New 2,2′-Substituted 4,4′-Dimethoxy-6,6′-dimethyl[1,1′-biphenyls], Inducing a Strong Helical Twisting Power in Liquid Crystals

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Abstract: Based on the stabilisation of the molecular motion by the chiral residue, novel optically active biphenylic chiral dopants for nematic liquid crystals were developed. This molecular congestion was obtained by introducing mesogenic residues on the 2,2′-positions of the chiral biphenyl; this led to a novel molecular architecture that was found to be efficient. The synthesised optically active biphenyls were characterised with very short cholesteric pitches when used as chiral dopants in nematic liquid crystals. The synthesis of the enatiomerically pure biphenyl dopants and their preliminary physicochemical characterisations are described.

Keywords: asymmetric synthesis · biaryls · helical structures · liquid crystals

Introduction

The most striking consequence of the macroscopic helical structure of cholesteric mesophases is the selective circularly polarised light reflection and the angular dependence of the reflected wavelength. The reflected light can range from few nm to the entire UV-visible-IR spectral range. Based on this property unique to cholesteric liquid crystals, applications mainly in reflective displays, reflective polarisers, diffusive reflectors, optical filters and so forth still arouse great interest.[1] The rapid growth of these applications and their mother technologies is mainly driven by material development, as the width and the wavelength of reflected light are directly related to molecular parameters. In addition, the understanding and the control of the interactions between the chiral dopant and the nematic host are important in order to design and develop materials with definite properties. Here the helical twisting power (HTP), which is the quantitative measure of the cholesteric guest–host interactions, is the most important parameter of cholesteric chiral induction.

The HTP, given in Equation (1), is directly dependent on the chiral dopant molecular structure.[2] In Equation (1) HTP [μm^{-1}] is the helical twisting power for small concentrations; p [μm] is the pitch of induced helix, + for P, − for M helicies; x_i is the mole fraction of conformer I.

$$\mathrm{HTP} = \left[\frac{\mathrm{d}p^{-1}}{\mathrm{d}x}\right]_{x=0} \cong \frac{p-1}{x} = \sum_i x_i(\mathrm{HTP})_i \qquad (1)$$

Since the chiral guest and the achiral host compounds are not necessarily compatible at the molecular scale, their binary solution is frequently characterised by undesirable changes of the thermotropic properties with respect to the pure liquid-crystalline host material, like, for example, a depression of the clearing point. Those changes could in turn have negative effects on the physicochemical properties of the host, such as a decrease of the birefringence. Therefore, a chiral dopant is sought so that only very small concentrations are necessary to obtain large HTP values.

Binaphthol derivatives are examples of such efficient chiral dopants.[3] However, applications of chiral binaphthols are strongly limited by their relatively poor photostability when they are exposed to strong light sources such as those used in projection systems.

Chiral biphenyls[4] could represent a stable alternative to binaphthols, taking into account their weaker molecular polarisability. Besides biphenyls are from the chemical access point of view obtainable by a wide variety of synthetic methods, such as symmetrical or unsymmetrical coupling reactions performed on benzene functional derivatives, which are commercially available in a broad assortment. This offers the possibility to access various biphenyl-based chemical structures. Nevertheless chiral biphenyl derivatives synthesised so far, bearing mesogenic residues at 4,4′-positions,[5] are compatible with liquid crystal (LC) molecular ar-

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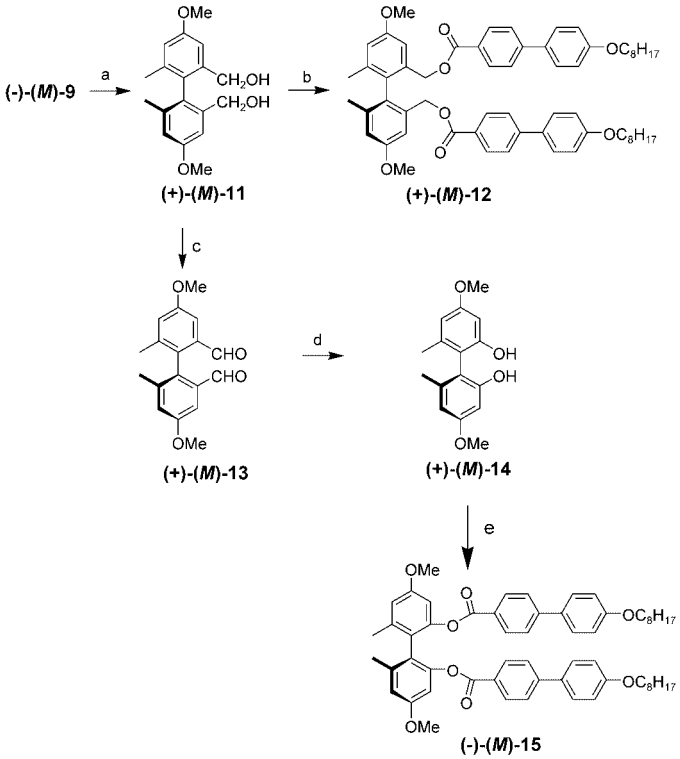
chitecture and have provided mixtures with a relatively small HTP when they are used as doping agents in nematic liquid crystals.

When analysing the molecular structures of the chiral dopants reported in literature it appears that the ones bearing overcrowded molecular structure around the chiral centres generally induce strong HTP in nematic hosts. As such chiral dopants are binaphthol,[6] Taddols,[7] butanetetraol[8a] and pyrrolidine[8b] derivatives. Based on this, we anticipated that moving mesogenic residues from 4,4′- to 2,2′-positions on the chiral biphenyl could lead to novel chiral dopants with high HTP. In fact in this novel molecular design of chiral biphenyl the sought overcrowding around the chiral group is increased and therefore better stabilisation of biphenyl dihedral angle could be induced due to the increase of intramolecular steric interactions at the 2,2′-positions.

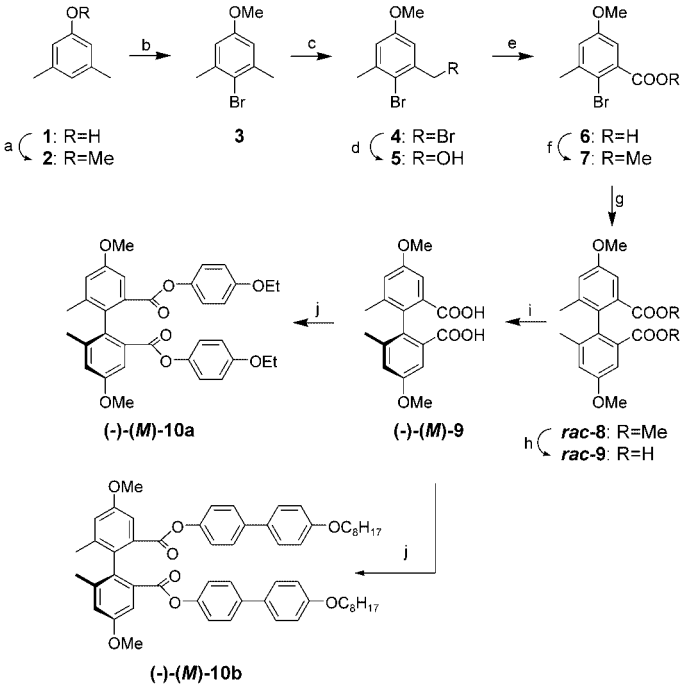
We present here the synthesis of first examples of such enantiomerically pure biphenyl dopants and preliminary results of their pitch measurements in a nematic host. The molecular overcrowding of the optically active group and its influence on the cholesteric pitch is briefly discussed by comparison of the length of the mesogenic residues and their linking nature to the optically active biphenyl core.

Results and Discussion

Synthesis: The synthesetic routes to the chiral dopants **10**, **12** and **15** are shown in Schemes 1 and 2. The common



Scheme 2. Reaction conditions: a) BH_3/THF, 0 °C (96 %); b) 4′octyloxy[1,1′-bipheyl]-4-carboxylic acid, $(CoCl)_2$, Et_3N, DMAP (27 %); c) PCC, DCM (88 %); d) *m*CPBA, DCM, $NaHCO_3$ (20 %); e) 4′-octyloxy(1,1′-biphenyl)-4-carboxylic acid, $(COCl)_2$, Et_3N, CH_3SO_2Cl, THF, −25 °C (73 %).



Scheme 1. Reaction conditions: a) KOH, MeOH, Me_2SO_4 (84 %); b) CCl_4, Br_2, −5 °C (85 %); c) CCl_4, NBS;AIBN; reflux (92 %); d) dioxane water, $CaCO_3$, reflux (95 %); e) acetone, $KMnO_4$, reflux (85 %); f) $SOCl_2$, MeOH (93 %); g) Cu, DMF, reflux (92 %); h) NaOH, water, reflux (97 %); i) brucine, MeOH, acetone, HCl (38 %); j) THF, CH_3SO_2Cl,Et_3N, −25 °C; **10a**: *p*-ethoxyphenol (63 %), **10b**: 4′-octyloxy(1,1′-biphenyl)-4-ol (59 %).

parent step of these syntheses involves the preparation of enantiomerically pure 4,4′-dimethoxy-6,6′-dimethyl(1,1′-biphenyl)-2,2′-dicarboxylic acid **9**, which was prepared from 3,5-dimethylphenol (Scheme 1). Phenol protection with dimethyl sulphate (84 % yield), followed by aromatic bromination *para* to the methoxy group with bromine in carbon tetrachloride (85 % yield) and benzylic bromination with NBS (92 % yield) led to the benzylbromide **4**. Compound 4 was then hydrolysed to the corresponding benzyl alcohol **5** using aqueous calcium carbonate (95 % yield) followed by benzylic oxidation using $KMnO_4$ to give the benzoic acid **6** (85 % yield). After esterification via the acid chloride (93 % yield), the resulting methyl ester **7** was submitted to Ullmann coupling reaction. The obtained racemic biphenyl dicarboxylic ester **8** (92 % yield) was saponified to the racemic acid *rac*-**9** (97 % yield).

For the optical resolution of racemic dicarboxylic acid *rac*-**9** we followed the procedure developed by Suda et al.[9] Hence upon treatment of *rac*-**9** with one mole equivalent of brucine in an acetone/methanol mixture under reflux followed by cooling, the (+)-*M* isomer was exclusively obtained in 38 % yield. Evaporation of the solvent of the mother liquor to dryness and recrystallisation from acetone, gave exclusively the (−)-*P* isomer in 31 % yield.

The acid (−)-(*M*)-**9** was then esterified with *p*-ethoxyphenol (63 % yield) or 4′-octyloxy(1,1′-biphenyl)-4-ol (59 % yield) to givethe optically active dopants (−)-(*M*)-**10a** and (−)-(*M*)-**10b**, respectively.

Despite the variation of the molecular structure of the mesogenic residues, the molecular nature of their linking groups to the biphenyl core could also have a strong effect on the molecular overcrowding of the optically active biphenyl. In order to study the effect of this structural change, the dicarboxylic acid (−)-(*M*)-**9** was reduced to the diol (+)-(*M*)-**11** with BH_3/THF followed by esterification with 4′-octyloxy(1,1′-biphenyl)-4-carboxylic acid, to give the diester (+)-(*M*)-**12** (Scheme 2).

Along this line the dibenzylalcohol (+)-(*M*)-**11** was converted into the dialdehyde (+)-(*M*)-**13** by using PCC (PCC = pyridinium chlorochromate, followed by Baeyer–Villiger rearrangement and hydrolysis to obtain the known optically active biphenol (+)-(*M*)-**14**[10]. Esterification with 4′-octyloxy(1,1′-biphenyl)-4-carboxylic acid afforded the chiral dopant (−)-(*M*)-**15**.

Helical twisting power measurements: The $HTP = 1/px$ of the optically active biphenyls, given in Table 1, were measured in ROTN 3010 nematic mixture (from Rolic Technology, Allschwil Switzerland), where p is the pitch in μm and x is the mole fraction.

Table 1. Helical twisting powers of chiral biphenyls in ROTN3010.

	Pitch[a] [μm]	HTP [$g\,mm^{-1}\,mmol^{-1}$]	Screw sense
(−)-(*M*)-10a	7.4	8	right
(−)-(*M*)-10b	2.3	39	left
(+)-(*M*)-12	7.3	13	left
(−)-(*M*)-15	1.8	50	left

[a] The pitch was measured in a solution of 1% of dope in nematic ROTN3010.

A global analysis of the obtained results shows that relatively high HTPs are obtained by using the new 2,2′-substituted optically active biphenyls as chiral dopants. By increasing the length of the mesogenic residues and varying the nature of their linking groups to the chiral residue it was possible to achieve HTP up to $50\,g\,mm^{-1}\,mmol^{-1}$ into the nematic host ROTN 3010. This confirms our assumption relative the chiral dopant intramolecular congestion as an efficient molecular architecture concept for achieving high HTPs. In addition, only a slight molecular decoupling of the chiral residue from the mesogenic groups led to a drastic decrease of the HTP. By comparison with (−)-(*M*)-**15**, the strong decrease of HTP observed for (+)-(*M*)-**12** (from 50 to $13\,g\,mm^{-1}\,mmol^{-1}$) could be attributed to the insertion of the two methylene groups, which reduces the molecular overcrowding and dihedral angle stability of the chiral biphenyl dopant.

Among the synthesised chiral dopants that all have the same absolute biphenyl configuration, it is interesting to point out that only compound (−)-(*M*)-**10a** induces cholesteric helix with an opposite helix sign. Here, even if an approach to the explanation of this behaviour needs more systematic variation of the molecular structure of the chiral dopant, it is reasonable to attribute it to a different intermolecular chiral induction mechanism. Taking into account the short mesogenic residue axis in (−)-(*M*)-**10a**, interactions with the LC host may differ from the other chiral dopants for which better defined segregation with LC host molecules is allowed through the long mesogenic residue axis.

Conclusion

In this paper we demonstrated that chiral biphenyls with appropriate molecular architecture are able to induce a large HTP into nematic liquid crystals. The efficiency of these novel chiral dopants is attributed to the intramolecular congestion in the chiral biphenyl residue induced by rigid grafting of the 2,2′-positions with long mesogenic residues. From the chemical point of view, if the chemistry of biphenyls is varied, the optical resolution has to be further improved in order to foresee their commercial and practical use in modern cholesteric devices.

Experimental Section

General remarks: ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz on a Bruker AC-200 instrument. Chemical shifts are reported relative to $CHCl_3$. Infrared spectra were recorded on a Perkin–Elmer Spectrum One. Optical rotations were measured on a Perkin–Elmer 241 MC Polarimeter. Melting points are uncorrected. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from P_2O_5. Hexane and dimethylformamide were dried over 4 Å molecular sieves. Flash chromatography was performed over Merck silica gel Si 60 (40–63 μm). Elemental analyses were performed by the Service Central de Microanalyse at the CNRS, Institut de Chimie, Strasbourg (France). Pitches were determined following the method of Grandjean-Cano using an Olympus BH-2 Microscope.

1-Methoxy-3,5-dimethylbenzene (2): Dimethyl sulphate (48 mL, 0.50 mol) was added slowly to a solution of 3,5-dimethylphenol (61 g, 0.50 mol) and potassium hydroxide (29 g, 0.52 mol) in methanol (250 mL). The exothermic reaction was kept at reflux for 1 h. Then the solvent was evaporated and the residue dissolved in diethyl ether (200 mL). The organic layer was washed with aqueous sodium hydroxide solution (10%, 3 × 50 mL) and with brine (3 × 50 mL). The organic phase was dried over ($MgSO_4$) and concentrated in vacuum. The crude material was distilled to give 57.8 g of **2** as colourless oil (0.42 mol, 84%). ^1H NMR ($CDCl_3$): $\delta = 2.31$ (s, 1H), 3.79 (s, 3H), 6.55 (s, 2H), 6.62 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 21.6$, 55.2, 111.8, 122.6, 139.3, 159.8 ppm.

2-Bromo-5-methoxy-1,3-dimethylbenzene (3): A solution of bromine (20.6 mL, 0.40 mol) in CCl_4 (200 mL) was added dropwise to a solution of **2** (55 g, 0.40 mol) in CCl_4 (800 mL) at −5 °C. A solution of aqueous sodium hydroxide (10%, 400 mL) was added slowly and the two layers were separated. The organic phase was washed with brine (2 × 200 mL) and dried over $MgSO_4$, and the solvent was evaporated in vacuum. Compound **3** was obtained as colourless oil (73 g, 0.34 mol, 85%). ^1H NMR ($CDCl_3$): $\delta = 2.39$ (s, 6H), 3.76 (s, 3H), 6.65 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 24.1$, 55.3, 113.9, 118.3, 139.1, 158.2 ppm.

2-Bromo-1-(bromomethyl)-5-methoxy-3-methylbenzene (4): A mixture of **3** (86 g, 0.40 mol), NBS (71 g, 0.40 mol) and AIBN (0.2 g) in CCl_4 (500 mL) was heated for 4 h at reflux. The reaction mixture was cooled to 0 °C and filtered, and the organic phase was washed successively with saturated sodium bicarbonate (200 mL), water (2 × 100 mL) and brine (2 × 100 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuum to give 108 g of **4** as a white solid (0.37 mol, 92%). M.p. 75–76 °C; ^1H NMR ($CDCl_3$): $\delta = 2.41$ (s, 3H), 3.80 (s, 3H), 4.61 (s, 2H), 6.77 (d, $J = 3$ Hz, 1H), 6.85 ppm (d, $J = 3$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 24.0$, 34.8, 55.6, 114.0, 117.0, 117.6, 138.0, 140.4, 158.4 ppm.

(2-Bromo-5-methoxy-3-methylphenyl)methanol (5): A mixture of **4** (50 g, 0.20 mol), 1,4-dioxane (150 mL), water (150 mL) and calcium carbonate (50 g, 0.50 mol) was heated for 10 h at reflux. The mixture was filtered

and concentrated in vacuum, then diluted with methylene chloride (150 mL). The organic layer was washed with HCl (2 M, 50 mL) and a solution of saturated sodium bicarbonate (50 mL), dried ($MgSO_4$) and concentrated in vacuum to give 43.9 g of compound **5** as white crystals (0.19 mol, 95%). M.p. 48–49 °C; ^{1}H NMR ($CDCl_3$): $\delta = 2.39$ (s, 3H), 3.80 (s, 3H), 4.72 (s, 2H), 6.75 (d, $J = 3$ Hz, 1H), 6.91 ppm (d, $J = 3$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 23.5$, 55.5, 65.4, 111.4, 115.6, 139.3, 141.1, 140.4, 158.6 ppm.

2-Bromo-5-methoxy-3-methylbenzoic acid (6): A solution of $KMnO_4$ (16.6 g, 105 mmol) in water (350 mL) was added slowly to a solution of alcohol **5** (12.2 g, 52.5 mmol) in acetone (250 mL), which was kept at reflux for further 30 minutes. The mixture was cooled down and acidified with HCl (2 M, 50 mL). The brown precipitate was dissolved by adding a solution of saturated sodium bicarbonate (100 mL) and acetone was evaporated in vacuum. Ammonia (150 mL) was added. The mixture was filtered over celite and acidified with concentrated HCl. The product was extracted with diethyl ether (3×50 mL), the combined organic phases were dried ($MgSO_4$) and concentrated in vacuum to obtain 13.5 g of the acid **6** as white crystals (0.55 mol, 85%). M.p. 129 °C; IR (KBr): $\tilde{\nu} = 926$, 1159, 1277, 1411, 1682, 2631, 2563–3125 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.45$ (s, 3H), 3.82 (s, 3H), 6.98 (d, $J = 2.6$ Hz, 1H), 7.26 (d, $J = 2.6$ Hz, 1H), 10.3 ppm (br s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 23.1$, 55.6, 111.7, 112.2, 118.2, 136.3, 139.9, 157.8, 168.0 ppm.

Methyl 2-bromo-5-methoxy-3-methylbenzoate (7): A mixture of acid **6** (9.5 g, 37 mmol) and thionyl chloride (20 mL) was heated at reflux for 3 h. The mixture was concentrated in vacuum; methanol (50 mL) and pyridine (10 mL) were added and altogether stirred for 2 h at room temperature. The mixture was concentrated in vacuum, dissolved in methylene chloride (50 mL), washed successively with HCl (2 M, 20 mL) and brine (2×30 mL), dried ($MgSO_4$) and filtered, and the solvents were evaporated in vacuum. The crude product was purified by flash chromatography (hexane/ethyl acetate, 40:60) to give 8.8 g of ester **7** as a white solid (34 mmol, 93%). M.p. 49–51 °C; IR (KBr): $\tilde{\nu} = 856$, 1146, 1245, 1438, 1593, 1727, 2845, 2955, 3006 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.39$ (s, 3H), 3.76 (s, 3H), 3.90 (s, 3H), 6.89 (d, $J = 3.1$ Hz, 1H), 6.97 ppm (d, $J = 3.1$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 24.0$, 52.6, 55.6, 113.0, 113.6, 119.4, 134.5, 140.8, 158.1, 167.6 ppm.

Dimethyl 4,4′-dimethoxy-6,6′-dimethyl(1,1′-biphenyl)-2,2′-dicarboxylate (*rac*-8): A mixture of ester **7** (11 g, 43 mmol) and freshly activated copper powder[11] (10 g) in DMF (50 mL) was heated to reflux for 3 h under argon atmosphere. The mixture was cooled down to room temperature, filtered over celite by washing the residue with ethyl acetate (5× 10 mL). DMF was extracted with water (10×30 mL). Then the organic phase was washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated in vacuum. The crude product was purified by flash chromatography (hexane/ethyl acetate, 80/20) to give 7.2 g of diester ***rac*-8** as a white solid (20 mmol, 92%). M.p. 73–74 °C; IR (KBr): $\tilde{\nu} = 860$, 1014, 1173, 1234, 1435, 1605, 1723, 2838, 2951 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.88$ (s, 6H), 3.59 (s, 6H), 3.86 (s, 6H), 6.98 (d, $J = 2.7$ Hz, 2H), 7.34 ppm (d, $J = 2.7$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 20.4$, 51.8, 55.2, 111.8, 119.7, 130.7, 133.2, 138.7, 157.9, 167.5 ppm.

4,4′-Dimethoxy-6,6′-dimethyl(1,1′-biphenyl)-2,2′-dicarboxylic acid (*rac*-9): A mixture of diester **8** (5.0 g, 14 mmol) and sodium hydroxide (5.6 g, 140 mmol) in water (50 mL) was heated at reflux for 3 h. The solution was cooled down to room temperature and acidified with HCl_{conc} until pH 1 was attained. The white precipitate was extracted with ethyl acetate, and the organic layer washed with saturated sodium bicarbonate (50 mL) and brine (2×50 mL), dried over $MgSO_4$ and concentrated in vacuum to obtain 4.5 g of *rac*-**9** as white crystals (13.6 mmol, 97%): m.p. 202–204 °C; IR (KBr): $\tilde{\nu} = 795$, 852, 942, 1147, 1240, 1313, 1459, 1602, 1667, 1689, 2524–2984 cm^{-1}; 1H NMR (CDCl3): $\delta = 1.85$ (s, 6H), 3.86 (s, 6H), 7.04 (d, $J = 2.1$ Hz, 2H), 7.29 (d, $J = 2.1$ Hz, 2H), 10.56 ppm (br s, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 20.4$, 55.4, 112.7, 121.6, 129.1, 134.5, 138.6, 158.0, 172.8 ppm.

4,4′-Dimethoxy-6,6′-dimethyl(1,1′-biphenyl)-2,2′-dicarboxylic acid ((−)-(*M*)-9 and (+)-(*P*)-9): A mixture of diacid *rac*-**9** (3.7 g, 11 mmol) and brucine (4.2 g, 11 mmol) was dissolved at reflux in methanol (5 mL) and acetone (10 mL). The solution was allowed to cool down slowly and the precipitated crystals were filtered off by washing with cold methanol (2 mL) in order to obtain (*M*)-**9**-brucine salt (3.1 g, 39%), $[\alpha]_D^{20} = +59$ ($c = 1$ in CH_2Cl_2). The mother liquor was concentrated in vacuum and the residue crystallised in acetone in order to obtain (*P*)-**9**-brucine salt (2.6 g, 33%), $[\alpha]_D^{20} = -41$ ($c = 1$ in CH_2Cl_2). The nonracemic salts were hydrolysed separately by shaking them at room temperature in a separation funnel containing a mixture of ethyl acetate/hydrochloric acid (1 M) 1:1. The aqueous phases were extracted with ethyl acetate the obtained organic layers were washed with saturated sodium bicarbonate (50 mL) and brine (2× 50 mL), dried over $MgSO_4$ and concentrated in vacuum to obtain 1.4 g of (−)-(*M*)-**9** (4.3 mmol, 38%), $[\alpha]_D^{20} = -20$ ($c = 1$ in EtOH) and 1.1 g of (+)-(*P*)-**9** (3.5 mmol, 31%), $[\alpha]_D^{20} = +19$ ($c = 1$ in EtOH); m.p. 202–204 °C; IR and NMR spectra were identical to those of *rac*-**9**.

4,4′-Dimethoxy-6,6′-dimethyl(1,1′-biphenyl)-2,2′-dimethanol ((+)-(*M*)-11 and (−)-(*P*)-11): A solution of BH_3/THF 1 M (20 mL, 20 mmol) was added slowly at 0 °C to diacid (−)-(*M*)-**9** or (+)-(*P*)-**9** (1.56 g, 4.73 mmol) dissolved in THF (60 mL). The mixture was stirred at room temperature for 12 h before being hydrolysed at 0 °C with saturated aqueous NH_4Cl (5 mL). The mixture was filtered, extracted with ethyl acetate and the organic layer washed with brine (2×20 ml), dried ($MgSO_4$) and concentrated in vacuum to obtain 1.37 g (4.53 mmol, 96%) as white crystals of respectively (+)-(*M*)-**11**: $[\alpha]_D^{20} = +15$ ($c = 1$ in EtOH) or (−)-(*P*)-**11**: $[\alpha]_D^{20} = -13$ ($c = 1$ in EtOH); m.p. 79–82 °C; IR (KBr): $\tilde{\nu} = 867$, 999, 1173, 1305, 1439, 1604, 2840, 2944, 3257 cm^{-1} (br); ^{1}H NMR ($CDCl_3$): $\delta = 1.84$ (s, 6H), 3.84 (s, 6H), 4.16 (AB, $J = 11.5$ Hz, $\Delta\nu = 24$ Hz, 4H), 6.79 (d, $J = 2.4$ Hz, 2H), 6.89 ppm (d, $J = 2.4$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 20.3$, 55.1, 63.2, 111.9, 115.4, 130.1, 138.0, 140.2, 158.8 ppm.

4,4′-Dimethoxy-6,6′-dimethyl(1,1′-biphenyl)-2,2′-dicarbaldehyde ((+)-(*M*)-13 and (−)-(*P*)-13): A mixture of alcohol (+)-(*M*)-**11** or (−)-(*P*)-**11** (0.80 g, 2.9 mmol) and PCC (2.6 g, 12 mmol) in methylene chloride (20 mL) was stirred at room temperature for 45 minutes and afterwards filtered over silica gel and washed with ethyl acetate/hexane 50:50 in order to obtain 0.77 g (2.6 mmol, 88%) of (+)-(*M*)-**13**: $[\alpha]_D^{20} = +32$ ($c = 1$ in EtOH) or (−)-(*P*)-**13**: $[\alpha]_D^{20} = -30$ ($c = 1$ in EtOH); m.p. 95–98 °C; IR (KBr): $\tilde{\nu} = 867$, 947, 1147, 1305, 1391, 1600, 2854, 2925, 2958 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.95$ (s, 6H), 3.90 (s, 6H), 7.13 (dd, $J = 2.7$, 0.6 Hz, 2H), 7.39 (d, $J = 2.7$ Hz, 2H), 9.55 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 19.8$, 55.5, 108.4, 123.1, 132.7, 136.1, 139.7, 159.5, 191.3 ppm.

4,4′-Dimethoxy-6,6′-dimethyl(1,1′-biphenyl)-2,2′-diol ((+)-(*M*)-14 or (−)-*P*-14): A mixture of aldehyde (+)-(*M*)-**13** or (−)-(*P*)-**13** (224 mg, 0.75 mmol) and *m*CPBA (1.3 g, 7.5 mmol) in methylene chloride (10 mL) was stirred at room temperature for 20 h. The excess *m*CPBA was reduced by adding $Na_2S_2O_3$ 1 M (10 mL). The mixture was washed with a saturated solution of $NaHCO_3$ (3×10 mL). The organic layer was stirred in Na_2CO_3 1 M (5 mL) for 30 minutes at room temperature and then extracted with methylene chloride (3×5 mL) and concentrated in vacuum; the residue was purified by preparative chromatography (ethyl acetate/hexane 40:60) to obtain 30 mg (0.11 mmol, 20%) of respectively (+)-(*M*)-**14**: $[\alpha]_D^{20} = +15$ ($c = 1$ in EtOH) or (−)-(*P*)-**14**: $[\alpha]_D^{20} = -13$ ($c = 1$ in EtOH); m.p. 155–160 °C; IR (KBr): $\tilde{\nu} = 837$, 977, 1156, 1343, 1305, 1579, 2842, 2957, 3338 cm^{-1} (br); ^{1}H NMR ($CDCl_3$): $\delta = 1.97$ (s, 6H), 3.81 (s, 6H), 4.80 (s, 2H), 6.47 (AB, $J = 2.4$ Hz, 2H), 6.50 ppm (AB, $J = 2.4$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 11.6$, 55.8, 99.2, 109.2, 112.7, 141.0, 156.2, 161.5 ppm.

Bis(4-ethoxyphenyl) 4,4′-Dimethoxy-6,6′-dimethyl(1,1′-biphenyl)-2,2′-dicarboxylate ((−)-(*M*)-10a): Oxalyl chloride (0.5 mL, 6 mmol) was added slowly to a solution of (−)-(*M*)-**9** (0.3 g, 0.9 mmol) in CH_2Cl_2 (2 mL) at 0 °C and stirred for 3 h at room temperature. The solvent was evaporated in vacuum and the residue dissolved in benzene (5 mL). *p*-Ethoxyphenol (190 mg, 1.38 mmol), freshly distilled pyridine (1 mL) and DMAP (8 mg) were added. The mixture was stirred at room temperature for 5 minutes, and then heated to 65 °C for 3 h. The cold mixture was dissolved in EtOAc (5 mL), washed successively with HCl 2 M (5 mL), Na_2CO_3 1 M (5 mL) and brine (2×5 mL), dried over $MgSO_4$ and evaporated in vacuum. The residue purified by flash chromatography (ethyl acetate/hexane 20:80) to obtain 110 mg (0.19 mmol, 63%) of (−)-(*M*)-**10a**: $[\alpha]_D^{20} = -77$ ($c = 1$ in CH_2Cl_2); pitch = +7.4 μm (1% in ROTN 3010); IR (KBr): $\tilde{\nu} = 854$, 1009, 1171, 1314, 1465, 1505, 1603, 1741, 2927, 2979 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.39$ (t, $J = 3.5$ Hz, 6H), 2.02 (s, 6H), 3.88 (s, 6H), 3.98 (q, $J = 3.5$ Hz, 4H), 6.80 (d, $J = 1.8$ Hz, 8H), 7.06 (d, $J = 1.3$ Hz, 2H), 7.50 ppm (d, $J = 1.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 15.2$, 20.8, 55.8, 64.2, 112.8, 120.6, 115.4, 122.9, 131.2, 133.6, 139.5, 144.5, 156.9, 158.7,

166.6 ppm; elemental analysis calcd (%) for $C_{34}H_{34}O_8$: C 71.5, H 6.0; found C 71.5, H 6.2.

Bis[4′-(octyloxy)(1,1′-biphenyl)-4-yl]-4,4′-dimethoxy-6,6′-dimethyl(1,1′-biphenyl)-2,2′-dicarboxylate ((−)-(*M*)-10b): Compound (−)-(*M*)-**10b** was prepared according the procedure described above ((−)-(*M*)-**10a**). 4′-Octyloxy(1,1′-biphenyl)-4-ol was used instead of *p*-ethoxyphenol. After flash chromatography (ethyl acetate/hexane 20:80) 157 mg (0.18 mmol, 59%) of (−)-(*M*)-**10b** $[\alpha]_D^{20} = -147$ ($c = 1$ in CH_2Cl_2) were obtained; pitch = −2.3 μm (1% in ROTN 3010); m.p. 80–82 °C; IR (KBr): $\tilde{\nu} = 857$, 997, 1166, 1318, 1466, 1603, 1728, 1746, 2852, 2922 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.96$ (t, $J = 6.9$ Hz, 6H), 1.2–1.9 (m, 24H), 2.07 (s, 6H), 3.88 (s, 6H), 3.98 (t, $J = 6.4$ Hz, 4H), 6.90 (d, $J = 3.2$ Hz, 4H), 6.94 (d, $J = 3.2$ Hz, 4H), 7.06 (d, $J = 2.4$ Hz, 2H), 7.42 (d, $J = 5.1$ Hz, 4H), 7.46 (d, $J = 5.1$ Hz, 4H), 7.52 ppm (d, $J = 2.7$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 14.1$, 20.3, 22.8, 26.0, 29.3, 31.7, 55.3, 68.0, 112.4, 120.3, 114,7, 121.7, 127.5, 128.0, 130.4, 131.7, 133.2, 138.5, 139.1, 149.5, 158.2, 158.6, 165.9 ppm; $C_{58}H_{66}O_8$: calcd. C 78.1, H 7.5; found C 77.9, H 7.5.

Bis[4′-(octyloxy)(1,1′-biphenyl)-4-carbonyloxymethyl]-4,4′-dimethoxy-6,6′-dimethyl(1,1′-biphenyl)-−2,2′-diyl ((+)-(*M*)-12): Oxalyl chloride (0.5 mL, 6 mmol) was added slowly to a solution of 4′-octyloxy(1,1′-biphenyl)-4-carboxylic acid (0.3 g, 0.9 mmol) in CH_2Cl_2 (5 mL) at 0 °C and stirred for 3 h at room temperature. The solvent was evaporated in vacuum and the residue dissolved in CH_2Cl_2 (5 mL). Benzylic alcohol (+)-(*M*)-**11** (100 mg, 0.33 mmol), triethylamine (0.3 mL, 2 mmol) and DMAP (8 mg) were added at 0 °C. The mixture was stirred at room temperature for 12 h. The cold mixture was washed successively with HCl 1 M (5 mL), $NaHCO_3$ 1 M (5 mL) and brine (2 × 5 mL), dried over $MgSO_4$ and evaporated in vacuum. After flash chromatography (ethyl acetate/hexane 20:80) 225 mg (0.25 mmol, 27%) of (+)-(*M*)-**12** $[\alpha]_D^{20} = +29$ ($c = 1$ in CH_2Cl_2) were obtained. Pitch = −7.3 μm (1% in ROTN 3010); m.p. 80–84 °C; IR (KBr): $\tilde{\nu} = 827$, 1096, 1157, 1248, 1372, 1467, 1604, 1713, 2854, 2925 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.91$ (t, $J = 6.3$ Hz, 6H), 1.2–1.9 (m, 24H), 1.95 (s, 6H), 3.85 (s, 6H), 3.96 (t, $J = 6.2$ Hz, 4H), 4.98 (AB, $J = 12.9$ Hz, $\Delta\nu = 19$ Hz, 4H), 6.86 (d, $J = 2.0$ Hz, 2H), 6.93 (d, $J = 8.3$ Hz, 4H), 7.00 (d, $J = 2.0$ Hz, 2H), 7.46 (d, $J = 8.9$ Hz, 4H), 7.52 (d, $J = 8.3$ Hz, 4H), 8.00 ppm (d, $J = 8.1$ Hz, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 14.1$, 20.1, 22.5, 26.0, 29.2, 29.4, 31.8, 55.1, 64.9, 68.1, 111.9, 115.2, 114.9, 126.3, 128.2, 130.1, 128.0, 129.8, 131.9, 135.5, 138.4, 145.1, 158.9, 159.4, 166.1 ppm; elemental analysis calcd (%) for $C_{58}H_{66}O_8$: C 78.4, H 7.7; found C 78.2, H 7.7.

Bis[4′-(octyloxy)(1,1′-biphenyl)-4-carbonyloxy]-4,4′-dimethoxy-6,6′-dimethyl(1,1′-biphenyl)-2,2′-diyl ((−)-(*M*)-15): A solution of 4′-octyloxy(1,1′-biphenyl)-4-carboxylic acid (175 mg, 0.5 mmol), triethylamine (0.14 mL, 0.98 mmol) and methylsulfonyl chloride (37 μL, 0.48 mmol) in THF (2 mL) was stirred between −25 °C and −35 °C for 1 h. Biphenol (+)-(*M*)-**14** (40 mg, 0.15 mmol) and DMAP (4 mg) dissolved in THF (2 mL) were added. The mixture was stirred at room temperature for 24 h, filtered over celite and purified by preparative TLC (ethyl acetate/hexane 20:80) to obtain 96 mg (0.11 mmol, 73%) of (−)-(*M*)-**15** $[\alpha]_D^{20} = -238$ ($c = 1$ in CH_2Cl_2); pitch = −1.8 μm (1% in ROTN 3010); m.p. 63–66 °C; IR (KBr): $\tilde{\nu} = 823$, 998, 1078, 1139, 1182, 1251, 1314, 1463, 1603, 1733, 2853, 2921 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.89$ (t, $J = 6.2$ Hz, 6H), 1.2–1.9 (m, 24H), 2.09 (s, 6H), 3.76 (s, 6H), 4.00 (t, $J = 6.5$ Hz, 4H), 6.71 (AB, $J = 2.3$ Hz, $\Delta\nu = 5$ Hz, 4H), 7.97 (d, $J = 8.9$ Hz, 4H), 7.54 (d, $J = 8.9$ Hz, 4H), 7.56 (d, $J = 8.6$ Hz, 4H), 7.92 ppm (d, $J = 8.6$ Hz, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 14.1$, 19.9, 22.7, 26.1, 29.3, 29.4, 31.8, 55.4, 68.2, 105.5, 113.4, 114.9, 121.1, 126.4, 127.6, 128.3, 130.5, 132.1, 139.9, 145.5, 149.9, 159.2, 159.5, 164.7 ppm; elemental analysis calcd (%) for $C_{58}H_{66}O_8$: C 78.2, H 7.5; found C 77.5, H 7.6.

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[11] Activation of copper powder: Prior to use the copper powder (10 g) was stirred in a solution of iodine (2 g) in acetone (50 mL). As soon as the mixture became colourless the liquid was decanted and the copper powder was washed once with a mixture of acetone/HCl_{conc} 1/1 (50 mL), then with acetone (5 × 50 mL). The copper powder was dried in vacuum at 170 °C for 2 h.

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