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A Greek cross dodecaphenylene: sparteine-mediated asymmetric synthesis of chiral D_2-symmetric π-conjugated tetra-*o*-phenylenes

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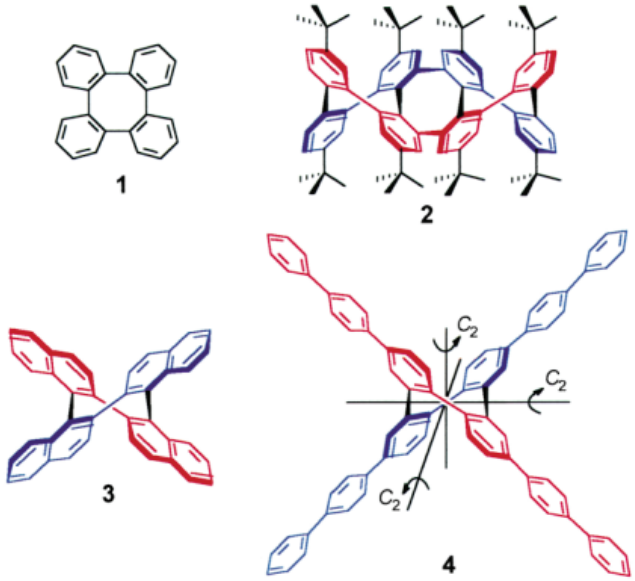
Abstract: The asymmetric synthesis of a chiral, nonracemic π-conjugated system with D_2 point group of symmetry, dodecaphenylene **4** is described. In the key step, (−)-sparteine- and Cu(II)-mediated oxidation of 2,2′-dilithio-1,1′-biaryls in ether gives the corresponding dimers, tetra-*o*-phenylenes, in 80% isolated yields and 50–60% ee's. X-Ray crystallography confirms the structure of rac-**4** and its molecular shape of a Greek cross. The torsional angles between the benzene rings in the tetra-*o*-phenylene core of rac-**4** are in the 56.5–71.0° range. However, CD and UV spectra of **4** in CH_2Cl_2 are consistent with significant conjugation between the four terphenyl moieties.

Keywords: asymmetric synthesis, biaryl, chiral, sparteine, π-conjugated

1. Introduction

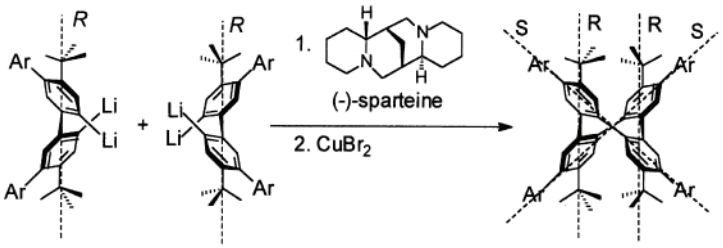
There is a growing interest in chiral π-conjugated molecules, directed at the design of organic materials. [1] The chirality may provide not only additional electronic properties but also allow for the control of packing and π–π interactions in the solid as well. [2, 3, & 4] Molecular shapes and enantiomeric excesses, ee ≫ 0%, are important factors. Therefore, asymmetric synthesis of novel chiral π-conjugated molecules is the first step toward efficient preparation of organic materials with interesting properties.



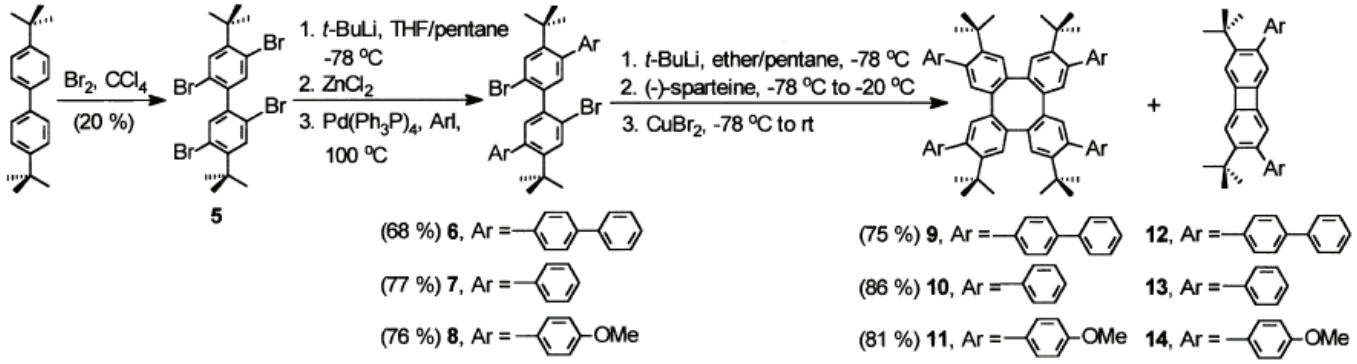
One of our approaches relies on chiral derivatives of tetra-*o*-phenylene **1** (tetrabenzo [a,c,e,g]cyclooctatetraene), a saddle shaped molecule, e.g. short π-conjugated double helices **2** and **3**. [5, 6, & 7] Such tetra-*o*-phenylene-based chiral π-conjugated molecules may possess extraordinarily high barriers for racemization and relatively high symmetry, such as D_2 point groups of symmetry in **2** and **3**. [5, 7, & 8] In addition to double helices, a different substitution pattern of **1** may lead to molecules with the shape of Greek cross, but chiral. A novel dodecaphenylene **4**, chiral π-conjugated molecule with D_2 point group of symmetry, may be viewed as a molecule with two perpendicularly crossed hexaphenylenes. Compared to spiro-linked oligophenyls and tetrahedrally linked o ligo(phenylenevinylenes), which have favorable morphology and optical properties for light emitting diodes, [9 & 10] **4** is designed to possess chirality and π-conjugation between the crossed chains.

There are only three examples of nonracemic tetra-*o*-phenylenes; they are prepared in rather low yields either from nonracemic biaryls or via resolution of racemates. [7 & 8] In this work, we describe an efficient asymmetric synthesis for chiral tetra-*o*-phenylenes, based upon (−)-sparteine- and $CuBr_2$-mediated coupling of 2,2′-dilithiobiaryls (Scheme 1). [11 & 12] Two aryl–aryl CC bonds are formed and the configuration of four chiral axes is set. For the tetra-*o*-phenylene ring to be formed, the two chiral axes originating from the 2,2′-dilithiobiaryl must have identical configuration (e.g., *R*) but opposite to the two new axes (e.g., *S*) which are associated with the newly formed CC bonds (Scheme 1). [7]

The synthesis and characterization (including X-ray crystallography) of the Greek cross π-conjugated dodecaphenylene **4** are reported.



Scheme 1. Enantioselective synthesis of tetra-*o*-phenylenes. Intercepted lines indicate chiral axes (*R* and *S*).



Scheme 2. Synthesis of tetra-*o*-phenylenes **9**–**11**.

2. Results and discussion

Synthesis of tetra-*o*-phenylenes **9**–**11** is outlined in Scheme 2).

Bromination of 4,4′-di-*tert*-butylbiphenyl gives 2,2′,5,5′-tetrabromo-4,4′-di-*tert*-butylbiphenyl (**5**) in ~20% yield. [13 & 14] In **5**, one would expect that Li/Br exchange at the 2,2′-sites will be favored by the ion triplet formation. [15] However, treatment of **5** with *t*-BuLi in THF at −78°C gives predominantly the 5,5′-dilithio derivative of **5**, as evidenced by both proton and deuteron quenching experiments. [16] It may be speculated that this remarkable selectivity for the Li/Br exchange at the 5,5′-sites is caused by steric acceleration. [17 & 18]

Following selective Li/Br exchange at the 5,5′-sites in **5** and transmetallation with $ZnCl_2$, the Negishi coupling with iodoaryls gives the corresponding 5,5′-diarylated compounds **6**–**8** in 68–77% yields. The selectivity between C–Br vs. C–I oxidative addition is sufficient to permit the use of only small excess (2.5 vs 2 equiv.) iodoaryls. [19] This is especially important in the case of **6**, where the greater excess of 4-iodobiphenyl and/or inaccurate stoichimetry of *t*-BuLi leads to increased contamination with nearly insoluble *p*-quaterphenyl side product, complicating the purification process.

In the next step, **6**–**8** are treated with *t*-BuLi (4 equiv.) and (−)-sparteine (2 equiv.) in ether/pentane at −78°C. The reaction mixture is briefly (30 min) allowed to attain −20°C, and then it is cooled to −78°C. After addition of $CuBr_2$ (6 equiv.), the vigorously stirred reaction mixture is allowed to attain ambient temperature overnight. Following aqueous workup, ^{1}H NMR analyses of the reaction mixtures reveal that tetra-*o*-phenylenes **9**–**11** are the predominant products (~90% yield) and only minor amounts of the biphenylene side prod-

Table 1. Synthesis of tetra-*o*-phenenylenes **9**–**11** and biphenylenes **12**–**14**

R	Procedure[a]	(**9**–**11**)/(**12**–**14**)[b] (crude)	ee (%) (crude)	ee (%) (LC)	Yield (%)[c] (**9**–**11**)	Yield (%)[c] (**12**–**14**)
4-C_6H_4Ph	A	8:1–3:1	49–59	57–64	75	6
	B	3:1	–	–	40	8
	C	7:1	35	–	–	–
	D	1:3–4:1	8–9	–	–	–
	E	1:20	–	–	–	40–50
Ph	A	8:1	50	54	86	3
	B	2:1	–	–	55	4
4-$MeOC_6H_4$	A	7:1	50	56	81	3
	B	4:1	–	–	31	7

[a] A=pentane/ether/(−)-sparteine, −20°C, 30 min; B=pentane/ether (no (−)-sparteine); C=pentane/ether/(−)-sparteine, −78°C, 30 min; D=pentane/THF/(−)-sparteine, −20°C, 30 min; E=pentane/THF (no (−)-sparteine).
[b] Molar ratios from ^{1}H NMR analyses.
[c] Isolated yields of pure compounds.

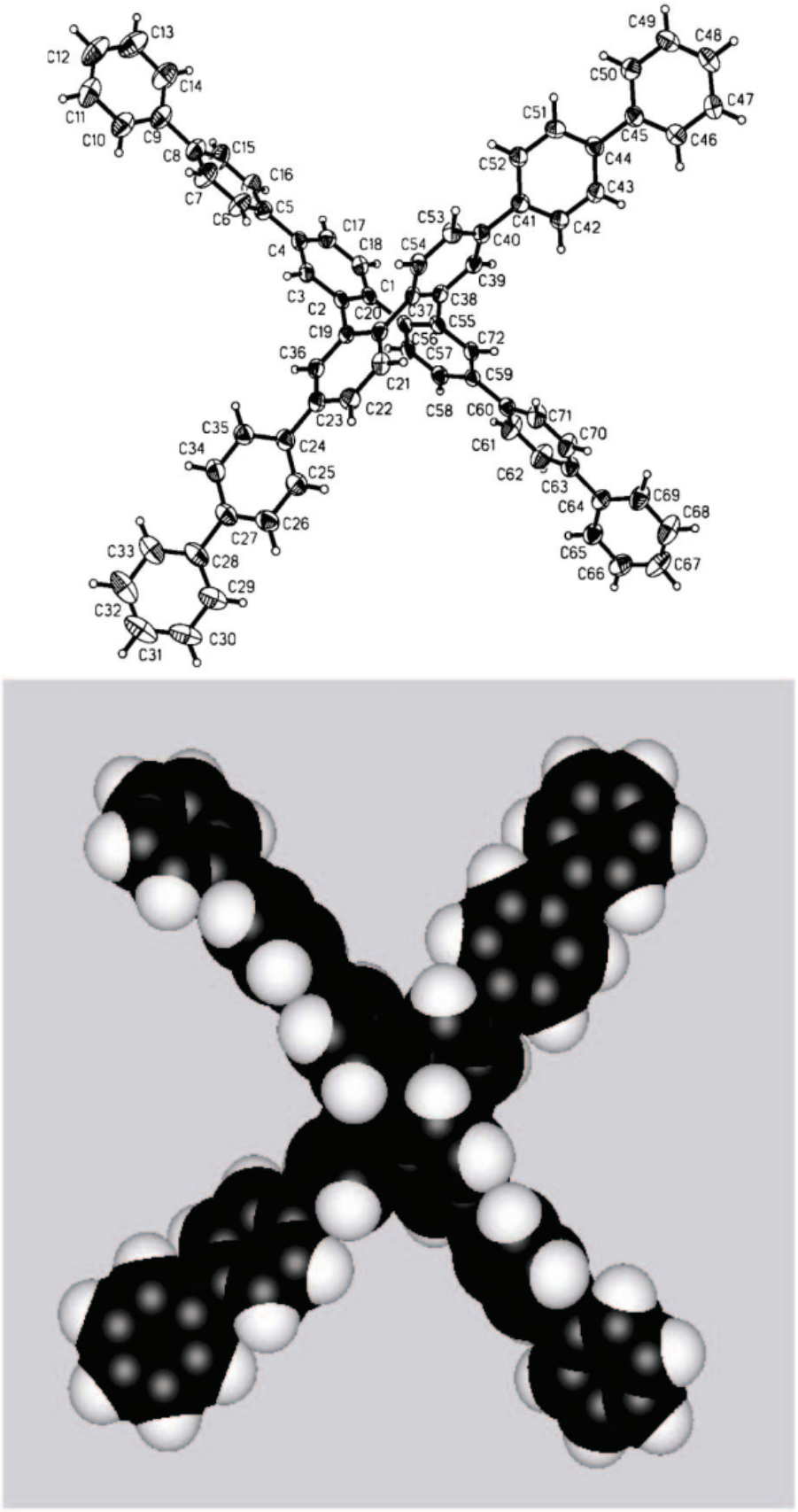


Figure 1. Molecular conformation for **4** as determined by a single crystal X-ray crystallography. The disordered molecules of solvent of crystallization (chloroform) are not shown. Top part: Ortep plot, carbon atoms are depicted with ellipsoids representing 50% probability level. Bottom part: space filling plot.

Table 2. Selected interatomic distances (Å), angles (deg), and torsional angles (deg) for **4** (space group $P2_1/n$).

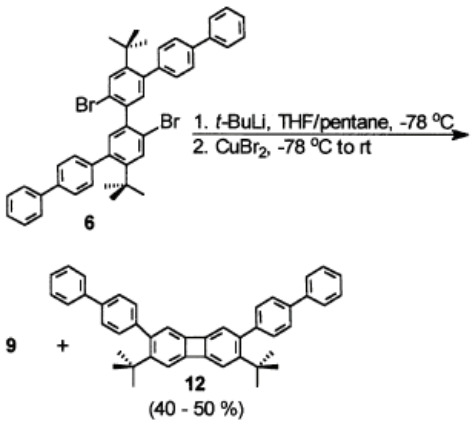
Hexaphenylene A		Hexaphenylene B	
C(12)—C(67)	24.3	C(31)–C(48)	24.2
C(12)—C(1)–C(67)	176.5	C(31)–C(37)–C(48)	167.3
C(12)—C(56)–C(67)	175.9	C(31)–C(20)–C(48)	168.0
α-torsions (within the tetra-*o*-phenylene moiety):[a]			
C(18)—C(1)–C(56)—C(57)	−58.1(4)	C(21)–C(20)–C(37)–C(54)	−58.6(4)
C(2)–C(1)–C(56)—C(55)	−63.5(4)	C(19)–C(20)–C(37)–C(38)	−65.6(4)
β-torsions:			
C(3)–C(4)–C(5)–C(6)	13.8(4)	C(53)–C(40)–C(41)–C(52)	−41.0(4)
C(17)—C(4)–C(5)–C(16)	15.2(4)	C(39)–C(40)–C(41)–C(42)	−40.0(4)
C(72)—C(59)–C(60)—C(71)	11.7(4)	C(36)–C(23)–C(24)–C(35)	−30.5(4)
C(58)—C(59)–C(60)—C(61)	11.0(4)	C(22)–C(23)–C(24)–C(25)	−31.0(4)
χ-torsions:			
C(7)–C(8)–C(9)–C(10)	−38.6(5)	C(51)–C(44)–C(45)–C(50)	−27.8(4)
C(15)—C(8)–C(9)–C(14)	−41.2(5)	C(43)–C(44)–C(45)–C(46)	−28.3(4)
C(62)—C(63)–C(64)—C(65)	−32.8(5)	C(34)–C(27)–C(28)–C(33)	−32.7(5)
C(70)—C(63)–C(64)—C(69)	−32.8(5)	C(26)–C(27)–C(28)–C(29)	−30.7(5)

[a] Other torsional angles within the tetra-*o*-phenylene moiety are: C(1)–C(2)–C(19)–C(20)=71.0(3), C(3)–C(2)–C(19)–C(36)=63.5(3), C(37)–C(38)–C(55)–C(56)=66.9(4), C(39)–C(38)–C(55)–C(72)=56.5(3).

ucts **12**–**14** (<10% yield) are formed (Table 1, procedure A). The ee's of about 50% are reproducibly obtained. Nonracemic **9**–**11** are isolated in about 80% yields (Table 1, procedure A). Analogous reactions, but without sparteine, give racemic **9**–**11**; however, the admixtures of **12**–**14** are somewhat increased but they are still relatively minor (<15% yield) (Table 1, procedure B).

The reaction conditions for synthesis of **9** and **12** are further studied. For procedure A (Table 1), 2–3 fold increase in the number of equivalents of *t*-BuLi and/or (−)-sparteine and/or $CuBr_2$ has no effect on ee's or yields. However, vigorous stirring after the addition of $CuBr_2$ is essential for high ee. When (−)-sparteine is added and kept at −78°C, without equilibriation at −20°C, the ee of **9** is significantly decreased (Table 1, procedure C).

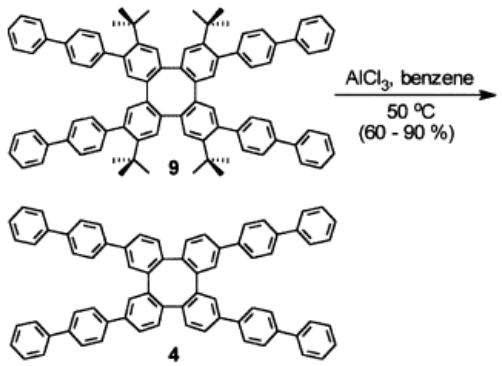
Change of solvent from ether/pentane to pentane/THF affects ee and/or product distribution. [20] With (−)-sparteine (Table 1, procedure D), tetra-*o*-phenylene **9** is still a major product but its ee of 8–9% is rather low. Without (−)-sparteine (Table 1, procedure E), biphenylene **12** becomes the dominant product (**9**:**12**, 1:20), which is isolated in 40–50% yield (Eq. (1)). [21]



(1)

Overall, (−)-sparteine mediated coupling of 2,2′-dilithiobiaryls provides a practical synthesis of nonracemic tetra-*o*-phenylenes in high chemical yields and moderate ee's.

Fractional crystallization of nonracemic **9** (ee 50–60%) gives optically pure **9** ($[\alpha]_D^{rt} = +170$) in 20–30% yield from **6**. Removal of *tert*-butyl groups from **9** (ee 0 or 100%) using $AlCl_3$ in benzene, [13] gives dodecaphenylene **4** in 60–90% yield (Eq. (2)). (Low solubility of rac-**4** in common organic solvents leads to lower isolated yields.) Starting from the optically pure **9**, nonracemic **4** ($[\alpha]_D^{rt} = +62$) is obtained; however, ee of **4** could not be determined by NMR spectroscopy (see Section 4).



(2)

NMR spectra for **4**–**14** show the expected numbers of resonances and spin coupling patterns. For biphenylene products **12**–**14**, the selected aromatic protons and carbons are significantly upfield-shifted compared to **9**–**11**, as expected. [21] In MS (EI), **12**–**14** show the expected isotopic clusters at M^+; isotopic clusters at *m*/*z* corresponding to $2M^+$ are either not detected or their intensity is negligible. For **4** and **9**–**11**, isotopic clusters at *m*/*z* corresponding to M^+ are found; only negligible, if any, intensities of monocharged ions at the *m*/*z* corresponding to $(M/2)^+$ are detected. For all compounds, **4**–**14**, high resolution MS (either EI or FAB) give the expected exact masses for M^+ (within 2.7 ppm).

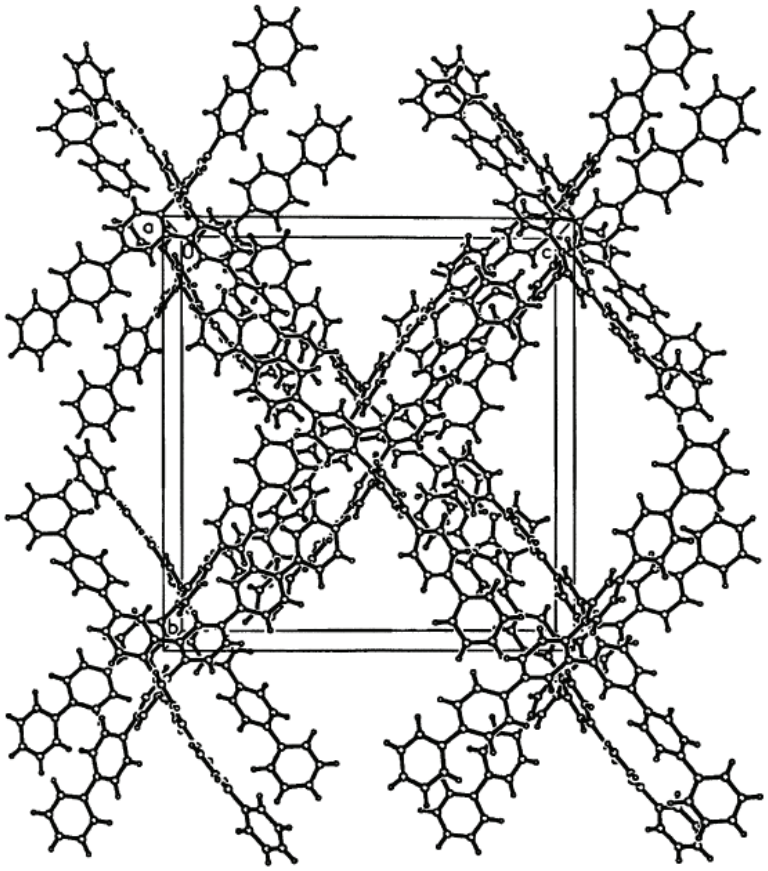


Figure 2. Crystal packing for **4** (view along *a*-axis). The disordered molecules of chloroform are not shown.

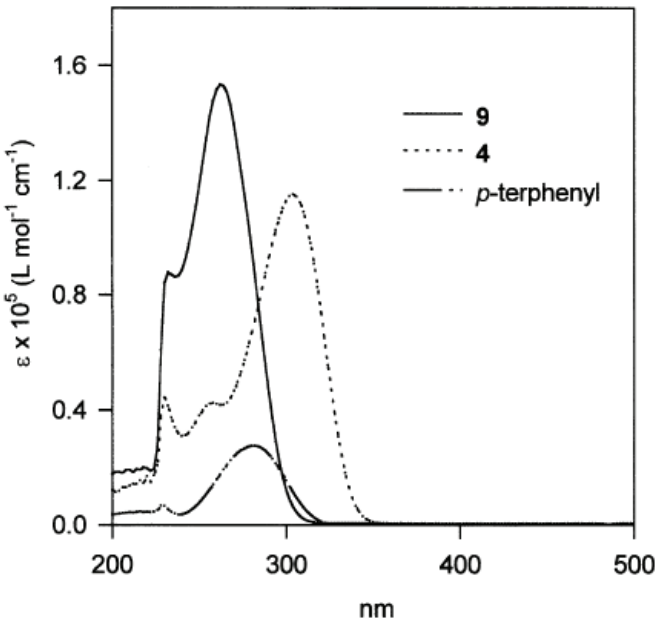


Figure 3. UV–vis spectra for **4**, **9**, and *p*-terphenyl in CH_2Cl_2. λ_{max}/nm ($\log(\varepsilon_{max}$/L mol^{-1} cm^{-1})): 4, 228 (4.77), 256 (4.75), 302 (5.18); 9, 232 (4.96), 262 (5.20); *p*-terphenyl, 280 (4.51).

The structure of rac-**4** was confirmed by single crystal X-ray analysis (Fig. 1). The molecule has very approximate D_2 point group of symmetry; all 72 carbon atoms are non-equivalent. The torsion angles between benzene rings within the tetra-*o*-phenylene moiety are in the (±)56.5–71.0° range, similar to that in **1**. [22] For the remaining benzene rings, the torsion angles are in the (±)11.0–41.2° range. The space filling plot shows that **4** has the molecular shape of a Greek cross (Fig. 1). The two crossing *p*-hexaphenylenes are designated as **A** and **B** (Table 2). Both **A** and **B** are about 2.4 nm long; **A** is more planar and less bent compared to **B** (Table 2). While the out-of-plane twisting within the tetra-*o*-phenylene moiety is unavoidable in each of the *p*-hexaphenylenes, the four *p*-terphenyl arms could adopt near planar conformations. [23]

The crystal of rac-**4** contains 4.5 molecules of chloroform per asymmetric unit. The crystal structure possesses large voids filled with badly disordered molecules of chloroform. The solvent accessible volume is slightly over a third (0.37) of the total volume (Fig. 2). [24]

UV/vis spectra for **4**, **9**, and *p*-terphenyl in methylene chloride are shown in Fig. 3. [25] The bathochromic shifts for **4** vs *p*-terphenyl vs **9** (22 and 18 nm, respectively) are rather substantial. This suggests that conjugation between the four *p*-terphenyl arms in **4** is significant, considering the relatively large torsion angles between benzene rings within the tetra-*o*-phenylene core. However, the presence of *tert*-butyl groups

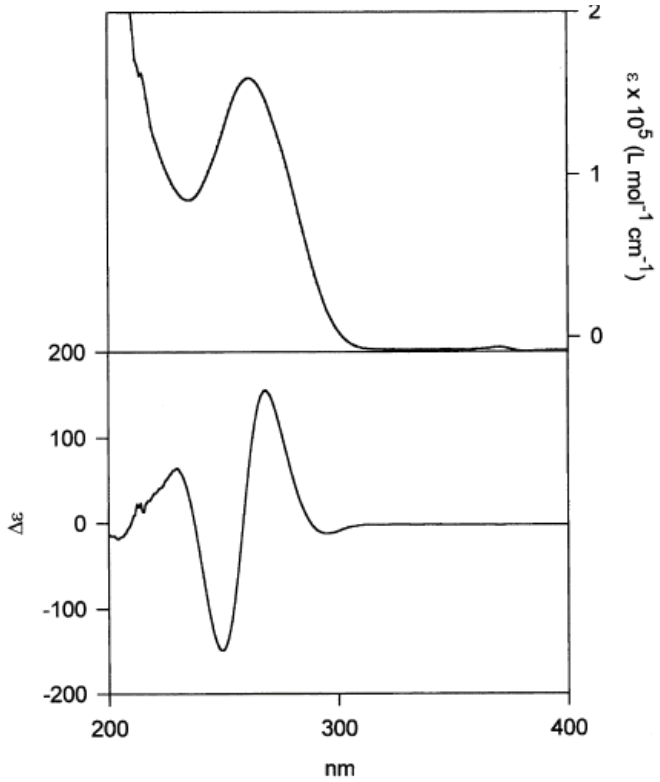


Figure 4. UV–vis (top) and CD (bottom) spectra for **9** (95+% ee) in CH_2Cl_2. CD, λ_{max}/nm ($\Delta\varepsilon_{max}$/L mol^{-1} cm^{-1}): 249.5 (−149), 258.5 (0), 268.5 (155).

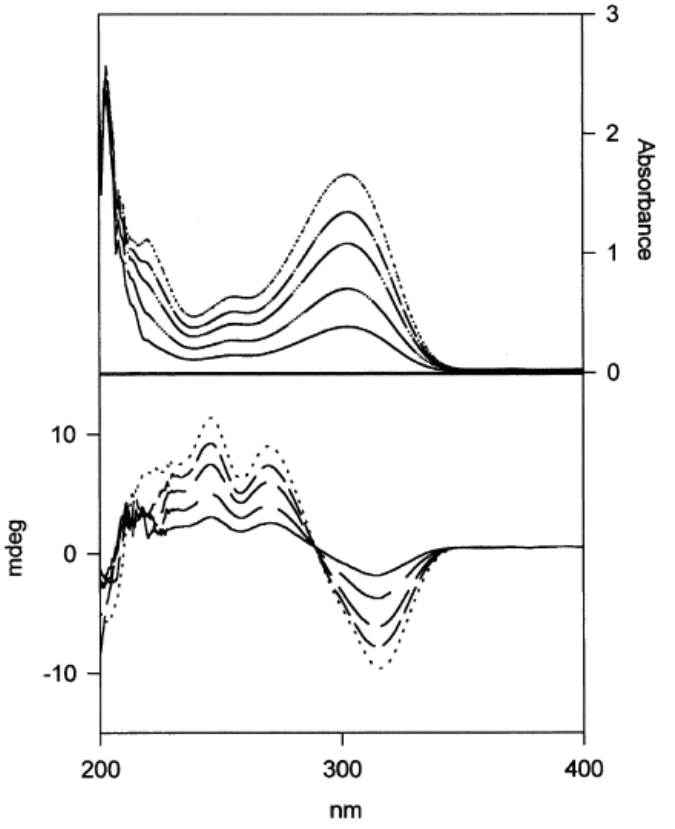


Figure 5. UV–vis (top) and CD (bottom) spectra for **4** (undetermined ee) in CH_2Cl_2. CD, the approximate concentrations are 25, 50, 75, 100, and 125 μM.

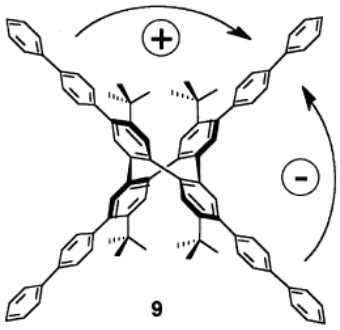


Figure 6. Selected exciton chiralities between the long-axis-polarized electronic transitions for the diagonal (positive) and proximate (negative) biphenyl chromophores in **9**.

in **9** disrupts conjugation between the biphenyl moieties and the tetra-*o*-phenylene core. These observations are confirmed by CD spectra of **9** and **4** (Figure 4 and Figure 5). For **9**, one prominent positive couplet (positive at long λ and negative at short λ cotton effects) is centered at 259 nm. For **4**, the long wavelength couplet, centered at 289 nm, is negative. The exciton coupling model would predict the same signs for the long wavelength couplets in **4** and **9**, providing that both compounds possess identical configurations. [26] The couplet inversion in **4** might suggest that the exciton coupling model, which assumes negligible interchromophoric conjugation, is not applicable to **4**. [7, 8, & 27]

Assuming that biphenyl chromophores in **9** are unconjugated and their long-axis polarized transitions are dominant, [28] exciton coupling model may be used to infer absolute configuration of **9**. [26] Positive and negative exciton chiralities, which are predicted for **9**, involve either diagonal or proximate pairs of biphenyl chromophores (Fig. 6).

(Exciton chiralities of biphenyls within the *p*-hexaphenylenes are nil, because each two such biphenyls are alligned parallel to each other.) As the interchromophoric distances for the diagonal pairs are shorter, compared to the proximate pairs, the exciton chirality of the diagonal pair of biphenyl chromophores is expected to be dominant. Therefore, the exciton chirality for the diagonal pair should be positive to be consistent with the positive couplet centered at 259 nm in the CD spectrum of **9**; i.e. the absolute configuration of **9** may tentatively be assigned as shown in Fig. 6. Also, this would suggest selectivity of (−)-sparteine toward (*R*)-2,2′-dilithiobiaryls (Scheme 1).

3. Conclusion

Chiral derivatives of π-conjugated tetra-*o*-phenylenes are prepared in good yields and moderate ee's via (−)-sparteine mediated asymmetric synthesis. As *p*-terphenyl has excellent quantum yields of fluorescence and its selected radical cation salts are good electrical conductors, [23 and 29] the Greek cross dodecaphenylene **4**, with four conjugated *p*-terphenyl arms within a chiral molecule, is a promising target for LEDs and electrical conductors.

4. Experimental

4.1. General procedures

Ether and tetrahydrofuran (THF) for use on the vacuum line were distilled from sodium/benzophenone under a nitrogen atmosphere. $CuBr_2$ was dried under vacuum at 70°C overnight prior to use. Ag(fod) was prepared as described by Wenzel, Bettes, Sadlowski, and Sievers. [30] $ZnCl_2$ (99.999%, ultra dry) was obtained from Alfa (Johnson–Mathey). *t*BuLi (pentane) and *n*BuLi (hexane) were obtained from either Aldrich or Acros; prior to use, their concentrations were determined by titration with *N*-pivaloyl-*o*-toluidine. [31] All other commercially available chemicals, including MeOD (99.5+%D), were obtained from Aldrich. Column chromatography was carried out on TLC grade silica gel (Aldrich), using 0–20 psig pressure. Preparative TLC (PTLC) was carried out using Analtech silica plates (tapered with a preadsorbent zone). Standard techniques for synthesis under inert atmosphere, using Schlenk glassware and gloveboxes (Mbraun and Vacuum Atmospheres), were employed.

NMR spectra were obtained using Bruker and Omega spectrometers (^{1}H, 500 and 300 MHz) using $CDCl_3$ as solvent. The chemical shift references were as follows: ^{1}H (TMS) 0.0 ppm and ^{13}C ($CDCl_3$) 77.0 ppm. Typical 1D FID was subjected to exponential multiplication with an exponent of 0.1 Hz (for ^{1}H) and 1.0–2.0 Hz (for ^{13}C).

IR spectra were obtained using a Nicolet Avatar 360 FT-IR instrument, equipped with an ATR sampling accessory (Spectra Tech). A few drops of the compound in CH_2Cl_2 were applied to the surface of a ZnSe ATR plate horizontal parallelogram (45°, Wilmad). After the solvent evaporated, the spectrum was acquired (16 scans, 1 cm^{-1} resolution).

UV–vis absorption spectra were recorded at ambient temperature using the diode-array Hewlett Packard (HP 8450A and HP 8452A) spectrophotometers. The Lambert–Beer plots for **4**, **9**, and *p*-terphenyl in CH_2Cl_2 were obtained using 10-mm pathlength quartz cells (six concentrations, $R = 0.999$).

Concurrent UV–vis and CD spectra for **4** (at 24°C) and **9** (at 26°C) in CH_2Cl_2 were obtained using Applied Photophysics Pistar 180 CDF Spectrometer at the University of North Carolina Macromolecular Interactions Facility. The spectra were obtained at **5** approximate concentrations (25, 50, 75, 100, and 125 μM), using 1-mm pathlength cells.

Optical rotations were measured with Autopol III (Rudolph Research) at ambient temperature.

Elemental analyses were carried out by M-H-W Laboratories, P.O. Box 15149, Phoenix, Arizona 85060 and Quantitative Technologies, P.O. Box 470, Salem Industrial Park, Bldg. 5, Whitehouse, NJ 08888.

4.1.1. ^{1}H NMR spectra with chiral shift reagents [32]. Spectrum for racemate (~3 mg) in $CDCl_3$ (0.4–0.5 mL) was first obtained; then, Ag(fod) and ytterbium tris [3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] (Yb(hfpc)) were added until baseline separation between the resonances of the enantiomers (in equilibrium with diastereomeric complexes) was attained. Typical amounts of the chiral tetra-*o*-phenylene derivative (**9**–**11**), Ag(fod), and Yb(hfpc), giving the optimum trade-off between dispersion and line width, were 3, 20, 20 mg, respectively. For samples with ee $\gg$ 0%, a small amount racemate was added to verify the resolution of resonances for the enantiomers.

4.1.2. X-Ray crystallography. Colorless needles (approximate dimensions 0.25×0.05×0.01 mm [3]) of rac-**4** were obtained from chloroform solution by slow evaporation. A crystal was placed onto a tip of a 0.1 mm diameter glass capillary and mounted on a Bruker SMART Platform CCD system for data collection at 173 (2) K. A low temperature transfer was needed because the crystals rapidly lost solvent.

The initial structure solution and refinement revealed the major sites of five chloroform molecules, one of which was disordered over an inversion center. However, the modeling of disorder for the solvent molecules was not successful as the minor sites could not be refined ($R = 0.19$). Therefore, the data set was corrected for disordered solvent using the program PLATON/SQUEEZE. [33] The total potential solvent accessible volume is 2515.5 Å [3] with 415 electrons, corresponding to 4.5 chloroform molecules per asymmetric unit. With the understanding that the exact amount of solvent is unknown (leading to incorrect values of F(000), formula, formula weight, etc.), the refinement using the corrected data was satisfactory; crystal data for rac-**4** were as follows: $C_{72}H_{48}$, M = 913.10, monoclinic, $a = 13.561(1)$, $b = 23.301(2)$, $c = 21.764(2)$ Å, $\beta = 92.269(2)$, $V = 6871.7(11)$ Å [3], $T = 173(2)$ K, space group $P2_1/n$, $Z = 4$, MoK ($\lambda = 0.71073$ Å). Structure was solved by direct methods and refined by full-matrix least-squares on F^2. Total of 12114 reflections was observed and 6238 reflections with $I > 2\sigma(I)$ were recorded. Refinement statistics with 649 parameters was as follows: $wR = 0.1871$ ($I > 2\sigma(I)$), $R = 0.0701$ ($I > 2\sigma(I)$), GOF = 1.040.

4.1.3. 2,2′,5,5′-Tetrabromo-4,4′-di-*tert*-butylbiphenyl (5) and quenching experiments. Br_2 (30.0 g, 9.7 mL, 0.188 mol, 10 equiv.) in CCl_4 (7 mL) was added dropwise to 4,4′-*tert*-butylbiphenyl (5.0 g, 18.8 mmol, 1 equiv.) and Fe powder (70 mg) in CCl_4 (17 mL) in an ice bath. After 6 h at 0°C–ambient temperature, $Na_2S_2O_{3aq}$ was added. Extraction with chloroform (3×70 mL), drying over $MgSO_4$, and concentration in vacuo, gave white solid (16.0 g). After several recrystallizations from toluene, the pure product **5** as white crystals (2.52 g, 23%) was obtained. Mp 258–260°C. ^{13}C{^{1}H}DEPT(135°)NMR (125 MHz, $CDCl_3$): 149.6 (q), 139.4 (q), 137.4, 132.0, 122.4 (q), 120.9 (q), 36.7 (q), 29.5. LR/HR EIMS, *m*/*z* (ion type, % RA for *m*/*z* = 100–600, deviation for the formula): 690.20908 ($(M+6)^+$, 63%, 0.3 ppm for $^{12}C_{20}{}^1H_{22}{}^{79}Br_1{}^{81}Br_3$), 581.8421 ($(M+4)^+$, 93%, 0.8 ppm for $^{12}C_{20}{}^1H_{22}{}^{79}Br_2{}^{81}Br_2$), 579.8433 ($(M+2)^+$, 64%, −0.5 ppm for $^{12}C_{20}{}^1H_{22}{}^{79}Br_3{}^{81}Br_1$), 577.8451 ($M^+$, 16%, −0.7 ppm for $^{12}C_{20}{}^1H_{22}{}^{79}Br_4$); 566.8182 ($(M+4-CH_3)^+$, 100%), 562.8221 ($(M-CH_3)^+$, 17%). IR ($cm^{-1}$): 3001.7, 2987.7, 2970.6, 2949.2, 2868.0 (CH).

t-BuLi (1.48 M in pentane, 0.27 mL, 0.40 mmol, 4 equiv.) was

added to **5** (58.2 mg, 0.100 mmol, 1 equiv.) in THF (3 mL) at −78°C. After 2 h, the reaction mixture containing fine white precipitate was quenched with either MeOH or MeOD (0.1 mL). Aqueous workup gave 44–47 mg of pale yellow solids. MeOH quench: ^{1}H NMR (300 MHz, $CDCl_3$): 7.650 (d, J = 2 Hz, 2H), 7.367 (dd, J_1 = 8, J_2 = 2 Hz, 2H), 7.168 (d, J = 8 Hz, 2H), 1.357 (s, 18H). GC MS (CI): *m*/*z*, 424 ($(M+2)^+$). MeOD quench: 7.652 (s, 2H), 7.170 (s, 2H), 1.359 (s, 18H). GC MS (CI): *m*/*z*, 426 ($(M+2)^+$).

4.1.4. 2,2′-Dibromo-5,5′-bis(4-biphenylyl)-4,4′-di-*tert*-butylbiphenyl (6). The reaction was setup in a heavy-wall Schlenk vessel equipped with an 8-mm PTFE vacuum stopcock (Chemglass). *t*-BuLi (1.83 M in pentane, 9.4 mL, 16.2 mmol, 4.0 equiv.) was added to a solution of 2,2′,5,5′-tetrabromo-4,4′-di-*tert*-butylbiphenyl (2.50 g, 4.30 mmol, 1 equiv.) in THF (110 mL) at −78°C. A large amount of a white precipitate was formed. After the reaction mixture was stirred for 2 h at −78°C, $ZnCl_2$ (1.464 g, 10.7 mmol, 2.5 equiv.) was added under nitrogen gas stream. After 10–30 min at −78°C, the reaction mixture was allowed to attain ambient temperature. The resultant solution (pale yellow to pale red colors) was transferred to an argon-filled glovebox. Following the addition of 4-iodobiphenyl (3.01 g, 10.7 mmol, 2.5 equiv.) and $Pd(Ph_3P)_4$ (0.298 g, 0.258 mmol, 0.06 equiv.), the reaction mixture was kept at 100°C for 12–24 h. Subsequently, when the ambient temperature was attained, the reaction mixture was quenched with water. Chloroform was added (150 mL), and then the organic layer was washed with water (3×120 mL) and dried over $MgSO_4$. Concentration in vacuo afforded crude product (3.921 g). Purification by column chromatography (silica, hexane/benzene from 3:1 to 1:1) gave 2.343 g of white solid, of which 2.083 g was crystallized from chloroform/hexane (1:3, v/v) to give 1.901 g (68%) of **6** as white crystals. Mp 293–295°C. Anal. calcd for $C_{44}H_{40}Br_2$: C, 72.53; H, 5.53. Found: C, 70.66; H, 5.58. ^{1}H NMR (500 MHz, $CDCl_3$): 7.761 (s, 2H), 7.637 (d, J = 7 Hz, 4H), 7.558 (bd, J = 7 Hz, 4H), 7.452 (t, J = 8 Hz, 4H), 7.354 (t, J = 7 Hz, 2H), ~7.32 (br, 4H), 6.989 (s, 2H), 1.240 (s, 18H). ^{13}C{^{1}H}DEPT(135°)NMR (125 MHz, $CDCl_3$): 149.4 (q), 142.8 (q), 140.75 (q), 140.69 (q), 139.7 (q), 137.9 (q), 135.2, 130.8, 130.5 (br), 128.8, 127.3, 127.0, 125.9 (br), 122.2 (q), 36.5 (q), 32.4. LR/HR EIMS, *m*/*z* (ion type, % RA for *m*/*z* = 100–750, deviation for the formula): 730.1461 ($(M+4)^+$, 55%, −0.7 ppm for $^{12}C_{44}{}^1H_{40}{}^{81}Br_2$), 728.1472 ($(M+2)^+$, 100%, 0.6 ppm for $^{12}C_{44}{}^1H_{40}{}^{81}Br_1{}^{79}Br_1$), 726.1479 ($M^+$, 50%, 2.5 ppm for $^{12}C_{44}{}^1H_{40}{}^{79}Br_2$). IR ($cm^{-1}$): 3037.0, 2954.9, 2870.2 (CH).

4.1.5. 2,2′-Dibromo-5,5′-diphenyl-4,4′-di-*tert*-butyl-biphenyl (7). The procedure similar to that described above, using 2,2′,5,5′-tetrabromo-4,4′-di-*tert*-butylbiphenyl (1.50 g, 2.58 mmol, 1 equiv.) and iodobenzene (1.31 g, 0.72 mL, 6.44 mmol, 2.5 equiv.), afforded 1.77 g of crude product. Filtration through a silica plug (hexane) and crystallization from chloroform/methanol (5:2, v/v) afforded 1.144 g (77%) of white powder. Mp 251–252°C (after formation of needle crystals at ~230°C). Anal. calcd for $C_{32}H_{32}Br_2$: C, 66.68; H, 5.60. Found: C, 66.64; H, 5.62. ^{1}H NMR (500 MHz, $CDCl_3$): 7.733 (s, 2H), ~7.30 (br, 8H), ~7.23 (br, 2H), 6.934 (s, 2H), 1.193 (s,18H). ^{13}C{^{1}H}DEPT(135°)NMR (125 MHz, $CDCl_3$): 149.2 (q), 143.8 (q), 141.0 (q), 137.8 (q), 135.1, 130.7, 130.0 (br), 127.3 (br), 126.8, 122.2 (q), 36.5 (q), 32.3. LR/HR EIMS, *m*/*z* (ion type, % RA for *m*/*z* = 100–580, deviation for the formula): 578.0848 ($(M+4)^+$, 53%, 2.7 ppm for $^{12}C_{32}{}^1H_{32}{}^{81}Br_2$), 576.0873 ($(M+2)^+$, 100%, 3.7 ppm for $^{12}C_{32}{}^1H_{32}{}^{81}Br_1{}^{79}Br_1$), 574.0873 ($M^+$, 49%, 0.3 ppm for $^{12}C_{32}{}^1H_{32}{}^{79}Br_2$). IR ($cm^{-1}$): 3060.0, 2962.8, 2953.0, 2867.4 (CH).

4.1.6. 2,2′-Dibromo-5,5′-bis(4-methoxyphenyl)-4,4′-di-*tert*-butylbiphenyl (8). The procedure similar to that described above, using 2,2′,5,5′-tetrabromo-4,4′-di-*tert*-butylbiphenyl (1.50 g, 2.58 mmol, 1 equiv.) and 4-iodoanisole (1.508 g, 6.44 mmol, 2.5 equiv.), afforded 1.97 g of crude product. Filtration through a silica plug (hexane/chloroform, 2:1, v/v) and crystallization from chloroform/methanol (5:1, v/v) afforded 1.24 g (76%) of white powder. Mp 266–268°C (after formation of needle crystals at 255–257°C). ^{1}H NMR (500 MHz, $CDCl_3$): 7.720 (s, 2H), ~7.15 (br, 4H), 6.928 (s, 2H), 6.850 (bd, $J \approx 8$ Hz, 4H), 3.832 (s, 6H), 1.202 (s, 18H). ^{13}C{^{1}H}DEPT(135°)NMR (125 MHz, $CDCl_3$): 158.5 (q), 149.5 (q), 140.7 (q), 137.8 (q), 135.9 (q), 135.6, 131.0 (br), 130.6, 122.0 (q), 112.6 (br), 55.2, 36.4 (q), 32.3. LR/HR EIMS, *m*/*z* (ion type, % RA for *m*/*z* = 100–640, deviation for the formula): 636.1063 ($(M+2)^+$, 100%, 0.0 ppm for $^{12}C_{34}{}^1H_{36}O_2{}^{81}Br_1{}^{79}Br_1$), 634.1068 ($M^+$, 48%, −2.2 ppm for $^{12}C_{34}{}^1H_{36}O_2{}^{79}Br_2$). IR ($cm^{-1}$): 3000.0, 2955.5, 2833.6 (CH).

4.1.7. General procedures: 2,7,10,16-tetra-*tert*-butyl-3,6,11,15-tetrakis(4-biphenylyl)tetra-*o*-phenylene (9). *Procedure A*. *t*-BuLi (1.43 M in pentane, 0.26 mL, 0.37 mmol, 4.1 equiv.) was added dropwise to a suspension of **6** (65.0 mg, 0.0892 mmol, 1 equiv.) in ether (8 mL) at −78°C. After 2 h at −78°C, (−)-sparteine (42 mg, 0.18 mmol, 2 equiv.) was added. After 20 min at −78°C, the reaction mixture was kept at −20°C for 30 min. Subsequently, the pale yellow solution (with a negligible amount of white precipitate) was slowly recooled to −78°C, and then $CuBr_2$ (125 mg, 0.536 mmol, 6 equiv.) was added. After 2 h at −78°C, the reaction mixture was allowed to warm to ambient temperature overnight. The resultant purple solution with some yellow precipitate was quenched with water. After washing the organic layer with HCl_{aq} (15%, 4×20 mL), $NaHCO_{3aq}$ (sat., 2×20 mL), and water (2×20 mL), the colorless solution was dried over $MgSO_4$. Filtration and concentration in vacuo gave the crude product as a pale yellow solid (52.9 mg). ^{1}H NMR analysis revealed a mixture of **9** and **12** (8:1), with 55% ee for **9**. For the analogous three reactions, each starting from 130 mg of **6**, 49, 51, and 59% ee were obtained; the **9**:**12** ratios were 3:1, 5:1, and 3:1, respectively. After NMR analyses, all four crude mixtures were combined (311 mg). Purification by flash chromatography (silica, hexane/chloroform, from 5/1 to 4/1) yielded **9** (248 mg, 81, 64% ee).

Rapid crystallization **9** (248 mg, 64% ee) from chloroform/methanol (4/1) gave white crystals (138 mg, 74% ee). Recrystallization from chloroform/hexane gave the crystals (39 mg, 24% ee) and solid from mother liquor (94.4 mg, 31%, 95+% ee). $[\alpha]_D^{rt}$ = +168 (c = 0.015, chloroform). Mp (under argon) for enantiomer of **9** is not well defined: 270°C (crystalline), 281°C (glass/wax), 341–344°C (clear).

Another reaction starting from 246 mg of **6** yielded 261 mg of **9** and **12** (7:1). Purification by flash chromatography (chloroform/hexane, 1/4) gave two fractions, F1 (less polar), **12**, 27.1 mg (14%) and F2 (more polar), **9**, 136 mg (71, 57% ee). Crystallization of F1 from chloroform/methanol (4/1) yielded white crystals of **12** (11.2 mg, 6%). Several recrystallizations of 125 mg of F2 yielded white solid of **9** (45.2 mg, 23%, 95+% ee) with $[\alpha]_D^{rt} = +171$ (c = 0.015, chloroform) and identical melting behavior, as the sample described in the preceding paragraph.

Procedure B. *t*-BuLi (1.74 M in pentane, 0.97 mL, 1.69 mmol, 4.1 equiv.) was added dropwise to a suspension of **6** (300 mg, 0.411 mmol, 1 equiv.) in ether (40 mL) at −78°C. After 2 h at −78°C, the reaction mixture was kept at −20°C for 15 min. After the resultant yellow solution was recooled to −78°C, $CuBr_2$ (552 mg, 2.47 mmol, 6 equiv.) was added. After 2 h at −78°C, the reaction mixture was allowed to warm to ambient temperature overnight, yielding a purple mixture. The usual aqueous workup, including extraction with chloroform (150 mL), gave the crude product as a pale yellow solid (273 mg). ^{1}H NMR analysis revealed a mixture of **9** and **12** (3:1). Purification by flash chromatography (silica, hexane/benzene, from 6:1 to pure benzene) yielded **9** (105 mg, 45%) and **12** (22.6 mg, 10%). Recrystallizations of **9** and **12** from chloroform/methanol (2:1 — 3:1) gave white solids: 93.5 mg, 40% and 18.4 mg, 8%. Mp (under argon) for rac-**9** is not well defined: 250°C (cubic crystal), 265°C (waxy), 315°C (clear).

Procedure C. *t*-BuLi (1.50 M in pentane, 0.49 mL, 0.735 mmol, 4.1 equiv.) was added dropwise to a suspension of **6** (130 mg, 0.178 mmol, 1 equiv.) in ether (16 mL) at −78°C. After 1.5 h at −78°C, the reaction mixture was kept at −25–(−30) °C for 30 min. After the resultant yellow solution was recooled to −78°C (no precipitate), (−)-sparteine (84 mg, 0.36 mmol, 2 equiv.) in ether (2 mL) was added. After 2 h at −78°C, $CuBr_2$ (250 mg, 1.08 mmol, 6 equiv.) was added. After 2 h at −78°C, the reaction mixture was allowed to warm to ambient temperature overnight, yielding a purple solution with yellow precipitate. The usual aqueous workup, including extraction with chloroform (40 mL), gave the crude product (104 mg). ^{1}H NMR analysis revealed a mixture of **9** and **12** (7:1), with 35% ee for **9**.

Procedure D. This procedure is analogous to the Procedure A, except ether is replaced with THF as a solvent. For three reactions, each starting with 130, 130, and 65 mg of **6**, the following results were obtained: **9**:**12**, 1:3—4:1 and 8–9% ee for **9**.

Procedure E. This procedure is analogous to the Procedure B, except ether is replaced with THF as a solvent. Starting with 130 mg of **6**, mixture of **9** and **12** (pale yellow oil, 144 mg, ≈1:20) was obtained. Purification by flash chromatography (silica, chloroform/hexane, 1:6) yielded **12** (60.9 mg); recrystallization from chloroform/methanol (3:2, v/v) gave 52.2 mg of **12** (52%, mp 263–264°C). Another reaction on the identical scale yielded a similar mixture of **9** and **12** (~1:20); after column chromatography and recrystallization, 40.3 mg (40%) of **12** was obtained.

4.1.8. Tetra-*o*-phenylene 9. Calcd for $C_{88}H_{80}$: C, 92.91; H, 7.09. Found: C, 92.43; H, 7.48. ^{1}H NMR (500 MHz, $CDCl_3$, COSY cross-peak): 7.657 (d, J = 7 Hz, 8H, 7.449), 7.568 (bd, J = 8 Hz, 8H, 7.4), 7.449 (t, J = 8 Hz, 8H, 7.657, 7.345), 7.4 (bs, 8H, 7.568), 7.388 (s, 4H, 6.970), 7.345 (t, J = 7 Hz, 4H, 7.449), 6.971 (s, 4H, 7.388), 1.263 (s, 36 H); 328 K: 7.653 (d, J = 7 Hz, 8H), 7.566 (d, J = 8 Hz, 8H), 7.441 (t, J = 8 Hz, 8H), 7.396 (s, 4H), 7.391 (bd, J ≈ 7 Hz, 8H), 7.338 (t, J = 7 Hz, 4H), 6.970 (s, 4H), 1.272 (s, 36H). ^{13}C{^{1}H}DEPT(135°)NMR (125 MHz, $CDCl_3$): 146.6 (q), 144.1 (q), 140.88 (q), 140.85 (q), 140.4 (q), 139.2 (q), 137.8 (q), 134.1, 130.6, 129.1, 128.7, 127.2, 127.0, 125.8, 36.4 (q), 32.9. LR EIMS, m/z (ion type, % RA for m/z = 100–1250): 1136.5 (M^+, 100%), 1137.5 ($(M+1)^+$, 95%), 1138.5 ($(M+2)^+$, 45%), 1139.5 ($(M+3)^+$, 15%), 568 (<5%); calcd: 1136.626 (100%), 1137.629 (99%), 1138.633 (49%), 1139.636 (16%). LR/HR FABMS, m/z (ion type, % RA for m/z = 200–1500, deviation for the formula): 1137.6262 ($(M+1)^+$, 98%, 2.7 ppm for $^{12}C_{87}{}^{13}C_1{}^1H_{80}$), 1136.6229 ($M^+$, 100%, 2.7 ppm for $^{12}C_{88}{}^1H_{80}$), 568 (not observed). IR (cm^{-1}): 3026.8, 2958.7, 2904.5, 2868.8 (CH).

4.1.9. Biphenylene 12. ^{1}H NMR (500 MHz, $CDCl_3$): 7.647 (d, J = 7 Hz, 4H), 7.562 (d, J = 8 Hz, 4H) 7.448 (t, J = 8 Hz, 4H), 7.345 (t, J = 7 Hz, 2H), 7.296 (d, J = 8 Hz, 4H), 6.972 (s, 2H), 6.301 (s, 2H), 1.161 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 149.8, 147.6, 146.9, 144.7, 140.80, 140.65, 139.2, 130.2, 128.8, 127.2, 127.0, 126.1, 121.7, 116.6, 37.1, 32.9. LR/HR EIMS, m/z (ion type, % RA for m/z = 100–1250, deviation for the formula): 569.3157 ($(M+1)^+$, 56%, 1.1 ppm for $^{12}C_{43}{}^{13}C_1{}^1H_{40}$), 568.3120 ($M^+$, 100%, 1.8 ppm for $^{12}C_{44}{}^1H_{40}$), 1136 (not observed up to 300°C on the probe). IR (cm^{-1}): 3028.7, 2962.7, 2867.4 (CH).

4.1.10. 2,7,10,16-Tetra-*tert*-butyl-3,6,11,15-tetraphenyltetra-*o*-pheny1ene (10) and 2,7-di-*tert*-butyl-3,6-diphenylbiphenylene (13). *Procedure A*. Starting from 40 and 400 mg of **7**, crude mixtures of **10** and **13** (6:1 and 10:1), with 50% ee for **10**, were obtained. Purification of the crude mixture from the 400-mg scale reaction (328 mg) by flash chromatography (benzene/hexane, 1/5) gave two fractions, F1 (less polar) and F2 (more polar).

F1: **13**, 31.3 mg. Preparative TLC (silica, chloroform/hexane, 1/6) and crystallization (chloroform/methanol, 1/1) yielded 7.5 mg (3%) of pure **13**. Mp 215–216°C.

F2: **10**, 249 mg, 86%, 54% ee, $[\alpha]_D^{rt} = +70$ (c = 0.003, chloroform), mp 401–404°C.

Procedure B. Starting from 400 mg of **7**, crude mixture of rac-**10** and **13** (423 mg, 5:1) was obtained. Purification by flash chromatography (benzene/hexane, 1/5) gave two fractions, F1 (less polar) and F2 (more polar).

F1: **13**, 33.5 mg (12%). Crystallization (chloroform/methanol, 3:1, v/v) yielded 12.6 mg (4%) of pure **13**.

F2: rac-**10**, 217 mg (75%). Crystallization (benzene/chloroform/methanol, 1:1:1, v/v) yielded 158.4 mg (55%) of rac-**10**. Mp (under argon) 442–443°C.

4.1.11. Tetra-*o*-pheny1ene 10. Anal. calcd for $C_{64}H_{64}$: C, 92.26; H, 7.74. Found: C, 91.96; H, 7.46. ^{1}H NMR (500 MHz, $CDCl_3$): 7.341 (s, 4H), 7.30 (bm, 20 H), 6.893 (s, 4H), 1.206 (s, 36H). $^{13}C\{^1H\}$DEPT(135°)NMR (125 MHz, $CDCl_3$): 146.4 (q), 145.0 (q), 140.8 (q), 140.7 (q), 137.8 (q), 134.0, 130.2 (br), 129.0, 127.1, 126.4, 36.4 (q), 32.8. LR/HR EIMS, *m*/*z* (ion type, % RA for *m*/*z* = 100–870, deviation for the formula): 833.5037 ($(M+1)^+$, 70%, 0.5 ppm for $^{12}C_{63}{}^{13}C_1{}^1H_{64}$), 832.5003 ($M^+$, 100%, 0.7 ppm for $^{12}C_{64}{}^1H_{64}$). IR (cm^{-1}): 2953.6, 2868.4 (CH).

4.1.12. Biphenylene 13. ^{1}H NMR (500 MHz, $CDCl_3$): 7.33–7.20 (m, 10H), 6.942 (s, 2H), 6.246 (s, 2H), 1.114 (s, 18H). $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$): 149.7, 147.3, 146.8, 145.6, 141.0, 129.7, 127.4, 126.4, 121.7, 116.5, 37.0, 32.8. LR/HR EIMS, *m*/*z* (ion type, % RA for *m*/*z* = 100–900, deviation for the formula): 417.2541 ($(M+1)^+$, 34%, −0.9 ppm for $^{12}C_{31}{}^{13}C_1{}^1H_{32}$), 416.2505 ($M^+$, 100%, −0.3 ppm for $^{12}C_{32}{}^1H_{32}$), 832 (not observed up to 300°C on the probe). IR (cm^{-1}): 2955.5, 2867.2 (CH).

4.1.13. 2,7,10,16-Tetra-*tert*-butyl-3,6,11,15-tetrakis(4-methoxyphenyl)tetra-*o*-phenylene (11) and 2,7-di-*tert*-butyl-3,6-bis(4-methoxyphenyl)biphenylene (14). *Procedure A*. Starting from 56.6 and 400 mg of **8**, crude mixtures of **11** and **14** (11:1 and 15:1), with 50% ee for **11**, were obtained. Purification of the crude mixture from the 400-mg scale reaction (322 mg) by flash chromatography (chloroform/hexane, from 1/4 to 1:1) gave two fractions, F1 (less polar) and F2 (more polar).

F1: **14**, 25.8 mg. Crystallization (chloroform/methanol, 1/1) yielded 8.9 mg (3%) of pure **14** (^{1}H NMR).

F2: **11**, 242 mg, 81%, 56% ee, $[\alpha]_D^{rt} = +86$ (*c* = 0.004, chloroform), mp 395–402°C (purity by ^{1}H NMR).

Procedure B. Starting from 400 mg of **8**, crude mixture of rac-**11** and **14** (421 mg, 7:1) was obtained. Purification by flash chromatography (chloroform/hexane, from 1/2 to 1/1) gave two fractions, F1 (less polar) and F2 (more polar).

F1: **14**, 24.6 mg. Crystallization (chloroform/methanol, 1/1) yielded 19.5 mg (7%) of pure **14** (^{1}H NMR). Mp 218–219°C.

F2: rac-**11**, 217 mg, 47%. Crystallization (chloroform/methanol, 1/1) yielded 91.5 mg, 31%) of pure rac-**11** (^{1}H NMR). Mp (under argon) 393–394°C.

4.1.14. Tetra-*o*-phenylene 11. Anal. calcd for $C_{68}H_{72}O_4$: C, 85.67; H, 7.61. Found: C, 85.38; H, 7.62. ^{1}H NMR (500 MHz, $CDCl_3$): 7.326 (s, 4H), 7.213 (bd, $J \approx 6$ Hz, 8H), 6.892 (s, 4H), 6.851 (bd, $J \approx 8$ Hz, 8H), 3.832 (s, 12H), 1.216 (s, 36H); 328 K: 7.323 (s, 4H), 7.201 (bd, $J \approx 8$ Hz, 8H), 6.880 (s, 4H), 6.848 (d, J = 9 Hz, 8H), 3.835 (s, 12H), 1.218 (s, 36H). $^{13}C\{^1H\}$DEPT(135°)NMR (125 MHz, $CDCl_3$): 158.2 (q), 146.7 (q), 140.7 (q), 140.3 (q), 137.8 (q), 137.2 (q), 134.5, 131.1, 129.0, 112.5, 55.2, 36.3 (q), 32.8. LR EIMS, *m*/*z* (ion type, % RA for *m*/*z* = 100–1250): 952.5 (100), 953.5 (75) 953.5 ($(M+1)^+$, 75%), 952.5 (M^+, 100%), 476 (<4%). LR/HR FABMS, *m*/*z* (ion type, % RA for *m*/*z* = 200–1200, deviation for the formula): 953.5465 ($(M+1)^+$, 74%, −0.1 ppm for $^{12}C_{67}{}^{13}C_1{}^1H_{72}O_4$), 952.5414 ($M^+$, 100%, 1.7 ppm for $^{12}C_{68}{}^1H_{72}O_4$), 476 (not observed). IR (cm^{-1}): 2998.3, 2956.5, 2905.4, 2869.1, 2833.4 (CH).

4.1.15. Biphenylene 14. ^{1}H NMR (500 MHz, $CDCl_3$): 7.115 (d, J = 9 Hz, 4H), 6.919 (s, 2H), 6.849 (d, J = 9 Hz, 4H), 6.236 (s, 2H), 3.830 (s, 6H), 1.114 (s, 18H). $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$): 158.2, 149.7, 147.7, 146.8, 140.7, 137.9, 130.7, 122.1, 116.4, 112.8, 55.2, 37.0, 32.8. LR/HR EIMS, *m*/*z* (ion type, % RA for *m*/*z* = 100–1000, deviation for the formula): 477.2737 ($(M+1)^+$, 34%, 2.5 ppm for $^{12}C_{33}{}^{13}C_1{}^1H_{36}O_2$), 476.2704 ($M^+$, 100%, 2.4 ppm for $^{12}C_{34}{}^1H_{36}O_2$), 952 (not observed at 75°C, <2% at 100°C on the probe). IR (cm^{-1}): 2999.8, 2953.5, 2905.7, 2866.4, 2833.8 (CH).

4.1.16. 3,6,11,15-Tetrakis(4-biphenylyl)tetra-*o*-phenylene (4). Tetra-*o*-pheny1ene **9** (31 mg, 0.027 mmol, $[\alpha]_D^{rt} = +171$) and $AlCl_3$ (~20 mg) in dry benzene (2 mL) were stirred at 50°C for 3 h. Following the usual aqueous workup with chloroform (2×15 mL), the crude product was treated with charcoal in chloroform, and then recrystallized from chloroform/methanol (1:1, v/v) to yield 21.9 mg (88%) of white solid. Mp (under argon) 290°C (crystalline appearance), 350°C (wax), 362–364°C (clear). $[\alpha]_D^{rt} = +62$ (*c* = 0.006, chloroform).

Starting from rac-**9** (40 mg, 0.035 mmol), 18.8 mg (59%) of rac-**4** was obtained. Mp (under argon) 430–433°C. Anal. calcd for $C_{72}H_{48}$: C, 94.70; H, 5.30. Found: C, 94.40; H, 5.36.

^{1}H NMR (500 MHz, EM = −1.2, GB = 0.8, $CDCl_3$, COSY cross-peak): Ring A (1,2,4-Ph): 7.657 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 4H, 7.603, 7.384), 7.603 (d, J = 2 Hz, 4H, 7.657, 7.384), 7.384 (d, J = 8 Hz, 4H, 7.657, 7.603); Ring B (1,4-Ph): 7.718 (d, J = 8 Hz, 8H, 7.657), 7.657 (d, J = 8 Hz, 8H, 7.718); Ring C (Ph): 7.628 (d, J = 8 Hz, 8H, 7.442, 7.344), 7.442 (t, J = 8 Hz, 8H, 7.628, 7.344), 7.344 (t, J = 8 Hz, 4H, 7.628, 7.442). $^{13}C\{^1H\}$DEPT(135°)NMR (125 MHz, $CDCl_3$): 142.3 (q), 140.8 (q), 140.6 (q), 140.4 (q), 139.9 (q), 139.5 (q), 130.1, 128.9, 128.2, 127.63, 127.59, 127.49, 127.2, 126.2. LR/HR EIMS, *m*/*z* (ion type, % RA for *m*/*z* = 100–1000, deviation for the formula): 913.3789 ($(M+1)^+$, 79%, 0.1 ppm for $^{12}C_{71}{}^{13}C_1{}^1H_{48}$), 912.3761 ($M^+$, 100%, −0.6 ppm for $^{12}C_{72}{}^1H_{48}$), 456.2 (M^{2+}, 15%). IR (cm^{-1}): 3055.2, 3027.8 (CH).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 160101. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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