Asymmetric Synthesis of Axially Dissymmetric 1,1′-Binaphthyls *via* an Intramolecular Ullmann Coupling Reaction of (*R*)- and (*S*)-2,2′-Bis(1-bromo-2-naphthylcarbonyloxy)-1,1′-binaphthyl[1,2]

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(Received May 7, 1981)

An Ullmann reaction of the chiral bifunctional substrate containing two 1-bromo-2-naphthyl moieties, (*S*)-2,2′-bis(1-bromo-2-naphthylcarbonyloxy)-1,1′-binaphthyl, gives an intramolecularly coupled 12-membered cyclic diester in a 36% isolated yield. The intramolecular coupling reaction proceeds with virtually complete diastereoselectivity to induce *S*-chirality into the newly formed bond between the two naphthyl units.

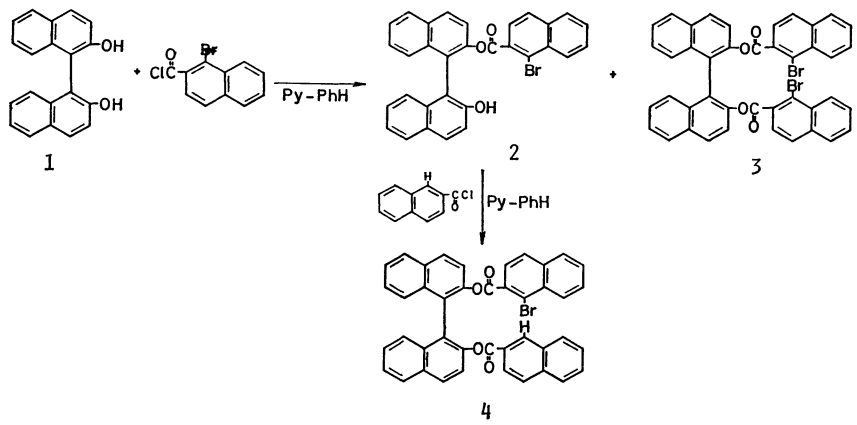
A number of 2,2′-disubstituted 1,1′-binaphthyls have been resolved into atropisomers, and proved to be highly resistant to thermal racemization.[3] The axially dissymmetric binaphthyl structure would be effective for chiral recognition because of its steric bulkiness and structural rigidity.[4,5] Having only the C_2 axis for the element of chirality, and thus minimizing the possibility of complex diastereomeric interactions, the biaryl moiety may also be useful for the elucidation of the mechanism of asymmetric induction. Thus, much attention has recently been centered on asymmetric reactions by the use of axially dissymmetric biaryl derivatives; in some cases a remarkable success has been accomplished.[6,7]

Although there are a number of methods currently available for the synthesis of biaryls,[8] direct routes to their atropisomers are limited:[7a,9] optical resolution of racemates has been adopted in conventional practices for the preparation of the prerequisite atropisomeric binaphthyl skeletons. In 1971, Jacques *et al.*[10] showed that the readily available 1,1′-binaphthyl-2,2′-diol (**1**) can be easily resolved into its antipodes *via* a phosphate ester. We have for some time been trying to utilize the axial dissymmetry of atropisomeric **1** for asymmetric synthesis of other biaryls, and here we wish to describe copper-promoted Ullmann biaryl coupling of 1-bromo-2-naphthoates of **1**.[1]

Results and Discussion

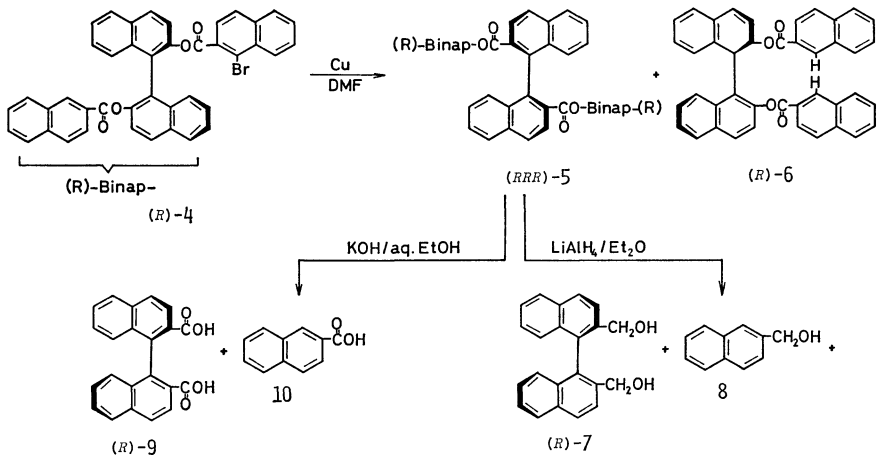
The synthesis of 1-bromo-2-naphthoates of **1** (**3** and **4**, and their atropisomers) is outlined in Scheme 1. 1-Bromo-2-naphthoyl chloride, prepared from 1-bromo-2-naphthoic acid[11] by reaction with thionyl chloride, was allowed to react with **1** in pyridine-benzene to give the corresponding monoester **2** and diester **3**. Each ester product was cleanly separated by column chromatography on alumina; benzene eluted the latter only, while ethanol–benzene could be used to liberate the former. The hydroxy ester (**2**) was in turn treated with 2-naphthoyl chloride to yield the mixed diester **4**. Optically active substrates were synthesized by use of (*S*)- and (*R*)-**1**.

Although the optical yield was poor, the Ullmann coupling reaction of the chiral substrates, (*R*)- and (*S*)-**4**, induced (*R*)- and (*S*)-chirality, respectively, into the newly formed 1,1′-binaphthyl bond, as evidenced as follows: In a typical reaction, (*R*)-**4** was treated with freshly activated copper powder in gently refluxing DMF under nitrogen. Debromination of the substrate ((*R*)-**4**) was completed within 5 h by heating under reflux to give a 15:85 mixture of the reduction ((*R*)-**6**) and the coupled product ((*RRR*)-**5**) in an almost quantitative yield (Scheme 2). Reductive cleavage of the ester linkage of the coupled product ((*RRR*)-**5**) with lithium aluminum hydride (LAH) in boiling ether gave a sample of (*R*)-2,2′-bis(hydroxymethyl)-1,1′-binaphthyl ((*R*)-**7**), which had $[\alpha]_{546}^{23}$ +3.5° (*c* 0.8, acetone). This value corresponds to the optical purity of 4% on the assumption that the enantiomerically pure (*R*)-**7** has the value of $[\alpha]_{546}^{23}$ +86° (*vide infra*). The diol was transformed into (*R*)-α-methoxy-α-trifluoromethylphenylacetic acid ester ((*R*)-MTPA ester);[12] an ^{1}H NMR spectral study of

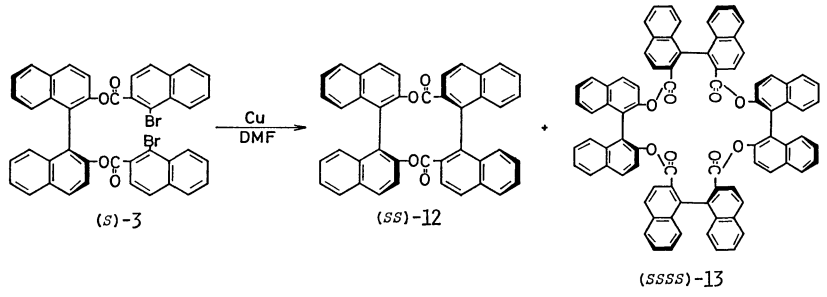


1 2 3 4

Scheme 1.



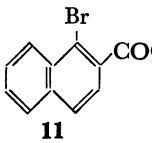
Scheme 2.



Scheme 3.

the ester in the presence of a chiral shift reagent, Eu(fod)$_3$, also showed the % e.e. of the sample to be 4—6%. Any significant racemization of the substrate ((*R*)-**4**) or products ((*RRR*)-**5** and (*R*)-**6**) under the reaction conditions was ruled out by considering the optical purity of the recovered (*R*)-**1**. Alternatively, (*R*)-1,1′-binaphthyl-2,2′-dicarboxylic acid (*R*)-**9** of 3% optical purity[13] was obtained *via* a hydrolytic treatment of a similar Ullmann product with KOH in boiling aq ethanol.

We have previously shown that an Ullmann coupling of *C*-chiral alcohol esters of 1-bromo-2-naphthoic acid induces axial dissymmetry into the 1,1′-binaphthyl bonds, but that the highest optical yield attained is only 13%.[9a] These and above results may imply that intermolecular Ullmann coupling of chiral substrates of type **11** is discouraging for asymmetric synthesis of binaphthyl atropisomers.



(R*: Chiral substituent)

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On the other hand, we have found that copper-promoted reaction of bifunctional substrates, (*S*)- and (*R*)-**3**, is promising: Ullmann products from these diesters were hydrolyzed by heating under reflux with KOH in aq ethanol to give **9**'s in *ca.* 45% chemical yields. The apparent net optical yield for the joining of two binaphthyl units was estimated to be 30—45% on the basis of optical rotations of the recovered diacids. It seemed that these rather high asymmetric inductions should be attributed to *intramolecular* interactions of the substrates, as the *intermolecular* coupling of atropisomeric **4** scarcely induced axial dissymmetry.

Thus, we tried an attempt to enhance the unimolecular debromination of the diester, (*S*)-**3**. To a well stirred suspension of copper powder in gently refluxing DMF was slowly added a sample of (*S*)-**3** over 1 h period, and then heating was continued for another 5 h. As judged by TLC and HPLC, however, the intended intramolecular Ullmann coupling of (*S*)-**3** to **12** was accompanied by the formation of serious amounts of reduction product ((*S*)-**6**), dimeric ((*SSS*)-**5** and (*SSSS*)-**13**), and other higher oligomeric products (Scheme 3). It should be pointed out here that careful HPLC analysis, including variation of column and eluant, showed only one peak for the intramolecularly coupled product (**12**).[14] A chromatography of the Ullmann product on a silica-gel column using chloroform (1% ethanol) as the eluant gave a 36% isolated yield of the intramolecularly coupled cyclic diester ((*SS*)-**12**) as a white powder. The compound was characterized by elemental analysis, mass, IR, and other spectral studies as well as chemical transformation. Thus, treatment of the cyclic diester with LAH in ether–THF gave only two diols, (*S*)-**7** and (*S*)-**1**, the specific rotations being $[\alpha]_{546}^{23}$ −86.0° (*c* 1.4, acetone) and $[\alpha]_{D}^{24}$ −34.9°

(c 1.03, THF), respectively. These values compare well with literature ones claimed for enantiomerically pure samples; $[\alpha]_{546}^{23}$ −83.0° for (S)-**7**[11] and $[\alpha]_D^{25}$ −33.3° for (S)-**1**.[6,15] Furthermore, within the limits of the NMR detection at 60 MHz, the (R)-MTPA esters of these diols showed, in the presence of $Eu(fod)_3$, no indication of the presence of (R)-diols.

These observations unequivocally indicate that the two 1,1'-binaphthyl axes in the cyclic diester (**12**) have an *SS*-configuration of high enantiomeric purity. This leads to the conclusion that intramolecular Ullmann coupling of (S)-**3** proceeds, though under rather severe reaction conditions, with a virtually complete diastereoselectivity to give cyclic diester of *SS*-configuration ((*SS*)-**12**). An inspection of CPK models of the cyclic diester **12** suggests that two sets of Naph–COO–Naph moieties of (*SS*)-**12** arrange to a double helix-like structure to accommodate the 12-membered cyclic diester as schematically shown in Fig. 1, while those of (*SR*)-counterpart must be bent to a highly strained right angle in order to form the cycle (Fig. 2), thus strongly favoring the *SS*-configuration over *SR*-isomer. In conclusion, the origin of the remarkable diastereoselectivity in the intramolecular coupling may be attributed to the steric requirements of the product cyclic diester, while at present there is no basis for mechanistic conclusions with regard to the Ullmann reaction.

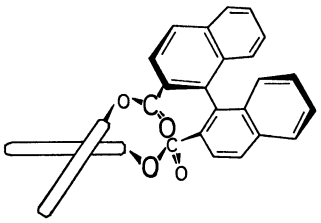

Fig. 1. (*SS*)-**12**.

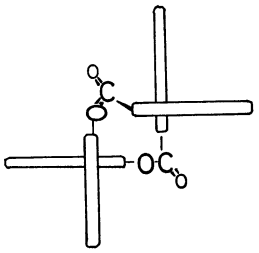

Fig. 2. (*SR*)-**12**.

It is interesting that both of the newly formed 1,1'-binaphthyl bonds in the cyclic dimer ((*SSSS*)-**13**) have also *SS*-chirality of rather high optical purity, though the paucity of the sample has been retarding the elucidation of their accurate structures. Further work along this line is in progress.

Experimental

Measurements. IR spectra were obtained on a Shimadzu IR 430 spectrophotometer. NMR spectra were determined on a Hitachi R-24A instrument using hexamethyldisiloxane as an internal standard in CCl_4 unless otherwise stated. Mass spectra were recorded on a JEOL JMS-D300 double focusing mass spectrometer with direct sample injection. Optical rotations were recorded on a Union PM-101 automatic digital polarimeter in a 1-cm cell at ambient temperature. High performance liquid chromatography (HPLC) was carried out on a JASCO TRIROTAR-III and/or JASCO FAMILIC-100 instrument using columns packed with JASCO SC-01 (ODS), HP-01 (styrene-divinylbenzene), and WC-03 (Carbowax 400) with conventional eluants. Molecular weight was determined in benzene solution with a Hitachi-Perkin-Elmer 115 vapor pressure osmometer. All melting points were corrected.

Materials. Analytical and preparative TLC were carried out on Merck Silica Gel 60H. Solvents for experiments requiring anhydrous conditions were distilled from CaH_2 and stored under nitrogen. 1-Bromo-2-naphthoic acid[11] (mp 188—190 °C), racemic **1**[17] (mp 217—218 °C), and 2-naphthoyl chloride[18] (bp 130—131 °C/400 Pa, mp 51.3—52.3 °C) were prepared according to the reported methods.

1-Bromo-2-naphthoyl Chloride: A mixture of 1-bromo-2-naphthoic acid (5.95 g, 23.7 mmol) and 10 ml† of thionyl chloride was refluxed for 3 h, and the resulting brown-red solution was evaporated to dryness. The residue was dissolved in hot cyclohexane, filtered hot from activated charcoal, and recrystallized to give pale yellow, feather-like crystals: yield, 5.40 g (84.5%); mp 82.5—83.5 °C; IR (KBr) 1780 cm^{-1} (>C=O). Found: C, 49.30; H, 2.10; halogen, 43.07%. Calcd for $C_{11}H_6BrClO$: C, 49.02; H, 2.24; halogen, 42.80%.

Resolution of **1**: The method of Jacques *et al.*[10] and Kyba *et al.*[6] was slightly modified. To a stirred solution of racemic **1** (50 g, 0.175 mol) in CH_2Cl_2 (200 ml) and pyridine (150 ml) was added dropwise 20 ml of $POCl_3$. The mixture was refluxed for 3 h, and then volatiles were evaporated under slightly reduced pressure. The residue was dissolved in a hot Na_2CO_3 (60 g) solution in water (2 l††). An amount of activated charcoal was added, and the mixture was filtered hot. The filtrate was made acidic by addition of 50 ml concd HCl, and the resulting white slurry was stirred overnight at room temperature. The white precipitate was collected and dried in a rotatory evaporator *in vacuo* to give 52.4 g (85.7% yield) of the acid phosphate of **1**. Resolution of the binaphthyl acid phosphate with cinchonine gave, after successive two runs of crystallization from MeOH–H_2O followed by HCl treatment, a 12.0 g sample of (+)-acid (46% yield): $[\alpha]_D^{22}$ +605° and $[\alpha]_{546}^{22}$ +717° (c 1.16, MeOH) (lit,[6] $[\alpha]_{546}^{25}$ +722° (c 0.9, MeOH). The levorotatory acid was recovered from the mother filtrate: 8.3 g (32% yield); $[\alpha]_D^{22}$ −608°; $[\alpha]_{546}^{22}$ −721° (c 0.824, MeOH) (lit,[6] $[\alpha]_{546}^{25}$ −734° (c 0.9, MeOH)). The (+)- and (−)-phosphoric acid were treated with LAH in THF[6] to give (S)-(−)- and (R)-(+)-**1**, respectively.

(S)-1: 8.69 g (88% yield based on the (+)-phosphoric acid); mp 209—210 °C (PhMe); $[\alpha]_D^{22}$ −35.0° (c 1.18, THF).

(R)-1: 5.72 g (84% yield); mp 208—210 °C (PhH); $[\alpha]_D^{23}$ +34.6° (c 0.892, THF).

2-Hydroxy-2'-(1-bromo-2-naphthylcarbonyloxy)-1,1'-binaphthyl (2): To a stirred, water-chilled solution of racemic **1** (1.0 g, 3.49 mmol) in PhH(20 ml)–pyridine(5 ml) was slowly added 0.945 g (3.51 mmol) of 1-bromo-2-naphthoyl chloride. The mixture was stirred overnight at ambient temperature and finally heated under reflux for 3 h. The reaction was quenched with 50 ml of 2 M (1 M=1 mol dm^{-3})

† 1 ml=1 cm^3.

†† 1 l=1 dm^3.

HCl, and extracted with portions of PhH. The combined extracts were washed successively with 2 M HCl, 1 M Na_2CO_3, and then H_2O, and dried over Na_2SO_4. The organic phase was concentrated to a *ca.* 5 ml volume, which was chromatographed on alumina column (Wako-Activated Alumina, 300 mesh). After a small amount of **3** (*vide infra*) was eluted with PhH, 1.32 g of **2** was recovered by use of PhH–EtOH (10:1) eluant (73% yield based on **1**): mp 202—203 °C (PhH); IR (KBr) 3450 (–OH) and 1735 cm^{-1} (>C=O). Found: C, 72.01; H, 3.88; Br, 15.60%. Calcd for $C_{31}H_{19}O_3Br$: C, 71.68; H, 3.69; Br, 15.38%.

Similar reactions of (*S*)- and (*R*)-**1** gave their corresponding atropisomeric **2**.

(S)-**2**: Mp 179—180 °C (PhH); $[\alpha]_D^{22}$ −32.0° (*c* 0.874, acetone); IR (KBr) 3450 (–OH) and 1730 cm^{-1} (>C=O). Found: C, 71.56; H, 3.69; Br, 15.72%.

(R)-**2**: Mp 177—178 °C (PhH); $[\alpha]_D^{23}$ +34.1° (*c* 1.38, acetone).

2,2′-Bis(1-bromo-2-naphthylcarbonyloxy)-1,1′-binaphthyl (**3**): Following the procedure used for the preparation of **2**, a 93% yield of **3** was obtained by the reaction of 2.2 g (8.16 mmol) of 1-bromo-2-naphthoyl chloride and **1** (1.10 g, 3.84 mmol) in PhH(20 ml)–pyridine(5 ml): yield, 2.69 g; mp 226.5—227 °C; IR (KBr) 1745 cm^{-1} (>C=O). Found: C, 67.04; H, 3.34; Br, 21.55%. Calcd for $C_{42}H_{24}O_4Br_2$: C, 67.04; H, 3.21; Br, 21.24%.

(S)-**3**: Mp 180—182 °C; $[\alpha]_D^{22}$ +34.7° (*c* 0.922, acetone); IR (KBr) 1750 cm^{-1} (>C=O). Found: C, 66.81; H, 3.16; Br, 20.84%.

(R)-**3**: Mp 177—180 °C; $[\alpha]_D^{24}$ −33.5° (*c* 1.08, acetone).

2,2′-Bis(2-naphthylcarbonyloxy)-1,1′-binaphthyl (**6**): Mp 211—213 °C; IR (KBr) 1730 cm^{-1} (>C=O). Found: C, 84.73; H, 4.46%. Calcd for $C_{42}H_{26}O_4$: C, 84.83; H, 4.40%.

2-(2-Naphthylcarbonyloxy)-2′-(1-bromo-2-naphthylcarbonyloxy)-1,1′-binaphthyl (**4**): A mixture of 3.71 g (7.14 mmol) of **2** and 1.41 g (7.40 mmol) of 2-naphthoyl chloride in PhH-(40 ml)–pyridine(5 ml) was stirred overnight at ambient temperature and then refluxed for 3 h. The reaction mixture was diluted with 50 ml of PhH, to which was added 100 ml of 2 M HCl. The solid was filtered off and recrystallized from $CHCl_3$ to give 3.86 g (5.73 mmol) of **4**: yield 80.3%; mp 248—249 °C; IR (KBr) 1725 and 1745 cm^{-1} (>C=O). Found: C, 74.66; H, 3.68; Br, 12.12%. Calcd for $C_{42}H_{25}O_4Br$: C, 74.89; H, 3.74; Br, 11.86%.

Optically active **4**'s were soluble in benzene and purified by alumina column chromatography.

(S)-**4**: Vitreous powder; $[\alpha]_D^{24}$ ≈0°; $[\alpha]_{436}^{24}$ +20.3° (*c* 1.03, acetone); IR (KBr) 1730 cm^{-1} (>C=O, broad).

(R)-**4**: Vitreous powder; $[\alpha]_{436}^{24}$ −18.9° (*c* 2.17, acetone).

Ullmann Reaction of (R)-**4**. Just prior to the reaction, 1.0 g of copper powder (200 mesh, Junsei Chemical Co.) was pretreated for activation according to a literature procedure,[19] except that all manipulations were carried out under nitrogen and that the acetone-moist powder was further washed with several portions of PhH. The copper powder and 0.524 g (0.778 mmol) of (*R*)-**4** were charged into a 30 ml round-bottomed flask equipped with a reflux condenser topped with nitrogen inlet. The whole system was evacuated and refilled with nitrogen, and then 10 ml of DMF was added to the flask. The mixture was magnetically stirred and heated to gentle reflux under nitrogen. After 5 h heating, the cooled mixture was diluted with 50 ml of PhH, and solids were filtered off. The filtrate was washed with 2 M HCl and then water, and dried over Na_2SO_4. Evaporation of the solvent *in vacuo* afforded a pale yellow residue, 0.458 g (0.770 mmol, calculated as **6**), which was comprised of a 15:85 mixture of (*R*)-**6** and (*RRR*)-**5**, as judged from the peak areas of UV absorption at 254 nm on HPLC (JASCO SC-01 column, MeCN/H_2O (98/2) eluant). A negative Beilstein test confirmed the absence of the unreacted ester. A preparative TLC of an aliquot of the Ullmann product (0.40 g) using PhH as eluant gave 21 mg of (*R*)-**6** and 0.302 g of (*RRR*)-**5**. The (*RRR*)-**5** melted gradually over a temperature range of 150—160 °C (dec); $[\alpha]_D^{23}$ +91.8° (*c* 1.0, acetone). Found: C, 84.85; H, 4.31%. Calcd for $C_{84}H_{50}O_8$: C, 84.98; H, 4.24%.

The (*RRR*)-**5** (0.25 g) was boiled with 0.2 g of LAH in ether for 3 h. The reaction was worked up as usual, and a preparative TLC with $CHCl_3$/AcOEt (4/1) enabled the recovery of (*R*)-**7** (36 mg, $[\alpha]_{546}^{23}$ +3.5° (*c* 0.8, acetone)), (*R*)-**1** (80 mg, $[\alpha]_D^{23}$ +35.2° (*c* 0.90, THF)), and **8** (26 mg). The diol ((*R*)-**7**) was completely acylated in CCl_4 with excess acid chloride of (*R*)-(+)-MTPA in the presence of excess 4-dimethylaminopyridine to give the diastereomeric pair of di-(*R*)-MTPA ester.[12b] NMR ($CDCl_3$): δ 3.33 (3H, $-OCH_3$), 2H at 4.76 ($-CH_2-$ for (*RR*)-isomer) and 4.82 ($-CH_2-$ for (*SR*)-isomer), 7.25 (10H, –Ph), and 6.7—8.1 (12H, Naphthyl). Addition of $Eu(fod)_3$ caused separation of the $-OCH_3$ signal, where the induced downfield shift for the (*SR*)-ester was larger than that for the (*RR*)-isomer.

Ullmann Reaction of (R)- *and* (S)-**3**. *Procedure A*: The following example is typical. As above, a mixture of (*R*)-**3** (1.00 g, 1.33 mmol) and activated copper powder (prepared from 1.2 g of Cu) in 10 ml of DMF was refluxed for 5 h with vigorous stirring under nitrogen. The organic residue obtained weighed 0.785 g, $[\alpha]_D^{24}$ +70.4° (*c* 0.83, PhH). This sample was refluxed with 2 g of KOH in 95% aq EtOH (20 ml) for 5 h. After the solvent was evaporated, the residue was dissolved in 30 ml of H_2O and made acidic with concd HCl to give a white precipitate. The mixture was extracted with portions of ether. Combined ether extracts were then extracted with 1 M Na_2CO_3; after usual work-up of the aq layer, 2-naphthoic acids ((*R*)-**9**+**10**) were recovered (0.42 g, 92% yield) while diol ((*R*)-**1**) was obtained from the ether layer (0.34 g, 89%, $[\alpha]_D^{24}$ +33.2° (*c* 1.00, THF)). After a TLC (EtOH/28% NH_4OH/H_2O= 16/3/1) of the acid mixture, 0.203 g of diacid ((*R*)-**9**, 44.6% yield based on (*R*)-**3**) and 0.140 g of monoacid (**10**) were obtained.

(R)-**9**: $[\alpha]_D^{24}$ +34.0° (*c* 0.78, 0.1 M NaOH); mp 255—265 °C (dec).

In another run, 0.302 g (0.401 mmol) of (*S*)-**3** was treated with Cu (1 g) in 10 ml of DMF at 120—130 °C for 10 h. The specific rotation of the diacid ((*S*)-**9**) was $[\alpha]_D^{24}$ −49.4° (*c* 0.85, 0.1 M NaOH); the yield was 60 mg.

Procedure B: To a well stirred, gently refluxing suspension of freshly activated copper powder (prepared from 3 g of Cu) in 50 ml of DMF was slowly added (*S*)-**3** (1.54 g, 2.05 mmol) over 1 h period under nitrogen, and heating was continued for another 5 h. The pale yellow organic residue (1.21 g, $[\alpha]_D^{24}$ −196.5° (*c* 1.11, PhH)) was analyzed by HPLC (JASCO SC-01 column, MeCN) to show the presence of, in the order of elution, (*SS*)-**12** (1.00), (*S*)-**6** (0.20), (*SSSS*)-**13** (0.21), (*SSS*)-**5** (0.19), and other higher oligomeric products (in parentheses are shown relative peak areas of UV absorption at 254 nm). A chromatography on a silica-gel column (Wako Gel C-200) using $CHCl_3$ (1% EtOH) as eluant gave 0.437 g of (*SS*)-**12** and 40 mg of (*SSSS*)-**13** as well as trace amounts of (*S*)-**6** and (*SSS*)-**5**.

(SS)-*Tetranaphtho*[*2,1*-b:*1,2*-d:*2,1*-h:*1,2*-j][*1,6*]*dioxacyclododeca-2,4,8,10-tetraene-7,12-dione* ((SS)-**12**): Mp >350 °C; $[\alpha]_D^{23}$ −457.6° (*c* 0.507, PhH); IR (KBr) 1752 cm^{-1} (>C=

O); MS (70 eV), *m/e* (%), 592 (M^+, 27.1), 280 (8.3), 268 (26.6), 252 (4.2), and 239 (4.2). Found: C, 85.41; H, 3.81%. Calcd for $C_{42}H_{24}O_4$: C, 85.12; H, 4.08%.

The cyclic diester ((*SS*)-**12**, 0.332 g, 0.56 mmol) was treated with 0.15 g of LAH in ether(30 ml)–THF(10 ml). After a TLC ($CHCl_3$/AcOEt=4/1), 0.149 g (0.474 mmol) of (*S*)-**7** ($[\alpha]_{546}^{23}$ −86.0° (*c* 1.43, acetone)) and 0.124 g (0.433 mmol) of (*S*)-**1** ($[\alpha]_D^{24}$ −34.9° (*c* 1.03, THF)) were recovered.

(SSSS)-***13***: Mp >400 °C; M.W. 1220 (calibrated with (*SS*)-**12** (M.W.=592)); $[\alpha]_D^{25}$ ≈0° (*c* 0.304, PhH); $[\alpha]_{436}^{24}$ −291° (*c* 0.134, PhH); IR (KBr) 1745 cm^{-1} (>C=O). Found: C, 84.75; H, 3.63%. Calcd for $C_{84}H_{48}O_8$: C, 85.12; H, 4.08%.

LAH treatment of the cyclic dimer (*ca.* 30 mg) gave a *ca.* 8 mg sample of (*S*)-**7**, the specific rotation of which was estimated to be $[\alpha]_{546}^{23}$ −75——85° (acetone).

(*S*)-***6***: MS (70 eV), *m/e* (%), 594 (M^+, 22.3), 440 (2.5), 268 (2.7), 156 (8.1), and 155 (56.3).

The (*SSS*)-**5** was inferred from its retention volume on HPLC and IR spectrum.

We are grateful to Professor Shozo Yamaguchi and Dr. Kuninobu Kabuto in our University for helpful suggestions and kind offering of reagents for the preparation of the (*R*)-MTPA esters. This work was partly supported by a Grant-in-Aid for Scientific Research No. 465280 from the Ministry of Education, Science and Culture.

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