Chiral Tolans: A New Family of Ferroelectric Liquid Crystals. Synthesis and Mesomorphic Properties

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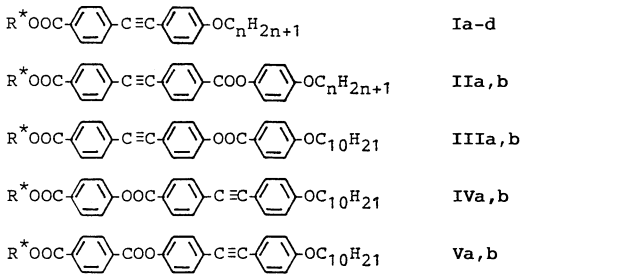
Diphenylacetylene homologues having a chiral alkyl group, synthesized by a palladium-catalyzed coupling reaction, provide a new series of liquid crystalline materials which form chiral smectic C (SmC*) phases exhibiting ferroelectric properties. Mesomorphic properties of the compounds composed of three aromatic rings is strongly affected by the position of an acetylenic linkage and the direction of an ester linking unit. The effect of variations in terminal chain length on the thermal stabilities of the smectic A (SmA) and SmC* the two and three aromatic ring systems has been systematically studied.

Owing to the utility based on the ferroelectric properties of SmC* liquid crystalline compounds, they have been received a considerable amount of attention. Clark and Langerwall showed[1] in 1980 that the SmC* liquid crystals exhibit ferroelectric properties and extremely fast response to an applied electric field. Considerable interest in the synthesis of new SmC* liquid crystalline materials suitable for application to microelectric devices has continued since then. The fast switching is based on a spontaneous polarization, *Ps*, and the switching time (τ) is inversely proportionate to it (Eq. 1).

$$\tau = \frac{\eta}{Ps \cdot E} \quad \eta\text{: viscosity, } E\text{: electric field} \qquad (1)$$

As it was pointed out that the size of a dipole moment near the asymmetric center almost decides the *Ps*, the investigations on chiral groups[2] were the forcus of the synthesis of the liquid crystalline compounds; research on chiral Sm liquid crystals was not attached weight to a core so much as that on nematic liquid crystals. Hence not many investigations have been reported about the effect of core structures on mesomorphic properties except of the cores such as benzylideneaniline, phenylpyrimidine, and biphenyl which are frequently adopted for the core of the SmC* liquid crystalline compounds. Currently the core structure is receiving an attention[3] aiming at decreasing viscosities, η, and at improving orientation of liquid crystalline molecules because too large *Ps* results in losing bistability.[4]

Previously we have showed[5] that tolan (diphenylacetylene) is competent to a core structure for liquid crystalline compounds. No examples of SmC* liquid crystalline compounds incorporating a tolan structure have appeared so far in literatures. The present paper describes the synthesis of the tolan homologues, **I** and **II**, and the analogues, **III**, **IV**, and **V**, as well as systematic studies about the effect of molecular structures on mesomorphism.

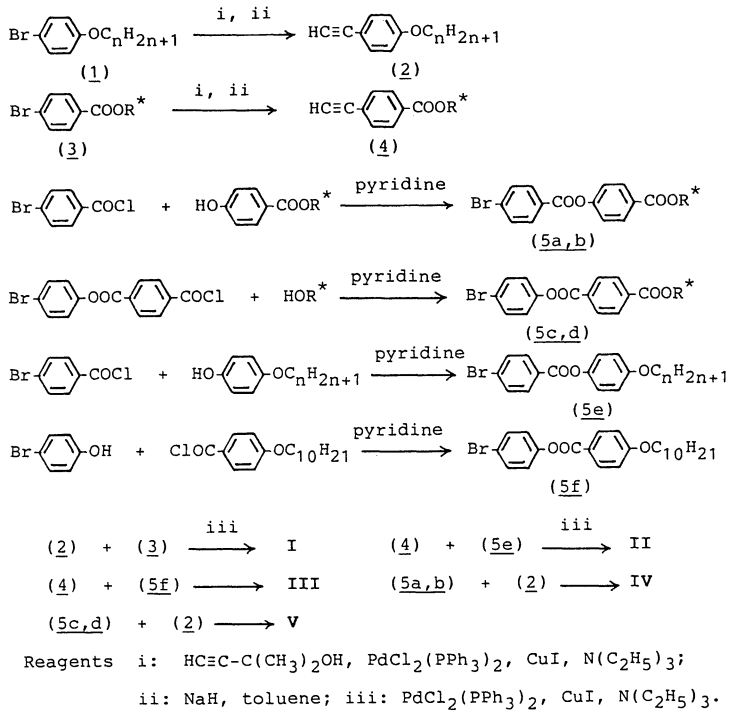


a: R^*= (S)-$C_2H_5CH(CH_3)CH_2$-; b: R^*= (R)-$C_6H_{13}CH(CH_3)$-;
c: R^*= (S)-$C_2H_5CH(CH_3)(CH_2)_3$-; d: R^*= (S)-$C_2H_5CH(CH_3)(CH_2)_5$-;

Results and Discussion

The synthetic routes of compounds **I**—**V** are shown in Scheme 1.

Terminal acetylene compounds **2** and **4** were prepared by the coupling reaction of arylbromides with 2-methyl-3-butyn-2-ol using a palladium catalyst,[6] followed by the elimination of acetone.[7] Compounds **I**—**V** were obtained in good yields by the coupling of **2** or **4** with esters (**5**—**f**) using a palladium catalyst and purified by column chromatography. Purification of **I** and **IV** may be easily performed due to their blue fluorescence on irradiation with UV light (254 nm). Thermal behaviors and transition temperatures of **I**—**V** were determined with a polarizing microscope and a differential scanning calorimeter. Mesophases were identified by comparison with textures reported in the literatures.[8] The SmC* phases observed for **I**, **II**, and **IV** were confirmed by measuring dynamic response to a changing external electric field, and the others were determined by a contact method with **IV**. Colored schlieren textures having fluidity for chiral nematic (N*) phases, forcal-conic fan textures for SmA phases, and forcal-conic fan textures having stripes corresponding to the helical pitch for SmC* phases were observed. Melting points and mesomorphic transition temperatures for the homologue series, **I** and **II**, are summarized in Tables 1 and 2.



Scheme 1.

Table 1. Phase Transition Temperatures[a] for Compounds **I**

Compound **I**	Transition Temperatures[b]/°C					
	Mp[c]	S1	SmC*	SmA	N*	Iso
a n= 5	49 [39]			.(41)[d]	.(42)	.
6	40 [15]			. 52		.
7	36 [26]		.(27)	. 52		.
8	51 [29]		.(33)	. 58		.
9	58 [37]		.(39)	. 58		.
10	54 [39]		.(41)	. 60		.
11	65 [50]			.(60)		.
12	59 [43]		.(45)	. 61		.
b n=10	78 [72]					.
c n= 8	54 [<25]	.(49)		. 61		.
d n= 8	58 [<25]	.(51)		. 62		.

a) In heating process. b) Mp: melting point, S1: unidentified smectic phase, SmC*: chiral smectic C, SmA: smectic A, N*: chiral nematic, Iso: isotropic liquid. c) [ ]: Temperature of crystallization. d) ( ): Monotropic transition.

Table 2. Phase Transition Temperatures for Compounds **II**

Compound **II**	Transition Temperatures/°C				
	Mp	SmC*	SmA	N*	Iso
a n= 8	84 [65]	. 120	.159	.176	.
10	91 [67]	. 122	.158	.168	.
b n= 6	92 [57]	. (62)	.122		.
7	83 [58]	. 85	.117		.
8	84 [57]	. 90	.117		.
9	87 [67]	. 99	.112		.
10	87 [72]	. 102	.112		.
11	91 [73]	. 107	.109		.
12	91 [75]	. 105	.109		.

Abbreviations and footnotes, see Table 1.

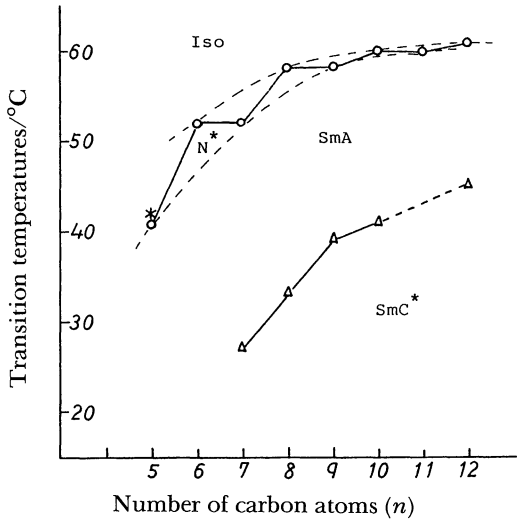


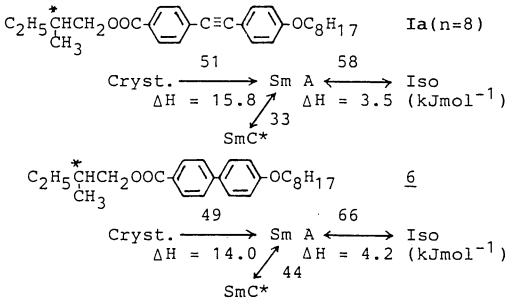
Fig. 1. Plots of transition temperatures against the number of carbon atoms (n) in the alkoxyl chain of homologous series **Ia**.

The homologue series of **Ia** [R=(*S*)-2-methylbutyl] shows a sequence, Iso-N*-SmA or Iso-SmA-SmC*. Figure 1 shows that the thermal stability of the SmA, and SmC* phases increase as the alkyl chain length increases.[9] The Iso-SmA transition temperatures clearly exhibit the normal trend, that is odd-even alternation whose amplitude decays according to an increase in the number of carbons, n. When the alkyl chain has five carbon atoms, a N* phase forms. However **Ib** which has a bulky lateral group in the neighbourhood of the core forms no mesophases, and **Ic** and **Id** which have long terminal chains exhibit no

SmC* phase.

It is known that the core length of liquid crystalline molecules gives strong influences to the thermal stabilitiy of mesophases. Hence we expected that **Ia** (n=8) would form more stable mesophases than biphenyl derivatives[6] because the diphenylacetylene structure may have a longer rigid core with the similar rigidity and polarity to those of biphenyl. As shown in Scheme 2, however, **Ia** showed just the same sequence of mesophases with almost the same thermal stabilities and transition enthalpies (ΔH) as biphenyl derivative **6**. This fact may indicate that for the thermal stabilities of smectic phases formed by these compounds the dipole-dipole and quadrupole-quadrupole interactions[10] are more important than the dispersion interactions[11] and the excluded molecular volume effect based on the rod-like structure model theory.[12]

Different from **I** the homologue series **IIa** and **IIb** exhibit the phase sequences of Iso-N*-SmA-SmC* and Iso-SmA-SmC*. The mesomorphic trends of the homologue series **IIb** are shown in Fig. 2. The Iso-



Scheme 2.

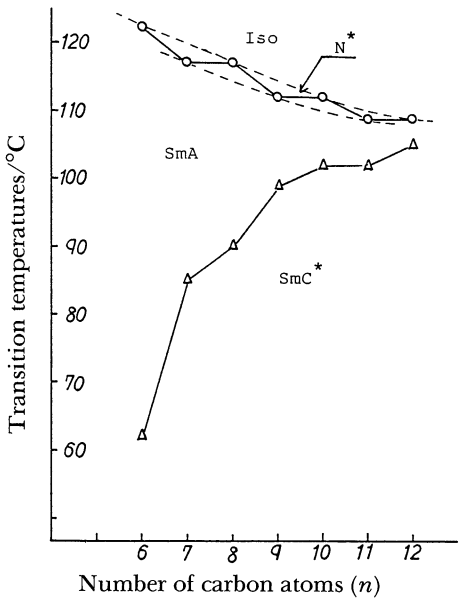
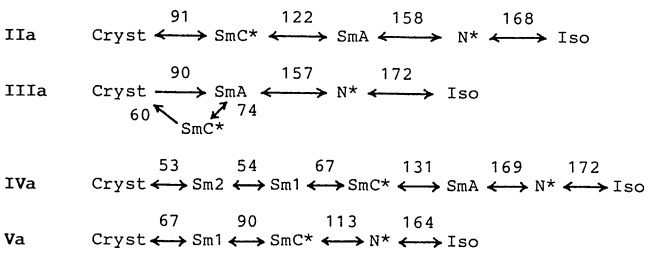
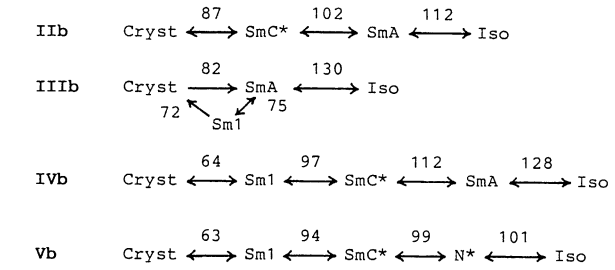


Fig. 2. Plots of transition temperatures against the number of carbon atoms (n) in the alkoxyl chain of homologous series **IIb**.



Scheme 3. Phase sequences and transition temperatures of series **a** (abbreviations, see Table 1).



Scheme 4. Phase sequences and transition temperatures of series **b** (abbreviations, see Table 1).

SmA transition temperatures for **IIb** showed odd-even alternation, and the transition temperatures are reduced with an increase in the number of carbons, n, whereas the SmA-SmC* transition temperatures increase with odd-even alternation as the number of carbons increase. The thermal stabilities of the SmC* phases of **II** were higher than those of **I** composed of two aromatic rings.

The thermal stabilities of the SmC* phases are strongly affected by the polar groups in the core.[13] In order to investigate in more details the effect of the linking group(-COO-) in the core on the phase transition temperatures, analogues **IIIa—Va** and **IIIb—Vb** having the same terminal chiral group and alkyl chain have been synthesized. Their mesomorphic properties as well as those of **II** are listed in Schemes 3 and 4, which reveal that there are some characteristic tendencies for the mesomorphic transition of analogue series **a** and **b** bearing 2-methylbutyl and 1-methylheptyl, respectively, as the chiral group. The thermal stabilities of the SmA phases are in the order of **IV>II≈III** for series **a**, and of **III≈IV>II** for series **b**; those of the SmC* phases are in the order of **IV>II>V** for series **a**, and of **IV>II≈V** for series **b**. The order of the thermal stabilities of SmA phases differs from that of SmC* phases. The results obtained in the present work, thus, reveal that the thermal stabilities of both the SmA and SmC* phases are strongly affected by the position and direction of the polar linking group in the core, while their effects on the SmA are essentially different from those on the SmC* phases.

Experimental

IR spectra were obtained with a HITACHI 270-30

Infrared Spectrophotometer and ^{1}H NMR spectra were recorded on a JEOL JNM-PX60. Transition temparatures were measured, and mesomorphic properties were observed using a NIKON OPTIPHOTPOL polarising microscope in conjunction with a Mettler FP82 heating stage and a Shimadzu DT-308 differential scanning calorimeter. The rate of heating or cooling was fixed to 5 °C min^{-1}.

***p*-Alkoxyphenylacetylens (2).** 1-Bromo-4-(octyloxy)benzene (**1**, n=8) (66.7 g, 234 mmol) and 2-methyl-3-butyn-2-ol (29.6 g, 352 mmol) were dissolved in triethylamine (200 ml) under an atmosphere of nitrogen. Copper(I) iodide (160 mg), triphenylphosphine (1.0 g) and dichloroibis(triphenylphosphine)palladium (520 mg) were added to the stirred solution. The solution was heated to 90 °C for 16 h. After cooling the precipitate of triethylammonium bromide was filtered off and washed with benzene. The combined filtrates were evaporated under a reduced pressure, and the residue wes chromatographed on a column (SiO_2, CH_2Cl_2) to yield 4-(*p*-octyloxyphenyl)-2-methyl-3-butyn-2-ol (mp 61.9 °C). The elimination of acetone was performed with sodium hydride. To a solution of 4-(*p*-octyloxyphenyl)-2-methyl-3-butyn-2-ol (31.6 g, 110 mmol) in anhydrous toluene (220 ml) was added sodium hydride (350 mg) as a 60% dispersion in oil. The stirred suspension was slowly heated and distilled until the boiling point of the distillate reached 110 °C. After a standard work-up procedure, the residue was distilled in vacuo to leave **2** (n=8). The other acetylenes were prepared in the same manner. The physical constants and yields are summarized in Table 3.

Chiral *p*-(Aloxycarbonyl)phenylacetylenes (4). *p*-(1-Methylheptyloxycarbonyl)phenylacetylene (**4a**) was prepared by the coupling reaction of (*R*)-(1-methylheptyl *p*-bromobenzoate (**3a**) ($[\alpha]_D^{25}$=−31.0, *c* 5, $CHCl_3$) with 2-methyl-3-butyn-2-ol, followed by the elimination of acetone as descrived above for **2**. The physical constants and yields are shown in Table 5.

Ester 5. They were prepared by an esterification reaction between the selected acid chloride and phenols or alcohols in THF containing pyridine at room temperature during 24 h according to the literature method.[14] The ester obtained was purified by column chromatography or by recrystallization from ethanol. Transparent liquid or white crystalline products were obtained in 88—99% yields.

(*S*)-4-(2-Methylbutoxycarbonyl)phenyl 4-Bromobenzoate (5a). ^{1}H NMR ($CDCl_3$) δ=8.2—7.9 (m, 4H), 7.6 (d, 2H, *J*=8 Hz), 7.3 (d, 2H, *J*=9 Hz), 4.2 (d, 2H, *J*=6 Hz), and 2.1—0.7 (m, 9H); IR (KBr film) 2964 (CH), 1744 and 1720 (C=O) cm^{-1}; $[\alpha]_D^{25}$=+2.8 (*c* 5, $CHCl_3$).

(*R*)-4-(1-Methylheptyloxycarbonyl)phenyl 4-Bromobenzoate (5b). ^{1}H NMR ($CDCl_3$) δ=8.2—8.0 (m, 4H), 7.6 (d, 2H, *J*=8 Hz), 7.3 (d, 2H, *J*=9 Hz), 5.1 (m, 1H), and 2.1—0.7 (m, 16H); IR (KBr film) 2928 (CH), 1744 and 1714 (C=O) cm^{-1}, $[\alpha]_D^{25}$=−21.6 (*c* 5, $CHCl_3$).

(*S*)-2-Methylbutyl 4-(4-Bromophenoxycarbonyl)benzoate (5c). ^{1}H NMR ($CDCl_3$) δ=8.2 (S, 4H), 7.5 (d, 2H, *J*=9 Hz), 7.1 (d, 2H, *J*=9 Hz), 4.2 (d, 2H, *J*=6 Hz), and 2.1—0.7 (m, 9.H); IR (KBr disk) 2964 (CH), 1742 and 1720 (C=O) cm^{-1}; $[\alpha]_D^{25}$=+3.4 (*c* 5, $CHCl_3$); mp=46.4—47.7 °C.

(*R*)-1-Methylheptyl 4-(4-Bromophenoxycarbonyl)benzoate (5d). ^{1}H NMR ($CDCl_3$) δ=8.2 (S, 4H), 7.5 (d, 2H, *J*=9 Hz), 7.1 (d, 2H, *J*=9 Hz), 5.2 (m, 1H), and 2.1—0.7 (m, 17H); IR (KBr disk) 2932 (CH), 1744 and 1720 (C=O) cm^{-1}; $[\alpha]_D^{25}$=−25.4 (*c* 5, $CHCl_3$); mp=50.7—52.5 °C.

4-(Decyloxy)phenyl 4-Bromobenzoate (5e). ^{1}H NMR ($CDCl_3$) δ=8.0 (d, 2H, *J*=8 Hz), 7.6 (d, 2H, *J*=8 Hz), 7.0 (d, 2H, *J*=9 Hz), 6.8 (d, 2H, *J*=9 Hz), 3.9 (t, 2H, *J*=6 Hz), 2.2—0.7 (m, 19H); IR (KBr disk) 2920 (CH), 1742 (C=O) cm^{-1}; mp=98.6—99.7 °C.

4-Bromophenyl 4-(Decyloxy)benzoate (5f). ^{1}H NMR ($CDCl_3$) δ=8.1 (d, 2H, *J*=9 Hz), 7.5 (d, 2H, *J*=8 Hz), 7.1—6.9 (m, 4H), 4.0 (t, 2H, *J*=6 Hz), and 2.2—0.7 (m, 19H); IR (KBr disk) 2920 (CH), 1726 (C=O) cm^{-1}; mp=80.4—80.8 °C.

Chiral 4-Alkoxycarbonyl-4′-alkoxytolans I. (S)-2-Methylbutyl *p*-bromobenzoate (**3b**: $[\alpha]_D^{25}$=+4.3, *c* 5, $CHCl_3$) (1.56 g, 5.76 mmol) and *p*-(decyloxy)phenylacetylene (**2**, n=10) (1.50 g, 5.76 mmol) were dissolved in triethylamine (30 ml) under an atmosphere of nitrogen. Copper(I) iodide (6 mg), triphenylphosphine (100 mg) and dichlorobis(triphenylphosphine)palladium (50 mg) were added to the stirred solution. The solution was heated to 80 °C for 16 h. Afer cooling the precipitate formed was filtered off, and the solvent was removed by rotary evaporation. Ether was added to the residue, and the solution was washed with water and brine, then dried. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography and recrystallization from hexane. The other tolan derivatives were synthesized in the same manner. White crystalline products were obtained in 53—86 yields. ^{1}H NMR ($CDCl_3$) Compound **Ia** (n=10): δ=7.9 (d, 2H, *J*=8 Hz), 7.5 (d, 2H, *J*=8 Hz), 7.4 (d, 2H, *J*=9 Hz), 6.8 (d, 2H, *J*=9 Hz), 4.1 (d, 2H, *J*=6 Hz), 3.9 (t, 2H, *J*=9 Hz), and 2.2—0.7 (m, 28H). Compond **Ib** (n=10): δ=7.9 (d, 2H, *J*=8 Hz), 7.5 (d, 2H, *J*=8 Hz), 7.4 (d, 2H, *J*=9 Hz), 6.8 (d, 2H, *J*=9 Hz), 5.1 (m, 1H), 3.9 (t, 2H, *J*=6 Hz), and 2.1—0.6 (m, 35H). IR

Table 3. Spectral Data

Compound	Bp (°C)/mmHg	Yield/%[a]	IR(cm^{-1})		NMR δ[b]	$[\alpha]_D^{25}$[c]
			$\nu_{\equiv CH}$	$\nu_{C\equiv C}$	≡CH	
2 n=5	74—77/0.22	78	3292	2108	2.9	—
6	75—76/0.18	48	3292	2108	2.9	—
7	88—89/0.17	57	3300	2112	2.9	—
8	113—115/0.23	82	3296	2108	2.9	—
9	130—132/0.30	47	3320	2112	2.9	—
10	125—127/0.20	70	3316	2112	2.9	—
11	28.1[d]	80	3288	2112	2.9	—
12	26.9—27.4[d]	68	3316	2108	2.9	—
4a	79—81/0.23	67	3292	2112	3.2	+5.6
4b	110—111/0.15	63	3300	2112	3.2	−40.0

a) Yields from **1** or **3**. b) In $CDCl_3$. c) In $CHCl_3$. d) Melting points.

Table 4. Elemental Analyses and $[\alpha]_D^{25}$ for Compounds I

Compounds I	Calcd(%)		Found(%)		$[\alpha]_D^{25}$ ($CHCl_3$)
	C	H	C	H	
a n= 5	79.33	7.99	79.39	7.85	+2.8
6	79.56	8.22	79.62	7.95	+3.7
7	79.77	8.43	79.88	8.49	+3.6
8	79.96	8.63	80.26	8.42	+3.1
9	80.40	8.51	80.14	8.81	+3.3
10	80.32	8.99	80.05	8.78	+3.3
11	80.48	9.15	80.76	8.80	+3.0
12	80.63	9.30	80.74	9.06	+3.0
b n=10	80.77	9.45	80.94	9.28	−33.9
c n= 8	80.32	8.99	80.39	9.24	+3.4
d n= 8	80.63	9.30	80.68	9.48	+2.7

(KBr disk) Compound **Ia** (n=10): 2924 (CH), 2216 (C≡C), and 1714 (C=O) cm^{-1}. Compound **Ib** (n=10): 2920 (CH), 2216 (C≡C), and 1710 (C=O) cm^{-1}.

Other physical constants are summarized in Table 4.

Chiral 4-Alkoxycarbonyl-4′-(*p*-alkoxyphenoxycarbonyl)-tolans II. Chiral tolans **II** were prepared by the coupling reaction of chiral *p*-(alkoxycarbonyl)phenylacetylens (**4**) with 4′-alkoxyphenyl 4-bromobenzoate (**5e**) as described above for **I**. The other tolans were obtained in the same manner. White crystalline products were obtained in 65—93% yields. ($CDCl_3$) Compound **IIa** (n=10): δ=8.8—8.0 (m, 4H), 7.7—7.5 (m, 4H), 7.1 (d, 2H, J=9 Hz), 6.9 (d, 2H, J=9 Hz), 4.2 (d, 2H, J=6 Hz), 4.0 (t, 2H, J=6 Hz), and 2.3—0.7 (m, 28H).

Compound **IIb** (n=10): =8.2—7.9 (m, 4H), 7.7—7.5 (m, 4H), 7.1 (d, 2H, J=9 Hz), 6.9 (d, 2H, J=9 Hz), 5.2 (m, 1H), 3.9 (t, 2H, J=6 Hz), and 2.0—0.7 (m, 35H). IR (KBr disk) Compound **IIa** (n=10): 2922 (CH), 1736 and 1720 (C=O) cm^{-1}. Compound **IIb** (n=10): 2920 (CH), 1736, 1720 and 1704 (C=O) cm^{-1}.

Chiral 4-[*p*-(Alkoxycarbonyl)phenoxycarbonyl-4′-(decyloxy)tolans IV. Chiral tolans **IV** were prepared by the coupling reaction of *p*-decyloxyphenylacetylene (**2**) (n=10) with chiral esters (**5a** and **5b**) as described above for **I**. White crystalline products were obtained in 77 and 71% yields, respectively.

Comopound **IVa:** IR (KBr disk) 2920 (CH), 2216 (C≡C), 1736 and 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.2—8.0 (m, 4H), 7.7—7.2 (m, 6H), 6.9 (d, 2H, J=9 Hz), 4.2 (d, 2H, J=6 Hz), 4.0 (t, 2H, J=6 Hz), and 2.1—0.6 (m, 28H); Calcd for $C_{37}H_{44}O_5$: C, 78.14; H, 7.80%. Found: C, 78.42; H, 7.88%; $[\alpha]_D^{25}$=+2.0 (*c* 5, $CHCl_3$).

Table 5. Elemental Analyses and $[\alpha]_D^{25}$ for Compounds II

Compounds II	Calcd(%)		Found(%)		$[\alpha]_D^{25}$ ($CHCl_3$)
	C	H	C	H	
a n= 8	77.75	7.46	78.01	7.60	+2.8
10	78.14	7.80	78.33	7.55	+2.6
b n= 6	77.95	7.63	78.06	7.50	−31.3
7	78.14	7.80	78.19	7.62	−30.8
8	78.32	7.96	78.31	7.85	−30.1
9	78.49	8.11	78.59	8.02	−28.8
10	78.65	8.25	78.91	8.35	−28.6
11	78.81	8.39	78.79	8.54	−27.6
12	78.96	8.52	79.06	8.61	−27.1

Compound **IVb:** IR (KBr disk) 2924 (CH), 2216 (C≡C), 1738 and 1718 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ=8.1—8.0 (m, 4H), 7.6—7.1 (m, 6H), 6.8 (d, 2H, J=9 Hz), 5.1 (m, 1H), 3.9 (t, 2H, J=6 Hz), and 2.1—0.7 (m, 35H); Calcd for $C_{40}H_{50}O_5$: C, 78.65; H, 8.25. Found: C, 78.73; H, 8.10%; $[\alpha]_D^{25}$=−20.2 (*c* 5, $CHCl_3$).

Chiral 4-[*p*-Alkoxycarbonyl)phenylcarbonyloxy]-4′-(decyloxy)tolans V. Chiral tolans **V** were prepared by the coupling reaction of *p*-decyloxyphenylacetylene (**2**) (n=10) with chiral esters (**5a** and **5b**) as described above for **I**. White crystalline products were obtained in 50 and 46% yields, respectively.

Compound **Va:** IR (KBr disk) 2924 (CH), 2216 (C≡C), 1740 and 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.2 (s, 4H), 7.6—7.1 (m, 6H), 6.8 (d, 2H, J=9 Hz), 4.2 (d, 2H, J=6 Hz), 4.0 (t, 2H, J=6 Hz), and 2.1—0.6 (m, 28H); Calcd for $C_{37}H_{44}O_5$: C, 78.14; H, 7.80%. Found: C, 78.17; H, 7.67%; $[\alpha]_D^{25}$=+2.3 (*c* 5, $CHCl_3$).

Compound **Vb:** IR (KBr disk) 2928 (CH), 2216 (C≡C), 1736 and 1716 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.2 (s, 4H), 7.6—7.1 (m, 6H), 6.8 (d, 2H, J=9 Hz), 5.2 (m, 1H), 4.0 (t, 2H, J=6 Hz), and 2.4—0.4 (m, 35H); Calcd for $C_{40}H_{50}O_5$: C, 78.65; H, 8.25%. Found: C, 78.80; H, 8.26%; $[\alpha]_D^{25}$=−20.2 (*c* 5, $CHCl_3$).

Chiral 4-Alkoxycarbonyl-4′(*p*-alkoxyphenylcarbonyloxy)-tolans III. Chiral tolans **III** were prepared by the coupling reaction of chiral *p*-(alkoxycarbonyl)phenylacetylenes (**4a** and **4b**) with ester **5f** as described above for **I**. White crystalline products were obtained in 65 and 72% yields, respectively.

Compound **IIIa:** IR (KBr disk) 2920 (CH), 2216 (C≡C), and 1724 (broad, C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.2—7.9 (m, 4H), 7.6—7.5 (m, 4H), 7.2 (d, 2H, J=8 Hz), 6.9 (d, 2H, J=9 Hz), 4.0—3.9 (m, 4H), and 2.1—0.7 (m, 28H); Calcd for $C_{37}H_{44}O_5$: C, 78.14; H, 7.80%. Found: C, 78.01; H, 7.52%; $[\alpha]_D^{25}$=+2.5 (*c* 5, $CHCl_3$).

Compound **IIIb:** IR (KBr disk) 2924 (CH), 2216 (C≡C), and 1718 (broad, C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.2—7.9 (m, 4H), 7.7—7.4 (m, 4H), 7.2 (d, 2H, J=8 Hz), 6.9 (d, 2H, J=9 Hz), 5.2 (m, 1H), 4.0 (t, 2H, J=6 Hz), and 2.1—0.6 (m, 35H); Calcd for $C_{40}H_{50}O_5$: C, 78.65; H, 8.25%. Found: C, 78.72; H, 8.26%; $[\alpha]_D^{25}$=−26.1 (*c* 5, $CHCl_3$).

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