Supplementary information

Tightening or Loosening a pH-Sensitive double-Lasso Molecular Machine Readily Synthesized from an Ends-Activated [c2]Daisy Chain

Camille Romuald\textsuperscript{a}, Ana Ardá Freire\textsuperscript{b}, Caroline Clavel\textsuperscript{a}, Jesús Jiménez-Barbero\textsuperscript{*b} and Frédéric Coutrot\textsuperscript{*a}

\textsuperscript{a}Institut des Biomolécules Max Mousseron (IBMM), UMR 5247 CNRS-Universités Montpellier 2 et 1, Bâtiment de Recherche Max Mousseron, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l’Ecole Normale, 34296 Montpellier Cedex 5, France. Fax: +33 467-14-43-44; Tel: +33 467-14-72-97; E-mail: frederic.coutrot@univ-montp2.fr – http://www.glycorotaxane.fr

\textsuperscript{b}Centro de Investigaciones Biológicas (CIB-CSIC), Ramiro de Maetzu, 9 – E28040 Madrid, Spain. E-mail: jjbarbero@cib.csic.es

A. Synthesis of the stoppering azido precursor 1 ........................................................................ 3
   1) Preparation of the anhydride 7............................................................................................ 3
   2) Preparation of the 1,2,3,4-tetra-O-acetyl-\( \beta \)-D-glucuronic acid 8................................. 4
   3) Preparation of the 1-azido-2,3,4-tri-O-acetyl-\( \beta \)-D-glucuronic acid 9 ......................... 4
   4) Preparation of the pentafluorophenol 1-azido-2,3,4-tri-O-acetyl-\( \beta \)-D-glucuronic ester 1 .... 5

B. Synthesis of the alkyne pseudo [c2]Daisy chain 2 ................................................................. 5
   1) Preparation of the tridec-2-yn-1-ol 10 ............................................................................. 5
   2) Preparation of the tridec-12-yn-1-ol 11 ........................................................................... 6
   3) Preparation of the 13-bromotridec-1-yn 12 ..................................................................... 6
   4) Preparation of the phthalimide 13 .................................................................................... 7
   5) Preparation of the tridec-12-yn-1-amine 14 .................................................................... 7
   6) Preparation of the crown ether 15 .................................................................................... 8
   7) Preparation of the compound 16 ..................................................................................... 8
   8) Preparation of the compound 2 ....................................................................................... 9

C. Synthesis of the non-interlocked threads 5u and 6u ............................................................ 10
   1) Preparation of the compound 17 ..................................................................................... 10
   2) Preparation of the compound 18 .................................................................................... 10
   3) Preparation of the thread 19 ........................................................................................... 11
4) Preparation of the thread 20 ................................................................. 12
5) Preparation of the thread 5u ............................................................... 13
6) Preparation of the thread 6u ............................................................... 14

D. Synthesis of the double-lasso .............................................................. 15
   1) Preparation of the activated rotaxane dimer 3 .................................... 15
   2) Preparation of the double-lasso 4a-b ............................................... 16
   3) Preparation of the double-lasso 5a-b ............................................... 17
   4) Preparation of the double-lasso 6a-b ............................................... 18
   5) Reprotonation procedure of 6a-b ................................................... 18

E. Molecular Modeling ............................................................................... 18

F. Stack plot $^1$H NMR (400 MHz, 298K) of double-lasso 5 in different solvents .......... 22

G. NMR Spectra ...................................................................................... 22
General Methods. All reactions were carried out under an atmosphere of argon unless otherwise indicated. All reagents were used as received without further purification. Dichloromethane was distilled over P₂O₅ and was degassed by bubbling Ar for 20 min. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates. Compounds were visualized by dipping the plates in an ethanolic solution of 10% sulphuric acid, ninhydrine or an aqueous solution of KMNO₄, followed by heating. ¹H NMR and ¹³C NMR spectra were obtained on a spectrometer (respectively at 400.13 MHz and 100.62 MHz). Chemical shifts of ¹H NMR and ¹³C NMR are given by using CHCl₃, CH₂Cl₂, CH₃OH, CH₃CN and DMSO as references (7.27 ppm, 5.32 ppm, 3.31 ppm, 1.94 ppm and 2.50 ppm respectively for ¹H spectrum, and 77.0 ppm, 54.0 ppm, 49.15 ppm, 118.26 ppm, and 39.51 ppm respectively for ¹³C spectrum). ¹H assignments were deduced from 2D ¹H-¹H NMR COSY experiments. ¹³C assignments were deduced from 2D ¹³C-¹H NMR HMQC experiments. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), br (broad), d (doublet), t (triplet), q (quartet), m (multiplet). Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded respectively on a ZQ Micromass apparatus, a MALDI and a Q-TOF Micromass apparatus supplied with an ESI source (Waters, 2001).

A. Synthesis of the stoppering azido precursor 1

1) Preparation of the anhydride 7

To a suspension of D-glucuronic acid (1.97 g, 10.15 mmol, 1 eq.) in 30 mL of acetic anhydride at 5°C was added slowly in portions iodine (260 mg, 1.015 mmol, 0.1 equiv). The suspension was stirred 1 h at 5°C and then 4 h at room temperature. The solution was co-evaporated with toluene and the solid residue was triturated with diethyl ether. A white powder was obtained (3.21 g) with a yield of 78%.

¹H NMR (400 MHz, CDCl₃, 298K): δ = 5.79 (d, 1H, ³JHH = 8.3 Hz, H₁), 5.35 (t, 1H, ³JHH = ³JHH = ³JHH = 8.3 Hz, H₂), 5.27 (t, 1H, ³JHH = ³JHH = 3JHH = 8.3 Hz, H₃), 5.10 (t, 1H, ³JHH = ³JHH = 8.3 Hz, H₄), 4.31 (d, 1H, ³JHH = 3JHH = 8.3 Hz, H₅), 2.25 (s, 3H, COOCH₃), 2.29 & 2.10 & 2.04 & 2.03 & 2.02 (5*s, 5*3H, CH₃CO).

¹³C NMR (CDCl₃, 298K): δ = 169.7 & 169.3 & 169.1 & 168.6 (C₁OCH₃), 164.7 & 162.5 (COOCH₃), 91.3 (C₁), 72.9 (C₂), 71.2 (C₃), 70.0 (C₄), 67.9 (C₅), 22.0 (COOCH₃), 20.6 & 20.4 & 20.4 (CH₃CO).

2) Preparation of the 1,2,3,4-tetra-O-acetyl-β-D-glucuronic acid 8

The anhydride 7 (1.40 g, 3.46 mmol) was stirred overnight at room temperature in 60 mL of a solution consisting of THF / water 2:1. The THF was then evaporated and the aqueous solution was extracted with dichloromethane (3 x 50 mL). The organic phase was dried over MgSO₄, filtered and evaporated to afford the acid compound 8 (1.23 g) in a quantitative yield.

Rf (AcOEt/éther de pétrole 4:1) 0.0

1H NMR (400 MHz, CDCl₃, 298K): δ = 5.81 (d, 1H, 3JH₃-H₂ = 6.9 Hz, H₁), 5.39 (t, 1H, 3JH₃-H₄ = 3JH₃-H₄ = 8.7 Hz, H₃), 5.29 (t, 1H, 3JH₄-H₃ = 3JH₄-H₃ = 8.7 Hz, H₄), 5.13 (dd, 1H, 3JH₂-H₁ = 6.9 Hz, 3JH₂-H₃ = 8.7 Hz, H₂), 4.32 (d, 1H, 3JH₅-H₃ = 8.7 Hz, H₅), 2.14 & 2.07 & 2.04 & 2.02 (4*s, 4*3H, CH₃CO).

13C NMR JMOD (100 MHz, CDCl₃, 298K): δ = 170.0 & 169.7 & 169.6 & 169.3 & 168.9 (C₆ COCH₃), 91.2 (C₁), 72.4 (C₃), 71.8 (C₅), 70.0 (C₂), 68.5 (C₄), 20.7 & 20.5 & 20.5 & 20.4 (CH₃CO).

MS (ESI): [M+Na]+ calcd for [C₁₂ H₂₃O₁₁ Na]: 385.28, found: 385.10

3) Preparation of the 1-azido-2,3,4-tri-O-acetyl-β-D-glucuronic acid 9

To a solution of the 1,2,3,4-tetra-O-acetyl-β-D-glucuronic acid 8 (3.93 g, 10.847 mmol, 1 equiv) in 25 mL of dichloromethane at 5°C were added trimethylsilylalazine (3.57 mL, 27.117 mmol, 2.5 equiv) and tin(IV) chloride (5.4 mL, 5.423 mmol, 1M in CH₂Cl₂). The reaction was allowed to stir overnight at 5°C. A saturated aqueous solution of NaHCO₃ was then added and the reaction mixture was stirred 20 min before separating the two layers. After a second wash with saturated NaHCO₃, the combined aqueous layers were acidified with hydrochloric acid 12M and extracted with dichloromethane (3 x 30 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated to yield the compound 9 (2.85 g, 75%, ratio α/β: 17/83) as a colorless solid.

β isomer: 1H NMR (400 MHz, CDCl₃, 298K): δ = 5.30 (t, 1H, 3JH₃-H₂ = 3JH₃-H₄ = 9.2 Hz, H₁), 5.26 (t, 1H, 3JH₄-H₃ = 3JH₄-H₅ = 9.2 Hz, H₄), 4.96 (t, 1H, 3JH₂-H₁ = 3JH₂-H₃ = 9.2 Hz, H₂), 4.76 (d, 1H, 3JH₁-H₂ = 9.2 Hz, H₁), 4.18 (d, 1H, 3JH₅-H₃ = 9.2 Hz, H₅), 2.07 & 2.04 & 2.02 (3*s, 3*3H, CH₃CO).

13C NMR JMOD (100 MHz, CDCl₃, 298K): δ = 170.2 & 170.0 & 169.4 & 168.3 (C₆ COCH₃), 87.7 (C₁), 73.5 (C₃), 71.9 (C₅), 70.3 (C₂), 68.8 (C₄), 20.4 & 20.4 (CH₃CO).

MS (ESI): [M+Na]+ calcd for [C₁₂ H₂₃N₃O₁₁ Na]: 368.25, found: 368.00
4) Preparation of the pentafluorophenol 1-azido-2,3,4-tri-O-acetyl-β-D-glucuronic ester 1

To a cooled solution (0°C) of the 1-azido-2,3,4-tri-O-acetyl-β-D-glucuronic acid 9 (2.84 g, 8.224 mmol, 1 equiv) in 30 mL of dichloromethane was added oxalyl chloride (1.44 mL, 16.449 mmol, 2 equiv). 3 mL of DMF was then slowly added to the stirring solution and evolution of gas was observed. The pale yellow solution was stirred for 30 min at 0°C and then for 2 h at room temperature. The solution was evaporated to give a solid, which was diluted in 30 mL of dichloromethane and added pentfluorophenol (1.82 g, 9.869 mmol, 1.2 equiv). The mixture was allowed to stir overnight at room temperature. The solution was washed with a saturated aqueous solution of NaHCO₃ (2 x 30 mL). After separation, the aqueous layer was extracted with dichloromethane (2 x 30 mL). The organic layers were combined, dried over MgSO₄, and concentrated. The crude was purified by chromatography on silica gel column (gradient elution petroleum ether/AcOEt 9:1 to 1:1) to yield the compound 1 as a colorless solid (2.32 g, 56%) and as a unique β stereoisomer.

Rf (petroleum ether/AcOEt 1:1) 0.68

H NMR (400 MHz, CDCl₃, 298K): δ = 5.44 (t, 1H, J₃H₃-H₂ = J₃H₃-H₄ = 9.2 Hz, H₃), 5.32 (t, 1H, J₄H₄-H₃ = J₄H₄-H₅ = 9.2 Hz, H₄), 5.05 (t, 1H, J₅H₅-H₄ = J₅H₅-H₁ = 9.2 Hz, H₅), 4.83 (d, 1H, J₁H₁-H₂ = 9.2 Hz, H₁), 4.54 (d, 1H, J₁H₁-H₃ = 9.2 Hz, H₃), 2.11 & 2.06 & 2.05 (3*s, 3*3H, CH₃CO).

C NMR JMOD (100 MHz, CDCl₃, 298K): δ = 170.0 & 169.1 & 169.0 (COCH₃), 162.5 (C₆), 88.2 (C₁), 73.8 (C₃), 71.7 (C₃), 70.1 (C₂), 68.7 (C₄), 20.5 & 20.4 & 20.2 (CH₂CO).

B. Synthesis of the alkyne pseudo [c2]Daisy chain 2

1) Preparation of the tridec-2-yn-1-ol 10

To a stirred solution of 1-dodecyne (5g, 30.064 mmol, 1 equiv) in anhydrous THF at 5°C was added, under Argon, n-BuLi (20.7 mL, 33.077 mmol, 1.6 M in THF, 1.1 equiv). After 30 min at 5°C, paraformaldehyde was added by portions. The solution was further stirred during 1h at 5°C, then during one night at room temperature. The reaction mixture was quenched with 120 mL of 1:1 water/saturated water with NH₄Cl. The biphasic solution was separated and the aqueous layer

extracted twice with 100 mL of ethyl acetate. The organic layers were then combined, dried over MgSO₄ and concentrated to afford compound 10 in a quantitative yield (5.90 g) as a yellow oil.

Rᶠ (petroleum ether /AcOEt 9:1) 0.21

¹H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 4.25 (t, 2H, 5J_H-H = 2.0 Hz, H₁), 2.21 (tt, 2H, 5J_H-H = 2.0 Hz, 3J_H-H = 7.2 Hz, H₂), 1.55-1.46 (m, 2H, H₃), 1.42-1.33 (m, 2H, H₆), 1.33-1.20 (m, 12H, H₇ H₈ H₉ H₁₀ H₁₁ H₁₂), 0.89 (t, 3H, 3J_H-H = 6.9 Hz, H₁₃).

¹³C NMR J MOD (CDCl₃, 100 MHz, 298K) : δ (ppm) = 86.6 & 78.2 (C₂ C₃), 51.4 (C₄), 31.9 & 29.6 & 29.5 & 29.3 & 29.1 & 28.9 & 28.6 & 22.7 (C₅ C₆ C₇ C₈ C₉ C₁₀ C₁₁ C₁₂), 18.7 (C₁₃), 14.1 (C₁₄).

2) Preparation of the tridec-12-yn-1-ol II

To dry ethylene-1,2-diamine (80 mL) at 0-5°C under argon was added NaH (11.90 g, 0.297 mol, 10 equiv, 60% in oil). The mixture was allowed to warm slowly at 60°C and stirred for 3h to give a deep blue mixture. Then, it was cooled to 45°C before adding dropwise the tridec-2-yn-1-ol 10 (5.84 g, 29.749 mmol, 1 equiv). The solution was stirred at 60°C for one night before being cooled to 0°C. 100 mL of water and 100 mL of diethyl ether were introduced slowly; then HCl 12M was added until pH 1. Aqueous layer was extracted with diethyl ether (4x100 mL). The organic layers were combined, dried and concentrated. The crude oil was purified by chromatography on a silicagel column (solvent elution: petroleum ether/AcOEt 1:1) to give the desired product (3.56 g, 61%) as a yellow oil.

Rᶠ (petroleum ether /AcOEt 1:1) 0.71

¹H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 3.63 (t, 2H, 3J_H-H = 6.6 Hz, H₁), 2.18 (td, 2H, 3J_H-H = 7.1 Hz, 4J_H-H = 2.6 Hz, H₂), 1.94 (t, 1H, 4J_H-H = 2.6 Hz, H₃), 1.62-1.47 (m, 4H, H₂ H₄ H₅ H₁₂), 1.43-1.23 (m, 14H, H₆ H₇ H₈ H₉ H₁₀ H₁₁ H₁₂).

¹³C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 84.4 (C₁₂), 68.0 (C₁₁), 62.2 (C₁), 32.4 (C₂) 29.4 & 29.3 & 29.2 & 28.9 & 28.5 & 28.2 (C₃ C₄ C₅ C₆ C₇ C₈ C₉ C₁₀), 25.6 (C₁₁).

3) Preparation of the 13-bromotridec-1-ynyl 12

To a solution of the tridec-12-ynyl 11 (2.40 g, 12.226 mmol, 1 equiv) in 40 mL of dry dichloromethane were added the tetrabromomethane (8.11 g, 24.451 mmol, 2 equiv) and the triphenylphosphine (6.41 g, 24.451 mmol, 2 equiv). The mixture was stirred at room temperature for 1h; then, the solvent was removed under reduced pressure. A solution of petroleum ether / ethyl acetate (9:1) was added and the resulted precipitate was filtered and washed abundantly. The filtrate was evaporated and the crude was purified by chromatography on a silicagel column (elution: petroleum ether/AcOEt 9:1) to give the brominated product 12 (3.07 g, 97%) as a yellow oil.

Rᶠ (petroleum ether /AcOEt 97:3) 0.50
\(^{1}\)H NMR (CDCl\(_3\), 400 MHz, 298K) : \(\delta\) (ppm) = 3.42 (t, 2H, \(^3\)J\(_{H1\text{-}H2}\) = 6.9 Hz, H\(_6\)), 2.19 (td, 2H, \(^3\)J\(_{H1\text{-}H10}\) = 7.1 Hz, \(^4\)J\(_{H1\text{-}H10}\) = 2.7 Hz, H\(_{11}\)), 1.95 (t, 1H, \(^4\)J\(_{H1\text{-}H11}\) = 2.7 Hz, H\(_{12}\)), 1.90-1.81 (m, 2H, H\(_2\)), 1.57-1.48 (m, 2H, H\(_{10}\)), 1.48-1.23 (m, 14H, H\(_{1}\)), 1.23 (m, 14H, H\(_{9}\)), 1.62 (m, 2H, H\(_{3}\)), 1.56 (m, 2H, H\(_{13}\)).

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz, 298K) : \(\delta\) (ppm) = 168.0 (C\(_4\)), 133.5 (C\(_{17}\)), 131.9 (C\(_{15}\)), 122.8 (C\(_{16}\)), 84.4 (C\(_{12}\)), 68.0 (C\(_{13}\)), 37.7 (C\(_1\)), 29.2 & 29.2 & 28.9 & 28.8 & 28.5 & 28.3 & 28.2 & 26.6 (C\(_2\) C\(_3\) C\(_4\) C\(_5\) C\(_6\) C\(_7\) C\(_8\) C\(_9\) C\(_{10}\)), 18.1 (C\(_{11}\)).

4) Preparation of the phthalimide 13

Potassium phthalimide (3.40 g, 18.34 mmol, 1.5 equiv) was added to a solution of the 13-bromotridec-1-yn 12 (3.17 g, 12.230 mmol, 1 equiv) in 60 mL of DMF. After stirring for 4 h at 70°C, the solvent was removed in vacuo. The solid residue was suspended in dichloromethane and filtered through a layer of silica gel. The filtrate was evaporated to give the desired product (3.98 g) in a quantitative yield as a yellow oil.

R\(_F\) (Petroleum ether/AcOEt 75/25) 0.50

\(^{1}\)H NMR (CDCl\(_3\), 400 MHz, 298K) : \(\delta\) (ppm) = 7.87-7.81 (m, 2H, H\(_{16}\)), 7.73-7.68 (m, 2H, H\(_{17}\)), 3.67 (t, 2H, \(^3\)J\(_{H1\text{-}H2}\) = 7.4 Hz, H\(_1\)), 2.17 (td, 2H, \(^3\)J\(_{H1\text{-}H10}\) = 7.8 Hz, \(^4\)J\(_{H1\text{-}H10}\) = 2.6 Hz, H\(_{11}\)), 1.94 (t, 1H, \(^4\)J\(_{H1\text{-}H11}\) = 2.6 Hz, H\(_{12}\)), 1.72-1.62 (m, 2H, H\(_2\)), 1.56-1.47 (m, 2H, H\(_{10}\)), 1.42-1.22 (m, 14H, H\(_3\) H\(_4\) H\(_5\) H\(_6\) H\(_7\) H\(_8\) H\(_9\)).

\(^{13}\)C NMR JMOD (CDCl\(_3\), 100 MHz, 298K) : \(\delta\) (ppm) = 168.0 (C\(_4\)), 133.5 (C\(_{17}\)), 131.9 (C\(_{15}\)), 122.8 (C\(_{16}\)), 84.4 (C\(_{12}\)), 68.0 (C\(_{13}\)), 37.7 (C\(_1\)), 29.2 & 29.2 & 28.9 & 28.8 & 28.5 & 28.3 & 28.2 & 26.6 (C\(_2\) C\(_3\) C\(_4\) C\(_5\) C\(_6\) C\(_7\) C\(_8\) C\(_9\) C\(_{10}\)), 18.1 (C\(_{11}\)).

5) Preparation of the tridec-12-yn-1-amine 14

Hydrazine monohydrate (2.14 g, 42.805 mmol, 3.5 equiv) was added to a solution of the phthalimide 13 (3.98 g, 12.230 mmol, 1 equiv) in 60 mL of ethanol. The mixture was stirred at reflux for 4 h, and then cooled to room temperature. An aqueous solution of KOH 1N (100 mL) was added and the solvent was removed in vacuo. The solution was extracted with dichloromethane (2x100 mL); then, the organic layers were combined, dried over MgSO\(_4\) and concentrated to yield the desired product (2.10 g, 88 %) as a yellow solid.

R\(_F\) (CH\(_2\)Cl\(_2\)/MeOH 9:1) 0

\(^{1}\)H NMR (CDCl\(_3\), 400 MHz, 298K) : \(\delta\) (ppm) = 2.67 (t, 2H, \(^3\)J\(_{H1\text{-}H2}\) = 7.0 Hz, H\(_1\)), 2.18 (td, 2H, \(^3\)J\(_{H1\text{-}H10}\) = 7.2 Hz, \(^4\)J\(_{H1\text{-}H10}\) = 2.7 Hz, H\(_{11}\)), 1.93 (t, 1H, \(^4\)J\(_{H1\text{-}H11}\) = 2.7 Hz, H\(_{12}\)), 1.56-1.47 (m, 2H, H\(_{10}\)), 1.47-1.34 (m, 4H, H\(_2\) H\(_6\)), 1.34-1.21 (m, 12H, H\(_3\) H\(_4\) H\(_5\) H\(_6\) H\(_7\) H\(_8\)).
**6) Preparation of the crown ether 15**

This compound has been synthesized according to the procedure described by S. J. Cantrill, G. J. Youn, J. F. Stoddart. [2]

**1H NMR (400 MHz, CDCl3, 298K):** \( \delta \) (ppm) = 9.83 (s, 1H, H\(_7\)), 7.43 (dd, 1H, \(3^J_{H7-H6} = 8.2 \text{ Hz, } 4^J_{H7-H3} = 1.9 \text{ Hz, } H_3\)), 7.38 (d, 1H, \(4^J_{H6-H7} = 1.9 \text{ Hz, } H_2\)), 6.94-6.86 (m, 4H, H\(_{15}\) H\(_{16}\) H\(_{17}\) H\(_{18}\)), 4.24-4.20 (m, 4H, H\(_8\) H\(_{12}\) H\(_{21}\) H\(_{22}\)), 3.86-3.84 (m, 8H, H\(_9\) H\(_{12}\) H\(_{21}\) H\(_{22}\)).

**13C NMR (100 MHz, CDCl3, 298K):** \( \delta \) (ppm) = 190.9 (C\(_1\)), 154.3 & 149.1 & 148.8 (C\(_4\) C\(_5\) C\(_14\)), 130.2 (C\(_2\)), 126.9 (C\(_7\)), 121.4 & 113.9 (C\(_{15}\) C\(_{16}\) C\(_{17}\) C\(_{18}\)), 111.8 (C\(_6\)), 110.9 (C\(_3\)), 71.5 & 71.4 & 71.3 & 69.7 & 69.5 & 69.4 & 69.4 & 69.3 (CH\(_3\)O).

**MS (ESI):** [M+Na]\(^+\) calcd for C\(_{25}\)H\(_{42}\)O\(_9\): 499.52, found: 499.27

**7) Preparation of the compound 16**

A solution of the crown ether aldehyde 15 (5.78 g, 12.134 mmol, 1 equiv) and the tridec-12-yne-1-amine 14 (2.37 g, 12.134 mmol, 1 equiv) in 200 mL of toluene was heated under reflux for 30 h using a Dean-Stark apparatus. The solvent was then evaporated to give a yellow oil. The mixture was diluted with MeOH (150 mL), and then NaBH\(_4\) (2.30 g, 60.670 mmol, 5 equiv) was added portionwise at 0-5°C. Stirring was maintained at room temperature for a further 5 h. Then, an aqueous solution of HCl 5M (100 mL) was added to the reaction mixture. Methanol was evaporated, and the residue was

diluted with dichloromethane (100 mL) and washed with an aqueous solution of NaOH 5M (100 mL). The two layers were separated and the aqueous layer was extracted with dichloromethane (2x200 mL). The organic layers were combined, dried over MgSO₄ and concentrated. The crude (6.73 g) was directly engaged in the following reaction.

Rf (CH₂Cl₂/MeOH 9:1) 0.1

1H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 6.90-6.80 (m, 7H, H_D H_E H_N H_O H_P H_Q), 4.19-4.10 (m, 8H, H_C H_L H_S H_X), 3.95-3.89 (m, 8H, H_I H_K H_T H_W), 3.84 (s, 8H, H_I H_J H_U H_V), 3.70 (s, 2H, H_I), 2.60 (t, 2H, 3J_H4-H5 = 7.3 Hz, H_3), 2.18 (td, 2H, 3J_H5-H6 = 7.1 Hz, 4J_H13-H12 = 2.7 Hz, H_13), 1.94 (t, 1H, 3J_H15-H13 = 2.7 Hz, H_15), 1.57-1.45 (m, 4H, H_I H_12), 1.44-1.34 (m, 2H, H_1), 1.33-1.23 (m, 12H, H_S H_T H_R H_O)

13C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 148.3 & 148.2 & 147.2 (C_A C_F C_M C_R), 132.8 (C_C), 120.7 & 120.2 & 113.4 & 113.3 (C_B C_D C_E C_N C_O C_R C_O), 83.9 (C_14), 70.5 (C_I C_J C_U C_V), 69.2 (C_H C_K C_T C_W), 68.6 (C_G C_L C_S C_X), 67.8 (C_15), 52.9 (C_C), 48.6 (C_3), 29.2 & 28.9 & 28.9 & 28.8 & 28.4 & 27.9 & 26.7 (C_C C_G C_R C_S C_T C_U C_V C_W), 17.7 (C_13).

MS (ESI): [M+H]**; calcd for [C_{15}H_{38}N_{10}O_{6}]**: 656.4, found : 656.3

8) **Preparation of the compound 2**

A solution of HCl 2M in diethyl ether (20 mL, 0.2 mol, 19 equiv) was added to the amine 16 (6.73 g, 10.59 mmol, 1 equiv). The mixture was stirred for 30 min, and then diethyl ether was evaporated to give a solid. To a solution of the previous solid in milliQ water (50 mL) was added NH₄PF₆ (5.12 g, 31.77 mmol, 3 equiv) and dichloromethane (50 mL). The biphasic solution was stirred vigorously for 30 min; then, the two phases were separated and the aqueous layer was extracted with dichloromethane (3x30 mL). The organic layers were then combined, dried over MgSO₄ and concentrated. The crude was purified by chromatography on a silicagel column (solvent elution CH₂Cl₂/MeOH 98:2) to yield the compound 2 (8.40 g, 87% over the two steps) as a white solid.

Rf (CH₂Cl₂/MeOH 9:1) 0.54

1H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 6.93 (dd, 1H, 3J_H6-H7 = 1.5 Hz, 4J_H5-H6 = 8.4 Hz, H_D), 6.87-6.72 (m, 5H, H_E H_N H_O H_P H_Q), 6.60 (d, 1H, 3J_H8-H9 = 1.5 Hz, H_B), 4.52-4.28 (m, 2H, H_I), 4.52-3.59 (m, 24H, CH₂O_DB24CS), 3.58-3.30 (m, 2H, H_S), 2.19 (td, 2H, 3J_H13-H12 = 7.1 Hz, 4J_H13-H15 = 2.7 Hz,
H<sub>13</sub>), 1.96 (t, 1H, J<sub>H5,H13</sub> = 2.7 Hz, H<sub>5</sub>), 1.73-1.63 (m, 2H, H<sub>4</sub>), 1.57-1.48 (m, 2H, H<sub>12</sub>), 1.44-1.35 (m, 2H, H<sub>11</sub>), 1.35-1.16 (m, 12H, H<sub>3</sub>H<sub>6</sub>H<sub>7</sub>H<sub>8</sub>H<sub>9</sub>H<sub>10</sub>).

13C NMR JMOD (CDCl<sub>3</sub>, 100 MHz, 298K) : δ (ppm) = 147.6 & 147.5 & 146.2 & 146.0 (C<sub>A</sub> C<sub>F</sub> C<sub>M</sub> C<sub>O</sub>), 124.7 (C<sub>9</sub>), 122.9 (C<sub>D</sub>), 121.0 & 120.9 & 112.9 & 112.5 & 111.7 (C<sub>B</sub> C<sub>E</sub> C<sub>N</sub> C<sub>O</sub> C<sub>P</sub> C<sub>O</sub>), 72.2 & 71.8 & 70.9 & 70.8 & 70.7 & 67.0 (C<sub>15</sub>), 52.1 (C<sub>1</sub>), 48.8 (C<sub>3</sub>), 29.3 & 29.0 & 28.6 & 28.4 & 26.6 (C<sub>4</sub> C<sub>5</sub> C<sub>6</sub> C<sub>7</sub> C<sub>8</sub> C<sub>9</sub> C<sub>10</sub> C<sub>11</sub> C<sub>12</sub>), 18.3 (C<sub>13</sub>).

MS (ESI): [M-2PF<sub>6</sub>]<sup>+</sup>; calcd for [C<sub>76</sub>H<sub>116</sub>N<sub>2</sub>O<sub>16</sub>]<sup>+</sup>: 656.42, found: 656.38

MS (MALDI): [M-1H-2PF<sub>6</sub>]<sup>+</sup> calcd for [C<sub>75</sub>H<sub>115</sub>N<sub>2</sub>O<sub>16</sub>]: 1311.82, found: 1311.8

C. Synthesis of the non-interlocked threads 5u and 6u

1) Preparation of the compound 17

The compound 1 (200 mg, 0.391 mmol, 2 equiv) and the 1,12-diaminododecane (39 mg, 0.1955 mmol, 1 equiv) were stirred in 5 mL of dichloromethane at reflux for one night. The organic layer was washed successively with an aqueous solution of HCl 1M (2x5 mL), and with a saturated aqueous solution of NaCl (2x5 mL), then dried over MgSO<sub>4</sub> and concentrated under vacuo to afford the compound 17 (155 mg, 93%) as a white solid.

R<sub>f</sub> (petroleum ether /AcOEt 1:1) 0.28

1H NMR (400 MHz, CDCl<sub>3</sub>, 298K): δ = 6.49 (t, 2H, J<sub>H7,H8</sub> = 5.8 Hz, H<sub>7</sub>), 5.24 (t, 2H, J<sub>H3,H4</sub> = 9.3 Hz, H<sub>3</sub>), 5.08 (t, 2H, J<sub>H4,H5</sub> = 9.3 Hz, H<sub>5</sub>), 4.87 (t, 2H, J<sub>H2,H3</sub> = 9.3 Hz, H<sub>2</sub>), 4.77 (d, 2H, J<sub>H1,H2</sub> = 9.3 Hz, H<sub>1</sub>), 3.99 (d, 2H, J<sub>H5,H6</sub> = 9.3 Hz, H<sub>6</sub>), 3.21-3.12 (m, 4H, H<sub>8</sub>), 2.03 & 2.00 & 1.96 (3*6H, CH<sub>3</sub>CO), 1.50-1.40 (m, 4H, H<sub>4</sub>), 1.29-1.15 (m, 16H, H<sub>10</sub> H<sub>11</sub> H<sub>12</sub> H<sub>13</sub>).

13C NMR JMOD (100 MHz, CDCl<sub>3</sub>, 298K): δ = 169.7 & 169.3 & 169.1 (COCH<sub>3</sub>), 165.5 (C<sub>6</sub>), 87.6 (C<sub>1</sub>), 74.1 (C<sub>3</sub>), 71.6 (C<sub>3</sub>), 70.3 (C<sub>2</sub>), 69.0 (C<sub>4</sub>), 39.1 (C<sub>8</sub>), 29.3 & 29.2 & 29.0 & 26.6 (C<sub>9</sub> C<sub>10</sub> C<sub>11</sub> C<sub>12</sub> C<sub>13</sub>), 20.4 & 20.3 & 20.3 (CH<sub>3</sub>CO).

MS (ESI): [M+H]<sup>+</sup> calcd for [C<sub>36</sub>H<sub>55</sub>N<sub>8</sub>O<sub>16</sub>]: 855.37, found: 855.46

2) Preparation of the compound 18
To a solution of compound 2 (300 mg, 0.0374 mmol, 1 equiv) in dichloromethane (15 mL) were added Boc₂O (245 mg, 1.122 mmol, 3 equiv) and DIEA (0.145 mL, 1.122 mmol, 3 equiv). The solution was stirred during 3 h at room temperature. The organic layer was washed successively with an aqueous solution of HCl 1M (2x30 mL), a saturated aqueous solution of NaHCO₃ (2x30 mL), then dried over MgSO₄ and concentrated under vacuo. The crude was purified by chromatography on a silicagel column (solvent elution CH₂Cl₂/MeOH 98:2) to yield the N-Boc protected compound 18 (272 mg, 96%) as a white solid.

Rf (CH₂Cl₂/MeOH 9:1) 0.74

H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 6.94-6.70 (m, 7H, H₅ H₆ H₇ H₈ H₉ H₁₀ H₁₁), 4.38-4.27 (br s, 2H, H₁₂), 4.21-4.09 (m, 8H, H₁₃ H₁₄ H₁₅ H₁₆), 3.95-3.87 (m, 8H, H₁₇ H₁₈ H₁₉ H₂₀), 3.83 (s, 8H, H₁ H₂ H₃ H₄), 3.20-3.00 (m, 2H, H₁₁), 2.18 (td, 2H, J₁₃-H₁₂ = 7.1 Hz, J₁₅-H₁₄ = 2.7 Hz, H₁₃), 1.94 (t, 1H, J₁₄-H₁₅ = 7.1 Hz, H₁₄), 1.57-1.18 (m, 18H, H₁₁ H₁₂ H₁₃ H₁₄ H₁₅ H₁₆), 1.45 (s, 9H, H₂).

C NMR (CDCl₃, 100 MHz, 298K) : δ (ppm) = 148.8 & 147.9 (C₁₇ C₁₈ C₁₉), 131.9 (C₁), 121.4 & 114.6 & 113.8 (C₁₃ C₁₄ C₁₅ C₂₂ C₂₃ C₂₄), 79.3 (CO₂(CH₃)₃), 71.1 (C₁₆ C₁₇ C₁₈ C₁₉), 69.8 (C₁₀ C₂₄ C₂₅ C₂₆), 69.3 (C₂₂ C₂₃ C₂₄), 68.0 (C₁₅), 51.4 (C₁), 46.3(C₁₇), 29.5 & 29.4 & 29.3 & 29.0 & 28.7 & 26.8 (C₃ C₄ C₅ C₆ C₇ C₈ C₉ C₁₀ C₁₁ C₁₂), 28.4 ((CH₃)₃CCO), 18.4 (C₁₃).

MS (ESI): [M+H]⁺; calcd for [C₁₃H₂₆NO₁₀]⁺: 756.5, found : 756.5

3) Preparation of the thread 19

In a typical procedure, Cu(CH₂CN)₂PF₆ (36 mg, 0.0966 mmol, 1 equiv) and 2,6-lutidine (1 mg, 0.0097 mmol, 0.1 equiv) were added successively to a solution of the azido compound 17 (41 mg, 0.048 mmol, 0.5 equiv) and the alkyne compound 18 (73 mg, 0.0966 mmol, 1 equiv) in 4 mL of dry dichloromethane. The mixture was stirred for 24 h at room temperature, after which time the solvent was evaporated under vacuo. The crude was then directly purified by chromatography on a silicagel column (solvent gradient elution CH₂Cl₂ /acetone 1:0 to 3:7) to afford the thread 19 (80 mg, 70%) as a yellow solid.

Rf (CH₂Cl₂/MeOH 9:1) 0.63

H NMR (CDCl₃, 400 MHz, 298K) : δ (ppm) = 7.79 (s, 2H, H₁₄), 7.17-7.05 (m, 10H, H₂₂ H₂₃ H₂₄ H₂₅ H₂₆), 7.02 (br s, 2H, H₂₃), 6.94 (dd, 2H, J₁₆-H₁₇ = 1.4 Hz, J₁₇-H₁₈ = 8.3 Hz, H₁₈), 6.84 (t, 2H, J₁₇-H₁₈ = 5.7 Hz, H₁₉), 5.99 (d, 2H, J₁₉-H₂₀ = 9.5 Hz, H₂₀), 5.60 (t, 2H, J₁₉-H₂₀ = J₁₉-H₂₁ = 9.5 Hz, H₂₁), 5.50 (t, 2H, J₁₉-H₂₁ = J₁₉-H₂₂ = 9.5 Hz, H₂₂), 5.32 (t, 2H, J₁₉-H₂₂ = J₁₉-H₂₃ = 9.5 Hz, H₂₃), 5.21 (t, 2H, J₁₉-H₂₃ = J₁₉-H₂₄ = 9.5 Hz, H₂₄), 4.34 (s, 4H, H₂₅), 4.30-4.22 (m, 18H, H₁₁-H₁₆ H₂₆ H₂₇-H₃₂), 3.77-3.68 (m, 16H, H₁₁-H₁₆ H₂₆ H₂₇-H₃₂), 3.59 (s, 16H, H₁₁-H₁₆ H₂₆ H₂₇-H₃₂), 3.20-3.12 (br t, 4H, H₂₇-H₂₈), 3.11-3.04 (m, 4H, H₂₈), 2.66 (t, 4H, J₁₉-H₁₉ = 7.5 Hz, H₁₉), 1.99 & 1.97 & 1.78 (3*H, 3*H, 3*H, 3*H, 3*H)
CH₃(CO), 1.66-1.56 (m, 4H, H₁₇), 1.51-1.34 (m, 8H, H₂₉), 1.45 (s, 18H, C(CH₃)₃), 1.33-1.19 (m, 44H, H₁₀ H₁₁ H₁₂ H₁₃ H₁₈ H₂₀ H₂₁ H₂₂ H₂₃).

¹³C NMR JMOD (CD₂CN, 100 MHz, 298K) : δ (ppm) = 170.7 & 170.2 & 169.6 (COCH₃), 166.4 (C₈), 149.4 & 149.1 & 148.9 & 147.9 (C₁₅ C₆ C₇ C₈ C₉), 135.3 (C₈), 124.1 & 124.1 & 117.6 & 117.5 & 117.4 (C₈ C₉ C₁₀ C₁₁ C₁₂ C₁₃), 122.8 (C₁₄), 121.5 (C₁₄), 116.5 (C₈), 85.4 (C₁), 79.9 (C(CH₃)₃), 75.9 (C₅), 72.8 (C₇), 70.8 (C₂), 69.8 (C₆), 69.5 & 69.4 & 69.2 & 68.3 & 68.2 & 67.9 & 67.8 & 67.8 (CH₂O_{DB24C8}), 50.0 (C₂₈), 47.5 (C₂₀), 39.7 (C₈), 30.2 & 30.1 & 30.1 & 29.9 & 29.9 & 29.8 & 29.6 & 27.4 (C₉ C₁₀ C₁₁ C₁₂ C₁₃ C₁₇ C₁₈ C₁₉ C₂₀ C₂₁ C₂₂ C₂₃ C₂₄ C₂₅), 28.5 ((C₃H₃)C), 25.9 (C₁₆), 20.8 & 20.7 & 20.3 (CH₃CO).


4) Preparation of the thread 20

The thread 19 (75 mg, 0.0317 mmol, 1 equiv) was suspended in 2 mL of iodomethane and stirred for 4 days at room temperature. Then, iodomethane was evaporated under reduced pressure and the obtained solid was washed with diethyl ether to give a yellow solid. NH₄PF₆ (31 mg, 0.1901 mmol, 6 equiv) and 5 mL of dichloromethane were added to a suspension of the previous product in 5 mL of miliQ water. The resulted bilayer solution was vigorously stirred for 30 min. After separation, the aqueous layer was extracted twice with 5 mL of dichloromethane. The organic layers were combined, dried over MgSO₄ and concentrated to obtain the thread 20 (71 mg, 84%) as a yellow solid.

Rf (CH₃Cl/MeOH 9:1) 0.51

¹H NMR (CD₂CN, 400 MHz, 298K) : δ (ppm) = 8.53 (s, 2H, H₁₄), 7.01-6.85 (m, 14H, H₇ H₈ H₉ H₁₀ H₁₁ H₁₂ H₁₃ H₁₄), 6.81 (dd, 2H, ¹J_HD-HB = 1.4 Hz, ¹J_HD-HF = 8.1 Hz, H₂₀), 6.15-6.11 (m, 2H, H₁₅), 5.56-5.51 (m, 4H, H₁₆ H₁₇), 5.41-5.34 (m, 2H, H₈), 4.32 (d, 2H, ¹J_H₁₅-H₁₆ = 10.0 Hz, H₂₁), 4.31 (s, 4H, H₂₈), 4.16-4.09 (m, 16H, H₁₀ H₁₁ H₁₂ H₁₃ H₁₄), 4.14 (s, 6H, H₂₉), 3.80-3.75 (m, 16H, H₁₃ H₁₅ H₁₆ H₁₇), 3.65 (s, 16H, H₁₇ H₁₈ H₁₉), 3.18-3.07 (m, 8H, H₂₀ H₂₁), 2.79 (t, 4H, ¹J_H₁₆-H₁₇ = 7.7 Hz, H₂₂), 1.99 & 1.99 & 1.91 (3s, 3*H, CH₃(CO)), 1.74-1.64 (m, 4H, H₁₈), 1.51-1.34 (m, 12H, H₁₉ H₂₀ H₂₁), 1.44 (s, 18H, C(CH₃)₃), 1.33-1.17 (m, 40H, H₁₀ H₁₁ H₁₂ H₁₃ H₁₄ H₂₀ H₂₁ H₂₂ H₂₃ H₂₄).

¹³C NMR JMOD (CD₂CN, 100 MHz, 298K) : δ (ppm) = 170.6 & 170.1 & 170.0 (COCH₃), 165.4 (C₈), 149.4 & 149.4 & 149.3 & 148.4 & 146.9 (C₁₅ C₁₆ C₁₇ C₈ C₉ C₁₀), 133.9 (C₈), 127.8 (C₁₄), 122.8 & 121.6 & 115.7 & 115.6 & 115.5 & 114.8 (C₉ C₁₀ C₁₁ C₁₂ C₁₃ C₁₄ C₈ C₁₅ C₁₆ C₁₇), 87.8 (C₁), 79.8 (C(CH₃)₃), 76.2 (C₇), 72.1 (C₉), 70.7 (C₂), 69.2 (C₈), 70.4 & 69.7 & 69.6 & 69.5 & 69.4 (CH₂O_{DB24C8}), 50.0 (C₂₈), 47.4 (C₂₉), 39.8 (C₈), 38.9 (C₂₀), 30.3 & 30.2 & 30.2 & 30.1 & 30.0 & 29.9 & 29.9 & 29.7 & 29.7 & 27.4 (C₉ C₁₀ C₁₁ C₁₂ C₁₃ C₁₇ C₁₈ C₁₉ C₂₀ C₂₁ C₂₂ C₂₃ C₂₄ C₂₅), 28.6 ((CH₃)C), 23.8 (C₁₆), 20.8 & 20.7 & 20.5 (CH₃CO).
5) Preparation of the thread 5u

A suspension of the N-Boc protected compound 20 (71 mg, 0.0281 mmol, 1 equiv) in 3 mL of HCl 2M in diethyl ether was stirred for 1 hour. The mixture was then evaporated and washed with diethyl ether to give a solid. NH₄PF₆ (27 mg, 0.1686 mmol, 6 equiv) and 3 mL of dichloromethane were added to a suspension of the previous product in 3 mL of milliQ water. The resulted bilayer solution was vigorously stirred for 30 min. After separation, the aqueous layer was extracted twice with 5 mL of dichloromethane. The organic layers were combined, dried over MgSO₄ and concentrated to obtain the thread 5u (68 mg, 78 %) as a pale yellow solid.

Rf (CH₂Cl₂/Methanol 9:1) 0.40

1H NMR (CD₂CN, 400 MHz, 298K) : δ (ppm) = 8.52 (s, 2H, H₁₄), 7.07-6.91 (m, 14H, H₆ H₈ H₁₄ H₁₆ H₁₇ H₁₈ H₂₀ H₂₂ H₂₃), 6.89 (t, 2H, 3J_H₂₅_H₂₆ = 5.9 Hz, H₇), 6.16-6.12 (m, 2H, H₁), 5.57-5.52 (m, 4H, H₂ H₃), 5.41-5.34 (m, 2H, H₄), 4.32 (d, 2H, 3J_H₂₅-H₂₆ = 10.0 Hz, H₃), 4.19-4.09 (m, 16H, H₆ H₈ H₁₄ H₁₆ H₁₇ H₁₈ H₂₀ H₂₂ H₂₃), 4.14 (s, 6H, H₂₉), 4.04 (s, 4H, H₃₀), 3.84-3.75 (m, 16H, H₁₆ H₁₇ H₁₈ H₁₉), 3.67 & 3.66 (2s, 16H, H₂₀ H₂₂ H₂₃ H₂₅), 3.14-3.07 (m, 4H, H₈), 2.94 (t, 4H, 3J_H₂₆_H₂₇ = 7.6 Hz, H₂₆), 2.80 (t, 4H, 3J_H₁₆-H₁₇ = 7.6 Hz, H₁₇), 1.99 & 1.99 & 1.91 (3s, 3H, CH₃CO), 1.74-1.65 (m, 4H, H₁₇), 1.65-1.56 (m, 4H, H₂₃), 1.46-1.35 (m, 8H, H₉ H₁₈), 1.35-1.19 (m, 40H, H₁₀ H₁₁ H₁₂ H₁₃ H₁₄ H₂₀ H₂₁ H₂₂ H₂₃).

13C NMR (CD₂CN, 100 MHz, 298K) : δ (ppm) = 170.6 & 170.1 & 170.0 (COCH₃), 165.5 (C₆), 150.3 & 149.5 & 149.4 & 149.4 & 146.9 (C₁₅ C₁₆ C₁₇ C₁₈), 127.8 (C₁₄), 125.0 (C₇), 124.5 & 122.7 & 122.7 & 116.8 & 115.5 & 115.4 & 115.0 (C₈ C₉ C₁₀ C₁₁ C₁₂ C₁₃ C₁₄ C₁₅), 87.8 (C₄), 76.2 (C₃), 72.1 (C₇), 70.7 (C₅), 69.2 (C₄), 70.7 & 70.6 & 70.6 & 69.8 & 69.8 & 69.7 & 69.6 & 69.5 & 69.4 (CH₃O_3PB₄C₄8), 52.1 (C₂₈), 48.5 (C₂₆), 39.8 (C₈), 38.9 (C₂₉), 30.2 & 30.2 & 30.1 & 30.0 & 29.9 & 29.9 & 29.7 & 29.6 & 29.5 & 27.4 & 27.2 & 26.9 & 26.6 (C₉ C₁₀ C₁₁ C₁₂ C₁₃ C₁₄ C₁₅ C₁₆ C₁₇ C₁₈ C₁₉ C₂₀ C₂₁ C₂₂ C₂₃ C₂₄ C₂₅), 23.7 (C₁₆), 20.8 & 20.7 & 20.5 (CH₃CO).

MS (ESI): [M-3PF₆]⁺; calcd for [C₁₁₄H₁₇₆F₆N₁₀O₃₂]⁺: 780.74, found: 781.08

13
A solution of the thread 5u (68 mg, 2.447.10^{-5} mol) in 5 mL of dichloromethane was washed with 5 mL of an aqueous solution of NaOH 1M. After separation, the aqueous layer was extracted twice with 5 mL of dichloromethane and the combined organic phases were dried over MgSO_4 and then evaporated to obtain product 6u as a pale yellow solid (61 mg, quantitative).

R_f (CH_2Cl_2/MeOH 9:1) 0.40

^1^H NMR (CD_3CN, 400 MHz, 298K) : δ (ppm) = 8.54 (s, 2H, H_14), 7.02-6.82 (m, 16H, H_7 H_8 H_9 H_E H_N H_O H_P H_Q), 5.58-5.50 (m, 4H, H_2 H_3), 5.42-5.34 (m, 2H, H_4), 4.32 (d, 2H, J_H5-H4 = 9.9Hz, H_5), 4.17-4.07 (m, 16H, H_L H_M H_N H_P H_Q), 4.14 (s, 6H, H_29), 3.80-3.74 (m, 16H, H_O H_P H_Q), 3.65 & 3.65 (2*s, 16H, H_I H_J H_K H_L H_M H_N H_O H_P H_Q), 3.64 (s, 4H, H_28), 3.14-3.07 (m, 4H, H_8), 2.79 (t, 4H, J_H16-H17 = 7.7 Hz, H_16), 2.51 (t, 4H, J_H26-H25 = 7.0 Hz, H_25), 1.99 & 1.99 & 1.91 (3*s, 3*6H, CH_3CO), 1.74-1.64 (m, 4H, H_17), 1.50-1.34 (m, 12H, H_9 H_18 H_25), 1.34-1.18 (m, 40H, H_10 H_11 H_12 H_13 H_19 H_20 H_21 H_22 H_23 H_24).

^13^C NMR JMOD (CD_3CN, 100 MHz, 298K) : δ (ppm) = 170.6 & 170.1 & 170.0 (COCH_3), 165.4 (C_6), 149.6 & 149.5 & 149.3 & 147.0 (C_15 C_A C_F C_M C_R), 136.1 (C_c), 126.6 (C_14), 122.8 & 122.7 & 122.0 & 115.7 & 115.6 & 115.4 & 115.4 (C_B C_D C_E C_N C_O C_P C_Q), 87.9 (C_1), 76.2 (C_3), 72.1 (C_2), 70.8 (C_2), 69.2 (C_4), 70.6 & 69.8 & 69.7 & 69.7 & 69.6 & 69.5 & 69.5 (CH_2O_DB24CB), 53.9 (C_28), 49.9 (C_26), 39.9 (C_8), 39.0 (C_29), 30.8 & 30.3 & 30.3 & 30.2 & 30.2 & 30.1 & 29.9 & 29.7 & 29.3 & 28.1 & 27.5 & 27.2 (C_9 C_10 C_11 C_12 C_13 C_17 C_18 C_19 C_20 C_21 C_22 C_23 C_24 C_25), 23.8 (C_16), 20.8 & 20.8 & 20.5 (CH_3CO).
**D. Synthesis of the double-lasso**

1) *Preparation of the activated rotaxane dimer 3*

![Diagram of rotaxane dimer 3]

In a typical procedure, Cu(CH$_3$CN)$_4$PF$_6$ (73 mg, 0.1955 mmol, 1 equiv) and 2,6-lutidine (2 mg, 0.01955 mmol, 0.1 equiv) were added successively to a solution of the azido compound 1 (100 mg, 0.1955 mmol, 1 equiv) and the alkyne compound 2 (157 mg, 0.1955 mmol, 1 equiv) in 2 mL of dry dichloromethane. The mixture was stirred for 24 h at room temperature after which time the solvent was evaporated under vacuo. The crude was then directly purified by chromatography on a silica gel column (solvent gradient elution CH$_2$Cl$_2$ / acetone 1:0 to 3:7) to afford the rotaxane dimer 3 (239 mg, 93%) as a yellow solid.

**RF** (CH$_2$Cl$_2$/MeOH 9:1) 0.49

$^1$H NMR (CD$_3$CN, 400 MHz, 298K) : δ (ppm) = 7.82 (s, 2H, H$_7$), 6.95-6.85 & 6.69-6.56 (m, 4H, H$_{20}$), 6.85-6.71 (m, 12H, H$_6$ H$_9$ H$_8$ H$_7$ H$_5$ H$_4$ H$_3$ H$_2$ H$_1$), 6.42 (d, 2H, $^3$J$_{HE,HD}$ = 8.3 Hz, H$_b$), 6.11 (d, 2H, $^3$J$_{HE,HG}$ = 9.3 Hz, H$_i$), 5.77 (t, 2H, $^3$J$_{HE,HG}$ = 9.3 Hz, H$_2$), 5.62 (t, 2H, $^3$J$_{HE,HG}$ = 9.3 Hz, H$_2$), 5.56 (t, 2H, $^3$J$_{HE,HG}$ = 9.3 Hz, H$_2$), 4.97 (d, 2H, $^3$J$_{HE,HG}$ = 9.3 Hz, H$_2$), 4.58-4.40 (m, 4H, H$_{21}$), 4.33-3.64 (m, 48H, CH$_3$O$_{DB24C8}$), 3.47-3.34 (m, 4H, H$_{19}$), 2.68 (t, 4H, $^3$J$_{HE,HG}$ = 7.3 Hz, H$_9$), 2.05 & 2.00 & 1.81 (3*$s$, 3*$s$H, CH$_3$CO), 1.75-1.67 (m, 4H, H$_{18}$), 1.67-1.58 (m, 4H, H$_{18}$), 1.40-1.18 (m, 28H, H$_{11}$ H$_{12}$ H$_{13}$ H$_{14}$ H$_{15}$ H$_{16}$ H$_{17}$).

$^{13}$C NMR JMOD (CD$_3$CN, 100 MHz, 298K) : δ (ppm) = 170.6 & 170.3 & 169.6 & 164.0 (COCH$_3$), 164.0 (C$_6$), 148.6 & 147.0 & 146.9 (C$_5$ C$_A$ C$_F$ C$_M$ C$_K$), 126.2 (C$_7$), 123.5 & 122.9 & 120.5 & 114.0 & 112.9 & 112.6 & 112.6 (C$_8$ C$_D$ C$_E$ C$_N$ C$_O$ C$_Q$), 121.5 (C$_9$), 85.6 (C$_4$), 74.5 (C$_3$), 72.7 (C$_2$), 70.3 (C$_2$), 69.3 (C$_3$), 73.0 & 72.9 & 72.9 & 72.1 & 71.4 & 71.3 & 71.2 & 70.9 & 70.9 & 69.9 & 69.2 & 68.3 & 68.3 & 67.8 & 67.8 (C$_{H2O_{DB24C8}}$), 52.7 (C$_{21}$), 49.7 (C$_{19}$), 30.1 & 30.0 & 29.9 & 29.8 & 29.6 & 29.4 & 27.2 & 27.1 (C$_{10}$ C$_{11}$ C$_{12}$ C$_{13}$ C$_{14}$ C$_{15}$ C$_{16}$ C$_{17}$ C$_{18}$), 25.9 (C$_9$), 20.7 & 20.6 & 20.3 (CH$_3$CO).

**HRMS (ESI):** [M-2PF$_6$]$^{1+}$; calcd for [C$_{112}$H$_{144}$F$_{10}$N$_{9}$O$_{34}$]$:^{1+}$: 1167.4813, found : 1167.5016
2) Preparation of the double-lasso 4a-b

To a stirred solution of the rotaxane dimer 3 (104 mg, 0.0396 mmol, 1 equiv) in 80 mL of dichloromethane (C = 5.10^-4 M) was added the dodecane-1,12-diamine (7.92 mg, 0.0396 mmol, 1 equiv). The solution was stirred for 4 days at room temperature, then evaporated and the crude was purified by chromatography on silica gel column (solvent gradient elution CH$_2$Cl$_2$ to CH$_2$Cl$_2$/acetone 3:7) to give the double-lasso 4a-b (32 mg) as a yellow solid in 33% yield.

R$_f$ (CH$_3$Cl/MeOH 9:1) 0.48

$^1$H NMR (CD$_3$CN, 400 MHz, 298K) : δ (ppm) = 7.78 (s, 2H, H$_{1d}$), 7.04-6.85 & 6.70-6.54 (m, 4H, H$_{15}$), 6.84-6.70 (m, 16H, H$_3$ H$_6$ H$_9$ H$_{10}$ H$_{11}$ H$_{12}$ H$_{13}$), 6.44 & 6.43 (2* d, 2H, $^3$J$_{HH-HD} = 8.3$ Hz, H$_6$), 5.99 & 5.99 (2* d, 2H, $^3$J$_{HH-H2} = 9.5$ Hz, H$_1$), 5.61 & 5.60 (2* t, 2H, $^3$J$_{HH-H1} = 9.5$ Hz, H$_2$), 5.49 (t, 4H, $^3$J$_{HH-H2} = 3^*J_{HH-H4} = 9.5$ Hz, H$_3$), 5.32 & 5.32 (2* t, 2H, $^3$J$_{HH-H4} = 9.5$ Hz, H$_2$), 4.58-4.39 (m, 4H, H$_{26}$), 4.23 & 4.22 (2* d, 2H, $^3$J$_{HH-H4} = 9.5$ Hz, H$_3$), 4.34-3.61 (m, 48H, CH$_2$O$_{DB24C8}$), 3.49-3.34 (m, 4H, H$_{26}$), 3.09-2.96 (m, 4H, H$_{8}$), 2.65 (t, 4H, $^3$J$_{HH-H17} = 7.4$ Hz, H$_{16}$), 1.98 & 1.97 & 1.79 & 1.79 (4* s, 18H, CH$_3$CO), 1.76-1.66 (m, 4H, H$_{25}$), 1.66-1.55 (m, 4H, H$_{17}$), 1.41-1.14 (m, 48H, H$_9$ H$_{10}$ H$_{11}$ H$_{12}$ H$_{13}$ H$_{18}$ H$_{19}$ H$_{20}$ H$_{21}$ H$_{22}$ H$_{23}$ H$_{24}$).

$^{13}$C NMR JMOD (CD$_3$CN, 100 MHz, 298K) : δ (ppm) = 170.7 & 170.1 & 169.7 (C(OCH$_3$)), 166.2 (C$_6$), 149.4 & 148.6 & 147.1 & 146.9 (C$_{15}$ C$_{A}$ C$_{F}$ C$_{M}$ C$_{R}$), 126.2 (C$_C$), 121.5 (C$_{1d}$), 123.5 & 123.5 & 121.6 & 114.1 & 113.0 & 112.9 & 112.7 & 112.6 (C$_B$ C$_D$ C$_E$ C$_N$ C$_O$ C$_P$ C$_Q$), 85.5 (C$_I$), 76.0 (C$_S$), 72.9 (C$_3$), 70.8 (C$_2$), 69.8 (C$_4$), 72.9 & 71.5 & 71.3 & 71.3 & 71.2 & 71.0 & 68.4 & 68.2 & 67.9 & 67.9 (CH$_2$O$_{DB24C8}$), 52.7 (C$_{28}$), 49.7 (C$_{26}$), 39.7 (C$_8$), 30.3 & 30.3 & 29.9 & 29.8 & 29.8 & 29.5 & 29.5 & 29.4 & 29.1 & 27.9 & 27.0 & 26.9 (C$_9$ C$_{10}$ C$_{11}$ C$_{12}$ C$_{13}$ C$_{17}$ C$_{18}$ C$_{19}$ C$_{20}$ C$_{21}$ C$_{22}$ C$_{23}$ C$_{24}$ C$_{25}$), 25.9 (C$_{16}$), 20.8 & 20.8 & 20.4 (CH$_3$CO).

HRMS (ESI): [M-2PF$_6$]$:^+$; calc'd for [C$_{112}$H$_{76}$F$_{10}$O$_{32}$]$^+$: 1083.5991, found: 1083.5991
3) Preparation of the double-lasso 5a-b

The double-lasso 4a-b (28 mg, 0.0114 mmol) was suspended in 3 mL of iodomethane and stirred for four days at room temperature. Then, iodomethane was evaporated under reduced pressure and the obtained solid was washed with diethyl ether to give a yellow solid. NH₄PF₆ (11 mg, 0.0683 mmol, 6 equiv) and 5 mL of dichloromethane were added to a suspension of the previous product in 5 mL of milliQ water. The resulted bilayer solution was vigorously stirred for 30 min. After separation, the aqueous layer was extracted twice with 5 mL of dichloromethane. The organic layers were combined, dried over MgSO₄ and concentrated to afford the double-lasso 5a-b (32 mg) in a quantitative yield as a yellow solid.

\[ \text{RF (CH}_3\text{Cl)} / \text{MeOH 9:1) 0.43} \]

\[ ^1H \text{ NMR (CD}_3\text{CN, 400 MHz, 298K)}: \delta (ppm) = 8.50 (s, 2H, H_{14}), 7.00-6.88 & 6.71-6.57 (m, 4H, H_{22}), 6.84 (t, 2H, ^3J_{HH,HD} = 6.0 Hz, H_{21}), 6.88-6.71 (m, 12H, H_{8} H_{9} H_{18} H_{19} H_{16} H_{17}), 6.42 (d, 2H, ^3J_{HE,HD} = 8.4 Hz, H_{6b}), 6.15 (d, 2H, ^3J_{HH,HE} = 9.4 Hz, H_{1}), 5.59-5.49 (m, 4H, H_{3} H_{1}), 5.37 & 5.36 (2s, 2H, ^3J_{HH,HH} = 9.4 Hz, H_{3}), 4.58-4.40 (m, 4H, H_{28}), 4.31 (d, 2H, ^3J_{HH,HH} = 9.4 Hz, H_{8}), 4.36-3.63 (m, 48H, CH_{3}O)_{DB24C8}, 4.13 (s, 6H, H_{29}), 3.48-3.35 (m, 4H, H_{26}), 3.11-3.02 (m, 4H, H_{9}), 2.78 (t, 4H, ^3J_{HH,HH} = 7.6 Hz, H_{16}), 1.99 & 1.99 & 1.98 & 1.91 (4s, 18H, CH_{3}CO), 1.78-1.63 (m, 8H, H_{17} H_{23}), 1.46-1.33 (m, 12H, H_{9} H_{8} H_{24}), 1.33-1.13 (m, 36H, H_{10} H_{11} H_{12} H_{13} H_{19} H_{20} H_{21} H_{22} H_{23}). \]

\[ ^{13}C \text{ NMR JMOD (CD}_2\text{CN, 100 MHz, 298K)}: \delta (ppm) = 170.6 & 170.1 & 170.0 (COCH_{3}), 165.4 (C_{8}), 148.6 & 148.6 & 147.1 & 147.0 & 146.9 (C_{15} C_{A} C_{F} C_{M} C_{R}), 127.6 (C_{14}), 126.2 (C_{C}), 123.5 & 121.6 & 114.1 & 112.9 & 112.7 & 112.6 (C_{B} C_{D} C_{E} C_{N} C_{O} C_{P} C_{Q}), 87.9 (C_{1}), 76.2 (C_{9}), 72.1 (C_{5}), 70.7 (C_{2}), 69.2 (C_{4}), 72.9 & 72.9 & 71.5 & 71.5 & 71.3 & 71.2 & 71.0 & 68.4 & 68.2 & 68.0 & 67.9 (CH_{3}O)_{DB24C8}, 52.7 (C_{28}), 49.7 (C_{26}), 39.9 (C_{8}), 38.9 (C_{29}), 30.4 & 30.4 & 30.0 & 30.0 & 29.9 & 29.8 & 29.7 & 29.3 & 29.3 & 27.5 & 27.1 & 27.0 (C_{9} C_{10} C_{11} C_{12} C_{13} C_{17} C_{18} C_{19} C_{20} C_{21} C_{22} C_{23} C_{24} C_{25}), 23.8 (C_{16}), 20.8 & 20.7 & 20.5 (CH_{3}CO). \]

HRMS (ESI): [M-3PF_{6}]^+; caled for [C_{114}H_{176}F_{6}N_{10}O_{32}P]^+: 780.7365, found : 780.7440
4) Preparation of the double-lasso 6a-b

A solution of the double-lasso 5a-b (22 mg, 7.917.10^-6 mol) in 5 mL of dichoromethane was washed with 5 mL of an aqueous solution of NaOH 1M. After separation, the aqueous layer was extracted twice with 5 ml of dichlorométhane and the combined organic phases were dried over MgSO₄ and then evaporated to obtain product 6a-b as a yellow solid (20 mg, quantitative).

\[ R_f \ (CH_3Cl/MeOH \ 9:1) \ 0.46 \]

\[ ^1H \ NMR \ (CD_3CN, \ 400 \ MHz, \ 298K) : \delta \ (ppm) = 9.54 \ & \ 9.51 (2^s, 2H, H_{14}), \ 7.04 \ & \ 7.00 (2^t, 2H, J_{H7-H8} = 6.0 \ & \ 5.7 \ Hz, H_7), \ 6.96-6.71 (m, 14H, H_{B-D}), \ 6.19 \ & \ 6.16 (2^d, 2H, J_{H1-H2} = 9.2 \ Hz, H_1), \ 5.58-5.50 (m, 2H, H_4), \ 4.40 \ & \ 4.39 (2^d, 2H, J_{H5-H4} = 9.2 \ Hz, H_5), \ 4.36 \ & \ 4.36 (2^s, 6H, H_{29}), \ 4.28-3.10 (m, 48H, CH_2O_{DB24C8}), \ 3.74-3.56 (m, 4H, H_{28}), \ 3.24-3.10 (m, 4H, H_{26}), \ 3.08-2.95 \ & \ 2.73-2.63 (2^s, 4H, H_6), \ 2.53-2.42 (m, 4H, H_{16}), \ 2.00 \ & \ 1.99 (2^s, 18H, CH_3CO), \ 1.76-1.49 (m, 8H, H_{17-H25}), \ 1.49-0.57 (m, 48H, H_9-H_{16}, H_{18}, H_{19}, H_{20}, H_{21}, H_{22}, H_{23}-H_{34}). \]

5) Reprotonation procedure of 6a-b

The double-lasso 6a-b (20 mg, 7.917.10^-6 mol) was suspended in 2 mL of a solution of HCl 2M in diethyl ether and stirred for 30 min at room temperature. After evaporation, the solid was washed with diethyl ether. Then, NH₄PF₆ (6.4 mg, 3.959.10^-5 mol, 5 equiv) and 2 mL of dichloromethane were added to a suspension of the previous product in 2 mL of milliQ water. The resulted bilayer solution was vigorously stirred for 30 min. After separation, the aqueous layer was extracted twice with 3 mL of dichloromethane. The organic layers were combined, dried over MgSO₄ and concentrated to obtain the double-lasso 5a-b (20 mg, 89%) as a yellow solid.

E. Molecular Modeling

NMR: NMR spectra were acquired on a Bruker Avance spectrometer operating at 500MHz. For DOSY experiments the standard Bruker sequence with double stimulated echoes and 3 spoil gradients for convection compensation was employed. Pulse field gradients were incremented in 64 steps from 2% to 95% of the maximum gradient strength. 48 scans were
used for each increment with a gradients length of 1.8 ms and a diffusion time of 200 ms. The spectra were processed by using Bruker’s Topspin2.0 software, and the diffusion coefficients were obtained directly from the spectra. Different solvents (CDCl$_3$, CD$_3$CN and DMSO-d6) and temperatures (from 298 to 278K) were employed. In DMSO and CDCl$_3$, diffusion coefficient between the protonated and non-protonated species does not change (see for example figures 1, 2 and 3). However, a significant variation was observed in CD$_3$CN at 278K (figure 4).

Figure 1. $^1$H and DOSY spectra (500 MHz, CD$_3$CN at 295K). In black: spectra corresponding to the protonated species and, in red, spectra corresponding to the non protonated species. The diffusion coefficients of both compounds under these conditions is $1.23 \times 10^{-9}$ (from value in the abscise axe -8.907).

Figure 2. $^1$H and DOSY spectra (500 MHz, CDCl$_3$ at 295K). In black: spectra corresponding to the protonated species and, in red, spectra corresponding to the non protonated species. The diffusion coefficients of both compounds under these conditions is $8.00 \times 10^{-10}$ (from value in the abscise axe -9.097).
Figure 3. $^1$H and DOSY spectra (500 MHz, DMSO at 295K). In black: spectra corresponding to the protonated species and, in red, spectra corresponding to the non protonated species. The diffusion coefficients of both compounds under these conditions is $2.05 \times 10^{-10}$ (from value in the abscise axe -9.688).

Figure 4. Partial DOSY spectra (500 MHz, CD$_3$CN, 278 K) of the protonated double-lasso macrocycle 5 (in blue) and the deprotonated double-lasso macrocycle 6 (in black). The diffusion coefficients of protonated compound 5 and deprotonated compound 6 are respectively $8.93 \times 10^{-10}$ and $9.66 \times 10^{-10}$ under these conditions.

Modeling: The structures of compounds 5a, 5b, 6a and 6b were built in Maestro. As a starting point for the two interlocked DB24C8 units (in 5a and 5b), we took the crystallographic structure of a dibenzo-24-crown-8-ether deposited in the Cambridge crystallographic Data Centre (CCDC) with the TEVBEB CCDC code. The structures were submitted to minimization by use of conjugate gradients and/or Monte Carlo Torsional Sampling Conformational Search (MCMM) with the OPLS2005 force field with electrostatic treatment for acetonitrile, and 1500 minimum number of steps. The modeling of compounds 5 and 6 was carried out in using a continuum solvent model: (Generalized-Born/Surface Area, GB/SA). The actual counterions were not included in the calculations, given the lack of proper parameters of the force field for PF$_6^-$.
employing other simple counterions, such as phosphate (Figure 5). None effect in the results was observed.

Figure 5. OPLS2005 minimised structure of compound 5b with H$_2$PO$_4^-$ counterions on the triazolium.
F. Stack plot and partial zoomed stack plot $^1$H NMR (400 MHz, 298K) of double-lasso 5 in different solvents
NMR Spectra
$^1$H NMR (400 MHz, CDCl$_3$, 298 K)
JMOD $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K)

![Chemical Structure](image)
$^1$H NMR (400 MHz, CDCl$_3$, 298 K)
JMOD $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K)

Electronic Supplementary Material (ESI) for Chemical Science
This journal is © The Royal Society of Chemistry 2012
$^1$H NMR (400 MHz, CDCl$_3$, 298 K)

![Chemical structure diagram](image-url)
JMOD $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K)
$^1$H NMR (400 MHz, CDCl$_3$, 298 K)
JMOD $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K)
$^1$H NMR (400 MHz, CDCl$_3$, 298 K)
JMOD $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K)
$^1$H NMR (400 MHz, CDCl$_3$, 298 K)
JMOD $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K)
$^1$H NMR (400 MHz, CDCl$_3$, 298 K)
JMOD $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K)
$^1$H NMR (400 MHz, CDCl$_3$, 298 K)
JMOD $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K)
$^1$H NMR (400 MHz, CDCl$_3$, 298 K)
JMOD $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K)
$^1$H NMR (400 MHz, CDCl$_3$, 298 K)
JMOD $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K)
$^1$H NMR (400 MHz, CDCl$_3$, 298 K)
JMOD $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K)
JMOD $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$, 298 K)
^1^H NMR (400 MHz, CDCl\textsubscript{3}, 298 K)
JMOD $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K)
$^1$H NMR (400 MHz, CDCl$_3$, 298 K)
JMOD $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K)
$^1$H NMR (400 MHz, CD$_3$CN, 298 K)
JMOD $^{13}$C NMR (100 MHz, CD$_3$CN, 298 K)
$^1$H NMR (400 MHz, CD$_3$CN, 298 K)
$^1$H NMR (400 MHz, CD$_3$CN, 298 K)
JMOD $^{13}$C NMR (100 MHz, CD$_3$CN, 298 K)
$^1$H NMR (400 MHz, CD$_3$CN, 298 K)
$\textsuperscript{1}H$ NMR (400 MHz, $\text{CD}_3\text{CN}$, 298 K)
$^1$H NMR (400 MHz, CD$_3$CN, 298 K)
JMOD $^{13}$C NMR (100 MHz, CD$_3$CN, 298 K)
$^1$H NMR (400 MHz, CD$_3$CN, 298 K)
JMOD $^{13}$C NMR (100 MHz, CD$_3$CN, 298 K)
$^1$H NMR (400 MHz, CD$_3$CN, 298 K)