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Synthesis and mesomorphic properties of liquid crystalline [1]benzothieno[3,2-*b*][1]benzothiophene derivatives

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Two new series of chiral aliphatic and aromatic esters of 7-decyl[1]benzothieno[3,2-*b*][1]benzothiophene-2-carboxylic acid were synthesized and their mesomorphic behaviour studied. While the chiral aliphatic esters exhibited only the SmA phase, the antiferroelectric SmC_A^* phase was found for esters with chiral 4-hydroxybenzoates; for one homologue a ferroelectric SmC* phase was also observed. Introduction of lateral substituents in the 3-position of the 4-hydroxybenzoic acids (methoxy, fluoro, chloro, and bromo) led to a reduction of the polymorphism and only the SmA phase remained.

1. Introduction

Ferro- and antiferro-electric mesogens usually contain a convenient aromatic core structure [1–3]. The geometry, polarizability, molecular conformation, length-to-breadth ratio, and so on, of the core substantially affect the mesomorphic behaviour of the liquid crystalline materials. Liquid crystals containing a 2,5-disubstituted thiophene unit in the core due to their bent structure have lower symmetry, which generally leads to a lowering of transition temperatures and clearing points and the preferential formation of nematic phases [4]. Nonetheless several examples of thiophene-based ferro- and antiferro-electric liquid crystals are known [5–9]. However, thiophene-containing liquid crystals often show lower viscosities, higher birefrigence and faster switching times than their related benzene analogues [10, 11].

The introduction of fused thiophene cores, benzothiophene and thienothiophene, led to the destabilization of mesophases [12, 13]. On the other hand, we found that benzothiophene [14] and the benzofused thienofuran ring [15] can be successfully introduced into the core of liquid crystals, which then exhibited ferroelectric phases in a broad temperature interval. The even higher fused thiophene system of [1]benzothieno[3,2-*b*][1]benzothiophene (**1**), see scheme 1, was introduced recently into the core of liquid crystals [16–18]. Unlike thiophene, substitution of this core in the long axis preserves the linearity of the molecular structure, and the introduction of various achiral chains led to the formation of the SmA phase [18]. The presence of a chiral alkyl chain had a pronounced effect on the mesomorphic behaviour: a rather wide antiferroelectric SmC_A^* phase just below the SmA phase was found [18]. The antiferroelectric behaviour was observed in structures possessing a polar ketone functional group.

The aim of the present paper is to continue the investigation of structures based on this heterocyclic core because these materials are relatively simple but substantially different from common antiferroelectric materials [2]. In order to exploit the pool of available chiral alcohols, the synthesis of new materials is based on the introduction of an ester moiety in the core. For the design of new materials we modified the general structure of ketones exhibiting the SmC_A^* phase by replacing the acyl group for an ester functionality derived of the model 7-decyl[1]benzothieno[3,2-*b*][1]benzothiophene-2-carboxylic acid (**2**), see scheme 1. Here we report the synthesis of a series of [1]benzothieno[3,2-*b*][1]benzothiophene-2-carboxylic acid esters in order to establish the influence of molecular structures on the mesomorphic properties in these compounds.

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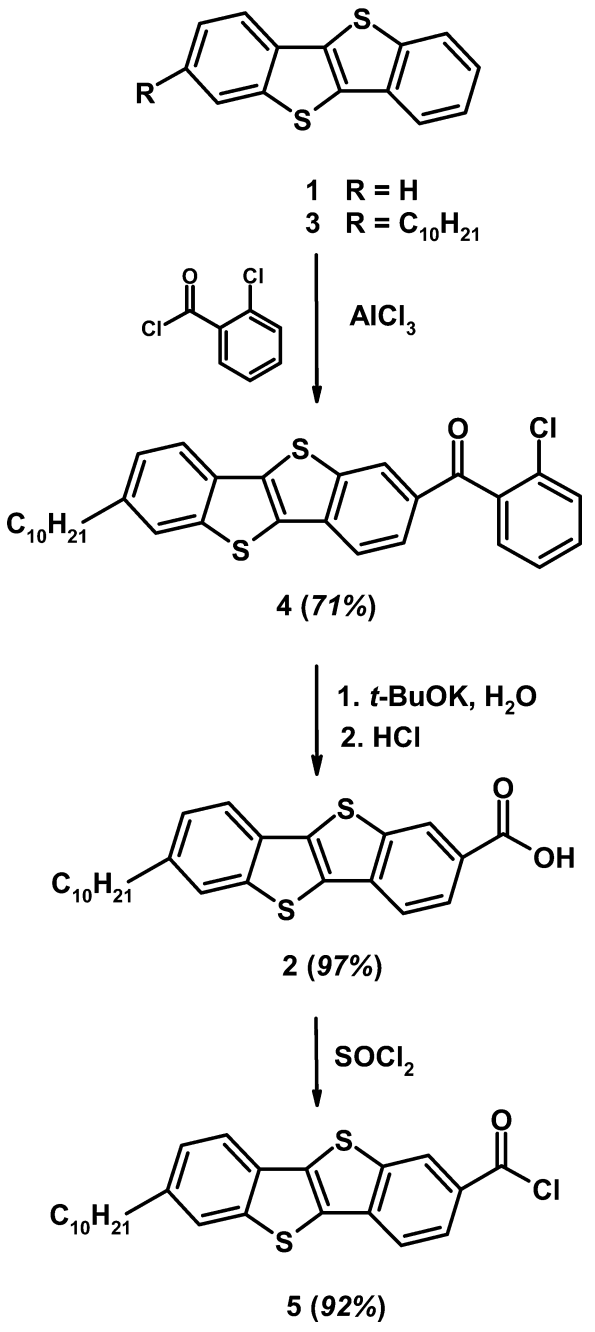


Scheme 1. Preparation of 7-decyl[1]benzothieno[3,2-*b*][1]benzothiophene-2-carbonyl chloride (**5**).

2. Synthesis

We have already reported methods for the selective introduction of an alkyl chain into position 2 of heterocycle **1** and effective methods for selective acylation of such alkyl derivatives [18, 19]. According to these procedures, 2-decyl[1]benzothieno[3,2-*b*][1]benzothiophene (**3**) was obtained in two steps from parent heterocycle **1** in an overall yield of 87%. A wide range of methods for the introduction of the carboxylic group in the aromatic system is known [20] and many of them are based on the Lieben haloform reaction [21] of the corresponding aryl methyl ketones. However, cleavage of (7-decyl[1]benzothieno[3,2-*b*][1]benzothien-2-yl)ethan-1-one (which was easily obtained by acetylation of **3** with acetyl chloride by the method described earlier [19]) with sodium hypobromite proceeded very slowly and acid **2** was isolated in a very low yield. Thus, a different method for the preparation of acid **2** was developed (scheme 1). The key step of the reaction sequence is based on the selective cleavage of non-enolizable aryl (2-chlorophenyl) ketones in a strongly basic medium [22]. The desired intermediate 2-chlorophenyl (7-decyl[1]benzothieno[3,2-*b*][1]benzothiophene-2-yl) ketone (**4**) was synthesized by a selective acylation of **3** with 2-chlorobenzoyl chloride in 71% yield.

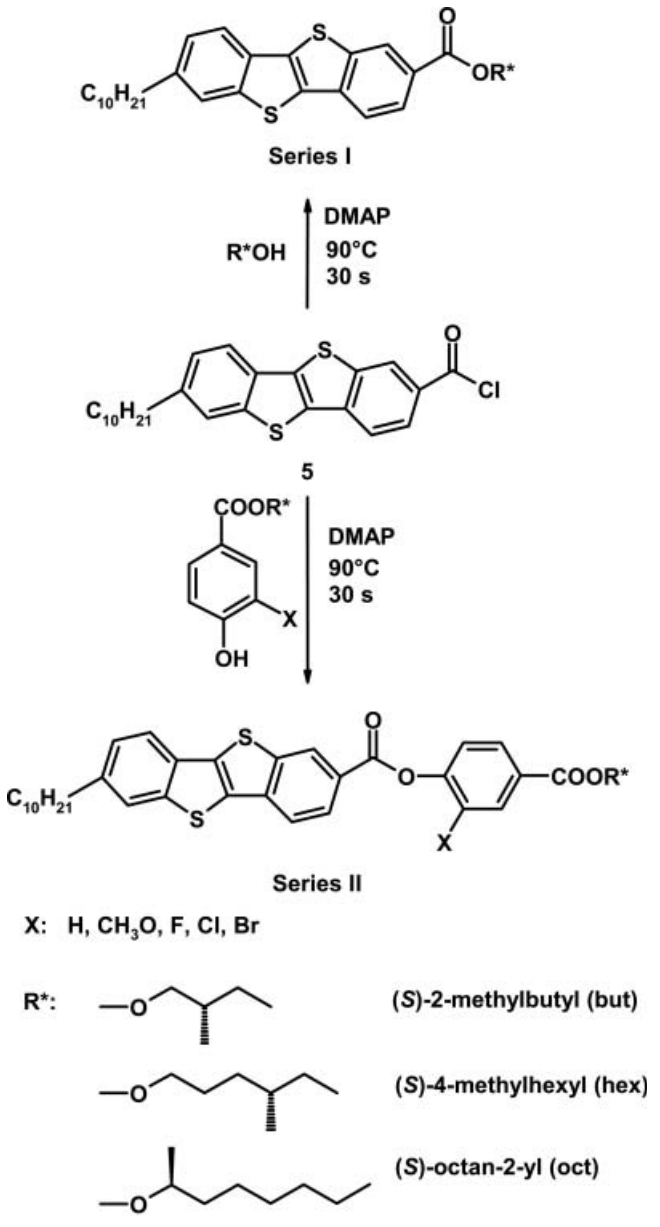
Heating **4** with a mixture of potassium hydroxide and potassium *tert*-butoxide afforded the required acid **2** (yield 97%). Chloride **5**, which served as the key reactive intermediate in the syntheses of various series of mesogenic esters, was obtained by a standard procedure from acid **2** and thionyl chloride. Acylation of (*S*)-2-methylbutan-1-ol (but), (*S*)-4-methylhexan-1-ol (hex), and (*S*)-octan-2-ol (oct) with **5** led to the formation of an aliphatic ester series (series **I**) (scheme 2).

The same acylation procedure was used for preparation of the series **II**, which was obtained from chloride **5** and chiral alkylesters of 4-hydroxybenzoic acid **6**. Intermediate 4-hydroxybenzoates **6** were prepared from the corresponding 4-hydroxybenzoic acids **7** by a reaction sequence that permitted the maximum exploitation of the starting chiral alcohols, *vide supra*. The hydroxy group of 4-hydroxybenzoic acid was first protected with methyl chloroformate to form aryl methyl carbonate **8** (scheme 3). The resulting protected acid was subsequently transformed to the acyl chloride, which acylated the chiral alcohols. Finally, the hydroxy group of the intermediate ester was deprotected with aq. ammonia to afford esters **6**.

4-Hydroxybenzoic acid, 4-hydroxy-3-methoxybenzoic acid and 3-chloro-4-hydroxybenzoic acid were commercial products. 3-Bromo-4-hydroxybenzoic acid was prepared by bromination of 4-hydroxybenzoic acid [23]. 3-Fluoro-4-hydroxybenzoic acid was prepared in a reaction sequence starting with 2-fluoroanisol involving bromination [24], lithiation followed by reaction with CO_2 [25], and deprotection of the hydroxy group [26].

3. Experimental results

The phase transition temperatures and associated enthalpies of all presented compounds were determined



Scheme 2. Preparation of chiral aliphatic (series **I**) and aromatic esters (series **II**) of 7-decyl[1]benzothieno[3,2-*b*][1]benzothiophene-2-carboxylic acid.

Table 1. Transition temperatures, T_{tr} (°C), and corresponding transition enthalpies, ΔH (J g^{-1}), evaluated from DSC on cooling at a rate of 5 K min^{-1} for aliphatic series **I**. M.p. is melting point, symbols • and – denote the existence or non-existence of the phase, respectively.

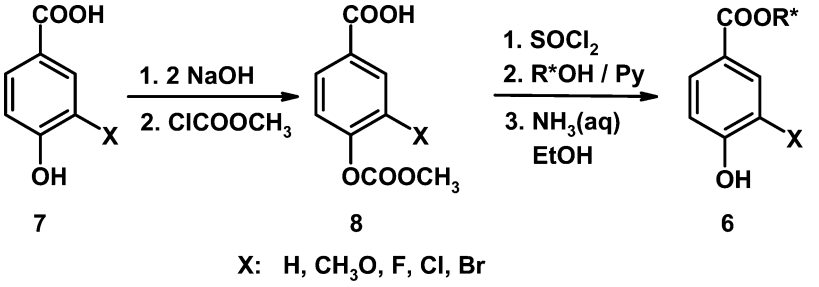
Compound	M.p. ΔH	Cr	T_{tr} ΔH	SmA	T_{tr} ΔH	I
I-but	57+16.9	•	46−13.7	•	128−12.4	•
I-hex	60+39.9	•	47−22.2	•	118−13.5	•
I-oct	84+35.2	•	68−35.2	—		•

from DSC study. The mesophases were identified from the texture observation in polarizing optical microscopy and from analysis of switching behaviour and dielectric properties. The mesophases, transition temperatures and associated enthalpy changes are summarized for aliphatic esters (series **I**) in table 1 and for aromatic esters (series **II**) in table 2.

For **I-but** and **I-hex** in series **I**, only the SmA phase and no SmC_A^* phase was detected while compound **I-oct** exhibits no mesophase. The melting points of all compounds are relatively low when compared with the previously reported ketones [18]. In contrast to these ketones, substitution of the chiral alkyl chain by an achiral chain, and transfer of the chirality to the ester moiety, led to the loss of the antiferroelectric phase.

In series **II**, in order to promote mesogenic behaviour, we extended the rigid molecular structure by the introduction of the 4-hydroxybenzoic acid unit, which is often found in antiferroelectric materials (e.g. MHPOBC [27]). The mesomorphic properties of compounds **II** are summarized in table 2.

All unsubstituted compounds **II-H** in series **II** exhibit a rather wide antiferroelectric SmC_A^* phase, together with the SmA phase. The compound **II-H-oct** also shows the ferroelectric SmC* phase. Introduction of lateral substituents (methoxy group denoted **M**, fluorine **F**, chlorine **Cl**, and bromine **Br**) into position 3 of the 4-hydroxybenzoic acid led to a remarkable lowering of the transition temperatures, however the chiral mesophases were lost and only the SmA phase remained.



Scheme 3. Preparation of chiral 3-substituted 4-hydroxybenzoates.

Table 2. Transition temperatures, T_{tr} (°C), and corresponding transition enthalpies, ΔH (J g^{-1}), evaluated from DSC on cooling at a rate of 5 K min^{-1} for the aromatic series **II**. M.p. is melting point, symbols • and – denote the existence or non-existence of the phase, respectively.

Compound	M.p. ΔH	Cr	T_{tr} ΔH	SmX	T_{tr} ΔH	SmC_A*	T_{tr} ΔH	SmC*	T_{tr} ΔH	SmA	T_{tr} ΔH	I
II-H-but	115+38.2	•	97−16.4	—		•	186−0.7			•	261−12.2	•
II-H-hex	121+40.5	•	94−12.4	—		•	196−0.6			•	248−18.0	•
II-H-oct	125+45.0	•	87−35.5			•	123−0.52	•	157−0.80	•	213−10.5	•
II-M-but	93+62.2	•	33−14.6			—				•	165−8.5	•
II-M-hex	39+12.6	•	30−10.7			—				•	148−7.3	•
II-M-oct	71+31.1	•	39−29.0			—				•	120−7.1	•
II-F-but	106+22.7	•	71−32.4			—				•	230−16.5	•
II-F-hex	121+29.0	•	86−15.1	•	96−10.6	—				•	218−31.4	•
II-F-oct	122+52.6	•	82−48.5			—				•	186−9.7	•
II-Cl-but	94+11.5	•	31−7.3			—				•	204−10.2	•
II-Cl-hex	102+39.5	•	79−45.8			—				•	190−11.8	•
II-Cl-oct	96+29.2	•	25−35.5			—				•	161−9.0	•
II-Br-but	100+22.7	•	35−28.7			—				•	196−33.8	•
II-Br-hex	88+11.8	•	35−26.4			—				•	182−8.1	•
II-Br-oct	74+51.6	•	29−15.6			—				•	150−11.5	•

The influence of the substituent on the transition temperatures is shown in figure 1 for materials from series **II**. The temperature ranges of mesophases measured on cooling are compared in a bar chart. The strongest influence on the transition temperatures was found for compounds bearing the methoxy group. For halogen substituents, a monotonous decrease of clearing points with halogen size was found for all the chiral alkyl chains used. In compound **II-H-oct** the SmC_A^* phase is monotropic, but not for **II-H-but** and **II-H-hex**.

The DSC plots are shown in figures 2 (*a*) and 2 (*b*) for compounds **II-H-but** and **II-H-oct**, respectively; the SmA–SmC_A^* phase transition, 2 (a), and the SmA–SmC* and SmC*–SmC_A^* phase transitions 2 (*b*) are shown in enlarged scales.

In the ferro- and antiferro-electric phases, the spontaneous quantities, dielectric and switching properties were studied. The temperature dependences of spontaneous polarization, $\mathbf{P}_S$, and spontaneous tilt angle, θ_S, are shown in figures 3 (*a*) and 3 (*b*), for compound **II-H-but** and **II-H-oct**, respectively. Values

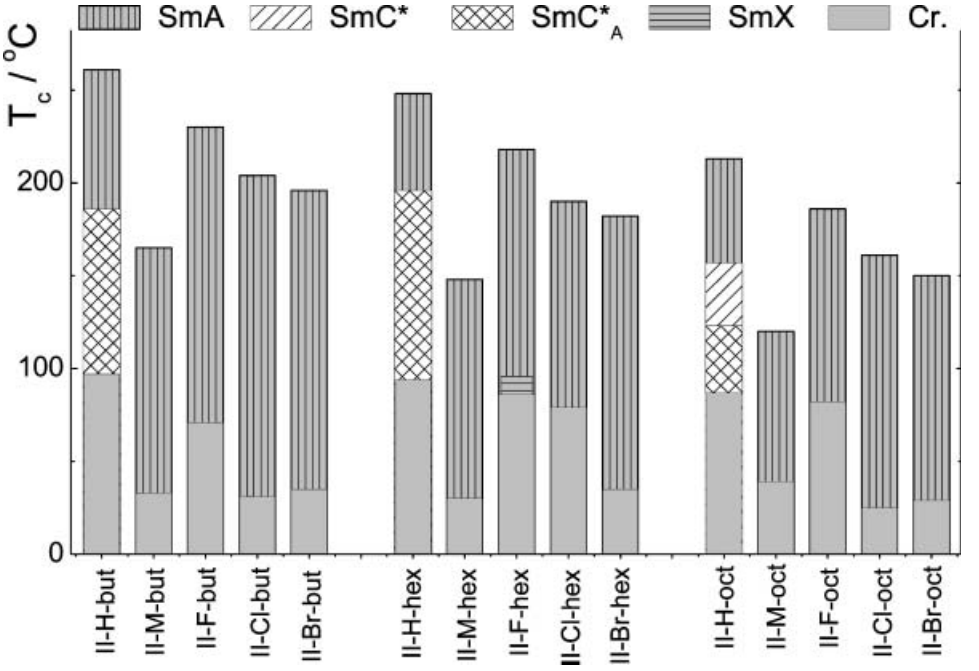


Figure 1. Dependence of transition temperatures on the lateral substitution for compounds of series **II** measured on cooling.

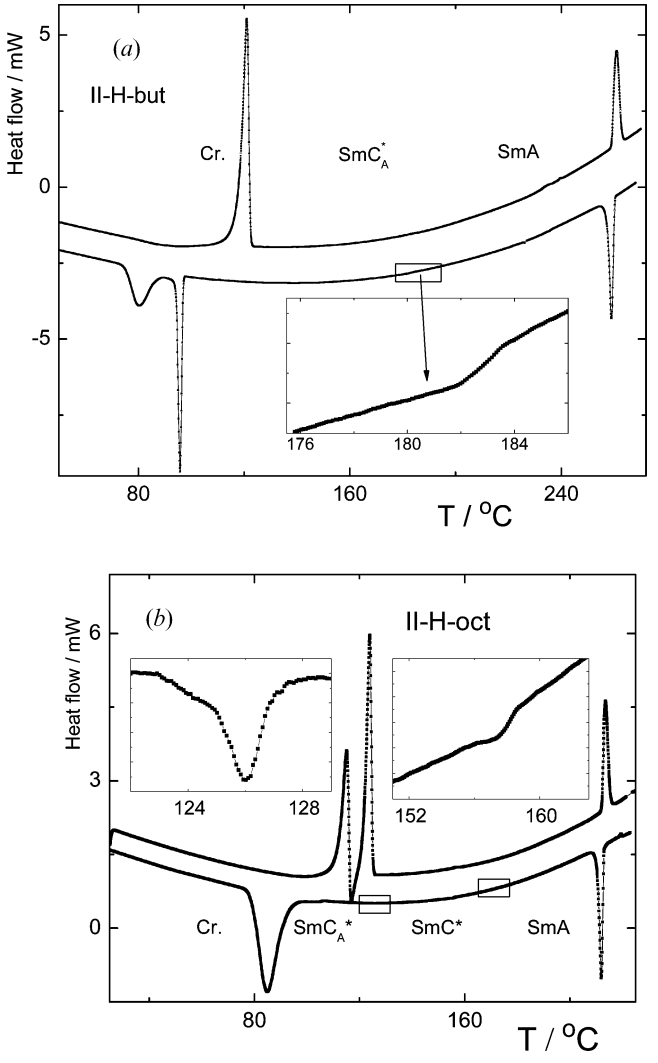


Figure 2. DSC thermograms for (*a*) **II-H-but** and (*b*) **II-H-oct**. Upper curves correspond to the second heating and lower to the second cooling run. In the insets the phase transitions SmA–SmC* and SmC*–SmC_A^* are shown in an enlarged scale.

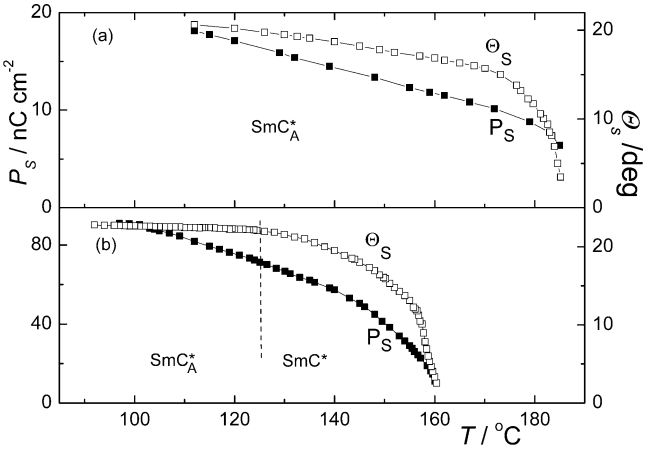


Figure 3. Temperature dependences of spontaneous polarization, $\mathbf{P}_S$, and spontaneous tilt angle, θ_S, for compound (*a*) **II-H-but** and (*b*) **II-H-oct**.

of $\mathbf{P}_s$ as well as θ_s increase continuously from zero as the temperature decreases from the SmA–SmC_A^* or the SmA–SmC* phase transitions; figure 3 (*a*) for **II-H-but** and 3 (*b*) for **II-H-oct**. This behaviour is a typical manifestation of a second order phase transition. The values of spontaneous polarization do not saturate at the low limit of the SmC_A^* phase for any of the compounds studied. For compound **II-H-oct** values of $\mathbf{P}_s$ reach 80 nC cm^{-2}. In this compound at the SmC*–SmC_A^* phase transition no anomaly in $\mathbf{P}_S(T)$, and $\theta_S(T)$ occurs, see figure 3 (*b*). In compounds exhibiting the SmA–SmC_A^* phase transition (**II-H-but** and **II-H-oct**), spontaneous polarization has only small values up to 20 nC cm^{-2}. For all three unsubstituted compounds **II-H**, values of the spontaneous tilt angle reach about 20 degrees at saturation. The existence of two peaks at low frequency switching current confirmed the antiferroelectric phase in **II-H-oct** (see figure 4). Only one peak was detected down to a frequency of 3 Hz in another two unsubstituted materials (**II-H-hex** and **II-H-but**) exhibiting the SmC_A^* phase.

The helical pitch of **II-H-oct** shows almost no dependence on the temperature except for the step change at the SmC_A^*–SmC* phase transition (figure 5). In the antiferroelectric SmC_A^* phase of **II-H-hex** and **II-H-but**, dechiralization lines are not seen but the samples become coloured at the SmA–SmC_A^* phase transition and the colours slightly change on cooling.

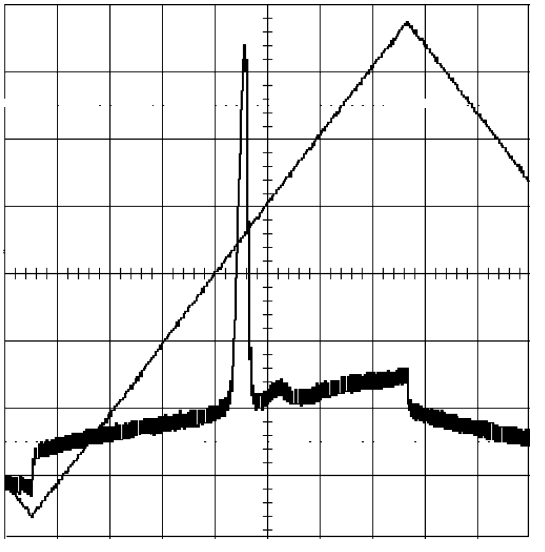


Figure 4. The switching current taken at 5 Hz, 120 V, and a temperature of $T = 115$°C for **II-H-oct**.

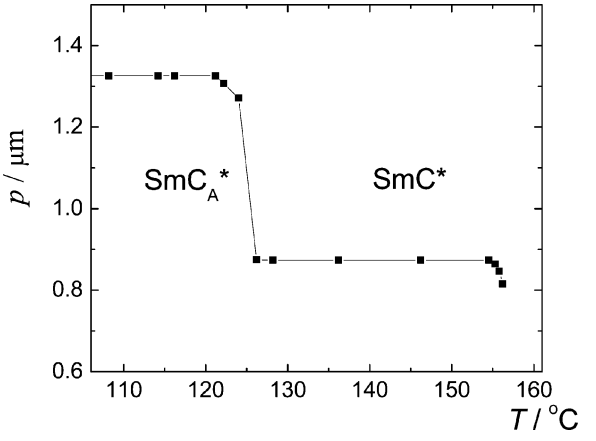


Figure 5. Temperature dependence of the helicoidal pitch length p for **II-H-oct**.

This indicates that the helix pitch length is short and comparable to the wavelength of the reflected light.

Dielectric spectroscopy data reveal a soft mode in the low temperature region of the SmA phase, above the phase transition temperature to the ferro- or antiferroelectric phase for all three non-substituted compound **II-H**. In the antiferroelectric SmC_A^* phase, a typical high frequency mode was detected for **II-H-but** (see figure 6). The relaxation frequency of this mode is about 50 kHz, decreasing with decreasing temperature, while the dielectric strength is very low. As the mode is very weak there is no possibility of obtaining values of dielectric strength $\Delta\varepsilon$ and relaxation frequency, f_r, over the whole temperature interval. For compound **II-H-hex** no mode was detected in the SmC_A^* phase. For the compound **II-H-oct**, a dielectric mode was found over the wide temperature range of the SmC* and SmC_A^* phases, see the 3-dimensional plot showing the imaginary part of dielectric permittivity in figure 7. The temperature dependences of the fitted values of $\Delta\varepsilon$ and f_r are shown in figure 8. In the $\Delta\varepsilon$ temperature dependence, the typical decrease at the SmC*–SmC_A^* phase transition is found, but the relaxation frequency is unusually low in the SmC_A^* phase.

4. Discussion and conclusions

Two structural types of new [1]benzothieno[3,2-*b*][1]benzothiophene-based esters were synthesized.

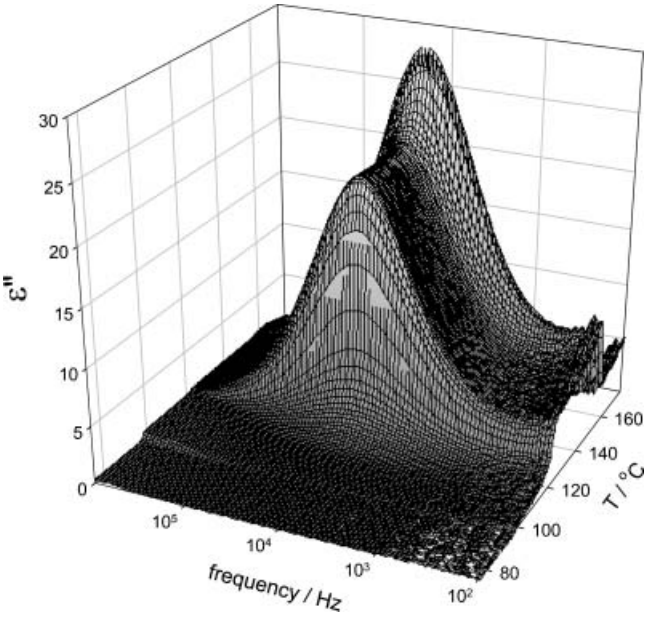


Figure 7. 3D plot of the imaginary part of the dielectric permittivity for **II-H-oct**.

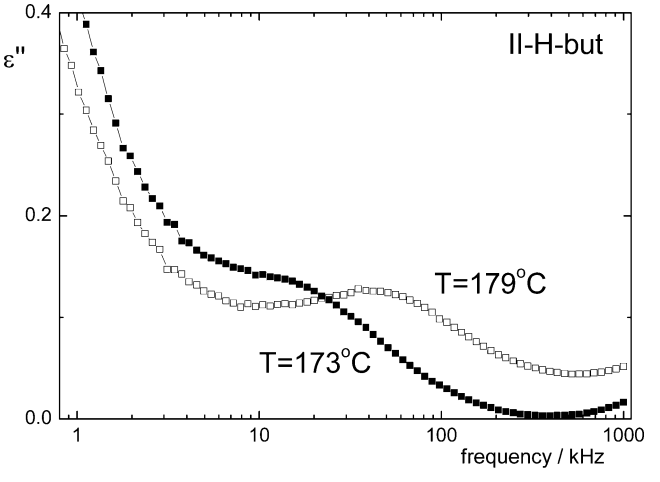


Figure 6. Frequency dependence of the imaginary part of the dielectric permittivity for **II-H-but**. Corresponding temperatures are indicated.

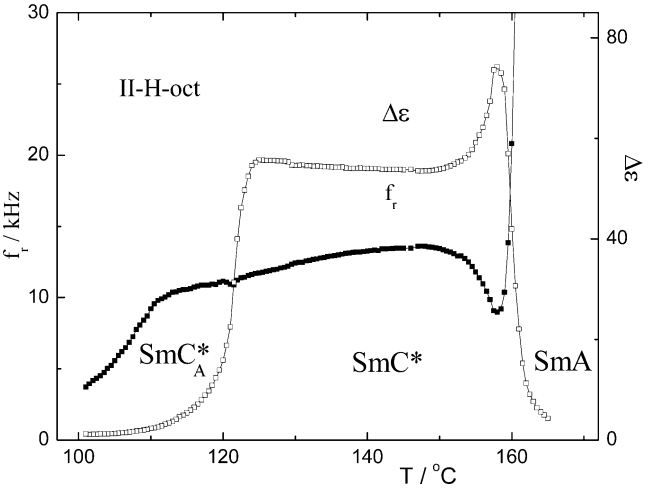


Figure 8. The fitted relaxation frequency f_r and dielectric strength $\Delta\varepsilon$ for compound **II-H-oct**.

In the series of chiral aliphatic esters of 7-decyl[1]-benzothieno[3,2-*b*][1]benzothiophene-2-carboxylic acid (series **I**), significant lowering of the transition temperatures in comparison with the previously reported ketones [18] was found; however only the SmA phase was observed and no SmC_A^* appeared. The elongation of the aromatic system by a 4-hydroxybenzoic acid unit led to a remarkable stabilization of the mesomophic properties. When chiral alkylesters of the unsubstituted 4-hydroxybenzoic acid were used, chiral SmC_A^* and SmC* phases were found, together with the SmA phase. On the other hand, the introduction of a lateral substituent in position 3 of the chiral alkyl esters of 4-hydroxybenzoic acid led to a complete loss of chiral liquid crystalline phases and only SmA phases appeared except for **II-F-hex**, where a low temperature more ordered smectic phase occurs. However, the transition temperatures were significantly lowered. The effect is strongest for the methoxy group. The transition temperatures for compounds containing halogen substituents show a monotonous decrease with the size of the halogen atom, which is obviously related to the decrease of the length-to-breadth ratio in such a way that the tilted phases are no longer stable.

Dielectric spectroscopy revealed the soft mode in the SmA phase just above the SmC* or SmC_A^* phases (see figures 7 and 8). In the SmC* phase the Goldstone mode occurs. In the SmC_A^* phase in **II-H-hex** no mode was found, in **II-H-but** a typical very weak high frequency mode was detected (figure 6), while in **II-H-oct** a weak mode with unusually low relaxation frequency occurs (figure 8). The difference in the relaxation frequency of modes found in the SmC_A^* phase is so large that we may speculate that the modes occurring in **II-H-but** and **II-H-oct** are of a different origin. One of them may arise from the antiphase fluctuations of the director in the adjacent layers (antiphase mode), and the other from in-phase fluctuations, which are dielectrically active due to non-compensated polarization in the adjacent layers because of the helical structure [28].

On cooling $\mathbf{P}_S$ and θ_S grow from zero below the SmA phase, θ_S reaching saturation at low temperatures, while $\mathbf{P}_S$ continues to increase. Neither of these quantities exhibit an anomaly at the SmC*–SmC_A^* phase transition. By contrast, the helix pitch length exhibits a significant jump at the transition to the SmC_A^* phase in **II-H-oct** (see figure 5).

New series of liquid crystalline [1]benzothieno[3,2-*b*][1]benzothiophene derivatives have been synthesized and their mesomorphic properties studied. Formation of the SmA phase appears to be typical mesomorphic behaviour for materials possessing this fused heterocyclic core [16–18], obviously due to their lamello–columnar alignment in the layers [29]. Synthesis and the study of the liquid crystalline behaviour of other [1]benzothieno[3,2-*b*][1]benzothiophenes will be the focus of further research.

5. Experimental

5.1. *Characterization*

Melting points of crystalline intermediates were determined on a Leica VM TG block. Elemental analyses were carried out on a Perkin-Elmer 2400 instrument. IR spectra were recorded on a Nicolet 740 FTIR spectrometer in chloroform or KBr. NMR spectra were measured on a Varian Gemini 300 HC (300 MHz for ^{1}H and 282 MHz for ^{19}F). Deuteriochloroform was used as solvent and the signal from the solvent served as an internal standard.

All synthesized materials were studied using DSC (Perkin–Elmer Pyris Diamond). The samples were prepared in a nitrogen atmosphere and hermetically closed in aluminium pans. The mass of the samples was 5–8 mg; cooling and heating rates of $5\,\mathrm{K\,min^{-1}}$ were applied.

Texture observation, dielectric measurements and measurements of spontaneous values were carried out on planar samples 6 μm thick of area $5 \times 5\,\mathrm{mm^2}$, filled into glass cells in the isotropic phase. The glasses substrates provided with transparent ITO electrodes and polyimide layers unidirectionally rubbed, which ensured the book-shelf (planar) geometry. The temperature was varied and stabilized with accuracy $\pm 0.1^\circ$C in a hot stage (Linkam) placed on the table of the polarising microscope.

The complex permittivity, ε^*, was measured by a Schlumberger 1260 impedance analyser in the frequency range 100 Hz–1 MHz. The frequency dispersions were measured on cooling at a rate of about $0.2\,\mathrm{K\,min^{-1}}$, keeping the temperature of the sample stable during frequency sweeps. Dielectric data were analysed using the Cole–Cole formula for the frequency dependent complex permittivity $\varepsilon^*(f) = \varepsilon' - \mathrm{i}\varepsilon''$:

$$\varepsilon^* - \varepsilon_\infty = \frac{\Delta\varepsilon}{1 + (\mathrm{i}f/f_\mathrm{r})^{(1-\alpha)}} - \mathrm{i}\frac{\sigma}{2\pi\varepsilon_0 f^n} + Af^m \quad (1)$$

where f_r is the relaxation frequency, $\Delta\varepsilon$ is the dielectric strength, α is the distribution parameter of the relaxation, ε_0 is the permittivity of a vacuum, ε_∞ is the high frequency permittivity and n, m, A are parameters of fitting. The second and third terms in the equation are used to eliminate a low frequency contribution from d.c. conductivity σ and a high frequency contribution due to resistance of the ITO electrodes, respectively.

The length of the helix pitch, p, has been established from the diffraction of He-Ne laser light on

dechiralization lines. Thick planar samples of 100 μm were used.

Spontaneous polarisation, $\mathbf{P}_S$, was determined from hysteresis loops detected during switching at a frequency of 60 Hz and an electric field of 40 V μm^{-1}. The frequency is high enough for direct switching between two saturated ferroelectric states to occur, without restoring the antiferroelectric state at zero electric field. In such a case a single hysteresis loop is observed [30]. The profile of the switching current was studied using memory oscilloscope leCroy 9304 with a triangular wave electric field of frequency down to 3 Hz.

Spontaneous tilt angle, θ_S, was determined on unwinding the helicoidal structure by measuring the angular difference between extinction positions of unwound structures in the square wave electric field 10 V μm^{-1}, 0.1 Hz.

5.2. *Synthesis*

5.2.1. *2-Decyl[1]benzothieno[3,2-b][1]benzothiophene (**3**)*

Decyl derivative **3** was prepared in the same way as described earlier [18] for the 2-dodecyl derivative. In the first step, heterocycle **1** (6.0 g, 25.0 mmol) was acylated with decanoyl chloride (18.6 g, 20 ml, 97.5 mmol) under aluminium chloride (14.0 g, 105 mmol) catalysis and 1-([1]benzothieno[3,2-*b*][1]benzothiophen-2-yl)decan-1-one was obtained (8.88 g, 90%), m.p. 174.0–176.2°C. ^{1}H NMR: 8.53 d, 1 H, $J(1,3)=1.4$ (H-1); 8.04 dd, 1 H, $J(1,3)=1.4$, $J(3,4)=8.3$ (3); 7.92 m, 3 H (H-4,H-6,H-9); 7.46 m, 2 H (H-7,H-8); 3.07 t, 2 H, $J=7.3$ (CH_2); 1.8 m, 2 H (CH_2); 1.48–1.23 m, 12 H ((CH_2)$_6$); 0.89 t, 3 H, $J=6.7$ (CH_3). Its reduction (8.8 g, 22.3 mmol) with hydrazine in the presence of sodium hydroxide [2] afforded 8.22 g (97%) of **3**, m.p. 112°C. ^{1}H NMR: 7.91 d, 1 H, $J(6,7)=7.7$ (H-6); 7.84 dd, 1 H, $J(7,9)=1.7$, $J(8,9)=7.7$ (H-9); 7.79 d, 1 H, $J(3,4)=8.2$ (H-4); 7.72 s, 1 H (H-1); 7.46 ddd, 1 H, $J(7,9)=1.7$, $J(6,7)=7.7$, $J(7,8)=8.2$ (H-7); 7.39 ddd, 1 H, $J(6,8)=1.7$, $J(8,9)=7.7$, $J(7,8)=8.2$ (H-8); 7.29 dd, 1 H, $J(1,3)=1.7$, $J(3,4)=8.2$ (H-3); 2.76 t, 2 H, $J=7.7$ (CH_2); 1.67 m, 2 H (CH_2); 1.42–1.22 m, 14 H ((CH_2)$_7$); 0.88 t, 3 H, $J=6.6$ (CH_3).

5.2.2. *2-Chlorophenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-yl ketone (**4**)*

To a solution of **3** (8.22 g, 21.6 mmol) in dichloromethane (600 ml) cooled to −20°C, aluminium chloride (17 g, 127.5 mmol) was added. After cooling to −78°C, 2-chlorobenzoyl chloride (11.73 g, 8.5 ml, 67.1 mmol) was added and the solution was stirred at −60 to −70°C for 3 h. The mixture was decomposed with water (150 ml); the organic phase was separated and the aqueous phase was extracted with dichloromethane (2 × 100 ml). The combined organic phases were washed with water (2 × 100 ml), a saturated solution of sodium hydrogencarbonate (100 ml) and brine (100 ml); it was dried over K_2CO_3. The crude product after evaporation was crystallized from ethyl acetate to afford 7.99 g (71%) of pure **4**, m.p. 119°C. ^{1}H NMR: 8.33 s, 1 H (H-1); 7.92 m, 2 H (H-3,H-6″); 7.82 d, 1 H, $J(3,4)=8.3$ (H-4); 7.73 s, 1 H (H-6); 7.52–7.38 m, 4 H (H-9,H-3″, H-4″,H-5″); 7.31 d, 1 H, $J(8,9)=8.0$ (H-8); 2.78 t, 2 H, $J=7.7$ (CH_2); 1.71 m, 2 H (CH_2); 1.35 m, 14 H (CH_2); 0.89 t, 3 H, $J=6.9$ (CH_3). IR: 3 031 w (C–H), 2 929 s (C–H), 2 856 m (C–H), 1 665 s (C=O), 1 589 s (C=C), 1 463 m (C=C), 1 291 s, 1 241 s. Anal. for $C_{31}H_{31}ClOS_2$ (519.17): calculated 71.72% C, 6.02% H, 6.83% Cl, 12.35% S; found 71.77% C, 5.96% H, 6.71% Cl, 12.40% S.

5.2.3. *7-Decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylic acid (**2**)*

Water (0.79 ml, 43.89 mmol) was added to a slurry of **4** (7.89 g, 15.20 mmol) and potassium *tert*-butoxide (17.3 g, 154.2 mmol) in diethyl ether (240 ml) and the mixture was vigorously stirred in a nitrogen atmosphere for 20 h. Acidification with 5% aq. hydrochloric acid to pH 1 left a precipitate, which was filtered, washed with diethyl ether (2 × 50 ml), methanol (2 × 50 ml) and dichloromethane (50 ml), and dried; 6.26 g (97%) of acid **2** was obtained, m.p. >300°C. Anal. for $C_{25}H_{28}O_2S_2$ (424.63): calculated 70.72% C, 6.65% H, 15.10% S; found 70.57% C, 6.46% H, 15.03% S. Spectral characterization of **2** could not be performed due to its negligible solubility in common solvents.

5.2.4. *7-Decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carbonyl chloride (**5**)*

Thionyl chloride (8.35 g, 5 ml, 70.2 mmol) was added to **2** (6.0 g, 14.13 mmol) in toluene (150 ml) and a catalytic amount of pyridine. The mixture was heated at reflux for 3 h and cooled; the solid was separated by filtration, washed with toluene (2 × 15 ml) and dried under reduced pressure to afford 5.75 g (92%) of chloride **5**. Cr–141–SmA–211–I. ^{1}H NMR: 8.70 d, 1 H, $J(1,3)=1.7$ (H-1); 8.13 dd, 1 H, $J(3,4)=8.5$, $J(1,3)=1.7$ (H-3); 7.90 d, 1 H, $J(3,4)=8.5$ (H-4); 7.84 d, 1 H, $J(8,9)=8.3$ (H-9); 7.74 s, 1 H (H-6); 7.32 d, 1 H, $J(8,9)=8.3$ (H-8); 2.78 t, 2 H, $J=7.7$ (CH_2); 1.71 q, 2 H, $J=7.7$ (CH_2); 1.35 m, 14 H (CH_2); 0.88 t, 3 H, $J=6.3$ (CH_3). IR: 2 954 w (C–H), 2 928 s (C–H), 2 855 m (C–H), 1 747 s (C=O), 1 590 m (C=C), 1 462 m (C=C). Anal. for $C_{25}H_{27}ClOS_2$ (443.07): calculated 67.77% C, 6.14% H, 8.00% Cl, 14.47% S; found 67.87% C, 6.23% H, 7.80% Cl, 14.36% S.

5.2.5. *4-[(Methoxycarbonyl)oxy]benzoic acid (**8H**) and derivatives*

4-Hydroxybenzoic acid (30 g, 0.217 mol) was dissolved in 10% aq. sodium hydroxide (170 ml). THF (150 ml) was added and the mixture was cooled to 0°C; methyl chloroformate (30.5 g, 25 ml, 0.324 mmol) was then added dropwise under stirring. After 15 min at 0°C and 1 h at 20°C, the mixture was acidified with diluted HCl to pH 1 and extracted with diethyl ether (4 × 150 ml). The combined organic phases were washed with brine and dried over $MgSO_4$. The crude product obtained after evaporation of the solvent was recrystallized from a methanol/water mixture (2/1). The product obtained was subsequently dehydrated by azeotropic distillation with toluene. Crystallization from toluene afforded 26.8 g (63%) of **8H**, m.p. 183°C, lit. 177–178°C [31]. The other substituted 4-[(methoxycarbonyl)oxy]benzoic acids were prepared in analogous manner.

3-Methoxy-4-[(methoxycarbonyl)oxy]benzoic acid (**8M**). Yield 64%, m.p. 157°C (toluene), lit. 159°C [32]. ^{1}H NMR (DMSO): 7.61 d, 1 H, *J*(2,6) = 1.7 (H-2); 7.56 dd, 1 H, *J*(5,6) = 8.3, *J*(2,6) = 1.7 (H-6); 7.31 d, 1 H, *J*(5,6) = 8.3 (H-5); 3.84 s, 3 H (OCH_3); 3.82 s, 3 H (OCH_3). IR (KBr): 3 433 m (O–H), 3 017 w (C–H), 2 962 w (C–H), 2 935 w (C–H), 1 768 s (C=O (OCOO)), 1 692 s (C=O (COOH)), 1 606 m (C=C), 1 513 m (C=C), 1 466 m (C=C), 1 442 m (C=C), 1 288 s (C–O), 1 273 s (C–O), 1 257 s (C–O), 1 222 s (C–O). Anal. for $C_{10}H_{10}O_6$ (226.18): calculated 53.10% C, 4.46% H; found 53.16% C, 4.49% H.

3-Fluoro-4-[(methoxycarbonyl)oxy]benzoic acid (**8F**). Yield 74%, m.p. 182.2–185.0°C (toluene). ^{1}H NMR: 7.97–7.90 m, 2 H (H-2,H-6); 7.36 t, 1 H, *J* = 7.9 (H-5); 3.96 s, 3 H (CH_3). IR (KBr): 3 430 w (O–H), 3 081 w (C–H), 2 983 w (C–H), 1 774 s (C=O (OCOO)), 1 704 m (C=O (COOH)), 1 599 w (C=C), 1 450 m (C=C), 1 284 s (C–O), 1 274 s (C–O), 1 202 m (C–F). Anal. for $C_9H_7FO_5$ (214.15): calculated 50.48% C, 3.29% H, 8.87% F; found 50.44% C, 3.37% H, 8.90% F.

3-Chloro-4-[(methoxycarbonyl)oxy]benzoic acid (**8Cl**). Yield 65%, m.p. 228°C (toluene). ^{1}H NMR (DMSO): 8.04 d, 1 H, *J*(2,6) = 1.9 (H-2); 7.95 dd, 1 H, *J*(2,6) = 1.9, *J*(5,6) = 8.4 (H-6); 7.58 d, 1 H, *J*(5,6) = 8.4 (H-5); 3.88 s, 3 H (CH_3). IR: 3 444 w (OH), 1 767 s (C=O (OCOO)), 1 701 m (C=O (COOH)), 1 443 w (C=C), 1 427 w (C=C), 1 284 s (C–O), 1 254 s (C–O). Anal. for $C_9H_7ClO_5$ (230.60): calculated 46.88% C, 3.06% H, 15.37% Cl; found 46.86% C, 2.97% H, 15.34% Cl.

3-Bromo-4-[(methoxycarbonyl)oxy]benzoic acid (**8Br**). Yield 94%, m.p. 215–220°C, dec. ^{1}H NMR (DMSO): 8.16 d, 1 H, *J*(2,6) = 2 (H-2); 7.97 dd, 1 H, *J*(5,6) = 8.5, *J*(2,6) = 2 (H-6); 7.55 d, 1 H, *J*(5,6) = 8.5 (H-1); 3.87 s, 3 H (CH_3). IR (KBr): 3 434 w (OH), 1 767 s (C=O (OCOO)), 1 699 m (C=O (COOH)), 1 443 m (C=C), 1 425 w (C=C), 1 299 m (C–O), 1 280 s (C–O), 1 253 s (C–O), 1 242 s (C–O). Anal. for $C_9H_7BrO_5$ (275.06): calculated 39.30% C, 2.57% H, 29.05% Br; found 39.24% C, 2.56% H, 29.21% Br.

5.2.6. *General procedure for the preparation of chiral alkyl 4-hydroxybenzoates **6***

To a slurry of protected acid **8** (0.7 mmol) in dry dichloromethane (3 ml), oxalyl chloride (0.52 g, 0.35 ml, 4.07 mmol) was added and the mixture heated at reflux for 4 h. The solvent was evaporated under reduced pressure, toluene (5 ml) was added and the remaining oxalyl chloride removed under reduced pressure together with the solvent. The crude chloride was dissolved in dichloromethane (3 ml), the corresponding chiral alcohol (0.65 mmol) and pyridine (59 mg, 0.06 ml, 0.74 mmol) were added and the mixture was stirred for 2.5 h. The reaction mixture was decomposed with water (0.2 ml) and stirring was continued for 4 h. The solvent was evaporated under reduced pressure, ethanol (3 ml) and ammonia (0.5 ml of 25% aq. solution) were added and the solution was stirred for 1 h, then acidified with 5% aq. HCl to pH 2–3 and extracted with dichloromethane (3 × 10 ml). The dichloromethane solutions were washed with 5% aq. sodium hydroxide (3 × 10 ml), the combined aqueous phase was acidified with 5% aq. HCl to pH 2–3 and extracted with dichloromethane (3 × 10 ml). The combined organic layers were washed with water and brine, and dried over $MgSO_4$. After evaporation of the solvent, pure product **6** was obtained in around 75% yield. For some compounds, column chromatography on silica gel with hexane/ethyl acetate mixture as eluant was used to conclude the product purification.

(S)-(2-Methylbutyl 4-hydroxybenzoate (**6H-but**). ^{1}H NMR: 7.96 d, 2 H, *J*(2,3) = 8.8 (H-2); 6.90 d, 2 H, *J*(2,3) = 8.8 (H-3); 5.29 s, 1 H (OH); 4.19 m, 1 H (OCH(H)); 4.11 m, 1 H (OC(H)H); 1.85 m, 1 H (C*–H); 1.52 m, 1 H (C*–CH(H)); 1.27 m, 1 H (C*–C(H)H); 1.00 d, 3 H (C*–CH_3); 0.95 t, 3 H (CH_3). Anal. for $C_{12}H_{16}O_3$ (208.26): calculated 69.21% C, 7.74% H; found 69.18% C, 7.79% H.

(S)-(4-Methylhexyl) 4-hydroxybenzoate (**6H-hex**). ^{1}H NMR: 7.96 d, 2 H, *J*(2,3) = 6.9 (H-2); 6.88 d, 2 H, *J*(2,3) = 6.9 (H-3); 5.77 s, 1 H (OH); 4.28 t, 2 H (OCH_2); 1.74 m, 2 H (CH_2); 1.48–1.30 m, 3 H (CH_2 + CH); 1.30–1.10 m, 2 H (CH_2); 0.90–0.85 m, 6 H (2 × CH_3). Anal. for $C_{14}H_{20}O_3$ (236.31): calculated 71.16% C, 8.53% H; found 71.11% C, 8.58% H.

(S)-(Octan-2-yl) 4-hydroxybenzoate (**6H-oct**). ^{1}H NMR: 7.95 d, 2 H, *J*(2,3) = 8.8 (H-2); 6.86 d, 2 H, *J*(2,3) = 8.8 (H-3); 5.82 s, 1 H (OH); 5.12 m, 1 H

(OC*H); 1.70 m, 1 H (C*–C(H)H); 1.59 m, 1 H (C*–CH(H)); 1.40–1.20 m, 8 H ($(CH_2)_4$); 1.32 d, 3 H (C*–CH_3); 0.87 t, 3 H (CH_3). Anal. for $C_{15}H_{22}O_3$ (250.34): calculated 71.97% C, 8.86% H; found 71.99% C, 8.91% H.

(S)-(2-Methylbutyl) 4-hydroxy-3-methoxybenzoate (**6M-but**). ^{1}H NMR: 7.64 dd, 1 H, $J(2,6) = 1.9$, $J(5,6) = 8.3$ (H-6); 7.56 d, 1 H, $J(2,6) = 1.9$ (H-2); 6.90 d, 1 H, $J(5,6) = 8.3$ (H-5); 6.02 s, 1 H (OH); 4.18 m, 1 H (OCH(H)); 4.09 m, 1 H (OC(H)H); 3.95 s, 3 H (OCH_3); 1.85 m, 1 H (C*–H); 1.52 m, 1 H (C*–CH(H)); 1.27 m, 1 H (C*–C(H)H); 1.00 d, 3 H (C*–CH_3); 0.95 t, 3 H (CH_3). Anal. for $C_{13}H_{18}O_4$ (238.28): calculated 65.53% C, 7.61% H; found 65.45% C, 7.59% H.

(S)-(4-Methylhexyl) 4-hydroxy-3-methoxybenzoate (**6M-hex**). ^{1}H NMR: 7.64 dd, 1 H, $J(2,6) = 1.8$, $J(5,6) = 8.3$ (H-6); 7.56 d, 1 H, $J(2,6) = 1.8$ (H-2); 6.90 d, 1 H, $J(5,6) = 8.3$ (H-5); 5.96 s, 1 H (OH); 4.27 t, 2 H (OCH_2); 3.94 s, 3 H (OCH_3); 1.74 m, 2 H (CH_2); 1.48–1.30 m, 3 H ($CH_2 + CH$); 1.30–1.10 m, 2 H (CH_2); 0.90–0.85 m, 6 H ($2 \times CH_3$). Anal. for $C_{15}H_{22}O_4$ (266.34): calculated 67.65% C, 8.33% H; found 67.58% C, 8.29% H.

(S)-(Octan-2-yl) 4-hydroxy-3-methoxybenzoate (**6M-oct**). ^{1}H NMR: 7.63 dd, 1 H, $J(2,6) = 1.9$, $J(5,6) = 8.3$ (H-6); 7.56 d, 1 H, $J(2,6) = 1.9$ (H-2); 6.93 d, 1 H, $J(5,6) = 8.3$ (H-5); 5.98 s, 1 H (OH); 5.12 m, 1 H (OC*H); 3.95 s, 3 H (OCH_3); 1.70 m, 1 H (C*–C(H)H); 1.59 m, 1 H (C*–CH(H)); 1.40–1.20 m, 8 H ($(CH_2)_4$); 1.32 d, 3 H (C*–CH_3); 0.87 t, 3 H (CH_3). Anal. for $C_{16}H_{24}O_4$ (280.36): calculated 68.55% C, 8.63% H; found 68.65% C, 8.58% H.

(S)-(2-Methylbutyl) 3-fluoro-4-hydroxybenzoate (**6F-but**). ^{1}H NMR: 7.76 m, 2 H (H-2,H-6); 7.04 m, 1 H (H-5); 6.16 s, 1 H (OH); 4.10 m, 1 H (OC(H)H); 4.18 m, 1 H (OCH(H)); 1.84 m, 1 H (C*–H); 1.51 m, 1 H (C*–CH(H)); 1.28 m, 1 H (C*–C(H)H); 1.00 d, 3 H (C*–CH_3); 0.95 t, 3 H (CH_3). ^{19}F NMR: −140.31 m. Anal. for $C_{12}H_{15}FO_3$ (226.25): calculated 63.71% C, 6.68% H; found 63.68% C, 6.60% H.

(S)-(4-methylhexyl) 3-fluoro-4-hydroxybenzoate (**6F-hex**). ^{1}H NMR: 7.76 m, 2 H (H-2,H6); 7.03 m, 1 H (H-5); 5.73 s, 1 H (OH); 4.27 t, 2 H (OCH_2); 1.74 m, 2 H (CH_2); 1.48–1.30 m, 3 H ($CH_2 + CH$); 1.30–1.10 m, 2 H (CH_2); 0.90–0.85 m, 6 H ($2 \times CH_3$). ^{19}F NMR: −140.45 m. Anal. for $C_{14}H_{19}FO_3$ (254.30): calculated 66.12% C, 7.53% H; found 66.02% C, 7.58% H.

(S)-(Octan-2-yl) 3-fluoro-4-hydroxybenzoate (**6F-oct**). ^{1}H NMR: 7.76 m, 2 H (H-2,H-6); 7.04 m, 1 H (H-5); 5.96 s, 1 H (OH); 5.11 m, 1 H (OC*H); 1.70 m, 1 H (C*–C(H)H); 1.59 m, 1 H (C*–CH(H)); 1.40–1.20 m, 8 H ($(CH_2)_4$); 1.32 d, 3 H (C*–CH_3); 0.87 t, 3 H (CH_3). ^{19}F NMR: −140.64 m. Anal. for $C_{15}H_{21}FO_3$ (268.33): calculated 67.14% C, 7.89% H; found 67.19% C, 7.93% H.

(S)-(2-Methylbutyl) 3-chloro-4-hydroxybenzoate (**6Cl-but**). ^{1}H NMR: 8.03 d, 1 H, $J(2,6) = 1.2$ (H-2); 7.89 dd, 1 H, $J(2,6) = 1.2$, $J(5,6) = 8.5$ (H-6); 7.06 d, 1 H, $J(5,6) = 8.5$ (H-5); 5.98 s, 1 H (OH); 4.18 m, 1 H (OCH(H)); 4.10 m, 1 H (OC(H)H); 1.85 m, 1 H (C*–H); 1.52 m, 1 H (C*–CH(H)); 1.28 m, 1 H (C*–C(H)H); 1.00 d, 3 H (C*–CH_3); 0.95 t, 3 H (CH_3). Anal. for $C_{12}H_{15}ClO_3$ (242.70): calculated 59.39% C, 6.23% H, 14.61% Cl; found 59.36% C, 6.26% H, 14.63% Cl.

(S)-(4-Methylhexyl) 3-chloro-4-hydroxybenzoate (**6Cl-hex**). ^{1}H NMR: 8.04 d, 1 H, $J(2,6) = 1.9$ (H-2); 7.89 dd, 1 H, $J(2,6) = 1.9$, $J(5,6) = 8.5$ (H-6); 7.05 d, 1 H, $J(5,6) = 8.5$ (H-5); 5.94 s, 1 H (OH); 4.27 t, 2 H (OCH_2); 1.74 m, 2 H (CH_2); 1.48–1.30 m, 3 H ($CH_2 + CH$); 1.30–1.10 m, 2 H (CH_2); 0.90–0.85 m, 6 H ($2 \times CH_3$). Anal. for $C_{14}H_{19}ClO_3$ (270.76): calculated 62.11% C, 7.07% H, 13.09% Cl; found 62.02% C, 6.99% H, 13.02% Cl.

(S)-(Octan-2-yl) 3-chloro-4-hydroxybenzoate (**6Cl-oct**). ^{1}H NMR: 8.02 d, 1 H, $J(2,6) = 1.9$ (H-2); 7.88 dd, 1 H, $J(2,6) = 1.9$, $J(5,6) = 8.5$ (H-6); 7.05 d, 1 H, $J(5,6) = 8.5$ (H-5); 5.97 s, 1 H (OH); 5.11 m, 1 H (OC*H); 1.70 m, 1 H (C*–C(H)H); 1.59 m, 1 H (C*–CH(H)); 1.40–1.20 m, 8 H ($(CH_2)_4$); 1.32 d, 3 H (C*–CH_3); 0.87 t, 3 H (CH_3). Anal. for $C_{15}H_{21}ClO_3$ (284.78): calculated 63.26% C, 7.43% H, 12.45% Cl; found 63.32% C, 7.44% H, 12.46% Cl.

(S)-(2-Methylbutyl) 3-bromo-4-hydroxybenzoate (**6Br-but**). ^{1}H NMR: 8.17 d, 1 H, $J(2,6) = 1.9$ (H-2); 7.92 dd, 1 H, $J(2,6) = 1.9$, $J(5,6) = 8.5$ (H-6); 7.05 d, 1 H, $J(5,6) = 8.5$ (H-5); 5.92 s, 1 H (OH); 4.18 m, 1 H (OCH(H)); 4.10 m, 1 H (OC(H)H); 1.85 m, 1 H (C*–H); 1.52 m, 1 H (C*–CH(H)); 1.28 m, 1 H (C*–C(H)H); 1.00 d, 3 H (C*–CH_3); 0.95 t, 3 H (CH_3). Anal. for $C_{12}H_{15}BrO_3$ (287.16): calculated 50.19% C, 5.27% H, 27.83% Br; found 50.13% C, 5.19% H, 27.64% Br.

(S)-(4-Methylhexyl) 3-bromo-4-hydroxybenzoate (**6Br-hex**). ^{1}H NMR: 8.18 d, 1 H, $J(2,6) = 1.9$ (H-2); 7.91 dd, 1 H, $J(2,6) = 1.9$, $J(5,6) = 8.5$ (H-6); 7.05 d, 1 H, $J(5,6) = 8.5$ (H-5); 5.99 s, 1 H (OH); 4.27 t, 2 H (OCH_2); 1.74 m, 2 H (CH_2); 1.48–1.30 m, 3 H ($CH_2 + CH$); 1.30–1.10 m, 2 H (CH_2); 0.90–0.85 m, 6 H ($2 \times CH_3$). Anal. for $C_{14}H_{19}BrO_3$ (315.21): calculated 53.35% C, 6.08% H, 25.35% Br; found 53.46% C, 6.13% H, 25.18% Br.

(S)-(Octan-2-yl) 3-bromo-4-hydroxybenzoate (**6Br-oct**). ^{1}H NMR: 8.17 d, 1 H, $J(2,6) = 1.9$ (H-2); 7.92 dd, 1 H, $J(2,6) = 1.9$, $J(5,6) = 8.5$ (H-6); 7.04 d, 1 H, $J(5,6) = 8.5$ (H-5); 5.93 s, 1 H (OH); 5.11 m, 1 H (OC*H); 1.70 m, 1 H (C*–C(H)H); 1.59 m, 1 H

(C*–CH(H)); 1.40–1.20 m, 8 H ($(CH_2)_4$); 1.32 d, 3 H (C*–CH_3); 0.87 t, 3 H (CH_3). Anal. for $C_{15}H_{21}BrO_3$ (329.24): calculated 54.72% C, 6.43% H, 24.27% Br; found 54.69% C, 6.52% H, 24.22% Br.

5.2.7. *General procedure for the preparation of 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylic acid esters, series **I** and **II***

Chiral alcohol (1 mmol) was dissolved in dry toluene (20 ml) and heated under a nitrogen atmosphere. After distilling off approx. 5 ml of toluene, the heating bath was removed and to the hot solution, chloride **5** (0.9 mmol) was added followed by DMAP (1.2 mmol). The mixture was stirred for approx. 30 s and the reaction was quenched by addition of 5% aq. hydrochloric acid (10 ml). After cooling, the layers were separated, and the aqueous layer was washed with dichloromethane (2 × 15 ml); the combined organic solution was washed with 5% aq. hydrochloric acid (10 ml) and brine (10 ml), and then dried over $MgSO_4$. After evaporation of the solvent the crude product was twice purified by column chromatography (silica gel, elution with dichloromethane hexane toluene (2/2/1) mixture) and crystallized from an ethanol/ethyl acetate mixture. The yield was about 70%.

(S)-(2-Methylbutyl) 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**I-but**). ^{1}H NMR: 8.60 s, 1 H (H-1); 8.11 d, 1 H, J(3,4) = 8.3 (H-3); 7.87 d, 1 H, J(3,4) = 8.3 (H-4); 7.81 d, 1 H, J(8,9) = 8.3 (H-9); 7.72 s, 1 H (H-6); 7.29 d, 1 H, J(8,9) = 8.3 (H-8); 4.28 m, 1 H (OCH(H)); 4.19 m, 1 H (OC(H)H); 2.77 t, 2 H, J = 7.7 (CH_2); 1.86 m, 1 H (C*–H); 1.7 m, 2 H (CH_2); 1.59 m, 1 H (C*–CH(H)); 1.40–1.20 m, 15 H ($(CH_2)_7$ + C*–C(H)H); 1.07 d, 3 H, J = 6.6 (C*–CH_3); 1.00 t, 3 H, J = 7.6 (CH_3); 0.89 t, 3 H, J = 6.2 (CH_3). IR: 2 963 m (C–H), 2 929 s (C–H), 2 857 m (C–H), 1 709 s (C = O), 1 596 m (C = C), 1 466 m (C = C), 1 279 s (C–O), 1 238 s (C–O). Anal. for $C_{30}H_{38}O_2S_2$ (494.76): calculated 72.83% C, 7.74% H, 12.96% S; found 72.75% C, 7.72% H, 13.04% S.

(S)-(4-Methylhexyl) 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**I-hex**). ^{1}H NMR: 8.61 d, 1 H, J(1,3) = 1.4 (H-1); 8.11 dd, 1 H, J(3,4) = 8.3, J(1,3) = 1.4 (H-3); 7.84 d, 1 H, J(3,4) = 8.3 (H-4); 7.82 d, 1 H, J(8,9) = 8.3 (H-9); 7.73 s, 1 H (H-6); 7.30 d, 1 H, J(8,9) = 8.3 (H-8); 4.37 t, 2 H, J = 6.9 (OCH_2); 2.78 t, 2 H, J = 7.7 (CH_2); 1.84 m, 2 H (CH_2); 1.62 m, 2 H (CH_2); 1.50–1.20 m, 19 H; 0.93 d, 3 H, J = 6.1 (C*–CH_3); 0.91 t, 3 H, J = 7.4 (CH_3); 0.89 t, 3 H, J = 6.9 (CH_3). IR: 2 960 m (C–H), 2 929 s (C–H), 2 856 m (C–H), 1 709 s (C = O), 1 596 m (C = C), 1 466 m (C = C), 1 280 s (C–O), 1 239 s (C–O). Anal. for $C_{32}H_{42}O_2S_2$ (522.81): calculated 73.52% C, 8.10% H, 12.27% S; found 73.50% C, 8.01% H, 12.42% S.

(S)-(Octan-2-yl) 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**I-oct**). m.p. 84°C. ^{1}H NMR: 8.61 s, 1 H (H-1); 8.12 d, 1 H, J(3,4) = 8.3 (H-3); 7.88 d, 1 H, J(3,4) = 8.3 (H-4); 7.83 d, 1 H, J(8,9) = 8.3 (H-9); 7.74 s, 1 H (H-6); 7.31 d, 1 H, J(8,9) = 8.3 (H-8); 5.22 m, 1 H (C*–H); 2.77 t, 2 H, J = 7.4 (CH_2); 1.85–1.60 m, 4 H (2 × CH_2); 1.38 d, 3 H, J = 6.3 (C*–CH_3); 1.40–1.15 m, 22 H ($(CH_2)_7$ + $(CH_2)_4$); 0.93–0.83 m, 6 H (2 × CH_3). IR: 3 022 w (C–H), 2 957 m (C–H), 2 930 s (C–H), 2 857 m (C–H), 1 705 s (C = O), 1 597 m (C = C), 1 467 m (C = C), 1 282 s (C–O), 1 241 s. Anal. for $C_{33}H_{44}O_2S_2$ (536.84): calculated 73.83% C, 8.26% H, 11.95% S; found 73.79% C, 8.33% H, 11.89% S.

4-[(S)-(2-Methylbutyl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**II-H-but**). ^{1}H NMR: 8.79 s, 1 H (H-1); 8.26 d, 1 H, J(3,4) = 8.5 (H-3); 8.16 d, 1 H, J(2′,3′) = 8.8 (H-2′); 7.95 d, 1 H, J(3,4) = 8.5 (H-4); 7.85 d, 1 H, J(8,9) = 8.0 (H-9); 7.75 s, 1 H (H-6); 7.36 d, 1 H (H-5′); 7.32 d, 1 H, J(8,9) = 8.0 (H-8); 4.24 m, 1 H (OCH(H)); 4.16 m, 1 H (OC(H)H); 2.78 t, 2 H (CH_2); 1.89 m, 1 H (C*–H); 1.71 m, 2 H (CH_2); 1.55 m, 1 H (C*–CH(H)); 1.27 m, 15 H ($(CH_2)_7$ + C*–C(H)H); 1.03 d, 3 H (C*–CH_3); 0.98 t, 3 H (CH_3); 0.88 t, 3 H (CH_3). IR: 3 041 w (C–H), 2 963 m (C–H), 2 929 m (C–H), 2 857 m (C–H), 1 734 m (C = O), 1 724 m (C = O), 1 596 m (C–C), 1 505 w (C–C), 1 465 w (C–C), 1 272 s (C–O), 1 162 s (C–O). Anal. for $C_{37}H_{42}O_4S_2$ (614.87): calculated 72.28% C, 6.89% H, 10.43% S; found 72.36% C, 6.81% H, 10.35% S.

4-[(S)-(4-Methylhexyl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**II-H-hex**). ^{1}H NMR: 8.80 s, 1 H (H-1); 8.26 d, 1 H, J(3,4) = 8.3 (H-3); 8.14 d, 1 H, J(2′,3′) = 8.8 (H-2′); 7.96 d, 1 H, J(3,4) = 8.3 (H-4); 7.85 d, 1 H, J(8,9) = 8.3 (H-9); 7.76 s, 1 H (H-6); 7.36 d, 1 H (H-5′); 7.31 d, 1 H, J(8,9) = 8.3 (H-8); 4.33 t, 2 H (OCH_2); 2.78 t, 2 H (CH_2); 1.85–1.65 m, 4 H (2 × CH_2); 1.50–1.15 m, 19 H (CH + 2 × CH_2 + $(CH_2)_7$); 0.92–0.85 m, 9 H (3 × CH_3). IR: 3 041 w (C–H), 2 961 m (C–H), 2 929 m (C–H), 2 857 w (C–H), 1 734 m (C = O), 1 724 m (C = O), 1 596 m (C–C), 1 505 w (C–C), 1 465 w (C–C), 1 272 s (C–O), 1 162 s (C–O). Anal. for $C_{39}H_{46}O_4S_2$ (642.92): calculated 72.86% C, 7.21% H, 9.97% S; found 72.87% C, 7.29% H, 10.05% S.

4-[(S)-(Octan-2-yl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-car-boxylate (**II-H-oct**). ^{1}H NMR: 8.80 d, 1 H, J(1,3) = 1.4 (H-1); 8.27 d, 1 H, J(3,4) = 8.5, J(1,3) = 1.4 (H-3); 8.15 d, 1 H, J(2′,3′) = 8.8 (H-2′); 7.97 d, 1 H, J(3,4) = 8.5 (H-4); 7.85 d, 1 H, J(8,9) = 8.3 (H-9); 7.76 s, 1 H (H-6); 7.35 d, 1 H (H-5′); 7.33 d, 1 H, J(8,9) = 8.0 (H-8); 5.18 m, 1 H (CH); 2.78 t, 2 H (CH_2); 1.80–1.60 m, 4 H (2 × CH_2);

1.40–1.20 m, 24 H ($(CH_2)_5+(CH_2)_7$); 1.35 d, 3 H (C*–CH_3); 0.95–0.85 m, 6 H ($2\times CH_3$). IR: 3024 w (C–H), 2930 s (C–H), 2857 m (C–H), 1734 s (C=O), 1712 s (C=O), 1596 m (C–C), 1505 w (C–C), 1466 w (C–C), 1272 s (C–O), 1162 s (C–O). Anal. for $C_{40}H_{48}O_4S_2$ (656.95): calculated 73.13% C, 7.36% H, 9.76% S; found 73.20% C, 7.39% H, 9.75% S.

3-Methoxy-4-[(S)-(2-methylbutyl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**II-M-but**). ^{1}H NMR: 8.81 s, 1 H (H-1); 8.27 d, 1 H, J(3,4) = 8.5 (H-3); 7.96 d, 1 H, J(3,4) = 8.5 (H-4); 7.85 d, 1 H, J(8,9) = 8.0 (H-9); 7.74 d, 1 H (H-6′); 7.73 s, 1 H (H-2′); 7.75 s, 1 H (H-6); 7.32 d, 1 H, J(8,9) = 8.0 (H-8); 7.27 d, 1 H (H-5′); 4.24 m, 1 H (OCH(H)); 4.16 m, 1 H (OC(H)H); 3.90 s, 3 H (OCH_3″); 2.78 t, 2 H (CH_2); 1.89 m, 1 H (C*–H); 1.71 m, 2 H (CH_2); 1.54 m, 1 H (C*–CH(H)); 1.27 m, 15 H ($(CH_2)_7$+C*–C(H)H); 1.03 d, 3 H (C*–CH_3); 0.98 t, 3 H (CH_3); 0.88 t, 3 H (CH_3). IR: 3031 w (C–H), 2963 m (C–H), 2929 m (C–H), 2857 m (C–H), 1738 s (C=O), 1715 s (C=O), 1596 m (C–C), 1507 m (C–C), 1465 m (C–C), 1415 m (C–C), 1288 s (C–O), 1277 s (C–O), 1266 s (C–O), 1174 s (C–O). Anal. for $C_{38}H_{44}O_5S_2$ (644.89): calculated 70.77% C, 6.88% H, 9.94% S; found 70.88% C, 6.89% H, 10.01% S.

3-Methoxy-4-[(S)-(4-methylhexyl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**II-M-hex**). ^{1}H NMR: 8.81 s, 1 H (H-1); 8.28 d, 1 H, J(3,4) = 8.5 (H-3); 7.97 d, 1 H, J(3,4) = 8.5 (H-4); 7.85 d, 1 H, J(8,9) = 8.0 (H-9); 7.74 d, 1 H (H-6′); 7.73 s, 1 H (H-2′); 7.75 s, 1 H (H-6); 7.32 d, 1 H, J(8,9) = 8.0 (H-8); 7.27 d, 1 H (H-5′); 4.33 t, 2 H (OCH_2); 3.90 s, 3 H (OCH_3″); 2.77 t, 2 H (CH_2); 1.85–1.65 m, 4 H ($2\times CH_2$); 1.50–1.15 m, 19 H ($CH+2\times CH_2+(CH_2)_7$); 0.92–0.86 m, 9 H ($3\times CH_3$). IR: 3022 m (C–H), 3018 m (C–H), 2961 m (C–H), 2929 s (C–H), 2857 m (C–H), 1737 m (C=O), 1715 m (C=O), 1597 m (C–C), 1507 m (C–C), 1465 m (C–C), 1415 m (C–C), 1289 s (C–O), 1278 s (C–O), 1266 s (C–O), 1174 s (C–O). Anal. for $C_{40}H_{48}O_5S_2$ (672.95): calculated 71.39% C, 7.19% H, 9.53% S; found 71.53% C, 7.24% H, 9.47% S.

3-Methoxy-4-[(S)-(octan-2-yl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**II-M-oct**). ^{1}H NMR: 8.81 s, 1 H (H-1); 8.28 d, 1 H, J(3,4) = 8.5 (H-3); 7.96 d, 1 H, J(3,4) = 8.5 (H-4); 7.85 d, 1 H, J(8,9) = 8.0 (H-9); 7.74 d, 1 H (H-6′); 7.73 s, 1 H (H-2′); 7.75 s, 1 H (H-6); 7.32 d, 1 H, J(8,9) = 8.0 (H-8); 7.27 d, 1 H (H-5′); 5.18 m, 1 H (CH); 3.90 s, 3 H (OCH_3″); 2.79 t, 2 H (CH_2); 1.80–1.60 m, 4 H ($2\times CH_2$); 1.40–1.20 m, 24 H ($(CH_2)_5+(CH_2)_7$); 1.36 d, 3 H (C*–CH_3); 0.95–0.85 m, 6 H ($2\times CH_3$). IR: 2945 m (C–H), 2930 s (C–H), 2857 m (C–H), 1738 s (C=O), 1710 s (C=O), 1596 m (C–C), 1507 m (C–C), 1465 m (C–C), 1415 m (C–C), 1289 s (C–O), 1277 s (C–O), 1266 s (C–O), 1175 s (C–O). Anal. for $C_{41}H_{50}O_5S_2$ (686.97): calculated 71.68% C, 7.34% H, 9.33% S; found 71.69% C, 7.26% H, 9.38% S.

3-Fluoro-4-[(S)-(2-methylbutyl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**II-F-but**). ^{1}H NMR: 8.80 d, 1 H, J(1,3) = 1.5 (H-1); 8.27 dd, 1 H, J(3,4) = 8.5, J(1,3) = 1.5 (H-3); 7.96 d, 1 H, J(3,4) = 8.5 (H-4); 7.92 m, 2 H (H-2′,H-6′); 7.84 d, 1 H, J(8,9) = 8.2 (H-9); 7.75 s, 1 H (H-6); 7.40 dd, 1 H, J(5′,6′) = 8.2 (H-5′); 7.32 d, 1 H, J(8,9) = 8.2 (H-8); 4.24 m, 1 H (OCH(H)); 4.16 m, 1 H (OC(H)H); 2.78 t, 2 H (CH_2); 1.88 m, 1 H (C*–H); 1.71 m, 2 H (CH_2); 1.53 m, 1 H (C*–CH(H)); 1.27 m, 15 H ($(CH_2)_7$+C*–C(H)H); 1.03 d, 3 H (C*–CH_3); 0.97 t, 3 H (CH_3); 0.88 t, 3 H (CH_3). ^{19}F NMR: −131.82 m. IR: 2963 m (C–H), 2929 s (C–H), 2857 m (C–H), 1743 s (C=O), 1720 s (C=O), 1596 m (C–C), 1508 m (C–C), 1465 m (C–C), 1432 m (C–C), 1288 s (C–O), 1275 s (C–O), 1262 s (C–O), 1184 s. Anal. for $C_{37}H_{41}FO_4S_2$ (632.86): calculated 70.22% C, 6.53% H, 10.13% S; found 70.34% C, 6.49% H, 10.10% S.

3-Fluoro-4-[(S)-(4-methylhexyl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**II-F-hex**). ^{1}H NMR: 8.78 s, 1 H (H-1); 8.24 d, 1 H, J(3,4) = 8.5 (H-3); 7.96 d, 1 H, J(3,4) = 8.5 (H-4); 7.92 m, 2 H (H-2′,H-6′); 7.83 d, 1 H, J(8,9) = 8.2 (H-9); 7.74 s, 1 H (H-6); 7.40 dd, 1 H, J(5′,6′) = 8.3 (H-5′); 7.31 d, 1 H, J(8,9) = 8.2 (H-8); 4.33 t, 2 H (OCH_2); 2.77 t, 2 H (CH_2); 1.85–1.65 m, 4 H ($2\times CH_2$); 1.50–1.15 m, 19 H ($CH+2\times CH_2+(CH_2)_7$); 0.92–0.86 m, 9 H ($3\times CH_3$). ^{19}F NMR: −131.88 m. IR: 3036 w (C–H), 2960 m (C–H), 2929 s (C–H), 2856 m (C–H), 1743 s (C=O), 1720 s (C=O), 1596 m (C–C), 1508 m (C–C), 1465 m (C–C), 1433 m (C–C), 1289 s (C–O), 1275 s (C–O), 1262 s (C–O), 1184 s. Anal for $C_{39}H_{45}FO_4S_2$ (660.91): calculated 70.88% C, 6.86% H, 9.70% S; found: 70.85% C, 6.77% H, 9.80% S.

3-Fluoro-4-[(S)-(octan-2-yl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**II-F-oct**). ^{1}H NMR: 8.80 s, 1 H (H-1); 8.26 d, 1 H, J(3,4) = 8.5 (H-3); 7.97 d, 1 H, J(3,4) = 8.5 (H-4); 7.92 m, 2 H (H-2′,H-6′); 7.85 d, 1 H, J(8,9) = 8.2 (H-9); 7.75 s, 1 H (H-6); 7.39 dd, 1 H, J(5′,6′) = 8.0 (H-5′); 7.33 d, 1 H, J(8,9) = 8.2 (H-8); 5.16 m, 1 H (CH); 2.78 t, 2 H (CH_2); 1.70–1.60 m, 4 H ($2\times CH_2$); 1.40–1.20 m, 24 H ($(CH_2)_5+(CH_2)_7$); 1.35 d, 3 H (C*–CH_3); 0.95–0.85 m, 6 H ($2\times CH_3$). ^{19}F NMR: −132.06 m. IR: 2930 s (C–H), 2857 m (C–H), 1743 s (C=O), 1715 s (C=O), 1596 m (C–C), 1508 m (C–C), 1466 m (C–C), 1432 m (C–C), 1290 s (C–O), 1274 s (C–O), 1262 s (C–O), 1185 s. Anal. for $C_{40}H_{47}FO_4S_2$ (674.94): calculated 71.18% C, 7.02% H, 9.50% S; found 71.23% C, 7.04% H, 9.42% S.

3-Chloro-4-[(S)-(2-methylbutyl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**II-Cl-but**). ^{1}H NMR: 8.83 d, 1 H, $J(1,3)=1.4$ (H-1); 8.20 d, 1 H, $J(2',6')=1.9$ (H-2'); 8.28 dd, 1 H, $J(3,4)=8.5$, $J(1,3)=1.4$ (H-3); 8.05 dd, 1 H, $J(5',6')=8.2$, $J(2',6')=1.9$ (H-6'); 7.97 d, 1 H, $J(3,4)=8.5$ (H-4); 7.85 d, 1 H, $J(8,9)=8.0$ (H-9); 7.76 s, 1 H (H-6); 7.43 d, 1 H, $J(5',6')=8.2$ (H-5'); 7.33 d, 1 H, $J(8,9)=8.0$ (H-8); 4.24 m, 1 H (OCH(H)); 4.16 m, 1 H (OC(H)H); 2.78 t, 2 H (CH_2); 1.87 m, 1 H (C*–H); 1.71 m, 2 H (CH_2); 1.53 m, 1 H (C*–CH(H)); 1.27 m, 15 H ($(CH_2)_7$+C*–C(H)H); 1.03 d, 3 H (C*–CH_3); 0.97 t, 3 H (CH_3); 0.88 t, 3 H (CH_3). IR: 3 027 w (C–H), 2 963 m (C–H), 2 929 s (C–H), 2 857 m (C–H), 1 741 s (C=O), 1 721 s (C=O), 1 596 m (C–C), 1 490 w (C–C), 1 465 m (C–C), 1 275 s (C–O), 1 251 s (C–O). Anal. for $C_{37}H_{41}ClO_4S_2$ (649.31): calculated 68.44% C, 6.36% H, 5.46% Cl, 9.88% S; found: 68.33% C, 6.37% H, 5.67% Cl, 9.92% S.

3-Chloro-4-[(S)-(4-methylhexyl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**II-Cl-hex**). ^{1}H NMR: 8.82 d, 1 H, $J(1,3)=1.1$ (H-1); 8.20 d, 1 H, $J(2',6')=1.9$ (H-2'); 8.29 dd, 1 H, $J(3,4)=8.5$, $J(1,3)=1.1$ (H-3); 8.04 dd, 1 H, $J(5',6')=8.5$, $J(2',6')=1.9$ (H-6'); 7.97 d, 1 H, $J(3,4)=8.5$ (H-4); 7.85 d, 1 H, $J(8,9)=8.3$ (H-9); 7.76 s, 1 H (H-6); 7.43 d, 1 H, $J(5',6')=8.5$ (H-5'); 7.33 d, 1 H, $J(8,9)=8.3$ (H-8); 4.33 t, 2 H (OCH_2); 2.78 t, 2 H (CH_2); 1.85–1.65 m, 4 H ($2\times CH_2$); 1.50–1.15 m, 19 H ($CH+2\times CH_2+(CH_2)_7$); 0.92–0.86 m, 9 H ($3\times CH_3$). IR: 3 027 w (C–H), 2 960 m (C–H), 2 929 s (C–H), 2 856 m (C–H), 1 741 s (C=O), 1 721 s (C=O), 1 595 m (C–C), 1 490 w (C–C), 1 465 m (C–C), 1 276 s (C–O), 1 251 s (C–O), 1 233 s (C–O). Anal. for $C_{39}H_{45}ClO_4S_2$ (677.37): calculated 69.15% C, 6.70% H, 5.23% Cl, 9.47% S; found 69.15% C, 6.70% H, 5.40% Cl, 9.52% S.

3-Chloro-4-[(S)-(octan-2-yl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**II-Cl-oct**). ^{1}H NMR: 8.83 d, 1 H, $J(1,3)=1.6$ (H-1); 8.28 dd, 1 H, $J(3,4)=8.5$, $J(1,3)=1.6$ (H-3); 8.19 d, 1 H, $J(2',6')=1.9$ (H-2'); 8.04 dd, 1 H, $J(5',6')=8.2$, $J(2',6')=1.9$ (H-6'); 7.97 d, 1 H, $J(3,4)=8.5$ (H-4); 7.85 d, 1 H, $J(8,9)=8.2$ (H-9); 7.75 s, 1 H (H-6); 7.42 d, 1 H, $J(5',6')=8.2$ (H-5'); 7.33 d, 1 H, $J(8,9)=8.2$ (H-8); 5.17 m, 1 H (CH); 2.78 t, 2 H (CH_2); 1.70–1.60 m, 4 H ($2\times CH_2$); 1.40–1.20 m, 24 H ($(CH_2)_5+(CH_2)_7$); 1.35 d, 3 H (C*–CH_3); 0.95–0.85 m, 6 H ($2\times CH_3$). IR: 3 027 w (C–H), 2 960 m (C–H), 2 930 s (C–H), 2 857 m (C–H), 1 741 s (C=O), 1 715 s (C=O), 1 595 m (C–C), 1 490 w (C–C), 1 466 m (C–C), 1 275 s (C–O), 1 251 s (C–O), 1 233 s (C–O). Anal. for $C_{40}H_{47}ClO_4S_2$ (691.39): calculated 69.49% C, 6.85% H, 5.13% Cl, 9.28% S; found 69.39% C, 6.85% H, 5.06% Cl, 9.22% S.

3-Bromo-4-[(S)-(2-methylbutyl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**II-Br-but**). ^{1}H NMR: 8.83 s, 1 H (H-1); 8.36 d, 1 H, $J(2',6')=1.9$ (H-2'); 8.30 dd, 1 H, $J(3,4)=8.5$ (H-3); 8.09 dd, 1 H, $J(5',6')=8.2$, $J(2',6')=1.9$ (H-6'); 7.97 d, 1 H, $J(3,4)=8.5$ (H-4); 7.85 d, 1 H, $J(8,9)=8.0$ (H-9); 7.76 s, 1 H (H-6); 7.43 d, 1 H, $J(5',6')=8.2$ (H-5'); 7.33 d, 1 H, $J(8,9)=8.0$ (H-8); 4.24 m, 1 H (OCH(H)); 4.16 m, 1 H (OC(H)H); 2.78 t, 2 H (CH_2); 1.87 m, 1 H (C*–H); 1.71 m, 2 H (CH_2); 1.53 m, 1 H (C*–CH(H)); 1.27 m, 15 H ($(CH_2)_7$+C*–C(H)H); 1.03 d, 3 H (C*–CH_3); 0.97 t, 3 H (CH_3); 0.88 t, 3 H (CH_3). IR: 3 026 w (C–H), 2 963 m (C–H), 2 929 s (C–H), 2 856 m (C–H), 1 740 s (C=O), 1 720 s (C=O), 1 595 m (C–C), 1 486 w (C–C), 1 465 m (C–C), 1 274 s (C–O), 1 250 m (C–O), 1 232 s (C–O). Anal. for $C_{37}H_{41}BrO_4S_2$ (693.77): calculated 64.06% C, 5.96% H, 11.52% Br, 9.24% S; found 64.18% C, 5.98% H, 11.46% Br, 9.12% S.

3-Bromo-4-[(S)-(4-methylhexyl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**II-Br-hex**). ^{1}H NMR: 8.83 d, 1 H, $J(1,3)=1.4$ (H-1); 8.36 d, 1 H, $J(2',6')=1.9$ (H-2'); 8.30 dd, 1 H, $J(1,3)=1.4$, $J(3,4)=8.5$ (H-3); 8.09 dd, 1 H, $J(5',6')=8.2$, $J(2',6')=1.9$ (H-6'); 7.97 d, 1 H, $J(3,4)=8.5$ (H-4); 7.85 d, 1 H, $J(8,9)=8.0$ (H-9); 7.76 s, 1 H (H-6); 7.43 d, 1 H, $J(5',6')=8.2$ (H-5'); 7.33 d, 1 H, $J(8,9)=8.0$ (H-8); 4.33 t, 2 H (OCH_2); 2.78 t, 2 H (CH_2); 1.85–1.65 m, 4 H ($2\times CH_2$); 1.50–1.15 m, 19 H ($CH+2\times CH_2+(CH_2)_7$); 0.92–0.86 m, 9 H ($3\times CH_3$). IR: 3 021 w (C–H), 2 960 m (C–H), 2 929 s (C–H), 2 856 m (C–H), 1 740 s (C=O), 1 720 s (C=O), 1 595 m (C–C), 1 486 w (C–C), 1 465 m (C–C), 1 275 s (C–O), 1 250 m (C–O), 1 232 s (C–O). Anal. for $C_{39}H_{45}BrO_4S_2$ (721.82): calculated 64.90% C, 6.28% H, 11.07% Br, 8.88% S; found 64.85% C, 6.31% H, 10.98% Br, 8.90% S.

3-Bromo-4-[(S)-(octan-2-yl)oxycarbonyl]phenyl 7-decyl[1]benzothieno[3,2-b][1]benzothiophene-2-carboxylate (**II-Br-oct**). ^{1}H NMR: 8.83 d, 1 H, $J(1,3)=1.4$ (H-1); 8.36 d, 1 H, $J(2',6')=1.9$ (H-2'); 8.30 dd, 1 H, $J(1,3)=1.4$, $J(3,4)=8.5$ (H-3); 8.09 dd, 1 H, $J(5',6')=8.2$, $J(2',6')=1.9$ (H-6'); 7.97 d, 1 H, $J(3,4)=8.5$ (H-4); 7.85 d, 1 H, $J(8,9)=8.0$ (H-9); 7.76 s, 1 H (H-6); 7.43 d, 1 H, $J(5',6')=8.2$ (H-5'); 7.33 d, 1 H, $J(8,9)=8.0$ (H-8); 5.17 m, 1 H (CH); 2.78 t, 2 H (CH_2); 1.70–1.60 m, 4 H ($2\times CH_2$); 1.40–1.20 m, 24 H ($(CH_2)_5+(CH_2)_7$); 1.36 d, 3 H (C*–CH_3); 0.95–0.85 m, 6 H ($2\times CH_3$). IR: 2 959 m (C–H), 2 930 s (C–H), 2 857 m (C–H), 1 741 s (C=O), 1 714 s (C=O), 1 595 m (C–C), 1 486 w (C–C), 1 466 m (C–C), 1 274 s (C–O), 1 250 m (C–O), 1 233 s (C–O). Anal. for $C_{40}H_{47}BrO_4S_2$ (735.85): calculated 65.29% C, 6.44% H, 10.86% Br, 8.71% S; found 65.26% C, 6.38% H, 10.89% Br, 8.83% S.

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