Published in European Journal of Organic Chemistry, Vol. 2015, Issue 3, 2015, p. 479-485
which should be used for any reference to this work

Preparation of Pillar[5]arene-Based [2]Rotaxanes from Acyl Chlorides and Amines

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Dedicated to Professor Mir Wais Hosseini on the occasion of his 60th birthday

Keywords: Supramolecular chemistry / Inclusion complexes / Rotaxanes / Pillar[5]arenes / Amides

Pillar[5]arene-based [2]rotaxanes have been prepared from the reactions of diacyl chloride reagents with various amine stoppers. The yields of the [2]rotaxanes are sensitive to the reaction conditions (solvent and stoichiometry) as well as to structural and electronic factors. In particular, the nature of the starting amine reagent has a dramatic influence on the yields of [2]rotaxanes; thus, the reaction outcome is not simply related to the binding constant of the diacyl chloride reagent with the pillar[5]arene. Indeed, the differences in the yields must be related to the different affinities for the various monoacylated intermediates. The yields of the [2]rotaxanes are also influenced by several structural factors such as the chain length of the diacyl chloride reagent and the size of the peripheral substituents of the pillar[5]arene building block. Finally, the preparation of [2]rotaxanes from alkyldiamine reagents and acyl chloride stoppers has also been investigated.

Introduction

Pillar[*n*]arenes are recently discovered macrocyclic compounds and are readily available.[1,2] Their host–guest chemistry has already been intensively investigated.[2] Owing to the electron-rich nature of their constitutive aromatic subunits, pillar[5]arenes exhibit interesting host–guest properties with π-electron-poor aromatic guests such as viologen[3] and imidazolium cations.[4] Along with charge-transfer interactions between the electron-rich cavities of pillar[5]arenes and π-electron-poor guest molecules, C–H···π interactions are also a driving force in the formation of inclusion complexes.[2] Simple alkyl-substituted guests are efficiently encapsulated in the cavities of pillar[5]arenes to generate pseudorotaxanes.[5,6] Such host–guest complexes are perfectly suited for the synthesis of [2]rotaxanes.[7] Stoddart and co-workers were the first to report the synthesis of a pillar[5]arene-containing [2]rotaxane, which was prepared by the treatment of a mixture of 1,4-dimethoxypillar[5]arene and 1,8-diaminooctane with 3,5-di-*tert*-butylbenzaldehyde under reductive amination conditions.[8] However, the yield was rather low (7%) because of the low association constant between the axle and the pillar[5]arene in the solvent system used for the reaction. Following this first example, other [2]rotaxanes have been prepared through the installation of bulky stoppers through various reactions. Examples include esterification reactions and copper-catalyzed alkyne–azide cycloadditions.[8] The [2]rotaxanes have been obtained in fair to very good yields. As part of this research, we now show that pillar[5]arene-based [2]rotaxanes can be readily obtained under reaction conditions involving acyl chloride and amine reagents to generate amides. The yields of the [2]rotaxanes are very sensitive to the reaction conditions as well as to structural and electronic factors. These different aspects have been investigated in details to provide key information for the design of pillar[5]arene-based [2]rotaxanes.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201403380.

Results and Discussion

Commercially available diacyl chloride reagents, namely, dodecanedioyl chloride (**1a**) and sebacoyl chloride (**1b**), have been selected as starting materials for the preparation of [2]rotaxanes. Their ability to form host–guest complexes

with 1,4-diethoxypillar[5]arene (**2**) was first evidenced by NMR spectroscopy binding studies in $CDCl_3$ at 25 °C. Continuous upfield shifts were observed for all the signals of **1a** and **1b** upon successive additions of macrocycle **2** (Figures 1 and S1). The formation of inclusion complexes of **1a** and **1b** with **2** locates the alkyl chains of guests **1a** and **1b** within the cavity of the pillar[5]arene host. As a result, the protons of the guests are exposed to a strong shielding effect owing to the proximity of the aromatic subunits of the host, in full agreement with the proposed formation of pseudorotaxanes. It can also be noted that the binding studies with **1a** and **1b** are particularly delicate, as

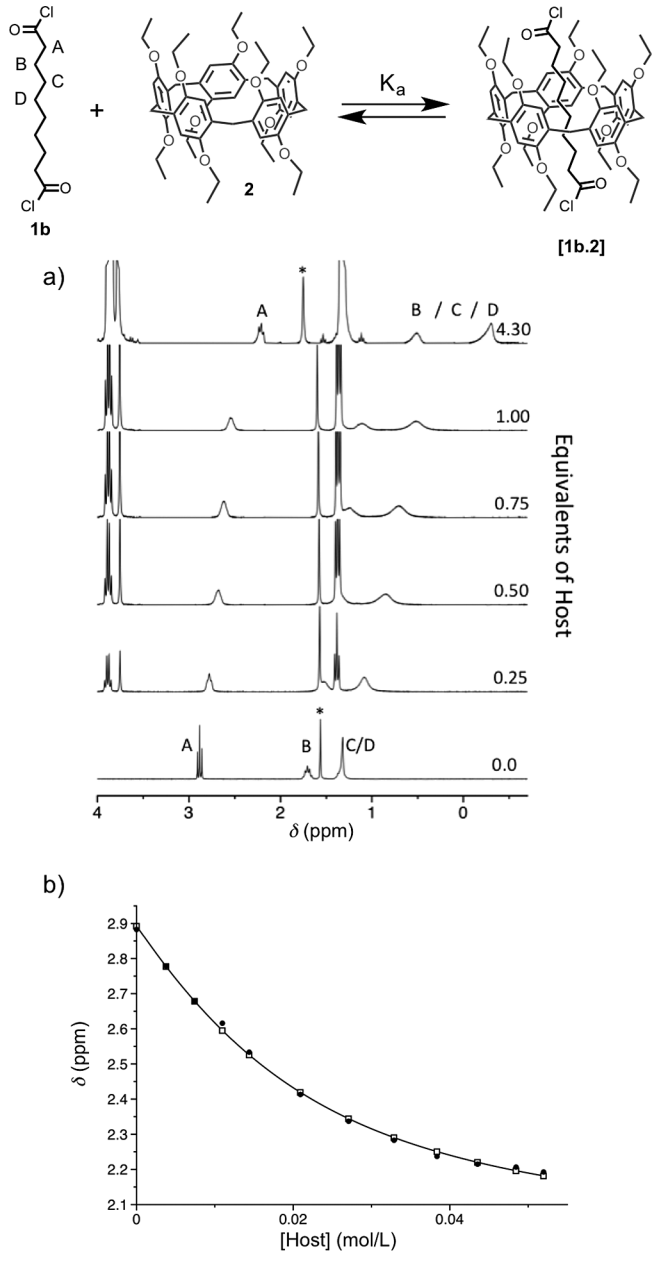
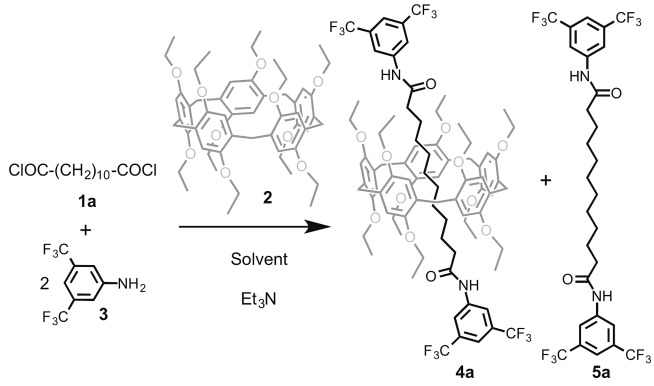


Figure 1. (a) ^{1}H NMR (300 MHz, $CDCl_3$, 298K) spectra recorded upon successive additions of **2** to a solution of **1b** (15 mM). (B) Chemical shift of H_A (calculated: □, experimental: ●) as a function of host concentration.

partial hydrolysis of the diacyl chloride reagents occurs during the experiments. This is clearly evidenced by the changes in chemical shift of the H_2O signal at the end of the titration because of the formation of HCl as well as by the apparition of minor peaks ascribed to the carboxylic acid derivatives that result from the hydrolysis of **1a** and **1b**. To limit this effect, the titration experiments were performed as quickly as possible. In this way, the hydrolysis products start to appear only at the very end of the experiments. The association constants (K_a) for the 1:1 complexes [**1a**–**2**] and [**1b**–**2**] were calculated on the basis of the complexation-induced changes in chemical shifts by using curve-fitting analysis (Figures 1 and S1). The $\log K_a$ values are 1.85(9) for **1a** and 1.87(5) for **1b**.

First, the reaction conditions for the preparation of [2]-rotaxanes from **1a**, **2**, and **3** were adjusted (Scheme 1, Table 1). The critical step is the threading of the diacyl chloride reagent, and the temperature and concentration conditions were adapted to favor the assembly of pseudorotaxane intermediates. For this reason, the reactions were systematically performed at low temperature (–15 °C) and at high concentration (0.14 to 0.40 M). The preparation of [2]rotaxane **4a** was attempted in different solvents (Table 1).



Scheme 1. Preparation of [2]rotaxane **4a** (see Table 1 for details).

Table 1. Isolated yields of [2]rotaxane **4a** and axle **5a** as a function of the solvent and the stoichiometry from the reaction of **1a** and **3** in the presence of **2** (see Scheme 1).

Entry	Solvent	**1a/2** ratio	Isolated yield [%]	
			4a	**5a**
1	CH_2Cl_2	1:2	–	62[a]
2	$ClCH_2CH_2Cl$	1:2	–	44[a]
3	pentane	1:2	1[a]	93[a]
4	tetrahydrofuran (THF)	1:2	6[a]	89[a]
5	toluene	1:2	10[a]	90[a]
6	$CHCl_3$	1:3	63[a]	33[a]
7	$CHCl_3$	1:2	45[a]	53[a]
8	$CHCl_3$	1:1	27[a] or [b]	70[a]
9	$CHCl_3$	2:1	18[b]	87[a]
10	$CHCl_3$	3:1	35[b]	87[a]

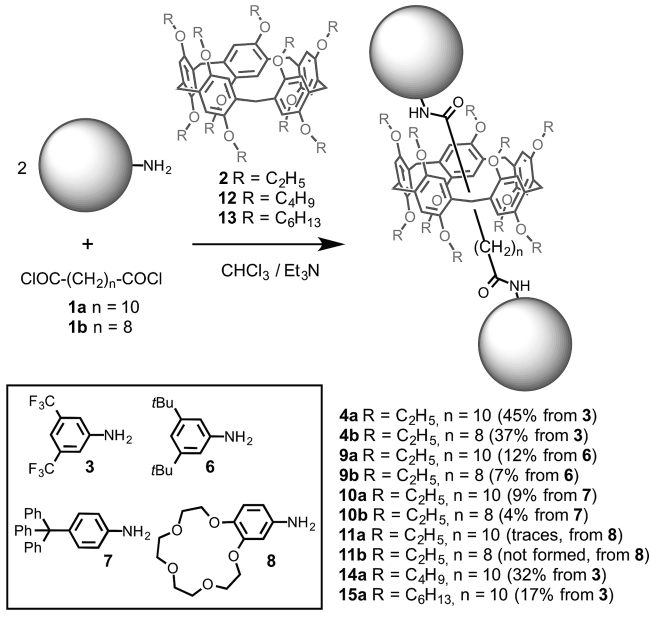
[a] Calculated from the starting amount of **1a**. [b] Calculated from the starting amount of **2**.

In all the cases, a solution of **1a** (1 equiv.), **2** (2 equiv.), **3** (2.5 equiv.), and Et_3N (3 equiv.) in the appropriate solvent was stirred for 1 h at –15 °C. The mixture was then allowed

to slowly warm to room temperature, and the solvents were evaporated. Purification by SiO_2 column chromatography followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) allowed us to isolate two products, namely, [2]rotaxane **4a** and axle **5a**, as well as unreacted pillar[5]arene **2**. The isolated yields of **4a** and **5a** are summarized in Table 1, Entries 1–5 and 7. The best results were obtained when the reaction was performed in $CHCl_3$ (Table 1, Entry 7). This solvent is unable to form inclusion complexes with macrocycle **2**, and there is no competition for the binding of the diacyl chloride reagent (**1a**) as for the other chlorinated solvents or pentane.[9] The effect of the stoichiometry on the yield of **4a** was also investigated. The results obtained by gradually changing the **1a/2** ratio from 3:1 to 1:3 are reported in Table 1, Entries 6–10. Compared with the yield of the reaction performed with an equimolar mixture of **1a** and **2**, increasing the amount of pillar[5]arene **2** clearly improved the yield of [2]rotaxane **4a**, as the formation of pseudorotaxanes is increasingly favorable (Table 1, Entries 6–8). A similar effect was also observed when the **1a/2** ratio was changed from 1:1 to 3:1 (Table 1, Entries 8–10). However, the effect is less pronounced in this case. A precipitate was observed during the course of the reactions with the 2:1 and 3:1 mixtures of **1a** and **2**. This partial precipitation may affect the equilibrium between threaded and unthreaded intermediates and, thus, influence the relative yields of **4a** and **5a**.

The reaction conditions used for the preparation of [2]rotaxane **4a** from amine **3** were then applied to amines **6**–**8** (Scheme 2). The same reactions were also performed with sebacoyl chloride (**1b**) as the diacyl chloride reagent. For all of these reactions, the initial host–guest ratio was the same (2:1). A compromise between the yield of [2]rotaxane and ease of purification prompted us to select this particular stoichiometry. However, it is clear that the yields of the [2]rotaxanes could be further improved by increasing the amount of pillar[5]arene, as for **4a** (see Table 1). The axles were also formed in these reactions but were not further characterized owing to their low solubility. Only the [2]rotaxanes were isolated and fully characterized (see Supporting Information).

Interestingly, the nature of the starting amine reagent has a dramatic influence on the yields of the [2]rotaxanes. The latter observation shows that the outcome of the reaction is not simply related to the binding constant of **1a** or **1b** with pillar[5]arene **2**. Indeed, the differences in yields must be related to the differences in the affinities of the various monoacylated intermediates for macrocycle **2**. This view is further supported by the fact that the best yields were obtained for aromatic amine **3**, which has electron-withdrawing groups. The electron-deficient aromatic ring may provide positive interactions with the electron-rich aromatic subunits of the pillar[5]arene and, thus, favor the formation of pseudorotaxanes. In contrast, pseudorotaxanes formed with monoacylated intermediates obtained from aromatic amines with slightly electron-donating substituents (**6** and **7**) are destabilized, and the yields of the [2]rotaxanes are lower. In the particular case of **8**, the stronger donating ability of the alkoxy groups almost completely prevents the formation of pseudorotaxane intermediates. Compound **11b** could not be detected, and [2]rotaxane **11a** formed in a very low yield. Pure **11a** was not isolated, and its presence was only confirmed by mass spectrometry.



Scheme 2. Preparation of [2]rotaxanes from **1a** and **1b**.

It is also interesting to note that the yields of the [2]rotaxane are influenced by the chain length of the starting diacyl chloride reagent (**1a** or **1b**); the yields are systematically higher when starting from the longer derivative (**1a**). As the affinities of **1a** and **1b** for pillar[5]arene **2** are similar (vide supra), this effect is likely related to steric factors that affect the kinetics of the reaction of the pseudorotaxane intermediates. As schematically shown in Figure 2, the relative yields of dumbbell **G** and [2]rotaxane **H** are exclusively related to the binding constant K'_a if the kinetics of the final acylations are the same for both monoacylated intermediates **E** and **F** ($k'_1 = k'_2$). However, if the reaction is slower for the pseudorotaxane intermediate **F** ($k'_1 > k'_2$) because of steric effects, intermediate **E** will be consumed faster. As a result, the equilibrium will be progressively displaced in favor of the unthreaded intermediate **E**; thus, the yield of dumbbell **G** will increase, and the yield of [2]rotaxane **H** will decrease.

To further investigate the influence of steric factors on the formation of [2]rotaxanes under our conditions, pillar[5]arene derivatives **12** and **13**, which are substituted with butyloxy and hexyloxy groups, respectively, were used as starting materials (Scheme 2). The reaction of diacyl chloride **1a** and amine **3** in the presence of pillar[5]arene **12** gave [2]rotaxane **14a** in 32% yield. Similarly, [2]rotaxane **15a** was obtained in 17% yield when the reaction was performed with the hexyloxy-substituted pillar[5]arene **13**. The size of the peripheral alkyl chains on both rims of the pillar[5]arene building blocks clearly affect the outcomes of these reactions, most likely because steric effects slow down the ki-

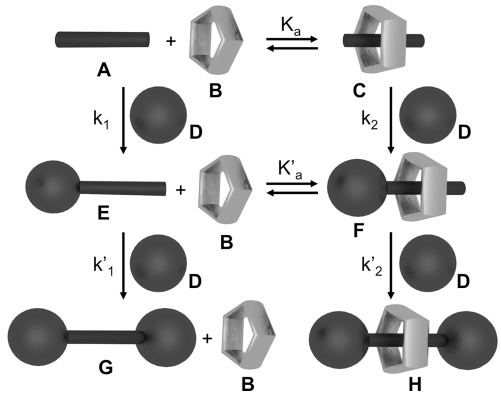
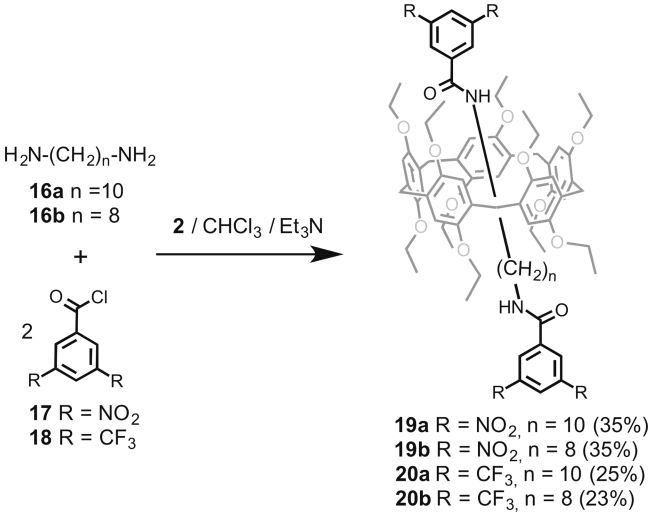


Figure 2. The relative yields of dumbbell (**G**) and [2]rotaxane (**H**) is related to both the binding constant K'_a and the difference in kinetics of the final acylation reactions involving the monoacylated intermediates **E** and **F** (k'_1 and k'_2).

netics of the acylation of the pseudorotaxane intermediate as size increases. In other words, the k'_1/k'_2 ratio (Figure 2) becomes less favorable for the formation of [2]rotaxanes as the size of the peripheral alkyl chains of the pillar[5]arene increase.

Finally, the preparation of [2]rotaxanes from alkyldiamine reagents **16a** and **16b** was also investigated (Scheme 3).



Scheme 3. Preparation of [2]rotaxanes from **16a** and **16b**.

The formation of host–guest complexes from pillar[5]arene derivatives and alkyldiamines is well established.[6] NMR spectroscopy binding studies with pillar[5]arene **2** in $CDCl_3$ provided log K_a values of 1.50(6) for **16a** and 1.45(7) for **16b**; these values are in good agreement with the data reported for related systems.[6] The treatment of **16a** and **16b** with 3,5-dinitrobenzoyl chloride (**17**) in the presence of pillar[5]arene **2** in $CHCl_3$ at –15 °C gave [2]rotaxanes **19a** and **19b**. [2]Rotaxanes **20a** and **20b** were obtained under similar conditions from 3,5-bis(trifluoromethyl)benzoyl chloride (**18**). The mechanically interlocked molecules **19a**, **19b**, **20a**, and **20b** were obtained in fair yields (23–35%). Unlike the yields of the [2]rotaxanes from **1a** and **1b**, the yields of the [2]rotaxanes from the alkyldiamines do not seem to be sensitive to the chain length of the starting alkyldiamine. However, the apparent absence of kinetic effects in this particular case is attributed to the limited solubility of **16a** in $CHCl_3$. Partial precipitations were observed for the reactions performed with **16a**, and this may also affect the formation of the pseudorotaxane intermediates. It is worth noting that the nature of the aromatic subunits of the stopper also plays a role in the outcome of the reactions. Here, the most electron-deficient aromatic stopper (**17**) again gave the best yields.

Conclusions

The couplings of acyl chlorides and amines to form amides have been used for the preparation of pillar[5]arene-containing [2]rotaxanes. All of the [2]rotaxanes have been obtained from the reactions of a difunctionalized reagent (**1a**, **1b**, **16a**, or **16b**) with complementary stoppers (**3**, **6**–**8**, and **17**–**18**), and the two stoppers were introduced in a single synthetic step. The stopper has a dramatic influence on the outcome of the reaction as it modulates the affinity of the monofunctionalized intermediate for the macrocyclic component. The best results were obtained when electron-deficient aromatic stoppers were introduced owing to their positive interactions with the electron-rich cavity of the pillar[5]arene receptor. The yield of the [2]rotaxane is also influenced by several structural factors such as the chain length of the diacyl chloride reagent or the size of the peripheral substituents of the pillar[5]arene building block. Indeed, these factors play a role in the relative kinetics of the final reactions between the stopper and the pseudorotaxane intermediate to form the [2]rotaxane and between the stopper and the unthreaded intermediate to form the dumbbell. In conclusion, the formation of pillar[5]arene-containing rotaxanes results from a combination of structural and electronic effects. The present study provides key design principles for the future preparation of more-elaborate [2]rotaxanes with additional functional subunits for various applications in the field of supramolecular chemistry.

Experimental Section

General: All reagents were used as purchased from commercial sources without further purification. Compounds **2**, **12**, and **13** were prepared according to previously reported procedures.[10] Evaporation and concentration were performed at water aspirator pressure, and drying was performed in vacuo at 10^{-2} Torr. Silica gel 60 (230–400 mesh, 0.040–0.063 mm) for column chromatography was purchased from Merck. Thin Layer Chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from Merck; visualization was achieved with UV light or $KMnO_4$ stain. NMR spectra were recorded with a Bruker AC 400 spectrometer with solvent peaks as reference. IR spectra were recorded with a Perkin–Elmer Spectrum One spectrometer. Elemental analyses were performed by the analytical service of the Chemistry Department of the University of Strasbourg (France). MALDI-TOF mass spectra were recorded by the analytical service of the School of Chemistry (Strasbourg, France).

Binding Studies: All of the ^{1}H NMR spectroscopy titration experiments were performed with a Bruker AC 300 spectrometer at 25(1) °C with samples in $CDCl_3$ (Sigma–Aldrich). The appropriate amount of pillar[5]arene **2** stock solution ($CDCl_3$, 230 mM) was added to 15 mM solutions of **1a**, **1b**, **16a**, and **16b** in $CDCl_3$. The association constants (K_a) of the complexes **2⊃1a**, **2⊃1b**, **2⊃16a**, and **2⊃16b** (Figure 1) were determined from the changes in the chemical shifts of the guests. The calculations were performed with the nonlinear least-squares regression analysis program HypNMR.[11]

Preparation of [2]Rotaxane 4a and Dumbbell 5a in Various Solvents: Dodecanedioyl dichloride (**1a**, 75 mg, 0.281 mmol), ethylpillar[5]arene **2** (0.50 g, 0.561 mmol), and triethylamine (88 mg, 0.842 mmol) were dissolved in the appropriate solvent (2 mL, see Tables 1 and 2). The mixture was stirred for 30 min at –15 °C, and 3,5-bis(trifluoromethyl)aniline (**3**, 161 mg, 0.702 mmol) was added. After 1 h, the reaction mixture was warmed to room temp., stirred overnight, and concentrated. Column chromatography (SiO_2, cyclohexane/Et_2O, 10:1) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave [2]rotaxane **4a** and the corresponding dumbbell **5a**. The isolated yields are indicated in Table 2.

Table 2. Isolated yields of [2]rotaxane **4a** and dumbbell **5a**.

Solvent	[2]Rotaxane **4a**	Dumbbell **5a**
CH_2Cl_2	–	114 mg (62%)
$ClCH_2CH_2Cl$	–	80 mg (44%)
Pentane	4 mg (1%)	170 mg (93%)
THF	26 mg (6%)	163 mg (89%)
Toluene	43 mg (10%)	165 mg (90%)
$CHCl_3$	195 mg (45%)	97 mg (53%)

Preparation of [2]Rotaxane 4a from Different 1a/2 Ratios: 3,5-Bis(trifluoromethyl)aniline (**3**, 2.5 equiv. relative to axle **1a**) was added to a solution of **1a**, **2** (see Tables 1 and 3), and Et_3N (3 equiv. relative to axle **1a**) in $CHCl_3$ (2 mL) at –15 °C. After 1 h, the mixture was warmed to room temp. and then stirred for 12 h, and the solvent was evaporated. The obtained solid was purified by silica gel chromatography (cyclohexane/Et_2O, 10:1) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2). The resulting products [2]rotaxane **4a** and dumbbell **5a** were obtained in various yields depending on the stoichiometry of **1a** and **2** (see Table 3).

Table 3. Isolated yields of [2]rotaxane **4a** and dumbbell **5a** depending on the stoichiometry of the starting materials **1a** and **2**.

Pillar[5]arene **2**	Axle **1a**	Yield [2]Rotaxane **4a**	Yield Dumbbell **5a**
Equiv. (mg; mmol)	Equiv. (mg; mmol)	mg (%)	mg (%)
1 (250; 0.281)	3 (225; 0.843)	152 (35)[a]	479 (87)[b]
1 (250; 0.281)	2 (150; 0.562)	78 (18)[a]	320 (87)[b]
1 (250; 0.281)	1 (75; 0.281)	117 (27)[a]	129 (70)[b]
2 (500; 0.561)	1 (75; 0.281)	195 (45)[b]	97 (53)[b]
3 (750; 0.842)	1 (75; 0.281)	273 (63)[b]	60 (33)[b]

[a] Calculated from the starting amount of pillar[5]arene **2**. [b] Calculated from the starting amount of **1a**.

General Procedure for the Preparation of [2]Rotaxanes from 1a and 1b: The appropriate amine stopper (**3**, **6**–**8**) was added to a solution of **1a** (75 mg, 0.281 mmol) or **1b** (67 mg, 0.281 mmol), pillar[5]arene **2** (0.50 g, 0.561 mmol), and Et_3N (87.6 mg, 0.842 mmol) in chloroform (2 ml) at –15 °C. The mixture was then slowly warmed to room temp. and concentrated. Purification by column chromatography (SiO_2, cyclohexane/Et_2O, 10:2) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) resulted in the isolation of the [2]rotaxanes (**9a**, **9b**, **10a**, **10b**, **11a**) as well as unreacted pillar[5]arene **2**.

[2]Rotaxane 4a and Dumbbell 5a: Compound **4a** was prepared from **1a**, **2**, and **3** (161 mg, 0.702 mmol) and obtained as a colorless glassy product (195 mg, 45%). IR (neat): $\tilde{\nu}$ = 1710 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 4 H), 7.59 (s, 2 H), 7.22 (s, 2 H), 6.90 (s, 10 H), 3.89 (m, 20 H), 3.75 (s, 10 H), 1.36 (t, J = 7 Hz, 30 H), 0.87 (m, 8 H), 0.53 (m, 4 H), 0.08 (m, 4 H), –0.14 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 149.7, 140.3, 132.1 (q, $^3J_{C,F}$ = 120 Hz), 128.7, 123.2 (q, $^2J_{C,F}$ = 1080 Hz), 118.6 (br), 116.4 (m), 114.8, 63.9, 36.4, 30.9, 29.6, 29.4, 29.2, 23.0, 15.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.96 ppm. MALDI-TOF MS: m/z = 1542.76 [M]$^+$. $C_{83}H_{98}F_{12}N_2O_{12}$·$Et_2O$ (1617.78): calcd. C 64.59, H 6.73, N 1.73; found C 64.84, H 6.51, N 1.97. The corresponding dumbbell **5a** was also isolated as a colorless solid (100 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 4 H), 7.59 (s, 2 H), 7.46 (br s, 2 H), 2.41 (t, J = 7 Hz, 4 H), 1.74 (m, 4 H), 1.31 (m, 12 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.07 ppm. MALDI-TOF MS: m/z = 653.09 [M]$^+$. ^{13}C NMR spectroscopy could not be performed owing to rapid gel formation from the solutions of dumbbell **5a**.

[2]Rotaxane 4b: This compound was prepared from **1b**, **2**, and **3** (161 mg, 0.702 mmol) and obtained as a colorless glassy product (0.157 g, 37%). IR (neat): $\tilde{\nu}$ = 1709 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 4 H), 7.60 (s, 2 H), 7.53 (s, 2 H), 6.90 (s, 10 H), 3.92 (m, 10 H), 3.85 (m, 10 H), 3.76 (s, 10 H), 1.36 (t, J = 7 Hz, 30 H), 0.98 (m, 4 H), 0.00 (m, 8 H), –0.14 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.6, 149.8, 140.4, 132.2 (q, $^3J_{C,F}$ = 120 Hz), 128.8, 123.4 (q, $^2J_{C,F}$ = 1080 Hz), 118.6 (br), 116.5 (m), 115.2, 64.2, 36.7, 29.3, 29.2, 29.1, 23.7, 15.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.98 ppm. MALDI-TOF MS: m/z = 1514.73 [M]$^+$. $C_{81}H_{94}F_{12}N_2O_{12}$·$2Et_2O$ (1663.85): calcd. C 64.22, H 6.59, N 1.76; found C 64.82, H 6.47, N 1.97.

[2]Rotaxane 9a: This compound was prepared from **1a**, **2**, and **6** (144 mg, 0.702 mmol) and obtained as a colorless glassy product (51 mg, 12%). IR (neat): $\tilde{\nu}$ = 1693 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (s, 4 H), 7.42 (s, 2 H), 7.18 (s, 2 H), 6.92 (s, 10 H), 4.00 (m, 10 H), 3.88 (m, 10 H), 3.77 (s, 10 H), 1.65 (t, J = 7 Hz, 4 H), 1.41 (t, J = 6 Hz, 30 H), 1.36 (s, 36 H), 0.59 (m, 4 H), 0.06 (m, 4 H), –0.38 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.5, 151.4, 149.7, 138.2, 128.5, 117.8, 114.4, 114.1, 63.8, 37.9, 34.9, 31.5, 30.3, 29.2, 29.1, 28.8, 25.5, 15.4 ppm. MALDI-TOF MS: m/z = 1495.99 [M]$^+$. $C_{95}H_{134}N_2O_{12}$·Et_2O (1570.21): calcd. C 75.73, H 9.25, N 1.79; found C 75.41, H 8.85, N 1.87.

[2]Rotaxane 9b: This compound was prepared from **1b**, **2**, and **6** (144 mg, 0.702 mmol) and obtained as a colorless glassy product (29 mg, 7%). IR (neat): $\tilde{\nu}$ = 1692 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 2 H), 7.57 (d, J = 1 Hz, 4 H), 7.17 (t, J = 1 Hz, 2 H), 6.93 (s, 10 H), 3.97 (m, 10 H), 3.85 (m, 10 H), 3.77 (s, 10 H), 1.65 (t, J = 6 Hz, 4 H), 1.38 (t, J = 6 Hz, 30 H), 1.36 (s, 36 H), 0.86 (m, 4 H), 0.48 (m, 4 H), –0.76 (s, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.1, 151.4, 149.8, 139.7, 128.8, 120.7, 115.3, 113.9, 64.3, 34.9, 31.5, 29.3, 28.2, 23.9, 15.4 ppm. MALDI-TOF MS: m/z = 1468.08 [M + H]$^+$.

[2]Rotaxane 10a: This compound was prepared from **1a**, **2**, and **7** (235 mg, 0.702 mmol) and obtained as a colorless glassy product (0.040 g, 9%). IR (neat): $\tilde{\nu}$ = 1693 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, J = 7 Hz, 4 H), 7.30–7.18 (m, 36 H), 6.90 (s, 10 H), 3.95 (m, 10 H), 3.85 (m, 10 H), 3.75 (s, 10 H), 1.38 (t, J = 7 Hz, 30 H), 0.89 (m, 4 H), 0.40 (m, 4 H), 0.30 (m, 4

H), –0.13 (m, 4 H), –0.29 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 149.7, 146.8, 142.1, 136.5, 131.6, 131.1, 128.5, 127.5, 125.9, 118.5, 114.7, 64.6, 63.8, 37.4, 30.5, 30.3, 29.7, 29.2, 25.0, 15.4 ppm. MALDI-TOF MS: *m*/*z* = 1755.96 $[M + H]^+$. $C_{117}H_{130}N_2O_{12}$ (1756.29): calcd. C 80.01, H 7.46, N 1.60; found C 79.79, H 7.78, N 1.50.

[2]Rotaxane 10b: This compound was prepared from **1b**, **2**, and **7** (235 mg, 0.702 mmol) and obtained as a colorless glassy product (0.02 g, 4%). IR (neat): $\tilde{\nu}$ = 1698 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (s, 2 H), 7.55 (d, *J* = 7 Hz, 4 H), 7.30–7.18 (m, 34 H), 6.91 (s, 10 H), 3.95 (m, 10 H), 3.84 (m, 10 H), 3.76 (s, 10 H), 1.37 (t, *J* = 7 Hz, 30 H), 0.90 (m, 4 H), 0.37 (m, 4 H), –0.63 (m, 4 H), –0.91 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.9, 149.8, 146.9, 142.0, 136.7, 131.7, 131.1, 128.8, 127.5, 125.9, 118.5, 115.2, 64.2, 63.8, 37.6, 30.3, 29.7, 29.3, 28.4, 15.4 ppm. MALDI-TOF MS: *m*/*z* = 1728.00 $[M + H]^+$. $C_{115}H_{126}N_2O_{12}$ (1728.24): calcd. C 79.92, H 7.35, N 1.62; found C 79.66, H 7.66, N 1.56.

[2]Rotaxane 11a: This compound was prepared from **1a**, **2**, and **8**. The pure compound could not be isolated owing to its very low yield, but its presence was confirmed by mass spectrometry. MALDI-TOF MS: *m*/*z* = 1651.20 $[M]^+$.

Preparation of [2]Rotaxanes from 1a, 3, and Pillar[5]arenes 12 and 13: Compound **3** (161 mg, 0.702 mmol) was added to a stirred solution of the appropriate pillar[5]arene (**12** or **13**, 0.561 mmol), **1a** (75 mg, 0.281 mmol), and Et_3N (88 mg, 0.842 mmol) in $CHCl_3$ (2 mL) at –15 °C. After 1 h, the mixture was warmed to room temp. and then stirred for 12 h, and the solvent was evaporated. Purification by column chromatography (SiO_2, cyclohexane/Et_2O, 10:2) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) allowed the isolation of the [2]rotaxanes (**14a**, **15a**) as well as the unreacted pillar[5]arene.

[2]Rotaxane 14a: This compound was prepared from **1a**, **3**, and pillar[5]arene **12** (657 mg) and obtained as a colorless glassy product (164 mg, 32%). IR (neat): $\tilde{\nu}$ = 1708 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (s, 4 H), 7.60 (s, 2 H), 7.33 (s, 2 H), 6.90 (s, 10 H), 3.87 (m, 10 H), 3.76 (m, 20 H), 1.79 (m, 10 H), 1.70 (m, 10 H), 1.48 (m, 20 H), 1.05 (m, 4 H), 0.95 (t, *J* = 7 Hz, 30 H), 0.72 (m, 4 H), 0.27 (m, 4 H), 0.10 (m, 4 H), –0.12 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 149.9, 140.4, 132.3 (q, $^3J_{C,F}$ = 120 Hz), 128.7, 123.2 (q, $^2J_{C,F}$ = 1080 Hz), 118.6 (br), 116.5 (m), 114.9, 68.5, 36.8, 32.1, 31.1, 30.3, 29.7, 29.3, 29.2, 23.6, 19.5, 14.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.98 ppm. MALDI-TOF MS: *m*/*z* = 1823.00 $[M]^+$. $C_{103}H_{138}F_{12}N_2O_{12}$ (1824.19): calcd. C 67.82, H 7.63, N 1.54; found C 68.30, H 7.81, N 1.63.

[2]Rotaxane 15a: This compound was prepared from **1a**, **3**, and pillar[5]arene **13** (815 mg) and obtained as a colorless glassy product (100 mg, 17%). IR (neat): $\tilde{\nu}$ = 1703 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 4 H), 7.59 (s, 2 H), 7.28 (s, 2 H), 6.89 (s, 10 H), 3.87 (m, 10 H), 3.75 (m, 20 H), 1.80 (m, 10 H), 1.70 (m, 10 H), 1.45 (m, 20 H), 1.32 (m, 40 H), 1.02 (m, 4 H), 0.89 (m, 30 H), 0.73 (m, 4 H), 0.30 (m, 4 H), 0.08 (m, 4 H), –0.09 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.3, 149.9, 140.4, 132.2 (q, $^3J_{C,F}$ = 120 Hz), 128.6, 122.3 (q, $^2J_{C,F}$ = 1080 Hz), 118.6 (br), 116.5 (m), 114.9, 68.8, 36.8, 31.8, 31.2, 29.9, 29.8, 29.4, 29.2, 25.9, 23.5, 22.6, 14.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.94 ppm. MALDI-TOF MS: *m*/*z* = 2103.32 $[M]^+$. $C_{123}H_{178}F_{12}N_2O_{12}$ (2104.72): calcd. C 70.19, H 8.52, N 1.33; found C 70.58, H 8.14, N 1.42.

General Procedure for the Preparation of [2]Rotaxanes from Dialkylamines: The appropriate acyl chloride stopper (**17** or **18**) was added to a solution of 1,10-diaminodecane (**16a**, 48.5 mg, 0.281 mmol) or 1,8-diaminooctane (**16b**, 40.5 mg, 0.281 mmol), pillar[5]arene **2** (0.50 g, 0.561 mmol), and Et_3N (87.6 mg, 0.842 mmol) in chloroform (2 ml) at –15 °C. The mixture was then allowed to slowly warm to room temp. and concentrated. Purification by column chromatography (SiO_2, cyclohexane/Et_2O, 3:1) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) allowed the isolation of the [2]rotaxanes (**19a**, **19b**, **20a**, and **20b**) as well as unreacted pillar[5]arene **2**.

[2]Rotaxane 19a: This compound was prepared from **2**, **16a**, and **17** (162 mg, 0.702 mmol) and obtained as a pale orange glassy product (143 mg, 35%). IR (neat): $\tilde{\nu}$ = 1673 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.21 (t, *J* = 2 Hz, 2 H), 9.03 (d, *J* = 2 Hz, 4 H), 6.94 (s, 10 H), 5.98 (t, *J* = 4 Hz, 2 H), 3.94 (m, 10 H), 3.87 (m, 10 H), 3.74 (s, 10 H), 2.53 (m, 2 H), 2.45 (m, 2 H), 1.39 (t, *J* = 7 Hz, 30 H), 0.69 (s, 4 H), 0.33 (s, 4 H), –0.09 (m, 4 H), –0.34 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0, 149.8, 148.7, 138.9, 128.9, 127.2, 120.7, 115.0, 64.1, 40.9, 30.7, 30.1, 29.3, 27.9, 26.1, 15.4 ppm. MALDI-TOF MS: *m*/*z* = 1451.57 $[M + H]^+$. $C_{79}H_{98}N_6O_{20}$ (1451.65): calcd. C 65.36, H 6.81, N 5.79; found C 65.08, H 6.80, N 5.79.

[2]Rotaxane 19b: This compound was prepared from **2**, **16b**, and **17** (162 mg, 0.702 mmol) and obtained as a pale orange glassy product (140 mg, 35%). IR (neat): $\tilde{\nu}$ = 1672 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.22 (t, *J* = 2 Hz, 2 H), 9.06 (d, *J* = 2 Hz, 4 H), 6.95 (s, 10 H), 6.19 (t, *J* = 4 Hz, 2 H), 3.94 (m, 10 H), 3.88 (m, 10 H), 3.75 (s, 10 H), 2.59 (m, 2 H), 2.44 (m, 2 H), 1.39 (t, *J* = 6 Hz, 30 H), –0.07 (m, 4 H), –0.22 (br s, 4 H), –0.54 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.9, 149.9, 148.7, 138.9, 129.1, 127.1, 120.8, 115.4, 64.4, 40.9, 29.3, 29.2, 28.1, 25.9, 15.4 ppm. MALDI-TOF MS: *m*/*z* = 1423.64 $[M + H]^+$. $C_{77}H_{94}N_6O_{20}$ (1423.60): calcd. C 64.96, H 6.66, N 5.90; found C 64.40, H 6.52, N 5.80.

[2]Rotaxane 20a: This compound was prepared from **2**, **16a**, and **18** (194 mg, 0.702 mmol) and obtained as a buff glassy product (100 mg, 23%). IR (neat): $\tilde{\nu}$ = 1670 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 4 H), 8.05 (s, 2 H), 6.92 (s, 10 H), 5.95 (t, *J* = 4 Hz, 2 H), 3.95 (m, 10 H), 3.88 (m, 10 H), 3.75 (s, 10 H), 2.63 (m, 2 H), 2.54 (m, 2 H), 1.39 (t, *J* = 6 Hz, 30 H), 0.52 (br. s, 4 H), 0.15 (broad s, 4 H), 0.03 (m, 4 H), –0.40 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1, 149.8, 137.8, 132.3 (q, $^3J_{C\text{-}F}$ = 120 Hz), 128.8, 127.3 (broad), 124.7 (m), 123.0 (q, $^2J_{C\text{-}F}$ = 1080 Hz), 119.0, 114.9, 64.0, 40.7, 30.6, 29.9, 29.2, 28.3, 26.0, 15.4 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.74 ppm. MALDI-TOF-MS: *m*/*z* calcd. for $C_{83}H_{98}O_{12}N_2F_{12}$ $[M]^+$: 1542.69, found 1542.63. $C_{83}H_{98}F_{12}N_2O_{12}$ (1543.66): calcd. C 64.58, H 6.40, N 1.82; found C 64.93, H 6.69, N 1.99.

[2]Rotaxane 20b: This compound was prepared from **2**, **16b**, and **18** (194 mg, 0.702 mmol) and obtained as a buff glassy product (107 mg, 25%). IR (neat): $\tilde{\nu}$ = 1670 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 4 H), 8.06 (s, 2 H), 6.92 (s, 10 H), 6.19 (t, *J* = 4 Hz, 2 H), 3.94 (m, 10 H), 3.87 (m, 10 H), 3.75 (s, 10 H), 2.71 (m, 2 H), 2.53 (m, 2 H), 1.37 (t, *J* = 8 Hz, 30 H), 0.03 (m, 4 H), –0.54 (m, 4 H), –0.64 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 149.9, 137.7, 132.2 (q, $^3J_{C\text{-}F}$ = 120 Hz), 129.0, 127.2 (br), 124.7 (m), 123.2 (q, $^2J_{C,F}$ = 1080 Hz), 115.3, 64.3, 40.8, 29.3, 28.8, 28.4, 25.8, 15.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.74 ppm. MALDI-TOF MS: *m*/*z* (%) = 1515.78 (100) $[M + H]^+$. $C_{81}H_{94}F_{12}N_2O_{12}$ (1515.60): calcd. C 64.19, H 6.25, N 1.85; found C 64.47, H 5.83, N 2.03.

Acknowledgments

The authors gratefully acknowledge financial support from the Swiss National Science Foundation (grant number 200020-140298), the International Center for Frontier Research in Chemistry (icFRC), and the LabEx Chimie des Systèmes Complexes. A. L.-P. thanks FUNDAYACUCHO and T. M. N. T. thanks the University of Strasbourg (IdEx 2013) for their fellowships. M. Schmitt is thanked for high-field NMR measurements and J.-M. Strub for the mass spectra.

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