

Synthesis of Optically Active Spiro Compounds with a 3,3′-(4*H*,4′*H*)-Spirobi(2*H*-naphtho[1,2-*b*]pyran) Skeleton and Their Applications as Chiral Dopants for Nematic Liquid Crystals

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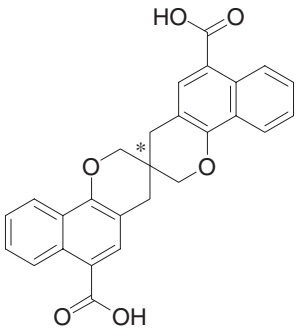
Chiral dopants with a spiro structure for nematic liquid crystals were synthesized from optically active 3,3′-(4*H*,4′*H*)-spirobi(2*H*-naphtho[1,2-*b*]pyran)-6,6′-dicarboxylic acid, and their helical twisting power (HTP) values were evaluated. Chiral dopants having the S configuration induced minus helices in the host nematic liquid crystals. It was found that the novel ester-linked spiro chiral dopants exhibited large molar HTP values. In particular, a chiral dopant with two pyrimidine structures in the side chain moiety showed the highest molar HTP value of 62.1 $\mu m^{-1} mol^{-1} kg$. In contrast, ether-linked chiral dopants showed relatively small molar HTP values.

Chirality is one of the most interesting subjects in the field of liquid crystals. Chiral nematic liquid crystals having macro helical structures are currently used in twisted nematic liquid crystal display devices. Generally, chiral nematic materials consist of a mixture of achiral host nematic liquid crystals and a chiral dopant with a large helical twisting power (HTP).[1,2] Helical structures are induced in chiral nematic liquid crystals by interactions between the host liquid crystalline molecules and the chiral dopant. Many optically active compounds with asymmetric carbons have been synthesized and used as dopants to induce chiral nematic phases.[1–8] It was reported that imine chiral dopants with two (*R*)-naphthylethylamine moieties showed the largest molar HTP value (40.0 $\mu m^{-1} mol^{-1} kg$) among chiral dopants with asymmetric carbons.[3] On the other hand, many biaryl chiral dopants with axial chirality exhibited larger HTP values than chiral dopants with asymmetric carbons.[2,9–13] In particular, the conformational fixation of 1,1′-binaphthalene-2,2′-diol (BINOL) derivatives has been shown to be effective in achieving large HTP values. In previous studies, conformational fixation was found to increase the molar HTP value of BINOL derivatives from 0.38 to 21 $\mu m^{-1} mol^{-1} kg$.[2,12] Goh and Akagi reported that a BINOL derivative tetra-substituted at the 2,2′,6,6′-positions showed a very large molar HTP value (209 $\mu m^{-1} mol^{-1} kg$), and also described the importance of molecular rigidity for inducing large HTP values.[13] Asymmetric metal complexes also exhibited relatively large HTP values.[14–18] In particular, Yagi et al. reported zinc bilinone dimers as chiral dopants that showed an unusually large molar HTP value (503.5 $\mu m^{-1} mol^{-1} kg$).[18] The conformations of the asymmetric metal complexes are rigid, causing large HTP values. This fixation is probably similar to the BINOL derivatives. Consequently, it can be considered that axial asymmetric chiral dopants having a fixed conformation will show large molar HTP values.

Optically active spiro compounds have a more rigid structure than general axially chiral compounds. Therefore, optically active spiro compounds have been used as chiral ligands for asymmetric synthesis[19] and as chiral dopants for smectic liquid crystalline mixtures.[20] However, the subject of optically active compounds with a spiro structure remains largely unexplored in the field of chiral dopants for nematic liquid crystals.

We recently reported the synthesis of a novel optically active spiro carboxylic acid, 3,3′-(4*H*,4′*H*)-spirobi(2*H*-naphtho[1,2-*b*]pyran)-6,6′-dicarboxylic acid (**1***, Figure 1).[21] The two naphthalene rings of **1*** are fixed by the spiro structure. In this paper, we report the HTP values of derivatives of **1*** and discuss their potential as chiral dopants for nematic liquid crystals CDEs**1**–**6** and CDEt**1**–**4** (Figures 2 and 3). The rigid structure of the spiro central portion probably minimizes conformational changes. The novel chiral dopants have two side chain moieties, which consist of some aromatic rings and an octyloxy group. The spiro central part and side chain moieties are connected by ester or ether linkages. Based on the interaction of the aromatic rings of the chiral dopants with those of the host liquid crystalline molecules, these novel dopants are expected to show large HTP values. Additionally, the relationship between molar HTP values of the chiral dopants and the length of the side chain moieties was investigated.



1*

Figure 1. Structure of **1***.

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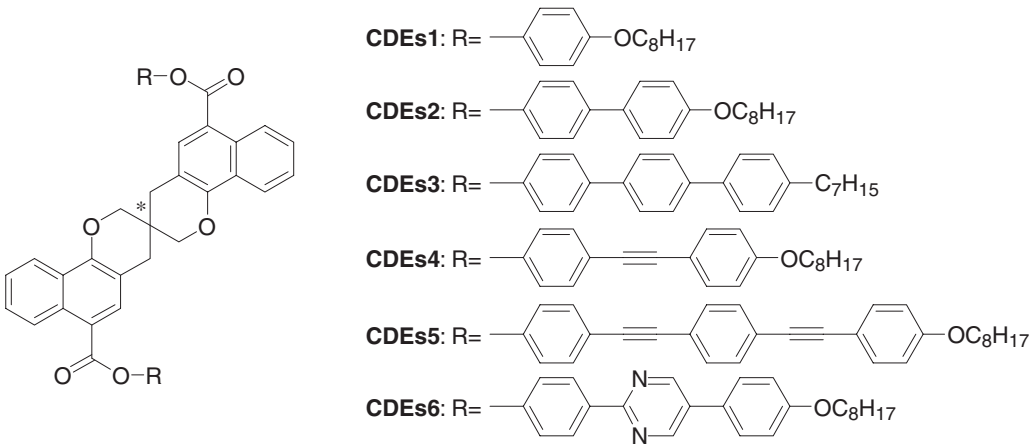


Figure 2. Structures of ester-linked chiral dopants (CDEs).

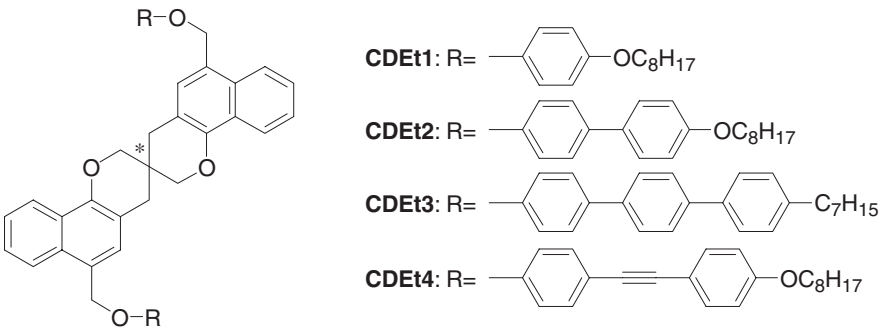


Figure 3. Structures of ether-linked chiral dopants (CDEt).

Results and Discussion

Compounds **1*** and **13*** were synthesized according to the published literature.[21] The precursors of the side chain moieties **7** and **12** were synthesized following Scheme 1. Tolan derivatives were synthesized using the Sonogashira cross-coupling reaction. The ester-linked chiral dopants CDEs**1**–**6** were derived from **1*** and phenols (Scheme 2). The ether-linked chiral dopants CDEt**1**–**4** were derived from **13*** and phenols (Scheme 3).

The chiral nematic liquid crystalline mixtures were prepared by adding the chiral dopant to the host nematic liquid crystal (ZLI-1132, Merck).[22] The helical pitch of the chiral nematic phase was measured using Cano wedge cells.[23] The HTP values were calculated based on eq 1, where p is the pitch of the chiral nematic phase (in μm) and c is the mass fraction of the chiral dopant. In order to describe the HTP per molecule, we used the value of the molar helical twisting power (MHTP), as defined in eq 2, where MW is the molecular weight of the chiral dopant.[6]

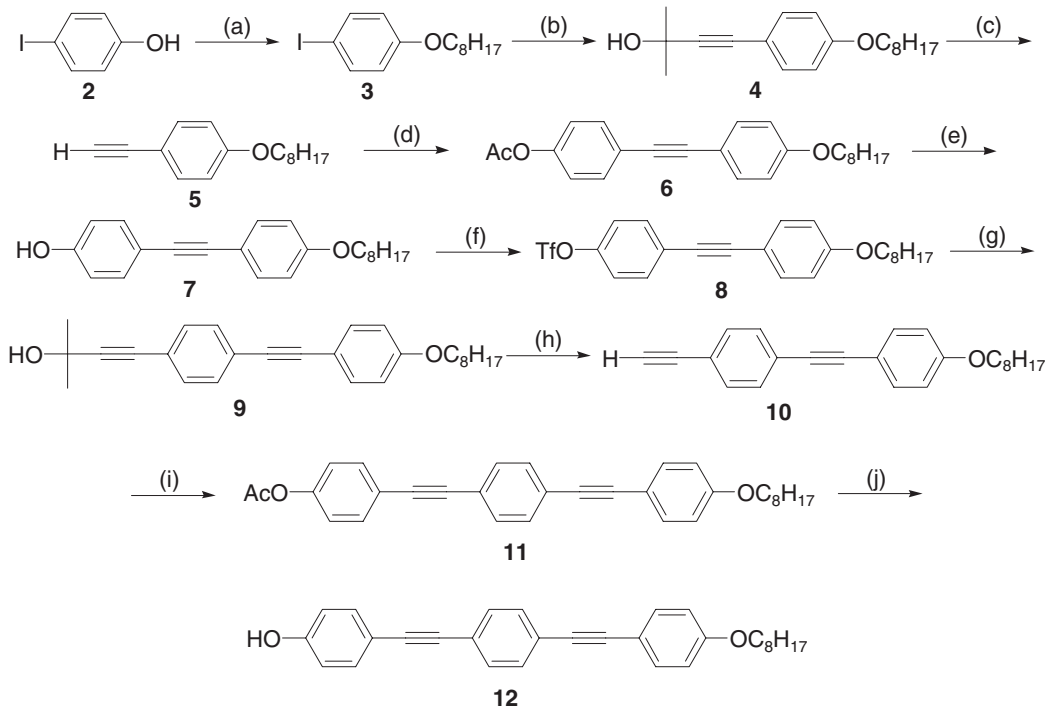
$$\mathrm{HTP} = (pc)^{-1} \quad (1)$$

$$\mathrm{MHTP} = \mathrm{HTP} \times \mathrm{MW} \times 10^{-3} \quad (2)$$

The helical senses of the chiral nematic phases were determined by the contact method using a reference mixture of the host liquid crystal and cholesteryl nonanoate, which features a left-handed helix (minus sense). The HTP and MHTP values of the new chiral dopants are summarized in Table 1. Additionally, PM3-optimized lengths of the rigid part of the side chain moiety (Figure 4) are also summarized in Table 1.

All novel chiral dopants derived from (*S*)-**1** induced a minus-sense helix, while chiral dopants derived from (*R*)-**1** induced a plus-sense helix. The absolute MHTP values of the ester-linked chiral dopants were in the order CDEs**6** > CDEs**5** > CDEs**3** > CDEs**4** > CDEs**2** > CDEs**1**. The MHTP value of CDEs**6** was the largest, at 62.1 $\mu m^{-1} mol^{-1} kg$. This is larger than those of general chiral dopants with asymmetric carbons,[1–8] and is also relatively large among chiral dopants with axial chirality.[2,9–13] It is thought that the large MHTP values are due to conformational fixation of chirality by the spiro structure. On the other hand, the absolute MHTP values of the ether-linked chiral dopants were in the order CDEt**3** > CDEt**4** > CDEt**2** > CDEt**1**. The order of the MHTP values of the ether-linked chiral dopants was similar to that of the ester-linked chiral dopants with regard to the side chain moiety. The absolute MHTP values of the ester- and ether-linked chiral dopants increased depending on the length of the rigid part of the side chain moiety (Figure 5).

It is known that aromatic rings of chiral dopants can interact with the aromatic rings of the host liquid crystalline molecule via π–π interactions. On the other hand, the side chain moieties of the ester- and ether-linked chiral dopants have rigid and linear rod-like structures. It is expected that chiral dopants with rod-like moieties are readily aligned in the same direction as the host liquid crystalline molecules, resulting in efficient interaction between the chiral dopants and the host liquid

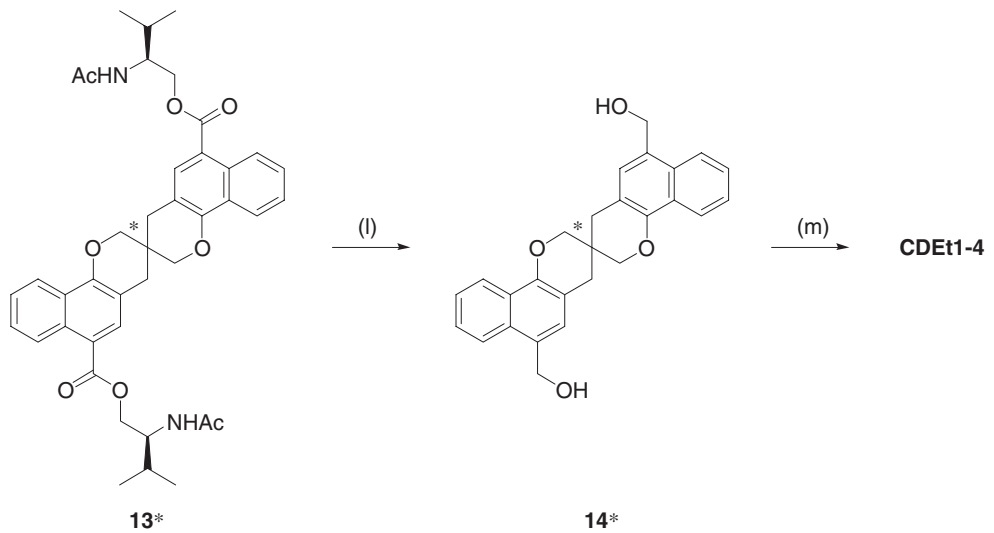


Scheme 1. Synthesis route of precursor of side chain moieties **7** and **12**: (a) 1-bromooctane, K_2CO_3, CH_3CN, reflux; (b) 2-methyl-3-butyn-2-ol, $[PdCl_2(PPh_3)_2]$, PPh_3, CuI, *N*,*N*-diisopropylamine, THF, 60 °C; (c) NaOH, dry toluene, reflux; (d) 4-iodophenyl acetate, $Pd(PPh_3)_4$, CuI, *N*,*N*-diisopropylamine, THF, 60 °C; (e) NaOHaq, THF, EtOH; (f) $(CF_3SO_2)_2O$, pyridine, dry CH_2Cl_2; (g) 2-methyl-3-butyn-2-ol, $[PdCl_2(PPh_3)_2]$, PPh_3, CuI, *N*,*N*-diisopropylamine, THF, 60 °C; (h) NaOH, dry toluene, reflux; (i) 4-iodophenyl acetate, $[PdCl_2(PPh_3)_2]$, PPh_3, CuI, *N*,*N*-diisopropylamine, THF, 60 °C; and (j) NaOHaq, THF, EtOH.

Scheme 2. Synthesis of ester-linked chiral dopants: (k) 1) $SOCl_2$, dry toluene, reflux, 2) phenols, Et_3N, dry CH_2Cl_2.

crystalline molecules (Figure 6). Therefore, the absolute MHTP values of the ester- and ether-linked chiral dopants increase depending on the length of the rigid part of the side chain moiety.

The MHTP values of the ester-linked chiral dopants were larger than those of the ether-linked chiral dopants. Ester linkages have strong polarity; therefore, ester-linked chiral dopants can interact more strongly with the host liquid crystalline molecules via dipole–dipole interactions. On the other hand, it is known that the dihedral angle between a conjugated ester linkage and an aromatic ring is almost 0°. Therefore, conformational fixation of the ester-linked chiral dopants is stronger than that of the ether-linked chiral dopants,



Scheme 3. Synthesis of ether-linked chiral dopants: (l) $LiAlH_4$, dry THF and (m) 1) MsCl, triethylamine, dry CH_2Cl_2, −20 °C, 2) phenols, K_2CO_3, CH_3CN, THF, 50 °C.

and the ester-linked chiral dopants showed larger MHTP values.

The MHTP value of CDEs**6** was 20% larger than that of CDEs**3**. It is suggested that a pyrimidine ring is useful for obtaining large MHTP values. The polar pyrimidine ring can interact with the liquid crystalline molecules via dipole–dipole interactions in addition to π–π interactions.

Table 1. Length of Rigid Part at Side Chain Moiety, HTP and MHTP Values of New Chiral Dopants

Chiral dopant	Optical purity /%	Length of rigid part at side chain moiety/Å	HTP[a] /μm^{-1}	MHTP[b] /$\mu m^{-1} mol^{-1} kg$
(*S*)-CDEs**1**	97.9	2.78	−21.1	−17.9
(*S*)-CDEs**2**	>99	7.05	−38.2	−38.2
(*S*)-CDEs**3**	>99	11.32	−46.1	−50.4
(*S*)-CDEs**4**	>99	9.59	−40.9	−42.8
(*S*)-CDEs**5**	>99	16.51	−40.9	−51.0
(*S*)-CDEs**6**	>99	11.39	−53.7	−62.1
(*S*)-CDEt**1**	94.9	2.78	−1.8	−1.5
(*R*)-CDEt**2**	>99	7.05	+7.6	+7.4
(*R*)-CDEt**3**	>99	11.32	+8.5	+9.0
(*S*)-CDEt**4**	>99	9.59	−6.0	−6.2

a) $HTP/\mu m^{-1} = (pc)^{-1}$; Measurement method: Cano wedge cell, measurement temperature: room temperature. *p*: helical pitch (μm), *c*: weight ratio of chiral dopant. b) $MHTP/\mu m^{-1} mol^{-1} kg = HTP \times MW \times 10^{-3}$; MW: molecular weight of the chiral dopant, host L.C.: ZLI-1132 (Merck).

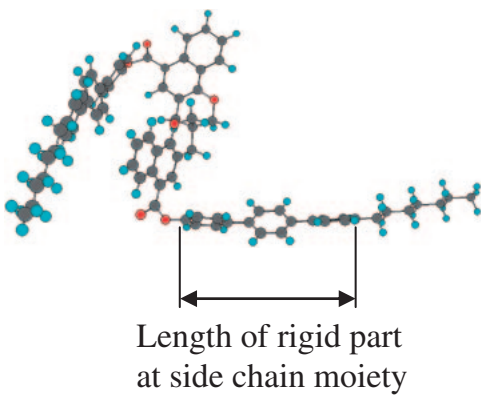


Figure 4. An example of the PM3-optimized length of the rigid part at the side chain moiety for (*S*)-CDEs**3**.

Conclusion

In conclusion, novel chiral dopants with an optically active 3,3′-(4*H*,4′*H*)-spirobi(2*H*-naphtho[1,2-*b*]pyran) skeleton were synthesized, and their MHTP values were evaluated. All chiral dopants with (*S*)-spiro skeletons induced minus-sense helices, while chiral dopants with (*R*)-spiro skeletons induced plus-sense helices. It was found that the ester-linked chiral dopants showed relatively large MHTP values, with the ester-linked chiral dopants containing two pyrimidine rings showing the largest MHTP values. It was also found that the MHTP values of the chiral dopants were proportional to the length of the rigid part of the side chain moiety. We were able to show that optically active spiro chiral dopants have the potential for inducing large MHTP values.

Experimental

Synthesis. Infrared (IR) spectra were recorded on a Perkin-Elmer 2000R spectrometer and SHIMADZU IRPrestige-21 spectrometer. ^1H and ^{13}C NMR spectra were measured on a Brucker DPX400 MHz (^1H: 400 MHz, ^{13}C: 100 MHz) spectrometer. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak. EI Mass spectroscopy was measured on a JEOL JMS-700AM. MALDI-TOF Mass spectroscopy was measured on a BRUKER DALTONICS autoflex III-2s. Specific rotations i.e., $[\alpha]_D$ were recorded on a JASCO

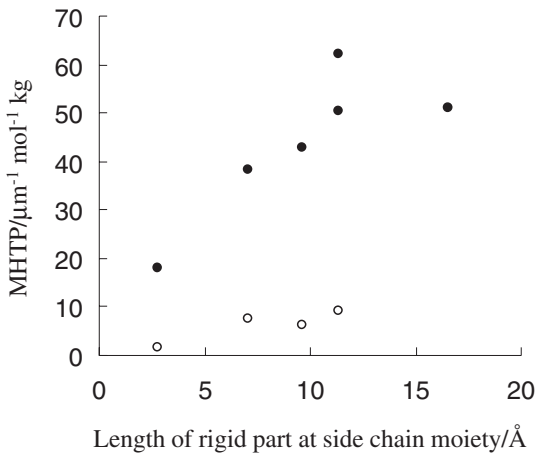


Figure 5. Relationship between absolute MHTP values and the length of the rigid part at the side chain moiety. The closed symbols and open symbols indicate ester-linked and ether-linked chiral dopants, respectively.

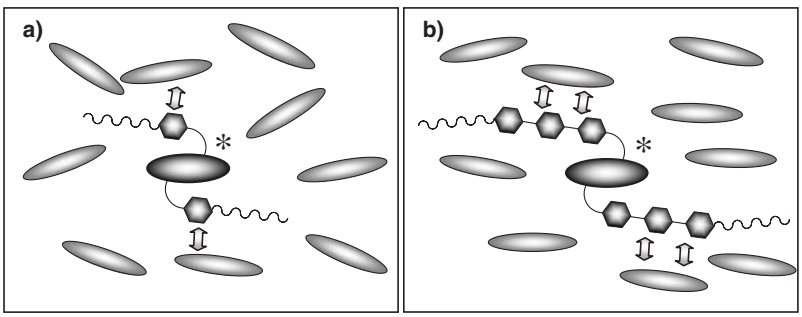


Figure 6. Image of the interaction between the chiral dopant molecule and the host liquid crystalline molecule. a) In the case of chiral dopants with short side chain and b) in the case of chiral dopants with long side chain.

DIP370 spectrometer and JASCO DIP1000 spectrometer. Elemental analyses were recorded on a Thermo Electron Corporation FlashEA 1112. The products were purified by preparative column chromatography on silica gel (silica gel 60N, spherical neutral, KANTO Chemical Co., Inc., Japan) or preparative TLC on silica gel (Wakogel B-5F, Wako Pure Chemical Industries, Ltd.). Commercially available chemicals were used without any purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl solution under argon.

4-Iodo-4-octyloxybenzene (3): Under argon, an acetonitrile solution (20 mL) of 1-bromooctane (3.51 g, 18.2 mmol) was added to a mixture of **2** (2.00 g, 9.09 mmol), K_2CO_3 (6.20 g, 44.9 mmol), and CH_3CN (50 mL). The reaction mixture was stirred for 1 day under reflux. After cooling the mixture, acetonitrile was evaporated. The residue was dissolved in ethyl acetate, 1 M HClaq (M = mol dm^{-3}) was added, and the phases were separated. The aqueous phase was washed with ethyl acetate, and the combined organic phases were washed with saturated $NaHCO_3$aq and brine and dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by reduced pressure distillation (200 °C, 5 mmHg) to give **3** (2.95 g, 8.89 mmol, 97.8%) as yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, $J = 6.4$ Hz, 3H, CH_3), 1.28–1.34 (m, 8H, CH_2), 1.39–1.46 (m, 2H, CH_2), 1.75 (quintet, $J = 6.8$ Hz, 2H, CH_2), 3.88 (t, $J = 6.8$ Hz, 2H, OCH_2), 6.65 (d, $J = 8.8$ Hz, 2H, aromatic), 7.52 (d, $J = 8.8$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 22.8, 26.1, 29.3, 29.4, 29.5, 31.9, 68.2, 82.5, 117.1, 138.3, 159.1. IR (neat, cm^{-1}): 2926, 2855, 1585, 1487, 1472, 1283, 1244, 1175, 819. MS (EI) m/z 332 $[M]^+$.

4-(4-Octyloxyphenyl)-2-methyl-3-butyn-2-ol (4): Under argon, a mixture of **2** (578 mg, 1.74 mmol), 2-methyl-3-butyn-2-ol (365 mg, 4.35 mmol), CuI (32 mg, 0.17 mmol), $[PdCl_2(PPh_3)_2]$ (119 mg, 0.17 mmol), PPh_3 (44 mg, 0.17 mmol), *N*,*N*-diisopropylamine (8 mL), and dry THF (8 mL) was stirred for 12 h at 60 °C. The solvent was evaporated, the residue was dissolved in $CHCl_3$, water was added, and the phases were separated. The organic phase was dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by column chromatography ($CHCl_3$) to give **4** (478 mg, 1.40 mmol, 95.4%) as light yellow solid. Mp: 61.7–61.9 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 6.8$ Hz, 3H, CH_3), 1.28–1.34 (m, 8H, CH_2), 1.40–1.44 (m, 2H, CH_2), 1.59 (s, 6H, CH_3), 1.75 (quintet, $J = 6.8$ Hz, 2H, CH_2), 2.75 (br, 1H, OH), 3.90 (t, $J = 6.4$ Hz, 2H, OCH_2), 6.79 (d, $J = 6.8$ Hz, 2H, aromatic), 7.32 (d, $J = 9.2$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.1, 22.7, 26.0, 29.2, 29.3, 29.4, 31.6, 31.8, 65.6, 68.0, 82.1, 92.5, 114.4, 114.7, 133.1, 159.1. IR (KBr, cm^{-1}): 3445, 2957, 2924, 2855, 1609, 1510, 1248, 1171, 837. MS (EI) m/z 288 $[M]^+$.

4-Octyloxyphenylacetylene (5): Under argon, a mixture of **3** (478 mg, 1.66 mmol), powdered NaOH (84 mg, 2.10 mmol), and dry toluene (15 mL) was stirred for 1 day under reflux. After cooling, the NaOH was removed by filtration, and toluene was evaporated. The crude product was purified by column chromatography (hexane) to give **5** (265 mg, 1.15 mmol, 82.1%) as colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 6.8$ Hz, 3H, CH_3), 1.26–1.36 (m, 8H, CH_2), 1.40–1.46 (m, 2H, CH_2), 1.77 (quintet, $J = 6.8$ Hz, 2H, CH_2), 2.98 (s, 1H, CH), 3.94 (t, $J = 6.4$ Hz, 2H, OCH_2), 6.82 (d, $J = 9.2$ Hz, 2H, aromatic), 7.41 (d, $J = 8.8$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 22.8, 26.1, 29.3, 29.4, 29.5, 31.9, 68.2, 83.9, 114.0, 114.6, 133.7, 159.7. IR (neat, cm^{-1}): 3296, 2926, 2855, 2106, 1605, 1504, 1497, 1288, 1248, 1169, 831. MS (EI) m/z 230 $[M]^+$.

4-(4-Octyloxyphenylethynyl)phenyl Acetate (6): Under argon, a mixture of **5** (95 mg, 0.412 mmol), 4-iodophenyl acetate (129 mg, 0.494 mmol), CuI (8 mg, 0.04 mmol), $[PdCl_2(PPh_3)_2]$ (28 mg, 0.04 mmol), PPh_3 (10 mg, 0.04 mmol), *N*,*N*-diisopropylamine (2 mL), and dry THF (2 mL) was stirred for 1 day at 60 °C. The solvent was evaporated, the residue was dissolved in $CHCl_3$, water was added, and the phases were separated. The organic phase was dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by preparative thin layer chromatography (toluene:hexane = 3:1) to give **6** (103 mg, 0.283 mmol, 68.7%) as white solid. Mp: 98.7–98.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 6.8$ Hz, 3H, CH_3), 1.28–1.30 (m, 8H, CH_2), 1.40–1.44 (m, 2H, CH_2), 1.76 (quintet, $J = 6.8$ Hz, 2H, CH_2), 2.26 (s, 3H, $COCH_3$), 3.91 (t, $J = 6.8$ Hz, 2H, OCH_2), 6.84 (d, $J = 8.8$ Hz, 2H, aromatic), 7.05 (d, $J = 8.4$ Hz, 2H, aromatic), 7.43 (d, $J = 8.8$ Hz, 2H, aromatic), 7.49 (d, $J = 8.4$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 21.1, 22.7, 26.1, 29.3, 29.3, 29.4, 31.9, 68.1, 87.2, 89.7, 114.6, 115.0, 121.4, 121.7, 132.6, 133.1, 150.3, 159.4, 169.1. IR (KBr, cm^{-1}): 2924, 2855, 1767, 1607, 1514, 1371, 1287, 1254, 1217, 1202, 1015, 912. MS (EI) m/z 364 $[M]^+$.

4-(4-Octyloxyphenylethynyl)phenol (7): A mixture of **6** (787 mg, 2.00 mmol), 3 M NaOHaq (2 mL, 6 mmol), 99% EtOH (20 mL), and THF (40 mL) was stirred for 12 h. After the THF and the ethanol were evaporated, 5 M hydrochloric acid was added, $CHCl_3$ was added, and the phases were separated. The organic phase was dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (toluene) to give **7** (577 mg, 1.79 mmol, 89.5%) as white solid. Mp: 115.0–115.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 7.2$ Hz, 3H, CH_3), 1.28–1.33 (m, 8H, CH_2), 1.40–1.45 (m, 2H, CH_2), 1.77 (quintet, $J = 6.8$ Hz, 2H, CH_2), 3.95 (t, $J = 6.4$ Hz, 2H, OCH_2), 5.46 (br, 1H, OH), 6.78 (d, $J = 8.8$ Hz, 2H, aromatic), 6.85 (d, $J = 8.8$ Hz, 2H, aromatic), 7.39 (d, $J = 8.4$ Hz, 2H, aromatic), 7.42 (d, $J = 8.8$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 22.8, 26.1, 29.3, 29.4, 29.5, 31.9, 68.3, 87.9, 88.2, 114.7, 115.5, 115.6, 116.1, 133.0, 133.2, 155.5, 159.1. IR (KBr, cm^{-1}): 3333, 2931, 2920, 2855, 1611, 1518, 1250, 833. MS (EI) m/z 322 $[M]^+$.

4-(4-Octyloxyphenylethynyl)phenyl Trifluoromethanesulfonate (8): A dry CH_2Cl_2 solution (6 mL) of trifluoromethanesulfonic anhydride (0.45 mL) was added to a mixture of **7** (628 mg, 1.95 mmol), pyridine (0.6 mL), and dry CH_2Cl_2, and was stirred for 1 h. Water and $CHCl_3$ was added, and the phases were separated. The aqueous phase was washed with $CHCl_3$, and the combined organic phases were washed with saturated $NaHCO_3$aq and brine and dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (toluene:hexane = 1:1) to give **8** (804 mg, 1.77 mmol, 90.8%) as white solid. Mp: 58.6–58.9 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.80 (t, $J = 6.8$ Hz, 3H, CH_3), 1.14–1.24 (m, 8H, CH_2), 1.32–1.37 (m, 2H, CH_2), 1.69 (quintet, $J = 7.2$ Hz, 2H, CH_2), 3.86 (t, $J = 6.4$ Hz, 2H, OCH_2), 6.77 (d, $J = 8.8$ Hz, 2H, aromatic), 7.14 (d, $J = 8.8$ Hz, 2H, aromatic), 7.35 (d, $J = 8.4$ Hz, 2H, aromatic), 7.46 (d, $J = 8.4$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 22.8, 26.2, 29.3, 29.4, 29.5, 32.0, 68.2, 86.2, 91.7, 114.4, 114.8, 117.3, 120.5, 121.6, 124.6, 133.3, 148.9, 159.8. IR (KBr, cm^{-1}): 2926, 2870, 2220, 1608, 1514, 1427, 1250, 1209, 1142, 881, 842. MS (EI) m/z 454 $[M]^+$.

2-Methyl-4-[4-(4-octyloxyphenylethynyl)phenyl]-3-butyn-2-ol (9): Under argon, a mixture of **8** (804 mg, 1.77 mmol), 2-methyl-3-butyn-2-ol (372 mg, 4.43 mmol), CuI (34 mg, 0.177 mmol),

$[PdCl_2(PPh_3)_2]$ (124 mg, 0.177 mmol), PPh_3 (46 mg, 0.177 mmol), *N*,*N*-diisopropylamine (8 mL), and dry THF (8 mL) was stirred for 12 h at 60 °C. The solvent was evaporated, the residue was dissolved in $CHCl_3$, water was added, and the phases were separated. The organic phase was dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by column chromatography ($CHCl_3$) to give **9** (601 mg, 1.55 mmol, 87.6%) as light white solid. Mp: 128.3–128.6 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 7.2$ Hz, 3H, CH_3), 1.28–1.33 (m, 8H, CH_2), 1.40–1.48 (m, 2H, CH_2), 1.61 (s, 6H, CH_3), 1.77 (quintet, $J = 8.0$ Hz, 2H, CH_2), 2.22 (br, 1H, OH), 3.94 (t, $J = 6.4$ Hz, 2H, OCH_2), 6.85 (d, $J = 8.4$ Hz, 2H, aromatic), 7.36 (d, $J = 8.0$ Hz, 2H, aromatic), 7.42 (d, $J = 8.0$ Hz, 2H, aromatic), 7.43 (d, $J = 8.4$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 22.8, 26.1, 29.3, 29.4, 29.5, 31.6, 31.9, 65.7, 68.2, 82.0, 87.8, 91.5, 95.5, 114.7, 114.9, 122.2, 123.7, 131.3, 131.7, 133.2, 159.5. IR (KBr, cm^{-1}): 3462, 2930, 2852, 2212, 1606, 1516, 1287, 1250, 1159, 962, 835. MS (EI) m/z 388 $[M]^+$.

4-(4-Octyloxyphenylethynyl)phenylacetylene (10): Under argon, a mixture of **9** (555 mg, 1.43 mmol), powdered NaOH (110 mg, 2.20 mmol), and dry toluene (20 mL) was stirred for 1 day under reflux. After cooling, the NaOH was removed by filtration, and toluene was evaporated. The crude product was purified by column chromatography ($CHCl_3$:hexane = 1:4) to give **10** (352 mg, 1.07 mmol, 74.8%) as light yellow solid. Mp: 98.8–99.4 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 6.8$ Hz, 3H, CH_3), 1.26–1.34 (m, 8H, CH_2), 1.43–1.47 (m, 2H, CH_2), 1.78 (quintet, $J = 7.6$ Hz, 2H, CH_2), 3.16 (s, 1H, CH), 3.96 (t, $J = 6.4$ Hz, 2H, OCH_2), 6.86 (d, $J = 8.8$ Hz, 2H, aromatic), 7.44–7.46 (m, 6H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 22.8, 26.2, 29.3, 29.4, 29.5, 32.0, 68.3, 78.8, 83.5, 87.7, 91.8, 114.7, 114.9, 121.6, 124.4, 131.4, 132.2, 133.2, 159.6. IR (KBr, cm^{-1}): 3273, 2945, 2857, 1514, 1287, 1250, 837, 827. MS (EI) m/z 330 $[M]^+$.

4-[4-(4-Octyloxyphenylethynyl)phenylethynyl]phenyl Acetate (11): Under argon, a mixture of **10** (300 mg, 0.909 mmol), 4-iodophenyl acetate (238 mg, 0.909 mmol), CuI (10 mg, 0.05 mmol), $[PdCl_2(PPh_3)_2]$ (35 mg, 0.05 mmol), PPh_3 (26 mg, 0.10 mmol), *N*,*N*-diisopropylamine (4 mL), and dry THF (4 mL) was stirred for 1 day at 60 °C. The solvent was evaporated, the residue was dissolved in $CHCl_3$, water was added, and the phases were separated. The organic phase was dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by preparative thin layer chromatography (toluene) to give **11** (410 mg, 0.884 mmol, 97.2%) as white solid. Mp: 180.8–181.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 6.8$ Hz, 3H, CH_3), 1.29–1.37 (m, 8H, CH_2), 1.42–1.47 (m, 2H, CH_2), 1.78 (quintet, $J = 6.8$ Hz, 2H, CH_2), 2.31 (s, 3H, $COCH_3$), 3.96 (t, $J = 6.4$ Hz, 2H, OCH_2), 6.84 (d, $J = 8.8$ Hz, 2H, aromatic), 6.87 (d, $J = 8.8$ Hz, 2H, aromatic), 7.09 (d, $J = 8.8$ Hz, 2H, aromatic), 7.45 (d, $J = 8.8$ Hz, 2H, aromatic), 7.48 (s, 4H, aromatic), 7.53 (d, $J = 8.8$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 21.3, 22.8, 26.2, 29.3, 29.4, 29.5, 32.0, 68.2, 87.9, 89.4, 90.3, 91.7, 114.7, 114.9, 120.9, 121.9, 122.6, 123.8, 131.5, 131.6, 132.9, 133.2, 150.7, 159.6, 169.3. IR (KBr, cm^{-1}): 2924, 2855, 1749, 1600, 1518, 1368, 1246, 1228, 1205, 1016, 837. MS (EI) m/z 464 $[M]^+$.

4-[4-(4-Octyloxyphenylethynyl)phenylethynyl]phenol (12): The mixture of **11** (410 mg, 0.884 mmol), 3 M NaOHaq (1 mL, 3 mmol), 99% EtOH (10 mL), and THF (20 mL) was stirred for 12 h. After the THF and the ethanol were evaporated, 1 M hydrochloric acid and $CHCl_3$ were added, and the phases were separated. The organic phase was dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by recrystallization (toluene) to give **12** (300 mg, 0.711 mmol, 80.4%) as light yellow solid. Mp: 183.4–183.9 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.86 (t, $J = 6.8$ Hz, 3H, CH_3), 1.26–1.30 (m, 8H, CH_2), 1.36–1.42 (m, 2H, CH_2), 1.71 (quintet, $J = 6.8$ Hz, 2H, CH_2), 3.95 (t, $J = 6.4$ Hz, 2H, OCH_2), 5.46 (br, 1H, OH), 6.81 (d, $J = 8.8$ Hz, 2H, aromatic), 6.97 (d, $J = 8.8$ Hz, 2H, aromatic), 7.39 (d, $J = 8.4$ Hz, 2H, aromatic), 7.48 (d, $J = 8.8$ Hz, 2H, aromatic), 7.52 (s, 4H, aromatic). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 14.0, 22.1, 25.5, 28.6, 28.6, 28.7, 31.2, 67.6, 87.1, 87.7, 91.5, 92.0, 112.2, 113.8, 114.9, 115.8, 122.3, 122.7, 131.3, 131.4, 133.0, 133.1, 158.3, 159.2. IR (KBr, cm^{-1}): 3489, 3190, 2924, 2855, 1604, 1520, 1285, 1250, 837, 532. MS (MALDI-TOF) m/z 422 $[M]^+$.

Bis(4-octyloxyphenyl) 3,3′-(4*H*,4′*H*)-Spirobi(2*H*-naphtho-[1,2-*b*]pyran)-6,6′-dicarboxylate ((*S*)-CDEs1): Under nitrogen, a mixture of (*S*)-(−)-**1** (25 mg, 0.057 mmol), dry toluene (2 mL) and thionyl chloride (0.5 mL) were refluxed for 20 h. After the thionyl chloride and the toluene were evaporated, the residue was dissolved in dry CH_2Cl_2 (4 mL). The solution was added to a mixture of 4-octyloxyphenol (35 mg, 0.16 mmol), Et_3N (0.2 mL), and dry CH_2Cl_2 (3 mL) at 0 °C, and stirred for 40 h. After the Et_3N was evaporated and CH_2Cl_2 and 1 M hydrochloric acid were added, the phases were separated. The organic phase was washed with saturated $NaHCO_3$aq and brine and dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by preparative TLC (CH_2Cl_2) to give a (*S*)-CDEs**1** (27 mg, 0.032 mmol, 56%) as white solid. Mp: 76.5–79.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.91 (t, $J = 6.8$ Hz, 6H, CH_3), 1.29–1.35 (m, 16H, CH_2), 1.43–1.50 (m, 4H, CH_2), 1.80 (quintet, $J = 6.8$ Hz, 4H, CH_2), 2.98 (s, 4H, $ArCH_2$), 3.97 (t, $J = 6.8$ Hz, 4H, $PhOCH_2$), 4.24 (d, $J = 11.2$ Hz, 2H, $ArOCH_2$), 4.40 (d, $J = 11.2$ Hz, 2H, $ArOCH_2$), 6.95 (d, $J = 9.2$ Hz, 4H, aromatic), 7.15 (d, $J = 8.8$ Hz, 4H, aromatic), 7.57 (dt, $J_1 = 1.2$ Hz, $J_2 = 8.4$ Hz, 2H, aromatic), 7.64 (dt, $J_1 = 1.2$ Hz, $J_2 = 6.8$ Hz, 2H, aromatic), 8.28 (s, 2H, aromatic), 8.40 (d, $J = 8.4$ Hz, 2H, aromatic), 9.09 (d, $J = 8.8$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 32.7, 47.7, 61.6, 62.3, 121.9, 124.3, 125.8, 126.1, 127.2, 128.0, 130.5, 134.2, 153.8. IR (neat, cm^{-1}): 3448, 2926, 1854, 1719, 1571, 1502, 1238, 1192, 1167, 1131, 1024, 969, 774. MS (MALDI-TOF) m/z 871 $[M + Na]^+$. $[\alpha]_D$ +7.8° ($CHCl_3$, c 0.530, 30.1 °C). Anal. Calcd for $C_{55}H_{60}O_8$: C, 77.80; H, 7.12%. Found: C, 77.98; H, 7.19%.

Other ester-linked chiral dopants were synthesized with the same manner as (*S*)-CDEs**1**.

Bis[4-(4-octyloxyphenyl)phenyl] 3,3′-(4*H*,4′*H*)-Spirobi(2*H*-naphtho[1,2-*b*]pyran)-6,6′-dicarboxylate ((*S*)-CDEs2): White solid. Mp: 134.2–135.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.80 (t, $J = 6.8$ Hz, 6H, CH_3), 1.19–1.24 (m, 16H, CH_2), 1.33–1.40 (m, 4H, CH_2), 1.71 (quintet, $J = 6.8$ Hz, 4H, CH_2), 2.77 (s, 4H, $ArCH_2$), 3.87 (t, $J = 6.4$ Hz, 4H, $PhOCH_2$), 4.05 (d, $J = 11.2$ Hz, 2H, $ArOCH_2$), 4.22 (d, $J = 10.8$ Hz, 2H, $ArOCH_2$), 6.85 (d, $J = 8.4$ Hz, 4H, aromatic), 7.17 (d, $J = 8.4$ Hz, 4H, aromatic), 7.39 (d, $J = 8.4$ Hz, 4H, aromatic), 7.45 (t, $J = 7.2$ Hz, 2H, aromatic), 7.48 (d, $J = 8.8$ Hz, 4H, aromatic), 7.54 (t, $J = 7.2$ Hz, 2H, aromatic), 8.18 (s, 2H, aromatic), 8.21 (d, $J = 8.4$ Hz, 2H, aromatic), 9.03 (d, $J = 8.8$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 22.8, 26.2, 29.4, 29.4, 29.5, 30.6, 32.0, 33.6, 68.2, 70.5, 112.3, 114.9, 118.0, 122.2, 122.3, 125.3, 125.9, 126.1, 127.8, 128.2, 128.4, 132.2, 132.8, 134.9, 138.7, 150.0, 153.9, 158.9, 165.5. IR (KBr, cm^{-1}): 2926, 2853, 1725, 1608, 1573, 1496, 1246, 1202, 1166, 1130, 1025, 968, 774. MS (MALDI-TOF) m/z 1023 $[M + Na]^+$. $[\alpha]_D$ +40.5° ($CHCl_3$, c 0.58, 17 °C). Anal. Calcd for

$C_{67}H_{68}O_8$: C, 80.37; H, 6.85%. Found: C, 80.36; H, 6.80%.

Bis{4-[4-(4-heptylphenyl)phenyl]phenyl} 3,3′-(4*H*,4′*H*)-Spirobi(2*H*-naphtho[1,2-*b*]pyran)-6,6′-dicarboxylate ((*S*)-CDEs3): White solid. Mp: 197.5–198.2 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 6.4$ Hz, 6H, CH_3), 1.29–1.39 (m, 16H, CH_2), 1.66 (quintet, $J = 7.2$ Hz, 4H, CH_2), 2.65 (t, $J = 7.6$ Hz, 4H, $PhCH_2$), 2.98 (s, 4H, $ArCH_2$), 4.24 (d, $J = 11.2$ Hz, 2H, $ArOCH_2$), 4.40 (d, $J = 10.8$ Hz, 2H, $ArOCH_2$), 7.27 (d, $J = 8.4$ Hz, 4H, aromatic), 7.34 (d, $J = 8.8$ Hz, 4H, aromatic), 7.56 (d, $J = 8.4$ Hz, 4H, aromatic), 7.59–7.71 (m, 16H, aromatic), 8.33 (d, $J = 6.8$ Hz, 4H, aromatic), 9.13 (d, $J = 8.4$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.3, 22.8, 29.4, 29.5, 30.8, 31.7, 32.0, 33.7, 35.8, 70.6, 112.3, 118.1, 122.2, 122.4, 125.3, 125.9, 126.2, 127.0, 127.5, 127.6, 128.3, 128.5, 129.0, 132.4, 135.0, 138.1, 138.6, 139.2, 140.3, 142.5, 150.6, 154.0, 165.5. IR (KBr, cm^{-1}): 2924, 2852, 1727, 1573, 1490, 1339, 1237, 1202, 1130, 968, 800, 773. MS (MALDI-TOF) m/z 1115 $[M + Na]^+$. $[\alpha]_D$ +71.7° ($CHCl_3$, c 0.211, 21 °C). Anal. Calcd for $C_{77}H_{72}O_6$: C, 84.58; H, 6.64%. Found: C, 84.17; H, 6.69%.

Bis[4-(4-octyloxyphenylethynyl)phenyl] 3,3′-(4*H*,4′*H*)-Spirobi(2*H*-naphtho[1,2-*b*]pyran)-6,6′-dicarboxylate ((*S*)-CDEs4): White solid. Mp: 82–95 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 6.8$ Hz, 6H, CH_3), 1.24–1.35 (m, 16H, CH_2), 1.39–1.46 (m, 4H, CH_2), 1.76 (quintet, $J = 6.8$ Hz, 4H, CH_2), 2.82 (s, 4H, $ArCH_2$), 3.91 (t, $J = 6.4$ Hz, 4H, OCH_2), 4.12 (d, $J = 10.8$ Hz, 2H, $ArOCH_2$), 4.29 (d, $J = 11.2$ Hz, 2H, $ArOCH_2$), 6.83 (d, $J = 8.8$ Hz, 4H, aromatic), 7.19 (d, $J = 8.8$ Hz, 4H, aromatic), 7.43 (d, $J = 8.8$ Hz, 4H, aromatic), 7.51–7.54 (m, 6H, aromatic), 7.59–7.63 (m, 2H, aromatic), 8.21 (s, 2H, aromatic), 8.28 (d, $J = 8.0$ Hz, 2H, aromatic), 9.09 (d, $J = 8.8$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 22.8, 26.1, 29.3, 29.3, 29.5, 30.5, 31.9, 33.5, 68.1, 70.4, 87.4, 89.8, 112.3, 114.6, 115.0, 117.6, 121.3, 122.1, 122.2, 125.2, 125.8, 126.1, 128.5, 132.3, 132.3, 133.1, 135.0, 150.7, 153.9, 159.4, 165.0. IR (KBr, cm^{-1}): 2926, 1728, 1574, 1512, 1248, 1200, 1165, 1128. MS (MALDI-TOF) m/z 1049 $[M + H]^+$. $[\alpha]_D$ +79.8° ($CHCl_3$, c 1.00, 28 °C). Anal. Calcd for $C_{71}H_{68}O_8$: C, 81.27; H, 6.53%. Found: C, 81.12; H, 6.61%.

Bis{4-[4-(4-octyloxyphenylethynyl)phenylethynyl]phenyl} 3,3′-(4*H*,4′*H*)-Spirobi(2*H*-naphtho[1,2-*b*]pyran)-6,6′-dicarboxylate ((*S*)-CDEs5): White solid. Mp: 202.2–202.7 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 7.2$ Hz, 6H, CH_3), 1.25–1.37 (m, 16H, CH_2), 1.42–1.49 (m, 4H, CH_2), 1.79 (quintet, $J = 7.2$ Hz, 4H, CH_2), 2.98 (s, 4H, $ArCH_2$), 3.97 (t, $J = 6.4$ Hz, 4H, OCH_2), 4.25 (d, $J = 11.2$ Hz, 2H, $ArOCH_2$), 4.41 (d, $J = 11.2$ Hz, 2H, $ArOCH_2$), 6.87 (d, $J = 9.2$ Hz, 4H, aromatic), 7.26 (d, $J = 8.4$ Hz, 4H, aromatic), 7.43–7.51 (m, 12H, aromatic), 7.55–7.67 (m, 8H, aromatic), 8.29 (s, 2H, aromatic), 8.32 (d, $J = 9.2$ Hz, 2H, aromatic), 9.09 (d, $J = 8.8$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.3, 22.8, 26.2, 29.3, 29.4, 30.8, 32.0, 33.7, 68.3, 70.6, 87.9, 89.5, 90.5, 91.7, 112.3, 114.7, 115.0, 117.8, 120.8, 122.3, 122.7, 123.8, 125.3, 125.8, 126.2, 128.6, 131.5, 131.7, 132.4, 133.0, 133.2, 135.0, 151.2, 154.1, 159.6, 165.0. IR (KBr, cm^{-1}): 2926, 2855, 1730, 1573, 1518, 1283, 1246, 1200, 1165, 1125, 835. MS (MALDI-TOF) m/z 1250 $[M + H]^+$. $[\alpha]_D$ +111° ($CHCl_3$, c 0.75, 28 °C). Anal. Calcd for $C_{87}H_{76}O_8 \cdot 0.5H_2O$: C, 83.03; H, 6.17%. Found: C, 83.16; H, 6.11%.

Bis{4-[5-(4-octyloxyphenyl)pyrimid-2-yl]phenyl} 3,3′-(4*H*,4′*H*)-Spirobi(2*H*-naphtho[1,2-*b*]pyran)-6,6′-dicarboxylate ((*S*)-CDEs6): White solid. Mp: 123.1–127.4 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 6.8$ Hz, 6H, CH_3), 1.29–1.35 (m, 16H, CH_2), 1.43–1.51 (m, 4H, CH_2), 1.81 (quintet, $J = 6.8$ Hz, 4H, CH_2), 2.92 (s, 4H, $ArCH_2$), 3.99 (t, $J = 6.4$ Hz, 4H, OCH_2), 4.19 (d, $J = 11.2$ Hz, 2H, $ArOCH_2$), 4.37 (d, $J = 11.2$ Hz, 2H, $ArOCH_2$), 7.02 (d, $J = 8.8$ Hz, 4H, aromatic), 7.39 (d, $J = 8.8$ Hz, 4H, aromatic), 7.53 (d, $J = 8.8$ Hz, 4H, aromatic), 7.57 (t, $J = 8.4$ Hz, 2H, aromatic), 7.63 (d, $J = 8.0$ Hz, 2H, aromatic), 8.29–8.32 (m, 4H, aromatic), 8.56 (d, $J = 8.4$ Hz, 4H, aromatic), 8.95 (s, 4H, aromatic), 9.11 (d, $J = 8.8$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 22.8, 26.2, 29.3, 29.4, 30.6, 31.9, 33.6, 68.3, 70.5, 112.3, 115.5, 117.8, 122.2, 125.3, 125.9, 126.1, 126.6, 127.9, 128.5, 129.5, 131.4, 132.4, 135.0, 135.1, 153.2, 154.0, 154.7, 160.0, 162.1, 165.0. IR (KBr, cm^{-1}): 2926, 2855, 1727, 1608, 1574, 1431, 1430, 1283, 1246, 1238, 1161, 1130, 1014, 968, 831, 773. MS (MALDI-TOF) m/z 1159 $[M]^+$. $[\alpha]_D$ +103° ($CHCl_3$, c 0.46, 27 °C). Anal. Calcd for $C_{75}H_{72}N_4O_8$: C, 77.83; H, 6.27; N, 4.84%. Found: C, 77.83; H, 6.22; N, 4.77%.

(*S*)- or (*R*)-6,6′-Bis(hydroxymethyl)-3,3′-(4*H*,4′*H*)-spirobi-(2*H*-naphtho[1,2-*b*]pyran) (14*): Under argon, a dry THF solution (16 mL) of **13*** (500 mg, 0.720 mmol) was added to a mixture of $LiAlH_4$ (164 mg, 4.32 mmol) and dry THF (14 mL), and was stirred for 6 h under reflux. The THF was evaporated, $CHCl_3$ and 1 M HClaq were added, and the phases were separated. The organic phase was washed with saturated $NaHCO_3$aq and brine and dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (toluene: ethyl acetate = 1:1) to give a **14*** (233 mg, 0.566 mmol, 78.6%) as colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.34 (br, 2H, OH), 2.52–2.62 (m, 4H, $ArCH_2$), 3.91 (d, $J = 10.8$ Hz, 2H, $ArOCH_2$), 4.09 (d, $J = 11.2$ Hz, 2H, $ArOCH_2$), 4.87 (s, 4H, CH_2), 6.93 (s, 2H, aromatic), 7.43–7.47 (m, 4H, aromatic), 7.96 (d, $J = 8.4$ Hz, 2H, aromatic), 8.19 (d, $J = 9.6$ Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 30.6, 33.7, 63.3, 70.2, 112.8, 122.3, 123.6, 125.4, 125.6, 126.5, 128.0, 128.8, 131.2, 149.0. IR (KBr, cm^{-1}): 3381, 1582, 1396, 1113, 1096, 762. MS (MALDI-TOF) m/z 412 $[M]^+$.

(*S*)-6,6′-Bis[(4-octyloxyphenyloxy)methyl]-3,3′-(4*H*,4′*H*)-spirobi(2*H*-naphtho[1,2-*b*]pyran) ((*S*)-CDEt1): Under argon, a dry CH_2Cl_2 (3 mL) solution of mesyl chloride (142 mg, 1.24 mmol) was added to a mixture of (*S*)-**14** (85 mg, 0.21 mmol), triethylamine (125 mg, 1.24 mmol), and dry CH_2Cl_2 (5 mL), and the mixture was stirred for 4 h at −20 °C. 1 M HClaq was added, and the phases were separated. The organic phase was washed with saturated $NaHCO_3$aq and brine and dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was used without further purification. The mixture of the crude product (123 mg), K_2CO_3 (579 mg, 4.13 mmol), 4-octyloxyphenol (137 mg, 0.618 mmol), THF (6 mL), and CH_3CN (3 mL) was stirred for 12 h under reflux. The solvents were evaporated, 1 M HClaq and $CHCl_3$ were added, and the phases were separated. The organic phase was washed with saturated $NaHCO_3$aq and brine and dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by preparative TLC (toluene:$CHCl_3$ = 2:1) to give a (*S*)-CDEt**1** (89 mg, 0.11 mmol, 53%) as white solid. Mp: 138.4–139.2 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 6.8$ Hz, 6H, CH_3), 1.28–1.44 (m, 20H, CH_2), 1.75 (quintet, $J = 6.8$ Hz, 4H, CH_2), 2.76 (s, 4H, $ArCH_2$), 3.90 (t, $J = 6.8$ Hz, 4H, OCH_2), 4.04 (d, $J = 10.8$ Hz, 2H, $ArOCH_2$), 4.23 (d, $J = 10.8$ Hz, 2H, $ArOCH_2$), 5.26 (s, 4H, $ArCH_2O$), 6.84 (d, $J = 9.2$ Hz, 4H, aromatic), 6.95 (d, $J = 8.8$ Hz, 4H, aromatic), 7.18 (s, 2H, aromatic), 7.47–7.52 (m, 4H, aromatic), 7.94–7.97 (m, 2H, aromatic), 8.24–8.26 (m, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.3, 22.8, 26.2, 29.4, 29.5, 30.8, 32.0, 33.9, 68.8, 69.3, 70.3, 112.8, 115.6, 115.9, 122.4, 123.9, 125.1, 125.5, 125.6, 126.6, 129.4, 131.7, 149.6, 153.1, 153.7. IR (KBr, cm^{-1}): 2924, 2855, 1582, 1506, 1225, 1178, 1113. MS (MALDI-TOF) m/z 820 $[M]^+$.

$[\alpha]_D$ −6.7° ($CHCl_3$, *c* 0.224, 32 °C). Anal. Calcd for $C_{55}H_{64}O_6$: C, 80.45; H, 7.86%. Found: C, 80.34; H, 7.83%.

Other ether-linked chiral dopants were synthesized in the same manner as (*S*)-CDEt**1**.

(*R*)-6,6′-Bis[4-(4-octyloxyphenyl)phenyloxymethyl]-3,3′-(4*H*,-4′*H*)-spirobi(2*H*-naphtho[1,2-*b*]pyran) ((*R*)-CDEt2): White solid. Mp: 129.5–130.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 6.4$ Hz, 6H, CH_3), 1.29–1.48 (m, 20H, CH_2), 1.78 (quintet, $J = 6.8$ Hz, 4H, CH_2), 2.65–2.75 (m, 4H, $ArCH_2$), 3.95 (t, $J = 6.4$ Hz, 4H, OCH_2), 4.00 (d, $J = 11.2$ Hz, 2H, $ArOCH_2$), 4.20 (d, $J = 11.2$ Hz, 2H, $ArOCH_2$), 5.31 (s, 4H, $ArCH_2O$), 6.93 (d, $J = 8.8$ Hz, 4H, aromatic), 7.05 (d, $J = 8.8$ Hz, 4H, aromatic), 7.17 (s, 2H, aromatic), 7.44–7.51 (m, 12H, aromatic), 7.94–7.96 (m, 2H, aromatic), 8.24–8.27 (m, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.3, 22.8, 26.2, 29.4, 29.5, 30.7, 32.0, 33.8, 68.2, 68.7, 70.3, 112.9, 114.9, 115.2, 122.4, 123.8, 124.8, 125.5, 125.7, 126.7, 127.8, 127.9, 129.5, 131.7, 133.3, 134.0, 149.7, 158.1, 158.5. IR (KBr, cm^{-1}): 2924, 2855, 1607, 1582, 1499, 1468, 1269, 1234, 1172, 1113, 995, 821. MS (MALDI-TOF) *m*/*z* 973 $[M]^+$. $[\alpha]_D$ −9.5° ($CHCl_3$, *c* 0.49, 28 °C). Anal. Calcd for $C_{67}H_{72}O_6$: C, 82.68; H, 7.46%. Found: C, 82.34; H, 7.55%.

(*R*)-6,6′-Bis{4-[4-(4-heptylphenyl)phenyl]phenyloxy}methyl-3,3′-(4*H*,4′*H*)-spirobi(2*H*-naphtho[1,2-*b*]pyran) ((*R*)-CDEt3): White solid. Mp: 195.4–196.2 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 6.8$ Hz, 6H, CH_3), 1.23–1.40 (m, 16H, CH_2), 1.65 (quintet, $J = 6.8$ Hz, 4H, CH_2), 2.64 (t, $J = 7.6$ Hz, 4H, $PhCH_2$), 2.73–2.82 (m, 4H, $ArCH_2$), 4.06 (d, $J = 10.8$ Hz, 2H, $ArOCH_2$), 4.25 (d, $J = 10.8$ Hz, 2H, $ArOCH_2$), 5.36 (s, 4H, $ArCH_2O$), 7.11 (d, $J = 8.8$ Hz, 4H, aromatic), 7.25 (d, $J = 8.4$ Hz, 4H, aromatic), 7.49–7.65 (m, 22H, aromatic), 7.96–8.00 (m, 2H, aromatic), 8.25–8.28 (m, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.3, 22.8, 29.4, 29.5, 30.8, 31.7, 32.0, 33.9, 35.8, 68.8, 70.3, 112.9, 115.3, 122.5, 123.8, 124.7, 125.6, 125.7, 126.7, 127.1, 127.4, 128.2, 129.0, 129.6, 131.7, 133.7, 138.2, 139.5, 139.6, 142.3, 149.7, 158.7. IR (KBr, cm^{-1}): 2924, 2853, 1607, 1582, 1510, 1491, 1464, 1234, 1177, 1113, 1098, 1005, 995, 806. MS (MALDI-TOF) *m*/*z* 1065 $[M]^+$. $[\alpha]_D$ −26.8° ($CHCl_3$, *c* 0.35, 28 °C). Anal. Calcd for $C_{77}H_{76}O_4$: C, 86.80; H, 7.19%. Found: C, 86.46; H, 7.24%.

(*S*)-6,6′-Bis[4-(4-octyloxyphenylethynyl)phenyloxymethyl]-3,3′-(4*H*,4′*H*)-spirobi(2*H*-naphtho[1,2-*b*]pyran) ((*S*)-CDEt4): White solid. Mp: 163.1–163.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, $J = 6.4$ Hz, 6H, CH_3), 1.28–1.46 (m, 20H, CH_2), 1.77 (quintet, $J = 7.6$ Hz, 4H, CH_2), 2.75 (s, 4H, $ArCH_2$), 3.93 (t, $J = 6.8$ Hz, 4H, OCH_2), 4.04 (d, $J = 11.2$ Hz, 2H, $ArOCH_2$), 4.24 (d, $J = 11.2$ Hz, 2H, $ArOCH_2$), 5.30 (s, 4H, $ArCH_2O$), 6.84 (d, $J = 8.8$ Hz, 4H, aromatic), 6.97 (d, $J = 8.8$ Hz, 4H, aromatic), 7.18 (s, 2H, aromatic), 7.42–7.53 (m, 12H, aromatic), 7.91–7.93 (m, 2H, aromatic), 8.25–8.27 (m, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 22.8, 26.2, 29.3, 29.4, 30.8, 31.9, 33.8, 68.2, 68.7, 70.3, 88.0, 88.4, 112.9, 114.6, 115.0, 115.5, 116.3, 122.4, 123.7, 124.4, 125.5, 125.7, 126.7, 129.6, 131.6, 133.0, 149.7, 158.8, 159.2. IR (KBr, cm^{-1}): 2924, 2853, 1607, 1514, 1281, 1242, 1171, 829. MS (MALDI-TOF) *m*/*z* 1021 $[M]^+$. $[\alpha]_D$ +28.5° ($CHCl_3$, *c* 0.40, 28 °C). Anal. Calcd for $C_{71}H_{72}O_6$: C, 83.50; H, 7.11%. Found: C, 83.11; H, 7.22%.

Helical Twisting Power Measurements. Helical pitch measurements of nematic liquid crystals were carried out according to the Cano wedge cell method. A typical procedure is described as follows. The chiral dopant (*S*)-CDEs**6** (2.87 mg) was added to ZLI-1132 (566.27 mg), and a homogeneous solution was prepared by heating the mixture to 120 °C with rotating followed by cooling to room temperature. Then the liquid crystalline mixture was inserted to three pieces of Cano wedge cells (E.H.C.) with different wedge angles (3, 5, and 7°). The sample cells were left at rest for 1day, and viewed through a polarizing microscope at room temperature. The distances (*a*) of the defect lines were measured in each sample cell, and helical pitch (*p*) was calculated based on eq 3 using average *a* value, where θ is the angle of the wedge cell.

$$p = 2 \times a \times \tan\theta \quad (3)$$

The other helical pitch measurements were also carried out in the same way. The weight ratio (*c*) of the liquid crystalline mixtures were (*S*)-CDEs**1** (0.0105), (*S*)-CDEs**2** (0.0108), (*S*)-CDEs**3** (0.0101), (*S*)-CDEs**4** (0.00509), (*S*)-CDEs**5** (0.00202), (*S*)-CDEs**6** (0.00504), (*S*)-CDEt**1** (0.0469), (*R*)-CDEt**2** (0.0104), (*R*)-CDEt**3** (0.00495), and (*S*)-CDEt**4** (0.00509). The HTP and MHTP values were calculated using the helical pitch (*p*) and the weight ratio of the chiral dopant (*c*) based on eq 1 and eq 2. The nematic to isotropic phase transition temperature (T_{NI}) of the above-mentioned liquid crystalline mixtures were almost the same as the T_{NI} of the host liquid crystal (72 °C).

The helical senses of the sample liquid crystalline mixtures were determined by the contact method using a reference mixture of the host liquid crystal and adequate amounts of cholesteryl nonanoate, which features a left-handed helix (minus sense). In this method, the sample mixture and reference mixture were contacted in the Cano wedge cell. In the case of a continuous contact surface, both mixtures have the same helix. Therefore, it was found that the helical sense of the sample mixture was minus sense. Conversely, in the case of a discontinuous contact surface, the helical sense of the sample mixture was plus sense.

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22 The host liquid crystalline mixture (ZLI-1132, Merck) consists of 4-(4-propylcyclohexyl)benzonitrile (24 wt %), 4-(4-pentylcyclohexyl)benzonitrile (36 wt %), 4-(4-heptylcyclohexyl)-benzonitrile (25 wt %), and 4-[4-(4-pentylcyclohexyl)phenyl]benzonitrile (15 wt %). The host liquid crystalline mixture shows a nematic liquid crystal phase in the range −6 to 70 °C.

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