AXIALLY CHIRAL SYNTHONS FOR DENDRIMER SYNTHESIS

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Received November 15, 1996
Accepted January 27, 1997

Axially chiral synthons for chiral dendrimer construction based on 2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylic acid were prepared, namely, chiral connecting units (**3**, **6**, **8**), chiral branching units (**10**, **12**, **14**), and chiral surface units (**5**, **17**). Regioselective chloromethylation of methyl 3′-acetoxymethyl-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (**7**) was also studied.
Key words: Dendrimers; Chiral synthons; Binaphthols.

Chemists have long sought ways to control the molecular structure of synthetic high-molecular weight compounds at a level comparable to that realized in biological macromolecules. Having such methods available might make it possible to finely tune the properties of materials thus obtained. One method recently discovered has already resulted in a new set of materials called dendrimers (Fig. 1) as witnessed by numerous review articles[1–8]. Some of these materials are now available commercially[9]. Dendrimers as highly ordered polymers are believed to provide solutions to a wide variety of technological and ecological problems, from removal of heavy metals pollutants from industrial wastes to their use as highly efficient drug delivery systems and even

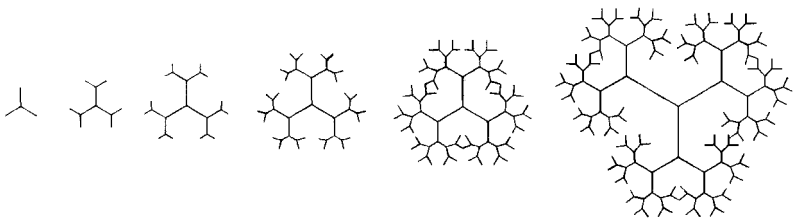

FIG. 1
Dendrimer with triple-branched core (G-0), up to generation five (G-5)

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the formation of artificial chemical cells and tissues[5,7]. Very recently dendrimers have been used as haemoprotein mimics[10,11], protein labels in electron microscopy[12], platform for deposition of monolayers[13], chemical sensors[14], light harvesting antennae[15], saccharide "sponge"[16], molecular architecture for photoinduced electron transfer[17], and unimolecular micelles[18].

Since the first synthesis of these multibranched cascade molecules has been published by Vögtle in 1978 (ref.[19]), numerous synthetic approaches to dendritic macromolecules have been developed, including divergent and convergent syntheses as well as one-step routes[7]. Recently self-assembly has been successfully used for a very efficient synthesis of dendrimers[20,21]. Not surprisingly, chiral dendrimers have attracted the attention of synthetic chemists as a model for biopolymers. As a matter of fact, the first "real" dendrimer of Denkewalter[22] was based on an amino acid and this type of building block has been used many times later[23–28]. Recently carbohydrates have been also used for the synthesis of chiral dendrimers[29–31] as well as non-natural building blocks[32–34]. Chiral dendrimers have been used as polymeric liquid crystals[35] and polymeric asymmetric catalysts[36,37].

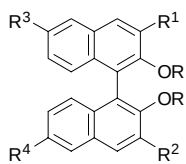
The extraordinary activity in the field of dendrimers, and of chiral dendrimers in particular, prompted us to disclose our synthetic approach to axially chiral building blocks well-suited for construction of chiral dendrimers. Here, we report on the synthesis of three types of 2,2′-binaphthalene-1,1′-diol (binaphthol) derivatives. They are currently used as axially chiral connectors, branching and finally surface units in the synthesis of axially chiral dendrimers which is under way in our laboratory.

RESULTS AND DISCUSSION

The synthesis starts from racemic or optically active 2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylic acid (**1**) prepared by modification of a solid-phase coupling reaction[38] followed by known resolution procedure[39].

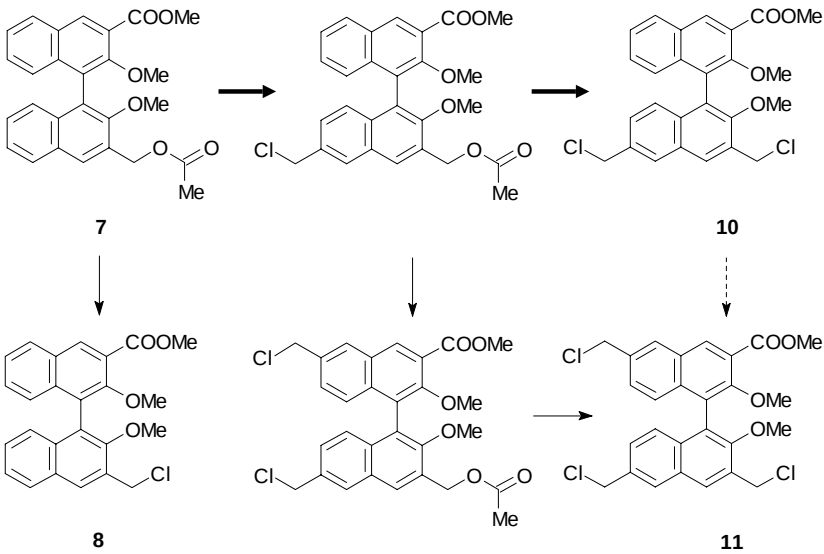
The free *R*- and *S*-hydroxy acids (**1**) were tetramethylated with methyl iodide in anhydrous dimethylformamide in the presence of potassium carbonate. The method is a modification of known procedure[40] and diester **2** was isolated in 88% yield for *R*-**2**, and 93% yield for *S*-**2**. Racemic **2** was prepared from known dimethyl 2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate[39] using methyl iodide and potasium carbonate in anhydrous acetone. Diester **2** was partially hydrolyzed following the method published for dimethyl terephthalate[41] and desired monoester **3** was isolated along with corresponding acid **1** and recovered diester **2** in 49, 45, and 50% yields for *R*,*S*-, *R*-, and *S*-**3**, respectively. The monoester *R*,*S*-**3** was alternatively prepared by deprotection of methyl phenacyl ester (see below). Analogously, methylation of known racemic[42–44] as well as chiral[45] 2,2′-dihydroxy-1,1′-binaphthalene-3-carboxylic acid its methyl ester proceed under known[40] conditions giving *R*,*S*-, *R*-, and *S*-**4** in 89, 94, and 83% yields, respectively. Hydrolyses of esters were performed using potassium hydroxide in methanol.

R,*S*- and *S*-**5** were isolated in 95 and 99% yields, respectively. Reduction of carboxyl group of **3** with the diborane–THF complex using known procedure[46,47] yielded alcohols **6** *R*,*S*, *R*, and *S* in 97, 81, and 87%, respectively. Acetylation of both racemic and chiral alcohols **6** with acetyl chloride proceeded very smoothly giving *R*,*S*-, *R*-, and *S*-**7** in 97, 94, and 99% yields, respectively. Racemic **6** was transformed to chloromethyl derivative *R*,*S*-**8** by treatment with excess of thionyl chloride in almost quantitative yield. Analogously, benzoate *R*,*S*-**9** was prepared using benzoyl chloride and 4-(dimethylamino)pyridine in dichloromethane again in quantitative yield. The key-step of our synthetic appropach was chloromethylation[48] of acetate **7**. We have reasoned that electron-donating group in 3′-position of binaphthalene moiety should direct the reaction regioselectively to 6′-position and it is exactly what we have observed. We have also found that chloromethylation of acetoxymethyl derivatives *R*,*S*- and *S*-**7** is accompanied by nucleophilic displacement of acetoxy group giving bis(chloromethyl) derivatives *R*,*S*- and *S*-**10**, both isolated in 50% yield. We have found that composition of reaction products mixtures obtained from the chloromethylation of **6**–**9** could be analysed by NMR spectroscopy only. The course of reaction can be expressed by the reac-



	R	R^1	R^2	R^3	R^4
(*R*,*S*), (*R*), (*S*) **1**	H	COOH	COOH	H	H
(*R*,*S*), (*R*), (*S*) **2**	CH_3	COOMe	COOMe	H	H
(*R*,*S*), (*R*), (*S*) **3**	CH_3	COOMe	COOH	H	H
(*R*,*S*), (*R*), (*S*) **4**	CH_3	COOMe	H	H	H
(*R*,*S*), (*S*) **5**	CH_3	COOH	H	H	H
(*R*,*S*), (*R*), (*S*) **6**	CH_3	COOMe	CH_2OH	H	H
(*R*,*S*), (*R*), (*S*) **7**	CH_3	COOMe	CH_2OAc	H	H
(R,S) **8**	CH_3	COOMe	CH_2Cl	H	H
(R,S) **9**	CH_3	COOMe	CH_2OCOPh	H	H
(*R*,*S*), (*S*) **10**	CH_3	COOMe	CH_2Cl	CH_2Cl	H
(*R*,*S*), (*S*) **11**	CH_3	COOMe	CH_2Cl	CH_2Cl	CH_2Cl
(*R*,*S*), (*S*) **12**	CH_3	COOMe	$CH_2OCH_2CH_2OH$	$CH_2OCH_2CH_2OH$	H
(*R*,*S*), (*S*) **13**	CH_3	COOH	$CH_2OCH_2CH_2OH$	$CH_2OCH_2CH_2OH$	H
(*R*,*S*), (*S*) **14**	CH_3	$COOCH_2COPh$	$CH_2OCH_2CH_2OH$	$CH_2OCH_2CH_2OH$	H
(R,S) **15**	CH_3	COOMe	$COOCH_2COPh$	H	H
(*R*,*S*), (*S*) **16**	CH_3	COOMe	CH_2OMe	CH_2OMe	H
(*R*,*S*), (*S*) **17**	CH_3	COOH	CH_2OMe	CH_2OMe	H

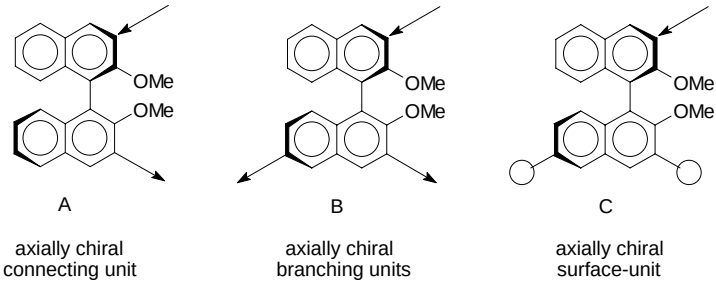
tion sequence shown in Scheme 1, where bold arrows indicate independently proven reactions, normal arrows indicate reactions deduced from NMR spectra, and dotted arrow indicates possible reaction. Compound **7** is chloromethylated in position 6′ first, then acetoxymethyl group is converted to chloromethyl group giving **10** as main product. At the same time the chloromethylation is proceeding further to position 6 and the intermediate thus formed is converted to tris(chloromethyl) derivative **11**. This compound is always present in reaction mixture and makes the purification of **10** difficult.



SCHEME 1

Bischloromethyl ester **10** was used as starting material for preparation of dendrimer branching unit. Reaction with silver oxide in ethylene glycol afforded a mixture of ester *R*,*S*- and *S*-**12** contaminated with ethylene glycol esters in total 77 and 78% yield, respectively. The mixture of both esters was found to be easily hydrolyzed with potassium hydroxide in water–methanol–THF mixture giving pure acids *R*,*S*- and *S*-**13** in 88 and 90% yields, respectively. These acids were further transformed to carboxyl-protected phenacyl esters *R*,*S*- and *S*-**14** by reaction[49] with (bromoacetyl)benzene in 73 and 78% isolated yields, respectively. Analogously, diester **15** was prepared in 91% yield from **3** and was found to be easily and selectively reduced with Zn in acetic acid back into starting *R*,*S*-**3** in quantitative isolated yield. This procedure will be useful in the later stages of dendrimer synthesis. Finally, bis(chloromethyl) ester was transformed to esters *R*,*S*- and *S*-**16** (yields 98 and 85%, respectively) using reaction with methanol and silver oxide. These ester were finally hydrolyzed to corresponding acids *R*,*S*- and *S*-**17** in 93 and 98%, respectively.

Thus, compounds **3**, **6**, and **8** can be regarded as axially chiral connecting units of type A, compounds **10**, **12**, and **14** as axially chiral branching units of type B and finally compounds **5** and **17** as axially chiral dendrimer surface-unit of type C as shown in Scheme 2. All these synthons are now used in our laboratory to construct chiral dendrimers.



SCHEME 2

EXPERIMENTAL

Melting points were taken on a Boetius apparatus and temperature data are uncorrected. NMR spectra (δ, ppm; *J*, Hz) with TMS as internal standard were measured on a Varian Gemini 300 HC spectrometer in $CDCl_3$ solutions at 298 °C. Mass spectra were recorded on a Jeol DX 303/DA 5000 mass spectrometer and infrared spectra (ν, cm^{-1}) on a Nicolet 750 FT IR spectrometer. Optical rotations were obtained with a JASCO Digital Polarimetr DIP370 in a 1 dm thermostatted cell. All solvents were distilled and dried before use.

(*R*,*S*)-2,2′-Dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylic Acid (*R*,*S*-**1**)

A mixture of finely ground 3-hydroxy-2-naphthoic acid (45.0 g, 239 mmol) and ferric chloride hexahydrate (130.0 g, 478 mmol) was heated to 60 °C (hydrogen chloride was evolved) for 25 h, cooled to ambient temperature. Hydrochloric acid (1 mol l^{-1}, 500 ml) was added and solid phase was filtered off and dissolved in 3% sodium hydroxide (1 000 ml). Cold aqueous solution was extracted with diethyl ether (100 ml) and then acidified with concentrated hydrochloric acid to pH 1. The solid phase was collected by filtration and washed with cold water. Raw acid was dried (8 h, 60 °C), dissolved by refluxing in tetrahydrofuran (200 ml). Triethylamine (40 ml) was added dropwise to the hot solution and set aside. Crystalline salt was collected after standing 2 days at ambient temperature and one day at –18 °C, the salt was redissolved in a minimum volume of 5% sodium hydroxide and the solution was acidified with concentrated hydrochloric acid to pH 1. The solid was filtered off, washed with water and dried *in vacuo* (250 Pa, 120 °C). In this way 40.2 g (90%) of acid **1** was obtained. This acid was again crystallized as salt with triethylamine (prepared as above using 35 g triethylamine in 180 ml tetrahydrofuran) and after the work-up described above, 30.0 g (67%) of pure yellow *R*,*S*-**1** was isolated (m.p. 337–340 °C with decomposition; ref.[39] gives m.p. > 285 °C).

Dimethyl (*R,S*)-2,2′-Dimethoxy-1,1′-binaphthalene-3,3′-dicarboxylate (**2**)

Procedure A: To dimethyl 2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate (25.0 g, 62 mmol) in anhydrous acetone (100 ml) solid anhydrous K_2CO_3 (34.1 g, 247 mmol) was added followed by methyl iodide (19 ml, 308 mmol). The reaction mixture was refluxed with stirring and every 24 h new portion of methyl iodide (19 ml, 308 mmol) was added until the fourth day when again K_2CO_3 (17.1 g, 123 mmol) was added and mixture was stirred and refluxed for the last 24 h, cooled, evaporated *in vacuo* diluted with water (100 ml) and left standing at 0 °C for 2 h. Filtration and drying at 70 °C yielded 26.58 g (100%) of pure *R,S*-**2**, m.p. 108–111 °C.

Procedure B: Pure acid **1** (24.0 g, 64 mmol) was suspended in dry DMF (250 ml) and anhydrous powdered K_2CO_3 (44.3 g, 320 mmol) was added at once with stirring. Evolution of carbon dioxide subsided within 20 min and was followed by addition of methyl iodide (31 ml, 500 mmol). Stirring was continued for next 24 h and the reaction was quenched by pouring onto mixture of ice and water (500 ml). The mixture was extracted with diethyl ether (3 × 250 ml) and combined organic phases were washed with ice water (250 ml), dried with $MgSO_4$ and evaporated *in vacuo* yielding 27.2 g of crude **2**. It was purified by column chromatography (150 g silica gel, elution with chloroform) and 25.7 g (93%) of pure **2** was isolated after drying *in vacuo* (250 Pa) at 70 °C (m.p. 108–111 °C).

Dimethyl (*R*)-2,2′-Dimethoxy-1,1′-binaphthalene-3,3′-dicarboxylate (*R*-**2**)

The diester *R*-**2** was prepared from pure *R*-**1** in 88% yield using procedure *B* as a glass[39], $[\alpha]_D^{25}$ +43.3° (*c* 1.0, THF); ref.[50] gives $[\alpha]_D^{23}$ +43.0° (*c* 1.0, THF).

Dimethyl (*S*)-2,2′-Dimethoxy-1,1′-binaphthalene-3,3′-dicarboxylate (*S*-**2**)

The diester *S*-**2** was prepared from pure *S*-**1** in 94% yield using procedure *B* as a glass[39], $[\alpha]_D^{25}$ –43.3° (*c* 1.0, THF).

Methyl Hydrogen (*R,S*)-2,2′-Dimethoxy-1,1′-binaphthalene-3,3′-dicarboxylate (**3**)

Procedure A: A solution of potassium hydroxide (3.58 g, 63.9 mmol) in 66% aqueous MeOH (30 ml) was added dropwise at ambient temperature to diester **2** (25.0 g, 58.1 mmol) dissolved in a mixture of THF (30 ml) and MeOH (40 ml). The reaction mixture was refluxed for 5 h, cooled and most of the solvents was evaporated, diluted with cold water (500 ml) and acidified with HCl (1 : 1) to pH ≈ 1. Solid products were collected by filtration, dried at 50 °C and chromatographed (silica gel, toluene–3% acetone).

Compound **3** was isolated in 49% yield; R_F 0.5 (chloroform–acetone 10 : 1). ^{1}H NMR spectrum ($CDCl_3$): 3.45 s, 3 H (OCH_3); 3.47 s, 3 H (OCH_3); 4.02 s, 3 H ($COOCH_3$); 7.12–7.55 m, 6 H (arom. H); 8.02 d, 1 H, *J* = 7.7 (arom. H); 8.06 d, 1 H, *J* = 8.8 (arom. H); 8.62 s, 1 H (arom. H); 8.94 s, 1 H (arom. H). ^{13}C NMR spectrum, APT ($CDCl_3$): CH_3 and CH: 53.16, 62.70, 63.08, 125.91, 126.12, 126.49, 126.82, 129.63, 129.95, 130.39, 134.70, 136.20; CH_2 and C: 122.15, 125.41, 125.83, 126.03, 130.20, 130.62, 136.07, 136.97, 154.31, 155.09, 167.28, 167.46. IR spectrum ($CHCl_3$): 1 733 (C=O); 3 205 (OH). Mass spectrum (EI), *m/z* (rel. int., %): 416 (M^+, 40); 384 (M – OCH_3^+, 100). For $C_{25}H_{20}O_6$ (416.4) calculated: 72.11% C, 4.84% H; found: 72.12% C, 5.11% H.

Ester **2** was obtained in 24% yield (5.95 g, 13.8 mmol); R_F 0.8 (chloroform–acetone 10 : 1).

Acid **1** was obtained in 24% yield (5.66 g, 14 mmol); R_F 0.2 (chloroform–acetone 10 : 1).

Procedure B: Diester *R,S*-**15** (20.0 mg, 37 μmol) was dissolved in warm glacial acetic acid (2 ml) and treated with zinc powder (5 mg, 76 μmol) at 20 °C. The reaction mixture was vigorously stirred for 5 h, then second portion of zinc powder (15 mg, 228 μmol) was added at once and stirring was continued for additional 15 h. All solids were filtered off and clear solution was evaporated *in vacuo*

to dryness giving *R,S*-**3** in almost quantitative yield with chromatographic and spectral properties identical with the product obtained by procedure *A*.

Methyl Hydrogen (*R*)-2,2′-Dimethoxy-1,1′-binaphthalene-3,3′-dicarboxylate (*R*-**3**)

Compound *R*-**3** was prepared using procedure *A* from *R*-**2** in 45% yield. Spectral data were in agreement with the data of racemic compound. For $C_{25}H_{20}O_6$ (416.4) calculated: 72.11% C, 4.84% H; found: 71.62% C, 5.09% H. $[\alpha]_D^{25}$ +46.5° (*c* 1.0, THF).

Methyl Hydrogen (*S*)-2,2′-Dimethoxy-1,1′-binaphthalene-3,3′-dicarboxylate (*S*-**3**)

Compound *S*-**3** was prepared using the same procedure as above for *R*-**3** from *S*-**2** in 50% yield. Spectral data correspond to those of racemic compound. For $C_{25}H_{20}O_6$ (416.4) calculated: 72.11% C, 4.84% H; found: 71.79% C, 5.10% H; $[\alpha]_D^{25}$ –47.6° (*c* 1.0, THF).

Methyl (*R,S*)-2,2′-Dimethoxy-1,1′-binaphthalene-3-carboxylate (*R,S*-**4**)

The mixture of *R,S*-methyl 2,2′-dihydroxy-1,1′-binaphthalene-3-carboxylate[44,45] (20.0 g, 58 mmol) and anhydrous K_2CO_3 (19.0 g, 137 mmol) in anhydrous acetone (200 ml) was stirred for 15 min, then methyl iodide (25 ml, 400 mmol) was added dropwise and the mixture was refluxed for 12 h. Additional methyl iodide (15 ml, 240 mmol) was added and the mixture was refluxed with stirring for total 120 h, cooled, the solid was filtered off, the filtrate evaporated and residual solid was crystallized from toluene–petroleum ether (1 : 1, 100 ml) giving 16.78 g (78%) of pure ester. The mother liquor was evaporated, chromatographed on silica gel using toluene–3% acetone and recrystallized giving second crop (2.53 g, 12%). Total yield was 89%, m.p. 99–102 °C. ^{1}H NMR spectrum ($CDCl_3$): 3.47 s, 3 H (CH_3); 3.80 s, 3 H (CH_3); 4.00 s, 3 H ($COOCH_3$); 7.06–7.51 m, 7 H (arom. H); 7.85–8.06 m, 3 H (arom. H); 8.52 s, 1 H (arom. H). ^{13}C NMR spectrum, APT ($CDCl_3$): CH_3 and CH: 52.95, 57.08, 62.34, 114.08, 124.31, 125.73, 126.08, 126.21, 127.41, 128.63, 128.85, 129.69, 130.64, 133.44; CH_2 and C: 119.14, 125.67, 127.85, 130.42, 134.62, 136.54, 155.01, 155.60, 167.79. IR spectrum ($CHCl_3$): 1 724 (C=O). Mass spectrum, *m/z* (rel. int., %): 372 (M^+, 100). For $C_{24}H_{20}O_4$ (372.4) calculated: 77.40% C, 5.41% H; found: 77.55% C, 5.52% H.

Methyl (*R*)-2,2′-Dimethoxy-1,1′-binaphthalene-3-carboxylate (*R*-**4**)

To (*R*)-2,2′-dihydroxy-1,1′-binaphthalene-3-carboxylic acid[47] (6.5 g, 19.7 mmol) in anhydrous acetone (70 ml), dry potassium carbonate (10.8 g, 79 mmol) was gradually added followed by methyl iodide (25 ml, 0.4 mol). The reaction mixture was stirred for 3 days at ambient temperature, then refluxed 12 h, additional portions of methyl iodide (6 ml, 96 mmol) and potassium carbonate (5.4 g, 38.3 mmol) were added and stirring under reflux was continued for another 24 h. The reaction mixture was cooled and the solid was filtered off. The filtrate was evaporated *in vacuo*, diluted with ice water (200 ml) and extracted with ether (3 × 100 ml). Combined organic layers were washed with water (150 ml), dried with $MgSO_4$, evaporated and dried for 2 h at 55 °C and 2 kPa yielding 6.86 g (94%) of glassy *R*-**4**. Its spectral data correspond to those of the racemic compound. For $C_{24}H_{20}O_4$ (372.4) calculated: 77.40% C, 5.41% H; found: 77.65% C, 5.51% H. $[\alpha]_D^{20}$ +87.9° (*c* 1.0, THF).

Methyl (*S*)-2,2′-Dimethoxy-1,1′-binaphthalene-3-carboxylate (*S*-**4**)

Compound *S*-**4** was prepared analogously from corresponding *S*-acid using the same procedure as above in 84% yield. Its spectral data correspond to those of racemic compound. For $C_{24}H_{20}O_4$ (372.4) calculated: 77.40% C, 5.41% H; found: 77.78% C, 5.63% H. $[\alpha]_D^{20}$ –93.6° (*c* 1.0, THF).

(*R*,*S*)-2,2′-Dimethoxy-1,1′-binaphthalene-3-carboxylic Acid (*R*,*S*-**5**)

Ester *R*,*S*-**4** (11.6 g, 31 mmol) was dissolved in methanol (150 ml) and treated with KOH (17.5 g, 311 mmol) with stirring. The resulting solution was refluxed for 4 h, cooled to ambient temperature and stirred for additional 16 h and then evaporated *in vacuo*. The residue was redissolved in water (400 ml), carefully acidified with 0.5 M HCl to pH 1, cooled in ice (2 h), precipitate collected, washed with water and dried at 50 °C for 5 h. Crystallization from acetone (50 ml) and toluene (5 ml) yielded (after 24 h drying *in vacuo* at 70 °C) 10.6 g (95%) of beige crystals, m.p. 197–200 °C. ^{1}H NMR spectrum ($CDCl_3$): 3.50 s, 3 H (OCH_3); 3.83 s, 3 H (OCH_3); 7.09 d, 1 H, J = 8.7 (arom. H); 7.19 d, 1 H, J = 8.8 (arom. H); 7.30 m, 1 H (arom. H); 7.39 m, 1 H (arom. H); 7.51 m, 2 H (arom. H); 7.92 d, 1 H, J = 7.7 (arom. H); 8.07 m, 2 H (arom. H), 8.93 s, 1 H (arom. H). ^{13}C NMR spectrum, APT ($CDCl_3$): CH_3 and CH: 57.00, 62.76, 113.86, 124.855, 125.26, 126.14, 126.72, 127.79, 128.79, 129,73, 130.29, 131.37, 135.84; CH_2 and C: 117.79, 121.42, 126.65, 129.65, 130.81, 134.20, 137.13, 154.08, 155.54, 167.30. IR spectrum ($CHCl_3$): 1 737 (C=O). Mass spectrum, *m/z* (rel. int., %): 358 (M^+, 100). For $C_{23}H_{18}O_4$ (358.4) calculated: 77.08% C, 5.06% H; found: 77.14% C, 5.07% H.

(*S*)-2,2′-Dimethoxy-1,1′-binaphthalene-3-carboxylic Acid (*S*-**5**)

The chiral acid was prepared from *S*-**4** in 99% yield as amorphous solid using the same method as described for the racemic compound. ^{1}H NMR, IR a MS data correspond to those of the racemic compound. For $C_{23}H_{18}O_4$ (358.4) calculated: 77.08% C, 5.06% H; found: 76.59% C, 5.14% H. $[\alpha]_D^{20}$ –62.2° (*c* 0.29, chloroform).

Methyl (*R*,*S*)-3′-Hydroxymethyl-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*R*,*S*-**6**)

Compound *R*,*S*-**3** (11.4 g, 27.4 mmol) was dissolved in anhydrous tetrahydrofuran (70 ml) under dry nitrogen and 1.0 M solution of BH_3 . THF complex in THF (41.0 ml) was added during 15 min maintaining temperature at –16 °C with stirring. Reaction mixture was stirred at –10 °C for 2 h and at 10 °C for another 2 h, then carefully quenched with ice–water (10 ml) followed by saturated $NaHCO_3$ (10 ml). Most of THF was evaporated *in vacuo* and the residue was partitioned between water (100 ml) and diethyl ether (50 ml). Aqueous phase was extracted twice with diethyl ether (50 ml), combined extracts were dried with $MgSO_4$, evaporated *in vacuo* and the crude product was chromatographed on silica gel using toluene–10% acetone. Methyl (*R*,*S*)-3′-hydroxymethyl-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*R*,*S*-**6**) 10.7 g (97%) was isolated as white solid, m.p. 127.5–131 °C. ^{1}H NMR spectrum ($CDCl_3$): 2.86 s, 1 H (OH); 3.34 s, 3 H (OCH_3); 3.43 s, 3 H (OCH_3); 3.99 s, 3 H ($COOCH_3$); 4.93 d, 1 H, J = 13.7 (OCH-H); 5.03 d, 1 H, J = 13.7 (OCH-H); 7.11–7.46 m, 6 H (arom. H); 7.87 d, 1 H, J = 8.2 (arom. H); 7.96 d, 1 H, J = 8.2 (arom. H); 8.03 s, 1 H (arom. H); 8.55 s, 1 H (arom. H). ^{13}C NMR spectrum, APT ($CDCl_3$): CH_3 and CH: 53.05, 61.49, 62.52, 125.60, 125.97, 126.20, 126.36, 126.96, 128.69, 128.89, 129.17, 129.71, 133.92; CH_2 and C: 62.56, 124.30, 127.22, 130.16, 131.21, 134.31, 134.72, 136.48, 154.96, 155.25, 167.60. IR spectrum ($CHCl_3$): 1 726.5 (C=O); 3 608 (OH). Mass spectrum, *m/z* (rel. int., %): 402 (M^+, 100). For $C_{25}H_{22}O_5$ (402.4) calculated: 74.61% C, 5.51% H; found: 74.37% C, 5.57% H.

Methyl (*R*)-3′-Hydroxymethyl-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*R*-**6**)

R-**6** was prepared using the same procedure as above and was isolated as a colourless glass in 81% yield. ^{1}H NMR, IR a MS data were identical with those of the racemic compounds. For $C_{25}H_{22}O_5$ (402.4) calculated: 74.61% C, 5.51% H; found: 74.94 %C, 5.62% H. $[\alpha]_D^{20}$ +5.9° (*c* 1.0, THF).

Methyl (*S*)-3′-Hydroxymethyl-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*S*-**6**)

S-**6** was prepared using the same procedure as above and was isolated as a colourless glass in 87% yield. ^{1}H NMR, IR a MS data were identical with those of the racemic compounds. For $C_{25}H_{22}O_5$ (402.4) calculated: 74.61% C, 5.51% H; found: 74.42 %C, 5.79% H. $[\alpha]_D^{20}$ –5.9° (*c* 1.0, THF).

Methyl (*R*,*S*)-3′-Acetoxymethyl-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*R*,*S*-**7**)

Pure *R*,*S*-**6** (4.90 g, 12.2 mmol) was dissolved in acetyl chloride (50 ml, 70 mmol) the mixture was refluxed for 2 h, coolled and evaporated *in vacuo* to dryness. The crude product was partitioned between diethyl ether (150 ml) and saturated solution of $NaHCO_3$ (50 ml). The aqueous phase was extracted with 50 ml of diethyl ether, combined extracts were dried with $MgSO_4$ and, after evaporation, subjected to column chromatography (50 g silica gel, toluene–5% acetone). After 2 h at 50 °C/2 kPa, 5.26 g (97%) of colourless glass *R*,*S*-**7** was obtained. R_F 0.5 (toluene–acetone 3 : 97). ^{1}H NMR spectrum ($CDCl_3$): 2.18 s, 3 H ($COCH_3$); 3.35 s, 3 H (OCH_3); 3.45 s, 3 H (OCH_3); 3.99 s, 3 H ($COOCH_3$); 5.38 d, 1 H, *J* = 13.2 (OCH-H); 5.43 d, 1 H, *J* = 13.2 (OCH-H); 7.12 d, 1 H, *J* = 8.3 (arom. H); 7.18 d, 1 H, *J* = 8.8 (arom. H); 7.23–7.48 m, 4 H (arom. H); 7.91 d, 1 H, *J* = 8.2 (arom. H); 7.97 d, 1 H, *J* = 8.2 (arom. H); 8.03 s, 1 H (arom. H); 8.55 s, 1 H (arom. H). ^{13}C NMR spectrum, APT ($CDCl_3$): CH_3 and CH: 21.17, 52.47, 61.27, 61.99, 125.13, 125.44, 125.61, 125.76, 126.76, 128.19, 128.58, 129.14, 129.97, 133.39; CH_2 and C: 62.43, 124.26, 125.05, 126.50, 129.43, 129.57, 130.40, 134.10, 135.85, 154.41, 154.79, 167.02, 170,91. IR spectrum ($CHCl_3$): 1 732 (C=O). Mass spectrum, *m/z* (rel. int., %): 444 (M^+, 100). For $C_{27}H_{24}O_6$. 1.5 H_2O (471.5) calculated: 68.78% C, 5.77% H; found: 68.82% C, 5.77% H.

Methyl (*R*)-3′-Acetoxymethyl-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*R*-**7**)

R-**7** was prepared in 94% yield using the same method as described for the racemic compound. Using diffusion of heptane into toluene solution of pure *R*-**7**, a crystalline product having m.p. 89–91 °C was obtained after three months at ambient temperature. ^{1}H NMR and IR data were identical with those of the racemic compound. For $C_{27}H_{24}O_6$ (444.5) calculated: 72.96% C, 5.44% H; found: 73.04% C, 5.46% H. $[\alpha]_D^{20}$ +6.0° (*c* 1.06, THF).

Methyl (*S*)-3′-Acetoxymethyl-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*S*-**7**)

S-**7**, m.p. 89.5–91 °C was prepared in 99% yield by the same method as described for racemic compound. ^{1}H NMR and IR data were identical with those of the racemic compound. For $C_{27}H_{24}O_6$ (444.5) calculated: 72.96% C, 5.44% H; found: 72.83% C, 5.51% H. $[\alpha]_D^{20}$ –5.9° (*c* 1.13, THF).

Methyl (*R*,*S*)-3′-Chloromethyl-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*R*,*S*-**8**).

Thionyl chloride (3 ml, 41 mmol) and *R*,*S*-**6** (1 g, 2.48 mmol) was slowly heated to reflux and then refluxed for 2 h. All volatiles were evaporated *in vacuo* and the solid residue was chromatographed on silica gel–chloroform. The amorphous product was obtained in nearly quantitative yield (1.05 g). R_F 0.8 (toluene–acetone 3 : 97). ^{1}H NMR spectrum ($CDCl_3$): 3.39 s, 3 H (OCH_3); 3.45 s, 3 H (OCH_3); 4.00 s, 3 H ($COOCH_3$); 4.81 d, 1 H, *J* = 11.5 (OCH-H); 5.01 d, 1 H, *J* = 11.5 (OCH-H); 7.16 d, 1 H, *J* = 8.7 (arom. H); 7.22 d, 1 H, *J* = 8.8 (arom. H); 7.26–7.48 m, 4 H (arom. H); 7.90 d, 1 H, *J* = 8.2 (arom. H); 7.98 d, 1 H, *J* = 8.2 (arom. H); 8.10 s, 1 H (arom. H); 8.57 s, 1 H (arom. H). ^{13}C NMR spectrum, APT ($CDCl_3$): CH_3 and CH: 53.08, 62.09, 62.59, 125.83, 126.05, 126.26, 126.38, 127.61, 128.81, 129.26, 129.76, 131.52, 134.05; CH_2 and C: 42.83, 124.98, 125.72, 127.04, 130.19, 131.05, 131.68, 134.93, 136.43, 155.02, 155.25, 167.59. IR spectrum ($CHCl_3$): 1 732 (C=O).

Mass spectrum, *m/z* (rel. int., %): 420 (M^+, 100), 422 (M^+ + 2, 30). For $C_{25}H_{21}ClO_4$ (420.9) calculated: 71.34% C, 5.03% H, 8.42% Cl; found: 71.00% C, 5.14% H, 8.61% Cl.

Methyl (*R*,*S*)-3′-(Benzoyloxymethyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*R*,*S*-**9**)

Pure **7** (0.5 g, 1.24 mmol) was dissolved in dry dichloromethane (5 ml) along with 4-(dimethylamino)pyridine (1.52 g, 12.4 mmol) and cooled to 0 °C. Benzoyl chloride (1.44 ml, 12.42 mmol) in dry dichloromethane (5 ml) was added dropwise with cooling. The reaction mixture was stirred for additional 2 h and temperature was allowed to rise to ambient and stirring was continued for 48 h, then poured into 10% aqueous solution of potassium carbonate (50 ml) and extracted with chloroform (3 × 20 ml). Combined organic phases were washed with 3% HCl (30 ml), dried with magnesium sulfate and evaporated. The crude material was subjected to chromatography on silica gel–chloroform and after 2 h of drying *in vacuo* at 50 °C glassy methyl (*R*,*S*)-3′-(benzoyloxymethyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*R*,*S*-**9**) in nearly quantitative yield (629 mg) was obtained. R_F 0.7 (toluene–acetone 3 : 97). ^{1}H NMR spectrum ($CDCl_3$): 3.40 s, 3 H (OCH_3); 3.47 s, 3 H (OCH_3); 4.00 s, 3 H ($COOCH_3$); 5.68 d, 1 H, *J* = 13.2 (OCH-H); 5.73 d, 1 H, *J* = 13.2 (OCH-H); 7.13–7.60 m, 9 H (arom. H); 7.92 d, 1 H, *J* = 8.4 (arom. H); 7.98 d, 1 H, *J* = 8.2 (arom. H); 8.14 m, 3 H (arom. H); 8.56 s, 1 H (arom. H). ^{13}C NMR spectrum, APT ($CDCl_3$): CH_3 and CH: 53.09, 62.04, 62.66, 125.77, 126.10, 126.24, 126.45, 127.42, 128.89, 129.11, 129.23, 129.78, 130.38, 130.74, 133.72, 134.04; CH_2 and C: 63.52, 124.95, 127.18, 130.16, 130.23, 131.09, 134.79, 136.52, 155.08, 155.55, 167.08, 167.64. IR spectrum ($CHCl_3$): 1 719 (C=O). Mass spectrum, *m/z* (rel. int., %): 506 (M^+, 46). For $C_{32}H_{26}O_6$ (506.6) calculated: 75.88% C, 5.17% H; found: 75.58% C, 5.19% H.

Methyl (*R*,*S*)-3′,6′-Bis(chloromethyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*R*,*S*-**10**)

Solution of *R*,*S*-**7** (2.2 g, 5.0 mmol) in anhydrous dichloromethane (20 ml) was treated successively with methoxymethyl chloride (1.6 g, 24.8 mmol) at –20 °C under vigorous stirring, then solution of $SnCl_4$ (1.43 ml, 12.42 mmol) in dichloromethane (15 ml) was added dropwise within 5 min. The reaction mixture was stirred for 3.5 h, allowed to warm to ambient temperature (1 h) and stirred another 30 min at this temperature. After quenching by addition of 5% HCl (10 ml), the organic layer was extracted with water (5 ml) and 3% aqueous solution of $NaHCO_3$ (5 ml), dried with $MgSO_4$, evaporated *in vacuo* and chromatographed on silica gel (toluene–3% acetone). Slow diffusion of hexane in toluene solution afforded crystalline crude material (1.8 g) that was recrystallized (the only procedure for separation of undesired methyl (*R*,*S*)-3′,6,6′-tris(chloromethyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate) giving 1.17 g (50%) of white crystals (m.p. 176–182 °C). R_F 0.7 (toluene–acetone 3 : 97). ^{1}H NMR spectrum ($CDCl_3$): 3.36 s, 3 H (OCH_3); 3.44 s, 3 H (OCH_3); 4.00 s, 3 H ($COOCH_3$); 4.71 s, 2 H (CH_2Cl); 4.72 s, 2 H (CH_2Cl); 4.83 d, 1 H, *J* = 11.5 (OCH-H); 4.96 d, 1 H, *J* = 11.5 (OCH-H); 7.10 d, 1 H, *J* = 8.8 (arom. H); 7.18 d, 1 H, *J* = 8.8 (arom. H); 7.26–7.40 m, 3 H (arom. H); 7.89 s, 1 H (arom. H); 7.96 s, 1 H (arom. H); 8.07 s, 1 H (arom. H); 8.53 s, 1 H (arom. H). ^{13}C NMR spectrum, APT ($CDCl_3$): CH_3 and CH: 53.24, 62.23, 62.76, 126.77, 127.12, 128.16, 128.50, 129.28, 129.78, 131.67, 134.16; CH_2 and C: 42.65, 46.63, 46.87, 124.80, 126.88, 129.97, 130.82, 132.44, 134.56, 134.99, 135.47, 136.04, 155.65, 155.84, 167.40. IR spectrum ($CHCl_3$): 1 727 (C=O). Mass spectrum, *m/z* (rel. int., %): 468 (M^+, 100), 470 (M^+ + 2, 70). For $C_{26}H_{22}O_4Cl_2$ (469.4) calculated: 66.53% C, 4.72% H, 15.11% Cl; found: 66.55% C, 4.79% H, 15.11% Cl.

Methyl (*S*)-3′,6′-Bis(chloromethyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*S*-**10**)

Solution of *S*-**7** (2.0 g, 4.5 mmol) in anhydrous dichloromethane (7 ml) was treated successively with methoxymethyl chloride (1.45 g, 22.5 mmol) at –60 °C under vigorous stirring. Then solution of

$SnCl_4$ (2.6 ml, 22.5 mmol) in dichloromethane (15 ml) was added within 5 min and the reaction mixture was stirred for 3.5 h, allowed to warm to ambient temperature (1 h) and stirred another 30 min. The mixture was quenched by addition of 5% HCl (10 ml). The organic layer was extracted with water (5 ml) and 3% aqueous solution of $NaHCO_3$ (5 ml), dried with $MgSO_4$, evaporated *in vacuo* and chromatographed on silica gel (dichloromethane) giving 1.65 g of yellowish material. Fourfold chromatography on silica gel (Kieselgel 60H) using heptane–ether–acetone–methanol (80 : 10 : 10 : 0.5) led to separation of following compounds:

Amorphous colourless methyl (*S*)-3′,6′-bis(chloromethyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*S*-**10**), 1.12 g (50%). ^{1}H NMR and IR data correspond to those of racemic compound. For $C_{26}H_{22}Cl_2O_4$ (469.4) calculated: 66.53% C, 4.72% H, 15.11% Cl; found: 66.55% C, 4.79% H, 15.11% Cl. $[\alpha]_D^{25}$ –7.2° (*c* 1, THF).

Methyl (*S*)-3′,6,6′-tris(chloromethyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*S*-**11**) 130 mg (5%), R_F 0.6 (toluene–acetone 3 : 97). ^{1}H NMR spectrum ($CDCl_3$): 3.38 s, 3 H (OCH_3); 3.44 s, 3 H (OCH_3); 4.00 s, 3 H ($COOCH_3$); 4.72 s, 2 H (CH_2Cl); 4.84 d, 1 H, *J* = 11.4 (OCH-H); 4.98 d, 1 H, *J* = 11.4 (OCH-H); 7.14 d, 1 H, *J* = 8.7 (arom. H); 7.18 d, 1 H, *J* = 8.4 (arom. H); 7.26–7.50 m, 3 H (arom. H); 7.90 s, 1 H (arom. H); 7.98 d, 1 H, *J* = 8.2 (arom. H); 8.08 s, 1 H (arom. H); 8.56 s, 1 H (arom. H). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 53.19, 62.18, 62.74, 126.36, 126.42, 126.94, 128.08, 128.50, 129.46, 129.89, 131.55, 134.31; CH_2 and C: 42.75, 46.95, 125.09, 125.75, 126.83, 130.23, 130.85, 132.47, 134.73, 134.95, 136.42, 155.12, 155.87, 167.64. IR spectrum ($CHCl_3$): 1 727 (C=O). Mass spectrum, *m/z* (rel. int., %): 515 (M^+, 30), 517 (M^+ + 2, 28), 517 (M^+ + 4, 10). $[\alpha]_D^{25}$ +42.6° (*c* 0.23, chloroform).

General Procedure for Monochloromethylation of Binaphthalenes **6**–**9**

3,3′-Disubstituted binaphthol (0.3 mmol) was dissolved in dry dichloromethane (2 ml) and treated with methoxymethyl chloride (97 mg, 1.5 mmol). The solution was cooled to –15 °C and $SnCl_4$ (85 μl, 0.75 mmol) dissolved in dry dichloromethane (4 ml) was added dropwise. The reaction mixture was stirred at –15 °C for 3.5 h, then at ambient temperature for 2 h and quenched by pouring onto a silica gel column. Fractions with intense blue luminiscence (excitation at 254 nm) eluated with dichloromethane were collected, evaporated and analyzed by NMR spectroscopy.

Methyl (*R*,*S*)-3′,6′-Bis(4-hydroxy-2-oxabutyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*R*,*S*-**12**)

R,*S*-**10** (470 mg, 1 mmol) and silver oxide (580 mg, 2.5 mmol) was refluxed in dry ethylene glycol (5 ml) with stirring for 1 h under nitrogen. The excess of ethylene glycol was distilled off under vacuum and residual material was chromatographed on silica gel (Kieselgel 60 H, chloroform–5% methanol) giving pure *R*,*S*-**12** (210 mg, 40%) and about 37% of 2-hydroxyethyl (*R*,*S*)-3′,6′-bis(4-hydroxy-2-oxabutyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (in a mixture with another unidentified product). ^{1}H NMR spectrum ($CDCl_3$): 2.27 s, 2 H (OH); 3.33 s, 3 H (OCH_3); 3.43 s, 3 H (OCH_3); 3.63 t, 2 H, *J* = 4.5 (CH_2); 3.77 t, 4 H, *J* = 4.4 (CH_2); 3.83 t, 2 H, *J* = 4.4 (CH_2); 3.99 s, 3 H ($COOCH_3$); 4.67 s, 2 H ($ArCH_2O$); 4.82 d, 1 H, *J* = 12.2 (OCH-H); 4.86 d, 1 H, *J* = 12.2 (OCH-H); 7.09–7.27 m, 3 H (arom. H); 7.33 t, 1 H, *J* = 7.6 (arom. H); 7.42 t, 1 H, *J* = 7.8 (arom. H); 7.86 s, 1 H (arom. H); 7.96 d, 1 H, *J* = 8.2 (arom. H); 8.05 s, 1 H (arom. H); 8.53 s, 1 H (arom. H). ^{13}C NMR spectrum, APT ($CDCl_3$): CH_3 and CH: 53.06, 61.75, 62.54, 126.20, 126.33, 126.41, 126.96, 127.42, 129.16, 129.72, 129.75, 133.91; CH_2 and C: 62.48, 62.49, 69.58, 72.21, 72.62, 73.79, 124.61, 125.62, 127.19, 130.16, 130.98, 132.35, 133.99, 135.26, 136.44, 154.95, 155.39, 167.63. IR spectrum ($CHCl_3$): 3 599 (OH); 3 479 (OH); 1 725 (C=O). Mass spectrum, *m/z* (rel. int., %): 520 (M^+, 100). For $C_{30}H_{32}O_8 \cdot H_2O$ (538.6) calculated: 66.90% C, 6.36% H; found: 66.79% C, 6.40% H.

Methyl (*S*)-3′,6′-Bis(4-hydroxy-2-oxabutyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*S*-**12**)

Product *S*-**12** was obtained from *S*-**10** (440 mg, 0.94 mmol) by the procedure described above for racemic compound. *S*-**12** (238 mg, 49%) was isolated along with 142 mg (29%) of 2-hydroxyethyl (*S*)-3′,6′-bis(4-hydroxy-2-oxabutyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (impure). ^{1}H NMR and IR data of *S*-**12** correspond to those of racemic compound. For $C_{30}H_{32}O_8$ (529.6) calculated: 68.04% C, 6.28% H; found: 68.21% C, 6.15% H; $[a]_D^{20}$ –6.2° (*c* 0.5, THF).

(*R*,*S*)-3′,6′-Bis(4-hydroxy-2-oxabutyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylic Acid (*R*,*S*-**13**)

A mixture of *R*,*S*-**12** (300 mg, 0.576 mmol), solution of KOH (323 mg, 5.76 mmol) in water (1.5 ml), methanol (2.5 ml), and tetrahydrofuran (5 ml) was stirred and refluxed for 1 h. Then it was stirred for another 12 h at ambient temperature, evaporated *in vacuo*, diluted with ice water (50 ml) and acidified with concentrated HCl to pH ≈ 1. The white precipitate obtained was extracted with chloroform (2 × 30 ml), the organic phase was dried with $MgSO_4$ and evaporated *in vacuo*. The residue was chromatographed on silica gel (chloroform–5% methanol) giving after drying (24 h, 250 Pa/50 °C) 257 mg (88%) of glassy *R*,*S*-**13**. ^{1}H NMR spectrum ($CDCl_3$): 3.30 s, 3 H (OCH_3); 3.38 s, 3 H (OCH_3); 3.64 t, 2 H, *J* = 4.5 (CH_2); 3.78 t, 4 H, *J* = 4.4 (CH_2); 3.83 q, 2 H, *J* = 3.1 (CH_2); 4.67 s, 2 H ($ArCH_2O$); 4.83 d, 1 H, *J* = 12.6 (OCH-H); 4.88 d, 1 H, *J* = 12.6 (OCH-H); 5.65 s, 2 H (OH); 7.08 d, 1 H, *J* = 8.6 (arom. H); 7.17 d, 1 H, *J* = 8.8 (arom. H); 7.24 d, 1 H, *J* = 10.4 (arom. H); 7.35 t, 1 H, *J* = 7.7 (arom. H); 7.47 t, 1 H, *J* = 7.8 (arom. H); 7.88 s, 1 H (arom. H); 8.00 d, 1 H, *J* = 8.2 (arom. H); 8.07 s, 1 H (arom. H); 8.83 s, 1 H (arom. H). ^{13}C NMR spectrum, APT ($CDCl_3$): CH_3 and CH: 61.79, 62.79, 126.14, 126.24, 127.24, 127.49, 129.74, 130.15, 130.30, 135.72; CH_2 and C: 62.27, 62.29, 69.43, 72.17, 72.56, 73.58, 122.76, 123.89, 126.43, 130.36, 130.95, 132.25, 133.72, 135.39, 136.92, 154.45, 155.39, 168.01. IR spectrum ($CHCl_3$): 1 736 (C=O). Mass spectrum (FAB, glycerol–thioglycerol), *m/z* (rel. int., %): 506.2 (M^+, 30), 445.2 ([$M - C_2H_5O_2^+$], 100). For $C_{29}H_{30}O_8$ (506.6) calculated: 68.00% C, 6.11% H; found: 67.95% C, 6.09% H.

(*S*)-3′,6′-Bis(4-hydroxy-2-oxabutyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylic Acid (*S*-**13**)

Procedure A: S-**13** was prepared according by the same procedure as racemic compound starting from *S*-**12**. Pure acid was isolated as a glassy material in 98% yield. The product was identical with that prepared by procedure *B*.

Procedure B: S-**13** was prepared from crude 2-hydroxyethyl (*S*)-3′,6′-bis(4-hydroxy-2-oxabutyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (300 mg, 576 μmol) and a solution of KOH (323 mg, 5.76 mmol) in water (1.5 ml) and methanol (2.5 ml). Pure (S)-3′,6′-bis(4-hydroxy-2-oxabutyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylic acid (*S*-**13**) was isolated in 90% yield. ^{1}H NMR and IR data correspond to those of racemic compound. For $C_{29}H_{30}O_8$ (506.6) calculated: 68.00% C, 6.11% H; found: 67.84% C, 6.09% H.

2-Oxoethyl-2-phenyl (*R*,*S*)-3′,6′-Bis(4-hydroxy-2-oxabutyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*R*,*S*-**14**)

To the mixture od phenacyl bromide (110 mg, 217 μmol) and potassium fluoride (28 mg, 0.478 mmol) in dry DMF (0.5 ml) a solution of acid *R*,*S*-**13** (43.4 mg, 0.217 mmol) in dry DMF (1.3 ml) was added dropwise and stirred for 12 h at ambient temperature. The reaction mixture was quenched with water (15 ml) and extracted with chloroform (3 × 15 ml). The organic phase was dried, evaporated *in vacuo* and subjected to chromatography (Kieselgel 60H, chloroform–2% methanol). After drying for 2 h at 40 °C and 2.5 kPa, 100 mg (73%) of a colourless glassy product was isolated. Using diffusion of heptane into a benzene solution of pure *R*,*S*-**14** at ambient temperature the crystalline

product m.p. 116–124 °C was obtained after three days. ^{1}H NMR spectrum ($CDCl_3$): 2.55 s, 2 H (OH); 3.36 s, 3 H (OCH_3); 3.48 s, 3 H (OCH_3); 3.60 t, 2 H, J = 4.3 (CH_2); 3.77 m, 4 H (CH_2); 3.83 t, 2 H, J = 4.4 (CH_2); 4.65 s, 2 H ($ArCH_2O$); 4.83 d, 1 H, J = 12.6 (OCH-H); 4.88 d, 1 H, J = 12.6 (OCH-H); 5.63 d, 1 H, J = 16.5 (H-CHCO); 5.70 d, 1 H, J = 16.5 (H-CHCO); 7.11–7.52 m, 7 H (arom. H); 7.61 t, 1 H, J = 7.4 (arom. H); 7.86 s, 1 H (arom. H); 7.98–8.00 m, 3 H (arom. H); 8.06 s, 1 H (arom. H); 8.76 s, 1 H (arom. H). ^{13}C NMR spectrum, APT ($CDCl_3$): CH_3 and CH: 61.74, 62.72, 126.19, 126.29, 126.41, 126.92, 127.35, 128.42, 129.31, 129.48, 129.71, 129.88, 134.51, 134.66; CH_2 and C: 62.44, 67.19, 69.53, 72.17, 72.58, 73.74, 124.56, 124.67, 127.29, 130.13, 130.95, 132.33, 133.96, 134.89, 135.26, 136.69, 155.14, 155.37, 166.13, 192.81. IR spectrum ($CHCl_3$): 3 598 (OH); 3 467 (OH); 1 735 (C=O); 1 704 (C=O). Mass spectrum, *m/z* (rel. int., %): 624 (M^+, 100). For $C_{37}H_{36}O_9$ (624.7) calculated: 71.14% C, 5.81% H; found: 70.97% C, 5.97% H.

2-Oxoethyl-2-phenyl (*S*)-3′,6′-Bis(4-hydroxy-2-oxabutyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*S*-**14**)

Compound *S*-**14** was prepared using the same procedure as for racemic compound and isolated in 78% yield as a glass. ^{1}H NMR and IR data correspond to those of racemic compound. For $C_{37}H_{36}O_9$ (624.7) calculated: 71.14% C, 5.81% H; found: 70.81% C, 5.81% H; $[\alpha]_D^{20}$ –23.6° (*c* 1, THF).

Methyl (2-Oxoethyl-2-phenyl) (*R*,*S*)-2,2′-Dimethoxy-1,1′-binaphthalene-3,3′-dicarboxylate (*R*,*S*-**15**)

A mixture of phenacyl bromide (48 mg, 0.24 mmol), potassium fluoride (31 mg, 0.528 mmol) and acid *R*,*S*-**4** (100 mg, 0.24 mmol) in dry DMF (2 ml) was stirred for 20 h at ambient temperature. The reaction mixture was evaporated *in vacuo* and chromatographed on a column of silica gel with chloroform as eluent. The crude product was further purified by preparative TLC (Kieselgel G, chloroform) giving 116 mg (90%) of *R*,*S*-**15** which, recrystallized from benzene–heptane (1 : 2), had m.p. 173.5–175.5 °C. ^{1}H NMR spectrum ($CDCl_3$): 3.52 s, 3 H (OCH_3); 3.54 s, 3 H (OCH_3); 3.99 s, 3 H ($COOCH_3$); 5.63 d, 1 H, J = 16.5 (H-CHCO); 5.70 d, 1 H, J = 16.5 (H-CHCO); 7.15–7.64 m, 9 H (arom. H); 7.96-8.02 m, 4 H (arom. H); 8.57 s, 1 H (arom. H); 8.78 s, 1 H (arom. H). ^{13}C NMR spectrum, APT ($CDCl_3$): CH_3 and CH: 53.00, 62.64, 62.83, 126.15, 126.21, 128.44, 129.14, 129.34, 129.51, 129.70, 129.93, 134.01, 134.52, 134.79; CH_2 and C: 67.21, 124.60, 125.51, 126.85, 126.98, 130.18, 134.95, 136.35, 136.61, 154.99, 155.19, 166.09, 167.53, 192.80. IR spectrum ($CHCl_3$): 1 730 (C=O), 1 705 (C=O). Mass spectrum, *m/z* (rel. int., %): 430 ([M – 105$^+$], 6), 119 ($PhCOCH_2^+$, 15), 105 ($PhCO^+$, 100). For $C_{33}H_{26}O_7$ (534.6) calculated: 74.15% C, 4.90% H; found: 74.17% C, 5.09% H.

Methyl (*R*,*S*)-3′,6′-Bis(methoxymethyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (**16**)

Procedure A: A stirred suspension of *R*,*S*-**10** (500 mg, 1.063 mmol) in a mixture of dry methanol (10 ml) and dioxane (5 ml) was treated with anhydrous $AlCl_3$ (425 mg, 3.19 mmol) under argon. The reaction mixture was heated to reflux for 20 min and then dry methanol (20 ml) was added. Another portion of dry methanol (10 ml) was added after 20 h of stirring followed by 5 ml of methanol after each 24 h until total 96 h of stirring was attained. The reaction mixture was evaporated *in vacuo* and filtered through a short column of silica gel using chloroform–acetone (10 : 1) as eluent. The eluated product was further purified using TLC plate (Kieselgel 60 PF_{254}, chloroform). Pure *R*,*S*-**16** (480 mg, 98%) was obtained after drying at 250 Pa/50 °C as white powder.

Procedure B: R,*S*-**10** (380 mg, 0.81 mmol) was suspended in dry methanol (6 ml) and silver oxide (464 mg, 2 mmol) was added under dry nitrogen. The reaction mixture was refluxed for 12 h with stirring, cooled, evaporated *in vacuo* and chromatographed on a column of silica gel in chloroform. After drying 354 mg (95%) of *R*,*S*-**16** was isolated. After recrystallization from methanol yielded 210 mg

(59%) of white crystals, m.p 118.5–120 °C. ^{1}H NMR spectrum ($CDCl_3$): 3.34 s, 3 H (OCH_3); 3.42 s, 6 H (OCH_3); 3.56 s, 3 H (OCH_3); 3.99 s, 3 H ($COOCH_3$); 4.57 s, 2 H (CH_2); 4.71 d, 1 H, *J* = 12.6 (OCH-H); 4.78 d, 1 H, *J* = 12.6 (OCH-H); 7.10–7.46 m, 5 H (arom. H); 7.86 s, 1 H (arom. H); 7.96 d, 1 H, *J* = 8.24 (arom. H); 8.06 s, 1 H (arom. H), 8.53 s, 1 H (arom. H). ^{13}C NMR spectrum, APT ($CDCl_3$): CH_3 and CH: 53.00, 58.87, 59.03, 61.76, 62.52, 126.15, 126.36, 126.43, 126.89, 127.40, 129.08, 129.58, 129.68, 133,77; CH_2 and C: 70.95, 75.30, 124.55, 125.75, 127.37, 130.19, 131.08, 132.57, 133.92, 135.39, 136.53, 155.00, 155.38, 167.67. IR spectrum ($CHCl_3$): 1 726 (C=O). Mass spectrum, *m/z* (rel. int., %): 460 (M^+, 25). For $C_{28}H_{28}O_6$ (460.5) calculated: 73.01% C, 6.13% H; found: 72.69% C, 6.05% H.

Methyl (*S*)-3′,6′-Bis(methoxymethyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (*S*-**16**)

Ester *S*-**16** was prepared from *S*-**10** using procedure *B* (see above) in 85% yield. ^{1}H NMR and IR data correspond to those of racemic compound. For $C_{28}H_{28}O_6$. 0.25 H_2O (465.0) calculated: 72.32% C, 6.18% H; found: 72.46% C, 6.28% H. $[\alpha]_D^{20}$ –7.9° (*c* 0.97, THF).

(*R*,*S*)- 3′,6′-Bis(methoxymethyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylic Acid (*R*,*S*-**17**)

Ester *R*,*S*-**16** (480 mg, 1.04 mmol) in tetrahydrofuran (5 ml) was hydrolyzed with a solution of KOH (1.17 g, 20 mmol) in water (1.5 ml) and methanol (2.5 ml) by 30 min reflux. All volatiles were evaporated *in vacuo*, water (50 ml) was added to the residue and acidified with concentrated HCl to pH ≈ 1. The precipitate was collected after two hours, washed with water and dried giving 430 mg (93%) of pure *R*,*S*-**17**. ^{1}H NMR spectrum ($CDCl_3$): 3.32 s, 3 H (OCH_3); 3.41 s, 3 H (OCH_3); 3.45 s, 3 H (OCH_3); 3.57 s, 3 H (OCH_3); 4.58 s, 2 H (CH_2); 4.72 d, 1 H, *J* = 12.6 (OCH-H); 4.78 d, 1 H, *J* = 12.6 (OCH-H); 7.10 d, 1 H, *J* = 8.6 (arom. H); 7.23 d, 1 H, *J* = 8.2 (arom. H); 7.25–7.53 m, 3 H (arom. H); 7.89 s, 1 H (arom. H); 8.04 d, 1 H, *J* = 8.2 (arom. H); 8.10 s, 1 H (arom. H); 8.92 s, 1 H (arom. H).^{13}C NMR spectrum, APT ($CDCl_3$): CH_3 and CH: 59.13, 59.35, 62.01, 63.11, 126.16, 126.52, 126.98, 127.55, 127.63, 130.12, 130.51, 130.55, 136.42; CH_2 and C: 70.95, 75.27, 121.66, 123.58, 126.24, 130.77, 131.23, 132.74, 133.70, 135.93, 137.34, 154.19, 155.59, 166.66. IR spectrum ($CHCl_3$): 3 195 (COOH), 1 737 (C=O). Mass spectrum, *m/z* (rel. int., %): 446 (M^+, 4). For $C_{27}H_{26}O_6$. 0.25 H_2O (451.0) calculated: 71.91% C, 5.92% H; found: 71.67% C, 5.73% H.

(*S*)-3′,6′-Bis(methoxymethyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylic Acid (*S*-**17**)

S-**17** was prepared in 98% yield from *S*-**16** using the same procedure as for racemic compound. ^{1}H NMR and IR data correspond to those of racemic compound. $[\alpha]_D^{20}$ –6.9° (*c* 0.26, THF). For $C_{27}H_{26}O_6$. 1.5 H_2O (473.5) calculated: 68.49% C, 6.17% H; found: 68.55% C, 6.16% H.

REFERENCES

1. Stibor I., Lellek V.: Chem. Listy *88*, 423 (1994).
2. Tomalia D. A., Naylor A. M., Goddard III W. A.: Angew. Chem., Int. Ed. Engl. *29*, 138 (1990).
3. Mekelburger H.-B., Jaworek W., Vogtle F.: Angew. Chem., Int. Ed. Engl. *31*, 1571 (1992).
4. Newkome G. R., Moorfield C. N., Baker G. R.: Aldrichim. Acta *25*, 31 (1992).
5. Tomalia D. A., Durst H. D.: Top. Curr. Chem. *165*, 193 (1993).
6. Issberner J., Moors R., Vogtle F.: Angew. Chem., Int. Ed. Engl. *33*, 2413 (1994).
7. Newkome G. R., Moorfield C. N. in: *Comprehensive Supramolecular Chemistry* (J.-M. Lehn, Ed.), Vol. 10, p. 777. Pergamon, Elsevier Science, Oxford 1996.
8. Bell T. W.: Science *271*, 1077 (1996).

9. O'Sullivan D. O.: Chem. Eng. News *1993*, August 16, 20.
10. Jiang D.-L., Aida T.: Chem. Commun. *1996*, 1523.
11. Dandliker P. J., Diederich F., Gisselbrecht J.-P., Louati A., Gross M.: Angew. Chem., Int. Ed. Engl. *34*, 272 (1995).
12. Qualmann B., Kessels M. M., Musiol H.-J., Sierralta W. D., Jungblut P. W., Moroder L.: Angew. Chem., Int. Ed. Engl. *35*, 909 (1996).
13. Bar G., Shai R., Citts R. W., Taylor T. N., Zawodzinski T. A., Jr.: Langmuir *12*, 1172 (1996).
14. Wells M., Crooks R. M.: J. Am. Chem. Soc. *118*, 3988 (1996).
15. Stewart G. M., Fox M. A.: J. Am. Chem. Soc. *118*, 4354 (1996).
16. James T. D., Shinmori H., Takeuchi M., Shinkai S.: Chem. Commun. *1996*, 705.
17. Sadamoto R., Tomioka N., Aida T.: J. Am. Chem. Soc. *118*, 3978 (1996).
18. Stevelmans S., van Hest J. C. M., Jansen J. F. G. A., van Boxtel D. A. F. J., de Brabander-van den Berg E. M. M., Meijer E. W.: J. Am. Chem. Soc. *118*, 7398 (1996).
19. Buhleier E., Wehner W., Vogtle F.: Synthesis *1978*, 155.
20. Huck W. T. S., van Veggel F. C. J. M., Reinhoudt D. N.: Angew. Chem., Int. Ed. Engl. *35*, 1213 (1996).
21. Zimmerman S. C., Zeng F., Reichert D. E. C., Kolotuchin S. V.: Science *271*, 1095 (1996).
22. Denkewalter R. G., Kolc J., Lukasavage W. J.: U.S. 4 289 872 (1985); Chem. Abstr. *102*, 79324 (1985).
23. Newkome G. R., Lin X., Weis C. D.: Tetrahedron Asymm. *10*, 957 (1991).
24. Twyman L. J., Beezer A. E., Mitchell J. C.: Tetrahedron Lett. *25*, 4423 (1994).
25. Pallin T. D., Tam J. P.: Chem.Commun. *1996*, 1345.
26. Niggemann M., Ritter H.: Acta Polym. *47*, 351 (1996).
27. Chow H.-F., Mak C. C.: Terahedron Lett. *33*, 5939, (1996).
28. McGrath D.V., Wu M.-J., Chaudry U.: Tetrahedron Lett. *37*, 6077 (1996).
29. Aoi K., Itoh K., Okada M.: Macromolecules *28*, 5391 (1995).
30. Ashton P. R., Boyd S. E., Brown C. L., Jayaraman M., Nepogodiev S. A., Stoddart J. F.: Chem. Eur. J. *2*, 1115 (1996).
31. Lindhorst T. K., Kieburg C.: Angew. Chem., Int. Ed. Engl. *35*, 1953 (1996).
32. Seebach D., Lapierre J.-M., Skobridis K., Greiveldinger G.: Angew. Chem., Int. Ed. Engl. *33*, 440 (1994).
33. Chow H.-F., Fok L. F., Mak C. C.: Tetrahedron Lett. *21*, 3547 (1994).
34. Murer P., Seebach D.: Angew. Chem., Int. Ed. Engl. *34*, 2116 (1995).
35. Bauer S., Fischer H., Ringsdorf H.: Angew. Chem., Int. Ed. Engl. *32*, 1589 (1993).
36. Brunner H., Altmann S.: Chem. Ber. *127*, 2285 (1994).
37. Bolm C., Derrier N., Seger A.: SYNLETT *1996*, 387.
38. Toda F., Tanaka K., Iwata S.: J. Org. Chem. *54*, 3007 (1989).
39. Cram D. J., Hegelson R. C., Peacock S. C., Kaplan L. J., Domeier L. A., Moreau P., Koga K., Mayer J. M., Chao Y., Siegel M. G., Hoffman D. H., Sogah G. D. Y.: J. Org. Chem. *43*, 1930 (1978).
40. Moneta W., Baret P., Pierre J. L.: Bull. Soc. Chim. Fr. *1988*, 995.
41. Holba V., Benko J., Kozankova J.: Collect. Czech. Chem. Commun. *45*, 255 (1980).
42. Hovorka M., Zavada J.: Org. Prep. Proced. Int. *23*, 200 (1991).
43. Hovorka M., Scigel J., Gunterova J., Tichy M., Zavada J.: Tetrahedron *48*, 9503 (1992).
44. Hovorka M., Zavada J.: Tetrahedron *48*, 9517 (1992).
45. Hovorka M., Stibor I., Holakovsky R., Smiskova I.: Czech. Appl. 64-96 (1996).
46. Arth C., Clemens M., Meise W.: Justus Liebigs Ann. Chem. *1994*, 259.

47. Yoon N. M., Pak C. S., Brown H. C., Krishnamurthy S., Stocky T. P.: J. Org. Chem. *38*, 2786 (1973).
48. Cram D. J., Helgeson R. C., Koga K., Kyba E. P., Madan K., Sousa L. R., Siegel M. G., Moreau P., Gokel G. W., Timko J. M., Sogah G. D. Y.: J. Org. Chem. *43*, 2758 (1978).
49. Clark J. H., Miller J. M.: Tetrahedron Lett. *7*, 599 (1977).
50. Akimoto H., Yamada S.: Terahedron *27*, 5999 (1971).