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Tetrahedron 62 (2006) 3370–3379
Tetrahedron

Synthesis of optically active amphiphilic tetrathiafulvalene derivatives

Elba Gomar-Nadal, Concepció Rovira and David B. Amabilino*

Departament de Nanociència Molecular i Materials Orgànics, Institut de Ciència de Materials de Barcelona (ICMAB), Consejo Superior de Investigaciones Científicas (CSIC), Campus Universitari, 08193 Bellaterra, Catalonia, Spain

Received 10 October 2005; revised 10 January 2006; accepted 17 January 2006

Available online 17 February 2006

Abstract—The synthesis and characterization of novel chiral tetrathiafulvalenes bearing two long alkyl chains at one end of the π-electron rich unit and different functional groups—ester, acid or thiolate—at the other extreme is described. The synthetic method requires the preparation of 1,3-dithiol derivatives with two stereogenic centers. Different routes and reaction conditions were explored to form these compounds, whose optimized synthesis involved the nucleophilic substitution of a chiral bromo methylene derivative with tetrabutylammonium bis(2-thioxo-1,3-dithiole-4,5-dithiolate)zincate. The tetrathiafulvalenes were prepared by coupling the 1,3-dithiol derivative with 4,5-bis(methoxycarbonyl)-1,3-dithiol-2-one or 4,5-bis(2-cyanotehylthio)-1,3-dithiol-2-thione. The products were fully characterized, including by circular dichroism spectroscopy, which confirmed their optical activity. They are promising candidates to be used as building blocks in supramolecular materials for molecular electronics, to produce systems with unique electrical, magnetic or optical properties that stem from their chirality.
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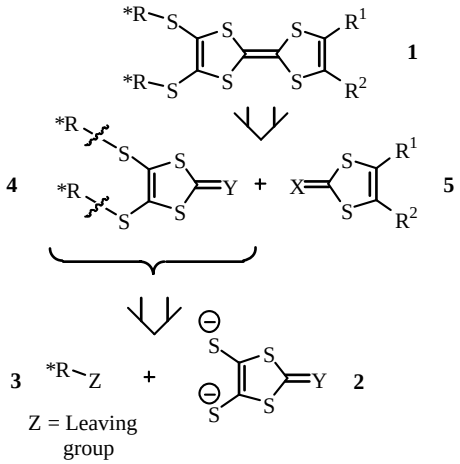
1. Introduction

The stereochemistry of molecular components has significant consequences for the properties of chemical systems of which they form a part, such us magnetic and conducting properties.[1] Tetrathiafulvalene (TTF) derivatives[2] are very versatile electro-active molecules widely used as building blocks to prepare organic metals, for supramolecular functions[3] and in molecular electronics.[4] The preparation of optically active compounds of this type offers, then, the creation of new substances with novel characteristics. Some chiral TTF derivatives have been previously reported.[5–8] These compounds have been used to form chiral conducting charge transfer complexes and salts mainly.[5,7] However, away from the constrictions of crystal space, they are also interesting for preparing multifunctional materials in the form of liquid crystals, thin films, self-assembled monolayers (SAMs), dendrimers and polymers for use in molecular (opto)electronic devices with new properties that arise from the chirality of the molecule, and in which (more often than not) an amphiphilic character is present.

In these systems it is often necessary to prepare components with long alkyl chains, which provide the amphiphilic nature, to ensure liquid crystallinity, solubility and processing characteristics in general. To the best of our knowledge, the synthetic routes to chiral TTFs reported to date have not incorporated long alkyl chains. The efficiency of the cyclic sulphate ester route to chiral TTFs suffers when the size of the substituent on the cyclic sulphate is increased.[5,8] To overcome these problems, we envisaged the preparation of TTFs of type **1** (see Scheme 1) introducing directly two chiral chains (**3**) by reaction of the readily available di-anion 2-thioxo-1,3-dithiole-4,5-



Scheme 1.

Keywords: Stereochemistry; Circular dichroism; Molecular electronics; π-Donor.
* Corresponding author. Tel.: +34 935801853; fax: +34 935805729; e-mail: amabilino@icmab.es

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doi:10.1016/j.tet.2006.01.056

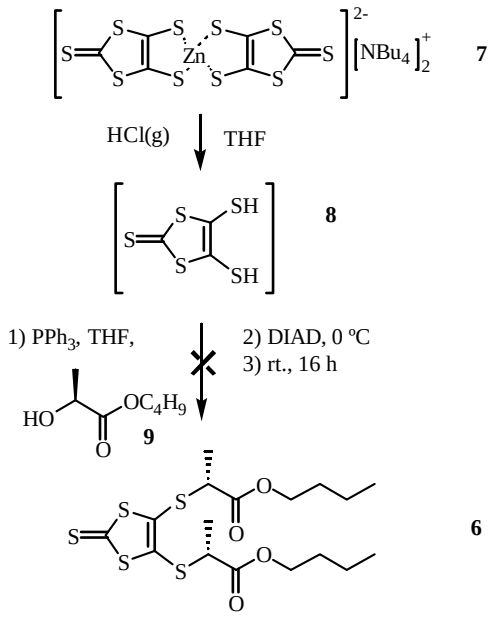
dithiolate (**2**), where a great body of literature exists for achiral components with long alkyl chains,[9] to give a 1,3-dithiole derivative with general structure **4**. Subsequently, coupling of 1,3-dithio-l,2-ones (or -thiones) **4** and **5** with trialkyl phosphites[10] would afford the desired compounds **1**.

Here, we describe the synthesis of new chiral TTFs of type **1** with two stereogenic centers in long alkyl chains at one extreme of the π-electron rich unit, and functional groups at the other that will help to incorporate the molecule into chemical systems.

2. Results and discussion

2.1. Synthesis of enantiomeric 1,3-dithiol-2-thiones

Different strategies were considered for the preparation of optically active 1,3-dithiol derivatives with two stereogenic centers and long alkyl chains (**4**). The synthesis of the chiral 1,3-dithiol-2-thione **6** (Scheme 2) was attempted, taking advantage of the stereoselectivity of the Mitsunobu[11,12] reaction for the introduction of stereogenic centers in the α-position to heteroatoms. A stable form of the synthon **2** is tetrabutylammonium bis(2-thioxo-1,3-dithiole-4,5-dithiolate)zincate[13] (**7**, Scheme 2). The complex was treated with dry hydrogen chloride in THF, and a change in color of the solution was observed—from purple to yellow, presumably resulting from decomplexation of the metal ion and the formation of the unstable[14] dithiol **8**. After bubbling nitrogen through the solution to eliminate the excess of hydrogen chloride, treatment of the intermediate with the lactate **9** under Mitsunobu reaction conditions[11,12] did not give the desired product (**6**) despite the fact that this type of coupling between alcohols and thiols has been reported in the past.[15]



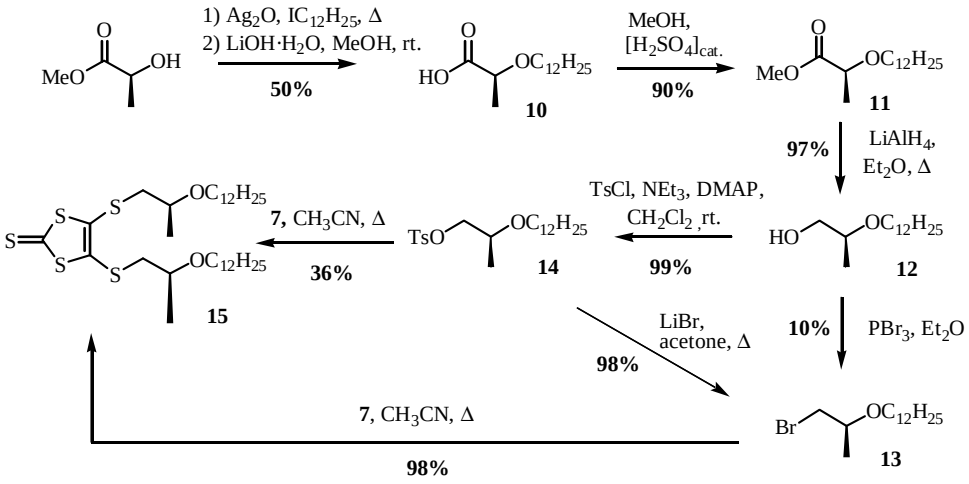
Scheme 2.

The direct reaction of alcohols and zinc complexes has also been reported using the Mitsunobu procedure.[16] However, treatment of the zinc complex with lactate **9** adding 4.1 equiv of acetic acid (or without adding any acid) under these conditions did not lead to the formation of **6** either, presumably because of the strength of the chelate. Another route explored to synthesize **6** was the mono-deprotection of 4,5-bis(2-cyanotehylthio)-1,3-dithiol-2-thione[17] with 1 equiv of CsOH and subsequent reaction of the resulting thiolate salt with lactate **9** under Mitsunobu conditions, but again no reaction was observed. The lack of success in all these reactions is most probably related to: (i) the role of the proton source[12] in the Mitsunobu reaction and (ii) the sterical impediment of the stereogenic center hindering the reactivity with the bulky (di)sulfide, a statement that was corroborated for the experimental data presented in this article (see below) and by Wallis and co-workers[8] research.

To avoid the possible reactivity problems caused by the proximity of the stereogenic carbon atom to the electrophilic group, a synthetic route where the introduction of the chiral 'tails' took place through a nucleophilic substitution one atom further from the chiral center was envisaged (Scheme 3). This synthetic pathway started with the preparation of the chiral acid **10** in two steps,[18] conversion to ester **11** whose treatment with $LiAlH_4$ led to alcohol **12**. Bromoderivative **13** was prepared by two methods (Scheme 3). The first one consisted of treating **12** with PBr_3,[19] which gave a mixture of the desired product (**13**) and the characteristic intermediates of the reaction,[20] which, even after passing HBr, were not completely transformed into the desired product, so very low yields were attained (~10%, Table 1). Alternatively, alcohol **12** was first tosylated and the functional group of the resulting product (**14**) was subsequently exchanged for bromide by reaction with LiBr in refluxing acetone, giving **13**. The yield of the reaction depends strongly on the refluxing time (Table 1). Long reaction times ensured a quantitative conversion of **14** to **13**. When NaBr was used, instead of LiBr, the reaction did not take place.

To optimize the reaction conditions to synthesize 4,5-bis((*S*)-2-dodecyloxy-propanyl)-1,3-dithiol-2-thione (**15**, Scheme 3), the synthesis of the analogous achiral thione 4,5-bis(decacyl)-1,3-dithiol-2-thione (**16**, Scheme 4) was used as a reference. The nucleophilic substitution reaction with the zinc complex **7** to form **16** gave higher yields using 1-bromodecane than tosylate **17** (Table 2). Addition of NaI to interchange the tosylate group for iodine in situ increased the yield of the reaction, which even so was lower than using 1-bromodecane as a starting material. Bromine and tosylate are both very good leaving groups for nucleophilic substitution reactions; so, the differences in yield observed are most likely due to steric impediment. [21]

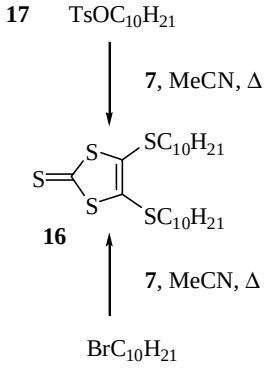
The same tendency was observed when the reactions were done with the analogous chiral reactants (Table 2). The efficiency of the reaction to form the chiral thione **15** (Scheme 3) was higher using the chiral bromide derivative (**13**) than the corresponding chiral tosylate (**14**). Comparing the reactions done under the same conditions for **15** and **16** the influence of the stereogenic carbon atom in the reaction (mentioned before) was evident. Longer refluxing times were necessary for the formation of the chiral 1,3-dithiol-2-



Scheme 3.

Table 1. Reaction conditions tested to produce **13**

Starting material	Reaction conditions	Yield **13** (%)
12	(1) PBr_3 in CCl_4; (2) 20 min; (3) HBr	11
	(1) PBr_3 in Et_2O; (2) 3 days; (3) HBr	9
14	(1) LiBr, acetone; (2) 2 h reflux	45
	(1) NaBr, acetone; (2) 3 h reflux	0
	(1) LiBr, acetone; (2) 20 h reflux	98



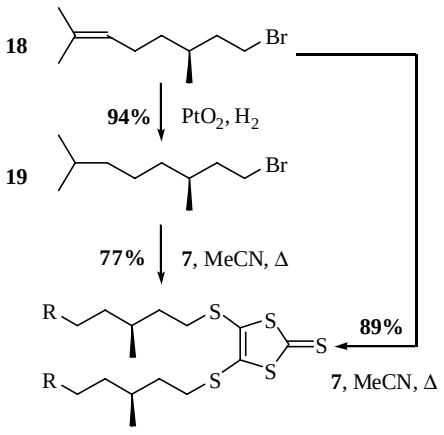
Scheme 4.

Table 2. Comparison of the reactions condition examined to form **15** and **16**

Starting material	Reaction conditions	Product	Isolated yield (%)
17	**7**, MeCN, reflux 3 h	**16**	3
	7, MeCN, NaI, reflux 3 h	**16**	60
$BrC_{10}H_{21}$	**7**, MeCN, reflux 3 h	**16**	87
14	(1) **7**, MeCN, reflux 2h; (2) NaI, reflux 1h	**15**	12
	7, MeCN, reflux 20 h	**15**	36
13	**7**, MeCN, reflux 20 h	**15**	98

thione (**15**) than for the comparable achiral thione (**16**) in order to have the same yield, because of the steric impediment created by the stereogenic center close to the electrophilic carbon atom. The thione **15** gave NMR and IR spectra in accord with the proposed structure. No evidence of the presence of diastereomers was observable. The laser desorption–ionization mass spectrum showed a characteristic peak corresponding to the addition of one of the alkyl substituent fragment at the thiol to the thione sulphur atom.

The preparation of 1,3-dithiol derivatives of type **4** (Scheme 1) which contain the stereogenic centers located further from the TTF moiety was achieved (Scheme 5) by reaction of the zinc complex **7** with (*S*)-(+)-citronellyl bromide (**18**) and **19**—that was obtained reducing **18** with Adam's catalyst. The chiral 1,3-dithiol-2-thiones **20** and **21** were formed in high yields (80–90%), which are comparable to the ones obtained with achiral bromides for the same refluxing times (see e.g., reaction of 1-bromodecane with **7**, in Table 2). The presence of a stereogenic atom two atoms away from the electrophilic carbon atom (one atom further away than in the synthesis of **15**) did not affect the yield of the reaction. Hence, the position of the stereogenic atom with respect to the atom on which the reaction takes place is important and can dramatically affect the yield of the reaction, to the point that we were unable to prepare the compound where the stereogenic center is adjacent to the electrophilic sulphur atoms.



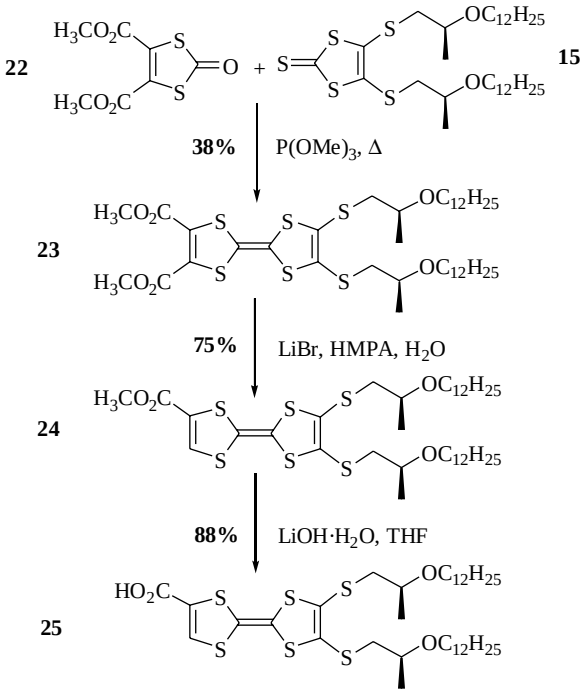
20 R = –CH=C(CH$_3$)$_2$

21 R = –CH$_2$CH(CH$_3$)$_2$

Scheme 5.

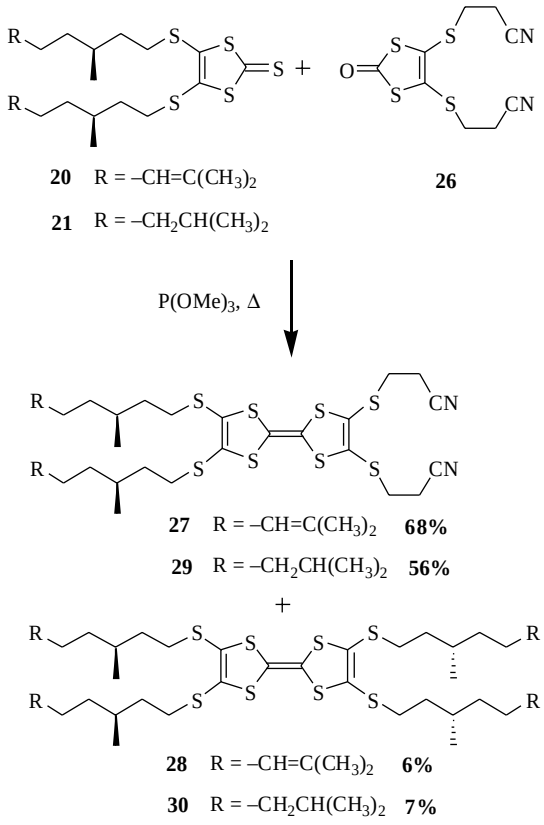
2.2. Synthesis and characterisation of chiral TTF derivatives

Coupling of the appropriate 1,3-dithio-2-thiones (or -ones) with trimethyl phosphite[10] allowed the preparation of chiral TTF derivatives of type **1** directly (Scheme 1). Thus, the cross-coupling reaction of **15** and 4,5-bis(methoxycarbonyl)-1,3-dithiol-2-one (**22**)[22] gave the chiral bisester TTF **23** in about 40% yield (Scheme 6), a good result considering that the symmetrical TTF derivatives are also formed during the reaction.[10] The redox properties of this TTF are those to be expected of a compound of this type with two strongly electron withdrawing ester groups at one extreme of the molecule. The first oxidation process—from neutral to cation radical—takes place at 683 mV, while further oxidation to the dication occurs at 1055 mV (in CH_2Cl_2, 0.1 M $[NBu_4][PF_6]$, Pt-electrodes and a Ag/AgCl electrode as reference). Treatment of the bisester **23** with an excess of LiBr in HMPA at 80 °C produced monodecarboxymethylation and basic hydrolysis of the resulting monoester **24** led to the chiral acid functionalized TTF **25** (Scheme 6). Monoester **24** exhibited oxidation waves at 635 and 1051 mV (conditions as for **23**).



Scheme 6.

In the same way as for the preparation of **23**, coupling of oxo compound **26** with either thione **20** or **21** leads to excellent yields of the corresponding TTFs **27** and **29**, respectively (Scheme 7), in which the stereogenic centers are one carbon further away from the π-electron rich core than in **23**, and here the propionitrile protecting groups are incorporated. This group can be sequentially removed using base,[17] and thus **27** and **29** are useful building blocks for a variety of structures, including chiral phthalocyanine TTF composite molecules.[22] The yield of **27** (68%) is notably high for this



Scheme 7.

type of coupling reaction. Cyclic voltammetry of **27** and **29** gave oxidation waves at identical positions, 650 and 1015 mV (in CH_2Cl_2, 0.1 M $[NBu_4][PF_6]$, Pt-electrodes and a Ag/AgCl electrode as reference).

All the TTF derivative compounds were identified clearly by laser desorption–ionization time-of-flight mass spectrometry, which shows the molecular ion peaks as the most abundant species in positive mode, with the exception of the carboxylic acid derivatives, which decarboxylate under the mass spectrometric conditions. The NMR spectra are also fully consistent with the structures of the compounds.

The optical activity of the TTF compounds was studied by circular dichroism (CD) spectroscopy, which provides direct information on the chromophores present in the molecule. It was not possible to use polarimetry to compare the optical activity because the ratio of absorption to rotation is too high. The CD spectra of representative examples of the two families of compounds, with the different stereogenic centers, are shown in Figure 1. Compound **23** shows a weak negative Cotton effect at 400 nm and a stronger positive one at 300 nm, below which the absorption becomes too strong to reliably measure the spectrum. The spectra of **24** and **25** are practically superimposable on this one. The TTF derivative **29** shows just one broad Cotton effect centerd on 350 nm. The slightly weaker Cotton effect in this compound compared with **23** is most likely due to the slightly larger distance between the stereogenic centre and the chromophore.

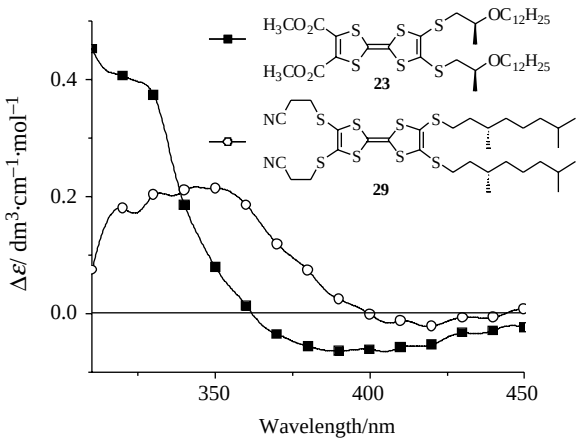


Figure 1. Circular dicroism spectra of **23** and **29** in THF.

3. Conclusion

In the synthesis of this series of chiral TTF derivatives using the routes described here the yield of the thione precursors depends critically on the position of the chiral center in the lateral chains. Steric interactions between the thiolate groups in 2-thioxo-1,3-dithiole-4,5-dithiolate and the incoming chiral electrophile mean that at least one methylene unit is necessary between the sulphur atom and the stereogenic center. Once formed, the TTFs show all the characteristics of this family of compounds, but also optical activity. This fact and their inherent chirality—which has important consequences during organization of π-functional molecules—makes them, and related compounds, very interesting for preparing multifunctional materials with new properties that arise from the chirality of the molecular building blocks.

4. Experimental

4.1. Materials and methods

Tetrabutylammonium bis(2-thioxo-1,3-dithiole-4,5-dithiolate)zincate (**7**),[13] 4,5-bis(methoxycarbonyl)-1,3-dithiol-2-one (**22**)[23] and 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one (**26**)[24] were synthesized using procedures reported in the literature. All other chemicals were commercial products and were used as obtained. Tetrahydrofuran (THF) and diethyl ether were distilled over sodium/benzophenone, acetone over K_2CO_3, and CH_2Cl_2 and MeCN over P_2O_5. Thin-layer chromatography (TLC) was performed on aluminium plates coated with Merck Silica gel 60 F254. Developed plates were air-dried and scrutinized under a UV lamp except for compounds **10** and **11** that were visualized by putting the plate in an iodine chamber. Silica gel 60 (35–70 mesh, SDS) was used for column chromatography.

Melting points were determined using a Melting Point SMP10, BIBBY Stuart Scientific instrument and are uncorrected. LDI-TOF-MS were obtained using a Kratos Kompact Maldi 2 K-probe (Kratos Analytical) operating with pulsed extraction of the ions in positive and linear high power mode. The samples were deposited directly onto a non-polished stainless steel sample plate from CH_2Cl_2 solution.

Infrared spectra were recorded on a Perkin Elmer FT-IR Spectrum One spectrometer. ^1H and ^{13}C NMR spectra were obtained using a Bruker Avance 250 spectrometer with deuterated solvent as lock and tetramethylsilane as internal reference. Polarimetry was performed using a Dr. Krenchen+Electronik Propol polarimeter in a 1 cm cell (20 mg/ml using as a solvent CH_2Cl_2). Cyclic voltammograms were recorded with the conventional three-electrode configuration in dry CH_2Cl_2 containing 0.1 M $[NBu_4][PF_6]$, as a supporting electrolyte, with Pt-electrodes and a Ag/AgCl electrode as a reference one.

4.1.1. (*S*)-2-Dodecyloxypropanoic acid (10). To a solution of (−)-methyl L-lactate (2.0 ml, 21 mmol) and 1-iodododecane (12.0 ml, 49 mmol) was added silver (I) oxide (6.53 g, 28 mmol). The mixture was sonicated for 10 min before refluxing for 24 h in the dark. The suspension was filtered through Celite, washed with diethyl ether, and the solvent was removed under vacuum. To the remaining oil (which contained the ester and by-products such as starting material, iodoalkane, alkanol, and alkyl ether) was added MeOH (70 ml), H_2O (30 ml) and $LiOH\cdot H_2O$ (2.80 g, 67 mmol), and the mixture was stirred overnight at room temperature. After this time, NaOH (aqueous, 75 ml, 3.5%) was added and the organic products were extracted with diethyl ether. The aqueous phase, which contains the salt of the chiral acid, was acidified with HCl (aqueous, 2 N). The product was extracted with CH_2Cl_2 (3×100 ml) and dried over $MgSO_4$, and the solvent evaporated. The colorless residue was purified by flash chromatography using hexane–EtOAc [9/1] mixture as eluent to obtain 2.60 g (50%) of a transparent oil. $[\alpha]_{546}^{25}$ (CH_2Cl_2, 20 mg/ml): −4.05 deg cm^2 g^{-1}. FT-IR (NaCl discs): 3300–2500 (w, OH), 2925 (s), 2855 (s), 1723 (s, C=O), 1462 (w), 1421 (w), 1371 (w), 1287 (w), 1241 (w), 1130 (m, C–O–C), 1013 (w), 932 (w), 828 (w), 721 (w), 658 (w), 561 (w), 523 (w), 489 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): 9.60 (br s, 1H, –O*H*), 3.99 (q, J=6.8 Hz, 1H, –C*H*(CH_3)), 3.60 (dt, J=8.8, 6.6 Hz, 1H, –OCH_2), 3.43 (dt, J=8.8, 6.6 Hz, 1H, –OCH_2), 1.61 (m, J=6.8 Hz, 2H, –OCH$_2$CH_2), 1.45 (d, J=6.8 Hz, 3H, –CH(CH_3)), 1.40–1.20 (m, 18H, –(CH_2)$_9$CH$_3$), 0.89 (t, J=6.6 Hz, 3H, –(CH$_2$)$_9$CH_3) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 178.4 (*C*=O), 74.5 (–*C*H(CH_3)), 70.6 (–OCH_2), 31.9 (–O(CH$_2$)$_9$*C*H$_2$), 29.6 (–OCH$_2$*C*H$_2$), 29.6, 29.5, 29.4 and 29.3 (–O(CH$_2$)$_3$(*C*H$_2$)$_6$), 26.0 (–O(CH$_2$)$_2$*C*H$_2$), 22.7 (–*C*H$_2$CH$_3$), 18.3 (–CH(*C*H$_3$)), 14.0 (–(CH$_2$)$_{11}$*C*H$_3$) ppm.

4.1.2. Methyl (*S*)-2-dodecyloxypropanoate (11). A solution of (*S*)-2-dodecyloxypropanoic acid (**10**, 722 mg, 2.952 mmol) and sulphuric acid (three drops, 95–98%) in MeOH (45 ml) was refluxed for 5 h. After this time, the mixture was cooled to room temperature and $NaHCO_3$ (5 ml, saturated aqueous solution) was added. The MeOH was evaporated and the aqueous phase was extracted with CH_2Cl_2 (3×20 ml). The organic phase was washed with (3×100 ml) and dried over $MgSO_4$, and the solvent evaporated. The remaining oil (763 mg) was purified by flash chromatography using hexane–EtOAc [19/1] mixture as eluent to obtain 687 mg (90%) of a slightly yellow transparent oil. Anal. Calcd for $C_{16}H_{32}O_3$: C 70.54, H 11.84;

Found: C 70.05, H 11.98. $[\alpha]_{546}^{25}$ (CH_2Cl_2, 20 mg/ml): −45.43 deg cm^2 g^{-1}. FT-IR (NaCl discs): 2987 (w), 2925 (s), 2855 (s), 1758 (s, C=O), 1740 (m, C=O), 1460 (w), 1371 (w), 1330 (w), 1273 (w), 1202 (m, C–O), 1148 (m, C–O–C), 1075 (w), 982 (w), 843 (w), 754 (w), 722 (w), 656 (w) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): 4.00 (q, J=6.8 Hz, 1H, –C*H*(CH_3)), 3.74 (s, 3H, –CO_2C*H*$_3$), 3.54 (dt, J=8.9, 4.4 Hz, 1H, –OC*H*$_2$), 3.35 (dt, J=8.9, 4.4 Hz, 1H, –OC*H*$_2$), 1.59 (qi, J=7.0 Hz, 2H, –OCH_2C*H*$_2$), 1.39 (d, J=6.9 Hz, 3H, –CH(C*H*$_3$)), 1.40–1.20 (m, 18H, –(C*H*$_2$)$_9$$CH_3$), 0.88 (t, J=6.5 Hz, 3H, –$(CH_2)_{11}$C*H*$_3$) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 173.9 (*C*=O), 74.9 (–*C*H(CH_3)), 70.5 (–O*C*H$_2$), 51.7 (–CO_2*C*H$_3$), 31.9(–*C*H$_2$$CH_2$$CH_3$), 29.7 (–$OCH_2$*C*H$_2$), 29.7, 29.6, 29.6, 29.6, 29.4 and 29.3 (–(*C*H$_2$)$_6$(CH_2)$_2$$CH_3$), 26.0 (–($CH_2$)$_2$*C*H$_2$), 22.7 (–*C*H$_2$$CH_3$), 18.6 (–CH(*C*H$_3$)), 14.1 (–O($CH_2$)$_9$*C*H$_3$) ppm.

4.1.3. (*S*)-2-Dodecyloxypropan-1-ol (12). To a suspension of $LiAlH_4$ (39 mg, 1.03 mmol) in dry diethyl ether (15 ml) was added drop-wise a solution of methyl (*S*)-2-dodecyloxy-propanoate (**11**, 288 mg, 1.11 mmol) in dry diethyl ether (15 ml) during 15 min. The mixture was refluxed for 1 h. After this, the solution was cooled to room temperature and then to 0 °C introducing it in an ice bath, and H_2O was added drop-wise to eliminate the remaining $LiAlH_4$. The reaction product was filtered from the white sludge, the filtrate was dried over $MgSO_4$ and the solvent evaporated leaving a slightly yellow transparent oil (270 mg). The sludge in the filter funnel was dissolved in sulphuric acid (aqueous, 20%) and the resulting solution was extracted with diethyl ether. The organic phase was dried over $MgSO_4$ and the solvent evaporated. The residual oil obtained from the sludge treatment (85 mg) was combined with the first oil and they were purified by flash chromatography using hexane–EtOAc [3/1] mixture as eluent to obtain 240 mg (94%) of a slightly yellow transparent oil. Anal. Calcd for $C_{15}H_{32}O_2\cdot 1/4H_2O$: C 72.38, H 13.16; Found: C 72.43, H 13.29. $[\alpha]_{546}^{25}$ (CH_2Cl_2, 20 mg/ml): +27.12 deg cm^2 g^{-1}. FT-IR (NaCl discs): 3700–3200 (w, wide, OH), 2925 (s), 2855 (s), 1465 (w), 1374 (w), 1343 (w), 1147 (w), 1096 (m, C–O–C), 1048 (m), 989 (w), 915 (w), 834 (w), 721 (w) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): 3.65–3.35 (m, 5H, –CH_2C*H*(CH_3)OCH_2), 2.38 (br s, 1H, –O*H*), 1.58 (m, J=6.9 Hz, 2H, –OCH_2C*H*$_2$), 1.45–1.20 (m, 18H, –(C*H*$_2$)$_9$$CH_3$), 1.40 (d, J=6.1 Hz, 3H, –CH(C*H*$_3$)O), 0.88 (t, J=6.6 Hz, 3H, –O(CH_2)$_{11}$C*H*$_3$) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 75.8 (–*C*H(CH_3)), 68.9 (–*C*H_2OH), 66.3 (–O*C*H$_2$), 31.9 (–*C*$H_2$$CH_2$$CH_3$), 30.1 (–$OCH_2$*C*H$_2$), 29.7, 29.60, 29.5, 29.4 and 29.3 (–O(CH_2)$_3$(*C*H$_2$)$_6$), 26.2 (–O(CH_2)$_2$*C*H$_2$), 22.7 (–*C*$H_2$$CH_3$), 15.9 (–CH(*C*H$_3$)), 14.1 (–($CH_2$)$_{11}$*C*H$_3$) ppm.

4.1.4. 1-((*S*)-2-Bromo-1-methyl-etoxy)-dodecane (13). *Method A*. To a solution of (*S*)-2-dodecyloxy-propan-1-ol (**12**, 221 mg, 0.967 mmol) in diethyl ether (5 ml) at 0 °C under argon atmosphere was added drop-wise a solution of PBr_3 (0.100 ml, 1.064 mmol) in diethyl ether (5 ml) for 1 h. The reaction was then stirred for 2 days. The excess PBr_3 was destroyed with water, and the organic layer was separated, washed successively with equal volumes of H_2O, orthophosphoric acid (aqueous 85%), and $NaHCO_3$ (saturated aqueous solution) and twice with H_2O, and was dried over $MgSO_4$. The infrared spectrum of the residue obtained after evaporating the solvent showed the peaks at 1250, 950–1000, and 2400 cm^{-1} characteristic of partially converted phospite esters. Dry HBr gas was bubbled through the ether solution at a slow rate for about 15 min at room temperature. The diethyl ether solution was carefully washed with H_2O, $NaHCO_3$ (saturated aqueous solution), H_2O, dried over $MgSO_4$ and the solvent evaporated. The remaining oil (150 mg) was purified by flash chromatography using hexane–CH_2Cl_2 [1/1.5] mixture as eluent to obtain 28 mg (10%) of a slightly yellow transparent oil.

Method B. A solution of (*S*)-2-dodecyloxypropyl toluene-4-sulphonate (**14**, 358 mg, 1.098 mmol) and LiBr (2.3 g, 26 mmol) in acetone (10 ml) was refluxed overnight. The acetone was removed and diethyl ether (30 ml) was added. The diethyl ether solution was washed with H_2O, dried over $MgSO_4$ and the solvent evaporated. The remaining oil (358 mg) was purified as in Method A to give a yield of 94%. Anal. Calcd for $C_{15}H_{31}BrO$: C 58.62, H 10.17; Found: C 59.08, H, 10.36. $[\alpha]_{546}^{25}$ (CH_2Cl_2, 20 mg/ml): +4.09 deg cm^2 g^{-1}. FT-IR (NaCl discs): 2925 (s), 2854 (s), 1466 (w), 1376 (w), 1326 (w), 1229 (w), 1196 (w), 1140 (w), 1099 (m, C–O–C), 920 (w), 722 (w), 671 (w) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): 3.64 (sxd, J=6.1, 1.2 Hz, 1H, –C*H*(CH_3)), 3.50 (t, J=6.5 Hz, 2H, –OC*H*$_2$), 3.41 (dd, J=23.3, 10.2 Hz, 1H, –C*H*$_2$Br), 3.39 (dd, J=23.3, 10.2 Hz, 1H, –C*H*$_2$Br), 1.70–1.20 (m, 23H, –CH(C*H*$_3$)OCH_2(C*H*$_2$)$_{10}$-CH_3), 0.91 (t, J=6.7 Hz, 3H, –O(CH_2)$_{11}$C*H*$_3$) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 76.6 (–*C*H(CH_3)), 69.5 (–O*C*H_2(CH_2)$_{10}$), 36.5 (–*C*H_2Br), 32.0 (–*C*$H_2$$CH_2$-$CH_3$), 30.0 (–$OCH_2$*C*H$_2$), 29.7, 29.6, 29.5 and 29.4 (–(*C*H_2)$_6$(CH_2)$_2$$CH_3$), 26.2 (–O($CH_2$)$_2$*C*H$_2$), 22.7 (–*C*$H_2$$CH_3$), 19.0 (–CH(*C*H$_3$)), 14.1 (–O($CH_2$)$_{11}$*C*H$_3$) ppm.

4.1.5. (*S*)-2-Dodecyloxypropyl toluene-4-sulphonate (14). (*S*)-2-Dodecyloxypropan-1-ol (**12**, 195 mg, 0.853 mmol) is dissolved in CH_2Cl_2 (25 ml) and cooled in an ice bath (0 °C). NEt_3 (0.130 ml, 0.938 mmol) and dimethylamino-pyridine (DMAP, two small crystals) were then added, followed by the addition of toluene–*p*-sulphonyl chloride (TsCl, 179 mg, 0.938 mmol) in small portions with constant stirring. The resulting solution was stirred overnight. Ice (25 g), HCl (aqueous 10%, 5 ml) and H_2O (36 ml) are added and the mixture was stirred until the ice was melted. The organic layer was washed with H_2O (3×50 ml), dried over $MgSO_4$ and the solvent was evaporated. The remaining oil was purified by flash chromatography using hexane–CH_2Cl_2 [1/3] mixture as eluent to obtain 267 mg (84%) of a slightly yellow transparent oil. FT-IR (NaCl discs): 2925 (s), 2855 (s), 1919 (w), 1754 (w), 1599 (w), 1496 (w), 1457 (m), 1367 (s, –SO_2–), 1307 (w), 1292 (w), 1210 (w), 1188 (s, –SO_2–), 1178 (s, –SO_2–), 1098 (m, C–O–C), 1020 (w), 988 (m), 820 (m), 814 (m), 792 (w), 722 (w), 706 (w), 688 (w), 667 (m), 575 (w), 555 (m) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): 7.81 (d, J=8.4 Hz, 2H, $CH_3CCH_{ar}CH_{ar}$C–), 7.35 (d, J=8.4 Hz, 2H, $CH_3CCH_{ar}CH_{ar}$C–), 3.97 (dd, J=7.68, 3.28 Hz, 1H, –C*H*$_2$OTs), 3.93 (dd, J=7.68, 3.28 Hz, 1H, –C*H*$_2$OTs), 3.62 (sx, 1H, J=6.2 Hz, –C*H*(CH_3)), 3.43 (dt, J=8.8, 6.6 Hz, 1H, –OC*H*$_2$), 3.35 (dt, J=8.8, 6.6 Hz, 1H, –OC*H*$_2$), 2.46 (s, 3H, $CH_3CCH_{ar}CH_{ar}$C–), 1.50–1.20 (m, 18H, –(C*H*$_2$)$_9$$CH_3$), 1.12 (d, J=6.2 Hz, 3H, –CH(C*H*$_3$)), 0.89 (t, J=6.4 Hz, 3H, –O(CH_2)$_{11}$C*H*$_3$) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 144.7 (CH_3*C*$CH_{ar}CH_{ar}$C–), 133.4 ($CH_3CCH_{ar}CH_{ar}$*C*–), 129.7 (CH_3C*C*$H_{ar}CH_{ar}$C–), 127.9 (CH_3CCH_{ar}*C*H_{ar}C–), 72.8

(–*C*H(CH$_3$)), 72.7 (–*C*H$_2$CH(CH$_3$)), 69.6 (–O*C*H$_2$CH$_2$), 31.9 (–*C*H$_2$CH$_2$CH$_3$), 29.9 (–OCH$_2$*C*H$_2$), 29.6, 29.6, 29.4 and 29.3 (–(*C*H$_2$)$_6$(CH$_2$)$_2$CH$_3$), 26.0 (–O(CH$_2$)$_2$*C*H$_2$), 22.6 (–*C*H$_2$CH$_3$), 21.6 (*C*H$_3$CCH$_{ar}$CH$_{ar}$C–), 16.8 (–CH(*C*H$_3$)), 14.1 (–(CH$_2$)$_{11}$*C*H$_3$) ppm.

4.1.6. 4,5-Bis((*S*)-2-dodecyloxypropanyl)-1,3-dithiol-2-thione (15). A solution of the alkyl derivative (**13** or **14** see Table 2 and text, 4.1 mmol) and [Zn(dmit)$_2$][NBu$_4$]$_2$ (**7**, 1 mmol) in MeCN (5 ml for 100 mg of alkyl derivative) was refluxed under nitrogen overnight. MeCN was added and the resulting solution was extracted with hexane. The hexane phases were combined and washed with MeCN, H_2O and dried over $MgSO_4$, and the solvent was evaporated. The remaining oil was purified by flash chromatography using hexane–CH_2Cl_2 [1/2] mixture as eluent to obtain the product as a yellow oil (yield of 36 and 88% starting from **13** and **14**, respectively). LDI-TOF *m/z* (%): 877.7 (Adduct [Cycle=S–CH$_2$CH(CH$_3$)OC$_{12}$H$_{25}$]$^+$, 100). Anal. Calcd for $C_{33}H_{62}O_2S_5$: C 60.87, H 9.60; Found: C 61.39, H 9.86. $[\alpha]_{546}^{25}$ (CH_2Cl_2, 20 mg/ml): +36.6 deg cm^2 g^{-1}. FT-IR (NaCl discs): 2925 (s), 2854 (s), 1464 (w), 1373 (w), 1328 (w), 1136 (w), 1070 (s, C=S), 829 (w), 721 (w), 515 (w) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): 3.61 (sp, *J*=6.2 Hz, 2H, –C*H*(CH$_3$)), 3.46 (dt, *J*=8.8, 6.6 Hz, 2H, –OC*H*$_2$), 3.42 (dt, *J*=8.8, 6.6 Hz, 2H, –OC*H*$_2$), 3.05 (dd, *J*=15.6, 13.2 Hz, 2H, –SC*H*$_2$), 2.93 (dd, *J*=15.6, 13.2 Hz, 2H, –SC*H*$_2$), 1.57 (c, *J*=6.4 Hz, 4H, –C*H*$_2$(CH$_2$)$_7$CH$_3$), 1.40–1.20 (m, 42H, –CH(C*H*$_3$)O(CH$_2$)$_2$(C*H*$_2$)$_9$CH$_3$), 0.90 (t, *J*=6.4 Hz, 6H, –O(CH$_2$)$_{11}$C*H*$_3$) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 211.1 (*C*=S), 136.5 (*C*=*C*), 74.4 (–*C*H(CH$_3$)-OC$_{12}$H$_{25}$), 69.4 (–O*C*H$_2$(CH$_2$)$_{10}$CH$_3$), 42.7 (–*C*H$_2$-CH(CH$_3$)OC$_{12}$H$_{25}$), 31.9 (–O(CH$_2$)$_9$*C*H$_2$CH$_2$CH$_3$), 30.0 (–OCH$_2$*C*H$_2$(CH$_2$)$_{10}$), 29.7, 29.7, 29.5 and 29.4 (–O(CH$_2$)$_3$(*C*H$_2$)$_6$(CH$_2$)$_2$CH$_3$), 26.2 (–O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_8$-CH$_3$), 22.7 (–O(CH$_2$)$_{10}$*C*H$_2$CH$_3$), 19.3 (–CH(*C*H$_3$)OC$_{12}$-H$_{25}$), 14.1 (–O(CH$_2$)$_{11}$*C*H$_3$) ppm.

4.1.7. (*S*)-1-Bromo-3,7-dimethyloctane (19). To a solution of (*S*)-8-bromo-2,6-dimethyloct-2-ene ((*S*)-(+)-citronellyl bromide, **18**, 2 ml, 10 mmol) in EtOAc (15 ml) was added Adam's PtO_2 catalyst (40 mg, 0.176 mmol). H_2 gas was bubbled through the solution slowly for about 30 min and the reaction was left under H_2 atmosphere overnight. The suspension was filtered through Celite, washed with diethyl ether, and the solvent was removed under vacuum, leaving 2.1 g (94%) of a colourless transparent oil. FT-IR (NaCl discs): 2956 (s), 2928 (s), 2869 (m), 1465 (m), 1382 (w), 1366 (w), 1261 (w), 1217 (w), 1170 (w), 1011 (w), 933 (w), 649 (w), 568 (w), 488 (w) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): 3.47 (m, 2H, –C*H*$_2$Br), 1.87 (m, 1H, –C*H*(CH$_3$)), 1.75–1.42 (m, 3H, –C*H*(CH$_3$)C*H*$_2$CH$_2$Br), 1.35–1.15 (m, 6H, –(C*H*$_2$)$_3$CH(CH$_3$)$_2$), 0.88 (d, 3H, *J*=6.35 Hz, –CH(C*H*$_3$)), 0.86 (d, 6H, 6.52 Hz, –CH(C*H*$_3$)$_2$) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 40.14 (–*C*H$_2$CH(CH$_3$)$_2$), 39.21 (–*C*H$_2$CH$_2$Br), 36.75 (–*C*H$_2$CH(CH$_3$)(CH$_2$)$_2$Br), 32.13 (–C*H*(CH$_3$)(CH$_2$)$_2$Br), 31.70 (–*C*H$_2$Br), 27.98 (–*C*H(CH$_3$)$_2$), 24.58 (–*C*H$_2$CH$_2$CH(CH$_3$)$_2$), 22.70 and 22.60 (–CH(*C*H$_3$)$_2$) 18.99 (–CH(*C*H$_3$)(CH$_2$)$_2$Br) ppm.

4.1.8. 4,5-Bis((*S*)-3,7-dimethyloct-6-enylthio)-1,3-dithiole-2-thione (20). A solution of the (*S*)-8-bromo-2,6-dimethyloct-2-ene ((*S*)-(+)-citronellyl bromide, **18**, 1.4 ml, 7.1 mmol) and [Zn(dmit)$_2$][NBu$_4$]$_2$ (**7**, 1.6 g, 1.7 mmol) in MeCN (30 ml) under nitrogen was refluxed for 4 h. After this time, MeCN was added and the resulting solution was extracted with hexane. The hexane phases were combined and washed with MeCN, H_2O and dried over $MgSO_4$. The remaining oil was purified by flash chromatography using hexane–CH_2Cl_2 [3/1] mixture as eluent to obtain 1.5 g (89%) of a yellow oil. LDI-TOF *m/z* (%): 614.3 (Adduct [CycleS–R*]$^+$, 100). Anal. Calcd for $C_{23}H_{38}S_5$ C 58.17, H 8.07; Found: C 58.41, H 7.98. $[\alpha]_{546}^{25}$ (CH_2Cl_2, 20 mg/ml): 49.1 deg cm^2 g^{-1}. FT-IR (NaCl discs): 2962 (s), 2921 (s), 2853 (m), 1455 (m), 1378 (w), 1277 (w), 1069 (s, C=S), 886 (w), 515 (w) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): 5.08 (tsp, *J*=7.03, 1.34 Hz, 2H, –C*H*=C(CH$_3$)$_2$), 2.88 (m, 4H, –SC*H*$_2$–), 1.96 (m, 4H, –C*H*$_2$CH=C(CH$_3$)$_2$), 1.88–1.10 (m, 10H, –SCH$_2$C*H*$_2$C*H*(CH$_3$)C*H*$_2$–), 1.66 (d, *J*=10.12 Hz, 12H, –CH=C(C*H*$_3$)$_2$), 0.91 (d, *J*=6.35 Hz, 6H, –CH$_2$-CH(C*H*$_3$)CH$_2$–) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 211.6 (*C*=S), 136.2 (*C*=*C*), 131.4 (–CH=*C*(CH$_3$)$_2$), 124.3 (–*C*H=C(CH$_3$)$_2$), 36.7 (–S(CH$_2$)$_2$CH(CH$_3$)*C*H$_2$–), 36.6 (–SCH$_2$*C*H$_2$), 34.7 (–S(CH$_2$)$_2$*C*H(CH$_3$)–), 31.7 (–S*C*H$_2$–), 25.7 (–CH=C(*C*H$_3$)$_{trans}$(CH$_3$)$_{cis}$), 19.1 (–S(CH$_2$)$_2$-CH(*C*H$_3$)–), 17.65 (–CH=C(CH$_3$)$_{trans}$(*C*H$_3$)$_{cis}$) ppm.

4.1.9. 4,5-Bis((*S*)-3,7-dimethyloctylthio)-1,3-dithiole-2-thione (21). A solution of the (*S*)-1-bromo-3,7-dimethyl-octane (**19**, 2.1 g, 9.4 mmol) and [Zn(dmit)$_2$][NBu$_4$]$_2$ (**7**, 2.20 g, 2.3 mmol) in MeCN (30 ml) under nitrogen was refluxed for 3 h. After this time, MeCN was added and the resulting solution was extracted with hexane. The hexane phases were combined and washed with MeCN, H_2O and dried over $MgSO_4$. The remaining oil was purified by flash chromatography using hexane–CH_2Cl_2 [4/1] mixture as eluent to obtain 1.7 g (77%) of a yellow oil. Anal. Calcd for $C_{23}H_{42}S_5$ C 57.68, H. 8.84; Found: C 57.75, H 8.63. LDI-TOF *m/z* (%): 620.4 (Adduct [CycleS–R*]$^+$, 100). $[\alpha]_{546}^{25}$ (CH_2Cl_2, 20 mg/ml): 40.5 deg cm^2 g^{-1}. FT-IR (NaCl discs): 2955 (s), 2926 (s), 2868 (m), 1463 (m), 1283 (w), 1070 (s, C=S), 919 (w), 881 (w), 815 (w), 715 (w), 623 (w), 575 (w), 516 (w), 470 (w) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): 2.87 (m, 4H, –SC*H*$_2$–), 1.70–1.40 (m, 8H, –SCH$_2$C*H*$_2$C*H*(CH$_3$)(CH$_2$)$_3$C*H*(CH$_3$)$_2$), 1.30–1.00 (m, 12H, –C*H*$_2$CH$_2$C*H*$_2$CH(CH$_3$)$_2$), 0.88 (d, 6H, *J*=6.52 Hz, –S(CH$_2$)$_2$CH(C*H*$_3$)–), 0.85 (d, 12H, *J*=6.68 Hz, –CH(C*H*$_3$)$_2$) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 211.7 (*C*=S), 136.2 (*C*=*C*), 39.1 (–S*C*H$_2$–), 36.7 (–*C*H$_2$(CH$_2$)$_2$-CH(CH$_3$)$_2$), 34.7 (–SCH$_2$*C*H$_2$–), 32.1 (–S(CH$_2$)$_2$*C*H(CH$_3$)–), 27.9 (–*C*H(CH$_3$)$_2$), 24.6 (–*C*H$_2$CH$_2$CH(CH$_3$)$_2$), 22.7 and 22.6 (–CH(*C*H$_3$)$_2$), 19.20 (–S(CH$_2$)$_2$CH(*C*H$_3$)–) ppm.

4.1.10. 2,3-Bis((*S*)-2-dodecyloxy-propanylthio)-6,7-bis-(methoxycarbonyl)tetrathiafulvalene (23). A solution of 4,5-bis(methoxycarbonyl)-1,3-dithiol-2-one[22] (**22**, 163 mg, 0.295 mmol) and 4,5-bis((*S*)-2-dodecyloxy-propanyl)-1,3-dithiol-2-thione (**15**, 90 mg, 0.384 mmol) in freshly distilled trimethyl phosphite (4 ml) was brought to reflux for 3 h under an Ar atmosphere. The solvent is evaporated and the residual oil was purified by flash chromatography using hexane–CH_2Cl_2 [1/2] mixture as eluent to obtain 89 mg (38%) of **23** as a red oil. The symmetrical chiral TTF (18 mg, 8%) was also obtained as a side product of the reaction. Compound **23**: Anal. Calcd for $C_{40}H_{68}O_6S_6$ C 57.37, H. 8.19; Found: C 56.96, H 8.43. LDI-TOF *m/z* (%): 836.2 (M$^+$, 100) ppm.

FT-IR (NaCl disk): 2924 (w), 2853 (m), 1733 (m, C=O), 1579 (w), 1434 (w), 1375 (w), 1255 (m, C–O), 1135 (w), 1091 (w, C–O–C), 1027 (w), 765 (w), 470 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): 3.86 (s, 6H, $-CO_2CH_3$), 3.57 (sx, $J=6.1$ Hz, 2H, $-CH(CH_3)$), 3.50 (dt, 2H, $-OCH_2$), 3.44 (dt, 2H, $-OCH_2$), 3.03 (dd, $J=13.2$, 6.0 Hz, 2H, $-SCH_2$), 2.83 (dd, $J=13.2$, 6.0 Hz, 2H, $-SCH_2$), 1.57 (qi, $J=6.5$ Hz, 4H, $-OCH_2CH_2$), 1.40–1.20 (m, 42H, $-CH(CH_3)O(CH_2)_2(CH_2)_9$), 0.90 (t, $J=6.6$ Hz, 6H, $-CH_2CH_3$) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 159.9 ($-CO_2CH_3$), 132.0 and 128.10 (lateral C=C), 112.5 and 108.2 (central C=C), 74.6 ($-CH(CH_3)$), 69.3 ($-OCH_2$), 53.3 ($-CO_2CH_3$), 42.2 ($-SCH_2$), 31.9 ($-CH_2CH_2CH_3$), 30.1 ($-OCH_2CH_2$), 29.7, 29.7, 29.5 and 29.7 ($-O(CH_2)_3(CH_2)_6(CH_2)_2CH_3$), 26.2 ($-O(CH_2)_2CH_2$), 22.7 ($-CH_2CH_3$), 19.3 ($-CH(CH_3)$), 14.1 ($-CH_2CH_3$). $E_{1/2}(0/\cdot+)=683$ mV and $E_{1/2}(\cdot+/2+)=1055$ mV. Symmetrical chiral TTF: LDI-TOF *m/z* (%): 1236.7 (M^+, 100). FT-IR (NaCl discs): 2924 (s), 2854 (s), 1455 (w), 1373 (w), 1136 (w), 1099 (w), 805 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): 3.58 (sx, $J=6.0$ Hz, 4H, $-CH(CH_3)$), 3.51 (dt, 4H, $-OCH_2$), 3.50 (dt, 4H, $-OCH_2$), 3.04 (dd, $J=13.1$, 7.0 Hz, 4H, $-SCH_2$), 2.84 (dd, $J=13.1$, 7.0 Hz, 4H, $-SCH_2$), 1.57 (qi, 8H, $-OCH_2CH_2$), 1.40–1.20 (m, 84H, $-CH(CH_3)O(CH_2)_2(CH_2)_9$), 0.90 (t, $J=6.7$ Hz, 12H, $-CH_2CH_3$) ppm.

4.1.11. 2,3-Bis((*S*)-2-dodecyloxy-propanylthio)-6-methoxycarbonyltetrathiafulvalene (24). A solution of 2,3-bis((*S*)-2-dodecyloxy-propanylthio)-6,7-bis(methoxycarbonyl)tetrathiafulvalene (**23**, 194 mg, 0.262 mmol) and LiBr (289 mg, 3.327 mmol) in HMPA (3 ml) with a drop of H_2O was heated to 80 °C, causing evolution of gas (CH_3Br). When no more gas was evolved, the mixture was cooled to room temperature, H_2O (10 ml) was added and the aqueous phase was extracted successively with hexane until the organic phase was colorless. The combined organic fractions were washed with H_2O and were dried over $MgSO_4$, filtered, and evaporated to dryness, leaving an orange oil, which was purified by column chromatography on alumina using as eluent hexane–CH_2Cl_2 [1/1] mixture obtaining 134 mg (75%) of an orange oil. Anal. Calcd for $C_{38}H_{66}O_4S_6$ C 58.56, H. 8.54; Found: C 58.17, H 8.73. LDI-TOF *m/z* (%): 778.4 (M^+, 100). FT-IR (NaCl disk): 2925 (s), 2854 (s), 1716 (m, C=O), 1566 (w), 1538 (w), 1456 (w), 1374 (w), 1327 (w), 1284 (m, C–O), 1251 (m, C–O), 1199 (w), 1095 (m, C–O–C), 1060 (w, C–O–O), 890 (w), 761 (w), 727 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): 7.38 (s, 1H, C=C*H*), 3.84 (s, 3H, $-CO_2CH_3$), 3.58 (sx, $J=6.0$ Hz, 1H, $-CH(CH_3)$), 3.57 (sx, $J=6.0$ Hz, 1H, $-CH(CH_3)$), 3.51–3.44 (m, 4H, $-OCH_2$), 3.04 (dd, $J=13.2$, 6.0 Hz, 2H, $-SCH_2$), 2.85 (dd, $J=13.2$, 7.1 Hz, 1H, $-SCH_2$), 2.83 (dd, $J=13.2$, 7.1 Hz, 1H, $-SCH_2$), 1.58 (qi, $J=7.0$ Hz, 4H, $-OCH_2CH_2$) 1.40–1.20 (m, 42H, $-CH(CH_3)OCH_2CH_2(CH_2)_9$), 0.91 (t, $J=6.6$ Hz, 6H, $-CH_2CH_3$) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 159.77 (C=O), 131.8, 128.4, 128.2 and 127.6 (lateral C=C), 112.6 and 109.7 (central C=C), 74.6 ($-CH(CH_3)$), 69.3 ($-OCH_2$), 52.7 ($-CO_2CH_3$), 42.1 ($-SCH_2$), 32.0, 30.4, 30.1, 30.1, 29.9, 29.7, 29.7, 29.6 and 29.4 ($-O(CH_2)_3(CH_2)_6(CH_2)_2CH_3$), 26.3 ($-O(CH_2)_2CH_2$), 22.7 ($-CH_2CH_3$), 19.4 ($-CH(CH_3)$), 14.1 ($-CH_2CH_3$) ppm. $E_{1/2}(0/\cdot+)=593$ mV and $E_{1/2}(\cdot+/2+)=998$ mV.

4.1.12. 2,3-Bis((*S*)-2-dodecyloxy-propanylthio)-6-(carboxy)tetrathiafulvalene (25). $LiOH\cdot H_2O$ (500 mg, 12 mmol) in 5 ml H_2O was added drop-wise to a stirred solution of 2,3-bis((*S*)-2-dodecyloxy-propanyl)-6-methoxycarbonyltetrathiafulvalene (**24**, 617 mg, 0.792 mmol) in THF (50 ml). After stirring for 12 h, the mixture was diluted with ether (25 ml) and hydrochloric acid (0.5 M, 10 ml) was added. The dark organic phase was dried ($MgSO_4$) and the evaporation of the solvent gave 543 mg (88%) of purple oily solid. Anal. Calcd for $C_{37}H_{64}O_4S_6$ C 58.07, H 8.43; Found: C 57.77, H 8.21. LDI-TOF *m/z* (%): 764.4 ($[M]^+$, 40) and 720.3 ($[M-CO_2H]^+$, 100). FT-IR (KBr): 2924 (s), 2854 (s), 1712 (m, C=O free), 1682 (m, C=O bound), 1564 (m), 1531 (m), 1455 (m), 1417 (m), 1373 (m), 1289 (m), 1199 (w), 1135 (m), 1094 (m), 891 (w), 775 (w), 729 (m), 662 (d), 496 (d) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): 7.48 (br s, 1H, C=C*H*), 4.8 (br s, –O*H*), 3.60 (m, 2H, $-CH(CH_3)$), 3.49 (m, 4H, $-OCH_2$), 3.60 (dd, $J=12.9$, 7.0 Hz, 2H, $-SCH_2$), 2.85 (m, 2H, $-SCH_2$), 1.58 (m, 4H, $-OCH_2CH_2$) 1.40–1.20 (m, 19H, $-CH(CH_3)$-$OCH_2(CH_2)_{10}$), 0.91 (t, $J=6.5$ Hz, 3H, $-CH_2CH_3$) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 163.2 (C=O), 134.4, 128.5, 130.0 and 127.5 (lateral C=C), 112.1 and 110.3 (central C=C), 74.7 ($-CH(CH_3)$), 69.4 ($-OCH_2$), 42.0 ($-SCH_2$), 32.0, 30.1, 29.7, 29.6 and 29.4 ($-O(CH_2)_3(CH_2)_6(CH_2)_2$-$CH_3$), 26.2 ($-O(CH_2)_2CH_2$), 22.7 ($-CH_2CH_3$), 19.4 ($-CH(CH_3)$), 14.1 ($-CH_2CH_3$) ppm. $E_{1/2}(0/\cdot+)=586$ mV and $E_{1/2}(\cdot+/2+)=1050$ mV.

4.1.13. 2,3-Bis(2-cyanoethylthio)-6,7-bis((*S*)-3,7-dimethyloct-6-enylthio)tetrathiafulvalene (27). A solution of 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one[24] (**26**, 125 mg, 0.441 mmol) and 4,5-bis((*S*)-3,7-dimethyloct-6-enylthio)-1,3-dithiole-2-thione (**20**, 190 mg, 0.400 mmol) in freshly distilled trimethyl phosphite (4 ml) was brought to reflux for 7 h under an Ar atmosphere. Evaporation of solvent and purification of the residual oil by flash chromatography using hexane–CH_2Cl_2 [1/4] mixture as eluent gave 197 mg (68%) of **27** as an orange solid. The symmetrical chiral TTF **28** (18 mg, 6%) was also obtained as a side product of the reaction as an oily material. Compound **27**: mp: 64–65 °C. Anal. Calcd for $C_{32}H_{46}N_2S_8$ C 53.74, H. 6.48; Found: C 53.48, H 6.64. LDI-TOF *m/z* (%): 714.1 ($[M]^+$, 100). FT-IR (KBr): 2956 (s), 2923 (s), 2851 (s), 2249 (w, CN), 1473 (m), 1416 (m), 1379 (m), 1294 (w), 1264 (w), 1232 (w), 1127 (w), 891 (w), 800 (w), 771 (w), 728 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): 5.08 (tt, 2H, $J=7.02$, 1.30 Hz, $-CH=C(CH_3)_2$), 3.08 (t, 4H, $J=7.35$ Hz, $-CH_2CH_2CN$), 2.82 (m, 4H, $-SCH_2CH_2CH(CH_3)-$), 2.73 (t, 4H, $J=7.35$ Hz, $-CH_2CH_2CN$), 1.96 (sx, 4H, $J=7.02$ Hz, $(-CH_2CH=CCH_3)_2$), 1.70–1.00 (m, 10H, $-SCH_2CH_2$-$CH(CH_3)CH_2-$), 1.65 (d, 12H, $J=11.25$ Hz, $-C(CH_3)_2$), 0.90 (d, 6H, $J=6.35$ Hz, $-S(CH_2)_2CH(CH_3)-$) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 131.6 ($C=C(CH_3)_2$), 128.3, 128.1 (outer TTF C=C), 124.9 ($C=C(CH_3)_2$), 117.9 (CN), 114.6, 107.1 (central TTF C=C), 37.1, 37.0 ($-SCH_2-$), 34.5 ($-SCH_2CH_2-$), 32.0 ($-CH_2CH(CH_3)CH_2-$), 31.6 ($-CH_2$ $CH_2CHC(CH_3)_2$), 26.1 ($-CH(CH_3)$), 25.8 (CH_2CHC $(CH_3)_2$), 19.6 (CH_2CN), 19.3, 18.1 ($C(CH_3)_2$) ppm. $E_{1/2}(0/\cdot+)=650$ mV and $E_{1/2}(\cdot+/2+)=1015$ mV. Compound **28**: Anal. Calcd for $C_{46}H_{76}S_8$ C 62.38, H. 8.65; Found: C 62.43, H 8.50. LDI-TOF *m/z* (%): 884.4 ($[M]^+$, 100). FT-IR (KBr): 2956 (m), 2923 (s), 2853 (m), 1455 (w),

1377 (w), 1221 (w), 1073 (w), 825 (w), 772 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): 5.08 (tt, 4H, $J=7.18$, 1.50 Hz, $-CH{=}C(CH_3)_2$), 2.82 (m, 8H, $-SCH_2CH_2CH(CH_3)-$), 1.97 (m, 8H, $(-CH_2CH{=}CCH_3)_2$), 1.80–1.00 (m, 20H, $-SCH_2CH_2CH(CH_3)CH_2-$), 1.64 (d, 24H, $J=$ 19.75 Hz, $-C(CH_3)_2$), 0.90 (d, 12H, $J=6.35$ Hz, $-S(CH_2)_2$-$CH(CH_3)-$) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 131.6 ($C{=}C(CH_3)_2$), 128.3 (outer TTF C=C), 124.9 ($C{=}C(CH_3)_2$), 109.4 (central TTF C=C), 37.1 ($-SCH_2-$), 34.4 ($-SCH_2CH_2-$), 32.0 ($-CH_2CH(CH_3)CH_2-$), 31.7 ($-CH_2CH_2CHC(CH_3)_2$), 26.1 ($-CH(CH_3)$), 25.8 (CH_2-$CHC(CH_3)_2$), 19.4, 18.1 ($C(CH_3)_2$) ppm. $E_{1/2}(0/\cdot+)=$ 510 mV and $E_{1/2}(\cdot+/2+)=978$ mV.

4.1.14. 2,3-Bis(2-cyanoethylthio)-6,7-bis((*S*)-3,7-dimethyloctylthio)tetrathiafulvalene (29). A solution of 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one[24] (**26**, 858 mg, 3.03 mmol) and 4,5-bis((*S*)-3,7-dimethyloctylthio)-1,3-dithiole-2-thione (**21**, 1.44 g, 3.03 mmol) in freshly distilled trimethyl phosphite (10 ml) was brought to reflux for 4 h under an atmosphere of argon. After this time, the solvent was evaporated and the residual oil was purified by flash chromatography using CH_2Cl_2 as eluent to obtain 1.20 g (56%) of **29** as an orange solid. The symmetrical chiral TTF **30** (151 mg, 7%) was also obtained as a side product of the reaction. Compound **29**: mp: 76–77 °C. Anal. Calcd for $C_{32}H_{50}N_2S_8$ C 53.43, H. 7.01; Found: C 53.35, H 6.99. LDI-TOF *m/z* (%): 718.2 ($[M]^+$, 100). FT-IR (KBr): 2956 (s), 2923 (s), 2851 (m), 2249 (w, CN), 1473 (m), 1416 (m), 1380 (m), 1293 (w), 1264 (w), 1232 (w), 1126 (w), 891 (w), 800 (w), 770 (w), 728 (w) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): 3.06 (t, 4H, $J=7.06$ Hz, $-CH_2CH_2CN$), 2.82 (m, 4H, $-SCH_2CH_2CH(CH_3)-$), 2.72 (t, 4H, $J=7.06$ Hz, $-CH_2CN$), 1.70–1.35 (m, 8H, $-CH_2CH(CH_3)(CH_2)_3$-$CH(CH_3)_2$), 1.30–1.05 (m, 12H, $-(CH_2)_3CH(CH_3)_2$), 0.87 (d, 6H, $J=5.58$ Hz, $-CH_2CH(CH_3)CH_2-$), 0.84 (d, 12H, $J=6.70$ Hz, $-CH(CH_3)_2$) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 128.5, 128.2 (outer $C{=}C$), 117.9 (CN), 114.9, 107.0 (central C=C), 39.1, 37.3 ($-SCH_2-$), 34.7 ($-SCH_2CH_2-$), 32.5 ($-CH_2CH(CH_3)CH_2-$), 31.7 ($-CH_2(CH_2)_2CH(CH_3)_2$), 28.4 ($-CH(CH_3)_2$), 25.1 ($-CH_2$-$CH_2CH(CH_3)_2$), 23.2 ($-CH_2CH(CH_3)_2$), 23.1 ($-CH(CH_3)$), 19.8 (CH_2CN) and 19.4 ($CH(CH_3)_2$) ppm. $E_{1/2}(0/\cdot+)=$ 650 mV and $E_{1/2}(\cdot+/2+)=1015$ mV. Compound **30**: Anal. Calcd for $C_{46}H_{84}S_8$ C 61.82, H. 9.47; Found: C 62.08, H 9.18. LDI-TOF *m/z* (%): 892.4 ($[M]^+$, 100). ^1H NMR (250 MHz, $CDCl_3$): 2.81 (m, 8H, $-SCH_2CH_2$-$CH(CH_3)-$), 1.70–1.35 (m, 16H, $-CH_2CH(CH_3)(CH_2)_3$-$CH(CH_3)_2$), 1.30–1.05 (m, 24H, $-(CH_2)_3CH(CH_3)_2$), 0.88 (d, 12H, $J=5.03$ Hz, $-CH_2CH(CH_3)CH_2-$), 0.86 (d, 24H, $J=6.68$ Hz, $-CH(CH_3)_2$) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): 128.3 (outer $C{=}C$), 109.4 (central C=C) 38.9, ($-SCH_2-$), 34.6 ($-SCH_2CH_2-$), 32.5 ($-CH_2CH(CH_3)CH_2-$), 31.8 ($-CH_2(CH_2)_2CH(CH_3)_2$), 28.3 ($-CH(CH_3)_2$), 25.1 ($-CH_2CH_2CH(CH_3)_2$), 23.2 ($-CH_2CH(CH_3)^2$), 23.1 ($-CH(CH_3)$) and 19.5 ($CH(CH_3)_2$) ppm. $E_{1/2}(0/\cdot+)=$ 506 mV and $E_{1/2}(\cdot+/2+)=980$ mV.

Acknowledgements

This work was supported by the Programa General de Conocimento of the Dirección General de Investigación, Ciencia y Tecnología (Spain), under the project BQU2003-00760, DGR, Catalonia (Project 2005SGR00591), and the European Integrated Project project NAIMO (NMP4-CT-2004-500355). E.G.-N. is grateful to the Generalitat de Catalunya for a predoctoral grant.

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