New and Improved Synthesis of Optically Pure (*R*)- and (*S*)-2,2′-Dimethyl-1,1′-binaphthyl and Related Compounds

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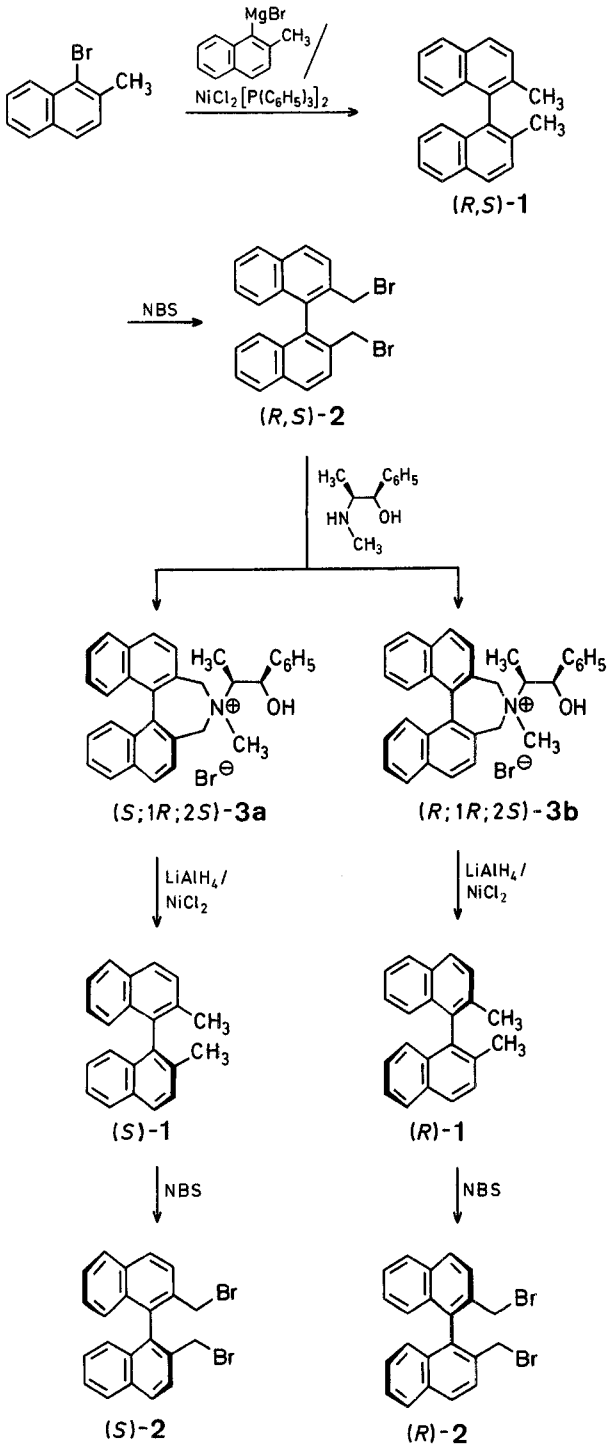
Axially disymmetric compounds containing a binaphthyl moiety have been extensively used in the past few years as chiral auxiliaries for asymmetric synthesis in the reduction of ketones by modified hydrides[1], addition of chelated organometallics to carbonyl compounds[2,3], chiral recognition in host-guest associations[4], catalytic hydrogenations[5], phase transfer catalysis[6], biogenetic type synthesis of limonene[7], reduction with NADH models[8]. At the same time, efforts have also been made to develop new syntheses of binaphthyl derivatives[5,9–15], or to improve the synthesis of useful binaphthyl precursors such as bis-2-naphthol[16].

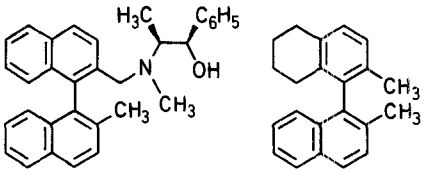
In that view, optically pure 2,2′-dimethyl-1,1′-binaphthyl (**1**) and 2,2′-bis[bromomethyl]-1,1′-binaphthyl (**2**), which have been considered as key intermediates in various studies[3,6,8,9,14,15,17] suffer from tedious access. The reported procedure[18] requires a 9–10 step reaction sequence starting from 1-bromo-2-methylnaphthalene, involving Ullmann coupling of 1-bromo-2-naphthoic acid methyl ester, which is sensitive to the experimental conditions, and resolution of 1,1′-binaphthyl-2,2′-dicarboxylic acid through the quinine salts of its two enantiomers, which requires careful crystallizations. (*S*)-**2** and (*R*)-**2** are obtained in ~ 13% and ~ 6% overall yield, respectively, and can be converted to (*S*)-**1** and (*R*)-**1** by reduction with lithium aluminium hydride[19].

In the present paper, we report a new and simpler alternative synthesis of these compounds, requiring only 4–5 steps from 1-bromo-2-methylnaphthalene. Under conditions similar to those reported[9], aryl-aryl coupling of 1-bromo-2 methylnaphthalene with its Grignard reagent in presence of a catalytic amount of bis[triphenylphosphine]dichloronickel, led to racemic 2,2′-dimethyl-1,1′-binaphthyl [(*R,S*)-**1**] in 73% overall yield after distillation. Treatment of (*R,S*)-**1** with *N*-bromosuccinimide, according to Ref.[17], led to the dibromide (*R,S*)-**2** in 58% yield after crystallization. In step 3, as we have previously described[6], (*R,S*)-**2** was treated with an excess of *l*-ephedrine (1*R*; 2*S*) in refluxing benzene/acetonitrile, leading quantitatively to a diastereoisomeric mixture of quaternary ammonium salts (*S*;1*R*;2S)-**3a** and (*R*;1*R*;2*S*)-**3b**, which were readily separated by crystallization because of their very good crystallinity and their markedly different solubilities. Thus, **3a** (sparingly soluble in all usual organic solvents) was obtained pure in 96% yield after a single crystallization, and **3b** was obtained from the mother liquor in 64% yield after 2 crystallizations. In step 4, reductive bis-de-*N*-benzylation of **3a** and **3b** was completed in refluxing tetrahydrofuran, with a large excess of lithium aluminium hydride and a catalytic amount of nickel chloride[20]. A simple acid-base extraction led respectively to (*S*)-**1** (89%) and (*R*)-**1** (87%) in the neutral extract and to recovered *l*-ephedrine in the basic extract.



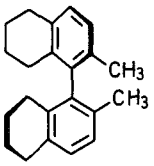
The above de-*N*-benzylation method was found to be more efficient than the catalytic reduction method using hydrogen over palladium-on-carbon or palladium(II) hydroxide-on-carbon where competitive hydrogenation of the naphthalene rings occurred. Several attempts at room temperature with hydrogen pressures of 1 to 15 bar resulted in the formation of mixtures of monodebenzylated amine **4a** or **4b**[14], the desired compound **1**, and the partially hydrogenated compound **5**

which could not be easily separated from **1** and was identified only by GC-MS of the mixture. However, under more drastic conditions (30 bar; 80 °C), complete transformation of **3b** into 2,2′-dimethyl-1,1′-bitetralyl [(*R*)-**6**] was observed (76% yield).

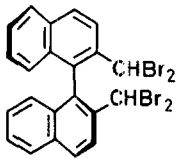


4a or **b**

5



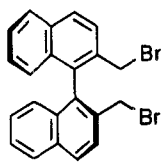
(*R*)-**6**



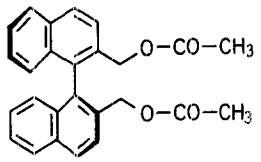
(*S*)-**7**

Treatment of crude (*S*)-**1** with *N*-bromosuccinimide led to optically pure dibromide (*S*)-**2** (34% yield after 2 crystallizations). Similar treatment of (*R*)-**1** led to optically pure (*R*)-**2** (38%). If needed, these yields could be optimized by recycling the crystallization residues or by converting them into other interesting binaphthyl derivatives. For example, the residue from crystallization of (*S*)-**2** was treated with a large excess of *N*-bromosuccinimide, to give optically pure 2,2′-bis[dibromomethyl]-1,1′-binaphthyl [(*S*)-**7**; 21.5%]. Racemic (*R,S*)-**7** which is a precursor of 1,1′-binaphthyl-2,2′-dialdehyde, has been previously prepared from (*R,S*)-**2** by this method[22].

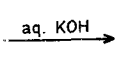
Other binaphthyl derivatives can be readily obtained from the dibromide **2**. As we have shown previously[23], hydrolysis of **2** with sodium carbonate in water/dioxan does not lead to 2,2′-bis[hydroxymethyl]-1,1′-binaphthyl (**9**), but to the corresponding ether oxide. Conversion of (*S*)-**2** to (*S*)-**9** was realized (88% yield) in two steps: The dibromide (*S*)-**2** was first converted to the diester (*S*)-**8** with potassium acetate and a catalytic amount of tetrabutylammonium bromide in dimethylformamide, (*S*)-**8** being then hydrolyzed to the diol (*S*)-**9**.

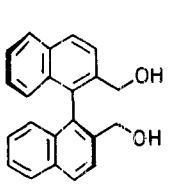


(*S*)-**2**



(*S*)-**8**





(*S*)-**9**

In conclusion, it can be pointed out that the two enantiomers of 2,2′-dimethyl-1,1′-binaphthyl presently obtained from 1-bromo-2-methylnaphthalene in a 4 step straight-forward synthesis, can be converted to most of the known functionalized products of this family, which are interesting precursors to various classes of chiral auxiliaries. The present synthetic approach has some remarkable features: (a), the aryl-aryl coupling is realized at the first step of the reaction sequence, (b) only distillation and crystallization operations are needed, (c) nor more than 2 crystallizations are required in order to obtain pure diastereoisomeric quaternary ammonium salts during the resolution process.

2,2′-Dimethyl-1,1′-binaphthyl [(*R,S*)-1]:

A solution of 1-bromo-2-methylnaphthalene (166 g, 0.75 mol) in 1:1 ether/benzene (600 ml) is added at room temperature under argon with magnetic stirring into a 2-l round-bottomed flask containing magnesium (20 g, 0.83 mol) in ether (~ 30 ml) and a few drops of 1,2-dibromoethane, at such a rate as to maintain a gentle reflux. When addition is completed (~ 4 h), the resulting Grignard solution is refluxed for 1 h, left at room temperature, transferred in portions in a 250-ml addition funnel under argon, and rapidly added to a 3-l round-bottomed flask equipped with a magnetic stirrer, containing 1-bromo-2-methylnaphthalene (148 g, 0.67 mol) and bis[triphenylphosphine]dichloronickel (5 g, 7.6 mmol) in ether (500 ml). When the addition is completed (~ 15 min.), the resulting dark brown solution is refluxed for 24 h, cooled at room temperature, and hydrolyzed with water (500 ml). After addition of 20% hydrochloric acid (500 ml), the organic phase is separated, washed with water (500 ml), and dried with magnesium sulfate. Filtration and evaporation of the solvents gives a crude product which is distilled (flame) under reduced pressure. Low boiling products (1-bromo-2-methylnaphthalene and 2-methylnaphthalene) are discarded. The high boiling fraction, a yellow glassy oil identified as (*R,S*)-**1** is used in the next step without further purification; yield: 138 g (73%); b.p. 190–210 °C/0.2 torr (Ref.[17], b.p. 160–170 °C/0.05 torr).

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 2.0 (s, 6H, CH_3); 6.8–8.2 ppm (m, 12 H_{arom}).

2,2′-Bis[bromomethyl]-1,1′-binaphthyl [(*R,S*)-2]:

(*R,S*)-**1** (138 g, 0.489 mol) is treated with *N*-bromosuccinimide (180 g, 1.011 mol) and benzoyl peroxide (1.8 g) in carbon tetrachloride (700 ml) as described[17]. Crystallization of the crude product from 1:3 benzene/hexane gives (*R,S*)-**2**; yield: 125 g (58%); m.p. 148–150 °C (Ref.[17], m.p. 148–149 °C).

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 4.25 (s, 4H, CH_2); 6.8–8.2 ppm (m, 12 H_{arom}).

Resolution Process: Ephedrinium Salts 3a and 3b[6]:

To a solution of (*R,S*)-**2** (88 g, 0.2 mol) and *l*-ephedrine (70 g, 0.425 mol) in benzene (500 ml), is added acetonitrile (1 l). The mixture is magnetically stirred for 24 h under reflux, then for 48 h at room temperature. On standing, a white precipitate deposits (partly insoluble salt **3a**), and analytical T.L.C. (silica, dichloromethane) of the clear upper solution shows no spot for the starting dibromide. Solvents are evaporated under vacuum and 95% ethanol (2 l) is added to the white solid residue, previously transferred to an Erlenmeyer flask. The mixture is boiled on a hot plate and concentrated to ~ 1 l. Crystallization occurs from the boiling solution, which is kept at room temperature overnight. The white crystals are filtered, washed with 95% ethanol, air dried giving pure (*S*; 1*R*; 2*S*)-**3a** (containing ~ 1 mol ethanol per mol, even after prolonged drying at 110 °C/0.1 torr); yield: 50.5 g (96%); m.p. 270–272 °C; $[\alpha]_Z^{22}$ (*c* 0.6, pyridine): + 291.4° (λ = 589 nm), + 302.2° (578 nm), + 343.2° (546 nm), + 565.8° (436 nm).

$C_{32}H_{30}BrNO \cdot C_2H_5OH$	calc.	C 71.57	H 6.36	N 2.46
(570.6)	found	71.73	6.34	2.47

M.S.: *m/e* = 411 ($M^+ - CH_3Br - H_2O$).

^{1}H-N.M.R. (DMSO-d_6/TMS): δ = 1.05 (t, *J* = 7.5 Hz, 3H, CH_3CH_2OH); 1.22 [d, *J* = 6.5 Hz, 3H, $NCH(CH_3)$]; 3.20 (s, 3H, NCH_3); 3.36 (s, H_2O from DMSO); 3.3–3.7 [m, 3H, $NCH(CH_3) + CH_3CH_2OH$]; 4.35 (t, *J* = 4.5 Hz, 1H, C_2H_5OH); 3.96, 4.76 (dd, *J* = 13 Hz, 2H, CH_2N); 4.04, 5.38 (dd, *J* = 13 Hz, 2H, CH_2N); 6.03 [d, *J* = 4.5 Hz, 1H, $CH(OH)C_6H_5$]; 6.22 (d, *J* = 4.5 Hz, 1H, OH); 7.2–8.5 ppm (m, 17 H_{arom}).

The mother liquor from the first crop is boiled on a hot plate and concentrated to ~ 800 ml. Water (1 l) is then slowly added to the boiling solution, which is concentrated again to ~ 1 liter, and left at

room temperature overnight. The resulting white powder is filtered, washed with water (200 ml), and air dried (weight 57 g). (Note: excess of *l*-ephedrine could be recovered from the mother liquor). The white solid is dissolved in boiling acetone (1–2 l), the resulting solution is filtered through paper and concentrated to ~ 300 ml on a hot plate. Crystallization occurs from the boiling solution, which is kept at room temperature overnight. The white crystals are filtered, rapidly washed with acetone, and air dried, giving pure (*R*;1*R*;2*S*)-**3b**; yield: 33.5 g (64%) (Note: a 78% yield was obtained in another experiment realized on smaller scale[6]); m.p. 217–225°C; $[\alpha]_\lambda^{22}$ (*c* 0.6, pyridine): −173.6° (λ = 589 nm), −183.8° (578 nm), −206.6° (546 nm), −300.5° (436 nm).

$C_{32}H_{30}BrNO$	calc.	C 73.28	H 5.77	N 2.67
(524.5)	found	73.36	5.69	2.65

M.S.: *m/e* = 411 ($M^+ - CH_3Br - H_2O$).

^{1}H-N.M.R. (DMSO-d_6/TMS): δ = 1.40 [d, *J* = 6.5 Hz, 3H, $NH(CH_3)$]; 3.23 (s, 3H, NCH_3); 3.33 (s, H_2O from DMSO); 3.3–3.7 [m, 1H, $NCH(CH_3)$]; 3.74, 4.88 (dd, *J* = 13 Hz, 2H, CH_2N); 4.54, 4.96 (dd, *J* = 13 Hz, 2H, CH_2N); 5.59 [d, *J* = 4.5 Hz, 1H, $CH(OH)C_6H_5$]; 6.27 (d, *J* = 4.5 Hz, 1H, OH); 7.2–8.5 ppm (m, $17H_{arom}$).

2,2′-Dimethyl-1,1′-binaphthyl [(*S*)-1 and (*R*)-1]:
To a solution of lithium aluminium hydride (19 g, 0.5 mol) in untreated tetrahydrofuran (1.8 l) are added crystalline **3a** (26.2 g, 0.05 mol) and dry nickel chloride (0.21 g). The magnetically stirred mixture is refluxed. Analytical T.L.C. (silica, 95:5 dichloromethane/methanol) of aliquots allows a control of the reaction, showing transformation of the primary product **4a**[14] into the desired hydrocarbon (*S*)-**1**. After 1 week reflux, the reaction is complete. The mixture is cooled at room temperature, carefully hydrolyzed with 1:1 tetrahydrofuran/water (100 ml), and filtered through fritted glass. The filtrate is evaporated to dryness and the residue dissolved in ether. The precipitated aluminium hydroxide is dissolved in 30% hydrochloric acid (600 ml) and the solution extracted with ether. The combined ether solution is extracted with 10% hydrochloric acid (2 × 100 ml), washed with water, dried with magnesium sulfate, filtered, and evaporated to give (*S*)-**1** as a glassy yellow oil; yield: 12.5 g (89%); $[\alpha]_D^{23}$: +17.5° (*c* 0.6, 95% ethanol).

Unchanged *l*-ephedrine is recovered after neutralization of the acidic extract and extraction with ether. A small amount of crude (*S*)-**1** is crystallized from methanol at −10°C, to give white crystals; m.p. 61–63°C. (Lit.[19], m.p. 64–67°C); $[\alpha]_\lambda^{23}$ (*c* 0.6; 95% ethanol): +18.9° (λ = 589 nm), +18.6° (578 nm), +25.3° (546 nm), +45.2° (436 nm). [Lit.[19], $[\alpha]_D^{22}$: +19° (*c* 1.3; ethanol)].

In the same manner, from **3b** (24.5 g, 0.047 mol), crude (*R*)-**1** is obtained after 24 h reflux with lithium aluminium hydride (18 g)/nickel chloride (0.18 g)/tetrahydrofuran (1.8 l); yield: 11.5 g (87%); $[\alpha]_D^{23}$: −16.4° (*c*, 2.5, 95% ethanol). Crystallization of a small amount of crude (*R*)-**1** from methanol at −10°C gives white crystals; m.p. 67–71°C; $[\alpha]_\lambda^{23}$ (*c* 0.9, 95% ethanol): −18.2° (λ = 589 nm), −19.8° (578 nm), −24.8° (546 nm), −46.5° (436 nm).

2,2′-Dimethyl-1,1′-bitetralyl [(*R*)-6]:
In a stainless steel 500 ml gas cylinder equipped with a thermocouple and a rocking heating jacket, are introduced a solution of **3b** (0.477 g, 0.9 mmol) in 95% ethanol (250 ml), and palladium hydroxide (0.5 g). The mixture is shaken at 80°C for 24 h under 30 bar pressure of hydrogen. The autoclave is opened at room temperature, the mixture is filtered on paper, the solution is evaporated to dryness, and the residue is dissolved in ether. The ether solution is extracted with 20% hydrochloric acid (2 × 100 ml), washed with water, and dried with magnesium sulfate. Filtration and evaporation of ether gives crude (*R*)-**6**; yield: 0.200 g (76%). Crystallization from a minimum of ether gives white crystals; m.p. 140–142°C; $[\alpha]_\lambda^{23}$ (*c* 1.2, chloroform): −15.9° (λ = 589 nm), −17.7° (578 nm), −20.1° (546 nm), −36.1° (436 nm).

$C_{22}H_{26}$	calc.	C 90.98	H 9.02
(290.5)	found	91.27	9.16

M.S.: *m/e* = 290 (M^+).

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 1.56 (m, 8H, $ArCH_2CH_2$); 1.69 (s, 6H, $ArCH_3$); 2.11 (m, 4H, $ArCH_2CH_2$); 2.80 (m, 4H, $ArCH_2CH_2$); 7.01 ppm (m, $4H_{arom}$).

2,2′-Bis[bromomethyl]-1,1′-binaphthyl[(*S*)-2 and (*R*)-2]:
To a solution of crude (*S*)-**1** (12.5 g, 44.3 mmol) in carbon tetrachloride (150 ml) are added *N*-bromosuccinimide (16.6 g, 93 mmol) and benzoyl peroxide (0.15 g). The magnetically stirred mixture is refluxed for 24 h. After filtration over fritted glass, the solution is evaporated and the residue dissolved in hot benzene (40 ml). When a mixture of hexane (80 ml)/pentane (30 ml) is slowly added to the hot benzene solution, crystallization occurs at room temperature within a few minutes. The crude crystals; yield: 9.55 g (49%); $[\alpha]_{546}^{23}$: −194.2° (*c* 1.1, benzene); m.p. 170–175°C are dissolved in boiling methyl ethyl ketone (50 ml) and the solution concentrated to ~ 10 ml on a hot plate. Crystallization occurs from the boiling solution. The mixture is kept at room temperature for 3 h. The crystals of pure (*S*)-**2** are filtered, washed with methyl ethyl ketone, and air-dried; yield: 6.65 g (34%); m.p.182–184°C (Ref.[18,19], m.p. 185.5–186.5°C, 183.5–185.5°C, respectively); $[\alpha]_\lambda^{23}$ (*c* 1, benzene): −159.2° (λ = 589 nm), −169.8° (578 nm), −198.6° (546 nm), −415.2° (436 nm); [Ref.[18], $[\alpha]_\lambda^{23}$ (*c* 1, benzene): −169.4° (λ = 578 nm), −199.1° (546 nm)].

The combined mother liquors from the crystallization are evaporated to dryness. The ^{1}H-N.M.R. spectrum of the residue (12.1 g) shows that it consists of ~ 30% unreacted (*S*)-**1** and 70% (*S*)-**2**.

In the same manner, from crude (*R*)-**1** (10.7 g, 30.9 mmol) is obtained crystalline (*R*)-**2** (from benzene/hexane); yield: 9.8 g (59%); m.p. 170–175°C; $[\alpha]_{546}^{23}$: +195.0° (*c* 1, benzene); which is recrystallized from methyl ethyl ketone to give pure (*R*)-**2**; yield: 6.30 g (38%); m.p. 182–184°C; $[\alpha]_\lambda^{23}$ (*c* 1, benzene): +163.0° (λ = 589 nm), +171.1° (578 nm); +200.2° (546 nm); +420.3° (436 nm).

2,2′-Bis[dibromomethyl]-1,1′-binaphthyl [(*S*)-7]:
The combined residue from the crystallizations of (*S*)-**2** (12.1 g) is treated with a large excess of *N*-bromosuccinimide (25 g) in refluxing carbon tetrachloride, with a catalytic amount of benzoyl peroxide for 2 weeks. After filtration and evaporation of the carbon tetrachloride, the residue is shaken with hot methyl ethyl ketone (30 ml), and then left at room temperature for 3 h. The white crystalline solid (*S*)-**7** is filtered, rapidly washed with methyl ethyl ketone, and air-dried; yield: 7.91 g [30% from initial (*S*)-**1**]. A second crystallization from methyl ethyl ketone gives pure (*S*)-**7**; yield: 5.7 g (22%); m.p. 221–223°C; $[\alpha]_\lambda^{25}$ (*c* 1, benzene): −161.5° (λ = 589 nm), −169.6° (578 nm), −194.6° (546 nm), −349.7° (436 nm), −575.6° (365 nm).

$C_{22}H_{14}Br_2$	calc.	C 44.18	H 2.36
(438.2)	found	44.43	2.36

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 6.13 (s, 2H, $ArCHBr_2$); 6.8–8.4 ppm (m, $12H_{arom}$).

2,2′-Bis[hydroxymethyl]-1,1′-binaphthyl [(*S*)-9]:
A solution of (*S*)-**2** (1.1 g, 2.5 mmol) in dimethylformamide (100 ml) is magnetically stirred at 80°C for 20 h with potassium acetate (1 g, 12 mmol) and tetrabutylammonium bromide (0.3 g). Extraction with ether gives crude *2,2′-bis[acetoxymethyl]-1,1′-binaphthyl* [(*S*)-**8**]; yield: 0.997 g (100%); $[\alpha]_{546}^{23}$: −94.4° (*c* 2.2, benzene).

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 1.82 (s, 6H, $OCOCH_3$); 4.83 (s, 4H, $ArCH_2$); 6.8–8.2 ppm (m, $12H_{arom}$).

The crude diester is hydrolyzed in refluxing aqueous 50% potassium hydroxide/dioxan for 24 h. Extraction with ether gives the crude diol, which is crystallized from benzene to give white crystals of (*S*)-**9**; yield: 0.690 g (88%); m.p. 166–168°C (Ref.[18], m.p. 168–169°C); $[\alpha]_\lambda^{24}$ (*c* 1, acetone): −67.5° (λ = 589 nm), −70.9° (578 nm), −83.1° (546 nm), −164.2° (436 nm) [Ref.[18], $[\alpha]_\lambda^{23}$ (*c* 1, acetone): −72.3° (λ = 578 nm), −83° (546 nm)].

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 3.33 (s, 2H, OH); 4.03, 4.37 (dd, *J* = 12 Hz, 4H, $ArCH_2$); 6.8–8.1 ppm (m, $12H_{arom}$).

Received: September 7, 1984

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