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Asymmetric synthesis of macrocyclic binaphthol dimers using a Sonogashira coupling reaction

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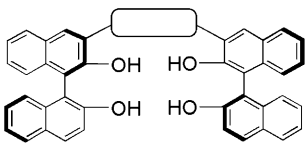
Abstract—Asymmetric synthesis of 24- and 26-membered macrocyclic binaphthol dimers was achieved by assembling a 3,3′-diethynyl-1,1′-bi-2-naphthol unit and 1,2- and 1,3-phenylene units with Sonogashira coupling reaction.

1. Introduction

1,1′-Bi-2-naphthol (BINOL) and their derivatives have been extensively used to provide a chiral environment in asymmetric synthesis.[1] Recently, bis-BINOLs **1** in which two BINOL units are connected at the 3 position by an appropriate tether have emerged as ligands for chiral catalysts of versatile utility.[2,3] Macrocyclic BINOL dimers **2** may also serve as potential ligands with a defined unambiguous chiral environment around the active metal center. Since the seminal work of Cram et al., BINOL-based macrocycles has been extensively studied in the molecular recognition field.[4] Recently, Diederich et al. have reported the synthesis of macrocyclic BINOL oligomers in which BINOL units are connected by 1,3-butadiyne units by using oxidative coupling of 3,3′-diethynyl-BINOL derivatives.[5] Herein, we report asymmetric syntheses of macrocyclic binaphthol dimers **8** and **10** by assembling 3,3′-diethynyl-BINOL units and 1,2- and 1,3-phenylene units via a Sonogashira coupling reaction.



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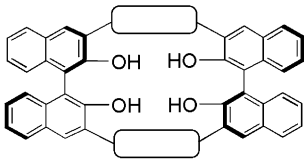

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Diethynylbinaphthol **4** was previously prepared from bi-2,2′-naphthol in four steps via the 3,3′-diiodo derivative.[5] A more straightforward and efficient method was developed by applying the regioselective ethynylation of phenols reported by Johnson et al.[6] (Scheme 1). Thus, treatment of (*R*)-BINOL with 1,1-dichloro-2,2-difluoroethene in aq. KOH–CH_2Cl_2 under phase-transfer conditions gave bis(dichlorodifluoroethyl) ether **3** in quantitative yield. When **3** was treated with BuLi (12 equiv.) at temperatures from −80°C to room temperature, the intermediately formed diethynyl ether derivative underwent clean rearrangement to give **4** in 90% yield. Etherification of **4** afforded bis-MOM derivative **5a** (89%) and dimethyl derivative **5b** (93%) in enantiomerically pure forms.

Our initial attempt to synthesize macrocyclic BINOL dimer **7a** by a single step reaction of terminal diyne **5a** and 1,2-diiodobenzene under the standard Sonogashira reaction conditions ($Pd(PPh_3)_4$ (10 mol%), CuI (20 mol%) in Et_3N at 60°C)[7] resulted in the formation of oligomeric coupling products. We then turned our attention to a two-step approach involving annulation of terminal diynes **5** and diiodides **6**. For the initial step of mono-alkynylation of 1,2- and 1,3-diiodobenzene, the cross-coupling was carried out in the presence of $Pd(PPh_3)_4$ (5 mol%) and CuI (10 mol%) at relatively low concentration (0.05 M) in Et_3N by using an excess of the diiodides (15 equiv.) in order to retard bis-alkynylation. Under these conditions, the reaction of 1,2-diiodobenzene with diyne **5a** and **5b** gave **6a** and **6b**

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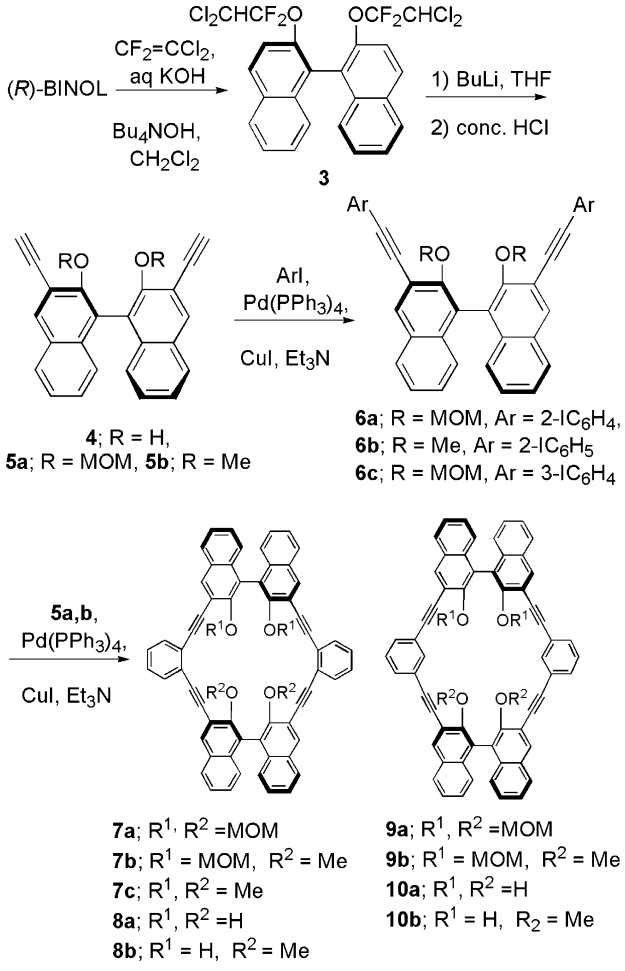

Scheme 1.

in 49 and 43% yield, respectively.[8] The cross-coupling reaction of **5a** with sterically less hindered 1,3-diiodobenzene gave **6c** in a higher yield of 80% under similar conditions. In these reactions, the diiodides used in excess could be recovered for the most part by distillation of the crude reaction mixture.[9]

When a mixture of diiodide **6a** and diyne **5a** was heated in the presence of $Pd(PPh_3)_4$ (4 mol%) and CuI (8 mol%) in Et_3N (0.005 M) at 60°C for 18 h, 24-membered annulation product **7a** was produced in 6% isolated yield together with the formation of oligomeric coupling products (entry 1 in Table 1). Slow addition of substrate(s) was found to be effective in retarding the undesirable oligomerization pathway. Thus, addition of **5a** (2.0 equiv.) during a 2.5 h period brought about the improved yield of **7a** (entry 2). Further improvement was observed when a mixture of both substrates were added to a suspension of $Pd(PPh_3)_4$ (10 mol%) and CuI (20 mol%) in Et_3N–benzene (entries 3–5). The best yield of 49% was achieved by the use of 1.5 equiv. of **5a** under these conditions (entry 4).

Table 1. Annulation of **6a** and **5a** leading to macrocycle **7a**[a]

Entry	Method[b]	**5a**	$Pd(PPh_3)_4$ (mol%)	Yield (%)
1	A	1.2	4	6
2	B	2.0	8	20
3	C	1.2	10	32
4	C	1.5	10	49
5	C	2.0	10	38

[a] Reactions were carried out by using 2 equiv. of CuI with respect to the catalyst at 60°C.

[b] Method A; a mixture of **6a**, **5a**, $Pd(PPh_3)_4$, and CuI in Et_3N (0.005 M) was stirred for 18 h. Method B; a solution of **5a** in THF–Et_3N (1:1) (0.05 M) was slowly (2.5 h) added to a mixture of **6a**, $Pd(PPh_3)_4$, and CuI in Et_3N (0.005 M) and the resulting mixture was stirred for 3.5 h. Method C; a benzene solution (0.05 M) of **6a** and **5a** was slowly (5 h) added to a suspension of $Pd(PPh_3)_4$ and CuI in Et_3N-benzene (1:1) (0.01 M) and the resulting mixture was stirred for 3 h.

The optimized conditions were successfully applied to annulation of diiodide **6a–c** and diynes **5a**,**b** (Table 2). The reactions of *O*,*O*′-dimethyl derivative **6b** with diynes **5a** and **5b** proceeded more efficiently than that of bis-MOM derivative **6a** to give the corresponding annulation products **7b** and **7c**, respectively (entries 2 and 3). 26-Membered macrocycles **9a**,**b** were also prepared, albeit in lower yields, by the reaction of bis-(3-iodophenyl) derivative **6c** with **5a**,**b** (entries 4 and 5). In spite of steric congestion around the MOM groups, removal of the protecting groups was effected simply by treating **7a**,**b** and **9a**,**b** with conc. HCl in refluxing MeOH–THF to furnish the corresponding macrocyclic BINOL dimers **8a**,**b** and **9a**,**b** in high yields (Table 2). Attempts to remove the methyl groups of **7c** using BBr_3 or HBr in acetic acid resulted in a complex mixture of unidentified products.

The ^1H and ^{13}C NMR spectra of symmetrical BINOL dimers **7a**, **7c**, **8a**, **9a**, and **10a** at room temperature contained a single set of resonances for four ethynylnaphthol moieties. The hydroxyl protons of **8a**,**b** and **10a**,**b** appeared as a relatively sharp singlet (half-width ca. 2 Hz), indicating the orientation of the hydroxy groups inside of the macrocycles. The structure of **8a** was unequivocally determined by X-ray analysis (Fig. 1). The solid-state structure shows a folded conformation with a single C_2 axis penetrating the ring. The torsional angle around the binaphthyl bond is 91–96°. Distances between two oxygen atoms are 3.7–3.9, 5.8, 3.3–3.5, and 3.8° for O1–O2, O1–O3, O1–O4, and O2–O4, respectively. Two naphthol moieties in a BINOL unit are inequivalent. One of the naphthol moieties and the corresponding one in another BINOL unit arranges nearly in a parallel with distance of 4.4–4.8 Å. Higher symmetry of **8a** observed in the NMR analyses implies rapid flipping of the macrocyclic rings on the NMR time scale, leading to the averaged resonances derived from the two naphthol moieties.

We have described an asymmetric synthesis of novel macrocyclic binaphthol dimers **8a**,**b** and **10a**,**b** by using

Table 2. Synthesis of macrocyclic BINOL dimers **8** and **10**[a]

Entry	Diiodide	Diyne	Annulation product	Yield (%)	Deprotection product	Yield (%)
1	**6a**	**5a**	**7a**	49	**8a**	71
2	**6b**	**5a**	**7b**	60	**8b**	89
3	**6b**	**5b**	**7c**	55	–	–
4	**6c**	**5a**	**9a**	35	**10a**	77
5	**6c**	**5b**	**9b**	42	**10b**	92

[a] Annulation reaction was carried out by using a diyne (1.5 equiv.), $Pd(PPh_3)_4$ (10 mol%), and CuI (20 mol%) in Et_3N and benzene at 60°C according to method C. Deprotection was effected by treatment of an annulation product with conc. HCl in refluxing MeOH–THF for 2–3 h.

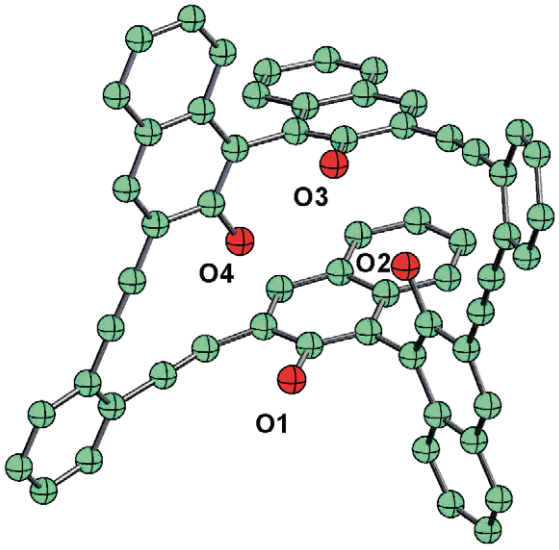

Figure 1. X-Ray structure of macrocyclic binaphthol dimer **8a**.[10]

a Sonogashira coupling reaction. The coupling reaction of 3,3′-diethynylbinaphthol derivatives **5**, which were prepared straightforwardly in three steps from (*R*)-BINOL, with diiodobenzenes gave diarylation products **6** in reasonable yields. Annulation of **6** with **5** proceeded successfully by carrying out the Sonogashira coupling again under high dilution conditions. Final deprotection of the annulation products furnished the corresponding macrocyclic binaphthol dimers **8a**,**b** and **10a**,**b**, which could be utilized as ligands of structurally defined chiral catalysts. An application of these chiral macrocycles to molecular recognition is also promising.

2. Experimental

2.1. (*R*)-2,2′-Bis(2,2-dichloro-1,1-difluoroethoxy)-1,1′-binaphthyl (*R*)-3

To a mixture of (*R*)-1,1′-bi-2-naphthol (432 mg, 1.5 mmol) in CH_2Cl_2 (1.5 mL) and water (3.0 mL) were added aqueous 4 M KOH (1.5 mL) and aqueous 40% $Bu_4N^+OH^-$ (950 mg, 1.46 mmol). 1,1′-Dichloro-2,2′-difluoroethene (0.6 mL, 6.5 mmol) was cannulated into the mixture at 0°C. After being stirred vigorously at rt for 24 h, the reaction mixture was poured into water and extracted twice with ether. The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by silica gel flash chromatography (5% ethyl acetate in hexane) to give 795 mg (96%) of (*R*)-**3**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.40 (2H, dd, $J=4.1$ and 6.1 Hz), 7.22 (2H, d, $J=8.5$ Hz), 7.32 (2H, dt, $J=1.3$ and 6.8 Hz), 7.50 (2H, dt, $J=1.3$ and 6.8 Hz), 7.64 (2H, br d, $J=9.3$ Hz), 7.93 (2H, d, $J=8.3$ Hz), 8.00 (2H, d, $J=9.1$ Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 67.4 (t, $J=42$ Hz), 119.8 (t, $J=295$ Hz), 119.9, 124.1, 125.9, 126.3, 127.0, 127.9, 130.0, 131.4, 133.6, 145.6; IR (liquid film) 820, 765 cm^{-1}.

2.2. 3,3′-Diethynyl-1,1′-bi-2-naphthol (*R*)-4

To a solution of (*R*)-**3** (786 mg, 1.40 mmol) in THF (14 mL) was added BuLi (16.8 mmol, 10.5 mL, 1.6 M in hexane) at −78°C under an argon atmosphere. After being stirred for 6 h at the same temperature, the reaction mixture was allowed to warm slowly to rt during 11 h. The mixture was diluted with ether, poured into aqueous 1N HCl, and extracted twice with ether. The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by silica gel flash chromatography (10% ethyl acetate in hexane) to give 426 mg (90%) of (*R*)-**4**: $[\alpha]_D^{22}=+232$ (*c* 0.750, THF); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.51 (2H, s), 5.71 (2H, s), 7.1–7.15 (2H, m), 7.30 (2H, ddd, $J=1.2$, 6.6, and 8.4 Hz), 7.37 (2H, ddd, $J=1.2$, 6.6, and 8.4 Hz), 7.85 (2H, br d, $J=8.40$ Hz), 8.18 (2H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 78.7, 83.9, 110.9, 113.2, 124.5, 124.6, 128.20, 128.22, 128.3, 133.8, 134.4, 151.3; IR (KBr disk) 3470, 2100, 750 cm^{-1}; MS (EI) *m*/*z* (relative intensity) 334 (M^+, 86), 305 (26), 276 (24), 88 (126), 61 (100); HRMS (EI) calcd for $C_{24}H_{14}O_2$: 334.0994, found 334.0991.

2.3. 3,3′-Diethynyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl (*R*)-5a

To a solution of (*R*)-**4** (403 mg, 1.20 mmol) in CH_2Cl_2 (12 mL) at 0°C was added *i*-Pr_2NEt (0.50 mL, 2.88 mmol) and chloromethyl methyl ether (0.275 mL, 3.60 mmol). After being stirred for 19 h, the reaction mixture was poured into aqueous NH_4Cl and extracted twice with ether. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel flash chromatography (10% ethyl acetate in hexane) to give 353 mg (70%) of (*R*)-**5a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.52 (6H, s), 3.33 (2H, s), 4.88 (2H, d, $J=6.0$ Hz), 5.08 (2H, d, $J=6.0$ Hz), 7.2 (2H, m), 7.30 (2H, ddd, $J=1.9$, 7.2, and

8.4 Hz), 7.42 (2H, ddd, $J=1.9$, 7.2, and 8.4 Hz), 7.83 (2H, br d, $J=$ca. 8.5 Hz), 8.19 (2H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 56.0, 80.5, 81.6, 98.8, 116.2, 125.6, 125.7, 126.4, 127.5, 127.6, 130.1, 133.9, 135.2, 153.3; IR (KBr disk) 3270, 2100, 1155 cm^{-1}; MS (EI) m/z (relative intensity) 422 (M^+, 25), 391 (16), 377 (16), 346 (50), 274 (27), 59 (100); HRMS (EI) calcd for $C_{28}H_{22}O_4$: 422.1518, found 422.1511.

2.4. 3,3′-Diethynyl-2,2′-dimethoxy-1,1′-binaphthyl (*R*)-5b

To a mixture of (*R*)-**4** (336 mg, 1.00 mmol) and K_2CO_3 (414 mg, 3.00 mmol) in acetone (10 mL) at rt was added dimethyl sulfate (378 mg, 3.00 mmol). The resulting mixture was heated under reflux for 16 h. The solvent was removed in vacuo. The residue was treated with aqueous 1N HCl and extracted twice with ether. The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by silica gel flash chromatography (10% ethyl acetate in hexane) to give 242 mg (67%) of (*R*)-**5b**: mp 158–160°C (recrystallized from benzene and hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.36 (2H, s), 3.66 (6H, s), 7.09 (2H, d, $J=8.5$ Hz), 7.26 (2H, br t, $J=$ca. 8 Hz), 7.40 (2H, br t, $J=$ca. 8 Hz), 7.84 (2H, d, $J=8.1$ Hz), 8.19 (2H, s); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 61.2, 80.5, 81.6, 116.1, 125.4, 125.6, 126.3, 127.4, 127.8, 130.0, 133.9, 135.3, 153.4; IR (KBr disk) 3280, 3250, 1240 cm^{-1}. Anal calcd for $C_{26}H_{18}O_2$: C, 86.17; H, 5.01. Found: C, 85.90; H, 5.20.

2.5. (*R*)-3,3′-Bis(2-iodophenylethynyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl (*R*)-6a. (A representative procedure for palladium(0)-catalyzed cross-coupling of diynes 5a,b with a diiodobenzene)

To a stirred solution of **5a** (1.03 g, 2.43 mmol) and 1,2-diiodobenzene (12.4 g, 36.5 mmol) in triethylamine (50 mL) at rt under argon atmosphere was added CuI (46 mg, 0.24 mmol) and $Pd(PPh_3)_4$ (140 mg, 0.12 mmol). The resulting mixture was stirred for 6 h at 60°C and concentrated in vacuo. The residue was dissolved in benzene, poured into aqueous 1N HCl, and extracted twice with the solvent. The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by silica gel flash chromatography (10% ethyl acetate in hexane) to give, in the order of elution, 10.3 g (86% recovery) of 1,2-diiodobenzene and 984 mg (49%) of (*R*)-**6a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.50 (6H, s), 5.03 (2H, d, $J=6.1$ Hz), 5.28 (2H, d, $J=6.1$ Hz), 7.03 (2H, m), 7.25-7.35 (8H, m), 7.44 (2H, m), 7.55 (2H, m), 7.89 (2H, m), 8.32 (2H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 56.0, 90.0, 95.5, 99.2, 100.6, 116.9, 125.6, 125.9, 126.6, 127.3, 127.6, 127.8, 129.5, 129.7, 130.2, 132.7, 133.9, 134.7, 138.7, 152.7; IR (KBr disk) 2200, 750 cm^{-1}.

2.6. (*R*)-3,3′-Bis(2-iodophenylethynyl)-2,2′-dimethoxy-1,1′-binaphthyl (*R*)-6b

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.77 (6H, s), 7.03 (2H, br t, $J=7.8$ Hz), 7.16 (2H, d, $J=8.2$ Hz), 7.25–7.35 (2H, m), 7.42 (2H, t, $J=7.2$ Hz), 7.59 (2H, br d, $J=$ca. 8.5 Hz), 7.90 (4H, m), 7.89 (2H, d, $J=8.2$ Hz), 8.31 (2H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 61.7, 90.1, 95.5, 100.6, 117.0, 124.9, 125.4, 125.7, 127.4, 127.8, 127.9, 129.5, 130.0, 130.2, 132.8, 134.0, 134.7, 138.8, 155.5; IR (KBr disk) 2200, 750 cm^{-1}.

2.7. (*R*)-3,3′-Bis(3-iodophenylethynyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl (*R*)-6c

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.54 (6H, s), 4.96 (2H, d, $J=6.1$ Hz, 5.18 (2H, d, $J=6.1$ Hz), 7.12 (2H, t, $J=7.8$ Hz), 7.27 (2H, t, $J=8.5$ Hz), 7.34 (2H, t, $J=8.0$ Hz), 7.47 (2H, t, $J=7.4$ Hz), 7.54 (2H, d, $J=7.7$ Hz), 7.70 (2H, d, $J=7.8$ Hz), 7.89 (2H, d, $J=8.2$ Hz), 7.95 (2H, s), 8.25 (2H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 56.1, 87.7, 91. 9, 93.7, 98.9, 116.8, 125.2, 125.6, 125.9, 126.5, 127.4, 127.6, 129.9, 130.3, 130.6, 133.9, 134.4, 137.4, 140.1, 153.0; IR (KBr disk) 775, 745 cm^{-1}.

2.8. Macrocyclic binaphthyl dimer (*R*,*R*)-7a (A representative procedure for palladium(0)-catalyzed macrocyclic annulation)

To a stirred suspension of CuI (19.3 mg, 0.100 mmol), and $Pd(PPh_3)_4$ (57.9 mg, 0.050 mmol) in triethylamine (25 mL) and benzene (25 mL) at 60°C under argon atmosphere was added a benzene (10 mL) solution of **6a** (414 mg, 0.500 mmol) and **5a** (325 mg, 0.750 mmol) slowly during 5 h. The resulting mixture was stirred further for 3 h at 60°C and then concentrated in vacuo. The residue was dissolved in benzene and ethyl acetate (1:1), poured into aqueous 1N HCl, and extracted twice with the solvents. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica gel flash chromatography (8–12% ethyl acetate in hexane) to give 223 mg (49%) of (*R*)-**7a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (12H, s), 4.87 (4H, d, $J=5.9$ Hz), 5.52 (4H, d, $J=5.9$ Hz), 7.17 (4H, d, $J=8.5$ Hz), 7.26 (4H, t, $J=7.5$ Hz), 7.4 (8H, m), 7.65 (4H, m), 7.82 (4H, d, $J=8.2$ Hz), 8.22 (4H, s); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 56.0, 90.5, 92.3, 98.7, 117.1, 125.2, 125.4, 125.9, 126.6, 127.2, 127.4, 128.2, 130.1, 132.9, 134.2, 134.7, 152.5; IR (KBr disk) 2200, 745 cm^{-1}.

2.9. Macrocyclic binaphthyl dimer (*R*,*R*)-7b

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.92 (6H, s), 3.80 (6H, s), 4.68 (2H, d, $J=6.1$ Hz), 5.44 (2H, d, $J=6.1$ Hz), 7.12 (4H, br d, $J=$ca. 8.5 Hz), 7.23 (4H, m), 7.35–7.45 (8H, m), 7.69 (4H, m), 7.78 (2H, d, $J=8.2$ Hz), 7.82 (2H, d, $J=8.2$ Hz), 8.21 (2H, s), 8.21 (2H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 55.3, 61.6, 90.0, 90.1, 92.1, 92.4, 98.7, 117.0, 117.3, 125.1, 125.2, 125.3, 125.4, 125.7, 125.9, 126.2, 126.6, 127.0, 127.25, 127.30, 127.7, 128.2, 130.0 (2C), 132.7, 133.0, 133.9, 134.1, 134.2, 134.5, 134.9, 152.6, 155.6; IR (KBr disk) 2200, 750 cm^{-1}.

2.10. Macrocyclic binaphthyl dimer (*R*,*R*)-7c

Mp 265–276°C (recrystallized from benzene and hexane) $[\alpha]_D^{24}=-231$ (c 1.00, $CHCl_3$); ^{1}H NMR (500 MHz,

$CDCl_3$) δ 3.63 (12H, s), 7.08 (4H, d, J=8.5 Hz), 7.23 (4H, br t, J=ca. 8 Hz), 7.35–7.45 (8H, m), 7.70 (4H, m), 7.82 (4H, d, J=8.2 Hz), 8.20 (4H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 61.2, 90.1, 92.1, 117.2, 125.0, 125.2, 125.4, 125.7, 125.2, 127.7, 128.2, 123.0, 132.7, 134.0, 134.5, 155. 5; IR (KBr disk) 2200, 750 cm^{-1}.

2.11. Macrocyclic binaphthyl dimer (*R*,*R*)-9a

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.48 (12H, s), 4.91 (4H, d, J=4.9 Hz), 5.15 (4H, d, J=4.9 Hz), 7.25–7.35 (8H, m), 7.4–7.45 (6H, m), 7.55 (4H, br d, J=ca. 8 Hz), 7.88 (4H, d, J=8.1 Hz), 8.15 (2H, s), 8.23 (4H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 56.0, 87.6, 92.9, 98.9, 117.1, 123.7, 125.3, 125.8, 126.6, 127.2, 127.7, 128.3, 128.6, 130.2, 133.5, 133.9, 137.7, 154.2; IR (KBr disk) 2200, 790, 750 cm^{-1}.

2.12. Macrocyclic binaphthyl dimer (*R*,*R*)-9b

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.45 (6H, s), 3.71 (6H, s), 4.88 (2H, d, J=4.9 Hz), 5.13 (2H, d, J=4.9 Hz), 7.25–7.7 (18H, m), 7.83 (4H, m), 8.09 (2H, s), 8.19 (4H, s).

2.13. Macrocyclic binaphthol dimer (*R*,*R*)-8a. (A representative procedure for deprotection of the MOM groups)

To a solution of (*R*,*R*)-**7a** (184 mg, 0.186 mmol) in THF (20 mL) and methanol (2 mL) was added conc. HCl (1 mL) and the mixture was heated under reflux for 2 h. The mixture was poured into water and extracted twice with $CHCl_3$. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Recrystallization of the crude reside from $CHCl_3$ and hexane gave 103 mg (71% yield) of (*R*,*R*)-**8a**. Concentration of the mother liquor and purification of the residue by silica gel flash chromatography (2% ethyl acetate in benzene) gave additional 43 mg (29%) of (*R*,*R*)-**8a**: mp 280°C (decompose); $[\alpha]_D^{25}$= +445 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.20 (4H, br s), 7.05 (4H, d, J=8.2 Hz), 7.2–7.3 (8H, m), 7.42 (4H, m), 7.68 (4H, m), 7.71 (4H, d, J=7.8 Hz), 8.10 (4H, s); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 89.1, 94.3, 111.8, 113.4, 124.1, 124.5, 125.5, 127.7, 128.1, 128.3, 128.6, 131.6, 133.4, 133.8, 151.2; IR (KBr disk) 3480 (br), 2200, 750 cm^{-1}; MS *m*/*z* (relative intensity) 816 (M^+, 65), 697 (4), 149 (100); HRMS (FAB) calcd for $C_{60}H_{32}O_4$, 816.2300, found 816.2301.

2.14. Macrocyclic binaphthol dimer (*R*,*R*)-8b

Mp 250°C (decompose) (recrystallized from $CHCl_3$ and hexane); $[\alpha]_D^{25}$=−51.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.58 (6H, s), 6.10 (2H, s), 7.07 (2H, d, J=8.4 Hz, 7.14 (2H, d, J=8.3 Hz), 7.22 (2H, br t, J=ca. 7 Hz), 7.27 (2H, br t, J=ca. 7 Hz), 7.31 (1H, br t, J=ca. 7 Hz), 7.36 (2H, br t, J=ca. 7 Hz), 7.42 (4H, m), 7.70 (4H, m), 7.78 (2H, d, J=8.1 Hz), 7.81 (2H, d, J=8. 2 Hz), 8.16 (2H, s), 8.18 (2H, s); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 61.4, 87.7, 90.9, 92.0, 94.9, 112.0, 114.3, 116.7, 124.2, 124.4, 124.6, 125.2, 125.6, 125.8, 127.2, 127.7, 127.8, 128.1, 128.2, 128.3, 128.5, 128.6, 129.9, 132.3, 132. 5, 133.1, 133.9, 134.1, 134.6, 150.5, 155.4; IR (KBr disk) 3500 (br), 2200, 750 cm^{-1}; HRMS (FAB) calcd for $C_{62}H_{36}O_4$, 844.2613, found 844.2630. Anal calcd for $C_{62}H_{36}O_4(H_2O)_2$: C, 84.54; H, 4.58. Found: C, 84.97; H, 4.82.

2.15. Macrocyclic binaphthol dimer (*R*,*R*)-10a

Mp 250°C (decompose) (recrystallized from $CHCl_3$ and hexane); $[\alpha]_D^{25}$=−1160 (*c* 0.35, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.96 (4H, br s), 7.14 (4H, d, J=8.3 Hz), 7.29 (4H, t, J=7.4 Hz), 7.46 (4H, t, J=7.7 Hz), 7.59 (4H, d, J=7.7 Hz), 7.74 (2H, m), 7.88 (4H, d, J=8.1 Hz), 8.00 (2H, s), 8.18 (4H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 85.1, 95.2, 112.0, 113.3, 123.1, 124.2, 125.2, 125.9, 127.8, 128.3, 128.6, 128.9, 130.6, 132.8, 134.0, 151.2; IR (KBr disk) 3490 (br), 2200, 745 cm^{-1}; HRMS (FAB) calcd for $C_{60}H_{32}O_4$, 816.2300, found 816.2305. Anal calcd for $C_{60}H_{32}O_4$: C, 88.22; H, 3.95. Found: C, 88.02; H, 4.34.

2.16. Macrocyclic binaphthol dimer (*R*,*R*)-10b

Mp 250°C (decompose) (recrystallized from $CHCl_3$ and hexane); $[\alpha]_D^{25}$=−1280 (*c* 0.17, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.54 (6H, s), 6.00 (2H, s), 7.13 (4H, d, J=8.6 Hz), 7.17 (2H, d, J=8.7 Hz), 7.24–7.29 (4H, m), 7.35 (2H, t, J=8.8 Hz), 7.40 (2H, d, J=7.6 Hz), 7.42 (2H, d, J=6.6 Hz), 7.53 (2H, t, J=1.8 Hz), 7.55 (2H, t, J=1.6 Hz), 7.84 (2H, d, J=8.1 Hz), 7.88 (2H, d, J=8.1 Hz), 8.07 (2H, s), 8.16 (2H, s), 8.19 (2H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 61.3, 85.0, 87.6, 93.0, 95.3, 112.2, 113.7, 117.4, 123.0, 124.0, 124.2, 124.2, 124.5, 125.2, 125.8, 127.3, 127.7, 128.1, 128.3, 128.6, 128.7, 130.1, 130.16, 130.19, 132.7, 133.9, 134.1, 138.0, 151.3, 156.7; IR (KBr disk) 3510 (br), 745 cm^{-1}; HRMS (FAB) calcd for $C_{62}H_{36}O_4$, 844.2613, found 844.2639.

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8. When the coupling reaction leading to **6a** was carried out by using 20 mol% of the catalyst and 20 equiv. of 1,2-diiodobenzene, the product yield was improved to 59%.
9. For example, 86% of 1,2-diiodobenzene was recovered in the reaction of **5a**.
10. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC Number: 213427. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].