

Selected Paper

Synthesis of [2]- and [3]Rotaxanes by an End-Capping Approach Utilizing Urethane Formation

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Several axle-shaped *sec*-ammonium salts having hydroxy groups at the terminal ends were allowed to react with 3,5-dimethylphenyl isocyanate in the presence of dibenzo-24-crown-8 ether (DB24C8) in $CHCl_3$ by the catalysis of dibutyltin dilaurate to afford the corresponding [2]rotaxanes in good yields. Several Lewis acids other than dibutyltin dilaurate were effective for the end-capping. Although *N*,*N*-dimethylacetamide was not a suitable solvent, the use of chlorobenzene and nitromethane as solvents gave the [2]rotaxane in high yields. When a C_2-chiral 26-membered crown ether, prepared from biphenyl-2,2′,6,6′-tetrol and L-tartaric acid, was employed instead of DB24C8, the corresponding optically active [2]rotaxane was isolated in 47% yield. The present method was successfully applied to the synthesis of [3]rotaxane by employing hexamethylene diisocyanate. Thus, end-capping by acid-catalyzed urethane formation from alcohol and isocyanate was demonstrated to be an effective protocol for the synthesis a variety of rotaxanes, based on the *sec*-ammonium salt/crown ether recognition motif.

Rotaxanes have recently attracted increasing attention for the last two decades, because they are expected to be indispensable motifs for nanometer-level devices or new materials with unusual viscoelastic properties.[1] Several recognition motifs that can be exploited for rotaxane synthesis have been reported to date. Among them, *sec*-ammonium salt/crown ether system is the most versatile couple for the design of interlocked molecules, because the synthetic methods of *sec*-ammonium salts and crown ethers are well established and some of them are commercially available.[2] Numerous end-capping methods have been investigated for the *sec*-ammonium/crown motif, including amide formation,[3a,b] ester formation,[3c,d] 1,3-dipolar cycloaddition,[3e] Wittig reaction,[3f] disulfide formation by oxidation of thiol,[3g] thiol–disulfide interchange reaction,[3h,i] radical Michael addition,[3j] and urea formation.[3k,l] The ester-forming and disulfide-forming protocols ascertain high yields and have high functional-group tolerance. However, from viewpoint of further applications, ester[3c,d] and disulfide[3g–i] groups are not sufficiently stable towards nucleophiles and electrophiles as well as reducing and oxidizing agents. Although other protocols form stable linkages, such as C=C bonds,[3f] the yields are often considerably low.

Urethanes are known to be more stable than esters and disulfides towards chemical reagents, heating, and light irradiation.[4] In general, they can be readily prepared by the addition of alcohols to isocyanates under mild conditions in high yields. In addition, isocyanates can be prepared from amines, and a large number of them are commercially available. Therefore, synthetic methods of rotaxanes by utilizing urethane formation should be promising for the fabrication of interlocked systems with high durability. In this paper, we report on a novel synthetic procedure for [2]- and [3]rotaxanes by end-capping utilizing urethane formation from alcohols and isocyanates (Scheme 1).

Results and Discussion

1. Synthesis of Axles. Axle-shaped *sec*-ammonium salts having a hydroxy group at the end and a bulky end-capping group at the other end (**1** and **2** in Fig. 1) were synthesized as reported previously.[3c,5] Axles having a nitro group (**3a**) and a carbomethoxy group (**3b**) were synthesized according to Scheme 2. The treatment of 5-*t*-butylsalicylaldehyde (**4**) with 4-nitrobenzyl chloride in the presence of NaH gave the aldehyde (**5a**) in 54% yield. Reductive amination of **5a** with 3-amino-1-propanol afforded hydroxypropylamine (**6a**) in 65% yield, which was further treated with HPF_6 to produce ammonium salt (**3a**) in 79% yield. Methoxycarbonyl-substituted axle (**3b**) was similarly synthesized in high yield by using methyl 4-bromomethylbenzoate instead of 4-nitrobenzyl chloride, as shown in Scheme 2.

2. Synthesis of Wheel. C_2-Chiral 26-membered crown ether (**9**) was synthesized from optically active biphenol[6] (**7**) which was prepared from biphenyl-2,2′,6,6′-tetrol and L-tartaric acid (Scheme 3). Cesium ion-templated cyclization of **7** with ditosylate (**8**) gave **9** in 43% yield. The ^{1}H NMR, IR, and mass spectral data were consistent with the structure of **9**.

3. Synthesis of Rotaxanes. The addition of dibenzo-24-crown-8 ether (DB24C8) to a suspension of **1** (0.10 mmol) in $CDCl_3$ (0.60 mL) resulted in a colorless clear solution. The for-

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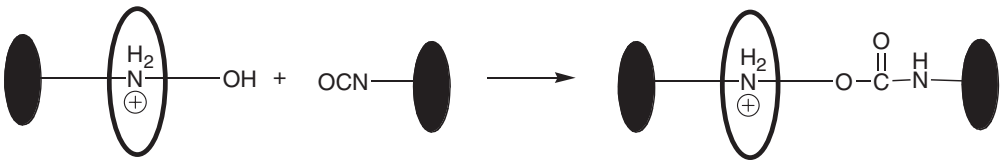


Scheme 1. A schematic representation of the synthetic protocol for [2]rotaxanes utilizing urethane formation from alcohol and isocyanate based on *sec*-ammonium/crown motif.

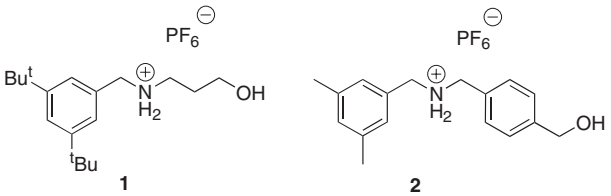
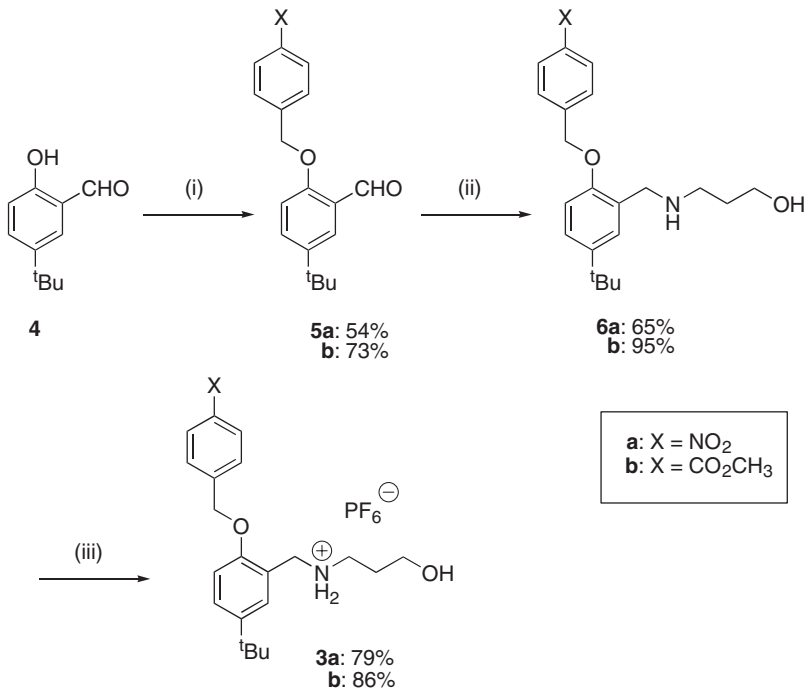
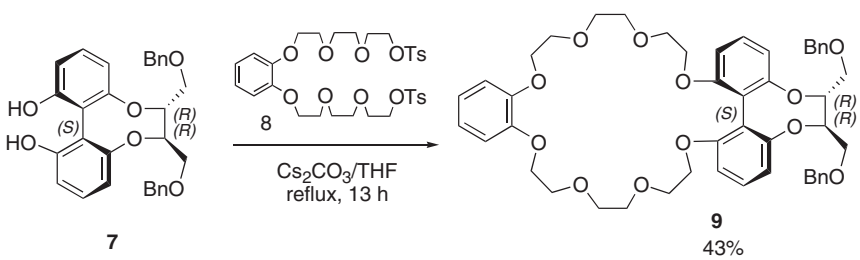


Fig. 1.

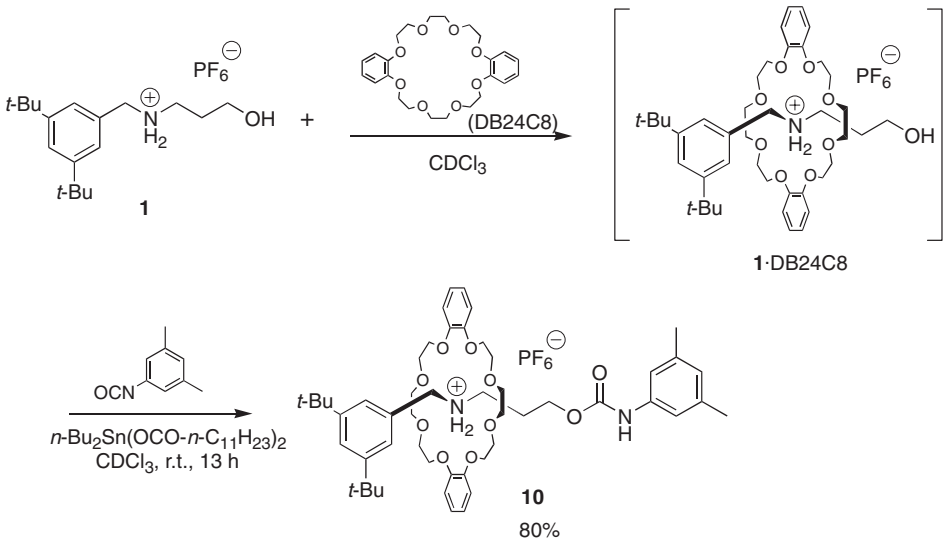
mation of the corresponding pseudorotaxane (**1**·DB24C8) was confirmed by ^{1}H NMR. 3,5-Dimethylphenyl isocyanate was added, and the resulting solution was allowed to stand at ambient temperature for 13 h. However, no reaction proceeded under these conditions. Although, in general, urethane formation is known to proceed at higher temperature without a catalyst, rotaxane synthesis should be conducted at low temperature, because the ratio of pseudorotaxane formation is lowered at high temperatures.[3i] Upon the addition of a catalytic amount of dibutyltin dilaurate (0.010 mmol), a reaction of the hydroxy group of **1**·DB24C8 with 3,5-dimethylphenyl isocyanate started. After 13 h, the reaction mixture was subjected to preparative GPC



Scheme 2. Reagents and conditions: (i) 4-nitrobenzyl chloride for **5a**, methyl 4-bromomethylbenzoate for **5b**, NaH/DMF, 100 °C; (ii) 3-amino-1-propanol/toluene, then $NaBH_4$/MeOH; (iii) 5% HPF_6aq, 0 °C.



Scheme 3. Synthesis of optically-active 26-membered crown ether (**9**).



Scheme 4. Synthesis of [2]rotaxane (**10**).

Table 1. Effect of Catalyst on the Yield of [2]Rotaxane (**10**)

Entry	Catalyst	Yield of **10**/%[a)]	Unreacted **1**/%[a)]
1	n-$Bu_2Sn(OCO$-n-$C_{11}H_{23})_2$	87	13
2	n-Bu_2SnCl_2	85	14
3	$Et_2O \cdot BF_3$	79	0
4	CF_3SO_3H	81	0
5	CF_3CO_2H	56	44

a) Estimated by ^{1}H NMR.

to give [2]rotaxane (**10**) in 80% yield (Scheme 4). The structure of **10** was confirmed by ^{1}H NMR, IR, and mass spectroscopies along with an elemental analysis.

The effect of a catalyst on the yield of rotaxane was examined by using **1**, DB24C8, and 3,5-dimethylphenyl isocyanate as the building blocks for **10**. A catalytic amount of an acid (0.010 mmol) was added to a mixture of **1** (0.10 mmol), DB24C8 (0.12 mmol), and 3,5-dimethylphenyl isocyanate (0.15 mmol) in $CHCl_3$ (0.60 mL). The reaction mixture was allowed to stand at room temperature for 13 h and then evaporated to dryness. The mixture of the residue and naphthalene (0.10 mmol) was dissolved in $CDCl_3$ (0.60 mL). The yield of **10** was estimated by the ^{1}H NMR, and is summarized in Table 1. In the case of dibutyltin dilaurate, **10** was formed in 87% yield along with 13% of unreacted **1** (entry 1). Similarly, dibutyltin dichloride gave **10** in 85% yield and 14% of unreacted **1** (entry 2). Diethyl ether–boron trifluoride (1/1) and trifluoromethanesulfonic acid afforded **10** in 79% and 81% yields, respectively (entries 3 and 4). However, in these cases, no unreacted **1** was observed. In both cases, the adduct of **1** and 3,5-dimethylphenyl isocyanate was formed in ca. 20% yield. This means that the yields of **10** do not increase even if the reaction times are prolonged. The use of trifluoroacetic acid resulted in a reaction rate slower than those of other catalysts under the same conditions (entry 5). Thus, several typical Lewis and Bronsted acids are available for this end-capping protocol utilizing urethane formation. The organotin reagents can be taken as the best among them from the viewpoints of both the yield and the reaction rate.

Table 2. Effect of Solvent on the Yield of [2]Rotaxane (**10**)

Entry	Solvent	Yield of **10**/%[a)]	Unreacted **1**/%[a)]
1	Chloroform	87	13
2	Chlorobenzene	90	9
3	Nitromethane	83	8
4	*N*,*N*-Dimethylacetamide	0	4

a) Estimated by ^{1}H NMR.

Table 3. Effect of Feed Ratio of DB24C8 on the Yield of [2]Rotaxane (**10**)

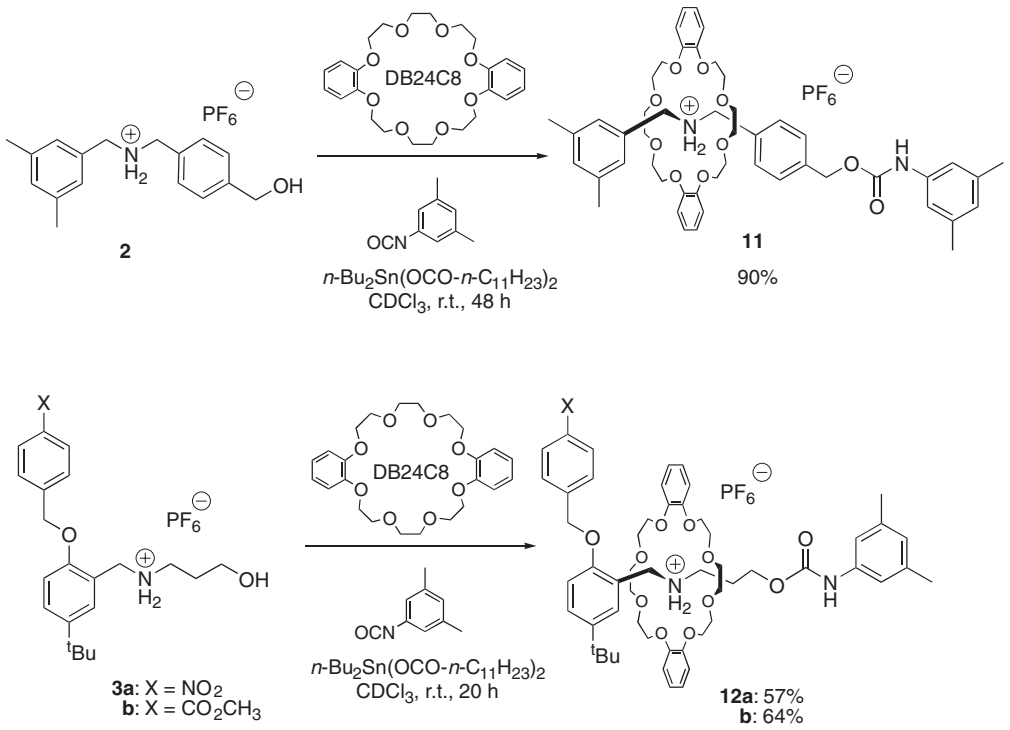
Entry	Feed ratio of DB24C8 to **1**	Yield of **10**/%[a)]	Unreacted **1**/%[a)]
1	1.0	81	19
2	1.2	87	13
3	2.0	89	11

a) Estimated by ^{1}H NMR.

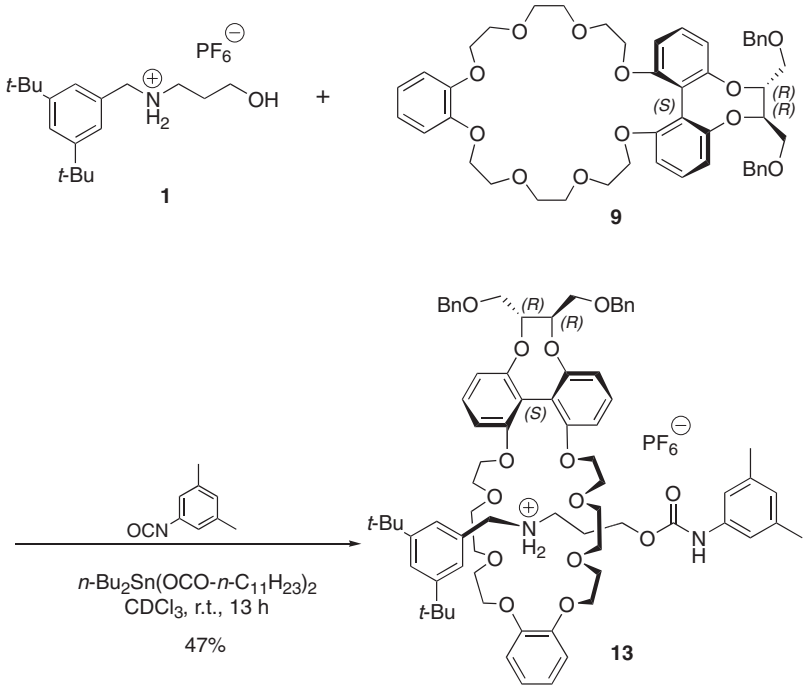
The effect of a solvent on the yield of rotaxane was investigated under conditions similar to those employed in Table 1. The results are summarized in Table 2. Chlorobenzene and nitromethane gave good results, similarly to that obtained with chloroform (entries 1–3). However, **10** was not yielded at all by use of *N*,*N*-dimethylacetamide. Instead, the adduct of **1** and 3,5-dimethylphenyl isocyanate was formed in 96% yield. This is accounted for by the fact that *N*,*N*-dimethylacetamide prevents the hydrogen-bonding interaction, which is the main driving force for the complexation between *sec*-ammonium salt and crown ether[7] (entry 4).

The effect of the feed ratio of DB24C8 to **1** on the yield of **10** was examined. As shown in Table 3, the yield of **10** increased with an increase in the feed ratio of DB24C8. However, there was no appreciable difference in the yield of **10** between the feed ratios of 2.0 and 1.2.

Three axles other than **1** were employed for the synthesis of [2]rotaxanes (Scheme 5). When axle (**2**), which is longer than **1**, was employed, **11** was obtained in 90% isolated yield. The high



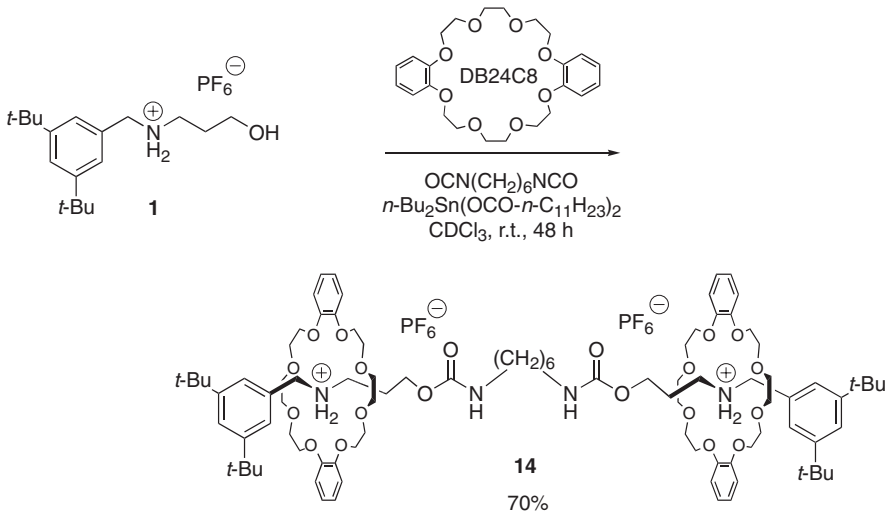
Scheme 5. Synthesis of [2]rotaxane (**11** and **12**).



Scheme 6. Synthesis of optically-active [2]rotaxane (**13**).

yield suggests that the distance between the *sec*-ammonium salt and hydroxy group has almost no effect on the yield of rotaxane. The use of **3a** resulted in a lower yield (57%) of **12a**, which can be attributed to a steric repulsion between the DB24C8 ring and the 4-nitrobenzyloxy group attached to the axle. Similarly, [2]rotaxane, having a 4-methoxycarbonylphenylmethoxy group on the axle component (**12b**), was obtained in 64% yield under the same conditions. Thus, this protocol has high tolerance to the structure of the axle component, although the axles having bulky substituents reduce the yield of rotaxane.

To examine the effect of the structure of the wheel component, the C_2-chiral 26-membered crown ether (**9**) was employed for rotaxane synthesis (Scheme 6). The corresponding optically active [2]rotaxane (**13**) was obtained in 47% isolated yield. The



Scheme 7. Synthesis of [3]rotaxane (**14**).

structure of **13** was confirmed by ^{1}H NMR, IR, and FAB mass spectroscopies. The yield of **13** was lower than those with the 24-membered crown ethers. This result is explained by the fact that the 26-membered crown ether has much lower association constants with *sec*-ammonium salts than those with the 24-membered ones.[8] In fact, the yield of 47% is comparable to that reported for [2]rotaxane synthesis with a 26-membered crown ether having a binaphthyl unit.[3k] The present end-capping protocol thus tolerates a structural modification of wheel component. Furthermore, **9** has two benzyl ether-protected hydroxy groups on its outer rim, which can be utilized as a scaffold for introducing of additional functional groups.[9]

Bifunctional isocyanates can be used for [3]rotaxane synthesis by this end-capping method. Hexamethylene diisocyanate was allowed to react with the pseudorotaxane (**1**·DB24C8) by the catalysis of dibutyltin dilaurate. The corresponding [3]rotaxane (**14**) was isolated in 70% yield (Scheme 7).

In summary, the end-capping protocol utilizing acid-catalyzed urethane-formating reaction was examined in the synthesis of various [2]- and [3]rotaxanes. The method is based on the *sec*-ammonium salt/crown ether recognition motif. Several acids were effective for rotaxane synthesis. Furthermore, the present protocol has a high tolerance for modifications of the stuctures of both the axle and wheel components.

Experimental

General. The melting points were measured on a Yanagimoto micro melting-point apparatus and were uncorrected. IR spectra were recorded on a JASCO FT-IR model 230 spectrometer. ^{1}H and ^{13}C NMR measurements were performed on JEOL JNM-GX-270 and JNM-L-400 spectrometers in $CDCl_3$ with tetramethylsilane as an internal reference. FAB-MS measurements were performed on a Finnigan TSQ-70 instrument. For preparative HPLC, a JAICO LC-908 system using columns JAIGEL 1 (ϕ 20 mm × 600 mm) and JAIGEL 2 (ϕ 20 mm × 600 mm) was used.

5-*t*-Butyl-2-(4-nitrophenylmethoxy)benzaldehyde (5a). To a suspension of NaH (60% in oil, 536 mg, 13.4 mmol) in DMF (20 mL) was added dropwise a solution of 5-*t*-butylsalicylaldehyde (**4**, 2.01 g, 11.2 mmol) in DMF (10 mL) at room temperature under an Ar atmosphere. After the evolution of H_2 had stopped, 4-nitrobenzyl chloride (6.87 g, 40.2 mmol) was added to the resulting yellow suspension. The mixture was stirred at 100 °C for 24 h. After being cooled to room temperature, the mixture was poured into water (100 mL) and extracted with ethyl acetate (200 mL × 1). The extract was washed with water (100 mL × 1) and brine (100 mL × 1), dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The residue was subjected to SiO_2 column chromatography (eluent: hexane/ethyl acetate (9/1)) to afford 5-*t*-butyl-2-(4-nitrophenylmethoxy)benzaldehyde (**5a**) as a yellow heavy oil (1.69 g, 54%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 10.55 (s, 1H, CHO), 8.27 (d, J = 9 Hz, 2H, ArH), 7.90 (d, J = 3 Hz, 1H, Ar), 7.63 (d, J = 9 Hz, 1H, ArH), 7.57 (dd, J = 9, 3 Hz, 1H, ArH), 6.92 (d, J = 9 Hz, 1H, ArH), 5.28 (s, 2H, $ArCH_2O$), 1.31 (s, 9H, *t*-Bu). IR (NaCl) 1728 ($\nu_{C=O}$), 1520 ($\nu_{N=O}$), 1346 ($\nu_{N=O}$) cm^{-1}.

2-(4′-Methoxycarbonylphenylmethoxy)-5-*t*-butylbenzaldehyde (5b). 73% yield. A white solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ 10.57 (s, 1H, CHO), 8.08 (d, J = 8 Hz, 2H, Ar), 7.88 (d, J = 2.6 Hz, 1H, ArH), 7.57–7.50 (m, 3H, ArH), 6.94 (d, J = 9 Hz, 1H, Ar), 5.24 (s, 2H, $ArCH_2O$), 3.93 (s, 3H, CH_3OCO), 1.31 (s, 9H, *t*-Bu). IR (NaCl) 1707 ($\nu_{C=O}$), 1684 ($\nu_{C=O}$) cm^{-1}.

Amino Alcohol (6a). A mixture of aldehyde (**5a**, 2.10 g, 6.70 mmol), 3-amino-1-propanol (503 mg, 6.70 mmol), and toluene (50 mL) was refluxed for 2 h in a flask equipped with a Dean–Stark apparatus. After evaporation of the solvent, $NaBH_4$ (633 mg, 16.7 mmol) was added portionwise to a solution of the residue in methanol (50 mL) with stirring. The mixture was stirred for 20 h at room temperature. After evaporation of the solvent, the residue was poured into water (50 mL), and extracted with $CHCl_3$ (30 mL × 3). The extract was washed with aqueous 10% NaOH (30 mL × 1), and brine (30 mL × 1), dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The residue was subjected to SiO_2 column chromatography (eluent: $CHCl_3$/methanol (9/1)) to afford amino alcohol (**6a**) as a yellow heavy oil (1.61 g, 65%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.26 (d, J = 9 Hz, 2H, ArH), 7.59 (d, J = 9 Hz, 2H, ArH), 7.29–7.20 (m, 2H, ArH), 6.78 (d, J = 9 Hz, 1H, ArH), 5.19 (s, 2H, $ArCH_2O$), 3.86 (s, 2H, $ArCH_2N$), 3.81 (t, J = 5 Hz, 2H, CH_2OH), 2.90 (t, J = 6 Hz, 2H, NCH_2CH_2), 2.04–1.67 (m, 5H, NH_2, OH and $CH_2CH_2CH_2$), 1.30 (s, 9H, *t*-Bu). IR (NaCl) 3306 (ν_{N-H} and ν_{O-H}), 1521 ($\nu_{N=O}$), 1345 ($\nu_{N=O}$) cm^{-1}.

Amino Alcohol (6b). 95% yield. A colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.07 (d, J = 8 Hz, 2H, ArH), 7.48 (d, J = 9 Hz, 2H, ArH), 7.26–7.20 (m, 2H, ArH), 6.81 (d, J = 9 Hz, 1H,

ArH), 5.14 (s, 2H, $ArCH_2O$), 3.93 (s, 3H, CH_3OCO), 3.85 (s, 2H, $ArCH_2N$), 3.81 (t, $J = 5$ Hz, 2H, CH_2OH), 2.87 (t, $J = 6$ Hz, 2H, NCH_2CH_2), 1.73–1.66 (m, 5H, NH_2, OH and $CH_2CH_2CH_2$), 1.30 (s, 9H, *t*-Bu). IR (NaCl) 1722 ($\nu_{C=O}$), 1612 ($\nu_{C=O}$) cm^{-1}.

Axle (3a). To a solution of amino alcohol (**6a**, 1.60 g, 4.30 mmol) in methanol (10 mL) was slowly added dropwise an aqueous 5% HPF_6 solution (72 mL) at 0 °C. The resulting yellow paste was collected and dissolved in $CHCl_3$ (50 mL). The solution was washed with water (50 mL × 1), dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The resulting yellow solid was recrystallized from hexane/ethyl acetate to affored axle (**3a**) as a yellowish-white solid (1.76 g, 79%). Mp 131–133 °C. ^{1}H NMR (270 MHz, CD_3CN) δ 8.25 (d, $J = 9$ Hz, 2H, ArH), 7.58 (d, $J = 8.9$ Hz, 2H, ArH), 7.46–7.43 (m, 2H, Ar), 7.13 (br s, 2H, NH_2), 6.97 (d, $J = 9$ Hz, 1H, ArH), 5.31 (s, 2H, $ArCH_2O$), 4.24 (t, $J = 5.8$ Hz, 2H, $ArCH_2N$), 3.66 (t, 2H, $J = 6$ Hz, CH_2OH), 3.22–3.12 (m, 2H, NCH_2CH_2), 2.18 (br s, 1H, OH), 1.86–1.78 (m, 2H, $CH_2CH_2CH_2$), 1.29 (s, 9H, *t*-Bu). IR (KBr) 3559, 3220, and 3189 (ν_{O-H}), 1531 ($\nu_{N=O}$), 1346 ($\nu_{N=O}$), 851 and 559 (ν_{P-F}) cm^{-1}. FAB-MS (matrix: mNBA) m/z 373 [$(M - PF_6)^+$]. Found: C, 48.96; H, 5.67; N, 5.45%. Calcd for $C_{21}H_{29}F_6N_2O_4P$: C, 48.65; H, 5.65; N, 5.40%.

Axle (3b). 86% yield. A white solid. Mp 121–124 °C. ^{1}H NMR (270 MHz, CD_3CN) δ 8.02 (d, $J = 9$ Hz, 2H, ArH), 7.59 (d, $J = 9$ Hz, 2H, ArH), 7.44–7.41 (m, 2H, ArH), 6.97 (d, $J = 8.9$ Hz, 1H, ArH), 5.26 (s, 2H, $ArCH_2O$), 4.21 (s, 2H, $ArCH_2N$), 3.87 (s, 3H, CH_3OCO), 3.64 (t, $J = 6$ Hz, 2H, CH_2OH), 3.15 (t, $J = 6.1$ Hz, 2H, NCH_2CH_2), 2.18 (br s, 1H, OH), 1.85–1.76 (m, 2H, $CH_2CH_2CH_2$), 1.28 (s, 9H, *t*-Bu). IR (KBr) 3228 and 3190 (ν_{O-H}), 1728 ($\nu_{C=O}$), 850 and 559 (ν_{P-F}) cm^{-1}. FAB-MS (matrix: mNBA) m/z 386 [$(M - PF_6)^+$]. Found: C, 51.87; H, 5.95; N, 2.70%. Calcd for $C_{23}H_{32}F_6NO_4P$: C, 51.98; H, 6.07; N, 2.64%.

26-Membered Chiral Crown Ether (9). A mixture of diol (**7**, 845 mg, 1.74 mmol) and cesium carbonate (2.26 g, 6.96 mmol) in THF (44 mL) was refluxed under Ar atmosphere for 30 min. To the resulting white suspension was added dropwise a solution of ditosylate (**8**, 1.18 g, 1.74 mmol) in THF (26 mL). The mixture was refluxed for 13 h. After being cooled to room temperature, the mixture was filtered. The filtrate was extracted with $CHCl_3$ (100 mL × 1). The extract was washed with 2 M HCl (50 mL × 1) and water (50 mL × 1), dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The residue was subjected to Al_2O_3 column chromatography (eluent: hexane/ethyl acetate (1/1)) to afford crown ether (**9**) as a colorless heavy oil (620 mg, 43%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.38–7.16 (m, 12H, ArH), 6.90 (s, 4H, ArH), 6.82 (dd, $J = 7$, 1 Hz, 2H, ArH), 6.72 (dd, $J = 7$, 1 Hz, 2H, ArH), 4.55 (s, 4H, CH_2Ph), 4.20–3.56 (m, 30H, CH_2O and CHO). FAB-MS (matrix: mNBA) m/z 822.3 [M^+]. Found: C, 66.13; H, 5.90%. Calcd for $C_{48}H_{54}O_{12}\cdot(H_2O)_{0.5}$: C, 66.00; H, 6.22%.

[2]Rotaxane (10). To a solution of axle (**1**, 0.10 mmol), DB24C8 (54 mg, 0.12 mmol), and 3,5-dimethylphenyl isocyanate (22 mg, 0.15 mmol) in $CHCl_3$ (0.60 mL) was added dibutyltin dilaurate (6.3 mg, 0.010 mmol). The mixture was stirred at room temperature for 13 h and was evaporated to dryness. The residue was subjected to preparative GPC (eluent: $CHCl_3$) to afford [2]rotaxane (**10**) as a white foamy solid (81 mg, 80%). Mp 72–75 °C. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.41 (br s, 1H, NHCO), 7.33 (t, $J =$ 2.0 Hz, 1H, ArH), 7.29 (d, $J = 2.0$ Hz, 2H, ArH), 7.05 (s, 2H, ArH), 6.89 (s, 8H, ArH of DB24C8), 6.65 (s, 1H, ArH), 4.71 (m, 2H, CH_2), 4.4–3.3 (m, 28H, CH_2 of DB24C8 and dumbbell), 2.25 (s, 6H, CH_3), 1.85 (m, 2H, CH_2), 1.19 (s, 18H, *t*-Bu). IR (NaCl) 3304 (ν_{N-H}), 1710 ($\nu_{C=O}$), 843 and 557 (ν_{P-F}) cm^{-1}. FAB-MS (matrix: mNBA) m/z 874.1 [$(M - PF_6)^+$]. For elemental analysis, recrystallization was carried out by use of $CHCl_3$/hexane. Found: C, 60.95; H, 7.26; N, 2.38%. Calcd for $C_{51}H_{73}F_6N_2O_{10}P\cdot(C_6H_{14})_{0.5}$: C, 61.06; H, 7.59; N, 2.64%.

[2]Rotaxane (11). 90% yield. A white foamy solid. Mp 75–80 °C. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.57 (br s, 2H, NH_2), 7.4–6.65 (m, 18H, ArH), 5.09 (s, 2H, $ArCH_2O$), 4.59 (m, 2H, $ArCH_2N$), 4.41 (m, 2H, $ArCH_2N$), 4.10 (m, 8H, CH_2 of DB24C8), 3.75 (m, 8H, CH_2 of DB24C8), 3.41 (m, 8H, CH_2 of DB24C8), 2.26 (s, 6H, CH_3), 2.14 (s, 6H, CH_3). IR (NaCl) 3394 and 3151 (ν_{N-H}), 1710 ($\nu_{C=O}$), 843 and 557 (ν_{P-F}) cm^{-1}. FAB-MS (matrix: mNBA) m/z 851.4 [$(M - PF_6)^+$]. Found: C, 57.73; H, 6.35; N, 2.56%. Calcd for $C_{50}H_{63}F_6N_2O_{10}P\cdot(H_2O)_{2.5}$: C, 57.63; H, 6.58; N, 2.69%.

[2]Rotaxane (12a). 57% yield. A clear pale yellow film. ^{1}H NMR (270 MHz, CD_3CN) δ 8.08 (d, $J = 9$ Hz, 2H), 7.50 (d, $J = 9$ Hz, 1H), 7.40–7.37 (m, 2H), 7.22–7.18 (m, 2H), 6.98 (s, 2H), 6.91–6.84 (m, 9H), 6.70 (s, 1H), 6.58 (d, $J = 9$ H, 1H), 4.96 (s, 2H), 4.66–4.61 (m, 2H), 4.13–3.97 (m, 11H), 3.86–3.80 (m, 4H), 3.72–3.61 (m, 10H), 3.57–3.49 (m, 3H), 2.23 (s, 6H), 2.04–1.96 (m, 2H), 1.18 (s, 9H). IR (KBr) 3397 (ν_{N-H}), 1730 ($\nu_{C=O}$), 1506 ($\nu_{N=O}$), 1346 ($\nu_{N=O}$), 844 and 557 (ν_{P-F}) cm^{-1}. FAB-MS (matrix: mNBA) m/z 969.9 [$(M - PF_6)^+$]. Found: C, 56.09; H, 5.92; N, 3.67%. Calcd for $C_{54}H_{70}F_6N_3O_{13}P\cdot(CHCl_3)_{0.5}$: C, 55.77; H, 6.05; N, 3.58%.

[2]Rotaxane (12b). 64% yield. A colorless film. ^{1}H NMR (270 MHz, CD_3CN) δ 7.87 (d, $J = 8$ Hz, 2H), 7.41–7.35 (m, 4H), 7.20–7.16 (m, 2H), 6.98 (s, 2H), 6.91–6.88 (m, 9H), 6.70 (s, 1H), 6.56 (d, $J = 8.6$ Hz, 1H), 4.92 (s, 2H), 4.63–4.58 (m, 2H), 4.13–3.97 (m, 11H), 3.84–3.79 (m, 7H), 3.71–3.61 (m, 10H), 3.54–3.48 (m, 3H), 2.23 (s, 6H), 2.01–1.96 (m, 2H), 1.17 (s, 9H). IR (KBr) 3391 (ν_{N-H}), 1722 ($\nu_{C=O}$), 1613 ($\nu_{C=O}$), 844 and 557 (ν_{P-F}) cm^{-1}. FAB-MS (matrix: mNBA) m/z 981.5 [$(M - PF_6)^+$]. Found: C, 56.91; H, 6.05; N, 2.44%. Calcd for $C_{56}H_{73}F_6N_2O_{13}P\cdot(CHCl_3)_{0.5}$: C, 57.18; H, 6.24; N, 2.36%.

Chiral [2]Rotaxane (13). To a solution of axle (**1**, 42.3 mg, 0.10 mmol), crown ether (**9**, 91.8 mg, 0.110 mmol), and 3,5-dimethylphenyl isocyanate (22 mg, 0.15 mmol) in $CHCl_3$ (0.60 mL) was added dibutyltin dilaurate (6.3 mg, 0.010 mmol). The mixture was stirred at room temperature for 66 h. After evaporation, the residue was subjected to preparative GPC (eluent: $CHCl_3$) to afford chiral [2]rotaxane (**13**) as a colorless heavy oil (66 mg, 47%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.42 (t, $J = 2$ Hz, 1H, ArH), 7.37–7.25 (m, 13H, ArH), 7.10 (t, $J = 7.8$ Hz, 1H, ArH), 6.98–6.79 (m, 10H, ArH), 6.67 (br s, 1H, NH), 6.34 (d, $J = 7.8$ Hz, 1H, ArH), 4.7–3.0 (m, 40H, CH_2 and CH), 2.25 (s, 6H, CH_3), 1.99 (m, 2H, CH_2), 1.25 (s, 18H, *t*-Bu). IR (KBr) 3395 (ν_{N-H}), 1729 ($\nu_{C=O}$), 1613 ($\nu_{C=O}$), 843 and 557 (ν_{P-F}) cm^{-1}. FAB-MS (matrix: mNBA) m/z 1247.6 [$(M - PF_6)^+$]. Found: C, 63.63; H, 7.04; N, 2.27%. Calcd for $C_{75}H_{95}F_6N_2O_{14}P\cdot(H_2O)_1$: C, 63.82; H, 6.93; N, 1.98%.

[3]Rotaxane (14). To a solution of axle (**1**, 85 mg, 0.20 mmol), DB24C8 (180 mg, 0.40 mmol), and hexamethylene diisocyanate (16 μL, 0.10 mmol) in $CHCl_3$ (1.0 mL) was added dibutyltin dilaurate (12 μL, 0.020 mmol). The mixture was stirred at room temperature for 48 h and was evaporated to dryness. The residue was subjected to preparative GPC (eluent: $CHCl_3$) to afford [2]rotaxane (**10**) as a white solid (140 mg, 70%). ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.35–7.27 (m, 6H, ArH), 6.87 (s, 16H, ArH of DB24C8), 4.69–4.67 (m, 4H, $ArCH_2N$), 4.27–3.02 (m, 60H, CH_2), 2.03–0.90 (m, 44H, CH_2 and *t*-Bu). IR (NaCl) 3426 (ν_{N-H}), 1729 ($\nu_{C=O}$), 843 and 557 (ν_{P-F}) cm^{-1}. FAB-MS (matrix: mNBA): m/z 1621.4 [$(M - 2PF_6)^+$]. Found: C, 55.39; H, 6.94; N,

2.81%. Calcd for $C_{92}H_{140}F_{12}N_4O_{20}P_2 \cdot (CHCl_3)_1$: C, 54.99; H, 7.00; N, 2.76%.

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