Electronic Supplementary Material (ESI) for ChemComm.


**Electronic Supplementary Information**

# Maximizing the [*c2*]daisy chain to lasso ratio through competitive self-templating clipping reactions

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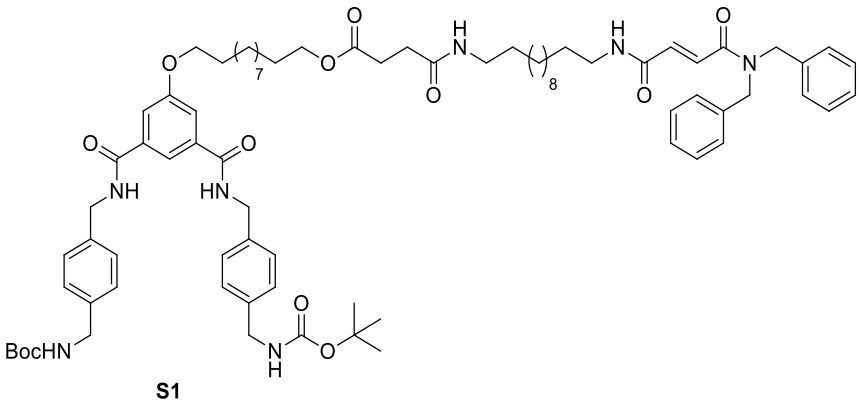
## 1. General experimental section

Unless stated otherwise, all reagents were purchased from Aldrich Chemicals and used without further purification. HPLC grade solvents (Scharlab) were nitrogen saturated, dried and deoxygenated using the Innovative Technology Inc. Pure-Solv 400 Solvent Purification System. Column chromatography was carried out using silica gel (60 Å, 70-200 μm, SDS) as stationary phase, and TLC was performed on precoated silica gel on aluminun cards (0.25 mm thick, with fluorescent indicator 254 nm, Fluka) 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 at 298 K on a Bruker Avance 400 and 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 $Me_4Si$ 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 or two-dimensional NMR experiments (COSY, NOESY, ROESY and HSQC). Abbreviations of coupling patterns are as follows: b, broad; s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet. Coupling constants *(J)* are expressed in Hz. High-resolution mass spectra (HRMS) were obtained using a time-of-flight (TOF) instrument equipped with electrospray ionization (ESI).

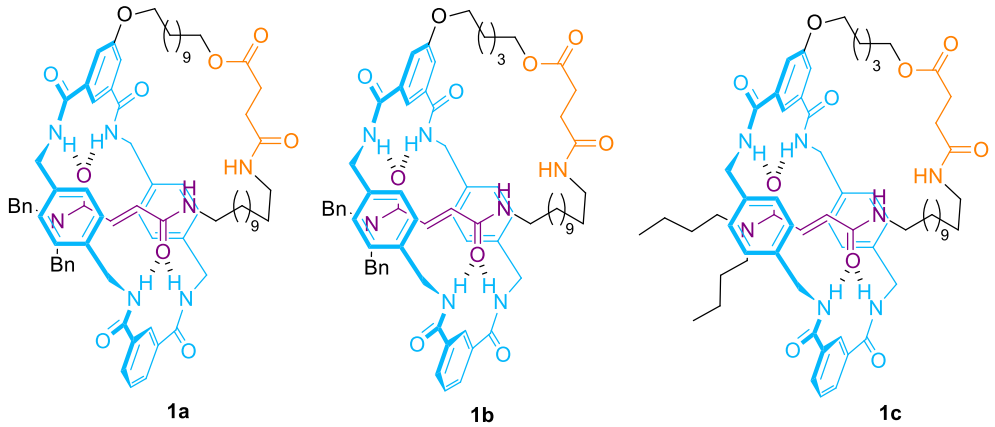
## 2. Synthesis of S1



S1

Precursor **S1** was synthesized following the described procedure reported in A. Saura-Sanmartin, A. Martinez-Cuezva, A. Pastor, D. Bautista and J. Berna, *Org. Biomol. Chem.*, 2018, **16**, 6980.

## 3. Synthesis of lasso rotaxanes 1a-c



**1a** **1b** **1c**

Lasso rotaxanes **1a-c** were synthesized following the described procedure reported in A. Saura-Sanmartin, A. Martinez-Cuezva, A. Pastor, D. Bautista and J. Berna, *Org. Biomol. Chem.*, 2018, **16**, 6980.

## 4. Screening of the clipping reaction

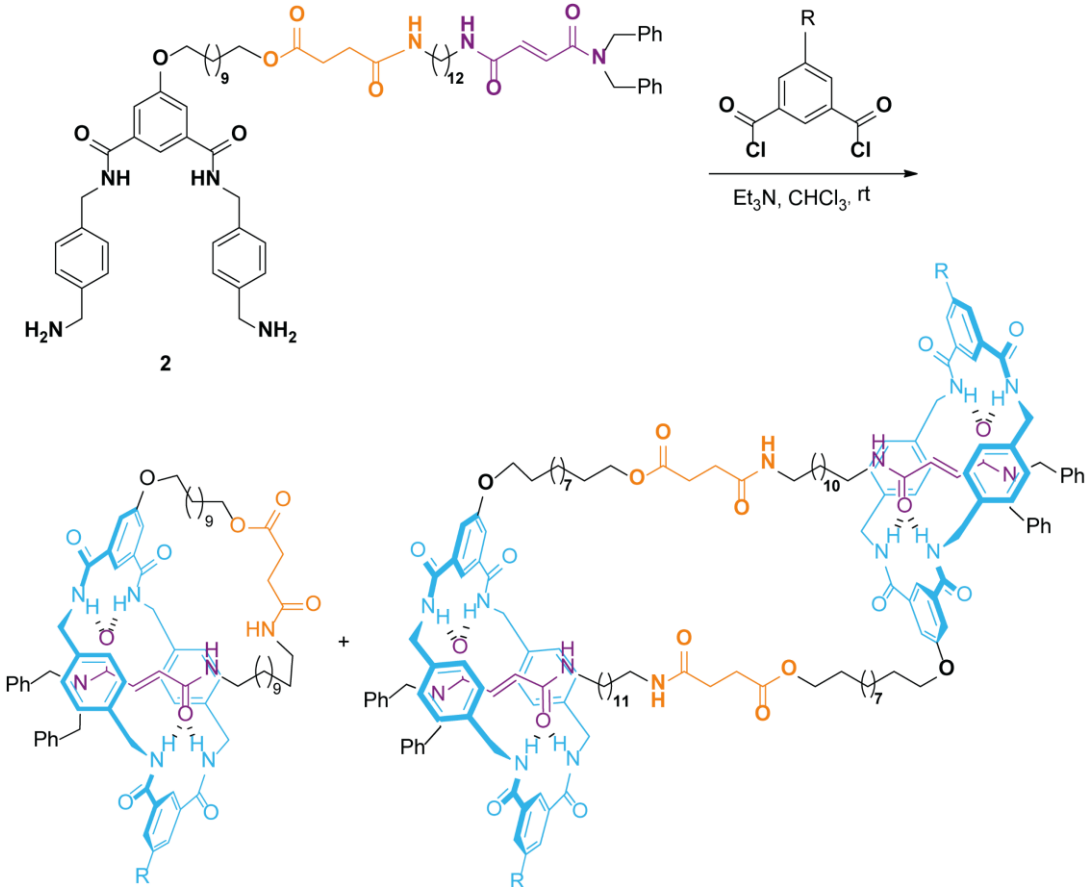



**Table S1.** Screening of the clipping reaction using chloroform and mixtures with $CH_3CN$.

| Entry | R | [2] (mM) | Amount of 2 (g) | $CHCl_3$ volume (mL) | $CH_3CN$ volume (mL) | Yield of lasso rotaxane (%)[a] | Yield of [*c2*]daisy chain rotaxane (%)[a] | Global yield (%) |
|---|---|---|---|---|---|---|---|---|
| **1** | H | 1.1 | 0.20 | 150 | 10 | 7.0 | - | 7.0 |
| **2** | H | 1.1 | 0.20 | 140 | 20 | 6.2 | - | 6.2 |
| **3** | H | 1.1 | 0.20 | 130 | 30 | 4.1 | - | 4.1 |
| **4** | $^t$Bu | 1.1 | 0.20 | 160 | - | 22.1 | - | 22.1 |
| **5** | $^t$Bu | 2.2 | 0.20 | 80 | - | 16.3 | 0.4 | 16.7 |
| **6** | $^t$Bu | 4.4 | 0.20 | 40 | - | 9.9 | 1.2 | 11.1 |
| **7** | $^t$Bu | 8.8 | 0.20 | 20 | - | 4.4 | 3.1 | 7.5 |
| **8** | $^t$Bu | 17.6 | 0.20 | 10 | - | - | - | |

[a] Average isolated yields of two independent reactions.

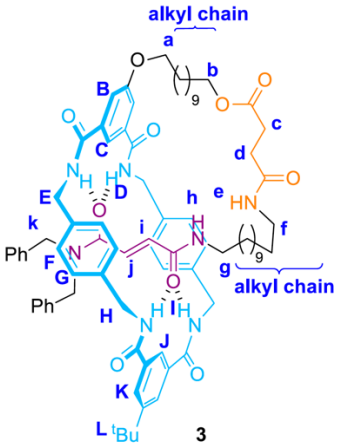
**Table S2.** Clipping reaction using TCE, DCM and mixtures with $CH_3CN$.

| Entry | R | [2] (mM) | $C_2H_2Cl_4$ volume (mL) | $CH_2Cl_2$ volume (mL) | $CH_3CN$ volume (mL) | Yield of lasso rotaxane (%)[a] | Yield of [*c2*]daisy chain rotaxane (%)[a] |
|---|---|---|---|---|---|---|---|
| **1** | $^t$Bu | 1.1 | - | 150 | 10 | 3.1 | - |
| **2** | $^t$Bu | 1.1 | - | 140 | 20 | 2.6 | - |
| **3** | $^t$Bu | 1.1 | - | 130 | 30 | 2.0 | - |
| **4** | $^t$Bu | 8.8 | - | 20 | - | 2.4 | - |
| **5** | $^t$Bu | 1.1 | 150 | - | 10 | 3.5 | - |
| **6** | $^t$Bu | 8.8 | 20 | - | - | 2.8 | - |

[a] Average isolated yields of two independent reactions.

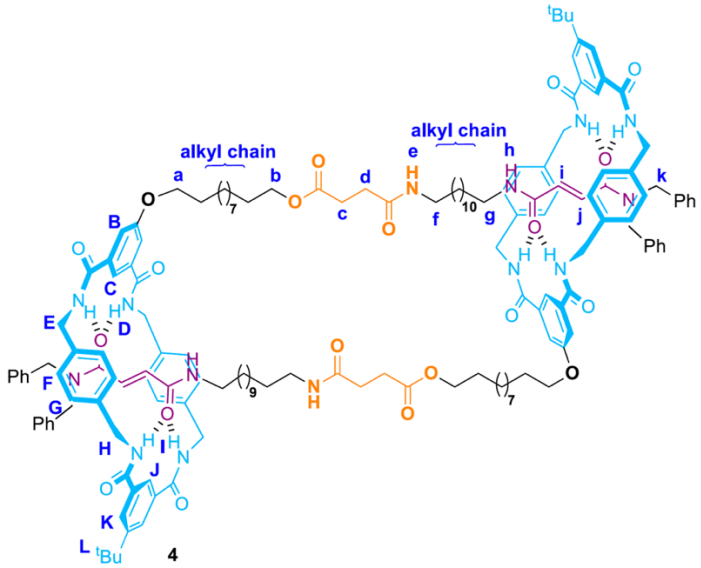
**5. Clipping reaction to afford lasso rotaxane 3 and [*c2*]daisy chain rotaxane 4**

To a solution of precursor **S1** (0.20 g, 0.17 mmol) in dichloromethane (10 mL) was added trifluoroacetic acid (1.4 mL, 17.4 mmol). The mixture was stirred for 24 hours. The resulting salt was neutralized by using Amberlyst® A21. To a solution of the resulting diamine **2** in chloroform (20 mL; 8.8 mM) was added $Et_3N$ (0.16 mL, 1.15 mmol) under a nitrogen-gas atmosphere. A solution of 5-(*tert*-butyl)isophtaloyl dichloride (4.41 mg, 0.17 mmol) in chloroform (4 mL) was added dropwise for a period of 4 hours by using a motor-driven syringe pump. The crude of reaction was filtered over Celite® for remove unsoluble polymers, and sequentially washed with an aqueous solution of HCl 1 N (2 x 100 mL), a saturated solution of $NaHCO_3$ (2 x 100 mL) and brine (75 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The solid crude was purified by silica-gel chromatography eluting with $CH_2Cl_2$/$CH_3OH$ (99.5/0.5-98/2) to obtain **3** (Rf = 0.3, $CHCl_3$/MeOH 98/2) and **4** (Rf = 0.2, $CHCl_3$/MeOH 98/2). Compound **4** was submited to a further purification by preparative TLC employing a $CHCl_3$/MeOH (98/2) mixture as eluent.




*Lasso rotaxane **3**:* obtained as a white solid (10.21 mg, 4.4% yield[1]); m. p. > 300ºC; $^{1}$H NMR (401 MHz, $CDCl_3$, 298 K) δ (ppm) = 8.27 (s, 1H, $H_J$), 8.22-8.21 (d, *J* = 1.3 Hz, 2H, $H_B$), 8.07 (s, 1H, $H_C$), 7.70 (d, *J* = 1.1 Hz, 2H, $H_K$), 7.61 – 7.57 (m, 4H, $NH_{D+I}$), 7.34 – 7.31 (m, 3H, $H_{Ph}$ + $NH_h$), 7.22 – 7.09 (m, 6H, $H_{Ph}$), 6.90 (s, 8H, $H_{F+G}$) 6,79 – 6.74 (m, 2H, $H_{Ph}$), 6.11 (t, *J* = 5.5 Hz, 1H, $NH_e$), 6.05 (d, *J* = 14.6 Hz, 1H, $H_j$), 5.87 (d, *J* = 14.4 Hz, 1H, $H_i$), 4.51 – 4.22 (m, 12H, $H_{E+H+k}$), 4.10 – 4.02 (m, 4H, $H_{a+b}$), 3.18 – 3.06 (m, 4H, $H_{f+g}$), 2.56 (t, *J* = 6.6 Hz, 2H, $H_c$), 2.36 (t, *J* = 6.4 Hz, 2H, $H_d$), 1.85 – 1.75 (m, 2H, $H_{alkyl\ chain}$), 1.61 – 1.55 (m, 2H, $H_{alkyl\ chain}$), 1.50 – 1.12 (43H, $H_{L+alkyl\ chain}$); $^{13}$C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm) = 173.2 (CO), 171.7 (CO), 166.8 (CO), 166.1 (CO), 165.9 (CO), 165.1 (CO), 160.0 (C), 152.8 (C), 137.6 (C), 137.4 (C), 136.0 (CH), 135.2 (C), 134.9 (C), 133.5 (C), 133.4 (CH), 129.4 (CH), 129.1 (CH), 129.0 (CH), 128.7 (CH), 128.5 (CH), 128.3 (CH), 126.9 (CH), 125.9 (CH), 121.2 (CH), 117.6 (CH), 116.0 (CH), 68.4 ($CH_2$), 64.9 ($CH_2$), 51.4 ($CH_2$), 50.9 ($CH_2$), 43.9 ($CH_2$), 43.8 ($CH_2$), 40.3 ($CH_2$), 39.7 ($CH_2$), 35.2 (C), 31.3 ($CH_3$), 31.3 ($CH_2$), 30.0 ($CH_2$), 29.5 ($CH_2$), 29.4 ($CH_2$), 29.3 ($CH_2$), 29.2 ($CH_2$), 29.12 ($CH_2$), 29.05, 28.9 ($CH_2$), 28.84 ($CH_2$), 28.79 ($CH_2$), 28.5 ($CH_2$), 26.8 ($CH_2$), 25.72 ($CH_2$), 25.68 ($CH_2$); HRMS (ESI) calcd for $C_{81}H_{104}N_7O_{10}$ $[M + H]^+$ 1334.7839, found 1334.7857.

[1] A 22.1% yield was obtained by using the conditions previously reported in A. Saura-Sanmartin, A. Martinez-Cuezva, A. Pastor, D. Bautista and J. Berna, *Org. Biomol. Chem.*, 2018, **16**, 6980.




*[c2]daisy chain rotaxane **4**:* obtained as a white solid (7.21 mg, 3.1% yield); m. p. > 300ºC; $^{1}$H NMR (401 MHz, $CDCl_3$, 298 K) δ (ppm) = 9.05 (s, 2H, $H_J$), 8.29 (s, 2H, $H_C$), 8.21 (d, *J* = 1.2 Hz, 4H, $H_B$), 7.68 – 7.50 (m, 14H, $H_K$ + $H_{Ph}$ + $NH_{D+I}$), 7.32 – 7.19 (m, 10H, $H_{Ph}$ + $NH_h$), 7.08 – 7.00 (m, 22H, $H_{F+G+Ph}$), 6.66 – 6.62 (m, 4H, $H_{Ph}$), 6.11 (d, *J* = 14.6 Hz, 2H, $H_j$), 5.98 – 5.90 (m, 4H, $H_i$ + $NH_e$), 5.00 (s, 4H, $H_E$), 4.80 (s, 4H, $H_{E'}$), 4.26 (s, 4H, $H_k$), 4.19 (s, 4H, $H_{k'}$), 4.14 (t, *J* = 6.1 Hz, 4H, $H_a$), 4.06 (t, *J* = 6.6 Hz, 4H, $H_b$), 3.88 (bs, 8H, $H_H$), 3.46 – 3.39 (m, 4H, $H_f$), 3.21 – 3.16 (m, 4H, $H_g$), 2.65 (t, *J* = 6.6 Hz, 4H, $H_c$), 2.45 (t, *J* = 6.5 Hz, 4H, $H_d$), 1.81 – 1.18 (m, 94H, $H_{L+alkyl\ chain}$); $^{13}$C NMR (151 MHz, $CDCl_3$, 298 K) δ (ppm) = 173.1 (CO), 171.6 (CO), 166.3 (CO), 166.0 (CO), 165.9 (CO), 165.7 (CO), 159.6 (C), 152.5 (C), 137.8 (C), 136.5 (C), 135.8 (C), 134.6 (CH), 134.4 (CH), 134.2 (C), 133.0 (CH), 129.4 (CH), 129.3 (CH), 129.2 (CH), 129.0 (CH), 128.8 (CH), 128.74 (CH), 128.67 (CH), 126.8 (CH), 125.8 (CH), 117.2 (CH), 115.7 (CH), 68.5 ($CH_2$), 64.9 ($CH_2$), 51.3 ($CH_2$), 50.7 ($CH_2$), 48.5 ($CH_2$), 44.2 ($CH_2$), 43.7 ($CH_2$), 40.3 ($CH_2$), 39.9 ($CH_2$), 39.8 ($CH_2$), 39.6 ($CH_2$), 39.5 ($CH_2$), 35.1 (C), 31.4 ($CH_2$), 31.3 ($CH_3$), 31.2 ($CH_2$), 30.2 ($CH_2$), 29.62 ($CH_2$), 29.56 ($CH_2$), 29.5 ($CH_2$), 29.33 ($CH_2$), 29.27 ($CH_2$), 29.25 ($CH_2$), 29.14 ($CH_2$), 28.5 ($CH_2$), 27.2 ($CH_2$), 26.82 ($CH_2$), 26.77 ($CH_2$), 26.0 ($CH_2$), 25.8 ($CH_2$); HRMS (ESI) calcd for $C_{162}H_{207}N_{14}O_{20}$ $[M + H]^+$ 2668.5606, found 2668.5633.

## 6. NMR diffusion experiments

The PGSE NMR diffusion measurements were performed on a 600 MHz Bruker AVANCE spectrometer. The sample was not spun and the airflow was disconnected. The values reported are the average of three different measurements ($\Delta$ = 50/100, 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 1.2 and 5.4 ms. The number of scans was 32 and the experimental time was ca. 90 min. All of the observed data leading to the reported *D*-values afforded lines whose correlation coefficients were above 0.999.

**Table S3.** Diffusion coefficients, *D* ($m^2\ s^{-1}$) and hydrodynamic radii, $r_H$ (Å), for 2 x $10^{-3}$ M solutions in $CDCl_3$ at 298 K of compounds **1a-c**,[a] **3** and **4**.

| Entry | **Compound** | $\boldsymbol{D}$ [b]/$\mathbf{10^{-10}}$ | $\boldsymbol{r_H}$ [c] |
|---|---|---|---|
| 1 | **1c (monomer)** | 5.67 | 6.9 |
| 2 | **1b (monomer)** | 5.31 | 7.4 (7.5)[d] |
| 3 | **1a (monomer)** | 5.10 | 7.7 |
| 4 | **3 (monomer)** | 5.04 | 7.8 |
| 5 | **4 (dimer)** | 3.74 | 10.5 (9.1)[e] |

$\eta$ ($CDCl_3$, 298 K) = 0.556 x $10^{-3}$ Kg $s^{-1}$ $m^{-1}$ [According to the following reference: U. B. Kadam, A. P. Hiray, A. B. Sawant and M. Hasan, *J. Chem. Thermodynamics*, 2006, **38**, 1675]. [a] Data previously reported in A. Saura-Sanmartin, A. Martinez-Cuezva, A. Pastor, D. Bautista and J. Berna, *Org. Biomol. Chem.*, 2018, **16**, 6980. [b] Experimental error: ± 3%. [c] Calculated from the Stokes-Einstein equation (see below); standard deviation: ± 0.1 Å. [d] Calculated from the X-Ray structure [According to the following reference: A. Macchioni, G. Ciancaleoni, C. Zuccaccia and D. Zuccaccia, *Chem. Soc. Rev.*, 2008, **37**, 479]. [e] Calculated from the modelized structure (see below).

The Stokes-Einstein equation: $D = (k_B T)/(6\pi\eta r_H)$. In this equation, *D* = diffusion coefficient, $k_B$ = Boltzman constant, *T* = temperature in degrees Kelvin, $\eta$ = viscosity of the solution (for diluted solutions, the viscosity of the solvent can be used), and $r_H$ = hydrodynamic radius (the radius of a hypothetical hard sphere that diffuses with the same speed as the particle under examination) [See: J. T. Edward, *J. Chem. Educ.* 1970, **47**, 261].

The hydrodynamic radius ($r_H$) is similar to $r_{vdW}$ only for compact molecules without any inlet. Otherwise $r_H$ is greater than $r_{vdW}$. The upper limit of $r_H$ is frequently the $r_{x\text{-}Ray}$ that can be deduced from the X-Ray structure by simply dividing the volume of the crystallographic cell by the number of contained molecules, assuming the latter has a spherical shape [According to the following reference: A. Macchioni, G. Ciancaleoni, C. Zuccaccia and D. Zuccaccia, *Chem. Soc. Rev.*, 2008, **37**, 479].

The ratio of diffusion coefficients for two different molecular species is inversely proportional to the square-root or to the cubic-root of the ratio of their molecular weights for rod-like and spherical molecules, respectively. The determined diffusion data fullfilled this relationship assuming that **4** is a dimer of **3** (Table S2) [See P. Timmerman, J.-L. Wiedmann, K. A. Jolliffe, L. J. Prins, D. N. Reindhoudt, S. Shinkai, L. Frish, Y. Cohen *J. Chem. Soc. Perkin Trans. 2*, 2000, 2077].

**Table S4.** Ratio between the diffusion coeficients of **3** and **4** and values of the corresponding cubic and square roots of the inverse quotients of their respective molecular weights.

| Entry | **a/b** | $\sqrt[3]{\frac{M_b}{M_a}}$ | $\boldsymbol{D_a/D_b}$ | $\sqrt[2]{\frac{M_b}{M_a}}$ |
|---|---|---|---|---|
| 1 | **3 / 4** | 1.26 | 1.35 | 1.41 |

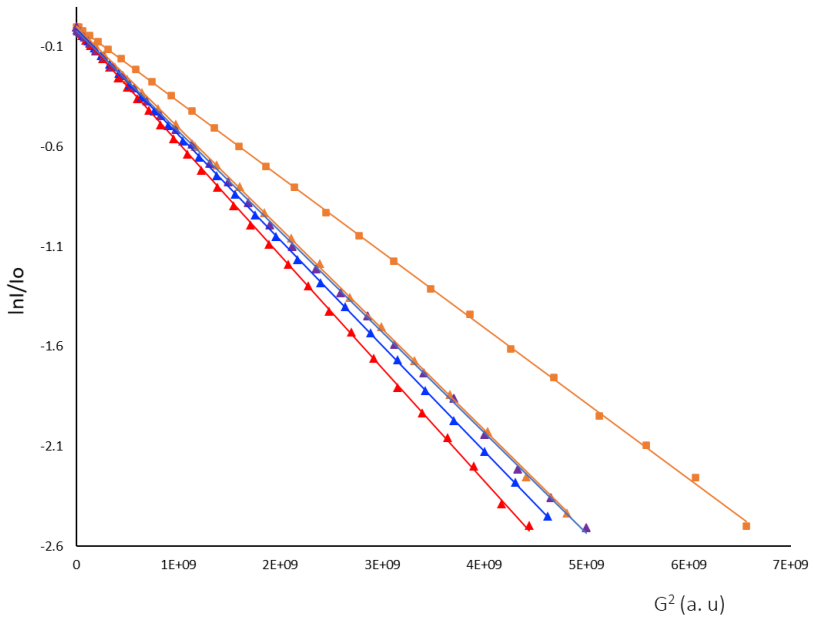



**Figure S1.** NMR diffusion experiments (600 MHz, 298 K, $2\cdot10^{-3}$ M in $CDCl_3$) of **1c** (▲), **1b** (▲), **1a** (▲), **3** (▲) and **4** (■). Plots of the observed intensity changes $\ln(I/I_o)$ as a function of $G^2$ (arbitrary units) showing the different translation rates depending on their molecular sizes. The calculated lines have been adjusted to compensate the different values of Δ and δ for every measurement.

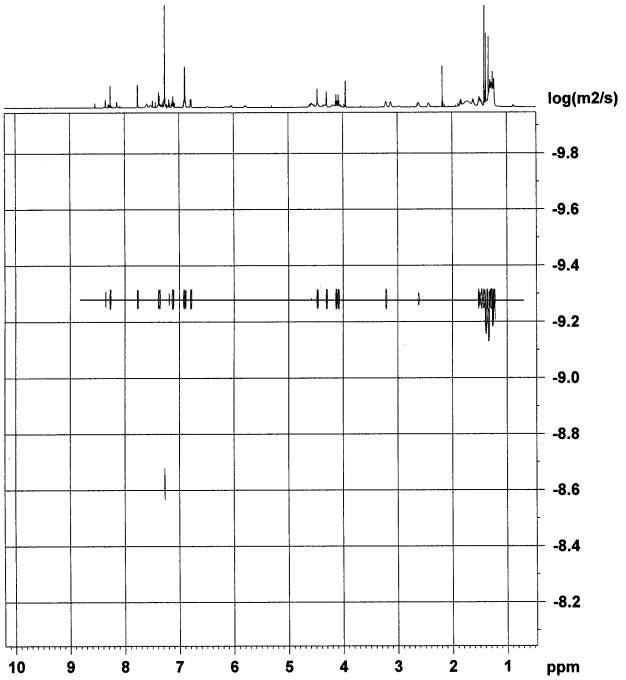



**Figure S2.** DOSY 2D TXI of compound **3**.

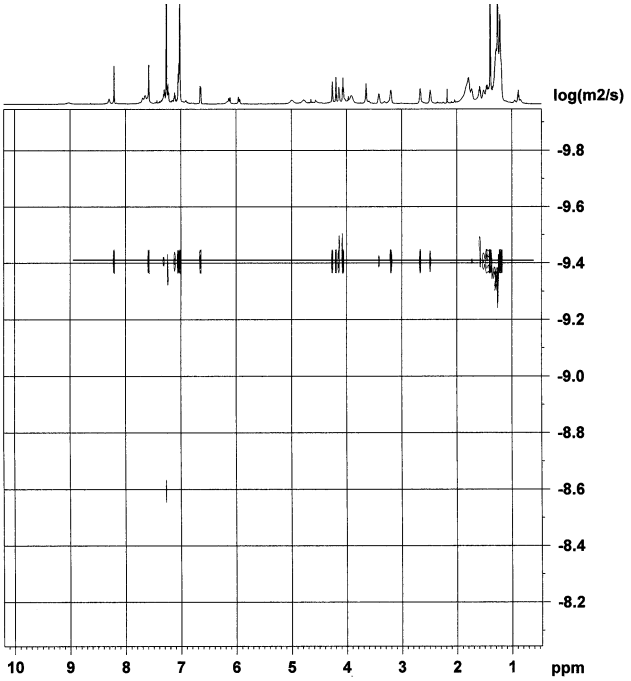



**Figure S3.** DOSY 2D TXI of compound **4**.

## 7. Molecular Mechanics calculations of 4

Theoretical MM2 calculations of [*c2*]daisy chain rotaxane **4** were performed using the Chem3D® Pro 12.0 software (CambridgeSoft), in which the hydrogen atoms between the macrocyclic components and the templating arms were selected as a restriction. The first minimization of the energy was performed considering dimethylamide as stoppers by using a minimum RMS gradient of 0.100 after 10000 iterations. Then, the dimethyl stoppers groups were exchanged for dibenzyl motifs. A rapid minimization of the stopper groups were carried out (minimum RMS gradient of 0.100 and 1000 iterations). An additional minimization of the energy of the complete dimeric structure **4** was performed (minimum RMS gradient of 0.100 and 10000 iterations).

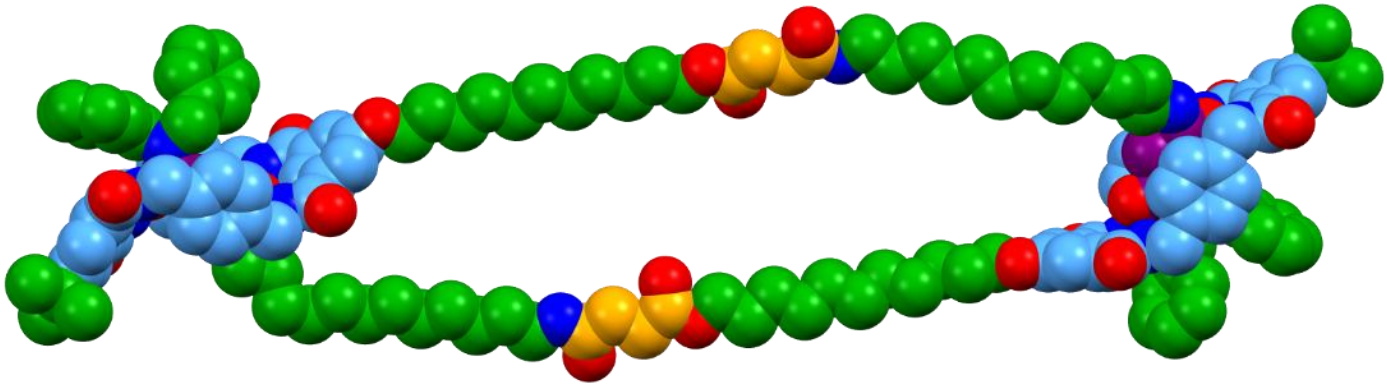


**Figure S4.** Computed model of [*c2*]daisy chain rotaxane **4** by using MM2.

| Atom | X | Y | Z |
|---|---|---|---|
| **C** | 62.508 | -19.802 | -5.193 |
| **H** | 65.126 | -14.253 | -8.055 |
| **C** | 19.18 | 4.15 | -7.316 |
| **C** | 25.006 | 5.234 | -7.419 |
| **H** | 17.411 | 5.232 | -6.859 |
| **H** | 72.985 | -15.932 | -8.004 |
| **C** | 72.436 | -15.215 | -4.636 |
| **C** | 61.728 | -22.054 | -9.7 |
| **H** | 23.24 | 4.637 | -6.439 |
| **H** | 66.293 | -16.166 | -7.127 |
| **C** | 62.728 | -21.744 | -8.847 |
| **H** | 20.93 | 2.275 | -5.236 |
| **C** | 18.191 | 4.134 | -5.221 |
| **H** | 13.37 | -1.016 | -8.302 |
| **C** | 26.283 | 3.567 | -8.4 |
| **C** | 68.901 | -17.588 | -5.538 |
| **H** | 62.872 | -19.643 | -11.17 |
| **H** | 71.842 | -14.281 | -4.762 |
| **H** | 66.493 | -16.988 | -10.25 |

| | | | |
|---|---|---|---|
| **C** | 65.774 | -14.826 | -8.76 |
| **O** | 65.864 | -16.678 | -6.283 |
| **C** | 18.204 | 4.559 | -6.492 |
| **N** | 66.704 | -18.021 | -4.862 |
| **H** | 24.588 | 2.553 | -10.366 |
| **H** | 24.857 | 6.294 | -7.149 |
| **C** | 62.771 | -16.367 | -10.308 |
| **C** | 63.423 | -19.089 | -4.521 |
| **H** | 70.633 | -15.149 | -7.838 |
| **H** | 65.019 | -18.616 | -11.226 |
| **O** | 61.941 | -18.046 | -7.712 |
| **C** | 65.049 | -20.618 | -5.082 |
| **C** | 57.087 | -19.129 | -8.108 |
| **O** | 59.601 | -18.068 | -11.258 |
| **H** | 65.192 | -17.525 | -7.078 |
| **C** | 62.848 | -20.95 | -5.801 |
| **H** | 63.15 | -14.537 | -9.338 |
| **C** | 63.134 | -16.809 | -6.941 |
| **C** | 62.31 | -18.687 | -11.055 |
| **H** | 61.306 | -22.454 | -5.84 |
| **H** | 65.743 | -19.608 | -7.053 |
| **N** | 61.124 | -20.666 | -6.636 |
| **H** | 65.941 | -18.428 | -8.487 |
| **H** | 59.279 | -14.274 | -3 |
| **C** | 62.341 | -23.882 | -7.889 |
| **H** | 61.683 | -16.187 | -10.302 |
| **C** | 70.141 | -17.172 | -5.23 |
| **H** | 25.104 | -4.67 | -7.23 |
| **N** | 61.31 | -18.899 | -9.99 |
| **C** | 63.251 | -17.558 | -10.702 |
| **C** | 59.79 | -20.883 | -6.42 |
| **C** | 68.327 | -22.118 | -9.717 |
| **H** | 57.405 | -17.988 | -9.879 |
| **C** | 21.839 | 0.574 | -8.419 |
| **H** | 64.435 | -22.31 | -6.179 |
| **H** | 23.876 | 0.01 | -8.438 |
| **C** | 15.945 | -1.751 | -8.805 |
| **C** | 66.683 | -21.584 | -8.168 |
| **H** | 43.407 | -13.268 | -10.959 |
| **H** | 60.453 | -13.673 | -1.156 |
| **C** | 65.41 | -16.783 | -10.267 |
| **H** | 27.045 | -7.402 | -11.548 |
| **C** | 23.963 | 1.894 | -10.991 |
| **C** | 47.798 | -15.733 | -9.982 |
| **N** | 19.647 | -0.315 | -6.776 |
| **H** | 17.379 | 4.444 | -4.543 |
| **H** | 48.164 | -15.12 | -10.839 |
| **H** | 36.462 | -11.087 | -11.262 |
| **C** | 40.777 | -13.483 | -10.907 |

| | | | |
|---|---|---|---|
| **O** | 49.917 | -6.803 | -1.541 |
| **H** | 61.467 | -19.444 | -5.237 |
| **C** | 25.156 | -4.425 | -12.162 |
| **C** | 39.561 | -13.636 | -11.828 |
| **C** | 27.846 | -1.781 | -9.523 |
| **H** | 60.753 | -20.43 | -8.575 |
| **H** | 37.826 | -2.816 | -7.891 |
| **H** | 25.569 | 1.593 | -8.245 |
| **H** | 47.953 | -5.387 | -3.072 |
| **H** | 52.065 | -8.26 | -1.072 |
| **O** | 68.482 | -15.03 | -9.25 |
| **H** | 21.785 | -0.299 | -13.143 |
| **H** | 32.858 | -1.55 | -9.042 |
| **H** | 50.996 | -18.486 | -9.643 |
| **H** | 63.099 | -18.2 | -3.963 |
| **H** | 32.404 | -11.007 | -13.374 |
| **H** | 24.633 | -6.504 | -11.743 |
| **C** | 64.584 | -17.718 | -10.761 |
| **C** | 17.639 | -0.514 | -9.879 |
| **C** | 24.26 | 3.014 | -7.358 |
| **C** | 68.108 | -20.939 | -10.314 |
| **C** | 21.459 | -2.605 | -7.088 |
| **C** | 22.407 | 0.343 | -12.498 |
| **C** | 64.919 | -15.685 | -9.668 |
| **C** | 68.897 | -16.262 | -7.425 |
| **H** | 59.248 | -14.254 | -2.995 |
| **C** | 63.638 | -20.532 | -9.101 |
| **H** | 61.868 | -18.485 | -12.055 |
| **H** | 57.212 | -20.068 | -6.222 |
| **C** | 64.718 | -19.448 | -4.509 |
| **C** | 64.127 | -21.358 | -5.716 |
| **C** | 70.869 | -16.457 | -6.171 |
| **C** | 68.317 | -16.997 | -6.61 |
| **C** | 57.743 | -19.839 | -7.161 |
| **O** | 18.138 | -0.356 | -12.061 |
| **C** | 59.078 | -19.157 | -9.355 |
| **H** | 34.629 | -12.343 | -13.188 |
| **H** | 62.041 | -16.758 | -6.833 |
| **C** | 61.809 | -21.756 | -6.546 |
| **N** | 66.699 | -15.641 | -7.946 |
| **O** | 55.78 | -18.778 | -7.854 |
| **C** | 68.055 | -15.677 | -8.321 |
| **C** | 63.591 | -15.44 | -9.791 |
| **H** | 55.178 | -8.758 | -2.01 |
| **C** | 68.076 | -18.309 | -4.73 |
| **H** | 62.204 | -22.031 | -7.55 |
| **H** | 22.007 | -1.735 | -9.96 |
| **H** | 66.278 | -14.044 | -9.368 |
| **H** | 25.825 | -7.475 | -13.784 |

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|---|---|---|---|
| **H** | 27.787 | -5.837 | -12.033 |
| **N** | 63.927 | -19.302 | -8.26 |
| **C** | 63.97 | -17.682 | -6.867 |
| **O** | 68.51 | -18.962 | -3.809 |
| **C** | 59.953 | -18.728 | -10.307 |
| **H** | 66.094 | -20.97 | -5.039 |
| **C** | 57.824 | -18.711 | -9.164 |
| **H** | 20.433 | -2.806 | -7.425 |
| **C** | 24.108 | 4.313 | -7.037 |
| **C** | 59.001 | -20.272 | -7.345 |
| **N** | 51.203 | -7.951 | -3.012 |
| **H** | 70.69 | -17.636 | -4.31 |
| **H** | 33.269 | -9.528 | -13.922 |
| **H** | 23.821 | 1.025 | -6.675 |
| **C** | 63 | -18.142 | -7.603 |
| **H** | 60.469 | -13.68 | -1.155 |
| **O** | 59.35 | -21.222 | -5.345 |
| **C** | 20.164 | 3.323 | -6.91 |
| **N** | 64.207 | -15.993 | -4.871 |
| **H** | 22.959 | 2.268 | -5.863 |
| **H** | 60.133 | -23.331 | -10.282 |
| **H** | 27.188 | 3.25 | -8.945 |
| **H** | 63.967 | -22.686 | -7.387 |
| **H** | 40.245 | -3.511 | -7.25 |
| **H** | 51.275 | -8.263 | -3.981 |
| **H** | 53.387 | -9.29 | -3.675 |
| **H** | 66.307 | -17.332 | -5.552 |
| **C** | 61.269 | -24.083 | -8.666 |
| **H** | 67.049 | -19.145 | -10.363 |
| **C** | 67.177 | -20.1 | -9.835 |
| **C** | 72.338 | -16.105 | -5.893 |
| **H** | 19.167 | 2.982 | -3.743 |
| **C** | 59.514 | -13.964 | -1.944 |
| **C** | 65.472 | -19.365 | -8.108 |
| **C** | 63.06 | -22.753 | -8.012 |
| **H** | 58.779 | -12.293 | -2.046 |
| **H** | 47.212 | -6.939 | -2.531 |
| **C** | 25.378 | 2.654 | -8.016 |
| **H** | 41.941 | -5.803 | -6.064 |
| **H** | 57.877 | -14.05 | -1.205 |
| **C** | 66.416 | -20.401 | -8.763 |
| **H** | 62.536 | -14.726 | -5.146 |
| **H** | 42.936 | -5.422 | -3.764 |
| **H** | 67.243 | -17.174 | -6.77 |
| **C** | 52.371 | -8.134 | -2.136 |
| **H** | 36.449 | -1.414 | -6.306 |
| **H** | 72.595 | -14.345 | -7.224 |
| **H** | 40.55 | -4.549 | -4.339 |
| **H** | 57.252 | -10.469 | -1.933 |

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|---|---|---|---|
| **H** | 72.788 | -17.989 | -4.788 |
| **C** | 73.136 | -17.411 | -5.672 |
| **H** | 63.278 | -16.072 | -2.511 |
| **C** | 58.392 | -13.043 | -1.287 |
| **H** | 38.185 | -3.712 | -4.94 |
| **C** | 32.581 | -1.904 | -8.021 |
| **C** | 54.481 | -9.608 | -1.823 |
| **C** | 33.772 | -1.75 | -7.064 |
| **O** | 45.563 | -5.721 | -4.193 |
| **H** | 74.217 | -17.204 | -5.5 |
| **C** | 55.143 | -10.933 | -2.248 |
| **C** | 50.072 | -7.271 | -2.641 |
| **H** | 54.284 | -9.626 | -0.725 |
| **C** | 59.726 | -20.047 | -8.49 |
| **C** | 46.721 | -6.363 | -4.549 |
| **H** | 38.829 | -2.194 | -5.625 |
| **H** | 34.734 | -3.615 | -7.661 |
| **H** | 61.649 | -19.099 | -9.013 |
| **C** | 62.668 | -15.289 | -3.037 |
| **C** | 73.032 | -15.354 | -7.053 |
| **C** | 70.171 | -15.906 | -7.19 |
| **C** | 49.02 | -7.174 | -3.742 |
| **H** | 39.571 | -5.038 | -6.619 |
| **H** | 52.501 | -10.273 | -2.464 |
| **H** | 73.49 | -14.919 | -4.431 |
| **H** | 55.274 | -10.941 | -3.357 |
| **H** | 34.034 | -0.67 | -6.968 |
| **C** | 64.592 | -16.52 | -6.078 |
| **H** | 60.993 | -14.829 | -3.464 |
| **C** | 40.946 | -4.043 | -5.251 |
| **H** | 37.163 | -4.31 | -7.165 |
| **C** | 61.188 | -15.379 | -2.493 |
| **H** | 61.687 | -15.146 | -1.498 |
| **H** | 33.463 | -2.086 | -6.045 |
| **C** | 43.329 | -4.881 | -4.658 |
| **H** | 63.168 | -14.303 | -2.846 |
| **H** | 72.066 | -15.727 | -3.72 |
| **C** | 56.987 | -12.66 | -1.93 |
| **H** | 73.06 | -18.079 | -6.561 |
| **C** | 60.109 | -14.328 | -1.998 |
| **H** | 74.111 | -15.183 | -6.836 |
| **H** | 35.832 | -2.887 | -5.514 |
| **H** | 53.013 | -7.225 | -2.194 |
| **H** | 32.289 | -2.978 | -8.084 |
| **C** | 47.713 | -6.429 | -3.388 |
| **C** | 53.159 | -9.378 | -2.585 |
| **C** | 42.218 | -4.776 | -5.726 |
| **H** | 62.133 | -16.447 | -4.823 |
| **C** | 37.442 | -3.254 | -6.939 |

| | | | |
|---|---|---|---|
| **H** | 41.212 | -3.003 | -4.945 |
| **H** | 46.328 | -16.687 | -11.274 |
| **H** | 47.802 | -15.073 | -9.082 |
| **H** | 50.313 | -15.54 | -9 |
| **C** | 36.181 | -2.481 | -6.493 |
| **C** | 31.918 | -9.205 | -12.242 |
| **C** | 45.366 | -15.007 | -10.258 |
| **C** | 23.845 | -3.695 | -11.808 |
| **H** | 26.46 | -5.848 | -14.167 |
| **C** | 46.355 | -16.188 | -10.277 |
| **H** | 23.364 | -4.151 | -10.913 |
| **H** | 56.135 | -13.306 | -1.581 |
| **C** | 52.673 | -17.156 | -9.246 |
| **C** | 38.567 | -3.248 | -5.88 |
| **C** | 42.971 | -14.208 | -10.547 |
| **C** | 39.841 | -3.995 | -6.329 |
| **C** | 50.239 | -16.436 | -9.66 |
| **C** | 28.069 | -0.009 | -10.759 |
| **H** | 45.297 | -14.616 | -9.215 |
| **H** | 38.908 | -11.588 | -11.486 |
| **H** | 52.958 | -17.195 | -10.325 |
| **H** | 23.118 | -3.755 | -12.65 |
| **H** | 25.835 | -4.418 | -11.278 |
| **C** | 43.955 | -15.364 | -10.764 |
| **H** | 25.662 | -3.856 | -12.979 |
| **H** | 53.424 | -17.876 | -7.341 |
| **C** | 35.133 | -11.382 | -12.932 |
| **H** | 53.25 | -19.152 | -8.594 |
| **C** | 30.718 | -8.77 | -13.105 |
| **H** | 42.79 | -14.071 | -9.456 |
| **C** | 15.114 | -4.051 | -8.221 |
| **H** | 46.034 | -16.945 | -9.523 |
| **H** | 43.615 | -3.859 | -4.314 |
| **H** | 55.199 | -18.381 | -9.807 |
| **C** | 28.476 | -7.542 | -13.197 |
| **H** | 38.074 | -12.813 | -10.463 |
| **H** | 44.286 | -6.632 | -5.532 |
| **H** | 44.009 | -15.614 | -11.85 |
| **C** | 14.131 | -2.922 | -10.224 |
| **O** | 46.951 | -6.817 | -5.648 |
| **H** | 29.317 | -8.533 | -11.447 |
| **H** | 28.833 | -6.893 | -14.032 |
| **H** | 13.853 | -1.995 | -6.876 |
| **C** | 29.679 | -7.943 | -12.322 |
| **C** | 44.571 | -5.61 | -5.189 |
| **H** | 49.501 | -6.67 | -4.614 |
| **H** | 48.485 | -17.413 | -8.787 |
| **C** | 48.771 | -16.902 | -9.737 |
| **H** | 32.443 | -8.299 | -11.858 |

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|---|---|---|---|
| **H** | 14.233 | -4.731 | -8.173 |
| **H** | 45.771 | -14.182 | -10.892 |
| **C** | 38.461 | -12.611 | -11.49 |
| **C** | 37.271 | -12.571 | -12.442 |
| **C** | 18.307 | -0.299 | -6.497 |
| **H** | 23.281 | -0.532 | -5.266 |
| **C** | 22.627 | 2.017 | -10.934 |
| **C** | 24.937 | -5.877 | -12.614 |
| **H** | 50.933 | -17.695 | -8.037 |
| **C** | 34.144 | -10.48 | -12.171 |
| **H** | 35.451 | -10.883 | -13.877 |
| **C** | 62.824 | -15.619 | -4.542 |
| **H** | 54.435 | -11.762 | -2.011 |
| **C** | 26.15 | -6.511 | -13.324 |
| **H** | 28.044 | -8.461 | -13.659 |
| **H** | 31.549 | -9.767 | -11.352 |
| **C** | 55.064 | -17.99 | -8.772 |
| **H** | 21.06 | 0.225 | -5.283 |
| **C** | 56.509 | -11.227 | -1.591 |
| **H** | 43.58 | -16.273 | -10.236 |
| **H** | 52.842 | -16.108 | -8.904 |
| **H** | 22.183 | -4.186 | -8.289 |
| **H** | 30.166 | -7.025 | -11.917 |
| **H** | 50.575 | -16.127 | -10.678 |
| **H** | 25.741 | -2.273 | -9.091 |
| **H** | 30.225 | -9.678 | -13.526 |
| **O** | 41.749 | -14.461 | -11.202 |
| **C** | 16.486 | -1.414 | -7.621 |
| **C** | 19.168 | 3.322 | -4.792 |
| **C** | 22.947 | -1.225 | -9.69 |
| **O** | 17.946 | -0.042 | -5.232 |
| **C** | 14.724 | -2.681 | -8.817 |
| **C** | 28.274 | -2.582 | -8.434 |
| **C** | 51.181 | -17.523 | -9.111 |
| **N** | 36.325 | -11.635 | -12.111 |
| **C** | 23.744 | 0.259 | -12.59 |
| **C** | 30.308 | -1.414 | -8.248 |
| **H** | 19.929 | 1.181 | -12.588 |
| **O** | 28.703 | 0.86 | -11.314 |
| **N** | 19.693 | 0.421 | -10.575 |
| **C** | 16.608 | -1.372 | -9.928 |
| **H** | 15.893 | -4.556 | -8.835 |
| **H** | 56.979 | -12.796 | -3.043 |
| **C** | 24.546 | 0.978 | -11.786 |
| **C** | 21.733 | -1.573 | -6.271 |
| **H** | 30.42 | 0.34 | -9.415 |
| **H** | 48.773 | -8.218 | -4.05 |
| **C** | 32.92 | -10.084 | -13.018 |
| **H** | 34.673 | -9.555 | -11.839 |

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|---|---|---|---|
| **C** | 21.221 | 2.953 | -7.931 |
| **N** | 24.179 | -2.292 | -11.57 |
| **H** | 24.662 | -1.777 | -12.305 |
| **O** | 37.158 | -13.302 | -13.395 |
| **C** | 27.368 | -6.793 | -12.425 |
| **H** | 31.09 | -8.163 | -13.965 |
| **C** | 24.258 | -1.754 | -10.317 |
| **C** | 22.915 | -0.115 | -8.953 |
| **C** | 23.277 | 1.965 | -6.884 |
| **H** | 48.671 | -17.655 | -10.554 |
| **H** | 33.803 | -11.007 | -11.247 |
| **H** | 25.052 | -1.848 | -6.231 |
| **C** | 26.056 | 0.856 | -11.851 |
| **C** | 20.62 | -0.693 | -5.73 |
| **H** | 29.674 | -2.867 | -6.856 |
| **C** | 18.438 | -0.122 | -10.912 |
| **O** | 31.476 | -1.155 | -7.562 |
| **C** | 26.093 | 4.863 | -8.111 |
| **H** | 20.163 | 0.256 | -9.646 |
| **C** | 24.009 | -2.074 | -6.506 |
| **H** | 42.623 | -4.254 | -6.626 |
| **H** | 20.094 | -1.226 | -4.909 |
| **C** | 28.686 | -0.817 | -9.849 |
| **C** | 23.734 | -3.079 | -7.355 |
| **H** | 39.149 | -14.67 | -11.74 |
| **H** | 26.427 | 1.898 | -11.711 |
| **H** | 44.989 | -5.047 | -6.056 |
| **H** | 14.805 | -3.537 | -10.863 |
| **H** | 13.921 | -1.957 | -10.74 |
| **N** | 25.97 | -3.068 | -8.442 |
| **H** | 26.051 | -0.756 | -10.344 |
| **C** | 13.598 | -2.051 | -7.958 |
| **C** | 53.574 | -18.096 | -8.425 |
| **H** | 24.069 | -5.896 | -13.318 |
| **C** | 27.275 | -3.403 | -8.019 |
| **H** | 26.39 | 0.574 | -12.876 |
| **H** | 26.901 | -1.956 | -10.058 |
| **H** | 39.892 | -13.497 | -12.885 |
| **C** | 17.542 | -0.568 | -7.586 |
| **H** | 12.656 | -2.641 | -8.023 |
| **C** | 29.836 | -0.569 | -9.197 |
| **N** | 26.661 | -0.087 | -10.882 |
| **H** | 24.182 | -0.409 | -13.35 |
| **O** | 25.446 | -1.499 | -9.853 |
| **O** | 20.578 | 0.185 | -8.675 |
| **H** | 16.106 | -1.811 | -6.672 |
| **N** | 22.076 | 1.772 | -7.714 |
| **H** | 60.647 | -24.984 | -8.548 |
| **H** | 13.163 | -3.471 | -10.158 |

| | | | |
|---|---|---|---|
| **C** | 20.32 | 1.327 | -11.557 |
| **H** | 64.967 | -15.726 | -4.245 |
| **C** | 35.019 | -2.547 | -7.508 |
| **H** | 35.369 | -2.163 | -8.496 |
| **H** | 56.426 | -11.126 | -0.482 |
| **C** | 20.145 | 2.932 | -5.626 |
| **H** | 65.313 | -17.73 | -3.3 |
| **H** | 62.624 | -24.645 | -7.143 |
| **H** | 19.169 | 4.518 | -8.355 |
| **H** | 66.144 | -21.876 | -7.252 |
| **C** | 60.981 | -23.164 | -9.596 |
| **H** | 68.703 | -20.656 | -11.197 |
| **C** | 29.422 | -2.327 | -7.784 |
| **O** | 41.063 | -12.435 | -10.379 |
| **C** | 65.77 | -18.576 | -3.862 |
| **H** | 16.29 | -1.766 | -10.906 |
| **C** | 21.826 | 1.202 | -11.642 |
| **C** | 22.442 | -3.349 | -7.619 |
| **H** | 66.257 | -19.194 | -3.077 |
| **H** | 24.468 | -4.478 | -8.861 |
| **C** | 18.247 | -0.096 | -8.659 |
| **C** | 67.602 | -22.442 | -8.639 |
| **H** | 69.096 | -22.808 | -10.098 |
| **H** | 67.754 | -23.417 | -8.144 |
| **H** | 26.837 | 5.616 | -8.419 |
| **C** | 23.022 | -1.338 | -5.971 |
| **H** | 19.168 | 0.539 | -8.588 |
| **H** | 22.179 | 2.791 | -10.289 |
| **H** | 61.47 | -21.386 | -10.533 |
| **H** | 15.543 | -3.939 | -7.2 |
| **C** | 24.84 | -3.899 | -7.986 |
| **H** | 55.423 | -16.937 | -8.707 |
| **O** | 27.485 | -4.275 | -7.206 |
| **H** | 20.03 | 2.369 | -11.288 |
| **H** | 64.188 | -20.549 | -10.053 |
| **H** | 64.46 | -21.2 | -8.797 |
| **H** | 20.658 | 2.811 | -8.881 |
| **H** | 21.844 | 3.853 | -8.123 |
| **H** | 61.44 | -19.884 | -7.214 |
| **H** | 19.948 | -0.069 | -7.721 |

## 8. High resolution Mass Spectra of rotaxanes 3 and 4

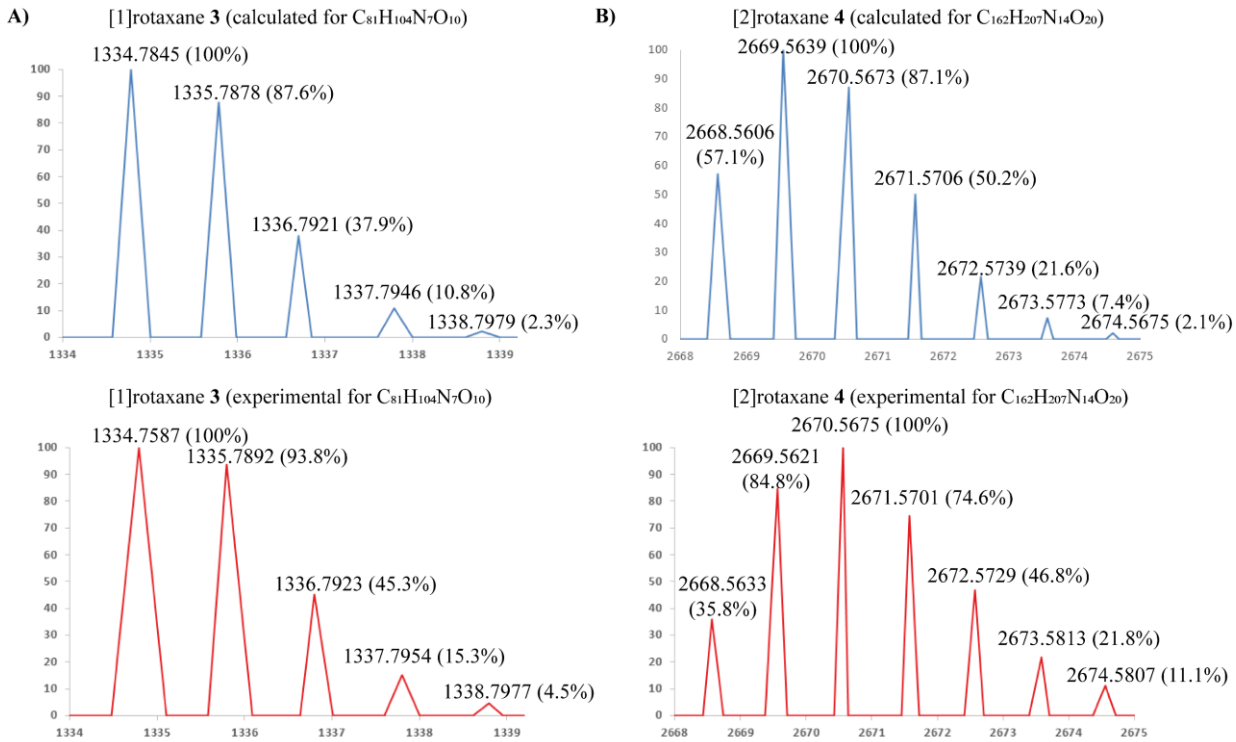
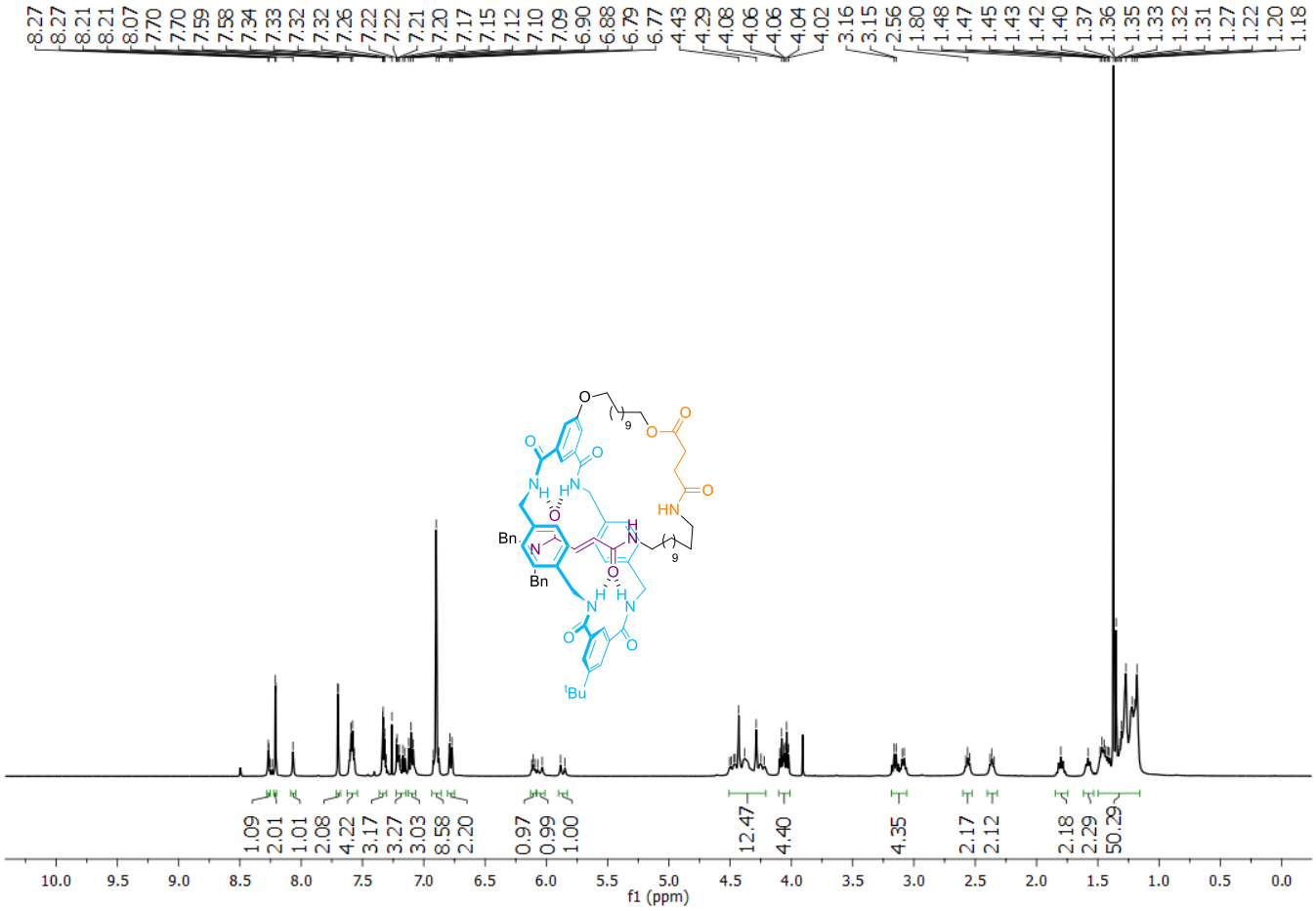


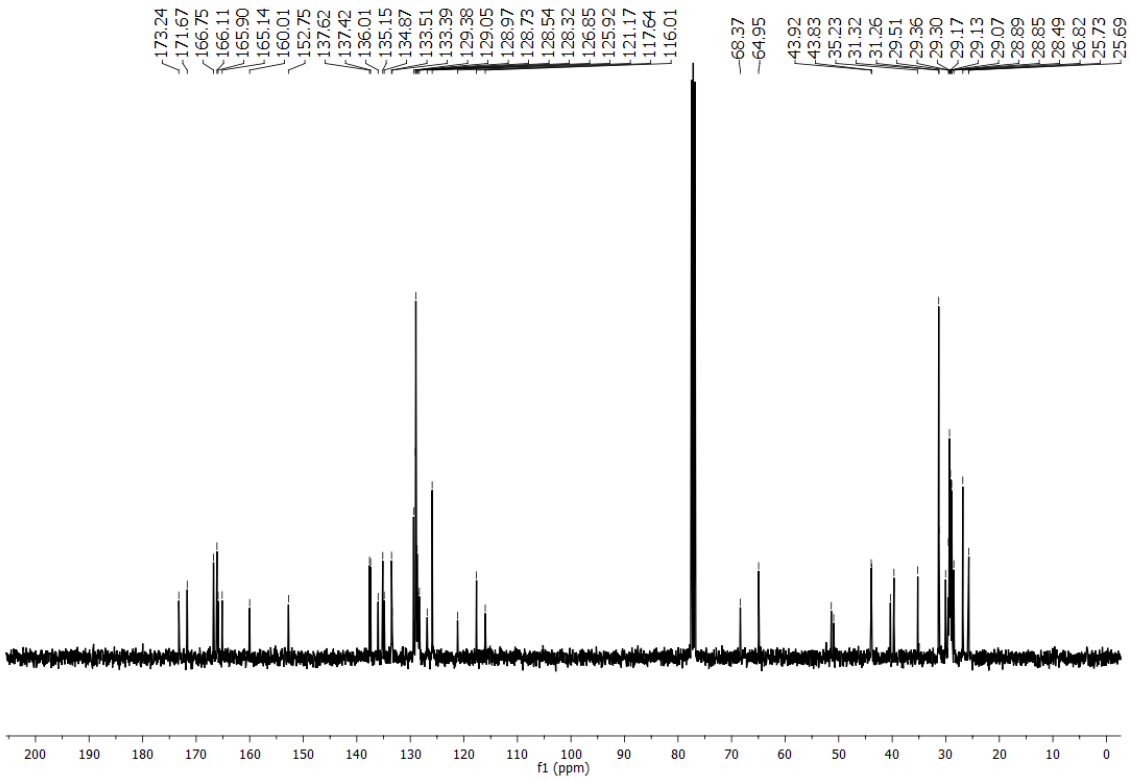

**Figure S5.** Calculated (above) and experimental (below) high resolution mass spectra ($ESI^+$) of: A) lasso rotaxane **3** and B) [*c2*]daisy chain rotaxane **4**.

## 9. $^{13}$C NMR spectra of synthesized compounds

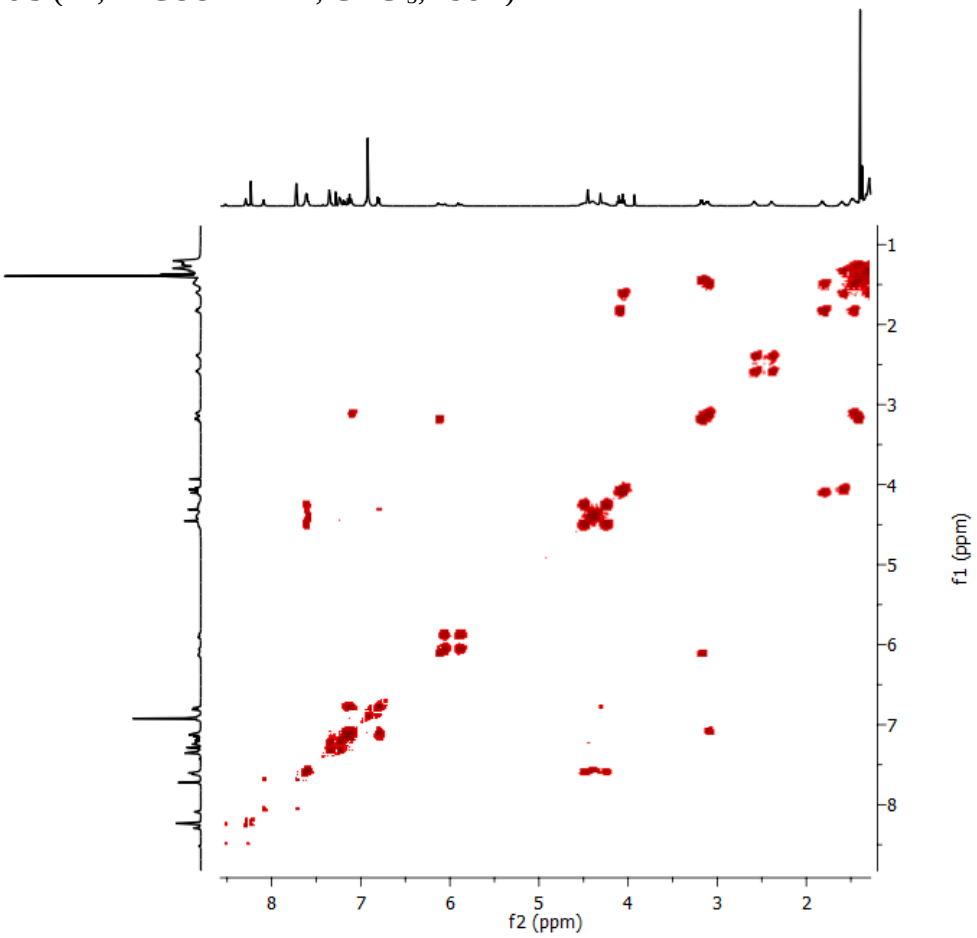
**Lasso rotaxane 3** ($^{1}$H NMR, 401 MHz, $CDCl_3$, 298K)



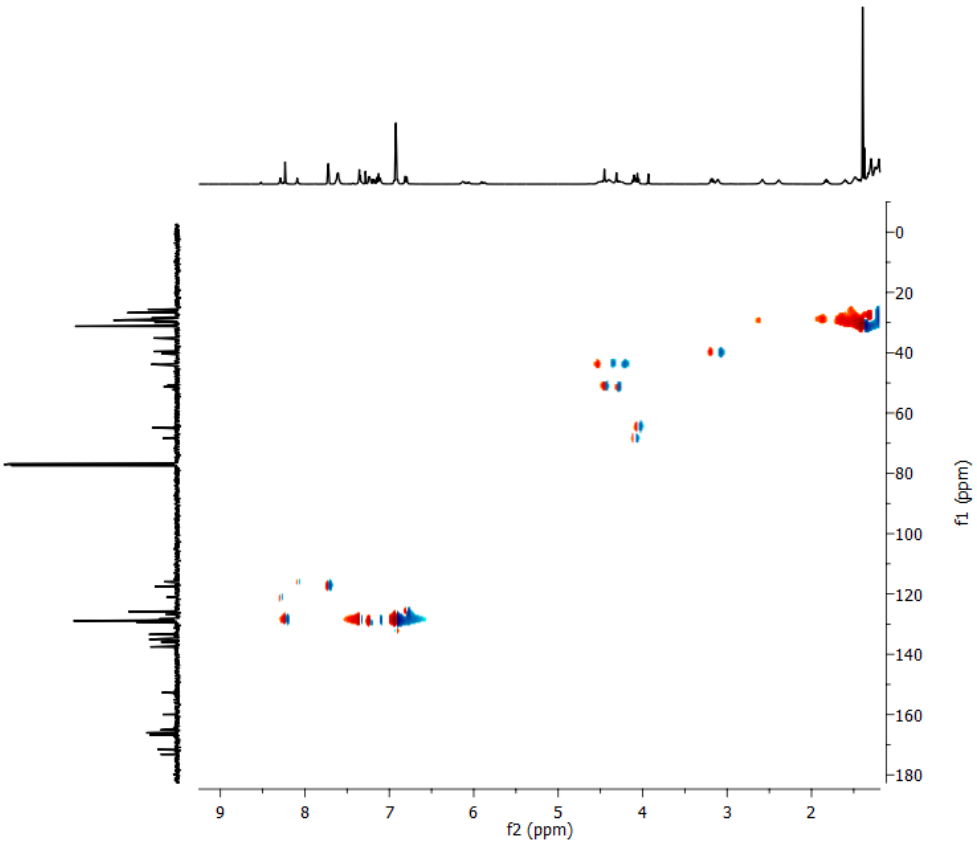

**Lasso rotaxane 3** ($^{13}$C NMR, 101 MHz, $CDCl_3$, 298K)



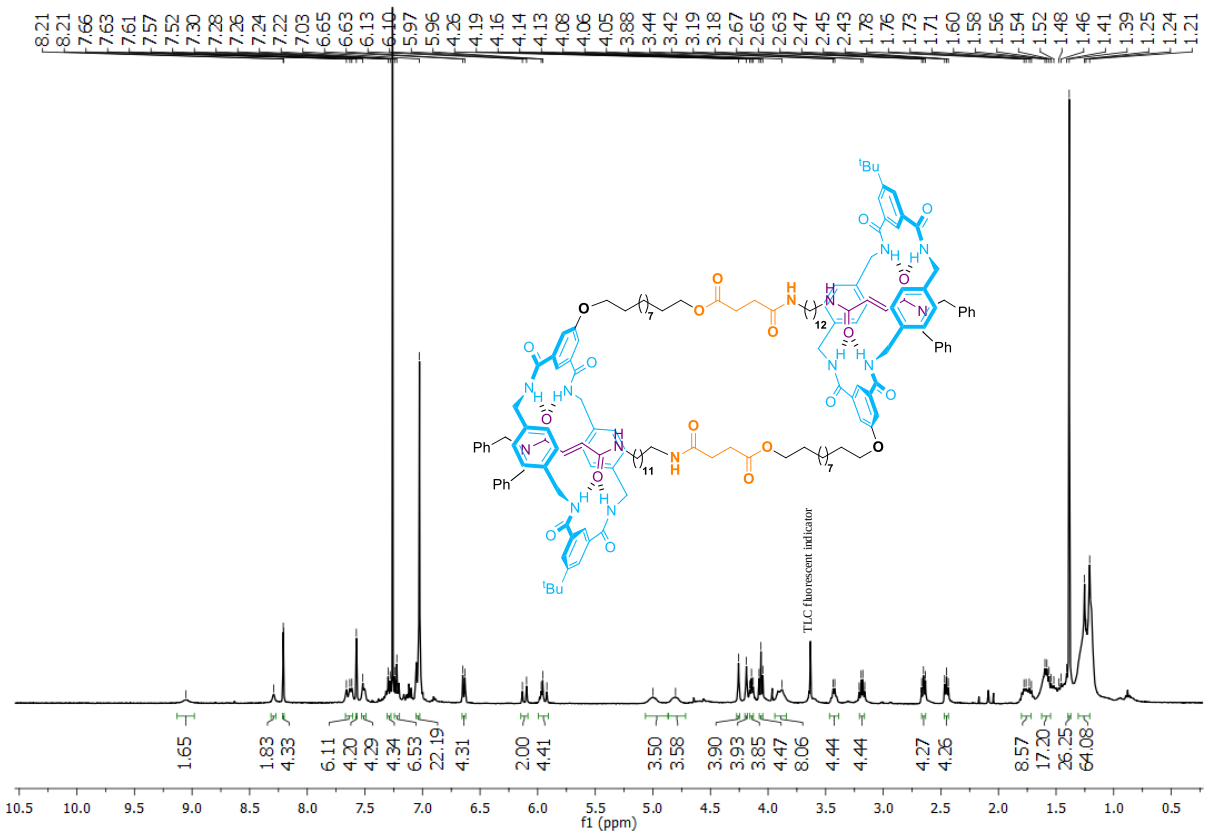
**Lasso rotaxane 3** ($^{1}$H,$^{1}$H-COSY NMR, $CDCl_3$, 298K)



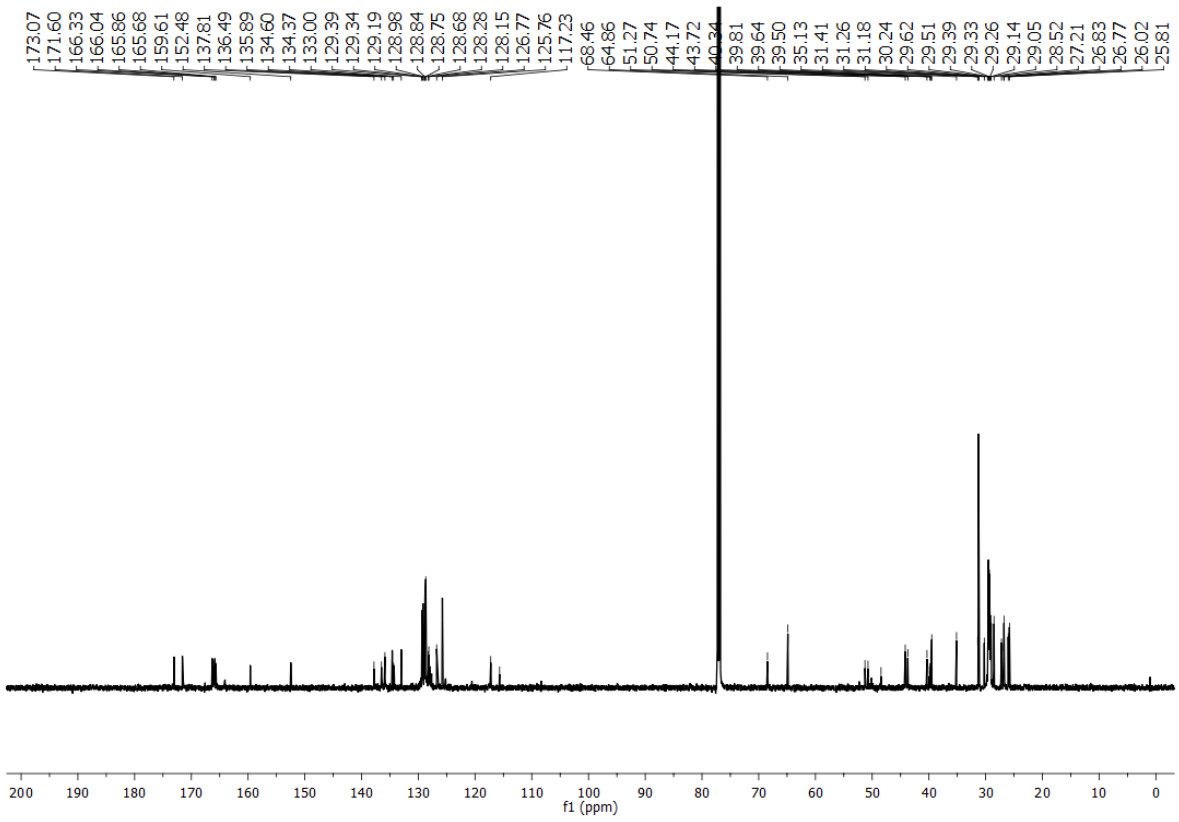

**Lasso rotaxane 3** ($^{1}$H,$^{13}$C-HSQC NMR, $CDCl_3$, 298K)



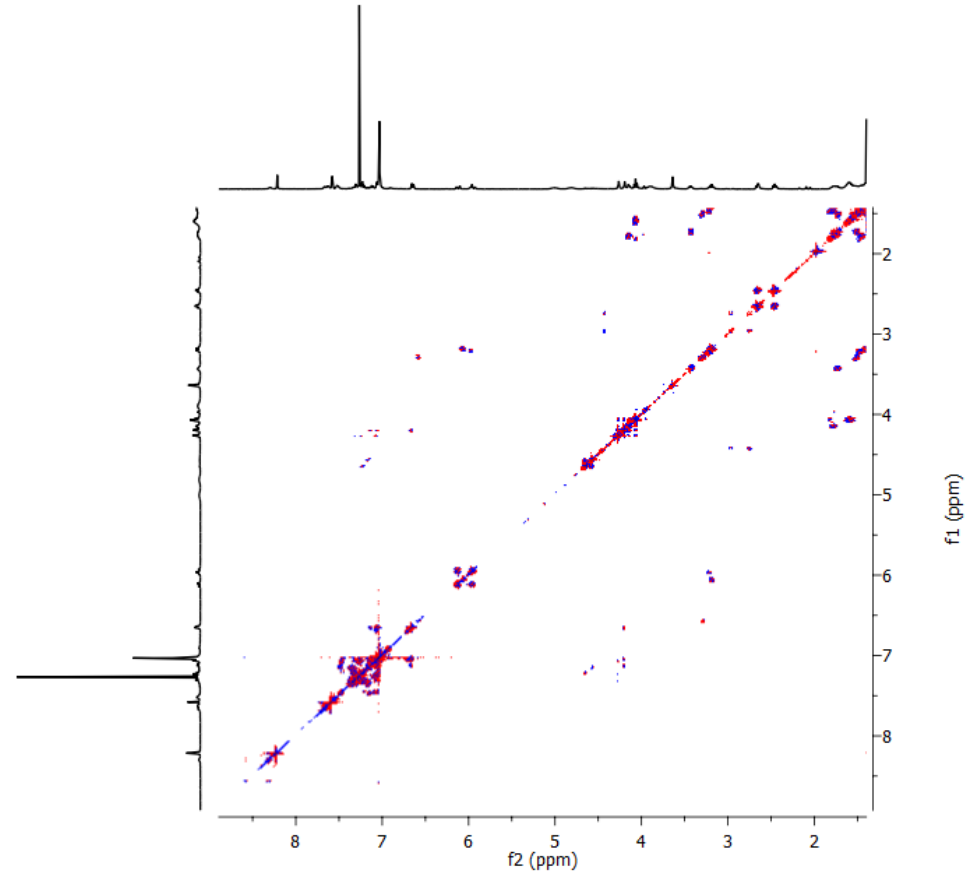
**[*c2*]Daisy chain rotaxane 4** ($^{1}$H NMR, 401 MHz, $CDCl_3$, 298K)



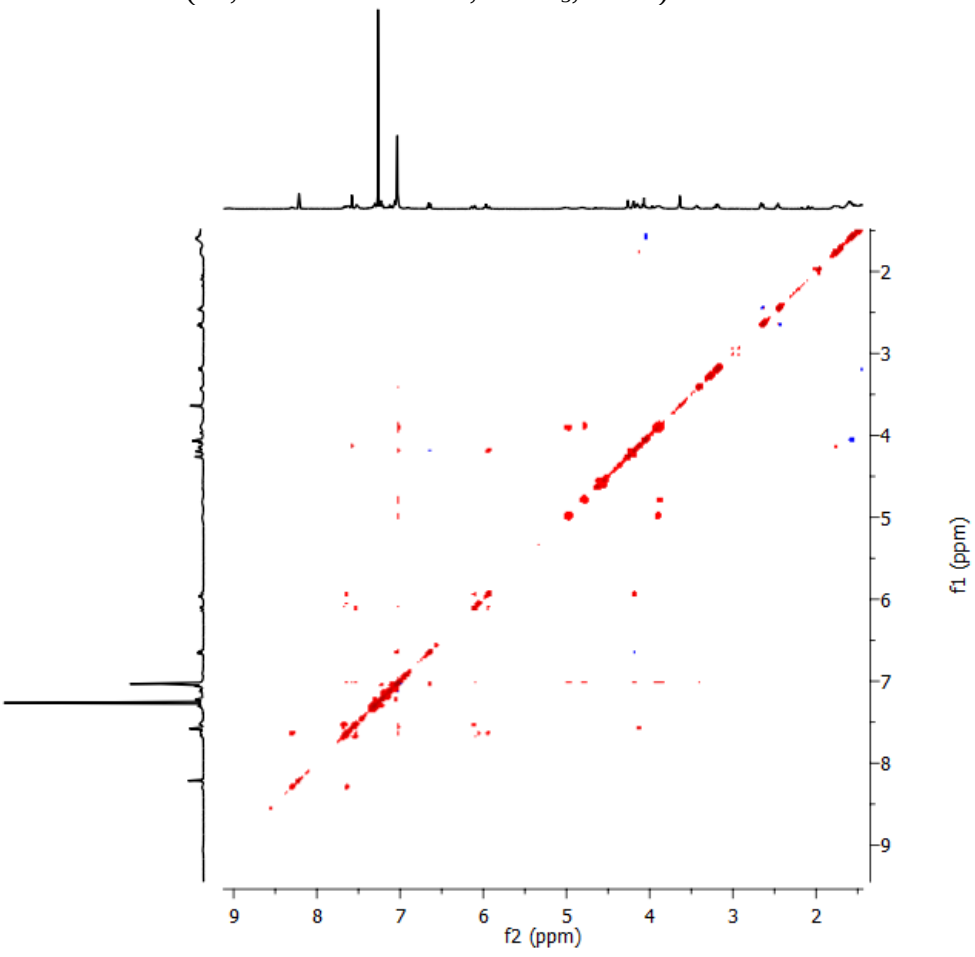

**[*c2*]Daisy chain rotaxane 4** ($^{13}$C NMR, 151 MHz, $CDCl_3$, 298K)



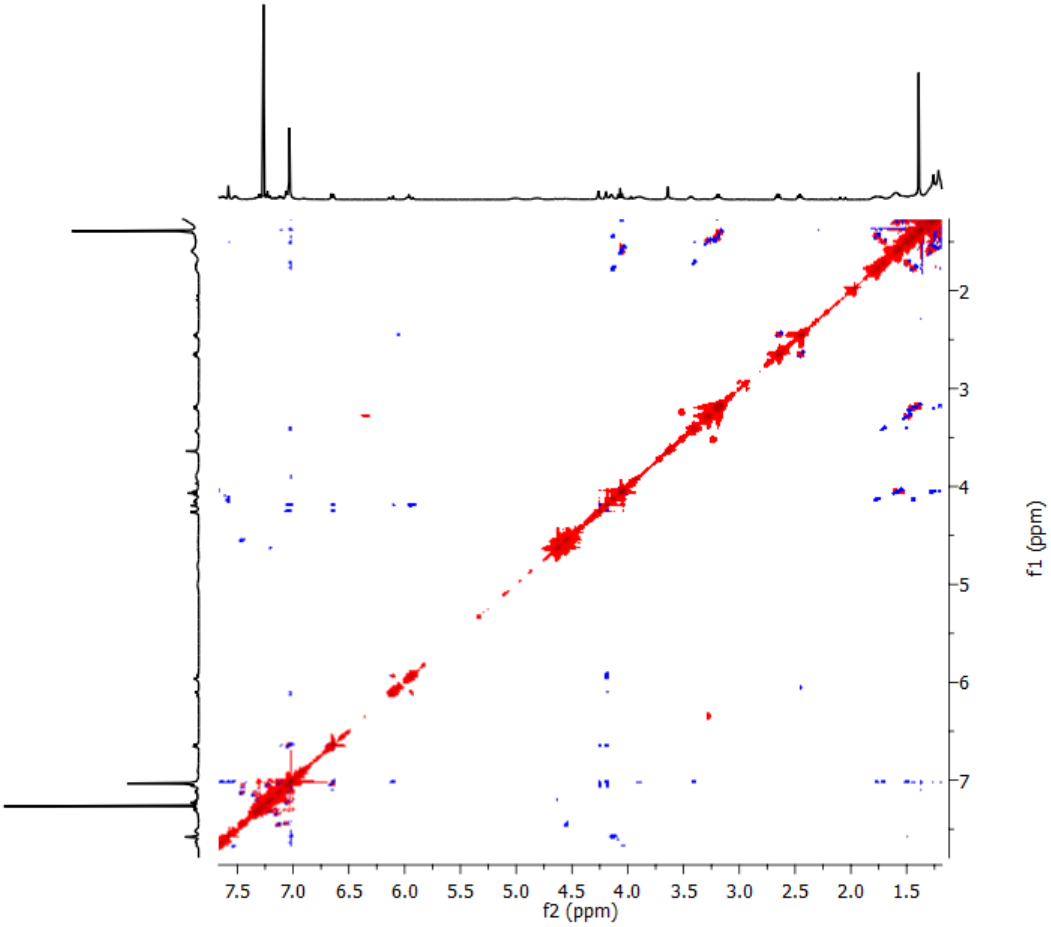
**[*c2*]Daisy chain rotaxane 4** ($^1$H,$^1$H-COSY NMR, $CDCl_3$, 298K)



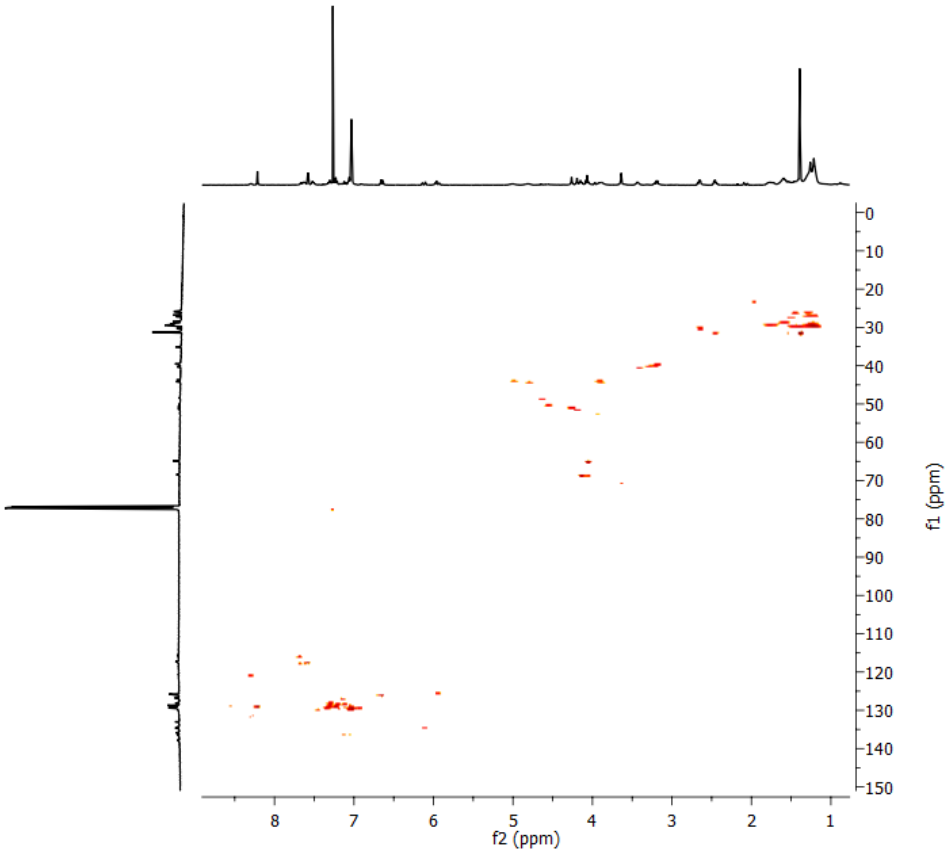

**[*c2*]Daisy chain rotaxane 4** ($^1$H,$^1$H-NOESY NMR, $CDCl_3$, 298K)



**[*c2*]Daisy chain rotaxane 4** ($^{1}$H,$^{1}$H-ROESY NMR, $CDCl_3$, 298K)




**[*c2*]Daisy chain rotaxane 4** ($^{1}$H,$^{13}$C-HSQC NMR, $CDCl_3$, 298K)



## 10. Member numbering of cyclic [1]rotaxane 3 and [2]rotaxane 4