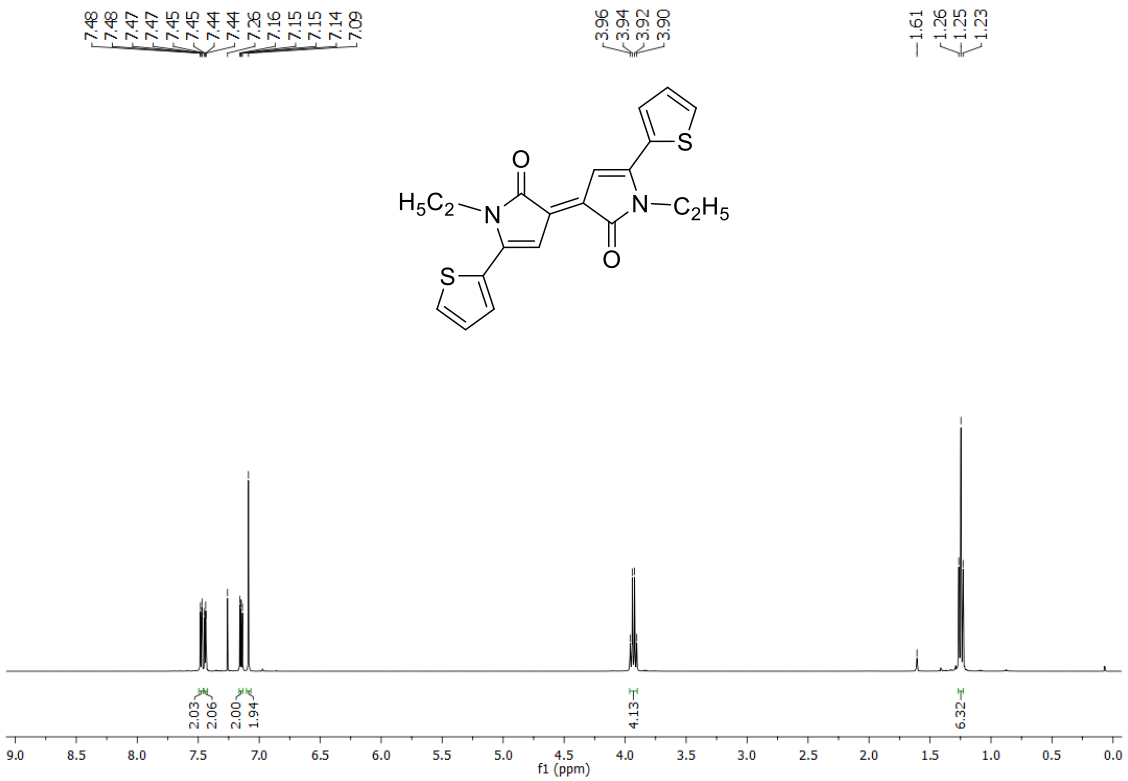
Thread **2c** (^{1}H,^{1}H-COSY, 400 MHz, $CDCl_3$, 298 K)



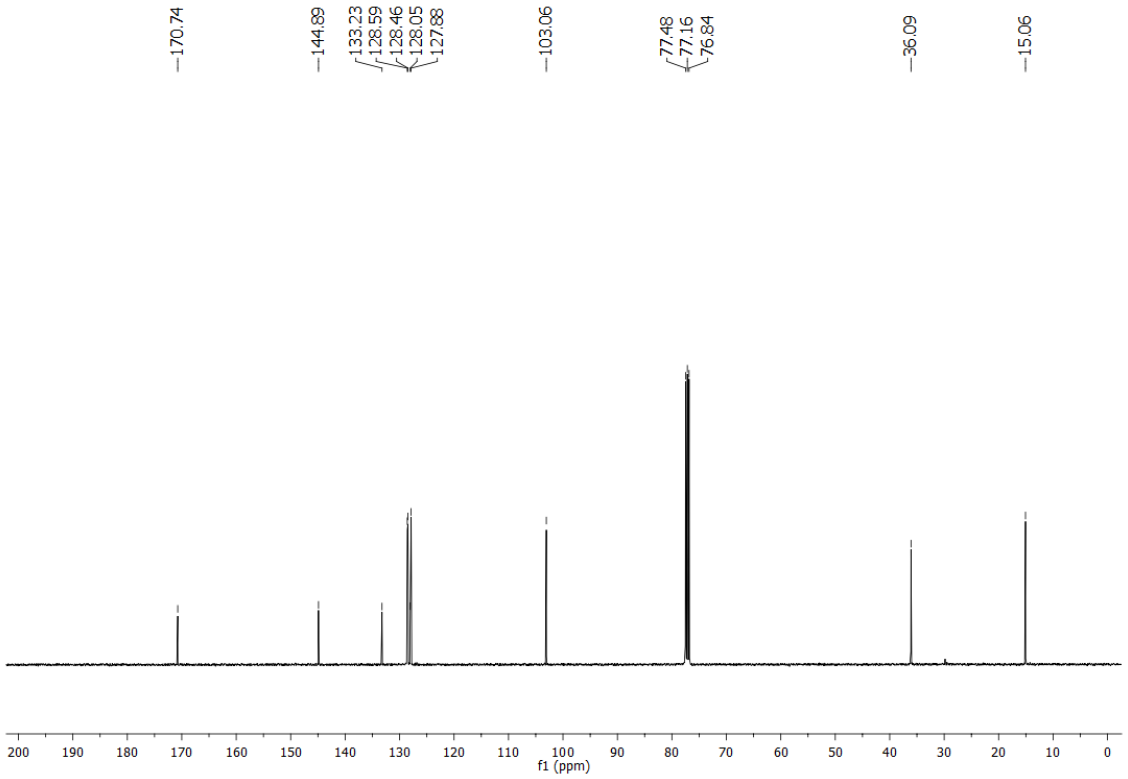
Thread **2c** (^{1}H,^{1}H-NOESY, 400 MHz, $CDCl_3$, 298 K)



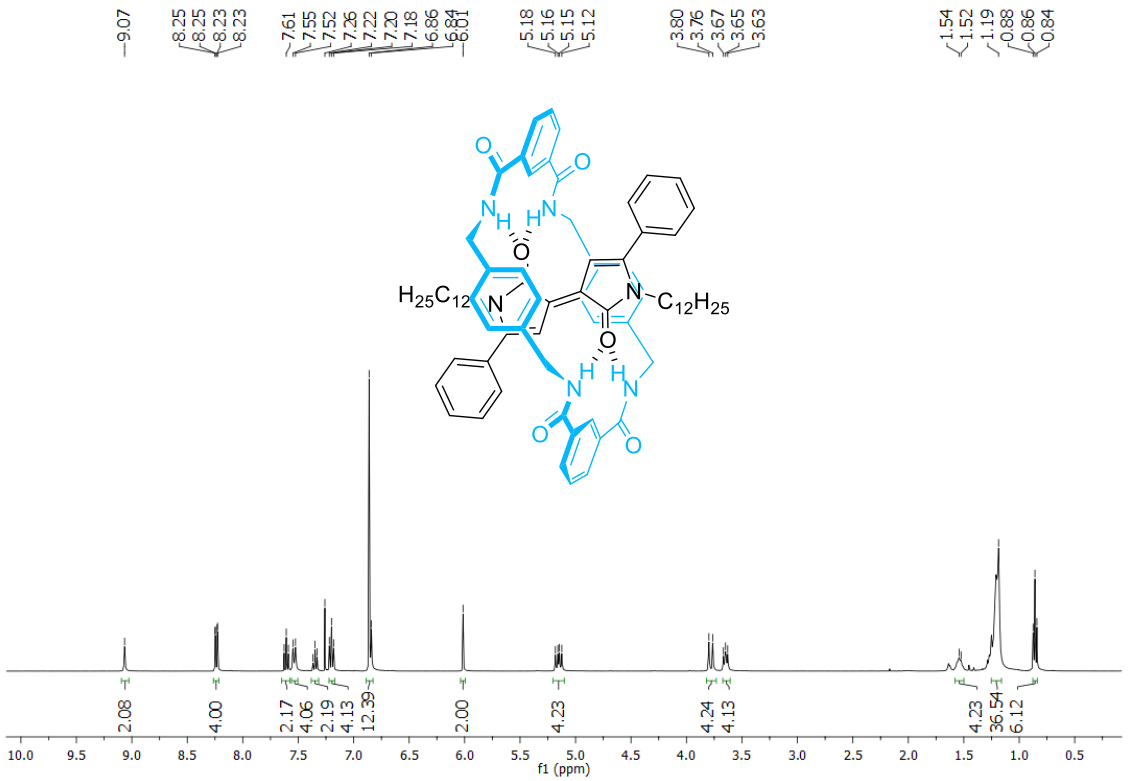
Thread **2d** (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



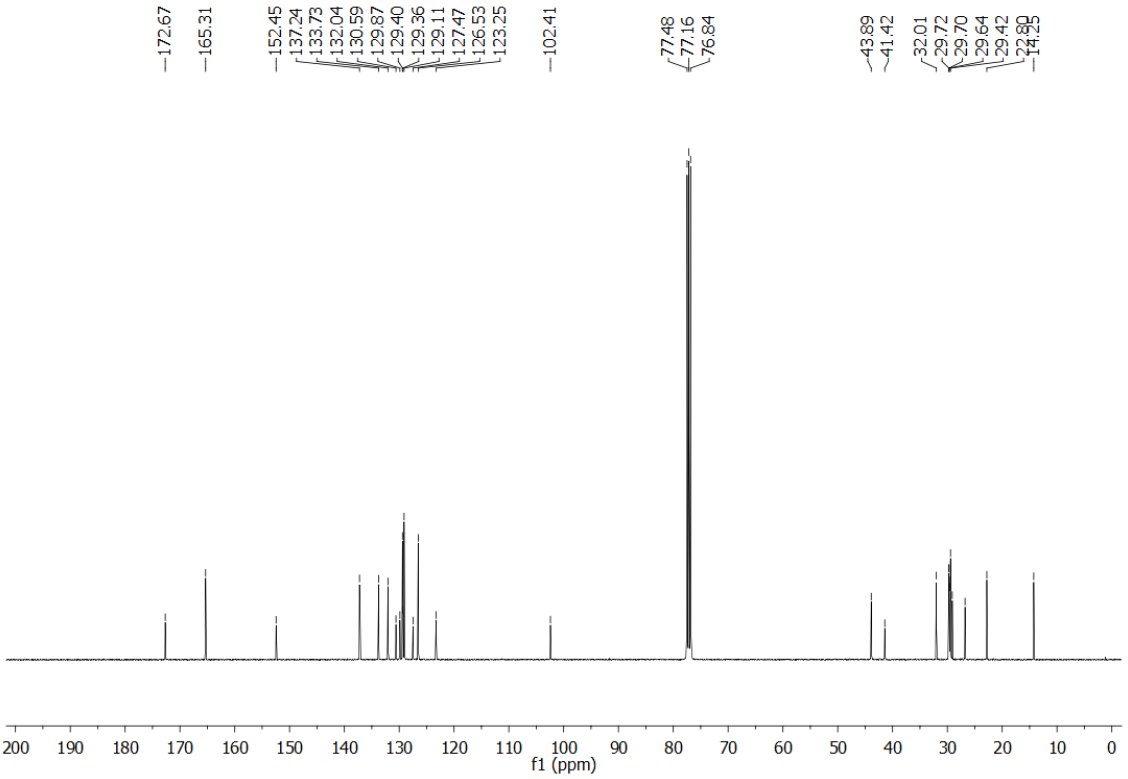
Thread **2d** (^{13}C RMN, 100 MHz, $CDCl_3$, 298 K)



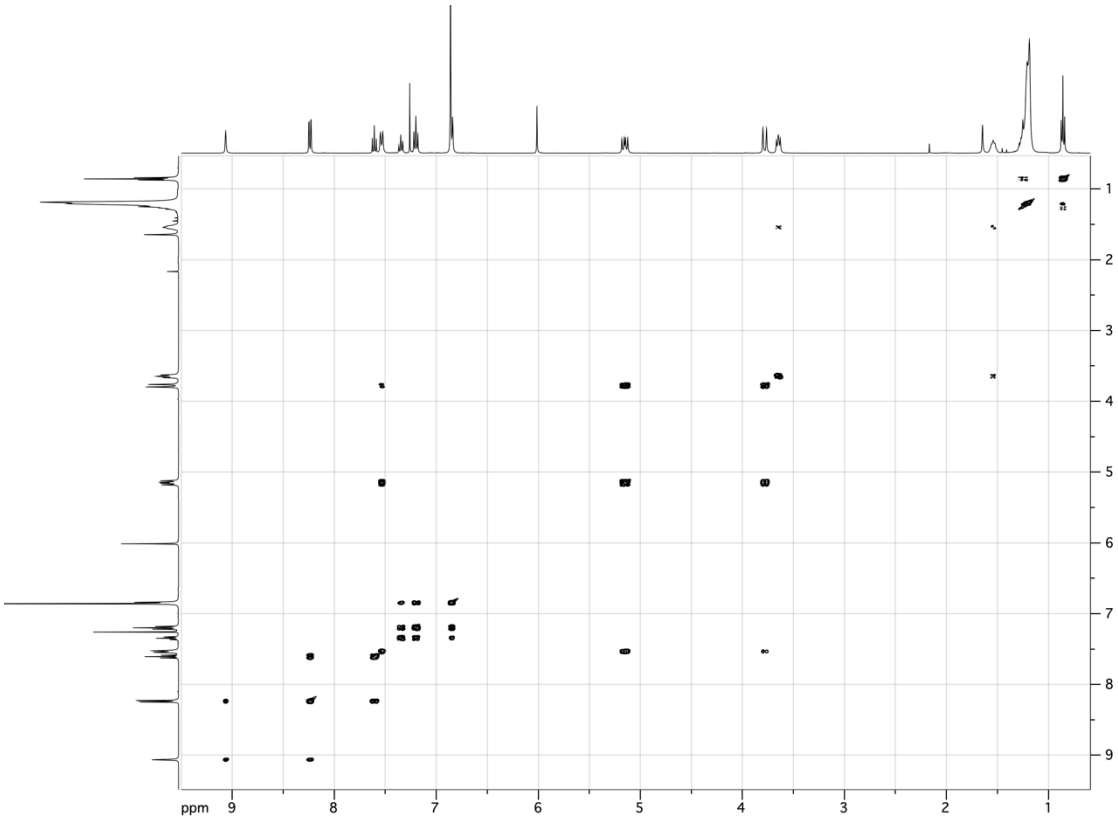
Rotaxane **3a** (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



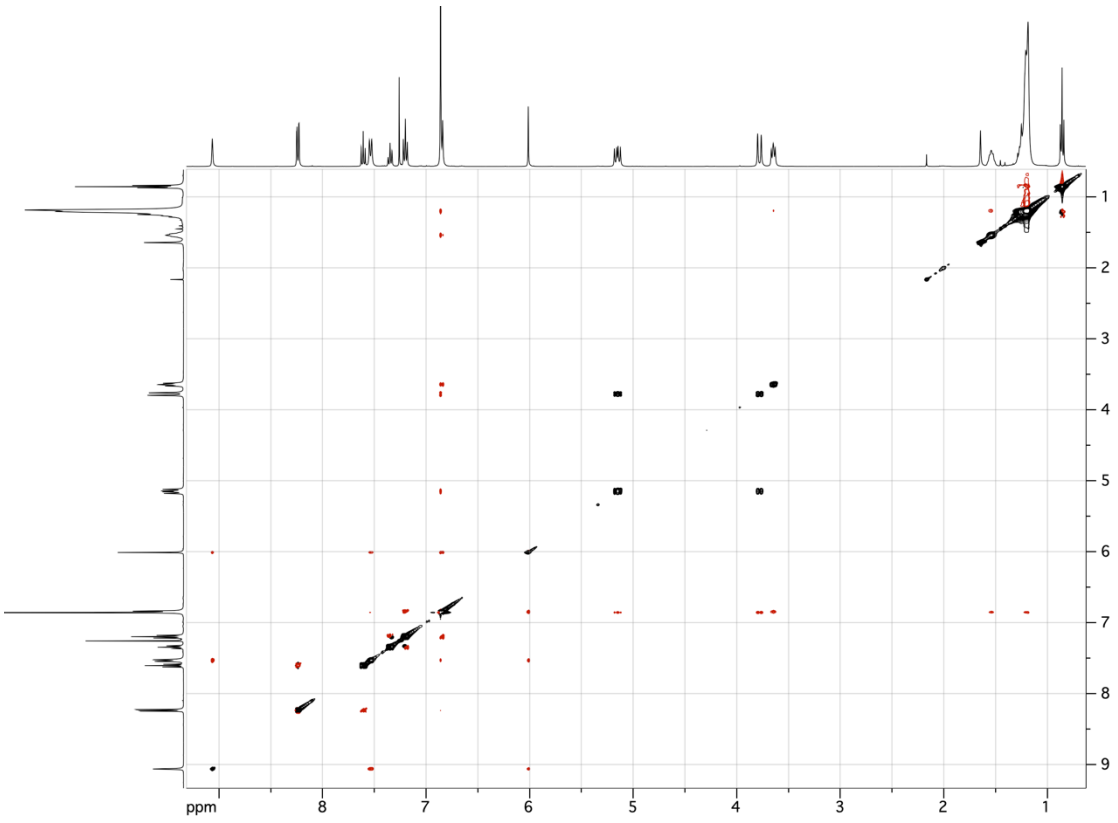
Rotaxane **3a** (^{13}C RMN, 100 MHz, $CDCl_3$, 298 K)



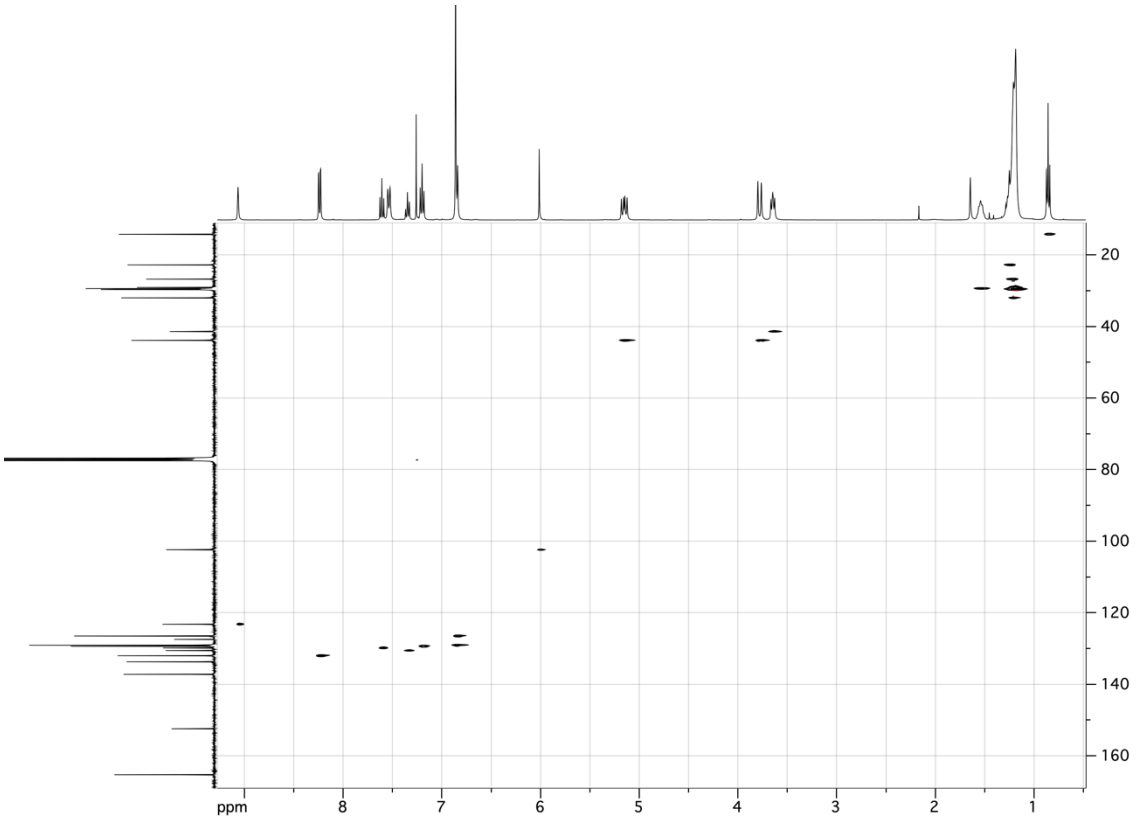
Rotaxane **3a** (^{1}H,^{1}H-COSY, 400 MHz, $CDCl_3$, 298 K)



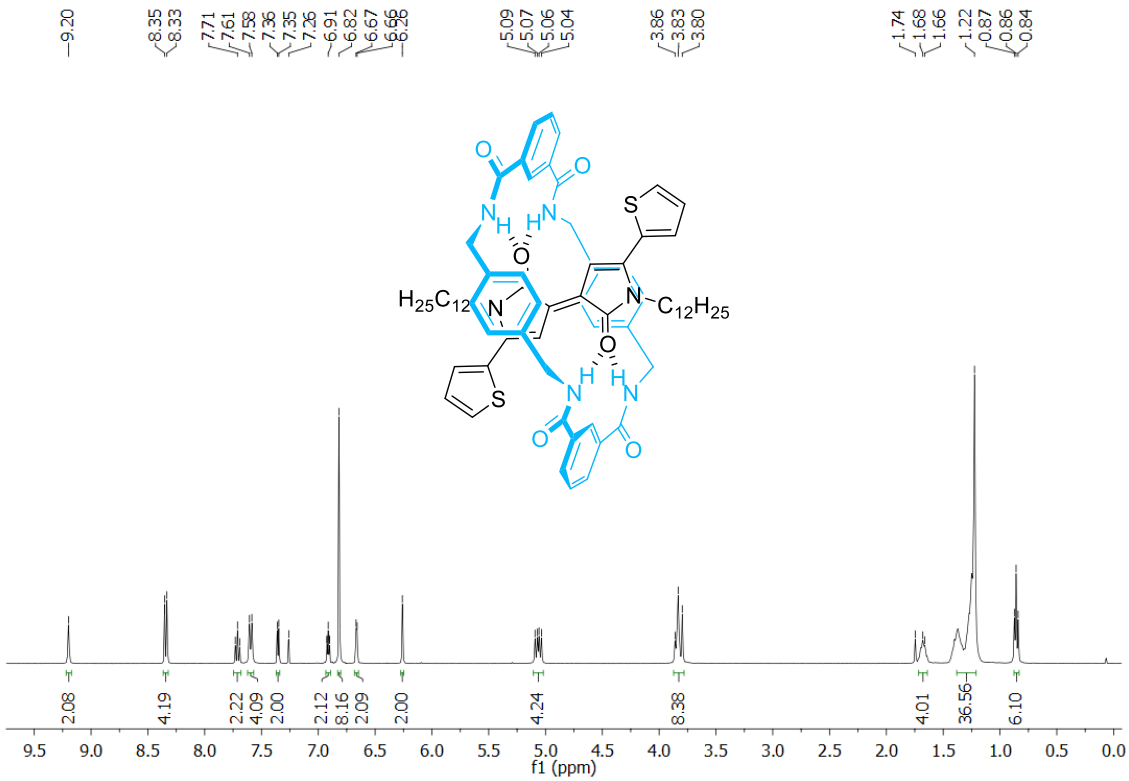
Rotaxane **3a** (^{1}H,^{1}H-NOESY, 400 MHz, $CDCl_3$, 298 K)



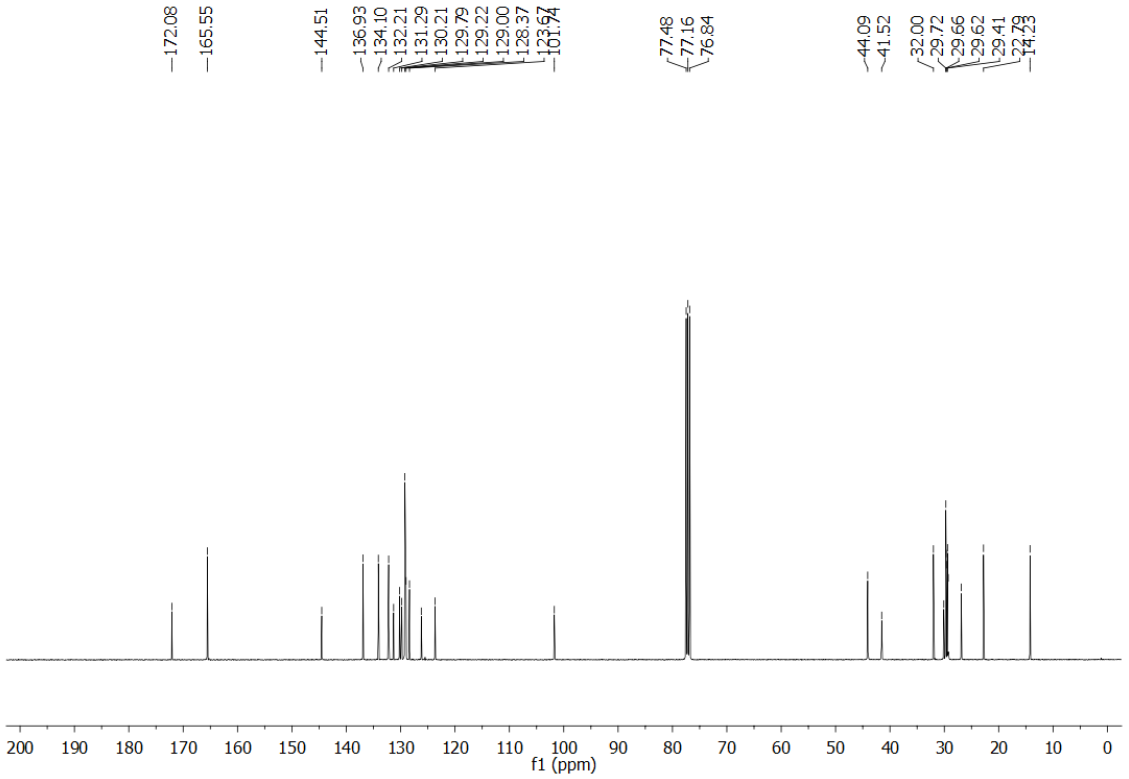
Rotaxane **3a** (HSQC, 400 MHz, $CDCl_3$, 298 K)



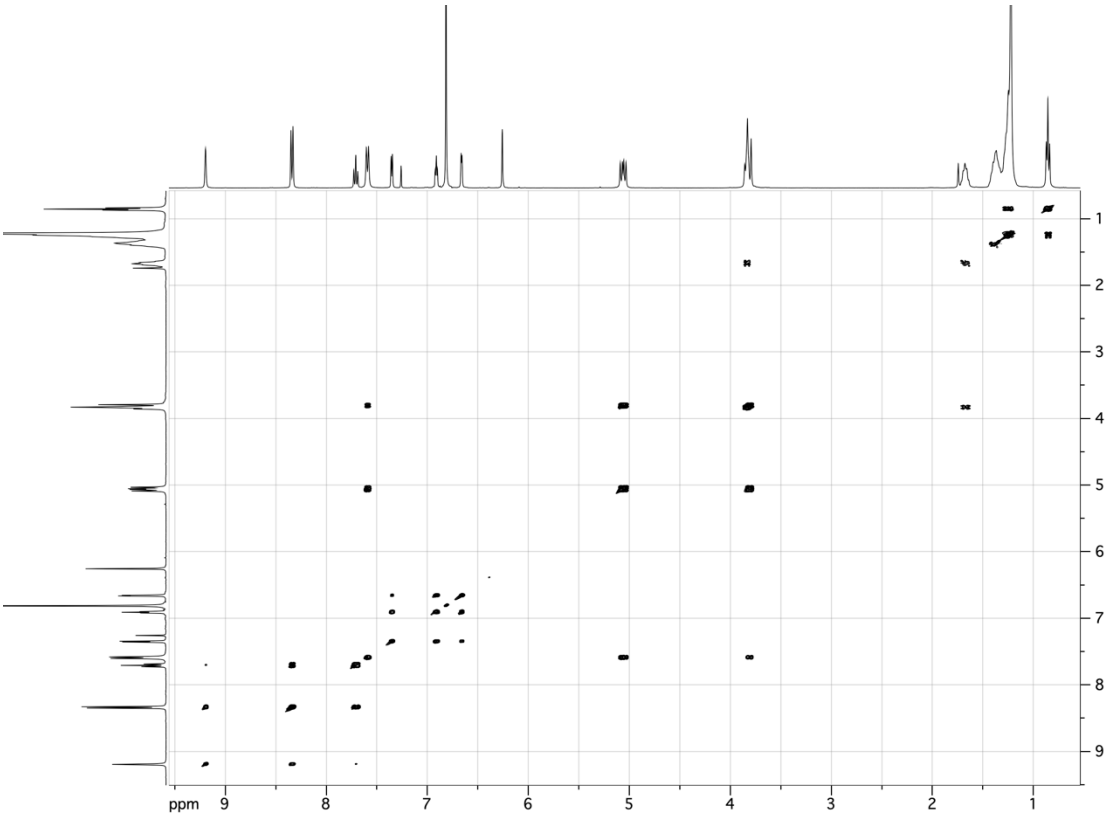
Rotaxane **3b** (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



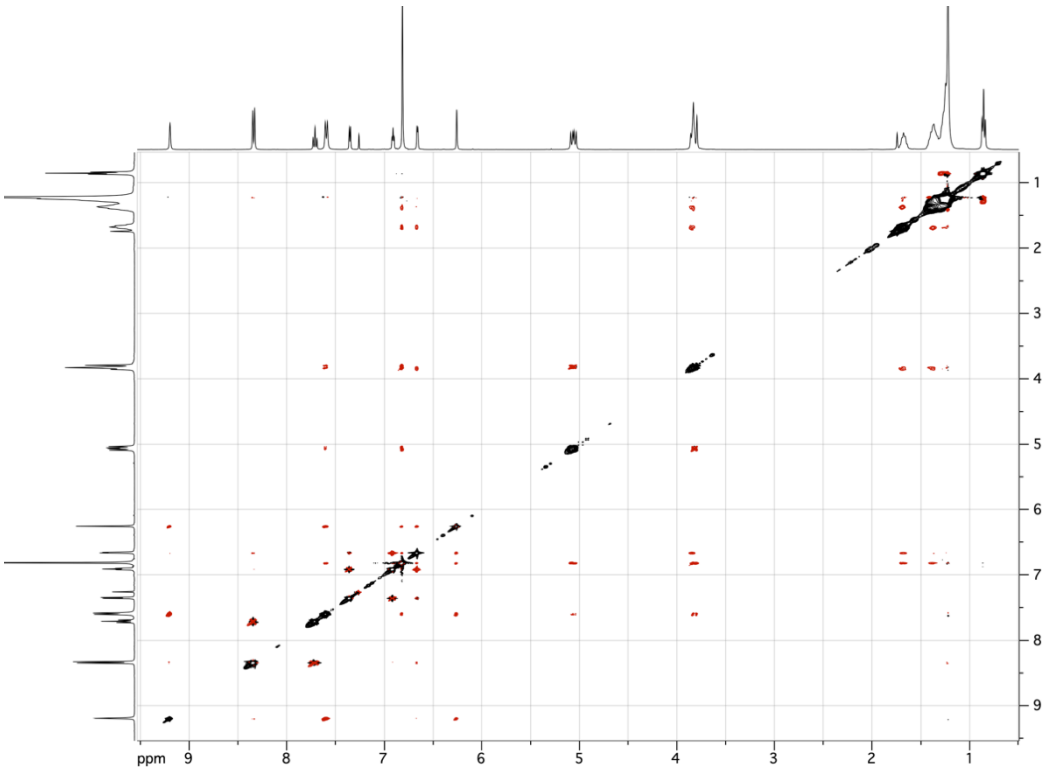
Rotaxane **3b** (^{13}C RMN, 100 MHz, $CDCl_3$, 298 K)



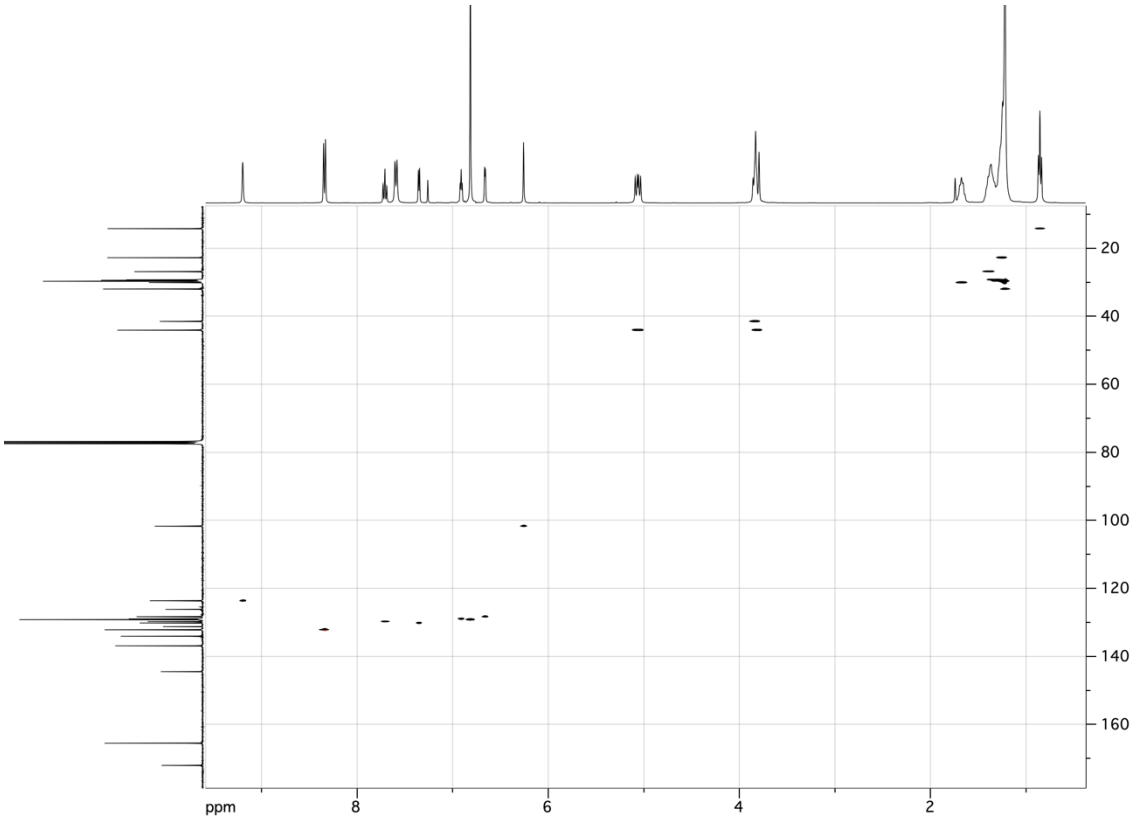
Rotaxane **3b** (^{1}H,^{1}H-COSY, 400 MHz, $CDCl_3$, 298 K)



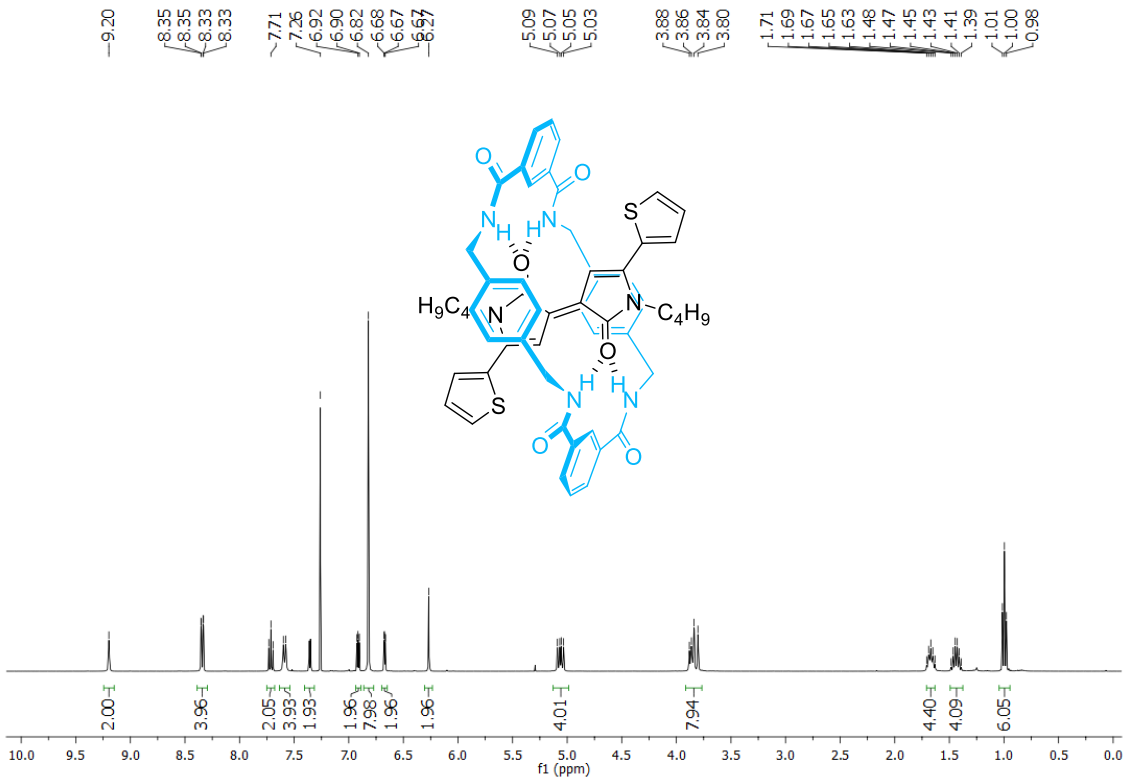
Rotaxane **3b** (^{1}H,^{1}H-NOESY, 400 MHz, $CDCl_3$, 298 K)



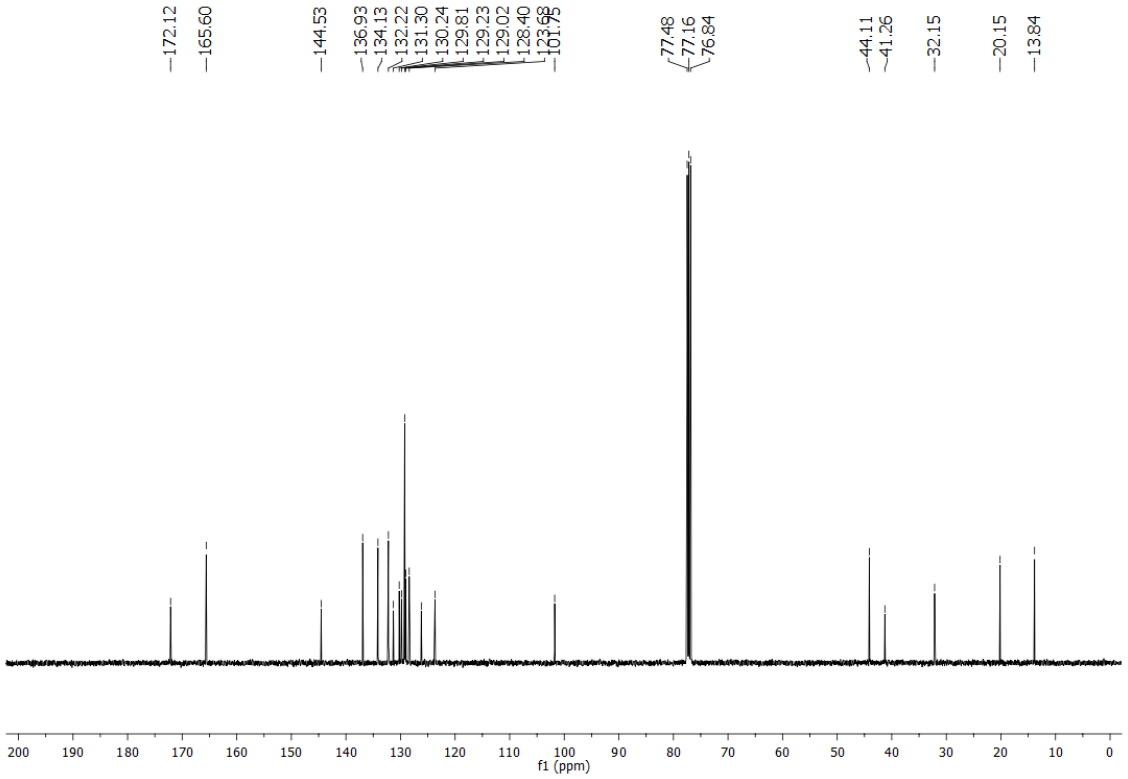
Rotaxane **3b** (HSQC, 400 MHz, $CDCl_3$, 298 K)



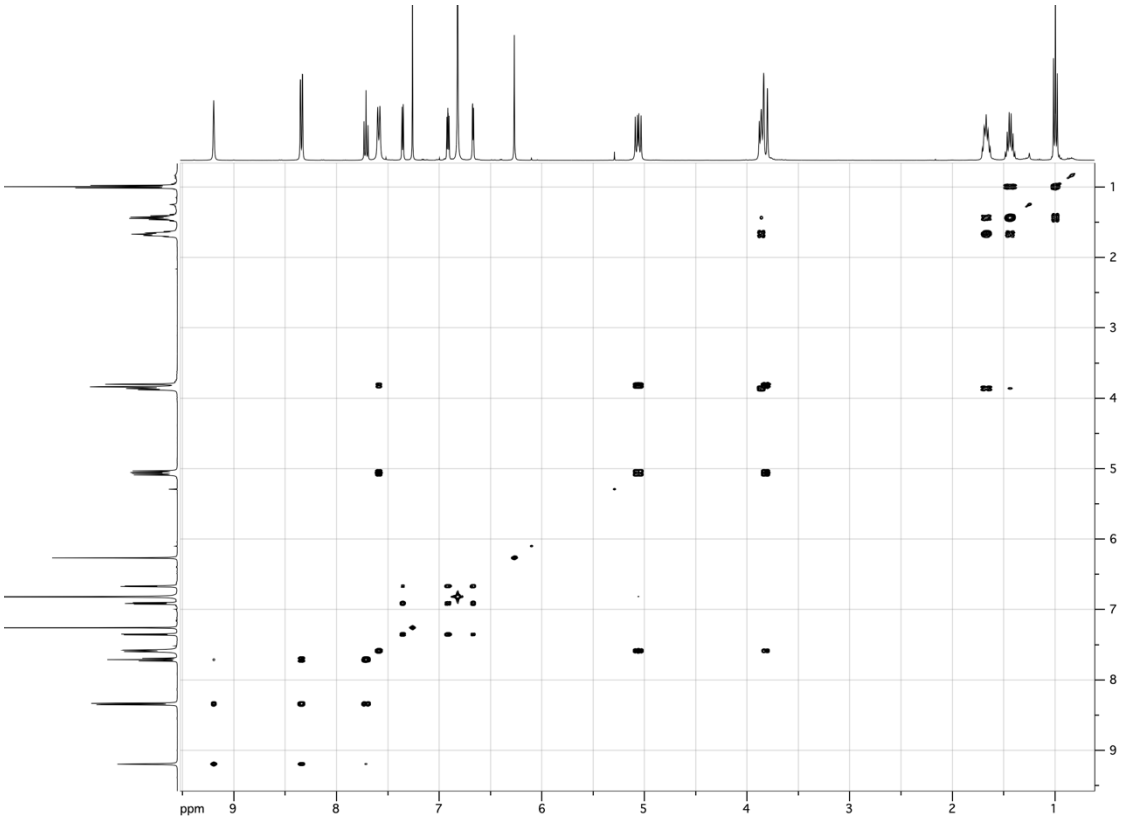
Rotaxane **3c** (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



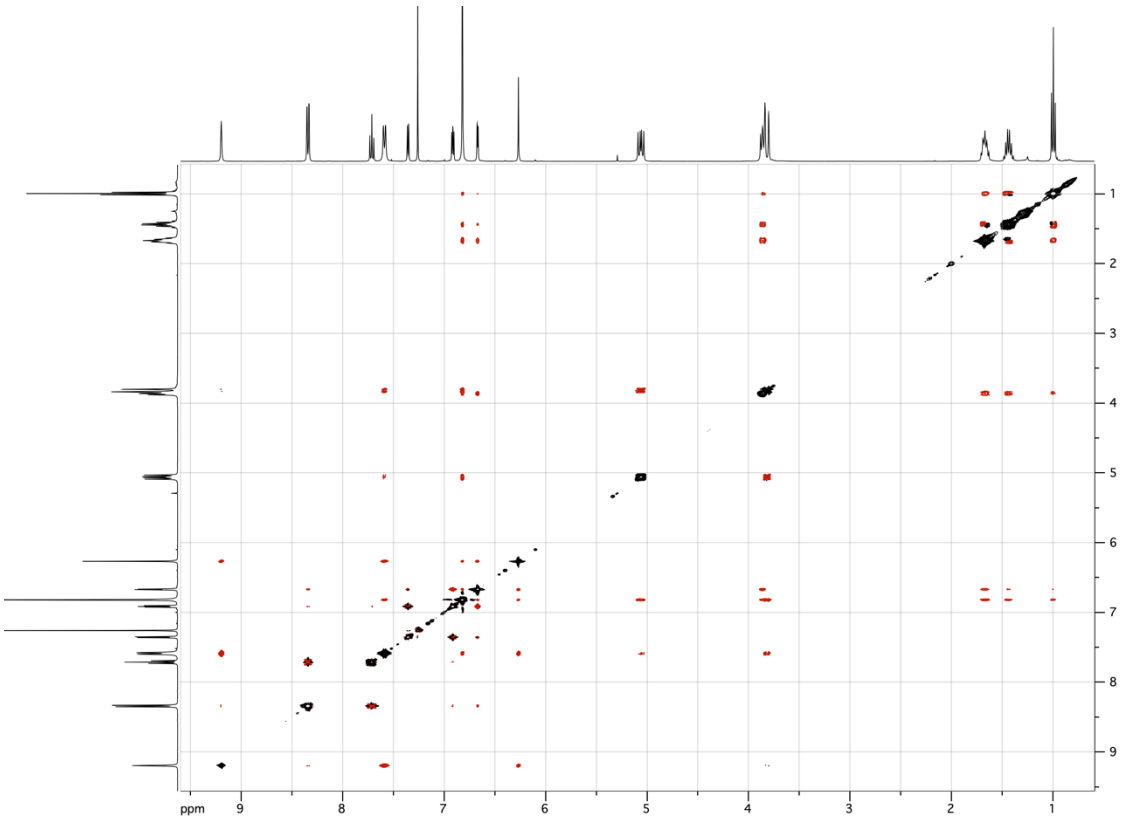
Rotaxane **3c** (^{13}C RMN, 100 MHz, $CDCl_3$, 298 K)



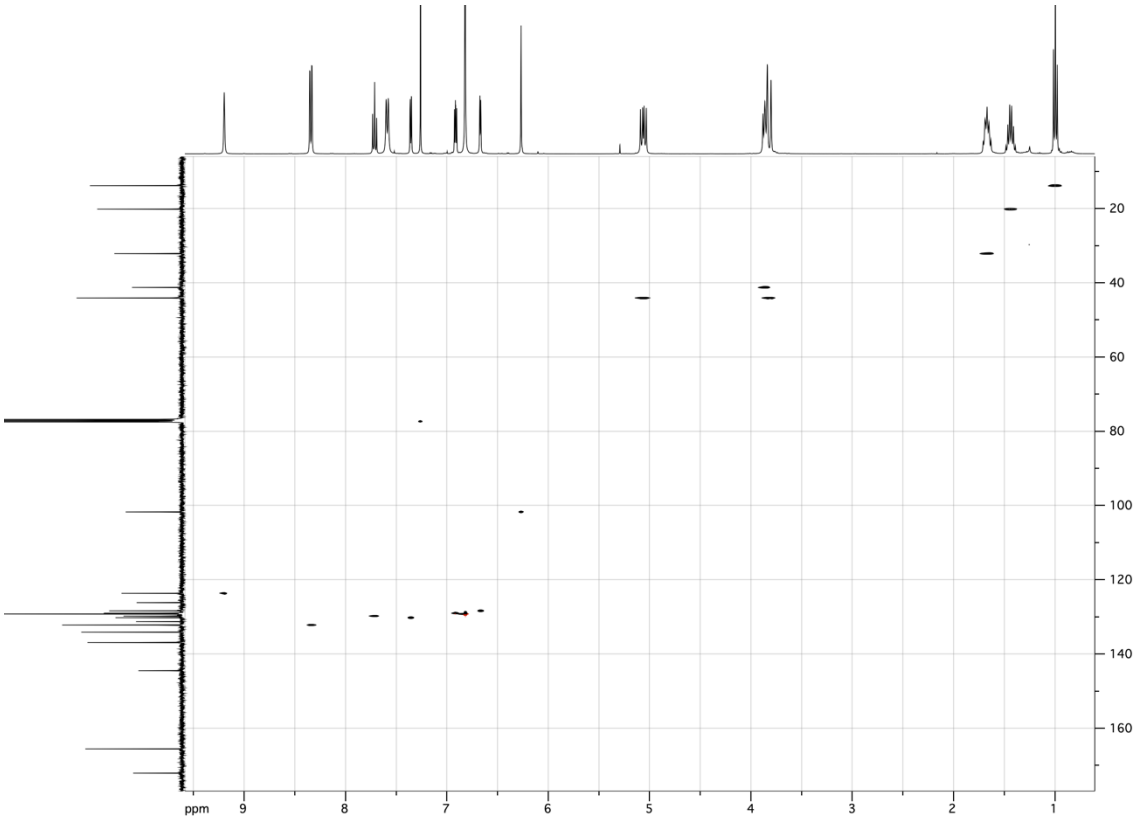
Rotaxane **3c** (^{1}H,^{1}H-COSY, 400 MHz, $CDCl_3$, 298 K)



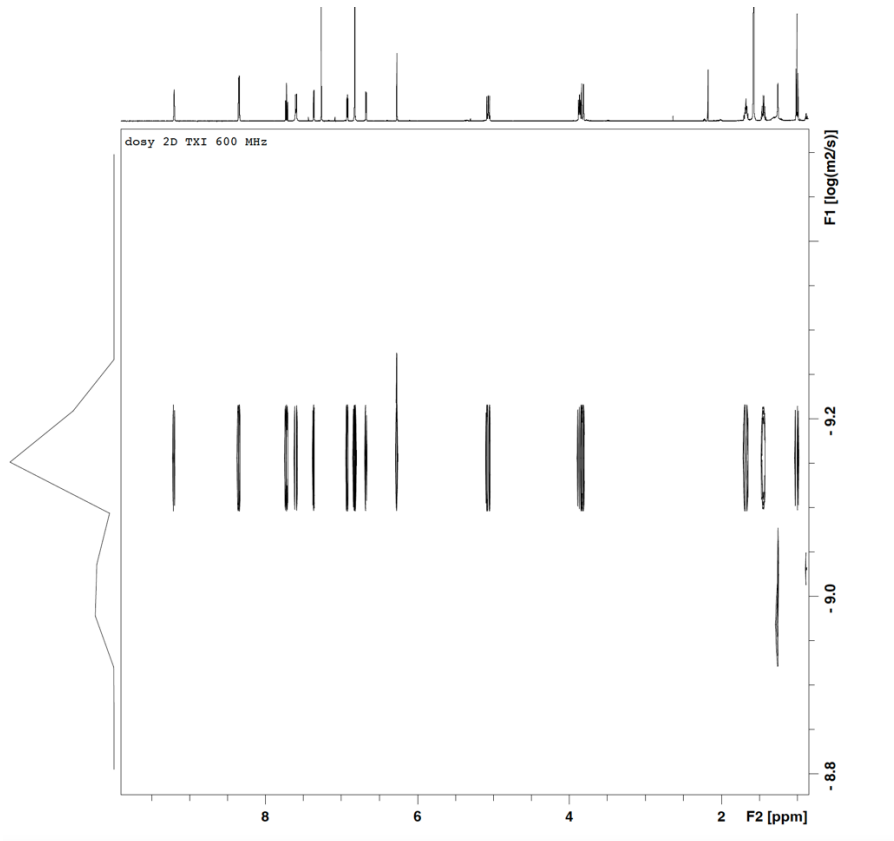
Rotaxane **3c** (^{1}H,^{1}H-NOESY, 400 MHz, $CDCl_3$, 298 K)



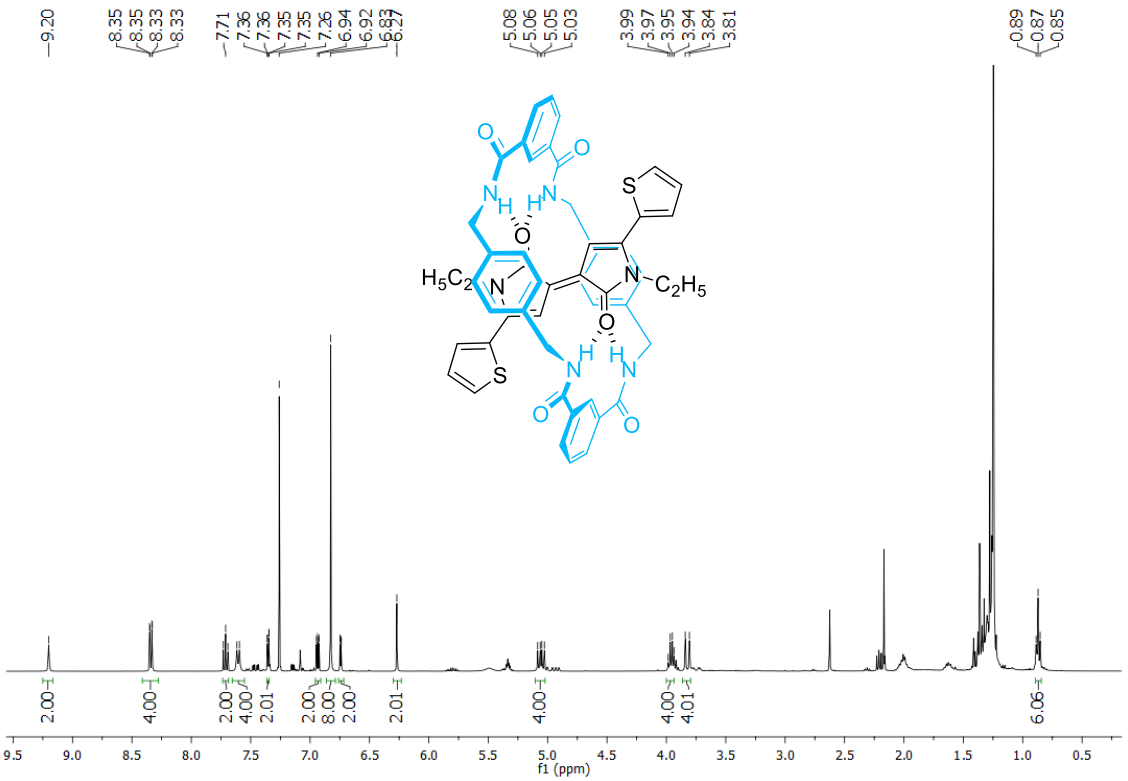
Rotaxane **3c** (HSQC, 400 MHz, $CDCl_3$, 298 K)



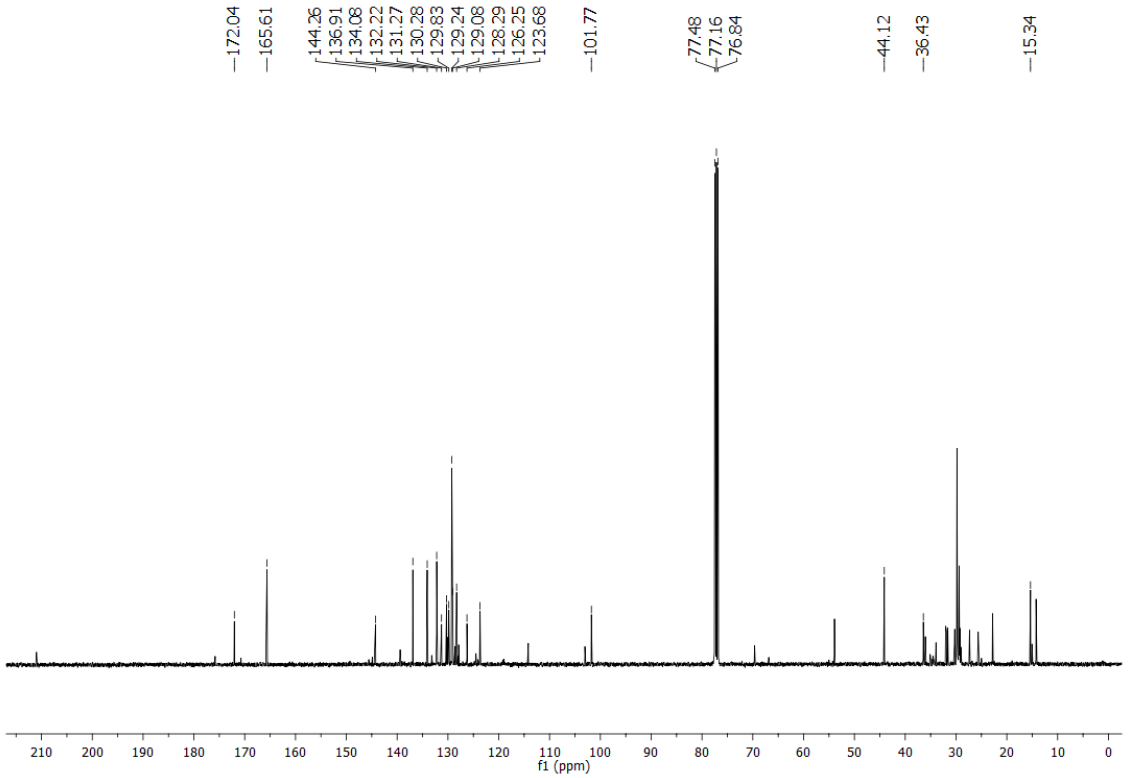
Rotaxane **3c** (DOSY 2D, 600 MHz, $CDCl_3$, 298 K).



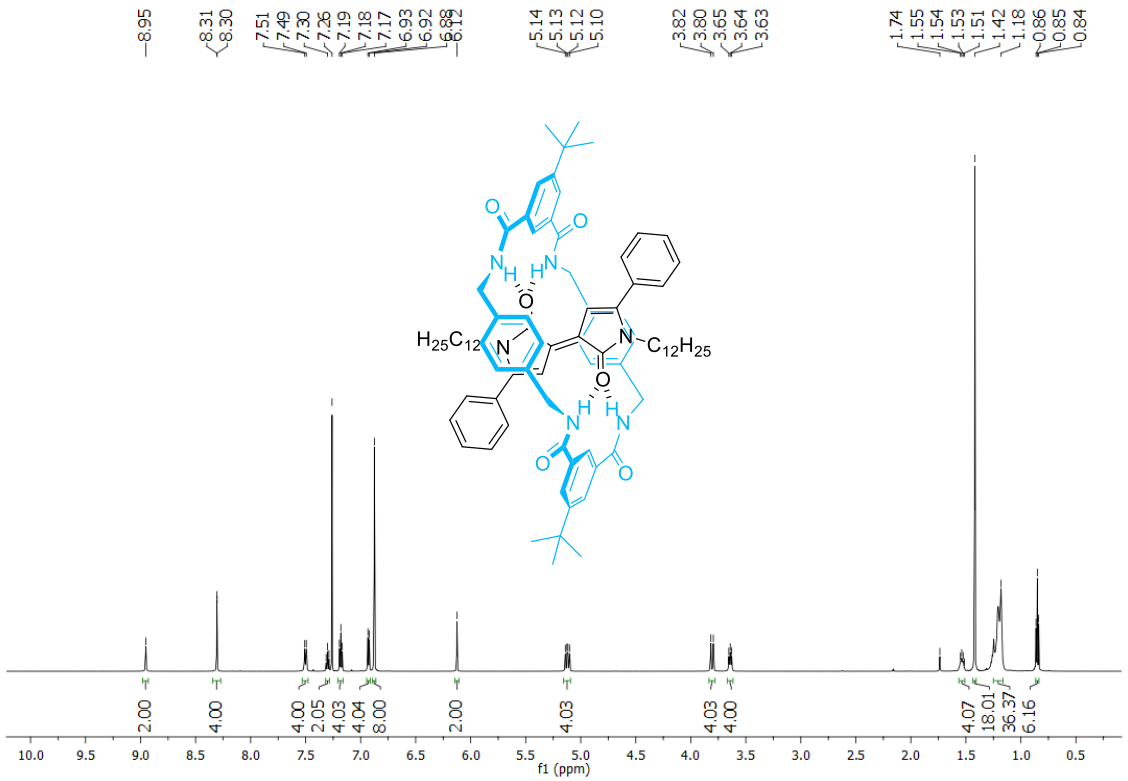
Rotaxane **3d** (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



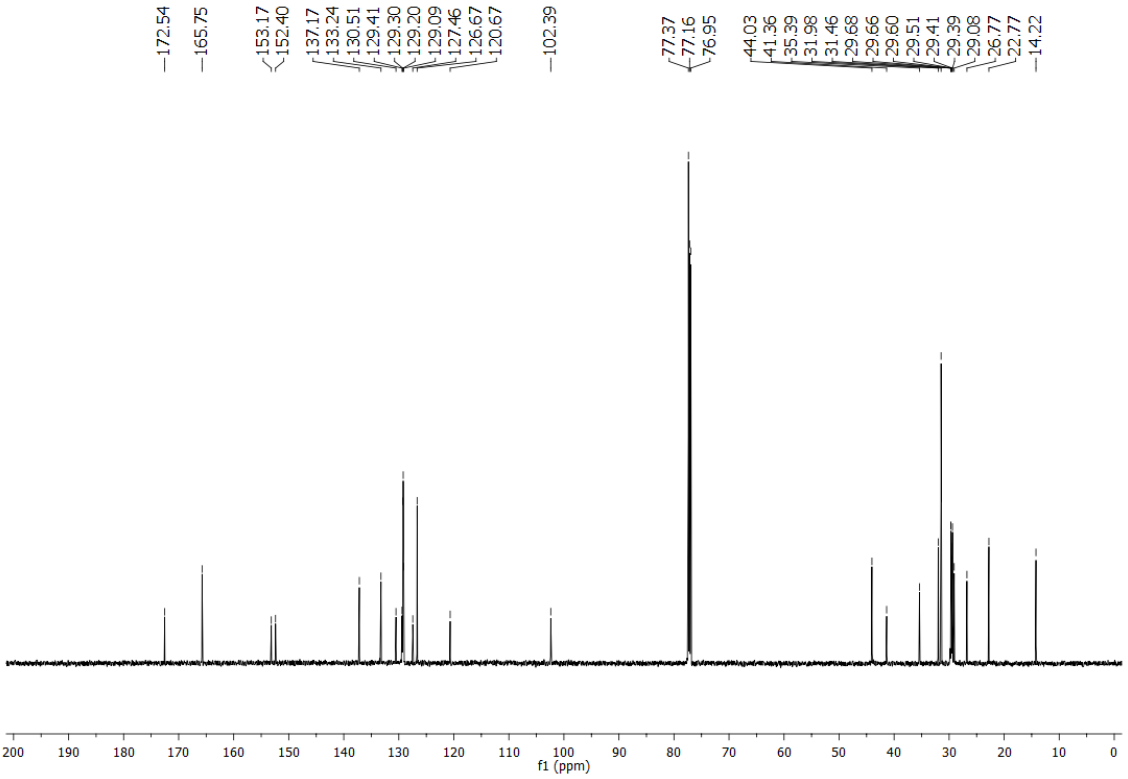
Rotaxane **3d** (^{13}C NMR, 100 MHz, $CDCl_3$, 298 K)



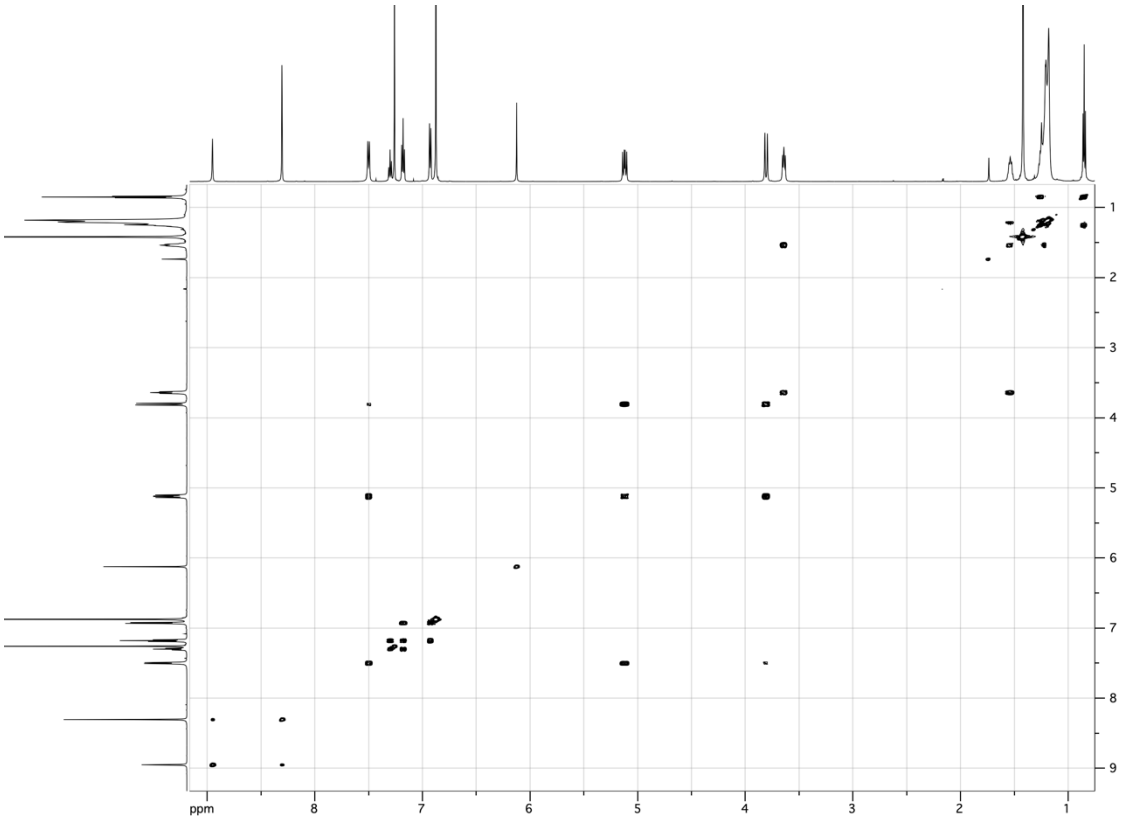
Rotaxane **3e** (^{1}H NMR, 600 MHz, $CDCl_3$, 298 K)



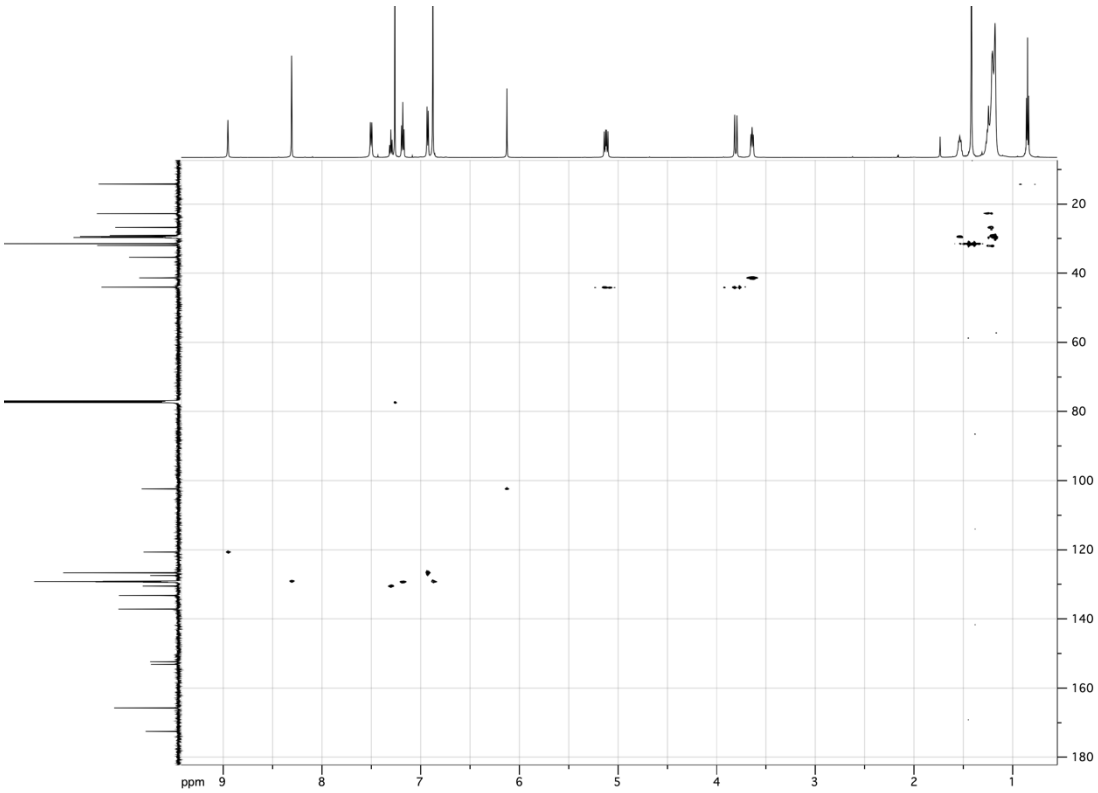
Rotaxane **3e** (^{13}C RMN, 150 MHz, $CDCl_3$, 298 K)



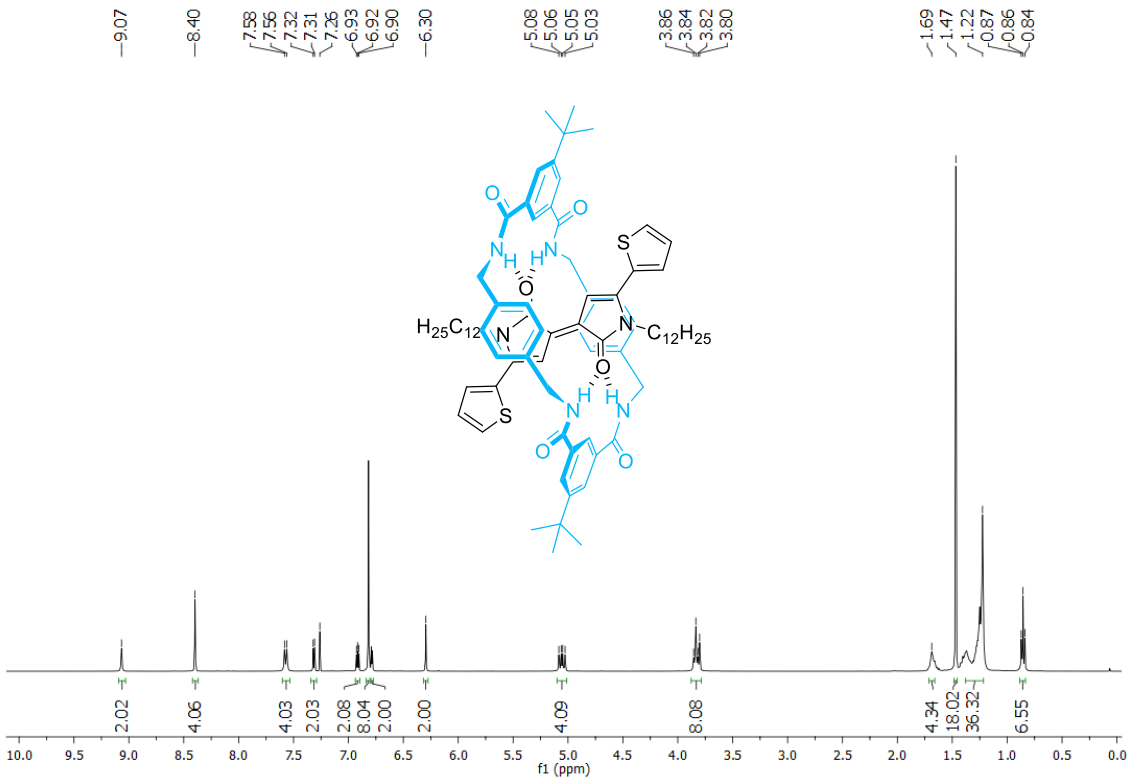
Rotaxane **3e** (^{1}H,^{1}H-COSY, 600 MHz, $CDCl_3$, 298 K)



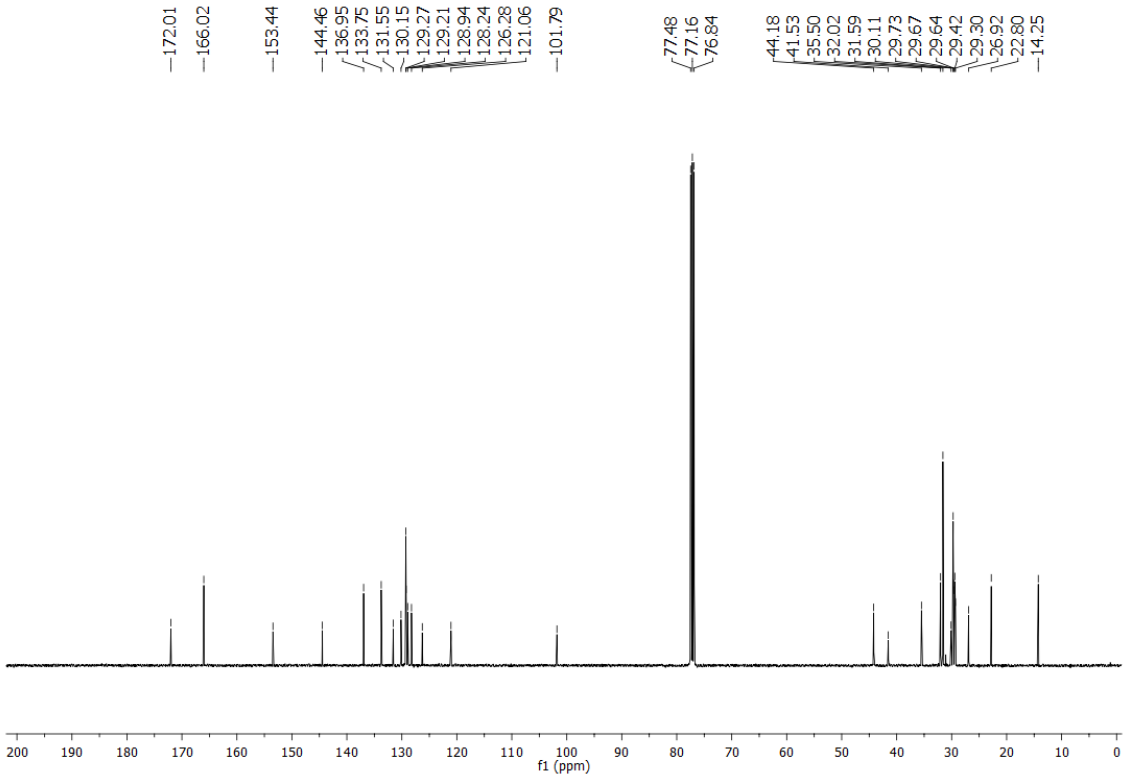
Rotaxane **3e** (HSQC, 600 MHz, $CDCl_3$, 298 K)



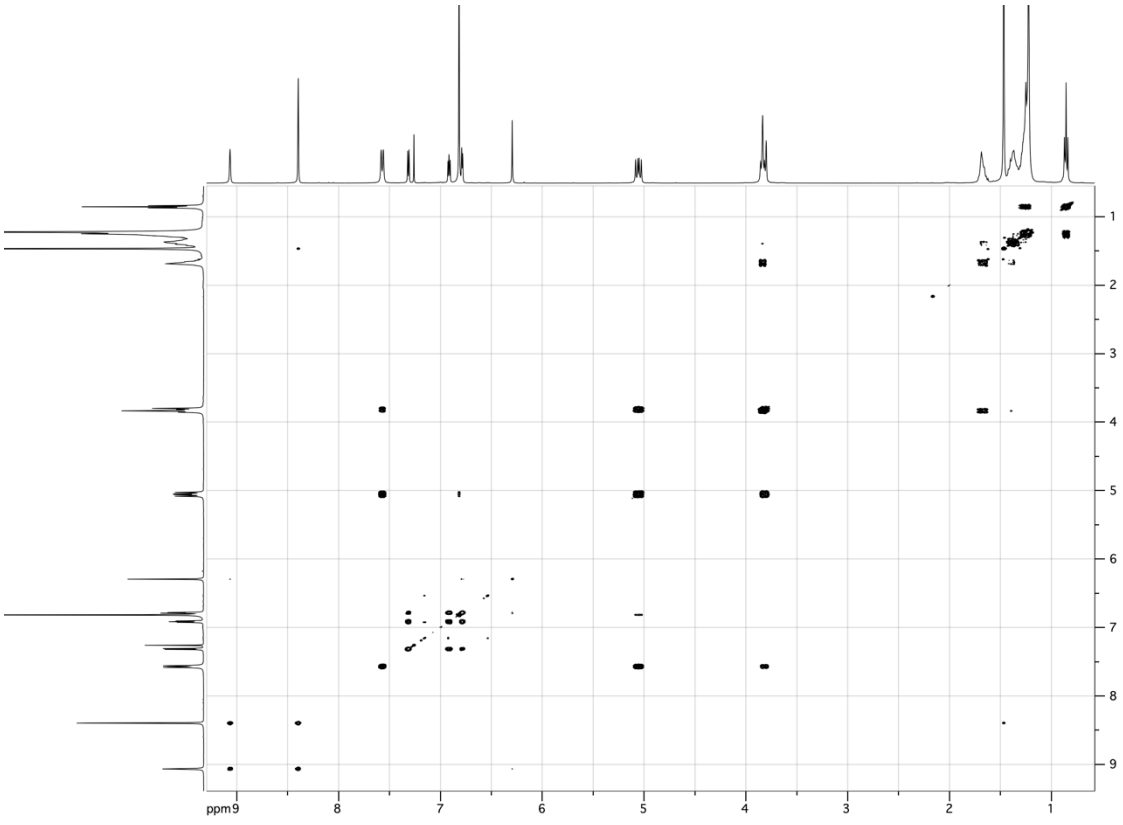
Rotaxane **3f** (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



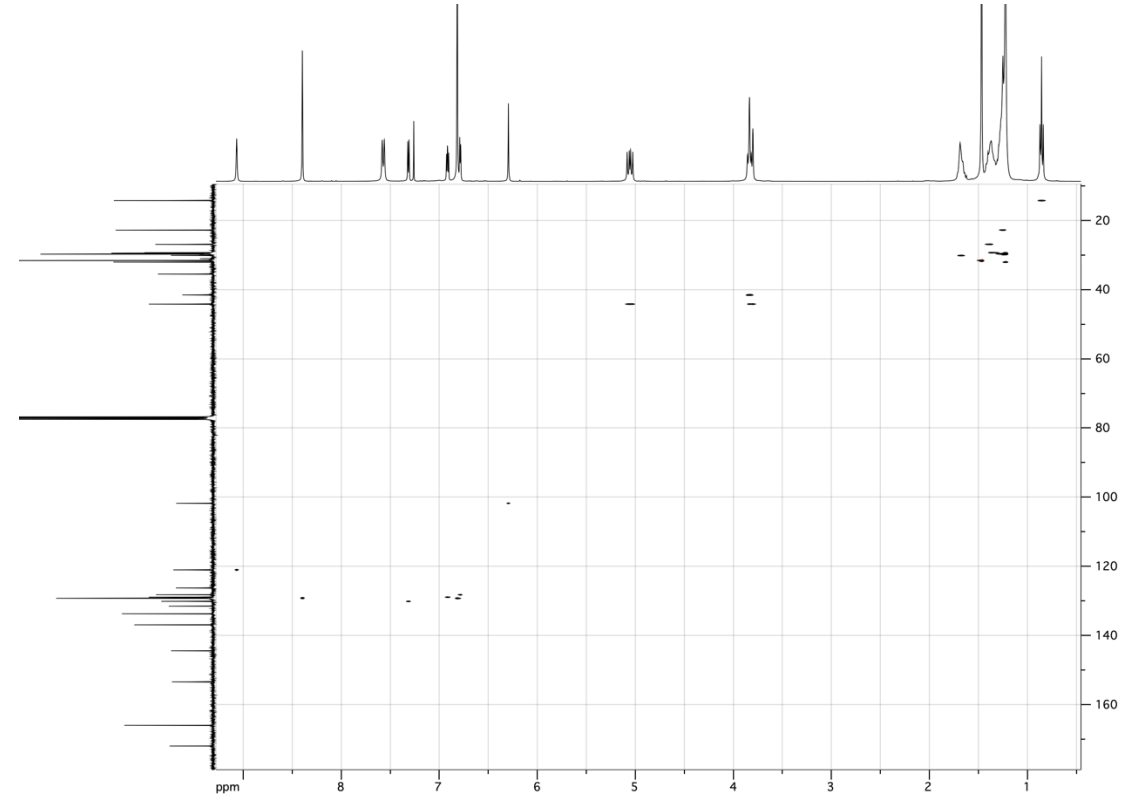
Rotaxane **3f** (^{13}C RMN, 100 MHz, $CDCl_3$, 298 K)



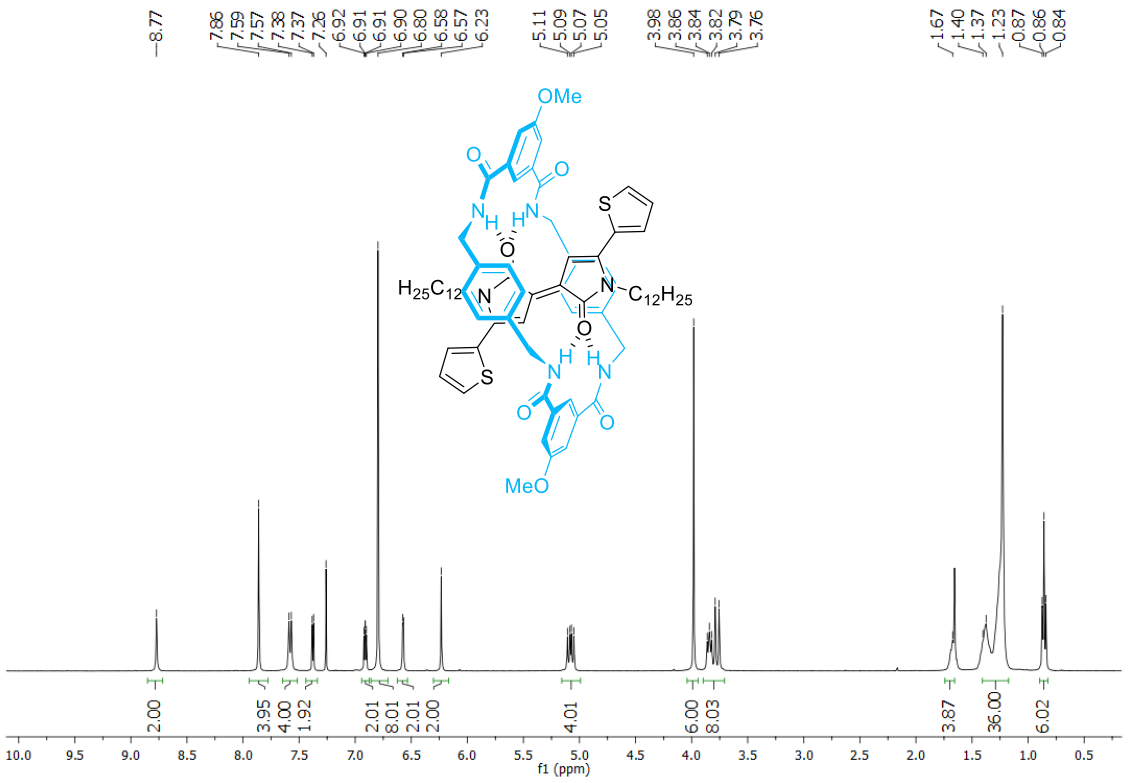
Rotaxane **3f** (^{1}H,^{1}H-COSY, 400 MHz, $CDCl_3$, 298 K)



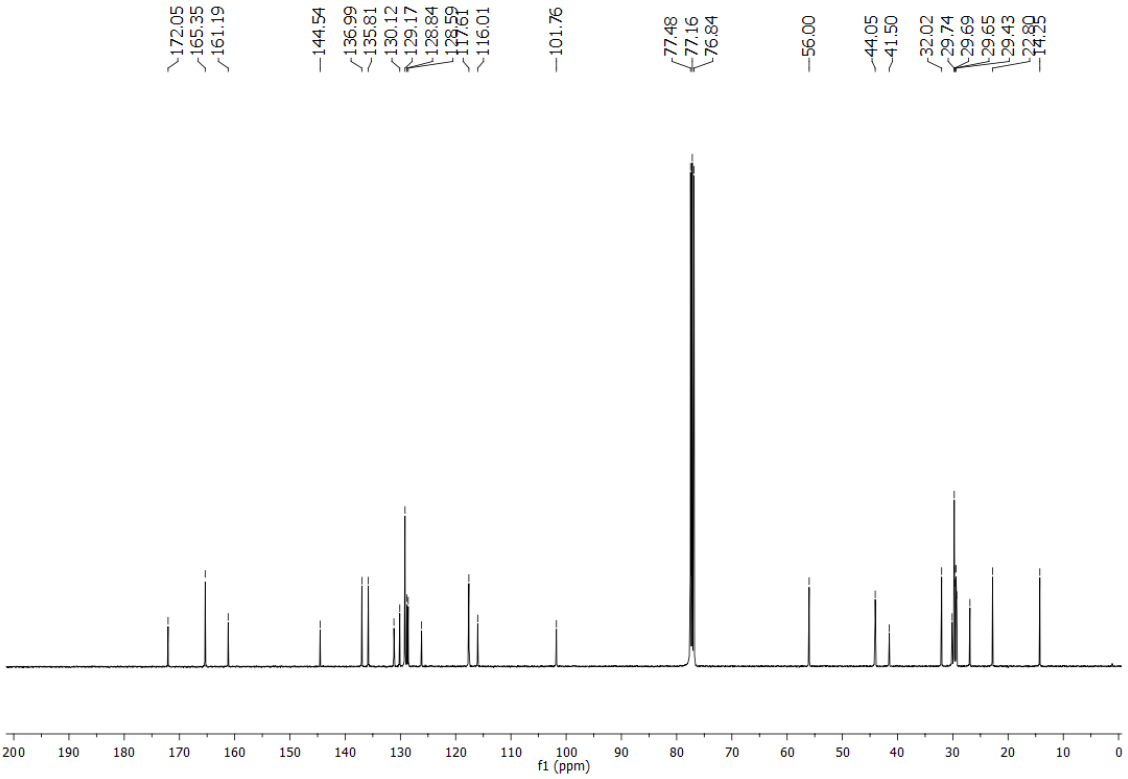
Rotaxane **3f** (HSQC, 400 MHz, $CDCl_3$, 298 K)



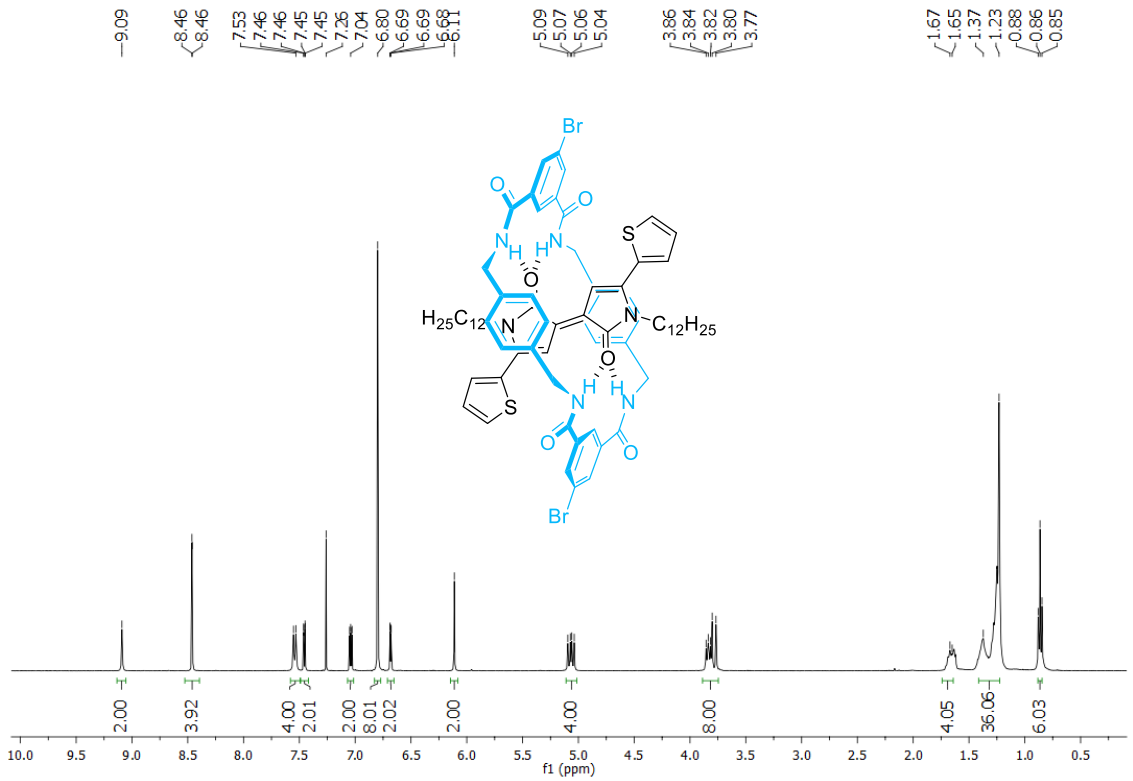
Rotaxane **3g** (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



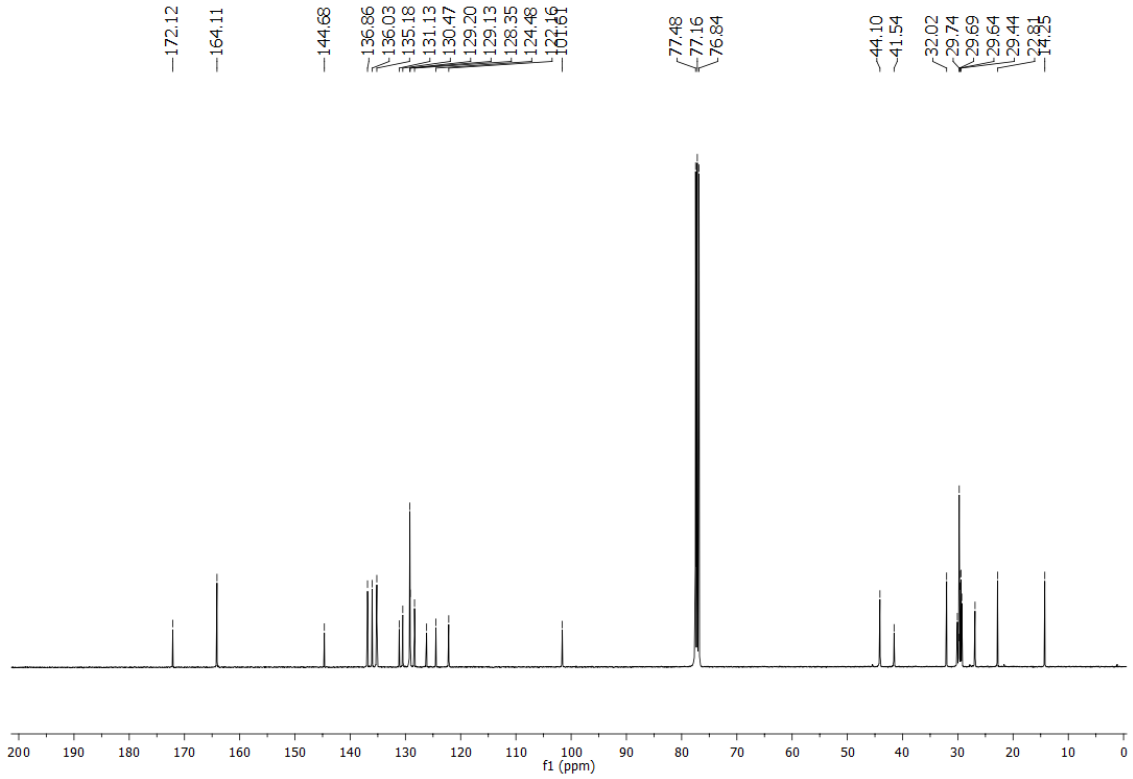
Rotaxane **3g** (^{13}C RMN, 100 MHz, $CDCl_3$, 298 K)



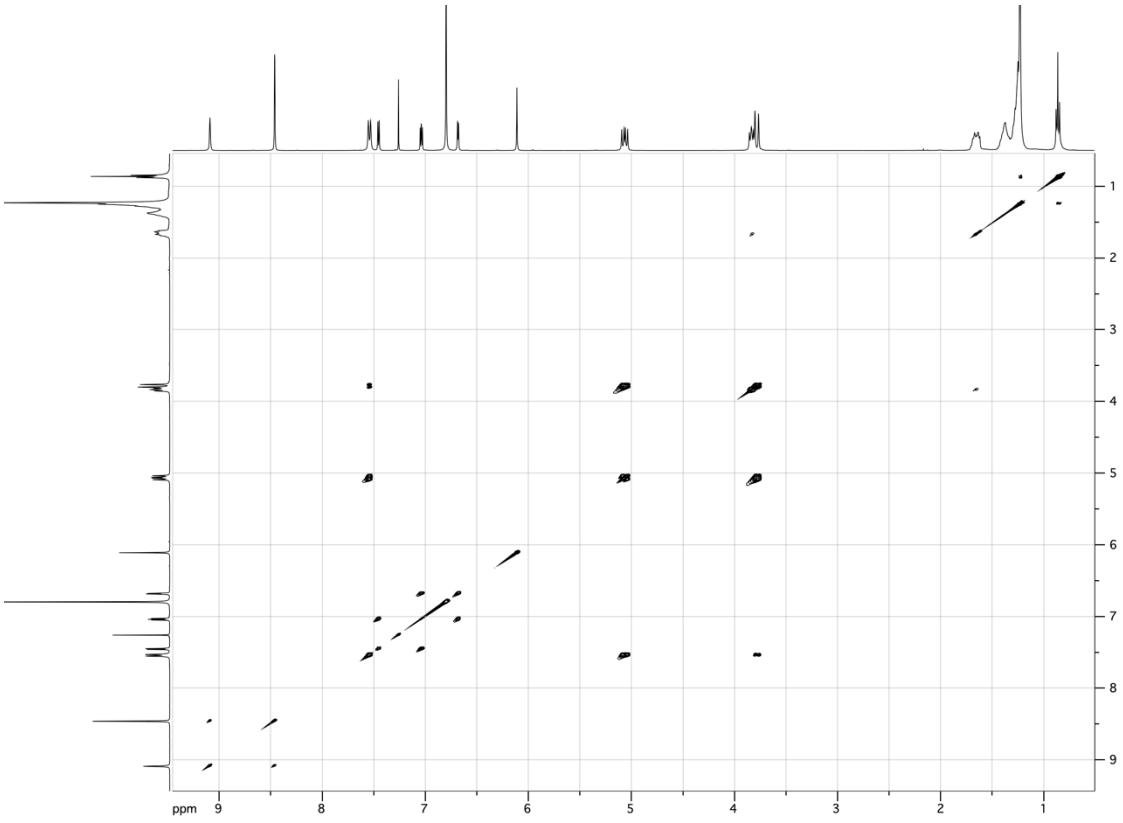
Rotaxane **3h** (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



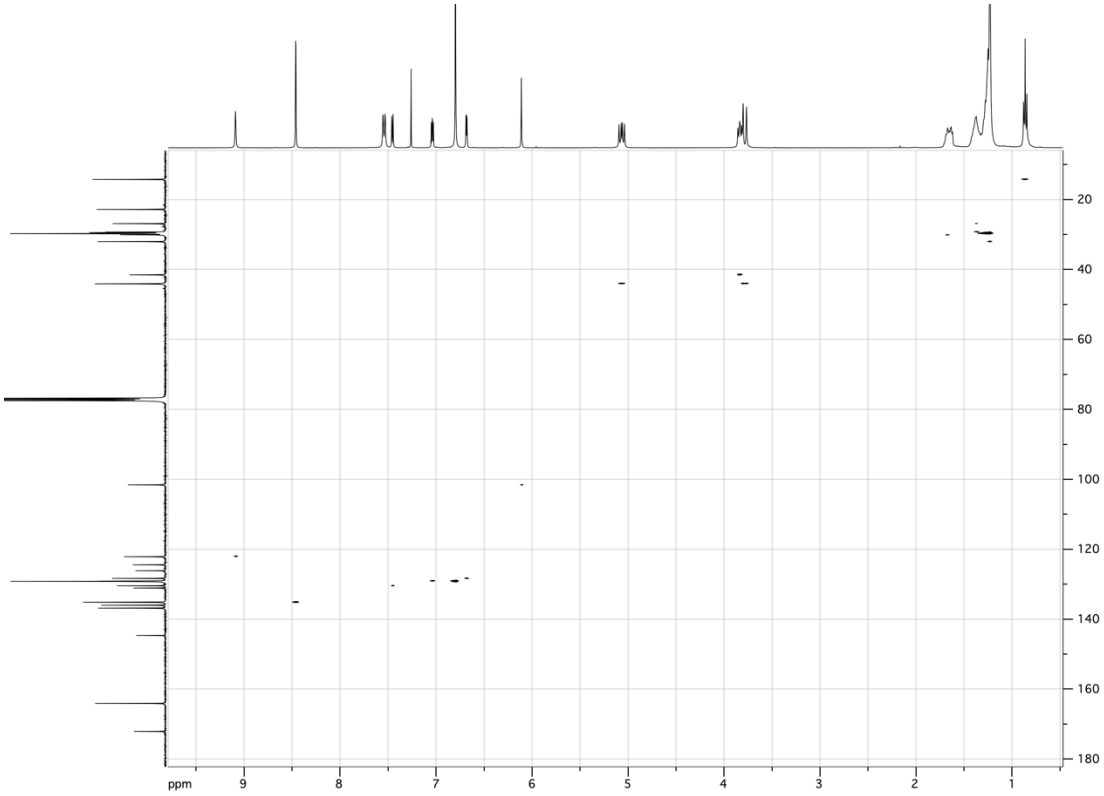
Rotaxane **3h** (^{13}C RMN, 100 MHz, $CDCl_3$, 298 K)



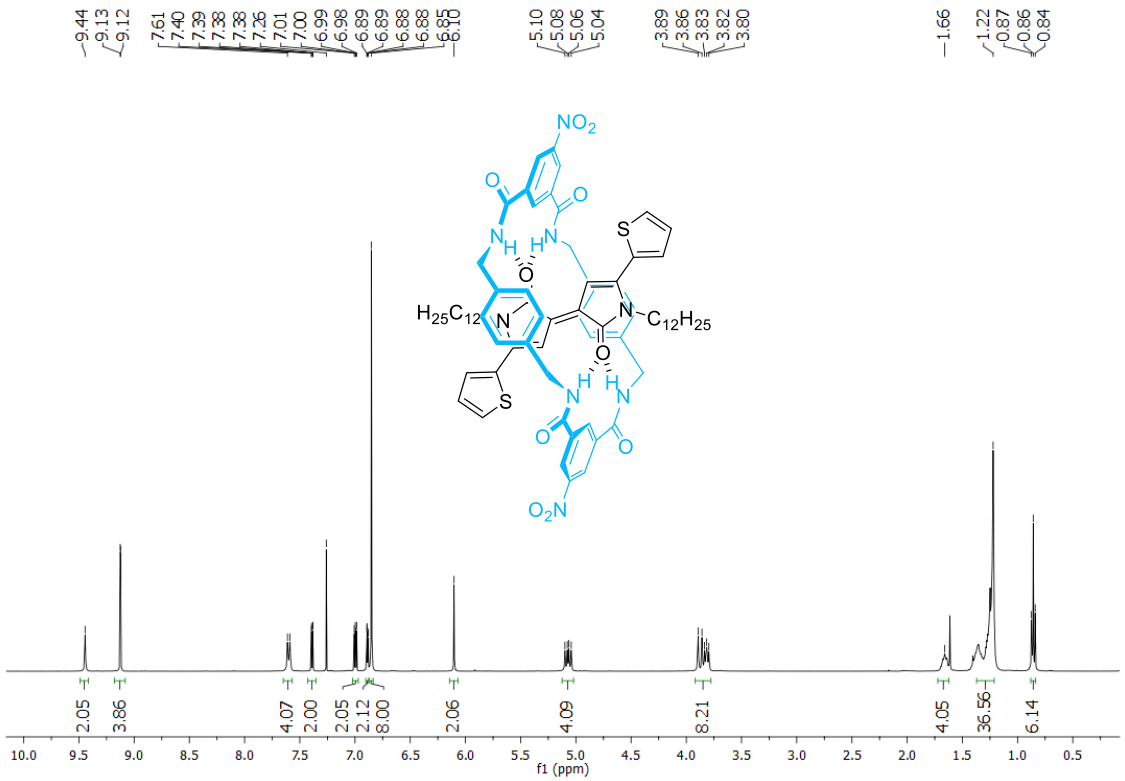
Rotaxane **3h** (^{1}H,^{1}H-COSY, 400 MHz, $CDCl_3$, 298 K)



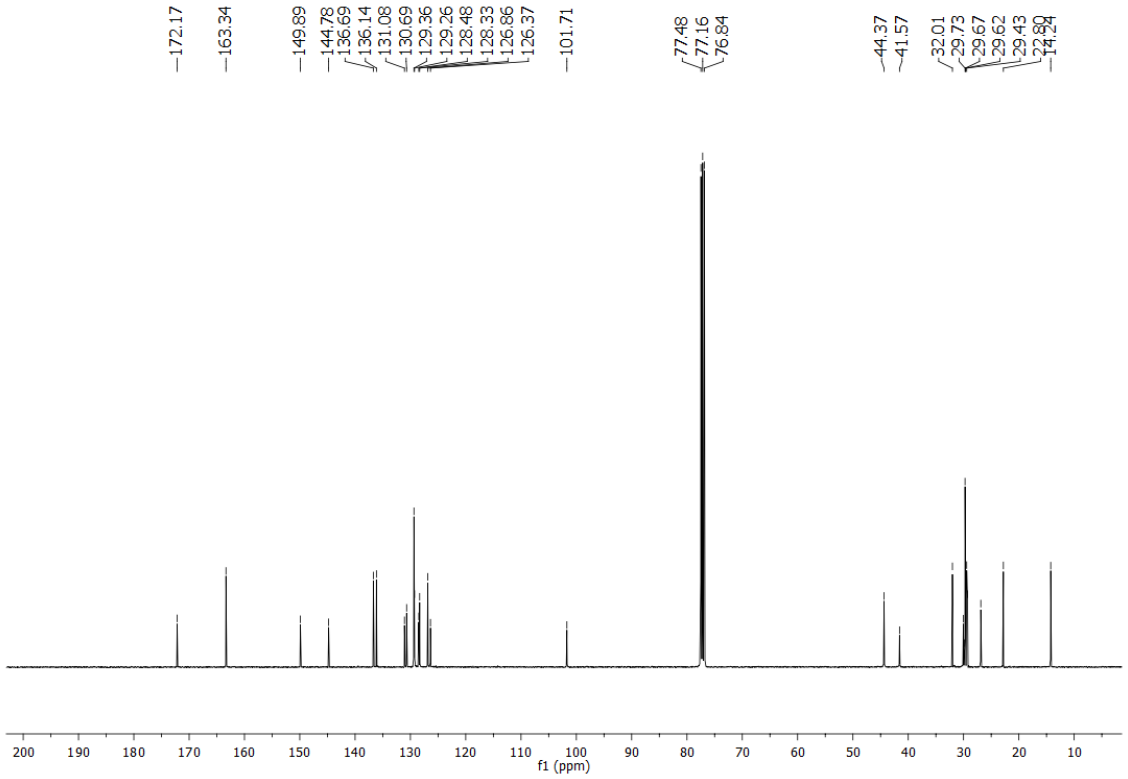
Rotaxane **3h** (HSQC, 400 MHz, $CDCl_3$, 298 K)



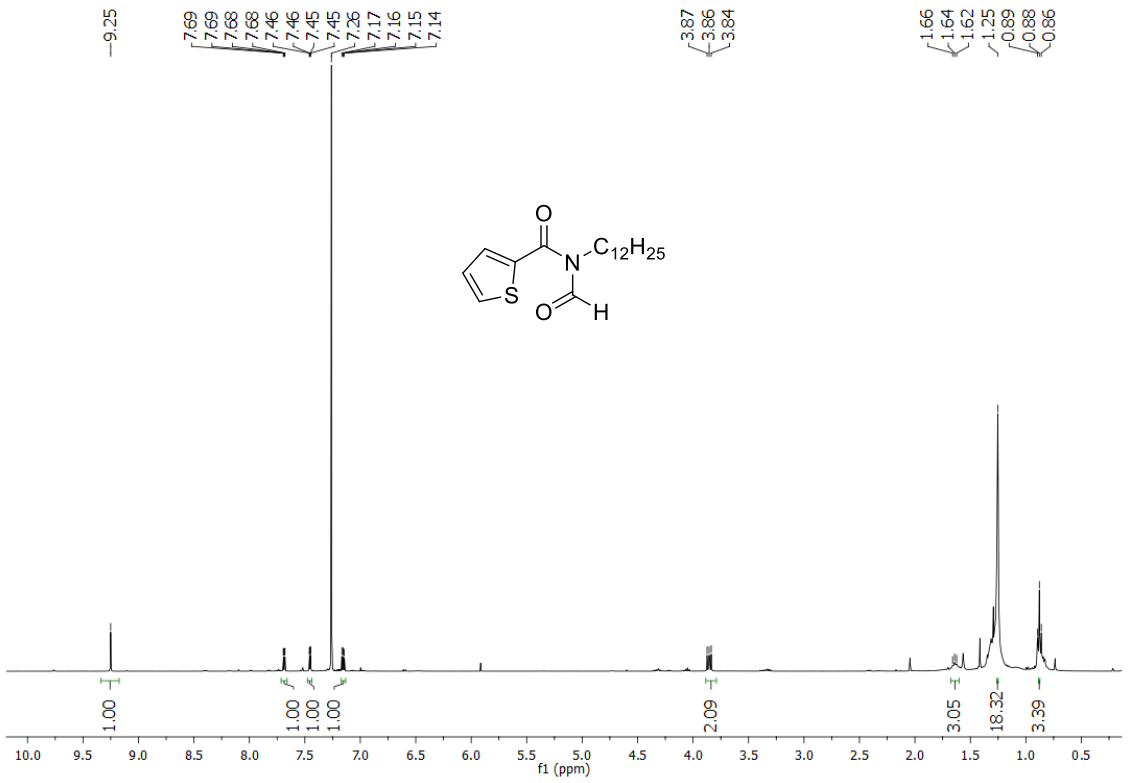
Rotaxane **3i** (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



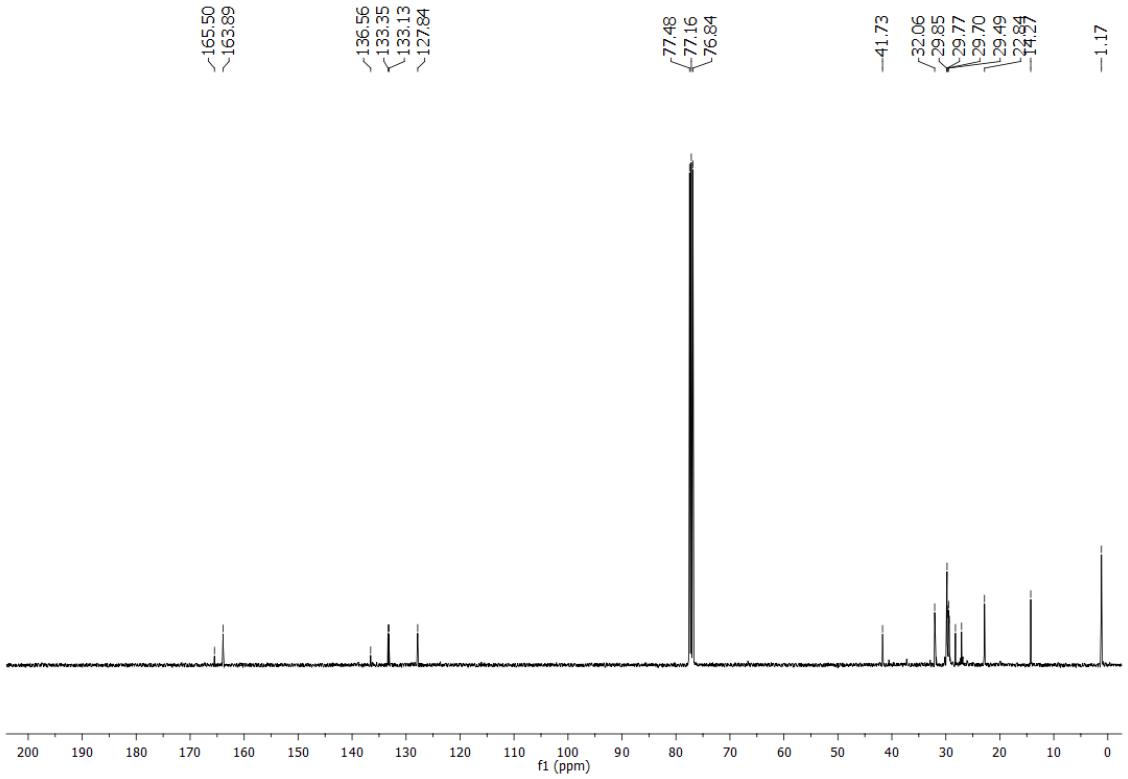
Rotaxane **3i** (^{13}C RMN, 100 MHz, $CDCl_3$, 298 K)



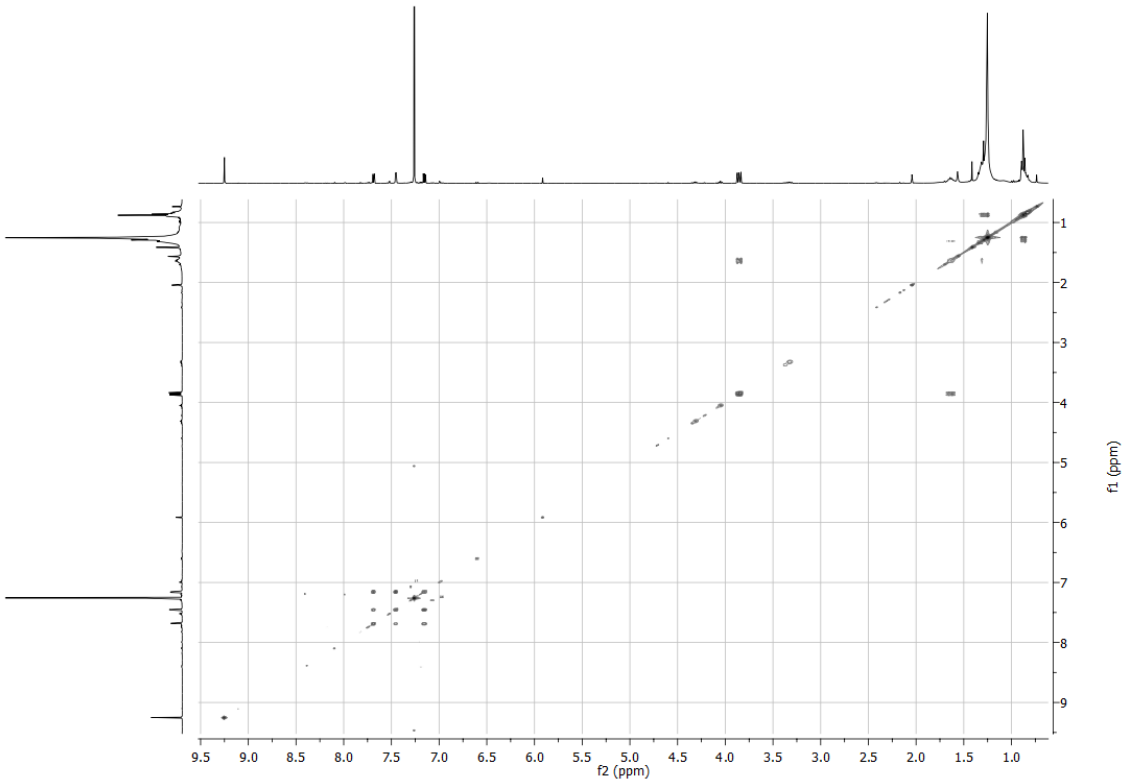
N-Dodecyl-*N*-formylthiophene-2-carboxamide (**4**) (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



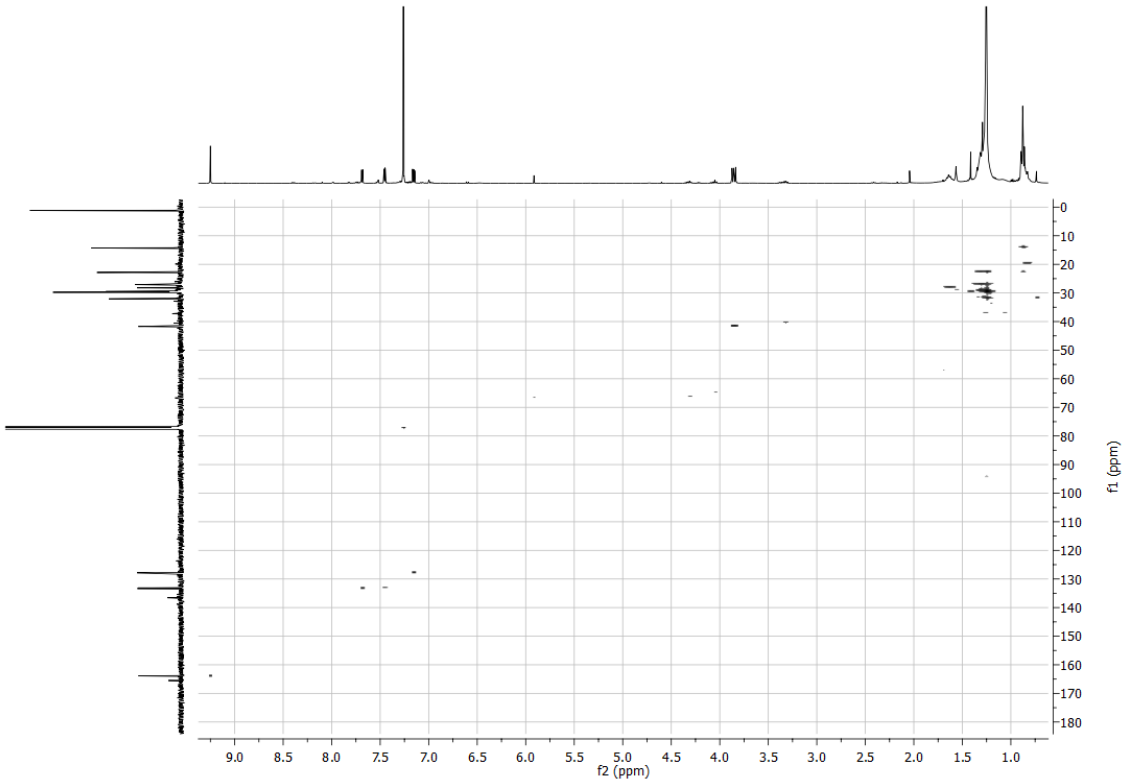
N-Dodecyl-*N*-formylthiophene-2-carboxamide (**4**) (^{13}C RMN, 100 MHz, $CDCl_3$, 298 K)



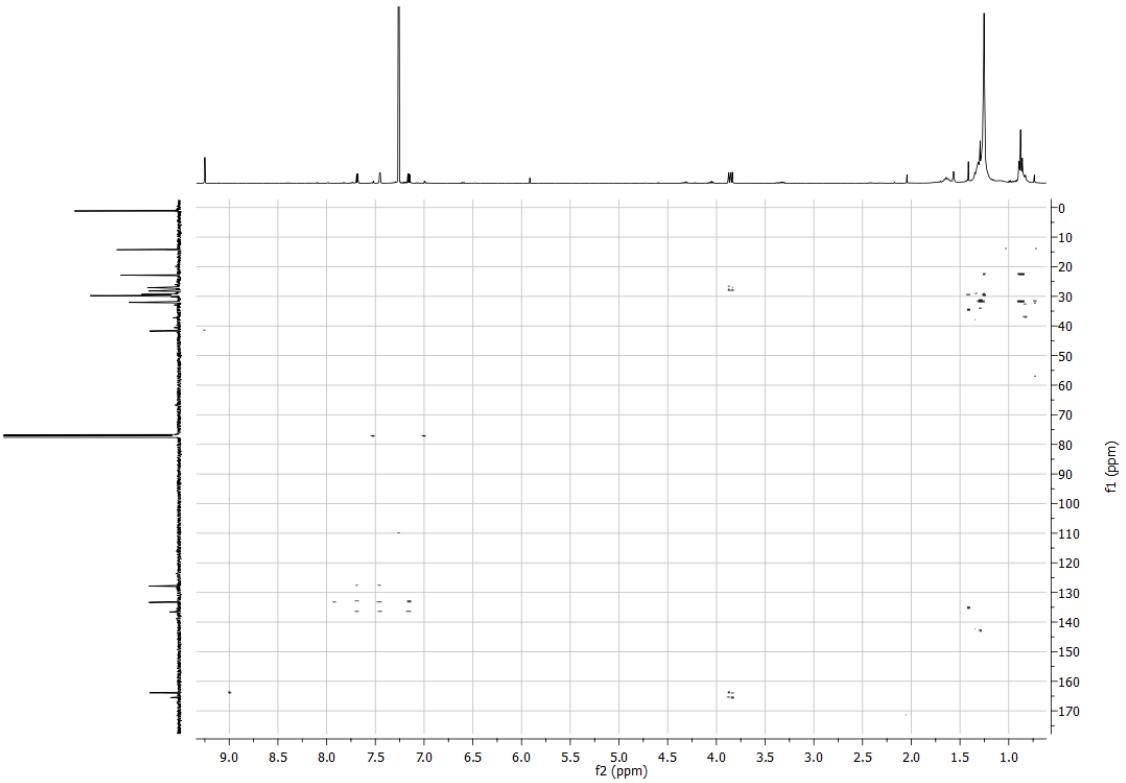
N-Dodecyl-*N*-formylthiophene-2-carboxamide (**4**) (^{1}H,^{1}H-COSY, 400 MHz, $CDCl_3$, 298 K)



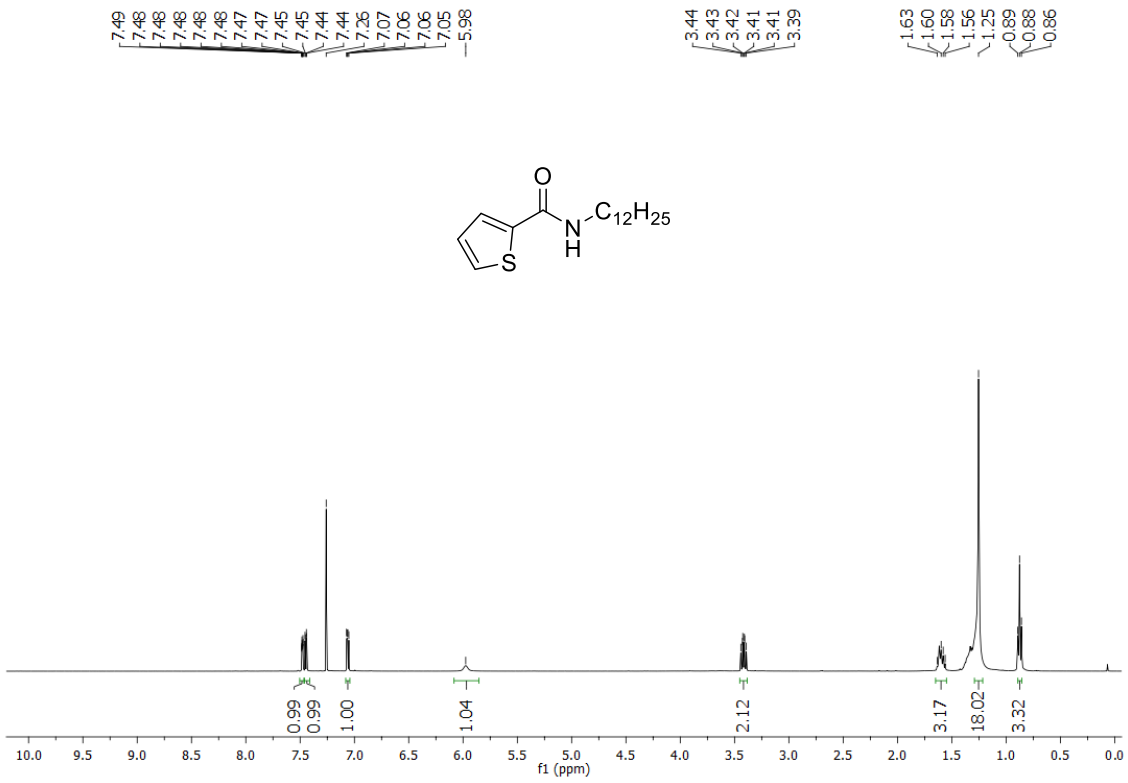
N-Dodecyl-*N*-formylthiophene-2-carboxamide (**4**) (HSQC, 400 MHz, $CDCl_3$, 298 K)



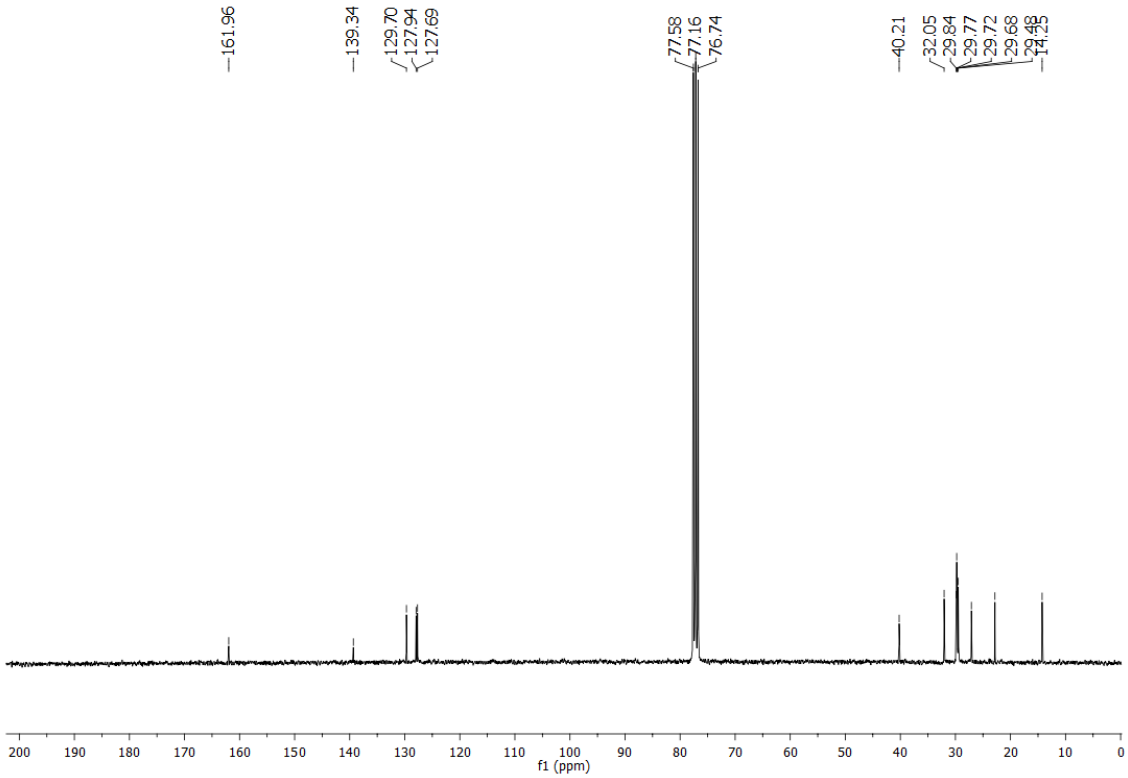
N-Dodecyl-*N*-formylthiophene-2-carboxamide (**4**) (HMBC, 400 MHz, $CDCl_3$, 298 K)



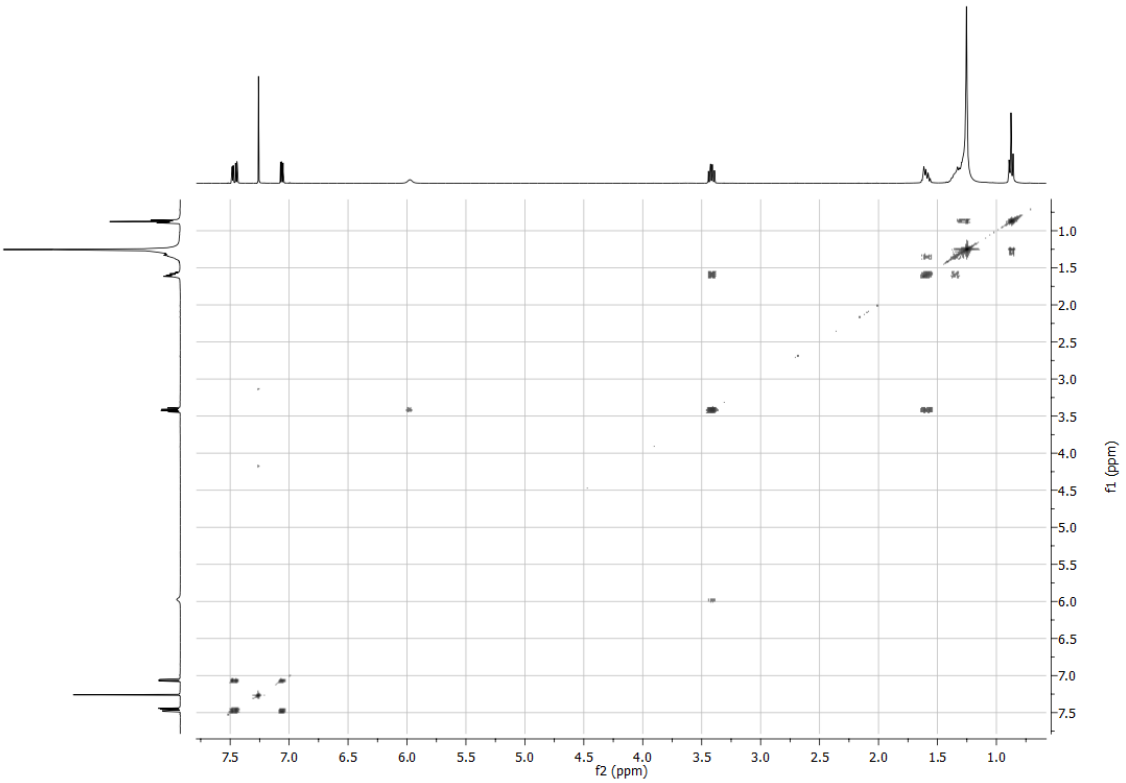
N-Dodecylthiophene-2-carboxamide (**5**) (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



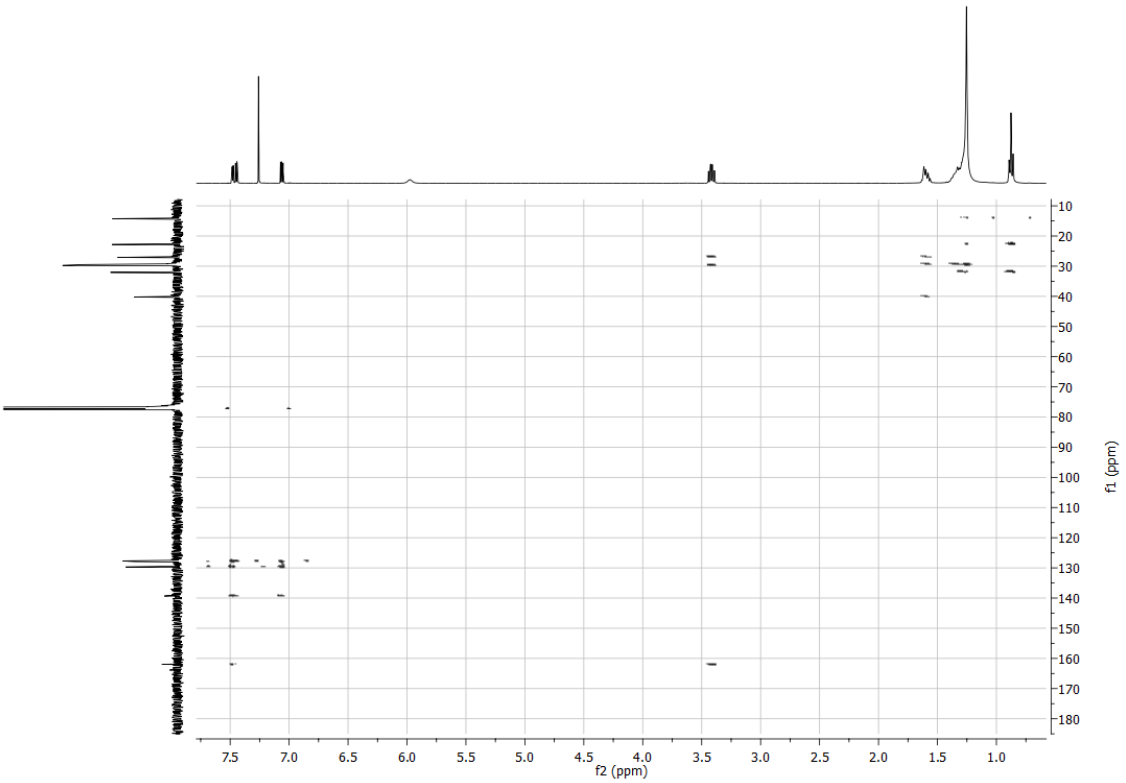
N-Dodecylthiophene-2-carboxamide (**5**) (^{13}C RMN, 75 MHz, $CDCl_3$, 298 K)



N-Dodecylthiophene-2-carboxamide (**5**) (^{1}H,^{1}H-COSY, 400 MHz, $CDCl_3$, 298 K)



N-Dodecylthiophene-2-carboxamide (**5**) (HMBC, 400 MHz, $CDCl_3$, 298 K)



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