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Enantiomeric Recognition of Amino Acid Salts by Macrocyclic Crown Ethers Derived from Enantiomerically Pure 1,8,9,16-Tetrahydroxytetraphenylenes

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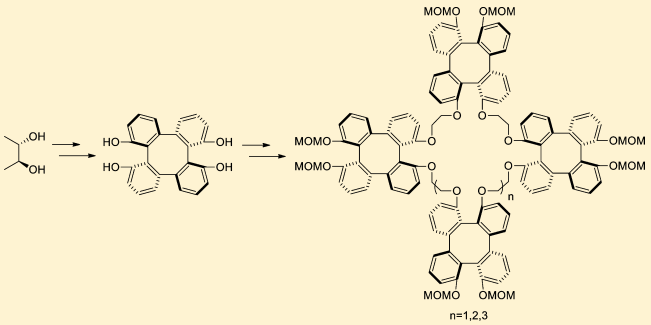
Supporting Information

ABSTRACT: Asymmetric synthesis of (*R*,*R*)- and (*S*,*S*)-1,8,9,16-tetrahydroxytetraphenylenes was achieved from starting material (2*R*,3*R*)-butane-2,3-diol and (2*S*,3*S*)-butane-2,3-diol respectively by utilizing a center-to-axis strategy. A series of crown ether compounds **20**, **24**, and **25** and their corresponding enantiomers derived from chiral tetrahydroxytetraphenylene were synthesized in enantiomerically pure forms. Enantiomeric recognition properties of these hosts toward L- and D-amino acid methyl ester hydrochloride were studied by the UV spectroscopy titration. The tetramer hosts (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** and (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**20** exhibited the best enantioselectivities toward L- and D-alanine methyl ester hydrochloride salt with K_L/K_D = 4.1 and K_D/K_L = 3.9, respectively. The new chiral macrocyclic hosts would further enrich the host−guest chemistry.



INTRODUCTION

Tetraphenylene (**1**),[1] featuring a unique saddle shaped structure, possesses a ground state D_{2d} geometry and exhibits an extraordinarily high barrier for the central cyclooctatetraene (COT) ring inversion (Figure 1).[2] Therefore, substituted

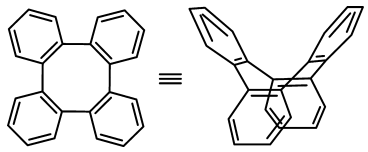


Figure 1. Chemical structure of tetraphenylene **1**.

tetraphenylene **1** derivatives can lead to chirality. We have designed and synthesized five different hydroxytetraphenylenes[3−7] as building blocks to investigate their 3-dimensional scaffolds constructed by noncovalent bonds.[2,4,8]

Generally, optically active tetraphenylene can be realized through four methods: (a) lithiation with metal-assisted coupling reaction;[9] (b) ligand-induced coupling reaction;[10] (c) rhodium-catalyzed [2 + 2+2] cycloaddition,[11] and (d) resolution of racemic substituted tetraphenylene.[3,4,6] Among these, the ee value of the chiral products in the first three approaches cannot reach up to 100% even after several recrystallizations. The tedious work would be carried out after resolution to achieve enantiopure targeted compounds. In this study, the chiral pieces were synthesized following the chiron approach starting with enatiomerically pure butane-2,3-diols. Owing to their unique structures and intriguing properties, optically pure and racemic substituted tetraphenylenes could be applied in the field of asymmetric catalytic hydrogenation,[4] organic catalysis,[12] liquid crystals,[13] and molecular devices,[14] etc.

Herein, we report the synthesis of enantiopure 1,8,9,16-tetrahydroxytetraphenylene in an asymmetric manner, as well as the study of chiral marcrocyclic compounds based on optically pure tetraphenylene structures toward chiral recognition of amino acid methyl ester hydrochloride salts.

RESULTS AND DISCUSSION

Asymmetric Synthesis of Chiral 1,8,9,16-Tetrahydroxytetraphenylenes. In our present program, we are working to develop a strategy toward enantiomeric construction of biaryl axis in optically pure forms through an intramolecular atropdiastereoselective Ullmann coupling utilizing a center-to-axis chirality transfer process. As shown in Scheme 1, we focused on the starting material (2*R*,3*R*)-butane-2,3-diol (**2**), which underwent tosylation to provide the corresponding

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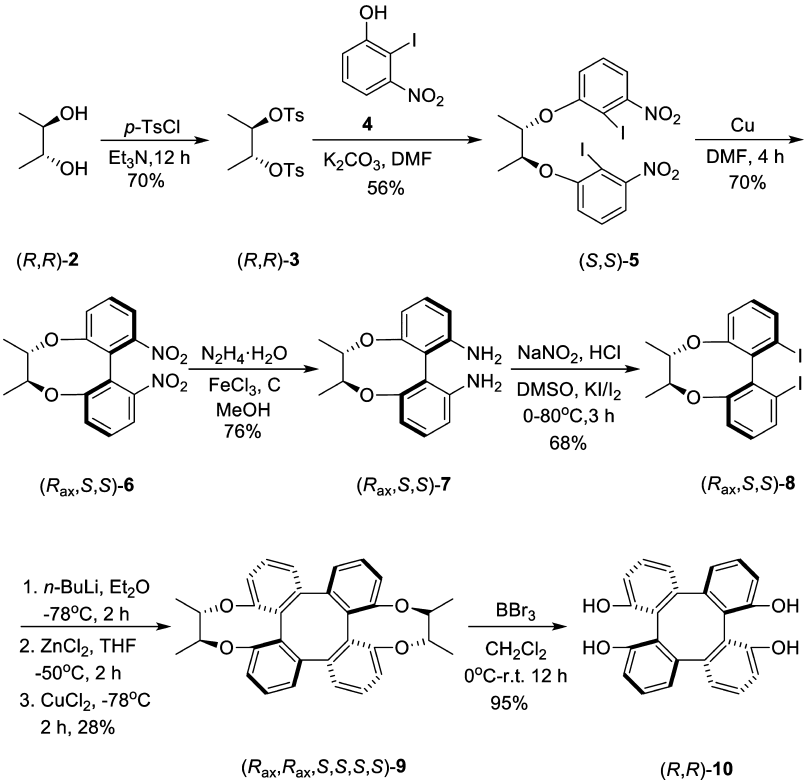
Scheme 1



ditosylate **3** in 70% yield. An S_N2 reaction between compound **3** and 2 equiv of 2-iodine-3-nitrophenol (**4**) was carried out to afford (*S*,*S*)-**5** in a moderate yield with inversion of configuration on (2*R*,3*R*)-**3**. Diiodide (*S*,*S*)-**5** was subjected to an intramolecular Ullmann reaction in refluxing DMF to lead to eight-membered ring formation, and the resulting **6** was confirmed to be diastereomerically pure by ^{1}H NMR spectroscopy. To establish the configuration of **6**, single crystals were prepared and characterized by an X-ray crystallographic analysis, which established the absolute configuration of (R_{ax},*S*,*S*)-**6** (Figure 2). Reduction of the dinitro group with $N_2H_4{\cdot}H_2O$ furnished diamine (R_{ax},*S*,*S*)-7 in 76% yield. The optically active diamine (R_{ax},*S*,*S*)-7 was converted to the corresponding diiodide (R_{ax},*S*,*S*)-**8** via a Sandmeyer reaction.

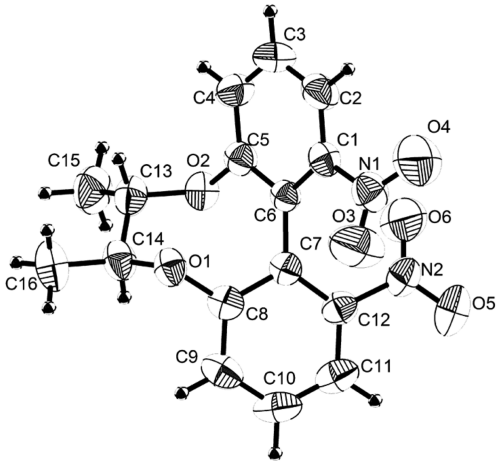


Figure 2. ORTEP drawing of (R_{ax},*S*,*S*)-**6**.

The structure of **8** was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy, and its absolute configuration was fully established by an X-ray crystallographic analysis (Figure 3).

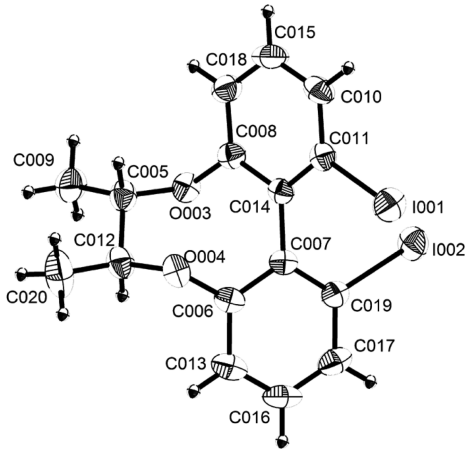


Figure 3. ORTEP drawing of (R_{ax},*S*,*S*)-**8**.

Then (R_{ax},*S*,*S*)-**8** was sequentially treated with *n*-BuLi, $ZnCl_2$, and $CuCl_2$ at −78 °C to room temperature for 12 h, leading to chiral tetraphenylene (R_{ax},R_{ax},*S*,*S*,*S*,*S*)-**9** in 28% yield. The molecular ion peak of (R_{ax},R_{ax},*S*,*S*,*S*,*S*)-**9** in its ESI mass spectrum was observed at *m*/*z* 477.2066, which is in good agreement with the theoretical value of 477.2060 for the molecular formula $C_{32}H_{28}O_4$ of (R_{ax},R_{ax},*S*,*S*,*S*,*S*)-**9**. Subsequently, the deprotection of (R_{ax},R_{ax},*S*,*S*,*S*,*S*)-**9** with boron tribromide furnished 1,8,9,16-tetrahydroxytetraphenylene (*R*,*R*)-**3** in 95%. (*R*,*R*)-Tetrahydroxytetraphenylene exhibited a specific rotation of $[\alpha]_D^{20}$ = +54.7 (*c* =1.10, MeOH).[4] In an

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analogous manner, 1,8,9,16-tetrahydroxytetraphenylene (*S*,*S*)-**10** was also obtained from the starting material (*S*,*S*)-**2**. (*S*,*S*)-Tetrahydroxytetraphenylene (**10**) exhibited a specific rotation of $[\alpha]_D^{20} = -55.3$ (c = 1.13, MeOH),[4] which is opposite to that of its (*R*,*R*)-counterpart (Figure 4).

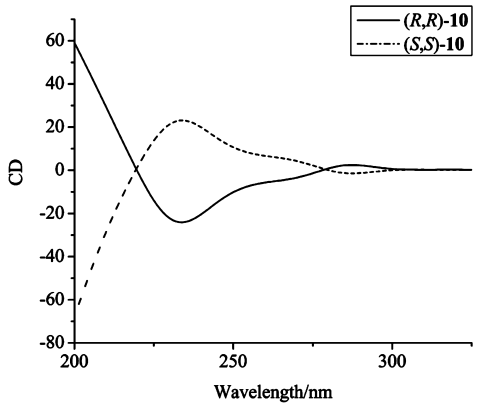


Figure 4. CD spectra of (*R*,*R*)-**10** (1.6×10^{-4} M, MeOH) and (*S*,*S*)-**10** (1.6×10^{-4} M, MeOH).

Synthesis of Macrocyclic Crown Ether Hosts. Enantiomeric recognition is one of the most remarkable features in host–guest chemistry.[15] During the past decades, the development of hosts has provided important information toward the better understanding of interaction between molecules.[16] Among various host molecules studied, chiral macrocyclic crown ethers demonstrated high efficiency in enantiomeric separations of amines, amino acids, and their derivatives.[17] We are interested in developing potential hosts with much more bigger cavity size and chiral axes in comparison to some well-documented hosts[16] in order to study the interaction between these hosts and guests. Herein, we envisioned that enantiomeric 1,8,9,16-tetrahydroxytetraphenylenes could be employed as excellent starting materials for the construction of chiral macrocyclic crown ethers, which in turn would act as hosts to recognize optically active ammonium salts because of their unique structures and enantiomeric purities.

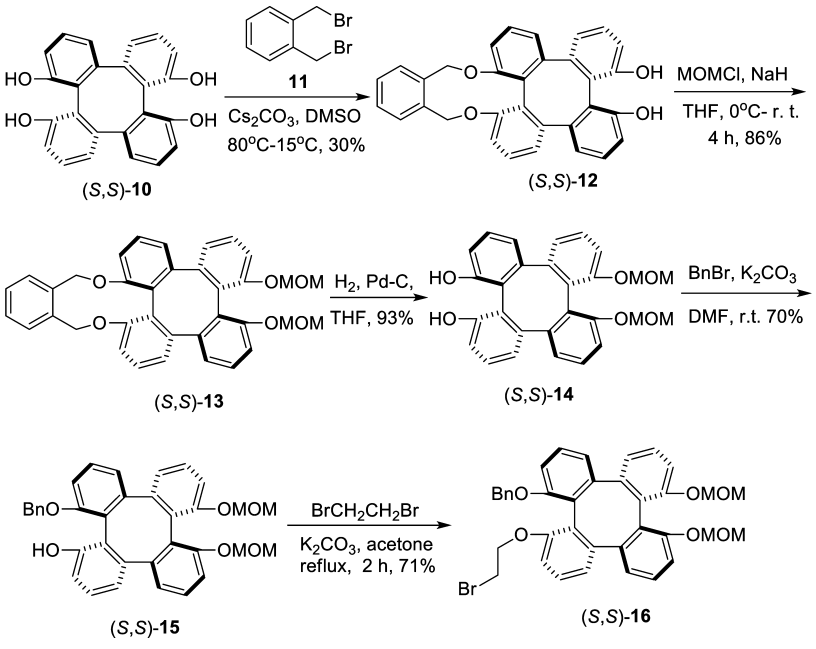
With (*S*,*S*)-1,8,9,16-tetrahydroxytetraphenylene in hand, we proceeded to protect the two proximal hydroxy groups with dibromide **11**. Then the unprotected hydroxy groups of (*S*,*S*)-**12**[12] (HRMS (ESI) m/z calcd for $C_{32}H_{22}O_4$ $[M + H]^+$ 471.1591, found 471.1593) were treated with sodium hydride and MOMCl to give (*S*,*S*)-**13**. Upon hydrogenolysis in the presence of palladium on charcoal, two hydroxy groups of (*S*,*S*)-**13** were released to afford (*S*,*S*)-**14**. Under a carefully controlled manner, (*S*,*S*)-**14** was further benzylated to give the monobenzyl (*S*,*S*)-**15** in 70% yield. Treatment of (*S*,*S*)-**15** with 1,2-dibromoethane gave (*S*,*S*)-**16** in 71% (Scheme 2).

Cross coupling between bromide monomer (*S*,*S*)-**16** and hydroxy monomer (*S*,*S*)-**15** provided the corresponding dimer (*S*,*S*,*S*,*S*)-**17** in 42% yield. Dimer (*S*,*S*,*S*,*S*)-**17** was hydrogenolyzed to remove the benzyl group to afford the hydroxy dimer (*S*,*S*,*S*,*S*)-**18**. Then (*S*,*S*,*S*,*S*)-**18** was readily converted to the bromide dimer (*S*,*S*,*S*,*S*)-**19** by 1,2-dibromoethane and K_2CO_3 in 52% yield (Scheme 3).

With the bromide dimer (*S*,*S*,*S*,*S*)-**19** in hand, it was allowed to react with hydroxy dimer (*S*,*S*,*S*,*S*)-**18** to successfully provide the corresponding tetramer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** in 40% yield (Scheme 4). Only one product was accordingly isolated and this compound (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** was fully characterized by ^{1}H NMR and ^{13}C NMR spectroscopy as well as HRMS. The tetramer (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**20**, enantiomer of tetramer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** was also synthesized in the same manner through a similar reaction sequence starting from material (*R*,*R*)-**10**. Figure 5 shows the circular dichroism (CD) spectra of the two antipodal tetramer (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**20** and (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20**.

Cross coupling between (*S*,*S*)-**14** and 2.0 equivalents of (*S*,*S*)-**16** in the presence of cesium carbonate in refluxing acetone provided the corresponding trimer (*S*,*S*,*S*,*S*,*S*,*S*)-**21**. The bromide trimer (*S*,*S*,*S*,*S*,*S*,*S*)-**23** was realized *via* the same

Scheme 2



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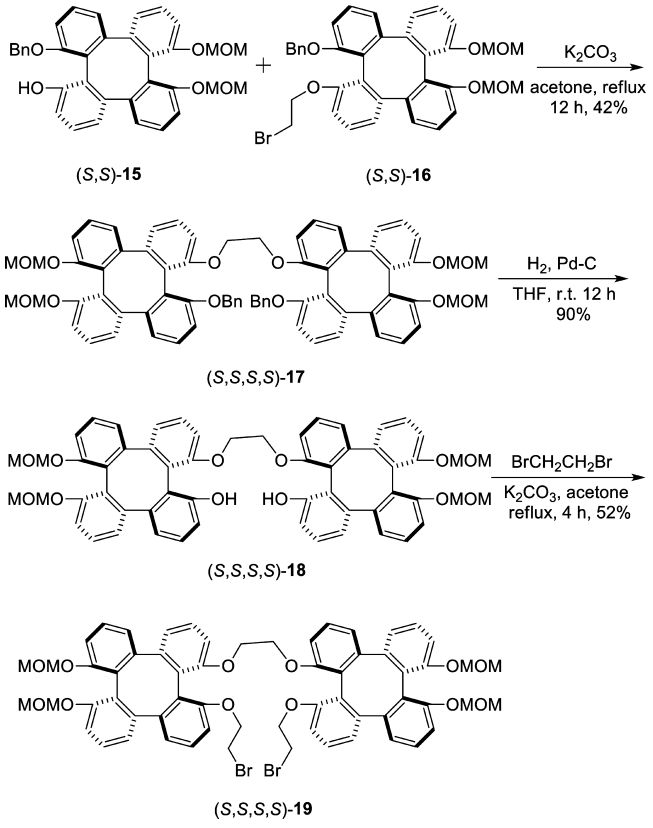
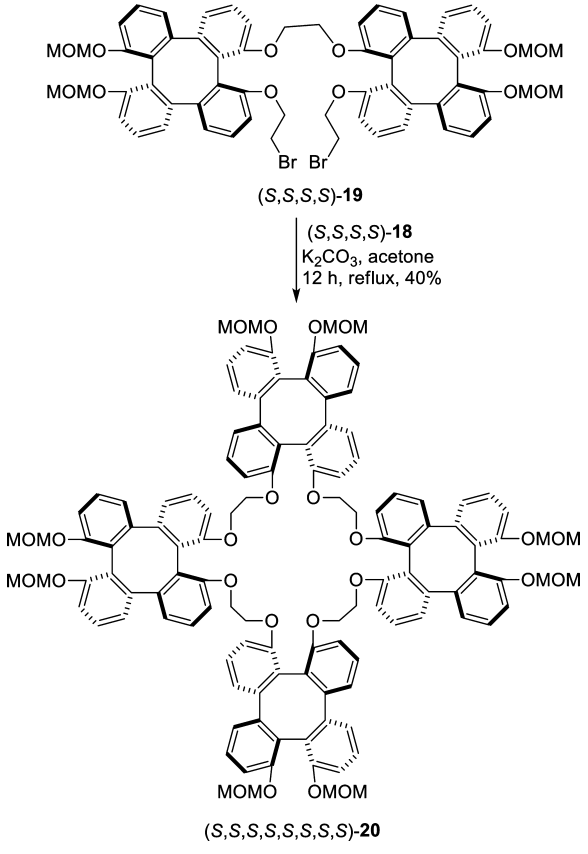
Scheme 3



Scheme 4



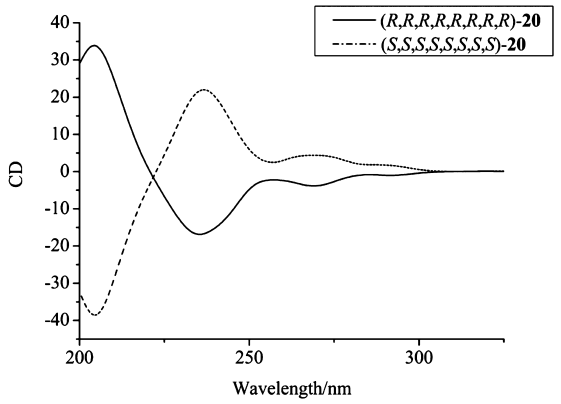
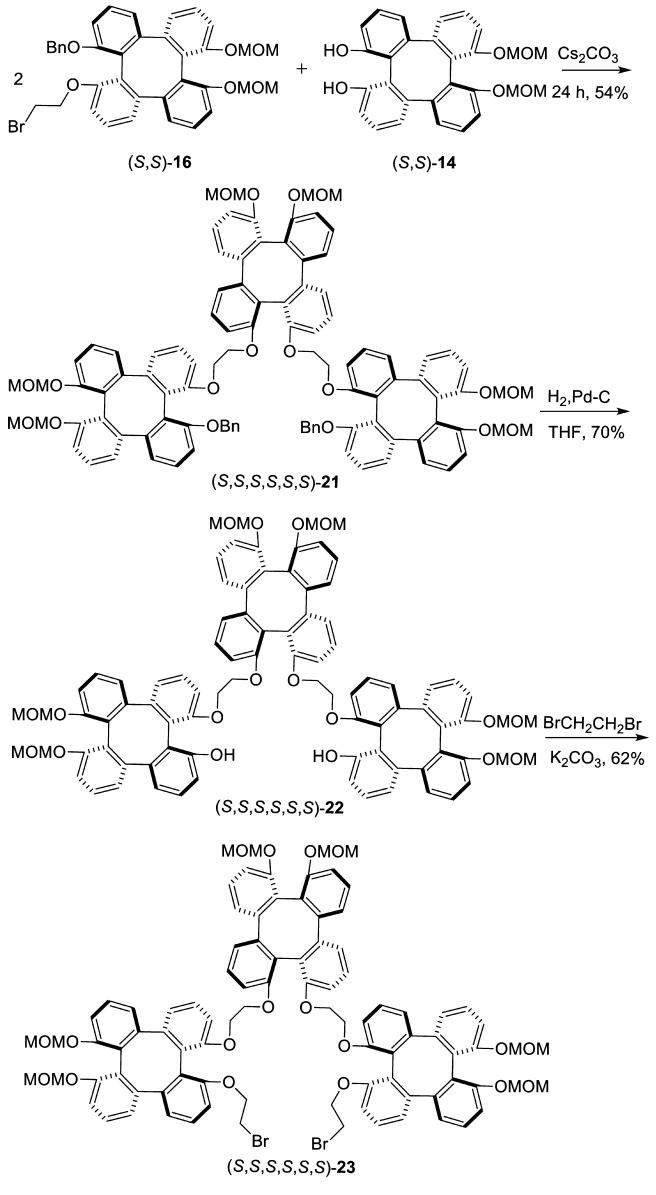


Figure 5. CD spectra of (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**20** (1.5×10^{-5} M, CH_3CN) and (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** (1.5×10^{-5} M, CH_3CN).

reaction sequence as mentioned previously, and is illustrated in Scheme 5.

Scheme 5



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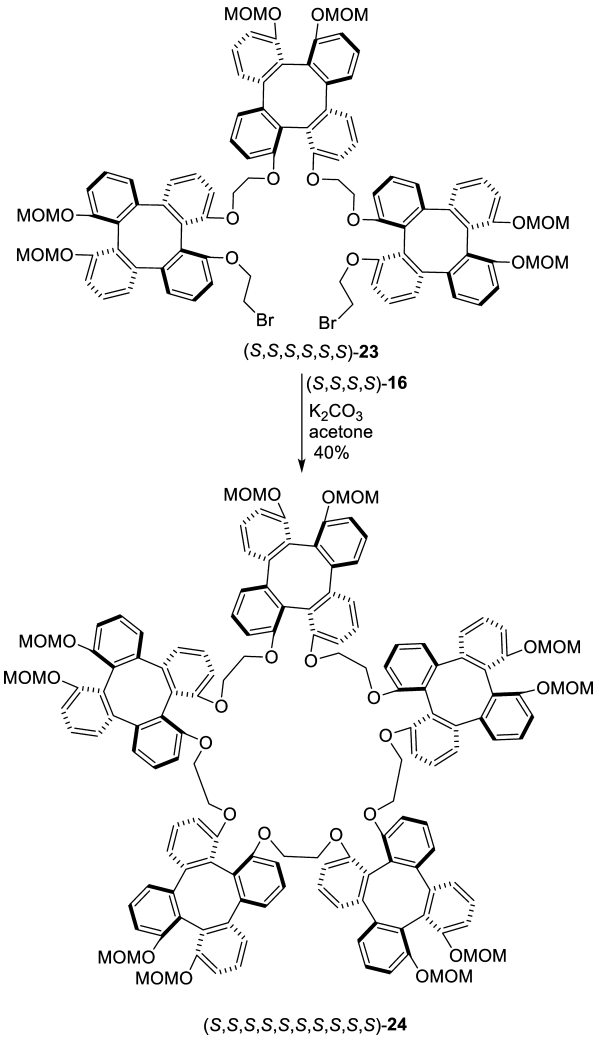
When the hydroxy dimer (*S*,*S*,*S*,*S*)-**18** was allowed to react with the dibromide trimer (*S*,*S*,*S*,*S*,*S*,*S*)-**23** in the presence of 20 equiv of potassium carbonate, the desired pentamer (*S*,*S*,*S*,-*S*,*S*,*S*,*S*,*S*,*S*)-**24** was afforded (Scheme 6).

Scheme 6



In an analogous manner, the pentamer (*R*,*R*,*R*,*R*,-*R*,*R*,*R*,*R*,*R*)-**24** was accomplished from the corresponding (*R*,*R*,*R*,*R*)-**18** and (*R*,*R*,*R*,*R*,*R*,*R*)-**23**. Circular dichroism (CD) spectra of the pentamers (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**24** and (*R*,*R*,*R*,-*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**24** displayed good agreement as an antipodal pair (Figure 6).

Hexamer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**25** together with (*R*,*R*,*R*,*R*,-*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**25** were furnished from the corresponding hydroxy trimer (*S*,*S*,*S*,*S*,*S*,*S*)-**22** or (*R*,*R*,*R*,*R*,*R*,*R*)-**22** and bromide trimer (*S*,*S*,*S*,*S*,*S*,*S*)-**23** or (*R*,*R*,*R*,*R*,*R*,*R*)-**23** under basic conditions in approximately 40% yield after refluxing for 12 h (Scheme 7). These two macrocycles were structurally characterized by ^{1}H NMR, ^{13}C NMR spectra and HRMS. As expected, circular dichroism (CD) spectra of (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,-*S*,*S*,*S*,*S*)-**25** and (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**25** also exhibited good agreement for an antipodal pair (Figure 7).

Enantiomeric Recognition Studies Using UV-Titration Method. With the potential hosts in hand, our interest then focused on utilizing these crown ethers to examine the enantiomeric recognition toward amino acids derivatives.

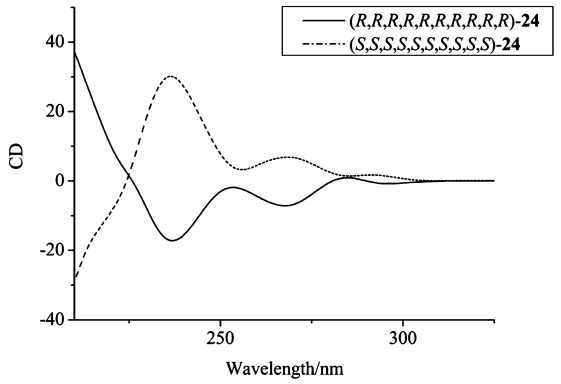
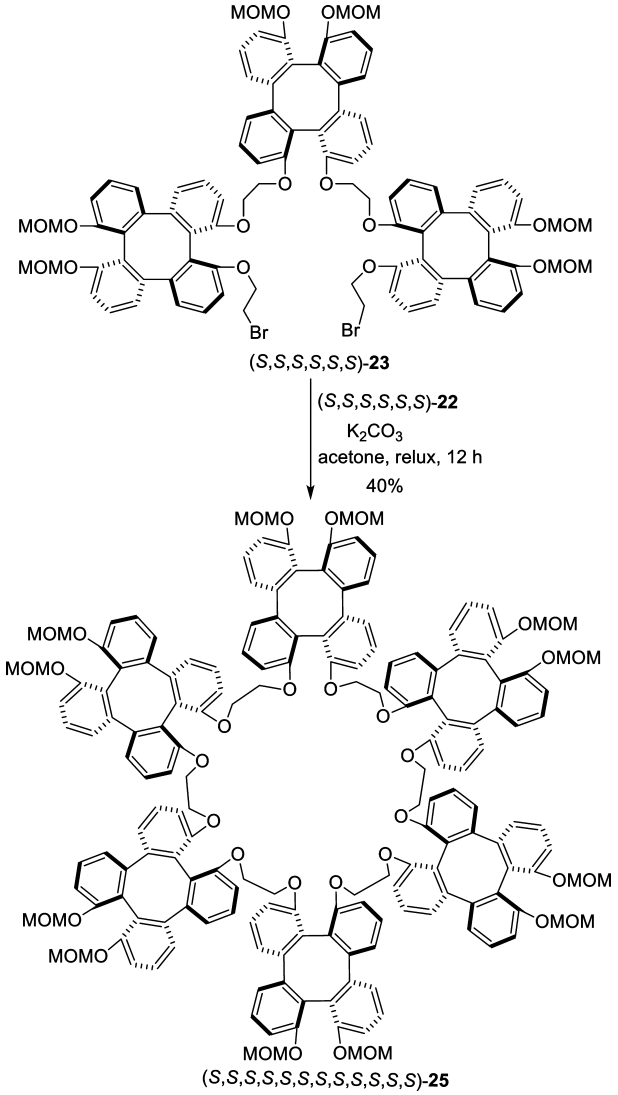


Figure 6. CD spectra of (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**24** (1.2×10^{-5} M, CH_3CN) and (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**24** (1.0×10^{-5} M, CH_3CN).

Scheme 7



Optically pure amino acid methyl ester hydrochloride salts Ala-OMe·HCl, Val-OMe·HCl, Pro-OMe·HCl, Leu-OMe·HCl, as well as Phe-OMe·HCl were employed as guests in our investigation of the binding behaviors with tetraphenylene hosts. The UV−vis spectroscopic method is a convenient and a widely used method for the study of binding phenomena.[18] In

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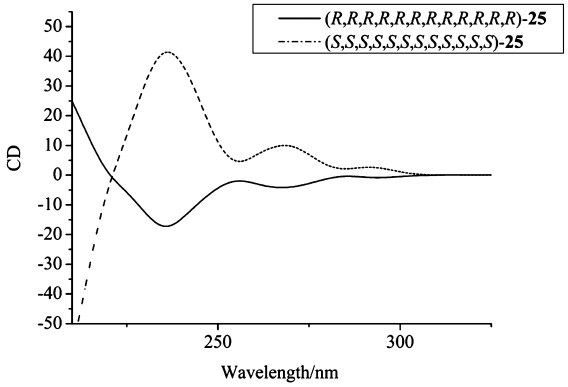

Figure 7. CD spectra of (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**25** (1.2 × 10^{-5} M, CH_3CN) and (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**25** (1.8 × 10^{-5} M, CH_3CN).

UV−vis spectroscopic titration experiments, varied concentrations of guest solution are added to the host system, which would lead to the absorptions intensities of the system in an either increased or decreased manner.

Under the conditions described herein, the combination of host tetramer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** with alanine methyl ester salt was first studied. When the concentration of (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** is 1.42 × 10^{-5} mol/L, the absorption increased upon the addition of the L-ALa-OMe·HCl salt (2.84−53.35 × 10^{-5} mol/L) to the host in CH_3CN-MeOH (95:5 v/v) at 20 °C (Figure 8). In this case, the absorption intensities at 284 nm were recorded.

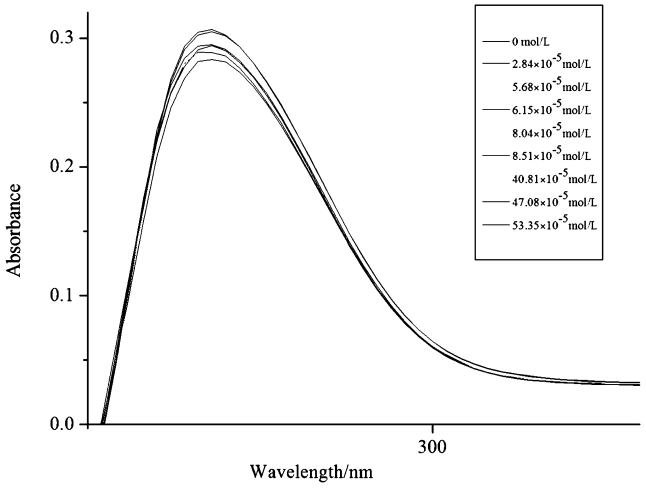

Figure 8. UV−vis spectra of (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** (1.42 × 10^{-5} mol/L) in the presence of L-ALa-OMe·HCl salt (2.84−53.4 × 10^{-5} mol/L).

The behavior of the tetramer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** and the alanine methyl ester salt during the titration indicated a 1:1 complexation, which was supported by the Job's plot based on the UV−vis spectroscopic changes (Figure 9), with *x* being referred to the proportion of host concentration in total host−guest solution.

This result was further confirmed by the strong host−guest [1 + 1] molecular ion peaks that appeared in the ESI-MS analysis of the host−guest system. The theoretical molecular weight of complex formed by the host and the guest was 2033.7657, and the measured value 2033.7653 was found.

Under the conditions employed, the concentration of tetramer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** (1.42 × 10^{-5} mol/L) is much

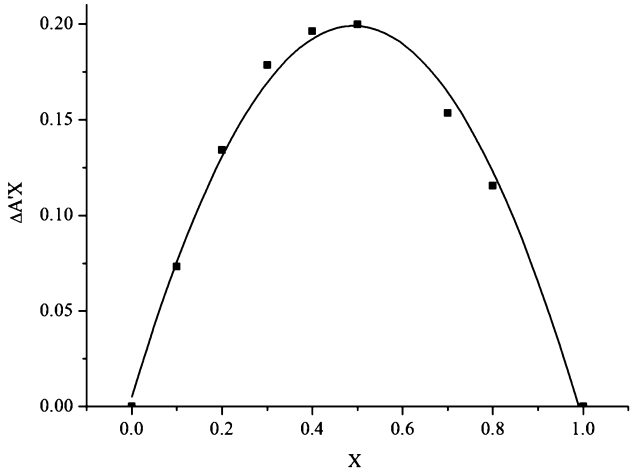

Figure 9. Job's plots for (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** and L-Ala-OMe·HCl salt.

smaller than that of the guest, i.e., $[H]_o \ll [G]_i$. Therefore, the binding constant of the complex system formed can be calculated according to the modified Benesi−Hildebrand equation.[19] Figure 10 displays the Benesi−Hildebrand plot

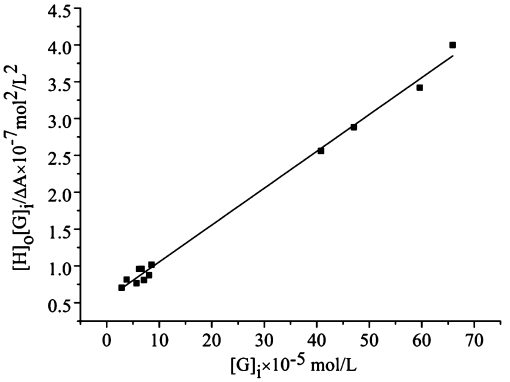

Figure 10. Typical plot of $[H]_o[G]_i/\Delta A$ vs $[G]_i$ for host−guest complexation of the (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-20 and L-Ala-OMe·HCl salt in CH_3CN−MeOH (95:5 v/v) at 20 °C.

for complexation between tetramer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** and L-alanine methyl ester salts. The binding constants (K_S) can be calculated from the slope ($1/\Delta\varepsilon$) and intercept ($1/K_S{\cdot}\Delta\varepsilon$) of linear regression. The binding constant of complex formed by tetramer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** and L-Ala-OMe·HCl salt was calculated to be 1.11 × 10^3 M^{-1} using the job plot.

In a similar manner, the affinities of 0.27 × 10^3 $M^{-1}$for the complex generated from tetramer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** with D-alanine methyl ester hydrochloride salts was obtained. According to these two corresponding binding constants, the enantioselectivity for the (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** was observed to be K_L/K_D = 4.1. Furthermore, tetramer (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**20** was used for binding with L- and D-Ala-OMe·HCl salts to check their binding affinities. When the concentration of tetramer (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**20** was fixed at 2.27 × 10^{-5} mol/L, the binding constants of the complexes formed by (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**20** and L-ALa-OMe·HCl together with (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**20** and D-ALa-OMe·HCl was calculated to be 0.27 × 10^3 M^{-1} and 1.06 × 10^3 M^{-1}, respectively. Therefore, the discrimination of two enantiomer of guests for the tetramer (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**20** were observed to be K_D/K_L = 3.9. These results indicated that tetramer (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**20** displayed a

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preference toward D-Ala-OMe·HCl, and the enantioselectivity was close to the results of (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20**.

In a similar manner, we systematically investigated the chiral discrimination ability of tetramer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20**, pentamer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**24**, hexamer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**25** with amino acid methyl esters hydrochloride as chiral organic ammonium salts. The binding constant (K_s), relative free energy changes ($-\Delta G_o$) along with the corresponding enantioselectivities of the hosts with guest molecules obtained from usual curve-fitting analyses are summarized in Table 1.

From the K_L/K_D value in Table 1, it can be seen that the hosts exhibited a preference for enantiomers with a configuration for L-guests. For tetramer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20**, the results suggested that the steric bulkiness of the ammonium guest is detrimental for good enantioselctivity. The best enantioselectivity from complexes formed by tetramer (*S*,*S*,*S*,*S*,-*S*,*S*,*S*,*S*)-**20** and alanine methyl ester salt is 4.1, and the hydrogen bonding π−charge interaction together with steric complementarity might be responsible for this result. Very weak $\pi-\pi$ interaction might be part of the binding force for the complexation of the phenyl alanine salts with hosts in view of the slightly larger binding constants than those of others (entries 9, 10, 19, 20, 29, and 30). The binding constants and the enantioselectivities decreased (entries 20−30) in comparison with the corresponding results in entries 1−10. The crown ether cavities as well as space conformation probably played very important role in these cases.

CONCLUSION

Asymmetric synthesis of optically active tetrahydroxytetraphenylene has been achieved from (2*R*,3*R*)-butane-2,3-diol or (2*S*,3*S*)-butane-2,3-diol. A series of chiral marcrocyclic crown ether type compounds were developed and their enantiomeric recognition properties toward a number of amino acid derivatives using UV-method were studied. The host tetramer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** exhibited the highest enantioselectivity toward alanine methyl ester salt with K_L/K_D equals 4.1. The larger cavity sizes of the pentamer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**24** and hexamer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**25** are believed to be responsible for weaker host−guest enantioselectivities, leading to a much lower degree of differentiation. Although the enantioselectivities are lower than 23.4 which was the best result we found from literature,[20] the new chiral macrocyclic hosts could further enrich the host−guest chemistry.

EXPERIMENTAL SECTION

(2*R*,3*R*)-Bis(4-methylbenzenesulfonate)butane [(2*R*,3*R*)-3] and (2*S*,3*S*)-3. In a dry round bottle, diol **2** (2.0 g, 22.2 mmol) and *p*-toluenesulfonyl chloride (12.7 g, 66.7 mmol) were dissolved in dichloromethane (20 mL) under nitrogen at 0 °C. Et_3N (9.2 mL, 66.7 mmol) was added dropwise within 30 min. The mixture was stirred at room temperature for 12 h. The reaction was quenched with water (100 mL) and was extracted with dichloromethane (40 mL × 3). The combined extracts were washed with brine (60 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EtOAc/hexanes, 1:6) to give pure **3** (6.2 g, 70%) as white solids: mp 116−119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (d, J = 6.32, 6 H), 2.45 (s, 6 H), 4.56 (m, 2 H), 7.32 (d, J = 8.0 Hz, 4 H), 7.73 (d, J = 8.3, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 21.8, 78.2, 128.0, 130, 133.6, 145.1; IR ν_{max}(film) cm^{-1} 3056.0, 2993.5, 1598.6, 1495.9, 1460.2, 1359.2, 1020.2, 854.4, 789.8, 775.9, 665.3. (2*R*,3*R*)-**3**: $[\alpha]_D^{20}$ = −12.6 (c = 0.70, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{18}H_{22}O_6S_2$ [M + Na]$^+$ 421.0750, found 421.0759. (2*S*,3*S*)-**3**: $[\alpha]_D^{20}$ = +13.8 (c = 0.75,

Table 1. Binding Constants (K_s), Free Energy Changes ($-\Delta G_o$), and Enantioselectivities K_L/K_D for Complexes between Ammonium Salts and Tetramer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-20, pentamer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-24, hexamer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-25 at 20 °C

entry	host[a]	guest	K_s(× 10^3 L/mol)	K_L/K_D	$-\Delta G_o$ (kJ/mol)
1	*S*-tetramer	L-Ala-OMe·HCl	K_L = 1.11 ± 0.07	4.1	17.0
2	*S*-tetramer	D-Ala-OMe·HCl	K_D = 0.27 ± 0.36		13.6
3	*S*-tetramer	L-Val-OMe·HCl	K_L = 1.64 ± 0.10	2.4	18.0
4	*S*-tetramer	D-Val-OMe·HCl	K_D = 0.67 ± 0.17		15.8
5	*S*-tetramer	L-Pro-OMe·HCl	K_L = 1.99 ± 0.15	1.7	18.5
6	*S*-tetramer	D-Pro-OMe·HCl	K_D = 1.14 ± 0.19		17.1
7	*S*-tetramer	L-Leu-OMe·HCl	K_L = 1.17 ± 0.17	1.1	17.2
8	*S*-tetramer	D-Leu-OMe·HCl	K_D = 1.03 ± 0.13		16.9
9	*S*-tetramer	L-Phe-OMe·HCl	K_L = 3.12 ± 0.07	1.0	19.6
10	*S*-tetramer	D-Phe-OMe·HCl	K_D = 3.04 ± 0.09		19.5
11	*S*-pentamer	L-Ala-OMe·HCl	K_L = 0.72 ± 0.08	1.1	16.0
12	*S*-pentamer	D-Ala-OMe·HCl	K_D = 0.65 ± 0.10		15.8
13	*S*-pentamer	L-Val-OMe·HCl	K_L = 0.73 ± 0.14	1.1	16.1
14	*S*-pentamer	D-Val-OMe·HCl	K_D = 0.63 ± 0.26		15.7
15	*S*-pentamer	L-Pro-OMe·HCl	K_L = 0.84 ± 0.18	1.6	16.4
16	*S*-pentamer	D-Pro-OMe·HCl	K_D = 0.51 ± 0.36		15.2
17	*S*-pentamer	L-Leu-OMe·HCl	K_L = 0.85 ± 0.24	1.3	16.4
18	*S*-pentamer	D-Leu-OMe·HCl	K_D = 0.62 ± 0.24		15.7
19	*S*-pentamer	L-Phe-OMe·HCl	K_L = 0.87 ± 0.08	1.4	16.5
20	*S*-pentamer	D-Phe-OMe·HCl	K_D = 0.63 ± 0.18		15.7
21	*S*-hexamer	L-Ala-OMe·HCl	K_L = 0.68 ± 0.16	1.1	15.9
22	*S*-hexamer	D-Ala-OMe·HCl	K_D = 0.65 ± 0.17		15.8
23	*S*-hexamer	L-Val-OMe·HCl	K_L = 0.69 ± 0.19	1.1	15.9
24	*S*-hexamer	D-Val-OMe·HCl	K_D = 0.63 ± 0.17		15.7
25	*S*-hexamer	L-Pro-OMe·HCl	K_L = 0.64 ± 0.23	1.0	15.7
26	*S*-hexamer	D-Pro-OMe·HCl	K_D = 0.62 ± 0.40		15.7
27	*S*-hexamer	L-Leu-OMe·HCl	K_L = 0.75 ± 0.17	1.1	16.1
28	*S*-hexamer	D-Leu-OMe·HCl	K_D = 0.71 ± 0.13		16.0
29	*S*-hexamer	L-Phe-OMe·HCl	K_L = 0.78 ± 0.14	1.0	16.2
30	*S*-hexamer	D-Phe-OMe·HCl	K_D = 0.75 ± 0.16		16.1

[a]Host[a], *s*-tetramer, *s*-pentamer, and *s*-hexamer indicated (*S*,*S*,*S*,*S*,*S*,*S*,-*S*,*S*)-**20**, (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**24** and (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**25**, respectively.

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CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{18}H_{22}O_6S_2$ $[M + Na]^+$ 421.0750, found 421.0759.

(2*S*,3*S*)-Bis(2-iodo-3-nitrophenoxyl)butane [(2*S*,3*S*)-5] and (2*R*,3*R*)-5. A dried round-bottom flask was loaded under Ar with 2-iodo-3-nitro-phenol **4** (7.9 g, 30.0 mmol), DMF (80 mL), and K_2CO_3 (8.2 g, 60.0 mmol). The reaction mixture was stirred at room temperature for 2 h and was followed by the addition of **3** (6.5 g, 16.3 mmol) in DMF (80 mL) within 0.5 h. The mixture was stirred at room temperature for a further 2 h and was then heated to 80 °C for 12 h. The reaction was quenched by water and was extracted with diethyl ether (150 mL × 3) and was washed with saturated sodium chloride solution (100 mL × 2). The organic layers were dried over $MgSO_4$, concentrated, and purified by column chromatography on silica gel (EtOAc/hexanes, 1:5) to give pure **5** (4.9 g, 56%) as yellow solids: mp 166−168 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 1.54 (d, J = 4.0 Hz, 6 H), 5.01 (s, 2 H), 7.36 (d, J = 8.0, 2 H), 7.44 (d, J = 7.8, 2 H), 7.58 (t, J = 7.2 Hz, 2 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 15.4, 78.9, 81.4, 117.2, 117.3, 131.4, 157.3, 159.3; IR ν_{max} (film) cm^{-1} 3093.4, 2986.0, 2881.4, 1584.1, 1528.7, 1450.3, 1265.1, 1056.4, 867.7, 790.7, 768.3, 735.9. (2*S*,3*S*)-**5**: $[\alpha]_D^{20}$ = +232.6 (c = 1.32, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{16}H_{14}I_2N_2O_6$ $[M + Na]^+$ 606.8833, found 606.8822; Anal. Calcd for $C_{16}H_{14}I_2N_2O_6$: C, 32.90; H, 2.42; N, 4.80. Found: C, 32.75; H, 2.41; N, 4.70. (2*R*,3*R*)-**5**: $[\alpha]_D^{20}$ = −203.3 (c = 1.02, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{16}H_{14}I_2N_2O_6$ $[M + Na]^+$ 606.8833, found 606.8826. Anal. Calcd for $C_{16}H_{14}I_2N_2O_6$: C, 32.90; H, 2.42; N, 4.80. Found: C, 32.74; H, 2.42; N, 4.69.

(6*S*,7*S*)-6,7-Dimethyl-1,12-dinitro-6,7-dihydrodibenzo[*e*,*g*]-[1,4]dioxocine [(R_{ax},6*S*,7*S*)-6] and (S_{ax},6*R*,7*R*)-6. To a solution of compound **5** (2.9 g, 5 mmol) in DMF (12.5 mL) was added Cu powder (3.2 g, 50 mmol). The mixture was then heated at 160 °C for 10 h with stirring. After that, the hot mixture was filtered through a pad of silica gel under reduced pressure. The flask and the silica gel pad were washed with hot DMF (50 mL). The collected filtrate was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexanes, 1:5) to give pure **6** (1.2 g, 70%) as a yellow solid: mp 225−227 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 1.40 (d, J = 5.6 Hz, 3 H), 4.05 (m, 1 H), 7.72 (t, J = 4.0 Hz, 2 H), 7.96 (t, J = 4.0 Hz, 1 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 18.8, 88.5, 121.1, 123.5, 129.3, 131.5, 149.4, 160.7; IR ν_{max} (film) cm^{-1} 3117.4, 3043.2, 2946.4, 2881.1, 1563.7, 1520.4, 1485.1, 1003.9, 858.2, 818.1, 767.7, 742.3, 718.9. (R_{ax},*S*,*S*)-**6**: $[\alpha]_D^{20}$ = −286.4 (c = 0.65, CH_2Cl_2); HRMS (EI) m/z calcd for $C_{16}H_{14}N_2O_6$ $[M + H]^+$331.0925, found 331.0932; Anal. Calcd for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.48. Found: C, 57.96; H, 4.44; N, 8.37. (S_{ax},*R*,*R*)-**6**: $[\alpha]_D^{20}$ = +303.7 (c = 0.7, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{16}H_{14}N_2O_6$ $[M + H]^+$ 331.0925, found 331.0951. Anal. Calcd for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.01; H, 4.27; N, 8.36.

(6*S*,7*S*)-6,7-Dimethyl-6,7-dihydrodibenzo[*e*,*g*][1,4]-dioxocine-1,12-diamine [(R_{ax},6*S*,7*S*)-7] and (S_{ax},6*R*,7*R*)-7. A mixture of compound **6** (0.3 g, 1 mmol), $FeCl_3$ (15.9 mg, 0.1 mmol), and activated charcoal (51.3 mg) was suspended in MeOH (25 mL) with stirring. The mixture was then heated to reflux for 1 h. Then hydrazine monohydrate (98%, 0.3 mL, 9.4 mmol) was added dropwise to the mixture. After being for another 3 h, the mixture was filtered through a pad of silica gel under reduced pressure without cooling. The flask and the pad were further washed with hot MeOH (5 mL). The filtrate was concentrated and purified by column chromatography on silica gel (EtOAc/hexanes, 1:4) to give pure **7** (0.2 g, 76%) as a light yellow oil: ^{1}H NMR (400 MHz, acetone-d_6) δ 1.28 (q, J = 1.6 Hz, 6 H), 3.77 (m, 2 H), 4.46 (brs, 4 H), 6.47 (dd, J = 0.9, 7.9 Hz, 2 H), 6.59 (dd, J = 0.9, 7.9 Hz, 2 H), 7.06 (t, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 19.2, 86.9, 111.5, 111.9, 115.4, 129.9, 146.7, 161.8; IR ν_{max} (film) cm^{-1} 3436.1, 3349.8, 3055.2, 2981.3, 2938.4, 2875.1, 1615.5, 1593.9, 1567.0, 1449.7, 1233.6, 1004.9, 855.3, 788.9, 723.5. (R_{ax},*S*,*S*)-**7**: $[\alpha]_D^{20}$ = −190.6 (c = 0.46, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{16}H_{18}N_2O_2$ $[M + H]^+$ 271.1441, found 271.1448. (S_{ax},*R*,*R*)-**7**: $[\alpha]_D^{20}$ = +185.5 (c = 0.40, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{16}H_{18}N_2O_2$ $[M + H]^+$ 271.1441, found 271.1445.

(6*S*,7*S*)-1,12-Diiodo-6,7-dimethyl-6,7-dihydrodibenzo[*e*,*g*]-[1,4]dioxocine[(R_{ax},*S*,*S*)-8] and (S_{ax},6*R*,7*R*)-8. Compound **7** (0.3 g, 1.2 mmol) was treated with a solution of 30% H_2SO_4 (12.6 mL) and DMSO (3.5 mL). The mixture was then cooled in an ice−acetone bath (<5 °C) with stirring. A solution of $NaNO_2$ (0.3 g, 3.6 mmol) was dropped to the mixture. The mixture was stirring for another 15 min after the addition. An aqueous solution of KI_3 (KI, 0.6 g, 3.6 mmol and I_2, 0.5g, 1.8 mmol) was added dropwise to the vigorous stirring mixture. The mixture was then warmed to room temperature. Subsequently, the mixture was heated to 80 °C for 2 h. The mixture was extracted with CH_2Cl_2 (20 mL × 3). The organic layer collected was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (CH_2Cl_2/hexanes, 1:6) to give pure **8** (0.4 g, 68%) as white solids: mp 194−197 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 1.28 (q, J = 2 Hz, 6 H), 3.81 (m, 2 H), 7.15 (t, J = 8 Hz, 2 H), 7.24 (dd, J = 1.2, 8.0 Hz, 2 H), 7.06 (dd, J = 1.2, 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 19.1, 88.2, 101.0, 123.0, 132.2, 135.8, 139.6, 160.5; IR ν_{max} (film) cm^{-1} 3070.7, 3049.0, 2912.6, 2890.3, 1573.4, 1555.9, 1547.5, 1442.0, 1250.2, 1041.8, 852.3, 831.8, 780.5, 756.0, 724.2, 575.0, 549.1. (R_{ax},*S*,*S*)-**8**: $[\alpha]_D^{20}$ = −102.1 (c = 0.78, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{16}H_{14}I_2O_2$ $[M + H]^+$ 492.9156, found 492.9167. Anal. Calcd for $C_{16}H_{14}I_2O_2$: C, 39.05; H, 2.87. Found: C, 38.88; H, 2.95. (S_{ax},*R*,*R*)-**8**: $[\alpha]_D^{20}$ = +105.3 (c = 0.80, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{16}H_{14}I_2O_2$ $[M + Na]^+$ 514.8975, found 514.8979 Anal. Calcd for $C_{16}H_{14}I_2O_2$: C, 39.05; H, 2.87. Found: C, 38.81; H, 2.96.

(R_{ax},R_{ax},2*S*,3*S*,12*S*,13*S*)-2,3,12,13-Tetramethyl-2,3,12,13-tetrahydrotetraphenyleno[1,16-*efg*:8,9-*e′f′g′*]bis([1,4]-dioxocine) [(R_{ax},R_{ax},2*S*,3*S*,12*S*,13*S*)-9] and (S_{ax},S_{ax},2*R*,3*R*,-12*R*,13*R*)-9. Compound **8** (0.5 g, 1 mmol) was suspended in dried Et_2O (14 mL) under nitrogen atmosphere. *n*-Butyllithium solution (1.6 M in hexanes, 1.5 mL, 2.2 mmol) was added to the mixture at −78 °C in a dropwise manner with stirring for 2 h. A solution of anhydrous $ZnCl_2$ (0.3 g, 2.4 mmol) in THF (2.3 mL) was injected in the mixture at −50 °C slowly with vigorous stirring for 2 h. After that, the anhydrous $CuCl_2$ (0.4 g, 3.0 mmol) was added to the solution at −78 °C for another 2 h. The mixture was then warmed to room temperature slowly and allowed to stir overnight at room temperature. The system was quenched with aqueous hydrochloric acid solution (6 M, 12 mL), and the aqueous solution was extracted with CH_2Cl_2 (50 mL × 3). The organic layers were combined and dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography on silica gel (CH_2Cl_2/hexanes, 1:3) to give pure **9** as white solids (66.7 mg, 28%): mp > 240 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 1.33 (dd, J = 1.8, 4.2 Hz, 12 H), 3.85 (m, 4 H), 6.87 (dd, J = 1.1, 7.6 Hz, 4 H), 7.07 (dd, J = 1.1, 7.6 Hz, 4 H), 7.27 (t, J = 7.8 Hz, 4 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 19.2, 87.5, 121.6, 126.1, 129.8, 131.1, 143.5, 159.4; IR ν_{max} (film) cm^{-1} 3017.7, 3019.7, 2883.2, 1512.1, 1480.1, 1215.8, 763.7, 669.2. (R_{ax},R_{ax},*S*,*S*,*S*,*S*)-**9**: $[\alpha]_D^{20}$ = −116.5 (c = 0.50, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{32}H_{28}O_4$ $[M + H]^+$ 477.2060, found 477.2066. (S_{ax},S_{ax},*R*,*R*,*R*,*R*)-**9**: $[\alpha]_D^{20}$ = +101.6 (c = 0.47, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{32}H_{28}O_4$ $[M + H]^+$ 477.2060, found 477.2064.

(*R*,*R*)-1,8,9,16-Tetrahydroxytetraphenylene [(*R*,*R*)-10] and (*S*,*S*)-10. Compound **9** (50.0 mg, 0.1 mmol) was suspended in CH_2Cl_2 (1 mL) under nitrogen atmosphere with stirring at 0 °C. Boron tribromide solution (0.5 M in CH_2Cl_2, 1.0 mL, 0.5 mmol) was injected slowly into the reaction mixture. The mixture was then allowed to warm to room temperature and stirred overnight. The reaction was quenched with water (5 mL), and the mixture was extracted with EtOAc (5 mL × 3) successively. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:2) to afford pure 1,8,9,16-tetrahydroxytetraphenylene (*R*,*R*)-**10** (41.4 mg, 95%) as colorless solids: mp > 300 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.53 (d, J = 7.2 Hz, 4 H), 6.60 (d, J = 7.2 Hz, 4 H), 6.96 (t, J = 7.6 Hz, 4 H); HRMS (EI) m/z calcd for $C_{24}H_{16}O_4$ $[M]^+$ 368.1043, found 368.1042. The ^{1}H and ^{13}C NMR spectroscopic and mass spectrometric data of (*S*,*S*)-**10** were consistent with (*R*,*R*)-**10**

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reported.[4] (*R*,*R*)-**10**: $[\alpha]_D^{20}$ = +54.7 (*c* =1.10, MeOH). (*S*,*S*)-**10**: $[\alpha]_D^{20}$ = −55.3 (*c* = 1.13, MeOH).[4]

5,22-Dihydrobenzo[*h*]tetraphenyleno[1,16-*bcd*][1,6]-dioxecine-13,14-dimethoxymethoxy [(*S*,*S*)-13] and (*R*,*R*)-13. To a stirring solution of (*S*,*S*)-**12** (220.0 mg, 0.5 mmol) in dried THF (5.8 mL) under nitrogen atmosphere was slowly added NaH (102.6 mg, 2.5 mmol) at 0 °C. After the solution was stirred for 15 min, MOMCl (106.2 μL, 1.4 mmol) was injected slowly. The mixture was stirred for 2 h and then diluted with water. The mixture was extracted with EtOAc (15 mL × 3) and washed with saturated brine solution (30 mL × 2) successively. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:5) to give pure (*S*,*S*)-**13** (224.0 mg, 86%) as colorless waxy solids: ^{1}H NMR (400 MHz, acetone-d_6) δ 3.17 (s, 6 H), 4.85 (d, *J* = 7.6 Hz, 2 H), 4.98 (d, *J* = 6.4, 2 H), 5.10 (d, *J* = 9.6, 2 H), 5.27 (d, *J* = 12.0, 2 H), 6.74 (d, *J* = 7.5, 2 H), 6.79 (d, *J* = 7.1, 2 H), 6.99 (d, *J* = 8.0, 2 H), 7.04 (d, *J* = 8.0, 2 H), 7.11 (t, *J* = 8.0, 4 H), 7.30 (m, 2 H), 7.46 (s, 2 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 55.8, 95.6, 114.8, 122.6, 123.4, 128.0,128.6, 128.8, 129.4, 132.3, 137.3, 144.1, 144.2, 155.2. (*S*,*S*)-**13**: $[\alpha]_D^{20}$ = −27.6 (*c* = 0.92, CH_2Cl_2); HRMS (ESI) *m*/*z* calcd for $C_{36}H_{30}O_6$ [M + Na]$^+$ 581.1935, found 581.1930. (*R*,*R*)-**13**: $[\alpha]_D^{20}$ = +25.8 (*c* = 0.89, CH_2Cl_2); HRMS (ESI) *m*/*z* calcd for $C_{36}H_{30}O_6$ [M + Na]$^+$ 581.1935, found 581.1943.

(*S*,*S*)-8,9-Bis(methoxymethoxy)tetraphenylene-1,16-diol [(*S*,*S*)-14] and (*R*,*R*)-14. To a solution of (*S*,*S*)-**13** (53.0 mg, 0.1 mmol) in THF (3 mL) was added palladium black catalyst (10 mol %). The mixture was stirred under hydrogen atmosphere for 2 h. The mixture was then filtered through Celite. The filtrate was concentrated and purified by column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:2) to give pure (*S*,*S*)-**14** (40.3 mg, 93%) as colorless waxy solid: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.25 (s, 6 H), 4.89 (d, *J* = 6.4 Hz, 2 H), 5.00 (d, *J* = 6.4 Hz, 2 H), 6.82 (d, *J* = 8 Hz, 2 H), 6.87 (d, *J* = 7.2 Hz, 2 H), 6.93 (d, *J* = 7.6 Hz, 2 H), 7.04 (d, *J* = 8 Hz, 2 H), 7.23 (dd, *J* = 8, 16 Hz, 4 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 55.7, 95.1, 114.4, 114.7, 120.8, 121.2, 121.9, 126.9, 128.4, 129.6, 142.9, 144.5, 152.5, 154.4. (*S*,*S*)-**14**: $[\alpha]_D^{20}$ = −19.3 (*c* = 0.86, CH_2Cl_2); HRMS (ESI) *m*/*z* calcd for $C_{28}H_{24}O_6$ [M + Na]$^+$ 479.1465, found 479.1462. (*R*,*R*)-**14**: $[\alpha]_D^{20}$ = +20.7 (*c* = 0.78, CH_2Cl_2); HRMS (ESI) *m*/*z* calcd for $C_{28}H_{24}O_6$ [M + Na]$^+$ 479.1465, found 479.1462.

(*S*,*S*)-16-(Benzyloxy)-8,9-bis(methoxymethoxy)-tetraphenylen-1-ol [(*S*,*S*)-15] and (*R*,*R*)-15. To a solution of (*S*,*S*)-**14** (80.0 mg, 0.2 mmol) in dried DMF (2 mL) under nitrogen atmosphere was added K_2CO_3 (25.8 mg, 0.2 mmol). The mixture was allowed to stir for 0.5 h at room temperature. Benzyl bromide (21.0 μL, 0.2 mmol) was dropped into the mixture slowly. The mixture was then stirred for another 3 h. The mixture was treated with water (20 mL) and extracted with EtOAc (15 mL × 3). The combined organic layer was washed with saturated brine solution (20 mL × 2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:6) to give pure (*S*,*S*)-**15** (65.0 mg, 70%) as colorless waxy solids: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.26 (d, *J* = 0.9 Hz, 6 H), 4.91 (dd, *J* = 4, 6.6 Hz, 2 H), 4.95 (s, 1 H), 5.01 (t, *J* = 6.4 Hz, 3 H), 6.82 (d, *J* = 8.0 Hz, 2 H), 6.94 (t, *J* = 8 Hz, 4 H), 7.04 (t, *J* = 8.4 Hz, 2 H), 7.16−7.30 (m, 9 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 55.7, 70.8, 95.1, 112.7, 114.1, 114.2, 114.3, 120.5, 121.9, 122.1, 123.4, 124.1, 127.0, 127.1, 127.8, 128.3, 128.3, 128.4, 128.7, 129.3, 137.0, 143.0, 143.2, 143.5, 145.0, 152.7, 154.4, 155.1. (*S*,*S*)-**15**: $[\alpha]_D^{20}$ = −44.2 (*c* = 0.96, CH_2Cl_2); HRMS (ESI) *m*/*z* calcd for $C_{35}H_{30}O_6$ [M + Na]$^+$ 569.1935, found 569.1941. (*R*,*R*)-**15**: $[\alpha]_D^{20}$ = +41.2 (*c* = 0.86, CH_2Cl_2); HRMS (ESI) *m*/*z* calcd for $C_{35}H_{30}O_6$ [M + Na]$^+$ 569.1935, found 569.1930.

(*S*,*S*)-1-(Benzyloxy)-16-(2-bromoethoxy)-8,9-bis-(methoxymethoxy)tetraphenylene [(*S*,*S*)-16] and (*R*,*R*)-16. Compound (*S*,*S*)-**15** (61.0 mg, 0.1 mmol) was dissolved in acetone (2 mL) under nitrogen atmosphere followed by the addition of K_2CO_3 (232.0 mg, 1.0 mmol). 1,2-Dibromoethane (4.0 M in acetone, 1.2 mL) was injected to the mixture. The mixture was then heated to reflux with stirring. After 1 h, the mixture was cooled and diluted with water (15 mL). The mixture was extracted with EtOAc (10 mL × 3). After concentration under reduced pressure, the residue was purified by column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:8) to give pure (*S*,*S*)-**16** (51.0 mg, 71%) as colorless waxy solids: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.28 (t, *J* = 8.0 Hz, 8 H), 4.03 (t, *J* = 6.0 Hz, 2 H), 4.89−5.02 (m, 6 H), 6.87 (t, *J* = 8.0 Hz, 3H), 6.95 (t, *J* = 4.8 Hz, 3 H), 7.04 (d, *J* = 8.0 Hz, 4 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 7.20−7.28 (m, 7 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 29.5, 55.7, 69.4, 70.5, 95.3, 111.9, 113.0, 114.3, 114.3, 121.0, 122.0, 122.2, 122.2, 126.5, 126.8, 127.2, 127.5, 128.3, 128.3, 137.7, 143.4, 143.5, 143.6, 143.7, 154.5, 154.5, 155.6, 155.8. (*S*,*S*)-**16**: $[\alpha]_D^{20}$ = −34.3 (*c* = 0.64, CH_2Cl_2); HRMS (ESI) *m*/*z* calcd for $C_{37}H_{33}BrO_6$ [M + Na]$^+$ 675.1353, found 675.1349. (*R*,*R*)-**16**: $[\alpha]_D^{20}$ = +31.3 (*c* = 1.02, CH_2Cl_2); HRMS (ESI) *m*/*z* calcd for $C_{37}H_{33}BrO_6$ [M + Na]$^+$ 675.1353, found 675.1345.

(*S*,*S*,*S*,*S*)-1,2-Bis(16-(benzyloxy)-8,9-bis(methoxymethoxy)-tetraphenylen-1-yloxy)ethane [(*S*,*S*,*S*,*S*)-17] and (*R*,*R*,*R*,*R*)-17. To a stirring solution of compounds (*S*,*S*)-**15** (50.0 mg, 0.1 mmol) and (*S*,*S*)-**16** (43.0 mg, 0.1 mmol) in acetone (1.4 mL) was added K_2CO_3 (188.0 mg, 1.4 mmol). The mixture was heated to reflux overnight. The mixture was cooled and was diluted with water (15 mL). The mixture was extracted with CH_2Cl_2 (15 mL × 3) successively. After removal of solvent, the residue was purified by column chromatography on silica gel (5 g, EtOAc/CH_2Cl_2/hexanes, 1:1:6) to give pure (*S*,*S*,*S*,*S*)-**17** (30.5 mg, 42%) as colorless waxy solids: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.24 (s, 6 H), 3.72 (s, 2 H), 4.79 (d, *J* = 5.6 Hz, 2 H), 4.88 (d, *J* = 6.4 Hz, 2 H), 4.99 (dd, *J* = 2.0, 6.6 Hz, 2 H), 6.49 (d, *J* = 8.0 Hz, 1 H), 6.78−6.91 (m, 5 H), 7.01 (d, *J* = 8.0 Hz, 4 H), 7.09 (t, *J* = 8.0 Hz, 1 H), 7.14−7.24 (m, 6 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 55.7, 68.3, 70.3, 95.2, 111.9, 112.8, 114.1, 121.1, 121.3, 122.1, 122.2, 126.5, 126.8, 126.9, 127.0, 127.4, 128.2, 128.3, 128.4, 137.6, 143.2, 143.3, 143.5, 143.6, 154.4, 155.6, 156.2. (*S*,*S*,*S*,*S*)-**17**: $[\alpha]_D^{20}$ = −38.9 (*c* = 0.72, CH_2Cl_2); HRMS (ESI) *m*/*z* calcd for $C_{72}H_{62}O_{12}$ [M + Na]$^+$ 1141.4133, found 1141.4129. (*R*,*R*,*R*,*R*)-**17**: $[\alpha]_D^{20}$ = +45.6 (*c* = 0.69, CH_2Cl_2); HRMS (ESI) *m*/*z* calcd for $C_{72}H_{62}O_{12}$ [M + Na]$^+$ 1141.4133, found 1141.4137.

(*S*,*S*,*S*,*S*)-16,16′-(Ethane-1,2-diylbis(oxy))bis(8,9-bis-(methoxymethoxy)tetraphenylen-1-ol) [(*S*,*S*,*S*,*S*)-18] and (*R*,*R*,*R*,*R*)-18. To a solution of compound (*S*,*S*,*S*,*S*)-**17** (21.3 mg, 20.0 μmol) in THF (3 mL) was added palladium black catalyst (10 mol %). The mixture was stirred under hydrogen atmosphere for 12 h. The mixture was then filtered through Celite. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:1) to give pure (*S*,*S*,*S*,*S*)-**18** (16.9 mg, 90%) as colorless waxy solids: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.25 (s, 6 H), 3.91 (d, *J* = 7.5 Hz, 1 H), 4.02 (d, *J* = 7.6 Hz, 1 H), 4.89 (t, *J* = 5.2 Hz, 2 H), 5.01 (t, *J* = 6.4 Hz, 2 H), 5.25 (s, 1 H), 6.74 (dd, *J* = 8.0, 20.8 Hz, 3 H), 6.82 (d, *J* = 11.2 Hz, 1 H), 6.89 (t, *J* = 8.0 Hz, 2 H), 7.03 (t, *J* = 7.2 Hz, 2 H), 7.12−7.24 (m, 4 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 55.7, 68.5, 95.2, 113.1, 114.1, 114.4, 114.7, 120.7, 122.0, 122.1, 122.3, 123.7, 124.5, 127.0, 127.1, 128.3, 128.3, 128.6, 129.4, 143.0, 143.3, 143.6, 144.7, 152.6, 154.4, 155.4. (*S*,*S*,*S*,*S*)-**18**: $[\alpha]_D^{20}$ = −62.3 (*c* = 0.83, Me_2CO); HRMS (ESI) *m*/*z* calcd for $C_{58}H_{50}O_{12}$ [M + Na]$^+$ 961.3194, found 961.3192. (*R*,*R*,*R*,*R*)-**18**: $[\alpha]_D^{20}$ = +62.3 (*c* = 0.95, Me_2CO); HRMS (ESI) *m*/*z* calcd for $C_{58}H_{50}O_{12}$ [M + Na]$^+$ 961.3194, found 961.3200.

(*S*,*S*,*S*,*S*)-1,2-Bis(16-(2-bromoethoxy)-8,9-bis-(methoxymethoxy)tetraphenylen-1-yloxy)ethane [(*S*,*S*,*S*,*S*)-19] and (*R*,*R*,*R*,*R*)-19. Compound (*S*,*S*,*S*,*S*)-**18** (32.0 mg, 34.0 μmol) was dissolved in acetone (3 mL) under nitrogen atmosphere followed by the addition of K_2CO_3 (142 mg, 1.0 mmol). 1,2-Dibromoethane (4.0 M in acetone, 0.7 mL) was injected to the mixture. The mixture was then heated to reflux with stirring. After 1 h, the solution was cooled and diluted with water (15 mL). The mixture was extracted with EtOAc (10 mL × 3). After concentration under reduced pressure, the residue was purified by column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:8) to give pure (*S*,*S*,*S*,*S*)-**19** (20.4 mg, 52%) as colorless waxy solids: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.24 (m, 8 H), 3.83−3.90 (m, 2 H), 3.99−4.08 (m, 2 H), 4.88 (t, *J* = 4.0 Hz, 2 H), 4.90 (d, *J* = 4.0 Hz, 2 H), 6.66 (dd, *J* = 8.0, 24.0 Hz, 1 H), 6.78 (d, *J* = 7.6 Hz, 1 H), 6.84 (d, *J* = 7.6 Hz, 1 H), 6.89 (dd, *J* = 4.0, 6.8 Hz, 2 H),

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7.02 (t, J = 8.2 Hz, 2 H), 7.06−7.27 (m, 4 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 29.7, 55.7, 68.9, 69.4, 95.2, 111.2, 113.0, 114.1, 114.1, 121.3, 121.9, 122.1, 122.2, 122.2, 126.6, 127.0, 127.3, 128.2, 128.3, 128.5, 143.1, 143.3, 143.5, 143.6, 154.3, 154.4, 155.3, 156.2. (*S*,*S*,*S*,*S*)-**19**: $[\alpha]_D^{20}$ = −20.7 (c = 0.78, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{62}H_{56}Br_2O_{12}$ [M + Na]$^+$ 1175.2011, found 1175.2011. (*R*,*R*,*R*,*R*)-**19**: $[\alpha]_D^{20}$ = +19.5 (c = 0.86, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{62}H_{56}Br_2O_{12}$ [M + Na]$^+$ 1175.2011, found 1175.2010.

Tetramer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-20 and (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-20. To a stirring solution of compounds (*S*,*S*,*S*,*S*)-**18** (25.0 mg, 25.0 μmol) and (*S*,*S*,*S*,*S*)-**19** (17.0 mg, 15.0 μmol) in acetone (1.0 mL), K_2CO_3 (80.0 mg, 0.6 mmol) was added. The mixture was heated to reflux overnight. The solution was cooled and was diluted with water (15 mL). After that, the mixture was partitioned between water and CH_2Cl_2 (15 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After removal of solvent, the residue was purified by column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:3−1:1:1) to give pure (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20** (11.5 mg, 40%) as colorless waxy solids: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.24 (s, 3 H), 3.76−3.84 (m, 2 H), 4.88 (d, J = 6.4 Hz, 2 H), 4.99 (d, J = 6.8 Hz, 2 H), 6.50 (d, J = 8.4 Hz, 1 H), 6.75 (d, J = 7.8 Hz, 1 H), 6.87 (d, J = 7.8 Hz, 1 H), 7.01 (d, J = 8.4 Hz, 1 H), 7.14 (t, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 55.7, 69.5, 95.2, 113.5, 114.1, 121.7, 122.2, 127.2, 128.3, 128.6, 143.3, 143.4, 154.3, 156.3; IR ν_{max} (film) cm^{-1} 3118.5, 2992.3, 2882.6, 1591.1, 1516.2, 1484.8, 1159.4, 1109.3, 1059.7, 857.5, 767.5, 745.6, 710.5. (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**20**: $[\alpha]_D^{20}$ = −18.1 (c = 0.92, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{120}H_{104}O_{24}$ [M + Na]$^+$ 1952.6844, found 1952.6846. (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**20**: $[\alpha]_D^{20}$ = +21.1 (c = 0.78, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{120}H_{104}O_{24}$ [M + Na]$^+$ 1952.6844, found 1952.6853.

(*S*,*S*,*S*,*S*,*S*,*S*)-16,16′-((((8,9-Bis(methoxymethoxy)-tetraphenylene-1,16-diyl)bis(oxy))bis(ethane-2,1-diyl))bis-(oxy))bis(1-(benzyloxy)-8,9-bis(methoxymethoxy)-tetraphenylene) [(*S*,*S*,*S*,*S*,*S*,*S*)-21] and (*R*,*R*,*R*,*R*,*R*,*R*)-21. To a stirring solution of compounds (*S*,*S*)-**14** (45.0 mg, 0.1 mmol) and (*S*,*S*)-**16** (130.0 mg, 0.2 mmol) in acetone (4 mL) was added Cs_2CO_3 (130.3 mg, 0.4 mmol). The mixture was heated to reflux 24 h. The mixture was cooled and was diluted with water (15 mL). The mixture was extracted with CH_2Cl_2 (15 mL × 3) successively. After removal of solvent, the residue was purified by column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:6) to give pure (*S*,*S*,*S*,*S*,*S*,*S*)-**21** (86.4 mg, 54%) as colorless waxy solids. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.25 (d, J = 2.0 Hz, 18 H), 3.68 (t, J = 8.0 Hz, 8 H), 4.80 (s, 4 H), 4.89 (dd, J = 3.6, 6.4 Hz, 6 H), 4.89 (dd, J = 3.6, 6.4 Hz, 6 H), 6.50 (dd, J = 8.4, 10.4 Hz, 4 H), 6.72−6.91 (m, 14 H), 6.97−7.12 (m, 10 H), 7.13−7.23 (m, 18 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 55.7, 68.4, 68.6, 70.4, 95.2, 112.0, 112.8, 113.1, 114.1, 121.1, 121.3, 121.4, 122.1, 122.2, 126.5, 126.8, 126.8, 127.0, 127.0, 127.4, 128.2, 128.2, 128.2, 128.3, 128.3, 128.4, 137.6, 143.2, 143.2, 143.4, 143.5, 143.4, 143.5,143.6, 154.3, 154.3, 155.6, 156.0, 156.2; IR ν_{max} (film) cm^{-1} 3117.4, 2993.2, 2882.1, 1615.0, 1590.7, 1520.9, 1487.6, 1160.8, 1059.4, 886.6, 858.2, 768.2, 624.5. (*S*,*S*,*S*,*S*,*S*,*S*)-**21**: $[\alpha]_D^{20}$ = −42.3 (c = 0.48, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{102}H_{88}O_{18}$[M + Na]$^+$ 1624.5897, found 1624.5879. (*R*,*R*,*R*,*R*,*R*,*R*)-**21**: $[\alpha]_D^{20}$ = +39.1 (c = 0.52, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{102}H_{88}O_{18}$[M + Na]$^+$ 1624.5897, found 1624.5890.

(*S*,*S*,*S*,*S*,*S*,*S*)-16,16′-((((8,9-Bis(methoxymethoxy)-tetraphenylene-1,16-diyl)bis(oxy))bis(ethane-2,1-diyl))bis-(oxy))bis(8,9-bis(methoxymethoxy)tetraphenylen-1-ol) [(*S*,*S*,*S*,*S*,*S*,*S*)-22] and (*R*,*R*,*R*,*R*,*R*,*R*)-22. Compound (*S*,*S*,*S*,*S*,*S*,*S*)-**22** was prepared from (*S*,*S*,*S*,*S*,*S*,*S*)-**21** (42.0 mg, 26.0 μmol) by using the same preparative method as that for compound (*S*,*S*)-**18**. Column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:1) gave pure (*S*,*S*,*S*,*S*,*S*,*S*)-**22** (26.1 mg, 70%) as colorless waxy solids: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.25 (s, 18 H), 3.74−3.81 (m, 8 H), 4.89 (dd, J = 2.8, 6.4 Hz, 6 H), 5.00 (m, 6 H), 6.59 (dd, J = 8.0, 20 Hz, 5 H), 6.76−6.79 (m, 6 H), 6.83−6.90 (m, 6 H), 7.01−7.04 (m, 6 H), 7.10−7.22 (m, 13 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 55.7, 55.7, 68.6, 68.8, 95.2, 113.4, 113.5, 114.0, 114.1, 114.3, 114.7, 120.6, 121.7, 122.1, 122.2, 122.2, 123.9, 124.8, 126.8, 126.9, 127.0, 127.1, 128.3, 128.5, 128.6, 129.3, 143.1, 143.2, 143.5, 143.6, 144.3, 152.6, 154.3, 154.4, 154.4, 155.5, 155.8; IR ν_{max} (film) cm^{-1} 3118.1, 2992.5, 1615.2, 1591.1, 1516.9, 1485.5, 1378.9, 1323.1, 1059.7, 857.6, 767.7. (*S*,*S*,*S*,*S*,*S*,*S*)-**22**: $[\alpha]_D^{20}$ = −27.6 (c = 0.32, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{88}H_{76}O_{18}$[M + Na]$^+$ 1443.4924, found 1443.4923. (*R*,*R*,*R*,*R*,*R*,*R*)-**22**: $[\alpha]_D^{20}$ = +26.5 (c = 0.34, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{88}H_{76}O_{18}$[M + Na]$^+$ 1443.4924, found 1443.4934.

(*S*,*S*,*S*,*S*,*S*,*S*)-16,16′-((((8,9-Bis(methoxymethoxy)-tetraphenylene-1,16-diyl)bis(oxy))bis(ethane-2,1-diyl))bis-(oxy))bis(1-(2-bromoethoxy)-8,9-bis(methoxymethoxy)-tetraphenylene) [(*S*,*S*,*S*,*S*,*S*,*S*)-23] and (*R*,*R*,*R*,*R*,*R*,*R*)-23. Compound (*S*,*S*,*S*,*S*,*S*,*S*)-**23** was prepared from (*S*,*S*,*S*,*S*,*S*,*S*)-**22** (38.0 mg, 26.7 μmol) by using the same preparative method as that for compound (*S*,*S*)-**19**. Column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:8) gave pure (*S*,*S*,*S*,*S*,*S*,*S*)-**23** (27.3 mg, 62%) as colorless waxy solids: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.22−3.26 (m, 22 H), 3.78−3.86 (m, 8 H), 4.96−4.01 (m, 4 H), 5.00 (m, 6 H), 4.87 (d, J = 6.4, 6 H), 4.98−5.00 (m, 6 H), 6.60 (q, J = 8.0 Hz, 4 H), 6.75 (d, J = 7.6 Hz, 4 H), 6.82−6.90 (m, 10 H), 7.01 (d, J = 8.4 Hz, 6 H), 7.10−7.27 (m, 12 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 29.8, 55.7, 68.8, 68.9, 69.1, 69.6, 69.7, 95.4, 112.5, 113.0, 113.0, 113.2, 113.3, 113.4, 114.3, 121.4, 121.6, 122.1, 122.2, 122.3, 122.3, 126.7, 127.2, 127.2, 127.3, 127.6, 128.3, 128.4, 124.5, 128.5, 143.3, 143.5, 143.6, 143.7, 143.8, 154.4, 154.5, 155.4, 156.2, 156.3. 156.4; IR ν_{max} (film) cm^{-1} 3117.4, 2993.2, 2882.1, 1615.0, 1590.7, 1520.9, 1487.6, 1181.0, 1160.8, 886.6, 858.2, 768.2, 749.0. (*S*,*S*,*S*,*S*,*S*,*S*)-**23**: $[\alpha]_D^{20}$ = −16.8 (c = 0.29, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{92}H_{82}Br_2O_{18}$ [M + Na]$^+$ 1657.3759, found 1657.3760. (*R*,*R*,*R*,*R*,*R*,*R*)-**23**: $[\alpha]_D^{20}$ = +12.6 (c = 0.21, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{92}H_{82}Br_2O_{18}$ [M + Na]$^+$1657.3759, found 1657.3763.

Pentamer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-24 and (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-24. To a stirring solution of compounds (*S*,*S*,*S*,*S*,*S*,*S*)-**23** (30.0 mg, 18.0 μmol) and (*S*,*S*,*S*,*S*)-**18** (17.0 mg, 18.0 μmol) in acetone (3.0 mL), K_2CO_3 (50.0 mg, 360.0 μmol) was added. The mixture was heated to reflux overnight. The mixture was cooled and was diluted with water (15 mL). After that, the mixture was partitioned between water and CH_2Cl_2 (15 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After removal of solvent, the residue was purified by column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:3−1:1:1) to give pure (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**24** (17.4 mg, 40%) as colorless waxy solids: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.24 (s, 6 H), 3.78 (s, 4 H), 4.88 (d, J = 6.5 Hz, 2 H), 4.99 (d, J = 6.5 Hz, 2 H), 6.53 (d, J = 8.0 Hz, 2 H), 6.75 (d, J = 8.0 Hz, 2 H), 6.85 (d, J = 7.6 Hz, 2 H), 7.01 (d, J = 7.6 Hz, 2 H), 7.11−7.16 (m, 4 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 55.7, 69.3, 95.3, 113.5, 114.2, 121.6, 122.2, 127.1, 127.2, 128.3, 128.5, 143.4, 143.5, 154.4, 156.2; IR ν_{max} (film) cm^{-1} 3118.1, 2991.7, 2882.8, 1615.5, 1566.0, 1513.2, 1484.1, 1060.8, 854.8, 767.5. (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**24**: $[\alpha]_D^{20}$ = −7.6 (c = 0.12, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{150}H_{130}O_{30}$ [M + Na]$^+$ 2434.8573, found 2434.8545. (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**24**: $[\alpha]_D^{20}$ = +6.8 (c = 0.09, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{150}H_{130}O_{30}$ [M + Na]$^+$ 2434.8573, found 2434.8556.

Hexamer (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-25 and (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-25. Compound (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**25** was prepared from (*S*,*S*,*S*,*S*,*S*,*S*)-**23** (18.0 mg, 11.0 μmol) and (*S*,*S*,*S*,*S*,*S*,*S*)-**22** (10.0 mg, 7.0 μmol) by using the same preparative method as that for compound (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**24**. Column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:6) gave pure (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**25** (8.1 mg, 40%) as colorless waxy solids: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.24 (s, 6 H), 3.61−3.80 (m, 4 H), 4.88 (d, J = 6.4 Hz, 2 H), 4.99 (d, J = 6.4 Hz, 2 H), 6.43 (d, J = 8.0 Hz, 1 H), 6.55 (d, J = 8.0 Hz, 2 H), 6.67−6.85 (m, 2 H), 6.91 (d, J = 8.0 Hz, 3 H), 6.97−7.16 (m, 3 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 56.0, 95.5, 113.8, 114.4, 121.9, 122.4, 127.3, 127.4, 128.6, 128.8, 143.6, 143.7, 154.6, 156.4; IR ν_{max} (film) cm^{-1} 3118.3, 3043.5, 2990.4, 2882.0, 1591.2, 1516.6, 1483.48, 1378.6, 1060.7, 858.1, 767.5, 710.4. (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**25**: $[\alpha]_D^{20}$ = −8.5 (c = 0.10, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{180}H_{156}O_{36}$ [M + Na]$^+$ 1470.5114, found 1470.5122. (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*)-**25**: $[\alpha]_D^{20}$ = +7.2 (c = 0.08, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{180}H_{156}O_{36}$ [M + Na]$^+$ 1470.5114, found 1470.5122.

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Crystallographic Details for (R_{ax},*S*,*S*)-6. Yellow crystals were grown from a solution of (*Rax*,*S*,*S*)-**6** in CH_2Cl_2 and *n*-hexane. A crystal of good quality was selected and mounted on a glass fiber. A total of 45768 reflections ($-9 \le h \le 8$, $-14 \le k \le 14$, $-18 \le l \le 18$) were collected at T = 296(2) K in the θ range from 2.12 to 25.24°, of which 2816 were unique R(int) = 0.0732; Mo Kα radiation (λ= 0.71073 Å). The residual peak and hole electron density were 0.532 and −0.269 e/Å^3. The absorption coefficient was 0.110 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.0728, wR_2 = 0.1596, and GOF = 1.023 [$I > 2\sigma(I)$]. $C_{16}H_{14}N_2O_6$, orthorhombic, space group $P2(1)2(1)2(1)$, a = 8.132(3) Å, b = 12.160(5) Å, c = 15.703(6) Å, α = 90°, β = 90°, γ = 90°, V= 1552.8(11)Å^3, Z = 4, ρ_{calcd} = 1.413 Mg/cm^3, F(000) = 688, $R(F)$ = 0.0561, w$R(F^2)$ = 0.1488.

Crystallographic Details for (R_{ax},*S*,*S*)-8. Colorless crystals were grown from a solution of (R_{ax},*S*,*S*)-**8** in CH_2Cl_2 and *n*-hexane. A crystal of good quality was selected and mounted on a glass fiber. A total of 27722 reflections ($-9 \le h \le 9$, $-17 \le k \le 17$, $-21 \le l \le 21$) were collected at T = 293(2) K in the θ range from 1.96 to 27.87°, of which 2197 were unique R(int) = 0.0555; Mo Kα radiation (λ = 0.71073 Å). The residual peak and hole electron density were 0.319 and −1.524 e/Å^3. The absorption coefficient was 3.918 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.0260, wR_2 = 0.0617, and GOF = 1.307 [$I > 2\sigma(I)$]. $C_{16}H_{14}N_2O_6$, orthorhombic, space group $P2(1)2(1)2(1)$, a = 7.2906(5) Å, b = 13.4966(8) Å, c = 16.3088(10) Å, α = 90°, β = 90°, γ = 90°, V= 1552.8(11)Å^3, Z = 4, ρ_{calcd}= 2.037 Mg/cm^3, F(000)= 928, $R(F)$= 0.0252, w$R(F^2)$= 0.0612.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Asymmetric synthesis of (*R*,*R*)- and (*S*,*S*)-1,8,9,16-tetrahydroxytetraphenylenes (**10**), enantiopure tetramer **20**, pentamer **24**, and hexamer **25**, complete experimental data of the X-ray crystallographic determination of (R_{ax},*S*,*S*)-**6** and (R_{ax},*S*,*S*)-**8**, and typical plots of hosts toward amino acid ester salts. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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