Atropisomerism of the C-1−C′-1 Axis of 2,2′,8,8′-Unsubstituted 1,1′-Binaphthyl Derivatives

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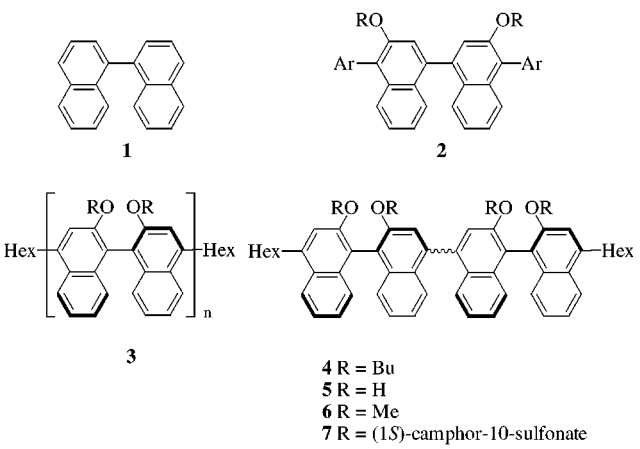
The Suzuki coupling of optically active (*S*)-binaphthyl bromide **10** with (*S*)-binaphthyl boronic acid **11** produced a diastereomeric mixture of tetrahydroxyquaternaphthyls **4**. The coupling products **4** as well as their derivatives **5**−**7** can be considered as members of the family of 1,1′-binaphthyl-3,3′-diols. The C-1−C′-1 axis of all these compounds was found to have an unusually high rotational barrier. Generally, the barrier is higher for derivatives having more bulky substituents at the 3 and 3′ positions.

Introduction

1,1′-Binaphthyl **1** and its derivatives bearing a C-1−C-1′ chiral axis are versatile auxiliaries and ligands for a wide range of asymmetric synthetic and catalytic reactions.[1] The high rotational barrier of the chiral axis is mainly due to the presence of substituents at the 2,2′ or 8,8′ positions on the binaphthyl nucleus.[2] In fact, 1,1′-binaphthyl derivatives without substituents at these locations are known to racemize at room temperature.[3] For example, 1,1′-binaphthyl has a half-life for racemization of 12 h at 20 °C.[3b] 1,1′-Binaphthyl-5,5′-dicarboxylic acid, which has a slightly more stable C-1−C-1′ axis, has a half-life for racemization of 4.5 h at 50 °C.[3a] Similarly, the half-lives for racemization of 1,1′-binaphthyl-4,4′-disubstituted compounds fall within a range of 2−50 h at room temperature.[3c] Herein, we report a high rotational barrier of the C-1−C-1′ axis in 4,4′-diaryl-1,1′-binaphthyl-3,3′-diol derivatives **2** at room temperature. The existence of a configurationally stable chiral axis in such compounds at room temperature may provide an opportunity for us to design new chiral, binaphthyl ligands based on structure **2**. As the ligating atoms are now located at the 3 and 3′ positions of the binaphthyl nucleus, such optically active, C_2 symmetrical 1,1′-binaphthyl-3,3′-diol derivatives **2**, when bound to a metal ion, will have a torsional angle that is different from that of the well-known 1,1′-binaphthyl-2,2′-diol (BINOL) or 1,1′-binaphthyl-2,2′-bis(diphenylphosphino) (BINAP) ligand.[4] It has previously been demonstrated that the torsional angle of binaphthyl-derived metal complexes has a strong influence on the reactivity and enantioselectivity in asymmetric reactions;[5] hence, ligands **2** having new geometrical attributes may have the potential to become a new class of chiral auxiliaries or catalysts in asymmetric synthesis.



1 **2** **3**

4 R = Bu
5 R = H
6 R = Me
7 R = (1*S*)-camphor-10-sulfonate

As part of our continuing program toward the construction of chiral rigid rodlike oligomers,[6] we are interested in preparing optically active 1,1′-binaphthyl-2,2′-diol oligomers **3** having the C-4 and C-4′ positions directly linked to each other. It is anticipated that a closer packing of the chiral binaphthyl units may impose some kind of macromolecular order along the oligomer main axis, which in turn may lead to an amplification of their chiroptical properties. As a result of this study, it was found that the dimeric species **4**−**7** of this series of oligomers existed as a mixture of diastereomers due to a restricted rotation of the carbon−carbon bond joining the two binaphthyl units. Structurally, these compounds may be considered as 4,4′-diaryl-1,1′-binaphthyl-3,3′-diol derivatives **2**. However, strictly speaking, they belong to the family of quaternaphthyls and are related to the series of octahydroxyquaternaphthyls[7] or hexahydroxy-

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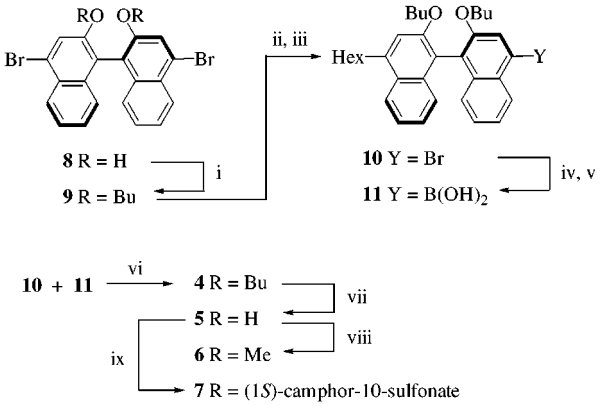
Scheme 1[a]



[a] Key: (i) Cs_2CO_3, *n*-C_4H_9I, acetone, 56 °C; (ii) 1-hexyne, $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, C_6H_6, 60 °C; (iii) H_2, PtO_2, EtOH/EtOAc; (iv) *n*-BuLi, THF, $B(OMe)_3$; (v) HCl; (vi) $Pd(PPh_3)_4$, aq Na_2CO_3, EtOH/toluene, 110 °C; (vii) BBr_3, CH_2Cl_2, 0 °C; (viii) Cs_2CO_3, MeI, acetone, 56 °C; (ix) (1*S*)-camphor-10-sulfonyl chloride, NEt_3, CH_2Cl_2, 0 °C.

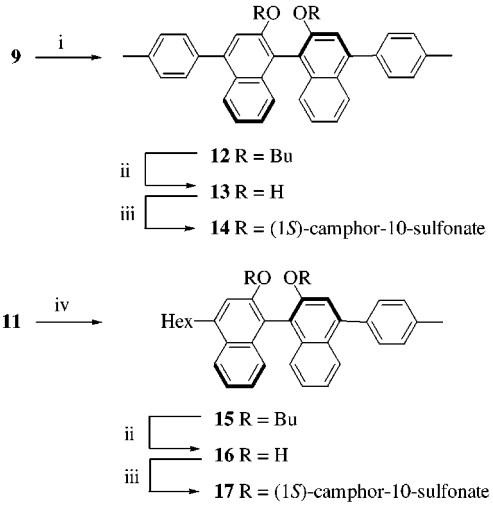
quaternaphthyls[8] reported by others. The latter compounds are known to exhibit multiple atropisomerism due to the chiral axes connecting the naphthyl subunits.

Results and Discussion

The Suzuki coupling reaction[9] was used to construct the dimeric binaphthyl derivatives **4**−**7**. Bis-O-butylation of (*S*)-4,4′-dibromo-1,1′-binaphthyl-2,2′-diol **8**[10] afforded the corresponding bis-*O*-butyl ether **9** in 89% yield (Scheme 1). An *n*-hexyl group was then installed to one end of the dibromide **9** via the Sonogashira coupling[11] with 1-hexyne, followed by saturation of the resulting carbon−carbon triple bond by catalytic hydrogenation to give a monobromide **10**. Metalation of the bromide **10** with *n*-butyllithium, followed by reaction of the intermediate organolithium derivative with trimethyl borate, then afforded the corresponding boronic acid **11**. This compound was not characterized but was immediately coupled to the monobromide **10** under the Suzuki conditions (2 M aqueous Na_2CO_3, $Pd(PPh_3)_4$, ethanol/toluene, 110 °C) to give an inseparable diastereomeric mixture (∼1:1) of the tetra-*O*-butyl ethers **4** in 90% yield. The mass spectrum of the mixture had a molecular ion peak at *m*/*z* 963 ($M + H^+$), which was consistent with the molecular formula of the dimeric structure. The formation of a diastereomeric mixture was suggested by ^1H and ^{13}C NMR spectroscopy. Hence, four sets of triplet signals, attributable to the methyl groups belonging to the *O*-butyl moieties, appeared at δ 0.62, 0.64, 0.69, and 0.70 in the ^1H NMR spectrum. Similarly, three ^{13}C NMR signals (δ 69.49, 69.62, and 69.73), instead of two, belonging to the methylene carbons adjacent to the oxygen atoms were also noted.

Treatment of the mixture of tetra-*O*-butyl ethers **4** with BBr_3 gave tetraphenols **5** as two separable products as revealed by thin-layer chromatography analysis. Although the two compounds could be separated by flash column chromatography (in less than 10 min) at 20 °C, the minor slower running component reappeared from a clean sample of the major faster running compound once the sample was allowed to stand at 20 °C (∼10 h). Likewise, the faster running component also appeared from a clean sample of the slower running fraction after prolonged standing at 20 °C. Hence, the two compounds are slowly interconverting and cannot be isolated in 100% purity. If the solvents of the two freshly separated samples were quickly evaporated under reduced pressure at 4 °C, one could obtain samples that were of reasonably good homogeneity for ^1H NMR spectral analysis. The two spectra (in $CDCl_3$) are nearly identical except that the faster running compound has a sharp aromatic singlet at δ 7.54. This signal, however, is presumably upfield shifted and merged with other aromatic signals for the slower running compound. The mass spectrum of the sample mixture gave the most abundant peak at *m*/*z* 738, which corresponded to the expected theoretical mass of the tetraphenol **5**. At this point, we suspected that the diastereomerism was due to a hindered rotation of the newly formed carbon−carbon bond joining the two chiral binaphthyl units. However, such an unusually high rotational barrier of the C-1−C′-1 bond at room temperature of binaphthyls without substituents at 2,2′,8,8′ positions was not anticipated. Therefore, it was necessary to confirm that the additional atropisomerism was not the result of a racemization of the original binaphthyl chiral axis in compounds **10** and **11** during their preparations.

Scheme 2[a]



[a] Key: (i) 4-tolylboronic acid, $Pd(PPh_3)_4$, aq Na_2CO_3, EtOH/toluene, 110 °C; (ii) BBr_3, CH_2Cl_2, 0 °C; (iii) (1*S*)-camphor-10-sulfonyl chloride, NEt_3, CH_2Cl_2, 0 °C; (vi) 4-bromotoluene, $Pd(PPh_3)_4$, aq Na_2CO_3, EtOH/toluene, 110 °C.

Using the enantiomerically pure (*S*)-aryl dibromide **9** as a model compound, the stereochemical integrity of the preexisting chiral axis during the various chemical transformations was assessed (Scheme 2). Hence, the dibromide **9** was coupled to 4-tolylboric acid [prepared from 4-bromotoluene via sequential treatment of *n*-BuLi, $B(OMe)_3$ and 1 M HCl] under the Suzuki conditions to give the ditolyl-substituted binaphthyl derivative **12** in 87% yield. Treatment of the bis-*O*-butyl ether **12** with BBr_3 in CH_2Cl_2 then provided the 4,4′-ditolyl binaphthyl-2,2′-diol **13** as a white solid in 80% yield. The stereo-

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chemistry of the C-1−C-1′ axis of compound **13** was then determined by an ^{1}H NMR method reported previously by us.[12] On the basis of our previous findings, the difference of the ^{1}H NMR chemical shift values of the two diastereotopic methylene protons adjacent to the sulfonyl moiety of the bis[(1*S*)-camphor-10-sulfonate] derived from an (*S*)-binaphthyl-2,2′-diol was known to be consistently smaller than 0.5 ppm, while that of the bis-sulfonate derived from an (*R*)-binaphthyl-2,2′-diol was larger than 1.0 ppm. This observation had also been independently confirmed by another group.[13] Hence, treatment of the diol **13** with (1*S*)-camphor-10-sulfonyl chloride and NEt_3 afforded the corresponding bis[(1*S*)-camphor-10-sulfonate] **14** in 77% yield. Examination of the ^{1}H NMR spectrum of the bis-sulfonate **14** showed the presence of only one AB system (δ 2.52, 2.95) due to the relevant methylene groups. As the chemical shift difference was less than 0.5 ppm, no racemization of the chiral axis had occurred in both the Suzuki coupling and BBr_3 deprotection reactions.

To show that the absolute configuration of the binaphthyl chiral axis also remained intact during the preparation of the aryl boronic acid **11** from the aryl bromide **10**, the absolute configuration of the boronic acid **11** was also determined. The boronic acid **11** was coupled to 4-bromotoluene under the Suzuki conditions to produce the unsymmetrical binaphthyl ether **15** in 92% yield. Deprotection (BBr_3, CH_2Cl_2) of the two butyl ether groups produced a 1,1′-binaphthyl-2,2′-diol **16**, which was similarly converted to the corresponding bis-[(1*S*)-camphor-10-sulfonate] **17**. The ^{1}H NMR spectrum of compound **17** exhibited two AB systems arising from the two different methylene groups adjacent to the sulfonyl moieties. Again, both the chemical shift differences were less than 0.5 ppm (correlation determined by ^{1}H−^{1}H 2D-COSY experiment); hence, there was no racemization of the binaphthyl chiral axis during the preparation of the boronic acid **11**. Therefore, it was concluded that the diastereomerism in the tetra-*O*-butyl ethers **4** must be due to the hindered rotation of the newly formed carbon−carbon axis.

As the fast interconversion between the two diastereomeric binaphthyl tetraphenols **5** at room temperature prevented us from conducting a thorough study of their individual spectroscopic and chiroptical properties, some configurationally stable derivatives of the tetraphenols **5** with more bulky substituents were prepared. Treatment of the diastereomeric tetraphenols **5** with excess methyl iodide in the presence of Cs_2CO_3 in acetone afforded a separable mixture of the diastereomeric tetra-*O*-methyl ethers **6** in 72% yield. The two compounds were configurationally stable at 20 °C for 24 h but were rapidly equilibrated in boiling toluene. The half-life for racemization of the newly formed axis was determined to be approximately 0.5 h at 56 °C in chloroform solution by ^{1}H NMR spectroscopic measurement. The ^{1}H NMR spectral data of the two diastereomers were slightly different from one another. Hence, for the faster running diastereomer, one of the aromatic singlets had a chemical shift value of δ 7.61, while that of the slower running diastereomer was downfield shifted to δ 7.64. Both compounds showed a positive first Cotton effect at around 240−245 nm and a negative second Cotton effect at 227−229 nm of comparable molar ellipticities in their circular dichroism (CD) spectra. This observation was consistent with the presence of the two (*S*)-configurated chiral axes in both diastereomers.[14] Unfortunately, no single crystals could be obtained for these compounds and hence the absolute configuration of the newly constructed chiral axis could not be ascertained due to the very similar nature of their CD spectra.

The tetraphenols **5** were also reacted with excess (1*S*)-camphor-10-sulfonyl chloride to give a mixture of diastereomeric tetrasulfonates **7** that could not be cleanly separated by column chromatography. However, enriched samples of the faster (∼90% purity) and slower (∼80% purity) running diastereomers could be obtained and they were shown to be configurationally stable at 20 °C. The ^{1}H NMR spectra of both diastereomers showed two AB systems arising from the diastereotopic methylene groups adjacent to the sulfonyl moiety. In both cases the chemical shift differences were less than 0.5 ppm, thus further confirming that no racemization occurred at the two original chiral axes. The specific rotations of the two compounds are slightly different from one another. Again we were unable to assign the absolute configuration of the newly formed carbon−carbon axis because of the poor crystallinity of the tetrasulfonates **7**.

In summary, we reported here an unexpected atropisomerism of the C-1−C′-1 axis of some 4,4′-diaryl-1,1′-binaphthyl-3,3′-diol derivatives. The configurational stability of the chiral axis was dependent on the steric size of the substituents at the 3 and 3′ positions. In general, compounds with more bulky substituents are configurationally more stable.

Experimental Section

General Methods. All reactions were conducted under a nitrogen atmosphere. Melting points were taken on a hot-plate microscope apparatus and were uncorrected. All physical measurements were performed at 20 °C unless otherwise stated. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in $CDCl_3$ unless otherwise stated. Mass spectra were obtained either by fast atom bombardment (FAB), liquid secondary ion mass spectrometry (L-SIMS) or electron ionization (EI) method. The reported molecular mass values (*m*/*z*), unless otherwise specified, were the most abundant monoisotopic mass. Optical rotations were measured at 589 nm. CD spectra were recorded in 1,2-dichloroethane as the solvent. Elemental analyses were carried out at MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge, U.K. All chemicals were purchased from commercial suppliers and used without further purification.

(*S*)-4,4′-Dibromo-2,2′-dibutoxy-1,1′-binaphthyl (9). A mixture of (*S*)-4,4′-dibromo-1,1′-binaphthyl-2,2′-diol **8**[10] (6.0 g, 13.5 mmol), *n*-butyl iodide (5.0 mL, 43.9 mmol), and cesium carbonate (10.0 g, 30.7 mmol) in dry acetone (50 mL) was stirred under reflux for 5 h. The mixture was filtered through a short pad of silica gel and washed with ethyl acetate (50 mL). The filtrate was concentrated on a rotary evaporator and the crude product chromatographed on silica gel (hexane/EtOAc = 50/1) to give the product **9** (6.7 g, 89%) as a white solid: mp 70−71 °C; R_f 0.74 (hexane/CH_2Cl_2 = 5/1); $[\alpha]^{25}_D$ = −79.7 (*c* = 1.24, $CHCl_3$); ^{1}H NMR 0.65 (t, *J* = 7.2 Hz, 6 H), 0.93−1.04 (m, 4 H), 1.34−1.44 (m, 4 H), 3.86−3.99 (m, 4 H), 7.12 (d, *J* = 8.4 Hz, 2 H), 7.22 (ddd, *J* = 0.9, 7.5, 7.7 Hz, 2 H), 7.39 (ddd, *J* = 1.2, 7.5, 7.7 Hz, 2 H), 7.72 (s, 2 H), 8.22 (d, *J* =

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8.4 Hz, 2 H); ^{13}C NMR 13.48, 18.67, 31.14, 69.43, 119.63, 119.73, 123.31, 124.81, 125.65, 126.94, 127.04, 127.66, 134.61, 154.06; MS (EI, *m*/*z*) 556 (M^+, 68). Anal. Calcd for $C_{28}H_{28}O_2Br_2$: C, 60.45; H, 5.07. Found: C, 60.42; H, 5.06.

(*S*)-4-Bromo-2,2′-dibutoxy-4′-hexyl-1,1′-binaphthyl (10). A mixture of the dibromide **9** (2.3 g, 4.1 mmol), 1-hexyne (0.47 mL, 4.1 mmol), $Pd(PPh_3)_2Cl_2$ (0.29 g, 0.41 mmol), and CuI (0.04 g, 0.21 mmol) in dry benzene (30 mL) and triethylamine (6 mL) was stirred under nitrogen at 60 °C for 12 h. The mixture was filtered through a short pad of silica gel and washed with ethyl acetate (75 mL). The solution was washed with 1 M HCl and saturated NaCl solution, dried (Na_2SO_4), and filtered. The solvents were removed in vacuo and the crude product purified by flash chromatography on silica gel (hexane/CH_2Cl_2 = 18/1) to give the monoacetylene compound (1.23 g, 54%) as a yellow oil: R_f 0.51 (hexane/CH_2Cl_2 = 5/1); $[\alpha]^{25}_D = -73.0$ (*c* = 1.13, $CHCl_3$); ^{1}H NMR 0.65 (t, *J* = 7.5 Hz, 6 H), 0.95−1.04 (m, 7 H), 1.36−1.40 (m, 4 H), 1.57−1.64 (m, 2 H), 1.70−1.77 (m, 2 H), 2.63 (t, *J* = 6.9 Hz, 2 H), 3.87−3.98 (m, 4 H), 7.11 (t, *J* = 8.1 Hz, 2 H), 7.19−7.24 (m, 2 H), 7.34−7.41 (m, 2 H), 7.54 (s, 1 H), 7.72 (s, 1 H), 8.21 (d, *J* = 8.4 Hz, 1 H), 8.34 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR 13.44, 13.66, 18.65, 19.42, 22.13, 30.98, 31.13, 31.17, 68.98, 69.36, 78.82, 95.54, 118.88, 119.68, 120.10, 120.29, 122.88, 123.05, 123.98, 124.71, 125.45, 125.77, 126.19, 126.48, 126.77, 126.92, 127.64, 129.37, 133.83, 134.73, 153.67, 154.10; MS (EI, *m*/*z*) 558 (M^+, 100). Anal. Calcd for $C_{34}H_{37}O_2Br$: C, 73.24; H, 6.69. Found: C, 73.21; H, 6.91. A sample of this internal acetylene (1.10 g, 1.97 mmol) was stirred under hydrogen in the presence of PtO_2 (0.08 g) in ethanol−ethyl acetate (20 mL, 1:1) mixture at room temperature for 1.5 h. The mixture was filtered through a short pad of Celite and the filtered cake washed with ethyl acetate (20 mL × 2). The filtrate was concentrated under reduced pressure and the residue purified by flash chromatography on silica gel (hexane/CH_2Cl_2 = 16/1) to give the titled compound **10** as a colorless oil (0.80 g, 73%); R_f 0.54 (hexane/CH_2Cl_2 = 5/1); $[\alpha]^{25}_D = -62.8$ (*c* = 1.89, $CHCl_3$); ^{1}H NMR 0.61 (t, *J* = 7.5 Hz, 3 H), 0.65 (t, *J* = 7.5 Hz, 3 H), 0.88−1.03 (m, 7 H), 1.32−1.57 (m, 10 H), 1.78−1.88 (m, 2 H), 3.08−3.23 (m, 2 H), 3.82−3.98 (m, 4 H), 7.11−7.40 (m, 7 H), 7.72 (s, 1 H), 8.03 (d, *J* = 8.4 Hz, 1 H), 8.21 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR 13.50, 13.56, 14.15, 18.65, 18.75, 22.72, 29.55, 30.91, 31.24, 31.40, 31.82, 33.61, 69.16, 69.69, 115.74, 117.71, 120.22, 121.36, 122.74, 123.15, 123.84, 124.73, 125.74, 125.98, 126.12, 126.68, 126.91, 127.64, 127.80, 134.47, 135.06, 140.70, 153.94, 154.30; MS (EI, *m*/*z*) 562 (M^+, 100). Anal. Calcd for $C_{34}H_{41}O_2Br$: C, 72.72; H, 7.36. Found: C, 73.14; H, 7.62.

Tetra-*O*-butyl Ethers (4). *n*-BuLi (0.78 mL, 1.6 M in hexane, 1.25 mmol) was added to a solution of the binaphthyl bromide **10** (0.35 g, 0.62 mmol) in dry THF (10 mL) at −78 °C under N_2. After 15 min, trimethyl borate (0.14 mL, 1.23 mmol) was added in one portion to the reaction mixture. The solution was then warmed to room temperature for 1 h and quenched with diluted HCl solution. The mixture was extracted with ethyl acetate (50 mL), washed with water and saturated NaCl solutions, dried (Na_2SO_4), and filtered. The solvent was removed in vacuo, and the crude boronic acid **11** was used immediately in the Suzuki coupling reaction without characterization.

A heterogeneous mixture of the above boronic acid **11**, the binaphthyl bromide **10** (0.22 g, 0.39 mmol), and $Pd(PPh_3)_4$ (0.05 g, 0.04 mmol) in ethanol/toluene (20 mL, 1:1) and aqueous Na_2CO_3 solution (2 M, 2 mL) was refluxed for 12 h. The mixture was cooled to room temperature and diluted with ethyl acetate (50 mL). The mixture was washed with 1 M HCl and saturated NaCl solutions, dried (Na_2SO_4), and filtered. The crude product was then purified by flash chromatography on silica gel (hexane/CH_2Cl_2 = 6/1) to give a diastereomeric mixture of the tetra-*O*-butyl ethers **4** as a colorless oil (0.34 g, 90%): R_f 0.26 (hexane/CH_2Cl_2 = 2/1); $[\alpha]^{25}_D = -73.7$ (*c* = 0.55, $CHCl_3$); ^{1}H NMR 0.62 (t, *J* = 7.8 Hz, 3 H), 0.64 (t, *J* = 7.8 Hz, 3 H), 0.69 (t, *J* = 7.2 Hz, 3 H), 0.70 (t, *J* = 7.2 Hz, 3 H), 0.88−1.11 (m, 14 H), 1.31−1.60 (m, 20 H), 1.89 (quintet, *J* = 7.2 Hz, 4 H), 3.15−3.25 (m, 4 H), 3.89−4.09 (m, 8 H), 7.11−7.45 (m, 14 H), 7.46−7.51 (m, 2 H), 7.59−7.63 (m, 2 H), 8.09 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR 13.55, 13.59, 13.69, 13.72, 14.15, 18.73, 18.77, 18.83, 18.96, 22.73, 29.58, 29.69, 30.92, 31.47, 31.58, 31.75, 31.84, 33.60, 69.49, 69.62, 69.73, 116.47, 116.51, 117.83, 118.07, 119.16, 120.84, 123.19, 123.24, 123.41, 123.50, 123.86, 125.62, 125.72, 125.92, 126.48, 126.66, 127.88, 127.91, 128.79, 134.60, 134.81, 134.83, 139.64, 139.75, 140.41, 140.44, 154.01, 154.05, 154.21, 154.26; MS (EI, *m*/*z*) 963 ($M + H^+$, 100). Anal. Calcd for $C_{68}H_{82}O_4$: C, 84.78; H, 8.58. Found: C, 85.10; H, 8.88.

Tetraphenols (5). BBr_3 (1.5 mL, 1.0 M in CH_2Cl_2, 1.50 mmol) was added to a solution of the tetra-*O*-butyl ethers **4** (0.23 g, 0.24 mmol) in anhydrous CH_2Cl_2 (10 mL) under N_2. The mixture was stirred at 0 °C for 2 h, quenched with 1 M HCl solution (20 mL), and extracted with ethyl acetate (50 mL). The organic layer was washed with saturated NaCl solution, dried ($MgSO_4$), and filtered. The filtrate was concentrated in vacuo and the residue purified by flash chromatography on silica gel (hexane/EtOAc = 6/1) to give the tetraphenols **5** as a mixture of diastereomers (0.16 g, 90%): mixed mp 123−125 °C; R_f 0.50 (faster running diastereomer) and 0.23 (slower running diastereomer) (hexane/EtOAc = 3/1); $[\alpha]^{25}_D = -52.5$ (*c* = 0.63, $CHCl_3$) (diastereomeric mixture); ^{1}H NMR (faster running isomer) 0.95 (t, *J* = 7.2 Hz, 6 H), 1.36−1.50 (m, 8 H), 1.50−1.63 (m, 4 H), 1.90 (quintet, *J* = 7.8 Hz, 4 H), 3.18 (t, *J* = 7.8 Hz, 4 H), 5.20 (s, 2 H), 5.22 (s, 2 H), 7.19−7.24 (m, 3 H), 7.28−7.45 (m, 11 H), 7.54 (s, 2 H), 7.60 (d, *J* = 8.1 Hz, 2 H), 8.12 (d, *J* = 8.1 Hz, 2 H); (slower running isomer) 0.95 (t, *J* = 7.2 Hz, 6 H), 1.34−1.50 (m, 8 H), 1.50−1.63 (m, 4 H), 1.90 (quintet, *J* = 7.8 Hz, 4 H), 3.18 (t, *J* = 7.8 Hz, 4 H), 5.23−5.29 (m, 4 H), 7.20−7.49 (m, 16 H), 7.60 (d, *J* = 8.1 Hz, 2 H), 8.13 (d, *J* = 7.8 Hz, 2 H); ^{13}C NMR (mixture) 14.16, 22.69, 29.64, 30.53, 31.79, 33.23, 108.67, 111.34, 117.51, 119.36, 119.65, 123.87, 124.19, 124.47, 124.69, 125.01, 127.20, 127.53, 128.26, 128.80, 133.79, 133.89, 141.10, 143.38, 152.21, 152.38, 152.48; MS (EI, *m*/*z*) 738 (M^+, 50). Anal. Calcd for $C_{52}H_{50}O_4$: C, 84.52; H, 6.82. Found: C, 84.09; H, 6.36.

Tetra-*O*-methyl Ethers (6). A mixture of the tetraphenols **5** (100 mg, 0.14 mmol), methyl iodide (50 μL, 0.80 mmol), and cesium carbonate (260 mg, 0.80 mmol) in dry acetone (10 mL) was stirred under reflux for 2 h. The mixture was filtered through a short pad of Celite and washed with ethyl acetate (20 mL × 2). The filtrate was concentrated on a rotary evaporator and the crude compound chromatographed on silica gel (hexane/CH_2Cl_2 = 5/1) to give the faster running (50 mg, 45%) and slower running diastereomer (30 mg, 27%) of **6** as white solids. Data for the faster running diastereomer **6**: mp 257−258 °C dec; R_f 0.22 (hexane/CH_2Cl_2 = 2/1); $[\alpha]^{25}_D = -99.5$ (*c* = 1.47, $CHCl_3$); ^{1}H NMR 0.96 (t, *J* = 6.9 Hz, 6 H), 1.35−1.50 (m, 8 H), 1.52−1.64 (m, 4 H), 1.92 (quintet, *J* = 7.2 Hz, 4 H), 3.14−3.30 (m, 4 H), 3.82 (s, 6 H), 3.87 (s, 6 H), 7.16−7.40 (m, 14 H), 7.61 (s, 2 H), 7.62−7.66 (m, 2 H), 8.10 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR 14.16, 22.73, 29.74, 30.93, 31.83, 33.77, 56.93, 57.03, 114.63, 116.32, 117.71, 119.67, 123.27, 123.54, 124.02, 125.69, 125.91, 126.12, 126.23, 126.86, 127.81, 128.70, 134.41, 134.57, 139.92, 140.95, 154.41, 154.65; MS (FAB, *m*/*z*) 795 ($M + H^+$, 50); HRMS (EI) calcd for $C_{56}H_{58}O_4$ 794.4332, found 794.4328. Data for the slower diastereomer **6** (0.03 g, 28%): mp 257−258 °C dec; R_f 0.06 (hexane/CH_2Cl_2 = 2/1); $[\alpha]^{25}_D = -55.2$ (*c* = 0.52, $CHCl_3$); ^{1}H NMR 0.96 (t, *J* = 6.9 Hz, 6 H), 1.35−1.50 (m, 8 H), 1.52−1.65 (m, 4 H), 1.92 (quintet, *J* = 7.2 Hz, 4 H), 3.17−3.28 (m, 4 H), 3.81 (s, 6 H), 3.86 (s, 6 H), 7.18−7.27 (m, 6 H), 7.32−7.43 (m, 8 H), 7.56−7.61 (m, 2 H), 7.64 (s, 2 H), 8.11 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR 14.17, 22.74, 29.76, 30.95, 31.84, 33.79, 56.90, 57.11, 114.56, 116.27, 117.72, 119.48, 123.37, 123.60, 124.03, 125.68, 126.06, 126.14, 126.23, 126.77, 127.87, 128.74, 134.32, 134.55, 139.90, 140.99, 154.37, 154.64; MS (FAB, *m*/*z*) 795 ($M + H^+$, 35); HRMS (EI) calcd for $C_{56}H_{58}O_4$ 794.4332, found 794.4329.

Tetrasulfonates (7). A mixture of the binaphthol dimer **5** (0.20 g, 0.27 mmol) and (1*S*)-camphor-10-sulfonyl chloride (0.27 g, 1.08 mmol) in dry CH_2Cl_2 (10 mL) and triethylamine (1.0 mL) was stirred at 0 °C for 3 h. The reaction mixture was diluted with water and extracted with CH_2Cl_2 (50 mL). The combined extracts were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo and purified by flash chromatography on silica gel

(hexane/EtOAc = 4/1) to give a 1:1 mixture of the diastereomeric tetrasulfonates **7** (0.37 g, 87%). Data for the faster running diastereomer **7**: mp 110−111 °C; R_f 0.34 (hexane/EtOAc = 2/1); $[\alpha]^{25}_D = +17.1$ (c = 0.46, $CHCl_3$); ^{1}H NMR 0.50 (s, 6 H), 0.55 (s, 6 H), 0.76 (s, 6 H), 0.79 (s, 6 H), 0.95 (t, J = 6.6 Hz, 6 H), 1.20−1.50 (m, 16 H), 1.50−1.62 (m, 4 H), 1.75−2.35 (m, 24 H), 2.46 (d, J = 15 Hz, 2 H), 2.56 (d, J = 15 Hz, 2 H), 2.80 (d, J = 15 Hz, 2 H), 2.99 (d, J = 15 Hz, 2 H), 3.12−3.28 (m, 4 H), 7.38−7.61 (m, 12 H), 7.68 (s, 2 H), 7.68−7.73 (m, 2 H), 7.87 (s, 2 H), 8.18 (d, J = 8.4 Hz, 2 H); ^{13}C NMR 14.11, 19.18, 19.30, 22.62, 24.85, 25.02, 26.66, 29.60, 30.53, 31.70, 33.18, 42.20, 42.62, 47.61, 49.12, 57.61, 120.75, 121.02, 123.68, 123.90, 124.22, 126.20, 126.68, 126.94, 127.07, 127.31, 127.73, 130.45, 131.08, 133.62, 139.22, 142.83, 145.17, 145.53, 213.07, 213.23; MS (FAB, m/z) 1596 ($M + H^+$, 60). Anal. Calcd for $C_{92}H_{106}O_{16}S_4$: C, 69.23; H, 6.69. Found: C, 69.37; H, 6.76. Data for the slower running diastereomer **7**: mp 111−112 °C; R_f 0.27 (hexane/EtOAc = 2/1); $[\alpha]^{25}_D = -6.4$ (c = 0.76, $CHCl_3$); ^{1}H NMR 0.58 (s, 6 H), 0.65 (s, 6 H), 0.80 (s, 6 H), 0.95 (t, J = 6.6 Hz, 6 H), 0.97 (s, 6 H), 1.18−1.62 (m, 20 H), 1.74−2.00 (m, 20 H), 2.17−2.32 (m, 4 H), 2.60 (d, J = 15 Hz, 2 H), 2.88 (d, J = 15 Hz, 2 H), 2.93 (d, J = 15 Hz, 2 H), 3.15−3.26 (m, 4 H), 3.25 (d, J = 15 Hz, 2 H), 7.36−7.68 (m, 14 H), 7.70 (s, 2 H), 7.95 (s, 2 H), 8.17 (d, J = 8.4 Hz, 2 H); ^{13}C NMR 14.11, 19.30, 19.39, 19.47, 19.61, 22.63, 24.91, 25.08, 26.67, 26.74, 29.59, 30.56, 31.70, 33.22, 42.20, 42.27, 42.63, 42.74, 47.54, 47.65, 48.74, 49.09, 57.66, 57.73, 120.59, 120.78, 123.37, 123.85, 124.11, 126.20, 126.51, 126.88, 127.02, 127.34, 127.48, 127.61, 130.40, 131.11, 133.71, 133.78, 139.24, 142.78, 144.99, 145.47, 212.95, 213.19; MS (FAB, m/z) 1595 (M^+, 30). Anal. Calcd for $C_{92}H_{106}O_{16}S_4$: C, 69.23; H, 6.69. Found: C, 69.62; H, 6.68.

(*S*)-2,2′-Dibutoxy-4,4′-bis(4-tolyl)-1,1′-binaphthyl (12). A heterogeneous mixture of 4-tolylboronic acid [prepared from 4-bromotoluene (0.50 g, 2.9 mmol)], the dibromide **9** (0.28 g, 0.50 mmol), and $Pd(PPh_3)_4$ (0.10 g, 0.09 mmol) in ethanol/toluene (20 mL, 1:1) and aqueous Na_2CO_3 (2 M, 2 mL) was refluxed for 12 h. The mixture was cooled to room temperature and extracted with ethyl acetate (50 mL). The mixture was washed with 1 M HCl and saturated NaCl solutions, dried (Na_2SO_4), and purified by flash chromatography on silica gel (hexane/CH_2Cl_2 = 10/1) to give the target compound **12** (0.25 g, 87%) as an oil: R_f 0.28 (hexane/CH_2Cl_2 = 5/1); $[\alpha]^{25}_D = -54.8$ (c = 1.79, $CHCl_3$); ^{1}H NMR 0.64 (t, J = 7.5 Hz, 6 H), 0.90−1.03 (m, 4 H), 1.33−1.45 (m, 4 H), 2.49 (s, 6 H), 3.90−4.02 (m, 4 H), 7.17−7.38 (m, 12 H), 7.53 (d, J = 7.8 Hz, 4 H), 7.88−7.93 (m, 2 H); ^{13}C NMR 13.59, 18.75, 21.27, 31.44, 69.53, 117.04, 120.13, 123.36, 125.87, 125.98, 126.05, 127.62, 128.97, 130.07, 134.73, 136.98, 138.15, 141.37, 154.00; MS (FAB, m/z) 578 (M^+, 100); HRMS (L-SIMS) calcd for $C_{42}H_{42}O_2$ 578.3183, found 578.3196.

(*S*)-4,4′-Bis-(4-tolyl)-1,1′-binaphthyl-2,2′-diol (13). BBr_3 (1.5 mL, 1.0 M in CH_2Cl_2, 1.5 mmol) was added to a solution of the bis-*O*-butyl ether **12** (0.28 g, 0.48 mmol) in CH_2Cl_2 (10 mL) under N_2 at 0 °C. The resulting mixture was stirred at 0 °C for 2 h, quenched with 1 M HCl solution (20 mL), and extracted with ethyl acetate (50 mL). The solution was washed with saturated NaCl solution, dried ($MgSO_4$), and filtered. The organic layer was concentrated in vacuo, and the residue was purified by flash chromatography on silica gel (hexane/EtOAc = 15/1) to give the target compound **13** (0.18 g, 80%) as a white solid: mp 224−225 °C; R_f 0.40 (hexane/EtOAc = 5/1); $[\alpha]^{25}_D = -35.8$ (c = 0.24, $CHCl_3$); ^{1}H NMR 2.49 (s, 6 H), 5.16 (s, 2 H), 7.28−7.37 (m, 12 H), 7.49 (d, J = 6 Hz, 4 H), 7.95−7.98 (m, 2 H); ^{13}C NMR 21.29, 110.22, 118.52, 123.96, 124.62, 126.79, 127.31, 128.03, 129.11, 129.81, 133.98, 136.96, 137.46, 143.84, 152.17; MS (FAB, m/z) 466 (M^+, 75); HRMS (L-SIMS) calcd for $C_{34}H_{26}O_2$ 466.1931, found 466.1930.

(*S*)-2,2′-Di-[(1*S*)-camphor-10-sulfonyloxy]-4,4′-bis-(4-tolyl)-1,1′-binaphthyl (14). A mixture of the binaphthol **12** (0.21 g, 0.45 mmol) and (1*S*)-camphor-10-sulfonyl chloride (0.45 g, 1.79 mmol) in dry CH_2Cl_2 (10 mL) and triethylamine (1.0 mL) was stirred at 0 °C for 3 h. The reaction mixture was diluted with water and extracted with CH_2Cl_2 (50 mL). The combined extracts were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo and purified by flash chromatography on silica gel (hexane/EtOAc = 4/1) to give the product **14** as a white solid (0.31 g, 77%): mp 121−122 °C; R_f 0.16 (hexane/EtOAc = 5/1); $[\alpha]^{25}_D = +7.2$ (c = 0.73, $CHCl_3$); ^{1}H NMR 0.51 (s, 6 H), 0.77 (s, 6 H), 1.24−1.35 (m, 4 H), 1.75−2.28 (m, 10 H), 2.49 (s, 6 H), 2.52 (d, J = 15 Hz, 2 H), 2.95 (d, J = 15 Hz, 2 H), 7.35−7.53 (m, 14 H), 7.73 (s, 2 H), 8.04−8.07 (m, 2 H); ^{13}C NMR 19.22, 19.33, 21.23, 24.77, 26.65, 42.16, 42.60, 47.51, 48.95, 57.57, 122.05, 122.13, 126.27, 126.50, 126.94, 127.36, 129.13, 129.97, 130.16, 133.74, 136.08, 137.71, 143.16, 145.24, 213.10; MS (FAB, m/z) 917 ($M + Na^+$, 10); HRMS (L-SIMS) calcd for $C_{54}H_{54}O_8S_2$ 894.3257, found 894.3274.

(*S*)-2,2′-Dibutoxy-4-hexyl-4′-(4-tolyl)-1,1′-binaphthyl (15). A heterogeneous mixture of the boronic acid **11** [prepared from **10** (0.30 g, 0.53 mmol)] and 4-bromotoluene (0.10 g, 0.58 mmol), $Pd(PPh_3)_4$ (0.08 g, 0.07 mmol) in ethanol/toluene (20 mL, 1:1), and aqueous Na_2CO_3 (2 M, 2 mL) was refluxed for 12 h. The mixture was cooled to room temperature and extracted with ethyl acetate (50 mL). The mixture was washed with 1 M HCl and saturated NaCl solutions, dried (Na_2SO_4), and filtered. The crude product was purified by flash chromatography on silica gel (hexane/CH_2Cl_2 = 10/1) to afford the product **15** as a colorless oil (0.28 g, 92%): R_f 0.37 (hexane/CH_2Cl_2 = 5/1); $[\alpha]^{25}_D = -55.2$ (c = 2.17, $CHCl_3$); ^{1}H NMR 0.76 (t, J = 7.5 Hz, 3 H), 0.79 (t, J = 7.2 Hz, 3 H), 1.04−1.21 (m, 4 H), 1.09 (t, J = 7.2 Hz, 3 H), 1.46−1.73 (m, 10 H), 2.03 (quintet, J = 7.2 Hz, 2 H), 2.60 (s, 3 H), 3.24−3.40 (m, 2 H), 4.01−4.17 (m, 4 H), 7.28−7.52 (m, 10 H), 7.67 (d, J = 8.1 Hz, 2 H), 8.03−8.08 (m, 1 H), 8.19−8.22 (m, 1 H); ^{13}C NMR 13.53, 13.59, 14.13, 18.70, 18.74, 21.21, 22.71, 29.54, 30.89, 31.40, 31.48, 31.81, 33.56, 69.38, 69.56, 116.40, 117.01, 119.07, 120.36, 123.14, 123.30, 123.75, 125.57, 125.78, 125.98, 126.39, 127.58, 127.80, 128.93, 130.03, 134.78, 134.82, 136.86, 138.15, 140.28, 141.22, 154.00, 154.11; MS (EI, m/z) 572 (M^+, 100); HRMS (EI) calcd for $C_{41}H_{48}O_2$ 572.3652, found 572.3655.

(*S*)-4-Hexyl-4′-(4-tolyl)-1,1′-binaphthyl-2,2′-diol (16). BBr_3 (1.8 mL, 1.0 M in CH_2Cl_2, 1.8 mmol) was added to a solution of the bis-*O*-butyl ether **15** (0.34 g, 0.59 mmol) in CH_2Cl_2 (10 mL) under N_2 at 0 °C. After 2 h, the mixture was quenched with 1 M HCl solution (20 mL) and extracted with ethyl acetate (50 mL). The solution was washed with saturated NaCl solution, dried ($MgSO_4$), and filtered. The organic layer was concentrated under reduced pressure and purified by flash chromatography on silica gel (hexane/EtOAc = 15/1) to give the titled compound **16** (0.25 g, 91%) as a white solid: mp 139−140 °C; R_f 0.31 (hexane/EtOAc = 5/1); $[\alpha]^{25}_D = -30.4$ (c = 0.39, $CHCl_3$); ^{1}H NMR 0.94 (t, J = 6.9 Hz, 3 H), 1.35−1.65 (m, 6 H), 1.90 (quintet, J = 7.2 Hz, 2 H), 2.49 (s, 3 H), 3.16 (t, J = 7.5 Hz, 2 H), 5.09 (br s, 2 H), 7.21−7.43 (m, 10 H), 7.49 (d, J = 7.8 Hz, 2 H), 7.93−7.98 (m, 1 H), 8.10 (d, J = 8.1 Hz, 1 H); ^{13}C NMR 14.13, 21.28, 22.67, 29.60, 30.50, 31.77, 33.18, 108.83, 110.38, 117.45, 118.44, 123.74, 123.88, 124.38, 124.63, 125.02, 126.74, 127.04, 127.21, 128.01, 128.17, 129.09, 129.81, 133.94, 134.07, 137.01, 137.43, 143.17, 143.71, 152.20, 152.39; HRMS (L-SIMS) calcd for $C_{33}H_{32}O_2$ 460.2401, found 460.2405.

(*S*)-2,2′-Di[(1*S*)-camphor-10-sulfonyloxy]-4-hexyl-4′-(4-tolyl)-1,1′-binaphthyl (17). A mixture of the binaphthol **16** (0.12 g, 0.26 mmol) and (1*S*)-camphor-10-sulfonyl chloride (0.26 g, 1.04 mmol) in dry CH_2Cl_2 (10 mL), and triethylamine (1.0 mL) was stirred at 0 °C for 3 h. The reaction mixture was diluted with water and extracted with CH_2Cl_2 (50 mL). The combined extracts were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo and purified by flash chromatography on silica gel (hexane/EtOAc = 4/1) to give the product **17** as a white solid (0.17 g, 74%): mp 72−73 °C; R_f 0.18 (hexane/EtOAc = 5/1); $[\alpha]^{25}_D = +28.3$ (c = 1.53, $CHCl_3$); ^{1}H NMR 0.49 (s, 3 H), 0.50 (s, 3 H), 0.76 (s, 6 H), 0.94 (t, J = 6.9, 3 H), 1.19−1.47 (m, 8 H), 1.50−1.58 (m, 2 H), 1.72−2.26 (m, 12 H), 2.41 (d, J = 15 Hz, 1 H), 2.47 (d, J = 15 Hz, 1 H), 2.48 (s, 3 H), 2.84 (d, J = 15 Hz, 1 H), 2.91 (d, J = 15 Hz, 1 H), 3.10−3.27 (m, 2 H), 7.34−7.57 (m, 10 H), 7.63 (s, 1 H), 7.69 (s, 1 H), 8.04 (d, J = 6 Hz, 1 H), 8.14 (d, J = 6 Hz, 1 H); ^{13}C NMR 14.11, 19.21, 19.27, 19.32, 19.37, 21.27, 22.63, 24.84, 26.71, 29.59, 30.55, 31.71, 33.17, 42.23, 42.66, 47.56, 48.89, 120.96, 122.17, 124.15,

126.13, 126.26, 126.49, 127.05, 127.17, 127.32, 127.42, 129.16, 130.02, 130.20, 130.44, 133.68, 133.84, 137.72, 142.66, 143.07, 145.32, 213.04, 213.14; HRMS (L-SIMS) calcd for ($C_{53}H_{60}O_8S_2$ + H^+) 889.3804, found 889.3839.

Determination of the Racemization Half-Life of the Central Chiral Axis of Compound 6. A solution of a freshly purified faster running diastereomer of the tetra-*O*-methyl ether **6** in $CDCl_3$ (~0.02 M) was placed in a sealed NMR tube. The tube was then immersed in a constant-temperature bath at 56 °C. The sample tube was removed at suitable times, and the ^{1}H NMR spectrum was recorded at 20 °C (acquistion time ~1 min). The relative amount of the faster and slower running diastereomers was then determined by the relative integration of the signals at δ 7.61 and 7.64. The half-life for the racemization of the central chiral axis was estimated by fitting the data using a simple equilibrium model provided by a TableCurve 2D (version 5) program.

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Supporting Information Available: Selected spectroscopic data (^{1}H and ^{13}C NMR, ^{1}H−^{1}H 2D-COSY, and CD) of the quaternaphthyl derivatives **4**−**7** and compounds **12**−**17** and a kinetic plot of the racemization of the central chiral axis of compound **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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