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Kenta Tojo[a]; Takuji Hirose[a]; Yoshio Aoki[a]
[a] Graduate School of Science and Engineering, Saitama University, Saitama 338-8570, Japan

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Synthesis of new chiral dopants derived from naproxen for nematic liquid crystals

Kenta Tojo, Takuji Hirose and Yoshio Aoki*

Graduate School of Science and Engineering, Saitama University, 255 Shimo-Ohkubo, Sakura-ku, Saitama 338-8570, Japan

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New chiral dopants were synthesised from naproxen and hexyloxyphenol or benzyloxyphenol, and their helical twisting power (HTP) and helical senses determined. Their HTP values were largely influenced by the position of the substituents and the type of linkage between the chiral centre and the core part. Ester-linked chiral dopants with 1,4-substitution of the benzene ring showed relatively large HTP values. However, ether-linked chiral dopants with 1,2-substitution showed larger molar HTP values than those with 1,4-substitution.

1. Introduction

Chirality is one of the most interesting subjects in the field of liquid crystals. Chiral nematic liquid crystals having macroscopic helical structure are currently used in twisted nematic liquid crystal display devices. In general, chiral nematic materials consist of achiral host mixtures of nematic liquid crystals and a chiral dopant with a large helical twisting power (HTP) (*1, 2*). The helical structure of the chiral nematic liquid crystals is induced by the interaction between the host liquid crystalline molecules and the chiral dopants. Twisted grain boundary (TGB) and blue phases are examples of specific liquid crystal phases with helical structures (*3, 4*). In many cases such phases are induced by addition of a chiral dopant to the host liquid crystal (*4, 5*). The TGB phase is a result of the frustration between molecular chirality and smectic layer ordering (*3*). The blue phase has a fluid lattice structure that is stabilised by lattice defects. The blue phase is usually found in a very narrow temperature range between an isotropic liquid phase and a chiral nematic phase of sufficiently short pitch (*4*).

Thus far, many chiral dopants have been synthesised, and their physical properties determined (*6–10*). In particular, chiral dopants with a methyl asymmetric frame have been widely investigated (*6, 7, 9, 10*). We have been investigating the relationship between the molecular structure of chiral dopants with a methyl or trifluoromethyl asymmetric frame and their HTP values (*6, 9*). For optically active 2-phenylpropionic acid derivatives, the HTP values were largely influenced by the linkage between the asymmetric frame and the core moiety (*6*). Optically active chiral dopants with a trifluoromethyl asymmetric frame, including 4,4,4-trifluoro-3-phenylbutanoic acid derivatives and 4,4,4-trifluoro-3-[4-(4-methoxyphenyl)phenyl]butanoic acid derivatives, gave rise to large HTP values (*9, 10*).

In most cases, chiral dopants consist of a chiral part, a core part and some substituents. Many chiral dopants with an asymmetric carbon have a linear structure, and their core moieties often consist of a 1,4-substituted benzene or a 1,4-substituted cyclohexane (Figure 1) (*1, 2, 6, 7, 9, 10*).

In this paper, we report the relationship between the molecular structures of new chiral dopants having two substituents and their HTP values.

2. Results and discussion

All new chiral dopants were derived from naproxen, which is one of the most used commercially available chiral compounds. The synthetic route to ester-linked chiral dopants (**1a**–**1c**, **2a**–**2c**) is shown in Scheme 1 and that to ether-linked chiral dopants (**5a**–**5c**, **6a**–**6c**) is shown in Scheme 2.

The chiral nematic liquid crystalline mixtures were prepared by adding the chiral dopant (1 wt %) to the host liquid crystal (ZLI-1132, Merck) (*11*). The helical pitches in the chiral nematic phases were measured using Cano wedge cells (*12*). The HTP can be calculated using

$$\mathrm{HTP} = (pc)^{-1}, \tag{1}$$

where p is the pitch of the chiral nematic phase in μm and c is the mass fraction of the chiral dopant (*13*). In order to describe the HTP per molecule, we have suggested the molar helical twisting power (MHTP), as defined by

$$\mathrm{MHTP} = \mathrm{HTP} \times M_\mathrm{d}/1000 \left(\mu\mathrm{m}^{-1}\ \mathrm{mol}^{-1}\ \mathrm{kg}\right), \tag{2}$$

where M_d is the molecular weight of the chiral dopant (*9*).

*Corresponding author. Email: aoki@apc.saitama-u.ac.jp

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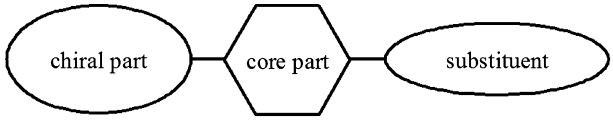
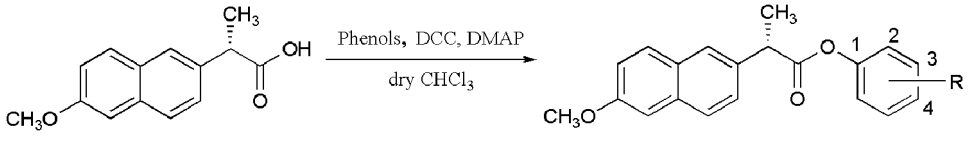


Figure 1. Schematic of typical chiral dopant structure.

The helical senses of the chiral nematic phases were determined by the contact method using a reference mixture prepared from the host liquid crystal and cholesteryl nonanoate, which has a negative helical sense (left-handed). The HTP and MHTP values and helical senses of the new chiral dopants are summarised in Table 1.

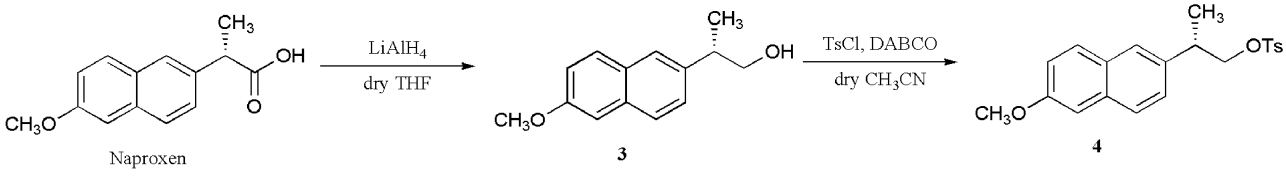
The 1,4-substituted chiral dopants (**1c**, **2c**, **5c** and **6c**) induced a negatively-sensed helix, whereas the 1,3-substituted chiral dopants (**1b**, **2b**, **5b** and **6b**) induced a positively-sensed helix. Most of the 1,2-substituted chiral dopants (**2a**, **5a** and **6a**) induced a negatively-sensed helix; however, **1a** induced a positively-sensed helix. These results suggest that the 1,4-substituted chiral dopants have a similar conformation regardless of the substituents and the linkage type, with the 1,3-substituted chiral dopants showing a similar tendency. The 1,2-substituted chiral dopants are probably influenced by steric hindrance between the chiral part and the substituent, with the magnitude of the steric hindrance strongly depending on the particular combination of chiral part and substituent. It can be seen that the helical senses depend on the substituent in the 1,2-substituted chiral dopants.

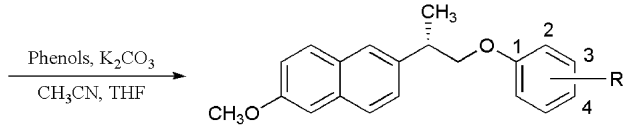
In most compounds, chiral dopants with a benzyloxy group showed larger MHTP values than those with a hexyloxy group. Specifically, it was found that chiral dopants with a benzyloxy group at the 2-position exhibited MHTP values that were about twice as large as those of the corresponding dopants with a hexyloxy group. In this system, the benzyloxy group strongly influences the MHTP value, whereas the hexyloxy group does not. A benzyloxy group has an aromatic ring which can interact with other host liquid crystalline molecules via $\pi-\pi$ interaction. These results suggest that the existence of an aromatic ring at the end of the molecule is important to obtain a large MHTP value.



1a, R = OC_6H_{13}, Substituted position = 1, 2
1b, R = OC_6H_{13}, Substituted position = 1, 3
1c, R = OC_6H_{13}, Substituted position = 1, 4
2a, R = OCH_2Ph, Substituted position = 1, 2
2b, R = OCH_2Ph, Substituted position = 1, 3
2c, R = OCH_2Ph, Substituted position = 1, 4

Scheme 1. Synthetic route of compounds **1** and **2**.

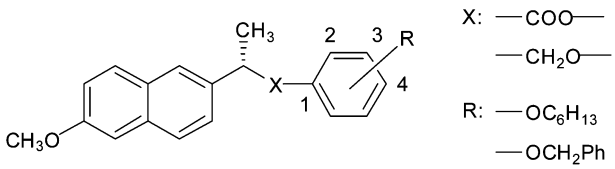




5a, R = OC_6H_{13}, Substituted position = 1, 2
5b, R = OC_6H_{13}, Substituted position = 1, 3
5c, R = OC_6H_{13}, Substituted position = 1, 4
6a, R = OCH_2Ph, Substituted position = 1, 2
6b, R = OCH_2Ph, Substituted position = 1, 3
6c, R = OCH_2Ph, Substituted position = 1, 4

Scheme 2. Synthetic route of compounds **5** and **6**.

Table 1. HTP and MHTP values of new chiral dopants.



Chiral dopant	X	R	Substituent positions	HTP/μm^{-1} [a]	MHTP/$\mu m^{-1}mol^{-1}kg$[a]
1a	–COO–	$-OC_6H_{13}$	1, 2	+2.55	+1.05
1b			1, 3	+3.52	+1.43
1c			1, 4	−9.60	−3.90
2a		$-OCH_2Ph$	1, 2	−3.19	−1.31
2b			1, 3	+4.79	+1.97
2c			1, 4	−8.58	−3.53
5a	$-CH_2O-$	$-OC_6H_{13}$	1, 2	−5.94	−2.33
5b			1, 3	+1.99	+0.78
5c			1, 4	−4.62	−1.81
6a		$-OCH_2Ph$	1, 2	−11.5	−4.58
6b			1, 3	+3.00	+1.20
6c			1, 4	−6.76	−2.70

[a]Measurement method: Cano wedge cell; host LC: ZLI-1132 (Merck); measurement temperature: rt. The weight ratio of the chiral dopant was 0.01.

In terms of substitution position, the absolute MHTP values in the ester-linked chiral dopants followed the order of 1,4-position >1,3-position >1,2-position. It can be seen that chiral dopants with a linear structure, i.e. the 1,4-substituted chiral dopants, show relatively large MHTP values. In other words, chiral dopants with a bent structure are likely to give lower MHTP values. In chiral dopants with an azobenzene moiety, it was reported that the trans isomer often showed larger HTP value than the cis isomer (*2, 14*). The trans isomer has a rod-like shape, which is similar to the host liquid crystalline molecules. On the other hand, the cis isomer has a bent shape, namely is not straight. Therefore, the interaction between the trans isomer and the host liquid crystalline molecule is probably stronger than that of the cis isomer. For the reason of the above-mentioned consideration, 1,4-substituted chiral dopants showed lager MHTP values than others. For the ether-linked chiral dopants substituted at different positions, the magnitude of the absolute MHTP values followed the order of 1,2-position >1,4-position >1,3-position. It should be noted that chiral dopants with a linear structure do not always show the largest MHTP values among the ether derivatives. These results suggest that steric congestion around the chiral centre gives rise to a large MHTP value. The 1,3-substituted chiral dopants show relatively small MHTP values, since their structures are not linear and do not have significant steric congestion.

3. Conclusions

The MHTP values and helical senses of the new chiral dopants are largely influenced by the substitution position, with 1,4-substituted chiral dopants showing relatively large HTP values. However, for the ether-linked chiral dopants, the 1,2-substituted chiral dopants showed larger MHTP values than the 1,4-substituted chiral dopants. These results suggest that 1,4-substituted chiral dopants do not always show the largest MHTP values.

4. Experimental

Commercially available chemicals from Wako and TCI were used without any purification. The syntheses of 2-hexyloxyphenol and 3-hexyloxyphenol were carried out in the usual way. All compounds were characterised by ^{1}H NMR (Bruker, AC-300P, AC-200), IR (JASCO FT/IR-460) and mass spectrometry (JEOL DX-303). Their specific rotations, i.e. $[\alpha]_D$ values, were determined using a JASCO DIP-370 instrument.

Syntheses

*(S)-(+)-2-Hexyloxyphenyl 2-[(6-methoxy)-2-naphtyl]propanoate (**1a**).*

Under nitrogen, 4-*N*,*N*-dimethylaminopyridine (45 mg, 0.37 mmol) was added to the mixture of naproxen (57 mg, 0.25 mmol) and 2-hexyloxyphenol (48 mg, 0.25 mmol) and dry chloroform (3 ml), and

the mixture was stirred for 10 min at room temperature. A dry chloroform solution (1 ml) of *N*,*N*′-dicyclohexylcarbodiimide (50 mg, 0.25 mmol) was added, and the reaction mixture was stirred for 10 h at room temperature. After toluene was added the resulting mixture was filtered. Hydrochloric acid (1M) was then added to the filtrate, and the phases were separated. The organic phase was washed with saturated sodium hydrogen carbonate and brine and dried over sodium sulfate. Removal of the solvent and purification by preparative TLC gave a colourless liquid. Yield: 89 mg (89%). IR (neat/cm^{-1}): 2934, 2871, 1762, 1606, 1501, 1260, 1127, 1115, 1071, 856, 745, 479. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): 0.87 (3 H, t, J=6.6 Hz, CH_3), 1.07–1.27 (6 H, m, CH_2), 1.46 (2 H, quintet, J=7.4 Hz, OCH$_2$CH_2), 1.71 (3 H, d, J=7.0 Hz, C*HCH_3), 3.82 (2 H, t, J=7.0 Hz, OCH_2), 3.90 (3 H, s, OCH_3), 4.12 (1 H, q, J=7.4 Hz, C*H), 6.79–6.95 (3 H, m, aromatic), 7.09–7.72 (3 H, m, aromatic), 7.54 (1 H, dd, J_1=1.8 Hz, J_2=8.5 Hz, aromatic), 7.74 (2 H, d, J=8.5 Hz, aromatic), 7.79 (1 H, d, J=1.5 Hz, aromatic). MS (EI): m/z 406 (M^+). $[\alpha]_D^{24}$ +54.7 (*c* 0.537 in $CHCl_3$).

*(S)-(+)-3-Hexyloxyphenyl 2-[(6-methoxy)-2-naphtyl]propanoate (**1b**).*

Quantities used were 4-*N*,*N*-dimethylaminopyridine (45 mg, 0.37 mmol), naproxen (57 mg, 0.25 mmol), 3-hexyloxyphenol (35 mg, 0.18 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (50 mg, 0.25 mmol) and the experimental procedure was as described for the preparation of **1a**. Yield: 58 mg (79%). M.p 50°C. IR (KBr/cm^{-1}): 2935, 1758, 1604, 1587, 1489, 1263, 1133, 1028, 859, 6.81. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): 0.89 (3 H, t, J=7.0 Hz, CH_3), 1.20–1.43 (6 H, m, CH_2), 1.68 (3 H, d, J=7.4 Hz, C*HCH_3), 1.73 (2 H, quintet, J=6.6 Hz, OCH$_2$CH_2), 3.88 (2 H, t, J=6.6 Hz, OCH_2), 3.91 (3 H, s, OCH_3), 4.07 (1 H, q, J=7.0 Hz, C*H), 6.51–6.73 (3 H, m, aromatic), 7.08–7.21 (3 H, m, aromatic), 7.49 (1 H, dd, J_1=1.8 Hz, J_2=8.5 Hz, aromatic), 7.72 (1 H, d, J=5.1 Hz, aromatic) 7.75 (1 H, d, J=5.5 Hz, aromatic), 7.76 (1 H, s, aromatic). MS (EI): m/z 406 (M^+). $[\alpha]_D^{24}$ +70.1 (*c* 0.265 in $CHCl_3$).

*(S)-(+)-4-Hexyloxyphenyl 2-[(6-methoxy)-2-naphtyl]propanoate (**1c**).*

Quantities used were 4-*N*,*N*-dimethylaminopyridine (63 mg, 0.52 mmol), naproxen (120 mg, 0.52 mmol), 4-hexyloxyphenol (101 mg, 0.52 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (119 mg, 0.57 mmol) and the experimental procedure was as described for the preparation of **1a**. Yield: 64 mg (37%). M.p. 144°C. IR (KBr/cm^{-1}): 2936, 1743, 1608, 150, 1206, 1145, 1032, 893, 858, 815. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): 0.90 (3 H, t, J=7.0 Hz, CH_3), 1.28–1.44 (6 H, m, CH_2), 1.67 (3 H, d, J=7.0 Hz, C*HCH_3), 1.73 (2 H, quintet, J=6.6 Hz, OCH$_2$CH_2), 3.88 (2 H, t, J=7.2 Hz, OCH_2), 3.90 (3 H, s, OCH_3), 4.06 (1 H, q, J=7.4 Hz, C*H), 6.80 (2 H, d, J=9.2 Hz, aromatic), 6.88 (2 H, d, J=9.2 Hz, aromatic), 7.12 (1 H, s, aromatic), 7.15 (1 H, dd, J_1=2.6 Hz, J_2=8.8 Hz, aromatic), 7.49 (1 H, dd, J_1=1.8 Hz, J_2=8.5 Hz, aromatic), 7.71 (1 H, d, J=5.1 Hz, aromatic), 7.74 (1 H, d, J=4.8 Hz, aromatic), 7.75 (1 H, s, aromatic). MS (EI) m/z 406 (M^+). $[\alpha]_D^{26}$ +85.4 (*c* 1.06 in $CHCl_3$).

*(S)-(+)-2-Benzyloxyphenyl 2-[(6-methoxy)-2-naphtyl]propanoate (**2a**).*

Quantities used were 4-*N*,*N*-dimethylaminopyridine (44 mg, 0.37 mmol), naproxen (56 mg, 0.24 mmol), 2-benzyloxyphenol (49 mg, 0.24 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (50 mg, 0.24 mmol) and the experimental procedure was as described for the preparation of **1a**. Yield: 32 mg (32%). M.p. 126°C. IR (KBr/cm^{-1}): 3033, 1753, 1605, 1503, 1453, 1258, 1230, 1137, 1112, 855, 754. ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si): 1.63 (3 H, d, J=6.8 Hz, C*HCH_3), 3.91 (3 H, s, OCH_3), 4.09 (1 H, q, J=7.3 Hz, C*H), 4.97 (2 H, s, OCH_2), 6.81–6.97 (4 H, m, aromatic), 7.08–7.17 (3 H, m, aromatic), 7.25–7.27 (3 H, m, aromatic), 7.40–7.47 (2 H, m, aromatic), 7.63 (2 H, dd, J_1=3.5 Hz, J_2=8.5 Hz, aromatic), 7.73 (1 H, s, aromatic). MS (EI): m/z 412 (M^+). $[\alpha]_D^{28}$ +62.7 (c 0.360 in $CHCl_3$).

*(S)-(+)-3-Benzyloxyphenyl 2-[(6-methoxy)-2-naphtyl]propanoate (**2b**).*

Quantities used were 4-*N*,*N*-dimethylaminopyridine (44 mg, 0.37 mmol), naproxen (56 mg, 0.24 mmol), 2-benzyloxyphenol (49 mg, 0.24 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (50 mg, 0.24 mmol) and the experimental procedure was as described for the preparation of **1a**. Yield: 83 mg (83%). M.p. 107°C. IR (KBr/cm^{-1}): 3004, 2940, 1753, 1605, 1588, 1486, 1262, 1228, 1144, 1012, 860, 819, 694. ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si): 1.68 (3 H, d, J=7.3 Hz, C*HCH_3), 3.92 (3 H, s, OCH_3), 4.08 (1 H, q, J=6.8 Hz, C*H), 4.98 (2 H, s, OCH_2), 6.58–6.62 (2 H, m, aromatic), 6.77–6.83 (1 H, m, aromatic), 7.14–7.21 (3 H, m, aromatic), 7.30–7.39 (5 H, m, aromatic), 7.49 (2 H, dd, J_1=1.6 Hz, J_2=8.5 Hz, aromatic), 7.71–7.76 (3 H, m, aromatic). MS (EI): m/z 412 (M^+). $[\alpha]_D^{28}$ +69.5 (*c* 1.17 in $CHCl_3$).

*(S)-(+)-4-Benzyloxyphenyl 2-[(6-methoxy)-2-naphtyl]propanoate (**2c**).*

Quantities used were 4-*N*,*N*-dimethylaminopyridine (44 mg, 0.37 mmol), naproxen (56 mg, 0.24 mmol), 2-benzyloxyphenol (49 mg, 0.24 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (50 mg, 0.24 mmol) and the experimental procedure was as described for the preparation of **1a**. Yield: 68 mg (68%). M.p. 122°C. IR (KBr/cm^{-1}): 2997, 2973, 2934, 1751, 1627, 1604, 1505, 1451, 1267, 1227, 1190, 1140, 1068, 1010, 843, 818. ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si): 1.68 (3 H, d, J=7.3 Hz, C*HCH_3), 3.93 (3 H, s, OCH_3), 4.04 (1 H, q, J=6.8 Hz, C*H), 5.01 (2 H, s, OCH_2), 6.89 (4 H, s, aromatic), 7.13–7.18 (2 H, m, aromatic), 7.33–7.38 (5 H, m, aromatic), 7.49 (2 H, dd, J_1=1.5 Hz, J_2=8.6 Hz, aromatic), 7.70–7.76 (3 H, m, aromatic). MS (EI): m/z 412 (M^+). $[\alpha]_D^{28}$ +84.1 (*c* 0.485 in $CHCl_3$).

*(S)-(−)-2-(6-Methoxy-2-naphtyl)propanol (**3**).*

Under nitrogen, naproxen (426 mg, 1.85 mmol) dissolved in dry tetrahydrofuran (8 ml) was added to the mixture of lithium aluminium hydride (147 mg, 3.70 mmol) and dry tetrahydrofuran (3 ml), and was heated under reflux for 2 h. After cooling to room temperature, 1M hydrochloric acid and ether were added, and the phases were separated. The aqueous phase was shaken with ether, and combined organic phases were washed with saturated sodium hydrogencarbonate and brine and dried over sodium sulfate. Removal of the solvent and purification by preparative TLC gave a white solid. Yield: 383 mg (95.6%). M.p. 93°C. IR (KBr/cm^{-1}): 2961, 1635, 1605, 1461, 1264, 1213, 1029, 854, 480. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): 1.28 (3 H, d, J=7.0 Hz, C*HCH_3), 1.92 (1 H, br, OH), 2.98 (1 H, sextet, J=7.0 Hz, C*H), 3.62–3.71 (2 H, m, C*HCH_2), 3.84 (3 H, s, OCH_3), 7.07 (1 H, d, J=2.6 Hz, aromatic), 7.11 (1 H, dd, J_1=2.7 Hz, J_2=9.1 Hz, aromatic), 7.27 (1 H, dd, J_1=1.6 Hz, J_2=8.6 Hz, aromatic), 7.64 (1 H, d, J=3.2 Hz, aromatic), 7.66 (1 H, d, J=2.7 Hz, aromatic). MS (EI): m/z 216 (M^+). $[\alpha]_D^{25}$ −19.3 (*c* 1.02 in $CHCl_3$).

*(S)-(−)-2-(6-Methoxy-2-naphtyl)propyl tosylate (**4**).*

Under nitrogen, 1,4-diazabicyclo[2.2.2]octane (174 mg, 1.56 mmol) dissolved in dry acetonitrile (1 ml) was poured into a mixture of **5** (280 mg, 1.30 mmol) and dry acetonitrile (4 ml) at room temperature, and a dry acetonitrile solution (1 ml) of tosyl chloride (270 mg, 1.43 mmol) was then added to the reaction mixture, followed by stirring for 2.5 h. Ether and 1M hydrochloric acid were added, and the phases were separated. The aqueous phase was shaken with ether, and the combined organic phases were washed with saturated sodium hydrogen carbonate and brine and dried over sodium sulphate. Removal of the solvent and purification by column chromatography gave a white solid. Yield: 344 mg (71.7%). M.p. 85°C. IR (KBr/cm^{-1}): 3418, 2952, 1607, 1335, 1188, 1174, 940, 857. ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si): 1.35 (3 H, d, J=6.8 Hz, C*HCH_3), 2.34 (3 H, s, Ar–CH_3), 3.21 (1 H, sextet, J=7.3 Hz, C*H), 3.92 (3 H, s, OCH_3), 4.13 (2 H, dd, J_1=1.9 Hz, J_2=6.8 Hz, C*HCH_2), 7.10–7.21 (5 H, m, aromatic), 7.43 (1 H, s, aromatic), 7.57–7.61 (3 H, m, aromatic), 7.63 (1 H, s, aromatic). MS (EI): m/z 370 (M^+). $[\alpha]_D^{27}$ −2.17 (c 1.03 in $CHCl_3$).

*(S)-(+)-2-[2-(2-Hexyloxyphenyloxy)-2-methylethyloxy]-6-methoxynaphthalene (**5a**).*

Under nitrogen, potassium carbonate (500 mg, 3.62 mmol) was added to a mixture of 2-hexyloxyphenol (74 mg, 0.38 mmol), acetonitrile (2 ml) and was then stirred for 5 min at room temperature. The tetrahydrofuran (1 ml) solution of **6** (141 mg, 0.382 mmol) was poured into the reaction mixture and was stirred for 3 days at 60°C. After cooling to room temperature, toluene and 1M hydrochloric acid were added, and the phases were separated. The aqueous phase was shaken with toluene, and the combined organic phases were washed with saturated sodium hydrogen carbonate and brine and dried over sodium sulfate. Removal of the solvent and purification by preparative TLC gave a colourless liquid. Yield: 32 mg (21.4%). IR (KBr/cm^{-1}): 2934, 1515, 1505, 1252, 1159, 1111, 1040, 829, 743. ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si): 0.89 (3 H, t, J=7.0 Hz, CH_3), 1.22–1.40 (6 H, m, CH_2), 1.51 (3 H, d, J=6.8 Hz, C*HCH_3), 1.75 (2 H, quintet, J=5.8 Hz, OCH$_2$CH_2), 3.34 (1 H, sextet, J=6.8 Hz, C*H), 3.90 (2 H, t, J=6.51 Hz, OCH_2), 3.91 (3 H, s, OCH_3), 4.00–4.27 (2 H, m, C*HCH_2), 6.87 (4 H, s, aromatic), 7.10–7.15 (3 H, m, aromatic), 7.42 (1 H, dd, J_1=1.5 Hz, J_2=8.3 Hz, aromatic), 7.67–7.71 (3 H, m, aromatic). MS (EI): m/z 392 (M^+). $[\alpha]_D^{27}$ +2.5 (*c* 0.262 in $CHCl_3$).

*(S)-(−)-2-[2-(3-Hexyloxyphenyloxy)-2-methylethyloxy]-6-methoxynaphthalene (**5b**).*

Quantities used were potassium carbonate (500 mg, 3.62 mmol), 3-hexyloxyphenol (50 mg, 0.26 mmol) and **6** (100 mg, 0.270 mmol) and the experimental

procedure was as described for the preparation of **5a**. Yield: 62 mg (60%). IR (neat/cm^{-1}): 2955, 2932, 2869, 1606, 1490, 1465, 1391, 1265, 1181, 1154, 1034, 851, 760, 686. ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si): 0.89 (3 H, t, J=6.8 Hz, CH_3), 1.20–1.38 (6 H, m, CH_2), 1.47 (3 H, d, J=6.8 Hz, C*HCH_3), 1.74 (2 H, quintet, J=5.9 Hz, OCH$_2$CH_2), 3.34 (1 H, sextet, J=7.3 Hz, C*H), 3.87 (2 H, t, J=6.3 Hz, OCH_2), 3.88 (3 H, s, OCH_3), 3.95–4.17 (2 H, m, C*HCH_2), 6.45 (2 H, s, aromatic), 6.49 (1 H, d, J=2.4 Hz, aromatic), 7.10–7.19 (3 H, m, aromatic), 7.37 (1 H, dd, J_1=1.5 Hz, J_2=8.3 Hz, aromatic), 7.62 (1 H, s, aromatic), 7.69 (2 H, d, J=8.3 Hz, aromatic). MS (EI): m/z 392 (M^+). $[\alpha]_D^{25}$ −6.5 (*c* 1.24 in $CHCl_3$).

*(*S*)-(−)-2-[2-(4-Hexyloxyphenyloxy)-2-methylethyloxy]-6-methoxynaphthalene (**5c**).*

Quantities used were potassium carbonate (500 mg, 3.62 mmol), 4-hexyloxyphenol (94 mg, 0.48 mmol) and **6** (176 mg, 0.475 mmol) and the experimental procedure was as described for the preparation of **5a**. Yield: 97 mg (52%). M.p. 59°C. IR (KBr/cm^{-1}): 2939, 2853, 1627, 1606, 1508, 1465, 1391, 1228, 1034, 1014, 852, 822. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): 0.91 (3 H, t, J=7.0 Hz, CH_3), 1.29–1.40 (6 H, m, CH_2), 1.47 (3 H, d, J=7.0 Hz, C*HCH_3), 1.74 (2 H, quintet, J=6.6 Hz, OCH$_2$CH_2), 3.34 (1 H, sextet, J=7.0 Hz, C*H), 3.89 (2 H, t, J=6.6 Hz, OCH_2), 3.91 (3 H, s, OCH_3), 3.94–4.13 (2 H, m, C*HCH_2), 6.81 (4 H, s, aromatic), 7.12 (1 H, s, aromatic), 7.15 (1 H, d, J=2.2 Hz, aromatic), 7.40 (1 H, dd, J_1=1.8 Hz, J_2=8.4 Hz, aromatic), 7.64 (1 H, s, aromatic), 7.70 (2 H, d, J=8.1 Hz, aromatic). MS (EI): m/z 392 (M^+). $[\alpha]_D^{25}$ −6.8 (c 1.02 in $CHCl_3$).

*(*S*)-(+)-2-[2-(2-Benzyloxyphenyloxy)-2-methylethyloxy]-6-methoxynaphthalene (**6a**).*

Quantities used were potassium carbonate (3.70 g, 26.8 mmol), 2-benzyloxyphenol (0.540 g, 2.70 mmol) and **6** (1.00 g, 2.70 mmol) and the experimental procedure was as described for the preparation of **5a**. Yield: 0.839 g (77.7%). M.p. 84°C. IR (KBr/cm^{-1}): 2953, 1605, 1508, 1463, 1389, 1377, 1259, 1241, 1221, 1124, 1032, 853, 743. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): 1.51 (3 H, d, J=7.0 Hz, C*HCH_3), 3.44 (1 H, sextet, J=7.0 Hz, C*H), 3.91 (3 H, s, OCH_3), 4.08–4.25 (2 H, m, C*HCH_2), 5.02 (2 H, s, OCH_2), 6.83–6.93 (4 H, m, aromatic), 7.10 (1 H, s, aromatic), 7.13 (1 H, d, J=2.6 Hz, aromatic), 7.27–7.37 (5 H, m, aromatic), 7.41 (2 H, dd, J_1=1.5 Hz, J_2=8.5 Hz, aromatic), 7.62–7.68 (3 H, m, aromatic). MS (EI): m/z 400 (M^+). $[\alpha]_D^{28}$ +5.9 (*c* 0.79 in $CHCl_3$).

*(*S*)-(−)-2-[2-(3-Benzyloxyphenyloxy)-2-methylethyloxy]-6-methoxynaphthalene (**6b**).*

Quantities used were potassium carbonate (690 mg, 5.00 mmol), 3-benzyloxyphenol (100 mg, 0.500 mmol) and **6** (185 mg, 0.500 mmol) and the experimental procedure was as described for the preparation of **5a**. Yield: 62 mg (31%). M.p. 93°C. IR (KBr/cm^{-1}): 2961, 1601, 1489, 1460, 1388, 1181, 1158, 1011, 855, 770, 691. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): 1.46 (3 H, d, J=7.0 Hz, C*HCH_3), 3.34 (1 H, sextet, J=6.6 Hz, C*H), 3.87 (3 H, s, OCH_3), 3.96–4.15 (2 H, m, C*HCH_2), 4.98 (2 H, s, OCH_2), 6.48–6.56 (3 H, m, aromatic), 7.09–7.19 (3 H, m, aromatic), 7.26–7.41 (6 H, m, aromatic), 7.62 (1 H, s, aromatic), 7.68 (2 H, d, J=8.5 Hz, aromatic). MS (EI): m/z 400 (M^+). $[\alpha]_D^{29}$ −7.8 (*c* 0.95 in $CHCl_3$).

*(*S*)-(−)-2-[2-(4-Benzyloxyphenyloxy)-2-methylethyloxy]-6-methoxynaphthalene (**6c**).*

Quantities used were potassium carbonate (3.70 g, 26.8 mmol), 4-benzyloxyphenol (0.540 g, 2.70 mmol) and **6** (1.00 g, 2.70 mmol) and the experimental procedure was as described for the preparation of **5a**. Yield: 0.513 g (47.5%). M.p. 100°C. IR (KBr/cm^{-1}): 2968, 2909, 1607, 1229, 1211, 1034, 855, 823, 739. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): 1.47 (3 H, d, J=7.0 Hz, C*HCH_3), 3.34 (1 H, sextet, J=6.6 Hz, C*H), 3.91 (3 H, s, OCH_3), 3.94–4.13 (2 H, m, C*HCH_2), 4.99 (2 H, s, OCH_2), 6.81 (2 H, d, J=9.2 Hz, aromatic), 6.88 (2 H, d, J=9.2 Hz, aromatic), 7.10–7.17 (3 H, m, aromatic), 7.29–7.42 (5 H, m, aromatic), 7.63 (1 H, s, aromatic), 7.79 (2 H, d, J=8.1 Hz, aromatic). MS (EI): m/z 400 (M^+). $[\alpha]_D^{28}$ −9.3 (*c* 0.95 in $CHCl_3$).

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