VOLUME 67, NUMBER 22

JOC Articles

NOVEMBER 1, 2002

© Copyright 2002 by the American Chemical Society

Well-Defined Enantiopure 1,1′-Binaphthyl-Based Oligomers: Synthesis, Structure, Photophysical Properties, and Chiral Sensing

Ling Ma, Peter S. White, and Wenbin Lin*

Department of Chemistry, CB#3290, University of North Carolina, Chapel Hill, North Carolina 27599

wlin@unc.edu

Received January 30, 2002

A series of well-defined enantiopure 1,1′-binaphthyl-based oligomers linked through their 6,6′-positions, ranging from quaternaphthol to decanaphthol, have been synthesized by Suzuki and Stille coupling reactions. These novel oligonaphthyls have been characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy and high-resolution mass spectrometry. A combination of X-ray structural and CD studies suggests that these oligonaphthyls adopt zigzag but not helical conformations. As the chain length increases, the compounds show enhanced fluorescence. The fluorescence intensity of oligonaphthols is almost 2 orders of magnitude higher than that of 1,1′-bi-2-naphthol and can be effectively and enantioselectively quenched with *trans*-1,2-diaminocyclohexane with an enantioselectivity factor of 1.24. The present work thus demonstrates the potential of constructing chiral sensory materials based on well-defined enantiopure oligonaphthols.

Introduction

There has been tremendous interest in well-defined conjugated oligomers because they serve as excellent models for the synthesis, properties, and characterization of their larger polymeric congeners.[1] The past decade has witnessed many creative synthetic strategies toward and important property studies of a variety of conjugated oligomeric materials. Among them, optically active oligonaphthyls and polybinaphthyls have been examined for second-order nonlinear optical and electroluminescent applications.[2,3] Polybinaphthyls have also been extensively applied in asymmetric catalysis and have shown good to excellent enantioselectivities for hetero-Diels–Alder reactions, organozinc addition to aldehydes, 1,3-dipolar cycloaddition, and reduction of ketones.[4] More recently, polybinaphthyls containing both BINOL and BINAP functionalities have been shown to be excellent asymmetric catalysts for tandem diethylzinc addition and hydrogenation of acetyl benzaldehydes to produce corresponding chiral diols.[5]

Pu et al. have recently reported interesting enantioselective fluorescence quenching of 1,1′-binaphthyl-derived dendrimers by chiral amino alcohols by virtue of greatly enhanced fluorescence efficiency of the dendritic species vs that of 1,1′-bi-2-naphthol (BINOL).[6] Fluorescence-based molecular sensors provide many advantages, including multiple modes of detection (such as quenching, enhancing, and lifetime), extremely high sensitivity, relatively low cost, and easy availability.[7] Numerous reports on chiral discrimination based on fluorescence techniques have appeared over the past decade, and a variety of chiral luminescent materials, including inorganic complexes, organic molecules, and enzymes have been used.[8] We envision that it may be advantageous to use well-defined enantiopure oligonaphthols as chiral

(1) (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537. (b) Müllen, K.; Wegner, G.; *Adv. Mater.* **1998**, *10*, 433. (c) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350.

(2) Pu, L. *Chem. Rev.* **1998**, *98*, 2405−2494.

(3) Zheng, L.; Urian, R. C.; Liu, Y.; Jen, A. K.-Y.; Pu, L. *Chem. Mater.* **2000**, *12*, 13−15.

(4) (a) Pu, L. *Chem Eur. J.* **1999**, *5*, 2227−2232. (b) Hu, Q.-S.; Huang, W.-S.; Vitharana, D.; Zheng, X.-F.; Pu, L. *J. Am. Chem. Soc.* **1997**, *119*, 12454−12464. (c) Huang, W.-S.; Hu, Q.-S.; Zheng, X.-F.; Anderson, J.; Pu, L. *J. Am. Chem. Soc.* **1997**, *119*, 4313−4314. (d) Hu, Q.-S.; Vitharana, D.; Zheng, X.-F.; Wu, C.; Kwan, C. M. S.; Pu, L. *J. Org. Chem.* **1996**, *61*, 8370−8377. (e) Fan, Q. H.; Liu, G. H.; Deng, G. J.; Chen, X. M.; Chan, A. S. C. *Tetrahedron Lett.* **2001**, *42*, 9047−9050.

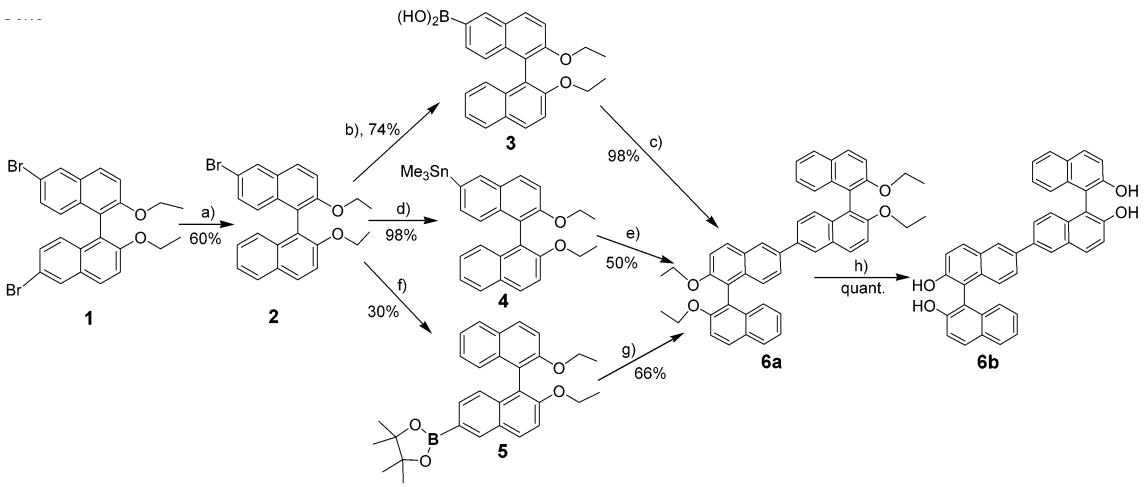
(5) Yu, H.-B.; Hu, Q.-S.; Pu, L. *J. Am. Chem. Soc.* **2000**, *122*, 6500−6501.

(6) (a) Yorozu, T.; Hayashi, K.; Irie, M. *J. Am. Chem. Soc.* **1981**, *103*, 5480−5484. (b) Avnir, D.; Wellner, E.; Ottolenghi, M. *J. Am. Chem. Soc.* **1989**, *111*, 2001−2003. (c) Gong, L.-Z.; Hu, Q.-S.; Pu, L. *J. Org. Chem.* **2001**, *66*, 2358−2367. (d) Pugh, V. J.; Hu, Q.-S.; Pu, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 3638−3641. (e) Pugh, V. J.; Hu, Q.-S.; Zuo, X.; Lewis, F. D.; Pu, L. *J. Org. Chem.* **2001**, *66*, 6136−6140.

(7) (a) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983. (b) D'Souza, F.; Deviprasad, G. R.; Hsieh, Y. Y. *Chem. Commun.* **1997**, *6*, 533−534. (c) Narita, M.; Mima, S.; Ogawa, N.; Hamada, F. *Anal. Sci.* **2001**, *17*, 379−385.

10.1021/jo0255680 CCC: $22.00 © 2002 American Chemical Society
Published on Web 04/02/2002

SCHEME 1. Synthesis of Quaternaphthyls[a]



[a] Reagents and conditions. (a) (i) 1 equiv BuLi, THF, −78 °C, 2 h; (ii) H_2O. (b) (i) BuLi, THF, −78 °C, 2 h; (ii) $B(OEt)_3$, rt, overnight; (iii) 2 N HCl. (c) **2**, $Pd(PPh_3)_4$, K_2CO_3, THF, reflux, 72 h. (d) (i) Na and Me_3SnCl, DME, 0 °C; (ii) cannulated (i) into **2**, DME, reflux, overnight. (e) **2**, $PdCl_2(PPh_3)_2$, LiCl, toluene, reflux, 65 h. (f) $PdCl_2$(dppf), dioxane, NEt_3 and pinacolborane, reflux, 36 h. (g) $Pd(PPh_3)_4$, K_2CO_3, toluene, reflux, 40 h. (h) BBr_3, from 0 °C to rt, overnight.

luminescence-based sensory materials because of enhanced fluorescence efficiency of oligonaphthols vs BINOL, the lowering of molecular symmetry, and possible cooperative effects of multiple chiral units. We are also interested in studying the correlation between X-ray structure and CD spectra of these well-defined enantiopure oligonaphthols. We report in this article the synthesis and characterization of a series of binaphthyl-based oligomers, from quaternaphthyls to decanaphthyls, and enantioselective fluorescence quenching of hexanaphthols by C2-symmetric chiral substrate *trans*-1,2-diaminocyclohexane.

Results and Discussion

1. Synthesis and Characterization of 1,1′-Binaphthyl-Based Oligomers. Biaryls and their oligoaryl and polyaryl homologues are of great current interest because of their applications in polymers, advanced materials, liquid crystals, and medicines.[9] Among numerous synthetic methods developed for oligoaryls, Stille[10] and Suzuki[11] coupling reactions are two of the most commonly used catalytic methods. We have thus used Stille and Suzuki coupling reactions to synthesize 1,1′-binaphthyl-based oligomers in this work.

The syntheses of 1,1′-binaphthyl-based oligomers started from enantiomerically pure 6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthyl, **1**. Scheme 1 outlines the synthesis of enantiopure quaternaphthyl **6**. First, lithium−halogen exchange of (*R*)-**1** with 1 equiv of *n*-BuLi followed by quenching with water afforded (*R*)-6-bromo-2,2′-diethoxy-1,1′-binaphthyl, **2**, in 60% yield. This method gives a much higher yield than the monobromination of binaphthyl (cf. 13%).[12] (*R*)-**2** underwent lithium−halogen exchange with *n*-BuLi, followed by reaction with $B(OEt)_3$ and hydrolysis with 2 N HCl to form (*R*)-2,2′-diethoxy-1,1′-binaphthyl-6-boronic acid, (*R*)-**3**, in 74% yield. Suzuki coupling of (*R*)-**2** and (*R*)-**3** in the presence of 1 M aqueous K_2CO_3 and $Pd(PPh_3)_4$ in THF yielded (*R*,*R*)-**6a** as a white solid in 98% yield. Alternatively, (*R*,*R*)-**6a** was synthesized via a Stille coupling reaction in 50% yield between (*R*)-**2** and (*R*)-6-trimethylstannyl-2,2′-diethoxy-1,1′-binaphthyl, (*R*)-**4**, in the presence of $PdCl_2(PPh_3)_2$ and LiCl in toluene. (*R*)-**4** was prepared from (*R*)-**2** in 98% yield by reacting with sodium trimethyltin in DME. (*S*,*S*)-**6a** was synthesized in 66% yield by Suzuki coupling of (*S*)-**2** and monoboronic ester (*S*)-**5**, which was obtained in 30% yield by treating (*S*)-6-bromo-2,2′diethoxy-1,1′-binaphthyl with pinacolborane in the presence of $PdCl_2$(dppf) and triethylamine in dioxane. Compound **6a** was readily deprotected with BBr_3 in dichloromethane to give the quaternaphthol product **6b**. All the intermediates and products **6a** and **6b** have been characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and HRMS.

Enantiopure hexanaphthyl **9a** was synthesized by a Stille coupling between **1** and **4** in THF in 36% yield (Scheme 2). An alternative Stille coupling between (*R*)-**2** and (*R*)-6, 6′-bis(trimethylstannyl)-2,2′-diethoxy-1,1′-binaphthyl, **7**, gave (*R*,*R*,*R*)-**9a** in 27% yield. Compound **7** was obtained in 89% yield by treating **1** with $NaSnMe_3$ in DME. Both (*R*,*R*,*R*)- and (*S*,*S*,*S*)-enantiomers of **9a** were synthesized in a much improved 83% yield from a Suzuki coupling between **2** and 2,2′-diethoxy-1,1′-binaphthyl-6,6′-diboronic acid, **8**, which was obtained in 50% yield via lithium−halide exchange of **1** with *n*-BuLi followed by reaction with triethylborate and hydrolysis with 2 N HCl. Hexanaphthol **9b** was prepared in quantitative yield by treating **9a** with BBr_3 in dichloromethane.

To synthesize octanaphthyls, it is necessary to have access to monobromo-quaternaphthyl **10**. We envisioned that it would not be viable to synthesize **10** via mono-

(8) (a) Irie, M.; Yorozu, T.; Hayashi, K. *J. Am. Chem. Soc.* **1978**, *100*, 2236−2237. (b) James, T. D.; Sandanayake, K. R. A. S.; Shinkai, S. *Nature* **1995**, *374*, 345−347. (c) Gafni, Ari. *J. Am. Chem. Soc.* **1980**, *102*, 7367−7368.

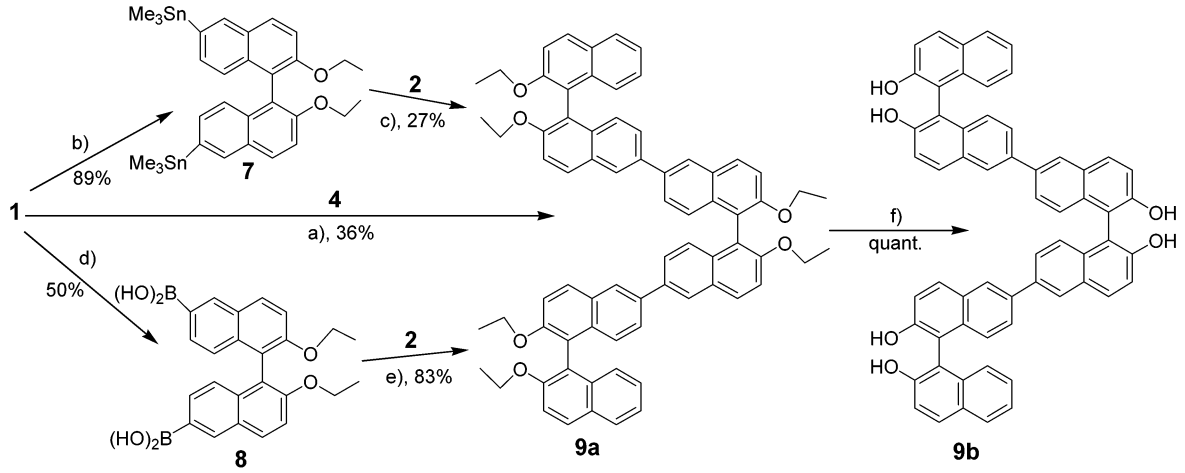
(9) Stanforth, S. P. *Tetrahedron*, **1998**, *54*, 263−303.

(10) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508−524.

(11) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483.

(12) Simonet, J.; Belloncle, C.; Fabre, B.; Cauliez, P. *Synth. Metals* **1998**, *93*, 115−122.

SCHEME 2. Synthesis of Hexanaphthyls[a]



[a] Reagents and conditions. (a) **4**, $PdCl_2(PPh_3)_2$, THF, reflux, 60 h. (b) (i) Na and Me_3SnCl, DME, 0 °C; (ii) cannulated (i) into **1**, DME, reflux, overnight. (c) **2**, $PdCl_2(PPh_3)_2$, THF, reflux, 84 h. (d) (i) BuLi, THF, −78 °C, 2 h; (ii) $B(OEt)_3$, rt, overnight; (iii) HCl. (e) **2**, $Pd(PPh_3)_4$, K_2CO_3, THF, reflux, 69 h. (f) BBr_3, from 0 °C to rt.

bromination of quaternaphthyls due to potential difficulty in controlling the regioselectivity of the reaction and subsequent separation of the products. Instead, a Suzuki coupling of **3** with excess amounts of **1** afforded **10** in 64% yield along with **9a** in 16% yield. With **10** in hand, we were able to prepare trimethylstannyl-substituted quaternaphthyl **11** in 44% yield, which was used for Stille coupling with **10** to give **15a** in 13% yield. The monoboronic acid intermediate **12** was also synthesized in 40% yield, and subsequent Suzuki coupling with **10** gave **15a** in 8% yield. Beginning with **10**, the overall yields of **15a** are only 5.7 and 3.2% for the above Stille and Suzuki couplings, respectively. We have also attempted the synthesis of **15a** by Negishi coupling using monoiodo-substituted quaternaphthyl **13**. Compound **13** was quantitatively prepared from **10** via lithiation with *n*-BuLi followed by iodination with I_2. Lithium−halogen exchange of **10** followed by transmetalation with $ZnCl_2$ afforded an organozincate that was coupled with **13** in the presence of $Pd(PPh_3)_4$ in THF to afford **15a** in 10%. Finally, we were able to obtain **15a** in 32% yield by a Suzuki coupling between **13** and monoboronic ester intermediate **14**, which was synthesized in 53% yield via a Pd-catalyzed coupling reaction between monoiodo-substituted quaternaphthyl **13** and pinacolborane. This approach gives an overall yield of 16%, the highest yield among all four methods we have tried. The octa(hydroxyl) product **15b** was also prepared in quantitative yield by treating **15a** with BBr_3 in dichloromethane.

We have failed to synthesize decanaphthyl via Suzuki coupling reactions between either **8** and **10** or **8** and **13**, presumably as a result of the insolubility of the monoboronic acid intermediate. To overcome such a solubility problem, we have converted **8** into (*R*)-2,2′-diethoxy-1,1′-binaphthyl-6,6′-bis-1,3,2-dioxaborane, **16**, in 98% yield by refluxing **8** with 1,3-propanediol in toluene. Suzuki coupling of **13** and **16** in the presence of $Pd(PPh_3)_4$ and K_2CO_3 in toluene gave the desired ethoxy-protected decanaphthyl, which is insoluble in common solvents such as diethyl ether, ethyl acetate, acetone, acetonitrile, and methanol and only sparingly soluble in chloroform and methlyene chloride. The insolubility of ethoxy-protected decanaphthyl has hindered its purification. Fortunately, we have noticed that the oligonaphthols are generally more soluble than their ethoxy-protected oligonaphthyls. With this in mind, the crude product from the above reaction was deprotected with BBr_3 in CH_2Cl_2 to give pure **17** in 24% overall yield after silica gel chromatography.

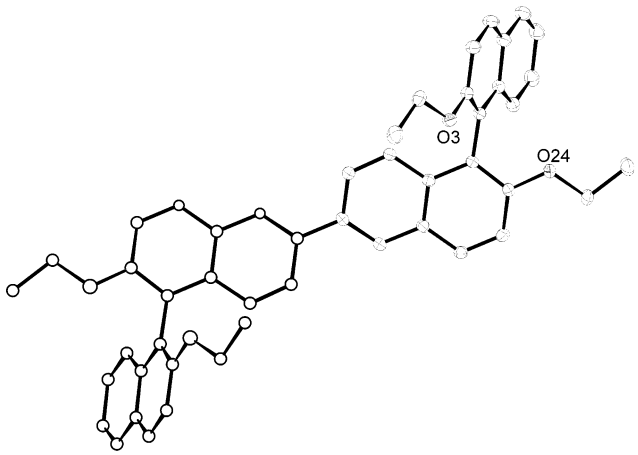


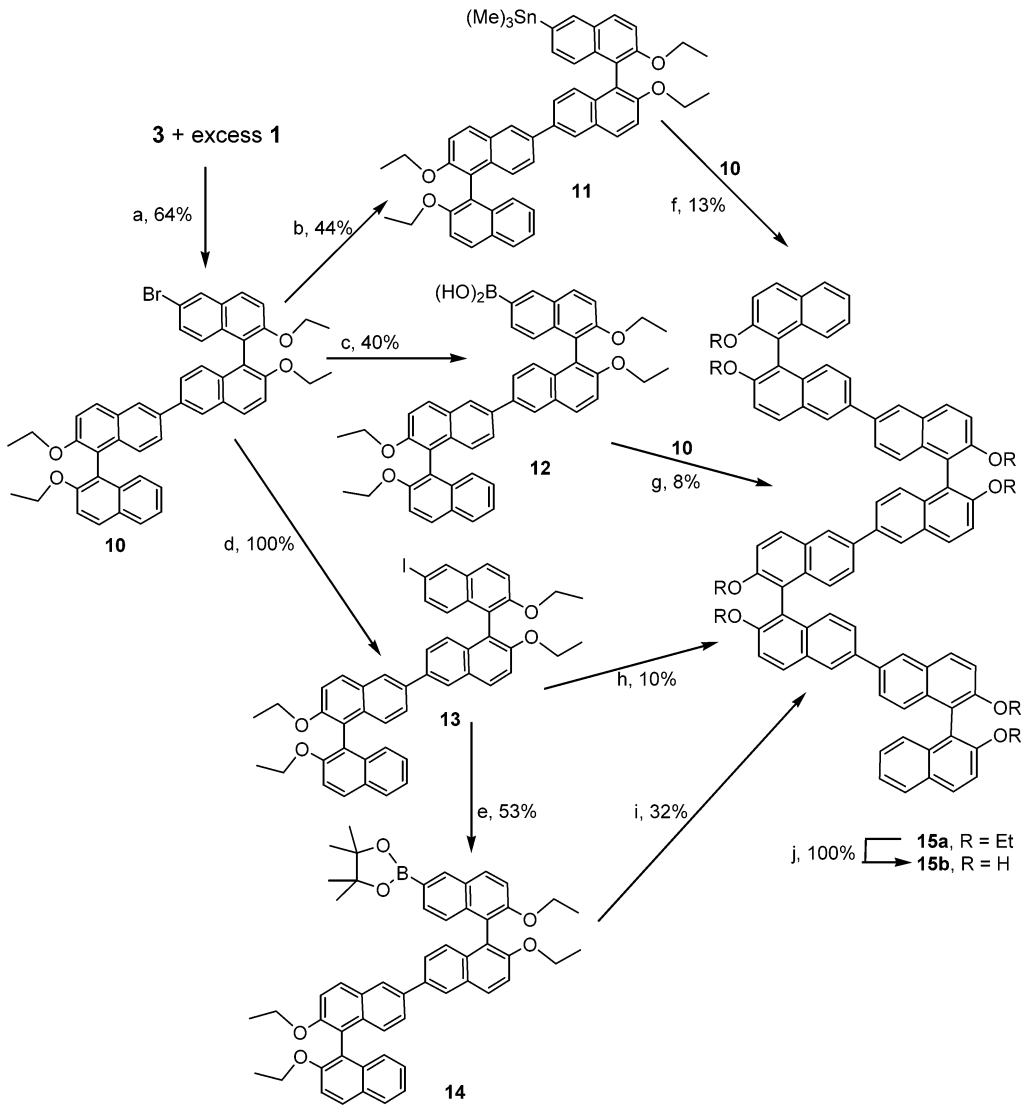
FIGURE 1. X-ray single-crystal structure of (*R*,*R*)-**6a**. The asymmetric unit is shown by ellipsoids at 30% probability.

2. X-ray Structure of Tetranaphthyl 6a. We attempted to grow single crystals of these 1,1-binaphthyl-based oligomers but have only obtained diffraction-quality single crystals of (*R*,*R*)-**6a**. Compound (*R*,*R*)-**6a** crystallizes in the chiral space group *I*2 with half of the molecule in the asymmetric unit (Figure 1).[14] The two 1,1′-binaphthyl units in (*R*,*R*)-**6a** are related by a 2-fold axis. The dihedral angle between the 1- and 1′-naphthyl rings is 115.6°, while the dihedral angle between the 6- and 6′-naphthyl rings is 23.2°. All the bond angles and distances are normal.

(13) Miura, Y.; Yamano, E.; Miyazawa, A.; Tashiro, M. *J. Chem. Soc., Perkin Trans. 2* **1995**, 359−364.

(14) Crystal data for (*R*)-**6a**: monoclinic, space group *I*2, $a = 21.09(2)$ Å, $b = 7.441(3)$ Å, $c = 12.453(7)$ Å, $\beta = 112.160(1)°$, $U = 1809.6(16)$ Å^3, and $Z = 4$.

SCHEME 3. Synthesis of Octanaphthyls[a]



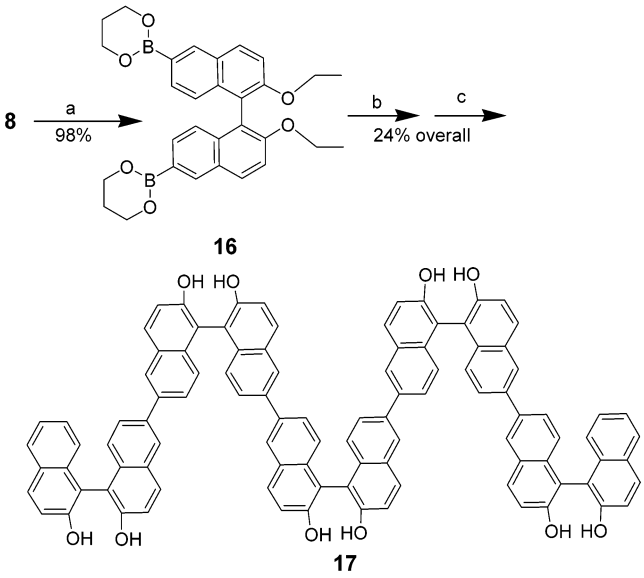
[a] Reagents and conditions. (a) $Pd(PPh_3)_4$, 1 M K_2CO_3, THF, reflux, 90 h. (b) (*i*) Na, Me_3SnCl, DME, 0 °C; (*ii*) cannulated (*i*) into **10**, DME, reflux, overnight. (c) (*i*) BuLi, THF, −78 °C, 3 h; (*ii*) $B(OEt)_3$, rt, overnight; (*iii*) HCl. (d) (*i*) BuLi, THF, −78 °C, 3 h, (*ii*) I_2, THF. (e) Pinacolborane, $PdCl_2$(dppf), NEt_3, dioxane, reflux, 30 h. (f) $PdCl_2(PPh_3)_2$, THF, reflux, 80 h. (g) $Pd(PPh_3)_4$, 1 M K_2CO_3, THF, reflux, 60 h. (h) (*i*) **10**, BuLi, THF, −78 °C, 1 h; (*ii*) $ZnCl_2$, THF, 20 min, warm to rt, 3 h; (*iii*) **13**, $Pd(PPh_3)_4$, THF, reflux, 60 h. (i) $Pd(PPh_3)_4$, 2 M K_2CO_3, toluene, reflux, 46 h. (j) BBr_3, CH_2Cl_2, from 0 °C to rt overnight.

3. Spectroscopic Studies of 1,1′-Binaphthyl-Based Oligomers. UV spectra of oligonaphthols are similar to that of 1,1′-binaphthol. Their molar extinction coefficients have increased drastically with the growth of the chain, especially for the longer wavelength absorptions, which increase by about 2 orders of magnitude (Table 1). Additionally, the oligonaphthols exhibit red-shifted and broadened bands probably as a result of excitonic coupling.

We have measured the optical rotation of these oligonaphthols in THF. As shown in Table 2, the specific optical rotation increases as the chain grows. The specific optical rotation of quaternaphthol is about three times that of 1,1′-binaphthol (+36 (c = 1, THF) for (*R*)-1,1′-binaphthol) but with a reversed sign. The specific optical rotations of hexanaphthol, octanaphthol, and decanaphthol are about 8, 10, and 14 times that of 1,1′-binaphthol, respectively. The molar optical rotation also increases steadily as the oligomer chain grows, which is in good agreement with the existence of multichiral groups.

The circular dichroism (CD) spectra of both enantiomers of the oligonaphthyls were measured in acetonitrile solution. In contrast to binaphthol, which shows only one bisignate band corresponding to the ^1B absorption band in its UV−vis spectrum, the oligonaphthyls exhibit two additional Cotton effects, whose intensities increase as the oligomer chain grows (Figure 2). The major bisignate band lies around 260 nm and corresponds to the ^1L_a transition, while the minor one lies around 330 nm and corresponds to the ^1L_b transition. The corresponding (*R*)- and (*S*)-enantiomers show exact mirror images in their CD spectra as shown in Figures 3−6, respectively. The remarkable similarity between the CD spectra of oligonaphthyls ranging from quaternaphthyl to decanaphthyl suggests that the chirality originates only from 1,1′-binaphthol and that these oligonaphthyls adopt zigzag

SCHEME 4. Synthesis of Decanaphthyls[a]



[a] Reagents and conditions. (a) Propane-1,3-diol, toluene, reflux. (b) **13**, $Pd(PPh_3)_4$, K_2CO_3, toluene, reflux, 50 h. (c) BBr_3, CH_2Cl_2, from 0 °C to rt, overnight.

TABLE 1. UV Spectral Data of Oligonaphthols

compound	concn (mol/L)	peaks (nm)	abs (AU)	ϵ (cm^2/mol) $\times 10^{-5}$
(*R*)-binaphthol	1.0×10^{-5}	230	0.65062	0.65
		290	0.026733	0.027
		334	0.061386	0.062
(*R*,*R*)-**6b**	7.0×10^{-6}	230	0.99237	1.4
		262	0.55214	0.79
		318	0.22894	0.33
(*R*,*R*,*R*)-**9b**	8.8×10^{-6}	230	1.20720	1.4
		266	1.02100	1.2
		314	0.49165	0.56
(*R*,*R*,*R*,*R*)-**15b**	8.8×10^{-6}	230	1.97620	2.25
		264	2.08330	2.37
		314	1.06800	1.21
(*R*,*R*,*R*,*R*,*R*)-**17**	5.0×10^{-6}	230	1.04270	2.09
		264	1.21450	2.43
		312	0.61555	1.23

TABLE 2. Optical Rotation Data of Chiral Binaphthyl-based Oligomers

compound	concn (g/100 mL)	$[\alpha]_D$ (°)	$[\phi]_D$ (°)
(*R*,*R*)-**6b**[a]	0.5	−94.1	−5370
(*R*,*R*,*R*)-**9b**	0.5	−291.8	−24947
(*S*,*S*,*S*,*S*)-**15b**	0.02	+356.5	+40614
(*R*,*R*,*R*,*R*,*R*)-**17**	0.01	−486.5	−69256

[a] (*S*,*S*)-**6b** at 0.1 g/100 mL gives $[\alpha]_D$ and $[\phi]_D$ of +99.7 and +5690, respectively.

(rather than helical) conformations in solution because of the lack of new chirality.

In contrast to 1,1′-binaphthol, the oligonaphthols emit strong blue light upon UV irradiation. Figure 7 shows the fluorescence spectra of 1,1′-binaphthol and its oligomers in acetonitrile at 5.0×10^{-7} M. When excited at 325 nm, the emission spectra of oligonaphthols are almost identical with two major peaks around 380 and 395 nm. At the same molar concentration, the fluorescence intensity increases steadily from quaternaphthol to octanaphthol but decreases when going from octanaphthol to decanaphthol. Quantum yields of oligonaphthols, on the other hand, decrease as the chain grows. Table 3 shows the relative intensity of the emission and the calculated quantum yields with 9,10-diphenylanthracene as the reference.

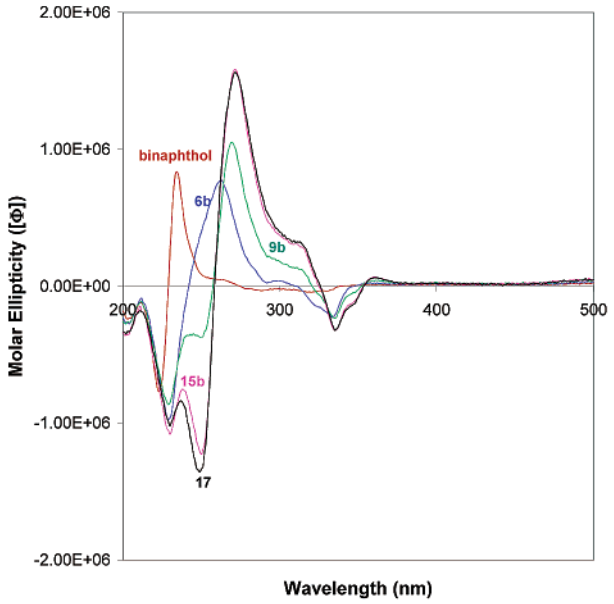


FIGURE 2. CD spectra of (*S*)-oligonaphthols.

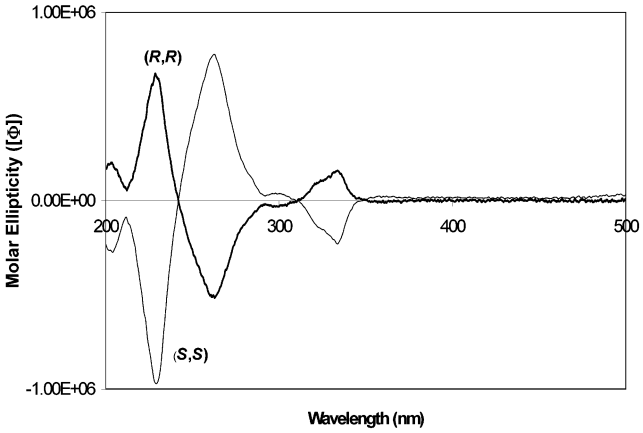


FIGURE 3. CD spectra of (*R*,*R*)- and (*S*,*S*)-**6b**.

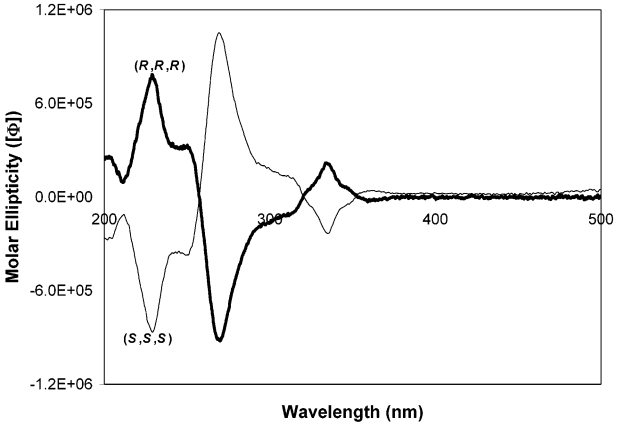


FIGURE 4. CD spectra of (*R*,*R*,*R*)- and (*S*,*S*,*S*)-**9b**.

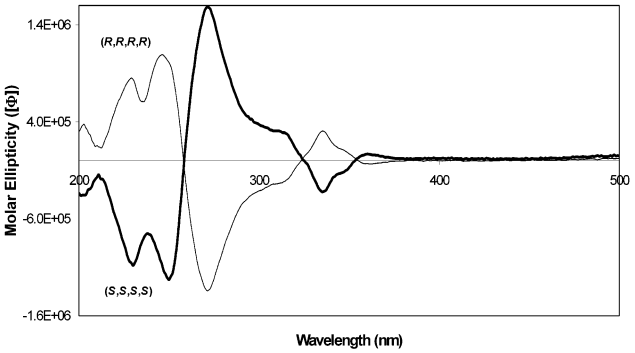


FIGURE 5. CD spectra of (*R*,*R*,*R*,*R*)- and (*S*,*S*,*S*,*S*)-**15b**.

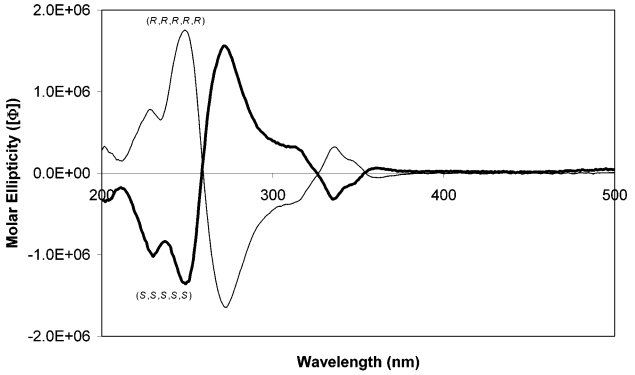


FIGURE 6. CD spectra of (*R*,*R*,*R*,*R*,*R*)- and (*S*,*S*,*S*,*S*,*S*)-**17**.

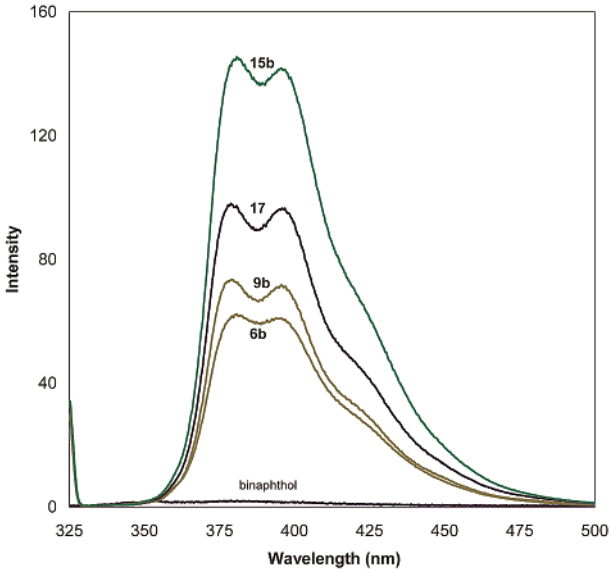


FIGURE 7. Fluorescence spectra of oligonaphthols.

4. Enantioselective Fluorescence Quenching of Chiral Amines. The greatly enhanced fluorescence intensity of enantiopure oligonaphthols prompts us to examine their potential utility as chiral fluorescence sensors. We have studied representative fluorescence quenching of hexanaphthol by 1,2-diaminocyclohexane in a mixed solvent of benzene and hexane (v/v: 20/80). Stern−Völmer plots of (*R*,*R*,*R*)- and (*S*,*S*,*S*)-**9b** in the presence of (*R*,*R*)- and (*S*,*S*)-1,2-diaminocyclohexane are shown in Figures 8 and 9, respectively. The Stern−Völmer constant for (*S*,*S*,*S*)-hexanaphthol at a concentration of 5.0 × 10^{-7} M is 10 446 M^{-1} (K^S_{sv}) in the presence of (*S*,*S*)-1,2-diaminocyclohexane and 12 611 M^{-1} (K^R_{sv}) in the presence of (*R*,*R*)-1,2-diaminocyclohexane. The enantioselectivity factor K^R_{sv}/K^S_{sv} is 1.21 for (*S*,*S*,*S*)-**9b**. The Stern−Völmer constant for (*R*,*R*,*R*)-hexanaphthol at a concentration of 5.0 × 10^{-7} M is 10 303 M^{-1} (K^R_{sv}) in the presence of (*R*,*R*)-1,2-diaminocyclohexane and 13 147 M^{-1} (K^S_{sv}) in the presence of (*S*,*S*)-1,2-diaminocyclohexane. The enantioselectivity factor K^S_{sv}/K^R_{sv} is 1.27 for (*R*,*R*,*R*)-**9b**. The opposite trend of quenching efficiency for the

TABLE 3. Fluorescence Intensities and Quantum Yields of Oligonaphthols

compound	fluorescence peaks (nm)	rel intensity	quantum yield
1,1′-binaphthol	383	1	0.1
6b	381	15	0.5
	394	15	
9b	379	44	0.34
	396	42	
15b	381	86	0.32
	396	83	
17	379	53	0.21
	396	51	

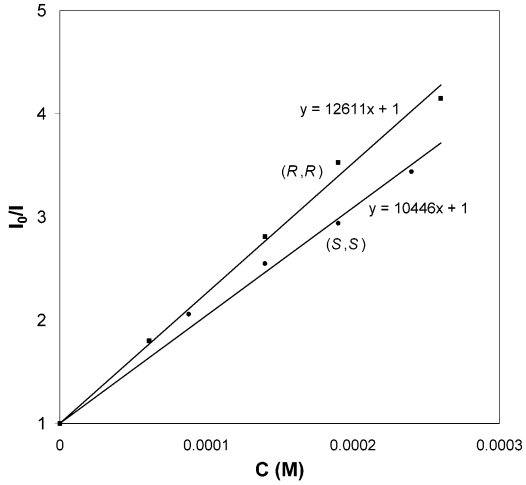


FIGURE 8. Stern−Völmer plot of (*S*,*S*,*S*)-hexanaphthol in the presence of (*R*,*R*)- and (*S*,*S*)-1,2-diaminocyclohexane.

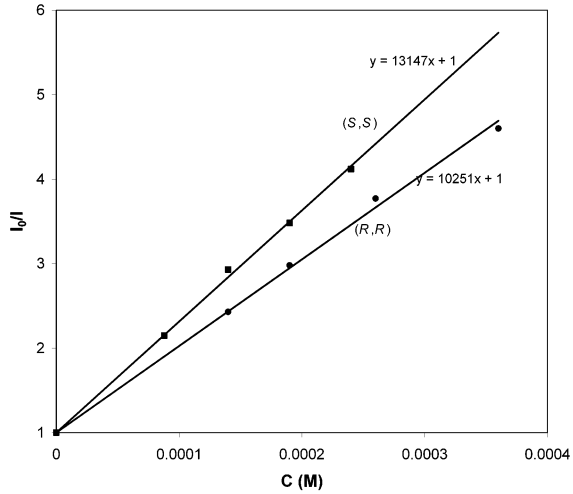


FIGURE 9. Stern−Völmer plot of (*R*,*R*,*R*)-hexanaphthol in the presence of (*R*,*R*)- and (*S*,*S*)-1,2-diaminocyclohexane.

opposite enantiomer of **9b** indicates that **9b** exhibits a chirality-based luminescence-quenching selectivity for 1,2-diaminocyclohexane guest molecules. This result is very interesting given the *C*2-symmetric nature of 1,2-diaminocyclohexane guest molecules. The level of enantioselectivity observed for **9b** also compares favorably with other BINOL-derived systems.[6]

Conclusion

A new series of well-defined enantiopure 1,1′-binaphthyl-based oligomers have been synthesized and characterized. These oligonaphthyls show significantly increased specific and molar optical rotations as the chain grows. Exciton coupling leads to a red-shifted, broadened band in the UV−visible spectra and red-shifted Cotton effects and increased molar ellipticities in their CD spectra. These results are consistent with the presence of multichiral groups and an enhancement of conjugation. Oligonaphthols exhibit significantly enhanced fluorescence intensity compared to that of 1,1′-binaphthol, but the quantum yield decreases from quaternaphthol to decanaphthol. Hexanaphthol exhibits interesting enantioselectivity for fluorescence quenching by chiral 1,2-diaminocyclohexane. This work thus suggests the potential for designing chiral fluorescence sensors based on well-defined, enantiopure oligonaphthols.

Experimental Section

General Procedures and Materials. All reactions were carried out under a nitrogen atmosphere. Solvents and reagents were reagent grade and used without further purifications unless otherwise stated. Solvents for spectroscopic measurements are spectroscopy or HPLC grade. THF was freshly distilled from sodium benzophenone ketyl, while CH_2Cl_2 was freshly distilled from CaH_2 under nitrogen; Et_3N was distilled from KOH and stored over KOH pellets under nitrogen.

(*R*)-6-Bromo-2,2′-diethoxy-1,1′-binaphthyl, (*R*)-2. To a THF (180 mL) solution of (*R*)-6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthyl (15.48 g, 30.94 mmol) at −78 °C was slowly added *n*-BuLi (22.5 mL, 1.6 M in hexanes, 36 mmol). After stirring at −78 °C for 2 h, the resulting greenish yellow solution was quenched with H_2O. Upon being evaporated to dryness, the residue was extracted with ethyl acetate, washed with brine, and then dried over $MgSO_4$. The crude product was purified by flash chromatography (hexane/toluene) on silica gel to yield pure (*R*)-**2** (7.7 g, 60%) as a white solid. $[\alpha]_D = 41.60$ (*c* 0.5, THF). ^{1}H NMR ($CDCl_3$): δ 8.03 (d, $^4J = 1.83$ Hz, H5), 7.96(d, $^3J = 9.16$ Hz, H5′), 7.86 (d, d, $^3J = 7.94$ Hz, $^3J = 9.16$ Hz, H4, H4′), 7.44 (d, d, $^3J = 8.55$ Hz, $^3J = 9.16$ Hz, H3, H3′), 7.34 (ddd, $^3J = 7.84$ Hz, $^3J = 7.74$ Hz, $^4J = 1.22$ Hz, H6′), 7.26 (m, H7, H7′), 7.12 (d, $^3J = 8.55$ Hz, H8′), 7.05 (d, $^3J = 9.16$ Hz, H8), 4.07(m, $-CH_2-$), 1.09(m, $-CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.82, 154.49, 134.22, 132.91, 130.50, 129.94, 129.59, 129.52, 129.42, 128.40, 128.11, 127.64, 126.44, 125.43, 123.73, 121.10, 120.04, 117.42, 116.91, 115.82, 65.36, 65.33, 15.21, 15.15. MS (EI) for $C_{24}H_{21}BrO_2$: calcd, 420.0725; found, 420.0724 (M^+).

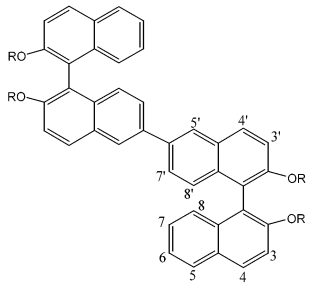
(*R*)-2,2′-Diethoxy-1,1′-binaphthyl-6-boronic Acid, (*R*)-3. To a THF (60 mL) solution of (*R*)-**2** (3.4 g, 8.1 mmol) at −78 °C was slowly added *n*-BuLi (10 mL, 1.6 M in hexanes, 16 mmol). After stirring at −78 °C for 2 h, the resulting greenish yellow solution was cannulated into a solution of $B(OEt)_3$ (9 mL) in THF (20 mL). The mixture was warmed to room temperature and stirred overnight. Excess 2 N HCl was then added at 0 °C. The mixture was extracted with ethyl acetate and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel (methylene chloride/methanol) to give pure (*R*)-**3** (2.3 g, 74%) as a white solid. $[\alpha]_D = 32$ (*c* 0.5, THF). ^{1}H NMR ($CDCl_3$): δ 8.80 (s, $-B(OH)_2$), 8.10 (d, $J = 9.16$ Hz, 1 H), 7.97(d, $^3J = 8.55$ Hz, 1 H), 7.96 (d, $^3J = 9.16$ Hz, 1 H), 7.88 (d, $^3J = 7.94$ Hz, 1 H), 7.45 (d, d, $^3J = 7.94$ Hz, $^3J = 9.16$ Hz, 2 H), 7.33 (ddd, $^3J = 6.72$ Hz, $^3J = 7.32$ Hz, $^4J = 1.2$ Hz, 1 H), 7.21 (m, 4 H), 4.07(m, $-CH_2-$), 1.07(m, $-CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.98, 154.57, 138.13, 136.92, 134.34, 131.13, 130.70, 129.49, 129.37, 128.83, 128.05, 126.31, 125.67, 125.24, 125.04, 123.66, 120.66, 120.61, 116.05, 115.63, 65.45, 65.18, 15.24, 15.17. MS (ESI) for $C_{24}H_{24}BO_4$: calcd, 387.25; found, 387.20 ($[M + H]^+$).

(*R*)-6-Trimethylstannyl-2,2′-diethoxy-1,1′-binaphthyl, (*R*)-4. To a DME (5.5 mL) suspension of sodium (0.7 g, 30 mmol) at 0 °C was added Me_3SnCl (0.72 g, 3.6 mmol). After stirring at 0 °C for 7 h, the mixture was centrifuged and the resulting greenish yellow clear solution was cannulated into a round-bottom flask charged with (*R*)-**2** (0.35 g, 0.83 mmol). The mixture was refluxed overnight. After being cooled to room temperature, the mixture was evaporated to dryness and the residue extracted with ethyl acetate. After being dried over $MgSO_4$ and concentrated under vacuum, the crude product was purified by flash chromatography on silica gel (hexane/ethyl acetate) to give pure (*R*)-**4** (414 mg, 98%) as a sticky solid. $[\alpha]_D = -163.9$ (*c* 0.6, THF). ^{1}H NMR ($CDCl_3$): δ 7.99 (s, H5), 7.95 (d, $^3J = 9.2$ Hz, H5′), 7.92 (d, $^3J = 9.2$ Hz, H4), 7.86 (d, $^3J = 8.5$ Hz, H4′), 7.42 (d, d, $^3J = 9.2$ Hz, $^3J = 8.5$ Hz 2H, H3, 3′), 7.31 (m, 2H, H6′, H7), 7.20 (ddd, $^3J = 8.5$ Hz, $^3J = 1.2$ Hz, H7′), 7.14 (d, $^3J = 8.5$ Hz, H8′), 7.11 (d, $^3J = 8.5$ Hz, H8), 4.10 (m, $-OCH_2$-), 1.13(m, $-CH_3$), 0.40(t, $J = 27.2$, Me_3Sn-). ^{13}C-{^{1}H} ($CDCl_3$): δ 154.76, 154.69, 136.64, 136.32, 134.58, 134.53, 133.02, 129.61, 129.57, 129.43, 129.25, 128.18, 126.42, 125.89, 125.10, 123.78, 120.98, 120.83, 116.20, 116.07, 65.50, 65.43, 15.40, 15.38, −9.10. MS (EI) for $C_{27}H_{30}O_2Sn$: calcd, 506.1268; found, 506.1267 (M^+).

(*S*)-6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolyl)-2,2′-diethoxy-1,1′-binaphthyl, (*S*)-5. To a solution of (*S*)-**2** (712 mg, 1.69 mmol) and $PdCl_2$(dppf) (50 mg, 0.06 mmol) in dioxane (8 mL) were added triethylamine (0.8 mL) and pinacolborane (0.5 mL, 3.5 mmol). The mixture was heated to reflux for 36 h and then evaporated to dryness under vacuum. The residue was extracted with EtAc, washed with brine, and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel (hexane/EtAc) to give pure (*S*)-**5** (230 mg, 30% yield) as white solid. ^{1}H NMR ($CDCl_3$): δ 8.40 (s, 1 H), 7.99 (d, $J = 8.55$ Hz, 1 H), 7.94 (d, $^3J = 9.16$ Hz, 1 H), 7.86 (d, $^3J = 7.94$ Hz, 1 H), 7.57 (d, $^3J = 8.55$ Hz, 1 H), 7.42 (d, $^3J = 9.16$ Hz, 1 H), 7.41 (d, $^3J = 9.16$ Hz, 1 H), 7.31 (ddd, $^3J = 8.55$ Hz, $^3J = 7.32$ Hz, $^4J = 1.22$ Hz, 1 H), 7.19 (ddd, $^3J = 8.55$ Hz, $^3J = 8.55$ Hz, $^4J = 1.22$ Hz, 1 H), 7.12 (d, $^3J = 8.55$ Hz, 2 H), 4.04 (m, 4 H, $-OCH_2-$), 1.37 (s, 12 H, $-BO_2C_2Me_4$), 1.05 (m, 6 H, $-CH_3$). ^{13}C{^{1}H} ($CDCl_3$): δ 155.54, 154.55, 136.64, 136.11, 134.38, 130.82, 130.24, 129.46, 129.28, 128.81, 127.98, 126.25, 125.69, 124.81, 123.63, 120.80, 120.58, 116.12, 115.68, 83.91 [C−($BO_2C_2Me_4$)], 65.42, 65.23, 25.13, 25.07, 15.22, 15.16. MS (EI) for $C_{30}H_{33}BO_4$: calcd, 468.2472; found, 468.2473 (M^+).

Tetranaphthyl, 6a. Method A. To a solution of (*R*)-**4** (118 mg, 0.233 mmol), $PdCl_2(Ph_3)_2$ (10 mg, 0.015 mmol), and LiCl (60 mg, 1.4 mmol) in toluene (8 mL) was added (*R*)-**2** (102 mg, 0.242 mmol). The mixture was refluxed under N_2 for 65 h, allowed to cool to room temperature, and concentrated to dryness under vacuum. The residue was extracted with $CHCl_3$ and washed with H_2O. The organic extract was dried with $MgSO_4$ and then evaporated to dryness. Purification of the crude product by flash chromatography on silica gel (ethyl acetate/hexane) yielded (*R*)-**6a** (80 mg, 50%) as a white solid. **Method B.** A mixture of (*R*)-**3** (490 mg, 1.27 mmol), (*R*)-**2** (696 mg, 1.65 mmol), and $Pd(PPh_3)_4$ (70 mg, 0.06 mmol) in THF (6 mL), and 1 M K_2CO_3 (5.5 mL) was heated to reflux for 72 h. The mixture was extracted with CH_2Cl_2, washed with brine, and dried over $MgSO_4$. The crude product was purified by flash

chromatography on silica gel to give pure (*R*)-**6a** (848 mg, 98%) as a white solid.



Method C. To a solution of (*S*)-**5** (197 mg, 0.42 mmol), (*S*)-**2** (196 mg, 0.46 mmol), and $Pd(PPh_3)_4$ (45 mg, 0.04 mmol) in toluene (4 mL) was added degassed 1 M K_2CO_3 (4 mL). The mixture was heated to reflux for 40 h and then evaporated to dryness under vacuum. The residue was extracted with EtAc, washed with brine, and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel to give pure (*S*)-**6a** (188 mg, 66% yield) as a white solid. $[\alpha]_D = -12.20$ for (*R*)-**6a** (*c* = 0.5, THF). ^{1}H NMR ($CDCl_3$): δ 8.11 (d, J = 1.8 Hz, 2H, H5), 7.97 (d, J = 9.02 Hz, 2H, H4), 7.92 (d, J = 9.02 Hz, 2H, H4′), 7.84 (d, J = 8.12 Hz, 2H, H5′), 7.50 (dd, J = 8.56 Hz, J = 1.80 Hz, 2H, H7), 7.41 (d, d, J = 9.017 Hz, J = 9.017 Hz, 4H, H3, H3′), 7.30 (ddd, 2H, H6′), 7.19 (m, 6H, H8, H8′, H7′), 4.08 (m, $-OCH_2-$), 1.05 (m, $-CH_3$). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 154.63, 156.57, 136.31, 134.42, 133.52, 129.79, 129.63, 129.49, 129.37, 128.07, 126.35, 126.31, 126.12, 125.89, 125.76, 123.70, 120.83, 120.78, 116.40, 116.10. MS (EI) for $C_{48}H_{42}O_4$: calcd, 682.3083; found, 682.3076 (M^+).

Quaternaphthol, 6b. To a stirred solution of **6a** (0.843 g, 1.23 mmol) in CH_2Cl_2 (30 mL) was added dropwise BBr_3 (7.0 mL, 74 mmol) at 0 °C. After being stirred at room temperature for 12 h, the mixture was poured into ice−water. The product was extracted with CH_2Cl_2, washed with brine, and dried over $MgSO_4$. Pure **6b** as an off-white solid was obtained upon evaporation of CH_2Cl_2 under vacuum (0.7 g, 100%). (*R*,*R*)-**6b**, $[\alpha]_D = -94.06$ (*c* 0.5, THF). (*S*,*S*)-**6b**, $[\alpha]_D = +99.70$ (*c* 0.1, THF). ^{1}H NMR ($CDCl_3$): δ 8.14 (d, ^4J = 1.37 Hz, 2 H), 8.01 (d ^3J = 9.16 Hz, 2 H), 7.97 (d, ^3J = 8.70 Hz, 2 H), 7.90 (d, ^3J = 7.79 Hz, 2 H), 7.642 (d, ^3J = 8.70 Hz, 2 H), 7.638 (d, ^3J = 8.70 Hz, 2 H), 7.36 (m, 6 H), 7.25 (d, ^3J = 8.70 Hz, 2 H), 7.20 (d, ^3J = 8.24 Hz, 2 H), 5.31 (s, OH), 5.29 (s, OH). ^{13}C NMR ($CDCl_3$): δ 153.07, 152.97, 136.67, 133.63, 132.83, 131.85, 131.68, 129.99, 129.67, 128.66, 127.78, 127.34, 126.62, 125.17, 124.42, 124.32, 118.52, 118.02, 111.17, 111.01. MS (EI) for $C_{40}H_{26}O_4$: calcd, 570.1831; found, 570.1831 (M^+).

***(R)*-6,6′-Bis(trimethylstannyl)-2,2′-diethoxy-1,1′-binaphthyl, (*R*)-7.** To a DME (16 mL) solution of sodium (1.2 g, 52 mmol) at 0 °C was added Me_3SnCl (3.0 g, 15 mmol). After stirring at 0 °C for 6.5 h, the resulting greenish yellow solution was centrifuged and cannulated into a round-bottom flask charged with (*R*)-**1** (840 mg, 1.68 mmol). The mixture was heated to reflux for 12 h, cooled to room temperature, and evaporated to dryness under vacuum. The residue was extracted with ethyl acetate and dried over $MgSO_4$. Upon being evaporated to dryness, the crude product was purified by flash chromatography on silica gel (hexane/EtAc) to give pure (*R*)-**7** (980 mg, 89%) as a white solid. $[\alpha]_D = -64.80$ (*c* 0.5, THF). ^{1}H NMR ($CDCl_3$): δ 8.06 (s, 2 H, H5), 7.98 (d, ^3J = 9.16 Hz, 2 H, H4), 7.47 (d, ^3J = 9.16 Hz, 2 H, H3), 7.37 (dd, ^3J = 8.55 Hz, ^4J = 1.22 Hz, 2 H, H7), 7.18 (d, ^3J = 8.55 Hz, 2 H, H8), 4.10 (q, $-OCH_2-$), 1.14 (t, $-CH_3$), 0.39 [t, $-Sn(CH_3)_3$]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.67, 136.55, 136.20, 134.45, 132.92, 129.46, 129.10, 124.99, 120.77, 116.06, 65.42, 15.34, −9.20. MS (EI) for $C_{30}H_{38}O_2Sn_2$: calcd, 666.0916; found, 666.0913 (M^+).

***(R)*-2,2′-Diethoxy-1,1′-binaphthyl-6,6′-diboronic Acid, (*R*)-8.** To a THF (125 mL) solution of (*R*)-**1** (6.7 g, 13.4 mmol) at −78 °C was slowly added *n*-BuLi (25 mL, 1.6 M in hexanes, 40 mmol). After stirring at −78 °C for 2 h, the resulting greenish yellow solution was cannulated into a solution of $B(OEt)_3$ (10.5 mL, 61.7 mmol) in THF (25 mL). The mixture was warmed to room temperature and then refluxed overnight. The reaction was quenched with excess amounts of 2 N HCl at 0 °C. Upon being evaporated to dryness, the residue was extracted with EtAc and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel (methylene chloride/methanol) to give the pure (*R*)-**8** (2.9 g, 50%) as a white solid. $[\alpha]_D = -39.5$ (*c* 0.1, MeOH). ^{1}H NMR (DMSO-d_6): δ 8.42 (s, 2 H), 8.10 [s, 4 H, $-B(OH)_2$], 8.05 (d, J = 9.16 Hz, 2 H), 7.59 (d, J = 9.16 Hz, 4 H), 6.87 (d, J = 8.55 Hz, 2 H), 4.11 (m, 4 H, $-OCH_2-$), 1.04 (t, 6 H, $-CH_3$). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 155.49, 136.34, 135.57, 131.77, 130.84, 129.79, 129.18, 124.38, 120.11, 116.21, 65.14, 15.80. MS (EI) for $C_{24}H_{25}B_2O_6$: calcd, 431.07; found, 431.20 ($[M + H]^+$).

***(R,R,R)*-Hexanaphthyl, (*R,R,R*)-9a. Method A.** To a solution of (*R*)-**4** (243 mg, 0.475 mmol) and $PdCl_2(PPh_3)_2$ (20 mg, 0.028 mmol) in THF (8 mL) was added (*R*)-**1** (116 mg, 0.23 mmol). The mixture was refluxed for 63 h. Upon being cooled to rt and evaporated to dryness, the residue was extracted with $CHCl_3$ and washed with H_2O. The organic extract was dried over $MgSO_4$ and then evaporated to dryness. Purification of the crude product by flash chromatography on silica gel (hexane/methylene chloride) yielded (*R*,*R*,*R*)-**9a** (86 mg, 36%) as a white solid. **Method B.** To a solution of (*R*)-**7** (108 mg, 0.16 mmol) and $PdCl_2(PPh_3)_2$ (10 mg, 0.014 mmol) in THF (5 mL) was added (*R*)-**2** (140 mg, 0.33 mmol). The mixture was refluxed for 84 h. Similar workup afforded (*R*,*R*,*R*)-**9a** in 27% yield (44 mg). **Method C.** A mixture of (*R*)-**8** (1.84 g, 4.28 mmol), (*R*)-**2** (3.62 g, 8.59 mmol), and $Pd(PPh_3)_4$ (500 mg, 0.433 mmol) in THF (26 mL) and 1 M K_2CO_3 (22 mL) was refluxed for 69 h. Similar workup gave (*R*,*R*,*R*)-**9a** in 83% yield (3.6 g). $[\alpha]_D = -160.7$ (*c* 0.5, THF). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.151 (d, J = 1.951 Hz, 2 H), 8.141 (d, J = 1.951 Hz, 2 H), 8.01 (d, J = 8.778 Hz, 2 H), 7.99 (d, J = 9.266 Hz, 2 H), 7.95 (d, J = 8.779 Hz, 2 H), 7.87 (d, J = 8.291 Hz, 2 H), 7.59 (m, 4 H), 7.46 (d, J = 9.266 Hz, 2 H), 7.44 (d, 8.779, 4 H), 7.323 (m, 4 H), 7.25 (m, 6 H), 4.07 (m, $-OCH_2-$), 1.08 (m, $-CH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.65, 154.62, 154.57, 136.33, 136.30, 134.40, 133.52, 129.79, 129.65, 129.61, 129.49, 129.34, 128.03, 126.33, 126.30, 126.15, 126.09, 125.87, 125.74, 123.67, 120.86, 120.80, 120.76, 116.42, 116.11, 65.47, 65.42, 15.25, 15.22. MS (FAB) for $C_{72}H_{62}O_6$ *m*/*z*: calcd, 1022.4546; found, 1022.4545 (M^+).

Hexanaphthol 9b. To a stirred solution of **9a** (1.51 g, 1.48 mmol) in CH_2Cl_2 (55 mL) was added dropwise BBr_3 (9.0 mL, 95 mmol) at 0 °C. After being stirred at room temperature overnight, the mixture was poured into ice−water. The product was extracted with CH_2Cl_2, washed with brine, and dried over $MgSO_4$. Evaporation of CH_2Cl_2 afforded pure **9b** as an off-white solid (1.26 g, 100%). $[\alpha]_D = -291$ (*c* 0.5, THF). ^{1}H NMR ($CDCl_3$): δ 8.15 (d, ^4J = 2.44 Hz, 2 H), 8.14 (d, ^4J = 2.44 Hz, 2 H), 8.02 (d ^3J = 9.16 Hz, 2 H), 8.01 (d, ^3J = 8.55 Hz, 2 H), 7.97 (d, ^3J = 8.55 Hz, 2 H), 7.90 (d, ^3J = 7.94 Hz, 2 H), 7.64 (m, 4 H), 7.39 (m, 6 H), 7.32, (m, 6 H), 7.24 (d, ^3J = 8.55 Hz, 2 H), 7.19 (d, ^3J = 8.94 Hz, 2 H), 5.13 (OH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 153.08, 152.96, 136.73, 136.64, 133.62, 132.81, 131.94, 131.86, 131.69, 130.01, 129.99, 129.68, 128.66, 127.78, 127.41, 127.32, 126.62, 125.16, 124.39, 124.31, 118.54, 118.51, 118.00, 111.15, 111.06, 110.98. MS (EI) for $C_{60}H_{38}O_6$ *m*/*z*: calcd, 854.2668; found, 854.2671 (M^+).

Monobromo-tetranaphthyl 10. A mixture of (*R*)-**3** (1.839 g, 4.76 mmol), (*R*)-**1** (5.0 g, 10 mmol), and $Pd(PPh_3)_4$ (700 mg, 0.6 mmol) in THF (50 mL) and 1 M K_2CO_3 (43 mL) was refluxed for 4 days. The mixture was extracted with $CHCl_3$, washed with brine, and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel (methylene chloride/hexane) to give pure (*R*,*R*)-**10** (2.35 g, 64% yield) as a white solid and **9a** (0.7 g, 16%) as a byproduct. $[\alpha]_D = -261.7$ (*c* 0.5, THF). ^{1}H NMR ($CDCl_3$): δ 8.133 (s, 1 H), 8.128 (s, 1 H), 8.01 (d, ^4J = 2.29 Hz, 1 H), 7.99 (d, ^3J = 9.16 Hz, 2 H), 7.95 (d,

^3J = 8.70 Hz, 1 H), 7.87 (d, ^3J = 6.87 Hz, 1 H), 7.85 (d, ^3J = 8.70 Hz, 1 H), 7.58 (m, 2 H), 7.44, (m, 4 H), 7.32 (m, 2 H), 7.21 (m, 3 H), 7.16 (d, ^3J = 8.70 Hz, 1 H), 7.06 (d, ^3J = 8.70 Hz, 1 H), 4.07 (m, $-OCH_2-$), 1.06 (m, $-CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.86, 154.66, 154.57, 136.42, 136.19, 134.40, 133.55, 133.33, 132.93, 130.53, 129.93, 129.84, 129.75, 129.56, 129.50, 129.33, 128.42, 128.01, 127.65, 126.31, 126.24, 125.99, 125.90, 125.87, 125.72, 123.66, 121.11, 120.85, 120.26, 117.46, 116.98, 116.47, 116.20, 116.14, 65.48, 65.43, 65.36, 15.23, 15.19, 15.15. MS (EI) for $C_{48}H_{41}BrO_4$ *m*/*z*: calcd, 760.2188; found, 760.2190 (M^+).

Trimethylstannyl-Substituted Tetranaphthyl 11. To a DME (10 mL) solution of sodium (0.8 g, 35 mmol) at 0 °C was added Me_3SnCl (0.9 g, 4.5 mmol) under nitrogen. After 5 h of stirring at this temperature, the resulting greenish yellow solution was cannulated into a round-bottom flask charged with monobromo-substituted tetranaphthyl (200 mg, 0.26 mmol). The mixture was heated to reflux and stirred overnight. After it had cooled to room temperature, the mixture was concentrated under vacuum. The mixture was then extracted with chloroform, and the organic layer was dried over $MgSO_4$. After filtration, the filtrate was concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (hexane/methylene chloride) to give the pure product (98 mg, 44%) as a white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.14 (s, 2 H), 8.01 (s, 1 H), 7.98 (d, ^3J = 7.23 Hz, 2 H), 7.94 (d, ^3J = 8.53 Hz, 2 H), 7.88 (d, ^3J = 7.73 Hz, 1 H), 7.58 (m, 2 H), 7.44 (m, 4 H), 7.33 (m, 2 H), 7.25 (m, 4 H), 7.16 (d, ^3J = 8.51 Hz, 1 H), 4.07 (m, $-OCH_2-$), 1.09 (m, $-CH_3$), 0.33 [t, $-Sn-(CH_3)_3$]. MS (EI) for $C_{51}H_{50}O_4Sn$: calcd, 844.2731; found, 844.2735 (M^+).

Tetranaphthyl-boronic Acid 12. To a solution of (*R*,*R*)-**10** (105 mg, 0.138 mmol) in 2.5 mL of THF at −78 °C was added dropwise *n*-BuLi (0.45 mL, 1.6 M in hexane, 0.72 mmol). After stirring for 3 h at this temperature in a dry ice/acetone bath, the resulting yellow solution was cannulated into a solution of $B(OEt)_3$ (0.6 mL, 4 mmol) in THF (3 mL). The mixture was warmed to room temperature and stirred overnight. Excess 2 N HCl was then added at 0 °C. Then, the mixture was extracted with methylene chloride, and the organic layer was dried over $MgSO_4$. After filtration, the filtrate was concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (methylene chloride) to give the title compound (42 mg, 42%) as a white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.80 (s, $-B(OH)_2$), 8.16 (s, 2 H), 8.10 (d, ^3J = 8.55 Hz, 1 H), 7.98 (m, 4 H), 7.88 (d, ^3J = 7.94 Hz, 1 H), 7.60 (m, 2 H), 7.46 (m, 5 H), 7.34 (m, 2 H), 7.24 (m, 4 H), 4.07 (m, $-CH_2-$), 1.09 (m, $-CH_3$).

Monoiodo-tetranaphthyl 13. To a solution of **10** (1.0 g, 1.3 mmol) in 30 mL THF at −78 °C was added dropwise *n*-BuLi (2.5 mL, 1.6 M in hexane, 4 mmol). After stirring at −78 °C for 3 h, a solution of I_2 (1.9 g, 7.5 mmol) in 12 mL of THF was added dropwise and the mixture was stirred for 2.5 h. Upon warming of the mixture to rt, the reaction was quenched with saturated aqueous sodium thiosulfate solution and the mixture stirred for 2 h at room temperature. The product was extracted with methylene chloride, washed with brine, and dried over $MgSO_4$. Compound **10** (1.06, 100%) was obtained after removing the solvent under vacuum. $[\alpha]_D$ = −279 (*c* 0.5, THF). ^1H NMR ($CDCl_3$): δ 8.25 (d, ^4J = 1.83 Hz, 1 H), 8.133 (s, 1 H), 8.130 (s, 1 H), 7.99 (d, ^3J = 8.54 Hz, 2 H), 7.95 (d, ^3J = 9.16 Hz, 1 H), 7.87 (d, ^3J = 7.94 Hz, 1 H), 7.82 (d, ^3J = 8.55 Hz, 1 H), 7.57 (m, 2 H), 7.44, (m, 4 H), 7.32 (m, 2 H), 7.21 (m, 3 H), 7.15 (d, ^3J = 8.55 Hz, 1 H), 6.92 (d, ^3J = 9.16 Hz, 1 H), 4.06 (m, $-OCH_2-$), 1.07 (m, $-CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.98, 154.66, 154.56, 136.66, 136.41, 136.19, 134.69, 134.40, 133.54, 133.33, 133.25, 131.13, 129.87, 129.78, 129.74, 129.62, 129.49, 129.36, 128.34, 128.05, 127.65, 126.34, 126.27, 126.05, 126.01, 125.93, 125.90, 125.74, 123.69, 120.96, 120.79, 119.91, 116.66, 116.42, 116.18, 116.10, 88.74, 65.47, 65.42, 65.35, 15.26, 15.23, 15.18. MS (EI) for $C_{48}H_{41}IO_4$ *m*/*z*: calcd, 808.2050; found, 808.2053 (M^+).

(*S*,*S*)-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolyl)-tetranaphthyl, (*S*,*S*)-14. To a solution of (*S*,*S*)-**13** (1.02 g, 1.26 mmol) and $PdCl_2$(dppf) (40 mg, 0.049 mmol) in dioxane (11 mL) was added NEt_3 (2 mL) and pinacolborane (0.4 mL, 2.7 mmol). The mixture was refluxed for 30 h and then concentrated under vacuum. The residue was extracted with ethyl acetate, washed with brine, and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel (hexane/EtAc) to give pure (*S*,*S*)-**14** (530 mg, 53% yield) as a pale yellow solid. $[\alpha]_D$ = 88.67 (*c* 0.1, THF). ^1H NMR ($CDCl_3$): δ 8.42 (s, 1 H), 8.14 (s, 2 H), 8.00 (m, 2 H), 7.95 (d, ^3J = 9.16 Hz, 1 H), 7.87 (d, ^3J = 7.94 Hz, 1 H), 7.58 (m, 3 H), 7.43, (m, 4 H), 7.32 (m, 2 H), 7.21 (m, 5 H), 4.06 (m, $-OCH_2-$), 1.37 (s, 12H), 1.07 (m, $-CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.57, 154.64, 154.61, 154.56, 136.67, 136.32, 136.30, 136.13, 134.40, 133.49, 130.89, 130.29, 129.78, 129.60, 129.49, 129.34, 128.83, 128.02, 126.32, 126.28, 126.09, 125.86, 125.74, 124.83, 123.67, 120.86, 120.79, 120.70, 120.54, 116.46, 116.11, 115.70, 83.91, 65.47, 65.42, 65.27, 25.14, 25.08, 15.22. MS (EI) for $C_{54}H_{53}BO_6$ *m*/*z*: calcd, 808.4; found, 808.5 (M^+).

Octanaphthyl, 15a. Method A. A mixture of (*R*,*R*)-**11** (98 mg, 0.116 mmol), $PdCl_2(PPh_3)_2$ (10 mg, 0.014 mmol), and (*R*,*R*)-**10** (95 mg, 0.125 mmol) in THF (5 mL) was refluxed for 72 h. After the mixture was cooled to room temperature and concentrated under vacuum, the residue was extracted with $CHCl_3$, washed with H_2O, and dried over $MgSO_4$. Purification of the crude product by flash chromatography on silica gel (hexane/methylene chloride) yielded (*R*,*R*,*R*,*R*)-**15a** (21 mg, 13%) as a white solid. **Method B.** To a mixture of (*R*,*R*)-**12** (40 mg, 0.055 mmol), $Pd(PPh_3)_4$ (10 mg, 0.01 mmol), and (*R*,*R*)-**10** (42.4 mg, 0.056 mmol) in THF (2.3 mL) was added 1 M K_2CO_3 (2 mL). The mixture was refluxed for 60 h. Similar workup afforded (*R*,*R*,*R*,*R*)-**15a** in 8% (6 mg) yield. **Method C.** To a stirred solution of **10** (73 mg, 0.096 mmol) in THF (1.5 mL) at −78 °C was added *n*-BuLi (0.1 mL, 1.6 M in hexane, 0.16 mmol). The resulting mixture was stirred for 1 h, and then a solution of $ZnCl_2$ in THF (0.5 M) was added. The reaction mixture was stirred for 20 min, slowly warmed to room temperature, and stirred at rt for 3 h. This solution was then cannulated into a solution of **13** (80 mg, 0.099 mmol) and 5 mol % $Pd(PPh_3)_4$ in THF (2 mL). The resulting mixture was refluxed for 60 h. Similar workup afforded **15a** in 10% (12 mg) yield. **Method D.** To a mixture of (*S*,*S*)-**14** (198 mg, 0.25 mmol), $Pd(PPh_3)_4$ (10 mg, 0.01 mmol), and (*S*,*S*)-**13** (220 mg, 0.27 mmol) in toluene (5.5 mL) was added 2 M K_2CO_3 (4.1 mL). The mixture was refluxed for 46 h. Similar workup afforded (*S*,*S*,*S*,*S*)-**15a** in 32% (109 mg) yield. **(*R*,*R*,*R*,*R*)-15a.** $[\alpha]_D$ = −1117 (*c* 0.1, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 8.14 (s, 6 H), 7.99 (m, 6 H), 7.94 (d, J = 9.16 Hz, 2 H), 7.86 (d, J = 7.94 Hz, 2 H), 7.58 (m, 6 H), 7.44 (m, 8 H), 7.31 (m, 2 H), 7.25 (m, 4 H), 7.19 (m, 6 H), 4.07 (m, $-OCH_2-$), 1.07 (m, $-CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.63, 154.60, 154.55, 136.32, 136.30, 134.39, 133.49, 129.78, 129.63, 129.58, 129.47, 129.32, 128.01, 126.31, 126.14, 126.08, 125.86, 125.74, 123.66, 120.83, 120.78, 120.76, 120.74, 116.42, 116.10, 65.46, 65.42, 15.25, 15.21. MS (FAB) for $C_{72}H_{62}O_6$ *m*/*z*: calcd, 1362.6010; found, 1362.6014 (M^+).

(*S*,*S*,*S*,*S*)-Octanaphthol, (*S*,*S*,*S*,*S*)-15b. To a solution of (*S*,*S*,*S*,*S*)-**15a** (15 mg, 0.01 mmol) in CH_2Cl_2 (16 mL) was slowly added BBr_3 (0.5 mL, 5 mmol) at 0 °C. After stirring at rt overnight, the mixture was poured into ice−water and the product was extracted with CH_2Cl_2, washed with brine, and dried over $MgSO_4$. The crude product was passed through a short column (hexane/EtAc) to afford pure (*S*,*S*,*S*,*S*)-**15b** (11 mg, 95%) as an off-white solid. $[\alpha]_D$ = +356 (*c* 0.02, THF). ^1H NMR ($CDCl_3$): δ 8.16 (s, 6 H), 8.04 (m, 6 H), 7.99 (d, J = 8.55 Hz, 2 H), 7.90 (d, J = 7.94 Hz, 2 H), 7.65 (m, 6 H), 7.41 (m, 8 H), 7.29 (m, 10 H), 7.20 (d, J = 8.55 Hz, 2 H), 5.13 (s, −OH), 5.09 (s, −OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.10, 152.98, 136.76, 136.73, 136.66, 133.59, 132.80, 131.99, 131.91, 131.74, 130.03, 129.69, 128.67, 127.79, 127.42, 127.34, 126.67, 126.64, 125.15, 124.38, 124.32, 118.54, 118.00, 111.08, 110.99, 110.91. MS (FAB) for $C_{80}H_{50}O_8$: calcd, 1138.3506; found, 1138.3505 (M^+).

(*R*)-2,2′-Diethoxy-1,1′-binaphthyl-6,6′-bis-1,3,2-dioxaborane, (*R*)-16. A mixture of (*R*)-**8** (626 mg, 1.46 mmol) and propane-1,3-diol (1.2 mL, 16.6 mmol) in dry toluene (16 mL) was heated to reflux overnight. After removing the solvent under vacuum, the resulting residue was extracted with diethyl ether, washed with water, and dried over $MgSO_4$. Evaporation of the solvent afforded pure (*R*)-**16** as a light yellow solid (732 mg, 98%). $[\alpha]_D = -12.0$ (*c* 0.1, THF). ^{1}H NMR ($CDCl_3$): δ 8.37 (s, 2 H), 7.99 (d, 2 H, $J = 9.16$ Hz), 7.57 (d, $J = 8.55$ Hz, 2 H), 7.41 (d, $J = 8.55$ Hz, 2 H), 7.13 (d, $J = 8.55$ Hz, 2 H), 4.17 (t, 8 H, $-BOCH_2-$), 4.04 (t, 4 H, $-OCH_2-$), 2.04 (m, 4 H, $-CH_2-$), 1.04 (t, 6 H, $-CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.23, 135.86, 135.14, 130.13, 128.93, 127.48 (br), 124.71, 120.63, 115.63, 65.30, 62.21, 27.72, 15.19. MS (EI) for $C_{40}H_{26}O_4$: calcd, 510.19; found, 510.30 (M^+).

(*R*,*R*,*R*,*R*,*R*)-Decanaphthol, (*R*,*R*,*R*,*R*,*R*)-17. A mixture of (*R*)-**16** (66 mg, 0.129 mmol), (*R*,*R*)-**13** (220 mg, 0.27 mmol), and $Pd(PPh_3)_4$ (20 mg, 0.017 mmol) in toluene (3.6 mL) and 2 M K_2CO_3 (3.4 mL) was heated to reflux for 50 h. Upon being evaporated to dryness, the residue was extracted with $CHCl_3$, washed with brine, and dried over $MgSO_4$. The crude product was directly treated with BBr_3 in CH_2Cl_2 at 0 °C. After being stirred at rt overnight, the mixture was poured into ice−water. The organic layer was extracted with CH_2Cl_2, washed with brine, and dried over $MgSO_4$. After filtration and evaporation, the residue was purified by flash chromatography on silica gel (methylene chloride/methanol) to give the pure (*R*,*R*,*R*,*R*,*R*)-**17** (45 mg, 24% yield) as an off-white solid. $[\alpha]_D = -486$ (*c* 0.01, THF). ^{1}H NMR (CD_3OD): δ 8.10 (s, 8 H), 7.88 (m, 8 H), 7.84 (d, $^3J = 9.16$ Hz, 2 H), 7.79 (d, $^3J = 7.94$ Hz, 2 H), 7.54 (m, 8 H), 7.26 (m, 8 H), 7.21 (m, 2 H), 7.12 (m, 8 H), 7.05 (m, 6 H), 4.87 (OH). $^{13}C\{^1H\}$ NMR (CD_3OD): δ 153.11, 153.08, 153.01, 135.52, 134.64, 133.72, 129.72, 129.74, 129.57, 129.39, 129.24, 127.82, 125.96, 125.51, 125.43, 125.34, 125.29, 124.64, 122.65, 118.46, 118.06, 114.94. MS (FAB) for $C_{72}H_{62}O_6$: calcd, 1422.4343; found, 1422.4343 (M^+).

Acknowledgment. We acknowledge NSF (CHE-9875544) for financial support. W.L. is an Alfred P. Sloan Fellow, an Arnold and Mabel Beckman Young Investigator, and a Cottrell Scholar of Research Corp. We thank Suk Joong Lee for generating the cover graphic.

Supporting Information Available: General experimental procedures and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JO0255680