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M. Parra[a]; J. Vergara[a]; C. Zúñiga[a]; E. Soto[b]; T. Sierra[c]; J. L. Serrano[c]
[a] Facultad de Ciencias Químicas, Departamento de Química Orgánica, Universidad de Concepción, Concepción, Chile [b] Facultad de Ciencias Químicas y Farmacéuticas, Departamento de Química Orgánica y Físico-Química, Universidad de Chile, Santiago, Chile [c] Facultad de Ciencias-Instituto de Ciencia de Materiales de Aragón, Química Orgánica, Universidad de Zaragoza-C.S.I.C., 50009-Zaragoza, España

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New chiral Schiff's bases with a 1,3,4-thiadiazole ring in the mesogenic core: synthesis, mesomorphic and ferroelectric properties

M. PARRA*†, J. VERGARA†, C. ZÚÑIGA†, E. SOTO‡, T. SIERRA§ and J. L. SERRANO§

†Facultad de Ciencias Químicas, Departamento de Química Orgánica, Universidad de Concepción, Casilla 160-C, Concepción, Chile

‡Facultad de Ciencias Químicas y Farmacéuticas, Departamento de Química Orgánica y Físico-Química, Universidad de Chile, Olivos 1007, Independencia, Santiago, Chile

§Facultad de Ciencias-Instituto de Ciencia de Materiales de Aragón, Química Orgánica, Universidad de Zaragoza-C.S.I.C., 50009-Zaragoza, España

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Two new homologous series of chiral esters derived from Schiff's bases containing a 1,3,4-thiadiazole unit (series **6** and **7**) were synthesized and their liquid crystalline and ferroelectric properties investigated. All the compounds of series **6** exhibit SmC*–SmA dimorphism and the compounds of series **7** exhibit a SmC* phase. All the compounds of these series are ferroelectric liquid crystals.

1. Introduction

Ferroelectric liquid crystals (FLCs) have attracted considerable attention since their discovery in 1975 [1]. The interest in these materials is due to their potential application in fast switching devices [2, 3].

The 2-amino-1,3,4-thiadiazoles are interesting systems for the design and synthesis of liquid crystalline compounds with a classical rod-like structure. We have previously reported the synthesis and mesomorphic properties of 1,3,4-thiadiazole derivatives which exhibit broad smectic C (SmC) temperature ranges [4, 5]. In addition, a thiadiazole ring can contribute significantly to the molecular dipole moment from the dipole moment contained in the plane of the heterocycle. Both of these aspects are relevant in the design of new compounds as ferroelectric liquid crystals.

Our interest in the relationship between molecular structure and mesomorphic and ferroelectric behaviour has led us to design new chiral molecules which incorporate 1,3,4-thiadiazole in the mesogenic core. Only a few examples of FLCs containing a five-membered heterocycle have been reported in the literature; these include chiral pyrazole and isoxazole derivatives [6], and chiral thiadiazole derivatives [7–9]. We have now synthesized and investigated the mesomorphic and ferroelectric properties of two novel series of chiral Schiff's bases derived from 2-amino-1,3,4-thiadiazole (series **6a**–**c** and series **7a**–**c**). In order to achieve the non-centrosymmetry in the SmC phase necessary for ferroelectric behaviour, one of the terminal groups is a chiral ester chain (either benzoate-like or alkanoate-like) derived from (*S*)-ethyl lactate. The other terminal substituent is an alkoxy group with the number of carbon atoms kept constant at $n=10$.

2. Synthesis

The synthesis of all the compounds is outlined in schemes 1 and 2. The 2-*n*-alkoxypropanoic acids **1a**–**c** were prepared by alkylation of (*S*)-ethyl lactate with an excess of the appropiate *n*-alkyl iodide in the presence of Ag_2O; the resulting esters were saponified, according to the procedure described elsewhere [10, 11]. These chiral acids **1a**–**c** were reduced to the corresponding alcohols **2a**–**c** with lithium aluminum hydride [12–14]. The homologous series **3a**–**c** was obtained by reaction of **2a**–**c** with 4-formylbenzoic acid chloride [15, 16].

The amino thiadiazole **4** and Schiff's bases **5** were synthesized according to methods previously described [15, 17, 18]. The homologous series **6a**–**c** was obtained by condensation of **4** with an excess of the corresponding chiral precursor **3** [15, 18]. Esterification of **5** with the corresponding chiral 2-*n*-alkoxypropanoic acid **1**, gave the homologous series **7a**–**c** [19].

*Corresponding author. Email: mparra@udec.cl

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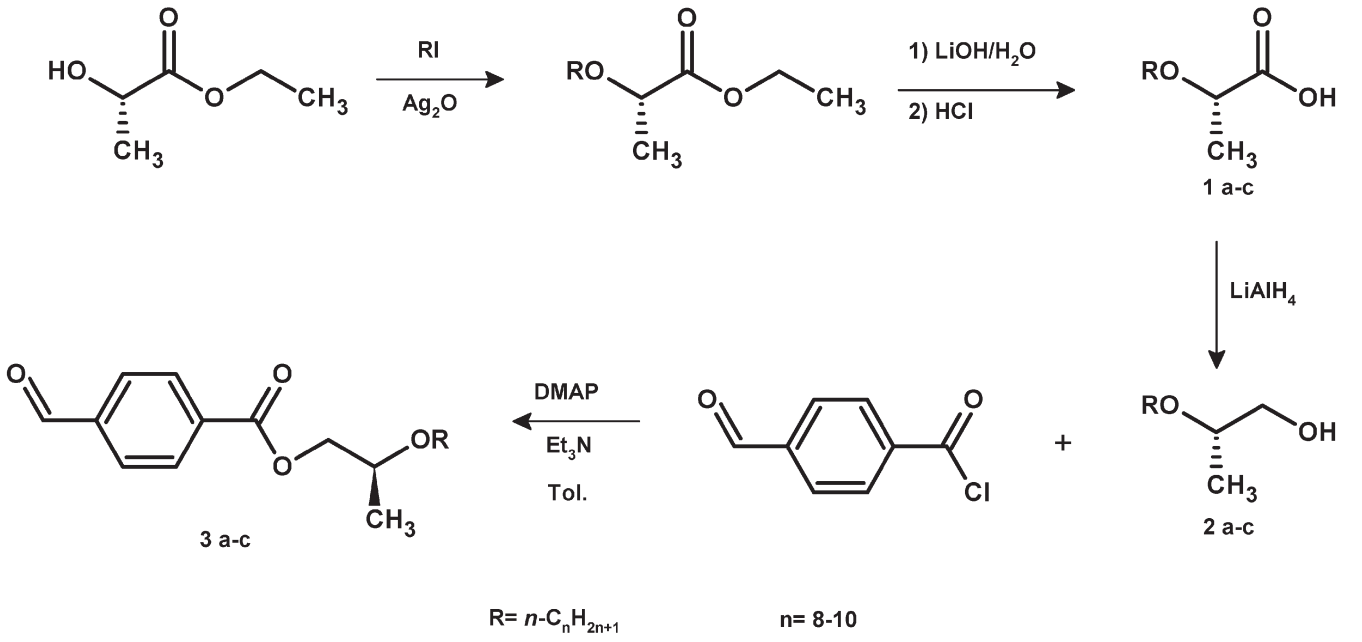


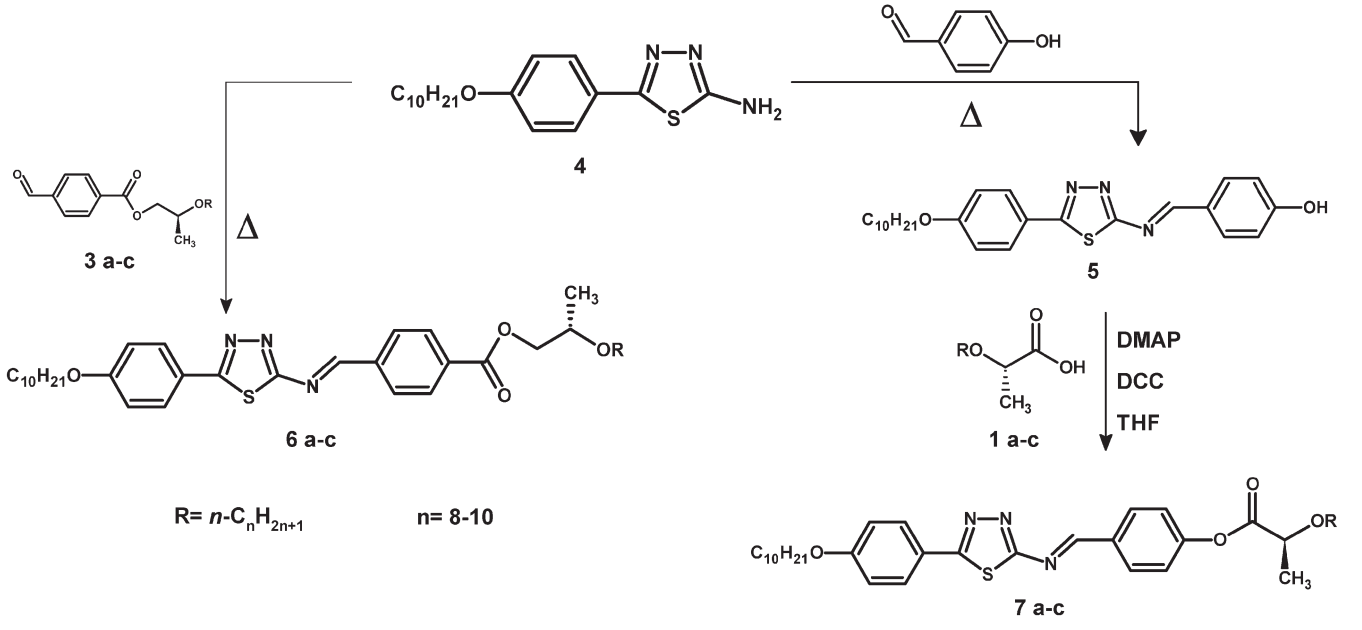
Scheme 1. Synthetic route for chiral precursors **1**–**3**.

3. Results and discussion

3.1. *Mesomorphic properties*

The optical, thermal and thermodynamic data for the compounds **6** and **7** are gathered in the table; a graphical representation of the mesomorphic behaviour is presented in figure 1. All compounds in series **6a**–**c** and **7a**–**c** show mesomorphic properties. Enantiotropic phase sequences are observed for compounds **6a**–**c** (Cr–SmC*–SmA–I and for compounds **7a**–**c** (Cr–SmC*–I).

Compounds of the series **6a**–**c** have lower melting points and higher clearing temperatures than the corresponding compounds of series **7a**–**c**. Compounds **6a**,**b** exhibit broader SmC* and SmA temperature



Scheme 2. Synthetic route for chiral Schiff's bases **6a**–**c** and **7a**–**c**.

Table. Transition temperatures and enthalpies for compounds of series **6a–c** and series **7a–c**. Cr=crystal, SmC*=chiral smectic C, SmA=smectic A, I=isotropic.

Compound R=n-C_nH_{2n+1}	Transition	Temperature /°C	ΔH/kJ mol^{-1}
6a (n=8)	Cr–SmC*	88.2	22.7
	SmC*–SmA	150[a]	—
	SmA–I	155.3	5.9
6b (n=9)	Cr–SmC*	90.9	26.6
	SmC*–SmA	152.6	0.6
	SmA–I	158.2	3.2
6c (n=10)	Cr–SmC*	91.3	24.2
	SmC*–SmA	142[a]	—
	SmA–I	144.1	5.0
7a (n=8)	Cr–SmC*	94.8	17.9
	SmC*–I	140[a]	—
7b (n=9)	Cr–SmC*	100.8	20.7
	SmC*–I	139[a]	—
7c (n=10)	Cr–SmC*	99.8	24.0
	SmC*–I	138[a]	—

[a]Optical microscopy data.

ranges than compound **6c**, which has a lower clearing temperature, reduced SmC* and SmA temperature ranges and decreased mesomorphic stability.

All compounds of the series **7a–c** have a lower mesomorphic temperature range and a lower mesomorphic stability than the corresponding compounds of the series **6a–c**.

Compounds of series **6a–c** and **7a–c** have the same central rigid core and the same achiral alkoxy chain. The difference between these series is in the lateral chiral ester chain. The results show that the position of the carbonyl function of the ester group has a profound influence on the mesomorphic properties. While compounds of series **6** exhibit SmC*–SmA dimorphism with broad mesomorphic ranges, compounds of series **7** display only a SmC* phase. It seems likely that, in comparison with compounds **7a–c**, the increased mesogenic character of compounds **6a–c** is due to the carbonyl group which is coplanar with the aromatic rigid core; these compounds therefore have a major conjugated character and a major polarizability, both of which favour mesophase formation and, in particular, smectic phases [20].

3.2. *Textures observed by polarizing optical microscopy*

The mesophases exhibited by Schiff's bases of series **6** and **7** were identified according to their optical textures which were observed by polarizing optical microscopy (POM). The SmC* and SmA phases were determined from textural observations by thermal microscopy under the polarizing microscope using heating and cooling cycles. Phase transition temperatures observed through thermal microscopy were found to be in reasonable agreement with the corresponding DSC thermograms.

The SmA phase of series **6** compounds was characterized by the formation of the typical focal-conic fan texture. The SmC* phase exhibited by series **6** compounds showed a schlieren texture with four-brush singularities coexisting with a pseudo-homeotropic texture, which is characteristic of the SmC* phase, see figure 2 (*a*) [21]. The SmC* phase of series **7** compounds was identified by the appearance of a broken focal-conic texture with dechiralization lines, characterisitic of the SmC* phase, see figure 2 (*b*). The striations on the focal-conic domains in the SmC* phase are due to pitch bands and dechiralization lines [22].

3.3. *Ferroelectric properties*

Both series of compounds were observed under electric fields in 5 μm ITO/polyimide-coated cells (Linkam), in which aligned samples were obtained. When a voltage of 70 V_{pp} was applied, ferroelectric switching was clearly detected for all compounds of series **6** and **7**. However, the current peak due to inversion of the spontaneous polarization was barely detected, being masked by the high conductivity and capacitance of the materials. The appearance of the peak was short-lived, so, accurate measurement of $\mathbf{P}_s$ values was not carried out. Decomposition of the materials probably took place under the effect of the electric field.

4. Experimental

4.1. *Characterization*

The structures of the compounds were confirmed by ^{1}H NMR, ^{13}C NMR (Bruker AC-250P) and FTIR (Nicolet 550) spectra; the purity of the final products was evaluated by thin layer chromatography.

Transition temperatures and textures of mesophases were determined by optical microscopy using an Ortholux Pol BK-11 polarizing microscope equipped with a Mettler FP 800 hot stage. Transition temperatures and enthalpies were investigated by differential scanning calorimetry using a Rheometric DSC-V calorimeter. Samples were encapsulated in aluminium pans and studied at a scanning rate of 5°C min^{-1} during heating and cooling. The instrument was calibrated using an indium standard (156.6°C, 28.44 J g^{-1}).

Cells used for ferroelectric measurements were coated with polyimide and carried indium tin oxide (ITO) electrodes.

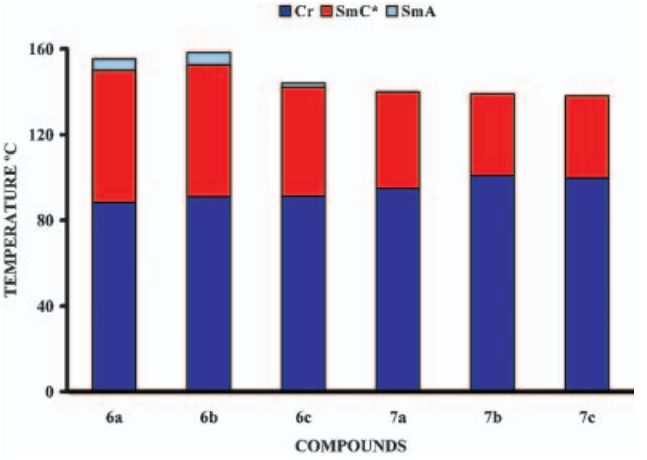


Figure 1. Plot of transition temperatures versus the number of carbon atoms in the ester chain of series **6** and **7** compounds.

4.2. *Synthesis*

4.2.1. (S)-2-n-Alkoxypropanoic acids (1a–c). The compounds of this series were synthesized according to a previously described procedure [10, 11].

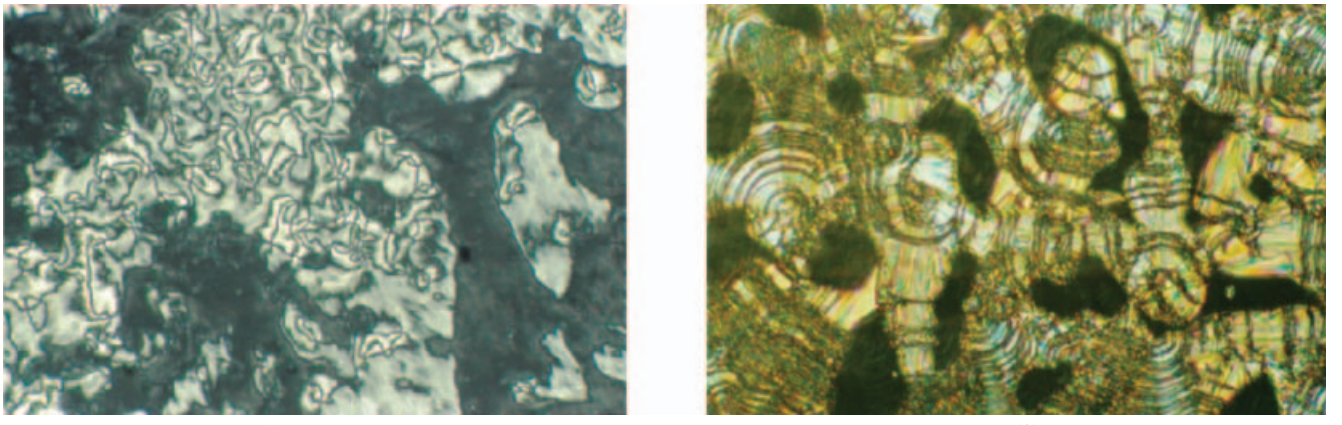
4.2.2. (S)-2-n-Alkoxypropanols (2a–c). The compounds of this series were synthesized by the method described in references [12–14].

4.2.3. (S)-2-(n-Alkoxy)propyl-4-formylbenzoates (3a–c). These compounds were synthesized using the procedure described in references [15, 16]. Products were obtained in liquid form, and were used in subsequent reaction without further purification. The purity of these compounds was evaluated by TLC. The following yields were obtained. **3a** 80%; **3b** 90%; **3c** 82%.

3a: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm=10.10 (s, 1H, O=C<u>H</u>); 7.93 (d, J=7.76 Hz, 2H, arom. H); 7.22 (d, J=7.64 Hz, 2H, arom. H); 4.32 (m, 1H, C<u>H</u> of the chiral chain); 3.52 (d, J=6.85 Hz, 2H, $CO_2C\underline{H}_2$); 1.42 (d, J=6.83 Hz, 3H, methyl branch); 1.28 (m, 14H, 7 CH_2); 0.88 (t, J=6.27 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm=191.5 (O=<u>C</u>H); 165.2 (C=O); 137.7, 130.1 (quaternary arom. C); 129.0, 128.1 (arom. C); 73.1 (<u>C</u>H of the chiral chain); 69.4 ($CO_2\underline{C}H_2$); 17.0 (methyl branch); 30.1, 29.4, 28.6, 26.1, 22.6 (aliph. C); 14.0 (CH_3). IR (film): cm^{-1}=1720 (C=O); 2928 (C_{sp^3}–H); 1460 (C=C).

3b: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm=10.06 (s, 1H, O=C<u>H</u>); 7.95 (d, J=7.72 Hz, 2H, arom. H); 7.23 (d, J=7.60 Hz, 2H, arom. H); 4.30 (m, 1H, C<u>H</u> of the chiral chain); 3.54 (d, J=6.82 Hz, 2H, $CO_2C\underline{H}_2$); 1.40 (d, J=6.80 Hz, 3H, methyl branch); 1.24 (m, 16H, 8 CH_2); 0.85 (t, J=6.25 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm=190.9 (O=<u>C</u>H); 165.0 (C=O); 138.0, 130.0 (quaternary arom. C); 128.9, 128.1 (arom. C); 73.0 (<u>C</u>H of the chiral chain); 68.2 ($CO_2\underline{C}H_2$); 17.0 (methyl branch); 30.7, 29.4, 28.5, 26.1, 22.6 (aliph. C); 13.9 (CH_3). IR (film): cm^{-1}=1718 (C=O); 2927 (C_{sp^3}–H); 1459 (C=C).

3c: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm=10.09 (s, 1H, O=C<u>H</u>); 7.96 (d, J=7.75 Hz, 2H, arom. H); 7.25 (d, J=7.65 Hz, 2H, arom. H); 4.33 (m, 1H, C<u>H</u> of the chiral chain); 3.55 (d, J=6.85 Hz, 2H, $CO_2C\underline{H}_2$); 1.41 (d, J=6.83 Hz, 3H, methyl branch); 1.27 (m, 18H, 9 CH_2); 0.90 (t, J=6.28 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm=191.5 (O=<u>C</u>H); 165.8 (C=O);



(*a*) (*b*)

Figure 2. Mesophase textures of the SmC* phase obtained on cooling. (*a*) Schlieren coexisting with a pseudo-homeotropic texture at 156°C for compound **6b**. (*b*) Broken focal-conic with dechiralization lines (SmC*) at 132°C for compound **7c**.

137.7, 130.1 (quaternary arom. C); 128.9, 128.1 (arom. C); 73.1 (CH of the chiral chain); 69.4 ($CO_2\underline{C}H_2$); 17.1 (methyl branch); 30.0, 29.4, 28.6, 26.1, 22.6 (aliph. C); 14.0 (CH_3). IR (film): cm^{-1}=1719 (C=O); 2929 (C_{sp^3}–H); 1461 (C=C).

4.2.4. 5-(4-n-Decyloxy)phenyl 2-amino-1,3,4-thiadiazole (4). This compound was synthesized according to reference [4].

4.2.5. 5-(4-n-decyloxy)phenyl-2-(4-hydroxy)benzylidene-amino-1,3,4-thiadiazole(5). This compound was prepared from 4-hydroxybenzaldehyde and 5-(4-*n*-decyloxy)phenyl-2-amino-1,3,4-thiadiazole (**4**) by the procedure describe in references [15, 18].

4.2.6. (S)-2-(n-Alkoxy)propyl 4-{[5-(4-n-decyloxyphenyl-1,3,4-thiadiazol-2-yl)imino]methyl} benzoate (6a–c). These compounds were synthesized by condensation of amino-thiadiazole **4** with chiral compounds of series **3a**–**c** using the procedure described in [15, 18]. A mixture of **4** (0.61 mmol, 0.2 g) and 0.91 mmol of the corresponding homologue of serie **3a**–**c** was heated in an oil bath at 120°C for 1 h. The residue was cooled and crystallized from ethanol with the following yields: **6a** (45%); **6b** (47%); **6c** (48%).

6a: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm=10.90 (s, 1H, N=C<u>H</u>); 8.17 (d, J=8.40 Hz, 2H, arom. H); 8.07 (d, J=8.43 Hz, 2H, arom. H); 7.90 (d, J=8.75 Hz, 2H, arom. H); 7.05 (d, J=8.80 Hz, 2H, arom. H); 4.33 (t, J=6.78 Hz, 2H, O<u>C</u>H$_2$); 4.00 (d, J=6.50 Hz, 2H, CO$_2$<u>C</u>H$_2$); 3.55 (m, 1H, C<u>H</u> of the chiral chain); 1.25 (m, 33H, 15 CH_2 and 3H of the methyl branch); 0.87 (t, J=6.83 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm=173.5 (C=O); 165.1 (N=CH); 166.8, 164.8, 161.7, 137.9, 133.9, 122.7 (quaternary arom. C); 130.1, 129.9, 129.2, 115.0 (arom. C); 73.1 (<u>C</u>H of the chiral chain); 69.5, 68.3 (O<u>C</u>H$_2$ and CO$_2$<u>C</u>H$_2$); 31.8, 30.0, 29.6, 29.3, 29.2, 29.1, 26.1, 25.9, 22.6 (aliph. C); 17.1 (methyl branch); 14.0 (2 CH_3). IR (KBr disk): cm^{-1}=1716 (C=O); 2925 (C_{sp^3}–H); 1610 (C=C).

6b: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm=9.90 (s, 1H, N=C<u>H</u>); 8.13 (d, J=8.40 Hz, 2H, arom. H); 8.05 (d, J=8.42 Hz, 2H, arom. H); 7.88 (d, J=8.73 Hz, 2H, arom. H); 7.01 (d, J=8.80 Hz, 2H, arom. H); 4.32 (t, J=6.77 Hz, 2H, O<u>C</u>H$_2$); 3.99 (d, J=6.51 Hz, 2H, CO$_2$<u>C</u>H$_2$); 3.53 (m, 1H, C<u>H</u> of the chiral chain); 1.23 (m, 35H, 16 CH_2 and 3H of the methyl branch); 0.86 (t, J=6.84 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm=172.5 (C=O); 165.0 (N=CH); 167.7, 165.3, 161.7, 138.2, 128.9, 122.8 (quaternary arom. C); 130.1, 129.9, 129.2, 115.0 (arom. C); 75.5 (<u>C</u>H of the chiral chain); 69.5, 68.3 (O<u>C</u>H$_2$ and CO$_2$<u>C</u>H$_2$); 31.8, 30.3, 29.5, 29.3, 29.1, 25.9, 22.6 (aliph. C); 17.1 (methyl branch); 14.1 (2 CH_3). IR (KBr disk): cm^{-1}=1717 (C=O); 2923 (C_{sp^3}–H); 1612 (C=C).

6c: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm=9.95 (s, 1H, N=C<u>H</u>); 8.10 (d, J=8.42 Hz, 2H, arom. H); 8.01 (d, J=8.40 Hz, 2H, arom. H); 7.85 (d, J=8.70 Hz, 2H, arom. H); 7.05 (d, J=8.81 Hz, 2H, arom. H); 4.30 (t, J=6.70 Hz, 2H, O<u>C</u>H$_2$); 3.98 (d, J=6.50 Hz, 2H, CO$_2$<u>C</u>H$_2$); 3.50 (m, 1H, C<u>H</u> of the chiral chain); 1.22 (m, 37H, 17 CH_2 and 3H of the methyl branch); 0.87 (t, J=6.85 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm=172.4 (C=O); 165.1 (N=CH); 167.9, 165.0, 161.6, 138.2, 134.9, 122.7 (quaternary arom. C); 130.1, 129.8, 129.2, 115.0 (arom. C); 77.5 (<u>C</u>H of the chiral chain); 69.5, 68.2 (O<u>C</u>H$_2$ and CO$_2$<u>C</u>H$_2$); 31.4, 30.3, 29.5, 29.3, 29.1, 26.1, 25.9, 22.6 (aliph. C); 17.1 (methyl branch); 14.1 (2 CH_3). IR (KBr disk): cm^{-1}=1714 (C=O); 2924 (C_{sp^3}–H); 1610 (C=C).

4.2.7. (S)-4-{[5-(4-n-decyloxyphenyl-1,3,4-thiadiazol-2-yl)imino]methyl}phenyl 2-(n-alkoxy) propanoates (7a–c). The general method of reference [19] was used. To a solution of 1.37 mmol (0.6 g) of Schiff's base **5** and 1.37 mmol of the required (*S*)-2-(*n*-alkoxy)propanoic acid (**1**) in 15 ml of dry THF, was added 1.37 mmol (0.17 g) of DMAP and 1.59 mmol (0.33g) of DCC. The mixture was stirred for 30 h at room temperature, and the dicyclohexylurea formed removed by filtration. The organic solution was washed with water (100 ml), twice with 0.2 M HCl (60 ml), and again with water (100 ml). The crude product obtained on evaporation of the filtrate was recrystallized several times using ethanol, giving the following yields: **7a** 39%; **7b** 35%; **7c** 39%.

7a: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm=9.28 (s, 1H, N=C<u>H</u>); 7.94 (d, J=8.58 Hz, 2H, arom. H); 7.83 (d, J=8.79 Hz, 2H, arom. H); 7.22 (d, J=8.55 Hz, 2H, arom. H); 6.91 (d, J=8.70 Hz, 2H, arom. H); 4.12 (q, J=6.81 Hz, 1H, C<u>H</u> of the chiral chain); 3.94 (t, J=6.50 Hz, 2H, O<u>C</u>H$_2$); 3.60–3.50 (m, 2H, diastero-topic H of O<u>C</u>H$_2$ of the chiral chain); 1.51 (d, J=6.87 Hz, 3H, methyl branch); 1.20 (m, 28H, 14 CH_2); 0.80 (t, J=6.38 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm=173.4 (C=O); 165.1 (N=CH); 172.1, 167.4, 154.4, 132.4, 129.5, 122.4 (quaternary arom. C); 131.5, 129.2, 122.1, 115.0 (arom. C); 74.9 (<u>C</u>H of the chiral chain); 70.8, 68.3 (2 O<u>C</u>H$_2$); 31.9, 29.5, 29.3, 26.0, 25.9, 22.6 (aliph. C); 17.5 (methyl branch); 14.8 (2 CH_3). IR (KBr disk): cm^{-1}=1767 (C=O); 2924 (C_{sp^3}–H); 1608 (C=C).

7b: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm=9.37 (s, 1H, N=C<u>H</u>); 7.96 (d, J=8.60 Hz, 2H, arom. H); 7.82 (d, J=8.79 Hz, 2H, arom. H); 7.21 (d, J=8.50 Hz, 2H, arom. H); 6.90 (d, J=8.75 Hz, 2H, arom. H); 4.14 (q, J=6.85 Hz, 1H, C<u>H</u> of the chiral chain); 3.92 (t, J=6.50 Hz, 2H, OC<u>H</u>$_2$); 3.63–3.46 (m, 2H, diasterotopic H of OC<u>H</u>$_2$ of the chiral chain); 1.52 (d, J=6.85 Hz, 3H, methyl branch); 1.19 (m, 30H, 15 CH_2); 0.81 (t, J=6.40 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm=172.7 (C=O); 165.2 (N=CH); 171.4, 167.4, 154.3, 132.3, 128.7, 122.7 (quaternary arom. C); 131.5, 129.1, 122.1, 115.0 (arom. C); 74.9 (<u>C</u>H of the chiral chain); 70.8, 68.2 (2 O<u>C</u>H$_2$); 31.8, 29.7, 29.5, 29.3, 25.9, 22.6 (aliph. C); 18.8 (methyl branch); 14.0 (2 CH_3). IR (KBr disk): cm^{-1}=1766 (C=O); 2923 (C_{sp^3}–H); 1606 (C=C).

7c: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm=9.32 (s, 1H, N=C<u>H</u>); 7.99 (d, J=8.40 Hz, 2H, arom. H); 7.84 (d, J=8.63 Hz, 2H, arom. H); 7.23 (d, J=8.30 Hz, 2H, arom. H); 6.93 (d, J=8.61 Hz, 2H, arom. H); 4.16 (q, J=6.76 Hz, 1H, C<u>H</u> of the chiral chain); 3.95 (t, J=6.55 Hz, 2H, OC<u>H</u>$_2$); 3.60–3.50 (m, 2H, diasterotopic H of OC<u>H</u>$_2$ of the chiral chain); 1.50 (d, J=6.88 Hz, 3H, methyl branch); 1.22 (m, 32H, 16 CH_2); 0.81 (t, J=6.44 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm=174.5 (C=O); 165.1 (N=CH); 172.7, 167.4, 161.6, 154.3, 132.4, 122.4 (quaternary arom. C); 131.5, 129.2, 122.2, 115.0 (arom. C); 75.0 (<u>C</u>H of the chiral chain); 70.9, 68.3 (2 O<u>C</u>H$_2$); 31.9, 29.3, 26.0, 25.6, 22.0 (aliph. C); 18.6 (methyl branch); 14.1 (2 CH_3). IR (KBr disk): cm^{-1}=1766 (C=O); 2922 (C_{sp^3}–H); 1608 (C=C).

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