JOC*Article*

Synthesis, Resolution, and Applications of 1,16-Dihydroxytetraphenylene as a Novel Building Block in Molecular Recognition and Assembly[1]

Jian-Feng Wen,[2] Wei Hong,[2] Ke Yuan,[3] Thomas C. W. Mak,[4] and Henry N. C. Wong*[,2,4,5]

Shanghai−Hong Kong Joint Laboratory in Chemical Synthesis, Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, 354 Feng Lin Road, Shanghai 200032, China, State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, 354 Feng Lin Road, Shanghai 200032, China, Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, and Central Laboratory, Institute of Molecular Technology for Drug Discovery and Synthesis, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

hncwong@cuhk.edu.hk

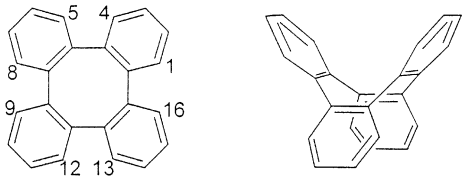
Received July 28, 2003

This paper concerns the synthesis of 1,16-dihydroxytetraphenylene (DHTP) (**2**) by employing a novel NBS bromination route. (±)-DHTP **2** was successfully resolved into its optical antipodes and converted to (±)-1,16-bis(diphenylphosphino)tetraphenylene (BPTP) (**26**), whose platinum complex BPTP−$PtCl_2$ (**27**) was also obtained. As a hydrogen bond donor, racemic and optically active DHTP **2** was allowed to assemble with 4,4′-bipyridine to form single crystals of good quality. X-ray Diffraction studies of these crystals revealed that the crystallographic packing of the hydrogen bonded complex between (±)-**2** and 4,4′-bipyridine was different from the one formed from (*S*)-**2** and 4,4′-bipyridine. It was found that an infinite zigzag chain with alternate chirality was formed in the assembly of (±)-**2** and 4,4′-bipyridine, while (*S*)-**2** and 4,4′-bipyridine failed to show the same assembly pattern. The reason (±)-**2** formed an alternate and zigzag chain with 4,4′-bipyridine was most likely due to the inherent stability of this supramolecular assembly. The chiral recognition between **2** and optically active BINAP under the direction of platinum(II) has also been examined. ^1H and ^{31}P NMR spectroscopic studies demonstrated that there was an obvious discrimination of **2** between the enantiomers of BINAP−$PtCO_3$.

Introduction

Tetraphenylene (**1**) is a structurally highly intriguing molecule that possesses a ground state D_{2d} geometry (Scheme 1). Several research teams have been actively engaged in the syntheses[6] and various physical[6,7] studies of **1** and its analogues.[8]

SCHEME 1



1 Tub-shape structure of **1**

In view of the interesting properties of tetraphenylene (**1**), we have commenced a program with the aim to prepare five tetraphenylenols **2**−**6**[9] as shown in Scheme 2. Due to the very high barrier to ring inversion of **1**,[7] it is worthy to note that **2**, **3**, and **5** could in principle be

(1) Taken in part from the doctoral thesis of J.F.W., Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, Shanghai, China, 2003.

(2) Shanghai−Hong Kong Joint Laboratory in Chemical Synthesis, The Chinese Academy of Sciences.

(3) State Key Laboratory of Organometallic Chemistry, The Chinese Academy of Sciences.

(4) Department of Chemistry, The Chinese University of Hong Kong.

(5) Institute of Molecular Technology for Drug Discovery and Synthesis, The Chinese University of Hong Kong.

(6) For reviews, see: (a) Mak, T. C. W.; Wong, H. N. C. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, P., Eds.; Pergamon Press: Oxford, 1996; Vol. 6, pp 351−369. (b) Mak, T. C. W.; Wong, H. N. C. *Top. Curr. Chem.* **1987**, *140*, 141−164. (c) Rajca, A.; Safronov, A.; Rajca, S.; Shoemaker, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 488−491. (d) Rajca, A.; Safronov, A.; Rajca, S.; Wongsriratanakul, J. *J. Am. Chem. Soc.* **2000**, *122*, 3351−3357. (e) Rajca, A.; Wang, H.; Bolshov, P.; Rajca, S. *Tetrahedron* **2001**, *57*, 3725−3735. (f) Rathore, R.; Magueres, P. L.; Lindeman, S. V.; Kochi, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 809−812. (g) Iyoda, M.; Kabir, S. H. M.; Vorasingha, A.; Kuwatani, Y.; Yoshida, M. *Tetrahedron Lett.* **1998**, *39*, 5393−5396. (h) Kabir, S. M. H.; Iyoda, M. *Synthesis* **2000**, 1839−1842. (i) Kabir, S. M. H.; Hasegawa, M.; Kuwatani, Y.; Yoshida, M.; Matsuyama, H.; Iyoda, M. *J. Chem. Soc., Perkin Trans. 1* **2001**, 159−165.

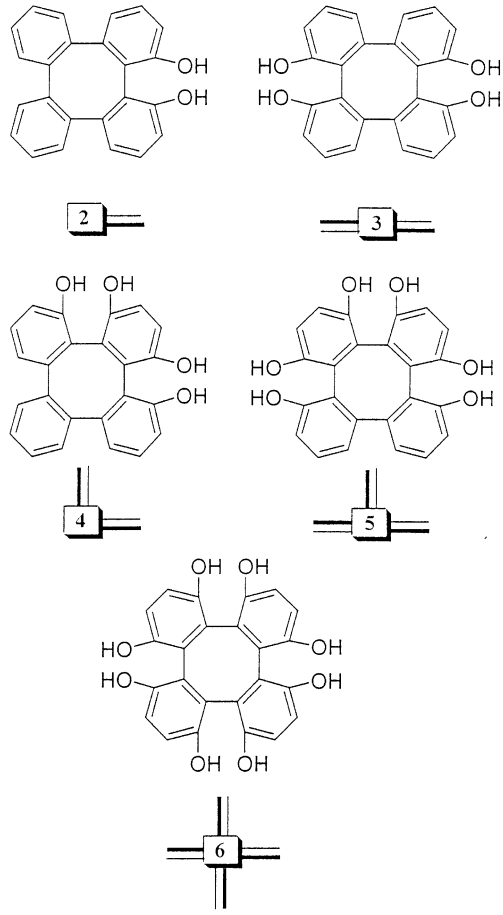
(7) (a) Figeys, H. P.; Dralants, A. *Tetrahedron Lett.* **1971**, 3901−3904. (b) Finder, C. J.; Chung, D.; Allinger, N. L. *Tetrahedron Lett.* **1972**, 4677−4680. (c) Gust, D.; Senkler, G. H., Jr.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1972**, 1345−1345. (d) Senkler, G. H., Jr.; Gust, D.; Riccobono, P. X.; Mislow, K. *J. Am. Chem. Soc.* **1972**, *94*, 8626−8627. (e) Rashi-Ranjbar, P.; Man, Y.-M.; Sandström, J.; Wong, H. N. C. *J. Org. Chem.* **1989**, *54*, 4888−4892.

(8) (a) Matsuura, A.; Komatsu, K. *J. Am. Chem. Soc.* **2001**, *123*, 1768−1769. (b) Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 1755−1759. (c) Marsella, M. J. *Acc. Chem. Res.* **2002**, *35*, 944−951 and references therein.

(9) Lai, C. W.; Lam, C. K.; Lee, H. K.; Mak, T. C. W.; Wong, H. N. C. *Org. Lett.* **2003**, *5*, 823−826.

10.1021/jo0302408 CCC: $25.00
Published on Web 10/14/2003

SCHEME 2



resolved into their optical antipodes. On the other hand, **4** and **6** are intrinsically achiral. Because of their nonplanar and defined three-dimensional structures, **2**−**6** are able to serve as chiral and nonchiral building blocks with their oxygen atoms being reactive sites. Geometrically, **3** is a linear unit containing reactive sites whose angle is 180°, while the reactive sites of **4** comprise an angle of 90° (Scheme 2). In this manner, the hydroxyl groups of these building blocks could be interconnected with guest molecules via noncovalent interaction[10] or with central metal linkages via covalent interaction,[11,12] forming ordered linear and two- and three-dimensional scaffolds.

We report herein our efforts in the synthesis and resolution of **2**. We also present the crystallographic packing features of **2** in its racemic and chiral forms with 4,4′-bipyridine, as well as the NMR study on the likely chiral recognition in the interaction between enantiomers of **2** and those of BINAP under the direction of platinum(II). Furthermore, as part of a continuing interest in the design of substituted tetraphenylenes, we would like to report the conversion of **2** through its corresponding triflate to a diphenylphosphine derivative and the use of this bis(diphenylphosphine) derivative in platinum(II) complexation.

Results and Discussion

Synthesis and Resolution of 1,16-Dihydroxytetraphenylene (DHTP) (2). Since the first successful synthesis of **1** was reported in 1943,[13] much effort has been devoted to the synthesis of **1** and its derivatives.[6] Following the earlier works of Mislow[14a] and our group,[14b] an eight-membered ring compound **9** could be constructed by bis-alkylation of the dibromide **7**[15] with the tetraester **8**[16] as can be seen in the retrosynthetic pathway shown in Scheme 3, which also illustrates that additional steps would convert **9** to the target molecule **2** via 1,16-dimethoxytetraphenylene (**13**). It is noteworthy that two hydroxyl groups must be introduced to carbon-1 and carbon-16 in a regiospecific manner. We have therefore chosen to begin the synthesis employing a known dibromide, namely, 2,2′-bis(bromomethyl)-6,6′-dimethoxybiphenyl (**7**),[15] as the precursor.

Compound **9** was only generated in a disappointing yield of 20% when toluene was used as the solvent. However, optimization procedures revealed that dioxane was much more superior as a solvent, and as a result, the yield was upgraded to 40%. After repeated trials of this cyclization step, it was eventually found that the molar ratio of starting materials was crucial to the reaction outcome. Thus, when we adjusted the molar ratio of **8**:potassium:**7** to 1:0.8:0.7, the yield of **9** was increased to 68% (Scheme 4). In the subsequent step, **9** was allowed to undergo concomitant saponification and decarboxylation[14b] with KOH in refluxing ethylene glycol to provide diacid **14** in 91% yield. Lead tetraacetate oxidation converted **14** into **10** in a meager 33% yield. Bromination of **10** expectedly furnished dibromide **15**,

(10) Inter alia, see: (a) *Comprehensive Supramolecular Chemistry*; Sauvage, J.-P., Hosseini, M. W., Eds.; Pergamon Press: Oxford, 1996; Vol. 9. (b) Fyfe, M. C. T.; Stoddart, J. F. *Acc. Chem. Res.* **1997**, *30*, 393−401. (c) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502−518. (d) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417−426.

(11) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 898−952.

(12) Quadrivalent metal BINOLates (BINOL is 1,1′-binaphthol) are well-known and have been shown to exhibit chiral recognition and asymmetric catalytic properties. For leading references, see: (a) Mikami, K.; Shimizu, M. *Chem. Rev.* **1992**, *92*, 1021−1050. (b) Terada, M.; Matsumoto, Y.; Nakamura, Y.; Mikami, K. *Inorg. Chim. Acta* **1999**, *296*, 267−272. (c) Mikami, K.; Matsukawa, S.; Volk, T.; Terada, M. *Angew. Chem., Int. Ed.*. **1997**, *36*, 2768−2771. (d) Corey, E. J.; Lee, T. W. *Chem. Commun.* **2001**, 1321−1329. (e) Corey, E. J.; Letavic, M. A.; Noe, M. C.; Sarshar, S. *Tetrahedron Lett.* **1994**, *35*, 7553−7556. (f) Shibasaki, M.; Kanai, M.; Funabashi, K. *Chem. Commun.* **2002**, 1989−1999. (g) Tanski, J. M.; Wolczanski, P. T. *Inorg. Chem.* **2001**, *40*, 2026−2033. (h) Kuntz, B. A.; Ramachandran, R.; Taylor, N. J.; Guan, J.; Collins, S. *J. Organomet. Chem.* **1995**, *497*, 133−142. (i) Boyle, T. J.; Barnes, D. L.; Heppert, J. A.; Morales, L.; Takusagawa, F.; Connolly, J. *Organometallics* **1992**, *11*, 1112−1126.

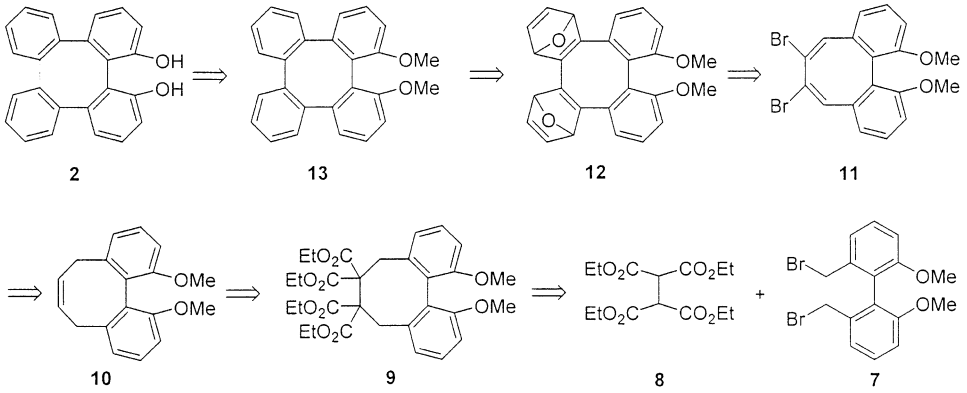
(13) Rapson, W. S.; Shuttleworth, R. G.; van Niejerk, J. *J. Chem. Soc.* **1943**, 326−327.

(14) (a) Dvorken, L. V.; Smyth, R. B.; Mislow, K. *J. Am. Chem. Soc.* **1958**, *80*, 486−492. (b) Wong, H. N. C.; Sondheimer, F. *J. Org. Chem.* **1980**, *45*, 2438−2440.

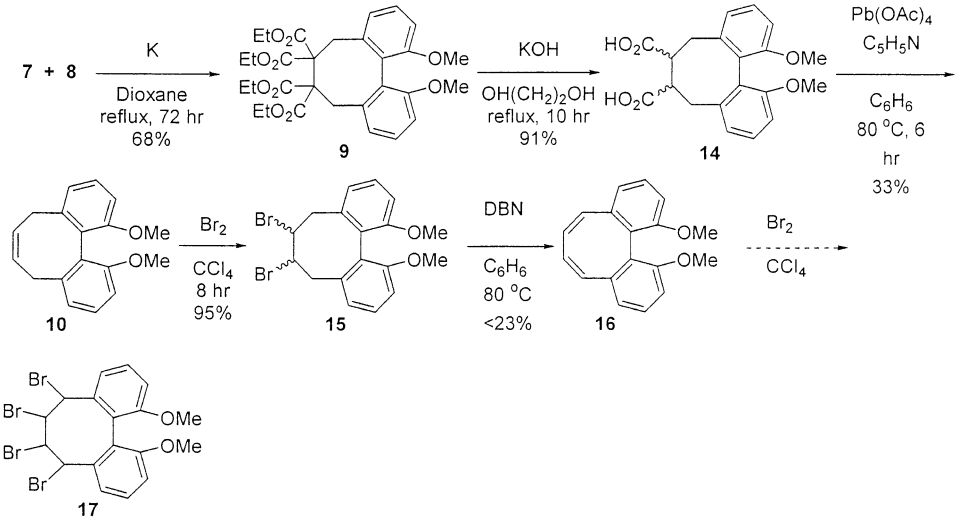
(15) (a) Zhang, A.-M. Ph.D. Thesis, Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, Shanghai, China, 2001. (b) Kanoh, S.; Muramoto, H.; Kobayashi, N.; Motoi, M.; Suda, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3659−3662. (c) Gajewski, J. J.; Jimenez, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 468−474. (d) Newman, M.; Lilje, K. C. *J. Org. Chem.* **1979**, *44*, 4944−4946. (e) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647−2650. (f) Tichy, M.; Budesinsky, M.; Gunterova, J.; Zavada, J.; Podiaha, J.; Cisarova, I. *Tetrahedron* **1999**, *35*, 7893−7906. (g) Godfrey, I. M.; Sargent, M. V.; Elix, J. A. *J. Chem. Soc., Perkin. Trans. 1* **1974**, 1353−1354. (h) Adams, R.; Baker, B. R. *J. Am. Chem. Soc.* **1941**, *63*, 535−537. (i) Johnstone, R. A. W.; Rose, M. E. *Tetrahedron* **1979**, *35*, 2169−2173. (j) Goleman, R. S.; Guernon, J. M.; Roland, J. T. *Org. Lett.* **2000**, *2*, 277−280. (k) Díaz, E.; Guzmàn, A.; Cruz, M.; Mares, J.; Ramíez, D. J.; Joseph-Nathan, P. *Org. Magn. Reson.* **1980**, *13*, 180−186. (l) Gruter, G. J. M.; Akkerman, O. S.; Bickelhanpt, F. *J. Org. Chem.* **1994**, *59*, 4473−4481.

(16) (a) Bischoff, C. A.; Rach, C. *Ber.* **1884**, *17*, 2781−2788. (b) Conrad, M.; Bischoff, C. A. *Liebig Ann. Chem.* **1882**, *214*, 68−72.

SCHEME 3



SCHEME 4



which upon dehydrobromination with DBN[14b] gave 1,12-dimethoxydibenzo[*a*,*c*]cyclooctene (**16**) in an extremely low yield (below 23%). Moreover, despite many attempts, we failed to obtain a sample of **16** with sufficient purity for ^{1}H NMR spectroscopic studies. Fortunately, the structure of **16** was substantiated unequivocally by an X-ray diffraction analysis (Figure 1). To complete the synthesis of **2**, a tetrabromide **17** was designed, which should be obtainable from **16**. However, to our surprise, all attempts to brominate **16** were unfruitful, and only intractable materials resulted. One explanation for this discrepancy is the likely competing electrophilic aromatic substitution of the benzene rings, leading to undesired aryl bromides.

In view of the low-yield reaction in the preparation of **16**, as well as the difficulty encountered in its bromination, we turned our attention to the radical-initiated bromination of **10**, in the hope of generating an appropriate bromide for further manipulation. This avenue was first explored by treatment of **10** with 2 molar equiv of NBS in the presence of dibenzoyl peroxide. It was found that this reaction afforded a mixture that was not easily identified by NMR spectroscopic studies. The mass spectrum of this mixture, on the other hand, did indicate the formation of a tribromide. It was fortunate that a chloroform solution of this mixture led to the formation of crystals suitable for an X-ray crystallographic analysis.

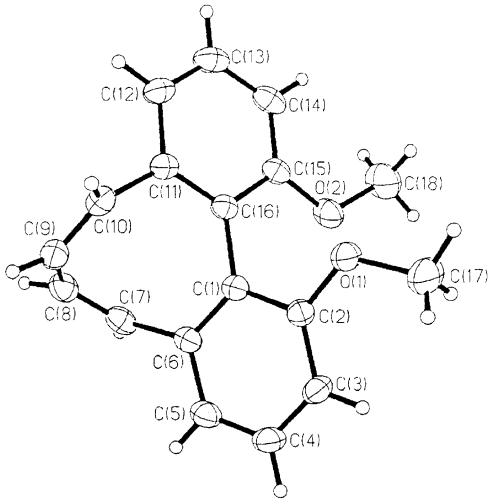
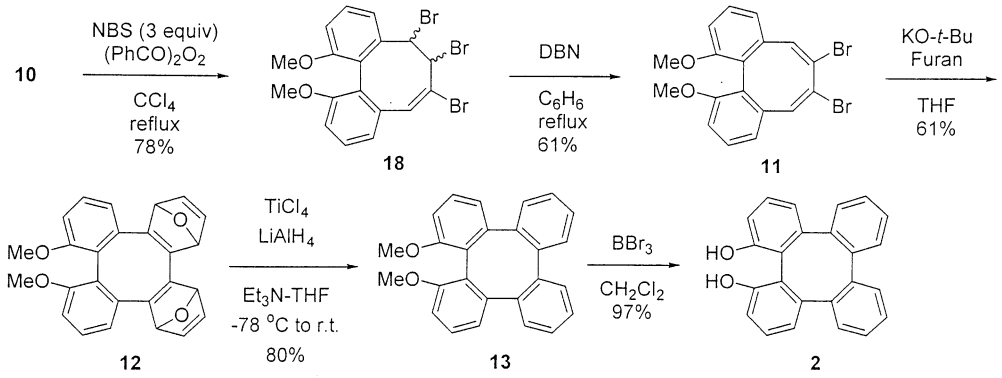


FIGURE 1. ORTEP drawing of **16**.

Thus, the X-ray diffraction result[17] depicted the structure of tribromide **18**, presumably formed through a radical mechanism whose full details are not yet known to us. The yield of **18** from **10** was further improved to 78% when 3 molar equiv of NBS were used (Scheme 5). It was also illustrated in Scheme 5 that dehydrobromination of

(17) Supporting Information.

SCHEME 5



18 with DBN led to the formation of dibromide **11**, which was the desired precursor for the preparation of **12**. Indeed, when **11** was allowed to undergo dehydrobromination with KO−*t*-Bu in the presence of furan,[14b] an unexpectedly high yield (61%) of the bis-endoxide **12** was afforded. From the dehydrobromination of **11** presumably a strained cyclic alkyne was generated, which underwent a Diels−Alder reaction with furan to form **12**. Deoxygenation of **12** with low-valent titanium[18] produced in situ by reduction of titanium(IV) chloride with lithium aluminum hydride in the presence of triethylamine furnished 1,16-dimethoxytetraphenylene (**13**) in 80% yield, whose structure was confirmed also by an X-ray diffraction study.[17] Eventually, the desired **2** was obtained in 97% yield by treatment of **13** with boron tribromide (Scheme 5).[19]

The observation of the antipodes of **2** was first realized through HPLC on a chiral column (Figure 2). It was also found that the diastereomeric bis-(*S*)-camphorsulfonates of (±)-**2**, namely, **19** and **20** were chromatographically separable using a 6:1 mixture of benzene and ethyl actate as an eluent. Due to the fact that the absolute configuration of the (*S*)-camphorsulfonyl group was defined, an X-ray crystallographic analysis of the less polar bis-camphorsulfonate **19** therefore led us to confirm the absolute structure of its appended **2** to be of (*S*)-configuration.[17] In this manner, the absolute stereochemistry of **20** with an appended (*R*)-**2** was also indirectly confirmed. Subsequent desulfonylation generated the enantiomerically pure (*S*)-**2** and (*R*)-**2**, whose optical purities were found to be >99% by HPLC on a chiral column.[20]

The circular dichroism (CD) spectra of (*S*)-**2** and (*R*)-**2** were also recorded in methanol (Figure 3). As can be seen, the CD spectrum of (*S*)-**2** showed strong bands at 196.6(−), 208.8(−), and 214.8(+) nm with a succession of weaker absorption bands at around 231.6(−) and 247.0(+) nm. On the other hand, the CD spectrum of (*R*)-**2** showed an almost opposite curve, i.e., strong bands at 196.6(+), 199.0(+), and 215.2(−) nm with weaker bands at 231.4(+) and 249.0(−) nm.

Synthesis of 1,16-Bis(diphenylphosphino)tetraphenylene (BPTP) (26). The quest for substituted tetraphenylenes that contain appropriate functional groups

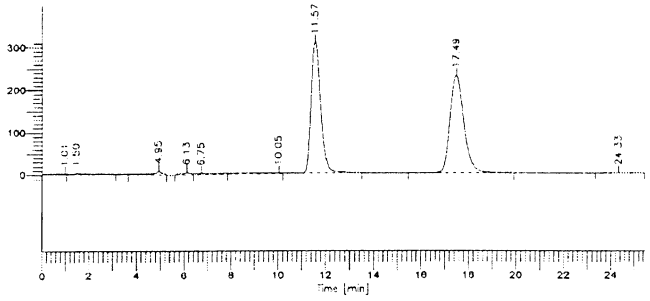


FIGURE 2. Resolution of (±)-**2** through chiral HPLC (AD column): retention times of (*S*)-**2** and (*R*)-**2** were 11.6 and 17.5 min, respectively.

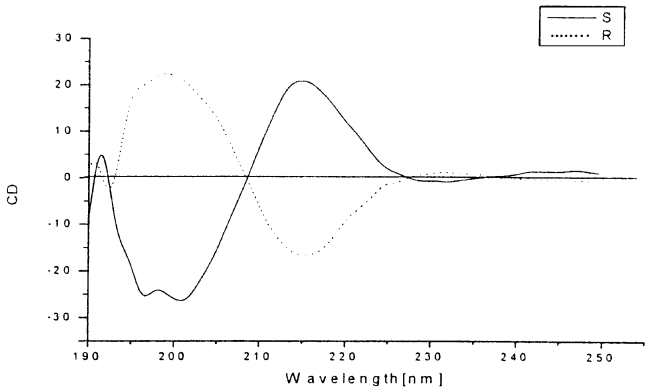
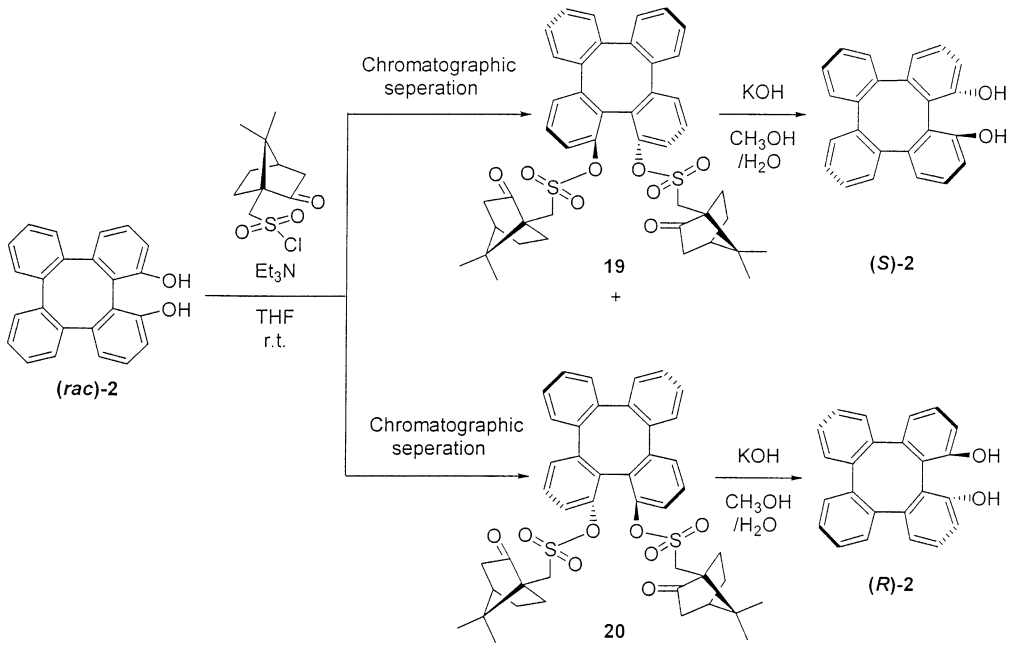


FIGURE 3. CD spectra of (*S*)-**2** and (*R*)-**2** in methanol.

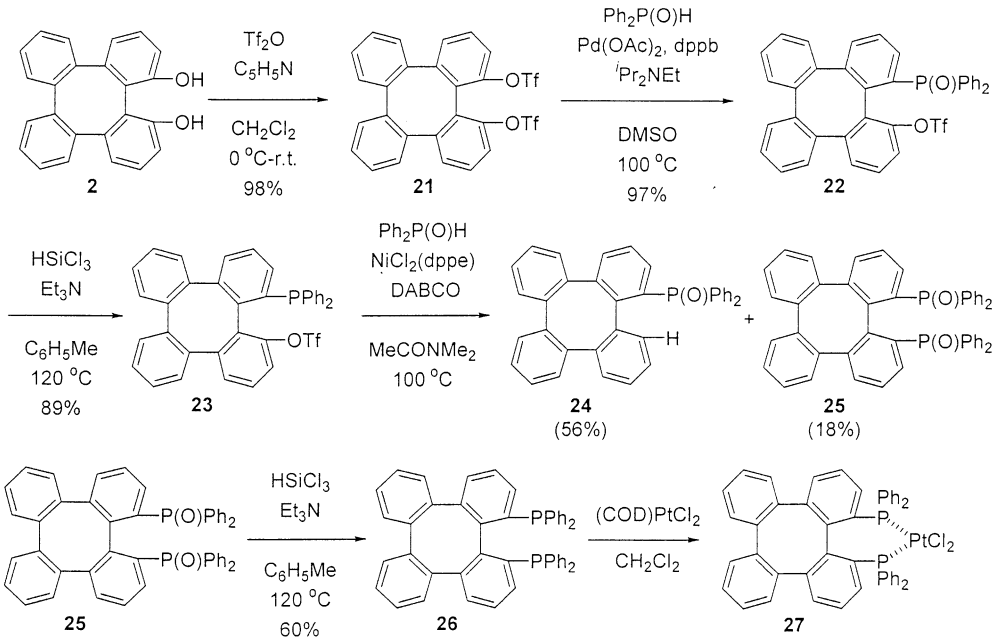
as metal coordination sites[21] prompted us to undertake the reaction sequence as shown in Scheme 7 in order to realize 1,16-bis(diphenylphosphino)tetraphenylene (**27**). The pivotal step in Scheme 7 is the palladium-catalyzed reaction, which is capable of converting triflates to other functionalities. Thus, **2** was readily converted into the bis-triflate **21** with triflic anhydride in the presence of pyridine.[22] Monophosphinylation of **21** with diphenylphospine oxide proceeded smoothly under Hayashi's conditions[23] to afford **22** in 97% yield. Reduction of **22** with trichlorosilane-triethylamine[24] gave the corresponding

(18) Xing, Y. D.; Huang, N. Z. *J. Org. Chem.* **1982**, *47*, 140−142.
(19) McOmie, J. F.; Watts, M. L.; West, D. E. *Tetrahedron* **1968**, *24*, 2289−2292.
(20) (a) Ng, M.-K.; Chow, H.-F.; Chan, T.-L.; Mak, T. C. W. *Tetrahedron Lett.* **1996**, *37*, 2979−2982. (b) Chow, H.-F.; Wan, C.-W.; Ng, M.-K. *J. Org. Chem.* **1996**, *61*, 8712−8714.
(21) Kumobayashi, H.; Miura, T.; Sayo, N.; Saito, T.; Zhang, X. *Synlett.* **2001**, 1055−1064.
(22) Cai, D.; Payack, J. F.; Bender, D. R.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *Org. Synth.* **1996**, *76*, 8−11.
(23) Uozumi, Y.; Tanahashi, A.; Lee, S.-Y.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945−1948.
(24) Takaya, H.; Akutagawa, S.; Noyori, R. *Org. Synth. Coll. Vol.* **1993**, *8*, 57−63.

SCHEME 6



SCHEME 7



phosphine **23** in 89% yield. A subsequent nickel-catalyzed coupling reaction[21] of **23** with diphenylphosphine oxide led to the desired bis-phosphinyltetraphenylene **25** in a meager 18% yield, together with a reduction product **24** in 56% yield. This result indicates that under this reaction condition, the first oxidative addition of nickel onto **23** would proceed effectively but the resulting organonickel triflate undergoes easily competing reduction steps to form **24**. Reduction of **25** with, again, trichlorosilane-triethylamine[24] eventually furnished BPTP **26** in 60% yield. As shown in Scheme 7, the conversion of **26** to a platinum complex was straightforward, giving BPTP−$PtCl_2$ **27**,[25] whose structure was substantiated by an X-ray diffraction analysis.[17] It can be seen that a seven-membered ring containing the diphosphine-chelated platinum that was linked to the tetraphenylene skeleton was formed.

Crystallographic Packing Features of Assembly between 4,4′-Bipyridine and (±)-2 as well as (*S*)-2. The propensity of **1** and its derivatives to function as hosts for a wide range of guest molecules via van der Waals interaction has been extensively investigated.[6a,b] The structural characteristics of the resulting clathrate inclusion complexes based on these tetraphenylene skeletons have also been discussed in details.[6a,b] Hydrogen bond interactions have also been utilized to construct a variety of supramolecular assemblies.[26] In light of the

(25) Tudor, M. D.; Becker, J. J.; White, P. S.; Gangé, M. R. *Organometallics* **2000**, *19*, 4376−4380.

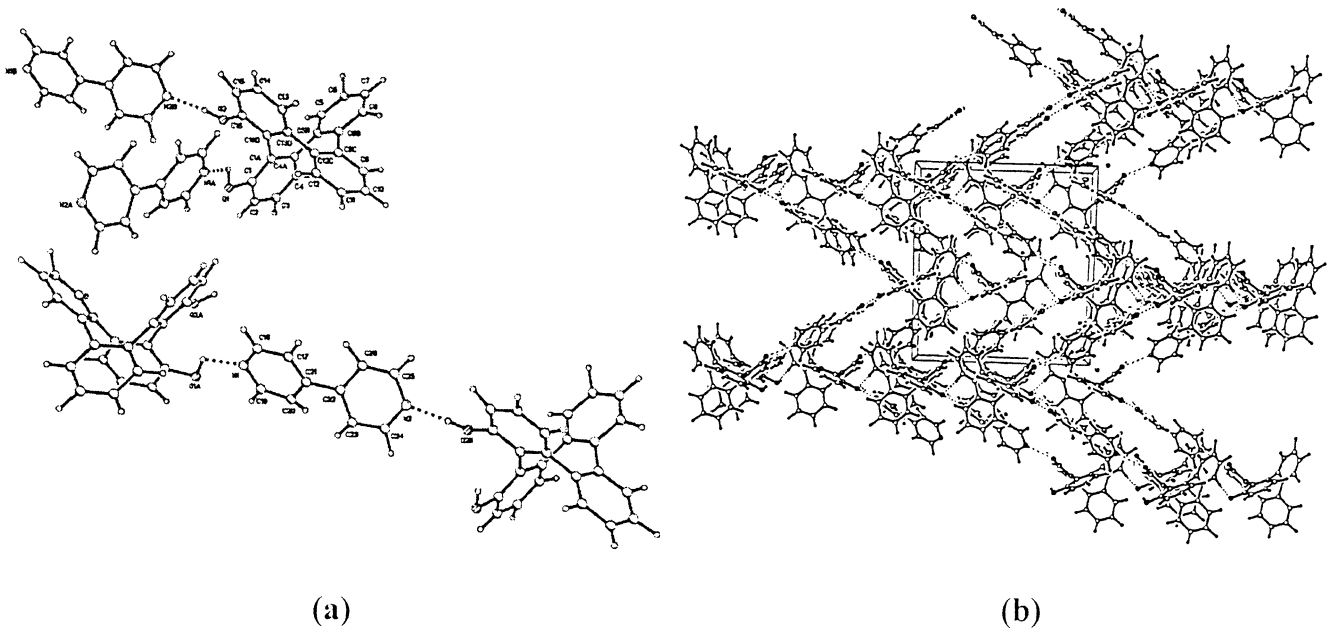


FIGURE 4. (a) Perspective view of the molecular aggregate of (±)-**2** and 4,4′-bipyridine. The thermal ellipsoids are drawn at the 35% probability level. (b) Perspective view of crystal packing (top view down the *c*-axis).

latter aspect, we considered it interesting to assess the likely assembly via hydrogen bond interactions between the hydrogen bond donor **2**, whose two phenolic hydroxyl groups are disposed with a specific geometry, and other hydrogen bond acceptors. In this context, we first attempted the molecular assembly between (±)-**2** and a linear hydrogen bond acceptor, namely, 4,4′-bipyridine. Thus, slow vaporization of a chloroform solution of (±)-**2** (1 molar equiv) and 4,4′-bipyridine (2 molar equiv) led to the formation of single crystals of sufficiently good quality for an X-ray crystallographic study (Figure 4). Despite the experimental molar ratio of 1:2, ^{1}H NMR spectroscopic analysis of a $CDCl_3$ solution of the single crystals nonetheless depicted that the molecular complex was composed of the hydrogen bond donor and acceptor at a molar ratio of 1:1. As can be seen from Figure 4, the molecular components in the molecular complex are linked via hydrogen bonds between the protons of the phenolic hydroxyl groups and the nitrogens of 4,4′-bipyridine. In the crystal packing, an infinite zigzag chain is formed, and many chains spread orderly in the *ab* plane. Furthermore, in each zigzag chain, (*S*)-**2** and (*R*)-**2** are connected alternately with 4,4′-bipyridine via hydrogen bond interaction, thereby resulting in a continuous heterochiral zigzag chain (Figure 5). Although in principle two types of zigzag arrangements consisting purely of either (*S*)-**2** or (*R*)-**2** could be formed, these infinite homochiral chains have not been observed in the crystal packing.

In a similar approach, single crystals were also readily grown form the dichloromethane solution of (*S*)-**2** (1 molar equiv) and 4,4′-bipyridine (2 molar equiv). Contrary to the aforementioned result, ^{1}H NMR spectroscopic analysis demonstrated that the composition of the molecular complex formed between (*S*)-**2** and 4,4′-bipyridine corresponded to a stoichiometric ratio of 1:2. The ORTEP drawing of this molecular complex is shown in Figure 6. As can be seen, the crystal packing pattern is consistent with the composition, in which two 4,4′-bipyridine are linked to one (*S*)-**2**. These discrete units, in turn, are not linked together by hydrogen bonding (Figure 6).

Chiral Recognition between 2 and BINAP. Gagné has examined the isomerization of a biphepPtX_2 complex (biphep is 2,2′-bis(diphenylphosphino)biphenyl and X_2 is 1,1′-binaphthol) to gain insight into the mechanism of diastereomeric interconversion.[25] We would like to report herein the results of our investigation of chiral recognition[12,27] between **2** and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) employing platinum(II) as a linker. In this connection, two chiral BINAP platinum complexes, namely, (*S*)-BINAP−$PtCO_3$ (*S*)-**28** and (*R*)-BINAP−$PtCO_3$ (*R*)-**28** were prepared according to Gagné's method.[25] Thus, reaction of (*S*)-BINAP or (*R*)-BINAP with (COD)$PtCl_2$ provided the corresponding BINAP−$PtCl_2$,

(26) (a) Fredericks, J. R.; Hamilton, A. D. In *Comprehensive Supramolecular Chemistry*; Sauvage, J.-P., Hosseini, M. W., Eds.; Pergamon Press: Oxford, 1996; Vol. 9, pp 565−594. (b) Toda, F. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Pergamon Press: Oxford, 1996; Vol. 6, pp 466−516. (c) Vaidhyanathan, R.; Natarajan, S.; Rao, C. N. R. *J. Mol. Struct.* **2002**, *608*, 123−133. (d) Zhang, J.-H.; Liao, J.; Cui, X.; Yu, K.-B.; Zhu, J.; Deng, J.-G.; Zhu, S.-F.; Wang, L.-X.; Zhou, Q.-L.; Chung, L.-W.; Ye, T. *Tetrahedron: Asymmetry* **2002**, *13*, 1363−1366. (e) Toda, F.; Senzaki, M.; Kuroda, R. *J. Chem. Soc., Chem. Commun.* **2002**, 1788−1789. (f) Hamilton, T. D.; Papaefstathiou, G. S.; MacGillivray, L. R. *J. Am. Chem. Soc.* **2002**, *124*, 11606−11607. (g) Holý, P.; Sehnal, P.; Tichý, M.; Závada, J.; Císařová, I. *Tetrahedron: Asymmetry* **2003**, *14*, 245−253.

(27) Some references for chiral recognition of optically active phenols (such as BINOL) via covalent interaction under direction of metal central linkages (such as Ti): (a) Boyle, T. J.; Eilerts, N. W.; Heppert, J. A.; Takusagawa, F. *Organometallics* **1994**, *13*, 2218−2229 and references therein. (b) Terada, M.; Matsumoto, Y.; Nakamura, Y.; Mikami, K. *Inorg. Chim. Acta* **1999**, *296*, 267−272. (c) Mikami, K.; Matsukawa, S.; Volk, T.; Terada, M. *Angew. Chem., Int. Ed.* **1997**, *36*, 2768−2771. (d) Huttenloch, M. E.; Dorer, B.; Rief, U.; Prosenc, M.-H.; Schmidt, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1997**, *541*, 219−232. (e) Balsells, J.; Carroll, P. J.; Walsh, P. J. *Inorg. Chem.* **2001**, *40*, 5568−5574. (f) Hanawa, H.; Hashimoto, T.; Maruoka, K. *J. Am. Chem. Soc.* **2003**, *125*, 1708−1709.

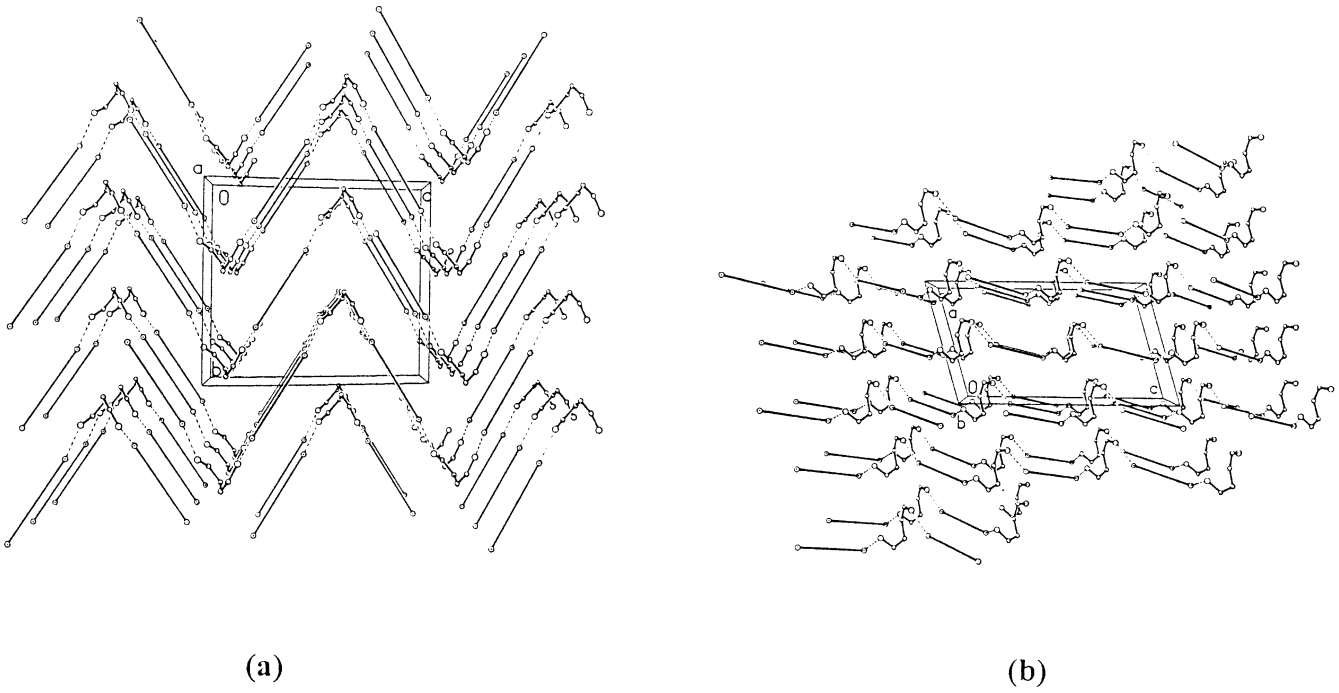


FIGURE 5. (a) Hydrogen bonding between the two molecular components in the crystal structure of (±)-**2**·$(C_5H_4N)_2$. The diol and 4,4′-bipyridine molecules are alternately linked by O−H···N hydrogen bonds to form a zigzag chain running parallel to the *c*-axis. The chains are arranged to form a pleated sheet whose mean plane is normal to the *b*-axis. For simplicity, the tetrol molecule is represented by its HO−C−C−C−C−OH fragment and the 4,4′-bipyridine molecule by a rigid rod. (b) View of the crystal structure of (±)-**2**·$(C_5H_4N)_2$ along the *b*-axis. For simplicity, the tetrol molecule is represented by its HO−C−C−C−C−OH fragment and the 4,4′-bipyridine molecule by a rigid rod.

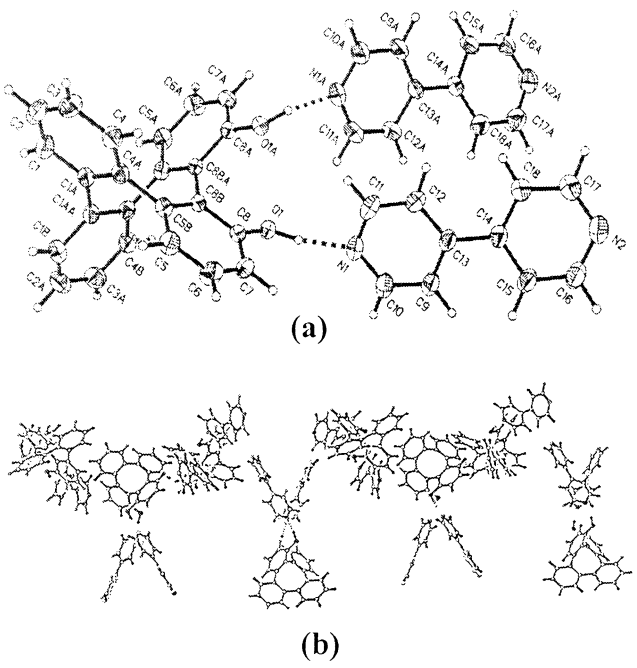


FIGURE 6. (a) ORTEP drawing of the molecular complex of (*S*)-**2** and 4,4′-bipyridine. (b) Perspective view of crystal packing.

which were converted readily to the desired (*S*)-**28** and (*R*)-**28**, respectively, by reaction with Ag_2CO_3 in wet dichloromethane under darkness. To examine the chiral factor involved in the interaction between **2** and BINAP−$PtCO_3$ **28**, we observed the reactions of (*S*)-**28** and (*R*)-**28** with (*S*)-**2**, (*R*)-**2**, and (±)-**2** by monitoring with ^{1}H NMR and ^{31}P NMR spectroscopic methods. The matches and molar quantities of these reactants are discussed below, and the reaction of **28** and **2**, forming **29**, is shown in Scheme 8. Experimentally, **28** and **2** were mixed in a NMR tube with $CDCl_3$ being the solvent. The mixture was irradiated with supersonic waves to afford a clear greenish solution, which was then studied by ^{1}H NMR and ^{31}P NMR spectroscopy.

The reaction between (*S*)-**2** and (*S*)-**28** was first chosen as an initial study (Figure 7). Figure 7a contains the ^{1}H NMR spectrum of **2**, where a pair of doublets Y and Z are characteristic. Figure 7b illustrates the ^{1}H NMR and ^{31}P NMR spectra of (*S*)-**28**, where peaks A and P_A are distinctive. When the molar ratio of (*S*)-**28** and (*S*)-**2** is 1:0.9, Figure 7c shows that in addition to the appearance of the original ^{1}H NMR absorption A and ^{31}P NMR absorption P_A in Figure 7b, new absorptions B, C, D, and P_B are observed, which eventually become the major peaks when the molar ratio of (*S*)-**28** and (*S*)-**2** is 1:1.6 as depicted in Figure 7d. It is worth mentioning that (*S*)-**28** and (*S*)-**2** reacted with each other completely at a molar ratio of 1:1 when the reaction was carried out in refluxing $CHCl_3$ (Figure 7e). However, it should be pointed out that in our ^{1}H NMR spectroscopic studies, the peaks are too complicated, making a detailed proton assignment difficult.

The next experiment concerned the mixing of (*S*)-**28** with (*R*)-**2** in an initial molar ratio of 1:1 (Figure 8). In this manner, it was observed that the reaction between these two chiral compounds was relatively slow and that

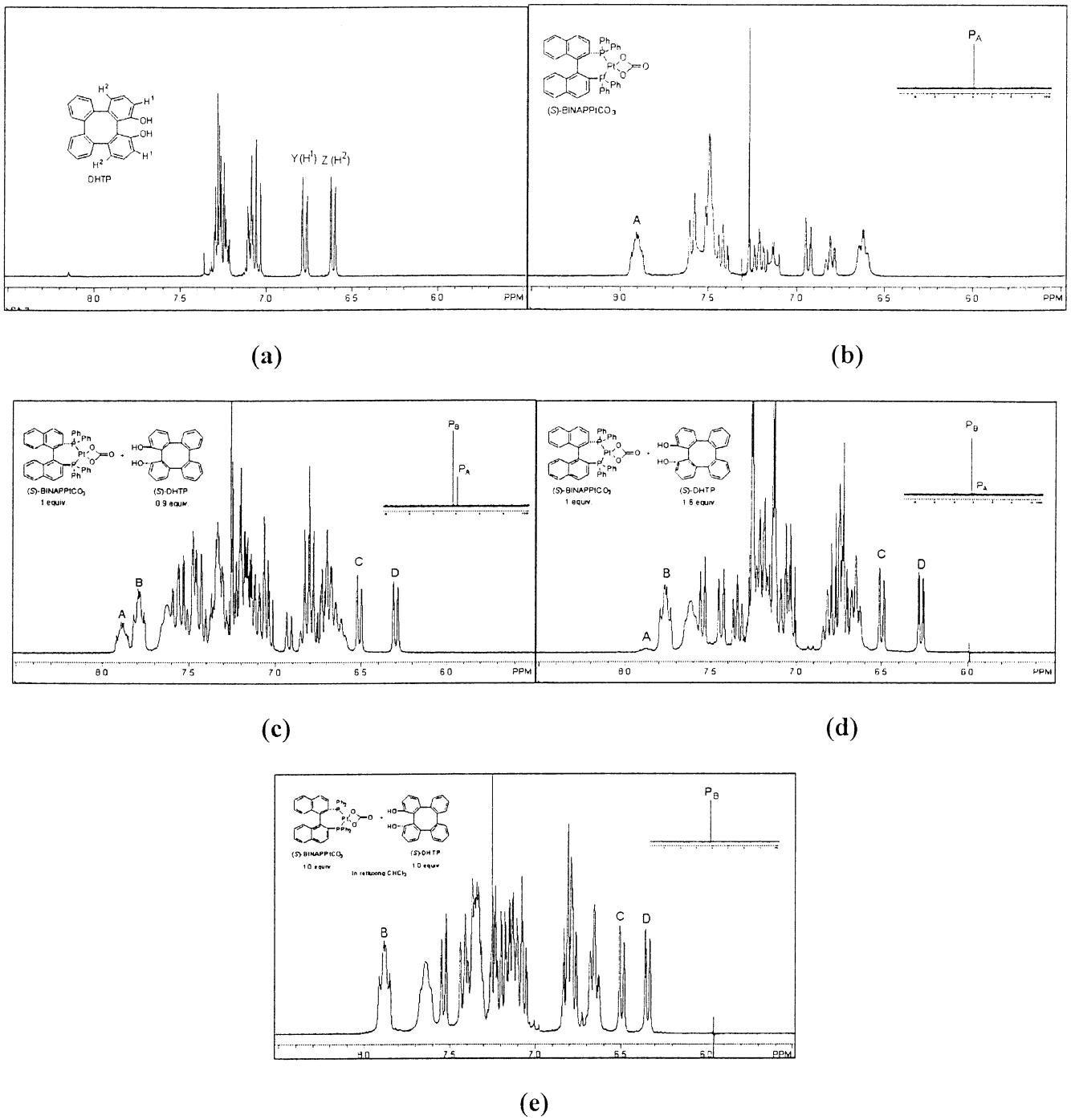
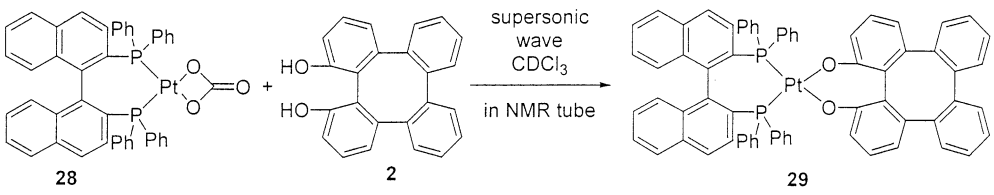


FIGURE 7. ^{1}H NMR spectra of the reaction mixtures of (*S*)-**28** and (*S*)-**2**, and at the top right corners of the spectra are the corresponding ^{31}P NMR spectra. (a) ^{1}H NMR spectrum of **2**. (b) ^{1}H NMR spectrum of (*S*)-**28**. (c) *S*-**2** and (*S*)-**28** mixed at a molar ratio of 1:0.9. (d) (*S*)-**2** and (*S*)-**28** mixed at a molar ratio of 1:1.6. (e) (*S*)-**2** and (*S*)-**28** mixed at an equal molar ratio and reacted in refluxing $CHCl_3$.

SCHEME 8



the time required for the mixture to become a greenish solution under supersonication was much longer. In comparison with the original ^{1}H NMR and ^{31}P NMR spectra of the starting materials (Figures 7a and 7b),

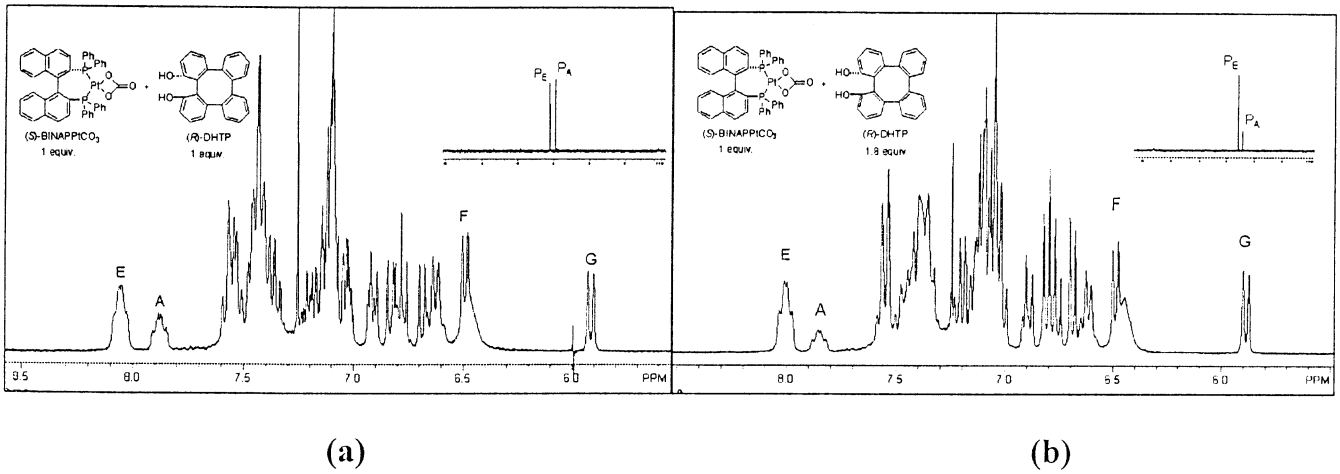


FIGURE 8. ^{1}H NMR spectra of the reaction mixtures of (*S*)-**28** and (*R*)-**2**, and at the top right corners of the spectra are the corresponding ^{31}P NMR spectra. (a) (*S*)-**28** and (*R*)-**2** mixed at a molar ratio of 1:1. (b) (*S*)-**28** and (*R*)-**2** mixed at a molar ratio of 1:1.8.

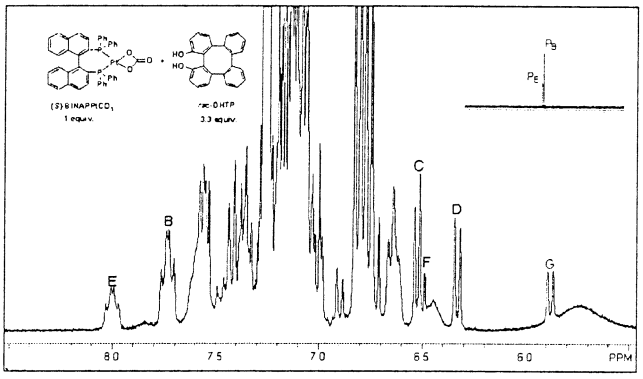


FIGURE 9. ^{1}H NMR spectrum of the reaction mixture of (*S*)-**28** and (±)-**2** at a molar ration of 1:3.3, and at the top right corner of the spectrum is the corresponding ^{31}P NMR spectrum.

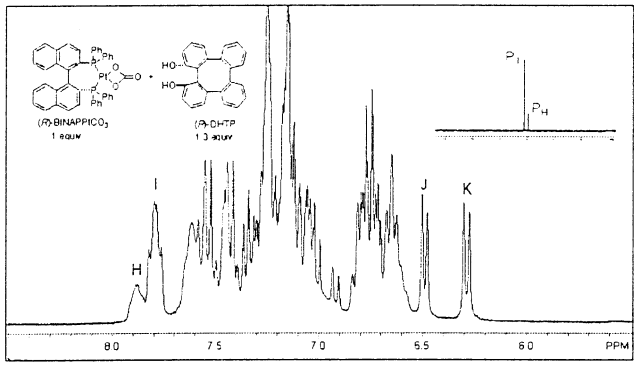


FIGURE 10. ^{1}H NMR spectrum of the reaction mixtures of (*R*)-**28** and (*R*)-**2** at a molar ratio of 1:1.3, and at the top right corner of the spectrum is the corresponding ^{31}P NMR spectrum.

Figure 8a shows new peaks E, F, G, and P_E, which do not abate significantly even when the number of molar equivalents of (*R*)-**2** was increased from 1 to 1.8 (Figure 8b), indicating that the reaction is not complete even in an excess of (*R*)-**2**. The result of the mixing of (*S*)-**28** with (*R*)-**2** nonetheless confirms that a relatively slower reaction has indeed taken place and that (*S*)-**28** does not recognize (*R*)-**2** so easily.

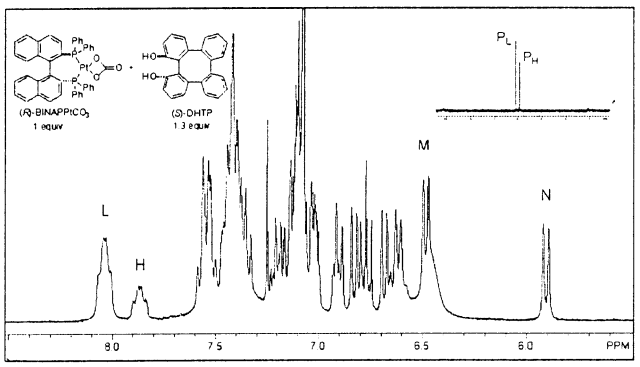


FIGURE 11. ^{1}H NMR spectrum of the reaction mixtures of (*R*)-**28** and (*S*)-**2** at a molar ratio of 1:1.3, and at the top right corner of the spectrum is the corresponding ^{31}P NMR spectrum.

When 1 molar equiv of (*S*)-**28** was allowed to mix with 3.3 molar equiv of (±)-**2**, the resulting ^{1}H NMR spectrum reveals a new set of proton NMR absorptions B, E, C, D, F, and G, as well as ^{31}P NMR absorptions P_B and P_E (Figure 9). The spectra are essentially a combined spectrum of Figures 7d and 8b, in which two diastereomers are formed and the one formed from (*S*)-**2** and (*S*)-**28** is the major component since B, C, D, and P_B are more distinct than E, F, G, and P_E. Again, the result of this experiment is reminiscent of the aforementioned fact that (*S*)-**28** is able to recognize (*S*)-**2** in a more efficient and rapid manner.

On the other hand, (*R*)-**28** also tends to demonstrate better chiral recognition of (*R*)-**2**. Thus, mixing of 1 molar equiv of (*R*)-**28** with 1.3 molar equiv of (*R*)-**2** led to a mixture whose ^{1}H NMR and ^{31}P NMR spectra show new peaks I, J, K, and P_I, in addition to the original peaks H and P_H shown by (*R*)-**28** (Figure 10), which are the same as A and P_A of (*S*)-**28**. These spectra are actually identical to those obtained from reaction between (*S*)-**2** and (*S*)-**28**, i.e., Figure 7c. It is also clear from this result that (*R*)-**28** exhibits a tangible recognition of (*R*)-**2**. On the contrary, the ^{1}H NMR and ^{31}P NMR spectroscopic results obtained from the reaction between 1 molar equiv of (*R*)-**28** and 1.3 molar equiv of (*S*)-**2** show new peaks L, M, N, and P_L, plus the original peaks H and P_H from (*R*)-**28**

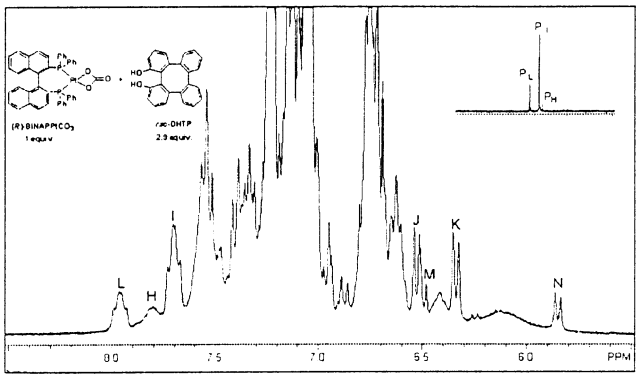


FIGURE 12. ^{1}H NMR spectrum of the reaction mixtures of (*R*)-**28** and (±)-**2** at a molar ratio of 1:2.9, and at the top right corner of the spectrum is the corresponding ^{31}P NMR spectrum.

TABLE 1. Results of Chiral Recognition between 2 and 28

	(*S*)-**2**	(*R*)-**2**
(*S*)-**28**	matched	mismatched
(*R*)-**28**	mismatched	matched

(Figure 11). From the peak heights of P_H and P_L, a conclusion can be drawn that the chiral recognition between (*R*)-**28** and (*S*)-**2** is not as effective as that between (*R*)-**28** and (*R*)-**2**. Finally, the reaction between 1 molar equiv of (*R*)-**28** and 2.9 molar equiv of (±)-**2** led to spectra showing peaks H, I, J, K, L, M, N, P_H, P_I, and P_L, with peaks I and P_I being the more noticeable absorptions (Figure 12), thereby showing a better chiral recognition of (*R*)-**2** by (*R*)-**28**. It is noteworthy that Figures 11 and 12 are in fact "enantiomeric" to Figures 8b and 9, respectively. In conclusion, Table 1 depicts a summary of results concerning the chiral recognition between **2** and **28**.

Conclusion

1,16-Dihydroxytetraphenylene (**2**) has been synthesized with an approximate overall yield of 4% in eight steps, featuring an unusual NBS bromination of 1,12-dimethoxy-5,8-dihydrodibenzo[*a*,*c*]cyclooctene (**10**). The enantiomers of **2** have also been obtained by a chromatographic separation of the corresponding diastereomeric bis(*S*)-camphorsulfonates, followed by a subsequent desulfonation step. We have also been successful in obtaining a bis-diphenylphosphine derivative of **2**, namely, (±)-**26**, whose platinum complex **27** was also prepared and characterized by X-ray crystallographic analysis. 4,4′-Bipyridine was utilized to realize two hydrogen bonded molecular complexes with (±)-**2** and (*S*)-**2**, whose crystal packing patterns are very much different. Chiral recognition experiments have also been performed by reacting **2** with **28**, and the spectroscopic results nevertheless point to the likelihood that (*S*)-**28** and (*R*)-**28** would recognize (*S*)-**2** and (*R*)-**2**, respectively.

Experimental Section

Tetraethyl 1,12-Dimethoxy-5,6,7,8-tetrahydrodibenzo-[*a*,*c*]cyclooctene-6,6,7,7-tetracarboxylate (9). A dry 250 mL round-bottomed flask fitted with a condenser and a dropping funnel was charged with dry argon and maintained under a positive pressure of argon. Dry freshly distilled dioxane (70 mL) was syringed into the flask, and then tetraethyl 1,1,2,2-ethanetetracarboxylate (**8**) (6.03 g, 19 mmol) and freshly cut potassium (1.37 g, 34 mmol) were placed in the reaction flask. After the reaction mixture was refluxed for 24 h, 2,2′-bis(bromomethyl)-6,6′-dimethoxybiphenyl (**7**) (5.00 g, 13 mmol) in dry dioxane (70 mL) was added dropwise slowly into the yellow suspension via the dropping funnel. After the addition was complete, the reaction mixture was refluxed for an additional 48 h. The reaction was quenched with water (70 mL) and acidified with 2 M hydrochloric acid to a pH value of 3. The mixture was extracted with ethyl acetate (2 × 150 mL), and the organic solution was washed with brine (2 × 100 mL) and dried over anhydrous sodium sulfate. Removal of the solvent and flash column chromatography on silica gel (petroleum ether/ethyl acetate 5:1) gave **9** as a white solid (4.72 g, 68%), mp 99−102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22 (t, 2H, J = 8.0 Hz), 6.84 (d, 4H, J = 8.0 Hz), 4.23−4.15 (m, 4H), 4.03−3.82 (m, 4H), 3.87 (d, 2H, J = 14.3 Hz), 3.72 (s, 6H), 3.39 (d, 2H, J = 14.4 Hz), 1.25 (t, 6H, J = 7.1 Hz), 0.99 (t, 6H, J = 7.2 Hz). ^{13}C NMR (100.4 MHz, $CDCl_3$): δ 169.8, 169.4, 157.3, 138.3, 127.7, 126.3, 123.1, 109.4, 62.9, 61.9, 61.1, 55.9, 36.6, 13.9, 13.4. MS (EI): *m*/*z* (relative intensity) 512 (100), 511 (96), 556 (M^+, 89), 557 (55), 436 (54), 350 (47), 437 (31), 409 (28). IR (KBr disk): 2984, 2904, 2839, 1730 (br), 1262, 1206 (br), 1095, 1037, 773, 755, 732 cm^{-1}. Anal. Calcd for $C_{30}H_{36}O_{10}$: C, 64.74; H, 6.52. Found: C, 64.37; H, 6.47.

1,12-Dimethoxy-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctandiene-6,7-dicarboxylicacid (14). To the mixture of potassium hydroxide (25.9 g, 0.46 mol) and ethylene glycol (120 mL) was added **9** (6.92 g, 12 mmol). The mixture was refluxed for 10 h and then cooled to room temperature. After being acidified to pH = 1 with 6 M hydrochloric acid, the solution was extracted with diethyl ether (3 × 100 mL) and the combined ethereal layer was washed with brine (3 × 100 mL) and dried over anhydrous sodium sulfate. Removal of ether gave the light yellow crude **14**, which was washed with a small amount of diethyl ether to give pure **14** as a white powder (4.02 g, 91%), mp 204−206 °C. ^{1}H NMR (300 MHz, CD_3COCD_3): δ 7.40−7.34 (m, 2H), 7.09−7.06 (m, 2H), 6.96−6.93 (m, 2H), 3.73−3.70 (m, 6H), 3.50 (br, 2H), 2.96−2.83 (m, 4H), 2.30−2.08 (m, 2H). ^{13}C NMR (75.3 MHz, CD_3COCD_3): δ 177.1, 158.9, 142.7, 130.6, 126.9, 122.7, 110.6, 56.7, 49.8, 35.3. MS (EI): *m*/*z* (relative intensity) 338 (100), 356 (M^+, 39), 91 (29), 249 (26), 235 (23), 265 (19), 251 (18), 310 (17). IR (KBr disk): 3100−2936 (br), 2835, 1699, 1584, 1464, 1436, 1263, 1074, 1085, 929, 790, 757, 736 cm^{-1}. HRMS (M^+): calcd for $C_{20}H_{20}O_6$ 356.1260, found 356.1269.

1,12-Dimethoxy-5,8-dihydrodibenzo[*a*,*c*]cyclooctene (10). To a mixture of lead tetraacetate (1.10 g, 2.37 mmol) and **14** (561 mg, 1.58 mmol) were added dry benzene (15 mL) and dry pyridine (0.3 mL, 3.7 mmol). The reaction mixture was stirred for 6 h at 80 °C. The dark mixture was filtered through a sintered glass funnel padded with a layer of silica gel, and the filter cake was washed thoroughly with benzene. The filtrate was washed sequentially with 2 M hydrochloric acid (2 × 25 mL) and water (2 × 25 mL). The benzene solution was dried with anhydrous sodium sulfate. Removal of the solvent and flash column chromatography on silica gel (petroleum ether/ethyl acetate 50:1) gave **10** as a white solid (140 mg, 33%), mp 142−143 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (t, 2H, J = 7.9 Hz), 6.84 (d, 4H, J = 7.9 Hz), 5.81−5.78 (m, 2H), 3.75 (s, 6H), 3.11−3.03 (m, 2H), 2.91 (d, 2H, J = 13.8 Hz). MS (EI): *m*/*z* (relative intensity) 266 (M^+, 100), 235 (59), 251 (19), 220 (19), 203 (16), 205 (16), 165 (15), 219 (15). IR (KBr disk): 3059, 3020, 2934, 2841, 1643, 1577, 1467, 1456, 1435, 1257, 1086, 1075, 768, 752, 730 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.98; H, 6.90.

1,12-Dimethoxy-6,7-dibromo-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene (15). To a solution of **10** (204 mg, 0.77 mmol) in carbon tetrachloride (4 mL) was added dropwise 0.54 M bromine in carbon tetrachloride (1.5 mL, 0.81 mmol) at

ambient temperature. After the addition was complete, the orange solution was stirred for 8 h at room temperature. After the solvent was removed on a rotary evaporator, the residual crude product was washed with a small amount of diethyl ether to supply **15** as a white solid (310 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (t, 2H, J = 7.9 Hz), 7.03 (d, 2H, J = 7.3 Hz), 6.91 (dd, 2H, J = 8.2, 0.6 Hz), 4.31−4.35 (m, 2H), 3.74 (s, 6H), 3.36 (dd, 2H, J = 13.9, 1.2 Hz), 2.84−2.93 (m, 2H). MS (EI): *m*/*z* (relative intensity) 265 (100), 426 (M^+, 48), 250 (36), 266 (36), 235 (27), 424 (25), 428 (25), 234 (24). HRMS (M^+): calcd for $C_{18}H_{18}Br_2O_2$ 423.9674, found 423.9683.

1,12-Dimethoxydibenzo[*a*,*c*]cyclooctene (16). Dibromide **15** (211 mg, 0.50 mmol) was dissolved in dry benzene (7 mL), and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (0.4 mL, 3 mmol) was added by a syringe. The reaction mixture was refluxed for 15 h and allowed to cool. The solution was treated successfully with 10% sulfuric acid (5 mL), water (2 × 10 mL), and brine (20 mL) and then dried over anhydrous sodium sulfate. Removal of the solvent and flash column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) gave **16** (38 mg, 29%), which was difficult to obtain in a sufficiently pure form for proton NMR spectroscopy but was characterized by HRMS and X-ray diffraction. HRMS (MNa^+): calcd for $C_{18}H_{16}O_2Na$ 287.1043, found 287.1049.

1,12-Dimethoxy-5,6,7-tribromo-5,6-dihydrodibenzo[*a*,*c*]-cyclooctene (18). To dry carbon tetrachloride (20 mL) were added **10** (146 mg, 0.55 mmol), *N*-bromosuccinimide (308 mg, 1.7 mmol), and benzoyl peroxide (11 mg, 0.05 mmol). The reaction mixture was refluxed for 10 h until the complete formation of succinimide floating upon the surface of carbon tetrachloride was evident. The succinimide was filtered off and washed thoroughly with carbon tetrachloride. After removal of the solvent, the mixture was solidified in *n*-hexane and washed with a minimum amount of diethyl ether to give **18** as a white solid (216 mg, 78%), which was directly used in the next step. Purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) gave a pure sample of **18** for characterization, mp 180−198 °C (sublimed). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39−7.49 (m, 3H), 6.81−7.02 (m, 3H), 6.85 (s, 1H), 5.20 (d, 1H, J = 11.1 Hz), 4.95 (d, 1H, J = 10.8 Hz), 3.80 (s, 3H), 3.77 (s, 3H). MS (EI): *m*/*z* (relative intensity) 263 (100), 262 (72), 189 (55), 232 (53), 264 (41), 233 (36), 343 (29), 248 (29). IR (KBr disk): 3050, 2999, 2930, 2834, 1573, 1461, 1265, 1099, 1076, 777, 753, 730 cm^{-1}. Anal. Calcd for $C_{18}H_{15}Br_3O_2$: C, 42.98; H, 3.00. Found: C, 43.15; H, 3.19.

1,12-Dimethoxy-6,7-dibromodibenzo[*a*,*c*]cyclooctene (11). To **18** (722 mg, 1.4 mmol) was added dry benzene (30 mL) by a syringe and then 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (1.8 mL, 14 mmol). The reaction mixture was refluxed for 12 h, allowed to cool, and washed successively with 2 M hydrochloric acid (2 × 30 mL) and brine (4 × 50 mL). The benzene solution was dried over anhydrous sodium sulfate. Removal of the solvent on a rotary evaporator and flash column chromatography on silica gel (petroleum ether/dichloromethane 3:1) gave **11** as a white solid (368 mg, 61%), mp 200−220 °C (sublimed). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (t, 2H, J = 8.0 Hz), 7.06 (s, 2H), 6.88 (d, 2H, J = 8.1 Hz), 6.80 (d, 2H, J = 7.8 Hz), 3.68 (s, 6H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ 157.8, 138.1, 136.3, 128.4, 125.5, 121.0, 120.0, 110.4, 56.1. MS (EI): *m*/*z* (relative intensity) 262 (100), 342 (39), 263 (38), 341 (38), 310 (31), 312 (31), 189 (28), 343 (28). IR (KBr disk): 3059, 3012, 2940, 2837, 1602, 1575, 1489, 1461, 1431, 1303, 1259, 1081, 867, 856, 781, 756, 731, 657 cm^{-1}. Anal. Calcd for $C_{18}H_{14}Br_2O_2$: C, 51.22; H, 3.34. Found: C, 51.43; H, 3.39.

1,4:5,8-Diepoxy-12,13-dimethoxy-1,4,5,8-tetrahydrotetraphenylene (12). To a solution of **11** (1.61 g, 3.8 mmol) in dry THF (10 mL) was added furan (15 mL, freshly distilled from sodium wire). A solution of potassium *tert*-butoxide (1.72 g, 15 mmol) in dry THF (25 mL) was added slowly into the reaction mixture via a dropping funnel under an argon atmosphere. After the addition was complete, the yellowish green suspension was stirred for 130 h at ambient temperature. The reaction mixture was quenched with water (30 mL). After most of the THF was removed on a rotary evaporator, the residual solution was extracted with ethyl acetate (2 × 50 mL). The organic layer was washed with water (30 mL) and dried over anhydrous sodium sulfate. Removal of the solvent and flash column chromatography on silica gel (petroleum ether/ethyl acetate 2:1) provided **12** as a yellow powder (920 mg, 61%), which was a mixture of several isomers and used in the next step without further purifcation. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44−6.40 (m, 10H), 5.78−5.22 (m, 4H), 3.68−3.52 (m, 6H). MS (EI): *m*/*z* (relative intensity) 69 (100), 226 (99), 131 (70), 239 (63), 329 (63), 270 (60), 293 (52), 294 (52). IR (KBr disk): 2998, 2835, 1733, 1573, 1459, 1428, 1254, 1128, 1115, 1074, 1028, 1017, 1028, 1017, 878, 823, 797, 787, 731, 703 cm^{-1}.

1,16-Dimethoxytetraphenylene (13). To dry THF (15 mL) was added dropwise titanium tetrachloride (2.5 mL, 23 mmol) at −78 °C, followed by lithium aluminum hydride (451 mg, 12 mmol) and triethylamine (4.5 mL, 32 mmol). The dark mixture was refluxed for 0.5 h and then cooled to room temperature. Compound **12** (910 mg, 2.3 mmol) in dry THF (25 mL) was added into the reaction flask via a dropping funnel. After the addition was complete, the reaction mixture was stirred for 39 h at ambient temperature. The reaction was quenched by carefully adding water (10 mL) and 6 M hydrochloric acid (5 mL). After most of the THF was removed on a rotary evaporator, the residual mixture was extracted with ethyl acetate (2 × 20 mL). The combined organic extract was washed with water (2 × 20 mL) and dried over anhydrous sodium sulfate. Removal of the solvent on a rotary evaporator and flash column chromatography on silica gel (petroleum ether/dichloromethane 2:1) gave **13** as a white solid (668 mg, 80%), mp 185−195 °C (sublimed). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27−7.18 (m, 8H), 7.13−7.10 (m, 2H), 6.79 (td, 4H, J = 8.5, 0.6 Hz), 3.68 (s, 6H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ 156.8, 143.3, 141.8, 141.5, 128.8, 128.2, 128.1, 127.1, 127.1, 126.3, 121.8, 110.2, 56.3. MS (EI): *m*/*z* (relative intensity) 364 (M^+, 100), 86 (83), 365 (29), 57 (28), 55 (25), 289 (21), 145 (16), 144 (14). IR (KBr disk): 3057, 2988, 2930, 2829, 1577, 1462, 1423, 1351, 1261, 1125, 1025, 865, 791, 761, 752, 734, 659, 558, 516 cm^{-1}. Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.61; H, 5.64.

1,16-Dihydroxytetraphenylene (2). To a solution of **13** (662 mg, 1.8 mmol) in dry dichloromethane (25 mL) was added 1 M boron tribromide in dichloromethane (10 mL, 10 mmol) via a dropping funnel at 0 °C. The reaction mixture was stirred for 18 h at ambient temperature. The reaction mixture was treated successively with 6 M hydrochloric acid (10 mL) and water (10 mL) and then extracted with dichloromethane (2 × 50 mL). The organic phase was dried over anhydrous sodium sulfate. Removal of the solvent and flash column chromatography on silica gel (petroleum ether/ethyl acetate 2:1) gave **2** as a white solid (595 mg, 97%), mp 200−220 °C (sublimed). ^{1}H NMR (300 MHz, CD_3COCD_3): δ 7.36−7.22 (m, 6H), 7.11−7.03 (m, 4H), 6.77 (dd, 2H, J = 8.1, 1.2 Hz), 6.61 (dd, 2H, J = 7.2, 1.2 Hz). MS (EI): *m*/*z* (relative intensity) 336 (M^+, 100), 289 (21), 337 (17), 307 (16), 308 (16), 40 (14), 145 (13), 144 (11). IR (KBr disk): 3499 (br), 1572, 1453, 1452, 1187, 1177, 1158, 1006, 901, 797, 761, 751, 738 cm^{-1}. Anal. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79. Found: C, 85.44; H, 4.95.

(*S*)-(+)-1,16-Bis[(*S*)-camphorsulfonyloxy]tetraphenylene (19) and (*R*)-(+)-1,16-Bis[(*S*)-camphorsulfonyloxy]-tetraphenylene (20). To a solution of (±)-**2** (299 mg, 0.89 mmol) and (*S*)-(+)-camphorsulfonyl chloride (97% ee, 2.31 g, 9.2 mmol) in THF (30 mL) was added dropwise triethylamine (1.3 mL, 9.3 mmol) at 0 °C. The resulting mixture was stirred for 42 h at room temperature until TLC indicated complete consumption of (±)-**2**. After most of the THF was removed on a rotary evaporator, the residue was treated with water (10 mL) and extracted with dichloromethane (2 × 20 mL). The organic solution was dried over anhydrous sodium sulfate. Removal of the solvent and flash column chromatograph on

silica gel (petroleum ether/ethyl acetate 6:1) yielded the crude product containing the two diastereomeric bissulfonates **19** and **20** in almost quantitative yield, which could be separated by repeated flash column chromatography with benzene and ethyl acetate (20:1) as the eluent followed by recrystallization from $CH_3OH-CH_2Cl_2$. Both diastereomeric bissulfonates **19** and **20** were obtained in over 94% (97.9% ee) and 97% (97.5% ee) yields, respectively. Single crystals of the less polar bissulfonate **19** were grown from CH_3OH, and its (*S*)-configuration was determined on the basis of an X-ray diffraction analysis. **Data of 19**, mp 239−240 °C. $[\alpha]^{20}_D$: +47.4 (c = 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41−7.27 (m, 10H), 7.22−7.13 (m, 4H), 3.20 (d, 2H, J = 15.3 Hz), 3.00 (d, 2H, J = 14.7 Hz), 2.42−2.34 (m, 4H), 2.13−2.00 (m, 4H), 1.95 (d, 2H, J = 18.6 Hz), 1.61−1.38 (m, 4H), 1.09 (s, 6H), 0.85 (s, 6H). MS (EI): *m*/*z* (relative intensity) 337 (100), 336 (96), 215 (77), 551 (59), 260 (49), 151 (49), 109 (48), 259 (47). IR (KBr disk): 3063, 2960, 1750 (vs), 1572, 1453, 1433, 1424, 1365, 1224, 1176, 1164, 1080, 1049, 912, 799, 761, 748, 576, 557, 513, 501 cm^{-1}. Anal. Calcd for $C_{24}H_{44}O_2$: C, 69.09; H, 5.80. Found: C, 69.01; H, 5.95. **Data of 20**, mp 206−207 °C. $[\alpha]^{20}_D$: +3.4 (c = 1.4, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47−7.25 (m, 10H), 7.21−7.11 (m, 4H), 3.54 (d, 2H, J = 15.0 Hz), 2.81 (d, 2H, J = 15.3 Hz), 2.42−2.33 (m, 2H), 2.21−1.97 (m, 6H), 1.92 (d, 2H, J = 18.6 Hz), 1.64−1.55 (m, 2H), 1.45−1.36 (m, 2H), 0.97 (s, 6H), 0.79 (s, 6H). Anal. Calcd for $C_{24}H_{16}O_2$: C, 69.09; H, 5.80. Found: C, 69.13; H, 6.01.

(*S*)-(+)-1,16-Dihydroxytetraphenylene ((*S*)-2). To a solution of **19** (141 mg, 0.18 mmol) in methanol (10 mL) and water (2 mL) was added potassium hydroxide (288 mg, 5.1 mmol). The reaction mixture was refluxed for 5 h and then allowed to cool. After most of the methanol was removed on a rotary evaporator, the residue mixture was acidified with 2 M hydrochloric acid to pH = 1 and then extracted with dichloromethane (2 × 20 mL). The organic layer was washed with brine (3 × 20 mL) and dried over anhydrous sodium sulfate. Removal of the solvent and flash column chromatography on silica gel (petroleum ether/ethyl acetate 2:1) gave (*S*)-**2** as a white solid (63 mg, 100%), with 97% purity and 99.3% ee as determined by chiral HPLC. The spectroscopic data of (*S*)-**2** were identical to those of (±)-**2**. $[\alpha]^{20}_D$: +66.2 (c = 1.0, CH_2Cl_2).

(*R*)-(−)-1,16-Dihydroxytetraphenylene ((*R*)-2). To a solution of **20** (155 mg, 0.20 mmol) in methanol (10 mL) and water (2 mL) was added potassium hydroxide (261 mg, 4.7 mmol). The reaction mixture was refluxed for 5 h and then allowed to cool. After most of the methanol was removed on a rotary evaporator, the residue was acidified with 2 M hydrochloric acid to pH = 1 and then extracted with dichloromethane (2 × 20 mL). The organic layer was washed with brine (3 × 20 mL) and dried over anhydrous sodium sulfate. Removal of the solvent and flash column chromatography on silica gel (petroleum ether/ethyl acetate 2:1) gave (*R*)-**2** as a white solid (69 mg, 100%), with a purity of 95% and 99.4% ee as determined by chiral HPLC. The spectroscopic data of (*R*)-**2** were identical to those of (±)-**2**. $[\alpha]^{20}_D$: −61.4 (c = 1.0, CH_2Cl_2).

1,16-Bis(trifluoromethanesulfonyloxy)tetraphenylene (21). To a solution of 1,16-dihydroxytetraphenylene (**2**) (116 mg, 0.35 mmol) in dry dichloromethane (15 mL) was added pyridine (1.5 mL, 13 mmol) and then trifluoromethane sulfonic anhydride (1.5 mL, 9.1 mmol) at 0 °C. After the addition, the reaction mixture was stirred for 69 h at ambient temperature. When TLC indicated the reaction was complete, water (5 mL) was added carefully. The mixture was extracted with dichloromethane (2 × 15 mL). The organic layer was washed sequentially with 1 M hydrochloric acid (10 mL) and brine (2 × 20 mL), dried over anhydrous sodium sulfate. Removal of the solvent on a rotary evaporator and flash column chromatography on silica gel (petroleum ether/ethyl acetate 50:1) gave **21** as a white solid (202 mg, 98%), mp 210−220 °C (sublimed). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (t, 2H, J = 8.1 Hz), 7.36−7.23 (m, 10H), 7.17−7.14 (m, 2H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ 145.9, 145.6, 140.5, 138.7, 130.3, 129.8, 129.5, 129.0, 128.2, 127.8, 127.3, 120.2, 120.1, 115.9. MS (EI): *m*/*z* (relative intensity) 299 (100), 600 (M^+, 38), 306 (37), 289 (27), 300 (24), 305 (23), 105 (21), 276 (20). IR (KBr disk): 1460, 1423 (vs), 1251, 1220 (vs), 1142 (vs), 1075, 920, 908, 809, 763, 751, 604, 513 cm^{-1}. Anal. Calcd for $C_{26}H_{14}O_6S_2F_6$: C, 52.00; H, 2.35. Found: C, 51.78; H, 2.40.

1-(Diphenylphosphinyl)-16-(trifluoromethanesulfonyloxy)tetraphenylene (22). To a mixture of **21** (61 mg, 0.10 mmol), diphenylphosphine oxide (60 mg, 0.30 mmol), palladium acetate (8 mg, 0.035 mmol), and 1,4-bis(diphenylphosphino)butane (dppb) (16 mg, 0.038 mmol) were added dry dimethyl sulfoxide (7 mL) and diisopropylethylamine (60 μL, 0.32 mmol). The mixture was heated with stirring at 100 °C for 24 h. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure (0.1 mmHg) to give a dark brown residue, which was diluted with ethyl acetate (25 mL). The ethyl acetate solution was washed with water (15 mL) and dried over anhydrous sodium sulfate. Removal of the solvent and flash column chromatography on silica gel (petroleum ether/ethyl acetate 2:1) provided **22** as a white solid (63 mg, 97%), mp 134−136 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64−7.03 (m, 23H), 6.80 (d, 1H, J = 7.2 Hz). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ 147.1, 144.8, 144.6, 143.9, 141.0, 140.9, 140.0, 139.8, 137.9, 137.8, 134.3, 133.6, 133.1, 133.1, 132.9, 132.7, 132.2, 132.2, 132.1, 132.1, 131.9, 131.9, 131.8, 131.6, 131.5, 131.3, 131.3, 130.7, 129.4, 129.4, 128.7, 128.6, 128.3, 128.3, 128.2, 128.2, 128.0, 127.9, 127.8, 127.5, 127.4, 127.4, 127.3, 127.2, 124.5, 120.2, 119.4, 116.0, 111.8. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 30.2. MS (ESI): *m*/*z* 653 (MH^+, 100), 675 (MNa^+, 28). IR (KBr disk): 3010, 1452, 1436, 1404 (vs), 1250, 1221 (vs), 1204 (vs), 1160, 1143 (vs), 1118, 1068, 917, 904, 812, 750, 696, 603, 533 (vs) cm^{-1}. HRMS (MNa^+): calcd for $C_{37}H_{24}F_3O_4PSNa$ 675.0977, found 675.0999.

1-(Diphenylphosphino)-16-(trifluoromethanesulfonyloxy)tetraphenylene (23). Under a dry argon atmosphere, **22** (77 mg, 0.12 mmol), dry toluene (8 mL), dry triethylamine (2 mL, 14 mmol), and trichlorosilane (∼1.5 mL, 15 mmol) were added sequentially into a 20 mL sealed tube with a Teflon screwcap cooled at 0 °C. The reaction mixture was stirred for 28 h at 120 °C in the sealed tube. After cooling to the room temperature, the reaction mixture was transferred to a 100 mL beaker and diluted with diethyl ether (100 mL). Addition of water resulted in a sticky suspension, which was filtered through a sintered glass funnel padded with silica gel. The organic phase was separated, washed with brine (3 × 50 mL), and then dried over anhydrous sodium sulfate. Removal of the solvent and flash column chromatography on silica gel (petroleum ether/ethyl acetate 50:1) gave **23** as a white solid (66 mg, 89%), with the recovery of the precursor **22** (10 mg). Compound **23** must be kept in an atmosphere of argon due to its instability in air. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39−6.97 (m, 20H), 6.89 (t, 1H, J = 7.5 Hz), 6.79 (t, 2H, J = 7.5 Hz), 6.06 (d, 1H, J = 7.5 Hz). ^{13}C NMR (75.3 MHz, CDCl3): δ 145.8, 143.2, 141.1, 140.8, 140.6, 139.2, 137.4, 137.3, 137.1, 135.2, 134.4, 134.1, 133.1, 133.0, 132.8, 130.6, 129.6, 129.3, 128.8, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.0, 127.5, 127.4, 127.2, 127.0, 120.1. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ −12.7. MS (ESI): *m*/*z* 637 (MH^+, 66). IR (KBr disk): 3400 (br), 3061, 2963, 2923, 2852, 1434, 1421, 1248, 1212, 1159, 1143, 921, 909, 829, 805, 745, 696, 601 cm^{-1}. HRMS (MH^+): calcd for $C_{37}H_{25}F_3O_3PS$ 637.1209, found 637.1206.

1,16-Bis(diphenylphosphinyl)tetraphenylene (25). To a mixture of diphenylphosphine oxide (167 mg, 0.83 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (133 mg, 1.0 mmol) was added *N*,*N*-dimethylacetamide (8 mL). The solution was degassed under vacuum and argon seven times and then charged with [1,2-bis(diphenylphosphino)ethane] nickel(II) chloride ($NiCl_2$·dppe, 22 mg, 0.024 mmol) and **23** (45 mg, 0.07 mmol). The reaction mixture was heated to 100 °C and stirred for

about 50 h at this temperature until the reaction solution became clear. The reaction mixture was allowed to cool, and *N*,*N*-dimethylacetamide was removed under reduced pressure (about 0.2 mmHg). The residue was diluted with ethyl acetate (15 mL), and the insoluble solid was removed by filtration. Removal of the solvent and flash column chromatography on silica gel (petroleum ether/ethyl acetate 1:1) gave **25** as a white solid (9 mg, 18%) and 1-diphenylphosphinyltetraphenylene (**24**) as a byproduct (20 mg, 56%). **Data of 25**, mp > 320 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84−7.77 (m, 4H), 7.56−6.91 (m, 26H), 6.73 (td, 2H, J = 7.5, 1.4 Hz), 6.11 (dd, 2H, J = 7.5, 0.9 Hz). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ 141.3, 140.9, 132.9, 132.7, 132.6, 132.5, 132.2, 131.6, 131.5, 131.4, 131.0, 130.9, 128.4, 128.3, 128.1, 128.1, 127.3, 127.0, 126.6, 126.5. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 28.7. MS (ESI): *m*/*z* 705 (MH^+, 100). IR (KBr disk): 3400 (br), 3051, 2923, 2852, 1647 (br), 1436 (vs), 1400 (m), 1210 (vs), 1195 (vs), 1147, 1116−1028 (br, vs), 748, 721, 696 (vs), 545 (vs), 532 (vs), 481 cm^{-1}. HRMS (MH^+): calcd for $C_{48}H_{35}O_2P_2$ 705.2107, found 705.2124. **Data of 24.** ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66−6.95 (m, 23H), 6.70−6.64 (m, 2H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ 145.2, 145.1, 144.3, 144.2, 141.6, 141.5, 141.5, 141.2, 141.2, 141.2, 141.1, 141.1, 141.1, 137.5, 137.4, 137.4, 134.3, 134.3, 134.2, 133.8, 133.7, 133.6, 133.3, 133.3, 133.0, 132.8, 132.8, 132.4, 132.3, 132.2, 132.1, 131.6, 131.5, 131.5, 131.4, 131.3, 131.1, 131.0, 130.8, 129.2, 129.1, 128.8, 128.8, 128.6, 128.6, 128.4, 128.4, 128.3, 128.3, 128.0, 127.7, 127.5, 127.4, 127.1, 127.0, 126.9, 126.3. MS (ESI): *m*/*z* 505 (MH^+, 100), 1031 ($2M+Na^+$, 34). HRMS (MNa^+): calcd for $C_{36}H_{25}OPNa$ 527.1535, found 527.1532.

1,16-Bis(diphenylphosphino)tetraphenylene (26). In a 20 mL tube sealed with a Teflon screwcap was placed **25** (14 mg, 0.02 mmol), dry toluene (5 mL), and dry triethylamine (2 mL, 14 mmol). Trichlorosilane (∼1.5 mL, 14 mmol) was added into the tube at 0 °C. The reaction mixture was kept at 120 °C in the sealed tube for 42 h. After cooling to room temperature, the reaction mixture was transferred to a 50 mL beaker and diluted with toluene (20 mL). Aqueous sodium hydroxide (10 M) was added to quench the reaction until the organic and aqueous layers became clear. The organic layer was separated, and the aqueous layer was extracted with warm toluene (2 × 20 mL). The combined organic layer was washed with 2 M hydrochloric acid (15 mL), saturated aqueous sodium hydrogen carbonate (20 mL), and brine (2 × 20 mL) and then dried over anhydrous sodium sulfate. Removal of the solvent gave the crude **26** as a yellow solid. Further purification by washing **26** with a minimum amount of toluene (2 × 0.5 mL) gave **26** as a white solid (8 mg, 60%). Due to its potential instability in air, compound **26** was used immediately in the next step after being characterized by ^{31}P NMR. ^{31}P NMR (121.5 MHz, C_6D_6): δ −11.5.

BPTP−$PtCl_2$ (27). A mixture of dichloro(1,5-cyclooctadiene)platinium (4.70 mg, 0.01 mmol) and **26** (8.00 mg, 0.01 mmol) in dichloromethane (2 mL) was stirred for 10 h at room temperature. After removal of the solvent, the residual powder was dried in a vacuum at 65 °C to give **27** (9.1 mg, 81%). Its structure was determined on the basis of X-ray diffraction analysis of a crystalline sample grown from dichloromethane. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ +10.6.

Assembly between 2 and 4,4′-Bipyridine. DHTP **2** [(±)-**2** or (*S*)-**2**] (1 molar equiv) and 4,4′-bipyridine (2 molar equiv) was dissolved in the solvent. The solvent was evaporated slowly at room temperature to afford crystal for the studies of proton NMR and X-ray diffraction. **Data for (±)-2 and 4,4′-bipyridine.** ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.71 (dd, 4H, J = 4.5, 1.5 Hz), 7.55 (dd, 4H, J = 4.5, 1.5 Hz), 7.29−7.10 (m, 10H), 6.90 (d, 2H, J = 8.4 Hz), 6.82 (d, 2H, J = 7.8 Hz), 5.56 (br) (integration values indicate the formation of molecular complex with a molar ratio of 1:1). **Data for (*S*)-2 and 4,4′-bipyridine.** ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.71 (dd, 2 × 4H, J = 4.5, 1.5 Hz), 7.55 (dd, 2 × 4H, J = 4.5, 1.5 Hz), 7.29−7.10 (m, 10H), 6.88 (d, 2H, J = 8.4 Hz), 6.78 (d, 2H, J = 7.8 Hz), 5.56 (br) (integration values indicate the formation of molecular complex with a molar ratio of 1:2).

(*S*)-BINAP−$PtCO_3$ ((*S*)-28). A mixture of (*S*)-BINAP−$PtCl_2$ (102 mg, 0.12 mmol) and silver carbonate (72 mg, 0.26 mmol) in wet dichloromethane (saturated in water, 30 mL) was stirred under darkness for 4.5 h. The insoluble solid was filtered, and the solvent was removed on a rotary evaporator to give (*S*)-**28** (97 mg, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93−7.86 (m, 4H), 7.59−7.38 (m, 16H), 7.23−7.09 (m, 4H), 6.92 (d, 2H, J = 5.7 Hz), 6.80 (d, 2H, J = 6.9 Hz), 6.64−6.59 (m, 4H). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 4.85 (J_{P-Pt} = 3648 Hz).

(*R*)-BINAP−$PtCO_3$ ((*R*)-28). The procedure for the preparation of (*R*)-**28** was similar to that for (*S*)-**28**. The spectroscopic data of (*R*)-**28** were identical with those of (*S*)-**28**.

Reaction between (*S*)-28 and (*S*)-2. Under an argon atmosphere, (*S*)-**28** (12 mg, 0.014 mmol), (*S*)-**2** (4 mg, 0.013 mmol), and dry $CDCl_3$ (0.5 mL) were added into a NMR tube. The yellowish green clear solution was treated with supersonic waves for 20 min and then characterized by ^{1}H NMR and ^{31}P NMR spectroscopy. In view of the complication of the proton NMR spectra, only characteristic peaks discussed in the article are reported (parts per million, peak multiplicities, relative integration, and coupling constant (Hz)). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92−7.85 (m, 2.15), 7.83−7.76 (m, 4.18), 6.51 (d, 2.15, J = 7.2 Hz), 6.30 (d, 2.0, J = 7.2 Hz) (the peak between 7.92 and 7.85 ppm almost completely disappeared when (*S*)-**2** was increased to 1.6 molar equiv). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 5.76 (s, 1.0), 4.79 (s, 0.5) (1.0 and 0.5 are the relative integration values of the two peaks; the peak at 4.79 ppm almost completely disappeared when (*S*)-**2** was increased to 1.6 molar equiv). HRMS (MNa^+): calcd for $C_{68}H_{46}O_2P_2{}^{190}PtNa$ 1169.2465, found 1169.2475.

Reaction between (*S*)-28 and (*S*)-2 at an Equal Molar Ratio in Refluxing $CHCl_3$. To a mixture of (*S*)-**28** (27 mg, 0.03 mmol) and (*S*)-**2** (10 mg, 0.03 mmol) was added dry chloroform (1 mL). The clear greenish solution was refluxed for 15 h. After removal of the solvent under reduced pressure, the residual yellow powder was dried in a vacuum at 70 °C. After 45 min, the powder was dissolved in dry $CDCl_3$ for the study of NMR. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91−7.85 (m, 4H), 7.66−7.61 (m, 4H), 7.53 (d, 2H, J = 6.9 Hz), 7.40−7.05 (m, 22H), 6.83−6.63 (m, 10H), 6.49 (d, 2H, J = 7.2 Hz), 6.34 (d, 2H, J = 8.1 Hz). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 5.52.

Reaction between (*S*)-28 and (*R*)-2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09−8.03 (m, 3.8), 7.91−7.84 (m, 2.14), 6.49 (d, J = 6.9 Hz), 5.91 (d, 2.0, J = 7.2 Hz) (the peak between 7.91 and 7.84 ppm diminished apparently when (*S*)-**2** was increased to 1.8 molar equiv). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 5.55 (s, 1.0), 4.77 (s, 0.5) (1.0 and 0.5 are the relative integration values of the two peaks, and the two values changed to 1.0 and 0.3 when (*S*)-**2** was increased to 1.8 molar equiv).

Reaction between (*S*)-28 and (±)-2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03−7.97 (m, 2.1), 7.76−7.70 (m, 4.8), 6.53 (d, J = 7.2 Hz), 6.50 (d, J = 7.5 Hz), 6.33 (d, 2.0, J = 7.8 Hz), 5.88 (d, J = 7.2 Hz). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 5.47 (s, 1.0), 4.86 (s, 1.89) (1.0 and 1.89 are the relative integration values of the two peaks).

Reaction between (*R*)-28 and (*R*)-2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91−7.85 (m, 1.5), 7.82−7.77 (m, 4.5), 6.46 (d, 2.2, J = 7.5 Hz), 6.29 (d, 2, J = 7.8 Hz) (the peak between 7.91 and 7.85 ppm almost completely disappeared when (*R*)-**2** was increased to 2.0 molar equiv). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 5.56 (s, 2.4), 4.81 (s, 1.0) (2.4 and 1.0 are the relative integration values of the two peaks; the peak at 4.81 ppm almost completely disappeared when (*R*)-**2** was increased to 2.0 molar equiv).

Reaction between (*R*)-28 and (*S*)-2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08−8.01 (m, 2.0), 7.90−7.83 (m, 0.9), 6.48 (d, J = 7.5 Hz), 5.91 (d, 1.0, J = 7.8 Hz). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 5.56 (s, 2.0), 4.75 (s, 1.0) (2.0 and 1.0 are the relative integration values of the two peaks).

Reaction between (*R*)-28 and (±)-2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99−7.93 (m, 1.0), 7.73−7.67 (m, 2.7), 6.53 (d, J = 7.8 Hz), 6.44 (d, J = 7.2 Hz), 6.34 (d, J = 7.8 Hz), 5.85 (d, J = 7.8 Hz). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 5.34 (s, 1.0), 4.76 (s, 2.2) (1.0 and 2.2 are the relative integration values of the two peaks).

Crystallographic Details. All structures were solved by direct methods (SHELXS-97) (Sheldrick, G. M. *SHELX-97 Programs for Crystal Structure Analysis*; University of Göttingen: Göttingen, Germany, 1998).

Crystallographic Details for 16. Colorless blocklike crystals were grown from a solution of **16** in $CHCl_3$. A crystal of approximate dimensions 0.53 × 0.48 × 0.32 mm^3 was selected and mounted on a glass fiber. A total of 6080 reflections ($-14 \le h \le 13$, $-8 \le k \le 6$, $-14 \le l \le 16$) were collected at T = 293(2) K in the θ range from 1.87 to 22.49°, of which 1917 were unique (R_{int} = 0.0192); Mo Kα radiation (λ = 0.71073 Å). The residual peak and hole electron density were 1.279 and −0.185 e/Å^3. The absorption coefficient was 0.076 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.0666 (all data), wR_2 = 0.1795, and GOF = 1.110 [$I > 2\sigma(I)$]. $C_{18}H_{16}O_2$, monoclinic, space group $P2_1/c$, a = 13.104(3) Å, b = 7.811(1) Å, c = 14.904(3) Å, α = 90°, β = 103.259(3)°, γ = 90°, V = 1485.0(5) Å^3, Z = 4, ρ_{calcd} = 1.182 g/cm^3, F(000) = 560, $R(F)$ = 0.0596, w$R(F^2)$ = 0.1713.

Crystallographic Details for 18. Colorless prismatic crystals were grown from a solution of **18** in $CHCl_3$. A crystal of approximate dimensions 0.20 × 0.20 × 0.30 mm^3 was selected and mounted on a glass fiber. A total of 3277 reflections were collected at T = 293(0) K in the 2θ range from 13.62 to 21.49°, of which 3073 were unique (R_{int} = 0.0066); Mo Kα radiation (λ = 0.71069 Å). The residual peak and hole electron density were 0.73 and −0.87 e/Å^3. The linear absorption coefficient, μ, for Mo Kα radiation was 69.5 cm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.055 (all data), wR_2 = 0.067, and GOF = 2.18 [$I > 3.00\sigma(I)$]. $C_{18}H_{15}O_2Br_3$, triclinic, space group $P\bar{1}(2)$, a = 9.420(4) Å, b = 11.697(5) Å, c = 9.226(3) Å, α = 106.56(3)°, β = 96.68(4)°, γ = 112.08(3)°, V = 874.0(7) Å^3, Z = 2, ρ_{calcd} = 1.911 g/cm^3, F(000) = 488.00.

Crystallographic Details for 13. Colorless crystals were grown from a solution of **13** in $CHCl_3$. A crystal of good quality was selected and mounted on a glass fiber. A total of 14 347 reflections ($-18 \le h \le 18$, $-13 \le k \le 17$, $-13 \le l \le 18$) were collected at T = 293(2) K in the θ range from 1.59 to 28.21°, of which 5558 were unique (R_{int} = 0.1682); Mo Kα radiation (λ = 0.71073 Å). The residual peak and hole electron density were 0.162 and −0.178 e/Å^3. The absorption coefficient was 0.406 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.3003 (all data), wR_2 = 0.0720, and GOF = 0.371 [$I > 2\sigma(I)$]. $C_{27}H_{21}Cl_3O_2$, monoclinic, space group $P2_1/c$, a = 14.304(2) Å, b = 13.250(2) Å, c = 14.068(2) Å, α = 90°, β = 116.378(3)°, γ = 90°, V = 2388.6(7) Å^3, Z = 4, ρ_{calcd} = 1.345 g/cm^3, F(000) = 1000, $R(F)$ = 0.0355, w$R(F^2)$ = 0.0498.

Crystallographic Details for 19. Colorless crystals were grown from a solution of **19** in CH_3OH. A crystal of approximate dimensions 0.35 × 0.24 × 0.17 mm^3 was selected and mounted on a glass fiber. A total of 27 018 reflections ($-10 \le h \le 12$, $-22 \le k \le 24$, $-27 \le l \le 24$) were collected at T = 293(2) K in the θ range from 1.45 to 28.18°, of which 9424 were unique (R_{int} = 0.2158); Mo Kα radiation (λ = 0.71073 Å). The residual peak and hole electron density were 0.654 and −0.413 e/Å^3. The absorption coefficient was 0.192 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.3396 (all data), wR_2 = 0.2849, and GOF = 0.898 [$I > 2\sigma(I)$]. $C_{44}H_{44}O_8S_2$, orthorhombic, space group $P2_12_12_1$, a = 9.7766(11) Å, b = 18.833(2) Å, c = 21.033(3) Å, α = 90°, β = 90°, γ = 90°, V = 3872.6(8) Å^3, Z = 4, ρ_{calcd} = 1.312 g/cm^3, F(000) = 1616, $R(F)$ = 0.0823, w$R(F^2)$ = 0.1862.

Crystallographic Details for 27. Colorless irregular-shaped crystals were grown from a solution of **27** in CH_2Cl_2. A crystal of approximate dimensions 0.166 × 0.057 × 0.051 mm^3 was selected and mounted on a glass fiber. A total of 24 037 reflections ($-14 \le h \le 14$, $-19 \le k \le 17$, $-26 \le l \le 27$) were collected at T = 293(2) K in the θ range from 1.77 to 25.50°, of which 8379 were unique (R_{int} = 0.1273); Mo Kα radiation (λ = 0.71073 Å). The residual peak and hole electron density were 1.134 and −1.579 e/Å^3. The absorption coefficient was 3.573 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.1342 (all data), wR_2 = 0.1273, and GOF = 0.976 [$I > 2\sigma(I)$]. $C_{50}H_{38}Cl_6P_2Pt$, orthorhombic, space group $P2_12_12_1$, a = 12.2983(7) Å, b = 15.9577(9) Å, c = 23.0064(14) Å, α = 90°, β = 90°, γ = 90°, V = 4510.7(5) Å^3, Z = 4, ρ_{calcd} = 1.632 g/cm^3, F(000) = 2192, $R(F)$ = 0.0819, w$R(F^2)$ = 0.1105.

Crystallographic Details for the Molecular Aggregate of (±)-2 and 4,4′-Bipyridine. Colorless irregular-shaped crystals were grown from a solution of (±)-**2** (1 molar equiv) and 4,4′-bipyridine (2 molar equiv) in CH_3Cl. A crystal of approximate dimensions 0.403 × 0.116 × 0.105 mm^3 was selected and mounted on a glass fiber. A total of 7621 reflections ($-13 \le h \le 8$, $-20 \le k \le 17$, $-22 \le l \le 22$) were collected at T = 293(2) K in the θ range from 2.44 to 28.39°, of which 4306 were unique (R_{int} = 0.0751); Mo Kα radiation (λ = 0.71073 Å). The residual peak and hole electron density were 0.152 and −0.140 e/Å^3. The absorption coefficient was 0.081 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.1175 (all data), wR_2 = 0.1094, and GOF = 0.892 [$I > 2\sigma(I)$]. $C_{34}H_{24}N_2O_2$, monoclinic, space group Cc, a = 9.9763(3) Å, b = 15.076(3) Å, c = 17.382(5) Å, α = 90°, β = 106.227(8)°, γ = 90°, V = 2510.1(12) Å^3, Z = 4, ρ_{calcd} = 1.303 g/cm^3, F(000) = 1032, $R(F)$ = 0.0591, w$R(F^2)$ = 0.0903.

Crystallographic Details for the Molecular Aggregate of (*S*)-2 and 4,4′-Bipyridine. Colorless irregular-shaped crystals were grown from a solution of (*S*)-**2** (1 molar equiv) and 4,4′-bipyridine (2 molar equiv) in CH_2Cl_2. A crystal of approximate dimensions 0.876 × 0.790 × 0.713 mm^3 was selected and mounted on a glass fiber. A total of 21 534 reflections ($-11 \le h \le 14$, $-10 \le k \le 14$, $-38 \le l \le 38$) were collected at T = 293(2) K in the θ range from 1.99 to 28.36°, of which 4224 were unique (R_{int} = 0.1029); Mo Kα radiation (λ = 0.71073 Å). The residual peak and hole electron density were 0.189 and −0.192 e/Å^3. The absorption coefficient was 0.077 mm^{-1}. The least-squares refinement converged normally with residuals of R_1 = 0.0661 (all data), wR_2 = 0.1047, and GOF = 0.903 [$I > 2\sigma(I)$]. $C_{44}H_{32}N_4O_2$, monoclinic, space group Cc, $P4_32_12$, a = 10.8989(6) Å, b = 10.8989(6) Å, c = 29.337(2) Å, α = 90°, β = 90°, γ = 90°, V = 3484.8(4) Å^3, Z = 4, ρ_{calcd} = 1.237 g/cm^3, F(000) = 1362, $R(F)$ = 0.0447, w$R(F^2)$ = 0.0985.

Acknowledgment. This work was supported by grants from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project CUHK 4264/00P), The Croucher Foundation (Hong Kong), and the Area of Excellence Scheme established under the University Grants Committee of the Hong Kong Special Administrative Region, China (Project No. AoE/P-10/01). J.F.W. thanks the Croucher Foundation (Hong Kong) for a Shanghai Studentship. The authors would like to thank Professors Xi-Yan Lu, Li-Xin Dai, Guo-Qiang Lin, and Xue-Long Hou for helpful discussion.

Supporting Information Available: Synthesis of 2,2′-bis(bromomethyl)-6,6′-dimethoxy biphenyl (**7**), complete experimental data of the X-ray crystallographic determination of **16**, **18**, **13**, **19**, **25**, **27**, and molecular complexes of 4,4′-bipyridine with (±)-**2** and (*S*)-**2**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0302408