A Building Block Method for the Synthesis of Higher Cycloamides

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Received August 29, 2000

Series of cyclic amides containing optically active helicene, (*P*)-1,12-dimethylbenzo[*c*]phenanthrene, are synthesized using a building block method. The building block consists of one (*P*)-helicene unit and one dianiline unit with its amino-terminal-protected with benzyloxycarbonyl and its acid terminal activated as acid chloride. The coupling with (*P*,*P*....)-[(n − 3) + (n − 2)]diamine followed by deprotection gives (*P*,*P*....)-[(n − 1) + n]diamine, which possesses n − 1 parts of (*P*)-helicene and n parts of dianiline. Cyclization of the (*P*,*P*....)-[(n − 1) + n]diamine with helicenediacid dichloride gives (*P*,*P*....)-[n + n]cycloamide. All the members of (*P*,*P*)-[2 + 2]cycloamide to (*P*,*P*,*P*,*P*,*P*,*P*,*P*,*P*,*P*,*P*)-[10 + 10]cycloamide are synthesized using this method, and are compared spectroscopically.

Previously, we reported the synthesis of cyclic amides containing optically active helicene, 1,12-dimethylbenzo-[*c*]phenanthrene-5,8-dicarboxylic acid (**8**).[1] The acid dichloride (*P*)-**6** derived from (*P*)-**8** was reacted with diamine **1**[2,3] by one-pot method, and (*P*,*P*....)-[n + n]cycloamides with n = 1, 2, 3, 4 were obtained. The (*P*,*P*....)-[n + n]-cycloamide is the cyclic amide which contains n parts of (*P*)-**8** and n parts of **1**. Some of the cycloamides show interesting properties: The [1 + 1]cycloamide forms stable monolayers on the water surface, which can be transferred on the solid support giving Langmuir−Blodgett films:[4] The [2 + 2]cycloamide catalyzes the asymmetric addition of diethyl zinc to aromatic aldehydes, and enantiomeric excesses up to 50% are attained.[1] We were then interested in the synthesis of higher cycloamides in order to compare their structures and properties with the lower cycloamides noted above. Described here is the synthesis of (*P*,*P*....)-[n + n]-cycloamide with n = 2 to 10 using a building block method.

The strategy of this synthesis is summarized in Scheme 1. Compound (*P*)-**3** containing one (*P*)-helicene moiety and one dianiline moiety is selected for the building block, in which the amino terminus is protected with benzyloxycarbonyl and the acid terminus activated as acid chloride. (*P*,*P*....)-[(n − 1) + n]Diamines (*P*,*P*....)-**4** are synthesized from diamine **1** or (*P*)-**2**. Coupling of **1** or (*P*)-**2** with (*P*)-**3** followed by deprotection gives (*P*,*P*)-[2 + 3]diamine (*P*,*P*)-**4** (n = 3) or (*P*,*P*,*P*)-[3 + 4]diamine (*P*,*P*,*P*)-**4** (n = 4), respectively, which can be used for the next chain elongation. One cycle of the operations adds two units of (*P*)-**8** and two units of **1** to the precursors giving series of (*P*,*P*....)-[(n − 1) + n]diamine, (*P*,*P*....)-**4**. Then, cyclization of (*P*,*P*....)-**4** with acid dichloride (*P*)-**6** gives (*P*,*P*....)-[n + n]cycloamide, (*P*,*P*....)-**7**. This two-directional chain elongation method using the building block has several advantages:[5,6] (i) All the members of the small-membered ring compounds to the large-membered ring compounds can be prepared in relatively short steps: (ii) Stereoisomers regarding the helicene moiety can be synthesized by simply changing the building block, (*P*)-**3** or (*M*)-**3**.

The building block (*P*)-**3** is synthesized as shown in Scheme 2. Reaction of dianiline **1** with 1 equiv of di(*tert*-butoxy) dicarbonate gives a mixture of monoprotected **1**, diprotected **1**, and the starting material **1**, which are readily separable by silica gel chromatography. It turned out that *tert*-butoxycarbonyl derivatives are much more easily separated than the corresponding benzyloxycarbonyl dianilines. The other amino group of the monoprotected **1** is then treated with benzyloxycarbonyl chloride, and removal of *tert*-butoxycarbonyl group gives **10**. Helicenedicarboxylic acid (*P*)-**8** is converted to the dimethyl ester, and selectively monohydrolyzed with barium hydroxide[7] giving (*P*)-**9** in a high yield. The coupling reaction of **10** with the acid chloride obtained from (*P*)-**9**

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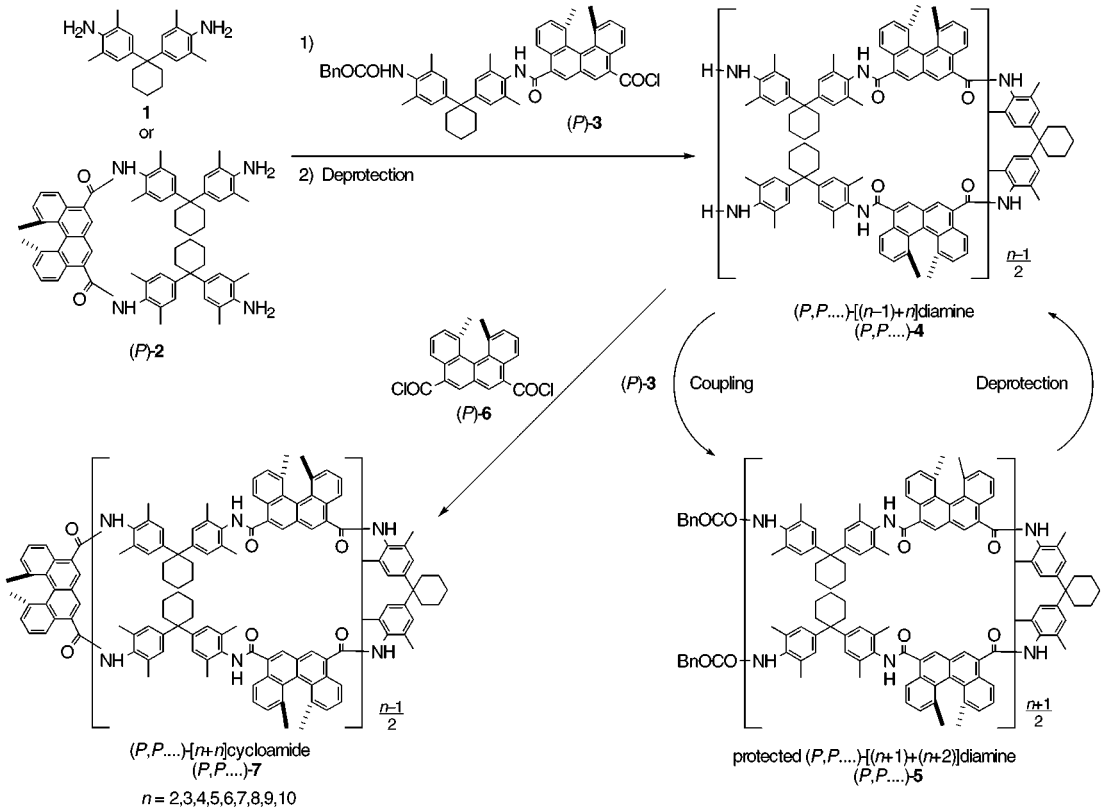
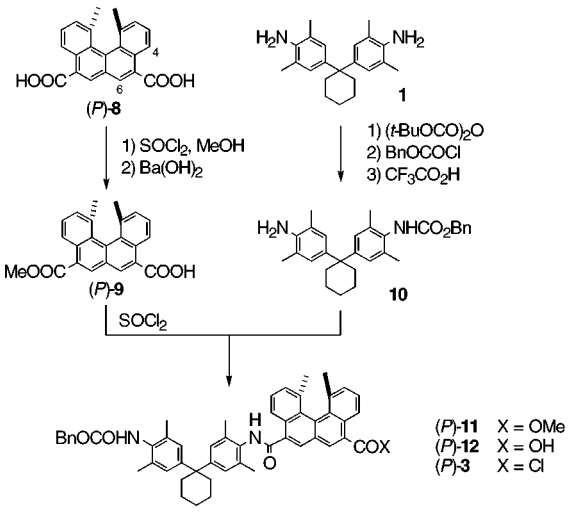
10.1021/jo0013047 CCC: $20.00
Published on Web 01/18/2001

Scheme 1



Scheme 2



gives methyl ester (*P*)-**11**, which is hydrolyzed to carboxylic acid (*P*)-**12**. Then, (*P*)-**12** is converted to the acid chloride (*P*)-**3** by treatment of its potassium salt with thionyl chloride in dichloromethane at room temperature for 12 h. The acid chloride (*P*)-**3** can be purified by silica gel chromatography.

The coupling reaction of **1** with (*P*)-**3** is conducted in *N*-methylpyrrolidone (NMP)[8] without base at room temperature for 24 h giving protected (*P*,*P*)-[2 + 3]diamine (*P*,*P*)-**5** ($n = 1$) in a high yield. *N*,*N*-Dimethylacetamide or HMPA is not effective. Reactions employing bases such as triethylamine, 4-(*N*,*N*-dimethylamino)pyridine, pyridine, K_2CO_3, ethyldiisopropylamine, or 1,8-bis(dimethylamino)naphthalene in dichloromethane or toluene give the product in less than 20% yield. The protecting group is removed by the treatment with trimethylsilyl iodide[9] in dichloromethane at 0 °C giving (*P*,*P*)-[2 + 3]diamine (*P*,*P*)-**4** ($n = 3$) in 86% yield from **1** (Scheme 3). The compound (*P*,*P*)-**4** ($n = 3$) is then converted to (*P*,*P*,*P*,*P*)-[4 + 5]diamine, (*P*,*P*,*P*,*P*,*P*,*P*)-[6 + 7]diamine, and (*P*,*P*,*P*,*P*,*P*,*P*,*P*,*P*)-[8 + 9]diamine by the sequences of the coupling and the deprotection. Since one cycle of the operation extends two (*P*)-helicene units, this series of synthesis gives acyclic diamines possessing even numbers of (*P*)-**8** moiety. The diamines of the odd number series are synthesized starting from (*P*)-[1 + 2]diamine (*P*)-**2**, which is obtained by the reaction of (*P*)-**6** and excess **1**. Reaction of (*P*)-**2** with (*P*)-**3** give (*P*,*P*)-[3 + 4]-diamine (*P*,*P*)-**4** ($n = 4$), which is converted to (*P*,*P*,*P*,*P*,*P*)-[5 + 6]diamine, (*P*,*P*,*P*,*P*,*P*,*P*,*P*)-[7 + 8]diamine, and (*P*,*P*,*P*,*P*,*P*,*P*,*P*,*P*,*P*)-[9 + 10]diamine. Their structures are determined by spectroscopic method as well as elemental analysis. Molecular weights are determined by MALDI-TOF MS. Cyclization of (*P*,*P*....)-[($n - 1$) + n]diamines ($n = 2,3,4,5,6,7,8,9,10$) with (*P*)-**6** is conducted under high dilution conditions. A solution of (*P*)-**6** in NMP and a solution of (*P*,*P*....)-[($n - 1$) + n]diamines ($n = 2,3,4,5,6,7,8,9,10$) in NMP are simultaneously added over a period of 12 h to NMP at room temperature, and the mixture is stirred for 12 h giving (*P*,*P*....)-[$n + n$]-cycloamides ($n = 2,3,4,5,6,7,8,9,10$) in acceptable yields. The 180-membered ring compound (*P*,*P*,*P*,*P*,*P*,*P*,*P*,*P*,*P*,*P*)-[10 + 10]cycloamide with molecular weight of 6308 is obtained by this method.

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(8) NMP is used in the synthesis of polyamides. Examples, Kim, Y. H. *J. Am. Chem. Soc.* **1992**, *114*, 4947. Shiotani, A.; Kohda, M. *J. Appl. Polym. Sci.* **1997**, *63*, 865.

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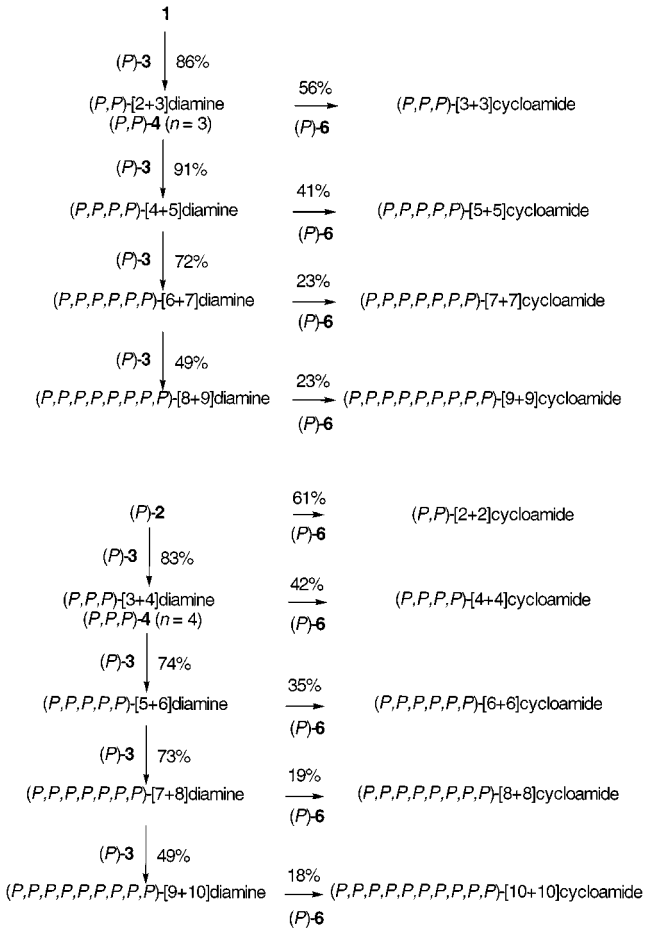
Scheme 3



Series of optically active cycloamides and their linear precursors being in hand, their spectroscopic behaviors are compared in regard to the "ring member number" and the "ring effect". The former treats the effect of the ring number, and the latter compares the cyclic and acyclic compounds. Such study was reported for synthetic cyclic polymers,[10] and here the cyclic oligomer is treated. ^{1}H NMR spectra of all the cycloamides show one sets of the benzo[*c*]phenanthrene protons. The chemical shifts of the cycloamides except (*P*,*P*)-[2 + 2]cycloamide are concentration dependent in $CDCl_3$, which may be due to aggregation in solution. Since the dependence is not observed in DMSO-d_6, the ^{1}H NMR comparison is conducted in this solvent to make the analysis simple. The chemical shifts of 4-H and 6-H at the benzo[*c*]phenanthrene moiety of the (*P*,*P*....)-[*n* + *n*]cycloamides, (*P*,*P*....)-**7**, (*n* = 1,2,3,4,5,6,7,8,9,10) as well as the (*P*,*P*....)-[(*n* − 1) + *n*]diamines, (*P*,*P*....)-**4**, (*n* = 2,3,4,5,6,7,8,9,10) are shown in Figure 1. While the chemical shifts of (*P*,*P*....)-**7** for *n* ≥ 4 are constant, the values are different for the compound with *n* = 1 to 3. It is also observed that the chemical shifts of the linear compounds are approximately constant, and are close to those of the higher cycloamides. The "ring effect" is therefore observed in the smaller compound than (*P*,*P*,*P*,*P*)-[4 + 4]cycloamide.

CD spectra of the cycloamides (*P*,*P*....)-**7** and diamines (*P*,*P*....)-**4** in $CHCl_3$ are summarized in Figures 2 and 3,

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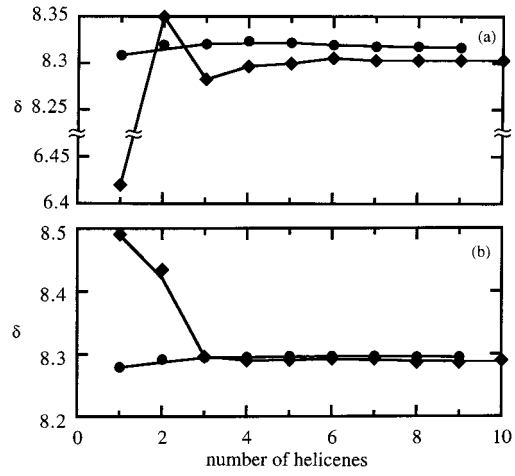

Figure 1. ^{1}H NMR (DMSO-d_6, 25 °C) chemical shifts of 6-H (a) and 4-H (b) at the benzo[*c*]phenanthrene moiety are plotted against the number of helicenes for (*P*,*P*....)-[*n* + *n*]cycloamides, (*P*,*P*....)-**7**, (*n* = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10) (♦) and (*P*,*P*....)-[(*n* − 1) + *n*]diamine, (*P*,*P*....)-**4**, (*n* = 2, 3, 4, 5, 6, 7, 8, 9, 10) (●) at the concentrations of 0.5 to 2.0 mM.

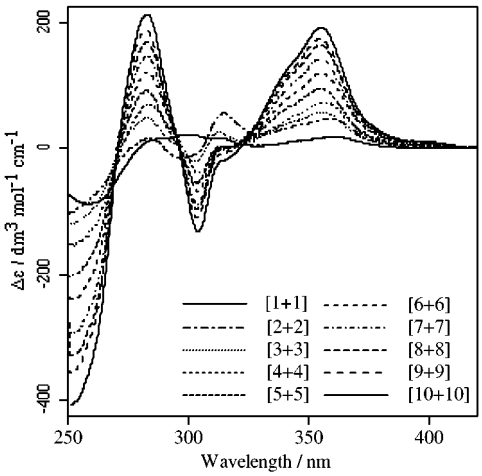

Figure 2. CD spectra ($CHCl_3$, 25 °C) of (*P*,*P*....)-[*n* + *n*]-cycloamide, (*P*,*P*....)-**7**, (*n* = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10) at the concentrations of 2.0 × 10^{-7} to 2.5 × 10^{-6} M except for (*P*)-**7** (*n* = 1) and (*P*,*P*)-**7** (*n* = 2), spectra of which were obtained at 1.4 × 10^{-5} and 1.0 × 10^{-5} M, respectively.

respectively, which are obtained at much lower concentrations compared to NMR. No concentration dependence of the spectra indicates that aggregation is negligible. (*P*,*P*....)-**7** of *n* ≥ 4 exhibit similar spectra, and the intensity increases in proportional to the number of helicene unit. CD spectra of the higher cycloamides are similar to (*P*,*P*....)-**4**, which suggests the similar structure of the higher cycloamide and the acyclic compounds. The "ring effect" can be seen more clearly when the values Δε/(number of helicene) at 305 nm for (*P*,*P*....)-**7** and (*P*,*P*....)-**4** are plotted against the number of helicene (Figure 4). The values of (*P*,*P*....)-**7** become constant at *n* ≥ 5, and are again close to those of the acyclic (*P*,*P*....)-**4**. Based on the results of the NMR and CD spectroscopy, it may reasonably be concluded that the large ring cycloamides (*n* ≥ 5) have flexible structures, and the "ring effect" appears for those for *n* ≤ 4 with the ring number of less than 72.

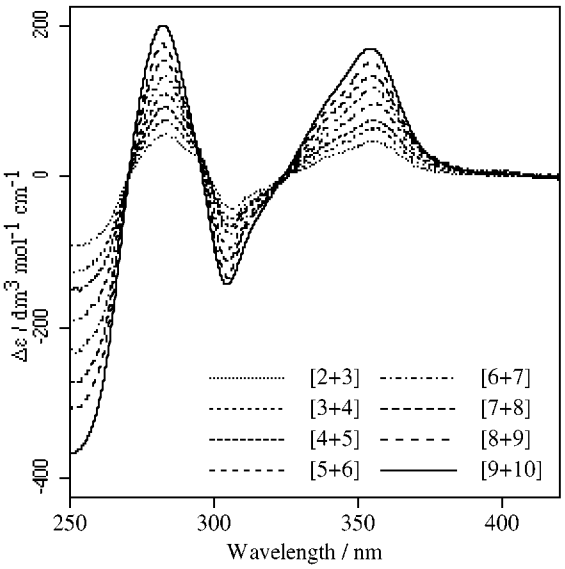

Figure 3. CD spectra ($CHCl_3$, 25 °C) of (*P*,*P*....)-[(*n* − 1) + *n*]diamine, (*P*,*P*....)-**4**, (*n* = 3, 4, 5, 6, 7, 8, 9, 10) at the concentrations of 2.5×10^{-6} to 8.0×10^{-6} M.

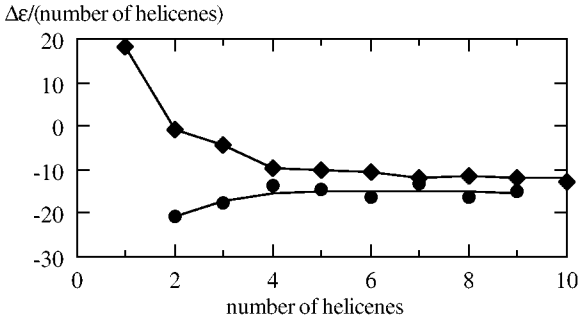

Figure 4. The values Δϵ/(number of helicenes) obtained from the CD ($CHCl_3$, 25 °C) absorption Δϵ at 305 nm are plotted against the number of helicenes for (*P*,*P*....)-[*n* + *n*]cycloamides, (*P*,*P*....)-**7**, (*n* = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10) (♦) and (*P*,*P*....)-[(*n* − 1) + *n*]diamines, (*P*,*P*....)-**4**, (*n* = 3, 4, 5, 6, 7, 8, 9, 10) (●).

Experimental Section

(*P*)-1-{3,5-Dimethyl-4-(benzyloxycarbonylamino)-phenyl}-1-{4-(8-chlorocarbonyl-1,12-dimethylbenzo[*c*]-phenanthrene-5-carbonylamino)-3,5-dimethylphenyl)cyclohexane, (*P*)-3. Potassium salt of (*P*)-**12** was prepared by mixing (*P*)-**12** (12 g, 15.3 mmol) in THF−MeOH (1:1, 150 mL) and 1.0 M KOH solution in MeOH (15.3 mL). After being stirred for 5 min, the solvents were removed, and the residue was dried at 80 °C for 2 days in vacuo. Under an argon atmosphere, to a solution of (*P*)-**12** potassium salt (410 mg, 0.50 mmol) in dichloromethane (5 mL) was added thionyl chloride (0.4 mL, 5.5 mmol), and the mixture was stirred at room temperature for 12 h. Solvents were evaporated in vacuo, and the residue was azeotropically dried twice with toluene (3 mL). The acid chloride (380 mg, 0.47 mmol, 94%) was purified by silica gel chromatography. $[\alpha]^{30}_D$ +231 (*c* 0.3, CH_2Cl_2). MS (FAB, NBA) *m*/*z* 802 ($M^+ + 1$). IR (CH_2Cl_2) 3413, 2936, 2861, 1753, 1731 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.46−1.64 (6H, m), 1.91 (3H, s), 1.92 (3H, s), 2.23 (6H, s), 2.23−2.30 (4H, m), 2.43 (6H, s), 5.18 (2H, s), 6.01 (1H, s), 7.02 (2H, s), 7.10 (2H, s), 7.30−7.44 (6H, m), 7.51 (1H, d, *J* = 7 Hz), 7.51 (1H, d, *J* = 7 Hz), 7.73 (1H, dd, *J* = 7, 8 Hz), 7.74 (1H, dd, *J* = 7, 8 Hz), 8.18 (1H, s), 8.47 (1H, d, *J* = 8 Hz), 8.74 (1H, d, *J* = 8 Hz), 8.94 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 19.2, 22.9, 23.2, 23.4, 26.3, 37.0, 45.4, 67.0, 122.4, 123.2, 123.4, 124.1, 127.0, 127.2, 128.1, 128.2, 128.5, 128.6, 128.7, 129.0, 129.1, 129.3, 129.7, 129.8, 130.8, 131.0, 131.1, 131.3, 131.9, 135.0, 135.0, 135.2, 135.3, 136.4, 137.0, 137.5, 147.1, 148.0, 154.3, 167.0, 167.3.

Typical Procedures for the Synthesis of Protected (*P*,*P*....)-[(*n* + 1) + (*n* + 2)]Diamine, (*P*,*P*....)-5. Under an argon atmosphere, to a 10 mM solution of (*P*,*P*,....)-[(*n* − 1) + *n*]diamine (*P*,*P*....)-**4** (0.04 mmol) in *N*-methylpyrrolidone (5 mL) was added (*P*)-**3** (0.12 mmol) in *N*-methylpyrrolidone (10 mL), and the mixture was stirred at room temperature for 12−24 h. Then water was added, and the resulting amorphous solid was collected in a Buchner funnel. The product was purified by alumina chromatography and GPC giving (*P*,*P*....)-**5**.

Typical Procedures for the Synthesis of (*P*,*P*....)-[(*n* − 1) + *n*]Diamine, (*P*,*P*....)-4. Under an argon atmosphere, to a 10 mM solution of (*P*,*P*....)-**5** (0.02 mmol) in dichloromethane (2 mL) was added trimethylsilyl iodide (0.04 × (*n* + 9) mmol), and the mixture was stirred at 0 °C for 6−12 h. The reaction was quenched by successively adding ethylenediamine (0.2 mL) in CH_2Cl_2 (2 mL) and water. After evaporating CH_2Cl_2, the resulting amorphous solid was diluted with chloroform. The organic layer was washed with saturated aqueous sodium sulfite, water, and brine and dried over sodium sulfate. Solvents were evaporated in vacuo, and the product was purified by alumina chromatography and GPC to give (*P*,*P*....)-**4**.

Protected (*P*,*P*,*P*)-[3 + 4]Diamine. Yield 83%. Mp >300 °C (toluene). Anal. Calcd for $C_{170}H_{168}N_8O_{10}$: C; 82.23, H; 6.82, N; 4.51%. Found: C; 82.31, H; 6.56, N; 4.62%. $[\alpha]^{26}_D$ +67 (*c* 1.0, $CHCl_3$). MS (FAB, NBA) Calcd for $^{12}C_{168}{}^{13}C_2H_{168}N_8O_{10}$: 2483.3. Found: 2484. UV−vis ($CHCl_3$) λ_{max} (ϵ) 304 nm (1.7×10^5). IR ($CHCl_3$) 3413, 3400−3200, 1717, 1668 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 10 mM) δ 1.40−1.70 (24H, m), 1.90 (18H, s), 2.18 (12H, s), 2.20−2.35 (16H, m), 2.38 (12H, s), 2.40 (24H, s), 5.12 (4H, s), 6.02 (2H, s), 7.01 (4H, s), 7.08 (4H, s), 7.15 (8H, s), 7.26−7.40 (10H, m), 7.43 (6H, t, *J* = 7 Hz), 7.48 (2H, s), 7.53 (4H, s), 7.60 (6H, t, *J* = 8 Hz), 8.04−8.11 (6H, m), 8.41 (6H, d, *J* = 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 10 mM) δ 18.7, 19.3, 19.3, 22.7, 22.9, 23.3, 26.3, 26.3, 37.0, 37.1, 45.4, 45.5, 67.0, 122.9, 124.0, 127.1, 127.1, 127.2, 127.3, 127.4, 128.2, 128.5, 129.4, 129.4, 130.0, 131.0, 131.0, 131.4, 134.4, 135.0, 135.0, 136.4, 137.1, 147.7, 154.3, 167.8, 167.8.

(*P*,*P*,*P*)-[3 + 4]Diamine, (*P*,*P*....)-4 (*n* = 4). Yield 100%. Mp >300 °C (toluene−methanol). Anal. Calcd for $C_{154}H_{156}N_8O_6$: C; 83.51, H; 7.10, N; 5.06%. Found: C; 83.19, H; 7.05, N; 4.69%. $[\alpha]^{26}_D$ +67 (*c* 0.55, $CHCl_3$). MS (FAB, NBA) Calcd for $^{12}C_{152}{}^{13}C_2H_{156}N_8O_6$: 2215.2. Found: 2215. UV−vis ($CHCl_3$) λ_{max} (ϵ) 302 nm (1.5×10^5). IR ($CHCl_3$) 3410, 3400−3200, 1667 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 20 mM) δ 1.40−1.65 (24H, m), 1.90 (18H, s), 2.12 (12H, s), 2.15−2.35 (16H, m), 2.38 (12H, s), 2.40 (24H, s), 3.40 (4H, br), 6.88 (4H, s), 7.08 (4H, s), 7.15 (8H, s), 7.40−7.45 (8H, m), 7.51 (2H, s), 7.54 (2H, s), 7.61 (6H, t, *J* = 8 Hz), 8.07 (4H, s), 8.09 (2H, s), 8.40 (6H, d, *J* = 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 20 mM) δ 18.2, 19.4, 23.1, 23.4, 26.6, 37.2, 37.3, 45.1, 45.6, 121.4, 122.7, 123.8, 127.0, 127.0, 127.2, 128.1, 128.3, 128.9, 129.1, 129.3, 129.8, 130.6, 131.0, 131.1, 134.1, 134.6, 134.9, 136.8, 137.4 139.9, 147.6, 148.7, 167.6. CD ($CHCl_3$) λ_{ext} ($\Delta\epsilon$) 356 nm (+65), 306 (−56), 283 (+78).

Protected (*P*,*P*,*P*,*P*)-[5 + 6]Diamine. Yield 87%. Mp >300 °C (toluene−methanol). Anal. Calcd for $C_{258}H_{252}N_{12}O_{14}\cdot 3H_2O$: C; 81.57, H; 6.85, N; 4.42%. Found: C; 81.53, H; 6.89, N; 4.44%. Found: C; 81.74, H; 6.92, N; 4.36%. $[\alpha]^{28}_D$ +64 (*c* 1.1, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{255}{}^{13}C_3H_{252}N_{12}O_{14}$+Na: 3767.9. Found: 3769. UV−vis ($CHCl_3$) λ_{max} (ϵ) 302 nm (2.5×10^5). IR ($CHCl_3$) 3412, 3400−3200, 1700, 1668 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 7 mM) δ 1.40−1.70 (36H, m), 1.91 (30H, s), 2.20 (12H, s), 2.20−2.40 (24H, m), 2.41 (60H, s), 5.13 (4H, s), 6.00 (2H, br), 7.00 (4H, s), 7.08 (4H, s), 7.15 (16H, s), 7.25−7.40 (10H, m), 7.40−7.55 (20H, m), 7.55−7.70 (10H, m), 8.08 (10H, s), 8.35−8.50 (10H, m). ^{13}C NMR (100 MHz, $CDCl_3$, 7 mM) δ 18.8, 19.4, 23.0, 23.4, 26.4, 37.2, 45.5, 45.6, 66.7, 122.7, 123.9, 126.9, 127.1, 127.2, 127.8, 127.9, 128.0, 128.3, 129.2, 129.3, 129.8, 131.0, 131.1, 134.1, 134.2, 134.8, 134.9, 135.0, 135.1, 136.3, 136.8, 147.6, 167.6.

(*P,P,P,P,P*)-[5 + 6]Diamine. Yield 85%. Mp >300 °C (toluene−methanol). Anal. Calcd for $C_{242}H_{240}N_{12}O_{10}\cdot 6H_2O$: C; 81.08, H; 7.09, N; 4.69%. Found: C; 81.18, H; 6.98, N; 5.14%. Found: C; 81.01, H; 6.83, N; 5.08%. Found: C; 80.88, H; 6.99, N; 4.73%. $[\alpha]^{28}_D$ +64 (*c* 2.0, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{239}{}^{13}C_3H_{240}N_{12}O_{10}$: 3476.9. Found: 3478. UV−vis ($CHCl_3$) λ_{max} (ϵ) 303 nm (2.5×10^5). IR ($CHCl_3$) 3411, 3400−3200, 1666 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 2 mM) δ 1.40−1.70 (36H, m), 1.90 (30H, s), 2.12 (12H, s), 2.20−2.35 (24H, m), 2.38 (12H, s), 2.40 (48H, s), 3,40 (4H, br), 6.88 (4H, s), 7.08 (4H, s), 7.15 (16H, s), 7.40−7.55 (20H, m), 7.55−7.70 (10H, m), 8.05−8.10 (10H, m), 8.35−8.45 (10H, m). ^{13}C NMR (100 MHz, $CDCl_3$, 2 mM) δ 18.1, 19.3, 23.1, 23.3, 26.5, 37.3, 45.0, 45.6, 121.3, 122.7, 123.8, 126.9, 127.1, 128.2, 129.0, 129.2, 129.7, 130.6, 131.0, 134.0, 134.5, 134.9, 136.7, 137.3, 139.8, 147.5, 148.7, 167.5. CD ($CHCl_3$) λ_{ext} ($\Delta\epsilon$) 356 nm (+97), 306 (−77), 284 (+110).

Protected (*P,P,P,P,P,P*)-[7 + 8]Diamine. Yield 86%. Mp >300 °C (toluene−methanol). Anal. Calcd for $C_{346}H_{336}N_{16}O_{18}$: C; 83.00, H; 6.76, N; 4.48%. Found: C; 83.20, H; 6.94, N; 4.29%. $[\alpha]^{21}_D$ +62 (*c* 0.46, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{342}{}^{13}C_4H_{336}N_{16}O_{18}$+Na: 5029.6. Found: 5029. UV−vis ($CHCl_3$) λ_{max} (ϵ) 303 nm (3.1×10^5). IR (KBr) 3400−3200, 1720, 1660 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6 at 90 °C) δ 1.40−1.65 (48H, m), 1.93 (42H, s), 2.14 (12H, s), 2.20−2.35 (32H, m), 2.36 (12H, s), 2.40 (72H, s), 5.09 (4H, s), 7.04 (4H, s), 7.10 (4H, s), 7.17 (24H, s), 7.25−7.40 (12H, m), 7.50−7.55 (14H, m), 7.69 (14H, t, *J* = 7 Hz), 8.28 (14H, br), 8.36 (14H, d, *J* = 8 Hz), 9.77 (14H, br). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 19.4, 23.0, 23.1, 23.4, 26.4, 26.5, 37.2, 45.5, 45.6, 67.0, 122.8, 123.9, 126.9, 127.2, 128.0, 128.4, 129.2, 129.3, 129.8, 131.0, 131.2, 134.2, 134.8, 134.9, 135.0, 136.9, 147.6, 167.6.

(*P,P,P,P,P,P*)-[7 + 8]Diamine. Yield 85%. Mp >300 °C (toluene−methanol). Anal. Calcd for $C_{330}H_{324}N_{16}O_{14}\cdot 10H_2O$: C; 80.59, H; 7.05, N; 4.56%. Found: C; 80.67, H; 6.98, N; 4.35%. Found: C; 80.94, H; 7.14, N; 4.39%. Found: C; 80.70, H; 7.03, N; 4.22%. $[\alpha]^{24}_D$ +67 (*c* 1.7, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{326}{}^{13}C_4H_{324}N_{16}O_{14}$: 4738.5. Found: 4738. UV−vis ($CHCl_3$) λ_{max} (ϵ) 303 nm (3.3×10^5). IR (KBr) 3450−3150, 1716, 1654 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6 at 90 °C) δ 1.45−1.65 (48H, m), 1.93 (42H, s), 2.07 (12H, s), 2.10−2.30 (16H, m), 2.30−2.38 (28H, m), 2.40 (72H, s), 4.10 (4H, br), 6.80 (4H, s), 7.05 (4H, s), 7.17 (24H, s), 7.52 (14H, d, *J* = 7 Hz), 7.69 (14H, t, *J* = 8 Hz), 8.21 (2H, s), 8.27 (2H, s), 8.28 (10H, s), 8.33−8.40 (14H, m), 9.70−9.80 (14H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2, 19.4, 23.1, 23.4, 26.5, 26.6, 37.3, 37.3, 45.1, 45.6, 121.4, 122.7, 123.8, 125.1, 127.0, 127.0, 127.1, 128.1, 128.3, 128.9, 129.1, 129.3, 129.8, 130.6, 131.0, 131.1, 134.1, 134.2, 134.6, 134.9, 136.8, 137.4, 139.9, 147.6, 148.8, 167.6. CD ($CHCl_3$) λ_{ext} ($\Delta\epsilon$) 356 nm (+126), 305 (−132), 283 (+136).

Protected (*P,P,P,P,P,P,P,P*)-[9 + 10]Diamine. Yield 68%. Mp >300 °C (toluene−methanol). Anal. Calcd for $C_{434}H_{420}N_{20}O_{22}\cdot 9H_2O$: C; 81.06, H; 6.87, N; 4.36%. Found: C; 80.87, H; 7.21, N; 4.22%. Found: C; 81.25, H; 7.11, N; 4.22%. Found: C; 81.09, H; 7.12, N; 4.33%. $[\alpha]^{21}_D$ +68 (*c* 1.0, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{429}{}^{13}C_5H_{420}N_{20}O_{22}$: 6268.2. Found: 6269. UV−vis ($CHCl_3$) λ_{max} (ϵ) 303 nm (4.1×10^5). IR ($CHCl_3$) 3411, 3350−3150, 1731, 1665 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6 at 90 °C) δ 1.40−1.65 (60H, m), 1.93 (54H, s), 2.14 (12H, s), 2.20−2.37 (52H, m), 2.40 (96H, s), 5.09 (4H, s), 7.04 (4H, s), 7.10 (4H, s), 7.17 (32H, s), 7.25−7.37 (12H, m), 7.52 (18H, d, *J* = 7 Hz), 7.69 (18H, t, *J* = 8 Hz), 8.28 (18H, br), 8.36 (18H, d, *J* = 8 Hz), 9.77 (18H, br). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 19.3, 23.0, 23.3, 26.4, 37.1, 45.5, 45.6, 66.9, 122.8, 124.0, 127.0, 127.2, 128.0, 128.4, 129.2, 129.4, 129.9, 131.1, 131.2, 134.2, 135.0, 136.9, 147.7, 167.9.

(*P,P,P,P,P,P,P,P*)-[9 + 10]Diamine. Yield 72%. Mp >300 °C (toluene−methanol). Anal. Calcd for $C_{418}H_{408}N_{20}O_{18}\cdot 14H_2O$: C; 80.30, H; 7.03, N; 4.48%. Found: C; 80.27, H; 7.19, N; 4.36%. Found: C; 80.03, H; 7.31, N; 4.31%. Found: C; 80.40, H; 6.83, N; 4.31%. $[\alpha]^{25}_D$ +75 (*c* 1.4, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{413}{}^{13}C_5H_{408}N_{20}O_{18}$: 6000.2. Found: 6001. UV−vis ($CHCl_3$) λ_{max} (ϵ) 303 nm (4.0×10^5). IR ($CHCl_3$) 3410, 3350−3150, 1666 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6 at 90 °C) δ 1.45−1.65 (60H, m), 1.92 (54H, s), 2.07 (12H, s), 2.10−2.37 (52H, m), 2.39 (96H, s), 4.07 (4H, br), 6.80 (4H, s), 7.04 (4H, s), 7.17 (32H, s), 7.52 (18H, d, *J* = 7 Hz), 7.69 (18H, t, *J* = 8 Hz), 8.28 (18H, s), 8.36 (18H, d, *J* = 8 Hz), 9.76 (18H, br). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 19.4, 23.1, 23.4, 26.5, 37.3, 45.1, 45.6, 66.9, 121.4, 122.7, 123.8, 126.9, 127.1, 128.3, 129.1, 129.3, 129.7, 131.1, 131.1, 134.1, 134.6, 134.9, 136.8, 137.4, 139.9, 147.6, 148.8, 167.6. CD ($CHCl_3$) λ_{ext} ($\Delta\epsilon$) 356 nm (+165), 305 (−133), 283 (+194).

Protected (*P,P*)-[2 + 3]Diamine, (*P,P*)-5 (*n* = 1). Yield 94%. Mp >300 °C (toluene). Anal. Calcd for $C_{126}H_{126}N_6O_8$: C; 81.70, H; 6.86, N; 4.54%. Found: C; 82.31, H; 6.56, N; 4.62%. $[\alpha]^{23}_D$ +59 (*c* 0.69, $CHCl_3$). MS (FAB, NBA) Calcd for $^{12}C_{125}{}^{13}C_1H_{126}N_6O_8$: 1852.0. Found: 1852. UV−vis ($CHCl_3$) λ_{max} (ϵ) 304 nm (9.6×10^4). IR (KBr) 3500−3200, 1717, 1661 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 28 mM) δ 1.40−1.70 (18H, m), 1.84 (6H, s), 1.85 (6H, s), 2.14 (12H, s), 2.20−2.30 (8H, m), 2.34 (24H, s), 5.06 (4H, s), 6.08 (2H, s), 7.00 (4H, s), 7.08 (4H, s), 7.15 (4H, s), 7.26−7.35 (10H, m), 7.38 (4H, d, *J* = 7 Hz), 7.53 (2H, t, *J* = 7 Hz), 7.55 (2H, t, *J* = 7 Hz), 7.60 (2H, br), 7.62 (2H, br), 8.00 (2H, s), 8.01 (2H, s), 8.35 (2H, d, *J* = 8 Hz), 8.37 (2H, d, *J* = 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 28 mM) δ 18.7, 19.3, 22.9, 23.3, 26.4, 37.1, 45.4, 45.6, 66.8, 122.6, 123.8, 126.8, 127.0, 127.1, 127.8, 127.9, 128.2, 128.3, 129.0, 129.2, 129.7, 130.9, 130.9, 131.0, 134.0, 134.8, 134.9, 135.0, 136.2, 136.7, 146.9, 147.5, 154.1, 167.5.

(*P,P*)-[2 + 3]Diamine, (*P,P*)-4 (*n* = 3). Yield 91%. Mp >300 °C (toluene). Anal. Calcd for $C_{110}H_{114}N_6O_4$: C; 83.40, H; 7.25, N; 5.31%. Found: C; 82.93, H; 7.45, N; 5.27%. $[\alpha]^{26}_D$ +68 (*c* 1.1, $CHCl_3$). MS (FAB, NBA) Calcd for $^{12}C_{109}{}^{13}C_1H_{114}N_6O_4$: 1583.9. Found: 1585. UV−vis ($CHCl_3$) λ_{max} (ϵ) 303 nm (7.6×10^5). IR (KBr) 3382, 3280, 1657 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 40 mM) δ 1.40−1.70 (18H, m), 1.93 (12H, s), 2.15 (12H, s), 2.20−2.35 (8H, m), 2.40 (12H, s), 2.42 (12H, s), 3.43(4H, br), 6.88 (4H, s), 7.08 (4H, s), 7.15 (4H, s), 7.43 (2H, s), 7.46 (4H, d, *J* = 8 Hz), 7.48 (2H, s), 7.64 (2H, t, *J* = 8 Hz), 7.64 (2H, t, *J* = 7 Hz), 8.11 (4H, s), 8.43 (2H, d, *J* = 8 Hz), 8.44 (2H, d, *J* = 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 40 mM) δ 18.2, 19.4, 19.4, 23.1, 23.4, 26.6, 37.2, 37.3, 45.1, 45.6, 121.4, 122.8, 123.8, 123.9, 127.0, 127.0, 127.2, 127.2, 128.4, 129.2, 129.3, 129.8, 130.5, 130.9, 131.2, 134.2, 134.3, 134.6, 134.9, 136.9, 137.3, 139.9, 147.5, 148.9, 167.5, 167.6. CD ($CHCl_3$) λ_{ext} ($\Delta\epsilon$) 356 nm (+47), 307 (−42), 284 (+57).

Protected (*P,P,P,P*)-[4 + 5]Diamine. Yield 97%. Mp >300 °C (toluene−methanol). Anal. Calcd for $C_{214}H_{210}N_{10}O_{12}$: C; 82.54, H; 6.79, N; 4.50%. Found: C; 82.49, H; 7.22, N; 4.41%. $[\alpha]^{28}_D$ +54 (*c* 0.83, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{211}{}^{13}C_3H_{210}N_{10}O_{12}$+Na: 3137.6. Found: 3138. UV−vis ($CHCl_3$) λ_{max} (ϵ) 302 nm (1.8×10^5). IR (KBr) 3450−3150, 1718, 1654 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 7 mM) δ 1.40−1.70 (30H, m), 1.92 (6H, s), 1.93 (18H, s), 2.19 (12H, s), 2.20−2.38 (20H, m), 2.39 (12H, s), 2.42 (36H, s), 5.13 (4H, s), 6.00 (2H, br), 7.00 (4H, s), 7.08 (4H, s), 7.15 (12H, s), 7.25−7.40 (10H, m), 7.40−7.50 (20H, m), 7.60−7.70 (10H, m), 8.05−8.15 (10H, m), 8.40−8.50 (10H, m). ^{13}C NMR (100 MHz, $CDCl_3$, 7 mM) δ 18.7, 19.3, 23.0, 23.3, 26.4, 37.1, 45.4, 45.6, 66.9, 122.7, 123.8, 126.8, 127.1, 127.8, 128.2, 128.3, 129.1, 129.2, 129.7, 130.9, 131.0, 134.0, 134.8, 134.9, 136.1, 136.7, 147.0, 147.5, 154.3, 167.5.

(*P,P,P,P*)-[4 + 5]Diamine. Yield 94%. Mp >300 °C (toluene−methanol). Anal. Calcd for $C_{198}H_{198}N_{10}O_8\cdot 6H_2O$: C; 80.51, H; 7.17, N; 4.74%. Found: C; 80.59, H; 6.83, N; 4.96%. Found: C; 80.76, H; 6.95, N; 4.79%. $[\alpha]^{25}_D$ +64 (*c* 2.0, $CHCl_3$). MS (FAB, NBA) Calcd for $^{12}C_{196}{}^{13}C_2H_{198}N_{10}O_8$: 2845.5. Found: 2846. UV−vis ($CHCl_3$) λ_{max} (ϵ) 302 nm (2.1×10^5). IR (KBr) 3400−3100, 1654 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 5 mM) δ 1.40−1.70 (30H, m), 1.90 (24H, s), 2.13 (12H, s), 2.20−2.35 (20H, m), 2.38 (12H, s), 2.41 (36H, s), 3,42 (4H, br), 6.87 (4H, s), 7.07 (4H, s), 7.15 (12H, s), 7.40−7.55 (16H, m), 7.55−7.65 (8H, m), 8.05−8.15 (8H, m), 8.35−8.45 (8H, m). ^{13}C NMR (100 MHz, $CDCl_3$, 5 mM) δ 18.1, 19.3, 23.1, 23.3, 26.5, 37.3, 45.0, 45.6, 121.3, 122.6, 123.7, 126.9, 127.1, 128.2, 129.0, 129.2, 129.7, 130.6, 131.0, 134.0, 134.5, 134.9, 136.7, 137.3, 139.8, 147.5, 148.7, 167.5. CD ($CHCl_3$) λ_{ext} ($\Delta\epsilon$) 356 nm (+76), 306 (−55), 284 (+86).

Protected (*P,P,P,P,P,P*)-[6 + 7]Diamine. Yield 86%. Mp >300 °C (toluene−methanol). Anal. Calcd for $C_{302}H_{294}N_{14}O_{16}$: C; 82.89, H; 6.77, N; 4.48%. Found: C; 82.91, H; 7.10, N; 4.36%. $[\alpha]^{20}_D$ +66 (*c* 0.75, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{299}{}^{13}C_3H_{294}N_{14}O_{16}$: 4375.3. Found: 4376. UV−vis ($CHCl_3$) λ_{max} (ϵ) 302 nm (3.0×10^5). IR (KBr) 3450−3150, 1710, 1660 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6 at 90 °C) δ 1.40−1.65 (42H, m), 1.94 (36H, s), 2.15 (12H, s), 2.20−2.37 (28H, m), 2.37 (12H, s), 2.41 (60H, s), 5.10, (4H, s), 7.04 (4H, s), 7.11 (4H, s), 7.18 (20H, s), 7.25−7.40 (10H, m), 7.53 (12H, d, J = 7 Hz), 7.70 (12H, t, J = 8 Hz), 8.28 (2H, s), 8.29 (10H, s), 8.34−8.40 (12H, m), 9.74 (2H, br), 9.77 (10H, br). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.8, 19.4, 23.0, 23.4, 26.5, 37.2, 45.5, 45.6, 66.9, 122.7, 123.9, 126.9, 127.0, 127.1, 128.0, 128.0, 128.4, 129.2, 129.3, 129.8, 131.0, 131.1, 134.1, 134.8, 134.9, 136.2, 136.9, 147.0, 147.6, 154.3, 167.6.

(*P,P,P,P,P,P*)-[6 + 7]Diamine. Yield 84%. Mp >300 °C (toluene−methanol). Anal. Calcd for $C_{286}H_{282}N_{14}O_{12}\cdot 7H_2O$: C; 81.14, H; 7.05, N; 4.63%. Found: C; 81.01, H; 7.19, N; 4.79%. Found: C; 81.13, H; 7.35, N; 4.90%. $[\alpha]^{26}_D$ +72 (*c* 0.87, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{283}{}^{13}C_3H_{282}N_{14}O_{12}$: 4107.2. Found: 4106. UV−vis ($CHCl_3$) λ_{max} (ϵ) 303 nm (3.0×10^5). IR (KBr) 3400−3100, 1654 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 1.40−1.60 (42H, m), 1.89 (36H, s), 2.04 (12H, s), 2.10−2.35 (40H, m), 2.38 (72H, s), 4.30 (4H, br), 6.78 (4H, s), 7.04 (4H, s), 7.18 (20H, s), 7.54 (12H, d, J = 7 Hz), 7.71 (12H, t, J = 8 Hz), 8.26−8.35 (24H, m), 10.02 (2H, br), 10.04 (10H, br). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2, 19.5, 23.1, 23.5, 26.5, 26.6, 37.2, 37.4, 45.1, 45.6, 121.4, 122.8, 123.9, 127.0, 127.0, 127.2, 128.4, 129.2, 129.4, 129.8, 130.6, 131.0, 131.2, 134.2, 134.6, 134.9, 136.9, 137.4, 139.9, 147.6, 148.9, 167.6. CD ($CHCl_3$) λ_{ext} ($\Delta\epsilon$) 356 nm (+120), 305 (−97), 284 (+132).

Protected (*P,P,P,P,P,P,P,P*)-[8 + 9]Diamine. Yield 70%. Mp >300 °C (toluene−methanol). Anal. Calcd for $C_{390}H_{378}N_{18}O_{20}\cdot 7H_2O$: C; 81.27, H; 6.86, N; 4.37%. Found: C; 81.27, H; 7.20, N; 4.20%. Found: C; 81.26, H; 7.18, N; 4.08%. Found: C; 81.13, H; 7.19, N; 4.23%. $[\alpha]^{23}_D$ +76 (*c* 0.36, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{386}{}^{13}C_4H_{378}N_{18}O_{20}$+K: 5676. Found: 5677. UV−vis ($CHCl_3$) λ_{max} (ϵ) 303 nm (3.9×10^5). IR ($CHCl_3$) 3406, 3400−3150, 1730, 1671 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6 at 90 °C) δ 1.40−1.65 (54H, m), 1.93 (48H, s), 2.14 (12H, s), 2.20−2.37 (48H, m), 2.39 (84H, s), 5.09, (4H, s), 7.04 (4H, s), 7.10 (4H, s), 7.17 (28H, s), 7.25−7.37 (10H, m), 7.52 (16H, d, J = 7 Hz), 7.69 (16H, t, J = 8 Hz), 8.28 (16H, s), 8.36 (16H, d, J = 8 Hz), 9.77 (16H, br). ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.7, 19.3, 22.9, 23.0, 23.3, 26.4, 26.4, 37.1, 37.1, 45.4, 45.5, 66.5, 122.8, 122.8, 124.0, 127.0, 127.2, 127.3, 128.1, 128.5, 129.0, 129.1, 129.3, 129.4, 129.9, 131.1, 131.2, 131.3, 134.3, 135.0, 135.1, 136.4, 137.0, 147.0, 147.8, 154.3, 167.8.

(*P,P,P,P,P,P,P,P*)-[8 + 9]Diamine. Yield 70%. Mp >300 °C (toluene−methanol). Anal. Calcd for $C_{374}H_{366}N_{18}O_{16}\cdot 12H_2O$: C; 80.43, H; 7.04, N; 4.51%. Found: C; 80.39, H; 7.14, N; 4.34%. Found: C; 80.57, H; 7.25, N; 4.46%. Found: C; 81.20, H; 7.19, N; 4.37%. $[\alpha]^{26}_D$ +48 (*c* 0.50, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{370}{}^{13}C_4H_{366}N_{18}O_{16}$: 5368.8. Found: 5369. UV−vis ($CHCl_3$) λ_{max} (ϵ) 303 nm (3.5×10^5). IR (KBr) 3411, 3400−3150, 1668 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6 at 90 °C) δ 1.40−1.65 (54H, m), 1.93 (48H, s), 2.07 (12H, s), 2.20−2.37 (48H, m), 2.39 (84H, s), 4.12, (4H, br), 6.80 (4H, s), 7.05 (4H, s), 7.17 (28H, s), 7.52 (16H, d, J = 7 Hz), 7.69 (16H, t, J = 8 Hz), 8.27 (2H, s), 8.28 (14H, s), 8.33−8.40 (16H, m), 9.77 (16H, br). ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.0, 19.2, 23.0, 23.3, 26.4, 26.4, 37.1, 37.2, 45.0, 45.6, 121.5, 122.8, 124.0, 127.1, 127.1, 127.3, 128.2, 128.4, 129.0, 129.3, 129.4, 129.9, 130.6, 131.1, 131.3, 134.3, 134.7, 135.1, 137.0, 137.5, 140.1, 147.8, 148.9, 167.8. CD ($CHCl_3$) λ_{ext} ($\Delta\epsilon$) 356 nm (+150), 305 (−132), 283 (+180).

Typical Procedures for Cyclization. A solution of (*P*)-**6** (0.01 mmol) in *N*-methylpyrrolidone (10 mL) was charged in a syringe. Also charged was 1 mM solution of (*P,P*....)-[(*n* − 1) + *n*]diamine, (*P,P*....)-**4** (0.01 mmol) in *N*-methylpyrrolidone (10 mL) in another syringe. Under an argon atmosphere, these solutions were simultaneously dropped over 12 h to *N*-methylpyrrolidone (30 mL, total 0.2 mM of the substrate) at room temperature. After standing for 12 h at the temperature, the reaction was quenched with water. The resulting amorphous solid was collected in a Buchner funnel. The product was purified by alumina chromatography and GPC giving (*P,P*....)-[*n* + *n*]cycloamide, (*P,P*....)-**7**. Analytical sample was obtained by recrystallization from toluene−ethanol.

(*P,P,P,P,P*)-[5 + 5]Cycloamide. Yield 41%. Mp >300 °C. Anal. Calcd for $C_{220}H_{210}N_{10}O_{10}\cdot 7H_2O$: C; 80.56, H; 6.88, N; 4.27%. Found: C; 80.36, H; 6.90, N; 4.36%. Found: C; 80.85, H; 7.08, N; 4.38%. $[\alpha]^{27}_D$ +112 (*c* 0.45, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{218}{}^{13}C_2H_{210}N_{10}O_{10}$: 3153.6. Found: 3155. UV−vis ($CHCl_3$) λ_{max} (ϵ) 302 nm (2.9×10^5). IR ($CHCl_3$) 3411, 3400−3200, 1666 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 2 mM) δ 1.50−1.70 (30H, m), 1.88 (30H, s), 2.20−2.50 (20H, m), 2.40 (60H, s), 7.18 (20H, s), 7.42 (10H, d, J = 7 Hz), 7.59 (10H, s), 7.61 (10H, t, J = 8 Hz), 8.00 (10H, s), 8.36 (10H, d, J = 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 2 mM) δ 19.4, 23.1, 23.4, 26.5, 37.2, 45.6, 122.8, 123.8, 127.2, 127.2, 128.5, 129.2, 129.2, 129.9, 131.0, 131.2, 134.2, 135.0, 136.9, 147.8, 167.7. CD ($CHCl_3$) λ_{ext} ($\Delta\epsilon$) 355 nm (+96), 302 (−54), 282 (+92).

(*P,P,P,P,P,P*)-[6 + 6]Cycloamide. Yield 35%. Mp >300 °C. Anal. Calcd for $C_{264}H_{252}N_{12}O_{12}\cdot 9H_2O$: C; 80.33, H; 6.89, N; 4.26%. Found: C; 80.26, H; 6.68, N; 4.43%. Found: C; 80.58, H; 7.01, N; 4.37%. $[\alpha]^{27}_D$ +105 (*c* 0.6, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{261}{}^{13}C_3H_{252}N_{12}O_{12}$: 3784.9. Found: 3785. UV−vis ($CHCl_3$) λ_{max} (ϵ) 302 nm (3.3×10^5). IR ($CHCl_3$) 3411, 3400−3200, 1667 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 3 mM) δ 1.50−1.70 (36H, m), 1.88 (36H, s), 2.20−2.50 (24H, m), 2.40 (72H, s), 7.14 (24H, s), 7.41 (12H, d, J = 7 Hz), 7.44 (12H, s), 7.60 (12H, t, J = 8 Hz), 8.02 (12H, s), 8.38 (12H, d, J = 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 3 mM) δ 19.4, 23.0, 23.4, 26.4, 37.1, 45.6, 122.8, 124.0, 127.2, 127.3, 128.5, 129.3, 129.3, 129.9, 131.0, 131.3, 134.2, 135.0, 137.0, 147.7, 167.6. CD ($CHCl_3$) λ_{ext} ($\Delta\epsilon$) 355 nm (+120), 302 (−68), 282 (+122).

(*P,P,P,P,P,P,P*)-[7 + 7]Cycloamide. Yield 23%. Mp >300 °C. Anal. Calcd for $C_{308}H_{294}N_{14}O_{14}\cdot 10H_2O$: C; 80.49, H; 6.89, N; 4.27%. Found: C; 80.47, H; 7.10, N; 4.41%. Found: C; 80.70, H; 7.11, N; 4.64%. $[\alpha]^{27}_D$ +120 (*c* 0.2, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{305}{}^{13}C_3H_{294}N_{14}O_{14}$: 4415.3. Found: 4416. UV−vis ($CHCl_3$) λ_{max} (ϵ) 301 nm (3.9×10^5). IR ($CHCl_3$) 3410, 3400−3200, 1666 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 1 mM) δ 1.50−1.70 (42H, m), 1.88 (42H, s), 2.20−2.50 (28H, m), 2.34 (84H, s), 7.15 (28H, s), 7.39 (14H, d, J = 7 Hz), 7.49 (14H, s), 7.57 (14H, t, J = 8 Hz), 8.00 (14H, s), 8.35 (14H, d, J = 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 1 mM) δ 19.4, 23.1, 23.4, 26.5, 37.2, 45.6, 122.8, 123.9, 127.1, 127.2, 128.4, 129.2, 129.2, 129.8, 131.0, 131.2, 134.1, 134.9, 136.8, 147.6, 167.6. CD ($CHCl_3$) λ_{ext} ($\Delta\epsilon$) 355 nm (+142), 303 (−89), 283 (+147).

(*P,P,P,P,P,P,P,P*)-[8 + 8]Cycloamide. Yield 19%. Mp >300 °C. Anal. Calcd for $C_{352}H_{336}N_{16}O_{16}\cdot 10H_2O$: C; 80.89, H; 6.87, N; 4.29%. Found: C; 80.89, H; 7.13, N; 4.45%. Found: C; 81.22, H; 7.04, N; 4.61%. $[\alpha]^{27}_D$ +92 (*c* 0.55, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{348}{}^{13}C_4H_{336}N_{16}O_{16}$: 5046.6. Found: 5046. UV−vis ($CHCl_3$) λ_{max} (ϵ) 302 nm (4.0×10^5). IR ($CHCl_3$) 3410, 3400−3200, 1666 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 2 mM) δ 1.50−1.70 (48H, m), 1.83 (48H, s), 2.20−2.50 (32H, m), 2.33 (96H, s), 7.14 (32H, s), 7.37 (16H, d, J = 7 Hz), 7.50−7.60 (32H, m), 8.00 (16H, s), 8.32 (16H, d, J = 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 2 mM) δ 19.4, 23.1, 23.4, 26.5, 37.2, 45.6, 122.7, 123.9, 127.1, 127.1, 128.3, 129.2, 129.2, 129.8, 131.0, 131.1, 134.1, 134.9, 136.8, 147.6, 167.6. CD ($CHCl_3$) λ_{ext} ($\Delta\epsilon$) 355 nm (+165), 302 (−99), 283 (+170).

(*P,P,P,P,P,P,P,P,P*)-[9 + 9]Cycloamide. Yield 23%. Mp >300 °C. Anal. Calcd for $C_{396}H_{378}N_{18}O_{18}\cdot 12H_2O$: C; 80.70, H; 6.88, N; 4.28%. Found: C; 80.62, H; 7.33, N; 4.47%. Found: C; 80.65, H; 7.34, N; 4.44%. $[\alpha]^{27}_D$ +92 (*c* 0.55, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{392}{}^{13}C_4H_{378}N_{18}O_{18}$: 5676.9. Found: 5679. UV−vis ($CHCl_3$) λ_{max} (ϵ) 301 nm (4.3×10^5). IR ($CHCl_3$) 3410, 3400−3200, 1665 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 1 mM) δ 1.50−1.70 (54H, m), 1.83 (54H, s), 2.20−2.50 (36H, m), 2.33 (108H, s), 7.14 (36H, s), 7.37 (18H, d, J = 7 Hz), 7.50−7.60 (36H, m), 7.98 (18H, s), 8.31 (18H, d, J = 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 1 mM) δ 19.4, 23.1, 23.4, 26.5, 37.2, 45.6, 122.7, 123.9, 127.1, 127.1, 128.3, 129.2, 129.2, 129.8, 131.0, 131.1, 134.1, 134.9, 136.8, 147.6, 167.6. CD ($CHCl_3$) λ_{ext} ($\Delta\epsilon$) 355 nm (+175), 302 (−108), 283 (+188).

(*P,P,P,P,P,P,P,P,P,P*)-[10 + 10]Cycloamide. Yield 18%. Mp >300 °C. Anal. Calcd for $C_{440}H_{420}N_{20}O_{20}\cdot 14H_2O$: C; 80.56, H; 6.88, N; 4.27%. Found: C; 80.25, H; 6.98, N; 4.52%. Found: C; 80.88, H; 6.98, N; 4.61%. $[\alpha]^{27}_D$ +72 (*c* 0.45, $CHCl_3$). MS (TOF, dithranol) Calcd for $^{12}C_{435}{}^{13}C_5H_{420}N_{20}O_{20}$: 6308.2. Found: 6309. UV−vis ($CHCl_3$) λ_{max} (ϵ) 301 nm (4.5×10^5). IR ($CHCl_3$) 3410, 3400−3200, 1667 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 1 mM) δ 1.50−1.70 (60H, m), 1.83 (60H, s), 2.20−2.50 (40H, m), 2.32 (120H, s), 7.13 (40H, s), 7.37 (20H, d, J = 7 Hz), 7.50−7.60 (40H, m), 7.98 (20H, s), 8.30 (20H, d, J = 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 1 mM) δ 19.4, 23.1, 23.4, 26.5, 37.2, 45.6, 122.7, 123.9, 127.0, 127.1, 128.3, 129.1, 129.2, 129.8, 131.0, 131.1, 134.1, 134.9, 136.8, 147.6, 167.5. CD ($CHCl_3$) λ_{ext} ($\Delta\epsilon$) 357 nm (+194), 304 (−122), 283 (+215).

Acknowledgment. 600 MHz NMR spectra were obtained by Dr. M. Ueno (Instrumental Analysis Center for Chemistry, Tohoku University). Elemental analyses were conducted by Ms. A. Sato (Graduate School of Pharmaceutical Sciences, Tohoku University). The authors thank JSPS and Toray Science Foundation for the financial support.

Supporting Information Available: Experimental procedures for the synthesis of (*P*)-**2**, (*P*)-**11**, and (*P*)-**12** as well as their physical data. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0013047