CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201000074

Using a Threading-Followed-by-Swelling Approach to Synthesize [2]Rotaxanes

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Abstract: We have developed a "threading-followed-by-swelling" protocol to synthesize [2]rotaxanes efficiently and atom economically. Our protocol employs *cis*-1-[(*Z*)-alk-1′-enyl]-2-vinylcyclopropane units as the termini of the threadlike components; these end groups are converted into more-sizable cycloheptadiene motifs, which function as stopper units, through Cope rearrangements at elevated temperature. We used this approach to synthesize [2]rotaxanes in good yield from [2]pseudorotaxanes featuring either one or two swellable termini to interlock three different types of macrocycle. The chiral centers created by the swelling process were "erased" by hydrogenating the cycloheptadiene termini into the corresponding cycloheptane units, affording achiral molecular [2]rotaxanes as the only final products.

Keywords: Cope rearrangement · NMR spectroscopy · rotaxanes · solvent-free synthesis · supramolecular chemistry

Introduction

Because rotaxanes have potential applicability as molecular actuators and switches within mesoscale molecular electronic devices,[1] there is interest in developing new methods and protocols for their synthesis. Although a diverse array of rotaxanes has been constructed using a range of molecular recognition systems,[2] the protocols that have been applied to the syntheses of these interlocked molecules have been limited primarily to threading-followed-by-stoppering,[3] slippage,[4] and clipping[5] methods (Figure 1). In the threading-followed-by-stoppering protocol, pseudorotaxanes are first generated in solution and then external stopper motifs are attached to the end groups to interlock the macrocycles. The slippage protocol relies on thermal energy to facilitate the passage of the macrocycle over the high potential energy barrier of the stopper unit to form the corresponding thermodynamically stable rotaxanes at lower temperature. In the clipping approach, a recognition site on the dumbbell-shaped component serves as a template to direct the formation of an encircling interlocked macrocycle. Synthetic approaches that do not fall within these three protocols are relatively rare. Notably, an elegant threading-followed-by-ring-shrinking approach[6] was developed, in which Pd^{II} ions were added to chelate a salophen motif of the macrocyclic unit within a [2]pseudorotaxane, thereby decreasing the cavity size of the macrocycle to such an extent that it became interlocked with the dumbbell-shaped thread (Figure 1). Conceptually, interlocking the macrocycle along the rodlike unit of the dumbbell-shaped component could also be achieved by swelling the volume of the terminal groups of the pseudorotaxane. There are, however, several difficulties associated with designing a system to prove the viability of this new "threading-followed-by-swelling" concept:[7] 1) the terminal group should be expanded without attaching any additional atoms or molecular motifs so that the "swelling" process can be separated conceptually from "stoppering", 2) to maintain sufficient binding affinity to the thread component, the size of the macrocycle should remain constant, but the size of the terminal group must be chosen carefully to ensure that the macrocycle can pass over it

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000074.

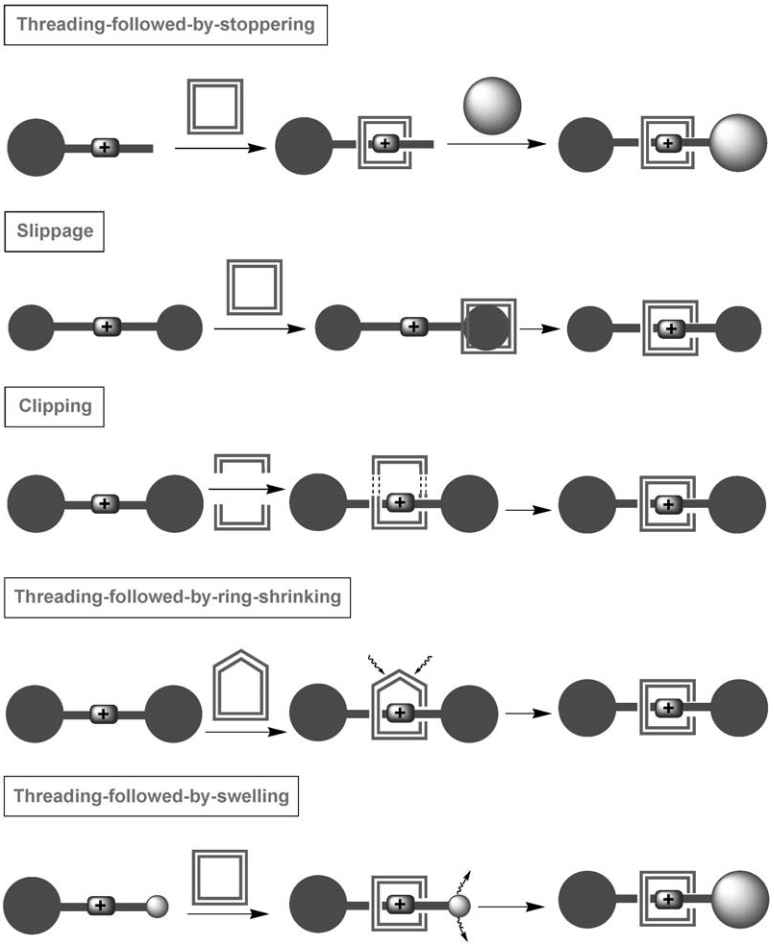


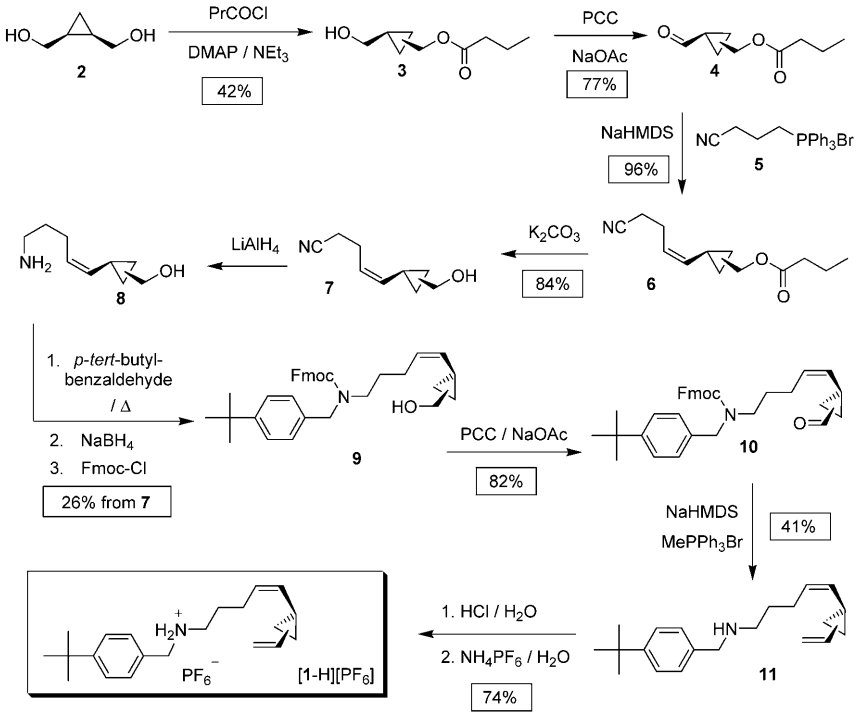
Figure 1. Cartoon representations of the general protocols for rotaxane synthesis.

prior to swelling but not after, and 3) the swelling of the terminal group must be initiated under simple and controllable conditions. Herein, we demonstrate a threading-followed-by-swelling protocol (Figure 1) for the synthesis of symmetrical and unsymmetrical molecular rotaxanes based on the recognition of dibenzylammonium ions (DBA^+) by three size-appropriate macrocyclic hosts, using *cis*-1-[(*Z*)-alk-1′-enyl]-2-vinylcyclopropane motifs as swellable terminal groups. We also report that this threading-followed-by-swelling protocol can be applied to the synthesis of these rotaxanes under solvent-free conditions.

Results and Discussion

Because of kinetic equilibrium between dumbbell-shaped and macrocyclic components and their pseudorotaxane complexes in solution, the efficiency of chemical reactions applied to interlock these components using a stoppering process is generally affected by the formation of interfering by-products.[8] Theoretically, the threading-followed-by-swelling approach is a clean and atom-economical[9] protocol—with no by-product disturbance—because the enlargement of the terminal group can be achieved by using an appropriate pericyclic reaction to rearrange its carbon atom skeleton. We chose the 1,2-divinylcyclopropane unit as the terminal group for the swelling thread because it can be converted into a bulkier cycloheptadiene motif through a Cope rearrangement. Because *trans*-1,2-divinylcyclopropane requires a high temperature—unfavorable for maintaining a complexed pseudorotaxane—to perform the desired Cope rearrangement reaction, *cis*-1,2-divinylcyclopropane, which rearranges very rapidly at room temperature, was our stopper unit of choice.[10] To slow down the rapid Cope rearrangement of the *cis*-1,2-divinylcyclopropane terminus, we chose to link its olefinic bond to the thread component in a *Z* configuration; unfavorable A-1,3 interactions of *cis*-1-[(*Z*)-alk-1′-enyl]-2-vinylcyclopropane units will disturb the alignment of the alkene orbitals and, thereby, significantly decrease the rate of rearrangement at room temperature.[11] Therefore, we aimed to synthesize and isolate the *cis*-1-[(*Z*)-alk-1′-enyl]-2-vinylcyclopropane-terminated threadlike salt **1**-H·PF_6 at room temperature and then demonstrate the threading-followed-by-swelling concept by initiating the Cope rearrangement reaction of its corresponding pseudorotaxane in solution at elevated temperature.

The racemic threadlike salt **1**-H·PF_6, featuring *p*-*tert*-butylphenyl and *cis*-1-[(*Z*)-alk-1′-enyl]-2-vinylcyclopropane units as terminal groups, was synthesized from *cis*-1,2-cyclopropanedimethanol[12] (Scheme 1). Monoesterification of the diol **2** gave a racemic mixture of the alcohol **3**, which was oxidized by using pyridinium chlorochromate (PCC) to provide the aldehyde **4**. By using sodium hexamethyl disilazide (NaHMDS) as the base, the Wittig reaction of **4** with (3-cyanopropyl)triphenylphosphonium bromide (**5**) provided the desired *Z* isomer of the alkene **6** in high yield. The ester protecting group of **6** was removed under basic conditions to produced the alcohol **7**. The nitrile function of **7** was reduced by $LiAlH_4$ to give the amino alcohol **8**, which was used in the following reaction without purification. Reduction of the imine formed from the reaction of *p*-*tert*-butylbenzaldehyde and **8** was followed by the protection of the resulting amine by using 9-fluorenylmethoxycarbonyl chlo-



Scheme 1. Synthesis of the threadlike salt **1**-H·PF_6. DMAP = 4-dimethylaminopyridine, PCC = pyridinium chlorochromate, NaHMDS = sodium hexamethyl disilazide, Fmoc-Cl = 9-fluorenylmethoxycarbonyl chloride.

The spectra of an equimolar mixture of the macrocycle **12** and the threadlike salt **1**-H·PF_6 (initial concentrations: 10 mM) in CD_3NO_2 at 318 K revealed the gradual consumption of the signals of the dialkenylcyclopropane-terminated [2]pseudorotaxane [**12**⊃**1**-H][PF_6] and the concomitant rise in the intensities of the signals of the cycloheptadiene-terminated [2]rotaxane **14**-H·PF_6 in terms of the changes in intensity of the signals of the two methylene groups adjacent to the ammonium center (Figure 3). Thus, heating an equimolar mixture of **12** and **1**-H·PF_6 in CH_3NO_2 (70 mM) at 318 K for 64 h, followed by ion exchange (NH_4PF_6/H_2O) and chromatographic processes, provided the [2]rotaxane **14**-H·PF_6 in an isolated yield of 61 %.

ride (Fmoc-Cl) to afford the alcohol **9**, which was then oxidized to give the aldehyde **10**. The Wittig reaction of **10** with methyltriphenylphosphonium bromide not only set up the desired *cis*-1-[(*Z*)-alk-1′-enyl]-2-vinylcyclopropane end group, but also removed the protecting Fmoc group to give the amine **11**, which was then protonated and subjected to ion exchange to give the threadlike salt **1**-H·PF_6. The macrocycles **12**,[13] **13**,[14] and dibenzo[24]crown-8 (DB24C8)[15] all form [2]pseudorotaxane-like complexes with DBA·PF_6 in low-polarity solvents. Thus, these three macrocycles were selected for the syntheses of three [2]rotaxanes by using the threading-followed-by-swelling approach. An equimolar mixture of **12** and the threadlike salt **1**-H·PF_6 (1 mM) in CD_3NO_2 underwent slow association/dissociation—on the ^{1}H NMR spectroscopic timescale—of the two species, as evidenced by the presence of three sets of resonances in the ^{1}H NMR spectrum (Figure 2b): one set for the free macrocycle **12** (cf., Figure 2a), one for the free salt **1**-H·PF_6 (cf., Figure 2c), and one for the 1:1 complex formed between **12** and **1**-H·PF_6. The characteristic upfield shift of the signal for the methylene protons adjacent to the NH_2^+ center in the complex formed between **12** and the threadlike cation **1**-H^+ (see the Supporting Information) suggested that the structure of the complex was most likely to be the [2]pseudorotaxane [**12**⊃**1**-H][PF_6]. Because the *p*-*tert*-butylphenyl unit is an effective stopper for the macrocycle **12**,[13] the association and dissociation of the complex [**12**⊃**1**-H][PF_6] must occur through passage of the *cis*-1-[(*Z*)-alk-1′-enyl]-2-vinylcyclopropane terminus of the threadlike component through the macrocycle.

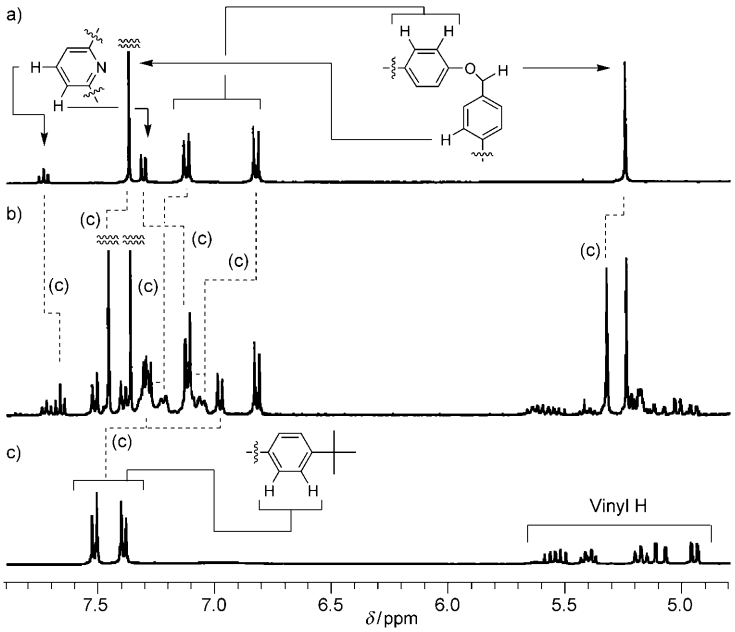


Figure 2. Partial ^{1}H NMR spectra (400 MHz, CD_3NO_2, 298 K) of a) macrocycle **12**, b) an equimolar mixture of **12** and **1**-H·PF_6 (1 mM), and c) **1**-H·PF_6. The descriptor (c) refers to the signals of the complexed states of macrocycle **12** and thread **1**-H·PF_6.

Single crystals suitable for X-ray crystallography were grown through the liquid diffusion of isopropyl ether into a solution of the [2]rotaxane **14**-H·PF_6 in MeCN. The solid-state structure[16,17] (Figure 4) reveals the expected [2]ro-

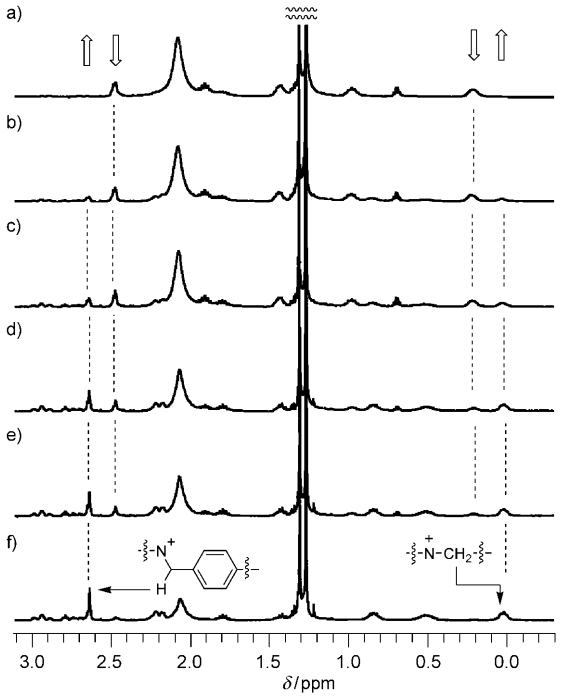


Figure 3. Partial ^{1}H NMR spectra (400 MHz, CD_3NO_2, 318 K) displaying the formation of the [2]rotaxane **14**-H·PF_6 from the [2]pseudorotaxane [**12**⊃**1**-H][PF_6] after reaction times of a) 0, b) 12, c) 18, d) 36, e) 48, and f) 64 h.

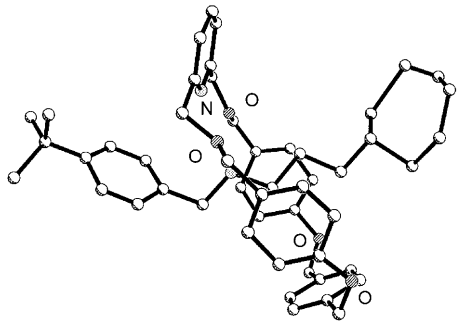


Figure 4. Ball-and-stick representation of the solid-state structure of the [2]rotaxane **14**$^+$.

taxane molecular geometry; the dumbbell-shaped component, with its *p-tert*-butylphenyl and cycloheptadiene stopper units, is threaded through the cavity of the macrocyclic moiety.

Because the racemic *cis*-1-[(*Z*)-alk-1′-enyl]-2-vinylcyclopropane-terminated threadlike salt **1**-H·PF_6 was employed in the threading-followed-by-swelling process, the resulting [2]rotaxane **14**-H·PF_6 was obtained as a racemate. The two enantiomers were converted into the same achiral [2]rotaxane **15**-H·PF_6 through the simple hydrogenation of the cycloheptadiene terminus into a cycloheptane moiety. This conversion was evidenced by the concomitant disappearance of the vinyl and allylic signals in the ^{1}H NMR spectra of the racemic [2]rotaxane **14**-H·PF_6 and the appearance of new signals for aliphatic protons ($\delta = 1.0$–1.5 ppm) in the ^{1}H NMR spectra of the [2]rotaxane **15**-H·PF_6 after hydrogenation (Figure 5). It was therefore not necessary to synthesize an optically pure threadlike salt because the final hydrogenation step erases the chirality from the [2]rotaxane. No signals from the free components were observed in the ^{1}H NMR spectrum recorded after heating a solution of the [2]rotaxane **15**-H·PF_6 in CD_3SOCD_3 at 343 K for 2 h, confirming the interlocked nature of the two components.

The ^{1}H NMR spectrum of an equimolar mixture of bis(*p-tert*-butylbenzyl)ammonium hexafluorophosphate and the macrocycle **13** in CD_3CN (8 mM) exhibited no signals that could be attributed to complex formation, even after heating at 323 K for 24 h. This suggests that, under such conditions, this macrocycle is incapable of passing over a *p-tert*-butylphenyl terminus. The formation of the pseudorotaxane [**13**⊃**1**-H][PF_6] in a solution of an equimolar mixture of the macrocycle **13** and the threadlike salt **1**-H·PF_6 in CD_3CN, with an association constant of 260 M^{-1}, therefore must have occurred as a result of the passage of the *cis*-1-[(*Z*)-alk-1′-enyl]-2-vinylcyclopropane terminus through the cavity of the macrocycle. Heating an equimolar mixture of **13** and **1**-H·PF_6 in CH_3NO_2 (70 mM) at 323 K for 48 h, followed by ion exchange (NH_4PF_6/H_2O) and chromatography processes, provided the [2]rotaxane **16**-H·PF_6 in an isolated yield of 86% (Scheme 2). The subsequent hydrogenation turned the racemic [2]rotaxane **16**-H·PF_6 into the achiral [2]rotaxane **17**-H·PF_6 in 85% yield. Thus, the threading-followed-by-swelling approach can also be applied to the efficient syntheses of [2]rotaxanes featuring the macrocycle **13** as an interlocked moiety.[18]

Because *p-tert*-butylphenyl and cycloheptane moieties are also effective stopper units for DB24C8,[19] we applied a similar complexation/swelling/hydrogenation sequence to an equimolar mixture of DB24C8 and **1**-H·PF_6. As expected,

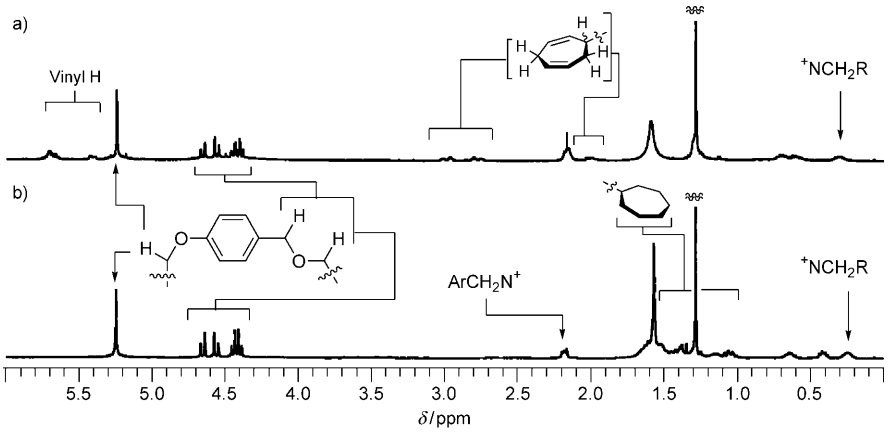
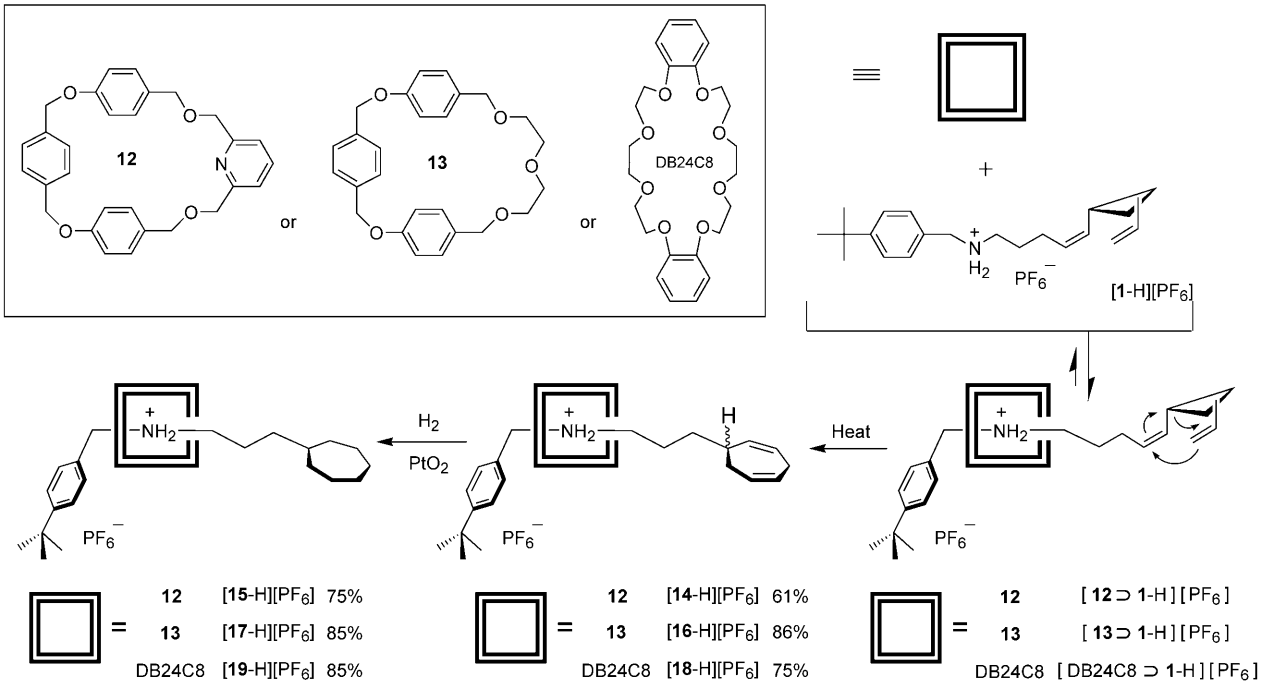


Figure 5. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of a) the racemic [2]rotaxane **14**-H·PF_6 and b) the achiral [2]rotaxane **15**-H·PF_6 obtained after the hydrogenation of **14**-H·PF_6.



Scheme 2. The threading-followed-by-swelling approach used to synthesize [2]rotaxanes featuring three types of interlocked macrocycles.

we obtained the desired achiral [2]rotaxane **19**-H·PF_6, in overall 64% yield after the swelling and hydrogenation reactions (Scheme 2).

Because this swelling process is initiated merely by heating, we suspected that the interlocking process could be performed under solvent-free conditions. We therefore concentrated an equimolar mixture of the macrocycle **12** and the threadlike salt **1**-H·PF_6 in $CDCl_3$ under reduced pressure at room temperature to afford a solid film, which we suspected contained predominately the [2]pseudorotaxane [**12**⊃**1**-H]-[PF_6].[20] After heating the solid film at 318 K for 72 h, we isolated the [2]rotaxane **14**-H·PF_6 in 45% yield after purification and counterion exchange. We applied the same solvent-free approach to synthesize the [2]rotaxanes **16**-H·PF_6 and **18**-H·PF_6 in isolated yields of 55 and 50%, respectively, after heating solid films presumably containing predominately the [2]pseudorotaxanes [**13**⊃**1**-H][PF_6] and [DB24C8⊃**1**-H][PF_6], respectively. The presence of greater amounts of unidentified by-products in the ^{1}H NMR spectra of the crude products obtained under solvent-free "swelling" conditions, relative to those obtained in solution, suggests that the rates of the side reactions may increase significantly when the free threadlike salt **1**-H·PF_6 and/or its corresponding [2]pseudorotaxanes are in close contact.

After confirming that our threading-followed-by-swelling protocol could be applied to the synthesis of asymmetrical [2]rotaxanes featuring one of three different macrocycles, we turned our attention to the construction of symmetrical [2]rotaxanes featuring two swellable stoppers from the threadlike salt **20**-H·PF_6 (Scheme 3). To avoid the genera-

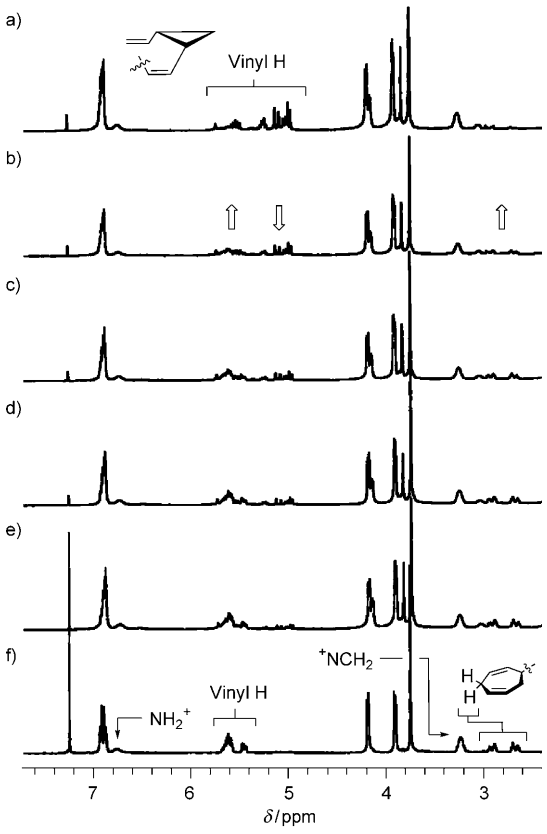
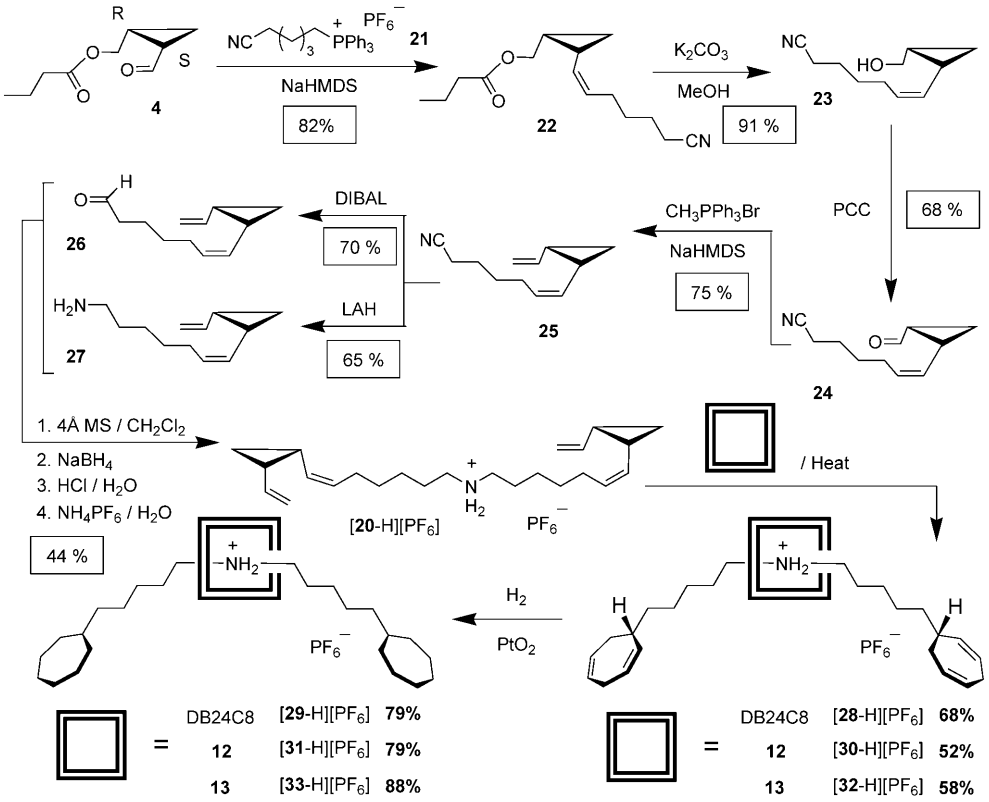


Figure 6. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 318 K) displaying the formation of the [2]rotaxane **28**-H·PF_6 from the [2]pseudorotaxane [DB24C8⊃**20**-H][PF_6] after reaction times of a) 0, b) 16, c) 40, d) 52, and e) 70 h; f) spectrum of the isolated product.



Scheme 3. The threading-followed-by-swelling approach used to synthesize symmetrical [2]rotaxanes. DIBAL = diisobutylaluminum hydride, MS = molecular sieves.

tion of **20**-H·PF_6 as a diastereoisomeric mixture, we synthesized the enantiomerically pure aldehyde **26** and amine **27** from the optically pure aldehyde **4**.[21]

The Wittig reaction of the optically pure aldehyde **4** and the nitrile **21** gave the *Z*-alkene **22**. Removal of the ester protecting group from **22** under basic conditions, followed by PCC oxidation, afforded the aldehyde **24**. The subsequent Wittig reaction of **24** with methylphosphonium bromide gave the nitrile **25**, which was reasonably stable under ambient conditions and could be converted into the aldehyde **26** and the amine **27** under DIBAL- and $LiAlH_4$-mediated reduction reactions, respectively. Reduction of the imine formed through condensation of the aldehyde **26** and the amine **27**, followed by protonation and ion exchange, gave the desired threadlike salt **20**-H·PF_6 as a colorless oil (Scheme 3).

When an equimolar mixture of the threadlike salt **20**-H·PF_6 and DB24C8 in $CDCl_3$ was heated at 318 K, the ^{1}H NMR spectra revealed a gradual decrease in intensity of the signals for the olefinic protons of the dialkenylcyclopropane-terminated [2]pseudorotaxane [DB24C8⊃**20**-H][PF_6] and a concomitant rise in the intensities of the signals for the olefinic protons of the symmetrical cycloheptadiene-terminated [2]rotaxane **28**-H·PF_6, (Figure 6), which was isolated in 68% yield after column chromatography and ion exchange. After reducing the two chiral cycloheptadiene termini of the [2]rotaxane **28**-H·PF_6 through hydrogenation, we obtained the achiral [2]rotaxane **29**-H·PF_6 in 79% yield (Scheme 3). We employed the same threading/swelling/hydrogenation approach using the macrocycles **12** and **13** and the threadlike salt **20**-H·PF_6 to obtain the achiral biscycloheptane-terminated [2]rotaxanes **31**-H·PF_6 and **33**-H·PF_6, respectively.

Single crystals suitable for X-ray crystallography were obtained by the liquid diffusion of hexane into a solution of the [2]rotaxane **29**-H·PF_6 in $CHCl_3$. The solid-state structure[22] (Figure 7) reveals the expected [2]rotaxane molecular geometry with one DB24C8 macrocycle trapped between two terminal cycloheptane stoppers.

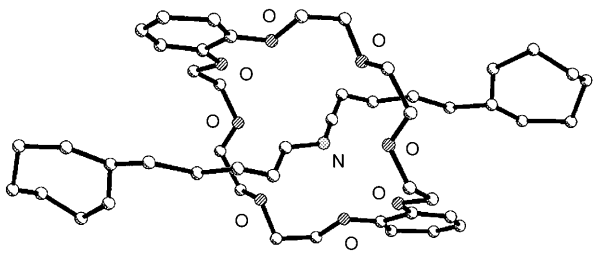


Figure 7. Ball-and-stick representation of the solid-state structure of the [2]rotaxane **29**$^+$.

Conclusion

The swelling of *cis*-1-[(*Z*)-alk-1′-enyl]-2-vinylcyclopropane termini is a mild and high-yielding method for the synthesis of symmetric and asymmetric [2]rotaxanes. Hydrogenation of the products of the threading-followed-by-swelling protocol provides achiral molecular [2]rotaxanes, that is, it erases the chiral information from the original cycloheptadiene termini. Because different types of macrocycles can be interlocked within [2]rotaxane structures when using this threading-followed-by-swelling approach, we believe that this protocol has the potential for application in the construction of more complicated interlocked systems in the future.

Experimental Section

General: All glassware, stirrer bars, syringes, and needles were either oven- or flame-dried prior to use. All reagents, unless otherwise indicated, were obtained from commercial sources. Anhydrous CH_2Cl_2 and MeCN were obtained by distillation from CaH_2 under N_2. Reactions were conducted under an N_2 or Ar atmosphere. Thin-layer chromatography (TLC) was performed on Merck 0.25 mm silica gel (Merck Art. 5715). Column chromatography was performed by using Kieselgel 60 (Merck, 70–230 mesh). Melting points were determined by using a Fargo MP-2D melting point apparatus. To obtain the NMR spectra, the deuterated solvent was used as the lock, whereas either the solvent's residual protons or TMS was employed as the internal standard. Chemical shifts are reported in parts per million (ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broad).

(±)-*cis*-1-Butyryloxymethyl-2-hydroxymethylcyclopropane (3): Butyryl chloride (7.39 mL, 7.5 g, 70 mmol) was slowly added to a mixture of **2** (7.7 g, 75.5 mmol), DMAP (0.46 g, 3.8 mmol), and Et_3N (23 mL, 16.7 g, 165 mmol) in CH_2Cl_2 (150 mL) at 0 °C. The mixture was stirred at room temperature for 2 h and was then partitioned between CH_2Cl_2 (300 mL) and water (300 mL). The organic phase was dried ($MgSO_4$) and concentrated to give a crude product that was purified chromatographically (SiO_2; EtOAc/hexane, 2:8) to afford **3** as a colorless oil (5.0 g, 42 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.22 (q, J = 5.2 Hz, 1H), 0.85 (td, J = 8.4, 5.6 Hz 1H), 0.95 (t, J = 7.2 Hz, 3H), 1.23–1.39 (m, 2H), 1.60–1.70 (m, 2H), 2.31 (t, J = 7.6 Hz, 2H), 3.38 (dd, J = 9.2, 12 Hz, 1H), 3.79 (dd, J = 9.2, 12 Hz, 1H), 3.86 (dd, J = 5.6, 12 Hz, 1H), 4.50 ppm (dd, J = 5.6, 12 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.2, 14.1, 14.8, 18.8, 19.1, 36.5, 62.6, 64.5, 172.9 ppm; HRMS (ESI): *m/z*: calcd for $C_9H_{17}O_3$: 173.1178 $[M+H]^+$; found: 173.1155.

(±)-*cis*-1-Butyryloxymethyl-2-formylcyclopropane (4): A mixture of the alcohol **3** (3.40 g, 19.8 mmol), NaOAc (0.950 g, 11.6 mmol), and PCC (8.4 g, 39 mmol) in CH_2Cl_2 (160 mL) was stirred at room temperature for 3 h and then filtered and partitioned between CH_2Cl_2 (200 mL) and water (200 mL). The organic phase was dried ($MgSO_4$) and concentrated to give the crude product, which was purified chromatographically (SiO_2; EtOAc/hexane, 5:95) to afford **4** as a colorless oil (2.6 g, 77 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, J = 7.2 Hz, 3H), 1.23–1.38 (m, 2H), 1.58–1.68 (m, 2H), 1.81–1.92 (m, 1H), 2.02–2.10 (m, 1H), 2.26 (t, J = 7.2 Hz, 2H), 3.94 (dd, J = 12, 9.2 Hz, 1H), 4.50 (dd, J = 12, 6 Hz, 1H), 9.51 ppm (d, J = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.2, 14.1, 18.8, 22.9, 27.0, 36.3, 62.3, 172.7, 199.1 ppm; HRMS (ESI): *m/z*: calcd for $C_9H_{14}KO_3$: 209.0580 $[M+K]^+$; found: 209.0568.

(±)-*cis*-1-Butyryloxymethyl-2-[(*Z*)-4-cyanobut-1-enyl]cyclopropane (6): NaHMDS (2 M in THF, 15 mL, 30 mmol) was added to a solution of (3-cyanopropyl)triphenylphosphonium bromide (11.6 g, 28.3 mmol) in THF (150 mL) at 0 °C. The mixture was stirred for 10 min and then the aldehyde **4** (2.80 g, 16.5 mmol) in THF (15 mL) was added to the ylide solution. After 3.5 h at 0 °C, the mixture was poured into petroleum ether (300 mL) to precipitate triphenylphosphine oxide. The suspension was filtered, the solvent was evaporated, and the residue was purified chromatographically (SiO_2; EtOAc/hexane, 5:95) to afford **6** as a colorless oil (3.5 g, 96 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.41–0.48 (m, 1H), 0.94 (t, J = 7.2 Hz, 3H), 1.01–1.12 (m, 1H), 1.37–1.47 (m, 1H), 1.58–1.75 (m, 3H), 2.28 (t, J = 7.2 Hz, 2H), 2.37–2.43 (m, 2H), 2.48–2.57 (m, 2H), 3.91 (dd, J = 8.4, 12 Hz, 1H), 4.18 (dd, J = 6.8, 12 Hz, 1H), 5.23 (t, J = 9.6 Hz, 1H), 5.45 ppm (dt, J = 8.4, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9, 14.1, 14.6, 17.4, 17.8, 18.8, 24.0, 36.4, 64.7, 119.0, 126.4, 131.0, 173.0 ppm; HRMS (ESI): *m/z*: calcd for $C_{13}H_{19}NaNO_2$: 244.1314 $[M+Na]^+$; found: 244.1263.

(±)-*cis*-1-[(*Z*)-4-Cyanobut-1-enyl]-2-hydroxymethylcyclopropane (7): A mixture of the ester **6** (3.50 g, 15.8 mmol) and K_2CO_3 (6.60 g, 47.5 mmol) in MeOH (16 mL) was stirred at room temperature for 30 min and then partitioned between CH_2Cl_2 (100 mL) and water (100 mL). The organic phase was dried ($MgSO_4$) and concentrated to give the crude product, which was purified chromatographically (SiO_2; EtOAc/hexane, 2:8) to afford **7** as a colorless oil (2.0 g, 84 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.14 (q, J = 5.2 Hz, 1H), 1.04 (td, J = 8, 5.2 Hz, 1H), 1.34–1.44 (m, 1H), 1.65–1.76 (m, 1H), 2.38–2.45 (m, 2H), 2.46–2.57 (m, 2H), 3.44 (dd, J = 8.8, 11.6 Hz, 1H), 3.77 (dd, J = 5.6, 11.6 Hz, 1H), 5.28 (dd, J = 10, 10.8 Hz, 1H), 5.45 ppm (dt, J = 10.8, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.8, 14.5, 17.9, 21.6, 23.9, 63.2, 119.3, 126.0, 131.7 ppm; HRMS (ESI): *m/z*: calcd for $C_9H_{14}NO$: 152.1075 $[M+H]^+$; found: 152.1120.

(±)-*cis*-1-[(*Z*)-5-Aminopent-1-enyl]-2-hydroxymethylcyclopropane (8): $LiAlH_4$ (1.30 g, 34.2 mmol) was added to a solution of the nitrile **7** (1.0 g, 6.6 mmol) in THF (150 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min and then at room temperature for 1 h. Water was added to the solution until a white suspension formed. The solids were filtered off and the filtrate was dried ($MgSO_4$) and concentrated to yield a yellow oil (0.88 g, 86 %), which was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.34 (q, J = 5.2 Hz, 1H), 0.99 (td, J = 8.4, 5.2 Hz, 1H), 1.31–1.42 (m, 1H), 1.54–1.75 (m, 3H), 2.14–2.31 (m, 2H), 2.75 (t, J = 6.8 Hz, 2H), 3.37 (dd, J = 11.6, 9.6 Hz, 1H), 3.78 (dd, J = 11.6, 5.6 Hz, 1H), 5.12 (dd, J = 10.8, 9.2 Hz, 1H), 5.46 ppm (dt, J = 10.8, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 14.4, 21.4, 25.3, 32.4, 41.4, 63.3, 128.7, 130.5 ppm; HRMS (ESI): *m/z*: calcd for $C_9H_{18}NO$: 156.1388 $[M+H]^+$; found: 156.1457.

(±)-(*Z*)-*N*-(9*H*-Fluoren-9-ylmethoxycarbonyl)-*N*-(4-*tert*-butylbenzyl)-5-(*cis*-2-hydroxymethylcyclopropyl)pent-4-en-1-amine (9): A solution of the amine **8** (1.15 g, 7.4 mmol) and 4-*tert*-butylbenzaldehyde (1.2 g, 7.4 mmol) in toluene (50 mL) was heated under reflux in a Dean–Stark apparatus for 16 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in MeOH (40 mL), cooled to 0 °C, and $NaBH_4$ (1.6 g, 42.3 mmol) was added. The solution was stirred at ambient temperature for 1 h before being partitioned between CH_2Cl_2 (150 mL) and water (150 mL). The organic phase was dried ($MgSO_4$) and concentrated to give a crude product, which was used in the next step without further purification. The crude amine was dissolved in THF (30 mL) and a solution of aqueous Na_2SO_4 (1 N, 30 mL) was added. The mixture was then cooled to 0 °C and Fmoc-Cl (1.9 g, 7.3 mmol) was added. The stirred mixture was warmed to room temperature over a period of 1 h and was then partitioned between CH_2Cl_2 (200 mL) and water (200 mL). The organic layer was dried and concentrated to give a crude product, which was purified chromatographically (SiO_2; MeOH/CH_2Cl_2, 2:98) to afford **9** as a colorless oil (1.2 g, 26 % from **7**). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.35 (q, J = 5.2 Hz, 1H), 0.98 (td, J = 8.4, 4.8 Hz, 1H), 1.28–1.43 (m, 11H), 1.56–1.72 (m, 2H), 1.89–2.02 (m, 1H), 2.11–2.20 (m, 1H), 3.01 (t, J = 7.6 Hz, 1H), 3.20–3.40 (m, 1H), 3.44 (t, J = 9.6 Hz, 1H), 3.71–3.79 (m, 1H), 4.18–4.27 (m, 1H), 4.32–4.45 (m, 2H), 4.48 (d, J = 6.0 Hz, 1H), 4.59 (d, J = 6.0 Hz, 1H), 5.03–5.15 (m, 1H), 5.24–5.33 (m, 0.5H), 5.39–5.47 (m, 0.5H), 7.01 (d, J = 7.6 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.28–7.36 (m, 3H), 7.36–7.41 (m, 2H), 7.45 (d, J = 7.2 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.71 (d, J = 7.2 Hz, 1H), 7.75 ppm (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 12.7, 14.4, 14.4, 21.1, 21.2, 25.0, 27.7, 28.0, 31.6, 34.7, 46.1, 46.6, 47.5, 47.6, 49.6, 50.2, 63.4, 63.5, 66.8, 67.3, 119.5, 124.3, 124.5, 125.0, 126.4, 126.5, 126.9, 127.1, 128.2, 128.4, 130.0, 134.0, 134.1, 140.7,

140.9, 143.4, 143.5, 149.5, 155.6 ppm; HRMS (ESI): *m/z*: calcd for $C_{35}H_{42}NO_3$: 524.3165 $[M+H]^+$: found: 524.3132.

(±)-(*Z*)-*N*-(9*H*-Fluoren-9-ylmethoxycarbonyl)-*N*-(4-*tert*-butylbenzyl)-5-(*cis*-2-formylcyclopropyl)pent-4-en-1-amine (10): A mixture of alcohol **9** (160 mg, 0.3 mmol), NaOAc (20 mg, 0.24 mmol), and PCC (200 mg, 0.93 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 3 h before being filtered and partitioned between CH_2Cl_2 (30 mL) and water (30 mL). The organic layer was dried ($MgSO_4$) and concentrated to give a crude product that was purified chromatographically (SiO_2; MeOH/CH_2Cl_2, 1:99) to afford **10** as a colorless oil (130 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.26$–1.42 (m, 12H), 1.55–1.67 (m, 1H), 1.83–1.95 (m, 1H), 2.02–2.29 (m, 3H), 2.96 (t, $J=7.2$ Hz, 1H), 3.21–3.32 (m, 1H), 4.18–4.27 (m, 1H), 4.35–4.42 (m, 2H), 4.47 (d, $J=6.8$ Hz, 1H), 4.60 (d, $J=5.6$ Hz, 1H), 5.22–5.34 (m, 1.5H), 5.42–5.50 (m, 0.5H), 7.01 (d, $J=8.0$ Hz, 1H), 7.09 (d, $J=8.0$ Hz, 1H), 7.20–7.24 (m, 1H), 7.27–7.41 (m, 5H), 7.44 (d, $J=7.2$ Hz, 1H), 7.59 (d, $J=7.2$ Hz, 1H), 7.69–7.77 (m, 2H), 9.25 ppm (d, $J=3.6$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=15.8$, 22.0, 25.2, 25.3, 27.6, 27.8, 30.4, 31.7, 34.7, 46.1, 46.9, 47.5, 47.7, 49.8, 50.2, 66.7, 67.3, 119.6, 124.3, 124.5, 125.0, 125.1, 125.7, 126.4, 126.6, 127.0, 127.2, 131.8, 131.9, 134.1, 140.8, 140.9, 143.4, 143.5, 149.6, 155.6, 155.9, 199.8, 199.9 ppm; HRMS (ESI): *m/z*: calcd for $C_{35}H_{40}NO_3$: 522.3008 $[M+H]^+$; found: 522.3028.

(±)-(*Z*)-*N*-(4-*tert*-Butylbenzyl)-5-(*cis*-2-ethenylcyclopropyl)pent-4-en-1-amine (11): NaHMDS (2 M in THF, 1.2 mL, 2.4 mmol) was added to a solution of methyltriphenylphosphonium bromide (700 mg, 2.5 mmol) in THF (150 mL) at −78 °C. The mixture was stirred for 10 min and a solution of the aldehyde **10** (400 mg, 0.77 mmol) in THF (15 mL) was added. The mixture was then stirred at 0 °C for 3 h before being poured into petroleum ether (300 mL) to precipitate triphenylphosphine oxide. After filtration, the organic solvent was evaporated and the residue purified chromatographically (SiO_2; MeOH/CH_2Cl_2, 0→2%) to give **11** as a colorless oil (93 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.54$ (q, $J=5.6$ Hz, 1H), 1.13 (td, $J=8.0$, 5.6 Hz, 1H), 1.30 (s, 9H), 1.58–1.86 (m, 4H), 2.18 (q, $J=7.2$ Hz, 2H), 2.67 (t, $J=7.2$ Hz, 2H), 3.75 (s, 2H), 4.97 (dd, $J=10.4$, 2 Hz, 1H), 5.02–5.13 (m, 2H), 5.41 (dt, $J=10.8$, 7.2 Hz, 1H), 5.47–5.58 (m, 1H), 7.25 (d, $J=8.4$ Hz, 2H), 7.33 ppm (d, $J=8.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=15.2$, 17.6, 22.8, 25.7, 29.8, 31.7, 34.8, 48.9, 53.5, 114.1, 125.0, 127.7, 128.8, 129.7, 135.9, 137.5, 149.5 ppm; HRMS (ESI): *m/z*: calcd for $C_{21}H_{32}N$: 298.2535 $[M+H]^+$; found: 298.2513.

(±)-(*Z*)-*N*-(4-*tert*-Butylbenzyl)-5-(*cis*-2-ethenylcyclopropyl)pent-4-en-1-ammonium hexafluorophosphate (1-H·PF$_6$): HCl (1 N, 1 mL) was added to a solution of the amine **11** (30 mg, 0.10 mmol) in CH_3CN (1 mL). The organic solvent was evaporated and the white precipitate was filtered off, dissolved in CH_3CN (1 mL), and treated with a solution of saturated aqueous NH_4PF_6 (2 mL). The organic solvent was evaporated and the precipitate collected to afford **1**-H·PF_6 as a white solid (33 mg, 74%). M.p. >175 °C decomp; ^{1}H NMR (400 MHz, CD_3CN): $\delta=0.59$ (q, $J=5.2$ Hz, 1H), 1.16 (td, $J=8.4$, 4.8 Hz, 1H), 1.32 (s, 9H), 1.66–1.89 (m, 4H), 2.15–2.24 (br, 2H), 3.02 (t, $J=7.6$ Hz, 2H), 4.11 (s, 2H), 4.97 (dd, $J=10.4$, 2.0 Hz, 1H), 5.09–5.20 (m, 2H), 5.39 (dt, $J=10.4$, 7.2 Hz, 1H), 5.50–5.60 (m, 1H), 7.37 (d, $J=8.4$ Hz, 2H), 7.50 ppm (d, $J=8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN): $\delta=15.2$, 17.9, 23.3, 24.8, 26.4, 31.2, 35.2, 48.2, 51.8, 114.2, 126.1, 127.7, 128.0, 129.9, 130.8, 138.3, 152.8 ppm; HRMS (ESI): *m/z*: calcd for $C_{21}H_{32}N$: 298.2529 [**1**-H]$^+$; found: 298.2542.

[2]Rotaxane 14-H·PF$_6$: A solution of the macrocycle **12** (45.4 mg, 0.1 mmol) and the threadlike salt **1**-H·PF_6 (44.4 mg, 0.1 mmol) in CH_3NO_2 (1.00 mL) was heated at 45 °C for 3 d. The yellow solution was concentrated to give a yellow residue that was purified chromatographically (SiO_2; hexane/EtOAc/MeOH, 10:10:0 then 10:10:1) to afford **14**-H·PF_6 as a white solid (55.0 mg, 61%). M.p. 173–175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.23$–0.31 (m, 2H), 0.54–0.72 (m, 4H), 1.26 (s, 9H), 1.80–2.01 (m, 1H), 2.10–2.20 (m, 4H), 2.70–2.83 (m, 1H), 2.92–3.05 (m, 1H), 4.38 (d, $J=9.6$ Hz, 2H), 4.44 (dd, $J=9.6$, 3.1 Hz, 2H), 4.54 (d, $J=11.6$ Hz, 2H), 4.64 (d, $J=11.6$ Hz, 2H), 5.23 (s, 4H), 5.35–5.46 (m, 1H), 5.62–5.73 (m, 3H), 6.81 (d, $J=8.3$ Hz, 2H), 6.83–6.92 (m, 4H), 7.09–7.20 (m, 6H), 7.24 (d, $J=8.3$ Hz, 2H), 7.39 (s, 4H), 7.60 ppm (t, $J=7.7$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=23.3$, 28.8, 31.2, 32.1, 32.5, 34.6, 36.8, 47.1, 50.4, 67.8, 73.9, 74.0, 115.8, 116.7, 122.1, 125.6, 127.2, 127.7, 128.1, 128.2, 128.3, 128.5, 129.1, 131.2, 134.7, 136.7, 138.1, 152.1, 155.3, 157.7 ppm {one extra aromatic signal appeared, presumably because of the existence of [C−H···π] and/or [$^+$N−H···π] interactions between the macrocycle's phenol rings and the $CH_2NH_2^+CH_2$ center under these conditions, thereby slowing the flipping of the phenol rings (see ref. [14]); when the interlocked macrocycle was DB24C8 (i.e., in **18**-H·PF_6), no additional aromatic signal was observed}; HRMS (ESI): *m/z*: calcd for $C_{50}H_{59}N_2O_4$: 751.4475 [**14**-H]$^+$; found: 751.4433.

[2]Rotaxane 15-H·PF$_6$: PtO_2 (1 mg, 4 μmol) was added to a solution of **14**-H·PF_6 (30 mg, 33.4 μmol) in THF (2 mL) and the mixture was stirred under a H_2 atmosphere for 30 min. After filtration, the organic solvent was evaporated and the residue was purified chromatographically (SiO_2; CH_2Cl_2/MeOH, 98:2) to afford **15**-H·PF_6 as a white solid (22.7 mg, 75%). M.p. 93–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta=0.19$–0.29 (m, 2H), 0.39–0.42 (m, 2H), 0.61–0.72 (m, 2H), 1.02–1.08 (m, 6H), 1.28 (s, 9H), 1.33–1.65 (m, 7H), 2.16–2.19 (m, 2H), 4.39 (d, $J=9.2$ Hz, 2H), 4.44 (d, $J=9.2$ Hz, 2H), 4.56 (d, $J=11.6$ Hz, 2H), 4.65 (d, $J=11.6$ Hz, 2H), 5.25 (s, 4H), 6.82 (d, $J=8.0$ Hz, 2H), 6.88–6.92 (m, 4H), 7.11–7.14 (m, 6H), 7.24 (d, $J=8.8$ Hz, 2H), 7.39 (s, 4H), 7.61 ppm (t, $J=7.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta=23.7$, 26.3, 28.5, 31.3, 34.1, 34.5, 34.7, 39.0, 47.3, 50.5, 67.8, 74.0, 74.1, 115.6, 116.6, 122.0, 125.5, 127.1, 127.6, 127.9, 128.2, 131.1, 136.6, 137.9, 151.9, 155.1, 157.5 ppm {one extra aromatic signal appeared, presumably because of the existence of [C−H···π] and/or [$^+$N−H···π] interactions between the macrocycle's phenol rings and the $CH_2NH_2^+CH_2$ center under these conditions, thereby slowing the flipping of the phenol rings (see ref. [14]); when the interlocked macrocycle was DB24C8 (i.e., in **19**-H·PF_6), no additional aromatic signal was observed}; HRMS (ESI): *m/z*: calcd for $C_{50}H_{63}N_2O_4$: 755.4788 [**15**-H]$^+$; found: 755.4773.

[2]Rotaxane 16-H·PF$_6$: A solution of **1**-H·PF_6 (30 mg, 0.07 mmol) and the macrocycle **13** (29 mg, 0.07 mmol) in CH_3NO_2 (1 mL) was stirred at 50 °C for 48 h. After evaporation of the solvent, the residue was purified chromatographically (SiO_2; MeOH/CH_2Cl_2, 0→1%) and the desired [2]rotaxane **16**-H·PF_6 was isolated as a white solid (51 mg, 86%). M.p. >210 °C decomp; ^{1}H NMR (400 MHz, CD_3NO_2): $\delta=-0.08$ to +0.06 (m, 2H), 0.49–0.67 (m, 2H), 0.88–1.01 (m, 2H), 1.35 (s, 9H), 2.06–2.17 (m, 1H), 2.24–2.38 (m, 2H), 2.62–2.68 (m, 2H), 2.76–2.87 (m, 1H), 2.95–3.12 (m, 3H), 3.32–3.41 (m, 2H), 3.50–3.60 (m, 2H), 3.60–3.69 (m, 2H), 4.38 (d, $J=9.2$ Hz, 2H; another doublet (2H) overlapped with the solvent peak), 5.26–5.38 (m, 4H), 5.56–5.63 (m, 1H), 5.68–5.83 (m, 3H), 6.85 (br, 2H), 7.00–7.06 (m, 2H), 7.08–7.15 (m, 2H), 7.18–7.31 (m, 6H), 7.41 (s, 4H), 7.59 ppm (d, $J=8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CD_3NO_2): $\delta=$ 25.5, 30.2, 32.0, 33.6, 34.1, 36.1, 38.7, 48.4, 52.5, 69.1, 71.0, 71.6, 75.0, 116.5, 117.4, 117.9, 127.0, 128.2, 128.8, 129.1, 129.7, 130.5, 130.6, 132.1, 132.4, 136.3, 138.2, 154.2, 158.7 ppm {two extra aromatic signals appeared, presumably because of the existence of [C−H···π] and/or [$^+$N−H···π] interactions between the macrocycle's phenol rings and the $CH_2NH_2^+CH_2$ center under these conditions, thereby slowing the flipping of the phenol rings (see ref. [14]); when the interlocked macrocycle was DB24C8 (i.e., in **18**-H·PF_6), no additional aromatic signal was observed}; HRMS (ESI): *m/z*: calcd for $C_{47}H_{60}NO_5$: 718.4471 [**16**-H]$^+$; found: 718.4465.

[2]Rotaxane 17-H·PF$_6$: PtO_2 (1 mg, 4 μmol) was added to a solution of **16**-H·PF_6 (20 mg, 23 μmol) in THF (0.5 mL) and the mixture stirred under a H_2 atmosphere for 30 min. After filtration, the organic solvent was evaporated and the residue purified chromatographically (SiO_2; MeOH/CH_2Cl_2, 1:99) to afford the [2]rotaxane **17**-H·PF_6 as a white solid (17 mg, 85%). M.p. 291–293 °C; ^{1}H NMR (400 MHz, CD_3NO_2): $\delta=-0.09$ to +0.02 (m, 2H), 0.36–0.44 (m, 2H), 0.82–0.95 (m, 2H), 1.16–1.27 (m, 2H), 1.34 (s, 9H), 1.41–1.75 (m, 11H), 2.62–2.67 (m, 2H), 3.01–3.09 (m, 2H), 3.32–3.39 (m, 2H), 3.52–3.59 (m, 2H), 3.61–3.68 (m, 2H), 4.39 (d, $J=9.6$ Hz, 2H; another doublet (2H) was covered by the solvent peak), 5.26–5.38 (m, 4H), 6.83 (br, 2H), 6.99–7.05 (m, 2H), 7.08–7.14 (m, 2H), 7.18–7.26 (m, 6H), 7.41 (s, 4H), 7.58 ppm (d, $J=8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CD_3NO_2): $\delta=25.7$, 27.8, 30.3, 32.0, 35.3, 36.0, 36.1, 40.8, 48.6, 52.5, 69.1, 71.0, 71.6, 75.0, 117.4, 117.8, 127.0, 128.7, 128.8, 130.5, 130.6, 132.0, 132.4, 138.2, 154.2, 158.7 ppm {two extra aromatic signals appeared, presumably because of the existence of [C−H···π] and/or [$^+$N−H···π] in-

teractions between the macrocycle's phenol rings and the $CH_2NH_2^+CH_2$ center under these conditions, thereby slowing the flipping of the phenol rings (see ref. [14]); when the interlocked macrocycle was DB24C8 (i.e., in **19**-H·PF_6), no additional aromatic signal was observed]; HRMS (ESI): *m/z*: calcd for $C_{47}H_{64}NO_5$: 722.4784 [**17**-H]$^+$; found: 722.4752.

[2]Rotaxane 18-H·PF_6: A solution of **1**-H·PF_6 (10 mg, 23 μmol) and DB24C8 (10.1 mg, 23 μmol) in $CHCl_3$ (0.5 mL) was stirred at 50 °C for 48 h. After evaporation of the solvent, the residue was purified chromatographically (SiO_2; MeOH/CH_2Cl_2, 1:99) to yield the [2]rotaxane **18**-H·PF_6 as a sticky colorless liquid (15 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86–1.06 (m, 2H), 1.26 (s, 9H), 1.32–1.42 (m, 2H), 1.73–1.93 (m, 2H), 2.10–2.21 (m, 1H), 2.56–2.67 (m, 1H), 2.80–2.91 (m, 1H), 3.07–3.20 (m, 2H), 3.33–3.49 (m, 4H), 3.56–3.68 (m, 4H), 3.75–3.88 (m, 8H), 4.03–4.15 (m, 4H), 4.17–4.30 (m, 4H), 4.49–4.59 (m, 2H), 5.14–5.21 (m, 1H), 5.48–5.60 (m, 3H), 6.81–6.97 (m, 8H), 7.14 (br, 2H), 7.27 (d, J = 8 Hz, 2H), 7.33 ppm (d, J = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 28.7, 31.6, 32.7, 32.9, 35.0, 36.6, 49.1, 52.1, 68.3, 70.2, 70.7, 112.5, 121.5, 125.2, 127.8, 127.9, 128.7, 128.8, 129.1, 134.5, 146.9, 152.0 ppm; HRMS (ESI): *m/z*: calcd for $C_{45}H_{64}NO_8$: 746.4631 [**18**-H]$^+$; found: 746.4634.

[2]Rotaxane 19-H·PF_6: PtO_2 (1 mg, 4 μmol) was added to a solution of **18**-H·PF_6 (20 mg, 22 μmol) in THF (0.5 mL) and the mixture stirred under a H_2 atmosphere for 30 min. After filtration, the organic solvent was evaporated and the residue purified chromatographically (SiO_2; MeOH/CH_2Cl_2, 1:99) to afford the [2]rotaxane **19**-H·PF_6 as a sticky colorless liquid (17 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77–0.92 (m, 2H), 1.04–1.54 (m, 24H), 3.03–3.14 (m, 2H), 3.38–3.46 (m, 4H), 3.58–3.66 (m, 4H), 3.77–3.90 (m, 8H), 4.07–4.15 (m, 4H), 4.20–4.28 (m, 4H), 4.53–4.59 (m, 2H), 6.83–6.76 (m, 8H), 7.15 (br, 2H), 7.30 (d, J = 8 Hz, 2H), 7.36 ppm (d, J = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 26.5, 28.7, 31.6, 34.4, 34.8, 35.0, 38.6, 49.4, 52.1, 68.3, 70.2, 70.7, 112.5, 121.5, 125.2, 128.9, 129.1, 146.9, 152.0 ppm; HRMS (FAB): *m/z*: calcd for $C_{45}H_{68}NO_8$: 750.4945 [**19**-H]$^+$; found: 750.4955.

(1*R*,2*R*)-*cis*-1-Butyryloxymethyl-2-[(*Z*)-6-cyanohex-1-enyl]cyclopropane (22): NaHMDS (2 M in THF, 41 mL, 82 mmol) was added to a solution of (5-cyanopentyl)triphenylphosphonium hexafluorophosphate (41.3 g, 82 mmol) in THF (400 mL) at 0 °C. The mixture was stirred for 10 min and then a solution of the optically pure aldehyde **4** (10.8 g, 63.5 mmol) in THF (55 mL) was added. After stirring at 0 °C for 3 h, petroleum ether (500 mL) was added to the mixture. The resulting precipitate was filtered off, the filtrate concentrated, and the residue purified chromatographically (SiO_2; hexane/EtOAc, 7:3) to afford the alkene **22** as a yellow oil (13.0 g, 82 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.39 (q, J = 5.3 Hz, 1H), 0.94 (t, J = 7.4 Hz, 3H), 1.04 (td, J = 8.3, 5.3 Hz, 1H), 1.35–1.40 (m, 1H), 1.52–1.71 (m, 7H), 2.16–2.23 (m, 2H), 2.28 (t, J = 7.4 Hz, 2H), 2.35 (t, J = 7.2 Hz, 2H), 3.95 (dd, J = 11.6, 8.0 Hz, 1H), 4.14 (dd, J = 11.6, 7.0 Hz, 1H), 5.08 (t, J = 10.0 Hz, 1H), 5.39 ppm (dt, J = 10.0, 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.4, 13.7, 14.3, 16.8, 17.1, 18.5, 24.9, 26.7, 28.5, 36.2, 64.9, 119.5, 128.5, 130.1, 173.5 ppm; HRMS (ESI): *m/z*: calcd for $C_{15}H_{23}NaNO_2$: 272.1627 [*M*+Na]$^+$; found: 272.1601.

(1*R*,2*R*)-*cis*-1-[(*Z*)-6-Cyanohex-1-enyl]-2-hydroxymethylcyclopropane (23): A mixture of alkene **22** (15.3 g, 61.4 mmol) and K_2CO_3 (25.3 g, 183 mmol) was stirred in MeOH (70 mL) at room temperature for 30 min and then partitioned between CH_2Cl_2 (300 mL) and H_2O (200 mL). The organic layer was dried ($MgSO_4$) and concentrated to give **23** as a colorless oil (10.0 g, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.39 (q, J = 5.3 Hz, 1H), 1.03 (td, J = 8.3, 5.3 Hz, 1H), 1.36–1.42 (m, 1H), 1.51–1.61 (m, 2H), 1.64–1.74 (m, 3H), 2.19–2.26 (m, 2H), 2.36 (t, J = 7.0 Hz, 2H), 3.46 (dd, J = 11.4, 9.0 Hz, 1H), 3.77 (dd, J = 11.4, 6.8 Hz, 1H), 5.14 (t, J = 10.3 Hz, 1H), 5.43 ppm (dt, J = 10.3, 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.2, 13.9, 16.9, 20.5, 24.7, 26.5, 28.3, 63.0, 119.5, 128.8, 129.7 ppm; HRMS (ESI): *m/z*: calcd for $C_{11}H_{17}NaNO$: 202.1208 [*M*+Na]$^+$; found: 202.1201.

(1*R*,2*R*)-*cis*-1-[(*Z*)-6-Cyanohex-1-enyl]-2-formylcyclopropane (24): A solution of alcohol **23** (10.0 g, 55.8 mmol) in CH_2Cl_2 (20 mL) was added to a mixture of PCC (28.4 g, 132 mmol), NaOAc (3.24 g, 39.5 mmol), and 4 Å molecular sieves (10.0 g) in CH_2Cl_2 (140 mL) and the mixture was stirred at room temperature for 2 h. After adding Celite (10.0 g) and diethyl ether (100 mL), the mixture was filtered through a pad of SiO_2. The filtrate was then concentrated and purified chromatographically (SiO_2; hexane/EtOAc, 7:3) to afford **24** as a colorless oil (6.7 g, 68 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42–1.46 (m, 2H), 1.53–1.60 (m, 2H), 1.63–1.69 (m, 2H), 2.10–2.27 (m, 4H), 2.34 (t, J = 7.0 Hz, 2H), 5.35 (t, J = 9.5 Hz, 1H), 5.48 (dt, J = 11.4, 7.0 Hz, 1H), 9.28 ppm (d, J = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.5, 17.2, 21.6, 24.9, 26.8, 28.3, 30.2, 119.5, 126.4, 131.9, 200.4 ppm; HRMS (ESI): *m/z*: calcd for $C_{11}H_{15}NaNO$: 200.1051 [*M*+Na]$^+$; found: 200.1021.

(1*S*,2*R*)-*cis*-1-[(*Z*)-6-Cyanohex-1-enyl]-2-ethenylcyclopropane (25): A mixture of NaHMDS (2 M in THF, 13.6 mL, 27 mmol) and methyltriphenylphosphonium bromide (9.8 g, 27 mmol) in THF (135 mL) was stirred at room temperature for 10 min and then cooled to −78 °C. A solution of aldehyde **24** (2.7 g, 15.2 mmol) in THF (16.2 mL) was added and the resulting mixture was stirred at −78 °C for 30 min before being poured into petroleum ether (300 mL) and filtered. The filtrate was concentrated and the residue purified chromatographically (SiO_2; hexane/EtOAc, 9:1) to afford **25** as a yellow oil (2.0 g, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.57 (q, J = 5.3 Hz, 1H), 1.16 (td, J = 8.2, 5.3 Hz, 1H), 1.51–1.59 (m, 2H), 1.65–1.81 (m, 4H), 2.19 (q, J = 7.3 Hz, 2H), 2.34 (t, J = 7.0 Hz, 2H), 4.99 (dd, J = 10.4, 2 Hz, 1H), 5.07–5.14 (m, 2H), 5.39 (dd, J = 11.0, 7.3 Hz, 1H), 5.48–5.57 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9, 17.1, 17.2, 22.5, 24.9, 26.6, 28.5, 114.4, 119.6, 129.2, 129.6, 137.7 ppm; HRMS (ESI): *m/z*: calcd for $C_{12}H_{17}NaN$: 198.1259 [*M*+Na]$^+$; found: 198.1226.

(1*R*,2*S*)-*cis*-1-Ethenyl-2-[(*Z*)-6-oxohex-1-enyl]cyclopropane (26): Diisobutylaluminum hydride (1.2 M in toluene, 6.6 mL, 7.9 mmol) was added to a solution of nitrile **25** (0.7 g, 4.0 mmol) in CH_2Cl_2 (41 mL) at −78 °C. After stirring at −78 °C for 30 min, HCl (1 N, 8 mL) was added and the mixture was slowly warmed to room temperature and partitioned between CH_2Cl_2 (30 mL) and H_2O (10 mL). The organic layer was washed with water (2×10 mL), dried ($MgSO_4$), and concentrated. The residue was purified chromatographically (SiO_2; hexane/EtOAc, 95:5) to afford **26** as a colorless oil (0.5 g, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.56 (q, J = 5.6 Hz, 1H), 1.15 (td, J = 8.3, 5.6 Hz, 1H), 1.37–1.46 (m, 2H), 1.60–1.83 (m, 4H), 2.16 (q, J = 7.3, 2H), 2.43 (t, J = 7.3, 2H), 4.98 (d, J = 8.8 Hz, 1H), 5.04–5.12 (m, 2H), 5.40 (dt, J = 10.9, 7.3 Hz, 1H), 5.48–5.57 (m, 1H), 9.74 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9, 17.3, 21.7, 22.5, 27.3, 29.1, 43.8, 114.3, 129.0, 129.9, 137.8, 202.5 ppm; HRMS (ESI): *m/z*: calcd for $C_{12}H_{18}NaO$: 201.1256 [*M*+Na]$^+$; found: 201.1234.

(1*S*,2*R*)-*cis*-1-[(*Z*)-7-Aminohept-1-enyl]-2-ethenylcyclopropane (27): $LiAlH_4$ (0.9 g, 23.7 mmol) was added in small portions to a solution of nitrile **25** (0.9 g, 5.1 mmol) in THF (100 mL) at 0 °C. The mixture was stirred at 0 °C for 5 h and then THF (50 mL), water (2 mL), and $MgSO_4$ (5 g) were sequentially added. The suspension was filtered and the filtrate was concentrated to afford **27** as a yellow oil (0.6 g, 65 %), which was used directly in the next reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.55 (q, J = 5.5 Hz, 1H), 1.14 (td, J = 8.2, 5.5 Hz, 1H), 1.29–1.47 (m, 6H), 1.69–1.72 (m, 1H), 1.77–1.83 (m, 1H), 2.13 (q, J = 6.7 Hz, 2H), 2.67 (t, J = 6.8 Hz, 2H), 4.98 (d, J = 9.2 Hz, 1H), 5.02–5.12 (m, 2H), 5.42 (dt, J = 10.4, 6.7 Hz, 1H), 5.49–5.58 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.8, 17.3, 22.4, 26.5, 27.6, 29.5, 33.8, 42.2, 114.1, 128.4, 130.6, 137.9 ppm; HRMS (ESI): *m/z*: calcd for $C_{12}H_{22}N$: 180.1752 [*M*+H]$^+$; found: 180.1719.

Bis[(*Z*)-7-((1*S*,2*R*)-2-ethenylcyclopropyl)hept-6-enyl]-ammonium hexafluorophosphate (20-H·PF_6): Aldehyde **26** (0.5 g, 2.8 mmol), amine **27** (0.6 g, 3.3 mmol), K_2CO_3 (210 mg, 1.5 mmol), and 4 Å molecular sieves (1 g) in CH_2Cl_2 (14.5 mL) were mixed at 0 °C and then stirred at room temperature for 16 h. The mixture was then filtered and the filtrate was concentrated. The residue was dissolved in MeOH (13 mL) at 0 °C and $NaBH_4$ (200 mg, 5.3 mmol) was added. The mixture was stirred at 0 °C for 4 h and was then partitioned between CH_2Cl_2 (30 mL) and water (10 mL). The organic layer was washed with water (2×10 mL), dried ($MgSO_4$), and concentrated. HCl (1 N, 2.9 mL) and an aqueous solution of saturated NH_4PF_6 (10 mL) were sequentially added to a solution of the crude amine (0.5 g, 1.4 mmol) in CH_3CN (10 mL). The organic solvent was evaporated under reduced pressure and the aqueous phase was then washed with CH_2Cl_2 (2×30 mL). The combined organic phases were dried ($MgSO_4$), concentrated, and purified chromatographically (SiO_2;

CH_2Cl_2/MeOH, 95:5) to afford **20**-H·PF_6 as a colorless oil (0.6 g, 44%). ^{1}H NMR (400 MHz, CD_3CN): δ = 0.57 (q, J = 5.5 Hz, 2H), 1.15 (td, J = 8.3, 5.5 Hz, 2H), 1.32–1.44 (m, 8H), 1.59–1.66 (m, 4H), 1.69–1.77 (m, 2H), 1.82–1.92 (m, 2H), 2.14–2.21 (m, 4H), 2.93 (t, J = 7.8 Hz, 4H), 4.96 (d, J = 10.2 Hz, 2H), 5.06–5.13 (m, 4H), 5.38–5.45 (m, 2H) , 5.51–5.64 ppm (m, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ = 15.3, 18.0, 23.2, 26.3, 26.4, 27.6, 29.5, 48.8, 113.9, 129.3, 130.4, 138.5 ppm; HRMS (ESI): m/z: calcd for $C_{24}H_{40}N$: 342.3161 [**20**-H]$^+$; found: 342.3131.

[2]Rotaxane 28-H·PF_6: A solution of **20**-H·PF_6 (50 mg, 0.1 mmol) and DB24C8 (91.8 mg, 0.2 mmol) in $CHCl_3$ (1.4 mL) was stirred at 45 °C for 70 h. After evaporating the solvent under reduced pressure, the residue was purified chromatographically (SiO_2; CH_2Cl_2/CH_3CN, 98:2) to give **28**-H·PF_6 as a white solid (65 mg, 68%). M.p. 113–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06–1.20 (m, 12H), 1.39–1.48 (m, 4H), 1.92–2.16 (m, 4H), 2.22–2.34 (m, 2H), 2.62–2.72 (m, 2H), 2.82–2.96 (m, 2H), 3.18–3.26 (m, 4H), 3.74 (s, 8H), 3.84–3.92 (m, 8H), 4.14–4.20 (m, 8H), 5.40–5.47 (m, 2H), 5.57–5.67 (m, 6H), 6.66–6.81 (br, 2H), 6.81–6.96 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.6, 26.7, 26.8, 28.4, 32.8, 35.9, 37.0, 48.6, 68.1, 70.5, 71.0, 112.6, 121.7, 127.3, 128.0, 129.5, 136.1, 147.2 ppm; HRMS (ESI): m/z: calcd for $C_{48}H_{72}NO_8$: 790.5258 [**28**-H]$^+$; found: 790.5226.

[2]Rotaxane 29-H·PF_6: PtO_2 (2 mg, 8 μmol) was added to a solution of **28**-H·PF_6 (62 mg, 66 μmol) in THF (2 mL) and the mixture was stirred under a H_2 atmosphere for 30 min. After filtration, the solvent was evaporated under reduced pressure and the residue purified chromatographically (SiO_2; CH_2Cl_2/MeOH, 98:2) to afford **29**-H·PF_6 as a white solid (49 mg, 79%). M.p. 148–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94–1.64 (m, 42H), 3.19–3.28 (m, 4H), 3.74 (s, 8H), 3.88–3.94 (m, 8H), 4.15–4.21 (m, 8H), 6.63–6.81 (br, 2H), 6.81–6.95 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.6, 26.7, 26.8, 26.9, 28.6, 34.6, 37.8, 39.1, 48.6, 68.0, 70.4, 71.0, 112.5, 121.6, 147.2 ppm; HRMS (ESI): m/z: calcd for $C_{48}H_{80}NO_8$: 798.5884 [**29**-H]$^+$; found: 798.5897.

[2]Rotaxane 30-H·PF_6: A solution of **20**-H·PF_6 (50 mg, 0.1 mmol) and the macrocycle **12** (93 mg, 0.2 mmol) in CH_3NO_2 (1.4 mL) was stirred at 45 °C for 62 h. After evaporating the solvent under reduced pressure, the residue was purified chromatographically (SiO_2; CH_2Cl_2/CH_3CN, 98:2) to afford **30**-H·PF_6 as a white solid (50 mg, 52%). M.p. 106–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.49–0.60 (m, 4H), 0.77–0.88 (m, 8H), 1.06–1.18 (m, 4H), 1.18–1.37 (m, 4H), 2.02–2.25 (m, 4H), 2.40–2.51 (m, 2H), 2.67–2.79 (m, 2H), 2.95–3.02 (m, 2H), 4.51 (s, 4H), 4.72 (s, 4H), 5.22 (s, 4H), 5.55–5.78 (m, 8H), 6.49–6.62 (br, 2H), 6.95 (d, J = 8.4 Hz, 4H), 7.16 (d, J = 8.4 Hz, 4H), 7.23 (d, J = 7.8 Hz, 2H), 7.32 (s, 4H), 7.72 ppm (t, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.9, 26.3, 26.8, 28.5, 32.9, 36.0, 37.1, 47.4, 67.8, 74.1, 74.2, 116.2, 122.4, 127.7, 127.8, 128.0, 128.3, 129.5, 130.9, 136.0, 136.4, 138.2, 155.4, 157.6 ppm; HRMS (ESI): m/z: calcd for $C_{53}H_{67}N_2O_4$: 795.5101 [**30**-H]$^+$; found: 795.5127.

[2]Rotaxane 31-H·PF_6: PtO_2 (1 mg, 4 μmol) was added to a solution of **30**-H·PF_6 (15 mg, 16 μmol) in THF (2 mL) and the mixture was stirred under a H_2 atmosphere for 30 min. After filtration, the solvent was evaporated under reduced pressure and the residue purified chromatographically (SiO_2; CH_2Cl_2/MeOH, 98:2) to afford **31**-H·PF_6 as a white solid (12 mg, 79%). M.p. 67–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.43–0.54 (m, 4H), 0.77–0.84 (m, 8H), 1.09–1.24 (m, 12H), 1.36–1.67 (m, 22H), 4.50 (s, 4H), 4.72 (s, 4H), 5.22 (s, 4H), 6.56 (br, 2H), 6.94 (d, J = 8.4 Hz, 4H), 7.15 (d, J = 8.4 Hz, 4H), 7.24 (d, J = 8.0 Hz, 2H), 7.32 (s, 4H), 7.71 ppm (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.0, 26.5, 26.7, 27.1, 28.6, 34.7, 38.1, 39.3, 47.5, 67.9, 74.2, 74.3, 116.2, 122.4, 127.8, 128.3, 130.9, 136.5, 138.2, 155.4, 157.6 ppm; HRMS (ESI): m/z: calcd for $C_{53}H_{75}N_2O_4$: 803.5727 [**31**-H]$^+$; found: 803.5711.

[2]Rotaxane 32-H·PF_6: A solution of **20**-H·PF_6 (50 mg, 0.1 mmol) and macrocycle **13** (86 mg, 0.2 mmol) in CH_3NO_2 (1.4 mL) was stirred at 45 °C for 84 h. After evaporating the solvent under reduced pressure, the residue was purified chromatographically (SiO_2; CH_2Cl_2/CH_3CN, 98:2) to afford **32**-H·PF_6 as a white solid (54 mg, 58%). M.p. 73–75 °C; ^{1}H NMR (400 MHz, CD_3NO_2): δ = 0.51–0.64 (m, 4H), 0.96–1.03 (m, 4H), 1.10–1.48 (m, 12H), 2.15–2.33 (m, 4H), 2.43–2.58 (m, 2H), 2.68–2.79 (m, 2H), 2.96–3.03 (m, 2H), 3.58–3.62 (m, 4H), 3.75–3.82 (m, 4H), 4.39 (s, 4H), 5.28 (s, 4H), 5.60–5.78 (m, 8H), 6.40–6.60 (br, 2H), 7.05 (d, J = 8.0 Hz, 4H), 7.26 (d, J = 8.0 Hz, 4H), 7.37 ppm (s, 4H); ^{13}C NMR (100 MHz, CD_3NO_2): δ = 27.6, 28.1, 29.6, 34.3, 37.4, 38.6, 48.9, 69.1, 71.6, 71.7, 75.0, 117.9, 129.1, 129.2, 129.6, 130.9, 131.2, 132.3, 137.9, 138.5, 159.2 ppm (one signal is missing, possibly because of signal overlap); HRMS (ESI): m/z: calcd for $C_{50}H_{68}NO_5$: 762.5097 [**32**-H]$^+$; found: 762.5055.

[2]Rotaxane 33-H·PF_6: PtO_2 (2 mg, 8 μmol) was added to a solution of **32**-H·PF_6 (54 mg, 59 μmol) in THF (2 mL) and the mixture was stirred under a H_2 atmosphere for 30 min. After filtration, the solvent was evaporated under reduced pressure and the residue was purified chromatographically (SiO_2; CH_2Cl_2/MeOH, 98:2) to afford **33**-H·PF_6 as a white solid (48 mg, 88%). M.p. 152–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.43–0.57 (m, 4H), 0.82–0.91 (m, 4H), 0.92–1.04 (m, 4H), 1.16–1.26 (m, 12H), 1.38–1.80 (m, 22H), 3.55–3.60 (m, 4H), 3.68–3.77 (m, 4H), 4.32 (s, 4H), 5.23 (s, 4H), 6.20–6.30 (br, 2H), 6.93 (d, J = 8.4 Hz, 4H), 7.12 (d, J = 8.4 Hz, 4H), 7.31 ppm (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.2, 26.4, 26.6, 27.1, 28.5, 34,7, 38.1, 39.2, 47.2, 67.8, 70.1, 73.9, 116.1, 127.6, 128.5, 130.5, 136.4, 157.4 ppm (one signal is missing, possibly because of signal overlap); HRMS (ESI): m/z: calcd for $C_{50}H_{76}NO_5$: 770.5723 [**33**-H]$^+$; found: 770.5712.

Acknowledgements

We thank the National Science Council (Taiwan) for financial support (NSC-98-2113M-002-004-MY3).

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[17] CCDC-760743 (**14**-H·PF_6) and 760744 (**29**-H·PF_6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Received: January 12, 2010
Published online: May 6, 2010

